Acyclic Quaternary Stereocenters via Catalytic Asymmetric Cross-Couplings with Unactivated Alkyl N-Hydroxyphthalimide Esters

Lian-Jie Li,[1] Jun-Chun Zhang,[1] Jia-Yu Tang,[1] Hui Yu,[1] and Ze-Peng Yang*,[1]

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

Supporting Information

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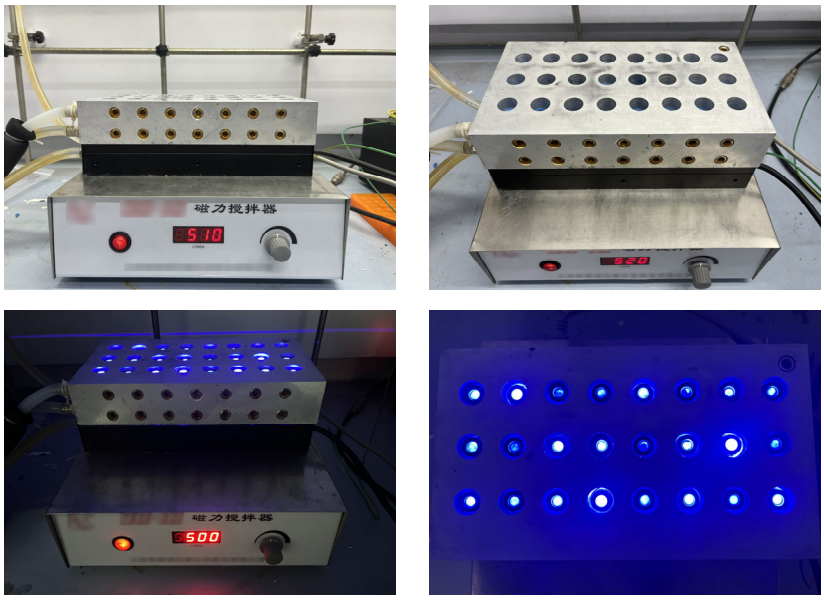
I. General Information

Unless otherwise noted, all 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 EA (ethyl acetate) was 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. An Agilent Carry5000 spectrometer was used to record the UV-vis spectra. 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 **Scheme 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.

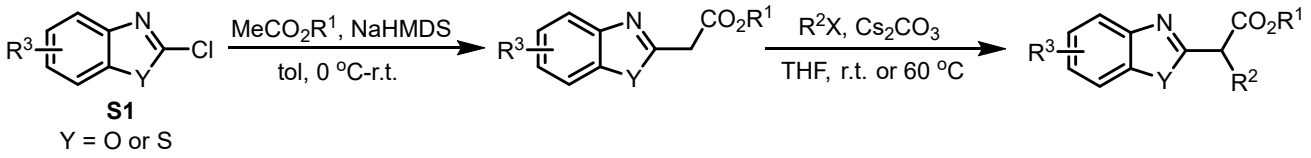


Scheme S1. Photoreaction Setup

II. Preparation of Benzoxazolyl Acetates and NHP Esters

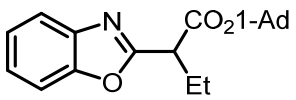
The yields have not been optimized.

General Procedure 1 (GP-1).



Preparation of Benzoxazolyl Acetates.[2] An oven-dried 100 mL round-bottom flask was charged with a stir bar, and then it was sealed with a rubber septum cap. The flask was placed under a nitrogen atmosphere by evacuating and backfilling the flask (three cycles), followed by the addition of NaHMDS (2.0 equiv) and anhydrous toluene (volume to generate a 1.0 M solution of **S1**) via syringe. The resulting solution was cooled to 0 °C using an ice bath, and then $MeCO_2R^1$ (2.0 equiv) was added by syringe within 10 min. The reaction mixture was stirred at 0 °C for 30 min, followed by the addition of **S1** (1.0 equiv) in anhydrous toluene (volume to generate a 2.0 M solution of the **S1**). The reaction was allowed to warm to room temperature and stirred for 3 hours and then quenched with saturated aqueous NH_4Cl. The aqueous phase was extracted with EtOAc, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was directly used for the next step without purification.

An oven-dried 100 mL round-bottom flask was charged with a stir bar, the crude product obtained above (1.0 equiv), and Cs_2CO_3 (1.5 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 THF (volume to generate a 1.0 M solution of the crude product) via syringe. Then R^2X (alkyl bromide or alkyl iodide) (1.5 equiv) was added via syringe over 10 min. The reaction was stirred at room temperature or 60 °C until the reaction was complete (monitored by TLC). The mixture was quenched by adding H_2O at 0 °C and extracted with EtOAc, 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.



Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (6.12 g, 40.0 mmol) and adamantan-1-yl acetate.

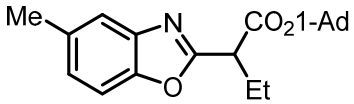
The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 6.41 g (18.9 mmol, 47% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.69 (m, 1H), 7.54 – 7.50 (m, 1H), 7.33 – 7.30 (m, 2H), 3.85 (t, *J* = 8.2 Hz, 1H), 2.24 – 2.16 (m, 2H), 2.15 – 2.12 (m, 3H), 2.09 – 2.07 (m, 6H), 1.64 – 1.61 (m, 6H), 1.03 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.5, 163.8, 150.9, 141.0, 124.8, 124.2, 120.0, 110.6, 82.3, 49.0, 41.1, 36.0, 30.8, 23.7, 11.9.

HRMS (ESI-MS) *m*/*z* [M+MeCN+Na]$^+$ calcd for $C_{23}H_{28}N_2NaO_3$: 403.1992, found: 403.1998.

FT-IR (film): 2960, 2920, 2820, 1726, 1455, 1253, 1044, 750 cm^{-1}.



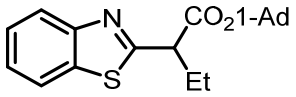
Adamantan-1-yl 2-(5-methylbenzo[*d*]oxazol-2-yl)butanoate. The title compound was synthesized according to **GP-1** from 2-chloro-5-methylbenzo[d]oxazole (1.67 g, 10.0 mmol) and adamantan-1-yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 2.40 g (6.8 mmol, 68% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 (s, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 3.82 (t, *J* = 6.6 Hz, 1H), 2.46 (s, 3H), 2.22 – 2.15 (m, 2H), 2.14 – 2.12 (m, 3H), 2.08 – 2.07 (m, 6H), 1.63 – 1.61 (m, 6H), 1.01 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.6, 163.8, 149.1, 141.2, 134.0, 125.9, 119.9, 109.9, 82.2, 49.0, 41.1, 36.0, 30.8, 23.6, 21.4, 11.9.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{22}H_{28}NO_3$: 354.2064, found: 354.2072.

FT-IR (film): 2959, 2914, 2816, 1726, 1450, 1264, 1056, 753 cm^{-1}.



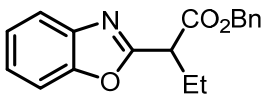
Adamantan-1-yl 2-(benzo[*d*]thiazol-2-yl)butanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzo[d]thiazole (0.85 g, 5.0 mmol) and adamantan-1-yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 0.71 g (2.0 mmol, 40% yield). Yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.38 – 7.35 (m, 1H), 4.02 (t, *J* = 7.6 Hz, 1H), 2.22 – 2.18 (m, 1H), 2.16 – 2.14 (m, 3H), 2.14 – 2.11 (m, 6H), 2.09 – 2.03 (m, 1H), 1.66 – 1.62 (m, 6H), 1.02 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.2, 169.1, 152.4, 135.3, 125.9, 124.9, 122.9, 121.5, 82.2, 53.9, 41.1, 36.1, 30.8, 27.5, 11.8.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{21}H_{26}NO_2S$: 356.1679, found: 356.1676.

FT-IR (film): 2958, 2913, 2822, 1727, 1452, 1260, 1055, 750 cm^{-1}.



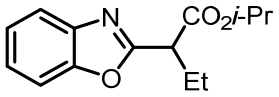
Benzyl 2-(benzo[*d*]oxazol-2-yl)butanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (1.53 g, 10.0 mmol) and benzyl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 1.24 g (4.2 mmol, 42% yield). Yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 – 7.69 (m, 1H), 7.49 – 7.46 (m, 1H), 7.32 – 7.26 (m, 7H), 5.21 – 5.15 (m, 2H), 4.00 (t, *J* = 7.2 Hz, 1H), 2.27 – 2.20 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.5, 162.9, 150.8, 140.9, 135.3, 128.4, 128.2, 128.0, 125.0, 124.3, 120.0, 110.5, 67.1, 47.8, 23.5, 11.8.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{18}H_{18}NO_3$: 296.1281, found: 296.1279.

FT-IR (film): 2958, 2911, 2826, 1726, 1451, 1252, 1045, 750 cm^{-1}.



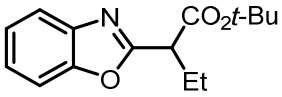
Isopropyl 2-(benzo[*d*]oxazol-2-yl)butanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (4.33 g, 28.3 mmol) and isopropyl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 2.57 g (10.4 mmol, 37% yield). Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.69 (m, 1H), 7.52 – 7.49 (m, 1H), 7.33 – 7.29 (m, 2H), 5.12 – 5.05 (m, 1H), 3.89 (t, *J* = 7.2 Hz, 1H), 2.26 – 2.17 (m, 2H), 1.23 – 1.19 (m, 6H), 1.02 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.2, 163.3, 150.8, 140.9, 124.9, 124.2, 120.0, 110.5, 69.2, 48.0, 23.6, 21.6, 21.5, 11.9.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{14}H_{18}NO_3$: 248.1281, found: 248.1274.

FT-IR (film): 2958, 2911, 2826, 1728, 1451, 1251, 1043, 753 cm^{-1}.



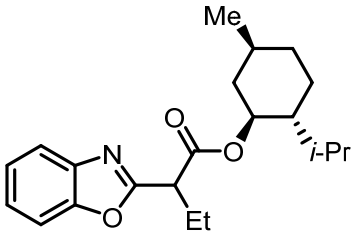
***tert*-Butyl 2-(benzo[*d*]oxazol-2-yl)butanoate.** The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (1.53 g, 10.0 mmol) and *tert*-butyl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 0.93 g (3.6 mmol, 36% yield). Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.69 (m, 1H), 7.54 – 7.49 (m, 1H), 7.33 – 7.29 (m, 2H), 3.85 (t, *J* = 7.2 Hz, 1H), 2.23 – 2.16 (m, 2H), 1.44 (s, 9H), 1.02 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.8, 163.7, 150.8, 141.0, 124.8, 124.2, 120.0, 110.5, 82.2, 48.9, 27.9, 23.6, 11.9.

HRMS (ESI-MS) *m*/*z* [M+MeCN+Na]$^+$ calcd for $C_{17}H_{22}N_2NaO_3$: 325.1523, found: 325.1515.

FT-IR (film): 2957, 2911, 2826, 1728, 1452, 1252, 1045, 750 cm^{-1}.



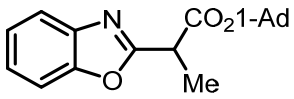
(*1S,2R,5S*)-2-Isopropyl-5-methylcyclohexyl 2-(benzo[*d*]oxazol-2-yl)butanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (1.83 g, 12.0 mmol) and *L*-menthyl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 1.83 g (5.3 mmol, 44% yield). Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.69 (m, 1H), 7.52 – 7.47 (m, 1H), 7.33 – 7.30 (m, 2H), 4.74 – 4.68 (m, 1H), 3.92 (t, *J* = 7.2 Hz, 1H), 2.26 – 2.20 (m, 2H), 2.04 – 1.98 (m, 1H), 1.75 – 1.60 (m, 3H), 1.50 – 1.43 (m, 1H), 1.32 – 1.26 (m, 1H), 1.06 – 0.99 (m, 4H), 0.99 – 0.89 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H), 0.85 – 0.79 (m, 1H), 0.77 (d, *J* = 7.2 Hz, 1H), 0.72 – 0.69 (m, 3H), 0.65 (d, *J* = 6.6 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.2, 163.5, 163.4, 150.8, 140.92, 140.90, 124.9, 124.28, 124.26, 119.99, 119.97, 110.5, 110.4, 75.82, 75.76, 48.3, 48.1, 46.8, 46.7, 40.6, 40.4, 34.1, 31.3, 26.0, 25.8, 23.4, 23.3, 23.2, 23.1, 21.93, 21.90, 20.59, 20.55, 16.0, 15.9, 11.90, 11.88.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{21}H_{30}NO_3$: 344.2220, found: 344.2214.

FT-IR (film): 2952, 2917, 2866 1729, 1450, 1239, 1173, 740 cm^{-1}.



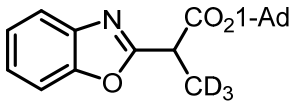
Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)propanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (1.53 g, 10.0 mmol) and adamantan-1-yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 1.80 g (5.5 mmol, 55% yield). Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.69 (m, 1H), 7.54 – 7.49 (m, 1H), 7.34 – 7.29 (m, 2H), 4.07 – 3.99 (q, *J* = 7.2 Hz, 1H), 2.16 – 2.12 (m, 3H), 2.09 – 2.06 (m, 6H), 1.69 (d, *J* = 7.2 Hz, 3H), 1.64 – 1.61 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.1, 164.6, 150.9, 141.0, 124.9, 124.2, 120.0, 110.5, 82.3, 41.7, 41.1, 36.0, 30.8, 15.1.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{20}H_{24}NO_3$: 326.1751, found: 326.1745.

FT-IR (film): 2958, 2912, 2826, 1726, 1451, 1252, 1047, 750 cm^{-1}.



Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)propanoate-3,3,3-*d*$_3$. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (0.62 g, 4.0 mmol) and adamantan-1-

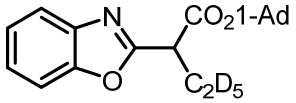
yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 0.80 g (2.4 mmol, 61% yield). Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.68 (m, 1H), 7.54 – 7.49 (m, 1H), 7.33 – 7.28 (m, 2H), 4.01 (s, 1H), 2.15 – 2.12 (m, 3H), 2.09 – 2.06 (m, 6H), 1.64 – 1.61 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.2, 164.6, 150.9, 141.0, 124.9, 124.2, 120.0, 110.5, 82.2, 41.5, 41.1, 36.0, 30.8.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{20}H_{21}D_3NO_3$: 329.1939, found: 329.1931.

FT-IR (film): 2938, 2907, 2849, 1726, 1456, 1271, 1180, 1039, 748 cm^{-1}.



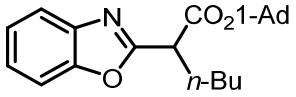
Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate-3,3,4,4,4-*d*$_5$. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (0.62 g, 4.0 mmol) and adamantan-1-yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 0.85 g (2.5 mmol, 62% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.69 (m, 1H), 7.53 – 7.49 (m, 1H), 7.33 – 7.29 (m, 2H), 3.83 (s, 1H), 2.14 – 2.11 (m, 3H), 2.09 – 2.06 (m, 6H), 1.64 – 1.60 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.5, 163.7, 150.8, 141.0, 124.8, 124.2, 119.9, 110.5, 82.2, 48.7, 41.1, 36.0, 30.7.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{21}H_{21}D_5NO_3$: 345.2221, found: 345.2221.

FT-IR (film): 2932, 2910, 2852, 1719, 1446, 1281, 1167, 1053, 753 cm^{-1}.



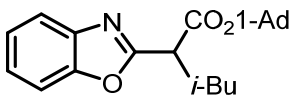
Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)hexanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (2.30 g, 15.0 mmol) and adamantan-1-yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 1.95 g (5.3 mmol, 35% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.69 (m, 1H), 7.53 – 7.50 (m, 1H), 7.33 – 7.29 (m, 2H), 3.91 (t, *J* = 7.7 Hz, 1H), 2.19 – 2.12 (m, 5H), 2.09 – 2.06 (m, 6H), 1.63 – 1.60 (m, 6H), 1.39 – 1.31 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.6, 163.9, 150.8, 141.0, 124.8, 124.2, 120.0, 110.5, 82.2, 47.5, 41.1, 36.0, 30.8, 29.9, 29.4, 22.3, 13.8.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{23}H_{30}NO_3$: 368.2220, found: 368.2222.

FT-IR (film): 2956, 2908, 2822, 1725, 1453, 1237, 1055, 751 cm^{-1}.



Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)-4-methylpentanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (2.30 g, 15.0 mmol) and adamantan-1-

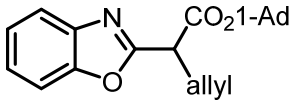
yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 1.54 g (4.2 mmol, 28% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.69 (m, 1H), 7.54 – 7.50 (m, 1H), 7.34 – 7.30 (m, 2H), 4.05 – 3.99 (m, 1H), 2.16 – 2.12 (m, 3H), 2.09 – 2.04 (m, 8H), 1.64 – 1.58 (m, 7H), 0.97 – 0.94 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.8, 164.0, 150.8, 141.0, 124.8, 124.2, 120.0, 110.6, 82.3, 45.7, 41.1, 38.9, 36.0, 30.8, 26.0, 22.3, 22.2.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{23}H_{29}NNaO_3$: 390.2040, found: 390.2046.

FT-IR (film): 2950, 2911, 2822, 1726, 1452, 1239, 1055, 751 cm^{-1}.



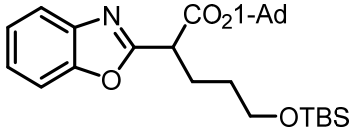
Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)pent-4-enoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (2.30 g, 15.0 mmol) and adamantan-1-yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 2.40 g (6.8 mmol, 46% yield). Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.70 (m, 1H), 7.53 – 7.49 (m, 1H), 7.33 – 7.30 (m, 2H), 5.88 – 5.80 (m, 1H), 5.17 – 5.13 (m, 1H), 5.06 – 5.03 (m, 1H), 4.02 (t, *J* = 7.8 Hz, 1H), 2.95 – 2.87 (m, 2H), 2.15 – 2.12 (m, 3H), 2.09 – 2.07 (m, 6H), 1.64 – 1.61 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.9, 163.2, 150.9, 141.0, 133.9, 124.9, 124.2, 120.0, 117.8, 110.6, 82.5, 47.1, 41.1, 36.0, 34.2, 30.8.

HRMS (ESI-MS) *m*/*z* [M+K]$^+$ calcd for $C_{22}H_{25}KNO_3$: 390.1466, found: 390.1467.

FT-IR (film): 2960, 2911, 2828, 1725, 1650, 1455, 1236, 1057, 751cm^{-1}.



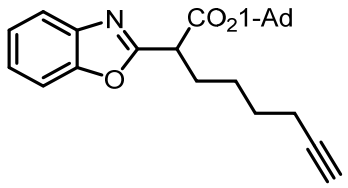
Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)-5-((*tert*-butyldimethylsilyl)oxy)pentanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (1.53 g, 10.0 mmol) and adamantan-1-yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 1.30 g (2.7 mmol, 27% yield). Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.68 (m, 1H), 7.54 – 7.49 (m, 1H), 7.34 – 7.29 (m, 2H), 3.97 (t, *J* = 7.2 Hz, 1H), 3.65 (t, *J* = 6.0 Hz, 2H), 2.28 – 2.19 (m, 2H), 2.15 – 2.12 (m, 3H), 2.10 – 2.07 (m, 6H), 1.65 – 1.57 (m, 8H), 0.88 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.6, 163.8, 150.9, 141.0, 124.8, 124.2, 120.0, 110.6, 82.3, 62.4, 47.2, 41.1, 36.1, 30.8, 30.3, 26.8, 25.9, 18.3, -5.3.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{28}H_{42}NO_4Si$: 484.2878, found: 484.2872.

FT-IR (film): 2960, 2912, 2825, 1725, 1455, 1233, 1043, 752 cm^{-1}.



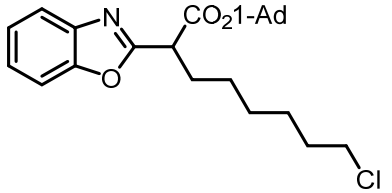
Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)oct-7-ynoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (0.49 g, 3.2 mmol) and adamantan-1-yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 0.66 g (1.7 mmol, 53% yield). Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 – 7.69 (m, 1H), 7.53 – 7.49 (m, 1H), 7.33 – 7.29 (m, 2H), 3.92 (t, *J* = 7.7 Hz, 1H), 2.20 – 2.14 (m, 4H), 2.14 – 2.12 (m, 3H), 2.09 – 2.07 (m, 6H), 1.90 (t, *J* = 2.7 Hz, 1H), 1.63 – 1.48 (m, 10H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.4, 163.6, 150.8, 141.0, 124.8, 124.2, 120.0, 110.5, 84.0, 82.4, 68.5, 47.3, 41.1, 36.0, 30.8, 29.6, 28.0, 26.3, 18.1.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{25}H_{30}NO_3$: 392.2220, found: 392.2221.

FT-IR (film): 2922, 2852, 2150, 1729, 1564, 1440, 1264, 1180, 1053, 750 cm^{-1}.



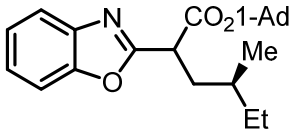
Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)-8-chlorooctanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (0.46 g, 3.0 mmol) and adamantan-1-yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 0.91 g (2.1 mmol, 71% yield). Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.69 (m, 1H), 7.54 – 7.49 (m, 1H), 7.34 – 7.30 (m, 2H), 3.90 (t, *J* = 7.7 Hz, 1H), 3.50 (t, *J* = 6.7 Hz, 2H), 2.17 – 2.12 (m, 5H), 2.09 – 2.06 (m, 6H), 1.76 – 1.73 (m, 2H), 1.64 – 1.61 (m, 6H), 1.44 – 1.36 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.5, 163.7, 150.8, 141.0, 124.8, 124.2, 120.0, 110.5, 82.3, 47.4, 45.0, 41.1, 36.0, 32.4, 30.8, 30.0, 28.4, 27.1, 26.5.

HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{25}H_{33}ClNO_3$: 430.2143, found: 430.2145.

FT-IR (film): 2960, 2911, 2823, 1728, 1430, 1235, 1037, 750 cm^{-1}.



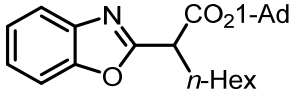
Adamantan-1-yl (*4S*)-2-(benzo[*d*]oxazol-2-yl)-4-methylhexanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (0.51 g, 3.3 mmol) and adamantan-1-yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 0.64 g (1.7 mmol, 50% yield). Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.69 (m, 1H), 7.54 – 7.50 (m, 1H), 7.34 – 7.30 (m, 2H), 4.06 – 4.00 (m, 1H), 2.26 – 2.18 (m, 1H), 2.15 – 2.12 (m, 3H), 2.09 – 2.06 (m, 6H), 1.97 – 1.88 (m, 1H), 1.64 – 1.60 (m, 6H), 1.44 – 1.41 (m, 1H), 1.31 – 1.14 (m, 2H), 0.93 – 0.85 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.9, 168.7, 164.2, 163.9, 150.83, 150.80, 141.0, 124.81, 124.78, 124.19, 124.18, 120.0, 110.6, 110.5, 82.2, 45.5, 41.08, 41.06, 36.9, 36.8, 36.0, 32.3, 32.2, 30.8, 29.2, 29.1, 18.8, 18.6, 11.08, 11.06.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{24}H_{32}NO_3$: 382.2377, found: 382.2376.

FT-IR (film): 2960, 2908, 2821, 1727, 1455, 1260, 1058, 750 cm^{-1}.



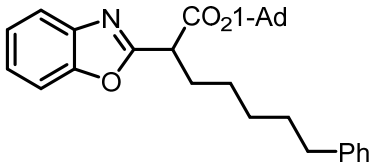
Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)octanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (0.51 g, 3.0 mmol) and adamantan-1-yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 0.62 g (1.6 mmol, 53% yield). Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.69 (m, 1H), 7.53 – 7.49 (m, 1H), 7.33 – 7.30 (m, 2H), 3.91 (t, *J* = 7.7 Hz, 1H), 2.18 – 2.12 (m, 5H), 2.09 – 2.07 (m, 6H), 1.64 – 1.60 (m, 6H), 1.40 – 1.32 (m, 4H), 1.28 – 1.24 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.6, 163.9, 150.8, 141.0, 124.8, 124.2, 120.0, 110.5, 82.2, 47.5, 41.1, 36.0, 31.5, 30.8, 30.2, 28.8, 27.2, 22.5, 14.0.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{25}H_{34}NO_3$: 396.2533, found: 396.2531.

FT-IR (film): 2962, 2911, 2822, 1728, 1439, 1238, 1055, 751 cm^{-1}.



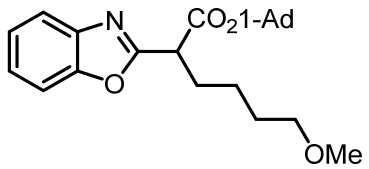
Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)-7-phenylheptanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (0.46 g, 3.0 mmol) and adamantan-1-yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 0.48 g (1.1 mmol, 35% yield). Colorless oil.

^{1}H NMR (600 MHz, Acetonitrile-d_3) δ 7.71 – 7.66 (m, 1H), 7.60 – 7.55 (m, 1H), 7.39 – 7.34 (m, 2H), 7.26 – 7.23 (m, 2H), 7.18 – 7.13 (m, 3H), 3.91 (t, *J* = 7.6 Hz, 1H), 2.57 (t, *J* = 7.8 Hz, 2H), 2.12 – 2.07 (m, 5H), 2.04 – 2.03 (m, 6H), 1.64 – 1.57 (m, 8H), 1.44 – 1.34 (m, 4H).

^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.2, 164.7, 151.5, 143.5, 141.8, 129.1, 129.0, 126.3, 125.8, 125.1, 120.4, 111.2, 82.4, 47.8, 41.6, 36.4, 36.0, 31.7, 31.5, 30.4, 29.2, 27.4.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{30}H_{36}NO_3$: 458.2690, found: 458.2687.

FT-IR (film): 2958, 2908, 2822, 1726, 1455, 1237, 1060, 750 cm^{-1}.



Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)-6-methoxyhexanoate. The title compound was synthesized according to **GP-1** from 2-chlorobenzoxazole (0.61 g, 4.0 mmol) and adamantan-1-yl acetate. The product was purified by column chromatography on silica gel (20:1 PE/EtOAc). 0.40 g (1.0 mmol, 25% yield). White solid.

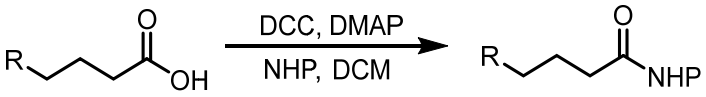
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.70 (m, 1H), 7.54 – 7.50 (m, 1H), 7.35 – 7.30 (m, 2H), 3.92 (t, *J* = 7.7 Hz, 1H), 3.36 (t, *J* = 6.5 Hz, 2H), 3.30 (s, 3H), 2.22 – 2.11 (m, 7H), 2.09 – 2.06 (m, 6H), 1.64 – 1.62 (m, 6H), 1.50 – 1.42 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.5, 163.7, 150.8, 141.0, 124.8, 124.2, 120.0, 110.6, 82.3, 72.3, 58.5, 47.4, 41.1, 36.0, 30.8, 30.0, 29.2, 24.0.

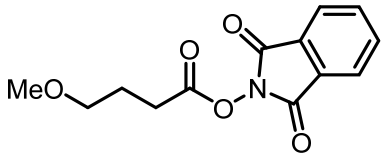
HRMS (ESI-MS) *m*/*z* [M+H]$^{+}$ calcd for $C_{24}H_{32}NO_4$: 398.2326, found: 398.2326.

FT-IR (film): 2961, 2912, 2825, 1728, 1455, 1238, 1055, 751 cm^{-1}.

General Procedure 2 (GP-2).



Preparation of NHP Esters.[3] An oven-dried 100 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 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.



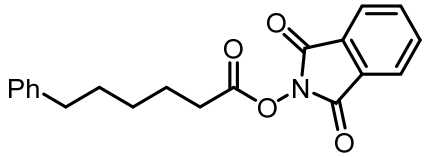
1,3-Dioxoisoindolin-2-yl 4-methoxybutanoate. The title compound was synthesized according to **GP-2** from 4-methoxybutanoic acid (1.18 g, 10.0 mmol) and *N*-hydroxyphthalimide. The product was purified by column chromatography on silica gel (10:1 PE/EtOAc). 1.45 g (5.5 mmol, 55% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 – 7.84 (m, 2H), 7.79 – 7.76 (m, 2H), 3.48 (t, *J* = 6.0 Hz, 2H), 3.36 (s, 3H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.05 – 2.00 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.5, 161.9, 134.7, 128.9, 123.9, 70.6, 58.6, 27.8, 24.7.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{13}H_{13}NNaO_5$: 286.0686, found: 286.0683.

FT-IR (film): 1817, 1785, 1729, 1446, 1264, 1160, 756 cm^{-1}.



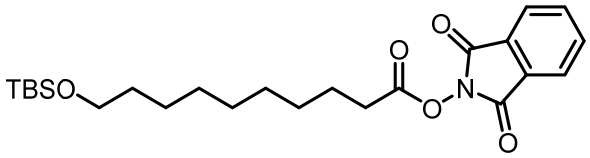
1,3-Dioxoisoindolin-2-yl 6-phenylhexanoate. The title compound was synthesized according to **GP-2** from 6-phenylhexanoic acid (2.0 g, 10.4 mmol) and *N*-hydroxyphthalimide. The product was purified by column chromatography on silica gel (10:1 PE/EtOAc). 2.3 g (6.8 mmol, 66% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 – 7.85 (m, 2H), 7.80 – 7.76 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 2.69 – 2.63 (m, 4H), 1.86 – 1.80 (m, 2H), 1.72 – 1.67 (m, 2H), 1.54 – 1.48 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.5, 161.9, 142.2, 134.7, 128.8, 128.3, 128.2, 125.6, 123.9, 35.6, 30.9, 30.8, 28.4, 24.5.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{20}H_{19}NNaO_4$: 360.1206, found: 360.1217.

FT-IR (film): 2938, 2922, 2832, 1809, 1774, 1737, 1456, 1370, 1264, 1069, 877, 745 cm^{-1}.



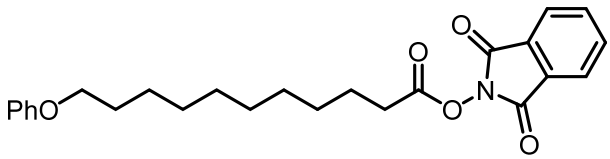
1,3-Dioxoisoindolin-2-yl 10-((*tert*-butyldimethylsilyl)oxy)decanoate. The title compound was synthesized according to **GP-2** from 10-((*tert*-butyldimethylsilyl)oxy)decanoic acid (6.64 g, 22.0 mmol) and *N*-hydroxyphthalimide. The product was purified by column chromatography on silica gel (10:1 PE/EtOAc). 4.3 g (9.6 mmol, 44% yield). Colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 – 7.86 (m, 2H), 7.79 – 7.76 (m, 2H), 3.59 (t, *J* = 6.6 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.80 – 1.75 (m, 2H), 1.52 – 1.48 (m, 2H), 1.45 – 1.41 (m, 2H), 1.35 – 1.29 (m, 8H), 0.89 (s, 9H), 0.39 (s, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.6, 162.0, 134.7, 128.9, 123.9, 63.3, 32.8, 30.9, 29.31, 29.30, 29.0, 28.8, 26.0, 25.7, 24.6, 18.3, -5.3.

HRMS (ESI-MS) *m*/*z* [M+H]$^+$ calcd for $C_{24}H_{38}NO_5Si$: 448.2514, found: 448.2511.

FT-IR (film): 1815, 1785, 1733, 1450, 1265, 1165, 756 cm^{-1}.



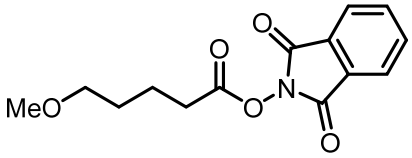
1,3-Dioxoisoindolin-2-yl 11-phenoxyundecanoate. The title compound was synthesized according to **GP-2** from 11-phenoxyundecanoic acid (4.6 g, 16.5 mmol) and *N*-hydroxyphthalimide. The product was purified by column chromatography on silica gel (10:1 PE/EtOAc). 4.2 g (9.9 mmol, 60% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 – 7.80 (m, 2H), 7.80 – 7.72 (m, 2H), 7.30 – 7.24 (m, 2H), 7.02 – 6.75 (m, 3H), 3.95 (t, *J* = 6.6 Hz, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 1.83 – 1.74 (m, 4H), 1.50 – 1.42 (m, 4H), 1.37 – 1.29 (m, 8H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.6, 162.0, 159.1, 134.7, 129.4, 128.9, 123.9, 120.4, 114.5, 67.8, 31.0, 29.4, 29.31, 29.25, 29.1, 28.8, 26.0, 24.6.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{25}H_{29}NNaO_5$: 446.1938, found: 446.1944.

FT-IR (film): 2955, 2917, 2832, 1811, 1780, 1740, 1455, 1372, 1268, 1080, 890, 745 cm^{-1}.



1,3-Dioxoisoindolin-2-yl 5-methoxypentanoate. The title compound was synthesized according to **GP-2** from 5-methoxypentanoic acid (9.50 g, 72.0 mmol) and *N*-hydroxyphthalimide. The product was purified by column chromatography on silica gel (10:1 PE/EtOAc). 12.2 g (44.0 mmol, 61% yield). White solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 – 7.87 (m, 2H), 7.80 – 7.77 (m, 2H), 3.43 (t, *J* = 6.2 Hz, 2H), 3.34 (s, 3H), 2.71 (t, *J* = 7.4 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.76 – 1.68 (m, 2H).

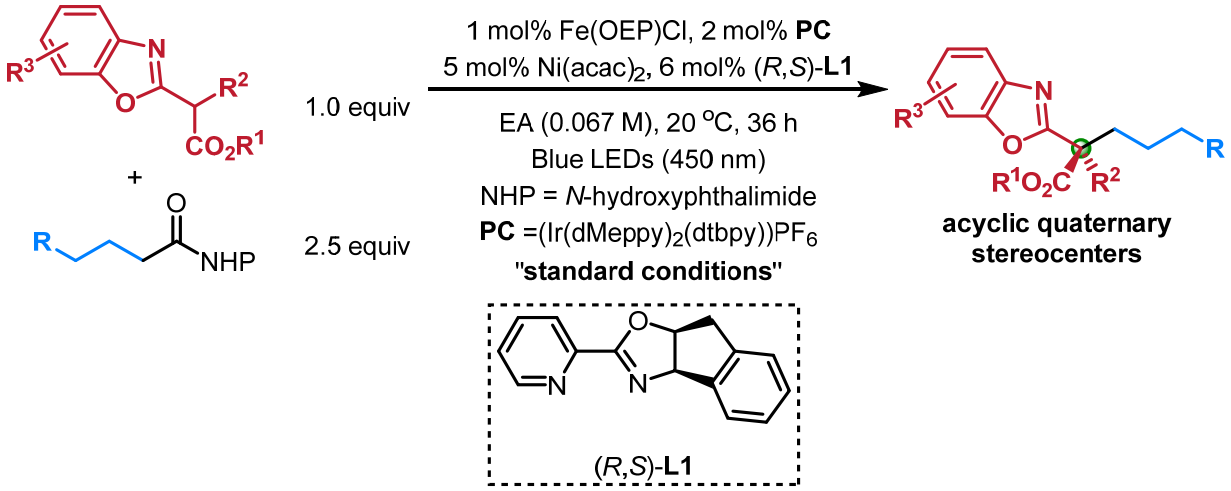
^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.5, 162.0, 134.7, 128.9, 123.9, 71.9, 58.6, 30.7, 28.6, 21.5.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{14}H_{15}NNaO_5$: 300.0842, found: 300.0841.

FT-IR (film): 1818, 1787, 1730, 1450, 1266, 1165, 755 cm^{-1}.

Other NHP esters are known compounds synthesized according to **GP-2** using the corresponding carboxylic acid and *N*-hydroxyphthalimide.[3]

III. Catalytic Enantioselective Cross-Couplings



General Procedure 3 (GP-3): Enantioselective cross-coupling of benzoxazolyl acetate and unactivated alkyl NHP ester.

Preparation of the Lewis acid catalyst solution: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with $Ni(acac)_2$ (2.5 mg, 0.010 mmol, 5.0 mol%), (*R*,*S*)-**L1** (2.8 mg, 0.012 mmol, 6.0 mol%), and a stir bar. Anhydrous EA (1.0 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 30 min, leading to a light blue solution.

Cross-coupling: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with Fe(OEP)Cl (1.3 mg, 0.0020 mmol, 1.0 mol%), $(Ir(dMeppy)_2(dtbpy))PF_6$ (3.9 mg, 0.0040 mmol, 2.0 mol%), NHP ester (0.50 mmol, 2.5 equiv), benzoxazolyl acetate (0.20 mmol, 1.0 equiv), and a stir bar. The Lewis acid catalyst solution (1.0 mL) and anhydrous EA (2.0 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 (**Scheme 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.

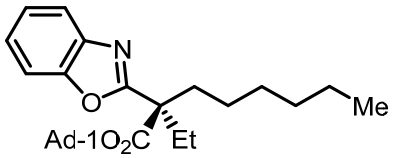
General Procedure 4 (GP-4): Enantioselective cross-coupling of benzoxazolyl acetate and unactivated alkyl NHP ester (72 hours).

The reaction time was extended from 36 to 72 hours, while following the same procedure as **GP-3**.

General Procedure 5 (GP-5): Enantioselective cross-coupling of benzoxazolyl acetate and unactivated alkyl NHP ester (96 hours).

The reaction time was extended from 36 to 96 hours, while following the same procedure as **GP-3**.

The racemic example was obtained by using (*rac*)-**L1** without further optimization.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyloctanoate (1). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 74.4 mg, 88% yield, 87% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.7 min (major), 5.6 min (minor).

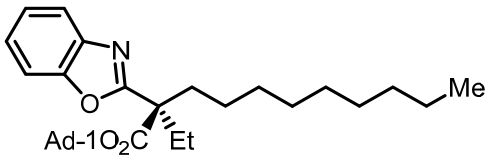
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 – 7.68 (m, 1H), 7.58 – 7.45 (m, 1H), 7.33 – 7.29 (m, 2H), 2.25 – 2.18 (m, 2H), 2.16 – 2.10 (m, 5H), 2.04 – 2.01 (m, 6H), 1.63 – 1.59 (m, 6H), 1.33 – 1.25 (m, 7H), 1.16 – 1.09 (m, 1H), 0.88 – 0.83 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 167.3, 150.7, 140.8, 124.6, 124.0, 119.9, 110.4, 81.7, 53.8, 41.1, 36.0, 33.0, 31.5, 30.7, 29.5, 26.6, 23.8, 22.5, 14.0, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{27}H_{38}NO_3$: 424.2846, found: 424.2840.

FT-IR (film): 2970, 2914, 2856, 1726, 1543, 1274, 1218, 1053, 748 cm^{-1}.

$[\alpha]^{20}_D$ = +1.3 (c 1.0, $CHCl_3$); 87% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethylundecanoate (2). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl decanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 82.7 mg, 89% yield, 86% 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 using (*R,S*)-**L1**: 4.0 min (minor), 5.6 min (major).

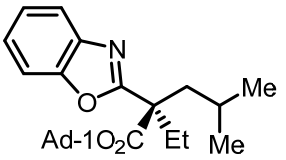
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.71 (m, 1H), 7.53 – 7.48 (m, 1H), 7.33 – 7.28 (m, 2H), 2.23 – 2.18 (m, 2H), 2.16 – 2.10 (m, 5H), 2.05 – 2.01 (m, 6H), 1.63 – 1.59 (m, 6H), 1.33 – 1.25 (m, 7H), 1.24 – 1.20 (m, 6H), 1.17 – 1.09 (m, 1H), 0.88 – 0.84 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 167.3, 150.7, 140.8, 124.6, 124.0, 119.9, 110.4, 81.7, 53.8, 41.1, 36.0, 33.0, 31.8, 30.7, 29.8, 29.5, 29.3, 29.2, 26.6, 23.8, 22.6, 14.1, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{30}H_{44}NO_3$: 466.3316, found: 466.3314.

FT-IR (film): 2955, 2907, 2851, 1723, 1564, 1450, 1215, 1049, 752 cm^{-1}.

$[\alpha]^{20}_D$ = +0.7 (c 1.0, $CHCl_3$); 86% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyl-4-methylpentanoate (3). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl 3-methylbutanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). White solid, 54.6 mg, 69% yield, 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 5.1 min (minor), 6.4 min (major).

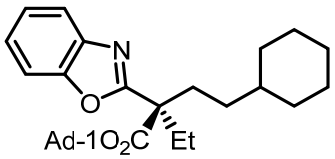
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.70 (m, 1H), 7.52 – 7.48 (m, 1H), 7.33 – 7.28 (m, 2H), 2.32 – 2.21 (m, 2H), 2.16 – 2.08 (m, 5H), 2.04 – 2.00 (m, 6H), 1.71 – 1.65 (m, 1H), 1.62 – 1.58 (m, 6H), 0.91 – 0.86 (m, 6H), 0.74 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.8, 167.5, 150.5, 140.8, 124.7, 124.1, 120.0, 110.4, 81.8, 53.4, 41.6, 41.1, 36.0, 30.7, 27.0, 24.2, 24.0, 23.5, 8.7.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{25}H_{34}NO_3$: 396.2533, found: 396.2530.

FT-IR (film): 2960, 2907, 2852, 1723, 1564, 1450, 1215, 1049, 752 cm^{-1}.

$[\alpha]^{20}_D$ = +2.6 (c 1.0, $CHCl_3$); 93% ee, from (*R,S*)-**L1**.



Adamantan-2-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-4-cyclohexyl-2-ethylbutanoate (4). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl 3-cyclohexylpropanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). White solid, 63.6 mg, 71% yield, 92% 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 using (*R,S*)-**L1**: 4.2 min (minor), 6.2 min (major).

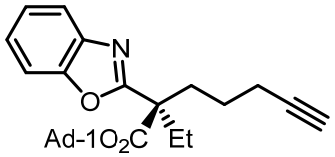
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.71 (m, 1H), 7.53 – 7.49 (m, 1H), 7.34 – 7.30 (m, 2H), 2.22 – 2.15 (m, 4H), 2.13 – 2.10 (m, 3H), 2.04 – 2.01 (m, 6H), 1.76 – 1.65 (m, 5H), 1.62 – 1.60 (m, 6H), 1.22 – 1.09 (m, 5H), 1.05 – 0.98 (m, 1H), 0.90 – 0.82 (m, 5H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 167.3, 150.7, 140.8, 124.6, 124.0, 120.0, 110.4, 81.7, 53.8, 41.1, 37.9, 36.1, 33.3, 33.2, 31.3, 30.8, 30.4, 26.6, 26.3, 8.4.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{29}H_{40}NO_3$: 450.3003, found: 450.2992.

FT-IR (film): 2907, 2852, 1729, 1557, 1450, 1222, 1049, 752 cm^{-1}.

$[\alpha]^{20}_D$ = +1.3 (c 0.8, $CHCl_3$); 92% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethylhept-6-ynoate (5). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl hex-5-ynoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). White solid, 51.5 mg, 64% yield, 88% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 10.8 min (major), 17.5 min (minor).

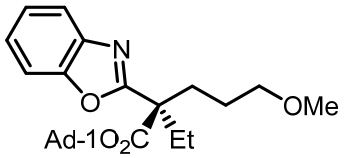
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.70 (m, 1H), 7.53 – 7.48 (m, 1H), 7.34 – 7.30 (m, 2H), 2.28 – 2.20 (m, 6H), 2.14 – 2.11 (m, 3H), 2.05 – 2.02 (m, 6H), 1.95 (t, *J* = 2.7 Hz, 1H), 1.63 – 1.60 (m, 6H), 1.58 – 1.52 (m, 1H), 1.43 – 1.37 (m, 1H), 0.89 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.3, 166.8, 150.7, 140.8, 124.8, 124.1, 120.0, 110.5, 83.8, 82.0, 68.7, 53.6, 41.1, 36.0, 32.4, 30.8, 26.8, 23.3, 18.7, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{26}H_{32}NO_3$: 406.2377, found: 406.2371.

FT-IR (film): 2966, 2907, 2856, 2176, 1733, 1564, 1450, 1264, 1211, 1046, 753 cm^{-1}.

$[\alpha]^{20}_D$ = –2.6 (c 0.3, $CHCl_3$); 88% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyl-5-methoxypentanoate (6). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl 4-methoxybutanoate. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil, 65.7 mg, 80% yield, 80% 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 (*R,S*)-**L1**: 6.3 min (major), 11.3 min (minor).

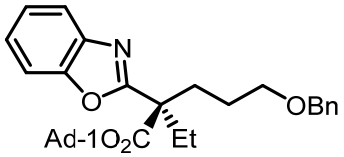
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.69 (m, 1H), 7.55 – 7.44 (m, 1H), 7.35 – 7.29 (m, 2H), 3.38 (t, *J* = 6.5 Hz, 2H), 3.30 (s, 3H), 2.25 – 2.17 (m, 4H), 2.14 – 2.10 (m, 3H), 2.05 – 2.02 (m, 6H), 1.63 – 1.58 (m, 7H), 1.47 – 1.39 (m, 1H), 0.89 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.4, 167.0, 150.7, 140.8, 124.7, 124.1, 120.0, 110.5, 81.9, 72.6, 58.5, 53.6, 41.1, 36.0, 30.8, 30.0, 26.9, 24.3, 8.5.

HRMS (ESI-MS) m/z $[M+K]^+$ calcd for $C_{25}H_{33}KNO_4$: 450.2041, found: 450.2035.

FT-IR (film): 2966, 2907, 2839, 1726, 1555, 1453, 1264, 1211, 1049, 748 cm^{-1}.

$[\alpha]^{20}_D$ = +1.5 (c 0.2, $CHCl_3$); 80% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-5-(benzyloxy)-2-ethylpentanoate (7). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl 4-(benzyloxy)butanoate. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil, 62.3 mg, 64% yield, 80% 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 (*R,S*)-**L1**: 5.7 min (major), 8.6 min (minor).

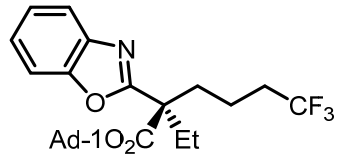
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.71 (m, 1H), 7.52 – 7.49 (m, 1H), 7.34 – 7.30 (m, 6H), 7.27 – 7.26 (m, 1H), 4.47 (s, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 2.26 – 2.21 (m, 4H), 2.13 – 2.09 (m, 3H), 2.05 – 2.02 (m, 6H), 1.65 – 1.59 (m, 7H), 1.51 – 1.46 (m, 1H), 0.89 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.4, 167.0, 150.7, 140.8, 138.5, 128.3, 127.6, 127.5, 124.7, 124.1, 120.0, 110.5, 81.9, 72.8, 70.3, 53.6, 41.1, 36.0, 30.8, 30.0, 26.9, 24.5, 8.6.

HRMS (ESI-MS) m/z $[M+K]^+$ calcd for $C_{31}H_{37}KNO_4$: 526.2354, found: 526.2358.

FT-IR (film): 2950, 2917, 2856, 1726, 1543, 1453, 1260, 1211, 1049, 752 cm^{-1}.

$[\alpha]^{20}_D$ = +0.9 (c 0.3, $CHCl_3$); 80% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyl-6,6,6-trifluorohexanoate (8). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl 5,5,5-trifluoropentanoate. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil, 53.4 mg, 60% yield, 86% 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 (*R,S*)-**L1**: 4.8 min (major), 9.6 min (minor).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.71 (m, 1H), 7.54 – 7.50 (m, 1H), 7.35 – 7.31 (m, 2H), 2.25 – 2.19 (m, 4H), 2.15 – 2.10 (m, 5H), 2.05 – 2.02 (m, 6H), 1.63 – 1.58 (m, 7H), 1.49 – 1.43 (m, 1H), 0.88 (t, *J* = 7.5 Hz, 3H).

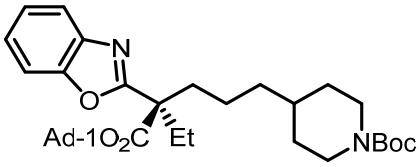
^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.1, 166.4, 150.7, 140.7, 126.9 (q, *J* = 276.5 Hz), 124.9, 124.2, 120.0, 110.5, 82.3, 53.6, 41.1, 36.0, 33.9 (q, *J* = 28.8 Hz), 32.4, 30.8, 27.0, 17.0, 8.5.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -66.2.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{25}H_{31}F_3NO_3$: 450.2251, found: 450.2254.

FT-IR (film): 2973, 2917, 2856, 1726, 1530, 1450, 1239, 1139, 756 cm^{-1}.

$[\alpha]^{20}_D$ = –1.8 (c 0.1, $CHCl_3$); 86% ee, from (*R,S*)-**L1**.



***tert*-Butyl (*R*)-4-(4-((adamantan-1-yloxy)carbonyl)-4-(benzo[*d*]oxazol-2-yl)hexyl)piperidine-1-carboxylate (9).** The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate 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 (1:15 EtOAc/hexanes). White solid, 93.6 mg, 83% yield, 80% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 7.6 min (major), 10.1 min (minor).

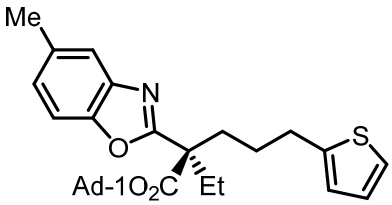
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.71 (m, 1H), 7.52 – 7.48 (m, 1H), 7.33 – 7.29 (m, 2H), 4.07 – 3.98 (m, 2H), 2.62 (t, *J* = 12.8 Hz, 2H), 2.23 – 2.17 (m, 2H), 2.14 – 2.09 (m, 5H), 2.03 – 2.00 (m, 6H), 1.62 – 1.56 (m, 8H), 1.43 (s, 9H), 1.36 – 1.24 (m, 4H), 1.18 – 1.12 (m, 1H), 1.05 – 0.98 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.5, 167.1, 154.8, 150.6, 140.8, 124.7, 124.1, 120.0, 110.4, 81.8, 79.1, 53.8, 44.0, 41.1, 36.6, 36.0, 35.5, 33.1, 32.1, 32.0, 30.7, 28.4, 26.7, 20.9, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{34}H_{49}N_2O_5$: 565.3636, found: 565.3633.

FT-IR (film): 2939, 2917, 2869, 1726, 1681, 1446, 1270, 1229, 733 cm^{-1}.

$[\alpha]^{20}_D$ = –0.8 (c 1.0, $CHCl_3$); 80% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-ethyl-2-(5-methylbenzo[*d*]oxazol-2-yl)-5-(thiophen-2-yl)pentanoate (10). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl 4-(thiophen-2-yl)butanoate.

The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil, 59.8 mg, 63% yield, 80% 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 using (*R,S*)-**L1**: 7.2 min (minor), 9.5 min (major).

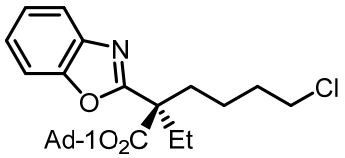
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.13 – 7.11 (m, 1H), 7.09 (d, *J* = 5.1 Hz, 1H), 6.89 (t, *J* = 5.2 Hz, 1H), 6.79 – 6.74 (m, 1H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.46 (s, 3H), 2.24 – 2.18 (m, 4H), 2.13 – 2.10 (m, 3H), 2.03 – 2.00 (m, 6H), 1.71 – 1.66 (m, 1H), 1.62 – 1.58 (m, 6H), 1.57 – 1.50 (m, 1H), 0.84 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.4, 167.0, 148.9, 144.7, 140.9, 133.9, 126.6, 125.8, 124.3, 122.9, 119.9, 109.8, 81.8, 53.6, 41.0, 36.0, 32.4, 30.7, 30.0, 26.7, 26.2, 21.4, 8.5.

HRMS (ESI-MS) m/z [M+Na]$^{+}$ calcd for $C_{29}H_{35}NNaO_3S$: 500.2230, found: 500.2220.

FT-IR (film): 2960, 2909, 2855, 1727, 1561, 1448, 1220, 1036, 751 cm^{-1}.

$[\alpha]^{20}_{D}$ = –1.0 (c 0.6 $CHCl_3$); 80% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-6-chloro-2-ethylhexanoate (11). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl 5-chloropentanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 62.2 mg, 73% 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 (*R,S*)-**L1**: 4.7 min (minor), 5.0 min (major).

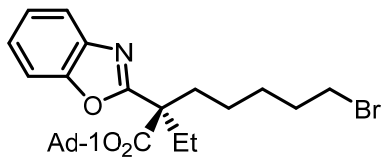
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.71 (m, 1H), 7.53 – 7.48 (m, 1H), 7.34 – 7.30 (m, 2H), 3.55 – 3.52 (m, 2H), 2.24 – 2.15 (m, 4H), 2.13 – 2.11 (m, 3H), 2.06 – 2.02 (m, 6H), 1.84 – 1.78 (m, 2H), 1.63 – 1.59 (m, 6H), 1.51 – 1.45 (m, 1H), 1.33 – 1.28 (m, 1H), 0.87 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.4, 166.9, 150.7, 140.8, 124.8, 124.1, 120.0, 110.5, 82.0, 53.7, 44.5, 41.1, 36.0, 32.7, 32.3, 30.8, 26.7, 21.3, 8.5.

HRMS (ESI-MS) m/z [M+H]$^{+}$ calcd for $C_{25}H_{33}ClNO_3$: 430.2143, found: 430.2137.

FT-IR (film): 2959, 2914, 2845, 1729, 1530, 1450, 1277, 1229, 1046, 745 cm^{-1}.

$[\alpha]^{20}_{D}$ = –0.7 (c 0.5, $CHCl_3$); 90% ee, from (*R,S*)-**L1**.



Aadamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-7-bromo-2-ethylheptanoate (12). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl 6-bromohexanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 67.7 mg, 70% 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 (*R,S*)-**L1**: 4.7 min (minor), 5.5 min (major).

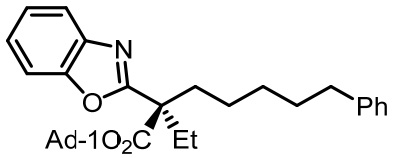
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.69 (m, 1H), 7.55 – 7.48 (m, 1H), 7.34 – 7.28 (m, 2H), 3.37 (t, *J* = 6.8 Hz, 2H), 2.22 – 2.18 (m, 2H), 2.17 – 2.11 (m, 5H), 2.05 – 2.01 (m, 6H), 1.88 – 1.83 (m, 2H), 1.63 – 1.59 (m, 6H), 1.50 – 1.44 (m, 2H), 1.35 – 1.30 (m, 1H), 1.21 – 1.14 (m, 1H), 0.87 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.5, 167.0, 150.7, 140.8, 124.7, 124.1, 120.0, 110.5, 81.9, 53.8, 41.1, 36.0, 33.7, 33.0, 32.4, 30.8, 28.3, 26.8, 23.1, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{26}H_{35}BrNO_3$: 488.1795, found: 488.1790.

FT-IR (film): 2910, 2859, 1726, 1550 1446, 1267, 1218, 1049 cm^{-1}.

$[\alpha]^{20}_D$ = –0.9 (c 0.5, $CHCl_3$); 86% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyl-7-phenylheptanoate (13). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl 6-phenylhexanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 69.7 mg, 72% yield, 86% 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 using (*R,S*)-**L1**: 6.6 min (minor), 9.7 min (major).

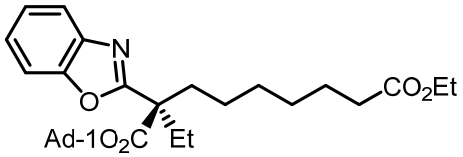
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 – 7.71 (m, 1H), 7.52 – 7.48 (m, 1H), 7.34 – 7.30 (m, 2H), 7.26 – 7.24 (m, 2H), 7.18 – 7.12 (m, 3H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.23 – 2.13 (m, 5H), 2.12 – 2.10 (m, 3H), 2.05 – 2.00 (m, 6H), 1.62 – 1.60 (m, 6H), 1.41 – 1.25 (m, 4H), 1.20 – 1.13 (m, 1H), 0.87 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 167.2, 150.6, 142.5, 140.7, 128.3, 128.2, 125.5, 124.7, 124.0, 119.9, 110.4, 81.7, 53.8, 41.1, 36.0, 35.8, 33.0, 31.1, 30.7, 29.4, 26.6, 23.7, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{32}H_{40}NO_3$: 486.3003, found: 486.2997.

FT-IR (film): 2973, 2928, 2852, 1729, 1560, 1456, 1256, 1147, 750 cm^{-1}.

$[\alpha]^{20}_D$ = +5.2 (c 0.5, $CHCl_3$); 86% ee, from (*R,S*)-**L1**.



1-(Adamantan-1-yl) 9-ethyl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethylnonanedioate (14). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1-(1,3-dioxoisoindolin-2-yl) 8-ethyl octanedioate. The product was purified by column chromatography on silica gel (1:10 EtOAc/hexanes). Colorless oil, 74.0 mg, 75% 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 (*R,S*)-**L1**: 10.4 min (minor), 11.8 min (major).

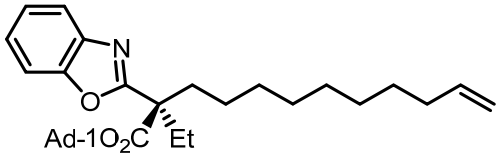
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.69 (m, 1H), 7.52 – 7.48 (m, 1H), 7.32 – 7.28 (m, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.25 (t, *J* = 7.5 Hz, 2H), 2.22 – 2.16 (m, 2H), 2.15 – 2.09 (m, 5H), 2.03 – 2.00 (m, 6H), 1.61 – 1.55 (m, 8H), 1.34 – 1.26 (m, 5H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.16 – 1.09 (m, 1H), 0.85 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.7, 170.5, 167.2, 150.6, 140.8, 124.6, 124.0, 119.9, 110.4, 81.7, 60.1, 53.8, 41.1, 36.0, 34.2, 33.0, 30.7, 29.5, 28.9, 26.6, 24.8, 23.7, 14.2, 8.5.

HRMS (ESI-MS) m/z [M+H]$^{+}$ calcd for $C_{30}H_{42}NO_5$: 496.3057, found: 496.3054.

FT-IR (film): 2966, 2907, 2868, 1733, 1720, 1564, 1450, 1264, 1211, 1046, 733 cm^{-1}.

$[\alpha]^{20}_{D}$ = –1.0 (c 1.0, $CHCl_3$); 86% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyldodec-11-enoate (15). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl undec-10-enoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 70.3 mg, 74% yield, 86% 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 using (*R,S*)-**L1**: 5.2 min (minor), 7.2 min (major).

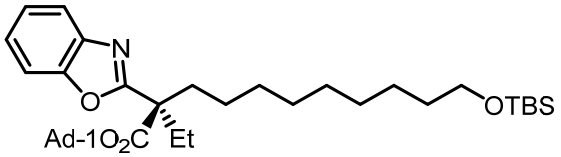
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.71 (m, 1H), 7.53 – 7.49 (m, 1H), 7.34 – 7.29 (m, 2H), 5.79 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.00 – 4.89 (m, 2H), 2.23 – 2.19 (m, 2H), 2.16 – 2.11 (m, 5H), 2.04 – 1.99 (m, 8H), 1.63 – 1.59 (m, 6H), 1.36 – 1.31 (m, 3H), 1.29 – 1.23 (m, 8H), 1.15 – 1.09 (m, 1H), 0.86 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 167.3, 150.7, 140.8, 139.2, 124.6, 124.0, 119.9, 114.1, 110.4, 81.7, 53.8, 41.1, 36.0, 33.8, 33.0, 30.7, 29.8, 29.3, 29.2, 29.0, 28.9, 26.6, 23.8, 8.5.

HRMS (ESI-MS) m/z [M+H]$^{+}$ calcd for $C_{31}H_{44}NO_3$: 478.3316, found: 478.3315.

FT-IR (film): 3011, 2917, 2852, 1729, 1639, 1567, 1450, 1226, 1218, 1049, 756 cm^{-1}.

$[\alpha]^{20}_D$ = +1.6 (c 1.0, $CHCl_3$); 86% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-11-((*tert*-butyldimethylsilyl)oxy)-2-ethylundecanoate (16). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl 10-((*tert*-butyldimethylsilyl)oxy)decanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 85.3 mg, 72% yield, 86% 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 using (*R,S*)-**L1**: 4.8 min (minor), 6.0 min (major).

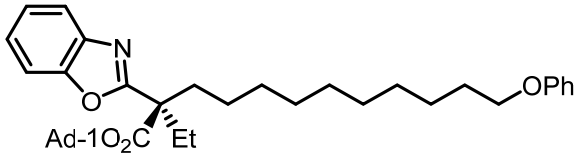
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.70 (m, 1H), 7.53 – 7.49 (m, 1H), 7.33 – 7.29 (m, 2H), 3.58 (t, *J* = 6.6 Hz, 2H), 2.23 – 2.18 (m, 2H), 2.15 – 2.10 (m, 5H), 2.05 – 2.01 (m, 6H), 1.62 – 1.59 (m, 6H), 1.50 – 1.46 (m, 2H), 1.35 – 1.18 (m, 15H), 0.88 (s, 9H), 0.04 (s, 6H) .

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 167.3, 150.7, 140.8, 124.6, 124.0, 120.0, 110.4, 81.7, 63.3, 53.8, 41.1, 36.1, 33.0, 32.9, 30.8, 29.8, 29.5, 29.4, 29.3, 26.6, 26.0, 25.8, 23.8, 18.4, 8.5, -5.3.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{36}H_{58}NO_4Si$: 596.4130, found: 596.4123.

FT-IR (film): 2952, 2922, 2859, 1726, 1453, 1239, 1087, 836, 748 cm^{-1}.

$[\alpha]^{20}_D$ = –0.7 (c 0.8, $CHCl_3$); 86% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyl-12-phenoxydodecanoate (17). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl 11-phenoxyundecanoate. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). White solid, 84.3 mg, 74% yield, 87% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 13.4 min (major), 15.3 min (minor).

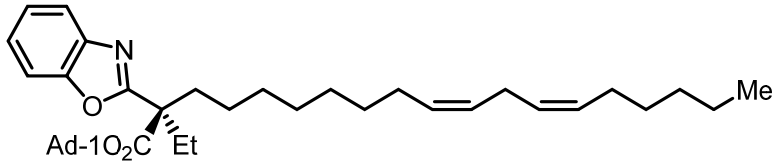
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.69 (m, 1H), 7.51 – 7.46 (m, 1H), 7.31 – 7.28 (m, 2H), 7.26 – 7.23 (m, 2H), 6.91 – 6.86 (m, 3H), 3.91 (t, *J* = 6.6 Hz, 2H), 2.22 – 2.17 (m, 2H), 2.14 – 2.09 (m, 5H), 2.03 – 2.00 (m, 6H), 1.76 – 1.72 (m, 2H), 1.61 – 1.57 (m, 6H), 1.43 – 1.38 (m, 2H), 1.30 – 1.23 (m, 11H), 1.14 – 1.06 (m, 1H), 0.85 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 167.3, 159.1, 150.7, 140.8, 129.4, 124.6, 124.0, 120.4, 120.0, 114.4, 110.4, 81.7, 67.8, 53.8, 41.1, 36.0, 33.0, 30.7, 29.8, 29.5, 29.44, 29.36, 29.28, 29.25, 26.6, 26.0, 23.8, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{37}H_{50}NO_4$: 572.3734, found: 572.3738.

FT-IR (film): 2922, 2850, 1726, 1550, 1453, 1260, 1222, 1049, 745 cm^{-1}.

$[\alpha]^{20}_D$ = +1.2 (c 0.6, $CHCl_3$); 87% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R,10Z,13Z*)-2-(benzo[*d*]oxazol-2-yl)-2-ethylnonadeca-10,13-dienoate (18). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate 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, 82.3 mg, 72% yield, 87% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 5.8 min (major), 6.2 min (minor).

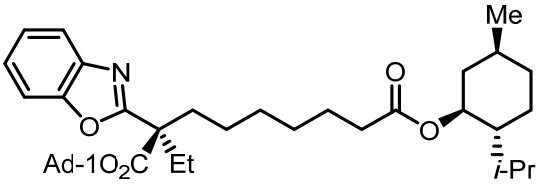
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.72 (m, 1H), 7.52 – 7.49 (m, 1H), 7.32 – 7.30 (m, 2H), 5.39 – 5.29 (m, 4H), 2.75 (t, *J* = 6.9 Hz, 2H), 2.22 – 2.19 (m, 2H), 2.15 – 2.10 (m, 5H), 2.04 – 2.02 (m, 8H), 1.62 – 1.60 (m, 6H), 1.34 – 1.25 (m, 17H), 1.16 – 1.11 (m, 1H), 0.89 – 0.85 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 167.3, 150.6, 140.8, 130.2, 130.0, 128.0, 127.9, 124.7, 124.0, 119.9, 110.4, 81.7, 53.8, 41.1, 36.0, 33.0, 31.5, 30.7, 29.8, 29.6, 29.3, 29.22, 29.18, 27.18, 27.16, 26.6, 25.6, 23.8, 22.5, 14.0, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{38}H_{56}NO_3$: 574.4255, found: 574.4237.

FT-IR (film): 3011, 2910, 2852, 1729, 1640, 1550, 1453, 1264, 1218, 756 cm^{-1}.

$[\alpha]^{20}_D$ = +1.9 (c 0.6, $CHCl_3$); 87% ee, from (*R,S*)-**L1**.



1-(Adamantan-1-yl) 9-((*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl) (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethylnonanedioate (19). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate 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 (1:15 EtOAc/hexanes). Colorless oil, 88.5 mg, 73% yield, 92.5:7.5 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALPAK IC-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 10.9 min (minor), 13.4 min (major).

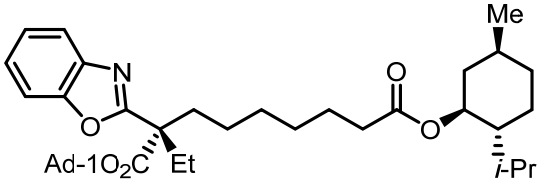
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.71 (m, 1H), 7.53 – 7.48 (m, 1H), 7.33 – 7.29 (m, 2H), 4.65 (td, *J* = 10.9, 4.4 Hz, 1H), 2.26 – 2.17 (m, 4H), 2.15 – 2.10 (m, 5H), 2.04 – 2.01 (m, 6H), 1.98 – 1.93 (m, 1H), 1.86 – 1.80 (m, 1H), 1.68 – 1.63 (m, 2H), 1.62 – 1.55 (m, 8H), 1.49 – 1.43 (m, 1H), 1.36 – 1.27 (m, 6H), 1.16 – 1.09 (m, 1H), 1.07 – 1.00 (m, 1H), 0.96 – 0.92 (m, 1H), 0.90 – 0.84 (m, 10H), 0.73 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.3, 170.6, 167.2, 150.6, 140.8, 124.7, 124.0, 120.0, 110.4, 81.7, 73.9, 53.8, 47.0, 41.1, 40.9, 36.0, 34.6, 34.2, 33.0, 31.3, 30.7, 29.5, 28.9, 26.6, 26.2, 25.0, 23.8, 23.4, 22.0, 20.7, 16.2, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{38}H_{56}NO_5$: 606.4153, found: 606.4148.

FT-IR (film): 2952, 2914, 2852, 1729, 1567, 1461, 1271, 1053, 753 cm^{-1}.

$[\alpha]^{20}_D$ = –10.1 (c 0.5, $CHCl_3$); 92.5:7.5 dr, from (*R,S*)-**L1**.



1-(Adamantan-1-yl) 9-((*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl) (*S*)-2-(benzo[*d*]oxazol-2-yl)-2-ethylnonanedioate (20). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate 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 (1:15 EtOAc/hexanes). Colorless oil, 89.1 mg, 74% yield, 7.5:92.5 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALPAK IC-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S,R*)-**L1**: 10.6 min (major), 13.5 min (minor).

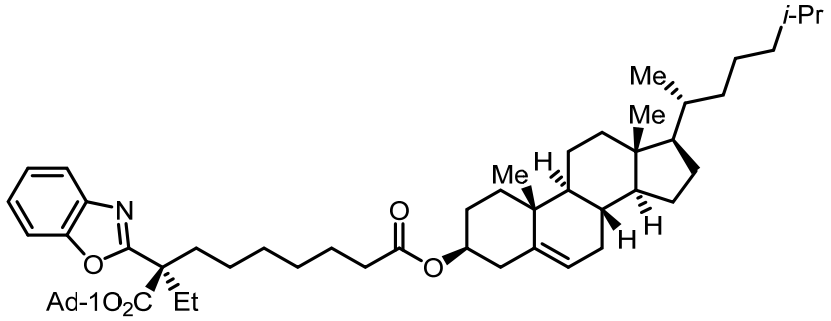
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.70 (m, 1H), 7.52 – 7.48 (m, 1H), 7.33 – 7.29 (m, 2H), 4.65 (td, *J* = 10.9, 4.4 Hz, 1H), 2.26 – 2.18 (m, 4H), 2.15 – 2.10 (m, 5H), 2.04 – 2.00 (m, 6H), 1.97 – 1.93 (m, 1H), 1.87 – 1.81 (m, 1H), 1.69 – 1.62 (m, 3H), 1.61 – 1.57 (m, 7H), 1.50 – 1.44 (m, 1H), 1.37 – 1.28 (m, 6H), 1.17 – 1.10 (m, 1H), 1.06 – 1.00 (m, 1H), 0.97 – 0.90 (m, 2H), 0.89 – 0.85 (m, 9H), 0.73 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.3, 170.6, 167.2, 150.6, 140.8, 124.7, 124.0, 119.9, 110.4, 81.7, 73.9, 53.8, 47.0, 41.1, 40.9, 36.0, 34.6, 34.2, 33.0, 31.3, 30.7, 29.5, 28.9, 26.6, 26.2, 25.0, 23.8, 23.4, 22.0, 20.7, 16.2, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{38}H_{56}NO_5$: 606.4153, found: 606.4145.

FT-IR (film): 2950, 2914, 2850, 1729, 1570, 1461, 1271, 1053, 753 cm^{-1}.

$[\alpha]^{20}_D$ = –17.3 (c 1.0, $CHCl_3$); 7.5:92.5 dr, from (*S,R*)-**L1**.



1-(Adamantan-1-yl) 9-((*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) (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethylnonanedioate (21). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate 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 (1:15 EtOAc/hexanes). White solid, 121.3 mg, 73% yield, 92.5:7.5 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALCEL OD-3 column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 8.0 min (major), 9.1 min (minor).

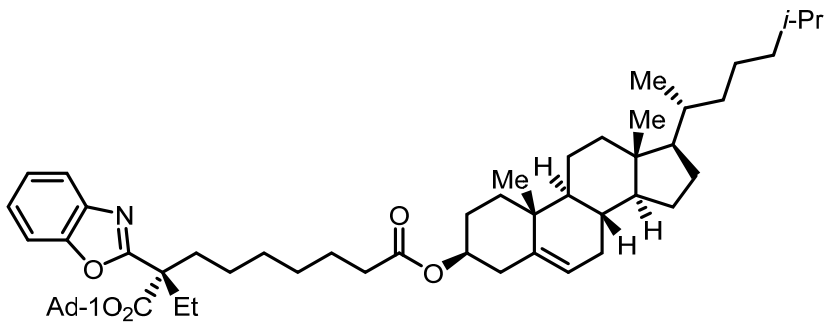
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.69 (m, 1H), 7.52 – 7.47 (m, 1H), 7.33 – 7.28 (m, 2H), 5.35 (d, *J* = 5.7 Hz, 1H), 4.65 – 4.53 (m, 1H), 2.31 – 2.28 (m, 2H), 2.25 – 2.18 (m, 4H), 2.14 – 2.10 (m, 5H), 2.03 – 2.01 (m, 6H), 1.99 – 1.92 (m, 2H), 1.87 – 1.78 (m, 4H), 1.62 – 1.59 (m, 6H), 1.57 – 1.43 (m, 8H), 1.36 – 1.28 (m, 8H), 1.16 – 1.06 (m, 8H), 1.03 – 0.98 (m, 5H), 0.98 – 0.89 (m, 6H), 0.87 – 0.84 (m, 8H), 0.66 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.1, 170.5, 167.2, 150.6, 140.8, 139.6, 124.6, 124.0, 122.5, 119.9, 110.4, 81.7, 73.6, 56.6, 56.1, 53.8, 50.0, 42.3, 41.1, 39.7, 39.5, 38.1, 36.9, 36.5, 36.1, 36.0, 35.7, 34.6, 33.0, 31.84, 31.80, 30.7, 29.5, 28.8, 28.2, 28.0, 27.8, 26.6, 24.9, 24.2, 23.8, 23.7, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{55}H_{82}NO_5$: 836.6188, found: 836.6188.

FT-IR (film): 2955, 2925, 2852, 1726, 1560, 1453, 1216, 1053, 748 cm^{-1}.

$[\alpha]^{20}_D$ = –23.7 (c 1.0, $CHCl_3$); 92.5:7.5 dr, from (*R,S*)-**L1**.



1-(Adamantan-1-yl) 9-((*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) (*S*)-2-(benzo[*d*]oxazol-2-yl)-2-ethylnonanedioate (22). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate 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 (1:15 EtOAc/hexanes). White solid, 121.7 mg, 73% yield, 7.5:92.5 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALCEL OD-3 column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S,R*)-**L1**: 8.0 min (minor), 9.1 min (major).

