Enantioselective Construction of Quaternary Stereocenters via Cooperative Photoredox/Fe/Chiral Primary Amine Triple Catalysis

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Supporting Information

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I. General Information

Unless otherwise noted, all the reagents and starting materials were purchased from commercial sources and used without further purification. Fe(OEP)Cl was prepared according to a known procedure.[1] Anhydrous MTBE (methyl *tert*-butyl ether) and $PhCF_3$ were purchased from *J&K* and stored under nitrogen. 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 tetramethylsilane, using 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. HRMS 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. Cyclic voltammograms were collected with a CorrTest CS310 electrochemical workstation. Emission intensities were recorded using a FLUOROLOG-3-11 Spectrophotometer. Flash column chromatography was performed using silica gel (particle size 200-400 mesh ASTM, purchased from Yantai, China).

The blue LEDs (450 nm) with a maximum capacity of 24 parallel reactions were purchased from www.howsuper-uvled.com. As shown in **Figure S1**, the reaction vials were irradiated by the LED chips underneath, and the temperature was controlled using the aluminum plate with continuous cryogenic circulation pumps.

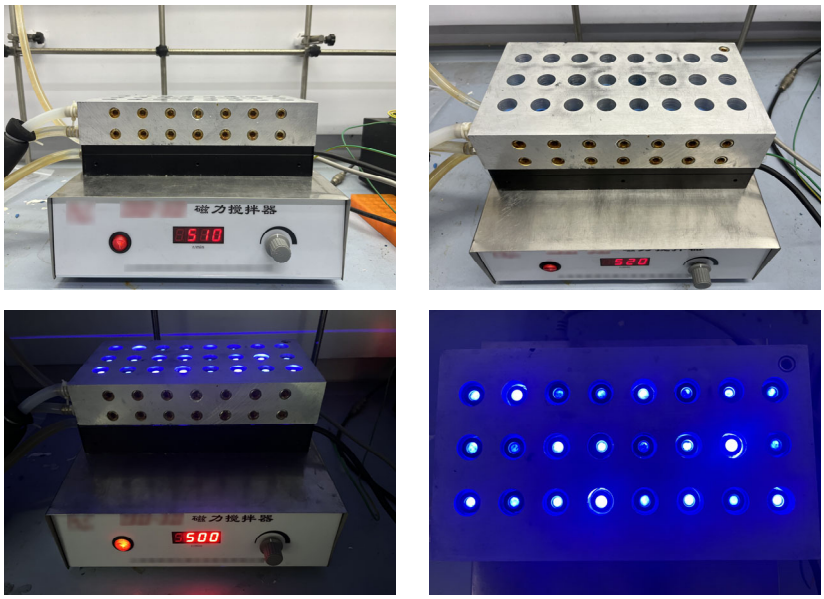
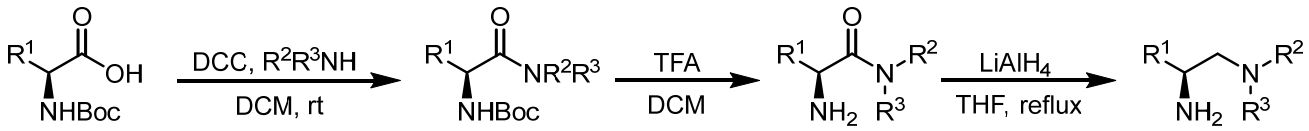


Figure S1. Photoreaction Setup

II. Preparation of Chiral Primary Amines

The yields have not been optimized.

General Procedure 1 (GP-1).

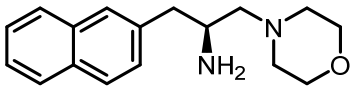


Preparation of Chiral Primary Amines.[2-4] An oven-dried 500 mL round-bottom flask was charged with a stir bar and Boc-protected amino acid (1.0 equiv), and then it was sealed with a rubber septum cap. The flask was placed under a nitrogen atmosphere by evacuating and backfilling the flask (three cycles), followed by the addition of anhydrous DCM (volume to generate a 0.50 M solution of the Boc-protected amino acid) via syringe. The resulting solution was cooled to 0 °C using an ice bath, and then DCC (1.05 equiv) in anhydrous DCM (volume to generate a 4.0 M solution of DCC) was added via syringe over 10 min. The reaction mixture was stirred at 0 °C for 30 min, followed by the addition of amine (1.5 equiv) in anhydrous DCM (volume to generate a 5.0 M solution of amine). The reaction was allowed to warm to room temperature and stirred overnight. The mixture was filtered through a pad of celite and washed with aqueous HCl (0.10 M), water, aqueous saturated $NaHCO_3$, and brine, and then dried over anhydrous Na_2SO_4 and filtered. The solution was then concentrated under reduced pressure to provide the amide compound, which was directly used for the next step without purification.

An oven-dried 200 mL round-bottom flask was charged with a stir bar, the amide compound (1.0 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 anhydrous DCM (volume to generate a 2.0 M solution of the amide compound) via syringe. The resulting solution was cooled to 0 °C using an ice bath, and then TFA (using a 1:1 volume ratio of TFA:DCM) was added via syringe over 10 min. The reaction was allowed to warm to room temperature and stirred overnight. The mixture was then concentrated under reduced pressure, and the solids obtained were dissolved with Et_2O. After standing at room temperature for several hours, crystals started to form and were collected using a Büchner funnel. The solids were dissolved in DCM, and the pH value of the solution was adjusted to ~12 by the addition of aqueous saturated Na_2CO_3 under an ice bath. The aqueous phase was extracted with DCM, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude amine intermediate was directly used for the next step without purification.

An oven-dried 250 mL two-neck round-bottom flask was charged with a stir bar, fitted with a reflux condenser attached to a nitrogen manifold, and then 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 a solution of amine intermediate in THF (volume to generate

a 0.50 M solution of the amine intermediate). The flask was cooled to 0 °C using an ice bath, followed by the addition of lithium aluminum hydride (3.0 equiv) through the open neck under a positive pressure of nitrogen. The reaction was stirred at 0 °C for 30 min and heated to reflux for 12 h. The mixture was then cooled to 0 °C, followed by the sequential dropwise addition of water, 15% aqueous NaOH, and water (1:1:3, depending on the grams of lithium aluminum hydride). The aqueous phase was extracted with EtOAc (40 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the target product.



(*S*)-1-Morpholino-3-(naphthalen-2-yl)propan-2-amine. The title compound was synthesized according to **GP-1** from (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(naphthalen-2-yl)propanoic acid (15.76 g, 50.0 mmol) and morpholine. The product was purified by column chromatography on silica gel (95:5 CH_2Cl_2/MeOH). 8.25 g (30.5 mmol, 61% yield). Yellow solid.

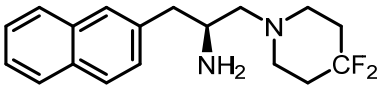
^{1}H NMR (400 MHz, Chloroform-d) δ 7.80 (d, *J* = 8.0 Hz, 3H), 7.66 (s, 1H), 7.50 – 7.41 (m, 2H), 7.34 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.75 – 3.64 (m, 4H), 3.34 – 3.25 (m, 1H), 2.94 – 2.85 (m, 1H), 2.65 (dd, *J* = 13.4, 8.4 Hz, 1H), 2.54 (dq, *J* = 11.5, 3.7 Hz, 2H), 2.43 – 2.25 (m, 4H), 1.60 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 136.6, 133.5, 132.2, 128.0, 127.63, 127.58, 127.4, 126.0, 125.3, 67.1, 65.4, 54.1, 48.9, 42.3.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{17}H_{23}N_2O$: 271.1805, found: 271.1798.

FT-IR (film): 3371, 2929, 2863, 2860, 1601, 1104, 852, 808, 752 cm^{-1}.

$[\alpha]^{20}_D$ = +137.0 (*c* 1.0, $CHCl_3$).



(*S*)-1-(4,4-Difluoropiperidin-1-yl)-3-(naphthalen-2-yl)propan-2-amine. The title compound was synthesized according to **GP-1** from (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(naphthalen-2-yl)propanoic acid (4.81 g, 30.0 mmol) and 4,4-difluoropiperidine. The product was purified by column chromatography on silica gel (95:5 CH_2Cl_2/MeOH). 5.10 g (16.8 mmol, 56% yield). Yellow solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 – 7.79 (m, 3H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.46 (tt, *J* = 6.8, 5.1 Hz, 2H), 7.35 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.28 (tt, *J* = 8.9, 4.5 Hz, 1H), 2.90 (dd, *J* = 13.3, 4.6 Hz, 1H), 2.73 – 2.60 (m, 3H), 2.52 – 2.46 (m, 2H), 2.43 – 2.32 (m, 2H), 2.08 – 1.89 (m, 4H), 1.60 (s, 2H).

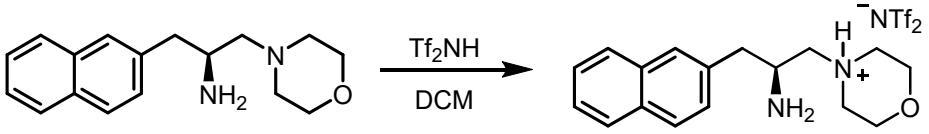
^{13}C NMR (101 MHz, Chloroform-d) δ 136.5, 133.5, 132.2, 128.0, 127.6, 127.5, 127.4, 126.0, 125.3, 122.0 (t, *J* =242.6f Hz), 63.9, 50.4 (t, *J* =5.6 Hz), 49.6, 42.3, 34.1 (t, *J* =22.8 Hz).

^{19}F NMR (376 MHz, Chloroform-d) δ -97.9.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{18}H_{23}F_2N_2$: 305.1824, found: 305.1814.

FT-IR (film): 3370, 2932, 2838, 2807, 1364, 953, 814, 742 cm^{-1}.

$[\alpha]^{20}_D$ = +138.2 (*c* 1.0, $CHCl_3$).



(*S*)-**A1**

Preparation of (*S*)-A1. An oven-dried 20 mL vial was equipped with a magnetic stir bar, (*S*)-1-morpholino-3-(naphthalen-2-yl)propan-2-amine (270 mg, 1.0 mmol, 1.0 equiv), Tf_2NH (281 mg, 1.0 mmol, 1.0 equiv), and was then sealed with a PTFE septum cap. The vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles), followed by the addition of anhydrous DCM (10 mL). The mixture was stirred for 60 min under room temperature and then concentrated in vacuum to obtain (*S*)**-A1**.

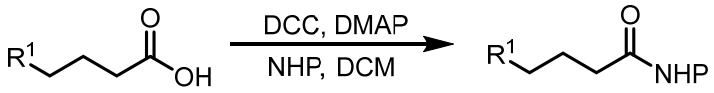
The corresponding chiral amines of **A3**-**A6** are known compounds.

III. Preparation of 1,3-Dicarbonyl Compounds and NHP Esters

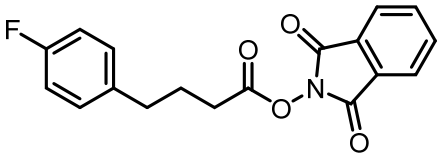
The yields have not been optimized.

Preparation of 1,3-Dicarbonyl Compounds. 24a, **25a**, **32a**, **33a**, **36a**, and **37a** are commercially available. The cyclic *β*-ketoesters **1a**,[5] **27a**,[6] **28a**,[7] and **38a**[8] were prepared by transesterification of the corresponding alcohol with **24a.** The cyclic *β*-ketoesters **26a**[7], cyclic *β*-ketoamides **29a**,[9] **30a**,[10] **31a**,[9] **34a**,[11] and **35a**[11] were prepared according to the corresponding literature.

General Procedure 2 (GP-2).



Preparation of NHP Esters.[12] An oven-dried 500 mL round-bottom flask was charged with a stir bar, carboxylic acid (1.0 equiv), *N*-hydroxyphthalimide (1.1 equiv), and DMAP (0.10 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 anhydrous DCM (volume to generate a 0.50 M solution of the carboxylic acid) via syringe. The resulting solution was cooled to 0 °C using an ice bath, and then DCC (1.1 equiv) in anhydrous DCM (volume to generate a 5.0 M solution of the DCC) was added via syringe over 10 min. The reaction was stirred at room temperature overnight. The mixture was filtered through a pad of celite, and the solution was then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the target product.



1,3-Dioxoisoindolin-2-yl 4-(4-fluorophenyl)butanoat*e*. The title compound was synthesized according to **GP-2** from 4-(4-fluorophenyl)butyric acid (5.41 g, 30.0 mmol) and *N*-hydroxyphthalimide. The product was purified by column chromatography on silica gel (6:1 PE/EtOAc). 6.87 g (21.0 mmol, 70% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.89 – 7.84 (m, 2H), 7.80 – 7.75 (m, 2H), 7.19 – 7.14 (m, 2H), 7.01 – 6.95 (m, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.3 Hz, 2H), 2.10 – 2.05 (m, 2H).

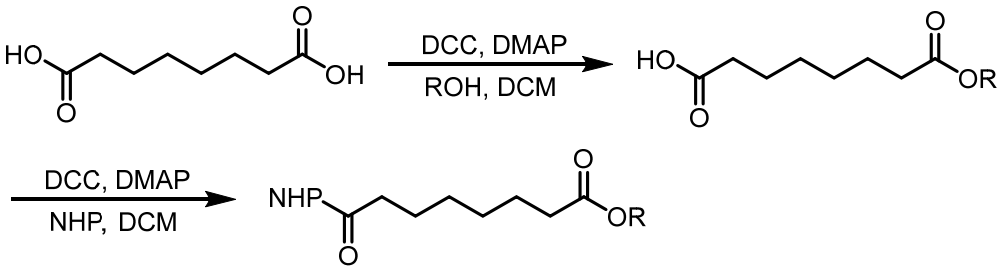
^{13}C NMR (151 MHz, Chloroform-d) δ 169.3, 161.9, 161.4 (d, *J* =243.9 Hz), 136.2 (d, *J* =3.3 Hz), 134.7, 129.9 (d, *J* =7.7 Hz), 128.8, 123.9, 115.2 (d, *J* =21.6 Hz), 33.6, 30.0, 26.3.

^{19}F NMR (565 MHz, Chloroform-d) δ -117.1.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{18}H_{15}FNO_4$: 328.0980, found: 328.0978.

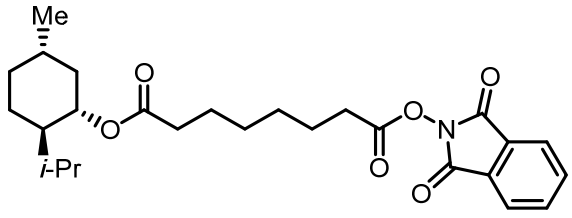
FT-IR (film): 2952, 2932, 1815, 1788, 1722, 1370, 1182, 873, 689 cm^{-1}.

General Procedure 3 (GP-3).



Preparation of NHP esters 20b and 22b.[12,13] An oven-dried 500 mL round-bottom flask was charged with a stir bar and adipic acid (1.0 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 anhydrous DCM (volume to generate a 0.50 M solution of the adipic acid) via syringe. The resulting solution was cooled to 0 °C using an ice bath, and then DCC (2.5 equiv) and DMAP (0.10 equiv) in anhydrous DCM (volume to generate a 4.0 M solution of the DCC) was added via syringe over 10 min. The mixture was stirred at 0 °C for 30 min, followed by the addition of ROH (2.5 equiv) in anhydrous DCM (volume to generate a 5.0 M solution of the ROH). The reaction was stirred at room temperature overnight. The mixture was filtered through a pad of celite and washed with aqueous HCl (0.10 M), water, aqueous saturated $NaHCO_3$, and brine, and then dried over anhydrous Na_2SO_4 and filtered. The solution was then concentrated under reduced pressure to provide the ester intermediate, which was directly used for the next step without purification.

An oven-dried 500 mL round-bottom flask was charged with a stir bar, the ester intermediate (1.0 equiv), *N*-hydroxyphthalimide (1.1 equiv), and DMAP (0.10 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 anhydrous DCM (volume to generate a 0.50 M solution of the ester intermediate) via syringe. The resulting solution was cooled to 0 °C using an ice bath, and then DCC (1.1 equiv) in anhydrous DCM (volume to generate a 5.0 M solution of the DCC) was added via syringe over 10 min. The reaction was stirred at room temperature overnight. The mixture was filtered through a pad of celite, and the solution was then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the target product.



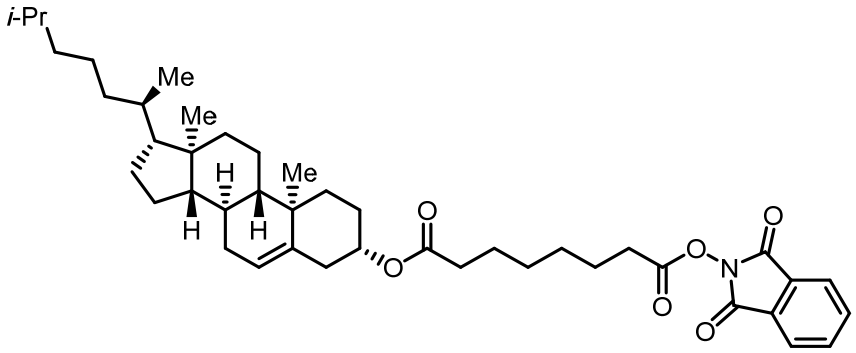
1-(1,3-Dioxoisoindolin-2-yl) 8-((*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl) octanedioate. The title compound was synthesized according to **GP-3** from adipic acid (7.30 g, 50.0 mmol) and *L*-Menthol. The product was purified by column chromatography on silica gel (8:1 PE/EtOAc). 7.56 g (16.5 mmol, 33% yield). Yellow solid.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.64 (td, *J* = 10.9, 4.4 Hz, 1H), 2.62 (t, *J* = 7.4 Hz, 2H), 2.28 – 2.24 (m, 2H), 1.95 – 1.91 (m, 1H), 1.83 (m, 1H), 1.75 (d, *J* = 7.5 Hz, 2H), 1.62 (m, 4H), 1.43 (d, *J* = 7.5 Hz, 3H), 1.37 – 1.30 (m, 3H), 1.04 – 0.97 (m, 1H), 0.95 – 0.89 (m, 1H), 0.85 (dd, *J* = 6.8, 2.8 Hz, 6H), 0.83 – 0.78 (m, 1H), 0.71 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-d) δ 173.0, 169.3, 161.8, 134.6, 128.78, 128.76, 123.8, 73.8, 46.9, 40.8, 34.4, 34.1, 31.2, 30.7, 28.5, 28.3, 26.1, 24.7, 24.4, 23.23, 21.9, 20.6, 16.2.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{26}H_{36}NO_6$: 458.2537, found: 458.2539.

FT-IR (film): 2952, 2926, 1820, 1788, 1747, 1722, 1370, 1182, 1055, 873, 689 cm^{-1}.



1-((*3S,8S,9S,10R,13R,14S,17R*)-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 title compound was synthesized according to **GP-3** from adipic acid (7.30 g, 50.0 mmol) and cholesterol. The product was purified by column chromatography on silica gel (6:1 PE/EtOAc). 13.07 g (19.0 mmol, 38% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.91 – 7.84 (m, 2H), 7.80 – 7.76 (m, 2H), 5.38 – 5.35 (m, 1H), 4.65 – 4.57 (m, 1H), 2.66 (t, *J* = 7.2 Hz, 2H), 2.32 – 2.27 (m, 4H), 2.01 – 1.92 (m, 2H), 1.86 – 1.76 (m, 5H), 1.67 – 1.62 (m, 2H), 1.59 – 1.44 (m, 8H), 1.42 – 1.31 (m, 6H), 1.27 – 1.22 (m, 1H), 1.18 – 1.04 (m, 7H), 1.00 (s, 3H), 1.00 – 0.92 (m, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.86 – 0.84 (m, 6H), 0.66 (s, 3H).

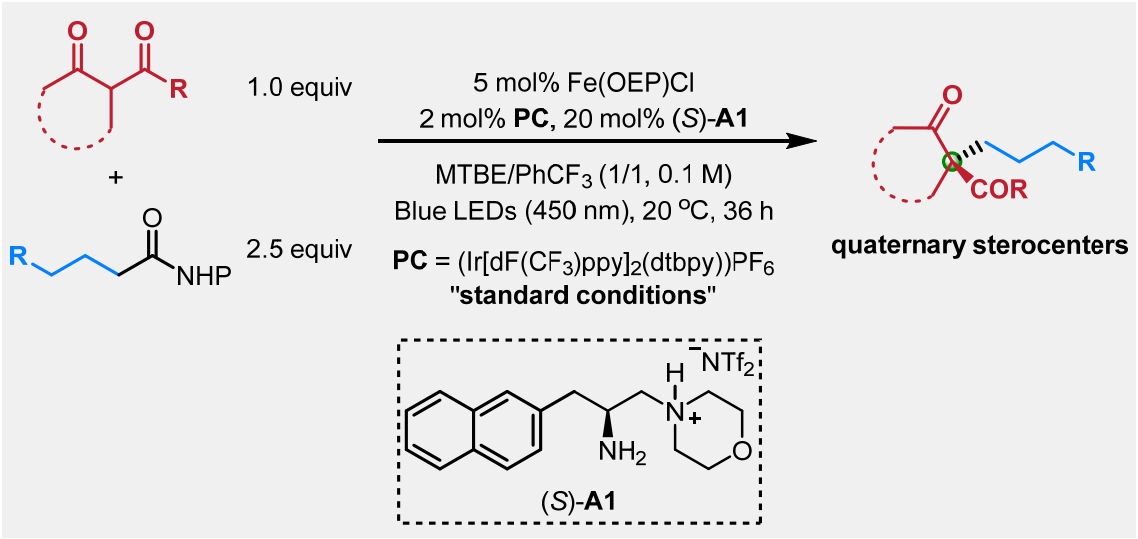
^{13}C NMR (151 MHz, Chloroform-d) δ 173.0, 169.5, 161.9, 139.7, 134. 7, 128.9, 123.9, 122.5, 73.7, 56.6, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 37.0, 36.6, 36.1, 35.8, 34.5, 31.9, 31.8, 30.9, 28.5, 28.4, 28.2, 28.0, 27.8, 24.7, 24.5, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{43}H_{62}NO_6$: 688.4572, found: 688.4579.

FT-IR (film): 2954, 2932, 1822, 1790, 1747, 1722, 1630, 1370, 1230, 1182, 1055, 932, 873, 744, 689 cm^{-1}.

Other NHP esters were synthesized according to **GP-2** from the corresponding carboxylic acid and *N*-hydroxyphthalimide.[14-17]

IV. Catalytic Enantioselective Cross-Couplings



General Procedure 4 (GP-4): Enantioselective cross-coupling of 1,3-dicarbonyl compound and unactivated alkyl NHP ester.

Cross-coupling: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with Fe(OEP)Cl (6.3 mg, 0.010 mmol, 5.0 mol%), $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (4.5 mg, 0.0040 mmol, 2.0 mol%), (*S*)-**A1** (22.0 mg, 0.040 mmol, 20 mol%), NHP ester (0.50 mmol, 2.5 equiv), 1,3-dicarbonyl compound (0.20 mmol, 1.0 equiv), and a stir bar. Anhydrous MTBE (1 mL) and $PhCF_3$ (1 mL) were added sequentially, and the vial was capped with a PTFE septum cap. The vial was transferred out of the glovebox and placed in the photoreactor (**Figure S1**). The reaction was irradiated with blue LEDs (450 nm) and was stirred at 20 °C for 36 hours.

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

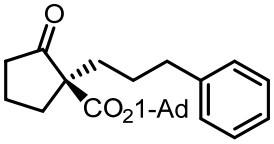
General Procedure 5 (GP-5): Enantioselective cross-coupling of 1,3-dicarbonyl compound and unactivated alkyl NHP ester (72 hours).

The reaction time was extended from 36 to 72 hours, while following the same procedure as **GP-4**.

General Procedure 6 (GP-6). Enantioselective cross-coupling of 1,3-dicarbonyl compound and unactivated alkyl NHP ester ($(Ir[dFppy]_2(bpy))PF_6$).

The photocatalyst was changed from $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ to $(Ir[dFppy]_2(bpy))PF_6$, and the reaction time was extended from 36 to 72 hours, while following the same procedure as **GP-4**.

The racemic example was obtained by using *(rac)*-**A1** as catalyst without further optimization.



Adamantan-1-yl (*S*)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxylate (1). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 55.5 mg, 73% yield, 94% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 10.9 min (major), 12.2 min (minor).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.27 (t, *J* = 8.6, 6.8 Hz, 2H), 7.20 – 7.14 (m, 3H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.46 – 2.33 (m, 2H), 2.26 – 2.17 (m, 1H), 2.16 – 2.14 (m, 3H), 2.06 – 2.05 (m, 6H), 2.00 – 1.70 (m, 5H), 1.65 – 1.64 (m, 6H), 1.60 – 1.48 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-d) δ 215.3, 170.0, 142.0, 128.4, 128.3, 125.8, 81.7, 61.0, 41.1, 37.9, 36.2, 36.1, 33.3, 33.0, 30.8, 26.6, 19.6.

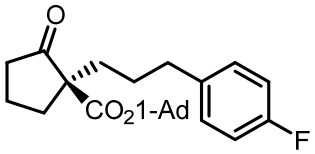
HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{25}H_{33}O_3$: 381.2424, found: 381.2414.

FT-IR (film): 2912, 2858, 1757, 1712, 1453, 1229, 1050, 732, 702 cm^{-1}.

$[\alpha]^{20}D$ = –12.5 (c 0.2, $CHCl_3$); 94% ee, from *(S)*-**A1**.

Gram-scale reaction: In a nitrogen-filled glovebox, an oven-dried 100 mL round-bottom flask was charged with Fe(OEP)Cl (157.5 mg, 0.25 mmol, 5.0 mol%), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (112.5 mg, 0.10 mmol, 2.0 mol%), (*S*)-**A1** (22.0 mg, 1.0 mmol, 20 mol%), 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (3.86 g, 12.5 mmol, 2.5 equiv), adamantan-1-yl 2-oxocyclopentane-1-carboxylate (1.31g, 5.0 mmol, 1.0 equiv), and a stir bar. Anhydrous MTBE (25 mL) and $PhCF_3$ (25 mL) were added sequentially, and the flask was capped with a rubber septum cap. The flask was transferred out of the glovebox and placed in an EtOH cooling bath at 20 °C. The reaction was irradiated with blue LEDs (450 nm) and was stirred at 20 °C for 96 hours. The reaction mixture was passed through a column of silica gel (~5 cm), and the flask, the septum, and the silica gel were rinsed with DCM. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil.

(*S*)-**A1**: 1.36 g, 72% yield, 95% ee.



Adamantan-1-yl (*S*)-1-(3-(4-fluorophenyl)propyl)-2-oxocyclopentane-1-carboxylate (2). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-

oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-(4-fluorophenyl)butanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 47.7 mg, 60% yield, 94% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 8.9 min (major), 9.9 min (minor).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 – 7.07 (m, 2H), 6.98 – 6.90 (m, 2H), 2.57 (t, *J* = 7.2 Hz, 2H), 2.45 – 2.34 (m, 2H), 2.22 – 2.16 (m, 1H), 2.15 – 2.13 (m, 3H), 2.05 – 2.04 (m, 6H), 1.99 – 1.78 (m, 4H), 1.71 – 1.65 (m, 1H), 1.65 – 1.63 (m, 6H), 1.57 – 1.46 (m, 2H).

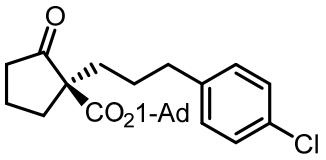
^{13}C NMR (151 MHz, Chloroform-*d*) δ 215.3, 170.0, 161.2 (d, *J* =243.4 Hz), 137.5 (d, *J* =3.3 Hz), 129.7 (d, *J* =7.7 Hz), 115.0 (d, *J* =21.0 Hz), 81.7, 60.9, 41.1, 37.9, 36.0, 35.3, 33.2, 33.1, 30.8, 26.7, 19.6.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -117.8.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{25}H_{31}FNaO_3$: 421.2149, found: 421.2154.

FT-IR (film): 2909, 2851, 1742, 1708, 1509, 1167, 1054, 752 cm^{-1}.

$[\alpha]^{20}_{D}$ = –9.8 (*c* 0.2, $CHCl_3$); 94% ee, from (*S*)-**A1**.



Adamantan-1-yl (*S*)-1-(3-(4-chlorophenyl)propyl)-2-oxocyclopentane-1-carboxylate (3). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-(4-chlorophenyl)butanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 51.3 mg, 62% yield, 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 9.4 min (major) 10.4 min (minor).

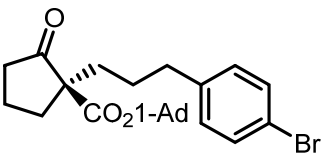
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 6.0 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.44 – 2.34 (m, 2H), 2.23 – 2.16 (m, 1H), 2.15 – 2.13 (m, 3H), 2.04 – 2.03 (m, 6H), 1.98 – 1.77 (m, 4H), 1.72 – 1.65 (m, 1H), 1.65 – 1.63 (m, 6H), 1.57 – 1.46 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 215.2, 169.9, 140.4, 131.5, 129.7, 128.4, 81.8, 60.9, 41.1, 37.9, 36.1, 35.5, 33.2, 33.1, 30.8, 26.5, 19.6.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{25}H_{32}ClO_3$: 415.2034, found: 415.2034.

FT-IR (film): 2910, 2850, 1746, 1713, 1489, 1229, 1150, 1053, 737 cm^{-1}.

$[\alpha]^{20}_{D}$ = –8.9 (*c* 0.2, $CHCl_3$); 93% ee, from (*S*)-**A1**.



Adamantan-1-yl (*S*)-1-(3-(4-bromophenyl)propyl)-2-oxocyclopentane-1-carboxylate (4). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-(4-bromophenyl)butanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 55.0 mg, 60% yield, 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 9.7 min (major), 10.7 min (minor).

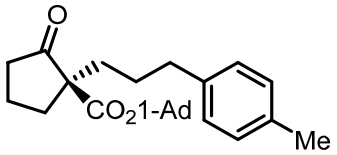
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.44 – 2.33 (m, 2H), 2.25 – 2.16 (m, 1H), 2.15 – 2.13 (m, 3H), 2.04 – 2.03 (m, 6H), 1.99 – 1.77 (m, 4H), 1.72 – 1.65 (m, 1H), 1.64 – 1.62 (m, 6H), 1.56 – 1.45 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 215.2, 169.9, 140.9, 131.3, 130.2, 119.5, 81.8, 60.8, 41.1, 37.9, 36.0, 35.5, 33.2, 33.1, 30.8, 26.4, 19.6.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{25}H_{35}BrNO_3$: 476.1795, found: 476.1783.

FT-IR (film): 2907, 2852, 1746, 1714, 1485, 1454, 1226, 1052, 755 cm^{-1}.

$[\alpha]^{20}_D$ = –10.3 (*c* 0.2, $CHCl_3$); 93% ee, from (*S*)-**A1**.



Adamantan-1-yl (*S*)-2-oxo-1-(3-(*p*-tolyl)propyl)cyclopentane-1-carboxylate (5). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-(*p*-tolyl)butanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 50.4 mg, 64% yield, 94% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 10.3 min (major), 11.1 min (minor).

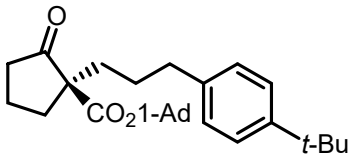
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 – 7.04 (m, 4H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.46 – 2.34 (m, 2H), 2.31 (s, 3H), 2.23 – 2.16 (m, 1H), 2.16 – 2.13 (m, 3H), 2.06 – 2.05 (m, 6H), 1.99 – 1.79 (m, 4H), 1.73 – 1.66 (m, 1H), 1.65 – 1.63 (m, 6H), 1.59 – 1.47 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 215.3, 169.9, 138.9, 135.1, 129.0, 128.2, 81.6, 61.0, 41.1, 37.9, 36.1, 35.7, 33.3, 33.0, 30.8, 26.8, 20.9, 19.6.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{26}H_{34}NaO_3$: 417.2400, found: 417.2402.

FT-IR (film): 2911, 2888, 2857, 1737, 1709, 1451, 1259, 1181, 1051, 751 cm^{-1}.

$[\alpha]^{20}_D$ = –9.9 (*c* 0.2, $CHCl_3$); 94% ee, from (*S*)-**A1**.



Adamantan-1-yl (*S*)-1-(3-(4-(*tert*-butyl)phenyl)propyl)-2-oxocyclopentane-1-carboxylate (6). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-(4-(*tert*-butyl)phenyl)butanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 53.3 mg, 61% yield, 96% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 7.0 min (major), 7.6 min (minor).

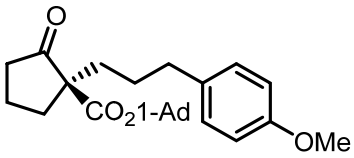
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.46 – 2.34 (m, 2H), 2.24 – 2.16 (m, 1H), 2.16 – 2.14 (m, 3H), 2.06 – 2.05 (m, 6H), 1.99 – 1.80 (m, 4H), 1.74 – 1.67 (m, 1H), 1.65 – 1.63 (m, 6H), 1.60 – 1.48 (m, 2H), 1.30 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 215.3, 170.0, 148.5, 138.9, 128.0, 125.2, 81.6, 61.0, 41.1, 37.9, 36.1, 35.6, 34.3, 33.4, 33.0, 31.4, 30.8, 26.7, 19.6.

HRMS (ESI-MS) *m*/*z* $[2M+NH_4]^+$ calcd for $C_{58}H_{84}NO_6$: 890.6293, found: 890.6297.

FT-IR (film): 2962, 2911, 2856, 1745, 1708, 1455, 1225, 1181, 1051, 751 cm^{-1}.

$[\alpha]^{20}_D$ = –11.2 (*c* 0.2, $CHCl_3$); 96% ee, from (*S*)-**A1**.



Adamantan-1-yl (*S*)-1-(3-(4-methoxyphenyl)propyl)-2-oxocyclopentane-1-carboxylate (7). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-(4-methoxyphenyl)butanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 58.2 mg, 71% yield, 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 13.6 min (major), 14.7 min (minor).

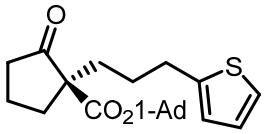
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.07 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 6.4 Hz, 2H), 3.77 (s, 3H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.45 – 2.33 (m, 2H), 2.24 – 2.16 (m, 1H), 2.15 – 2.13 (m, 3H), 2.05 – 2.04 (m, 6H), 1.98 – 1.78 (m, 4H), 1.72 – 1.65 (m, 1H), 1.64 – 1.63 (m, 6H), 1.57 – 1.45 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 215.3, 170.0, 157.7, 134.1, 129.2, 113.7, 81.6, 61.0, 55.2, 41.1, 37.9, 36.1, 35.2, 33.3, 33.0, 30.8, 26.9, 19.6.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{26}H_{35}O_4$: 411.2530, found: 411.2531.

FT-IR (film): 2909, 2851, 1748, 1712, 1515, 1453, 1238, 1177, 1055, 740 cm^{-1}.

$[\alpha]^{20}_D$ = –12.9 (*c* 0.2, $CHCl_3$); 95% ee, from (*S*)-**A1**.



Adamantan-1-yl (*R*)-2-oxo-1-(3-(thiophen-2-yl)propyl)cyclopentane-1-carboxylate (8). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-(thiophen-2-yl)butanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 48.6 mg, 63% yield, 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 10.2 min (major), 11.2 min (minor).

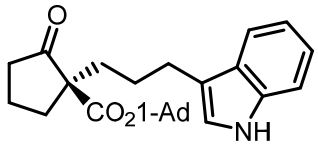
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (d, *J* = 5.2 Hz, 1H), 6.89 (d, *J* = 4.0 Hz, 1H), 6.77 (d, *J* = 3.6 Hz, 1H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.46 – 2.34 (m, 2H), 2.25 – 2.17 (m, 1H), 2.16 – 2.14 (m, 3H), 2.07 – 2.06 (m, 6H), 2.00 – 1.76 (m, 5H), 1.65 – 1.63 (m, 6H), 1.61 – 1.53 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.1, 169.9, 144.7, 126.7, 124.2, 122.9, 81.8, 60.9, 41.1, 37.8, 36.1, 33.1, 30.8, 30.2, 27.0, 19.6.

HRMS (ESI-MS) *m*/*z* [M+K]$^{+}$ calcd for $C_{23}H_{30}KO_3S$: 425.1547, found: 425.1550.

FT-IR (film): 2903, 2851, 1741, 1718, 1229, 1157, 1054, 690 cm^{-1}.

$[\alpha]^{20}_{D}$ = –12.0 (*c* 0.2, $CHCl_3$); 93% ee, from (*S*)-**A1**.



Adamantan-1-yl (*S*)-1-(3-(1*H*-indol-3-yl)propyl)-2-oxocyclopentane-1-carboxylate (9). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-(1*H*-indol-3-yl)butanoate. The product was purified by column chromatography on silica gel (1:6 EtOAc/hexanes). Colorless oil, 43.5 mg, 52% yield, 90% 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*)-**A1**: 9.6 min (minor), 10.7 min (major).

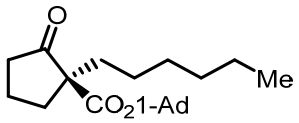
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.01 (s, 1H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.49 – 2.36 (m, 2H), 2.26 – 2.18 (m, 1H), 2.16 – 2.14 (m, 3H), 2.05 – 2.02 (m, 6H), 2.01 – 1.76 (m, 6H), 1.70 – 1.67 (m, 1H), 1.65 – 1.64 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.4, 170.0, 136.4, 127.5, 121.8, 121.3, 119.1, 118.9, 116.2, 111.0, 81.7, 61.2, 41.1, 37.9, 36.1, 33.7, 33.0, 30.8, 25.5, 25.3, 19.6.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{27}H_{34}NO_3$: 420.2533, found: 420.2534.

FT-IR (film): 3332, 2909, 2856, 1735, 1708, 1458, 1440, 1232, 1186, 1145, 1048, 745 cm^{-1}.

$[\alpha]^{20}_D$ = –1.3 (*c* 0.2, $CHCl_3$); 90% ee, from (*S*)-**A1**.



Adamantan-1-yl (*S*)-1-hexyl-2-oxocyclopentane-1-carboxylate (10). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 44.9 mg, 65% yield, 82% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 6.2 min (major), 6.6 min (minor).

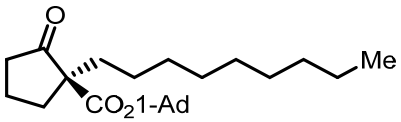
^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.49 – 2.31 (m, 2H), 2.27 – 2.17 (m, 1H), 2.17 – 2.14 (m, 3H), 2.08 – 2.07 (m, 6H), 2.02 – 1.81 (m, 4H), 1.65 – 1.63 (m, 6H), 1.54 – 1.44 (m, 1H), 1.32 – 1.22 (m, 7H), 1.21 – 1.13 (m, 1H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.5, 170.1, 81.6, 61.2, 41.1, 38.0, 36.1, 33.7, 33.0, 31.5, 30.8, 29.6, 24.7, 22.5, 19.6, 14.0.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{22}H_{34}NaO_3$: 369.2400, found: 369.2402.

FT-IR (film): 2953, 2911, 2853, 1748, 1716, 1456, 1226, 1153, 1049, 960 cm^{-1}.

$[\alpha]^{20}_D$ = –1.7 (*c* 0.2, $CHCl_3$); 82% ee, from (*S*)-**A1**.



Adamantan-1-yl (*S*)-1-nonyl-2-oxocyclopentane-1-carboxylate (11). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl decanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 50.5 mg, 65% yield, 82% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 6.3 min (major), 6.6 min (minor).

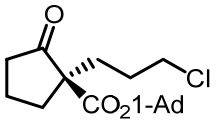
^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.47 – 2.32 (m, 2H), 2.24 – 2.16 (m, 1H), 2.16 – 2.13 (m, 3H), 2.07 – 2.06 (m, 6H), 2.01 – 1.80 (m, 4H), 1.64 – 1.63 (m, 6H), 1.53 – 1.45 (m, 1H), 1.36 – 1.14 (m, 14H), 0.86 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.5, 170.1, 81.6, 61.2, 41.1, 38.0, 36.1, 33.7, 33.0, 31.8, 30.8, 30.0, 29.5, 29.34, 29.25, 24.7, 22.6, 19.6, 14.1.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{41}O_3$: 389.3050, found: 389.3052.

FT-IR (film): 2911, 2850, 1750, 1714, 1457, 1220, 1154, 1054, 753 cm^{-1}.

$[\alpha]^{20}_D$ = –2.3 (*c* 0.2, $CHCl_3$); 82% ee, from (*S*)-**A1**.



Adamantan-1-yl (*R*)-1-(3-chloropropyl)-2-oxocyclopentane-1-carboxylate (12). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-chlorobutanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 40.6 mg, 60% yield, 86% 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*)-**A1**: 7.5 min (major), 8.2 min (minor).

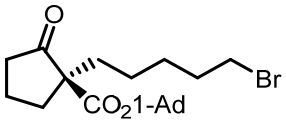
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.58 – 3.43 (m, 2H), 2.48 – 2.35 (m, 2H), 2.27 – 2.18 (m, 1H), 2.17 – 2.14 (m, 3H), 2.07 – 2.06 (m, 6H), 2.02 – 1.77 (m, 5H), 1.73 – 1.68 (m, 2H), 1.66 – 1.63 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 214.9, 169.9, 82.1, 60.4, 45.0, 41.1, 37.8, 36.1, 33.5, 31.1, 30.8, 28.1, 19.6.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{19}H_{28}ClO_3$: 339.1721, found: 339.1720.

FT-IR (film): 2956, 2910, 2852, 1746, 1718, 1453, 1257, 1049, 762 cm^{-1}.

$[\alpha]^{20}_D$ = –1.4 (*c* 0.2, $CHCl_3$); 86% ee, from (*S*)-**A1**.



Adamantan-1-yl (*S*)-1-(5-bromopentyl)-2-oxocyclopentane-1-carboxylate (13). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 6-bromohexanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 53.3 mg, 65% yield, 82% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 10.3 min (major), 11.0 min (minor).

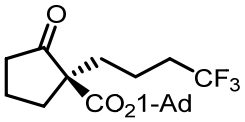
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.39 (t, *J* = 6.8 Hz, 2H), 2.49 – 2.34 (m, 2H), 2.26 – 2.17 (m, 1H), 2.17 – 2.14 (m, 3H), 2.07 – 2.06 (m, 6H), 2.00 – 1.79 (m, 5H), 1.65 – 1.61 (m, 6H), 1.53 – 1.35 (m, 4H), 1.30 – 1.12 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.3, 170.0, 81.8, 61.0, 41.2, 37.9, 36.1, 33.7, 33.4, 33.2, 32.4, 30.8, 28.5, 23.9, 19.6.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{21}H_{31}BrNaO_3$: 433.1349, found: 433.1344.

FT-IR (film): 2911, 2852, 1747, 1714, 1454, 1257, 1223, 1053, 966, 747 cm^{-1}.

$[\alpha]^{20}_D$ = –2.0 (*c* 1.0, $CHCl_3$); 82% ee, from (*S*)-**A1**.



Adamantan-1-yl (*R*)-2-oxo-1-(4,4,4-trifluorobutyl)cyclopentane-1-carboxylate (14). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 5,5,5-trifluoropentanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 48.4 mg, 65% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 6.7 min (major), 7.6 min (minor).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 2.48 – 2.38 (m, 2H), 2.24 – 2.18 (m, 1H), 2.16 – 2.15 (m, 3H), 2.10 – 2.07 (m, 1H), 2.07 – 2.06 (m, 6H), 2.05 – 1.98 (m, 2H), 1.94 – 1.80 (m, 3H), 1.72 – 1.66 (m, 1H), 1.65 – 1.63 (m, 6H), 1.59 – 1.53 (m, 1H), 1.51 – 1.43 (m, 1H).

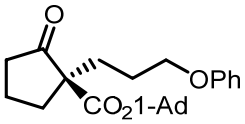
^{13}C NMR (151 MHz, Chloroform-*d*) δ 214.8, 169.7, 126.9 (q, *J* = 276.5 Hz), 82.1, 60.6, 41.1, 37.8, 36.0, 34.0 (q, *J* = 28.2 Hz), 33.2, 32.6, 30.8, 19.6, 17.5 (q, *J* = 3.3 Hz).

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

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{20}H_{31}F_3NO_3$: 390.2251, found: 390.2246.

FT-IR (film): 2912, 2855, 1747, 1713, 1453, 1256, 1134, 1052, 697 cm^{-1}.

$[\alpha]^{20}_D$ = –2.3 (*c* 0.2, $CHCl_3$); 92% ee, from (*S*)-**A1**.



Adamantan-1-yl (*R*)-2-oxo-1-(3-phenoxypropyl)cyclopentane-1-carboxylate (15). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-phenoxybutanoate. The product was purified by column chromatography on silica gel (1:10 EtOAc/hexanes). White solid, 50.6 mg, 64% yield, 82% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 15.6 min (minor), 17.1 min (major).

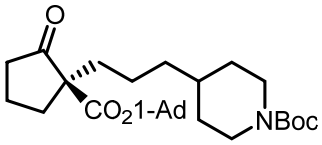
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 – 7.25 (m, 2H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 3.97 – 3.92 (m, 2H), 2.50 – 2.39 (m, 2H), 2.26 – 2.20 (m, 1H), 2.16 – 2.15 (m, 3H), 2.08 – 2.07 (m, 6H), 2.05 – 1.99 (m, 2H), 1.96 – 1.87 (m, 3H), 1.74 – 1.68 (m, 2H), 1.65 – 1.64 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 215.2, 170.0, 158.9, 129.4, 120.6, 114.5, 81.9, 67.7, 60.7, 41.1, 37.9, 36.1, 33.3, 30.8, 30.3, 24.8, 19.6.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{33}O_4$: 397.2373, found: 397.2373.

FT-IR (film): 2910, 2852, 1741, 1709, 1493, 1237, 1196, 1036, 750 cm^{-1}.

$[\alpha]^{20}_D$ = –1.6 (*c* 0.2, $CHCl_3$); 82% ee, from (*S*)-**A1**.



***tert*-Butyl (*S*)-4-(3-(1-((adamantan-1-yloxy)carbonyl)-2-oxocyclopentyl)propyl) piperidine-1-carboxylate (16).** The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate 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 (1:8 EtOAc/hexanes). Colorless oil, 54.6 mg, 56% yield, 82% 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*)-**A1**: 17.3 min (minor), 21.4 min (major).

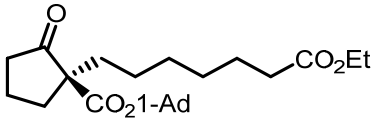
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.05 – 4.03 (m, 2H), 2.64 (t, *J* = 11.6 Hz, 2H), 2.45 – 2.33 (m, 2H), 2.23 – 2.16 (m, 1H), 2.16 – 2.14 (m, 3H), 2.06 – 2.05 (m, 6H), 2.00 – 1.72 (m, 5H), 1.64 – 1.62 (m, 6H), 1.60 – 1.59 (m, 1H), 1.53 – 1.45 (m, 1H), 1.44(s, 9H), 1.40 – 1.33 (m, 2H), 1.24 – 1.17 (m, 3H), 1.08 – 0.98 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.3, 170.1, 154.9, 81.7, 79.1, 61.1, 44.0, 41.2, 37.9, 36.8, 36.1, 35.6, 33.7, 33.1, 32.1, 30.8, 28.5, 21.7, 19.6.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{29}H_{46}NO_5$: 488.3371, found: 488.3378.

FT-IR (film): 2973, 2914, 2850, 1746, 1716, 1688, 1414, 1244, 1152, 1051, 737 cm^{-1}.

$[\alpha]^{20}_{D}$ = –1.9 (*c* 0.2, $CHCl_3$); 82% ee, from (*S*)-**A1**.



Adamantan-1-yl (*S*)-1-(7-ethoxy-7-oxoheptyl)-2-oxocyclopentane-1-carboxylate (17). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1-(1,3-dioxoisoindolin-2-yl) 8-ethyl octanedioate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Colorless oil, 52.6 mg, 63% yield, 82% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 17.7 min (major), 20.4 min (minor).

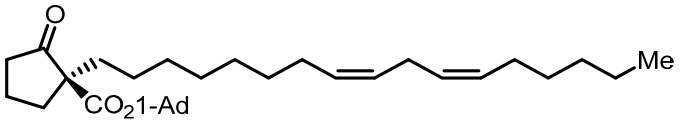
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.10 (q, *J* = 7.2 Hz, 2H), 2.46 – 2.33 (m, 2H), 2.26 (t, *J* = 7.6 Hz, 2H), 2.23 – 2.16 (m, 1H), 2.16 – 2.13 (m, 3H), 2.06 – 2.05 (m, 6H), 2.00 – 1.80 (m, 4H), 1.64 – 1.62 (m, 6H), 1.60 – 1.45 (m, 3H), 1.40 – 1.26 (m, 5H), 1.24 (t, *J* = 6.8 Hz, 3H), 1.20 – 1.12 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.4, 173.7, 170.1, 81.6, 61.1, 60.1, 41.1, 37.9, 36.1, 34.3, 33.6, 33.0, 30.8, 29.6, 28.8, 24.9, 24.5, 19.6, 14.2.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{25}H_{39}O_5$: 419.2792, found: 419.2779.

FT-IR (film): 2914, 2857, 1747, 1729, 1717, 1455, 1219, 1157, 1056, 747 cm^{-1}.

$[\alpha]^{20}_{D}$ = –0.9 (*c* 0.2, $CHCl_3$); 82% ee, from (*S*)-**A1**.



Adamantan-1-yl (*S*)-1-((*8Z,11Z*)-heptadeca-8,11-dien-1-yl)-2-oxocyclopentane-1-carboxylate (18). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl *(9Z,12Z)*-octadeca-9,12-dienoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 65.6 mg, 66% yield, 80% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 5.3 min (major), 5.7 min (minor).

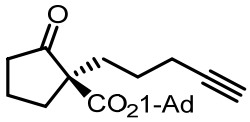
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.40 – 5.28 (m, 4H), 2.75 (t, *J* = 6.4 Hz, 2H), 2.45 – 2.34 (m, 2H), 2.24 – 2.16 (m, 1H), 2.16 – 2.14 (m, 3H), 2.07 – 2.06 (m, 6H), 2.03 – 1.79 (m, 8H), 1.64 – 1.63 (m, 6H), 1.51 – 1.45 (m, 1H), 1.31 – 1.23 (m, 15H), 1.18 – 1.12 (m, 1H), 0.86 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.4, 170.1, 130.2, 130.1, 128.0, 127.9, 81.5, 61.1, 41.1, 37.9, 36.1, 33.7, 33.0, 31.5, 30.8, 30.0, 29.6, 29.3, 29.24, 29.20, 27.19, 27.16, 25.6, 24.7, 22.5, 19.6, 14.0.

HRMS (ESI-MS) *m*/*z* $[2M+NH_4]^+$ calcd for $C_{66}H_{108}NO_6$: 1010.8171, found: 1010.8167.

FT-IR (film): 3010, 2954, 2914, 2853, 1750, 1717, 1454, 1053, 747 cm^{-1}.

$[\alpha]^{20}_D$ = –1.6 (*c* 0.2, $CHCl_3$); 80% ee, from (*S*)-**A1**.



Adamantan-1-yl (*S*)-2-oxo-1-(pent-4-yn-1-yl)cyclopentane-1-carboxylate (19). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl hex-5-ynoate. The product was purified by column chromatography on silica gel (1:10 EtOAc/hexanes). Colorless oil, 40.1 mg, 61% yield, 86% 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*)-**A1**: 9.1 min (major), 9.9 min (minor).

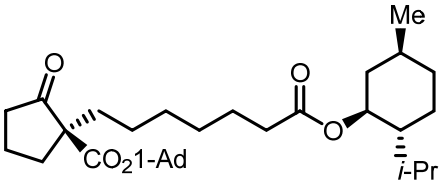
^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.51 – 2.33 (m, 2H), 2.25 – 2.18 (m, 3H), 2.16 – 2.14 (m, 3H), 2.07 – 2.06 (m, 6H), 2.03 – 1.80 (m, 5H), 1.65 – 1.63 (m, 7H), 1.62 – 1.58 (m, 1H), 1.49 – 1.37 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.0, 169.9, 83.9, 81.9, 68.6, 60.7, 41.1, 37.8, 36.1, 33.3, 32.9, 30.8, 23.9, 19.6, 18.8.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{21}H_{29}O_3$: 329.2111, found: 329.2113.

FT-IR (film): 3239, 2911, 2852, 1732, 1714, 1449, 1254, 1229, 1143, 852, 697 cm^{-1}.

$[\alpha]^{20}_D$ = –1.3 (*c* 0.2, $CHCl_3$); 86% ee, from (*S*)-**A1**.



Adamantan-1-yl (*S*)-1-(7-(((*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl)oxy)-7-oxoheptyl)-2-oxocyclopentane-1-carboxylate (20). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1-(1,3-dioxoisoindolin-2-yl) 8-((*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl) octanedioate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 65.6 mg, 62% yield, 91.5:8.5 dr.

HPLC analysis: The dr 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*)-**A1**: 11.5 min (major), 13.0 min (minor).

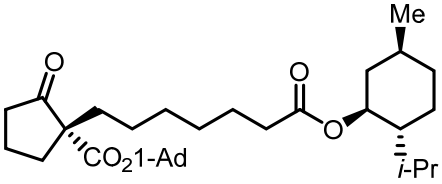
^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.66 (td, *J* = 10.8, 4.2 Hz, 1H), 2.46 – 2.34 (m, 2H), 2.26 (t, *J* = 7.8 Hz, 2H), 2.23 – 2.16 (m, 1H), 2.15 – 2.14 (m, 3H), 2.06 – 2.05 (m, 6H), 2.00 – 1.93 (m, 2H), 1.92 – 1.80 (m, 4H), 1.69 – 1.65 (m, 2H), 1.64 – 1.63 (m, 6H), 1.63 – 1.57 (m, 2H), 1.52 – 1.44 (m, 2H), 1.37 – 1.26 (m, 6H), 1.21 – 1.14 (m, 1H), 1.08 – 1.00 (m, 1H), 0.97 – 0.91 (m, 1H), 0.88 (t, *J* = 6.6 Hz, 6H), 0.87 – 0.81 (m, 1H), 0.74 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 215.4, 173.3, 170.1, 81.6, 73.9, 61.1, 47.0, 41.1, 40.9, 37.9, 36.1, 34.7, 34.3, 33.6, 33.0, 31.4, 30.8, 29.7, 28.9, 26.2, 25.0, 24.6, 23.4, 22.0, 20.7, 19.6, 16.3.

HRMS (ESI-MS) *m*/*z* $[M+K]^+$ calcd for $C_{33}H_{52}KO_5$: 567.3446, found: 567.3445.

FT-IR (film): 2954, 2912, 2853, 1747, 1728, 1711, 1457, 1262, 1225, 1170, 1150, 1052, 766 cm^{-1}.

$[\alpha]^{20}_D$ = –17.6 (*c* 0.2, $CHCl_3$); 91.5:8.5 dr, from (*S*)-**A1**.



Adamantan-1-yl (*R*)-1-(7-(((*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl)oxy)-7-oxoheptyl)-2-oxocyclopentane-1-carboxylate (21). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1-(1,3-dioxoisoindolin-2-yl) 8-((*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl) octanedioate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 63.4 mg, 60% yield, 9:91 dr.

HPLC analysis: The dr 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 (*R*)-**A1**: 11.7 min (minor), 12.7 min (major).

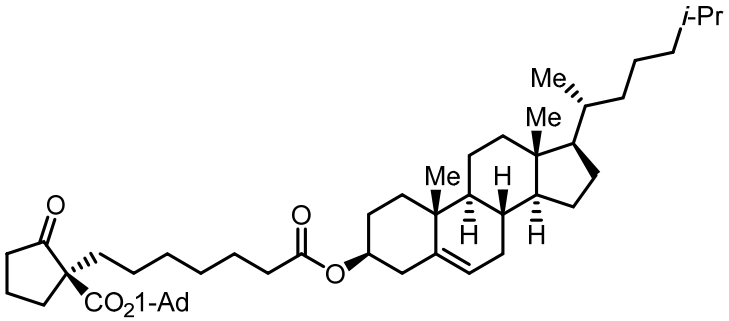
^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.67 – 4.63 (m, 1H), 2.46 – 2.34 (m, 2H), 2.24 (t, *J* = 7.2 Hz, 2H), 2.22 – 2.16 (m, 1H), 2.15 – 2.13 (m, 3H), 2.06 – 2.05 (m, 6H), 2.00 – 1.93 (m, 2H), 1.91 – 1.79 (m, 4H), 1.69 – 1.64 (m, 2H), 1.63 – 1.62 (m, 6H), 1.60 – 1.55 (m, 2H), 1.52 – 1.43 (m, 2H), 1.37 – 1.25 (m, 6H), 1.20 – 1.12 (m, 1H), 1.07 – 0.99 (m, 1H), 0.97 – 0.90 (m, 1H), 0.88 (t, *J* = 4.2 Hz, 6H), 0.86 – 0.81 (m, 1H), 0.74 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 215.3, 173.3, 170.1, 81.6, 73.9, 61.1, 47.0, 41.1, 40.9, 37.9, 36.1, 34.6, 34.2, 33.6, 33.0, 31.3, 30.8, 29.6, 28.9, 26.2, 25.0, 24.6, 23.4, 22.0, 20.7, 19.6, 16.3.

HRMS (ESI-MS) *m*/*z* [M+K]$^+$ calcd for $C_{33}H_{52}KO_5$: 567.3446, found: 567.3456.

FT-IR (film): 2953, 2912, 2850, 1746, 1726, 1709, 1457, 1262, 1225, 1170, 1150, 1052, 767 cm^{-1}.

$[\alpha]^{20}_D$ = –24.7 (*c* 0.2, $CHCl_3$); 9:91 dr, from (*R*)-**A1**.



Adamantan-1-yl (*S*)-1-(7-(((*3S,8S,9S,10R,13R,14S,17R*)-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)oxy)-7-oxoheptyl)-2-oxocyclopentane-1-carboxylate (22). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1-((*3S,8S,9S,10R,13R,14S,17R*)-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 (1:20 EtOAc/hexanes). White solid, 92.4 mg, 61% yield, 92:8 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 10.5 min (major), 12.0 min (minor).

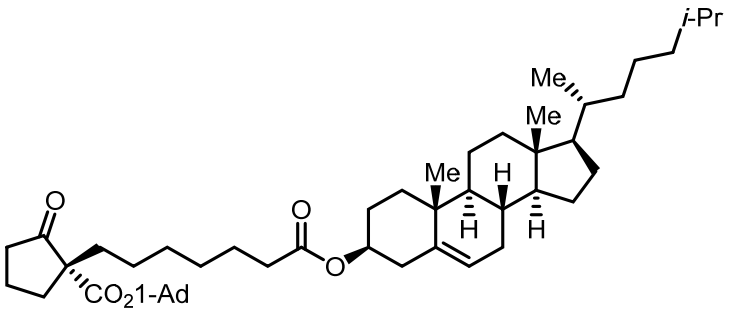
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.33 (d, *J* = 6.4 Hz, 1H), 4.68 – 4.51 (m, 1H), 2.46 – 2.33 (m, 2H), 2.33 – 2.16 (m, 5H), 2.16 – 2.12 (m, 3H), 2.06 – 2.05 (m, 6H), 2.02 – 1.79 (m, 9H), 1.64 – 1.67 (m, 1H), 1.64 – 1.62 (m, 6H), 1.61 – 1.41 (m, 10H), 1.38 – 1.23 (m, 9H), 1.21 – 1.04 (m, 8H), 1.01 (s, 3H), 0.99 – 0.92 (m, 2H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.85 (dd, *J* = 6.6, 2.0 Hz, 6H), 0.66 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.3, 173.1, 170.1, 139.7, 122.5, 81.6, 73.7, 61.1, 56.7, 56.1, 50.0, 42.3, 41.1, 39.7, 39.5, 38.1, 37.9, 37.0, 36.6, 36.2, 36.1, 35.8, 34.6, 33.6, 33.0, 31.88, 31.85, 30.8, 29.6, 28.8, 28.2, 28.0, 27.8, 24.8, 24.6, 24.3, 23.8, 22.8, 22.5, 21.0, 19.6, 19.3, 18.7, 11.8.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{50}H_{79}O_5$: 759.5922, found: 759.5933.

FT-IR (film): 2939, 2911, 2853, 1747, 1729, 1715, 1457, 1229, 1116, 1057, 803 cm^{-1}.

$[\alpha]^{20}_D$ = –46.1 (*c* 0.2, $CHCl_3$); 92:8 dr, from (*S*)-**A1**.



Adamantan-1-yl (*R*)-1-(7-(((*3S,8S,9S,10R,13R,14S,17R*)-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)oxy)-7-oxoheptyl)-2-oxocyclopentane-1-carboxylate (23). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-oxocyclopentane-1-carboxylate and 1-((*3S,8S,9S,10R,13R,14S,17R*)-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 (1:20 EtOAc/hexanes). White solid, 90.9 mg, 60% yield, 8.5:91.5 dr.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*)-**A1**: 11.0 min (minor), 11.7 min (major).

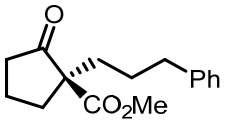
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.36 (d, *J* = 6.0 Hz, 1H), 4.66 – 4.53 (m, 1H), 2.46 – 2.33 (m, 2H), 2.33 – 2.16 (m, 5H), 2.16 – 2.14 (m, 3H), 2.07 – 2.06 (m, 6H), 2.02 – 1.79 (m, 9H), 1.64 – 1.63 (m, 6H), 1.61 – 1.41 (m, 10H), 1.38 – 1.23 (m, 10H), 1.21 – 1.04 (m, 8H), 1.01 (s, 3H), 0.99 – 0.93 (m, 2H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.85 (dd, *J* = 6.6, 2.0 Hz, 6H), 0.67 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.3, 173.1, 170.1, 139.7, 122.5, 81.6, 73.7, 61.1, 56.7, 56.1, 50.0, 42.3, 41.1, 39.7, 39.5, 38.1, 37.9, 37.0, 36.6, 36.2, 36.1, 35.8, 34.6, 33.6, 33.0, 31.88, 31.85, 30.8, 29.6, 28.8, 28.1, 28.0, 27.8, 24.9, 24.6, 24.3, 23.8, 22.8, 22.5, 21.0, 19.6, 19.3, 18.7, 11.8.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{50}H_{79}O_5$: 759.5922, found: 759.5933.

FT-IR (film): 2939, 2910, 2852, 1747, 1728, 1715, 1456, 1229, 1116, 1057, 802 cm^{-1}.

$[\alpha]^{20}_D$ = –30.9 (*c* 0.2, $CHCl_3$); 8.5:91.5 dr, from (*R*)-**A1.**



Methyl (*S*)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxylate (24). The title compound was synthesized according to **GP-4** from methyl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 36.4 mg, 70% yield, 90% 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*)-**A1**: 16.3 min (major), 17.3 min (minor).

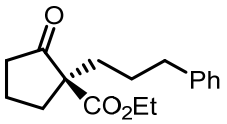
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 2H), 7.21 – 7.14 (m, 3H), 3.70 (s, 3H), 2.64 – 2.50 (m, 3H), 2.46 – 2.37 (m, 1H), 2.28 – 2.20 (m, 1H), 2.01 – 1.84 (m, 4H), 1.63 – 1.49 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 214.7, 171.5, 141.7, 128.331, 128.326, 125.9, 60.4, 52.5, 37.9, 36.0, 33.6, 32.7, 26.7, 19.6.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{16}H_{21}O_3$: 261.1485, found: 261.1485.

FT-IR (film): 2954, 2907, 2856, 1745, 1716, 1450, 1256, 1227, 1136, 751, 696 cm^{-1}.

$[\alpha]^{20}_D$ = –9.8 (*c* 0.2, $CHCl_3$); 90% ee, from (*S*)-**A1**.



Ethyl (*S*)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxylate (25). The title compound was synthesized according to **GP-4** from ethyl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 41.1 mg, 75% yield, 90% 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*)-**A1**: 13.6 min (major), 14.7 min (minor).

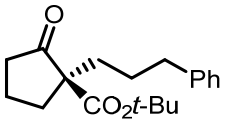
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.10 (m, 3H), 4.20 – 4.12 (m, 2H), 2.63 (t, *J* = 6.8 Hz, 2H), 2.57 – 2.48 (m, 1H), 2.45 – 2.36 (m, 1H), 2.23 (dt, *J* = 18.8, 8.2 Hz, 1H), 2.04 – 1.84 (m, 4H), 1.73 – 1.51 (m, 3H), 1.24 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 214.6, 170.9, 141.7, 128.23, 128.21, 125.7, 61.2, 60.3, 37.8, 36.0, 33.3, 32.7, 26.6, 19.5, 14.0.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{17}H_{23}O_3$: 275.1642, found: 275.1643.

FT-IR (film): 2962, 2907, 2856, 1745, 1716, 1450, 1256, 1227, 1136, 751, 692 cm^{-1}.

$[\alpha]^{20}_D$ = –10.8 (*c* 0.2, $CHCl_3$); 90% ee, from (*S*)-**A1**.



***tert*-Butyl (*S*)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxylate (26).** The title compound was synthesized according to **GP-4** from *tert*-butyl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 40.4 mg, 67% yield, 94% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 7.6 min (major), 8.3 min (minor).

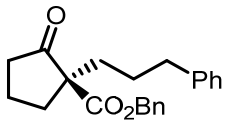
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.16 (m, 3H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.48 – 2.35 (m, 2H), 2.25 – 2.14 (m, 1H), 2.02 – 1.81 (m, 4H), 1.74 – 1.66 (m, 1H), 1.63 – 1.50 (m, 2H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.2, 170.3, 141.9, 128.4, 128.3, 125.8, 81.6, 60.9, 37.9, 36.2, 33.3, 32.9, 27.8, 26.6, 19.6.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{19}H_{27}O_3$: 303.1955, found: 303.1958.

FT-IR (film): 2961, 2922, 2861, 1747, 1717, 1451, 1223, 1177, 1141, 1027, 760, 740 cm^{-1}.

$[\alpha]^{20}_D$ = –10.2 (*c* 0.2, $CHCl_3$) (*c* 1.0, $CHCl_3$); 94% ee, from (*S*)-**A1**.



Benzyl (*S*)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxylate (27). The title compound was synthesized according to **GP-4** from benzyl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:10 EtOAc/hexanes). Colorless oil, 41.6 mg, 62% yield, 88% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 15.8 min (major), 16.8 min (minor).

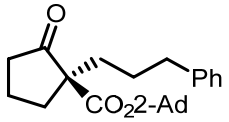
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.30 (m, 5H), 7.30 – 7.26 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 5.20 – 5.13 (m, 2H), 2.63 – 2.51 (m, 3H), 2.44 – 2.34 (m, 1H), 2.30 – 2.21 (m, 1H), 2.10 – 1.88 (m, 4H), 1.66 – 1.61 (m, 2H), 1.58 – 1.49 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 214.5, 170.8, 141.7, 135.7, 128.6, 128.32, 128.29, 128.2, 127.9, 125.8, 66.9, 60.5, 37.9, 36.0, 33.6, 32.8, 26.7, 19.6.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{25}O_3$: 337.1798, found: 337.1807.

FT-IR (film): 2956, 2922, 2861, 1746, 1716, 1454, 1259, 1219, 1139, 1113, 748, 695 cm^{-1}.

$[\alpha]^{20}_D$ = –7.8 (*c* 0.2, $CHCl_3$); 88% ee, from (*S*)-**A1**.



Adamantan-2-yl (*S*)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxylate (28). The title compound was synthesized according to **GP-5** from adamantan-2-yl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 57.0 mg, 75% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 12.5 min (major), 13.7 min (minor).

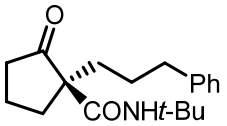
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 2H), 7.22 – 7.14 (m, 3H), 4.96 – 4.94 (m, 1H), 2.67 – 2.59 (m, 2H), 2.57 – 2.50 (m, 1H), 2.48 – 2.39 (m, 1H), 2.30 – 2.20 (m, 1H), 2.08 – 1.86 (m, 9H), 1.86 – 1.83 (m, 3H), 1.78 – 1.73 (m, 4H), 1.72 – 1.62 (m, 2H), 1.58 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 214.9, 170.4, 141.9, 128.33, 128.29, 125.8, 78.0, 60.5, 38.0, 37.3, 36.22, 36.20, 33.6, 32.9, 31.9, 31.8, 27.1, 26.9, 26.8, 19.7.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{33}O_3$: 381.2424, found: 381.2429.

FT-IR (film): 2905, 2853, 1743, 1716, 1453, 1229, 1145, 732, 696 cm^{-1}.

$[\alpha]^{20}_D$ = –12.3 (*c* 0.2, $CHCl_3$); 91% ee, from (*S*)-**A1**.



(*S*)-*N*-(*tert*-Butyl)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxamide (29). The title compound was synthesized according to **GP-4** from *N*-(*tert*-butyl)-2-oxocyclopentane-1-carboxamide and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:10 EtOAc/hexanes). Colorless oil, 36.2 mg, 60% 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*)-**A1**: 7.5 min (minor), 8.0 min (major).

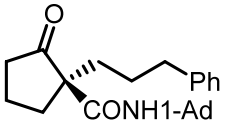
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 6.6 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 6.6 Hz, 2H), 6.41 (s, 1H), 2.68 – 2.59 (m, 2H), 2.56 – 2.51 (m, 1H), 2.33 – 2.24 (m, 2H), 1.82 – 1.70 (m, 4H), 1.61 – 1.49 (m, 3H), 1.28 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 221.1, 167.7, 141.5, 128.4, 128.3, 125.9, 61.2, 51.0, 38.7, 37.1, 35.7, 31.4, 28.6, 26.3, 19.1.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{19}H_{27}NNaO_2$: 324.1934, found: 324.1935.

FT-IR (film): 3385, 2969, 2930, 2868, 1719, 1670, 1518, 1453, 1153, 558 cm^{-1}.

$[\alpha]^{20}_D$ = +51.1 (*c* 0.2, $CHCl_3$); 92% ee, from (*S*)-**A1**.



(*S*)-*N*-(Adamantan-2-yl)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxamide (30). The title compound was synthesized according to **GP-4** from *N*-(adamantan-2-yl)-2-oxocyclopentane-1-carboxamide and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:10 EtOAc/hexanes). Colorless oil, 45.6 mg, 60% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 12.6 min (major), 14.0 min (minor).

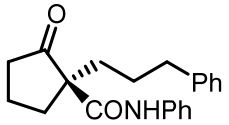
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.16 – 7.11 (m, 2H), 6.27 (s, 1H), 2.70 – 2.52 (m, 3H), 2.37 – 2.22 (m, 2H), 2.07 – 2.05 (m, 3H), 1.93 – 1.92 (m, 6H), 1.83 – 1.70 (m, 4H), 1.67 – 1.66 (m, 6H), 1.63 – 1.48 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 221.0, 167.3, 141.5, 128.4, 128.3, 125.8, 61.3, 51.7, 41.3, 38.7, 37.1, 36.3, 35.7, 31.3, 29.4, 26.2, 19.1.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{25}H_{37}N_2O_2$: 397.2850, found: 397.2852.

FT-IR (film): 3365, 2905, 2874, 2843, 1724, 1663, 1521, 1456, 1152, 743, 699, 573 cm^{-1}.

$[\alpha]^{20}_D$ = +48.1 (*c* 0.2, $CHCl_3$); 92% ee, from (*S*)-**A1**.



(*S*)-2-Oxo-*N*-phenyl-1-(3-phenylpropyl)cyclopentane-1-carboxamide (31). The title compound was synthesized according to **GP-4** from 2-oxo-*N*-phenylcyclopentane-1-carboxamide and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:10 EtOAc/hexanes). Colorless oil, 41.0 mg, 64% yield, 70% 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*)-**A1**: 15.0 min (major), 16.7 min (minor).

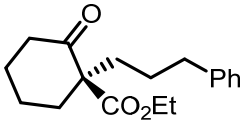
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.56 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.14 – 7.07 (m, 3H), 2.74 (dt, *J* = 13.2, 7.2 Hz, 1H), 2.60 (t, *J* = 6.6 Hz, 2H), 2.38 (t, *J* = 7.8 Hz, 2H), 1.96 – 1.85 (m, 4H), 1.70 – 1.66 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 220.9, 167.0, 141.2, 137.7, 128.9, 128.34, 128.29, 125.9, 124.2, 119.7, 61.2, 38.8, 37.0, 35.5, 31.2, 26.2, 18.9.

HRMS (ESI-MS) *m*/*z* $[M+K]^+$ calcd for $C_{21}H_{23}KNO_2$: 360.1360, found: 360.1375.

FT-IR (film): 3340, 2941, 2856, 1723, 1683, 1596, 1533, 1492, 1442, 1150, 684 cm^{-1}.

$[\alpha]^{20}_D$ = –134.7 (*c* 0.2, $CHCl_3$); 70% ee, from (*S*)-**A1**.



Ethyl (*R*)-2-oxo-1-(3-phenylpropyl)cyclohexane-1-carboxylate (32). The title compound was synthesized according to **GP-5** from ethyl 2-oxocyclohexane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 31.1 mg, 54% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 9.3 min (major), 10.7 min (minor).

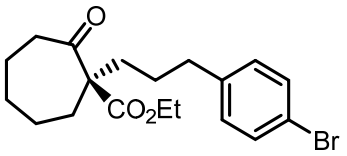
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (t, *J* = 7.2 Hz, 2H), 7.21 – 7.15 (m, 3H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.68 – 2.59 (m, 2H), 2.53 – 2.40 (m, 3H), 2.03 – 1.88 (m, 2H), 1.78 – 1.64 (m, 3H), 1.62 – 1.52 (m, 3H), 1.48 – 1.40 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.9, 172.0, 142.0, 128.4, 128.3, 125.7, 61.1, 60.8, 41.1, 36.1, 36.0, 34.3, 27.6, 26.0, 22.6, 14.1.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{18}H_{25}O_3$: 289.1798, found: 289.1799.

FT-IR (film): 2960, 2922, 2861, 1746, 1716, 1450, 1223, 1177, 1141, 1027, 760 cm^{-1}.

$[\alpha]^{20}_D$ = –12.7 (*c* 0.2, $CHCl_3$); 90% ee, from (*S*)-**A1.**



Ethyl (*R*)-1-(3-(4-bromophenyl)propyl)-2-oxocycloheptane-1-carboxylate (33). The title compound was synthesized according to **GP-5** from ethyl 2-oxocycloheptane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 30.4 mg, 40% 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*)-**A1**: 10.3 min (major), 12.0 min (minor).

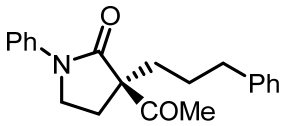
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.16 (q, *J* = 7.6 Hz, 2H), 2.66 – 2.52 (m, 3H), 2.49 – 2.41 (m, 1H), 2.12 (dd, *J* = 13.2, 8.8 Hz, 1H), 2.01 – 1.92 (m, 1H), 1.76 – 1.48 (m, 9H), 1.45 – 1.38 (m, 1H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.4, 172.5, 140.9, 131.3, 130.1, 119.5, 62.7, 61.0, 42.1, 35.6, 35.0, 33.0, 29.8, 26.2, 25.5, 24.9, 14.1.

HRMS (ESI-MS) *m*/*z* $[M+K]^+$ calcd for $C_{19}H_{25}BrKO_3$: 419.0619, found: 419.0621.

FT-IR (film): 2928, 2856, 1723, 1704, 1488, 1456, 1222, 1151, 1067, 1151, 1067, 1010, 794 cm^{-1}.

