Enantioselective Radical–Radical Cross-Couplings of β-Hydroxy Amides and *N*-Hydroxyphthalimide Esters via Ni/Photoredox Catalysis

Li-Li Zhang, Lian-Jie Li, Ning Wang, Hui Yu, and Ze-Peng Yang*

Shanghai Key Laboratory of Chemical Assessment and Sustainability, School of Chemical Science and Engineering, Tongji University, Shanghai 200092, People's Republic of China

Supporting Information

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I. General Information

Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. Anhydrous MTBE (methyl *tert*-butyl ether) and CF_3Ph ((trifluoromethyl)benzene) were purchased from *J&K* and stored under nitrogen. NHC was prepared according to the literature procedure, and all analytical data were consistent with the report.[1] Unless otherwise noted, all reactions were performed under an atmosphere of dry nitrogen.

NMR spectra were collected on a Bruker 400 MHz, or a Bruker 600 MHz spectrometer at ambient temperature; chemical shifts (δ) are reported in ppm downfield from tertramethylsilane, using the solvent resonance as the internal standard. HPLC analysis was performed on an Agilent 1260 Infinity II system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (4.6 × 250 mm, particle size 3 μm). FT-IR measurements were carried out on a Thermo Scientific Nicolet iS10 spectrometer. HR-MS were obtained from a Bruker micro TOF-II instrument. GC data were acquired by a Shimadzu GC-2030AF spectrometer. Optical rotation data were measured on a Rudolph AUTOPOL VI polarimeter. X-ray crystallographic analyses were carried out on a Bruker APEX-III CMOS diffractometer. Flash column chromatography was performed using silica gel (particle size 200-400 mesh ASTM, purchased from Yantai, China).

The blue LEDs (455 mm, 30 W) were purchased from www.taobao.com. As shown in **Figure S1**, the reaction vials were positioned 2-3 cm from the LEDs, and the temperature was controlled using a cooler (Greatwall DHJF-4002).

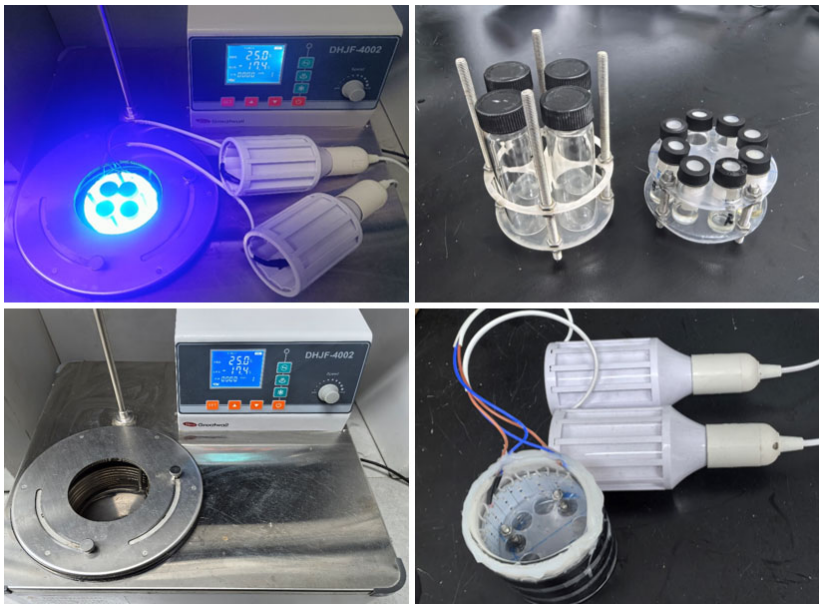
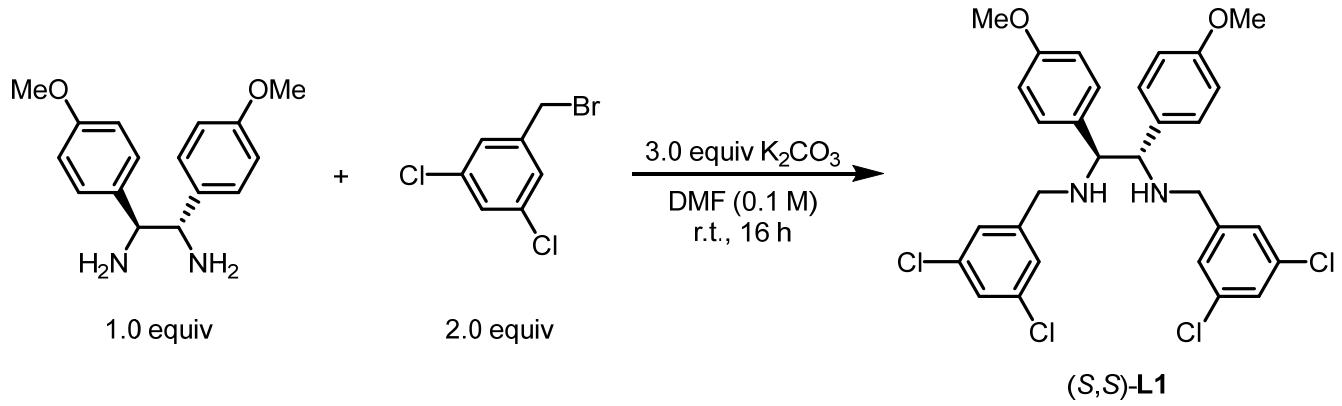


Figure S1. Photoreaction setup

II. Preparation of the Chiral Ligand

The yields have not been optimized.



(1*S*,2*S*)-*N*^{1},*N*^{2}-Bis(3,5-dichlorobenzyl)-1,2-bis(4-methoxyphenyl)ethane-1,2-diamine ((*S*,*S*)-L1).[2] An oven-dried 250 mL round-bottom flask was equipped with a magnetic stir bar, (1*S*,2*S*)-1,2-bis(4-methoxyphenyl)ethane-1,2-diamine (2.72 g, 10.0 mmol, 1.0 equiv), 1-(bromomethyl)-3,5-dichlorobenzene (4.76 g, 20.0 mmol, 2.0 equiv), potassium carbonate (4.15 g, 30.0 mmol, 3.0 equiv), and then it was sealed with a rubber septum cap. The flask was placed under a nitrogen atmosphere by evacuating and backfilling the flask (three cycles), followed by the addition of DMF (100 mL). The resulting mixture was stirred at room temperature for 16 h. Then, the reaction was quenched with water (100 mL), and the mixture was extracted with EA (50 mL x 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (1:5 EtOAc/hexanes) to afford the product as a white solid (3.47 g, 5.9 mmol, 59% yield, >99% ee).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 (t, *J* = 2.0 Hz, 2H), 7.08 (d, *J* = 1.9 Hz, 4H), 6.98 (d, *J* = 8.6 Hz, 4H), 6.75 (d, *J* = 8.6 Hz, 4H), 3.76 (s, 6H), 3.61 (d, *J* = 14.1 Hz, 2H), 3.60 (s, 2H), 3.43 (d, *J* = 14.1 Hz, 2H), 2.25 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.6, 144.1, 134.7, 132.4, 128.7, 126.9, 126.4, 113.6, 67.5, 55.1, 50.3.

FT-IR (film): 3311, 3059, 3024, 2998, 2951, 2907, 2833, 1611 cm^{-1}.

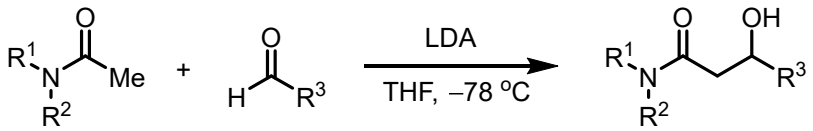
HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{30}H_{28}Cl_4N_2NaO_2$: 611.0797, found: 611.0795.

$[\alpha]^{10}_D$ = +6.9 (c 0.5, $CHCl_3$).

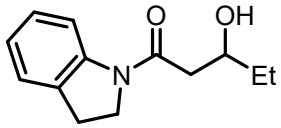
III. Preparation of β-Hydroxy Amides

The yields have not been optimized.

General Procedure 1 (GP-1).



Preparation of β-hydroxy amide from amide and aldehyde.[3] An oven-dried 250 mL round-bottom flask was charged with a magnetic stir bar, and then it was sealed with a rubber septum cap. The flask was placed under a nitrogen atmosphere by evacuating and backfilling the flask (three cycles), followed by the addition of diisopropylamine (1.1 equiv) and THF (volume to generate a 0.25 M solution of the amide). The solution was cooled to –78 °C and stirred for 5 min. *n*-Butyl lithium (2.5 M in hexanes, 1.1 equiv) was added slowly to the mixture, and the resulting solution was stirred for 30 minutes at –78 °C. The amide (1.0 equiv) was added, and the mixture was stirred for an additional 30 minutes. Then the aldehyde (1.5 equiv) was added. The resulting mixture was stirred at –78 °C for 80 minutes and then quenched with aqueous saturated NH_4Cl. The mixture was extracted three times with EtOAc, and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the target product.



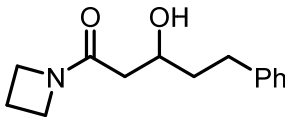
3-Hydroxy-1-(indolin-1-yl)pentan-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and propionaldehyde. The product was purified by column chromatography on silica gel (1:1 EtOAc/hexanes). 3.37 g (15.4 mmol, 77% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 4.11 – 4.05 (m, 1H), 4.02 – 3.96 (m, 2H), 3.89 (s, 1H), 3.17 (t, *J* = 8.5 Hz, 2H), 2.55 (dd, *J* = 16.5, 2.5 Hz, 1H), 2.43 (dd, *J* = 16.6, 9.4 Hz, 1H), 1.67 – 1.58 (m, 1H), 1.56 – 1.49 (m, 1H), 1.00 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.0, 142.4, 131.1, 127.5, 124.6, 123.9, 117.0, 69.2, 47.8, 41.7, 29.2, 27.8, 9.9.

FT-IR (film): 3670, 3307, 2970, 1642, 1398, 1055 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{13}H_{17}NNaO_2$: 242.1151, found: 242.1158.



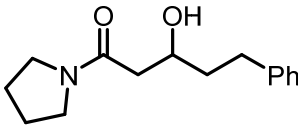
1-(Azetidin-1-yl)-3-hydroxy-5-phenylpentan-1-one. The title compound was synthesized according to **GP-1** from 1-(azetidin-1-yl)ethan-1-one (1.98 g, 20.0 mmol) and 3-phenylpropanal. The product was purified by column chromatography on silica gel (5:1 EtOAc/hexanes). 3.36 g (14.4 mmol, 72% yield). Yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.14 (m, 3H), 4.16 – 4.06 (m, 2H), 4.06 – 3.96 (m, 3H), 3.77 (s, 1H), 2.84 (ddd, *J* = 13.6, 9.8, 5.4 Hz, 1H), 2.70 (ddd, *J* = 13.8, 9.6, 6.8 Hz, 1H), 2.32 – 2.24 (m, 2H), 2.21 (dd, *J* = 12.5, 3.3 Hz, 1H), 2.12 (dd, *J* = 15.7, 9.0 Hz, 1H), 1.91 – 1.80 (m, 1H), 1.74 – 1.69 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.3, 141.9, 128.4, 128.2, 125.7, 67.3, 49.9, 47.7, 38.3, 36.8, 31.7, 15.0.

FT-IR (film): 3675, 2972, 1614, 1439, 1241, 1057, 698 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{14}H_{20}NO_2$: 234.1489, found: 234.1480.



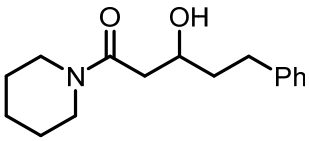
3-Hydroxy-5-phenyl-1-(pyrrolidin-1-yl)pentan-1-one. The title compound was synthesized according to **GP-1** from 1-(pyrrolidin-1-yl)ethan-1-one (2.26 g, 20.0 mmol) and 3-phenylpropanal. The product was purified by column chromatography on silica gel (5:1 EtOAc/hexanes). 3.61 g (14.6 mmol, 73% yield). Yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.24 – 7.14 (m, 3H), 4.15 – 4.01 (m, 1H), 3.95 (s, 1H), 3.45 (t, *J* = 6.9 Hz, 2H), 3.41 – 3.25 (m, 2H), 2.85 (ddd, *J* = 14.6, 9.7, 5.3 Hz, 1H), 2.71 (ddd, *J* = 13.7, 9.5, 6.9 Hz, 1H), 2.42 (dd, *J* = 16.3, 2.6 Hz, 1H), 2.30 (dd, *J* = 16.3, 9.4 Hz, 1H), 1.97 – 1.90 (m, 2H), 1.89 – 1.83 (m, 3H), 1.76 – 1.66 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.2, 142.1, 128.5, 128.3, 125.7, 67.3, 46.5, 45.4, 40.5, 38.2, 31.8, 25.9, 24.3.

FT-IR (film): 3678, 2975, 2912, 1611, 1450, 1049, 753, 708 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{15}H_{22}NO_2$: 248.1645, found: 248.1640.



3-Hydroxy-5-phenyl-1-(piperidin-1-yl)pentan-1-one. The title compound was synthesized according to **GP-1** from 1-(piperidin-1-yl)ethan-1-one (2.54 g, 20.0 mmol) and 3-phenylpropanal. The product was purified by column chromatography on silica gel (5:1 EtOAc/hexanes). 3.92 g (15.0 mmol, 75% yield). Yellow oil.

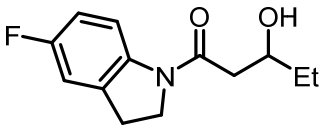
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (m, 2H), 7.23 – 7.20 (m, 2H), 7.19 – 7.14 (m, 1H), 4.46 (s, 1H), 4.08 – 3.98 (m, 1H), 3.65 – 3.47 (m, 2H), 3.36 – 3.28 (m, 2H), 2.86 (ddd, *J* = 14.6,

9.7, 5.3 Hz, 1H), 2.71 (ddd, *J* = 13.7, 9.5, 6.9 Hz, 1H), 2.45 (dd, *J* = 16.3, 2.5 Hz, 1H), 2.31 (dd, *J* = 16.4, 9.5 Hz, 1H), 1.93 – 1.83 (m, 1H), 1.75 – 1.68 (m, 1H), 1.66 – 1.61 (m, 2H), 1.58 – 1.50 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 142.1, 128.4, 128.3, 125.7, 67.3, 46.3, 42.4, 39.1, 38.1, 31.8, 26.2, 25.4, 24.3.

FT-IR (film): 3685, 2985, 2899, 1608, 1444, 1249, 1051, 698 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+K]$^+$ calcd for $C_{16}H_{23}KNO_2$: 300.1360, found: 300.1358.



1-(5-Fluoroindolin-1-yl)-3-hydroxypentan-1-one. The title compound was synthesized according to **GP-1** from 1-(5-fluoroindolin-1-yl)ethan-1-one (3.58 g, 20.0 mmol) and propionaldehyde. The product was purified by column chromatography on silica gel (1:1 EtOAc/hexanes). 3.60 g (15.2 mmol, 76% yield). White solid.

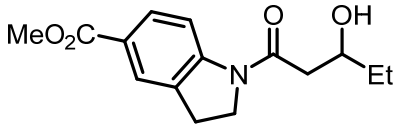
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.21 – 8.11 (m, 1H), 6.91 – 6.81 (m, 2H), 4.19 – 3.94 (m, 3H), 3.51 (s, 1H), 3.16 (t, *J* = 8.5 Hz, 2H), 2.54 (dd, *J* = 16.6, 2.5 Hz, 1H), 2.43 (dd, *J* = 16.5, 9.4 Hz, 1H), 1.69 – 1.58 (m, 1H), 1.54 – 1.48 (m, 1H), 0.99 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 159.4 (d, *J* = 242.6 Hz), 138.6 (d, *J* = 2.2 Hz), 133.2 (d, *J* = 8.3 Hz), 117.8 (d, *J* = 8.2 Hz), 113.7 (d, *J* = 22.6 Hz), 111.8 (d, *J* = 24.0 Hz), 69.2, 48.1, 41.6, 29.2, 27.8, 9.9.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -118.9.

FT-IR (film): 3516, 2977, 1632, 1481, 1405, 1241, 1062, 861 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{13}H_{17}FNO_2$: 238.1238, found: 238.1234.



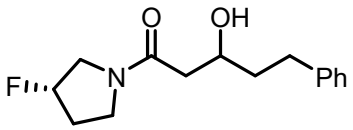
Methyl 1-(3-hydroxypentanoyl)indoline-5-carboxylate. The title compound was synthesized according to **GP-1** from methyl 1-acetylindoline-5-carboxylate (4.38 g, 20.0 mmol) and propionaldehyde. The product was purified by column chromatography on silica gel (2:1 EtOAc/hexanes). 3.93 g (14.2 mmol, 71% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.81 (s, 1H), 4.11 – 4.01 (m, 3H), 3.87 (s, 3H), 3.56 (s, 1H), 3.19 (t, *J* = 8.6 Hz, 2H), 2.56 (dd, *J* = 16.7, 2.6 Hz, 1H), 2.46 (dd, *J* = 16.7, 9.4 Hz, 1H), 1.67 – 1.56 (m, 1H), 1.55 – 1.49 (m, 1H), 0.99 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.5, 166.6, 146.4, 131.4, 130.0, 125.9, 125.5, 116.3, 69.1, 51.9, 48.3, 42.0, 29.2, 27.4, 9.9.

FT-IR (film): 3464, 2975, 1707, 1395, 1257, 1064, 768 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{15}H_{19}NNaO_4$: 300.1206, found: 300.1206.



1-((*S*)-3-Fluoropyrrolidin-1-yl)-3-hydroxy-5-phenylpentan-1-one. The title compound was synthesized according to **GP-1** from (*S*)-1-(3-fluoropyrrolidin-1-yl)ethan-1-one (2.62 g, 20.0 mmol) and 3-phenylpropanal. The product was purified by column chromatography on silica gel (5:1 EtOAc/hexanes). 3.98 g (15.0 mmol, 75% yield). Yellow oil.

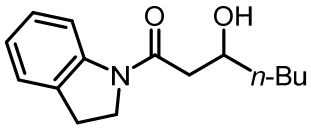
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 2H), 7.26 – 7.16 (m, 3H), 5.42 – 5.13 (m, 1H), 4.14 – 4.05 (m, 1H), 3.98 – 3.89 (m, 1H), 3.86 – 3.80 (m, 1H), 3.60 – 3.48 (m, 2H), 2.94 – 2.82 (m, 1H), 2.77 – 2.70 (m, 1H), 2.52 – 2.30 (m, 3H), 2.18 – 1.99 (m, 1H), 1.96 – 1.86 (m, 1H), 1.81 – 1.69 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.61, 171.56, 171.5, 171.3, 142.1, 128.5, 128.4, 125.8, 93.5, 92.1, 91.7, 90.3, 67.3, 67.2, 53.2, 52.9, 52.3, 52.1, 44.3, 44.2, 43.30, 43.27, 40.9, 40.8, 40.7, 40.6, 38.2, 38.1, 32.8, 32.5, 31.9, 31.8, 31.2, 30.9.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -177.2 (d, *J* = 51.5 Hz), -177.9 (d, *J* = 14.7 Hz).

FT-IR (film): 3670, 2977, 1612, 1454, 1050, 756, 709 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{15}H_{21}FNO_2$: 266.1551, found: 266.1549.



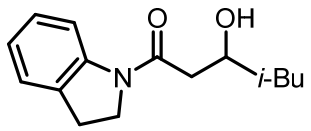
3-Hydroxy-1-(indolin-1-yl)heptan-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and pentanal. The product was purified by column chromatography on silica gel (1:1 EtOAc/hexanes). 3.90 g (15.8 mmol, 79% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.06 – 6.99 (m, 1H), 4.16 – 4.10 (m, 1H), 4.05 – 3.94 (m, 2H), 3.84 (s, 1H), 3.22 – 3.15 (m, 2H), 2.61 – 2.52 (m, 1H), 2.49 – 2.41 (m, 1H), 1.65 – 1.56 (m, 1H), 1.50 – 1.45 (m, 2H), 1.39 – 1.33 (m, 3H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.0, 142.4, 131.1, 127.5, 124.6, 123.9, 117.0, 67.8, 47.8, 42.2, 36.1, 27.8, 27.7, 22.6, 14.0.

FT-IR (film): 3675, 3508, 2905, 1637, 1411, 1072, 747 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{15}H_{22}NO_2$: 248.1645, found: 248.1643.



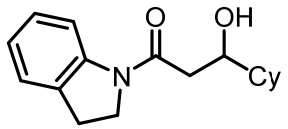
3-Hydroxy-1-(indolin-1-yl)-5-methylhexan-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and 3-methylbutanal. The product was purified by column chromatography on silica gel (1:1 EtOAc/hexanes). 4.15 g (16.8 mmol, 84% yield). White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 7.9 Hz, 1H), 7.18 (t, *J* = 8.1 Hz, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 4.38 – 4.17 (m, 1H), 4.07 – 3.94 (m, 2H), 3.85 (s, 1H), 3.18 (t, *J* = 8.4 Hz, 2H), 2.60 – 2.38 (m, 2H), 1.94 – 1.80 (m, 1H), 1.63 – 1.53 (m, 1H), 1.29 – 1.16 (m, 1H), 0.96 (d, *J* = 2.8 Hz, 3H), 0.94 (d, *J* = 2.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 142.5, 131.1, 127.5, 124.6, 124.0, 117.1, 65.9, 47.9, 45.5, 42.7, 27.9, 24.4, 23.3, 22.0.

FT-IR (film): 3508, 2967, 1642, 1408, 1072, 755 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{15}H_{22}NO_2$: 248.1645, found: 248.1632.



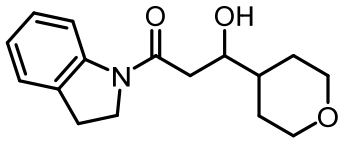
3-Cyclohexyl-3-hydroxy-1-(indolin-1-yl)propan-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and cyclohexanecarbaldehyde. The product was purified by column chromatography on silica gel (1:1 EtOAc/hexanes). 3.44 g (12.6 mmol, 63% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 4.10 – 3.99 (m, 2H), 3.94 – 3.89 (m, 1H), 3.48 (s, 1H), 3.20 (t, *J* = 8.5 Hz, 2H), 2.58 (dd, *J* = 16.5, 2.3 Hz, 1H), 2.48 (dd, *J* = 16.4, 9.7 Hz, 1H), 1.93 (d, *J* = 13.2 Hz, 1H), 1.81 – 1.76 (m, 2H), 1.73 – 1.66 (m, 2H), 1.51 – 1.41 (m, 1H), 1.30 – 1.23 (m, 2H), 1.20 – 1.15 (m, 1H), 1.11 – 1.05 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.4, 142.5, 131.1, 127.6, 124.6, 124.0, 117.1, 72.0, 47.9, 42.9, 39.3, 29.0, 28.5, 27.9, 26.5, 26.2, 26.1.

FT-IR (film): 3425, 2923, 1642, 1484, 1400, 1104, 750 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{17}H_{24}NO_2$: 274.1802, found: 274.1801.



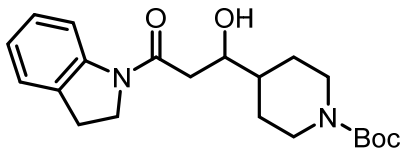
3-Hydroxy-1-(indolin-1-yl)-3-(tetrahydro-2*H*-pyran-4-yl)propan-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and tetrahydro-2*H*-pyran-4-carbaldehyde. The product was purified by column chromatography on silica gel (2:1 EtOAc/hexanes). 3.96 g (14.4 mmol, 72% yield). White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 8.1 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 4.07 – 3.97 (m, 4H), 3.92 (ddd, *J* = 9.3, 6.7, 2.4 Hz, 1H), 3.62 (s, 1H), 3.39 (t, *J* = 11.7, 2.4 Hz, 2H), 3.20 (t, *J* = 8.4 Hz, 2H), 2.61 (dd, *J* = 16.8, 2.3 Hz, 1H), 2.46 (dd, *J* = 16.5, 9.5 Hz, 1H), 1.94 – 1.81 (m, 1H), 1.78 – 1.69 (m, 1H), 1.59 – 1.53 (m, 1H), 1.52 – 1.39 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 142.4, 131.1, 127.6, 124.6, 124.1, 117.1, 71.5, 68.0, 67.7, 47.9, 40.2, 38.9, 28.88, 28.86, 27.9.

FT-IR (film): 3475, 2967, 1634, 1416, 1273, 1085, 763 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{16}H_{22}NO_3$: 276.1594, found: 276.1603.



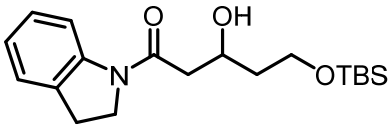
***tert*-Butyl 4-(1-hydroxy-3-(indolin-1-yl)-3-oxopropyl)piperidine-1-carboxylate.** The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and *tert*-butyl 4-formylpiperidine-1-carboxylate. The product was purified by column chromatography on silica gel (2:1 EtOAc/hexanes). 3.96 g (10.6 mmol, 53% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 8.4 Hz, 2H), 7.03 (t, *J* = 7.8 Hz, 1H), 4.19 – 4.11 (m, 2H), 4.03 – 3.96 (m, 2H), 3.92 (s, 1H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.69 – 2.64 (m, 2H), 2.56 (d, *J* = 16.4 Hz, 1H), 2.45 (dd, *J* = 16.4, 9.5 Hz, 1H), 1.88 (d, *J* = 13.0 Hz, 1H), 1.64 – 1.57 (m, 2H), 1.44 (s, 9H), 1.29 – 1.23 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.8, 154.7, 142.4, 131.1, 127.5, 124.6, 124.1, 117.0, 79.3, 71.1, 67.4, 47.9, 43.7, 41.2, 39.0, 28.4, 27.9, 27.8.

FT-IR (film): 3417, 2918, 1687, 1650, 1403, 1234, 1161, 760 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{21}H_{31}N_2O_4$: 375.2278, found: 375.2277.



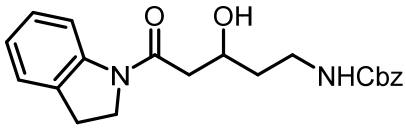
5-((*tert*-Butyldimethylsilyl)oxy)-3-hydroxy-1-(indolin-1-yl)pentan-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and 3-((*tert*-butyldimethylsilyl)oxy)propanal. The product was purified by column chromatography on silica gel (2:1 EtOAc/hexanes). 5.31 g (15.2 mmol, 76% yield). White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 4.48 – 4.30 (m, 1H), 4.18 – 3.97 (m, 2H), 3.93 – 3.80 (m, 2H), 3.19 (t, *J* = 8.5 Hz, 2H), 2.71 – 2.53 (m, 2H), 1.92 – 1.68 (m, 2H), 0.90 (s, 9H), 0.08 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.5, 142.6, 131.1, 127.5, 124.6, 123.9, 117.1, 66.8, 61.0, 48.0, 42.7, 38.8, 27.9, 25.9, 18.2, -5.4, -5.5.

FT-IR (film): 3529, 2957, 1642, 1418, 1247, 1088, 851, 760 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+K]$^{+}$ calcd for $C_{19}H_{31}KNO_3Si$: 388.1705, found: 388.1702.



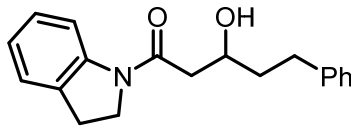
Benzyl (3-hydroxy-5-(indolin-1-yl)-5-oxopentyl)carbamate. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and benzyl (3-oxopropyl)carbamate. The product was purified by column chromatography on silica gel (3:1 EtOAc/hexanes). 5.08 g (13.8 mmol, 69% yield). White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.31 (m, 4H), 7.30 – 7.24 (m, 1H), 7.16 (t, *J* = 7.9 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 5.58 (s, 1H), 5.08 (s, 2H), 4.28 – 4.19 (m, 1H), 4.03 – 3.85 (m, 2H), 3.52 – 3.39 (m, 1H), 3.36 – 3.27 (m, 1H), 3.12 (t, *J* = 8.4 Hz, 2H), 2.57 – 2.43 (m, 2H), 1.83 – 1.62 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.4, 156.6, 142.3, 136.6, 131.2, 128.3, 127.9, 127.4, 124.5, 123.9, 116.9, 66.4, 66.3, 47.8, 42.0, 38.1, 35.8, 27.7.

FT-IR (film): 3498, 2990, 1684, 1486, 1252, 1059, 755 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{21}H_{24}N_2NaO_4$: 391.1628, found: 391.1629.



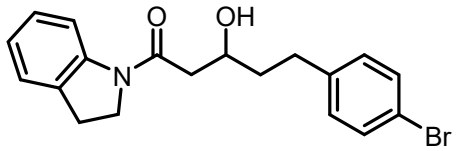
3-Hydroxy-1-(indolin-1-yl)-5-phenylpentan-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and 3-phenylpropanal. The product was purified by column chromatography on silica gel (1:1 EtOAc/hexanes). 5.02 g (17.0 mmol, 85% yield). White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.23 (m, 3H), 7.22 – 7.18 (m, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 4.26 – 4.16 (m, 1H), 4.11 (s, 1H), 3.98 (dt, *J* = 10.6, 8.2 Hz, 2H), 3.19 (t, *J* = 8.4 Hz, 2H), 2.99 – 2.86 (m, 1H), 2.82 – 2.71 (m, 1H), 2.56 (dd, *J* = 16.6, 3.1 Hz, 1H), 2.49 (dd, *J* = 16.7, 8.7 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.83 – 1.77 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 142.4, 142.0, 131.1, 128.5, 128.4, 127.6, 125.8, 124.6, 124.0, 117.1, 67.2, 47.9, 42.2, 38.0, 31.8, 27.9.

FT-IR (film): 3493, 2964, 1629, 1481, 1405, 1265, 1038, 755 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{19}H_{22}NO_2$: 296.1645, found: 296.1643.



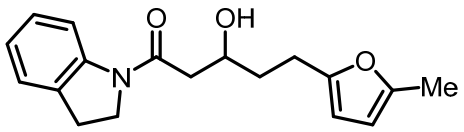
5-(4-Bromophenyl)-3-hydroxy-1-(indolin-1-yl)pentan-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and 3-(4-bromophenyl)propanal. The product was purified by column chromatography on silica gel (1:1 EtOAc/hexanes). 4.85 g (13.0 mmol, 65% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.17 (m, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 4.16 – 4.11 (m, 1H), 4.01 – 3.93 (m, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.87 – 2.82 (m, 1H), 2.73 – 2.69 (m, 1H), 2.54 – 2.45 (m, 2H), 1.92 – 1.86 (m, 1H), 1.75 – 1.71 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.7, 142.4, 140.9, 131.4, 131.1, 130.3, 127.6, 124.6, 124.1, 119.5, 117.1, 66.9, 47.8, 42.2, 37.8, 31.2, 27.9.

FT-IR (film): 3425, 2928, 1640, 1418, 1085, 760, 583 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{19}H_{20}BrNNaO_2$: 396.0570, found: 396.0564.



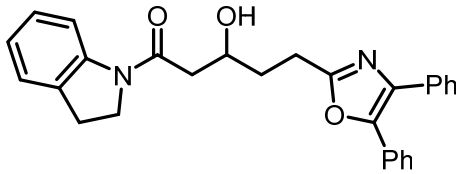
3-Hydroxy-1-(indolin-1-yl)-5-(5-methylfuran-2-yl)pentan-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and 3-(5-methylfuran-2-yl)propanal. The product was purified by column chromatography on silica gel (2:1 EtOAc/hexanes). 4.43 g (14.8 mmol, 74% yield). Yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 8.4 Hz, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 5.90 (d, *J* = 3.0 Hz, 1H), 5.84 (d, *J* = 1.6 Hz, 1H), 4.27 – 4.15 (m, 1H), 4.06 – 3.92 (m, 2H), 3.19 (t, *J* = 8.5 Hz, 2H), 2.88 – 2.79 (m, 1H), 2.75 – 2.66 (m, 1H), 2.59 – 2.43 (m, 2H), 2.25 (s, 3H), 2.06 – 1.73 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 153.8, 150.3, 142.5, 131.1, 127.6, 124.6, 124.0, 117.1, 105.9, 105.7, 67.1, 47.9, 42.1, 34.8, 27.9, 24.2, 13.5.

FT-IR (film): 3516, 2972, 1634, 1481, 1424, 1265, 1044, 759 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{18}H_{21}NNaO_3$: 322.1414, found: 322.1395.



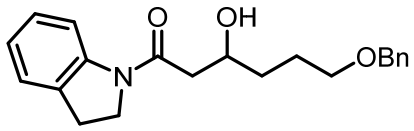
5-(4,5-Diphenyloxazol-2-yl)-3-hydroxy-1-(indolin-1-yl)pentan-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (1.61 g, 10 mmol) and 3-(4,5-diphenyloxazol-2-yl)propanal. The product was purified by column chromatography on silica gel (3:1 EtOAc/hexanes). 2.98 g (6.8 mmol, 68% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.1 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.35 (dd, *J* = 7.6, 5.7 Hz, 4H), 7.33 – 7.30 (m, 2H), 7.20 – 7.17 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 4.34 – 4.28 (m, 1H), 4.04 – 3.96 (m, 2H), 3.17 (t, *J* = 8.4 Hz, 2H), 3.15 – 3.11 (m, 1H), 3.08 – 3.02 (m, 1H), 2.65 (dd, *J* = 16.5, 2.9 Hz, 1H), 2.57 (dd, *J* = 16.5, 8.8 Hz, 1H), 2.13 (q, *J* = 7.2 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.5, 163.4, 145.2, 142.4, 134.8, 132.4, 131.2, 128.9, 128.6, 128.5, 128.4, 128.0, 127.9, 127.5, 126.4, 124.6, 124.0, 117.1, 67.2, 47.9, 42.1, 33.3, 27.9, 24.6.

FT-IR (film): 3574, 3418, 2937, 1657, 1572, 1429, 1072, 762, 663 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{28}H_{26}N_2NaO_3$: 461.1836, found: 461.1839.



6-(Benzyloxy)-3-hydroxy-1-(indolin-1-yl)hexan-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and 4-

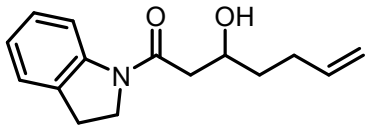
(benzyloxy)butanal. The product was purified by column chromatography on silica gel (2:1 EtOAc/hexanes). 5.29 g (15.6 mmol, 78% yield). White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 4.3 Hz, 4H), 7.30 – 7.26 (m, 1H), 7.24 – 7.18 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 4.53 (s, 2H), 4.24 – 4.14 (m, 1H), 4.05 – 3.94 (m, 2H), 3.64 – 3.48 (m, 2H), 3.18 (t, *J* = 8.4 Hz, 2H), 2.61 – 2.55 (m, 1H), 2.53 – 2.44 (m, 1H), 1.92 – 1.82 (m, 1H), 1.81 – 1.74 (m, 1H), 1.71 – 1.63 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 142.5, 138.4, 131.1, 128.3, 127.6, 127.50, 127.48, 124.6, 123.9, 117.1, 72.9, 70.2, 67.7, 47.9, 42.2, 33.2, 27.9, 25.9.

FT-IR (film): 3495, 2962, 1650, 1416, 1270, 1111, 737 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{21}H_{25}NNaO_3$: 362.1727, found: 362.1714.



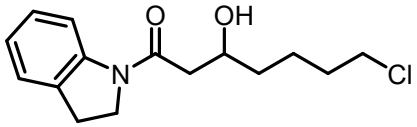
3-Hydroxy-1-(indolin-1-yl)hept-6-en-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and pent-4-enal. The product was purified by column chromatography on silica gel (1:1 EtOAc/hexanes). 3.28 g (13.4 mmol, 67% yield). White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.3 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 5.85 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.06 (dd, *J* = 17.1, 1.8 Hz, 1H), 4.98 (dd, *J* = 10.2, 1.8 Hz, 1H), 4.21 – 4.13 (m, 1H), 4.05 – 3.96 (m, 2H), 3.89 (s, 1H), 3.17 (t, *J* = 8.4 Hz, 2H), 2.55 (dd, *J* = 16.6, 2.8 Hz, 1H), 2.46 (dd, *J* = 16.6, 9.1 Hz, 1H), 2.32 – 2.25 (m, 1H), 2.22 – 2.12 (m, 1H), 1.77 – 1.64 (m, 1H), 1.60 – 1.48 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 142.4, 138.2, 131.1, 127.5, 124.6, 124.0, 117.0, 114.8, 67.3, 47.9, 42.1, 35.5, 29.8, 27.8.

FT-IR (film): 3508, 2907, 1640, 1405, 1267, 1062, 908, 754 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{15}H_{19}NNaO_2$: 268.1308, found: 268.1303.



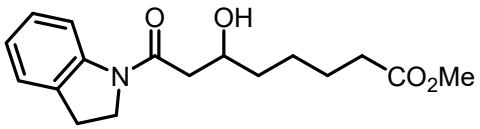
7-Chloro-3-hydroxy-1-(indolin-1-yl)heptan-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and 5-chloropentanal. The product was purified by column chromatography on silica gel (1:1 EtOAc/hexanes). 3.43 g (12.2 mmol, 61% yield). White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 2H), 7.02 (t, *J* = 7.8 Hz, 1H), 4.17 – 4.09 (m, 1H), 4.02 – 3.89 (m, 2H), 3.81 (s, 1H), 3.53 (t, *J* = 6.6 Hz, 2H), 3.14 (t, *J* = 8.5 Hz, 2H), 2.52 (dd, *J* = 16.6, 2.8 Hz, 1H), 2.43 (dd, *J* = 16.6, 9.1 Hz, 1H), 1.85 – 1.76 (m, 2H), 1.67 – 1.47 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 142.4, 131.1, 127.4, 124.5, 123.9, 116.9, 67.5, 47.8, 44.8, 42.1, 35.4, 32.4, 27.8, 22.9.

FT-IR (film): 3501, 2910, 1634, 1413, 1254, 1070, 747 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{15}H_{20}ClNNaO_2$: 304.1075, found: 304.1070.



Methyl 6-hydroxy-8-(indolin-1-yl)-8-oxooctanoate. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and methyl 6-oxohexanoate. The product was purified by column chromatography on silica gel (2:1 EtOAc/hexanes). 4.39 g (14.4 mmol, 72% yield). White solid.

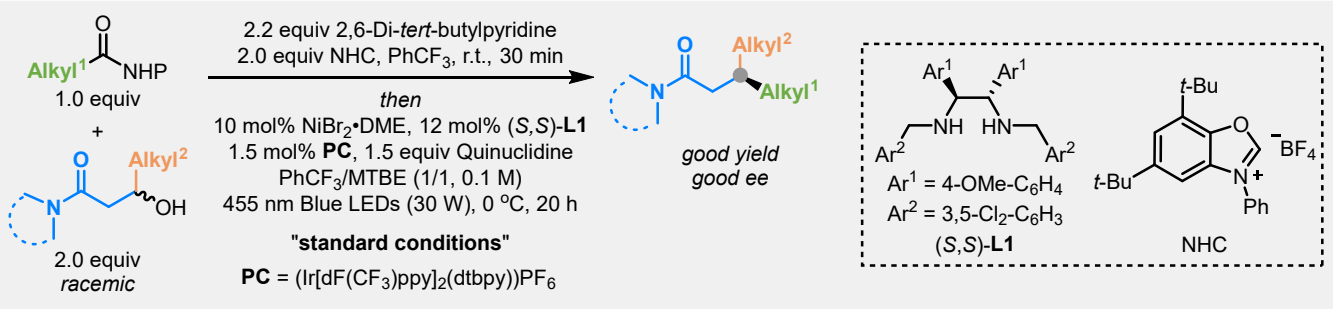
^1H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 2H), 7.03 (t, *J* = 7.7 Hz, 1H), 4.19 – 4.11 (m, 1H), 4.04 – 3.96 (m, 2H), 3.82 – 3.76 (m, 1H), 3.66 (s, 3H), 3.23 – 3.15 (m, 2H), 2.60 – 2.52 (m, 1H), 2.49 – 2.41 (m, 1H), 2.37 – 2.30 (m, 2H), 1.71 – 1.64 (m, 2H), 1.63 – 1.54 (m, 2H), 1.52 – 1.43 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 170.8, 142.4, 131.1, 127.5, 124.6, 124.0, 117.1, 67.6, 51.4, 47.9, 42.1, 35.9, 33.9, 27.9, 25.1, 24.8.

FT-IR (film): 3498, 2949, 1720, 1418, 1257, 1106, 757 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{17}H_{24}NO_4$: 306.1700, found: 306.1702.

IV. Catalytic Enantioconvergent Cross-Couplings



General Procedure 2 (GP-2): Enantioselective radical–radical cross-couplings of unactivated alkyl alcohols and *N*-hydroxyphthalimide (NHP) esters.

Preparation of the catalyst solution: In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a stir bar was charged with $NiBr_2$·DME (15.5 mg, 0.050 mmol, 10.0 mol%), (*S*,*S*)-**L1** (35.3 mg, 0.060 mmol, 12.0 mol%), and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (9.0 mg, 0.0075 mmol, 1.5 mol%). Anhydrous methyl *tert*-butyl ether (2.5 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 60 min at least, leading to a catalyst solution.

Preparation of the NHC-alcohol adduct solution: In a nitrogen-filled glovebox, a separate oven-dried 4 mL vial was charged with β-hydroxy amide (1.0 mmol, 2.0 equiv), NHC (395.2 mg, 1.0 mmol, 2.0 equiv), and a stir bar. (Trifluoromethyl)benzene (2.5 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (247.0 μL, 1.1 mmol, 2.2 equiv) was added dropwise, and the resulting solution was stirred at room temperature for another 30 min (a white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution.

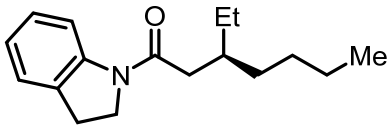
Cross-coupling: In a nitrogen-filled glovebox, an oven-dried 20 mL vial was charged with the NHP ester (0.50 mmol, 1.0 equiv), quinuclidine (83.5 mg, 0.75 mmol, 1.5 equiv), and a stir bar. The catalyst solution and NHC-alcohol adduct solution were transferred via syringe to the 20 mL reaction vial. The vial was transferred out of the glovebox and placed in an EtOH cooling bath at 0 °C for 5 min. Then the reaction was irradiated with blue LEDs (455 nm, 30 W) and was stirred at 0 °C for 20 hours.

Work-up: The reaction was stopped by ending the irradiation. The reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with EtOAc. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.

General Procedure 3 (GP-3): Enantioselective radical–radical cross-couplings of unactivated alkyl alcohols and NHP esters (30 hours).

The reaction time was extended from 20 to 30 hours, while following the same procedure as **GP-2**.

The racemic example was obtained by using 4,4'-di-*tert*-butyl-2,2'-bipyridine as the ligand without further optimization.



(*S*)-3-Ethyl-1-(indolin-1-yl)heptan-1-one (1). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl pentanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 95.8 mg, 74% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 14.9 min (major), 18.5 min (minor).

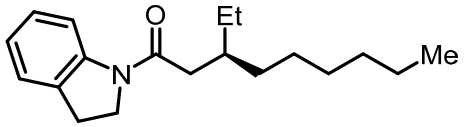
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 8.1 Hz, 2H), 7.00 (t, *J* = 8.0 Hz, 1H), 4.07 (t, *J* = 8.5 Hz, 2H), 3.19 (t, *J* = 8.4 Hz, 2H), 2.37 – 2.31 (m, 2H), 2.06 – 1.97 (m, 1H), 1.46 – 1.38 (m, 2H), 1.35 – 1.27 (m, 6H), 0.93 – 0.87 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.3, 143.2, 131.0, 127.5, 124.4, 123.4, 117.1, 48.2, 40.4, 35.7, 33.2, 28.9, 28.0, 26.3, 23.0, 14.1, 10.9.

FT-IR (film): 2920, 1665, 1472, 1396, 1267, 1062, 747 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{17}H_{25}NNaO$: 282.1828, found: 282.1823.

$[\alpha]^{16}_{D}$ = –13.2 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(indolin-1-yl)nonan-1-one (2). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 107.6 mg, 75% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 16.4 min (major), 22.1 min (minor).

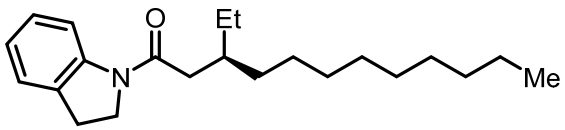
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 4.06 (t, *J* = 8.5 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.33 (d, *J* = 6.7 Hz, 2H), 2.09 – 1.95 (m, 1H), 1.44 – 1.39 (m, 2H), 1.38 – 1.33 (m, 2H), 1.31 – 1.26 (m, 8H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.3, 143.2, 131.0, 127.5, 124.4, 123.4, 117.1, 48.1, 40.4, 35.7, 33.4, 31.9, 29.6, 28.0, 26.7, 26.3, 22.6, 14.1, 10.9.

FT-IR (film): 2920, 1653, 1484, 1403, 1059, 750 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{19}H_{29}NNaO$: 310.2141, found: 310.2133.

$[\alpha]^{16}_{D}$ = –11.9 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(indolin-1-yl)dodecan-1-one (3). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl decanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 118.4 mg, 72% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (15% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 5.6 min (major), 6.5 min (minor).

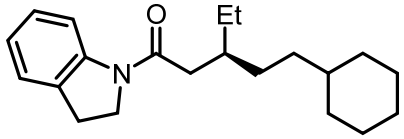
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 4.06 (t, *J* = 8.5 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.33 (d, *J* = 6.8 Hz, 2H), 2.04 – 1.99 (m, 1H), 1.44 – 1.39 (m, 2H), 1.37 – 1.33 (m, 3H), 1.30 – 1.23 (m, 13H), 0.90 (t, *J* = 7.5 Hz, 3H), 0.88 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.3, 143.2, 131.0, 127.5, 124.4, 123.4, 117.1, 48.1, 40.4, 35.7, 33.4, 31.9, 30.0, 29.7, 29.6, 29.3, 28.0, 26.7, 26.3, 22.7, 14.1, 10.9.

FT-IR (film): 2918, 1658, 1486, 1400, 1262, 1064, 752 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{22}H_{35}NNaO$: 352.2611, found: 352.2608.

$[\alpha]^{16}_{D}$ = –10.0 (c 0.5, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



(*S*)-5-Cyclohexyl-3-ethyl-1-(indolin-1-yl)pentan-1-one (4). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 3-cyclohexylpropanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 112.7 mg, 72% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 24.1 min (minor), 27.8 min (major).

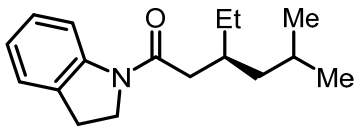
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 4.06 (t, *J* = 8.5 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.33 (d, *J* = 6.7 Hz, 2H), 2.01 – 1.95 (m, 1H), 1.72 – 1.66 (m, 6H), 1.65 – 1.59 (m, 1H), 1.43 – 1.35 (m, 4H), 1.22 – 1.14 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.88 – 0.82 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.3, 143.2, 131.0, 127.5, 124.4, 123.4, 117.1, 48.1, 40.3, 38.0, 35.9, 34.3, 33.5, 33.4, 30.5, 29.7, 28.0, 26.7, 26.4, 26.2, 10.8.

FT-IR (film): 2918, 1660, 1481, 1395, 1051, 747 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{21}H_{31}NNaO$: 336.2298, found: 336.2297.

$[\alpha]^{16}_{D}$ = –23.4 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(indolin-1-yl)-5-methylhexan-1-one (5). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 3-methylbutanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 81.6 mg, 63% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 15.1 min (major), 16.1 min (minor).

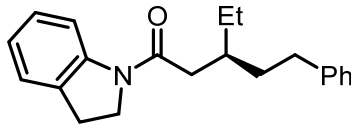
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 4.06 (t, *J* = 8.5 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.36 – 2.27 (m, 2H), 2.16 – 2.06 (m, 1H), 1.67 – 1.61 (m, 1H), 1.43 – 1.36 (m, 2H), 1.26 – 1.21 (m, 1H), 1.17 – 1.14 (m, 1H), 0.92 – 0.88 (m, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.2, 143.2, 131.0, 127.5, 124.4, 123.4, 117.1, 48.1, 43.2, 40.6, 33.3, 28.0, 26.5, 25.3, 23.0, 22.7, 10.6.

FT-IR (film): 2954, 1655, 1473, 1403, 1265, 1062, 744 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{17}H_{26}NO$: 260.2009, found: 260.2007.

$[\alpha]^{16}_{D}$ = +4.3 (c 0.5, $CHCl_3$); 92% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(indolin-1-yl)-5-phenylpentan-1-one (6). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 3-phenylpropanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 119.7 mg, 78% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (15% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 6.7 min (major), 7.5 min (minor).

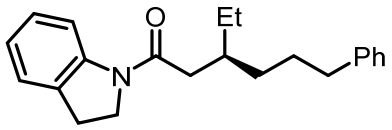
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.1 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.16 (m, 5H), 7.01 (t, *J* = 7.4 Hz, 1H), 4.10 – 3.94 (m, 2H), 3.17 (t, *J* = 8.5 Hz, 2H), 2.74 – 2.64 (m, 2H), 2.43 – 2.36 (m, 2H), 2.18 – 2.06 (m, 1H), 1.76 – 1.69 (m, 2H), 1.54 – 1.49 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.9, 143.1, 142.6, 131.0, 128.29, 128.27, 127.5, 125.6, 124.4, 123.4, 117.1, 48.1, 40.3, 35.6, 35.3, 33.2, 28.0, 26.2, 10.8.

FT-IR (film): 2970, 1653, 1598, 1398, 1265, 1067, 750, 698 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{21}H_{26}NO$: 308.2009, found: 308.2004.

$[\alpha]^{16}_{D}$ = –15.3 (c 0.5, $CHCl_3$); 92% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(indolin-1-yl)-6-phenylhexan-1-one (7). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 122.0 mg, 76% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 24.7 min (major), 28.4 min (minor).

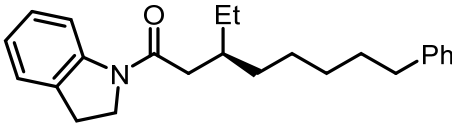
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.22 (m, 2H), 7.21 – 7.13 (m, 5H), 7.01 (t, *J* = 7.4 Hz, 1H), 4.03 (t, *J* = 8.5 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.42 – 2.28 (m, 2H), 2.17 – 2.06 (m, 1H), 1.75 – 1.60 (m, 2H), 1.48 – 1.38 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1, 143.2, 142.6, 131.0, 128.4, 128.2, 127.5, 125.6, 124.4, 123.4, 117.1, 48.1, 40.3, 36.2, 35.6, 33.1, 28.6, 28.0, 26.3, 10.9.

FT-IR (film): 2925, 1660, 1484, 1398, 1267, 752, 698 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{22}H_{28}NO$: 322.2165, found: 322.2167.

$[\alpha]^{16}_{D}$ = –7.7 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(indolin-1-yl)-8-phenyloctan-1-one (8). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 6-phenylhexanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 130.9 mg, 75% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 12.2 min (major), 17.7 min (minor).

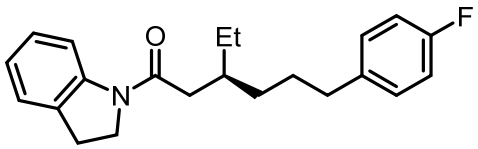
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.16 – 7.12 (m, 4H), 6.98 (t, *J* = 7.4 Hz, 1H), 4.02 (t, *J* = 8.5 Hz, 2H), 3.15 (t, *J* = 8.5 Hz, 2H), 2.61 – 2.55 (m, 2H), 2.33 – 2.29 (m, 2H), 2.03 – 1.98 (m, 1H), 1.63 – 1.58 (m, 2H), 1.43 – 1.37 (m, 2H), 1.36 – 1.31 (m, 5H), 1.28 – 1.26 (m, 1H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.2, 143.1, 142.8, 131.0, 128.3, 128.2, 127.5, 125.5, 124.4, 123.4, 117.0, 48.1, 40.3, 35.9, 35.7, 33.3, 31.5, 29.6, 28.0, 26.5, 26.3, 10.9.

FT-IR (film): 2931, 1655, 1484, 1395, 744, 687 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{24}H_{32}NO$: 350.2478, found: 350.2470.

$[\alpha]^{16}_{D}$ = –48.3 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-6-(4-fluorophenyl)-1-(indolin-1-yl)hexan-1-one (9). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-(4-fluorophenyl)butanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 110.2 mg, 65% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 14.8 min (minor), 15.4 min (major).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.16 (m, 2H), 7.12 (d, *J* = 5.7 Hz, 1H), 7.11 (d, *J* = 6.1 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 8.7 Hz, 2H), 4.03 (td, *J* = 8.9, 2.9 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.59 (td, *J* = 7.5, 1.9 Hz, 2H), 2.36 (dd, *J* = 15.6, 6.6 Hz, 1H), 2.30 (dd, *J* = 15.6, 6.8 Hz, 1H), 2.11 – 2.03 (m, 1H), 1.65 – 1.58 (m, 2H), 1.44 – 1.38 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 3H).

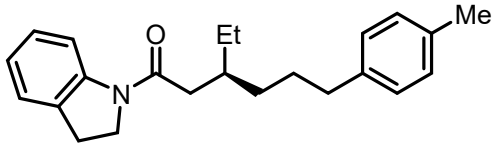
^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.0, 161.1 (d, *J* = 243.1 Hz), 143.1, 138.2 (d, *J* = 3.2 Hz), 131.0, 129.6 (d, *J* = 7.7 Hz), 127.5, 124.4, 123.4, 117.0, 114.9 (d, *J* = 21.0 Hz), 48.1, 40.2, 35.5, 35.2, 32.9, 28.7, 28.0, 26.3, 10.9.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -118.1.

FT-IR (film): 2967, 2899, 1653, 1507, 1484, 1400, 1218, 1064, 755 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{22}H_{27}FNO$: 340.2071, found: 340.2070.

$[\alpha]^{16}_{D}$ = –42.0 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(indolin-1-yl)-6-(*p*-tolyl)hexan-1-one (10). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-(*p*-tolyl)butanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 132.3 mg, 79% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 15.6 min (major), 16.5 min (minor).

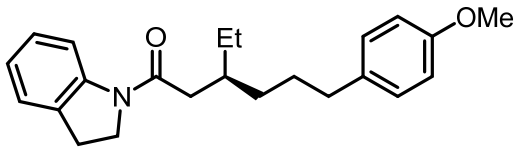
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.08 (s, 4H), 7.02 (t, *J* = 7.1 Hz, 1H), 4.07 – 4.00 (m, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.59 (td, *J* = 7.5, 2.7 Hz, 2H), 2.38 – 2.33 (m, 2H), 2.32 (s, 3H), 2.10 – 2.05 (m, 1H), 1.67 – 1.62 (m, 2H), 1.47 – 1.41 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.1, 143.1, 139.5, 135.0, 131.0, 128.9, 128.2, 127.5, 124.4, 123.4, 117.1, 48.1, 40.2, 35.7, 35.6, 33.1, 28.7, 28.0, 26.2, 20.9, 10.9.

FT-IR (film): 2970, 2915, 1663, 1484, 1400, 1262, 1054, 750 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{30}NO$: 336.2322, found: 336.2331.

$[\alpha]^{16}_D$ = –11.1 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(indolin-1-yl)-6-(4-methoxyphenyl)hexan-1-one (11). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-(4-methoxyphenyl)butanoate. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Yellow oil, 131.6 mg, 75% yield, 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (15% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 6.1 min (major), 6.8 min (minor).

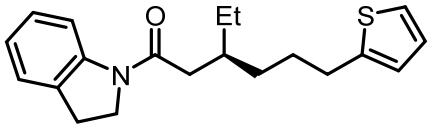
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.01 (t, *J* = 6.9 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 2H), 4.06 – 4.00 (m, 2H), 3.77 (s, 3H), 3.17 (t, *J* = 8.5 Hz, 2H), 2.59 – 2.53 (m, 2H), 2.33 (t, *J* = 7.1 Hz, 2H), 2.10 – 2.03 (m, 1H), 1.68 – 1.59 (m, 2H), 1.47 – 1.36 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.1, 157.6, 143.1, 134.7, 131.0, 129.2, 127.5, 124.4, 123.4, 117.0, 113.6, 55.2, 48.1, 40.2, 35.5, 35.2, 33.0, 28.8, 28.0, 26.2, 10.9.

FT-IR (film): 2964, 1658, 1510, 1403, 1244, 1038, 752 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{30}NO_2$: 352.2271, found: 352.2272.

$[\alpha]^{16}_D$ = –9.5 (c 0.5, $CHCl_3$); 93% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(indolin-1-yl)-6-(thiophen-2-yl)hexan-1-one (12). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-(thiophen-2-yl)butanoate. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Yellow oil, 124.3 mg, 76% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 20.0 min (major), 27.4 min (minor).

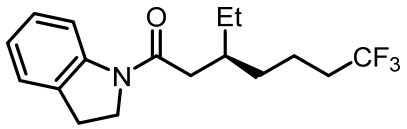
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.16 (m, 2H), 7.09 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.79 – 6.76 (m, 1H), 4.05 (t, *J* = 8.5 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.36 – 2.33 (m, 2H), 2.12 – 2.02 (m, 1H), 1.76 – 1.69 (m, 2H), 1.49 – 1.40 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 145.5, 143.1, 131.0, 127.5, 126.6, 124.4, 124.0, 123.4, 122.8, 117.1, 48.1, 40.2, 35.5, 32.9, 30.1, 29.0, 28.0, 26.3, 10.9.

FT-IR (film): 2964, 1653, 1479, 1400, 1262, 1075, 753, 690 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{20}H_{26}NOS$: 328.1730, found: 328.1723.

$[\alpha]^{16}_D$ = –29.2 (c 0.5, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-7,7,7-trifluoro-1-(indolin-1-yl)heptan-1-one (13). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 5,5,5-trifluoropentanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 101.7 mg, 65% yield, 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (15% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 8.3 min (major), 9.0 min (minor).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 4.05 (t, *J* = 8.5 Hz, 2H), 3.19 (t, *J* = 8.4 Hz, 2H), 2.40 (dd, *J* = 15.8, 6.2 Hz, 1H), 2.30 (dd, *J* = 15.8, 7.1 Hz, 1H), 2.16 – 2.02 (m, 3H), 1.65 – 1.55 (m, 2H), 1.47 – 1.39 (m, 4H), 0.92 (t, *J* = 7.4 Hz, 3H).

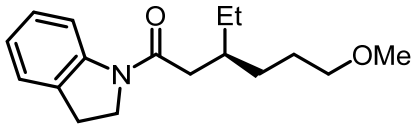
^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.7, 143.0, 131.0, 127.5, 127.2 (q, *J* = 276.5 Hz), 124.5, 123.5, 117.0, 48.1, 39.9, 35.2, 33.9 (q, *J* = 28.3 Hz), 32.5, 28.0, 26.0, 19.2 (q, *J* = 3.2 Hz), 10.8.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -66.3.

FT-IR (film): 2967, 1658, 1486, 1405, 1252, 1054, 750 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{17}H_{23}F_3NO$: 314.1726, found: 314.1723.

$[\alpha]^{16}_D$ = –25.0 (c 0.5, $CHCl_3$); 93% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(indolin-1-yl)-6-methoxyhexan-1-one (14). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-methoxybutanoate. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Yellow oil, 101.8 mg, 74% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 10.1 min (major), 12.3 min (minor).

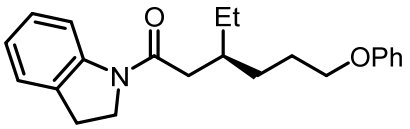
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 4.05 (t, *J* = 8.5 Hz, 2H), 3.37 (td, *J* = 6.6, 2.1 Hz, 2H), 3.32 (s, 3H), 3.18 (t, *J* = 8.4 Hz, 2H), 2.38 – 2.32 (m, 2H), 2.07 – 2.00 (m, 1H), 1.63 – 1.57 (m, 2H), 1.46 – 1.40 (m, 4H), 0.91 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.0, 143.1, 131.0, 127.5, 124.4, 123.4, 117.0, 73.1, 58.5, 48.1, 40.2, 35.5, 29.8, 28.0, 26.8, 26.3, 10.8.

FT-IR (film): 2931, 1658, 1478, 1398, 1114, 751 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{17}H_{26}NO_2$: 276.1958, found: 276.1952.

$[\alpha]^{16}_D$ = –13.4 (c 0.5, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(indolin-1-yl)-6-phenoxyhexan-1-one (15). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenoxybutanoate. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Yellow oil, 119.6 mg, 71% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (15% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 5.7 min (minor), 6.2 min (major).

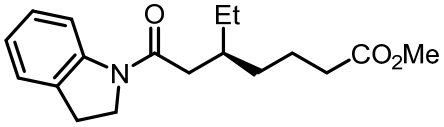
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.1 Hz, 1H), 7.28 (dd, *J* = 8.8, 7.2 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 7.4 Hz, 2H), 4.07 (t, *J* = 8.5 Hz, 2H), 4.02 – 3.96 (m, 2H), 3.20 (t, *J* = 8.5 Hz, 2H), 2.42 – 2.38 (m, 2H), 2.17 – 2.08 (m, 1H), 1.88 – 1.81 (m, 2H), 1.61 – 1.54 (m, 2H), 1.51 – 1.46 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 159.0, 143.1, 131.0, 129.4, 127.5, 124.4, 123.5, 120.5, 117.1, 114.5, 68.0, 48.1, 40.2, 35.5, 29.8, 28.0, 26.5, 26.3, 10.9.

FT-IR (film): 2938, 1598, 1481, 1403, 1234, 756, 690 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{28}NO_2$: 338.2115, found: 338.2116.

$[\alpha]^{16}_D$ = –26.2 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



Methyl (*S*)-5-ethyl-7-(indolin-1-yl)-7-oxoheptanoate (16). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl methyl glutarate. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). Yellow oil, 115.1 mg, 76% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (15% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 6.9 min (minor), 7.6 min (major).

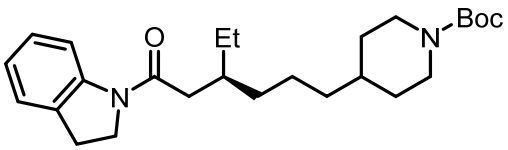
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 7.9 Hz, 1H), 7.20 – 7.12 (m, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 4.05 (t, *J* = 8.9 Hz, 2H), 3.65 (s, 3H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.39 – 2.26 (m, 4H), 2.08 – 2.00 (m, 1H), 1.70 – 1.63 (m, 2H), 1.45 – 1.37 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.2, 171.0, 143.1, 131.1, 127.5, 124.5, 123.5, 117.1, 51.5, 48.1, 40.1, 35.4, 34.3, 32.9, 28.0, 26.2, 22.1, 10.9.

FT-IR (film): 2957, 1736, 1653, 1478, 1408, 1169, 752 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{18}H_{26}NO_3$: 304.1907, found: 304.1907.

$[\alpha]^{16}_D$ = –22.1 (c 0.5, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



***tert*-Butyl (*S*)-4-(4-ethyl-6-(indolin-1-yl)-6-oxohexyl)piperidine-1-carboxylate (17).** The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and *tert*-butyl 4-(4-((1,3-dioxoisoindolin-2-yl)oxy)-4-oxobutyl)piperidine-1-carboxylate. The product was purified by column chromatography on silica gel (1:3 EtOAc/hexanes). Yellow oil, 145.5 mg, 68% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (20% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 10.6 min (minor), 13.5 min (major).

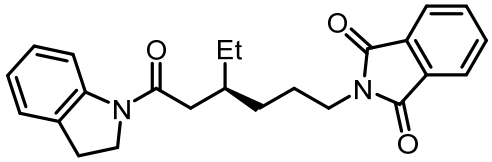
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.02 – 6.96 (m, 1H), 4.18 – 4.11 (m, 1H), 4.04 (t, *J* = 8.4 Hz, 2H), 3.17 (t, *J* = 8.4 Hz, 2H), 2.63 (s, 2H), 2.34 – 2.27 (m, 2H), 2.02 – 1.97 (m, 1H), 1.64 – 1.59 (m, 2H), 1.44 (s, 9H), 1.41 – 1.38 (m, 2H), 1.34 – 1.30 (m, 4H), 1.24 – 1.20 (m, 2H), 1.11 – 1.01 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.1, 154.8, 143.1, 131.0, 127.4, 124.4, 123.4, 117.0, 79.0, 48.1, 44.1, 40.2, 36.7, 35.9, 35.6, 33.5, 32.1, 28.4, 27.9, 26.2, 25.6, 23.6, 12.5, 10.8.

FT-IR (film): 2970, 2920, 1660, 1484, 1403, 1236, 1161, 755 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{26}H_{41}N_2O_3$: 429.3112, found: 429.3102.

$[\alpha]^{16}_{D}$ = –22.6 (c 0.5, $CHCl_3$); 92% ee, from (*S*,*S*)-**L1**.



(*S*)-2-(4-Ethyl-6-(indolin-1-yl)-6-oxohexyl)isoindoline-1,3-dione (18). The title compound was synthesized according to **GP-3** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-(1,3-dioxoisoindolin-2-yl)butanoate. The product was purified by column chromatography on silica gel (1:2 EtOAc/hexanes). Yellow oil, 105.3 mg, 54% yield, 87% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 15.8 min (major), 22.0 min (minor).

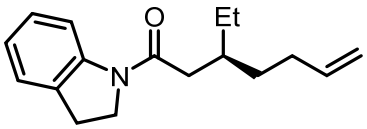
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.67 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.18 – 7.10 (m, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 4.04 (t, *J* = 8.8 Hz, 2H), 3.67 (t, *J* = 7.3 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.39 – 2.26 (m, 2H), 2.12 – 1.99 (m, 1H), 1.76 – 1.66 (m, 2H), 1.46 – 1.38 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 168.4, 143.1, 133.8, 132.1, 131.0, 127.4, 124.4, 123.4, 123.1, 117.0, 48.1, 40.0, 38.2, 35.2, 30.4, 28.0, 26.2, 25.6, 10.8.

FT-IR (film): 3301, 2974, 2893, 1649, 1386, 1059, 700 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{24}H_{26}N_2NaO_3$: 413.1836, found: 413.1824.

$[\alpha]^{16}_D$ = –17.9 (c 0.5, $CHCl_3$); 87% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(indolin-1-yl)hept-6-en-1-one (19). The title compound was synthesized according to **GP-3** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl pent-4-enoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 87.4 mg, 68% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 15.0 min (minor), 19.2 min (major).

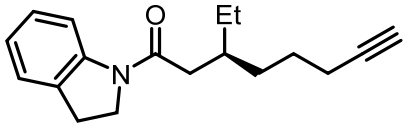
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.9 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 5.91 – 5.76 (m, 1H), 5.02 (dd, *J* = 17.2, 1.8 Hz, 1H), 4.94 (dd, *J* = 10.2, 2.0 Hz, 1H), 4.06 (t, *J* = 8.5 Hz, 2H), 3.19 (t, *J* = 8.5 Hz, 2H), 2.38 – 2.32 (m, 2H), 2.18 – 2.05 (m, 3H), 1.52 – 1.39 (m, 4H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 143.2, 138.9, 131.0, 127.5, 124.4, 123.4, 117.1, 114.4, 48.2, 40.2, 35.3, 32.7, 31.0, 28.0, 26.2, 10.8.

FT-IR (film): 2925, 1658, 1478, 1400, 903, 752 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{17}H_{23}NNaO$: 280.1672, found: 280.1664.

$[\alpha]^{16}_D$ = –20.1 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(indolin-1-yl)oct-7-yn-1-one (20). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl hex-5-ynoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 95.5 mg, 71% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 22.8 min (major), 24.9 min (minor).

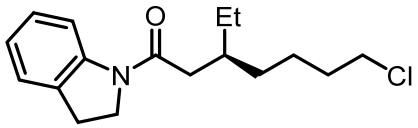
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 4.06 (t, *J* = 8.5 Hz, 2H), 3.19 (t, *J* = 8.5 Hz, 2H), 2.37 – 2.30 (m, 2H), 2.21 – 2.16 (m, 2H), 2.07 – 2.02 (m, 1H), 1.93 (t, *J* = 2.6 Hz, 1H), 1.59 – 1.54 (m, 2H), 1.50 – 1.45 (m, 2H), 1.45 – 1.39 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.9, 143.1, 131.0, 127.5, 124.5, 123.5, 117.1, 84.5, 68.3, 48.1, 40.2, 35.3, 32.6, 28.0, 26.2, 25.7, 18.7, 10.8.

FT-IR (film): 2959, 1655, 1486, 1405, 1265, 1072, 755 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{18}H_{24}NO$: 270.1852, found: 270.1844.

$[\alpha]^{16}_D$ = –28.4 (c 0.5, $CHCl_3$); 89% ee, from (*S*,*S*)-**L1**.



(*S*)-7-Chloro-3-ethyl-1-(indolin-1-yl)heptan-1-one (21). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 5-chloropentanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 111.3 mg, 76% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 13.5 min (minor), 16.5 min (major).

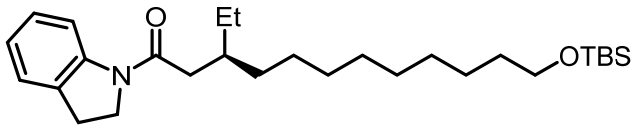
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 4.06 (t, *J* = 8.5 Hz, 2H), 3.54 (t, *J* = 6.6 Hz, 2H), 3.19 (t, *J* = 8.5 Hz, 2H), 2.40 – 2.29 (m, 2H), 2.07 – 1.98 (m, 1H), 1.81 – 1.74 (m, 2H), 1.49 – 1.39 (m, 6H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 143.1, 131.0, 127.5, 124.5, 123.5, 117.1, 48.2, 45.0, 40.2, 35.5, 32.7, 32.6, 28.0, 26.3, 23.9, 10.9.

FT-IR (film): 2933, 1658, 1593, 1481, 1401, 757 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{17}H_{24}ClNNaO$: 316.1439, found: 316.1438.

$[\alpha]^{16}_D$ = –11.8 (c 0.5, $CHCl_3$); 92% ee, from (*S*,*S*)-**L1**.



(*S*)-12-((*tert*-Butyldimethylsilyl)oxy)-3-ethyl-1-(indolin-1-yl)dodecan-1-one (22). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 10-((*tert*-butyldimethylsilyl)oxy)decanoate. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Yellow oil, 158.4 mg, 69% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (15% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 7.0 min (minor), 7.6 min (major).

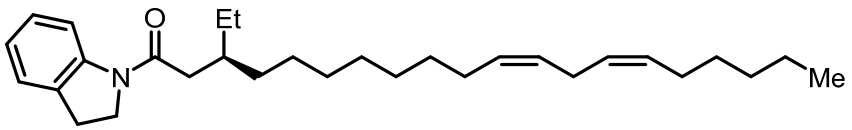
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.15 (m, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 4.05 (t, *J* = 8.4 Hz, 2H), 3.59 (t, *J* = 6.7 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.33 (d, *J* = 6.7 Hz, 2H), 2.05 – 1.97 (m, 1H), 1.50 (t, *J* = 7.1 Hz, 2H), 1.44 – 1.39 (m, 2H), 1.37 – 1.33 (m, 2H), 1.32 – 1.29 (m, 4H), 1.29 – 1.24 (m, 8H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.90 – 0.89 (m, 9H), 0.05 (s, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.2, 143.1, 131.0, 127.4, 124.4, 123.4, 117.0, 63.3, 48.1, 40.3, 35.7, 33.4, 32.8, 29.9, 29.6, 29.4, 28.0, 26.7, 26.3, 25.9, 25.7, 18.3, 10.9, -5.3.

FT-IR (film): 2925, 2853, 1663, 1484, 1400, 1098, 830, 755 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{28}H_{50}NO_2Si$: 460.3605, found: 460.3609.

$[\alpha]^{16}_D$ = –14.9 (c 0.5, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



(*S*,11*Z*,14*Z*)-3-Ethyl-1-(indolin-1-yl)icosa-11,14-dien-1-one (23). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl (9*Z*,12*Z*)-octadeca-9,12-dienoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 150.8 mg, 69% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 9.8 min (minor), 10.9 min (major).

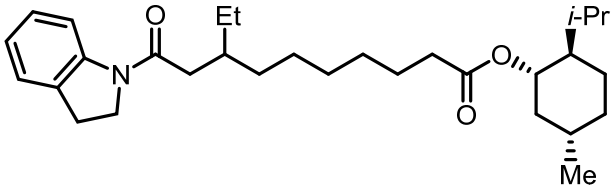
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 5.42 – 5.29 (m, 4H), 4.08 – 4.02 (m, 2H), 3.18 (t, *J* = 8.6 Hz, 2H), 2.77 (t, *J* = 7.0 Hz, 2H), 2.36 – 2.31 (m, 2H), 2.08 – 2.03 (m, 4H), 2.02 – 1.97 (m, 1H), 1.44 – 1.39 (m, 3H), 1.36 – 1.33 (m, 5H), 1.31 – 1.27 (m, 10H), 1.27 – 1.24 (m, 2H), 0.92 – 0.88 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.3, 143.2, 131.0, 130.2, 130.1, 127.9, 127.5, 124.4, 123.4, 117.1, 48.1, 40.4, 35.7, 33.4, 31.5, 29.9, 29.6, 29.5, 29.32, 29.28, 28.0, 27.20, 27.16, 26.7, 26.3, 25.6, 22.5, 14.0, 10.9.

FT-IR (film): 2923, 1660, 1484, 1402, 750 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{30}H_{47}NNaO$: 460.3550, found: 460.3544.

$[\alpha]^{16}_{D}$ = –12.1 (c 0.5, $CHCl_3$); 89% ee, from (*S*,*S*)-**L1**.



(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 8-ethyl-10-(indolin-1-yl)-10-oxodecanoate (24, 25). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1-(1,3-dioxoisoindolin-2-yl) 8-((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl) octanedioate. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Yellow oil; (*S*,*S*)-**L1**: 150.1 mg, 64% yield, 95:5 dr; (*R*,*R*)-**L1**: 147.7 mg, 63% yield, 5:95 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALPAK IG-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 15.4 min (major), 16.7 min (minor).

NMR data for the product from (*S*,*S*)-**L1**:

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.15 (m, 2H), 6.99 (t, *J* = 7.3 Hz, 1H), 4.71 – 4.59 (m, 1H), 4.06 (t, *J* = 8.3 Hz, 2H), 3.18 (t, *J* = 8.4 Hz, 2H), 2.33 (d, *J* = 6.7 Hz, 2H), 2.26 (t, *J* = 7.5 Hz, 2H), 2.04 – 1.94 (m, 2H), 1.89 – 1.82 (m, 1H), 1.71 – 1.64 (m, 4H), 1.63 – 1.58

(m, 2H), 1.52 – 1.45 (m, 1H), 1.43 – 1.39 (m, 2H), 1.35 – 1.27 (m, 6H), 1.09 – 1.01 (m, 2H), 0.94 – 0.84 (m, 11H), 0.75 (d, J = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.4, 171.2, 143.2, 131.0, 127.5, 124.4, 123.4, 117.1, 73.8, 48.1, 47.0, 40.9, 40.3, 35.7, 34.7, 34.3, 33.4, 31.3, 29.6, 29.1, 28.0, 26.5, 26.3, 26.2, 25.1, 23.4, 22.0, 20.7, 16.3, 10.9.

NMR data for the product from (*R*,*R*)-**L1**:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, J = 8.0 Hz, 1H), 7.18 (t, J = 8.1 Hz, 2H), 6.99 (t, J = 7.4 Hz, 1H), 4.66 (td, J = 10.9, 4.4 Hz, 1H), 4.06 (t, J = 8.5 Hz, 2H), 3.18 (t, J = 8.4 Hz, 2H), 2.35 – 2.31 (m, 2H), 2.26 (t, J = 7.5 Hz, 2H), 2.03 – 1.94 (m, 2H), 1.89 – 1.82 (m, 1H), 1.70 – 1.65 (m, 3H), 1.63 – 1.56 (m, 3H), 1.51 – 1.46 (m, 1H), 1.43 – 1.38 (m, 2H), 1.34 – 1.29 (m, 6H), 1.10 – 0.98 (m, 2H), 0.96 – 0.91 (m, 2H), 0.90 – 0.87 (m, 9H), 0.75 (d, J = 6.9 Hz, 3H).

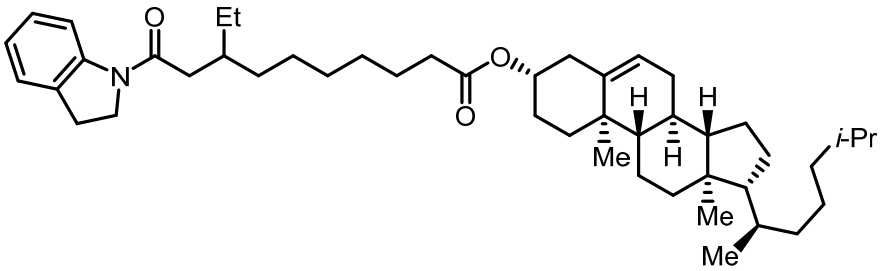
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.7, 171.5, 143.5, 131.3, 127.8, 124.7, 123.7, 117.4, 74.2, 48.5, 47.3, 41.3, 40.7, 36.0, 35.0, 34.6, 33.7, 31.7, 30.0, 29.9, 29.4, 28.3, 26.9, 26.61, 26.57, 25.4, 23.8, 22.3, 21.0, 16.6, 11.2.

FT-IR (film): 2923, 2858, 1728, 1660, 1486, 1457, 1400, 1174, 755 cm^{-1}.

HRMS (ESI-MS) m/z [M+H]$^{+}$ calcd for $C_{30}H_{48}NO_3$: 470.3629, found: 470.3633.

$[\alpha]^{16}_{D}$ = –110.3 (c 0.5, $CHCl_3$); 95:5 dr, from (*S*,*S*)-**L1**.

$[\alpha]^{16}_{D}$ = –73.6 (c 0.5, $CHCl_3$); 5:95 dr, from (*R*,*R*)-**L1**.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 8-ethyl-10-(indolin-1-yl)-10-oxodecanoate (26, 27). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1-((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl) 8-(1,3-dioxoisoindolin-2-yl) octanedioate. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). Yellow oil; (*S*,*S*)-**L1**: 199.4 mg, 57% yield, 95:5 dr; (*R*,*R*)-**L1**: 209.9 mg, 60% yield, 5:95 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALPAK AD-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 31.7 min (major), 49.5 min (minor).

NMR data for the product from (*S*,*S*)-**L1**:

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, J = 8.1 Hz, 1H), 7.19 – 7.14 (m, 2H), 6.99 (t, J = 7.4 Hz, 1H), 5.36 (d, J = 5.0 Hz, 1H), 4.65 – 4.56 (m, 1H), 4.05 (t, J = 8.5 Hz, 2H), 3.17 (t, J = 8.5 Hz, 2H), 2.33 – 2.29 (m, 4H), 2.25 (t, J = 7.5 Hz, 2H), 2.02 – 1.97 (m, 2H), 1.95 – 1.92 (m, 1H), 1.86 – 1.80 (m, 2H), 1.61 – 1.58 (m, 3H), 1.57 – 1.53 (m, 2H), 1.51 – 1.47 (m, 3H), 1.46 – 1.44 (m, 1H), 1.43 –

1.39 (m, 3H), 1.35 – 1.32 (m, 3H), 1.32 – 1.29 (m, 6H), 1.27 – 1.24 (m, 2H), 1.16 – 1.11 (m, 4H), 1.10 – 1.06 (m, 2H), 1.02 – 1.00 (m, 4H), 1.00 – 0.97 (m, 2H), 0.97 – 0.93 (m, 1H), 0.92 – 0.89 (m, 6H), 0.89 – 0.88 (m, 1H), 0.87 (d, *J* = 2.8 Hz, 3H), 0.85 (d, *J* = 2.8 Hz, 3H), 0.67 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.2, 171.1, 143.1, 139.6, 131.0, 127.4, 124.4, 123.4, 122.5, 117.0, 73.6, 56.6, 56.1, 49.9, 48.1, 42.2, 40.3, 39.7, 39.5, 38.1, 36.9, 36.5, 36.1, 35.7, 35.6, 34.6, 33.3, 31.83, 31.78, 29.5, 29.1, 28.2, 28.0, 27.9, 27.7, 26.5, 26.2, 25.0, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8, 10.9.

NMR data for the product from (*R*,*R*)-**L1**:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 8.2 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 5.40 – 5.34 (m, 1H), 4.65 – 4.58 (m, 1H), 4.05 (t, *J* = 8.4 Hz, 2H), 3.18 (t, *J* = 8.4 Hz, 2H), 2.36 – 2.29 (m, 4H), 2.26 (t, *J* = 7.5 Hz, 2H), 2.04 – 1.98 (m, 2H), 1.88 – 1.81 (m, 3H), 1.63 – 1.54 (m, 5H), 1.52 – 1.46 (m, 4H), 1.43 – 1.40 (m, 3H), 1.36 – 1.30 (m, 9H), 1.28 – 1.25 (m, 2H), 1.17 – 1.08 (m, 7H), 1.03 – 1.00 (m, 4H), 1.00 – 0.96 (m, 2H), 0.95 – 0.92 (m, 3H), 0.92 – 0.90 (m, 3H), 0.89 – 0.87 (m, 4H), 0.87 – 0.85 (m, 3H), 0.68 (s, 3H).

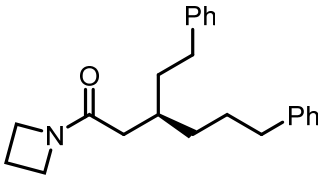
^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.1, 170.1, 142.1, 138.7, 129.9, 126.4, 123.4, 122.3, 121.5, 116.0, 72.6, 55.6, 55.1, 49.0, 47.1, 41.3, 39.3, 38.7, 38.5, 37.1, 35.9, 35.5, 35.1, 34.7, 34.6, 33.6, 32.4, 30.84, 30.80, 28.6, 28.5, 28.0, 27.2, 27.0, 26.9, 26.8, 25.5, 25.3, 24.0, 23.2, 22.8, 21.8, 21.5, 20.0, 18.2, 17.7, 10.8, 9.8.

FT-IR (film): 2938, 1733, 1660, 1405, 1049, 752 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+K]$^{+}$ calcd for $C_{47}H_{73}KNO_3$: 738.5222, found: 738.5236.

$[\alpha]^{16}_{D}$ = –82.7 (c 0.5, $CHCl_3$); 95:5 dr, from (*S*,*S*)-**L1**.

$[\alpha]^{16}_{D}$ = –124.8 (c 0.5, $CHCl_3$); 5:95 dr, from (*R*,*R*)-**L1**.



(*R*)-1-(Azetidin-1-yl)-3-phenethyl-6-phenylhexan-1-one (28). The title compound was synthesized according to **GP-2** from 1-(azetidin-1-yl)-3-hydroxy-5-phenylpentan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:2 EtOAc/hexanes). Yellow oil, 118.9 mg, 71% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 9.6 min (major), 14.5 min (minor).

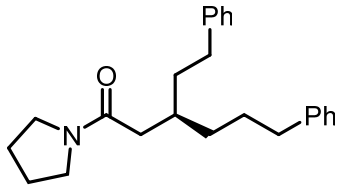
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.43 (m, 4H), 7.38 – 7.33 (m, 6H), 4.25 – 4.20 (m, 2H), 4.17 (t, *J* = 7.8 Hz, 2H), 2.81 – 2.73 (m, 4H), 2.44 – 2.35 (m, 2H), 2.23 – 2.16 (m, 3H), 1.86 – 1.77 (m, 4H), 1.63 – 1.57 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.6, 142.53, 142.50, 128.4, 128.28, 128.26, 128.2, 125.6, 50.1, 47.6, 36.1, 35.9, 35.7, 34.4, 33.4, 33.0, 28.4, 14.9.

FT-IR (film): 3301, 2974, 2893, 1649, 1386, 1059, 700 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{23}H_{30}NO$: 336.2322, found: 336.2321.

$[\alpha]^{16}_D$ = +15.6 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



(*R*)-3-Phenethyl-6-phenyl-1-(pyrrolidin-1-yl)hexan-1-one (29). The title compound was synthesized according to **GP-2** from 3-hydroxy-5-phenyl-1-(pyrrolidin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:2 EtOAc/hexanes). Yellow oil, 130.9 mg, 75% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 13.0 min (major), 17.2 min (minor).

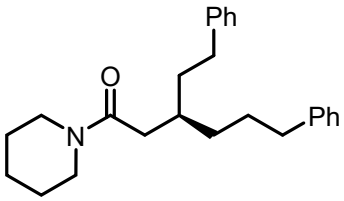
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.42 (m, 4H), 7.38 – 7.32 (m, 6H), 3.64 (t, *J* = 6.8 Hz, 2H), 3.53 (t, *J* = 6.7 Hz, 2H), 2.81 – 2.75 (m, 4H), 2.42 (d, *J* = 6.8 Hz, 2H), 2.32 – 2.24 (m, 1H), 2.13 – 2.06 (m, 2H), 2.04 – 1.97 (m, 2H), 1.87 – 1.79 (m, 4H), 1.66 – 1.59 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1, 142.64, 142.55, 128.34, 128.27, 128.23, 128.19, 125.60, 125.58, 46.7, 45.6, 39.5, 36.1, 35.8, 34.3, 33.5, 33.1, 28.4, 26.1, 24.3.

FT-IR (film): 3303, 2965, 2888, 1652, 1384, 1051, 710 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{24}H_{31}NNaO$: 372.2298, found: 372.2295.

$[\alpha]^{16}_D$ = +10.0 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



(*R*)-3-Phenethyl-6-phenyl-1-(piperidin-1-yl)hexan-1-one (30). The title compound was synthesized according to **GP-2** from 3-hydroxy-5-phenyl-1-(piperidin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:2 EtOAc/hexanes). Yellow oil, 137.9 mg, 76% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 14.6 min (major), 17.7 min (minor).

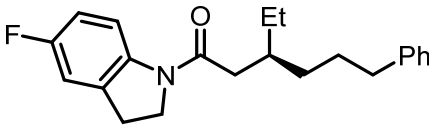
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.24 (m, 4H), 7.19 – 7.14 (m, 6H), 3.58 – 3.48 (m, 2H), 3.34 – 3.29 (m, 2H), 2.63 – 2.57 (m, 4H), 2.32 – 2.27 (m, 2H), 2.00 – 1.95 (m, 1H), 1.67 – 1.62 (m, 4H), 1.61 – 1.57 (m, 2H), 1.51 – 1.46 (m, 3H), 1.45 – 1.40 (m, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.7, 142.5, 128.4, 128.3, 128.24, 128.21, 125.62, 125.60, 46.8, 42.6, 38.0, 36.1, 35.6, 34.4, 33.4, 32.9, 28.4, 26.5, 25.6, 24.5.

FT-IR (film): 2923, 1637, 1437, 1254, 1059, 695 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+K]^+$ calcd for $C_{25}H_{33}KNO$: 402.2194, found: 402.2191.

$[\alpha]^{16}_D$ = +25.7 (c 0.5, $CHCl_3$); 92% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Ethyl-1-(5-fluoroindolin-1-yl)-6-phenylhexan-1-one (31). The title compound was synthesized according to **GP-2** from 1-(5-fluoroindolin-1-yl)-3-hydroxypentan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 123.7 mg, 73% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 16.9 min (major), 24.9 min (minor).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.21 (dd, *J* = 9.7, 5.0 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.18 – 7.13 (m, 3H), 6.86 (t, *J* = 8.1 Hz, 2H), 4.03 (td, *J* = 8.8, 2.8 Hz, 2H), 3.14 (t, *J* = 8.5 Hz, 2H), 2.61 (td, *J* = 7.5, 2.3 Hz, 2H), 2.35 – 2.24 (m, 2H), 2.07 – 2.01 (m, 1H), 1.67 – 1.62 (m, 2H), 1.45 – 1.38 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 3H).

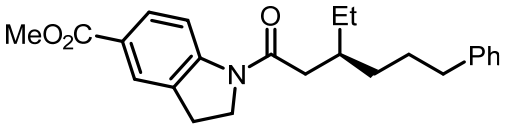
^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.8, 159.1 (d, *J* = 241.9 Hz), 142.6, 139.3, 133.0 (d, *J* = 8.5 Hz), 128.3, 128.2, 125.6, 117.7 (d, *J* = 8.0 Hz), 113.6 (d, *J* = 22.5 Hz), 111.6 (d, *J* = 23.9 Hz), 48.3, 40.0, 36.1, 35.6, 33.0, 28.6, 27.9, 26.2, 10.8.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -119.7.

FT-IR (film): 2931, 1655, 1484, 1398, 1239, 747, 696 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{27}FNO$: 340.2071, found: 340.2070.

$[\alpha]^{16}_D$ = –41.9 (c 0.5, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



Methyl (*S*)-1-(3-ethyl-6-phenylhexanoyl)indoline-5-carboxylate (32). The title compound was synthesized according to **GP-2** from methyl 1-(3-hydroxypentanoyl)indoline-5-carboxylate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). Yellow oil, 123.2 mg, 65% yield, 88% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 17.8 min (major), 25.4 min (minor).

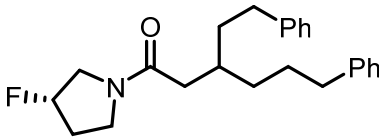
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.84 (s, 1H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.19 – 7.14 (m, 3H), 4.10 – 4.05 (m, 2H), 3.89 (s, 3H), 3.19 (t, *J* = 8.6 Hz, 2H), 2.66 – 2.60 (m, 2H), 2.37 – 2.31 (m, 2H), 2.08 – 2.04 (m, 1H), 1.68 – 1.61 (m, 2H), 1.45 – 1.40 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.6, 166.8, 147.1, 142.5, 131.2, 130.1, 128.3, 128.2, 125.8, 125.6, 125.0, 116.2, 51.9, 48.5, 40.3, 36.1, 35.4, 33.0, 28.6, 27.5, 26.2, 10.8.

FT-IR (film): 2970, 1715, 1395, 1260, 1078, 700 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{24}H_{30}NO_3$: 380.2220, found: 380.2214.

$[\alpha]^{16}_D$ = –18.4 (c 0.5, $CHCl_3$); 88% ee, from (*S*,*S*)-**L1**.



1-((*S*)-3-Fluoropyrrolidin-1-yl)-3-phenethyl-6-phenylhexan-1-one (33, 34). The title compound was synthesized according to **GP-2** from 1-((*S*)-3-fluoropyrrolidin-1-yl)-3-hydroxy-5-phenylpentan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:2 EtOAc/hexanes). (*S*,*S*)-**L1**: 122.9 mg, 67% yield, 96:4 dr; (*R*,*R*)-**L1**: 115.6 mg, 63% yield, 4:96 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALPAK AD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 10.9 min (major), 14.9 min (minor).

NMR data for the product from (*S*,*S*)-**L1**:

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.25 (m, 4H), 7.18 – 7.14 (m, 6H), 5.29 – 5.16 (m, 1H), 3.93 – 3.76 (m, 1H), 3.68 – 3.44 (m, 3H), 2.62 – 2.58 (m, 4H), 2.32 – 2.18 (m, 3H), 2.12 – 2.06 (m, 1H), 2.02 – 1.87 (m, 1H), 1.68 – 1.62 (m, 4H), 1.48 – 1.41 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.3 (d, *J* = 32.9 Hz), 142.5 (d, *J* = 3.3 Hz), 128.4, 128.30, 128.28, 128.2, 125.7, 93.4, 92.2, 92.0, 90.8, 53.2, 53.0, 52.4, 52.3, 44.3, 43.4, 39.5, 39.3, 36.10, 36.08, 35.8, 35.7, 34.3, 34.2, 33.5, 33.4, 33.1, 32.9, 32.7, 31.1, 30.9, 28.5, 28.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -177.1, -177.2, -177.70, -177.72.

NMR data for the product from (*R*,*R*)-**L1**:

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 4H), 7.20 – 7.14 (m, 6H), 5.31 – 5.14 (m, 1H), 3.96 – 3.73 (m, 1H), 3.68 – 3.43 (m, 3H), 2.63 – 2.57 (m, 4H), 2.31 – 2.19 (m, 3H), 2.16 – 2.06 (m, 1H), 2.01 – 1.86 (m, 1H), 1.70 – 1.62 (m, 4H), 1.49 – 1.41 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.3 (d, *J* = 33.4 Hz), 142.6 (d, *J* = 4.7 Hz), 128.44, 128.37, 128.35, 128.3, 125.7, 93.8, 92.3, 92.0, 90.6, 77.4, 53.3, 53.1, 52.5, 52.3, 44.4, 43.4, 39.6, 39.40, 39.37, 36.18, 36.15, 35.9, 35.8, 34.3, 34.2, 33.6, 33.5, 33.2, 33.0, 32.7, 31.2, 31.0, 28.52, 28.49.

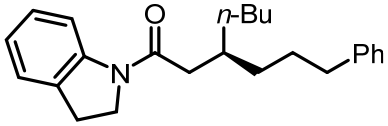
^{19}F NMR (376 MHz, $CDCl_3$) δ -178.08, -178.13, -178.67, -178.69.

FT-IR (film): 2919, 1643, 1572, 1441, 1253, 1037, 707 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{24}H_{31}FNO$: 368.2384, found: 368.2385.

$[\alpha]^{16}_D$ = +25.7 (c 0.5, $CHCl_3$); 96:4 dr, from (*S*,*S*)-**L1**.

$[\alpha]^{16}_D$ = +41.2 (c 0.5, $CHCl_3$); 4:96 dr, from (*R*,*R*)-**L1**.



(*S*)-1-(Indolin-1-yl)-3-(3-phenylpropyl)heptan-1-one (35). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)heptan-1-one and 1,3-

dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 123.9 mg, 71% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 16.8 min (minor), 18.0 min (major).

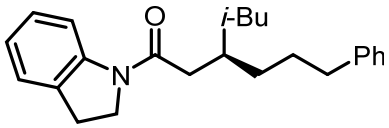
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.14 (m, 5H), 7.01 (t, *J* = 7.4 Hz, 1H), 4.03 (t, *J* = 8.5 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 2.34 (t, *J* = 5.7 Hz, 2H), 2.16 – 2.06 (m, 1H), 1.74 – 1.61 (m, 3H), 1.51 – 1.42 (m, 2H), 1.39 – 1.33 (m, 2H), 1.32 – 1.24 (m, 3H), 0.89 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1, 143.2, 142.7, 131.0, 128.4, 128.2, 127.5, 125.6, 124.4, 123.4, 117.1, 48.2, 40.7, 36.2, 34.2, 33.7, 33.6, 28.9, 28.6, 28.0, 23.0, 14.1.

FT-IR (film): 2921, 1656, 1597, 1481, 1402, 1264, 750, 696 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{24}H_{32}NO$: 350.2478, found: 350.2480.

$[\alpha]^{16}_{D}$ = –15.8 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



(*R*)-1-(Indolin-1-yl)-3-isobutyl-6-phenylhexan-1-one (36). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)-5-methylhexan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 118.7 mg, 68% yield, 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (15% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 5.8 min (minor), 6.2 min (major).

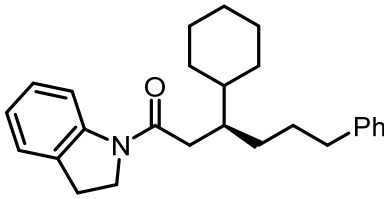
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.14 (m, 5H), 7.01 (t, *J* = 7.4 Hz, 1H), 4.03 (t, *J* = 8.5 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.68 – 2.56 (m, 2H), 2.40 – 2.29 (m, 2H), 2.24 – 2.16 (m, 1H), 1.70 – 1.60 (m, 4H), 1.49 – 1.39 (m, 2H), 1.25 – 1.17 (m, 1H), 0.90 (t, *J* = 6.5 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 143.2, 142.7, 131.0, 128.4, 128.2, 127.5, 125.6, 124.4, 123.4, 117.1, 48.2, 43.8, 41.0, 36.2, 34.1, 32.0, 28.5, 28.0, 25.4, 22.88, 22.86.

FT-IR (film): 3675, 2970, 1484, 1405, 1257, 1046, 752, 700 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{24}H_{32}NO$: 350.2478, found: 350.2484.

$[\alpha]^{16}_{D}$ = –18.2 (c 0.5, $CHCl_3$); 93% ee, from (*S*,*S*)-**L1**.



(*S*)-3-Cyclohexyl-1-(indolin-1-yl)-6-phenylhexan-1-one (37). The title compound was synthesized according to **GP-3** from 3-cyclohexyl-3-hydroxy-1-(indolin-1-yl)propan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 108.8 mg, 58% yield, 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (15% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 6.1 min (major), 6.8 min (minor).

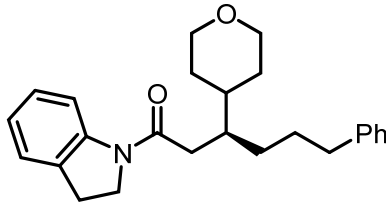
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.20 – 7.15 (m, 5H), 7.01 (t, *J* = 7.4 Hz, 1H), 4.06 – 4.02 (m, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.61 (t, *J* = 7.8 Hz, 2H), 2.43 (dd, *J* = 15.6, 5.6 Hz, 1H), 2.22 (dd, *J* = 15.6, 7.5 Hz, 1H), 2.07 – 2.01 (m, 1H), 1.76 – 1.72 (m, 2H), 1.68 – 1.62 (m, 5H), 1.48 – 1.42 (m, 2H), 1.40 – 1.34 (m, 1H), 1.25 – 1.19 (m, 2H), 1.15 – 1.09 (m, 1H), 1.06 – 0.98 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.5, 143.2, 142.7, 131.0, 128.4, 128.2, 127.5, 125.6, 124.4, 123.4, 117.1, 48.1, 40.2, 39.4, 37.6, 36.2, 31.0, 30.2, 29.4, 29.2, 28.0, 26.8, 26.7.

FT-IR (film): 3301, 2974, 2893, 1649, 1386, 1059, 700 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{26}H_{33}NNaO$: 398.2454, found: 398.2462.

$[\alpha]^{16}_{D}$ = –17.1 (c 0.5, $CHCl_3$); 93% ee, from (*S*,*S*)-**L1**.



(*S*)-1-(Indolin-1-yl)-6-phenyl-3-(tetrahydro-2*H*-pyran-4-yl)hexan-1-one (38). The title compound was synthesized according to **GP-3** from 3-hydroxy-1-(indolin-1-yl)-3-(tetrahydro-2*H*-pyran-4-yl)propan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Yellow oil, 116.9 mg, 62% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 36.3 min (major), 39.2 min (minor).

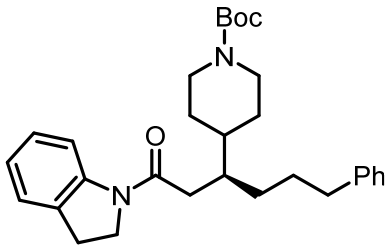
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.15 (m, 5H), 7.02 (t, *J* = 7.4 Hz, 1H), 4.03 (t, *J* = 8.8 Hz, 2H), 3.98 (dd, *J* = 11.2, 4.2 Hz, 2H), 3.36 (t, *J* = 11.7 Hz, 2H), 3.19 (t, *J* = 8.5 Hz, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.42 (dd, *J* = 15.9, 5.8 Hz, 1H), 2.26 (dd, *J* = 16.0, 6.9 Hz, 1H), 2.13 – 2.08 (m, 1H), 1.74 – 1.70 (m, 1H), 1.68 – 1.63 (m, 2H), 1.51 – 1.46 (m, 3H), 1.45 – 1.37 (m, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.8, 143.1, 142.4, 131.0, 128.4, 128.2, 127.5, 125.7, 124.5, 123.5, 117.1, 68.4, 48.0, 38.6, 37.6, 37.1, 36.1, 30.6, 29.9, 29.4, 29.2, 28.0.

FT-IR (film): 2938, 1650, 1478, 1398, 1091, 744 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{25}H_{31}NNaO_2$: 400.2247, found: 400.2241.

$[\alpha]^{16}_{D}$ = –6.1 (c 0.5, $CHCl_3$); 92% ee, from (*S*,*S*)-**L1**.



***tert*-Butyl (*S*)-4-(1-(indolin-1-yl)-1-oxo-6-phenylhexan-3-yl)piperidine-1-carboxylate (39).** The title compound was synthesized according to **GP-3** from *tert*-butyl 4-(1-hydroxy-3-(indolin-1-yl)-3-oxopropyl)piperidine-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:2 EtOAc/hexanes). Yellow oil, 123.8 mg, 52% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCPAK IC-3 column (15% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 5.5 min (major), 6.4 min (minor).

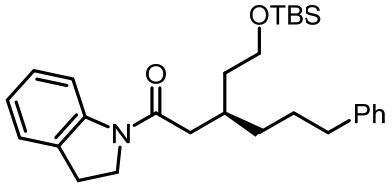
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.29 (m, 2H), 7.25 – 7.19 (m, 5H), 7.06 (t, *J* = 7.4 Hz, 1H), 4.22 – 4.14 (m, 2H), 4.09 – 4.04 (m, 2H), 3.23 (t, *J* = 8.5 Hz, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.44 (dd, *J* = 16.0, 5.9 Hz, 1H), 2.30 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.18 – 2.15 (m, 1H), 1.72 – 1.66 (m, 4H), 1.62 – 1.58 (m, 2H), 1.51 (s, 9H), 1.44 – 1.40 (m, 1H), 1.33 – 1.31 (m, 2H), 1.29 – 1.24 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.7, 154.8, 143.0, 142.4, 131.0, 128.3, 128.2, 127.5, 125.7, 124.5, 123.5, 117.0, 79.3, 48.0, 38.6, 38.4, 37.2, 36.0, 31.4, 29.6, 29.3, 28.4, 28.0.

FT-IR (film): 2969, 2913, 1650, 1468, 1263, 1217, 1159, 749 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{30}H_{40}N_2NaO_3$: 499.2931, found: 499.2925.

$[\alpha]^{26}_{D}$ = –8.9 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



(*R*)-3-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-1-(indolin-1-yl)-6-phenylhexan-1-one (40). The title compound was synthesized according to **GP-2** from 5-((*tert*-butyldimethylsilyl)oxy)-3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Yellow oil, 162.4 mg, 72% yield, 88% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 10.3 min (major), 11.7 min (minor).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.14 (m, 5H), 7.00 (t, *J* = 7.8 Hz, 1H), 4.05 – 3.97 (m, 2H), 3.67 (t, *J* = 6.9 Hz, 2H), 3.15 (t, *J* = 8.5 Hz,

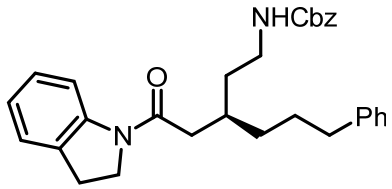
2H), 2.64 – 2.58 (m, 2H), 2.45 (dd, *J* = 15.5, 6.1 Hz, 1H), 2.33 (dd, *J* = 15.5, 7.3 Hz, 1H), 2.25 – 2.19 (m, 1H), 1.69 – 1.63 (m, 3H), 1.60 – 1.54 (m, 1H), 1.50 – 1.42 (m, 2H), 0.88 (s, 9H), 0.03 (s, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.8, 143.1, 142.5, 131.0, 128.3, 128.2, 127.4, 125.6, 124.4, 123.4, 117.0, 61.3, 48.0, 40.8, 36.7, 36.1, 33.8, 31.6, 28.6, 28.0, 25.9, 18.2, -5.4.

FT-IR (film): 2929, 1658, 1481, 1403, 1085, 835, 752 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{28}H_{42}NO_2Si$: 452.2979, found: 452.2963.

$[\alpha]^{16}_D$ = –17.2 (c 0.5, $CHCl_3$); 88% ee, from (*S*,*S*)-**L1**.



Benzyl (*R*)-(3-(2-(indolin-1-yl)-2-oxoethyl)-6-phenylhexyl)carbamate (41). The title compound was synthesized according to **GP-3** from benzyl (3-hydroxy-5-(indolin-1-yl)-5-oxopentyl)carbamate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:3 EtOAc/hexanes). Yellow oil, 134.0 mg, 57% yield, 87% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 21.8 min (major), 23.1 min (minor).

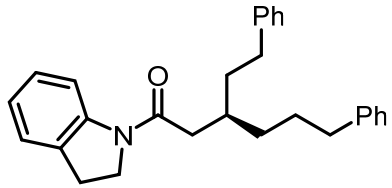
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.31 (m, 4H), 7.28 (d, *J* = 6.8 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.17 – 7.14 (m, 5H), 7.00 (t, *J* = 7.4 Hz, 1H), 5.35 (s, 1H), 5.11 – 5.02 (m, 2H), 4.00 – 3.92 (m, 2H), 3.32 – 3.25 (m, 1H), 3.17 – 3.11 (m, 3H), 2.60 (t, *J* = 7.7 Hz, 2H), 2.38 (dd, *J* = 16.2, 5.1 Hz, 1H), 2.29 (dd, *J* = 16.2, 7.8 Hz, 1H), 2.20 – 2.15 (m, 1H), 1.67 – 1.59 (m, 3H), 1.52 – 1.48 (m, 1H), 1.45 – 1.39 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 156.4, 142.9, 142.3, 136.7, 131.0, 128.4, 128.3, 128.2, 127.93, 127.89, 127.5, 125.7, 124.5, 123.6, 117.0, 66.4, 48.0, 40.4, 38.8, 36.0, 34.4, 34.2, 31.3, 28.7, 27.9.

FT-IR (film): 2931, 1713, 1481, 1405, 1239, 1049, 744, 697 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{30}H_{35}N_2O_3$: 471.2642, found: 471.2644.

$[\alpha]^{16}_D$ = –13.4 (c 0.5, $CHCl_3$); 87% ee, from (*S*,*S*)-**L1**.



(*R*)-1-(Indolin-1-yl)-3-phenethyl-6-phenylhexan-1-one (42). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)-5-phenylpentan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 137.0 mg, 69% yield, 87% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 17.6 min (major), 22.6 min (minor).

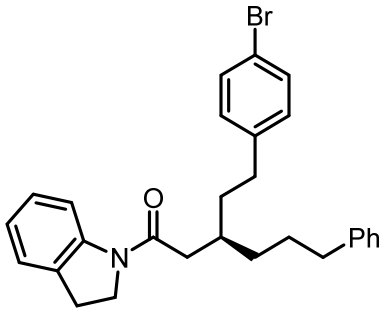
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.22 (m, 4H), 7.17 – 7.13 (m, 8H), 6.99 (t, *J* = 7.4 Hz, 1H), 3.95 (t, *J* = 8.5 Hz, 2H), 3.13 (t, *J* = 8.4 Hz, 2H), 2.62 – 2.59 (m, 4H), 2.38 – 2.34 (m, 2H), 2.22 – 2.17 (m, 1H), 1.70 – 1.65 (m, 4H), 1.51 – 1.46 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.7, 143.1, 142.5, 131.0, 128.4, 128.3, 128.2, 127.5, 125.7, 125.6, 124.4, 123.5, 117.1, 48.1, 40.6, 36.1, 35.7, 34.0, 33.5, 33.1, 28.5, 27.9.

FT-IR (film): 2923, 1653, 1478, 1400, 1254, 1044, 698 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{28}H_{32}NO$: 398.2478, found: 398.2470.

$[\alpha]^{16}_{D}$ = –12.2 (c 0.5, $CHCl_3$); 87% ee, from (*S*,*S*)-**L1**.



(*R*)-3-(4-Bromophenethyl)-1-(indolin-1-yl)-6-phenylhexan-1-one (43). The title compound was synthesized according to **GP-2** from 5-(4-bromophenyl)-3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:6 EtOAc/hexanes). Yellow oil, 166.3 mg, 70% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCPAK IC-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 14.9 min (major), 17.0 min (minor).

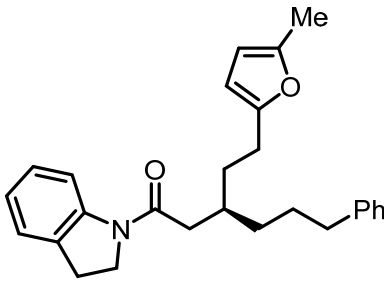
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.16 (m, 5H), 7.05 – 7.00 (m, 3H), 3.97 (t, *J* = 8.5 Hz, 2H), 3.17 (t, *J* = 8.5 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.60 – 2.56 (m, 2H), 2.39 – 2.34 (m, 2H), 2.21 – 2.16 (m, 1H), 1.70 – 1.65 (m, 4H), 1.52 – 1.47 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 143.0, 142.4, 141.4, 131.3, 131.0, 130.1, 128.4, 128.3, 127.5, 125.7, 124.5, 123.5, 119.3, 117.0, 48.1, 40.6, 36.1, 35.5, 33.9, 33.4, 32.5, 28.5, 28.0.

FT-IR (film): 2920, 1649, 1561, 1432, 1258, 1033, 701 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{28}H_{31}BrNO$: 476.1584, found: 476.1584.

$[\alpha]^{26}_{D}$ = –6.7 (c 0.5, $CHCl_3$); 89% ee, from (*S*,*S*)-**L1**.



(*R*)-1-(Indolin-1-yl)-3-(2-(5-methylfuran-2-yl)ethyl)-6-phenylhexan-1-one (44). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)-5-(5-methylfuran-2-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Yellow oil, 130.3 mg, 65% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 10.3 min (minor), 14.2 min (major).

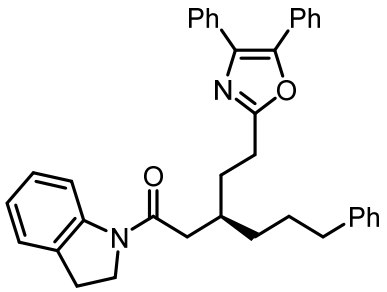
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.18 – 7.14 (m, 5H), 7.00 (t, *J* = 7.4 Hz, 1H), 5.83 (d, *J* = 3.0 Hz, 1H), 5.81 (d, *J* = 3.1 Hz, 1H), 3.98 (t, *J* = 8.5 Hz, 2H), 3.15 (t, *J* = 8.4 Hz, 2H), 2.62 – 2.58 (m, 4H), 2.35 (t, *J* = 6.6 Hz, 2H), 2.21 (s, 3H), 2.20 – 2.17 (m, 1H), 1.75 – 1.69 (m, 2H), 1.68 – 1.64 (m, 2H), 1.50 – 1.43 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 154.1, 150.1, 143.1, 142.5, 131.0, 128.3, 128.2, 127.5, 125.6, 124.4, 123.4, 117.0, 105.8, 105.3, 48.0, 40.4, 36.1, 33.7, 33.4, 32.1, 28.5, 27.9, 25.3, 13.4.

FT-IR (film): 2928, 1650, 1487, 1403, 1265, 752, 695 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{27}H_{32}NO_2$: 402.2428, found: 402.2421.

$[\alpha]^{16}_{D}$ = –1.9 (c 0.5, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



(*R*)-3-(2-(4,5-Diphenyloxazol-2-yl)ethyl)-1-(indolin-1-yl)-6-phenylhexan-1-one (45). The title compound was synthesized according to **GP-3** from 5-(4,5-diphenyloxazol-2-yl)-3-hydroxy-1-(indolin-1-yl)pentan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:2 EtOAc/hexanes). Colorless oil, 172.8 mg, 64% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 30.3 min (major), 34.9 min (minor).

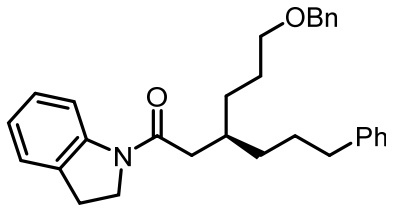
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.1 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 2H), 7.36 – 7.31 (m, 6H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.18 – 7.14 (m, 5H), 7.00 (t, *J* = 7.4 Hz, 1H), 4.00 (t, *J* = 8.6 Hz, 2H), 3.12 (td, *J* = 8.3, 2.7 Hz, 2H), 2.91 (t, *J* = 7.9 Hz, 2H), 2.63 (td, *J* = 7.5, 3.4 Hz, 2H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.32 – 2.27 (m, 1H), 2.04 – 1.96 (m, 2H), 1.74 – 1.67 (m, 2H), 1.56 – 1.49 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.4, 163.5, 145.2, 143.0, 142.4, 134.9, 132.5, 131.0, 129.0, 128.6, 128.5, 128.4, 128.32, 128.25, 128.0, 127.9, 127.5, 126.4, 125.7, 124.5, 123.5, 117.1, 48.1, 40.3, 36.1, 33.8, 33.4, 31.0, 28.6, 28.0, 25.7.

FT-IR (film): 3554, 3427, 2922, 1660, 1565, 1432, 1256, 765 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{37}H_{37}N_2O_2$: 541.2850, found: 541.2851.

$[\alpha]^{26}_D$ = –13.1 (c 0.5, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



(*R*)-6-(Benzyloxy)-1-(indolin-1-yl)-3-(3-phenylpropyl)hexan-1-one (46). The title compound was synthesized according to **GP-2** from 6-(benzyloxy)-3-hydroxy-1-(indolin-1-yl)hexan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Yellow oil, 165.4 mg, 75% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 14.5 min (major), 16.8 min (minor).

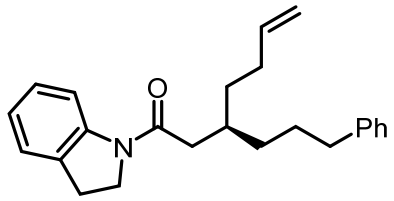
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.30 (m, 4H), 7.26 – 7.22 (m, 3H), 7.20 – 7.12 (m, 5H), 6.99 (t, *J* = 7.4 Hz, 1H), 4.47 (s, 2H), 4.03 – 3.93 (m, 2H), 3.45 (td, *J* = 6.6, 2.0 Hz, 2H), 3.12 (t, *J* = 8.5 Hz, 2H), 2.59 (td, *J* = 7.5, 2.7 Hz, 2H), 2.38 – 2.27 (m, 2H), 2.16 – 2.12 (m, 1H), 1.68 – 1.59 (m, 4H), 1.47 – 1.39 (m, 4H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.8, 143.1, 142.5, 138.5, 131.0, 128.31, 128.26, 128.2, 127.6, 127.42, 127.41, 125.6, 124.4, 123.4, 117.0, 72.8, 70.6, 48.0, 40.5, 36.1, 34.0, 33.5, 30.2, 28.6, 27.9, 26.8.

FT-IR (film): 2925, 1658, 1484, 1403, 1075, 700 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+K]$^+$ calcd for $C_{30}H_{35}KNO_2$: 480.2299, found: 480.2297.

$[\alpha]^{16}_D$ = –21.3 (c 0.5, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



(*R*)-1-(Indolin-1-yl)-3-(3-phenylpropyl)hept-6-en-1-one (47). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)hept-6-en-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 119.7 mg, 69% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 14.9 min (major), 16.3 min (minor).

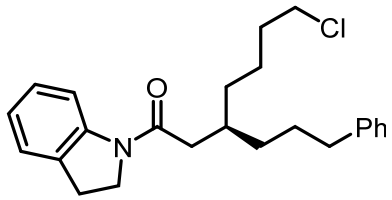
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.19 – 7.14 (m, 5H), 6.99 (t, *J* = 7.4 Hz, 1H), 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 4.99 (dd, *J* = 17.1, 1.9 Hz, 1H), 4.93 (dd, *J* = 10.2, 1.8 Hz, 1H), 4.00 (t, *J* = 8.5 Hz, 2H), 3.16 (t, *J* = 8.5 Hz, 2H), 2.63 – 2.58 (m, 2H), 2.35 – 2.32 (m, 2H), 2.17 – 2.12 (m, 1H), 2.08 – 2.04 (m, 2H), 1.68 – 1.62 (m, 2H), 1.48 – 1.41 (m, 4H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.8, 143.1, 142.5, 138.8, 131.0, 128.3, 128.2, 127.5, 125.6, 124.4, 123.4, 117.1, 114.4, 48.1, 40.5, 36.1, 33.8, 33.4, 33.1, 30.9, 28.5, 28.0.

FT-IR (film): 2931, 1655, 1478, 1395, 908, 747, 698 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{24}H_{30}NO$: 348.2322, found: 348.2329.

$[\alpha]^{16}_{D}$ = –19.9 (c 0.5, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



(*R*)-7-Chloro-1-(indolin-1-yl)-3-(3-phenylpropyl)heptan-1-one (48). The title compound was synthesized according to **GP-2** from 7-chloro-3-hydroxy-1-(indolin-1-yl)heptan-1-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 145.5 mg, 76% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-3 column (15% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 8.3 min (major), 10.2 min (minor).

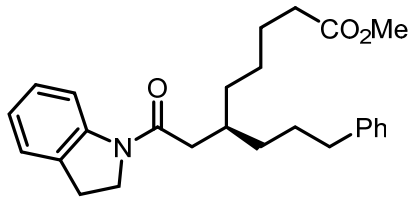
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.18 – 7.14 (m, 5H), 6.99 (t, *J* = 7.4 Hz, 1H), 4.01 – 3.96 (m, 2H), 3.51 (t, *J* = 6.6 Hz, 2H), 3.15 (t, *J* = 8.5 Hz, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 2.34 – 2.29 (m, 2H), 2.15 – 2.08 (m, 1H), 1.77 – 1.71 (m, 2H), 1.67 – 1.62 (m, 2H), 1.45 – 1.41 (m, 4H), 1.40 – 1.34 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.7, 143.0, 142.4, 131.0, 128.3, 128.2, 127.4, 125.6, 124.4, 123.4, 117.0, 48.0, 45.0, 40.4, 36.0, 33.9, 33.4, 32.9, 32.6, 28.5, 27.9, 23.8.

FT-IR (film): 2931, 1653, 1481, 1398, 752, 695 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{24}H_{30}ClNNaO$: 406.1908, found: 406.1903.

$[\alpha]^{16}_{D}$ = –11.2 (c 0.5, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.



Methyl (*S*)-6-(2-(indolin-1-yl)-2-oxoethyl)-9-phenylnonanoate (49). The title compound was synthesized according to **GP-2** from methyl 6-hydroxy-8-(indolin-1-yl)-8-oxooctanoate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:4 EtOAc/hexanes). Yellow oil, 144.5 mg, 71% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCPAK IG-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 11.3 min (minor), 14.5 min (major).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.19 – 7.14 (m, 5H), 6.99 (t, *J* = 7.4 Hz, 1H), 4.00 (t, *J* = 8.4 Hz, 2H), 3.63 (s, 3H), 3.16 (t, *J* = 8.5 Hz, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 2.32 – 2.28 (m, 4H), 2.13 – 2.09 (m, 1H), 1.66 – 1.59 (m, 4H), 1.44 – 1.39 (m, 2H), 1.39 – 1.35 (m, 2H), 1.34 – 1.30 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.1, 170.8, 143.0, 142.5, 131.0, 128.3, 128.2, 127.4, 125.6, 124.4, 123.4, 117.0, 51.4, 48.0, 40.5, 36.1, 34.0, 33.9, 33.46, 33.45, 28.5, 27.9, 26.1, 25.1.

FT-IR (film): 2928, 1739, 1658, 1481, 1400, 755, 695 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{26}H_{34}NO_3$: 408.2533, found: 408.2540.

$[\alpha]^{16}_{D}$ = –23.2 (c 0.5, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.

V. Effect of Reaction Parameters

General Procedure 4 (GP-4).

Preparation of the catalyst solution: In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a stir bar was charged with $NiBr_2$·DME (3.1 mg, 0.010 mmol, 10.0 mol%), (*S*,*S*)-**L1** (7.1 mg, 0.012 mmol, 12.0 mol%), and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.8 mg, 0.0015 mmol, 1.5 mol%). Anhydrous methyl *tert*-butyl ether (0.5 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 60 min at least, leading to a catalyst solution.

Preparation of the NHC-alcohol adduct solution: In a nitrogen-filled glovebox, a separate oven-dried 4 mL vial was charged with β-hydroxy amide (0.20 mmol, 2.0 equiv), NHC (79.1 mg, 0.20 mmol, 2.0 equiv), and a stir bar. (Trifluoromethyl)benzene (0.5 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (49.4 μL, 0.22 mmol, 2.2 equiv) was added dropwise, and the resulting solution was stirred at room temperature for another 30 min (a white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution.

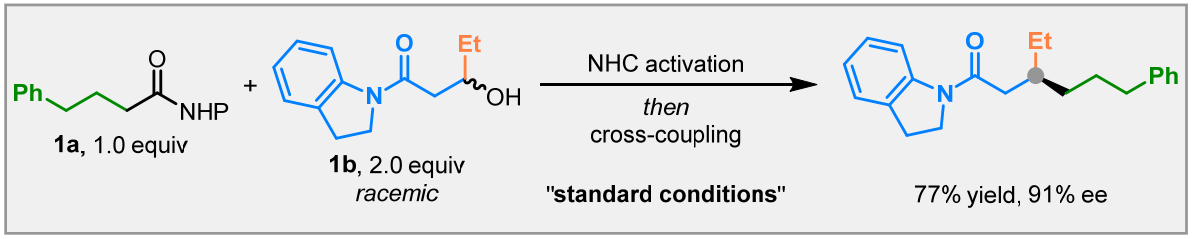
Cross-coupling: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with the NHP ester (0.10 mmol, 1.0 equiv), quinuclidine (16.7 mg, 0.15 mmol, 1.5 equiv), and a stir bar. The catalyst solution and NHC-alcohol adduct solution were transferred via syringe to the 4 mL reaction vial. The vial was transferred out of the glovebox and placed in an EtOH cooling bath at 0 °C for 5 min. Then the reaction was irradiated with blue LEDs (455 nm, 30 W) and was stirred at 0 °C for 20 hours.

Work-up: The reaction was stopped by ending the irradiation. The reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with EtOAc. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.

Figure S2: 3-Hydroxy-1-(indolin-1-yl)pentan-1-one was reacted with 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate according to **GP-4**. The yields were determined via GC analysis, with *n*-tetradecane as the internal standard. The ee values were determined via HPLC analysis after purification by preparative thin-layer chromatography.

Discussion: Throughout the optimization studies, we observed significant formation of hydro-decarboxylative product from **1a** and hydro-dehydroxylative product from **1b**, alongside the desired coupling product. The corresponding homocoupling products were either undetectable or present only in trace amounts.

Figure S2. Effect of reaction parameters. Standard reaction conditions: 2.2 equiv 2,6-bis(*tert*-butyl) pyridine, 2.0 equiv NHC, $PhCF_3$, r.t., and 30 min; then 10 mol% $NiBr_2$·DME, 12 mol% (*S*,*S*)-**L1**, 1.5 mol% (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (**PC**), 1.5 equiv quinuclidine, $PhCF_3$/MTBE (1/1, 0.1 M), 455 nm Blue LEDs (30 W), 0 °C, and 20 h. [a]Determined through GC analysis. [b]Determined through HPLC analysis.



entry	variation from the "**standard conditions**"	yield (%)[a]	ee (%)[b]
1	None	77	91
2	No Ni, **PC**, Quinuclidine, or light	0	–
3	No (*S*,*S*)-**L1**	37	0
4	**L2**, instead of (*S*,*S*)-**L1**	63	60
5	**L3**, instead of (*S*,*S*)-**L1**	46	-28
6	**L4**, instead of (*S*,*S*)-**L1**	32	0
7	**L5**, instead of (*S*,*S*)-**L1**	0	–
8	**L6**, instead of (*S*,*S*)-**L1**	55	15
9	THF, instead of MTBE	60	91
10	DME, instead of MTBE	49	91
11	Pure $PhCF_3$	26	90
12	Pure MTBE	62	89
13	NaOAc, instead of Quinuclidine	9	81
14	5.0 mol% $NiBr_2$•DME, 6.0 mol% (*S*,*S*)-**L1**	68	91
15	10 h, instead of 20 h	63	91
16	r.t., instead of 0 °C	23	88
17	0.05 M, instead of 0.1 M	71	90
18	3.0 mL air added (4.0 mL vial)	72	90
19	conducted outside of the glovebox	62	83
20	1.0 equiv H_2O added	68	80

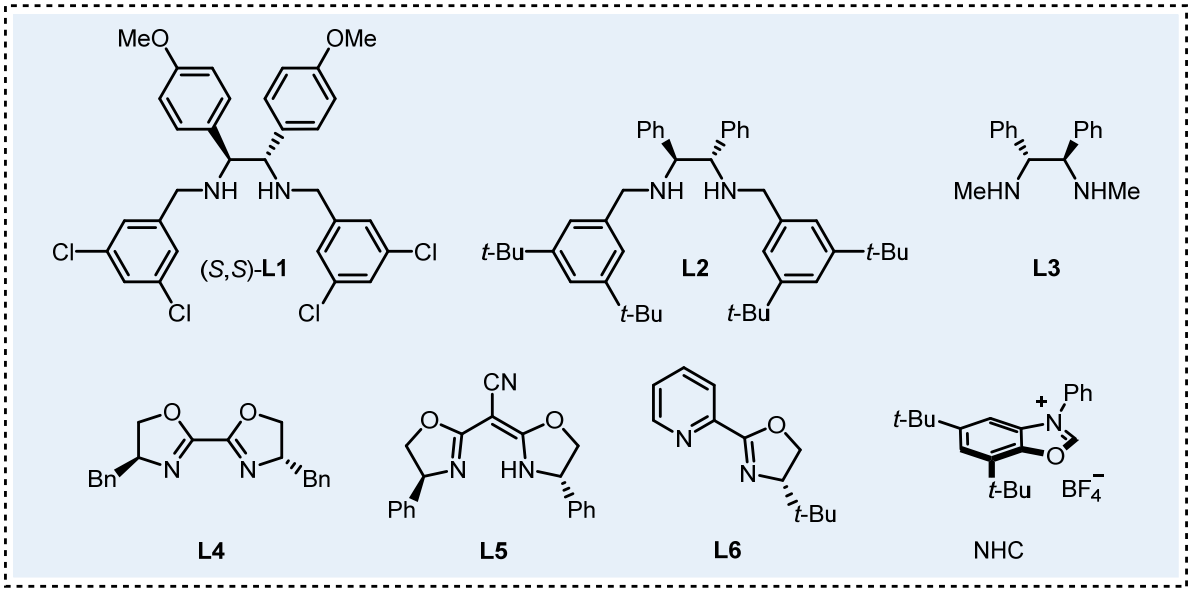
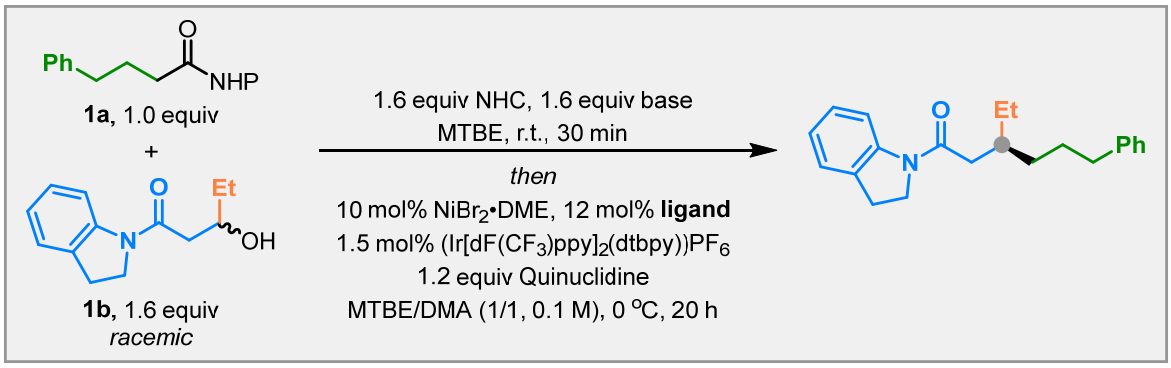
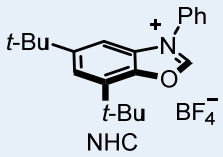
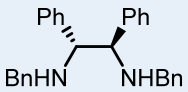


Figure S3. Evaluation of bases. [a]Determined through GC analysis. [b]Determined through HPLC analysis.



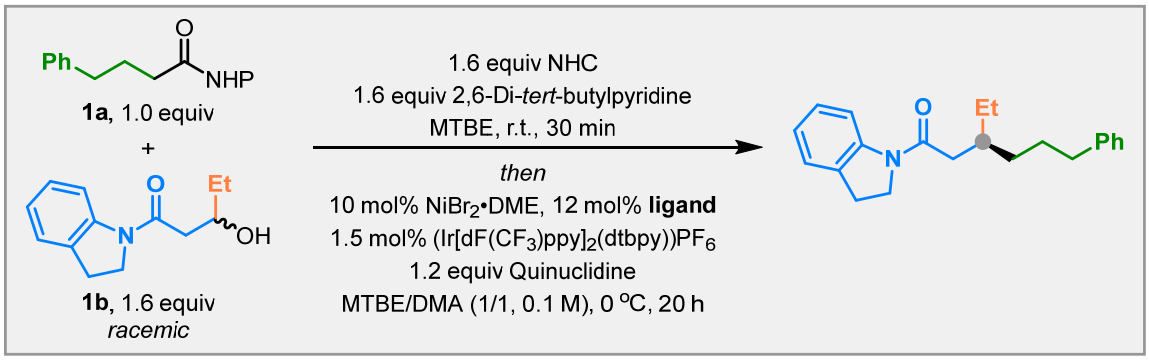
entry	base	yield (%)[a]	ee (%)[b]
1	pyridine	31	41
2	4-OMe-pyridine	26	40
3	4-Me-pyridine	42	37
4	4-COMe-pyridine	35	37
5	2,4,6-collidine	40	41
6	2,6-di-*tert*-butylpyridine	45	41
7	quinuclidine	21	39
8	NaOMe	<1	-
9	AcONa	<1	-

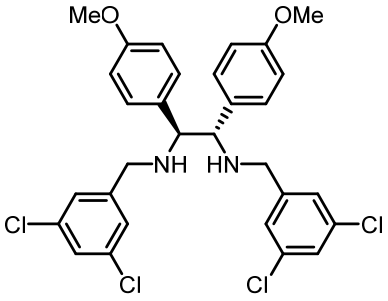




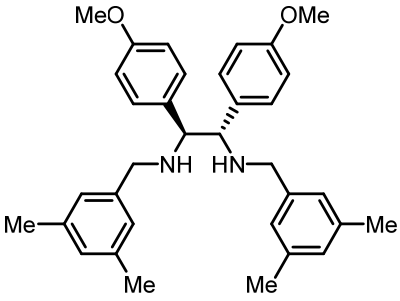
ligand

Figure S4. Evaluation of ligands. The yields were determined via GC analysis and the ee values were determined via HPLC analysis.

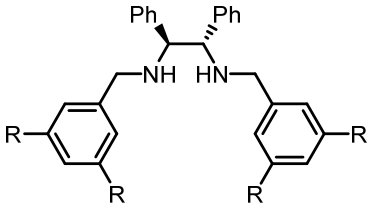




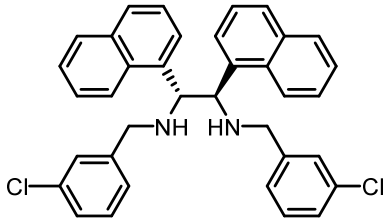
(*S*,*S*)-**L1**: 50% yield, 87% ee



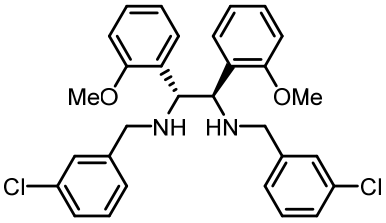
L2: 45% yield, 79% ee



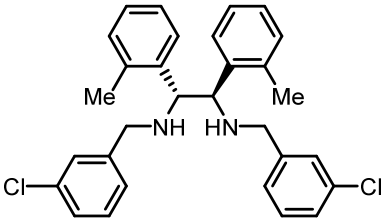
L3, R = Cl: 51% yield, 61% ee
L4, R = Me: 43% yield, 47% ee
L5, R = *t*-Bu: 42% yield, 56% ee



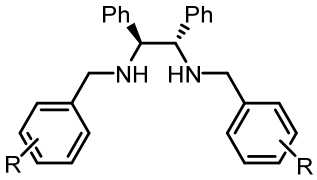
L6: 34% yield, -51% ee



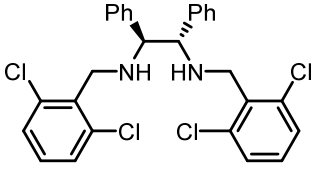
L7: 30% yield, -52% ee



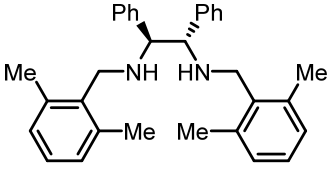
L8: 42% yield, -48% ee



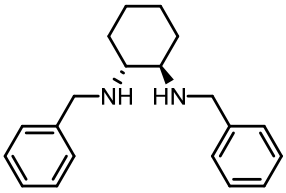
L9, R = 2-CF_3: 32% yield, 46% ee
L10, R = 2-Me: 42% yield, 49% ee
L11, R = 3-Ph: 31% yield, 50% ee
L12, R = 3-Cl: 45% yield, 54% ee
L13, R = 4-*t*-Bu: 43% yield, 44% ee



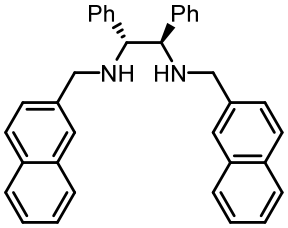
L14: 38% yield, 8% ee



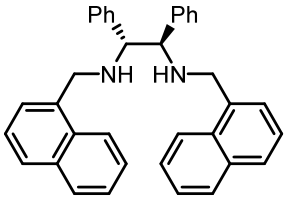
L15: 35% yield, 4% ee



L16: 25% yield, 36% ee

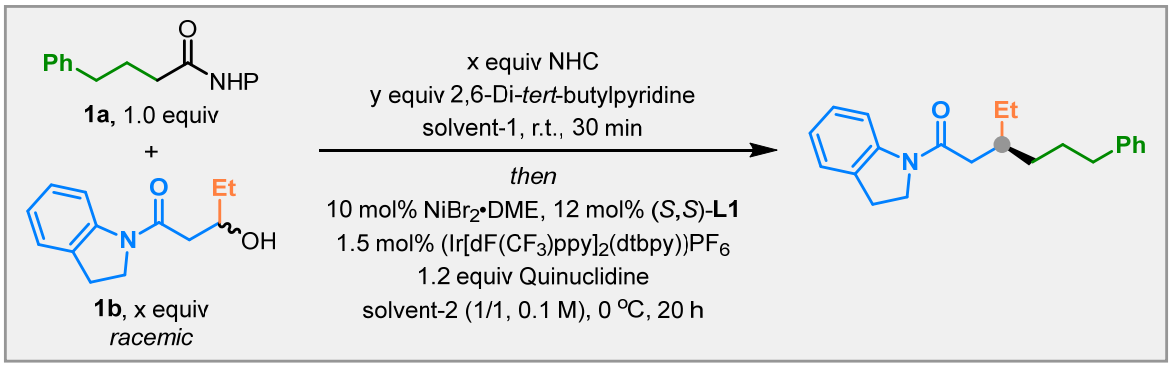


L17: 43% yield, -44% ee



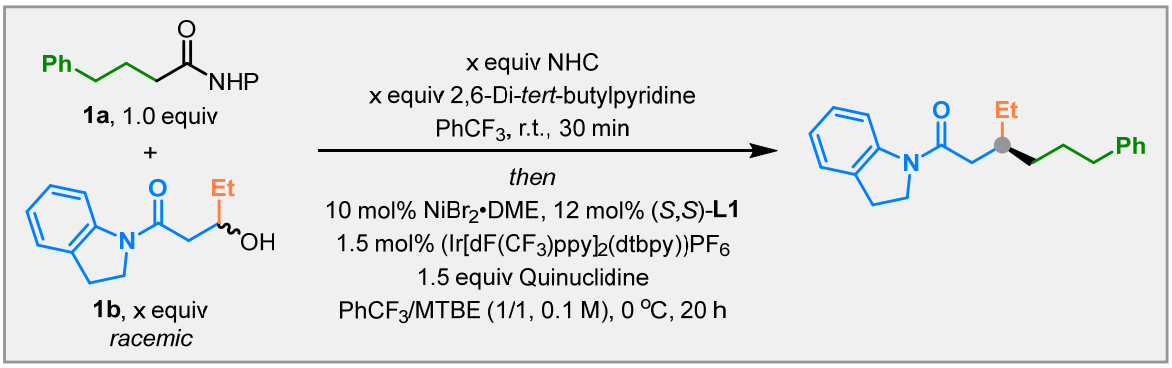
L18: 42% yield, -28% ee

Figure S5. Evaluation of solvents. [a]Determined through GC analysis. [b]Determined through HPLC analysis.



entry	x/y	base	yield (%)[a]	ee (%)[b]
1	1.6/1.6	MTBE/DMA	50	87
2	1.6/1.6	MTBE/$PhCF_3$	49	91
3	1.6/1.6	MTBE/MTBE	54	89
4	1.6/1.6	$PhCF_3$/$PhCF_3$	52	90
5	1.6/1.6	$PhCF_3$/THF	58	91
6	1.6/1.6	$PhCF_3$/MTBE	71	91
7	2.0/2.2	$PhCF_3$/MTBE	77	91
8	2.5/2.7	$PhCF_3$/MTBE	76	91

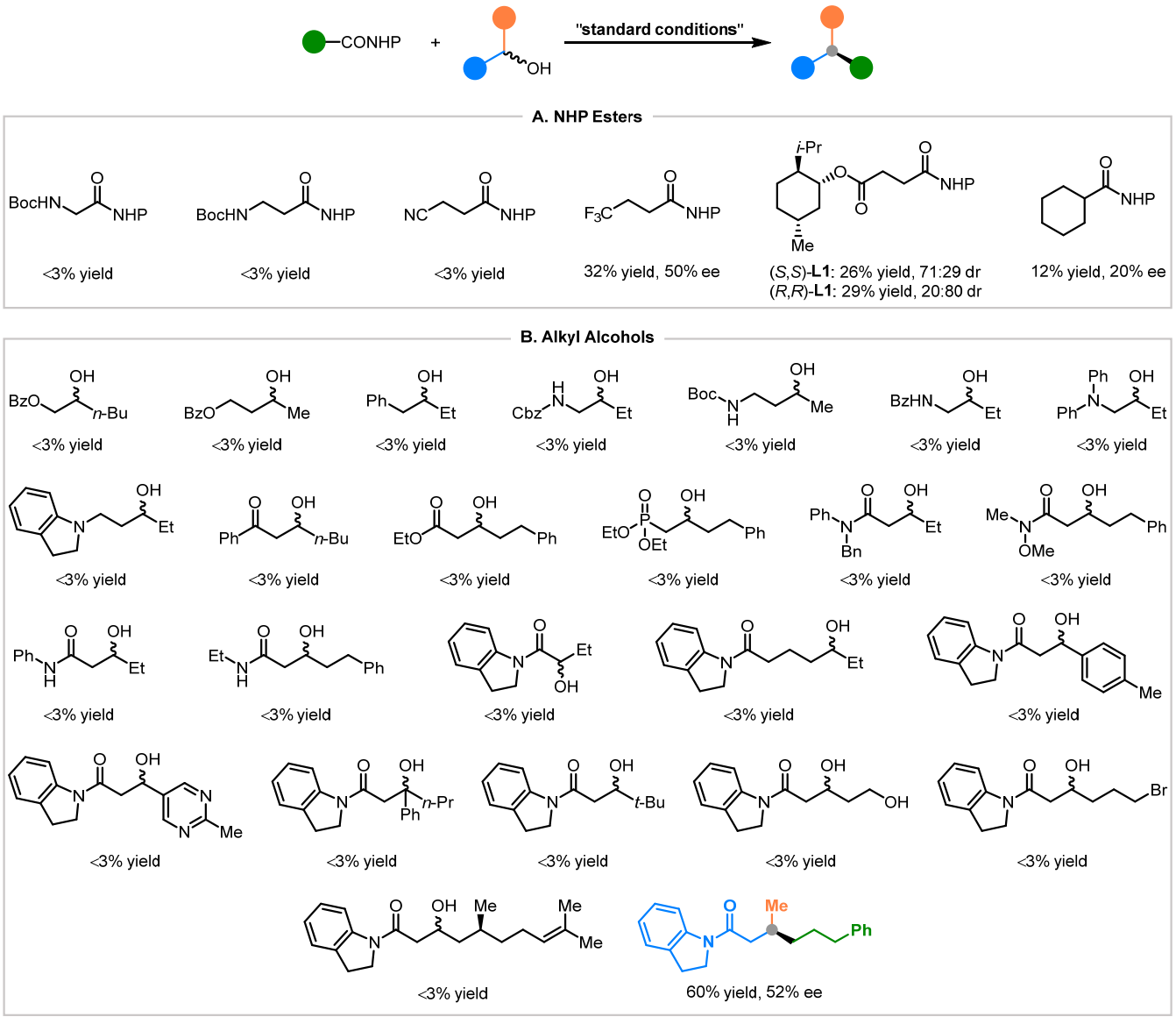
Figure S6. Evaluation of reagent loadings. [a]Determined through GC analysis. [b]Determined through HPLC analysis.



entry	x	yield (%)[a]	ee (%)[b]
1	1.5	68	91
2	1.2	56	91
3	1.0	43	90

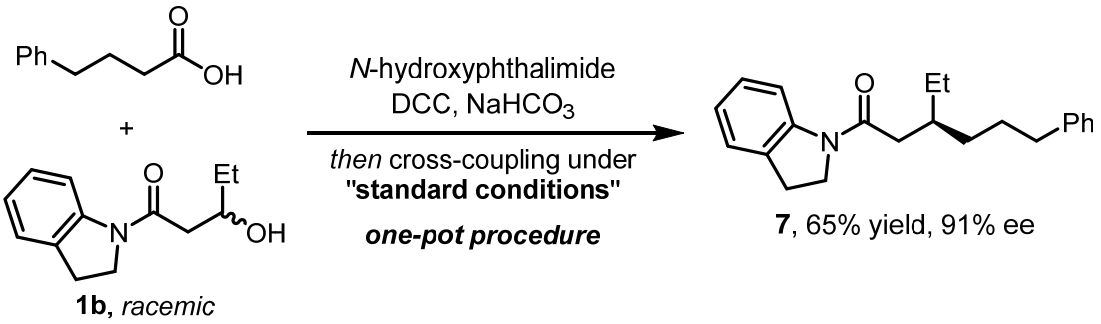
VI. Unsuccessful Examples

Figure S7. Unsucessful examples. The yields were either isolated yields or determined via GC analysis, and the ee values were determined via HPLC analysis.



VII. Applications

1. Catalytic asymmetric cross-coupling from alkyl carboxylic acid and alkyl alcohol.



Preparation of the NHP ester: In the air, an oven-dried 4 mL vial that contained a stir bar was charged with 4-phenylbutanoic acid (16.4 mg, 0.10 mmol, 1.0 equiv), *N*-hydroxyphthalimide (17.9 mg, 0.11 mmol, 1.1 equiv), DCC (22.7 mg, 0.11 mmol, 1.1 equiv), $NaHCO_3$ (10.1 mg, 0.12 mmol, 1.2 equiv), and anhydrous DCM (2.0 mL). The reaction mixture was stirred at room temperature for 2 hours, after which it turned to a white suspension. The reaction solution was drained by a rotary evaporator, the white solid was dried in vacuo for 30 min.