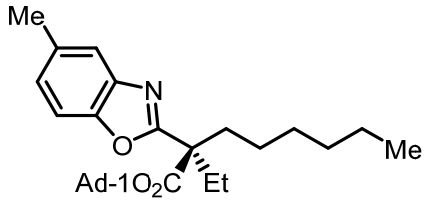
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 – 7.70 (m, 1H), 7.52 – 7.48 (m, 1H), 7.33 – 7.29 (m, 2H), 5.38 – 5.34 (m, 1H), 4.59 (tdd, *J* = 11.0, 6.8, 4.3 Hz, 1H), 2.31 – 2.27 (m, 2H), 2.25 – 2.18 (m, 4H), 2.15 – 2.10 (m, 5H), 2.03 – 2.01 (m, 6H), 2.01 – 1.91 (m, 2H), 1.85 – 1.81 (m, 3H), 1.62 – 1.60 (m, 6H), 1.58 – 1.43 (m, 8H), 1.40 – 1.21 (m, 10H), 1.17 – 1.04 (m, 8H), 1.02 – 0.93 (m, 6H), 0.92 – 0.90 (m, 3H), 0.88 – 0.84 (m, 9H), 0.67 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.1, 170.5, 167.2, 150.6, 140.8, 139.6, 124.7, 124.0, 122.5, 119.9, 110.4, 81.7, 73.7, 56.6, 56.1, 53.8, 50.0, 42.3, 41.1, 39.7, 39.5, 38.1, 36.9, 36.5, 36.1, 36.0, 35.8, 34.6, 33.0, 31.9, 31.8, 30.7, 29.5, 28.8, 28.2, 28.0, 27.8, 26.6, 24.9, 24.2, 23.8, 23.7, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{55}H_{82}NO_5$: 836.6188, found: 836.6188.

FT-IR (film): 2956, 2925, 2850, 1726, 1556, 1453, 1216, 1053, 750 cm^{-1}.

$[\alpha]^{20}_D$ = –31.1 (c 1.0, $CHCl_3$); 7.5:92.5 dr, from (*S,R*)-**L1**.



Adamantan-1-yl (*R*)-2-ethyl-2-(5-methylbenzo[*d*]oxazol-2-yl)octanoate (23). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(5-methylbenzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 70.0 mg, 80% yield, 85% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 5.7 min (major), 7.0 min (minor).

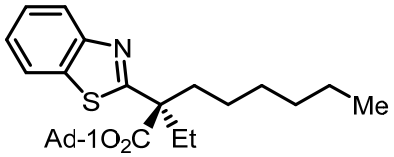
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 2.45 (s, 3H), 2.22 – 2.16 (m, 2H), 2.15 – 2.09 (m, 5H), 2.04 – 2.00 (m, 6H), 1.62 – 1.58 (m, 6H), 1.32 – 1.24 (m, 7H), 1.15 – 1.08 (m, 1H), 0.85 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.7, 167.4, 148.9, 141.0, 133.8, 125.7, 119.9, 109.8, 81.6, 53.8, 41.1, 36.0, 32.9, 31.5, 30.7, 29.5, 26.5, 23.8, 22.5, 21.4, 14.0, 8.5.

HRMS (ESI-MS) m/z $[M+K]^+$ calcd for $C_{28}H_{39}KNO_3$: 476.2562, found: 476.2565.

FT-IR (film): 2969, 2909, 2853, 1728, 1561, 1448, 1259, 1036, 754 cm^{-1}.

$[\alpha]^{20}_D$ = +7.6 (c 0.5, $CHCl_3$); 85% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*S*)-2-(benzo[*d*]thiazol-2-yl)-2-ethyloctanoate (24). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-(benzo[*d*]thiazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil, 27.6 mg, 32% yield, 82% 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 (*R,S*)-**L1**: 5.9 min (major), 6.4 min (minor).

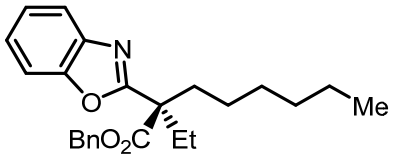
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.37 – 7.35 (m, 1H), 2.36 – 2.18 (m, 4H), 2.18 – 2.16 (m, 3H), 2.14 – 2.10 (m, 6H), 1.69 – 1.62 (m, 6H), 1.29 – 1.22 (m, 6H), 1.19 – 1.10 (m, 2H), 0.88 – 0.76 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.4, 172.3, 152.4, 135.4, 125.6, 124.6, 122.8, 121.3, 81.7, 57.9, 41.1, 37.6, 36.1, 31.5, 31.1, 30.8, 29.5, 24.4, 22.5, 14.0, 9.0.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{27}H_{38}NO_2S$: 440.2618, found: 440.2618.

FT-IR (film): 2966, 2912, 2853, 1726, 1560, 1450, 1266, 1050, 752 cm^{-1}.

$[\alpha]^{20}_D$ = +3.8 (c 0.4, $CHCl_3$); 82% ee, from (*R,S*)-**L1**.



Benzyl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyloctanoate (25). The title compound was synthesized according to **GP-3** from benzyl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 56.6 mg, 75% yield, 82% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 10.9 min (minor), 11.4 min (major).

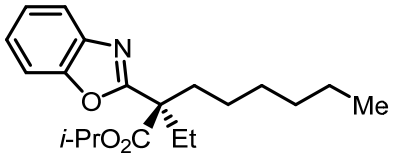
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 – 7.72 (m, 1H), 7.51 – 7.46 (m, 1H), 7.35 – 7.31 (m, 2H), 7.29 – 7.26 (m, 3H), 7.26 – 7.21 (m, 2H), 5.21 – 5.13 (m, 2H), 2.28 (q, *J* = 7.5 Hz, 2H), 2.25 – 2.18 (m, 2H), 1.28 – 1.16 (m, 7H), 1.14 – 1.08 (m, 1H), 0.86 – 0.81 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.8, 166.6, 150.7, 140.7, 135.6, 128.4, 128.1, 128.0, 124.9, 124.2, 120.1, 110.5, 66.9, 53.3, 33.0, 31.5, 29.4, 26.6, 23.8, 22.5, 14.0, 8.4.

HRMS (ESI-MS) m/z $[M+K]^+$ calcd for $C_{24}H_{29}KNO_3$: 418.1779, found: 418.1773.

FT-IR (film): 2962, 2933, 2850, 1740, 1550, 1461, 1222, 1077, 1018, 798, 750 cm^{-1}.

$[\alpha]^{20}_D$ = –1.2 (c 0.5, $CHCl_3$); 82% ee, from (*R,S*)-**L1**.



Isopropyl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyloctanoate (26). The title compound was synthesized according to **GP-3** from isopropyl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 50.1 mg, 76% yield, 80% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 7.6 min (major), 10.1 min (minor).

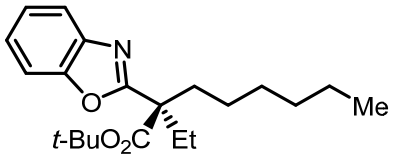
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.71 (m, 1H), 7.51 – 7.47 (m, 1H), 7.33 – 7.28 (m, 2H), 5.12 – 5.04 (m, 1H), 2.26 – 2.16 (m, 4H), 1.33 – 1.23 (m, 7H), 1.17 – 1.08 (m, 7H), 0.87 – 0.83 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.4, 166.9, 150.7, 140.8, 124.8, 124.1, 120.0, 110.4, 68.8, 53.2, 33.0, 31.5, 29.4, 26.6, 23.8, 22.5, 21.5, 14.0, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{20}H_{30}NO_3$: 332.2220, found: 332.2225.

FT-IR (film): 2939, 1731, 1271, 1243, 1168, 1139, 751 cm^{-1}.

$[\alpha]^{20}_D$ = +4.2(c 0.4, $CHCl_3$); 80% ee, from (*R,S*)-**L1**.



***tert*-Butyl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyloctanoate (27).** The title compound was synthesized according to **GP-3** from *tert*-butyl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 56.5 mg, 82% yield, 87% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.9 min (major), 5.3 min (minor).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.69 (m, 1H), 7.53 – 7.46 (m, 1H), 7.34 – 7.29 (m, 2H), 2.23 – 2.19 (qd, *J* = 7.6, 1.9 Hz, 2H), 2.17 – 2.12 (m, 2H), 1.38 (s, 9H), 1.33 – 1.29 (m, 2H), 1.28 – 1.23 (m, 5H), 1.15 – 1.09 (m, 1H), 0.87 – 0.83 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.0, 167.2, 150.6, 140.8, 124.7, 124.0, 120.0, 110.4, 81.6, 53.7, 32.9, 31.5, 29.5, 27.8, 26.5, 23.8, 22.5, 14.0, 8.5.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{21}H_{32}NO_3$: 346.2377, found: 346.2367.

FT-IR (film): 2952, 2914, 2852, 1729, 1567, 1461, 1271, 1060, 750 cm^{-1}.

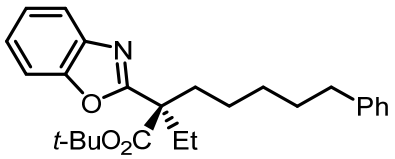
$[\alpha]^{20}_D$ = +1.9 (c 0.8, $CHCl_3$); 87% ee, from (*R,S*)-**L1**.

Gram-scale reaction:

Preparation of the Lewis acid catalyst solution: In a nitrogen-filled glovebox, an oven-dried 50 mL vial was charged with $Ni(acac)_2$ (62.5 mg, 0.250 mmol, 5.0 mol%), (*R,S*)-**L1** (70.0 mg, 0.30 mmol, 6.0 mol%), and a stir bar. Anhydrous EA (25.0 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 30 min, leading to a light blue solution.

Cross-coupling: In a nitrogen-filled glovebox, an oven-dried 150 mL round-bottom flask was charged with Fe(OEP)Cl (32.5 mg, 0.050 mmol, 1.0 mol%), $(Ir(dMeppy)_2(dtbpy))PF_6$ (97.5 mg, 0.10 mmol, 2.0 mol%), 1,3-dioxoisoindolin-2-yl heptanoate (3.44 g, 12.5 mmol, 2.5 equiv), *tert*-butyl 2-(benzo[*d*]oxazol-2-yl)butanoate (1.31 g, 5.0 mmol, 1.0 equiv), and a stir bar. The Lewis acid catalyst solution (25.0 mL) and anhydrous EA (50.0 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 120 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.

(*R,S*)-**L1**: 1.36 g, 79% yield, 86% ee.



***tert*-Butyl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyl-7-phenylheptanoate (28).** The title compound was synthesized according to **GP-4** from *tert*-butyl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl 6-phenylhexanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 55.4 mg, 68% yield, 85% 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 using (*R,S*)-**L1**: 9.5 min (minor), 11.1 min (major).

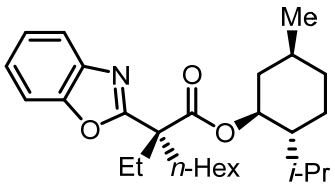
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.72 (m, 1H), 7.52 – 7.48 (m, 1H), 7.33 – 7.30 (m, 2H), 7.26 – 7.23 (m, 2H), 7.17 – 7.12 (m, 3H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.24 – 2.22 (m, 2H), 2.18 – 2.13 (m, 2H), 1.64 – 1.59 (m, 2H), 1.39 (s, 9H), 1.37 – 1.26 (m, 3H), 1.20 – 1.13 (m, 1H), 0.87 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.9, 167.2, 150.6, 142.5, 140.8, 128.4, 128.2, 125.6, 124.7, 124.1, 120.0, 110.4, 81.7, 53.7, 35.8, 32.9, 31.1, 29.4, 27.8, 26.5, 23.7, 8.5.

HRMS (ESI-MS) m/z $[M+Na]^+$ calcd for $C_{26}H_{33}NNaO_3$: 430.2353, found: 430.2356.

FT-IR (film): 2973, 2928, 2851, 1728, 1560, 1456, 1255, 1147, 748 cm^{-1}.

$[\alpha]^{20}_D$ = +1.2 (c 1.0, $CHCl_3$); 85% ee, from (*R,S*)-**L1**.



(*1S,2R,5S*)-2-Isopropyl-5-methylcyclohexyl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyloctanoate (29). The title compound was synthesized according to **GP-5** from (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 51.2 mg, 60% yield, 3:97 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALPAK IC-3 column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.4 min (minor), 4.7 min (major).

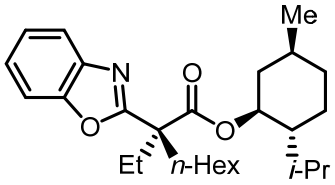
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 – 7.69 (m, 1H), 7.50 – 7.42 (m, 1H), 7.37 – 7.29 (m, 2H), 4.67 (td, *J* = 10.9, 4.3 Hz, 1H), 2.31 – 2.15 (m, 4H), 2.02 – 1.97 (m, 1H), 1.63 – 1.54 (m, 3H), 1.49 – 1.44 (m, 1H), 1.33 – 1.19 (m, 9H), 1.12 – 1.07 (m, 1H), 0.99 – 0.95 (m, 1H), 0.89 – 0.83 (m, 9H), 0.79 – 0.75 (m, 1H), 0.69 – 0.61 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.4, 167.0, 150.6, 140.7, 124.8, 124.1, 120.0, 110.3, 75.5, 53.2, 46.6, 40.3, 34.1, 32.6, 31.6, 31.3, 29.5, 26.0, 25.5, 23.8, 22.8, 22.6, 21.9, 20.6, 15.6, 14.0, 8.4.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{27}H_{42}NO_3$: 428.3159, found: 428.3150.

FT-IR (film): 2952, 2922, 2859, 1733, 1556, 1453, 1243, 808, 756 cm^{-1}.

$[\alpha]^{20}_D$ = –24.6 (c 0.8, $CHCl_3$); 3:97 dr, from (*R,S*)-**L1**.



(*1S,2R,5S*)-2-Isopropyl-5-methylcyclohexyl (*S*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyloctanoate (30). The title compound was synthesized according to **GP-5** from (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 2-(benzo[*d*]oxazol-2-yl)butanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 42.6 mg, 50% yield, 82:18 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALPAK IC-3 column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S,R*)-**L1**: 4.4 min (major), 4.7 min (minor).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.70 (m, 1H), 7.49 – 7.45 (m, 1H), 7.34 – 7.30 (m, 2H), 4.69 – 4.64 (m, 1H), 2.29 – 2.16 (m, 4H), 2.03 – 1.99 (m, 1H), 1.67 – 1.54 (m, 4H), 1.51 – 1.45

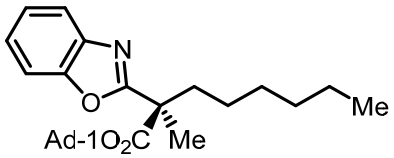
(m, 2H), 1.36 – 1.32 (m, 2H), 1.28 – 1.22 (m, 7H), 1.02 – 0.93 (m, 2H), 0.88 – 0.86 (m, 5H), 0.84 – 0.81 (m, 3H), 0.66 – 0.59 (m, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.5, 167.0, 150.6, 140.7, 124.8, 124.1, 120.0, 110.3, 75.5, 53.3, 46.6, 40.3, 34.1, 32.5, 31.5, 31.3, 29.4, 26.1, 25.5, 23.7, 22.8, 22.5, 22.0, 20.6, 15.6, 14.0, 8.3.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{27}H_{42}NO_3$: 428.3159, found: 428.3156.

FT-IR (film): 2950, 2918, 2860, 1732, 1555, 1455, 1240, 808, 755 cm^{-1}.

$[\alpha]^{20}_D$ = –20.8 (c 0.8, $CHCl_3$); 82:18 dr, from (*S*,*R*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-methyloctanoate (31). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)propanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). White solid, 66.2 mg, 81% yield, 80% 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 using (*R*,*S*)-**L1**: 4.8 min (minor), 6.0 min (major).

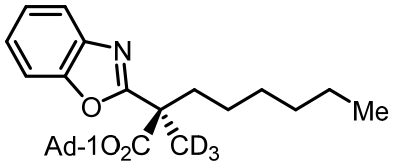
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.70 (m, 1H), 7.52 – 7.49 (m, 1H), 7.33 – 7.29 (m, 2H), 2.15 – 2.10 (m, 5H), 2.04 – 2.00 (m, 6H), 1.67 (s, 3H), 1.62 – 1.59 (m, 6H), 1.36 – 1.30 (m, 3H), 1.28 – 1.19 (m, 5H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.3, 167.9, 150.8, 140.9, 124.7, 124.0, 119.9, 110.4, 81.8, 49.7, 41.0, 36.7, 36.0, 31.5, 30.7, 29.5, 24.2, 22.5, 21.1, 14.0.

HRMS (ESI-MS) m/z $[2M+Na]^+$ calcd for $C_{52}H_{70}N_2NaO_6$: 841.5126, found: 841.5124.

FT-IR (film): 2952, 2922, 2859, 1726, 1560, 1453, 1243, 1040, 754 cm^{-1}.

$[\alpha]^{20}_D$ = +6.5 (c 0.5, $CHCl_3$); 80% ee, from (*R*,*S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-(methyl-*d*$_3$)octanoate (32). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)propanoate-3,3,3-*d*$_3$ and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). White solid, 63.3 mg, 77% yield, 80% 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 (*R*,*S*)-**L1**: 5.1 min (minor), 6.0 min (major).

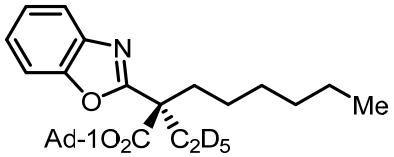
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.71 (m, 1H), 7.53 – 7.49 (m, 1H), 7.34 – 7.28 (m, 2H), 2.15 – 2.09 (m, 5H), 2.05 – 1.99 (m, 6H), 1.64 – 1.59 (m, 6H), 1.34 – 1.29 (m, 3H), 1.28 – 1.19 (m, 5H), 0.86 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.3, 167.9, 150.8, 140.8, 124.7, 124.1, 119.9, 110.5, 81.8, 49.5, 41.0, 36.7, 36.0, 31.5, 30.8, 29.5, 24.2, 22.6, 14.0.

HRMS (ESI-MS) m/z [M+H]$^+$ calcd for $C_{26}H_{33}D_3NO_3$: 413.2878, found: 413.2882.

FT-IR (film): 2938, 2907, 2849, 1726, 1536, 1271, 1180, 1039, 748 cm^{-1}.

$[\alpha]^{20}_D$ = +3.5 (c 0.5, $CHCl_3$); 80% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-(ethyl-*d*$_5$)octanoate (33). The title compound was synthesized according to **GP-3** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate-3,3,4,4,4-*d*$_5$ and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 67.2 mg, 79% yield, 85% 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 using (*R,S*)-**L1**: 4.8 min (minor), 6.4 min (major).

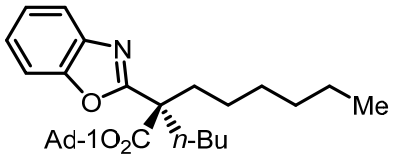
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.70 (m, 1H), 7.53 – 7.47 (m, 1H), 7.33 – 7.27 (m, 2H), 2.15 – 2.10 (m, 5H), 2.06 – 2.00 (m, 6H), 1.63 – 1.57 (m, 6H), 1.33 – 1.24 (m, 7H), 1.16 – 1.09 (m, 1H), 0.86 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 167.3, 150.6, 140.8, 124.6, 124.0, 119.9, 110.4, 81.7, 53.6, 41.1, 36.0, 33.0, 31.5, 30.7, 29.5, 23.8, 22.5, 14.0.

HRMS (ESI-MS) m/z [M+H]$^+$ calcd for $C_{27}H_{33}D_5NO_3$: 429.3160, found: 429.3150.

FT-IR (film): 2952, 2910, 2852, 1719, 1567, 1446, 1281, 1167, 1053, 753 cm^{-1}.

$[\alpha]^{20}_D$ = +1.5 (c 0.5, $CHCl_3$); 85% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-butyloctanoate (34). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)hexanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 58.3 mg, 65% yield, 85% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IG-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 6.0 min (minor), 6.5 min (major).

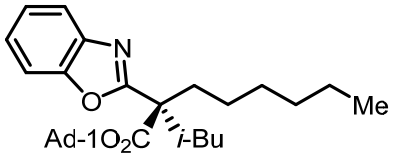
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 – 7.64 (m, 1H), 7.46 – 7.41 (m, 1H), 7.25 – 7.22 (m, 2H), 2.09 – 2.03 (m, 7H), 1.96 – 1.94 (m, 6H), 1.55 – 1.52 (m, 6H), 1.27 – 1.18 (m, 10H), 1.07 – 1.01 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.7, 167.5, 150.6, 140.8, 124.6, 124.0, 119.9, 110.4, 81.6, 53.4, 41.1, 36.0, 33.4, 33.1, 31.5, 30.7, 29.5, 26.1, 23.8, 22.9, 22.5, 14.0, 13.9.

HRMS (ESI-MS) m/z [M+Na]$^{+}$ calcd for $C_{29}H_{41}NNaO_3$: 474.2979, found: 474.2970.

FT-IR (film): 2952, 2917, 2856, 1726, 1564, 1450, 1271, 1205, 1046, 750 cm^{-1}.

$[\alpha]^{20}_{D}$ = –0.7 (c 0.6, $CHCl_3$); 85% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*S*)-2-(benzo[*d*]oxazol-2-yl)-2-isobutyloctanoate (35). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)-4-methylpentanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 56.7 mg, 63% yield, 83% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 3.9 min (major), 4.6 min (minor).

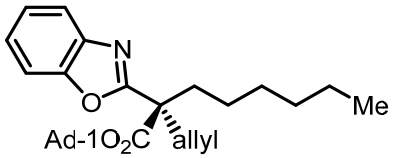
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.71 (m, 1H), 7.53 – 7.48 (m, 1H), 7.32 – 7.28 (m, 2H), 2.21 – 2.10 (m, 7H), 2.03 – 1.99 (m, 6H), 1.68 – 1.64 (m, 1H), 1.61 – 1.57 (m, 6H), 1.32 – 1.24 (m, 7H), 1.16 – 1.11 (m, 1H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H), 0.72 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.8, 167.7, 150.5, 140.8, 124.7, 124.0, 120.0, 110.4, 81.8, 52.9, 41.8, 41.0, 36.0, 33.8, 31.5, 30.7, 29.5, 24.2, 24.1, 24.0, 23.4, 22.6, 14.0.

HRMS (ESI-MS) m/z [M+H]$^{+}$ calcd for $C_{29}H_{42}NO_3$: 452.3159, found: 452.3166.

FT-IR (film): 2952, 2917, 2856, 1726, 1564, 1449, 1271, 1205, 1044, 750 cm^{-1}.

$[\alpha]^{20}_{D}$ = –0.5 (c 0.6, $CHCl_3$); 83% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*S*)-2-allyl-2-(benzo[*d*]oxazol-2-yl)octanoate (36). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)pent-4-enoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 59.7 mg, 69% yield, 86% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 4.5 min (major), 5.7 min (minor).

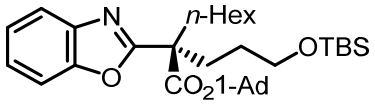
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.71 (m, 1H), 7.53 – 7.49 (m, 1H), 7.34 – 7.30 (m, 2H), 5.66 (ddt, *J* = 17.3, 10.2, 7.3 Hz, 1H), 5.12 – 5.03 (m, 2H), 2.93 (d, *J* = 7.2 Hz, 2H), 2.16 – 2.11 (m, 5H), 2.04 – 2.01 (m, 6H), 1.61 (t, *J* = 3.2 Hz, 6H), 1.33 – 1.24 (m, 7H), 1.19 – 1.14 (m, 1H), 0.85 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.1, 166.8, 150.7, 140.8, 132.5, 124.7, 124.1, 120.0, 118.9, 110.5, 82.0, 53.2, 41.1, 38.0, 36.0, 33.3, 31.5, 30.8, 29.4, 23.7, 22.5, 14.0.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{28}H_{38}NO_3$: 436.2846, found: 436.2845.

FT-IR (film): 2945, 2914, 2849, 1729, 1650, 1560, 1453, 1271, 1205, 1046, 890, 750 cm^{-1}.

$[\alpha]^{20}_D$ = +13.8 (c 0.5, $CHCl_3$); 86% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*S*)-2-(benzo[*d*]oxazol-2-yl)-2-(3-((*tert*-butyldimethylsilyl)oxy)propyl)octanoate (37). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)-5-((*tert*-butyldimethylsilyl)oxy)pentanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 69.5 mg, 62% yield, 86% 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 using (*R,S*)-**L1**: 5.0 min (minor), 5.5 min (major).

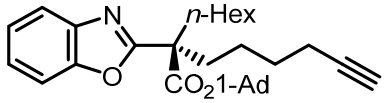
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.70 (m, 1H), 7.52 – 7.47 (m, 1H), 7.33 – 7.29 (m, 2H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.22 – 2.10 (m, 8H), 2.05 – 2.01 (m, 6H), 1.63 – 1.60 (m, 6H), 1.55 – 1.49 (m, 1H), 1.36 – 1.23 (m, 10H), 1.19 – 1.12 (m, 1H), 0.87 (s, 9H), 0.02 (s, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 167.3, 150.7, 140.9, 124.7, 124.0, 120.0, 110.5, 81.8, 63.0, 53.1, 41.1, 36.1, 33.5, 31.5, 30.8, 29.9, 29.5, 27.5, 25.9, 23.8, 22.6, 18.3, 14.0, -5.3.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{34}H_{54}NO_4Si$: 568.3817, found: 568.3818.

FT-IR (film): 2948, 2910, 2852, 1726, 1456, 1260, 1198, 1091, 836, 755 cm^{-1}.

$[\alpha]^{20}_D$ = +1.5 (c 0.5, $CHCl_3$); 86% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*S*)-2-(benzo[*d*]oxazol-2-yl)-2-hexyloct-7-ynoate (38). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)oct-7-ynoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 58.5 mg, 62% yield, 85% 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 (*R,S*)-**L1**: 6.1 min (minor), 6.7 min (major).

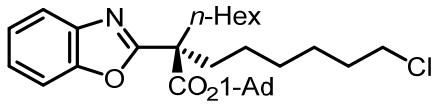
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.69 (m, 1H), 7.53 – 7.49 (m, 1H), 7.34 – 7.28 (m, 2H), 2.21 – 2.11 (m, 9H), 2.05 – 2.01 (m, 6H), 1.87 (t, *J* = 2.7 Hz, 1H), 1.63 – 1.59 (m, 6H), 1.58 – 1.53 (m, 2H), 1.45 – 1.40 (m, 1H), 1.31 – 1.24 (m, 8H), 1.14 – 1.08 (m, 1H), 0.85 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.5, 167.2, 150.6, 140.8, 124.7, 124.1, 120.0, 110.5, 84.1, 81.8, 68.4, 53.3, 41.1, 36.0, 33.4, 32.8, 31.5, 30.7, 29.5, 28.5, 23.8, 23.0, 22.5, 18.1, 14.0.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{31}H_{42}NO_3$: 476.3159, found: 476.3157.

FT-IR (film): 2948, 2914, 2849, 2176, 1729, 1560, 1456, 1267, 1171, 1045, 760 cm^{-1}.

$[\alpha]^{20}_D$ = +5.2 (c 0.6, $CHCl_3$); 85% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*S*)-2-(benzo[*d*]oxazol-2-yl)-8-chloro-2-hexyloctanoate (39). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)-8-chlorooctanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 66.5 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 (*R,S*)-**L1**: 5.2 min (minor), 6.4 min (major).

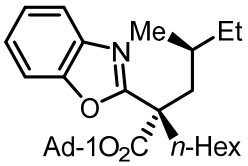
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.71 (m, 1H), 7.53 – 7.49 (m, 1H), 7.34 – 7.30 (m, 2H), 3.50 (t, *J* = 6.7 Hz, 2H), 2.16 – 2.11 (m, 6H), 2.05 – 2.01 (m, 6H), 1.75 – 1.70 (m, 2H), 1.63 – 1.59 (m, 6H), 1.44 – 1.40 (m, 2H), 1.35 – 1.25 (m, 11H), 1.17 – 1.09 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 167.3, 150.6, 140.7, 124.7, 124.1, 120.0, 110.5, 81.8, 53.4, 45.0, 41.1, 36.0, 33.5, 33.4, 32.5, 31.5, 30.7, 29.5, 29.1, 26.6, 23.9, 23.8, 22.6, 14.0.

HRMS (ESI-MS) m/z $[M+Na]^+$ calcd for $C_{31}H_{44}ClNNaO_3$: 536.2902, found: 536.2892.

FT-IR (film): 2950, 2914, 2859, 1730, 1560, 1456, 1271, 1180, 1053, 749 cm^{-1}.

$[\alpha]^{20}_D$ = +0.4 (c 0.4, $CHCl_3$); 82% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*S*)-2-(benzo[*d*]oxazol-2-yl)-2-((*S*)-2-methylbutyl)octanoate (40). The title compound was synthesized according to **GP-5** from adamantan-1-yl (*4S*)-2-(benzo[*d*]oxazol-2-yl)-4-methylhexanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 55.6 mg, 60% yield, 90:10 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALPAK AD-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 5.5 min (major), 6.5 min (minor).

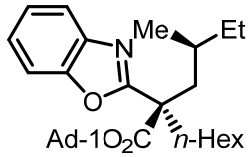
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.71 (m, 1H), 7.52 – 7.48 (m, 1H), 7.33 – 7.28 (m, 2H), 2.29 – 2.25 (m, 1H), 2.23 – 2.12 (m, 2H), 2.12 – 2.09 (m, 3H), 2.05 – 1.99 (m, 7H), 1.62 – 1.58 (m, 6H), 1.44 – 1.40 (m, 1H), 1.31 – 1.22 (m, 8H), 1.13 – 1.02 (m, 2H), 0.86 – 0.84 (m, 6H), 0.77 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.9, 167.7, 150.5, 140.8, 124.7, 124.0, 120.0, 110.4, 81.8, 53.0, 41.1, 39.9, 36.0, 33.9, 31.5, 30.7, 30.5, 30.4, 29.5, 24.0, 22.5, 20.3, 14.0, 11.2.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{30}H_{44}NO_3$: 466.3316, found: 466.3310.

FT-IR (film): 2948, 2914, 2862, 1719, 1560, 1453, 1271, 1208, 1046, 750 cm^{-1}.

$[\alpha]^{20}_D$ = –1.3 (c 0.5, $CHCl_3$); 90:10 dr, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-((*S*)-2-methylbutyl)octanoate (41). The title compound was synthesized according to **GP-5** from adamantan-1-yl (*4S*)-2-(benzo[*d*]oxazol-2-yl)-4-methylhexanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 46.4 mg, 50% yield, 19:81 dr.

HPLC analysis: The dr was determined via HPLC on a CHIRALPAK AD-3 column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S,R*)-**L1**: 5.6 min (minor), 6.6 min (major).

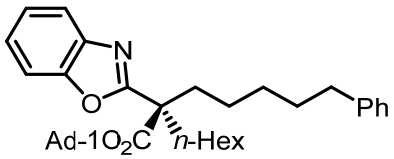
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.71 (m, 1H), 7.53 – 7.48 (m, 1H), 7.33 – 7.29 (m, 2H), 2.26 – 2.15 (m, 4H), 2.12 – 2.09 (m, 3H), 2.06 – 1.99 (m, 7H), 1.62 – 1.58 (m, 6H), 1.33 – 1.25 (m, 9H), 1.20 – 1.12 (m, 2H), 0.87 – 0.83 (m, 6H), 0.61 – 0.60 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.9, 167.8, 150.5, 140.9, 124.7, 124.0, 120.0, 110.4, 81.8, 52.9, 41.1, 39.9, 36.0, 33.6, 31.5, 30.9, 30.7, 30.3, 29.5, 24.0, 22.6, 19.8, 14.0, 11.3.

HRMS (ESI-MS) m/z $[M+MeCN+Na]^+$ calcd for $C_{32}H_{46}N_2NaO_3$: 529.3401, found: 529.3391.

FT-IR (film): 2950, 2907, 2860, 1720, 1555, 1455, 1270, 1210, 1046, 750 cm^{-1}.

$[\alpha]^{20}_D$ = +3.9 (c 0.5, $CHCl_3$); 19:81 dr, from (*S,R*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-(5-phenylpentyl)octanoate (42, *path a*). The title compound was synthesized according to **GP-4** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)octanoate and 1,3-dioxoisoindolin-2-yl 6-phenylhexanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 81.5 mg, 75% yield, 83% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 5.9 min (minor), 6.3 min (major).

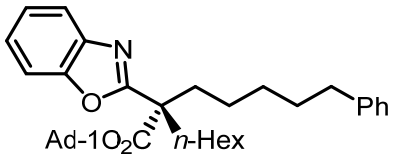
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 – 7.72 (m, 1H), 7.54 – 7.49 (m, 1H), 7.34 – 7.31 (m, 2H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.18 – 7.12 (m, 3H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.18 – 2.11 (m, 7H), 2.05 – 2.01 (m, 6H), 1.64 – 1.59 (m, 8H), 1.39 – 1.31 (m, 5H), 1.29 – 1.24 (m, 5H), 1.20 – 1.11 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 167.4, 150.6, 142.5, 140.8, 128.4, 128.2, 125.6, 124.7, 124.0, 120.0, 110.5, 81.7, 53.4, 41.1, 36.0, 35.8, 33.5, 33.4, 31.5, 31.1, 30.7, 29.5, 29.4, 23.9, 23.8, 22.6, 14.0.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{36}H_{48}NO_3$: 542.3629, found: 542.3631.

FT-IR (film): 2970, 2930, 2851, 1728, 1556, 1460, 1250, 1152, 750 cm^{-1}.

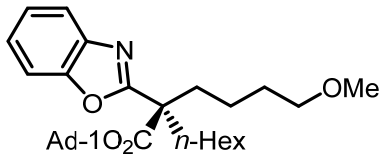
$[\alpha]^{20}_D$ = +5.3 (c 0.8, $CHCl_3$); 83% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*S*)-2-(benzo[*d*]oxazol-2-yl)-2-(5-phenylpentyl)octanoate (42, *path b*). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)-7-phenylheptanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 69.2 mg, 64% yield, -84% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC-3 column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 5.7 min (major), 6.4 min (minor).

$[\alpha]^{20}_D$ = – 7.5 (c 0.5, $CHCl_3$); -84% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-(4-methoxybutyl)octanoate (43, *path a*). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)octanoate and 1,3-dioxoisoindolin-2-yl 5-methoxypentanoate. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil, 67.3 mg, 70% 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 (*R,S*)-**L1**: 6.4 min (minor), 7.0 min (major).

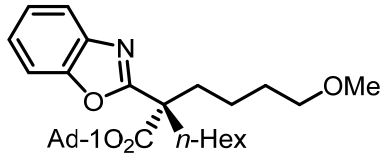
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.70 (m, 1H), 7.52 – 7.48 (m, 1H), 7.33 – 7.29 (m, 2H), 3.34 (t, *J* = 6.6 Hz, 2H), 3.28 (s, 3H), 2.18 – 2.13 (m, 4H), 2.12 – 2.10 (m, 3H), 2.04 – 1.99 (m, 6H), 1.62 – 1.57 (m, 8H), 1.32 – 1.24 (m, 8H), 1.20 – 1.10 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.5, 167.3, 150.6, 140.8, 124.7, 124.0, 120.0, 110.5, 81.8, 72.3, 58.5, 53.4, 41.1, 36.0, 33.3, 33.2, 31.5, 30.7, 29.8, 29.5, 23.8, 22.5, 20.6, 14.0.

HRMS (ESI-MS) m/z $[M+H]^+$ calcd for $C_{30}H_{44}NO_4$: 482.3265, found: 482.3268.

FT-IR (film): 2945, 2910, 2859, 1726, 1560, 1450, 1264, 1115, 1056, 753 cm^{-1}.

$[\alpha]^{20}_D$ = +2.1 (c 0.5, $CHCl_3$); 86% ee, from (*R,S*)-**L1**.



Adamantan-1-yl (*S*)-2-(benzo[*d*]oxazol-2-yl)-2-(4-methoxybutyl)octanoate (43, *path b*). The title compound was synthesized according to **GP-5** from adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)-6-methoxyhexanoate and 1,3-dioxoisoindolin-2-yl heptanoate. The product was purified by column chromatography on silica gel (1:15 EtOAc/hexanes). Colorless oil, 59.3 mg, 62% yield, -84% 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 (*R,S*)-**L1**: 6.5 min (major), 7.1 min (minor).

$[\alpha]^{20}_D$ = –2.2 (c 0.5, $CHCl_3$); -84% ee, from (*R,S*)-**L1**.

IV. Effect of Reaction Parameters

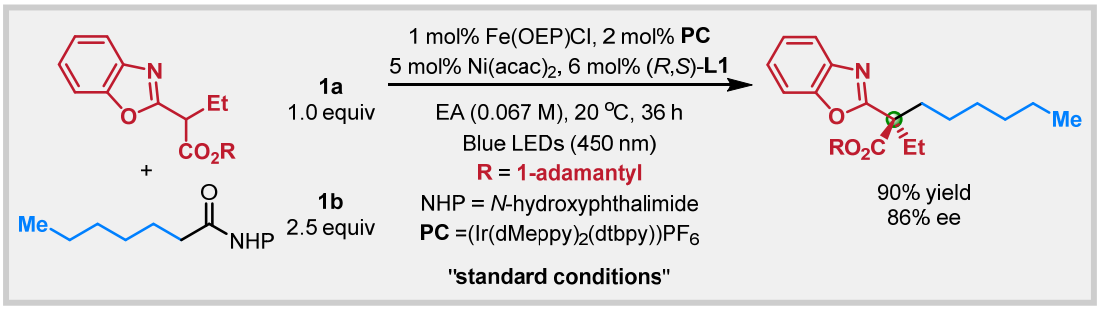
General Procedure 6 (GP-6).

Preparation of the Lewis acid catalyst solution: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with $Ni(acac)_2$ (1.3 mg, 0.005 mmol, 5.0 mol%), (*R,S*)-**L1** (1.4 mg, 0.006 mmol, 6.0 mol%), and a stir bar. Anhydrous EA (0.5 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 30 min, leading to a light blue solution.

Cross-coupling: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with Fe(OEP)Cl (0.6 mg, 0.001 mmol, 1.0 mol%), $(Ir(dMeppy)_2(dtbpy))PF_6$ (2.0 mg, 0.0020 mmol, 2.0 mol%), NHP ester (0.25 mmol, 2.5 equiv), benzoxazolyl acetate (0.10 mmol, 1.0 equiv), and a stir bar. The Lewis acid catalyst solution (0.5 mL) and anhydrous EA (1.0 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 (**Scheme 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 (26 μL, 0.10 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.

Table S1, S2 and S3: Adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate was reacted with 1,3-dioxoisoindolin-2-yl heptanoate according to **GP-6**. 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.



entry	variation from the "**standard conditions**"	yield (%)[a]	ee[b]
1	None	90	86
2	No Fe	20	20
3	No (*R*,*S*)-**L1**	53	0
4	No **PC**, Ni+(*R*,*S*)-**L1**, or light	0	–
5	Fe(TPP)Cl, instead of Fe(OEP)Cl	60	78
6	FePc, instead of Fe(OEP)Cl	22	80
7	Fe(III) Protoporphyrin IX, instead of Fe(OEP)Cl	13	20
8	Vitamin B12, instead of Fe(OEP)Cl	24	17
9	Co(Salen), instead of Fe(OEP)Cl	17	13
10	Co(TPP), instead of Fe(OEP)Cl	0	–
11	**L2**, instead of (*R*,*S*)-**L1**	86	84
12	**L3**, instead of (*R*,*S*)-**L1**	3	–
13	**L4**, instead of (*R*,*S*)-**L1**	56	0
14	**L5**, instead of (*R*,*S*)-**L1**	60	-35
15	**L6**, instead of (*R*,*S*)-**L1**	31	0
16	2.5 mol% $Ni(acac)_2$/3.0 mol % (*R*,*S*)-**L1**	90	83
17	$Ni(OTf)_2$, instead of $Ni(acac)_2$	0	–
18	0.5 mol% Fe(OEP)Cl	68	86
19	2.5 mol% Fe(OEP)Cl	72	86
20	5.0 mol% Fe(OEP)Cl	24	86
21	1.0 mol% **PC**	70	86
22	4CzIPN, instead of **PC**	0	–
23	$Ir(ppy)_2(dtbpy)PF_6$, instead of **PC**	69	86
24	18 h, instead of 36 h	72	86
25	10 °C, instead of 20 °C	73	86
26	30 °C, instead of 20 °C	76	86
27	MeCN, instead of EA	0	–
28	$PhCF_3$, instead of EA	8	78
29	1.0 mL air added	34	80
30	1.0 equiv H_2O added	78	86

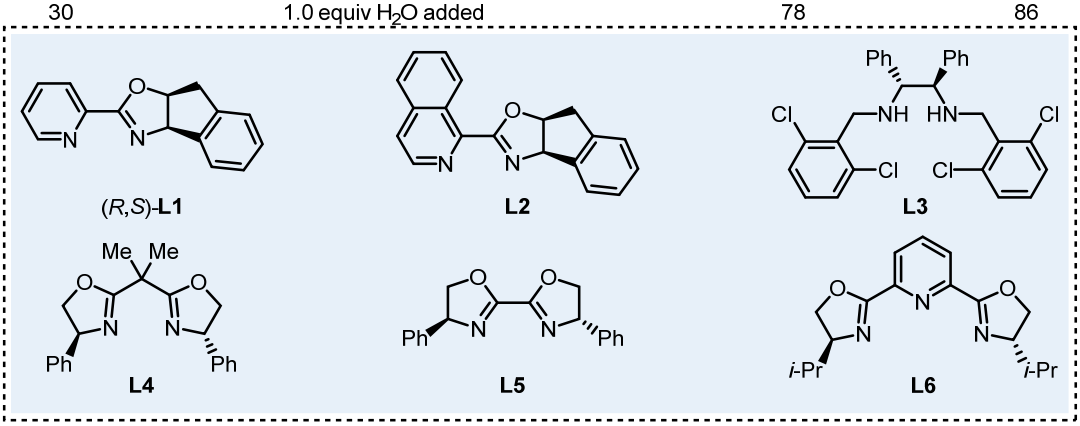
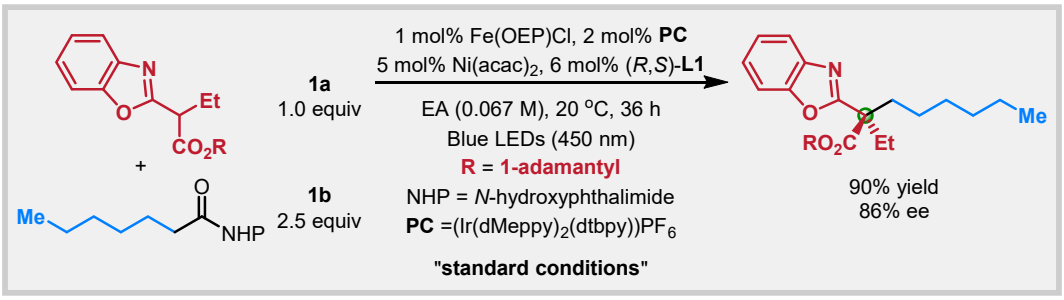
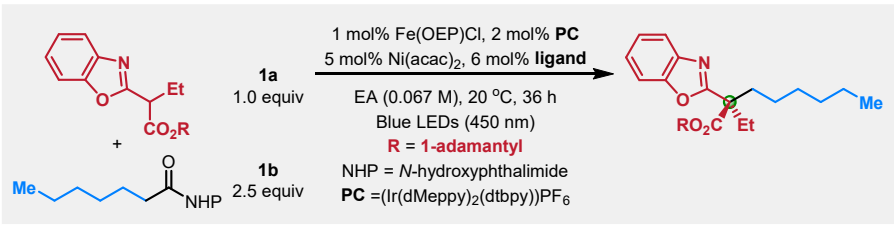


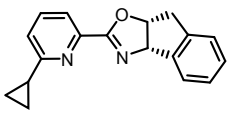
Table S1. Effect of Reaction Parameters.



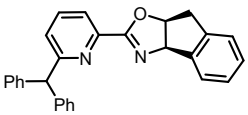
entry	variation from the "**standard conditions**"	yield (%)[a]	ee[b]
1	None	90	86
2	0 °C, instead of 20 °C	44	86
3	40 °C, instead of 20 °C	79	84
4	50 °C, instead of 20 °C	77	79
5	MeCN:EA=1:1, instead of EA	–	–
6	DCM:EA=1:1, instead of EA	–	–
7	TBME:EA=1:1, instead of EA	75	81
8	MeCN:EA=1:1, instead of EA	–	–
9	$PhCH_3$:EA=1:1, instead of EA	79	80
10	$PhCF_3$:EA=1:1, instead of EA	80	83
11	NMP:EA=1:1, instead of EA	–	–
12	MeOH:EA=1:1, instead of EA	–	–
13	DMF:EA=1:1, instead of EA	–	–
14	DMSO:EA=1:1, instead of EA	–	–
15	DME:EA=1:1, instead of EA	84	85
16	DCE:EA=1:1, instead of EA	–	–
17	CPME:EA=1:1, instead of EA	80	83
18	$CHCl_3$:EA=1:1, instead of EA	–	–
19	$Ni(TMHD)_2$, instead of $Ni(acac)_2$	87	84
20	$NiBr_2$•DME, instead of $Ni(acac)_2$	40	0
21	$NiCl_2$, instead of $Ni(acac)_2$	–	–
22	$Ni(OTf)_2$, instead of $Ni(acac)_2$	–	–
23	$Ni(OAc)_2$•$4H_2O$, instead of $Ni(acac)_2$	90	72
24	NiI_2, instead of $Ni(acac)_2$	11	0
25	$CuCl_2$, instead of $Ni(acac)_2$	–	–
26	$Cu(OTf)_2$, instead of $Ni(acac)_2$	–	–
27	$Cu(acac)_2$, instead of $Ni(acac)_2$	–	–
28	$MgCl_2$, instead of $Ni(acac)_2$	7	15
29	$Mg(OTf)_2$, instead of $Ni(acac)_2$	–	–
30	$Mg(acac)_2$•$2H_2O$, instead of $Ni(acac)_2$	–	–
31	$Yb(OTf)_3$, instead of $Ni(acac)_2$	–	–
32	$Er(acac)_3$, instead of $Ni(acac)_2$	–	–
33	$In(acac)_3$, instead of $Ni(acac)_2$	–	–
34	$Nd(acac)_3$, instead of $Ni(acac)_2$	–	–
35	$Ce(acac)_3$•$3H_2O$, instead of $Ni(acac)_2$	–	–
36	Ag(acac), instead of $Ni(acac)_2$	–	–
37	$Co(acac)_2$, instead of $Ni(acac)_2$	42	69
38	$Y(OTf)_3$, instead of $Ni(acac)_2$	–	–
39	$Sm(OTf)_3$, instead of $Ni(acac)_2$	–	–
40	$Gd(acac)_3$, instead of $Ni(acac)_2$	–	–
41	$La(acac)_3$•H_2O, instead of $Ni(acac)_2$	–	–
42	$Zn(acac)_2$, instead of $Ni(acac)_2$	12	9
43	$Lu(acac)_3$, instead of $Ni(acac)_2$	–	–
44	$Dy(acac)_3$, instead of $Ni(acac)_2$	–	–
45	$Mn(acac)_3$, instead of $Ni(acac)_2$	–	–
46	$Pr(acac)_3$, instead of $Ni(acac)_2$	–	–

Table S2. Extended table of reaction parameters (temperature, mixed solvent, and Lewis acid).

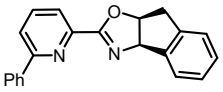




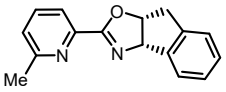
L7, 60% yield, -58% ee



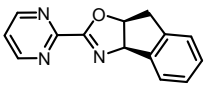
L8, 34% yield, 10% ee



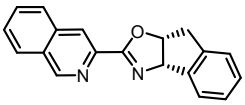
L9, 47% yield, 45% ee



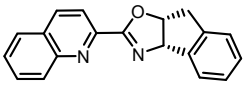
L10, 66% yield, -80% ee



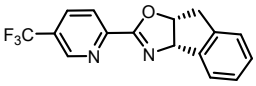
L11, 65% yield, 82% ee



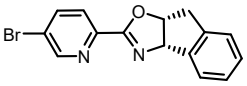
L12, 53% yield, -86% ee



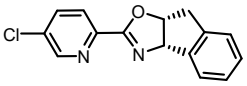
L13, 36% yield, -74% ee



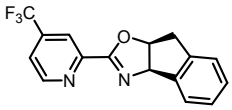
L14, 83% yield, -78% ee



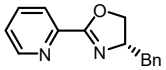
L15, 88% yield, -81% ee



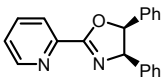
L16, 66% yield, -83% ee



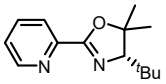
L17, 83% yield, 79% ee



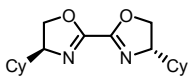
L18, 88% yield, -55% ee



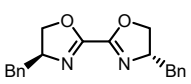
L19, 16% yield, 0% ee



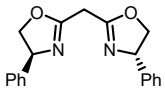
L20, 15% yield, 0% ee



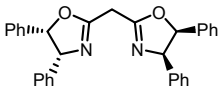
L21, 20% yield, -28% ee



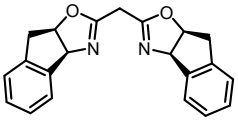
L22, 33% yield, -24% ee



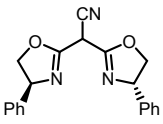
L23, 6% yield



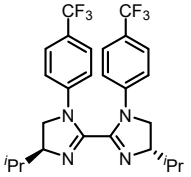
L24, <3% yield



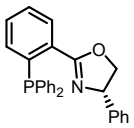
L25, 10% yield, -19% ee



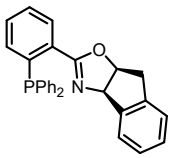
L26, <3% yield



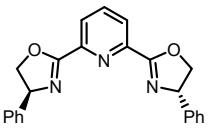
L27, 21% yield, -16% ee



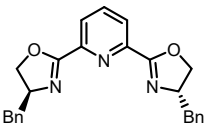
L28, 75% yield, 0% ee



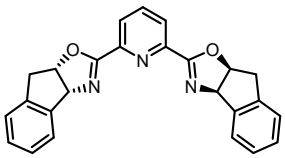
L29, 61% yield, 0% ee



L30, 20% yield, 0% ee



L31, 15% yield, 0% ee

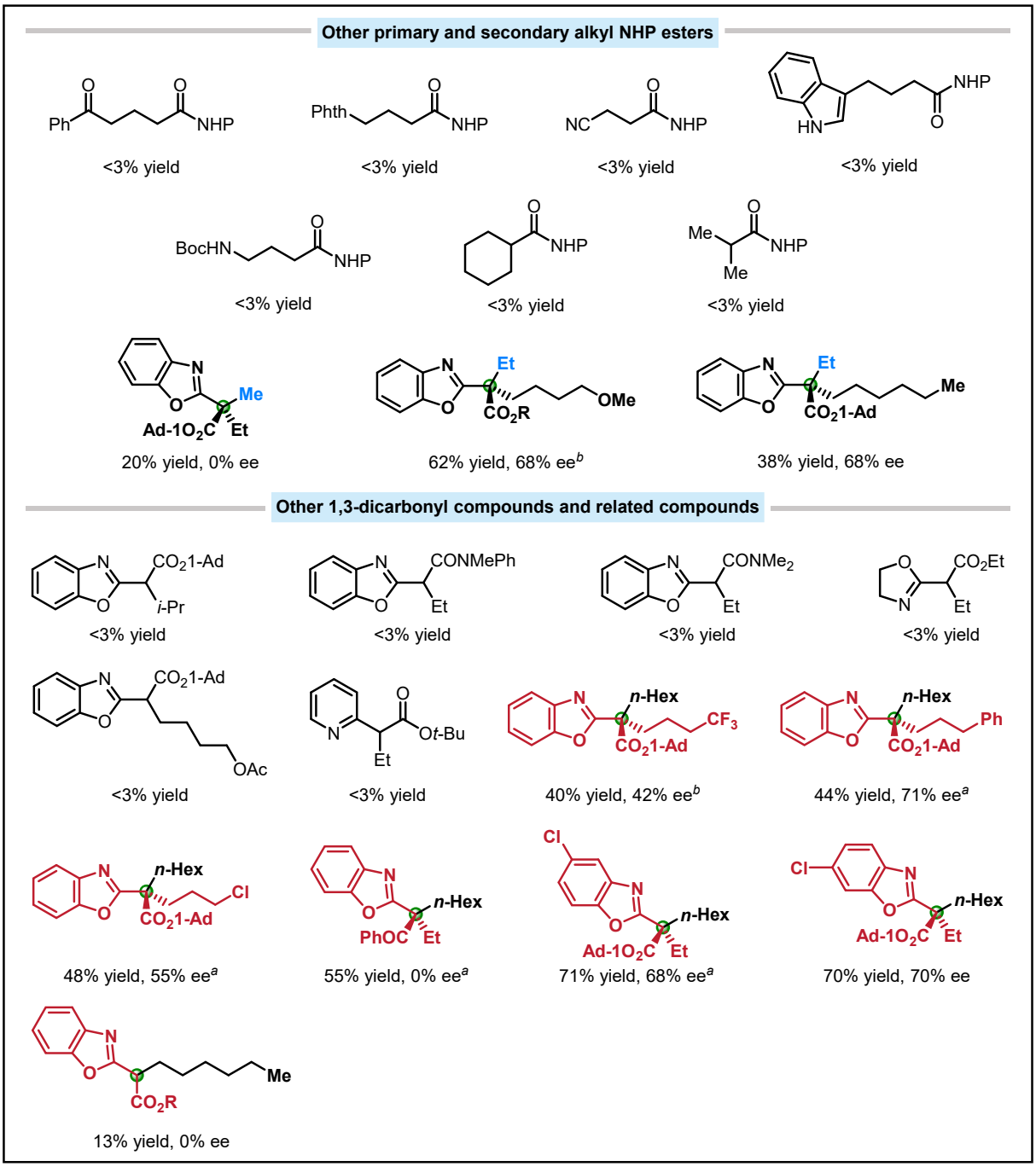


L32, <3% yield

Table S3. Extended table of reaction parameters (chial ligands).

V. Unsuccessful Examples

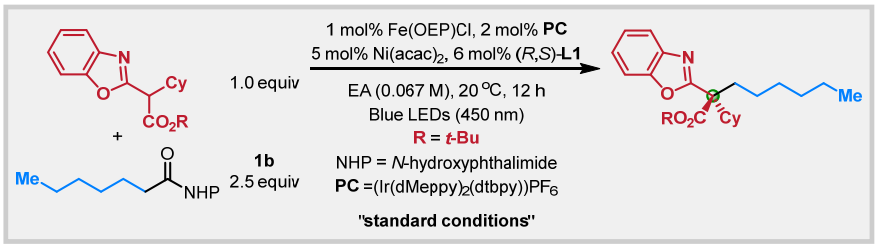
Scheme S2: The reactions were conducted according to **GP-3**. All yields are of purified products.



Scheme S2. Unsuccessful Examples. [a]The reaction was conducted for 72 hours rather than 36 hours. [b]The reaction was conducted for 96 hours rather than 36 hours.

General Procedure 7 (GP-7): Enantioselective cross-coupling of sterically hindered benzoxazolyl acetate and unactivated alkyl NHP ester (12 hours).

The reaction time was reduced from 36 to 12 hours, while following the same procedure as **GP-6**.



entry	variation from the "**standard conditions**"	yield (%)[a]	ee[b]
1	None	–	–
2	$Ni(TMHD)_2$, instead of $Ni(acac)_2$	–	–
3	$NiBr_2$•DME, instead of $Ni(acac)_2$	–	–
4	$NiCl_2$, instead of $Ni(acac)_2$	–	–
5	$Ni(OTf)_2$, instead of $Ni(acac)_2$	–	–
6	$Ni(OAc)_2$•$4H_2O$, instead of $Ni(acac)_2$	–	–
7	NiI_2, instead of $Ni(acac)_2$	–	–
8	**L2**, instead of (*R*,*S*)-**L1**	–	–
9	**L3**, instead of (*R*,*S*)-**L1**	–	–
10	**L4**, instead of (*R*,*S*)-**L1**	–	–
11	**L5**, instead of (*R*,*S*)-**L1**	–	–
12	**L6**, instead of (*R*,*S*)-**L1**	–	–
13	**L7**, instead of (*R*,*S*)-**L1**	–	–
14	**L8**, instead of (*R*,*S*)-**L1**	–	–
15	**L9**, instead of (*R*,*S*)-**L1**	–	–
16	**L10**, instead of (*R*,*S*)-**L1**	–	–
17	**L11**, instead of (*R*,*S*)-**L1**	–	–
18	**L12**, instead of (*R*,*S*)-**L1**	–	–
19	**L13**, instead of (*R*,*S*)-**L1**	–	–
20	**L14**, instead of (*R*,*S*)-**L1**	–	–
21	**L15**, instead of (*R*,*S*)-**L1**	–	–
22	**L16**, instead of (*R*,*S*)-**L1**	–	–
23	**L17**, instead of (*R*,*S*)-**L1**	–	–

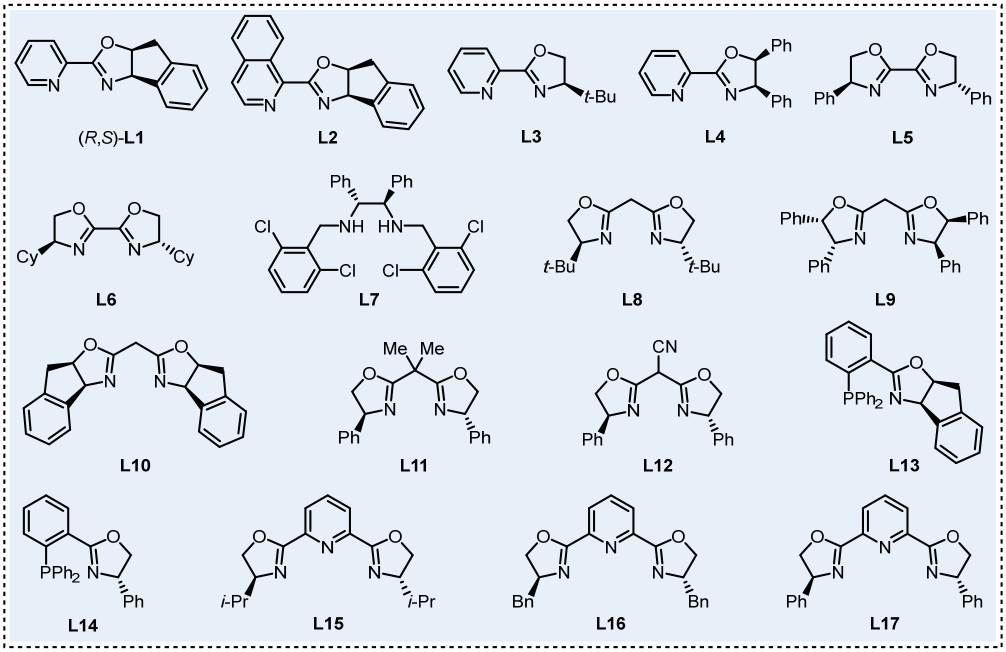
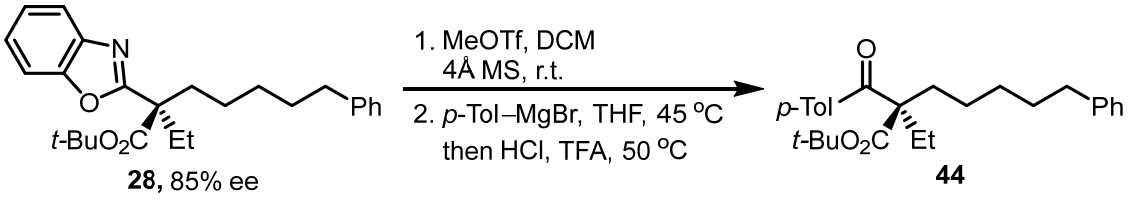


Table S4. Screenings for the coupling of Cy-substituted substrate.

VI. Applications



***tert*-Butyl (*R*)-2-ethyl-2-(4-methylbenzoyl)-7-phenylheptanoate (44).** In a nitrogen-filled glovebox, an oven-dried 10 mL vial was charged with *tert*-butyl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyl-7-phenylheptanoate (40.7 mg, 0.10 mmol, 1.0 equiv), 4Å molecular sieves (150 mg), and a stir bar. Anhydrous DCM (1 mL) was then added, and the mixture was stirred vigorously for 30 minutes at room temperature. Methyl trifluoromethanesulfonate (57 μL, 0.50 mmol, 5.0 equiv) was then added, and the vial was sealed with a PTFE septum cap. The reaction mixture was stirred at room temperature for 12 hours. After complete consumption of **28**, the mixture was concentrated to give the crude *N*-methylbenzoxazoliumsalt. The reaction vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles), followed by the addition of anhydrous THF (2 mL). The mixture was cooled to 0 °C, and a solution of *p*-TolMgBr (1.0 M in THF, 200 uL, 2.0 equiv) was added slowly. The resulting solution was stirred at 0 °C for 30 min, at which time the mixture was allowed to warm to 45 °C and stirred for 6 h. Subsequently, aqueous hydrochloric acid solution (4 mL, 1 M) and trifluoroacetic acid (74.0 μL, 1.0 mmol, 10.0 equiv) were added successively. After stirring for 3 h at 50 °C, the biphasic reaction mixture was cooled to 25 °C and extracted with EtOAc (3 x 5 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:15 EtOAc/hexanes) to afford the desired product. Colorless oil, 20.6 mg, 51% yield, 85% 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: 13.3 min (major), 14.2 min (minor).

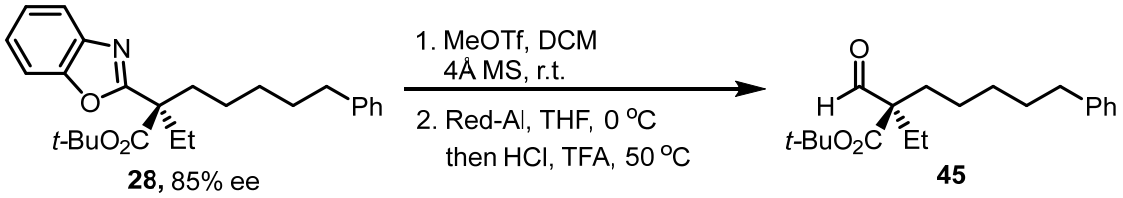
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 2H), 2.53 (t, *J* = 7.7 Hz, 2H), 2.38 (s, 3H), 2.08 – 1.96 (m, 4H), 1.61 – 1.52 (m, 3H), 1.30 (s, 9H), 1.19 – 1.15 (m, 1H), 1.05 (dt, *J* = 11.6, 4.6 Hz, 1H), 0.89 – 0.83 (m, 1H), 0.75 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 197.4, 173.0, 143.2, 142.6, 133.6, 129.0, 128.6, 128.4, 128.2, 125.6, 81.6, 61.5, 35.8, 31.5, 31.1, 29.6, 27.7, 25.2, 23.0, 21.5, 7.9.

HRMS (ESI-MS) *m*/*z* [M+K]$^{+}$ calcd for $C_{27}H_{36}KO_3$: 447.2296, found: 447.2296.

FT-IR (film): 2960, 2929, 2856, 1725, 1676, 1606, 1454, 1367, 1182, 1146, 748 cm^{-1}.

$[\alpha]^{20}_{D}$ = –5.8 (*c* 0.2, $CHCl_3$); 85% ee.



***tert*-Butyl (*R*)-2-ethyl-2-formyl-7-phenylheptanoate (45).** In a nitrogen-filled glovebox, an oven-dried 10 mL vial was charged with *tert*-butyl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyl-7-phenylheptanoate (40.7 mg, 0.10 mmol, 1.0 equiv), 4Å molecular sieves (150 mg), and a stir bar. Anhydrous DCM (1 mL) was then added, and the mixture was stirred vigorously for 30 minutes at room temperature. Methyl trifluoromethanesulfonate (57 μL, 0.5 mmol, 5.0 equiv) was then added, and the vial was sealed with a PTFE septum cap. The reaction mixture was stirred at room temperature for 12 hours. After complete consumption of **28**, the mixture was concentrated to give the crude *N*-methylbenzoxazoliumsalt. The reaction vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles), followed by the addition of anhydrous THF (2 mL). The mixture was cooled to 0 °C, and a solution of Red-Al (70% wt, 51 μL, 0.18 mmol, 1.8 equiv) was added slowly. The resulting solution was stirred at 0 °C for 30 min, at which time the mixture was allowed to warm to r.t. and stirred for 2 h. Subsequently, aqueous hydrochloric acid solution (4 mL, 1 M) and trifluoroacetic acid (74.0 μL, 1.0 mmol, 10.0 equiv) were added successively. After stirring for 3 h at 50 °C, the biphasic reaction mixture was cooled to 25 °C and extracted with EtOAc (3 x 5 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:20 EtOAc/hexanes) to afford the desired product. Colorless oil, 26.3 mg, 83% yield, 85% 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: 10.8 min (major), 12.6 min (minor).

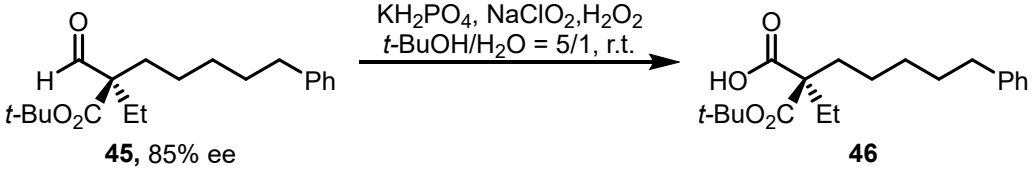
^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.74 (s, 1H), 7.23 – 7.20 (m, 2H), 7.13 – 7.08 (m, 3H), 2.53 (t, *J* = 7.7 Hz, 2H), 1.81 – 1.76 (m, 1H), 1.73 – 1.64 (m, 3H), 1.58 – 1.54 (m, 2H), 1.43 (s, 9H), 1.28 – 1.22 (m, 3H), 1.17 – 1.13 (m, 1H), 0.80 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 201.6, 171.4, 142.5, 128.4, 128.2, 125.6, 82.0, 61.7, 35.8, 32.4, 31.1, 29.7, 28.1, 25.8, 24.0, 8.7.

HRMS (ESI-MS) *m*/*z* [M+Na]$^{+}$ calcd for $C_{20}H_{30}NaO_3$: 341.2087, found: 341.2094.

FT-IR (film): 2969, 2930, 2856, 1725, 1703, 1456, 1364, 1274, 1146, 951, 754 cm^{-1}.

$[\alpha]^{20}_{D}$ = +1.1 (*c* 1.0, $CHCl_3$); 85% ee.



(*R*)-2-(*tert*-Butoxycarbonyl)-2-ethyl-7-phenylheptanoic acid (46). In a nitrogen-filled glovebox, an oven-dried 10 mL vial was charged with *tert*-butyl (*R*)-2-ethyl-2-formyl-7-phenylheptanoate (31.8 mg, 0.10 mmol, 1.0 equiv) and a stir bar. Next, *tert*-butanol:H_2O (2.5 mL: 0.5 mL), KH_2PO_4 (32.7 mg, 0.24 mmol, 2.0 equiv), hydrogen peroxide (0.1 mL, 30%), and $NaClO_2$ (43.4 mg, 0.48 mmol, 4.0 equiv) were added sequentially, and the vial was sealed with a PTFE septum cap. The reaction mixture was stirred at room temperature for 12 hours. The reaction was quenched with hydrochloric acid solution (1 mL, 1 M), 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 (1:9 MeOH/DCM) to afford the desired product. Colorless oil, 27.3 mg, 82% yield, 85% ee.

HPLC analysis: The literature indicates that ee remains constant throughout this process.[4]

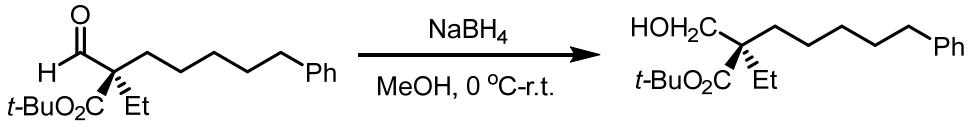
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 – 7.23 (m, 2H), 7.17 – 7.12 (m, 3H), 2.56 (t, *J* = 7.7 Hz, 2H), 2.00 – 1.91 (m, 2H), 1.84 – 1.75 (m, 2H), 1.61 – 1.56 (m, 2H), 1.48 (s, 9H), 1.33 – 1.26 (m, 3H), 1.17 – 1.11 (m, 1H), 0.83 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.2, 174.0, 142.4, 128.4, 128.2, 125.7, 84.0, 58.6, 36.7, 35.7, 31.0, 30.4, 29.2, 27.8, 25.0, 9.4.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{20}H_{30}NaO_4$: 357.2036, found: 357.2046.

FT-IR (film): 2974, 2923, 2856, 1725, 1703, 1455, 1367, 1275, 1148, 749 cm^{-1}.

$[\alpha]^{20}_D$ = +0.8 (*c* 0.3, $CHCl_3$); 85% ee.



45, 85% ee **47**

***tert*-Butyl (*R*)-2-ethyl-2-(hydroxymethyl)-7-phenylheptanoate (47).** An oven-dried 10 mL two-neck round-bottom flask was charged with a stir bar, and then sealed with two rubber septum caps. 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 *tert*-butyl (*R*)-2-ethyl-2-formyl-7-phenylheptanoate (31.8 mg, 0.10 mmol, 1.0 equiv) in MeOH (2 mL), and the flask was cooled to 0 °C using an ice bath. Sodium borohydride (5.7 mg, 0.15 mmol, 1.5 equiv) was added through the open neck under a positive pressure of nitrogen. The reaction mixture was stirred at 0 °C for 10 min, at which time the mixture was allowed to warm to r.t. and stirred for 1 h. Upon completion, aqueous saturated NH_4Cl solution (2 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 column chromatography (1:6 EtOAc/hexanes) on silica gel to give the desired product. Colorless oil, 27.2 mg, 85% 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: 5.8 min (major), 6.1 min (minor).

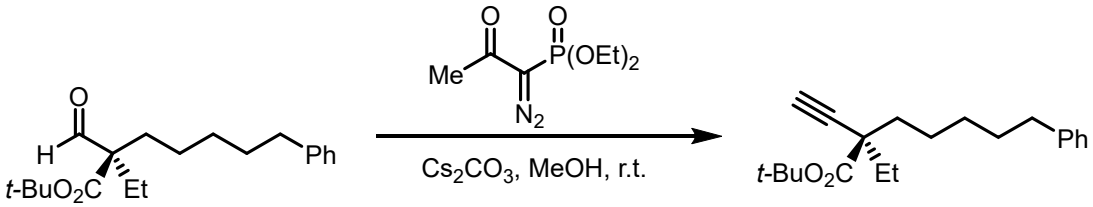
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.26 (m, 2H), 7.19 – 7.15 (m, 3H), 3.63 (s, 2H), 2.60 (t, *J* = 7.8 Hz, 2H), 2.13 (s, 1H), 1.65 – 1.60 (m, 3H), 1.58 – 1.53 (m, 2H), 1.50 – 1.47 (m, 1H), 1.46 (s, 9H), 1.34 – 1.29 (m, 3H), 1.27 – 1.24 (m, 1H), 0.86 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.3, 142.7, 128.4, 128.2, 125.6, 80.8, 64.8, 51.1, 35.9, 33.4, 31.3, 29.9, 28.1, 26.5, 24.0, 8.5.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{20}H_{32}NaO_3$: 343.2244, found: 343.2244.

FT-IR (film): 2969, 2930, 2858, 1717, 1454, 1366, 1246, 1144, 1038, 849, 746 cm^{-1}.

$[\alpha]^{20}_D$ = +1.8 (*c* 0.5, $CHCl_3$); 86% ee.



***tert*-Butyl (*R*)-2-ethyl-2-ethynyl-7-phenylheptanoate (48).** An oven-dried 10 mL vial was equipped with a magnetic stir bar, *tert*-butyl (*R*)-2-ethyl-2-formyl-7-phenylheptanoate (31.8 mg, 0.10 mmol, 1.0 equiv), Cs_2CO_3 (269.1 mg, 0.83 mmol, 8.3 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 MeOH (3 mL). Then, the Bestmann-Ohira reagent (64 mg, 0.33 mmol, 3.3 equiv) was added slowly. The reaction mixture was stirred at room temperature for 48 hours. The reaction was quenched with water (3 mL), and the aqueous phase was extracted with Et_2O (3 x 5 mL). The combined organic layers were concentrated, and the residue was purified by flash chromatography (1:20 EtOAc/hexanes) to afford the desired product. Colorless oil, 23.3 mg, 74% yield, 85% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD-3 column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained: 4.3 min (major), 4.8 min (minor).

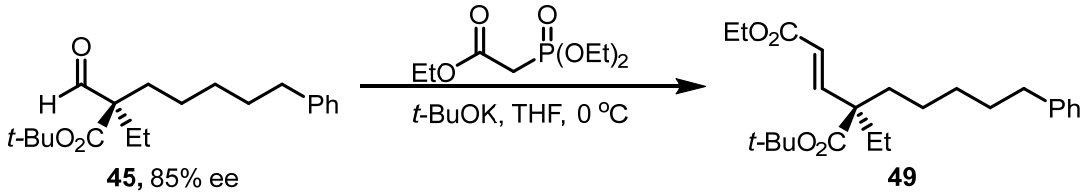
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.26 (m, 2H), 7.19 – 7.14 (m, 3H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.28 (s, 1H), 1.86 – 1.75 (m, 2H), 1.66 – 1.57 (m, 5H), 1.46 (s, 9H), 1.36 – 1.30 (m, 3H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.8, 142.7, 128.4, 128.2, 125.6, 84.4, 81.4, 71.9, 50.0, 39.0, 35.8, 32.6, 31.2, 29.3, 27.9, 25.1, 9.5.