$[\alpha]^{20}_D$ = –10.7 (*c* 0.2, $CHCl_3$); 92% ee, from (*S*)-**A1.**



(*R*)-3-Acetyl-1-phenyl-3-(3-phenylpropyl)pyrrolidin-2-one (34). The title compound was synthesized according to **GP-5** from 3-acetyl-1-phenylpyrrolidin-2-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). Colorless oil, 43.0 mg, 67% yield, 84% 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*)-**A1**: 15.6 min (minor), 19.7 min (major).

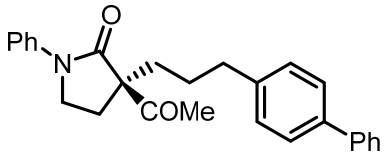
^{1}H NMR (600 MHz, Chloroform-d) δ 7.61 – 7.56 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.23 – 7.14 (m, 4H), 3.81 – 3.77 (m, 1H), 3.68 – 3.64 (m, 1H), 2.87 – 2.82 (m, 1H), 2.72 – 2.63 (m, 2H), 2.27 (s, 3H), 2.26 – 2.20 (m, 1H), 1.90 – 1.81 (m, 2H), 1.66 – 1.61 (m, 1H), 1.52 – 1.45 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 205.1, 171.4, 141.3, 139.1, 128.9, 128.41, 128.36, 126.0, 124.9, 119.9, 64.4, 46.0, 35.8, 34.7, 26.5, 25.9, 25.5.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{21}H_{23}NNaO_2$: 344.1621, found: 344.1625.

FT-IR (film): 2936, 1707, 1680, 1596, 1497, 1393, 1298, 1221, 755, 687 cm^{-1}.

$[\alpha]^{20}_D$ = –131.6 (*c* 0.2, $CHCl_3$); 84% ee, from (*S*)-**A1**.



(*R*)-3-(3-([1,1'-Biphenyl]-4-yl)propyl)-3-acetyl-1-phenylpyrrolidin-2-one (35). The title compound was synthesized according to **GP-5** from 3-acetyl-1-phenylpyrrolidin-2-one and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:8 EtOAc/hexanes). White solid, 48.4 mg, 61% yield, 83% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (20% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 17.6 min (minor), 19.1 min (major).

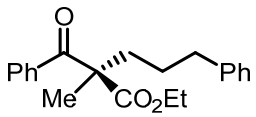
^{1}H NMR (400 MHz, Chloroform-d) δ 7.64 – 7.56 (m, 4H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.41 (m, 2H), 7.42 – 7.32 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 3.88 – 3.75 (m, 1H), 3.75 – 3.65 (m, 1H), 2.93 – 2.81 (m, 1H), 2.80 – 2.65 (m, 2H), 2.31 (s, 3H), 2.30 – 2.23 (m, 1H), 1.98 – 1.83 (m, 2H), 1.71 – 1.64 (m, 1H), 1.61 – 1.50 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 205.1, 171.4, 140.9, 140.5, 139.1, 139.0, 128.9, 128.8, 128.7, 127.2, 127.1, 127.0, 124.9, 119.9, 64.4, 46.0, 35.5, 34.8, 26.5, 25.9, 25.5.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{27}H_{27}NNaO_2$: 420.1934, found: 420.1939.

FT-IR (film): 2935, 1707, 1680, 1590, 1497, 1390, 1290, 1220, 740 cm^{-1}.

$[\alpha]^{20}_{D}$ = –135.3 (*c* 0.2, $CHCl_3$); 83% ee, from (*S*)-**A1.**



Ethyl (*R*)-2-benzoyl-2-methyl-5-phenylpentanoate (36). The title compound was synthesized according to **GP-6** from ethyl 2-methyl-3-oxo-3-phenylpropanoate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 20.1 mg, 31% yield, 96% ee.

HPLC analysis: The ee 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*)-**A1**: 6.4 min (minor), 7.4 min (major).

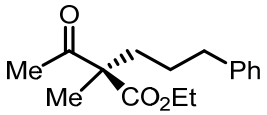
^{1}H NMR (400 MHz, Chloroform-d) δ 7.85 – 7.79 (m, 2H), 7.55 – 7.48 (m, 1H), 7.43 – 7.37 (m, 2H), 7.27 – 7.22 (m, 2H), 7.19 – 7.09 (m, 3H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.65 – 2.56 (m, 2H), 2.12 – 2.04 (m, 2H), 1.69 – 1.53 (m, 2H), 1.53 (s, 3H), 1.03 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.6, 174.3, 141.7, 135.7, 132.5, 128.4, 128.32, 128.27, 125.8, 61.2, 56.9, 36.0, 35.9, 25.5, 21.0, 13.7.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{21}H_{24}NaO_3$: 347.1618, found: 347.1621.

FT-IR (film): 2964, 2936, 1730, 1682, 1453, 1250, 1225, 1182, 1113, 740, 696 cm^{-1}.

$[\alpha]^{20}_{D}$ = +10.6 (*c* 0.2, $CHCl_3$); 96% ee, from (*S*)-**A1**.



Ethyl (*R*)-2-acetyl-2-methyl-5-phenylpentanoate (37). The title compound was synthesized according to **GP-5** from ethyl 2-methyl-3-oxobutanoate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 17.9 mg, 34% yield, 87% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*)-**A1**: 12.4 min (major), 13.0 min (minor).

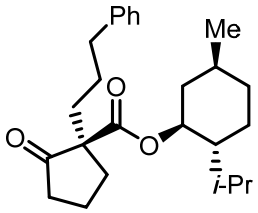
^{1}H NMR (600 MHz, Chloroform-d) δ 7.29 – 7.25 (m, 2H), 7.20 – 7.13 (m, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.66 – 2.59 (m, 2H), 2.10 (s, 3H), 1.96 – 1.91 (m, 1H), 1.82 – 1.76 (m, 1H), 1.55 – 1.47 (m, 2H), 1.32 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 205.6, 172.9, 141.7, 128.32, 128.29, 125.8, 61.2, 59.5, 36.0, 34.2, 26.02, 25.99, 18.8, 14.0.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{16}H_{23}O_3$: 263.1642, found: 263.1641.

FT-IR (film): 2982, 2935, 2867, 1734, 1709, 1709, 1453, 1258, 1236, 1172, 1101, 748, 697 cm^{-1}.

$[\alpha]^{20}_{D}$ = +9.8 (*c* 0.2, $CHCl_3$); 87% ee, from (*S*)-**A1**.



(*1S,2R,5S*)-2-Isopropyl-5-methylcyclohexyl (*S*)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxylate (38). The title compound was synthesized according to **GP-4** from (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 53.7 mg, 70% yield, 99:1 dr.

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*)-**A1**: 6.9 min (major), 7.3 min (minor).

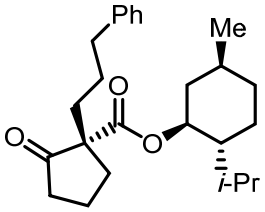
^{1}H NMR (400 MHz, Chloroform-d) δ 7.30 – 7.25 (m, 2H), 7.22 – 7.12 (m, 3H), 4.74 – 4.63 (m, 1H), 2.68 – 2.56 (m, 2H), 2.54 – 2.46 (m, 1H), 2.44 – 2.35 (m, 1H), 2.27 – 2.17 (m, 1H), 2.04 – 1.81 (m, 6H), 1.73 – 1.61 (m, 4H), 1.58 – 1.38 (m, 3H), 1.11 – 0.93 (m, 2H), 0.92 – 0.89 (m, 6H), 0.88 – 0.80 (m, 1H), 0.73 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 214.7, 170.6, 141.8, 128.30, 128.28, 125.8, 75.3, 60.5, 46.8, 40.5, 37.9, 36.2, 34.1, 33.4, 32.9, 31.3, 26.9, 25.9, 23.0, 21.9, 20.8, 19.6, 15.8.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{25}H_{37}O_3$: 385.2737, found: 385.2739.

FT-IR (film): 2954, 2930, 2866, 1751, 1713, 1447, 1229, 1142, 696 cm^{-1}.

$[\alpha]^{20}_{D}$ = –80.0 (*c* 0.2, $CHCl_3$); 99:1 dr, from (*S*)-**A1**.



(*1S,2R,5S*)-2-Isopropyl-5-methylcyclohexyl (*R*)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxylate (39). The title compound was synthesized according to **GP-4** from (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 2-oxocyclopentane-1-carboxylate and 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 29.1 mg, 38% yield, 37:63 dr.

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 (*R*)-**A1**: 6.8 min (minor), 7.2 min (major).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.30 – 7.25 (m, 2H), 7.22 – 7.13 (m, 3H), 4.72 – 4.63 (m, 1H), 2.67 – 2.57 (m, 2H), 2.55 – 2.47 (m, 1H), 2.43 – 2.34 (m, 1H), 2.27 – 2.17 (m, 1H), 2.03 – 1.80 (m, 6H), 1.72 – 1.64 (m, 3H), 1.61 – 1.39 (m, 4H), 1.09 – 0.92 (m, 2H), 0.92 – 0.88 (m, 6H), 0.87 – 0.79 (m, 1H), 0.75 – 0.69 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 214.6, 170.4, 141.9, 128.4, 128.3, 125.8, 75.4, 60.7, 46.8, 40.4, 37.7, 36.1, 34.2, 33.4, 32.7, 31.4, 26.8, 26.0, 23.0, 22.0, 20.8, 19.6, 15.9.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{25}H_{37}O_3$: 385.2737, found: 385.2734.

FT-IR (film): 2954, 2929, 2867, 1750, 1713, 1447, 1229, 1141, 696 cm^{-1}.

$[\alpha]^{20}_D$ = –40.7 (*c* 0.2, $CHCl_3$); 37:63 dr, from (*R*)-**A1**.

V. Effect of Reaction Parameters

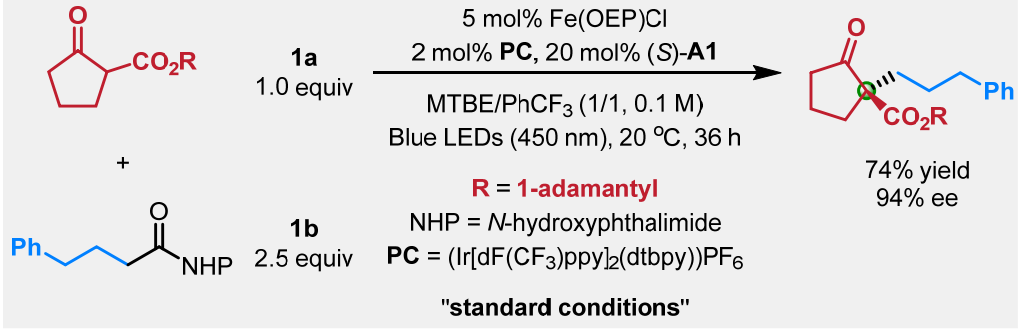
General Procedure 7 (GP-7).

Cross-coupling: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with Fe(OEP)Cl (6.3 mg, 0.010 mmol, 5.0 mol%), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (4.5 mg, 0.0040 mmol, 2.0 mol%), (*S*)-**A1** (22.0 mg, 0.040 mmol, 20 mol%), NHP ester (0.50 mmol, 2.5 equiv), 1,3-dicarbonyl compound (0.20 mmol, 1.0 equiv), and a stir bar. Anhydrous MTBE (1 mL) and $PhCF_3$ (1 mL) were added sequentially, and the vial was capped with a PTFE septum cap. The vial was transferred out of the glovebox and placed in the photoreactor (**Figure S1**). The reaction was irradiated with blue LEDs (450 nm) and was stirred at 20 °C for 36 hours.

Work-up: The reaction was stopped by ending the irradiation. Then, *n*-tetradecane (52 μL, 0.20 mmol, 1.0 equiv.) was added as an internal standard. The reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with DCM. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.

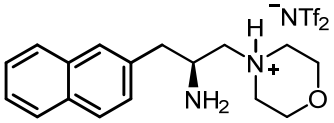
Figure S2: Adamantan-1-yl 2-oxocyclopentane-1-carboxylate was reacted with 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate according to **GP-7**. The yields were determined via GC analysis, with *n*-tetradecane as the internal standard. The ee values were determined via HPLC analysis after purification by preparative thin-layer chromatography.

Figure S2. Effect of Reaction Parameters

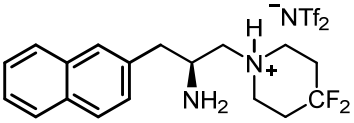


entry	variation from the **"standard conditions"**	yield (%)[a]	ee[b]
1	None	74	94
2	No Fe, **PC**, (*S*)-**A1**, or light	0	–
3	Fe(TPP)Cl, instead of Fe(OEP)Cl	37	78
4	FePc, instead of Fe(OEP)Cl	6	36
5	Fe(III) Protoporphyrin IX, instead of Fe(OEP)Cl	11	74
6	$Ni(acac)_2$+K[Tp*], instead of Fe(OEP)Cl	0	–
7	Vitamin B12, instead of Fe(OEP)Cl	2	–
8	Co(Salen), instead of Fe(OEP)Cl	3	–
9	Co(TPP), instead of Fe(OEP)Cl	0	–
10	**A2**, instead of (*S*)-**A1**	40	87
11	**A3**, instead of (*S*)-**A1**	47	86
12	**A4**, instead of (*S*)-**A1**	35	83
13	**A5**, instead of (*S*)-**A1**	21	88
14	**A6**, instead of (*S*)-**A1**	0	–
15	Pure MTBE	64	94
16	Pure $PhCF_3$	54	94
17	2.5 mol% Fe(OEP)Cl	65	94
18	1.0 mol% **PC**	58	94
19	18 h, instead of 36 h	53	94
20	10 °C, instead of 20 °C	54	95
21	30 °C, instead of 20 °C	60	94
22	0.05 M, instead of 0.1 M	56	95
23	1.0 mL air added	50	94
24	1.0 equiv H_2O added	62	93

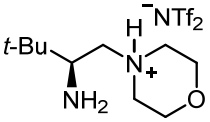
[a] Determined through GC analysis. [b] Determined through HPLC analysis.



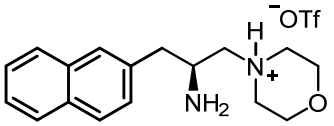
(S)-**A1**



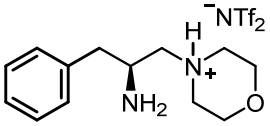
A3



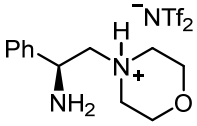
A5



A2



A4

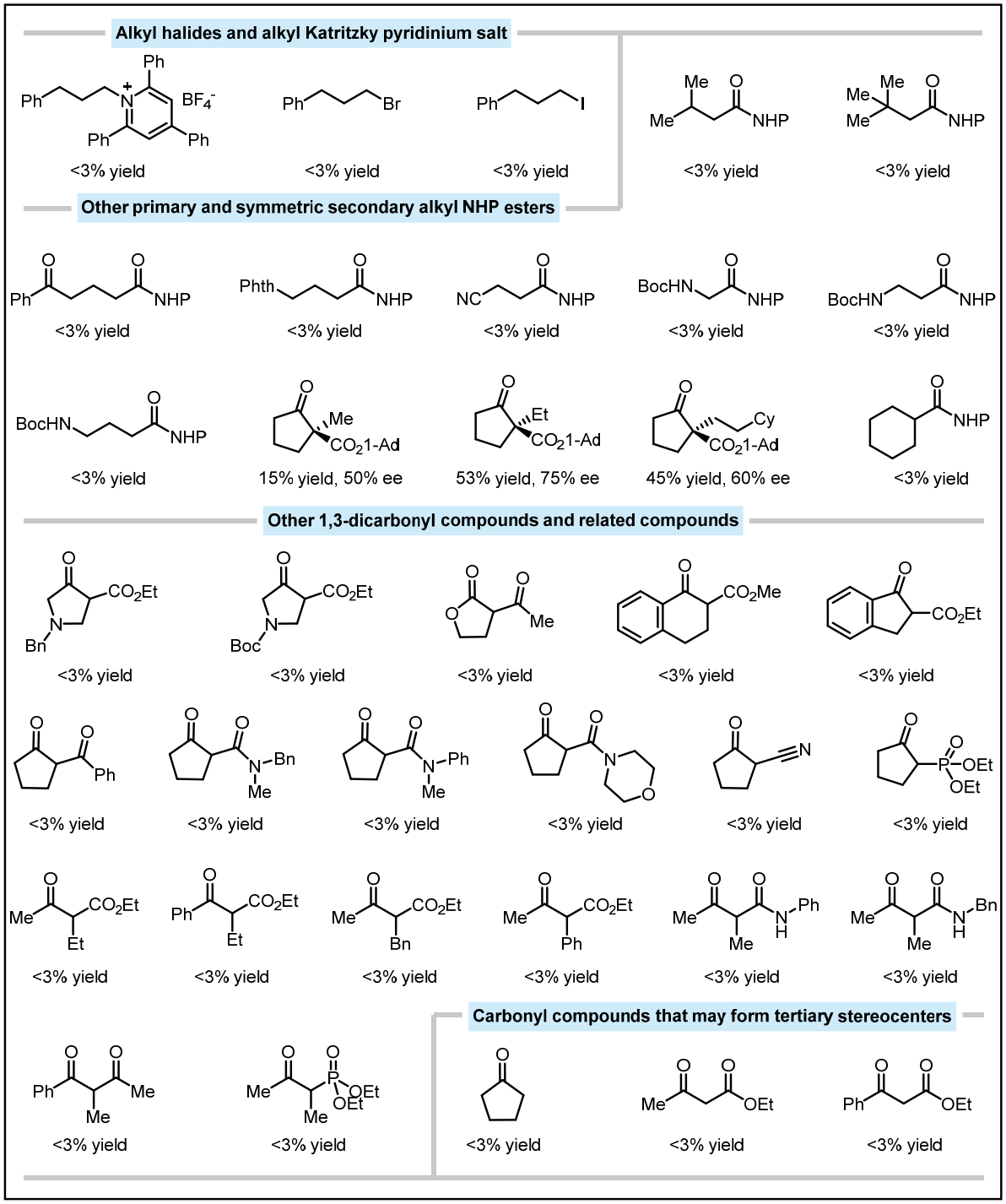


A6

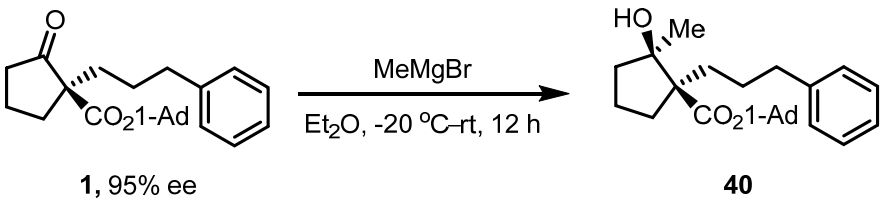
VI. Unsuccessful Examples

Figure S3: The reactions were conducted according to **GP-4**. All yields are of purified products.

Figure S3. Unsuccessful Examples



VII. Applications



1, 95% ee **40**

Adamantan-1-yl (*1S,2R*)-2-hydroxy-2-methyl-1-(3-phenylpropyl)cyclopentane-1-carboxylate (40). An oven-dried 10 mL vial was equipped with a magnetic stir bar and adamantan-1-yl (*S*)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxylate (76.0 mg, 0.20 mmol, 1.0 equiv), and was sealed with a PTFE septum cap. The vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles), followed by the addition of anhydrous Et_2O (1 mL). The mixture was cooled to –20 °C, and a solution of MeMgBr (3.0 M in Et_2O, 120 uL, 1.8 equiv) was added slowly. The resulting solution was stirred at –20 °C for 30 min, at which time the mixture was allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with water (5 mL), 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. Colorless oil, 72.1 mg, 91% yield, 97.5:2.5 dr, 95% ee (the relative configuration was determined by NOE experiments,[18] NOE shows no correlation between Me and 1-Ad).

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained: 7.1 min (minor), 7.7 min (major).

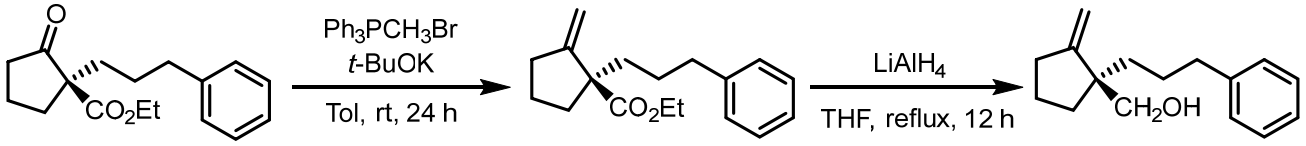
^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.25 (m, 2H), 7.21 – 7.14 (m, 3H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.19 – 2.13 (m, 3H), 2.09 – 2.05 (m, 6H), 2.05 – 1.94 (m, 3H), 1.87 – 1.80 (m, 1H), 1.74 – 1.67 (m, 2H), 1.67 – 1.64 (m, 6H), 1.64 – 1.55 (m, 3H), 1.45 – 1.32 (m, 2H), 1.23 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 174.5, 142.3, 128.4, 128.3, 125.7, 80.8, 80.6, 60.0, 41.4, 37.3, 36.4, 36.1, 31.4, 30.8, 28.9, 27.0, 25.8, 17.8.

HRMS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{26}H_{36}NaO_3$: 419.2557, found: 419.2554.

FT-IR (film): 3332, 2922, 2854, 1745, 1513, 1451, 1033, 778, 701 cm^{-1}.

$[\alpha]^{20}_D$ = –25.4 (*c* 0.2, $CHCl_3$); 97.5:2.5 dr, 95% ee.



25, 90% ee **41** **41'**

Ethyl (*R*)-2-methylene-1-(3-phenylpropyl)cyclopentane-1-carboxylate (41). An oven-dried 10 mL vial was equipped with a magnetic stir bar, methyltriphenylphosphonium bromide

(209.2 mg, 0.586 mmol, 2.93 equiv), *t*-BuOK (53.8 mg, 0.48 mmol, 2.4 equiv), and was sealed with a PTFE septum cap. The vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles), followed by the addition of anhydrous toluene (2 mL). The resulting solution was stirred at 0 °C for 60 min. Then, a solution of ethyl (*S*)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxylate (54.8 mg, 0.20 mmol, 90% ee, 1.0 equiv, 0.2 M in THF) was added slowly, at which time the mixture was allowed to warm to room temperature and stirred for 24 h. The reaction was quenched with water (5 mL), 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 (1:50 EtOAc/hexanes) to afford the desired product. Colorless oil, 44.0 mg, 81% yield, 90% ee.

HPLC analysis: The ee was determined after transforming the product to the corresponding alcohol.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.29 – 7.25 (m, 2H), 7.19 – 7.15 (m, 3H), 5.05 (t, *J* = 2.4 Hz, 1H), 5.00 (t, *J* = 2.4 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.65 – 2.55 (m, 2H), 2.43 – 2.37 (m, 1H), 2.36 – 2.30 (m, 2H), 2.05 – 1.99 (m, 1H), 1.78 – 1.72 (m, 1H), 1.67 – 1.62 (m, 1H), 1.60 – 1.52 (m, 3H), 1.52 – 1.46 (m, 1H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-d) δ 175.2, 155.2, 142.3, 128.3, 128.2, 125.7, 107.4, 60.5, 56.3, 38.7, 36.3, 35.1, 33.8, 27.5, 24.1, 14.1.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{18}H_{25}O_2$: 273.1849, found: 273.1847.

FT-IR (film): 2940, 2900, 1744, 1580, 1513, 1453, 1244, 1021, 820, 698 cm^{-1}.

$[\alpha]^{20}_D$ = -25.4 (*c* 0.2, $CHCl_3$); 90% ee.

(*R*)-(2-Methylene-1-(3-phenylpropyl)cyclopentyl)methanol (41'). An oven-dried 10 mL two-neck round-bottom flask was charged with a stir bar, fitted with a reflux condenser attached to a nitrogen manifold, and then sealed with a rubber septum cap. The flask was placed under a nitrogen atmosphere by evacuating and back-filling the flask (three cycles), followed by the addition of a solution of ethyl (*R*)-2-methylene-1-(3-phenylpropyl)cyclopentane-1-carboxylate (27.2 mg, 0.10 mmol, 90% ee, 1.0 equiv) in THF (2 mL), and the flask was cooled to 0 °C using an ice bath. Lithium aluminum hydride (11.4 mg, 0.30 mmol, 3.0 equiv) was added through the open neck under a positive pressure of nitrogen. The reaction mixture was stirred at 0 °C for 30 min and heated to reflux for 12 h. The mixture was then cooled to 0 °C, followed by the sequential dropwise addition of water, 15% aqueous NaOH, and water (1:1:3, depending on the grams of lithium tetrahydroaluminum). The aqueous phase was extracted with EtOAc (4 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (1:20 EtOAc/hexanes) on silica gel to give the desired product. Colorless oil, 20.7 mg, 90% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained: 10.7 min (minor), 11.5 min (major).

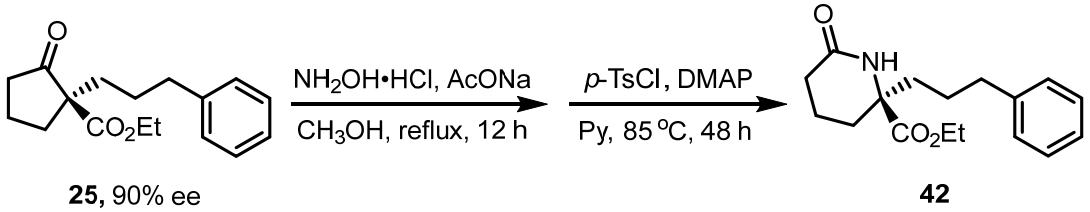
^{1}H NMR (600 MHz, Chloroform-d) δ 7.30 – 7.26 (m, 2H), 7.21 – 7.15 (m, 3H), 5.06 – 5.03 (m, 1H), 4.76 – 4.72 (m, 1H), 3.45 – 3.41 (m, 1H), 3.34 – 3.30 (m, 1H), 2.62 – 2.55 (m, 2H), 2.41 – 2.34 (m, 2H), 1.68 – 1.60 (m, 5H), 1.58 – 1.52 (m, 3H), 1.46 – 1.41 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-d) δ 156.9, 142.5, 128.4, 128.3, 125.7, 105.7, 68.1, 50.6, 36.7, 36.1, 34.6, 34.2, 26.4, 23.0.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{16}H_{22}NaO$: 253.1563, found: 253.1569.

FT-IR (film): 3332, 2922, 2854, 1580, 1513, 1451, 1033, 778, 701 cm^{-1}.

$[\alpha]^{20}_{D}$ = –20.4 (*c* 0.2, $CHCl_3$); 90% ee.



25, 90% ee **42**

Ethyl (*R*)-6-oxo-2-(3-phenylpropyl)piperidine-2-carboxylate (42). An oven-dried 10 mL vial was equipped with a magnetic stir bar, ethyl (*S*)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxylate (54.8 mg, 0.20 mmol, 1.0 equiv), sodium acetate (49.2 mg, 0.60 mmol, 3.0 equiv), and hydroxylamine hydrochloride (41.4 mg, 0.60 mmol, 3.0 equiv), and was then sealed with a PTFE septum cap. The vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles), followed by the addition of anhydrous MeOH (2 mL). The reaction was heated to reflux for 12 h and allowed to cool down to room temperature. The mixture was concentrated, and the residue was added to another oven-dried 10 mL vial that was equipped with *p*-TsCl (95.0 mg, 0.50 mmol, 2.5 equiv) and DMAP (0.5 mg, 0.0040 mmol, 2.0 mol%), and was then sealed with a PTFE septum cap. The vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles), followed by the addition of anhydrous pyridine (2 mL). The mixture was heated to 85 °C for 48 h, and then cooled down to room temperature. The mixture was concentrated under reduced pressure, and the crude material was diluted with DCM and washed with 1 M HCl and aqueous saturated $NaHCO_3$. The combined organic layers were then dried over Na_2SO_4, filtered, and concentrated, and the residue was purified by flash chromatography (1:2 EtOAc/hexanes) to afford the desired product. Colorless oil, 40.4 mg, 70% yield, 90% 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: 22.2 min (minor), 24.8 min (major).

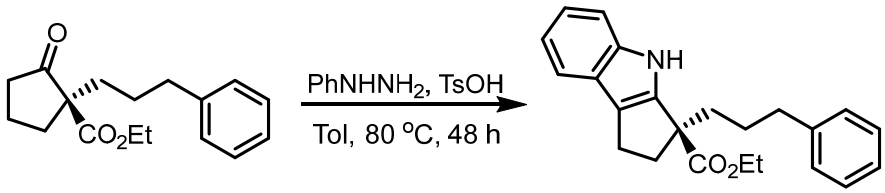
^{1}H NMR (400 MHz, Chloroform-d) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.16 (m, 1H), 7.15 – 7.09 (m, 2H), 6.10 (s, 1H), 4.21 – 4.13 (m, 2H), 2.64 – 2.56 (m, 2H), 2.41 – 2.26 (m, 2H), 2.22 – 2.16 (m, 1H), 1.83 – 1.61 (m, 6H), 1.57 – 1.49 (m, 1H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 173.1, 171.6, 141.1, 128.4, 128.3, 126.1, 62.7, 61.8, 39.5, 35.5, 30.9, 30.4, 25.1, 17.9, 14.2.

HRMS (ESI-MS) *m*/*z* $[M+K]^+$ calcd for $C_{17}H_{23}KNO_3$: 328.1310, found: 328.1309.

FT-IR (film): 3240, 2922, 2854, 1690, 1523, 1423, 1224, 1030, 922, 770, 698 cm^{-1}.

$[\alpha]^{20}_D$ = –12.9 (*c* 0.1, $CHCl_3$); 90% ee.



25, 90% ee **43**

Ethyl (*S*)-3-(3-phenylpropyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indole-3-carboxylate (43). An oven-dried 10 mL vial was equipped with a magnetic stir bar, ethyl (*S*)-2-oxo-1-(3-phenylpropyl)cyclopentane-1-carboxylate (54.8 mg, 0.20 mmol, 1.0 equiv), phenylhydrazine (23.6 uL, 0.24 mmol, 1.2 equiv), and was then sealed with a PTFE septum cap. The vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles), followed by the addition of anhydrous toluene (2 mL). The resulting solution was stirred at room temperature for 60 min, and TsOH (41.3 mg, 0.60 mmol, 3.0 equiv) was then added. The mixture was stirred at 80 °C for another 48 h. Upon completion, aqueous saturated NH_4Cl 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, 36.0 mg, 52% yield, 90% 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: 9.2 min (major), 9.9 min (minor).

^{1}H NMR (600 MHz, Chloroform-d) δ 8.03 (s, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.18 – 7.15 (m, 1H), 7.13 – 7.05 (m, 4H), 4.20 – 4.13 (m, 2H), 3.06 – 3.00 (m, 1H), 2.86 – 2.78 (m, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 2.45 – 2.40 (m, 1H), 2.02 – 1.97 (m, 1H), 1.91 – 1.85 (m, 1H), 1.66 – 1.57 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-d) δ 174.7, 143.1, 141.8, 141.0, 128.4, 128.3, 125.9, 124.3, 121.3, 119.6, 119.5, 118.9, 111.7, 61.0, 54.4, 38.8, 38.5, 35.9, 27.1, 22.9, 14.3.

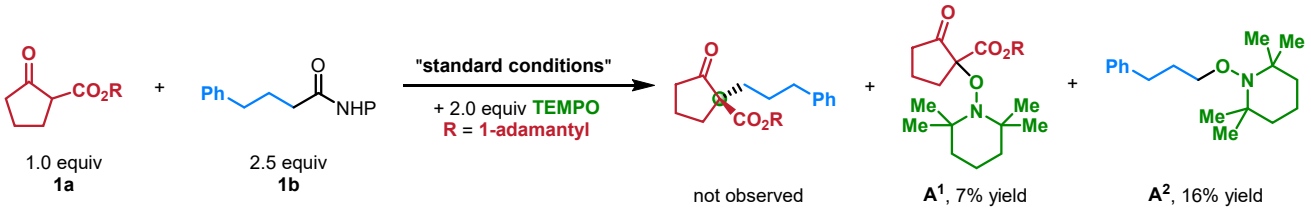
HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{26}NO_2$: 348.1958, found: 348.1950.

FT-IR (film): 3223, 2930, 2925, 2851, 1758, 1610, 1570, 1520, 1430, 1254, 1191, 1107, 932, 834, 731 cm^{-1}.

$[\alpha]^{20}_D$ = –8.3 (*c* 0.2, $CHCl_3$); 90% ee.

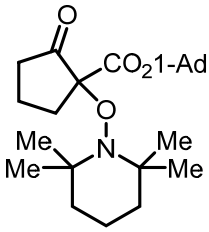
VIII. Mechanistic Experiments

1. Radical trapping experiment using TEMPO as the trapping agent.



Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with Fe(OEP)Cl (6.3 mg, 0.010 mmol, 5.0 mol%), (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (4.5 mg, 0.0040 mmol, 2.0 mol%), (*S*)-**A1** (22.0 mg, 0.040 mmol, 20 mol%), adamantan-1-yl 2-oxocyclopentane-1-carboxylate (52.4 mg, 0.20 mmol, 1.0 equiv), 1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (154.5 mg, 0.50 mmol, 2.5 equiv), TEMPO (62.4 mg, 0.40 mmol, 2.0 equiv), and a stir bar. Anhydrous MTBE (1 mL) and PhCF$_3$ (1 mL) were added sequentially, and the vial was capped with a PTFE septum cap. The vial was transferred out of the glovebox and placed in the photoreactor (**Figure S1**). The reaction was irradiated with blue LEDs (450 nm) and was stirred at 20 °C for 36 hours.

An ESI-MS analysis of the reaction was carried out, which confirmed no detection of the coupling product. The reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with DCM. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.



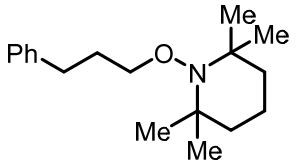
Adamantan-1-yl 2-oxo-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)cyclopentane-1-carboxylate (A^1). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 5.8 mg, 7% yield.

^{1}H NMR (400 MHz, Chloroform-d) δ 3.25 – 3.14 (m, 1H), 2.50 – 2.41 (m, 1H), 2.28 – 2.18 (m, 2H), 2.17 – 2.13 (m, 3H), 2.13 – 2.10 (m, 6H), 2.10 – 2.00 (m, 2H), 1.68 – 1.62 (m, 6H), 1.61 – 1.46 (m, 6H), 1.30 (s, 3H), 1.18 (s, 3H), 1.08 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-d) δ 214.9, 169.0, 89.1, 82.6, 41.2, 40.6, 40.4, 36.8, 36.0, 32.5, 32.4, 30.8, 29.8, 20.6, 20.5, 18.3, 16.9.

HRMS (ESI-MS) *m/z* [M+Na]$^+$ calcd for $C_{25}H_{39}NNaO_4$: 440.2771, found: 440.2767.

FT-IR (film): 2923, 2854, 1753, 1720, 1457, 1373, 1165, 1060, 852 cm^{-1}.



2,2,6,6-Tetramethyl-1-(3-phenylpropoxy)piperidine (A²). The product was purified by column chromatography on silica gel (1:12 EtOAc/hexanes). Colorless oil, 8.9 mg, 16% yield.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.32 – 7.27 (m, 2H), 7.22 – 7.18 (m, 3H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.37 (t, *J* = 7.8 Hz, 2H), 2.04 – 1.98 (m, 2H), 1.72 – 1.69 (m, 2H), 1.67 – 1.66 (m, 1H), 1.55 – 1.51 (m, 2H), 1.44 – 1.39 (m, 1H), 1.15 (s, 6H), 1.06 (s, 6H).

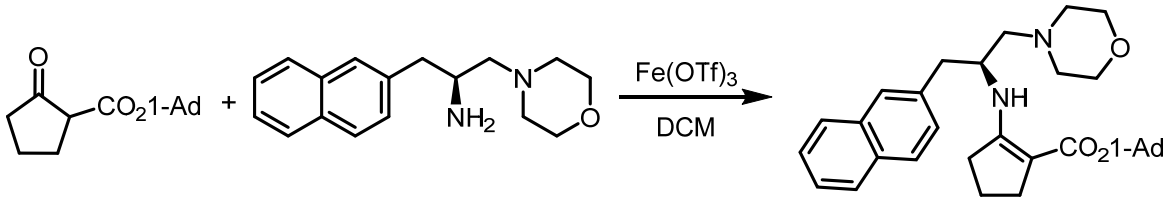
^{13}C NMR (151 MHz, Chloroform-d) δ 141.3, 128.44, 128.37, 126.0, 59.9, 38.9, 35.4, 32.3, 32.0, 26.9, 20.5, 16.9.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{18}H_{30}O$: 276.2322, found: 276.2335.

FT-IR (film): 2974, 2930, 2870, 1604, 1497, 1470, 1373, 1118, 701 cm^{-1}.

2. Cyclic Voltammograms Profiles.

Samples were prepared by mixing 0.050 mmol of the substrate in 10 mL of 0.1 M *n*-Bu_4NPF_6 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 solution was sparged with nitrogen for 3-5 minutes before data collection. $E_{1/2}$ was obtained using Origin.



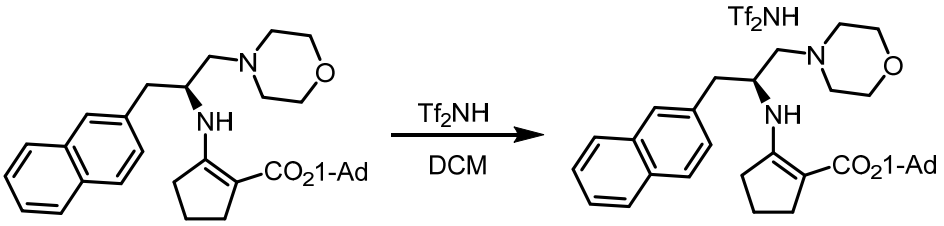
Adamantan-1-yl 2-(((*S*)-1-morpholino-3-(naphthalen-2-yl)propan-2-yl)amino)cyclopent-1-ene-1-carboxylate.[19] An oven-dried 20 mL vial was equipped with a magnetic stir bar, adamantan-1-yl 2-oxocyclopentane-1-carboxylate (524 mg, 2.0 mmol, 1.0 equiv), (*S*)-1-morpholino-3-(naphthalen-2-yl)propan-2-amine (540 mg, 2.0 mmol, 1.0 equiv), $Fe(OTf)_3$ (41 mg, 2.0 mmol, 0.10 equiv), and was then sealed with a PTFE septum cap. The vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles), followed by the addition of anhydrous DCM (5 mL). The reaction was stirred at room temperature, and the completion of the reaction was monitored by TLC. 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 DCM. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel (1:6 EtOAc/hexanes). Yellow oil, 720.3 mg, 72% yield.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.85 – 7.70 (m, 3H), 7.61 (s, 1H), 7.47 – 7.38 (m, 2H), 7.32 – 7.28 (m, 1H), 7.22 (s, 1H), 3.89 – 3.50 (m, 5H), 3.10 – 3.03 (m, 1H), 2.94 – 2.84 (m, 1H), 2.58 – 2.24 (m, 9H), 2.20 – 2.07 (m, 10H), 1.70 – 1.60 (m, 7H), 1.56 – 1.46 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 168.1, 162.5, 135.6, 133.5, 132.2, 128.2, 127.9, 127.8, 127.6, 127.5, 125.9, 125.4, 95.2, 78.1, 67,0, 63.4, 54.4, 54.2, 42.0, 41.3, 36.4, 32.4, 30.8, 29.5, 20.7.

HRMS (ESI-MS) *m*/*z* [M+K]$^{+}$ calcd for $C_{33}H_{42}KN_2O_3$: 553.2827, found: 553.2834.

FT-IR (film): 3370, 2932, 2838, 2808, 1742, 1592, 1259, 1167, 1054, 752, 727 cm^{-1}.



E

Preparation of E. An oven-dried 10 mL vial was equipped with a magnetic stir bar, adamantan-1-yl (*S*)-2-((2-morpholino-1-(naphthalen-2-yl)ethyl)amino)cyclopent-1-ene-1-carboxylate (500 mg, 1.0 mmol, 1.0 equiv), Tf_2NH (281 mg, 1.0 mmol, 1.0 equiv), and was then sealed with a PTFE septum cap. The vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles), followed by the addition of anhydrous DCM (3 mL). The mixture was stirred for 30 min at room temperature and then concentrated in vacuum to obtain **E** without further purification.

Cyclic voltammogram of Ferrocene. An oven-dried 20 mL beaker was equipped with ferrocene (9.3 mg, 0.050 mmol), *n*-Bu_4NPF_6 (387.4 mg, 1.0 mmol), and anhydrous MeCN (10 mL). The beaker was subjected to sonication and continuous nitrogen purge for deoxygenation for 5 min. 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.

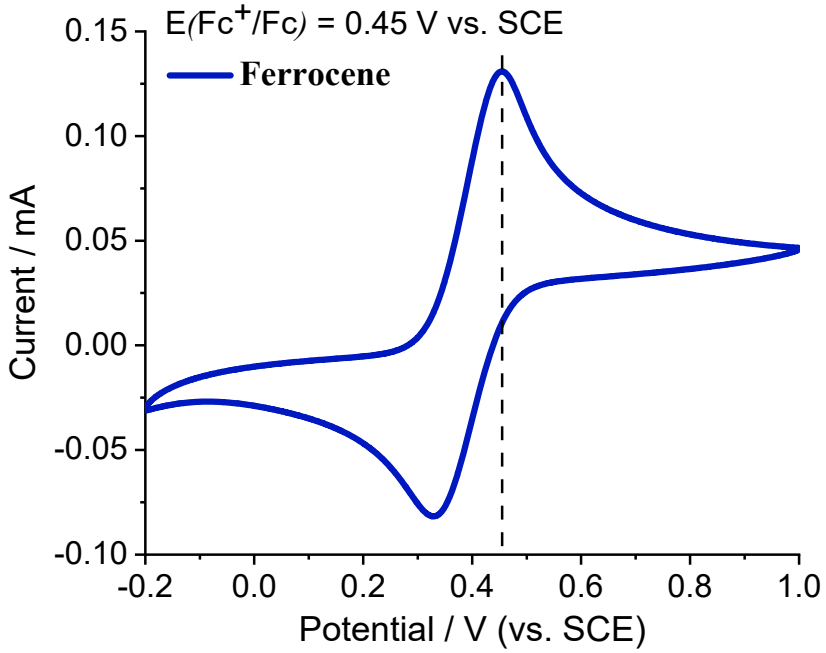


Figure S4. Cyclic voltammogram of ferrocene

Cyclic voltammogram of E. An oven-dried 20 mL beaker was equipped with **E** (39.8 mg, 0.050 mmol), *n*-Bu_4NPF_6 (387.4 mg, 1.0 mmol), and anhydrous MeCN (10 mL). The beaker was subjected to sonication and continuous nitrogen purge for deoxygenation for 5 min. 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.

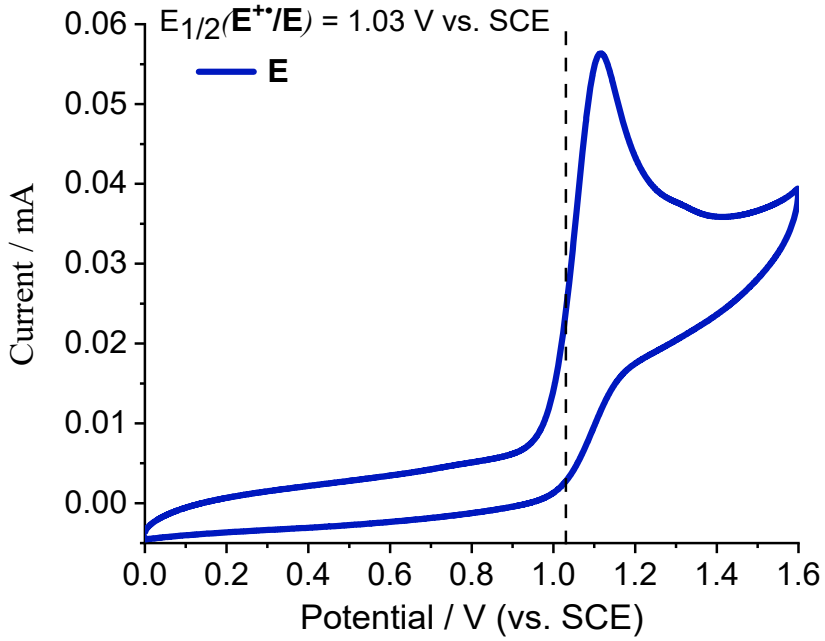


Figure S5. Cyclic voltammogram of **E**

Cyclic voltammogram of 1b. An oven-dried 20 mL beaker was equipped with **1b** (15.5 mg, 0.050 mmol), *n*-Bu_4NPF_6 (387.4 mg, 1.0 mmol), and anhydrous MeCN (10 mL). The beaker was subjected to sonication and continuous nitrogen purge for deoxygenation for 5 min. 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.

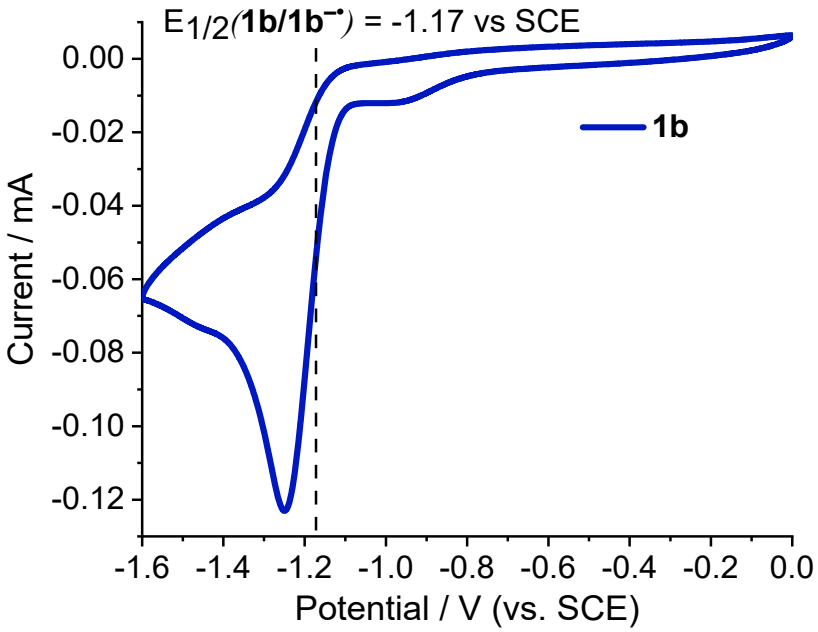


Figure S6. Cyclic voltammogram of **1b**

Cyclic voltammogram of 1b (in DMF). An oven-dried 20 mL beaker was equipped with **1b** (30.9 mg, 0.10 mmol), *n*-Bu_4NPF_6 (387.4 mg, 1.0 mmol), and anhydrous DMF (10 mL). The beaker was subjected to sonication and continuous nitrogen purge for deoxygenation for 5 min. 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.

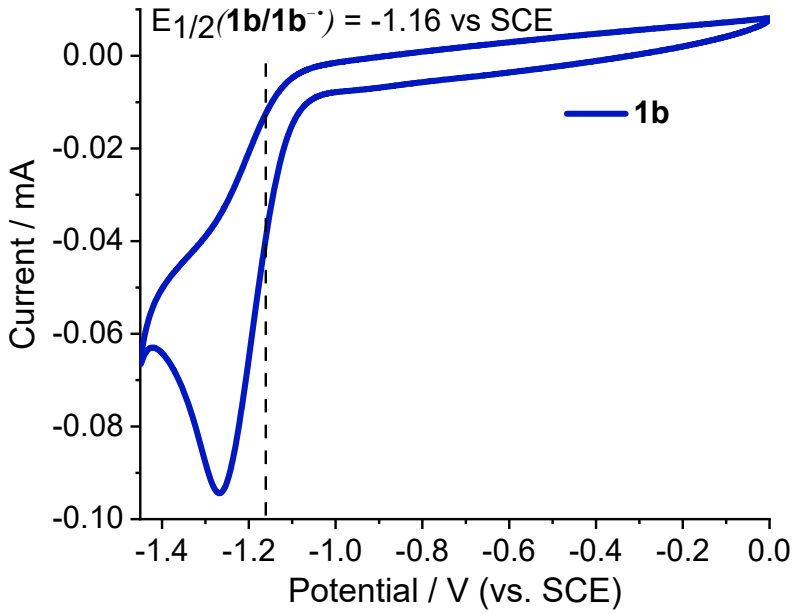


Figure S7. Cyclic voltammogram of **1b** (in DMF)

Cyclic voltammogram of Fe(OEP)Cl (in DMF). An oven-dried 20 mL beaker was equipped with Fe(OEP)Cl (31.2 mg, 0.050 mmol), *n*-Bu_4NPF_6 (387.4 mg, 1.0 mmol), and anhydrous DMF (10 mL). The beaker was subjected to sonication and continuous nitrogen purge for deoxygenation for 5 min. 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.

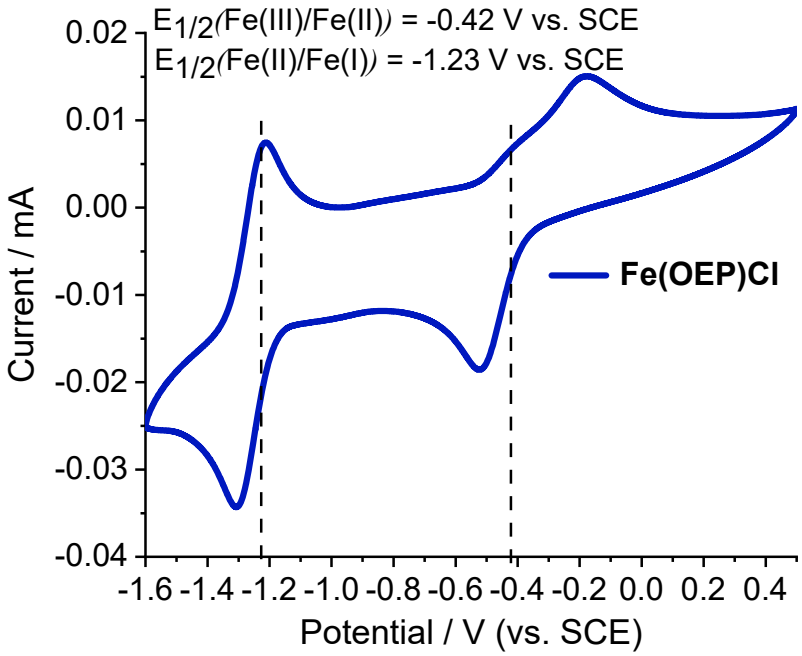


Figure S8. Cyclic voltammogram of Fe(OEP)Cl (in DMF)

Cyclic voltammogram of (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (in DMF). An oven-dried 20 mL beaker was equipped with (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (56.1 mg, 0.050 mmol), *n*-Bu$_4$NPF$_6$ (387.4 mg, 1.0 mmol), and anhydrous DMF (10 mL). The beaker was subjected to sonication and continuous nitrogen purge for deoxygenation for 5 min. 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.

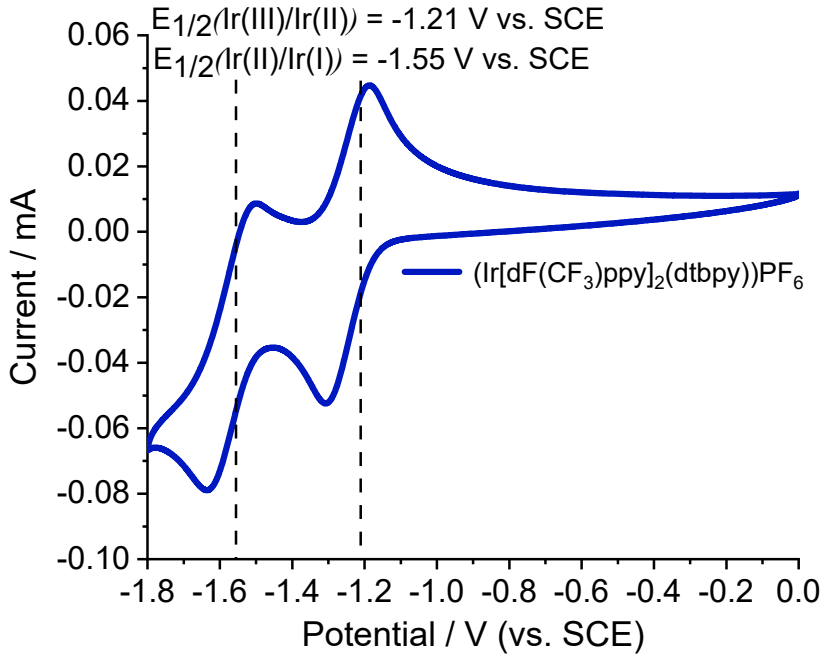


Figure S9. Cyclic voltammogram of (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (in DMF)

Discussion: These results obtained in DMF showed that the photocatalyst (Ir (II)) is capable of reducing Fe(OEP) (II) to Fe (I), which in turn can reduce **1b** to generate the primary radical species.

Cyclic voltammogram of Fe(OEP)Cl in the presence of 1b (in DMF). An oven-dried 20 mL beaker was equipped with *n*-Bu$_4$NPF$_6$ (387.4 mg, 1.0 mmol), Fe(OEP)Cl (31.2 mg, 0.050 mmol), **1b**, and anhydrous DMF (10 mL). The beaker was subjected to sonication and continuous nitrogen purge for deoxygenation for 5 min. 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.

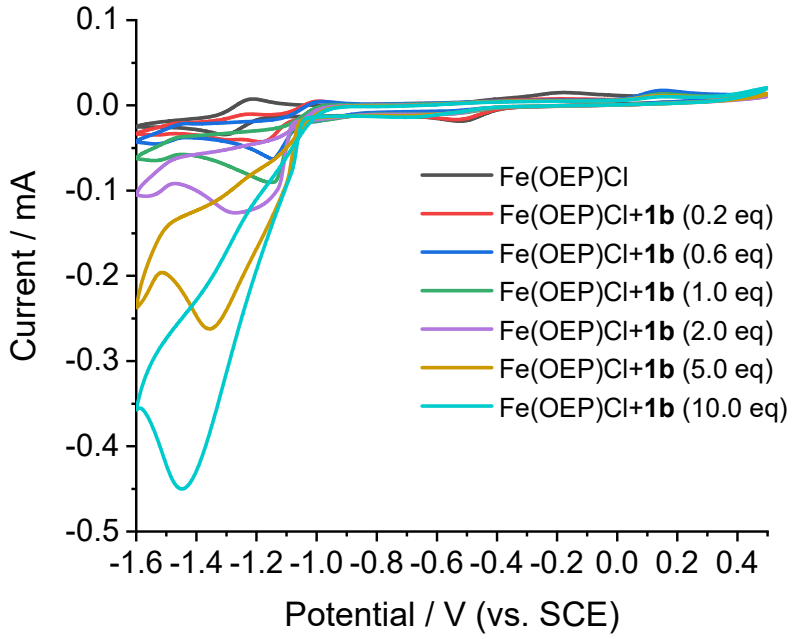


Figure S10. Cyclic voltammogram of Fe(OEP)Cl in the presence of **1b** (in DMF)**.** Conditions: (black curve) Fe(OEP)Cl (0.050 mmol); (red curve) Fe(OEP)Cl (0.050 mmol) and **1b** (0.010 mmol); (blue curve) Fe(OEP)Cl (0.050 mmol) and **1b** (0.030 mmol); (green curve) Fe(OEP)Cl (0.050 mmol) and **1b** (0.050 mmol); (purple curve) Fe(OEP)Cl (0.050 mmol) and **1b** (0.10 mmol) ; (brown curve) Fe(OEP)Cl (0.050 mmol) and **1b** (0.25 mmol); (light blue curve) Fe(OEP)Cl (0.050 mmol) and **1b** (0.50 mmol).

Discussion: Upon addition of **1b** to the mixture, the reduction peaks were considerably increased, while the oxidation peaks gradually disappeared. These observations also suggest that Fe (I) may reduce **1b**.

3. Stern–Volmer Luminescence Quenching Studies.

The fluorescence quenching experiments were carried out in degassed TBME: $PhCF_3$(1:1) at room temperature upon excitation by 380 nm light.

Emission quenching of [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 as a function of concentration of E. A 1.0×10^{-3} M solution of [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 (11.2 mg, 0.010 mmol) in anhydrous degassed TBME:$PhCF_3$ (1:1, 10 mL) and a 2.0×10^{-2} M solution of **E** (15.9 mg, 0.020 mmol) in anhydrous degassed TBME:$PhCF_3$ (1:1, 1 mL) were prepared in a nitrogen filled glovebox. To six sample vials were added 20 uL of 1.0×10^{-3} M solution of [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 and 0 uL, 10 uL, 40 uL, 80 uL, 200 uL, and 500 uL of 2.0×10^{-2} M solution of **E.** Anhydrous degassed TBME:$PhCF_3$ (1:1) was then added to each sample vial to a quantity of 2 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 the glove box. The cuvette caps were wrapped with parafilm and the quartz cuvettes were removed out of the glove box. The emission quenching of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1.0×10^{-5} M) as a function of the concentration of **E** in deaerated TBME:$PhCF_3$ with excitation at 380 nm is shown in **Figure S11.**

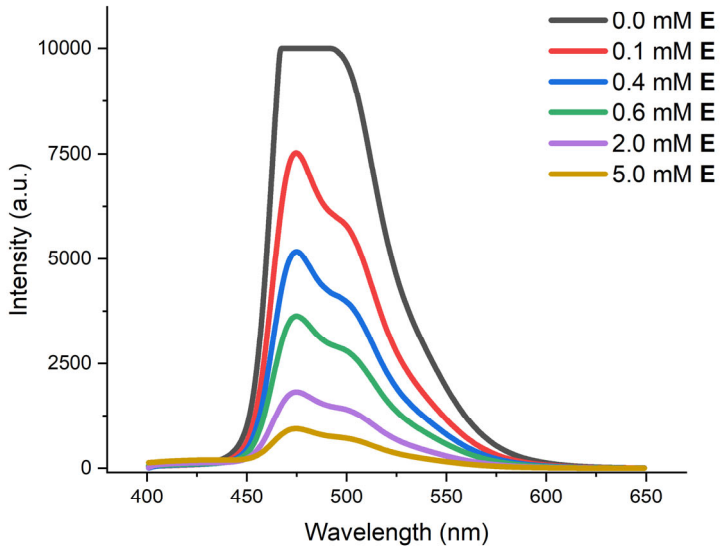


Figure S11. The emission quenching of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (0.01 mM) as a function of concentration of **E** in deaerated TBME:$PhCF_3$ (1:1) with excitation at 380 nm. Conditions: (black curve) **E** (0.0 mM); (red curve) **E** (0.1 mM); (blue curve) **E** (0.4 mM); (green curve) **E** (0.6 mM); (purple curve) **E** (2.0 mM); (yellow curve) **E** (5.0 mM).

Emission quenching of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ as a function of concentration of 1b. A 1.0×10^{-3} M solution of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (11.2 mg, 0.010 mmol) in anhydrous degassed TBME:$PhCF_3$ (1:1, 10 mL) and a 1.0×10^{-1} M solution of **1b** (30.9 mg, 0.10 mmol) in anhydrous degassed TBME:$PhCF_3$ (1:1, 1 mL) were prepared in a nitrogen filled glovebox. To six sample vials were added 10 uL of 1.0×10^{-3} M solution of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ and 0 uL, 20 uL, 40 uL, 120 uL and 160 uL of 1.0×10^{-1} M solution of **1b.** Anhydrous degassed TBME:$PhCF_3$ (1:1) was then added to each sample vial to a quantity of 2 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 $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (5.0×10^{-6} M) as a function of the concentration of **1b** in deaerated TBME:$PhCF_3$ (1:1) with excitation at 380 nm is shown in Figure **S12.**

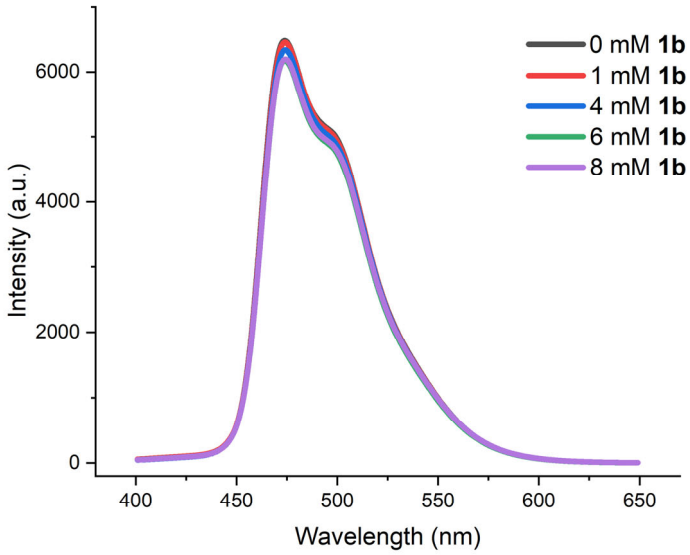
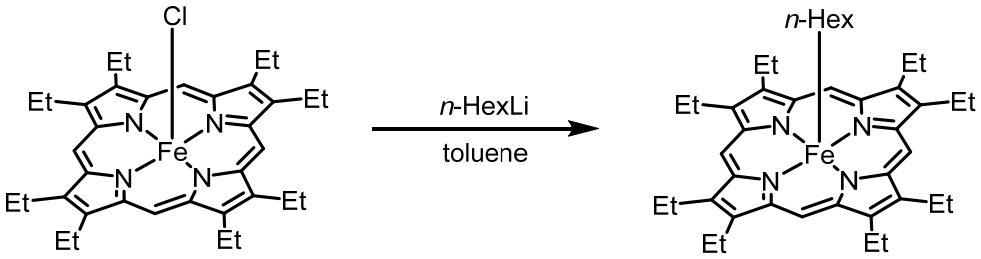


Figure S12. The emission quenching of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (0.005 mM) as a function of concentration of **1b** in deaerated TBME:PhCF$_3$ (1:1) with excitation at 380 nm. Conditions: (black curve) **1b** (0 mM); (red curve) **1b** (1 mM); (blue curve) **1b** (4 mM); (green curve) **1b** (6 mM); (purple curve) **1b** (8 mM).

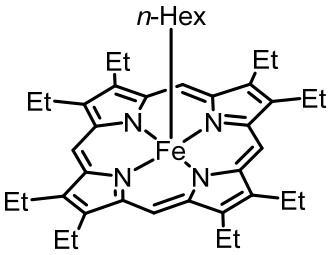
4. Isolation of catalytic intermediate and related studies.



Fe^1, 40% yield

Synthesis of Fe^1.[20] *Note: The compound **Fe^1** decomposes rapidly in the presence of O$_2$ and thus the following procedure was carried out either under an argon atmosphere using Schlenk technique or in a nitrogen-atmosphere glovebox.* To an oven-dried 50 mL Schlenk flask equipped with a stir bar was added Fe(OEP)Cl (311 mg, 0.50 mmol, 1.05 equiv) and toluene (15 mL). The resulting dark brown solution was sparged with argon for 15 minutes, after which it was cooled to 0 °C. Then, while the reaction mixture was stirred vigorously, *n*-HexLi (2.5 M in hexanes, 190 uL, 0.48 mmol) was added dropwise, resulting in an immediate color change to dark red. The resulting solution was stirred for 1 h at 0 °C, at which point H$_2$O (5 mL) was added. The aqueous layer was then separated and the organic layer was dried over Na$_2$SO$_4$, followed by filtration over basic alumina. The eluent was concentrated in vacuo while maintaining a temperature ≤ 30 °C and the resulting

dark red solids were purified via crystallization from 1:3 benzene:toluene at −20 °C, providing the title compound as a dark red crystalline solid (134.6 mg, 40% yield).

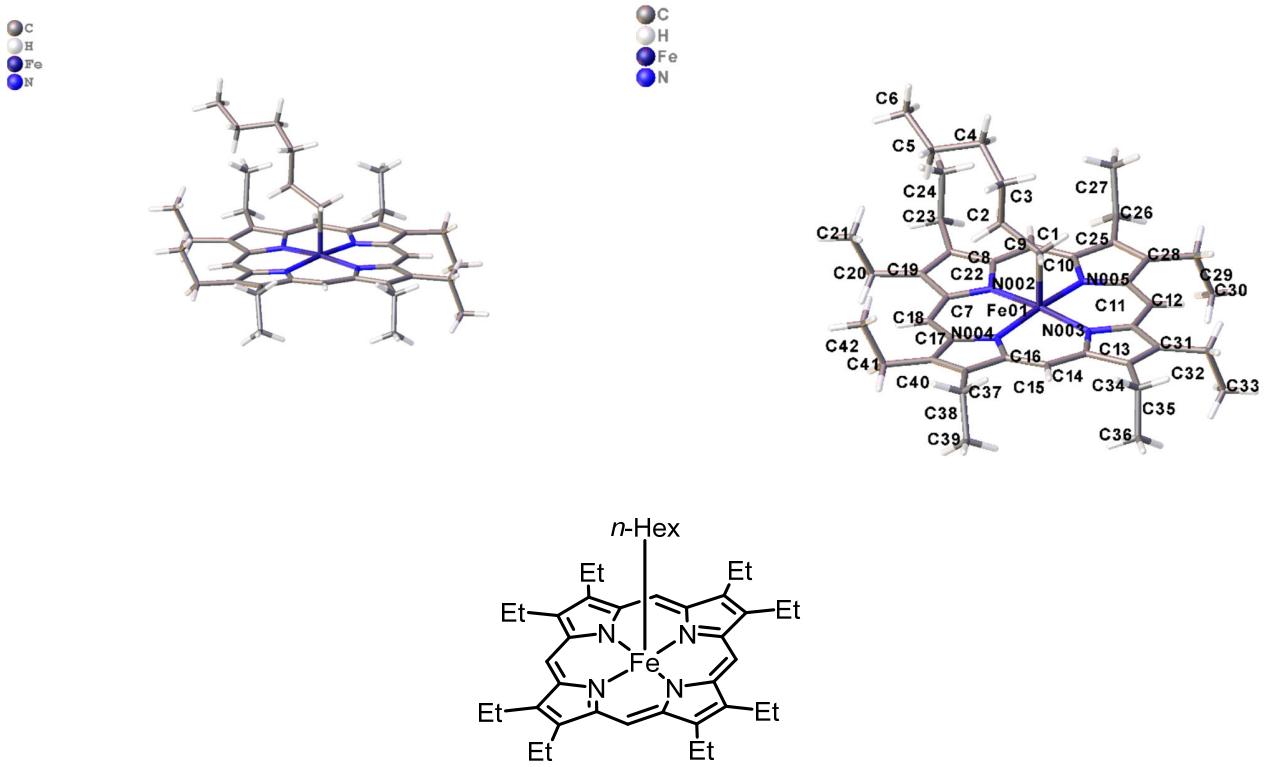


^{1}H NMR (400 MHz, Benzene-d6) δ 18.83 (s, 2H) Fe–γ–CH_2, 11.48 (s, 2H) Fe–δ–CH_2, 4.88 (s, 2H) Fe–ε–CH_2, 3.49 (t, J = 7.2 Hz, 3H) Fe–ζ–CH_3, 3.23 (s, 4H) OEP–*meso*-H, 2.15 – 2.22 (m, 8H) OEP–α–CH_2, -2.24 – -2.28 (m, 24H) OEP–β–CH_3, -2.33 – -2.40 (m, 8H) OEP–α'–CH_2, -58.53 (s, 2H) Fe–β–CH_2.

Fe–α–CH_2: No signal observed.[21]

HRMS (ESI-MS) m/z $[M]^+$ calcd for $C_{42}H_{57}FeN_4$: 673.3927, found: 673.3915.

X-ray crystallographic structure



CCDC: 2330035

***n*-Hex-Fe(OEP) (Fe^1).** X-ray quality crystals were obtained by slow evaporation of a saturated solution in benzene/toluene of a sample. A suitable crystal was selected and measured

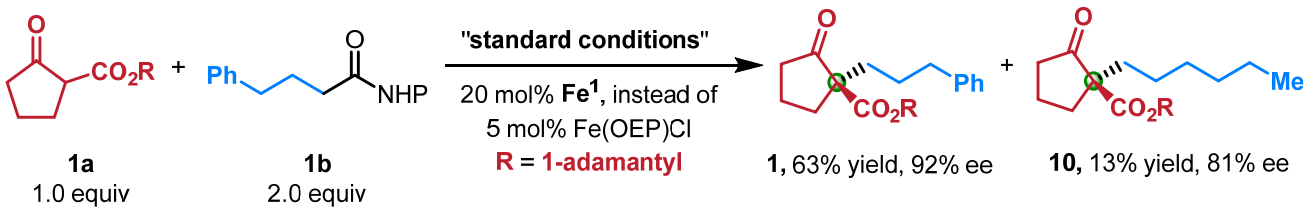
on a Bruker APEX-III CMOS diffractometer. The crystal was kept at 273.15 K during data collection.

Table S1. Crystal data for $C_{42}H_{57}FeN_4$.

Identification code	1
Empirical formula	$C_{42}H_{57}FeN_4$
Formula weight	673.76
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
a/Å	13.2137(13)
b/Å	13.4390(11)
c/Å	13.906(2)
α/°	97.254(4)
β/°	114.623(4)
γ/°	115.557(3)
Volume/Å^3	1878.9(4)
Z	2
ϱcalcg/cm^3	1.191
μ/mm^{-1}	0.435
F(000)	726.0
Crystal size/mm^3	0.23 × 0.22 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.57 to 50.936
Index ranges	-15 ≤ h ≤15, -14 ≤ k ≤ 16, -16 ≤ I ≤ 16
Reflections collected	36897
Independent reflections	6816 [R_{int} = 0.0741, R_{sigma} = 0.0483]
Data/restraints/parameters	6816/15/453
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0761, wR_2 = 0.1794
Final R indexes [all data]	R_1 = 0.1157, wR_2 = 0.2119
Largest diff. peak/hole / e Å^{-3}	0.53/-0.67

Table S2. Bond Lengths for n-HexFe(OEP).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.489(8)	C16	N004	1.375(5)
C1	Fe01	2.027(5)	C17	C18	1.384(6)
C2	C3	1.510(8)	C17	C40	1.447(6)
C3	C4	1.519(14)	C17	N004	1.365(5)
C4	C5	1.512(15)	C19	C20	1.485(6)
C5	C6	1.519(14)	C19	C22	1.363(7)
C7	C18	1.389(6)	C20	C21	1.512(8)
C7	C19	1.451(6)	C22	C23	1.500(7)
C7	N002	1.372(5)	C23	C24	1.530(9)
C8	C9	1.381(6)	C25	C26	1.505(6)
C8	C22	1.445(6)	C25	C28	1.356(7)
C8	N002	1.369(5)	C26	C27	1.513(9)
C9	C10	1.389(6)	C28	C29	1.498(7)
C10	C25	1.443(6)	C29	C30	1.506(10)
C10	N005	1.371(5)	C31	C32	1.497(7)
C11	C12	1.396(6)	C31	C34	1.362(7)
C11	C28	1.444(6)	C32	C33	1.501(8)
C11	N005	1.360(5)	C34	C35	1.503(6)
C12	C13	1.383(6)	C35	C36	1.507(8)
C13	C31	1.449(6)	C37	C38	1.513(7)
C13	N003	1.376(5)	C37	C40	1.357(7)
C14	C15	1.383(6)	C38	C39	1.492(8)
C14	C34	1.445(6)	C40	C41	1.495(7)
C14	N003	1.377(5)	C41	C42	1.511(9)
C15	C16	1.379(6)	Fe01	N002	1.983(3)
C16	C37	1.447(6)	Fe01	N003	1.984(4)
			Fe01	N004	1.991(4)
			Fe01	N005	1.994(4)



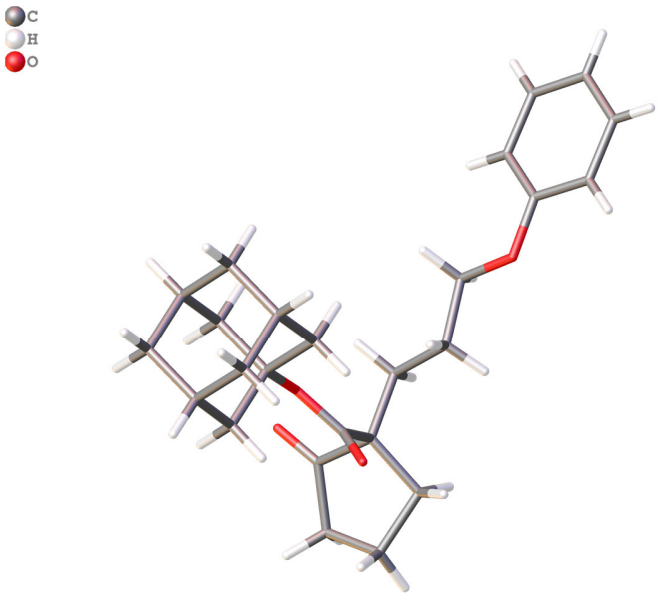
Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with **Fe**[1] (27 mg, 0.040 mmol, 20 mol%), (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (4.5 mg, 0.0040 mmol, 2.0 mol%), (*S*)-**A1** (22.0 mg, 0.040 mmol, 20 mol%), **1a** (52.4 mg, 0.20 mmol, 1.0 equiv), and **1b** (123.6 mg, 0.40 mmol, 2.0 equiv), and a stir bar. Anhydrous MTBE (1 mL) and PhCF$_3$ (1 mL) were added sequentially, and the vial was capped with a PTFE septum cap. The vial was transferred out of the glovebox and placed in the photoreactor (**Figure S1**). The reaction was irradiated with blue LEDs (450 nm) and was stirred at 20 °C for 36 hours. The reaction mixture was passed through a plug of silica gel, and the vial, the cap, and the silica gel were rinsed with DCM. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.

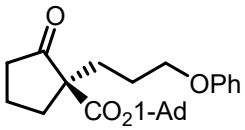
1, 47.6 mg, 63% yield, 92% ee.

10, 8.7 mg, 13% yield, 81% ee.

IX. Assignments of Absolute Configuration

The configuration of the coupling product illustrated in **Fig. 3A, entry 15**, using (*S*)-**A1**, was determined via X-ray crystallography.





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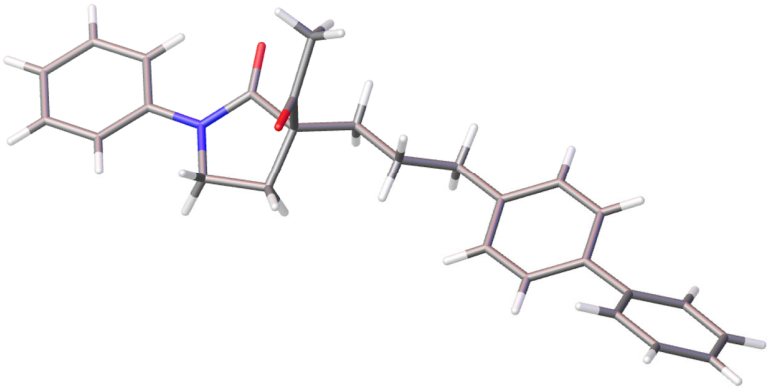
Adamantan-1-yl (*R*)-2-oxo-1-(3-phenoxypropyl)cyclopentane-1-carboxylate (Fig. 3A, entry 15). X-ray quality crystals were obtained by slow evaporation of a saturated solution in DCM/hexanes of a sample synthesized using (*S*)-**A1**. A suitable crystal was selected and measured on a Bruker APEX-III CMOS diffractometer. The crystal was kept at 100.0 K during data collection. The absolute stereochemistry was determined on the basis of the flack parameter.