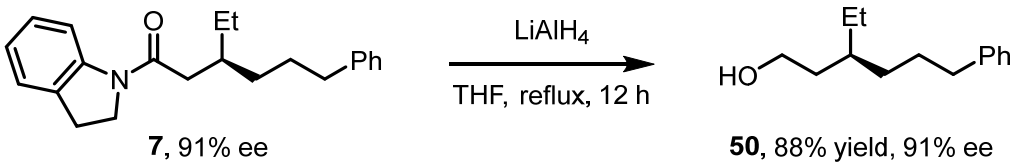
Preparation of the catalyst solution: In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a stir bar was charged with $NiBr_2$·DME (3.1 mg, 0.010 mmol, 10.0 mol%), (*S*,*S*)-**L1** (7.1 mg, 0.012 mmol, 12.0 mol%), and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.8 mg, 0.0015 mmol, 1.5 mol%). Anhydrous methyl *tert*-butyl ether (0.5 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 60 min at least, leading to a catalyst solution.

Preparation of the NHC-alcohol adduct solution: In a nitrogen-filled glovebox, a separate oven-dried 4 mL vial was charged with 3-hydroxy-1-(indolin-1-yl)pentan-1-one (43.8 mg, 0.20 mmol, 2.0 equiv), NHC (79.1 mg, 0.20 mmol, 2.0 equiv), and a stir bar. (Trifluoromethyl)benzene (0.5 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (49.4 μL, 0.22 mmol, 2.2 equiv) was added dropwise, and the resulting solution was stirred at room temperature for another 30 min (a white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution.

Cross-coupling: The reaction vial containing NHP ester was transferred into the glovebox, and quinuclidine (16.7 mg, 0.15 mmol, 1.5 equiv), the catalyst solution and NHC-alcohol adduct solution were added to the reaction vial. The vial was transferred out of the glovebox and placed in an EtOH cooling bath at 0 °C for 5 min. Then the reaction was irradiated with blue LEDs (455 nm, 30 W) and was stirred at 0 °C for 20 hours. Upon completion, the reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with EtOAc. The filtrate was concentrated, and the residue was purified by flash

chromatography (1:8 EtOAc/hexanes) to afford the desired product. Yellow oil, 20.9 mg, 65% yield, 91% ee.

2. Transformations of the coupling product.



7, 91% ee **50**, 88% yield, 91% ee

(*S*)-3-Ethyl-6-phenylhexan-1-ol (50). In a nitrogen-filled glovebox, a 10 mL Schlenk tube was equipped with a magnetic stir bar, (*S*)-3-ethyl-1-(indolin-1-yl)-6-phenylhexan-1-one (**7**, 91% ee, 32.1 mg, 0.10 mmol, 1.0 equiv), and THF (1 mL). The Schlenk tube was transferred out of the glovebox, and lithium aluminum hydride (1.0 M in THF, 200 uL, 0.20 mmol, 2.0 equiv) was added dropwise to the solution at 0 °C. Next, the reaction mixture was allowed to warm to room temperature, then it was heated to 80 °C and stirred for 12 h. Upon completion, the reaction mixture was cooled to 0 °C, and then quenched in turn with H_2O (10 uL), 15% aqueous NaOH (20 uL), and H_2O (30 uL). The reaction mixture was extracted with EtOAc (3 x 5 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:5 EtOAc/hexanes) to afford the desired product. Yellow oil, 18.1 mg, 88% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 7.8 min (minor), 9.1 min (major).

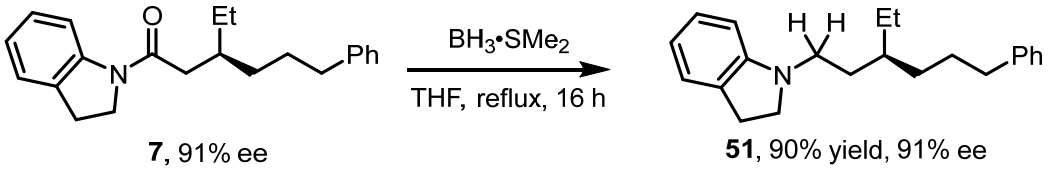
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 7.7 Hz, 2H), 7.20 – 7.16 (m, 3H), 3.65 (t, *J* = 7.0 Hz, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 1.64 – 1.58 (m, 2H), 1.54 – 1.50 (m, 2H), 1.44 – 1.40 (m, 1H), 1.34 – 1.29 (m, 4H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.7, 128.4, 128.2, 125.6, 61.2, 36.4, 36.3, 35.5, 32.8, 28.5, 25.9, 10.7.

FT-IR (film): 3670, 2925, 1455, 1049, 748, 700 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{14}H_{22}NaO$: 229.1563, found: 229.1545.

$[\alpha]^{16}_D$ = –5.3 (c 0.2, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



7, 91% ee **51**, 90% yield, 91% ee

(*S*)-1-(3-Ethyl-6-phenylhexyl)indoline (51). In a nitrogen-filled glovebox, a 10 mL Schlenk tube was equipped with a magnetic stir bar, (*S*)-3-ethyl-1-(indolin-1-yl)-6-phenylhexan-1-one (**7**, 91% ee, 32.1 mg, 0.10 mmol, 1.0 equiv), and THF (1 mL). The Schlenk tube was transferred out

of the glovebox, and borane-methyl sulfide complex (2.0 M in THF, 125 uL, 0.25 mmol, 2.5 equiv) was added dropwise to the solution at 0 °C. Next, the reaction mixture was allowed to warm to room temperature, then it was heated to 80 °C and stirred for 16 h. Upon completion, the reaction mixture was cooled to 0 °C, and then quenched with 15% aqueous NaOH (1.0 mL). The mixture was extracted with EtOAc (3 x 5 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:15 EtOAc/hexanes) to afford the desired product. Yellow oil, 27.6 mg, 90% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 7.8 min (minor), 9.1 min (major).

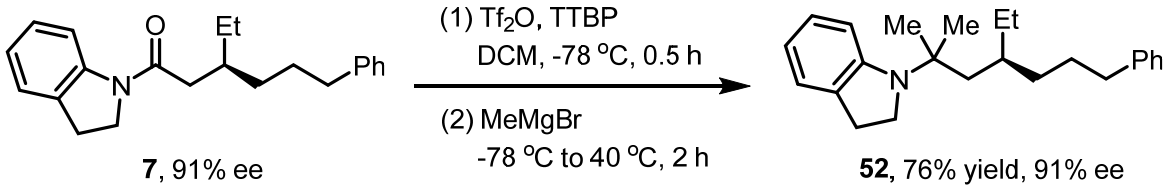
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.16 (m, 3H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.67 (s, 1H), 6.48 (s, 1H), 3.33 (t, *J* = 8.6 Hz, 2H), 3.04 (t, *J* = 7.8 Hz, 2H), 2.96 (t, *J* = 8.3 Hz, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.65 – 1.60 (m, 2H), 1.58 – 1.53 (m, 2H), 1.44 – 1.40 (m, 1H), 1.38 – 1.33 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.6, 142.7, 130.0, 128.4, 128.2, 127.2, 125.6, 124.3, 117.2, 106.9, 52.9, 47.1, 36.7, 36.3, 32.7, 30.3, 28.53, 28.49, 25.8, 10.8.

FT-IR (film): 2928, 1606, 1494, 1455, 744, 698 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{22}H_{29}NNa$: 330.2192, found: 330.2194.

$[\alpha]^{16}_{D}$ = –26.0 (c 0.2, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



7, 91% ee

52, 76% yield, 91% ee

(*S*)-1-(4-Ethyl-2-methyl-7-phenylheptan-2-yl)indoline (52). In a nitrogen-filled glovebox, an oven-dried 4 mL vial was equipped with a magnetic stir bar, (*S*)-3-ethyl-1-(indolin-1-yl)-6-phenylhexan-1-one (**7**, 91% ee, 32.1 mg, 0.10 mmol, 1.0 equiv), 2,4,6-tri-*tert*-butylpyrimidine (TTBP, 29.8 mg, 0.12 mmol, 1.2 equiv), and DCM (1 mL), and the vial was capped with a PTFE septum cap. The vial was transferred out of the glovebox, and trifluoromethanesulfonic anhydride (20 uL, 0.12 mmol, 1.2 equiv) was added dropwise to the solution at -78 °C. The reaction mixture was stirred at -78 °C for 0.5 h. Then, methylmagnesium bromide (1.0 M in THF, 400 uL, 0.40 mmol, 4.0 equiv) was added dropwise to the solution at -78 °C. Next, the reaction mixture was allowed to warm to room temperature, then it was heated to 40 °C and stirred for 2 h. Upon completion, saturated $NaHCO_3$ aqueous solution (5 mL) was added, and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:15 EtOAc/hexanes) to afford the desired product. Yellow oil, 25.5 mg, 76% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 23.7 min (major), 25.3 min (minor).

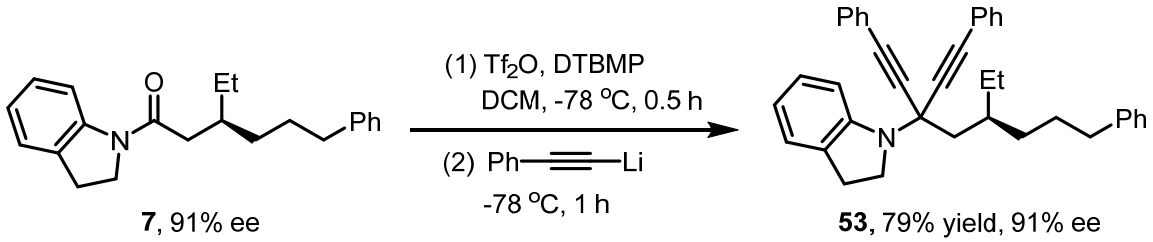
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.25 (m, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.16 – 7.12 (m, 2H), 7.06 – 7.02 (m, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.60 (t, *J* = 7.3 Hz, 1H), 3.43 (t, *J* = 8.5 Hz, 2H), 2.85 (t, *J* = 8.7 Hz, 2H), 2.54 (t, *J* = 7.7 Hz, 2H), 1.74 – 1.69 (m, 2H), 1.60 – 1.55 (m, 2H), 1.52 – 1.46 (m, 1H), 1.41 – 1.34 (m, 4H), 1.32 (s, 6H), 0.83 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.5, 142.8, 131.6, 129.1, 128.4, 128.2, 127.2, 126.6, 125.5, 124.3, 116.3, 110.4, 56.4, 49.6, 42.1, 36.3, 35.2, 34.0, 28.4, 28.2, 27.3, 26.1, 25.9, 10.8.

FT-IR (film): 2923, 1606, 1457, 737, 692 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{24}H_{34}N$: 336.2686, found: 336.2678.

$[\alpha]^{16}_D$ = –4.2 (c 0.2, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



7, 91% ee

53, 79% yield, 91% ee

(*S*)-1-(5-Ethyl-1,8-diphenyl-3-(phenylethynyl)oct-1-yn-3-yl)indoline (53). In a nitrogen-filled glovebox, an oven-dried 4 mL vial was equipped with a magnetic stir bar, (*S*)-3-ethyl-1-(indolin-1-yl)-6-phenylhexan-1-one (**7**, 91% ee, 32.1 mg, 0.10 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 24.6 mg, 0.12 mmol, 1.2 equiv), and DCM (1 mL), and the vial was capped with a PTFE septum cap. The vial was transferred out of the glovebox, and trifluoromethanesulfonic anhydride (20 uL, 0.12 mmol, 1.2 equiv) was added dropwise to the solution at -78 °C and stirred for 0.5 h. Then, lithium phenylacetylide (600 uL, 0.30 mmol, 3.0 equiv, 0.5 M in THF) was added dropwise to the solution at -78 °C. The reaction mixture was stirred at -78 °C for 1 h. Upon completion, saturated $NaHCO_3$ aqueous solution (5 mL) was added, and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:15 EtOAc/hexanes) to afford the desired product. Yellow oil, 40.1 mg, 79% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 11.0 min (major), 12.3 min (minor).

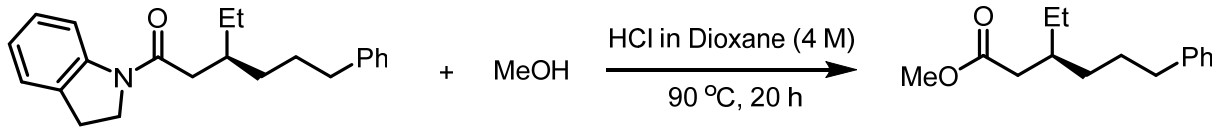
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.37 (m, 2H), 7.36 – 7.34 (m, 2H), 7.29 – 7.27 (m, 4H), 7.26 – 7.21 (m, 4H), 7.16 – 7.13 (m, 1H), 7.12 – 7.09 (m, 4H), 6.78 (t, *J* = 7.3 Hz, 1H) 3.57 (t, *J* = 7.9 Hz, 2H), 2.94 (t, *J* = 7.9 Hz, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.18 – 2.12 (m, 2H), 2.07 – 2.03 (m, 1H), 1.75 – 1.70 (m, 2H), 1.68 – 1.63 (m, 2H), 1.62 – 1.54 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.6, 142.8, 131.8, 131.70, 131.68, 128.3, 128.2, 126.5, 125.5, 124.2, 122.7, 122.6, 119.3, 112.9, 88.2, 88.1, 84.11, 84.08, 54.8, 50.7, 43.4, 36.4, 36.1, 34.1, 28.8, 28.1, 27.1, 10.8.

FT-IR (film): 2931, 1603, 1484, 1244, 744, 692 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{38}H_{38}N$: 508.2999, found: 508.2999.

[α]$^{16}_D$ = -–54.8 (c 0.2, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



7, 91% ee **54**, 83% yield, 91% ee

Methyl (*S*)-3-ethyl-6-phenylhexanoate (54). In a nitrogen-filled glovebox, a 10 mL Schlenk tube was equipped with a magnetic stir bar, (*S*)-3-ethyl-1-(indolin-1-yl)-6-phenylhexan-1-one (**7**, 91% ee, 32.1 mg, 0.10 mmol, 1.0 equiv), HCl solution (4.0 M in 1,4-dioxane, 0.7 mL, 2.8 mmol, 28 equiv), and methanol (0.7 mL). The Schlenk tube was transferred out of the glovebox, and the reaction mixture was stirred at 90 °C for 20 h. Upon completion, saturated $NaHCO_3$ aqueous solution (5 mL) was added, and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:10 EtOAc/hexanes) to afford the desired product. Yellow oil, 19.4 mg, 83% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 6.8 min (minor), 8.0 min (major).

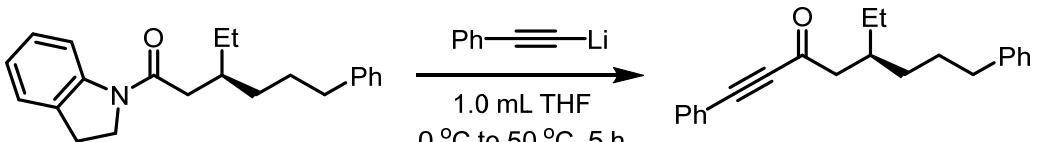
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.16 (m, 3H), 3.65 (s, 3H), 2.60 (t, *J* = 7.8 Hz, 2H), 2.26 – 2.23 (m, 2H), 1.87 – 1.82 (m, 1H), 1.64 – 1.57 (m, 2H), 1.40 – 1.34 (m, 2H), 1.34 – 1.29 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.0, 142.5, 128.3, 128.2, 125.6, 51.4, 38.6, 36.3, 36.1, 33.0, 28.4, 26.2, 10.7.

FT-IR (film): 3671, 2919, 1598, 1467, 1055, 745, 707 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{15}H_{22}NaO_2$: 257.1512, found: 257.1510.

[α]$^{16}_D$ = –12.6 (c 0.2, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



7, 91% ee **55**, 78% yield, 91% ee

(*S*)-5-Ethyl-1,8-diphenyloct-1-yn-3-one (55). In a nitrogen-filled glovebox, an oven-dried 4 mL vial was equipped with a magnetic stir bar, (*S*)-3-ethyl-1-(indolin-1-yl)-6-phenylhexan-1-one

(**7**, 91% ee, 32.1 mg, 0.10 mmol, 1.0 equiv), and THF (1 mL). The vial was transferred out of the glovebox, and lithium phenylacetylide (0.5 M in THF, 240 uL, 0.12 mmol, 1.2 equiv) was added dropwise to the solution at 0 °C. Next, the reaction mixture was allowed to warm to room temperature, then it was heated to 50 °C and stirred for 5 h. Upon completion, saturated $NaHCO_3$ aqueous solution (5 mL) was added, and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:15 EtOAc/hexanes) to afford the desired product. Yellow oil, 23.7 mg, 78% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 11.7 min (major), 13.5 min (minor).

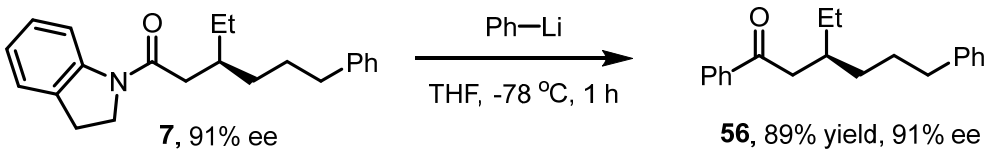
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 6.8 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.18 – 7.16 (m, 3H), 2.62 – 2.59 (m, 2H), 2.59 – 2.57 (m, 2H), 2.12 – 2.07 (m, 1H), 1.68 – 1.62 (m, 2H), 1.45 – 1.41 (m, 2H), 1.40 – 1.35 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 188.3, 142.4, 133.0, 130.6, 128.6, 128.34, 128.25, 125.7, 120.0, 90.5, 88.2, 50.0, 36.1, 35.9, 33.1, 28.6, 26.3, 10.8.

FT-IR (film): 3668, 2930, 1673, 1457, 1052, 756, 704 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{25}O$: 305.1900, found: 305.1903.

$[\alpha]^{16}_D$ = –7.9 (c 0.2, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



7, 91% ee

56, 89% yield, 91% ee

(*S*)-3-Ethyl-1,6-diphenylhexan-1-one (56). In a nitrogen-filled glovebox, an oven-dried 4 mL vial was equipped with a magnetic stir bar, (*S*)-3-ethyl-1-(indolin-1-yl)-6-phenylhexan-1-one (**7**, 91% ee, 32.1 mg, 0.10 mmol, 1.0 equiv), and THF (1 mL). The vial was transferred out of the glovebox, and phenyl lithium (0.5 M in Et_2O, 300 uL, 0.15 mmol, 1.5 equiv) was added dropwise to the solution at -78 °C. The reaction mixture was stirred at -78 °C for 1 h. Upon completion, saturated $NaHCO_3$ aqueous solution (5 mL) was added, and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:15 EtOAc/hexanes) to afford the desired product. Yellow oil, 24.9 mg, 89% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 10.2 min (major), 11.3 min (minor).

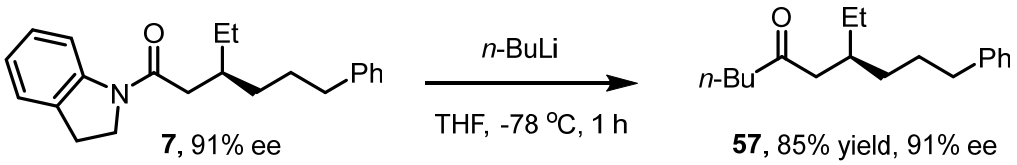
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 – 7.94 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 8.2 Hz, 3H), 2.93 – 2.83 (m, 2H), 2.61 – 2.58 (m, 2H), 2.14 – 2.08 (m, 1H), 1.67 – 1.60 (m, 2H), 1.43 – 1.35 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 200.6, 142.6, 137.5, 132.8, 128.5, 128.3, 128.2, 128.1, 125.6, 43.0, 36.2, 35.5, 33.3, 28.6, 26.4, 10.9.

FT-IR (film): 2928, 1681, 1603, 1450, 747, 690 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+K]$^+$ calcd for $C_{20}H_{24}KO$: 319.1459, found: 319.1455.

[α]$^{16}_D$ = –15.6 (c 0.2, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.



7, 91% ee

57, 85% yield, 91% ee

(*S*)-7-Ethyl-10-phenyldecan-5-one (57). In a nitrogen-filled glovebox, an oven-dried 4 mL vial was equipped with a magnetic stir bar, (*S*)-3-ethyl-1-(indolin-1-yl)-6-phenylhexan-1-one (**7**, 91% ee, 32.1 mg, 0.10 mmol, 1.0 equiv), and THF (1 mL). The vial was transferred out of the glovebox, and *n*-butyllithium (2.4 M in THF, 50 uL, 0.12 mmol, 1.2 equiv) was added dropwise to the solution at -78 °C. The reaction mixture was stirred at -78 °C for 1 h. Upon completion, saturated $NaHCO_3$ aqueous solution (5 mL) was added, and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:15 EtOAc/hexanes) to afford the desired product. Yellow oil, 22.1 mg, 85% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 25.3 min (major), 28.7 min (minor).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.18 (t, *J* = 5.6 Hz, 3H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 2.30 (t, *J* = 6.9 Hz, 2H), 1.91 (p, *J* = 6.5 Hz, 1H), 1.60 – 1.56 (m, 2H), 1.55 – 1.50 (m, 2H), 1.35 – 1.30 (m, 3H), 1.29 – 1.24 (m, 3H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H).

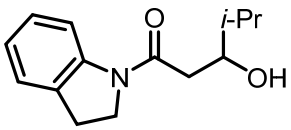
^{13}C NMR (151 MHz, Chloroform-*d*) δ 211.6, 142.6, 128.3, 128.2, 125.6, 47.3, 43.1, 36.1, 35.0, 33.1, 28.6, 26.3, 25.9, 22.3, 13.9, 10.8.

FT-IR (film): 2923, 1713, 1457, 1374, 1038, 745, 695 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{18}H_{29}O$: 261.2213, found: 261.2209.

[α]$^{16}_D$ = –9.8 (c 0.2, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.

3. Synthesis of a natural product.



3-Hydroxy-1-(indolin-1-yl)-4-methylpentan-1-one. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and isobutyraldehyde.

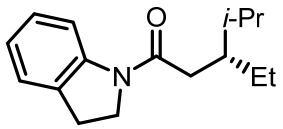
The product was purified by column chromatography on silica gel (1:1 EtOAc/hexanes). 3.82 g (16.4 mmol, 82% yield). White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.3 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 4.09 – 3.99 (m, 2H), 3.94 – 3.89 (m, 1H), 3.82 – 3.72 (m, 1H), 3.19 (t, *J* = 8.3 Hz, 2H), 2.60 – 2.54 (m, 1H), 2.50 – 2.41 (m, 1H), 1.84 – 1.74 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.3, 142.6, 131.1, 127.5, 124.6, 124.0, 117.1, 72.6, 48.0, 39.2, 33.0, 27.9, 18.5, 18.0.

FT-IR (film): 3502, 2876, 1725, 1396, 1261, 760 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{14}H_{20}NO_2$: 234.1489, found: 234.1492.



(*R*)-3-Ethyl-1-(indolin-1-yl)-4-methylpentan-1-one (58). In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a stir bar was charged with $NiBr_2$·DME (15.5 mg, 0.050 mmol, 10.0 mol%), (*R*,*R*)-**L1** (35.3 mg, 0.060 mmol, 12.0 mol%), and Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (9.0 mg, 0.0075 mmol, 1.5 mol%). Anhydrous methyl *tert*-butyl ether (2.5 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 60 min at least, leading to a catalyst solution. In a nitrogen-filled glovebox, a separate oven-dried 4 mL vial was charged with 3-hydroxy-1-(indolin-1-yl)-4-methylpentan-1-one (291.3 mg, 1.25 mmol, 2.5 equiv), NHC (494.0 mg, 1.25 mmol, 2.5 equiv), and a stir bar. (Trifluoromethyl)benzene (2.5 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (291.9 μL, 1.30 mmol, 2.6 equiv) was added dropwise, and the resulting solution was stirred at room temperature for another 30 min (a white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution. In a nitrogen-filled glovebox, an oven-dried 20 mL vial was charged with 1,3-dioxoisoindolin-2-yl propionate (109.5 mg, 0.50 mmol, 1.0 equiv), quinuclidine (83.5 mg, 0.75 mmol, 1.5 equiv), and a stir bar. The catalyst solution and NHC-alcohol adduct solution were transferred via syringe to the 20 mL reaction vial. The vial was transferred out of the glovebox and placed in an EtOH cooling bath at 0 °C for 5 min. Then the reaction was irradiated with blue LEDs (455 nm, 30 W) and was stirred at 0 °C for 30 hours. Upon completion, the reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with EtOAc. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 74.7 mg, 61% yield, 88% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L1**: 10.8 min (major), 12.8 min (minor).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.16 (m, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 4.08 (t, *J* = 8.5 Hz, 2H), 3.19 (t, *J* = 8.5 Hz, 2H), 2.37 (dd, *J* = 15.6, 5.7 Hz, 1H), 2.24 (dd, *J* =

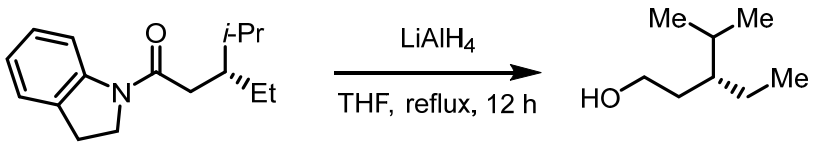
15.5, 7.5 Hz, 1H), 1.96 – 1.90 (m, 1H), 1.88 – 1.83 (m, 1H), 1.45 – 1.38 (m, 1H), 1.37 – 1.31 (m, 1H), 0.93 – 0.90 (m, 6H), 0.88 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.6, 143.2, 131.0, 127.5, 124.4, 123.4, 117.0, 48.1, 41.5, 36.9, 29.0, 28.0, 23.6, 19.4, 18.6, 11.9.

FT-IR (film): 2912, 1672, 1563, 1276, 1076, 789 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{16}H_{23}NNaO$: 268.1672, found: 268.1671.

[α]$^{25}_D$ = +9.8 (c 0.5, $CHCl_3$); 88% ee, from (*R*,*R*)-**L1**.



58, 88% ee **59**, 89% yield, 88% ee

(*R*)-3-Ethyl-4-methylpentan-1-ol (59). In a nitrogen-filled glovebox, a 10 mL Schlenk tube was equipped with a magnetic stir bar, (*R*)-3-ethyl-1-(indolin-1-yl)-4-methylpentan-1-one (**55**, 88% ee, 24.5 mg, 0.10 mmol, 1.0 equiv), and THF (1 mL). The Schlenk tube was transferred out of the glovebox, and lithium aluminum hydride (1.0 M in THF, 200 uL, 0.20 mmol, 2.0 equiv) was added dropwise to the solution at 0 °C. Next, the reaction mixture was allowed to warm to room temperature, then it was heated to 80 °C and stirred for 12 h. Upon completion, the reaction mixture was cooled to 0 °C, and then quenched in turn with H_2O (10 uL), 15% aqueous NaOH (20 uL), and H_2O (30 uL). The reaction mixture was extracted with EtOAc (3 x 5 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:5 EtOAc/hexanes) to afford the desired product. Yellow oil, 11.6 mg, 89% yield, 88% ee.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 3.68 – 3.58 (m, 2H), 1.88 (s, 1H), 1.73 – 1.67 (m, 1H), 1.58 – 1.50 (m, 1H), 1.44 – 1.37 (m, 1H), 1.34 – 1.28 (m, 1H), 1.24 – 1.17 (m, 1H), 1.15 – 1.10 (m, 1H), 0.86 (t, *J* = 7.5 Hz, 3H), 0.83 (d, *J* = 6.9 Hz, 3H), 0.82 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 62.0, 42.0, 33.3, 29.0, 23.3, 19.4, 18.7, 11.9.

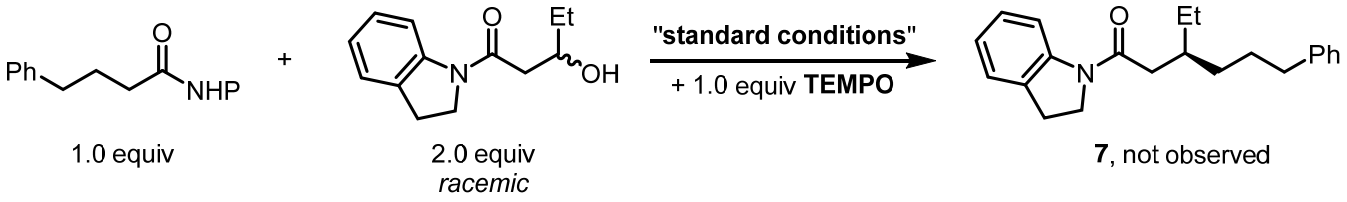
FT-IR (film): 3675, 2918, 1145, 988, 756 cm^{-1}.

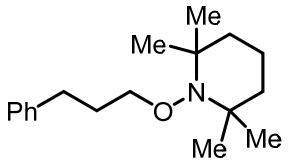
HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_8H_{18}NaO$: 153.1250, found: 153.1253.

[α]$^{25}_D$ = +7.2 (c 0.2, $CHCl_3$); 88% ee, from (*R*,*R*)-**L1**.

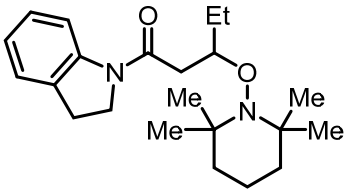
VIII. Mechanistic Experiments

1. Radical trapping experiment.



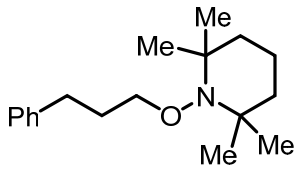


A[1], 28% yield



A[2], $[M+H]^+$ calcd: 359.2693
found: 359.2693

Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a stir bar was charged with $NiBr_2$·DME (6.2 mg, 0.020 mmol, 10.0 mol%), (*S*,*S*)-**L1** (14.2 mg, 0.024 mmol, 12.0 mol%), and Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (3.6 mg, 0.0030 mmol, 1.5 mol%). Anhydrous methyl *tert*-butyl ether (1.0 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 60 min at least, leading to a catalyst solution. Then, a separate oven-dried 4 mL vial was charged with 3-hydroxy-1-(indolin-1-yl)pentan-1-one (87.6 mg, 0.40 mmol, 2.0 equiv), NHC (158.2 mg, 0.40 mmol, 2.0 equiv), and a stir bar. (Trifluoromethyl)benzene (1.0 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (98.8 μL, 0.44 mmol, 2.2 equiv) was added dropwise, and the resulting solution was stirred at room temperature for another 30 min (a white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (61.8 mg, 0.20 mmol, 1.0 equiv), quinuclidine (33.4 mg, 0.30 mmol, 1.5 equiv), TEMPO (31.2 mg, 0.20 mmol, 1.0 equiv), and a stir bar. The catalyst solution and NHC-alcohol adduct solution were transferred via syringe to the 4 mL reaction vial. The vial was transferred out of the glovebox and placed in an EtOH cooling bath at 0 °C for 5 min. Then the reaction was irradiated with blue LEDs (455 nm, 30 W) and was stirred at 0 °C for 20 hours. The reaction was stopped by ending the irradiation. The reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with EtOAc. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.



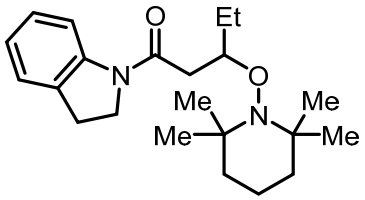
2,2,6,6-Tetramethyl-1-(3-phenylpropoxy)piperidine (A[1]). Colorless oil, 15.4 mg, 28% yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.8 Hz, 3H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.37 (t, *J* = 7.6 Hz, 2H), 2.01 (p, *J* = 7.6 Hz, 2H), 1.74 – 1.68 (m, 2H), 1.66 – 1.59 (m, 1H), 1.55 – 1.51 (m, 2H), 1.43 – 1.39 (m, 1H), 1.15 (s, 6H), 1.06 (s, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.4, 128.3, 128.2, 125.7, 76.1, 59.7, 39.6, 33.0, 32.7, 31.5, 30.5, 29.7, 20.1, 17.1.

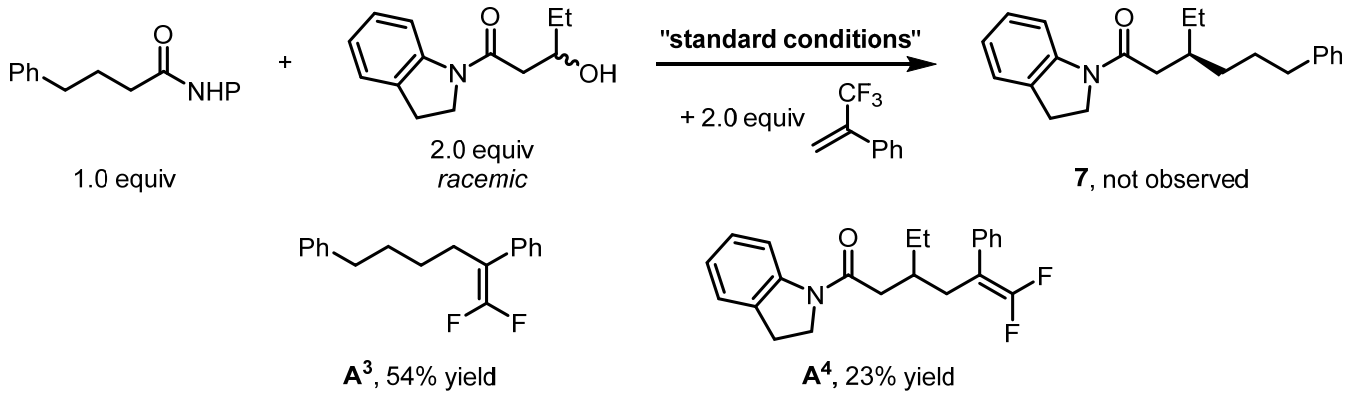
FT-IR (film): 2925, 1452, 1359, 1046, 700 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{18}H_{29}NNaO$: 298.2141, found: 298.2133.



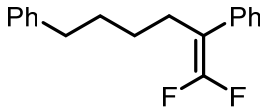
1-(Indolin-1-yl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentan-1-one (A[2]).

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{22}H_{35}N_2O_2$: 359.2693, found: 359.2693.



Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a stir bar was charged with $NiBr_2$·DME (6.2 mg, 0.020 mmol, 10.0 mol%), (*S*,*S*)-**L1** (14.2 mg, 0.024 mmol, 12.0 mol%), and Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (3.6 mg, 0.0030 mmol, 1.5 mol%). Anhydrous methyl *tert*-butyl ether (1.0 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 60 min at least, leading to a catalyst solution. Then, a separate oven-dried 4 mL vial was charged with 3-hydroxy-1-(indolin-1-yl)pentan-1-one (87.6 mg, 0.40 mmol, 2.0 equiv), NHC (158.2 mg, 0.40 mmol, 2.0 equiv), and a stir bar. (Trifluoromethyl)benzene (1.0 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (98.8 μL, 0.44 mmol, 2.2 equiv) was added dropwise, and the resulting solution was stirred at room temperature for another 30 min (a

white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (61.8 mg, 0.20 mmol, 1.0 equiv), quinuclidine (33.4 mg, 0.30 mmol, 1.5 equiv), (3,3,3-trifluoroprop-1-en-2-yl)benzene (68.8 mg, 0.40 mmol, 2.0 equiv), and a stir bar. The catalyst solution and NHC-alcohol adduct solution were transferred via syringe to the 4 mL reaction vial. The vial was transferred out of the glovebox and placed in an EtOH cooling bath at 0 °C for 5 min. Then the reaction was irradiated with blue LEDs (455 nm, 30 W) and was stirred at 0 °C for 20 hours. The reaction was stopped by ending the irradiation. The reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with EtOAc. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.



(6,6-Difluorohex-5-ene-1,5-diyl)dibenzene (A[3]). Colorless oil, 29.4 mg, 54% yield.

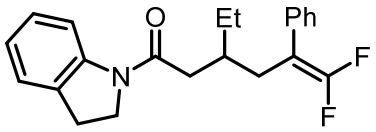
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 2.42 (ddt, *J* = 7.7, 5.3, 2.5 Hz, 2H), 1.64 – 1.59 (m, 2H), 1.43 – 1.38 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.6 (t, *J* = 288.3 Hz), 142.4, 133.7, 128.4, 128.33, 128.26, 128.2, 127.2, 125.7, 92.2 (t, *J* = 17.2 Hz), 35.5, 30.7, 27.4, 27.2 (t, *J* = 2.7 Hz).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -91.8.

FT-IR (film): 2933, 1728, 1497, 1228, 695 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{18}H_{19}F_2$: 273.1449, found: 273.1452.



3-Ethyl-6,6-difluoro-1-(indolin-1-yl)-5-phenylhex-5-en-1-one (A[4]). Colorless oil, 16.4 mg, 23% yield.

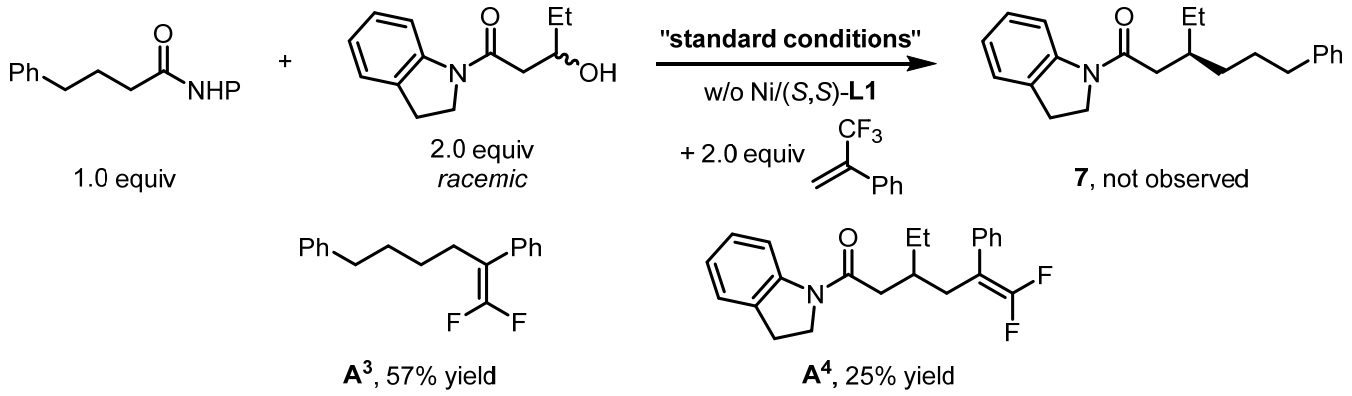
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 3.88 – 3.82 (m, 1H), 3.75 – 3.69 (m, 1H), 3.09 (t, *J* = 8.5 Hz, 2H), 2.58 – 2.51 (m, 2H), 2.34 – 2.22 (m, 2H), 2.10 – 2.05 (m, 1H), 1.46 – 1.41 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.3, 154.1 (dd, *J* = 290.8, 286.4 Hz), 143.0, 133.5, 130.9, 128.4, 128.3 (t, *J* = 3.3 Hz), 127.5, 127.2, 124.4, 123.4, 117.0, 91.0 (dd, *J* = 21.3, 12.9 Hz), 47.8, 39.4, 34.3, 31.1, 27.9, 26.1, 10.8.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.56, -90.64, -90.8, -90.9.

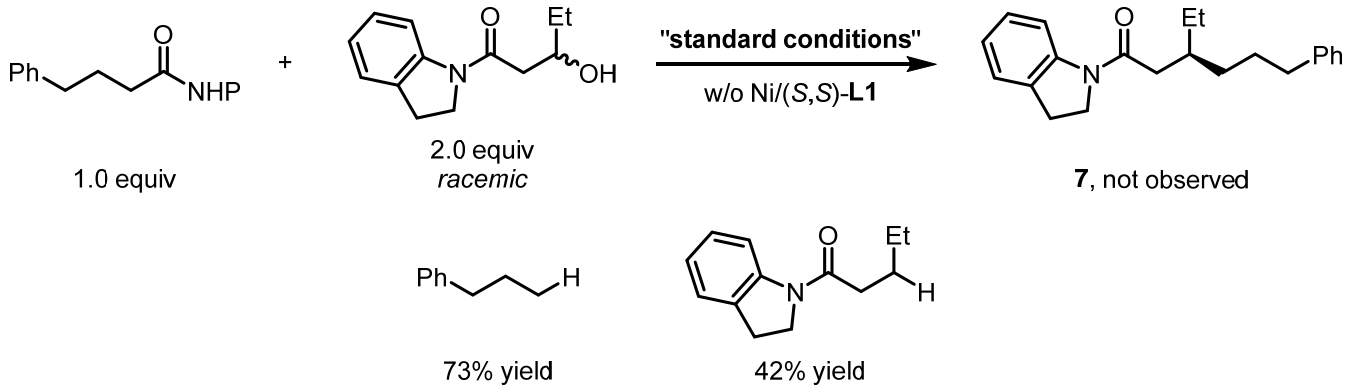
FT-IR (film): 2957, 1741, 1653, 1398, 1236, 1070, 768 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{22}H_{24}F_2NO$: 356.1820, found: 356.1824.

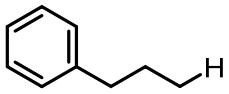


Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 3-hydroxy-1-(indolin-1-yl)pentan-1-one (43.8 mg, 0.20 mmol, 2.0 equiv), NHC (79.1 mg, 0.20 mmol, 2.0 equiv), and a stir bar. (Trifluoromethyl)benzene (0.5 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (49.4 μL, 0.22 mmol, 2.2 equiv) was added dropwise, and the resulting solution was stirred at room temperature for another 30 min (a white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (30.9 mg, 0.10 mmol, 1.0 equiv), quinuclidine (16.7 mg, 0.15 mmol, 1.5 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.8 mg, 0.0015 mmol, 1.5 mol%), (3,3,3-trifluoroprop-1-en-2-yl)benzene (34.4 mg, 0.20 mmol, 2.0 equiv), methyl *tert*-butyl ether (0.5 mL), and a stir bar. The NHC-alcohol adduct solution were transferred via syringe to the 4 mL reaction vial. The vial was transferred out of the glovebox and placed in an EtOH cooling bath at 0 °C for 5 min. Then the reaction was irradiated with blue LEDs (455 nm, 30 W) and was stirred at 0 °C for 20 hours. The reaction was stopped by ending the irradiation. The reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with EtOAc. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.

A^3: colorless oil, 15.5 mg, 57% yield; **A**^{4}: colorless oil, 8.9 mg, 25% yield.



Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 3-hydroxy-1-(indolin-1-yl)pentan-1-one (87.6 mg, 0.40 mmol, 2.0 equiv), NHC (158.2 mg, 0.40 mmol, 2.0 equiv), and a stir bar. (Trifluoromethyl)benzene (1.0 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (98.8 μL, 0.44 mmol, 2.2 equiv) was added dropwise, and the resulting solution was stirred at room temperature for another 30 min (a white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (61.8 mg, 0.20 mmol, 1.0 equiv), quinuclidine (33.4 mg, 0.30 mmol, 1.5 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.6 mg, 0.0030 mmol, 1.5 mol%), methyl *tert*-butyl ether (1.0 mL), and a stir bar. The NHC-alcohol adduct solution were transferred via syringe to the 4 mL reaction vial. The vial was transferred out of the glovebox and placed in an EtOH cooling bath at 0 °C for 5 min. Then the reaction was irradiated with blue LEDs (455 nm, 30 W) and was stirred at 0 °C for 20 hours. The reaction was stopped by ending the irradiation. The reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with EtOAc. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.



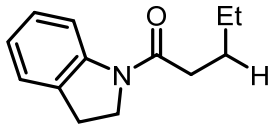
Propylbenzene. Colorless oil, 17.5 mg, 73% yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.21 – 7.18 (m, 3H), 2.61 (t, *J* = 7.8 Hz, 2H), 1.70 – 1.62 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.7, 128.5, 128.2, 125.6, 38.1, 24.6, 13.8.

FT-IR (film): 2959, 2928, 2868, 1499, 1450, 747, 692 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for C_9H_{13}: 121.1012, found: 121.1013.



1-(Indolin-1-yl)pentan-1-one. White solid, 17.1 mg, 42% yield.

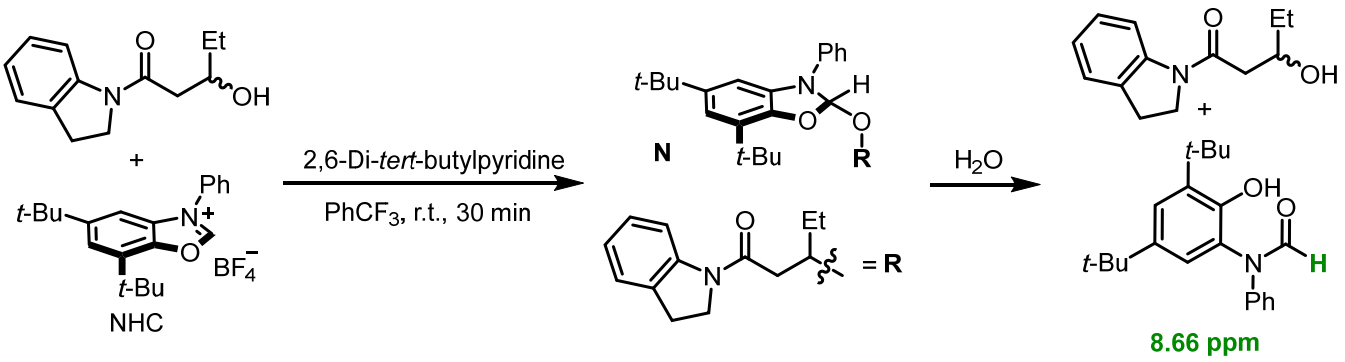
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.14 (m, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 4.03 (t, *J* = 8.8 Hz, 2H), 3.18 (t, *J* = 8.5 Hz, 2H), 2.40 (t, *J* = 7.5 Hz, 2H), 1.77 – 1.66 (m, 2H), 1.47 – 1.38 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.4, 143.1, 131.0, 127.5, 124.4, 123.4, 116.9, 47.9, 35.6, 28.0, 26.6, 22.5, 13.9.

FT-IR (film): 2951, 2866, 1655, 1476, 1398, 1244, 1111, 755 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+K]^+$ calcd for $C_{13}H_{17}KNO$: 242.0942, found: 242.0942.

2. Cyclic voltammograms profiles.



Preparation of the NHC-alcohol adduct (N) solution. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 3-hydroxy-1-(indolin-1-yl)pentan-1-one (21.9 mg, 0.10 mmol, 1.0 equiv), NHC (39.6 mg, 0.10 mmol, 1.0 equiv), and a stir bar. (Trifluoromethyl)benzene (1.0 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (24.7 μL, 0.11 mmol, 1.1 equiv) was added dropwise, and the resulting solution was stirred at room temperature for another 30 min (a white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution.

Note: *The solution of* ***N*** *was treated with water for 30 minutes, leading to the production of alkyl alcohol and amide. The concentration of* ***N*** *was determined by* ^{1}*H NMR analysis of the amide using 1,2-dibromoethane as the internal standard. The concentration of* ***N*** *is 0.073 M.*

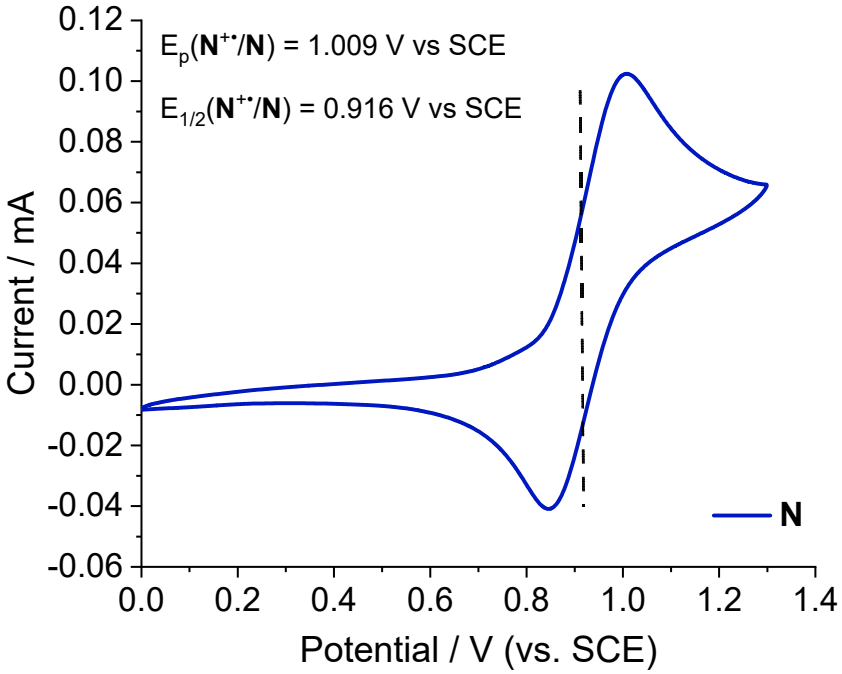


Figure S8. Cyclic voltammogram of **N**

Cyclic voltammogram of NHC-alcohol adduct (N). Cyclic voltammograms were collected with a CorrTest CS2350M electrochemical workstation. Samples were prepared by

mixing 0.050 mmol of **N** in 10 mL of 0.1 M *n*-Bu_4NPF_6 (387.4 mg, 1.0 mmol) in anhydrous MeCN. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, saturated calomel electrode (SCE) reference electrode, and a scan rate of 100 mV/s. The glassy carbon electrode was polished between each scan. The samples were sparged with N_2 for at least 15 minutes prior to data collection.

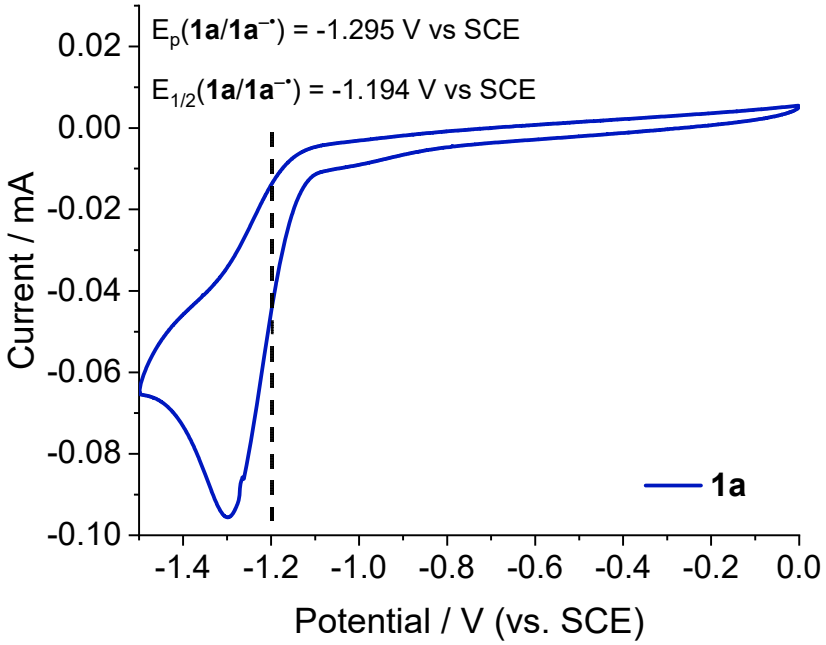
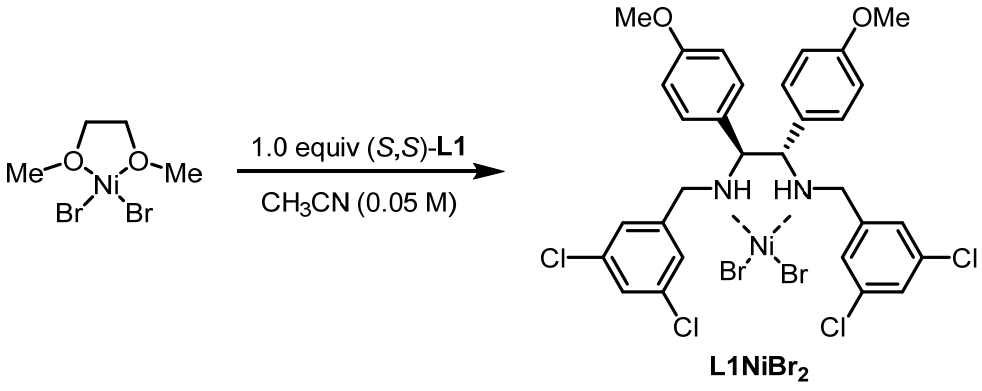


Figure S9. Cyclic voltammogram of **1a**

Cyclic voltammogram of NHP ester (1a). Cyclic voltammograms were collected with a CorrTest CS2350M electrochemical workstation. Samples were prepared by mixing 0.050 mmol of **1a** (15.5 mg) in 10 mL of 0.1 M *n*-Bu_4NPF_6 (387.4 mg, 1.0 mmol) in anhydrous MeCN. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, saturated calomel electrode (SCE) reference electrode, and a scan rate of 100 mV/s. The glassy carbon electrode was polished between each scan. The samples were sparged with N_2 for at least 15 minutes prior to data collection.



Preparation of L1NiBr$_2$: In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a stir bar was charged with (*S*,*S*)-**L1** (29.4 mg, 0.050 mmol, 1.0 equiv), NiBr$_2$·DME (15.4 mg, 0.050 mmol, 1.0 equiv), and dry CH$_3$CN (1.0 mL). The mixture was stirred at room temperature for 2 hours, leading to a red homogeneous solution.

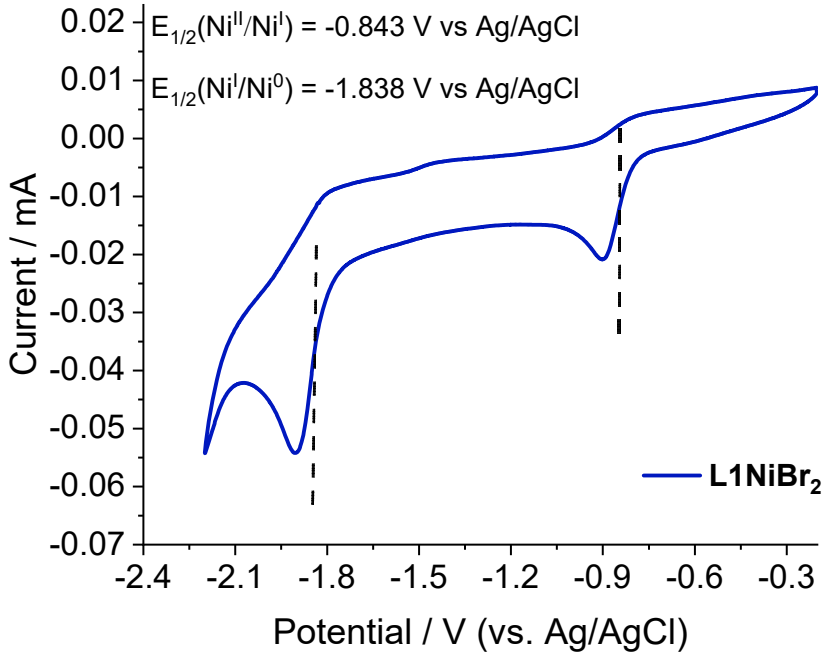


Figure S10. Cyclic voltammogram of **L1NiBr$_2$**

Cyclic voltammogram of L1NiBr$_2$. Cyclic voltammograms were collected with a CorrTest CS2350M electrochemical workstation. Samples were prepared by mixing 0.025 mmol of **L1NiBr$_2$** (0.5 mL solution of **L1NiBr$_2$**) in 10 mL of 0.1 M *n*-Bu$_4$NPF$_6$ (387.4 mg, 1.0 mmol) in anhydrous MeCN. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, Ag/AgCl reference electrode, and a scan rate of 100 mV/s. The glassy carbon electrode was polished between each scan. The samples were sparged with N$_2$ for at least 15 minutes prior to data collection.

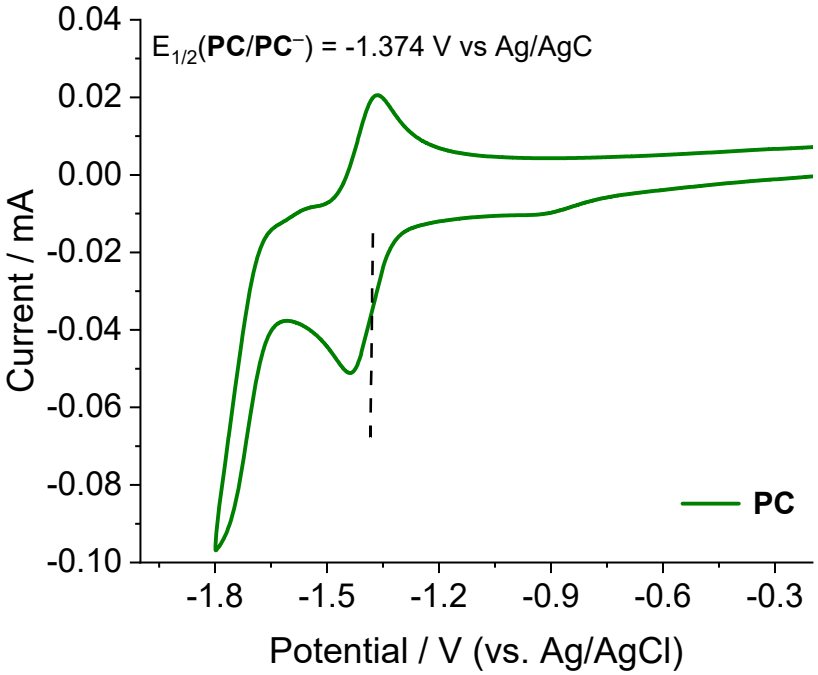


Figure S11. Cyclic voltammogram of **PC**

Cyclic voltammogram of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (PC). Cyclic voltammograms were collected with a CorrTest CS2350M electrochemical workstation. Samples were prepared by mixing 0.010 mmol of **PC** (11.2 mg) in 10 mL of 0.1 M *n*-Bu$_4$NPF$_6$ (387.4 mg, 1.0 mmol) in anhydrous MeCN. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, Ag/AgCl reference electrode, and a scan rate of 100 mV/s. The glassy carbon electrode was polished between each scan. The samples were sparged with N_2 for at least 15 minutes prior to data collection.

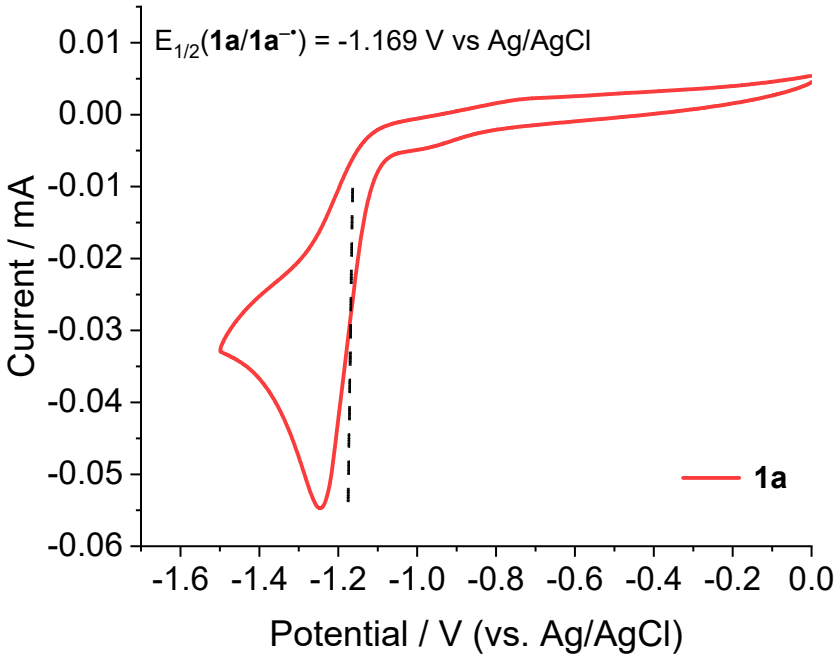


Figure S12. Cyclic voltammogram of **1a**

Cyclic voltammogram of NHP ester (1a). Cyclic voltammograms were collected with a CorrTest CS2350M electrochemical workstation. Samples were prepared by mixing 0.050 mmol of **1a** (15.5 mg) in 10 mL of 0.1 M *n*-Bu_4NPF_6 (387.4 mg, 1.0 mmol) in anhydrous MeCN. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, Ag/AgCl reference electrode, and a scan rate of 100 mV/s. The glassy carbon electrode was polished between each scan. The samples were sparged with N_2 for at least 15 minutes prior to data collection.

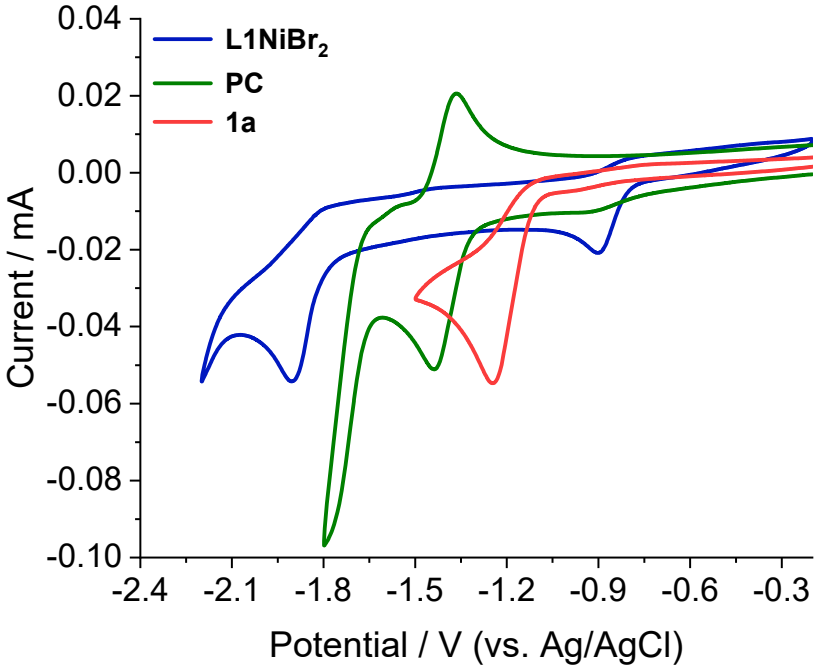


Figure S13. Cyclic voltammograms of **L1NiBr**$_2$ (blue line), **PC** (green line), and **1a** (red line)

3. Stern–Volmer luminescence quenching studies.

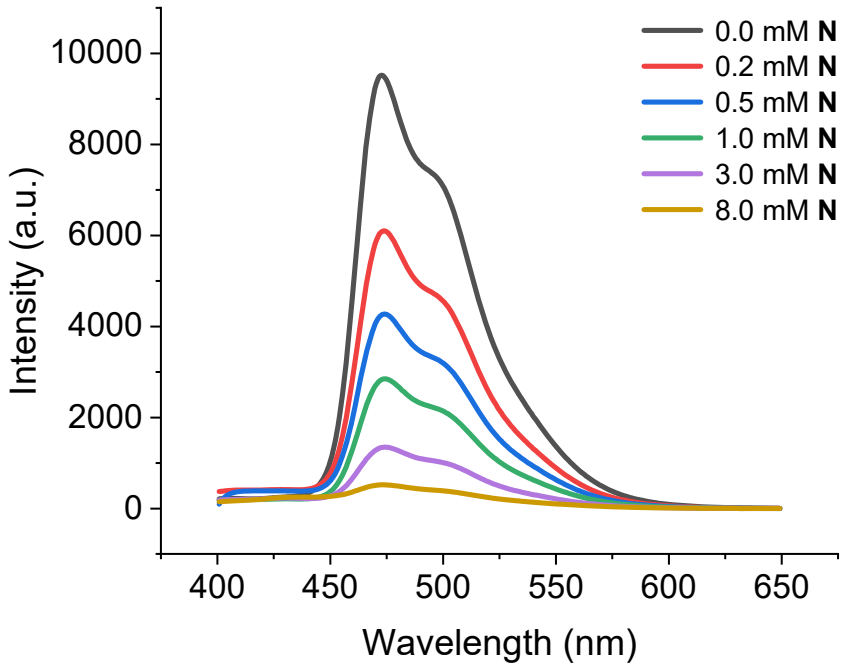


Figure S14. The emission quenching of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (0.005 mM) as a function of concentration of **N** in deaerated MTBE:PhCF$_3$ (1:1) with excitation at 455 nm. Conditions: (black curve) **N** (0.0 mM); (red curve) **N** (0.2 mM); (blue curve) **N** (0.5 mM); (green curve) **N** (1.0 mM); (purple curve) **N** (3.0 mM); (yellow curve) **N** (8.0 mM).

Emission quenching of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ as a function of concentration of N. A 1.0 mM solution of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (11.2 mg, 0.010 mmol) in anhydrous degassed MTBE:PhCF$_3$ (1:1, 10 mL) and a 73 mM solution of **N** were prepared in a nitrogen filled glovebox. To six sample vials were added 10 uL of 1.0 mM solution of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ and 0 uL, 5.5 uL, 13.7 uL, 27.4 uL, 82.2 uL, and 219.2 uL of 73 mM solution of **N.** Anhydrous degassed MTBE:PhCF$_3$ (1:1) was then added to each sample vial to a quantity of 2.0 mL. These were then transferred to a 3.5 mL quartz cuvette (path length: l = 10 mm) and sealed with Teflon caps under an atmosphere of nitrogen in glove box. The cuvette caps were wrapped with parafilm and the quartz cuvettes were removed out of the glove box. The emission quenching of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (0.005 mM) as a function of the concentration of **N** in deaerated MTBE:PhCF$_3$ (1:1) with excitation at 455 nm is shown in **Figure S14.**

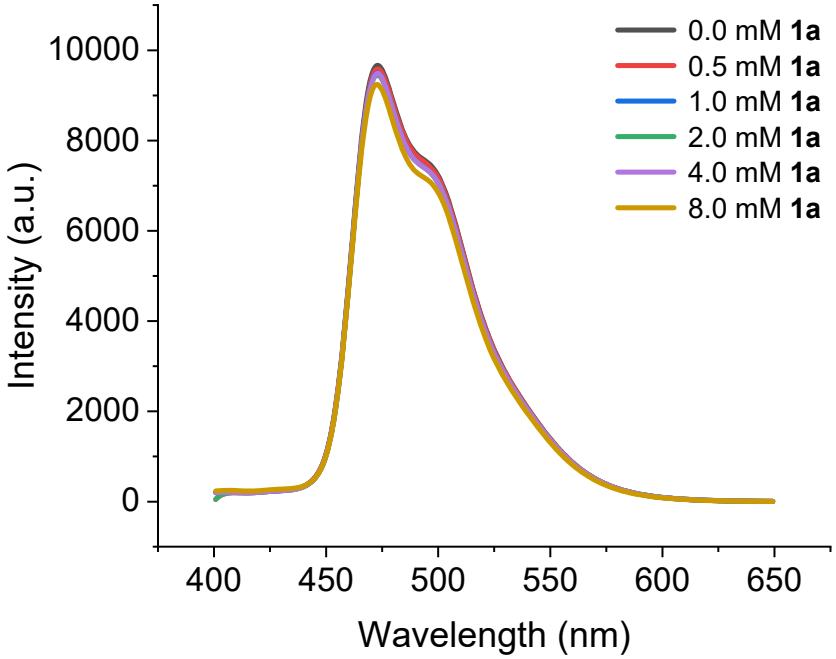
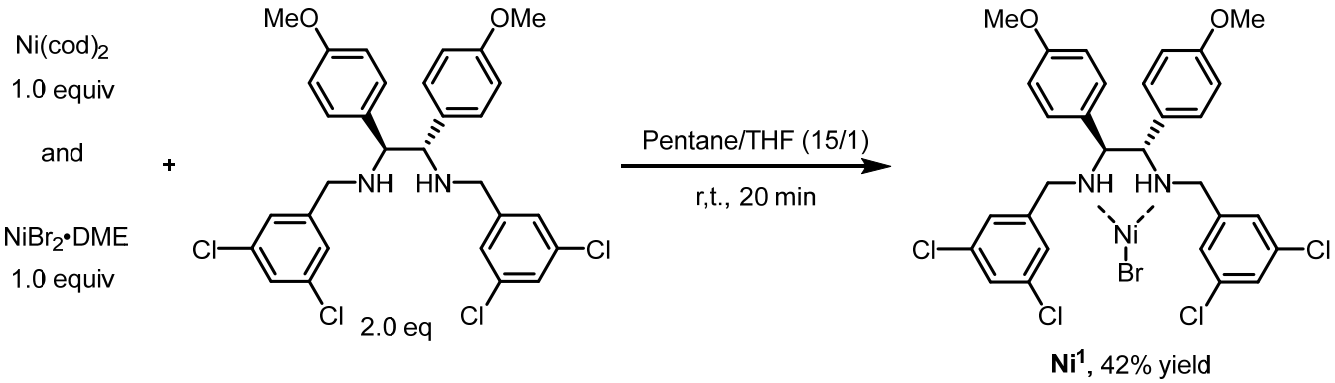


Figure S15. The emission quenching of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (0.005 mM) as a function of concentration of **1a** in deaerated MTBE:PhCF$_3$ (1:1) with excitation at 455 nm. Conditions: (black curve) **1a** (0.0 mM); (red curve) **1a** (0.5 mM); (blue curve) **1a** (1.0 mM); (green curve) **1a** (2.0 mM); (purple curve) **1a** (4.0 mM); (yellow curve) **1a** (8.0 mM).

Emission quenching of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ as a function of concentration of 1a. A 1.0 mM solution of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (11.2 mg, 0.010 mmol) in anhydrous degassed MTBE:PhCF$_3$ (1:1, 10 mL) and a 100 mM solution of **1a** (30.9 mg, 0.10 mmol) in anhydrous degassed MTBE:PhCF$_3$ (1:1, 1 mL) were prepared in a nitrogen filled glovebox. To six sample vials were added 10 uL of 1.0 mM solution of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ and 0 uL, 10 uL, 20 uL, 40 uL, 80 uL, and 160 uL of 100 mM solution of **1a.** Anhydrous degassed MTBE:PhCF$_3$ (1:1) was then added to each sample vial to a quantity of 2.0 mL. These were then

transferred to a 3.5 mL quartz cuvette (path length: l = 10 mm) and sealed with Teflon caps under an atmosphere of nitrogen in glove box. The cuvette caps were wrapped with parafilm and the quartz cuvettes were removed out of the glove box. The emission quenching of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (0.005 mM) as a function of the concentration of **1a** in deaerated MTBE:$PhCF_3$ (1:1) with excitation at 455 nm is shown in **Figure S15.**

4. Independently prepared nickel complexes.



Preparation of Ni¹: In a nitrogen-filled glovebox, an oven-dried 20 mL vial that contained a stir bar was charged with $Ni(COD)_2$ (68.8 mg, 0.25 mmol, 1.0 equiv), $NiBr_2$·DME (77.0 mg, 0.25 mmol, 1.0 equiv), (*S*,*S*)-**L1** (294.0 mg, 0.50 mmol, 2.0 equiv), dry pentane (15 mL), and THF (1 mL). The reaction was stirred at room temperature. After 20 min, a light green solid formed, which was filtered and washed with pentane (5 × 10 mL). The solid was dried in vacuo, affording **Ni¹** as a light green powder (152.3 mg, 42% yield), which was stored in the glovebox at −30 °C. This complex is not sensitive to dry air, but it degrades slowly in the presence of moisture.

Note: *The sample is paramagnetic. The ^1H and ^{13}C NMR spectra show signal broadening, preventing a comprehensive analytical characterization.*

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{30}H_{29}BrCl_4N_2NiO_2$: 725.9515, found: 725.9524.

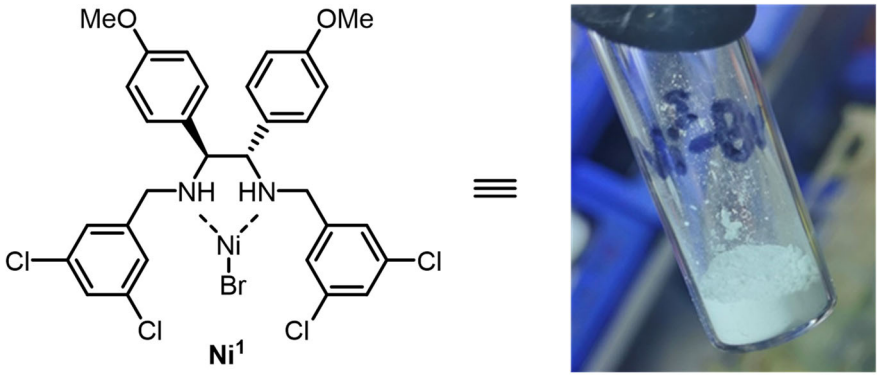
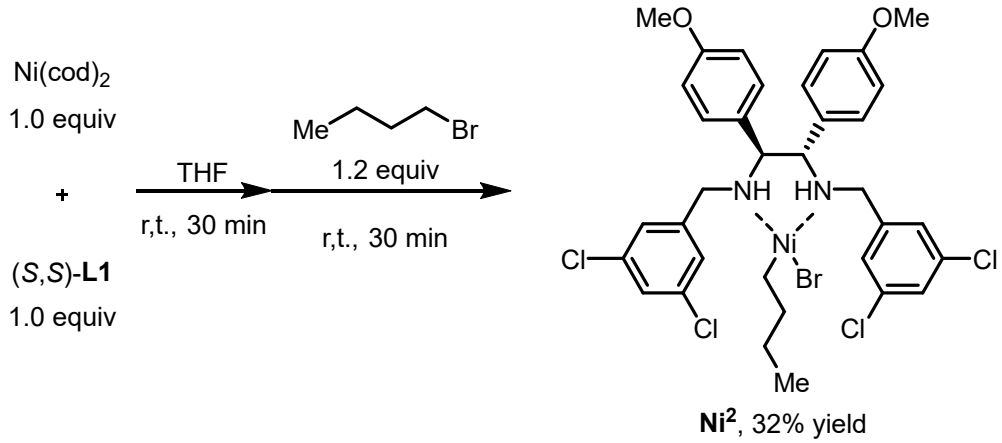


Figure S16. Picture of complex **Ni¹**



Preparation of Ni²: In a nitrogen-filled glovebox, an oven-dried 20 mL vial that contained a stir bar was charged with $Ni(COD)_2$ (137.5 mg, 0.50 mmol, 1.0 equiv), (*S*,*S*)-**L1** (294.0 mg, 0.50 mmol, 1.02 equiv), and dry THF (10 mL). The reaction was stirred at room temperature for 30 min, then 1-bromobutane (81.6 mg, 0.60 mmol, 1.2 equiv) was added. The reaction was stirred at room temperature for 30 min. The resulting grey solution was filtered and removed under reduced pressure to obtain a grey solid, which is washed with pentane (5 × 5 mL). The solid was dried in vacuo, affording **Ni²** a grey powder (125.1 mg, 32% yield). This complex remains stable in the solid state outside the glovebox for short periods of time, but it rapidly decomposes when stored in solution under aerobic conditions.

Note: *The sample is paramagnetic. The ^{1}H and ^{13}C NMR spectra show signal broadening, preventing a comprehensive analytical characterization.*

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{34}H_{38}BrCl_4N_2NiO_2$: 783.0219, found: 783.0220.

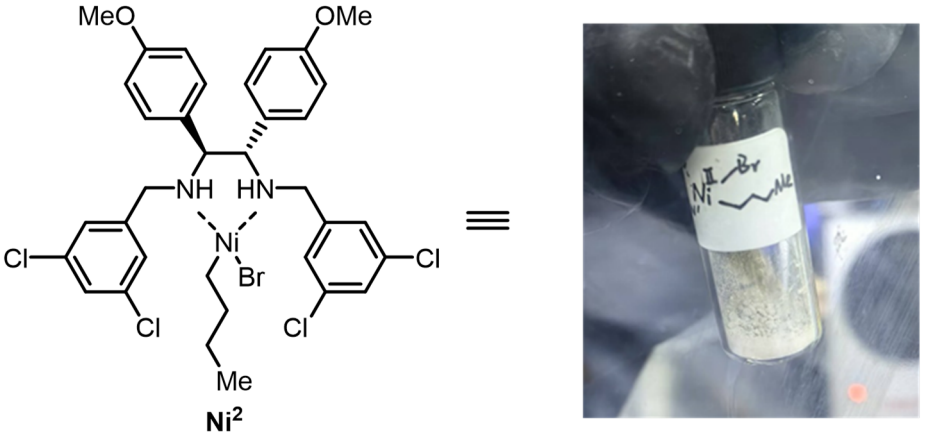
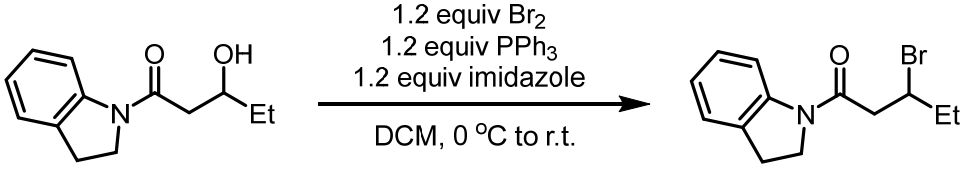


Figure S17. Picture of complex **Ni²**



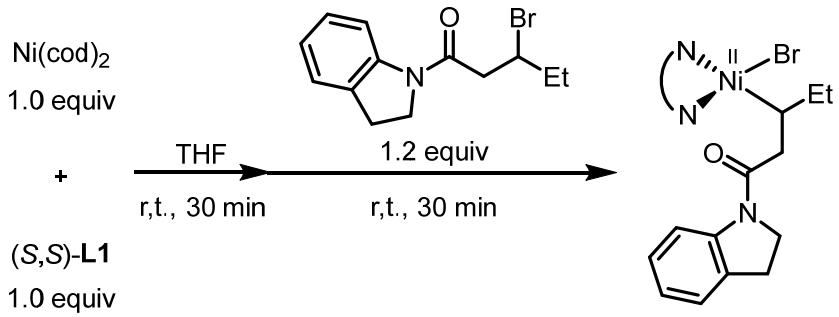
3-Bromo-1-(indolin-1-yl)pentan-1-one. To a solution of PPh_3 (3.13 g, 12.0 mmol, 1.2 equiv) and imidazole (0.82 g, 12.0 mmol, 1.2 equiv) in anhydrous DCM (50 mL), Br_2 (1.92 g, 12.0 mmol, 1.2 equiv) was added slowly. The reaction mixture was stirred at 0 °C for 10 min. Then, 3-hydroxy-1-(indolin-1-yl)pentan-1-one (2.19 g, 10.0 mmol, 1.0 equiv) was added dropwise. The mixture was stirred at 0 °C for another 1 h and then allowed to warm to room temperature. After stirring for 12 h, the mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with DCM (3 x 40 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (1:20 EtOAc/hexanes) to afford the desired product. Yellow oil, 1.0 g, 36% yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 4.12 – 4.08 (m, 1H), 4.06 – 3.98 (m, 2H), 3.22 (t, *J* = 8.5 Hz, 2H), 2.60 (dd, *J* = 16.6, 2.4 Hz, 1H), 2.47 (dd, *J* = 16.6, 9.5 Hz, 1H), 1.70 – 1.62 (m, 1H), 1.59 – 1.53 (m, 1H), 1.03 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 142.5, 131.1, 127.6, 124.6, 124.0, 117.1, 69.2, 47.9, 41.8, 29.2, 27.9, 10.0.

FT-IR (film): 2930, 1675, 1643, 1295, 979, 688 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{13}H_{16}BrNNaO$: 304.0307, found: 304.0311.



Ni^3, 28% yield

Preparation of Ni^3: In a nitrogen-filled glovebox, an oven-dried 20 mL vial that contained a stir bar was charged with $Ni(COD)_2$ (137.5 mg, 0.50 mmol, 1.0 equiv), (*S*,*S*)-**L1** (294.0 mg, 0.50 mmol, 1.02 equiv), and dry THF (10 mL). The reaction was stirred at room temperature for 30 min, then 3-bromo-1-(indolin-1-yl)pentan-1-one (168.6 mg, 0.60 mmol, 1.2 equiv) was added. The reaction was stirred at room temperature for 2 hours. The resulting black solution was filtered and removed under reduced pressure to obtain a black solid, which is washed with pentane (5 × 5 mL). The solid was dried in vacuo, affording **Ni^3** a black powder (129.8 mg, 28% yield). This complex remains stable in the solid state outside the glovebox for short periods of time, but it rapidly decomposes when stored in solution under aerobic conditions.

Note: *The sample is paramagnetic. The ^{1}H and ^{13}C NMR spectra show signal broadening, preventing a comprehensive analytical characterization.*

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{43}H_{45}BrCl_4N_3NiO_2$: 928.0746, found: 928.0748.

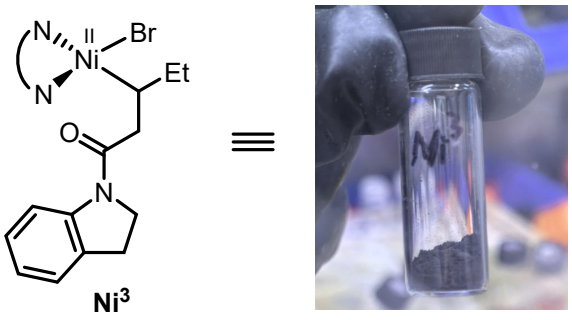


Figure S18. Picture of complex **Ni³**

5. UV-vis studies.

Preparation of Ni² solution: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with **Ni²** (0.8 mg, 0.001 mmol) and 1.0 mL MTBE:$PhCF_3$ (1:1). 100 μL of **Ni²** solution was transferred into a quartz cuvette followed by the addition of 2.5 mL MTBE:$PhCF_3$ (1:1). UV-vis absorption spectroscopy was subsequently performed at 20 °C.

Preparation of the standard reaction solution: In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a stir bar was charged with $NiBr_2$·DME (3.1 mg, 0.010 mmol, 10.0 mol%), (*S*,*S*)-**L1** (7.1 mg, 0.012 mmol, 12.0 mol%), and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.8 mg, 0.0015 mmol, 1.5 mol%). Anhydrous methyl *tert*-butyl ether (0.5 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 60 min at least, leading to a catalyst solution. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 3-hydroxy-1-(indolin-1-yl)pentan-1-one (43.8 mg, 0.20 mmol, 2.0 equiv), NHC (79.1 mg, 0.20 mmol, 2.0 equiv), and a stir bar. (Trifluoromethyl)benzene (0.5 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (49.4 μL, 0.22 mmol, 2.2 equiv) was added dropwise, and the resulting solution was stirred at room temperature for another 30 min (a white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 1,3-dioxoisoindolin-2-yl pentanoate (24.7 mg, 0.10 mmol, 1.0 equiv), quinuclidine (16.7 mg, 0.15 mmol, 1.5 equiv), and a stir bar. The catalyst solution and NHC-alcohol adduct solution were transferred via syringe to the 4 mL reaction vial. The vial was transferred out of the glovebox and placed in an EtOH cooling bath at 0 °C for 5 min. Then the reaction was irradiated with blue LEDs (455 nm, 30 W) and was stirred at 0 °C for 2, 4, and 6 hours. The reaction was stopped by ending the irradiation. The reaction mixture was transferred into a glovebox, where 100 μL of the reaction solution was transferred into a quartz cuvette followed by the addition of 2.5 mL MTBE:$PhCF_3$ (1:1). UV-vis absorption spectroscopy was subsequently performed at 20 °C.

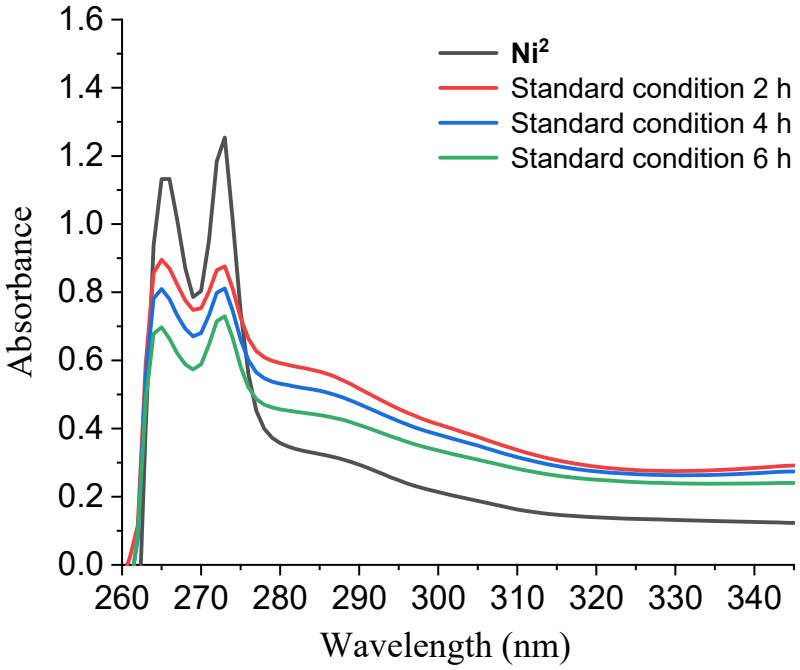
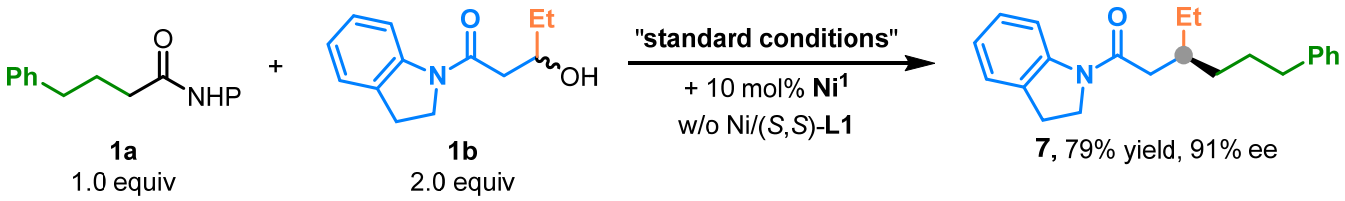


Figure S19. UV-vis spectra ((MTBE:$PhCF_3$ (1:1), 20 °C). Conditions: (black curve) **Ni²**; (red curve) Standard conditions 2 h; (blue curve) Standard conditions 4 h; (green curve) Standard conditions 6 h.

Discussion: Comparison of the UV−vis spectra shows that **Ni²** may be the predominant resting state for Ni catalytic cycle.

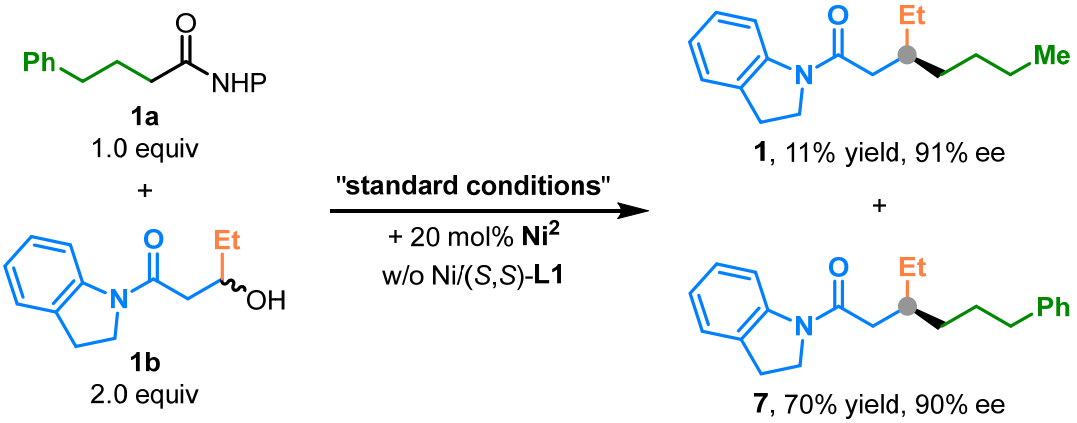
6. The reactivity and selectivity of Ni¹, Ni² and Ni³.



Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 3-hydroxy-1-(indolin-1-yl)pentan-1-one (43.8 mg, 0.20 mmol, 2.0 equiv), NHC (79.1 mg, 0.20 mmol, 2.0 equiv), and a stir bar. (Trifluoromethyl)benzene (0.5 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (49.4 μL, 0.22 mmol, 2.2 equiv) was added dropwise, and the resulting solution was stirred at room temperature for another 30 min (a white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (30.9 mg, 0.10 mmol, 1.0 equiv), quinuclidine (16.7 mg, 0.15 mmol, 1.5 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.8 mg, 0.0015 mmol, 1.5 mol%), **Ni¹** (7.2 mg, 0.010 mmol, 0.1 equiv), methyl *tert*-butyl ether (0.5 mL), and a stir bar.

The NHC-alcohol adduct solution was transferred via syringe to the 4 mL reaction vial. The vial was transferred out of the glovebox and placed in an EtOH cooling bath at 0 °C for 5 min. Then the reaction was irradiated with blue LEDs (455 nm, 30 W) and was stirred at 0 °C for 20 hours. The reaction was stopped by ending the irradiation. The reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with EtOAc. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.

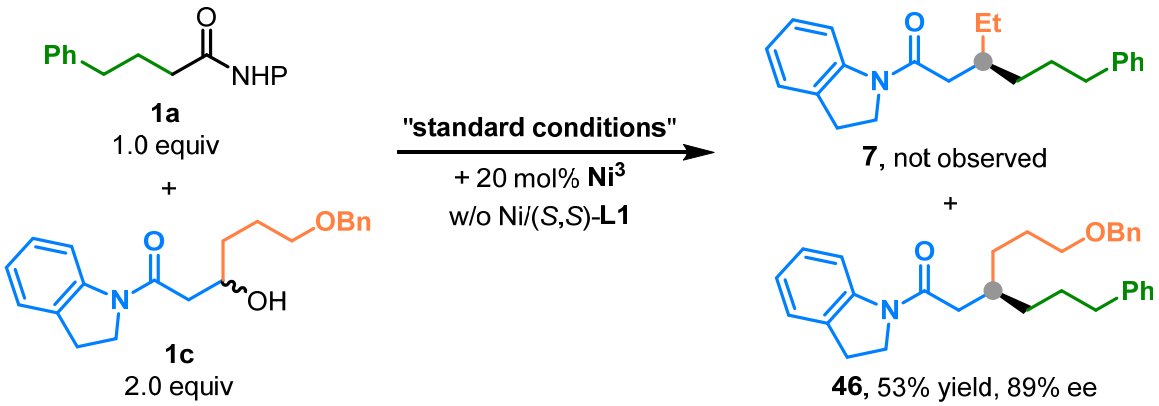
7, 25.4 mg, 79% yield, 91% ee.



Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 3-hydroxy-1-(indolin-1-yl)pentan-1-one (87.6 mg, 0.40 mmol, 2.0 equiv), NHC (158.2 mg, 0.40 mmol, 2.0 equiv), and a stir bar. (Trifluoromethyl)benzene (1.0 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (98.8 μL, 0.44 mmol, 2.2 equiv) was added dropwise, and the resulting solution was stirred at room temperature for another 30 min (a white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (61.8 mg, 0.20 mmol, 1.0 equiv), quinuclidine (33.4 mg, 0.30 mmol, 1.5 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (3.6 mg, 0.0030 mmol, 1.5 mol%), **Ni²** (31.2 mg, 0.040 mmol, 0.2 equiv), methyl *tert*-butyl ether (1.0 mL), and a stir bar. The NHC-alcohol adduct solution was transferred via syringe to the 4 mL reaction vial. The vial was transferred out of the glovebox and placed in an EtOH cooling bath at 0 °C for 5 min. Then the reaction was irradiated with blue LEDs (455 nm, 30 W) and was stirred at 0 °C for 20 hours. The reaction was stopped by ending the irradiation. The reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with EtOAc. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.

1, 5.7 mg, 11% yield, 91% ee.

7, 44.9 mg, 70% yield, 90% ee.



Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 6-(benzyloxy)-3-hydroxy-1-(indolin-1-yl)hexan-1-one (67.8 mg, 0.20 mmol, 2.0 equiv), NHC (79.1 mg, 0.20 mmol, 2.0 equiv), and a stir bar. (Trifluoromethyl)benzene (0.5 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (49.4 μL, 0.22 mmol, 2.2 equiv) was added dropwise, and the resulting solution was stirred at room temperature for another 30 min (a white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (30.9 mg, 0.10 mmol, 1.0 equiv), quinuclidine (16.7 mg, 0.15 mmol, 1.5 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.8 mg, 0.0015 mmol, 1.5 mol%), **Ni**^{3} (9.3 mg, 0.010 mmol, 0.1 equiv), methyl *tert*-butyl ether (0.5 mL), and a stir bar. The NHC-alcohol adduct solution was transferred via syringe to the 4 mL reaction vial. The vial was transferred out of the glovebox and placed in an EtOH cooling bath at 0 °C for 5 min. Then the reaction was irradiated with blue LEDs (455 nm, 30 W) and was stirred at 0 °C for 20 hours. The reaction was stopped by ending the irradiation. The reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with EtOAc. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.

46, 23.4 mg, 53% yield, 89% ee.

7. Kinetic isotope effect experiments.

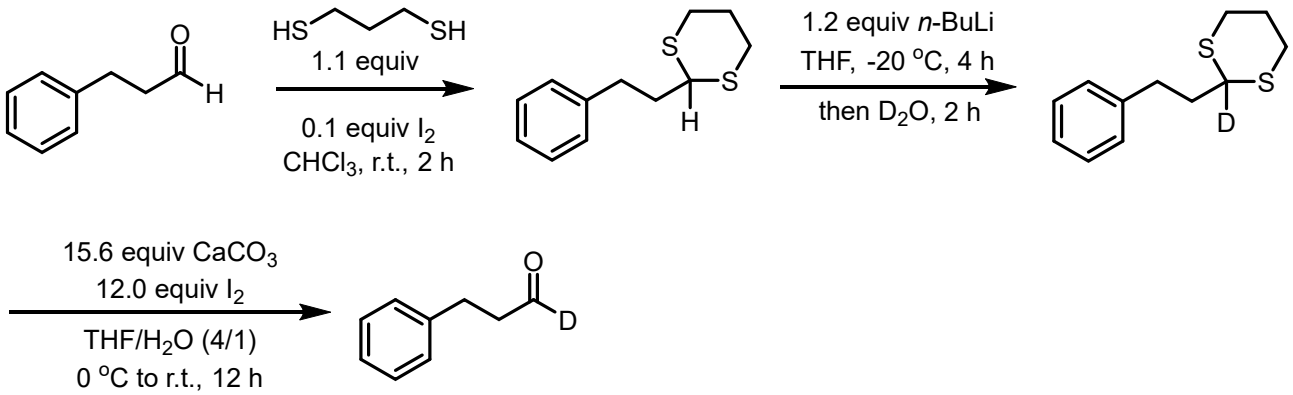
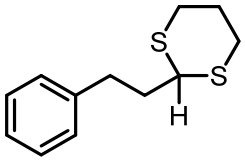


Figure S20. The synthetic route of 3-phenylpropanal-1-*d*



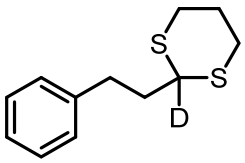
2-Phenethyl-1,3-dithiane. To a solution of 3-phenylpropanal (5.4 g, 40.0 mmol, 1.0 equiv) and iodine (1.0 g, 4.0 mmol, 0.1 equiv) in $CHCl_3$ (120 mL) was added propane-1,3-dithiol (4.8 g, 44.0 mmol, 1.1 equiv). The mixture was stirred at room temperature for 2 h. After the completion of reaction, the mixture was quenched with saturated $Na_2S_2O_3$ solution and extracted with DCM (3 x 50 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:8 EtOAc/hexanes) to afford the desired product. Yellow oil, 8.7 g, 97% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.26 (m, 2H), 7.24 – 7.19 (m, 3H), 4.01 (t, *J* = 7.0 Hz, 1H), 2.88 – 2.80 (m, 6H), 2.15 – 2.05 (m, 3H), 1.96 – 1.83 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 128.4, 128.3, 126.0, 46.4, 36.8, 32.4, 30.1, 25.9.

FT-IR (film): 2899, 1598, 1498, 1452, 1421, 1275, 744, 697 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{12}H_{16}NaS_2$: 247.0586, found: 247.0585.



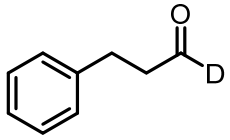
2-Phenethyl-1,3-dithiane-2-*d*. 2-Phenethyl-1,3-dithiane (7.8 g, 35.0 mmol, 1.0 equiv) was dissolved in anhydrous THF (150 mL), and *n*-BuLi (2.5 M in hexane, 16.8 mL, 42.0 mmol, 1.2 equiv) was added dropwise to the solution at -20 °C. The reaction mixture was stirred at -20 °C for 4 h, then quenched by D_2O (4 mL). After the mixture was stirred for 2 h at -20 °C, it was diluted with EtOAc (3 x 50 mL) and washed with brine (50 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:8 EtOAc/hexanes) to afford the desired product. Yellow oil, 7.7 g, 98% yield, >99% deuterium incorporation.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.24 – 7.18 (m, 3H), 2.89 – 2.80 (m, 6H), 2.20 – 2.06 (m, 3H), 1.95 – 1.81 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.8, 128.4, 128.3, 126.0, 46.0 (t, *J* = 23.3 Hz), 36.7, 32.4, 30.0, 25.9.

FT-IR (film): 2897, 1497, 1421, 1275, 898, 744, 692 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{12}H_{15}DNaS_2$: 248.0648, found: 248.0645.



3-Phenylpropanal-1-*d*. 2-Phenethyl-1,3-dithiane-2-*d* (7.6 g, 34.0 mmol, 1 equiv) was dissolved in THF/water (4:1, 250 mL) and cooled to 0 °C, then $CaCO_3$ (5.3 g, 530.4 mmol, 15.6

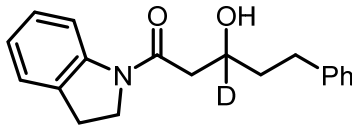
equiv) and iodine (103.6 g, 408.0 mmol, 12.0 equiv) were added. The mixture was stirred overnight at room temperature. After the reaction was completed, a saturated $Na_2S_2O_3$ solution was added and the mixture was stirred for 10 min. The mixture was filtered through Celite and extracted with EtOAc (3 x 50 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:6 EtOAc/hexanes) to afford the desired product. Colorless oil, 3.9 g, 85% yield, >99% deuterium incorporation.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.78 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2 (t, *J* = 26.8 Hz), 140.3, 128.5, 128.2, 126.2, 45.0 (t, *J* = 3.8 Hz), 28.0.

FT-IR (film): 3027, 1710, 1491, 1457, 1096, 731, 695 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+K]$^+$ calcd for C_9H_9DKO: 174.0426, found: 174.0436.



3-Hydroxy-1-(indolin-1-yl)-5-phenylpentan-1-one-3-*d*. The title compound was synthesized according to **GP-1** from 1-(indolin-1-yl)ethan-1-one (3.22 g, 20 mmol) and 3-phenylpropanal-1-*d*. The product was purified by column chromatography on silica gel (1:1 EtOAc/hexanes). 4.8 g (16.2 mmol, 81% yield, >99% deuterium incorporation). White solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.24 – 7.19 (m, 3H), 7.06 (t, *J* = 7.5 Hz, 1H), 4.28 – 4.09 (m, 1H), 4.03 – 3.93 (m, 2H), 3.20 (t, *J* = 8.5 Hz, 2H), 3.01 – 2.88 (m, 1H), 2.78 (m, 1H), 2.61 – 2.45 (m, 2H), 2.03 – 1.93 (m, 1H), 1.88 – 1.75 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 142.4, 142.0, 131.1, 128.5, 128.3, 127.5, 125.8, 124.6, 124.0, 117.1, 66.7 (t, *J* = 21.5 Hz), 47.8, 42.1, 37.9, 31.8, 27.8.

FT-IR (film): 3516, 2918, 1687, 1442, 1377, 1121, 752 cm^{-1}.

HRMS (ESI-MS) *m*/*z* [M+K]$^+$ calcd for $C_{19}H_{20}DKNO_2$: 335.1267, found: 335.1266.

General Procedure 5 (GP-5).

Preparation of the catalyst solution: In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a stir bar was charged with $NiBr_2$·DME (3.1 mg, 0.010 mmol, 10.0 mol%), (*S*,*S*)-**L1** (7.1 mg, 0.012 mmol, 12.0 mol%), and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.8 mg, 0.0015 mmol, 1.5 mol%). Anhydrous methyl *tert*-butyl ether (0.5 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 60 min at least, leading to a catalyst solution.

Preparation of the NHC-alcohol adduct solution: In a nitrogen-filled glovebox, a separate oven-dried 4 mL vial was charged with β-hydroxy amide (0.20 mmol, 2.0 equiv), NHC (79.1 mg, 0.20 mmol, 2.0 equiv), and a stir bar. (Trifluoromethyl)benzene (0.5 mL) was added, and the mixture was stirred at room temperature for 5 min. Next, 2,6-bis(*tert*-butyl) pyridine (49.4 μL, 0.22 mmol, 2.2 equiv) was added dropwise, and the resulting solution was stirred at room

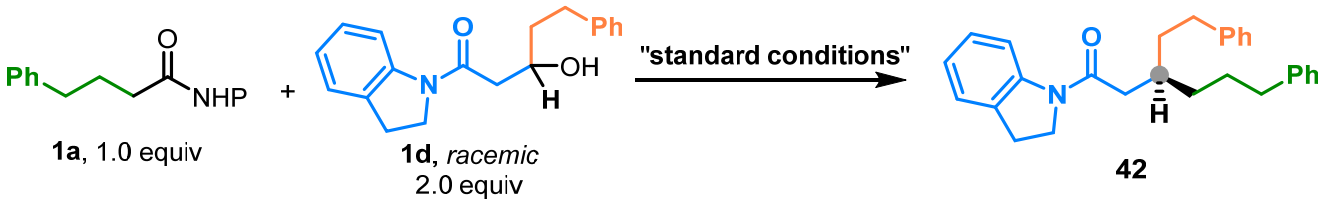
temperature for another 30 min (a white solid precipitated during this time). The suspension was filtered to furnish a homogeneous solution.

Cross-coupling: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with the NHP ester (0.10 mmol, 1.0 equiv), quinuclidine (16.7 mg, 0.15 mmol, 1.5 equiv), and a stir bar. The catalyst solution and NHC-alcohol adduct solution were transferred via syringe to the 4 mL reaction vial. The vial was transferred out of the glovebox and placed in an EtOH cooling bath at 0 °C for 5 min. Then the reaction was irradiated with blue LEDs (455 nm, 30 W) and was stirred at 0 °C.

Work-up: The reaction was stopped by ending the irradiation. The reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with EtOAc. The filtrate was concentrated, and the yield was determined via GC analysis with *n*–tetradecane as an internal standard.

Figure S21–S24: 1,3-Dioxoisoindolin-2-yl 4-phenylbutanoate was reacted with **1d** or **1d'** according to **GP-5**. Run five reactions in parallel, stopping one reaction every 10 minutes. Rate constants were calculated for each reaction using the initial rates method (<15% conversion). Error analysis was conducted using standard equations and calculations. The average value of k_H/k_D obtained through two parallel kinetic isotope effect experiments is 0.84.

The first parallel kinetic isotope effect experiments: k_H/k_D = 0.8279.



Time (min)	0	10	20	30	40	50
Yield (%)	0	2.7	4.8	7.2	9.5	11.3

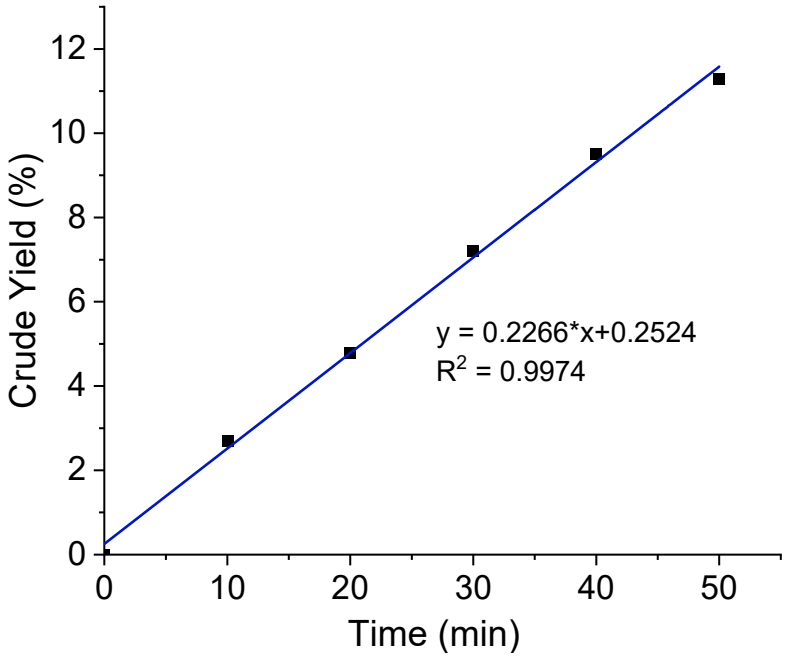
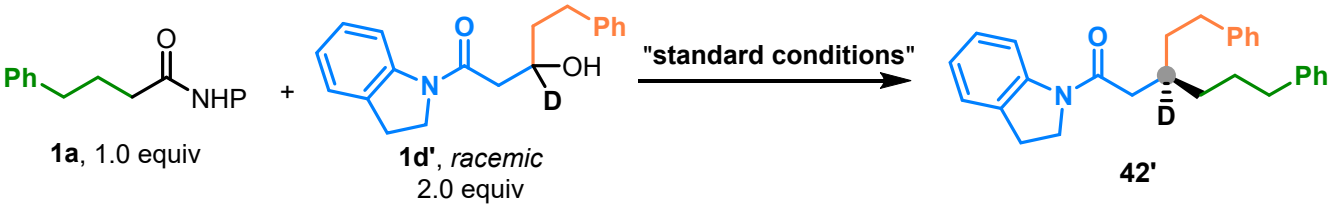


Figure S21. Kinetic profiles of the reaction between **1a** and **1d**



Time (min)	0	10	20	30	40	50
Yield (%)	0	2.5	5.4	8.2	10.5	13.8

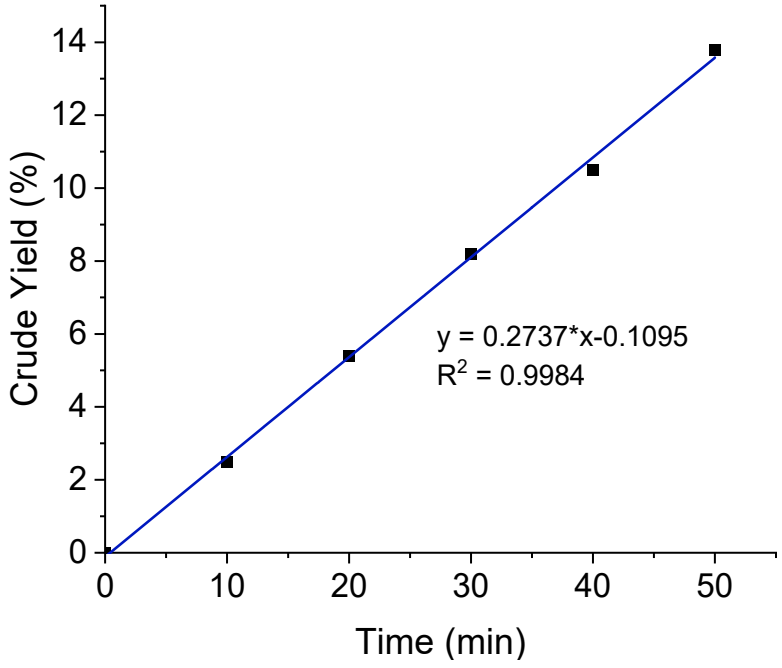
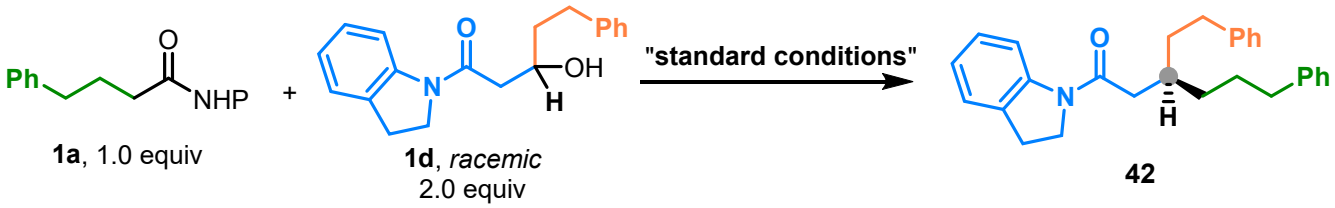


Figure S22. Kinetic profiles of the reaction between **1a** and **1d'**

The second parallel kinetic isotope effect experiments: k_H/k_D = 0.8514.



Time (min)	0	10	20	30	40	50
Yield (%)	0	2.6	4.5	6.9	9.2	10.8

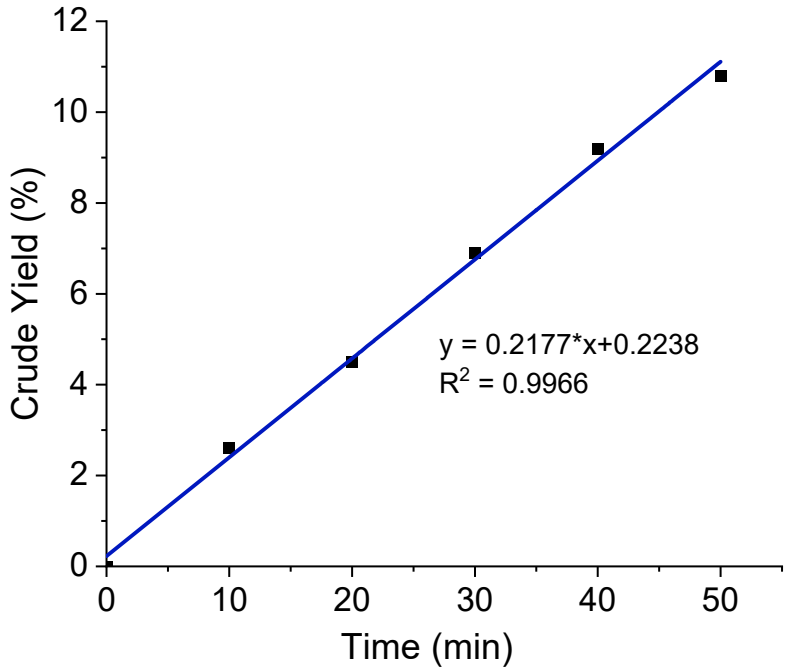
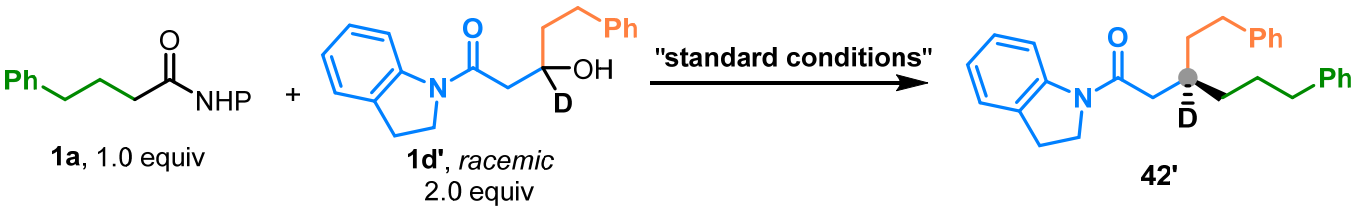


Figure S23. Kinetic profiles of the reaction between **1a** and **1d**



Time (min)	0	10	20	30	40	50
Yield (%)	0	2.5	5.2	8.2	10.0	12.8

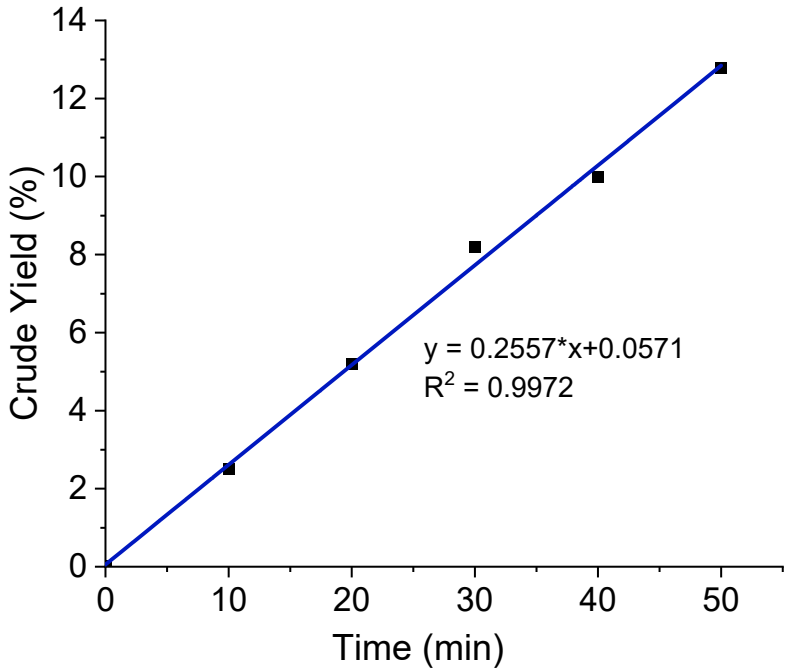
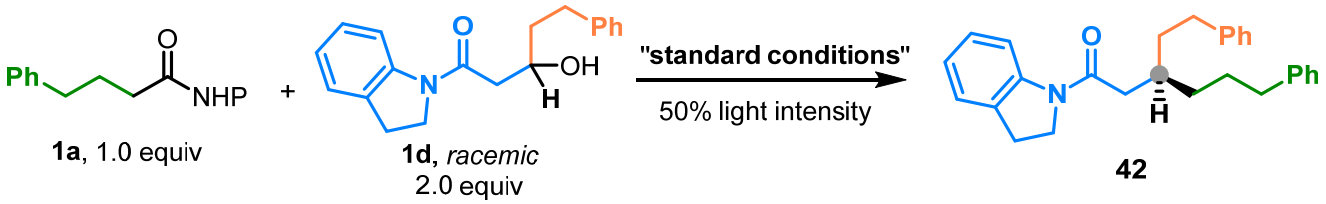


Figure S24. Kinetic profiles of the reaction between **1a** and **1d'**

Figure S25–S26: 1,3-Dioxoisoindolin-2-yl 4-phenylbutanoate was reacted with **1d** or **1d'** according to **GP-5** using 50% light intensity. Run five reactions in parallel, stopping one reaction every 15 minutes. Rate constants were calculated for each reaction using the initial rates method (<15% conversion). Error analysis was conducted using standard equations and calculations. The value of k_H/k_D obtained through parallel kinetic isotope effect experiments is 0.83.



Time (min)	0	15	30	45	60	75
Yield (%)	0	2.1	5.1	7.6	11.2	13.9

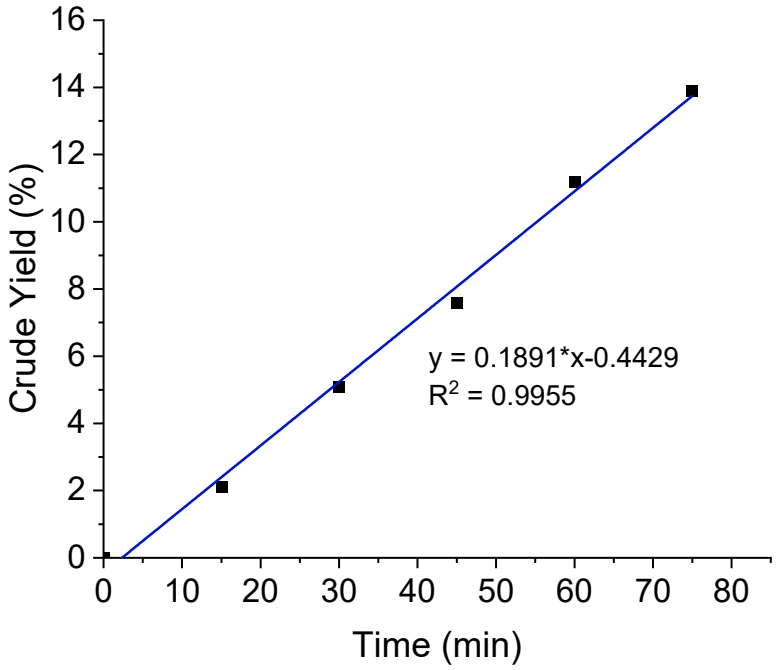
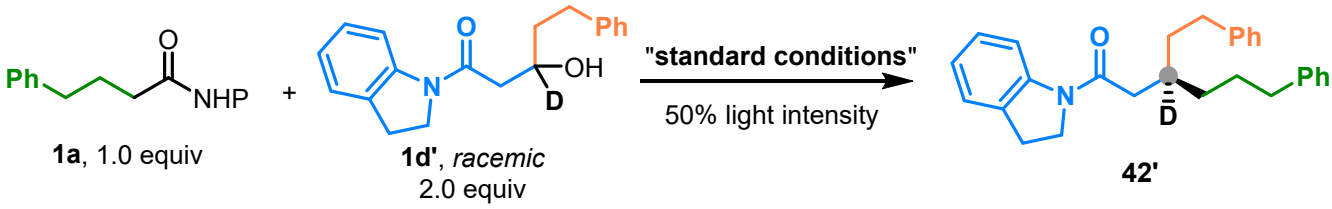


Figure S25. Kinetic profiles of the reaction between **1a** and **1d** using 50% light intensity



Time (min)	0	15	30	45	60	75
Yield (%)	0	2.2	6.1	9.2	13.4	16.7

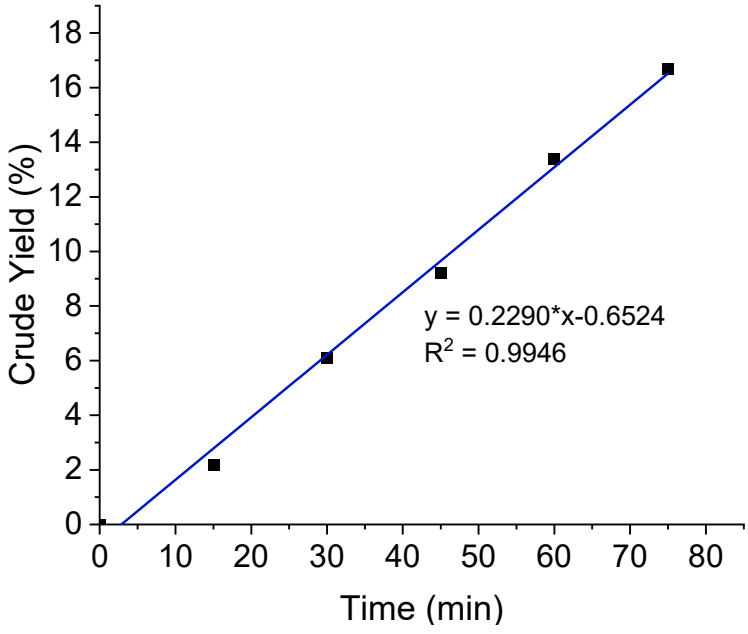
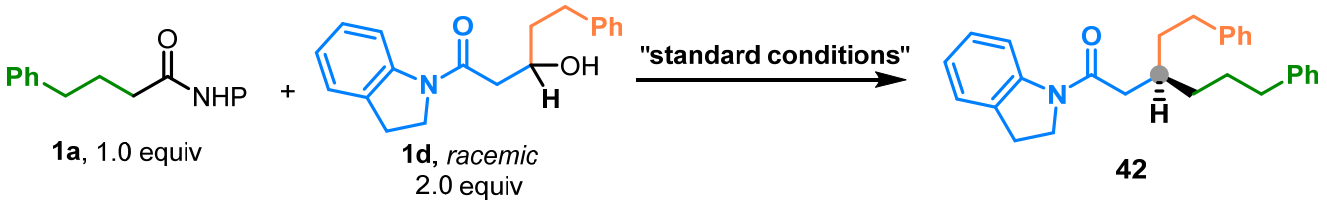


Figure S26. Kinetic profiles of the reaction between **1a** and **1d'** using 50% light intensity

Figure S27–S28: 1,3-Dioxoisoindolin-2-yl 4-phenylbutanoate was reacted with **1d** or **1d'** according to **GP-5**. Run five reactions in parallel, stopping one reaction every 10 minutes. Rate constants were calculated for each reaction using the initial rates method (<15% conversion). Error analysis was conducted using standard equations and calculations. The value of k_H/k_D obtained by measuring the consumption of **1a**: $k_H/k_D = 0.87$.



Time (min)	0	10	20	30	40	50
Consumption of **1a** (%)	0	5.2	5.3	8.6	11.9	12.3

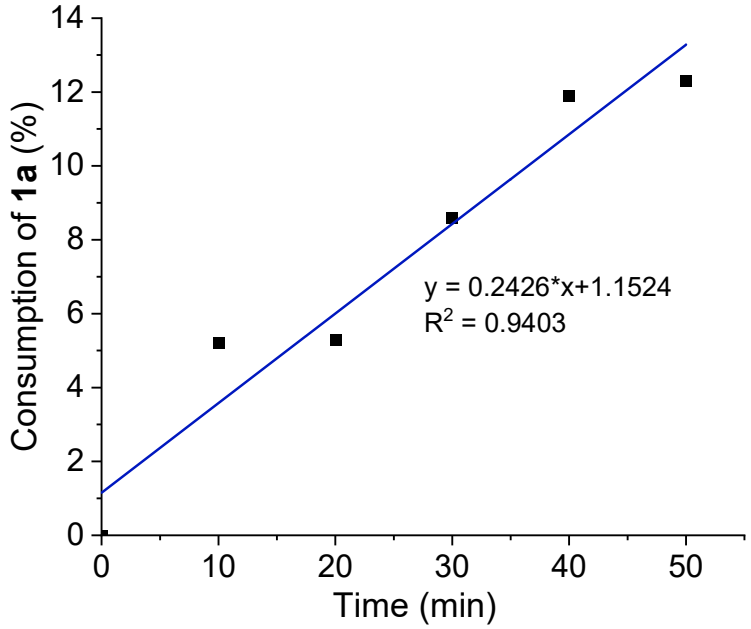
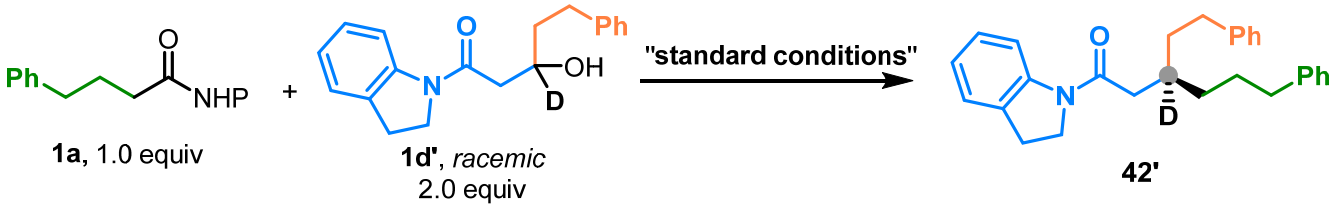


Figure S27. Kinetic profiles of the reaction between **1a** and **1d**



Time (min)	0	10	20	30	40	50
Consumption of **1a** (%)	0	4.9	5.4	7.2	12.3	14.8

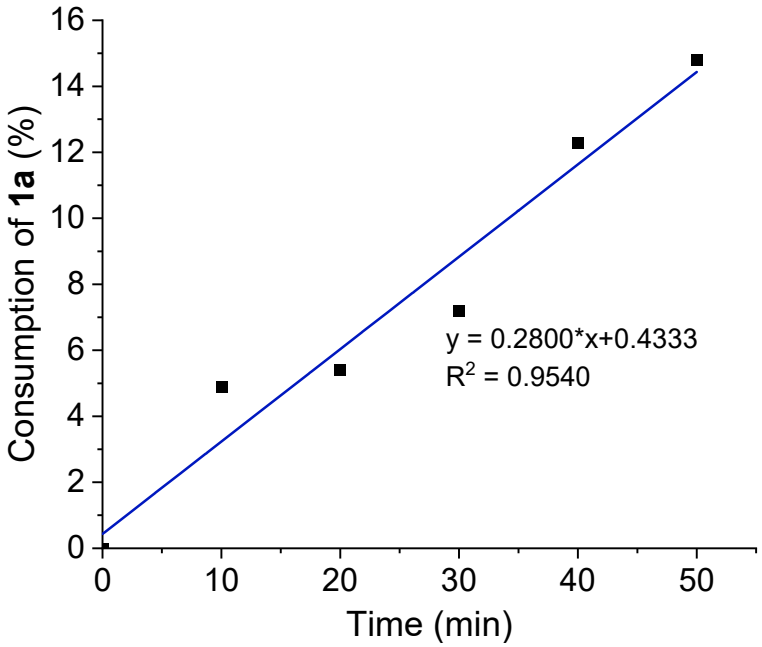
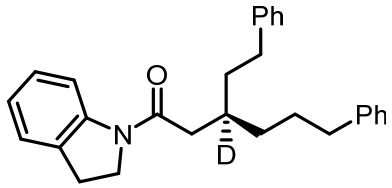


Figure S28. Kinetic profiles of the reaction between **1a** and **1d'**



(*R*)-1-(Indolin-1-yl)-3-phenethyl-6-phenylhexan-1-one-3-*d* (42'). The title compound was synthesized according to **GP-2** from 3-hydroxy-1-(indolin-1-yl)-5-phenylpentan-1-one-3-*d* and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Yellow oil, 139.3 mg, 70% yield, 87% ee.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.19 – 7.13 (m, 8H), 7.00 (t, *J* = 7.4 Hz, 1H), 3.96 (t, *J* = 8.5 Hz, 2H), 3.14 (t, *J* = 8.4 Hz, 2H), 2.65 – 2.59 (m, 4H), 2.41 – 2.33 (m, 2H), 1.72 – 1.65 (m, 4H), 1.51 – 1.47 (m, 2H).

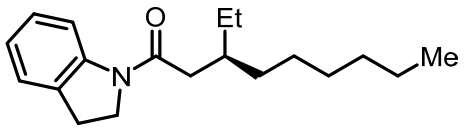
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 143.1, 142.5, 131.0, 128.4, 128.3, 128.2, 127.5, 125.7, 125.6, 124.4, 123.5, 117.1, 48.1, 40.5, 36.1, 35.6, 33.6 (t, *J* = 19.3 Hz), 33.4, 33.1, 28.5, 28.0.

FT-IR (film): 2924, 1656, 1472, 1403, 1256, 1044, 702 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{28}H_{31}DNO$: 399.2541, found: 399.2539.

Discussion: (1) Parallel reactions of **1d** (H) and **1d'** (D) afford coupling products with nearly identical yields and enantioselectivities. (2) KIE measurements (k_H/k_D = 0.87 from **1a** consumption) match those obtained from product formation. (3) Consistent KIE value (k_H/k_D = 0.83) was observed at reduced light intensity (50% light intensity). These collective results indicate that the rate-determining step is light-independent.

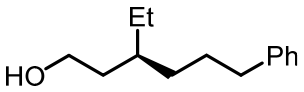
IX. Assignment of Absolute Configuration



(*S*)-3-Ethyl-1-(indolin-1-yl)nonan-1-one (Figure 2A, entry 2). The absolute configuration of this compound has been established by the literature.[4] It was obtained with (*S*,*S*)-**L1**. As shown below, the (*S*)-configuration was assigned by comparison with published optical rotation.

Optical rotation: $[\alpha]^{16}_{D}$ = –11.9 (c 0.5, $CHCl_3$); 90% ee, from (*S*,*S*)-**L1**.

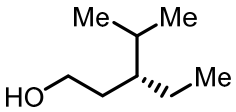
Lit.: $[\alpha]^{24}_{D}$ = +4.4 (c 1.0, $CHCl_3$); 90% ee for (*R*)-configuration.



(*S*)-3-Ethyl-6-phenylhexan-1-ol (Figure 3B, entry 50). The absolute configuration of this compound has been established by the literature.[4] It was obtained with (*S*,*S*)-**L1**. As shown below, the (*S*)-configuration was assigned by comparison with published optical rotation.

Optical rotation: $[\alpha]^{16}_{D}$ = –5.3 (c 0.5, $CHCl_3$); 91% ee, from (*S*,*S*)-**L1**.

Lit.: $[\alpha]^{24}_{D}$ = +2.2 (c 1.0, $CHCl_3$); 91% ee for (*R*)-configuration.



(*R*)-3-Ethyl-4-methylpentan-1-ol (Figure 3C, entry 59). The absolute configuration of this compound has been established by the literature.[5] It was obtained with (*R*,*R*)-**L1**. As shown below, the (*R*)-configuration was assigned by comparison with published optical rotation.

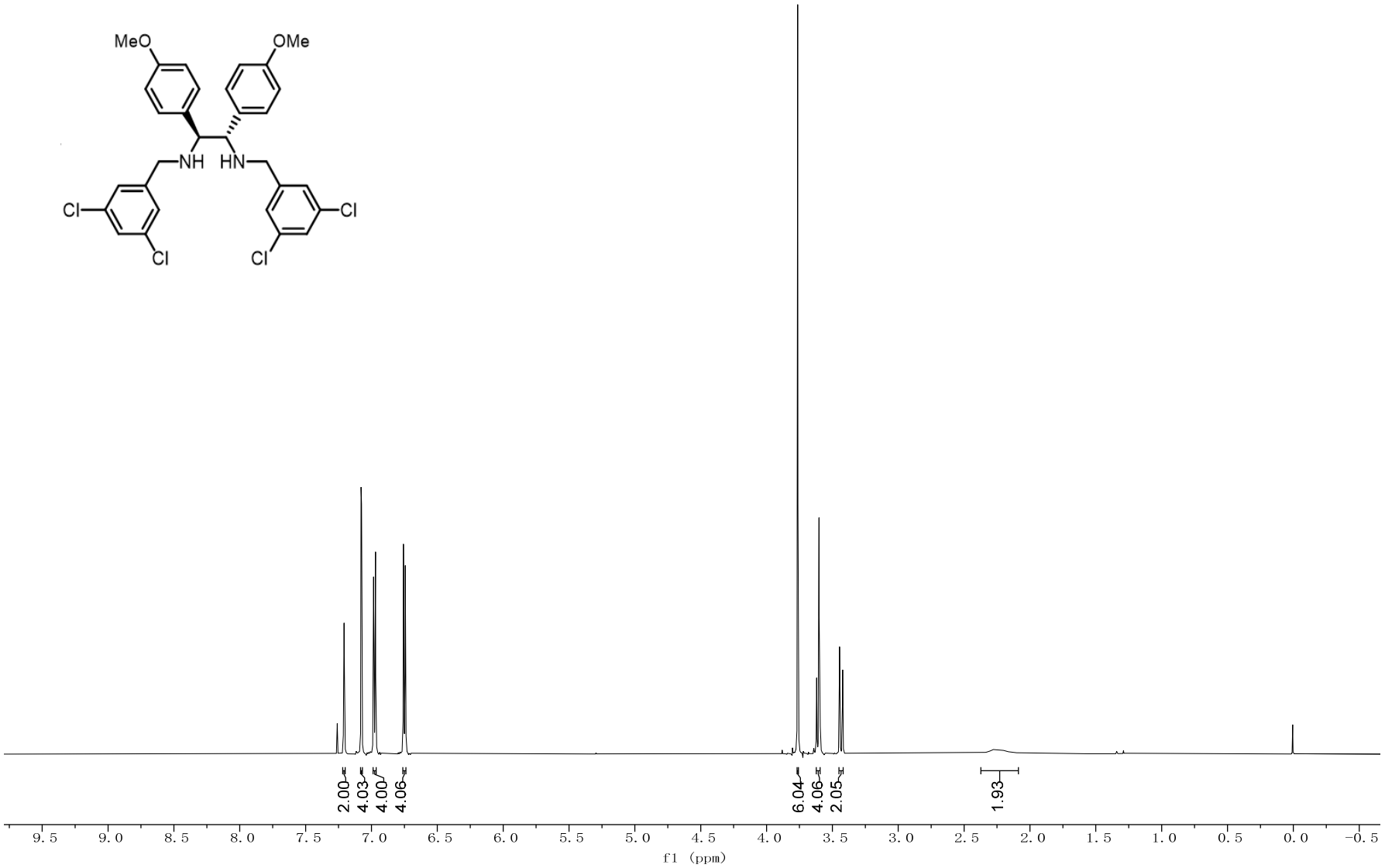
Optical rotation: $[\alpha]^{25}_{D}$ = +7.2 (c 0.2, $CHCl_3$); 88% ee, from (*R*,*R*)-**L1**.

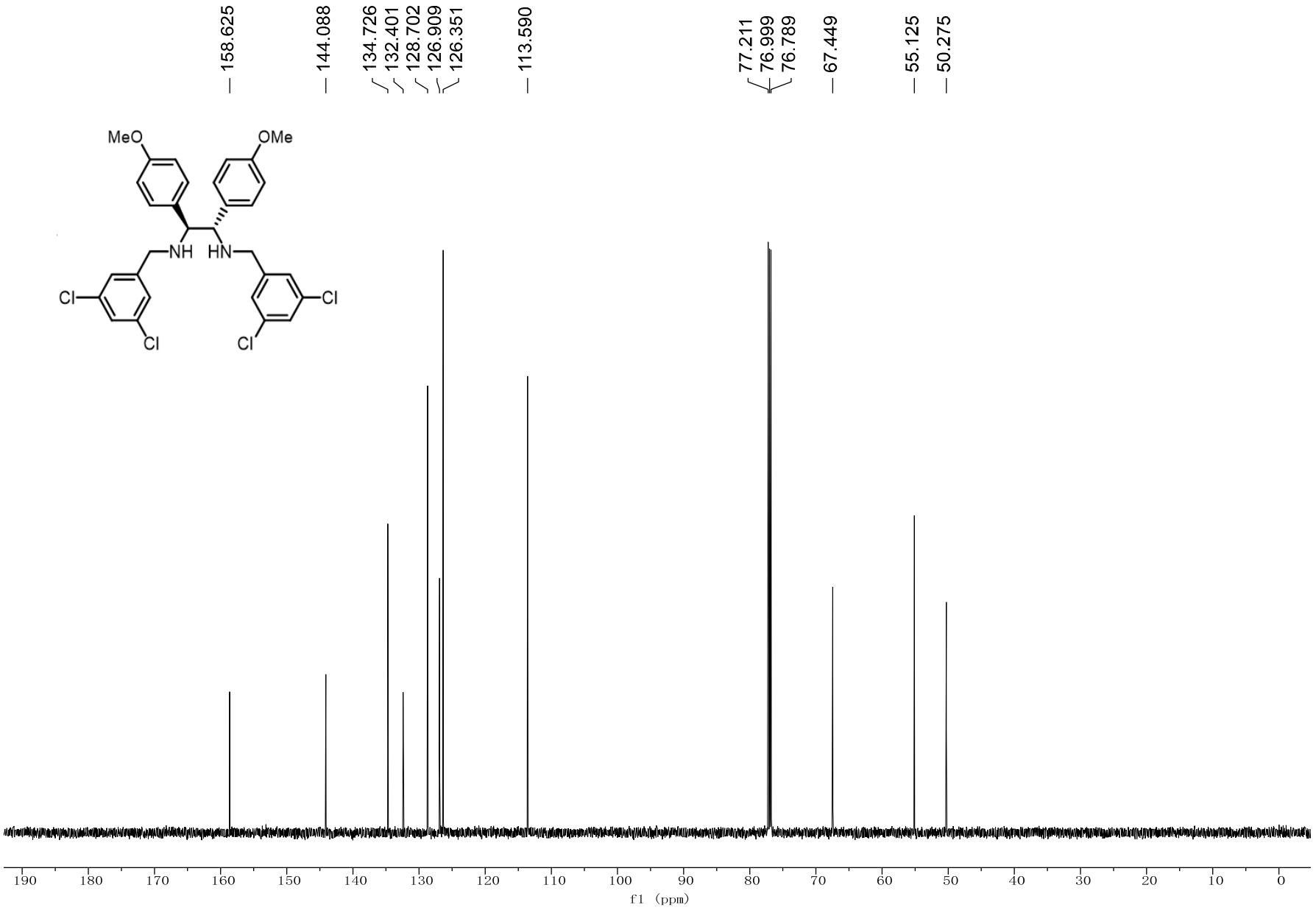
Lit.: $[\alpha]^{25}_{D}$ = –3.3 (c 1.0, $CHCl_3$); (*S*)-configuration (value of ee not provided).

X. References

(1) Dong, Z.; MacMillan, D. W. C. Metallaphotoredox-enabled deoxygenative arylation of alcohols. *Nature* **2021**, *598*, 451−456.
(2) Huang, Q.; Chen, Y.; Zhou, X.; Dai, L.; Lu, Y. Nickel-Hydride-Catalyzed Diastereo- and Enantioselective Hydroalkylation of Cyclopropenes. *Angew. Chem. Int. Ed.* **2022**, *61,* e202210560.
(3) Wilde, M. M. D.; Gravel, M. Bis(amino)cyclopropenylidenes as Organocatalysts for Acyl Anion and Extended Umpolung Reactions. *Angew. Chem. Int. Ed.* **2013**, *52*, 12651−12654.
(4) Huo, H.; Gorsline, B. J.; Fu, G. C. Catalyst-controlled doubly enantioconvergent coupling of racemic alkyl nucleophiles and electrophiles. *Science* **2020**, *367*, 559–564.
(5) Schiendorfer, M.; Mattay, J. Lower rim functionalized chiral resorc [4] arenes derived from citronellal and carvone. *Synthesis* **2005**, *16*, 2701–2712.