HRMS (ESI-MS) *m*/*z* [M+Na]$^+$ calcd for $C_{21}H_{30}NaO_2$: 337.2138, found: 337.2140

FT-IR (film): 2969, 2930, 2860, 2086, 1725, 1455, 1367, 1250, 1155, 1008, 794, 748 cm^{-1}.

$[\alpha]^{20}_D$ = +0.6 (*c* 0.5, $CHCl_3$); 85% ee.



5-(*tert*-Butyl) 1-ethyl (*R*,*E*)-4-ethyl-4-(5-phenylpentyl)pent-2-enedioate (49). An oven-dried 10 mL vial was equipped with a magnetic stir bar, triethyl phosphonoacetate (26.9 mg, 0.12 mmol, 1.2 equiv), *t*-BuOK (13.5 mg, 0.12 mmol, 1.2 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 THF (2 mL). The resulting solution was stirred at 0 °C for 60 min. Then, a solution of *tert*-butyl (*R*)-2-ethyl-2-formyl-7-phenylheptanoate (31.8 mg, 0.10 mmol, 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 2 h. The reaction was quenched with water (3 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 (1:20 EtOAc/hexanes) to afford the desired product. Colorless oil, 31.6 mg, 81% 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: 4.6 min (major), 5.0 min (minor).

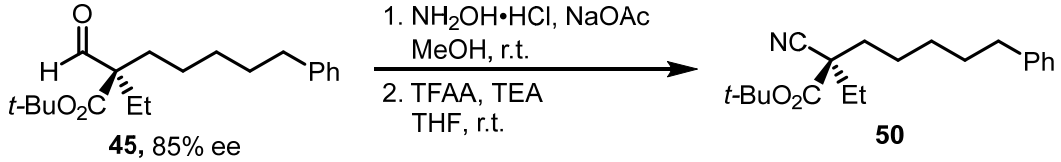
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 – 7.39 (m, 2H), 7.32 – 7.26 (m, 4H), 5.98 (d, *J* = 16.3 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.7 Hz, 2H), 1.94 – 1.79 (m, 3H), 1.76 – 1.72 (m, 3H), 1.59 (s, 9H), 1.50 – 1.39 (m, 6H), 1.39 – 1.28 (m, 1H), 0.95 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.2, 166.7, 150.2, 142.6, 128.4, 128.2, 125.6, 120.7, 81.0, 60.4, 53.1, 36.7, 35.8, 31.2, 29.9, 29.7, 28.0, 24.2, 14.2, 8.8.

HRMS (ESI-MS) *m*/*z* $[M+K]^+$ calcd for $C_{24}H_{36}KO_4$: 427.2245, found: 427.2246

FT-IR (film): 2975, 2930, 2860, 1718, 1647, 1455, 1366, 1262, 1241, 1140 1036, 749 cm^{-1}.

$[\alpha]^{20}_D$ = –0.9 (*c* 0.5, $CHCl_3$); 84% ee.



***tert*-Butyl (*R*)-2-cyano-2-ethyl-7-phenylheptanoate (50).** An oven-dried 10 mL vial was equipped with a magnetic stir bar, *tert*-butyl (*R*)-2-ethyl-2-formyl-7-phenylheptanoate (31.8 mg, 0.10 mmol, 1.0 equiv), sodium acetate (12.3 mg, 0.15 mmol, 1.5 equiv), and hydroxylamine hydrochloride (10.4 mg, 0.15 mmol, 1.5 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 mixture was stirred

at room temperature for 12 hours. The reaction was quenched with aqueous saturated $NaHCO_3$ solution, and the aqueous phase was extracted with DCM (3 x 5 mL). The combined organic layers were concentrated, and the residue was added to another oven-dried 10 mL vial, which 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 THF (2 mL), triethylamine (151.5 mg, 1.5 mmol, 10.0 equiv), and trifluoroacetic anhydride (211.5 mg, 0.75 mmol, 5.0 equiv). The reaction mixture was stirred at room temperature for 12 hours. Upon completion, aqueous saturated $NaHCO_3$ solution (2 mL) was added, and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic layers were then dried over Na_2SO_4, filtered, and concentrated, and the residue was purified by flash chromatography (1:20 EtOAc/hexanes) to afford the desired product. Colorless oil, 25.0 mg, 79% yield, 84% 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: 6.0 min (major), 8.0 min (minor).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 7.21 – 7.15 (m, 3H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.94 – 1.88 (m, 1H), 1.88 – 1.82 (m, 1H), 1.81 – 1.75 (m, 1H), 1.74 – 1.69 (m, 1H), 1.68 – 1.60 (m, 3H), 1.51 (s, 9H), 1.41 – 1.35 (m, 3H), 1.07 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.1, 142.3, 128.3, 128.2, 125.7, 119.6, 83.6, 51.4, 37.1, 35.6, 31.0, 28.8, 27.8, 25.2, 9.7.

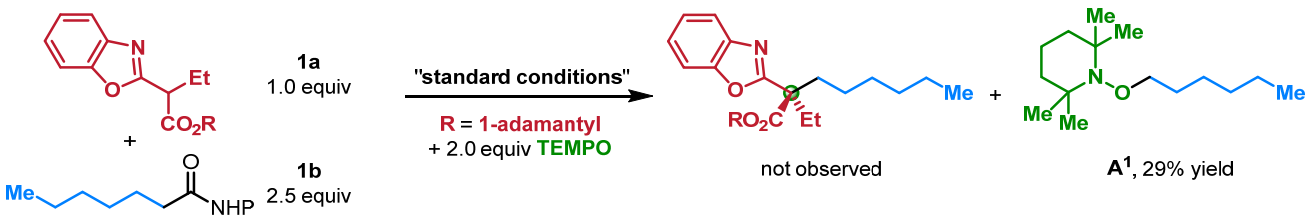
HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{20}H_{30}NO_2$: 316.2271, found: 316.2242.

FT-IR (film): 2973, 2930, 2859, 1732, 1456, 1369, 1256, 1148, 840, 749 cm^{-1}.

$[\alpha]^{20}_D$ = +2.4 (*c* 1.0, $CHCl_3$); 84% ee.

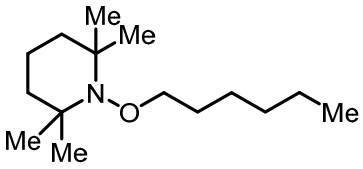
VII. Mechanistic Experiments

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 $Ni(acac)_2$ (2.5 mg, 0.010 mmol, 5.0 mol%), (*R,S*)-**L1** (2.8 mg, 0.012 mmol, 6.0 mol%), and a stir bar. Anhydrous EA (1.0 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 30 min, leading to a light blue solution. In a nitrogen-filled glovebox, another oven-dried 4 mL vial was charged with Fe(OEP)Cl (1.3 mg, 0.002 mmol, 1.0 mol%), $(Ir(dMeppy)_2(dtbpy))PF_6$ (3.9 mg, 0.0040 mmol, 2.0 mol%), 1,3-dioxoisoindolin-2-yl heptanoate (137.5 mg, 0.50 mmol, 2.5 equiv), adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate (67.8 mg, 0.20 mmol, 1.0 equiv), TEMPO (62.4 mg, 0.40 mmol, 2.0 equiv), and a stir bar. The Lewis acid catalyst solution (1.0 mL) and anhydrous EA (2.0 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 (**Scheme 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.



1-(Hexyloxy)-2,2,6,6-tetramethylpiperidine (A[1]). The product was purified by column chromatography on silica gel (1:20 EtOAc/hexanes). Colorless oil, 13.8 mg, 29% yield.

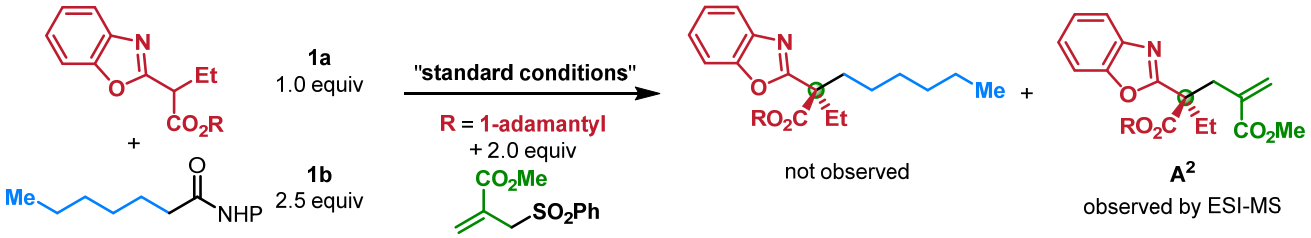
^{1}H NMR (600 MHz, Chloroform-*d*) δ 3.71 (t, *J* = 6.7 Hz, 2H), 1.53 – 1.42 (m, 6H), 1.38 – 1.24 (m, 8H), 1.18 – 1.06 (m, 12H), 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 59.6, 39.6, 33.1, 31.9, 28.7, 26.1, 22.6, 20.1, 17.2, 14.1.

HRMS (ESI-MS) *m/z* $[M+H]^+$ calcd for $C_{15}H_{32}NO$: 242.2478, found: 242.2477.

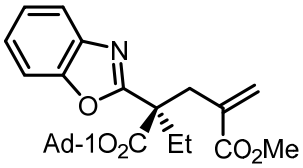
FT-IR (film): 2963, 2930, 2866, 1464, 1367, 1267, 1029, 758 cm^{-1}.

2. Radical trapping experiment using methyl 2-((phenylsulfonyl)methyl)acrylate as the trapping agent.



Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with $Ni(acac)_2$ (2.5 mg, 0.010 mmol, 5.0 mol%), (*R,S*)-**L1** (2.8 mg, 0.012 mmol, 6.0 mol%), and a stir bar. Anhydrous EA (1.0 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 30 min, leading to a light blue solution. In a nitrogen-filled glovebox, another oven-dried 4 mL vial was charged with Fe(OEP)Cl (1.3 mg, 0.002 mmol, 1.0 mol%), $(Ir(dMeppy)_2(dtbpy))PF_6$ (3.9 mg, 0.0040 mmol, 2.0 mol%), 1,3-dioxoisoindolin-2-yl heptanoate (137.5 mg, 0.50 mmol, 2.5 equiv), adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate (67.8 mg, 0.20 mmol, 1.0 equiv), methyl 2-((phenylsulfonyl)methyl)acrylate (96.0 mg, 0.40 mmol, 2.0 equiv), and a stir bar. The Lewis acid catalyst solution (1.0 mL) and anhydrous EA (2.0 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 (**Scheme S1**). The reaction was irradiated with blue LEDs (450 nm) and was stirred at 20 °C for 36 hours.

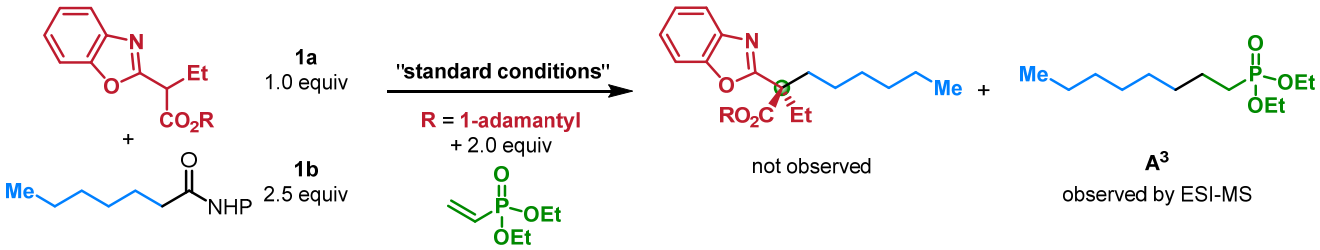
An ESI-MS analysis of the reaction was carried out, which confirmed no detection of the coupling product.



1-(Adamantan-1-yl) 5-methyl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyl-4-methylenepentanedioate (A²). The formation of **A²** was observed by ESI-MS.

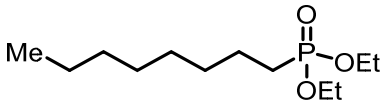
HRMS (ESI-MS) *m/z* $[M+Na]^+$ calcd for $C_{26}H_{31}NNaO_5$: 460.2094, found: 460.2094.

3. Radical trapping experiment using diethyl vinylphosphonate as the trapping agent.



Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with $Ni(acac)_2$ (2.5 mg, 0.010 mmol, 5.0 mol%), (*R*,*S*)-**L1** (2.8 mg, 0.012 mmol, 6.0 mol%), and a stir bar. Anhydrous EA (1.0 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 30 min, leading to a light blue solution. In a nitrogen-filled glovebox, another oven-dried 4 mL vial was charged with Fe(OEP)Cl (1.3 mg, 0.002 mmol, 1.0 mol%), $(Ir(dMeppy)_2(dtbpy))PF_6$ (3.9 mg, 0.0040 mmol, 2.0 mol%), 1,3-dioxoisoindolin-2-yl heptanoate (137.5 mg, 0.50 mmol, 2.5 equiv), adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate (67.8 mg, 0.20 mmol, 1.0 equiv), and a stir bar. The Lewis acid catalyst solution (1.0 mL) and anhydrous EA (2.0 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 (**Scheme 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.

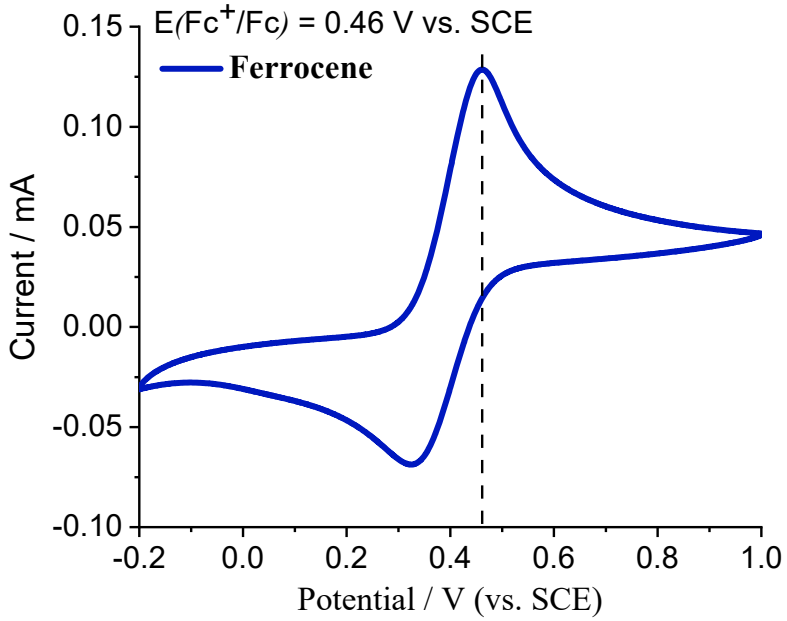


Diethyl octylphosphonate (A^3). The formation of A^3 was observed by ESI-MS.
HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{12}H_{27}NaO_3P$: 273.1590, found: 273.1595.

4. Cyclic Voltammograms Profiles.

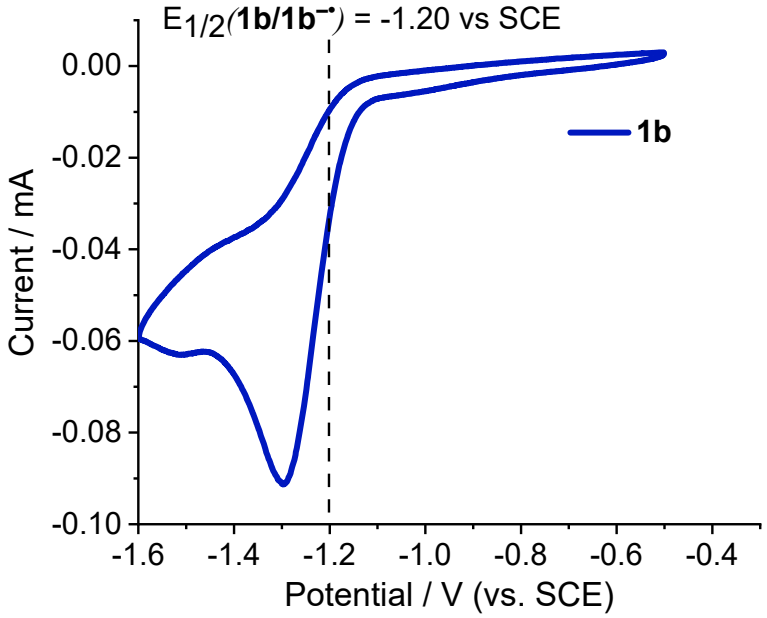
Samples were prepared by mixing 0.050 mmol of the substrate in 10 mL of 0.1 M *n*-Bu_4NPF_6 in anhydrous MeCN. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, saturated calomel electrode (SCE) reference electrode, and a scan rate of 100 mV/s. The solution was sparged with nitrogen for 3-5 minutes before data collection. $E_{1/2}$ was obtained using Origin.

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.



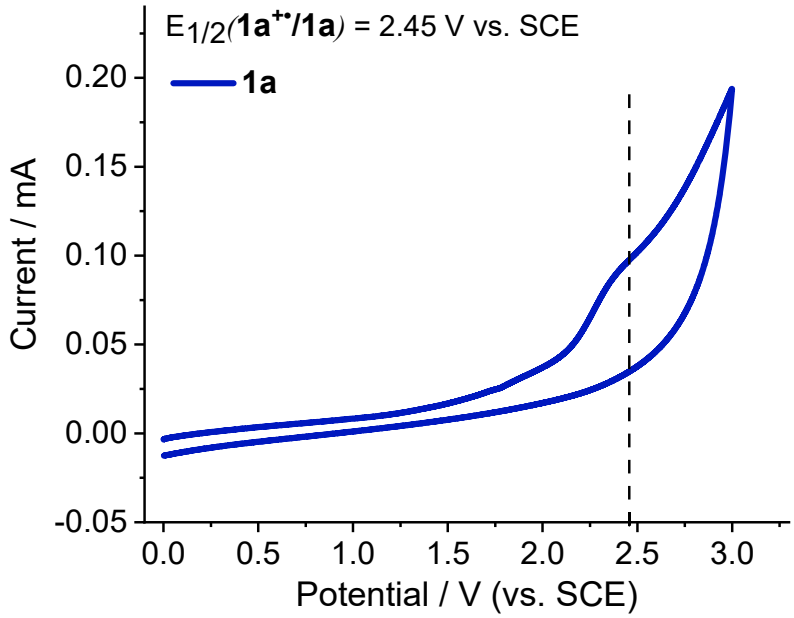
Scheme S3. Cyclic voltammogram of ferrocene

Cyclic voltammogram of 1b. An oven-dried 20 mL beaker was equipped with **1b** (13.8 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.



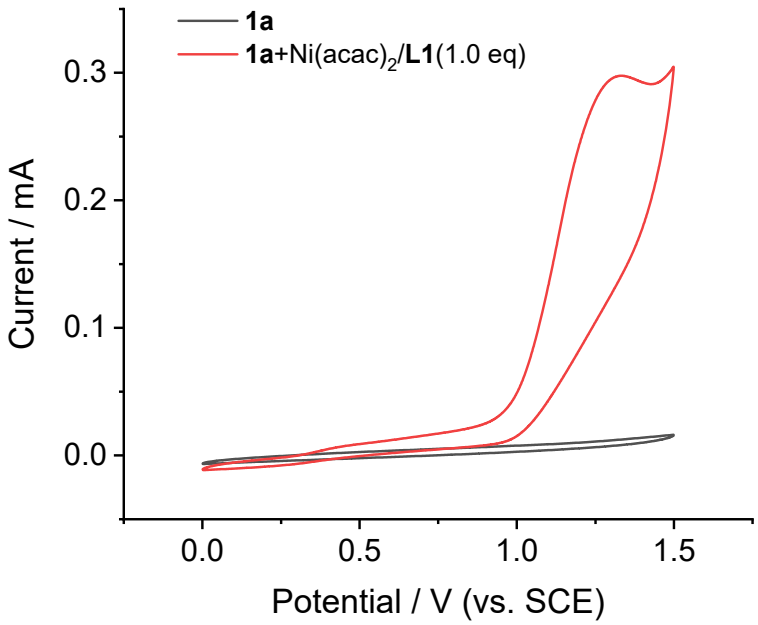
Scheme S4. Cyclic voltammogram of 1b

Cyclic voltammogram of 1a. An oven-dried 20 mL beaker was equipped with **1a** (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.

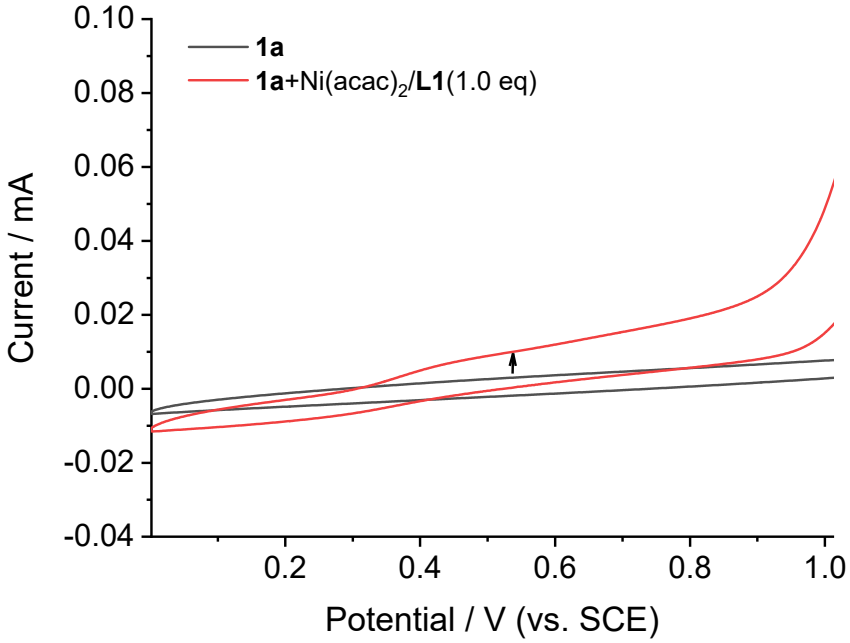


Scheme S5. Cyclic voltammogram of **1a**

Cyclic voltammogram of 1a in the presence of $Ni(acac)_2$/L1. An oven-dried 20 mL beaker was equipped with *n*-Bu_4NPF_6 (387.4 mg, 1.0 mmol), **1a** (101.7 mg, 0.30 mmol), $Ni(acac)_2$/**L1**, 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.



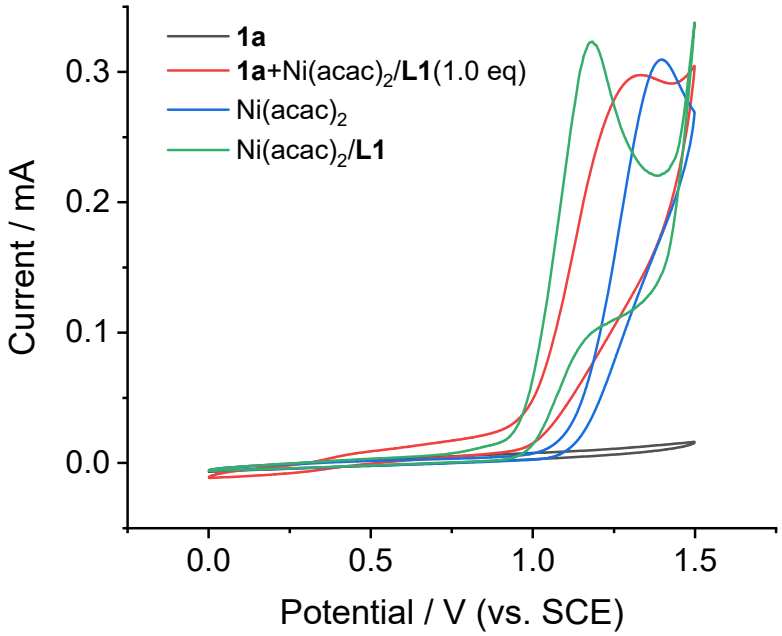
Scheme S6. Cyclic voltammogram of 1a in the presence of Ni(acac)$_2$/L1. Conditions: (black curve) **1a** (0.30 mmol); (red curve) **1a** (0.30 mmol) and Ni(acac)$_2$/**L1** (0.30 mmol).



Scheme S7. Cyclic voltammogram of 1a in the presence of Ni(acac)$_2$/L1. Conditions: (black curve) **1a** (0.30 mmol); (red curve) **1a** (0.30 mmol) and Ni(acac)$_2$/**L1** (0.30 mmol).

Discussion: The addition of Ni(acac)$_2$/**L1** significantly reduced the onset oxidation potential of **1a**.

Cyclic voltammogram of Ni(acac)$_2$ and Ni(acac)$_2$/L1. An oven-dried 20 mL beaker was equipped with *n*-Bu$_4$NPF$_6$ (387.4 mg, 1.0 mmol), Ni(acac)$_2$ (0.30 mmol) or Ni(acac)$_2$/**L1** (0.30 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.



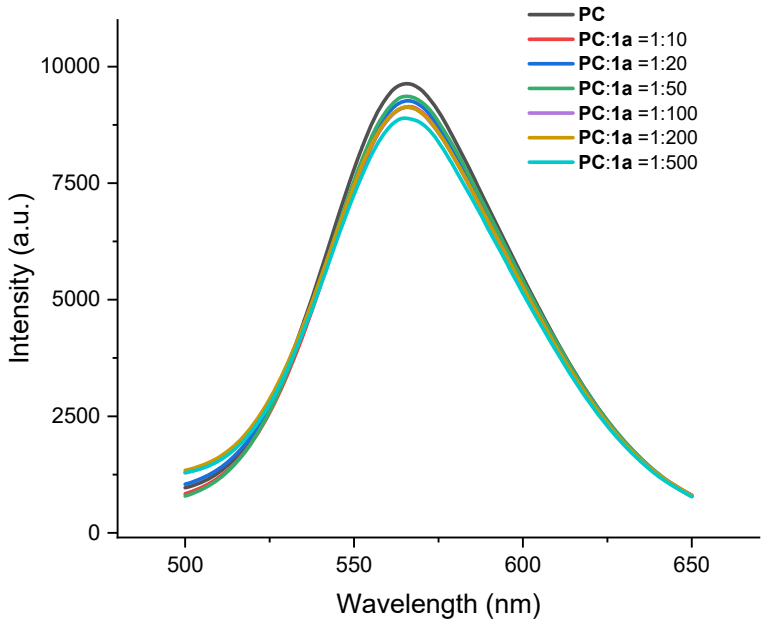
Scheme S8. Cyclic voltammogram of Ni(acac)$_2$ and Ni(acac)$_2$/L1. Conditions: (black curve) **1a** (0.30 mmol); (red curve) **1a** (0.30 mmol) and Ni(acac)$_2$/**L1** (0.30 mmol); (blue curve) Ni(acac)$_2$ (0.30 mmol); (green curve) Ni(acac)$_2$/**L1** (0.30 mmol).

5. Stern–Volmer Luminescence Quenching Studies.

The fluorescence quenching experiments were carried out in degassed EA at room temperature upon excitation by 450 nm light.

Emission quenching of (Ir(dMeppy)$_2$(dtbpy))PF$_6$ as a function of concentration of 1a. A 1.0×10^{-3} M solution of (Ir(dMeppy)$_2$(dtbpy))PF$_6$ (9.7 mg, 0.010 mmol) in anhydrous degassed EA (10 mL) and a 2.0×10^{-2} M solution of **1a** (13.6 mg, 0.040 mmol) in anhydrous degassed EA (2 mL) were prepared in a nitrogen filled glovebox. To six sample vials were added 20 uL of 1.0×10^{-3} M

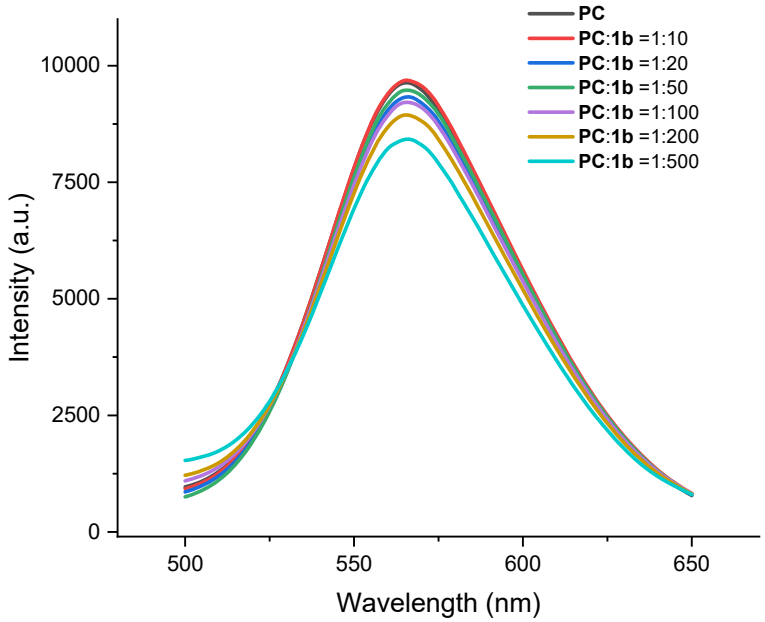
solution of $(Ir(dMeppy)_2(dtbpy))PF_6$ and 0 uL, 10 uL, 20 uL, 50 uL, 100 uL, 200 uL and 500 uL of 2.0×10^{-2} M solution of **1a**. Anhydrous degassed EA was then added to each sample vial to a quantity of 2 mL. These were then transferred to a 3.5 mL quartz cuvette (path length: l = 10 mm) and sealed 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 $(Ir(dMeppy)_2(dtbpy))PF_6$ (1.0×10^{-5} M) as a function of the concentration of **1a** in deaerated EA with excitation at 450 nm is shown in **Scheme S9.**



Scheme S9. The emission quenching of $(Ir(dMeppy)_2(dtbpy))PF_6$ (1.0×10^{-5} M) as a function of concentration of 1a in deaerated EA with excitation at 450 nm. Conditions: (black curve) **PC:1a** = 1:0; (red curve) **PC:1a** = 1:10; (blue curve) **PC:1a** = 1:20; (green curve) **PC:1a** = 1:50; (purple curve) **PC:1a** = 1:100; (yellow curve) **PC:1a** = 1:200; (light blue curve) **PC:1a** = 1:500.

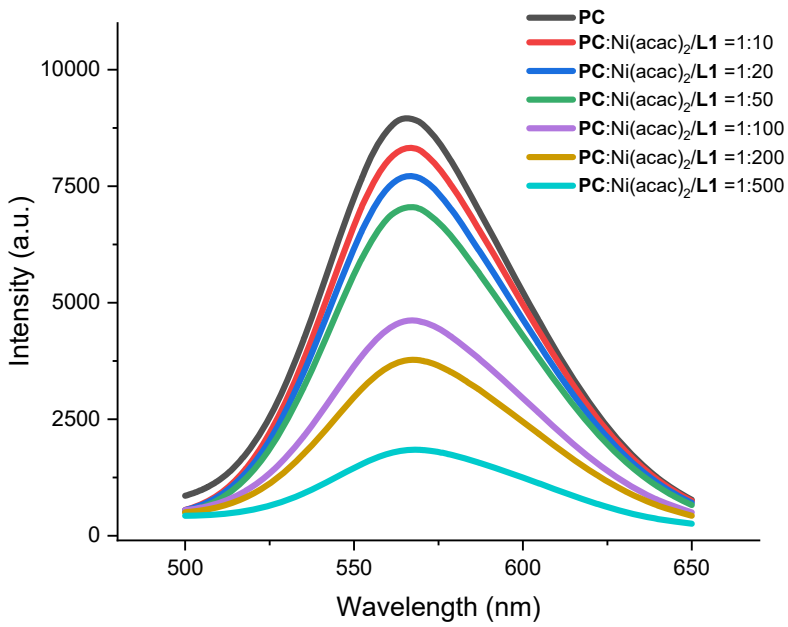
Emission quenching of $(Ir(dMeppy)_2(dtbpy))PF_6$ as a function of concentration of 1b. A 1.0×10^{-3} M solution of $(Ir(dMeppy)_2(dtbpy))PF_6$ (9.7 mg, 0.010 mmol) in anhydrous degassed EA (10 mL) and a 2.0×10^{-2} M solution of **1b** (11.0 mg, 0.040 mmol) in anhydrous degassed EA (2 mL) were prepared in a nitrogen filled glovebox. To six sample vials were added 20 uL of 1.0×10^{-3} M solution of $(Ir(dMeppy)_2(dtbpy))PF_6$ and 0 uL, 10 uL, 20 uL, 50 uL, 100 uL, 200 uL and 500 uL of 2.0×10^{-2} M solution of **1b**. Anhydrous degassed EA 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 $(Ir(dMeppy)_2(dtbpy))PF_6$ (1.0×10^{-5} M) as a function of the concentration of **1b** in deaerated EA with excitation at 450 nm is shown in **Scheme S10.**



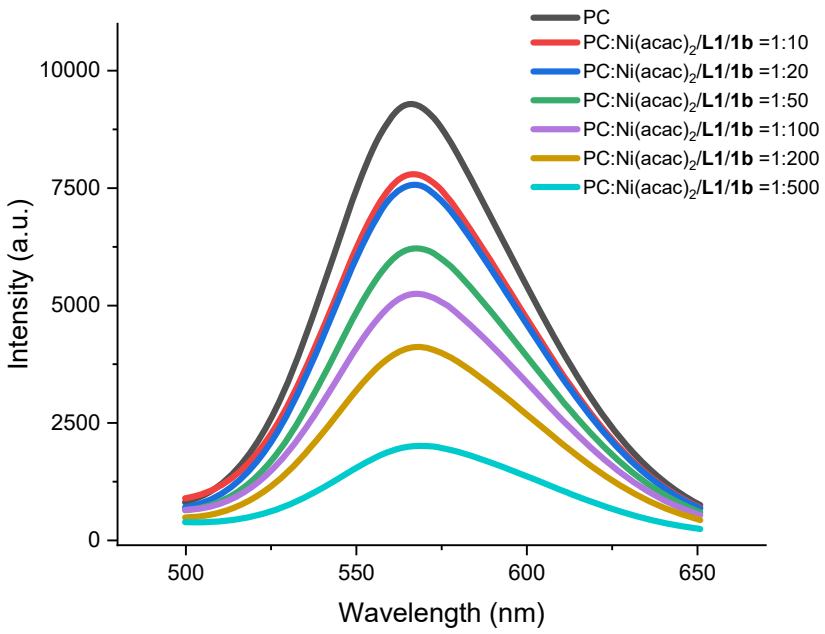
Scheme S10. The emission quenching of $(Ir(dMeppy)_2(dtbpy))PF_6$ (1.0×10^{-5} M) as a function of concentration of 1b in deaerated EA with excitation at 450 nm. Conditions: (black curve) **PC:1b** = 1:0; (red curve) **PC:1b** = 1:10; (blue curve) **PC:1b** = 1:20; (green curve) **PC:1b** = 1:50; (purple curve) **PC:1b** = 1:100; (yellow curve) **PC:1b** = 1:200; (light blue curve) **PC:1b** = 1:500.

Emission quenching of $(Ir(dMeppy)_2(dtbpy))PF_6$ as a function of concentration of $Ni(acac)_2$/L1. A 1.0×10^{-3} M solution of $(Ir(dMeppy)_2(dtbpy))PF_6$ (9.7 mg, 0.010 mmol) in anhydrous degassed EA (10 mL) and a 2.0×10^{-2} M solution of $Ni(acac)_2$/**L1** (0.040 mmol) in anhydrous degassed EA (2 mL) were prepared in a nitrogen filled glovebox. To six sample vials were added 20 uL of 1.0×10^{-3} M solution of $(Ir(dMeppy)_2(dtbpy))PF_6$ and 0 uL, 10 uL, 20 uL, 50 uL, 100 uL, 200 uL and 500 uL of 2.0×10^{-2} M solution of $Ni(acac)_2$/**L1**. Anhydrous degassed EA 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 $(Ir(dMeppy)_2(dtbpy))PF_6$ (1.0×10^{-5} M) as a function of the concentration of $Ni(acac)_2$/**L1** in deaerated EA with excitation at 450 nm is shown in **Scheme S11.**



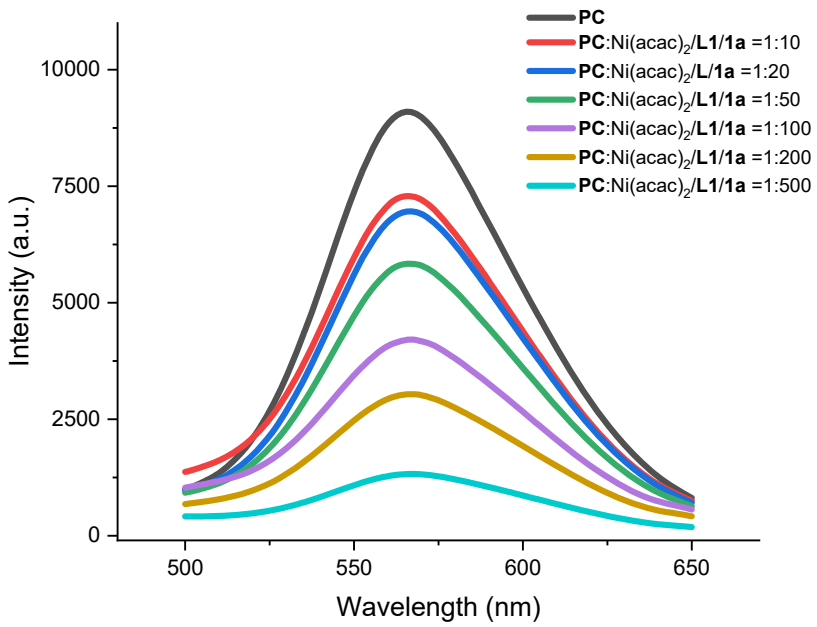
Scheme S11. The emission quenching of (Ir(dMeppy)$_2$(dtbpy))PF$_6$ (1.0×10^{-5} M) as a function of concentration of Ni(acac)$_2$/L1 in deaerated EA with excitation at 450 nm. Conditions: (black curve) **PC**:Ni(acac)$_2$/**L1** = 1:0; (red curve) **PC**:Ni(acac)$_2$/**L1** = 1:10; (blue curve) **PC**:Ni(acac)$_2$/**L1** = 1:20; (green curve) **PC**:Ni(acac)$_2$/**L1** = 1:50; (purple curve) **PC**:Ni(acac)$_2$/**L1** = 1:100; (yellow curve) **PC**:Ni(acac)$_2$/**L1** = 1:200; (light blue curve) **PC**:Ni(acac)$_2$/**L1** = 1:500.

Emission quenching of (Ir(dMeppy)$_2$(dtbpy))PF$_6$ as a function of concentration of Ni(acac)$_2$/L1/1b. A 1.0×10^{-3} M solution of (Ir(dMeppy)$_2$(dtbpy))PF$_6$ (9.7 mg, 0.010 mmol) in anhydrous degassed EA (10 mL) and a 2.0×10^{-2} M solution of Ni(acac)$_2$/**L1/1b** (0.040 mmol) in anhydrous degassed EA (2 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(dMeppy)$_2$(dtbpy))PF$_6$ and 0 uL, 10 uL, 20 uL, 50 uL, 100 uL, 200 uL and 500 uL of 2.0×10^{-2} M solution of Ni(acac)$_2$/**L1/1b**. Anhydrous degassed EA 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(dMeppy)$_2$(dtbpy))PF$_6$ (1.0×10^{-5} M) as a function of the concentration of **Ni(acac)$_2$/L1/1b** in deaerated EA with excitation at 450 nm is shown in **Scheme S12.**



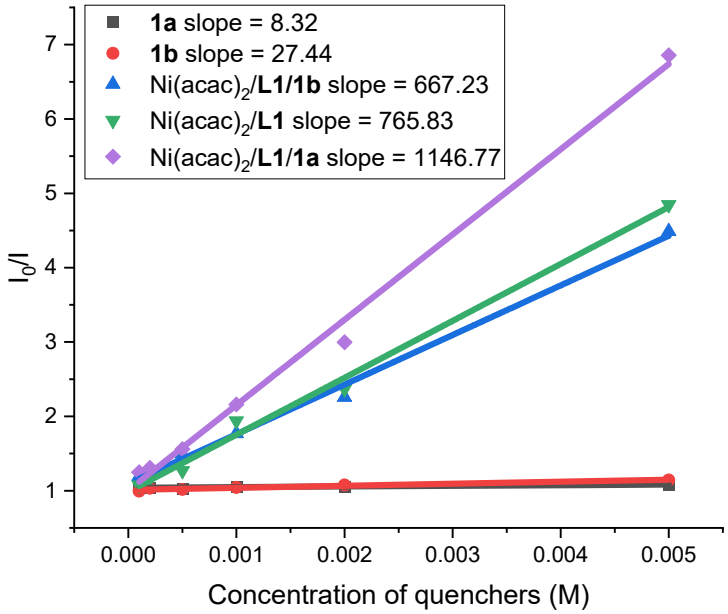
Scheme S12. The emission quenching of $(Ir(dMeppy)_2(dtbpy))PF_6$ (1.0×10^{-5} M) as a function of concentration of $Ni(acac)_2$/L1/1b in deaerated EA with excitation at 450 nm. Conditions: (black curve) **PC**:$Ni(acac)_2$/**L1/1b** = 1:0; (red curve) **PC**:$Ni(acac)_2$/**L1/1b** = 1:10; (blue curve) **PC**:$Ni(acac)_2$/**L1/1b** = 1:20; (green curve) **PC**:$Ni(acac)_2$/**L1/1b** = 1:50; (purple curve) **PC**:$Ni(acac)_2$/**L1/1b** = 1:100; (yellow curve) **PC**:$Ni(acac)_2$/**L1/1b** = 1:200; (light blue curve) **PC**:$Ni(acac)_2$/**L1/1b** = 1:500.

Emission quenching of $(Ir(dMeppy)_2(dtbpy))PF_6$ as a function of concentration of $Ni(acac)_2$/L1/1a. A 1.0×10^{-3} M solution of $(Ir(dMeppy)_2(dtbpy))PF_6$ (9.7 mg, 0.010 mmol) in anhydrous degassed EA (10 mL) and a 2.0×10^{-2} M solution of $Ni(acac)_2$/**L1/1a** (0.040 mmol) in anhydrous degassed EA (2 mL) were prepared in a nitrogen filled glovebox. To six sample vials were added 20 uL of 1.0×10^{-3} M solution of $(Ir(dMeppy)_2(dtbpy))PF_6$ and 0 uL, 10 uL, 20 uL, 50 uL, 100 uL, 200 uL and 500 uL of 2.0×10^{-2} M solution of $Ni(acac)_2$/**L1/1a**. Anhydrous degassed EA 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 $(Ir(dMeppy)_2(dtbpy))PF_6$ (1.0×10^{-5} M) as a function of the concentration of **$Ni(acac)_2$/L1/1a** in deaerated EA with excitation at 450 nm is shown in **Scheme S13.**



Scheme S13. The emission quenching of (Ir(dMeppy)$_2$(dtbpy))PF$_6$ (1.0×10^{-5} M) as a function of concentration of Ni(acac)$_2$/L1/1a in deaerated EA with excitation at 450 nm. Conditions: (black curve) **PC**:Ni(acac)$_2$/**L1/1a** = 1:0; (red curve) **PC**:Ni(acac)$_2$/**L1/1a** = 1:10; (blue curve) **PC**:Ni(acac)$_2$/**L1/1a** = 1:20; (green curve) **PC**:Ni(acac)$_2$/**L1/1a** = 1:50; (purple curve) **PC**:Ni(acac)$_2$/**L1/1a** = 1:100; (yellow curve) **PC**:Ni(acac)$_2$/**L1/1a** = 1:200; (light blue curve) **PC**:Ni(acac)$_2$/**L1/1a** = 1:500.

Discussion: As shown in **Scheme S14**, substrate **1a** and **1b** totally could not quench the excited state of (Ir(dMeppy)$_2$(dtbpy))PF$_6$. The complex of Ni(acac)$_2$/**L1**, Ni(acac)$_2$/**L1/1b**, and Ni(acac)$_2$/**L1/1a** could quench the excited state of (Ir(dMeppy)$_2$(dtbpy))PF$_6$. However, the quenching rate of Ni(acac)$_2$/**L1/1a** complex is much faster than Ni(acac)$_2$/**L1** complex and Ni(acac)$_2$/**L1/1b** complex.



Scheme S14. The emission quenching and Stern-Volmer plots of $(Ir(dMeppy)_2(dtbpy))PF_6$ (1.0×10^{-5} M) as a function of concentration of 1a (black curve), 1b (red curve), $Ni(acac)_2$/L1/1b (blue curve), $Ni(acac)_2$/L1 (green curve) and $Ni(acac)_2$/L1/1a (purple curve) in deaerated EA with excitation at 450 nm.

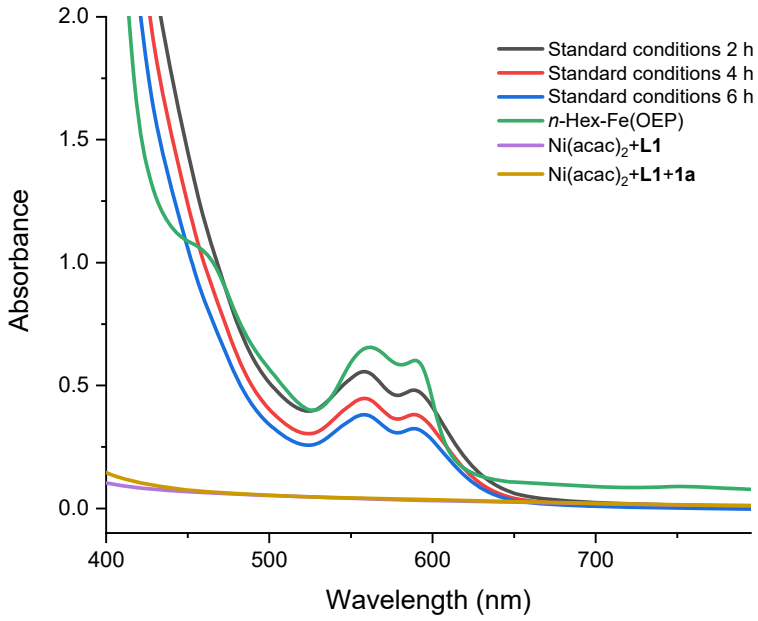
6. UV-vis studies.

Preparation of the standard reaction solution: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with $Ni(acac)_2$ (2.5 mg, 0.010 mmol, 5.0 mol%), (*R,S*)-**L1** (2.8 mg, 0.012 mmol, 6.0 mol%), and a stir bar. Anhydrous EA (1.0 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 30 min, leading to a light blue solution. In a nitrogen-filled glovebox, another oven-dried 4 mL vial was charged with Fe(OEP)Cl (1.3 mg, 0.002 mmol, 1.0 mol%), $(Ir(dMeppy)_2(dtbpy))PF_6$ (3.9 mg, 0.0040 mmol, 2.0 mol%), 1,3-dioxoisoindolin-2-yl heptanoate (137.5 mg, 0.50 mmol, 2.5 equiv), adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate (67.8 mg, 0.20 mmol, 1.0 equiv), and a stir bar. The Lewis acid catalyst solution (1.0 mL) and anhydrous EA (2.0 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 (**Scheme S1**). The reaction was irradiated with blue LEDs (450 nm) and was stirred at 20 °C for 2, 4, 6 hours. The reaction was stopped by ending the irradiation. The reaction mixture was transferred into a glovebox, where 500 μL of the reaction solution was transferred into a quartz cuvette followed by the addition of 2.5 mL EA. UV-vis absorption spectroscopy was subsequently performed at 20 °C.

Preparation of the *n*-Hex-Fe(OEP) catalyst solution: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with *n*-Hex-Fe(OEP) (0.7 mg, 0.001 mmol), and a stir bar. Anhydrous EA (1.5 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 30 min, leading to a light blue solution. Then 500 μL of the reaction solution was transferred to a quartz cuvette and 2.5 mL of EA was added. UV-vis absorption spectroscopy was subsequently performed at 20 °C.

Preparation of the Ni(acac)$_2$/L1 catalyst solution: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with Ni(acac)$_2$ (2.5 mg, 0.010 mmol, 5.0 mol%), (*R*,*S*)-**L1** (2.8 mg, 0.012 mmol, 6.0 mol%), and a stir bar. Anhydrous EA (3.0 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 30 min, leading to a light blue solution. Then 500 μL of the reaction solution was transferred to a quartz cuvette and 2.5 mL of EA was added. UV-vis absorption spectroscopy was subsequently performed at 20 °C.

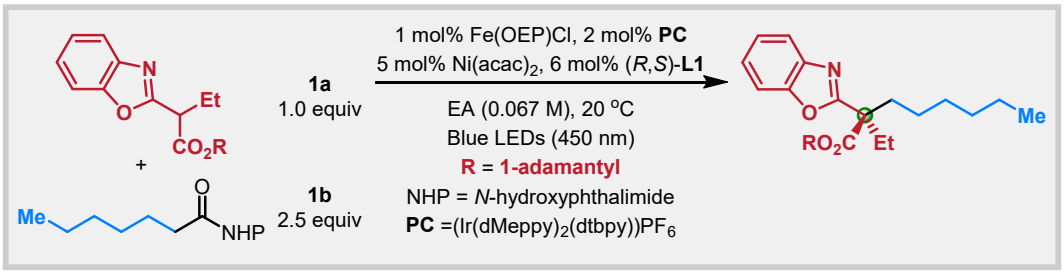
Preparation of the Ni(acac)$_2$/L1/1a catalyst solution: In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with Ni(acac)$_2$ (2.5 mg, 0.010 mmol, 5.0 mol%), (*R*,*S*)-**L1** (2.8 mg, 0.012 mmol, 6.0 mol%), adamantan-1-yl 2-(benzo[*d*]oxazol-2-yl)butanoate (67.8 mg, 0.20 mmol, 1.0 equiv), and a stir bar. Anhydrous EA (3.0 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 30 min, leading to a light blue solution. Then 500 μL of the reaction solution was transferred to a quartz cuvette and 2.5 mL of EA was added. UV-vis absorption spectroscopy was subsequently performed at 20 °C.



Scheme S15. UV-vis spectra (EA, 20 °C). Conditions: (black curve) Standard conditions 2 h; (red curve) Standard conditions 4 h; (blue curve) Standard conditions 6 h; (green curve) *n*-Hex-Fe(OEP); (purple curve) Ni(acac)$_2$/**L1**; (yellow curve) Ni(acac)$_2$/**L1**/**1a**.

Discussion: Comparison of the UV−vis spectra obtained during a coupling reaction after 2 h, 4 h, and 6 h shows that the *n*-Hex-Fe(OEP) species, represented by the green solid line, may be the predominant resting state for Fe during catalysis.

7. Control experiments investigating kinetic resolution.

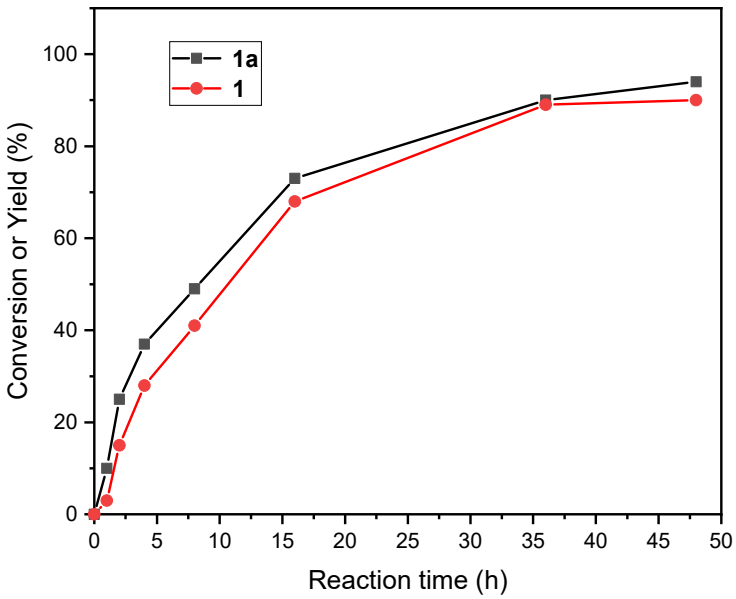


time	**1a** (recovery, ee)	**1** (yield, ee)
1 h	90%, 0%	3%, 86%
2 h	75%, 0%	15%, 86%
4 h	63%, 0%	28%, 86%
8 h	51%, 0%	41%, 86%
16 h	27%, 0%	68%, 86%
36 h	10%, 0%	89%, 86%

Table S5. Kinetic resolution studies

Procedure: Six parallel reactions were set up according to **GP-2**. Each reaction was stopped at a different duration. The recovery of **1a** and the yield of **1** were determined through GC analysis. The ee value of **1a** was determined via HPLC on a CHIRALPAK AD-3 column (5% *i*-PrOH in *n*-hexane, 1.0 mL/min); retention times for **1a**: 7.0 min and 8.5min. The ee value of **1** was determined via HPLC on a CHIRALPAK AD-3 column (2% *i*-PrOH in *n*-hexane, 1.0 mL/min); retention times for **1**: 4.5 min and 5.4 min.

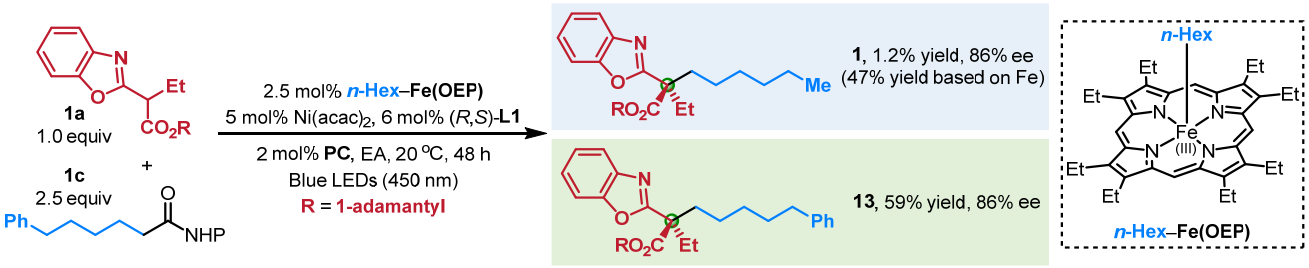
8. Time-course experiment.



Scheme S16. Time-course experiment. Conditions: (black curve) Conversion of **1a**; (red curve) Yield of **1**.

Procedure: Seven parallel reactions were set up according to **GP-2**. Each reaction was stopped at a different duration. The conversion of **1a** and the yield of **1** were determined through GC analysis.

9. Control experiment.



Procedure. In a nitrogen-filled glovebox, an oven-dried 10 mL vial was charged with $Ni(acac)_2$ (12.5 mg, 0.050 mmol, 5.0 mol%), (*R*,*S*)-**L1** (14 mg, 0.06 mmol, 6.0 mol%), and a stir bar. Anhydrous EA (2.5 mL) was added, and the vial was capped with a PTFE septum cap. The mixture was stirred at room temperature for 30 min, leading to a light blue solution. In a nitrogen-filled glovebox, an oven-dried 50 mL round-bottom flask was charged with ***n*-Hex–Fe(OEP)** (16.8 mg, 0.025 mmol, 2.5 mol%), $(Ir(dMeppy)_2(dtbpy))PF_6$ (19.4 mg, 0.020 mmol, 2.0 mol%), 1,3-dioxoisoindolin-2-yl heptanoate (0.69 g, 2.5 mmol, 2.5 equiv), adamantan-1-yl 2-

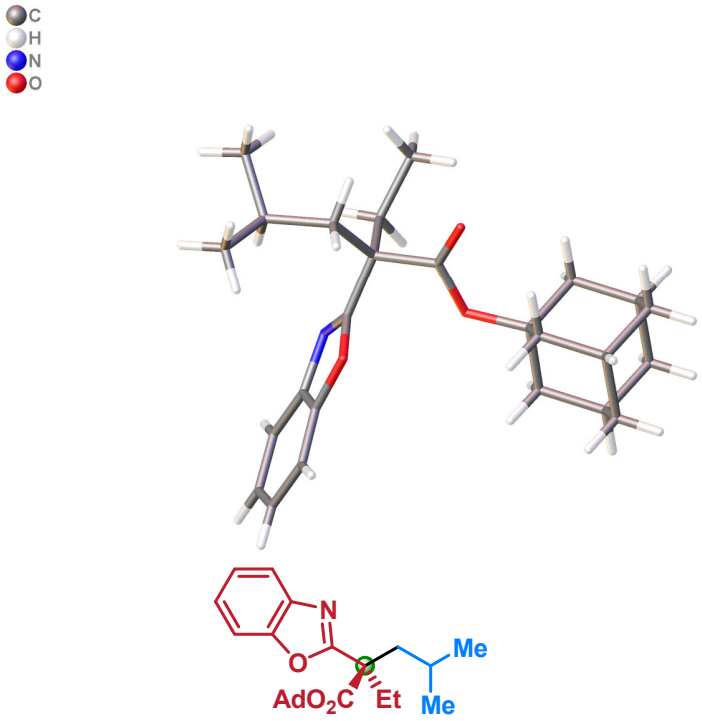
(benzo[*d*]oxazol-2-yl)butanoate (0.34 g, 1.0 mmol, 1.0 equiv), and a stir bar. The Lewis acid catalyst solution (2.5 mL) and anhydrous EA (12.5 mL) were added sequentially, and the flask was capped with a rubber septum cap. The flask was transferred out of the glovebox and placed in an EtOH cooling bath at 20 °C. The reaction was irradiated with blue LEDs (450 nm) and was stirred at 20 °C for 48 hours. The reaction mixture was passed through a plug of silica gel, and the flask, 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, 5.0 mg, 1.2% yield, 86% ee.

13, 284.2 mg, 59% yield, 86% ee.

VIII. Assignments of Absolute Configuration

The configuration of the coupling product illustrated in **Scheme 2A, entry 3**, using (*R,S*)-**L1**, was determined via X-ray crystallography.



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Adamantan-1-yl (*R*)-2-(benzo[*d*]oxazol-2-yl)-2-ethyl-4-methylpentanoate (Scheme 2A, entry 3). X-ray quality crystals were obtained by slow evaporation of a saturated solution in DCM/hexanes of a sample synthesized using (*R,S*)-**L1**. 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 S6. Crystal data for $C_{25}H_{33}NO_3$.

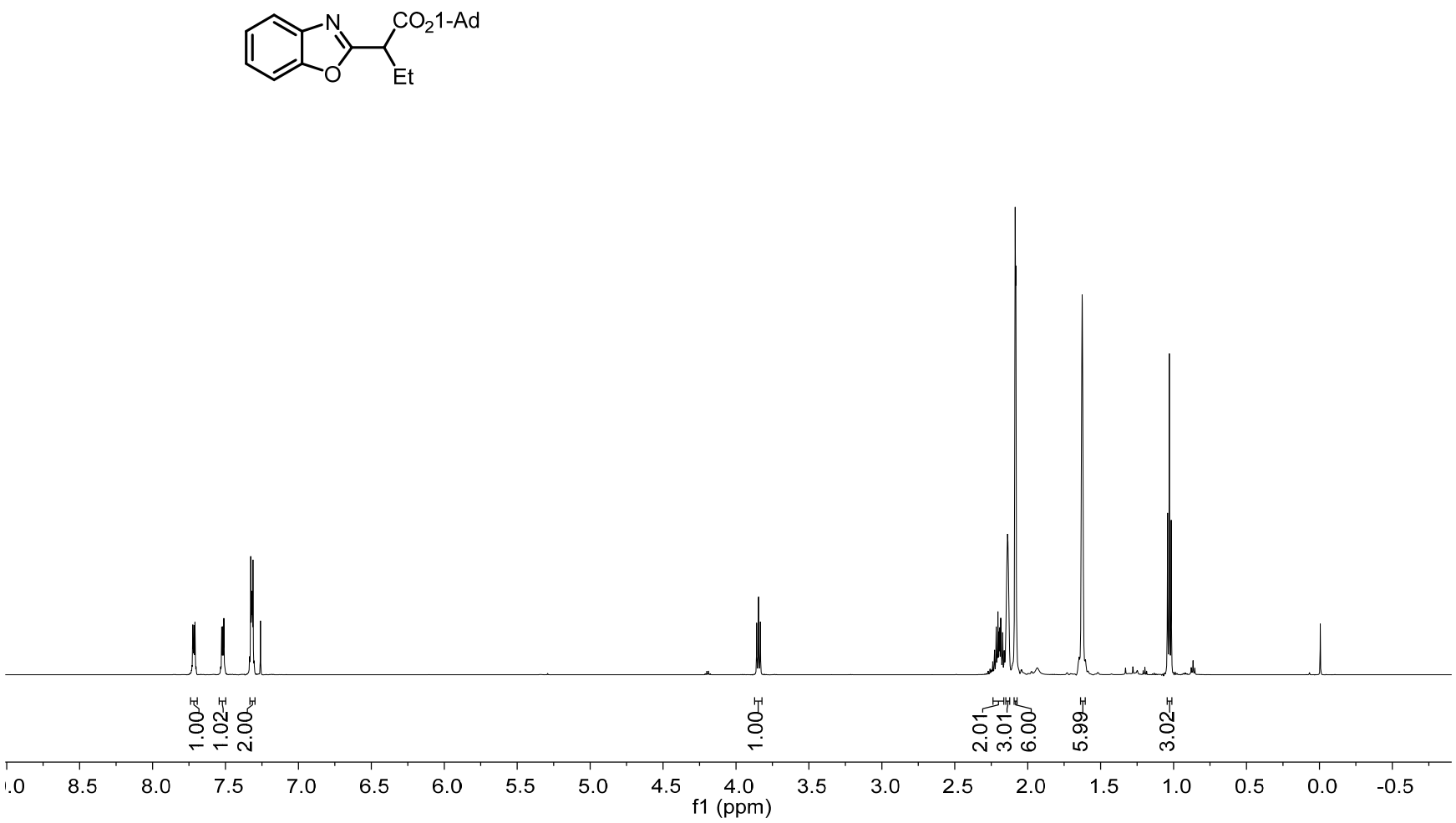
Identification code	cu_240620a_a
Empirical formula	$C_{25}H_{33}NO_3$
Formula weight	396.52
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.5604(2)
b/Å	19.5718(5)
c/Å	8.4661(2)

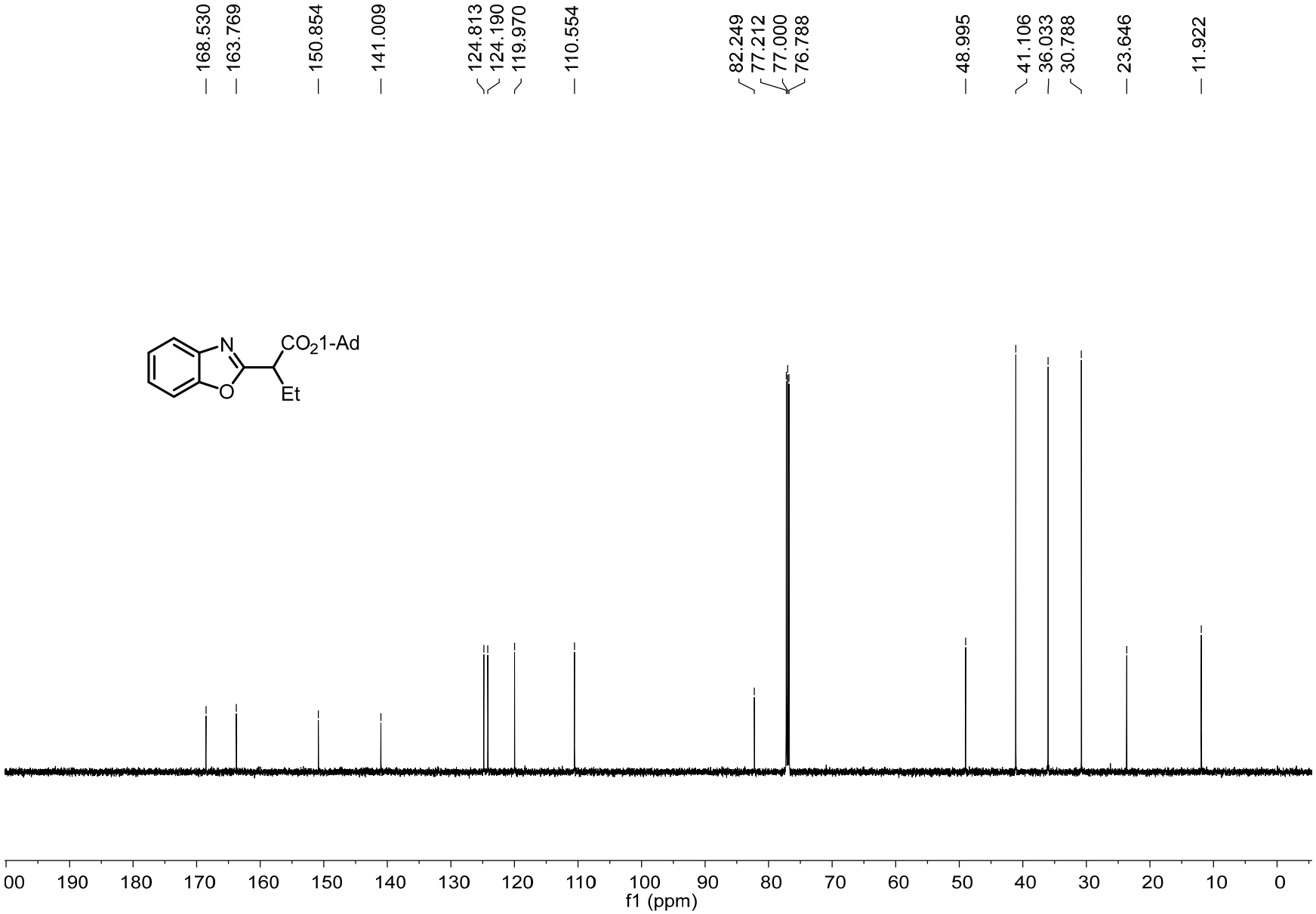
α/°	90
β/°	92.526(2)
γ/°	90
Volume/Å^3	1085.98(5)
Z	2
ρ_{calc}g/cm^3	1.210
μ/mm^{-1}	0.618
F(000)	428.0
Crystal size/mm^3	0.16 × 0.05 × 0.03
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.036 to 149.412
Index ranges	$-8 \le h \le 7$, $-24 \le k \le 24$, $-10 \le l \le 10$
Reflections collected	16293
Independent reflections	4404 [R_{int} = 0.0680, R_{sigma} = 0.0557]
Data/restraints/parameters	4404/1/266
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0492, wR_2 = 0.1134
Final R indexes [all data]	R_1 = 0.0568, wR_2 = 0.1202
Largest diff. peak/hole / e Å^{-3}	0.20/-0.22
Flack parameter	0.1 (2)

IX. References

1. D. Sahoo, M. G. Quesne, S. P. De Visser, S. P. Rath, *Angew. Chem. Int. Ed.* **2015**, *54*, 4796–4800.
2. Q. Zhang, J. Zhang, W. Zhu, R. Lu, C. Guo, *Nat. Commun.* **2024**, *15*, 4477.
3. L.-J. Li, J.-C. Zhang, W.-P. Li, D. Zhang, K. Duanmu, H. Yu, Q. Ping, Z.-P. Yang, *J. Am. Chem. Soc.* **2024**, *146*, 9404−9412.
4. X. Chang, J. Zhang, X. Cheng, X. Lv, C. Guo, *Adv. Sci.* **2024**, *11*, 2406764.