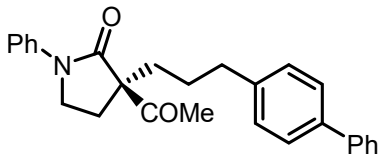
Table S3. Crystal data for $C_{25}H_{32}O_4$.

Identification code	231107a_a
Empirical formula	$C_{25}H_{32}O_4$
Formula weight	396.50
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.521 (4)
b/Å	11.117 (8)

c/Å	29.173 (19)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2115 (2)
Z	4
ρ_{calc}g/cm^3	1.245
μ/mm^{-1}	0.659
F(000)	856.0
Crystal size/mm^3	0.28 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.058 to 148.738
Index ranges	-7 ≤ h ≤ 7, -13 ≤ k ≤ 13, -36 ≤ l ≤ 35
Reflections collected	15305
Independent reflections	4196 [R_{int} = 0.0676, R_{sigma} = 0.0500]
Data/restraints/parameters	4196/0/262
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1044
Final R indexes [all data]	R_1 = 0.0512, wR_2 = 0.1094
Largest diff. peak/hole / e Å^{-3}	0.43/-0.22
Flack parameter	-0.12 (17)

The configuration of the coupling product illustrated in **Fig. 3B, entry 35**, using (*S*)-**A1**, was determined via X-ray crystallography.





CCDC: 2314298

(*R*)-3-(3-([1,1'-Biphenyl]-4-yl)propyl)-3-acetyl-1-phenylpyrrolidin-2-one (Fig. 3B, entry 28). X-ray quality crystals were obtained by slow evaporation of a saturated solution in DCM/hexanes of a sample synthesized using (*S*)-**A1**. A suitable crystal was selected and measured on a Bruker APEX-III CMOS diffractometer. The crystal was kept at 100.0 K during data collection. The absolute stereochemistry was determined on the basis of the flack parameter.

Table S4. Crystal data for $C_{27}H_{27}NO_2$.

Identification code	cu_231207a_0m_5
Empirical formula	$C_{27}H_{27}NO_2$
Formula weight	397.49
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$ (4)
a/Å	6.0417 (4)
b/Å	35.8990 (10)
c/Å	9.8580 (3)

α/°	90
β/°	94.775 (2)
γ/°	90
Volume/Å^3	2130.69 (11)
Z	4
ρ_{calc}g/cm^3	1.239
μ/mm^{-1}	0.606
F(000)	848.0
Crystal size/mm^3	0.250 × 0.150 × 0.050
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.92 to 149.24 (0.80 Å)
Index ranges	$-7 \le h \le 7$, $0 \le k \le 44$, $0 \le l \le 12$
Reflections collected	4380
Independent reflections	4380 [R_{int} = 0.0761, R_{sigma} = 0.0244]
Data/restraints/parameters	4196/0/262
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0872
Final R indexes [all data]	R_1 = 0.0376, wR_2 = 0.0886
Largest diff. peak/hole / e Å^{-3}	0.14/-0.22
Flack parameter	0.20 (17)

X. References

1. Sahoo, D.; Quesne, M. G.; De Visser, S. P.; Rath, S. P. Hydrogen-Bonding Interactions Trigger a Spin-Flip in Iron(III) Porphyrin Complexes. *Angew. Chem. Int. Ed.* **2015**, *54*, 4796–4800.
2. Rezayee, N. M.; Enemærke, V. J.; Linde, S. T.; Lamhauge, J. N.; Reyes-Rodríguez, G. J.; Jørgensen, K. A.; Lu, C.; Houk, K. N. An Asymmetric S_N2 Dynamic Kinetic Resolution. *J. Am. Chem. Soc.* **2021**, *143*, 7509–7520.
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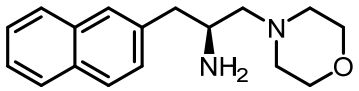
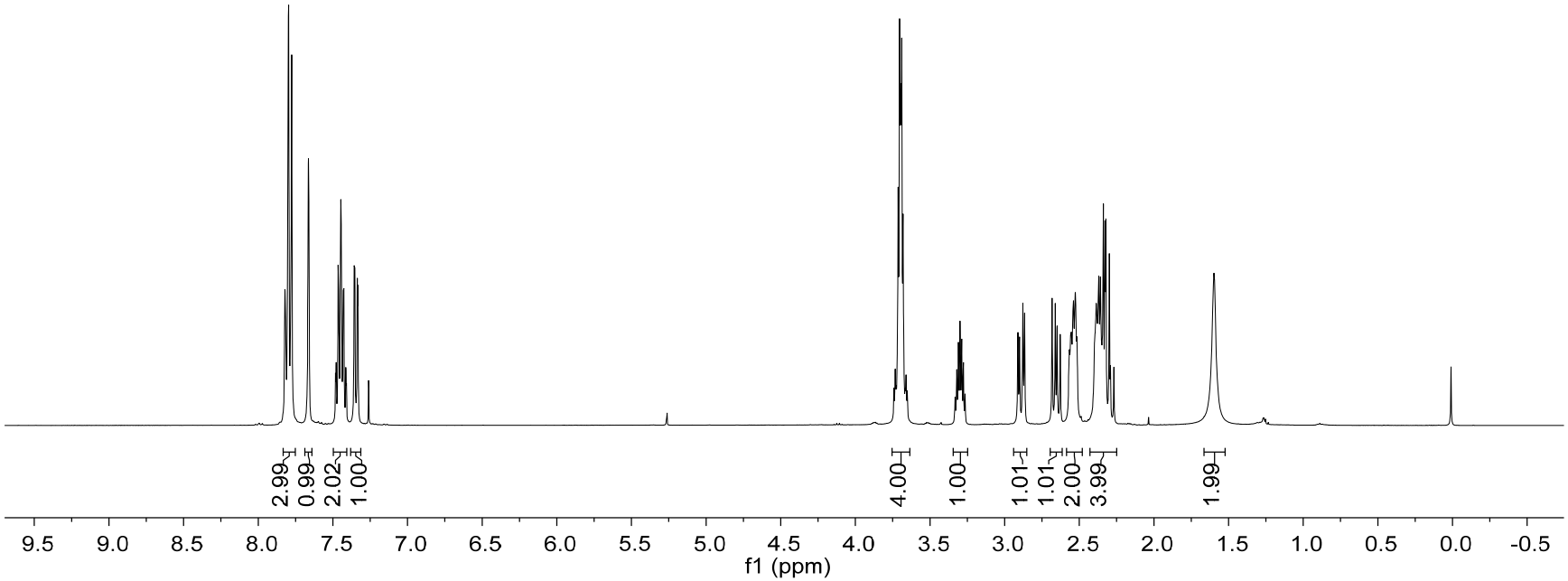
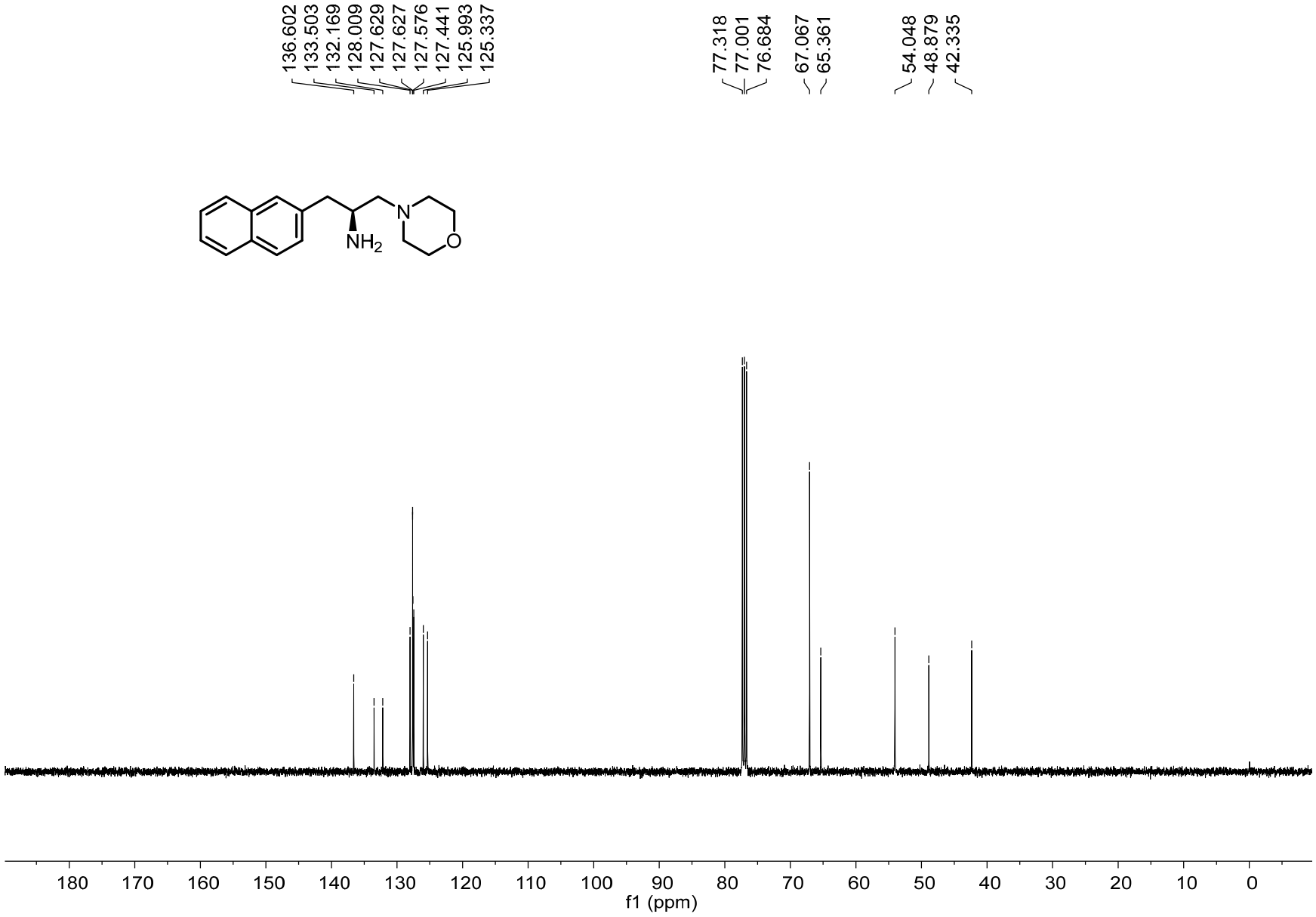
XI. NMR Spectra and Determination of Stereoselectivity



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127.441
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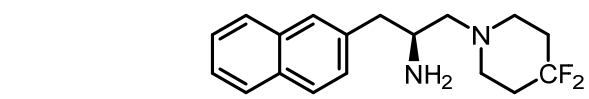
125.337
77.318
77.001
76.684
67.067
65.361
54.048
48.879
42.335
NH2
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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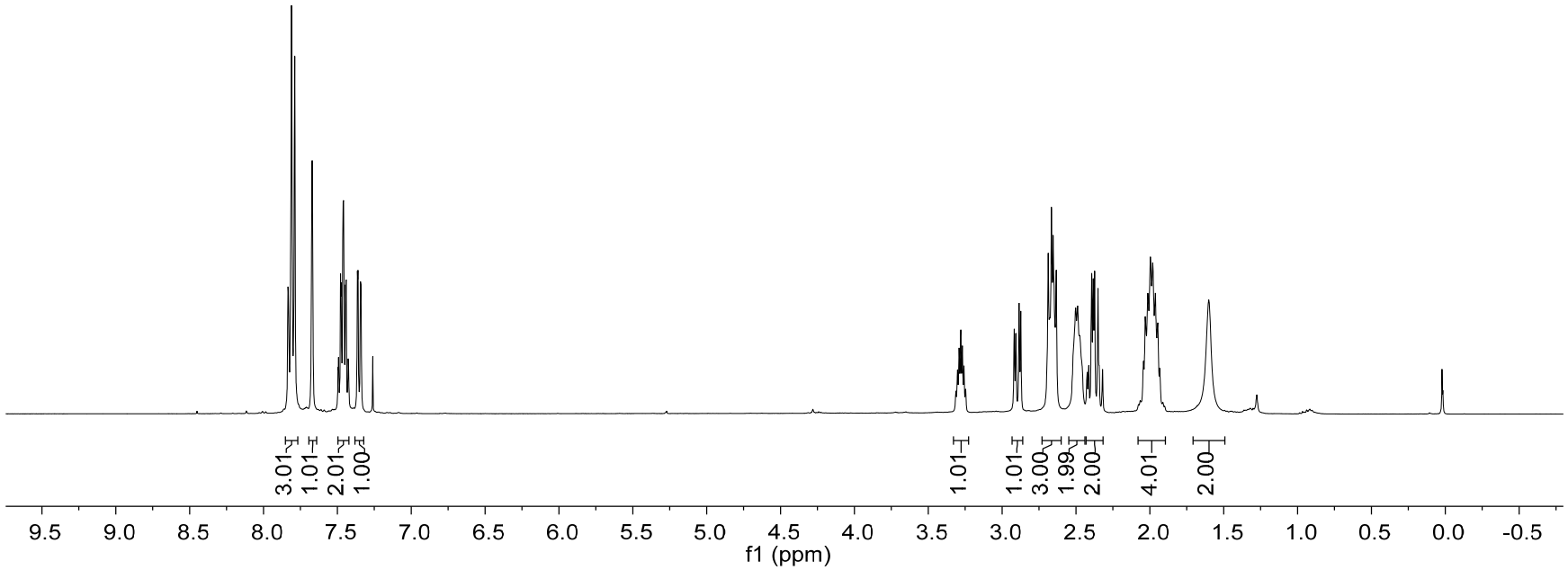
N
CF2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1.01
2.01
1.00
1.01
1.01
3.00
1.99
2.00
4.01
2.00
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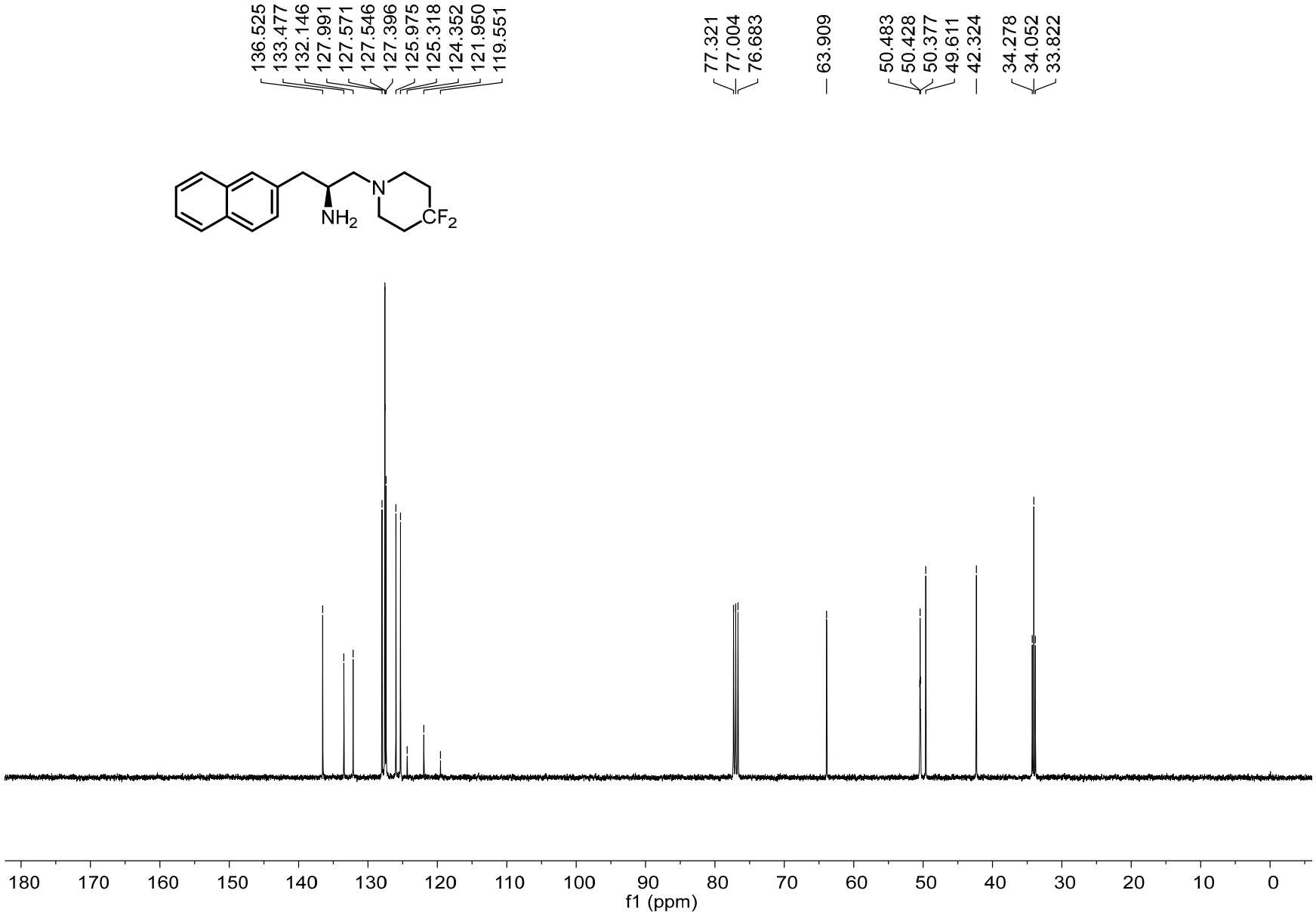
f1 (ppm)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125.975
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77.321
77.004
76.683
63.909
50.483
50.428
50.377
49.611
42.324
34.278
34.052
33.822
NH2
N
CF2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-97.879
NH2
N
CF2
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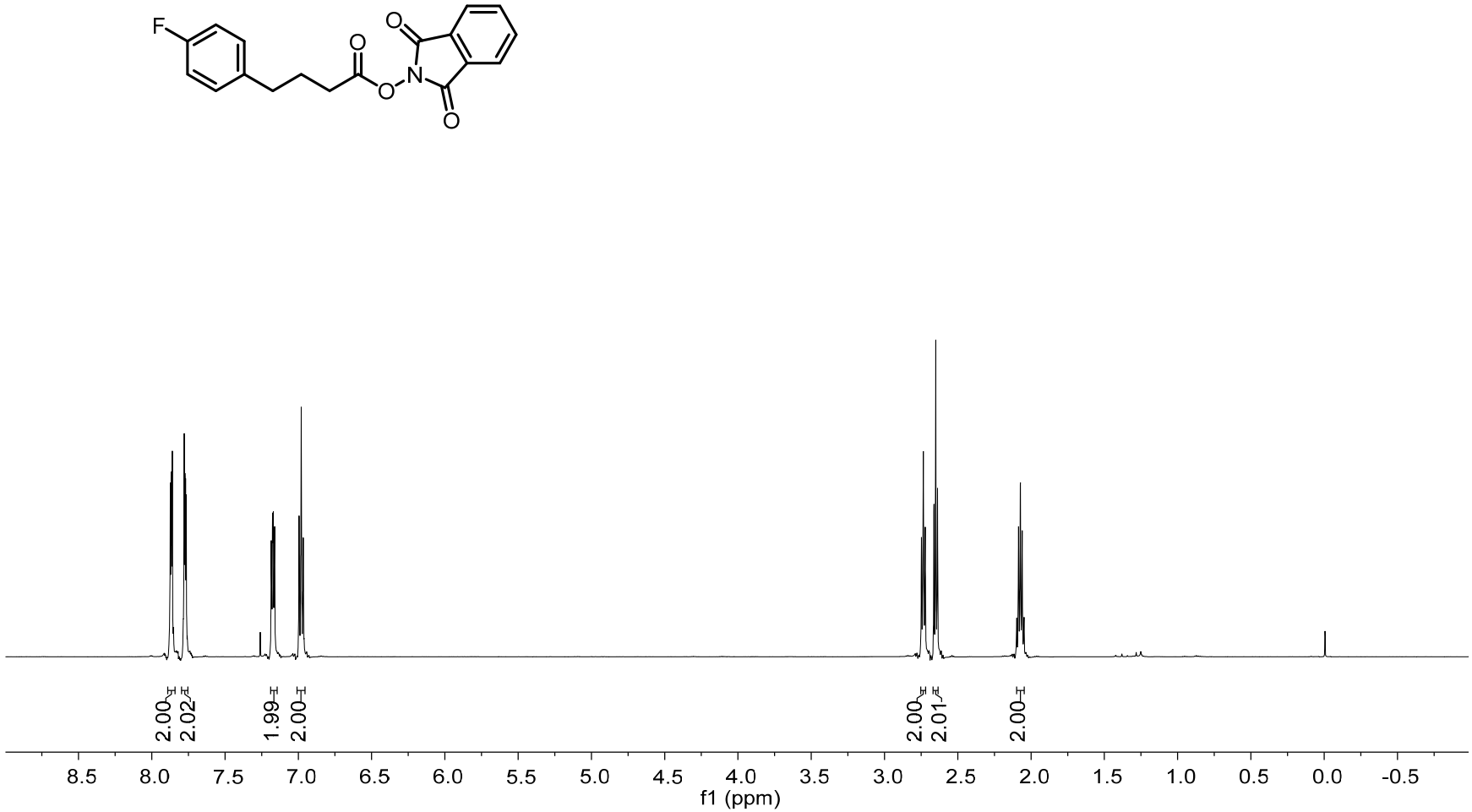
f1 (ppm)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O
O
N
O
O
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2.02
1.99
2.00
2.00
2.01
2.00
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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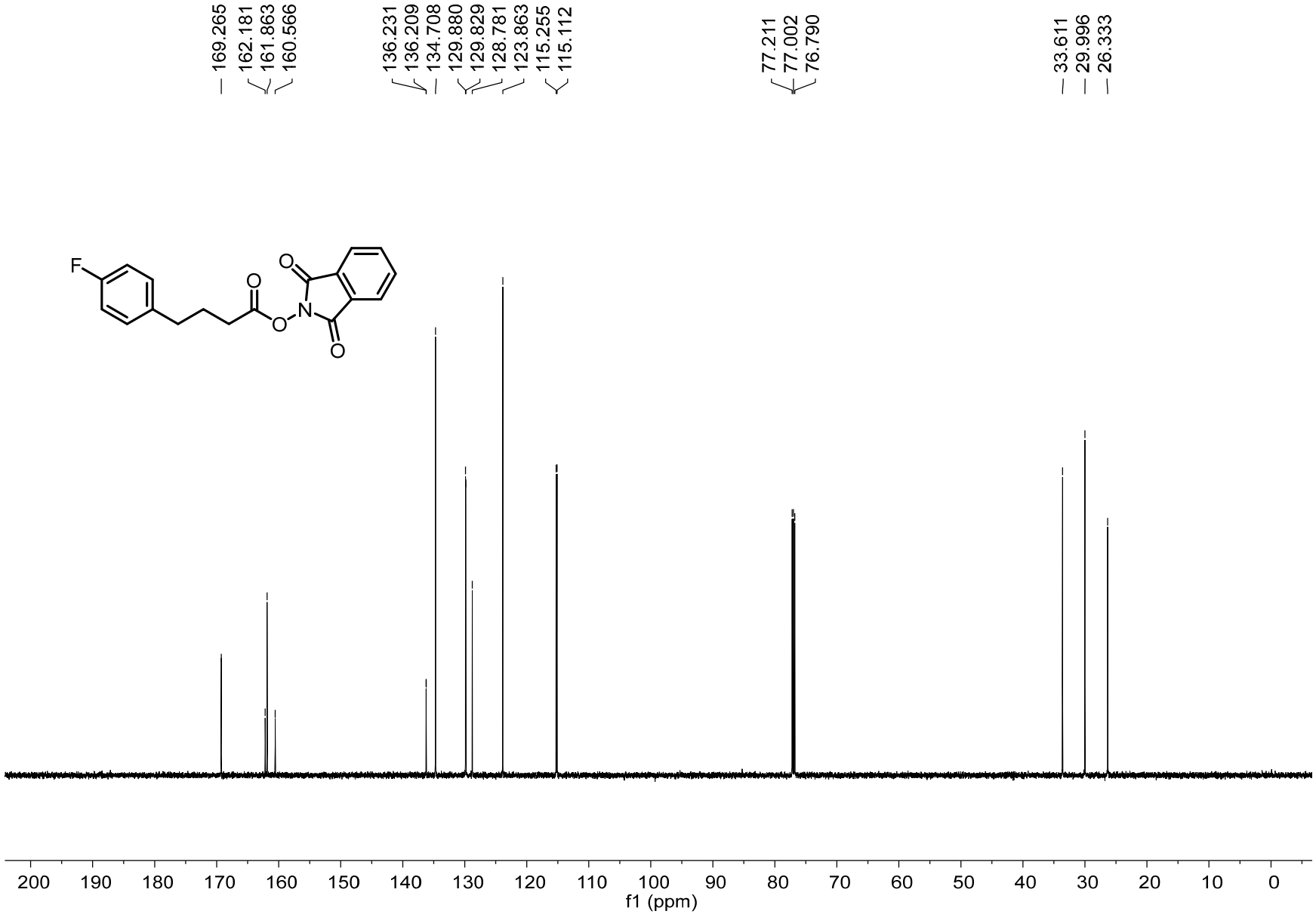
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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129.829
128.781
123.863
115.255
115.112
77.211
77.002
76.790
33.611
29.996
26.333
F
O
O
N
O
O
200
190
180
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130
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110
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90
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70
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50
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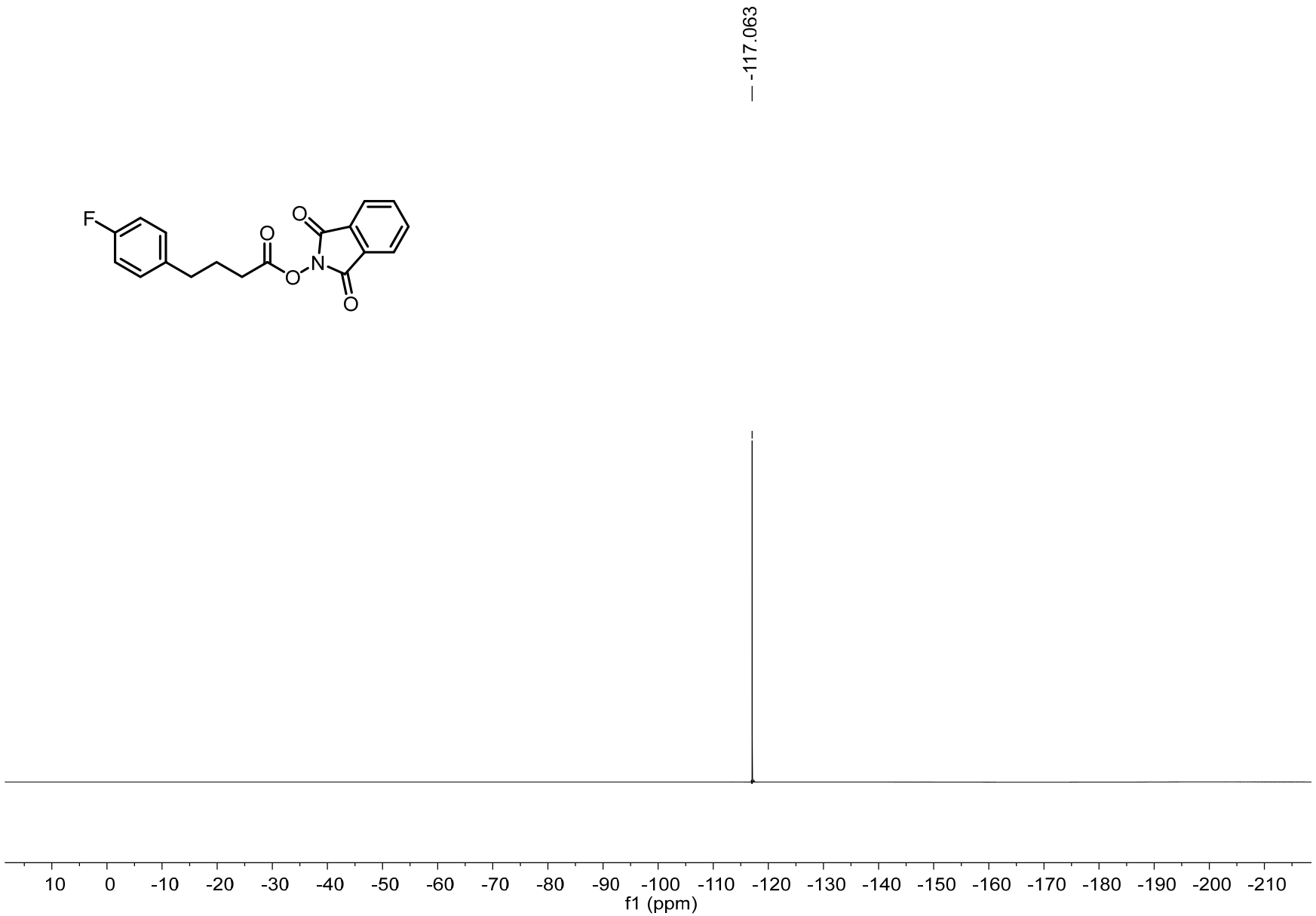
30
20
10
0
f1 (ppm)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O
N
O
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-10
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-30
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-50
-60
-70
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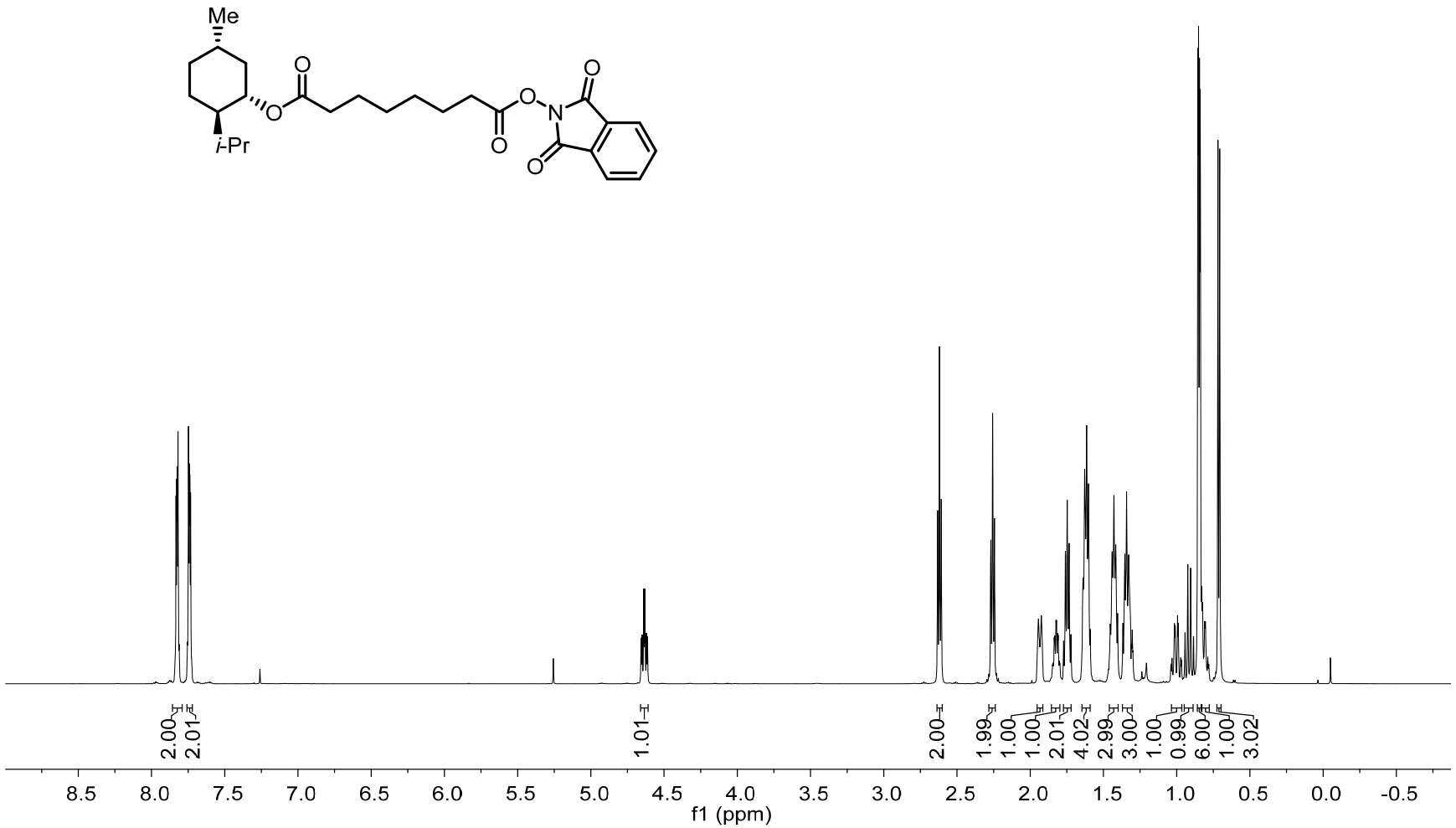
-170
-180
-190
-200
-210
f1 (ppm)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i-Pr
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O
O
O
O
N
O
O
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2.01
1.01
2.00
1.99
1.00
1.00
2.01
4.02
2.99
3.00
1.00
0.99
6.00
1.00
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
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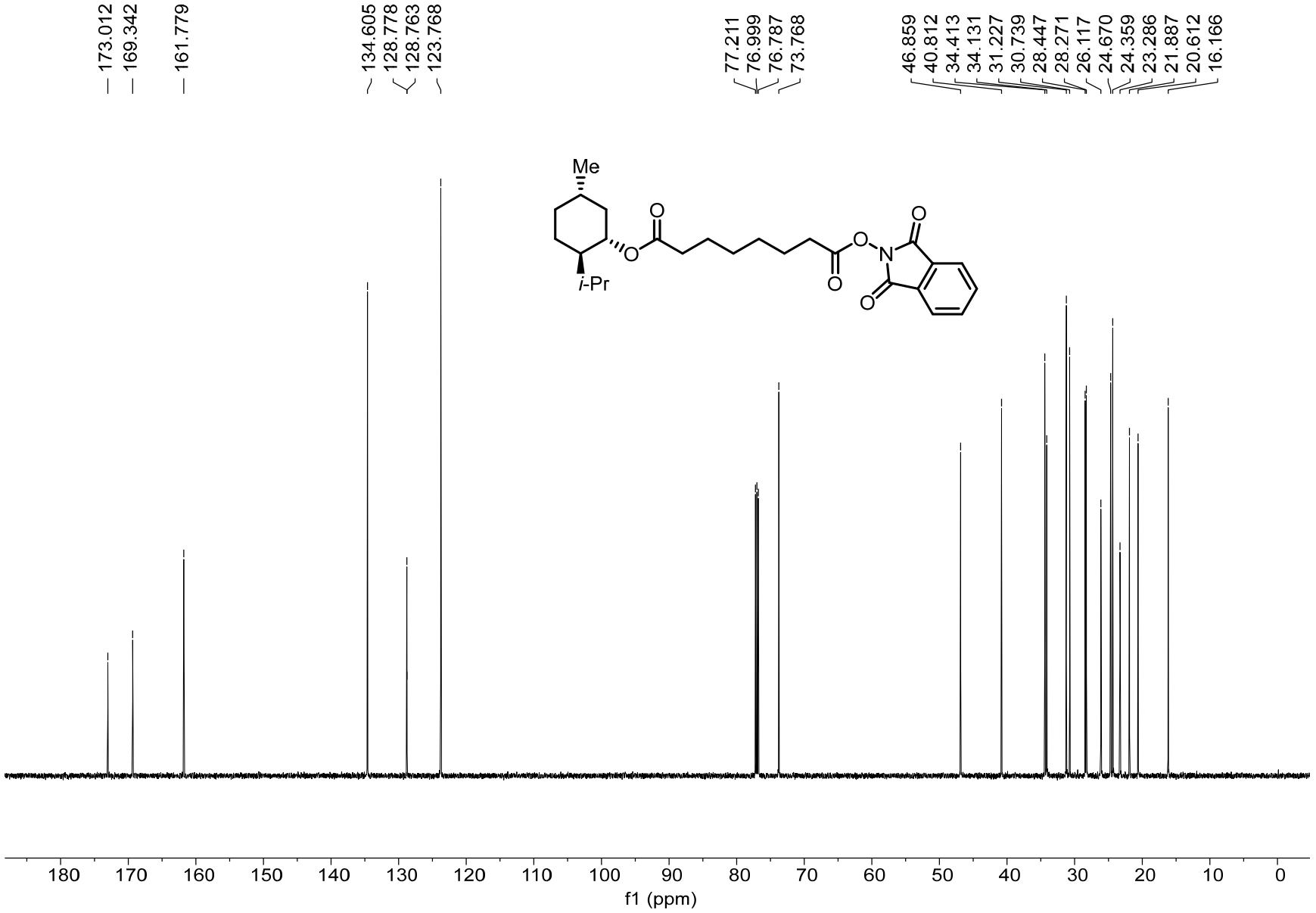
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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34.413
34.131
31.227
30.739
28.447
28.271
26.117
24.670
24.359
23.286
21.887
20.612
16.166
Me
i-Pr
O
O
O
O
O
N
O
O
180
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70
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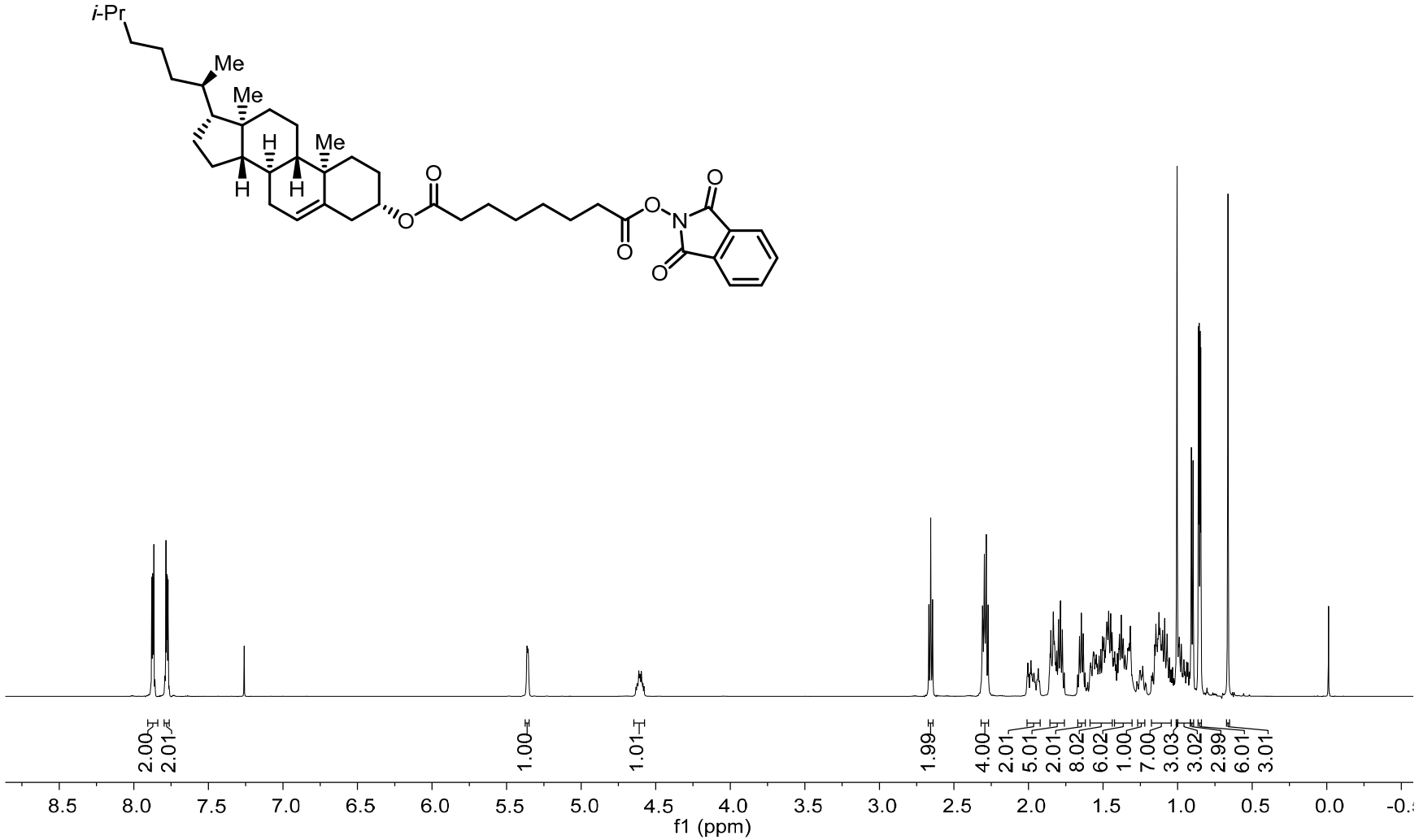
50
40
30
20
10
0
f1 (ppm)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H
Me
H
H
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5.01
2.01
8.02
6.02
1.00
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5.5
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4.5
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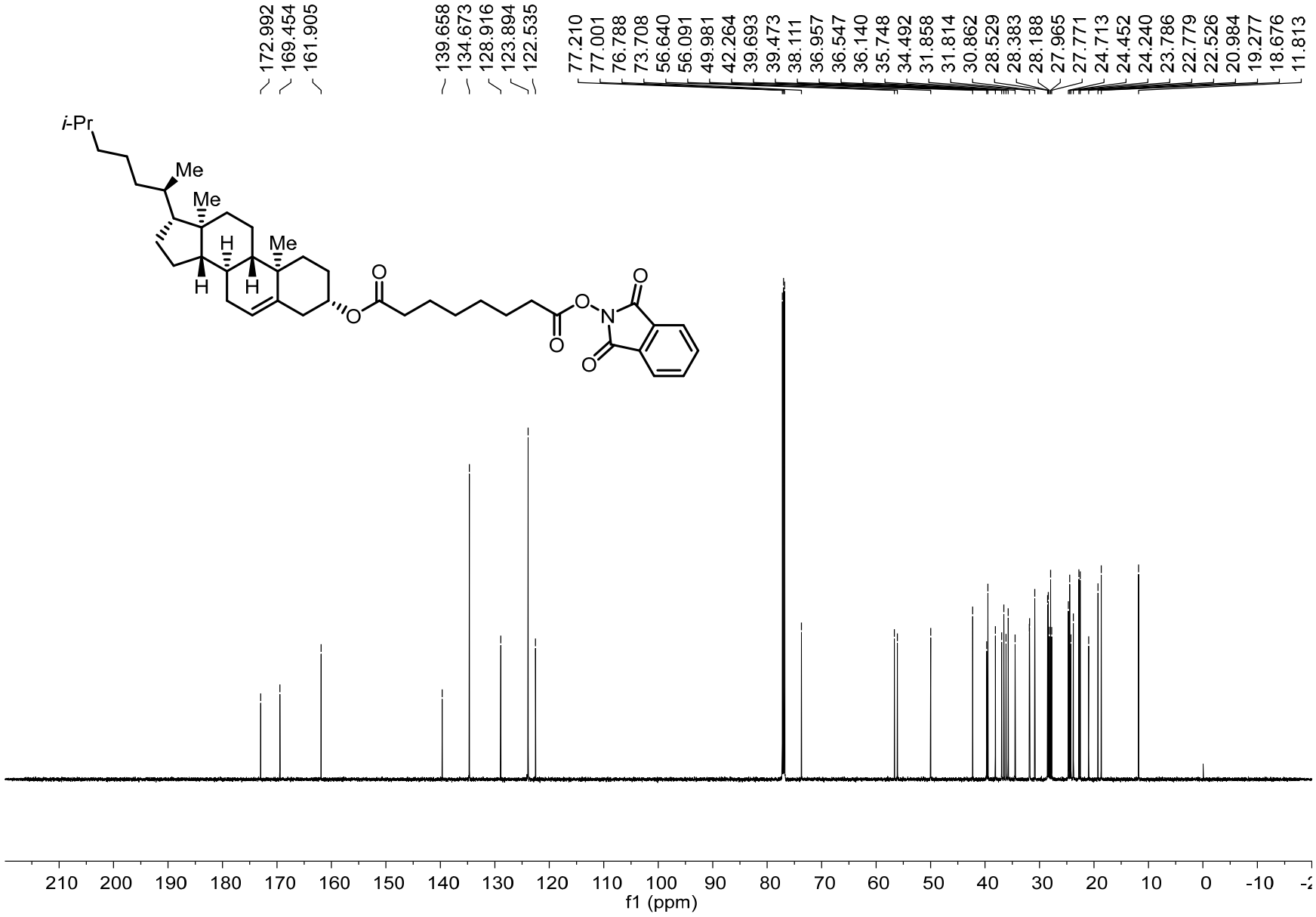
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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56.091
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42.264
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38.111
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36.547
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28.188
27.965
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24.713
24.452
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22.526
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19.277
18.676
11.813
i-Pr
Me
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Me
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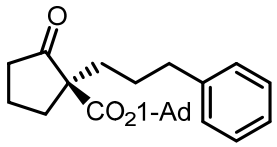
f1 (ppm)



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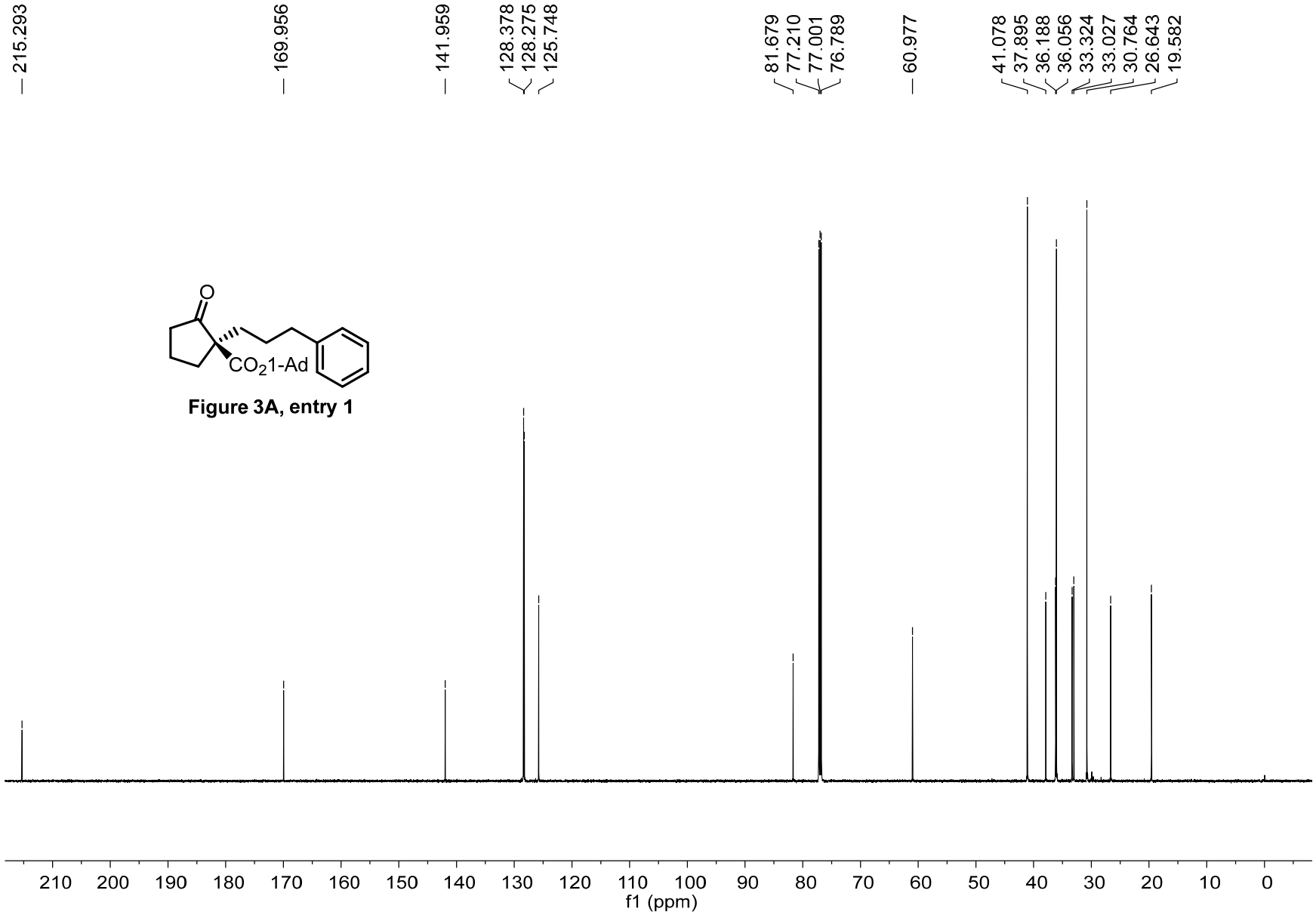

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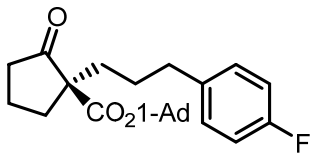

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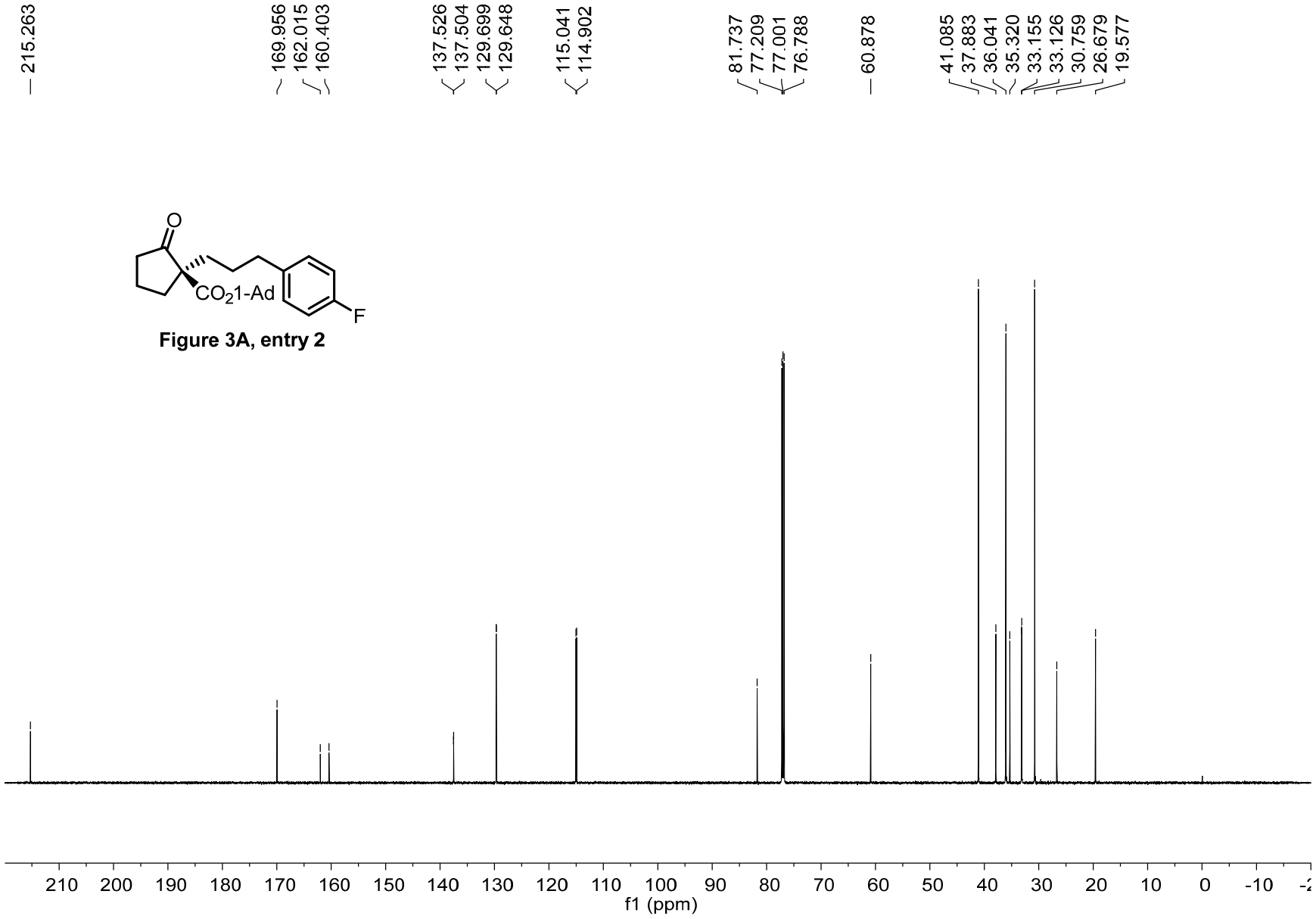

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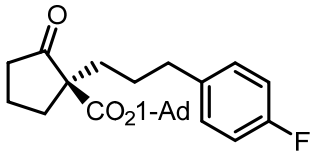

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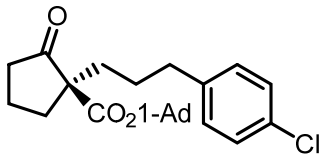

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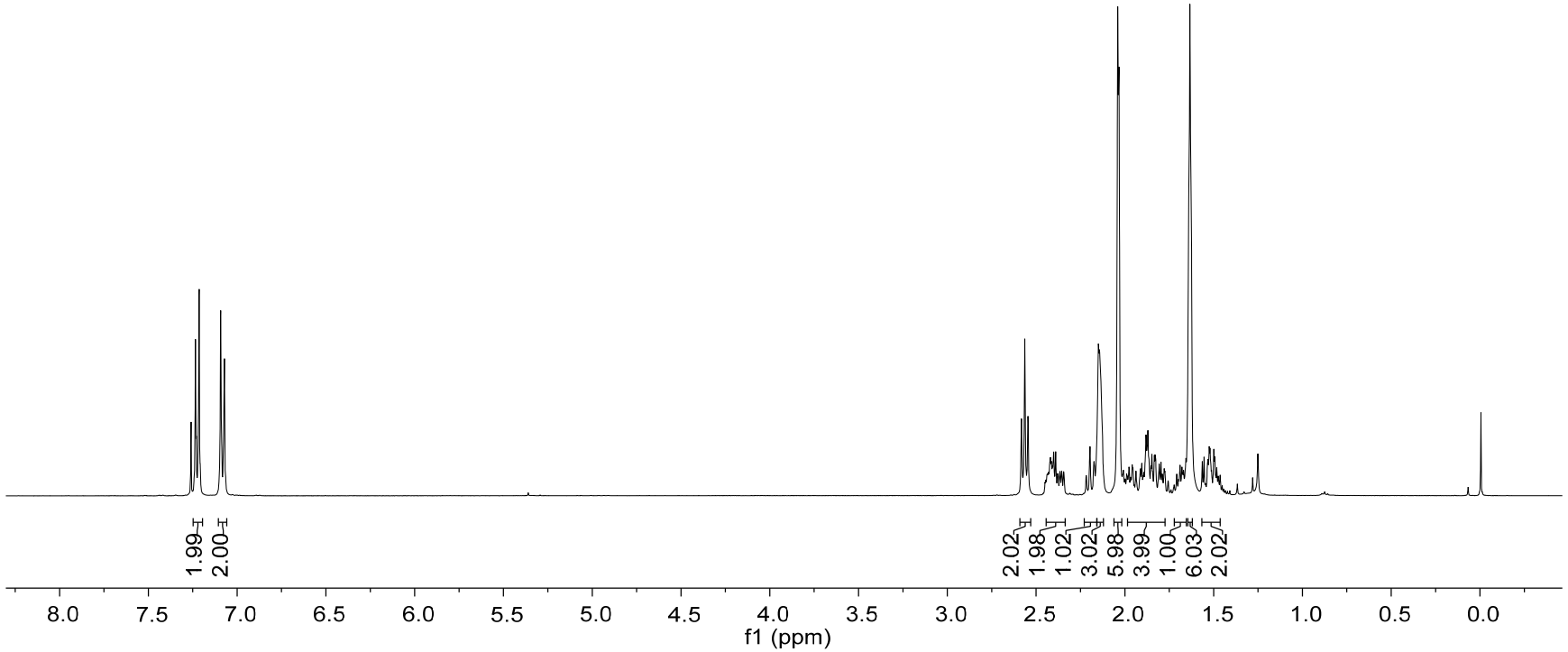

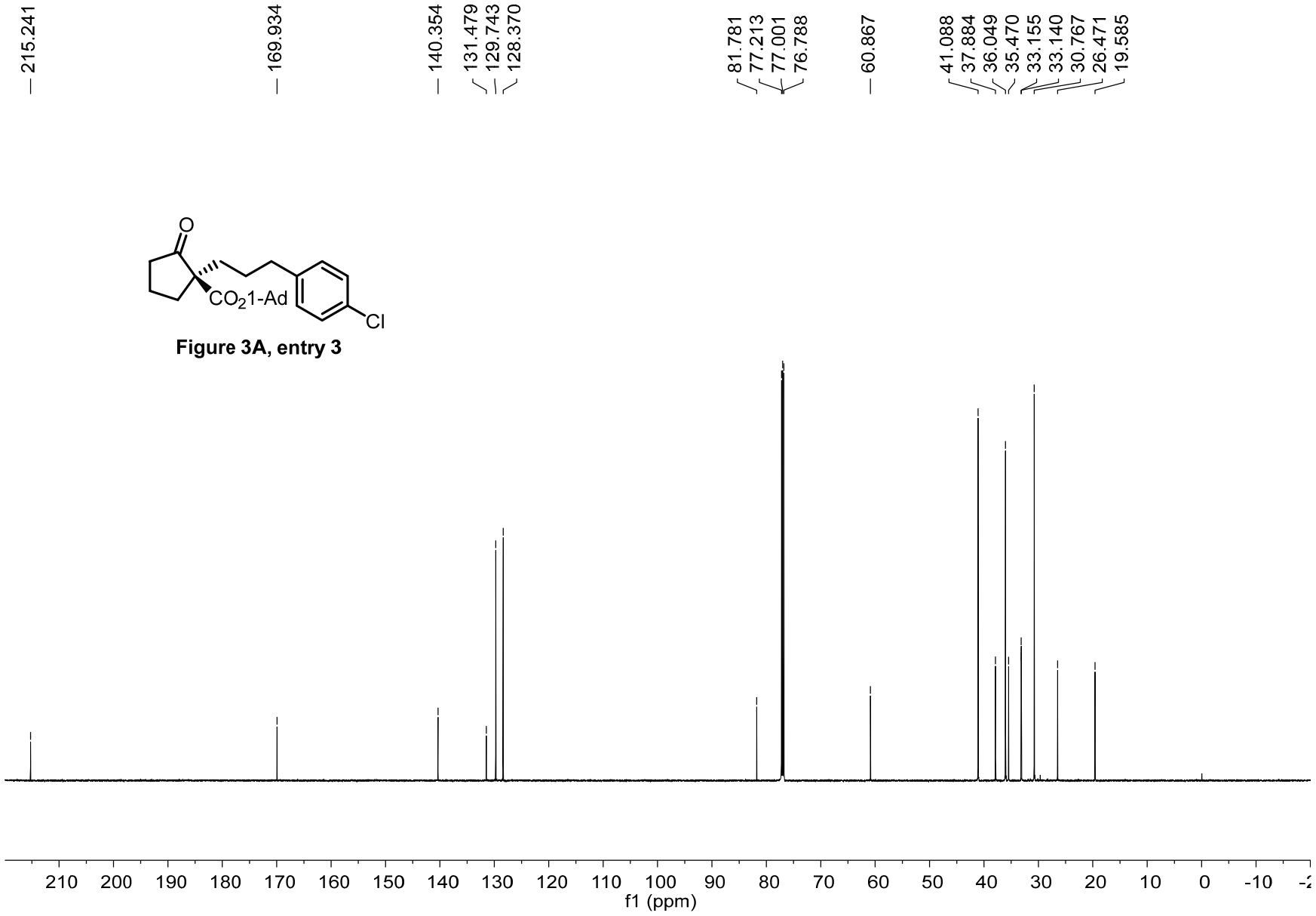

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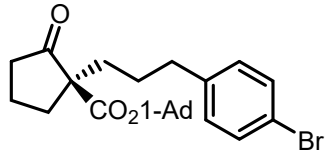

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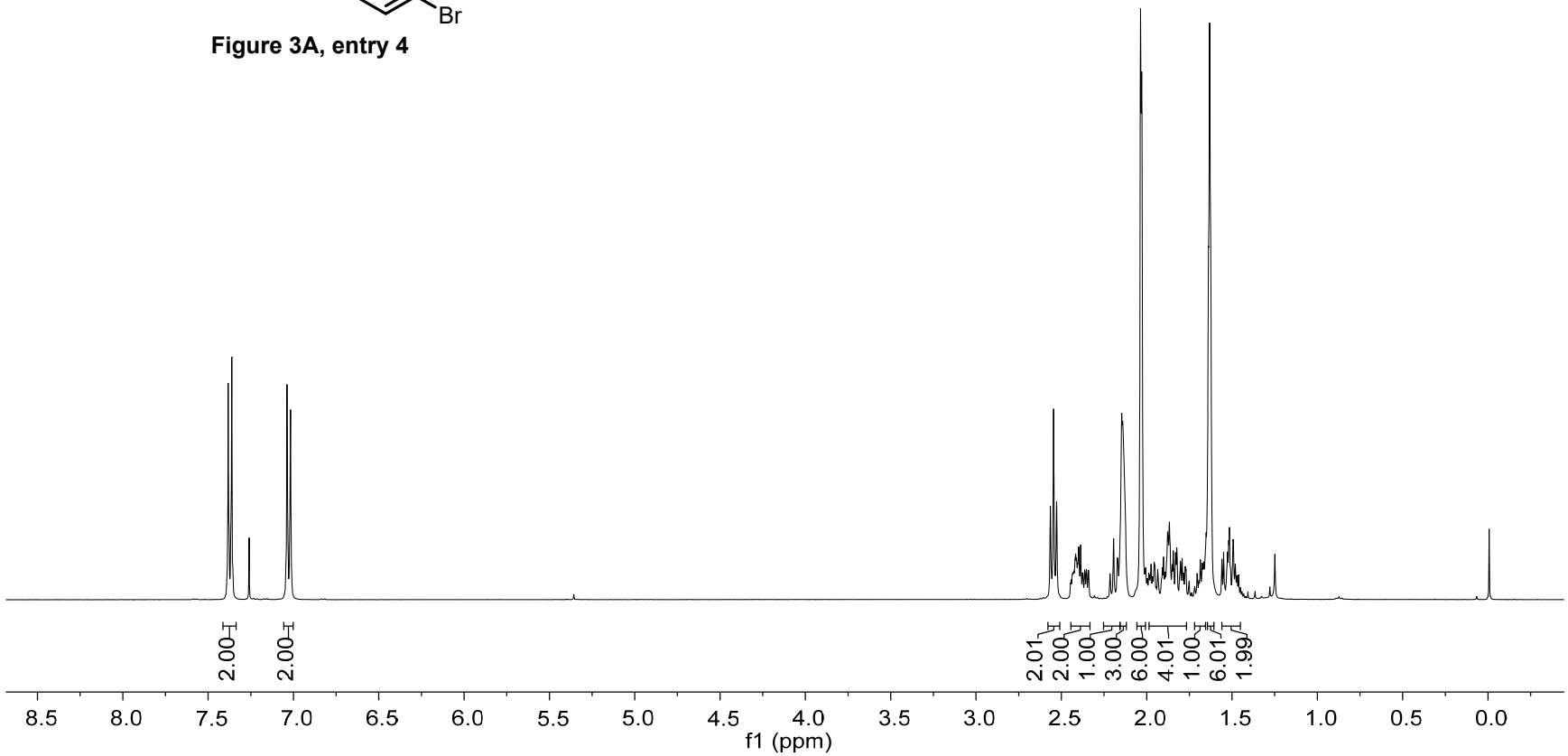

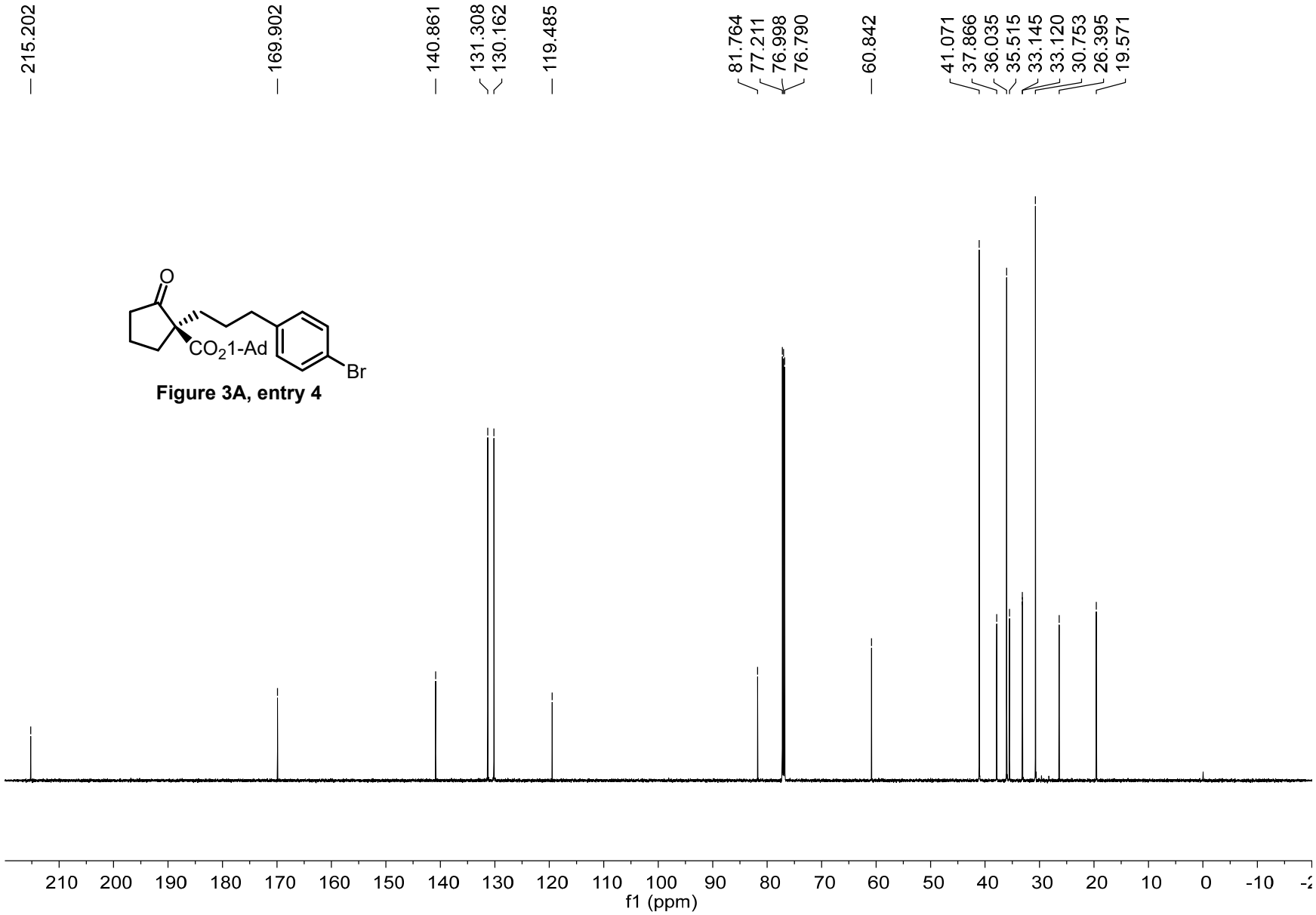

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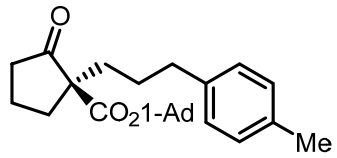

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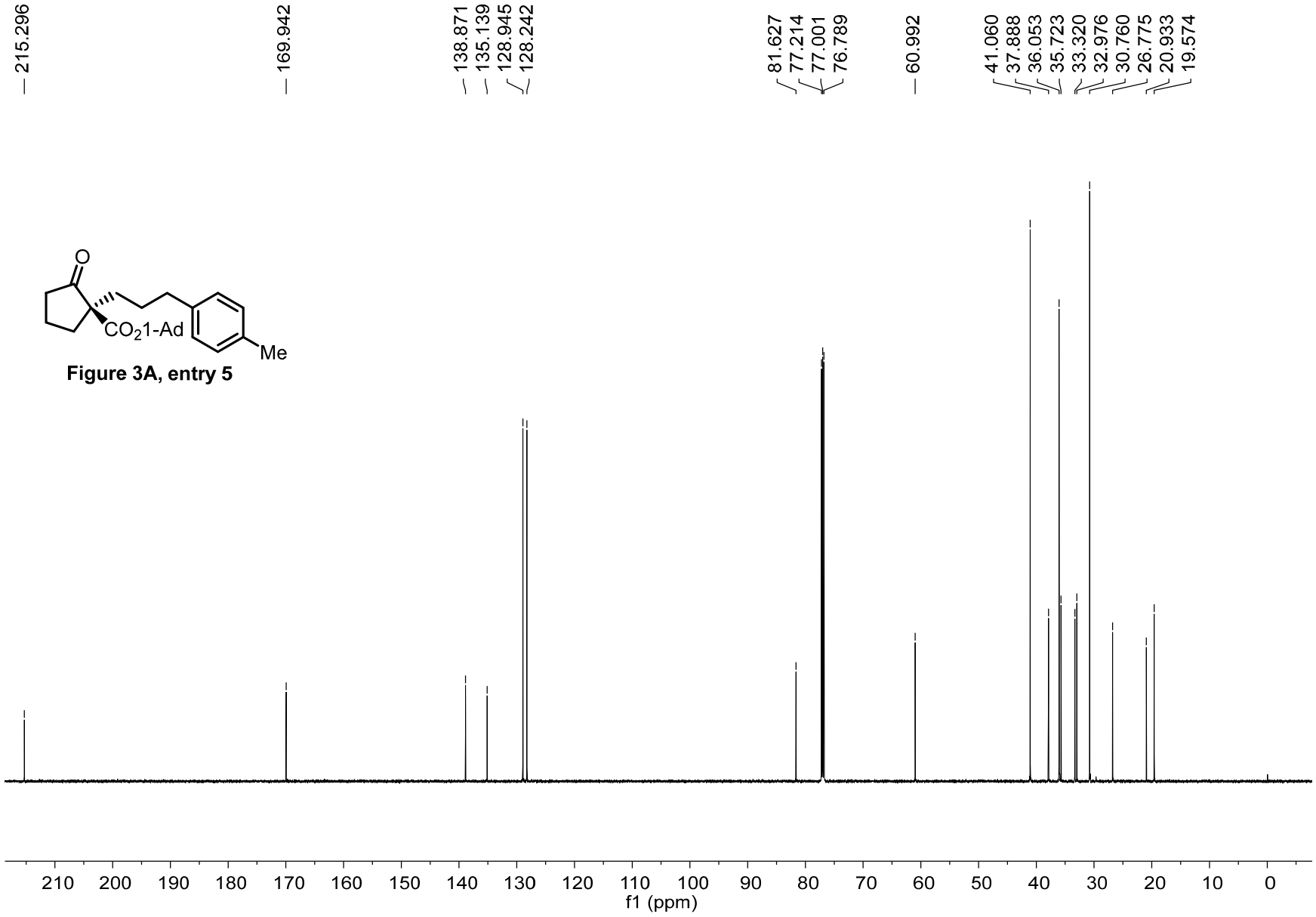

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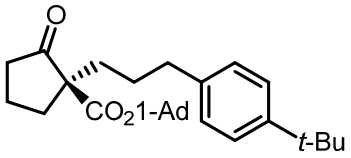

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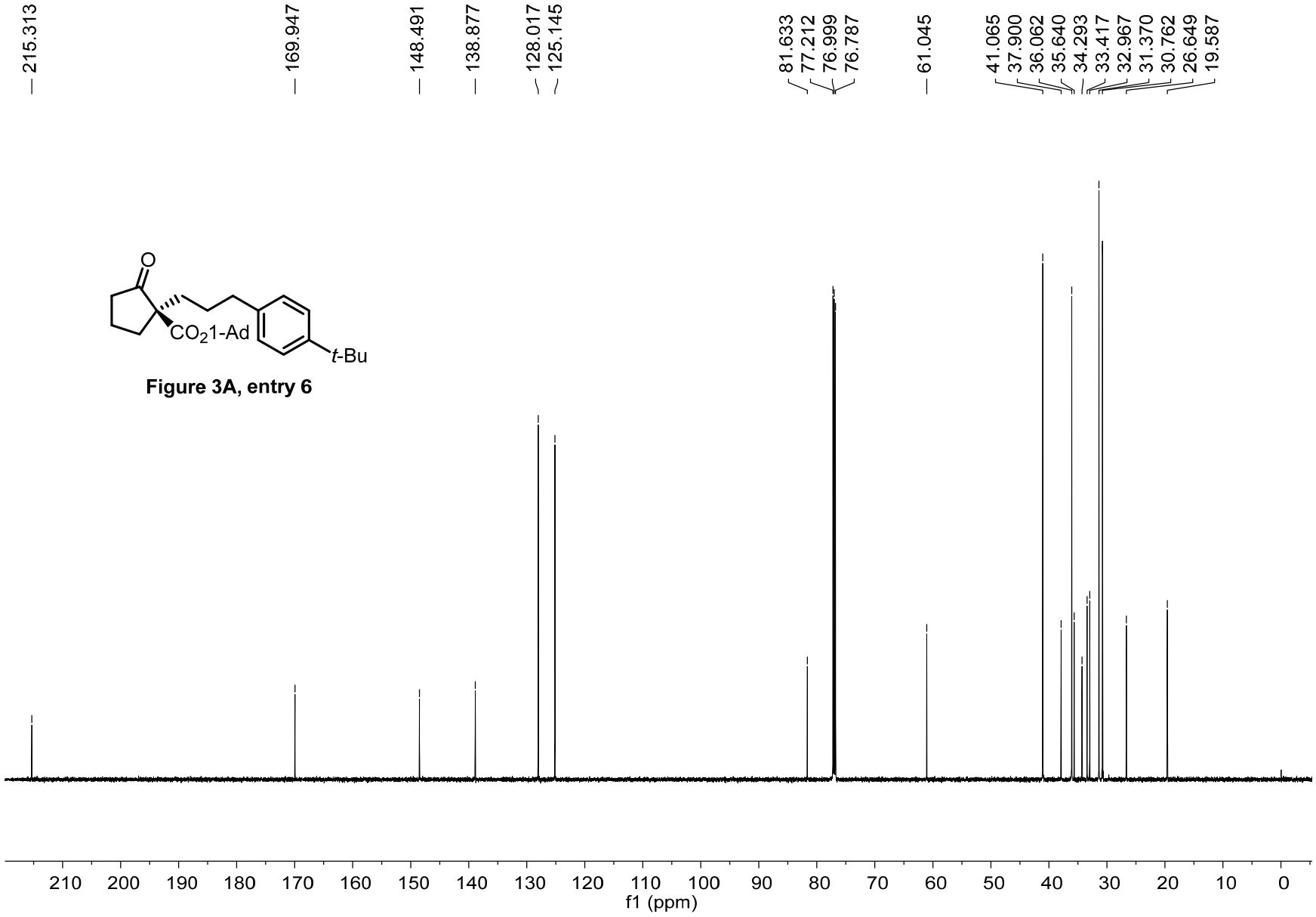

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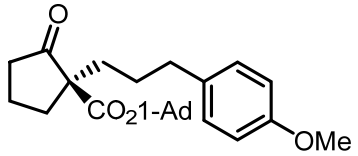