XI. NMR Spectra and Determination of Stereoselectivity

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134.726
132.401
128.702
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126.351
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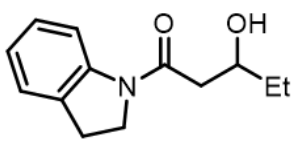
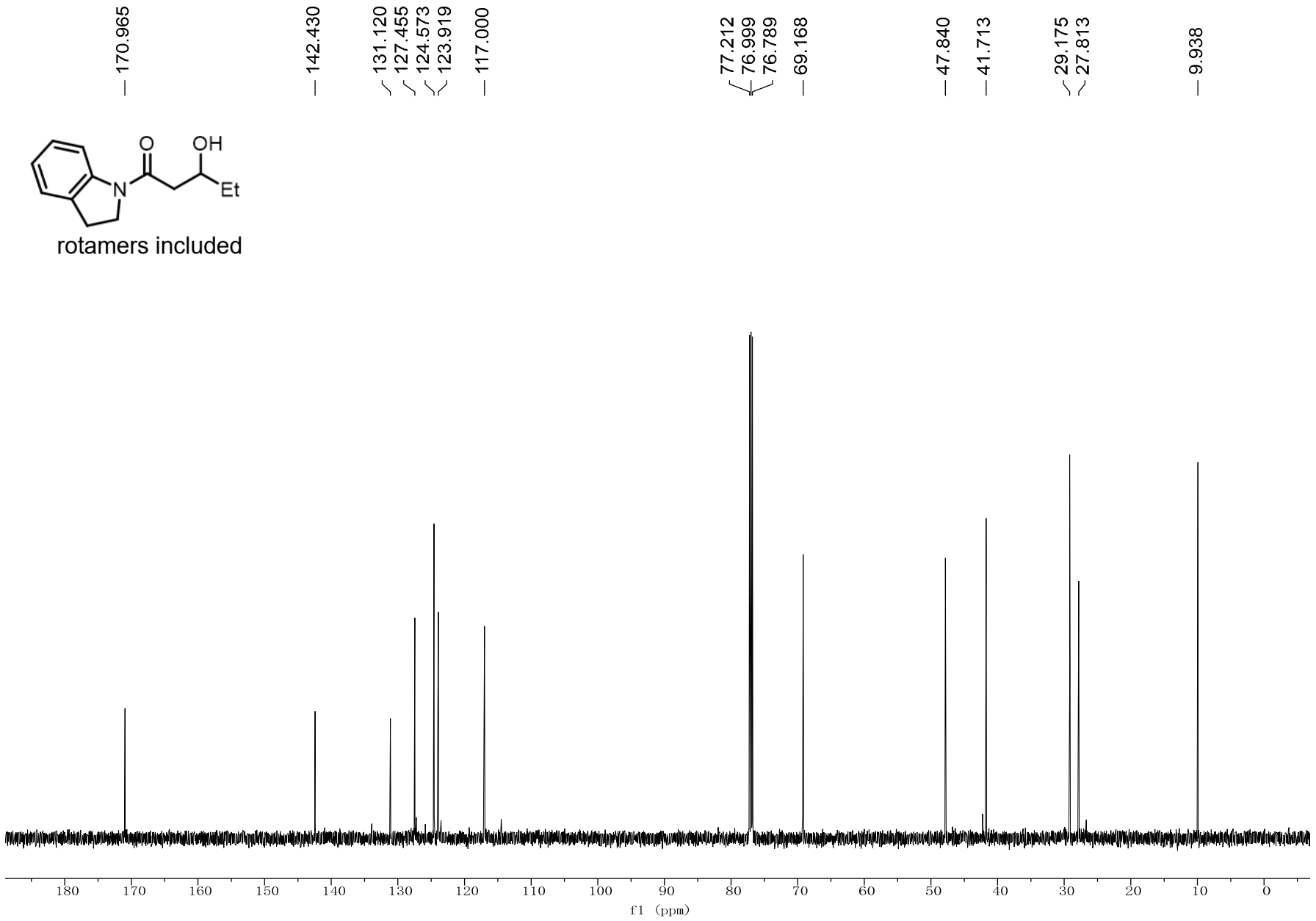
76.999
76.789
67.449
55.125
50.275
MeO
OMe
NH
HN
Cl
Cl
Cl
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



rotamers included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127.455
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41.713
29.175
27.813
9.938
O
OH
N
Et
rotamers included
180
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150
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130
120
110
100
90
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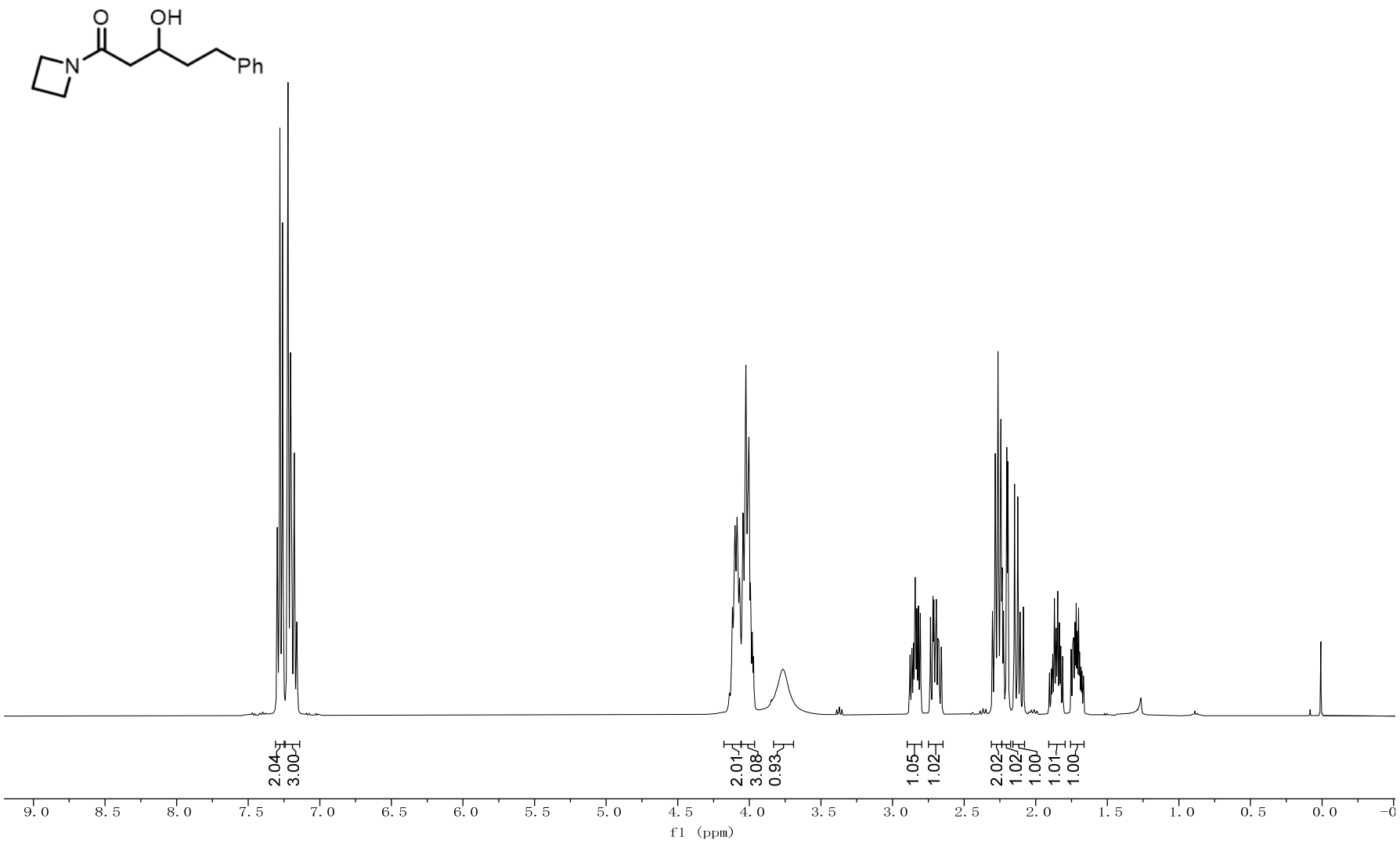
50
40
30
20
10
0
f1 (ppm)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OH
N
Ph
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1.01
1.00
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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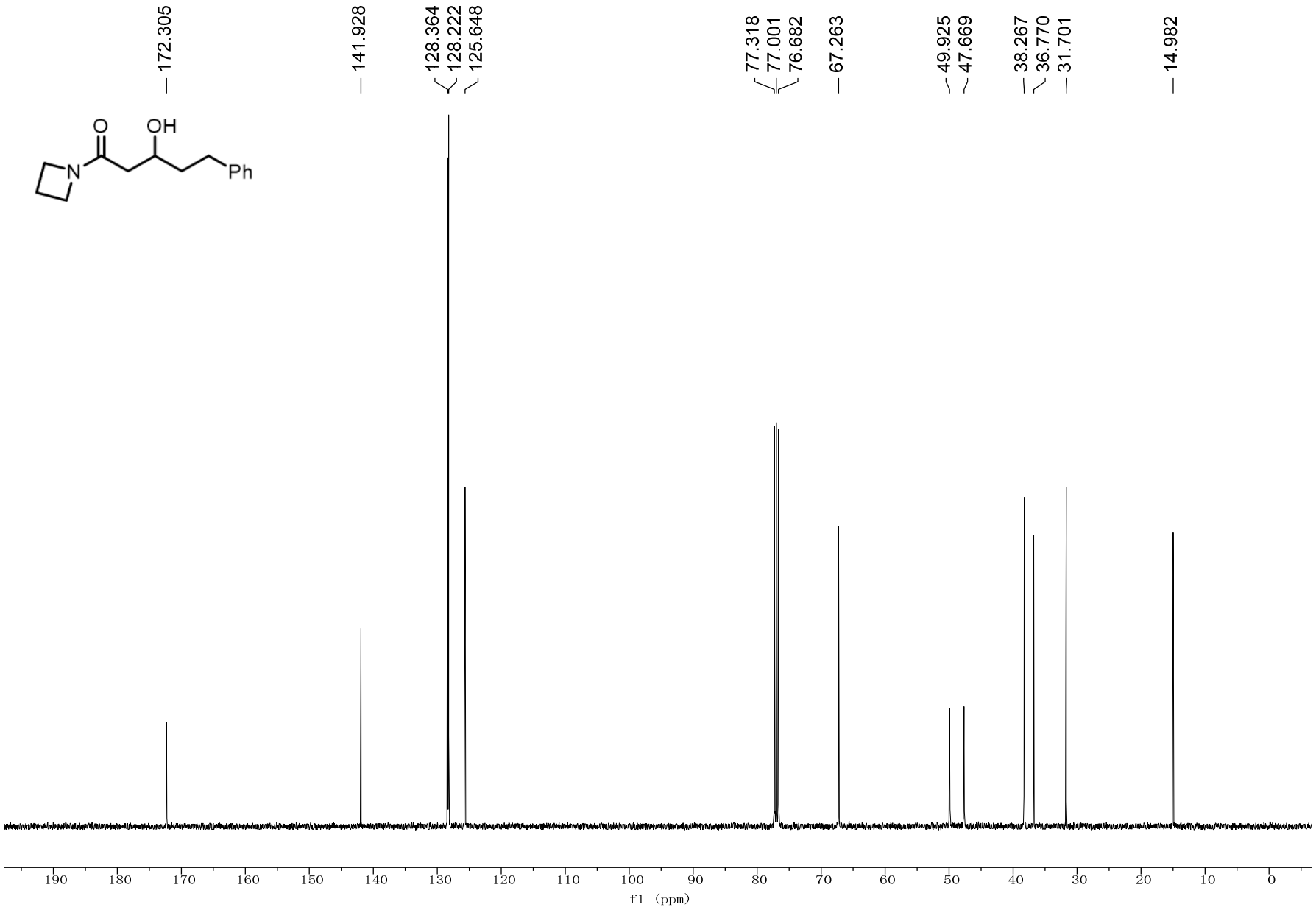
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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141.928
128.364
128.222
125.648
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77.001
76.682
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38.267
36.770
31.701
14.982
O
OH
N
Ph
190
180
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120
110
100
90
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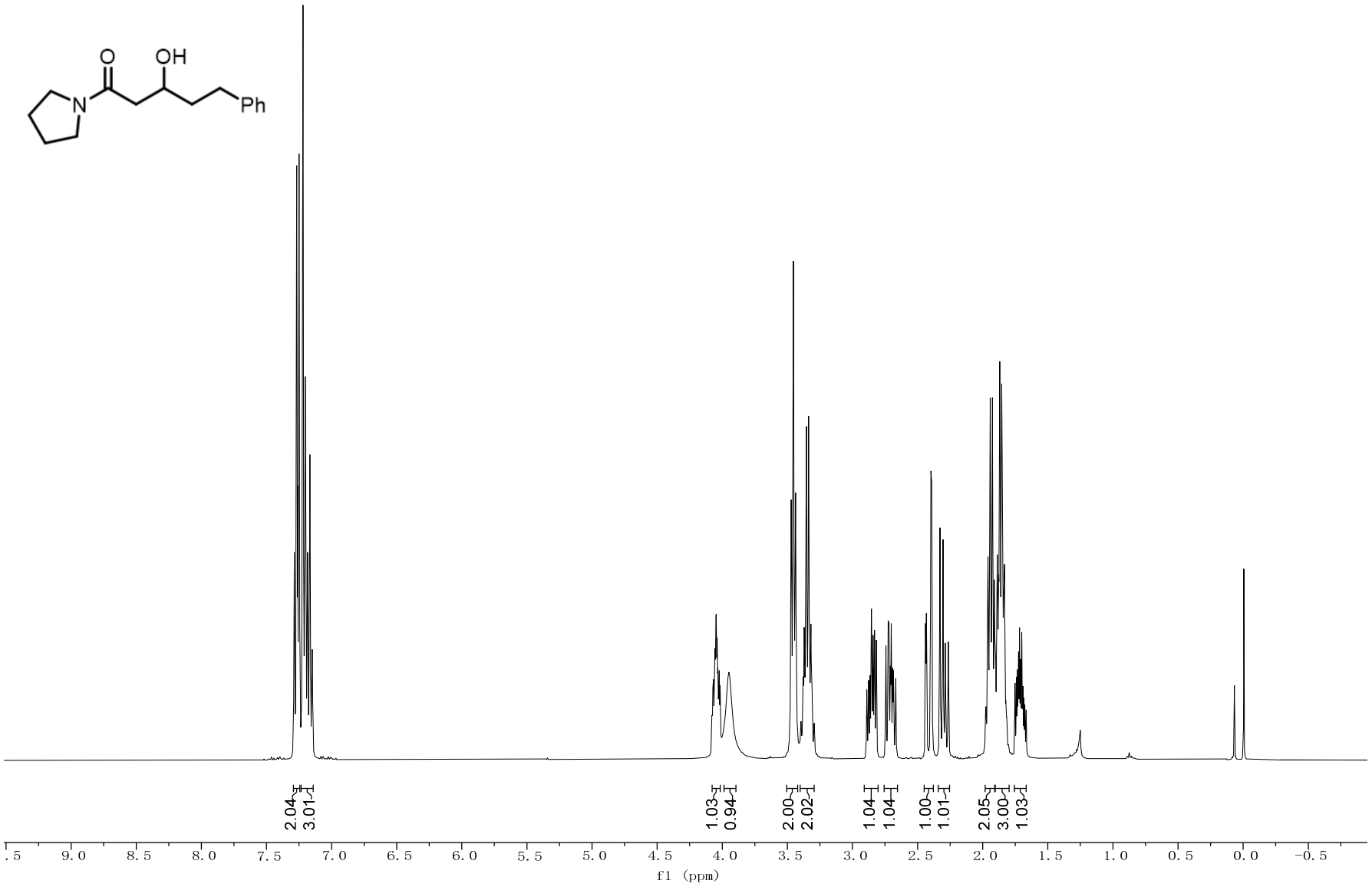
50
40
30
20
10
0
f1 (ppm)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OH
N
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1.04
1.00
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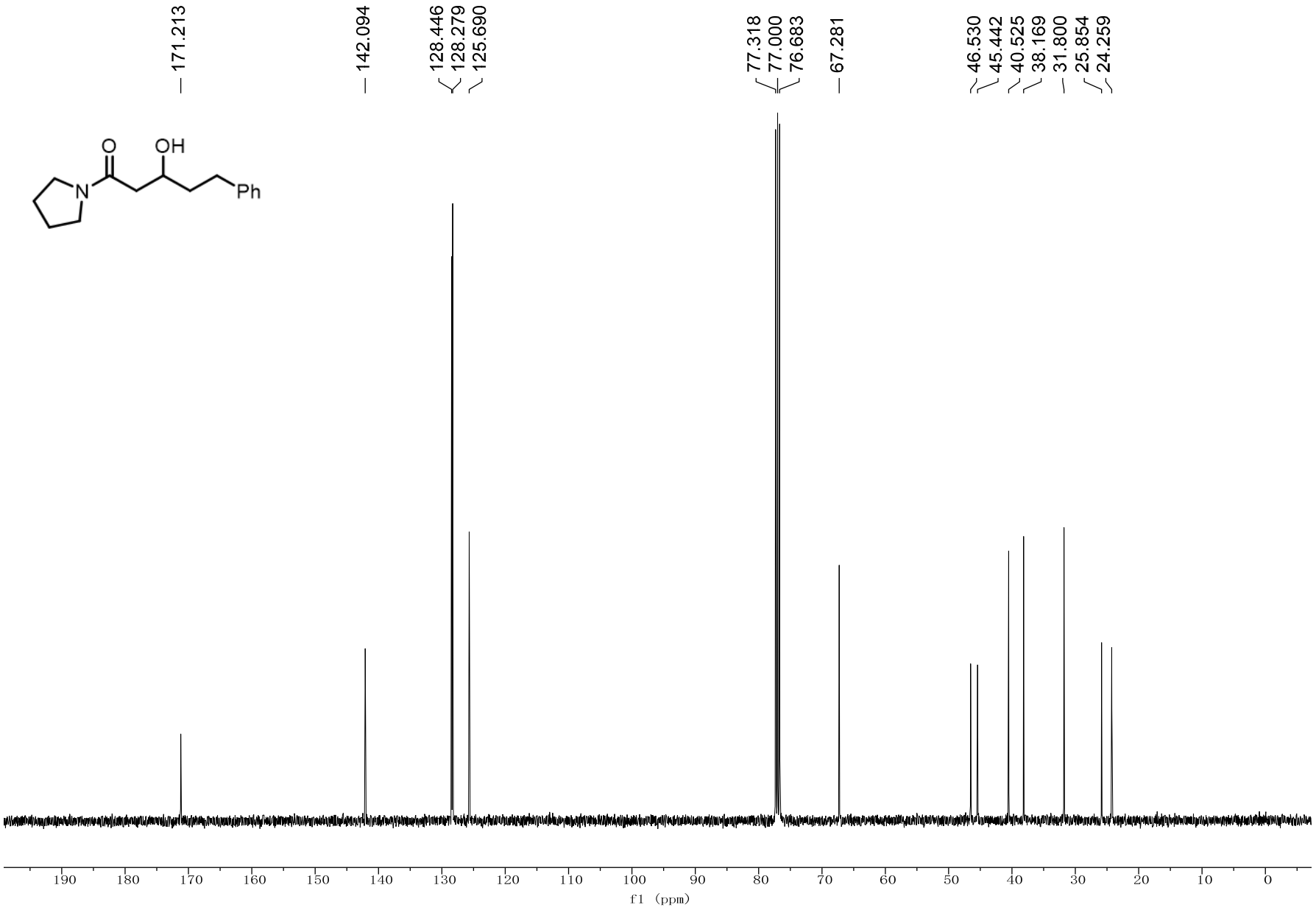
3.00
1.03
f1 (ppm)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25.854
24.259
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180
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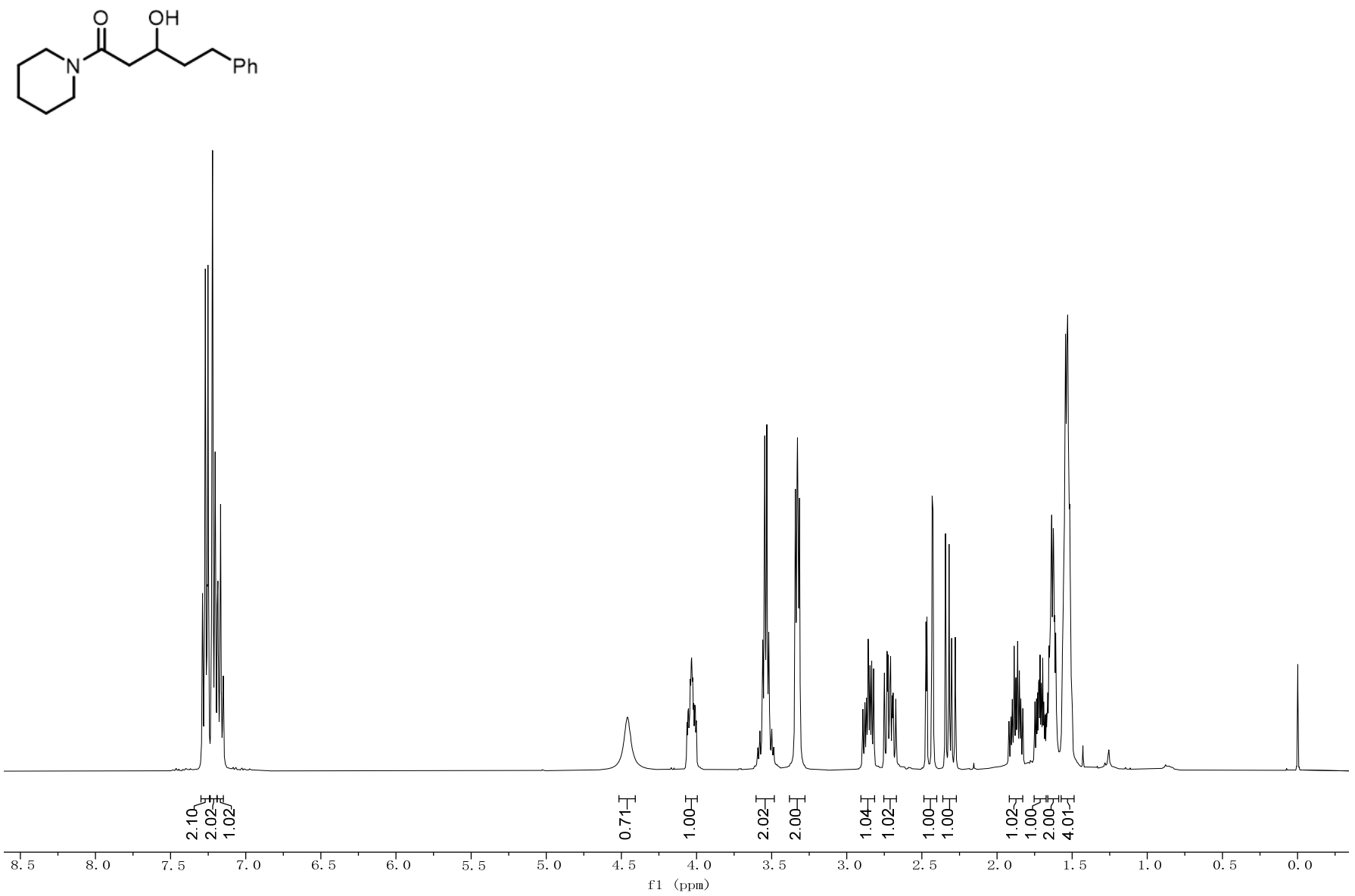
f1 (ppm)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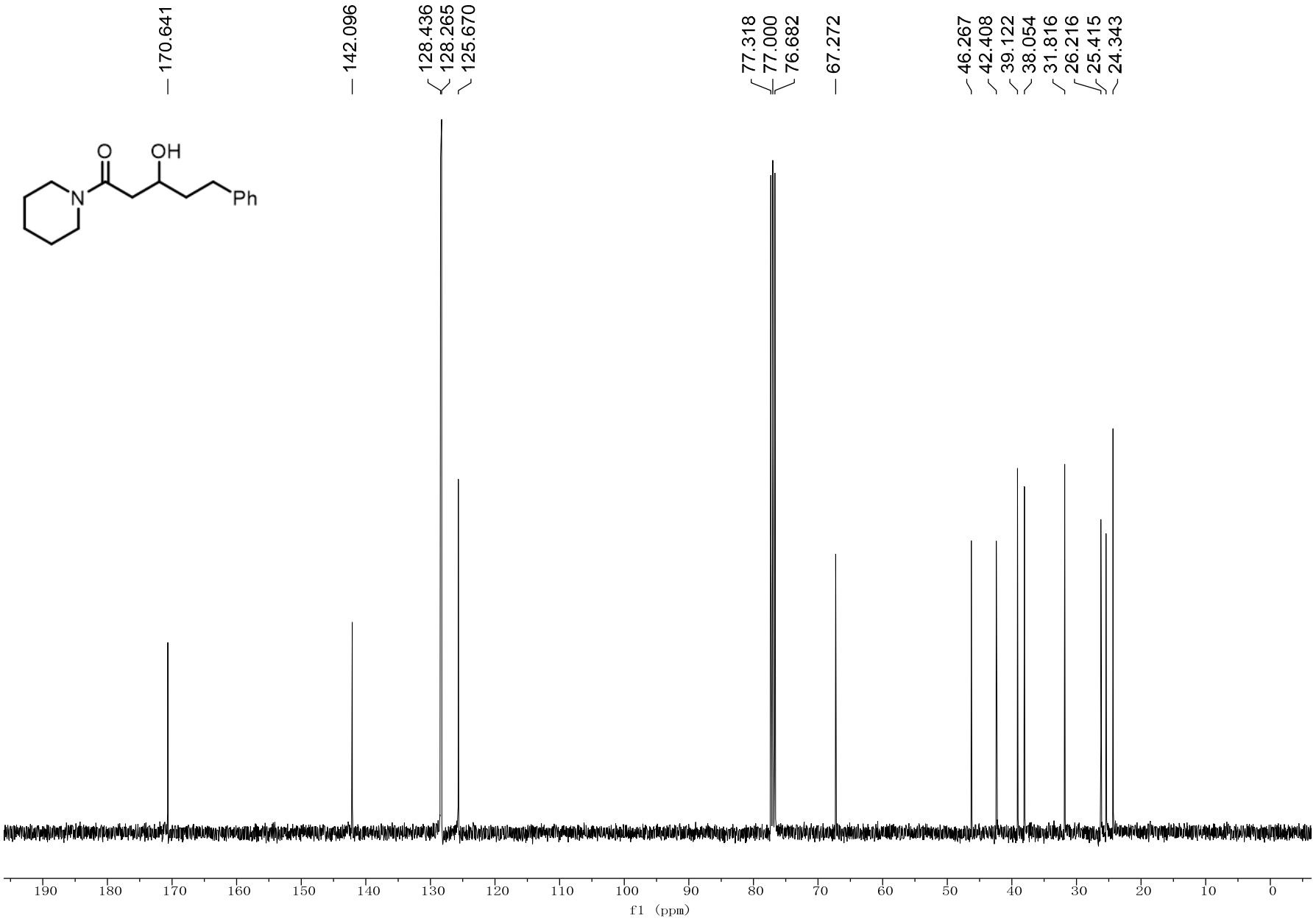
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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38.054
31.816
26.216
25.415
24.343
O
OH
N
Ph
190
180
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10
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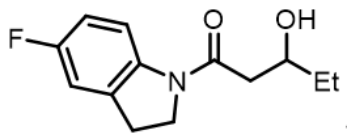
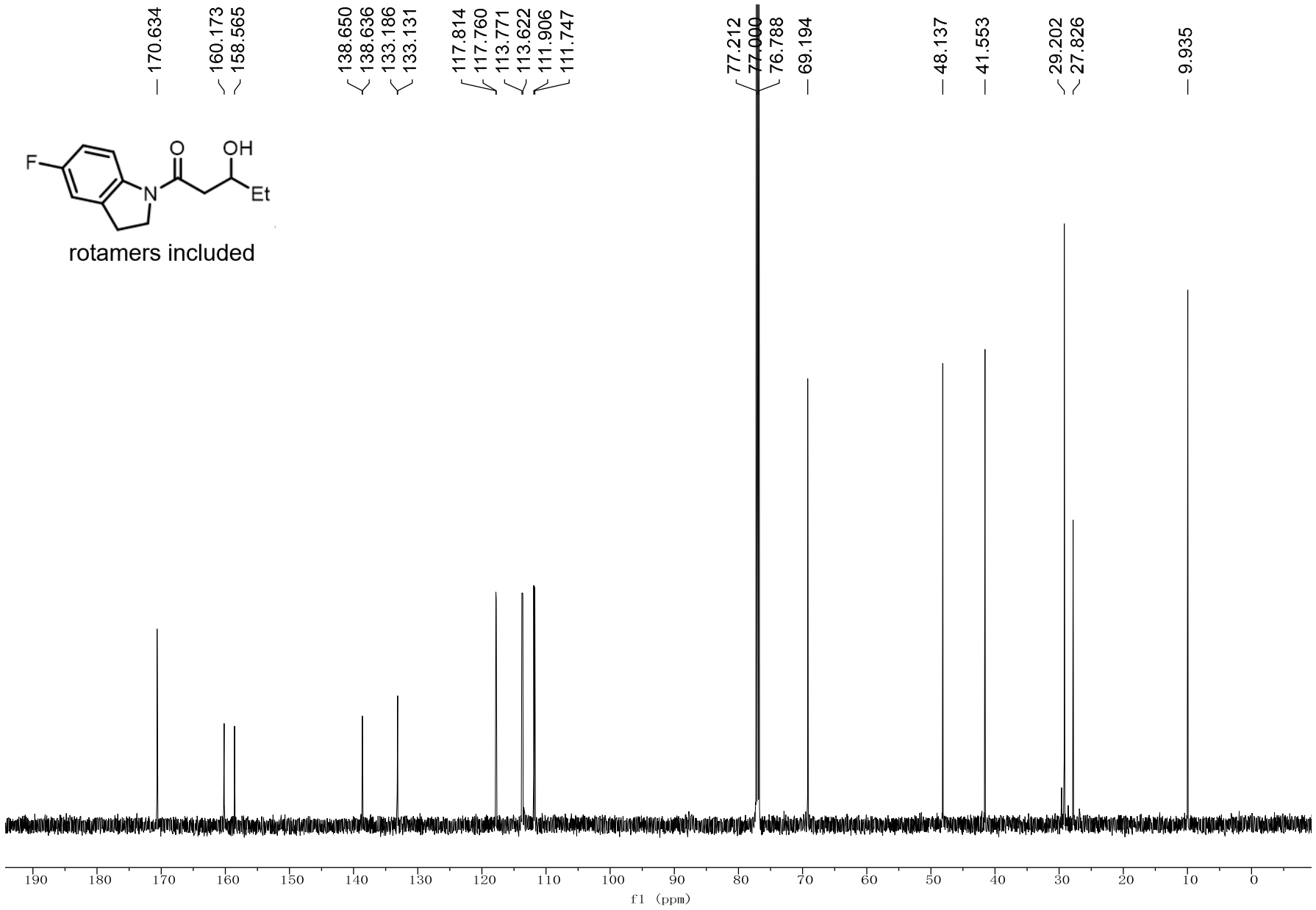
f1 (ppm)



rotamers included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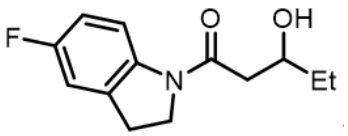
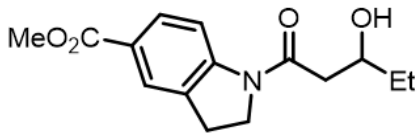
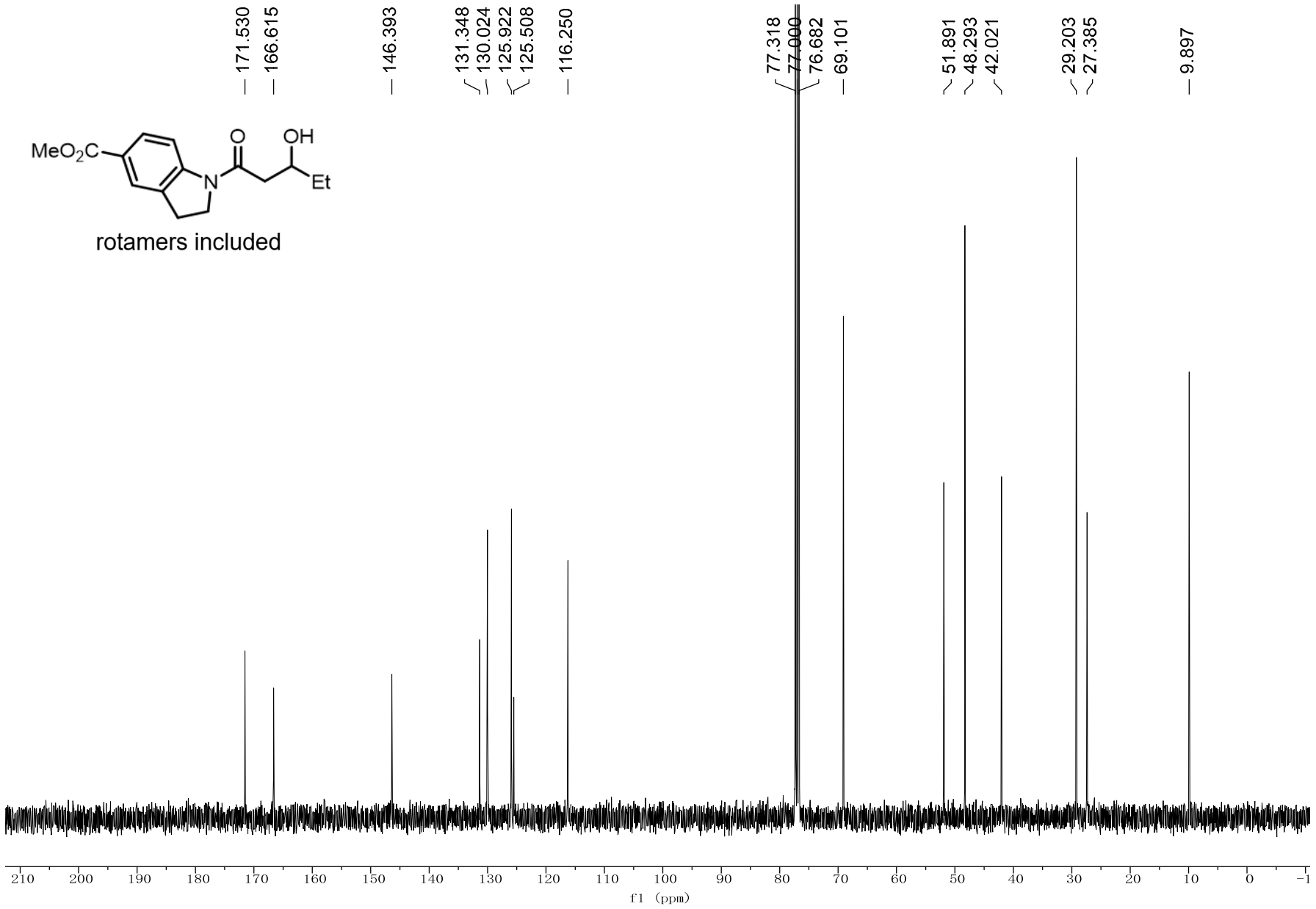
77.212
77.000
76.788
69.194
48.137
41.553
29.202
27.826
9.935
F
O
OH
N
Et
rotamers included
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

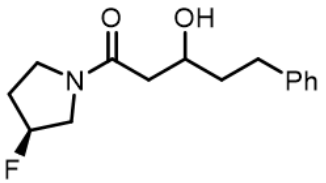


rotamers included

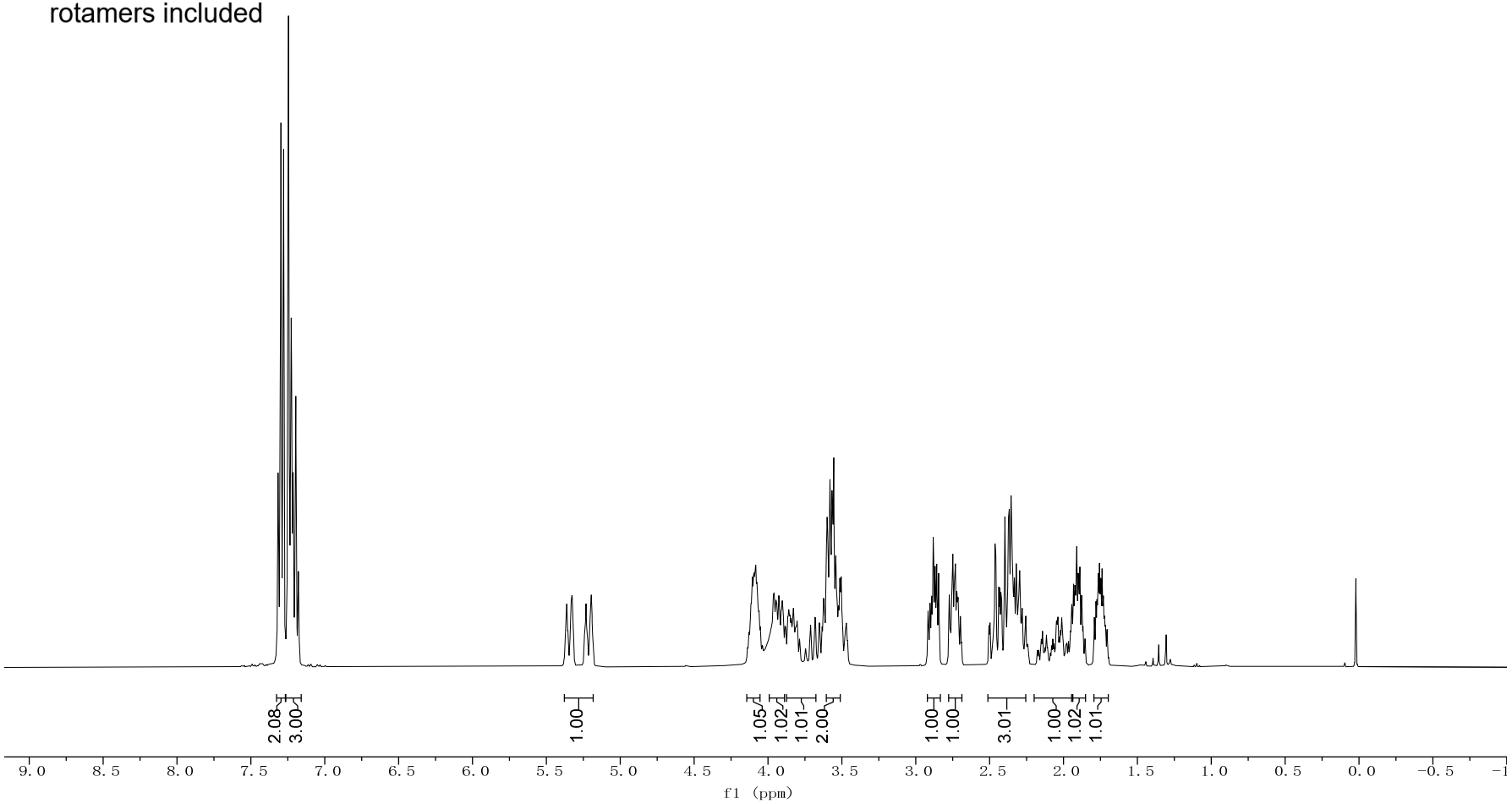


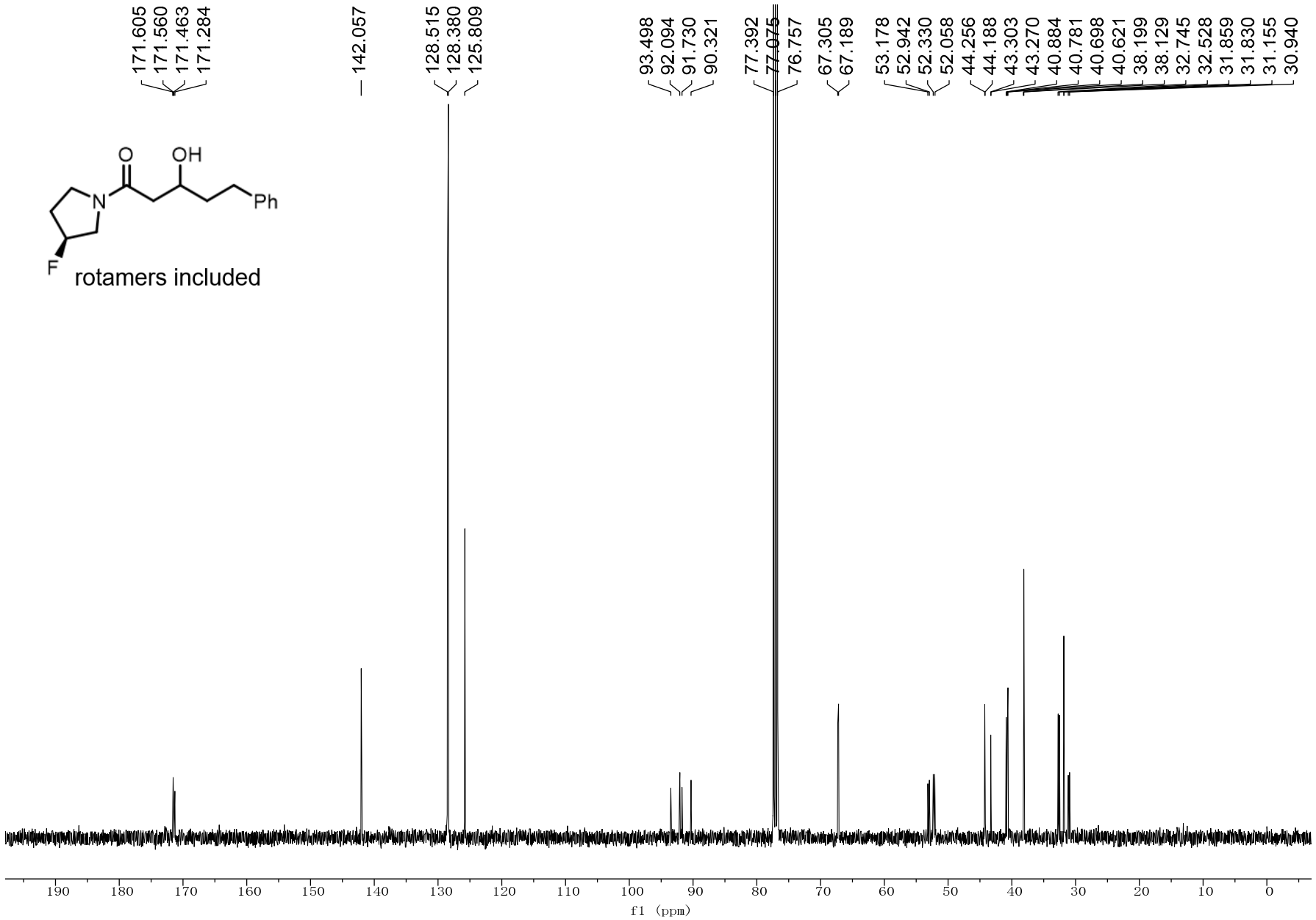
rotamers included

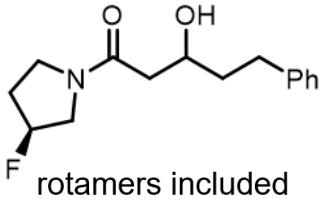

171.530
166.615
146.393
131.348
130.024
125.922
125.508
116.250
77.318
77.000
76.682
69.101
51.891
48.293
42.021
29.203
27.385
9.897
MeO2C
O
OH
N
Et
rotamers included
f1 (ppm)



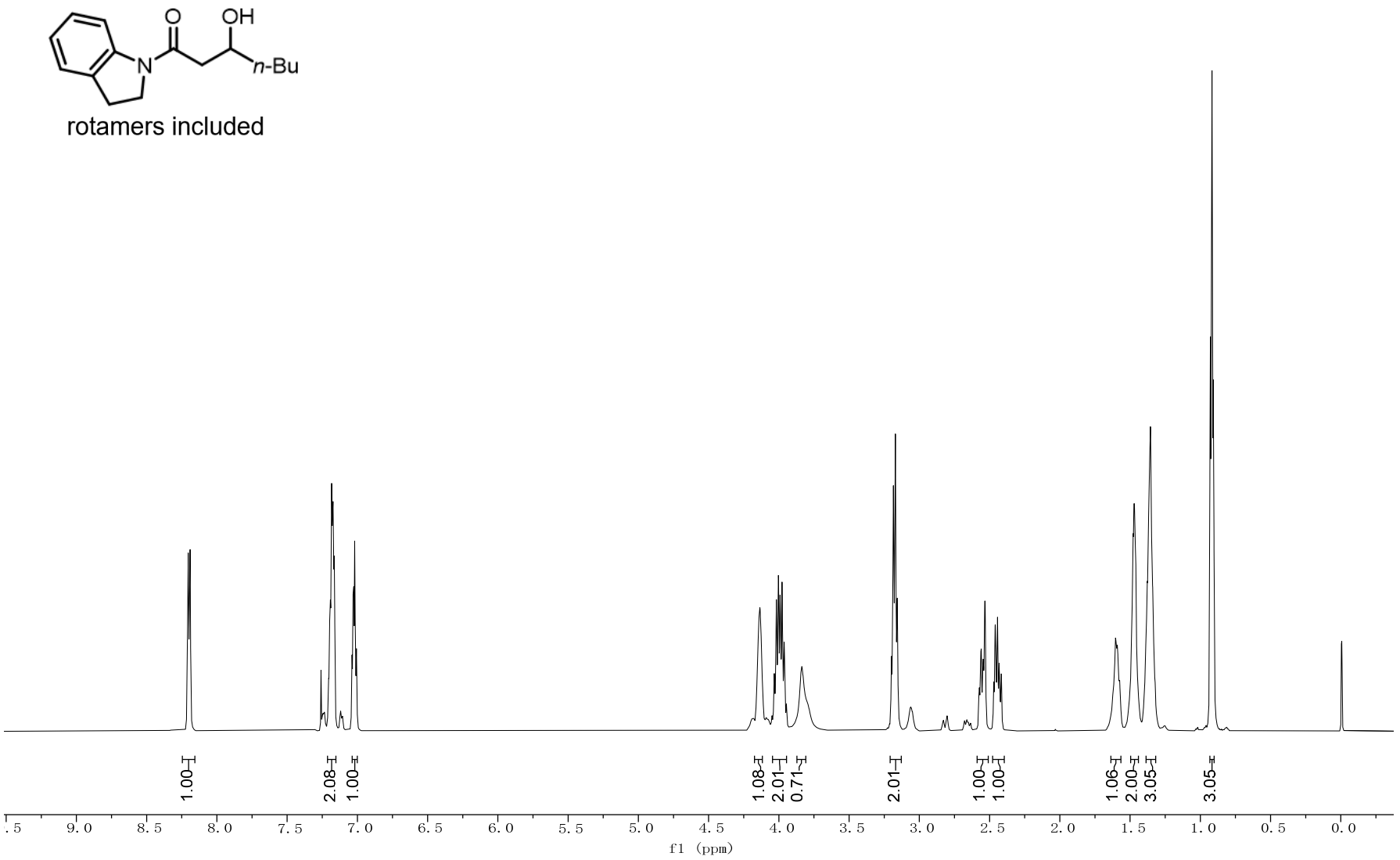
rotamers included

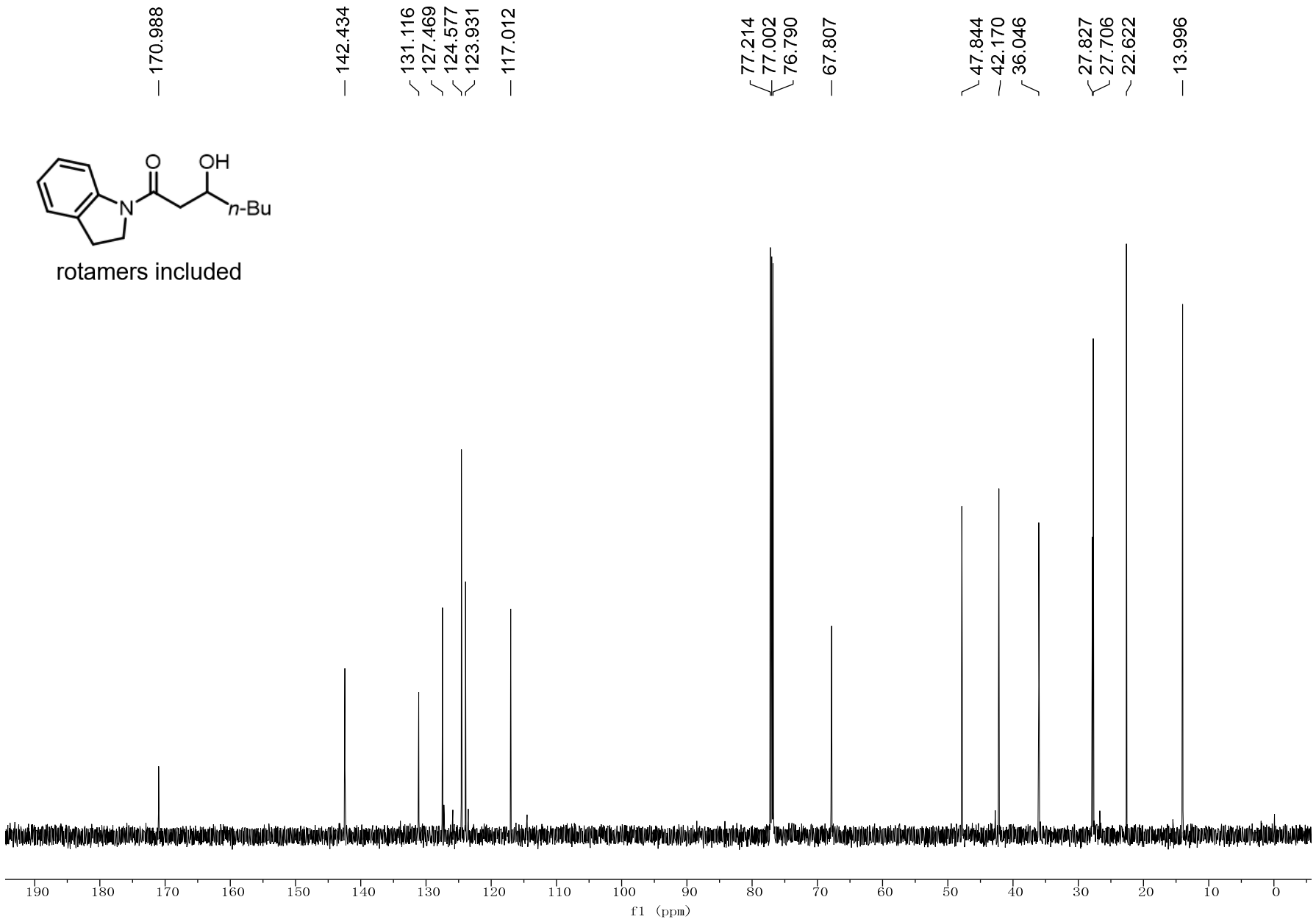


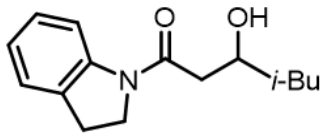

171.605
171.560
171.463
171.284
142.057
128.515
128.380
125.809
93.498
92.094
91.730
90.321
77.392
77.075
76.757
67.305
67.189
53.178
52.942
52.330
52.058
44.256
44.188
43.303
43.270
40.884
40.781
40.698
40.621
38.199
38.129
32.745
32.528
31.859
31.830
31.155
30.940
O
OH
N
Ph
F
rotamers included
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



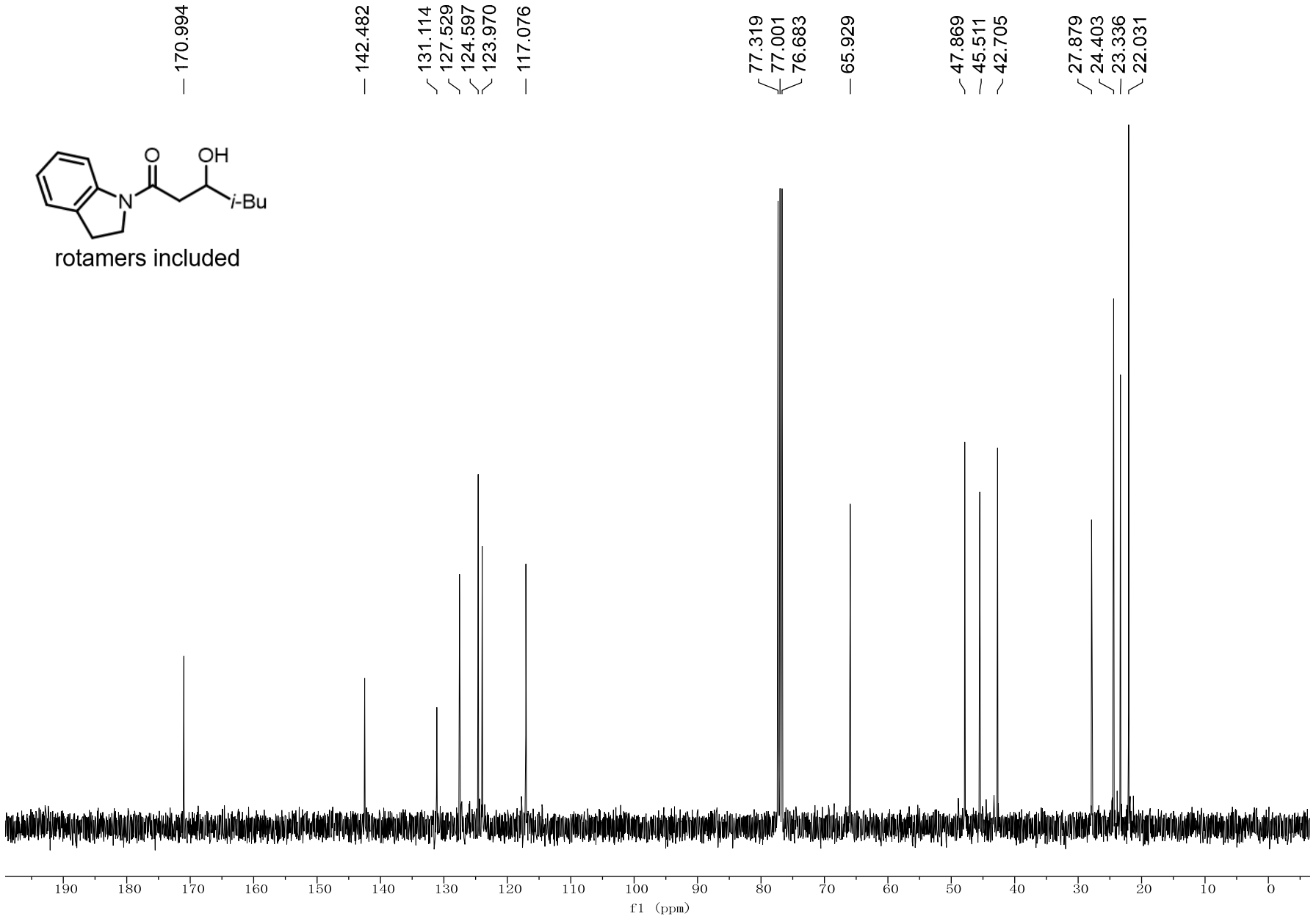
rotamers included

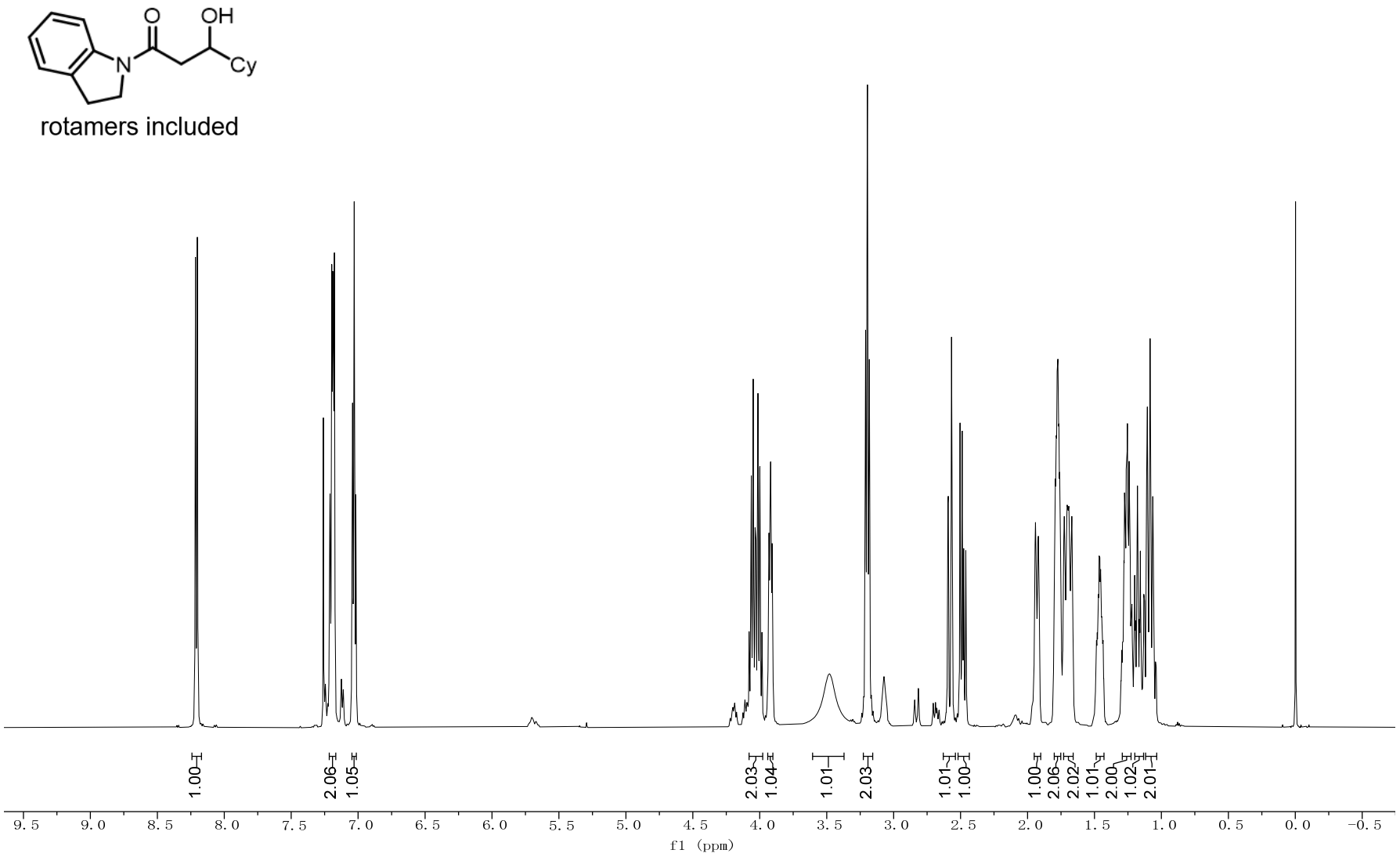

O
OH
N
n-Bu
rotamers included
1.00
2.08
1.00
1.08
2.01
0.71
2.01
1.00
1.00
1.06
2.00
3.05
3.05
f1 (ppm)

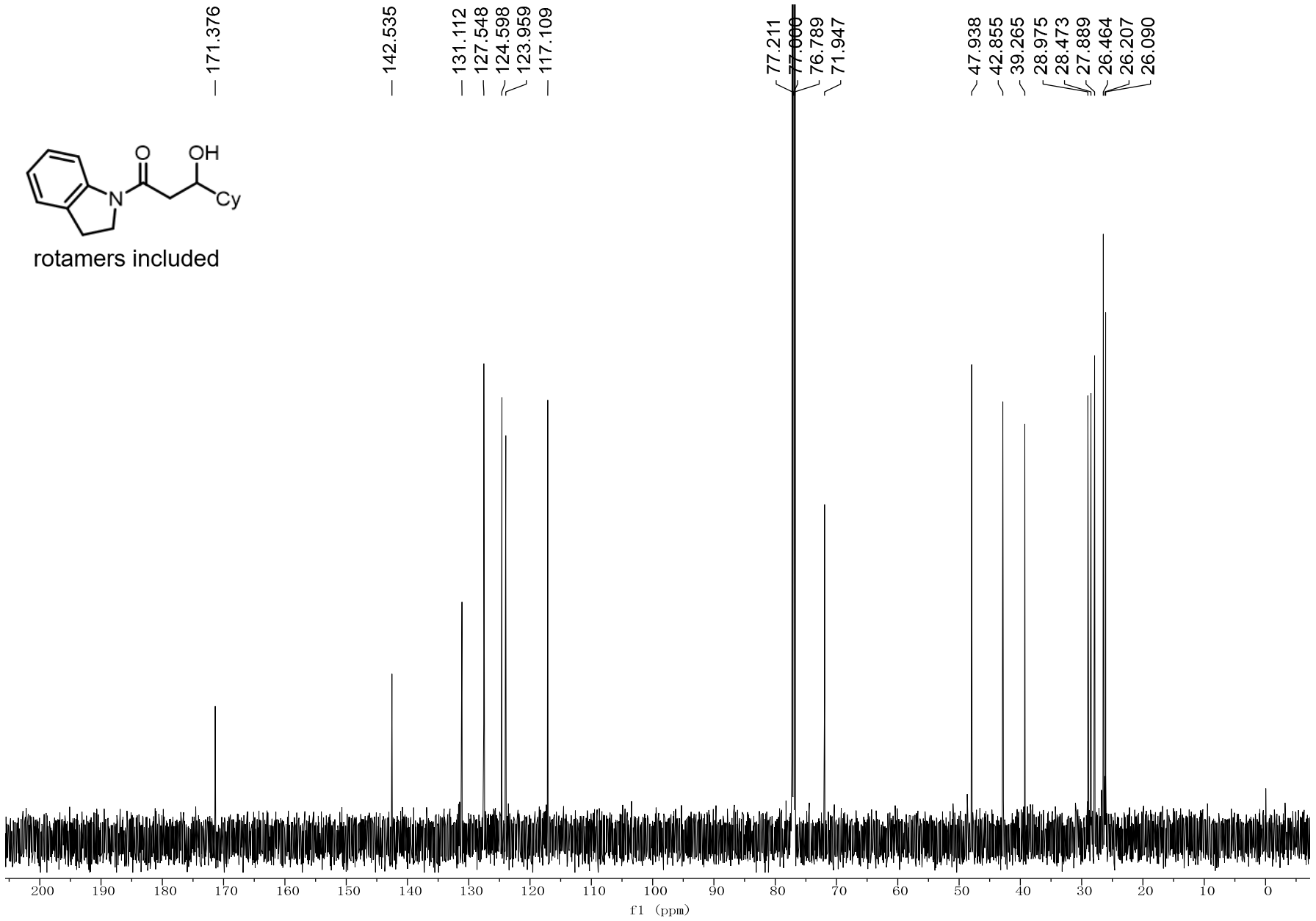

170.988
142.434
131.116
127.469
124.577
123.931
117.012
77.214
77.002
76.790
67.807
47.844
42.170
36.046
27.827
27.706
22.622
13.996
O
OH
N
n-Bu
rotamers included
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

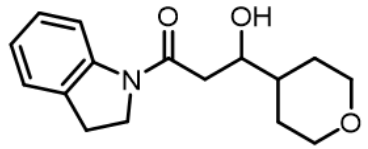


rotamers included

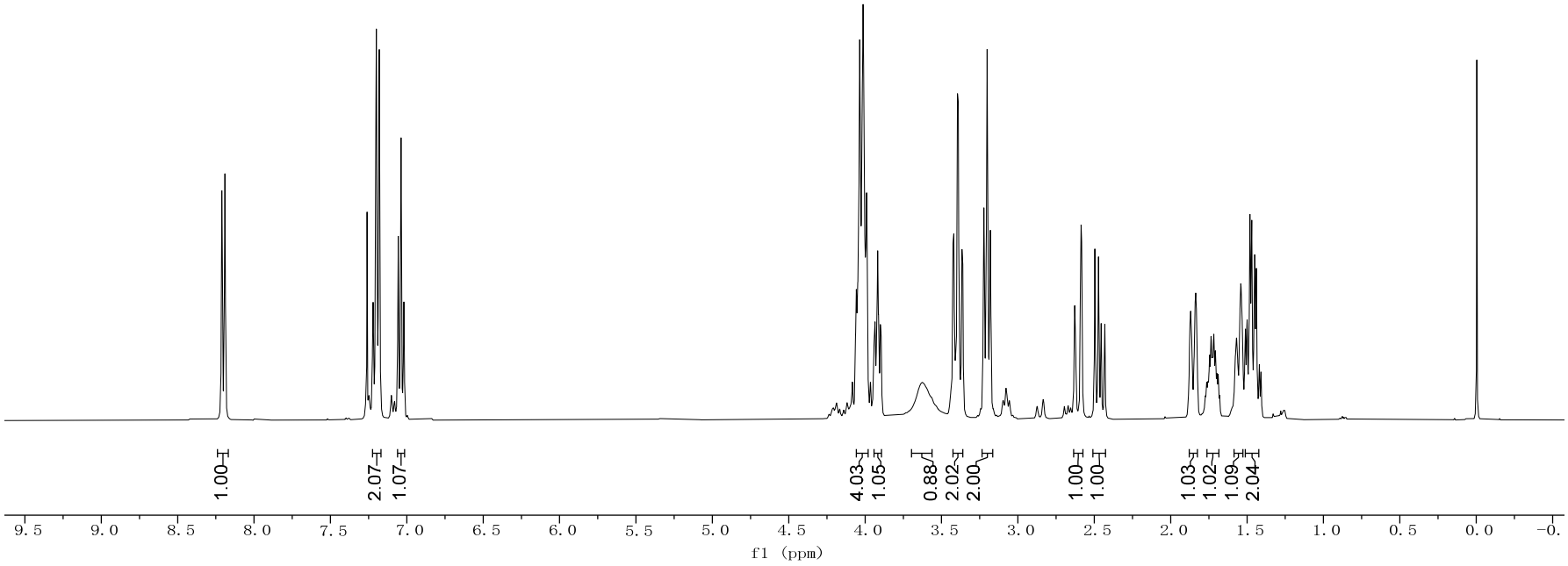

170.994
142.482
131.114
127.529
124.597
123.970
117.076
77.319
77.001
76.683
65.929
47.869
45.511
42.705
27.879
24.403
23.336
22.031
O
OH
N
i-Bu
rotamers included
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

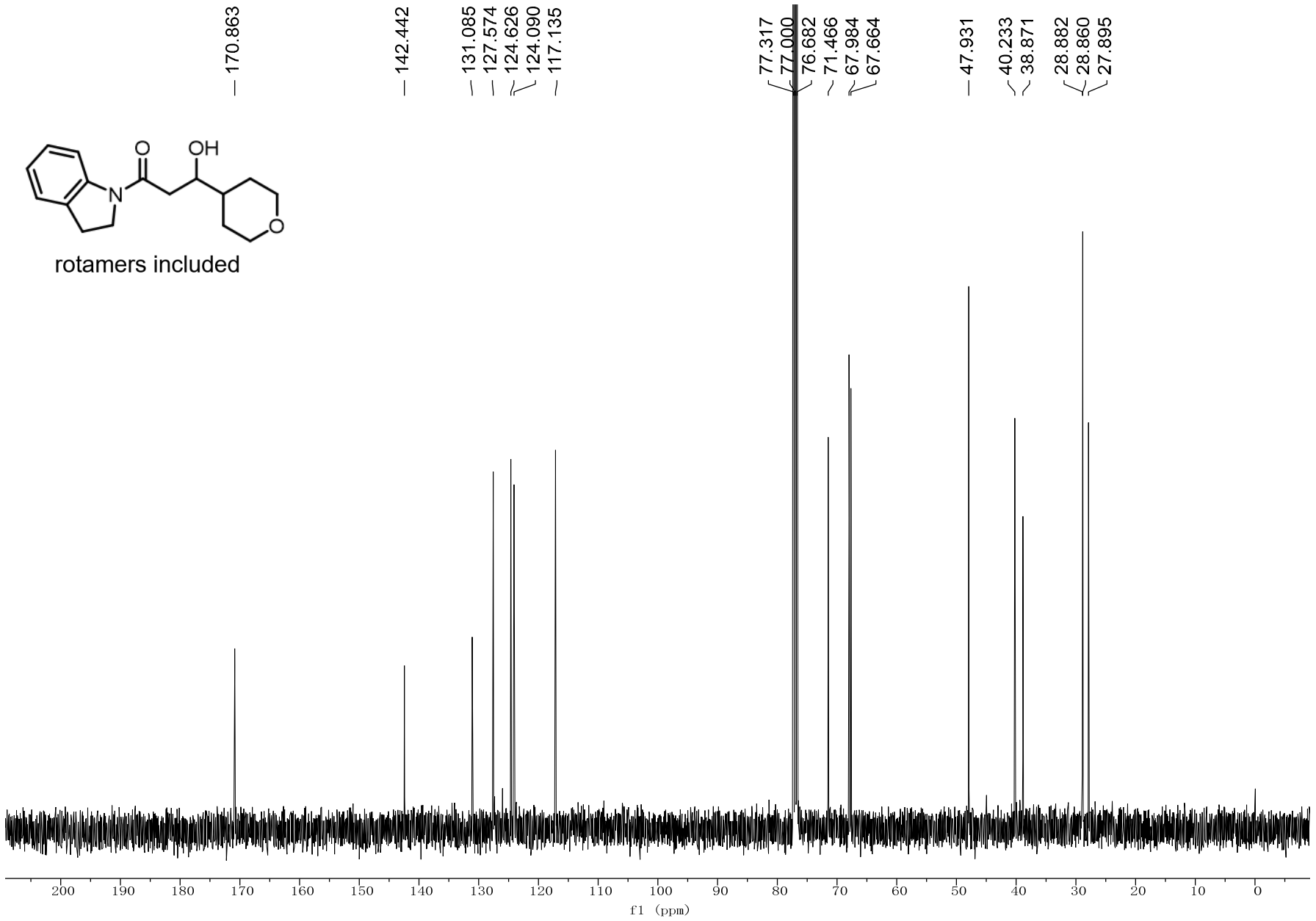

O
OH
N
Cy
rotamers included
1.00
2.06
1.05
2.03
1.04
1.01
2.03
1.01
1.00
1.00
2.06
2.02
1.01
2.00
1.02
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

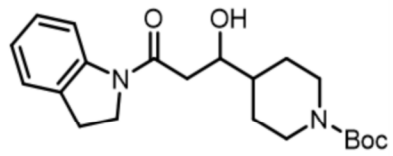

171.376
142.535
131.112
127.548
124.598
123.959
117.109
77.211
77.000
76.789
71.947
47.938
42.855
39.265
28.975
28.473
27.889
26.464
26.207
26.090
O
OH
N
Cy
rotamers included
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



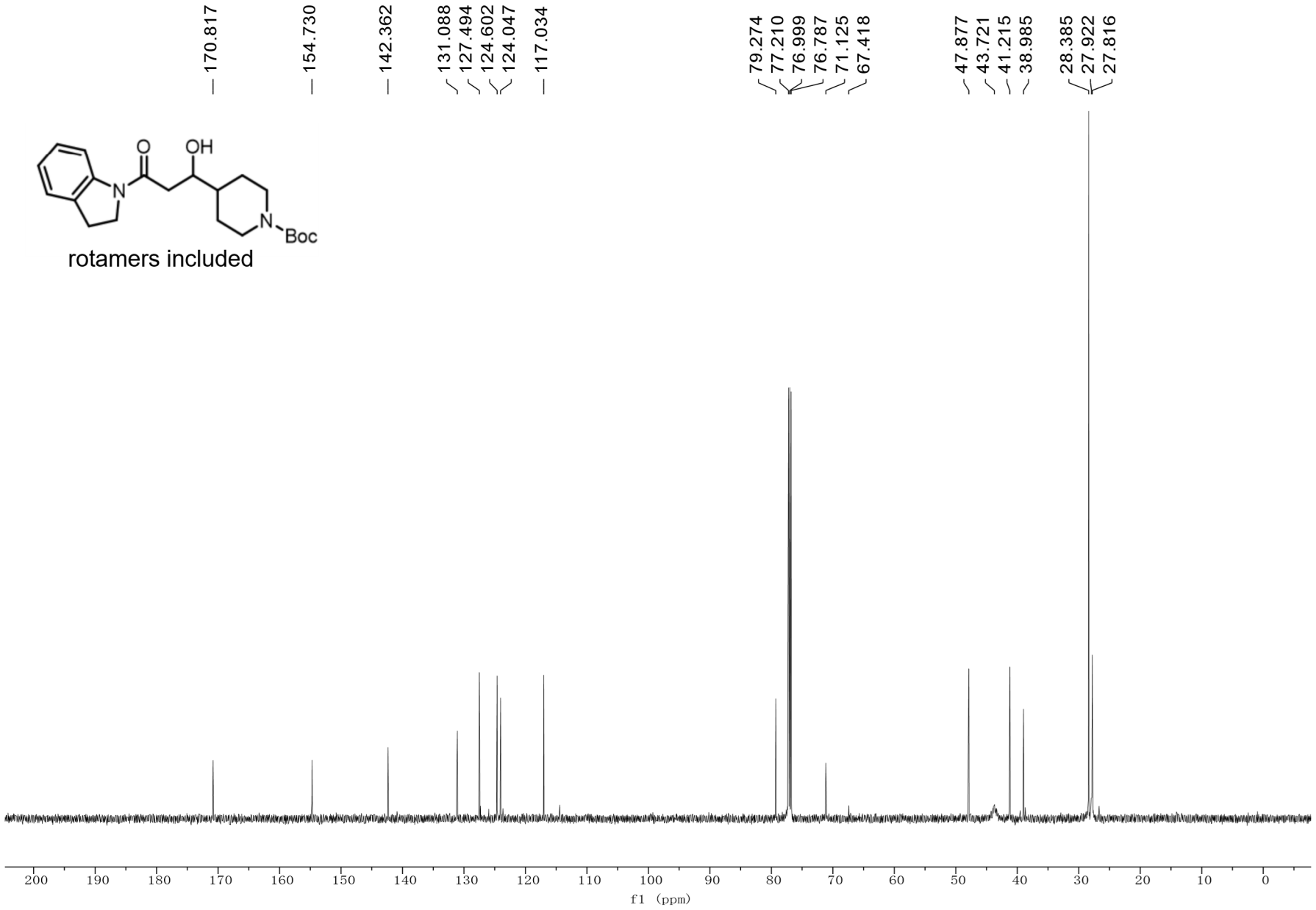
rotamers included

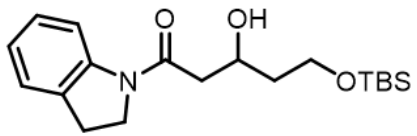



170.863
142.442
131.085
127.574
124.626
124.090
117.135
77.317
77.000
76.682
71.466
67.984
67.664
47.931
40.233
38.871
28.882
28.860
27.895
O
OH
N
O
rotamers included
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

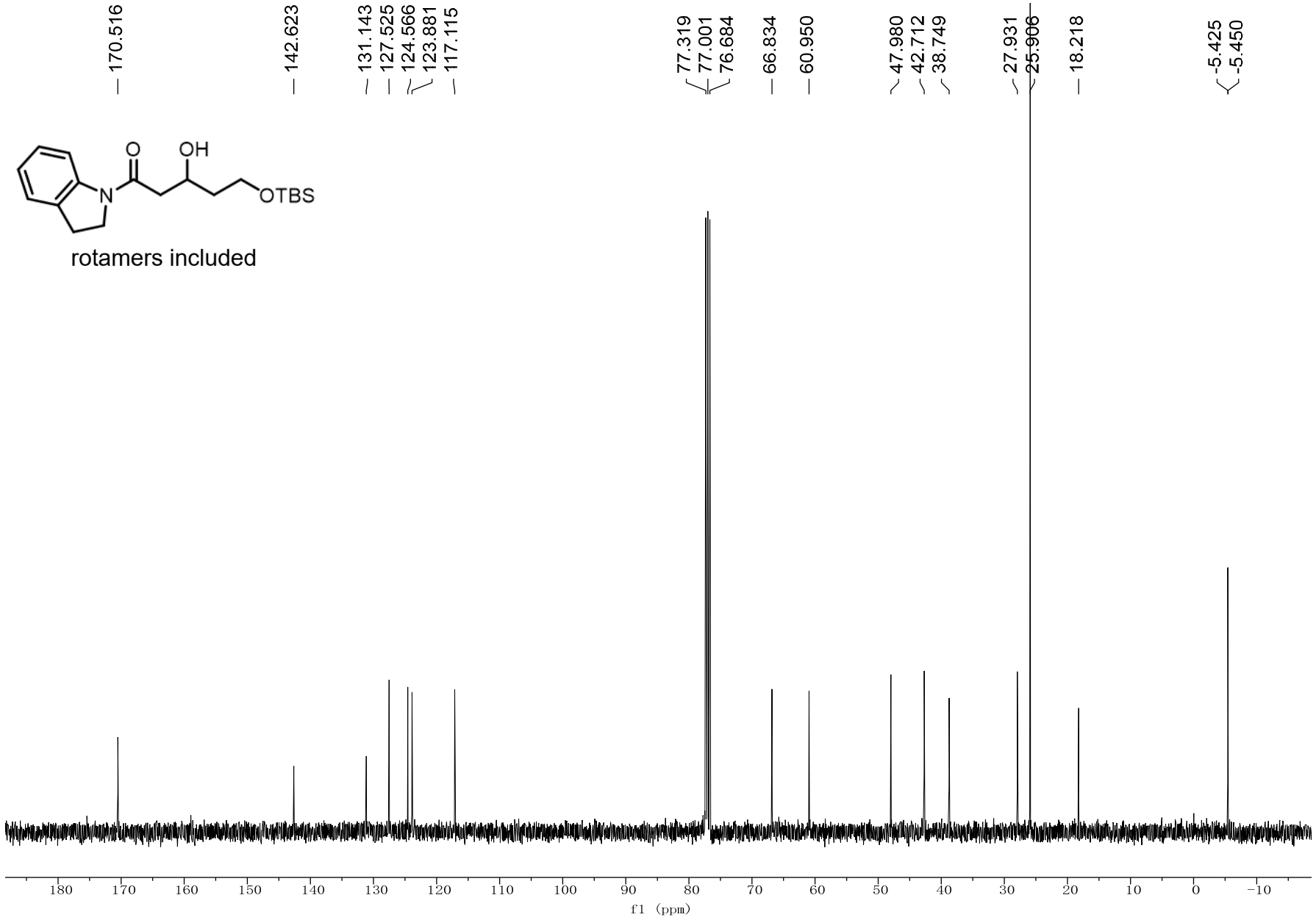


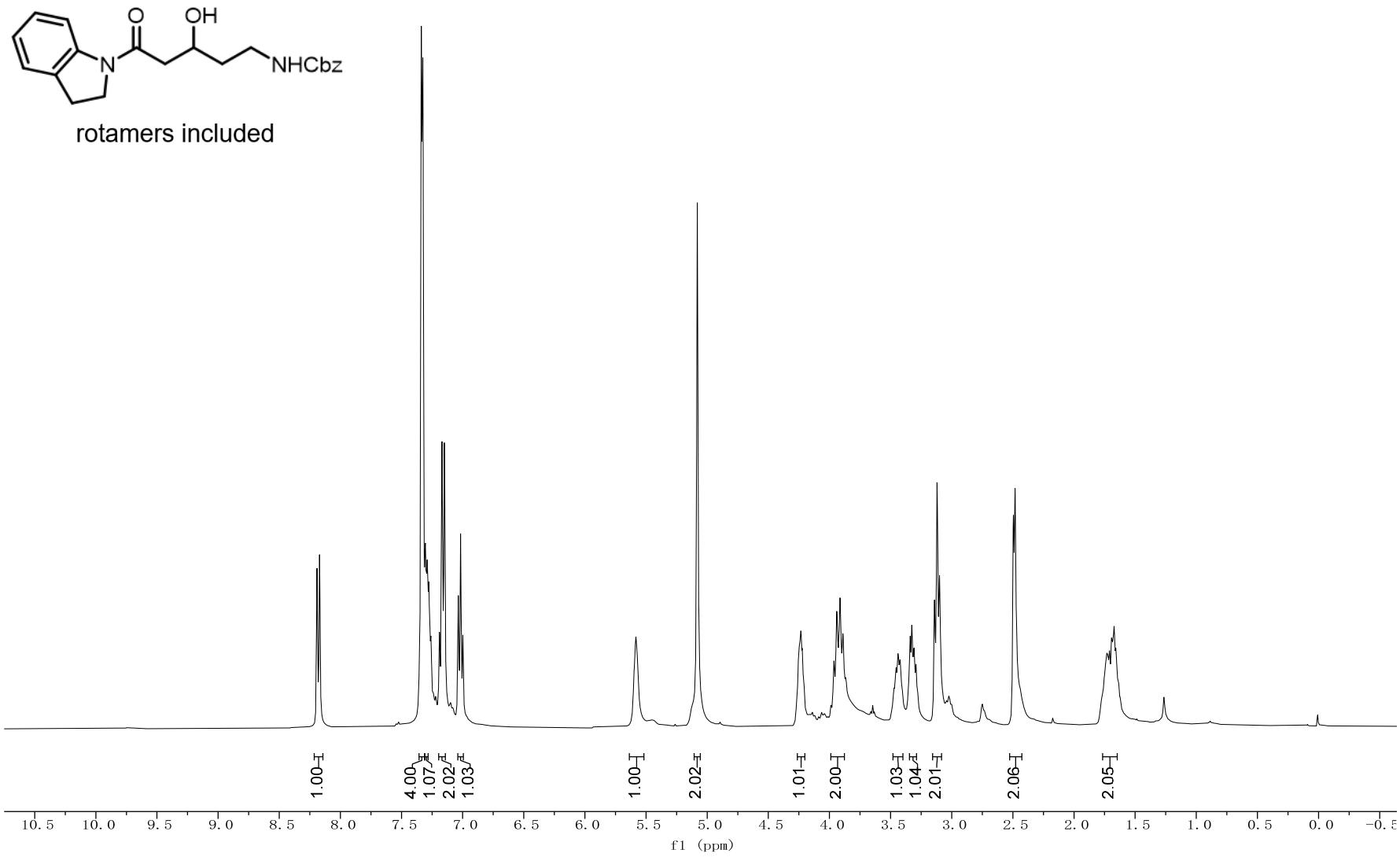
rotamers included

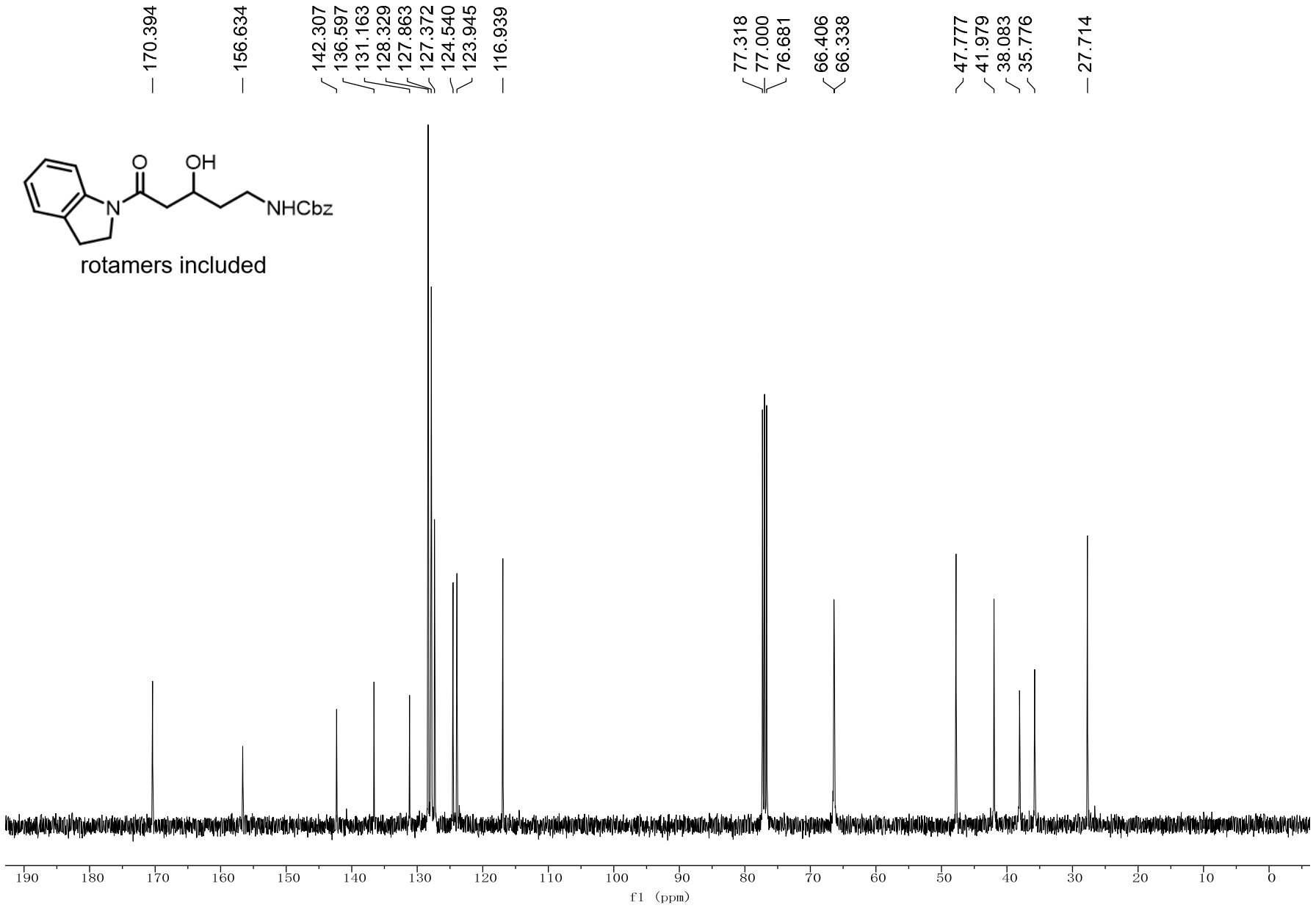

170.817
154.730
142.362
131.088
127.494
124.602
124.047
117.034
79.274
77.210
76.999
76.787
71.125
67.418
47.877
43.721
41.215
38.985
28.385
27.922
27.816
O
OH
N
N
Boc
rotamers included
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

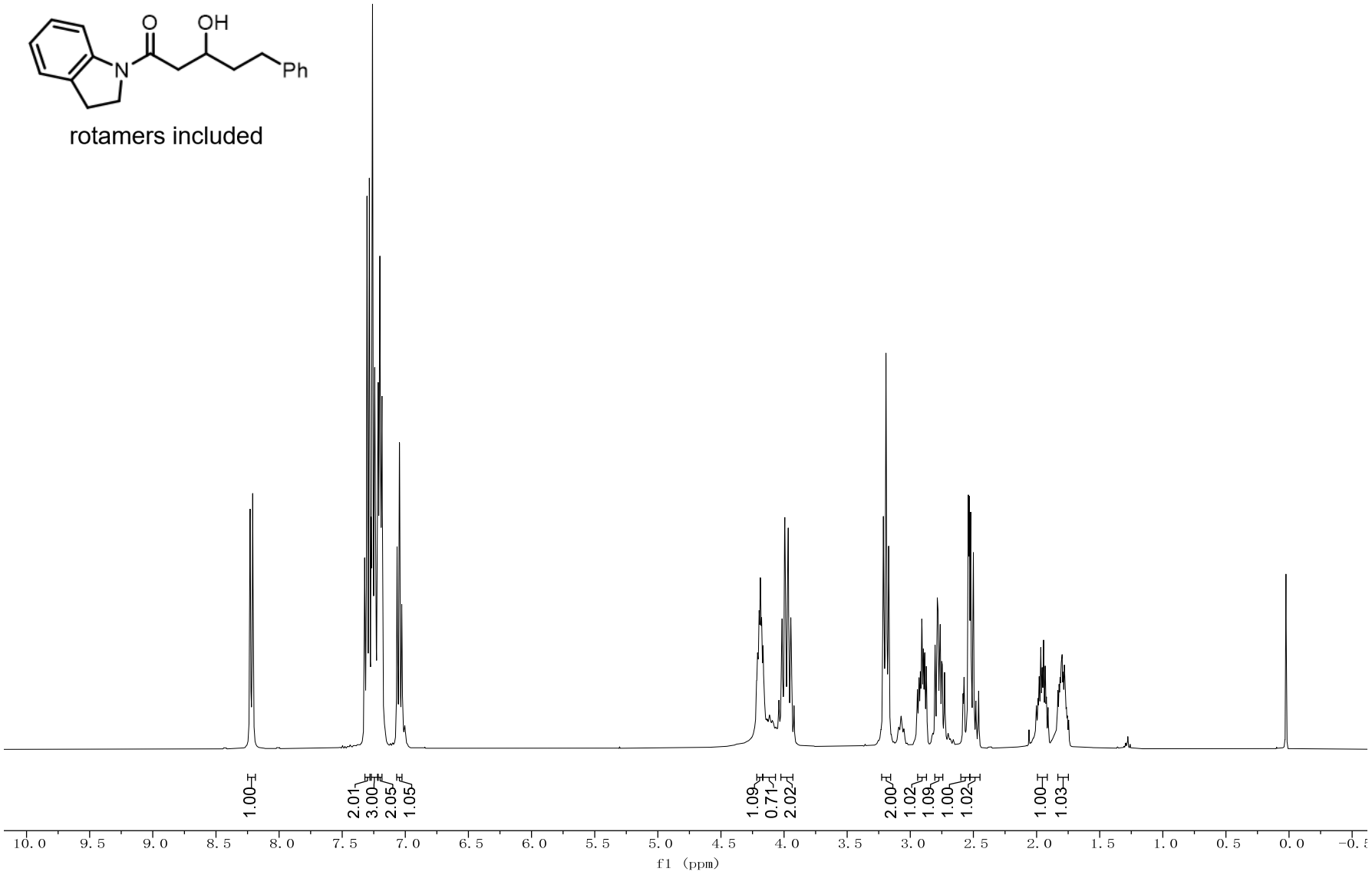


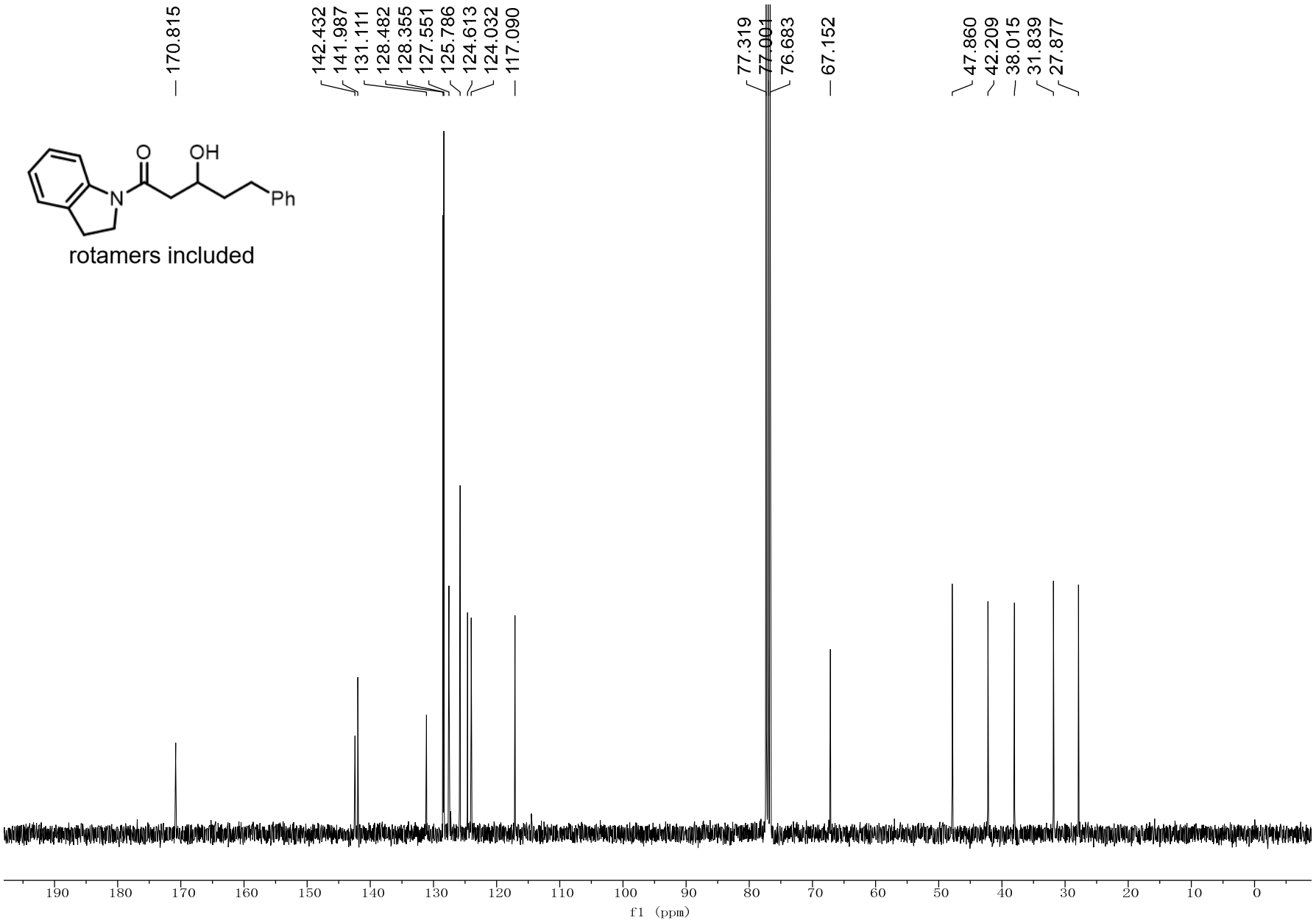
rotamers included

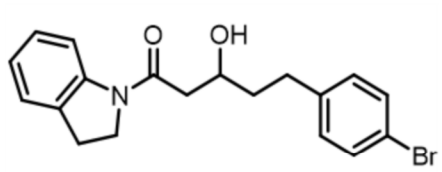

170.516
142.623
131.143
127.525
124.566
123.881
117.115
77.319
77.001
76.684
66.834
60.950
47.980
42.712
38.749
27.931
25.906
18.218
-5.425
-5.450
O
OH
N
OTBS
rotamers included
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


O
OH
N
NHCbz
rotamers included
1.00
4.00
1.07
2.02
1.03
1.00
2.02
1.01
2.00
1.03
1.04
2.01
2.06
2.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

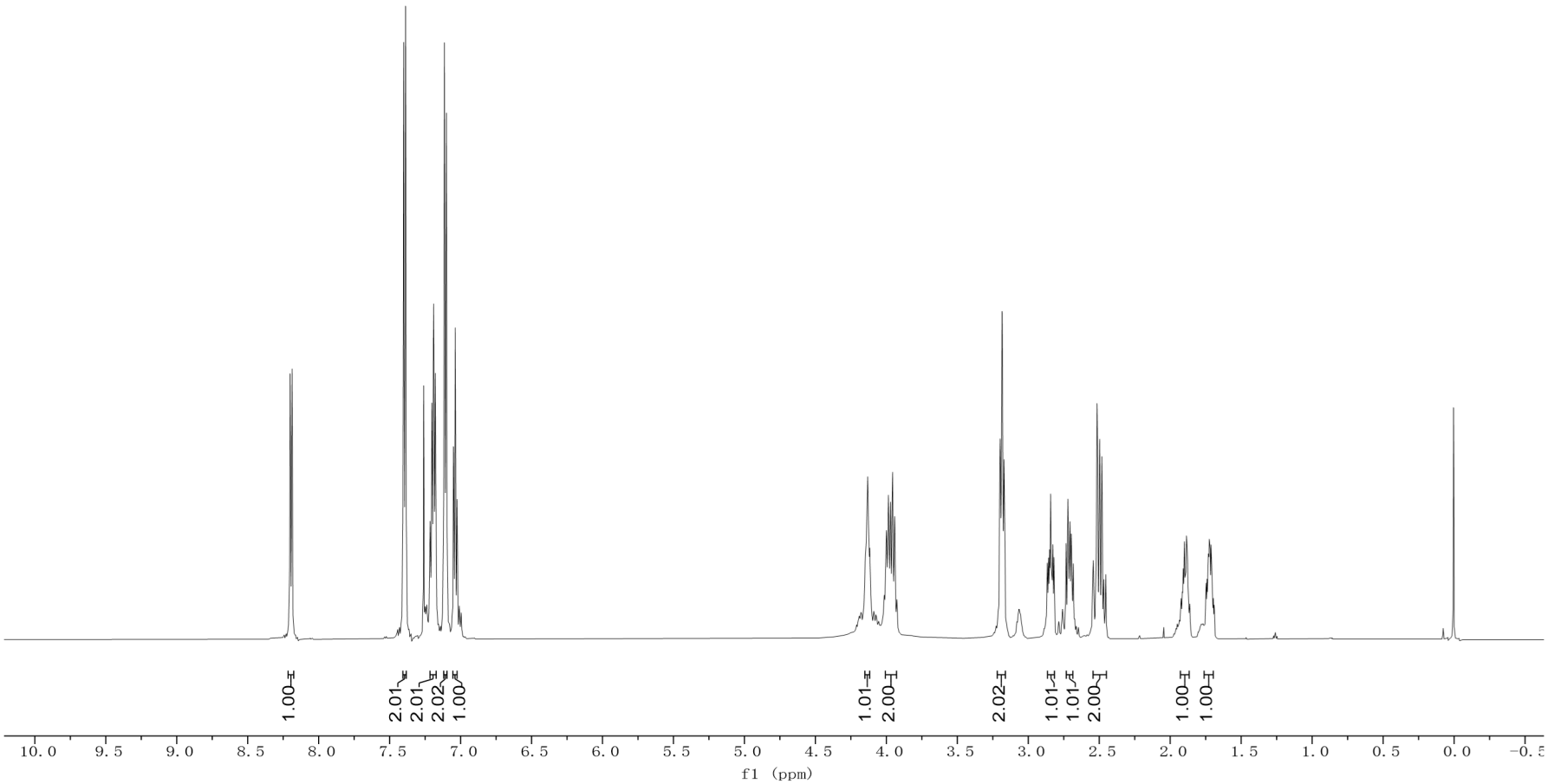

170.394
156.634
142.307
136.597
131.163
128.329
127.863
127.372
124.540
123.945
116.939
77.318
77.000
76.681
66.406
66.338
47.777
41.979
38.083
35.776
27.714
O
OH
N
NHCbz
rotamers included
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

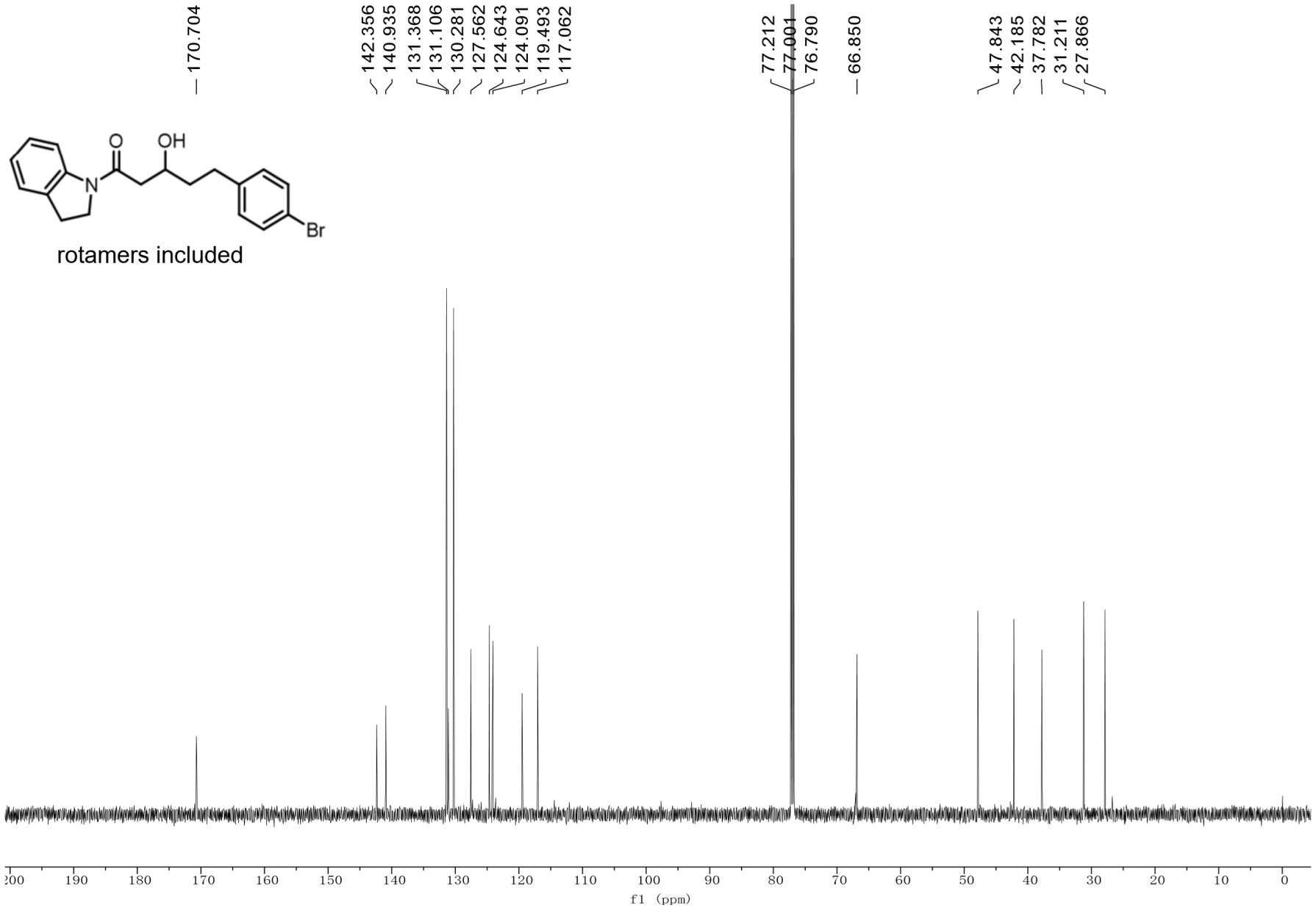

O
OH
N
Ph
rotamers included
1.00
2.01
3.00
2.05
1.05
1.09
0.71
2.02
2.00
1.02
1.09
1.00
1.02
1.00
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

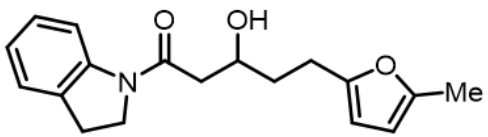

170.815
142.432
141.987
131.111
128.482
128.355
127.551
125.786
124.613
124.032
117.090
77.319
77.001
76.683
67.152
47.860
42.209
38.015
31.839
27.877
O
OH
N
Ph
rotamers included
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



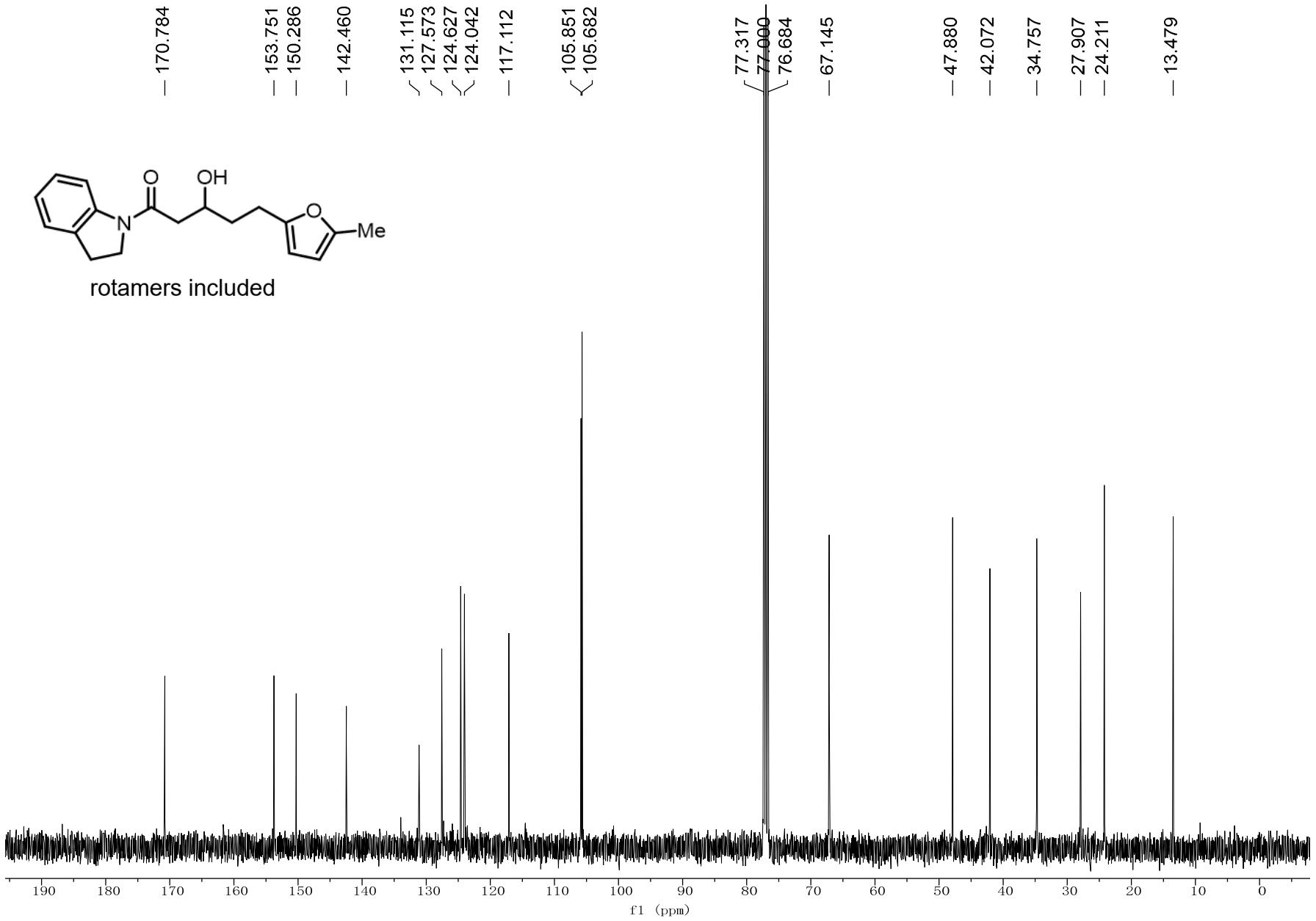
rotamers included




170.704
142.356
140.935
131.368
131.106
130.281
127.562
124.643
124.091
119.493
117.062
77.212
77.001
76.790
66.850
47.843
42.185
37.782
31.211
27.866
O
OH
N
Br
rotamers included
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



rotamers included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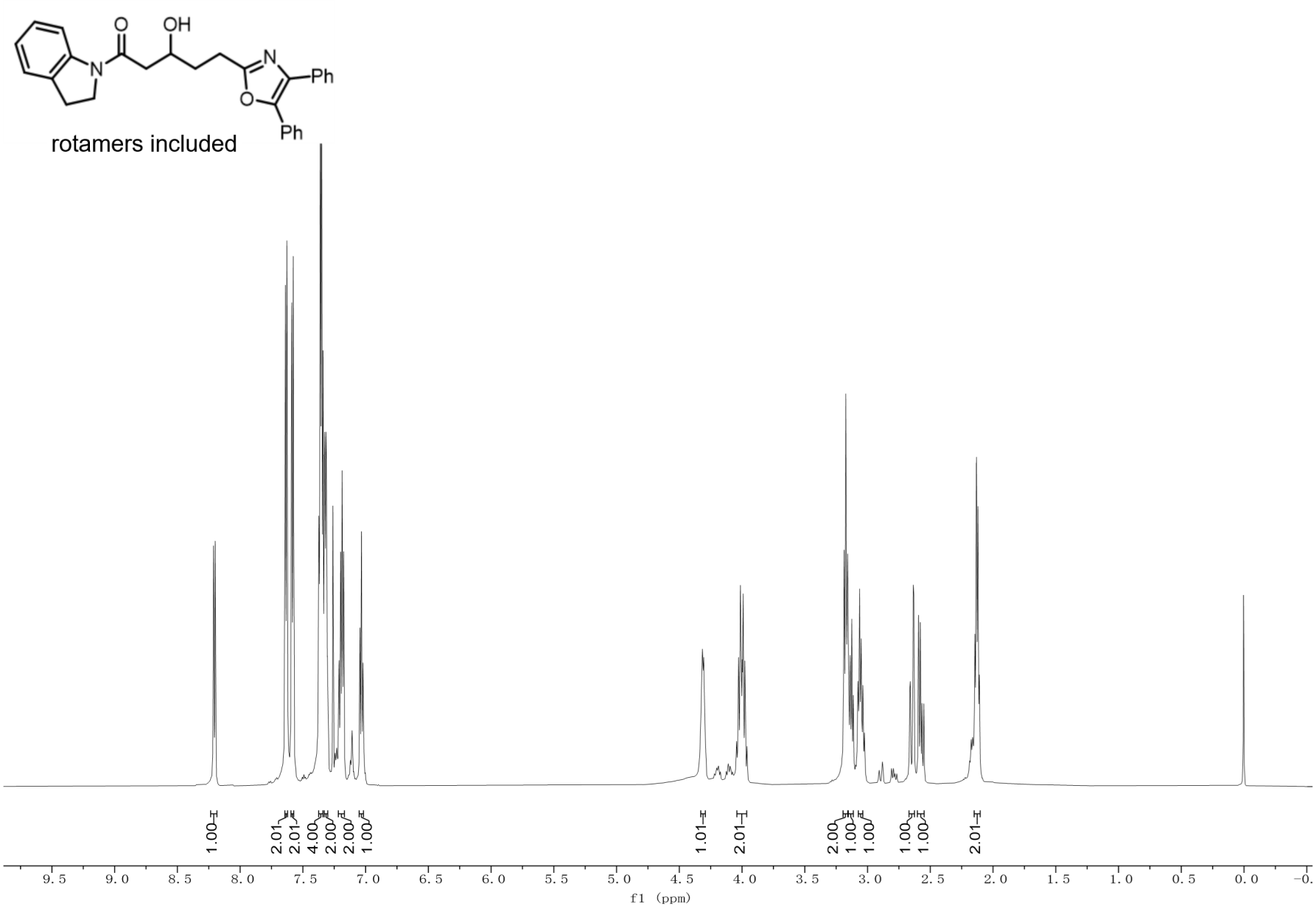
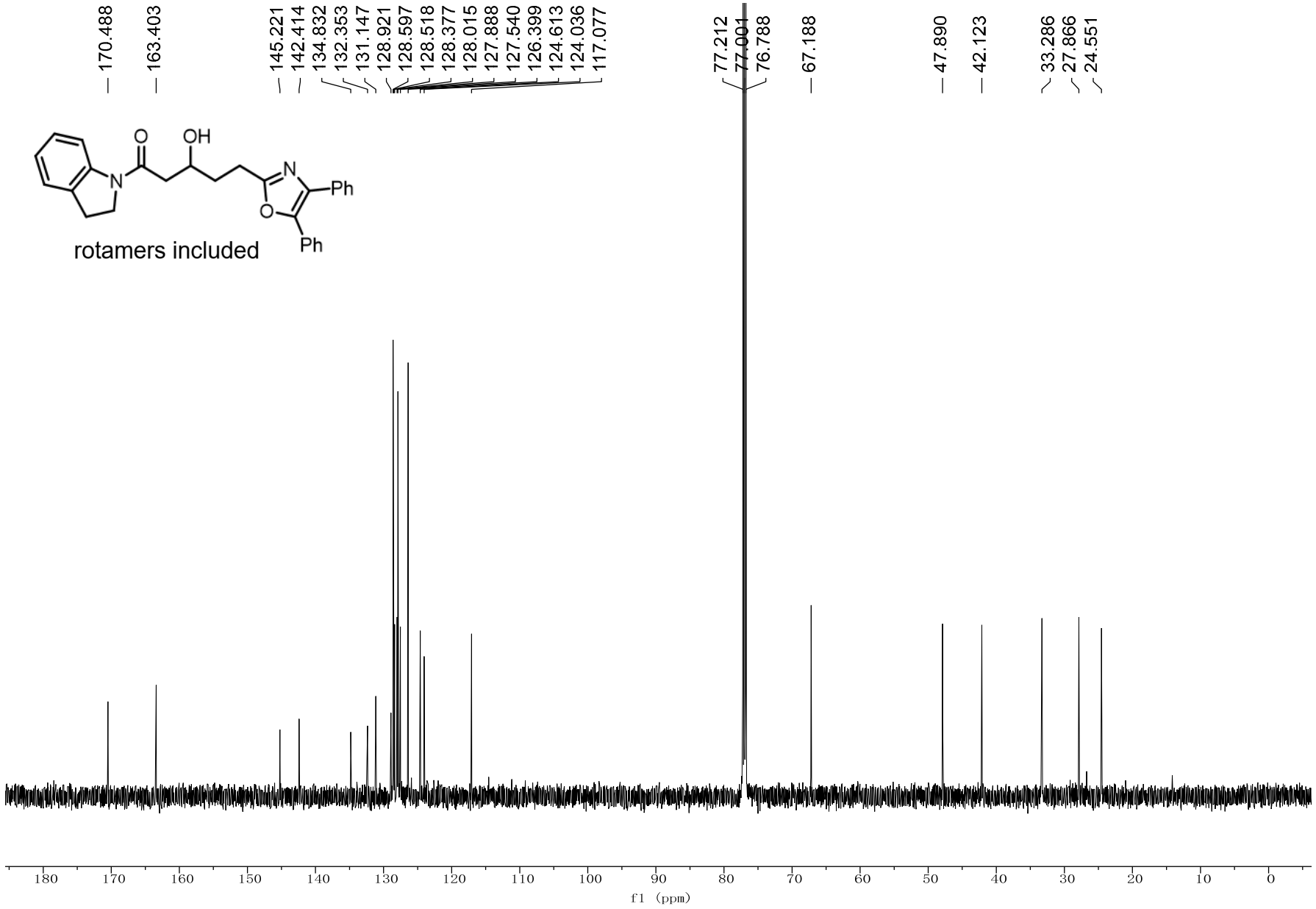
150.286
142.460
131.115
127.573
124.627
124.042
117.112
105.851
105.682
77.317
77.000
76.684
67.145
47.880
42.072
34.757
27.907
24.211
13.479
O
OH
N
O
Me
rotamers included
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OH
N
N
O
Ph
Ph
rotamers included
1.00
2.01
2.01
4.00
2.00
2.00
1.00
1.01
2.01
2.00
1.00
1.00
1.00
1.00
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.
f1 (ppm)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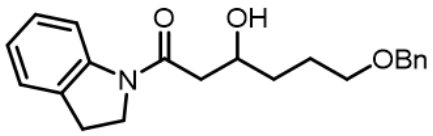
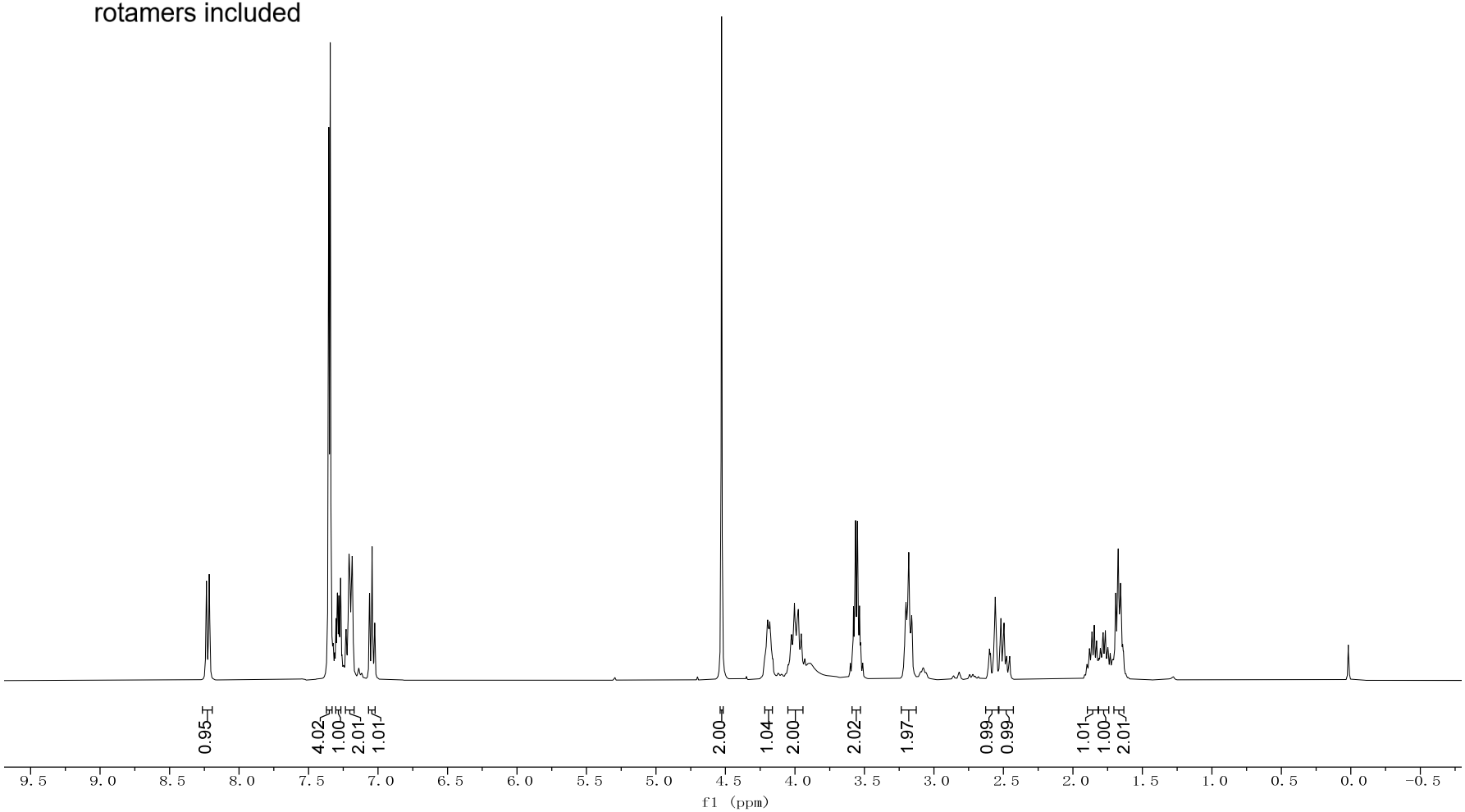
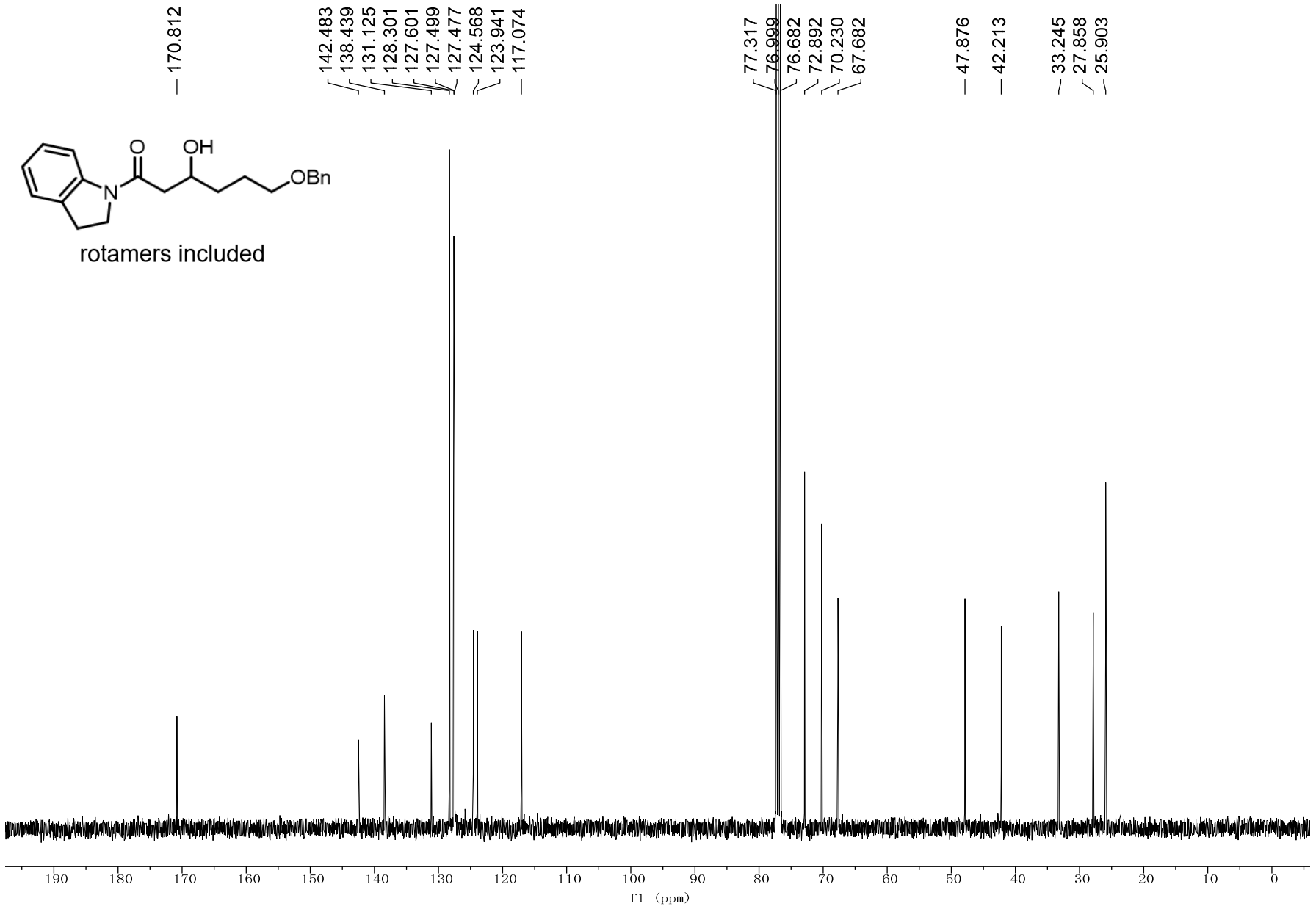
163.403
145.221
142.414
134.832
132.353
131.147
128.921
128.597
128.518
128.377
128.015
127.888
127.540
126.399
124.613
124.036
117.077
77.212
77.001
76.788
67.188
47.890
42.123
33.286
27.866
24.551
O
OH
N
N
O
Ph
Ph
rotamers included
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



rotamers included

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127.601
127.499
127.477
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123.941
117.074
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76.999
76.682
72.892
70.230
67.682
47.876
42.213
33.245
27.858
25.903
O
OH
N
OBn
rotamers included
190
180
170
160
150
140
130
120
110
100
90
80
70
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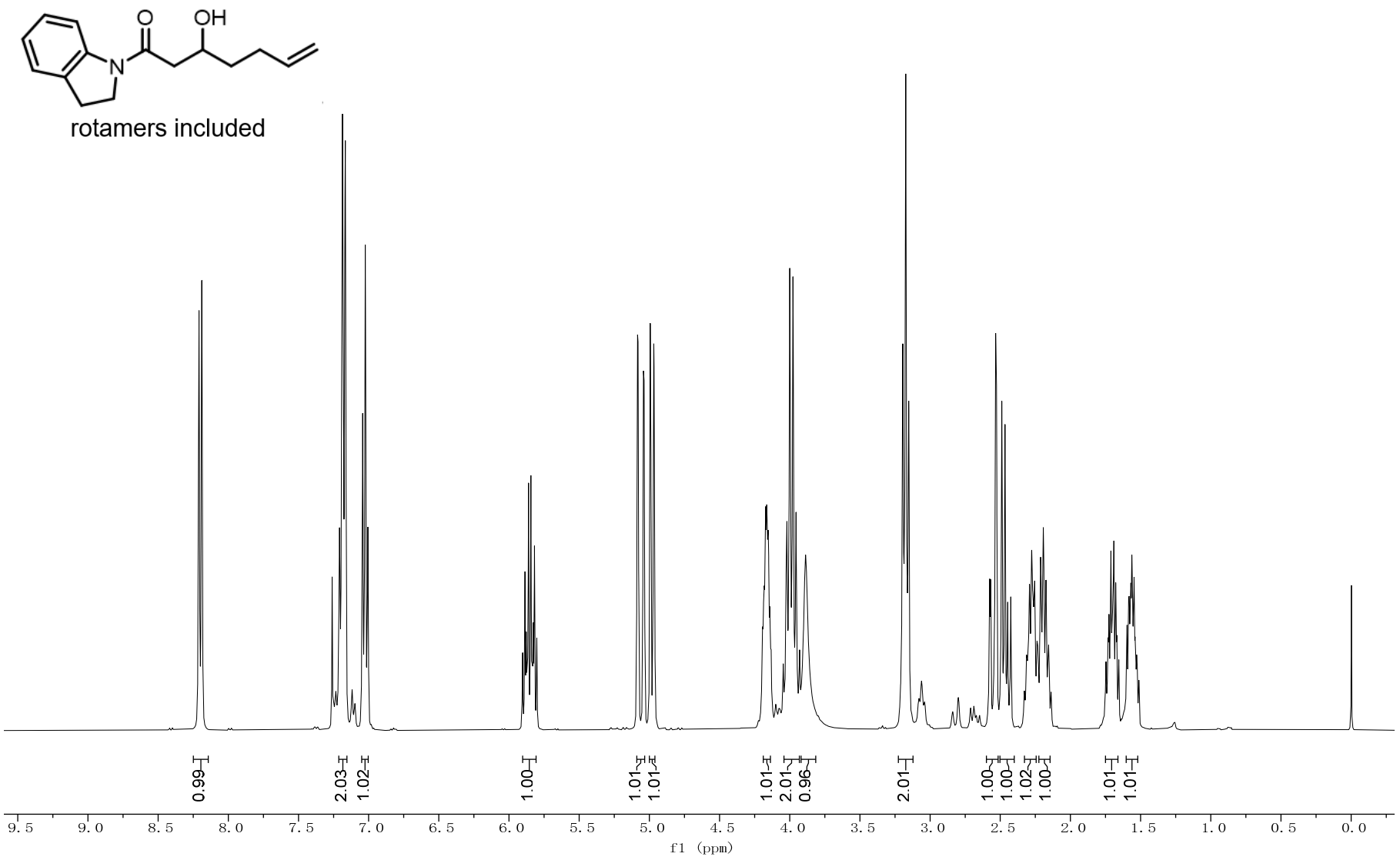
50
40
30
20
10
0
f1 (ppm)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OH
N
rotamers included
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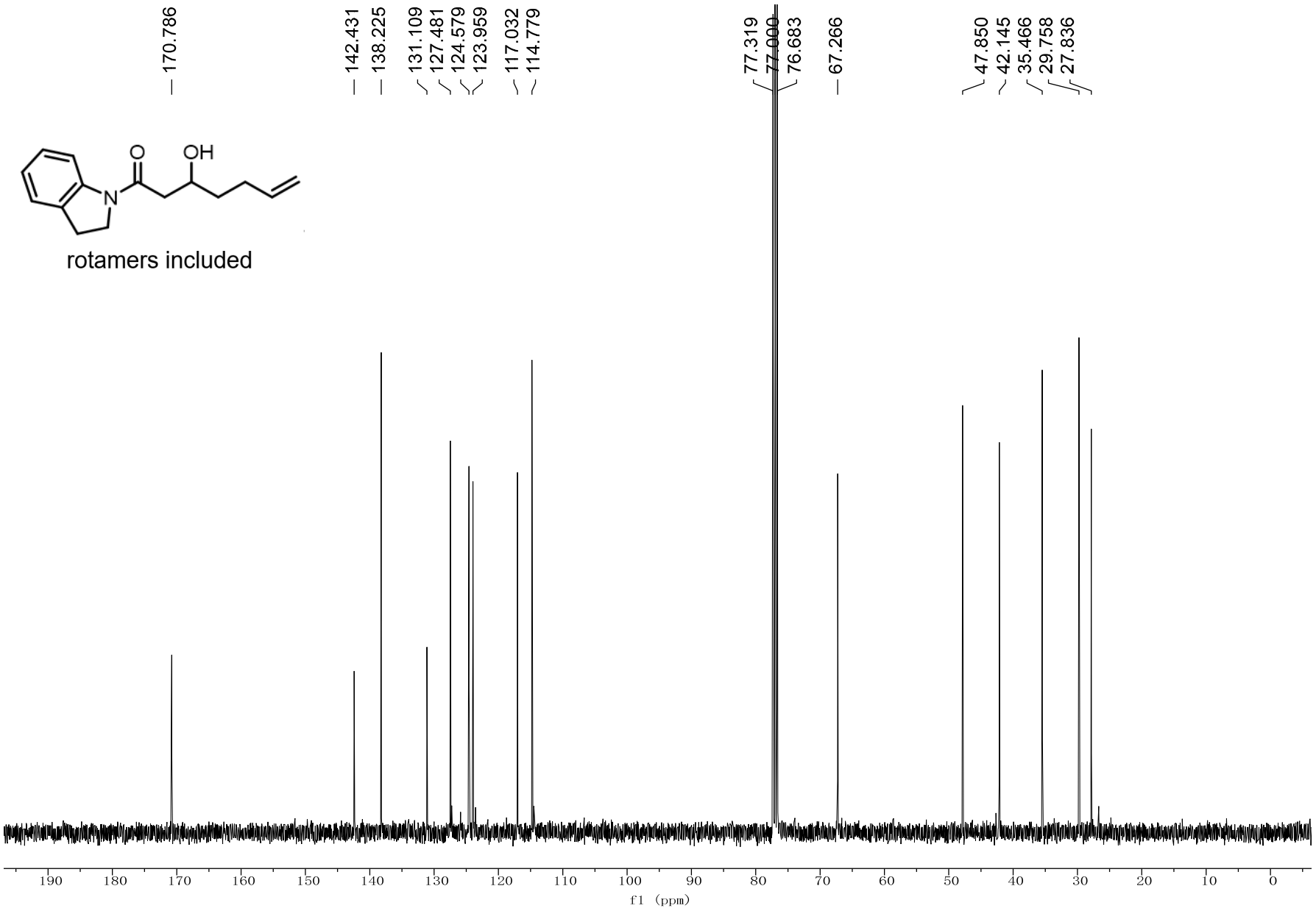
2.01
1.00
1.00
1.02
1.00
1.01
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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117.032
114.779
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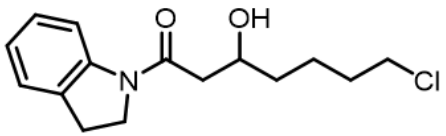
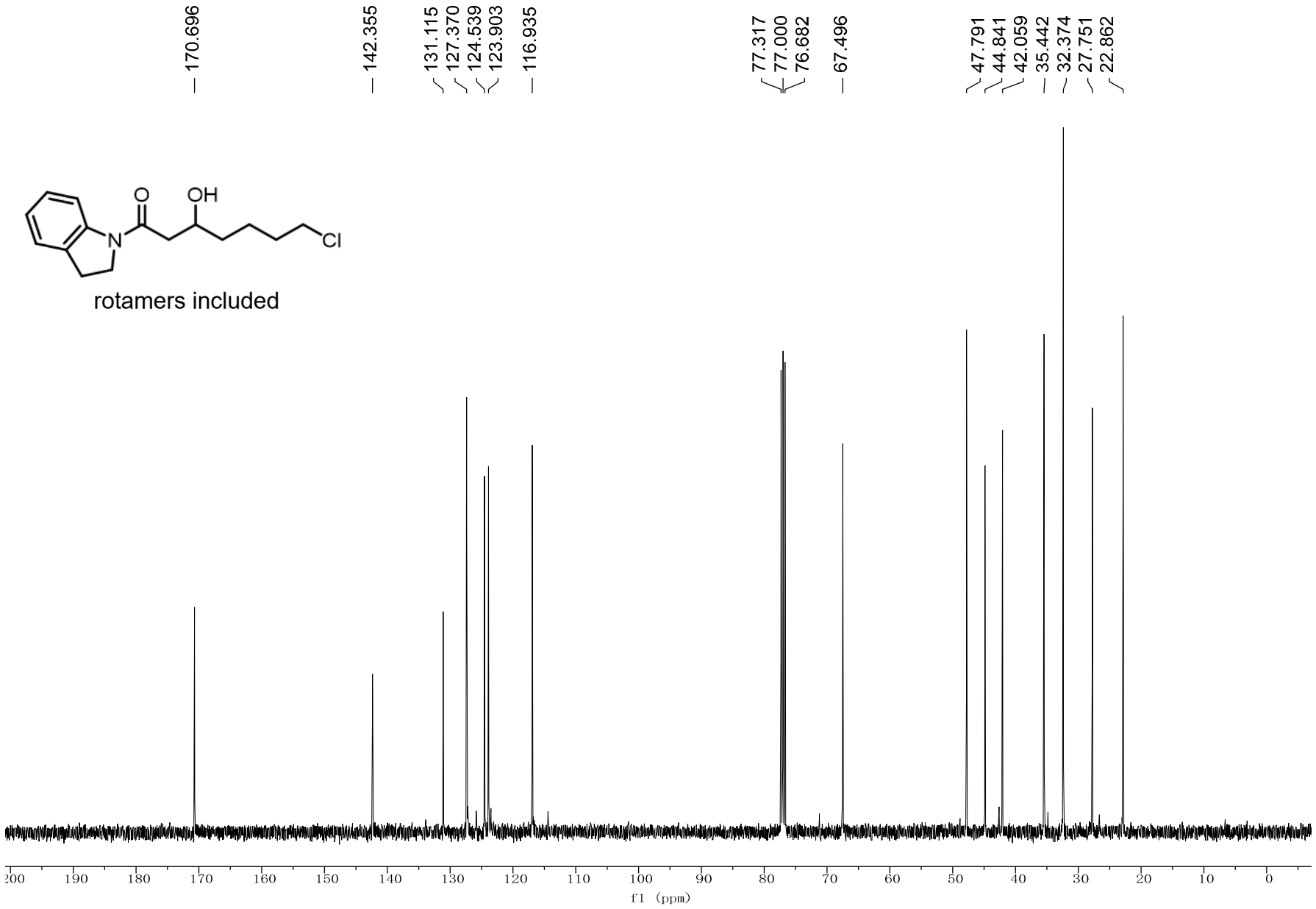
76.683
67.266
47.850
42.145
35.466
29.758
27.836
O
OH
N
rotamers included
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



rotamers included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77.317
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35.442
32.374
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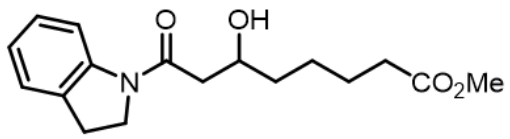
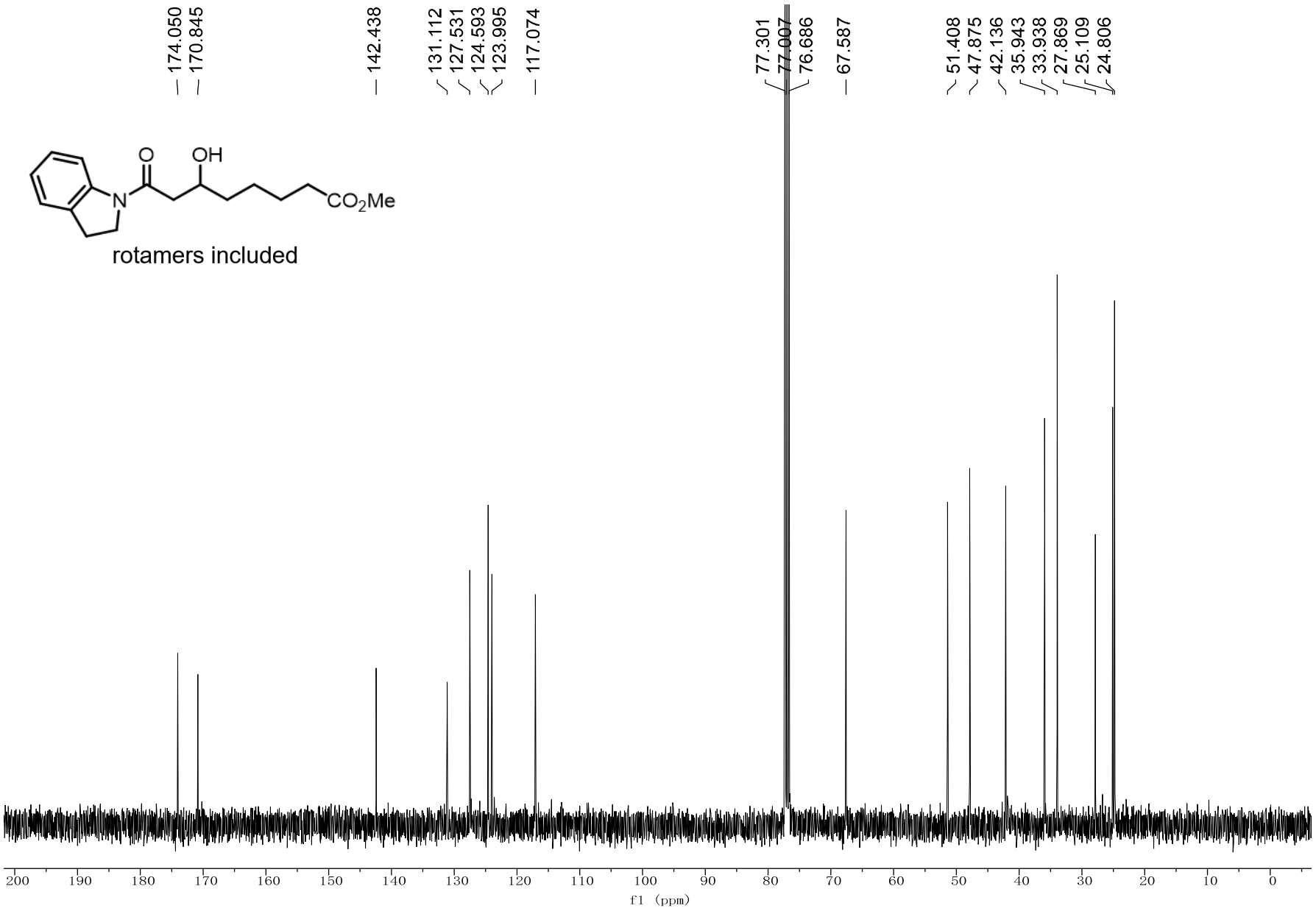
O
OH
N
Cl
rotamers included
f1 (ppm)



rotamers included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123.995
117.074
77.301
77.007
76.686
67.587
51.408
47.875
42.136
35.943
33.938
27.869
25.109
24.806
O
OH
N
CO2Me
rotamers included
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