X. NMR Spectra and Determination of Stereoselectivity

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163.769
150.854
141.009
124.813
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119.970
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77.212
77.000
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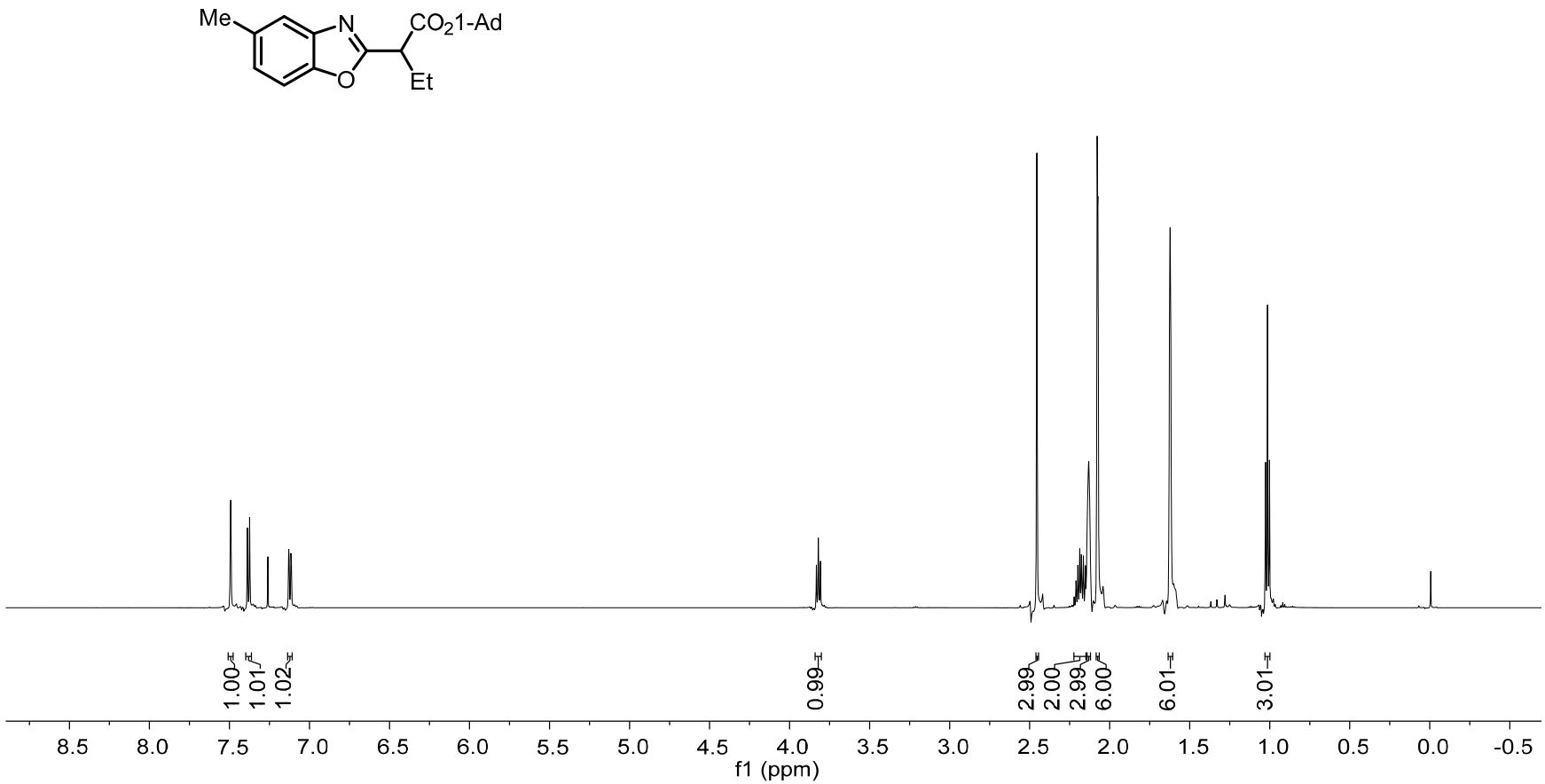
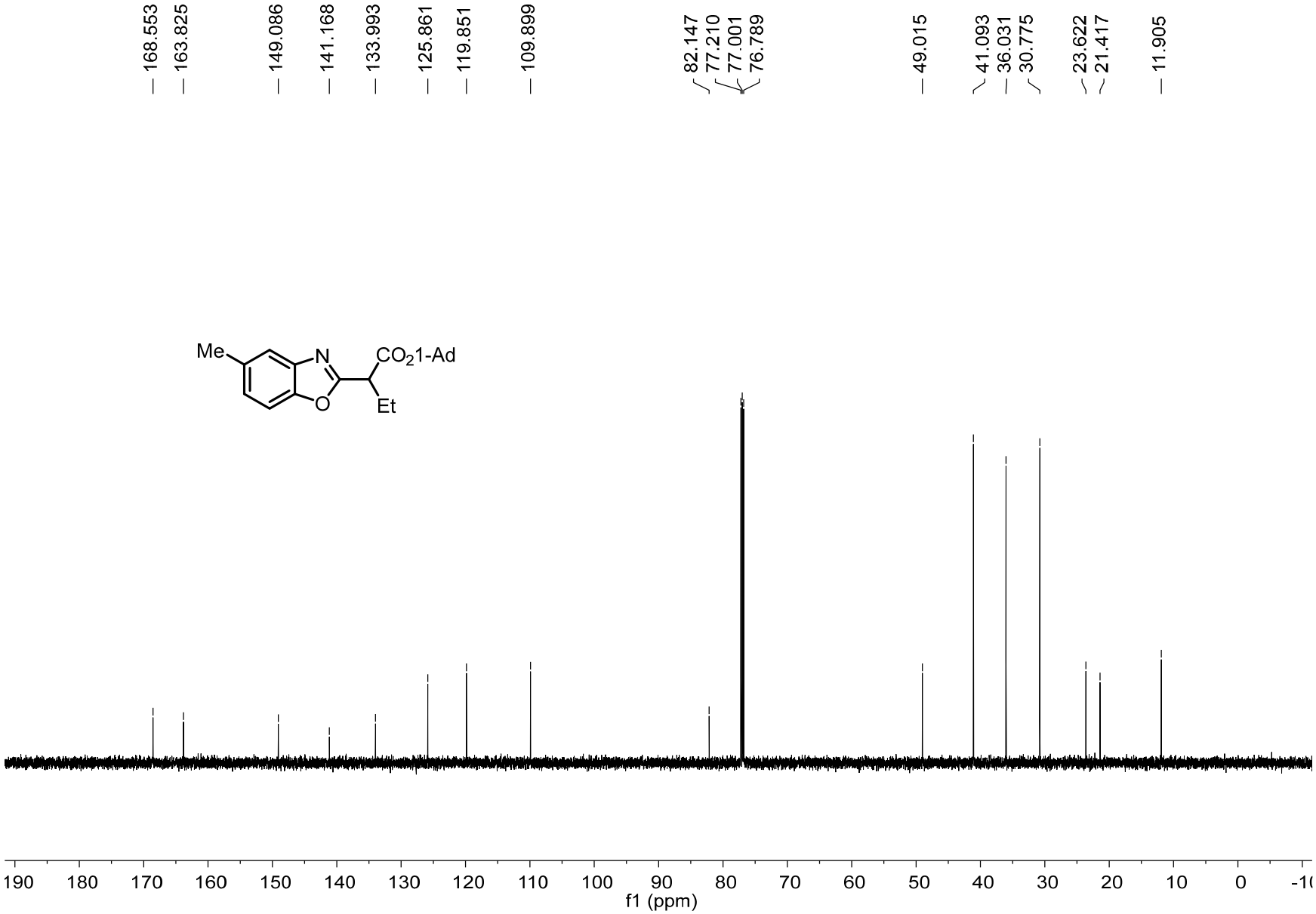
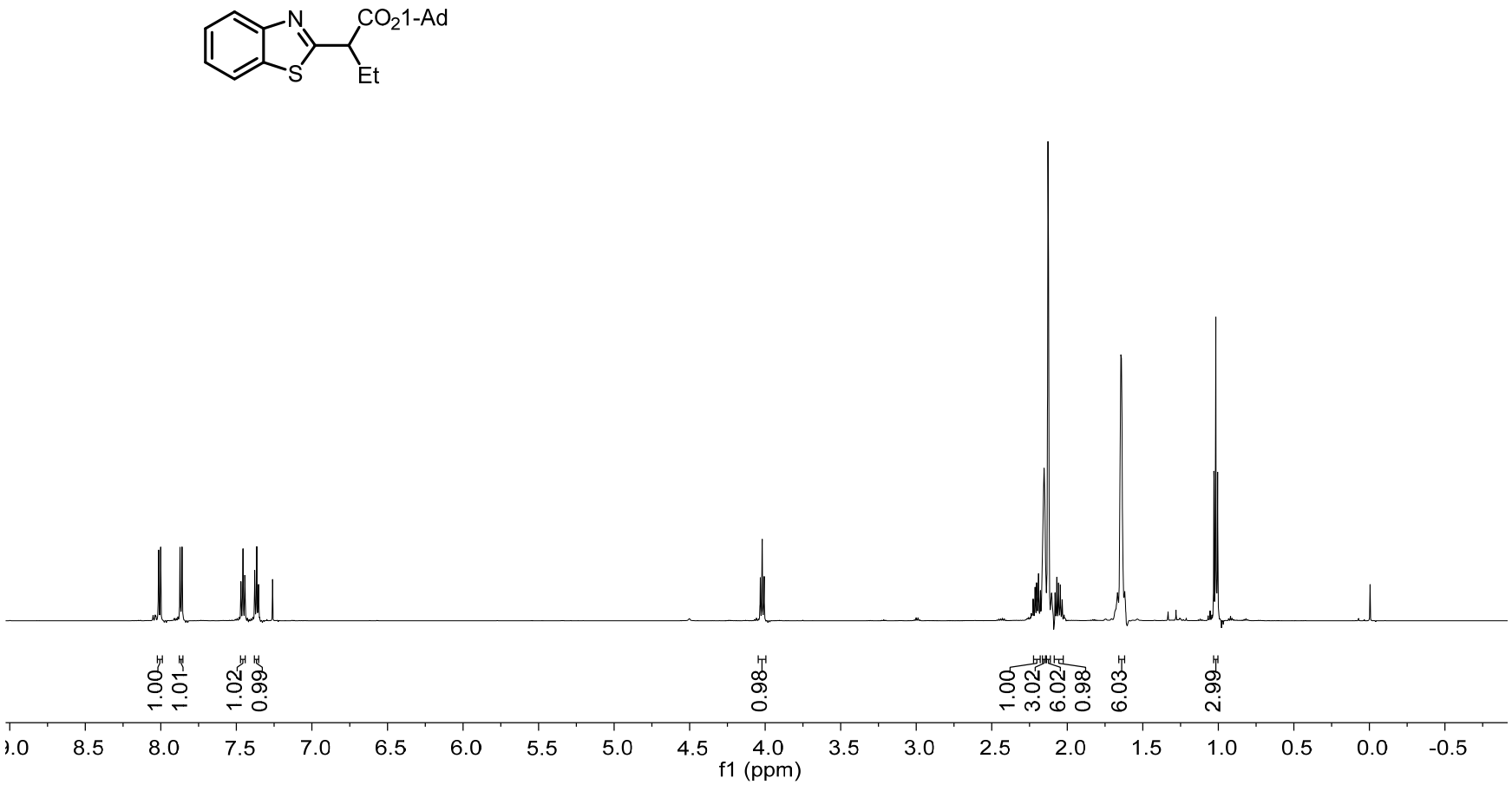
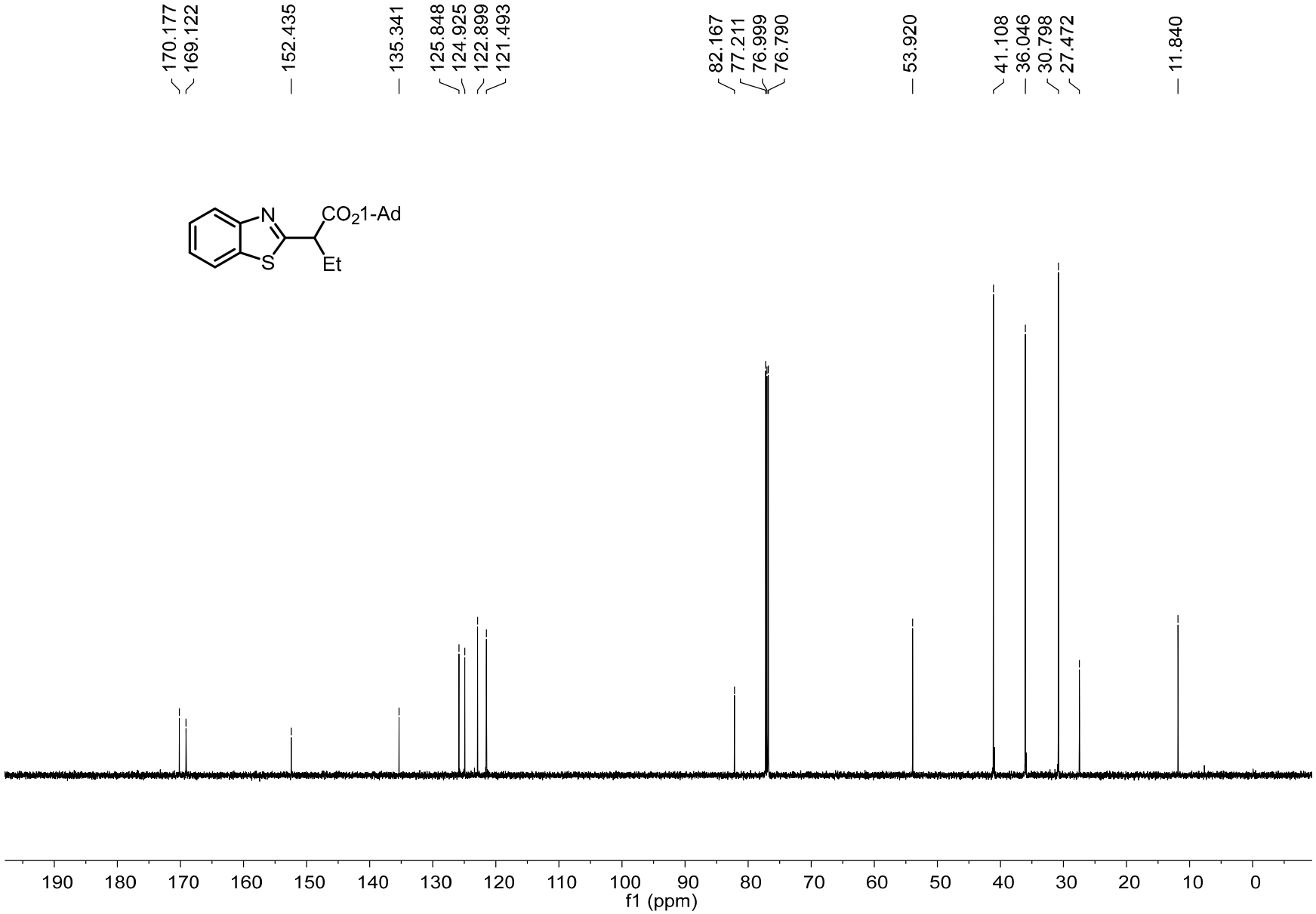
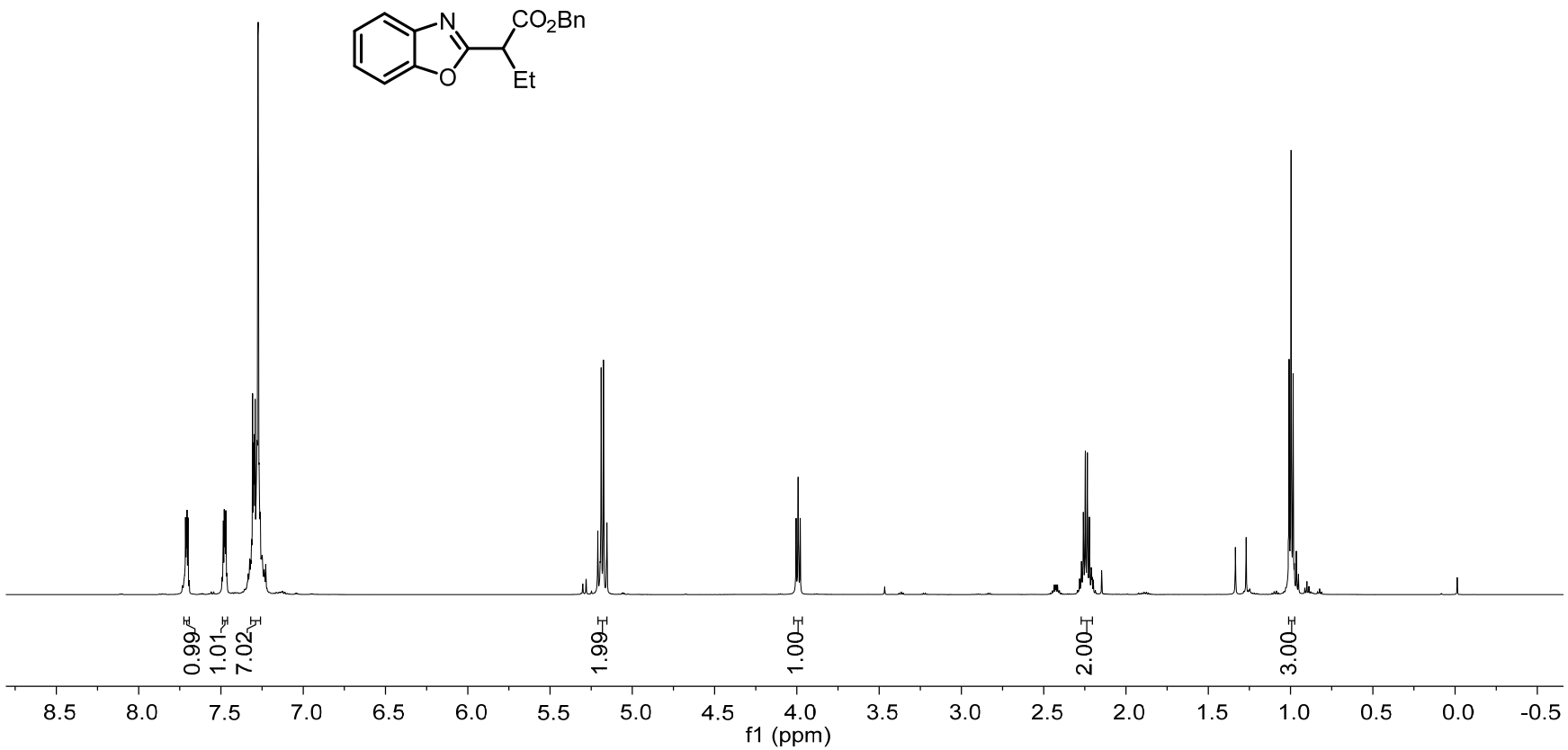
36.033
30.788
23.646
11.922
N
O
CO2
1-Ad
Et
f1 (ppm)

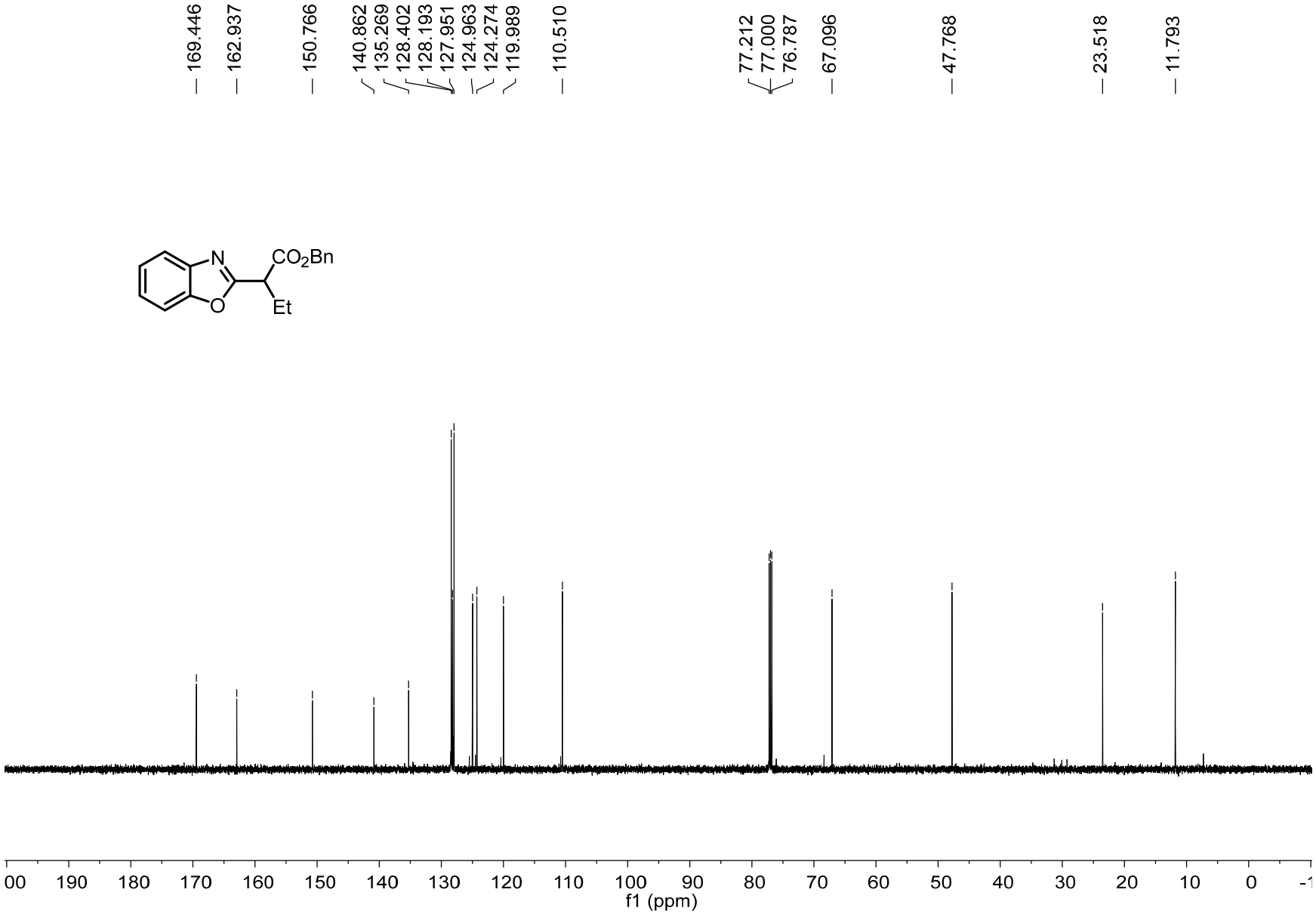

Me
N
O
CO2 1-Ad
Et
1.00
1.01
1.02
0.99
2.99
2.00
2.99
6.00
6.01
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

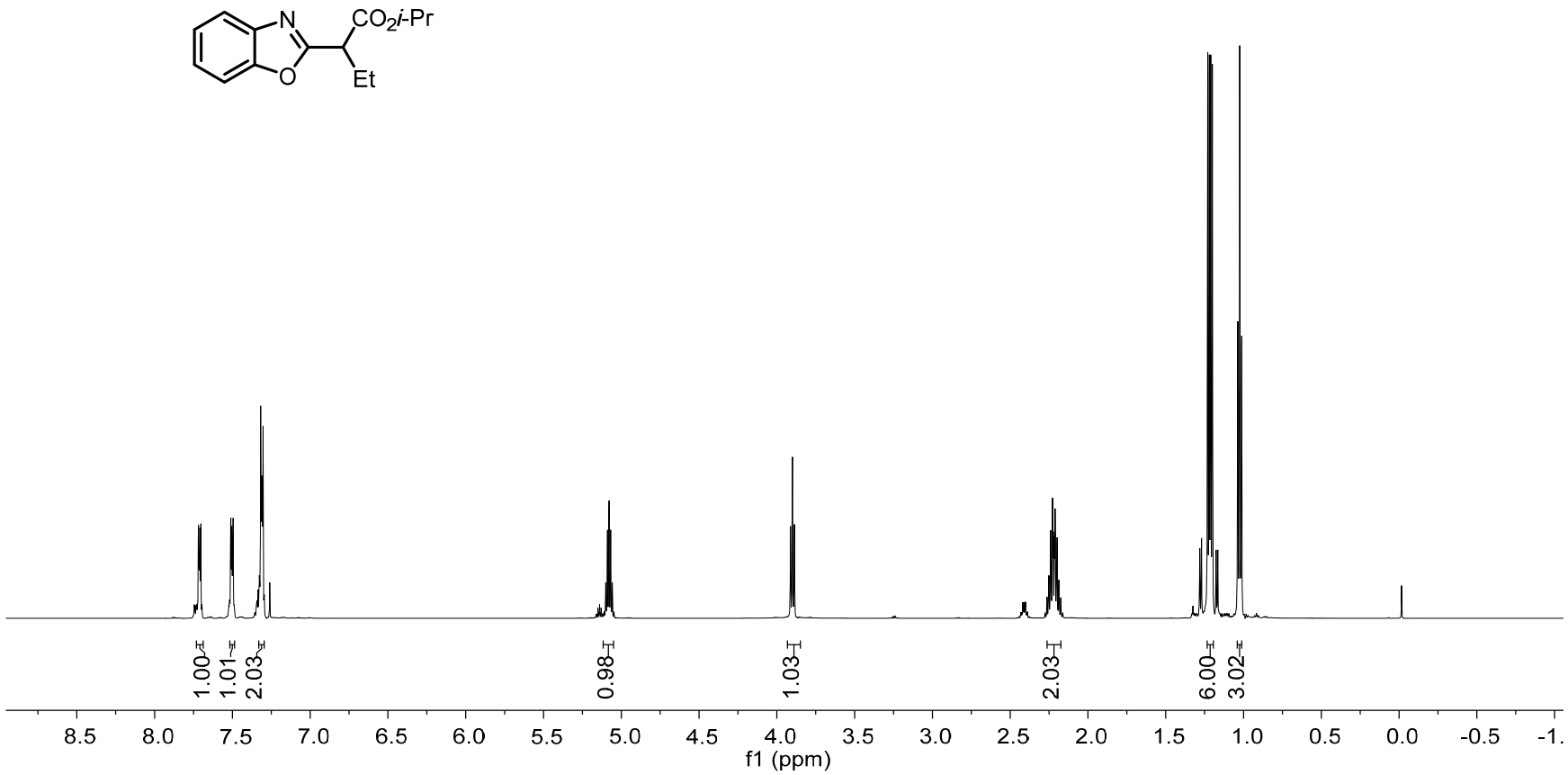

168.553
163.825
149.086
141.168
133.993
125.861
119.851
109.899
82.147
77.210
77.001
76.789
49.015
41.093
36.031
30.775
23.622
21.417
11.905
Me
N
O
CO2 1-Ad
Et
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

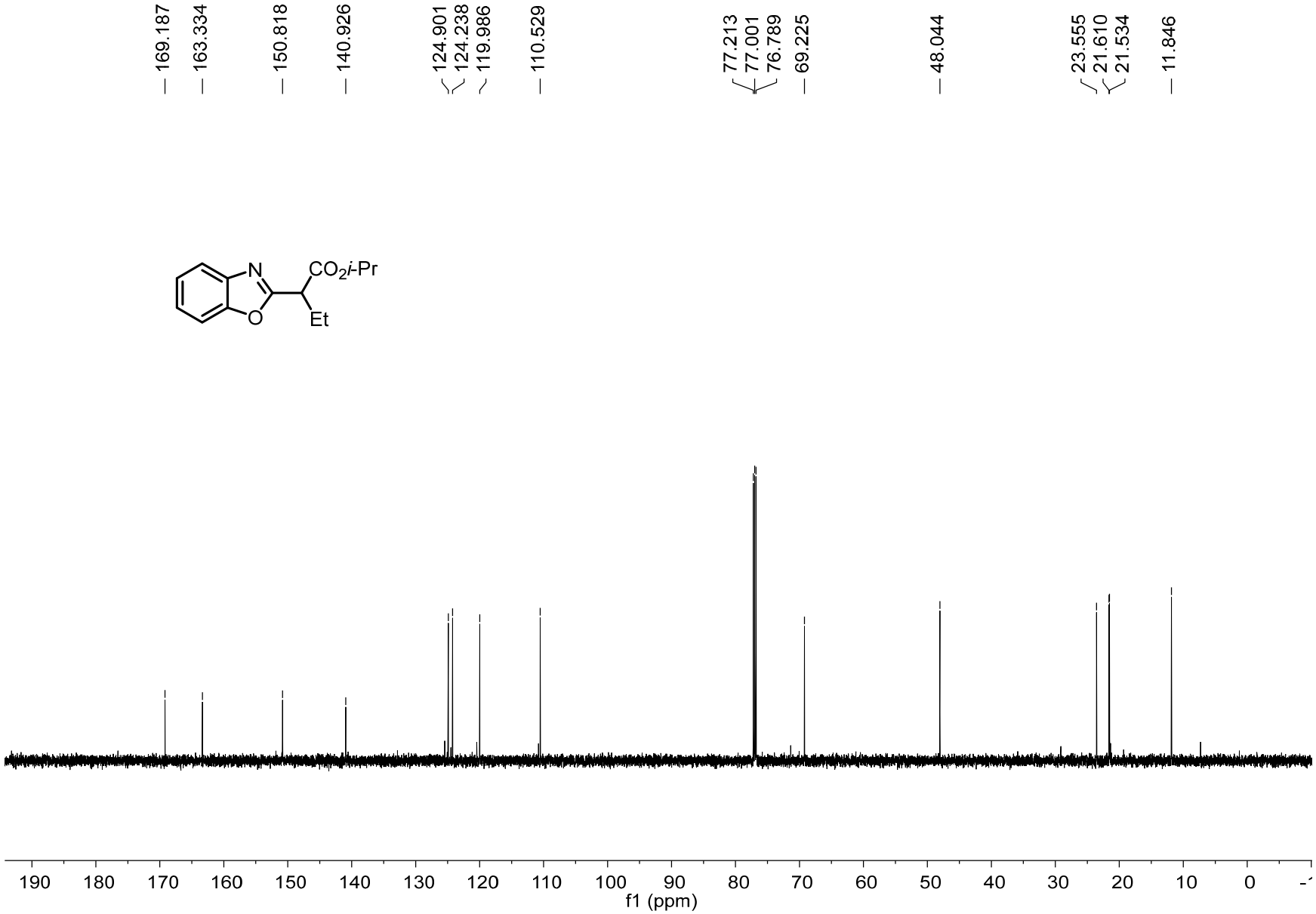

N
CO2 1-Ad
S
Et
1.00
1.01
1.02
0.99
0.98
1.00
3.02
6.02
0.98
6.03
2.99
f1 (ppm)

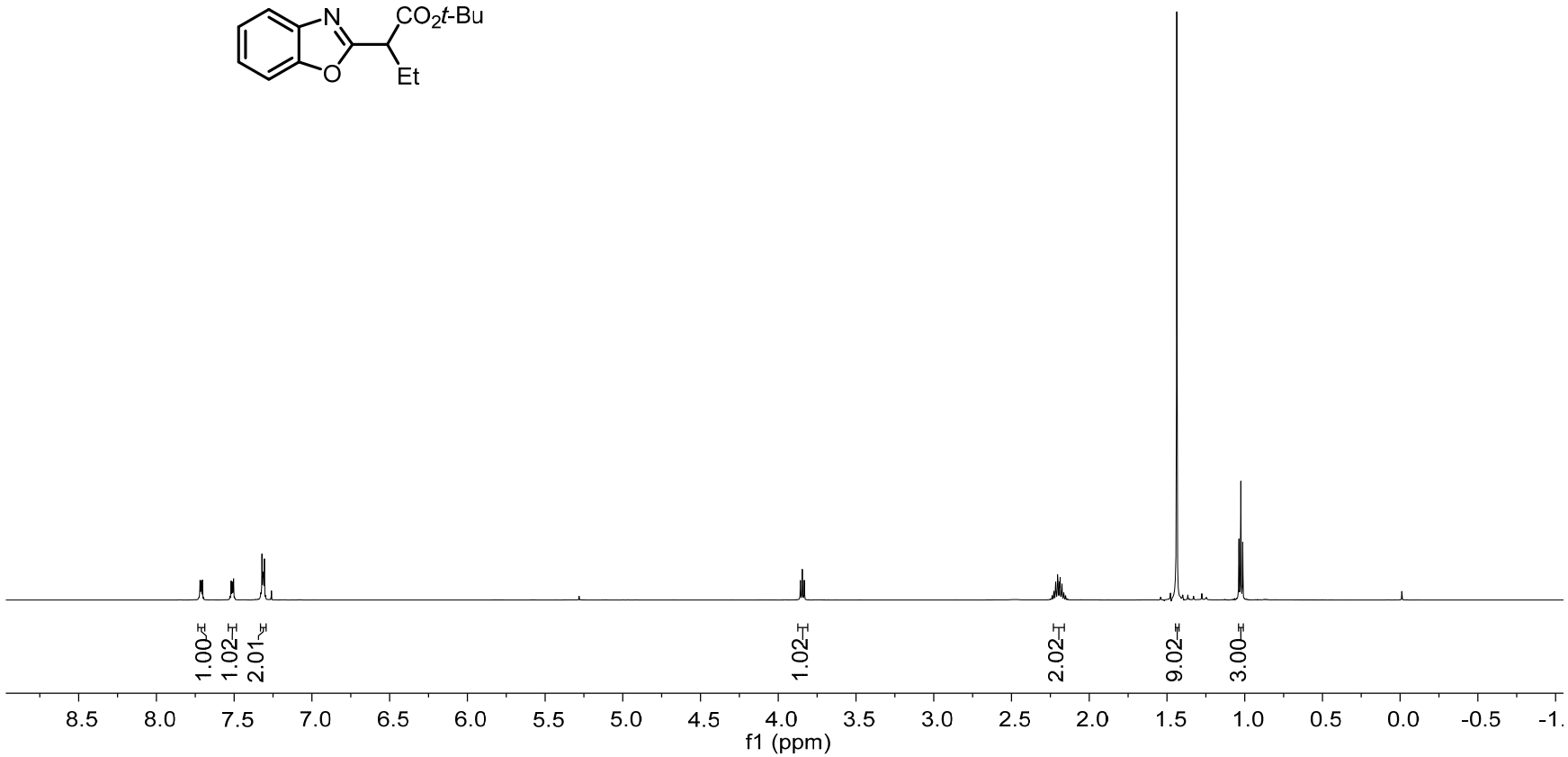

170.177
169.122
152.435
135.341
125.848
124.925
122.899
121.493
82.167
77.211
76.999
76.790
53.920
41.108
36.046
30.798
27.472
11.840
N
S
CO2
1-Ad
Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

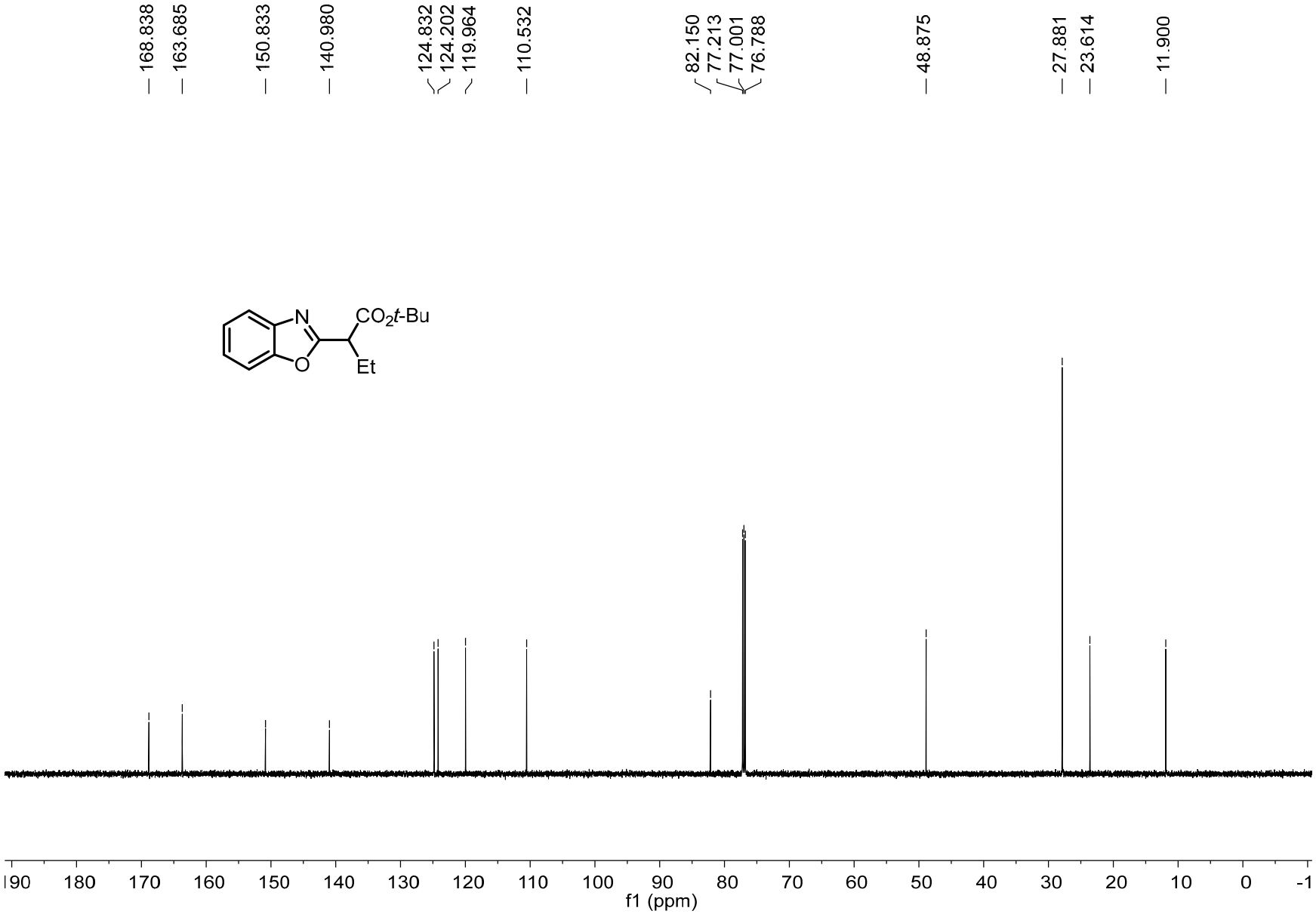

N
O
CO2Bn
Et
0.99
1.01
7.02
1.99
1.00
2.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

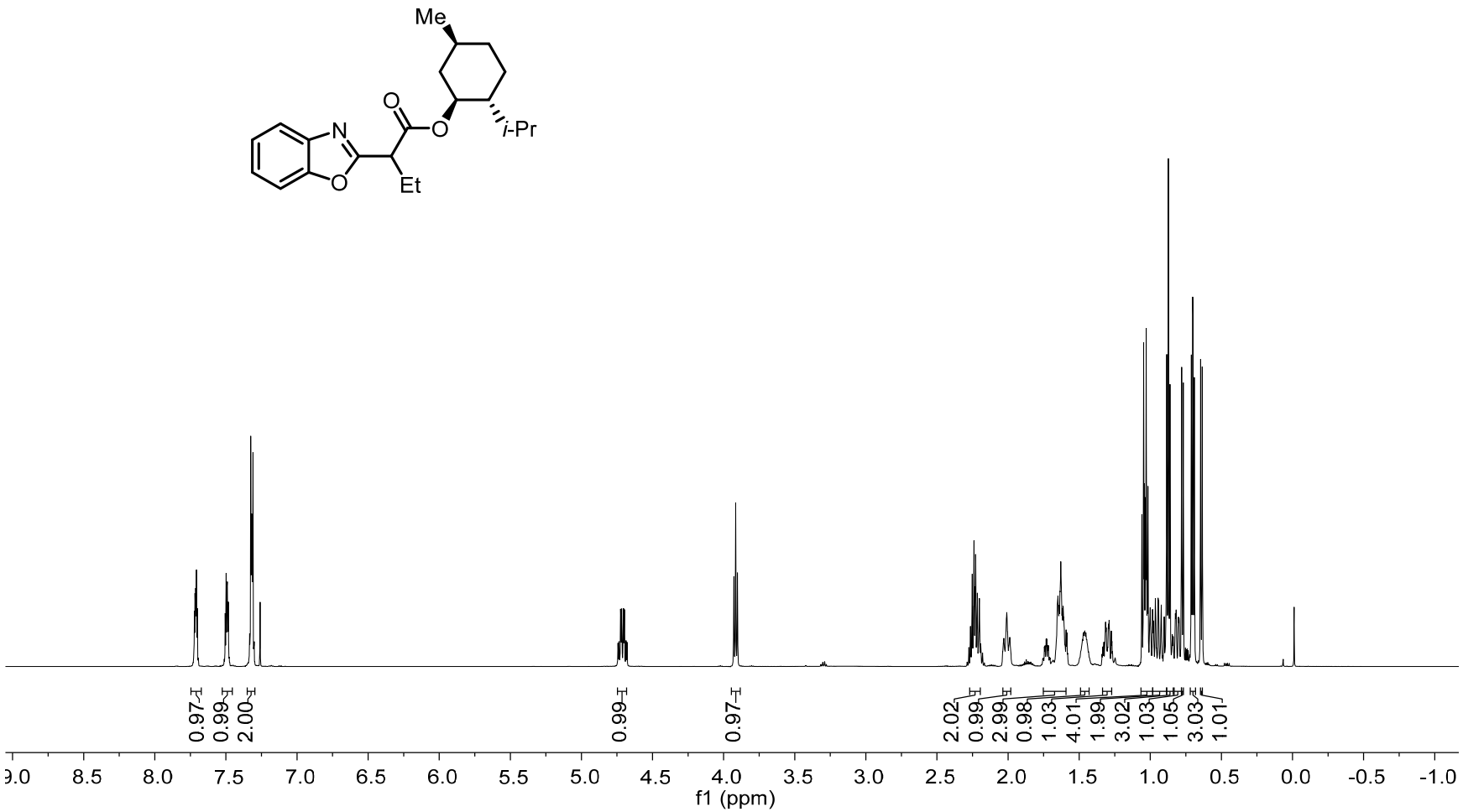

169.446
162.937
150.766
140.862
135.269
128.402
128.193
127.951
124.963
124.274
119.989
110.510
77.212
77.000
76.787
67.096
47.768
23.518
11.793
N
O
CO2Bn
Et
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

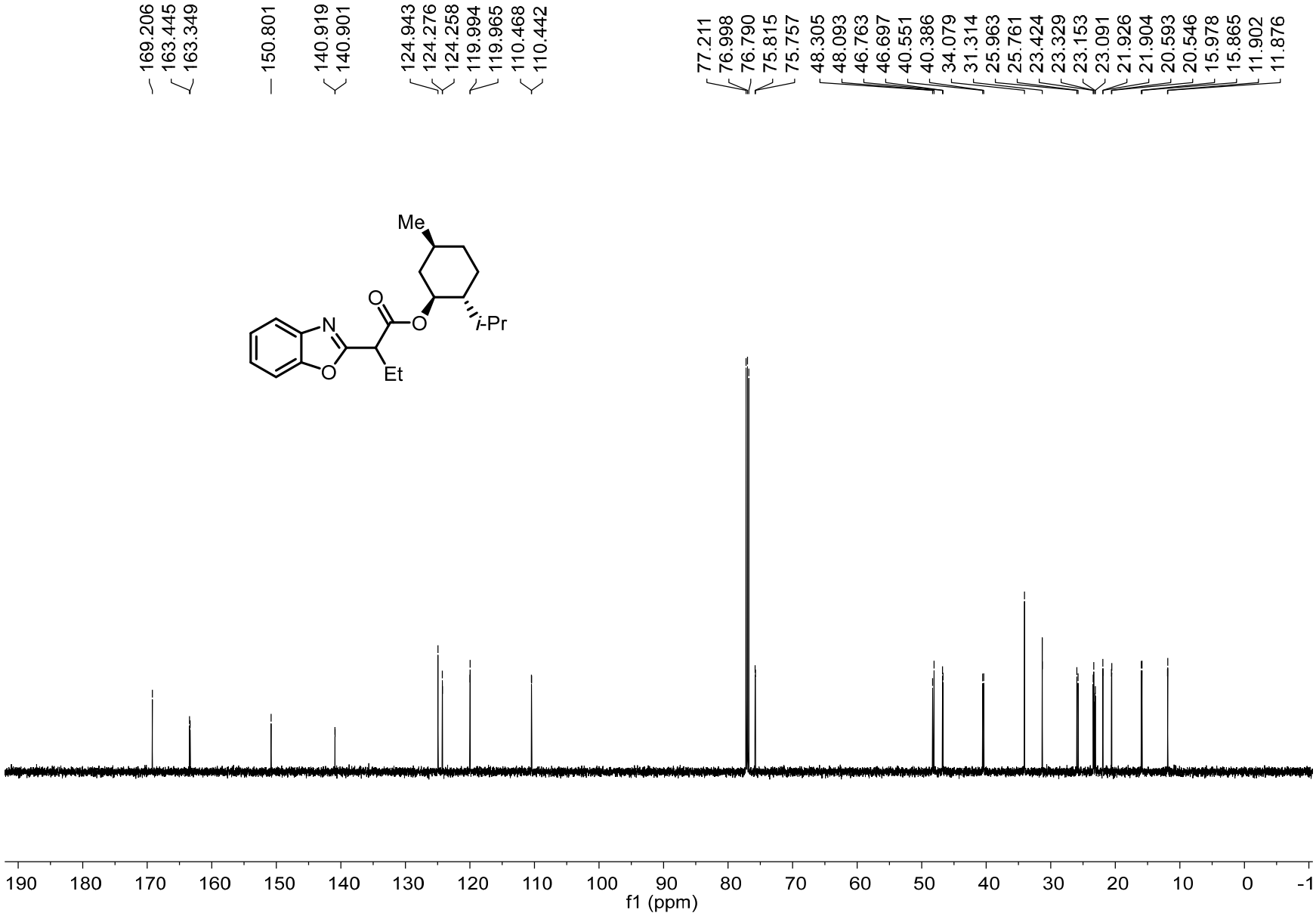

N
O
CO2i-Pr
Et
1.00
1.01
2.03
0.98
1.03
2.03
6.00
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

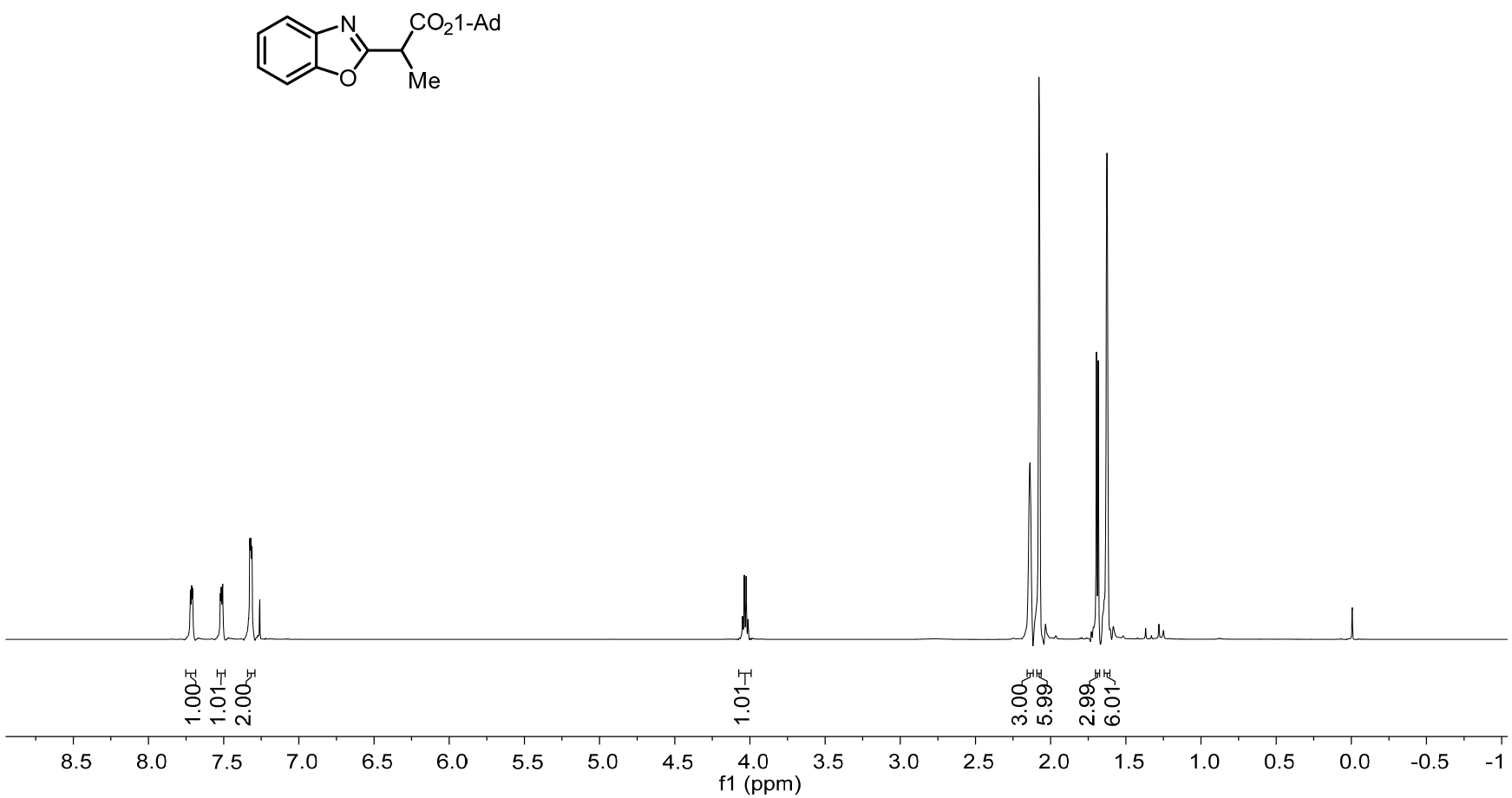

169.187
163.334
150.818
140.926
124.901
124.238
119.986
110.529
77.213
77.001
76.789
69.225
48.044
23.555
21.610
21.534
11.846
N
O
CO2i-Pr
Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

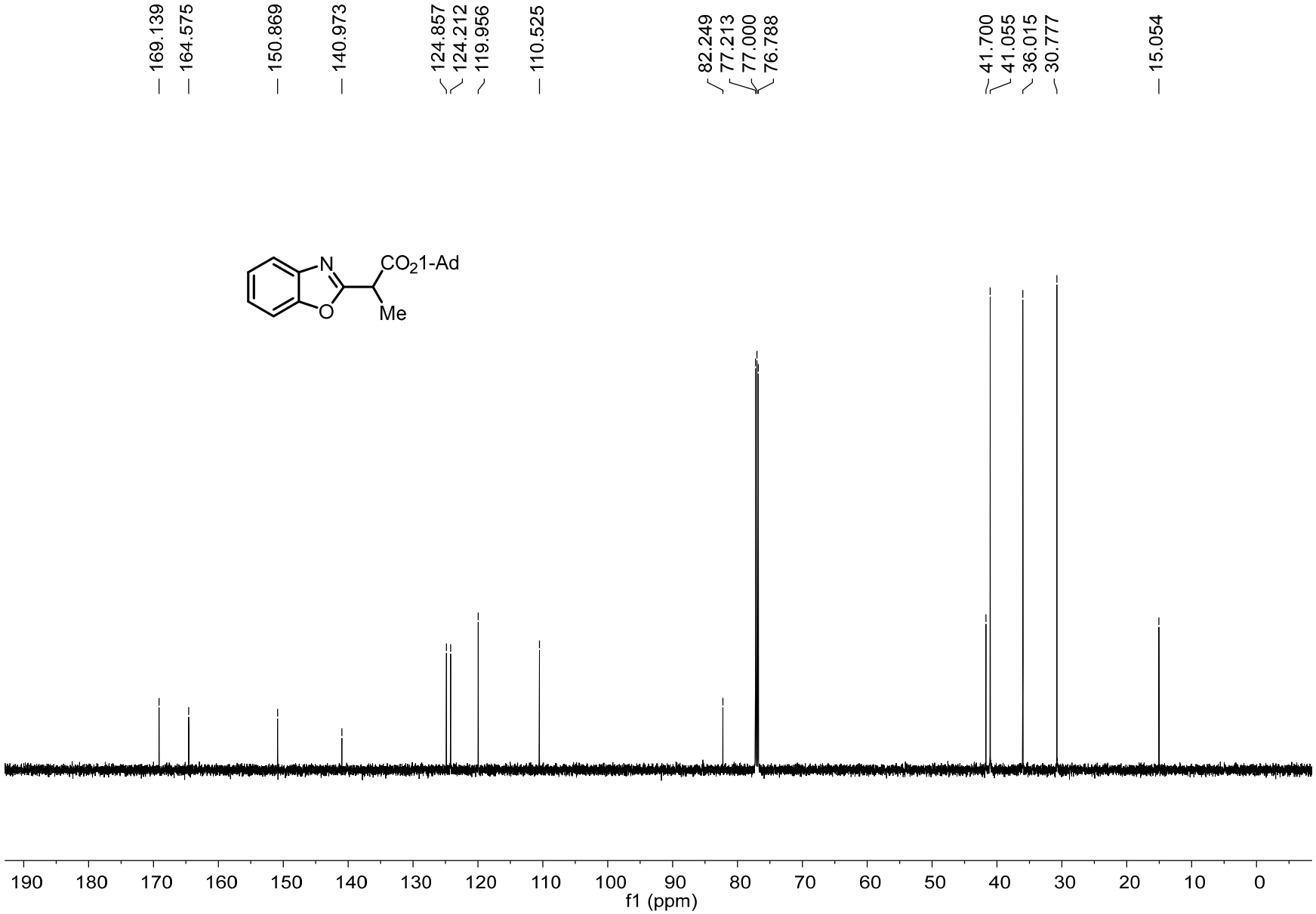

N
O
CO2t-Bu
Et
1.00
1.02
2.01
1.02
2.02
9.02
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

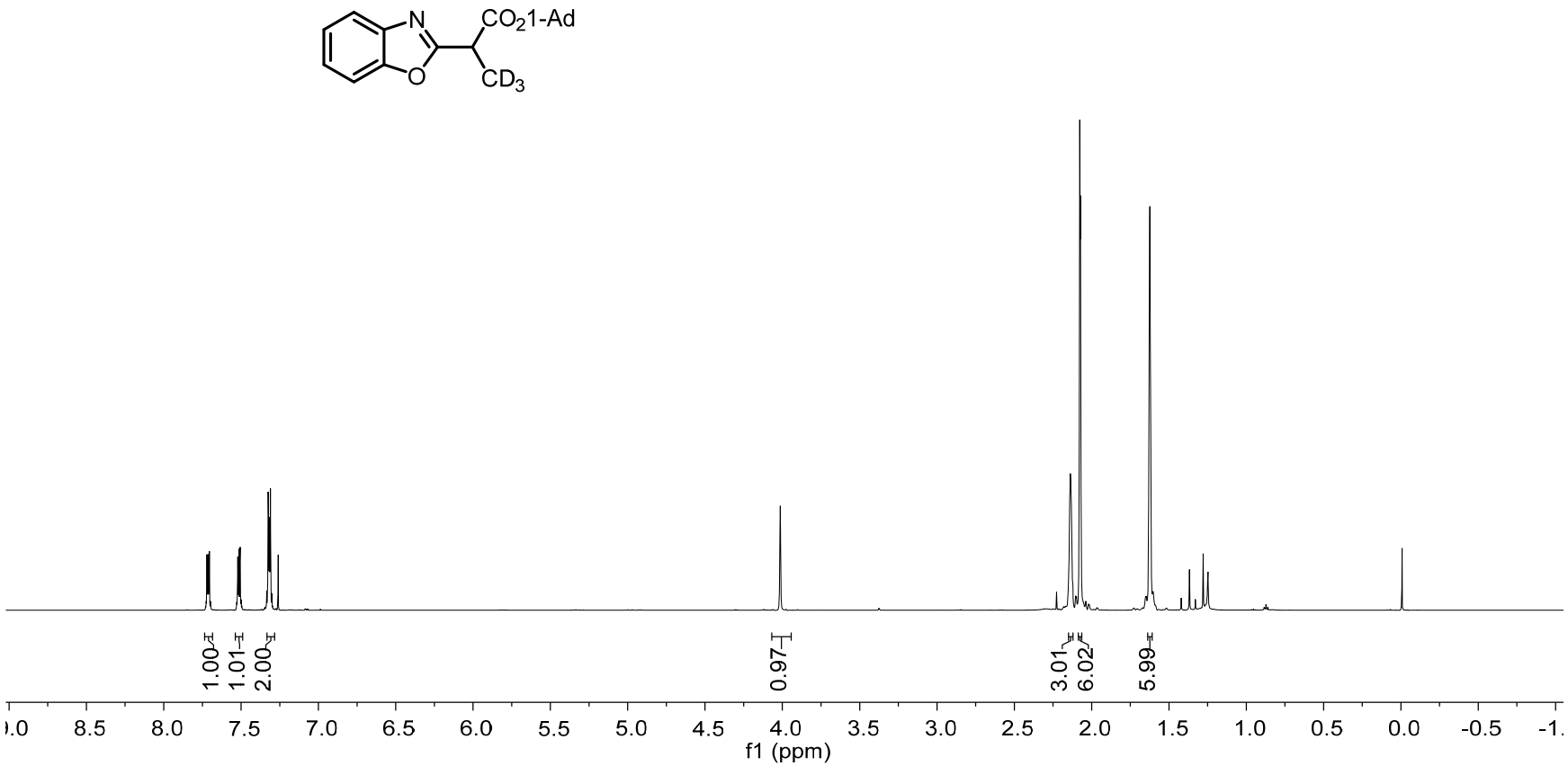

168.838
163.685
150.833
140.980
124.832
124.202
119.964
110.532
82.150
77.213
77.001
76.788
48.875
27.881
23.614
11.900
N
O
CO2t-Bu
Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

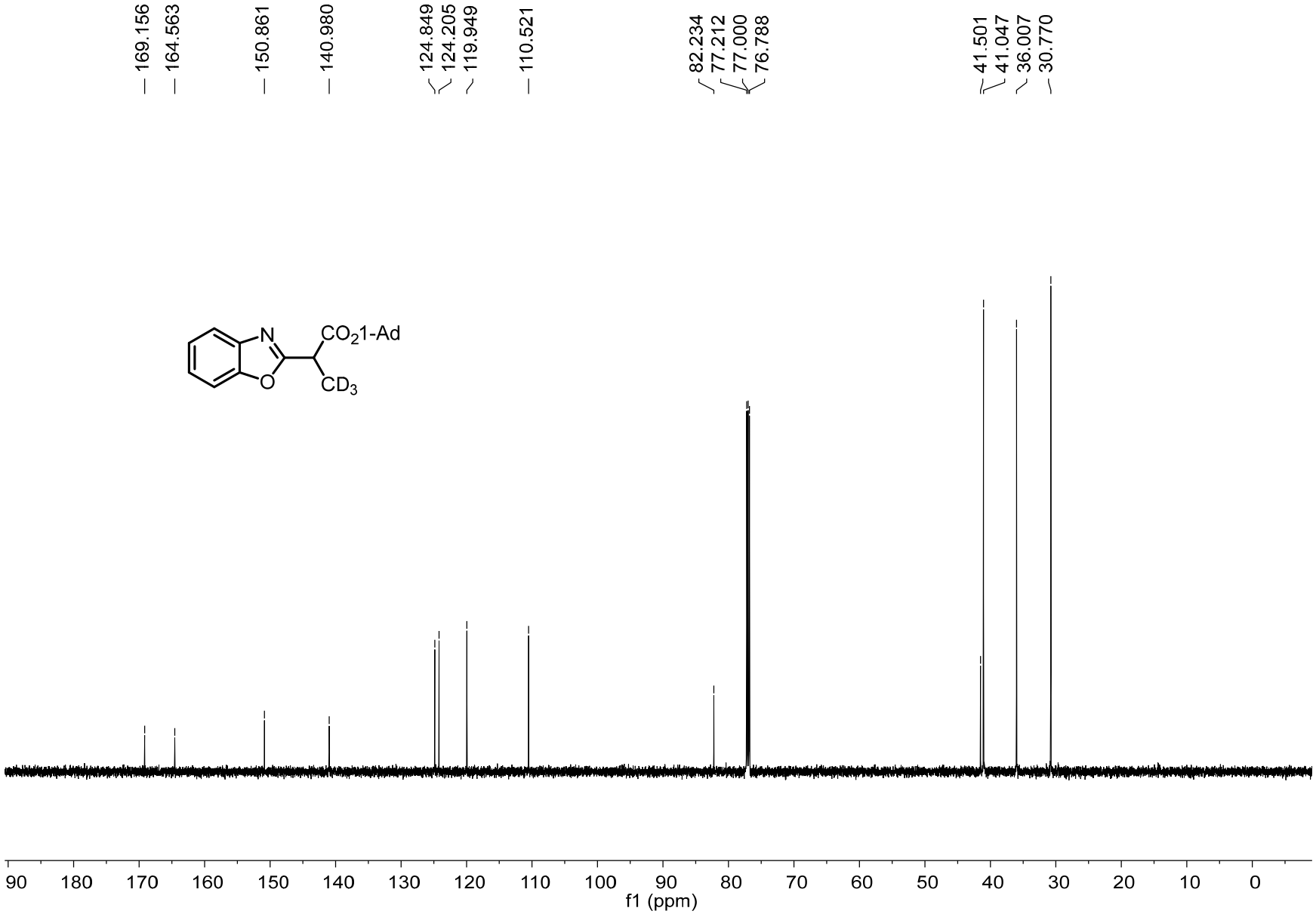

Me
O
O
N
O
i-Pr
Et
0.97
0.99
2.00
0.99
0.97
2.02
0.99
2.99
0.98
1.03
4.01
1.99
3.02
1.03
1.05
3.03
1.01
f1 (ppm)

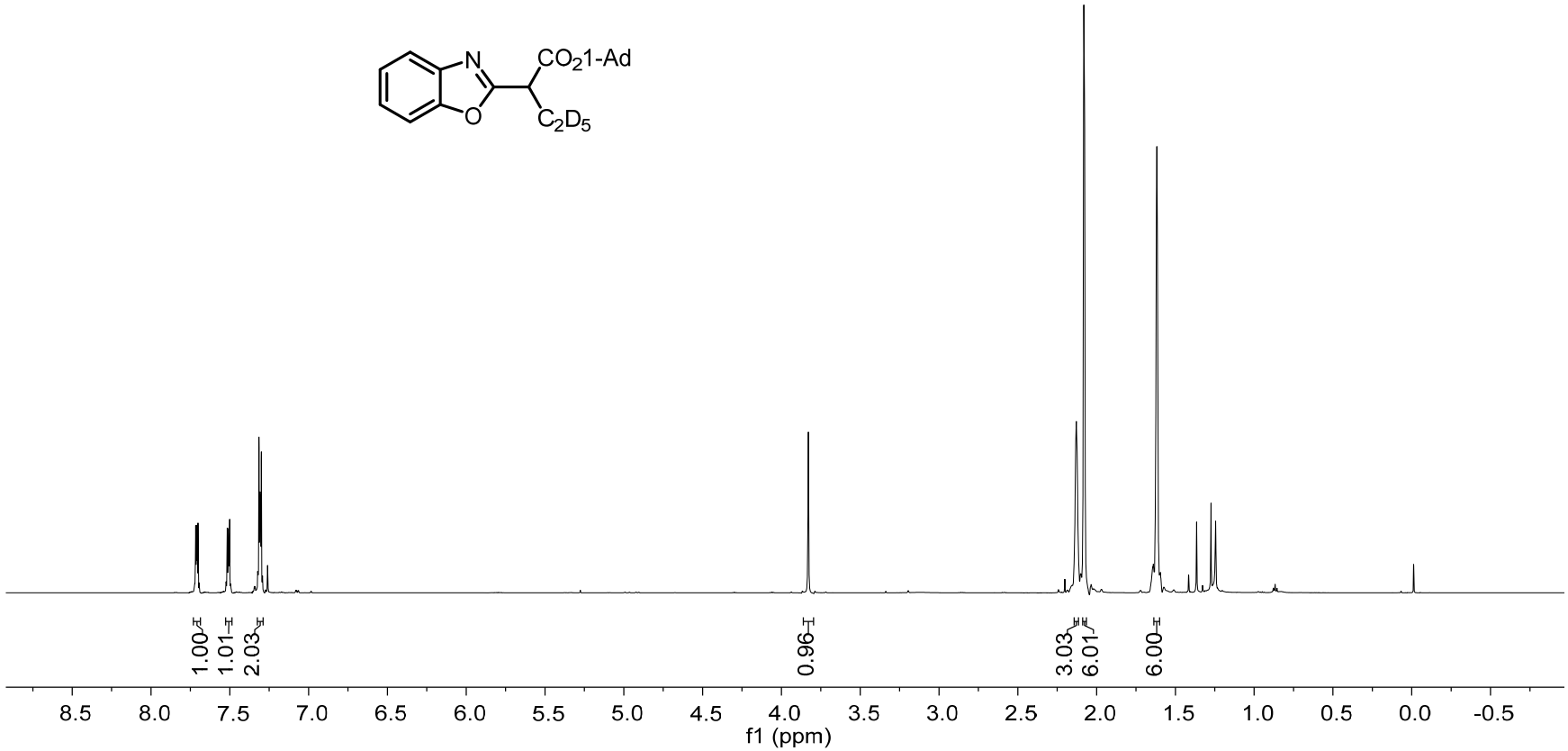

169.206
163.445
163.349
150.801
140.919
140.901
124.943
124.276
124.258
119.994
119.965
110.468
110.442
77.211
76.998
76.790
75.815
75.757
48.305
48.093
46.763
46.697
40.551
40.386
34.079
31.314
25.963
25.761
23.424
23.329
23.153
23.091
21.926
21.904
20.593
20.546
15.978
15.865
11.902
11.876
Me
O
O
N
O
i-Pr
Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

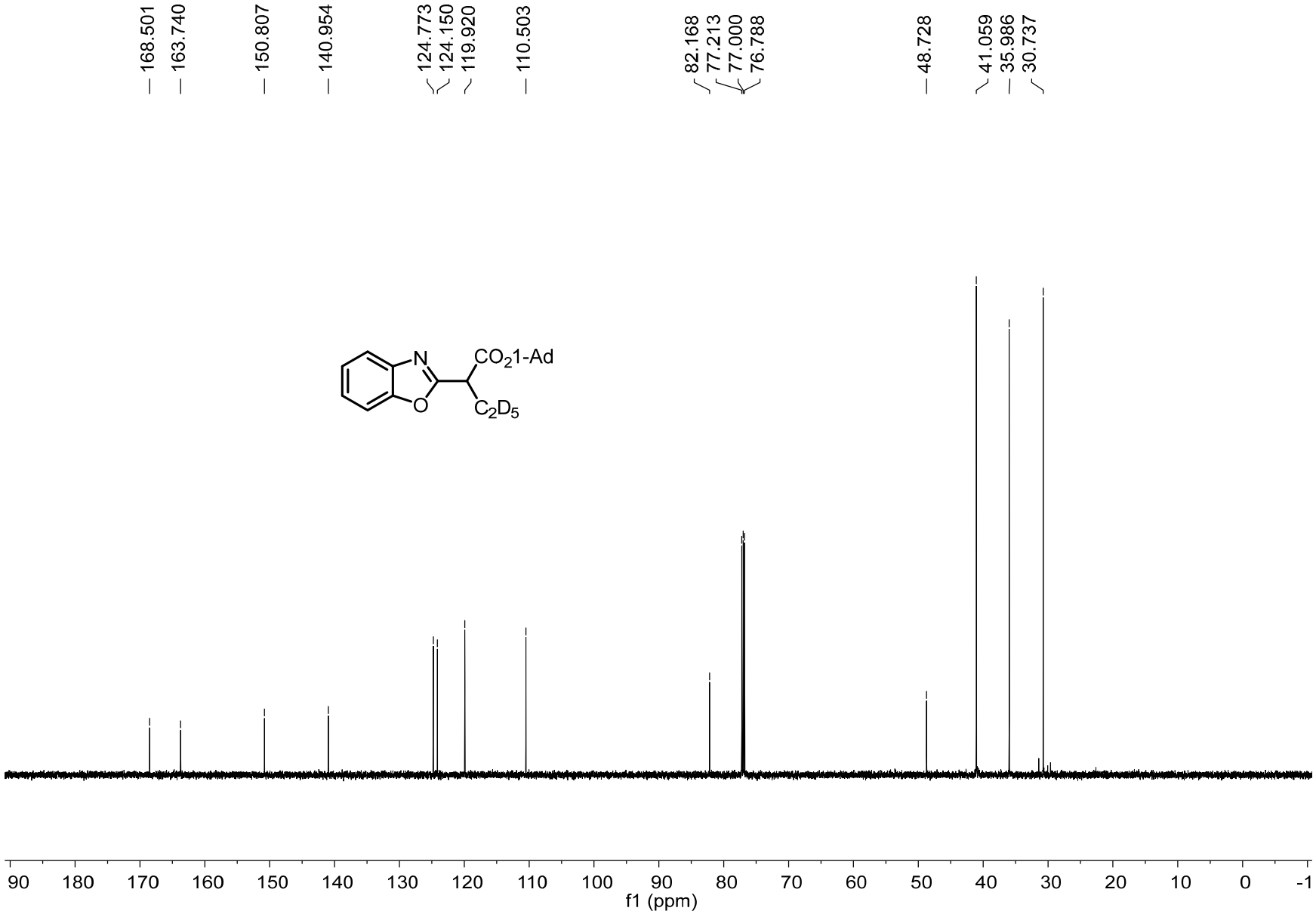

N
O
CO2 1-Ad
Me
1.00
1.01
2.00
1.01
3.00
5.99
2.99
6.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

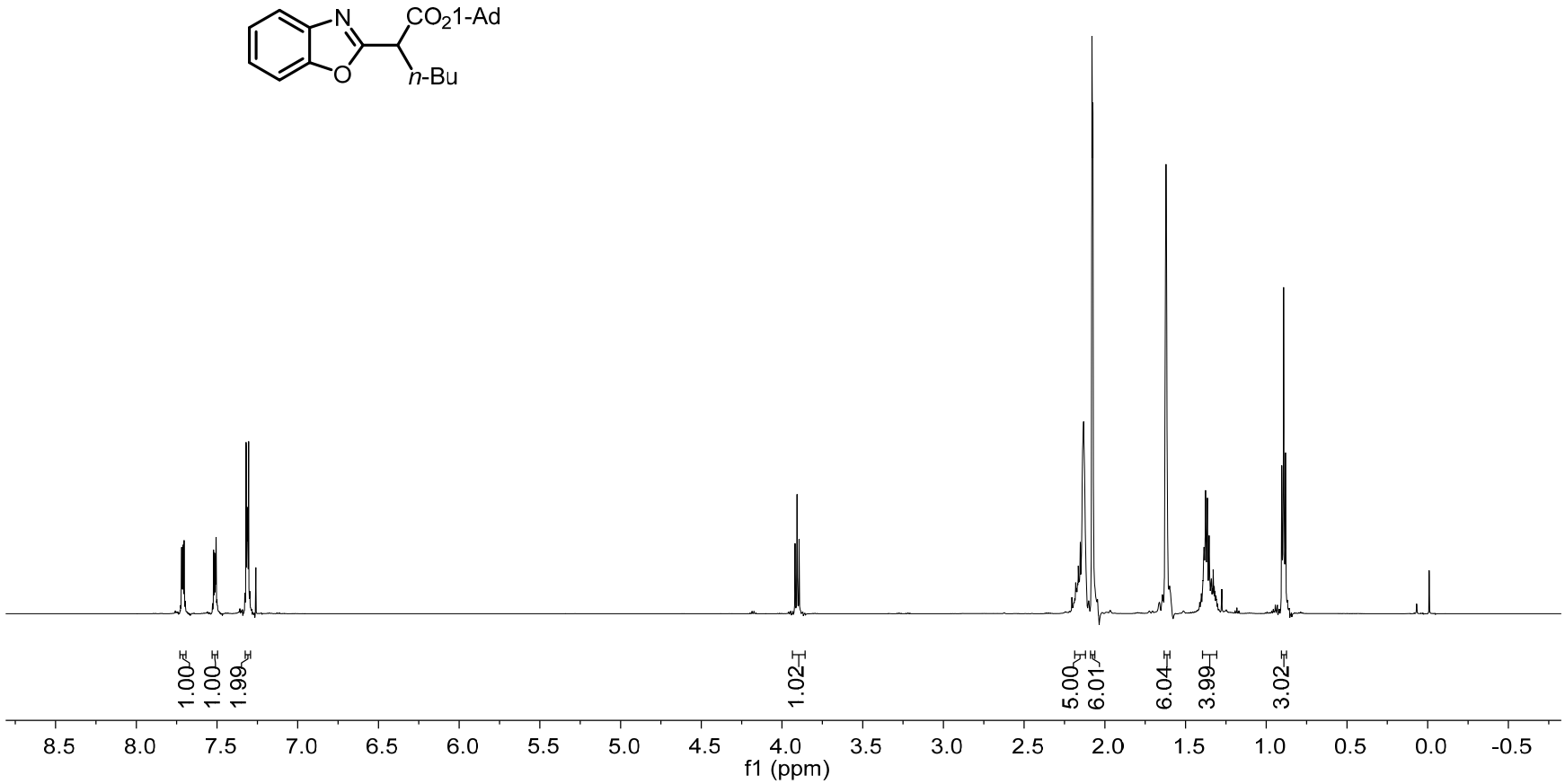

169.139
164.575
150.869
140.973
124.857
124.212
119.956
110.525
82.249
77.213
77.000
76.788
41.700
41.055
36.015
30.777
15.054
N
O
CO2 1-Ad
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

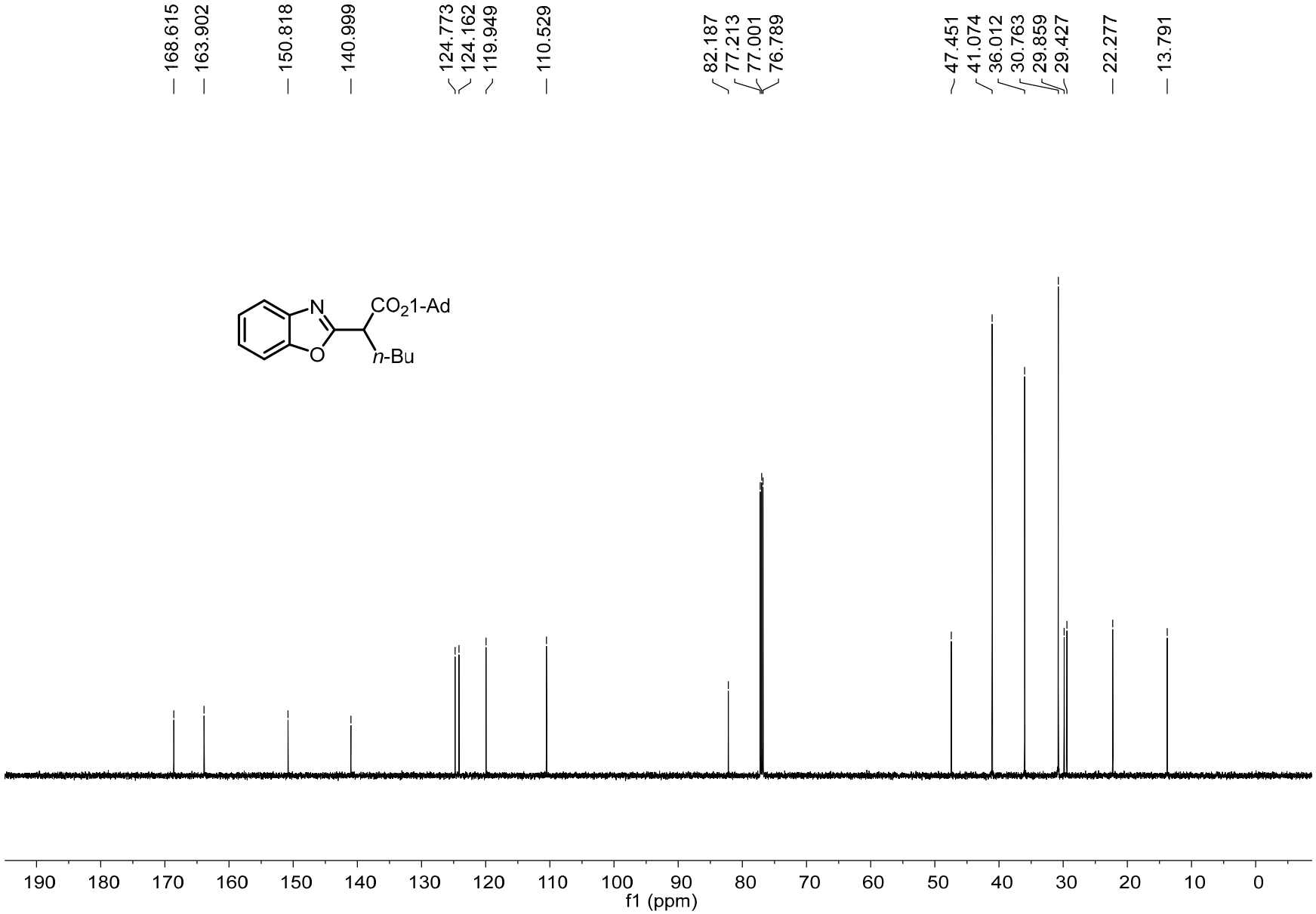

N
O
CO2 1-Ad
CD3
1.00
1.01
2.00
0.97
3.01
6.02
5.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