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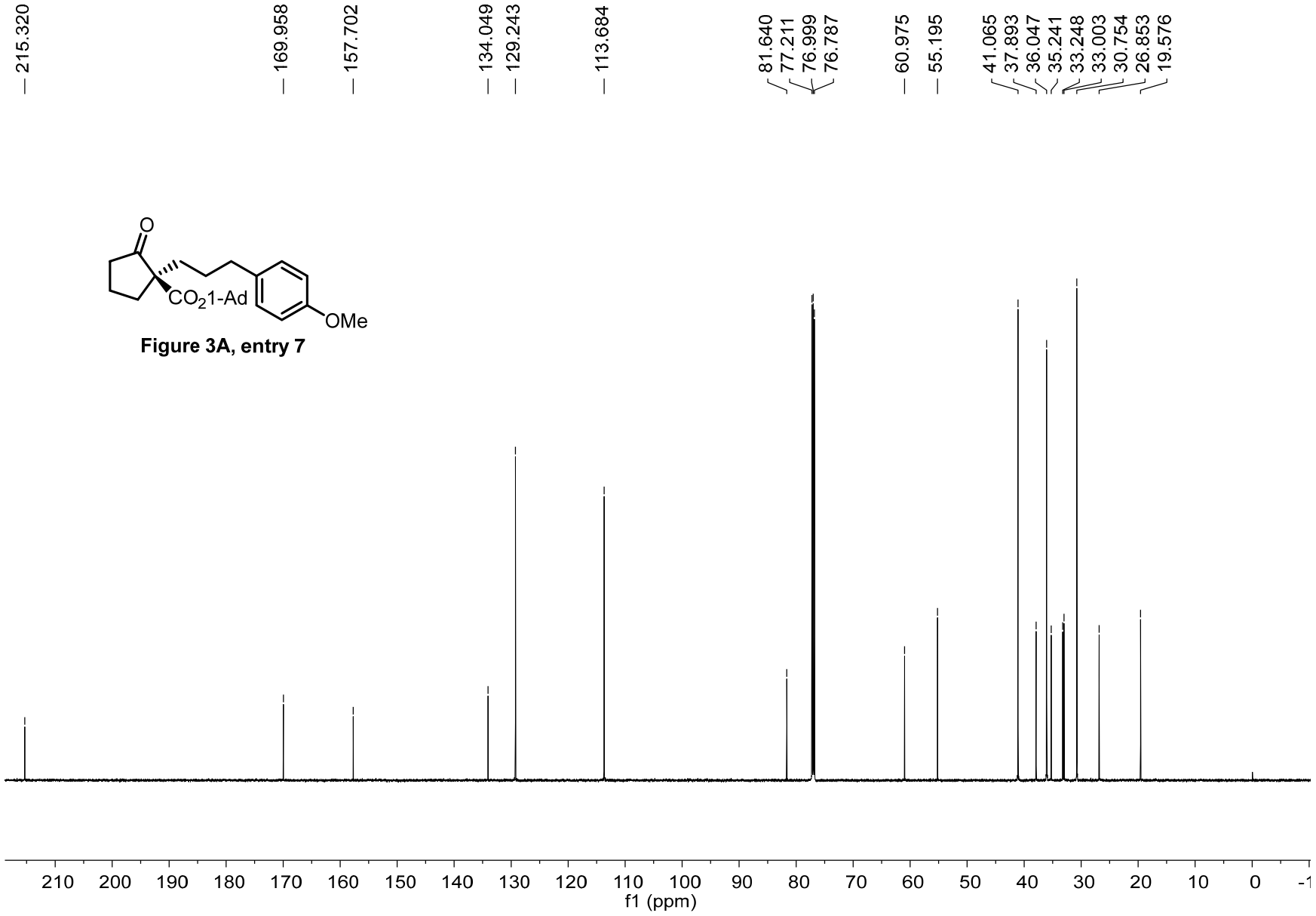

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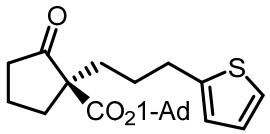

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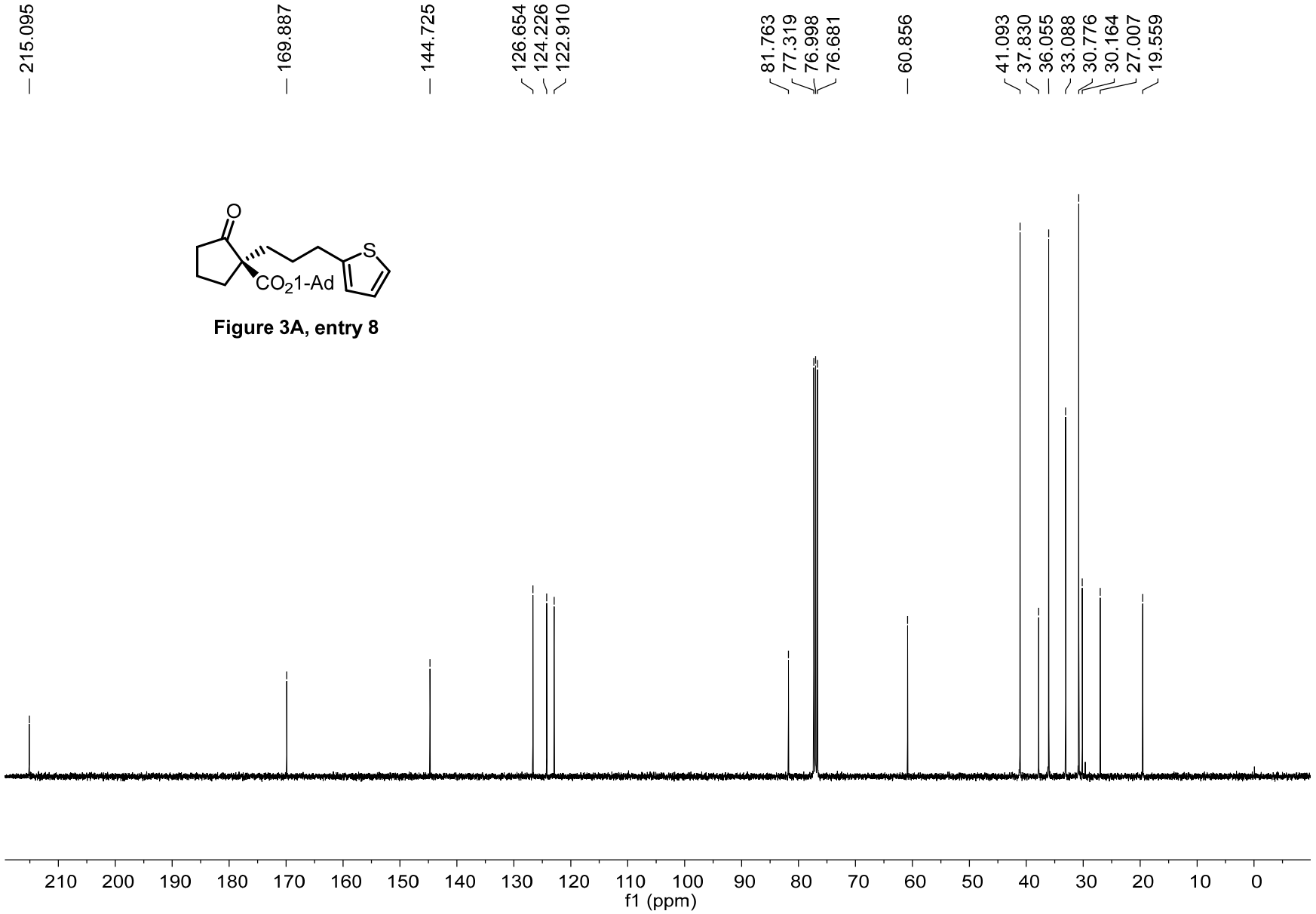

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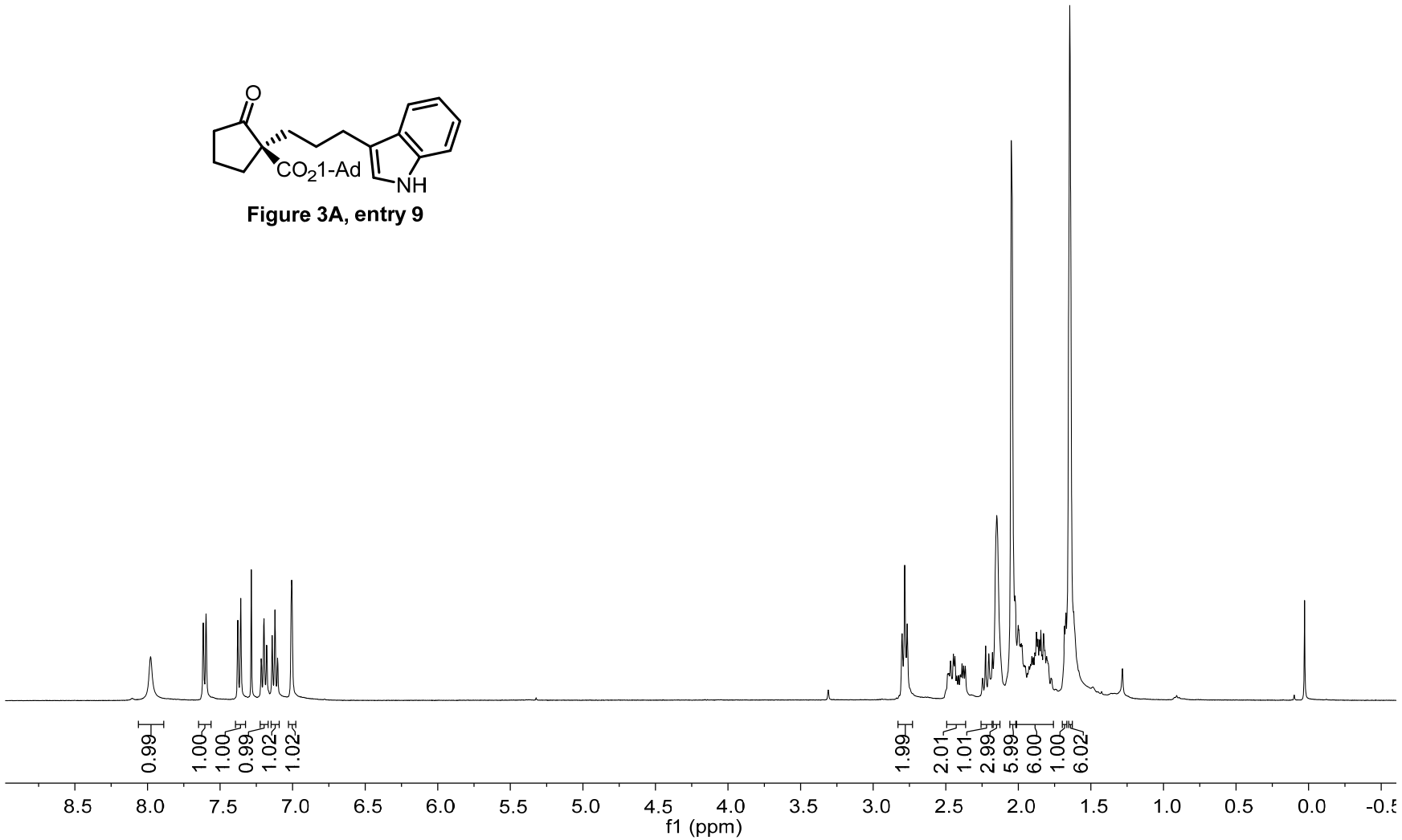

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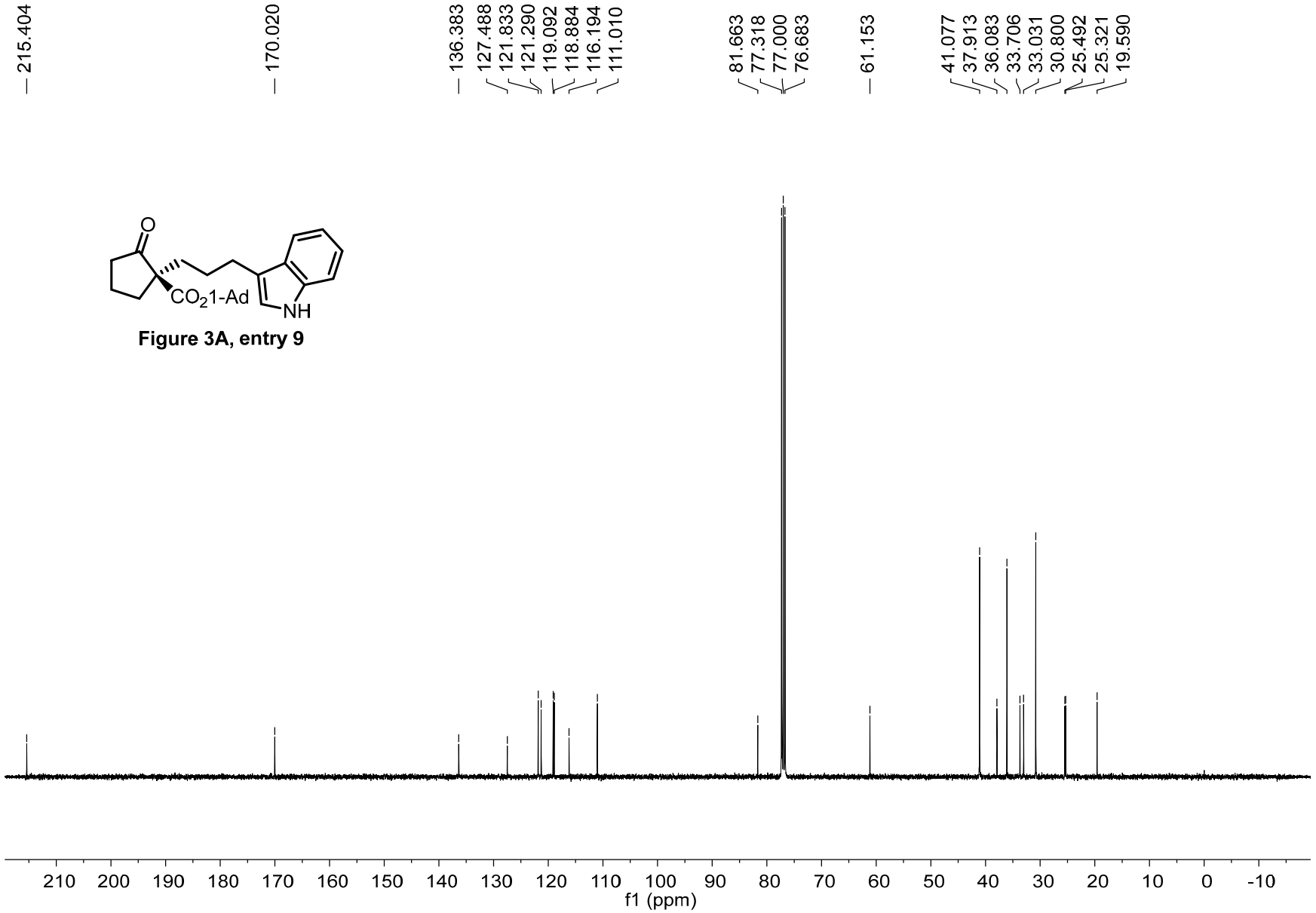

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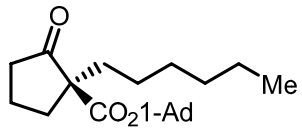

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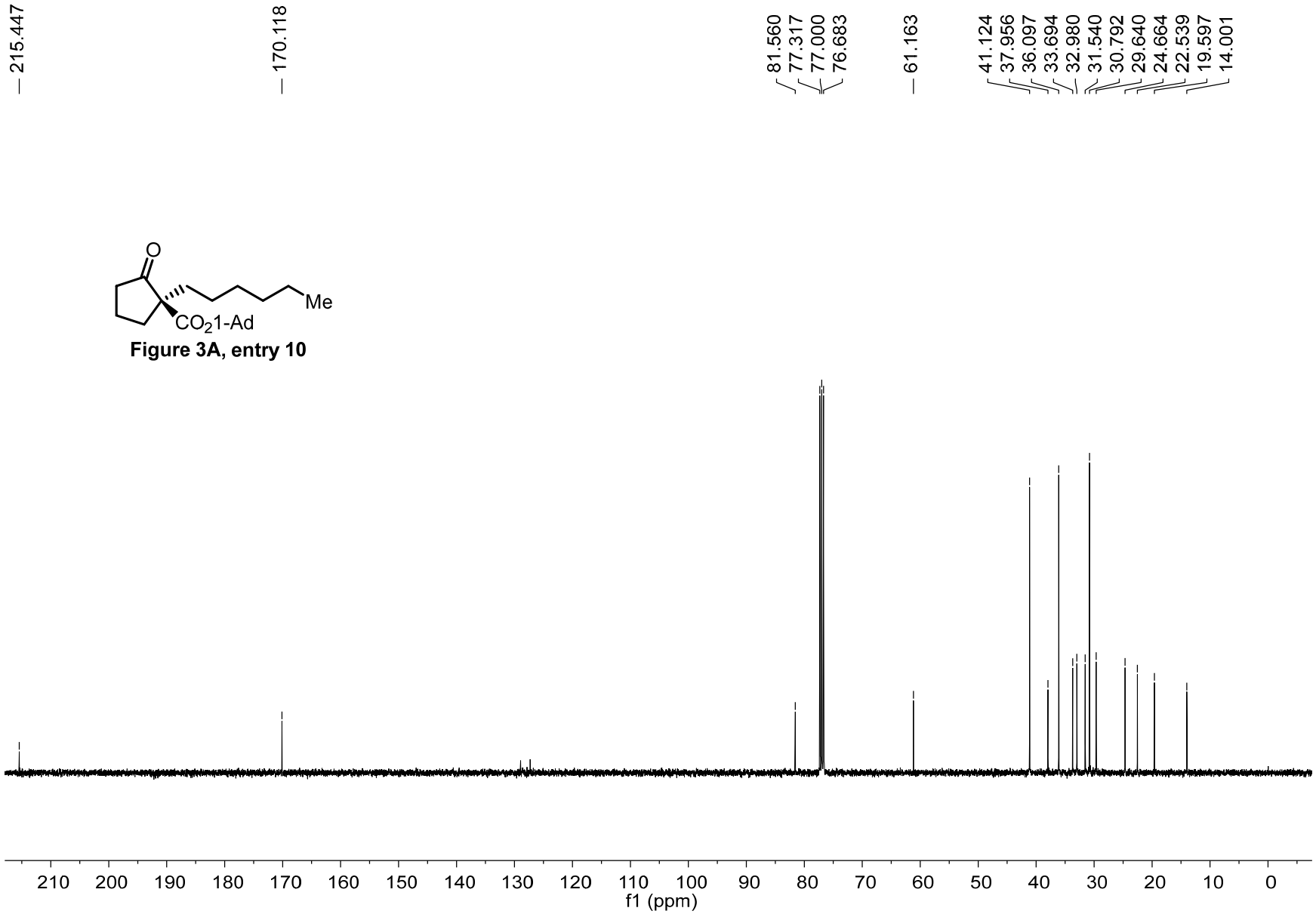

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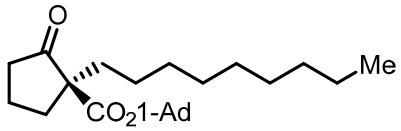

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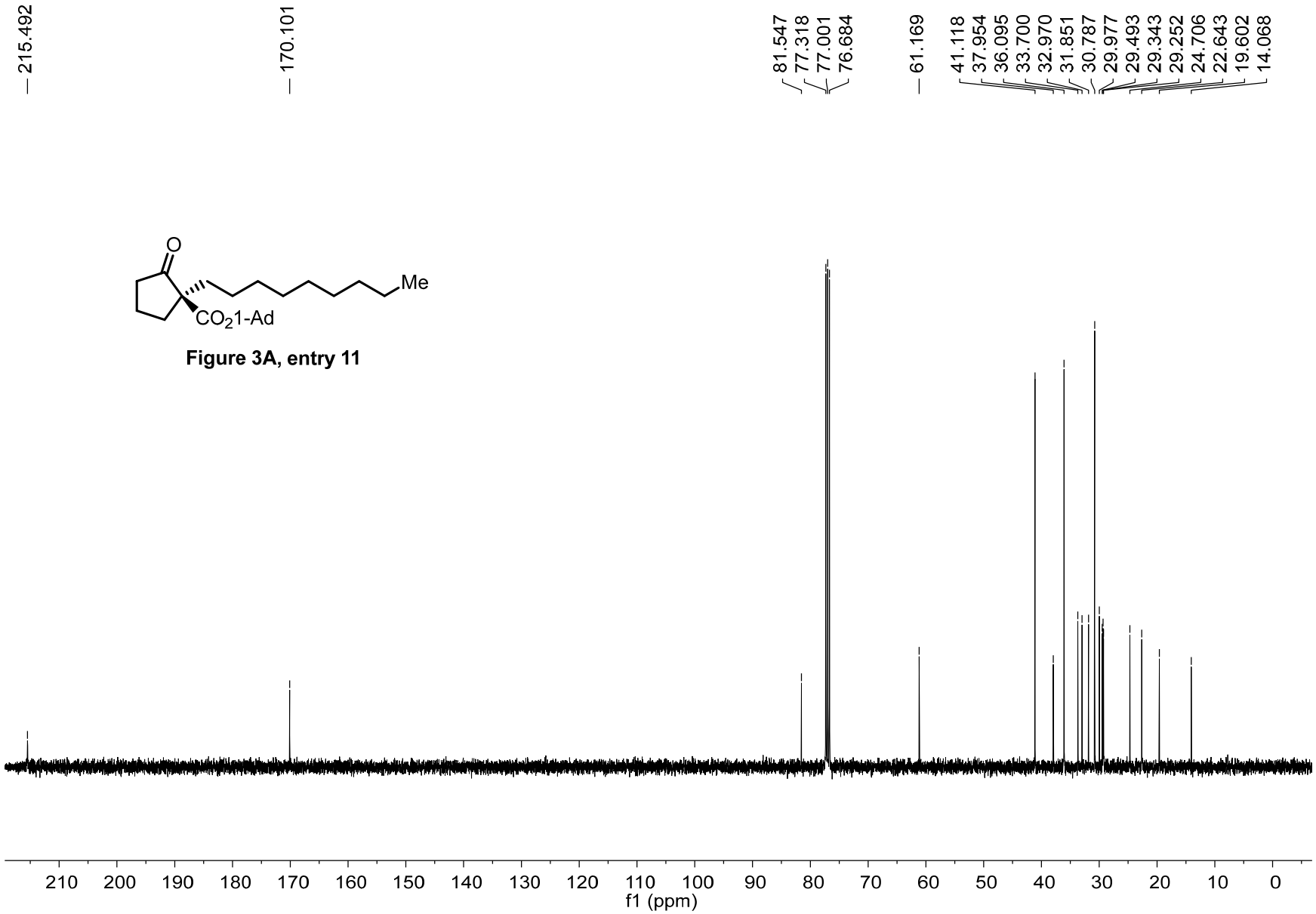

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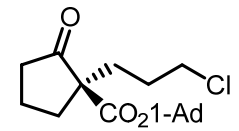

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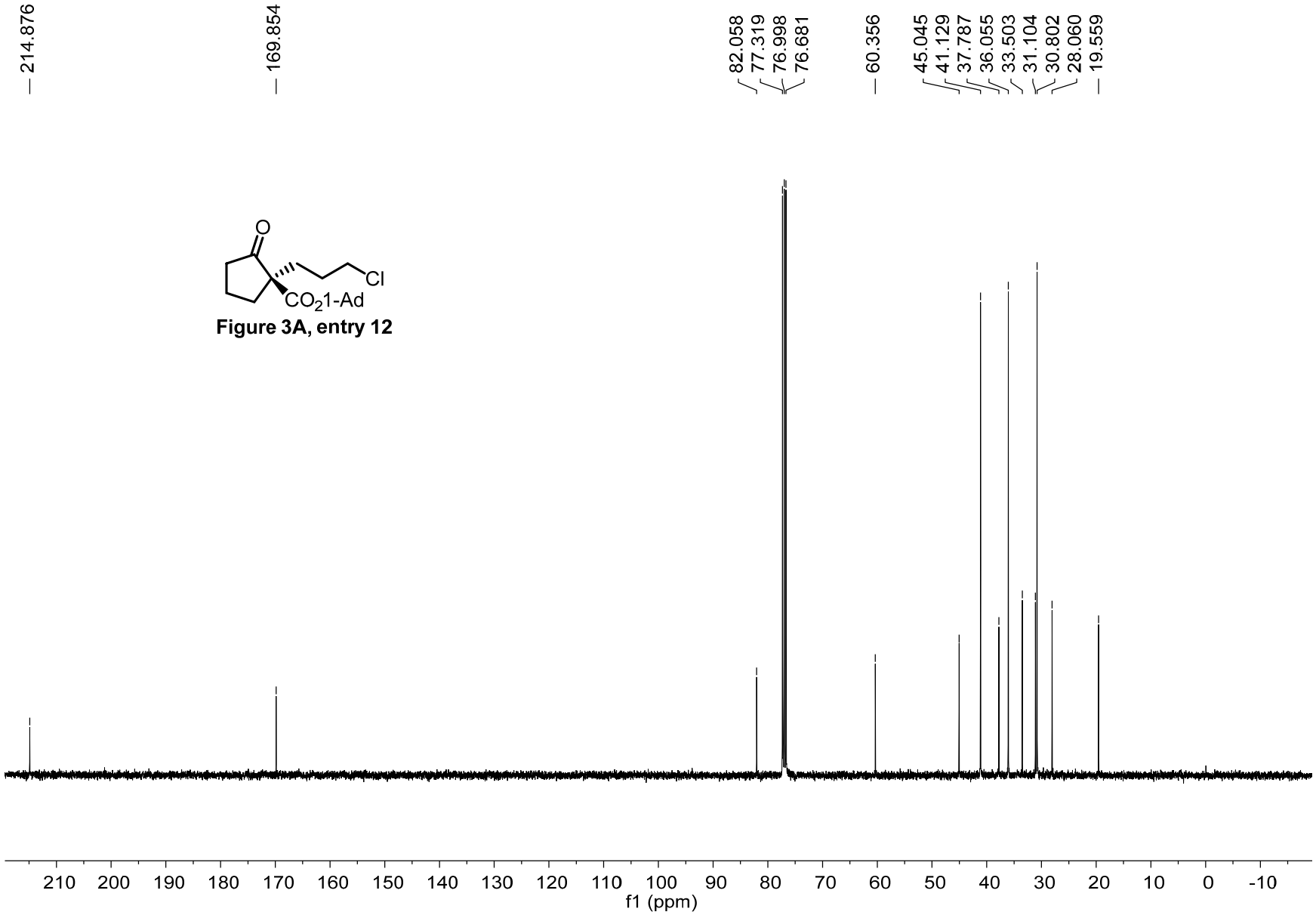

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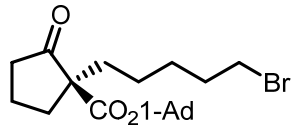

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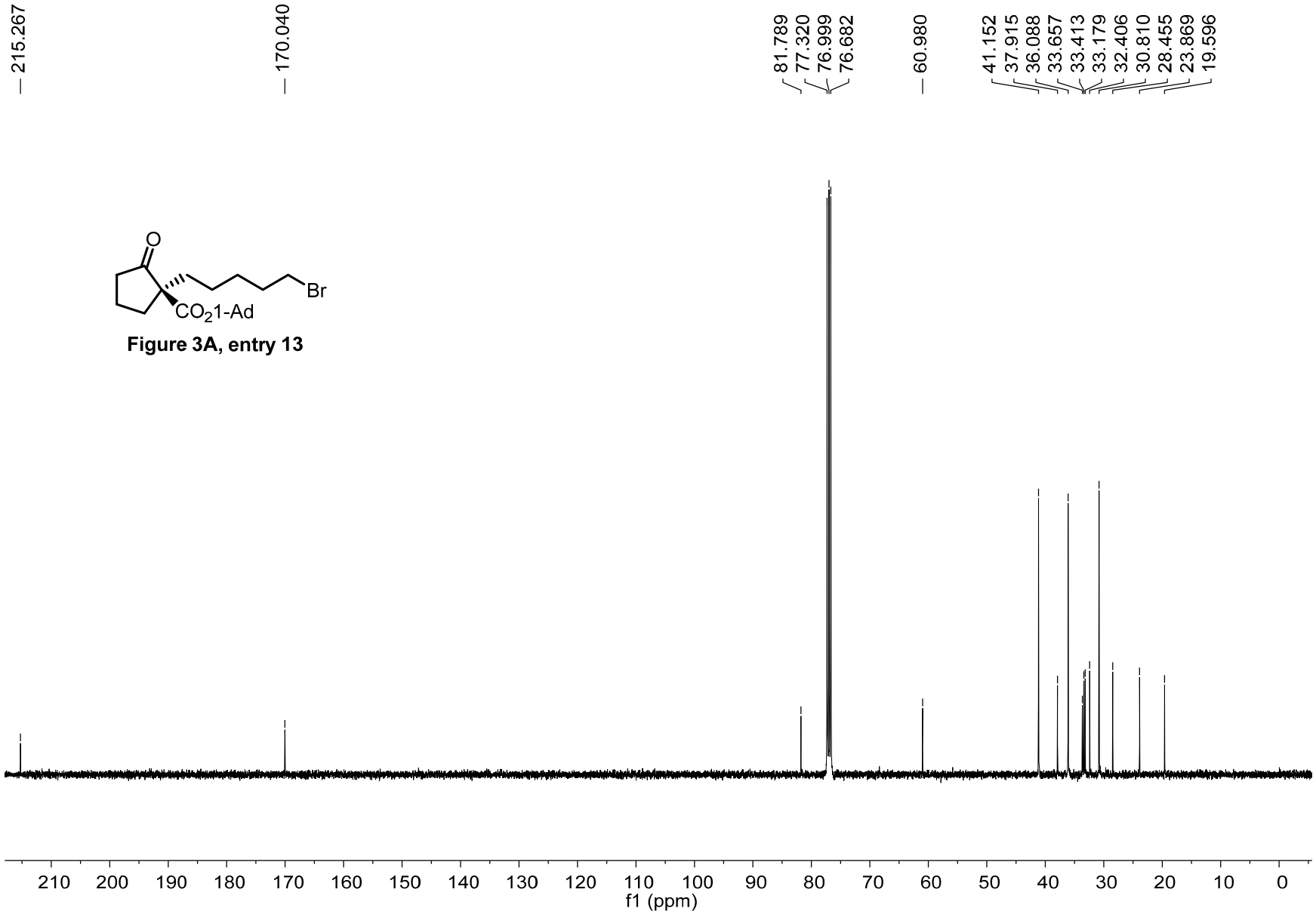

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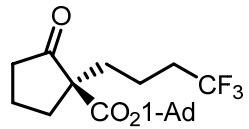

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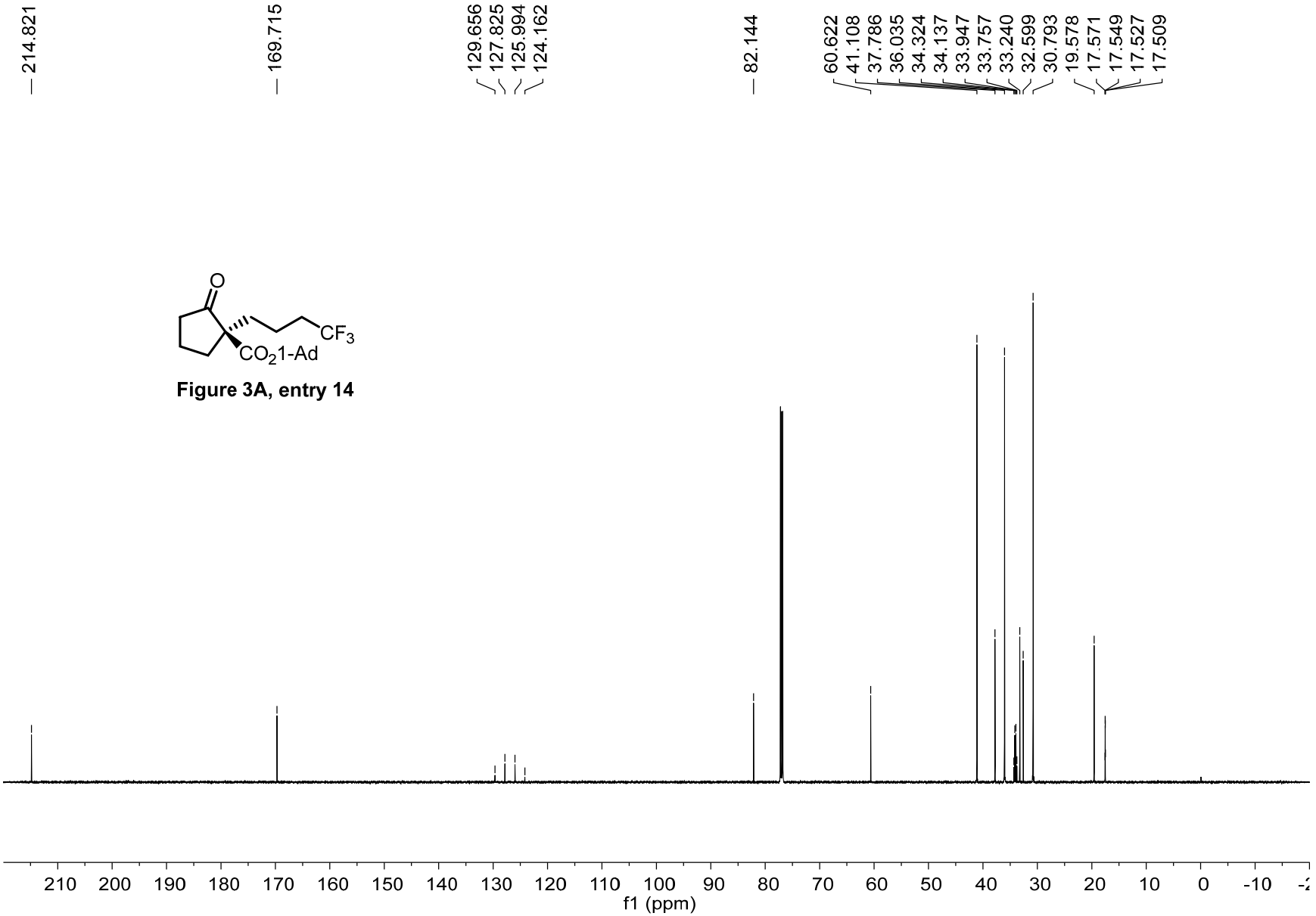

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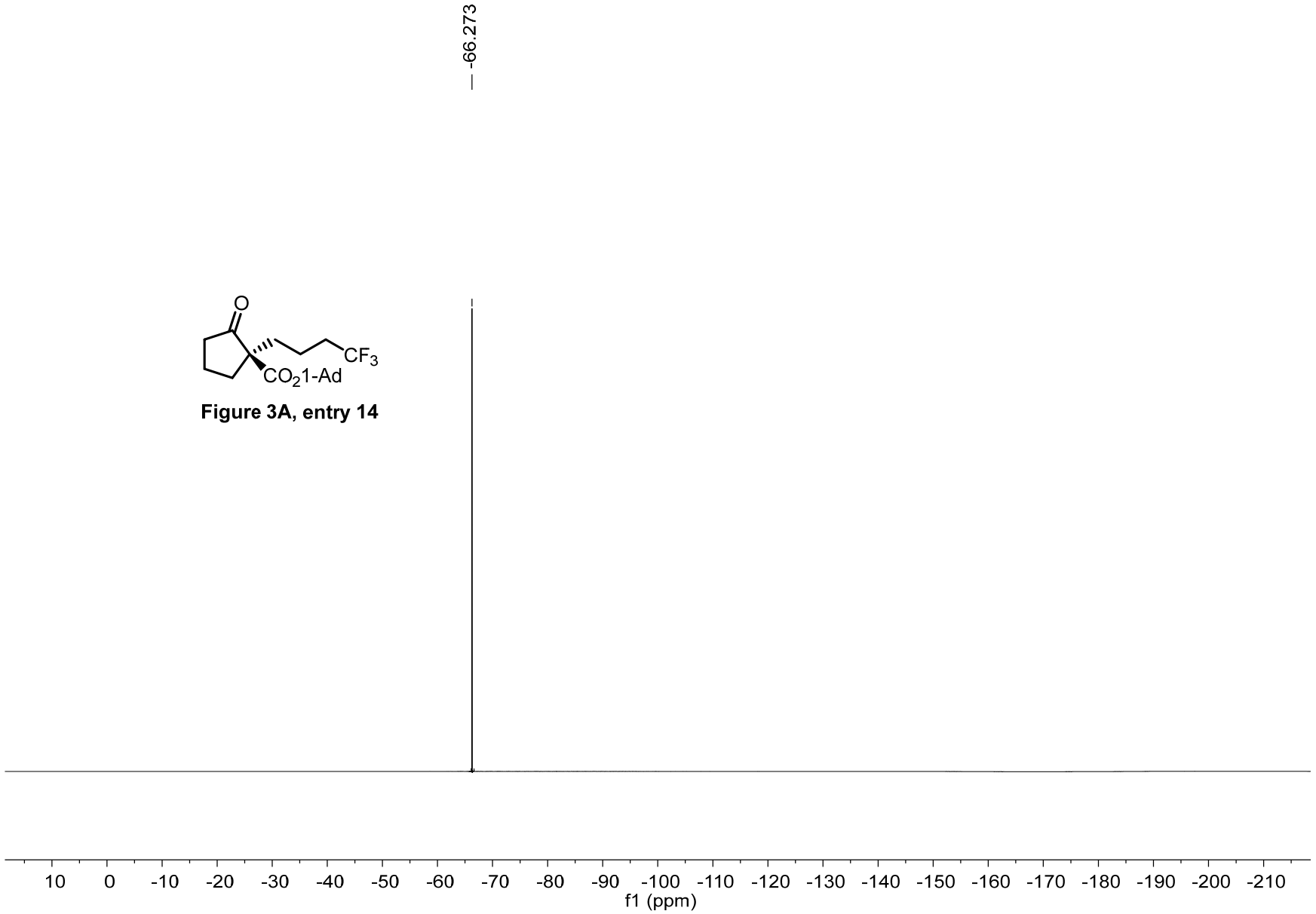

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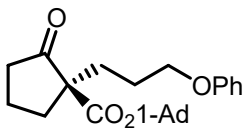

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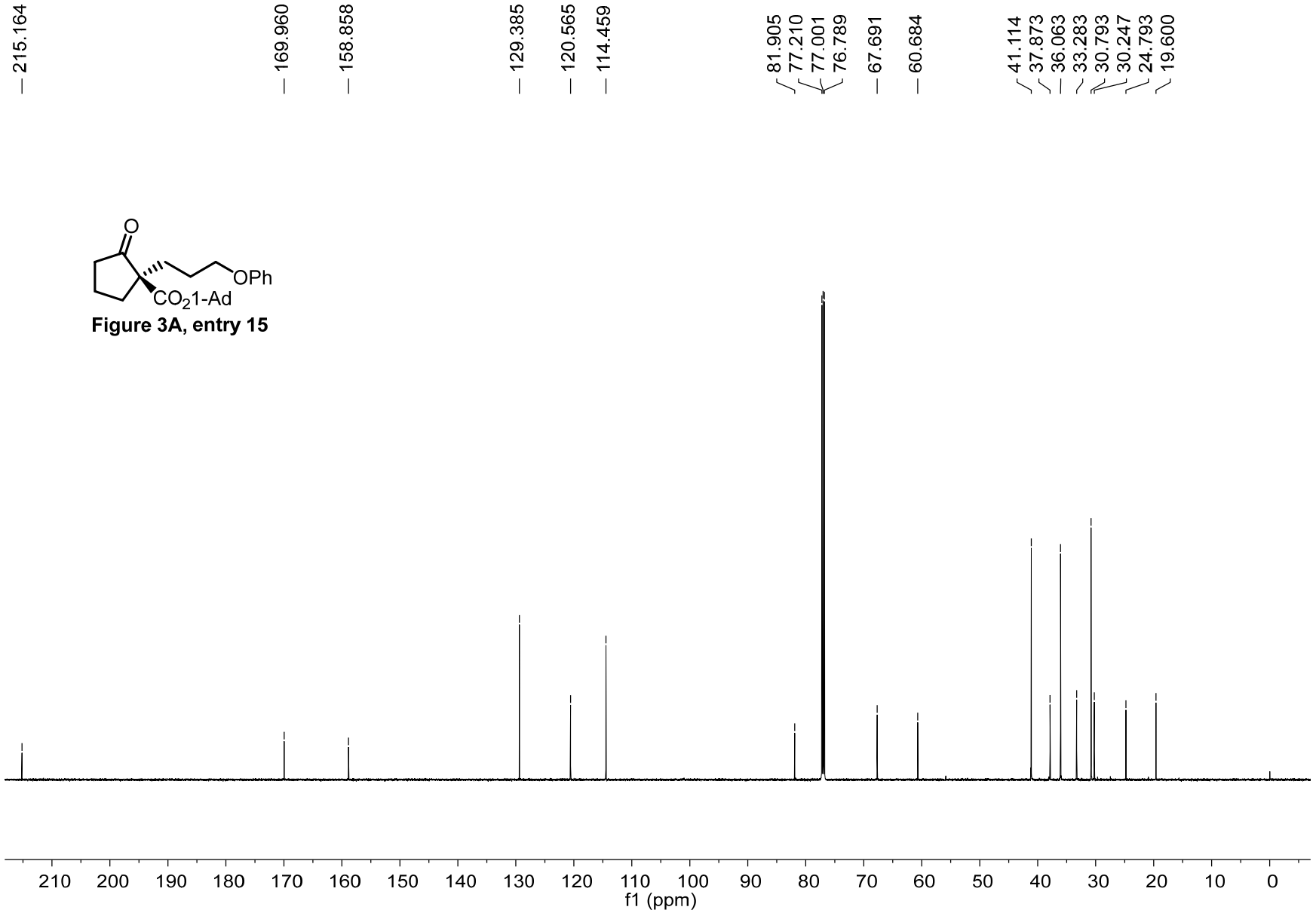

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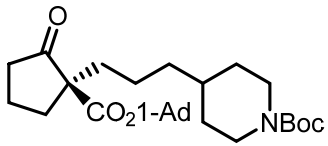

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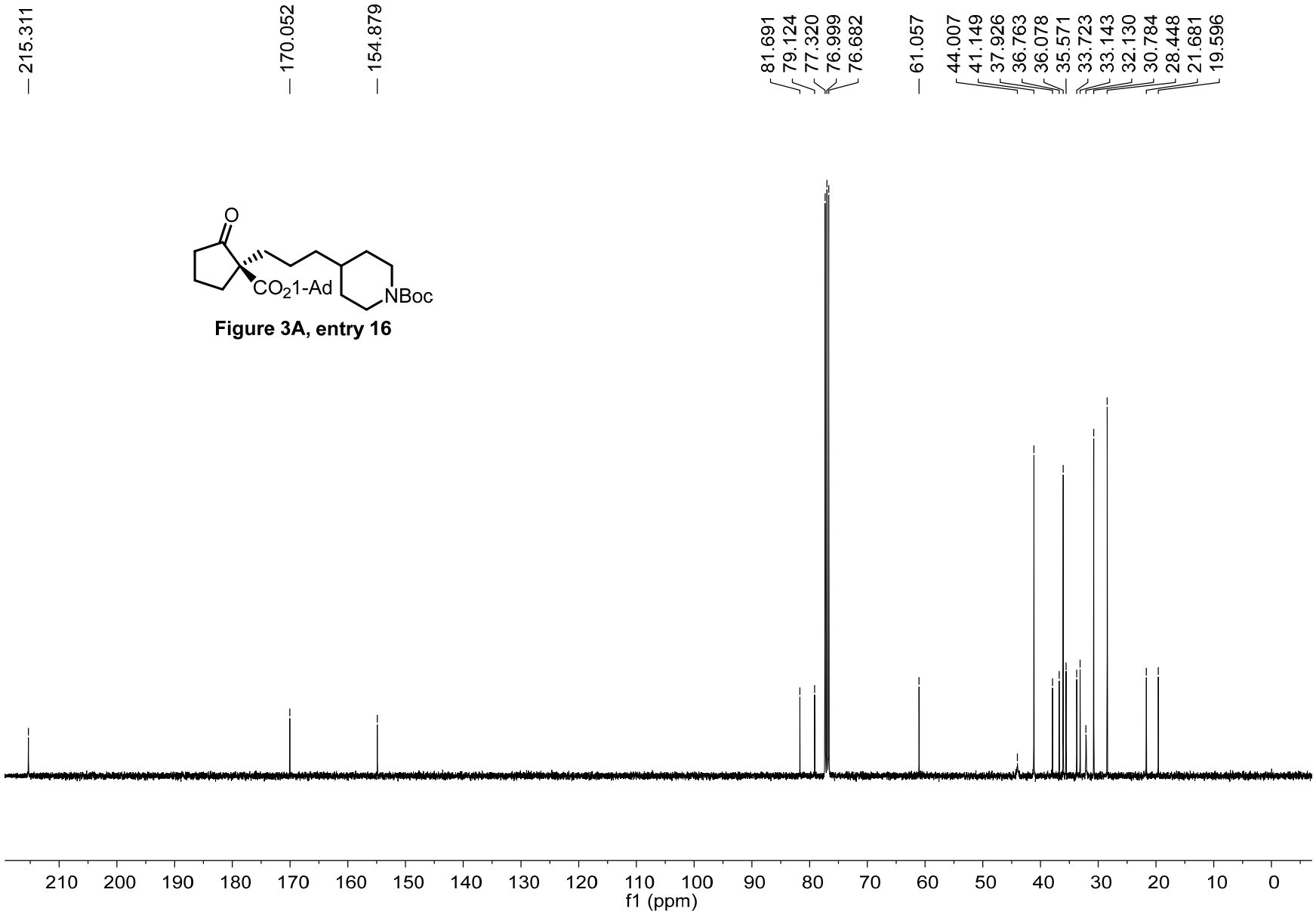

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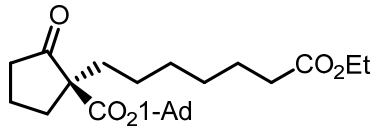

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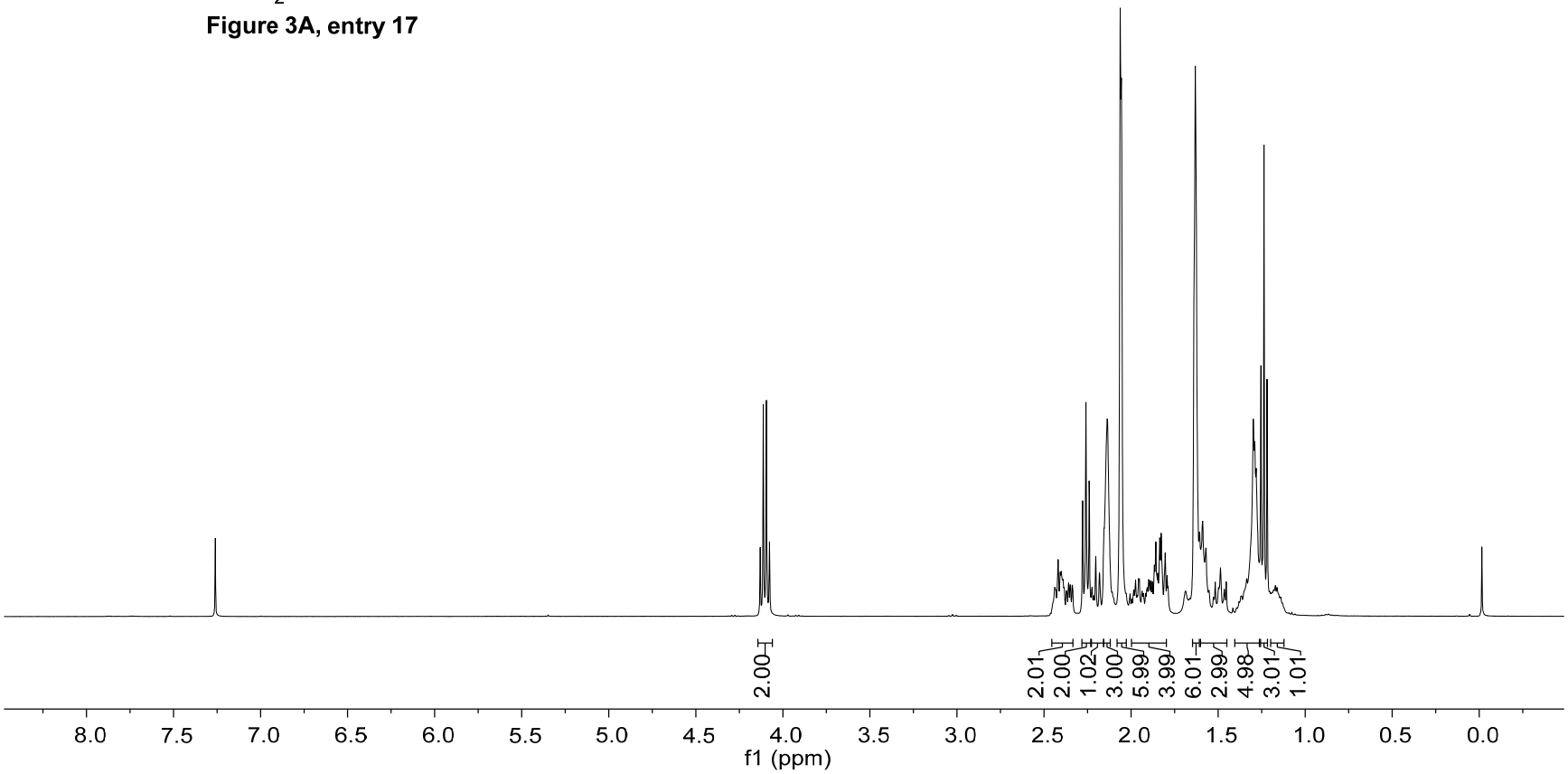

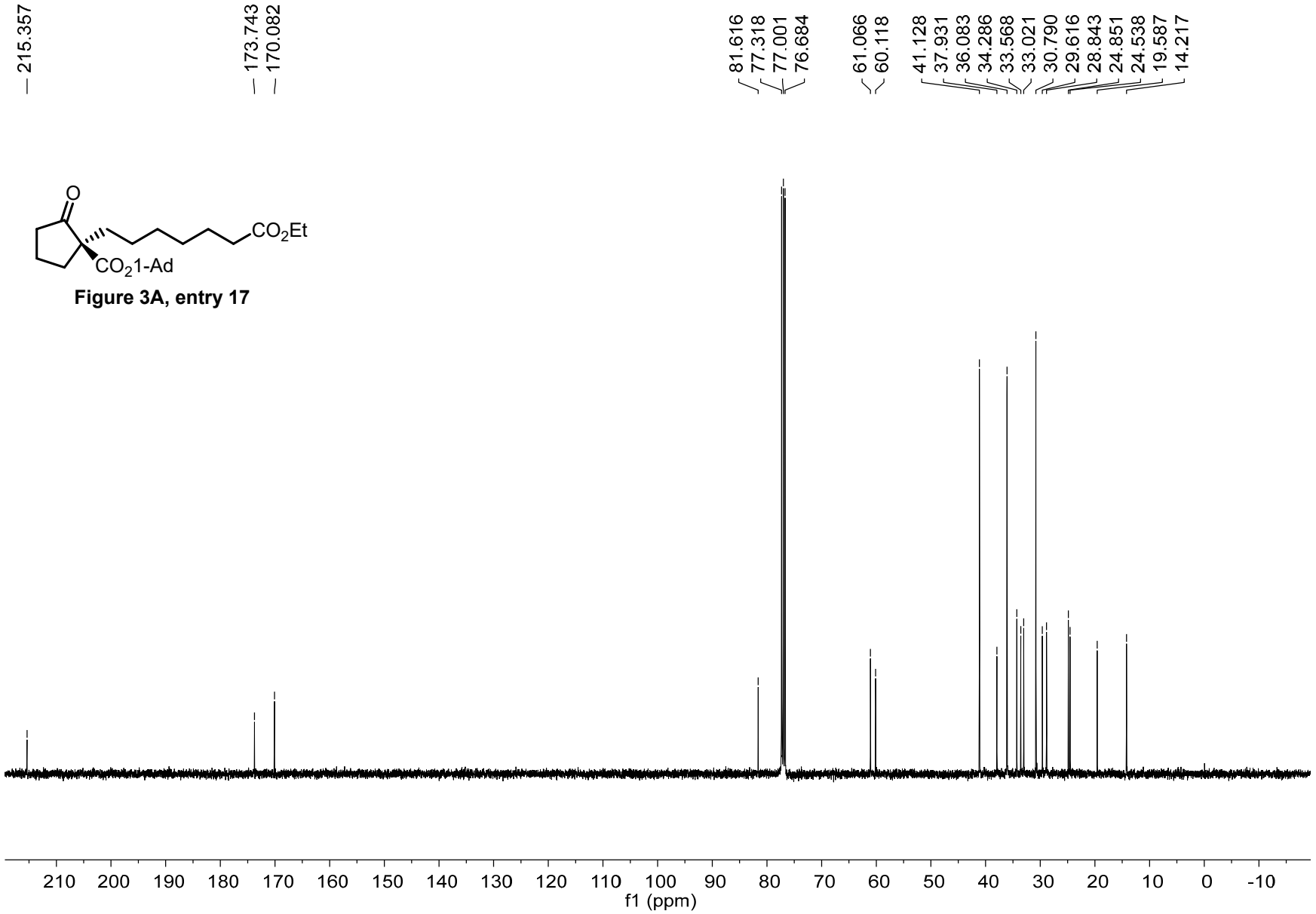

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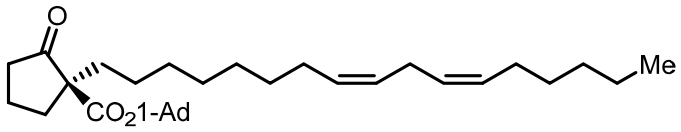

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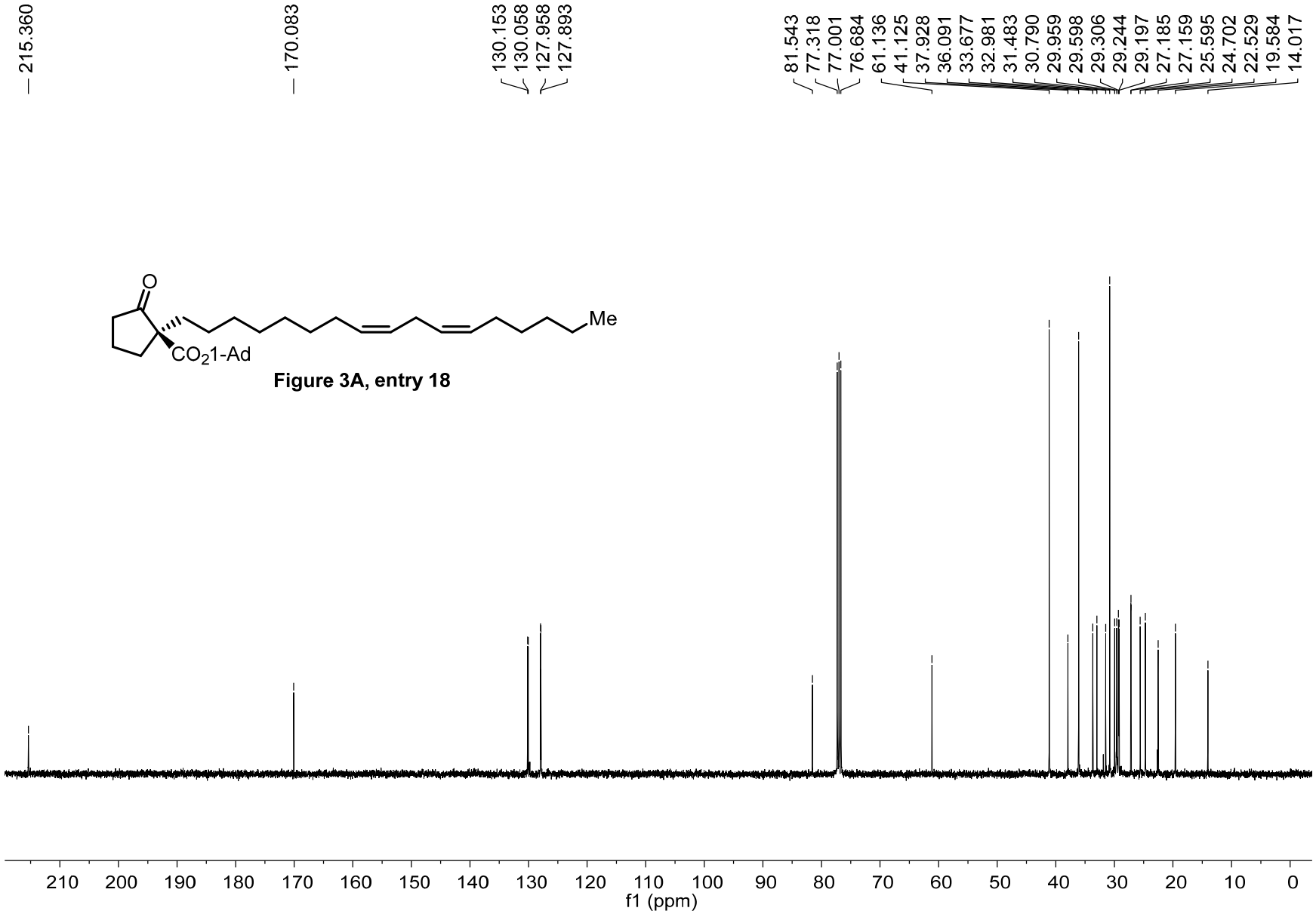

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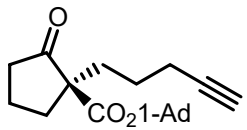

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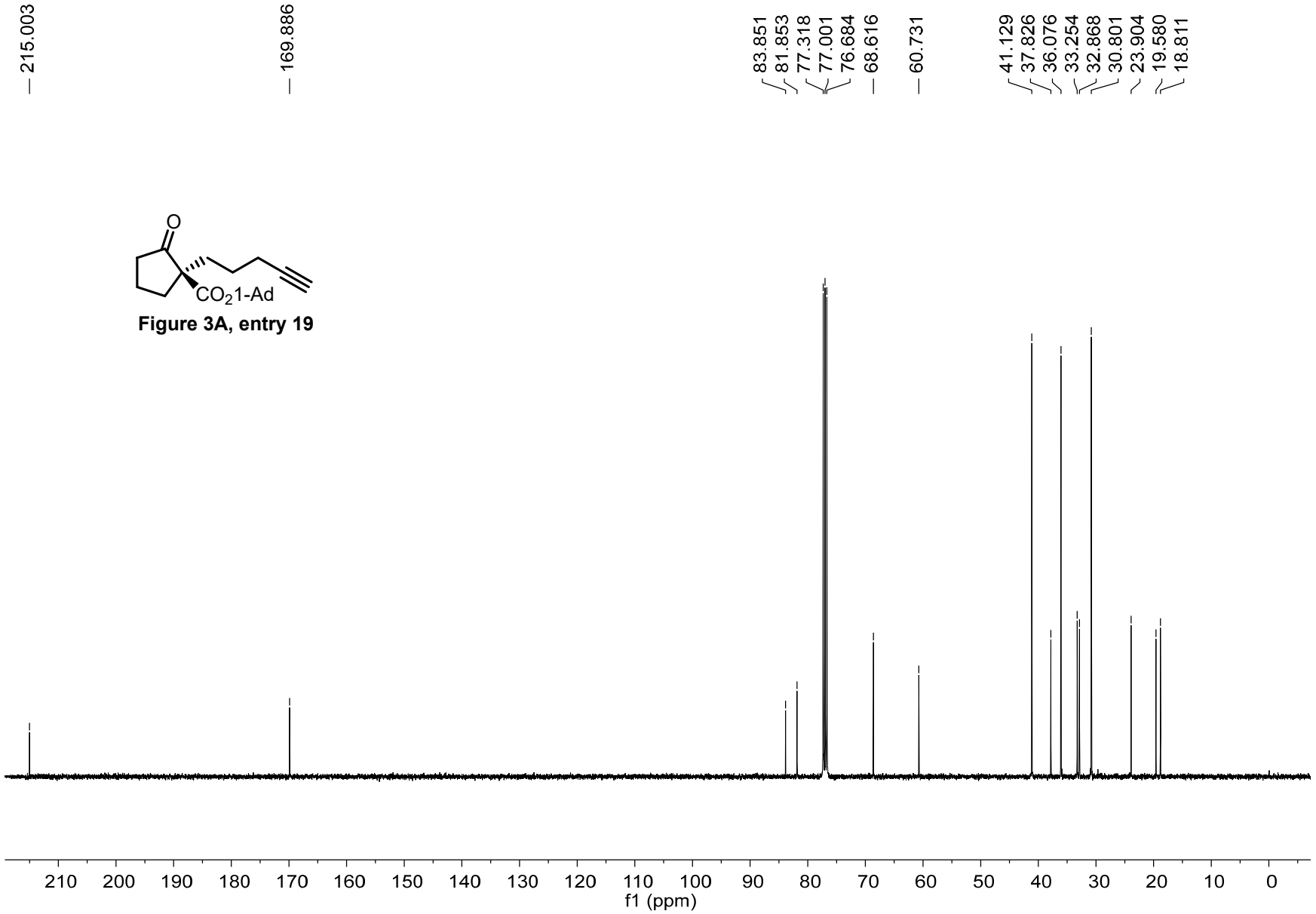

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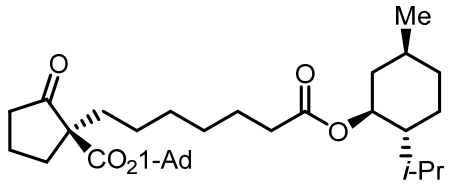

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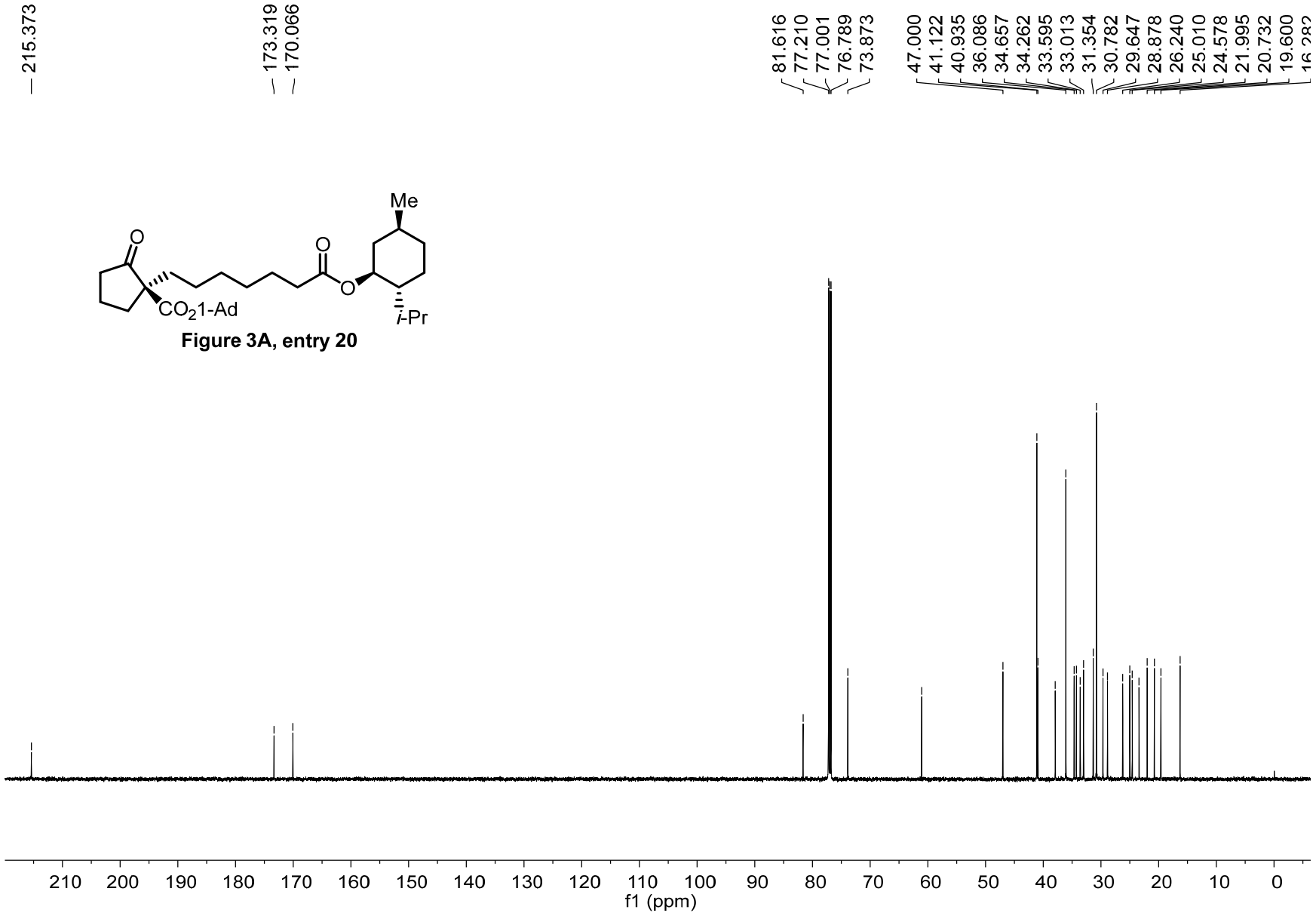

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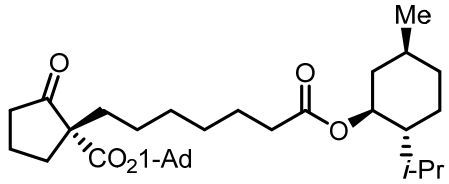

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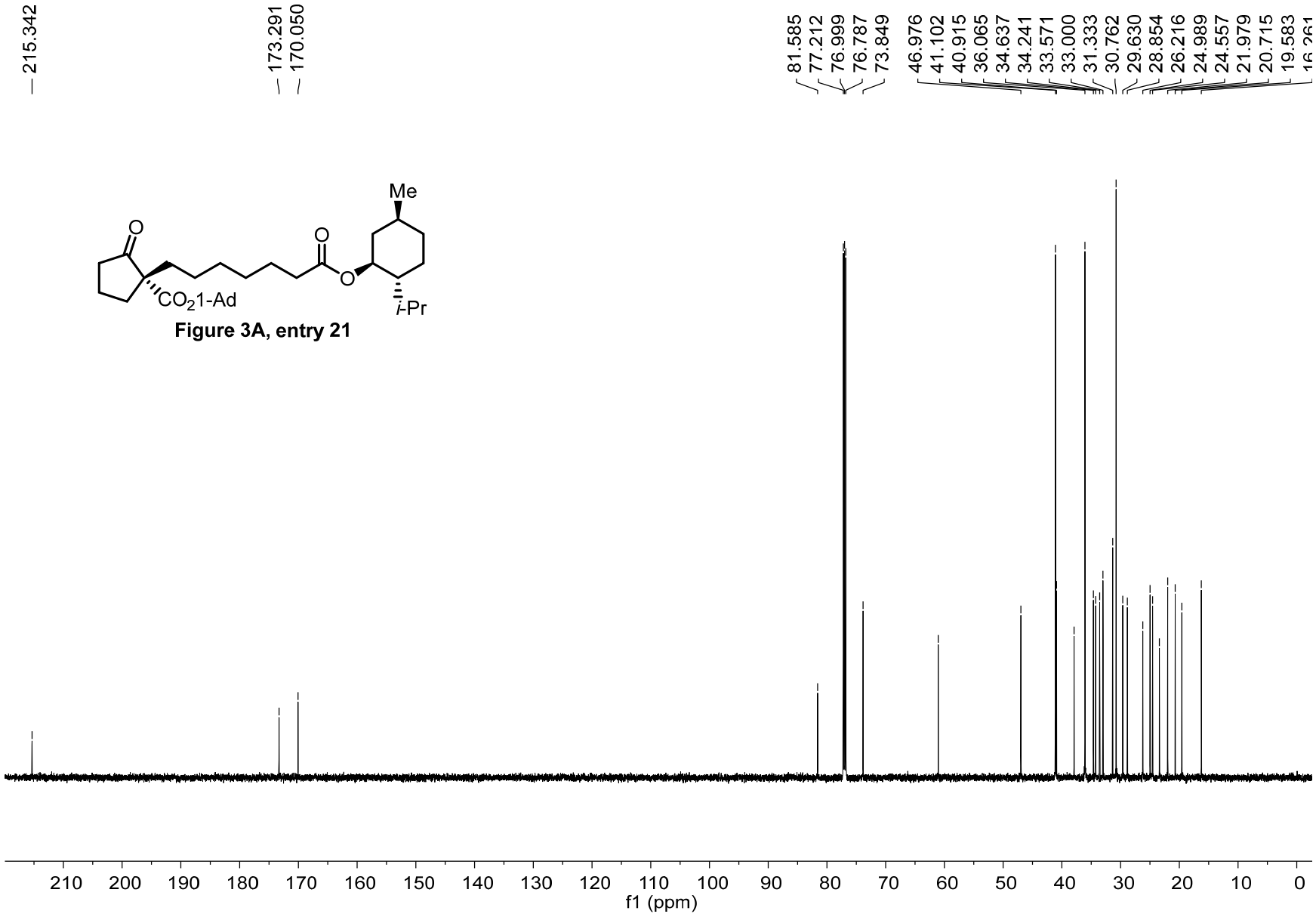

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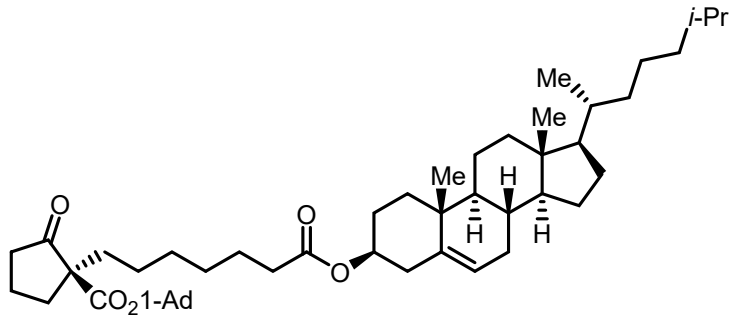
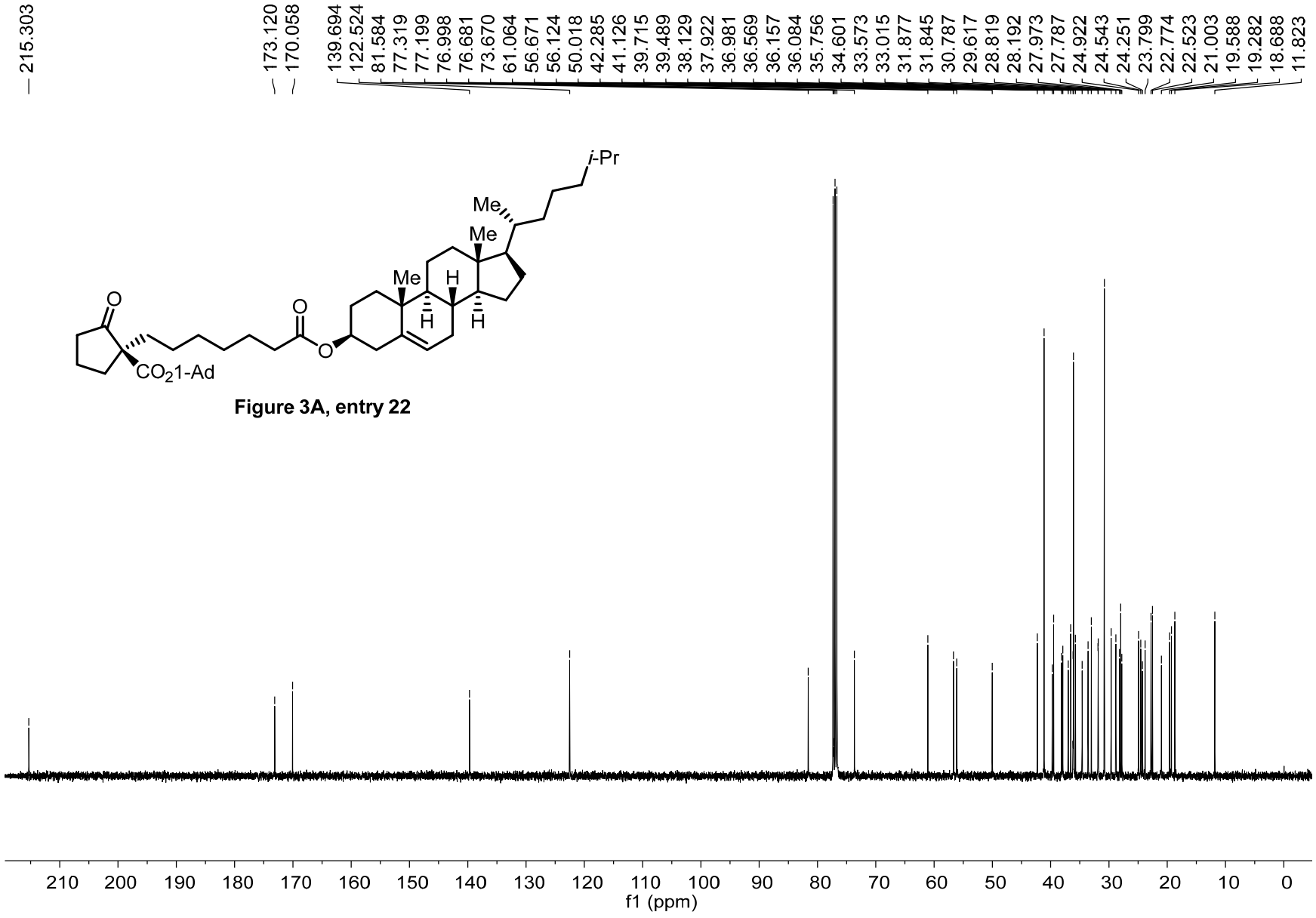


Figure 3A, entry 22



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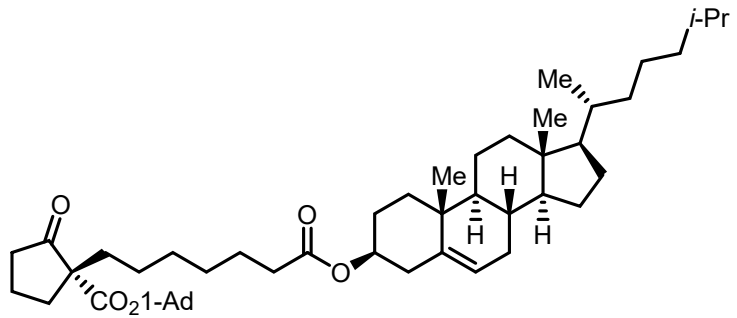