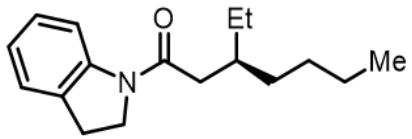


Figure 2A, entry 1

rotamers included

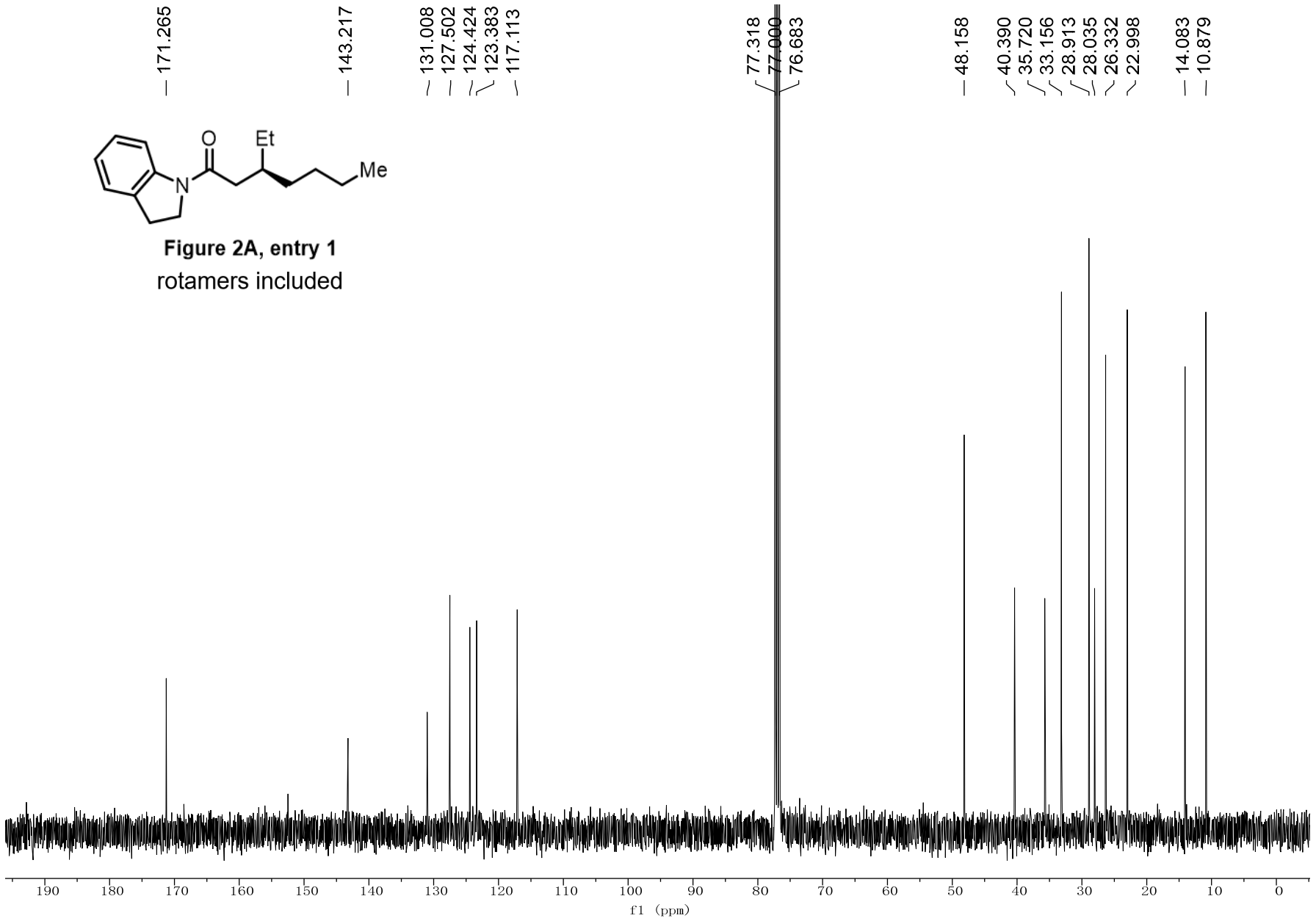


Figure 2A, entry 1
rotamers included

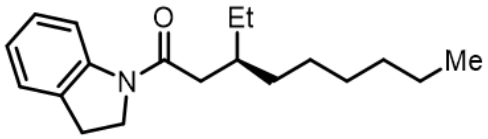


Figure 2A, entry 2
rotamers included

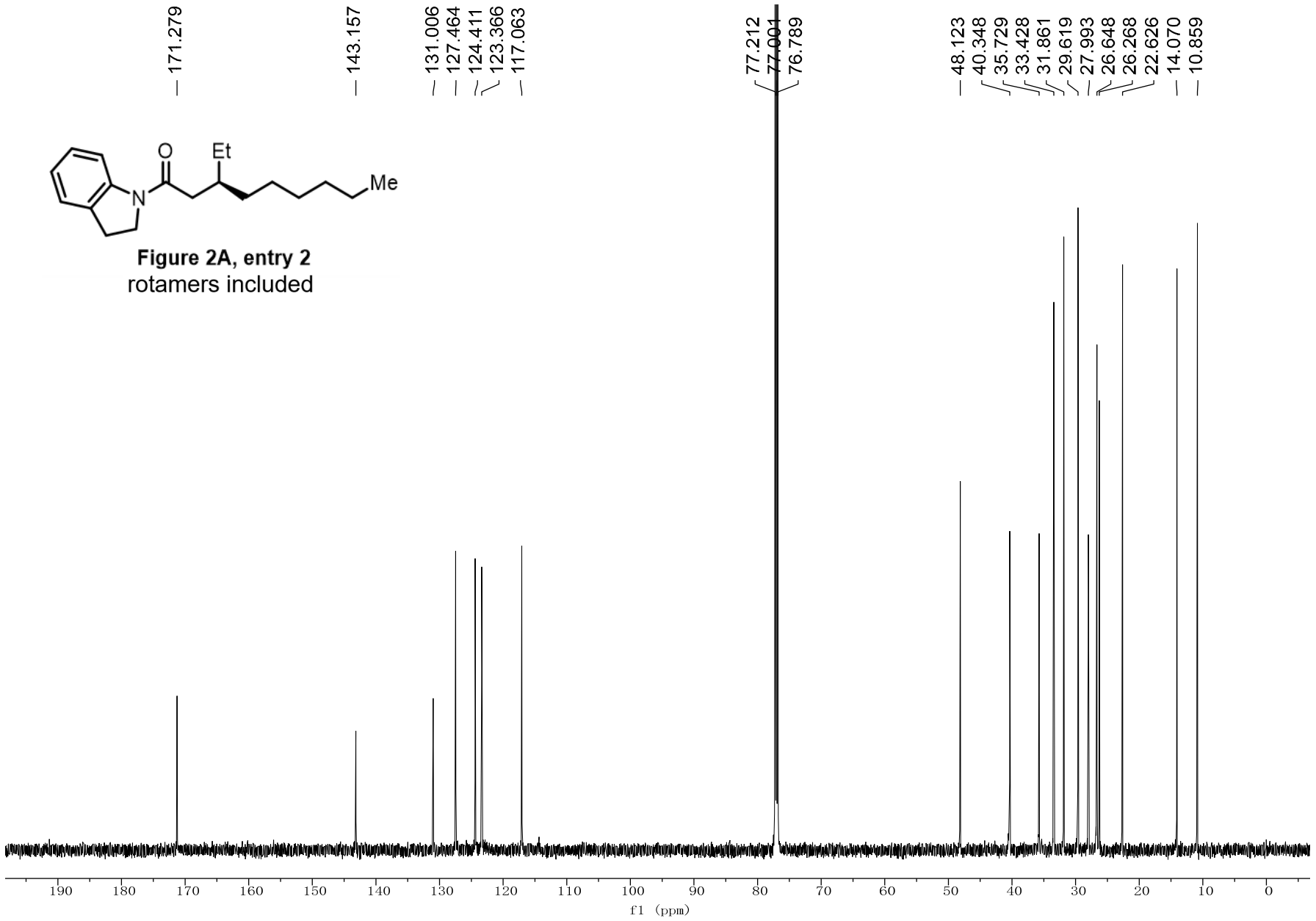


Figure 2A, entry 2
rotamers included

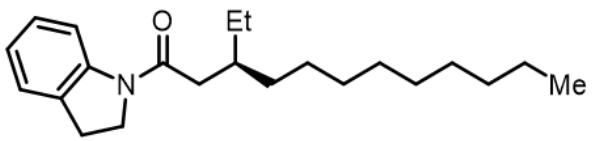


Figure 2A, entry 3
rotamers included

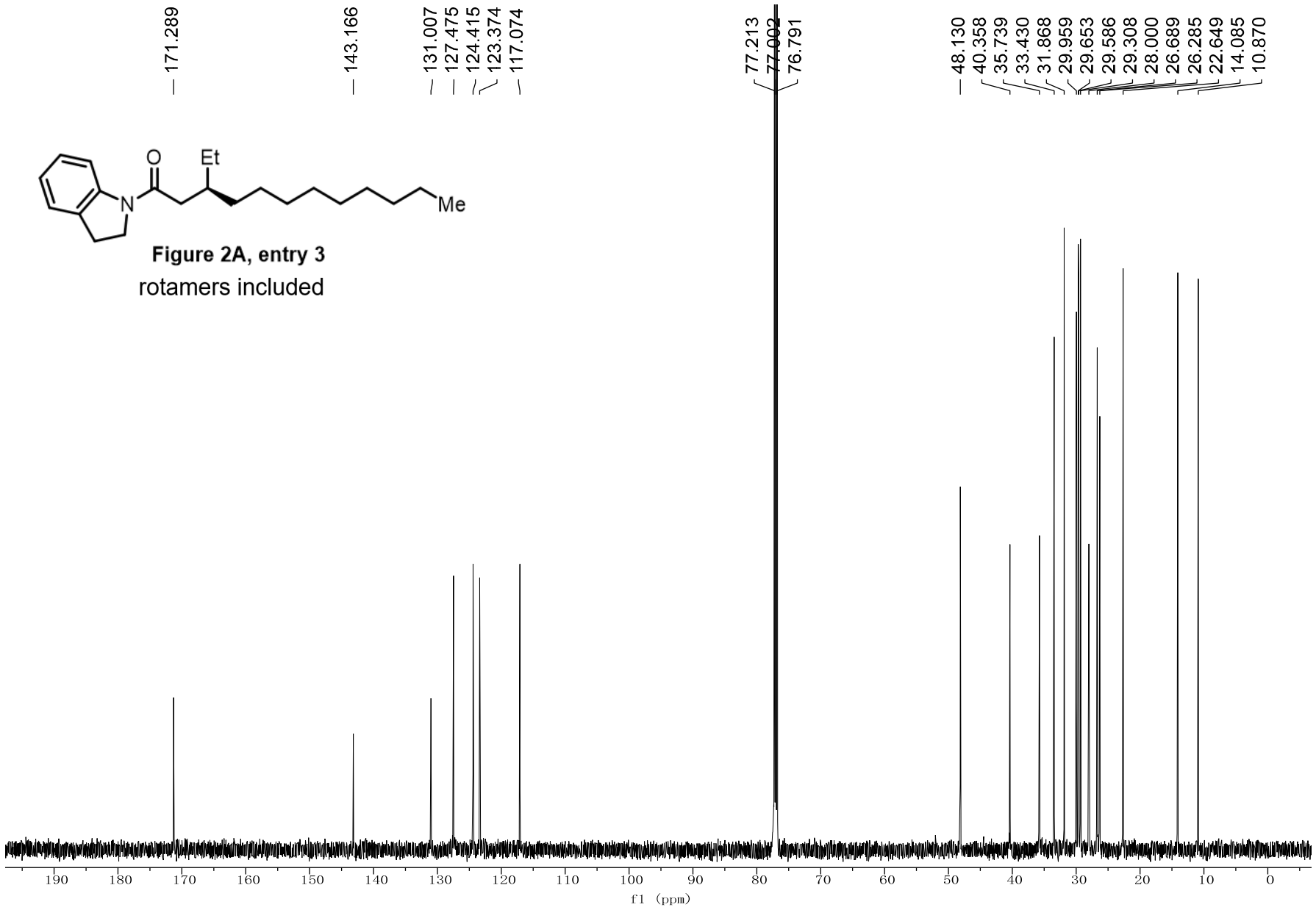


Figure 2A, entry 3

rotamers included

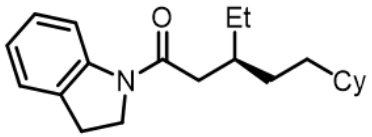


Figure 2A, entry 4
rotamers included

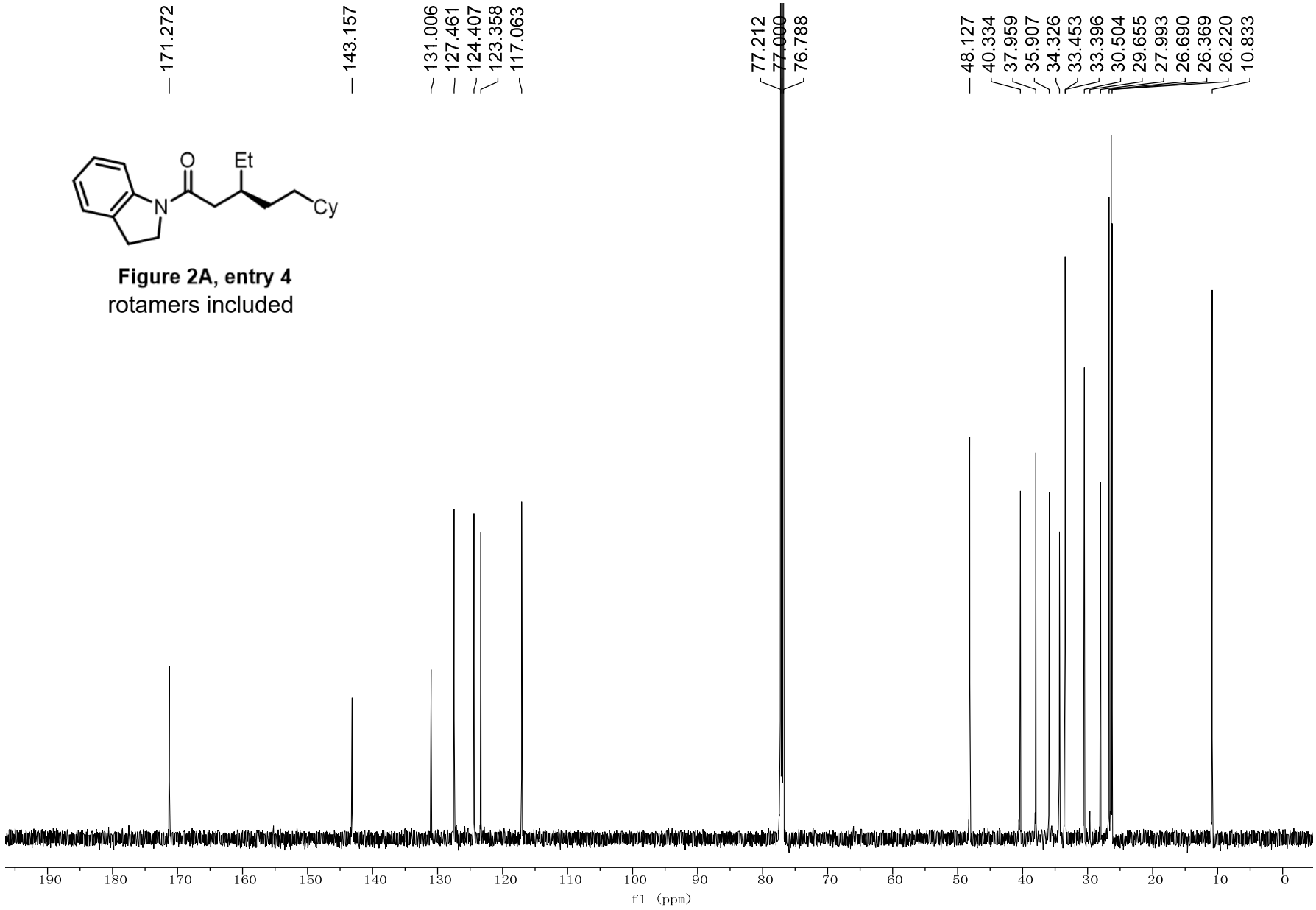


Figure 2A, entry 4
rotamers included

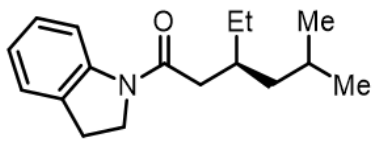


Figure 2A, entry 5
rotamers included

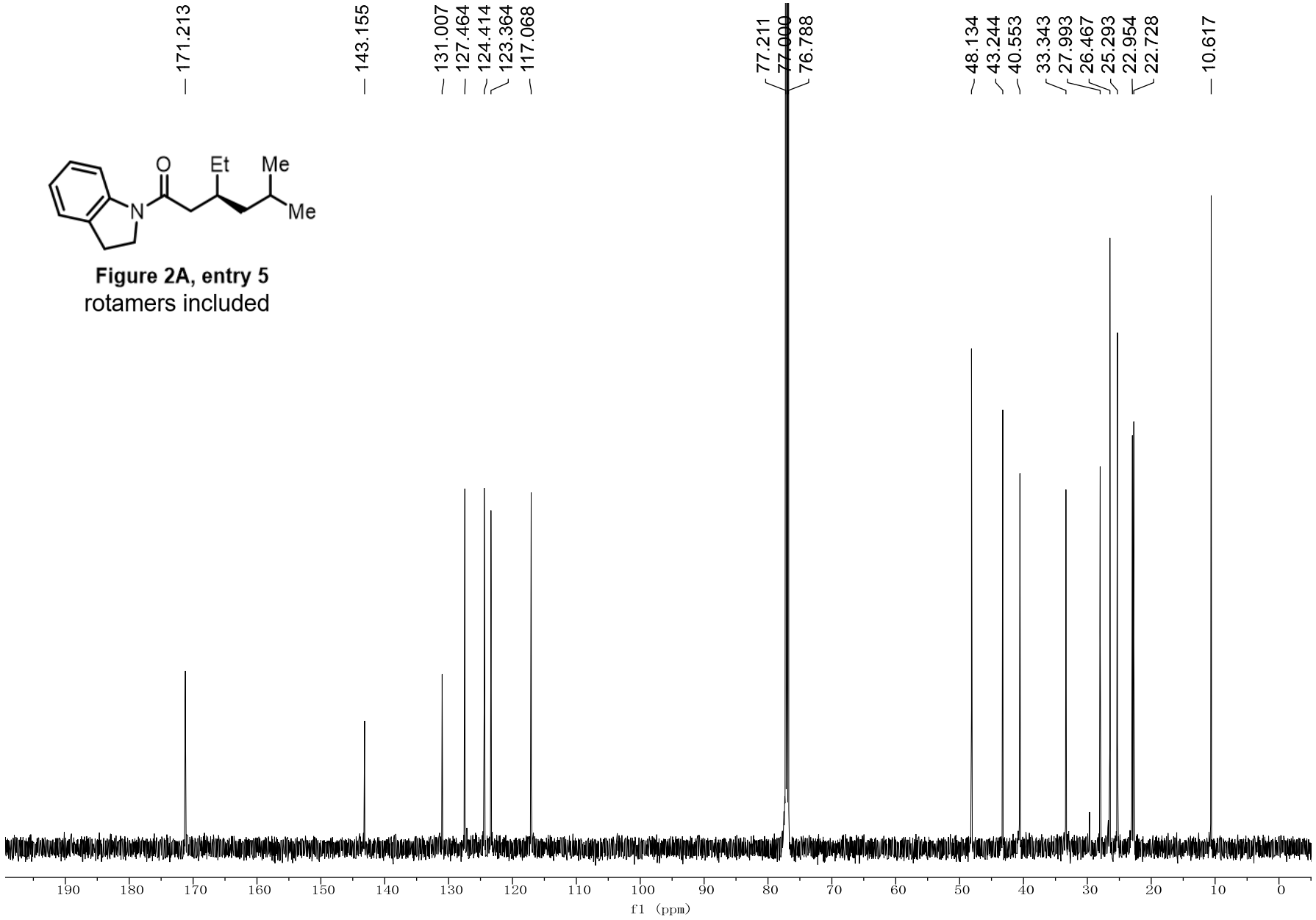


Figure 2A, entry 5
rotamers included

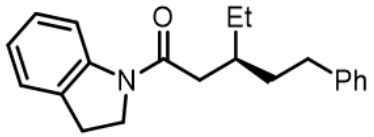


Figure 2A, entry 6
rotamers included

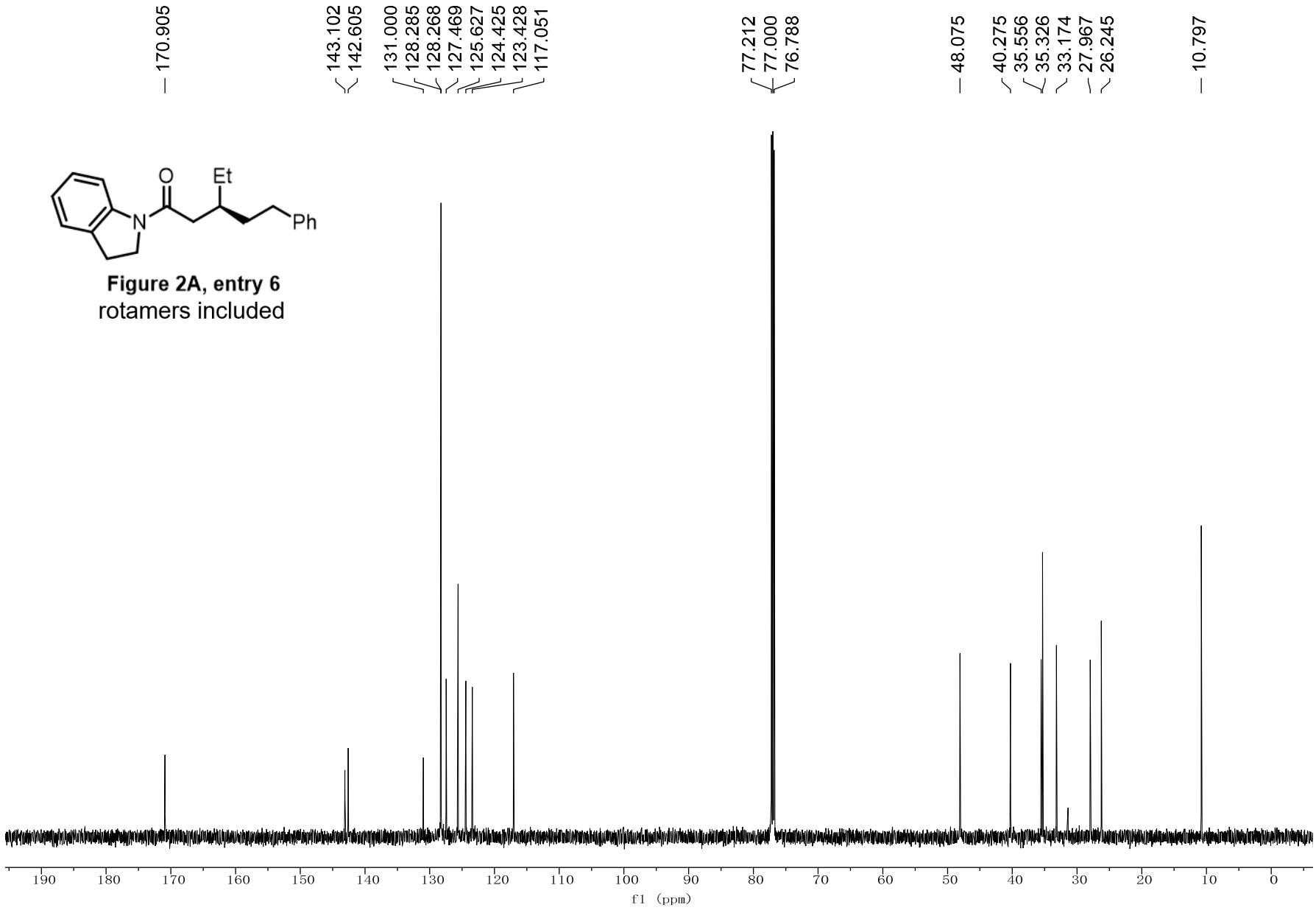


Figure 2A, entry 6
rotamers included

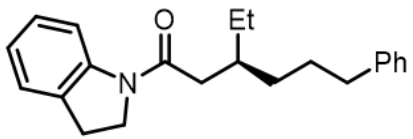
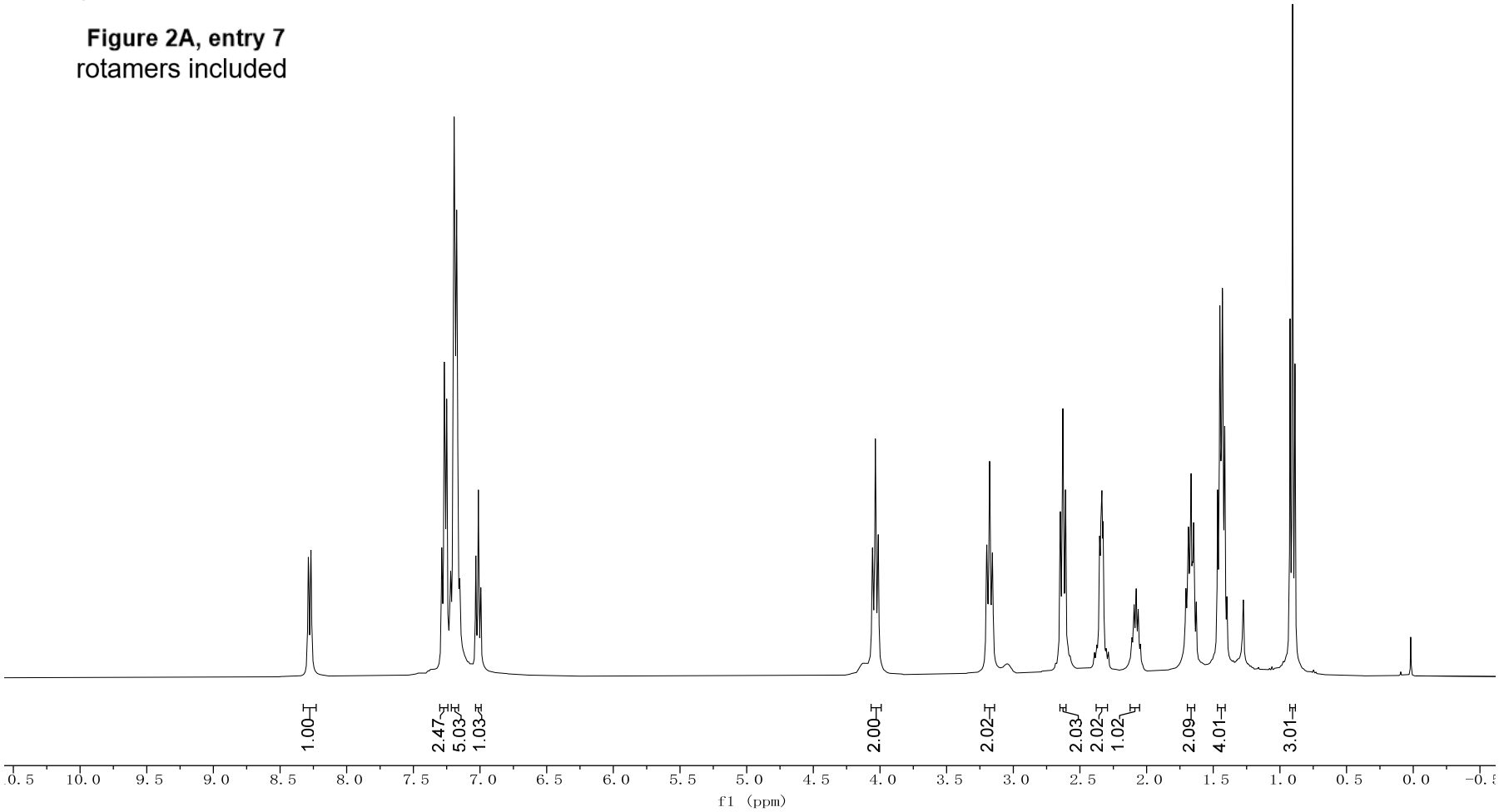


Figure 2A, entry 7
rotamers included



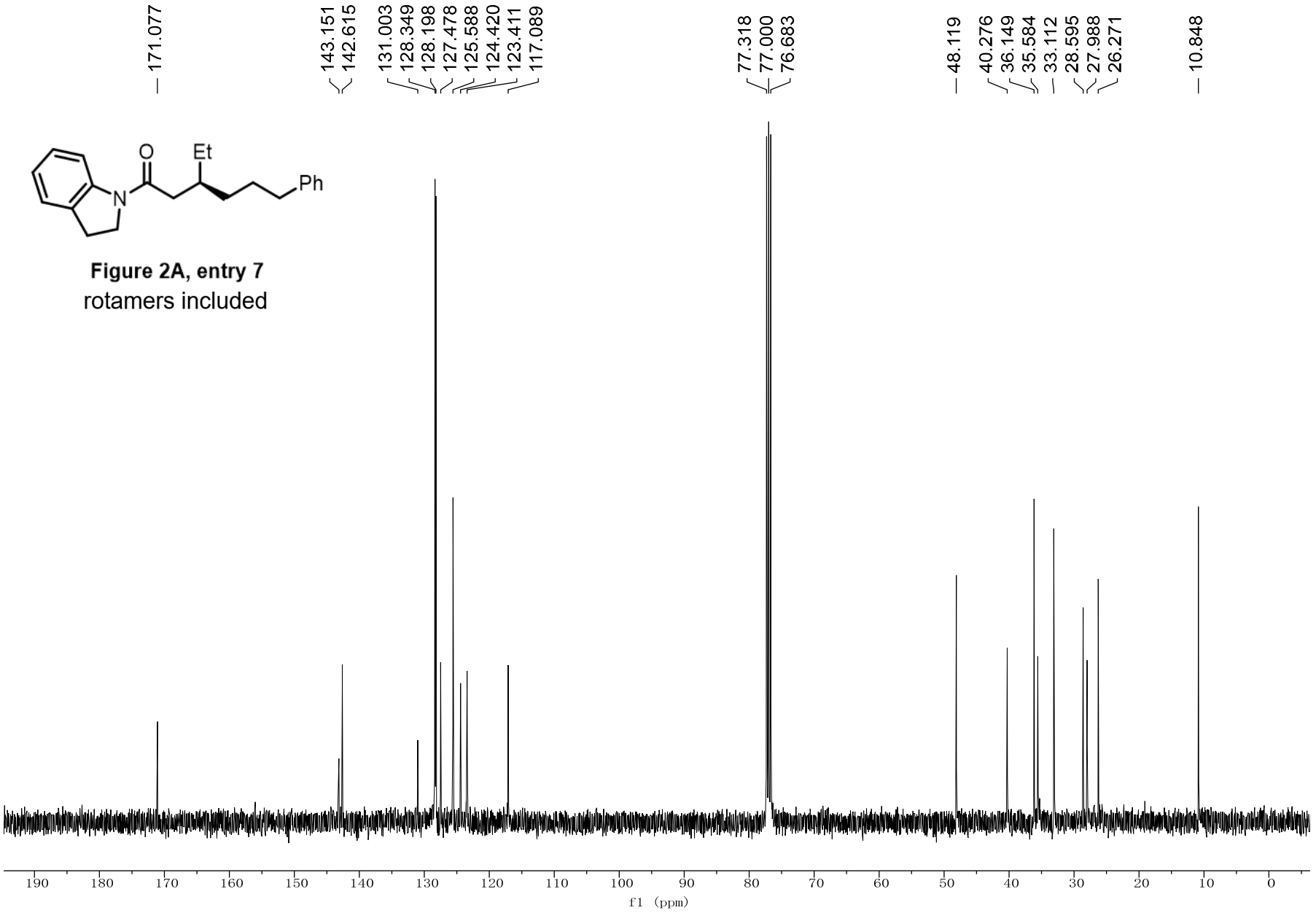


Figure 2A, entry 7
rotamers included

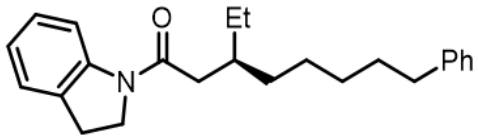
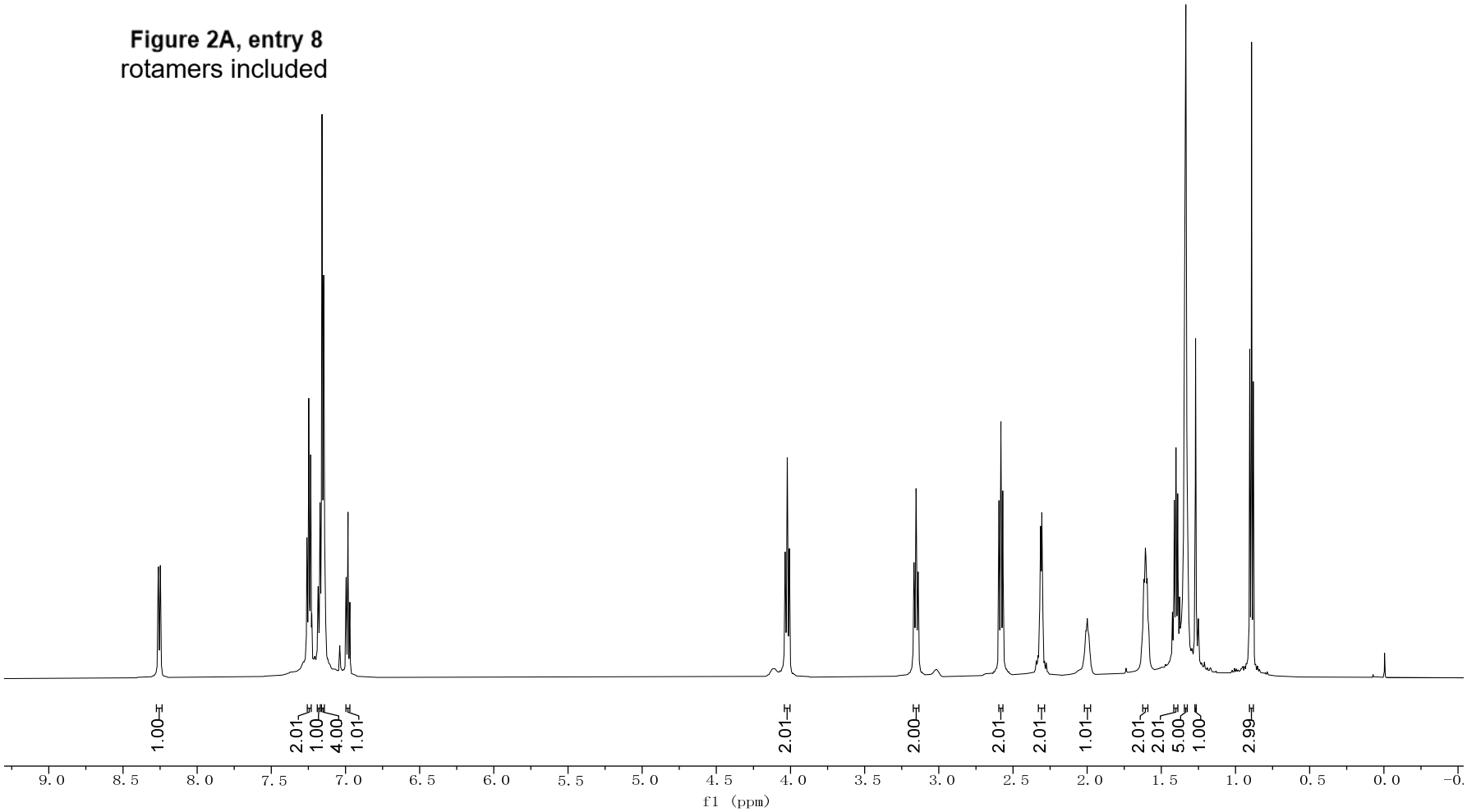


Figure 2A, entry 8
rotamers included



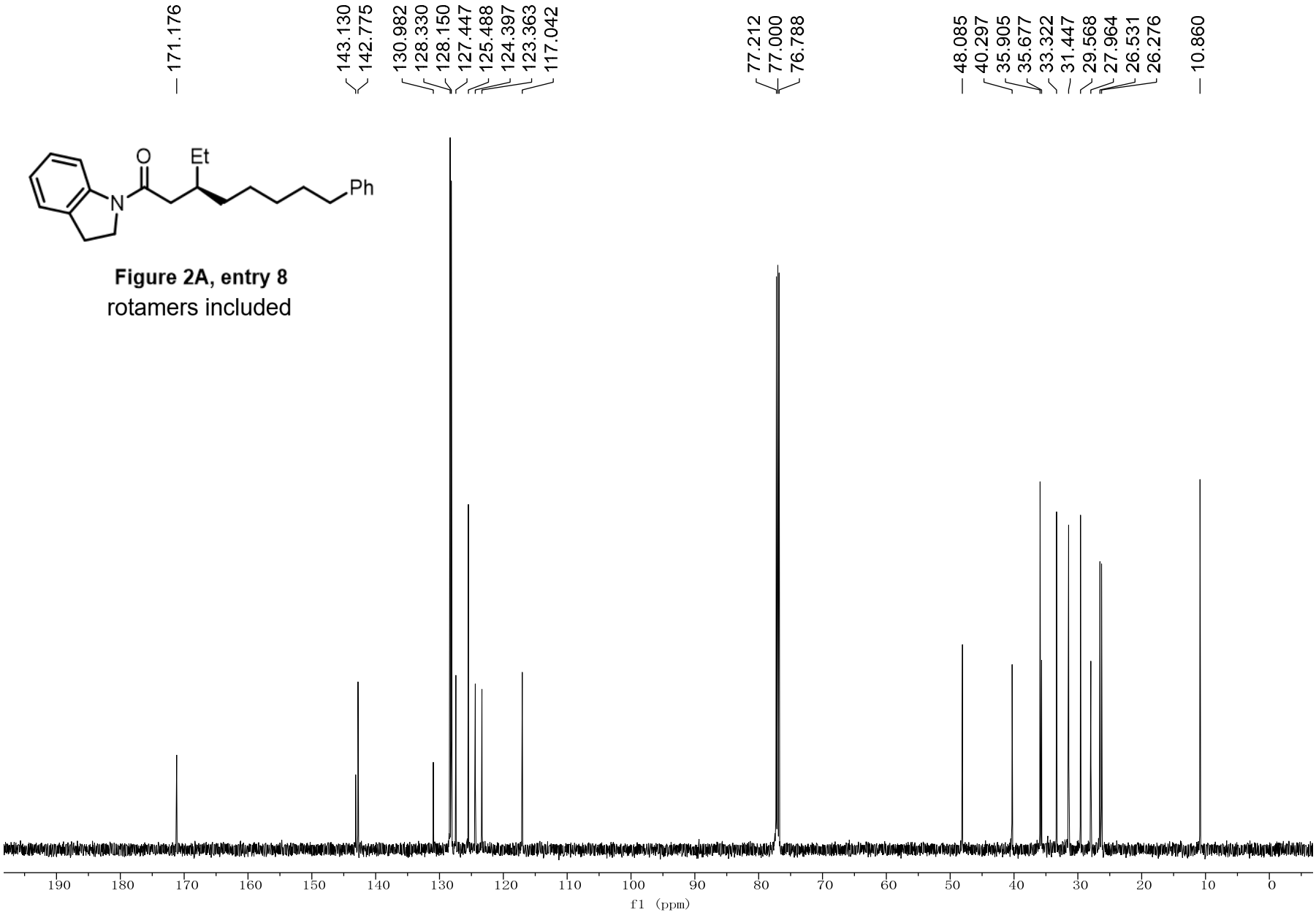


Figure 2A, entry 8
rotamers included

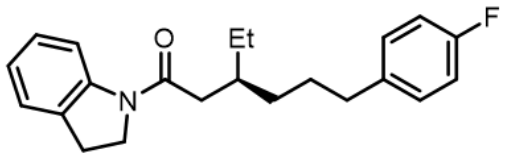


Figure 2A, entry 9
rotamers included

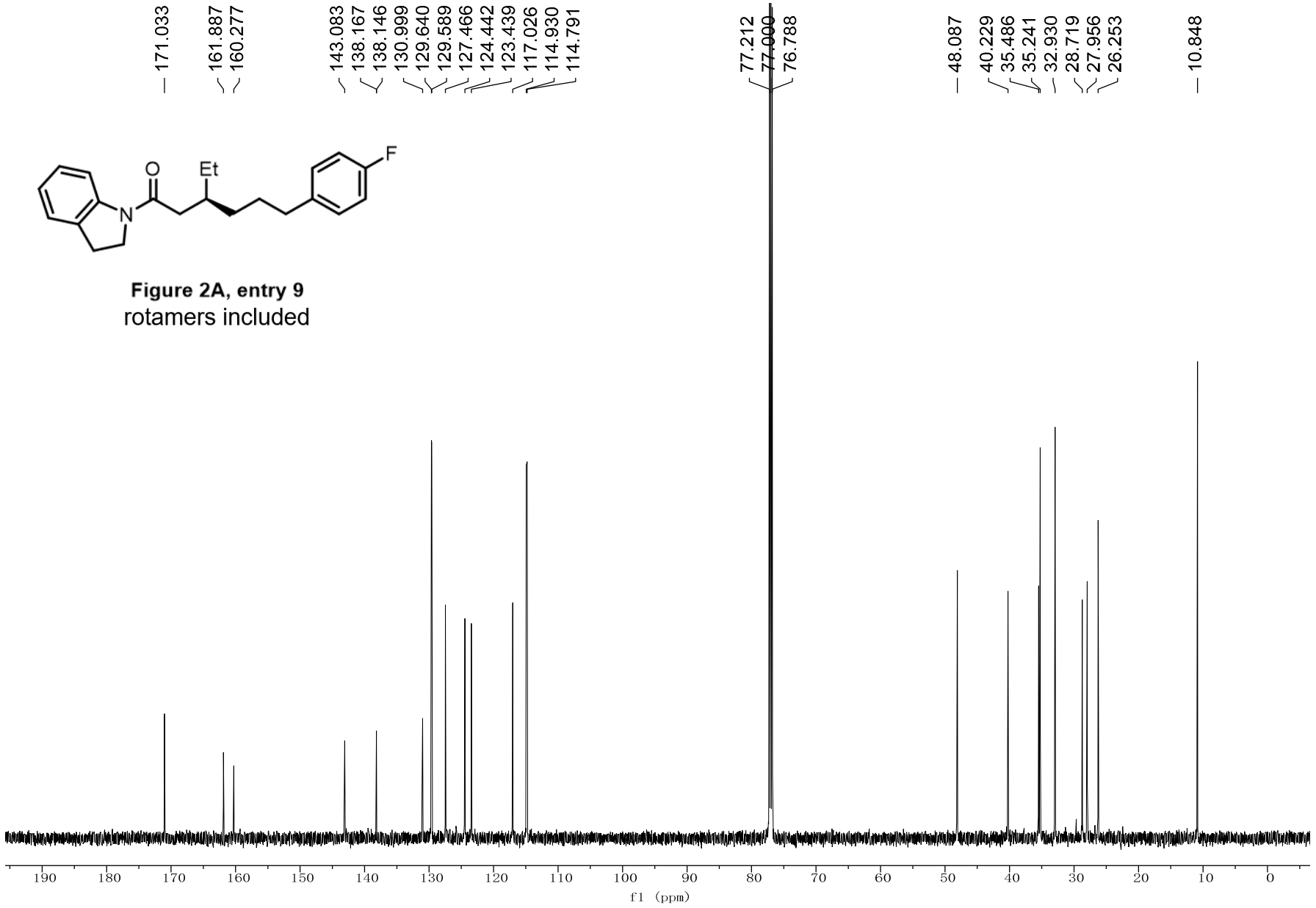


Figure 2A, entry 9
rotamers included

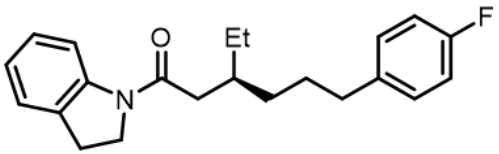


Figure 2A, entry 9
rotamers included

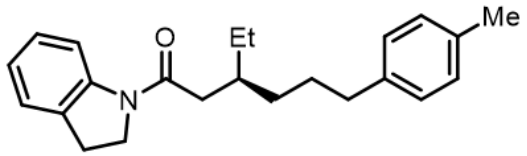


Figure 2A, entry 10
rotamers included

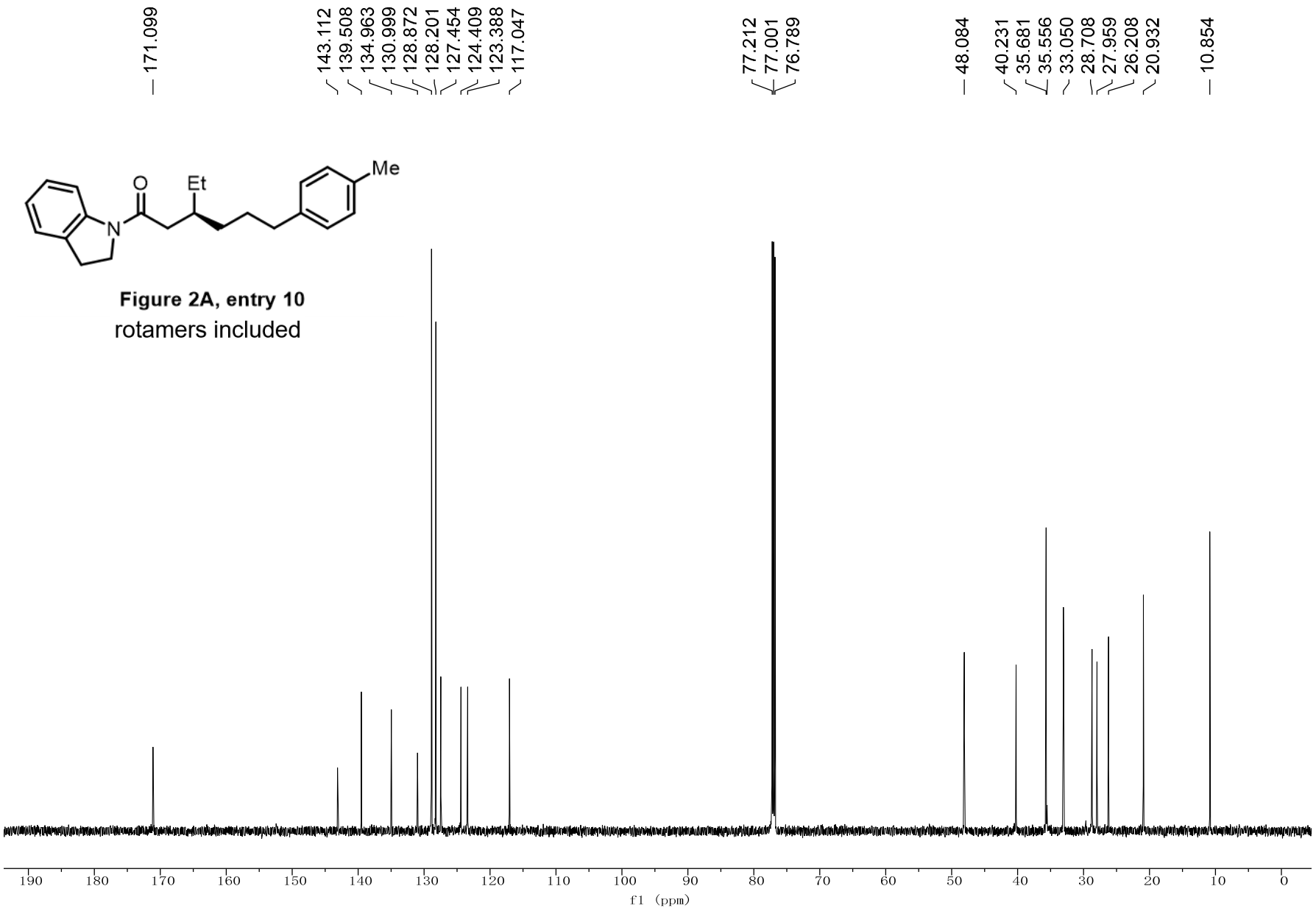


Figure 2A, entry 10
rotamers included

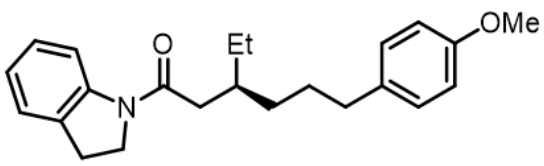


Figure 2A, entry 11
rotamers included

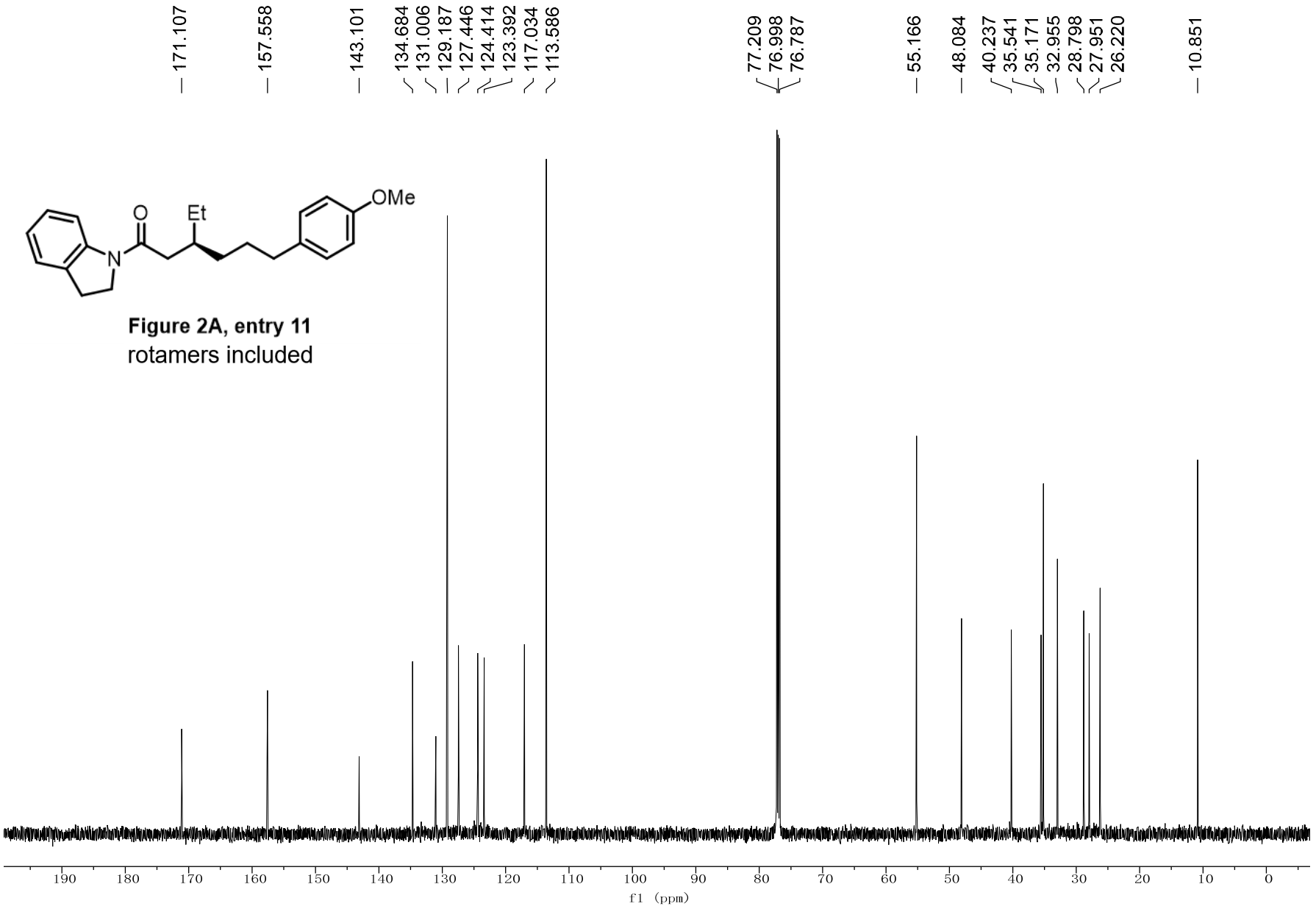


Figure 2A, entry 11
rotamers included

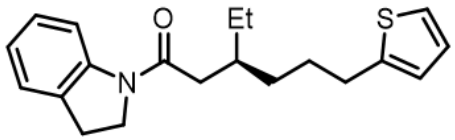


Figure 2A, entry 12
rotamers included

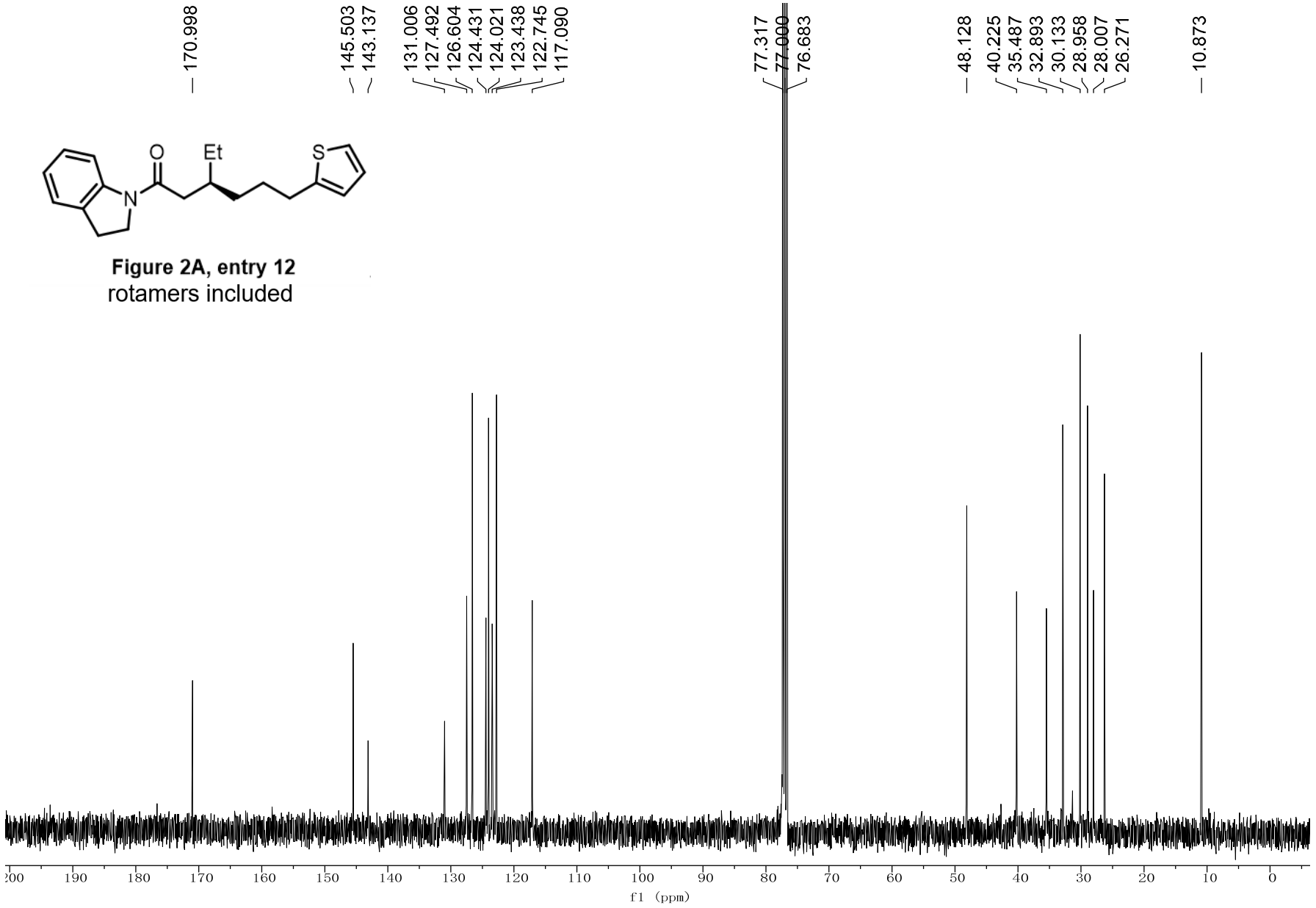


Figure 2A, entry 12
rotamers included

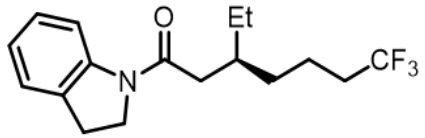
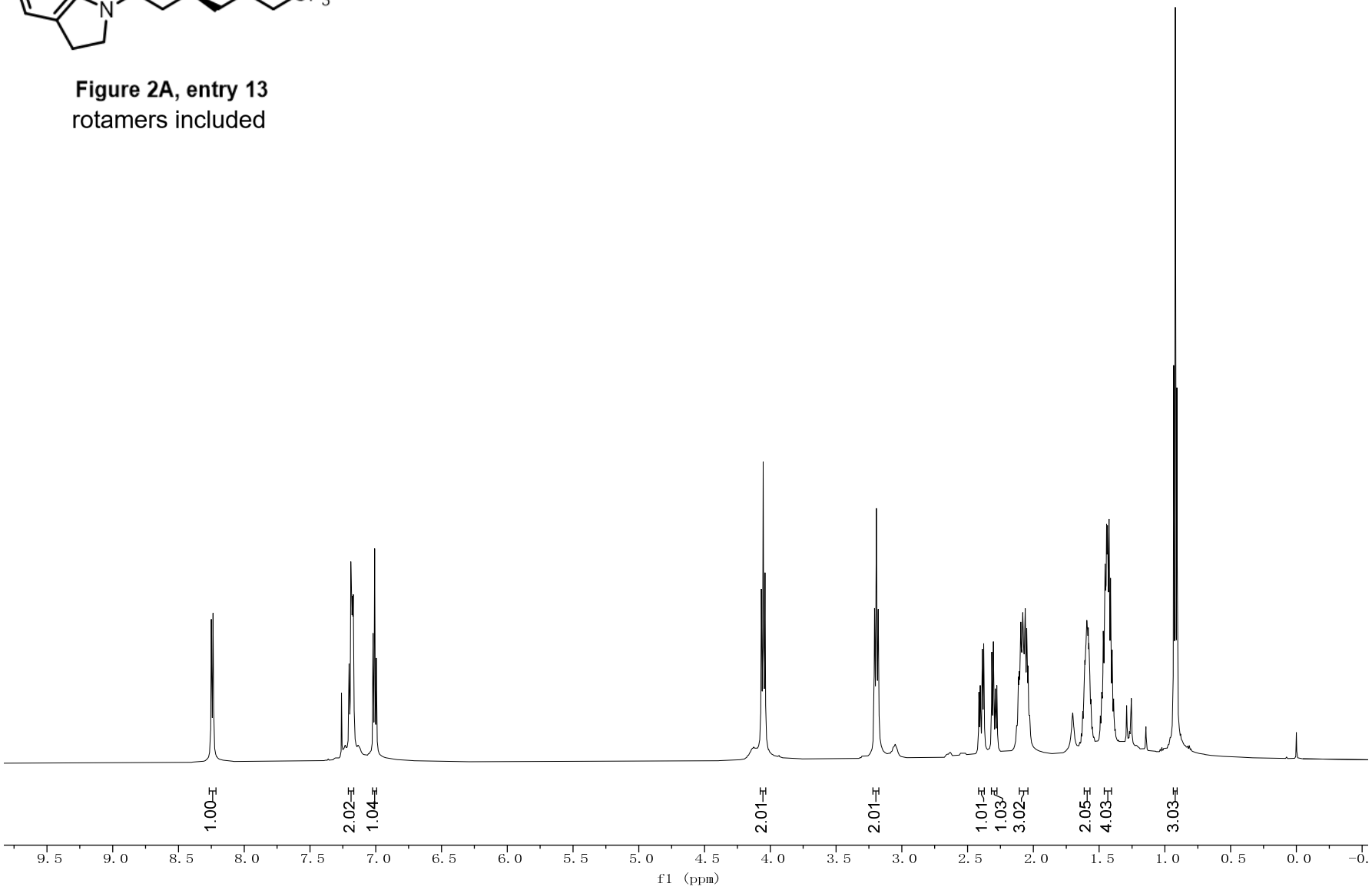


Figure 2A, entry 13
rotamers included



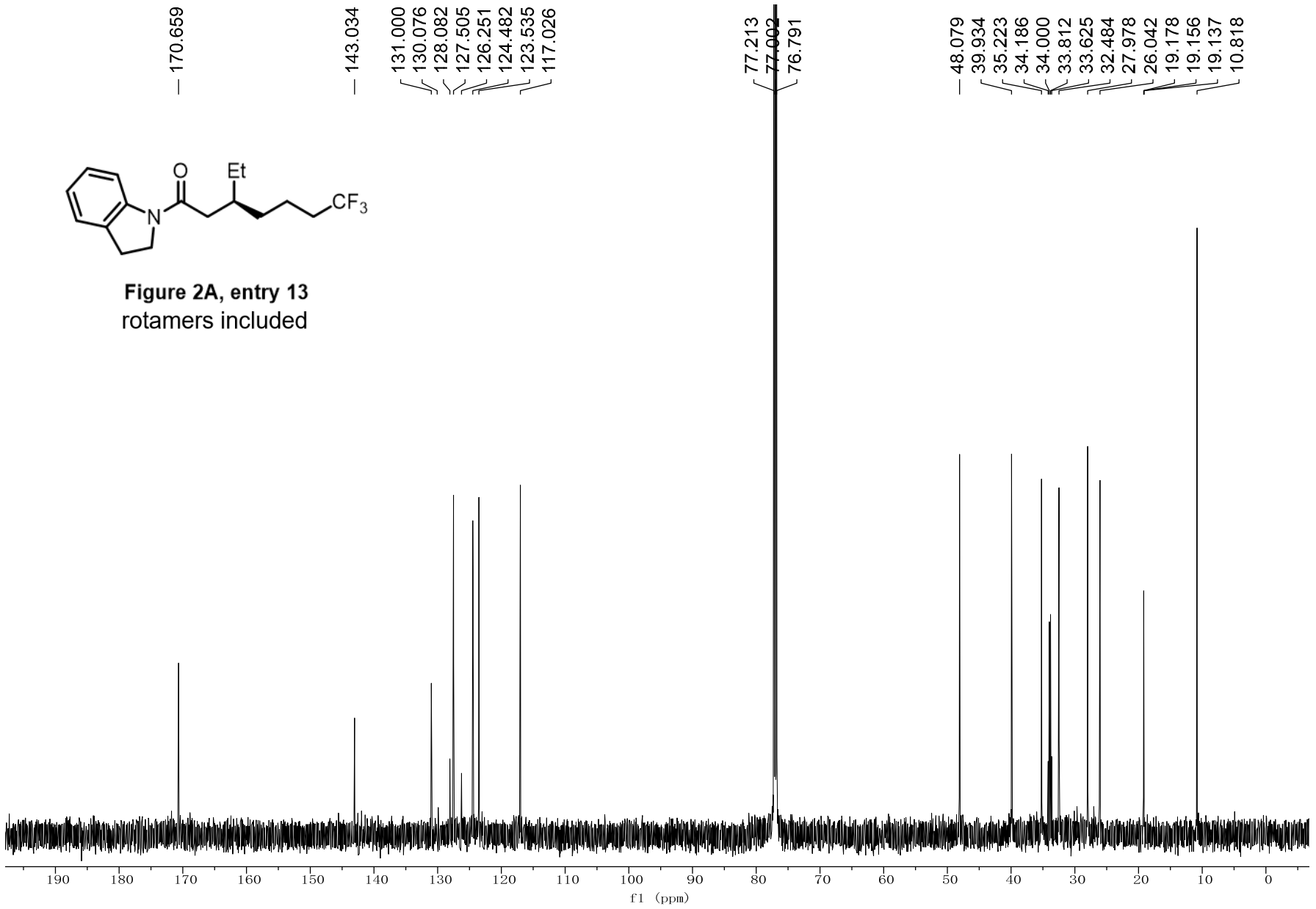
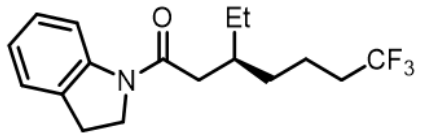
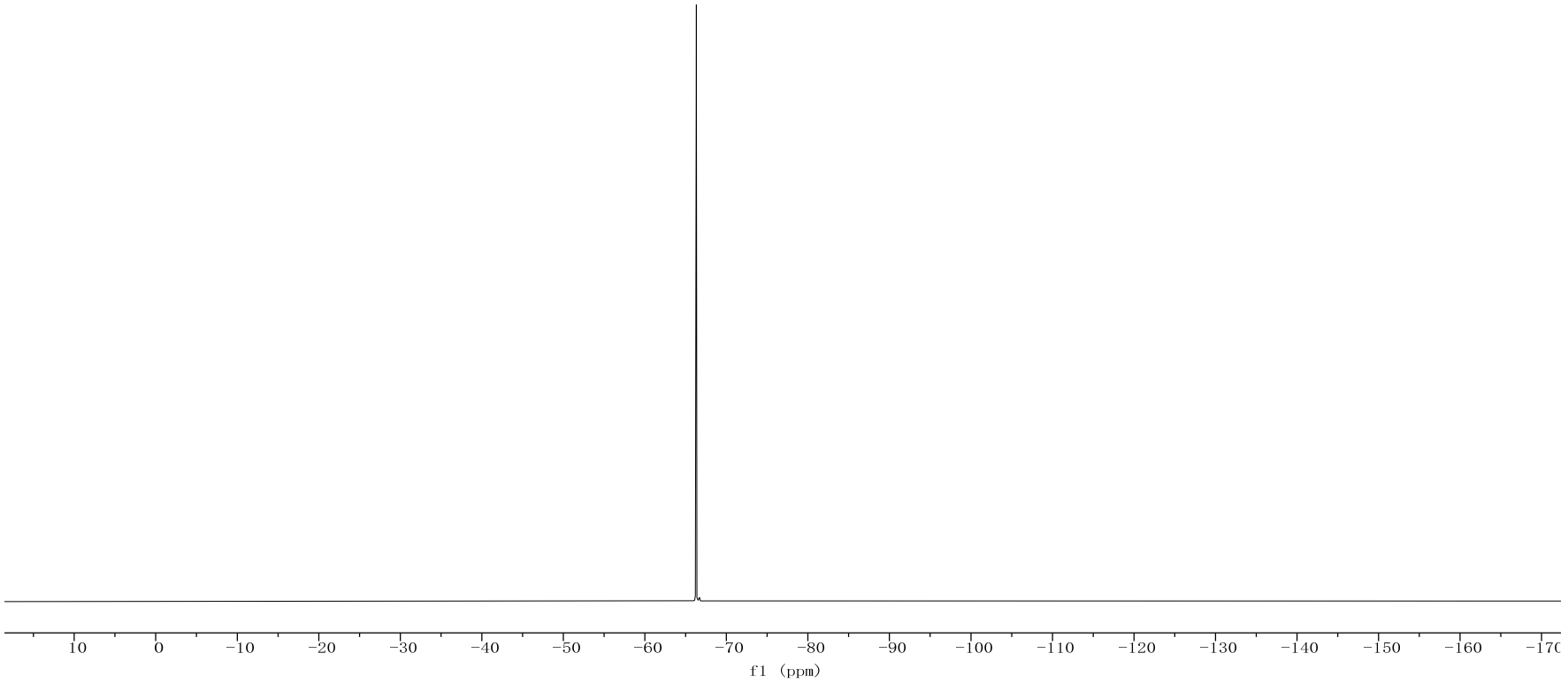


Figure 2A, entry 13
rotamers included



-66.321

Figure 2A, entry 13
rotamers included



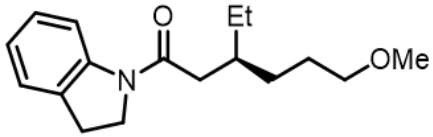
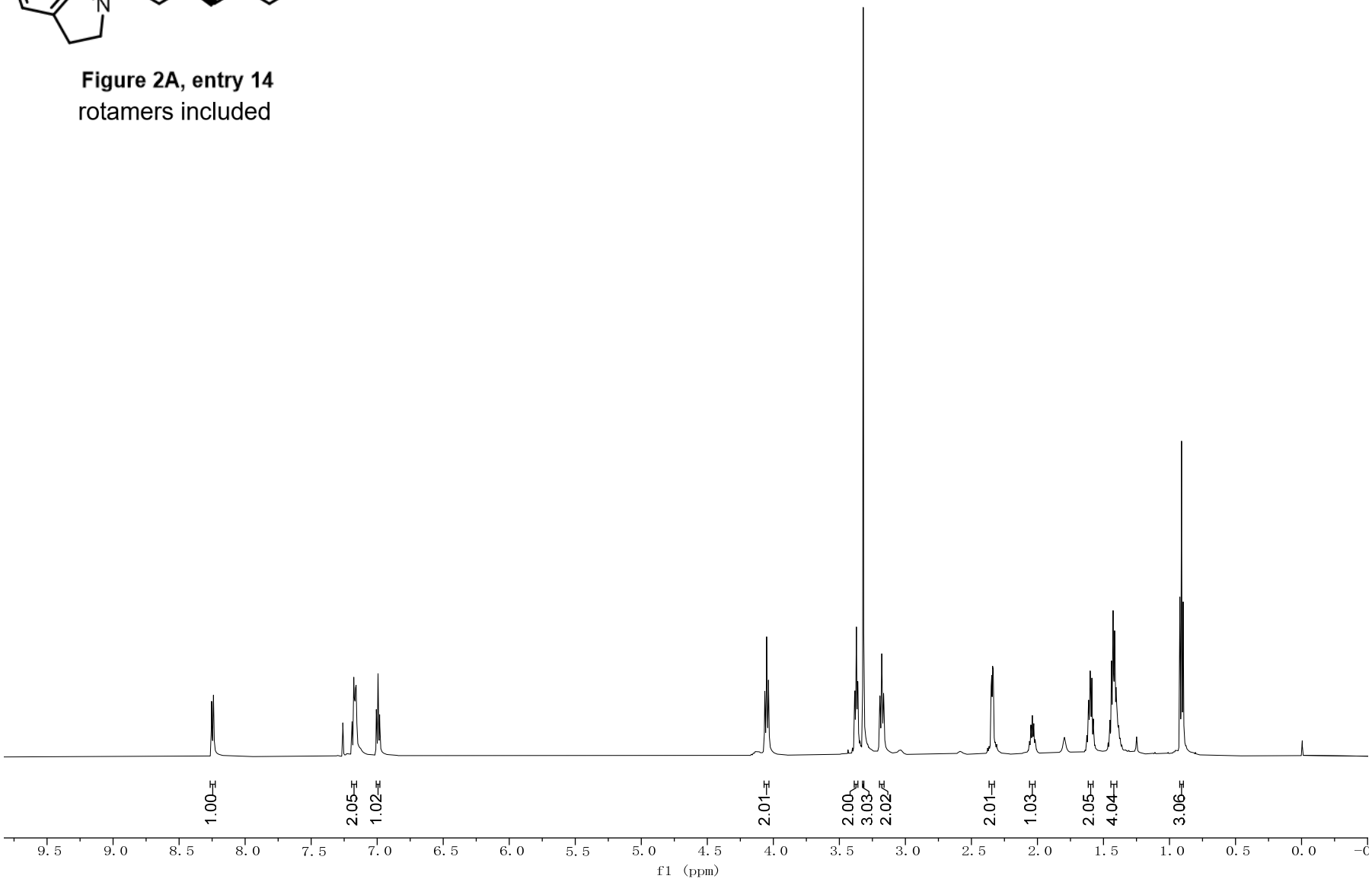


Figure 2A, entry 14
rotamers included



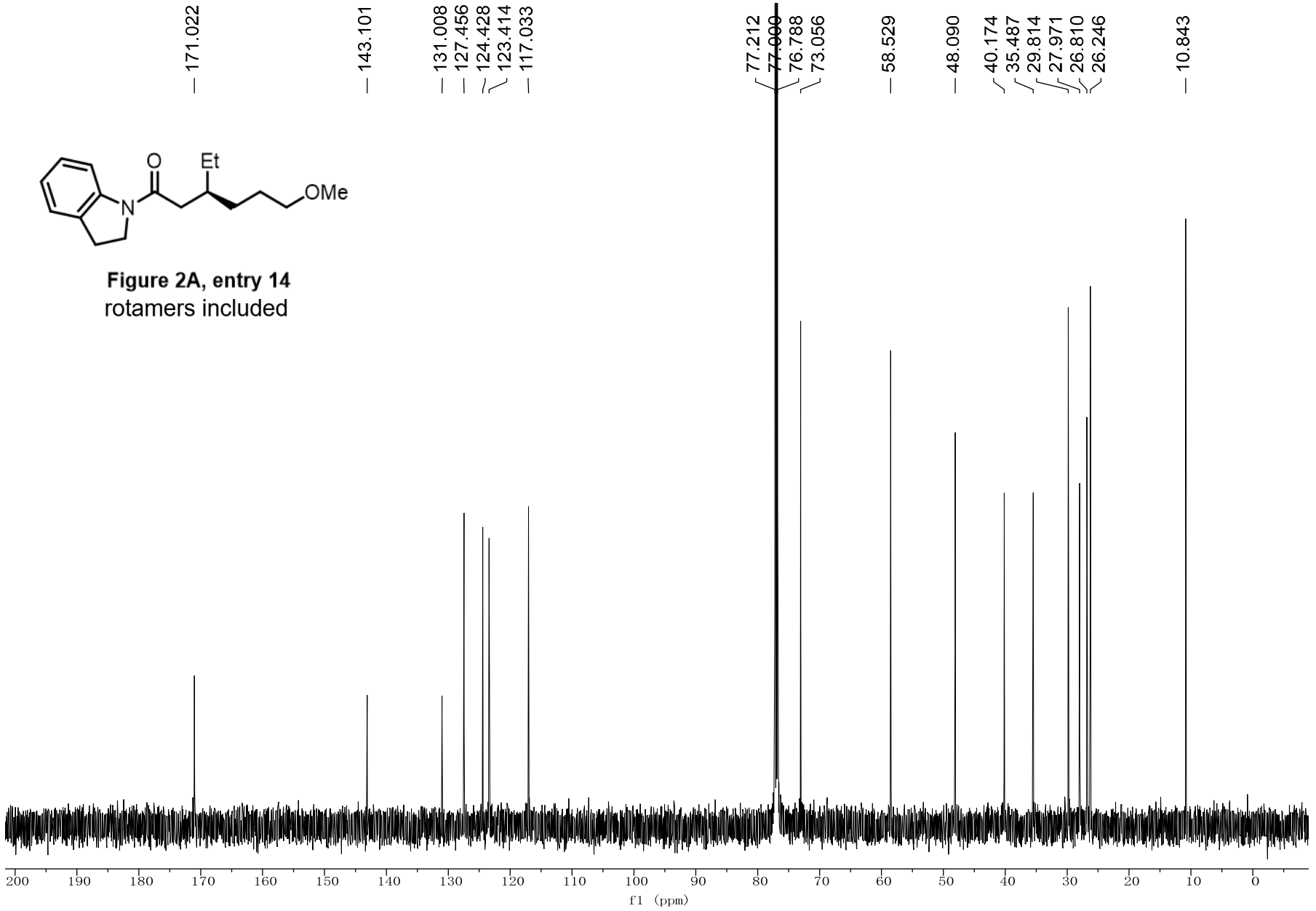


Figure 2A, entry 14
rotamers included

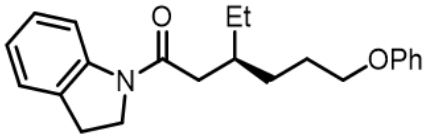


Figure 2A, entry 15
rotamers included

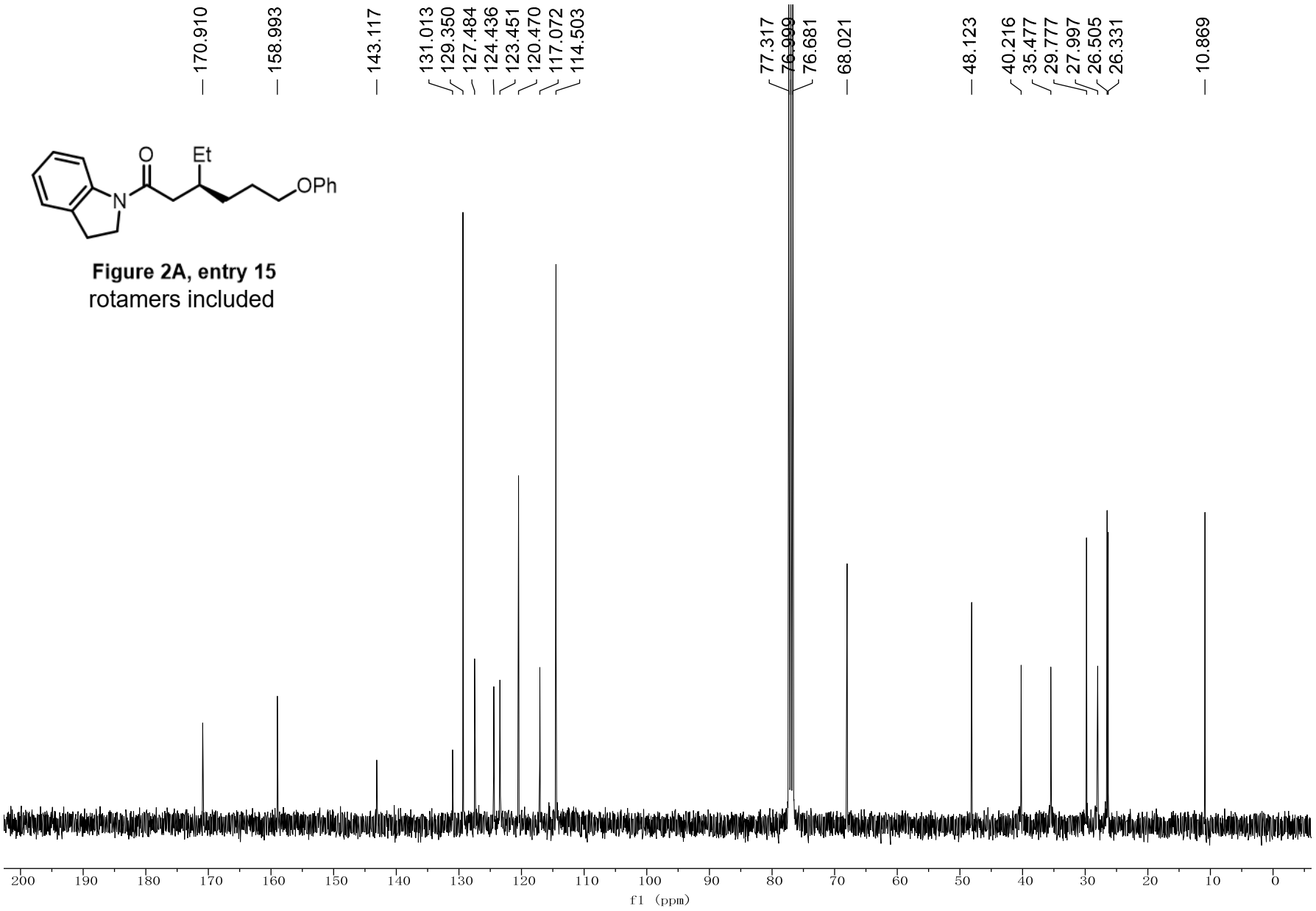


Figure 2A, entry 15
rotamers included

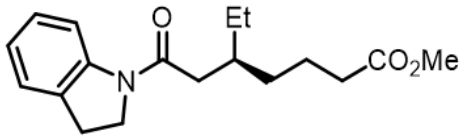
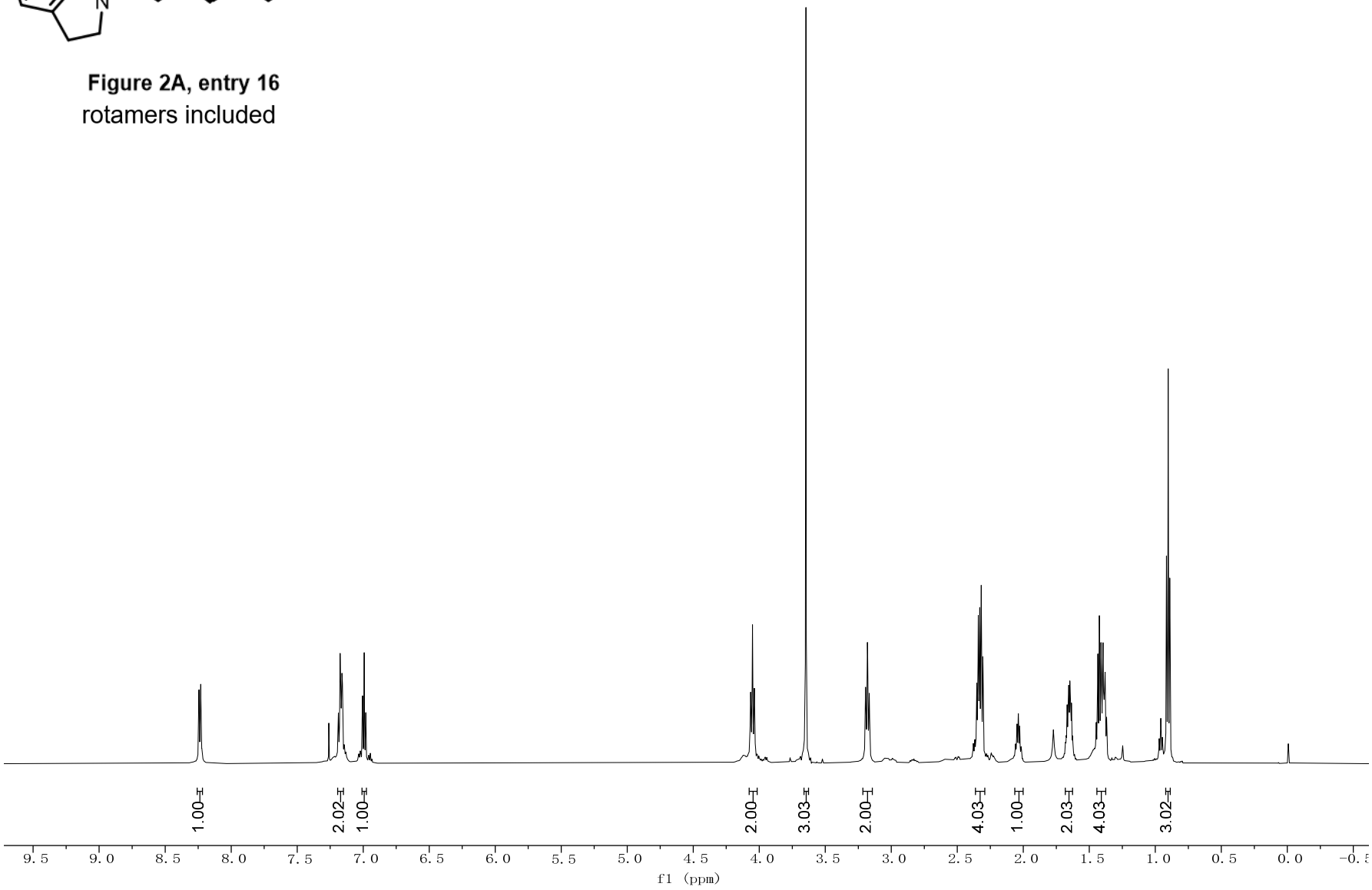


Figure 2A, entry 16
rotamers included



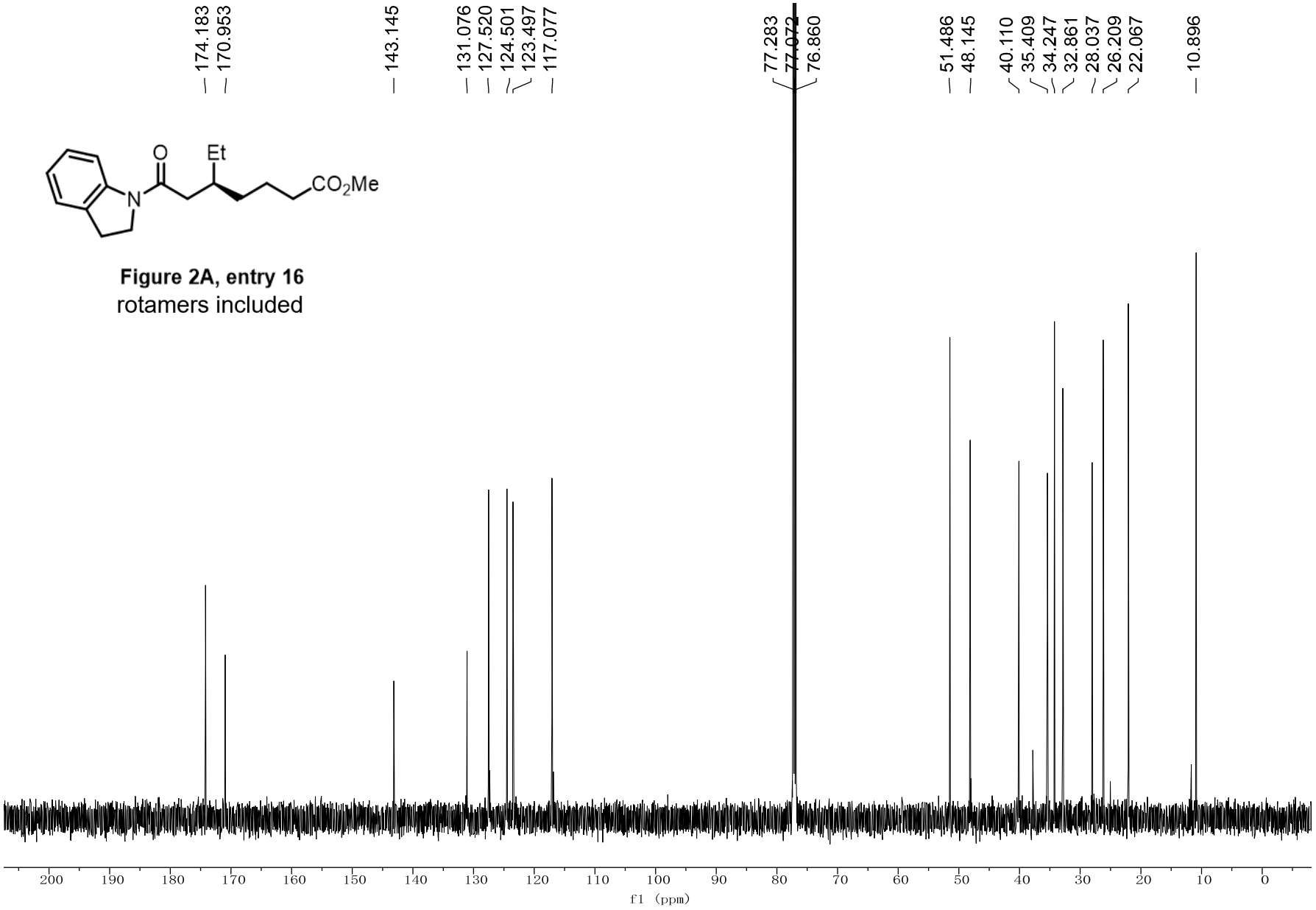


Figure 2A, entry 16
rotamers included

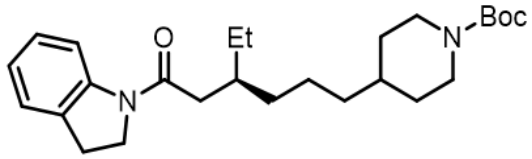
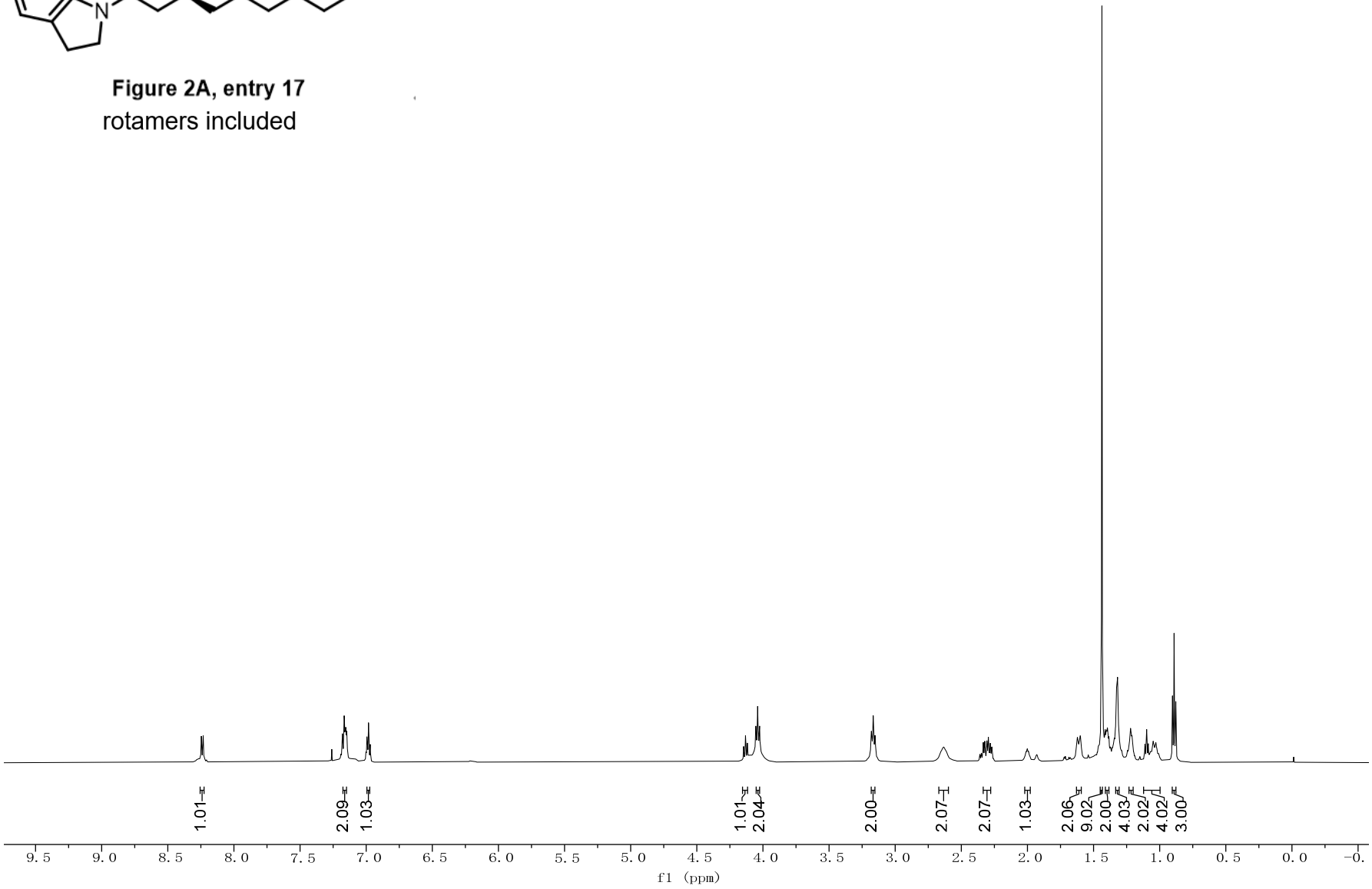


Figure 2A, entry 17
rotamers included



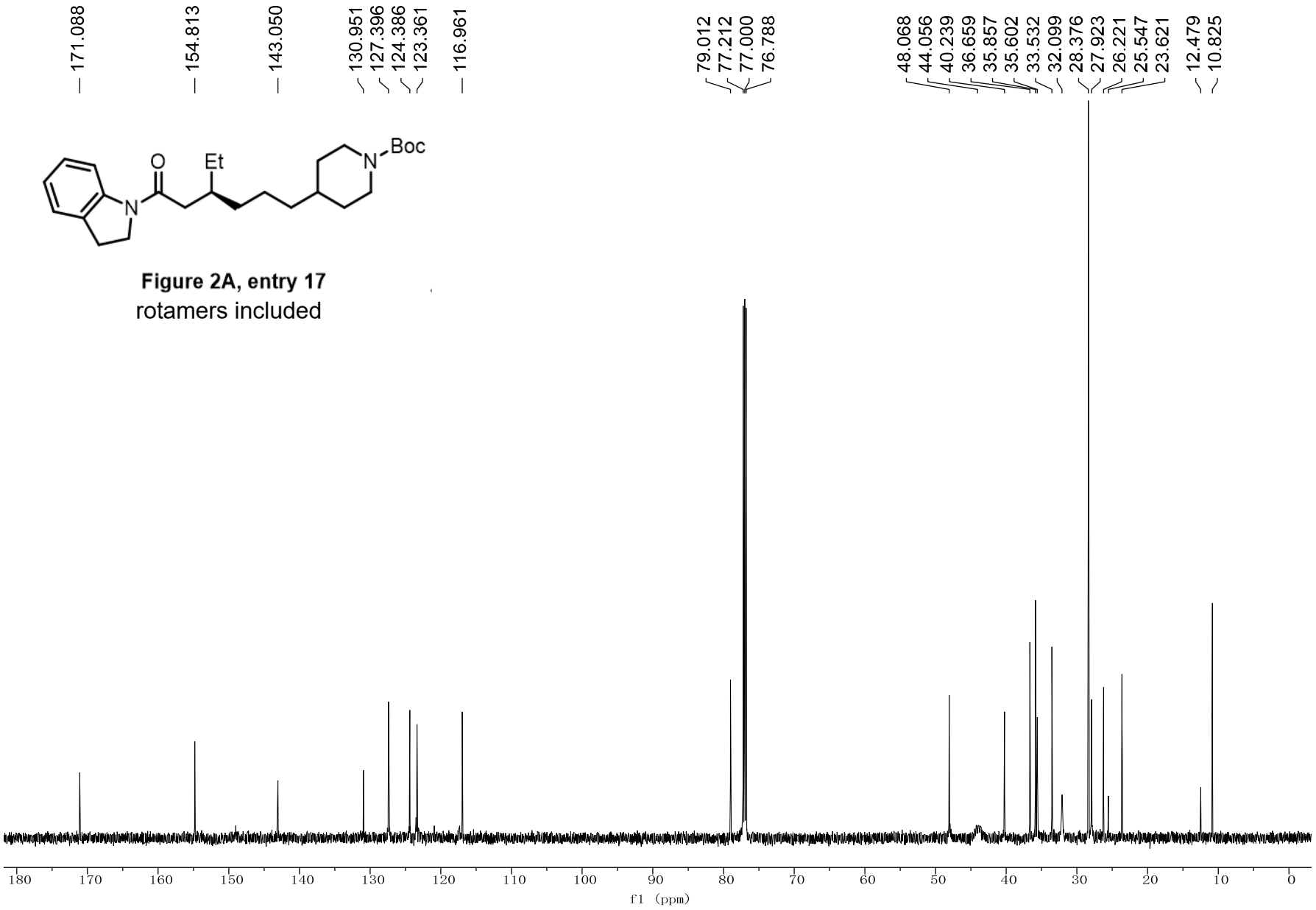


Figure 2A, entry 17
rotamers included

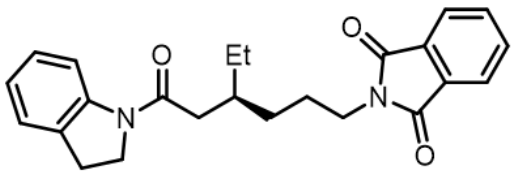


Figure 2A, entry 18
rotamers included

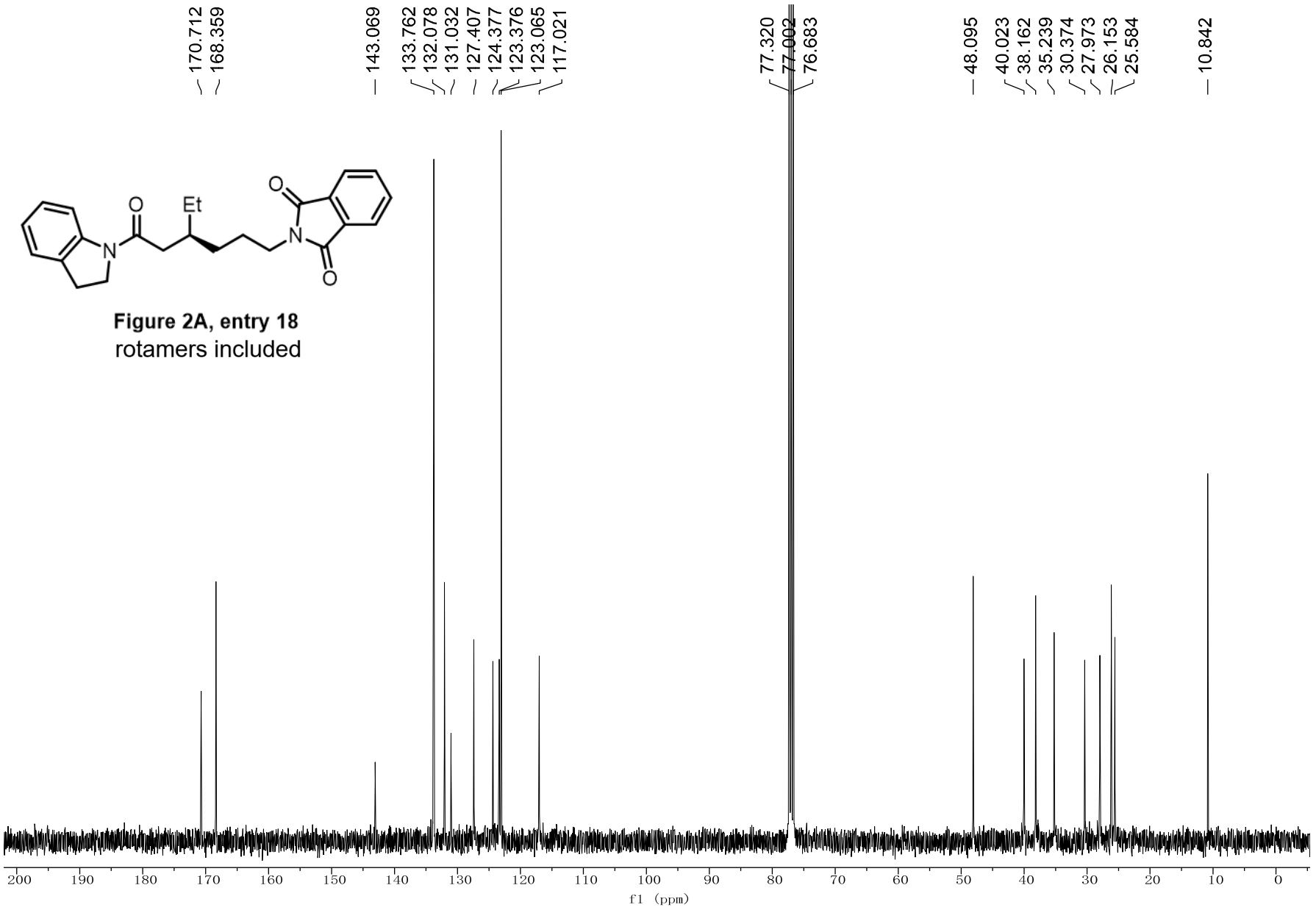


Figure 2A, entry 18
rotamers included

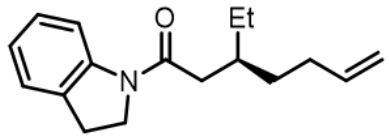
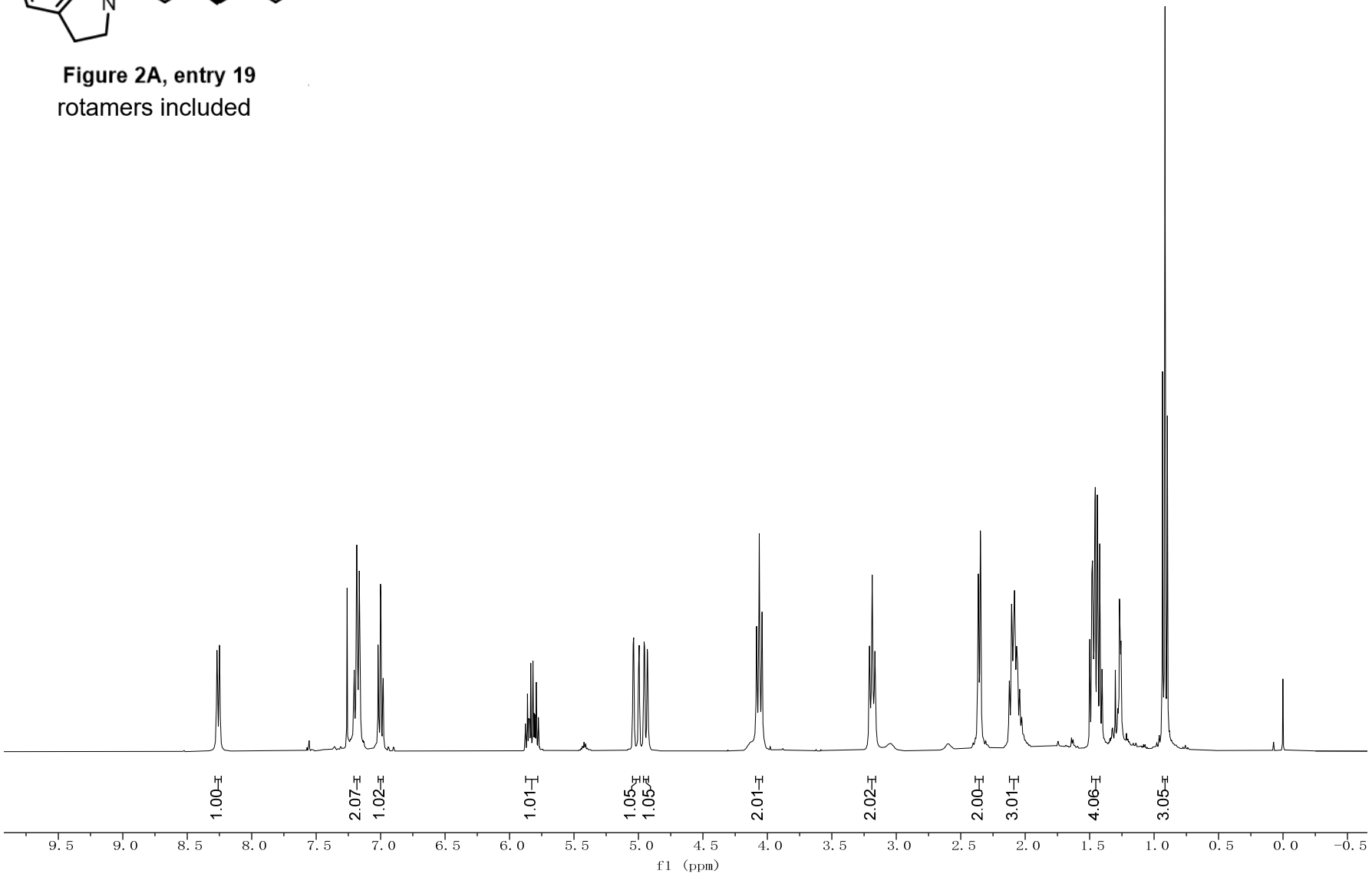


Figure 2A, entry 19
rotamers included



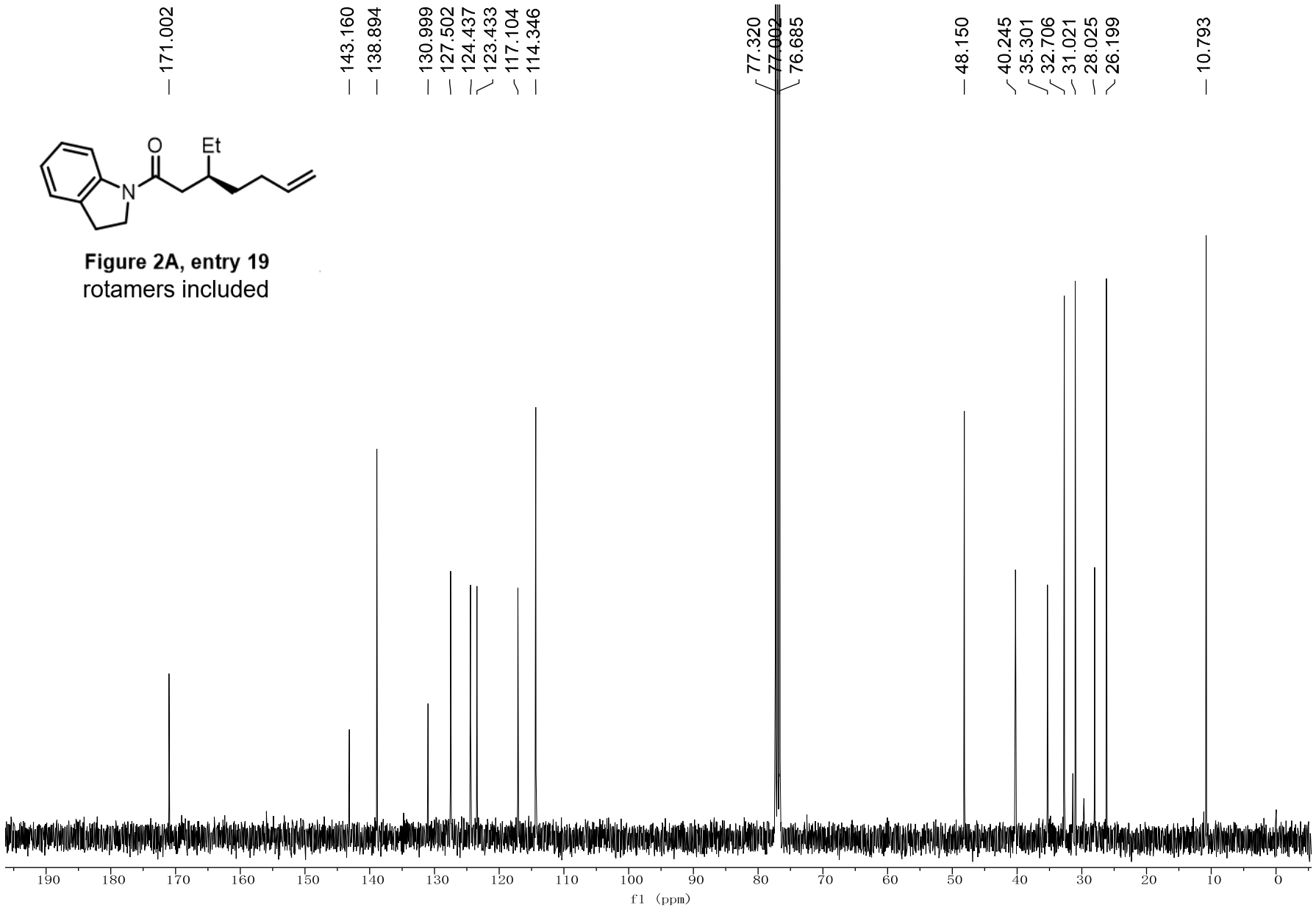


Figure 2A, entry 19
rotamers included

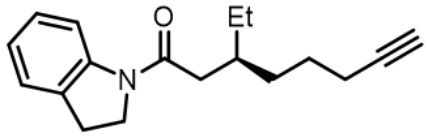
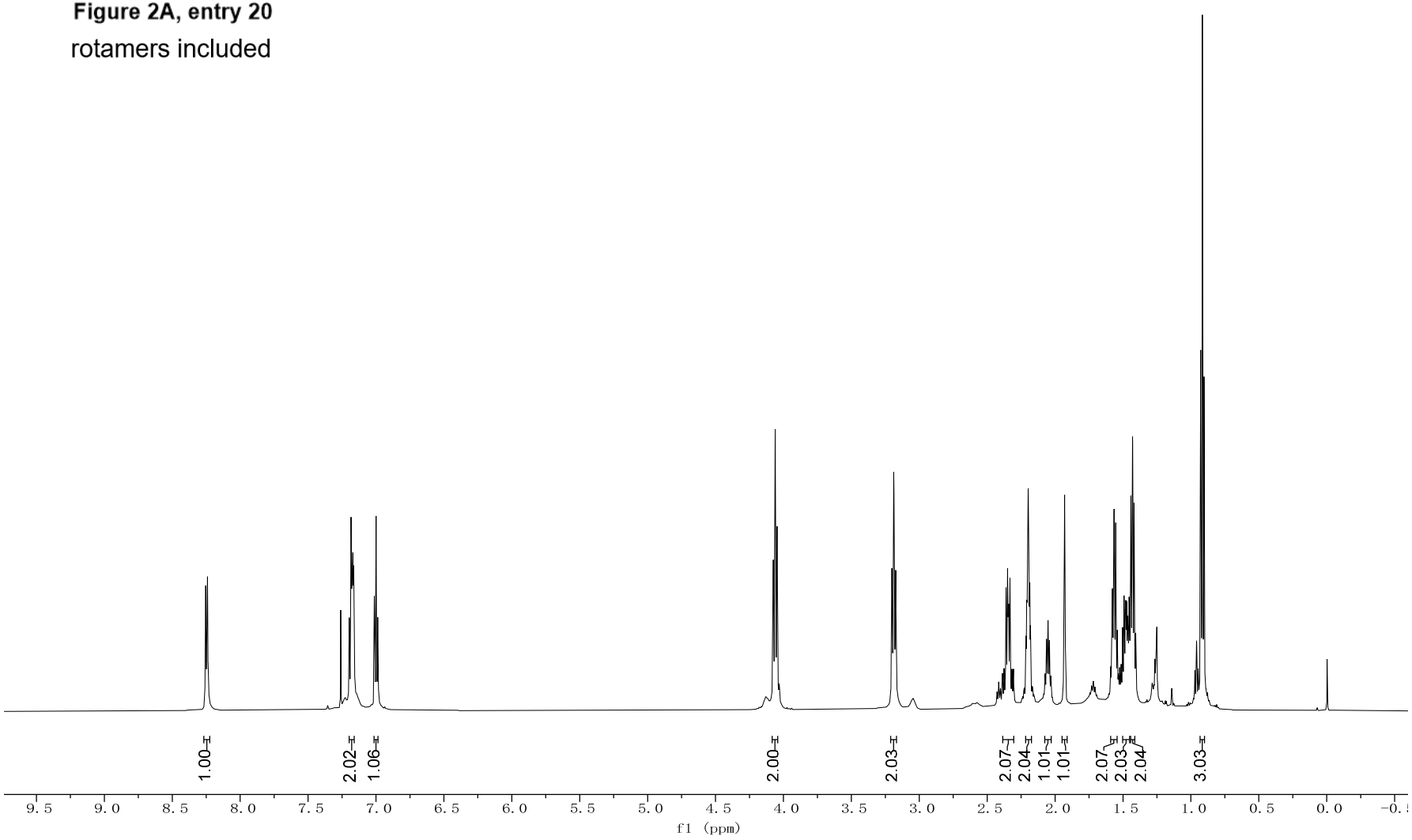


Figure 2A, entry 20

rotamers included



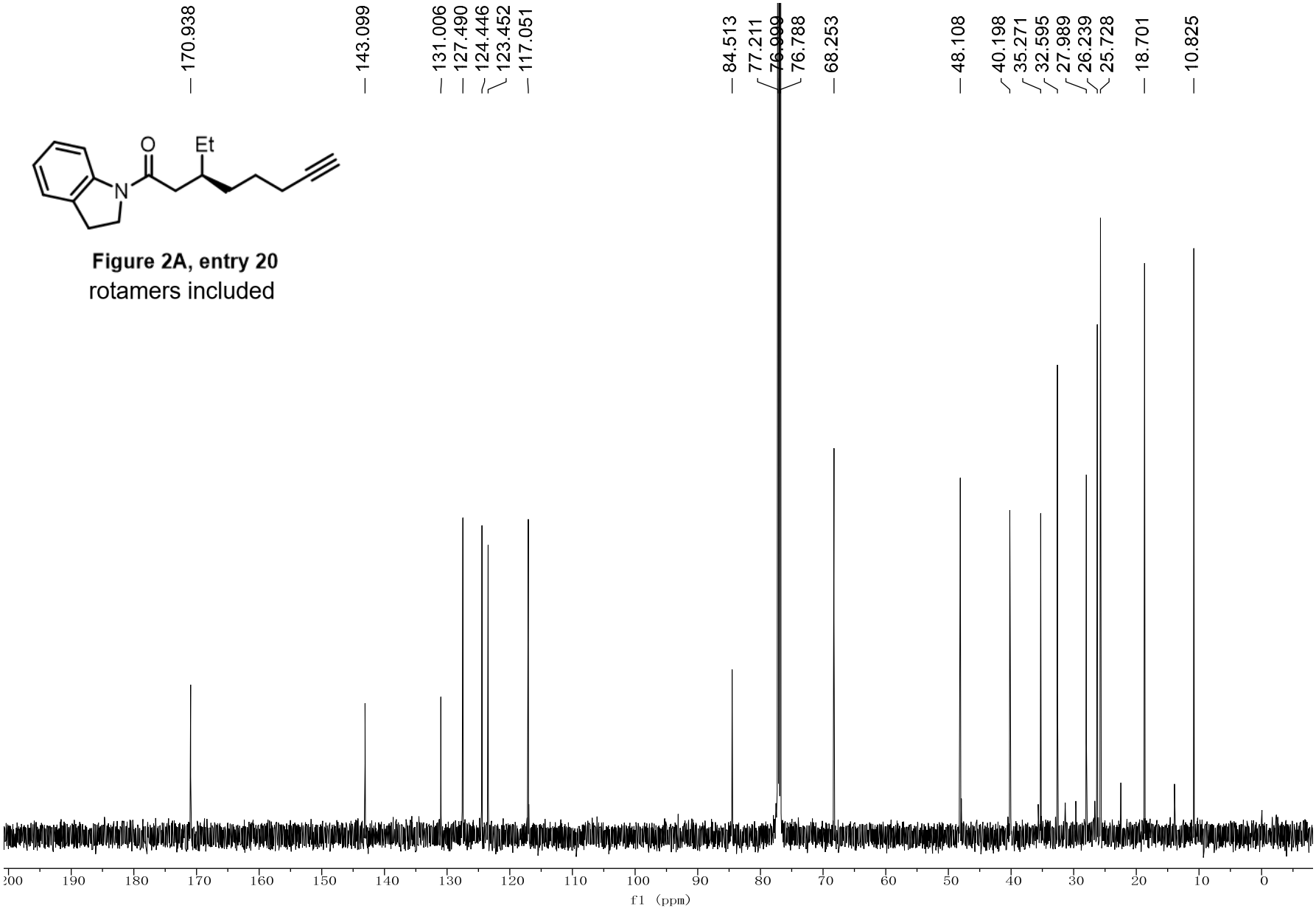


Figure 2A, entry 20
rotamers included

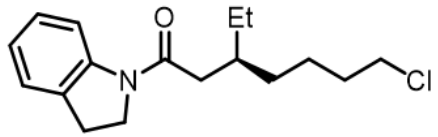
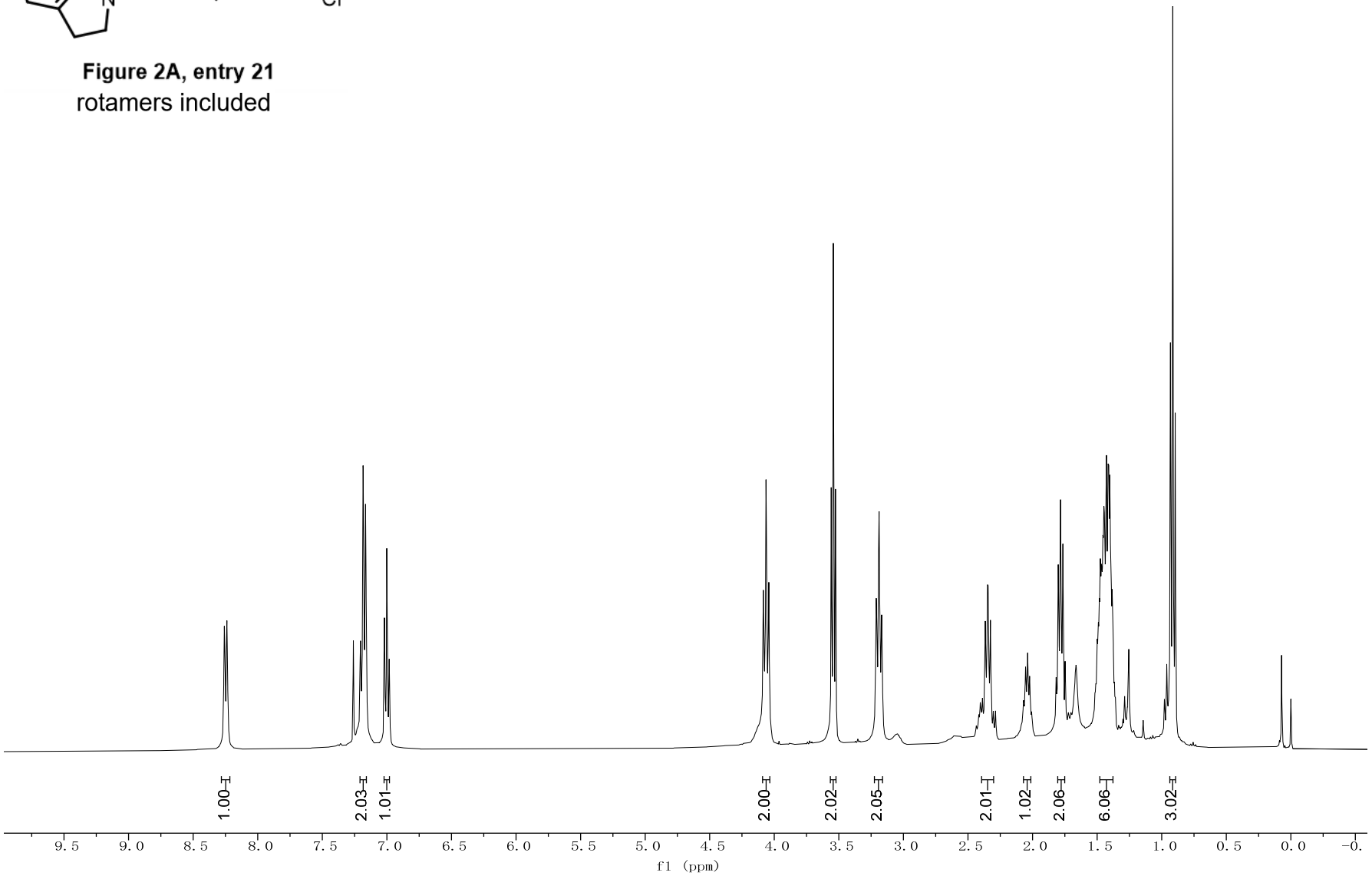


Figure 2A, entry 21
rotamers included



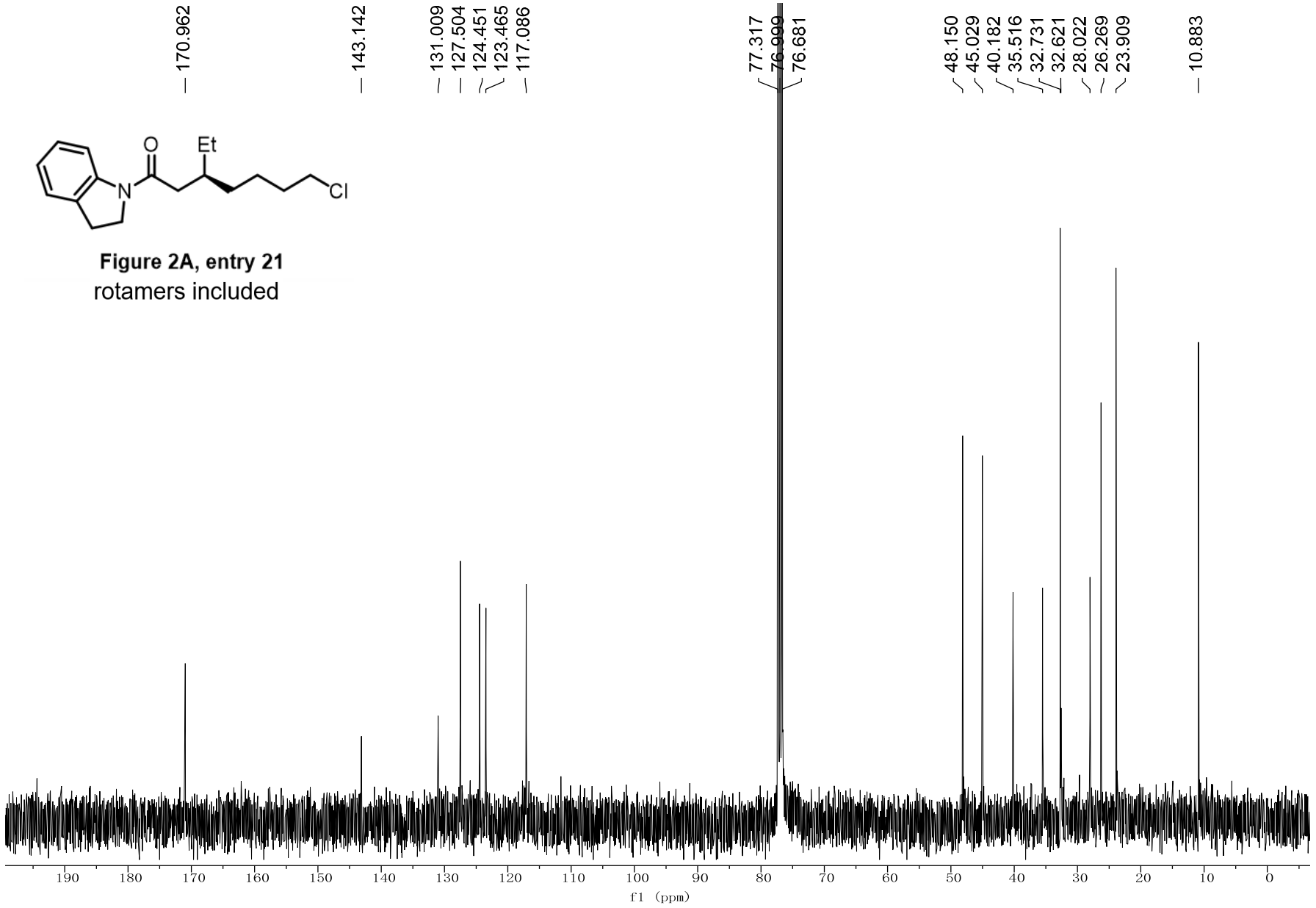


Figure 2A, entry 21
rotamers included

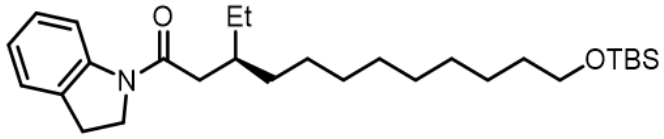
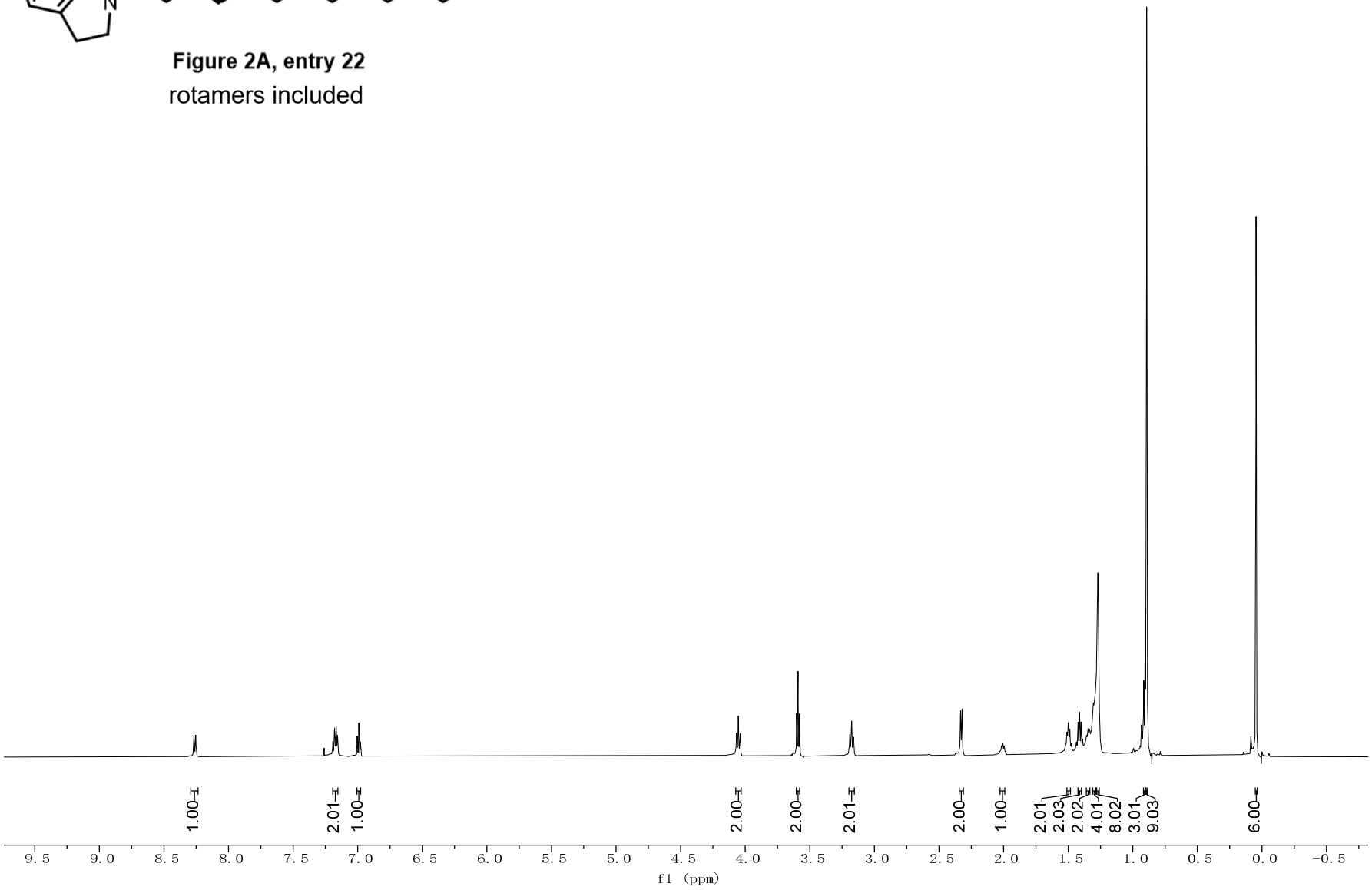


Figure 2A, entry 22

rotamers included



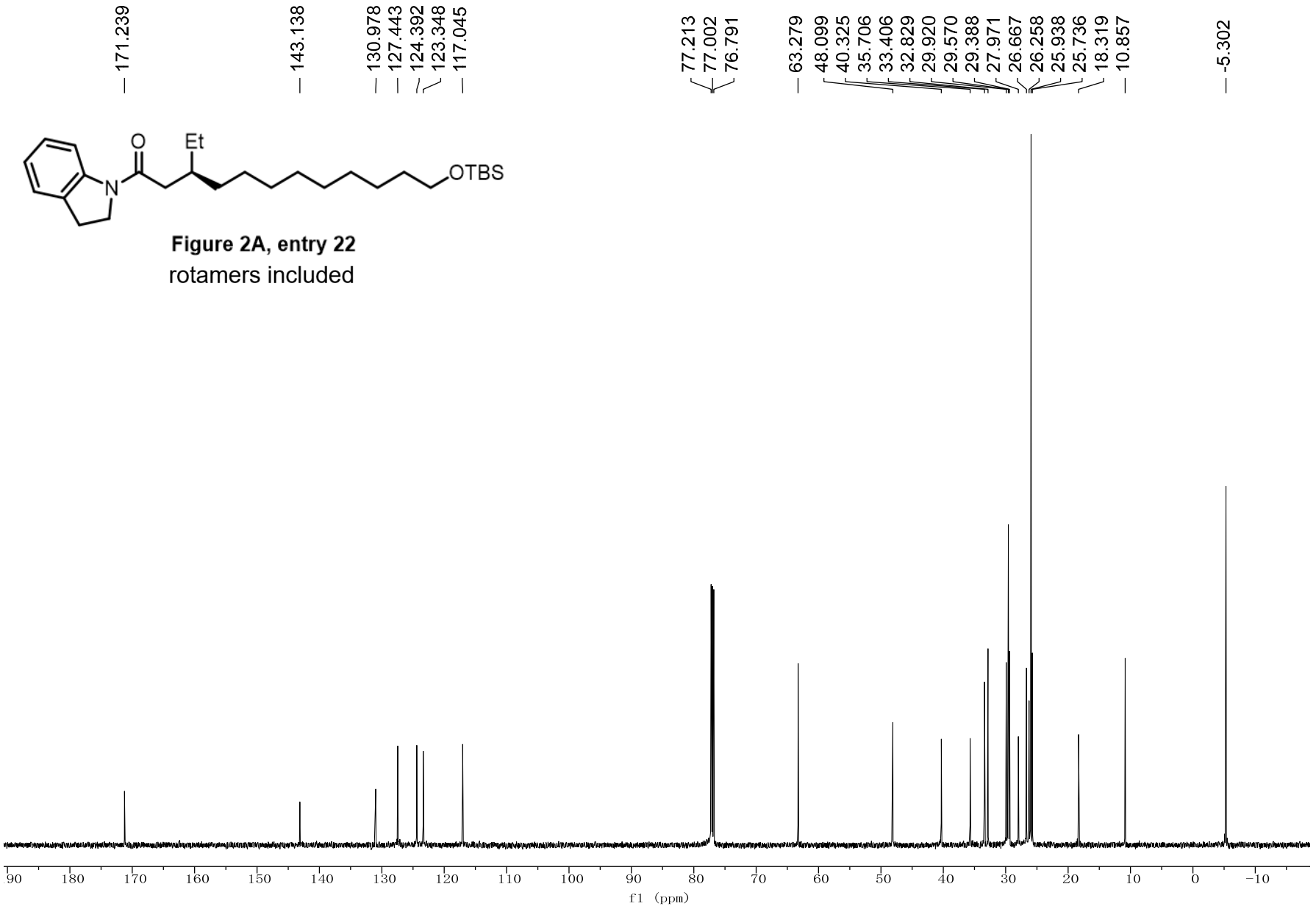


Figure 2A, entry 22
rotamers included

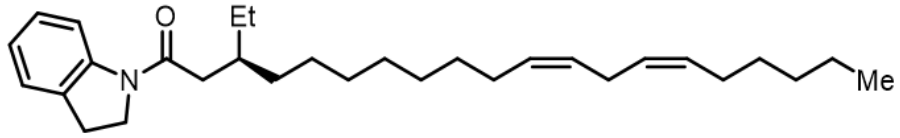
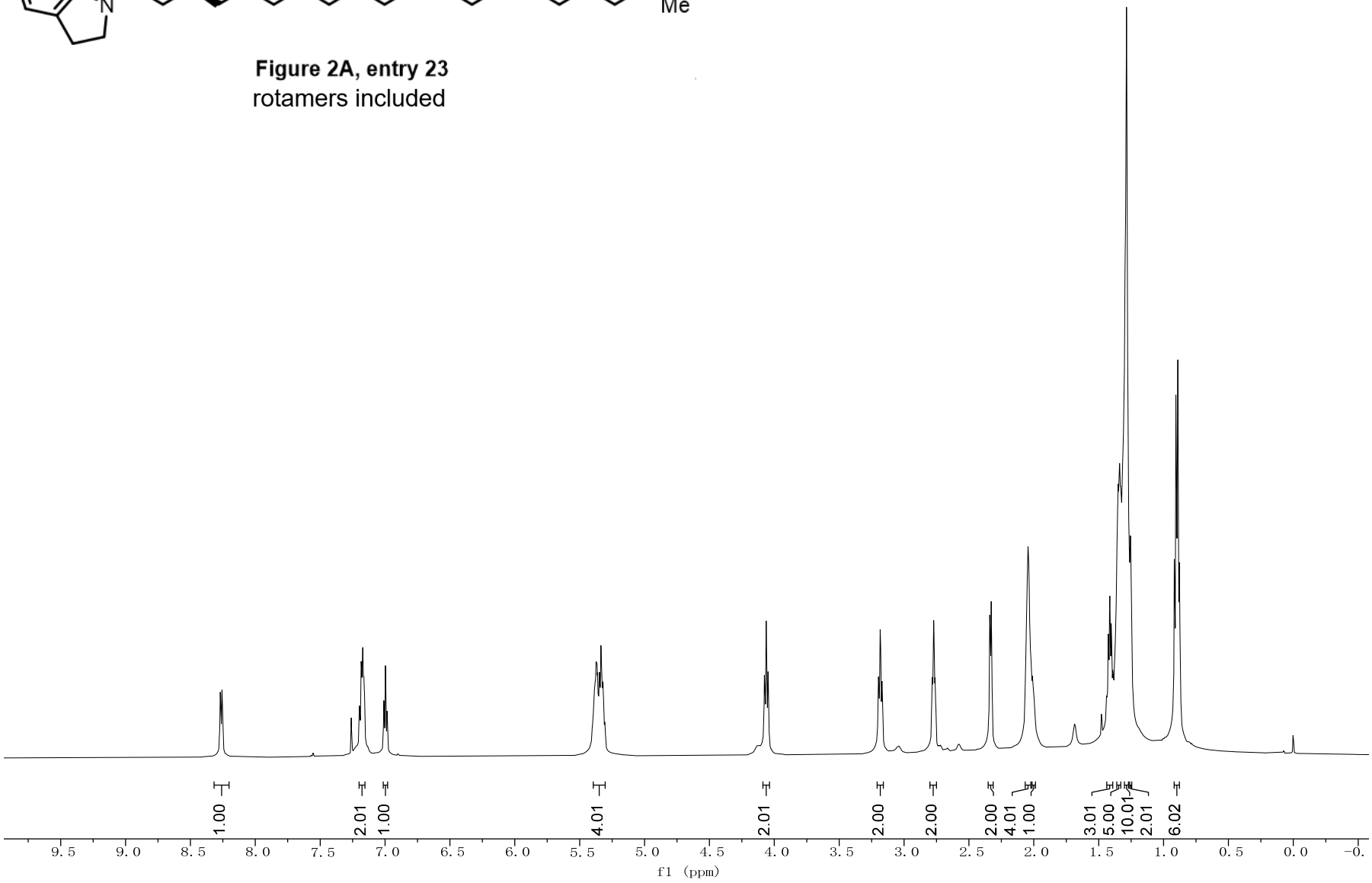


Figure 2A, entry 23
rotamers included



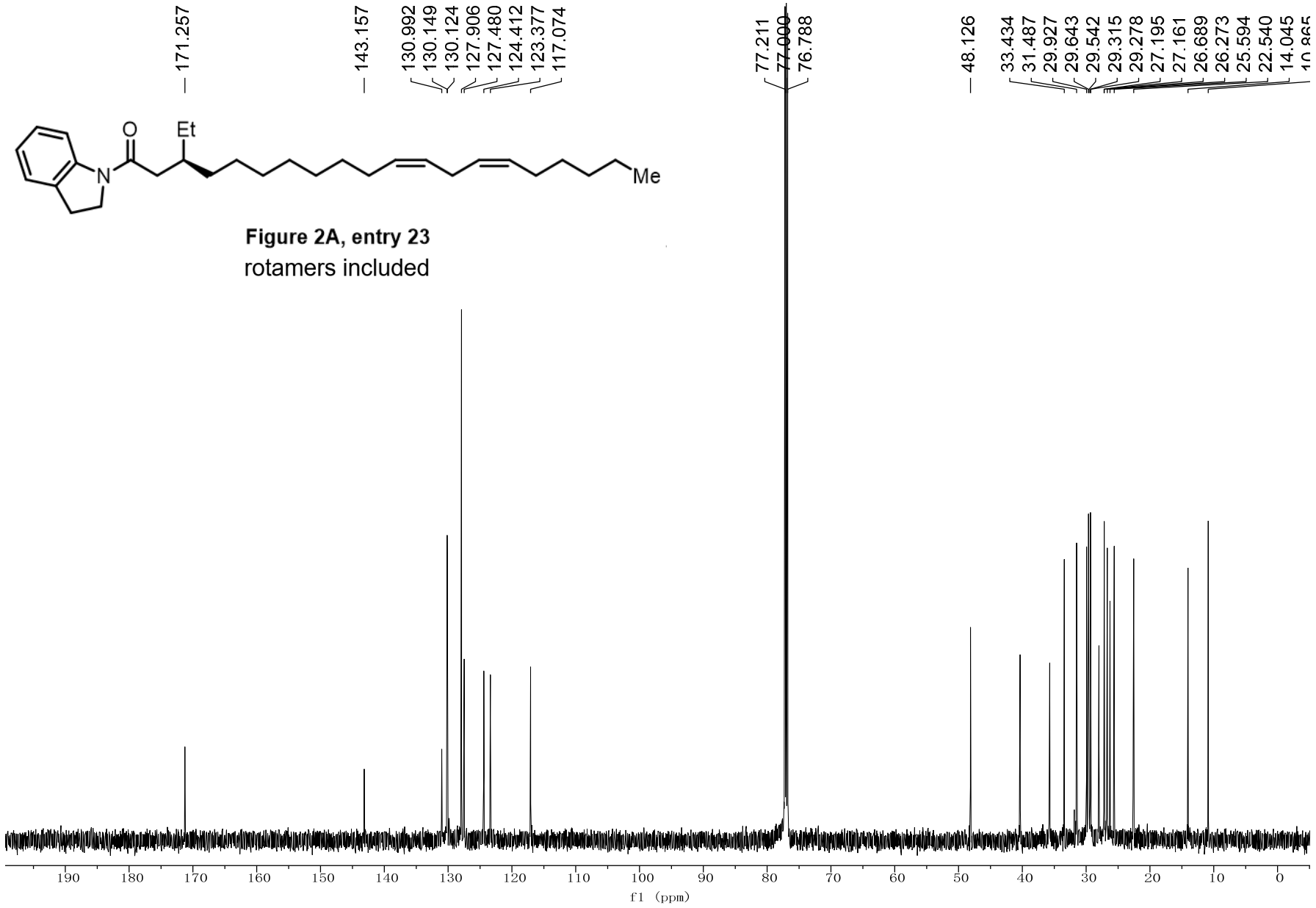


Figure 2A, entry 23
rotamers included

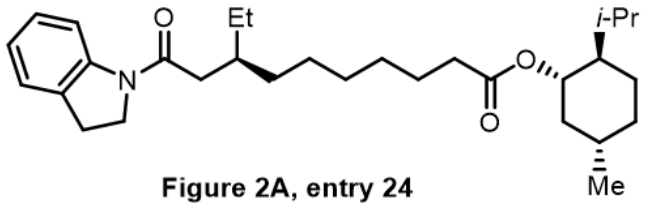
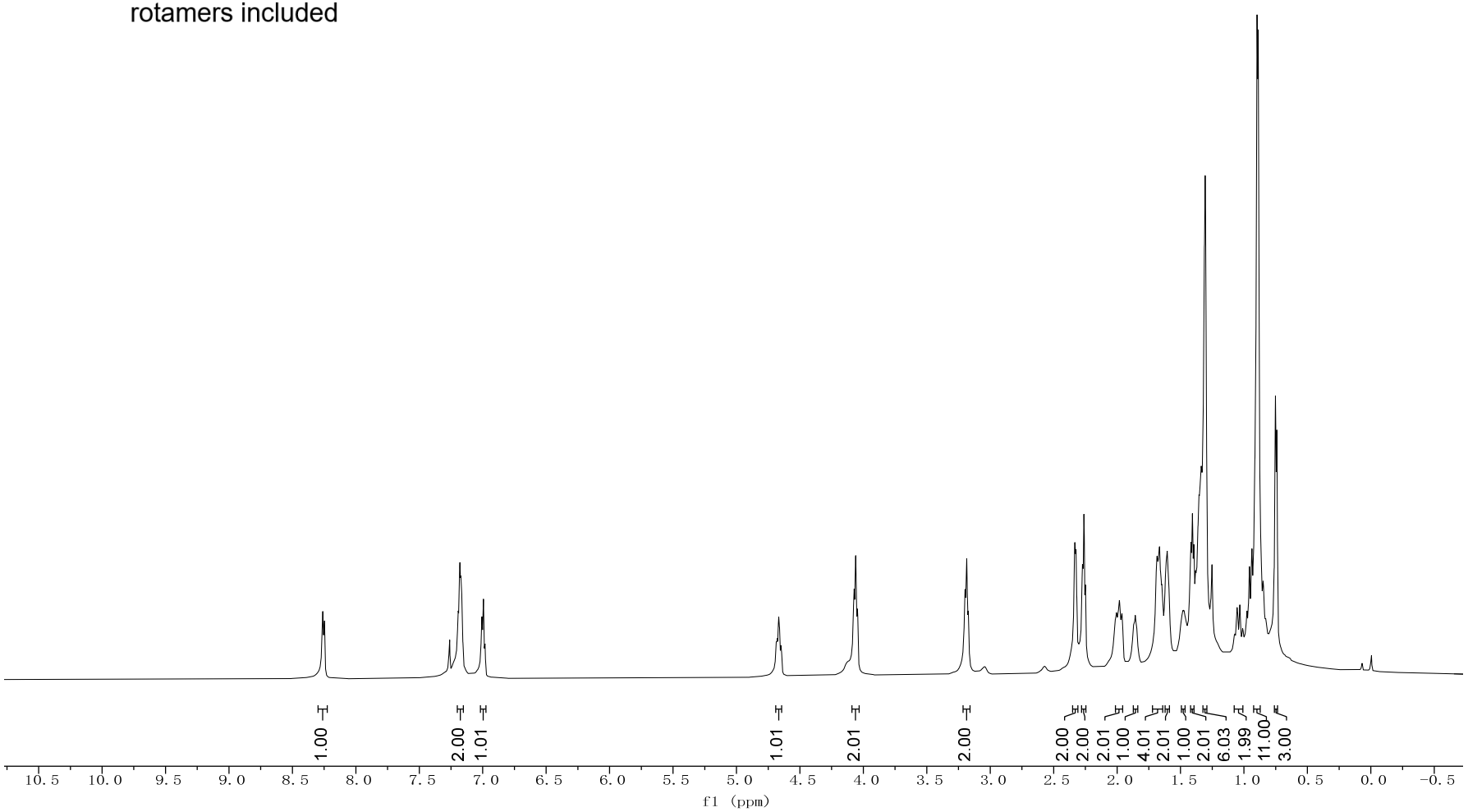