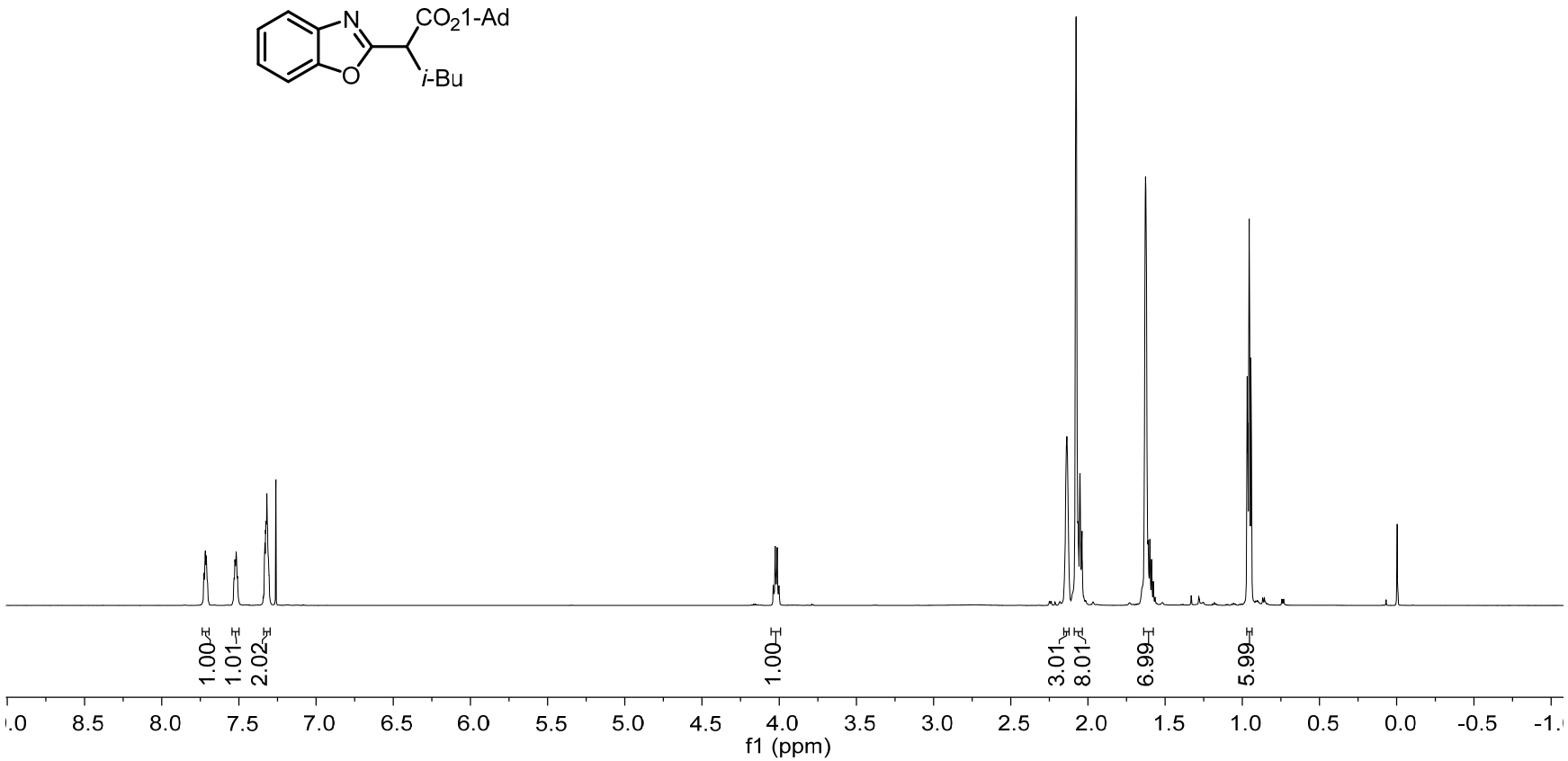

169.156
164.563
150.861
140.980
124.849
124.205
119.949
110.521
82.234
77.212
77.000
76.788
41.501
41.047
36.007
30.770
N
O
CO2 1-Ad
CD3
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

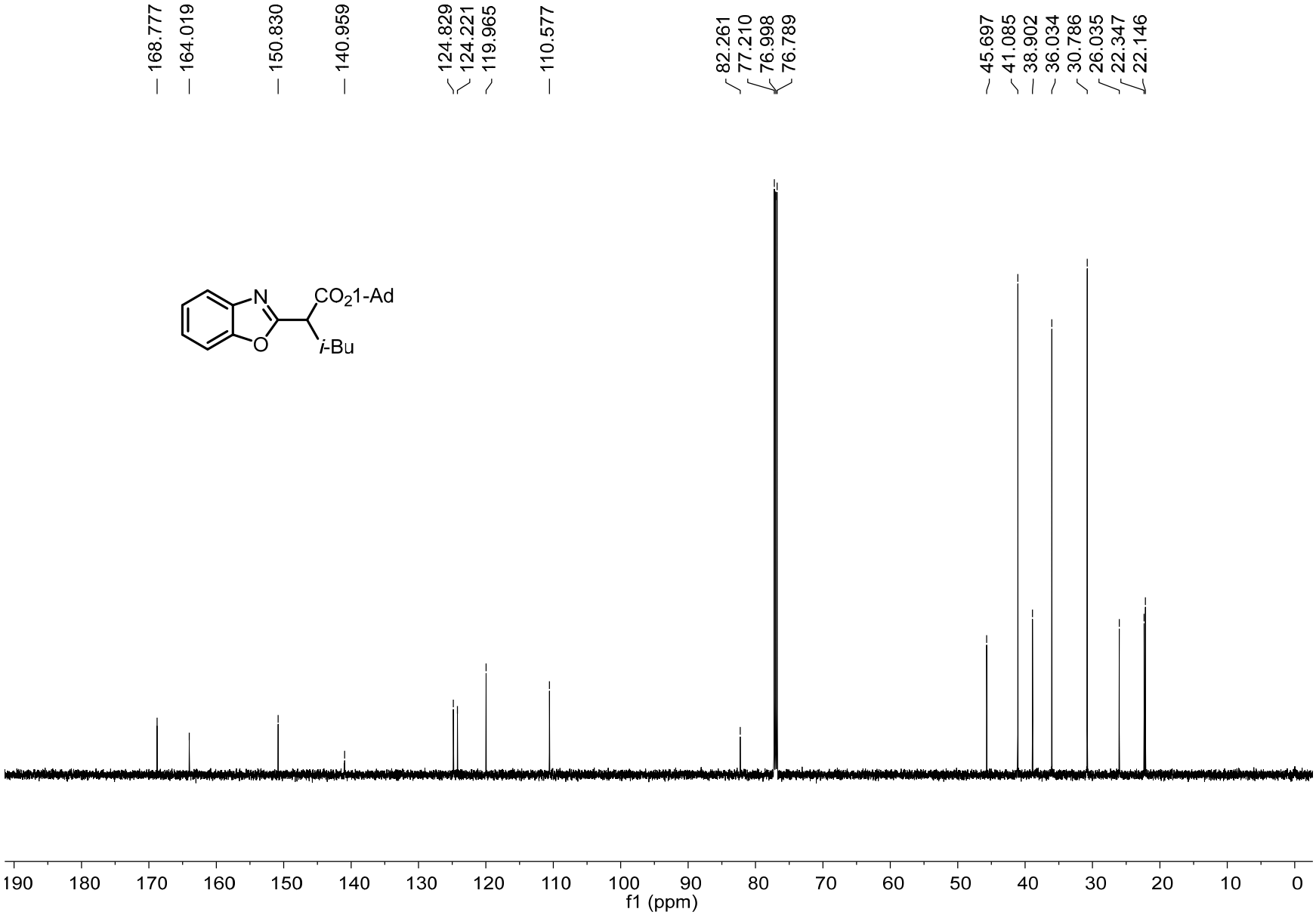

N
O
CO2 1-Ad
C2D5
1.00
1.01
2.03
0.96
3.03
6.01
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

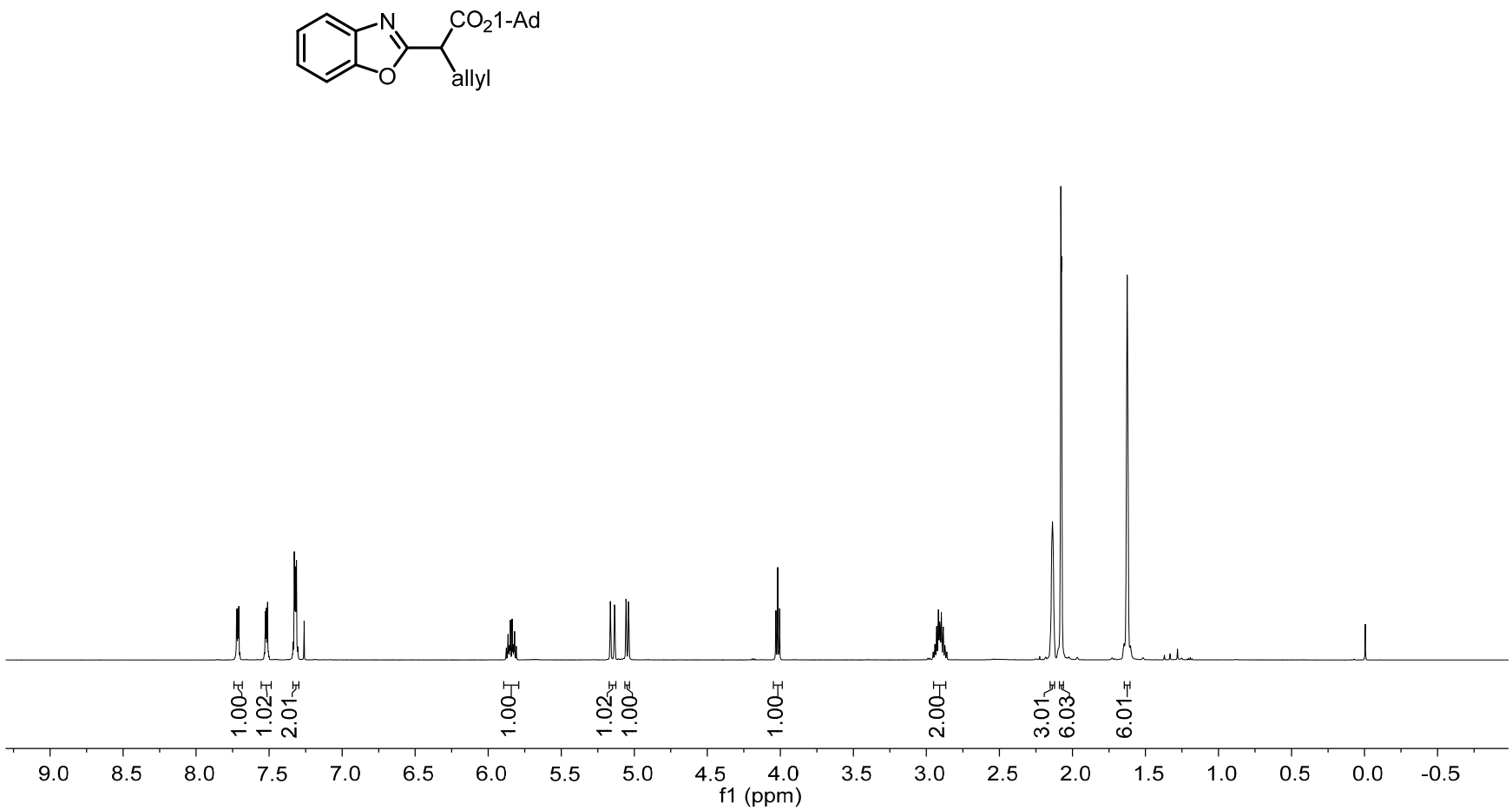

168.501
163.740
150.807
140.954
124.773
124.150
119.920
110.503
82.168
77.213
77.000
76.788
48.728
41.059
35.986
30.737
N
O
CO2 1-Ad
C2D5
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

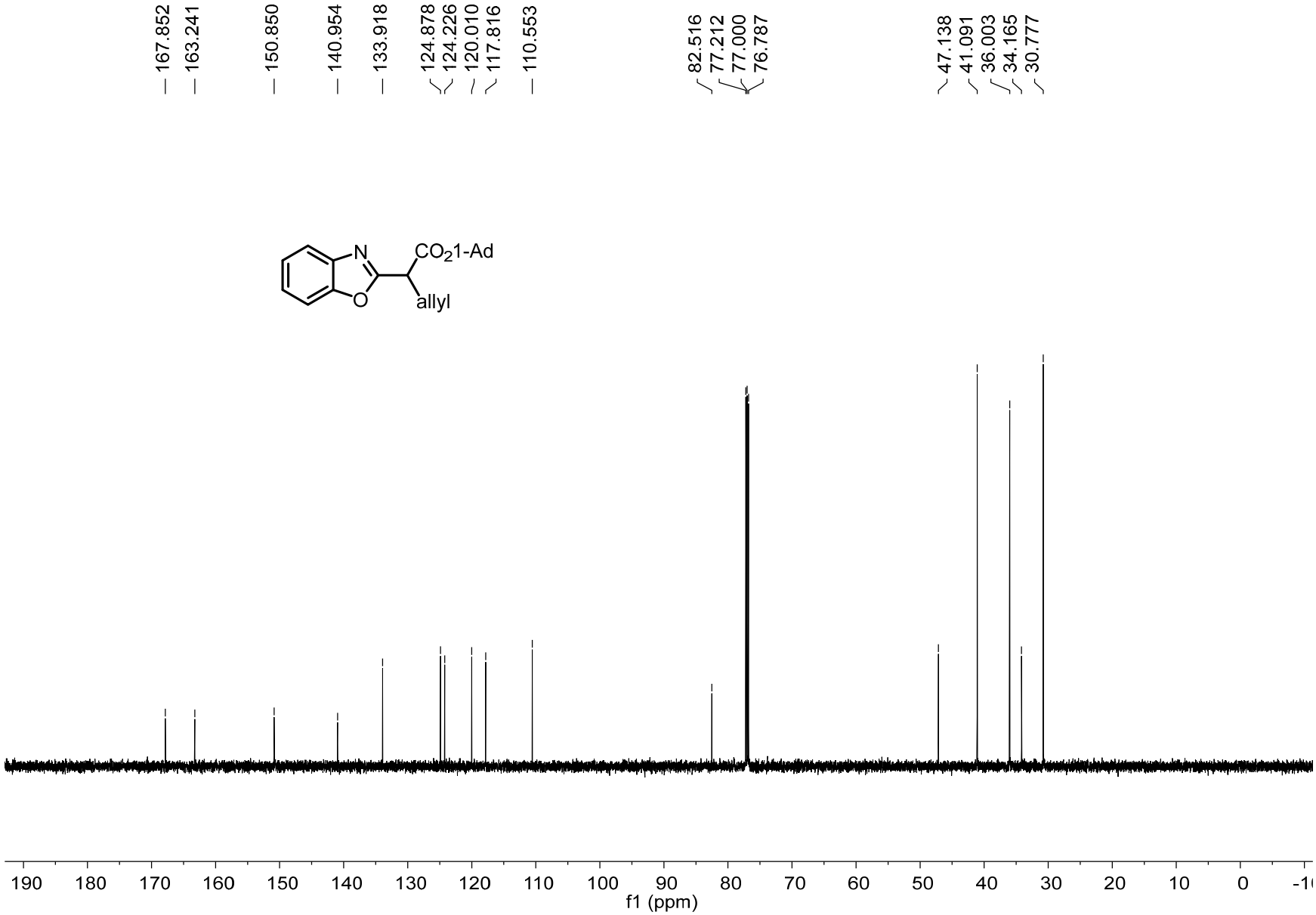

N
CO2 1-Ad
O
n-Bu
1.00
1.00
1.99
1.02
5.00
6.01
6.04
3.99
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

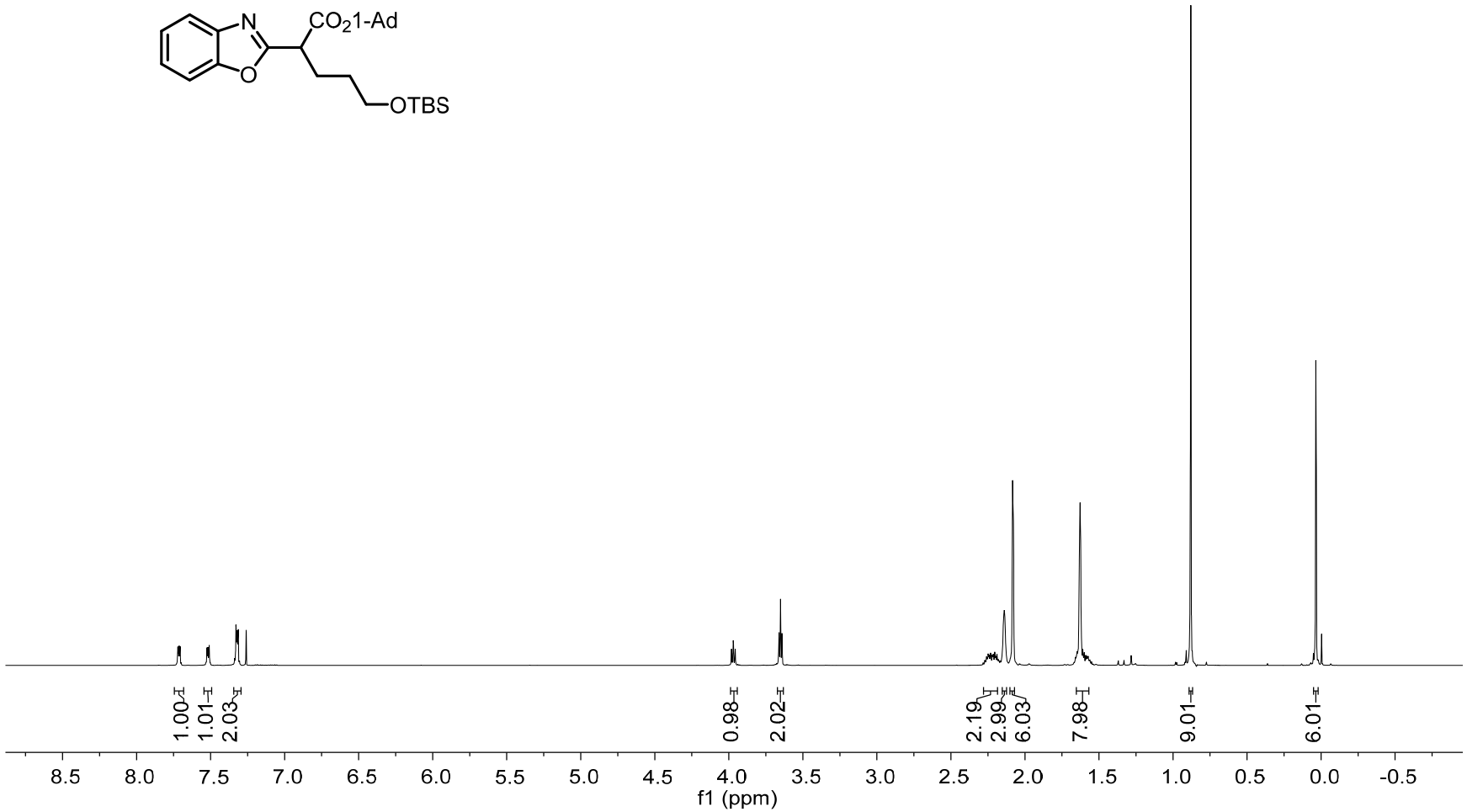

168.615
163.902
150.818
140.999
124.773
124.162
119.949
110.529
82.187
77.213
77.001
76.789
47.451
41.074
36.012
30.763
29.859
29.427
22.277
13.791
N
O
CO2 1-Ad
n-Bu
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

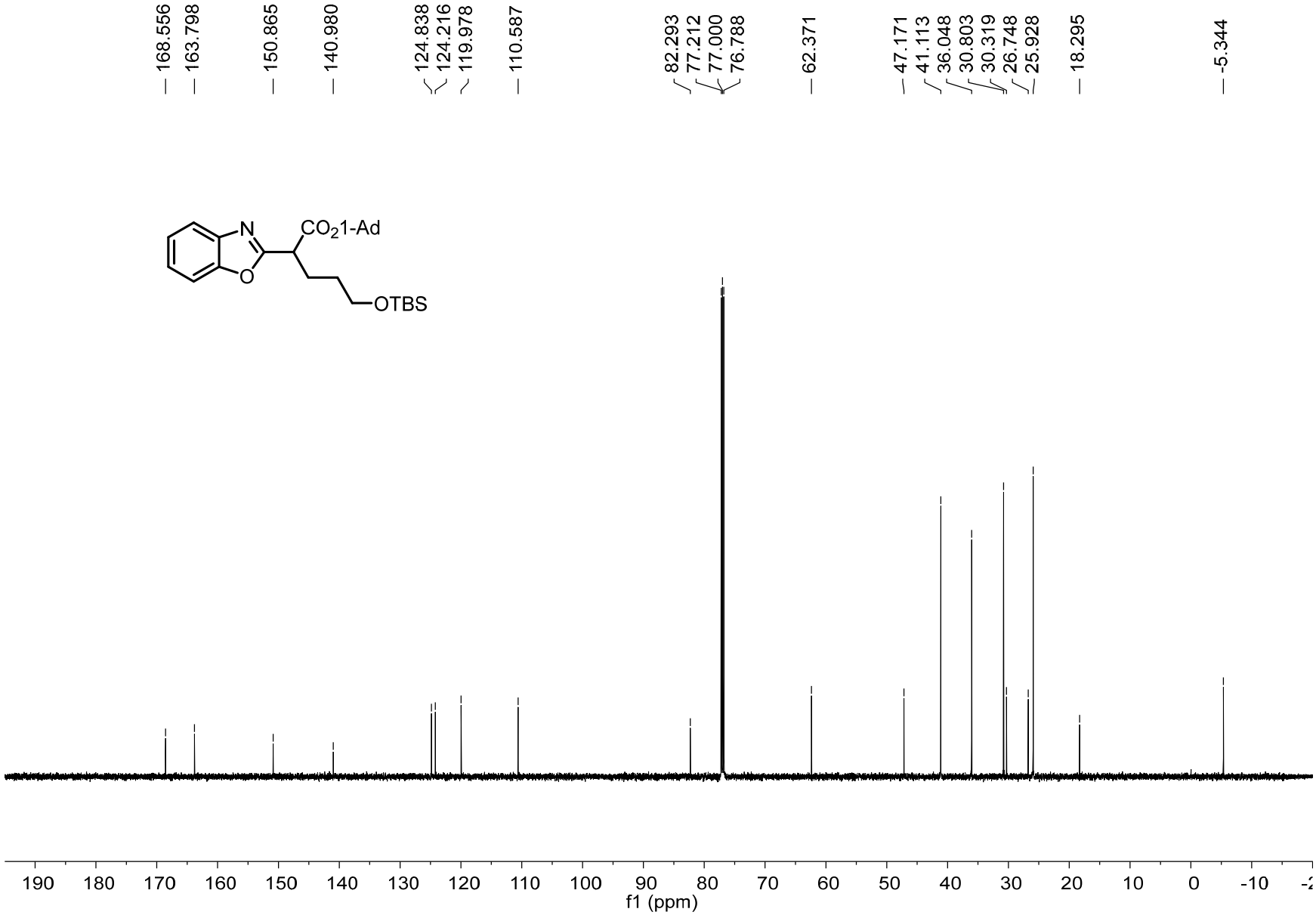

N
O
CO2 1-Ad
i-Bu
1.00
1.01
2.02
1.00
3.01
8.01
6.99
5.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

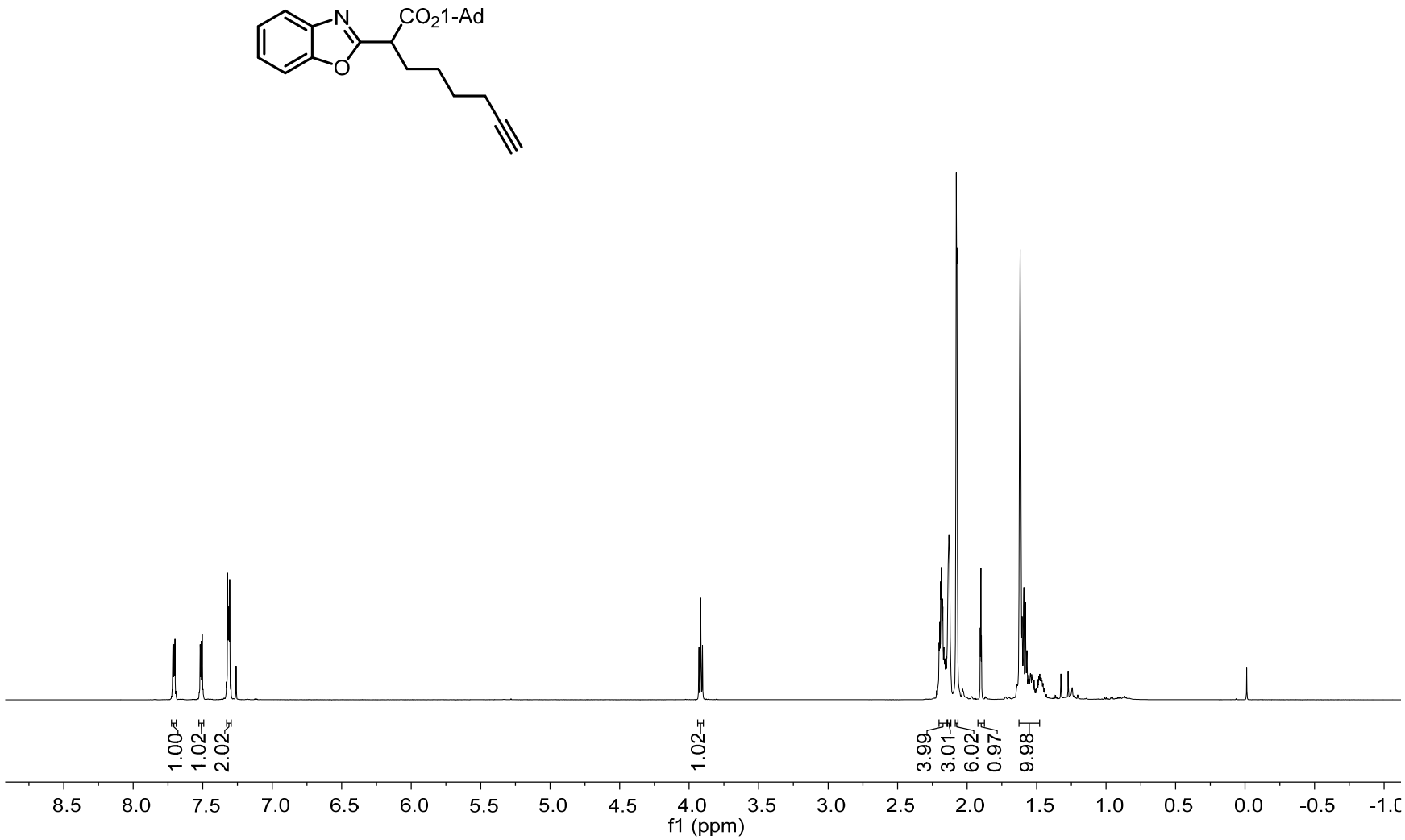

168.777
164.019
150.830
140.959
124.829
124.221
119.965
110.577
82.261
77.210
76.998
76.789
45.697
41.085
38.902
36.034
30.786
26.035
22.347
22.146
N
O
CO2 1-Ad
i-Bu
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

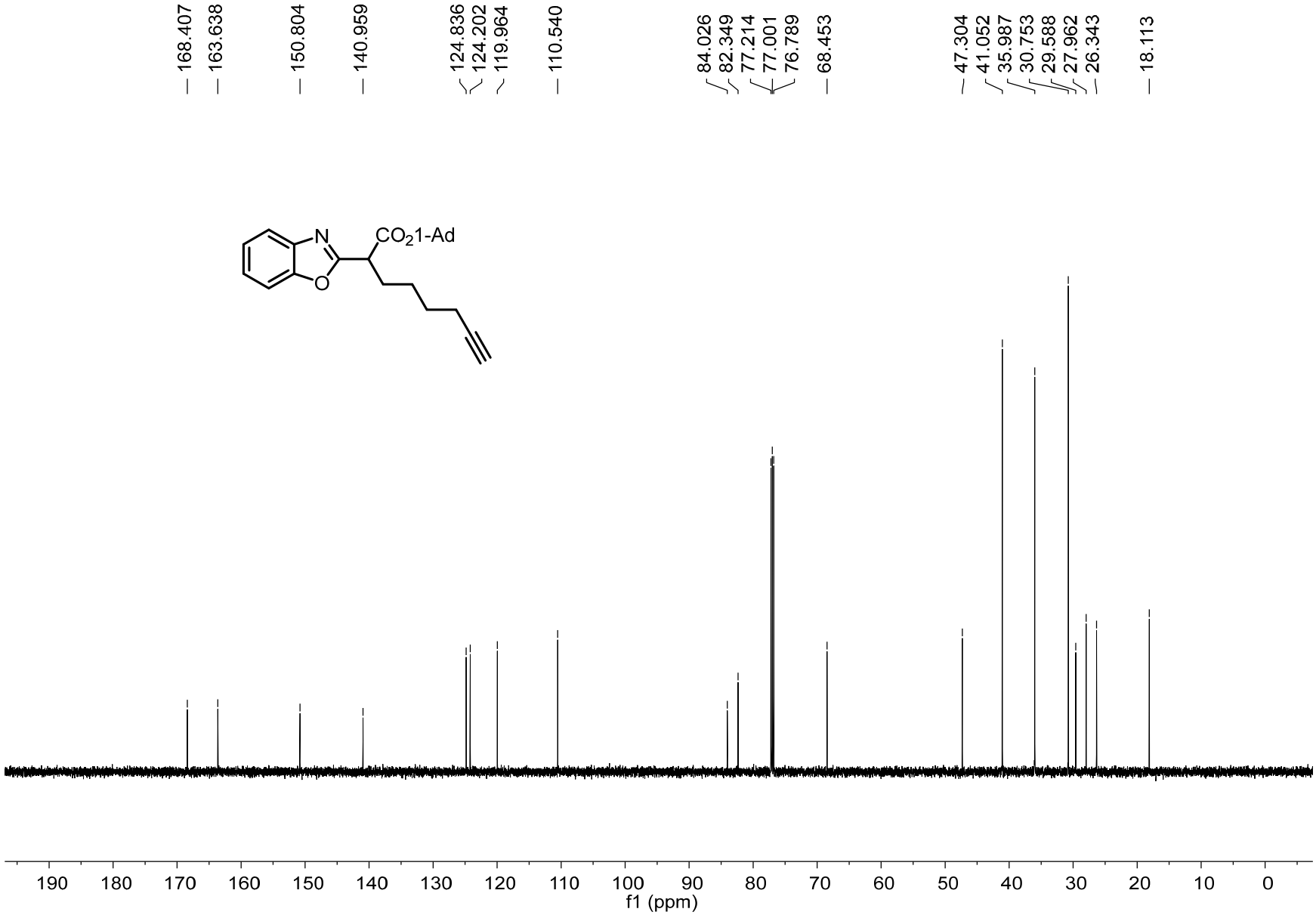

N
O
CO2 1-Ad
allyl
1.00
1.02
2.01
1.00
1.02
1.00
1.00
2.00
3.01
6.03
6.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

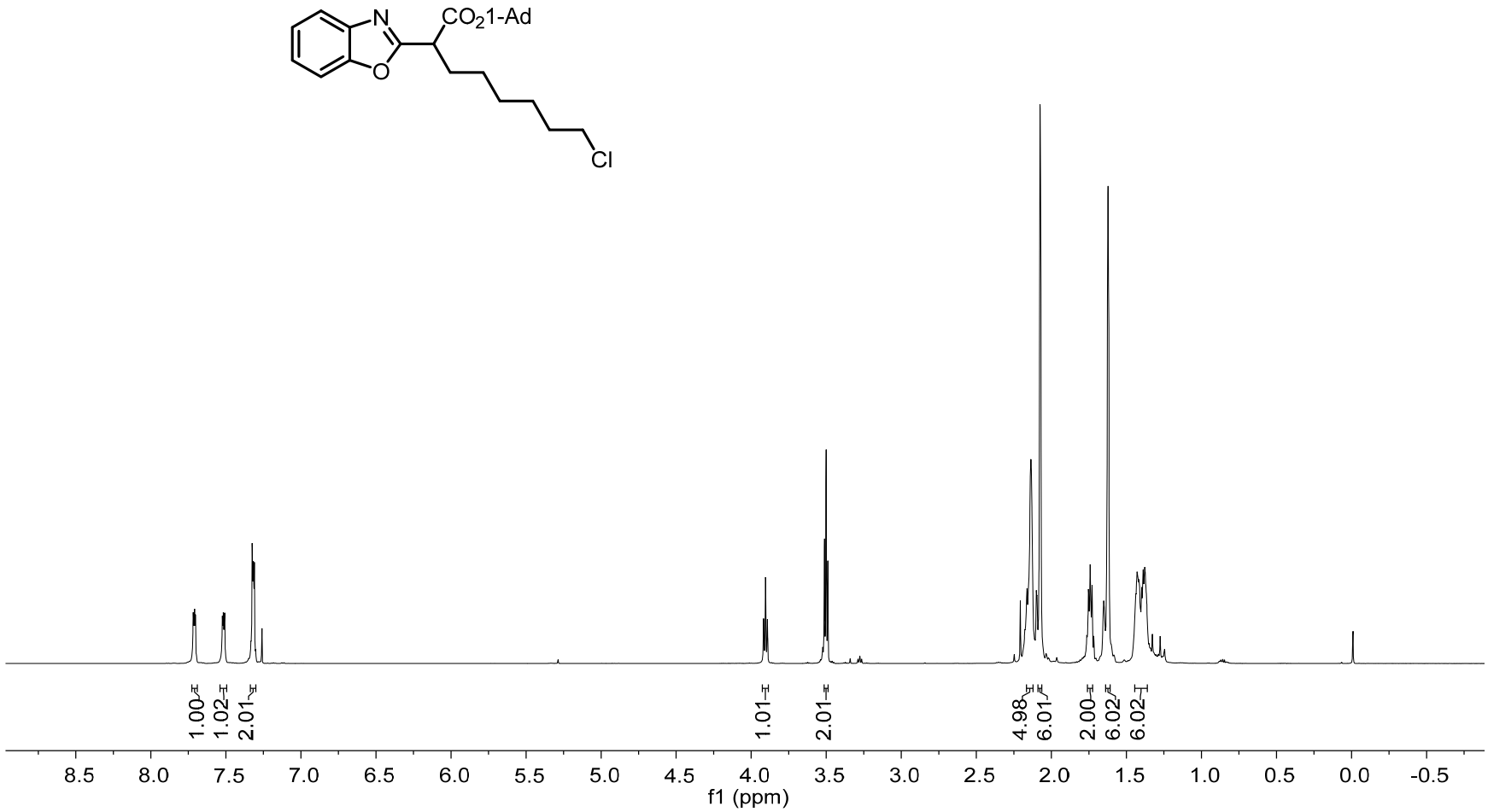

167.852
163.241
150.850
140.954
133.918
124.878
124.226
120.010
117.816
110.553
82.516
77.212
77.000
76.787
47.138
41.091
36.003
34.165
30.777
N
O
CO2
1-Ad
allyl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

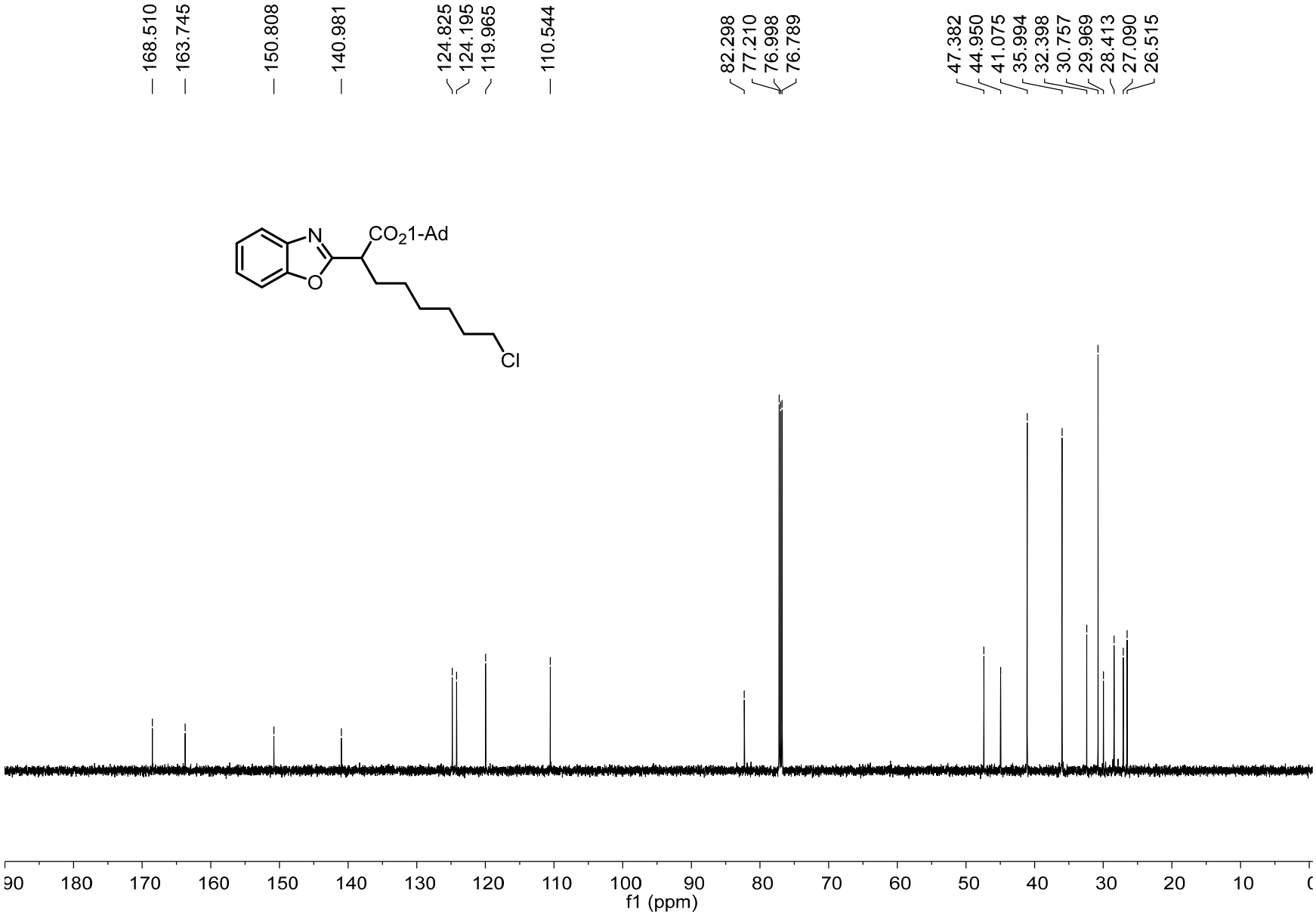

N
CO2 1-Ad
O
OTBS
1.00
1.01
2.03
0.98
2.02
2.19
2.99
6.03
7.98
9.01
6.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

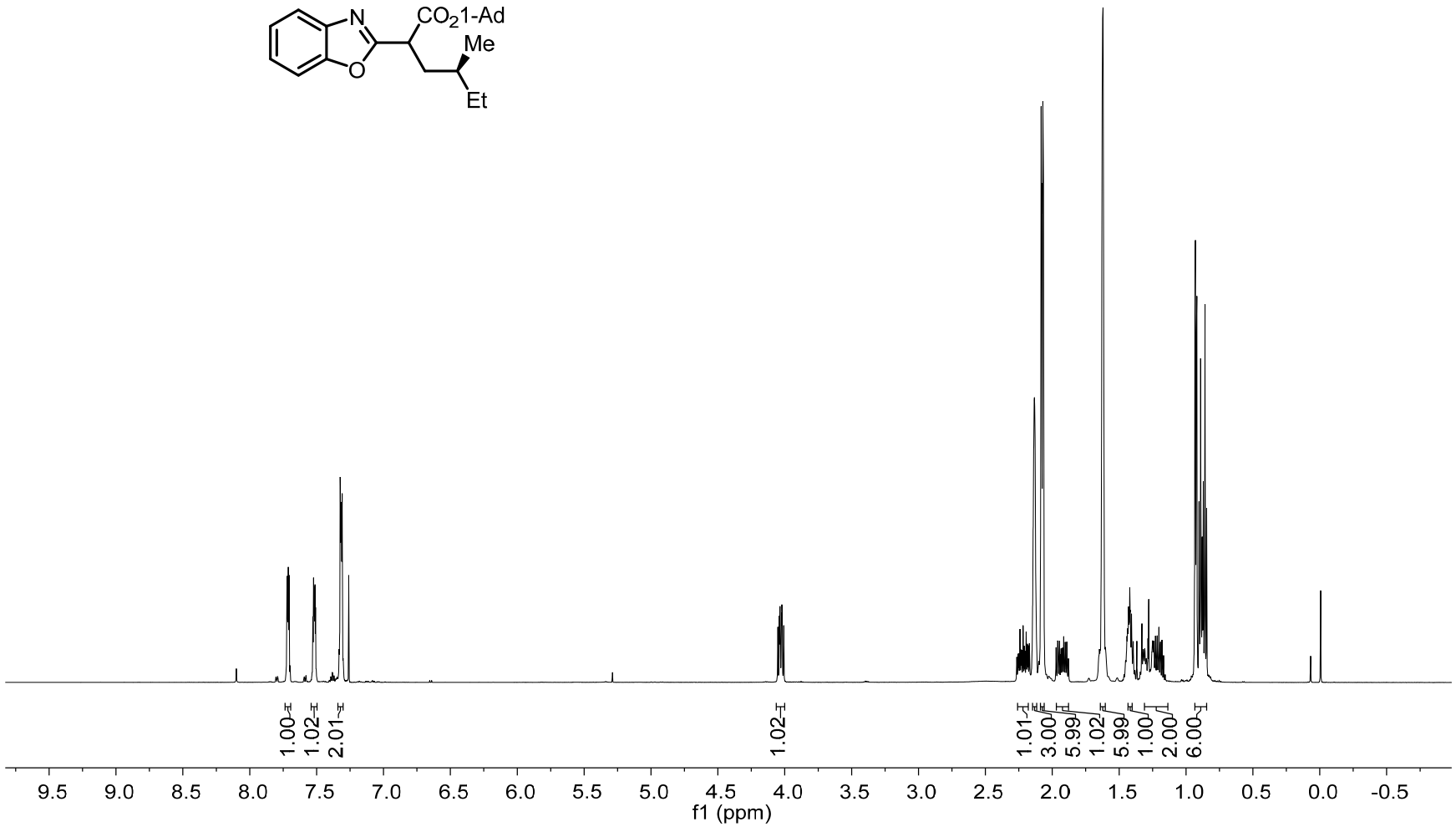

168.556
163.798
150.865
140.980
124.838
124.216
119.978
110.587
82.293
77.212
77.000
76.788
62.371
47.171
41.113
36.048
30.803
30.319
26.748
25.928
18.295
-5.344
N
O
CO2 1-Ad
OTBS
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

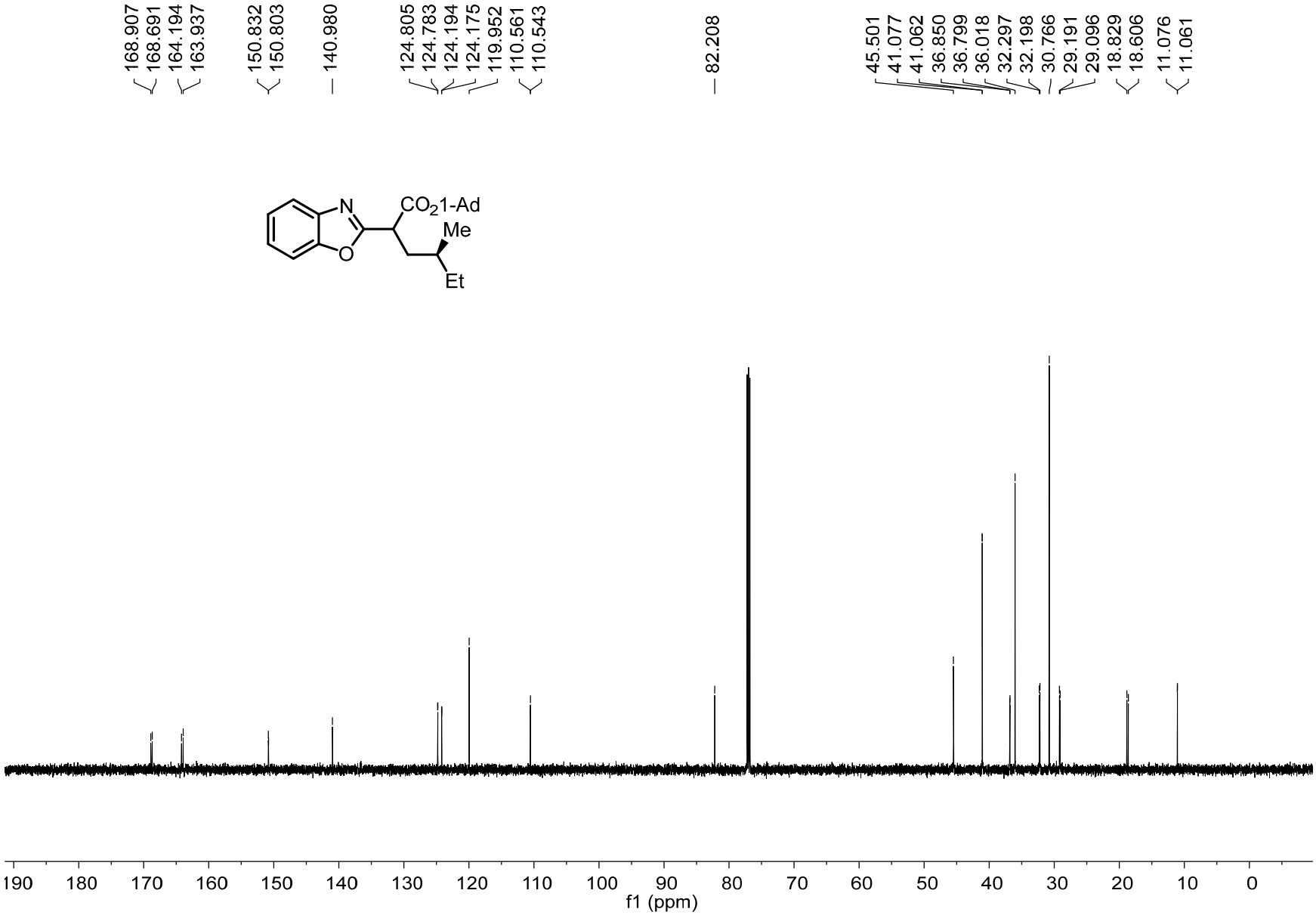

N
O
CO2 1-Ad
1.00
1.02
2.02
1.02
3.99
3.01
6.02
0.97
9.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

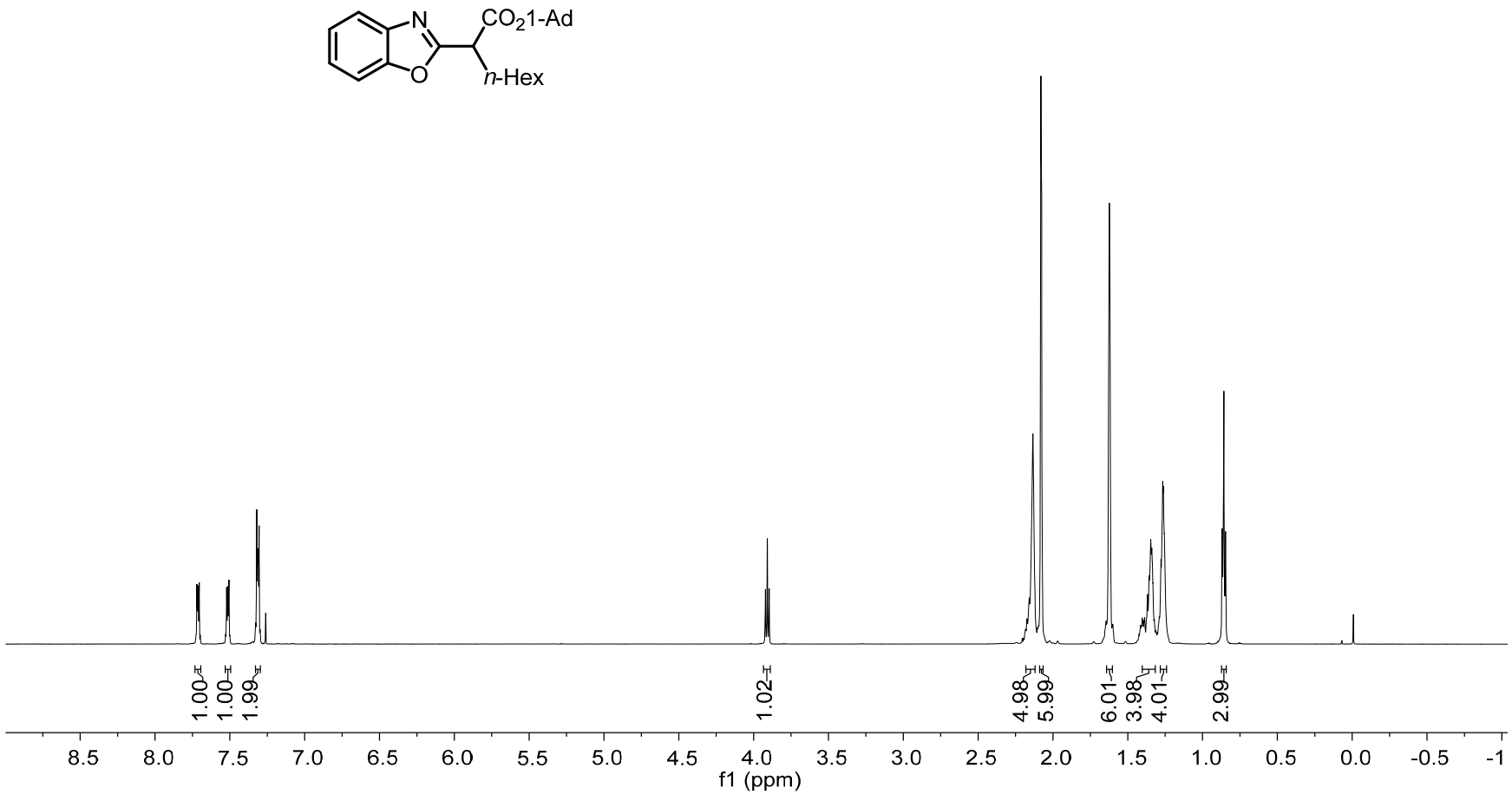

168.407
163.638
150.804
140.959
124.836
124.202
119.964
110.540
84.026
82.349
77.214
77.001
76.789
68.453
47.304
41.052
35.987
30.753
29.588
27.962
26.343
18.113
N
O
CO2 1-Ad
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

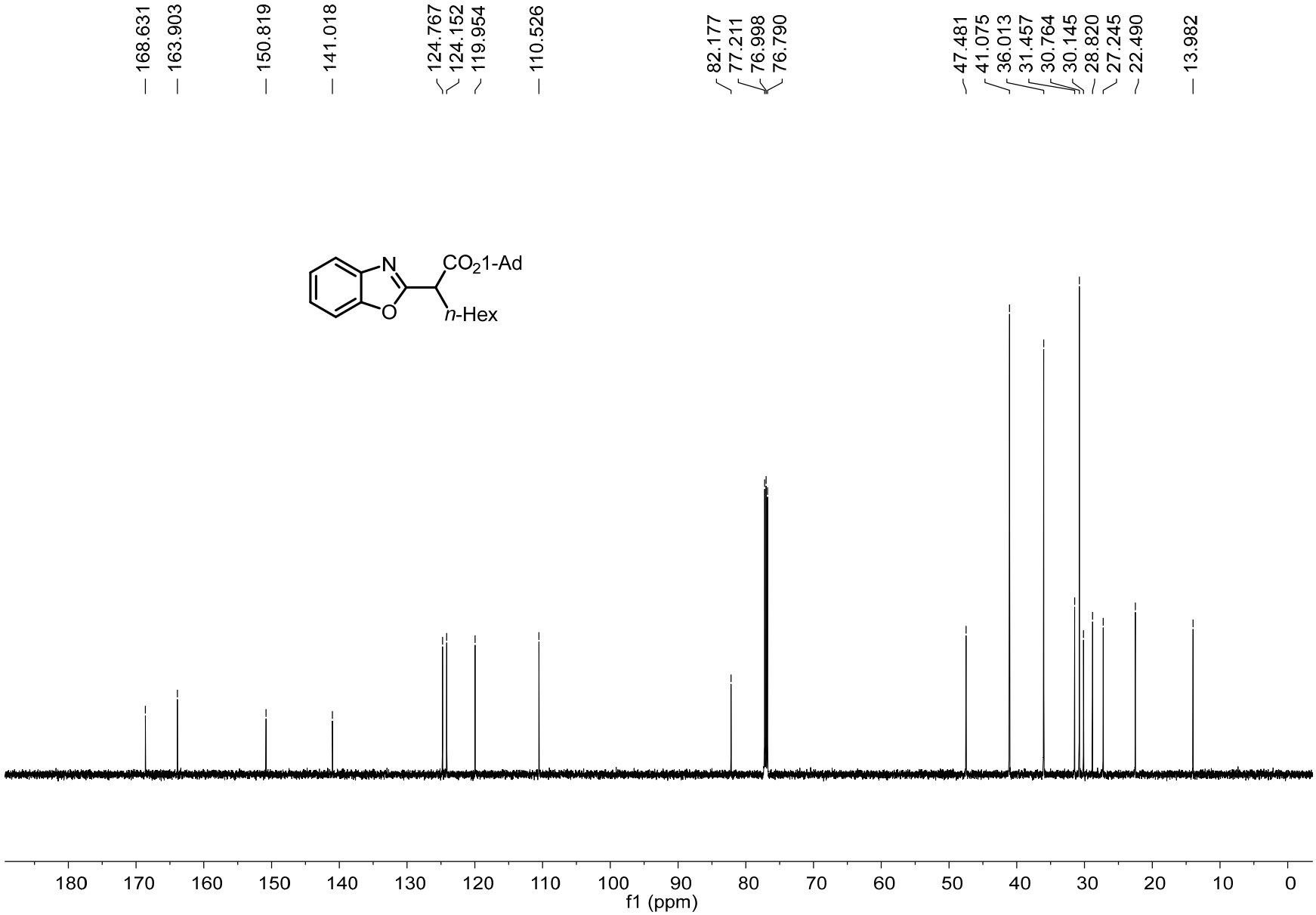

N
O
CO2 1-Ad
Cl
1.00
1.02
2.01
1.01
2.01
4.98
6.01
2.00
6.02
6.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

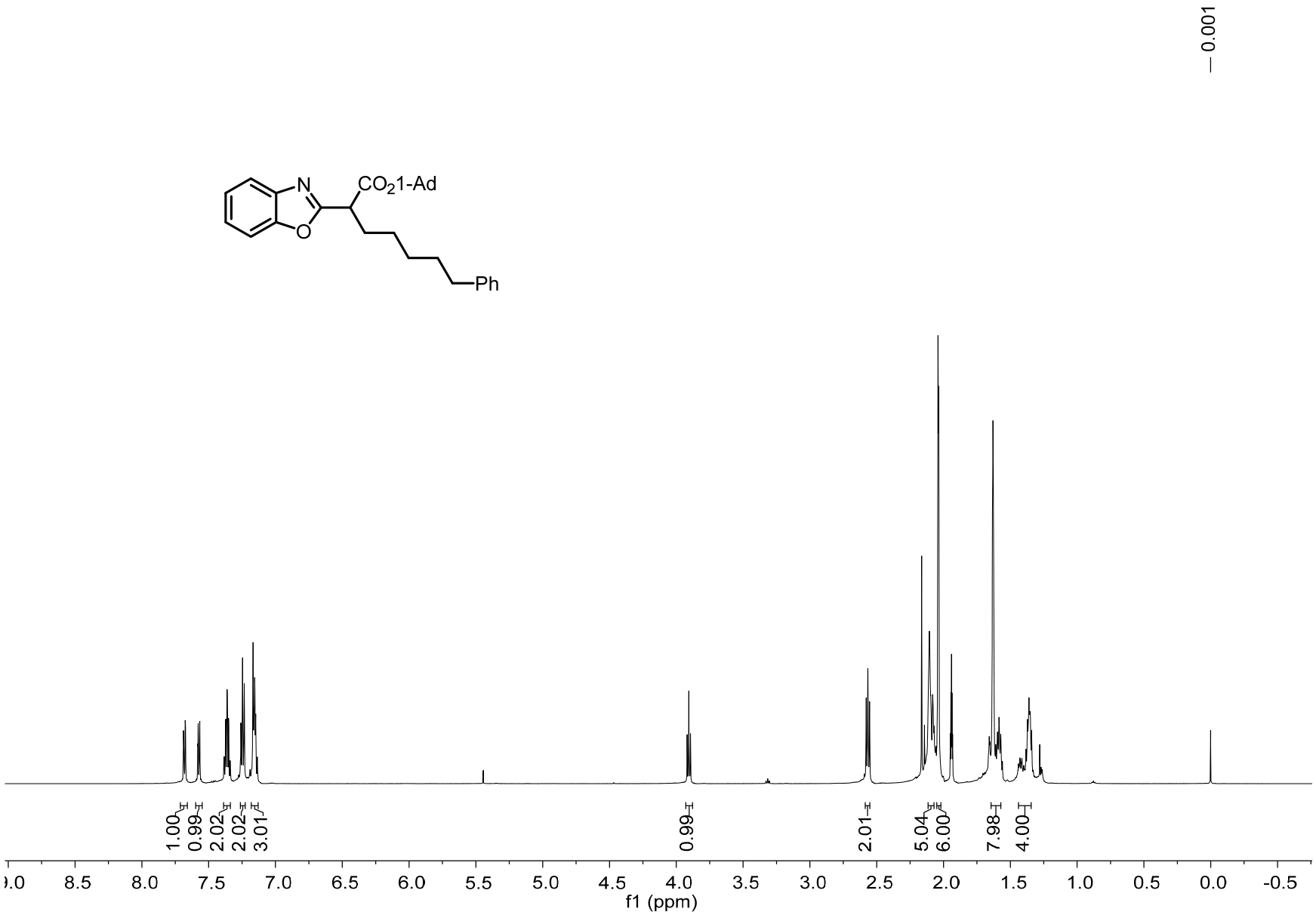

168.510
163.745
150.808
140.981
124.825
124.195
119.965
110.544
82.298
77.210
76.998
76.789
47.382
44.950
41.075
35.994
32.398
30.757
29.969
28.413
27.090
26.515
N
O
CO2
1-Ad
Cl
f1 (ppm)

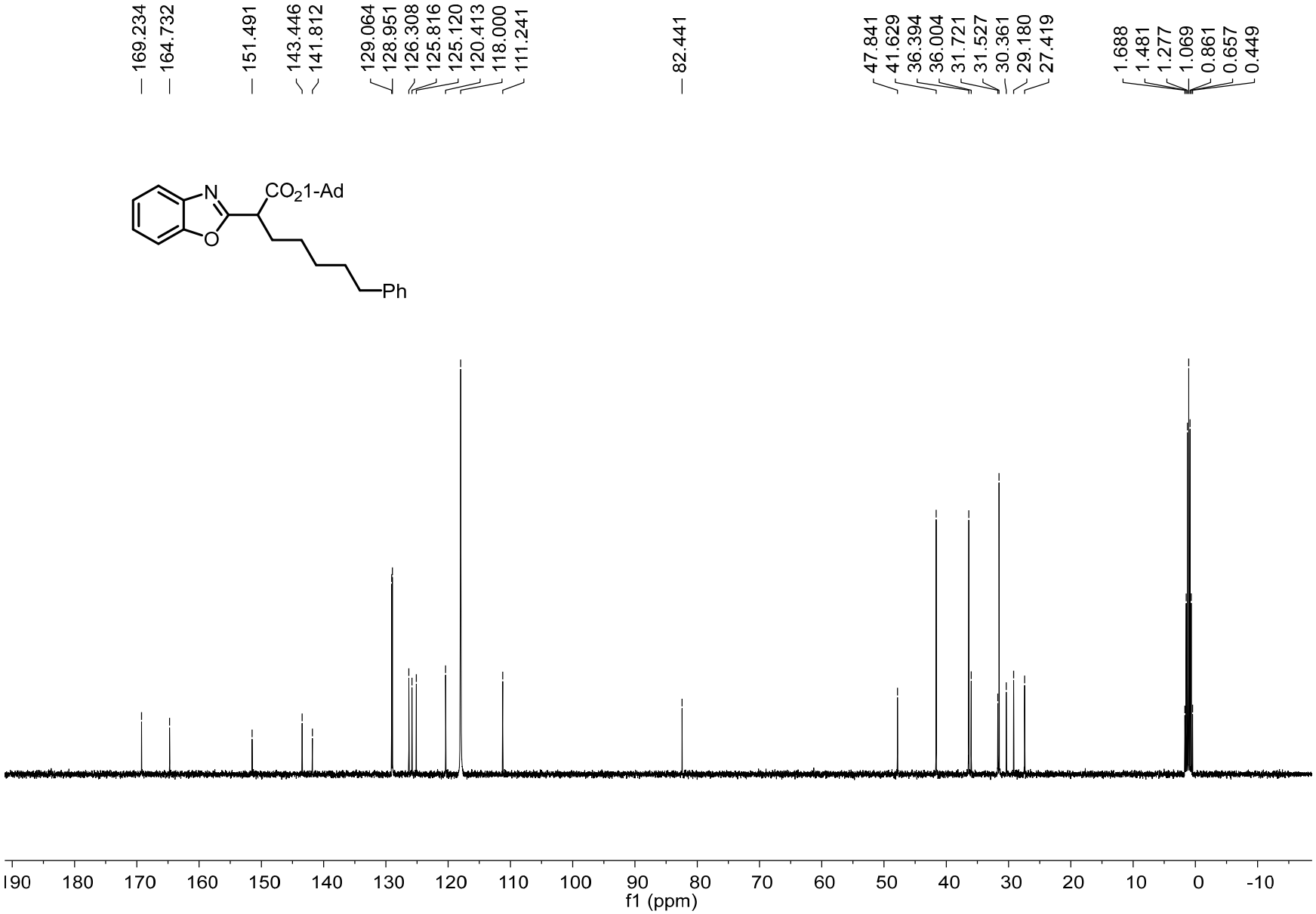

N
O
CO2 1-Ad
Me
Et
1.00
1.02
2.01
1.02
1.01
3.00
5.99
1.02
5.99
1.00
2.00
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

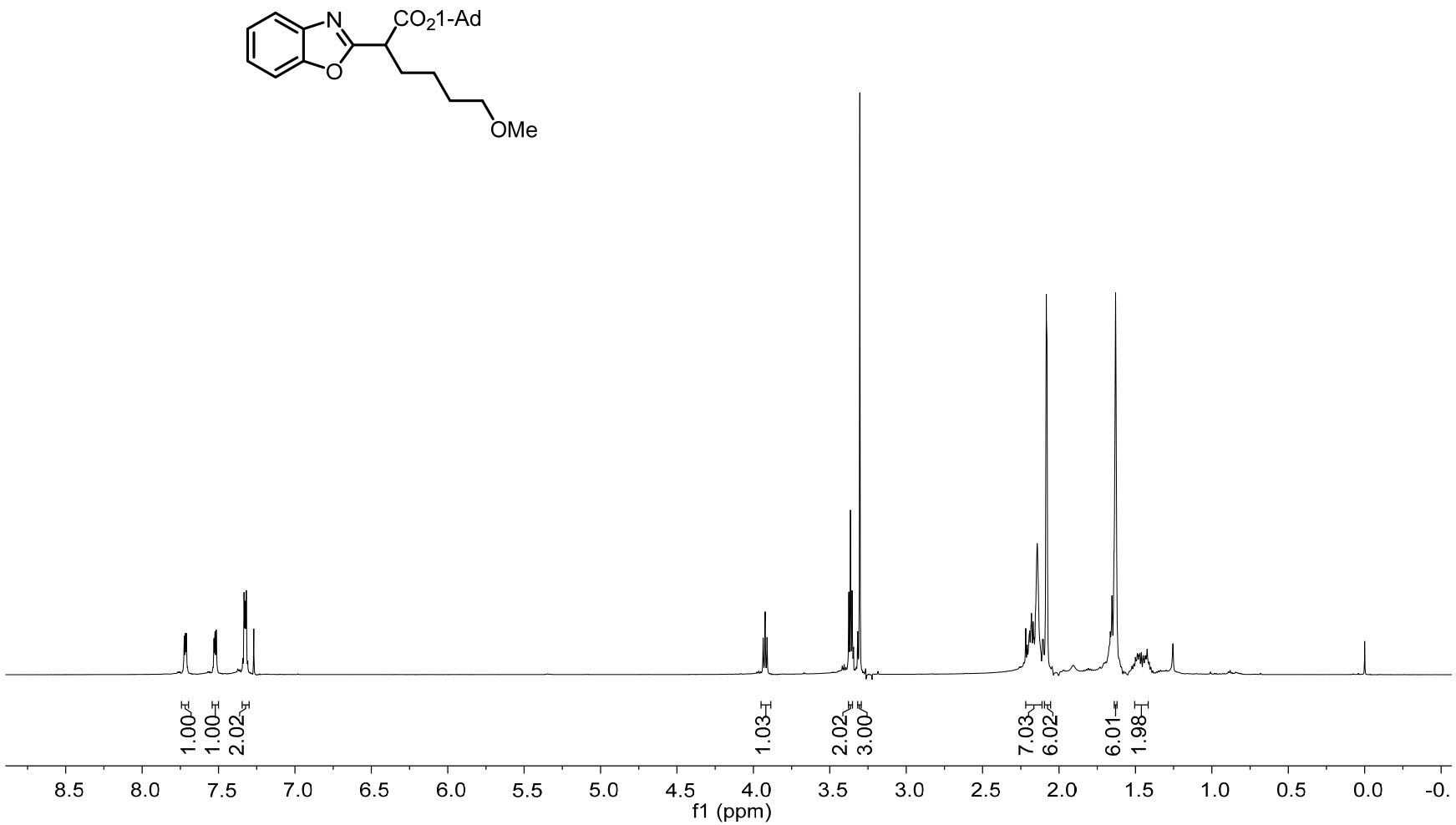

168.907
168.691
164.194
163.937
150.832
150.803
140.980
124.805
124.783
124.194
124.175
119.952
110.561
110.543
82.208
45.501
41.077
41.062
36.850
36.799
36.018
32.297
32.198
30.766
29.191
29.096
18.829
18.606
11.076
11.061
N
O
CO2 1-Ad
Me
Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

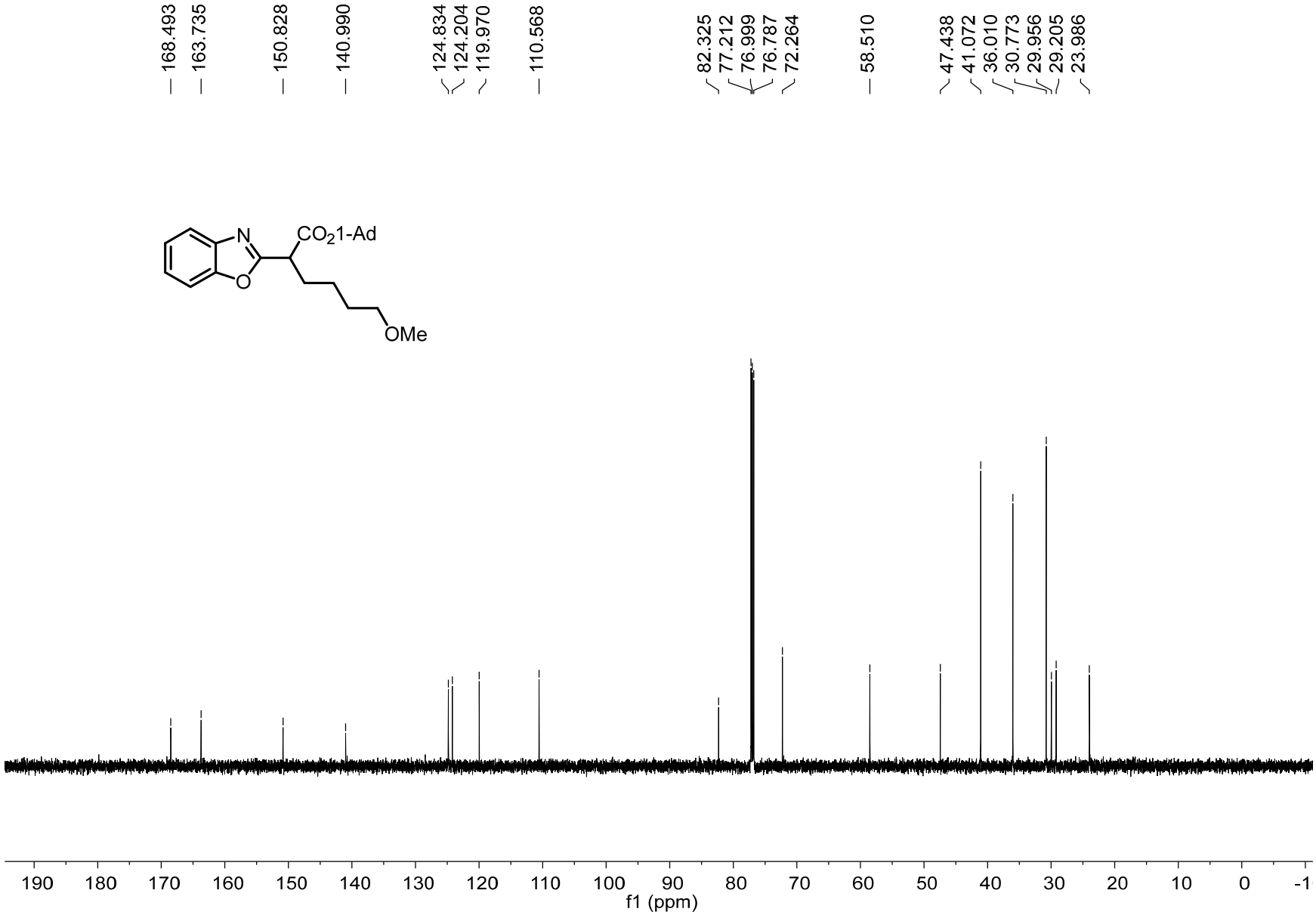

N
O
CO2 1-Ad
n-Hex
1.00
1.00
1.99
1.02
4.98
5.99
6.01
3.98
4.01
2.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

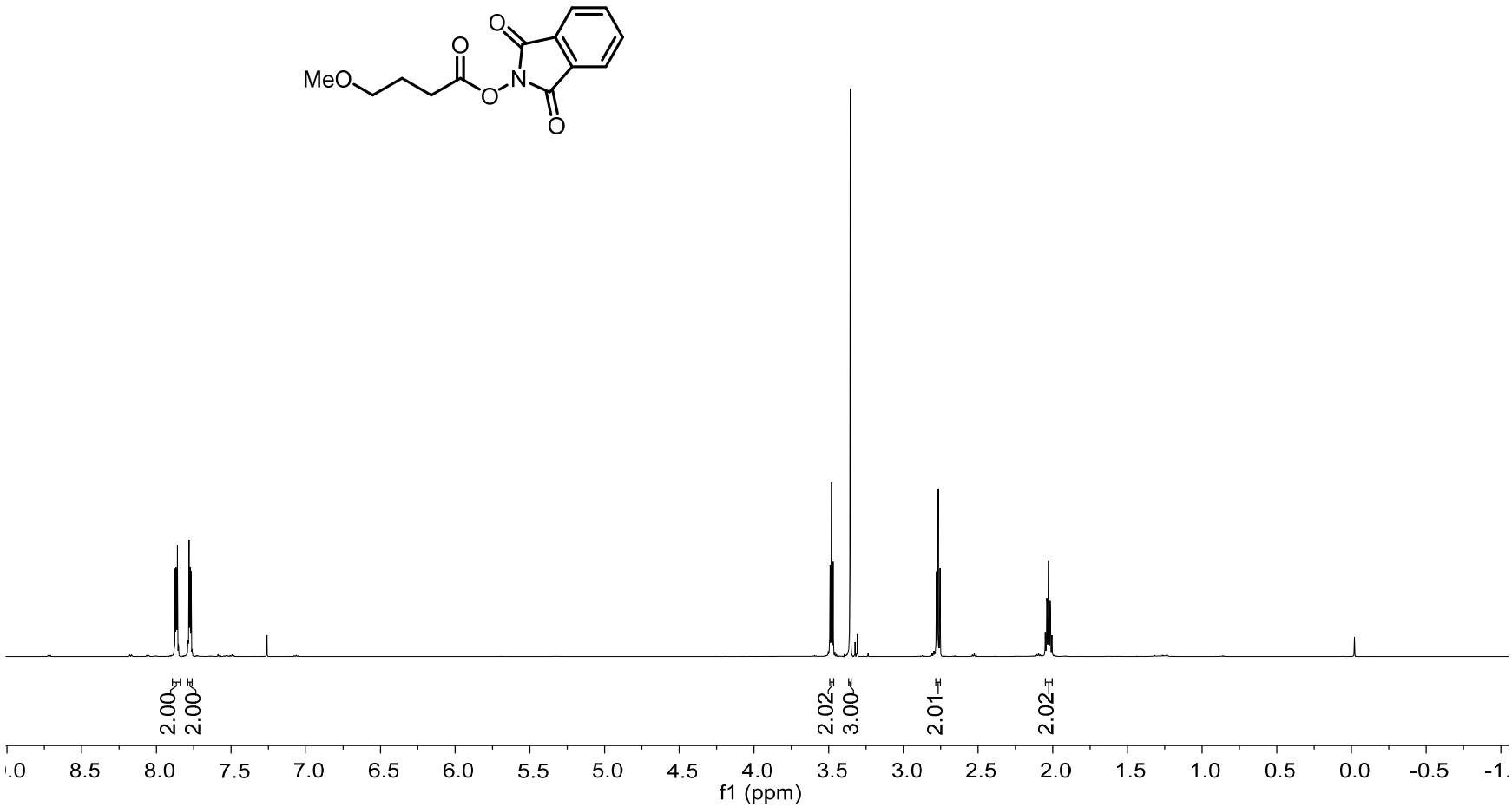

168.631
163.903
150.819
141.018
124.767
124.152
119.954
110.526
82.177
77.211
76.998
76.790
47.481
41.075
36.013
31.457
30.764
30.145
28.820
27.245
22.490
13.982
N
O
CO2 1-Ad
n-Hex
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