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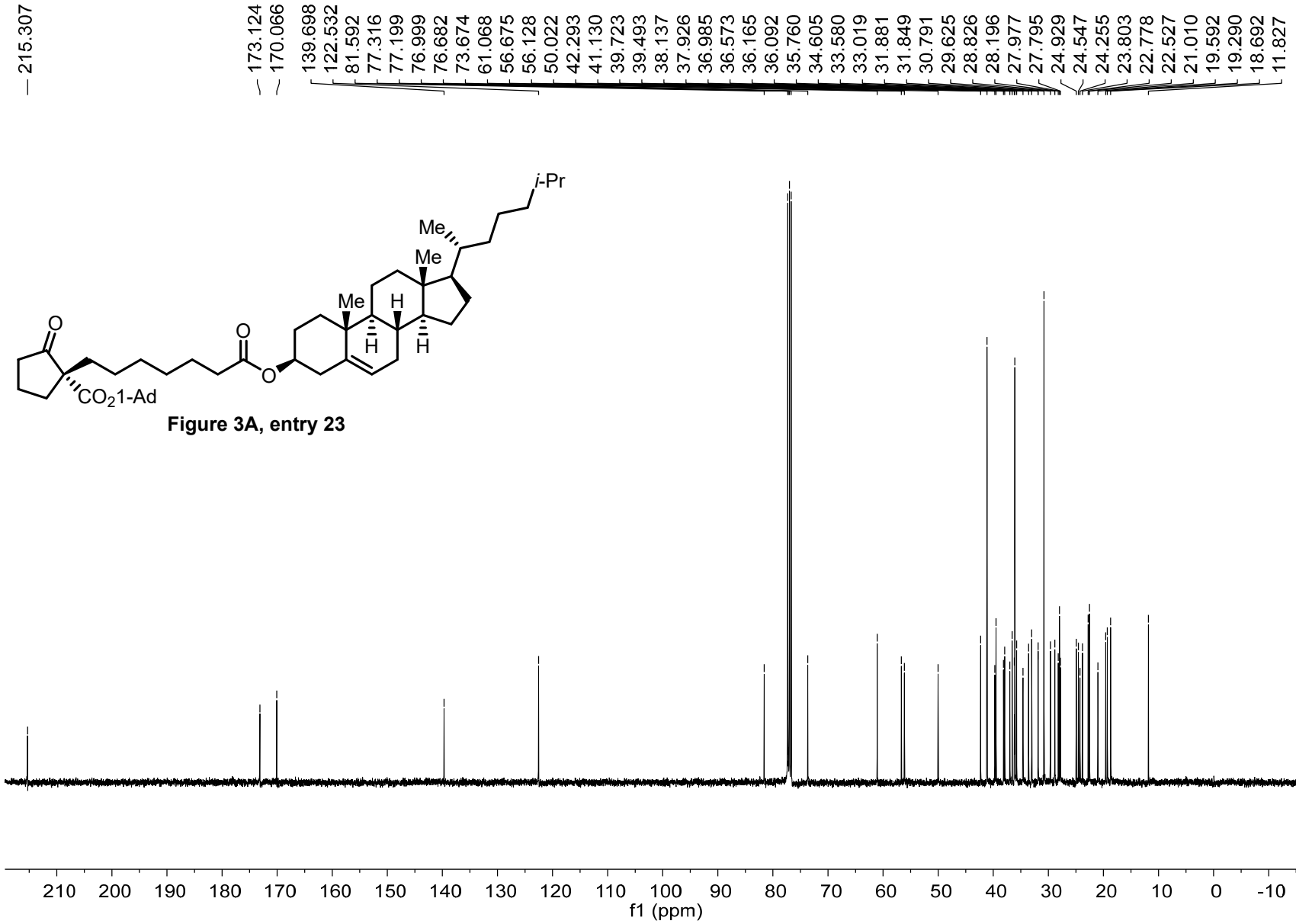

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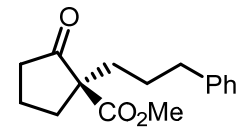
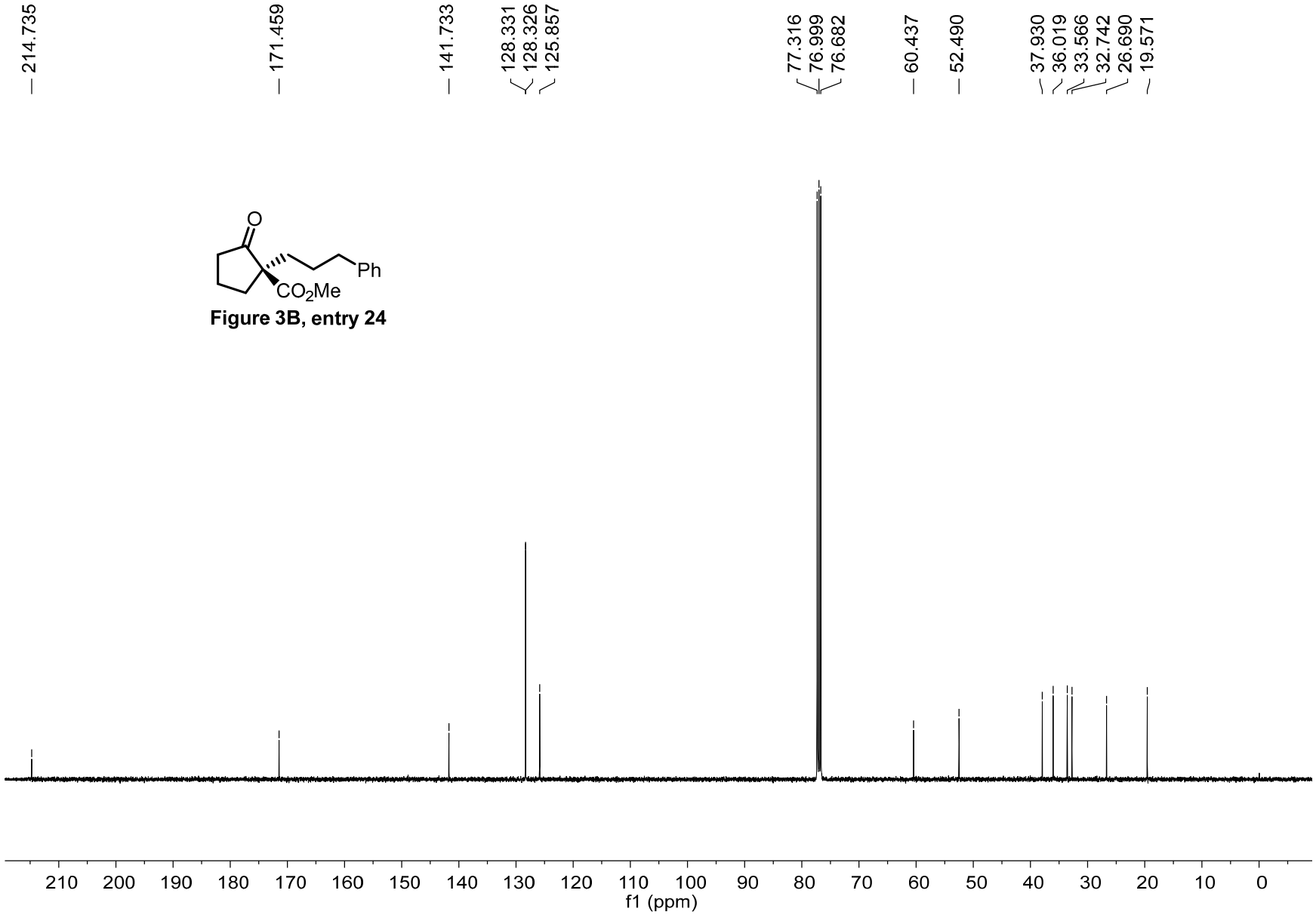


Figure 3B, entry 24



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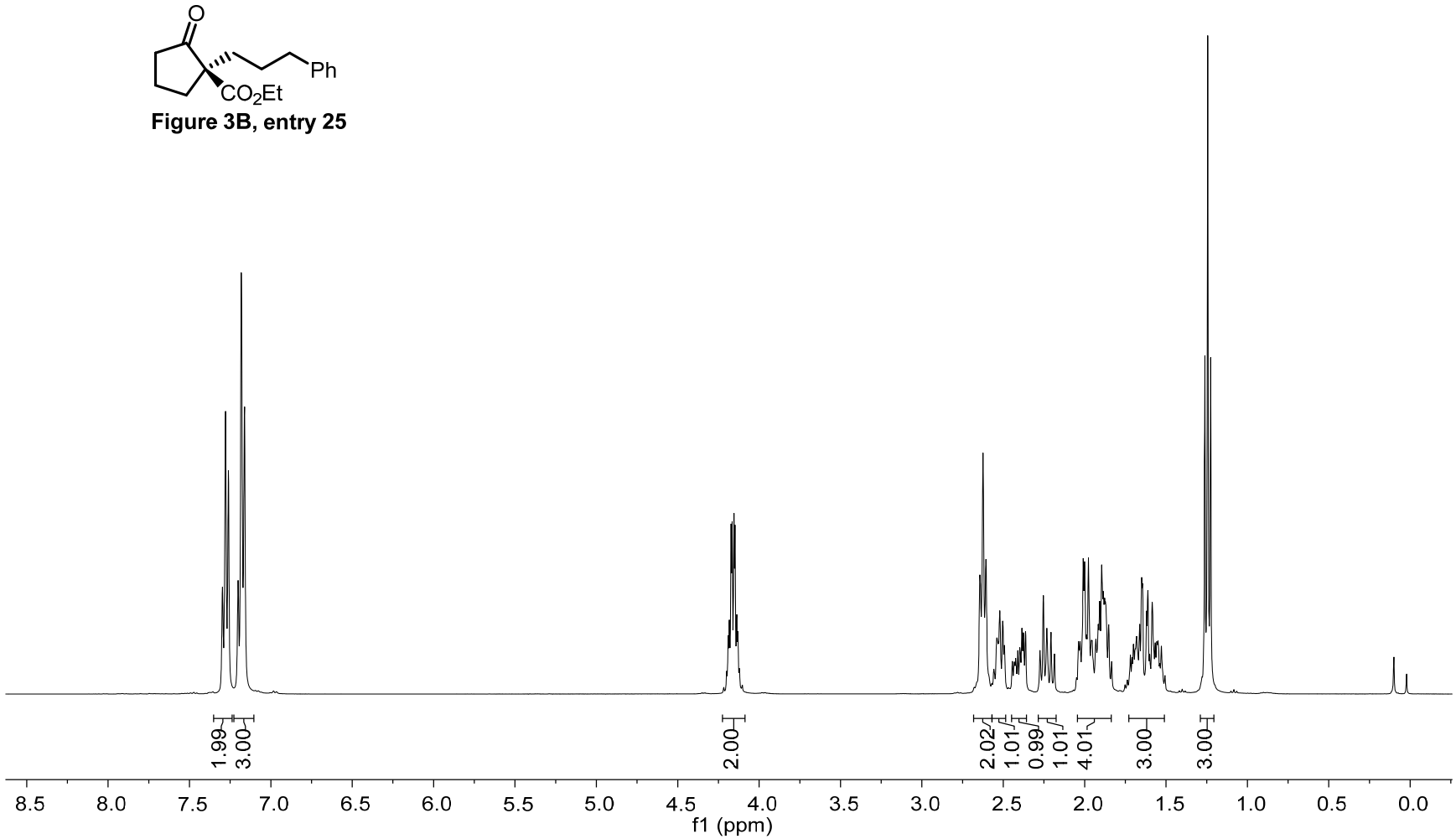

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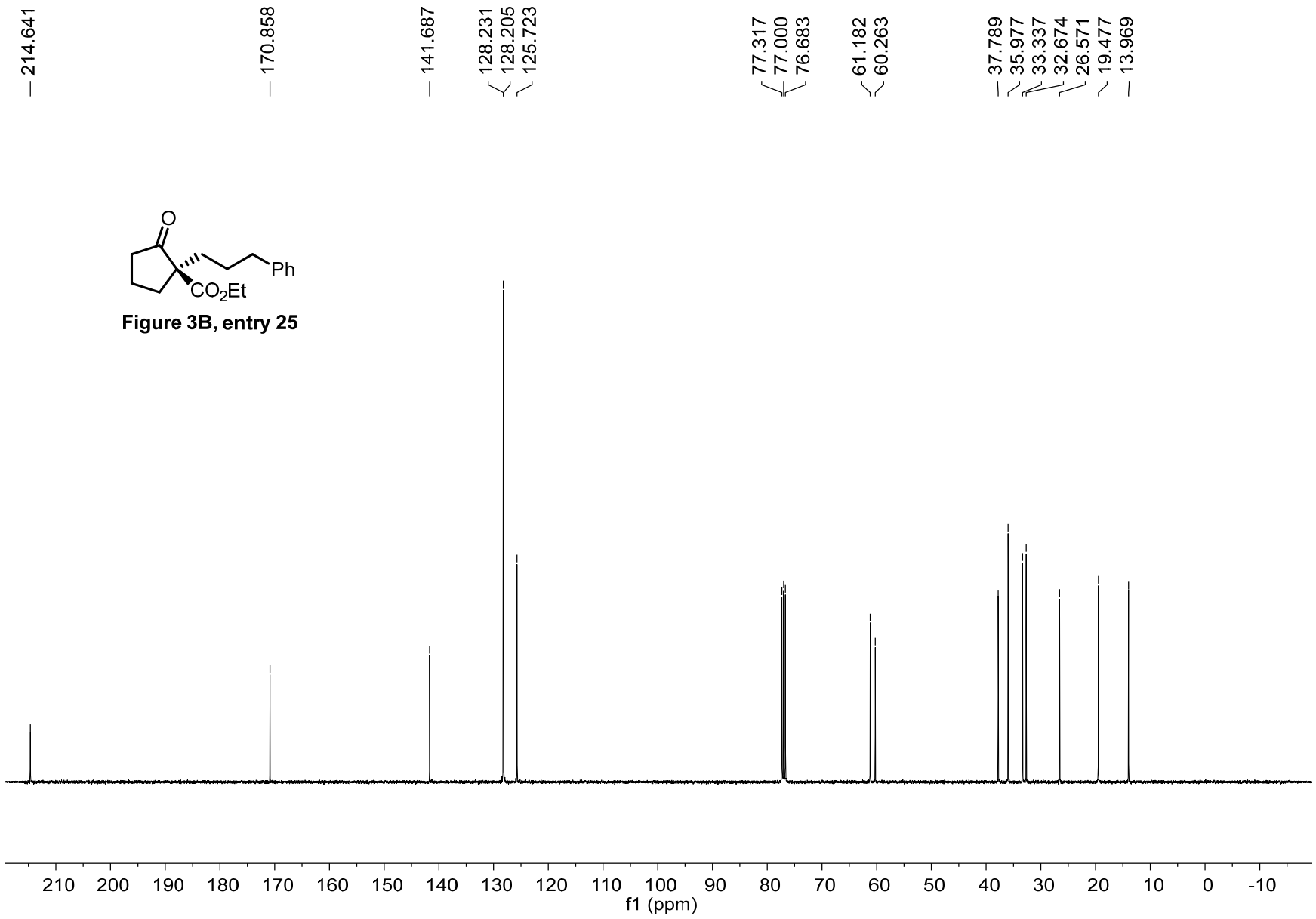

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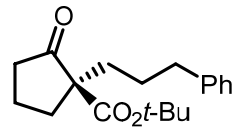

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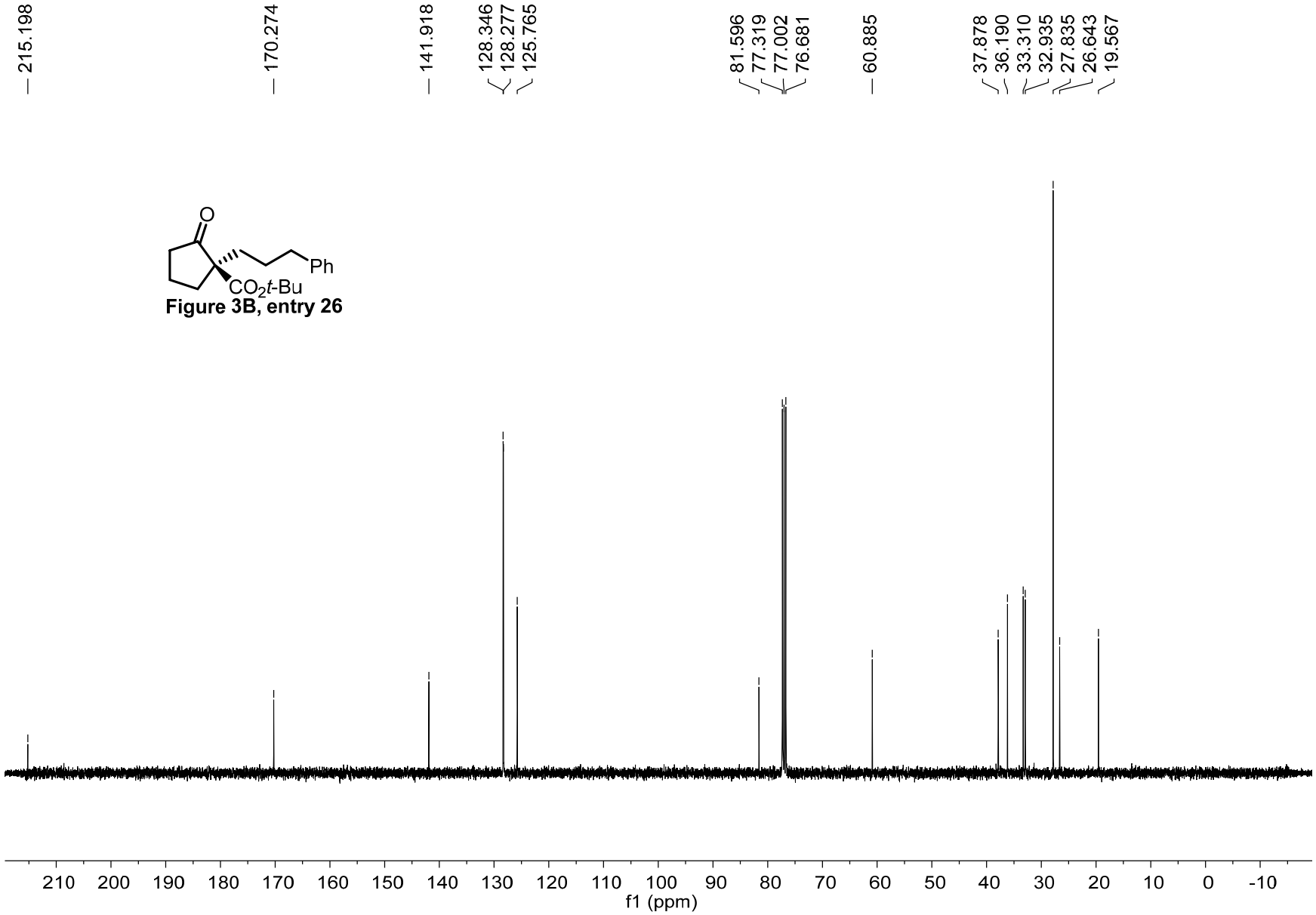

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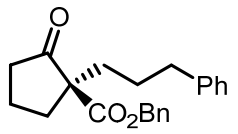

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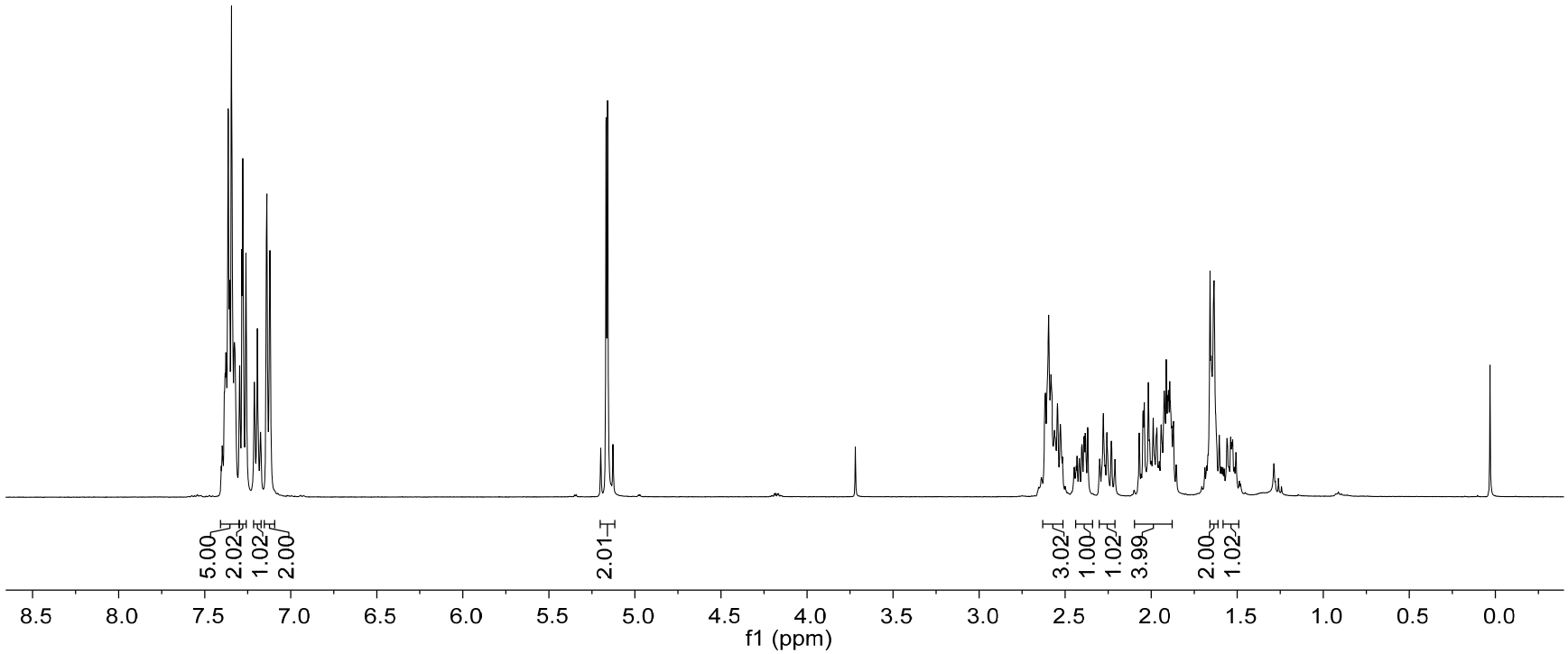

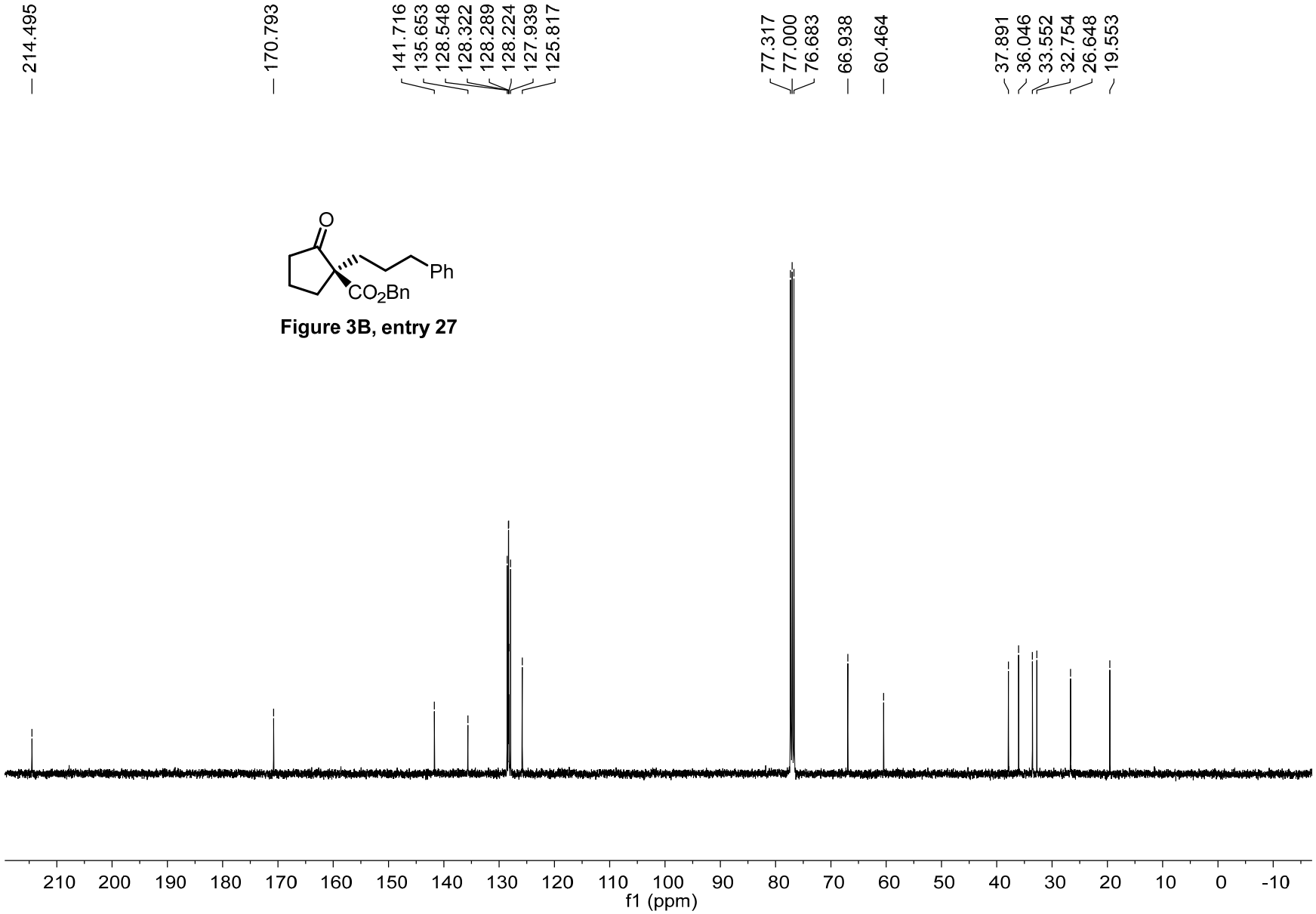

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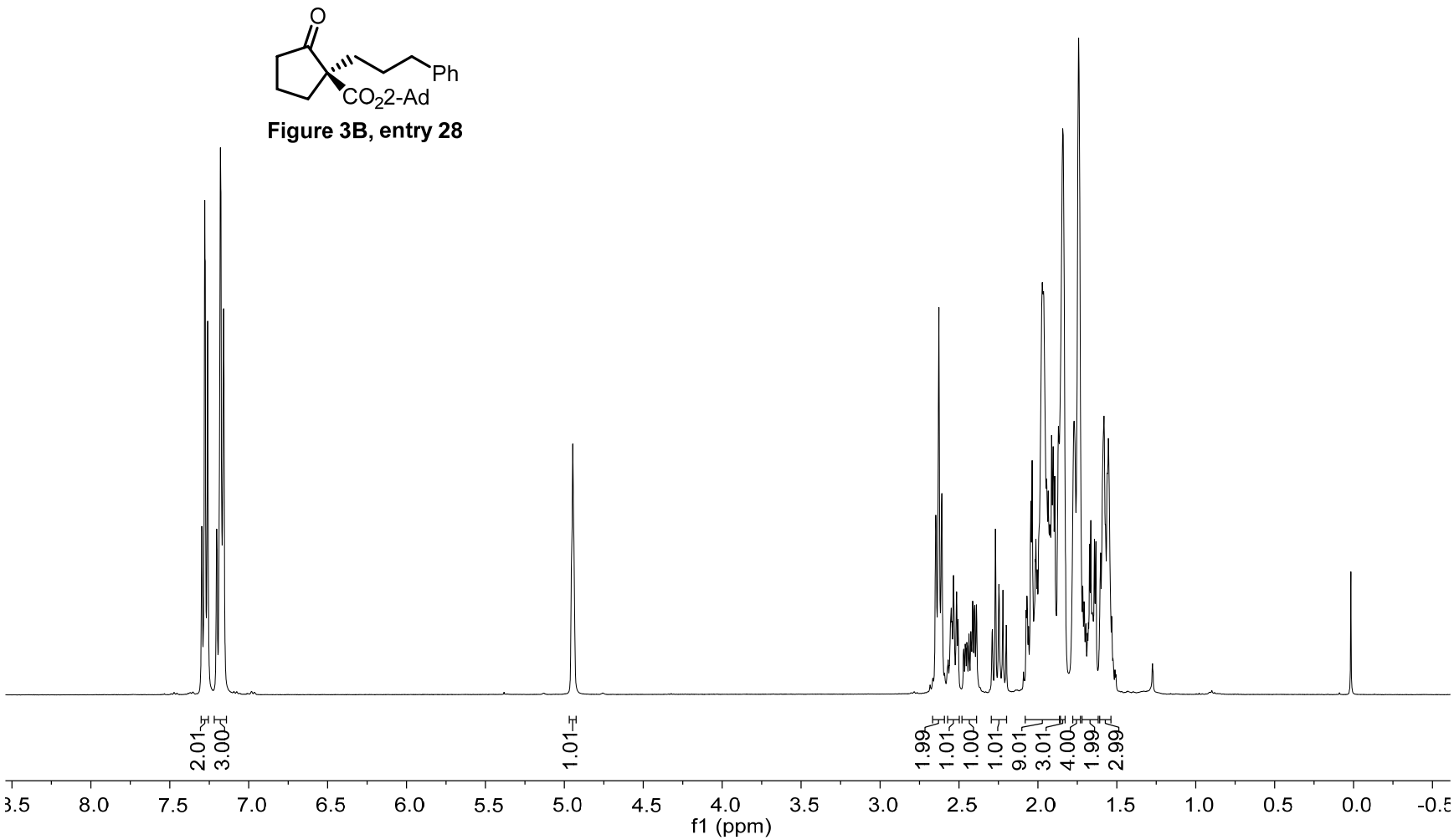

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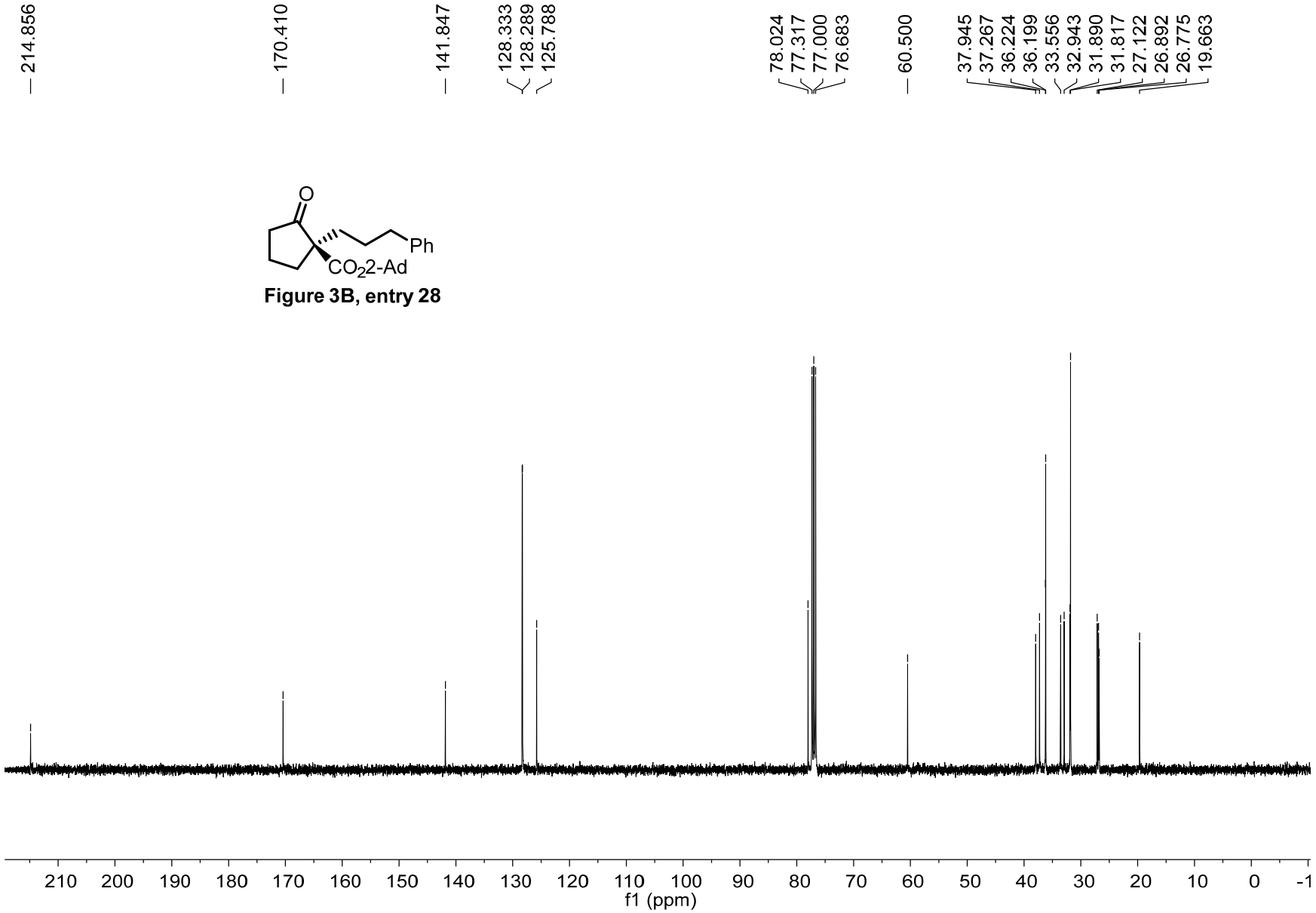

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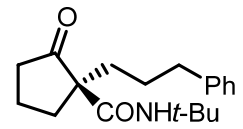

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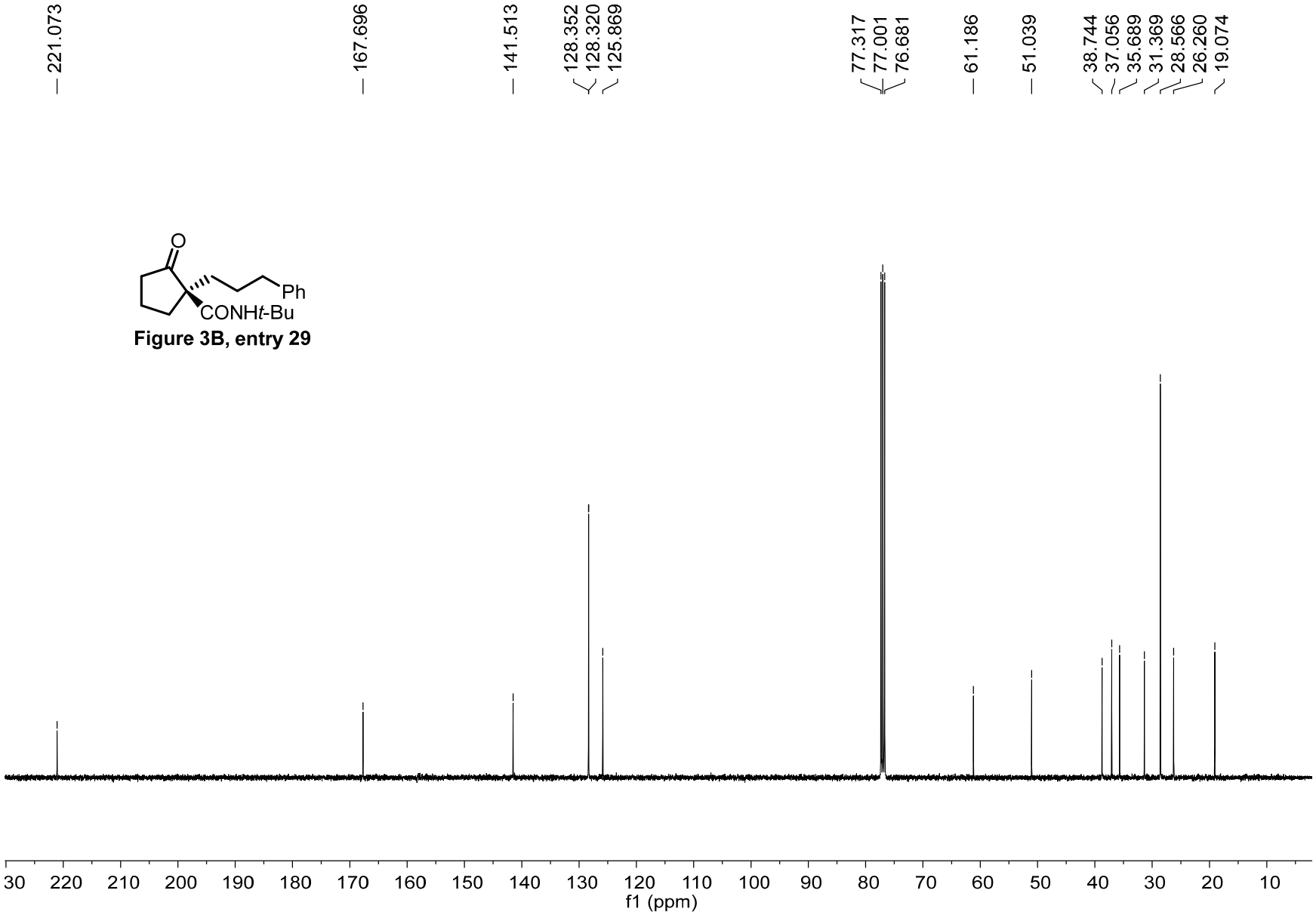

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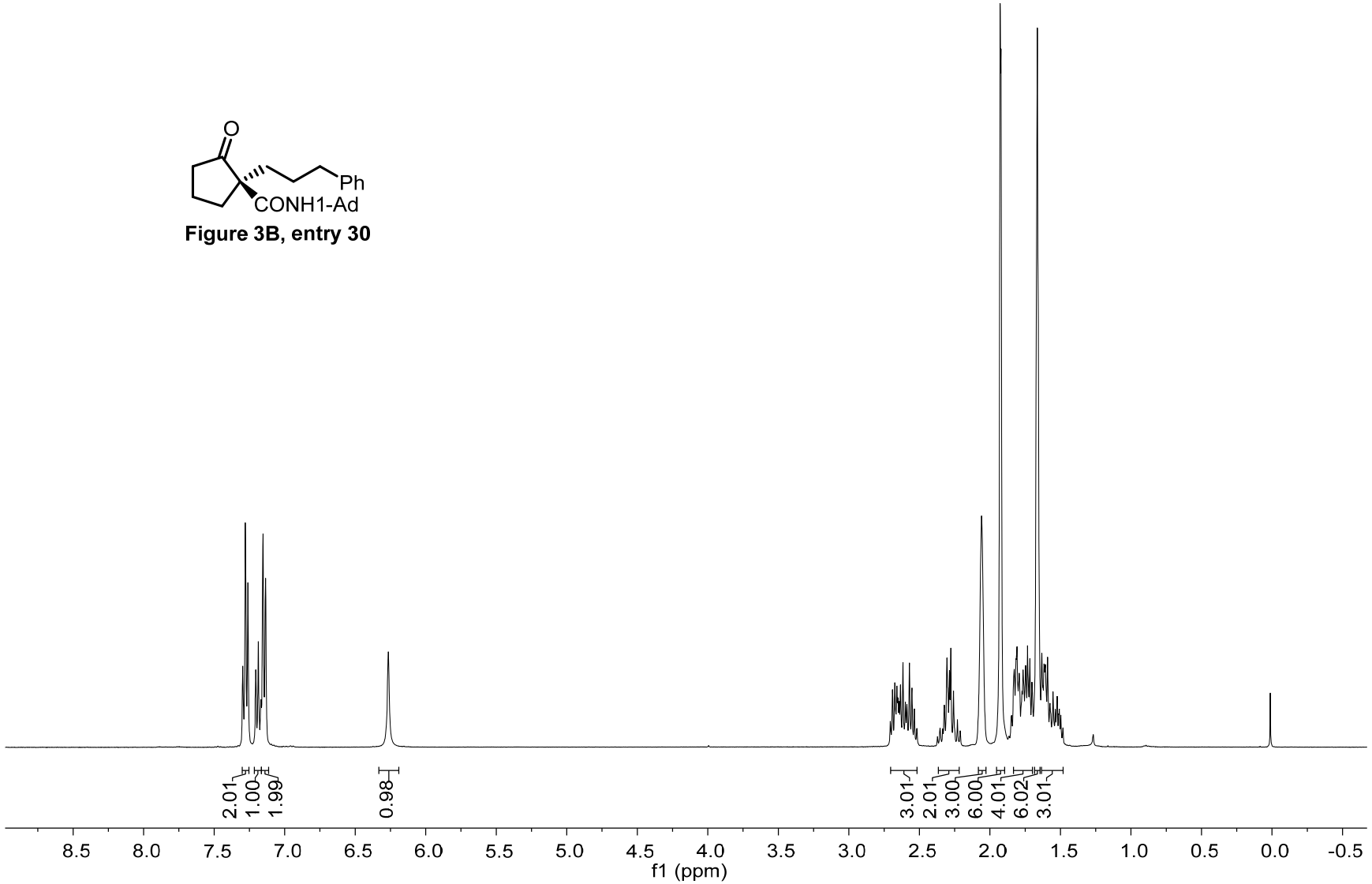

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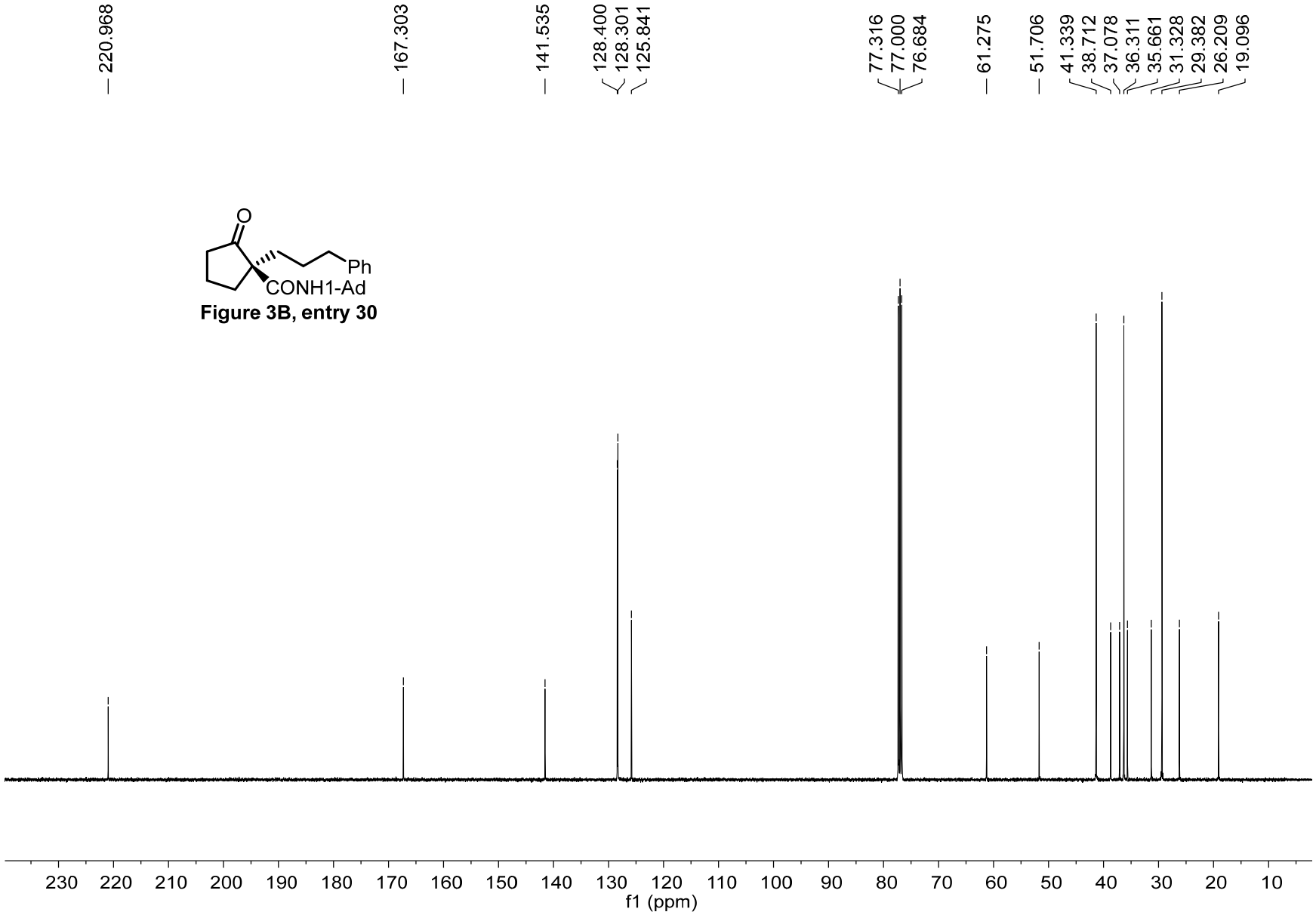

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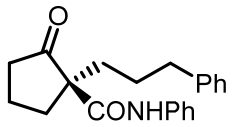

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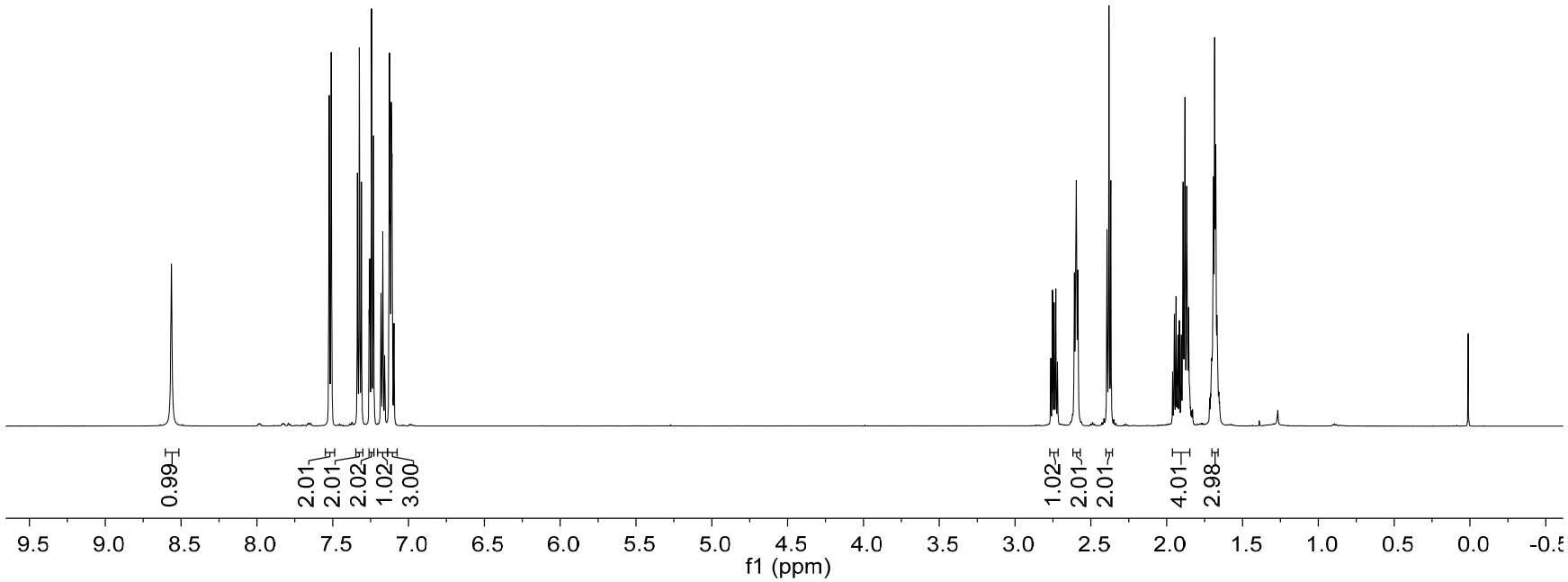

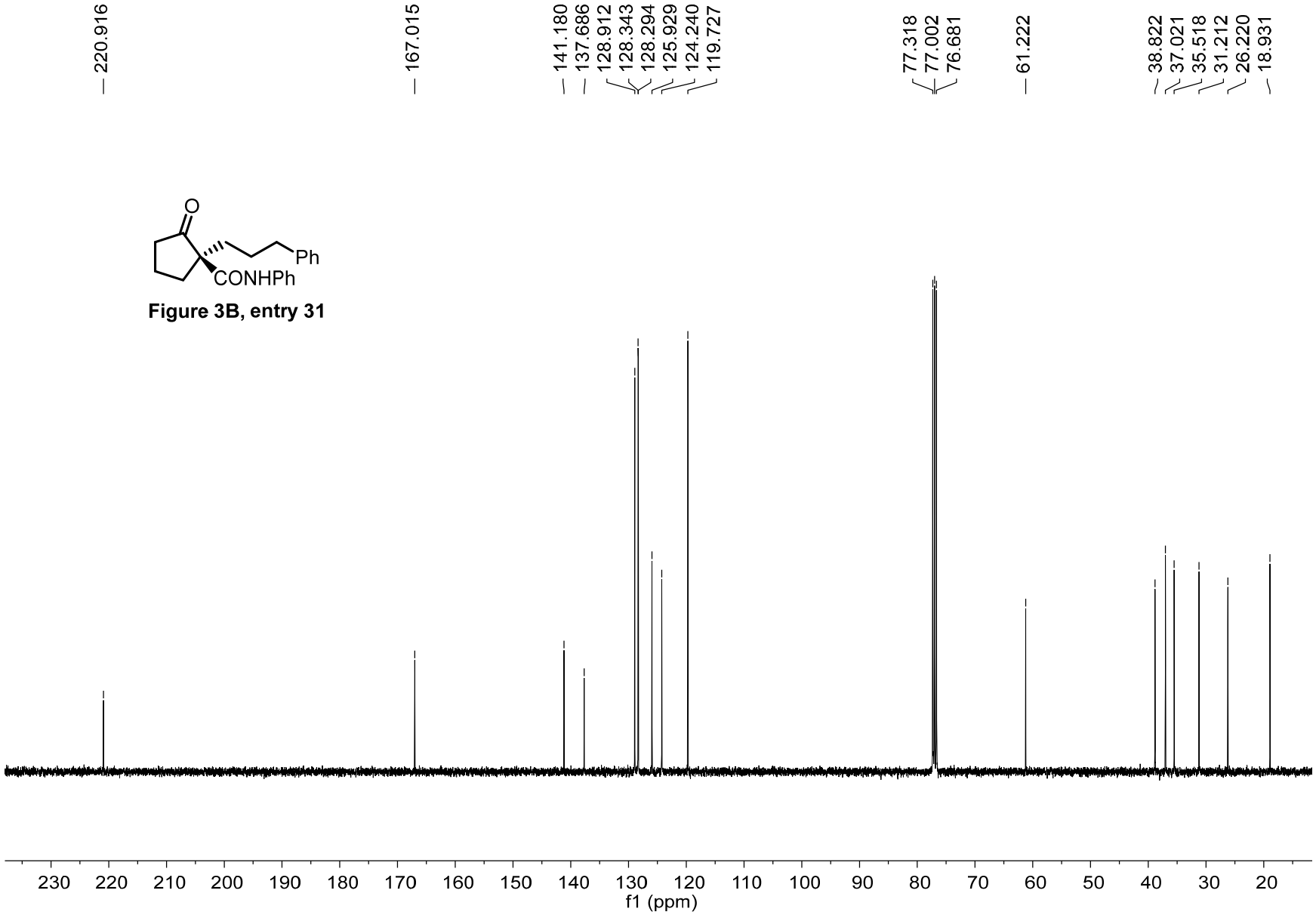

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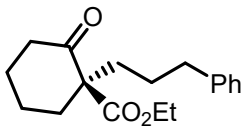

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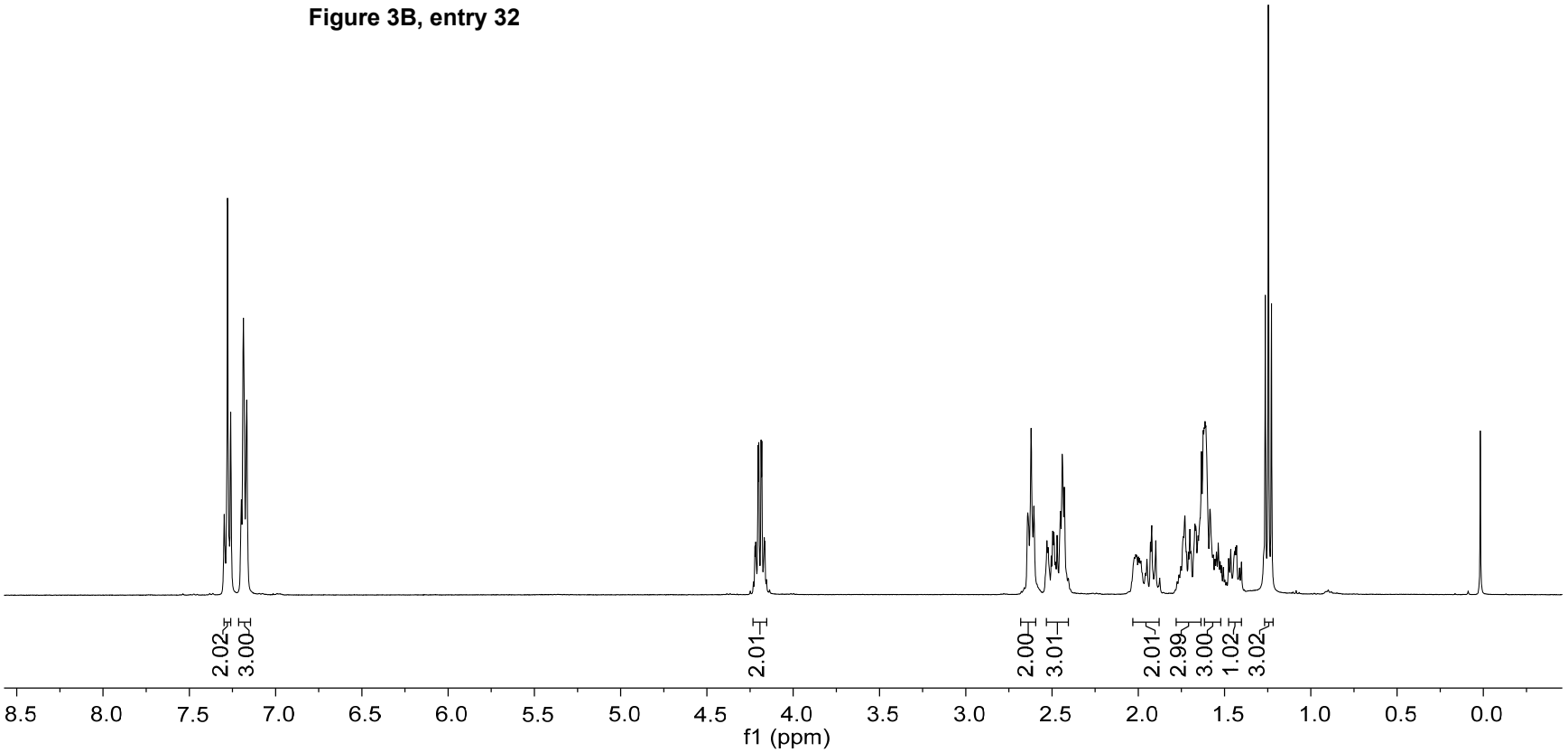

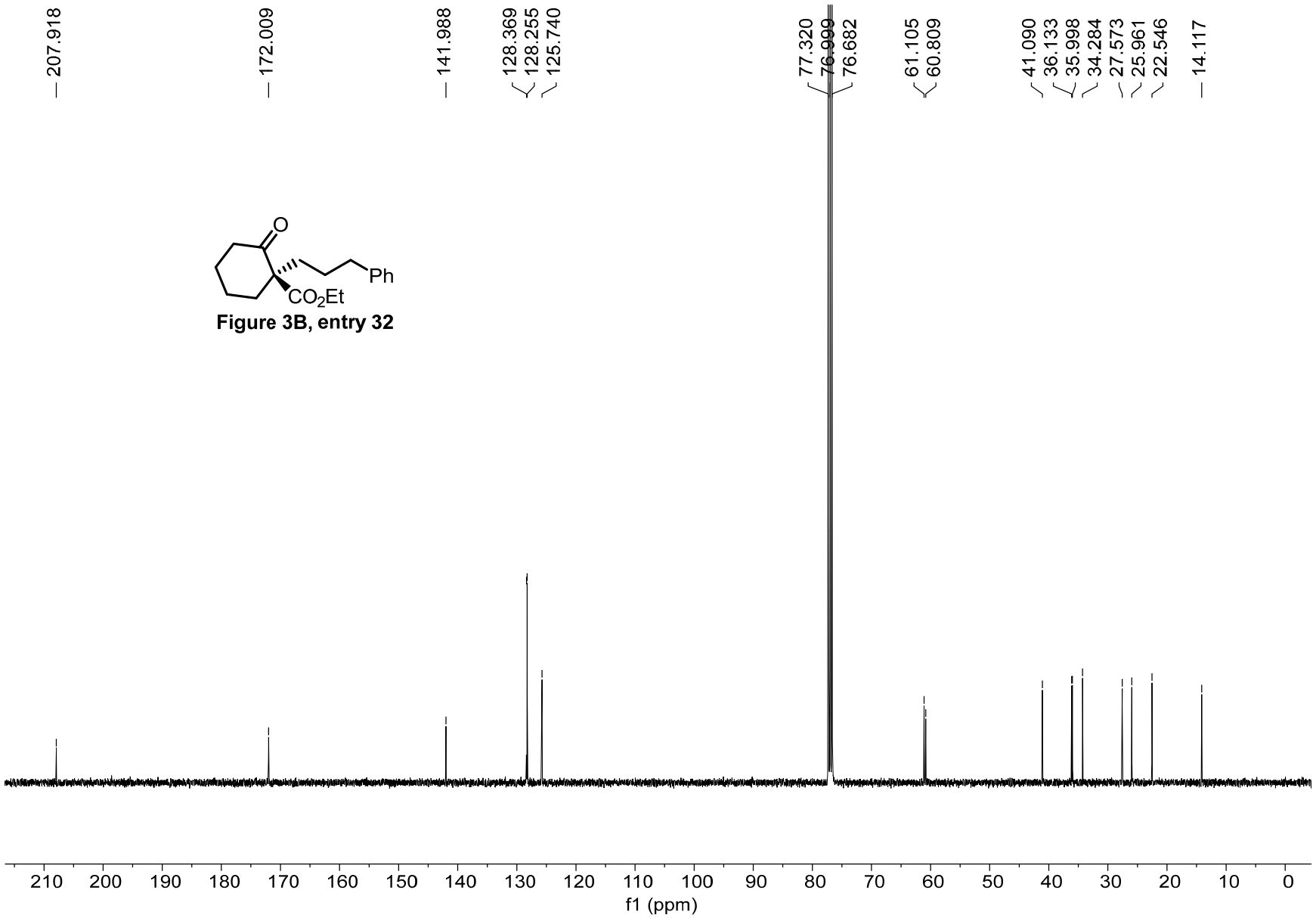

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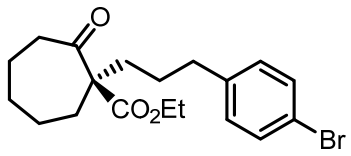

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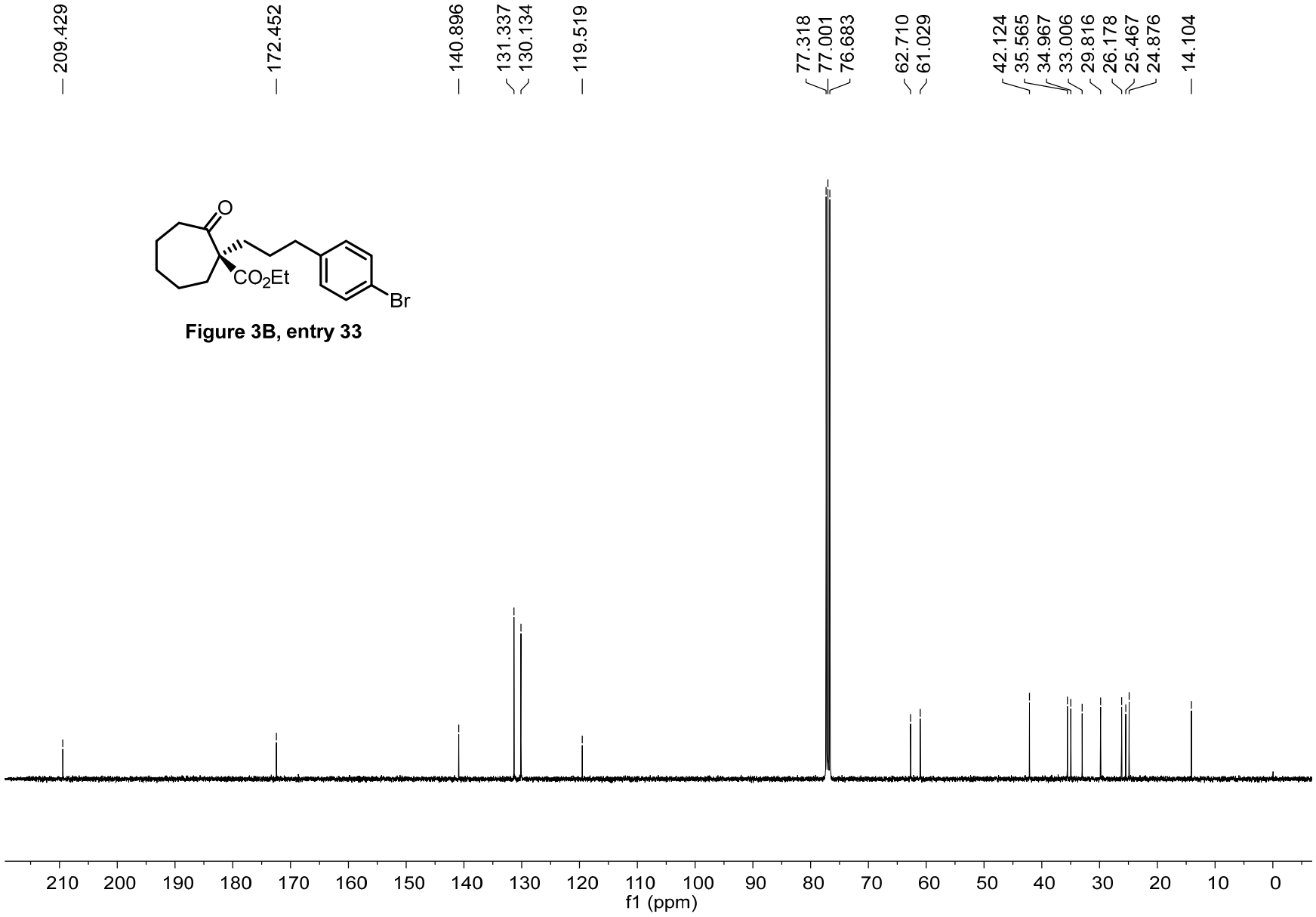

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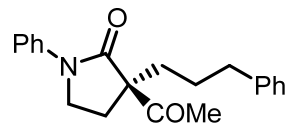

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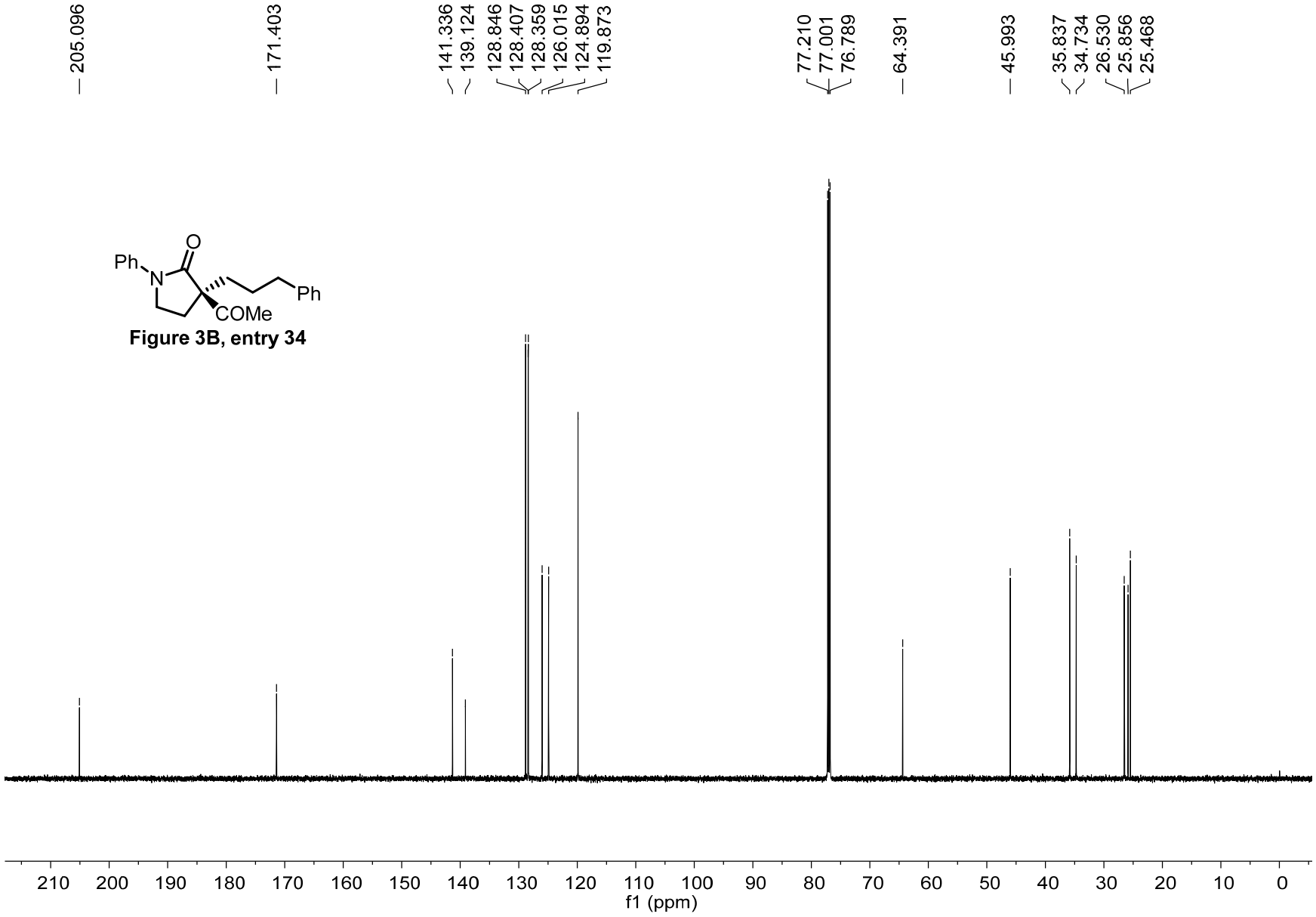

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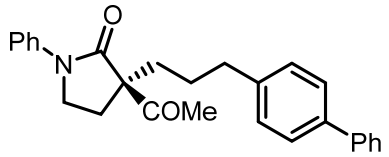