Figure 2A, entry 24

rotamers included



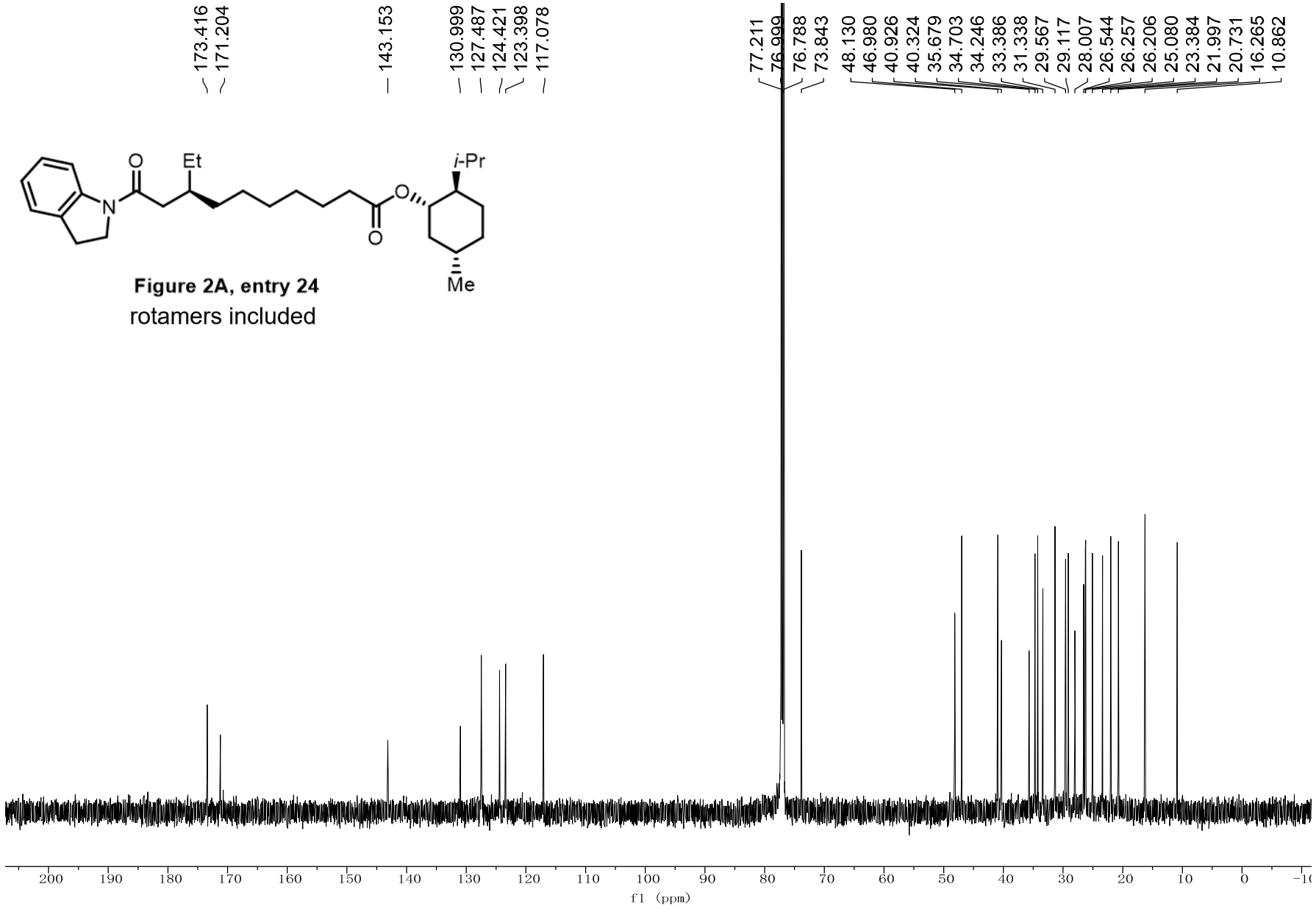


Figure 2A, entry 24

rotamers included

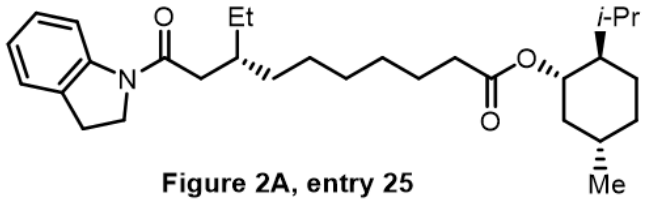


Figure 2A, entry 25
rotamers included

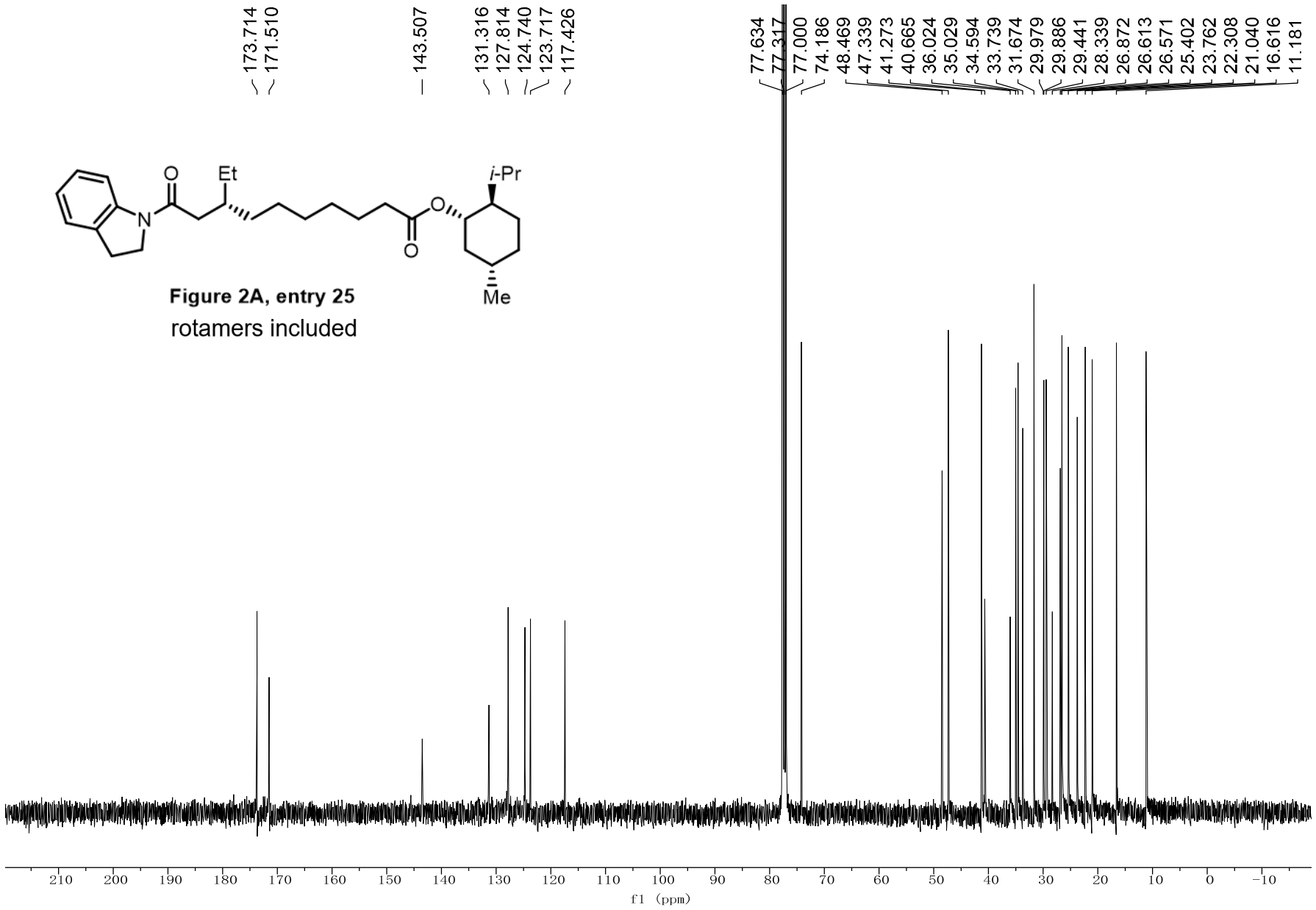


Figure 2A, entry 25

rotamers included

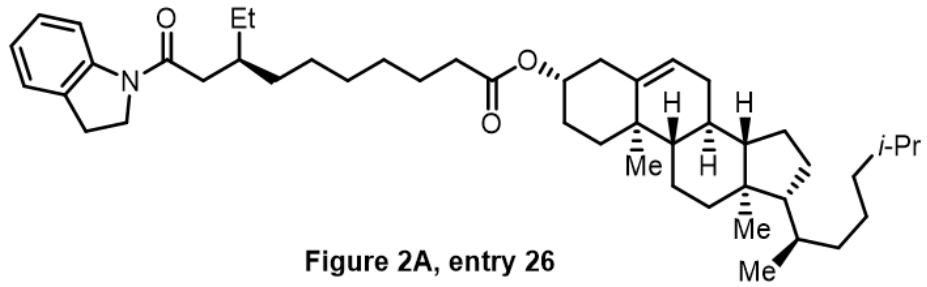


Figure 2A, entry 26
rotamers included

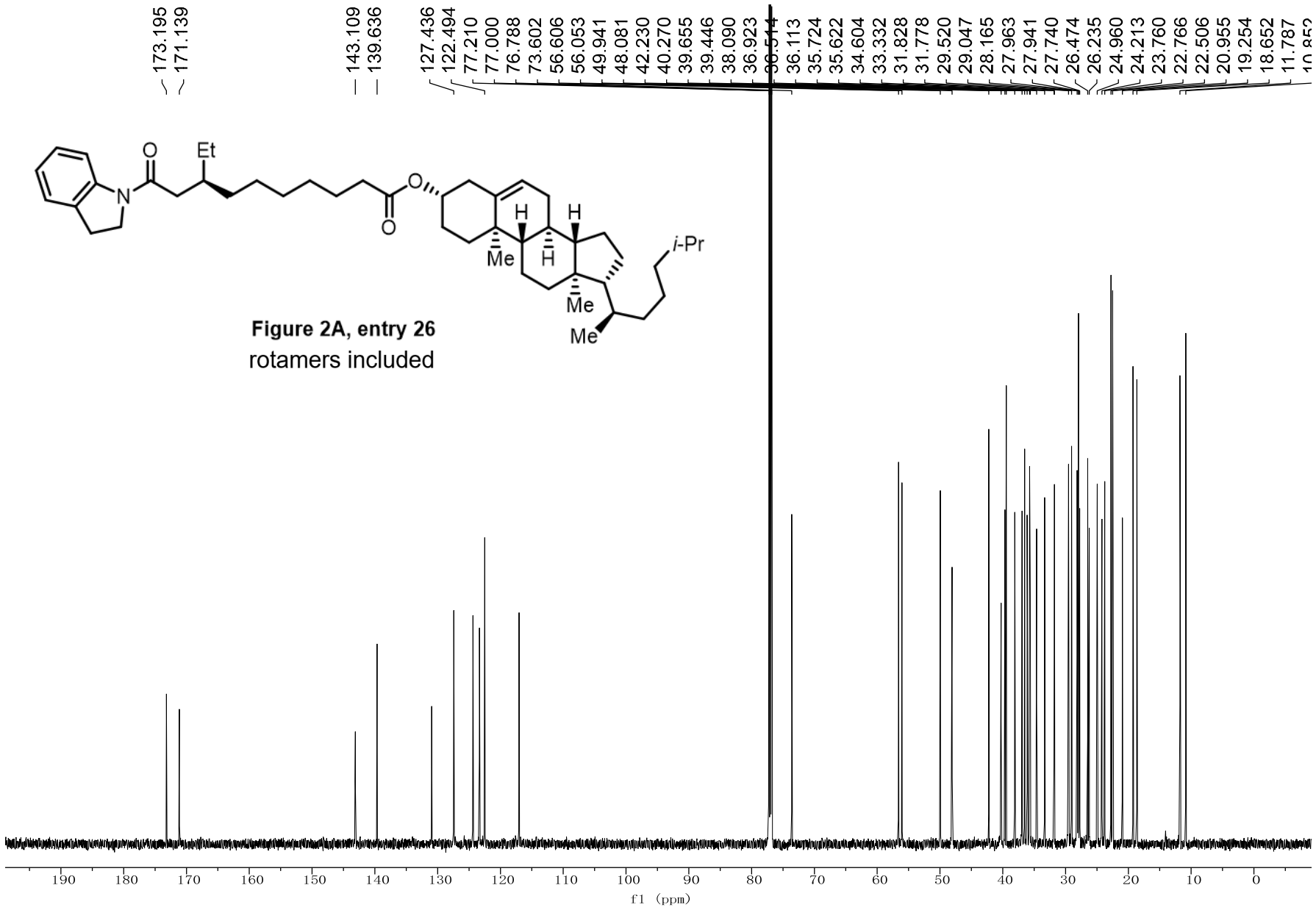


Figure 2A, entry 26
rotamers included

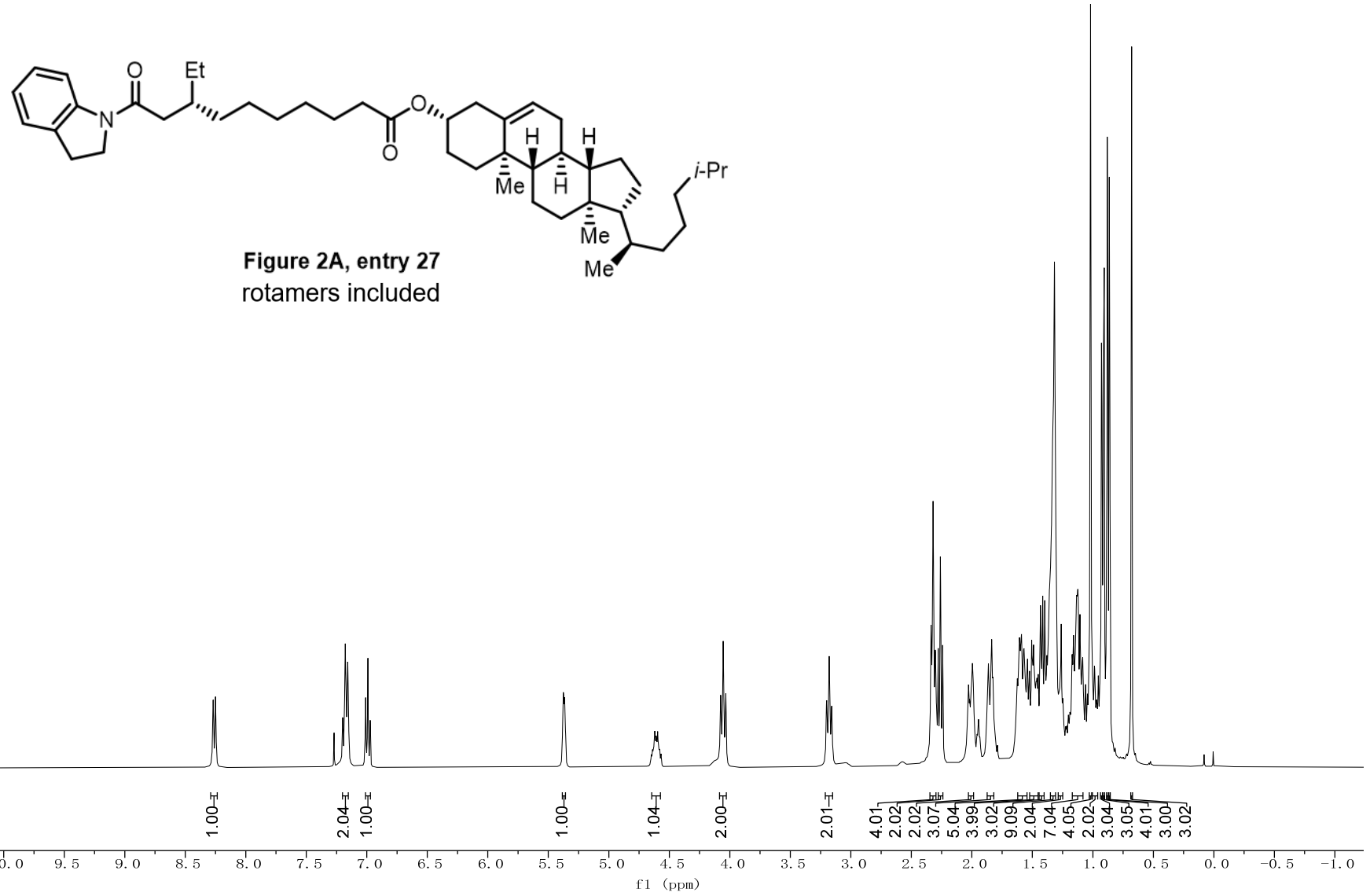


Figure 2A, entry 27
rotamers included

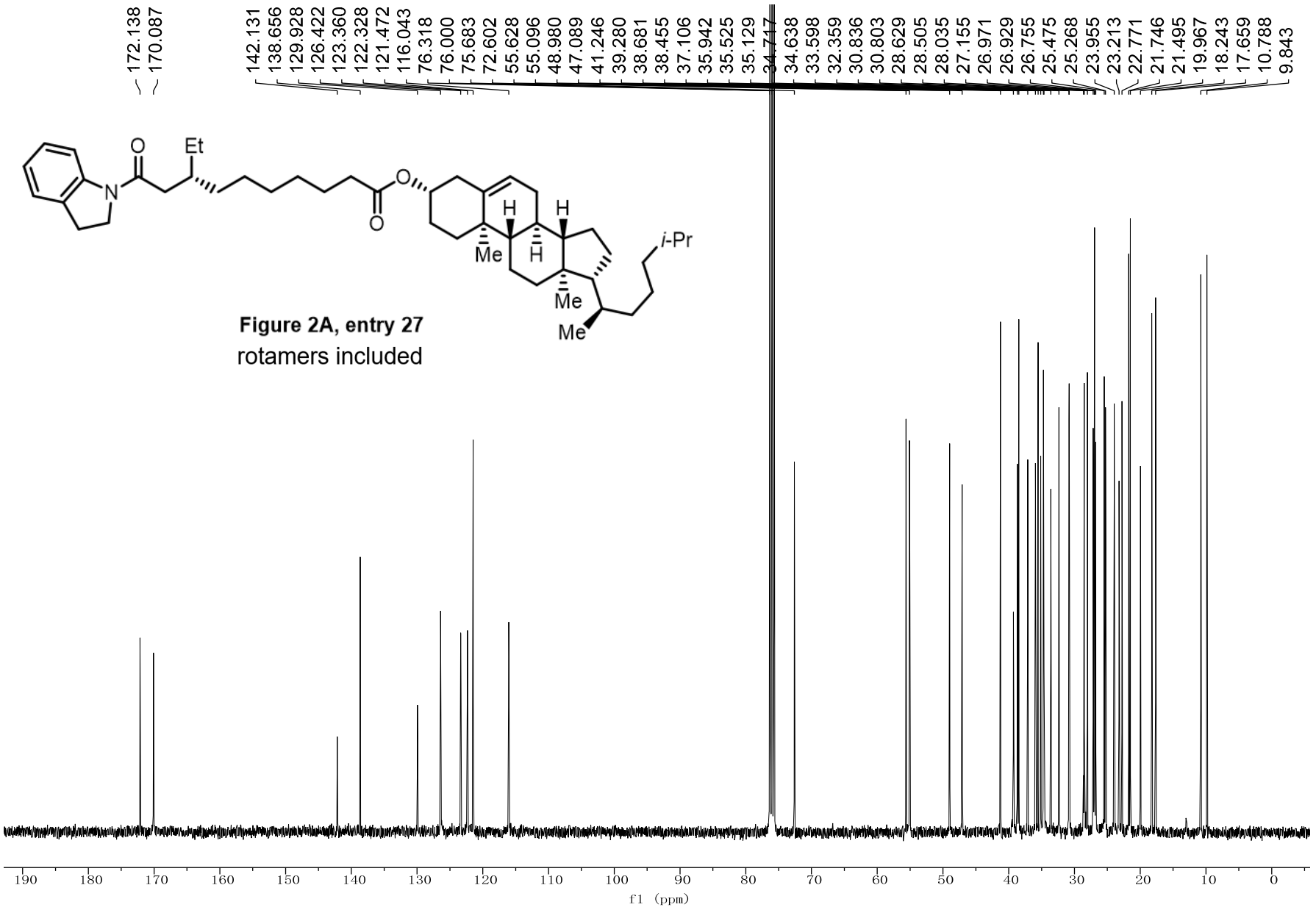


Figure 2A, entry 27
rotamers included

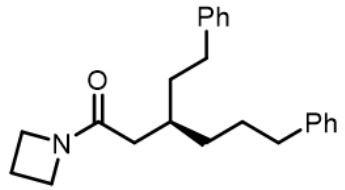
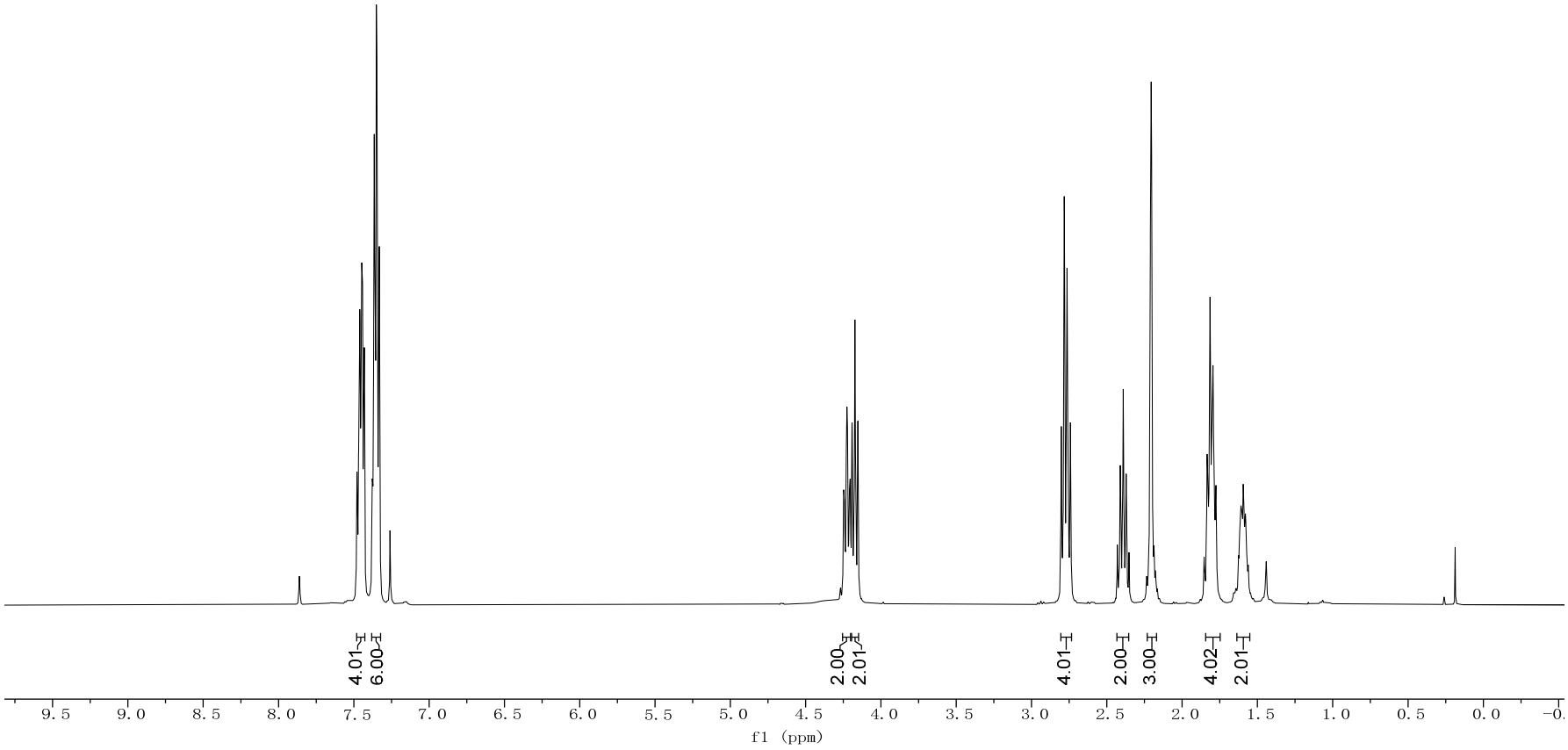


Figure 2B, entry 28



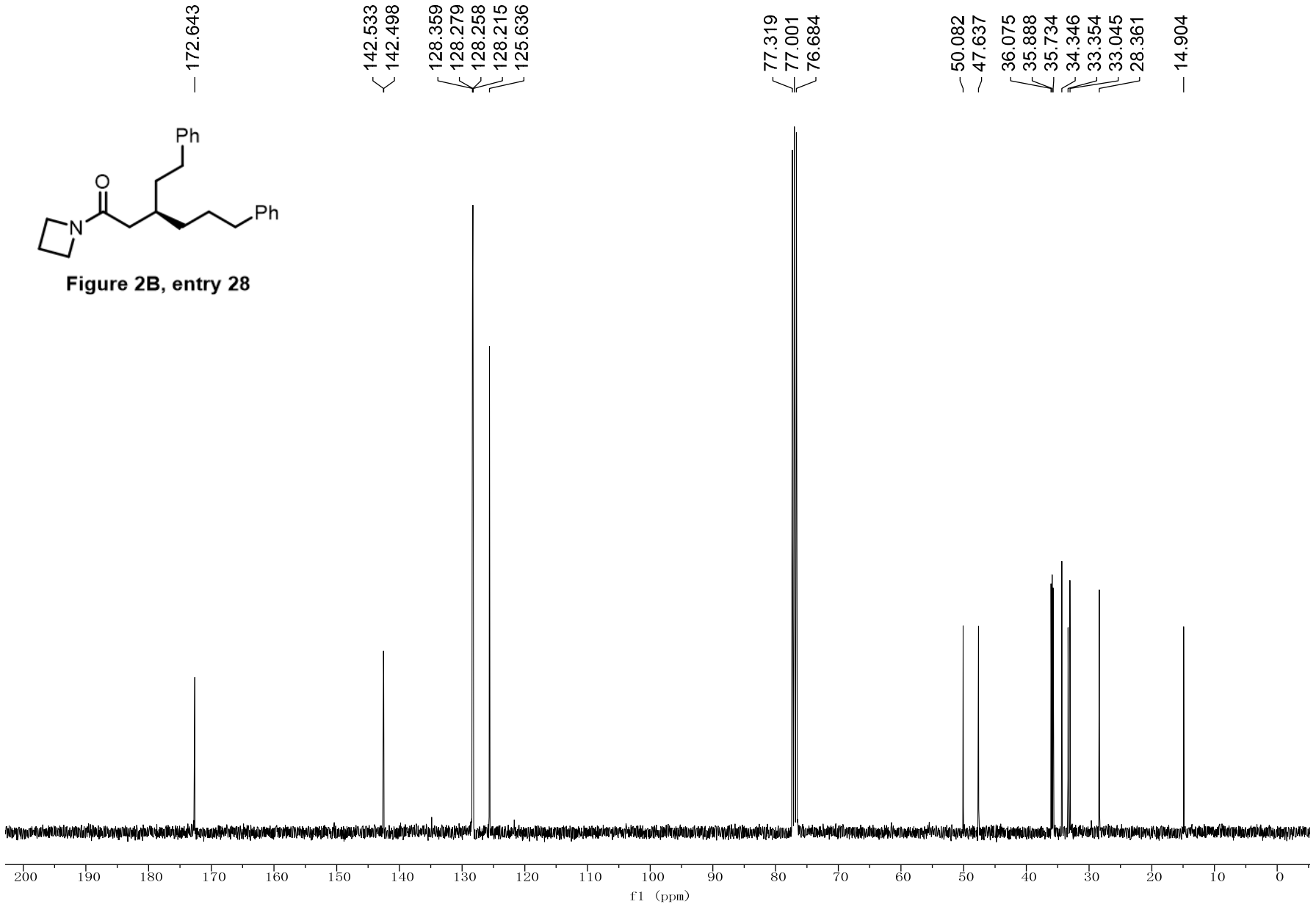


Figure 2B, entry 28

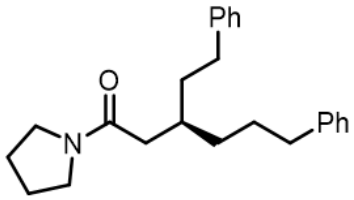
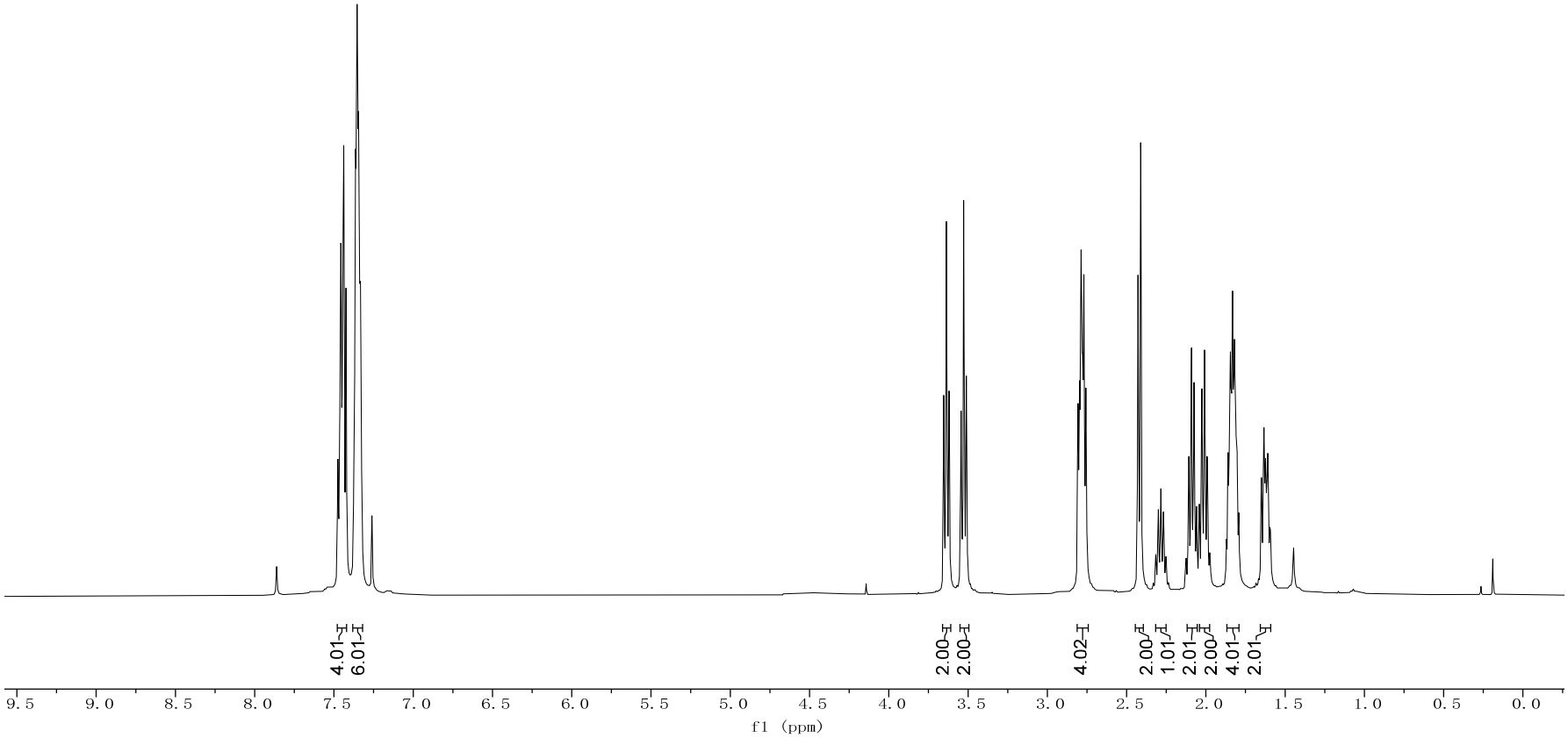


Figure 2B, entry 29



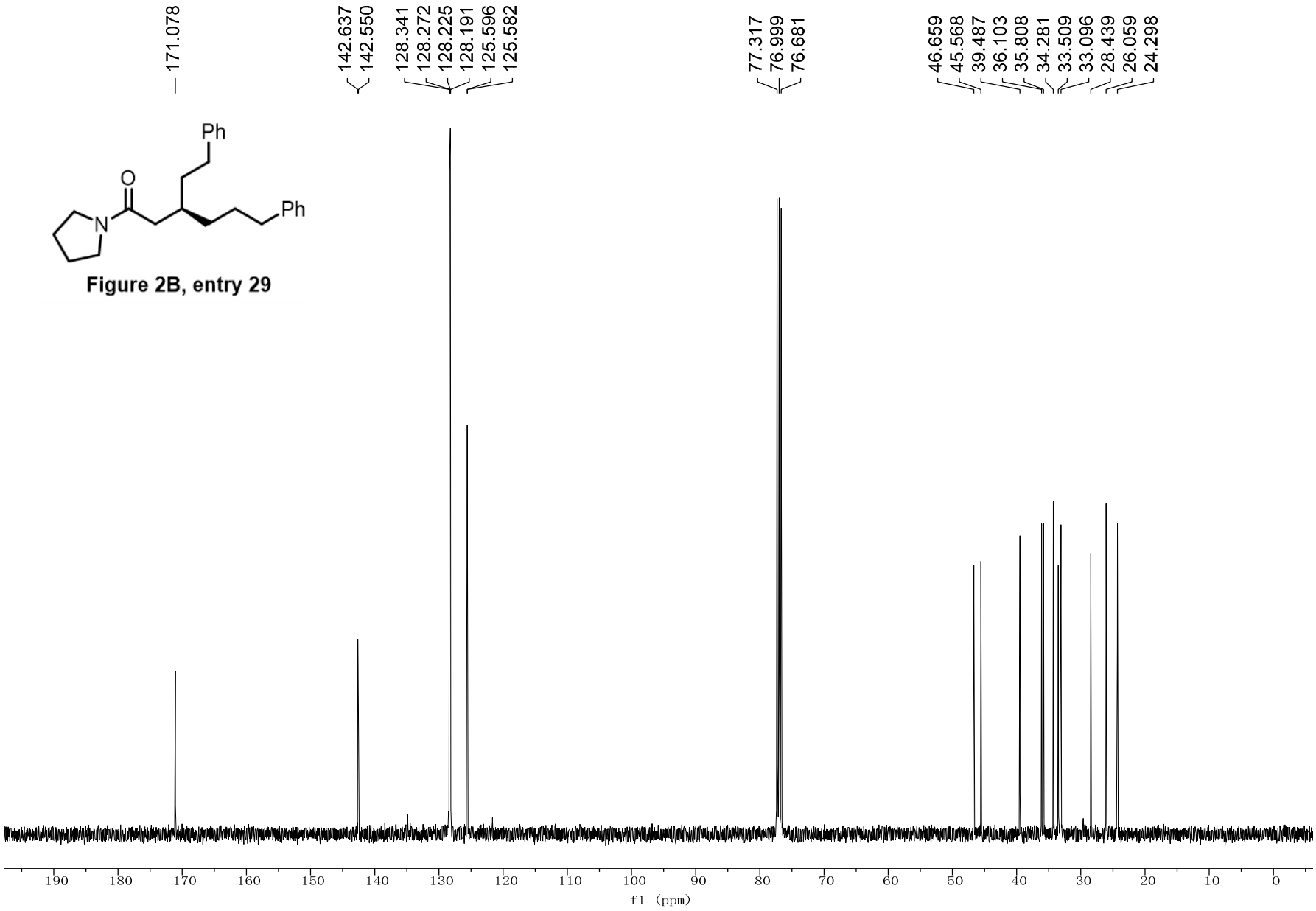


Figure 2B, entry 29

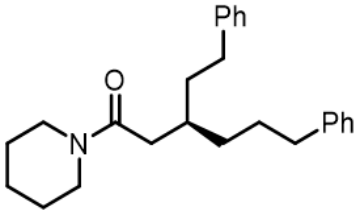
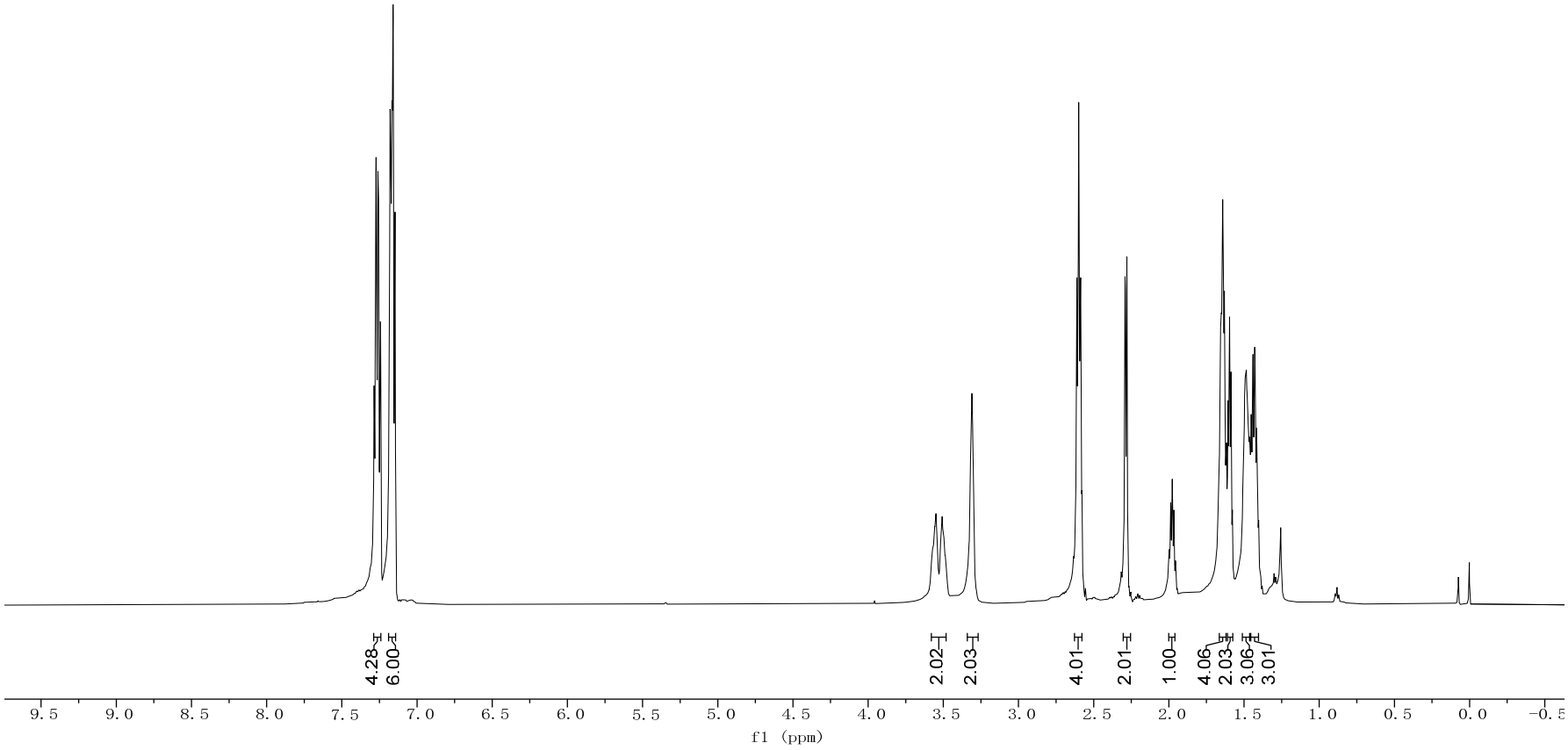


Figure 2B, entry 30



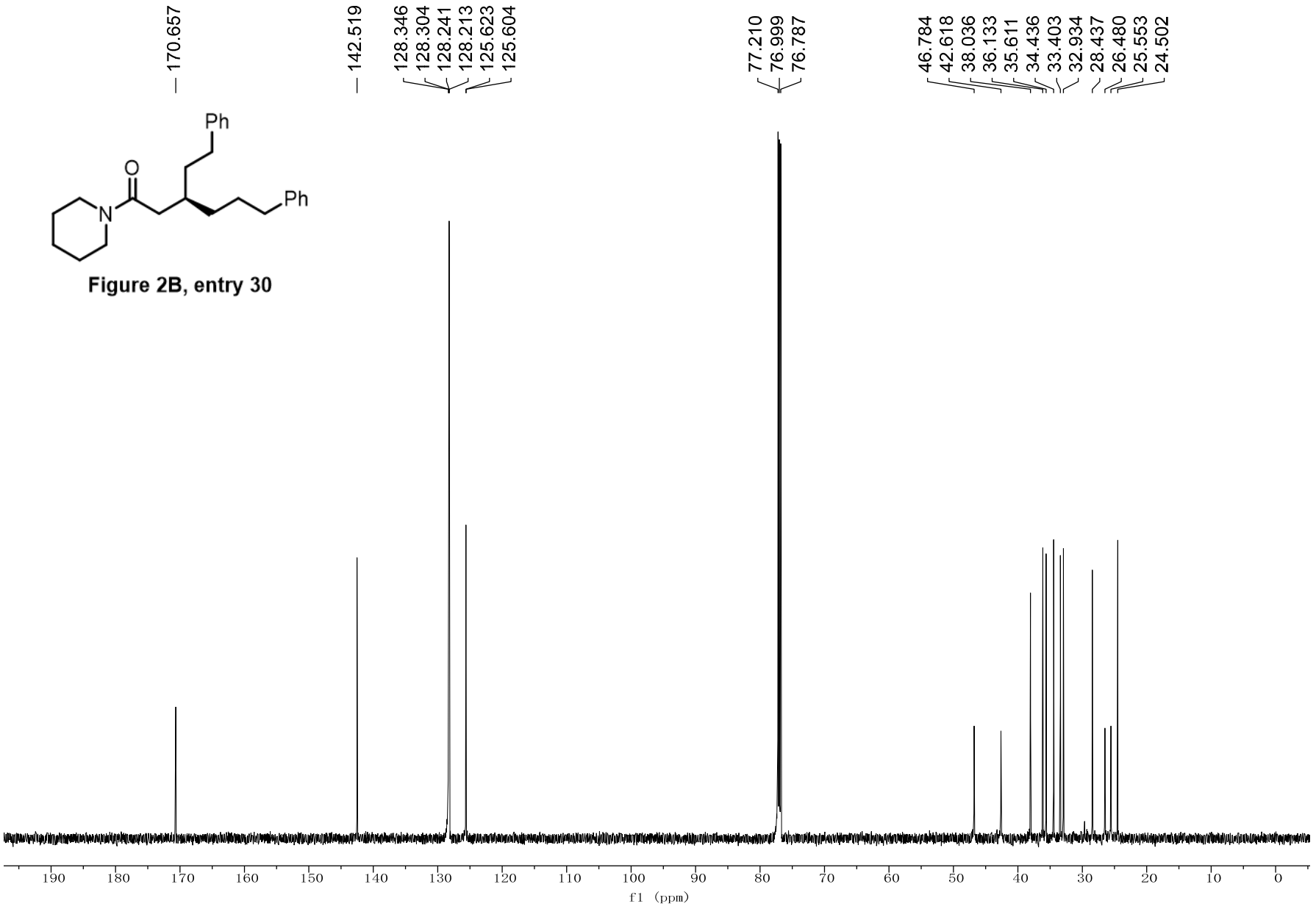


Figure 2B, entry 30

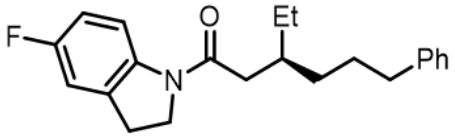
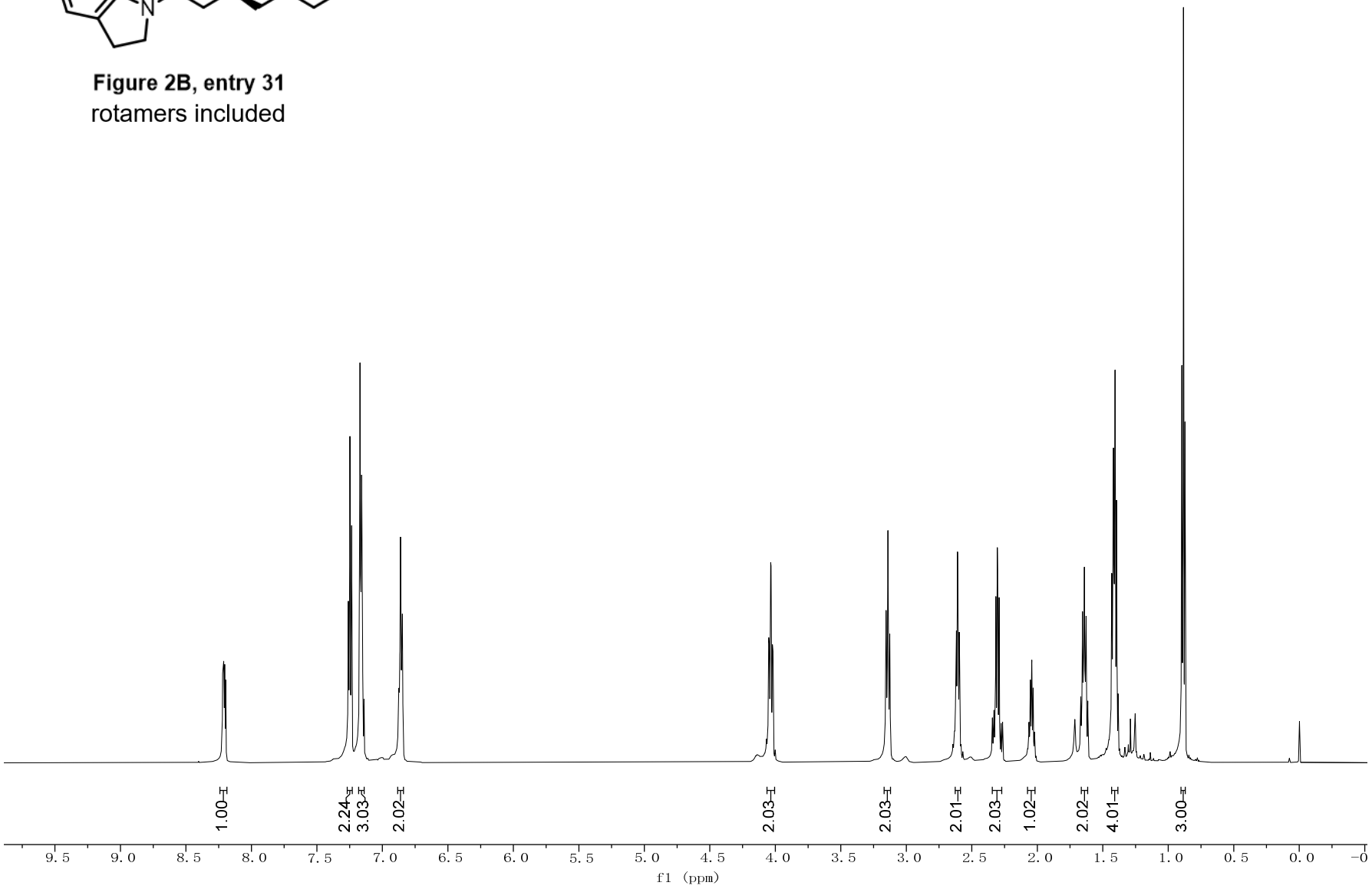


Figure 2B, entry 31
rotamers included



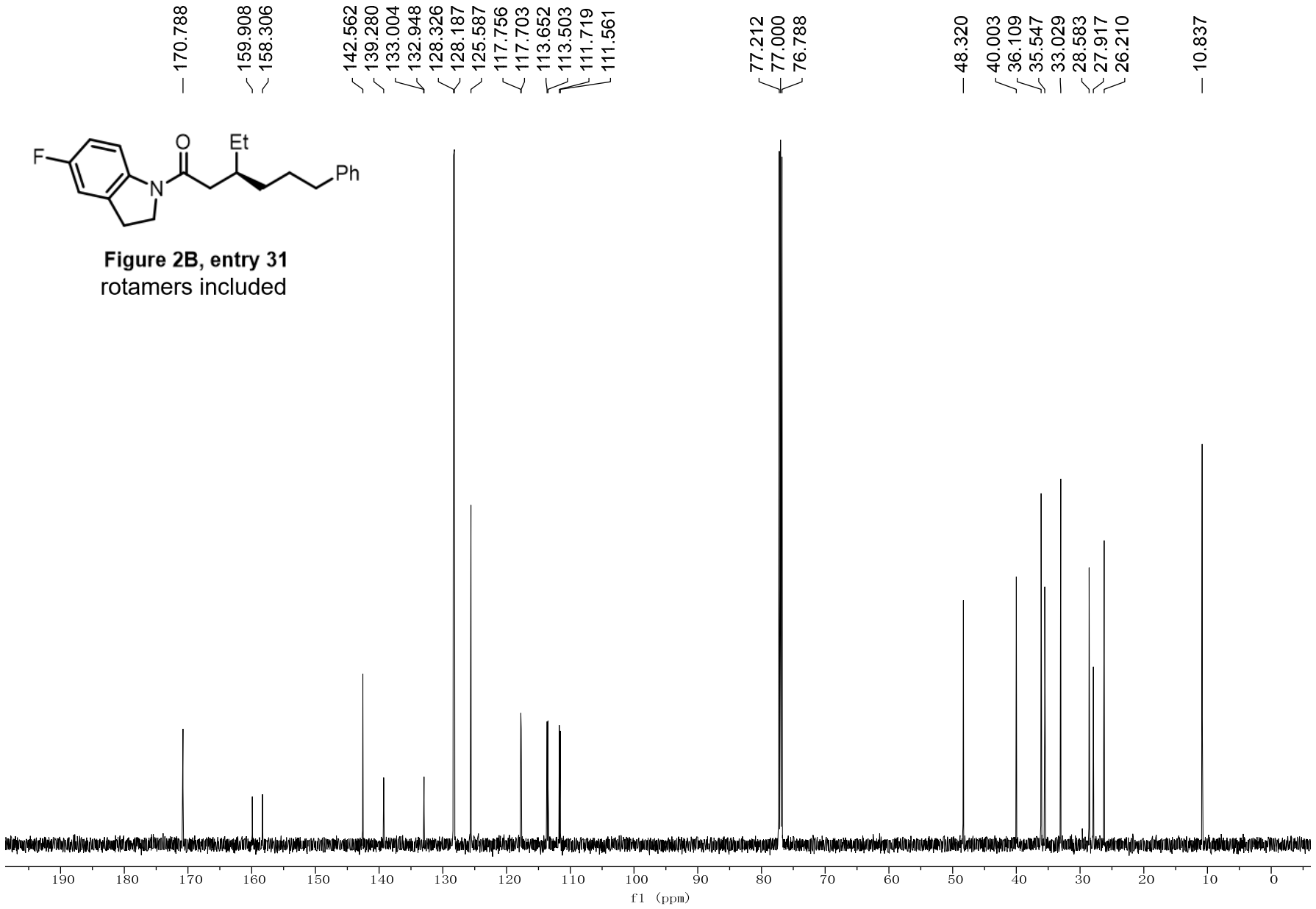


Figure 2B, entry 31
rotamers included

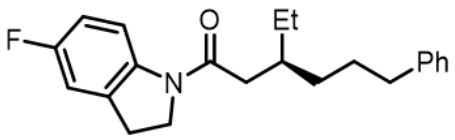


Figure 2B, entry 31

rotamers included

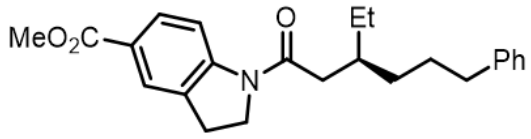
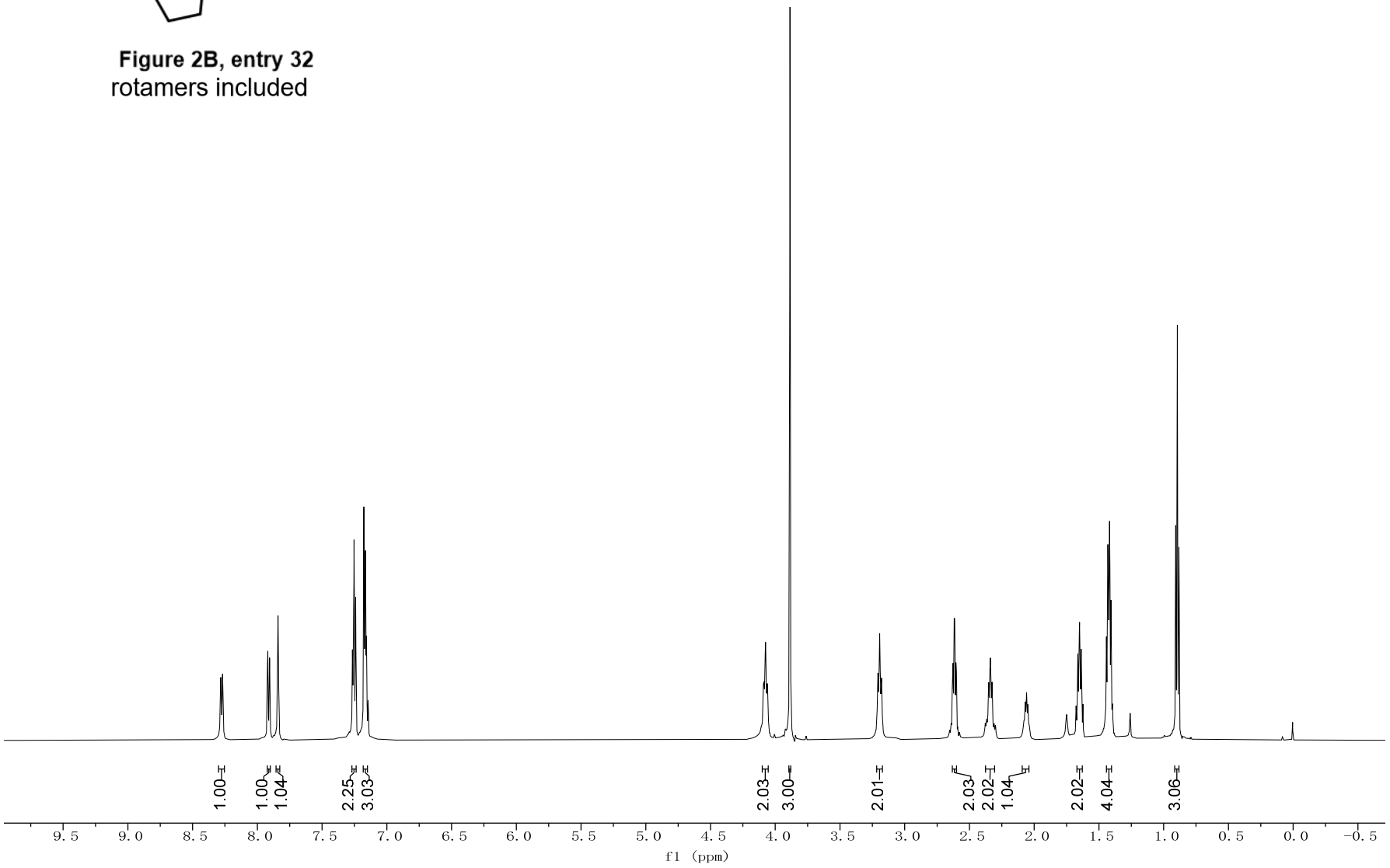


Figure 2B, entry 32
rotamers included



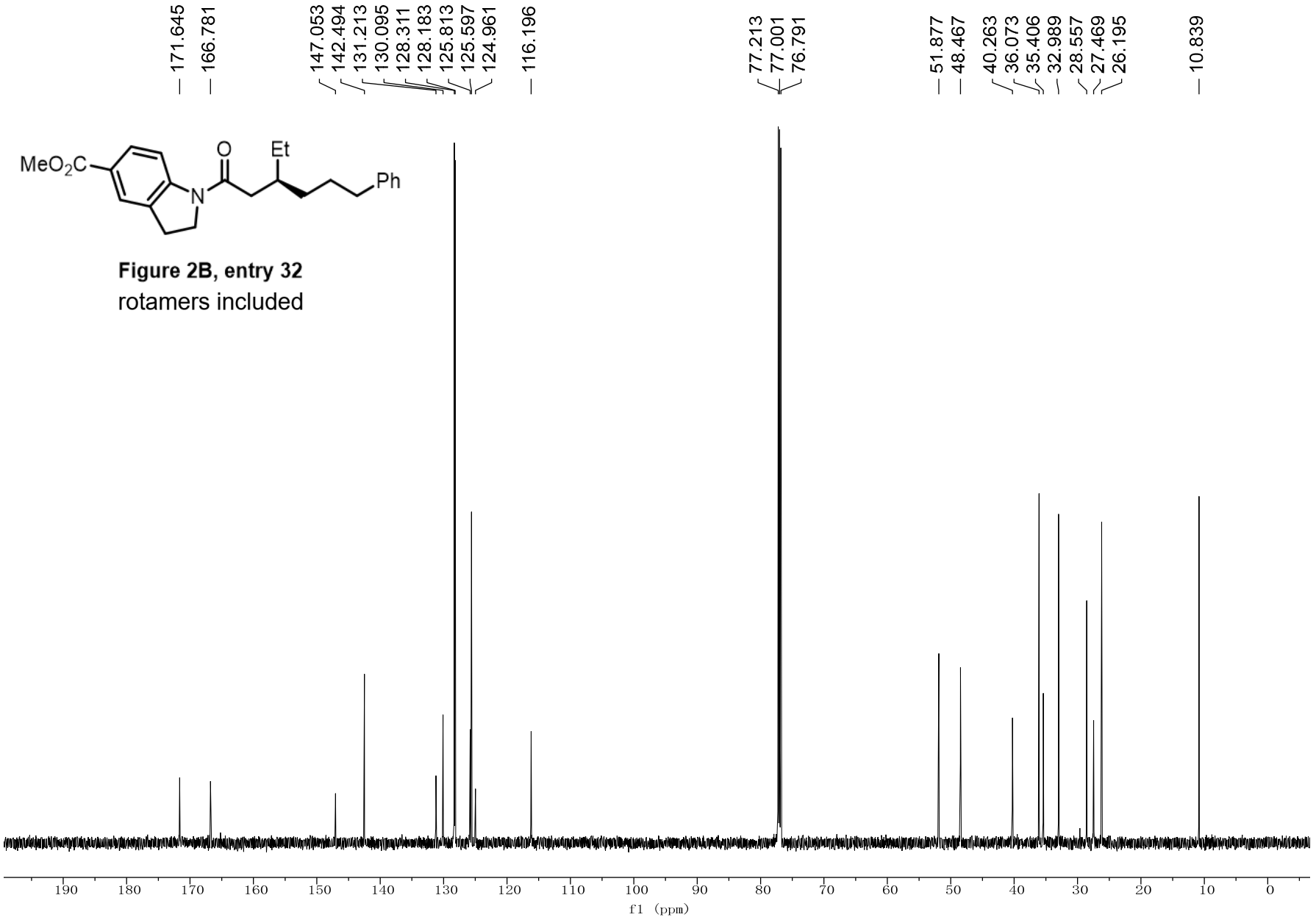


Figure 2B, entry 32
rotamers included

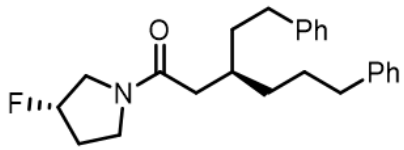
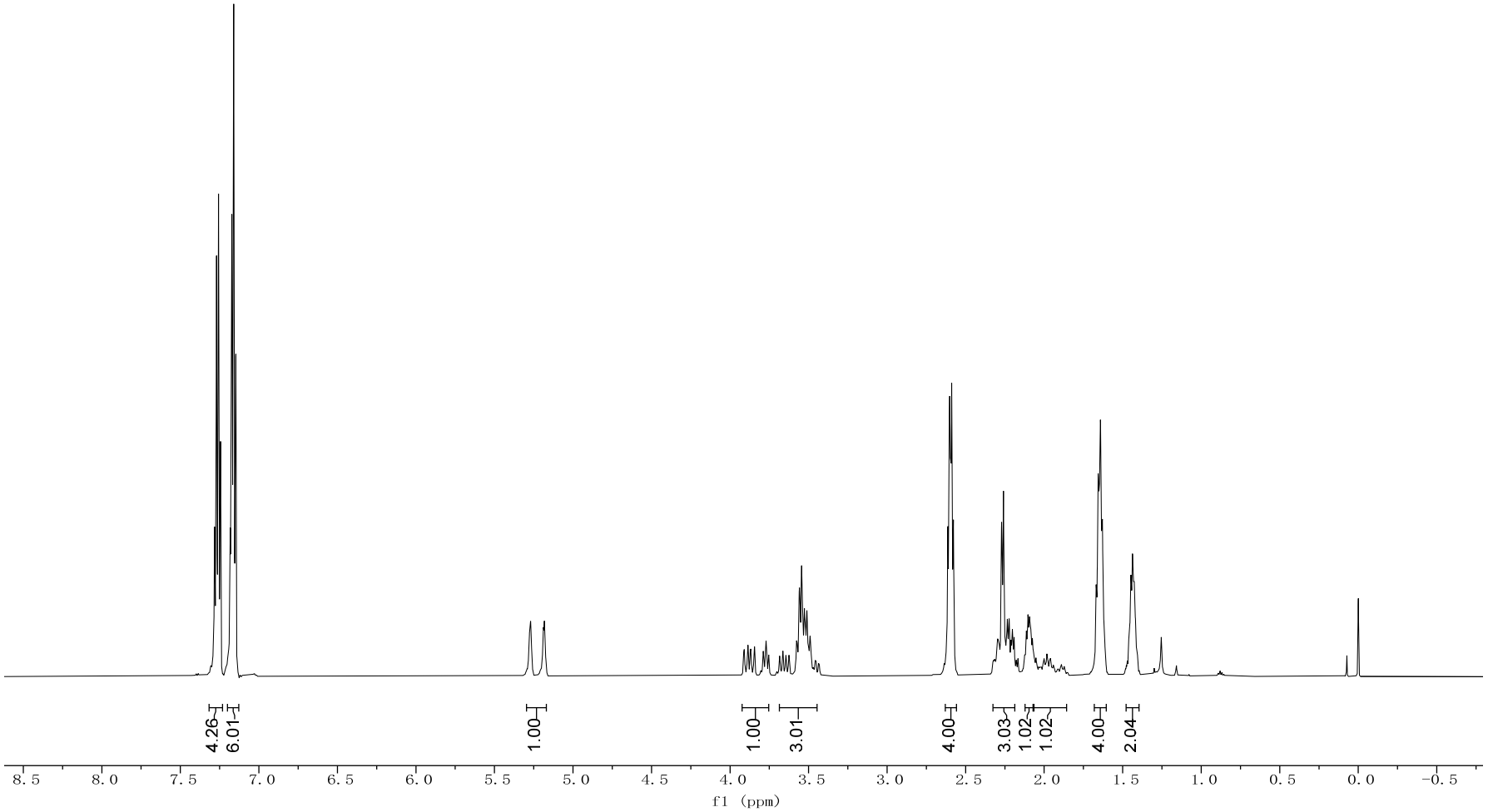


Figure 2B, entry 33
rotamers included



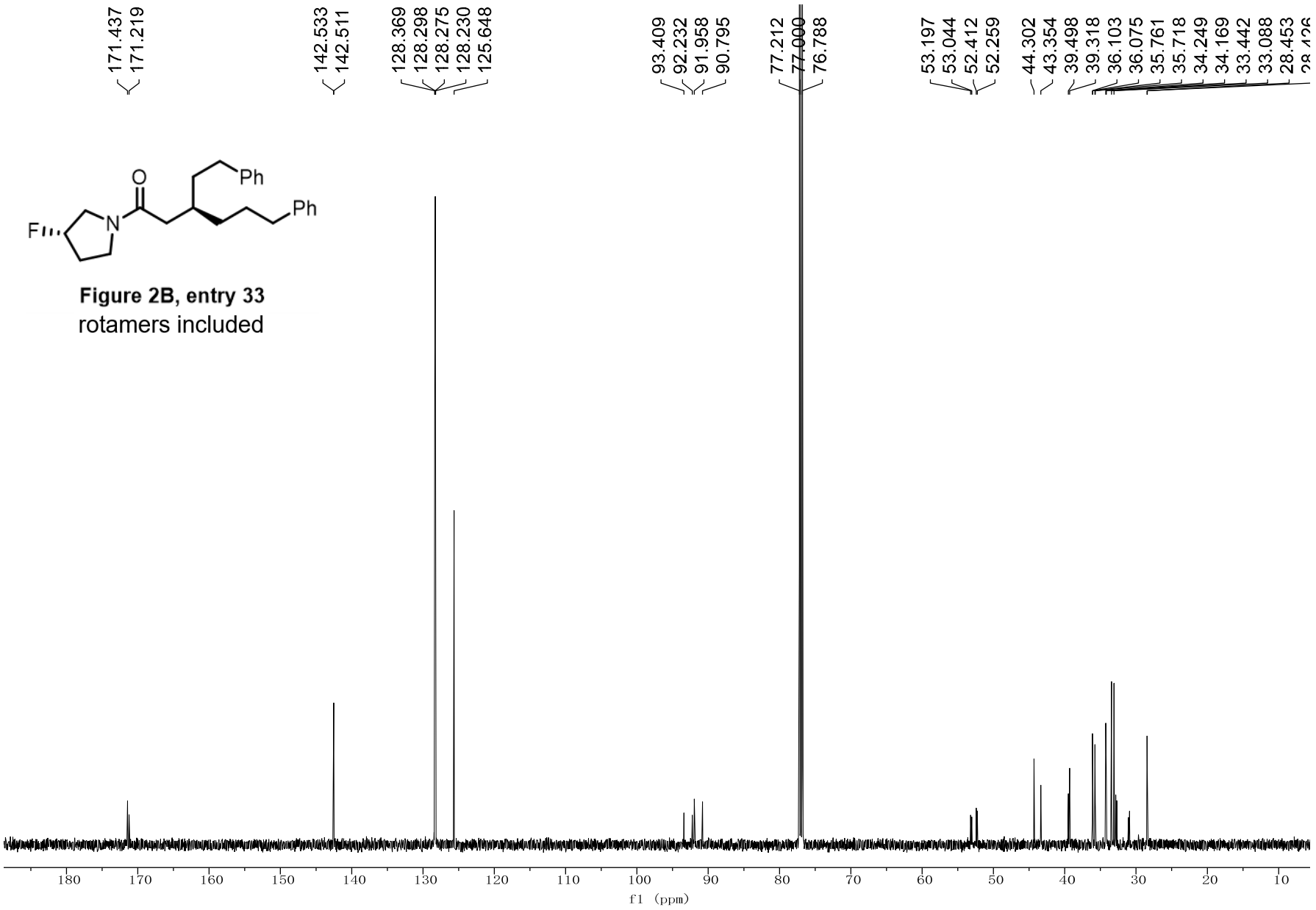


Figure 2B, entry 33
rotamers included

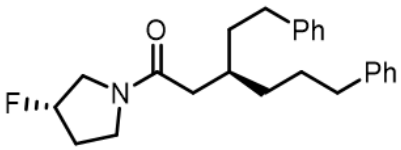
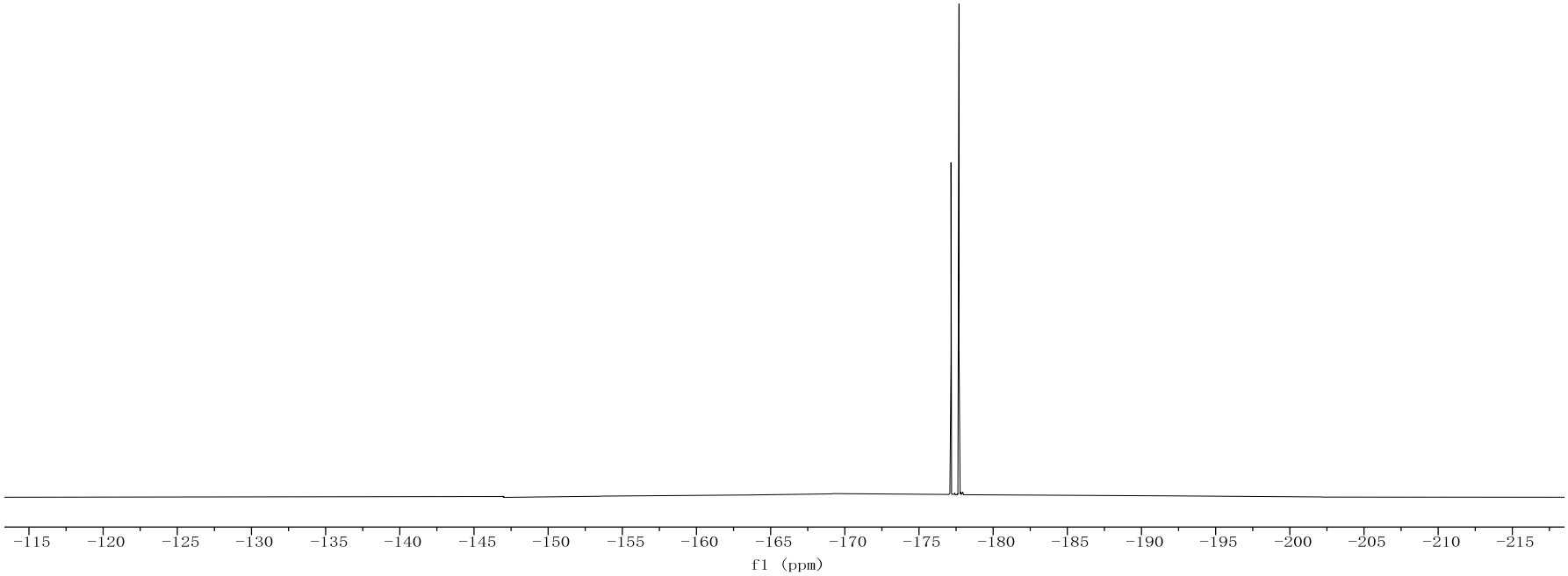


Figure 2B, entry 33
rotamers included

-177.103
-177.157
-177.695
-177.715



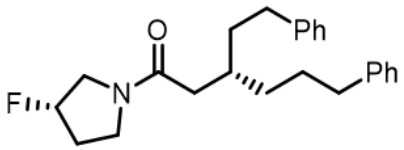
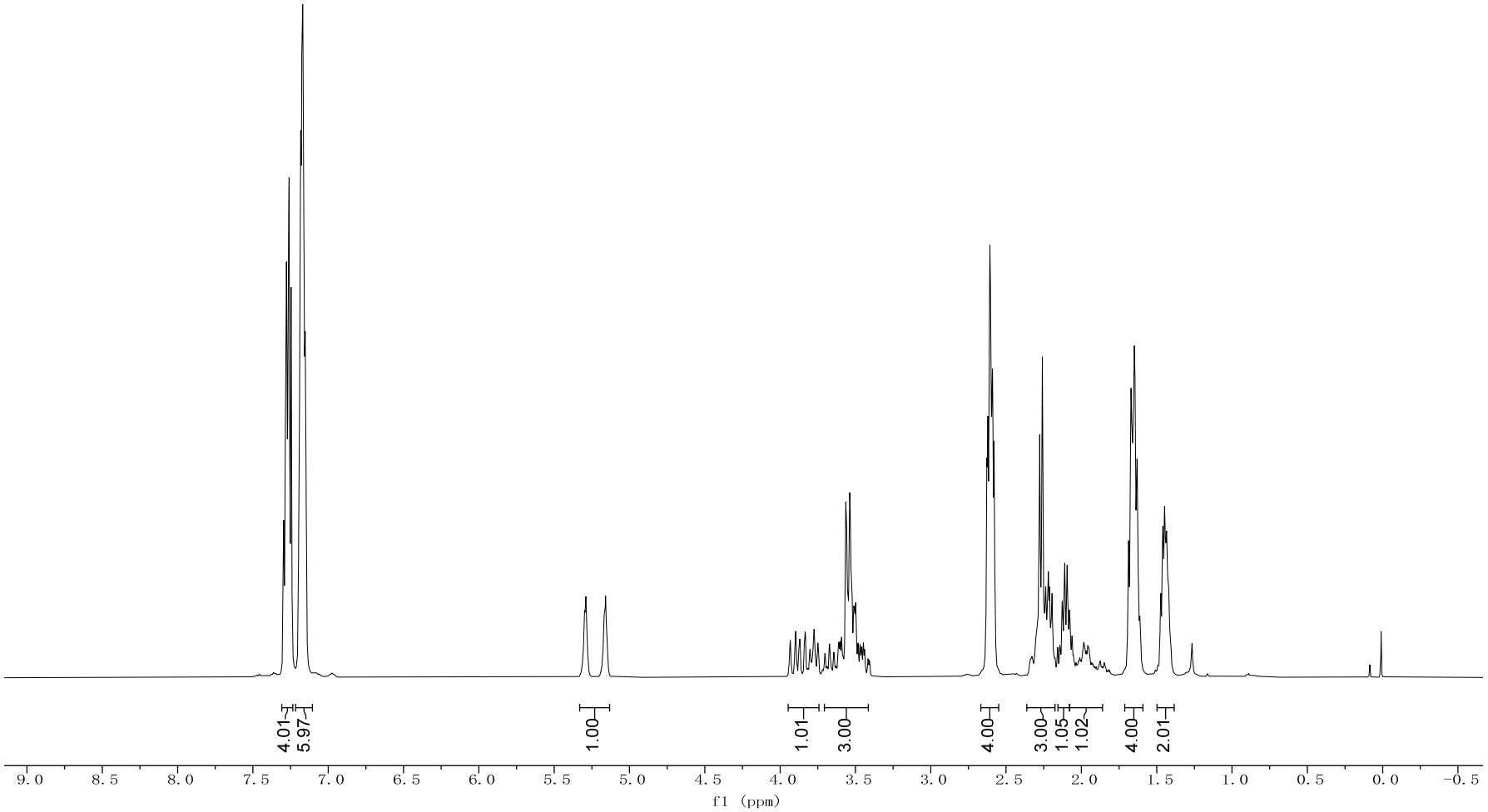


Figure 2B, entry 34
rotamers included



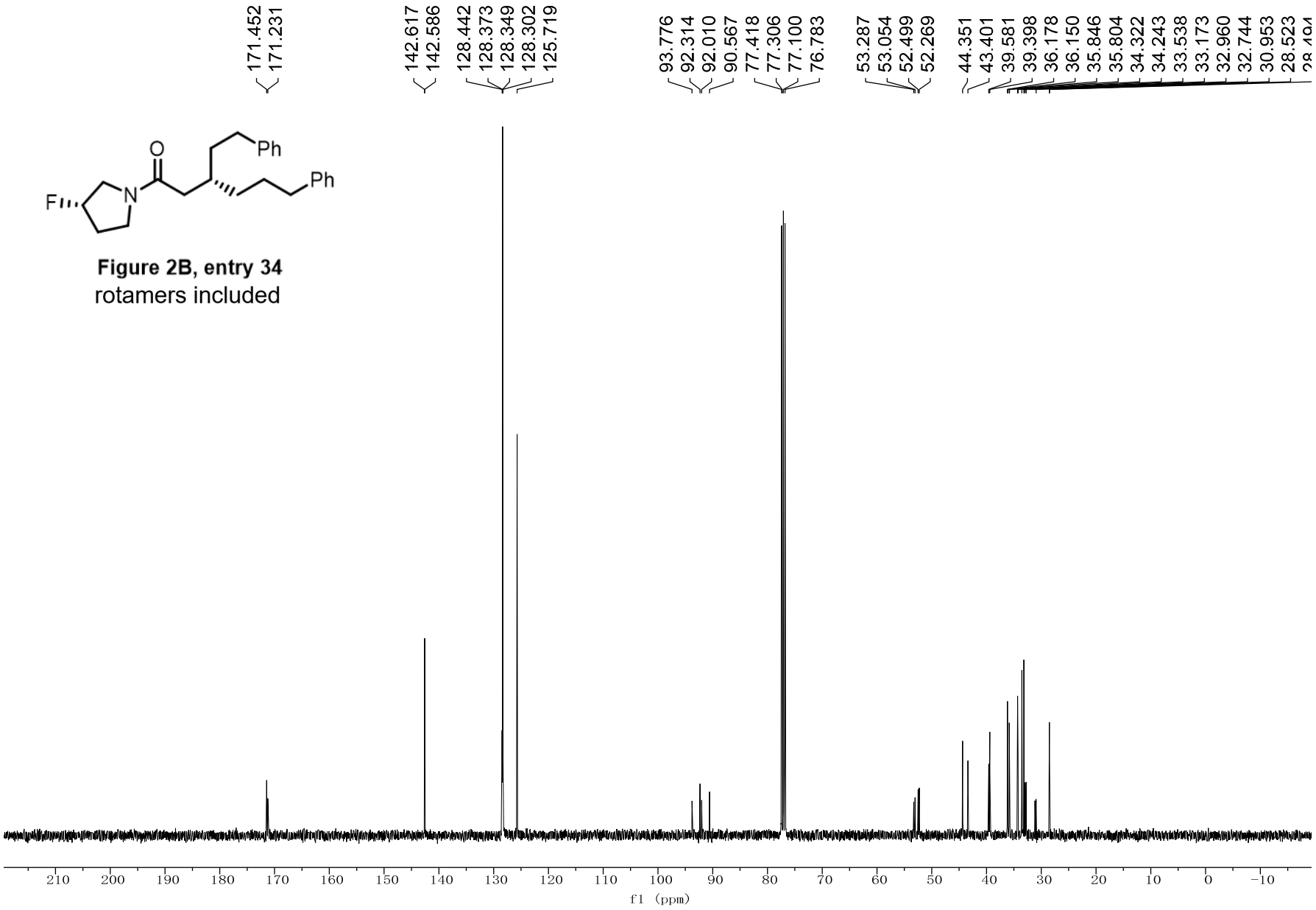


Figure 2B, entry 34
rotamers included

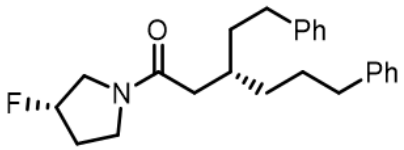


Figure 2B, entry 34
rotamers included

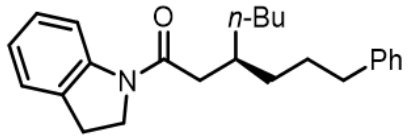
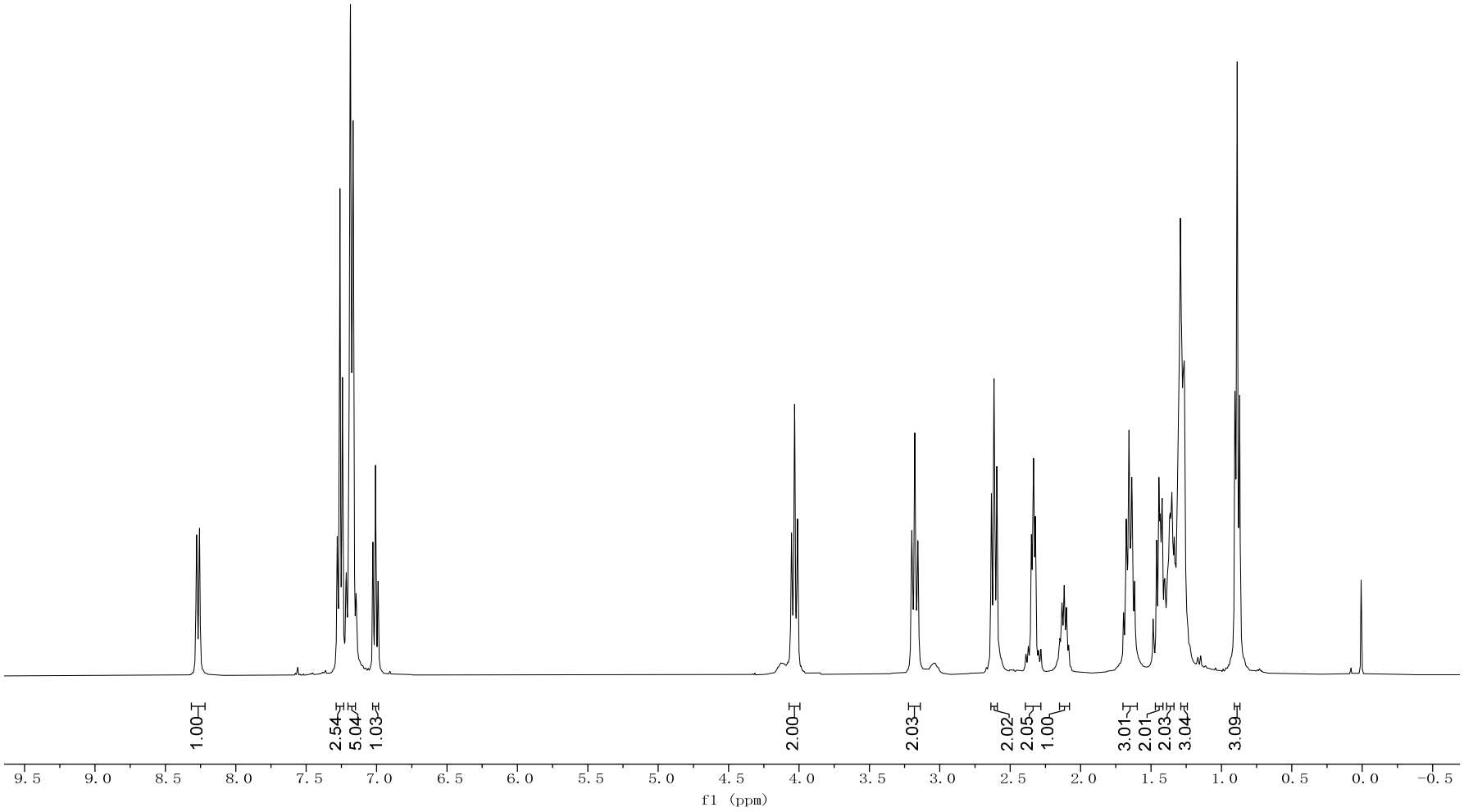


Figure 2B, entry 35
rotamers included



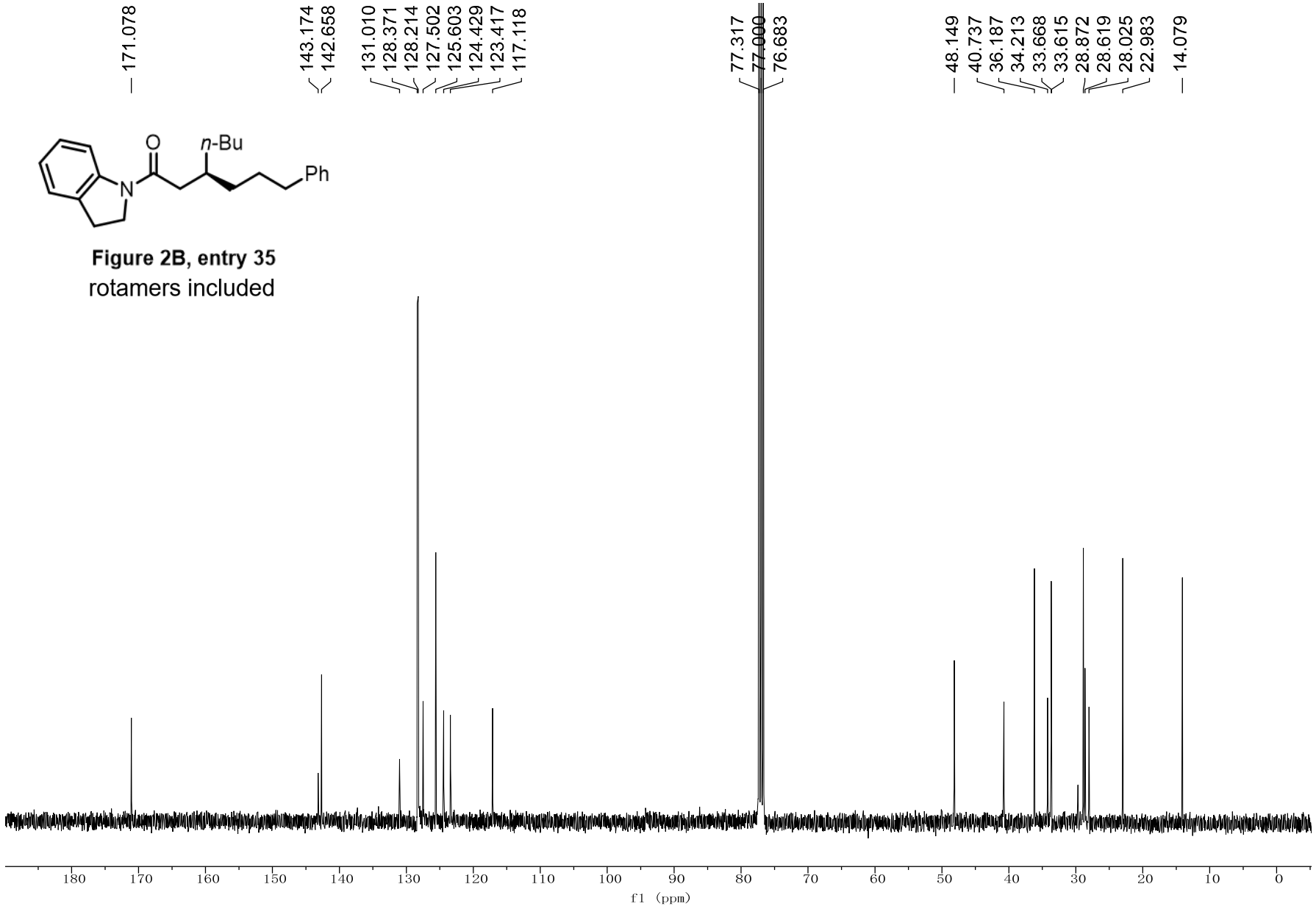


Figure 2B, entry 35
rotamers included

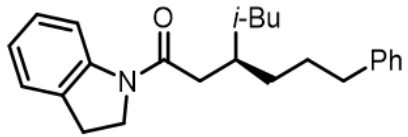
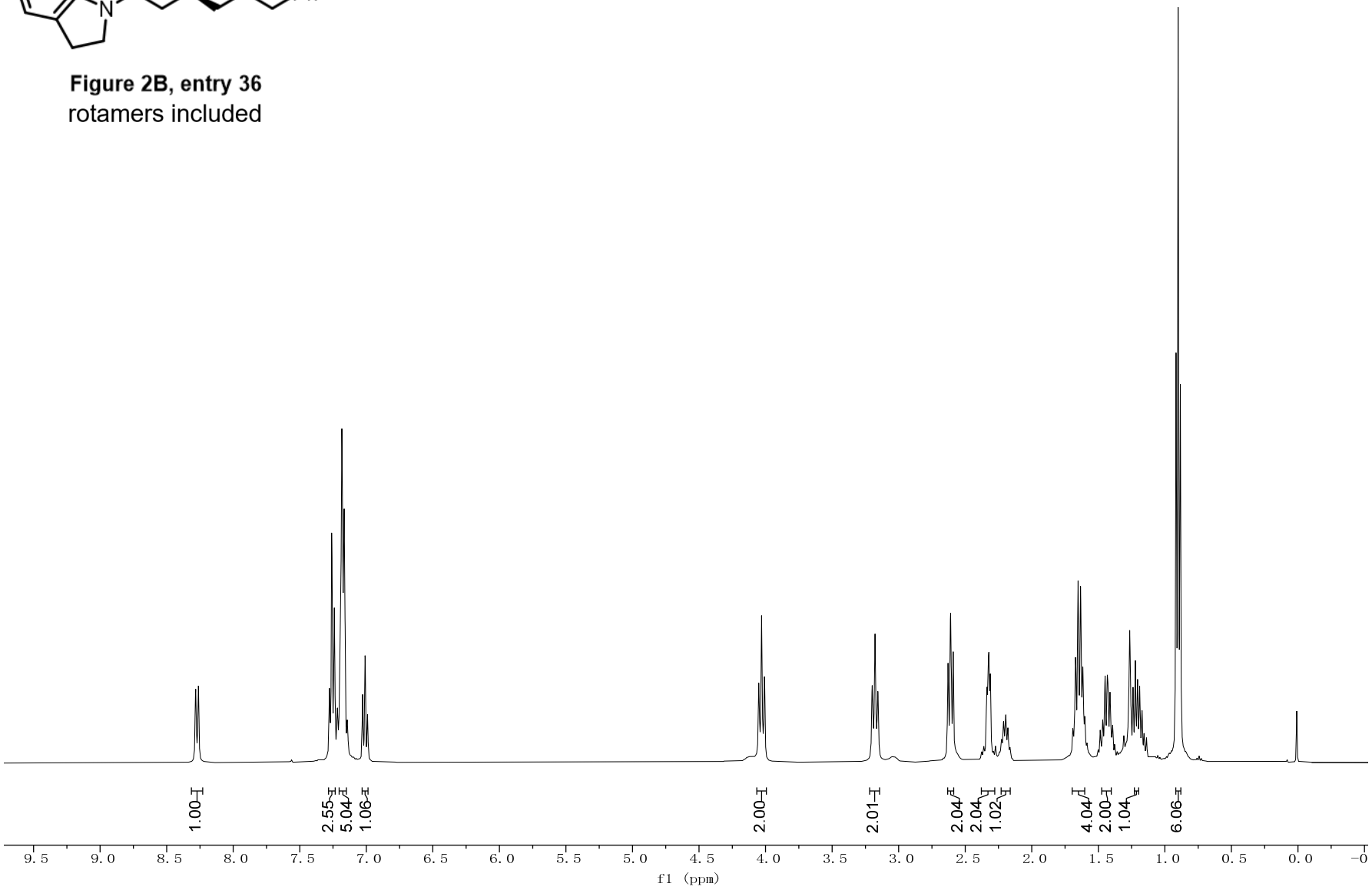


Figure 2B, entry 36
rotamers included



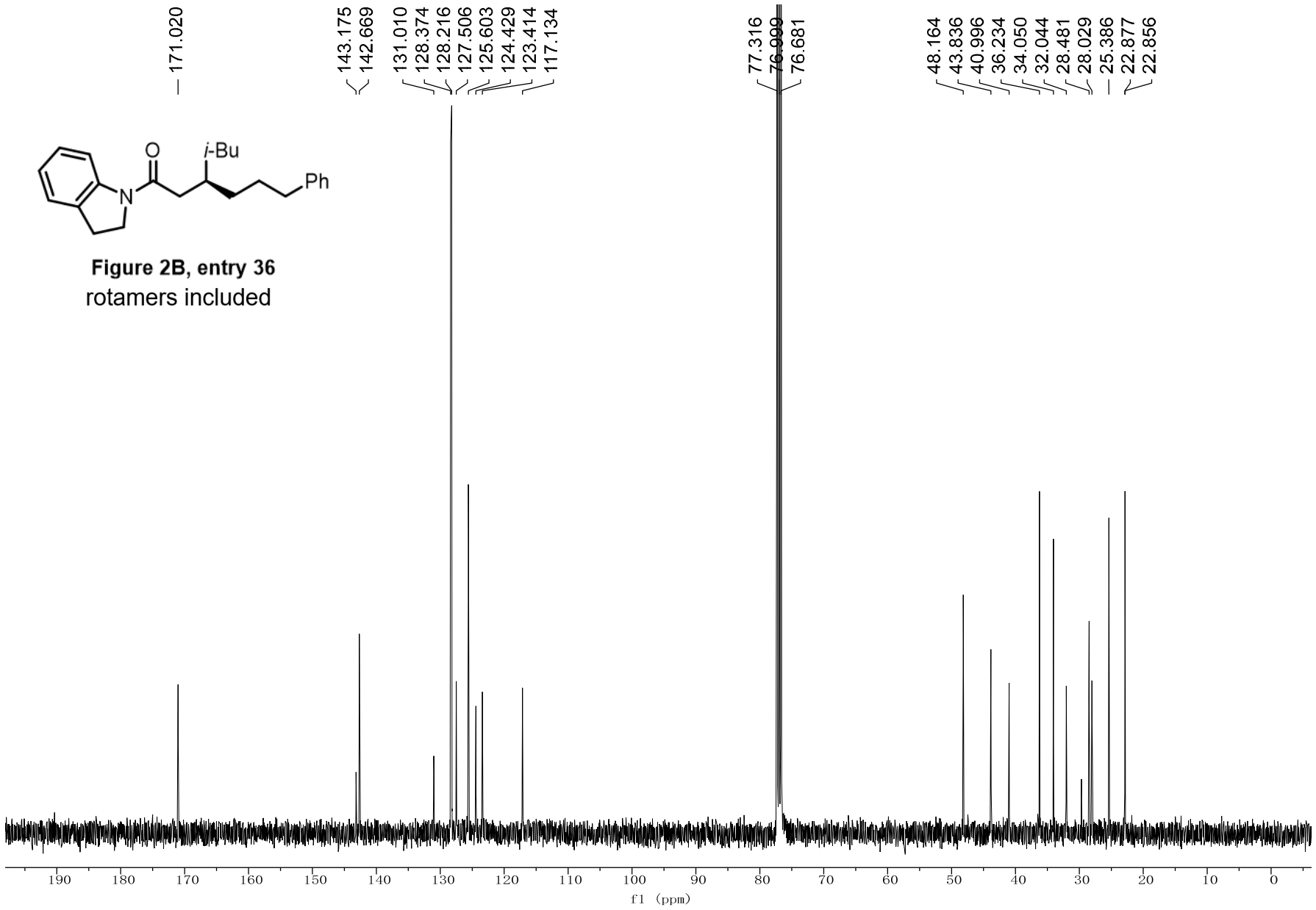


Figure 2B, entry 36
rotamers included

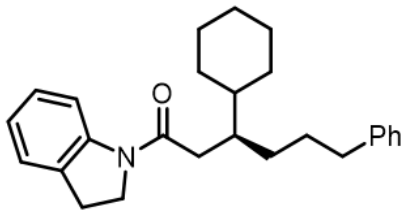


Figure 2B, entry 37
rotamers included

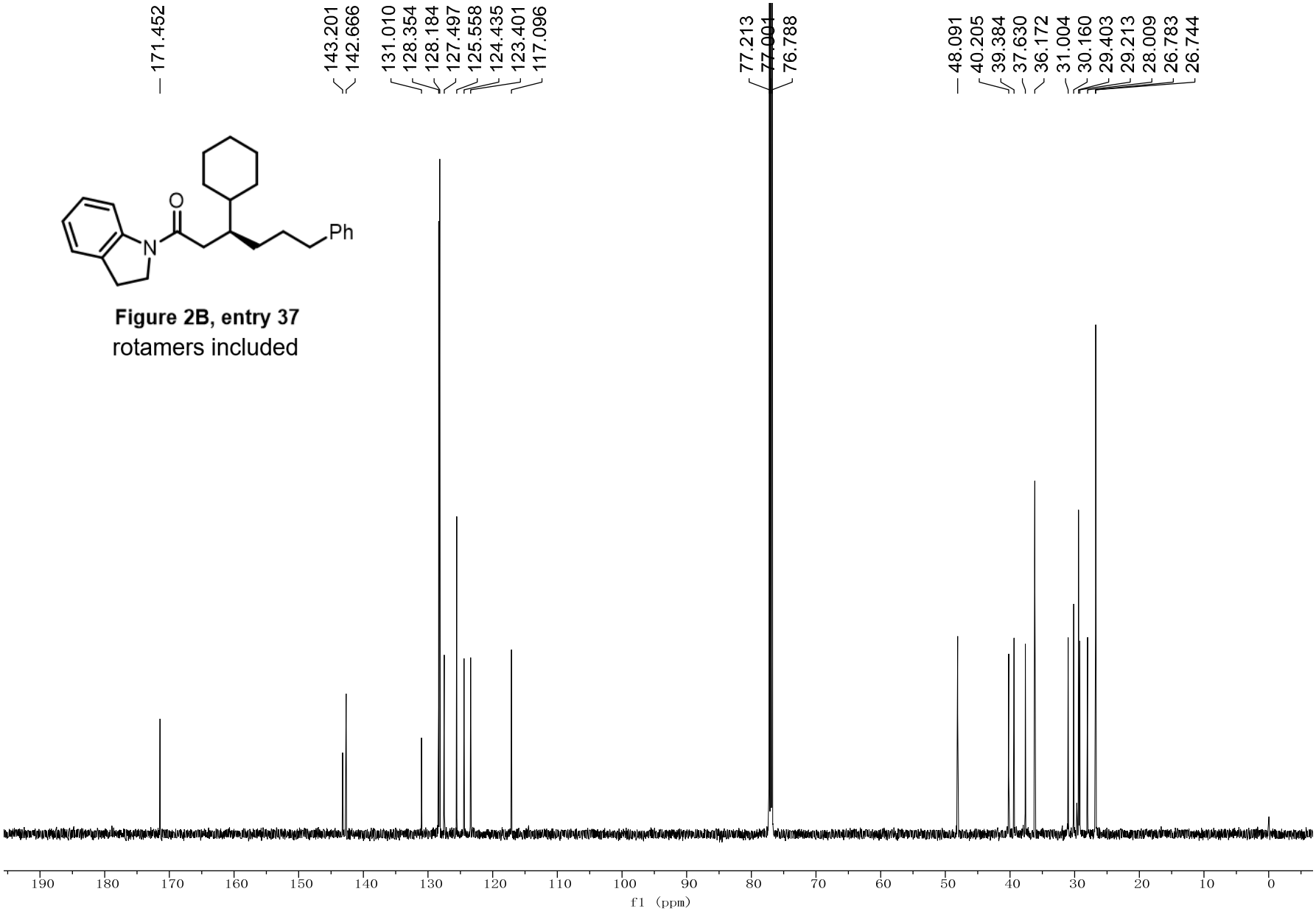


Figure 2B, entry 37
rotamers included

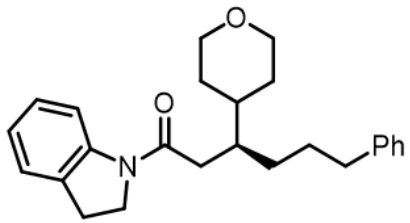
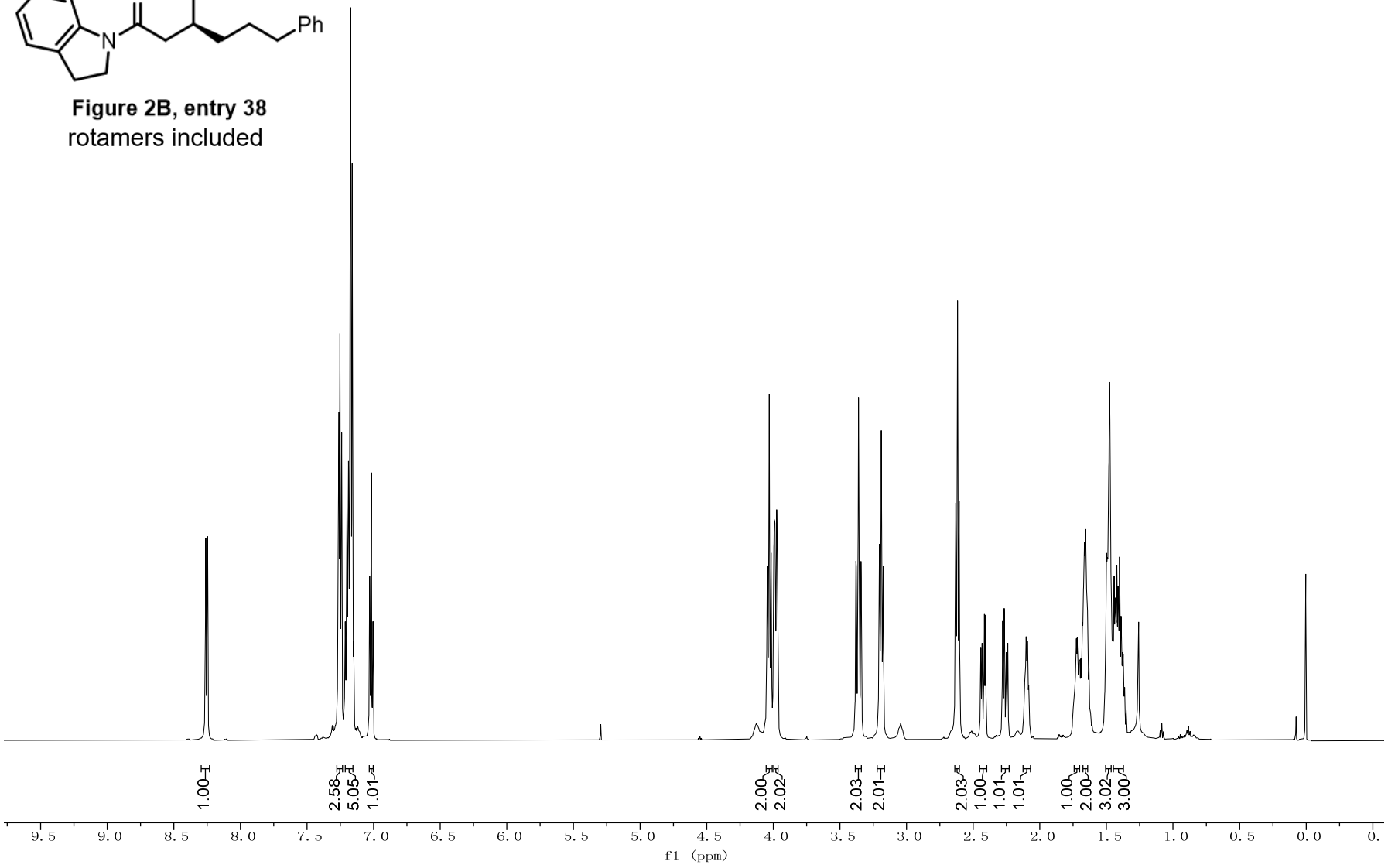


Figure 2B, entry 38
rotamers included



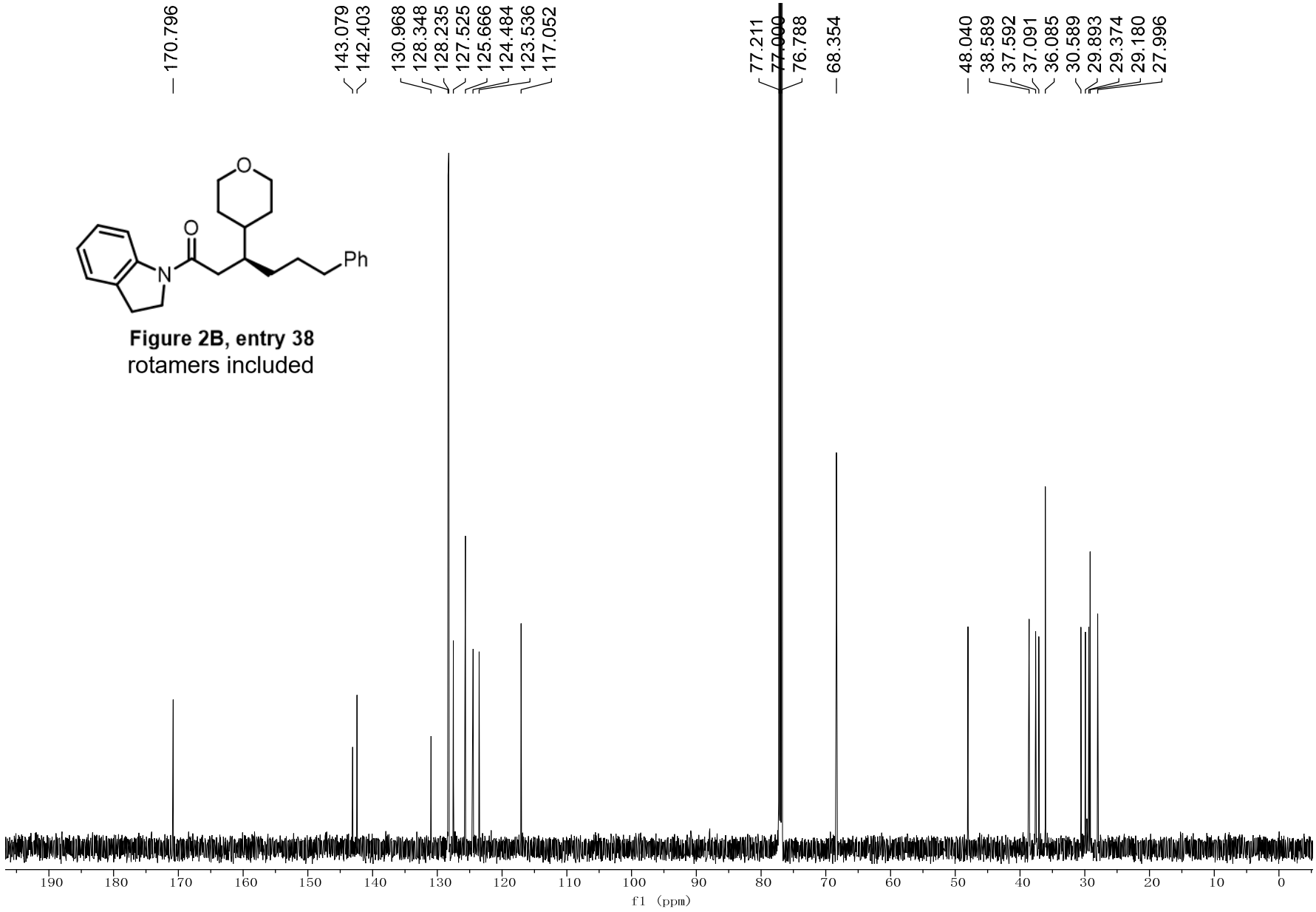


Figure 2B, entry 38
rotamers included

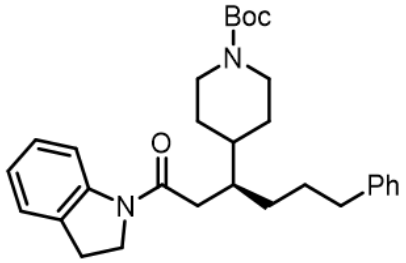
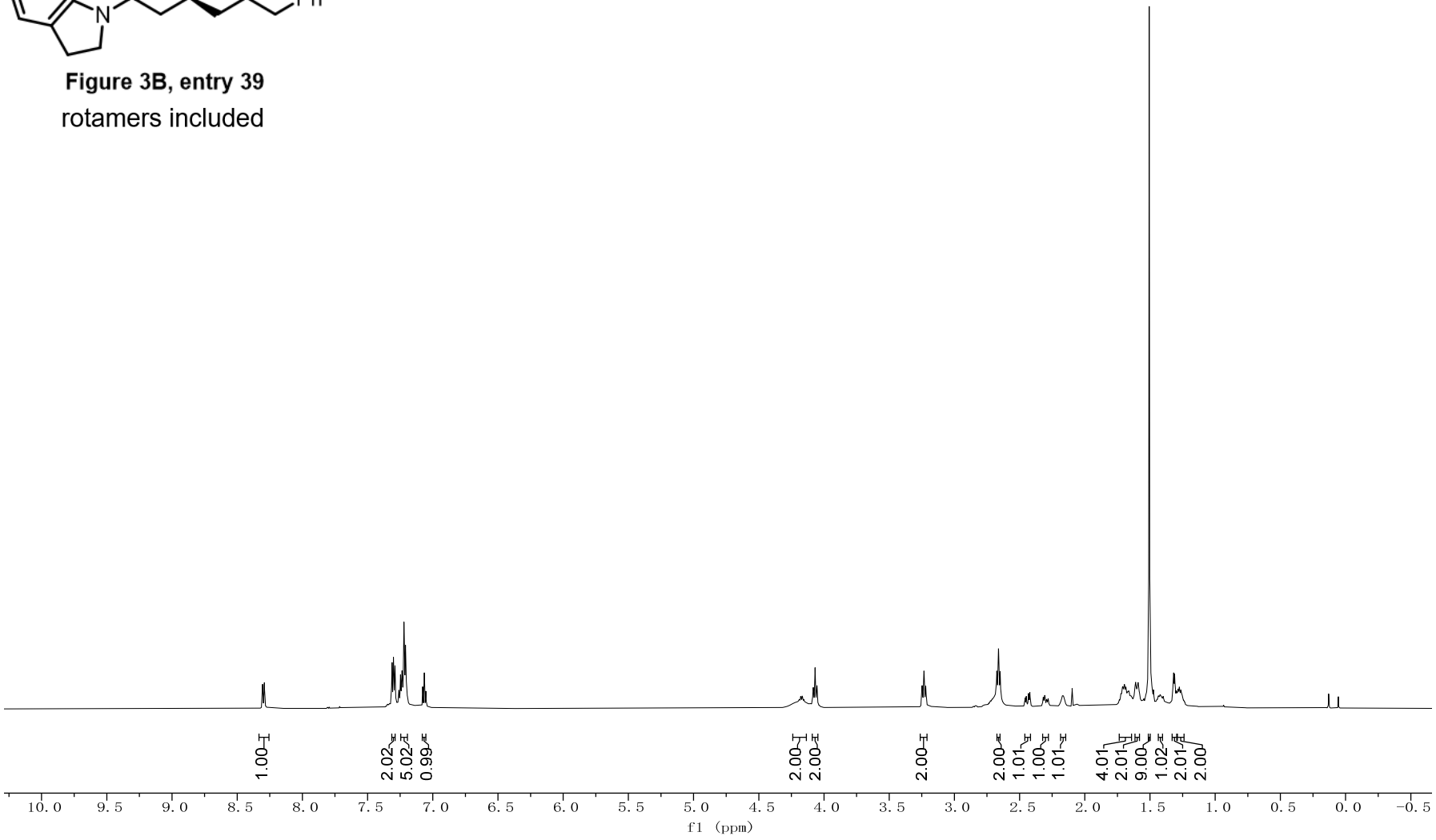


Figure 3B, entry 39

rotamers included



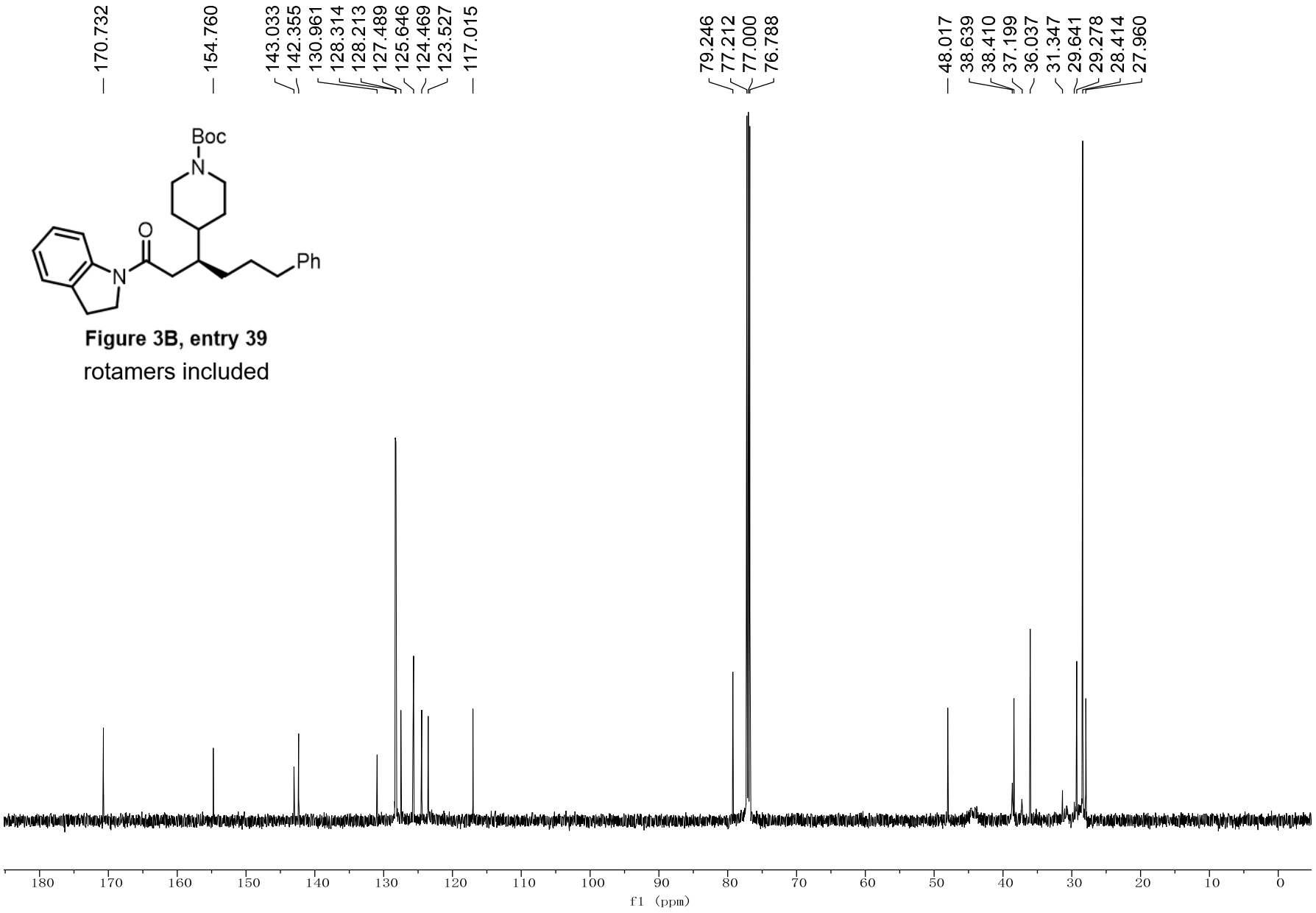


Figure 3B, entry 39

rotamers included

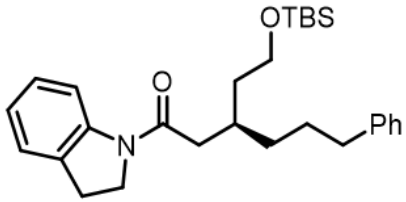


Figure 2B, entry 40

rotamers included

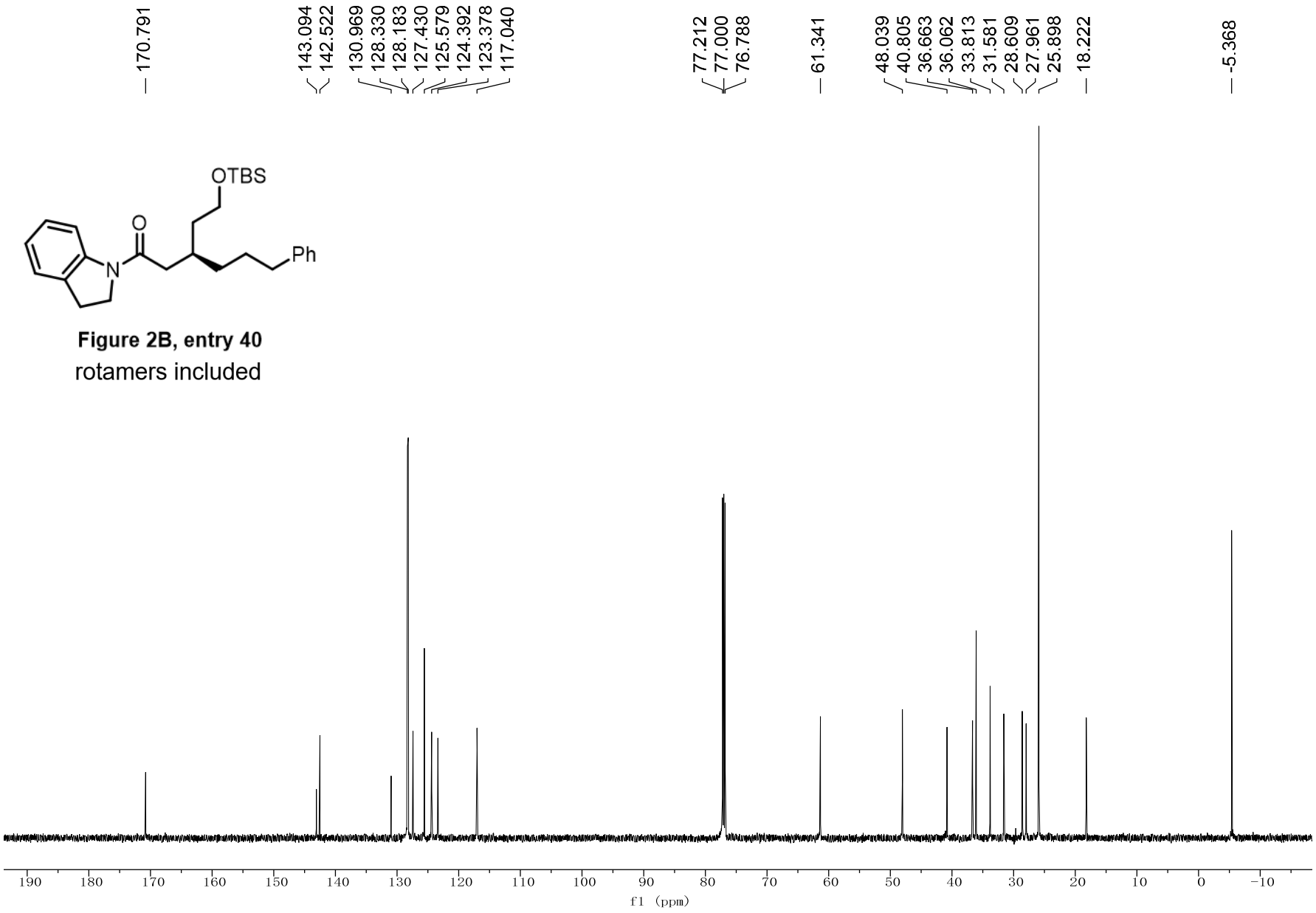


Figure 2B, entry 40
rotamers included

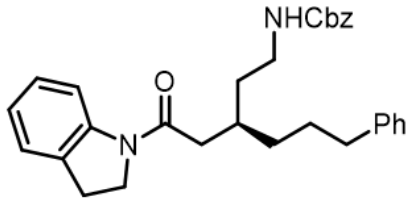
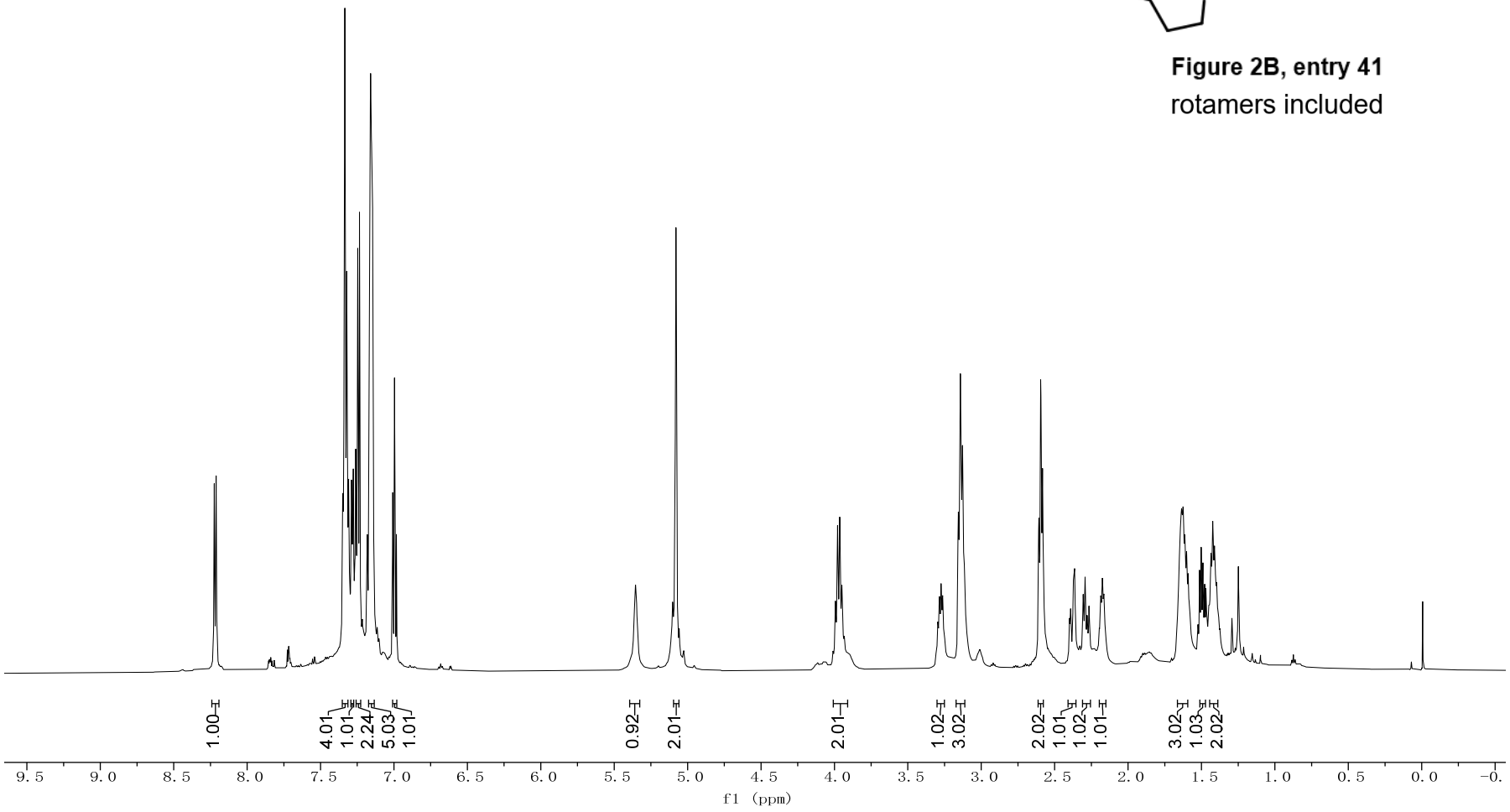


Figure 2B, entry 41
rotamers included



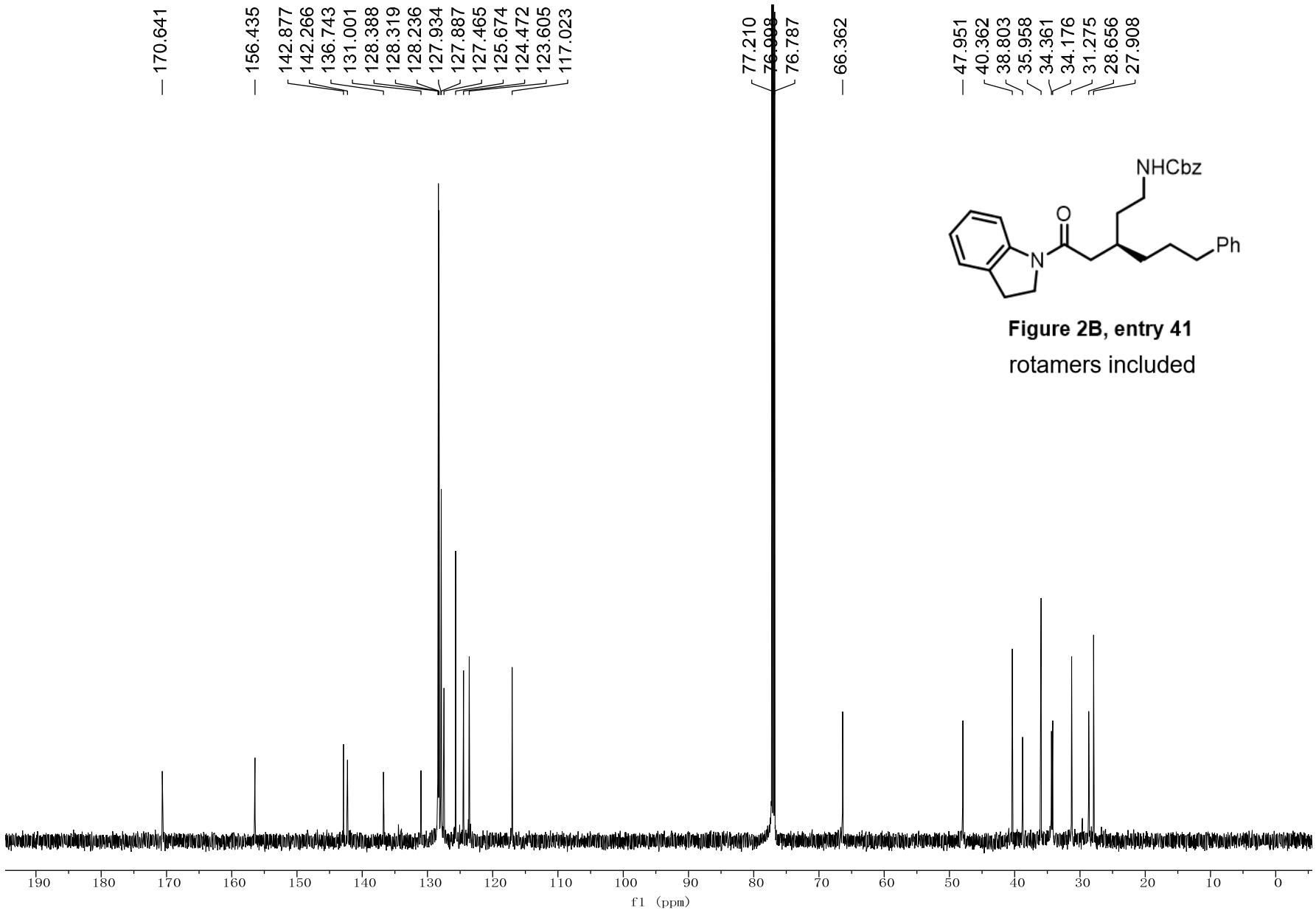


Figure 2B, entry 41

rotamers included

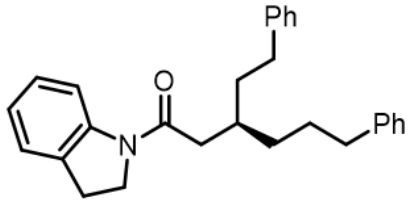
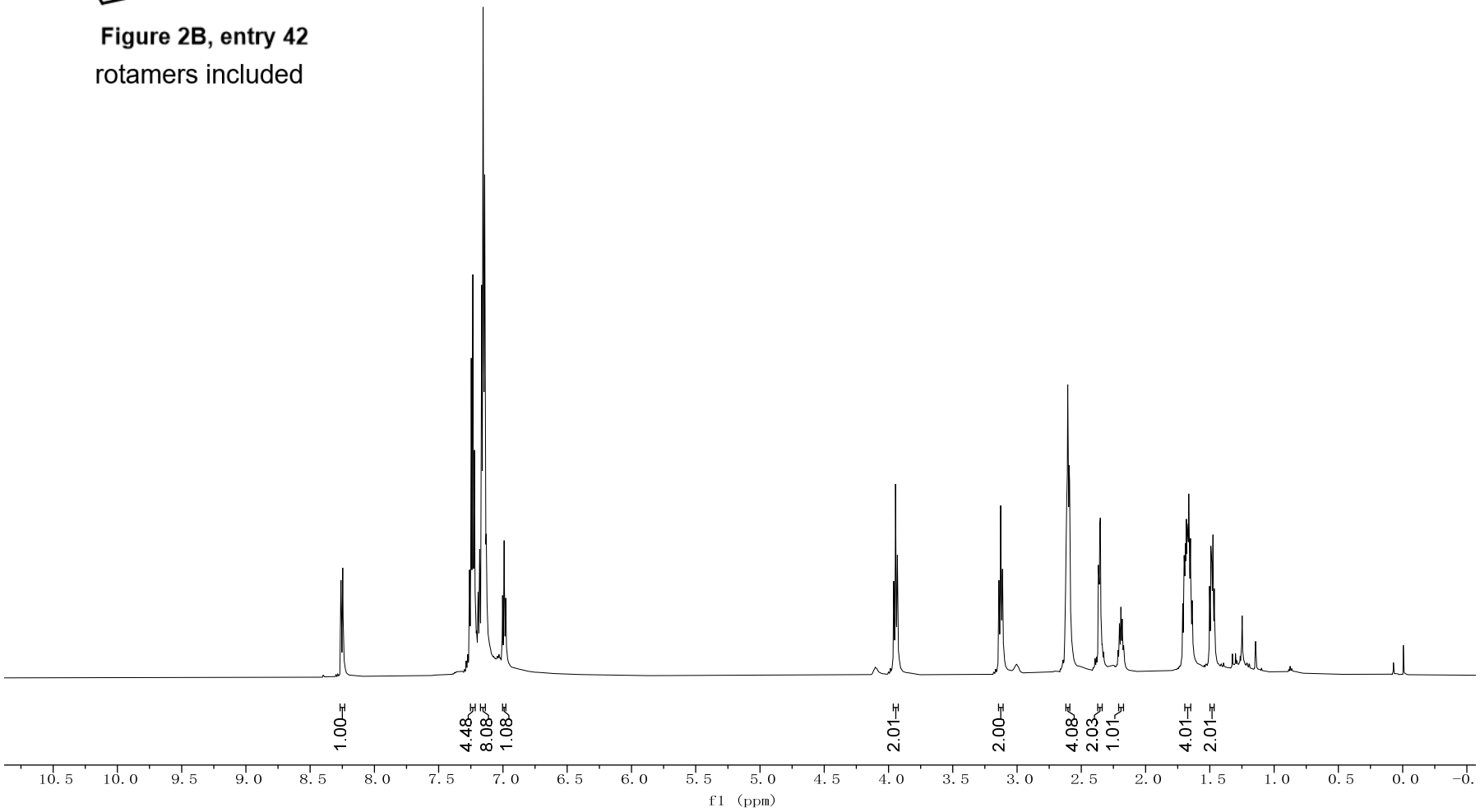


Figure 2B, entry 42

rotamers included



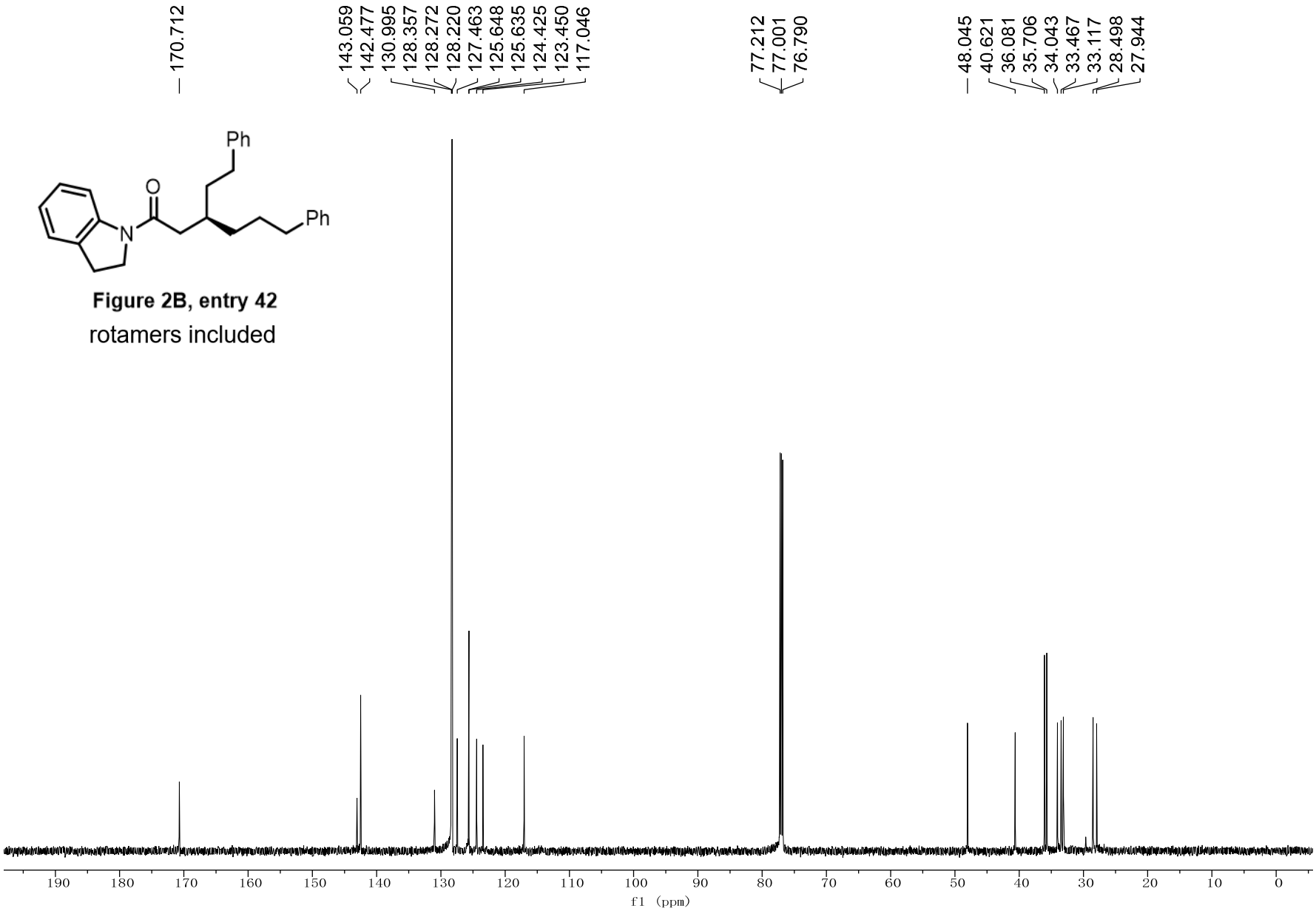


Figure 2B, entry 42

rotamers included

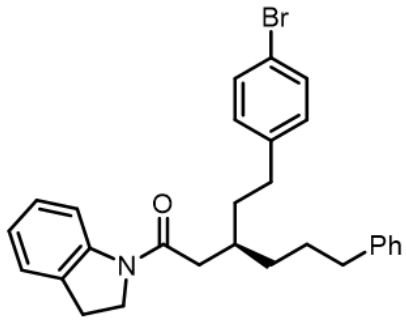
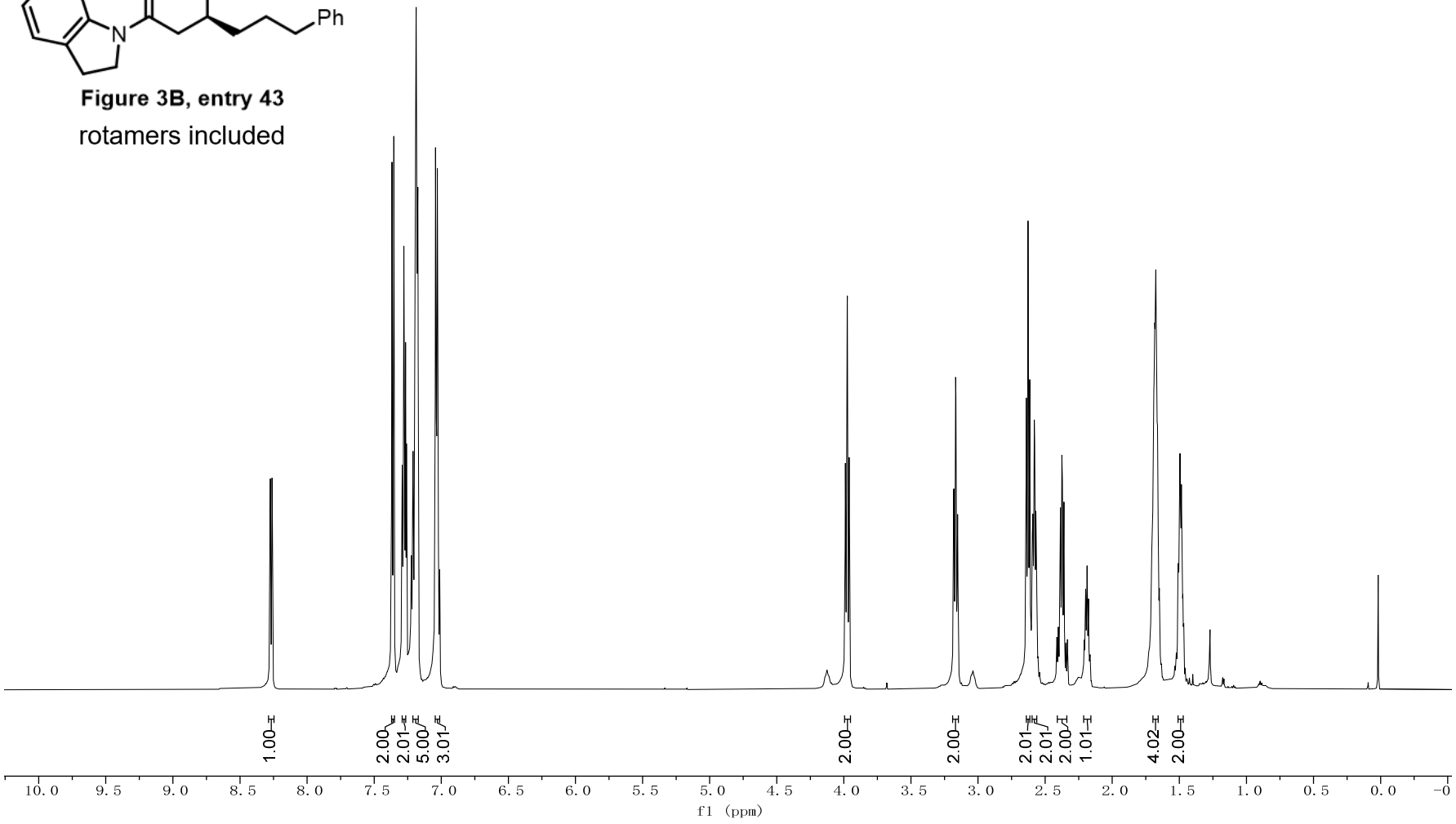


Figure 3B, entry 43

rotamers included



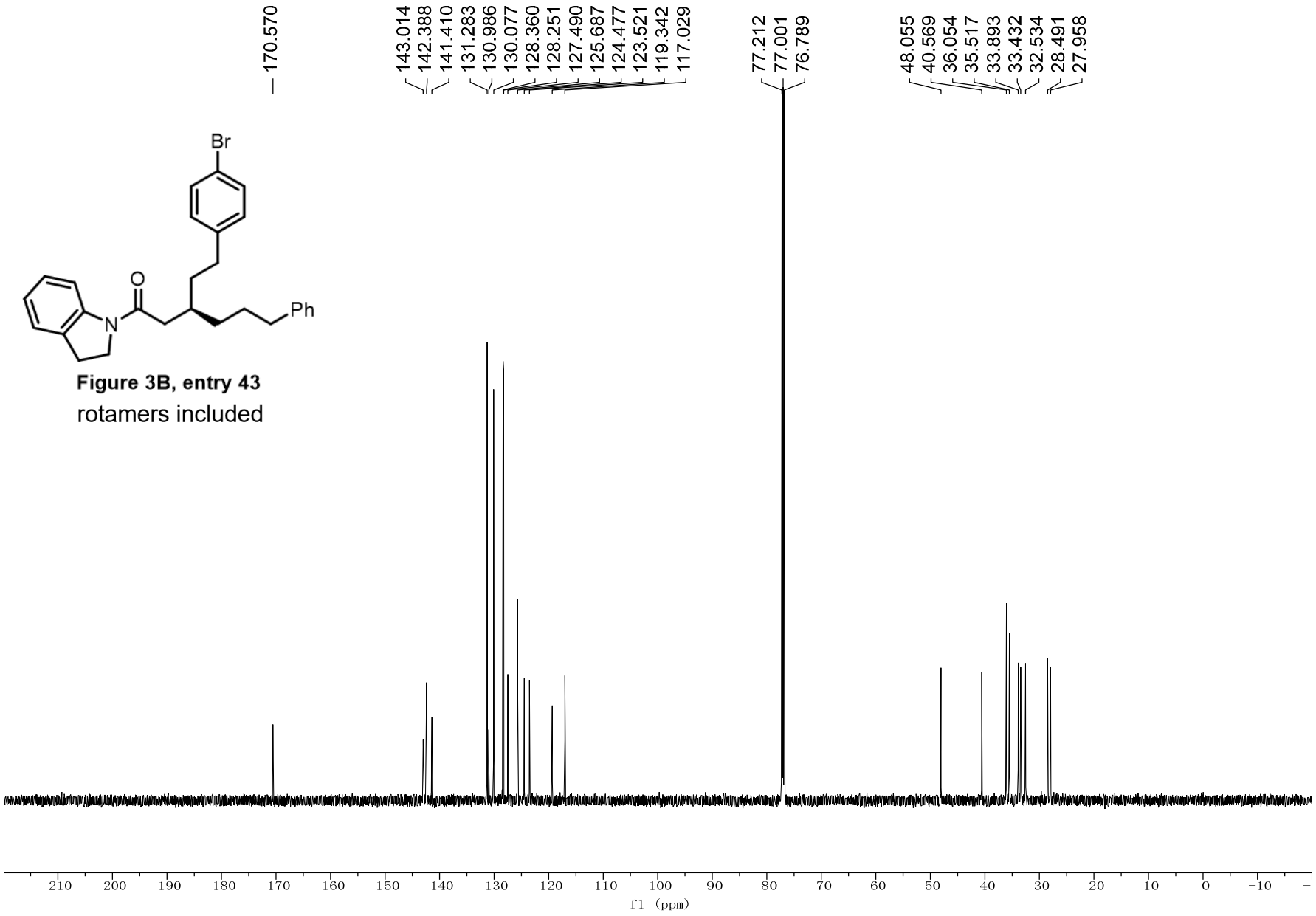


Figure 3B, entry 43

rotamers included

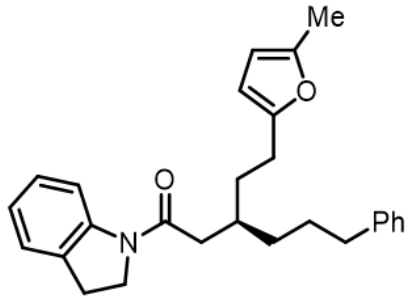


Figure 2B, entry 44

rotamers included

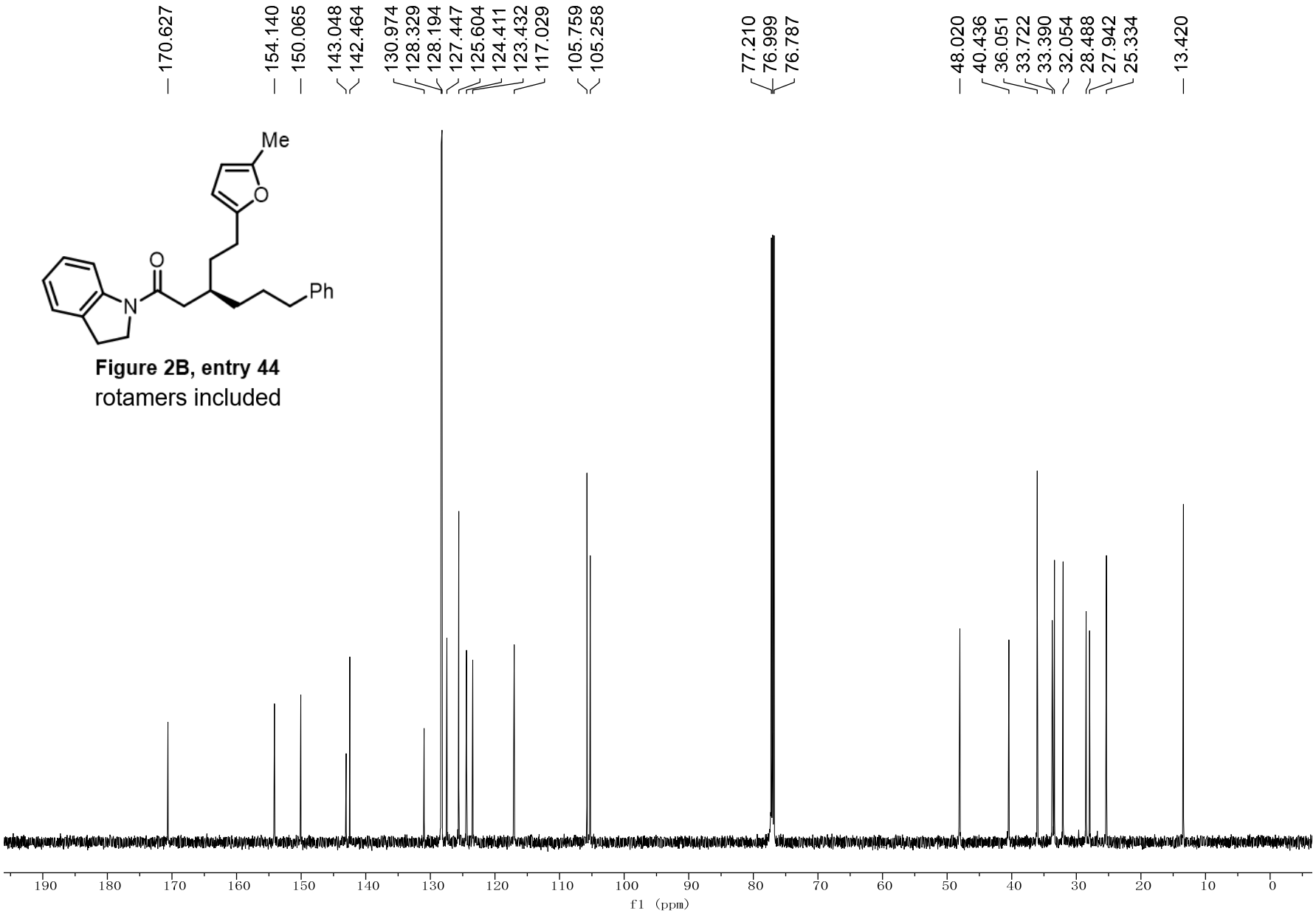


Figure 2B, entry 44
rotamers included

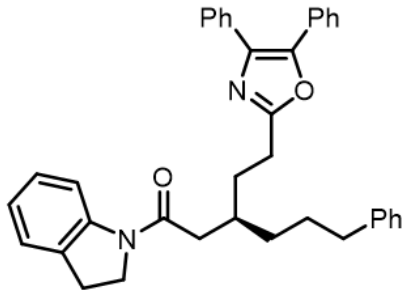
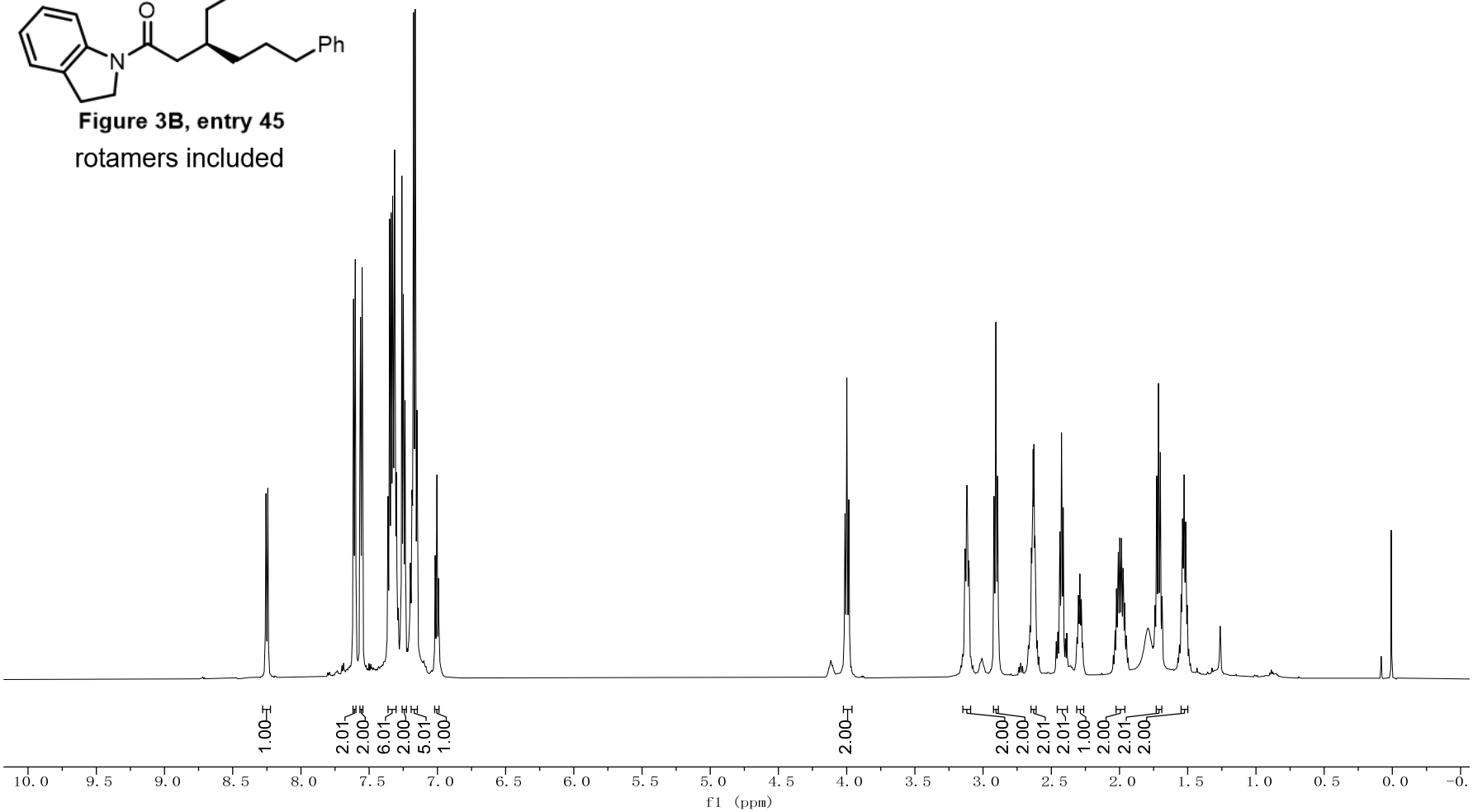