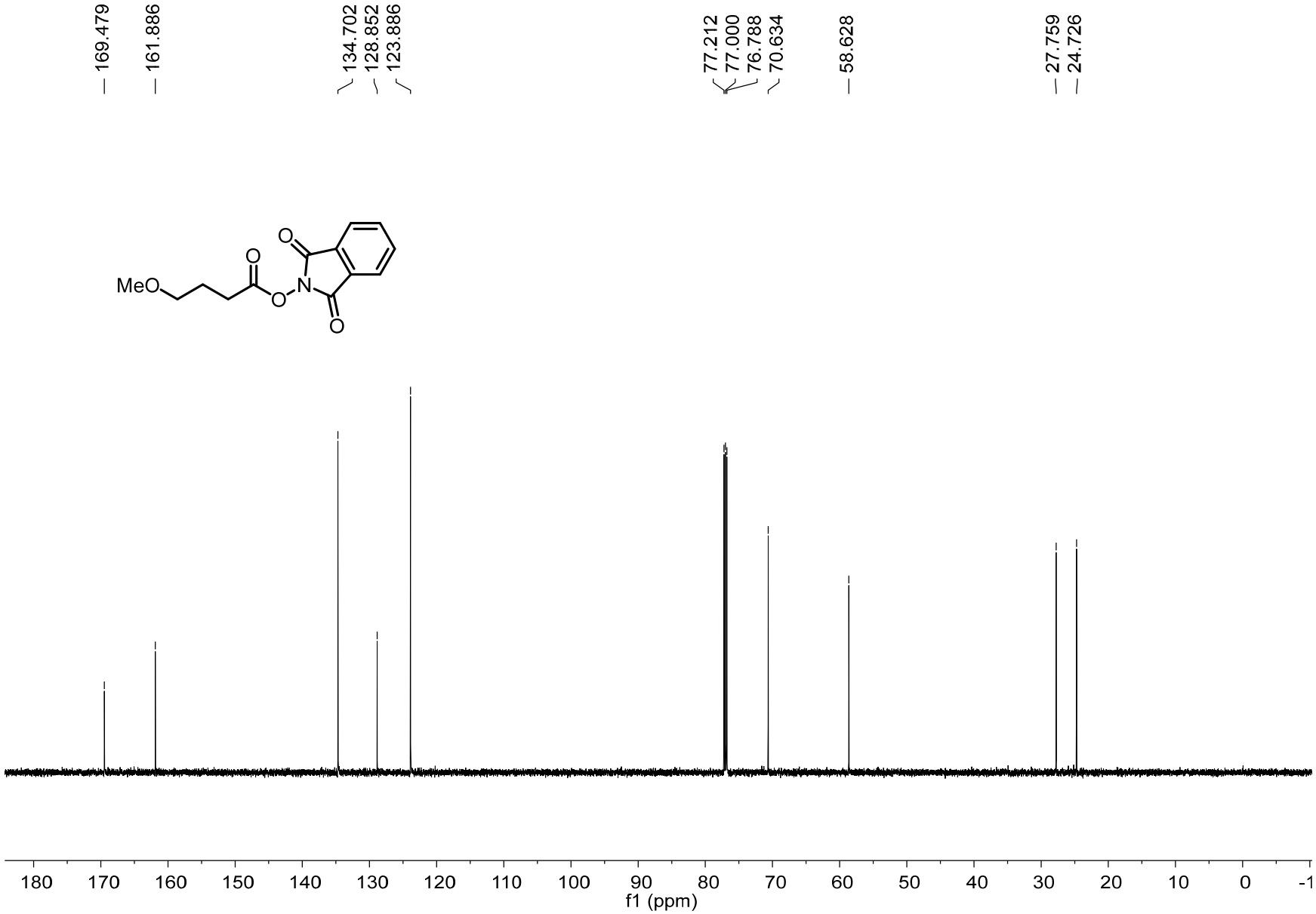

— 0.001
N
O
CO2 1-Ad
Ph
1.00
0.99
2.02
2.02
3.01
0.99
2.01
5.04
6.00
7.98
4.00
f1 (ppm)

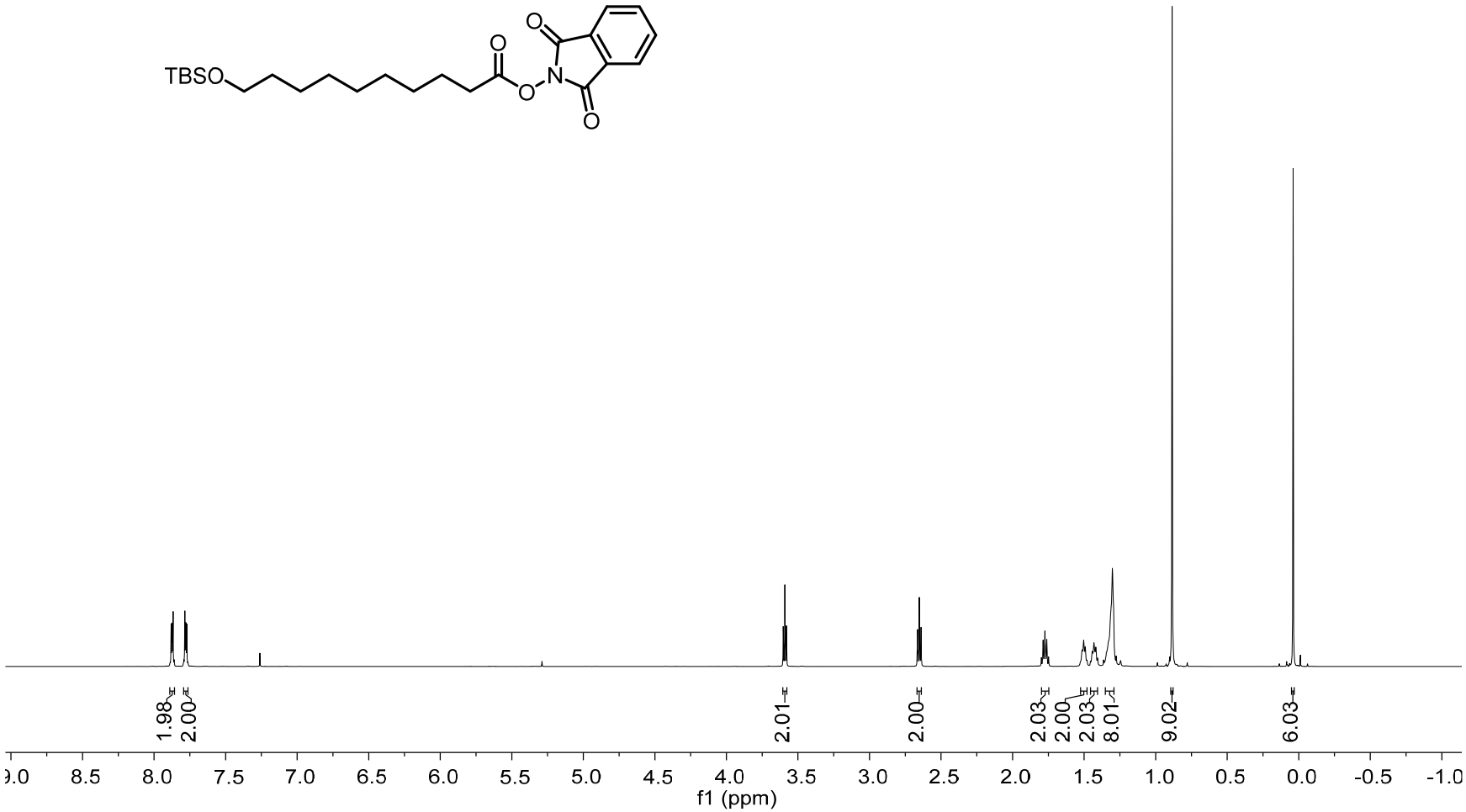

169.234
164.732
151.491
143.446
141.812
129.064
128.951
126.308
125.816
125.120
120.413
118.000
111.241
82.441
47.841
41.629
36.394
36.004
31.721
31.527
30.361
29.180
27.419
1.688
1.481
1.277
1.069
0.861
0.657
0.449
N
O
CO2
1-Ad
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

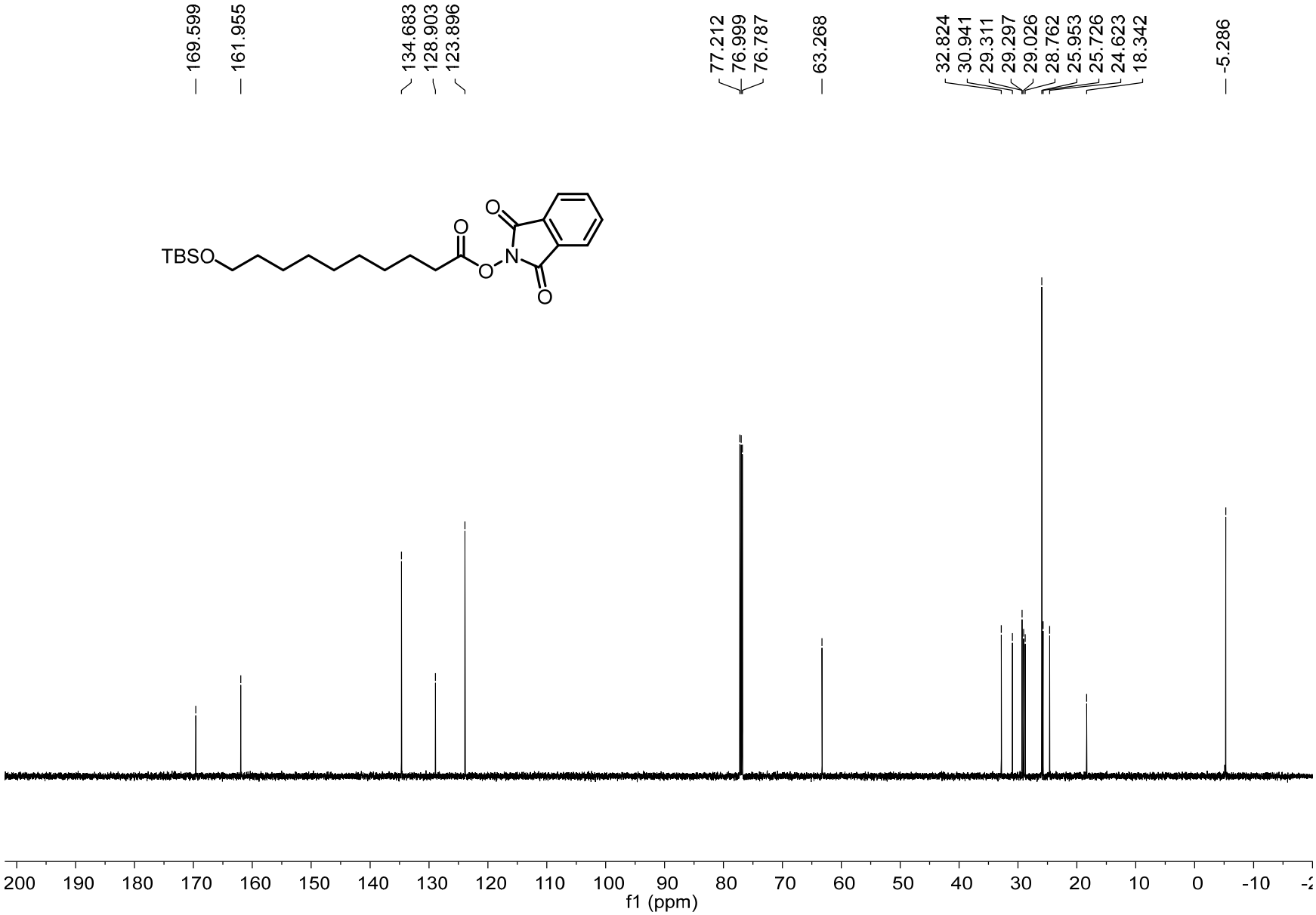

N
O
CO2 1-Ad
OMe
1.00
1.00
2.02
1.03
2.02
3.00
7.03
6.02
6.01
1.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

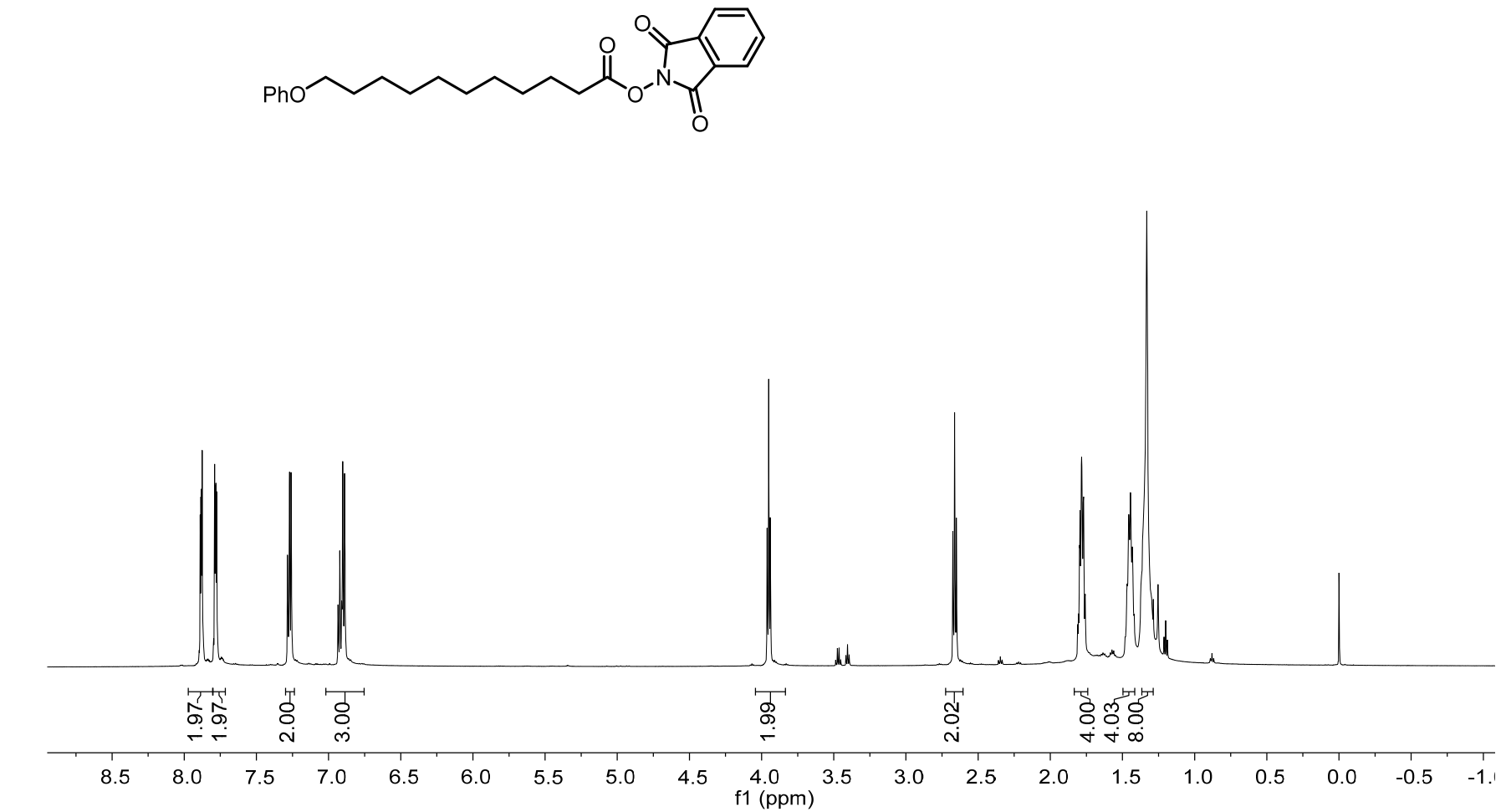

168.493
163.735
150.828
140.990
124.834
124.204
119.970
110.568
82.325
77.212
76.999
76.787
72.264
58.510
47.438
41.072
36.010
30.773
29.956
29.205
23.986
N
O
CO2 1-Ad
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

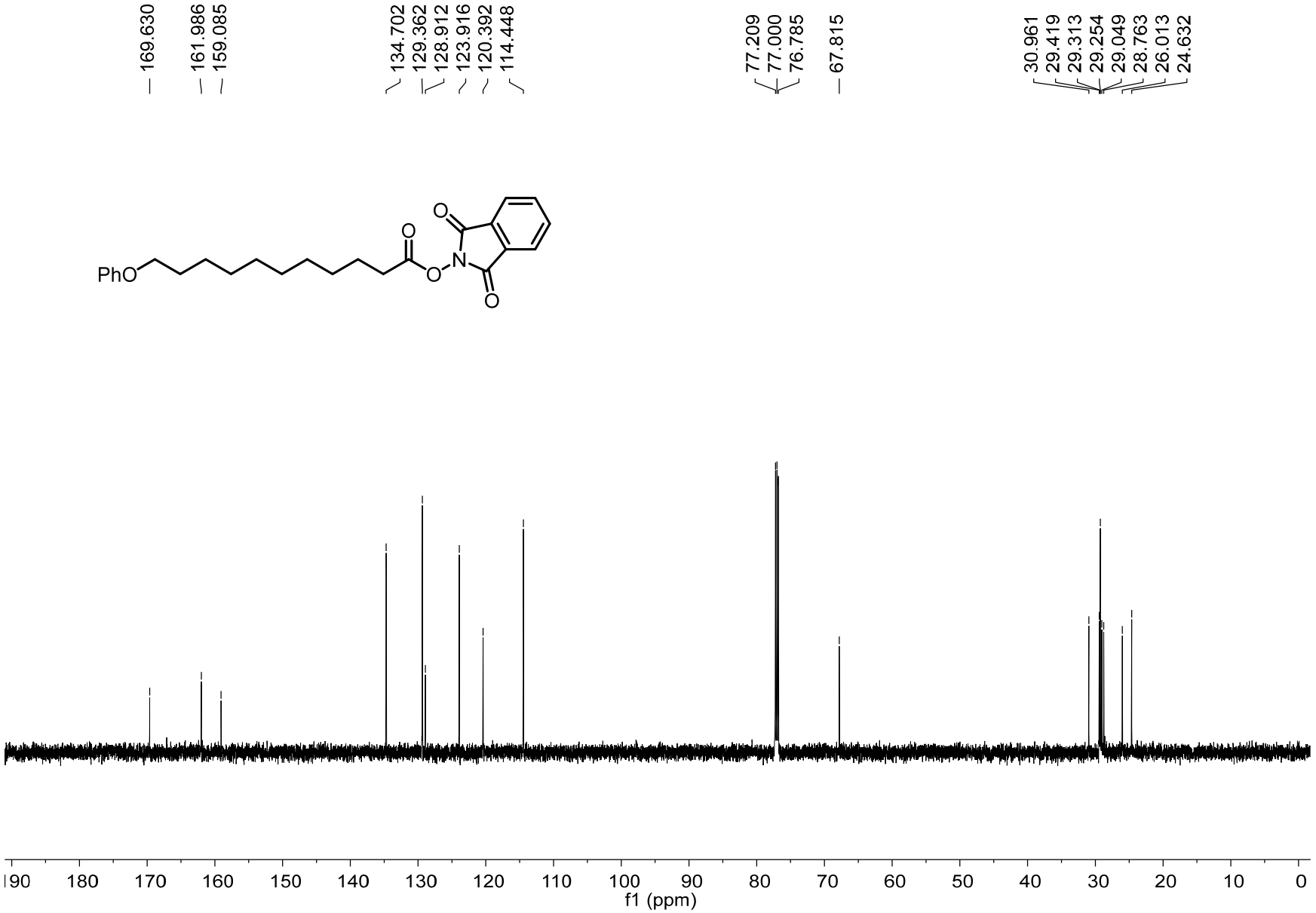

MeO
O
O
O
N
O
O
2.00
2.00
2.02
3.00
2.01
2.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

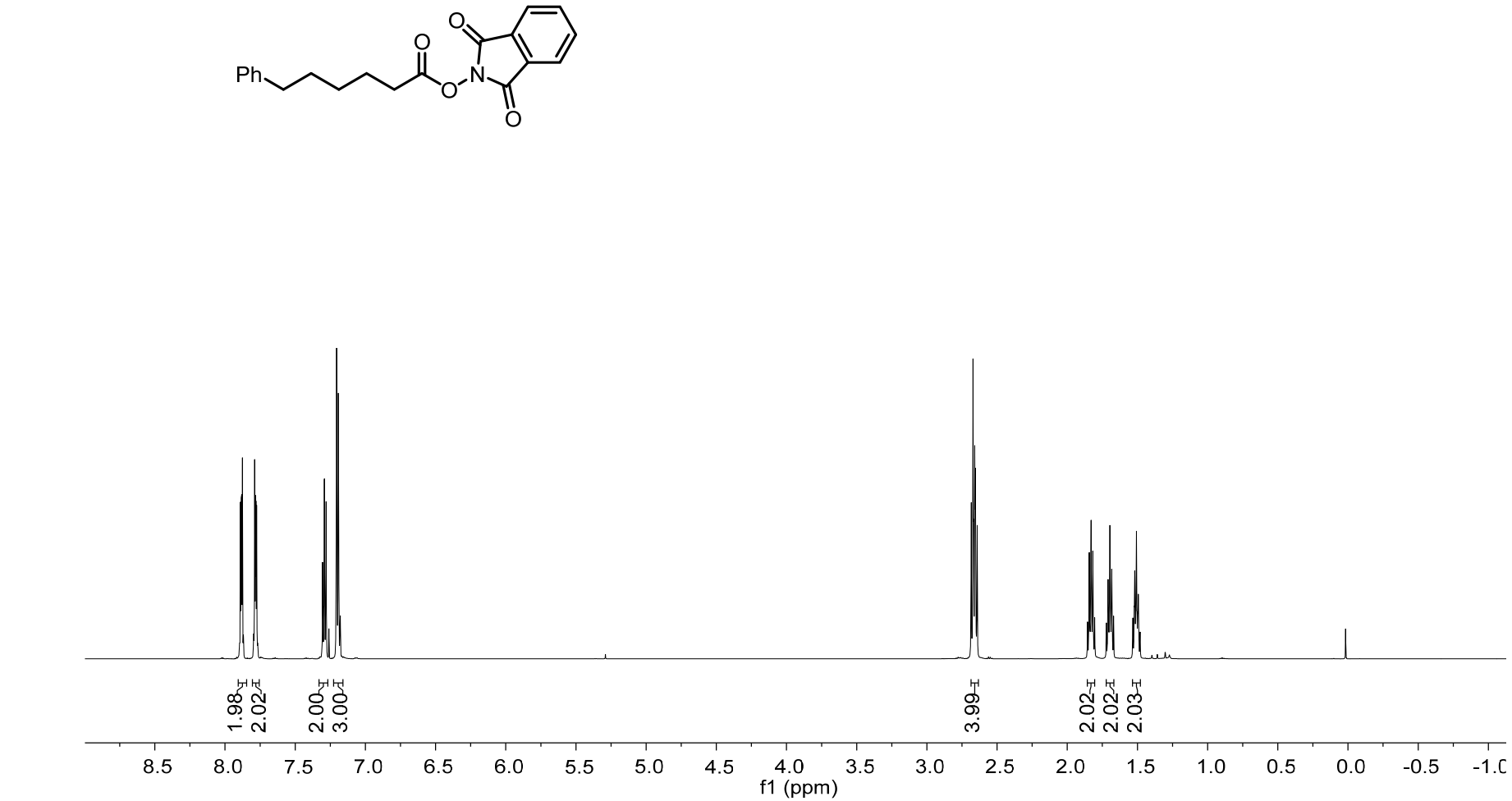

169.479
161.886
134.702
128.852
123.886
77.212
77.000
76.788
70.634
58.628
27.759
24.726
MeO
O
O
N
O
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

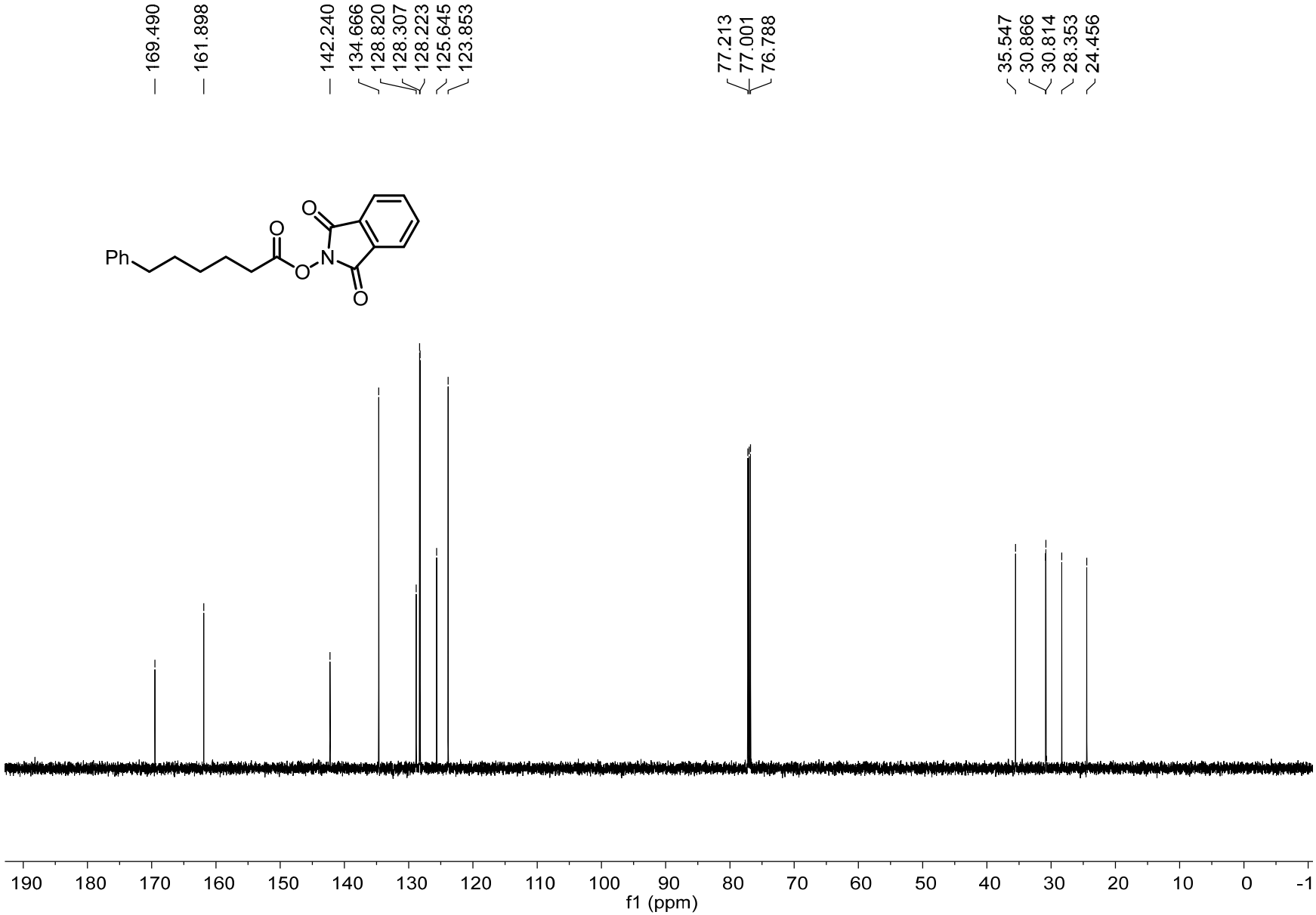

TBSO
O
O
N
O
O
1.98
2.00
2.01
2.00
2.03
2.00
2.03
8.01
9.02
6.03
f1 (ppm)

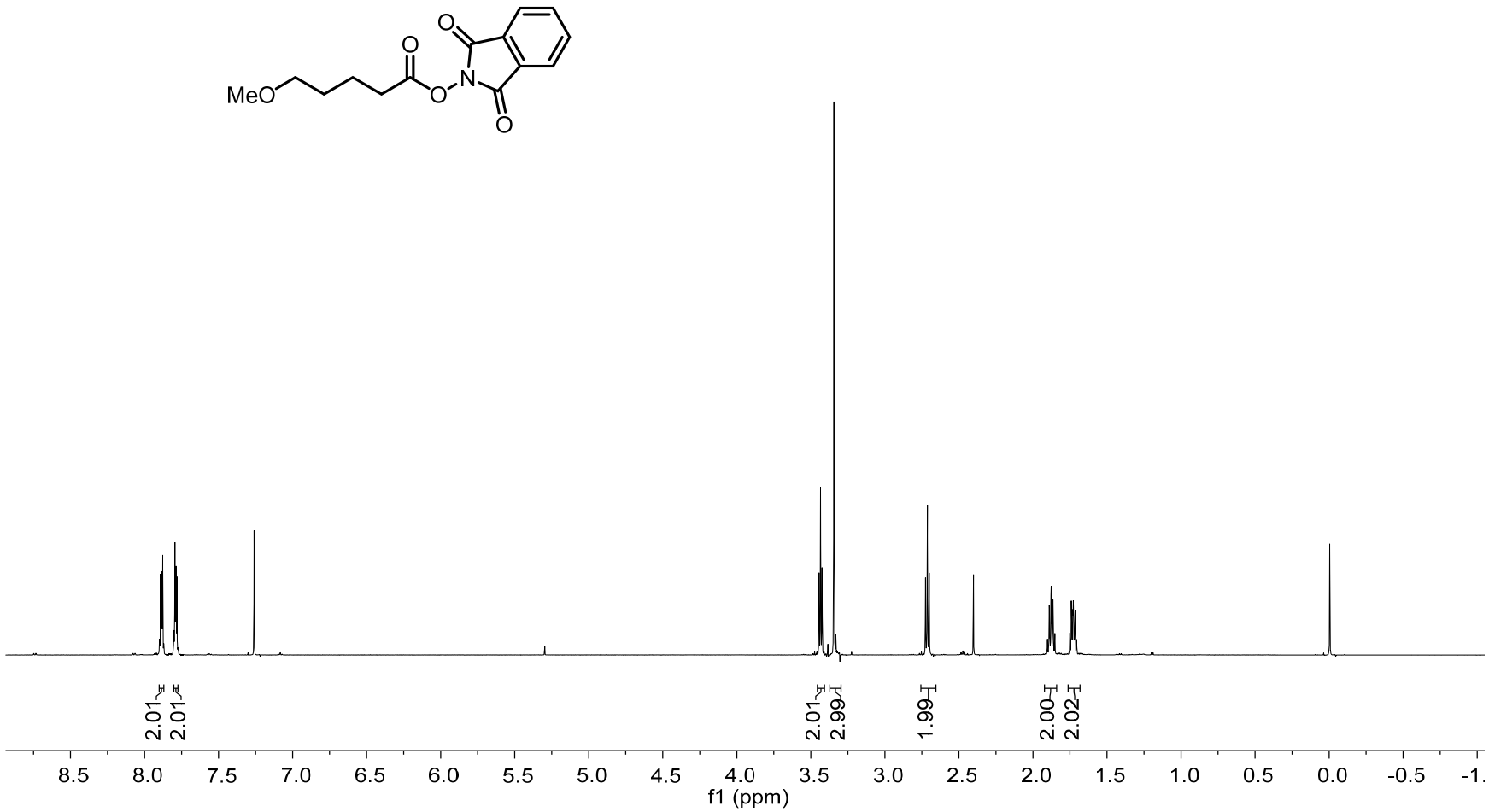

169.599
161.955
134.683
128.903
123.896
77.212
76.999
76.787
63.268
32.824
30.941
29.311
29.297
29.026
28.762
25.953
25.726
24.623
18.342
-5.286
TBSO
O
O
N
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

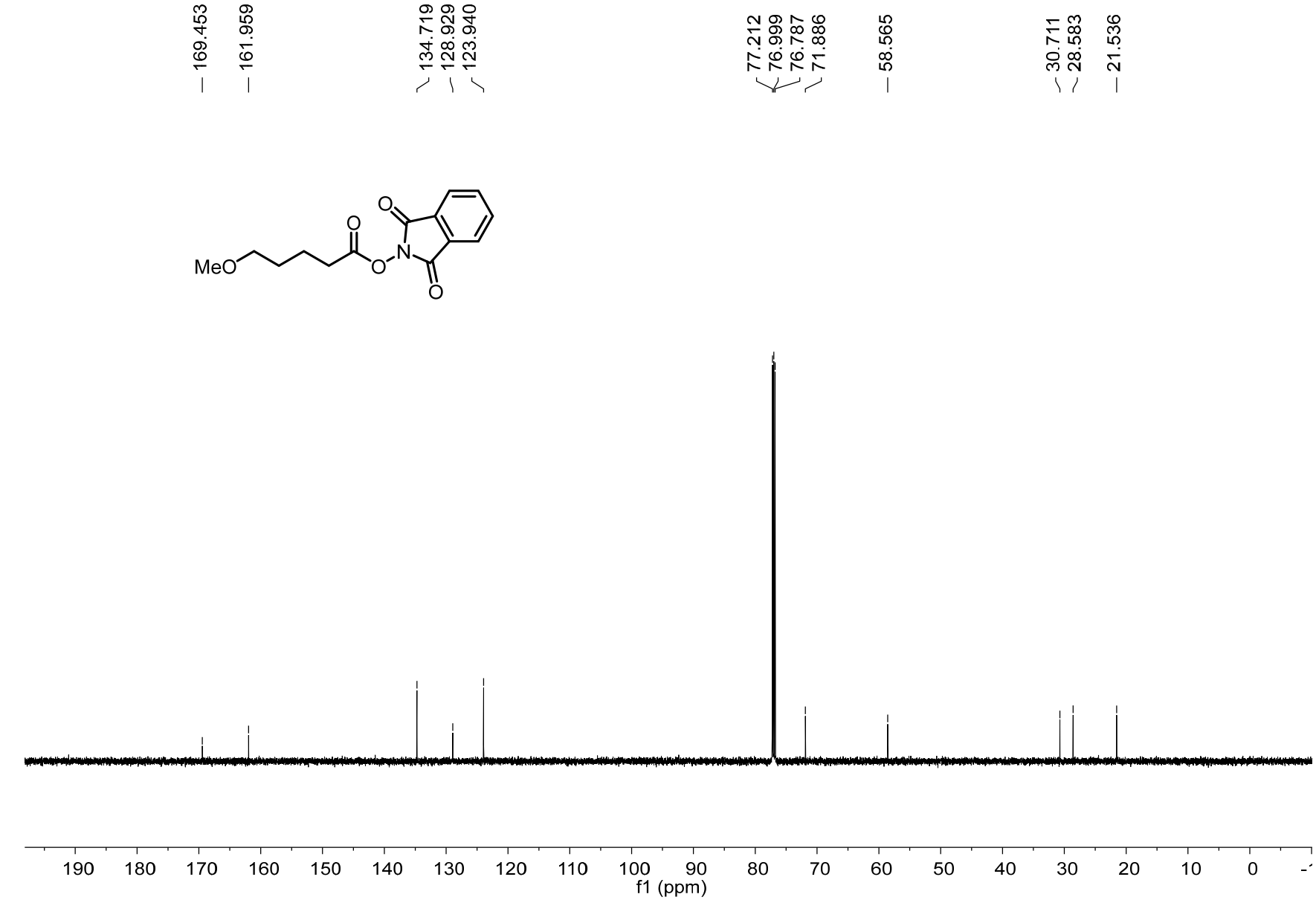

PhO
O
O
N
O
O
1.97
1.97
2.00
3.00
1.99
2.02
4.00
4.03
8.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

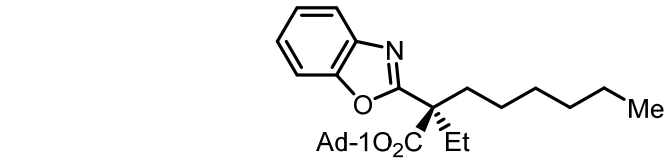

169.630
161.986
159.085
134.702
129.362
128.912
123.916
120.392
114.448
77.209
77.000
76.785
67.815
30.961
29.419
29.313
29.254
29.049
28.763
26.013
24.632
PhO
O
O
N
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
O
O
N
O
O
1.98
2.02
2.00
3.00
3.99
2.02
2.02
2.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

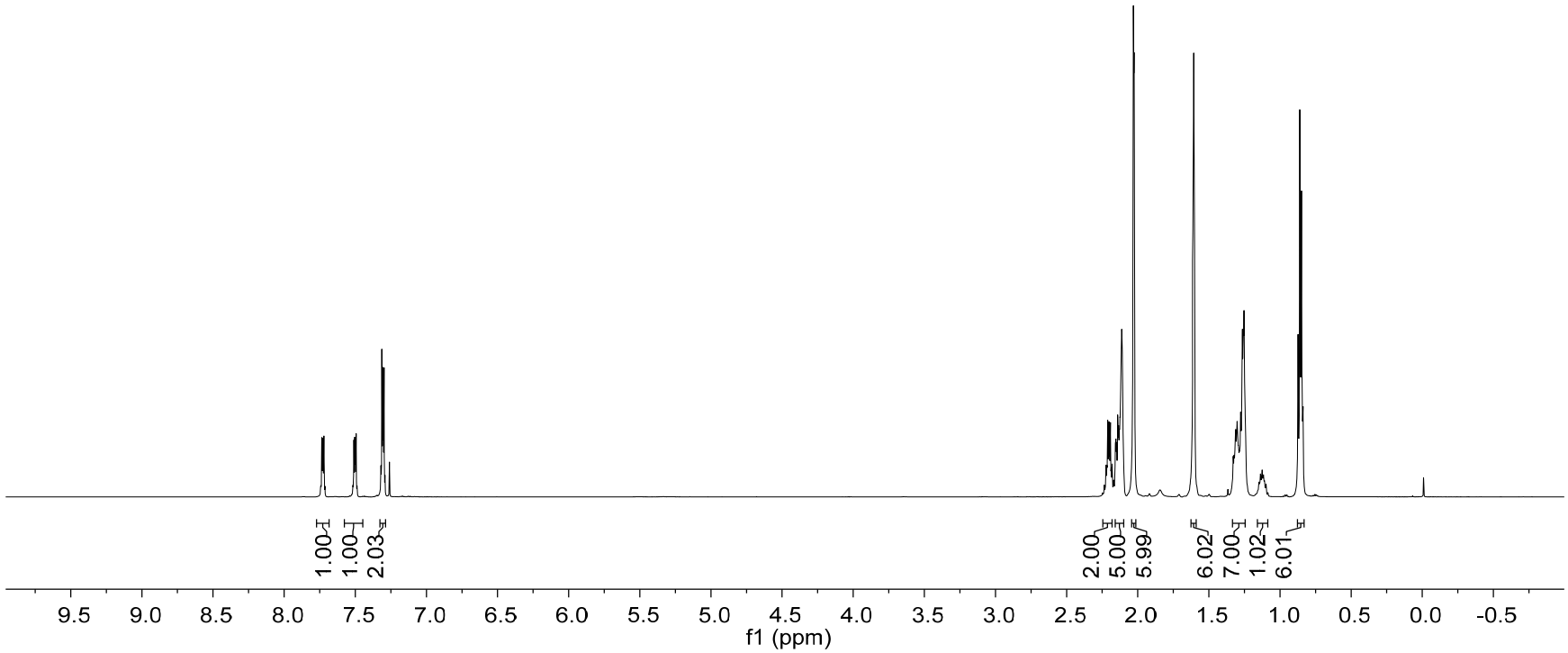

169.490
161.898
142.240
134.666
128.820
128.307
128.223
125.645
123.853
77.213
77.001
76.788
35.547
30.866
30.814
28.353
24.456
Ph
O
O
N
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

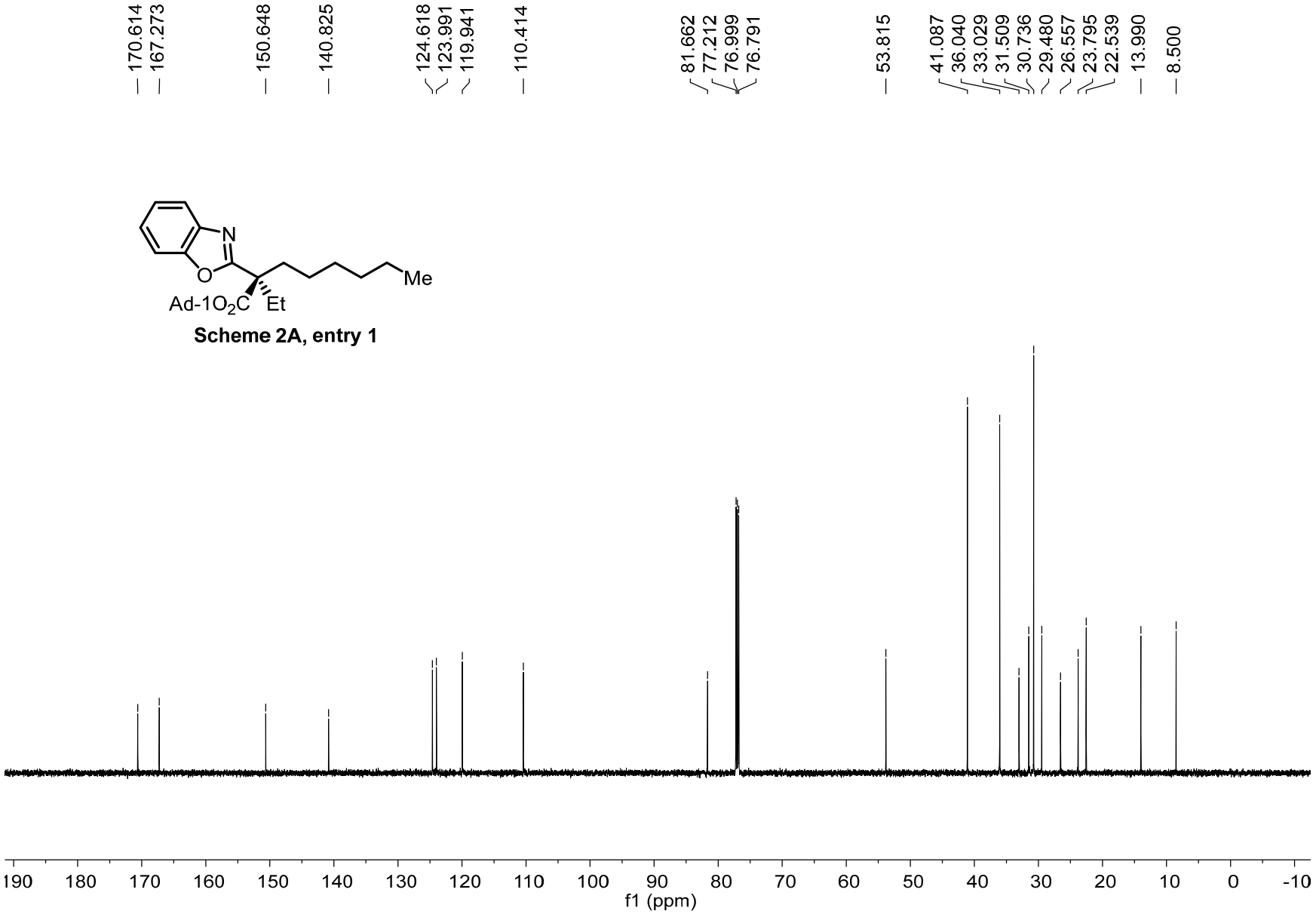

MeO
O
O
N
O
O
2.01
2.01
2.01
2.99
1.99
2.00
2.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

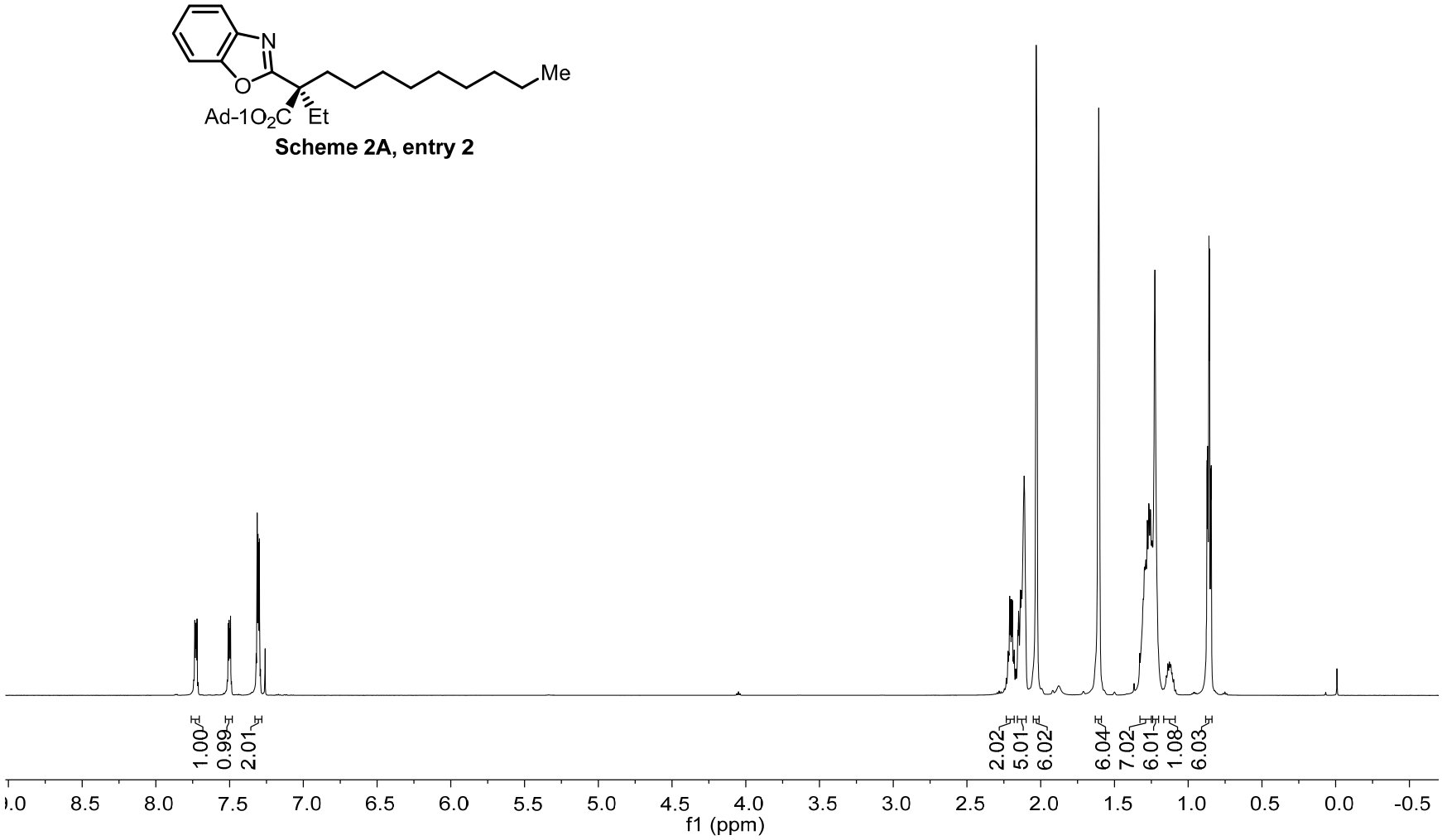

169.453
161.959
134.719
128.929
123.940
77.212
76.999
76.787
71.886
58.565
30.711
28.583
21.536
MeO
O
O
N
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



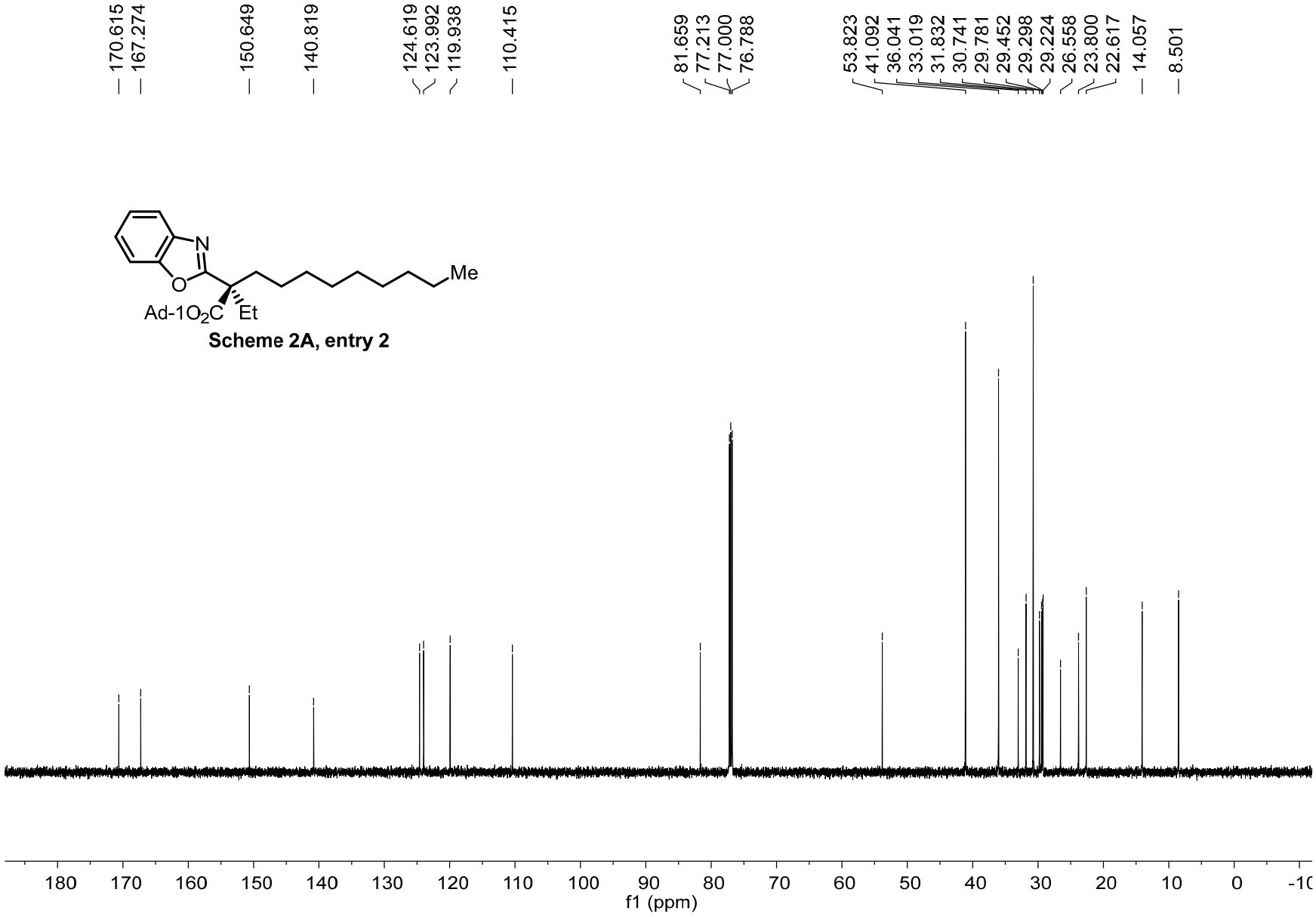
Scheme 2A, entry 1

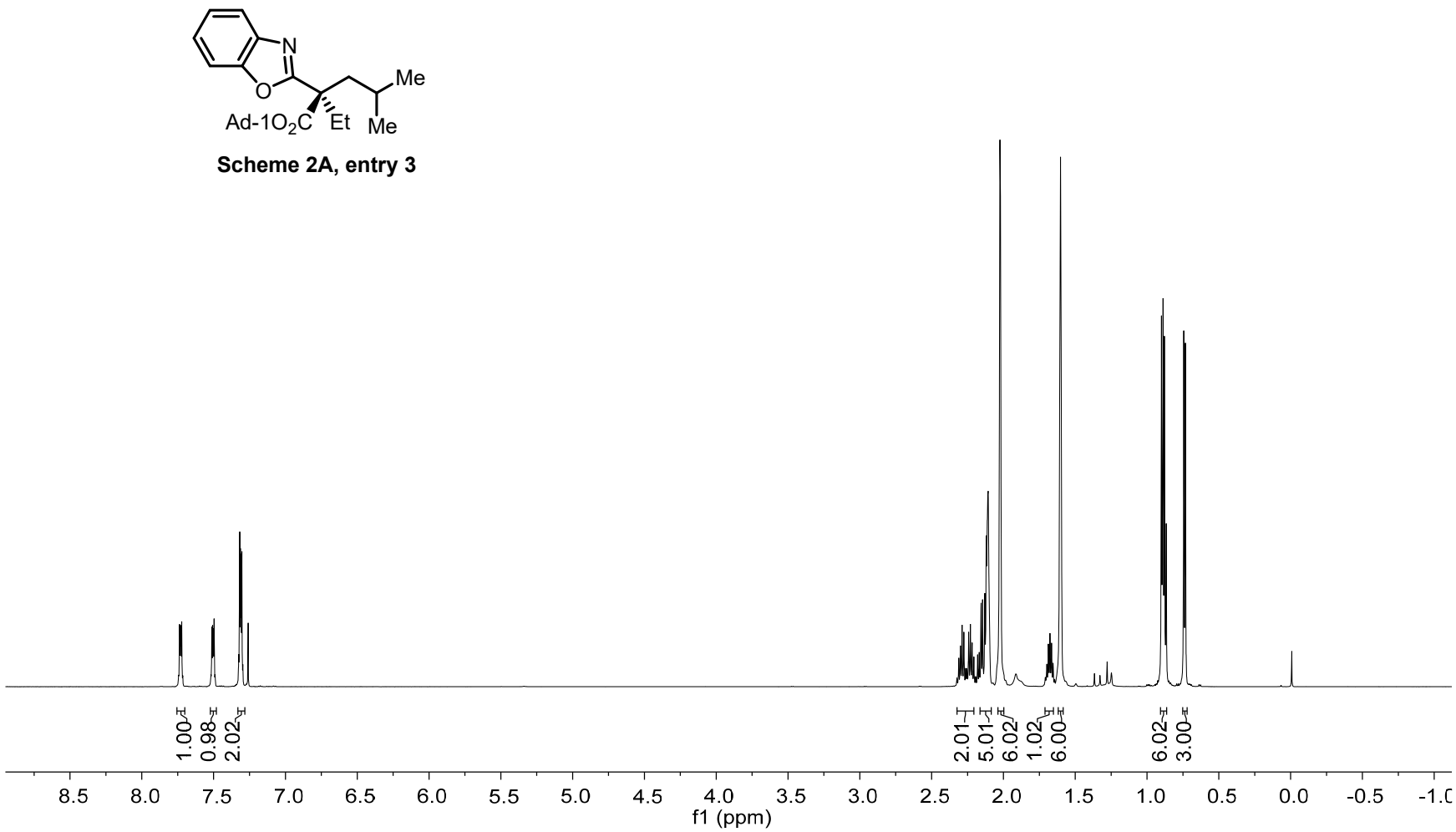



170.614
167.273
150.648
140.825
124.618
123.991
119.941
110.414
81.662
77.212
76.999
76.791
53.815
41.087
36.040
33.029
31.509
30.736
29.480
26.557
23.795
22.539
13.990
8.500
N
O
Me
Ad-1O2C
Et
Scheme 2A, entry 1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

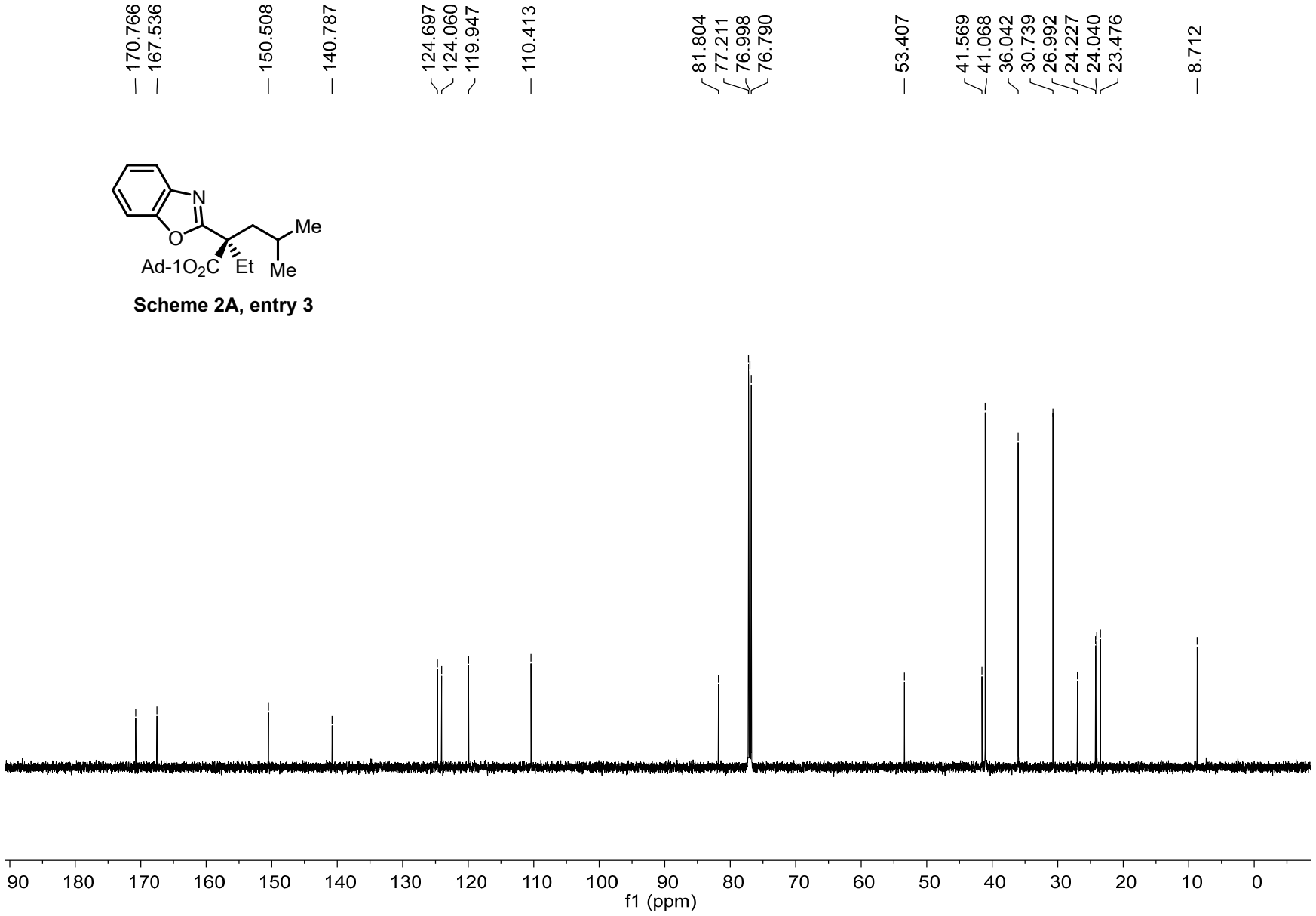


Scheme 2A, entry 2

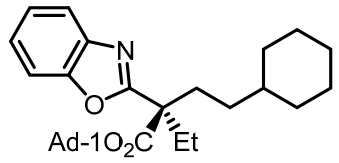

170.615
167.274
150.649
140.819
124.619
123.992
119.938
110.415
81.659
77.213
77.000
76.788
53.823
41.092
36.041
33.019
31.832
30.741
29.781
29.452
29.298
29.224
26.558
23.800
22.617
14.057
8.501
N
O
Me
Ad-1O2C Et
Scheme 2A, entry 2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