Figure 3B, entry 35

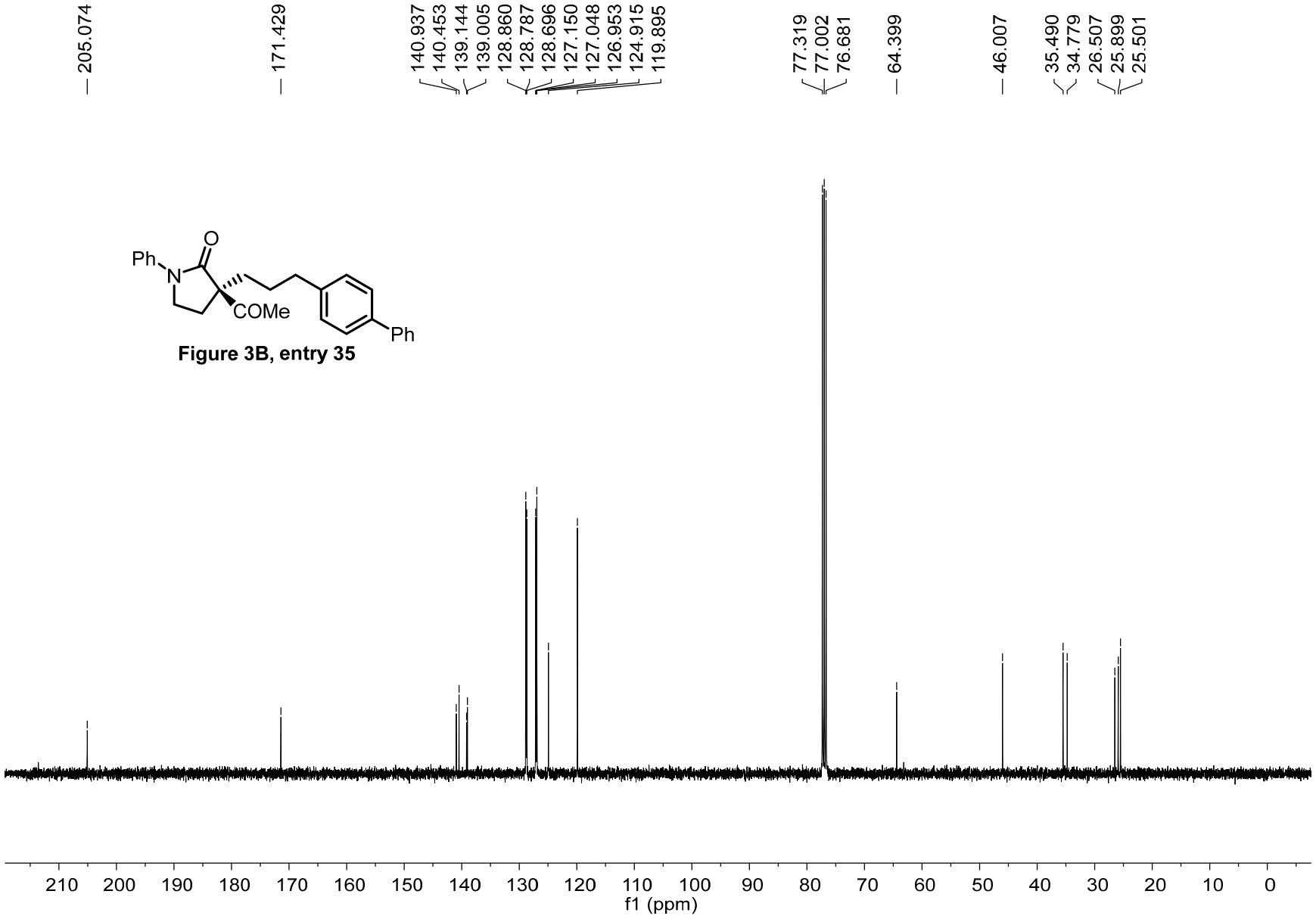


Figure 3B, entry 35

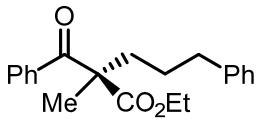


Figure 3B, entry 36

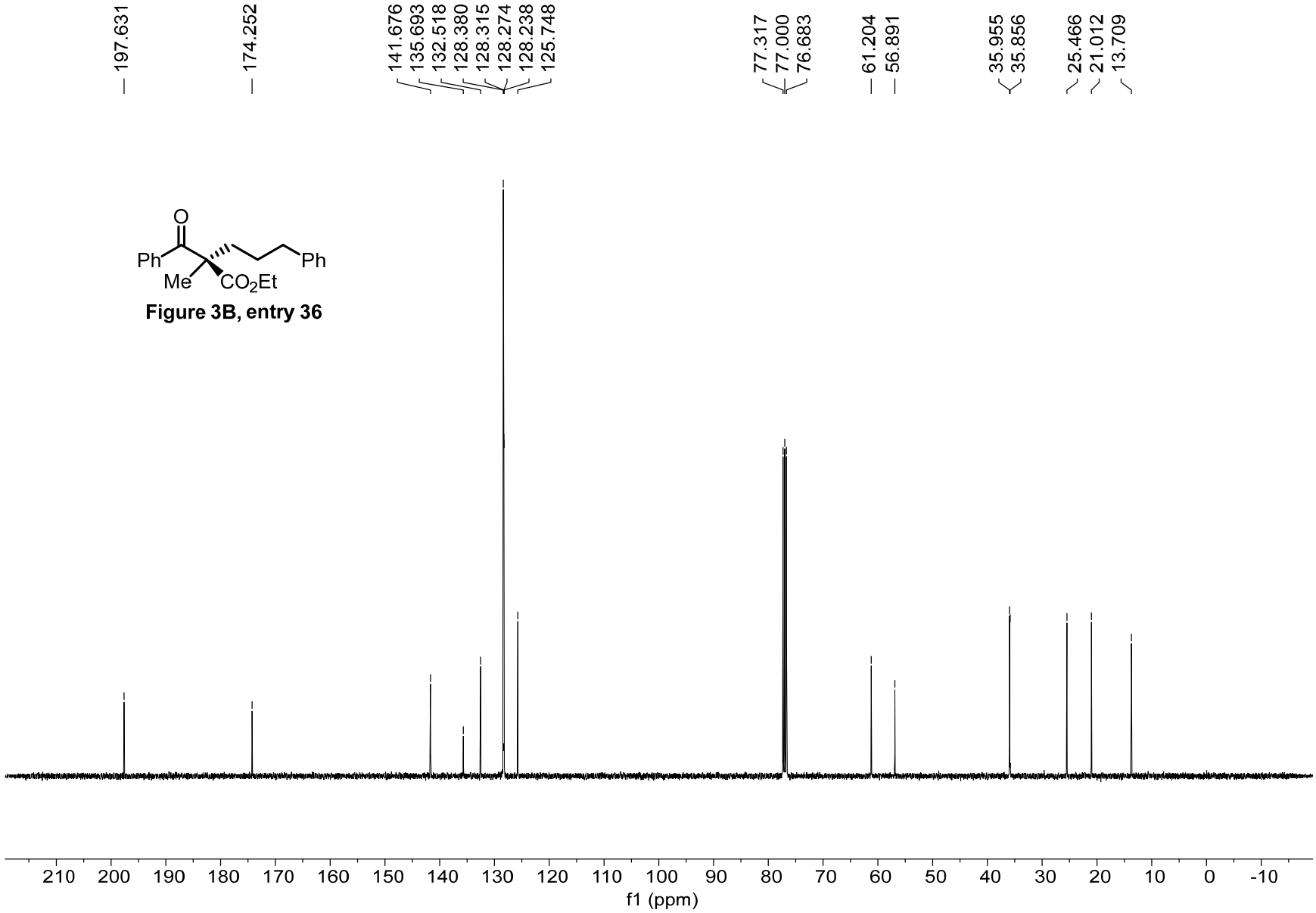


Figure 3B, entry 36

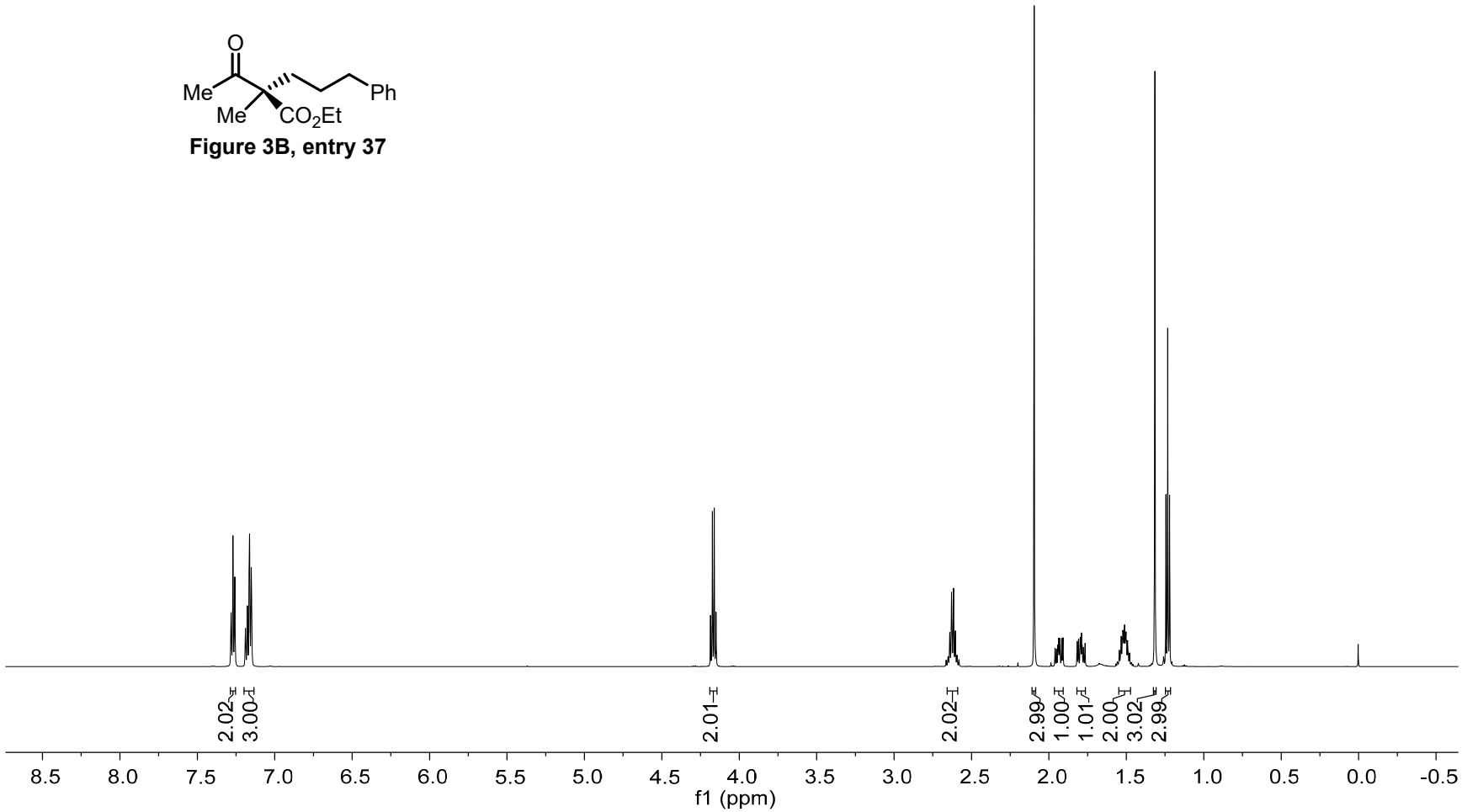


Figure 3B, entry 37

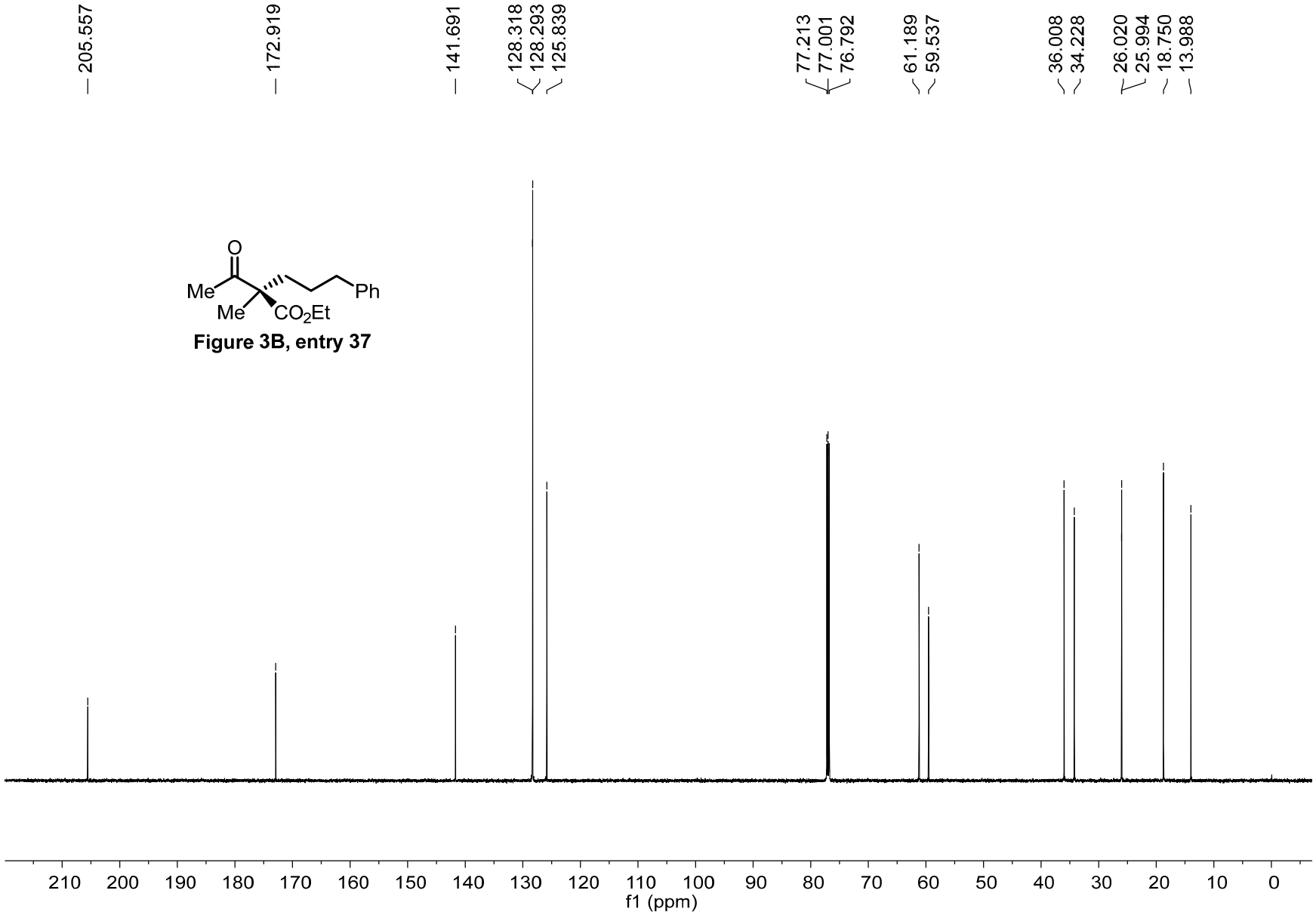


Figure 3B, entry 37

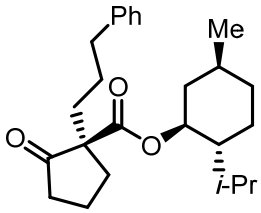


Figure 3B, entry 38

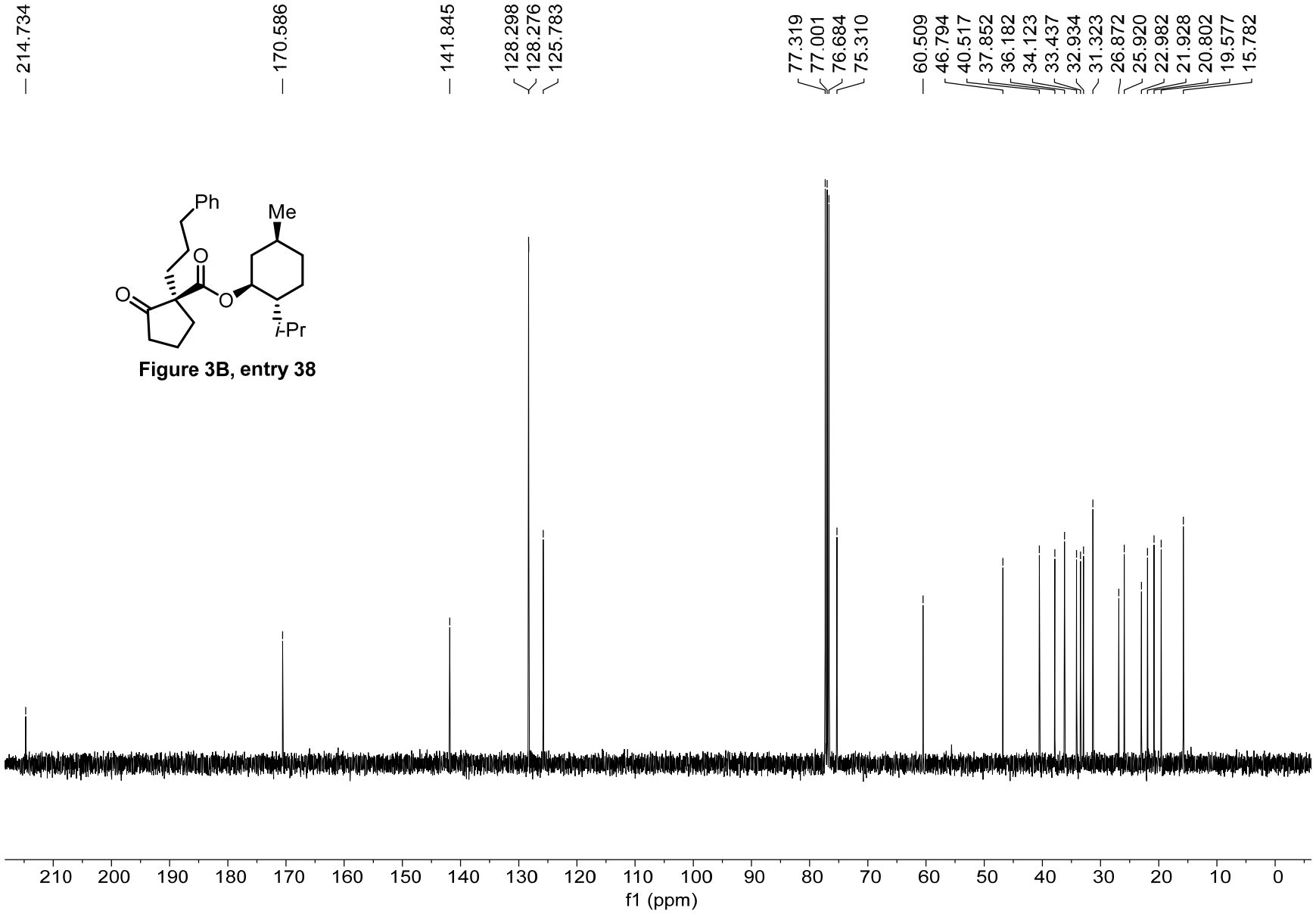


Figure 3B, entry 38

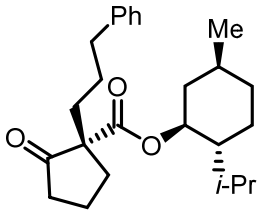


Figure 3B, entry 39

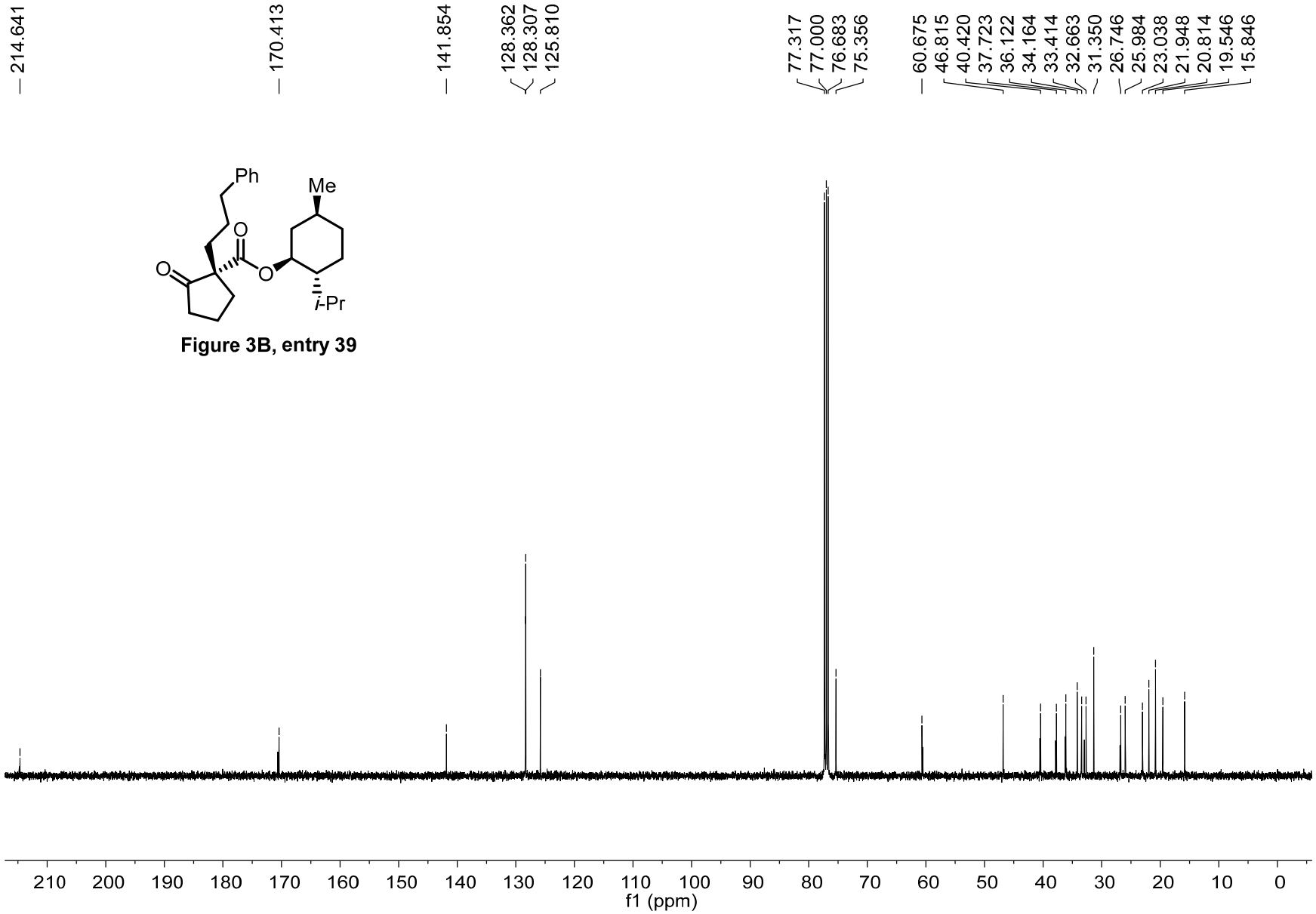


Figure 3B, entry 39

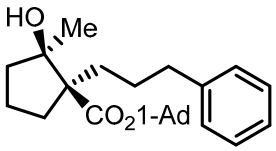
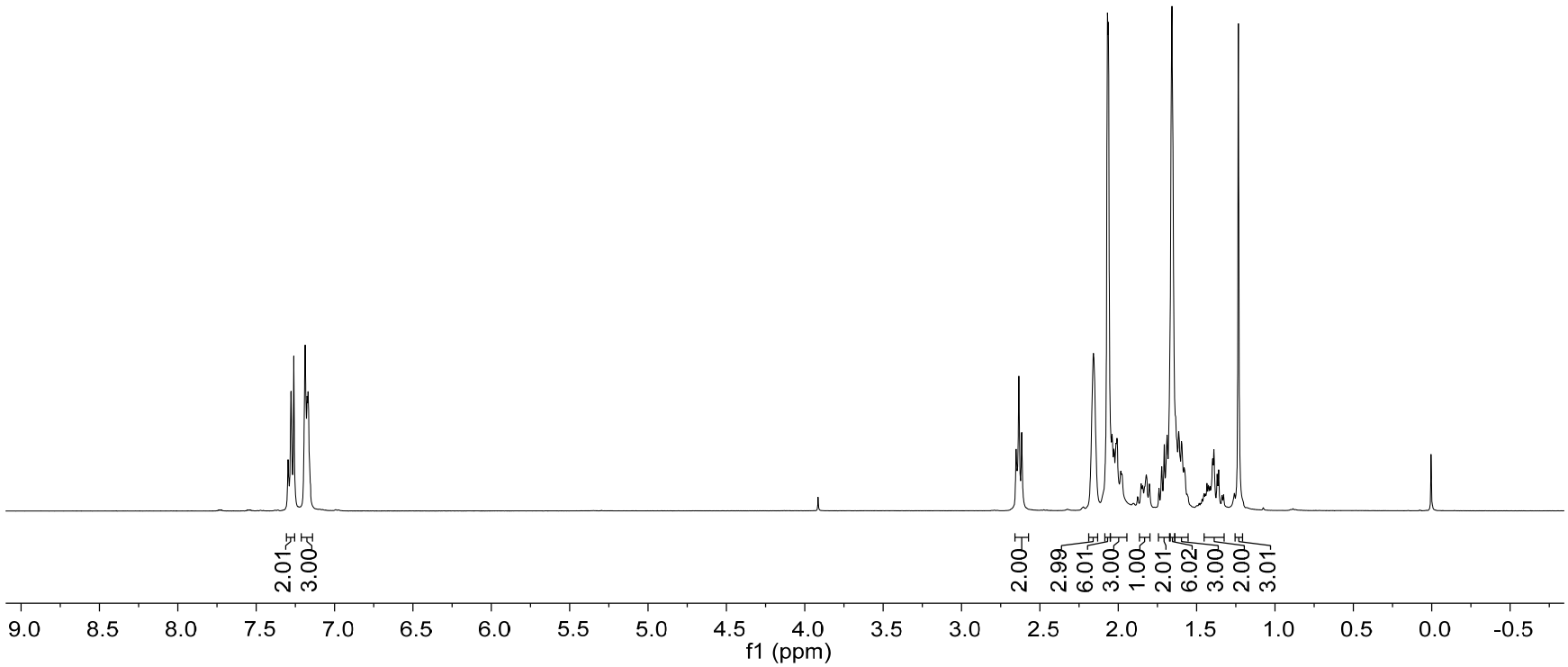


Figure 4, entry 40



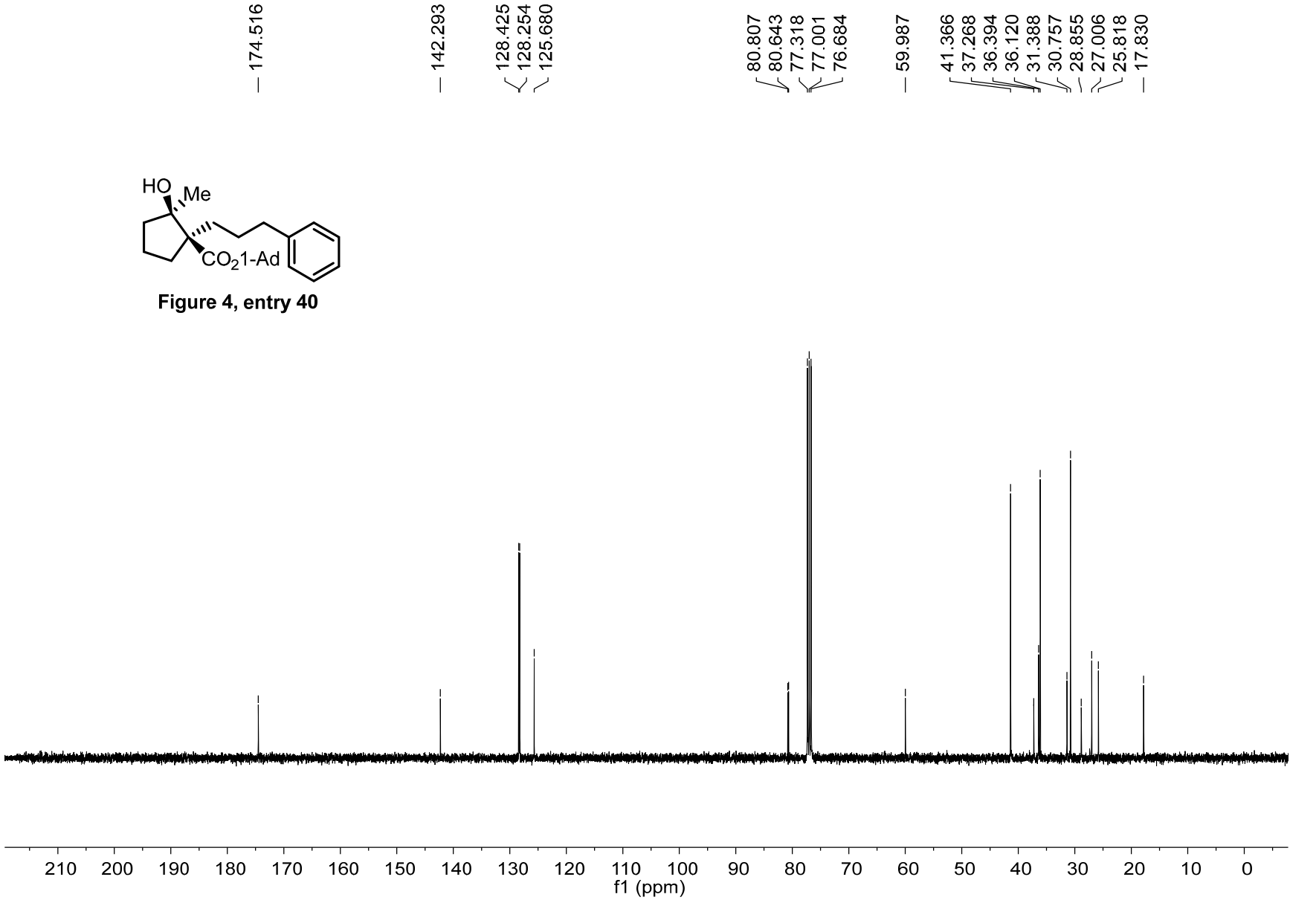


Figure 4, entry 40

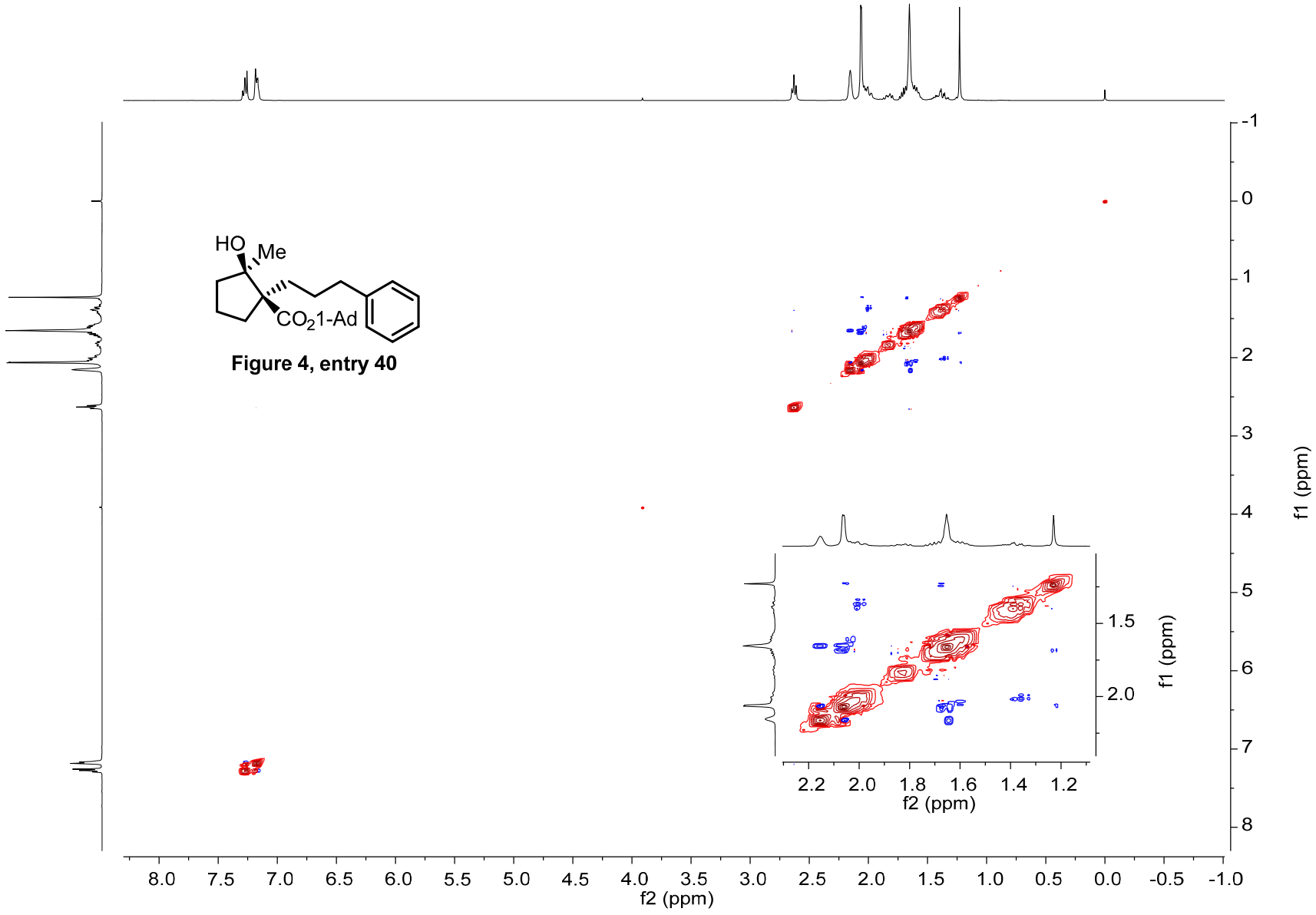


Figure 4, entry 40

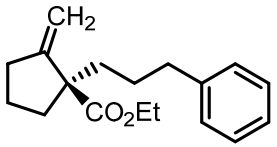
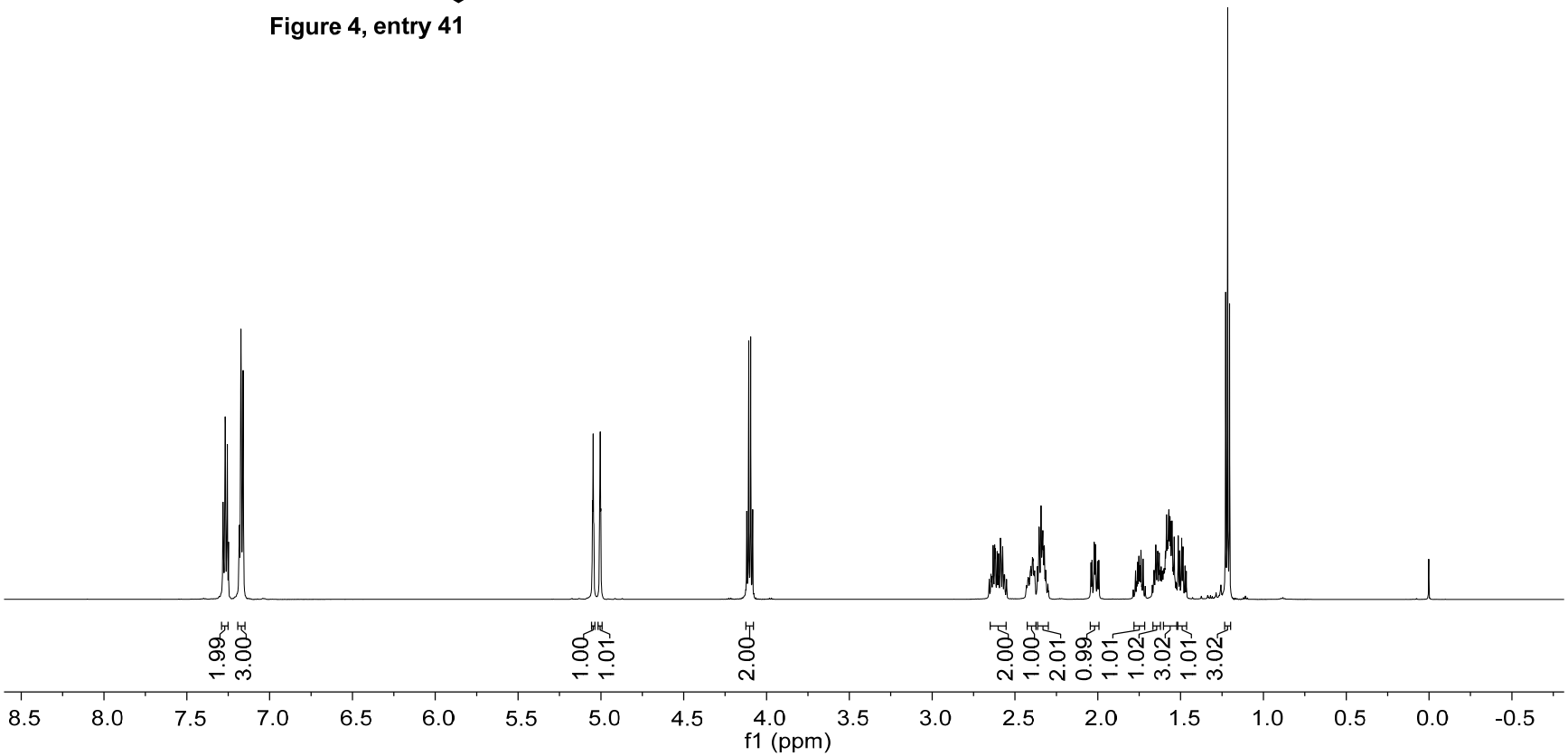


Figure 4, entry 41



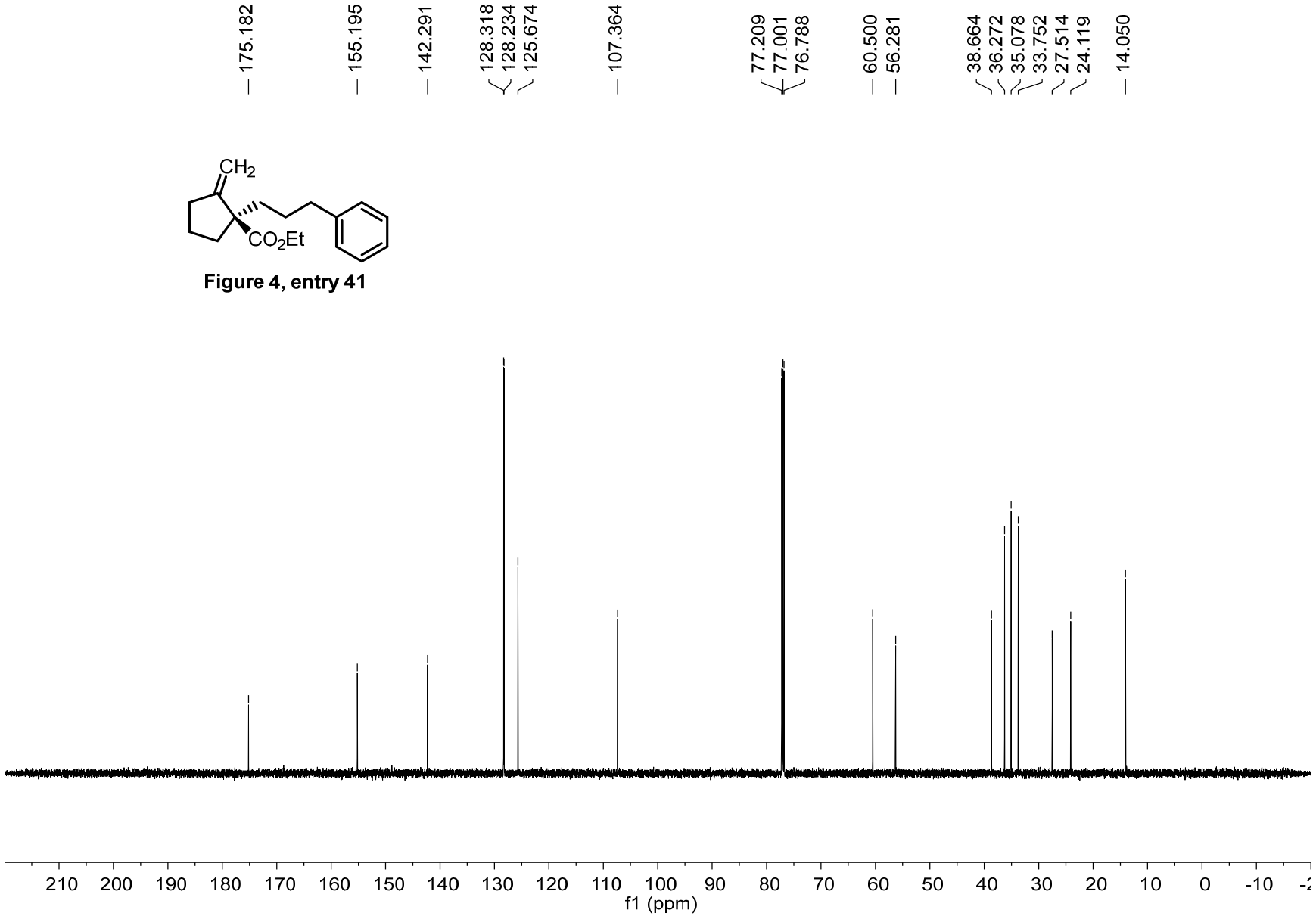


Figure 4, entry 41

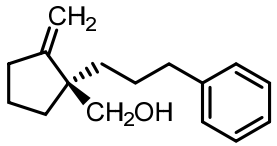
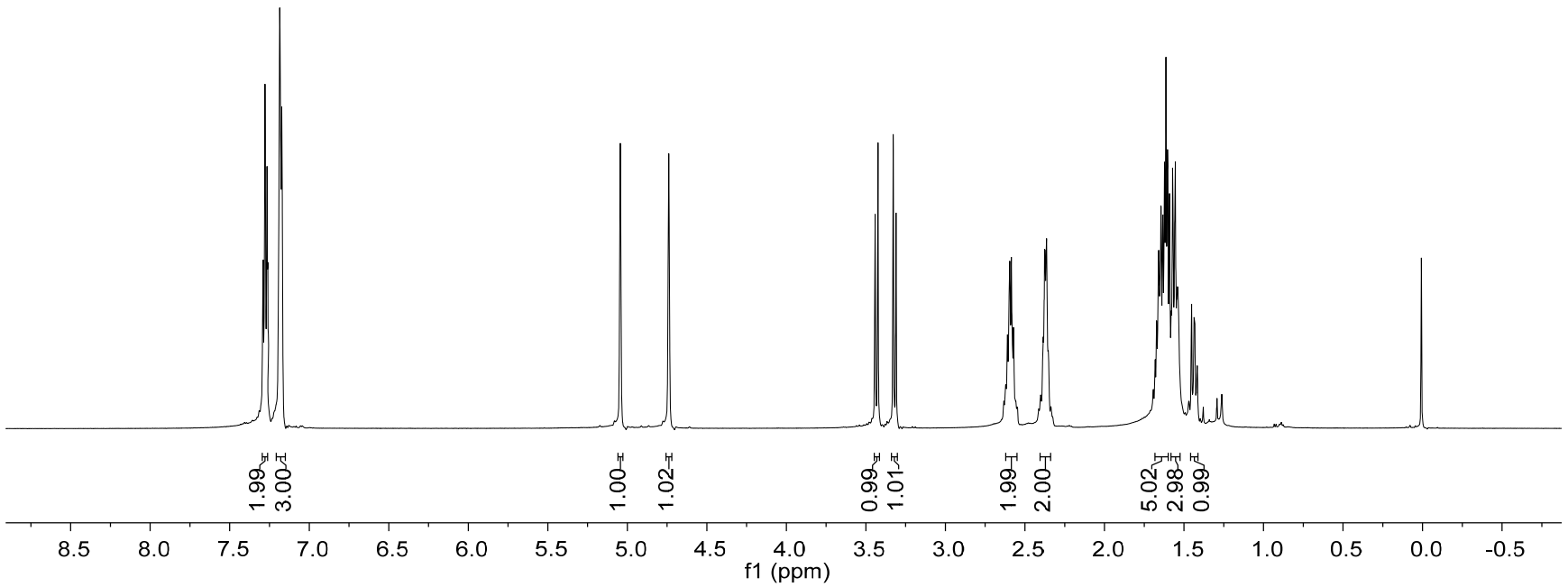


Figure 4, entry 41'



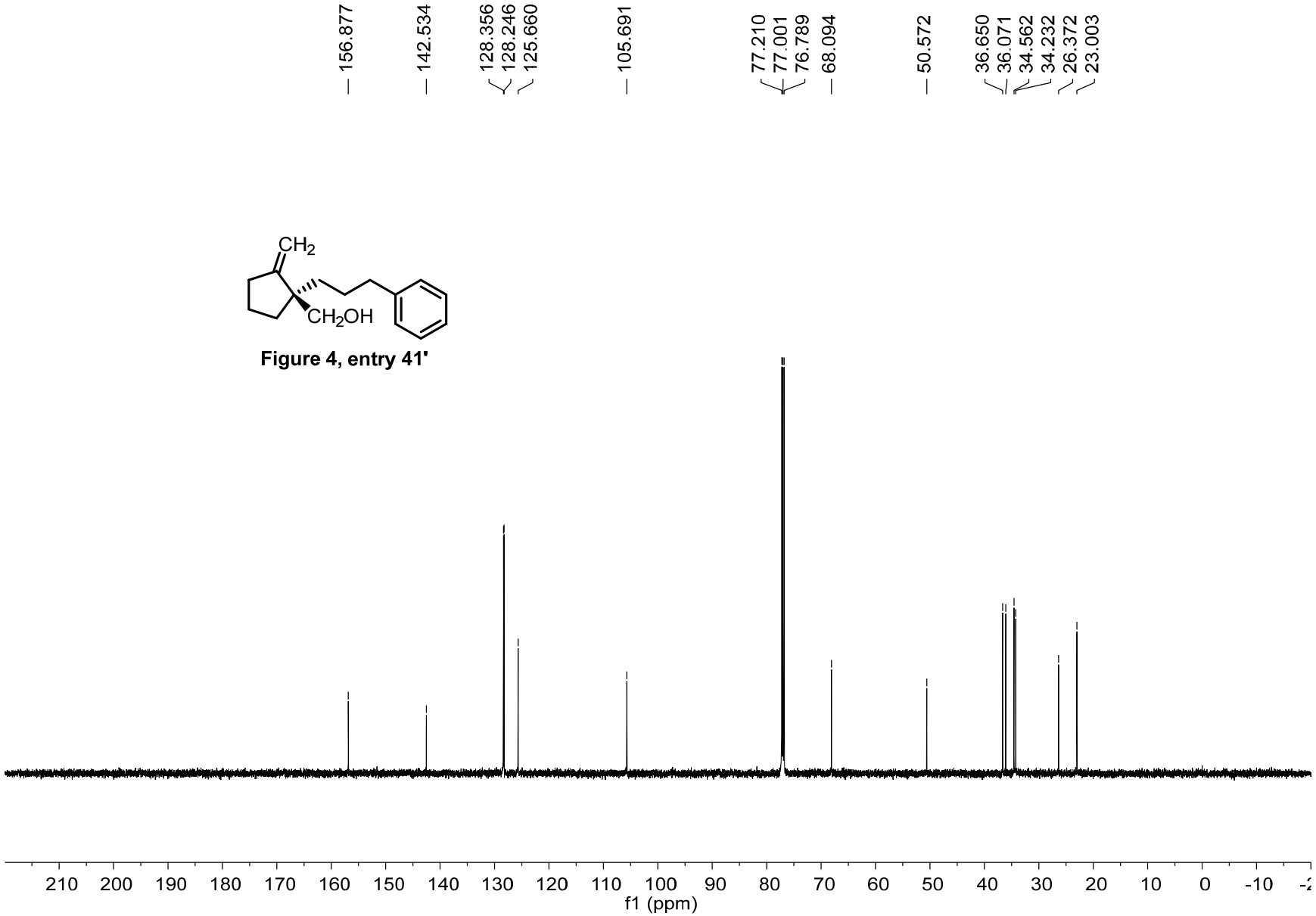


Figure 4, entry 41'

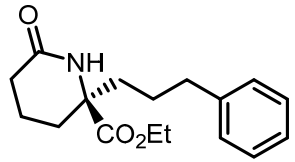


Figure 4, entry 42

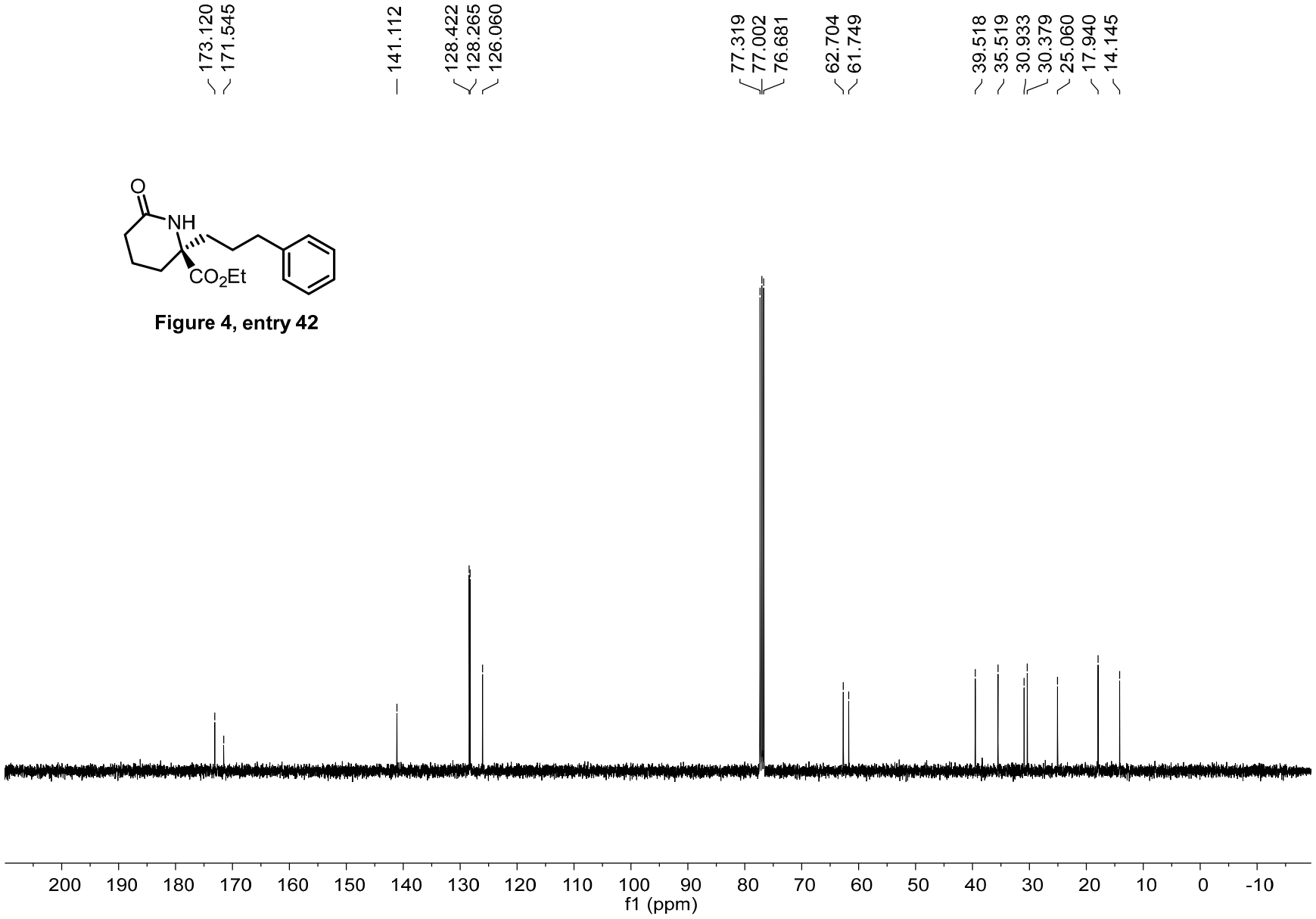


Figure 4, entry 42

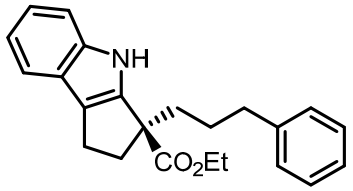
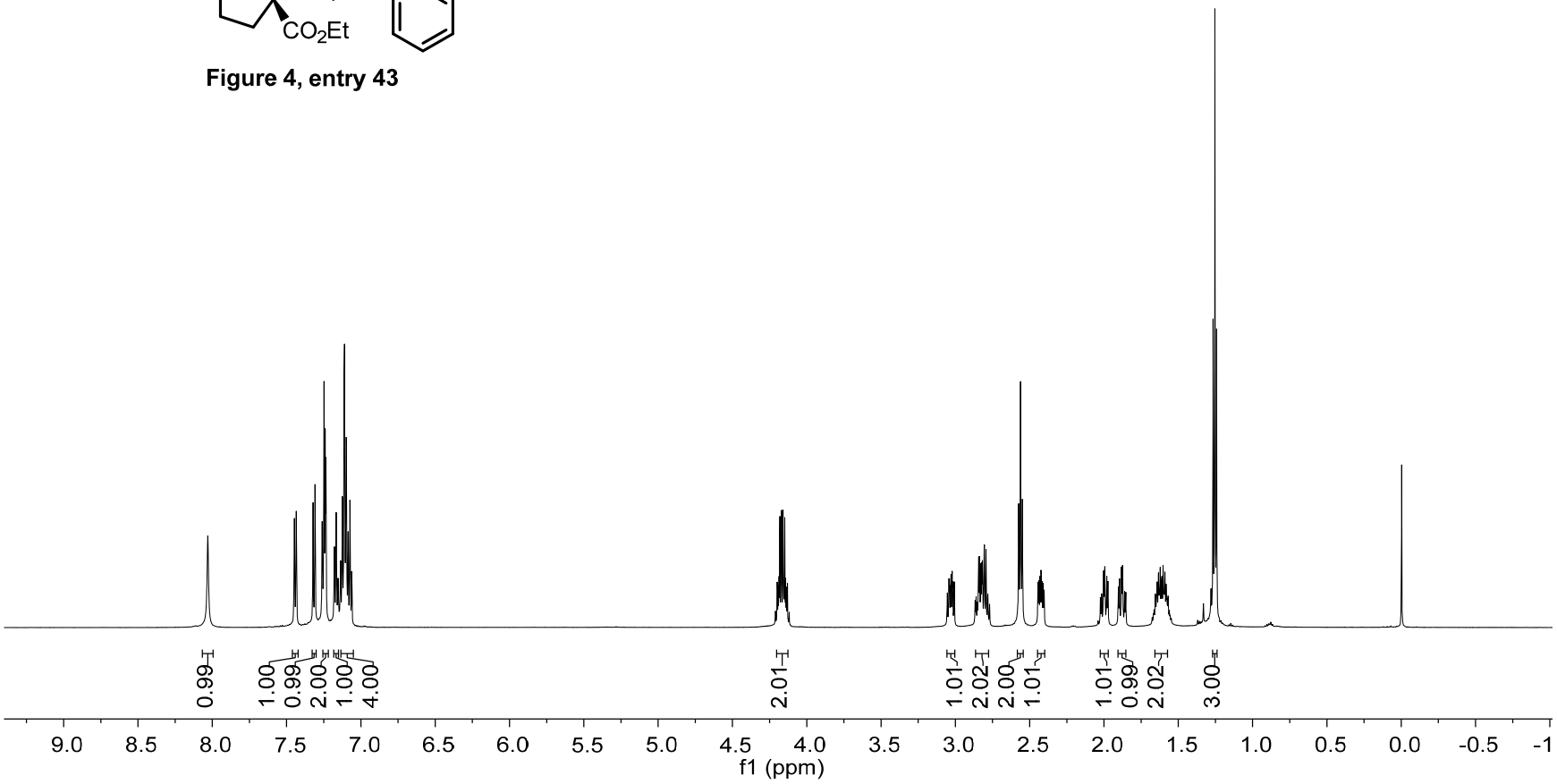


Figure 4, entry 43



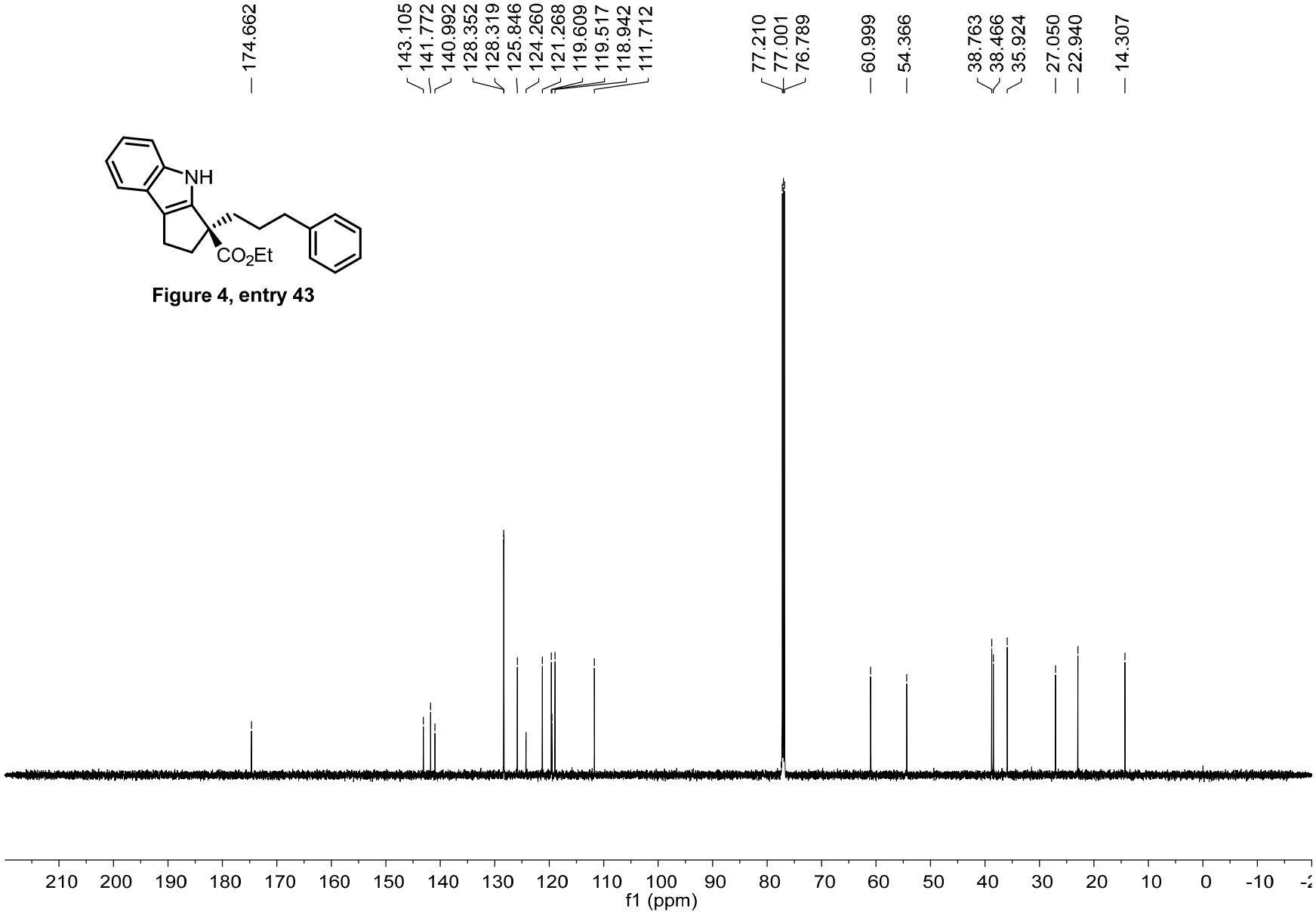


Figure 4, entry 43

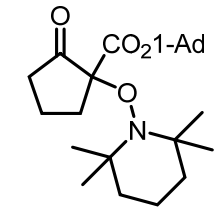
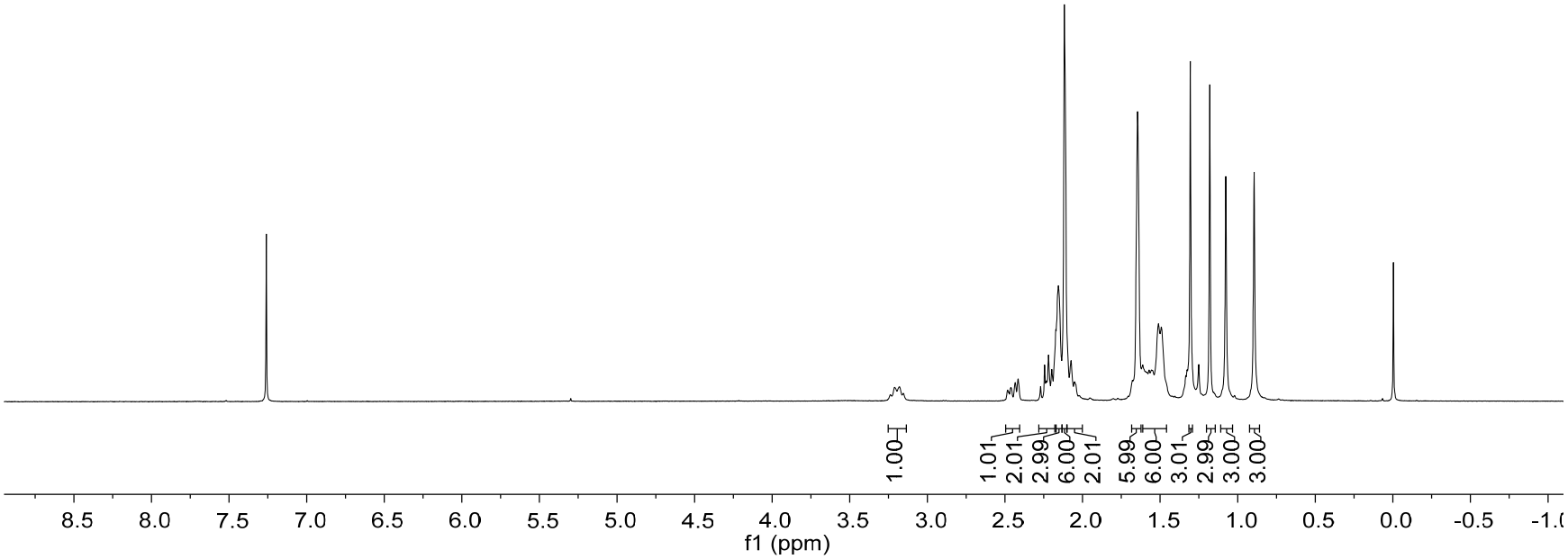


Figure 5A, entry A[1]



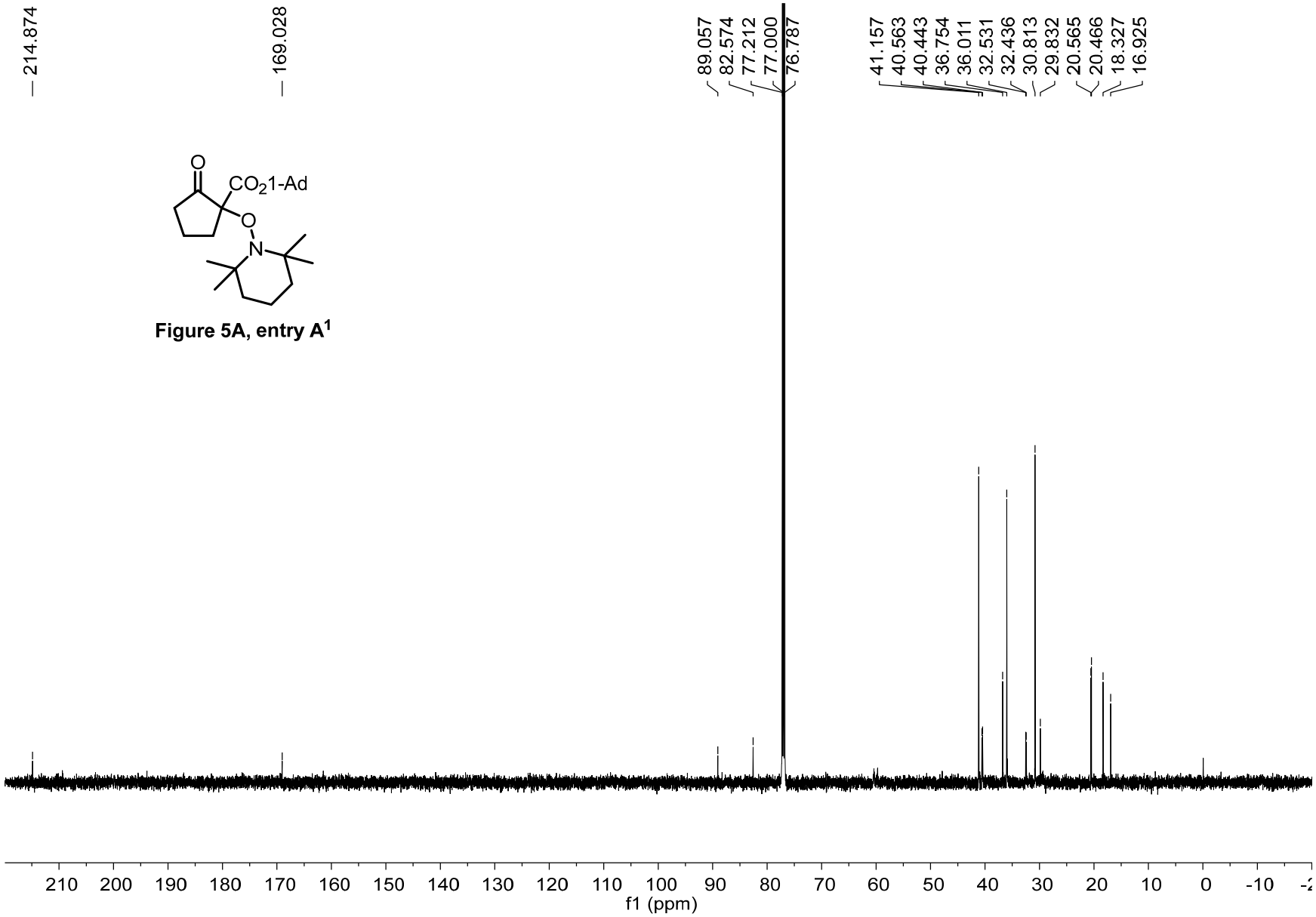


Figure 5A, entry A[1]

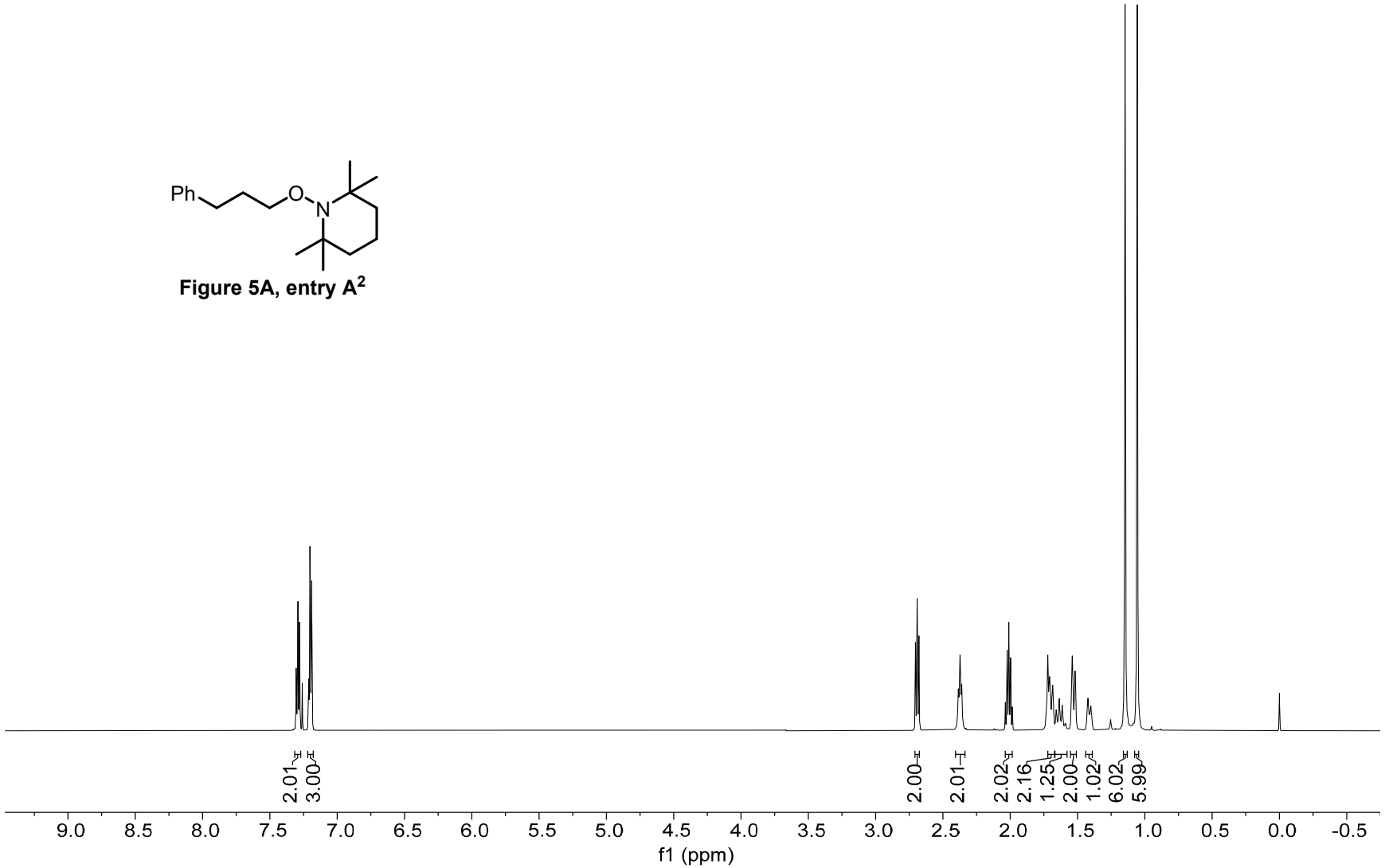


Figure 5A, entry A[2]

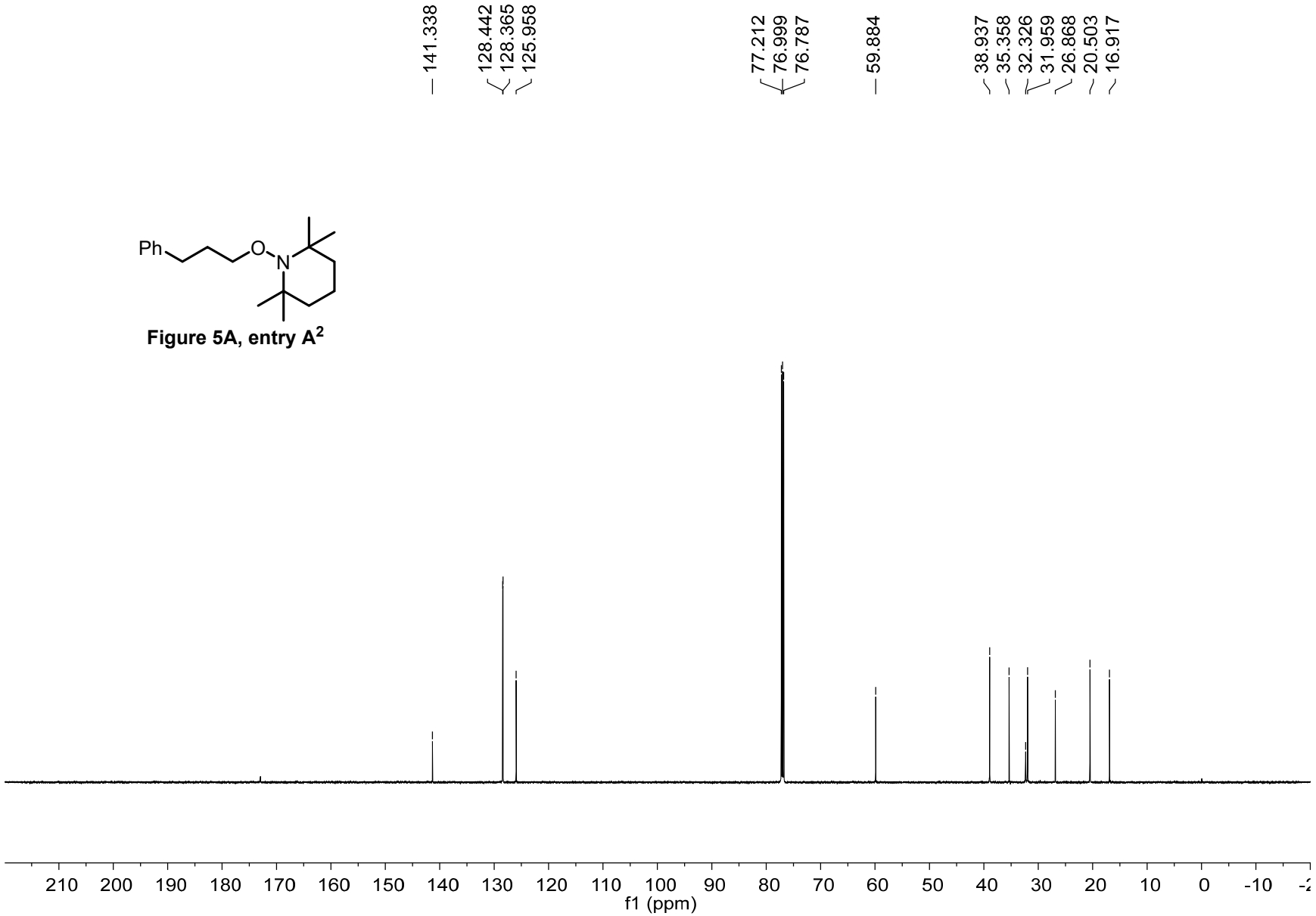
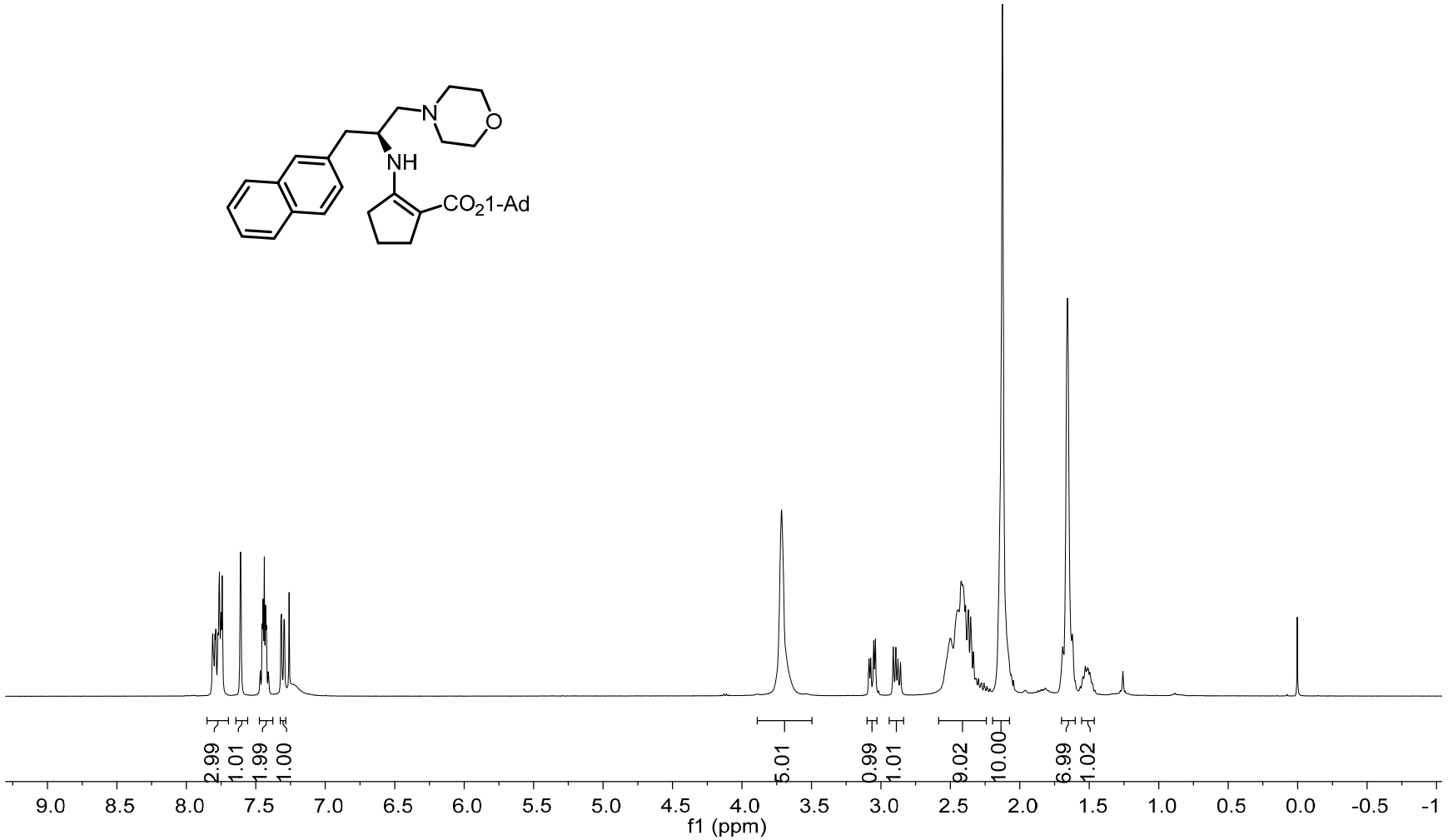
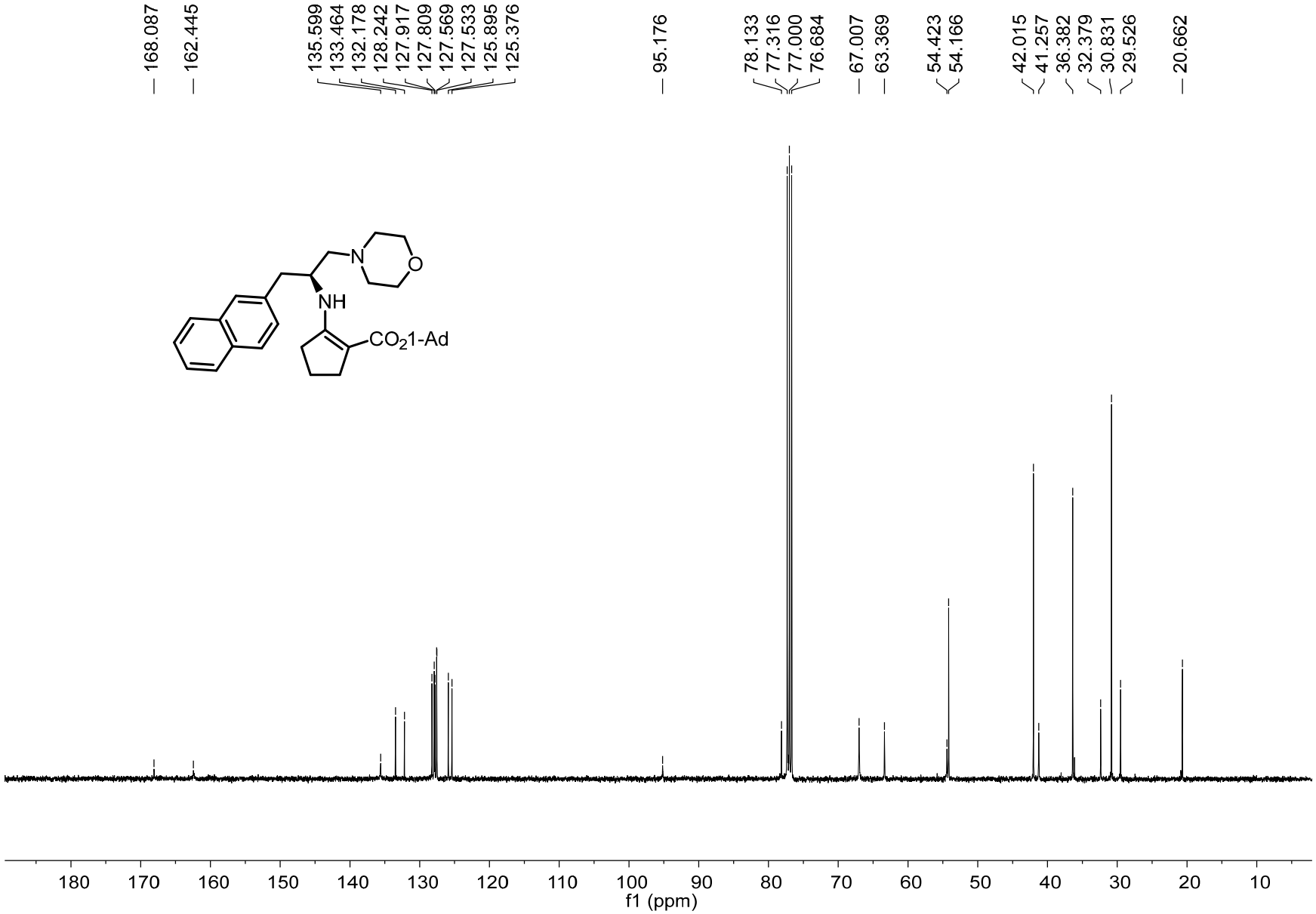


Figure 5A, entry A[2]


N
O
NH
CO2 1-Ad
2.99
1.01
1.99
1.00
5.01
0.99
1.01
9.02
10.00
6.99
1.02
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 -1
f1 (ppm)


168.087
162.445
135.599
133.464
132.178
128.242
127.917
127.809
127.569
127.533
125.895
125.376
95.176
78.133
77.316
77.000
76.684
67.007
63.369
54.423
54.166
42.015
41.257
36.382
32.379
30.831
29.526
20.662
N
O
NH
CO2 1-Ad
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

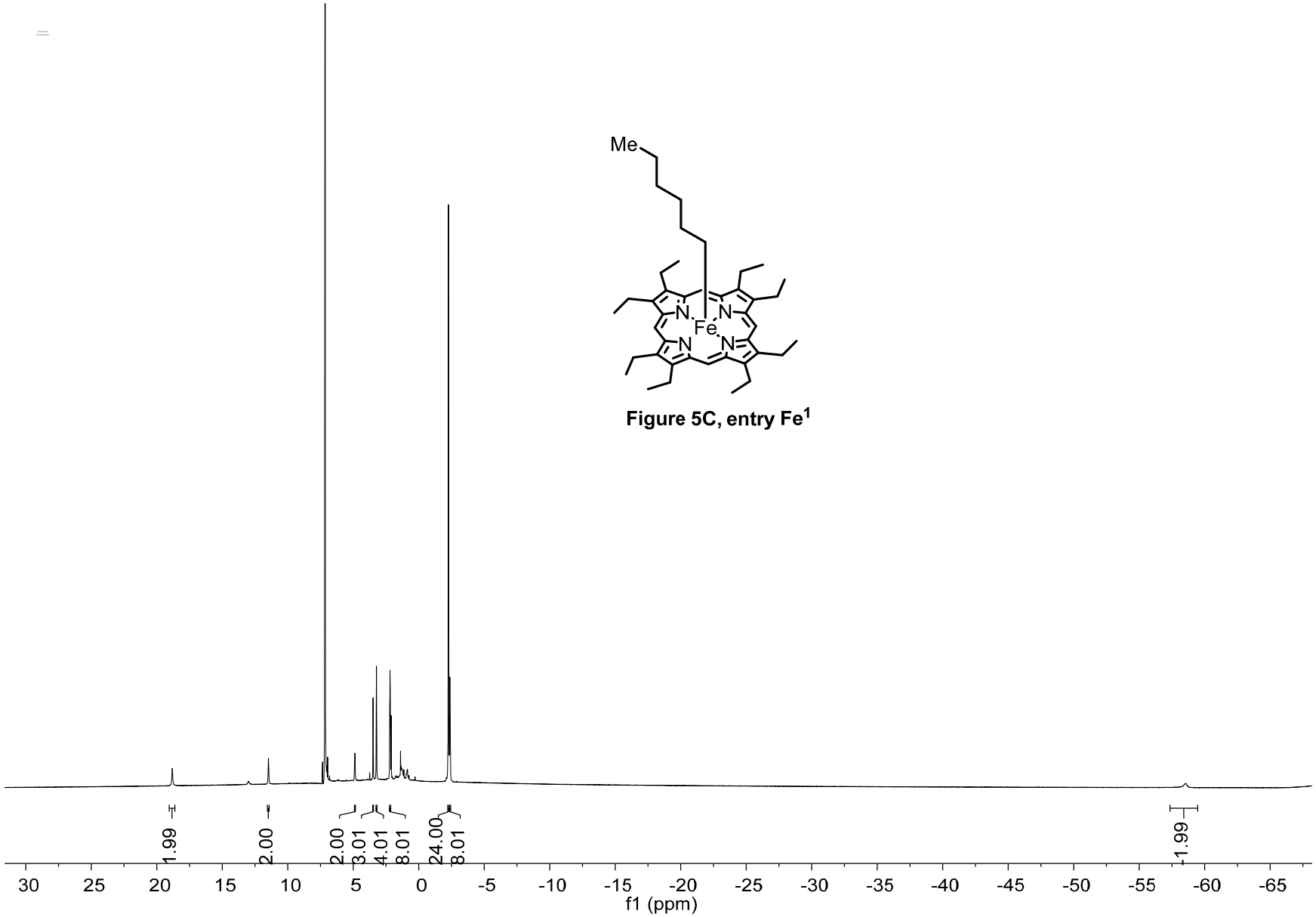


Figure 5C, entry Fe[1]