Figure 3B, entry 45

rotamers included



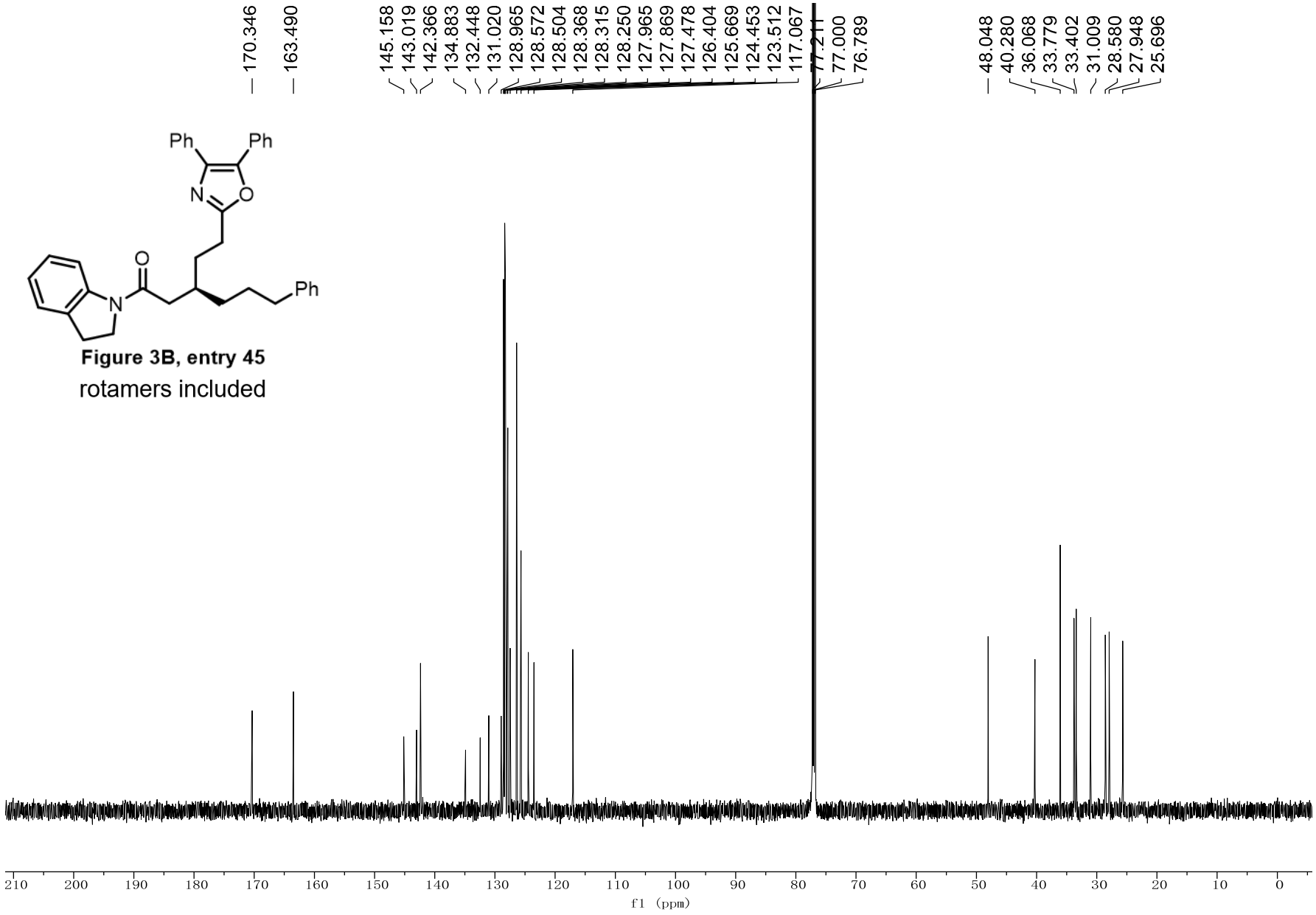


Figure 3B, entry 45

rotamers included

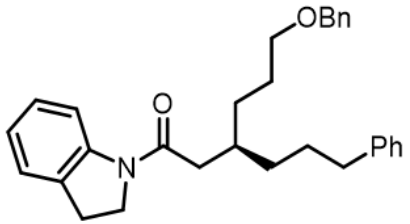
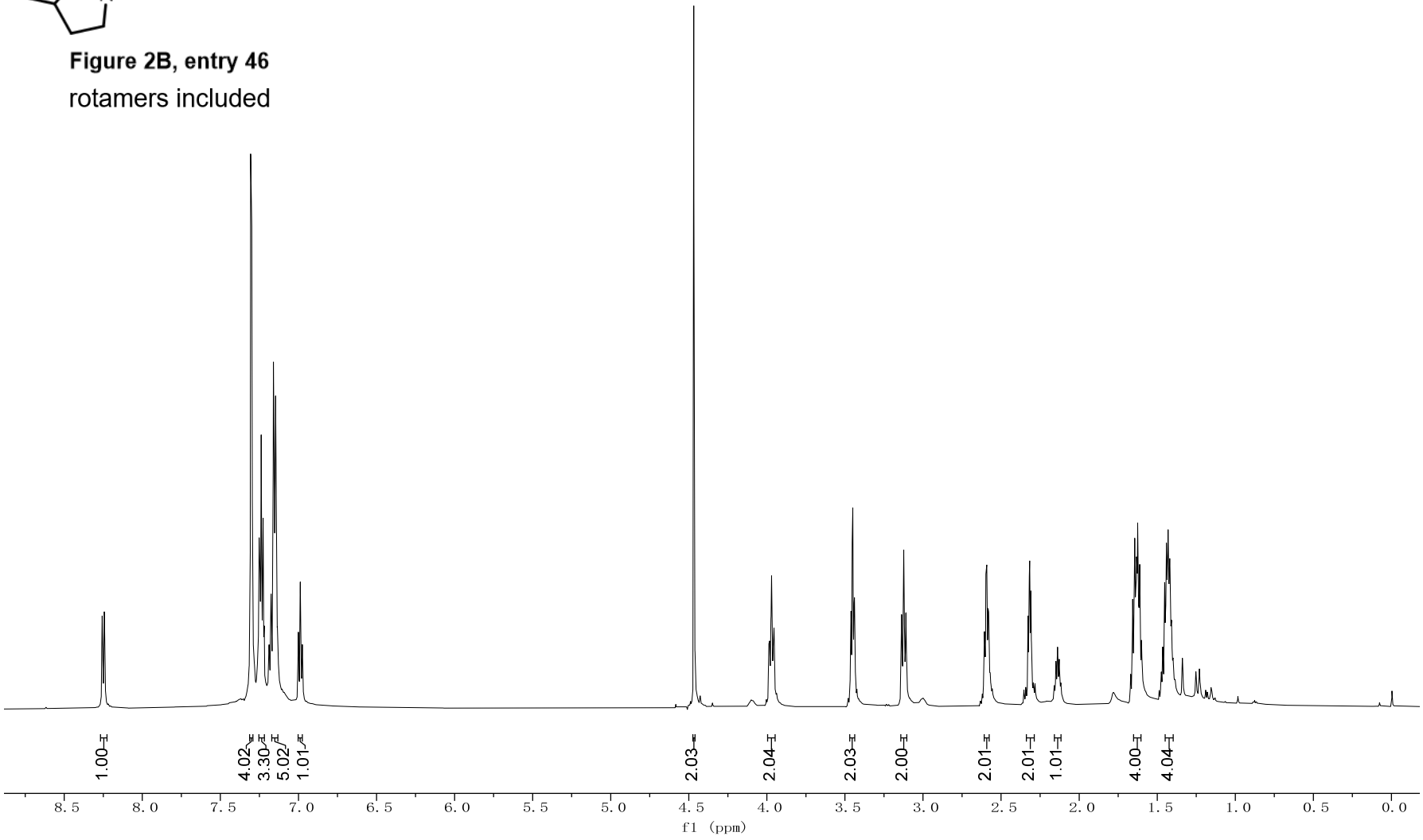


Figure 2B, entry 46

rotamers included



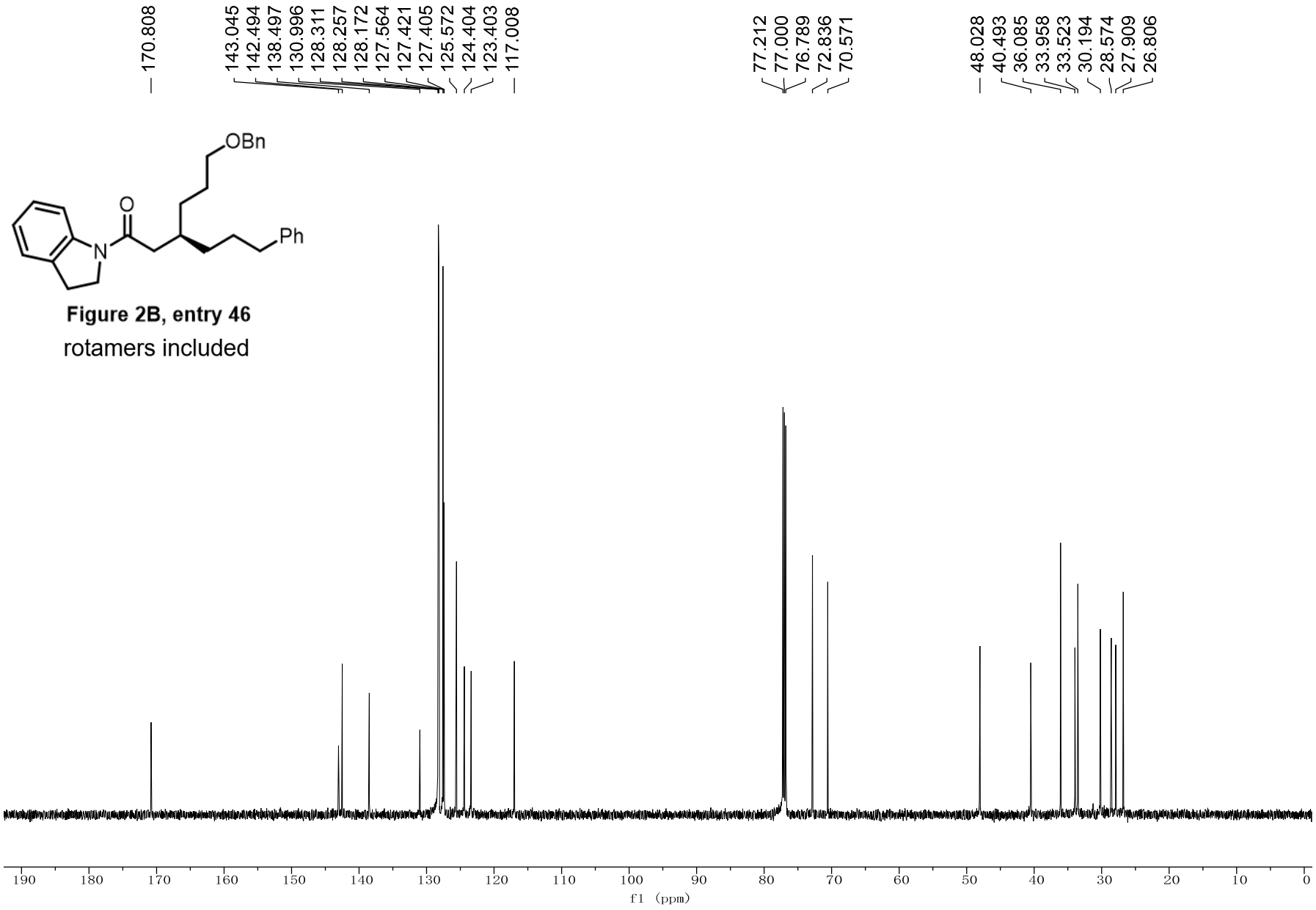


Figure 2B, entry 46

rotamers included

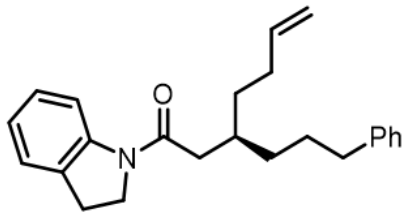
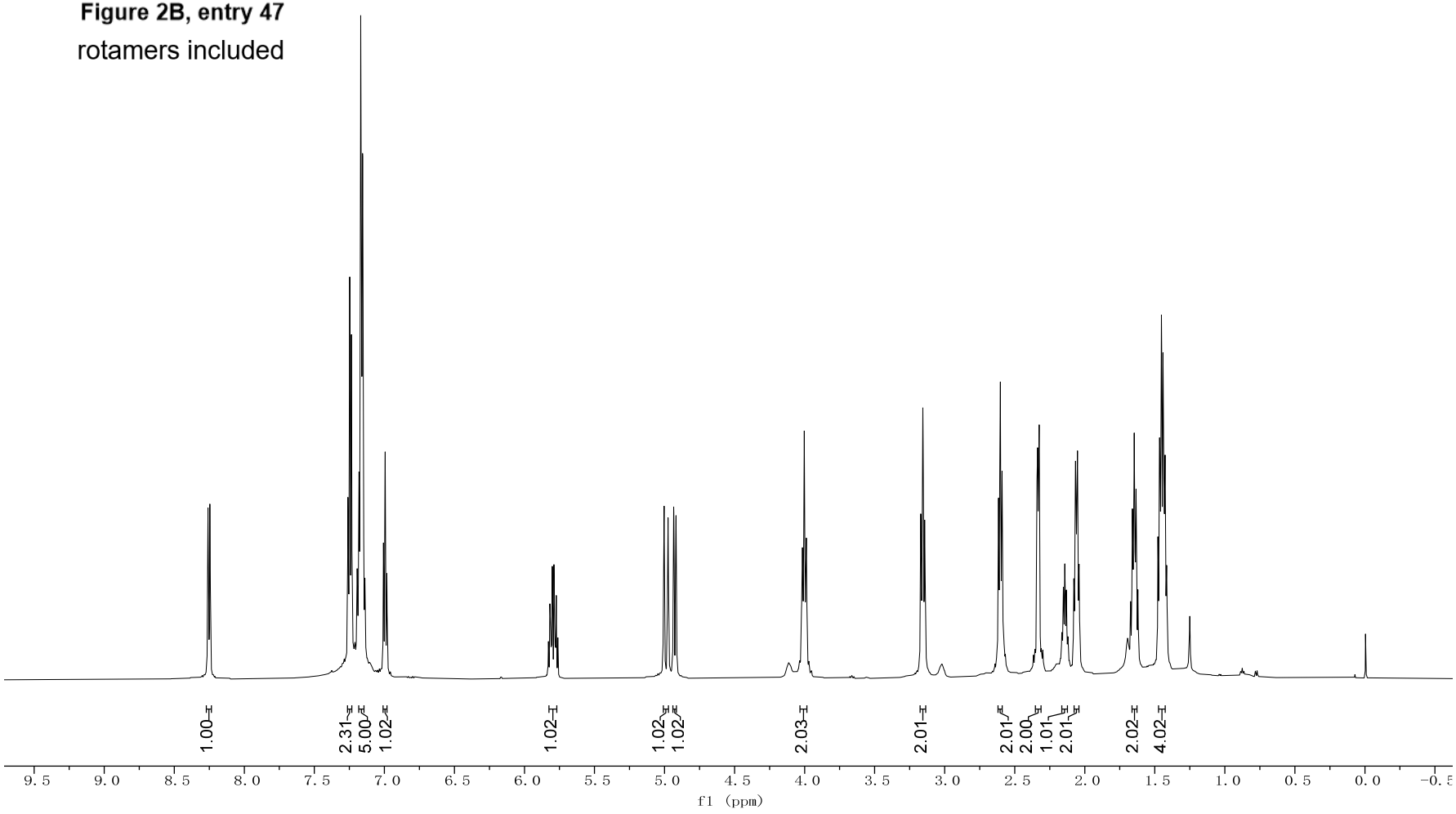


Figure 2B, entry 47

rotamers included



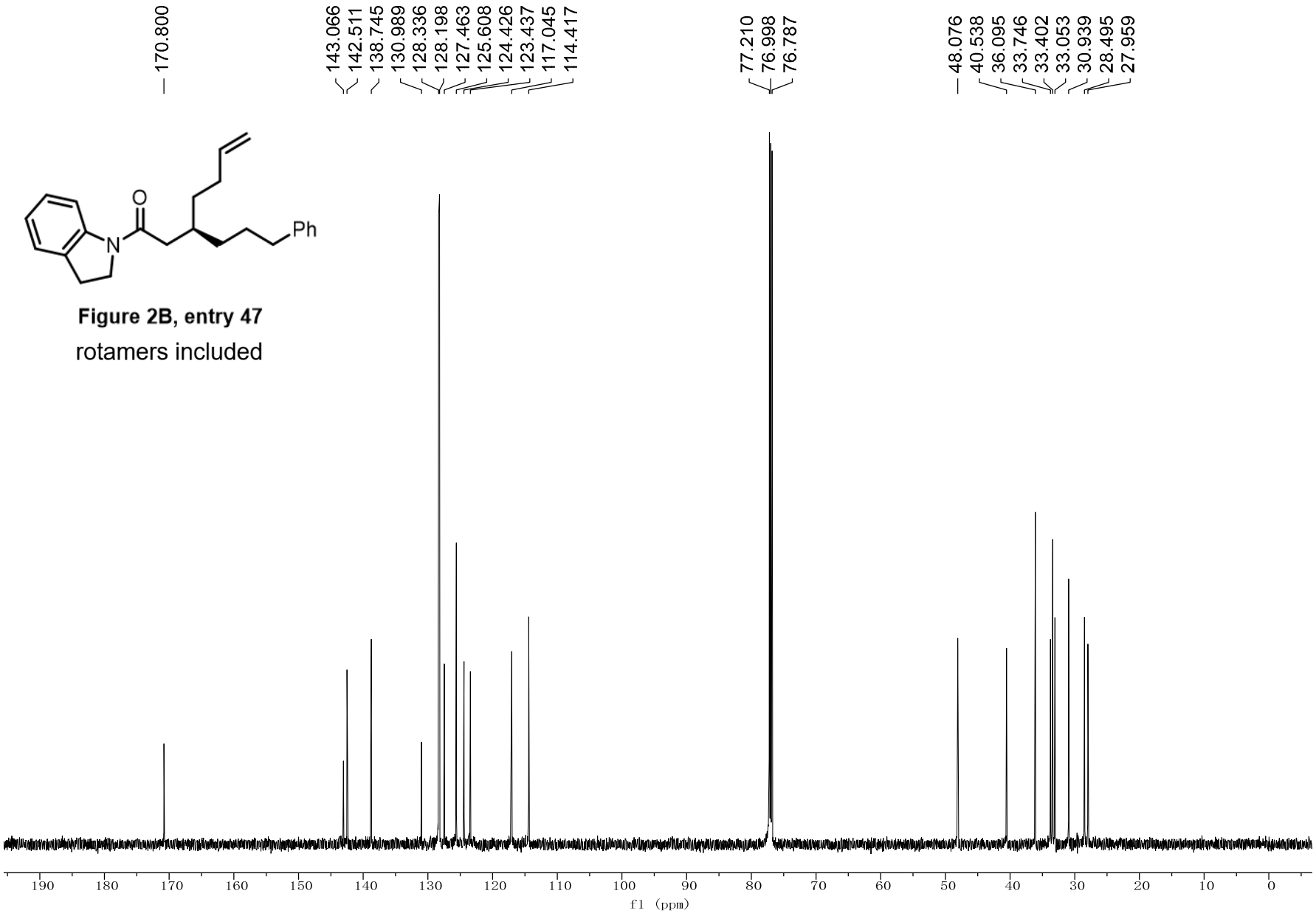


Figure 2B, entry 47

rotamers included

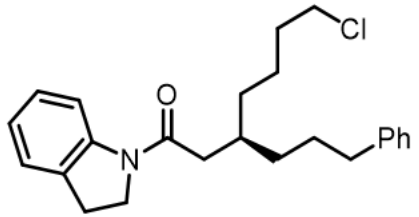
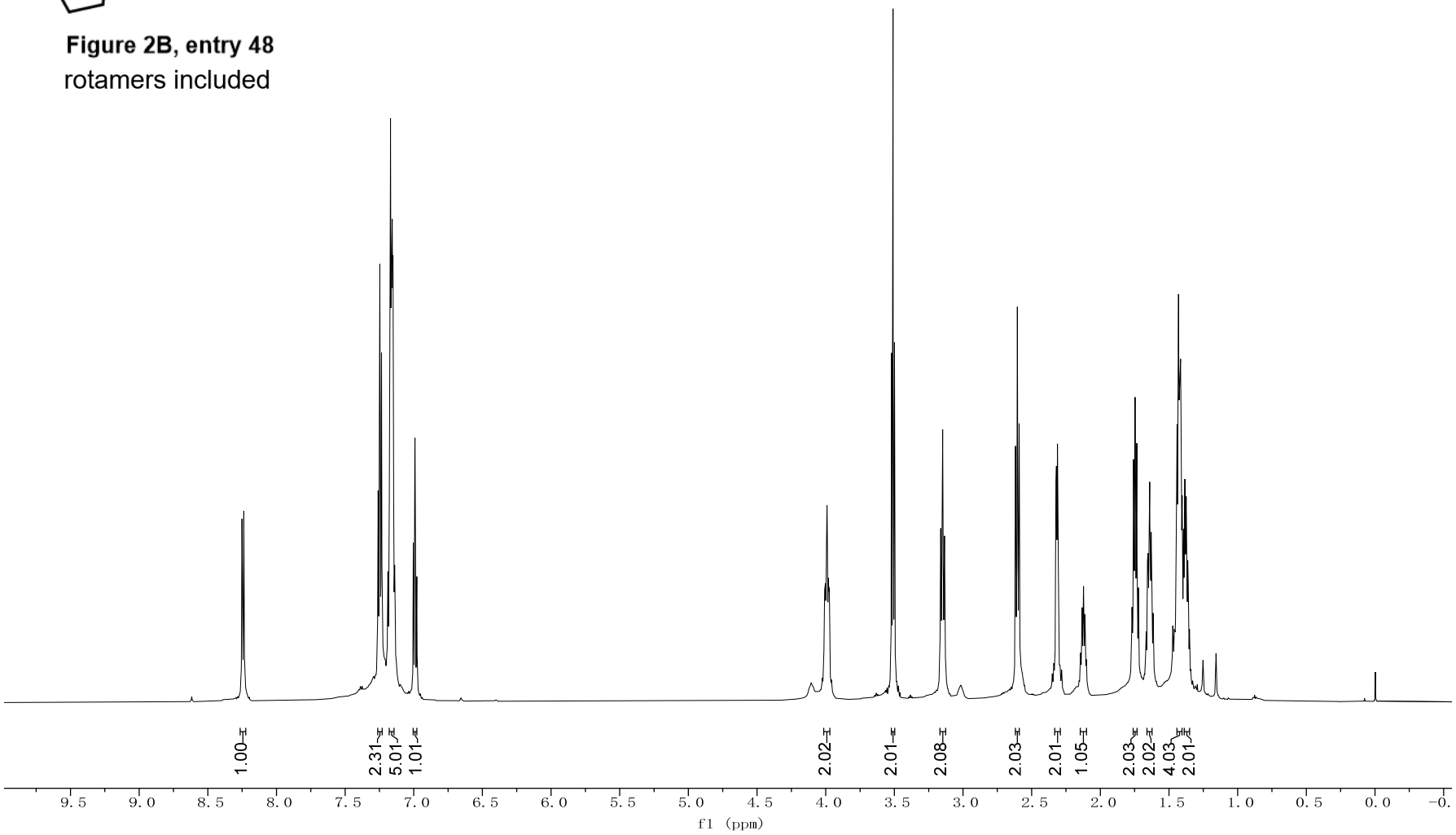


Figure 2B, entry 48
rotamers included



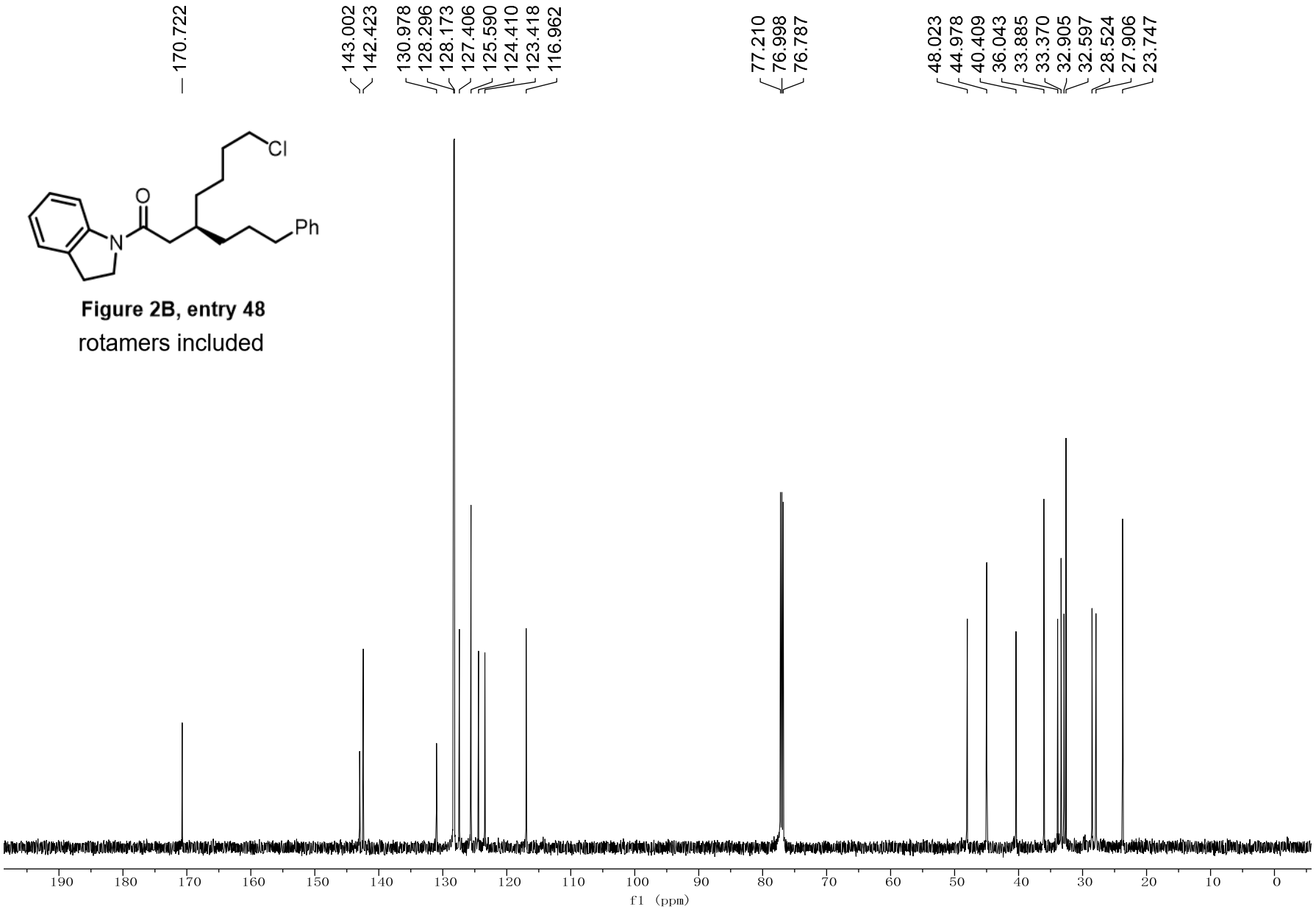


Figure 2B, entry 48

rotamers included

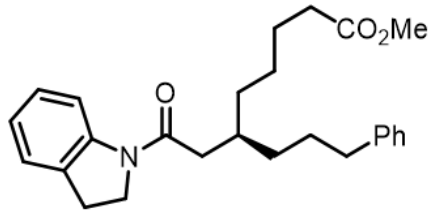


Figure 2B, entry 49

rotamers included

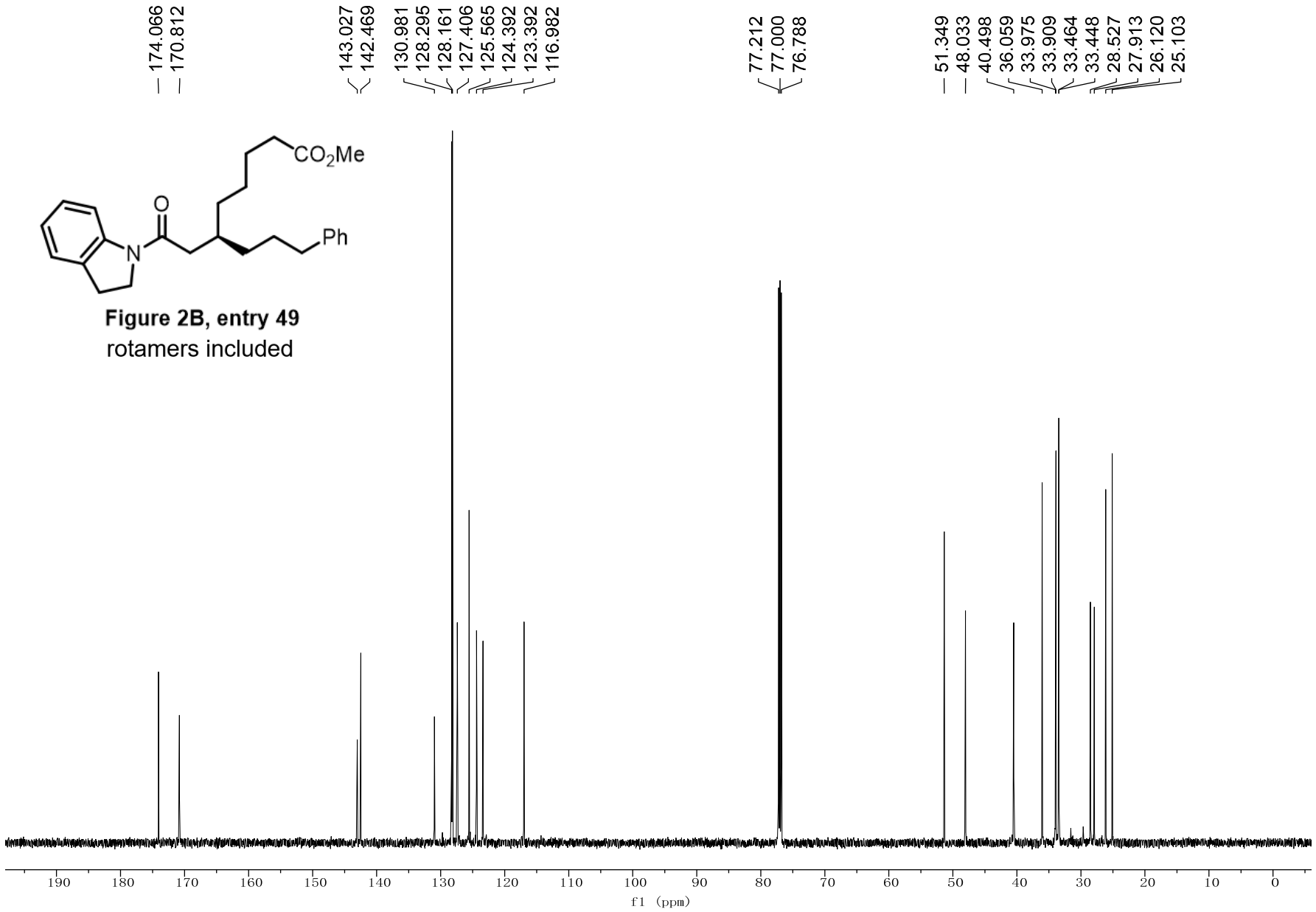


Figure 2B, entry 49
rotamers included

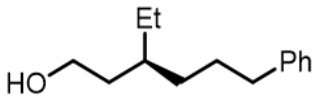
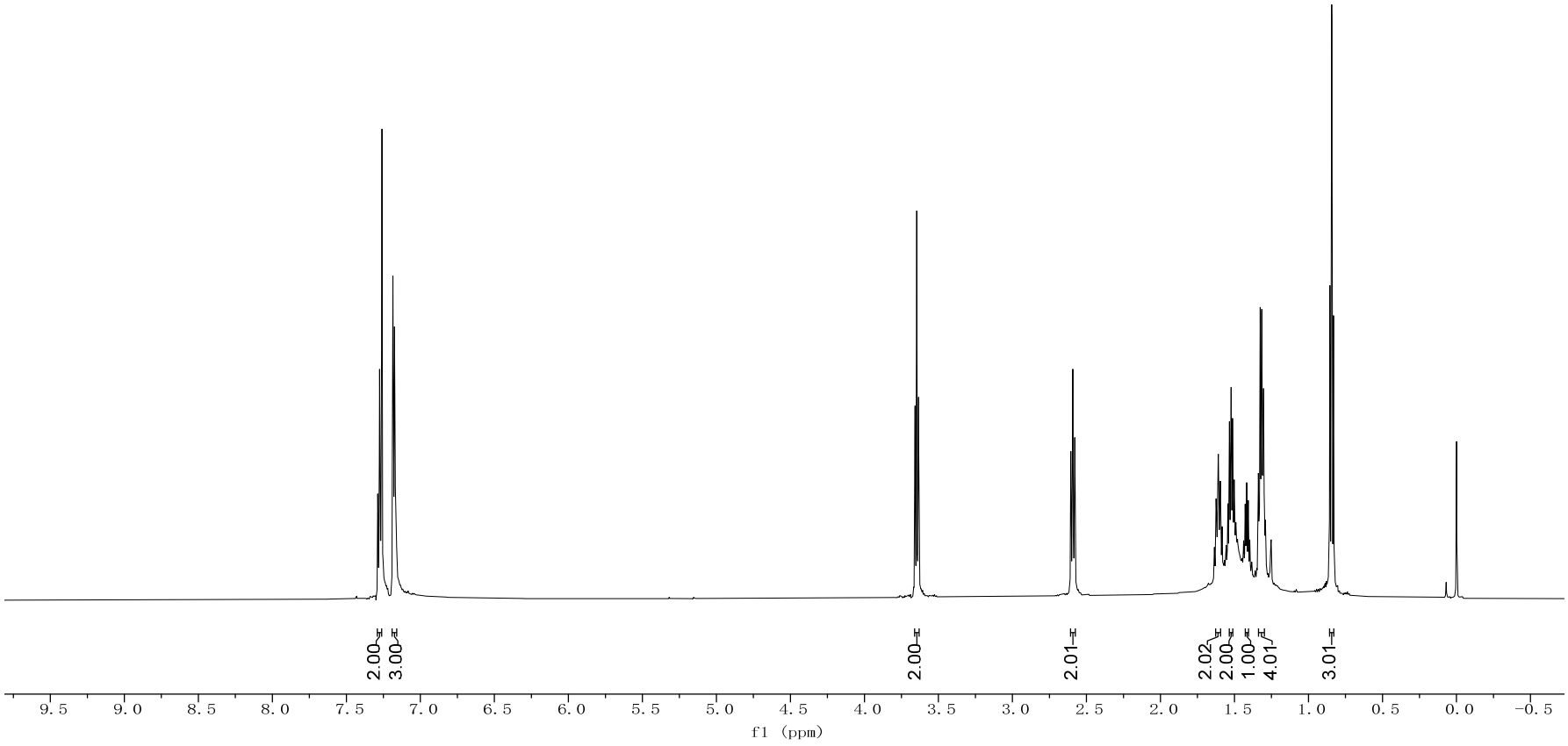


Figure 3B, entry 50



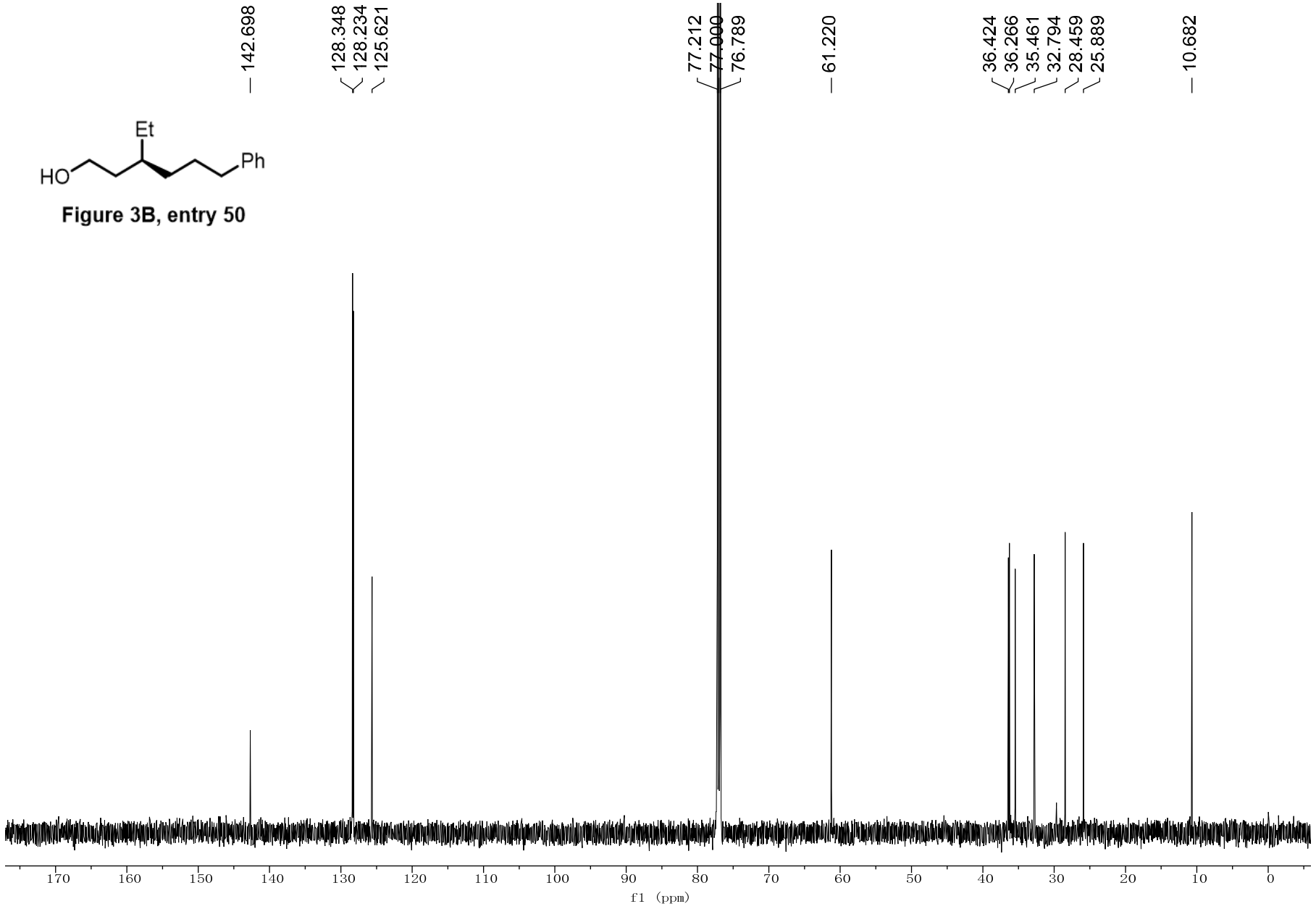


Figure 3B, entry 50

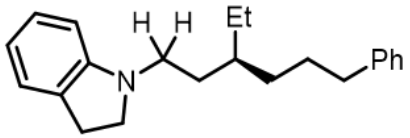
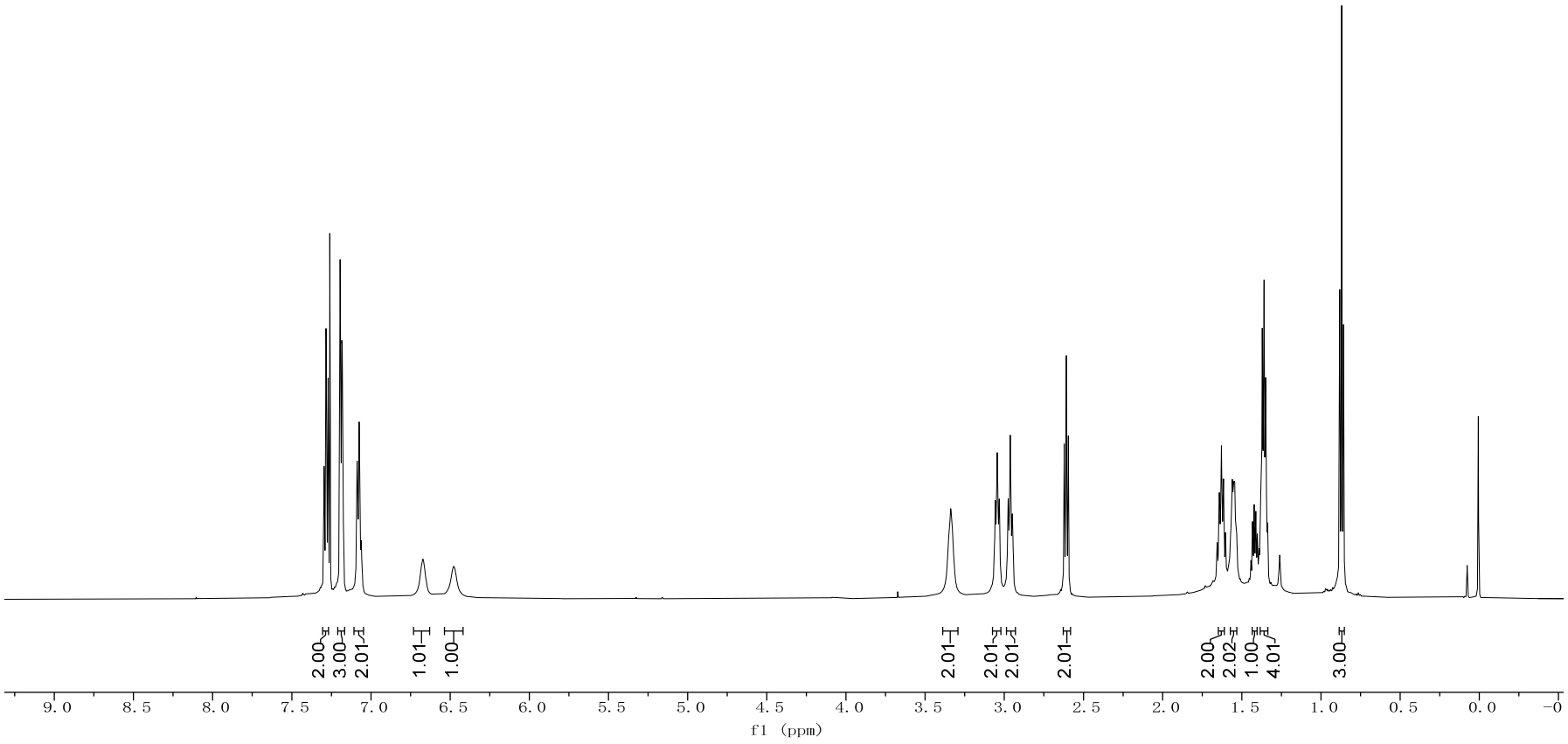


Figure 3B, entry 51



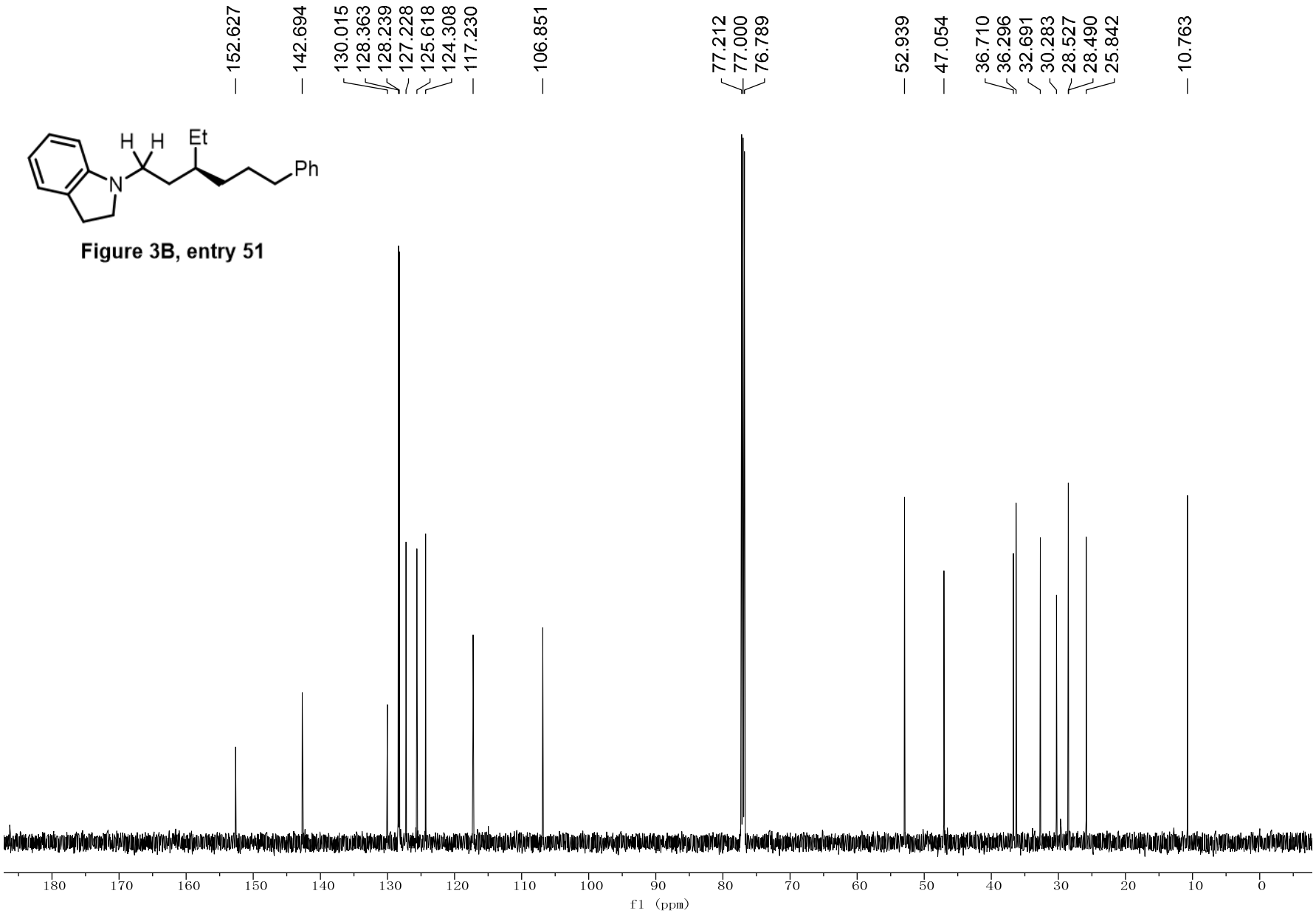


Figure 3B, entry 51

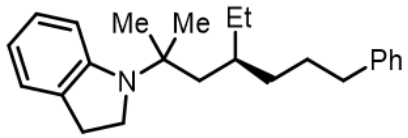
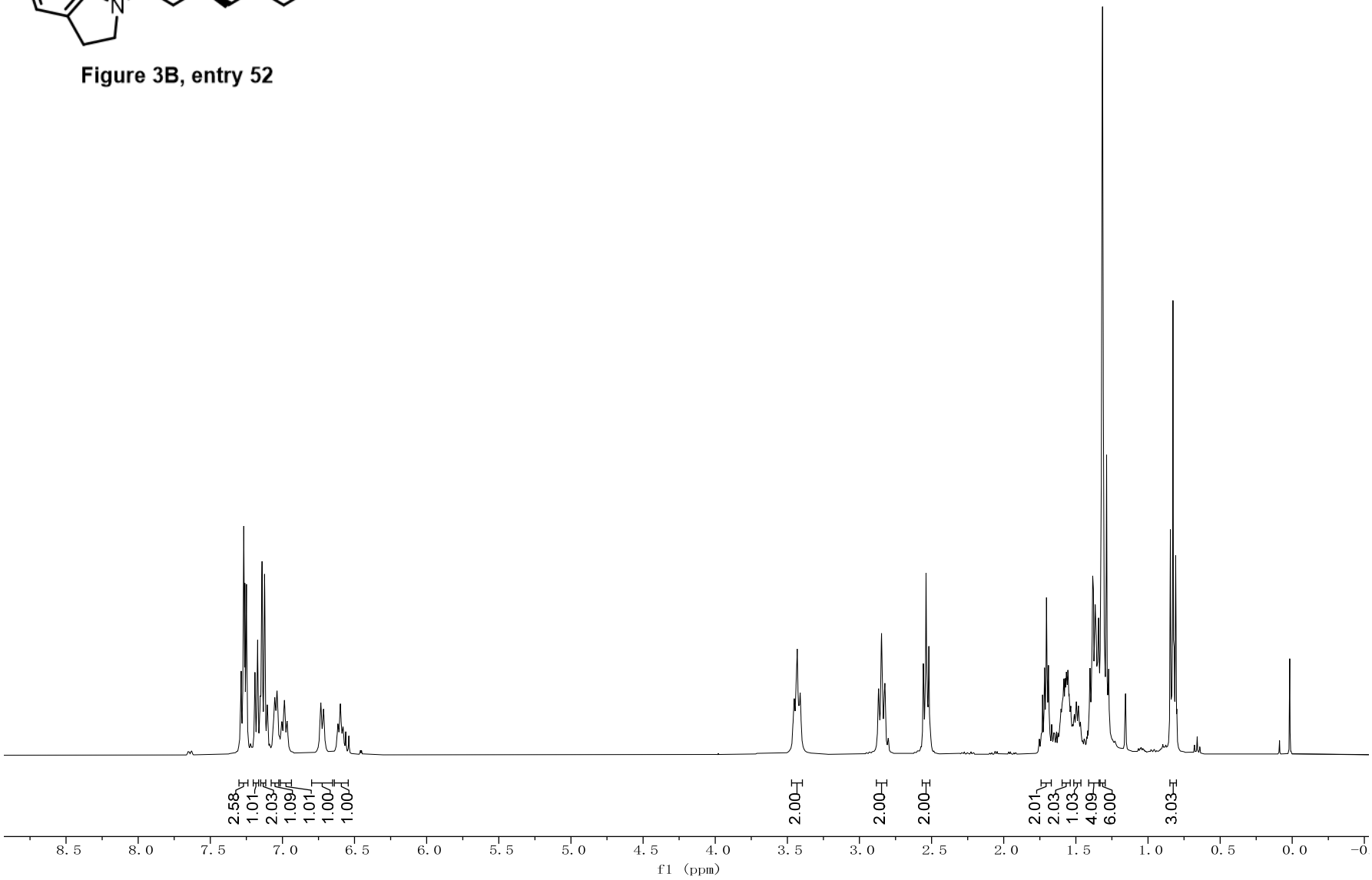


Figure 3B, entry 52



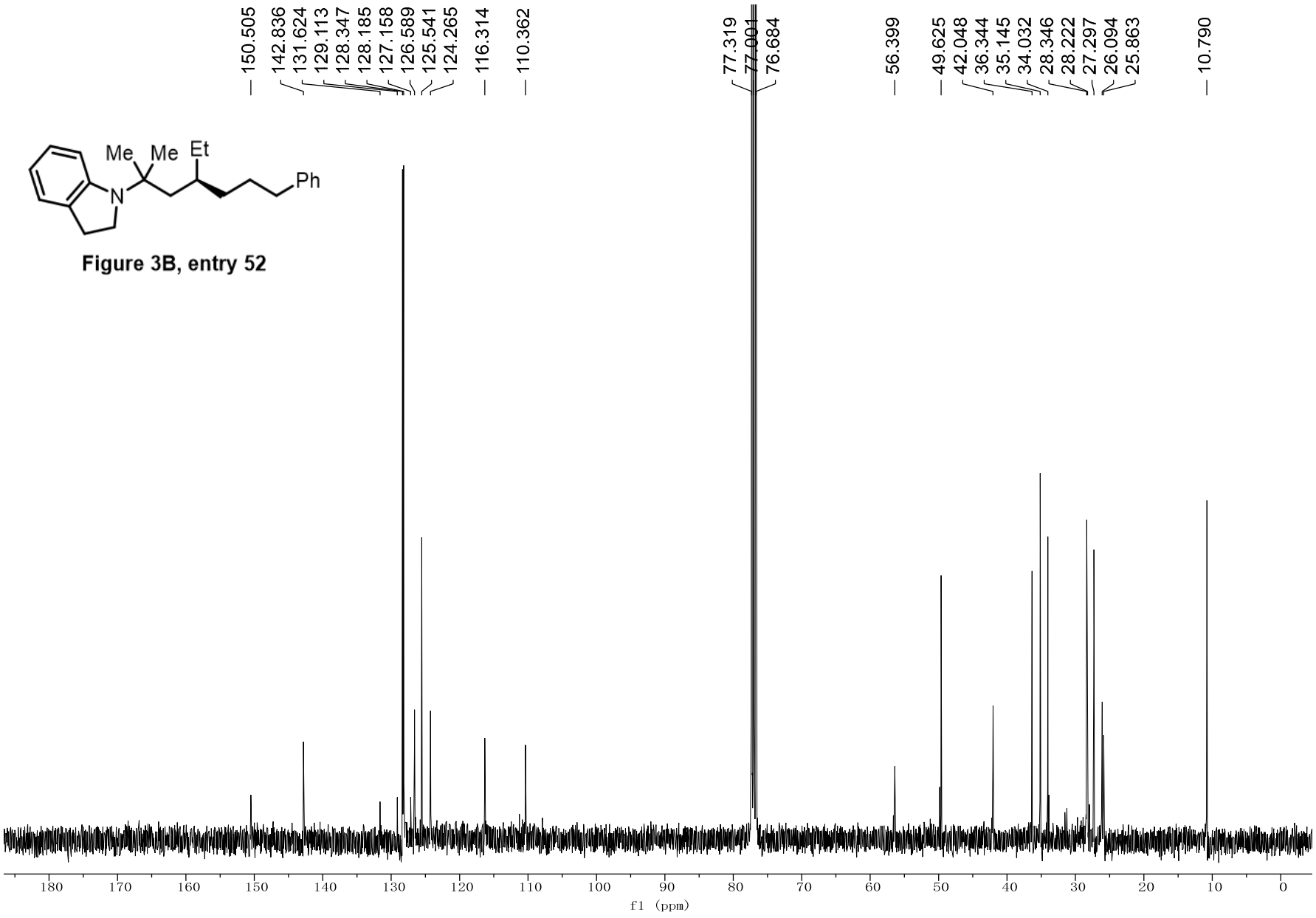


Figure 3B, entry 52

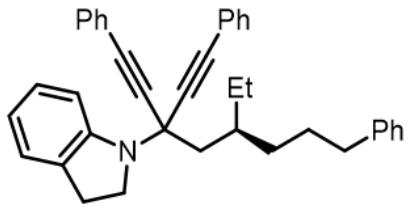
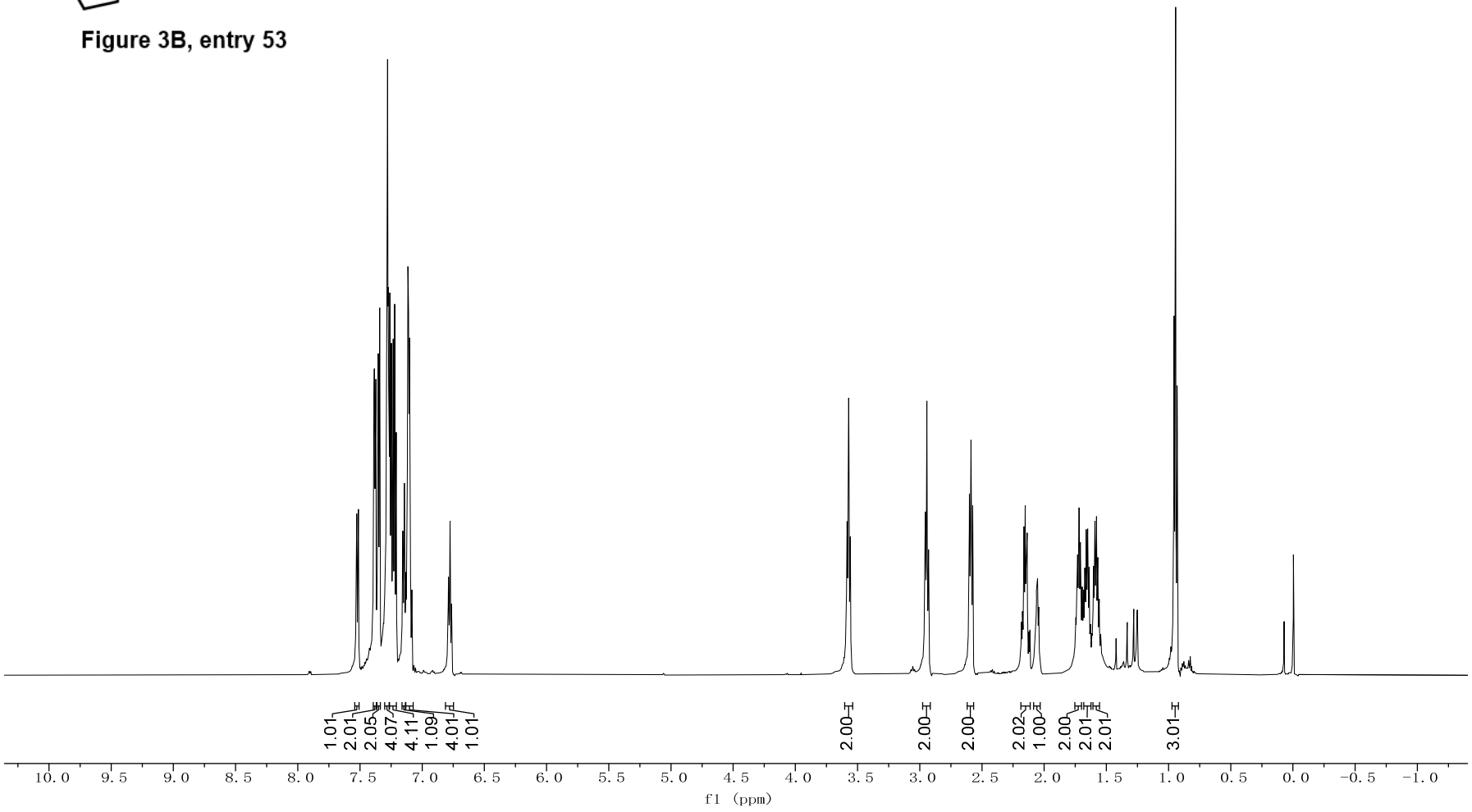


Figure 3B, entry 53



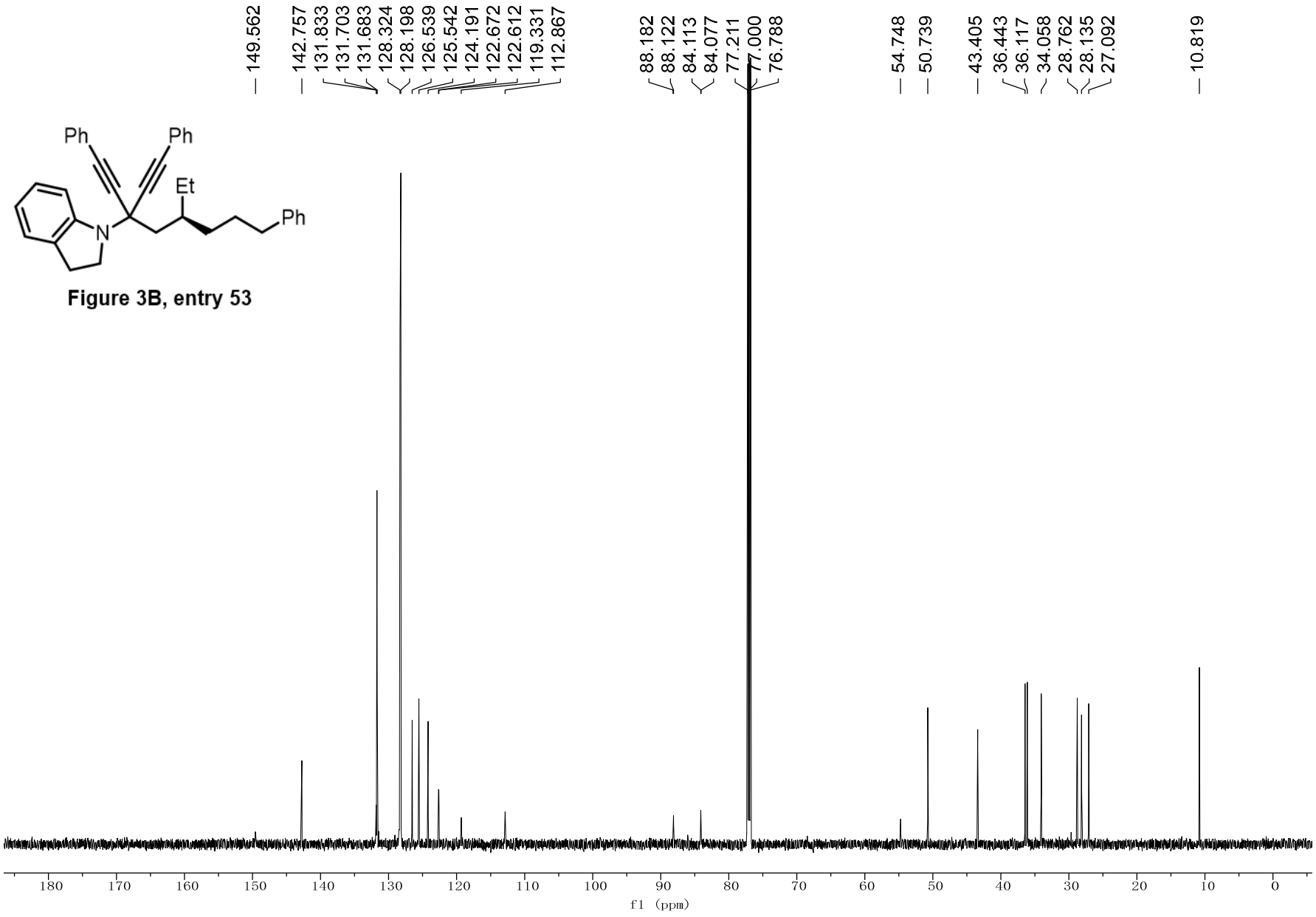


Figure 3B, entry 53

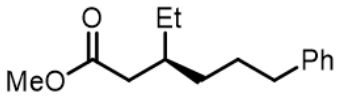


Figure 3B, entry 54

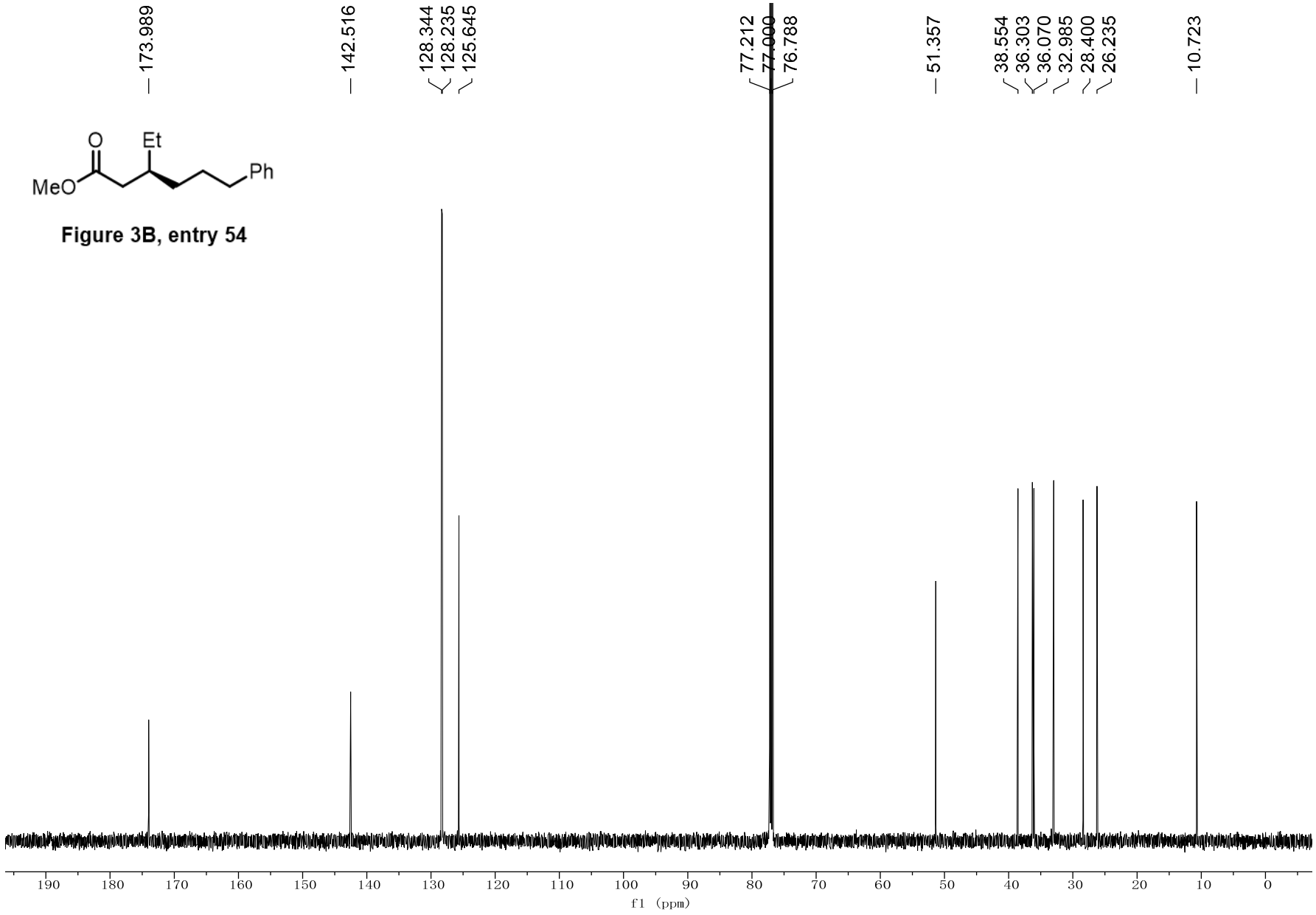


Figure 3B, entry 54

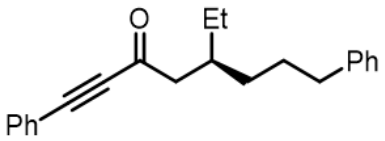
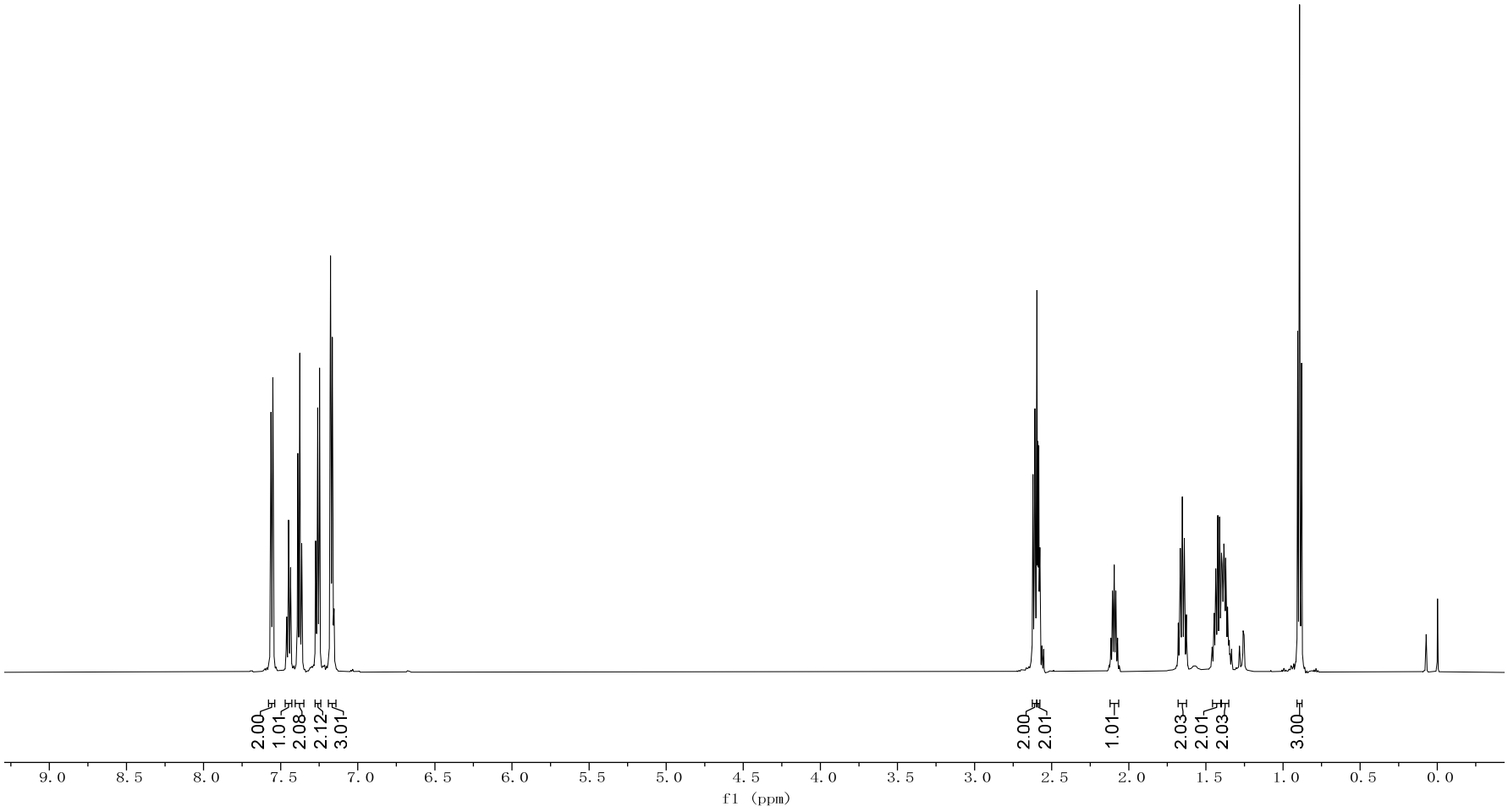


Figure 3B, entry 55



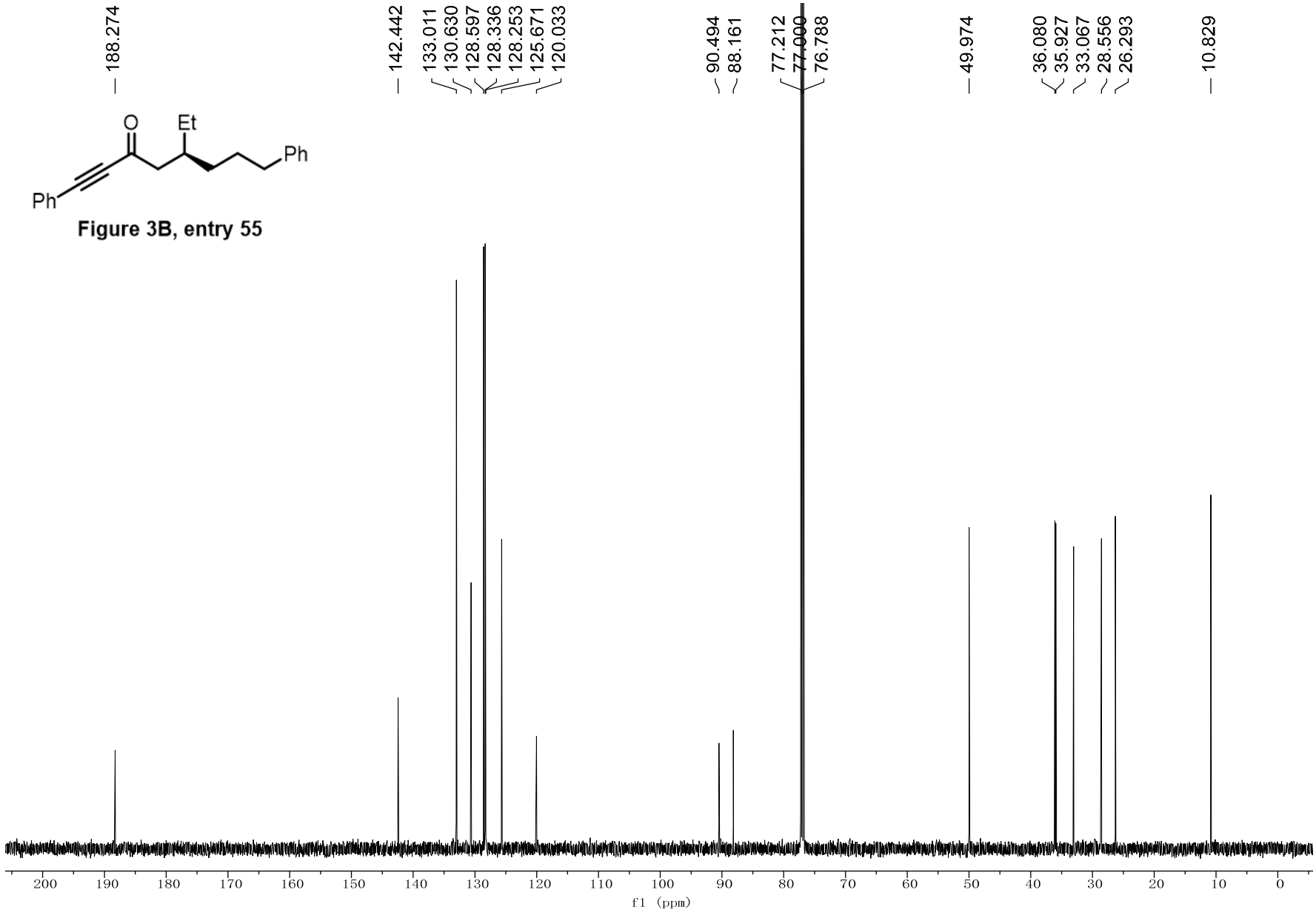


Figure 3B, entry 55

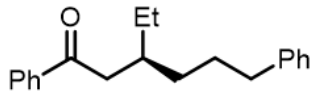


Figure 3B, entry 56

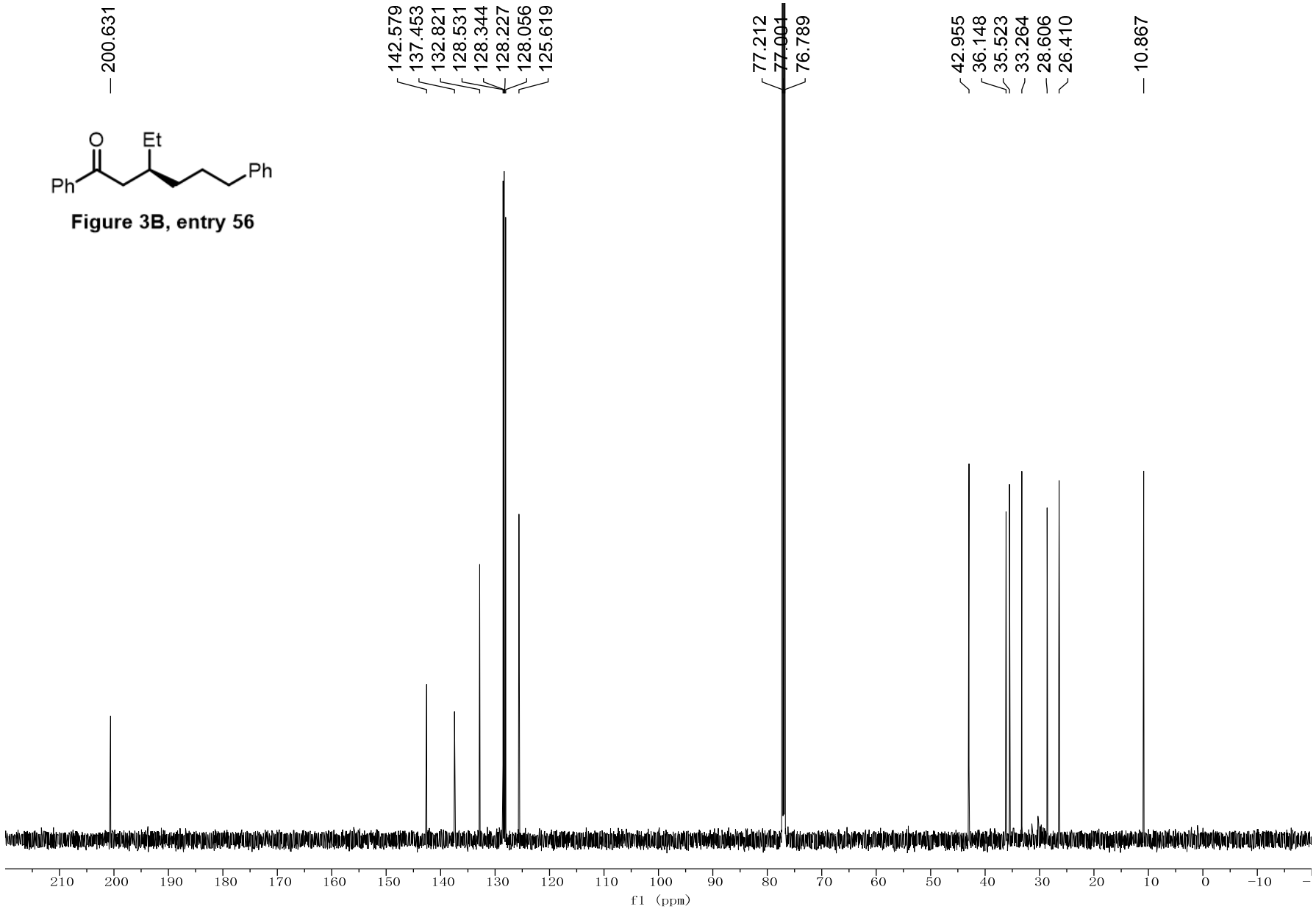


Figure 3B, entry 56

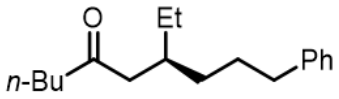
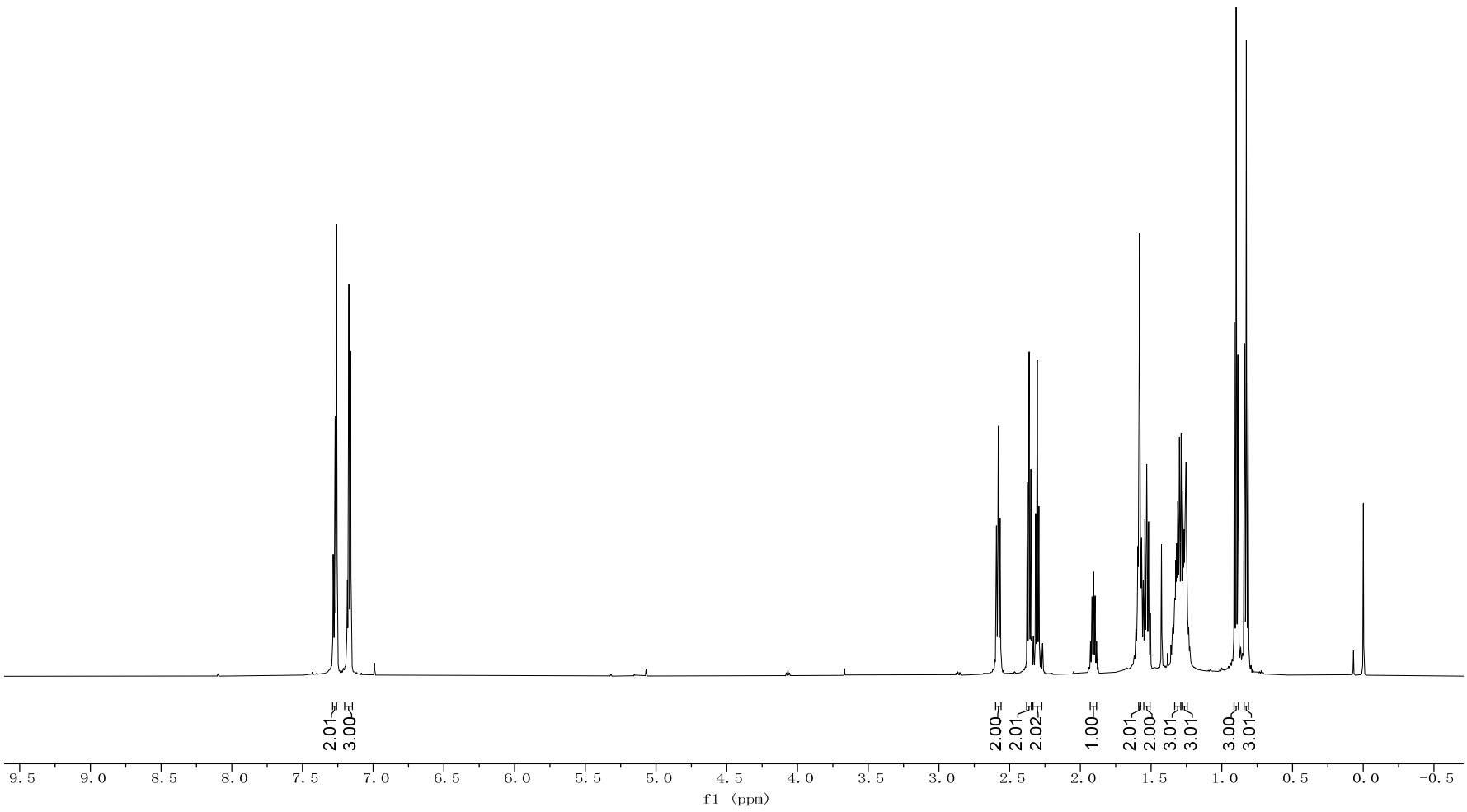


Figure 3B, entry 57



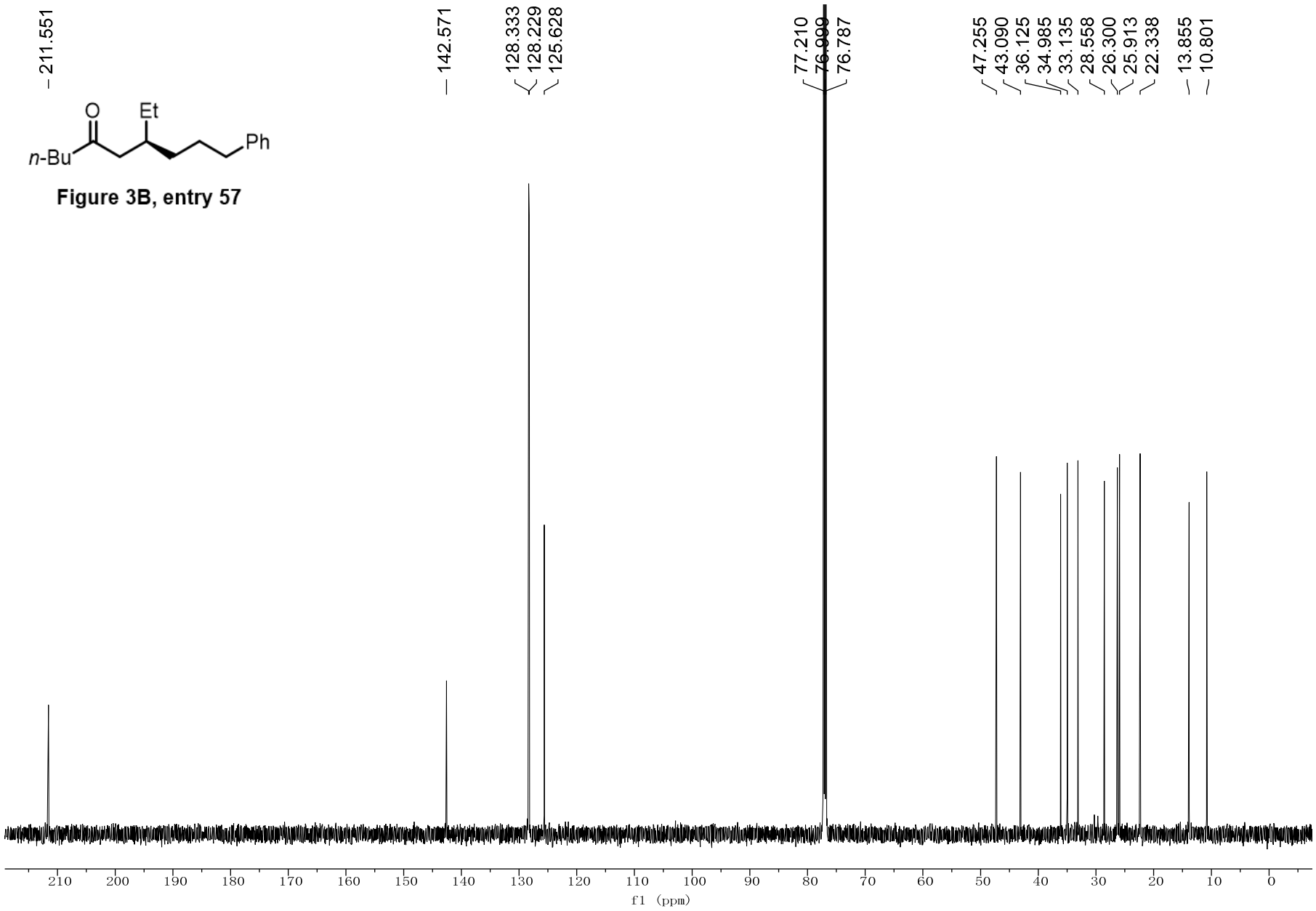
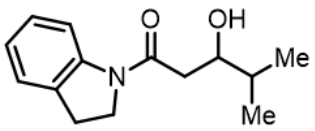
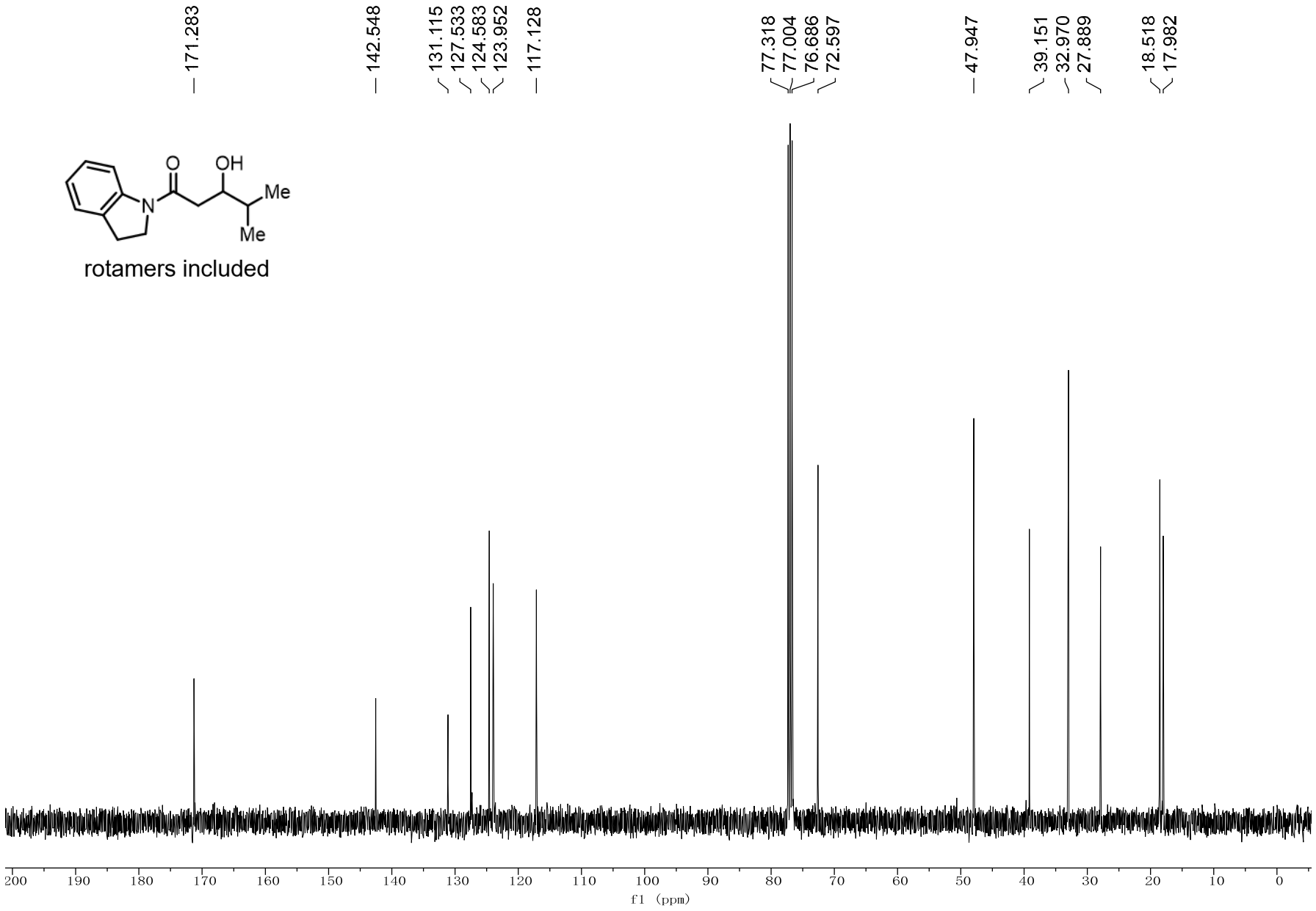


Figure 3B, entry 57



rotamers included


171.283
142.548
131.115
127.533
124.583
123.952
117.128
77.318
77.004
76.686
72.597
47.947
39.151
32.970
27.889
18.518
17.982
O
OH
N
Me
Me
rotamers included
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

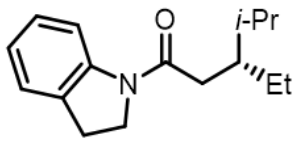
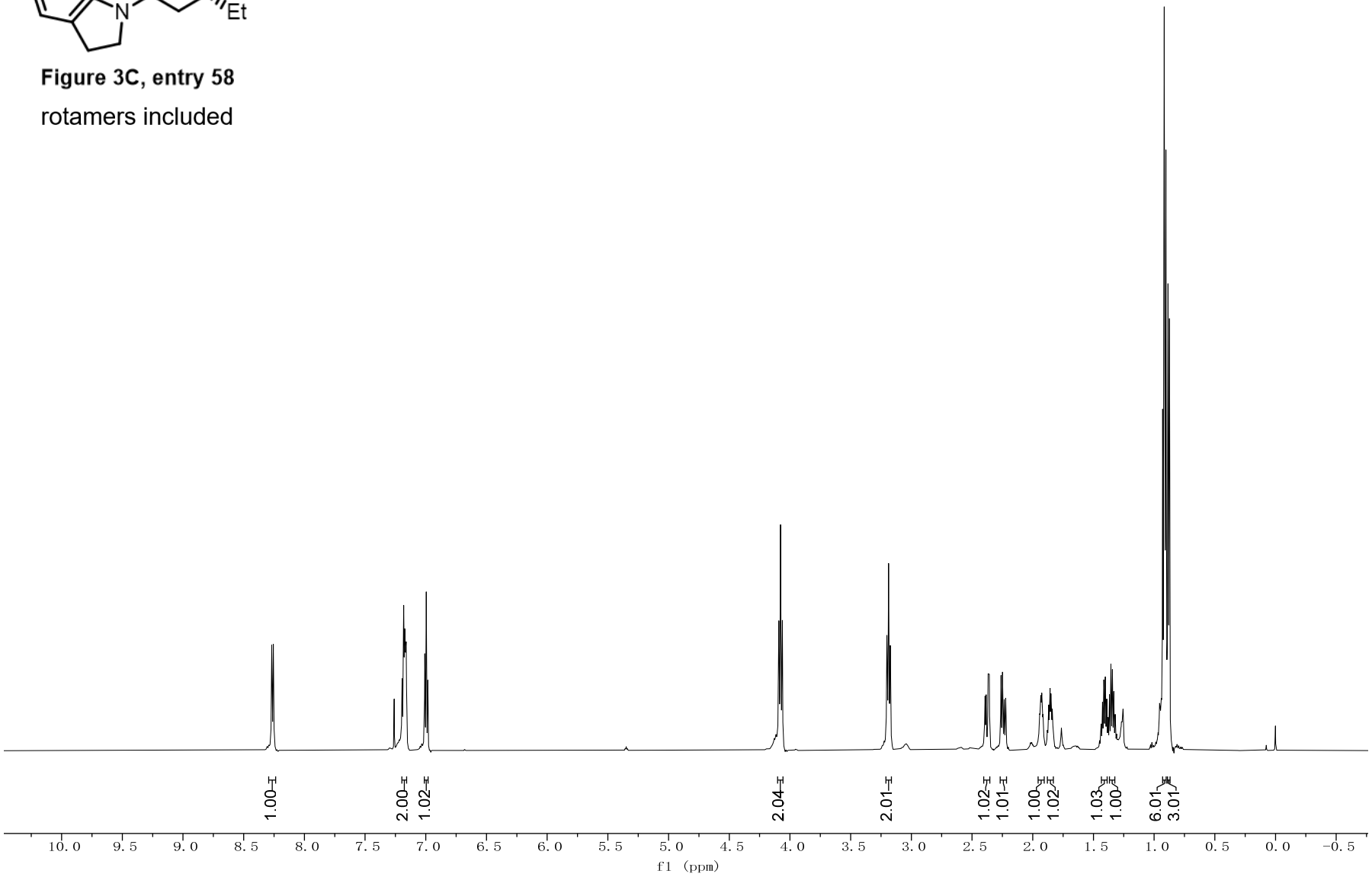


Figure 3C, entry 58

rotamers included



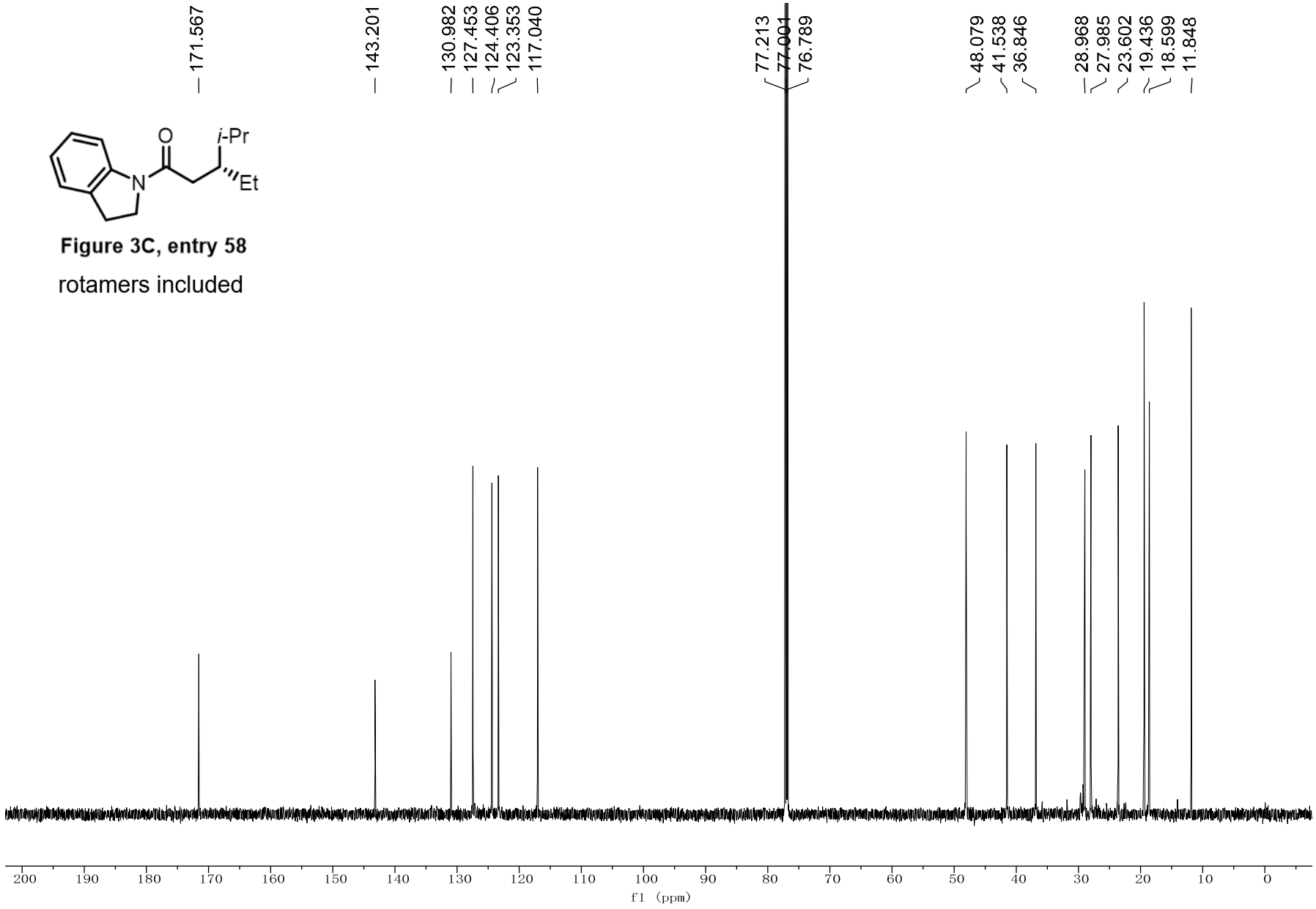


Figure 3C, entry 58

rotamers included

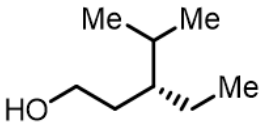
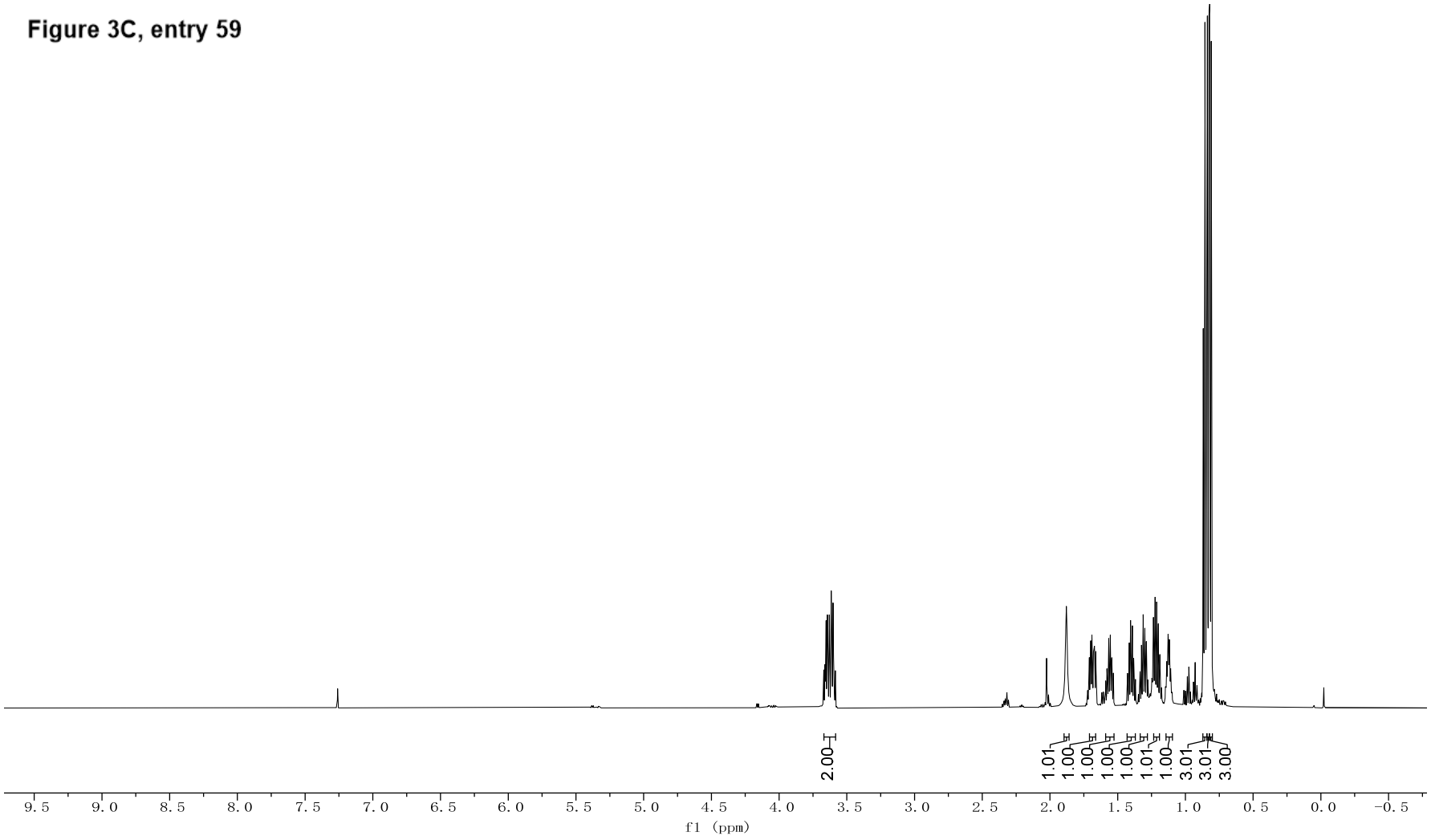


Figure 3C, entry 59



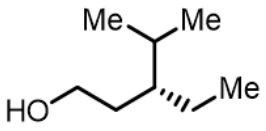


Figure 3C, entry 59

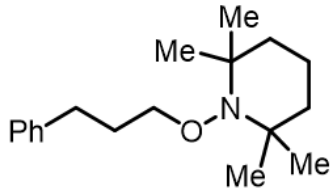
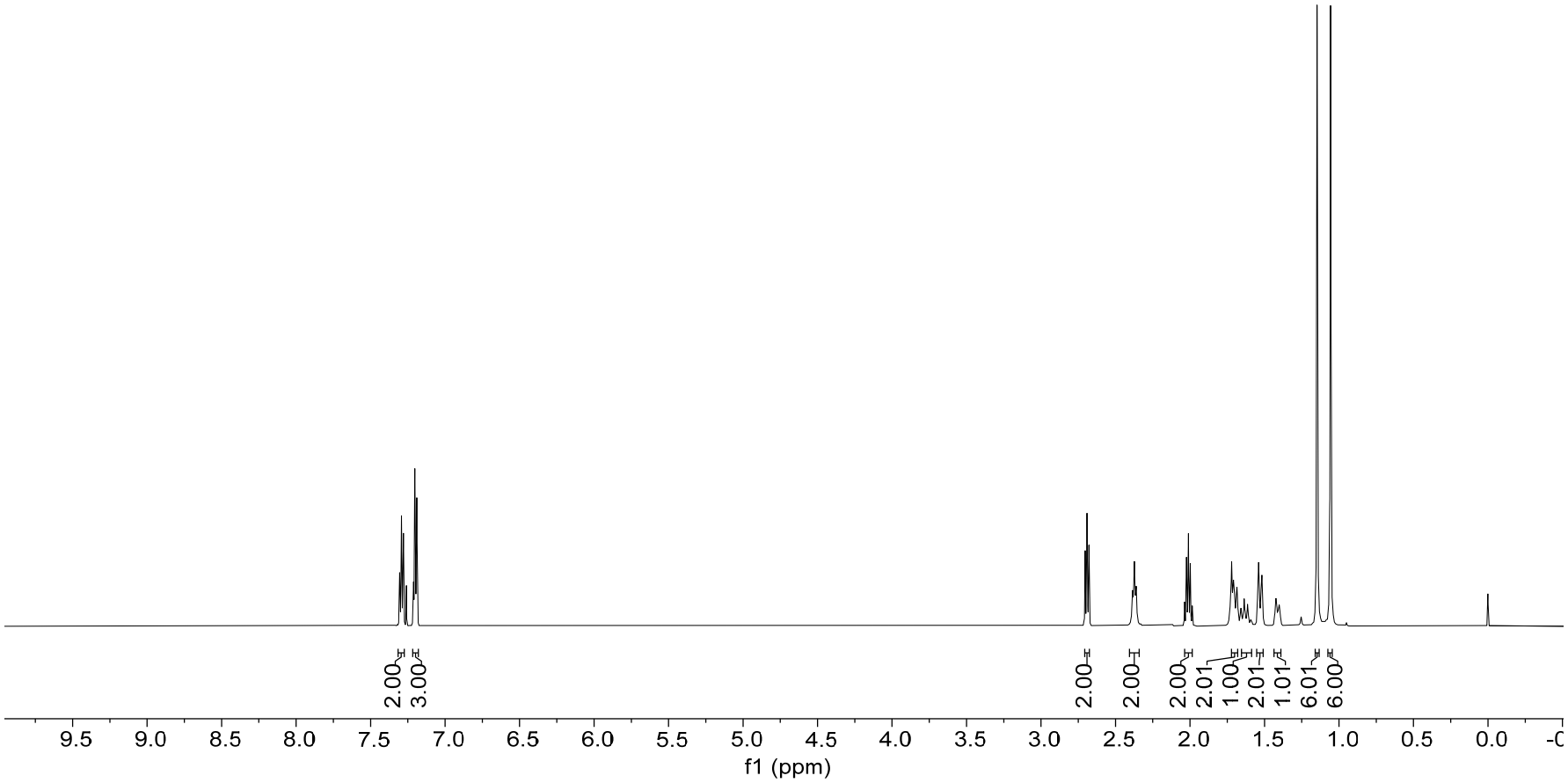

Me
Me
Ph
O
N
Me
Me

Figure 4A, A[1]


2.00
3.00
2.00
2.00
2.00
2.01
1.00
2.01
1.01
6.01
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

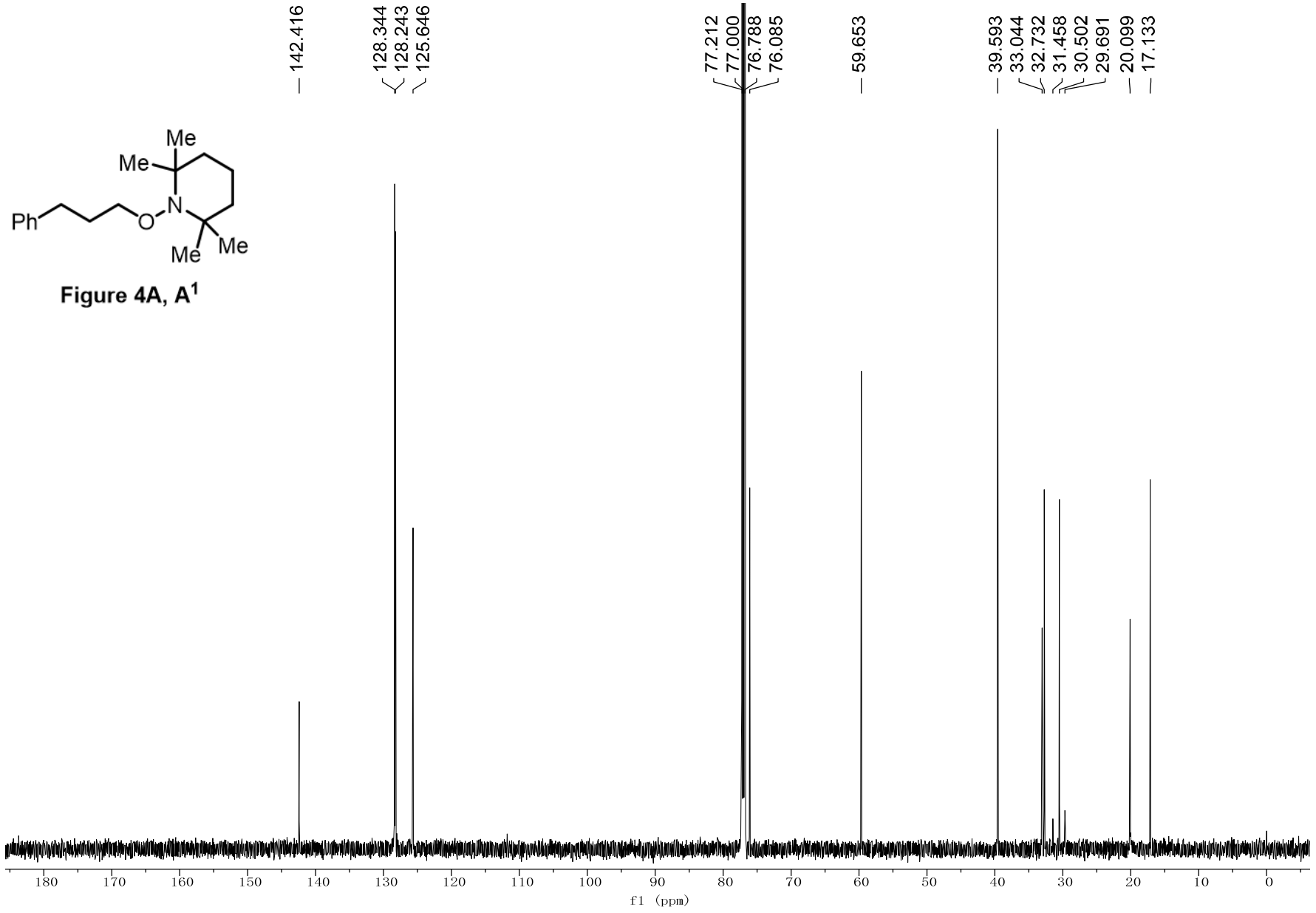

142.416
128.344
128.243
125.646
77.212
77.000
76.788
76.085
59.653
39.593
33.044
32.732
31.458
30.502
29.691
20.099
17.133
Me
Me
N
O
Ph
Me
Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Figure 4A, A[1]

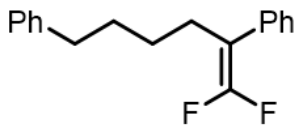
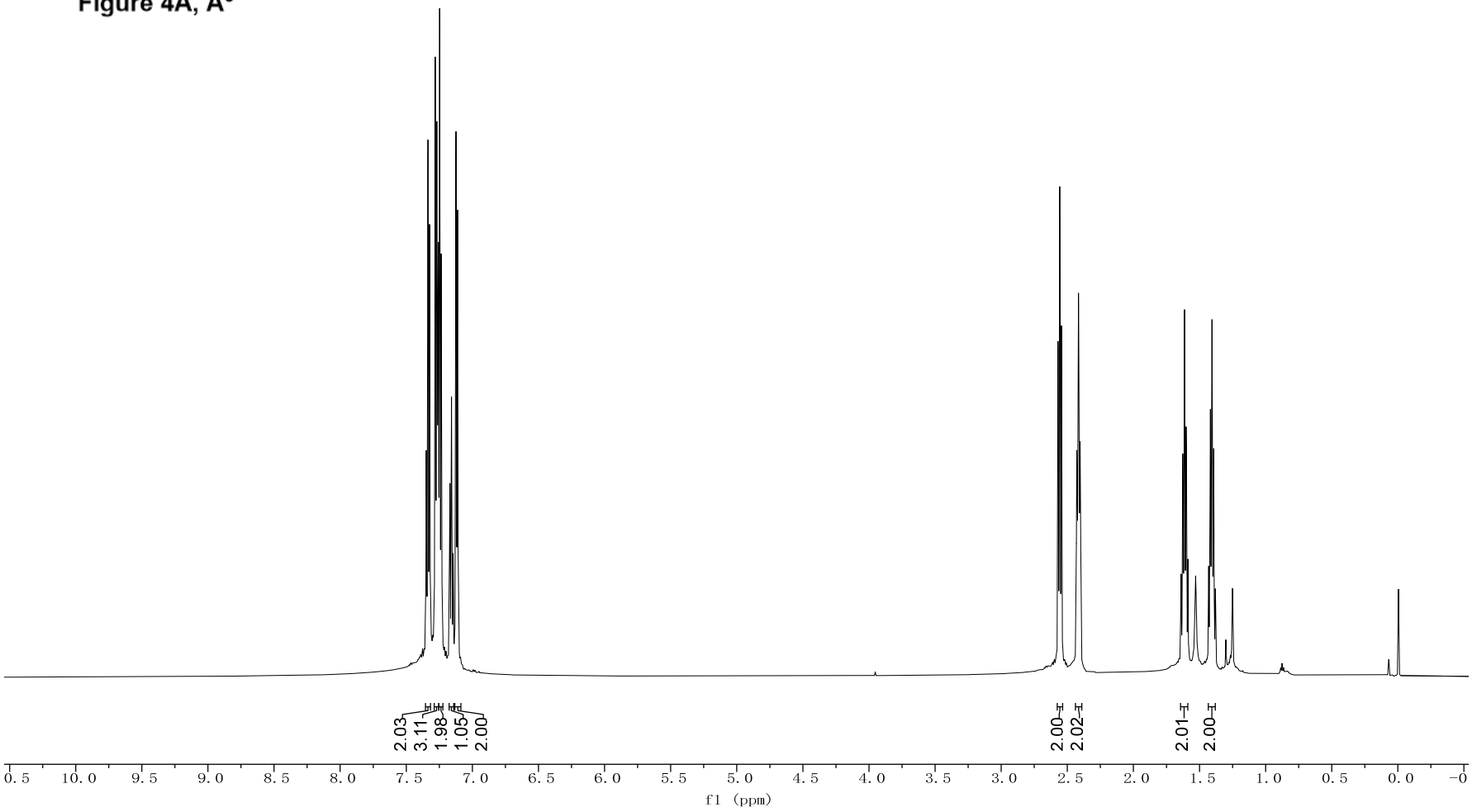


Figure 4A, A^3



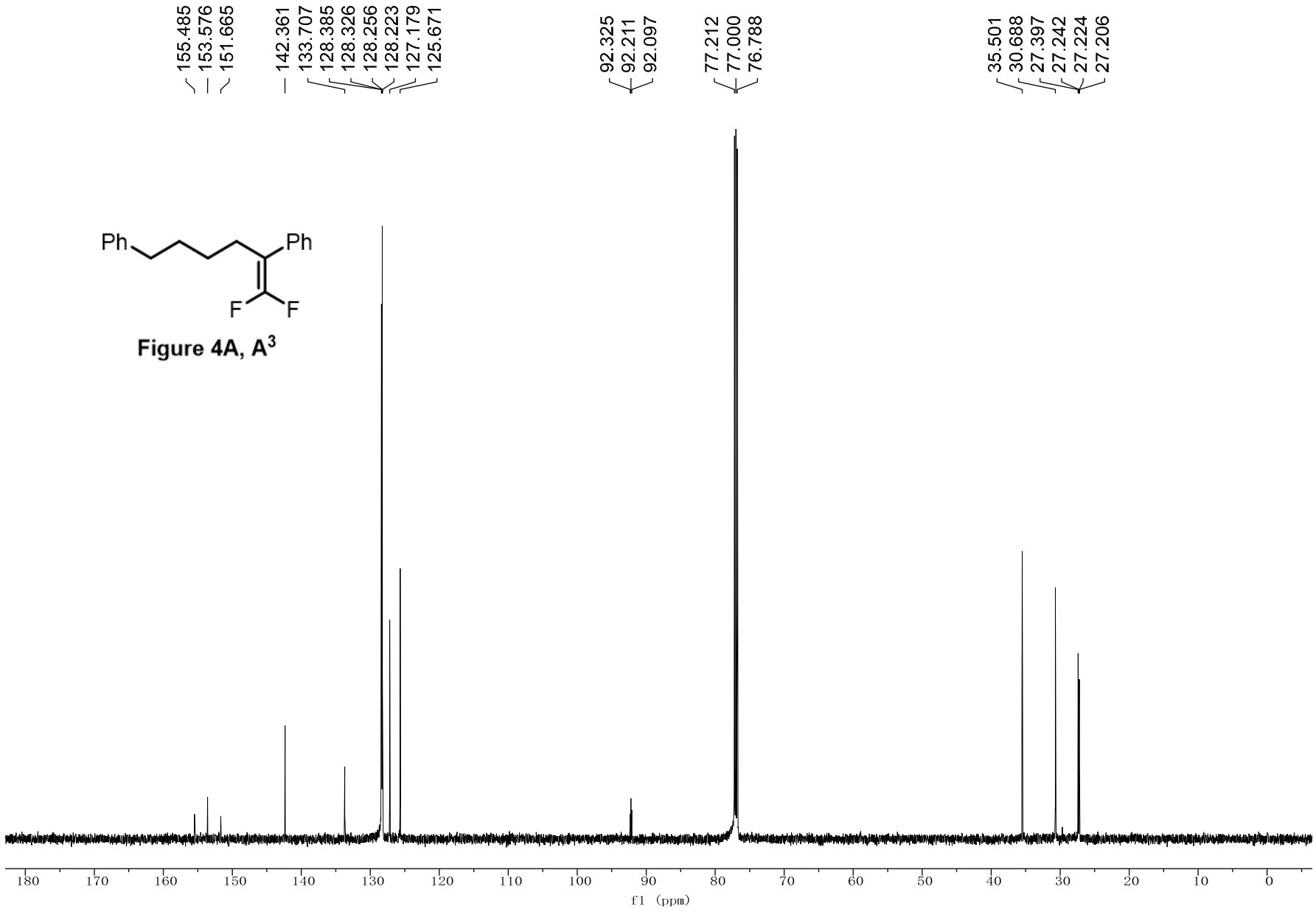

155.485
153.576
151.665
142.361
133.707
128.385
128.326
128.256
128.223
127.179
125.671
92.325
92.211
92.097
77.212
77.000
76.788
35.501
30.688
27.397
27.242
27.224
27.206
Ph
Ph
F
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Figure 4A, A^3

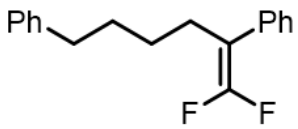

Ph
Ph
F
F

Figure 4A, A^3

-91.826
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

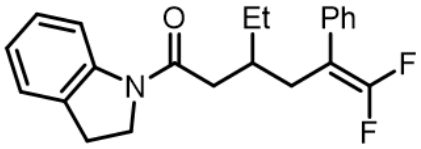


Figure 4A, A[4]
rotamers included

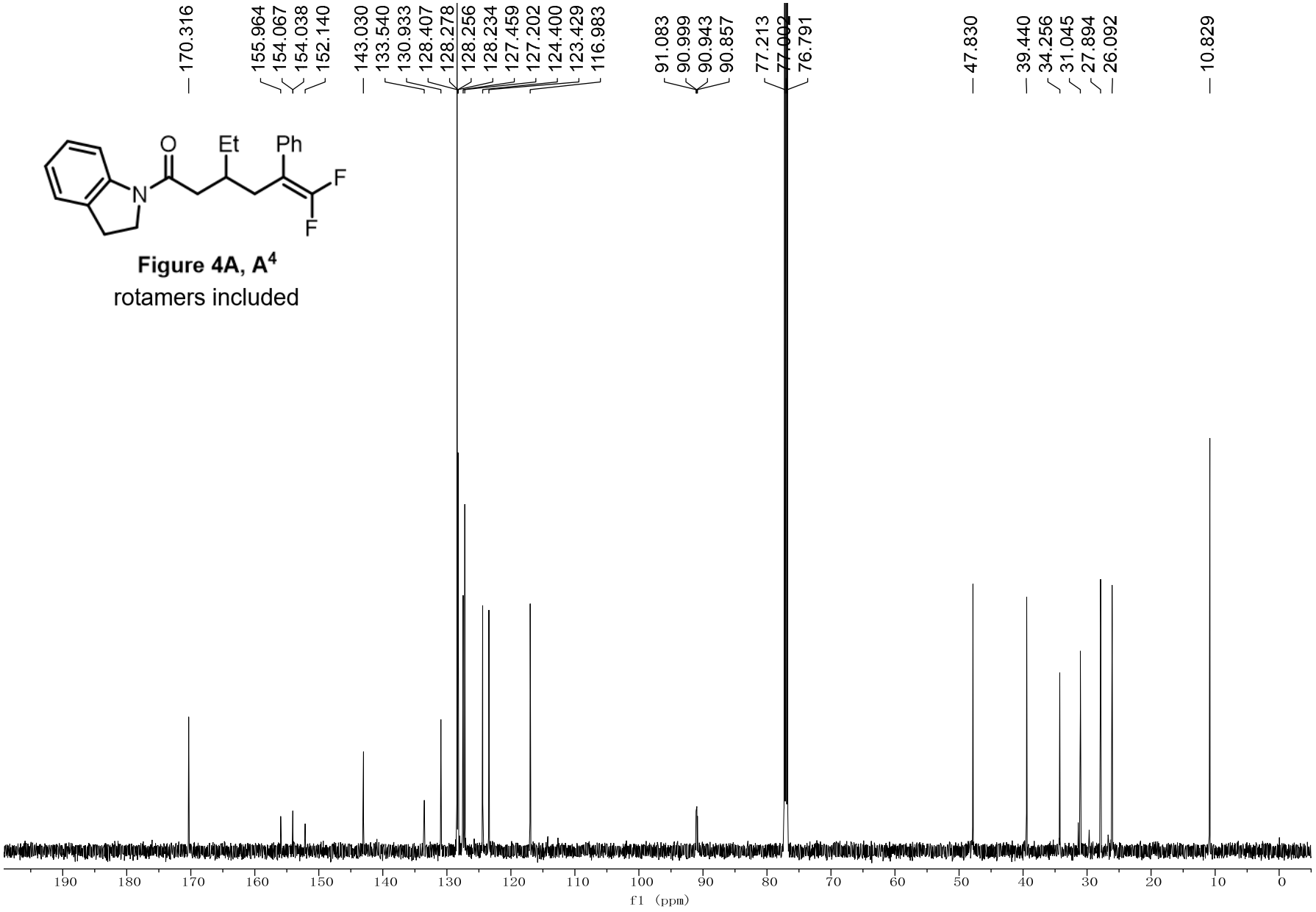


Figure 4A, A[4]
rotamers included

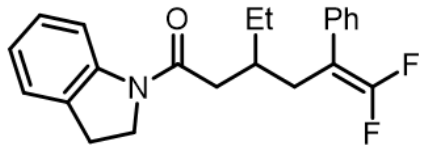
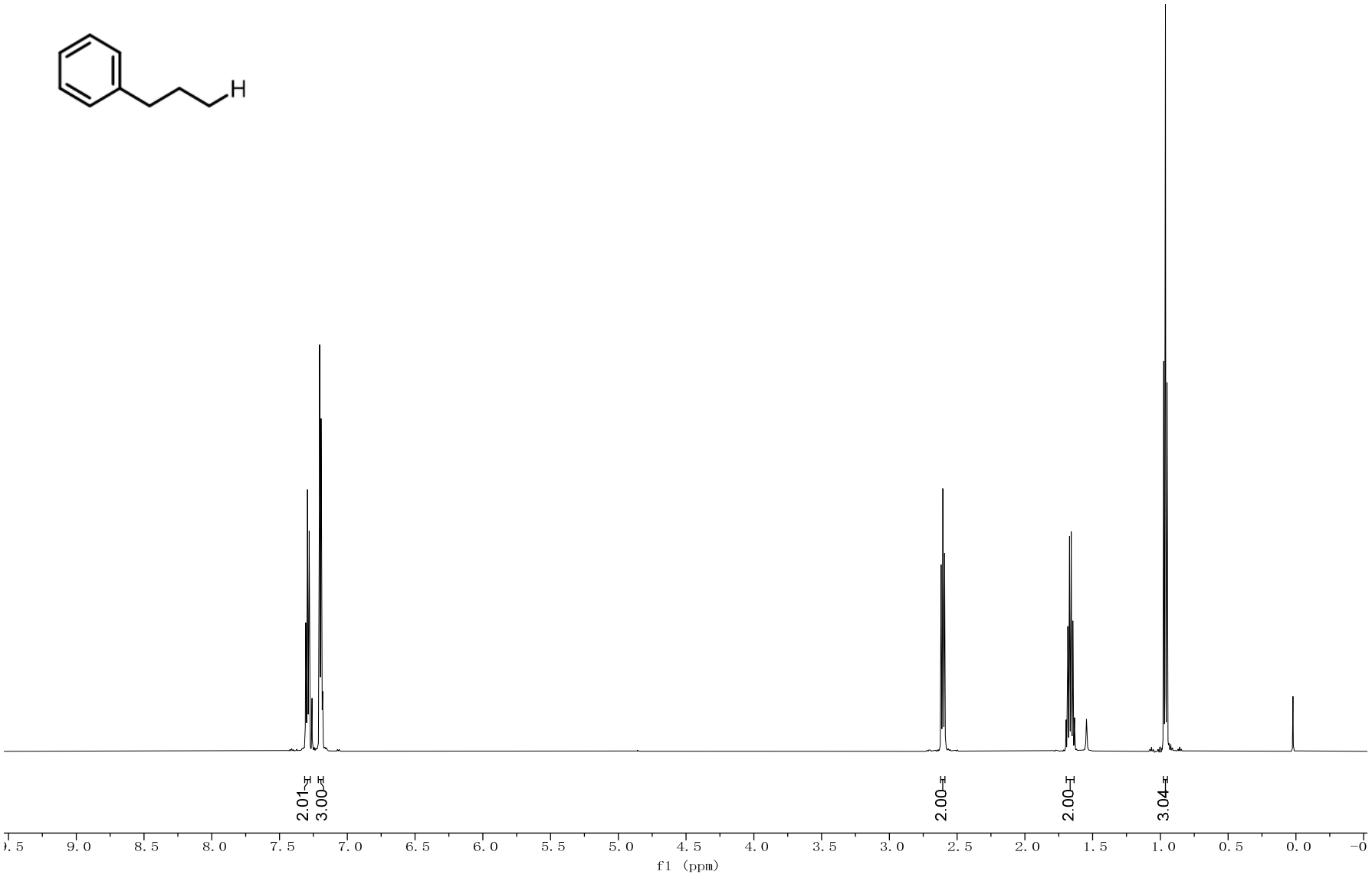
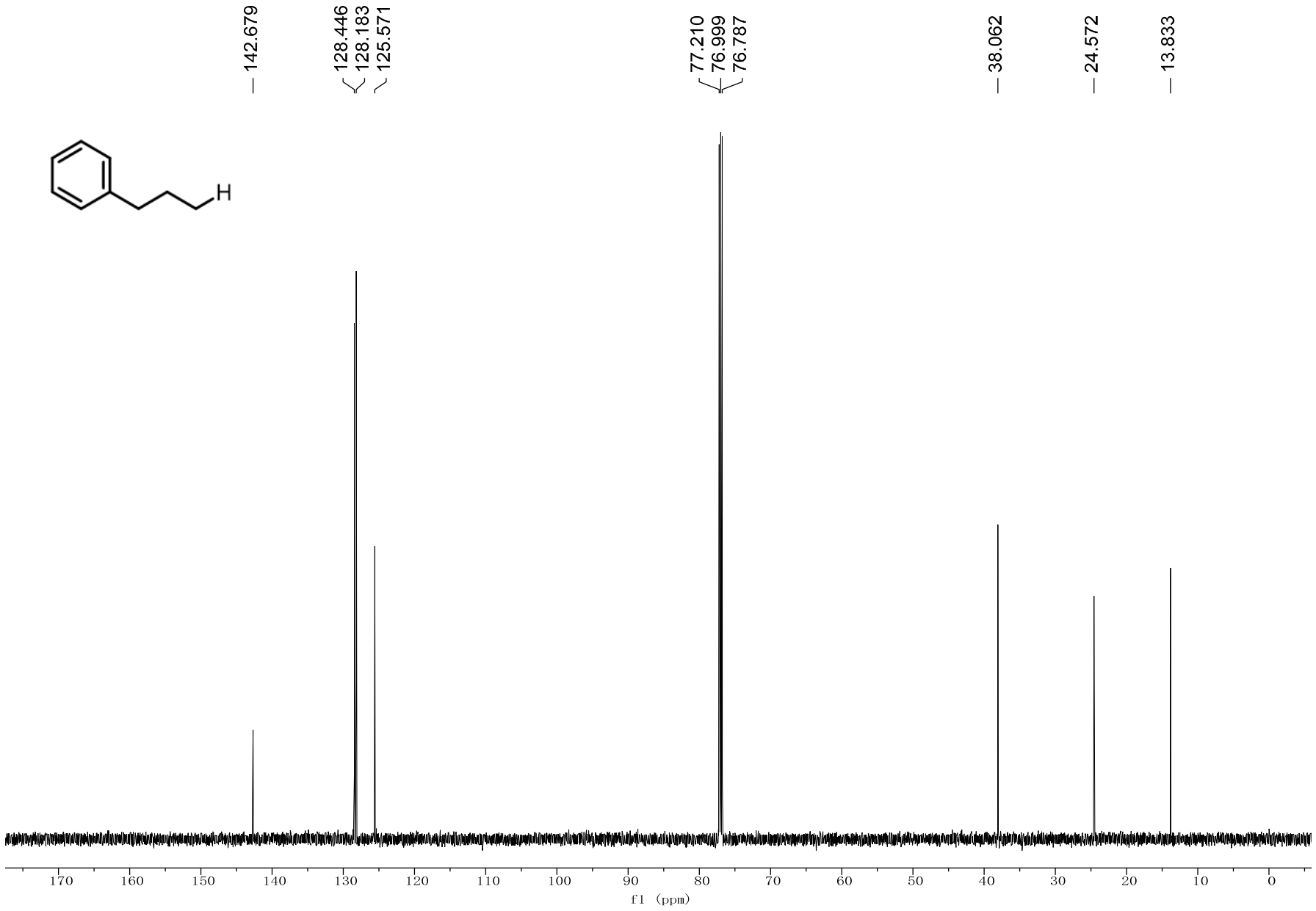
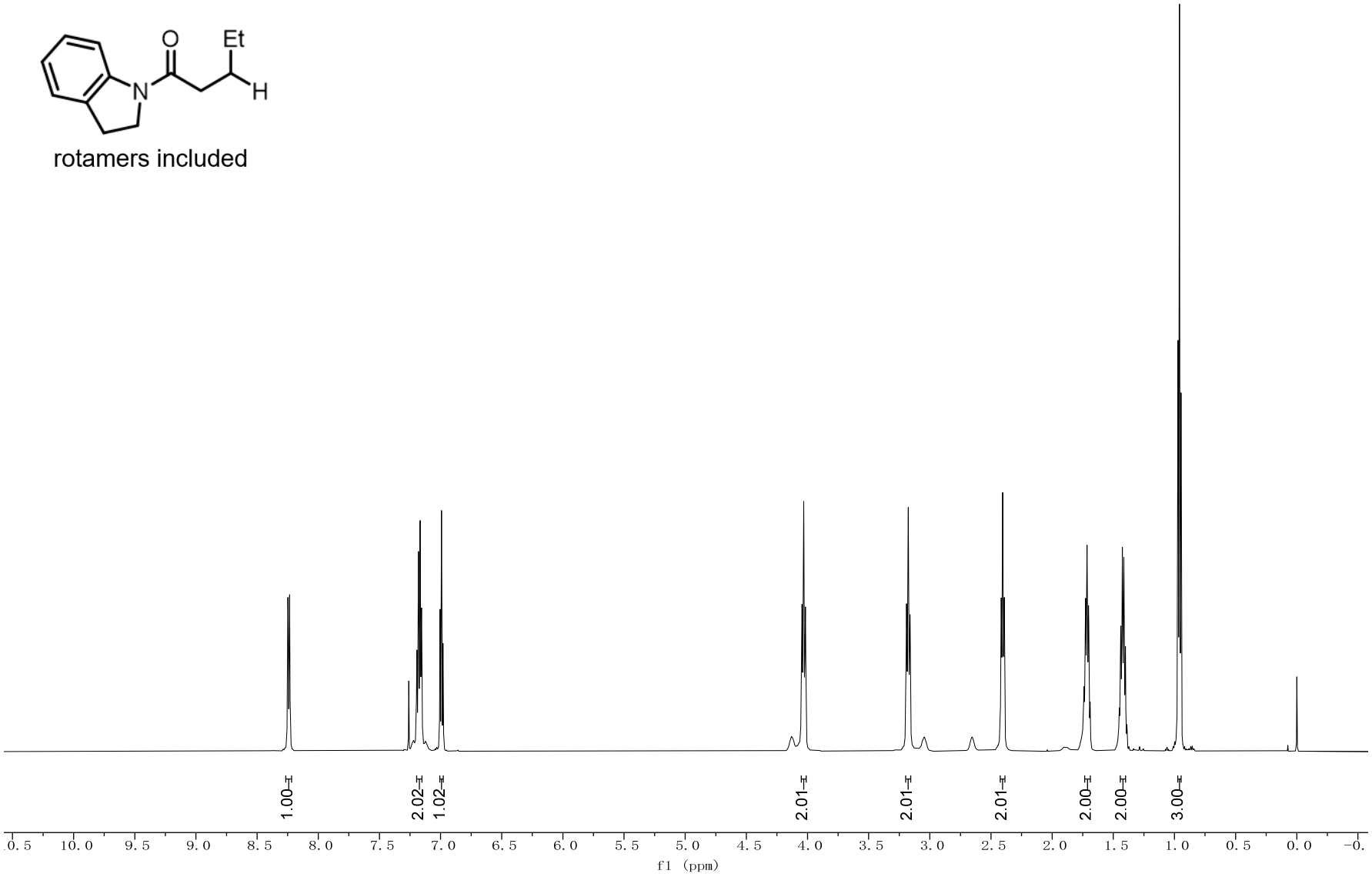
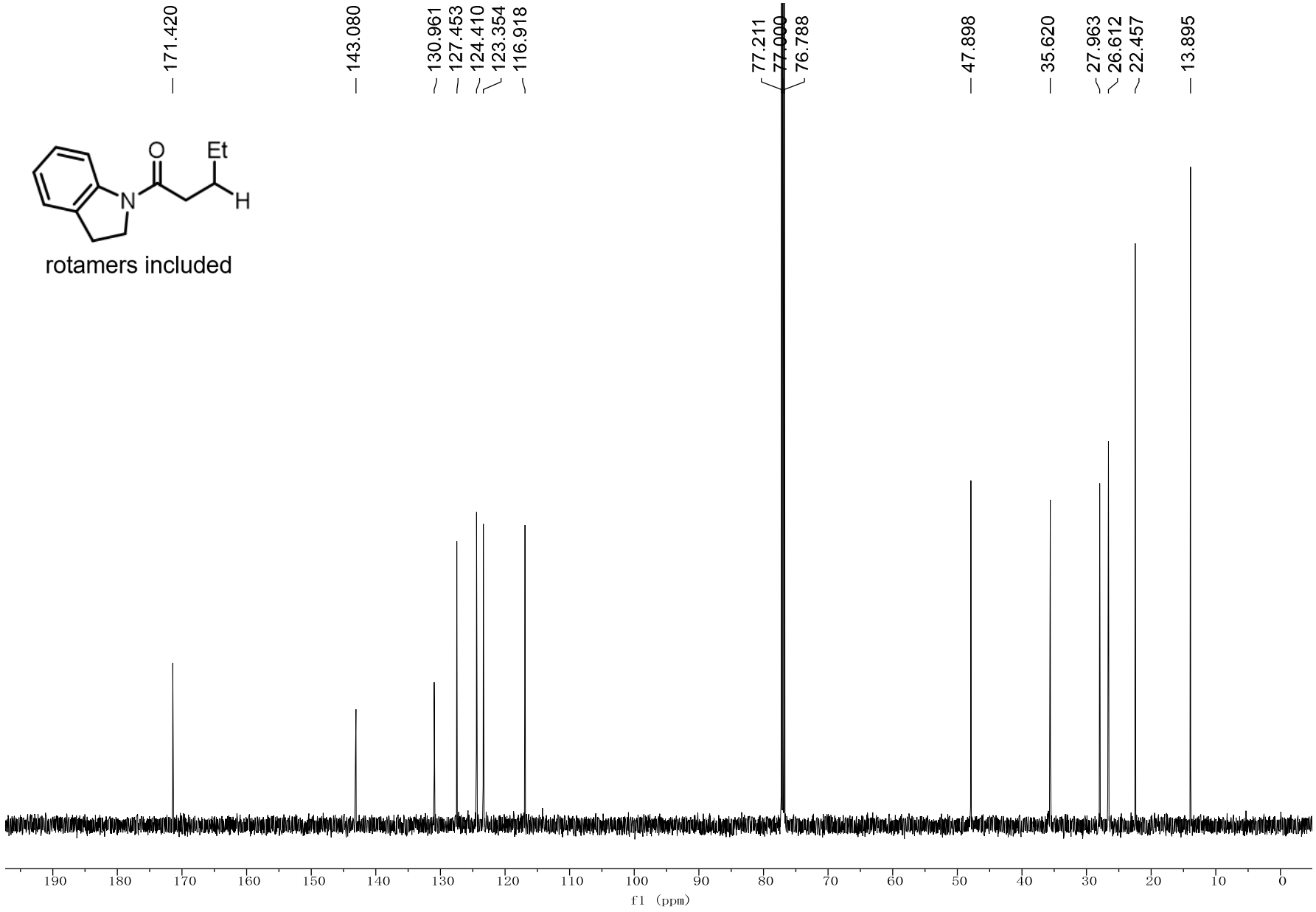


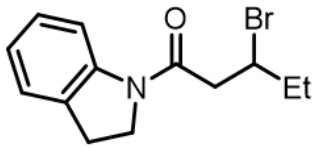
Figure 4A, A[4]
rotamers included


H
2.01
3.00
2.00
2.00
3.04
f1 (ppm)

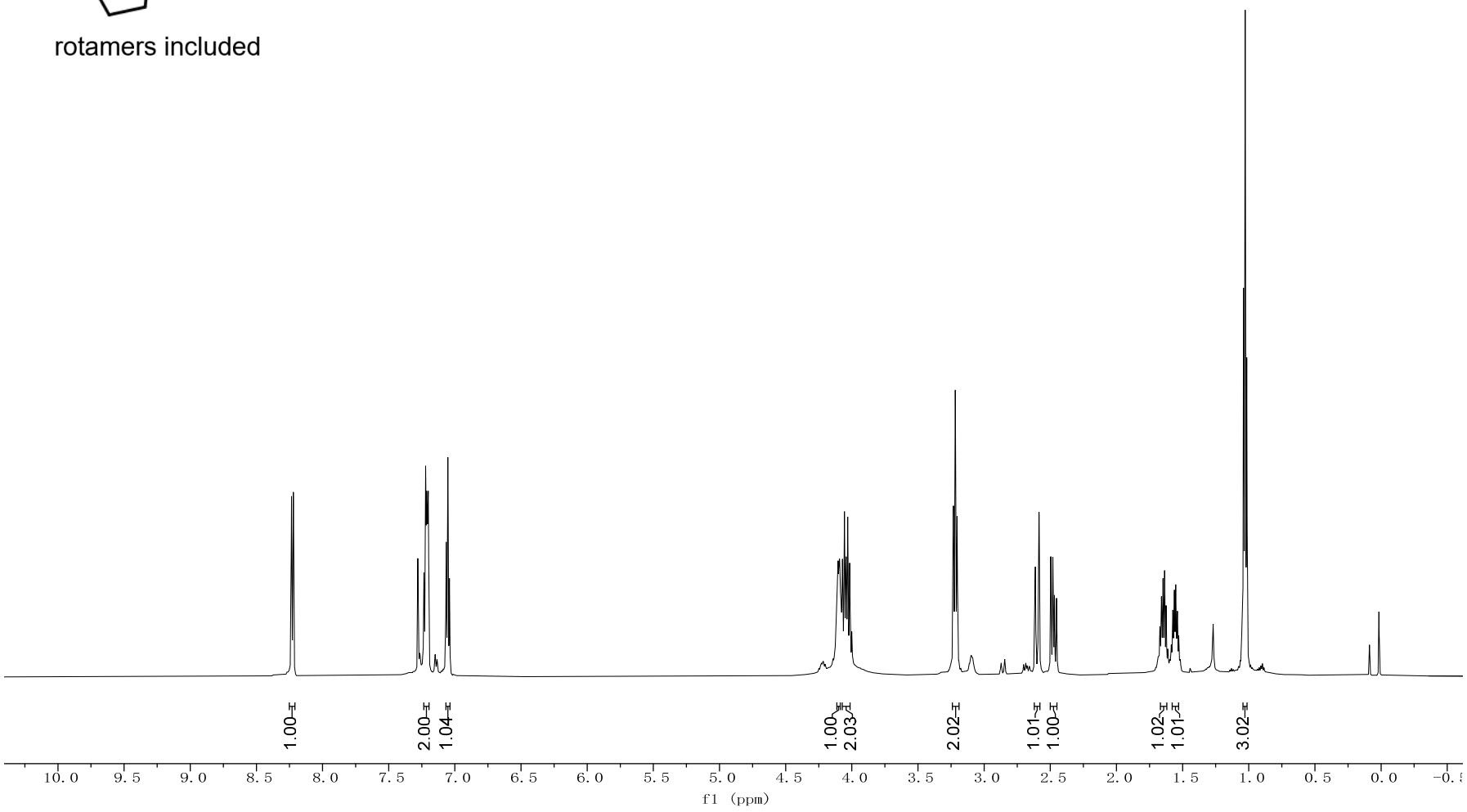

142.679
128.446
128.183
125.571
77.210
76.999
76.787
38.062
24.572
13.833
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

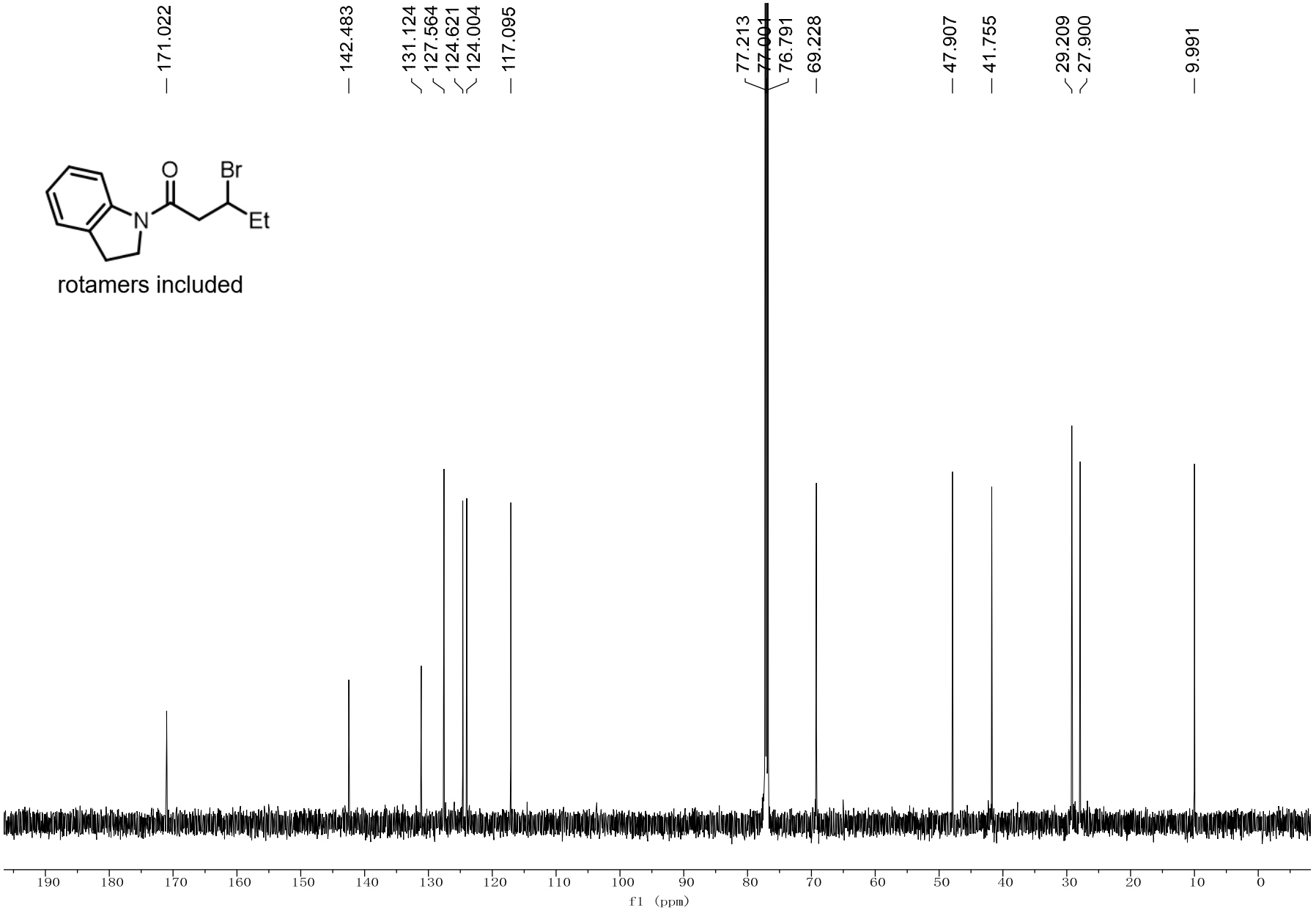

O
Et
N
H
rotamers included
1.00
2.02
1.02
2.01
2.01
2.01
2.00
2.00
3.00
f1 (ppm)