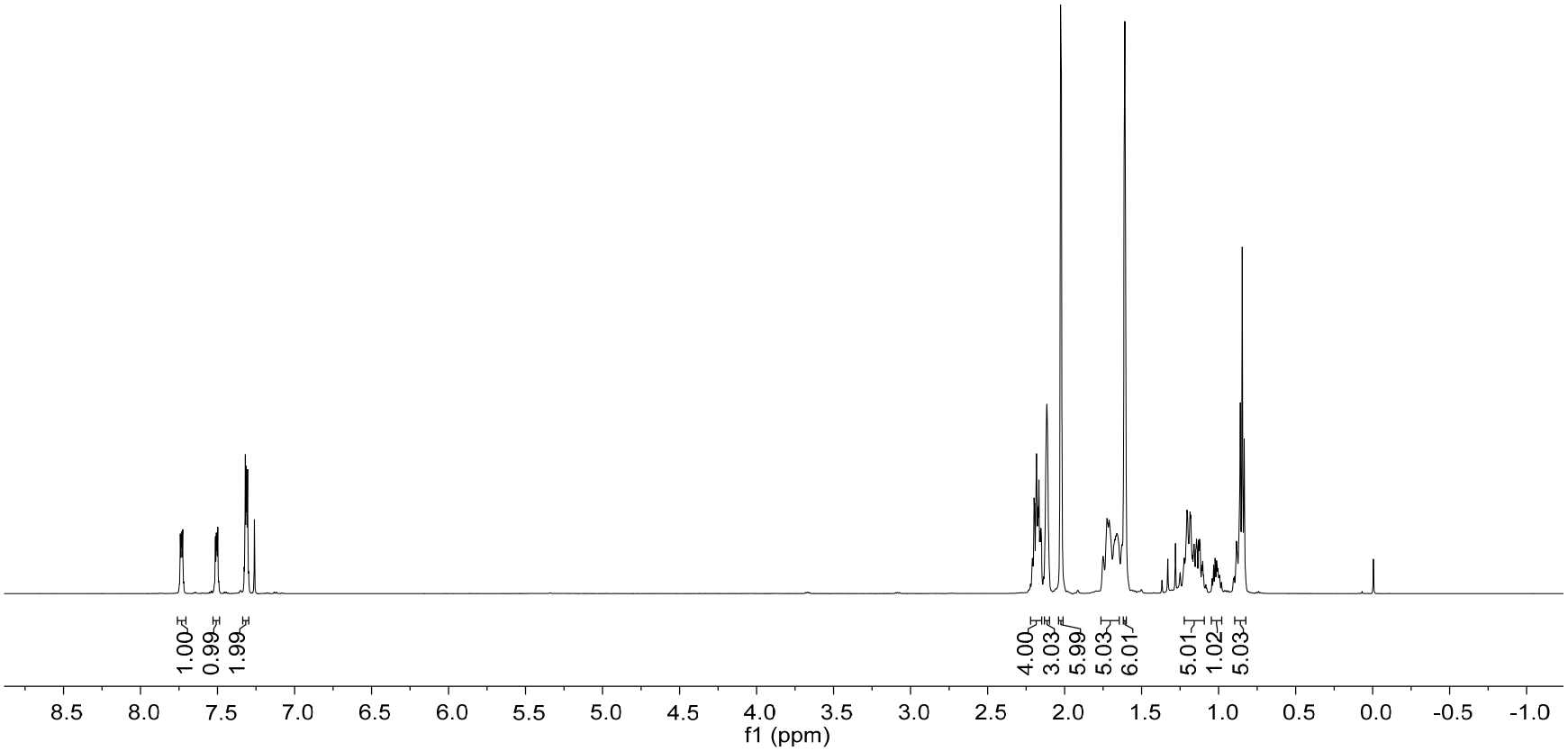
Scheme 2A, entry 3

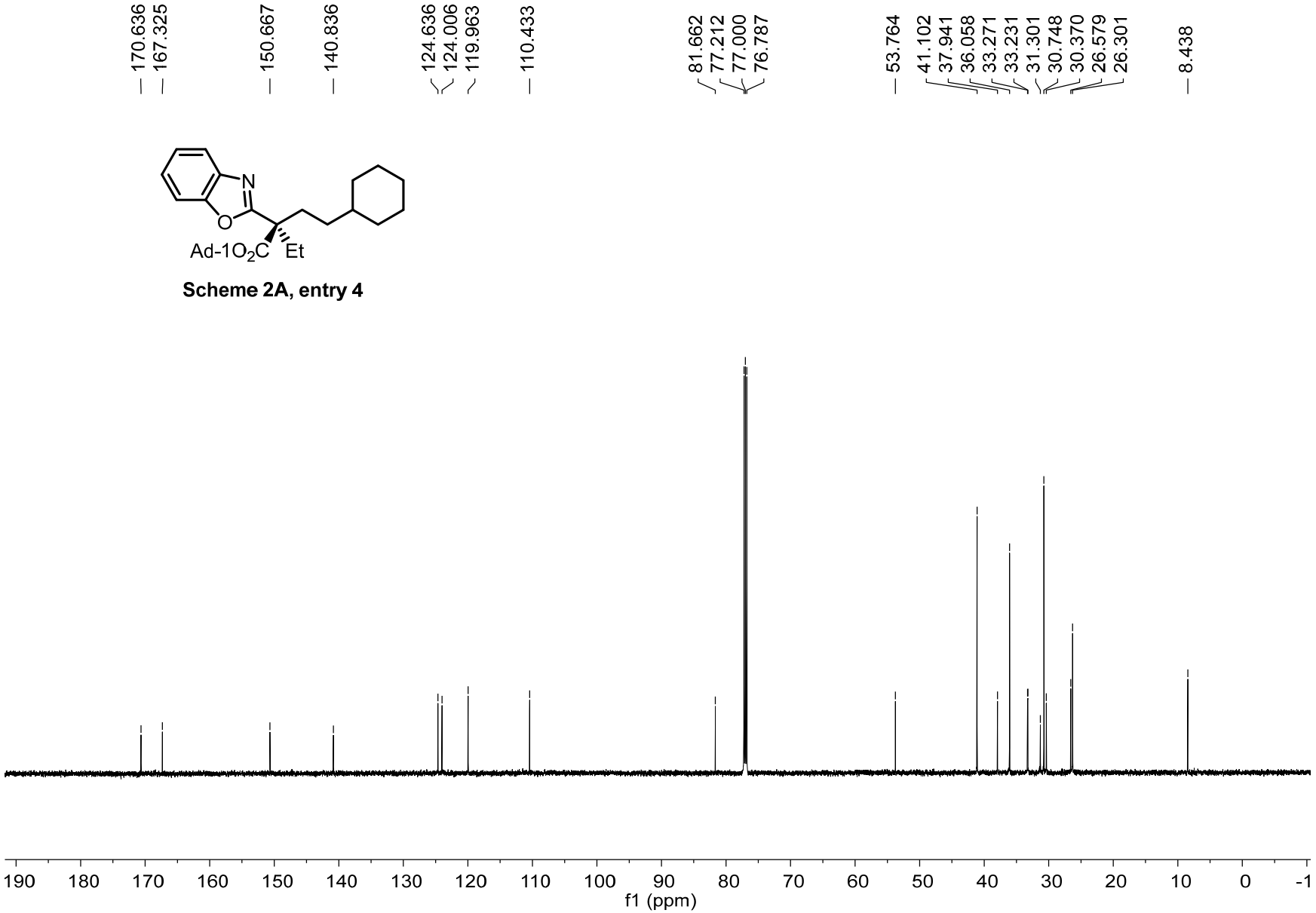


Scheme 2A, entry 3

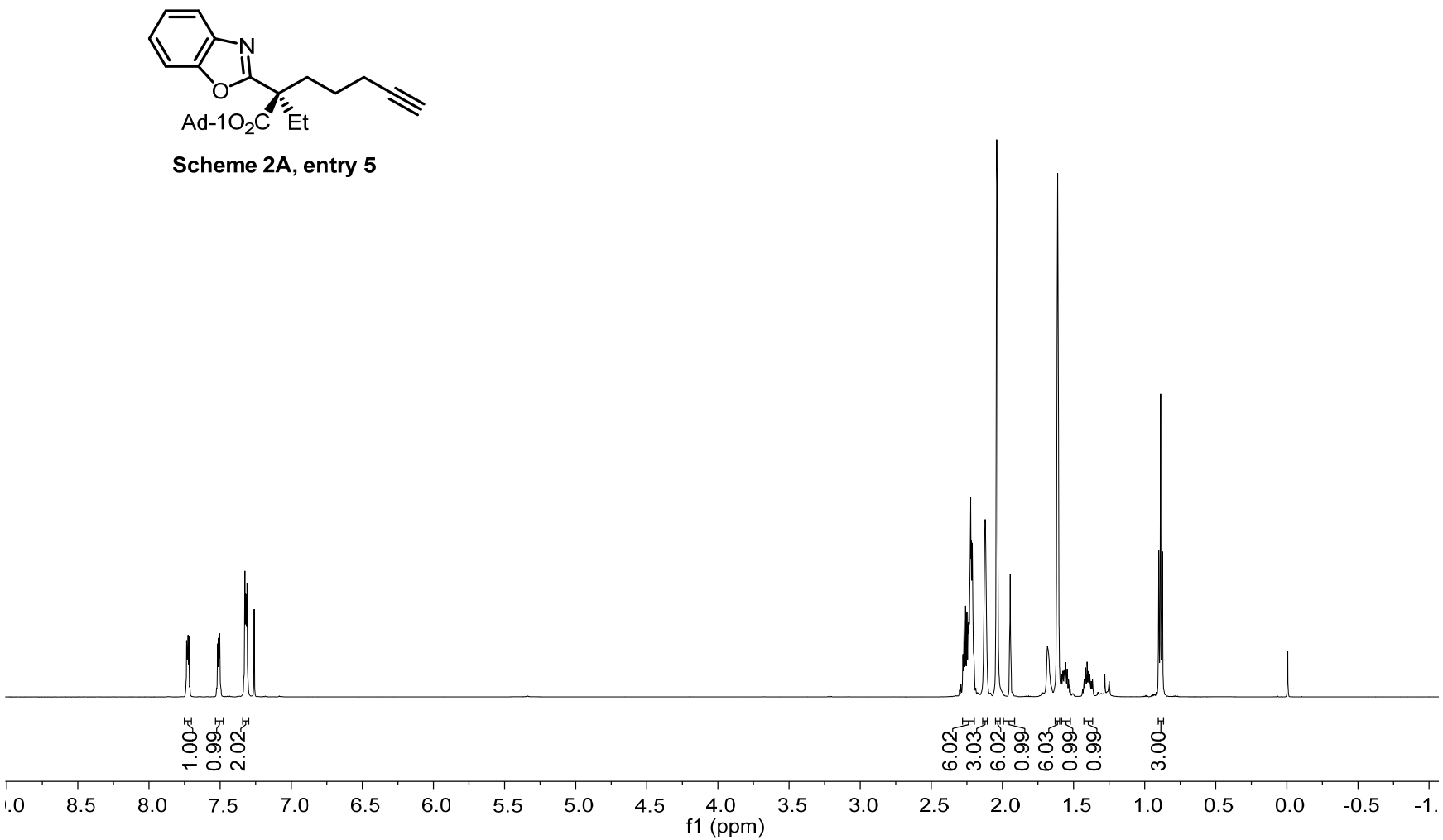


Scheme 2A, entry 4

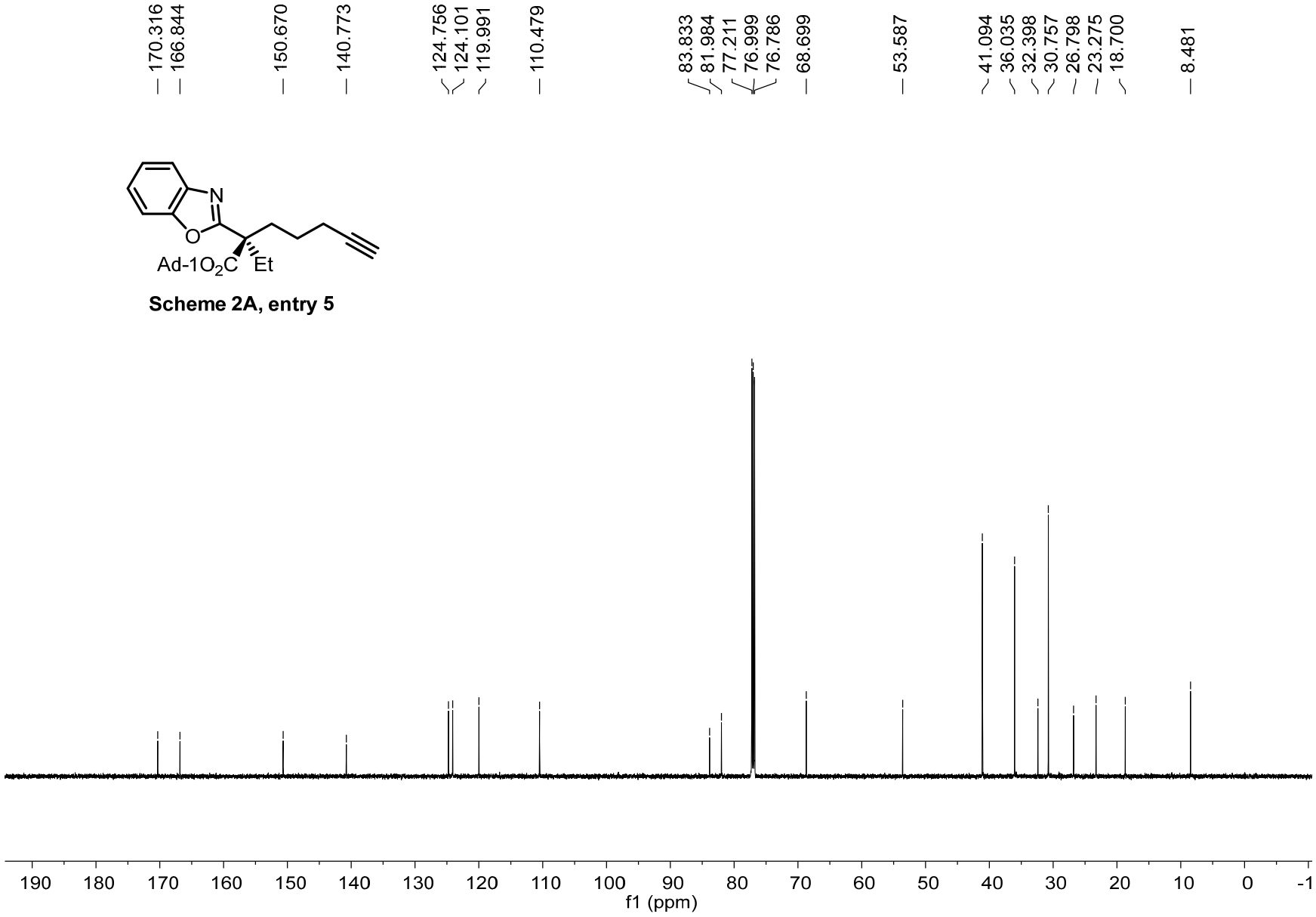




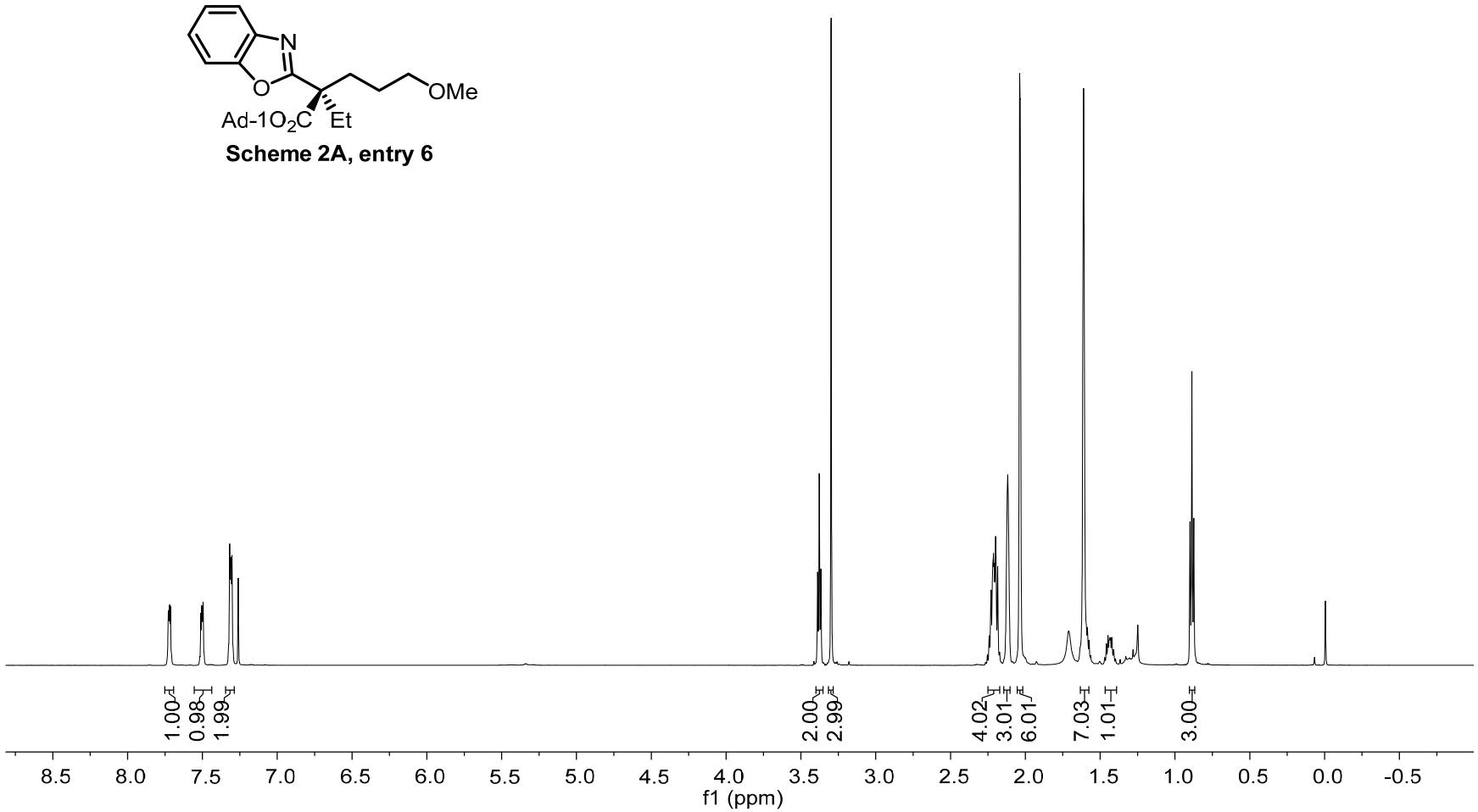
Scheme 2A, entry 4



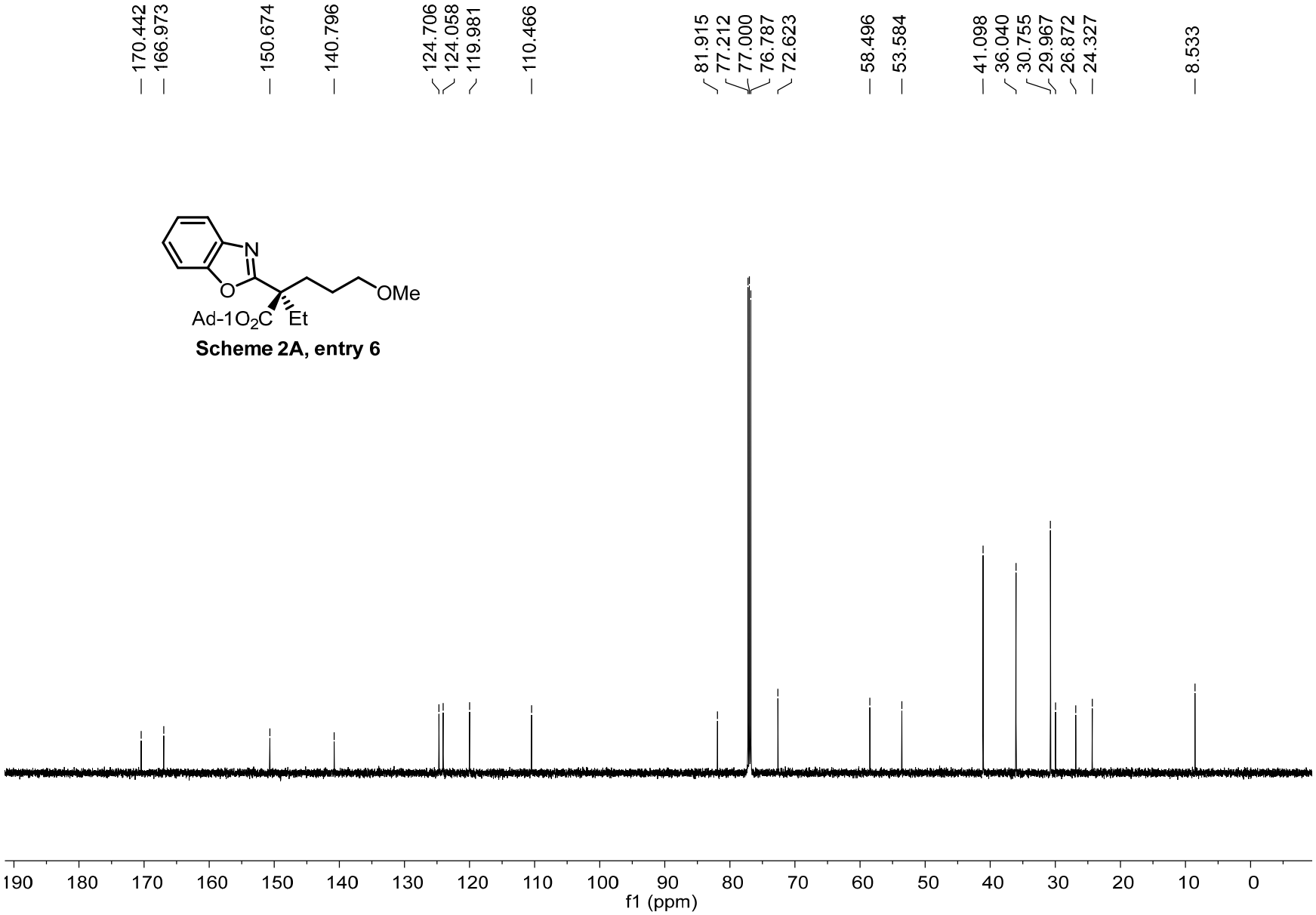
Scheme 2A, entry 5

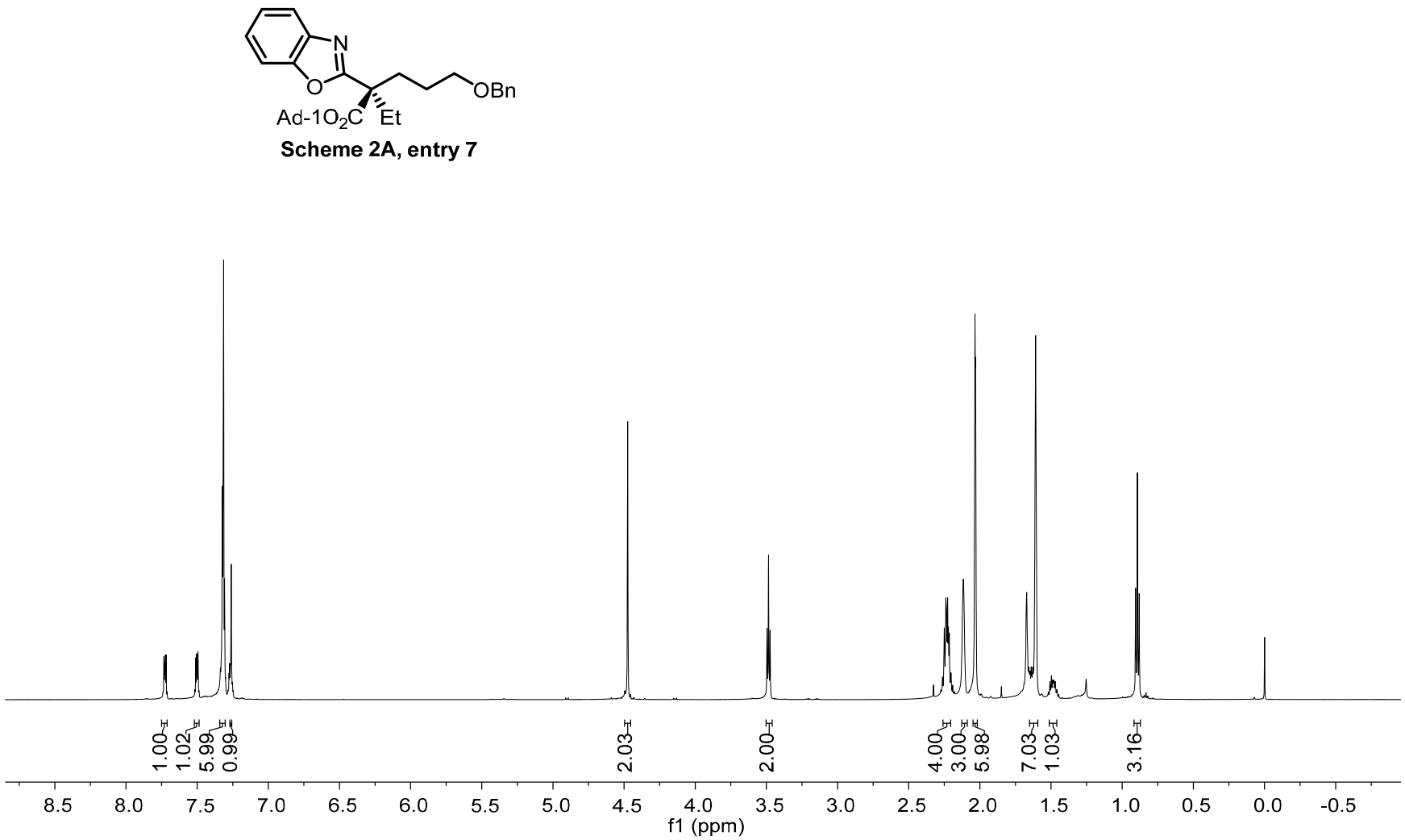


Scheme 2A, entry 5

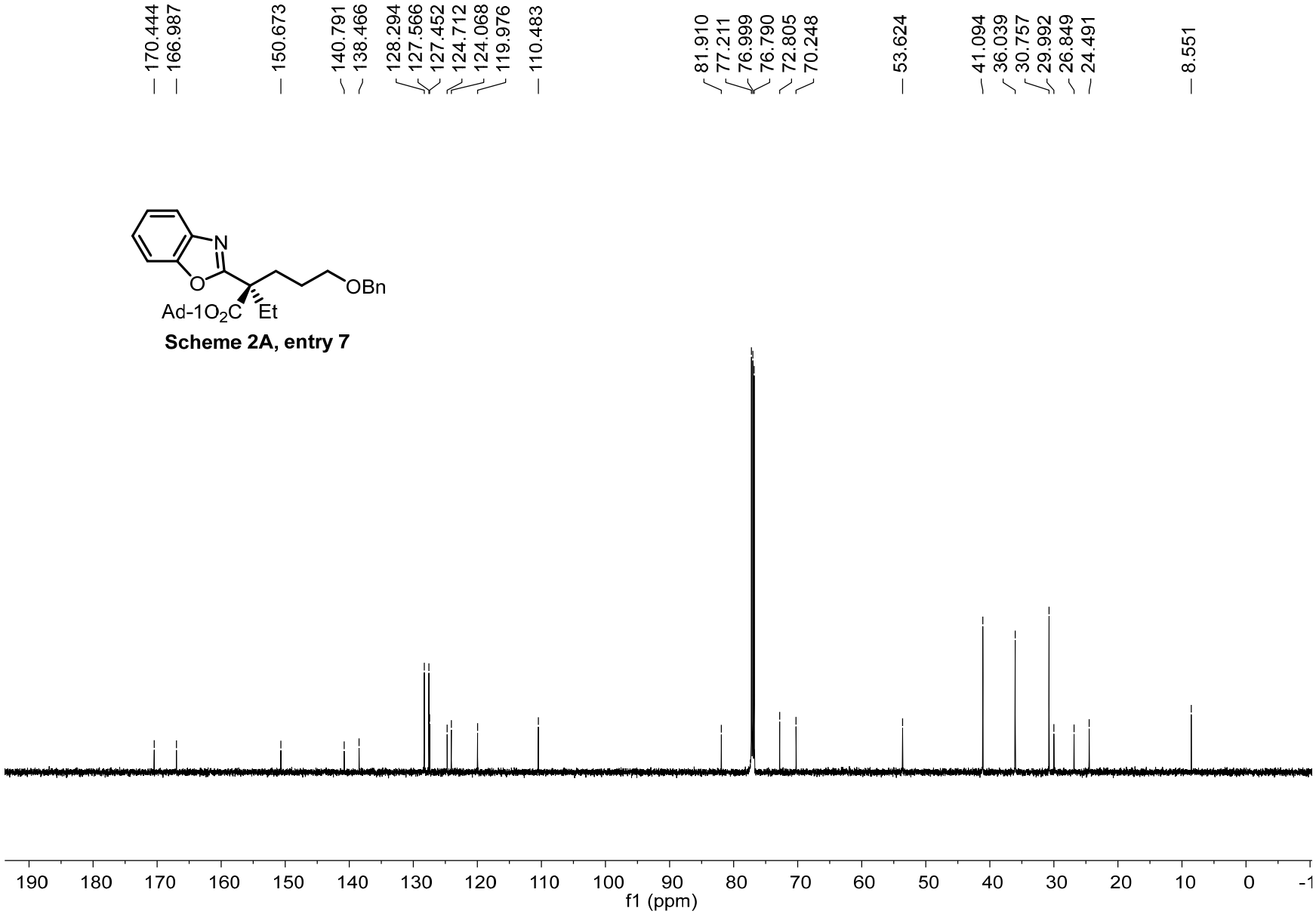


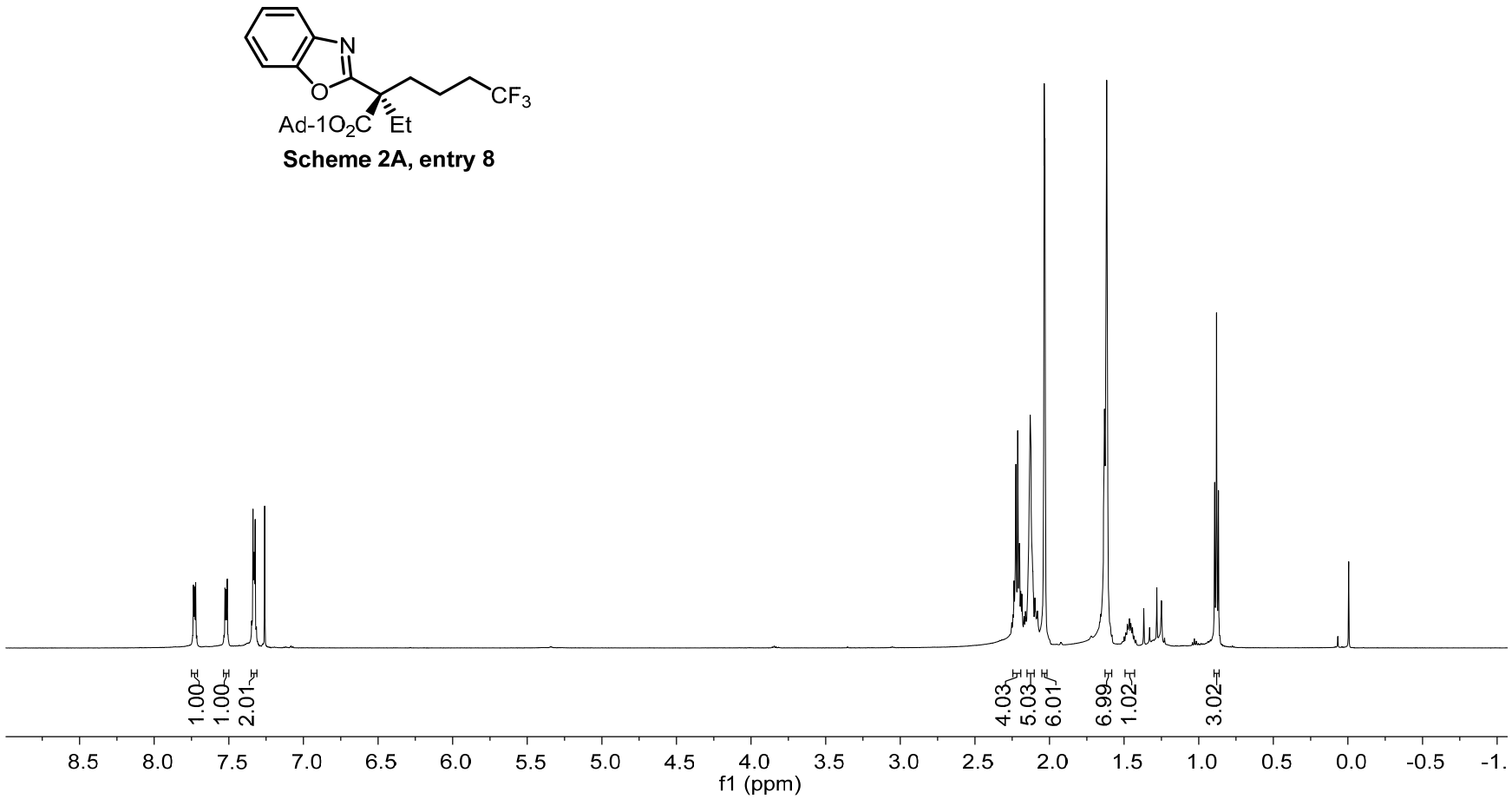
Scheme 2A, entry 6

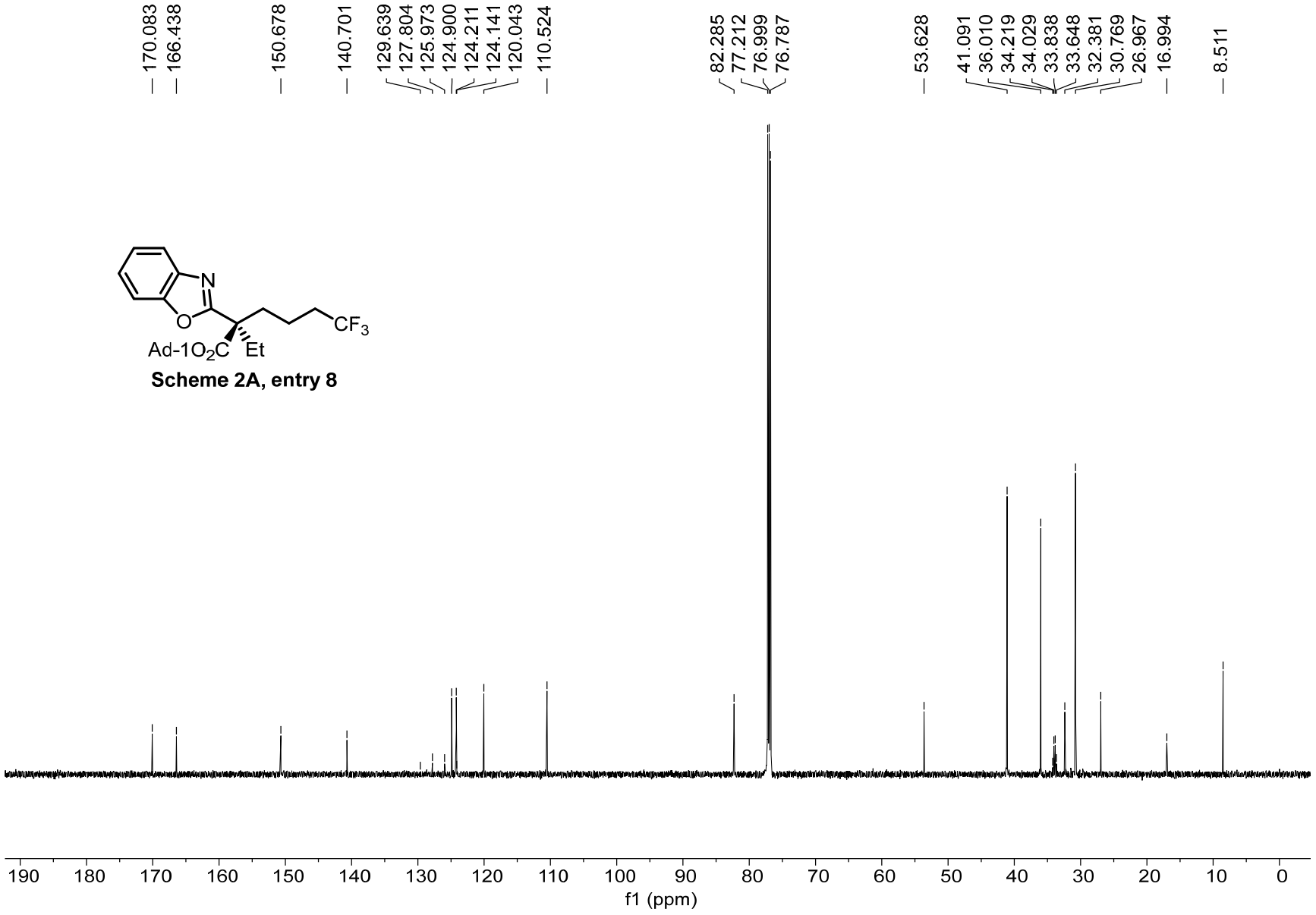

170.442
166.973
150.674
140.796
124.706
124.058
119.981
110.466
81.915
77.212
77.000
76.787
72.623
58.496
53.584
41.098
36.040
30.755
29.967
26.872
24.327
8.533
N
O
OMe
Ad-1O2C
Et
Scheme 2A, entry 6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

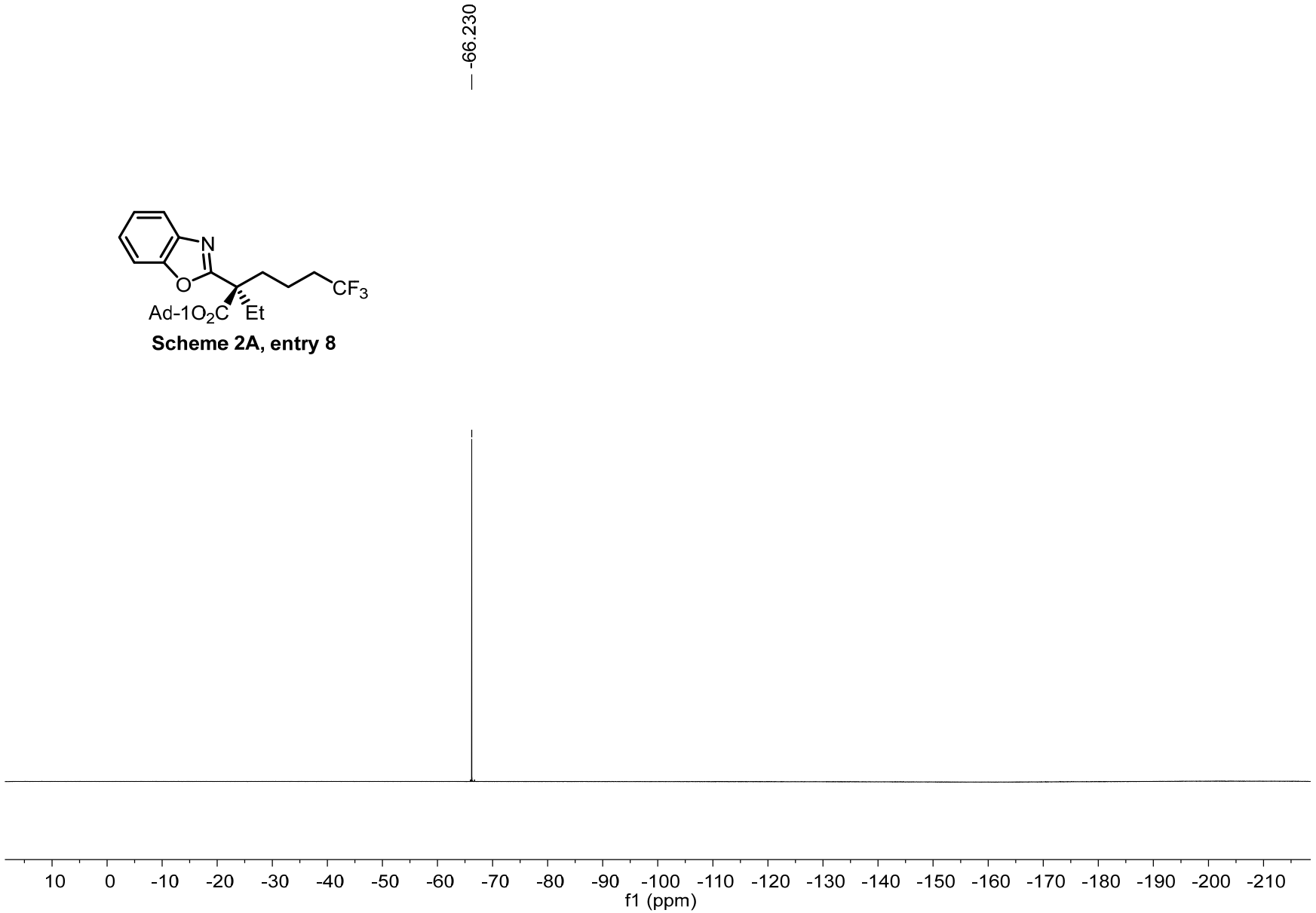


Scheme 2A, entry 7

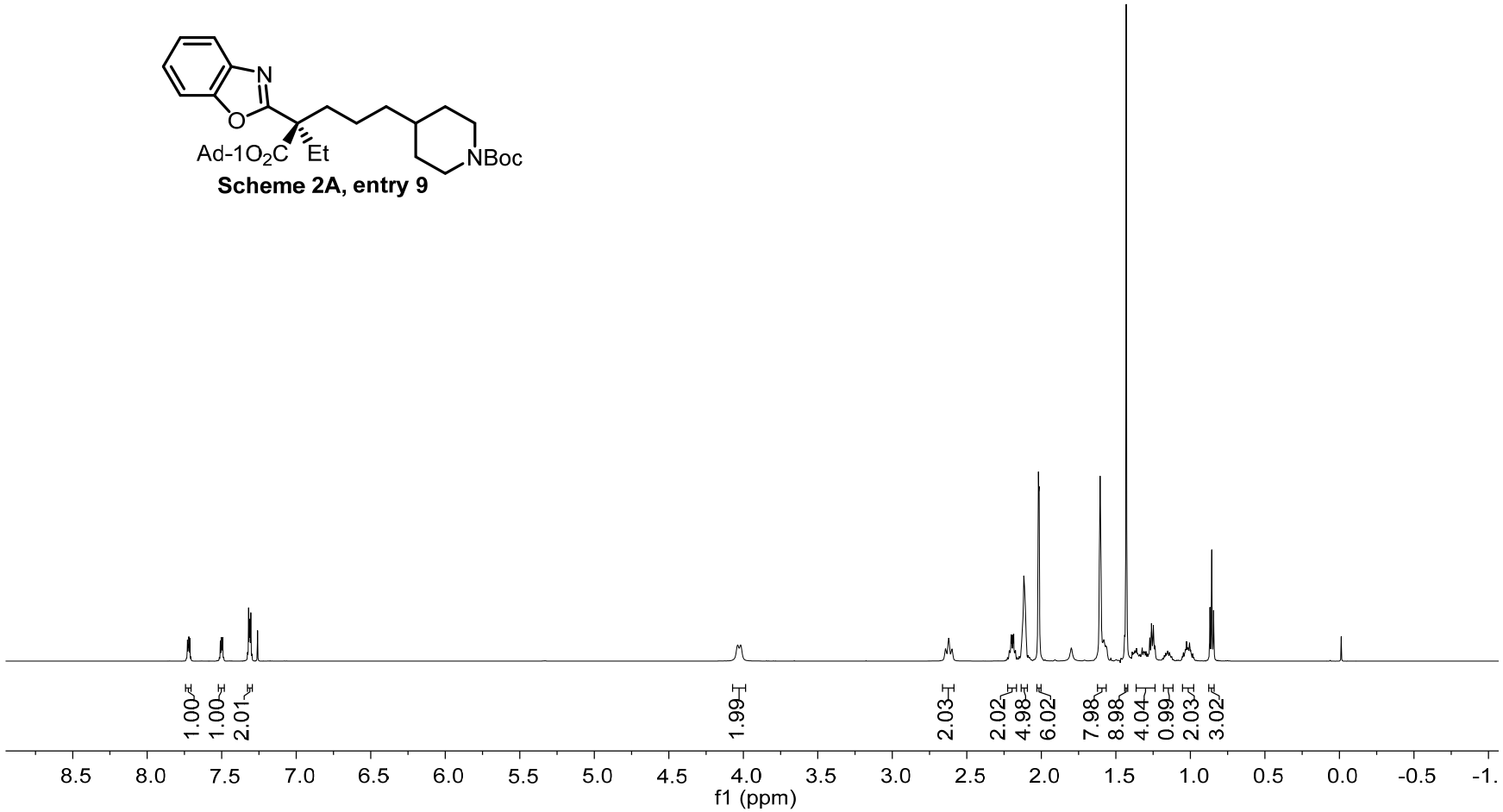

170.444
166.987
150.673
140.791
138.466
128.294
127.566
127.452
124.712
124.068
119.976
110.483
81.910
77.211
76.999
76.790
72.805
70.248
53.624
41.094
36.039
30.757
29.992
26.849
24.491
8.551
N
O
OBn
Ad-1O2C
Et
Scheme 2A, entry 7
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

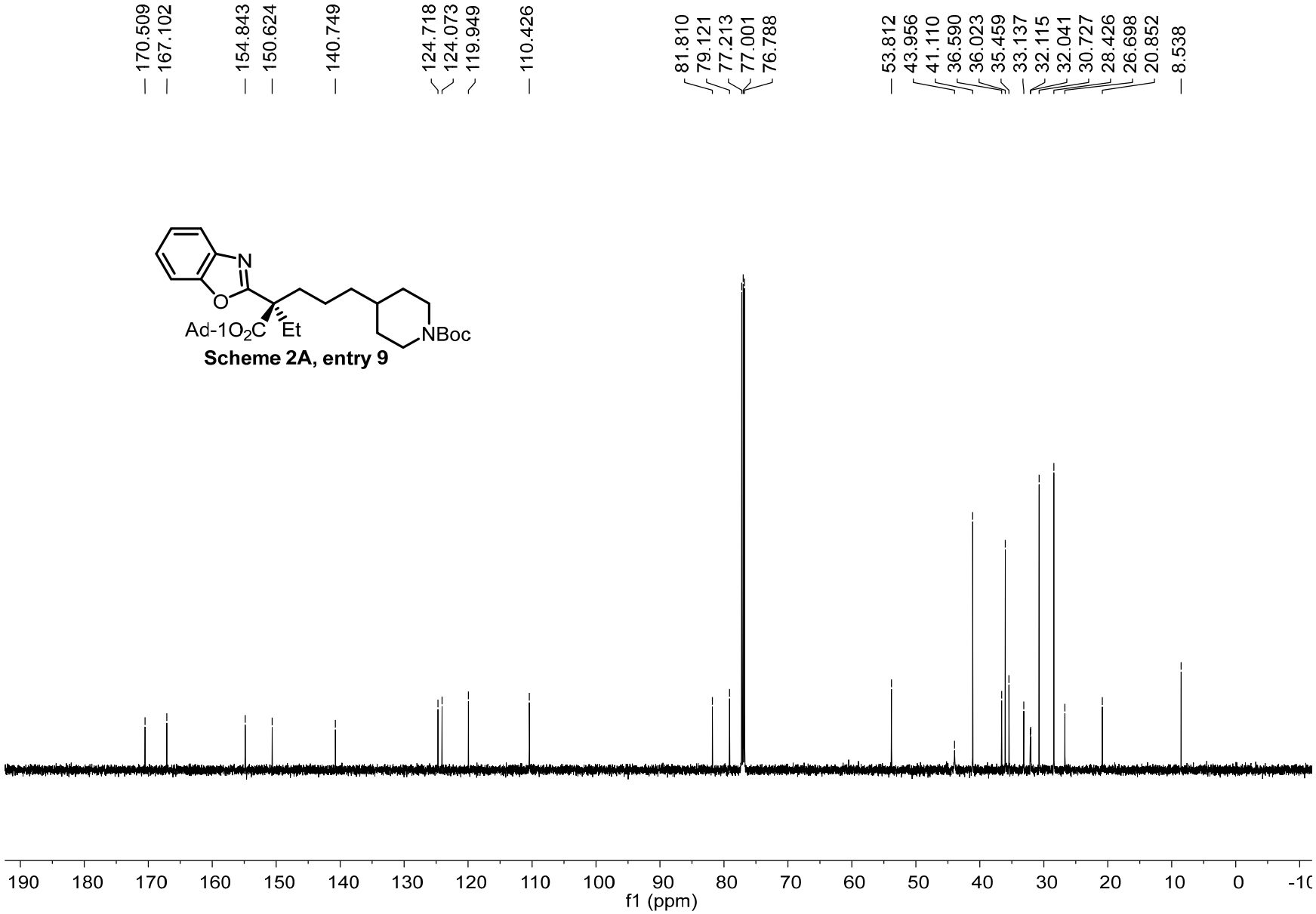

N
O
CF3
Ad-1O2C
Et
Scheme 2A, entry 8
1.00
1.00
2.01
4.03
5.03
6.01
6.99
1.02
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

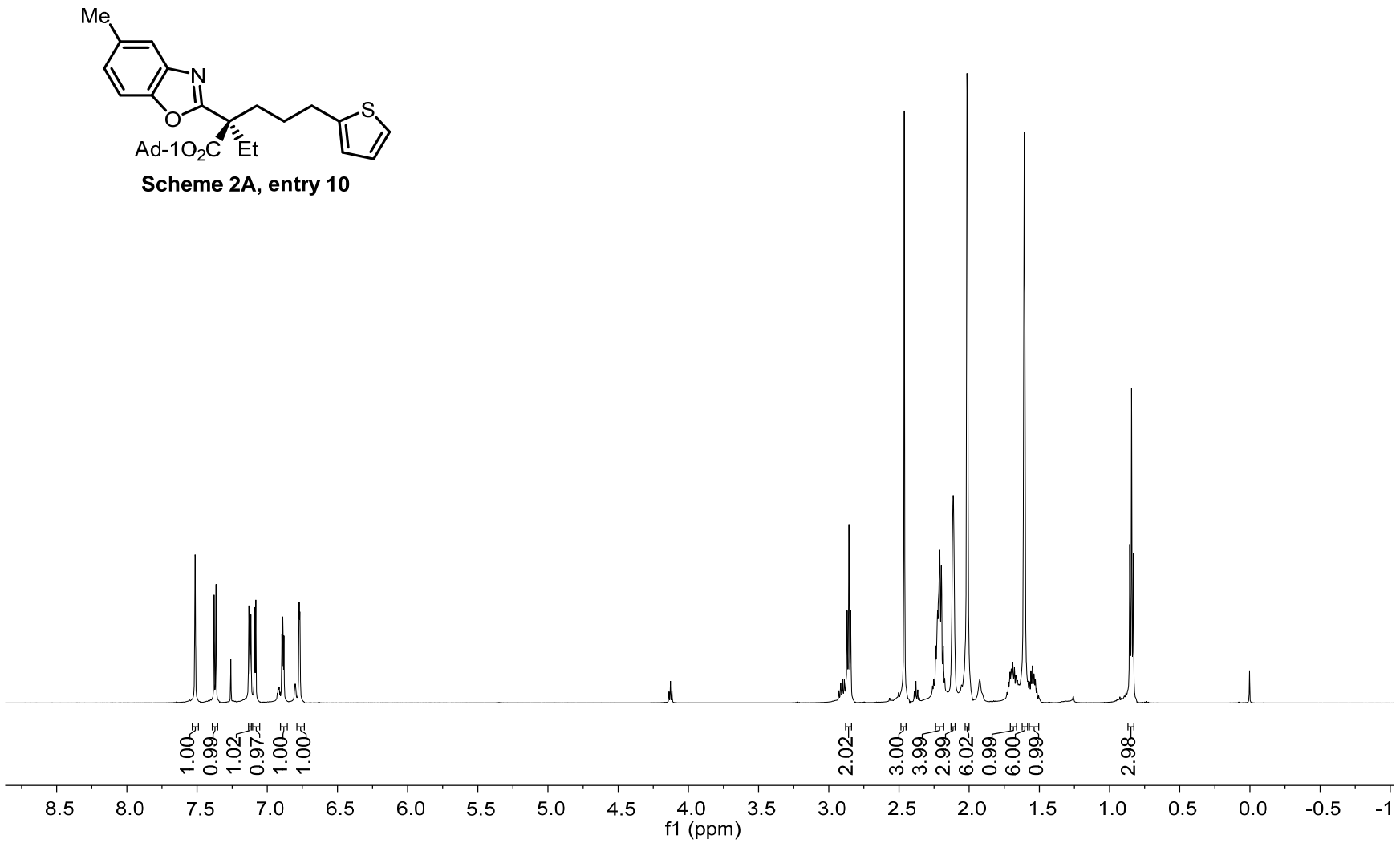

170.083
166.438
150.678
140.701
129.639
127.804
125.973
124.900
124.211
124.141
120.043
110.524
82.285
77.212
76.999
76.787
53.628
41.091
36.010
34.219
34.029
33.838
33.648
32.381
30.769
26.967
16.994
8.511
N
O
CF3
Ad-1O2C
Et
Scheme 2A, entry 8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



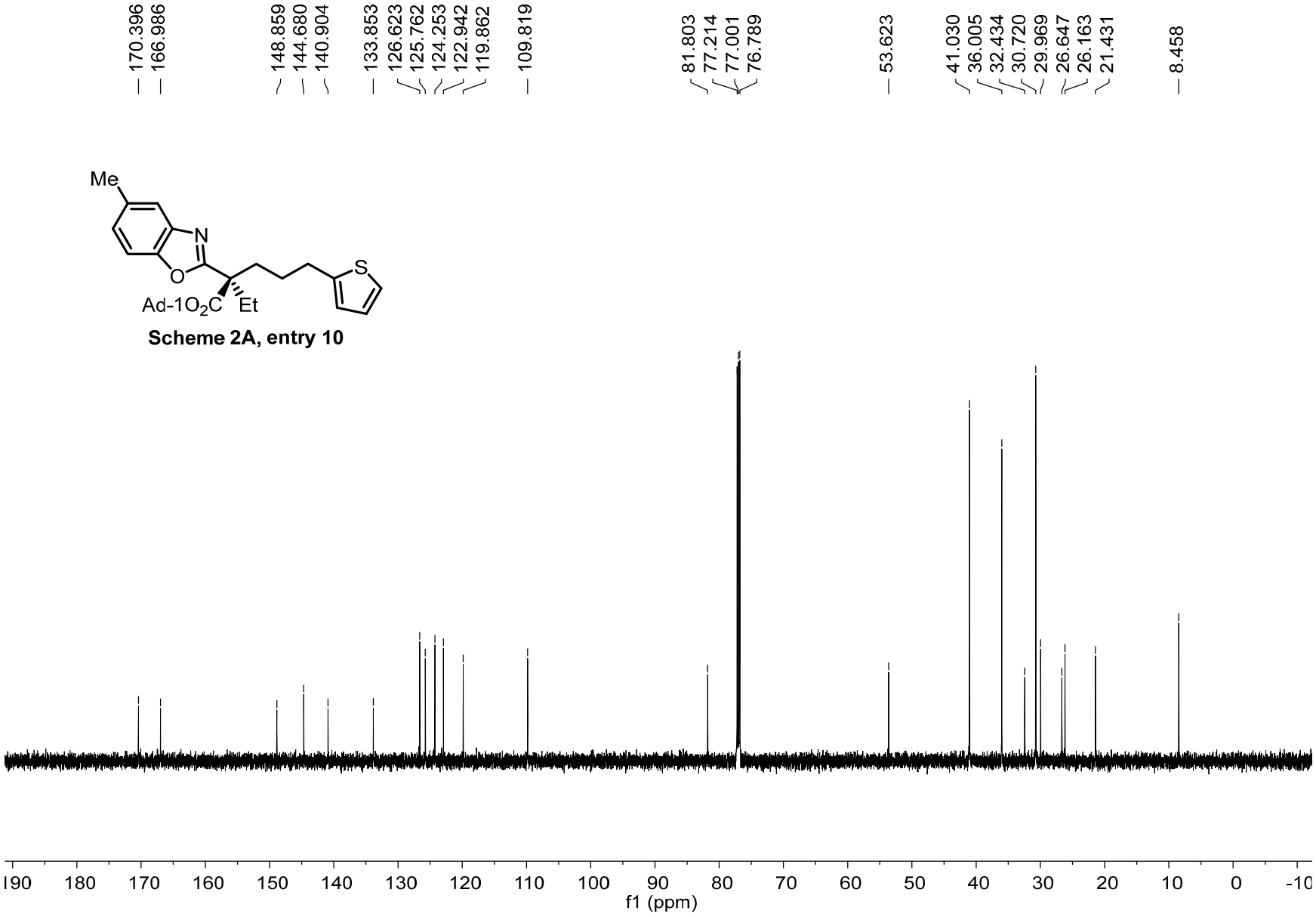
Scheme 2A, entry 8

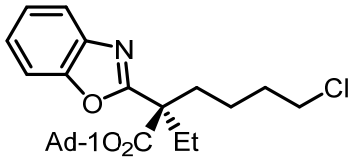

N
O
Ad-1O2C
Et
NBoc
Scheme 2A, entry 9
1.00
1.00
2.01
1.99
2.03
2.02
4.98
6.02
7.98
8.98
4.04
0.99
2.03
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)


170.509
167.102
154.843
150.624
140.749
124.718
124.073
119.949
110.426
81.810
79.121
77.213
77.001
76.788
53.812
43.956
41.110
36.590
36.023
35.459
33.137
32.115
32.041
30.727
28.426
26.698
20.852
8.538
N
O
Ad-1O2C
Et
NBoc
Scheme 2A, entry 9
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

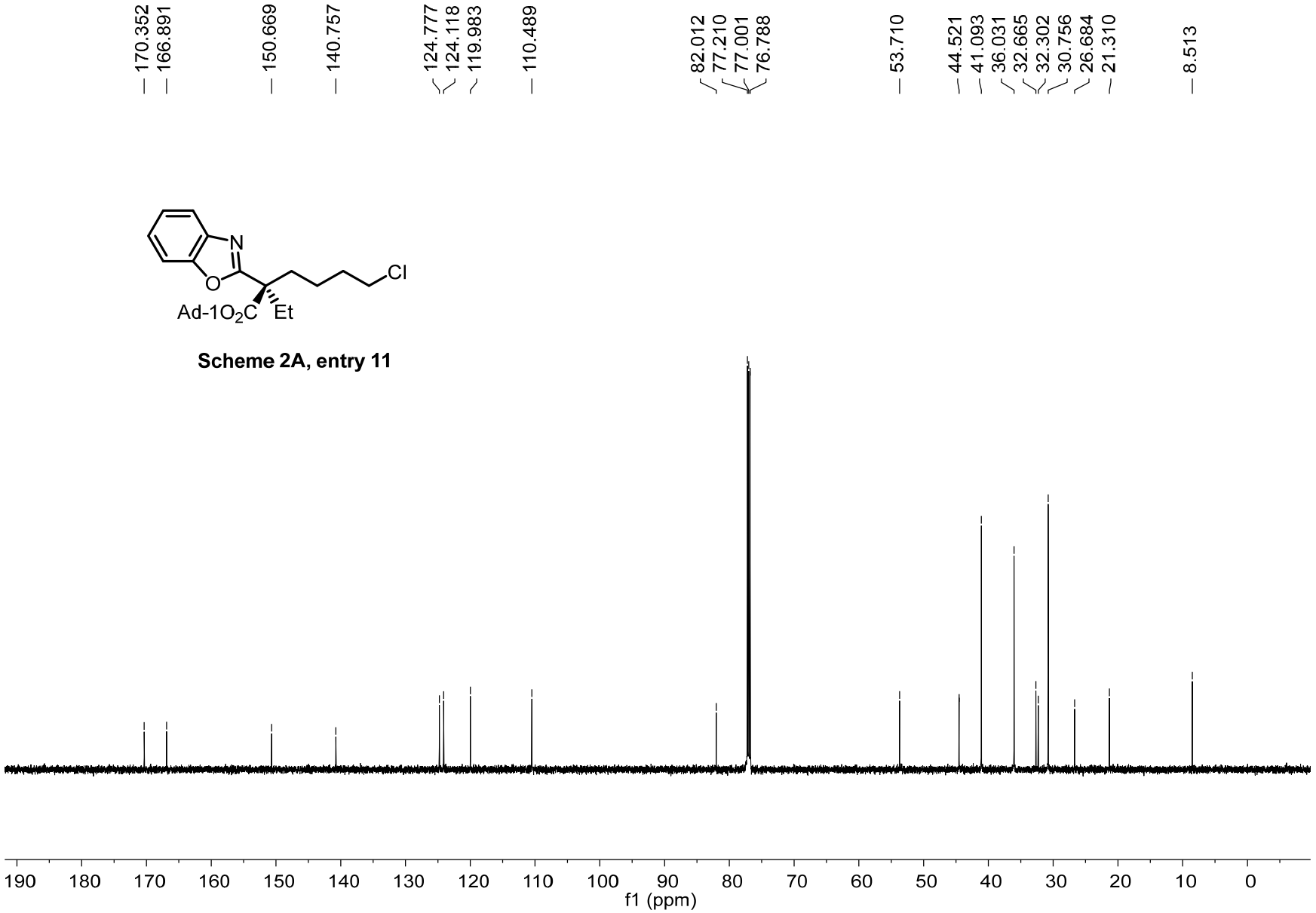


Scheme 2A, entry 10

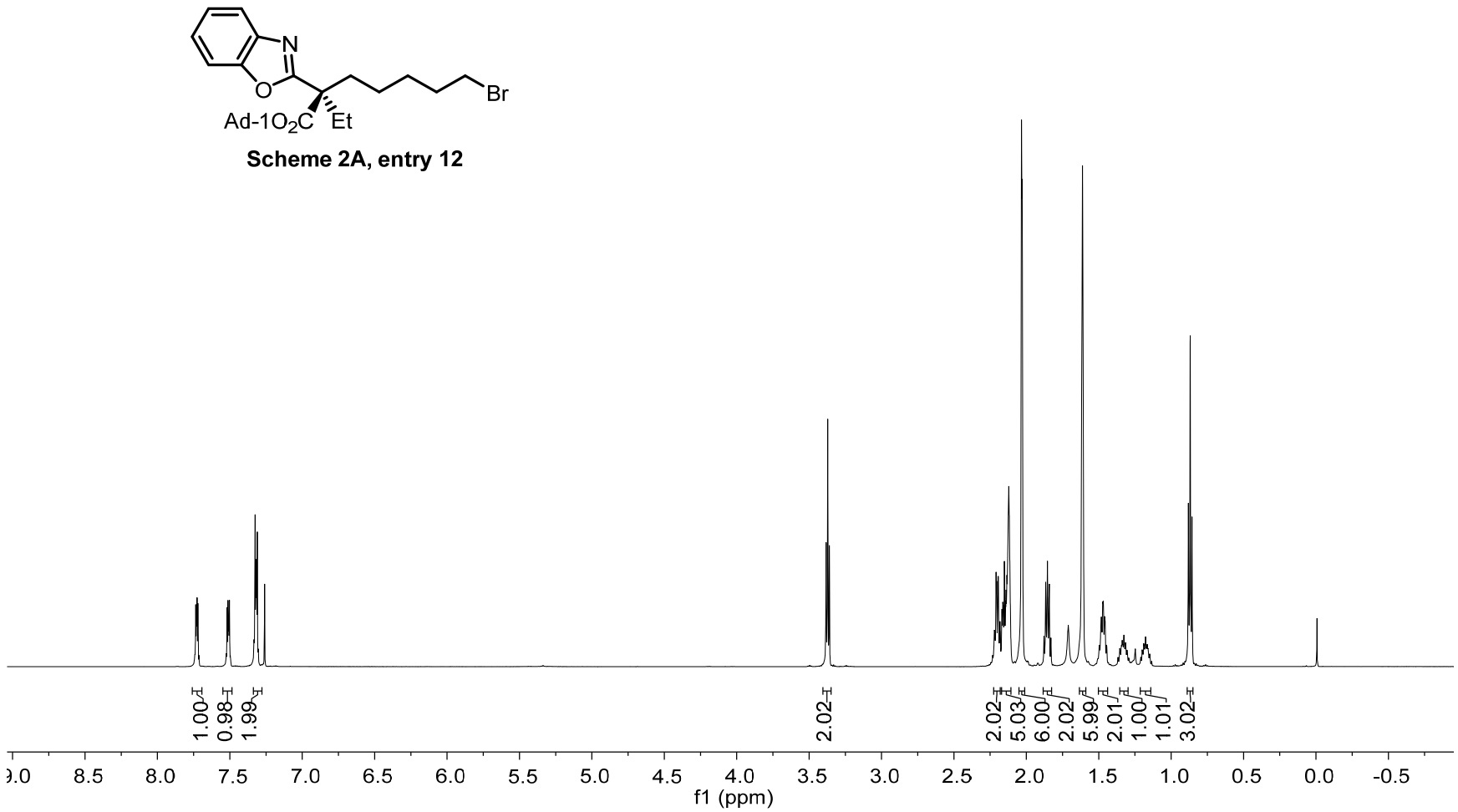

170.396
166.986
148.859
144.680
140.904
133.853
126.623
125.762
124.253
122.942
119.862
109.819
81.803
77.214
77.001
76.789
53.623
41.030
36.005
32.434
30.720
29.969
26.647
26.163
21.431
8.458
Me
N
O
S
Ad-1O2C
Et
Scheme 2A, entry 10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



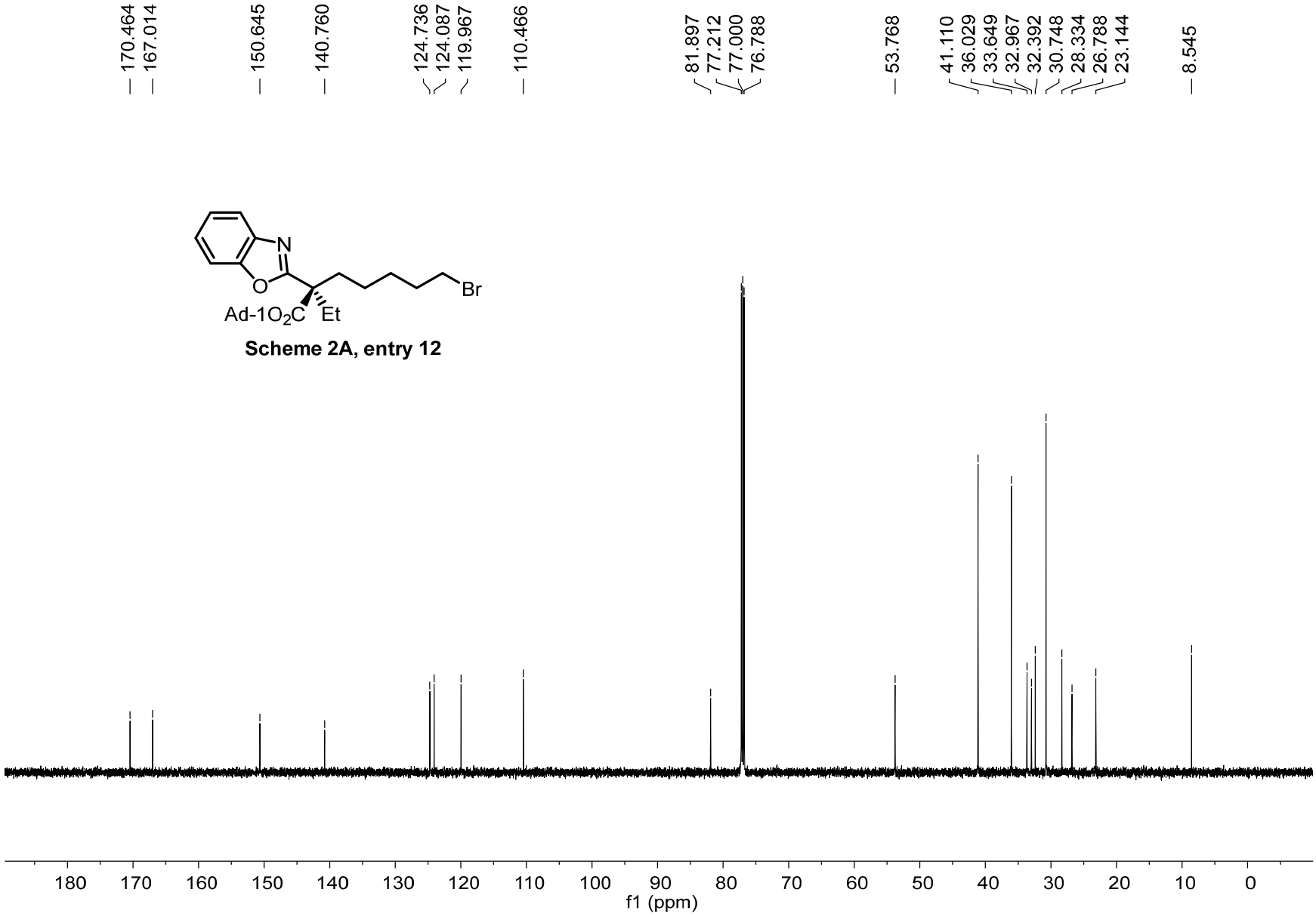
Scheme 2A, entry 11

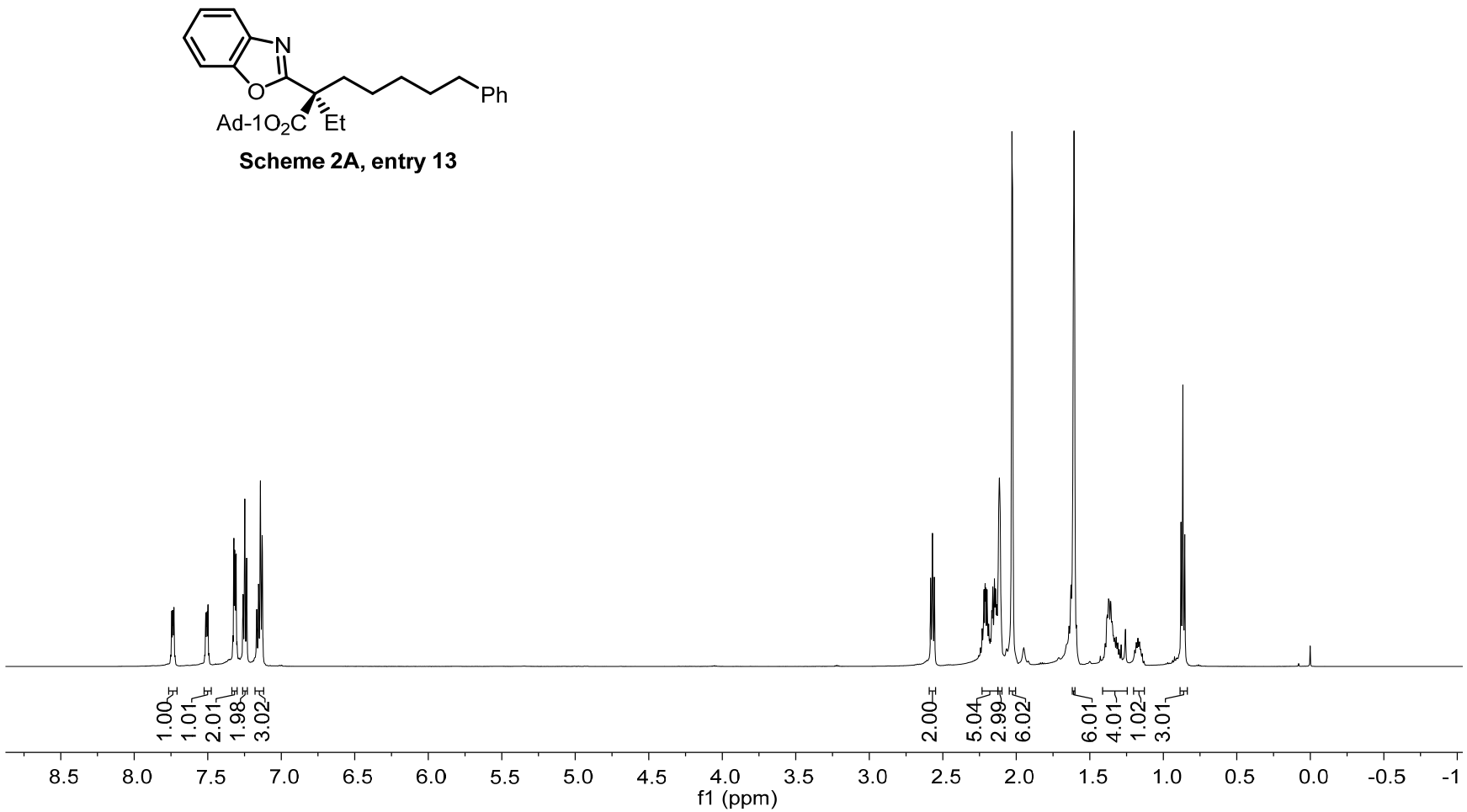


Scheme 2A, entry 11

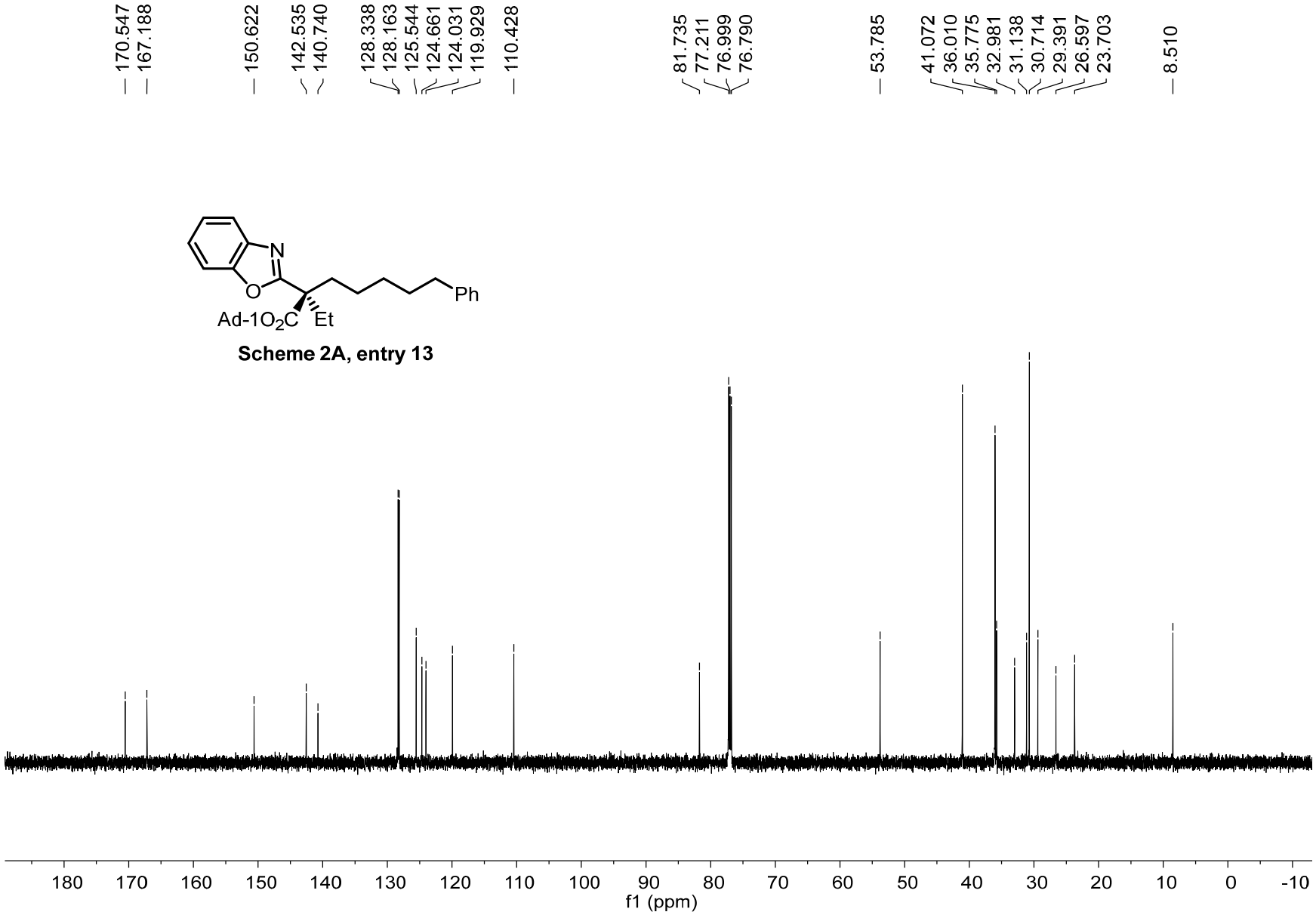


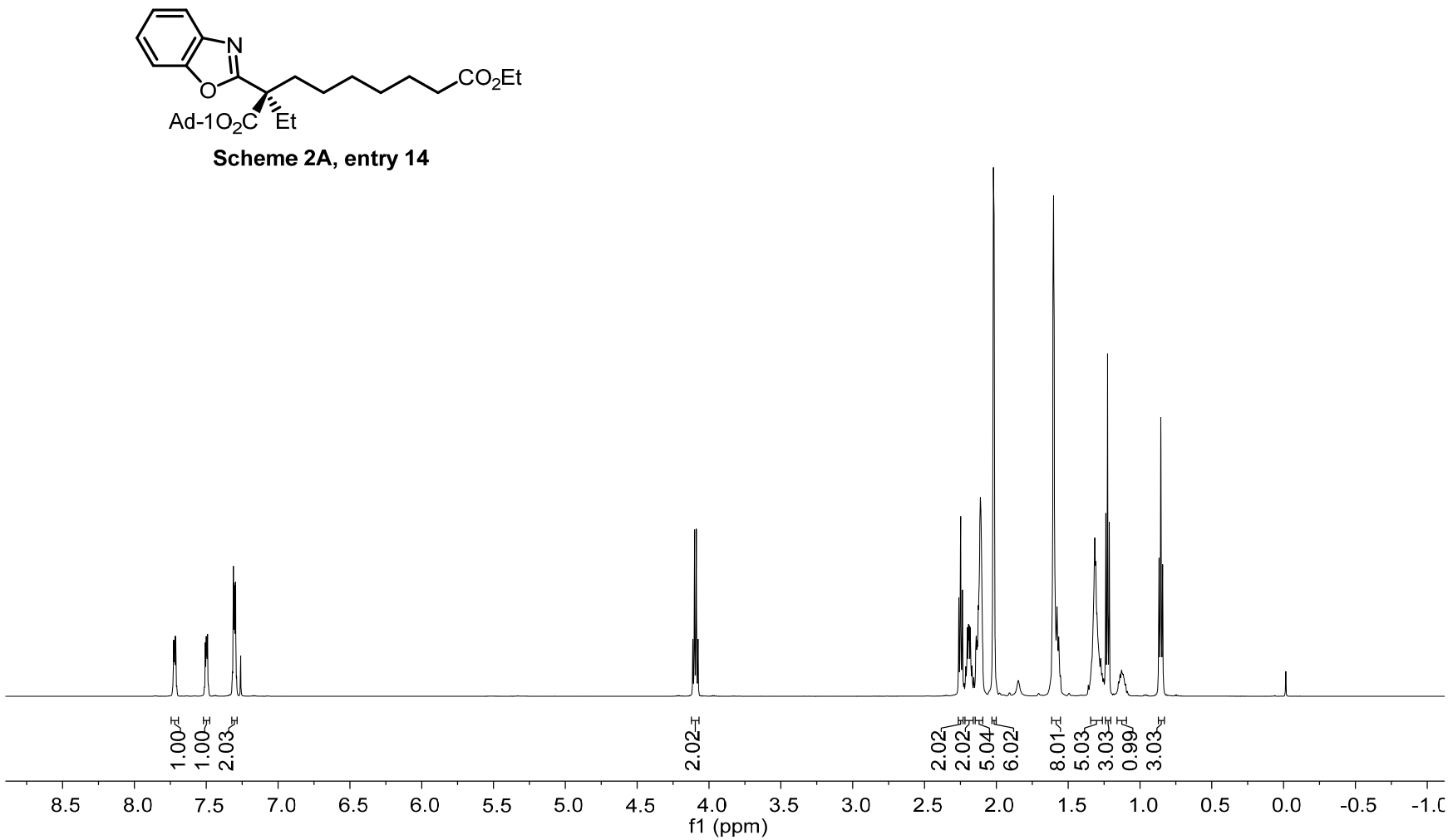
Scheme 2A, entry 12


170.464
167.014
150.645
140.760
124.736
124.087
119.967
110.466
81.897
77.212
77.000
76.788
53.768
41.110
36.029
33.649
32.967
32.392
30.748
28.334
26.788
23.144
8.545
N
O
Br
Ad-1O2C
Et
Scheme 2A, entry 12
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

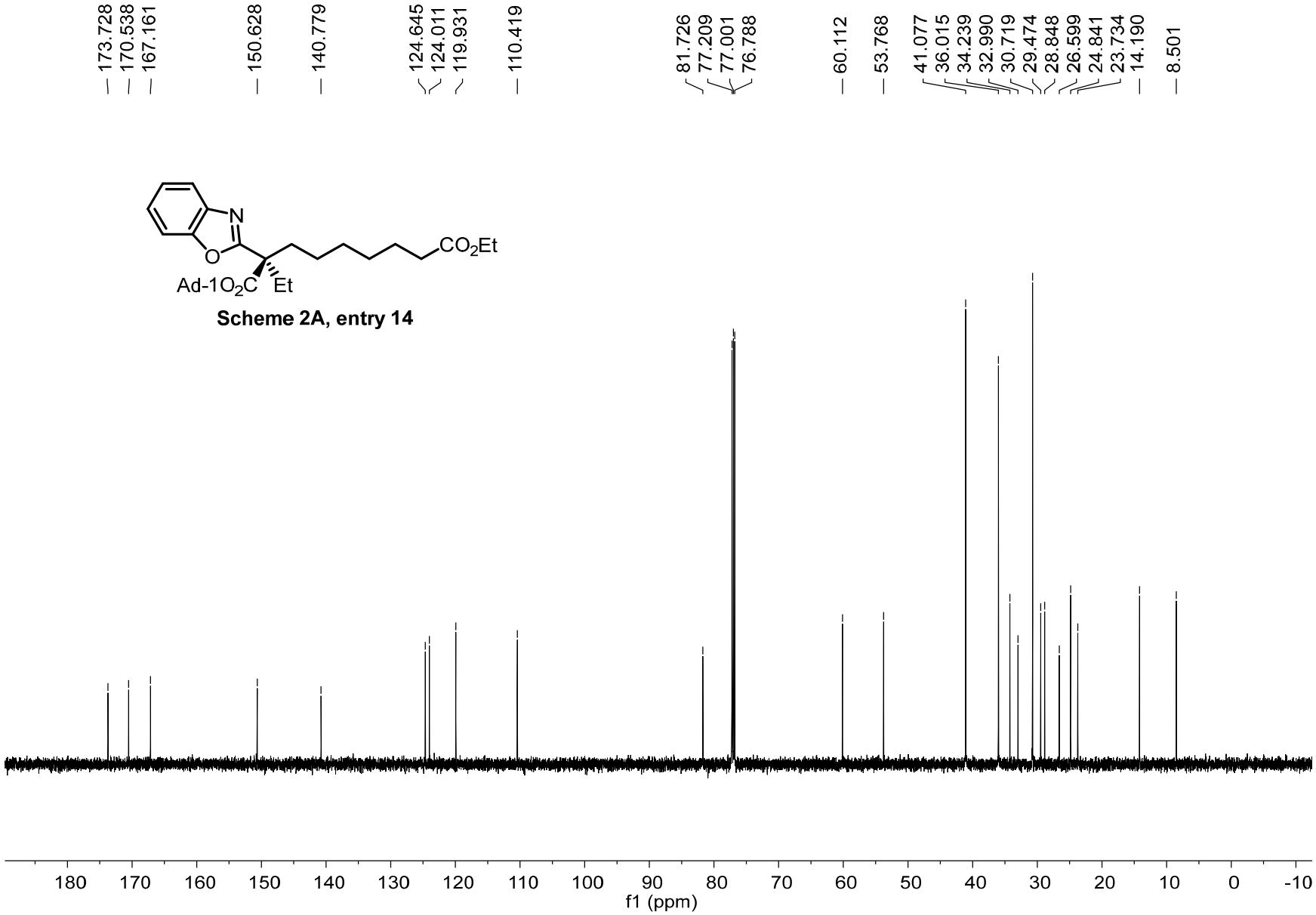


Scheme 2A, entry 13

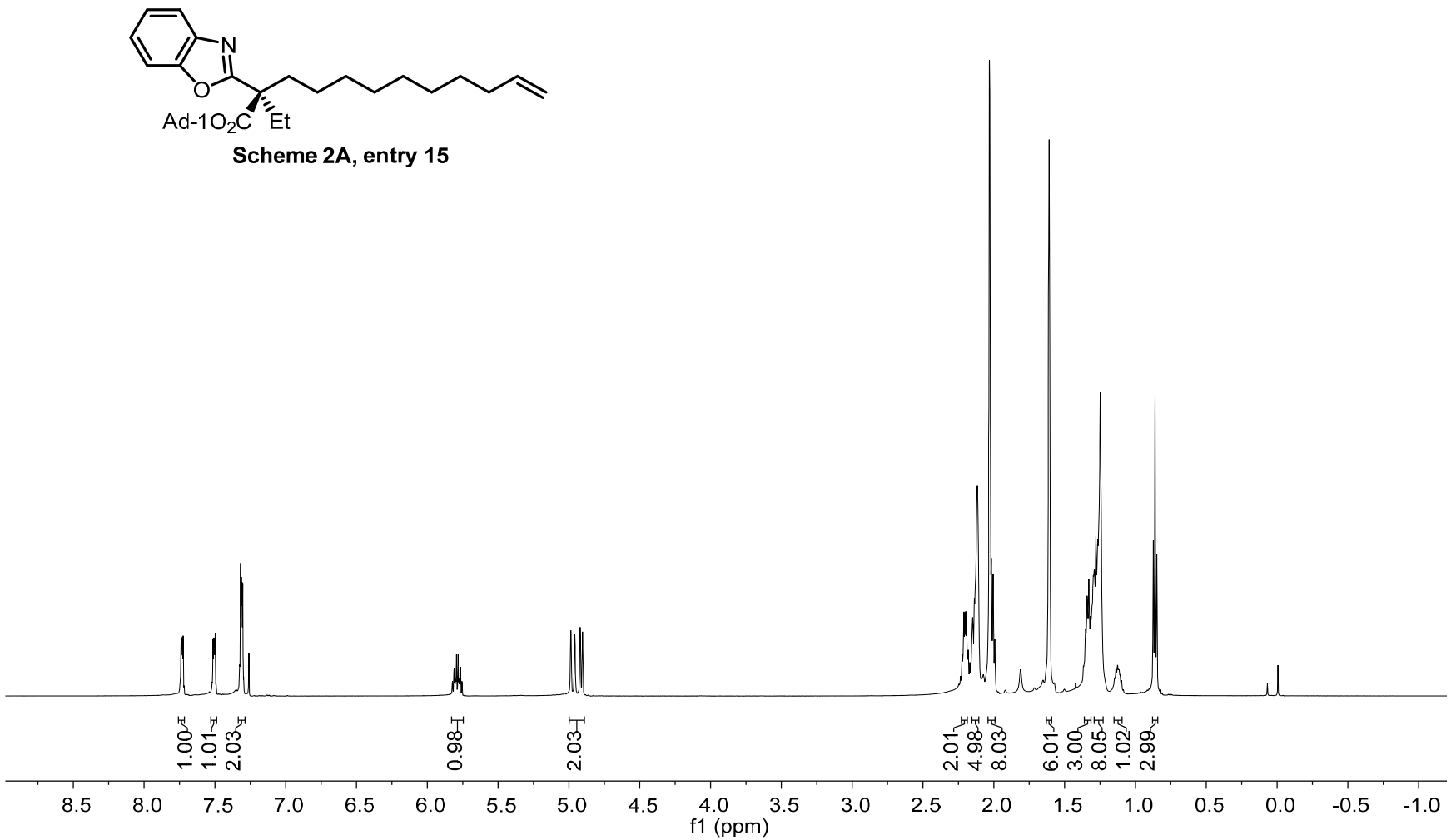

170.547
167.188
150.622
142.535
140.740
128.338
128.163
125.544
124.661
124.031
119.929
110.428
81.735
77.211
76.999
76.790
53.785
41.072
36.010
35.775
32.981
31.138
30.714
29.391
26.597
23.703
8.510
N
O
Ph
Ad-1O2C
Et
Scheme 2A, entry 13
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