Determination of Stereoselectivity

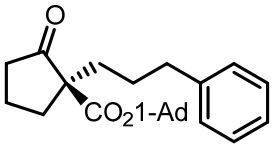
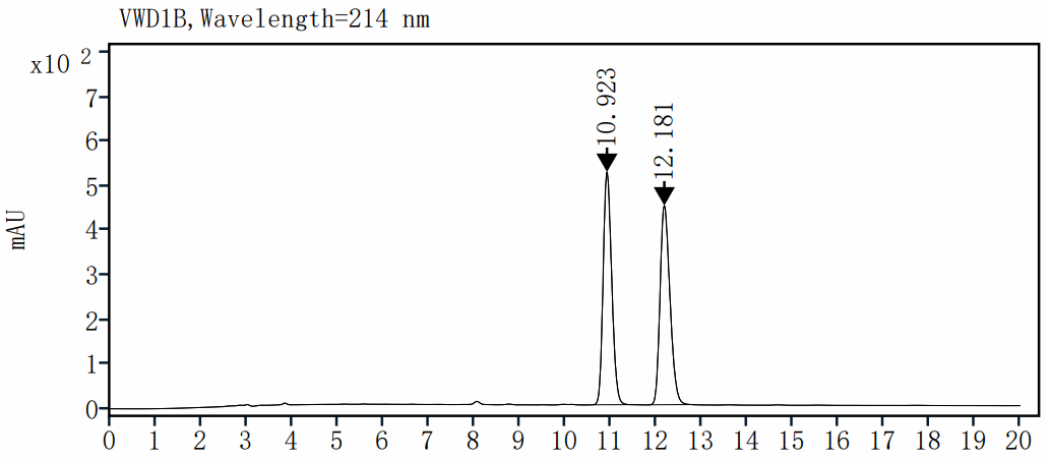
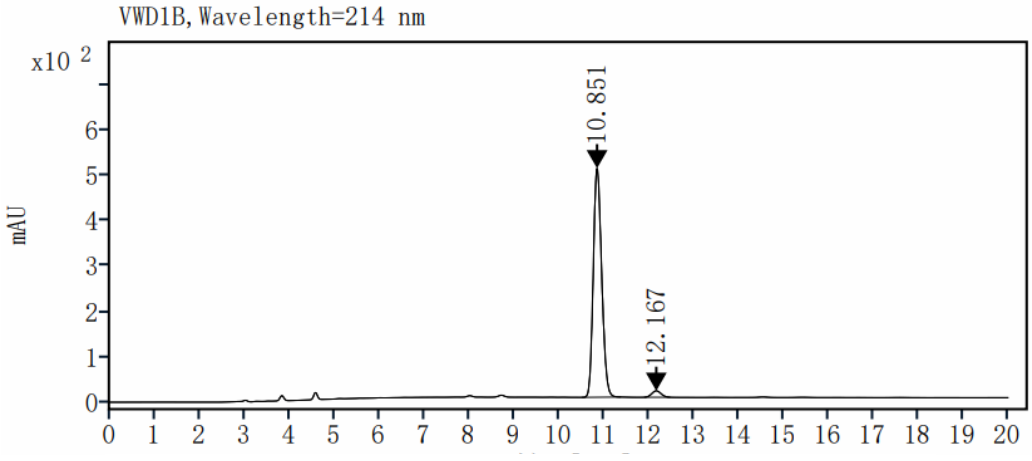


Figure 3A, entry 1
(*S*)-**A1**: 94% ee



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.923	MM m	6837.88	50.18
	12.181	MM m	6787.90	49.82



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.851	MM m	6567.11	97.00
	12.167	MM m	203.41	3.00

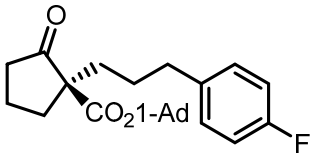
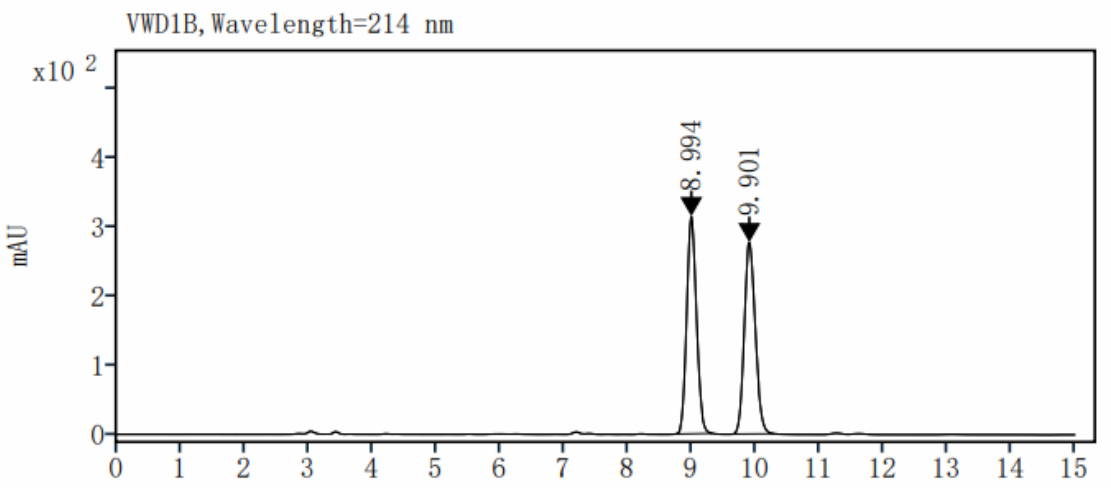
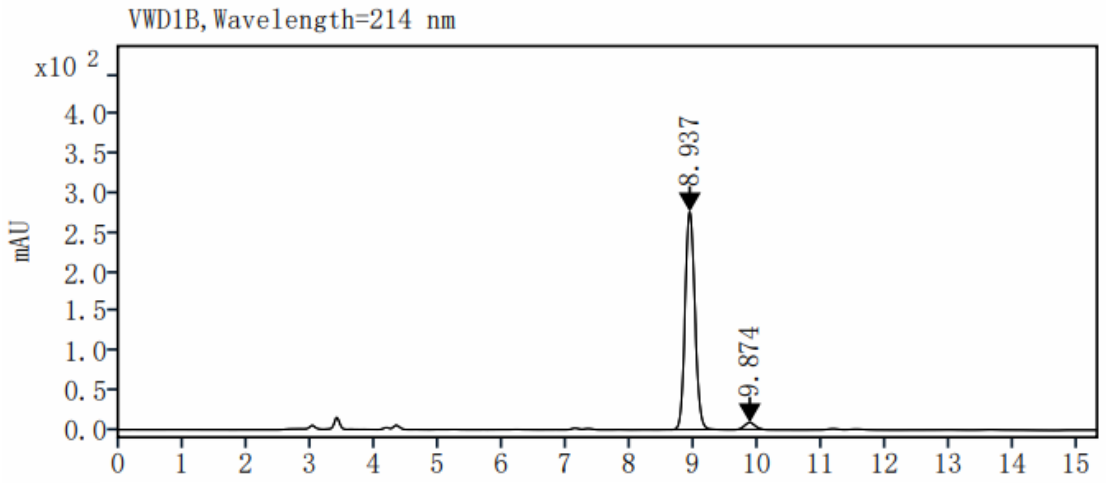


Figure 3A, entry 2
(*S*)-**A1**: 94% ee



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	8.994	MM m	3371.05	50.20
	9.901	MM m	3344.02	49.80



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	8.937	MM m	2940.45	96.87
	9.874	MM m	95.12	3.13

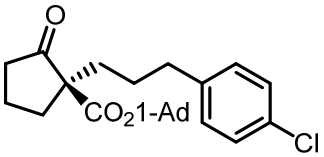
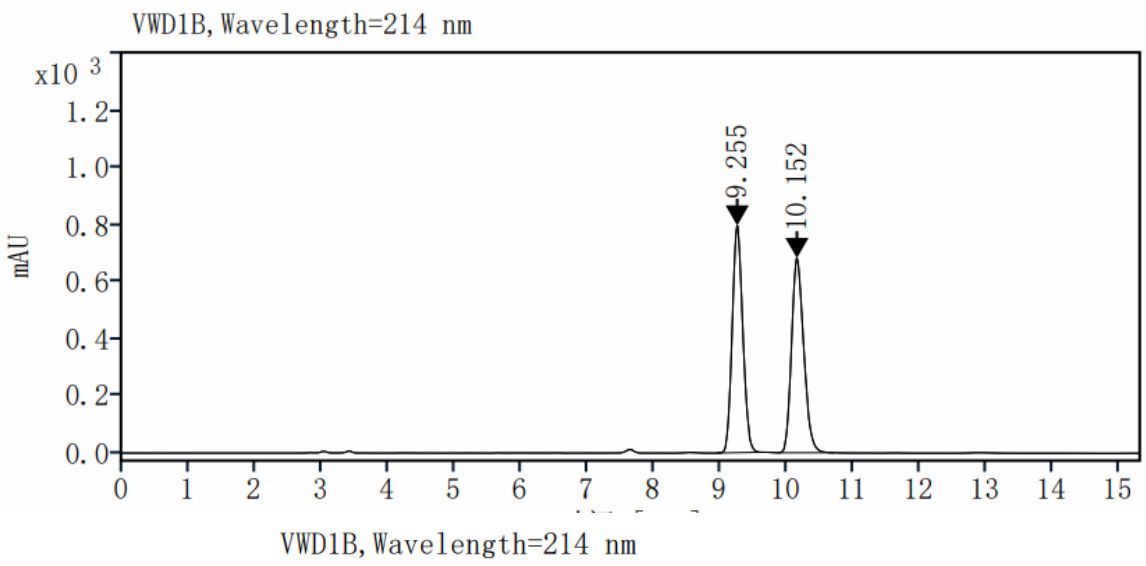
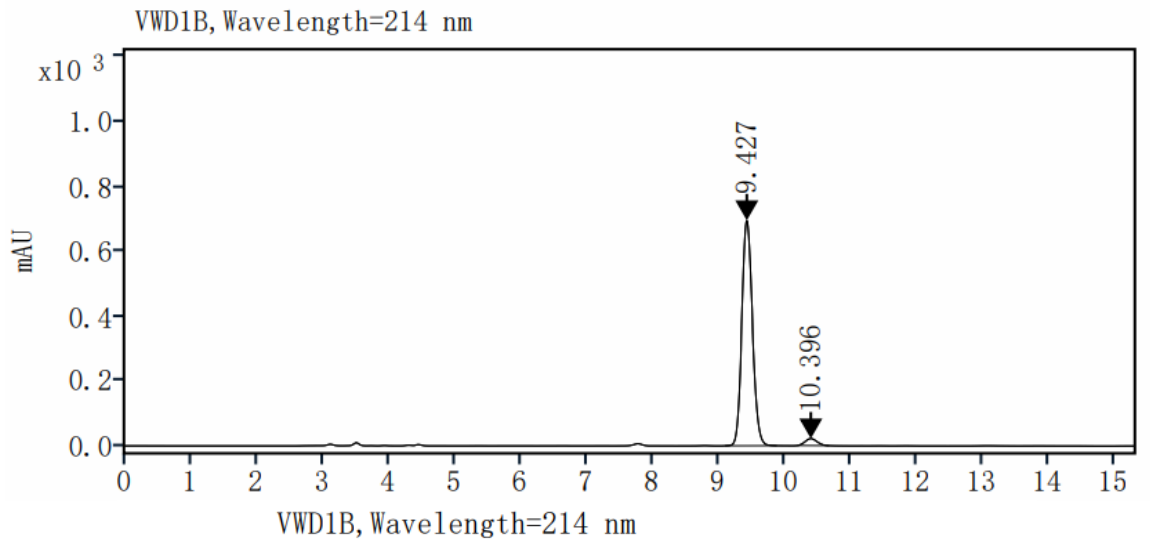


Figure 3A, entry 3
(*S*)-**A3**: 93% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.255	MM m	8802.24	50.16
	10.152	MM m	8745.76	49.84



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.427	MM m	7753.15	96.64
	10.396	MM m	269.28	3.36

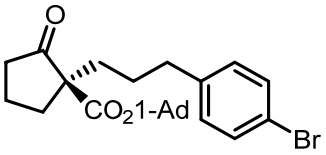
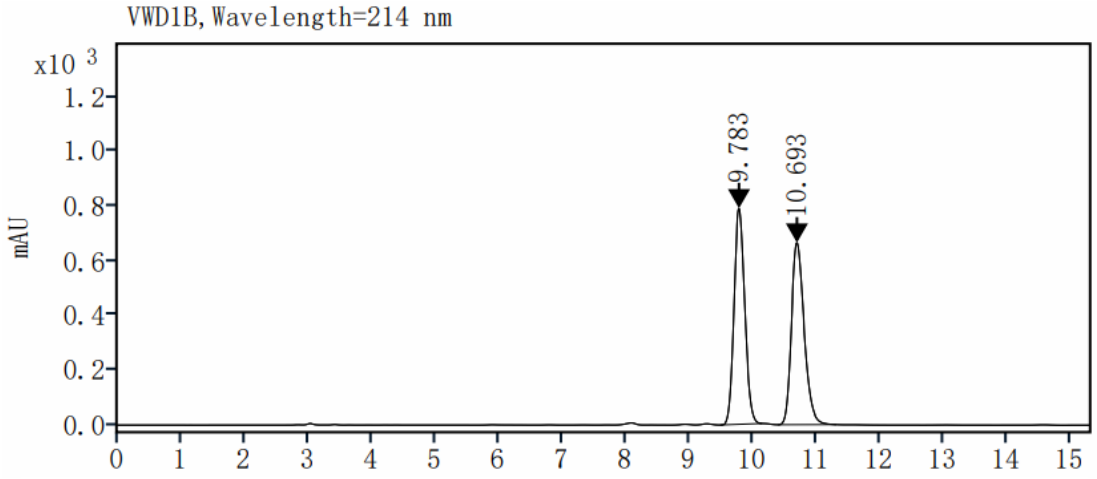
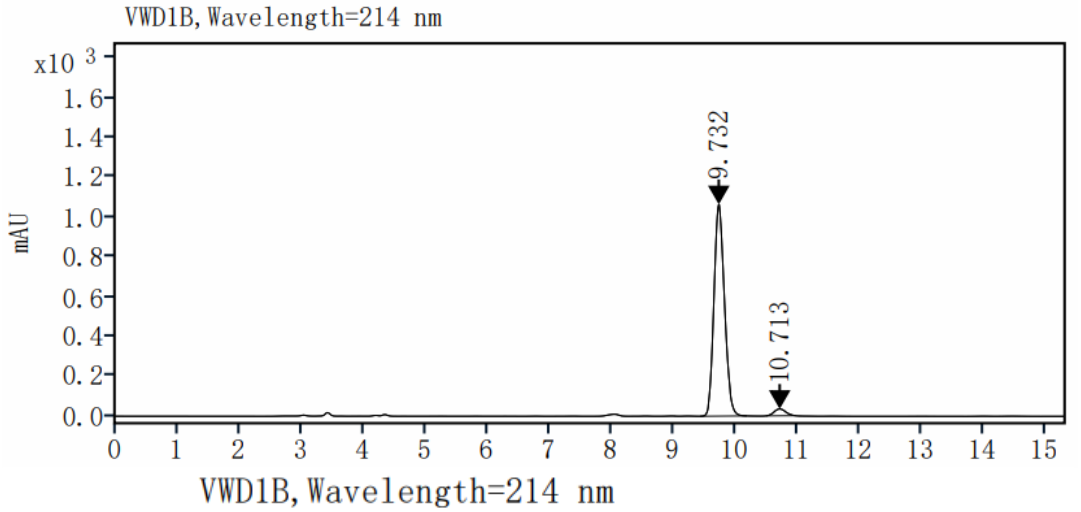


Figure 3A, entry 4
(*S*)-**A4**: 93% ee



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.783	MM m	9271.20	49.97
	10.693	MM m	9281.42	50.03



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.732	MM m	12576.91	96.58
	10.713	MM m	444.78	3.42

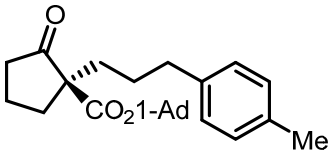
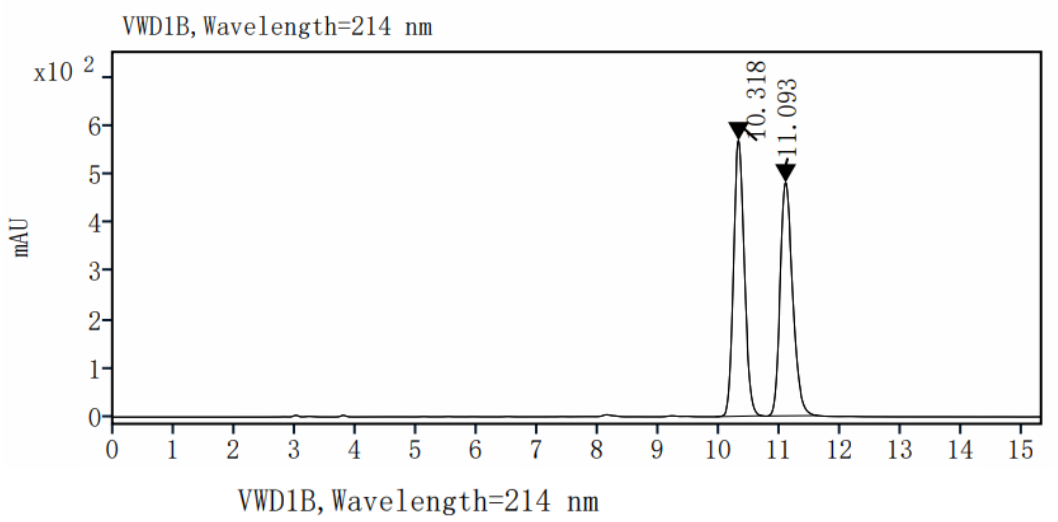
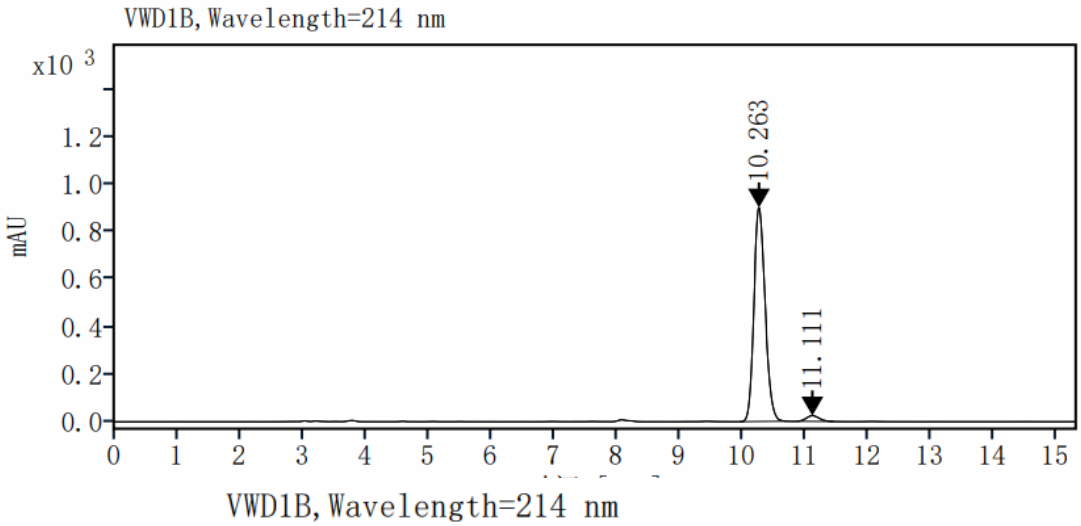


Figure 3A, entry 5
(*S*)-**A1**: 94% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.318	MM m	7061.81	50.45
	11.093	MM m	6935.88	49.55



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.263	MM m	11211.44	97.02
	11.111	MM m	344.05	2.98

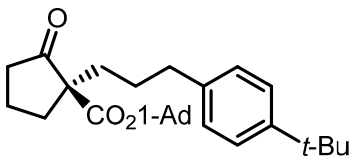
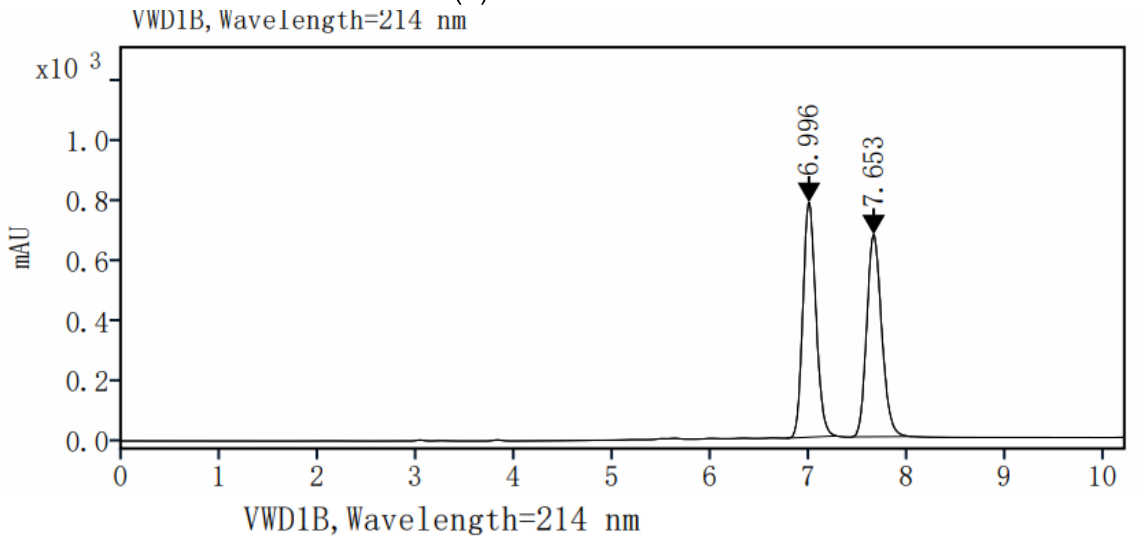
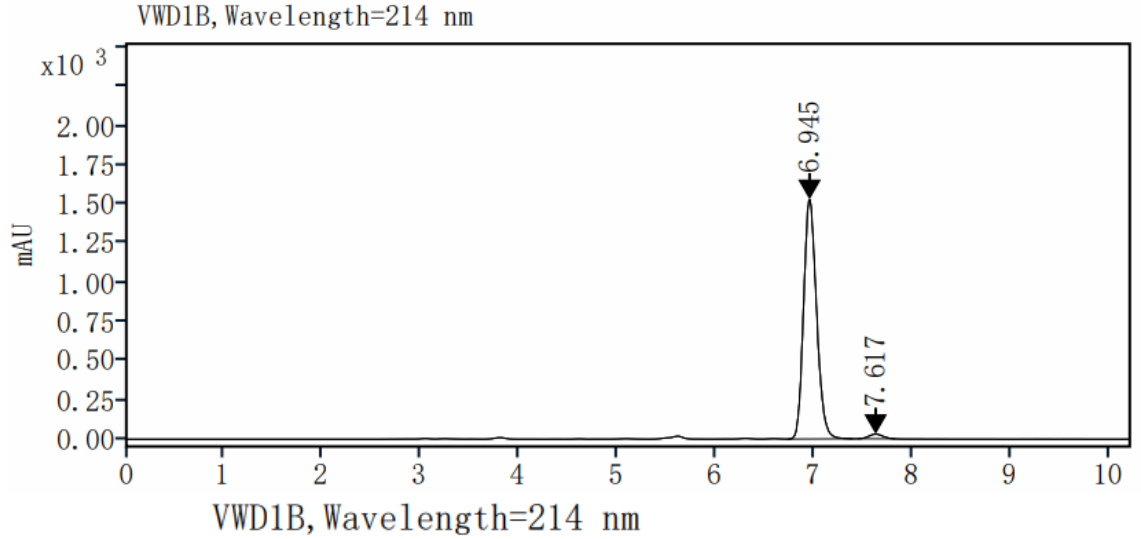


Figure 3A, entry 6
(*S*)-**A6**: 96% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.996	MM m	7194.55	50.16
	7.653	MM m	7148.70	49.84



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.945	MM m	14081.17	97.96
	7.617	MM m	292.75	2.04

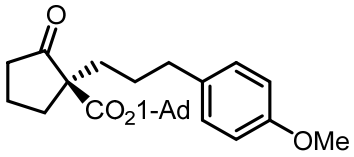
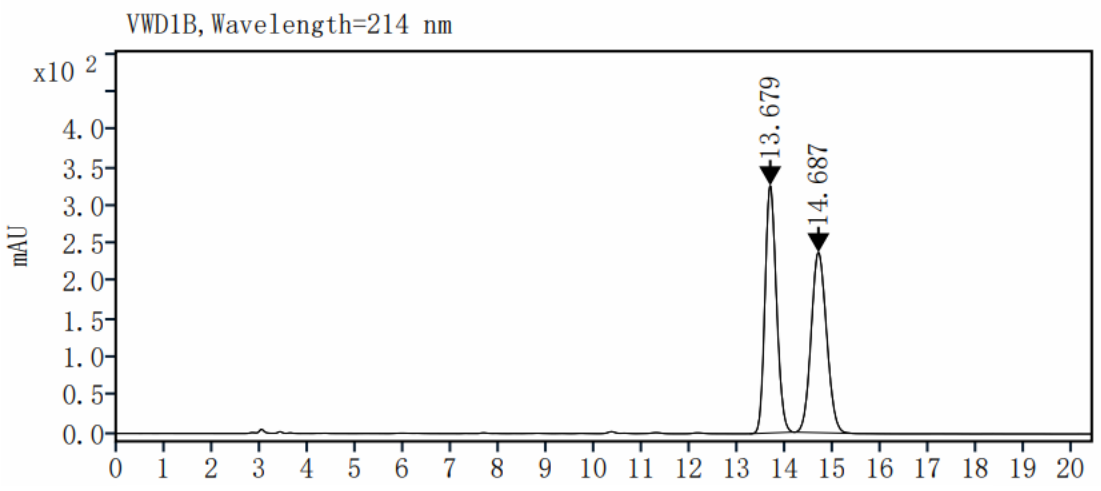
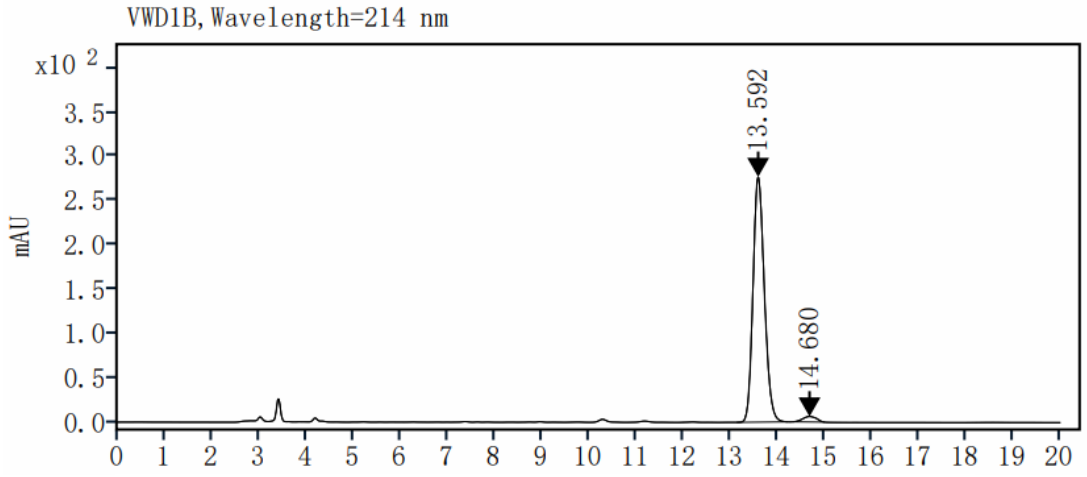


Figure 3A, entry 7
(*S*)-**A1**: 95% ee



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	13.679	MM m	5420.38	50.28
	14.687	MM m	5359.11	49.72



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	13.592	MM m	4644.23	97.39
	14.680	MM m	124.41	2.61

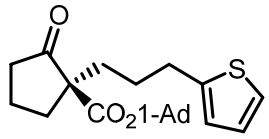
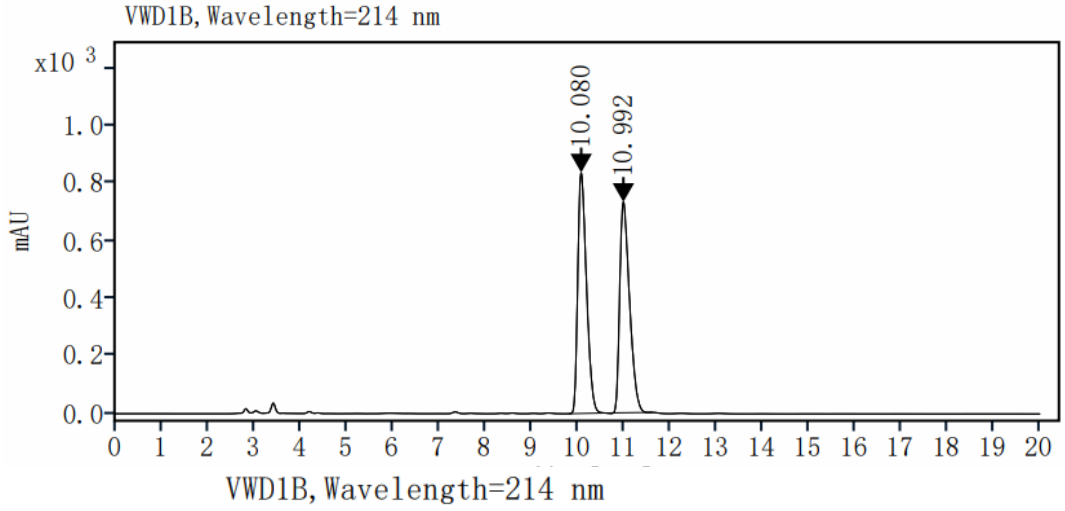
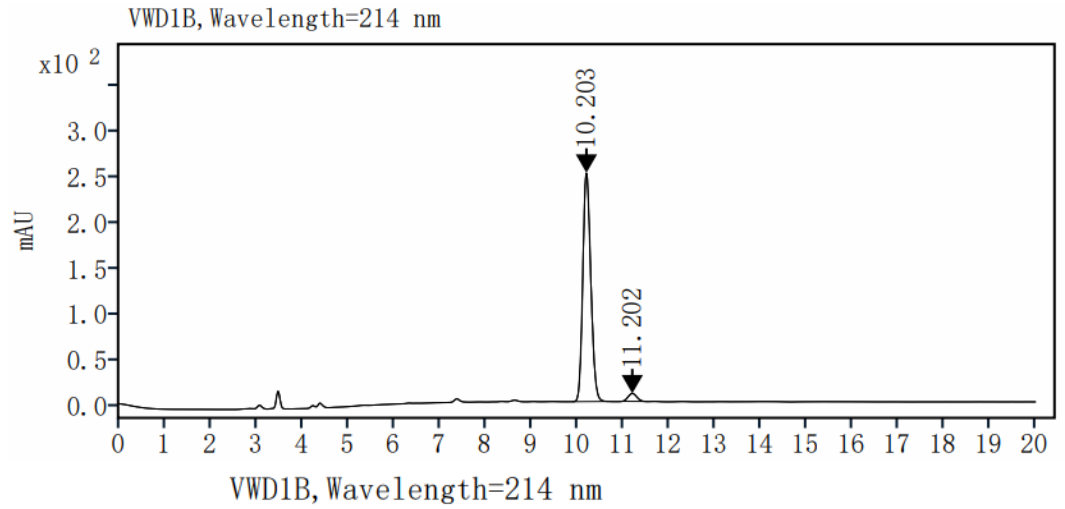


Figure 3A, entry 8
(*S*)-**A1**: 93% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.080	MM m	10937.90	50.35
	10.992	MM m	10783.73	49.65



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.203	MM m	3047.06	96.42
	11.202	MM m	113.07	3.58

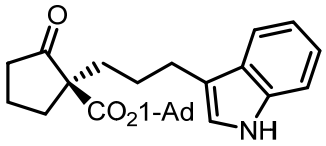
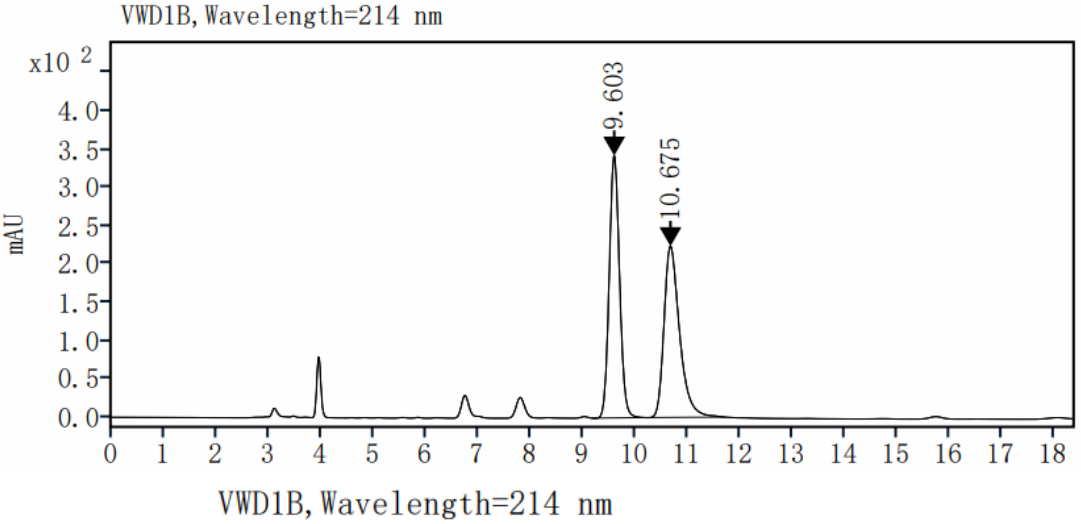
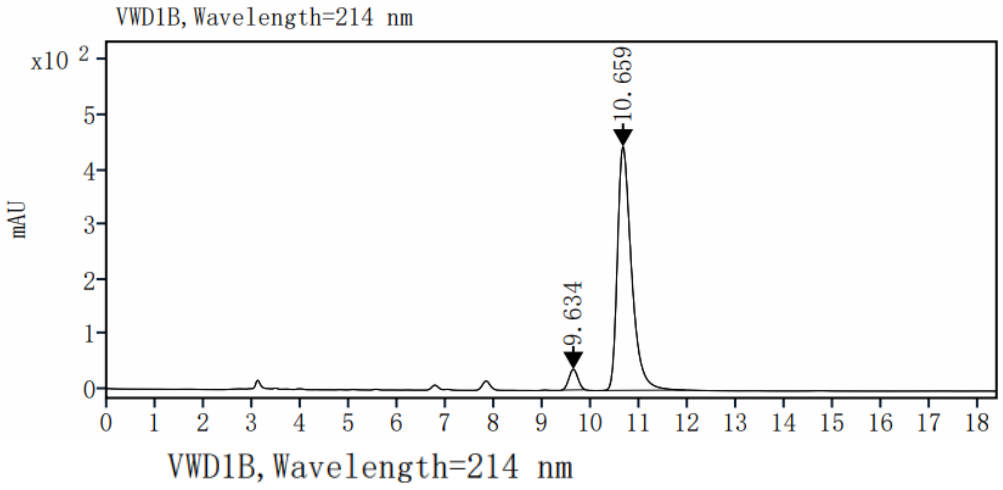


Figure 3A, entry 9
(*S*)-**A1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.603	MM m	4680.69	50.31
	10.675	MM m	4623.56	49.69



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.634	MM m	486.27	5.11
	10.659	MM m	9031.86	94.89

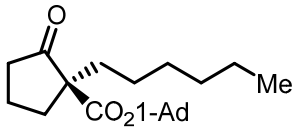
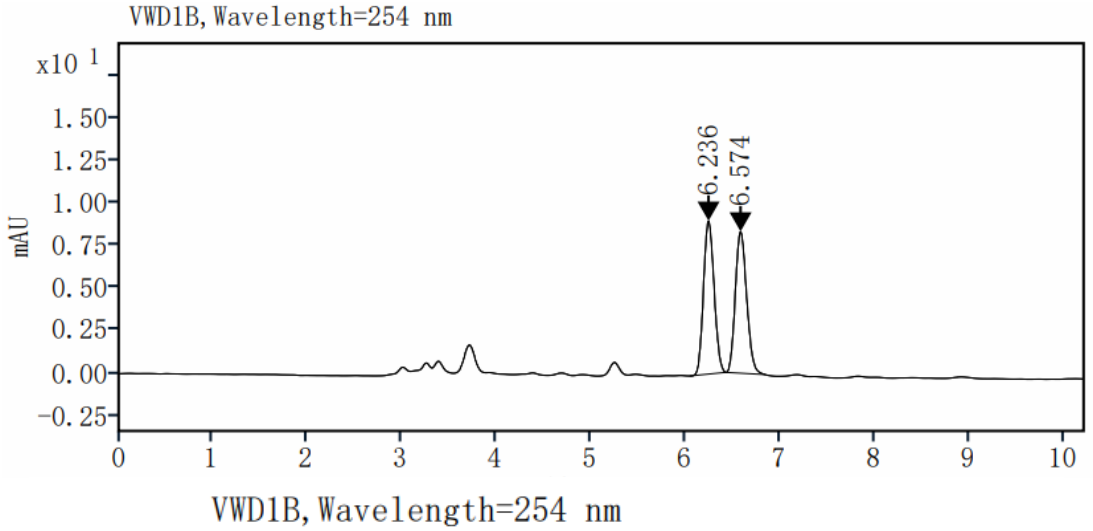
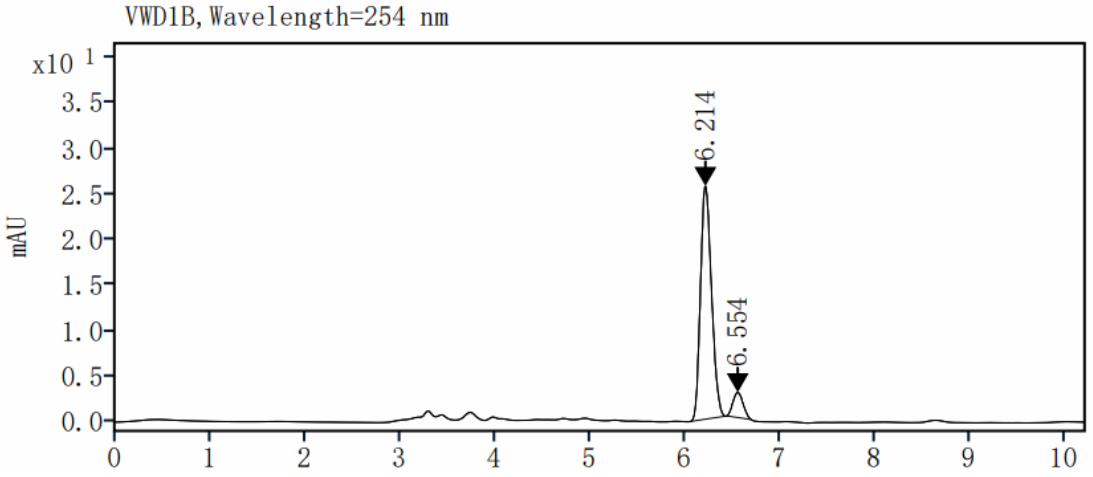


Figure 3A, entry 10
(*S*)-**A1**: 82% ee



VWD1B, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.236	MM m	70.10	50.19
	6.574	MM m	69.56	49.81



VWD1B, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.214	MM m	205.69	90.93
	6.554	MM m	20.53	9.07

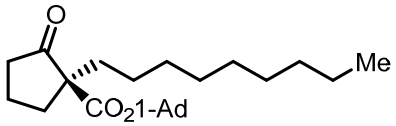
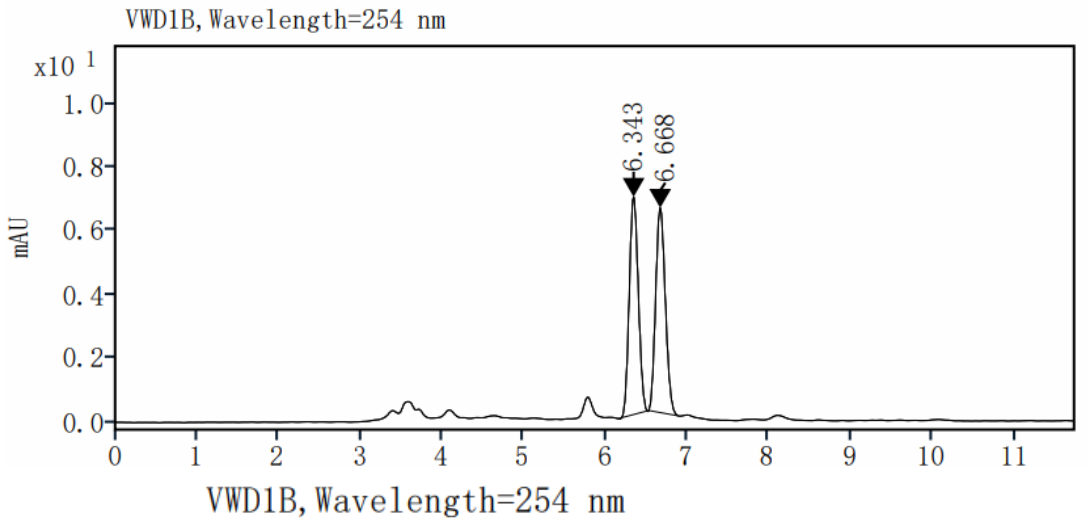
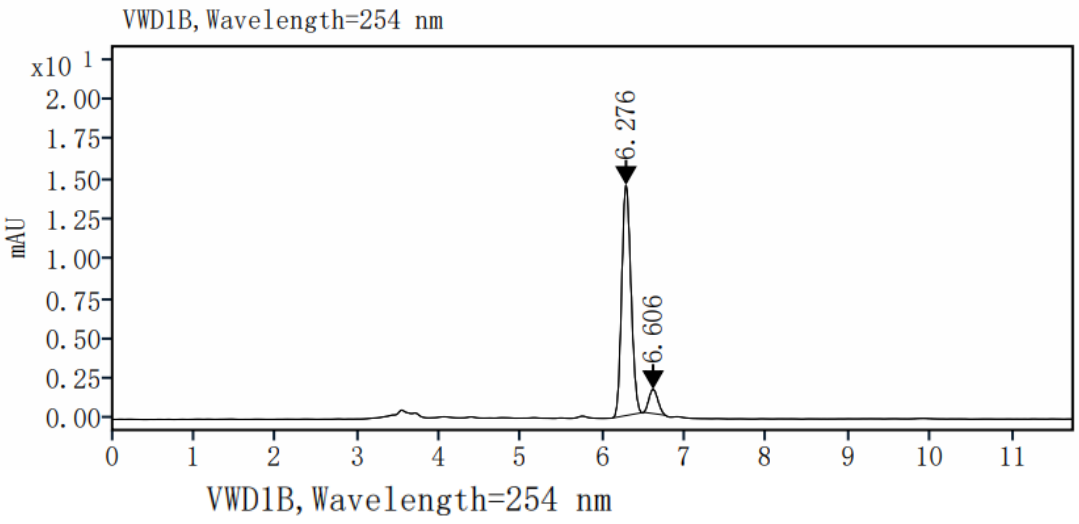


Figure 3A, entry 11
(*S*)-**A1**: 82% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.343	MM m	52.59	49.80
	6.668	MM m	53.00	50.20



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.276	MM m	113.73	90.76
	6.606	MM m	11.58	9.24

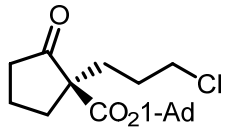
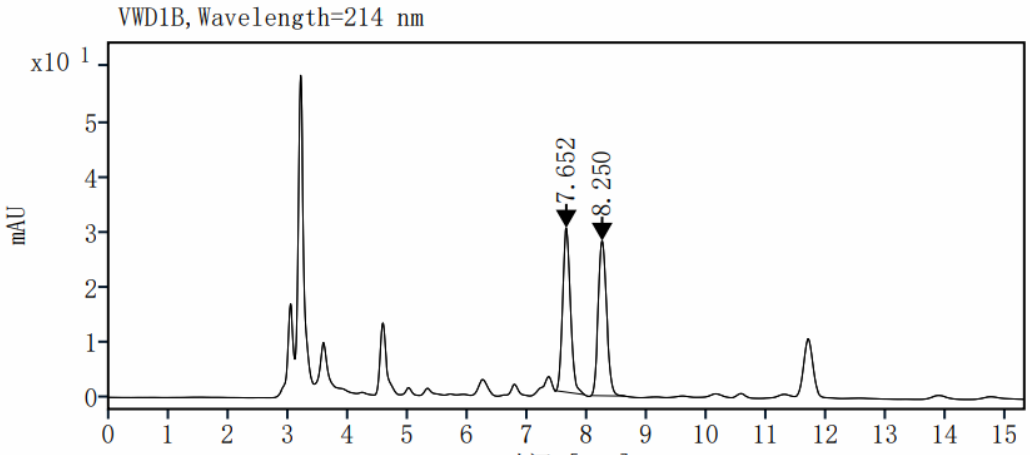
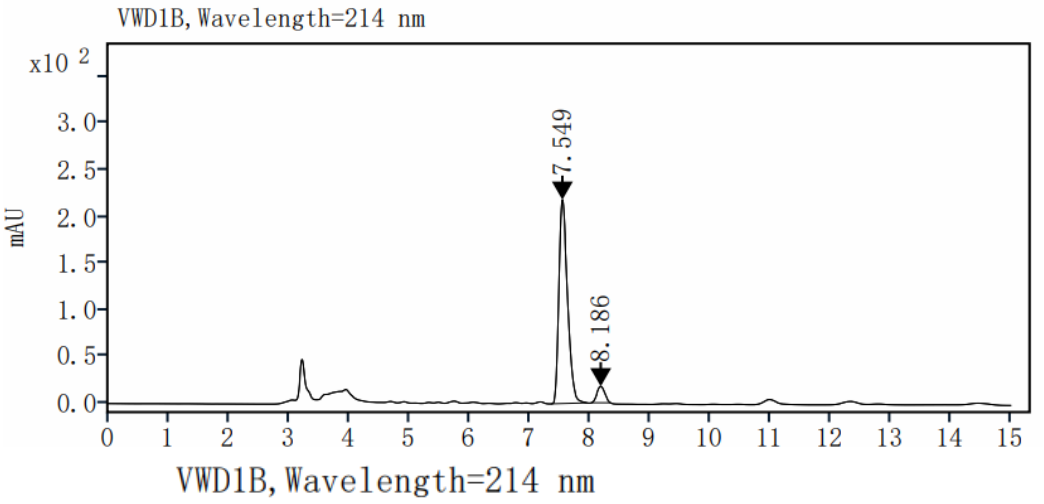


Figure 3A, entry 12
(*S*)-**A1**: 86% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.652	MM m	273.13	49.75
	8.250	MM m	275.83	50.25



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.549	MM m	2167.67	93.16
	8.186	MM m	159.07	6.84

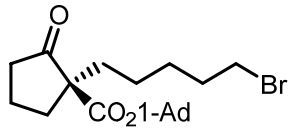
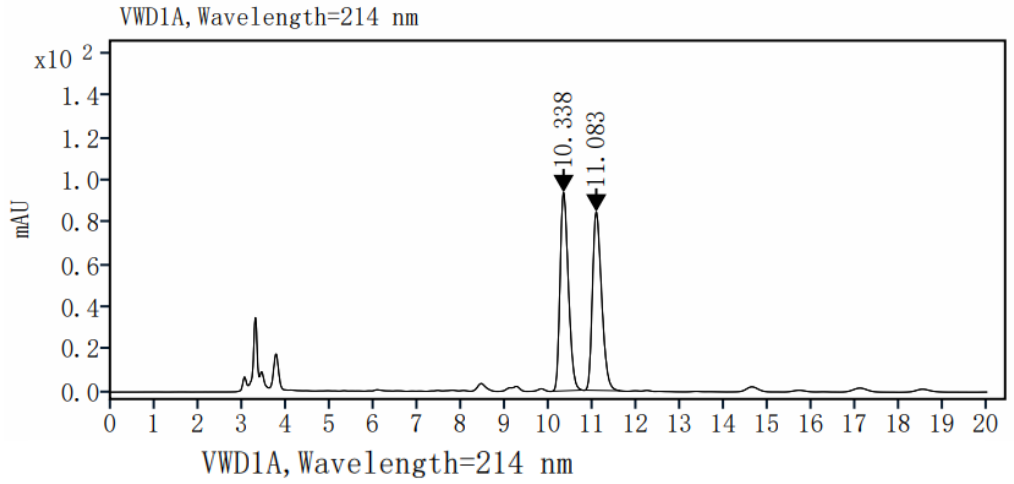
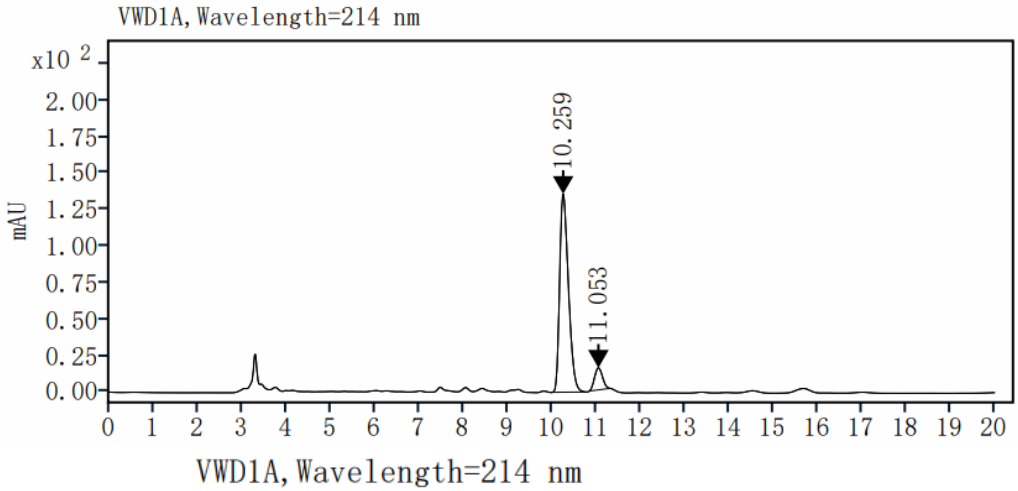


Figure 3A, entry 13
(*S*)-**A1**: 82% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.338	MM m	1240.57	50.26
	11.083	MM m	1227.96	49.74



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.259	MM m	1864.98	90.84
	11.053	MM m	188.04	9.16

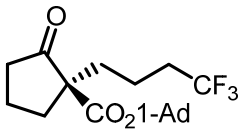
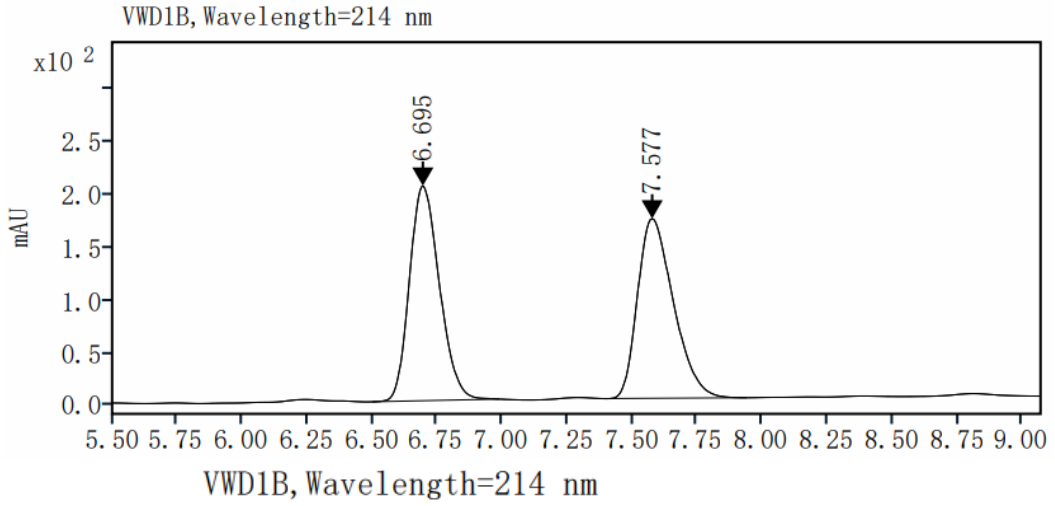
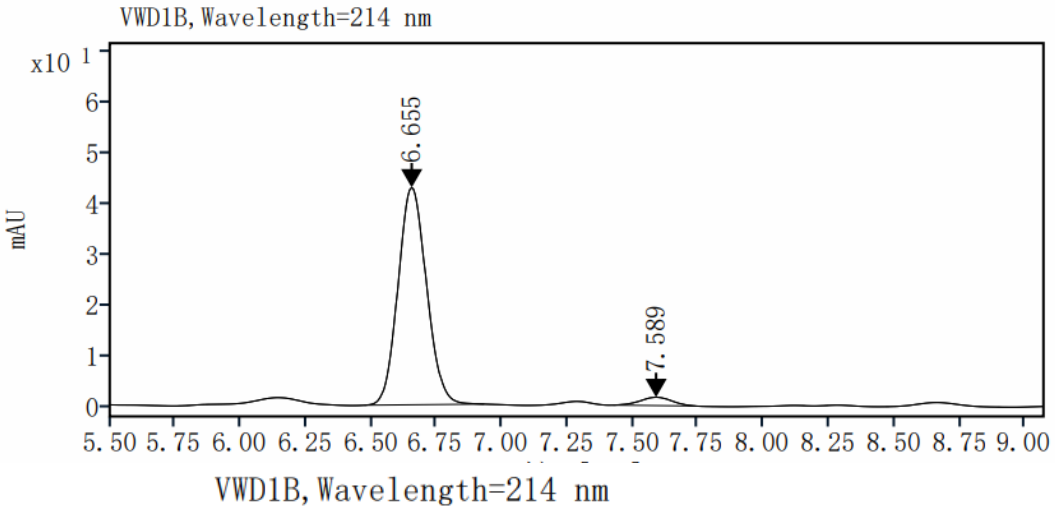


Figure 3A, entry 14
(*S*)-**A1**: 92% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.695	MM m	1624.02	49.98
	7.577	MM m	1625.50	50.02



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.655	MM m	325.11	95.92
	7.589	MM m	13.81	4.08

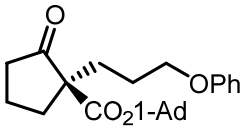
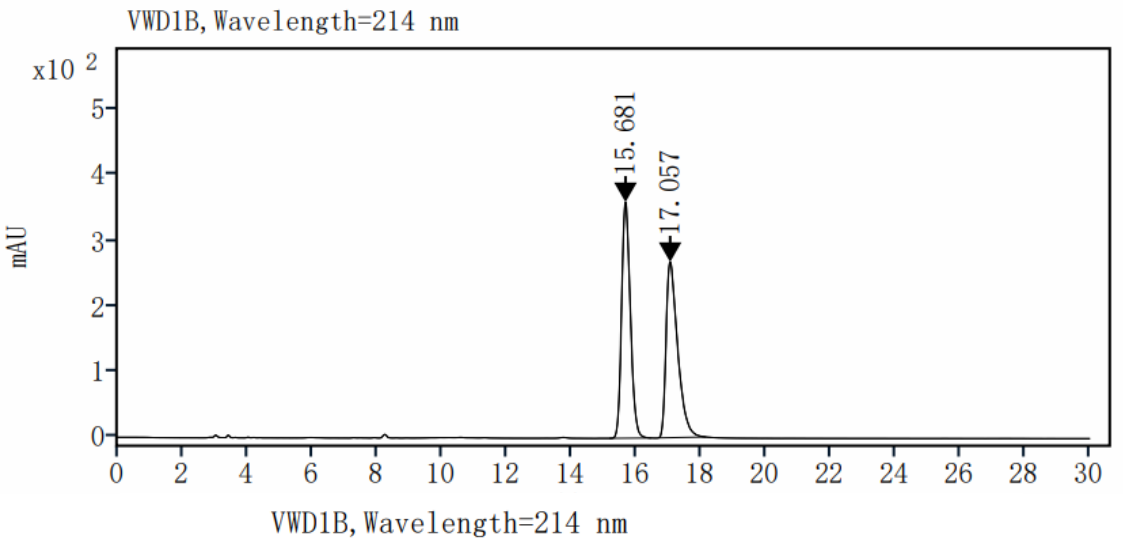
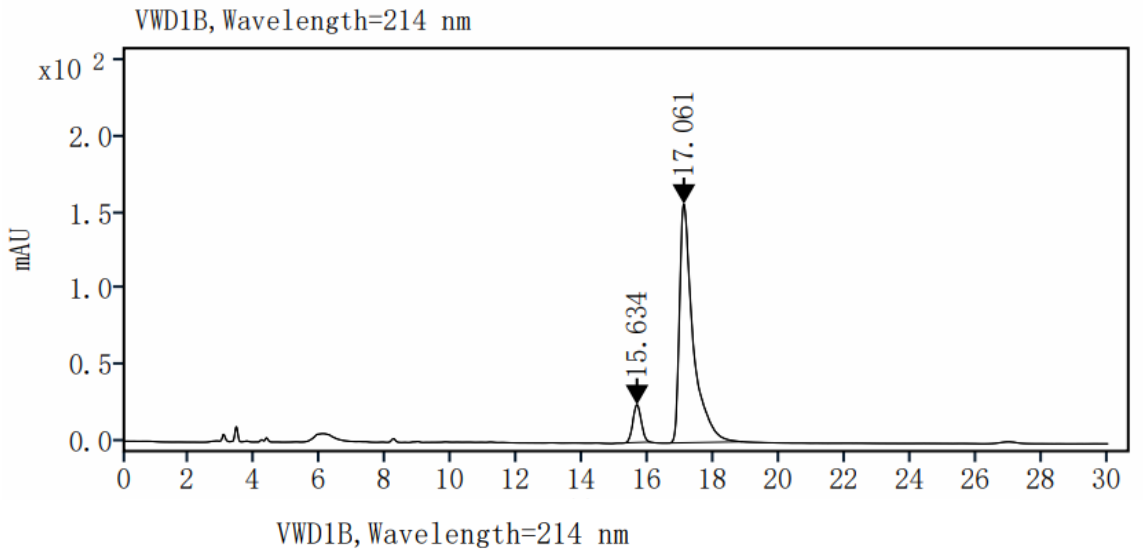


Figure 3A, entry 15
(*S*)-**A1**: 82% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.681	MM m	6740.66	50.30
	17.057	MM m	6659.93	49.70



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.634	MM m	444.05	8.92
	17.061	MM m	4532.93	91.08

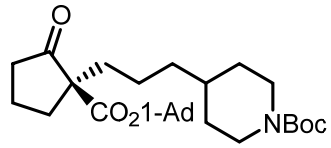
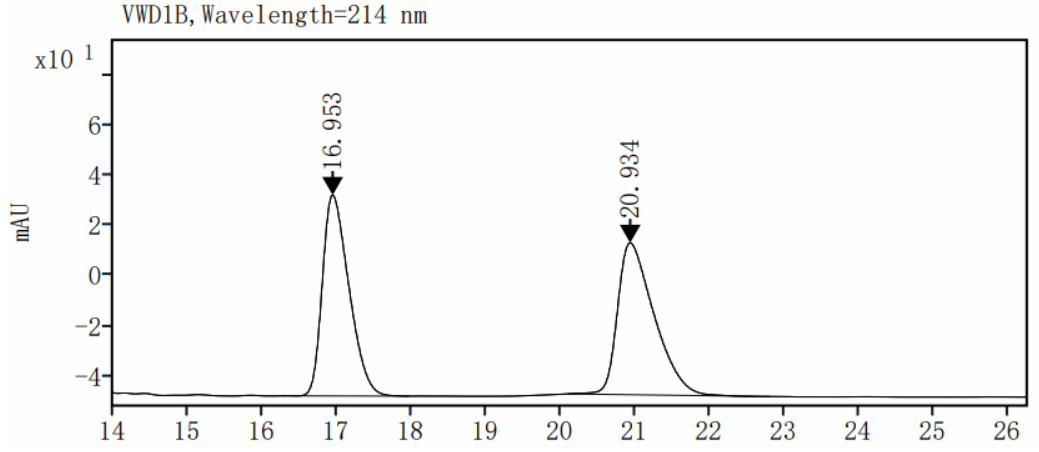
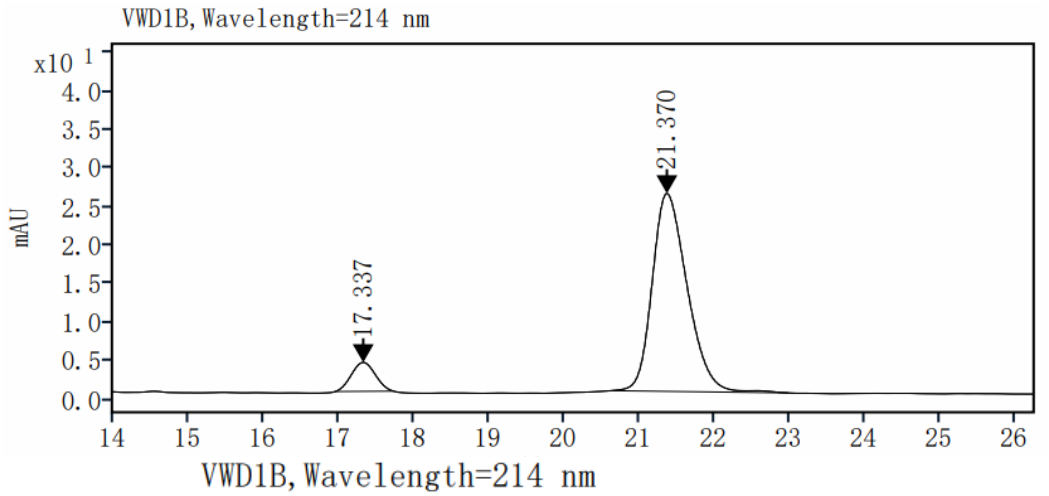


Figure 3A, entry 16
(*S*)-**A1**: 82% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	16.953	MM m	1984.48	49.09
	20.934	MM m	2057.85	50.91



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	17.337	MM m	82.90	9.07
	21.370	MM m	831.12	90.93

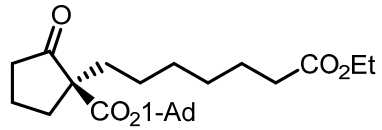
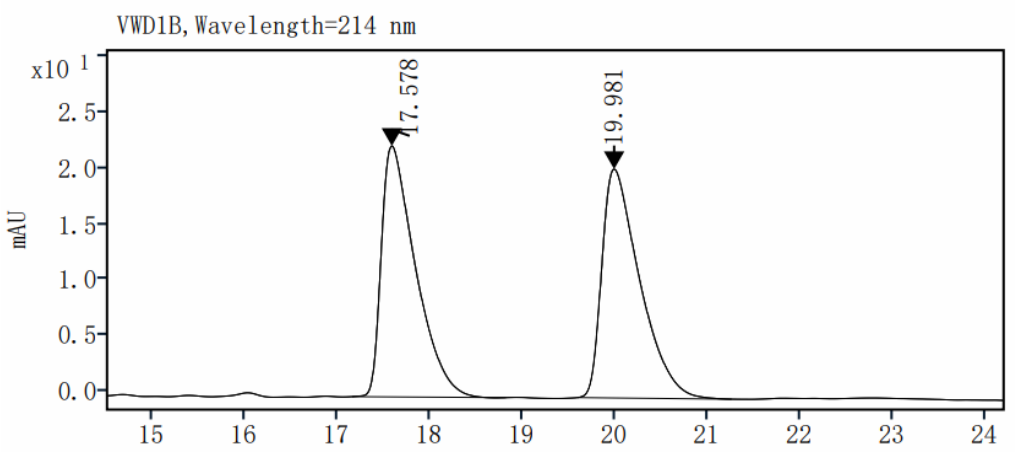
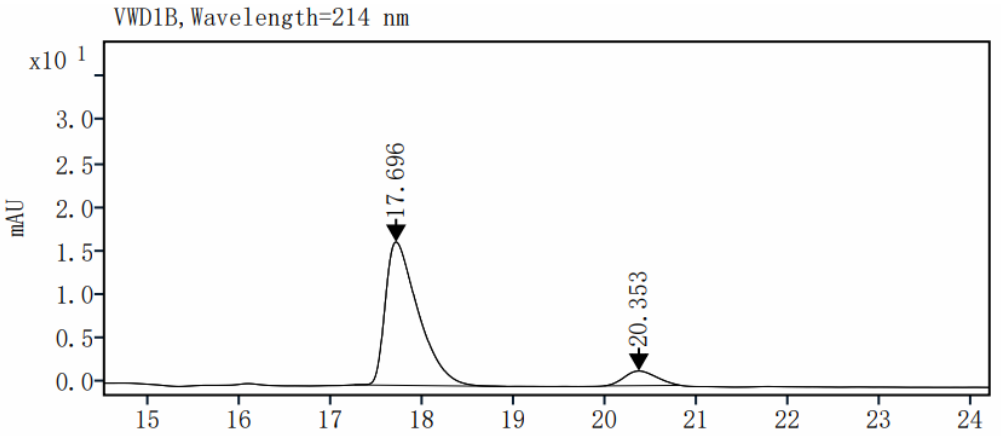


Figure 3A, entry 17
(*S*)-**A1**: 82% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	17.578	MM m	578.81	49.74
	19.981	MM m	584.95	50.26



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	17.696	MM m	411.46	90.90
	20.353	MM m	41.21	9.10

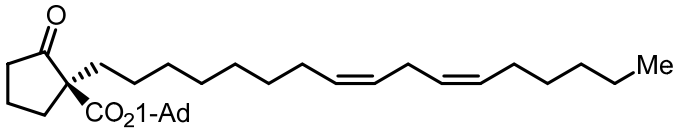
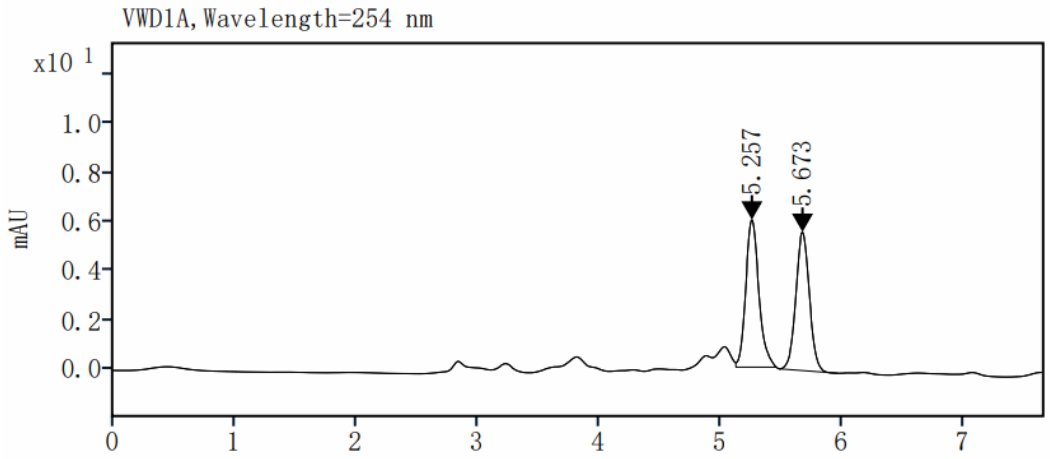
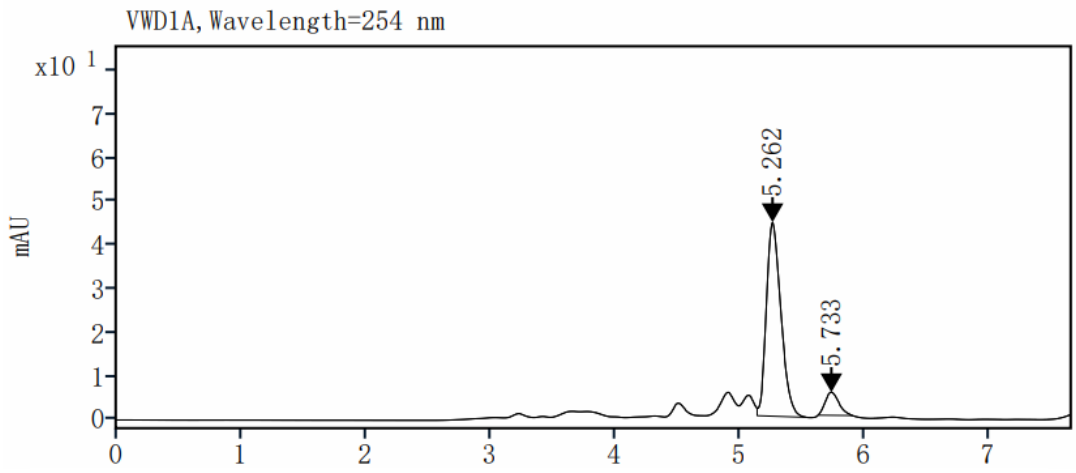


Figure 3A, entry 18
(*S*)-**A1**: 80% ee



VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.257	MM m	44.90	50.74
	5.673	MM m	43.59	49.26



VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.262	MM m	360.19	89.98
	5.733	MM m	40.11	10.02

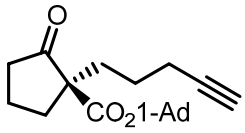
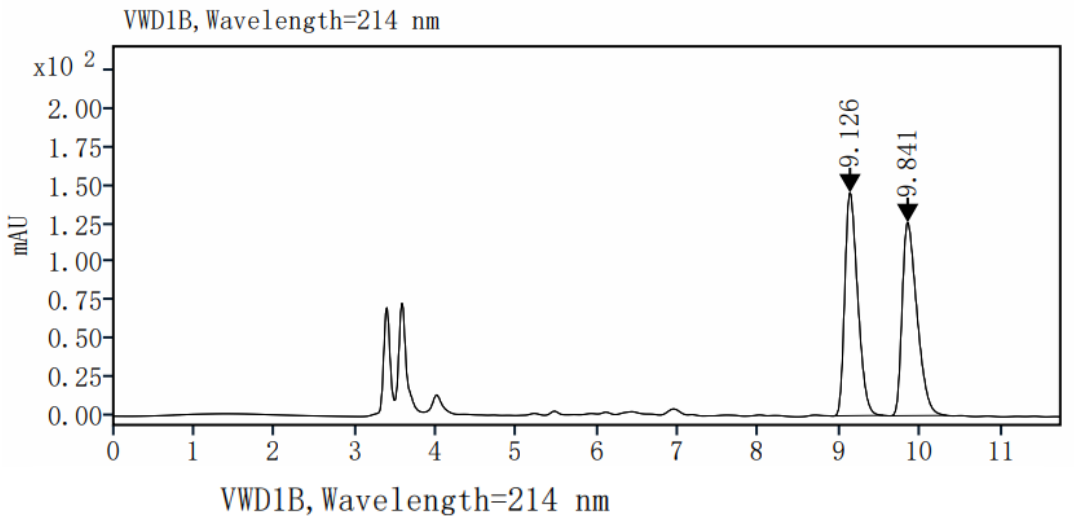
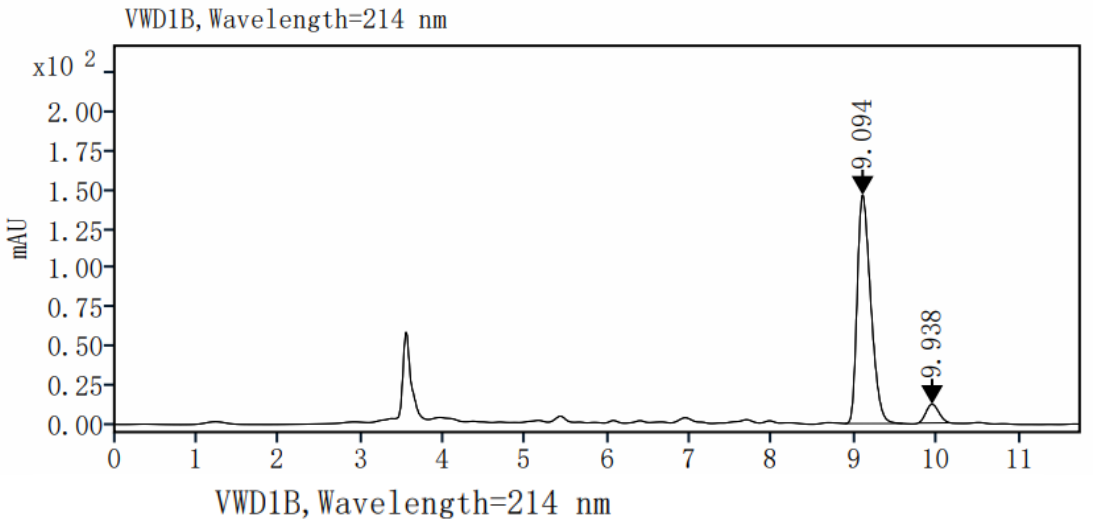


Figure 3A, entries 19
(*S*)-**A1**: 86% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.126	MM m	1618.47	50.02
	9.841	MM m	1616.88	49.98



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.094	MM m	1674.84	92.80
	9.938	MM m	129.90	7.20

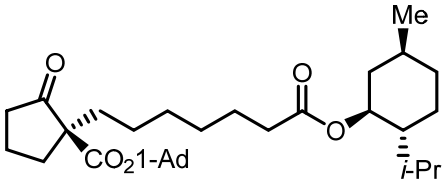
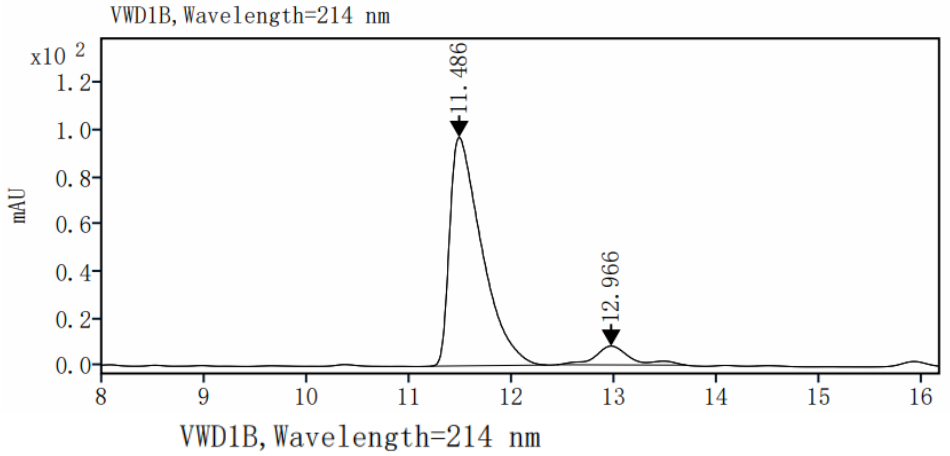
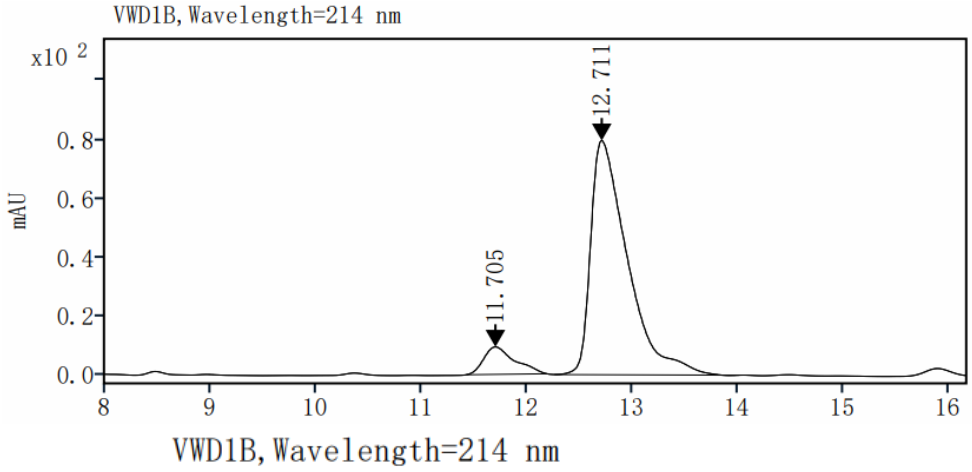