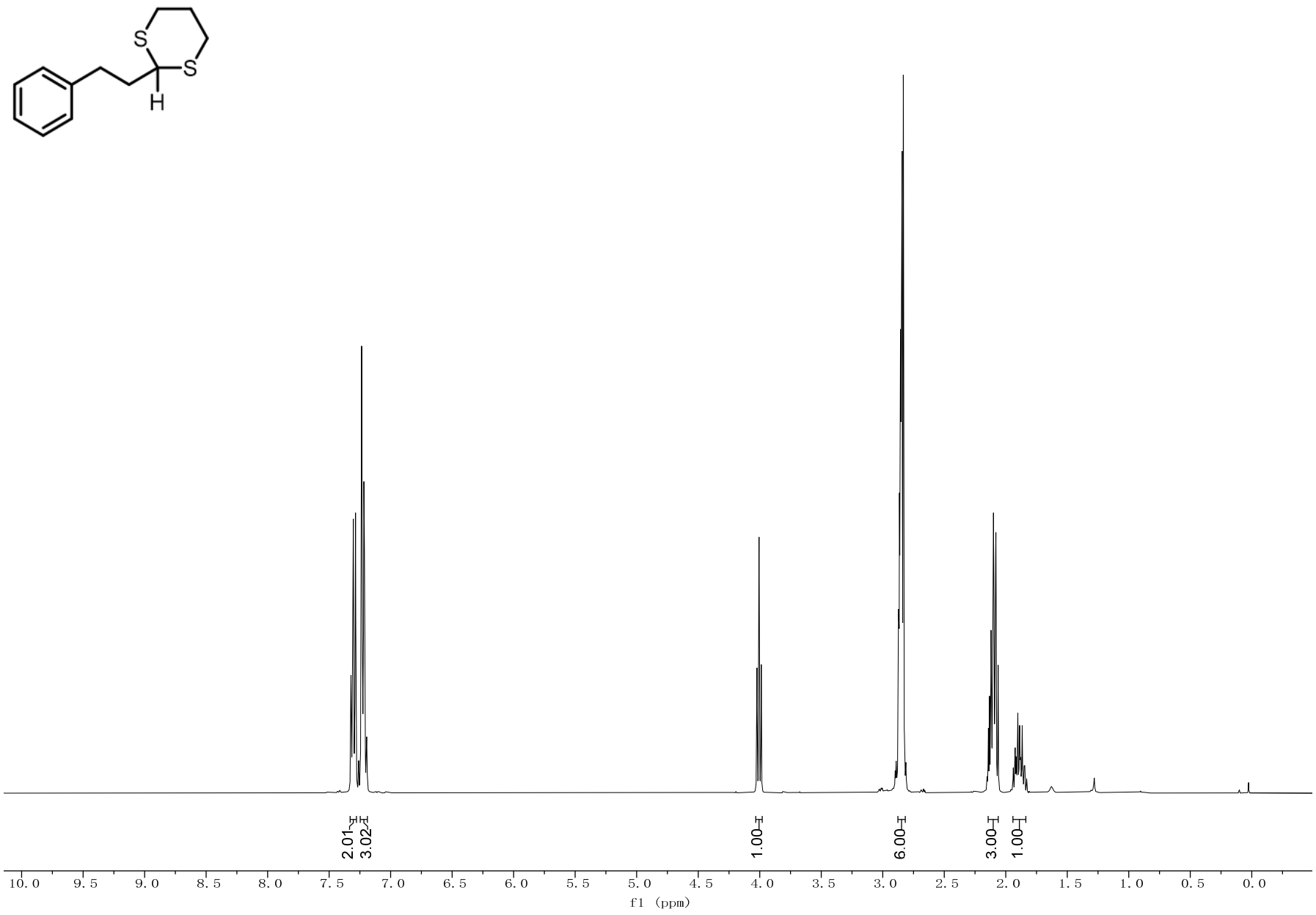

171.420
143.080
130.961
127.453
124.410
123.354
116.918
77.211
77.000
76.788
47.898
35.620
27.963
26.612
22.457
13.895
O
Et
N
H
rotamers included
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

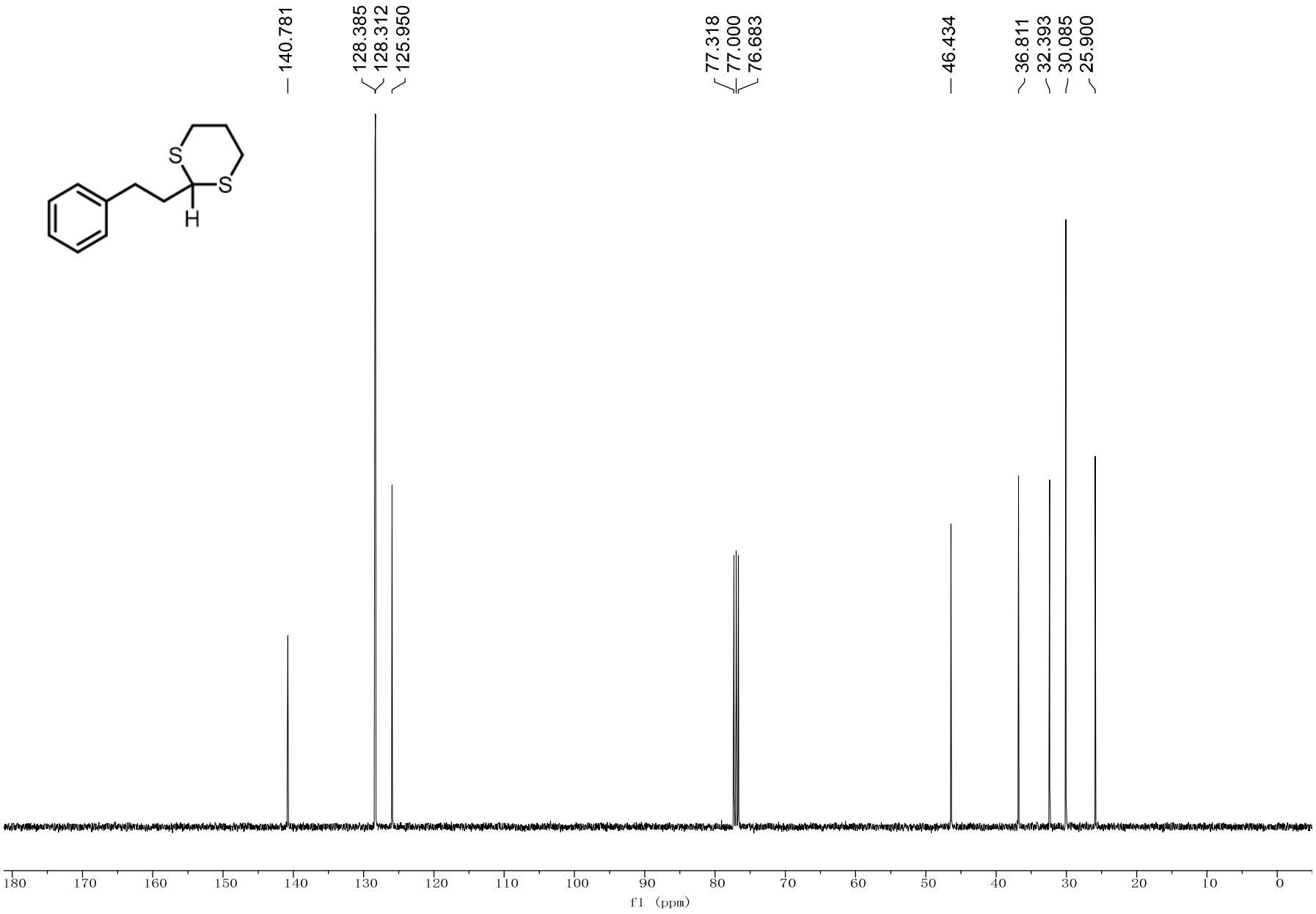


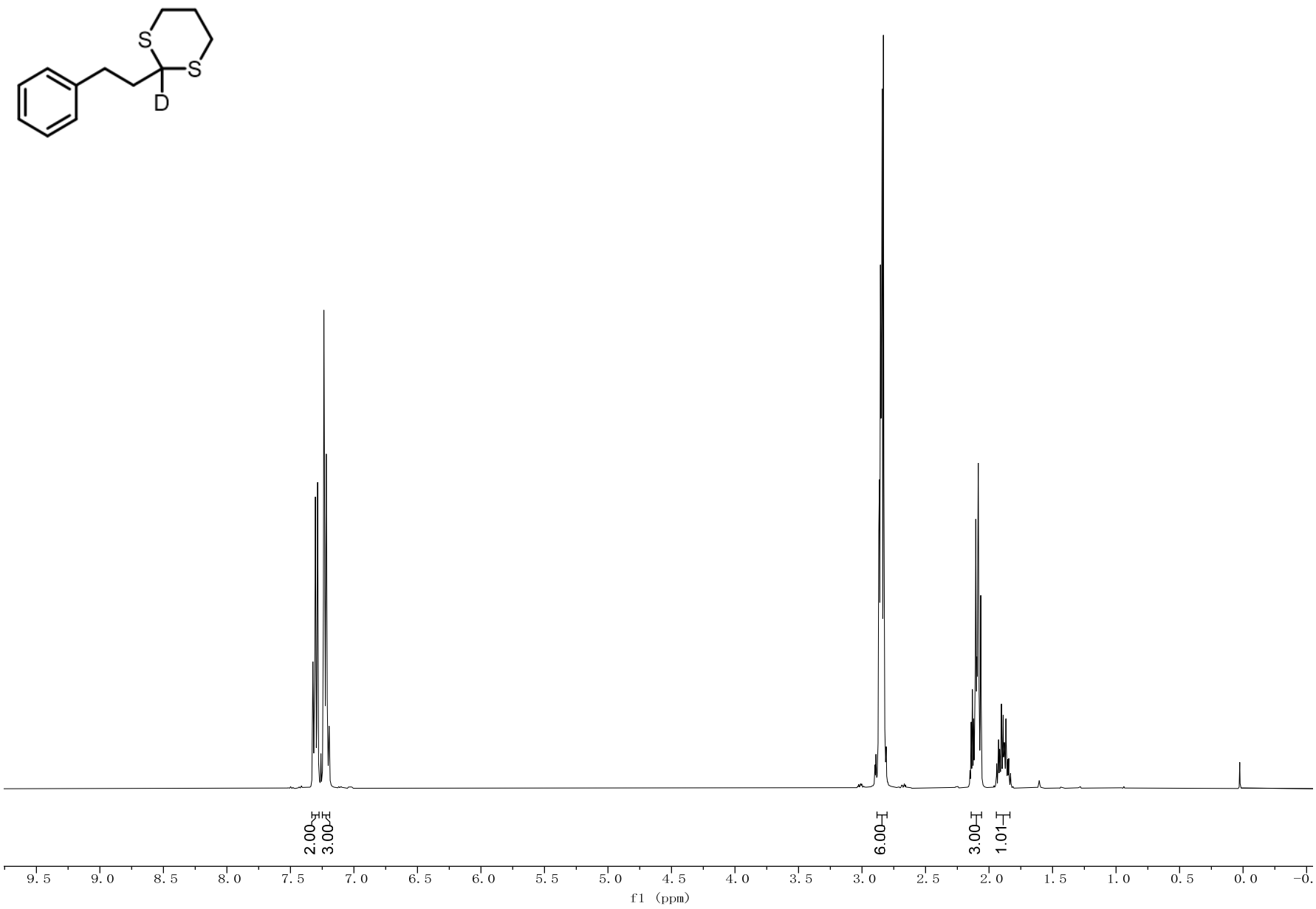
rotamers included

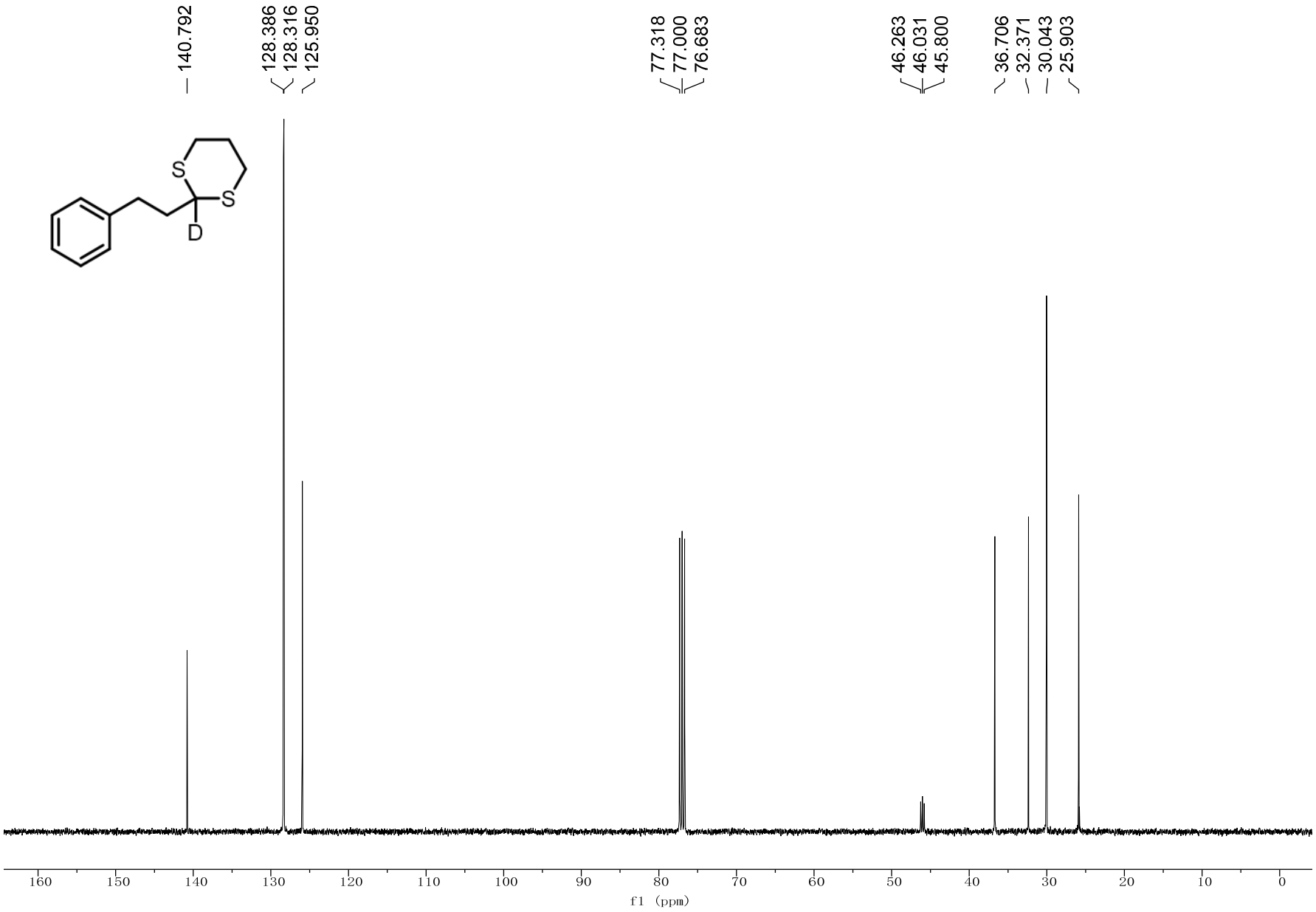


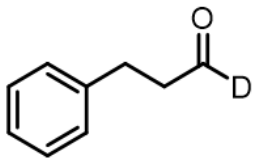

171.022
142.483
131.124
127.564
124.621
124.004
117.095
77.213
77.001
76.791
69.228
47.907
41.755
29.209
27.900
9.991
O
Br
N
Et
rotamers included
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

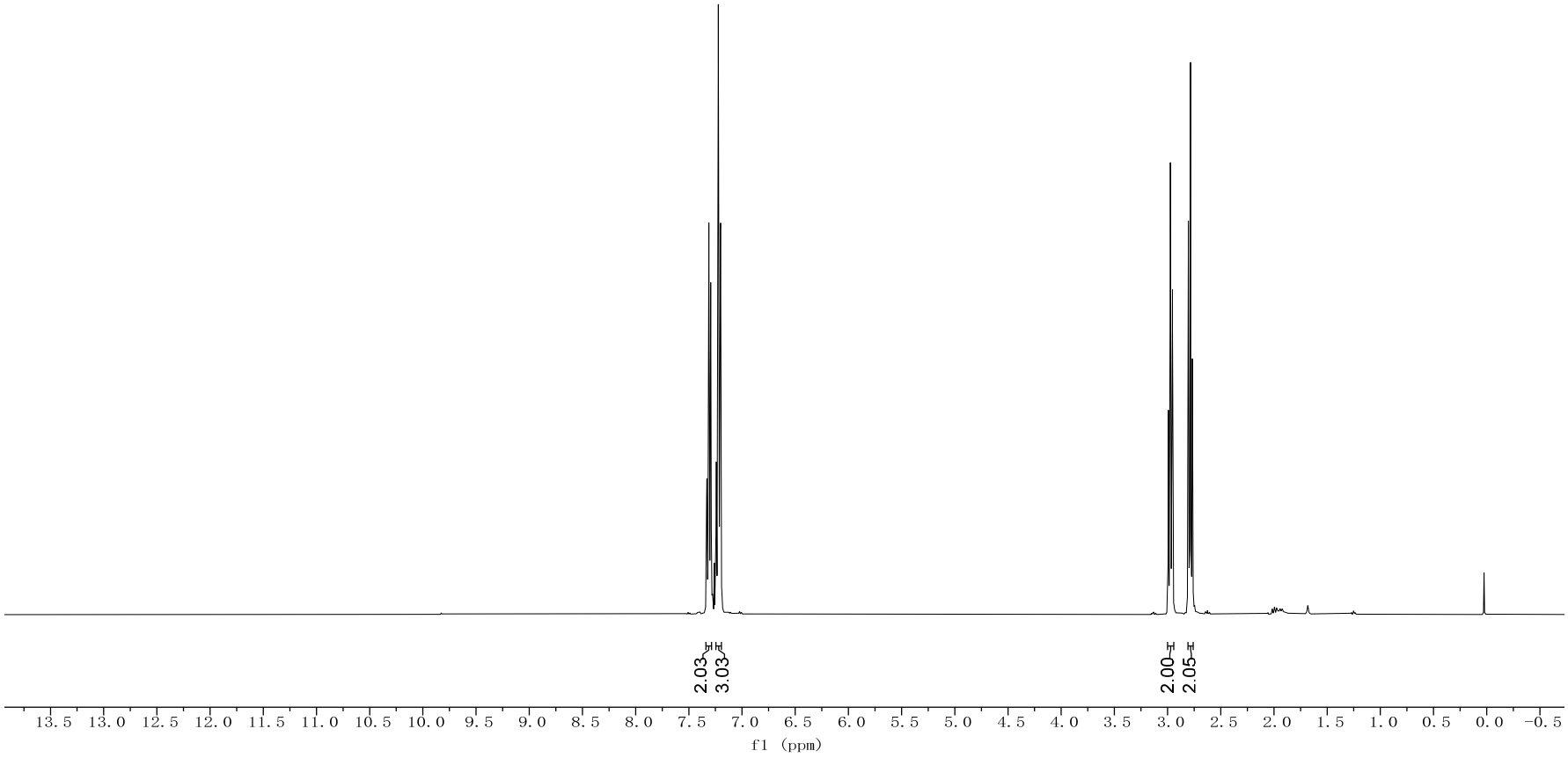

S
S
H
2.01
3.02
1.00
6.00
3.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

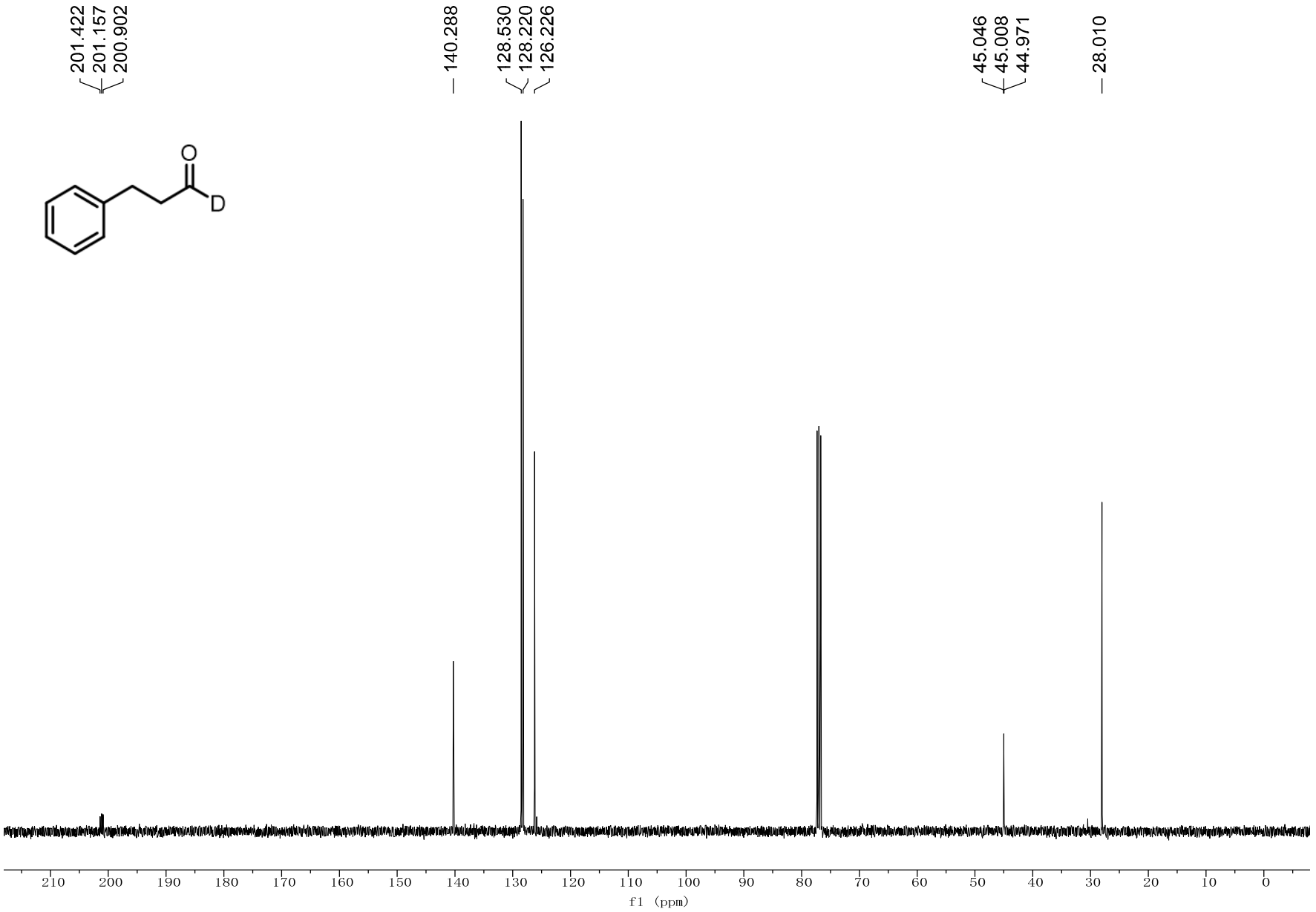

140.781
128.385
128.312
125.950
77.318
77.000
76.683
46.434
36.811
32.393
30.085
25.900
S
S
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

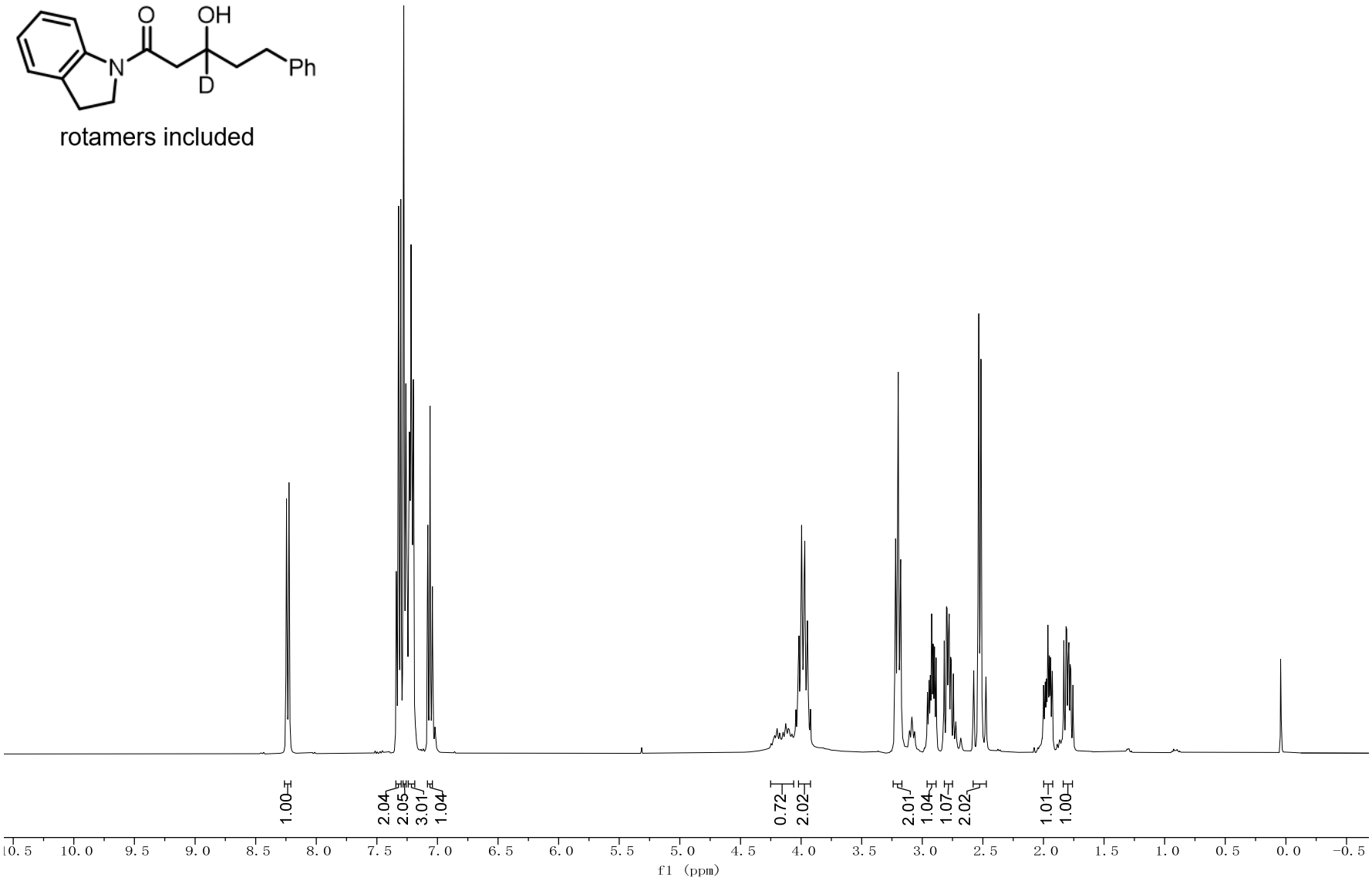

S
S
D
2.00
3.00
6.00
3.00
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

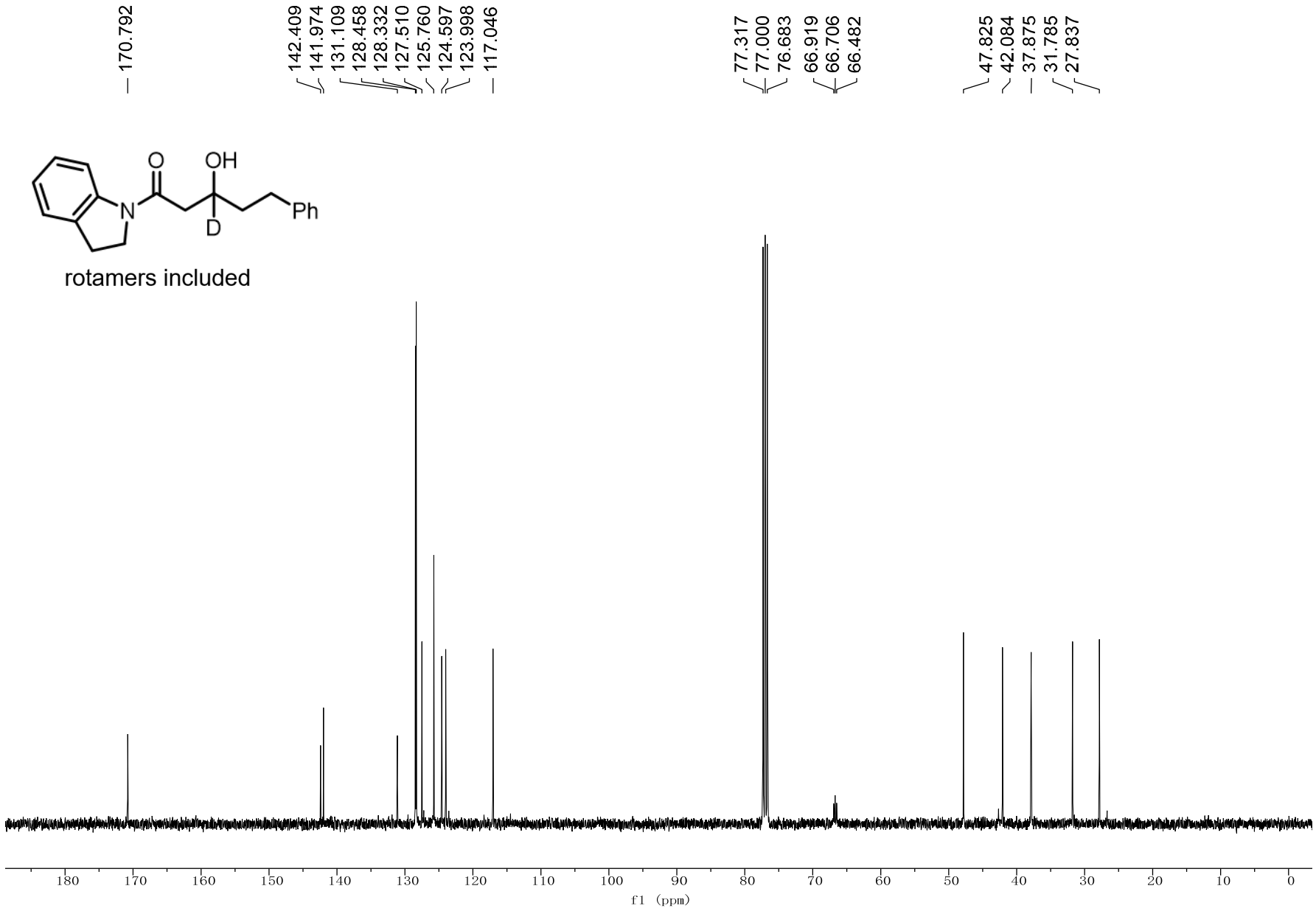

140.792
128.386
128.316
125.950
77.318
77.000
76.683
46.263
46.031
45.800
36.706
32.371
30.043
25.903
S
S
D
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
D


2.03
3.03
2.00
2.05
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


201.422
201.157
200.902
140.288
128.530
128.220
126.226
45.046
45.008
44.971
28.010
O
D
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OH
N
Ph
D
rotamers included
1.00
2.04
2.05
3.01
1.04
0.72
2.02
2.01
1.04
1.07
2.02
1.01
1.00
f1 (ppm)


170.792
142.409
141.974
131.109
128.458
128.332
127.510
125.760
124.597
123.998
117.046
77.317
77.000
76.683
66.919
66.706
66.482
47.825
42.084
37.875
31.785
27.837
O
OH
N
D
Ph
rotamers included
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

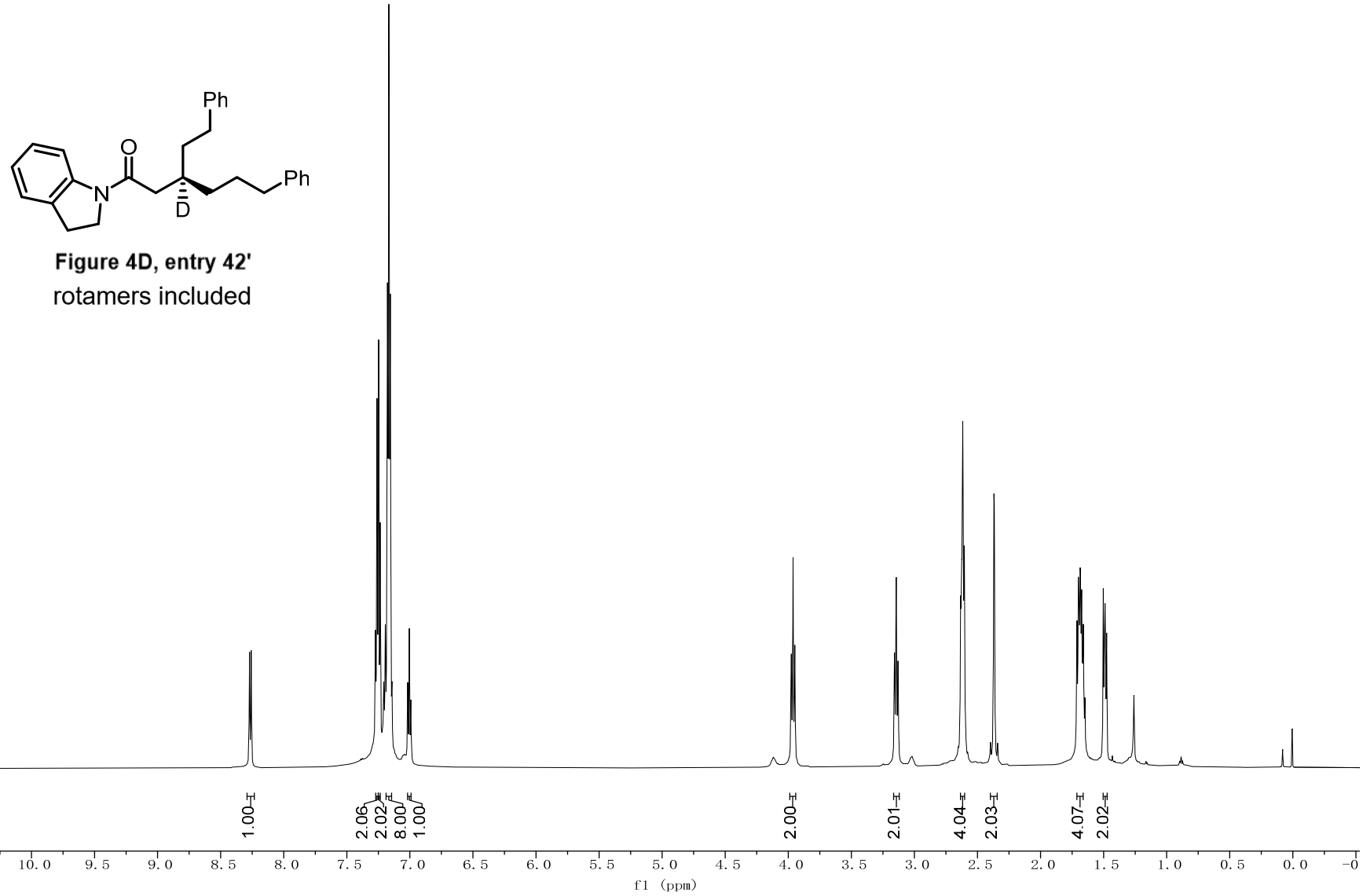


Figure 4D, entry 42'
rotamers included

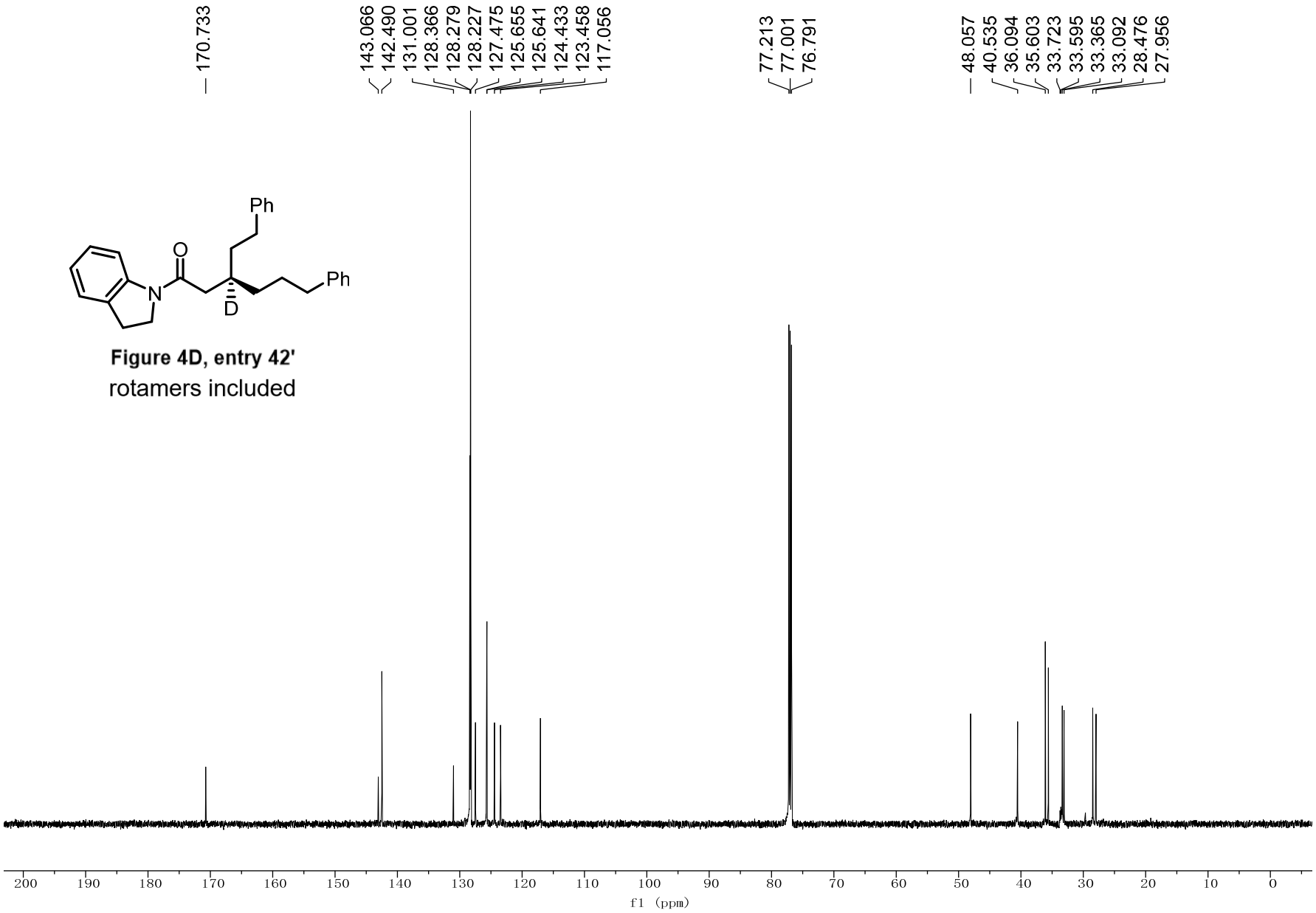


Figure 4D, entry 42'
rotamers included

Determination of Stereoselectivity

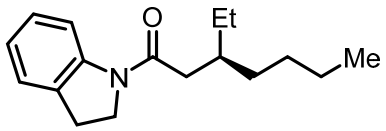
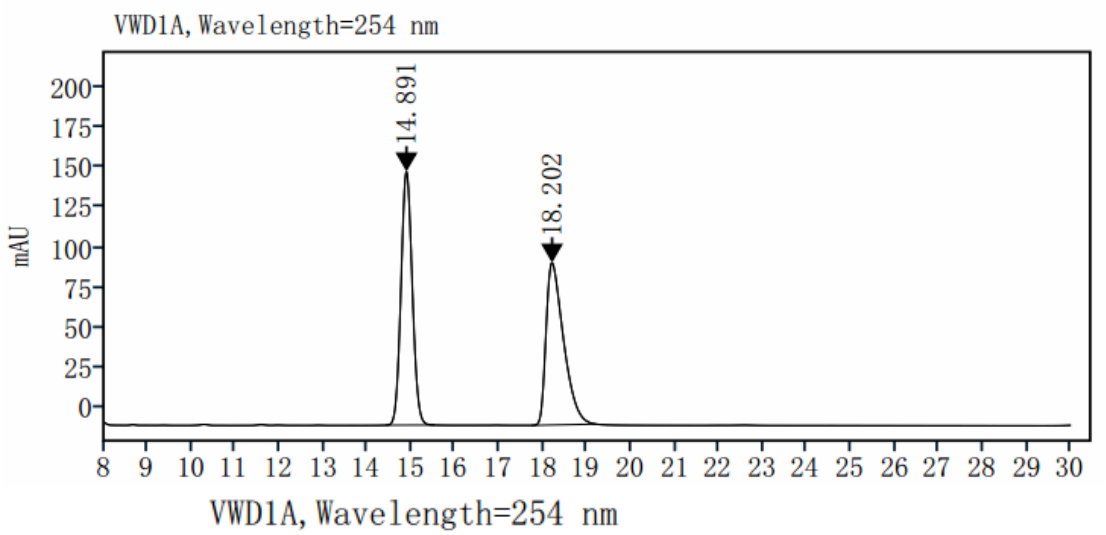
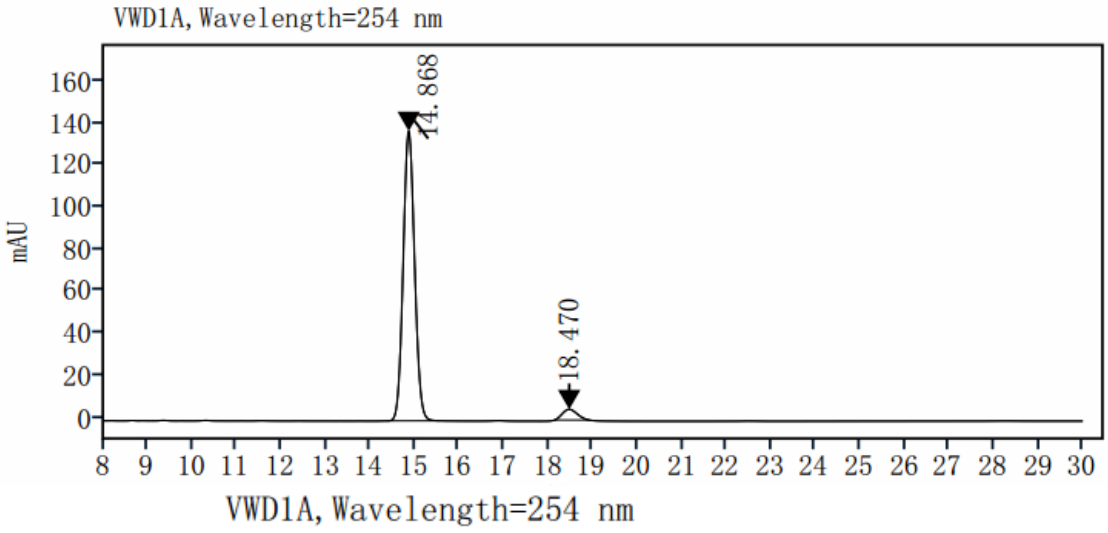


Figure 2A, entry 1
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	14.891	MM m	2804.99	49.99
	18.202	MM m	2805.90	50.01



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	14.868	MM m	2438.19	95.44
	18.470	MM m	116.52	4.56

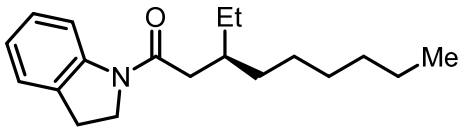
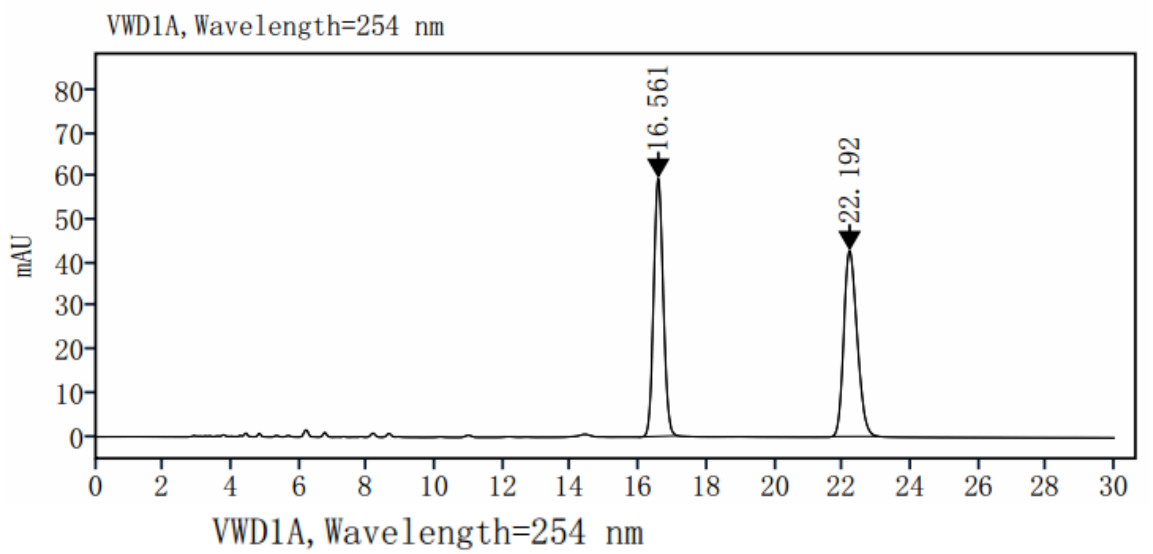
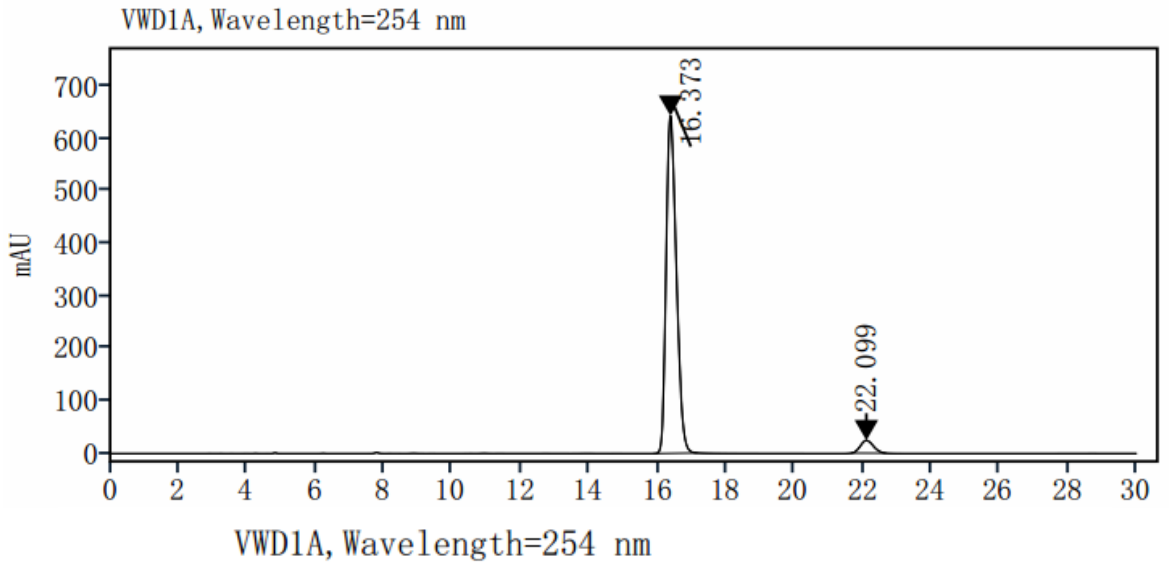


Figure 2A, entry 2
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	16.561	MM m	1161.58	49.83
	22.192	MM m	1169.40	50.17



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	16.373	MM m	13322.97	95.46
	22.099	MM m	634.26	4.54

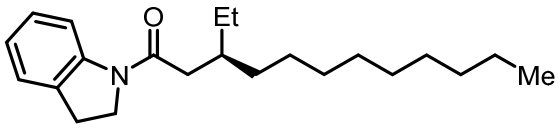
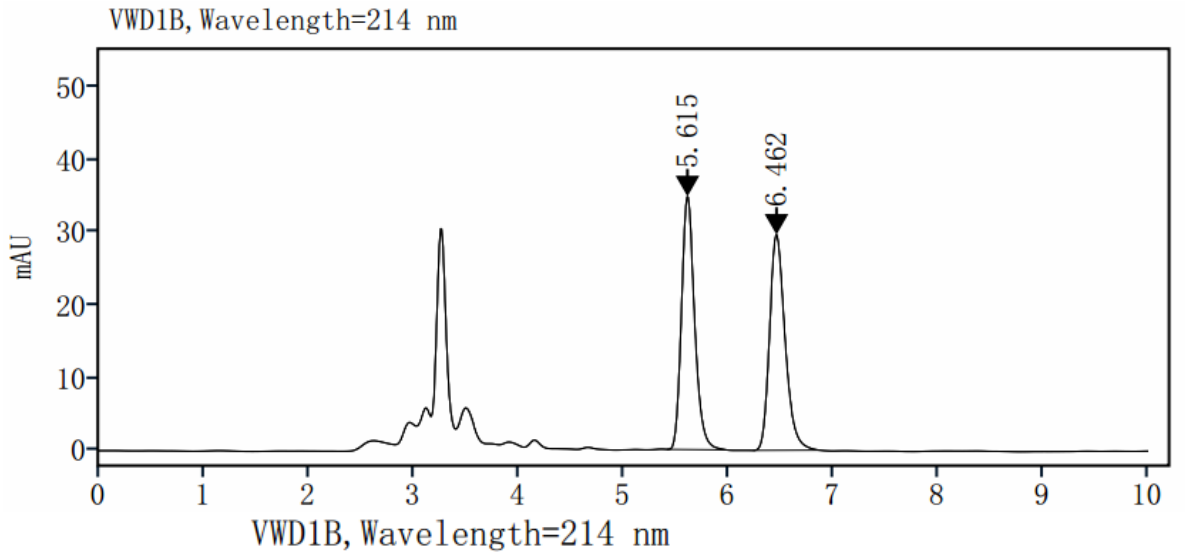
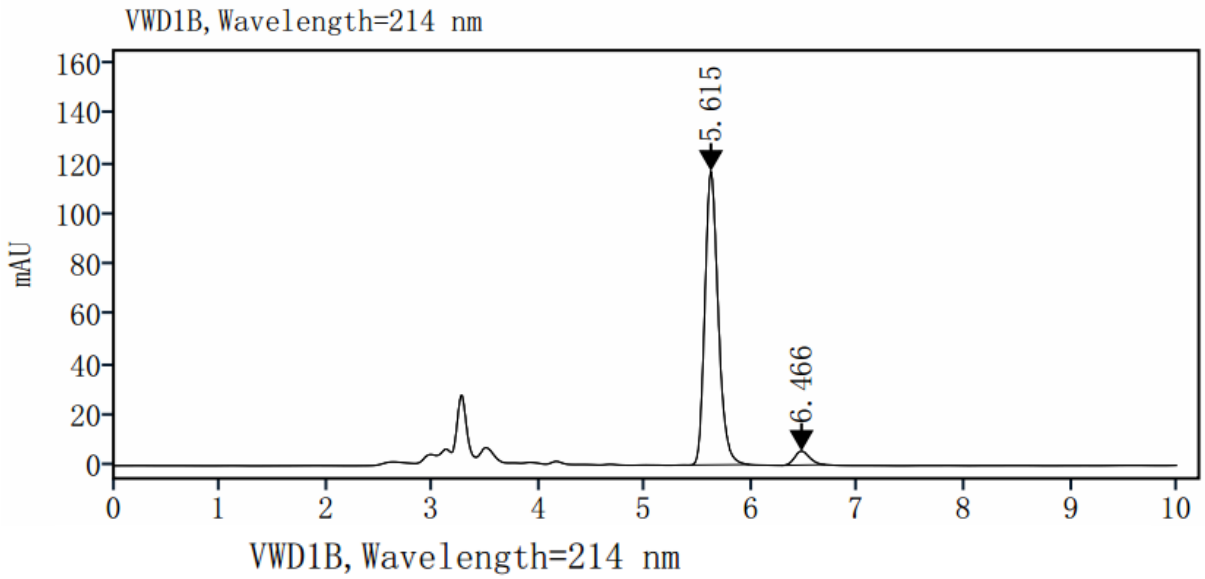


Figure 2A, entry 3
(*S*,*S*)-**L1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.615	MM m	302.27	49.80
	6.462	MM m	304.67	50.20



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.615	MM m	1020.44	94.97
	6.466	MM m	54.03	5.03

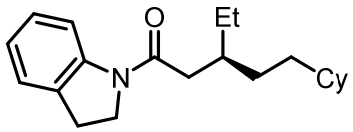
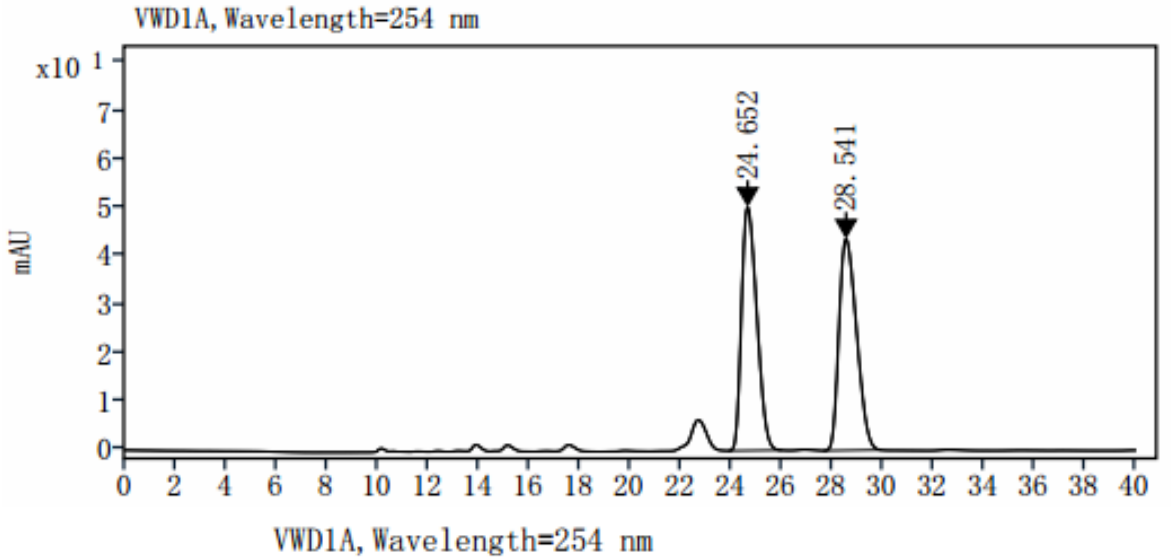
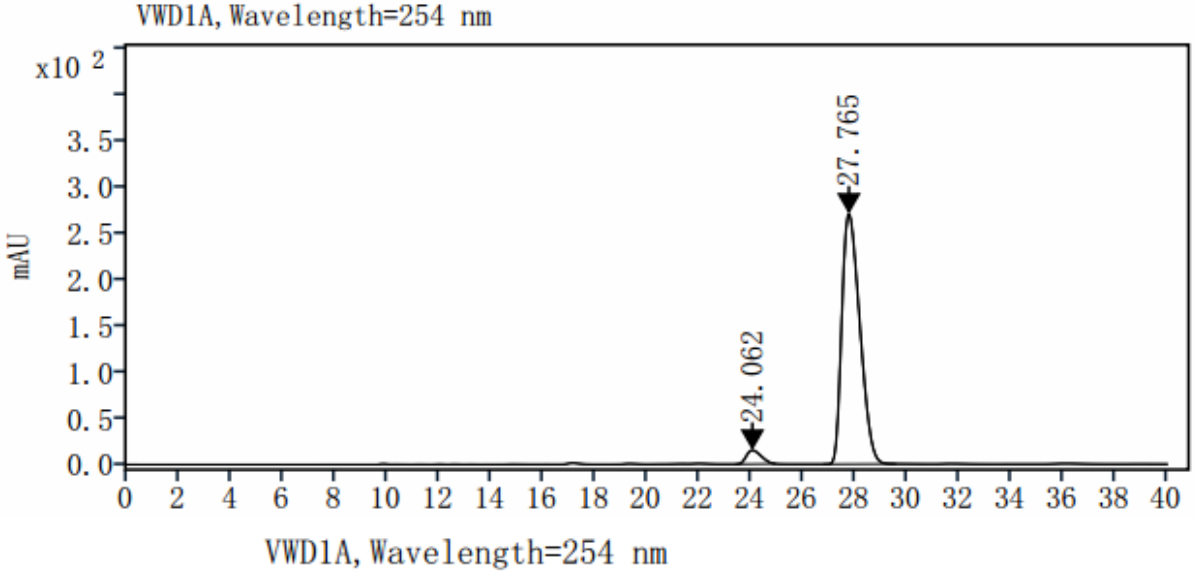


Figure 2A, entry 4
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	24.652	MM m	2110.90	50.03
	28.541	MM m	2108.19	49.97



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	24.062	MM m	590.96	4.35
	27.765	MM m	12998.70	95.65

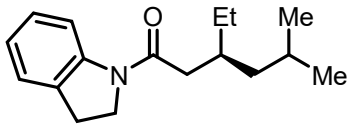
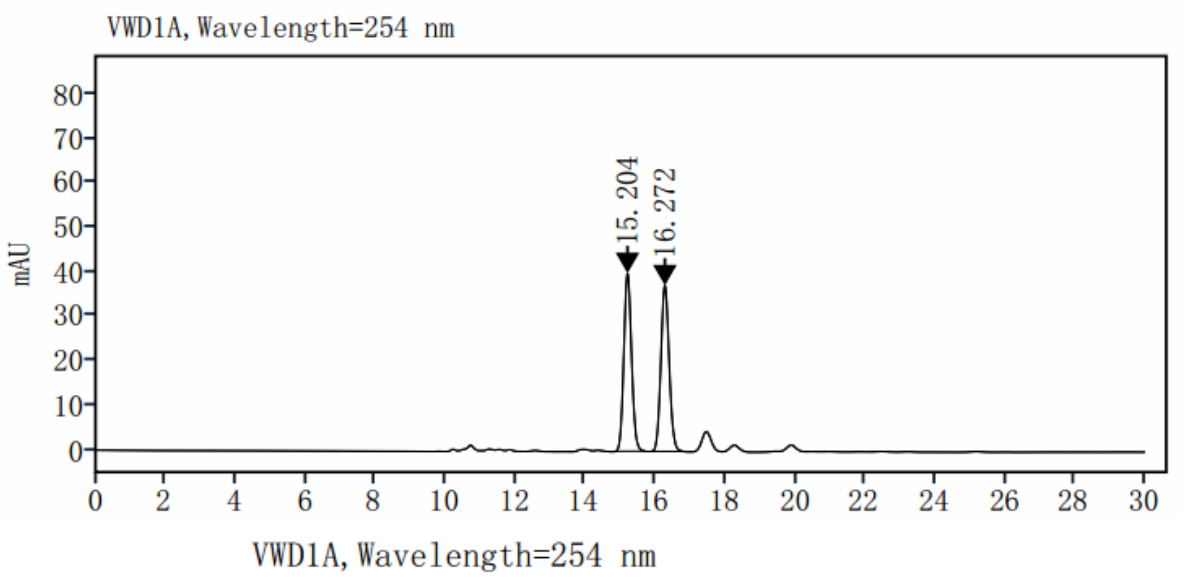
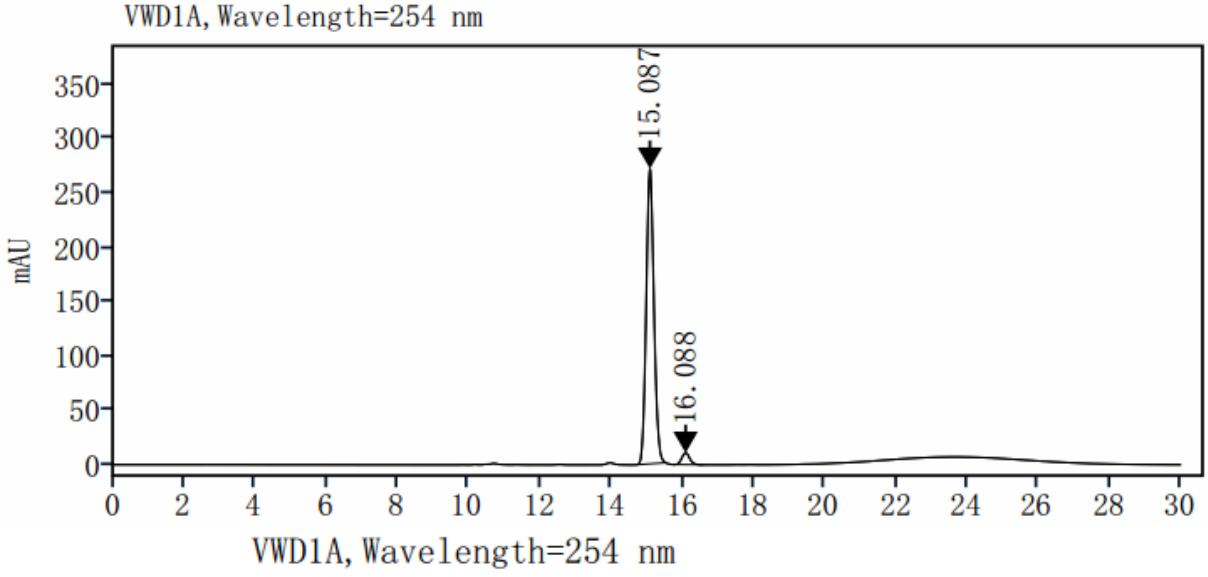


Figure 2A, entry 5
(*S*,*S*)-**L1**: 92% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.204	MM m	607.17	49.97
	16.272	MM m	608.02	50.03



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.087	MM m	4099.44	96.11
	16.088	MM m	166.09	3.89

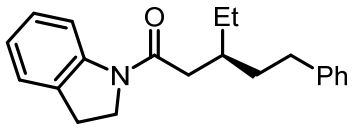
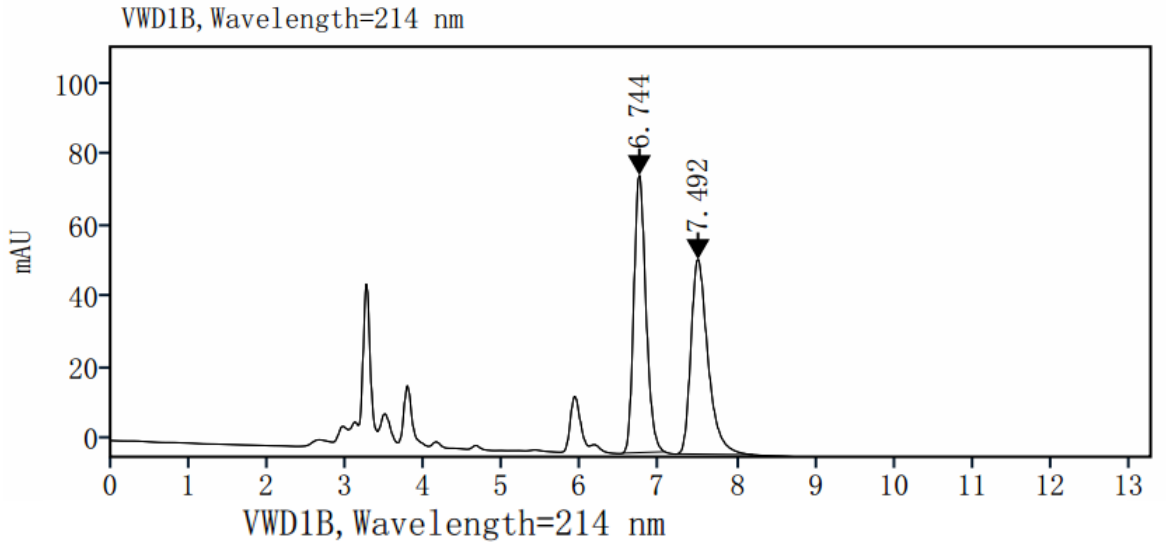
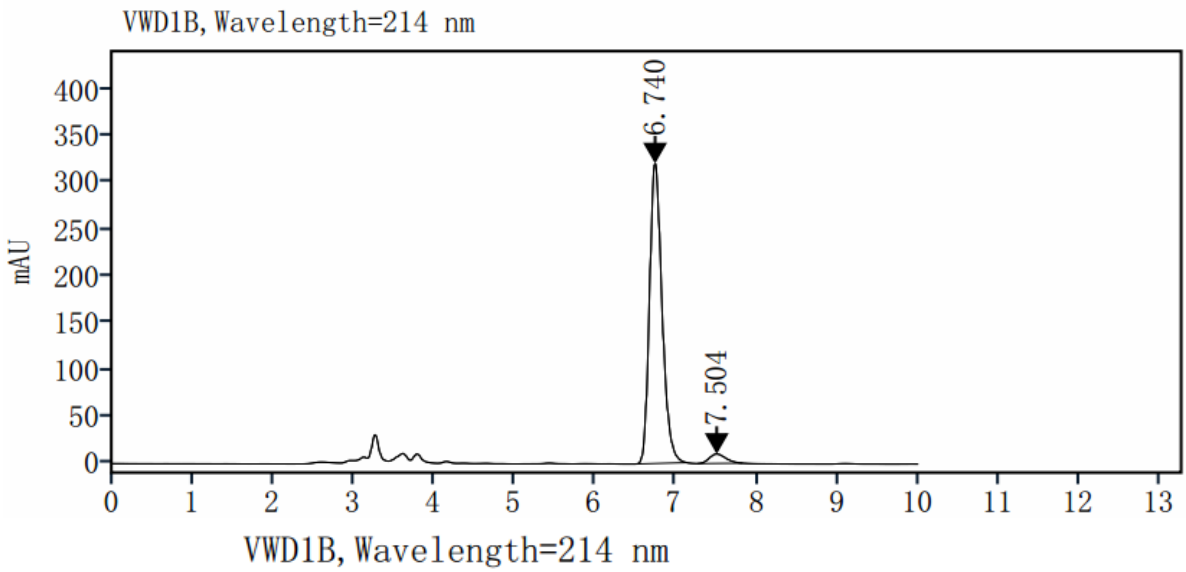


Figure 2A, entry 6
(*S*,*S*)-**L1**: 92% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.744	MM m	839.56	50.31
	7.492	MM m	829.18	49.69



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.740	MM m	3481.84	96.06
	7.504	MM m	142.96	3.94

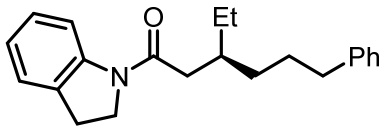
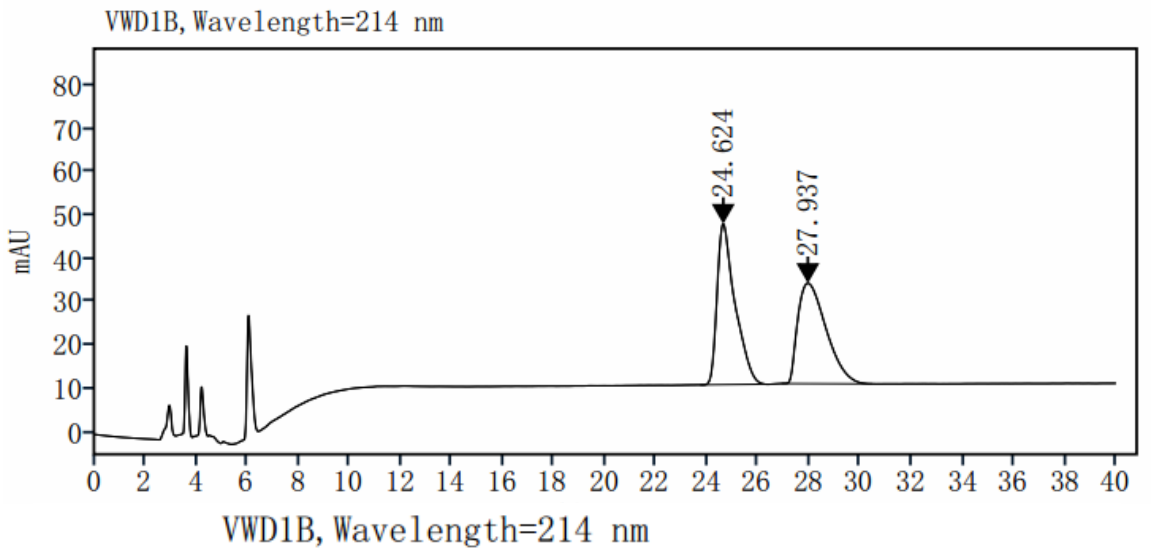
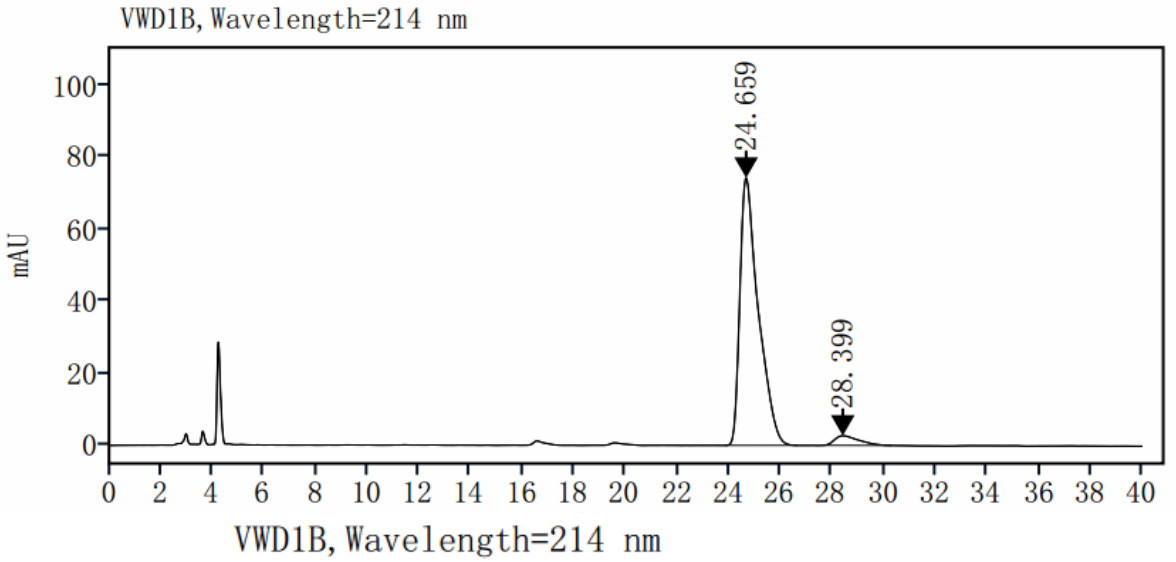


Figure 2A, entry 7
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	24.624	MM m	1806.51	50.29
	27.937	MM m	1785.98	49.71



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	24.659	MM m	3677.73	95.51
	28.399	MM m	172.73	4.49

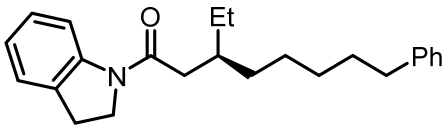
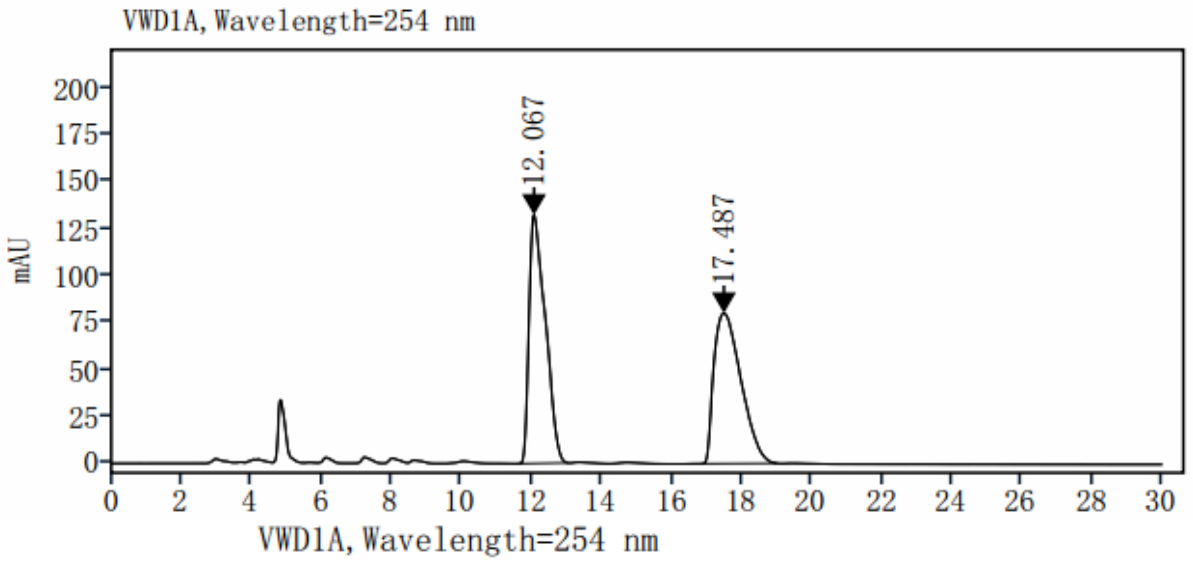
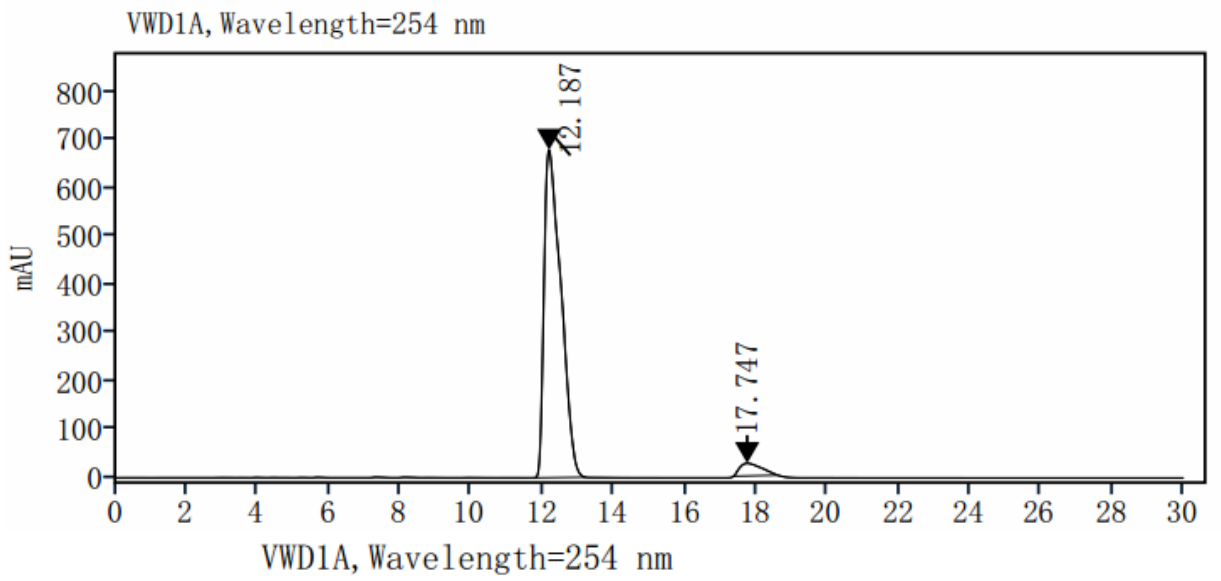


Figure 2A, entry 8
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	12.067	MM m	4280.92	49.85
	17.487	MM m	4306.03	50.15



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	12.187	MM m	22371.11	95.27
	17.747	MM m	1110.23	4.73

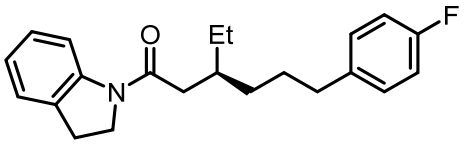
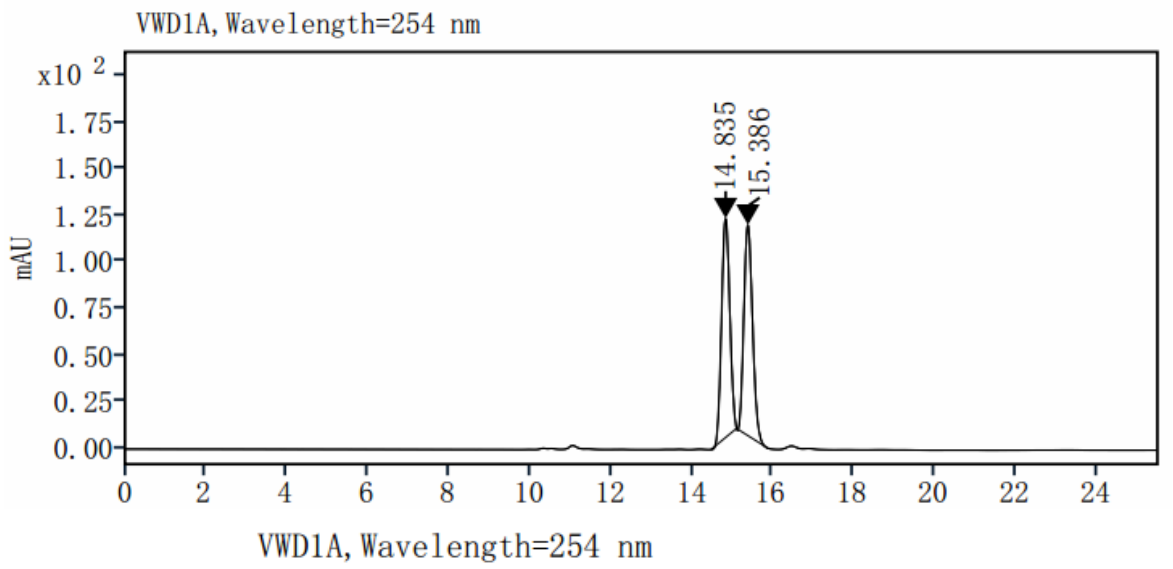
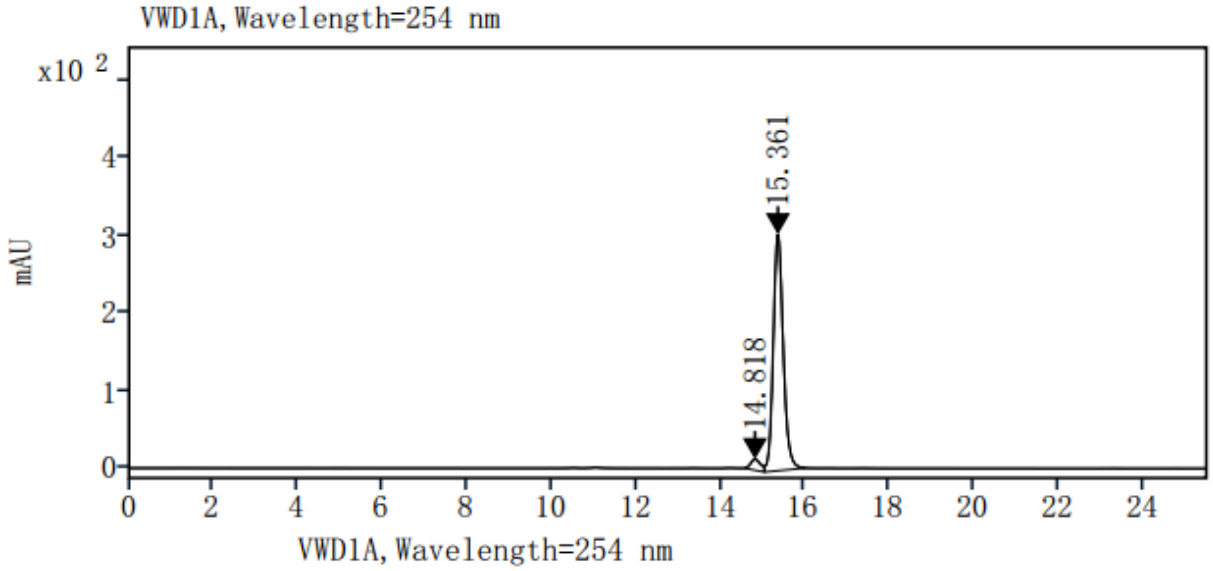


Figure 2A, entry 9
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	14.835	MM m	1654.66	49.62
	15.386	MM m	1680.09	50.38



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	14.818	MM m	237.46	4.51
	15.361	MM m	5025.93	95.49

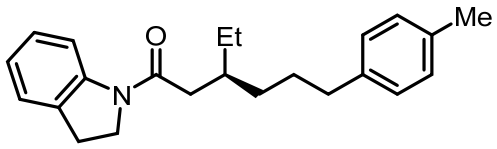
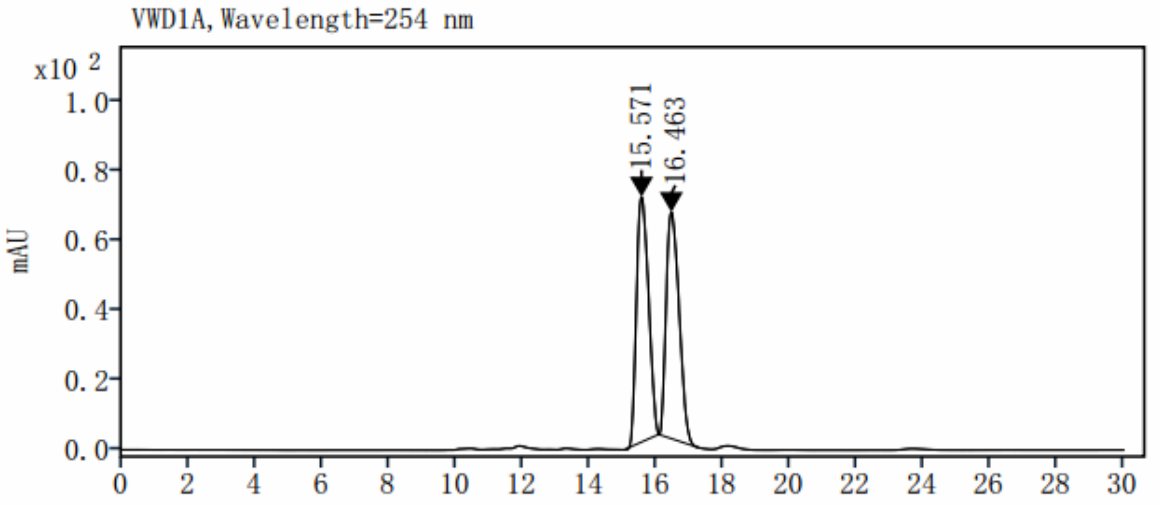
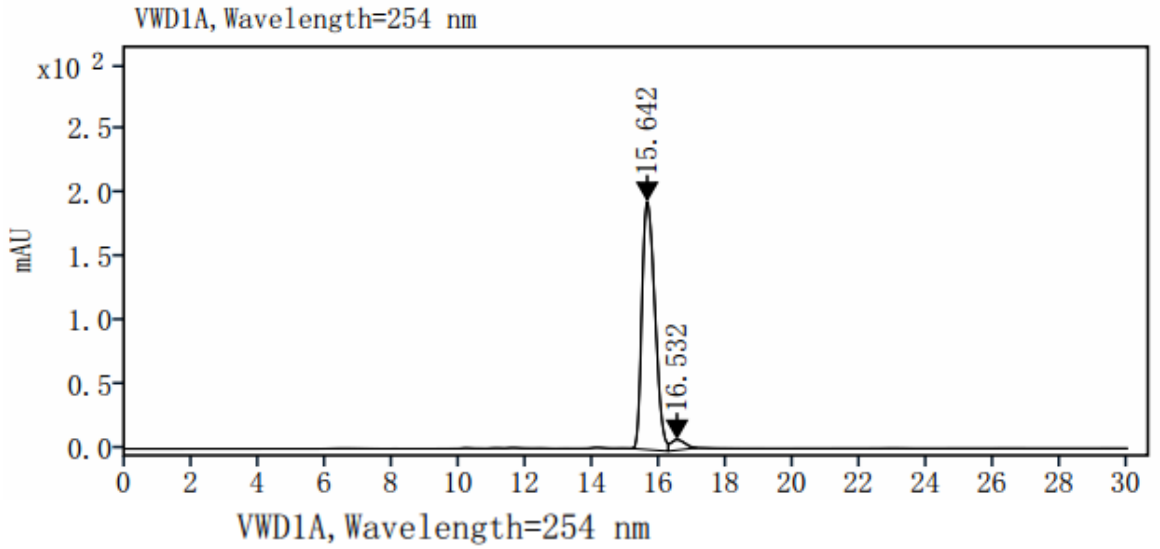


Figure 2A, entry 10
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.571	MM m	1762.85	50.05
	16.463	MM m	1759.46	49.95



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.642	MM m	5234.25	95.53
	16.532	MM m	244.92	4.47

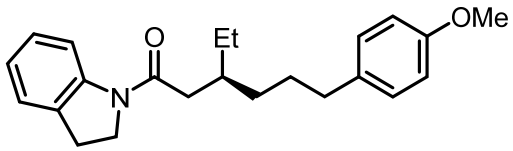
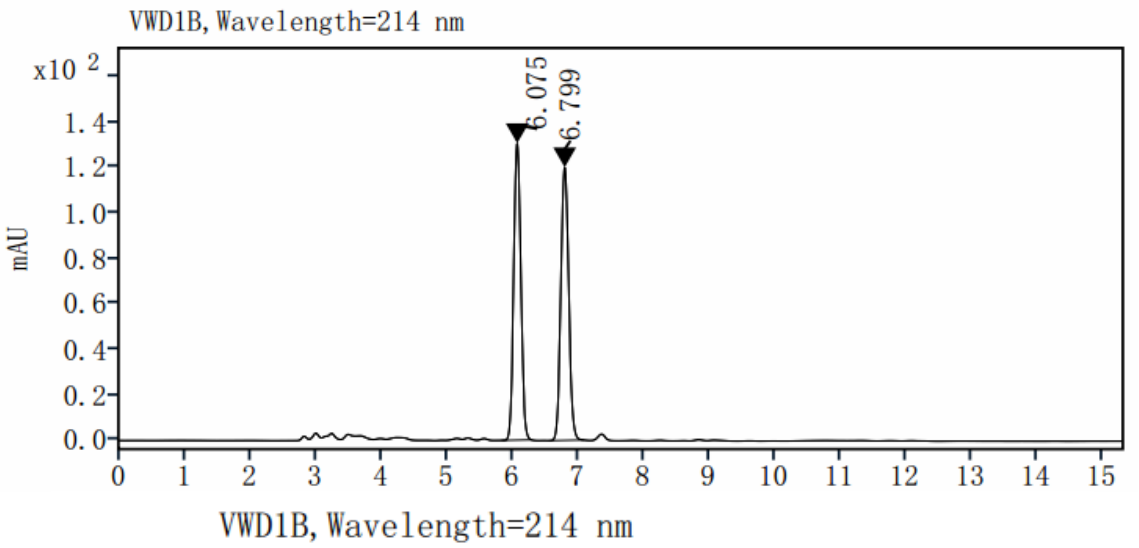
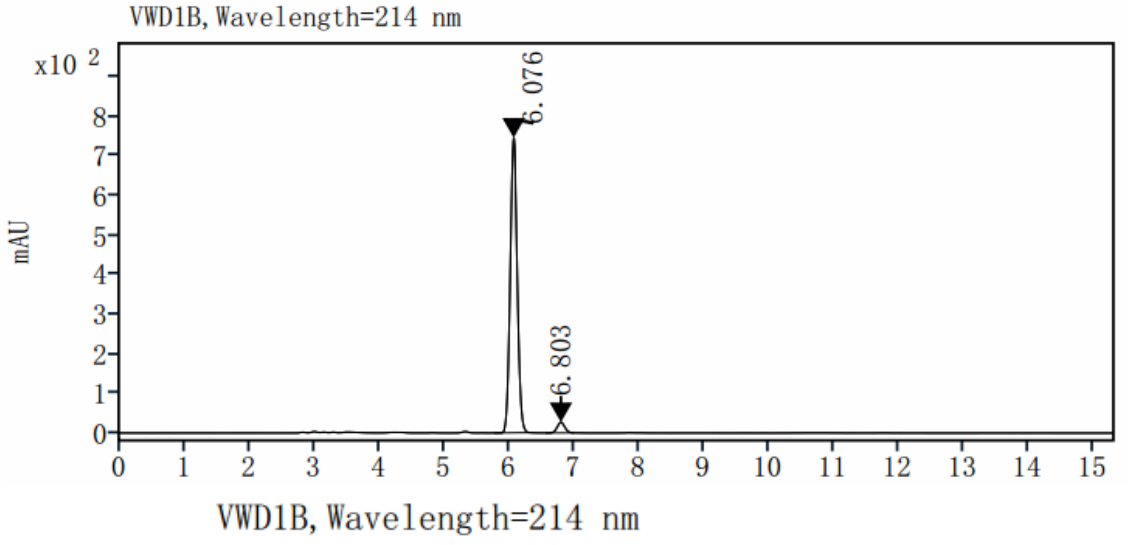


Figure 2A, entry 11
(*S*,*S*)-**L1**: 93% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.075	MM m	980.47	49.66
	6.799	MM m	993.71	50.34



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.076	MM m	5635.79	96.24
	6.803	MM m	220.34	3.76

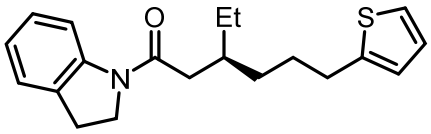
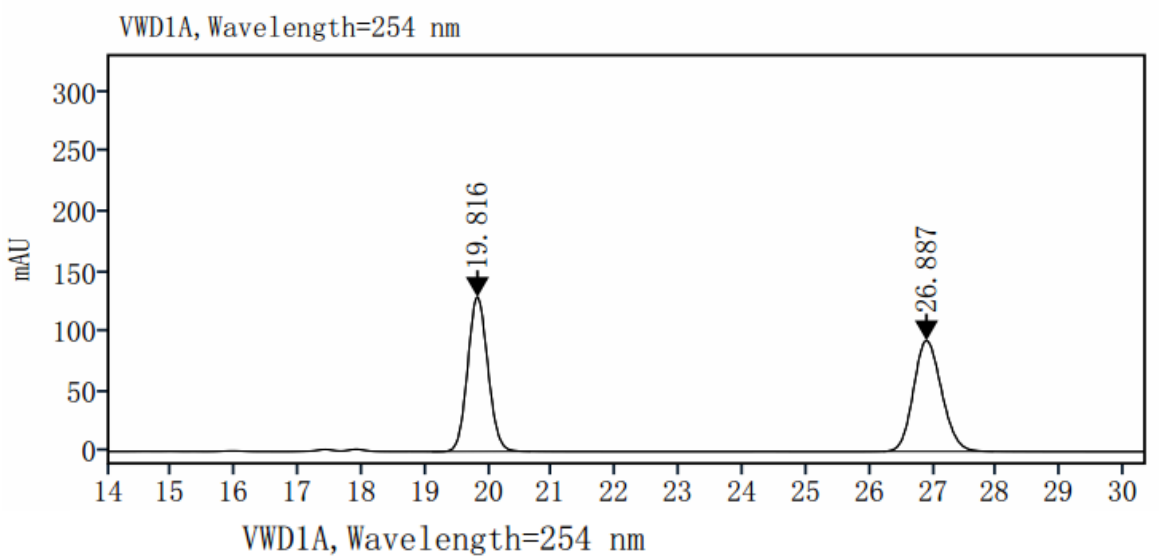
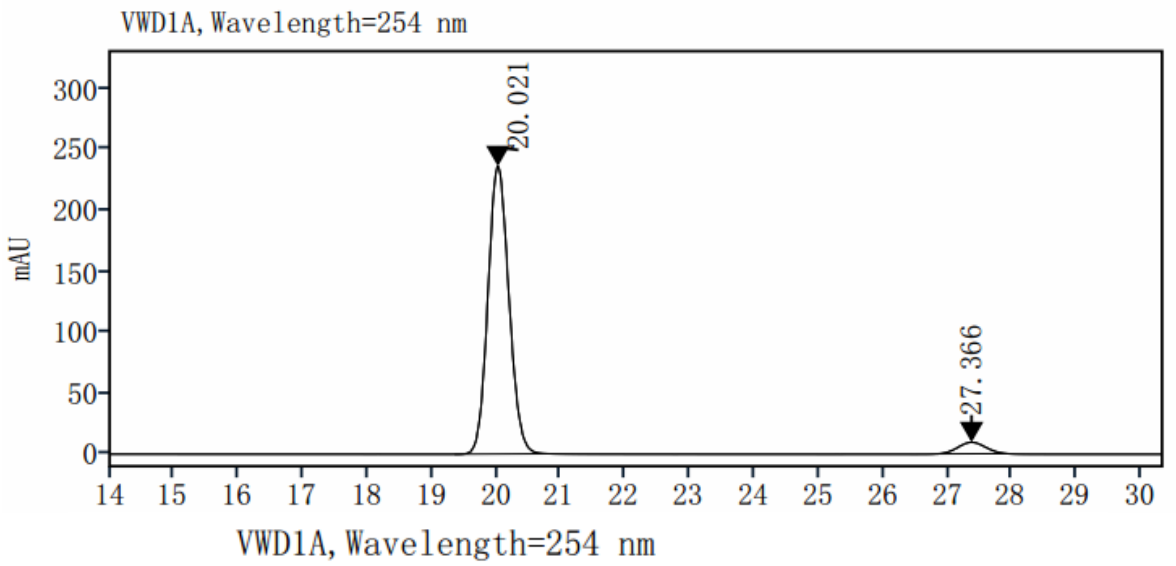


Figure 2A, entry 12
(*S*,*S*)-**L1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	19.816	MM m	2860.97	50.06
	26.887	MM m	2854.19	49.94



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	20.021	MM m	5351.99	95.05
	27.366	MM m	278.55	4.95

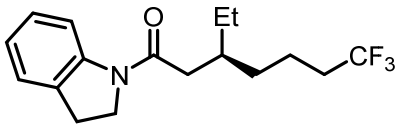
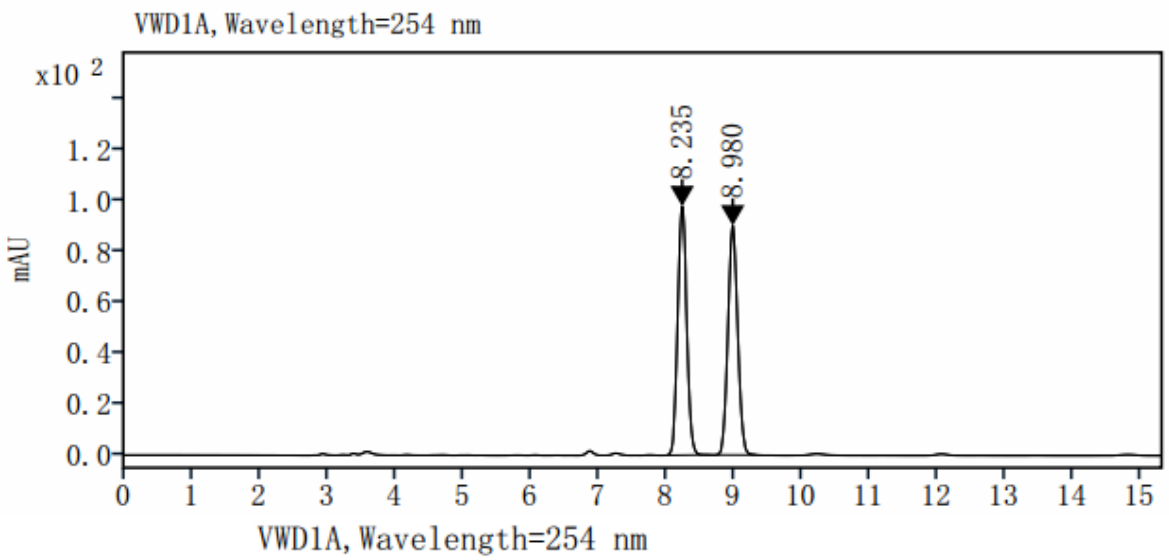
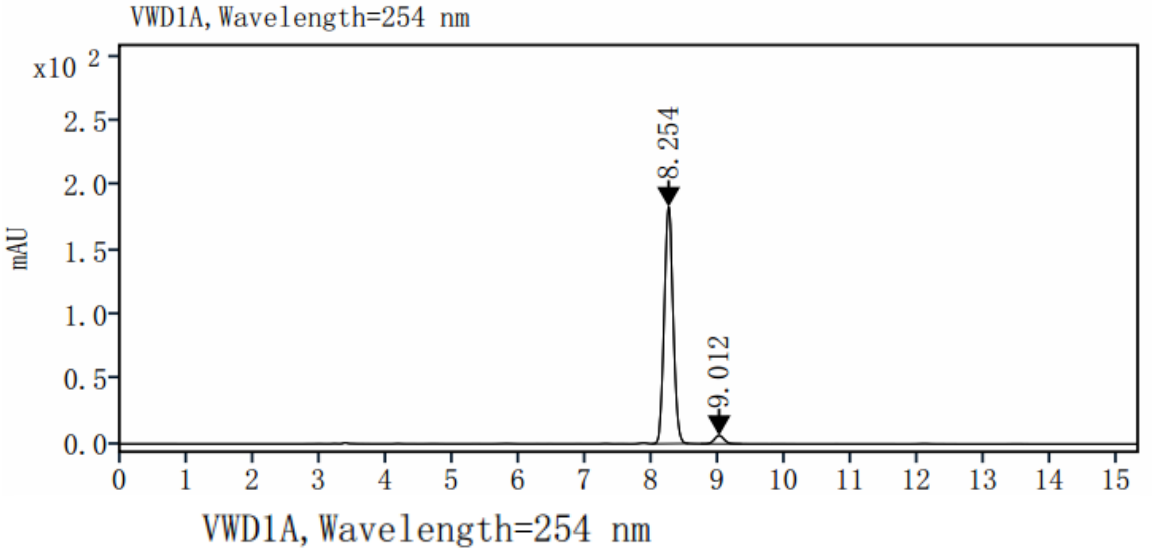


Figure 2A, entry 13
(*S*,*S*)-**L1**: 93% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	8.235	MM m	904.41	49.98
	8.980	MM m	904.99	50.02



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	8.254	MM m	1712.64	96.35
	9.012	MM m	64.85	3.65

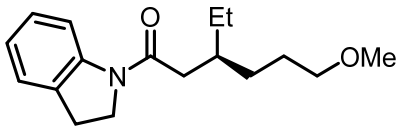
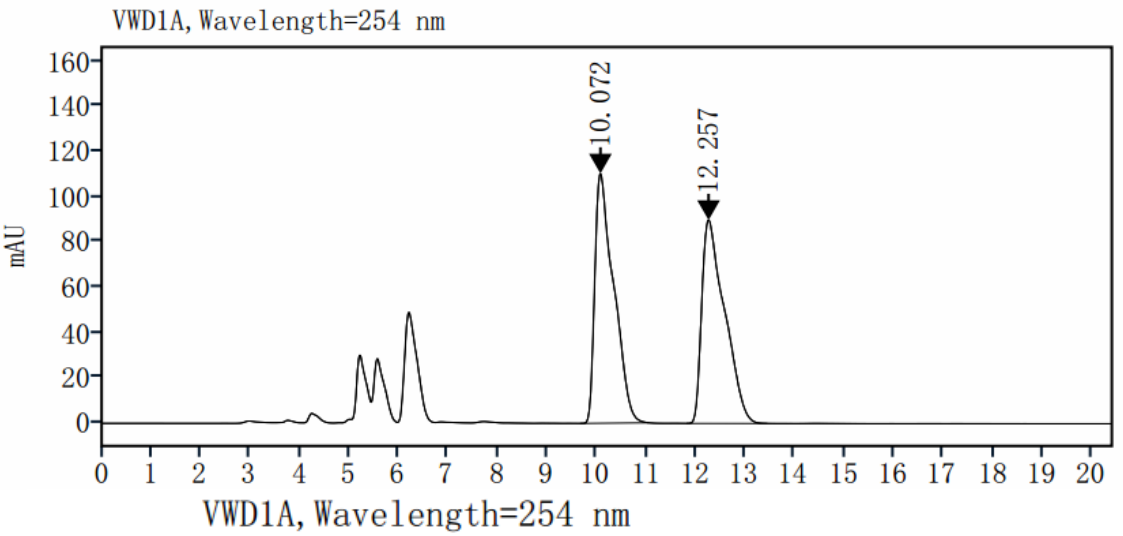
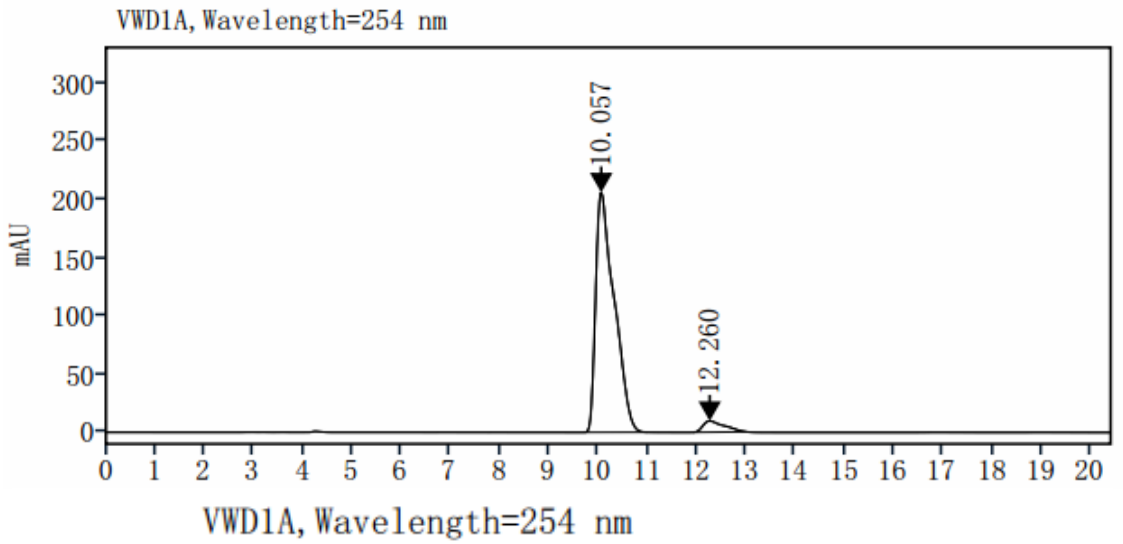


Figure 2A, entry 14
(*S*,*S*)-**L1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.072	MM m	2922.94	50.30
	12.257	MM m	2888.47	49.70



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.057	MM m	5397.64	94.90
	12.260	MM m	289.92	5.10

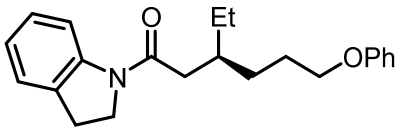
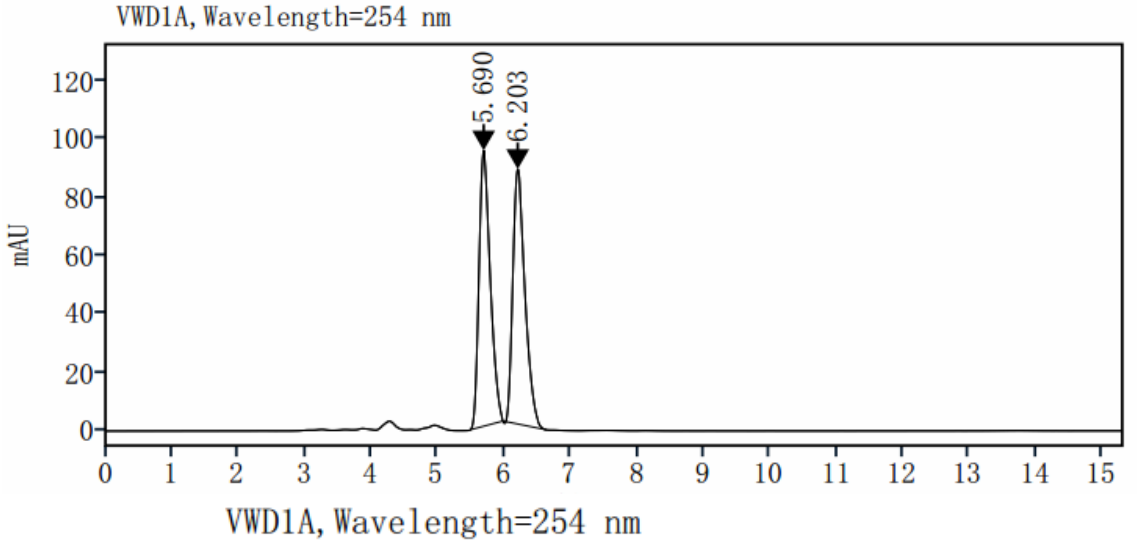
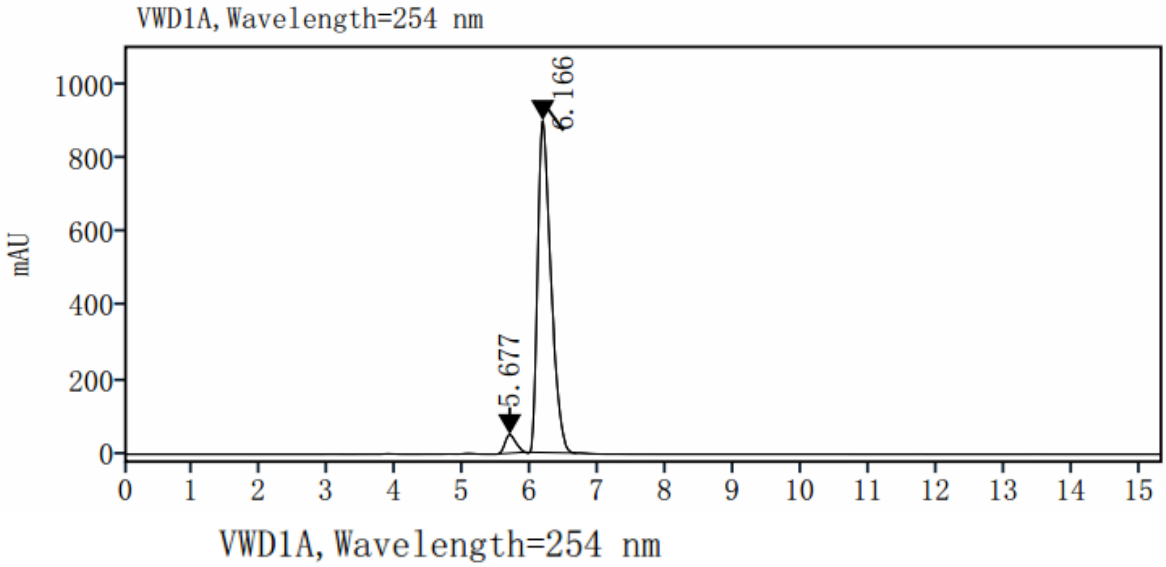


Figure 2A, entry 15
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.690	MM m	1118.81	50.14
	6.203	MM m	1112.71	49.86



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.677	MM m	557.60	4.37
	6.166	MM m	12211.86	95.63

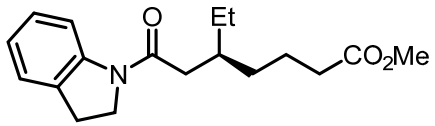
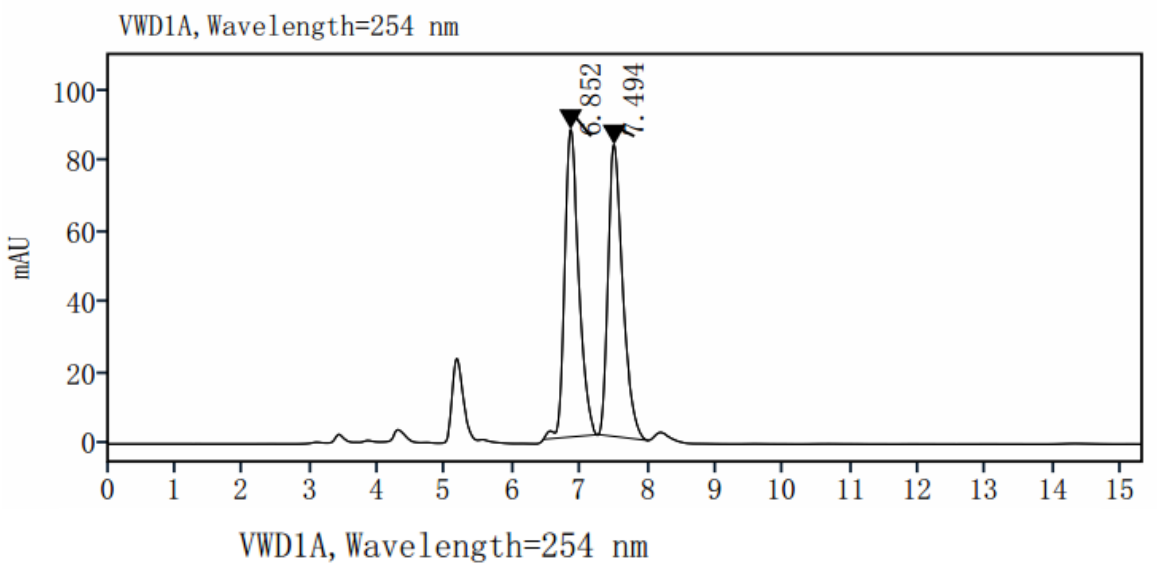
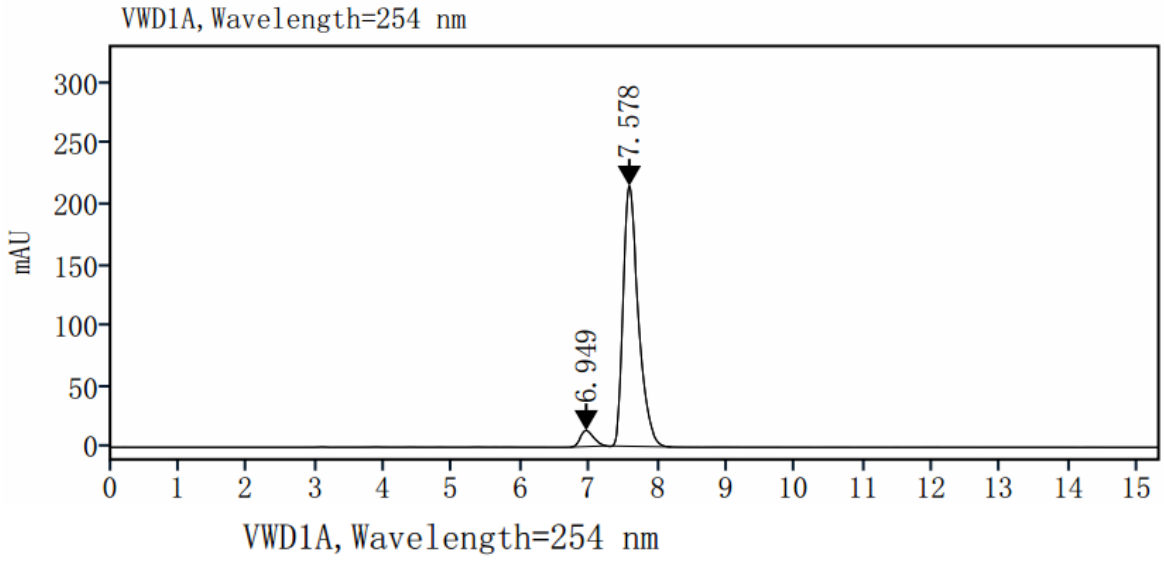


Figure 2A, entry 16
(*S*,*S*)-**L1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.852	MM m	1263.53	50.23
	7.494	MM m	1251.81	49.77



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.949	MM m	177.57	5.10
	7.578	MM m	3301.31	94.90

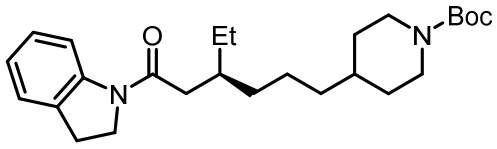
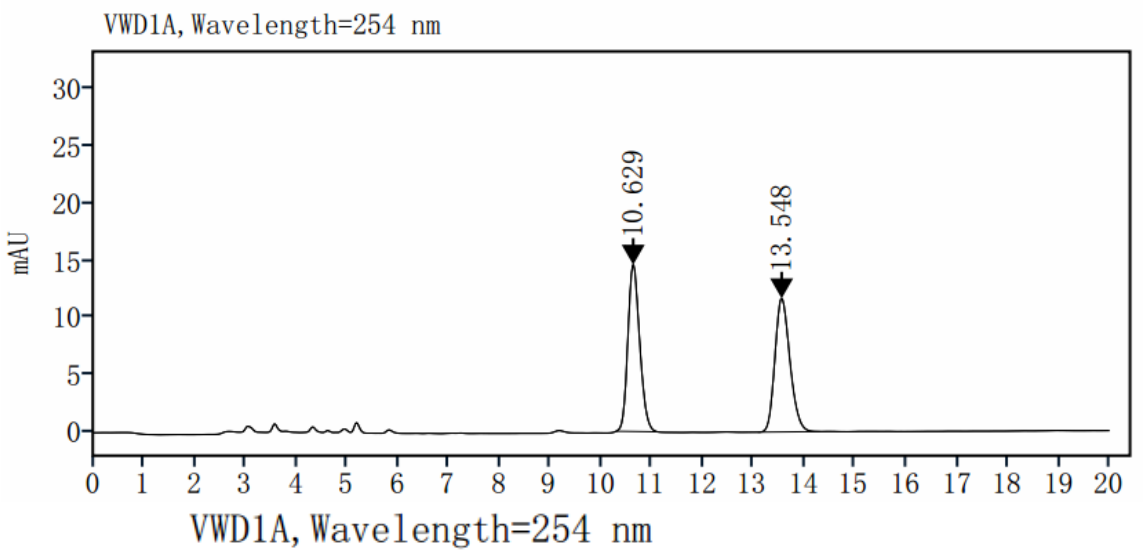
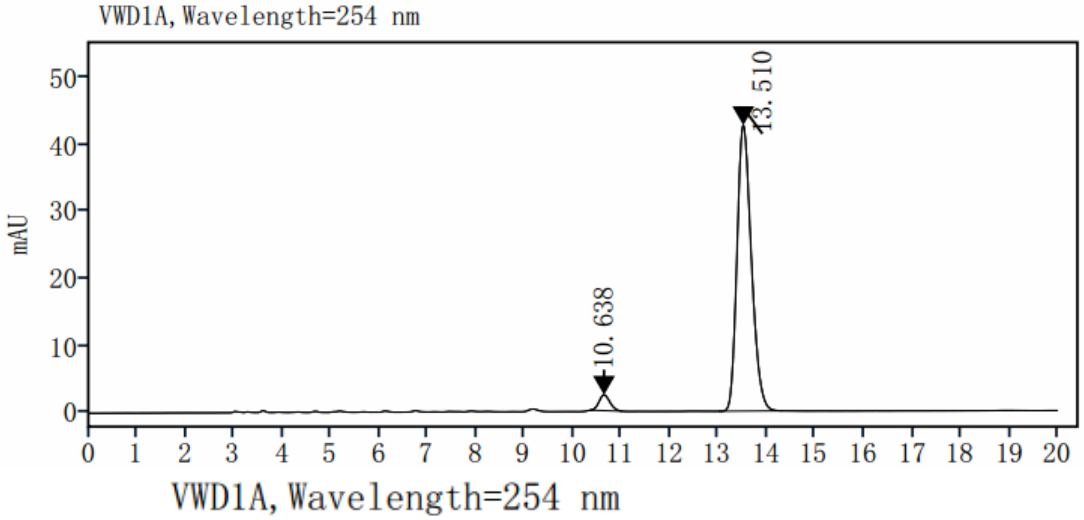


Figure 2A, entry 17
(*S*,*S*)-**L1**: 92% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.629	MM m	235.32	49.61
	13.548	MM m	239.01	50.39



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.638	MM m	36.89	4.04
	13.510	MM m	876.78	95.96

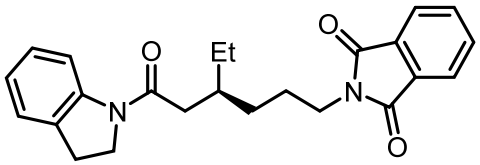
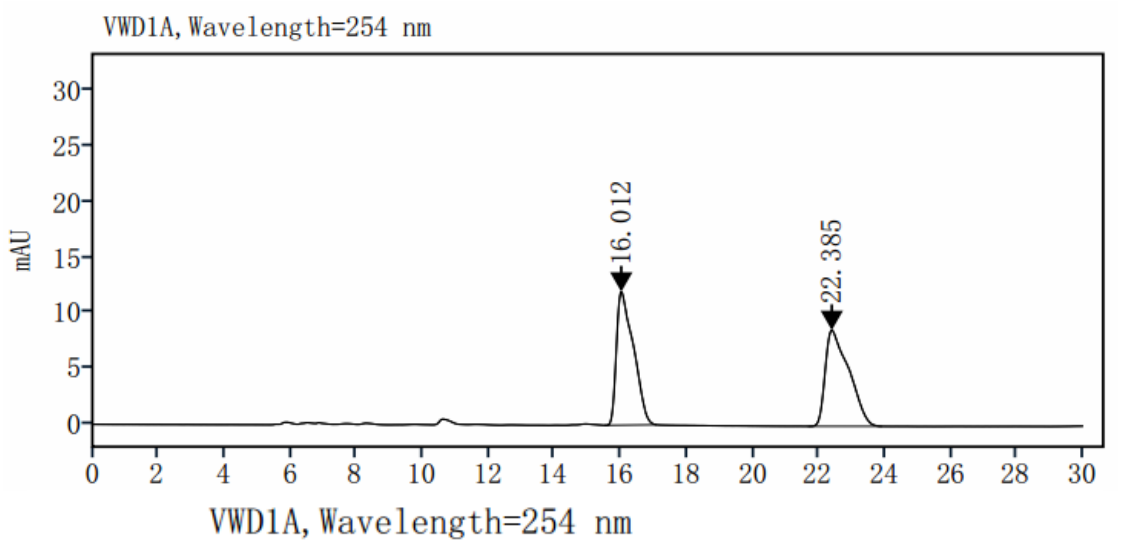
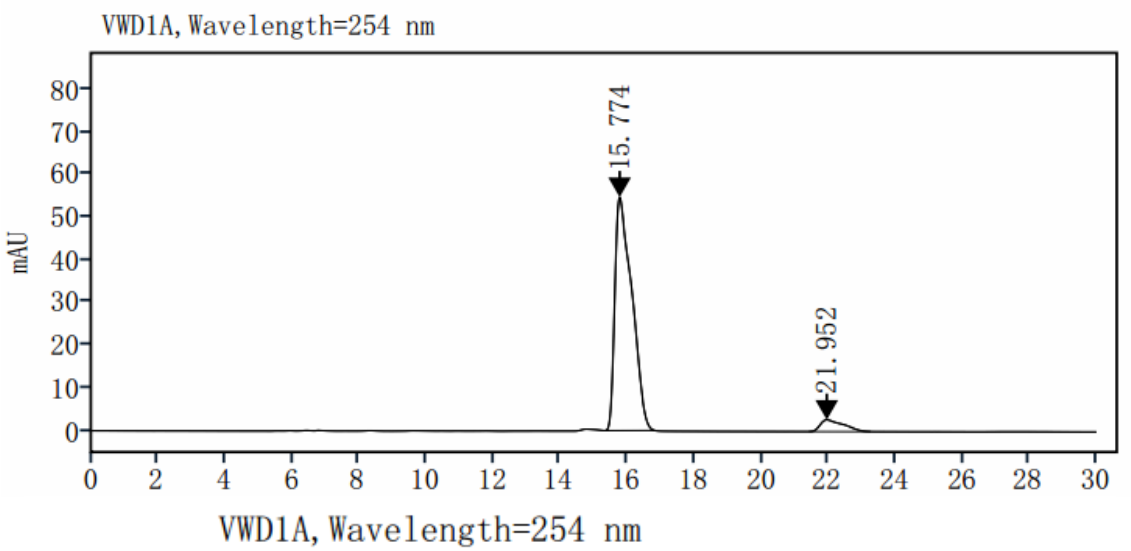


Figure 2A, entry 18
(*S*,*S*)-**L1**: 87% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	16.012	MM m	427.40	49.98
	22.385	MM m	427.79	50.02



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.774	MM m	1932.33	93.56
	21.952	MM m	133.02	6.44

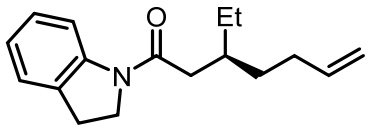
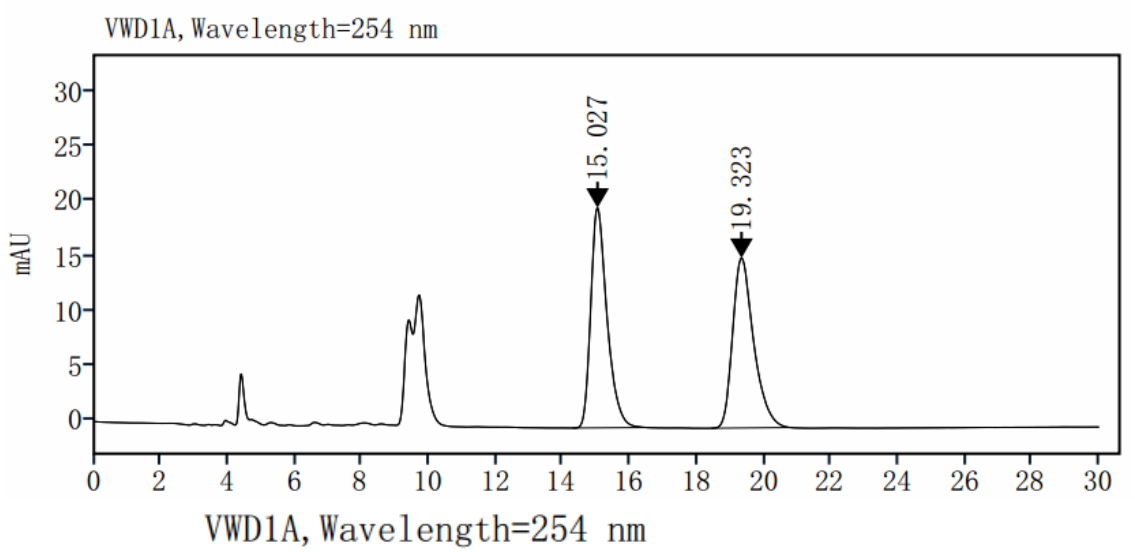
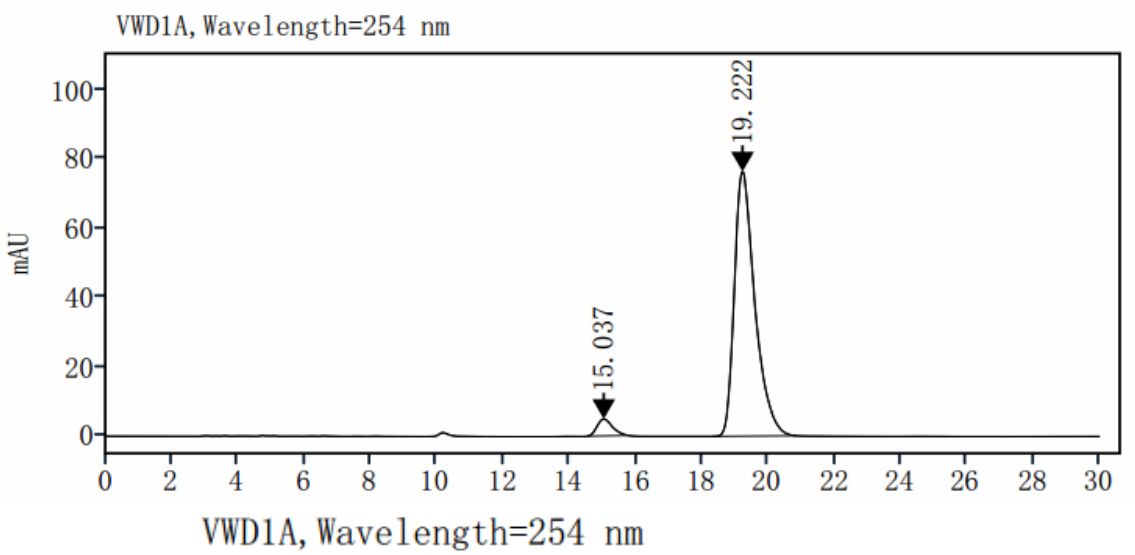


Figure 2A, entry 19
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.027	MM m	677.37	50.11
	19.323	MM m	674.44	49.89



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.037	MM m	155.54	4.51
	19.222	MM m	3290.09	95.49

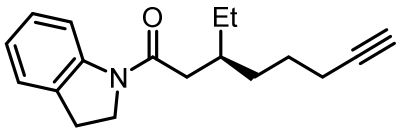
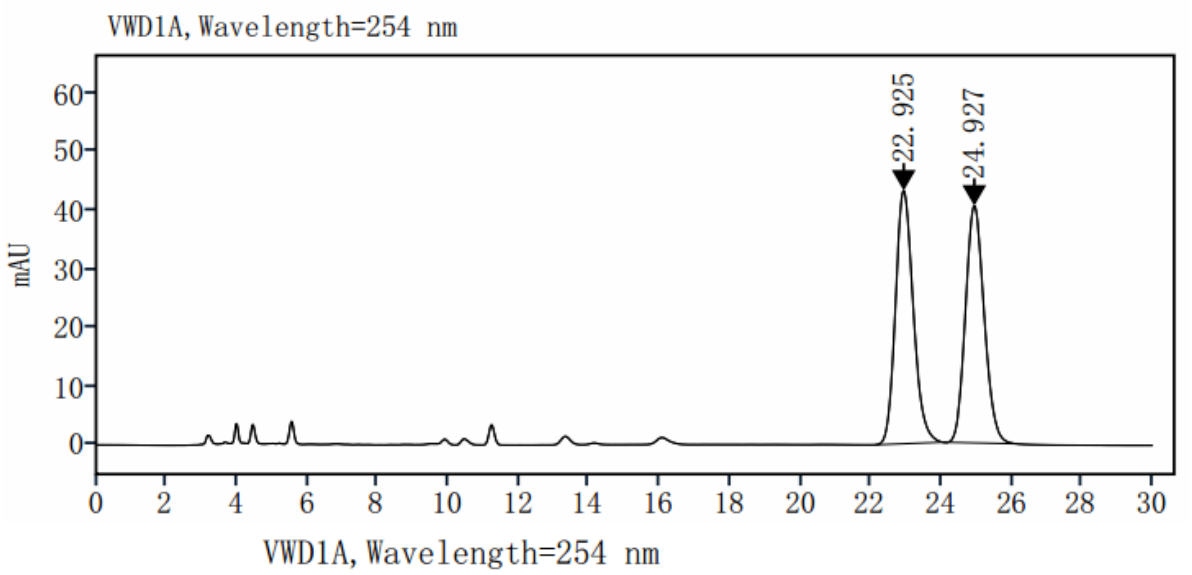
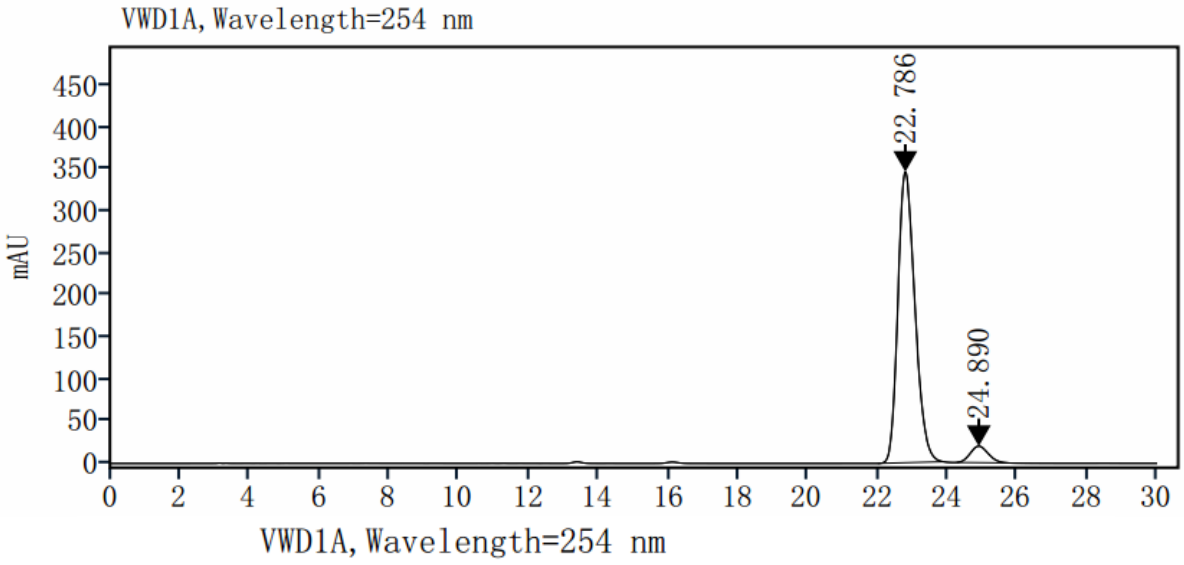


Figure 2A, entry 20
(*S*,*S*)-**L1**: 89% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	22.925	MM m	1521.66	50.39
	24.927	MM m	1498.02	49.61



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	22.786	MM m	11735.24	94.37
	24.890	MM m	700.38	5.63

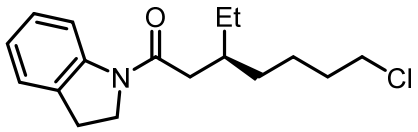
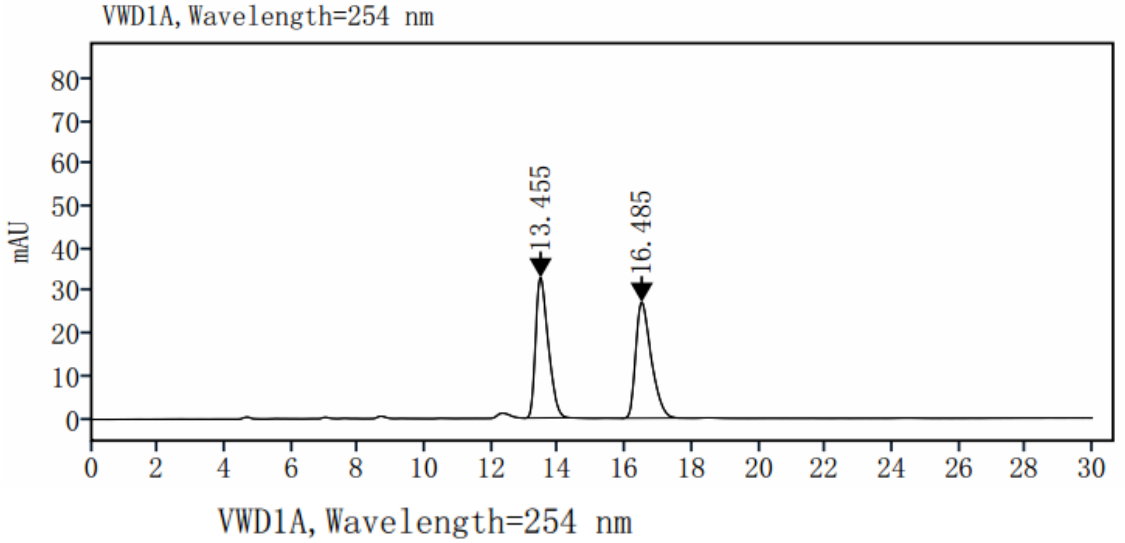
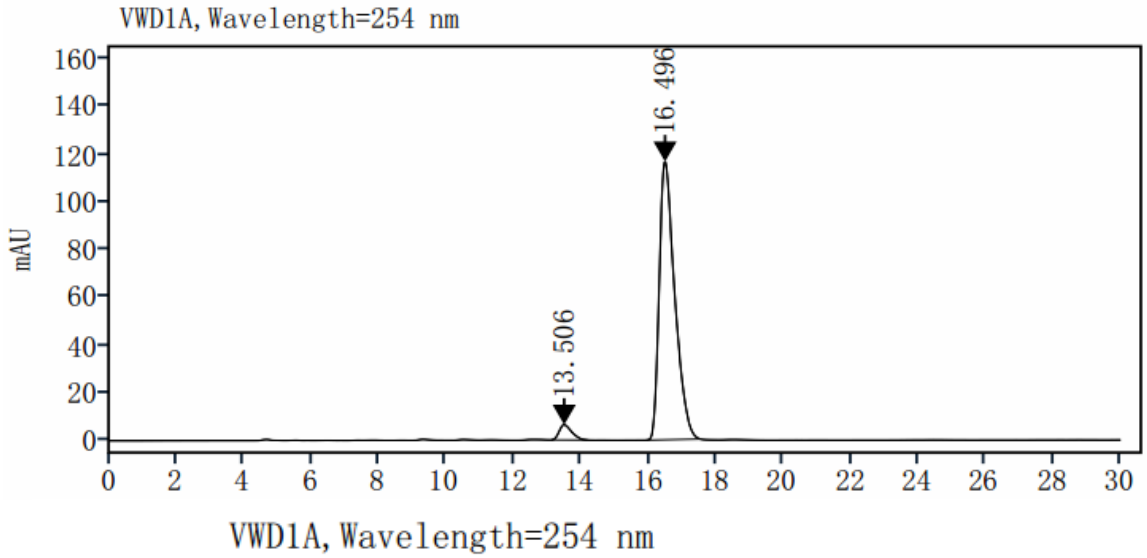


Figure 2A, entry 21
(*S*,*S*)-**L1**: 92% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	13.455	MM m	866.84	49.67
	16.485	MM m	878.43	50.33



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	13.506	MM m	164.27	4.22
	16.496	MM m	3732.50	95.78

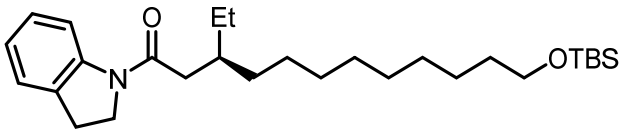
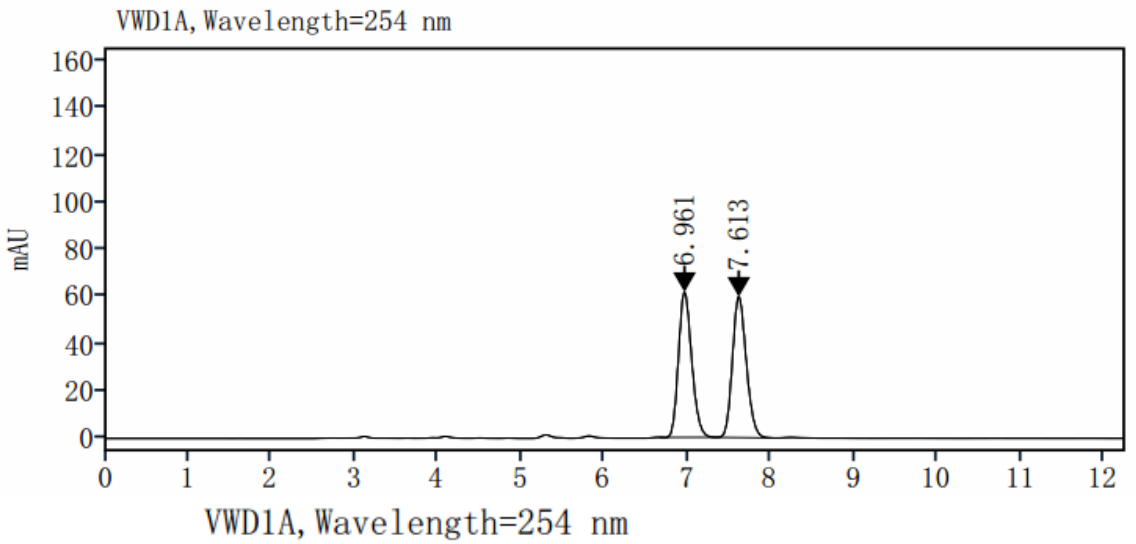
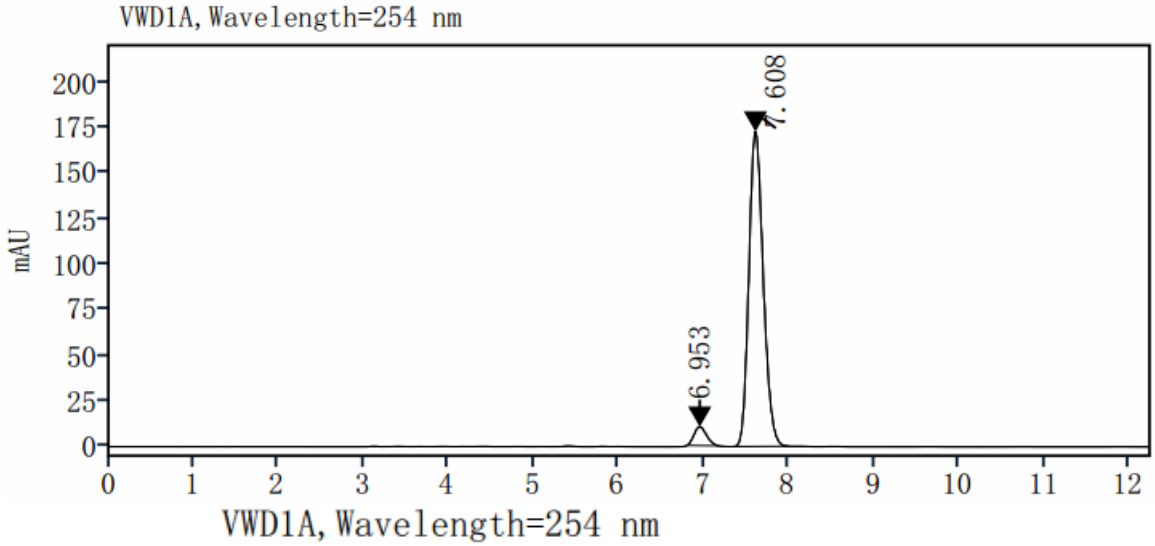


Figure 2A, entry 22
(*S*,*S*)-**L1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.961	MM m	681.74	49.51
	7.613	MM m	695.29	50.49



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.953	MM m	105.07	4.93
	7.608	MM m	2028.06	95.07

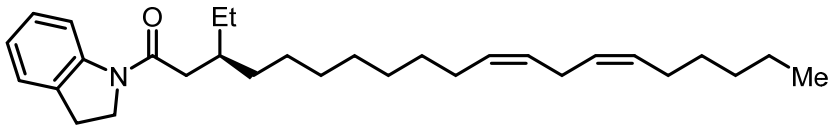
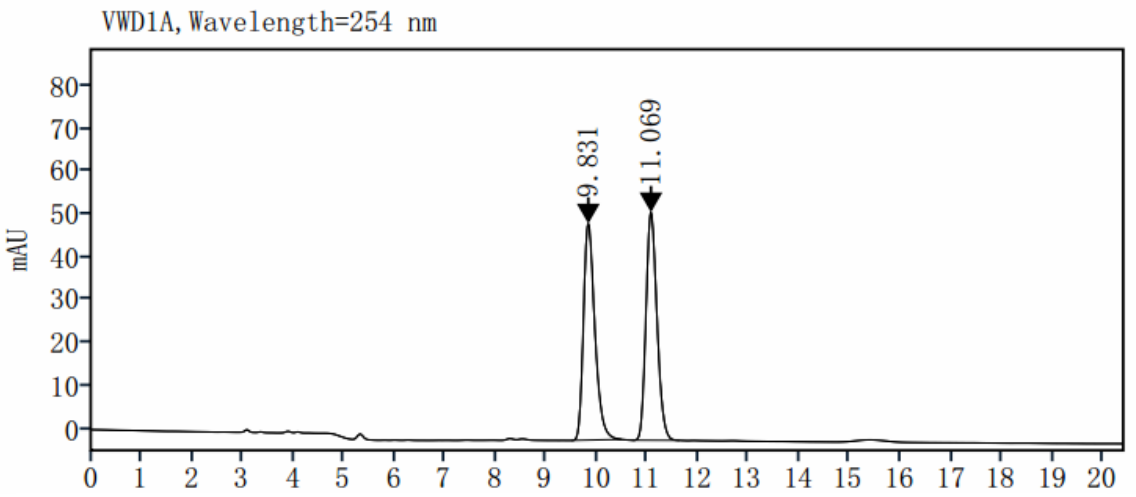
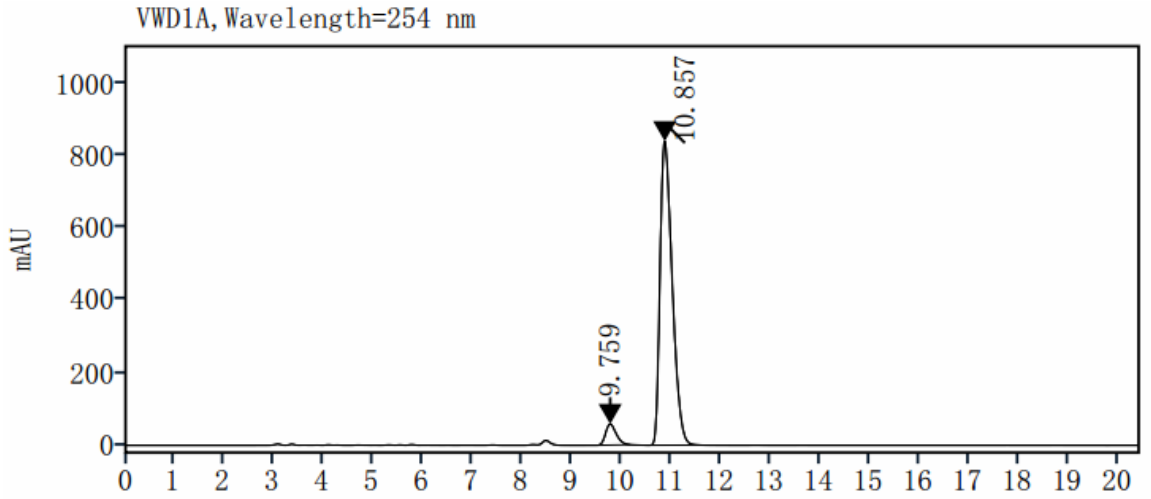


Figure 2A, entry 23
(*S*,*S*)-**L1**: 89% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.831	MM m	793.40	49.66
	11.069	MM m	804.32	50.34



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.759	MM m	862.33	5.70
	10.857	MM m	14272.30	94.30