Figure 3A, entries 20 and 21
(*S*)-**A1**: 91.5:8.5 dr
(*R*)-**A1**: 9:91 dr



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	11.486	MM m	2110.14	91.53
	12.966	MM m	195.24	8.47



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	11.705	MM m	189.97	8.98
	12.711	MM m	1924.52	91.02

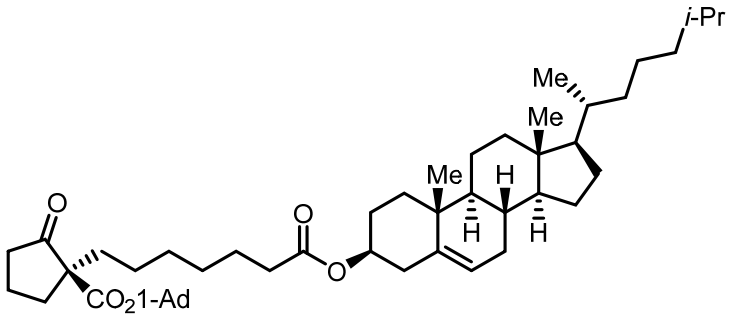
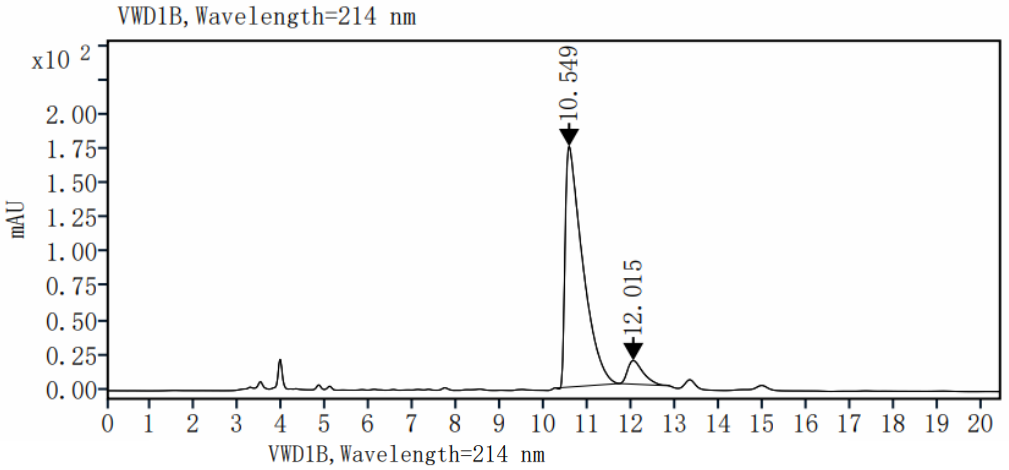
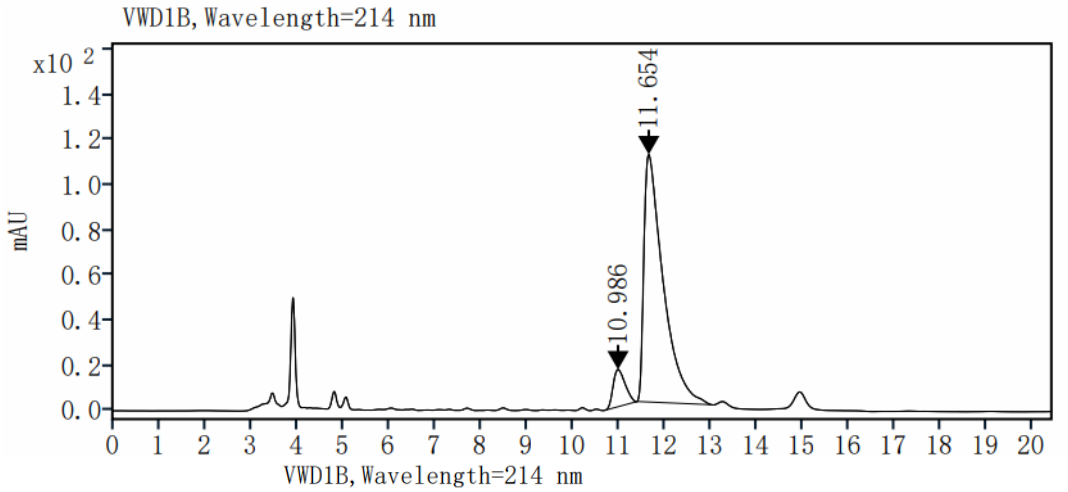


Figure 3A, entries 22 and 23
(*S*)-**A1**: 92:8 dr
(*R*)-**A1**: 8.5:91.5 dr



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.549	MM m	4892.29	91.99
	12.015	MM m	426.17	8.01



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.986	MM m	299.15	8.57
	11.654	MM m	3191.26	91.43

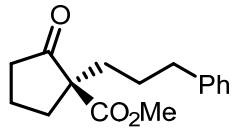
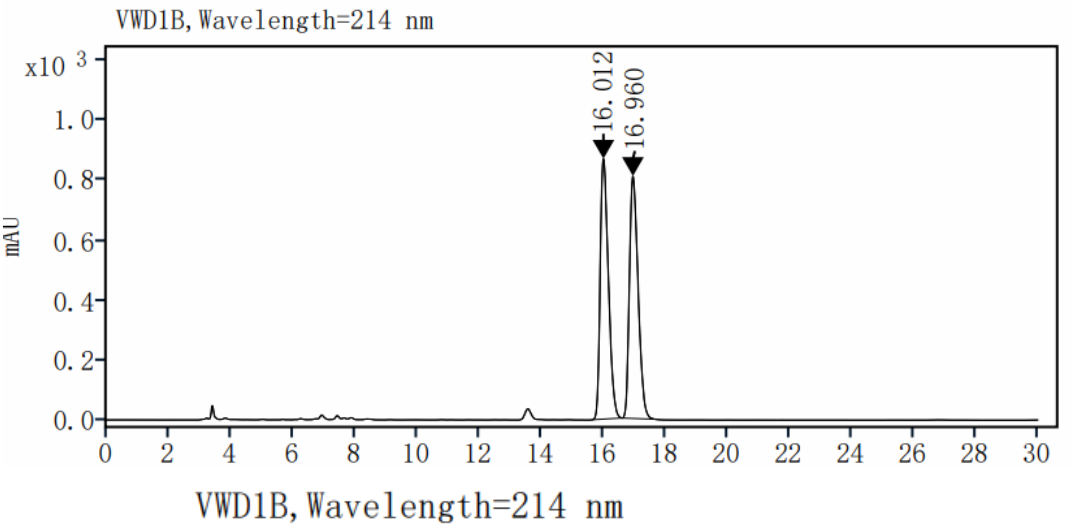
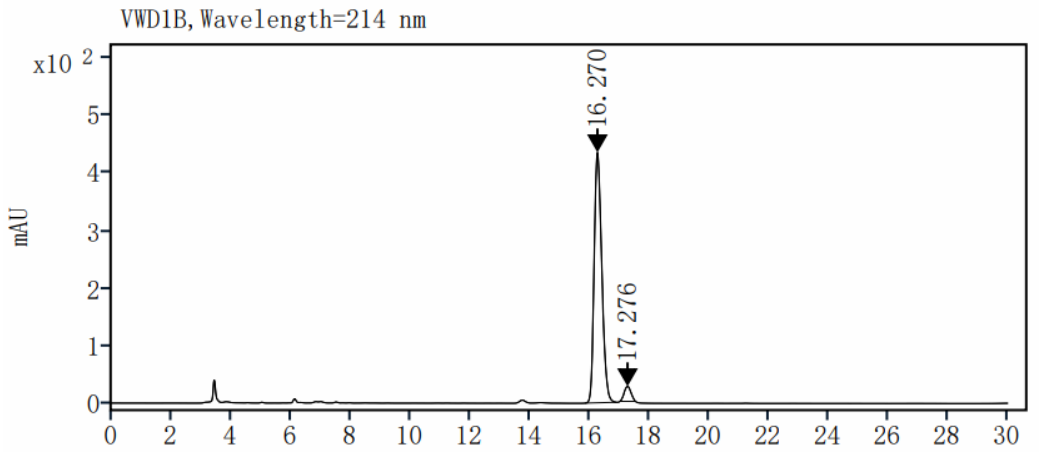


Figure 3B, entry 24
(*S*)-**A1**: 90% ee



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	16.012	MM m	15932.11	50.32
	16.960	MM m	15727.11	49.68



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	16.270	MM m	7738.30	94.93
	17.276	MM m	413.13	5.07

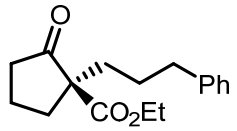
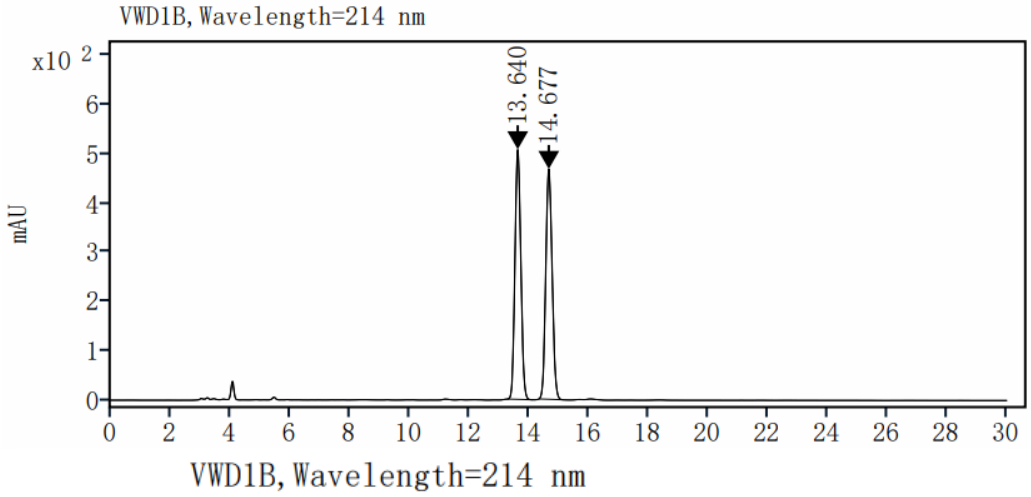
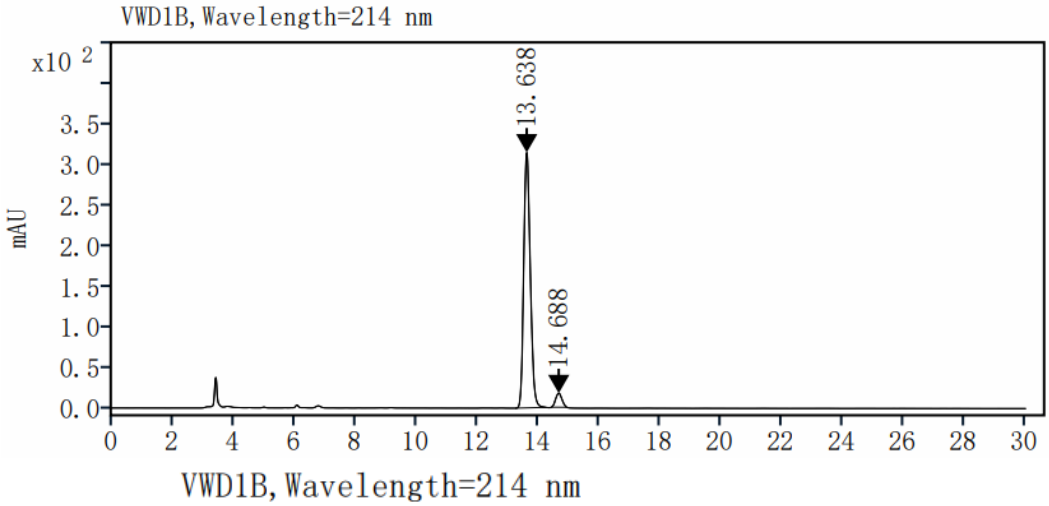


Figure 3B, entry 25
(*S*)-**A1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	13.640	MM m	6952.51	50.10
	14.677	MM m	6925.01	49.90



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	13.638	MM m	4699.92	94.97
	14.688	MM m	248.80	5.03

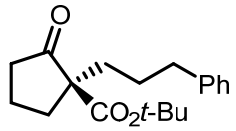
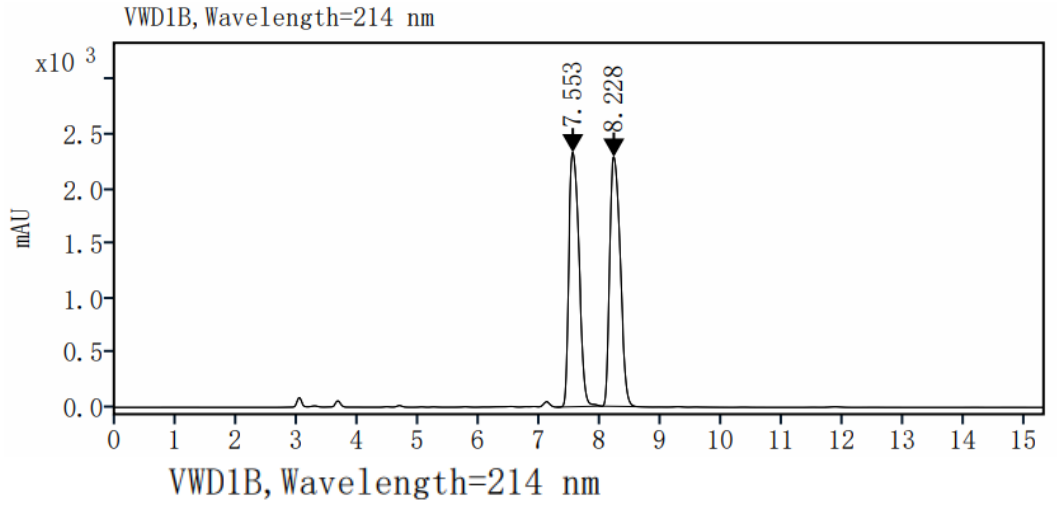
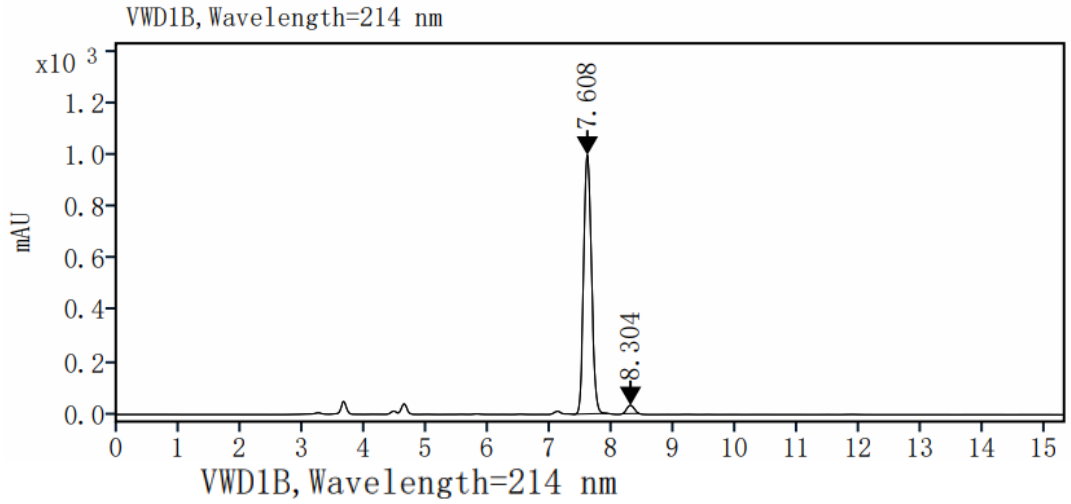


Figure 3B, entry 26
(*S*)-**A1**: 94% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.553	MM m	27114.41	49.45
	8.228	MM m	27719.46	50.55



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.608	MM m	8733.75	97.11
	8.304	MM m	260.29	2.89

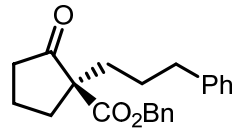
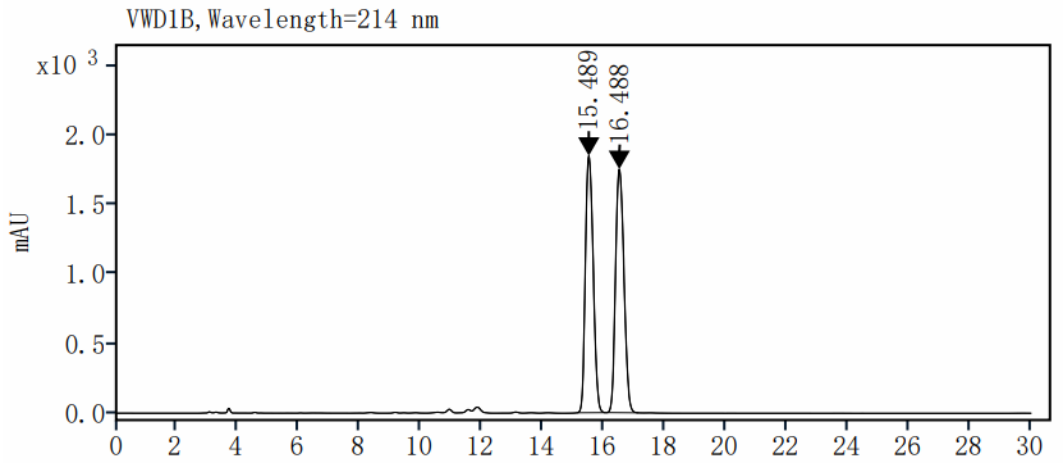
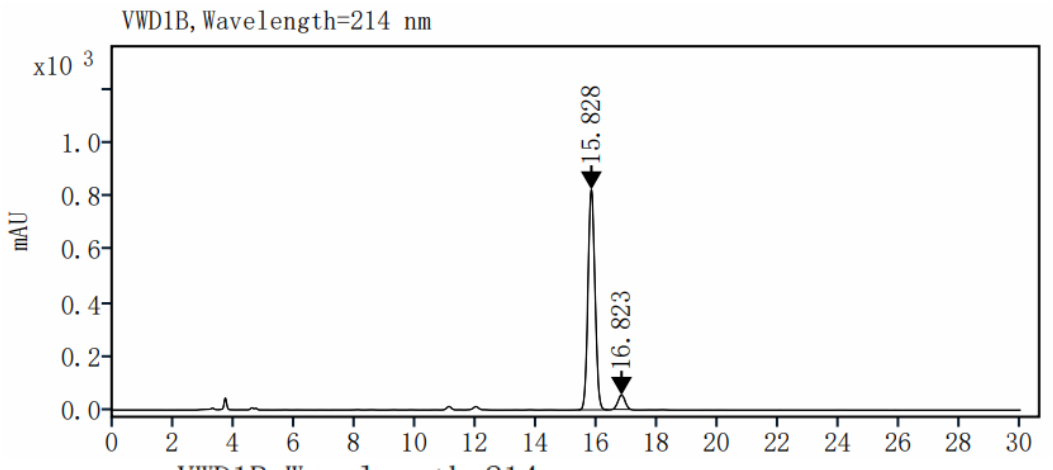


Figure 3B, entry 27
(*S*)-**A1**: 88% ee



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.489	MM m	33104.93	49.49
	16.488	MM m	33787.96	50.51



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.828	MM m	13293.30	93.82
	16.823	MM m	875.57	6.18

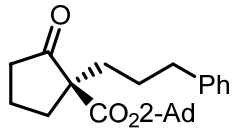
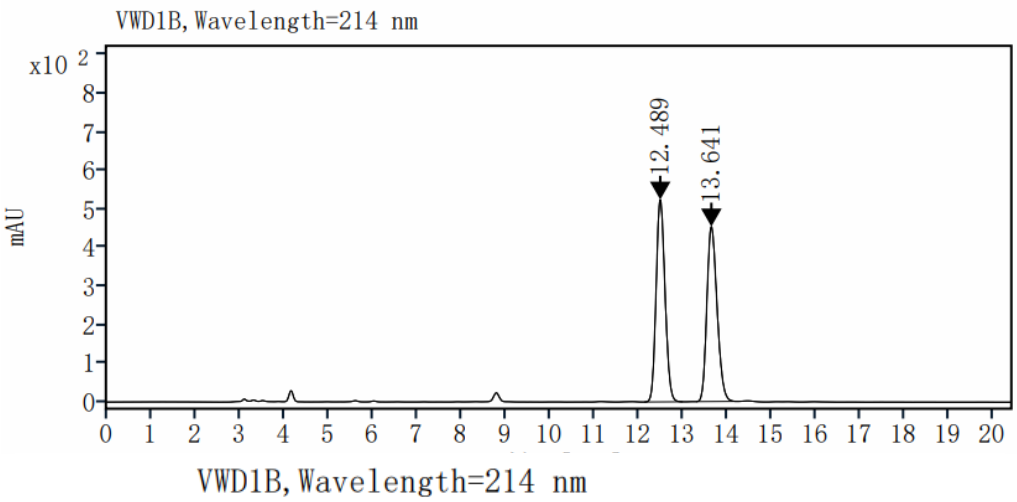
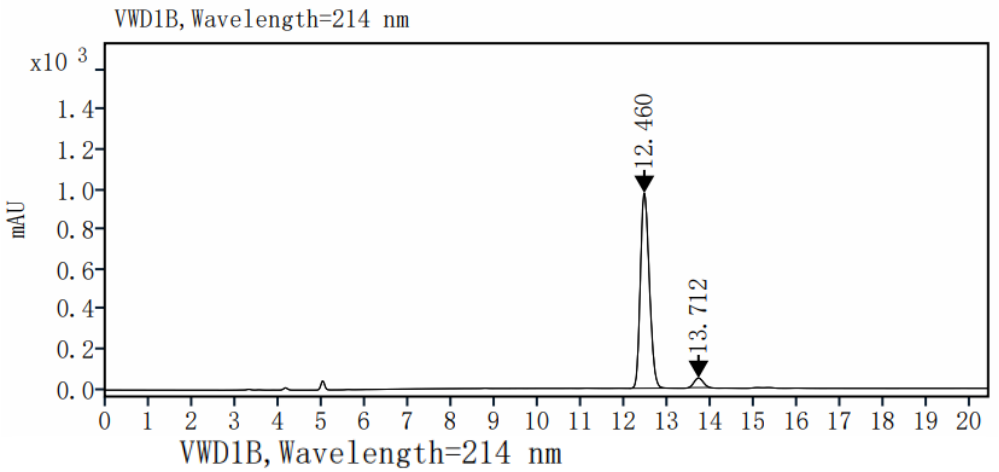


Figure 3B, entry 28
(*S*)-**A1**: 91% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	12.489	MM m	7345.12	50.27
	13.641	MM m	7266.05	49.73



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	12.460	MM m	14079.80	95.39
	13.712	MM m	680.32	4.61

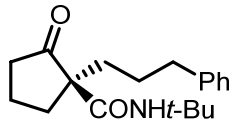
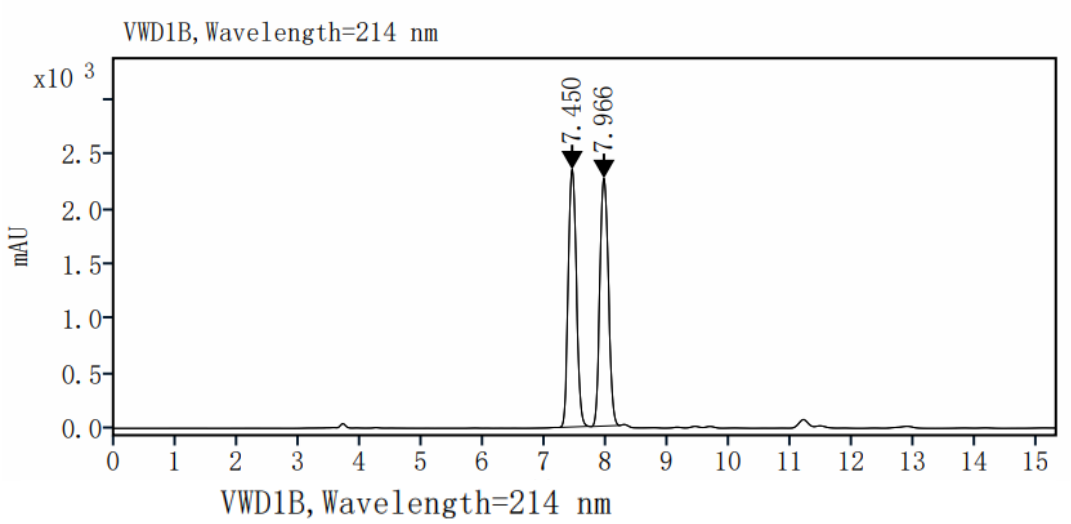
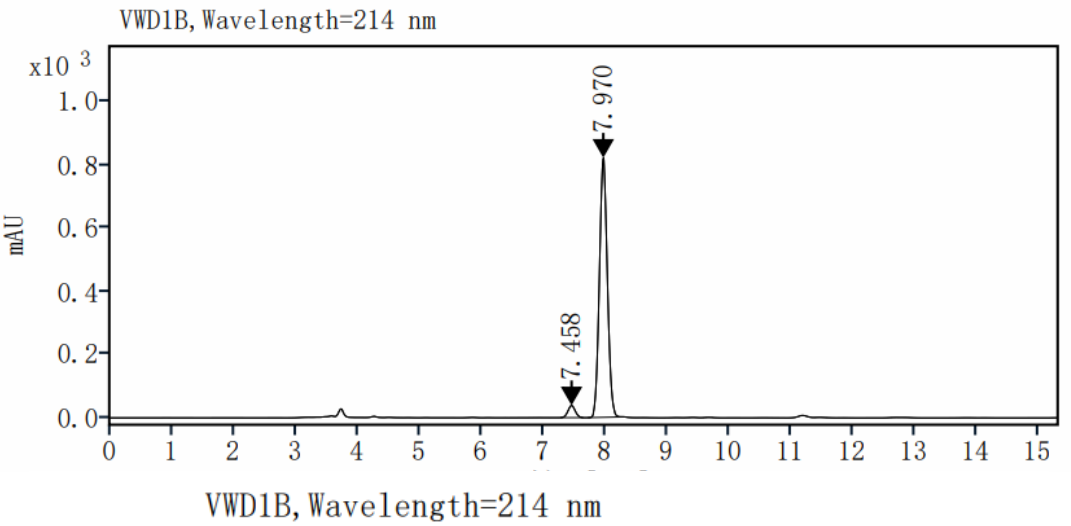


Figure 3B, entry 29
(*S*)-**A1**: 92% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.450	MM m	21559.06	49.62
	7.966	MM m	21887.10	50.38



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.458	MM m	318.29	4.15
	7.970	MM m	7359.86	95.85

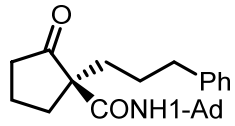
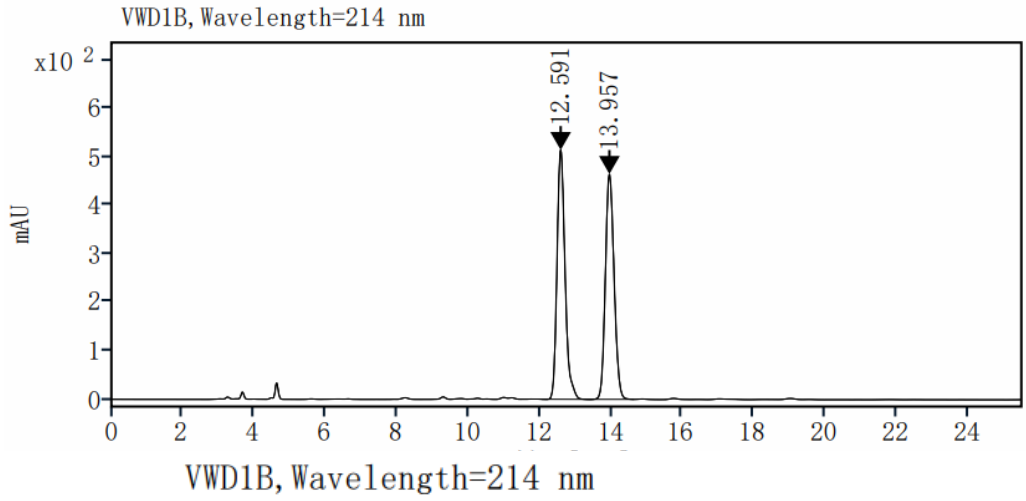
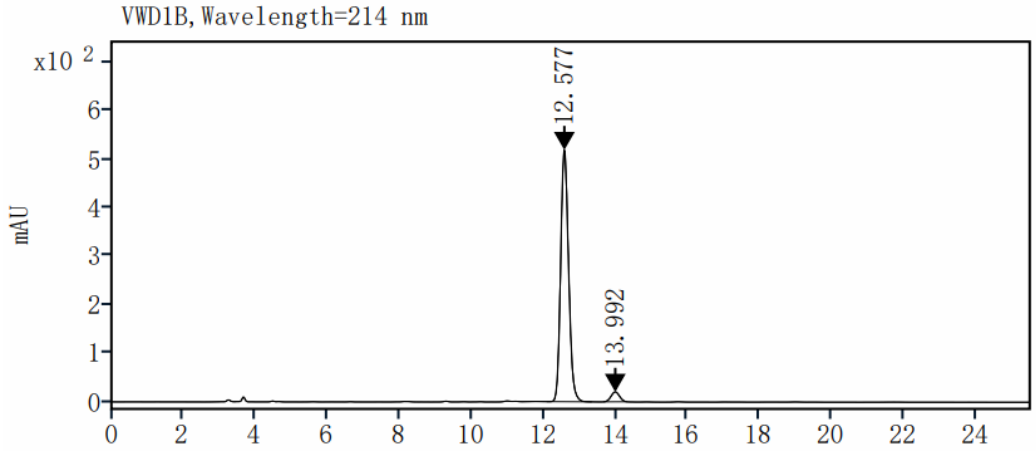


Figure 3B, entry 30
(*S*)-**A1**: 92% ee



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	12.591	MM m	8063.25	50.55
	13.957	MM m	7887.18	49.45



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	12.577	MM m	7938.75	95.99
	13.992	MM m	331.85	4.01

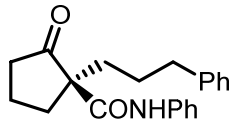
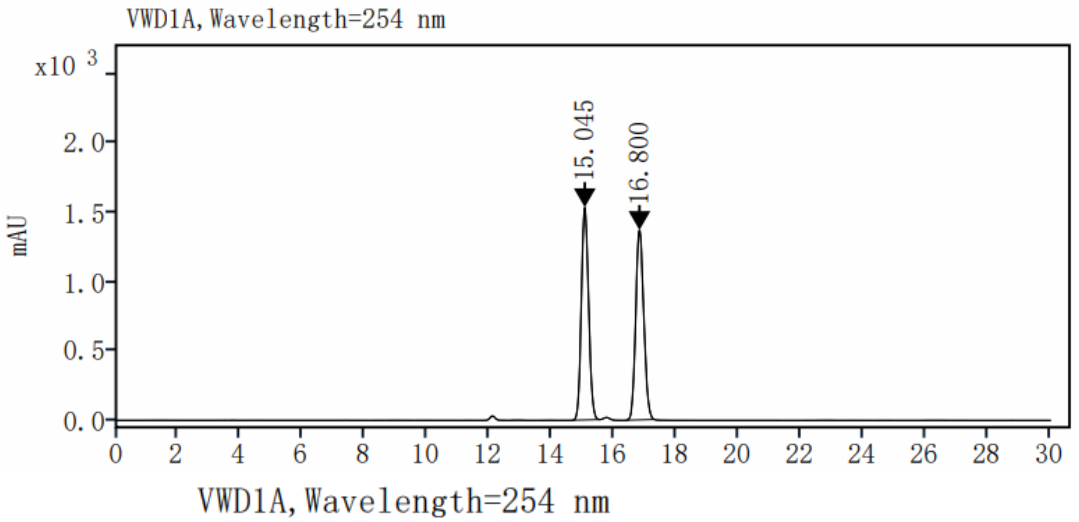
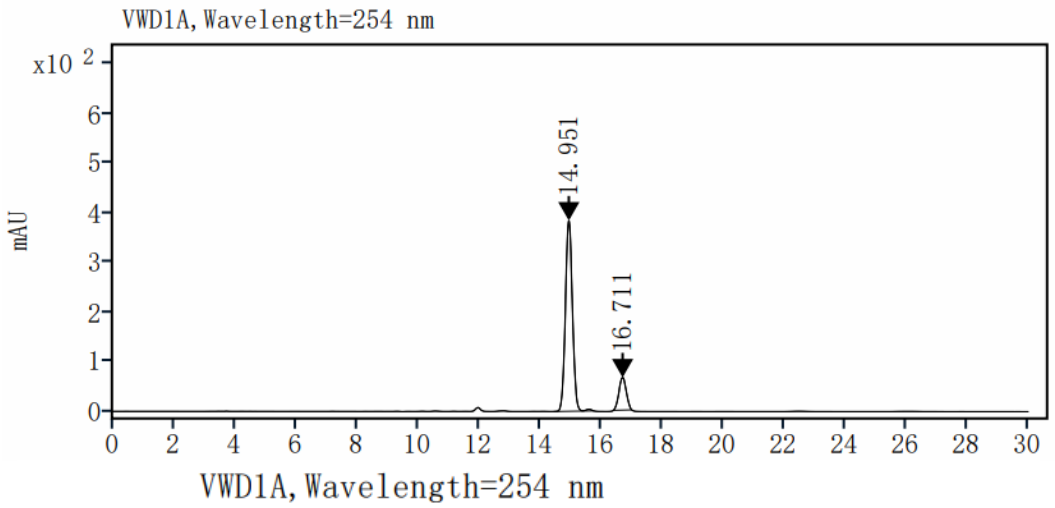


Figure 3B, entry 31
(*S*)-**A1**: 70% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.045	MM m	24902.23	50.14
	16.800	MM m	24763.62	49.86



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	14.951	MM m	6159.48	84.89
	16.711	MM m	1096.33	15.11

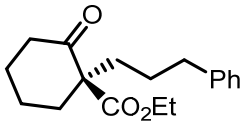
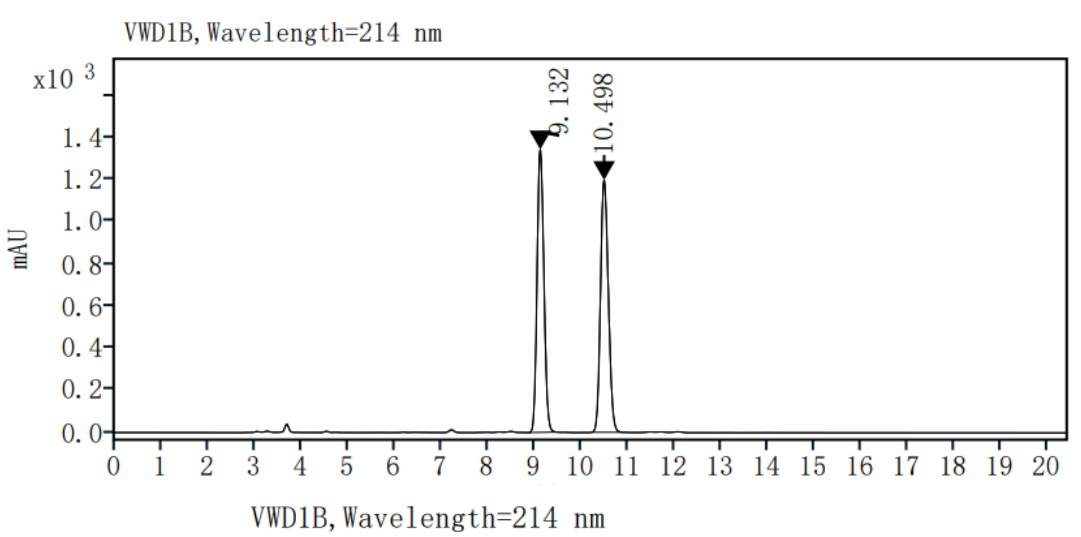
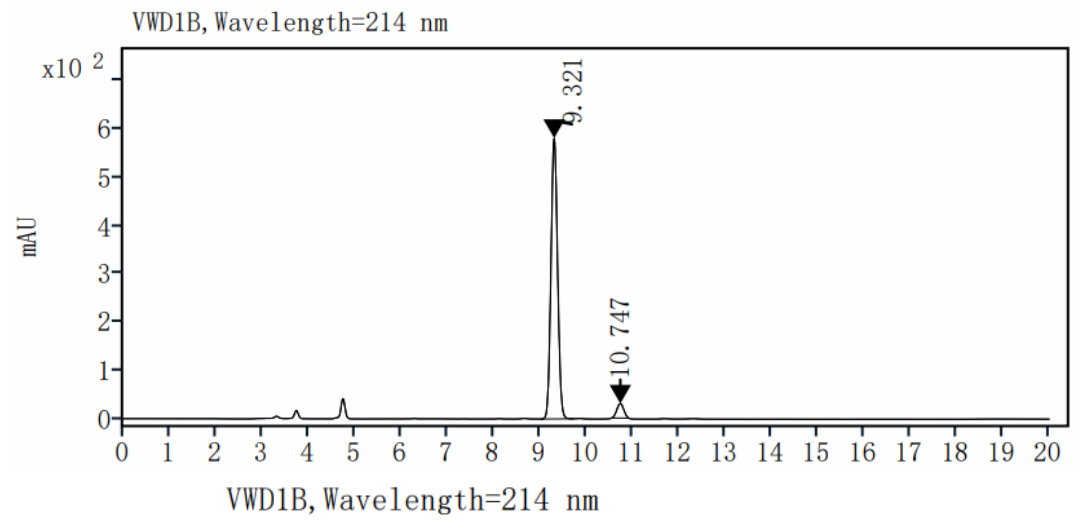


Figure 3B, entry 32
(*S*)-**A1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.132	MM m	13662.68	49.46
	10.498	MM m	13961.35	50.54



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.321	MM m	5767.20	94.84
	10.747	MM m	313.67	5.16

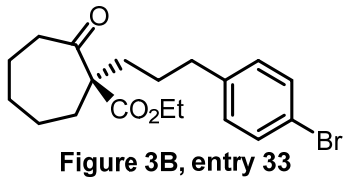
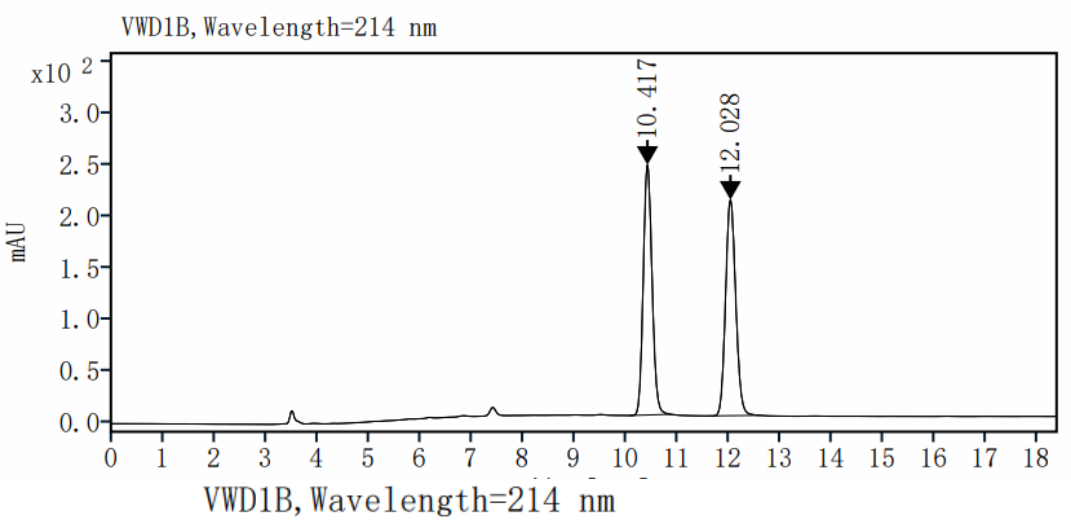
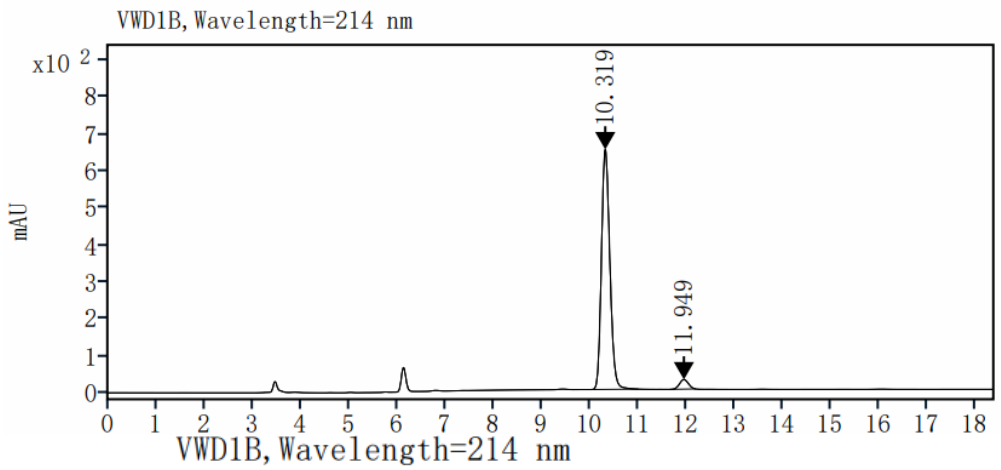


Figure 3B, entry 33
(*S*)-**A1**: 92% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.417	MM m	2856.58	50.09
	12.028	MM m	2846.06	49.91



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.319	MM m	7875.86	95.95
	11.949	MM m	332.49	4.05

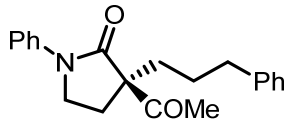
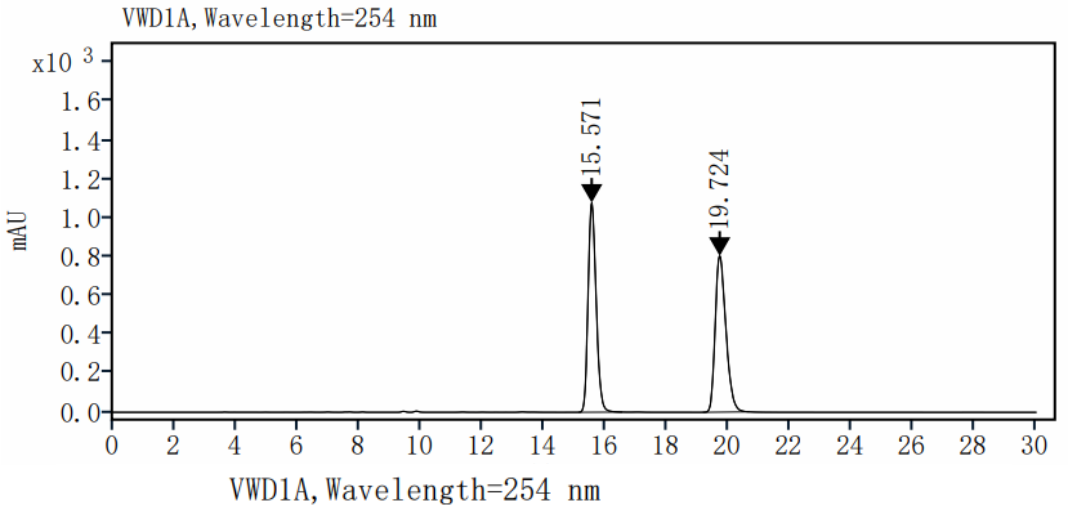
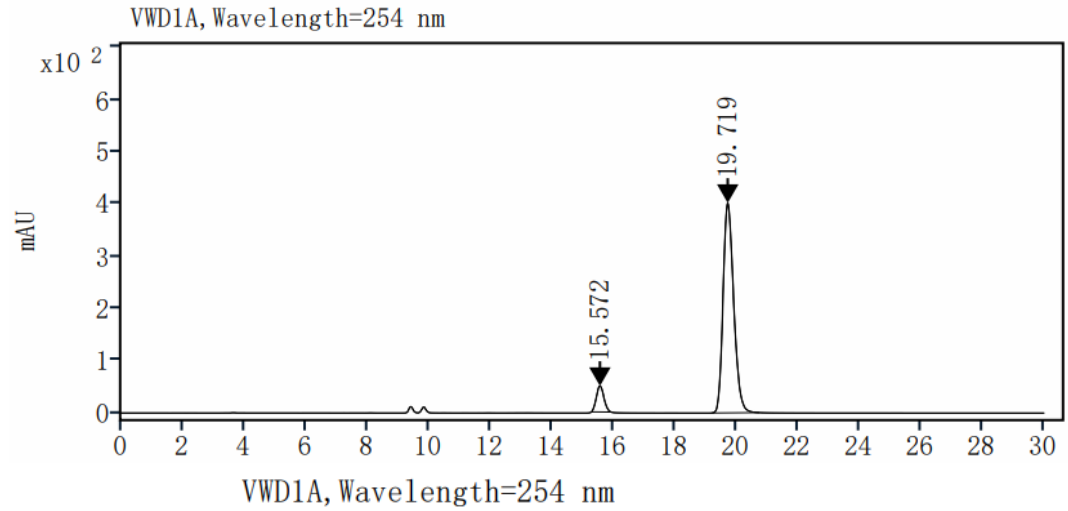


Figure 3B, entry 34
(*S*)-**A1**: 84% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.571	MM m	19612.79	50.18
	19.724	MM m	19475.36	49.82



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	15.572	MM m	844.67	8.07
	19.719	MM m	9625.08	91.93

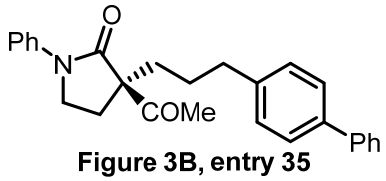
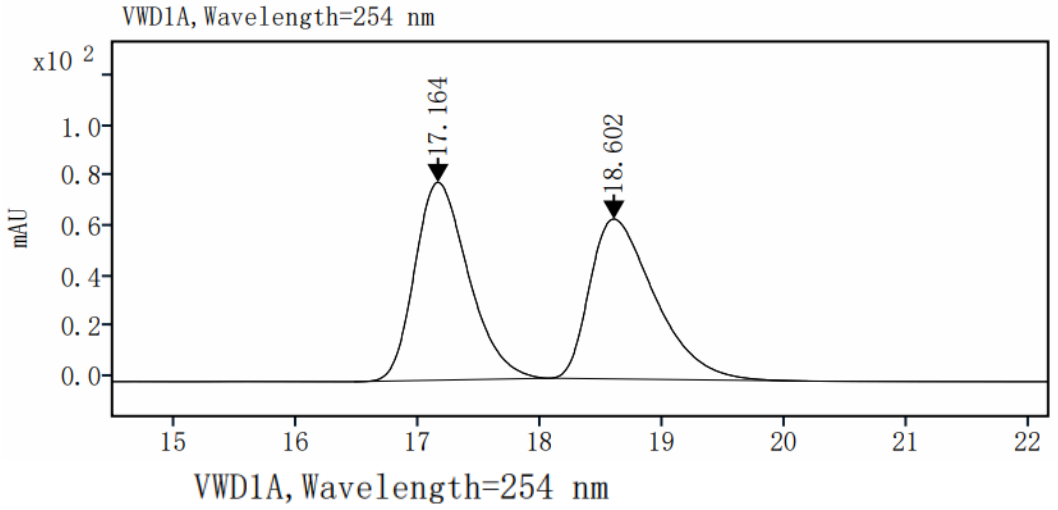
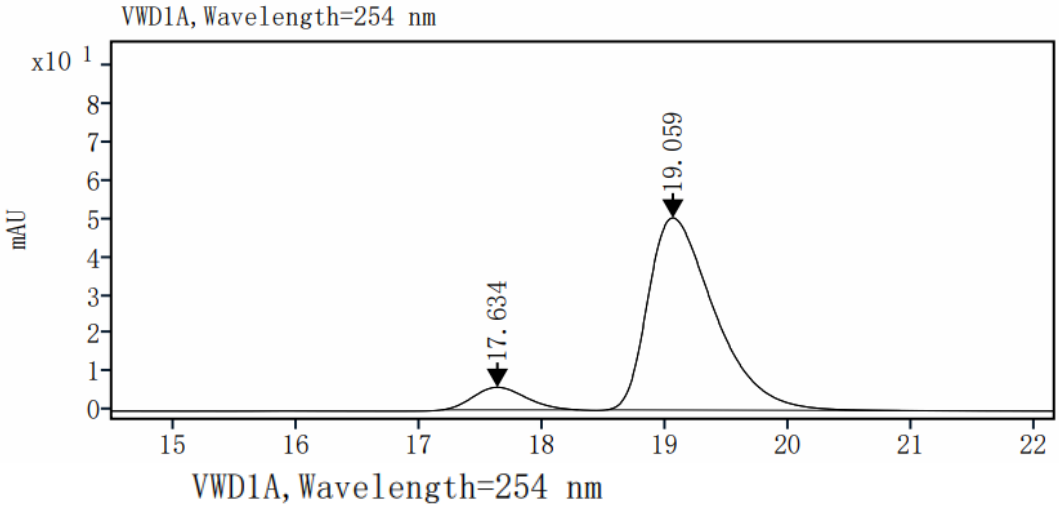


Figure 3B, entry 35
(*S*)-**A1**: 83% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	17.164	MM m	2412.75	50.51
	18.602	MM m	2363.74	49.49



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	17.634	MM m	173.98	8.47
	19.059	MM m	1879.21	91.53

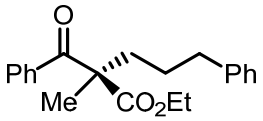
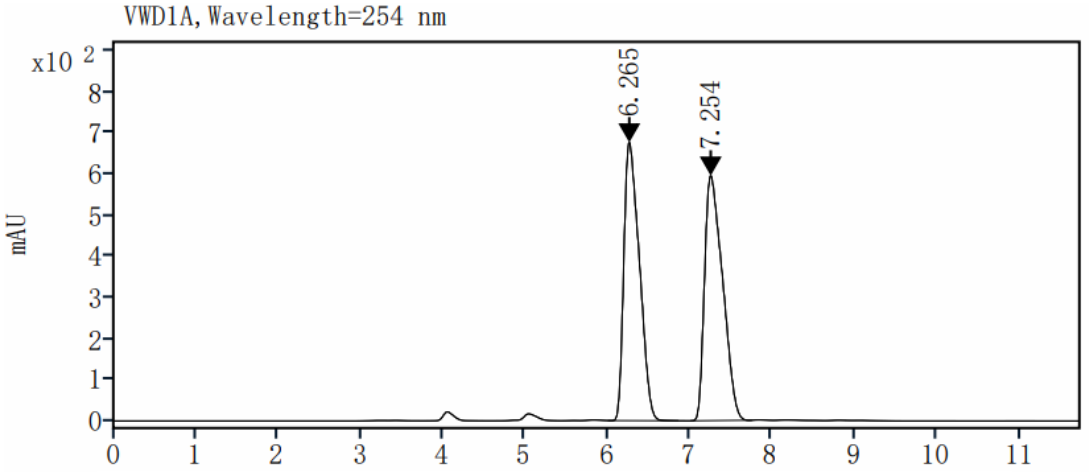
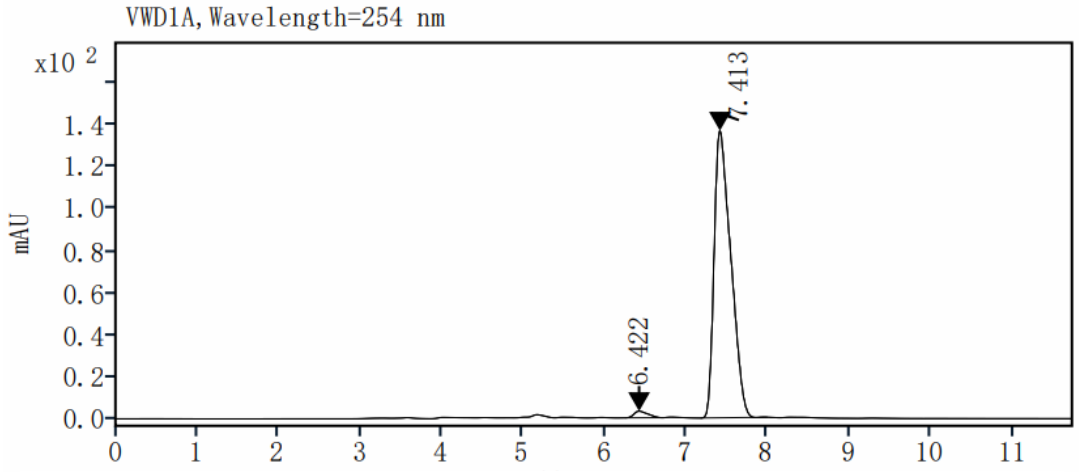


Figure 3B, entry 36
(*S*)-**A1**: 96% ee



VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.265	MM m	8883.88	49.46
	7.254	MM m	9078.71	50.54



VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.422	MM m	37.15	1.87
	7.413	MM m	1953.17	98.13

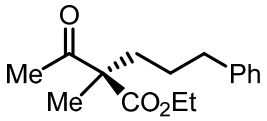
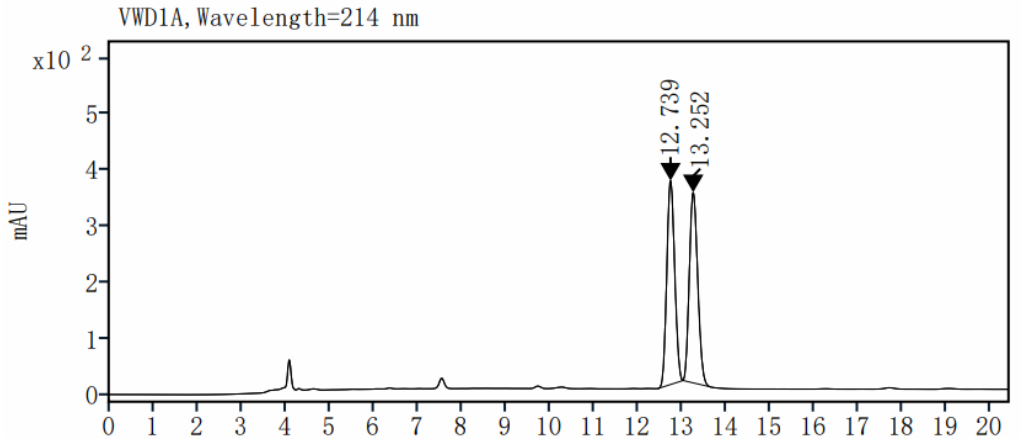
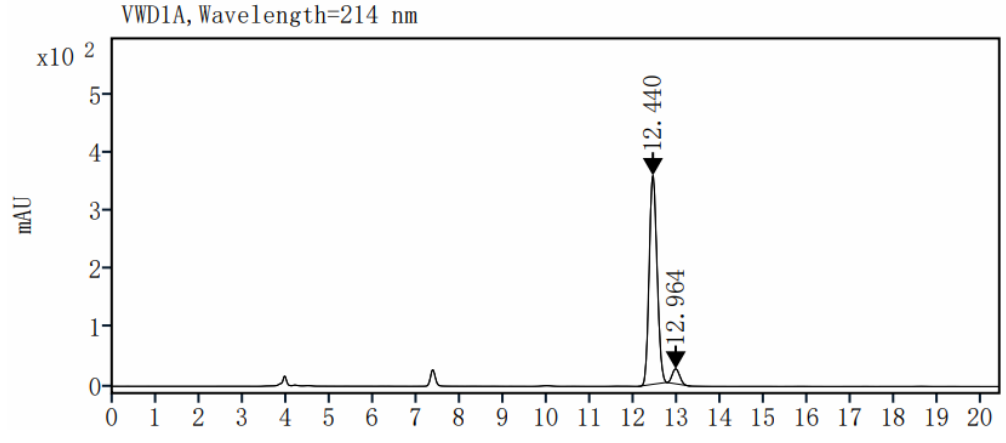


Figure 3B, entry 37
(*S*)-**A1**: 87% ee



VWD1A, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	12.739	MM m	4534.39	50.10
	13.252	MM m	4516.17	49.90



VWD1A, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	12.440	MM m	4502.86	93.70
	12.964	MM m	302.91	6.30

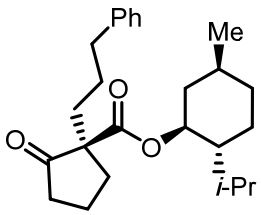
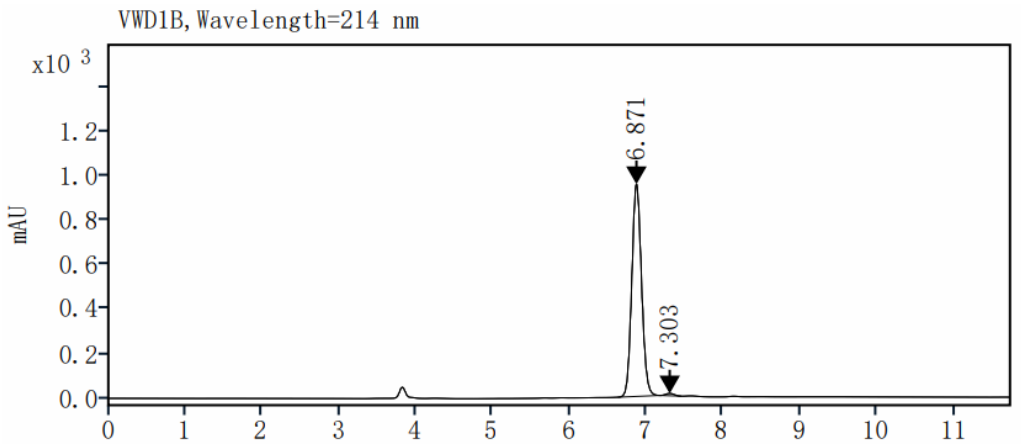
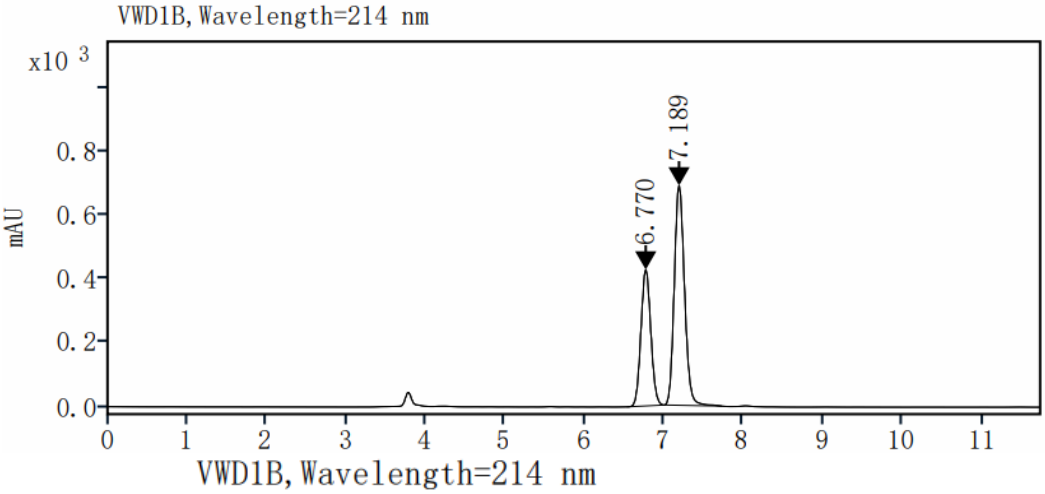


Figure 3B, entries 38 and 39
(*S*)-**A1**: 99:1 dr
(*R*)-**A1**: 37:63 dr



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.871	MM m	8397.80	99.05
	7.303	MM m	80.37	0.95



VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.770	MM m	3675.66	37.20
	7.189	MM m	6206.02	62.80

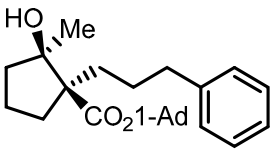
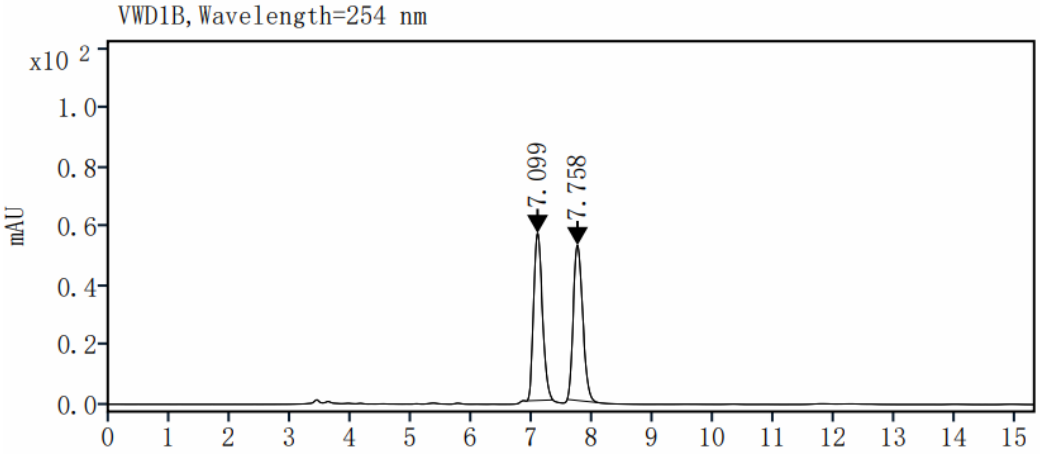
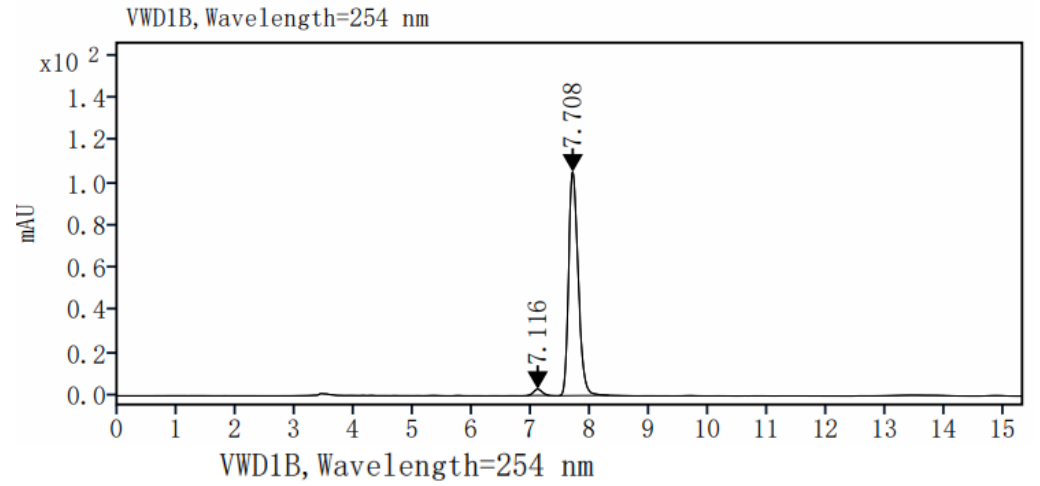


Figure 4, entry 40
95% ee



VWD1B, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.099	MM m	568.99	49.87
	7.758	MM m	571.93	50.13



VWD1B, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.116	MM m	29.41	2.42
	7.708	MM m	1186.79	97.58

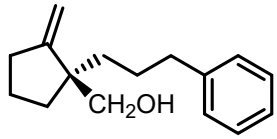
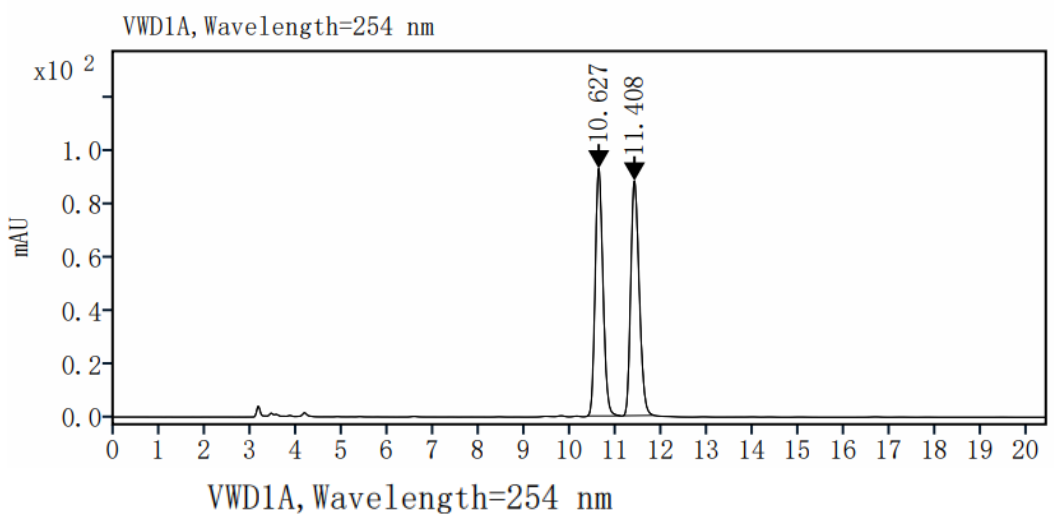
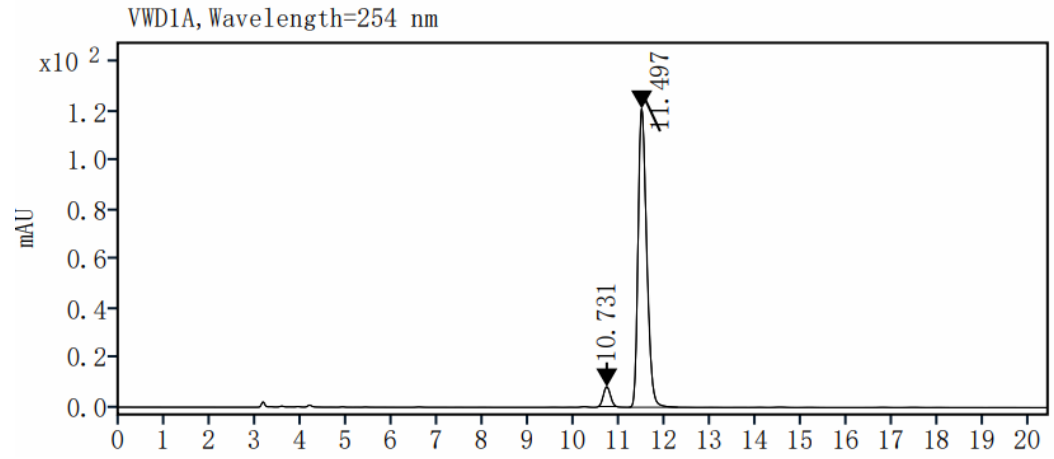


Figure 4, entry 41 (41')
90% ee



VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.627	MM m	1103.27	49.21
	11.408	MM m	1138.87	50.79



VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.731	MM m	85.67	5.10
	11.497	MM m	1595.43	94.90

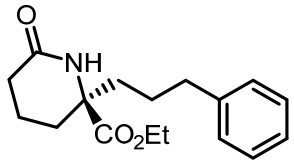
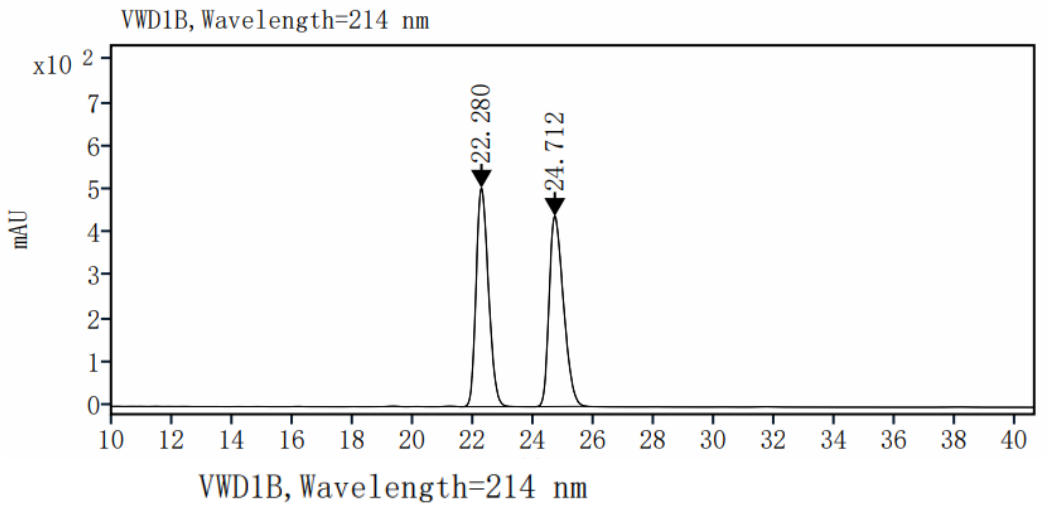
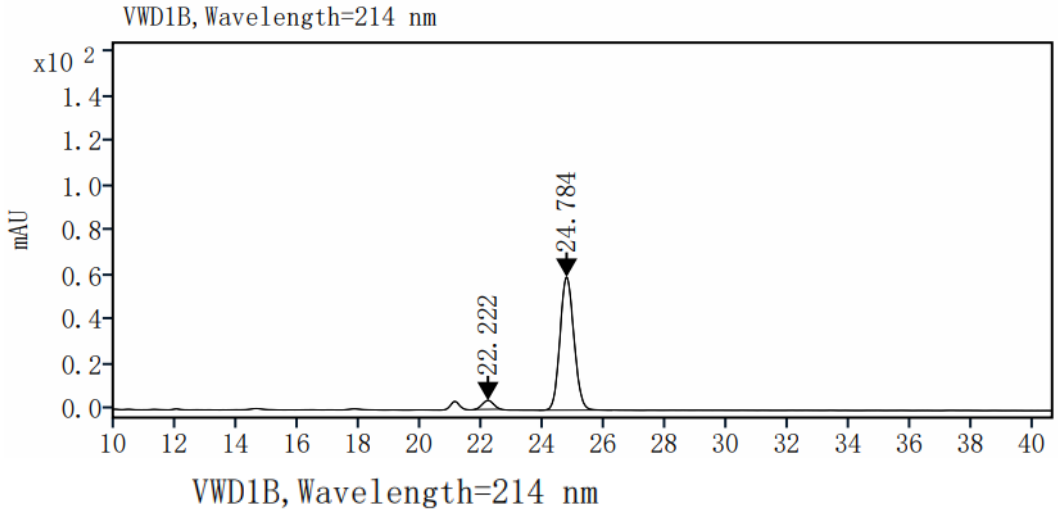


Figure 4, entry 42
90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	22.280	MM m	14406.01	49.69
	24.712	MM m	14587.14	50.31



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	22.222	MM m	100.54	5.06
	24.784	MM m	1885.13	94.94

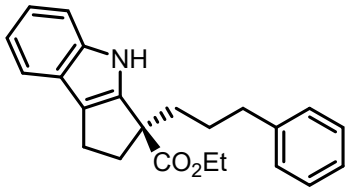
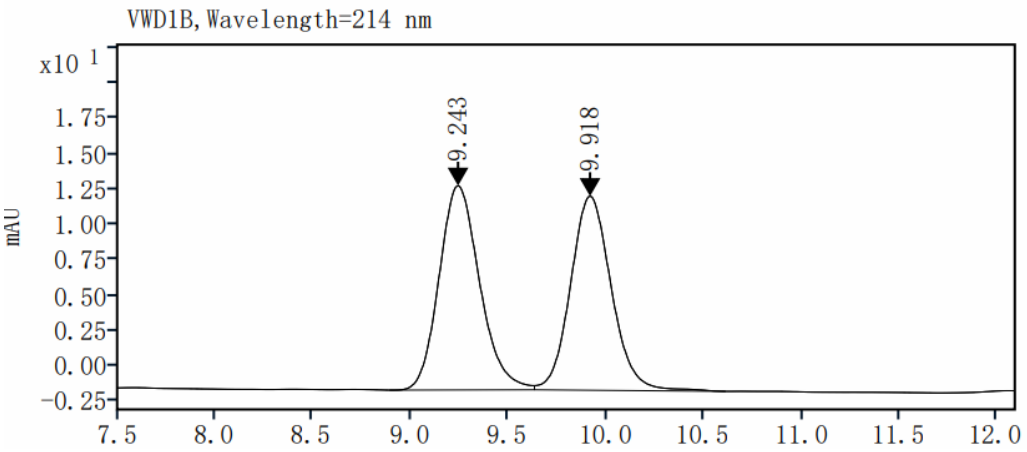
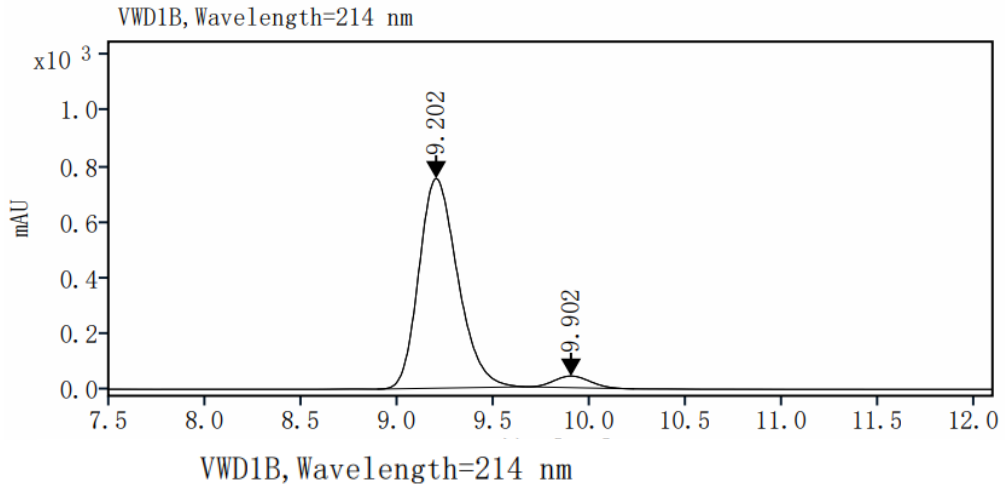


Figure 4, entry 43
90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.243	MM m	208.25	51.13
	9.918	MM m	199.03	48.87



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.202	MM m	10567.42	95.12
	9.902	MM m	541.65	4.88