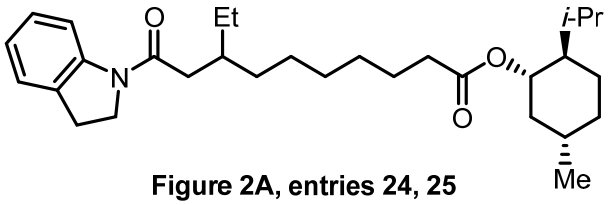
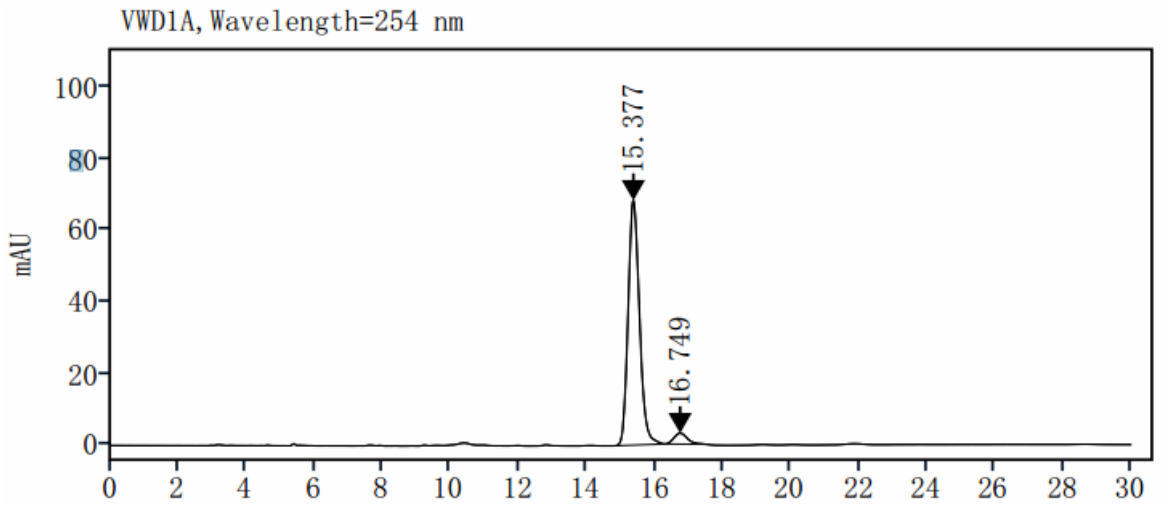
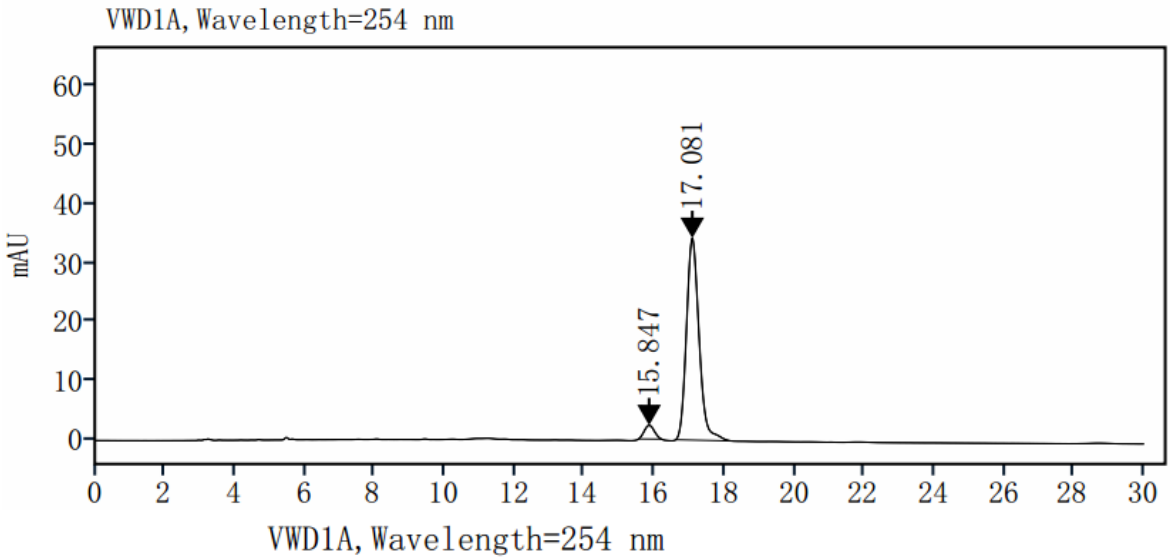


Figure 2A, entries 24, 25
(*S*,*S*)-**L1**: 95:5 dr, (*R*,*R*)-**L1**: 5:95 dr



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.377	MM m	1579.74	95.02
	16.749	MM m	82.74	4.98



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.847	MM m	46.21	5.10
	17.081	MM m	859.43	94.90

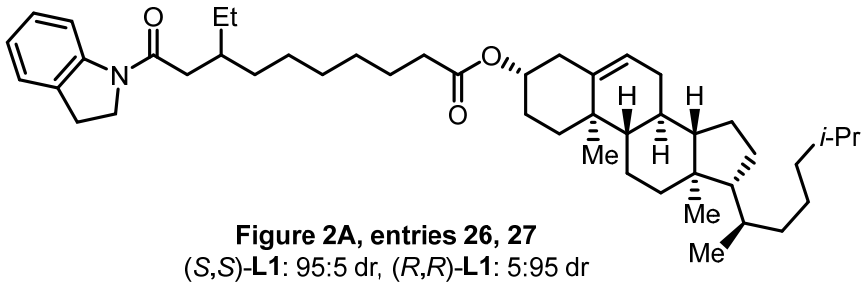
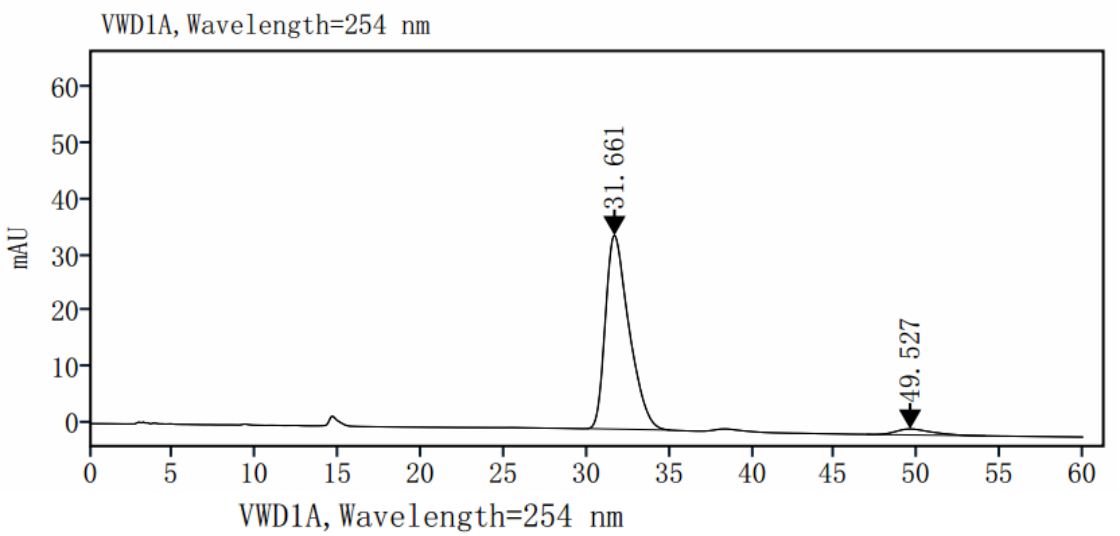
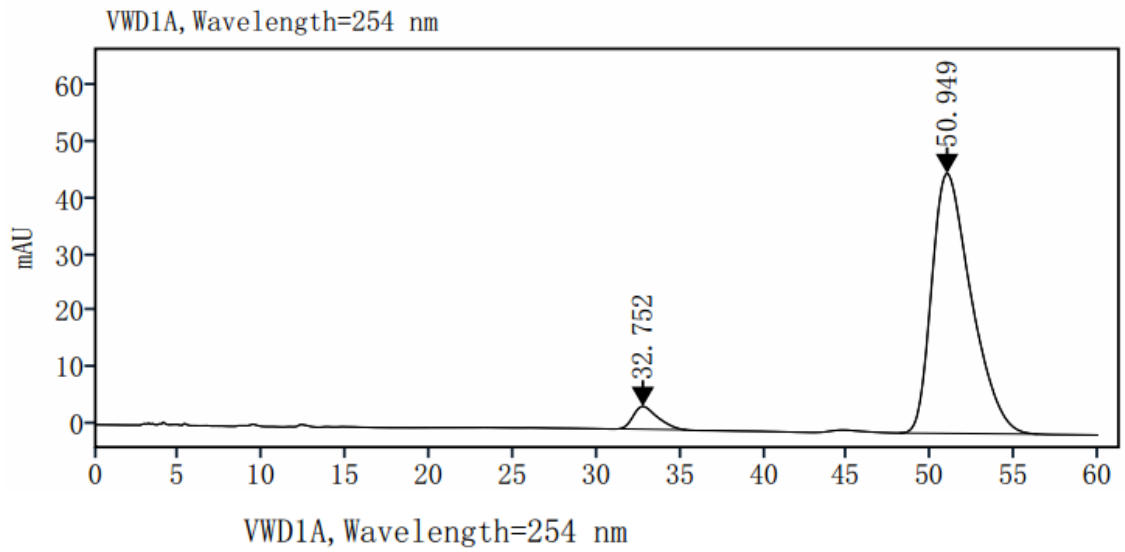


Figure 2A, entries 26, 27
(*S*,*S*)-**L1**: 95:5 dr, (*R*,*R*)-**L1**: 5:95 dr



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	31.661	MM m	3437.43	95.28
	49.527	MM m	170.28	4.72



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	32.752	MM m	408.95	5.14
	50.949	MM m	7546.77	94.86

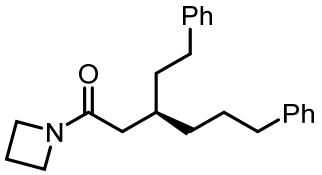
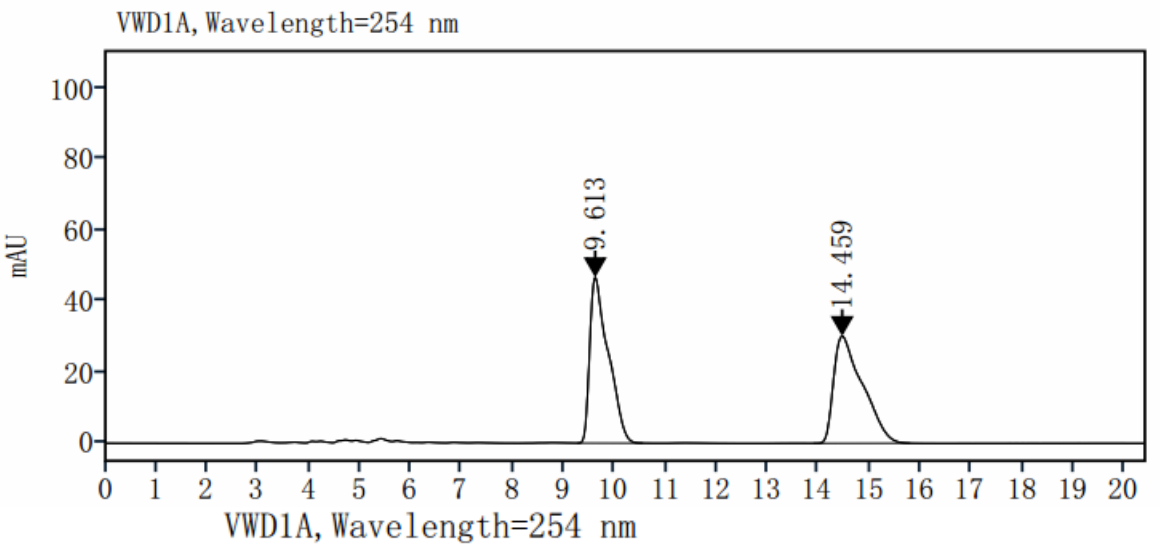
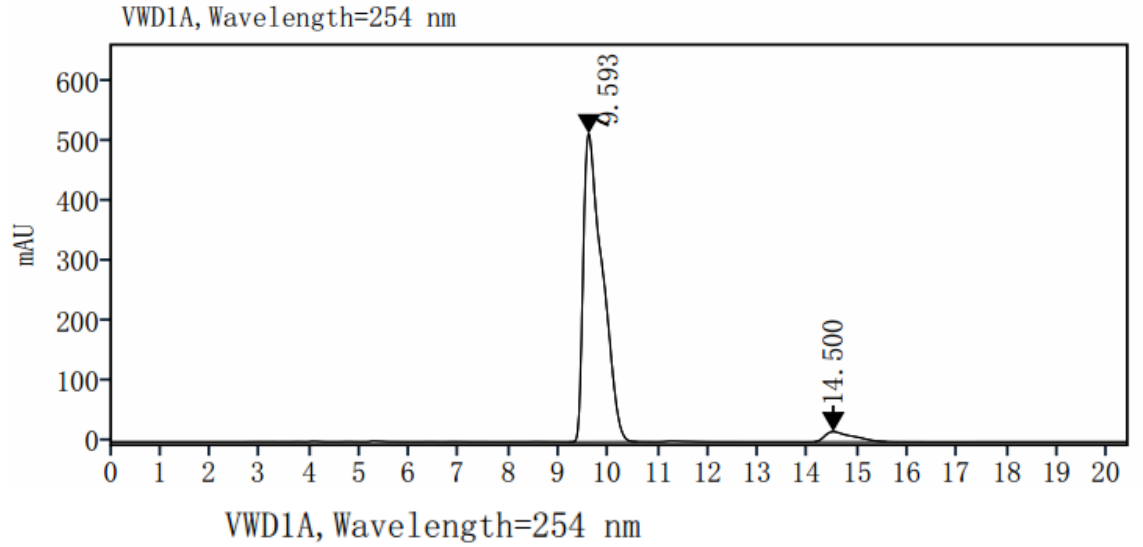


Figure 2B, entry 28
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.613	MM m	1181.67	49.80
	14.459	MM m	1191.16	50.20



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.593	MM m	13624.49	95.52
	14.500	MM m	638.36	4.48

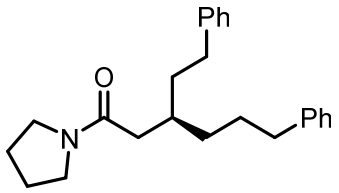
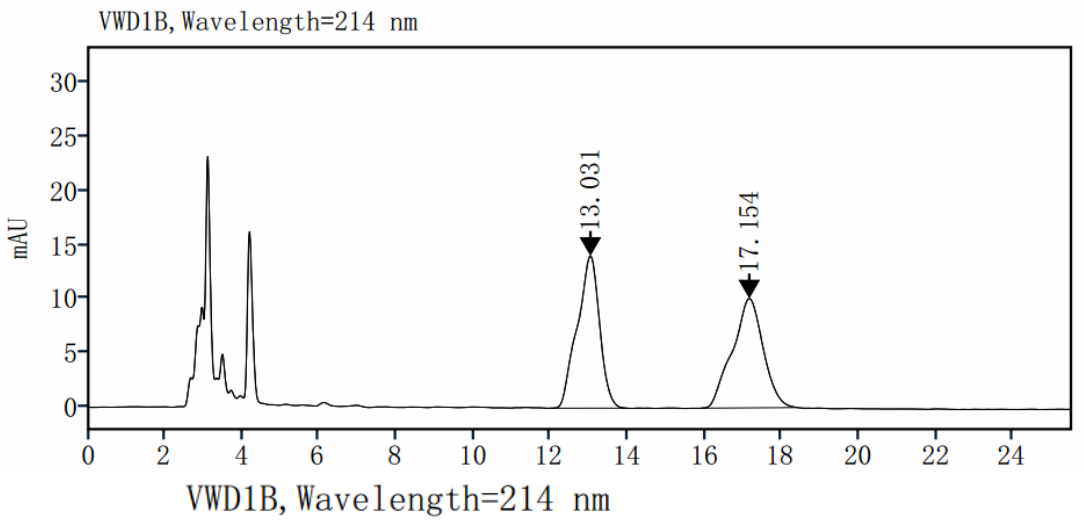
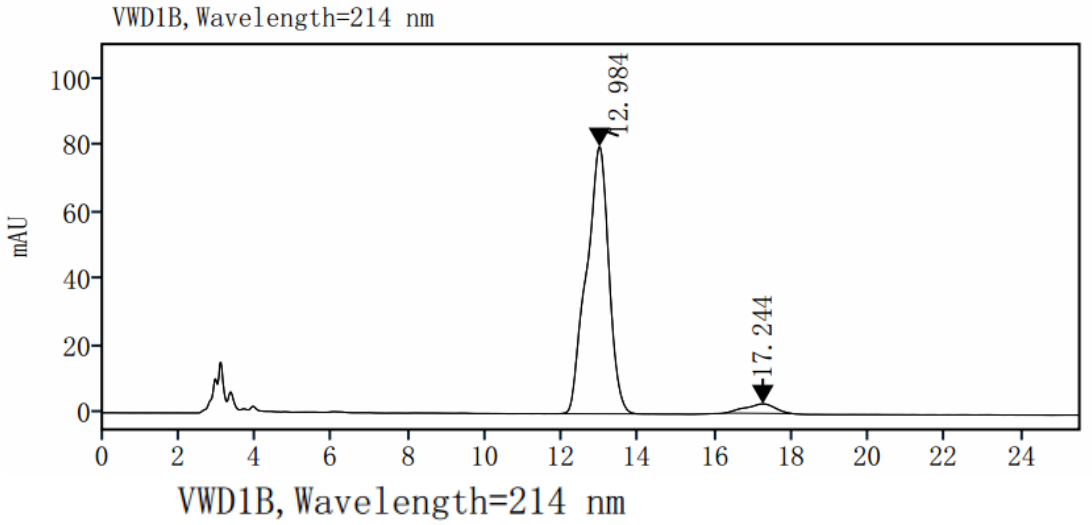


Figure 2B, entry 29
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	13.031	MM m	564.83	50.23
	17.154	MM m	559.69	49.77



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	12.984	MM m	3238.97	95.48
	17.244	MM m	153.22	4.52

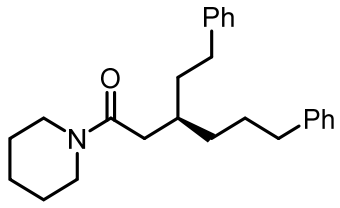
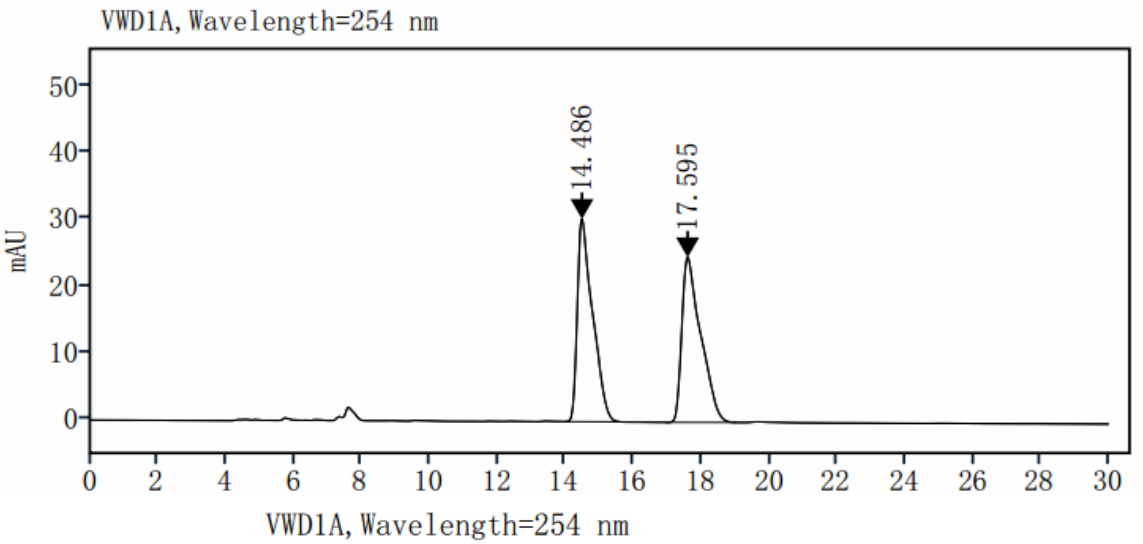
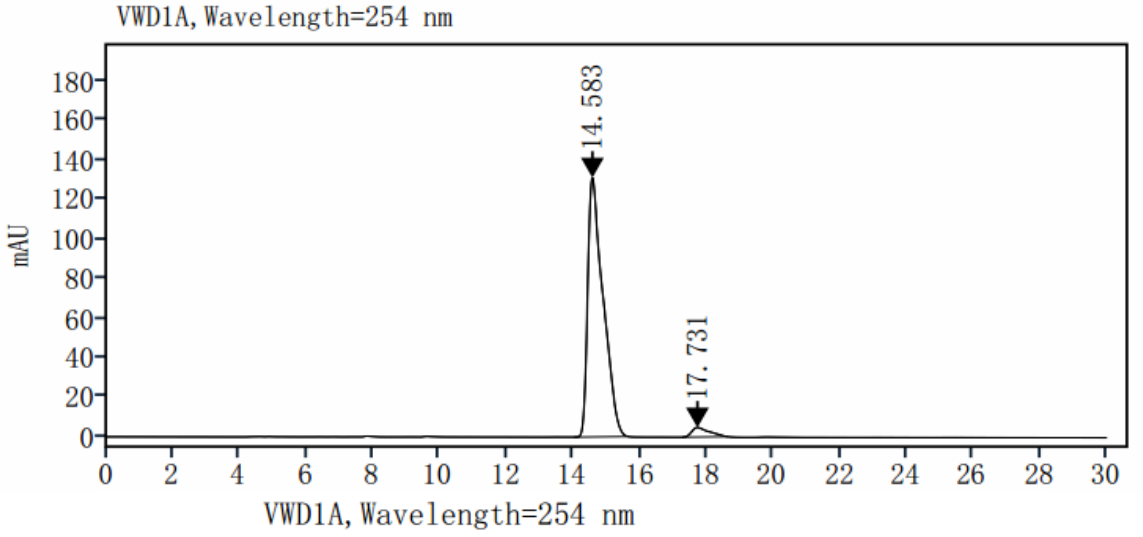


Figure 2B, entry 30
(*S*,*S*)-**L1**: 92% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	14.486	MM m	952.91	49.94
	17.595	MM m	955.04	50.06



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	14.583	MM m	4205.22	96.00
	17.731	MM m	175.09	4.00

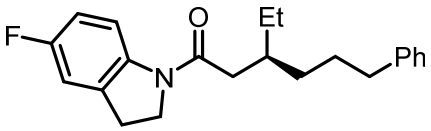
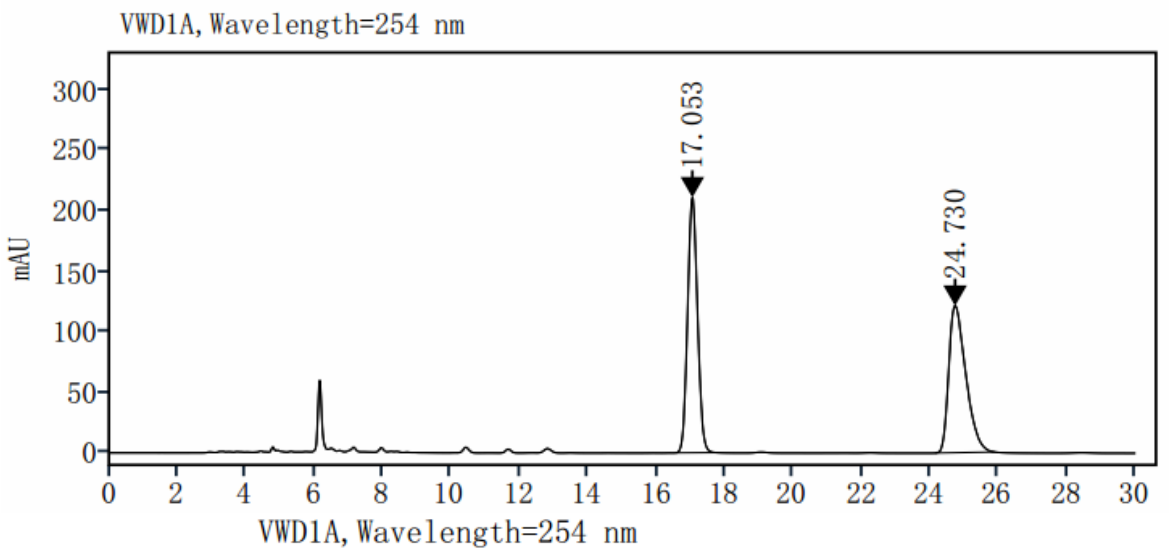
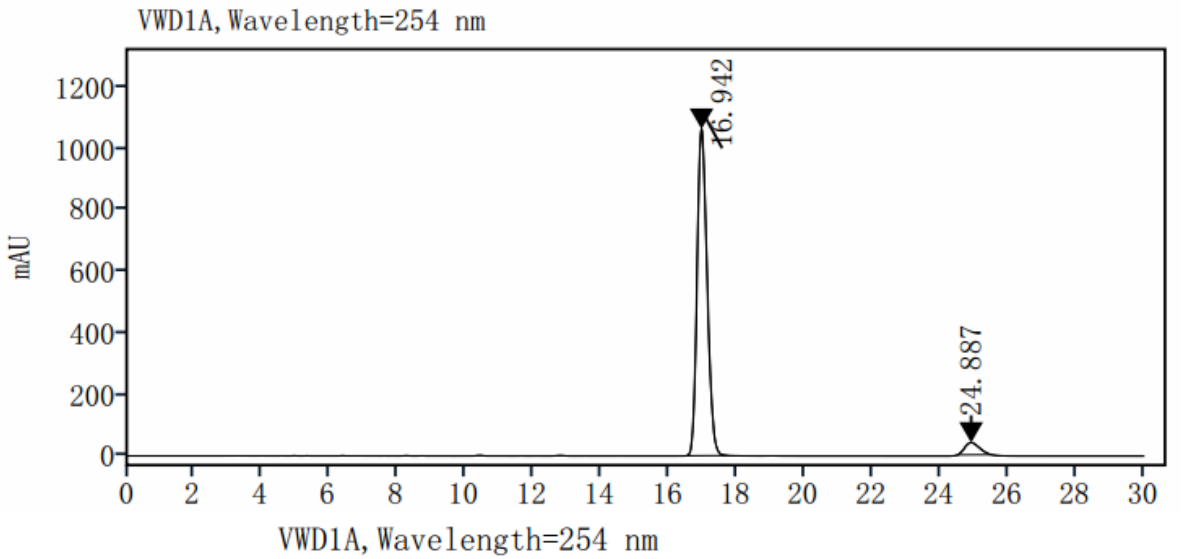


Figure 2B, entry 31
(*S*,*S*)-**L1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	17.053	MM m	4250.09	50.17
	24.730	MM m	4221.28	49.83



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	16.942	MM m	21855.89	94.89
	24.887	MM m	1177.94	5.11

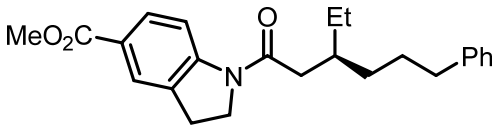
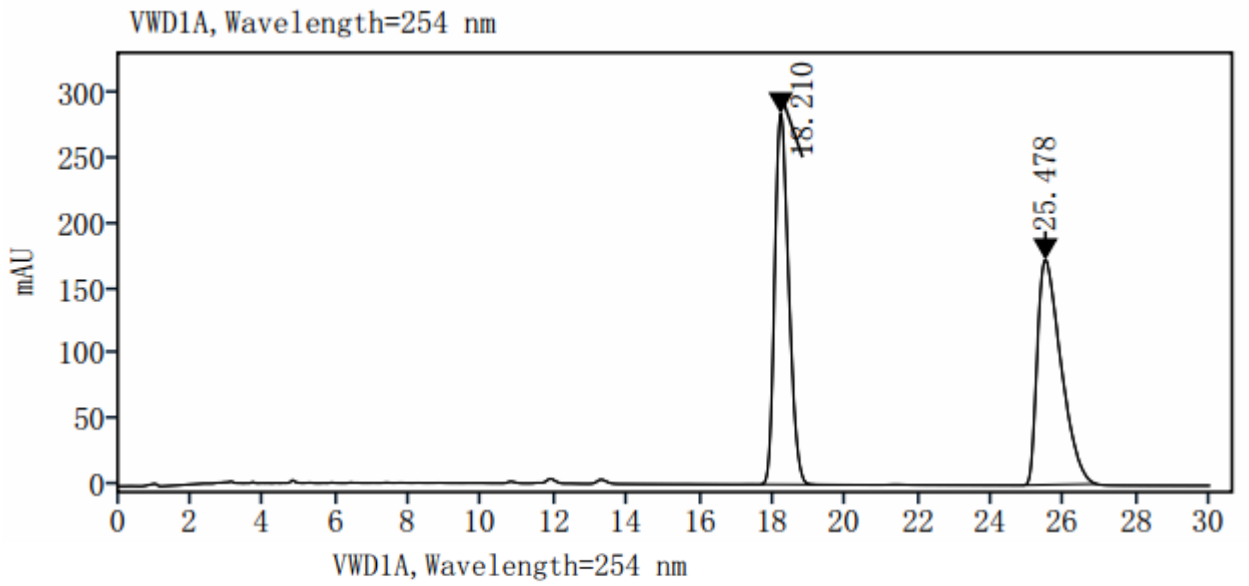
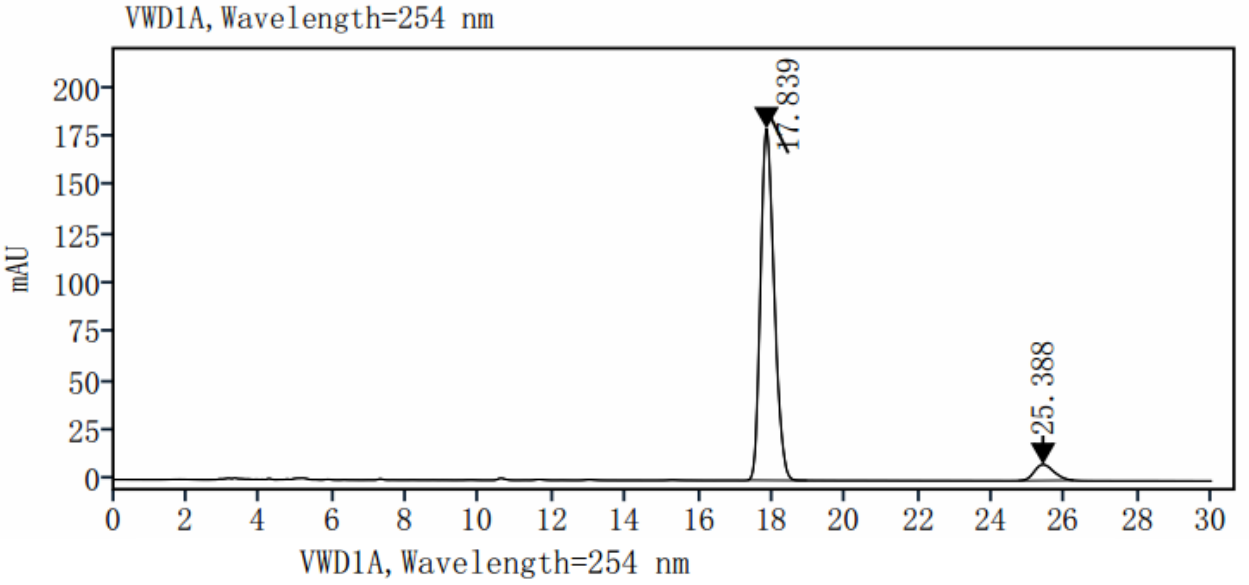


Figure 2B, entry 32
(*S*,*S*)-**L1**: 88% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	18.210	MM m	7566.52	49.31
	25.478	MM m	7779.36	50.69



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	17.839	MM m	4651.64	93.85
	25.388	MM m	304.80	6.15

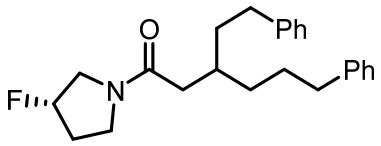
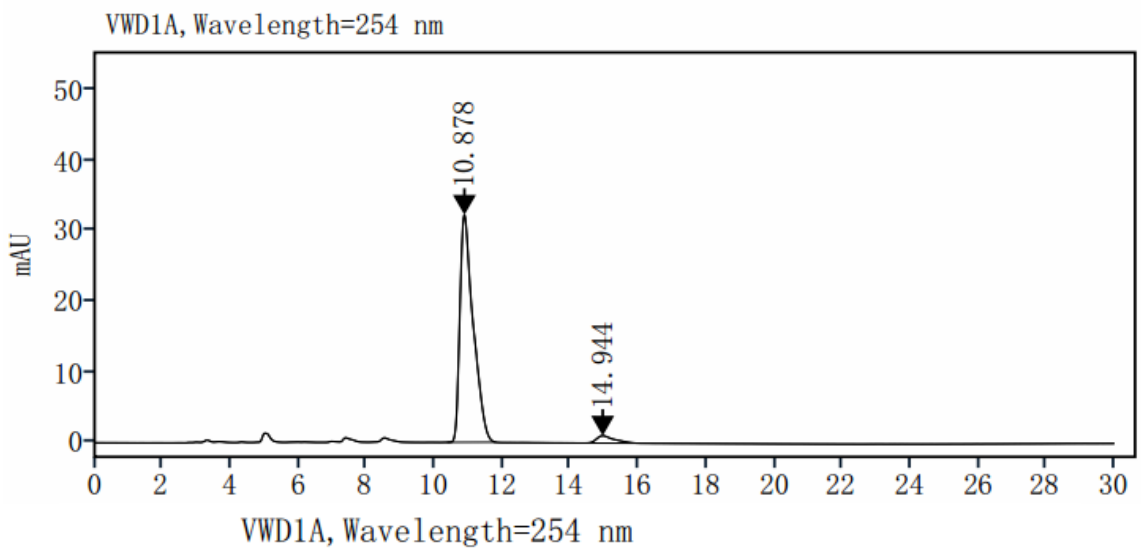
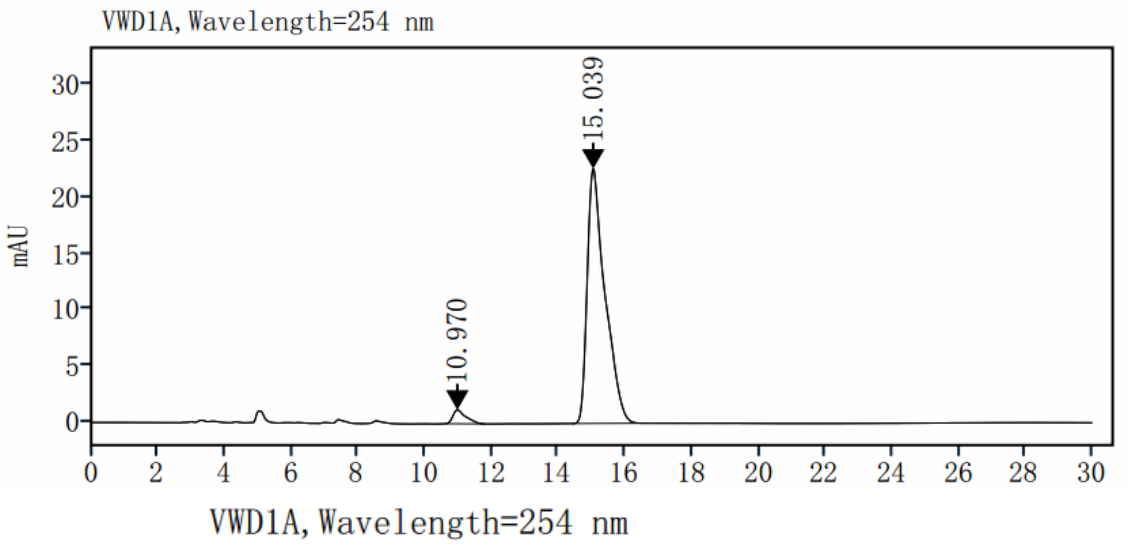


Figure 2B, entries 33, 34
(*S*,*S*)-**L1**: 96:4 dr, (*R*,*R*)-**L1**: 4:96 dr



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.878	MM m	874.21	95.90
	14.944	MM m	37.36	4.10



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.970	MM m	33.04	3.80
	15.039	MM m	837.22	96.20

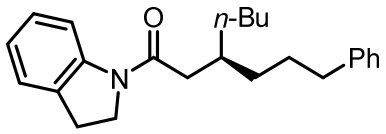
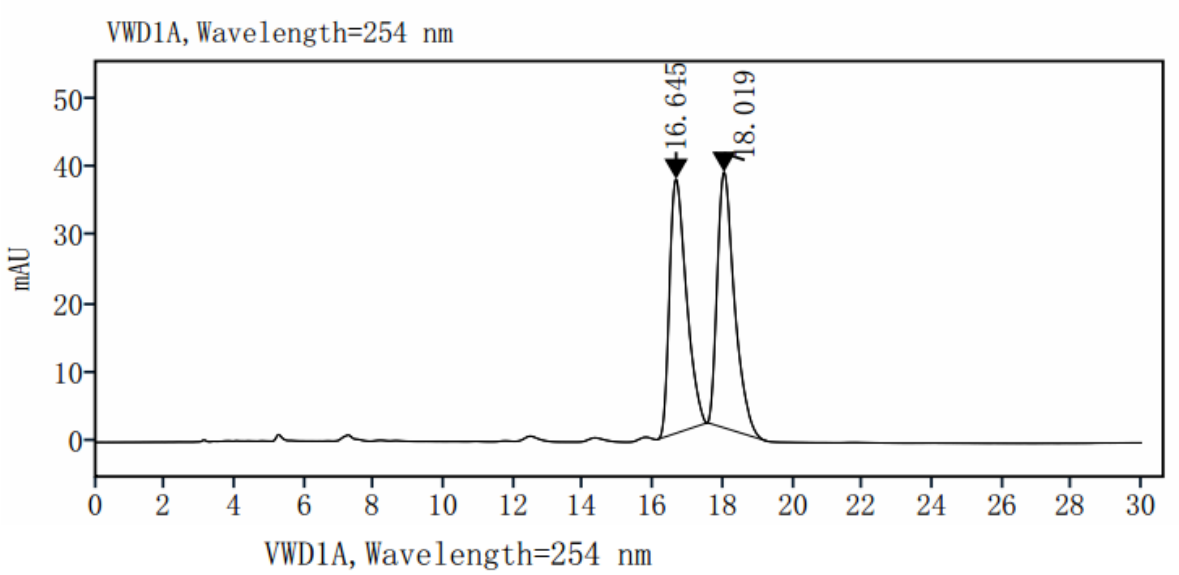
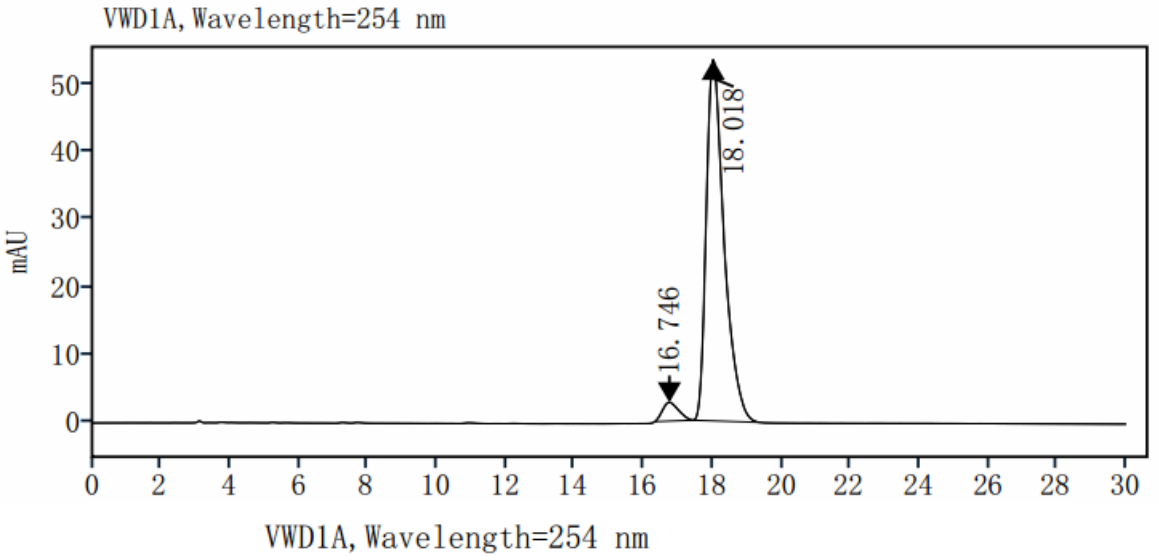


Figure 2B, entry 35
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	16.645	MM m	1245.42	49.33
	18.019	MM m	1279.08	50.67



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	16.746	MM m	88.98	4.43
	18.018	MM m	1917.69	95.57

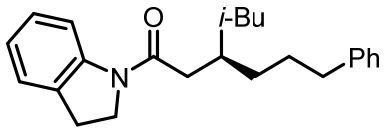
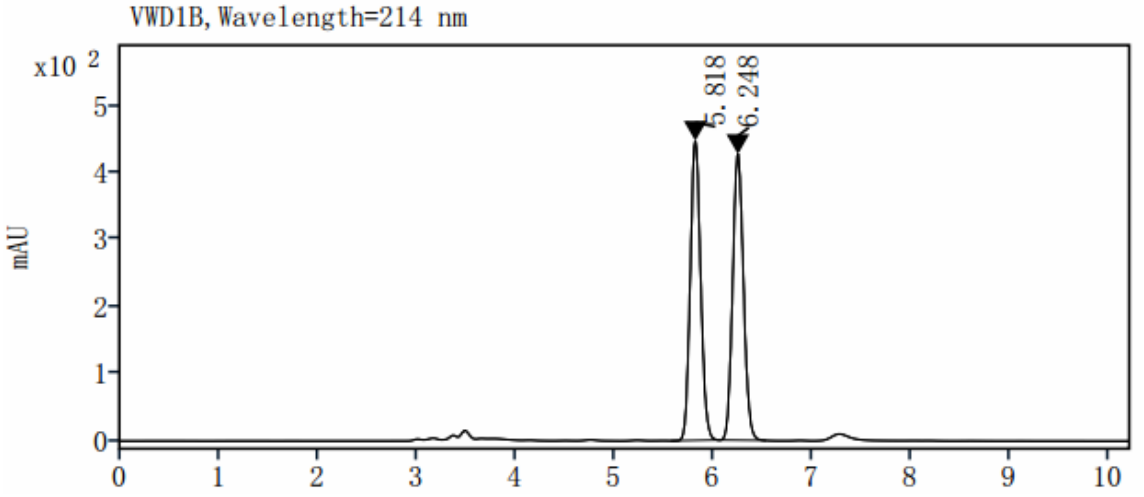
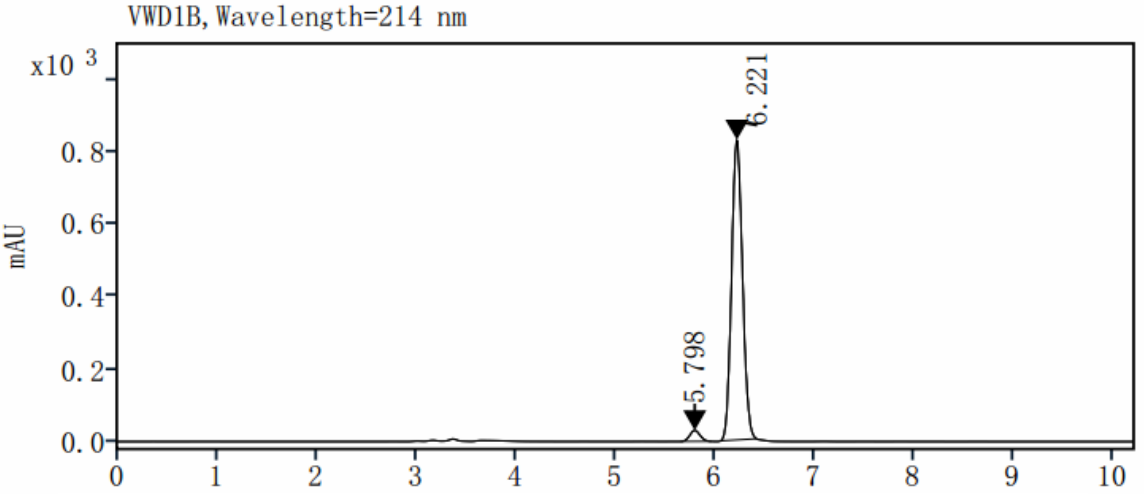


Figure 2B, entry 36
(*S*,*S*)-**L1**: 93% ee



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.818	MM m	3257.51	49.91
	6.248	MM m	3269.26	50.09



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.798	MM m	217.89	3.33
	6.221	MM m	6324.96	96.67

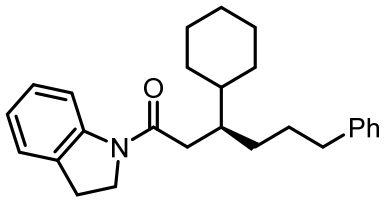
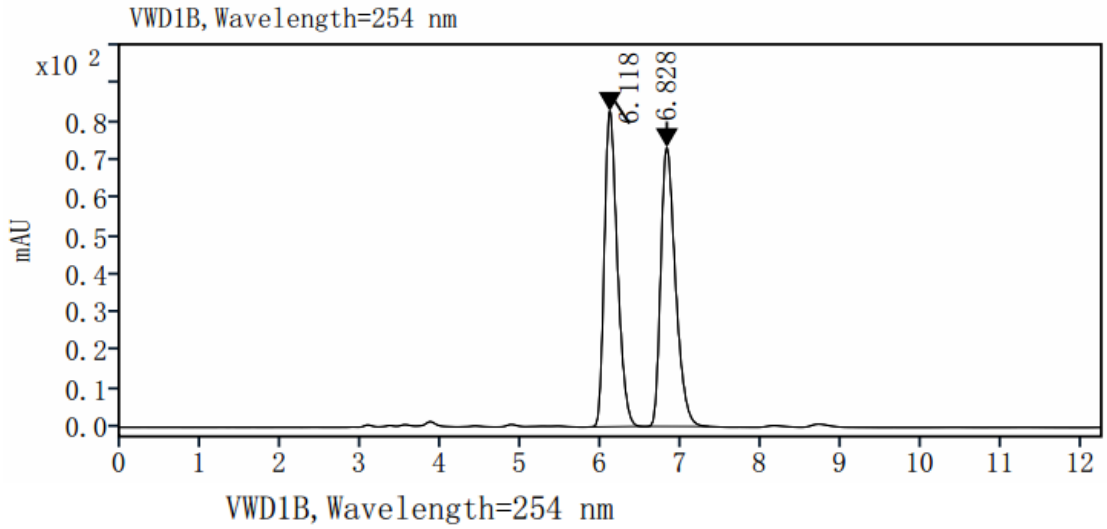
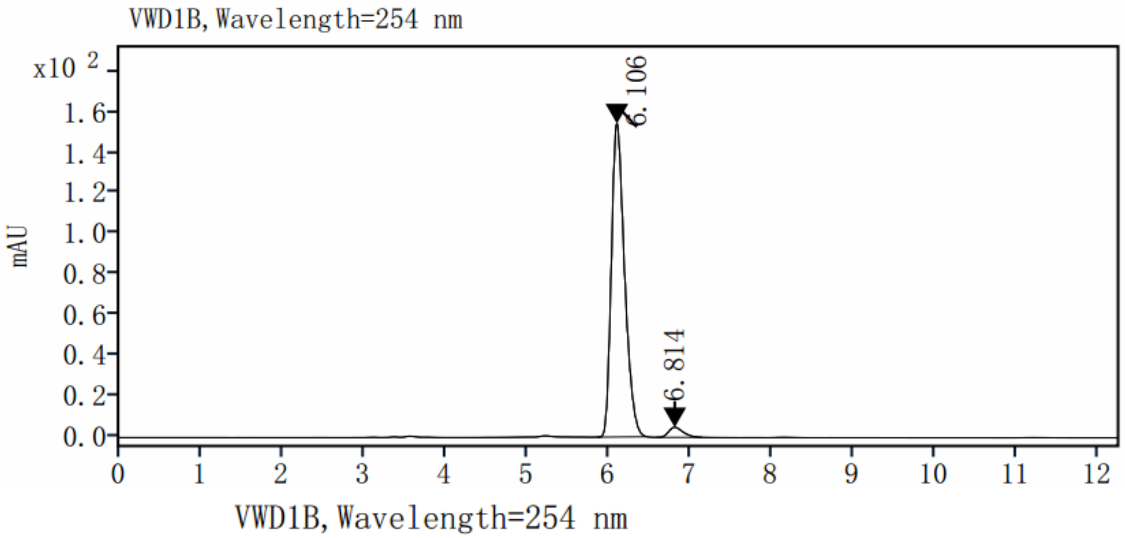


Figure 2B, entry 37
(*S*,*S*)-**L1**: 93% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.118	MM m	932.21	49.91
	6.828	MM m	935.71	50.09



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.106	MM m	1727.44	96.59
	6.814	MM m	61.02	3.41

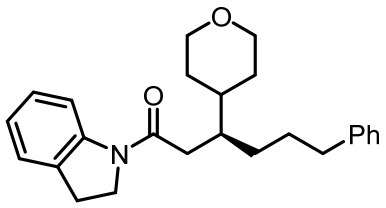
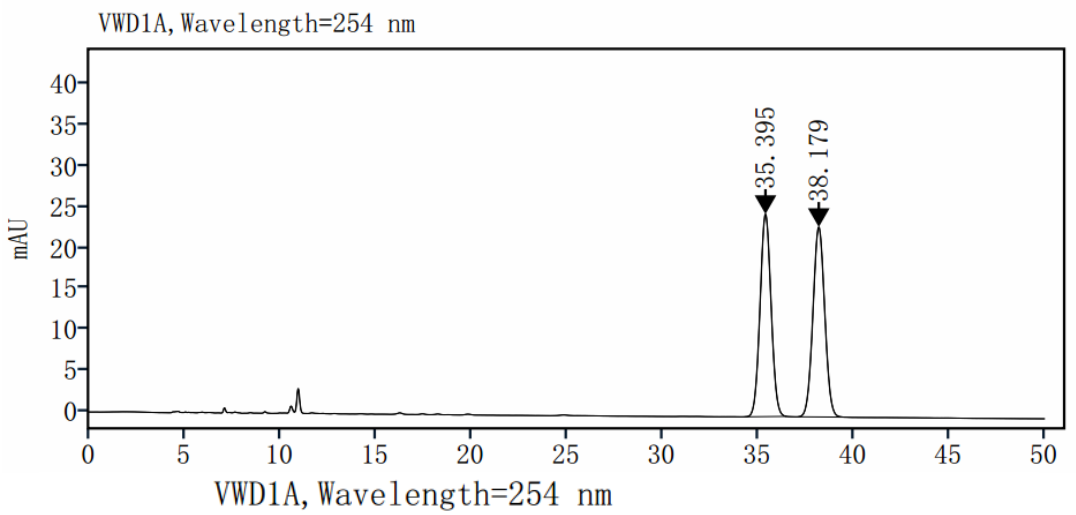
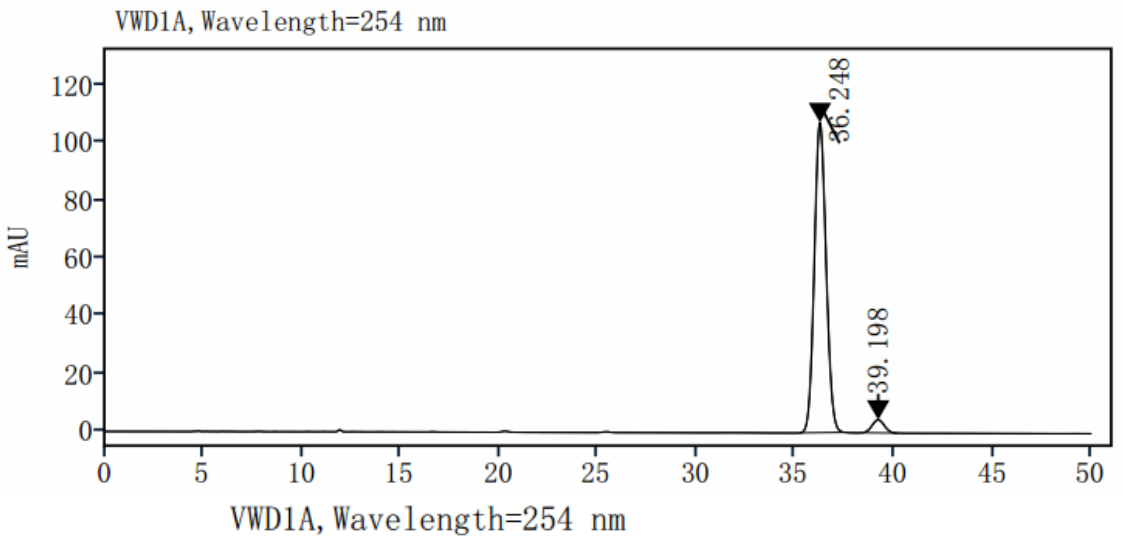


Figure 2B, entry 38
(*S*,*S*)-**L1**: 92% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	35.395	MM m	990.15	49.89
	38.179	MM m	994.44	50.11



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	36.248	MM m	4456.33	95.83
	39.198	MM m	193.78	4.17

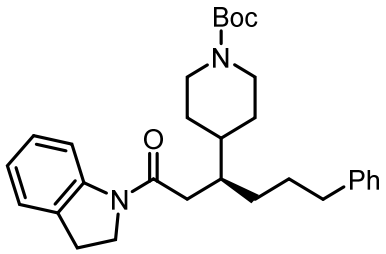
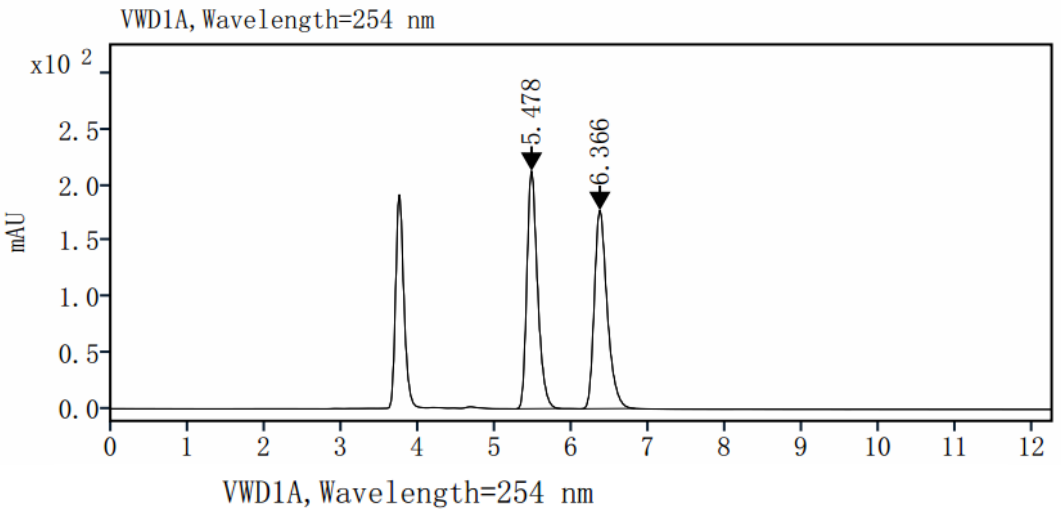
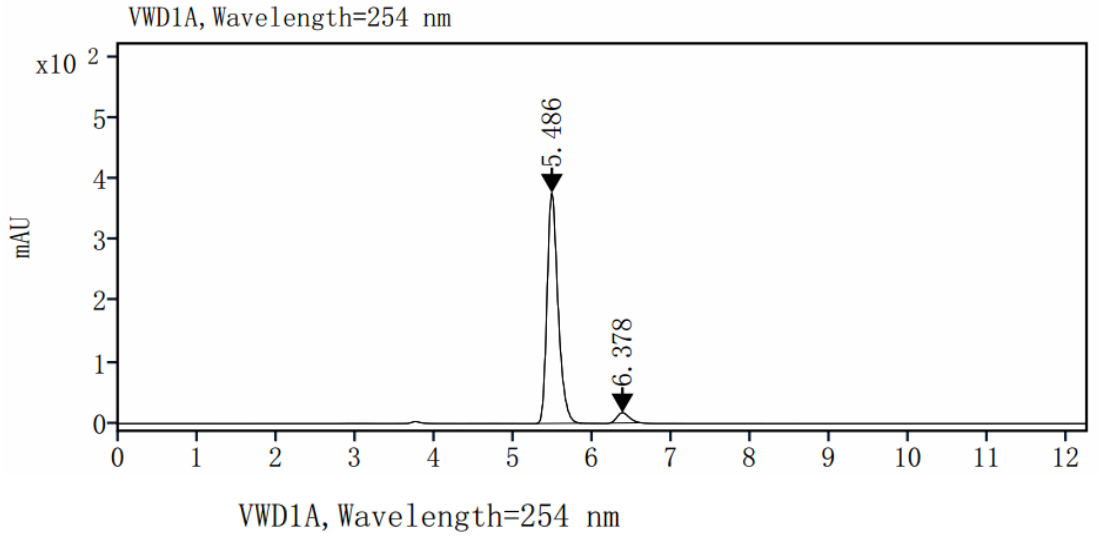


Figure 3B, entry 39
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.478	MM m	2049.52	49.68
	6.366	MM m	2076.01	50.32



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.486	MM m	3647.05	95.34
	6.378	MM m	178.07	4.66

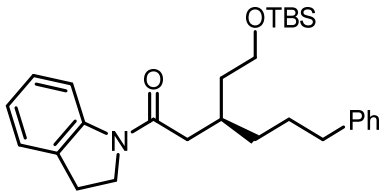
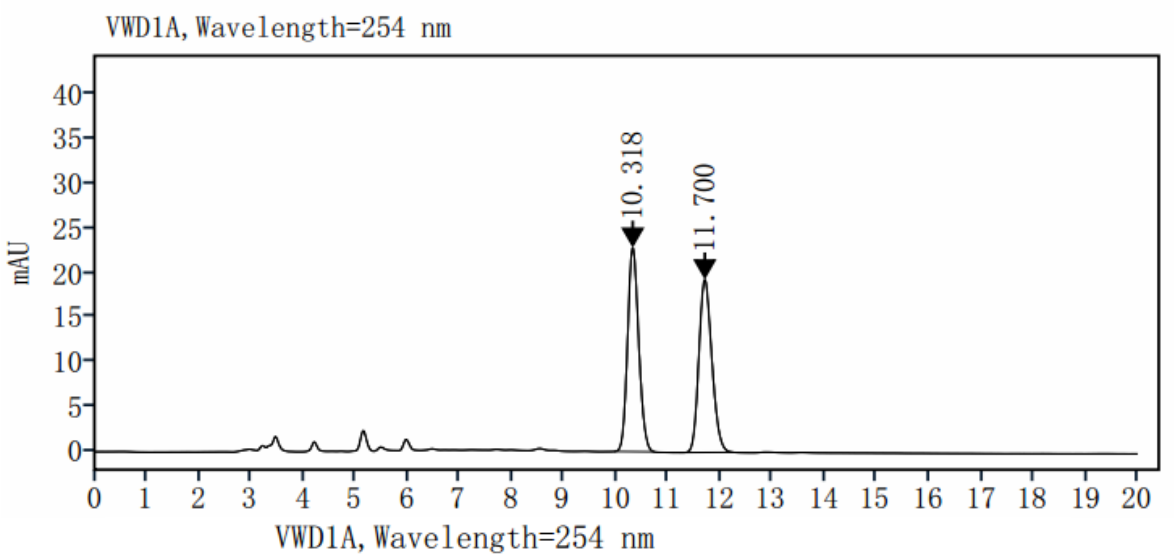
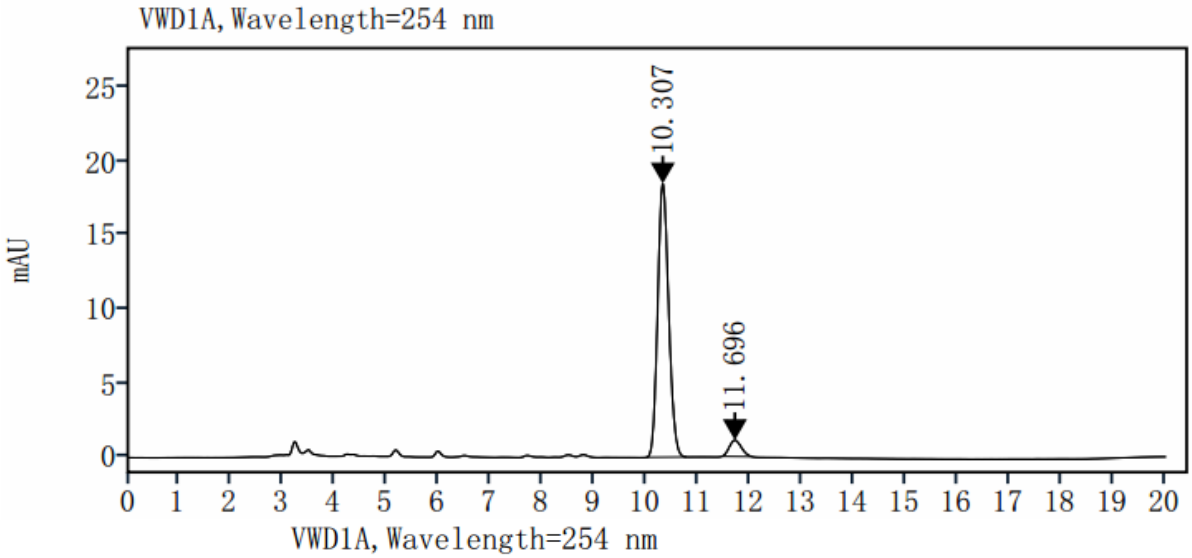


Figure 2B, entry 40
(*S*,*S*)-**L1**: 88% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.318	MM m	337.90	50.21
	11.700	MM m	335.01	49.79



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.307	MM m	271.06	93.90
	11.696	MM m	17.62	6.10

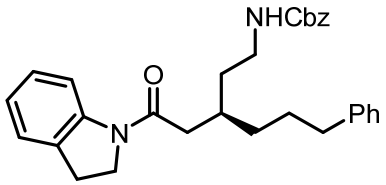
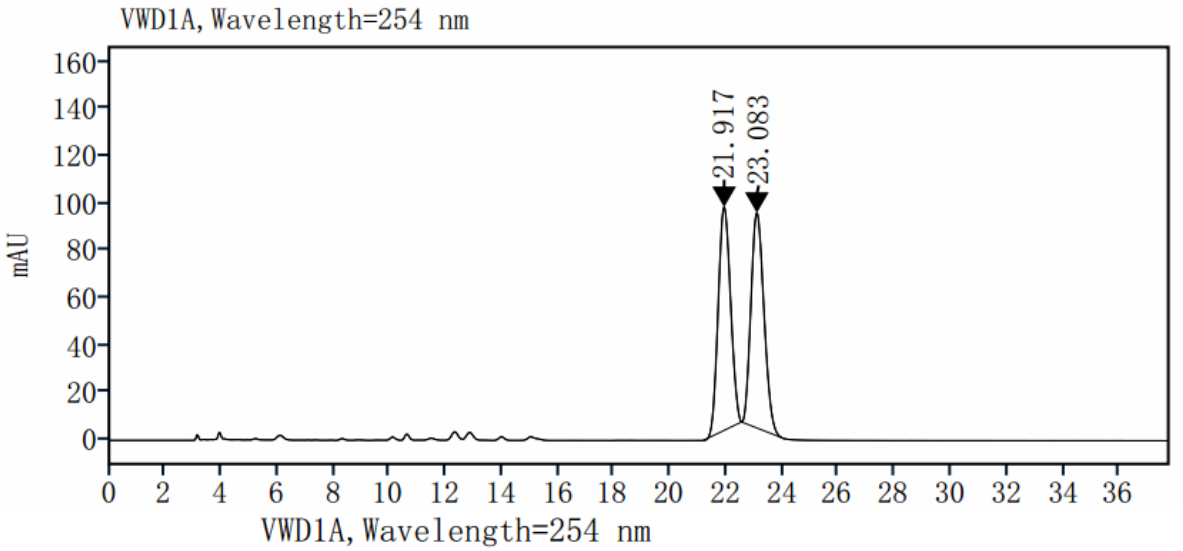
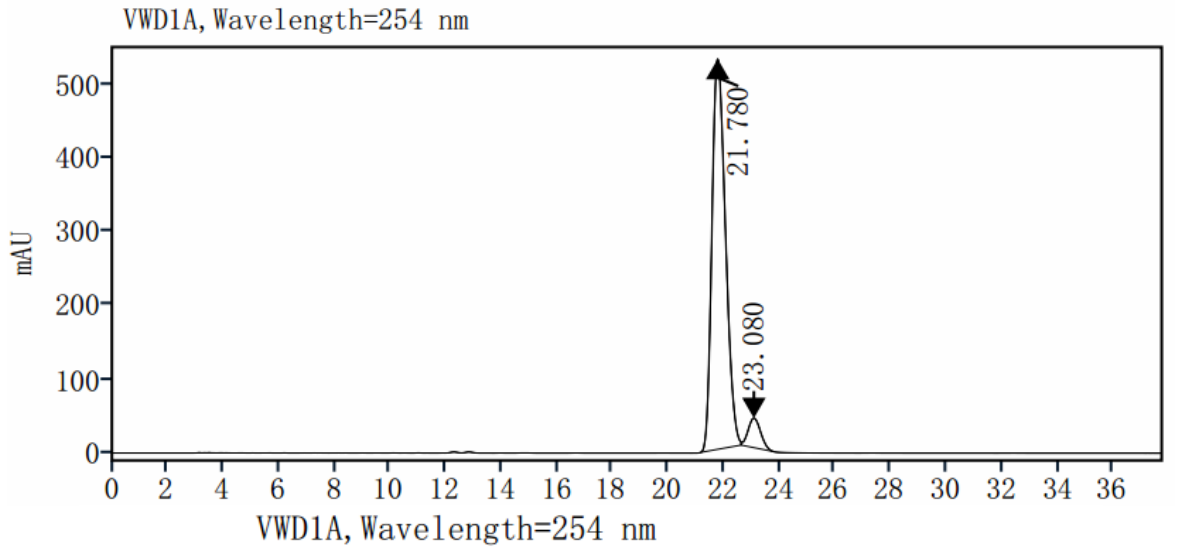


Figure 2B, entry 41
(*S*,*S*)-**L1**: 87% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	21.917	MM m	2884.83	49.58
	23.083	MM m	2934.29	50.42



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	21.780	MM m	17907.25	93.46
	23.080	MM m	1252.18	6.54

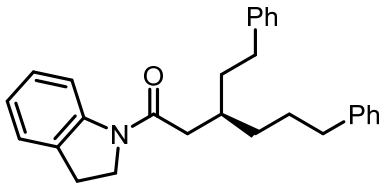
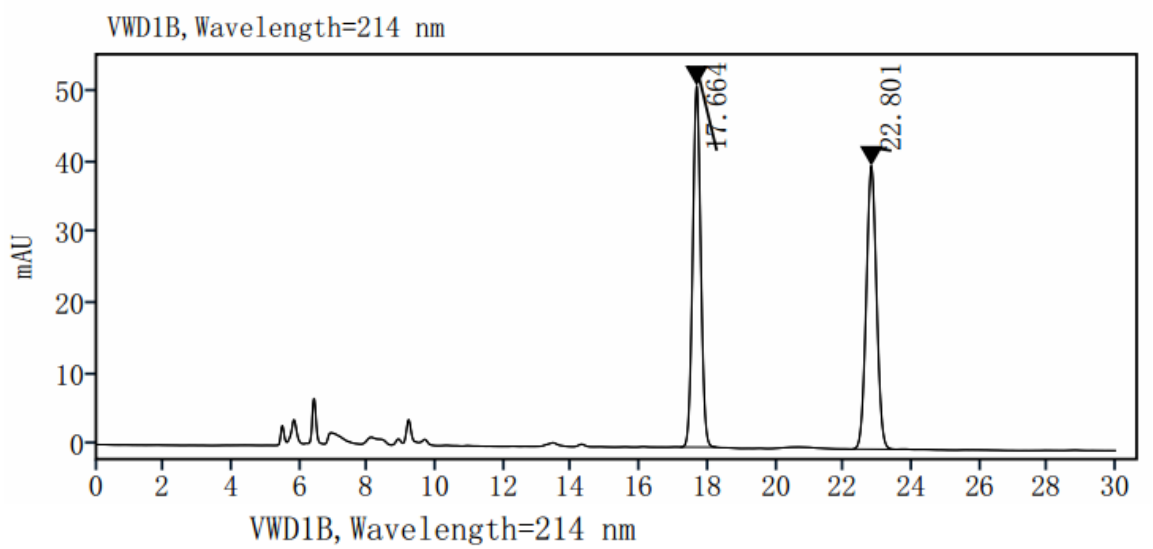
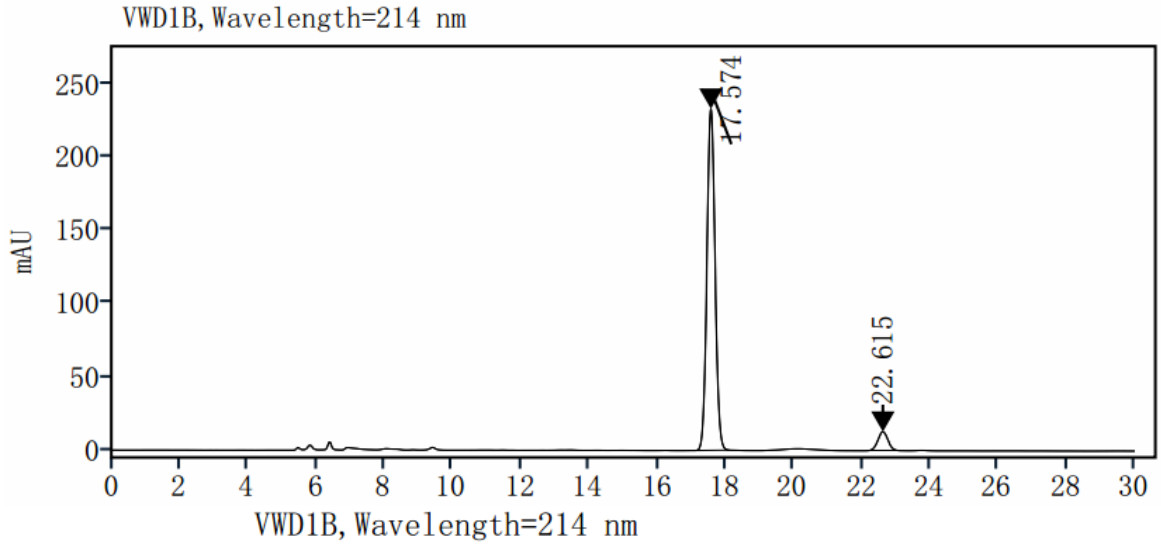


Figure 2B, entry 42
(*S*,*S*)-**L1**: 87% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	17.664	MM m	844.12	50.02
	22.801	MM m	843.50	49.98



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	17.574	MM m	3859.86	93.46
	22.615	MM m	256.88	6.54

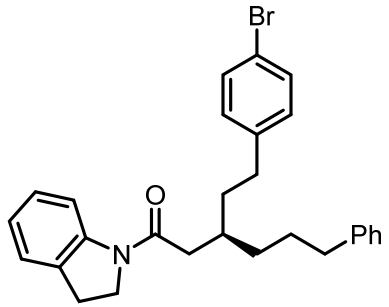
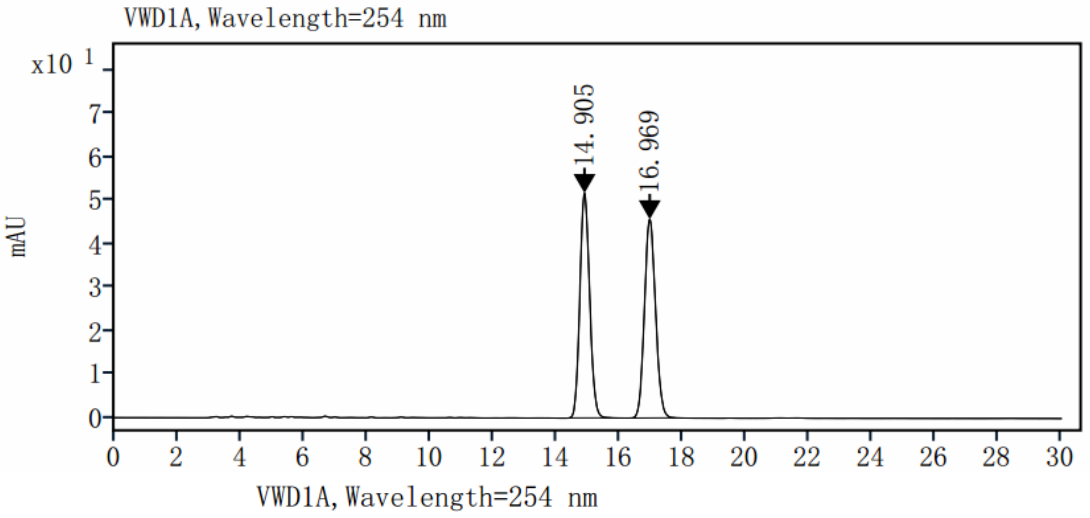
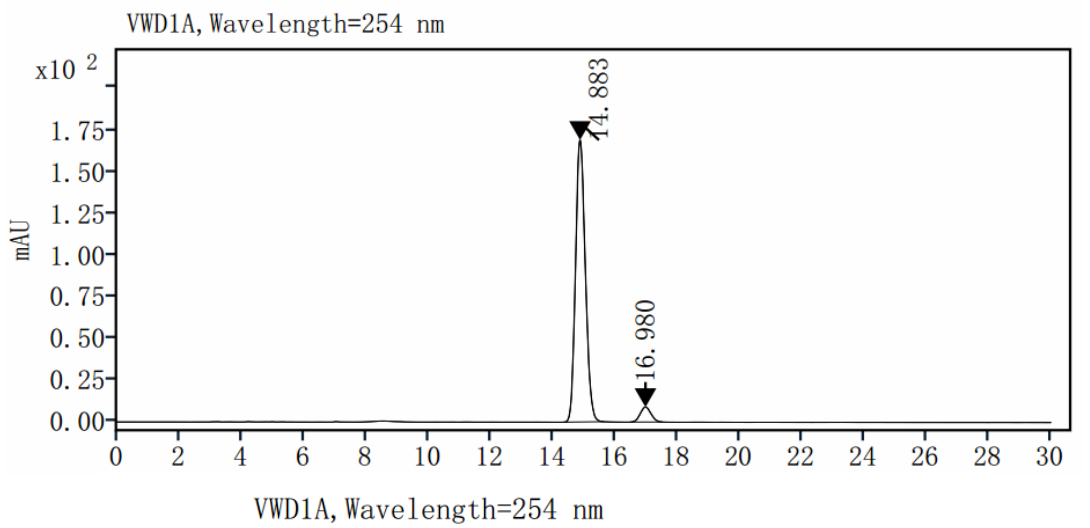


Figure 3B, entry 43
(*S*,*S*)-**L1**: 89% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	14.905	MM m	1113.91	49.91
	16.969	MM m	1117.99	50.09



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	14.883	MM m	3688.36	94.50
	16.980	MM m	214.67	5.50

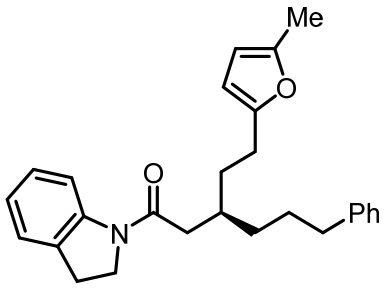
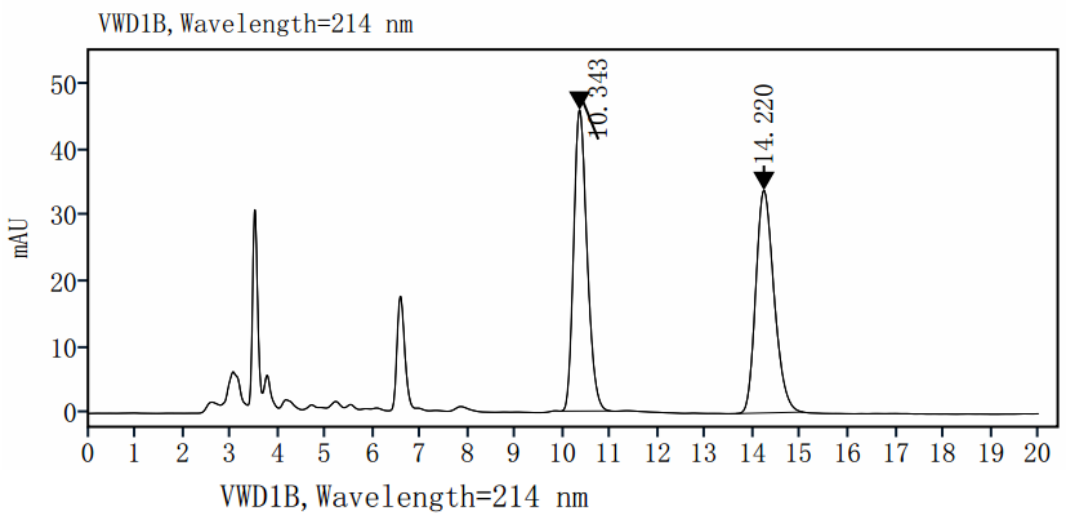
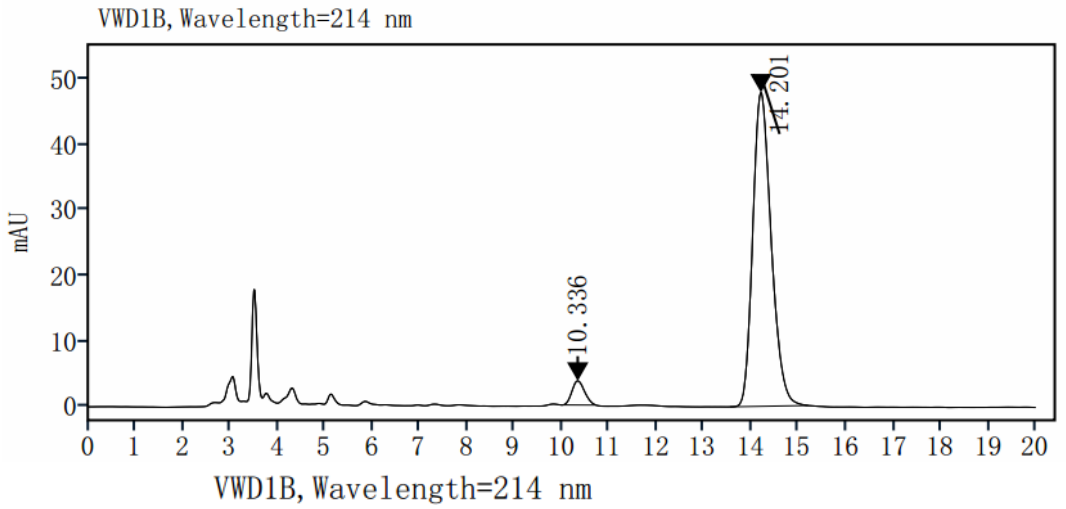


Figure 2B, entry 44
(*S*,*S*)-**L1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.343	MM m	894.56	49.71
	14.220	MM m	905.03	50.29



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.336	MM m	67.99	4.99
	14.201	MM m	1293.29	95.01

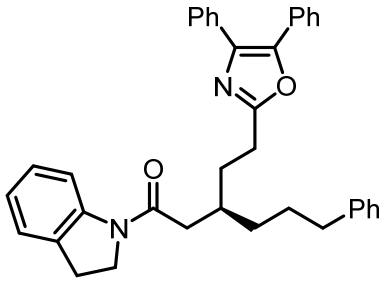
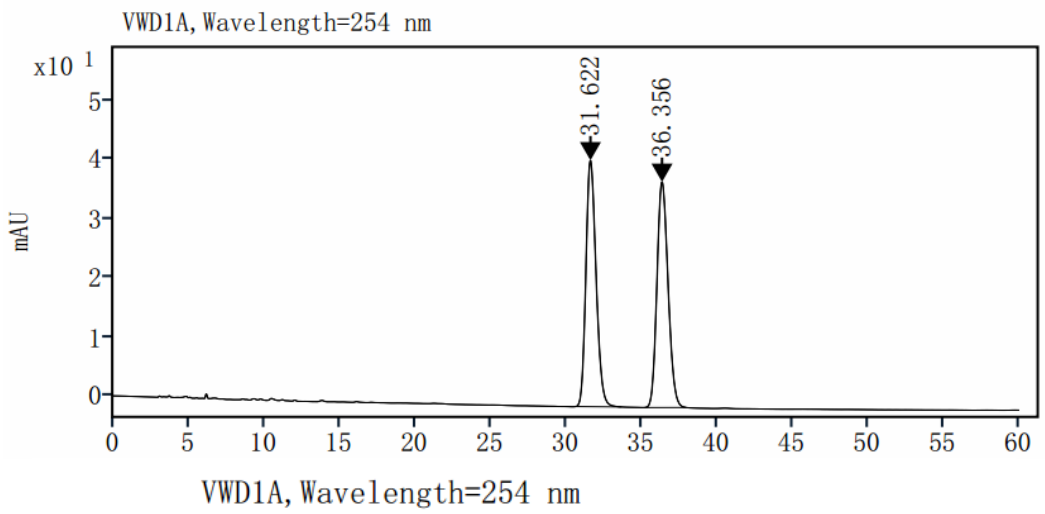
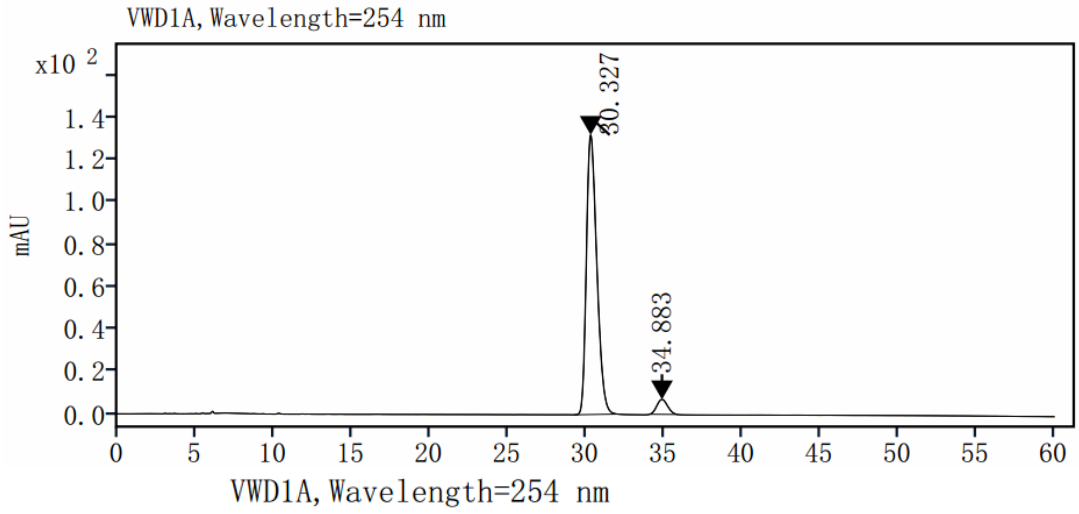


Figure 3B, entry 45
(*S*,*S*)-**L1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	31.622	MM m	1948.32	49.92
	36.356	MM m	1954.95	50.08



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	30.327	MM m	6130.97	94.81
	34.883	MM m	335.61	5.19

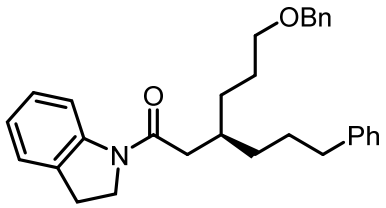
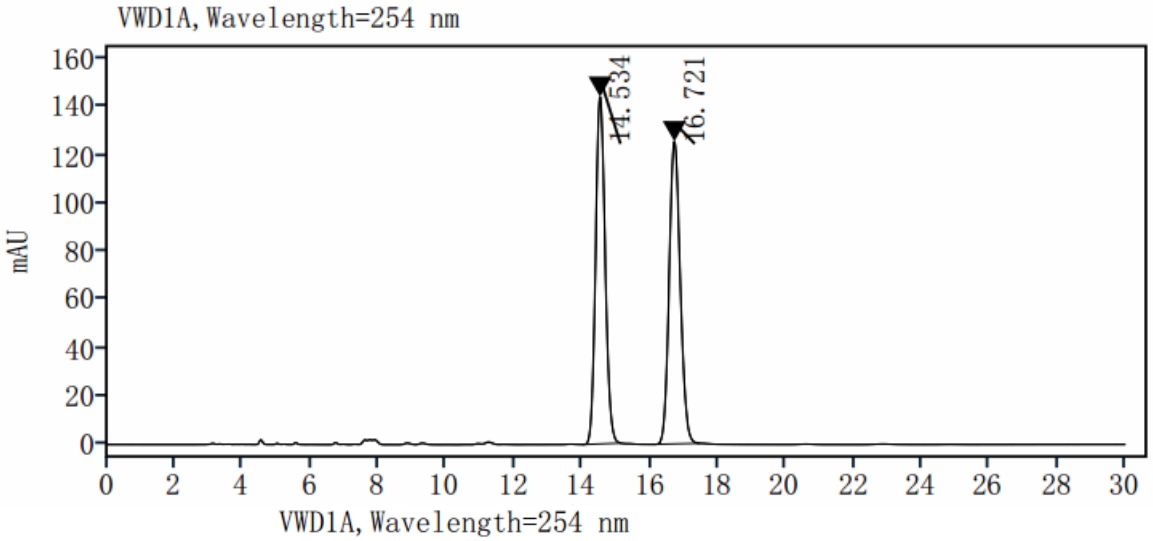
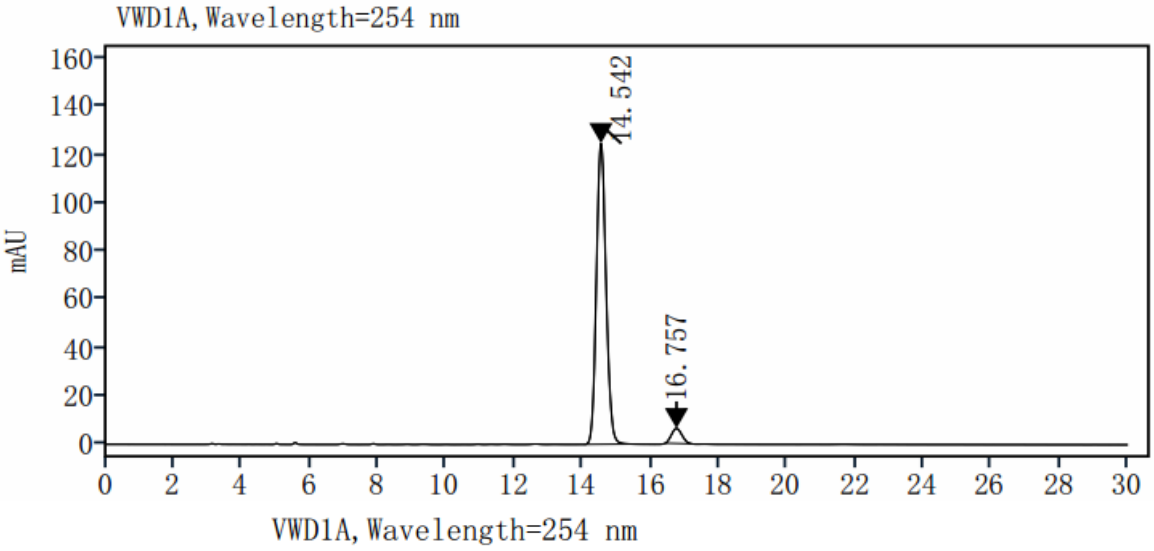


Figure 2B, entry 46
(*S*,*S*)-**L1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	14.534	MM m	2811.00	49.71
	16.721	MM m	2843.28	50.29



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	14.542	MM m	2449.21	94.87
	16.757	MM m	132.52	5.13

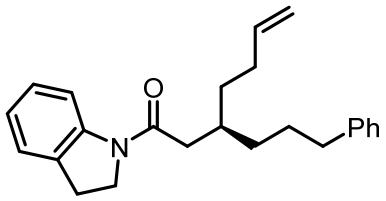
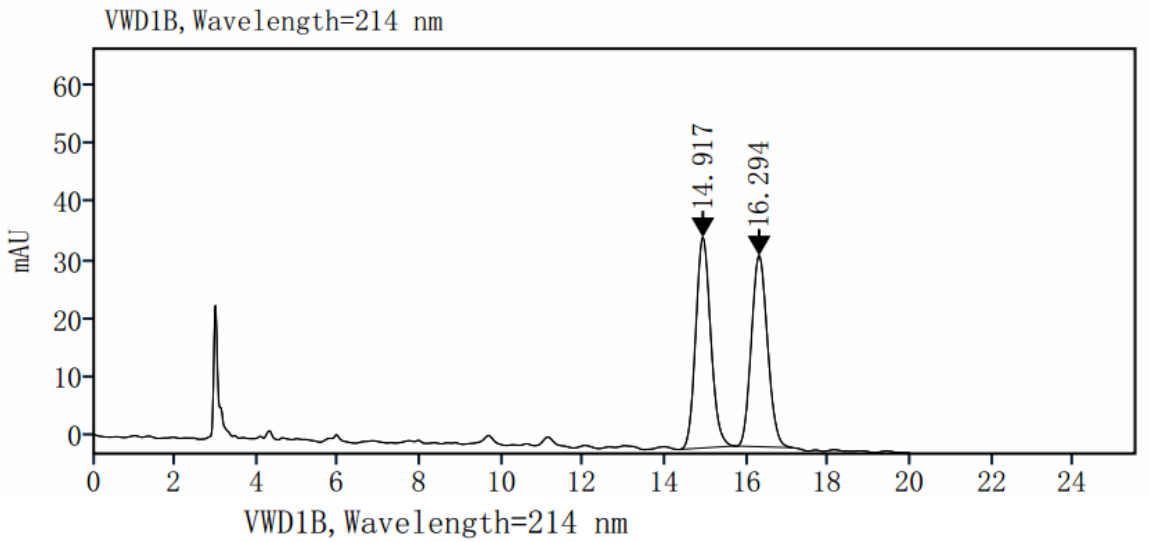
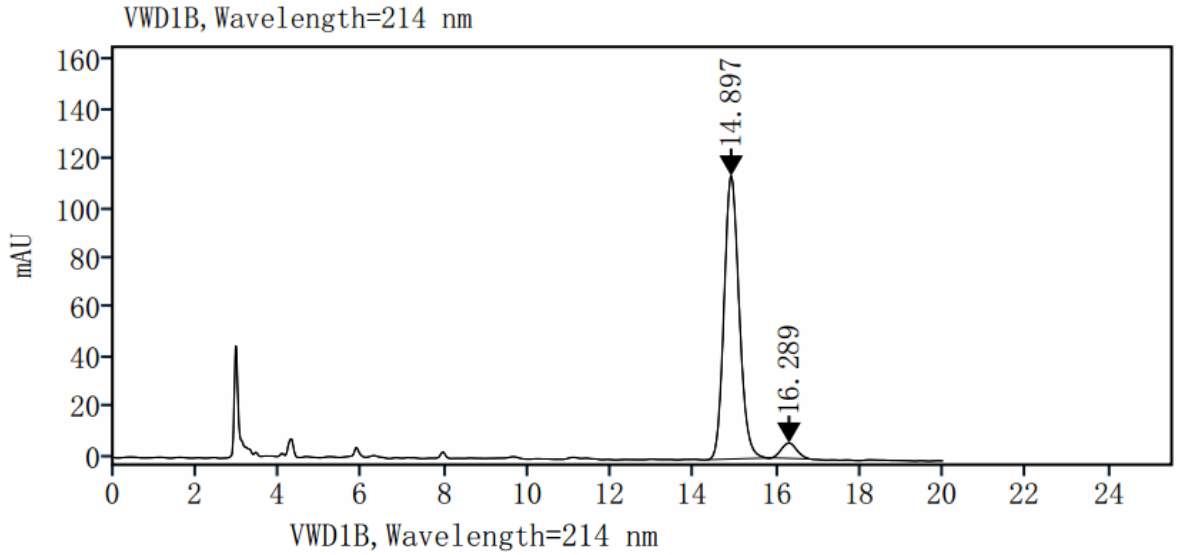


Figure 2B, entry 47
(*S*,*S*)-**L1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	14.917	MM m	920.68	50.56
	16.294	MM m	900.11	49.44



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	14.897	MM m	2882.19	94.79
	16.289	MM m	158.36	5.21

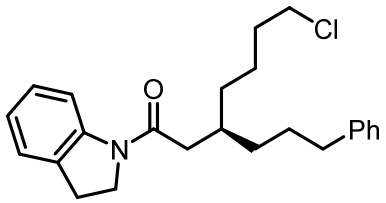
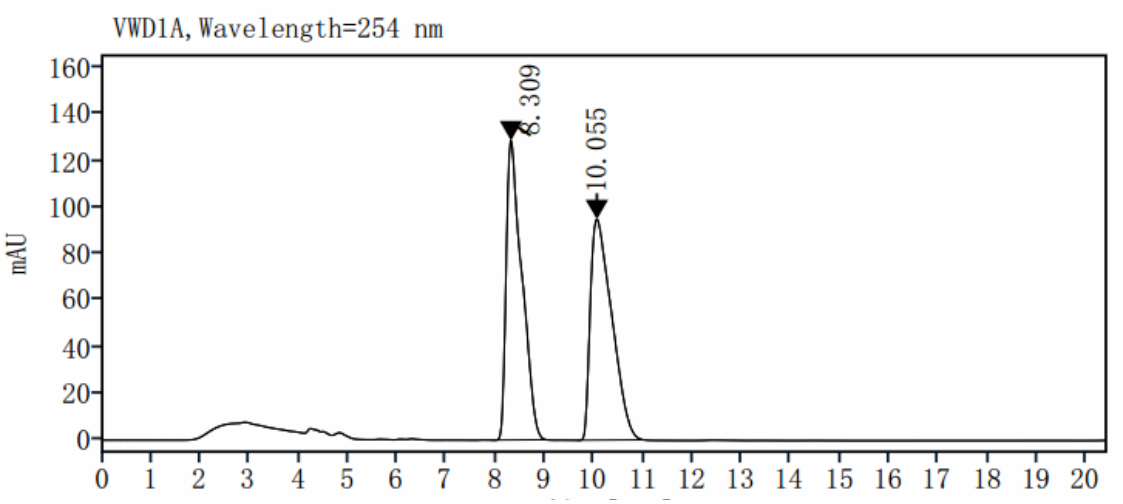
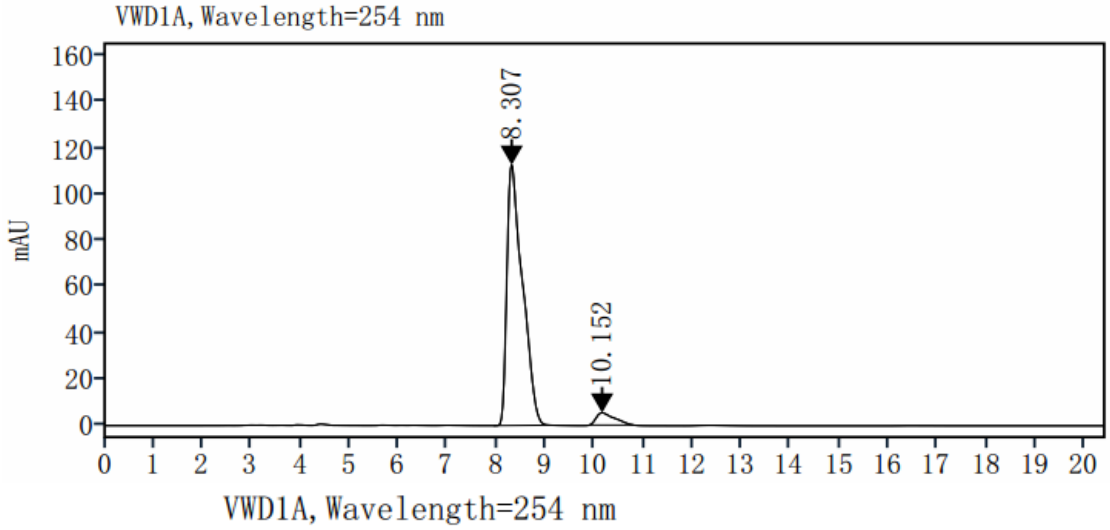


Figure 2B, entry 48
(*S*,*S*)-**L1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	8.309	MM m	2854.01	49.75
	10.055	MM m	2882.14	50.25



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	8.307	MM m	2493.07	94.77
	10.152	MM m	137.63	5.23

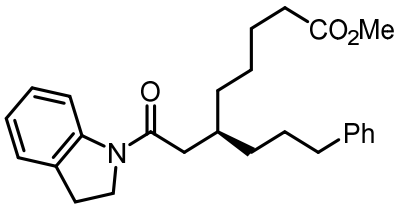
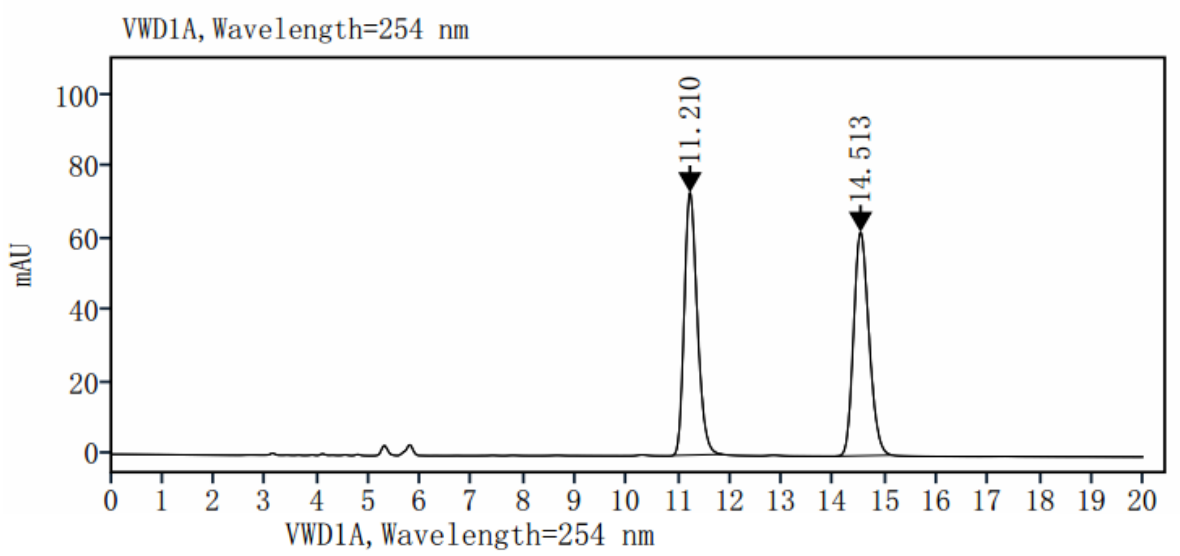
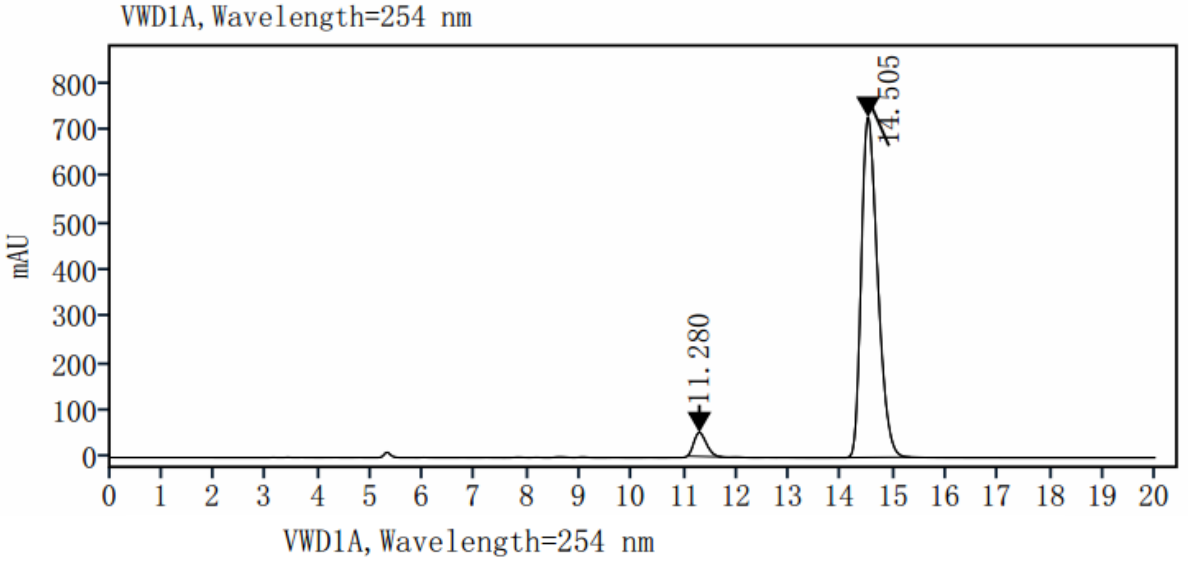


Figure 2B, entry 49
(*S*,*S*)-**L1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	11.210	MM m	1278.81	49.77
	14.513	MM m	1290.86	50.23



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	11.280	MM m	849.23	5.09
	14.505	MM m	15833.90	94.91

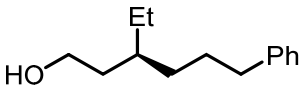
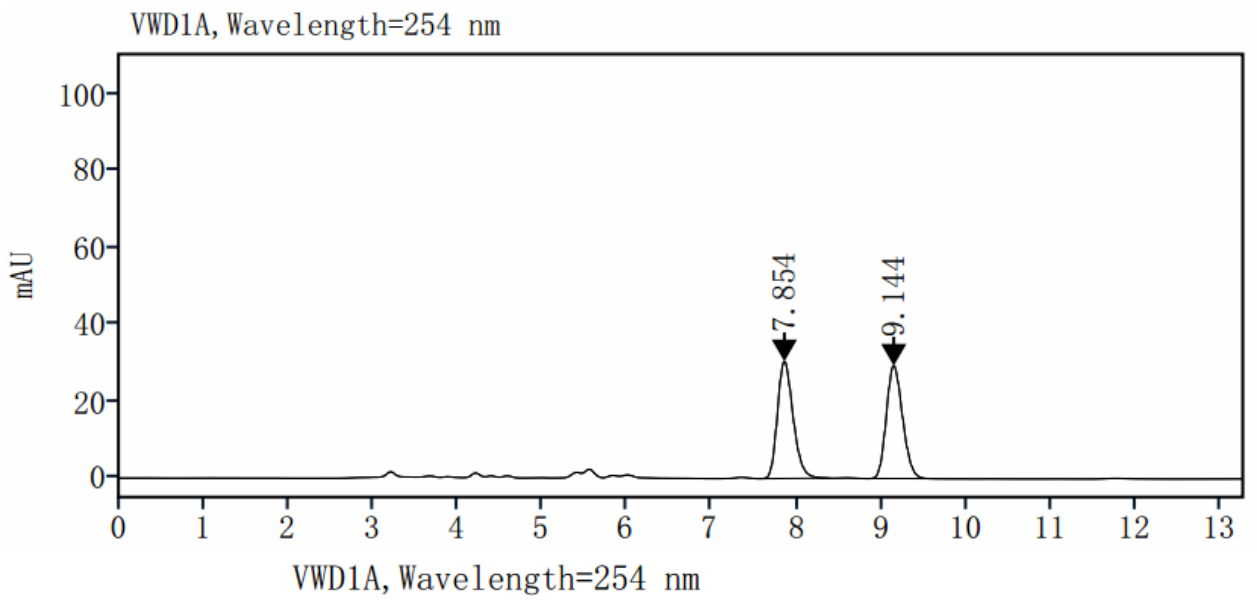
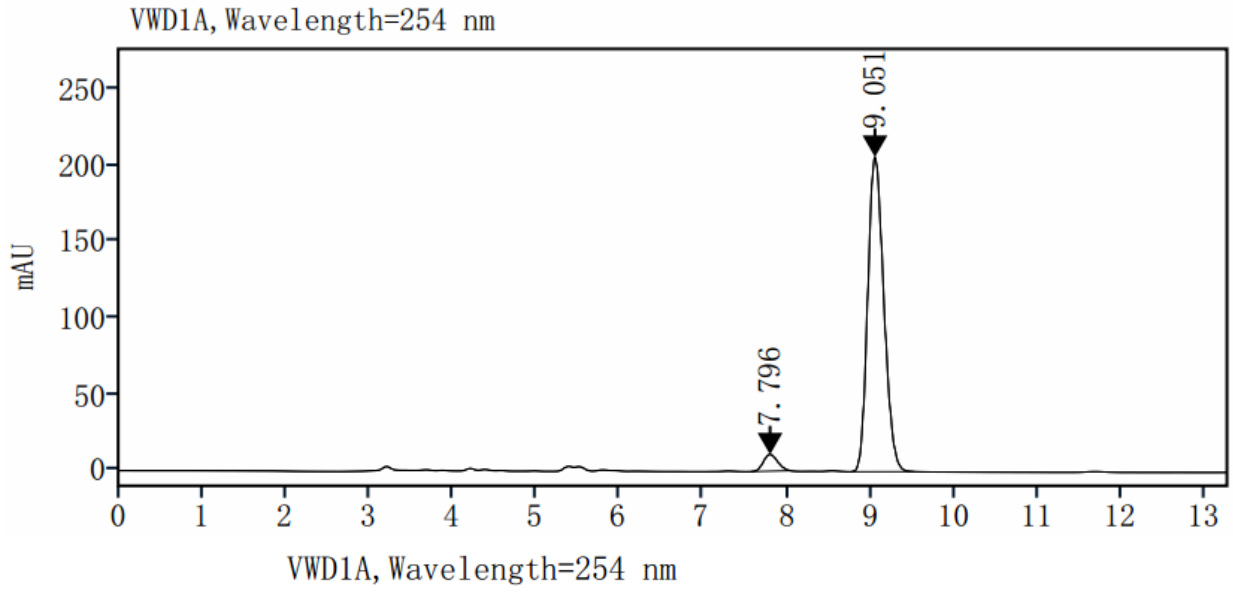


Figure 3B, entry 50
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.854	MM m	393.34	50.10
	9.144	MM m	391.83	49.90



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.796	MM m	129.75	4.50
	9.051	MM m	2755.05	95.50

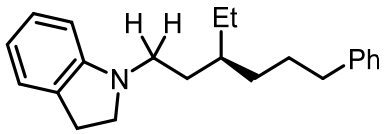
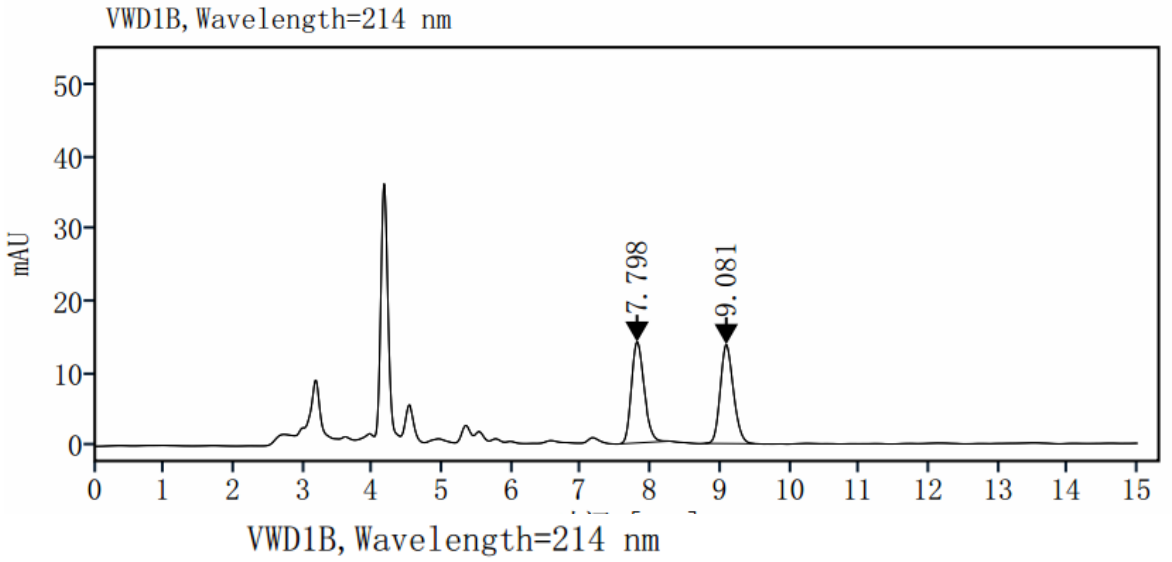
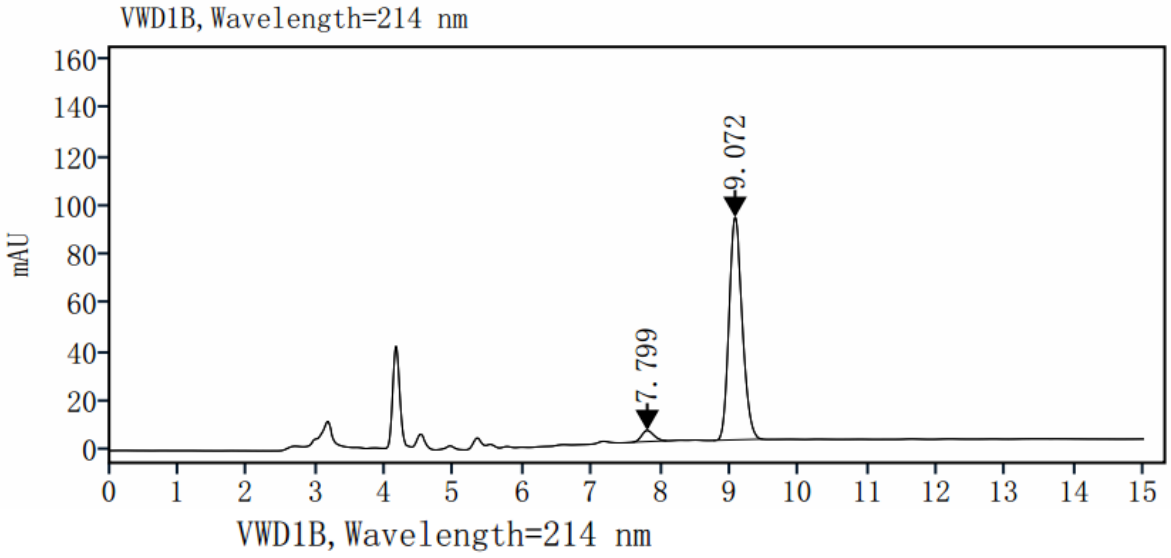


Figure 3B, entry 51
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.798	MM m	178.21	49.29
	9.081	MM m	183.34	50.71



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.799	MM m	55.97	4.41
	9.072	MM m	1214.12	95.59

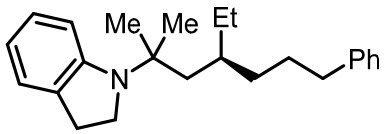
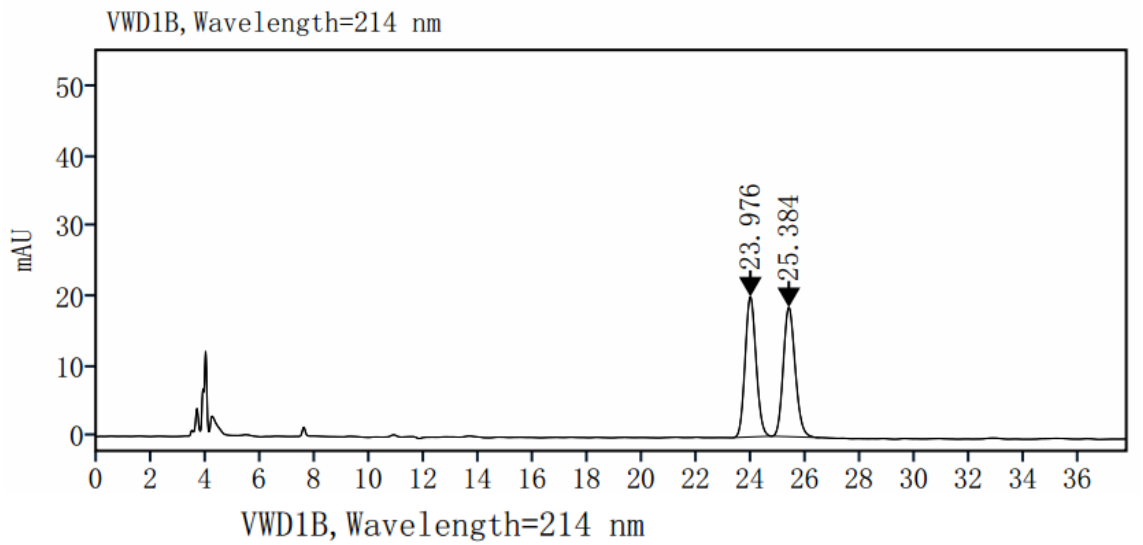
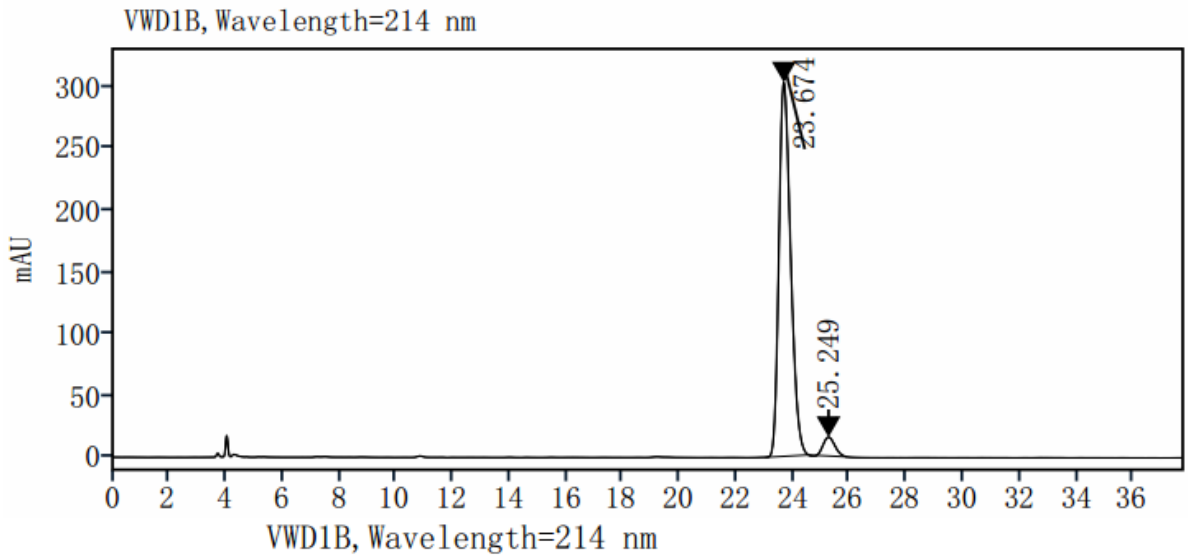


Figure 3B, entry 52
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	23.976	MM m	559.34	49.94
	25.384	MM m	560.75	50.06



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	23.674	MM m	8732.67	95.35
	25.249	MM m	425.96	4.65

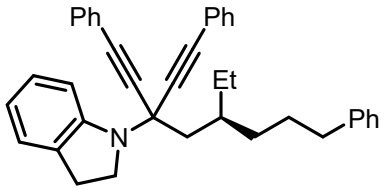
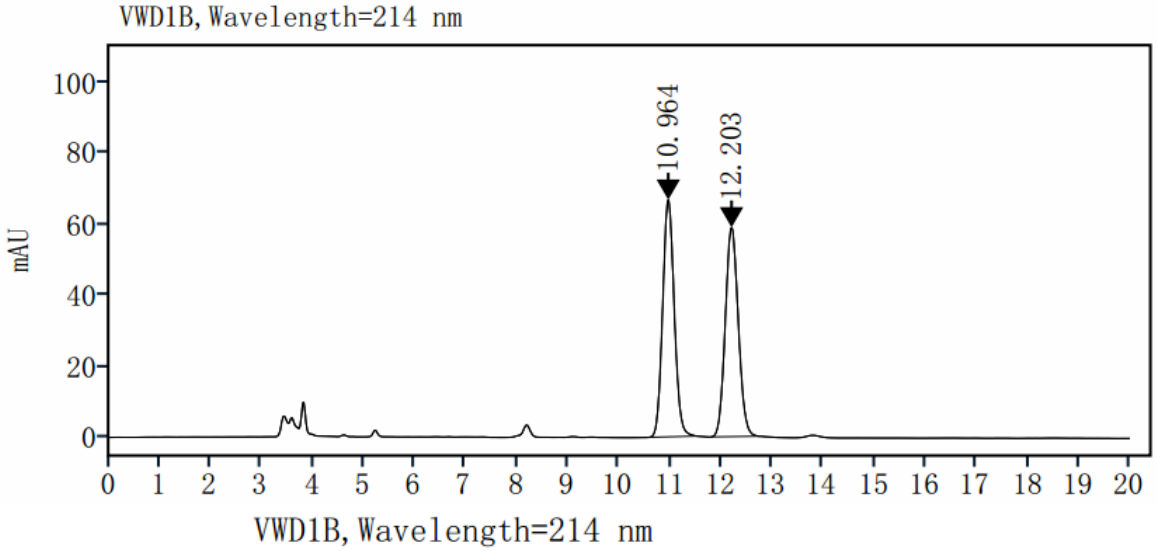
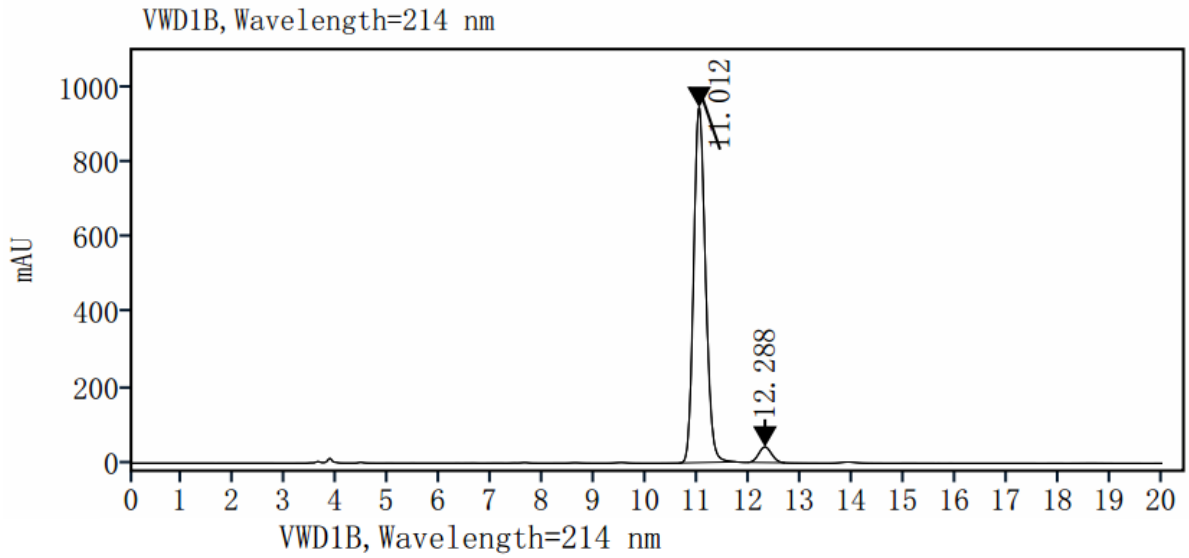


Figure 3B, entry 53
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.964	MM m	1051.32	50.23
	12.203	MM m	1041.57	49.77



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	11.012	MM m	15075.64	95.43
	12.288	MM m	722.27	4.57

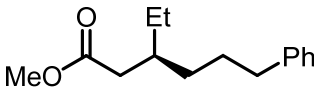
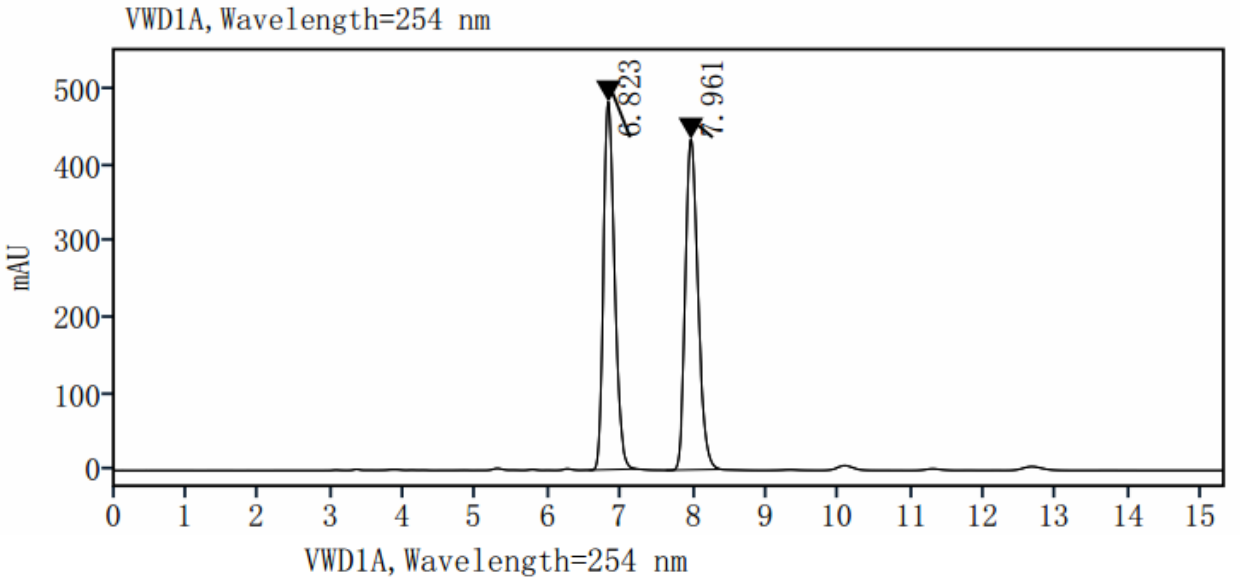
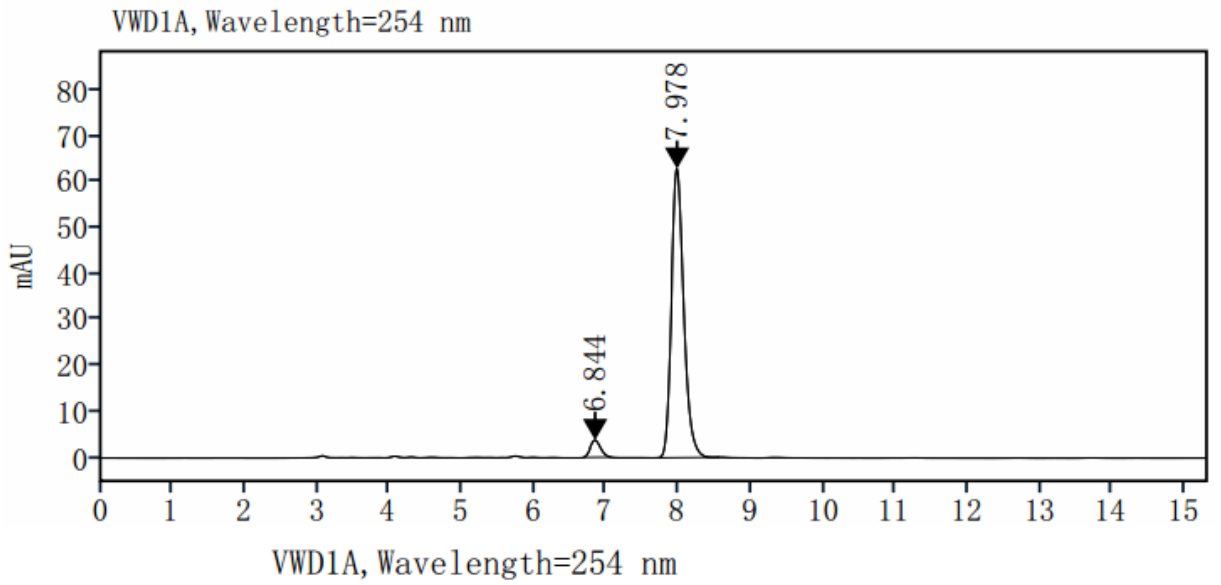


Figure 3B, entry 54
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.823	MM m	5129.18	49.49
	7.961	MM m	5234.41	50.51



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.844	MM m	36.89	4.68
	7.978	MM m	750.60	95.32

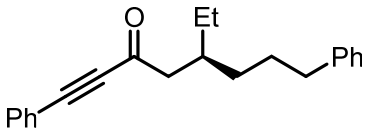
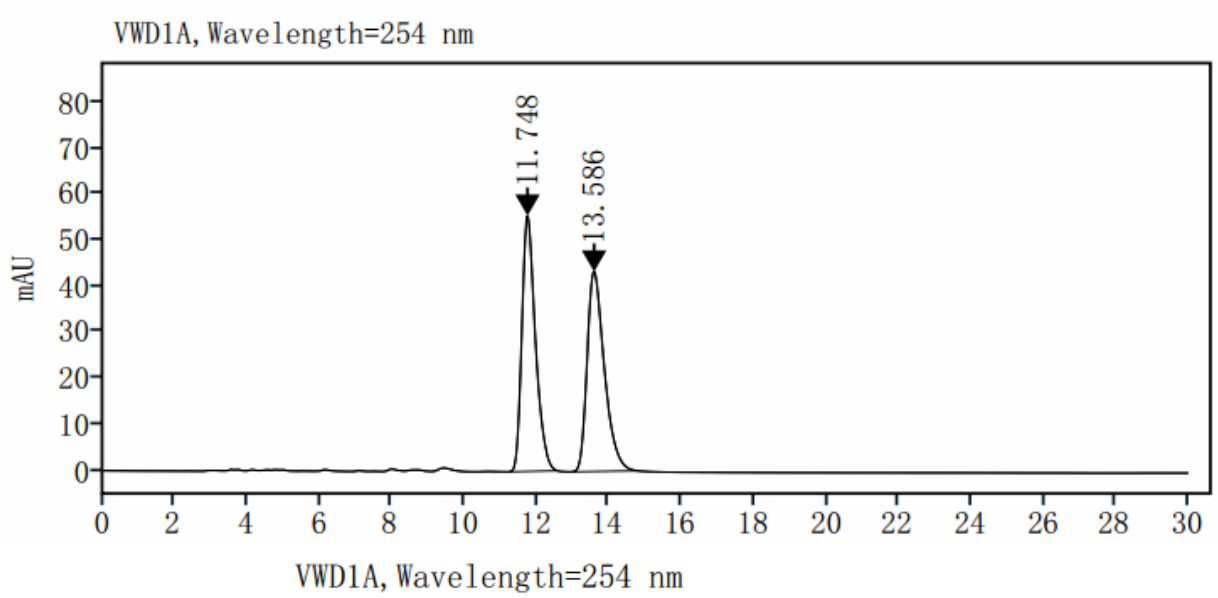
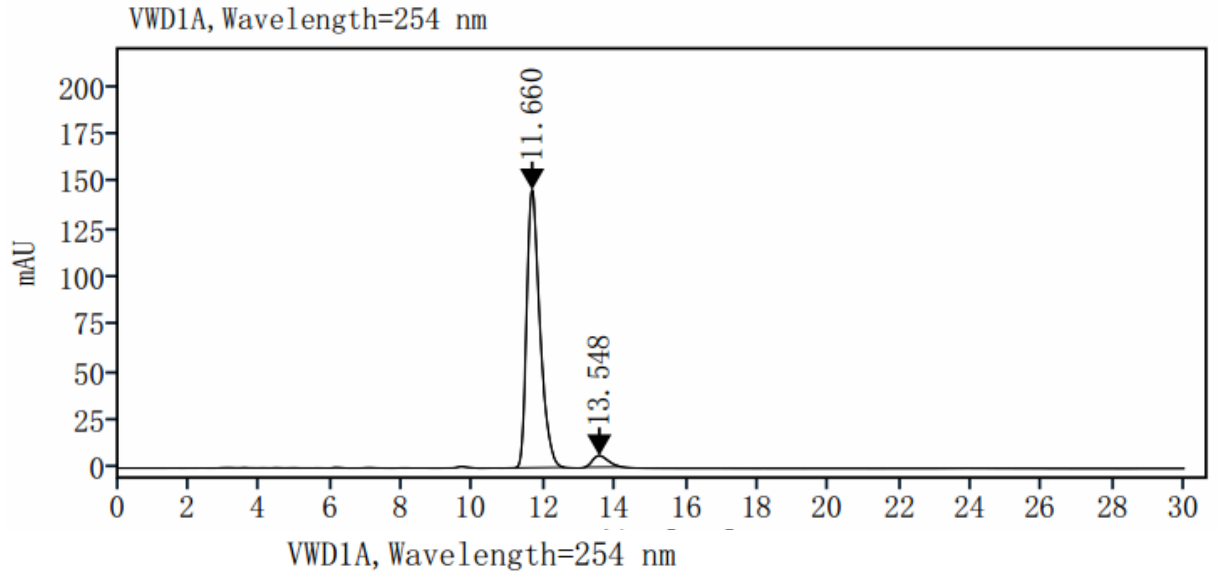


Figure 3B, entry 55
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	11.748	MM m	1444.79	50.11
	13.586	MM m	1438.47	49.89



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	11.660	MM m	3768.83	95.41
	13.548	MM m	181.23	4.59

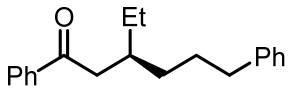
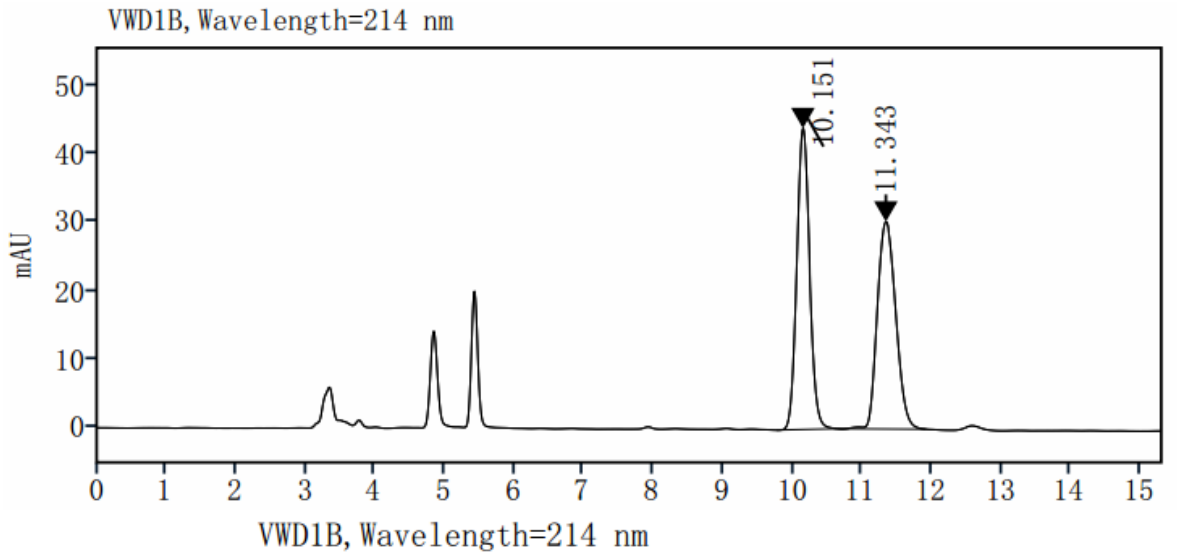
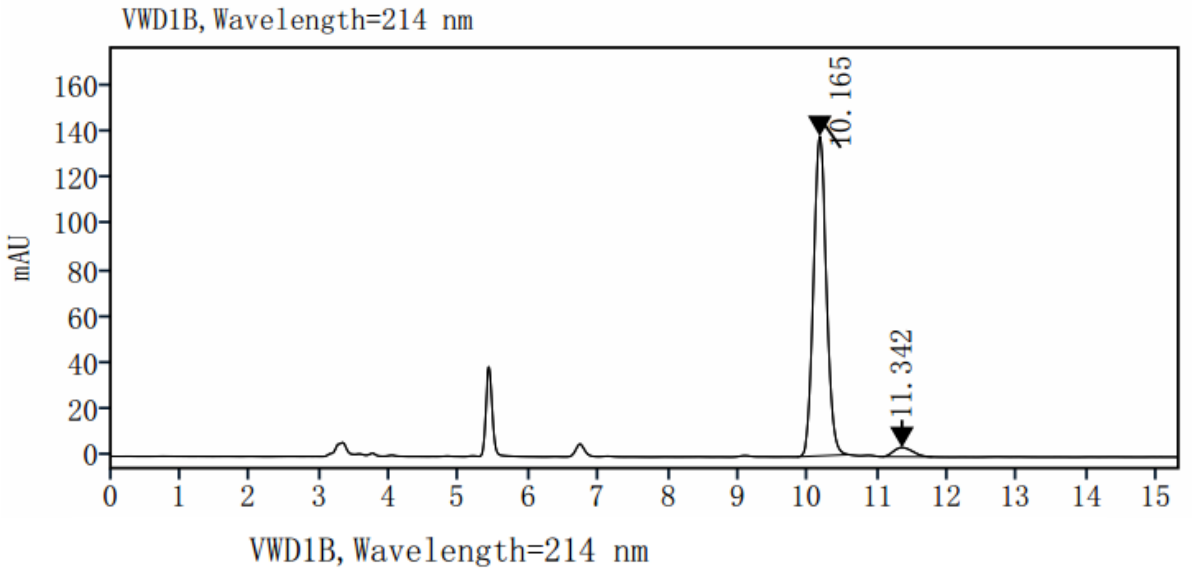


Figure 3B, entry 56
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.151	MM m	566.27	50.17
	11.343	MM m	562.43	49.83



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.165	MM m	1772.74	95.92
	11.342	MM m	75.47	4.08

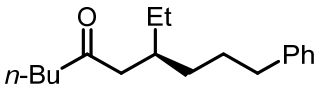
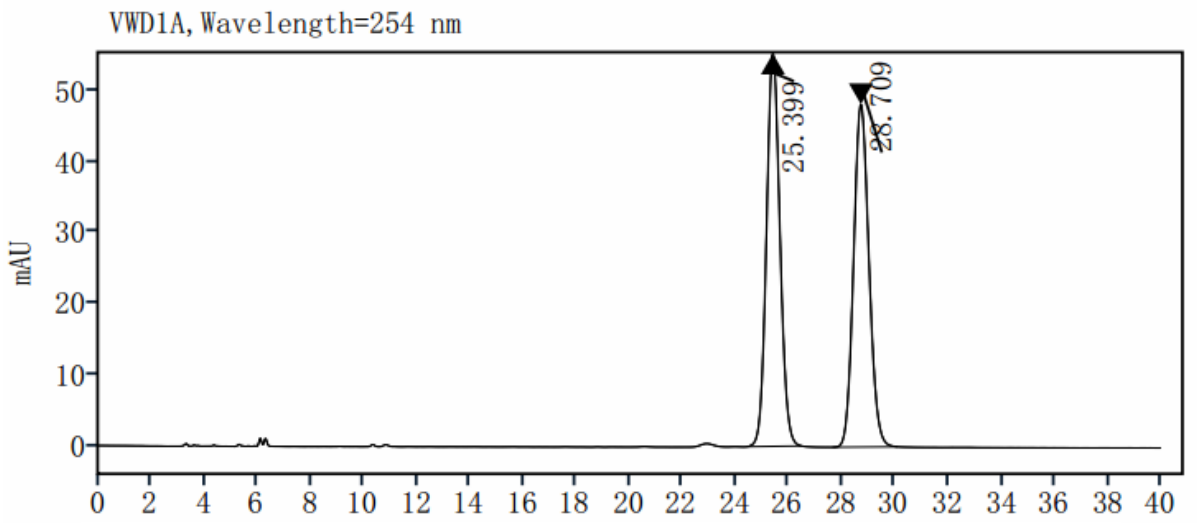
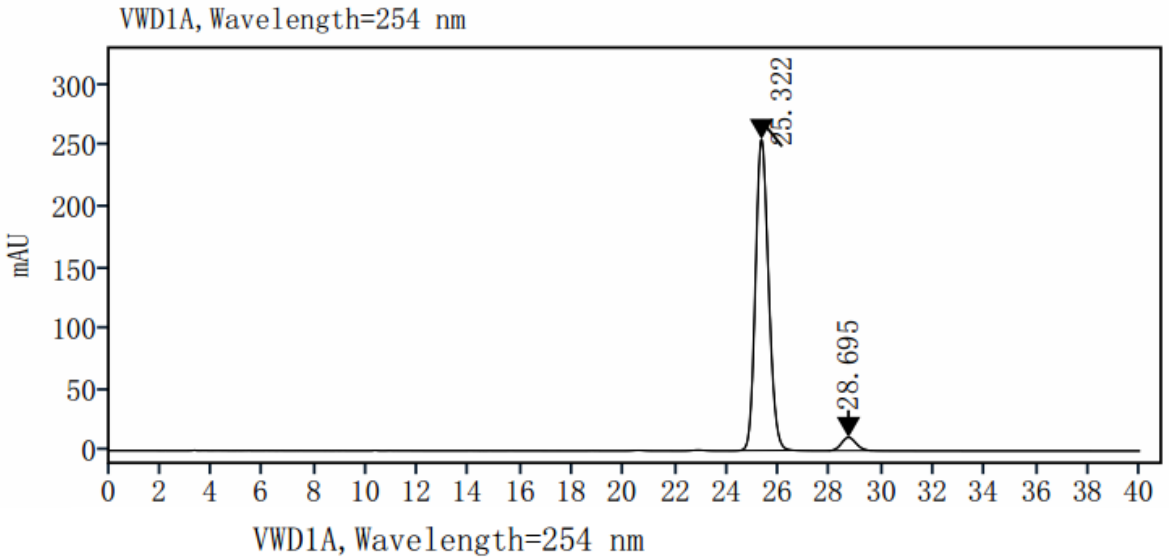


Figure 3B, entry 57
(*S*,*S*)-**L1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	25.399	MM m	1948.66	50.14
	28.709	MM m	1937.97	49.86



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	25.322	MM m	9004.32	95.47
	28.695	MM m	427.59	4.53

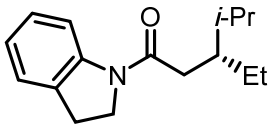
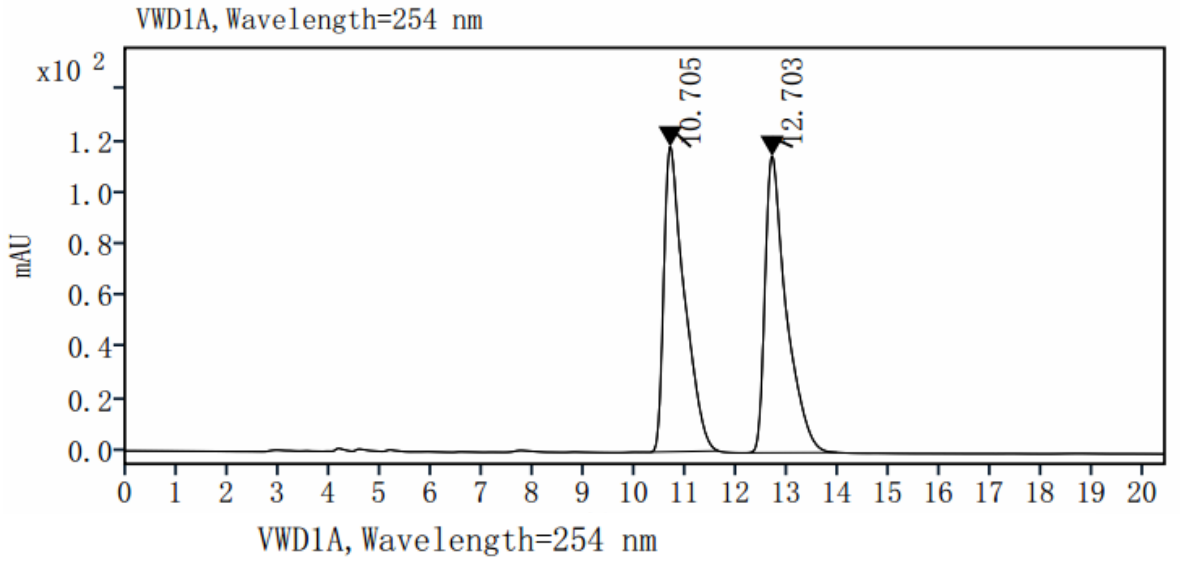
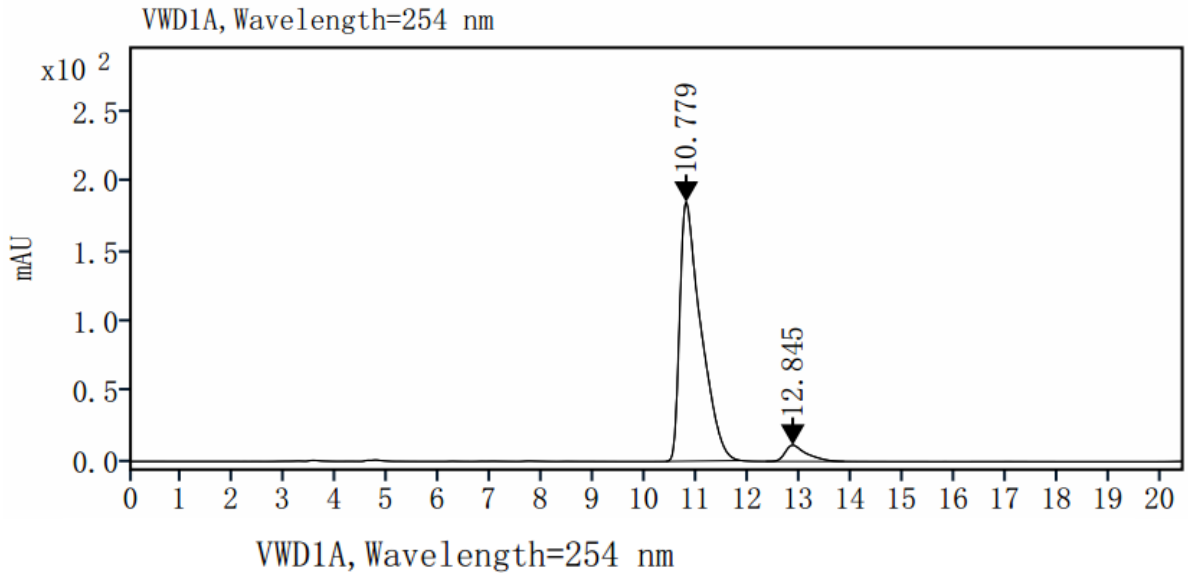


Figure 3C, entry 58
(*R*,*R*)-**L1**: 88% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.705	MM m	3314.85	49.78
	12.703	MM m	3344.42	50.22



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.779	MM m	5301.92	94.02
	12.845	MM m	337.50	5.98