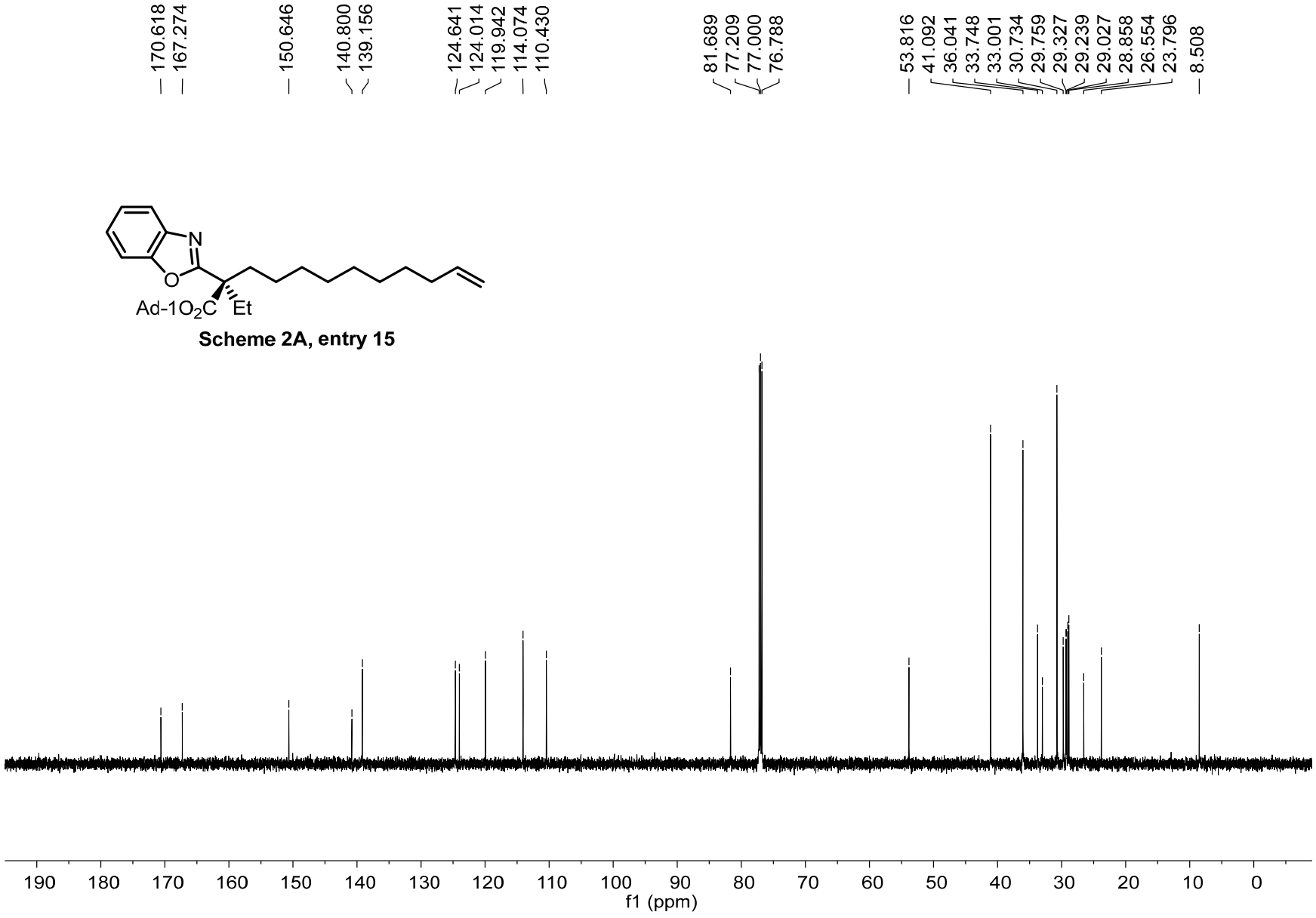
Scheme 2A, entry 14



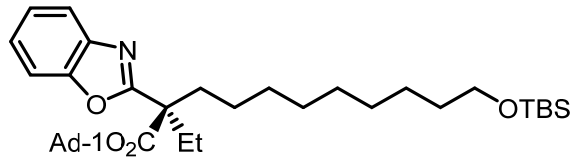
Scheme 2A, entry 14



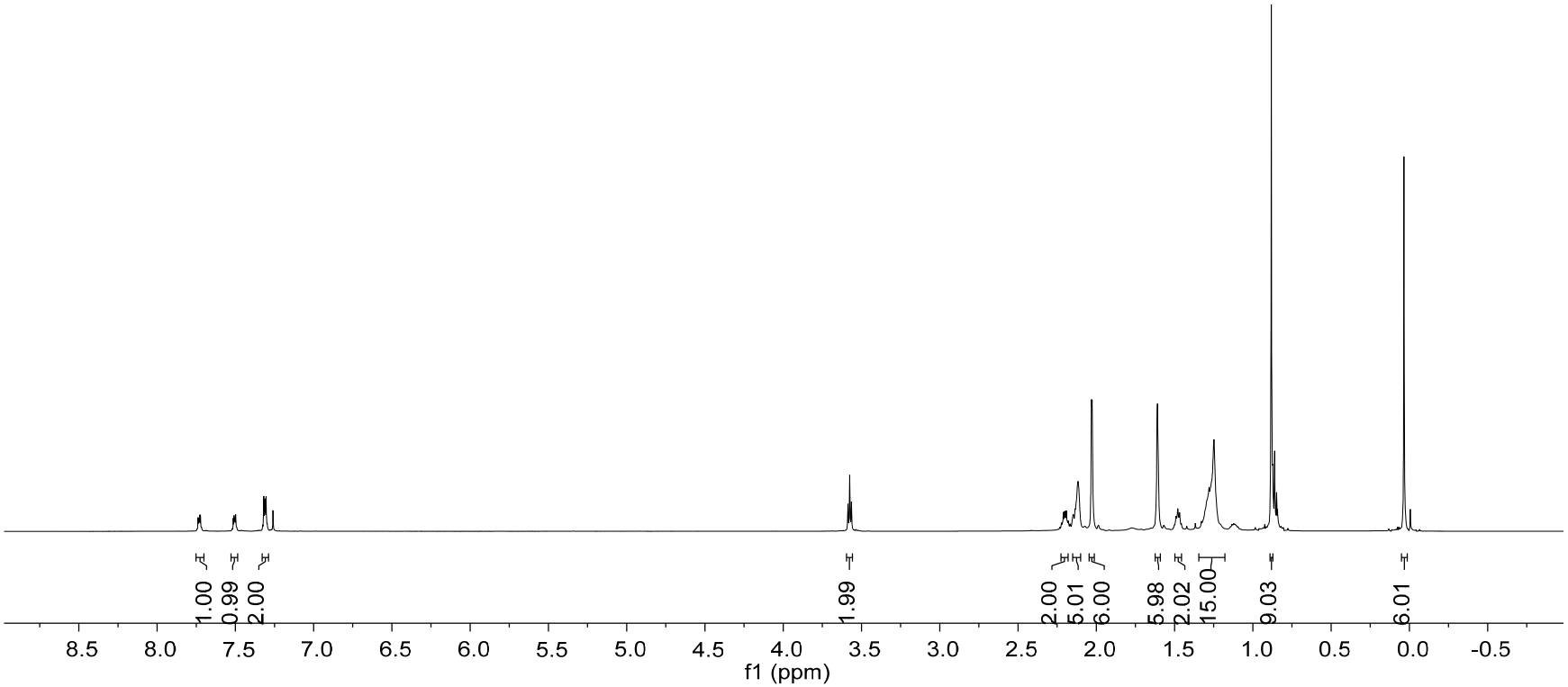
Scheme 2A, entry 15

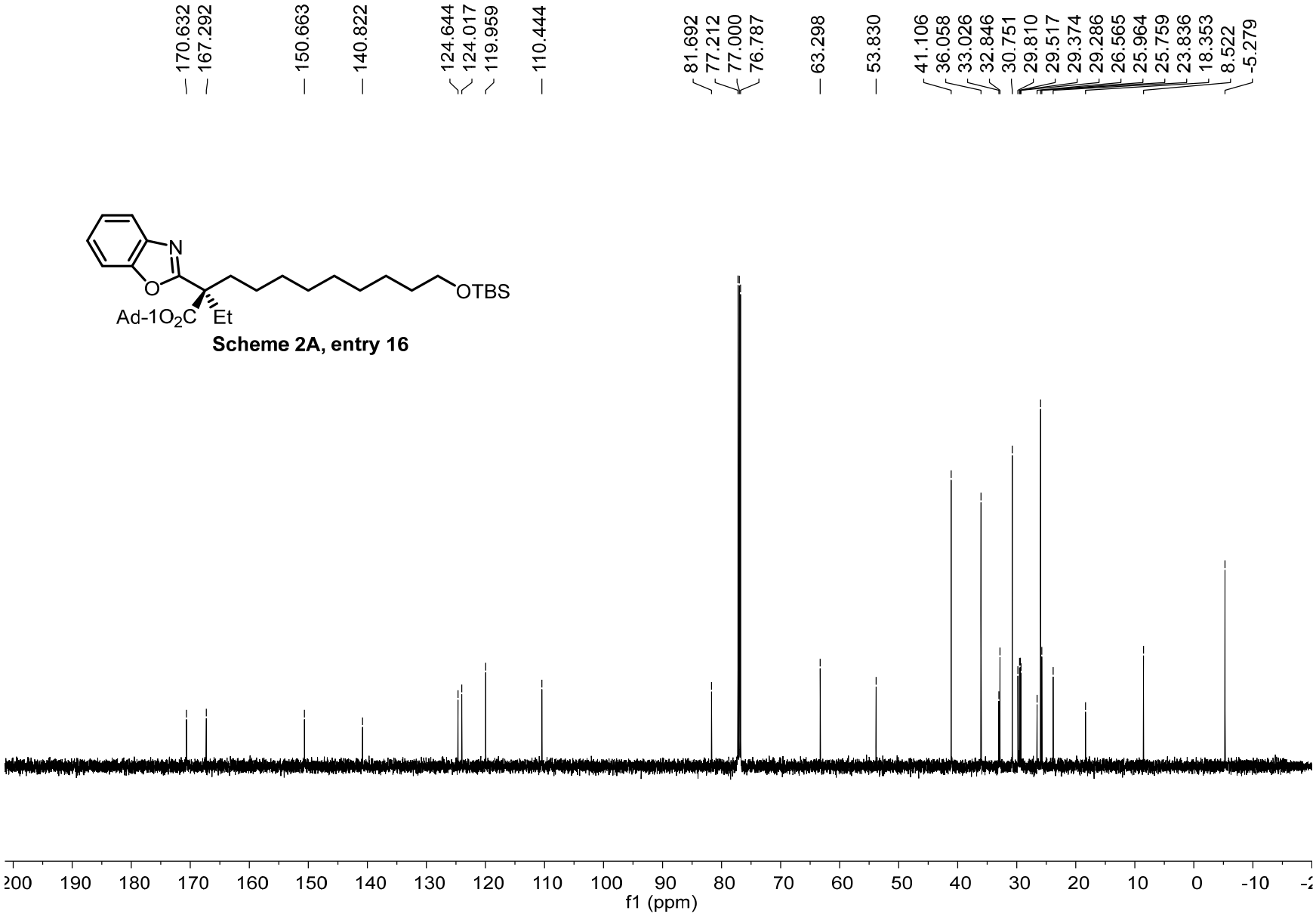


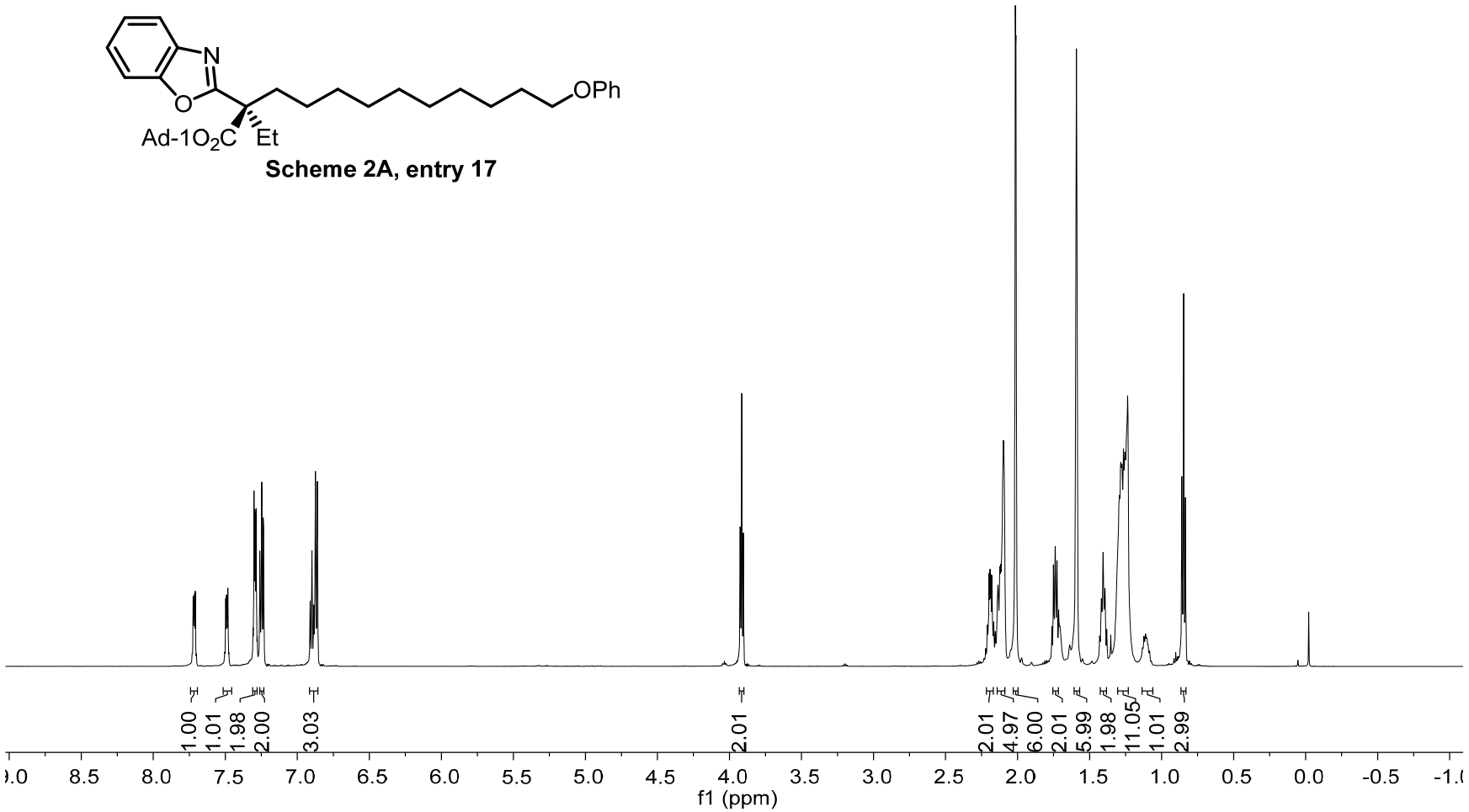
Scheme 2A, entry 15



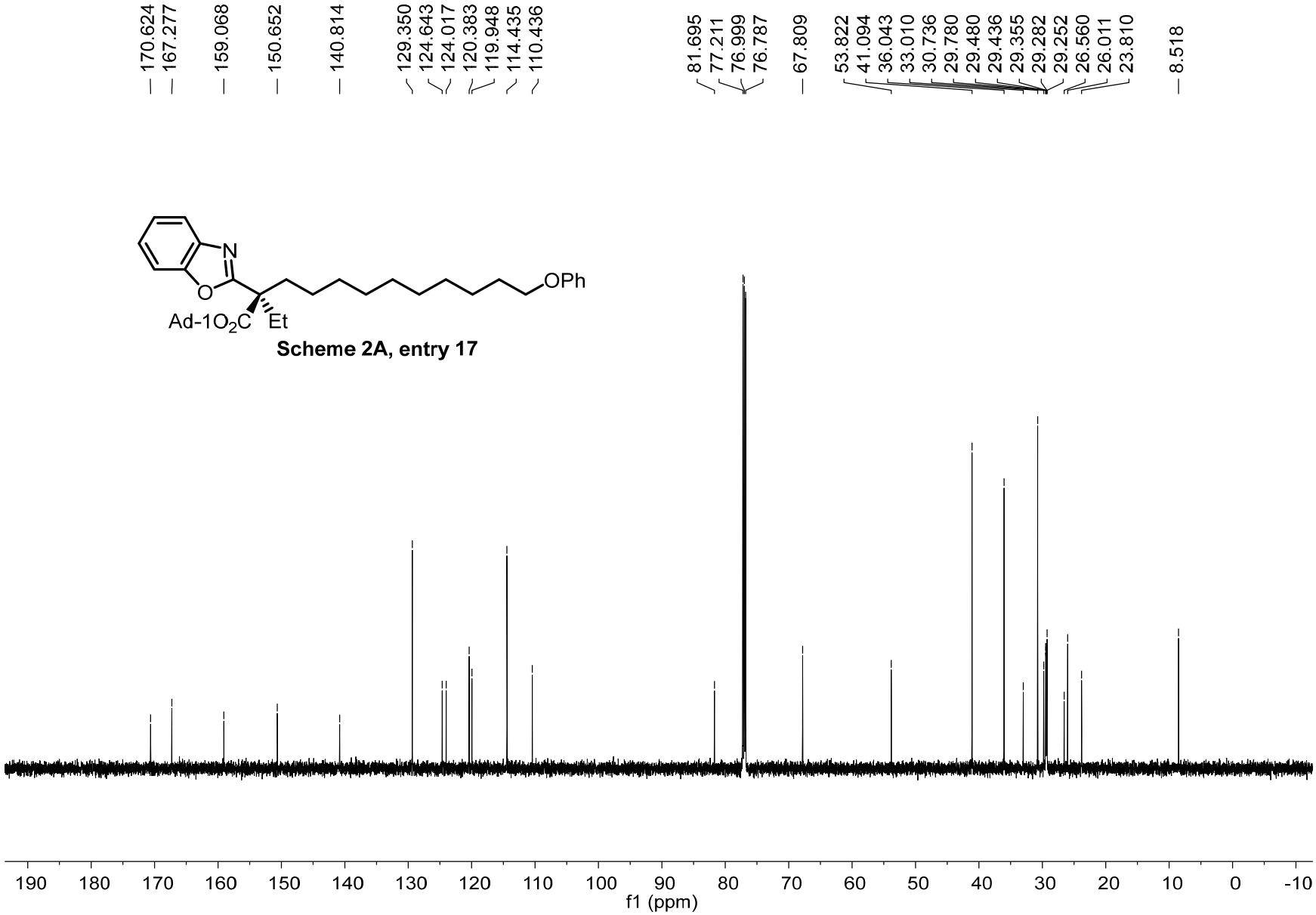
Scheme 2A, entry 16



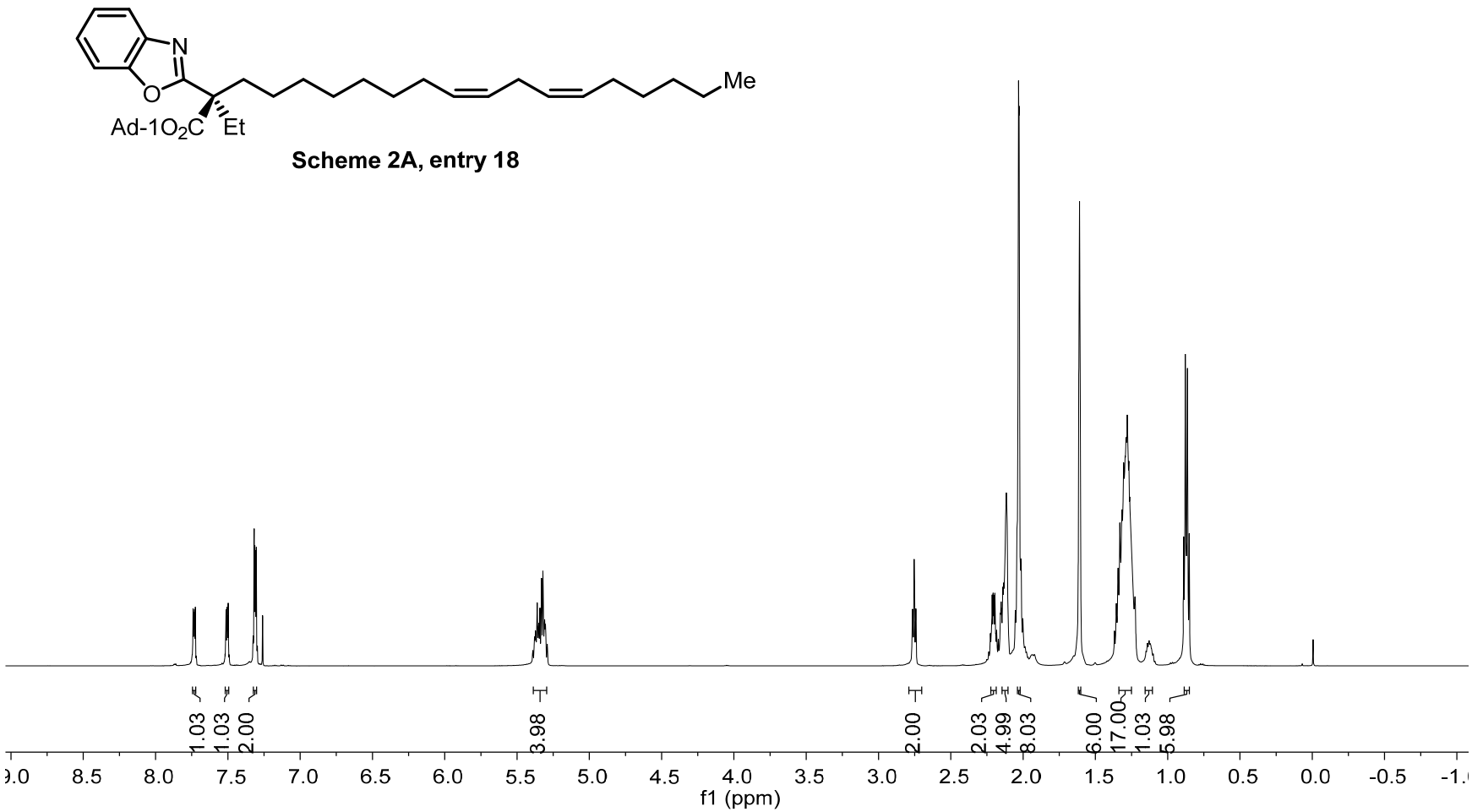

170.632
167.292
150.663
140.822
124.644
124.017
119.959
110.444
81.692
77.212
77.000
76.787
63.298
53.830
41.106
36.058
33.026
32.846
30.751
29.810
29.517
29.374
29.286
26.565
25.964
25.759
23.836
18.353
8.522
-5.279
N
O
OTBS
Ad-1O2C
Et
Scheme 2A, entry 16
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



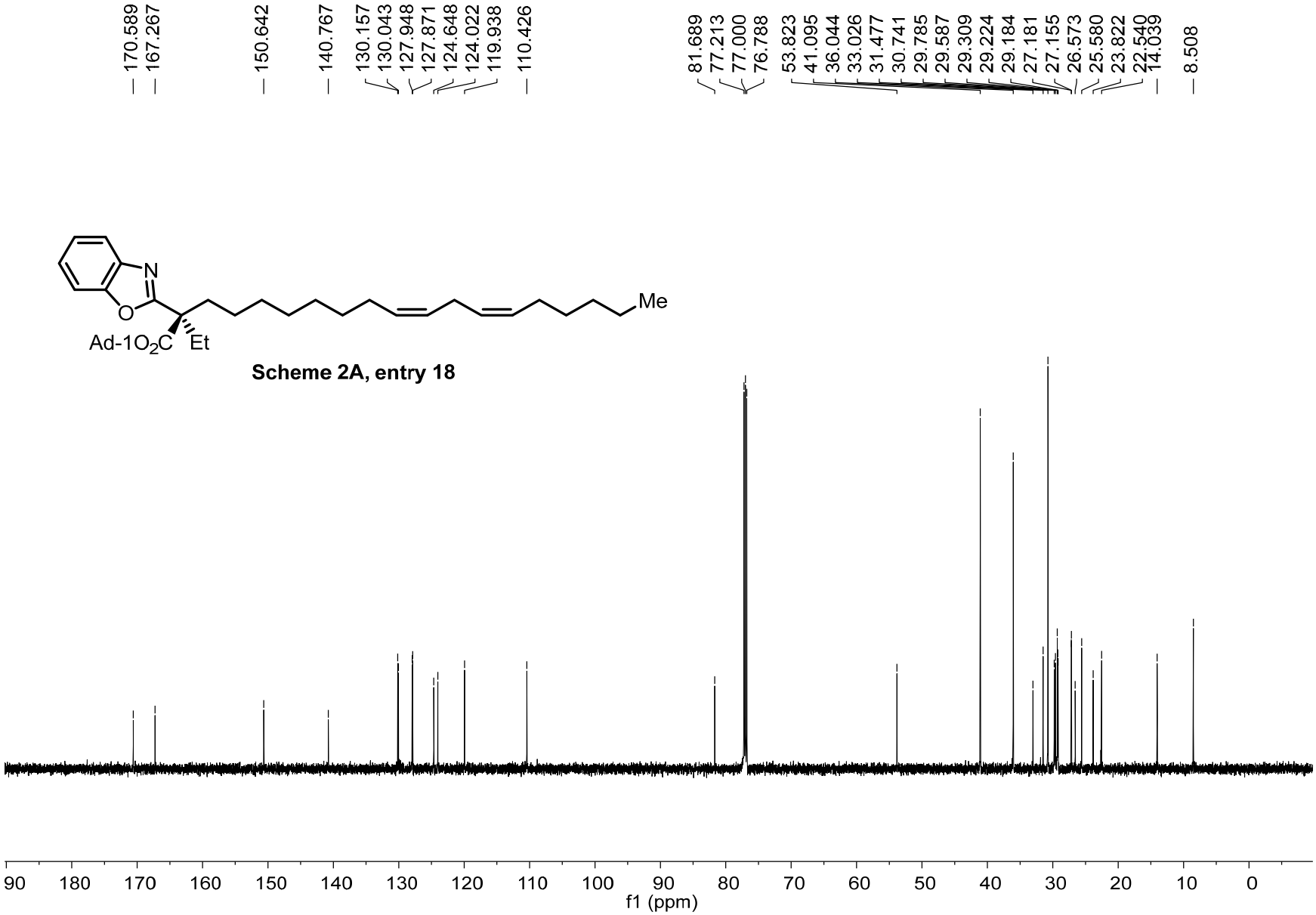
Scheme 2A, entry 17



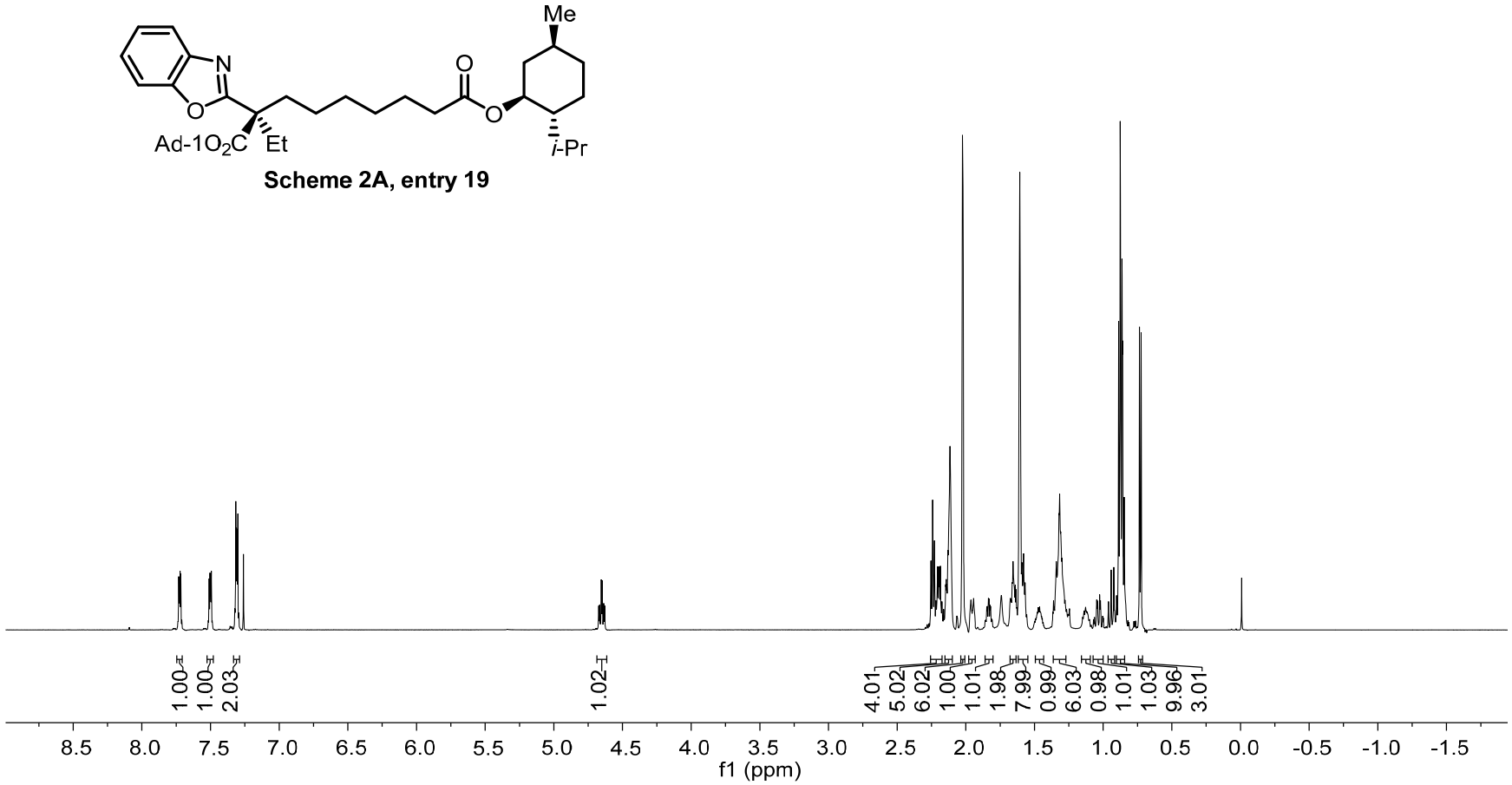
Scheme 2A, entry 17



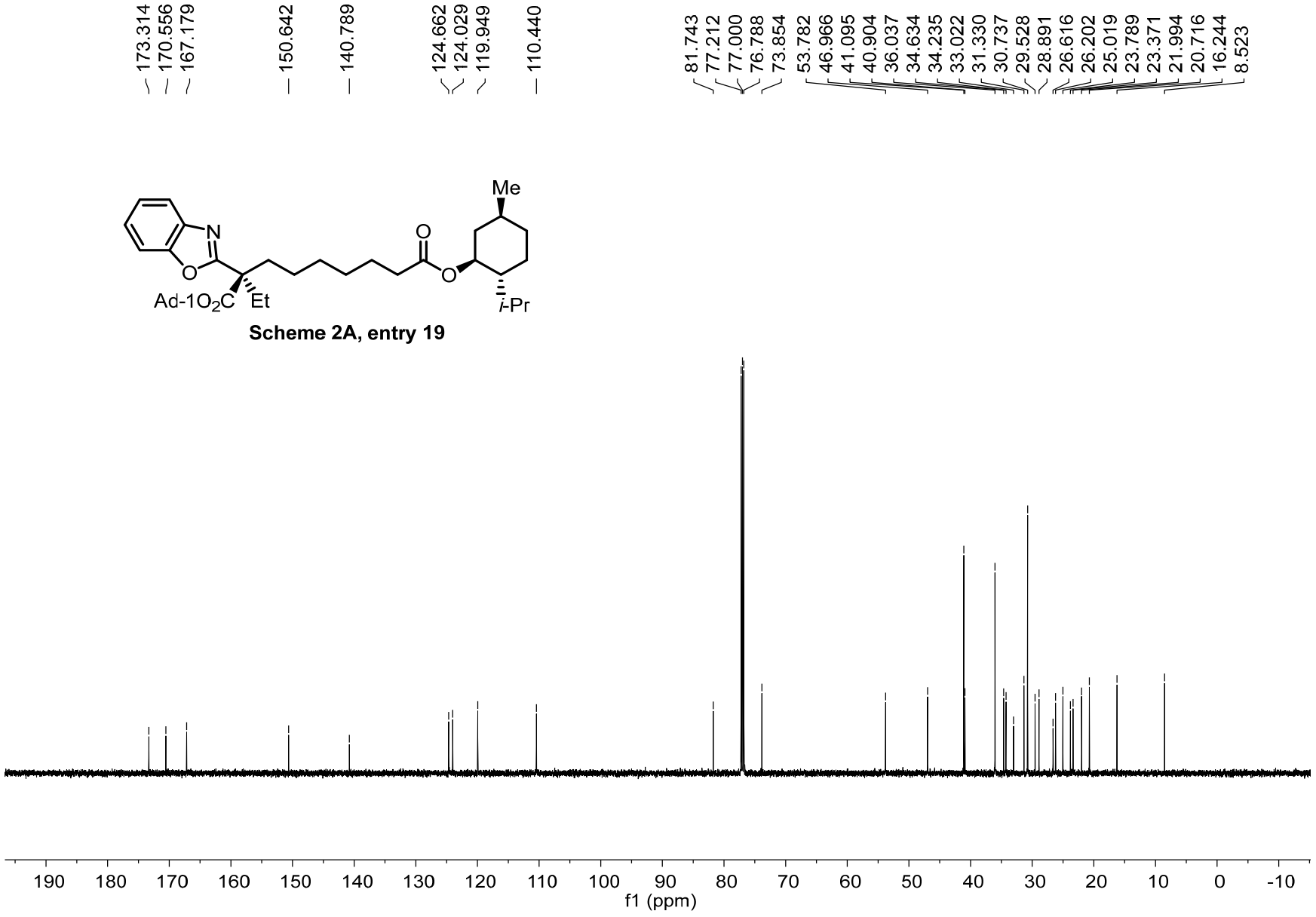
Scheme 2A, entry 18



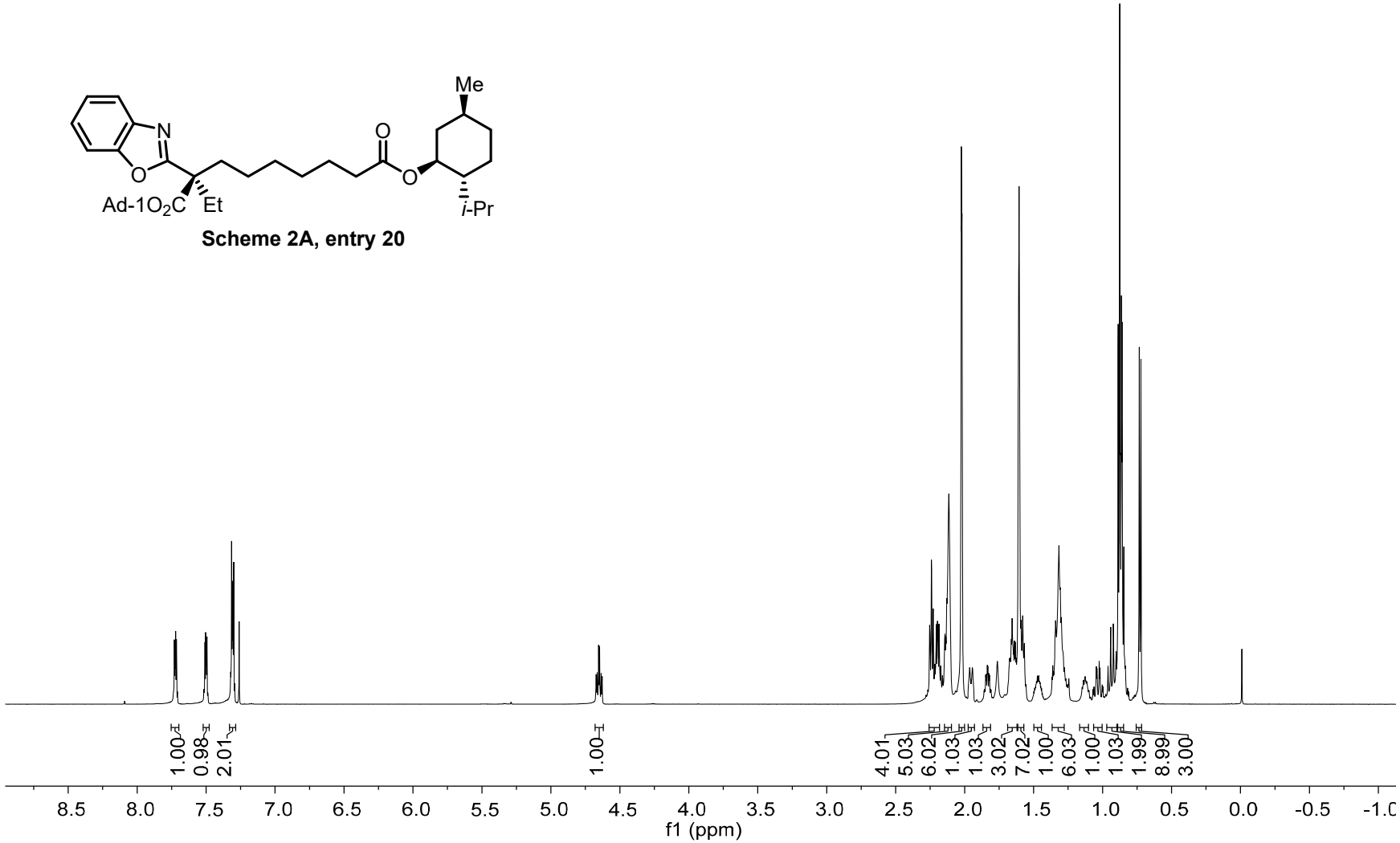
Scheme 2A, entry 18



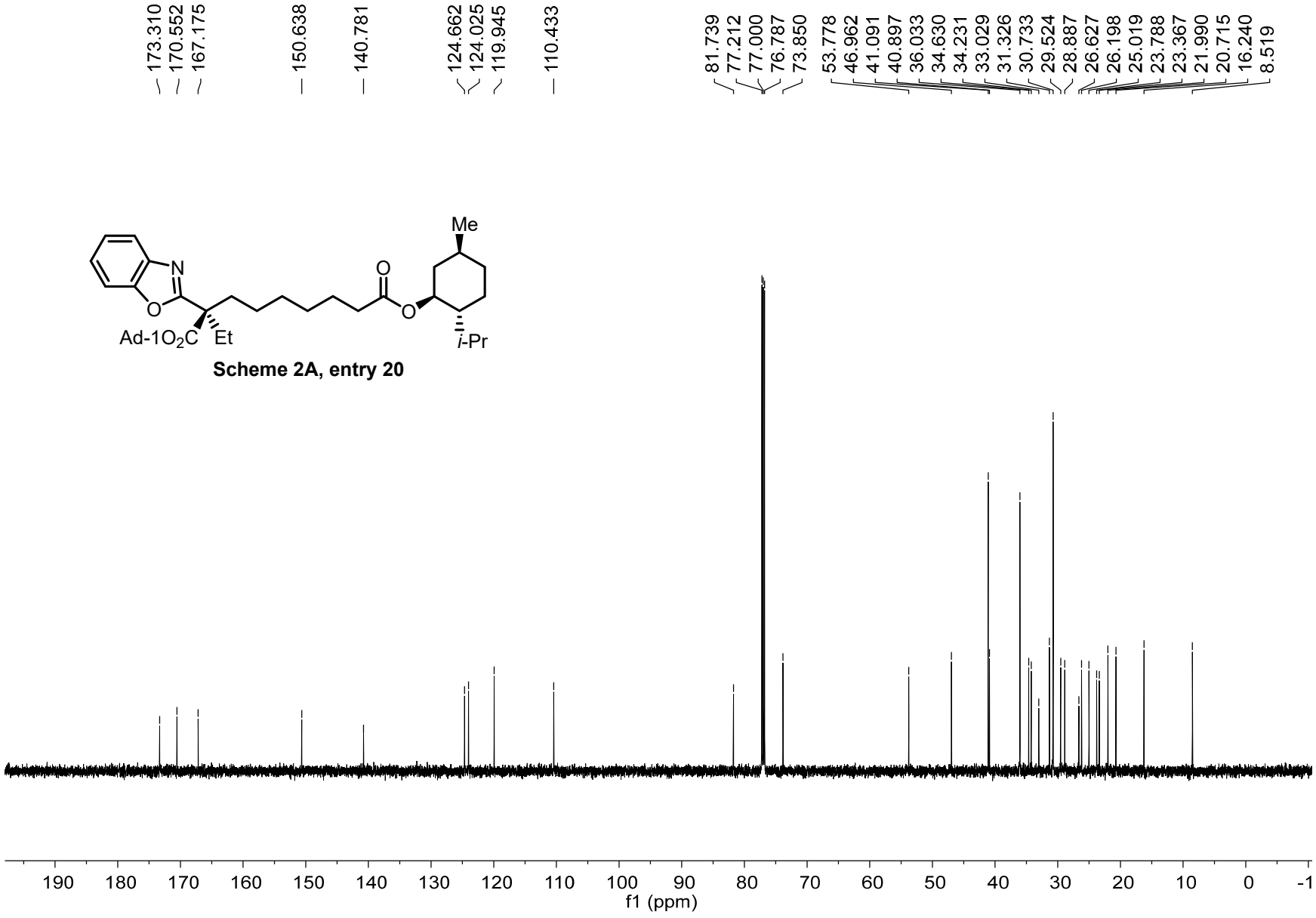
Scheme 2A, entry 19



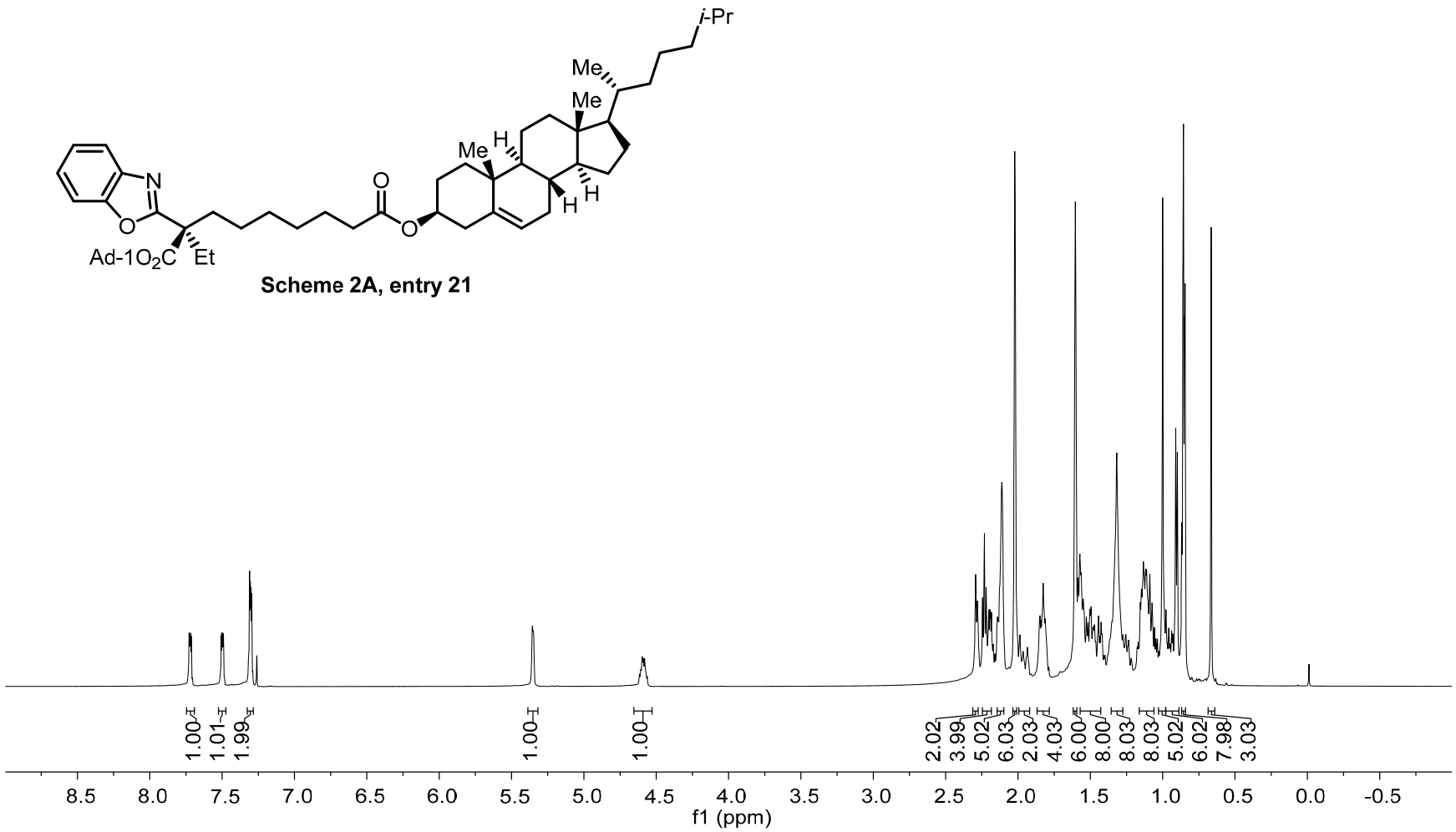
Scheme 2A, entry 19



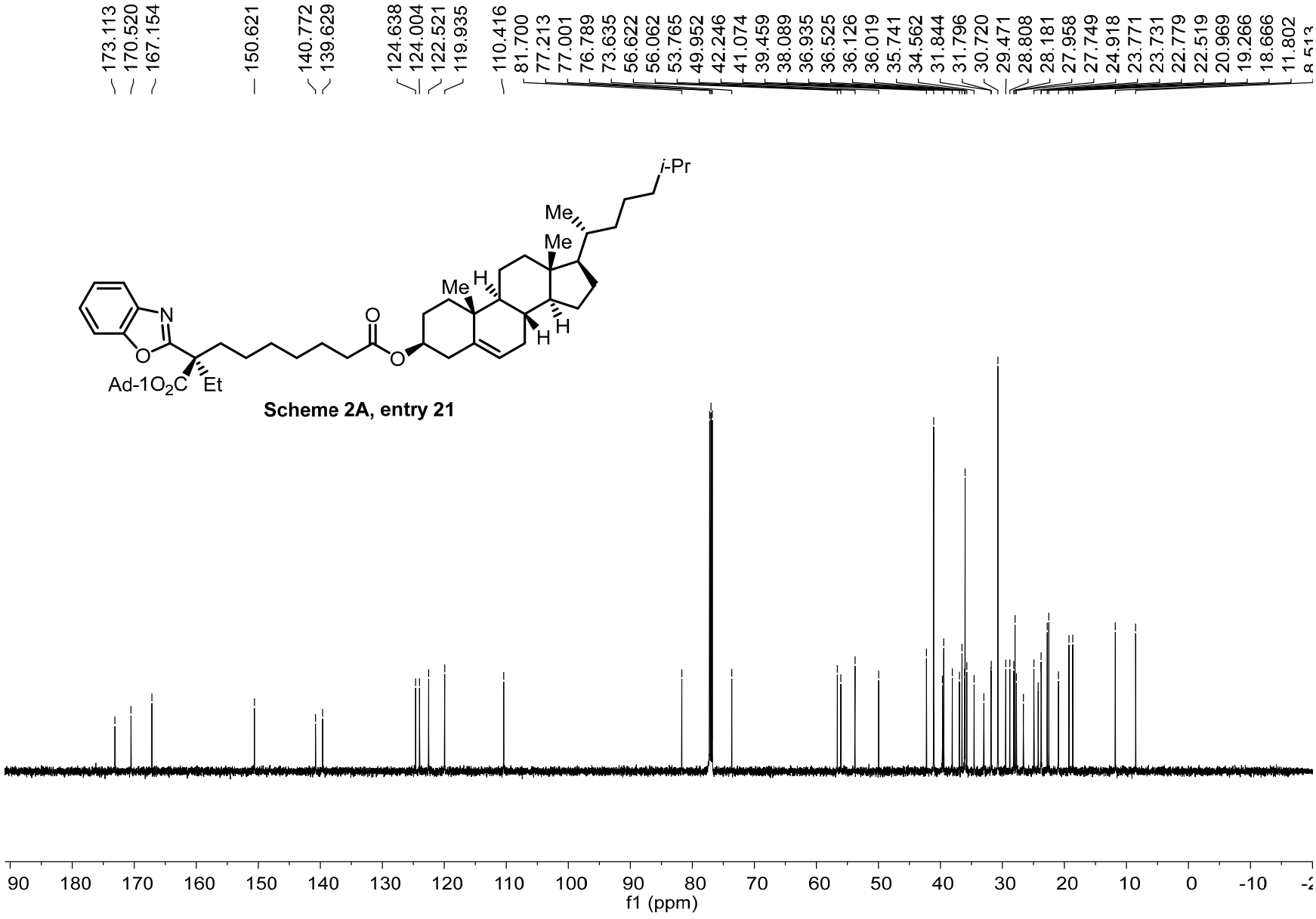
Scheme 2A, entry 20

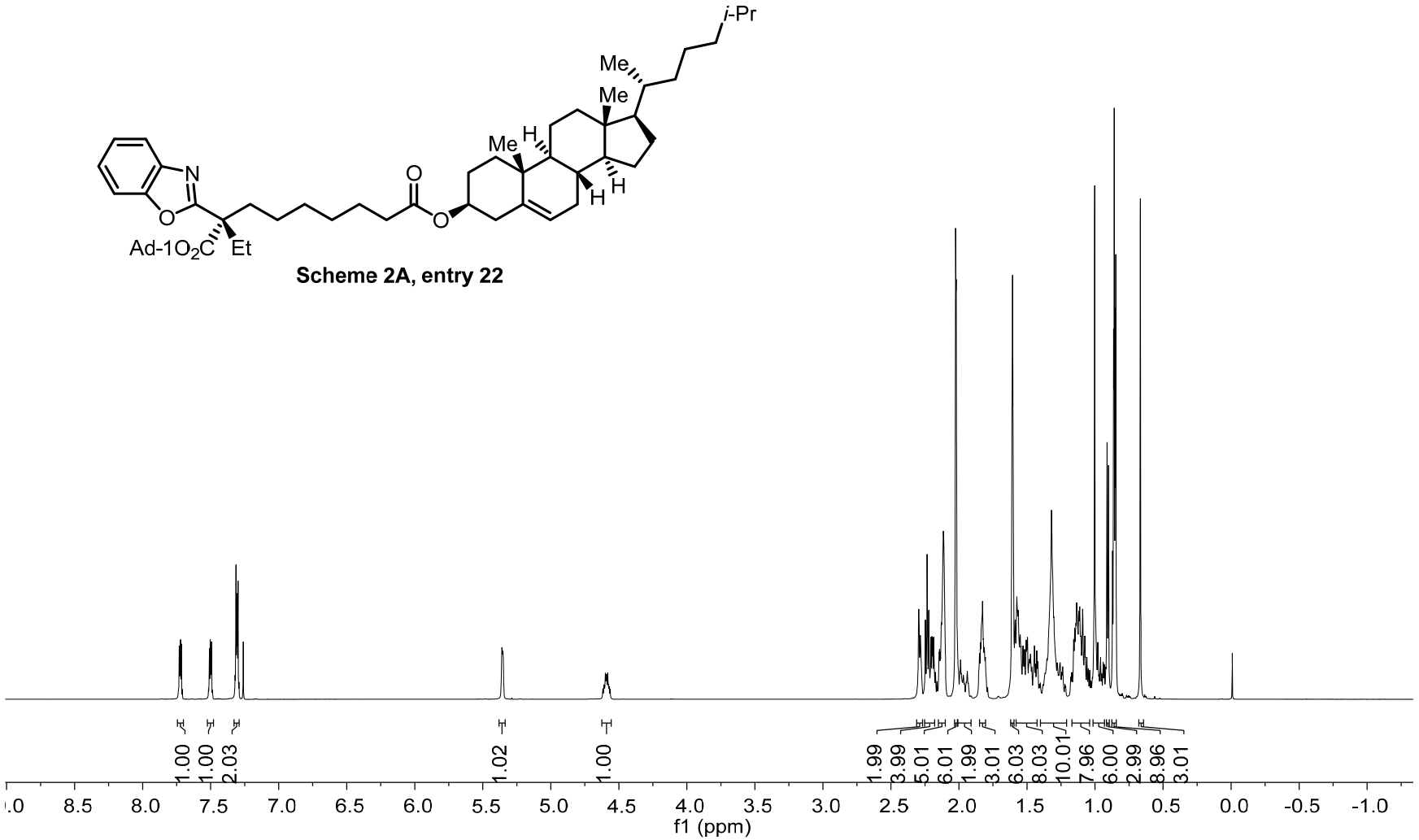


Scheme 2A, entry 20

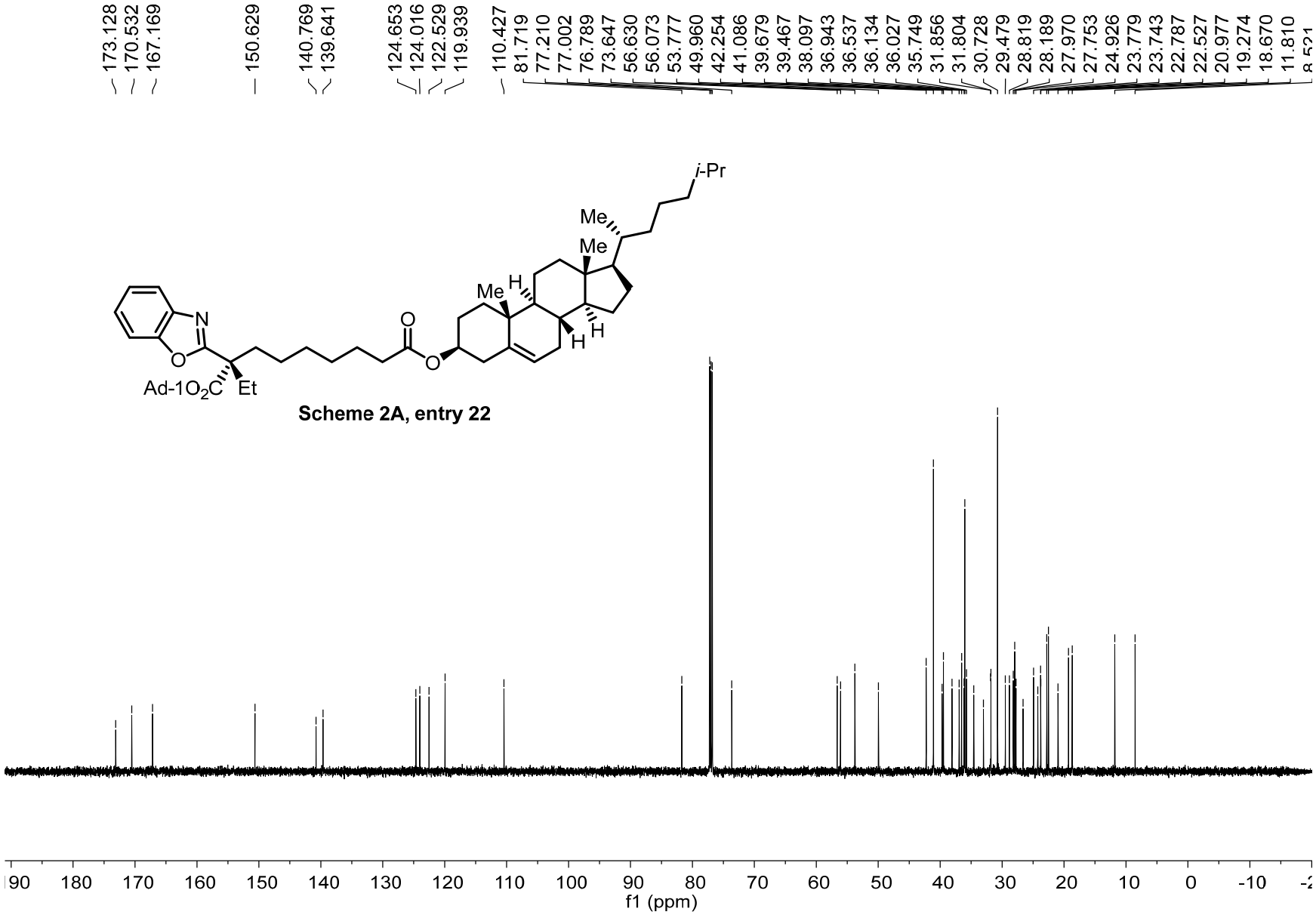


Scheme 2A, entry 21

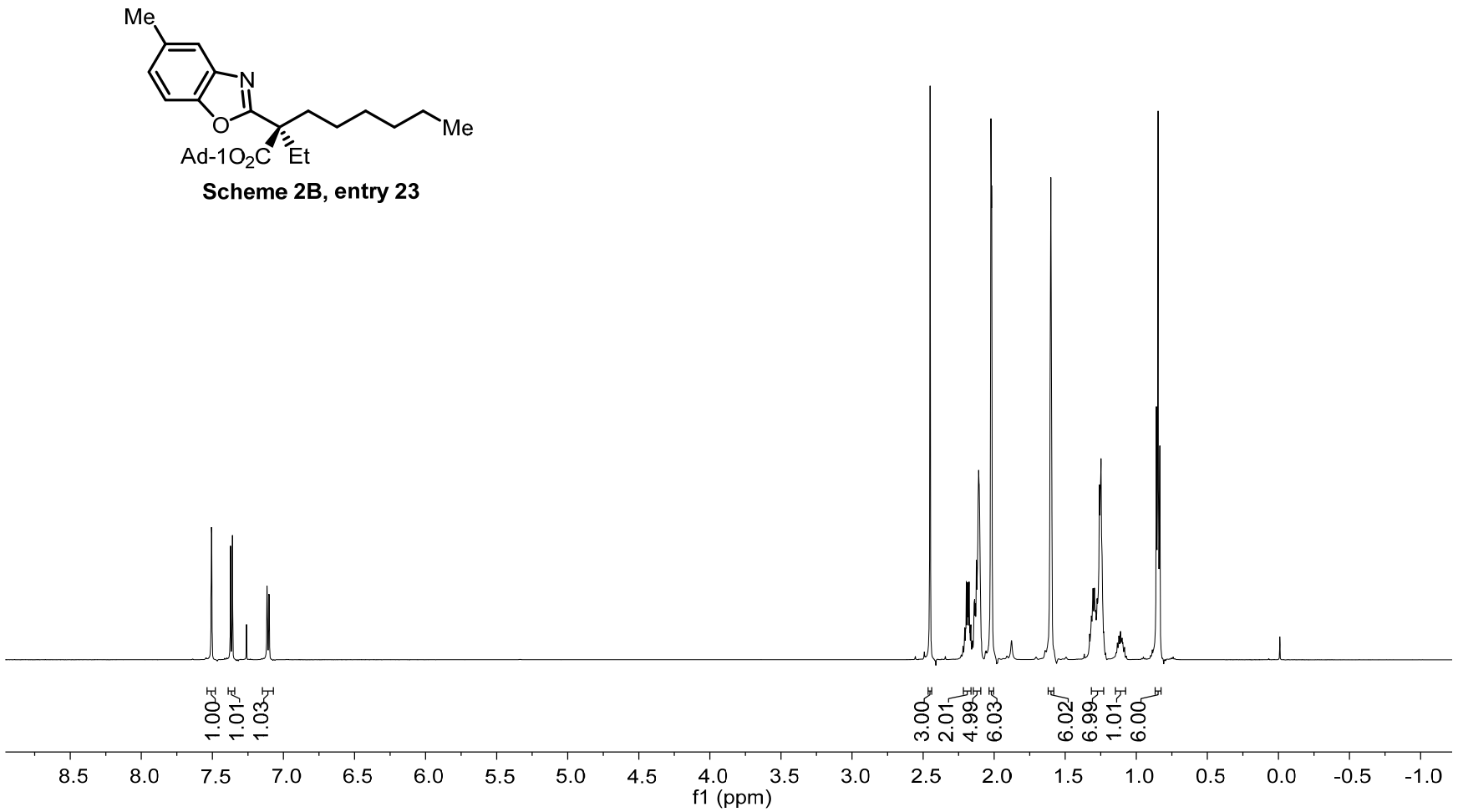

173.113
170.520
167.154
150.621
140.772
139.629
124.638
124.004
122.521
119.935
110.416
81.700
77.213
77.001
76.789
73.635
56.622
56.062
53.765
49.952
42.246
41.074
39.459
38.089
36.935
36.525
36.126
36.019
35.741
34.562
31.844
31.796
30.720
29.471
28.808
28.181
27.958
27.749
24.918
23.771
23.731
22.779
22.519
20.969
19.266
18.666
11.802
i-Pr
Me
Me
Me
H
H
H
N
O
O
O
Ad-1O2C
Et
Scheme 2A, entry 21
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

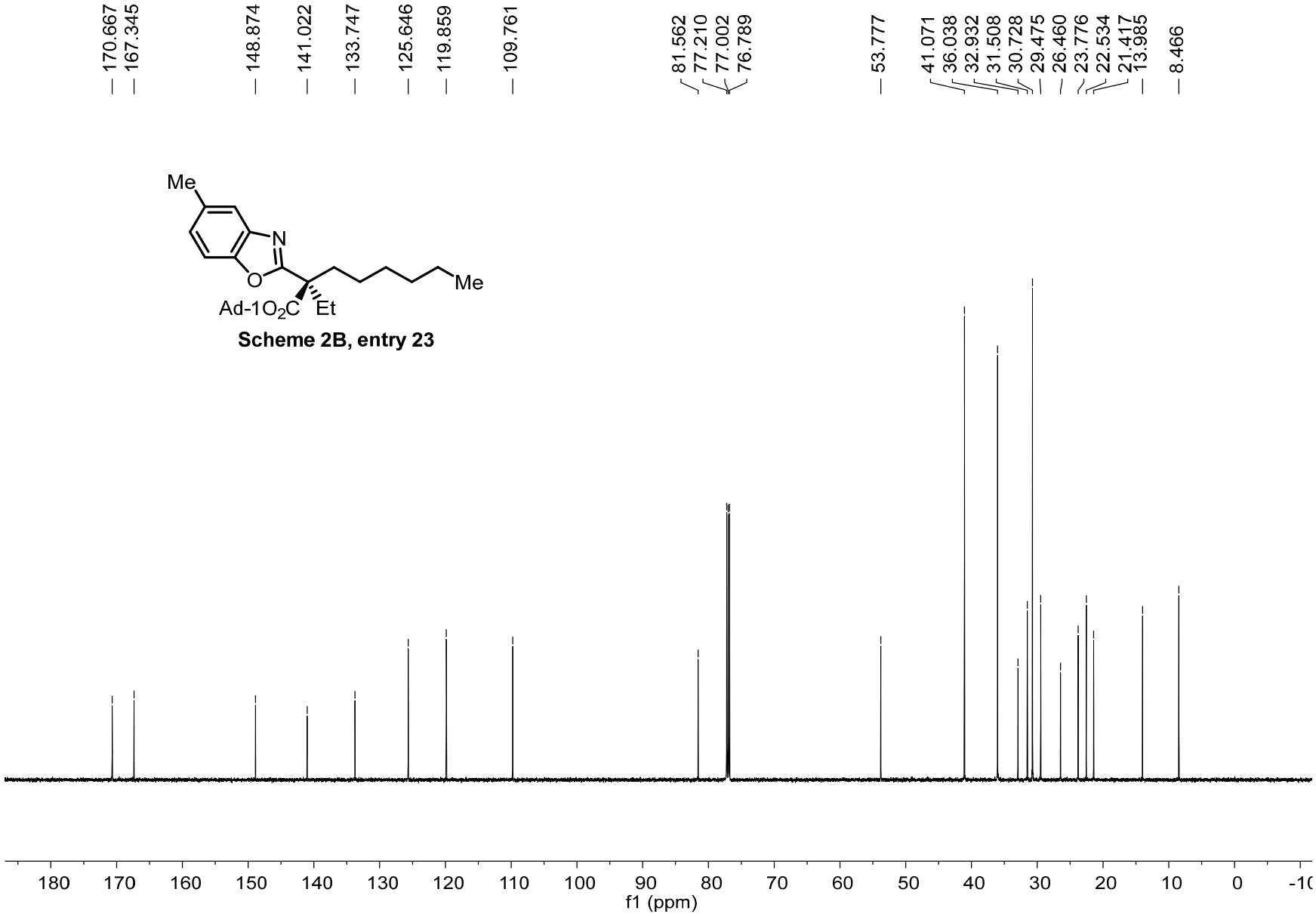


Scheme 2A, entry 22

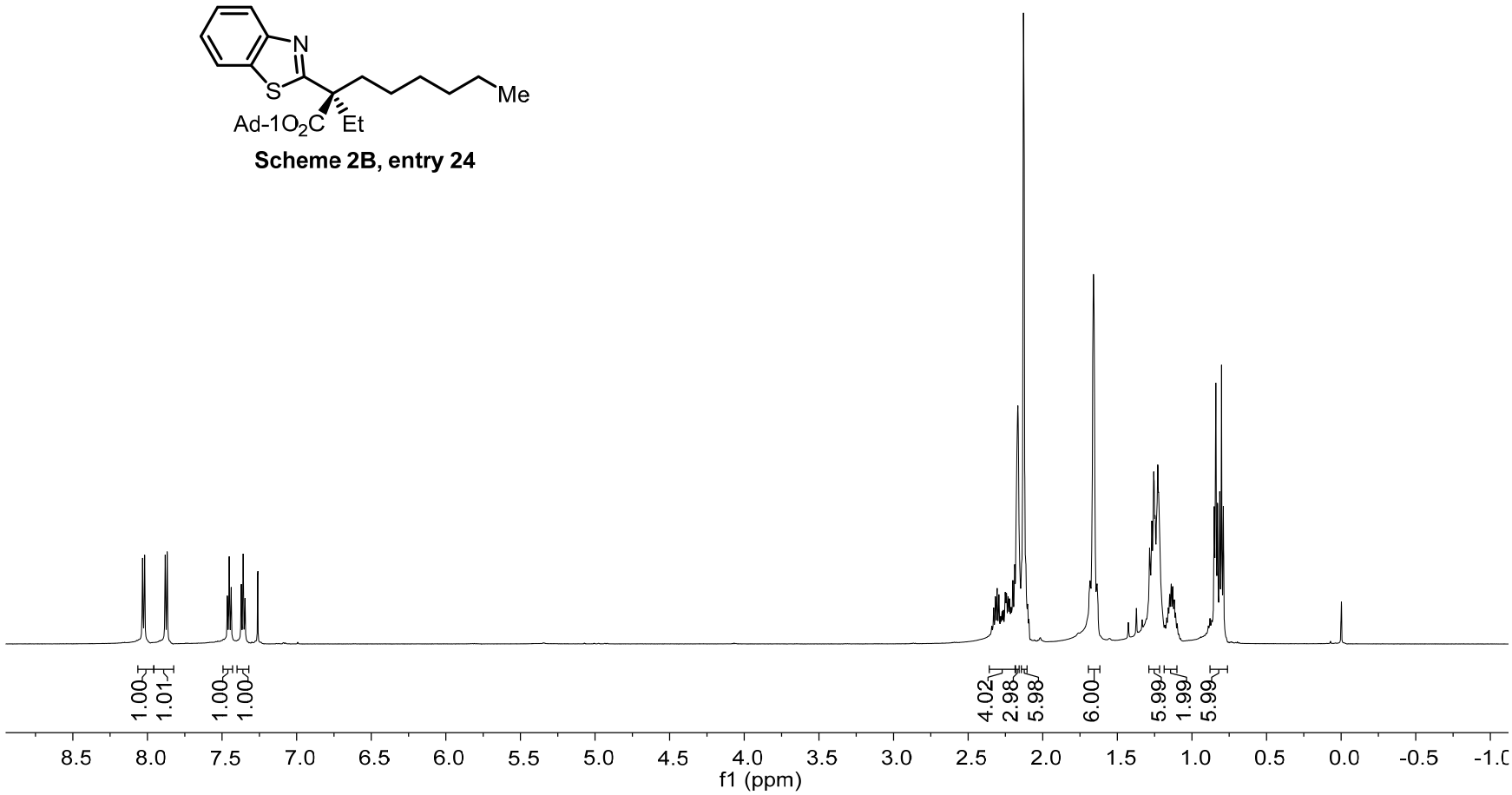


Scheme 2A, entry 22

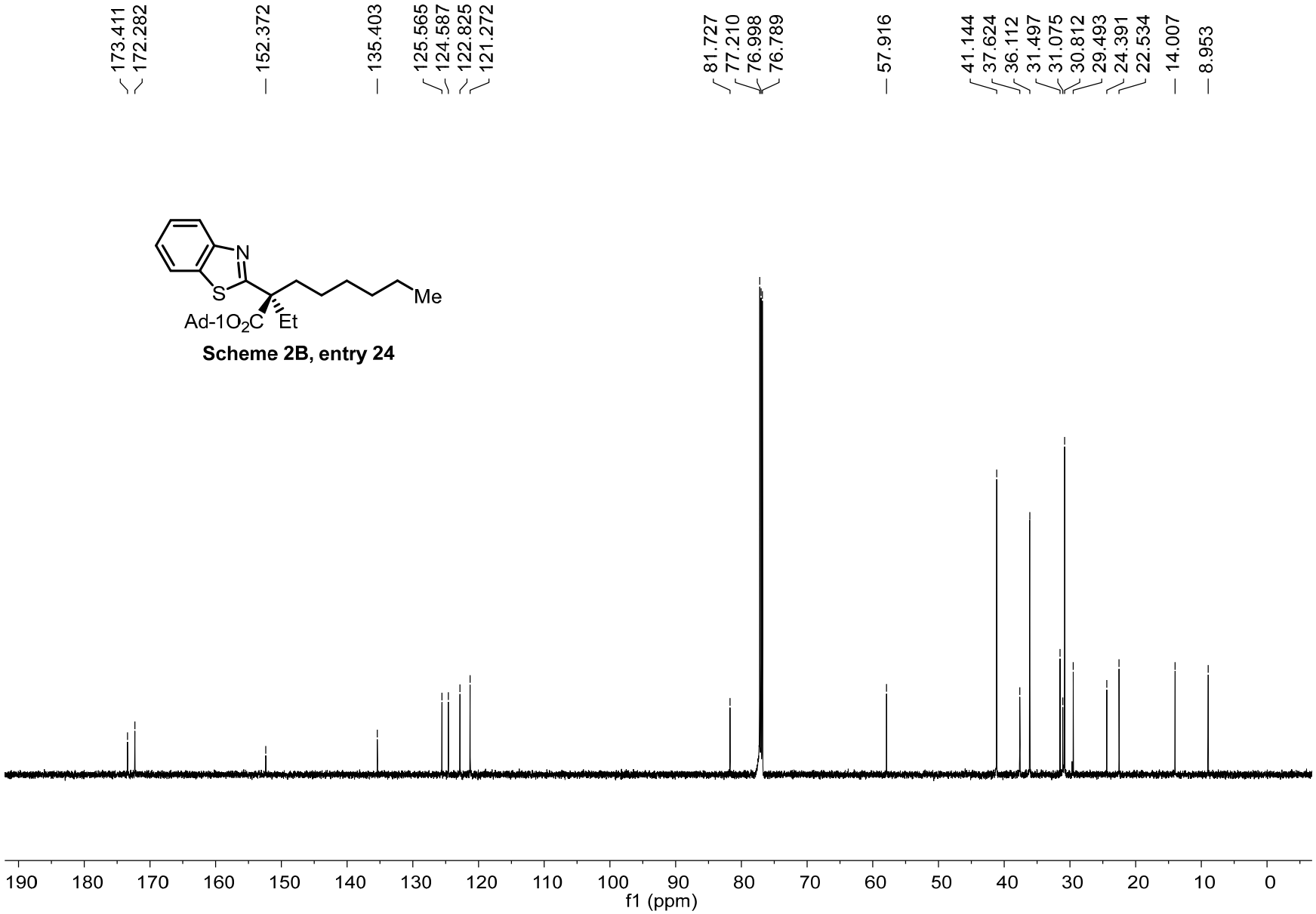

Me
N
O
Me
Ad-1O2C Et
Scheme 2B, entry 23
1.00
1.01
1.03
3.00
2.01
4.99
6.03
6.02
6.99
1.01
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

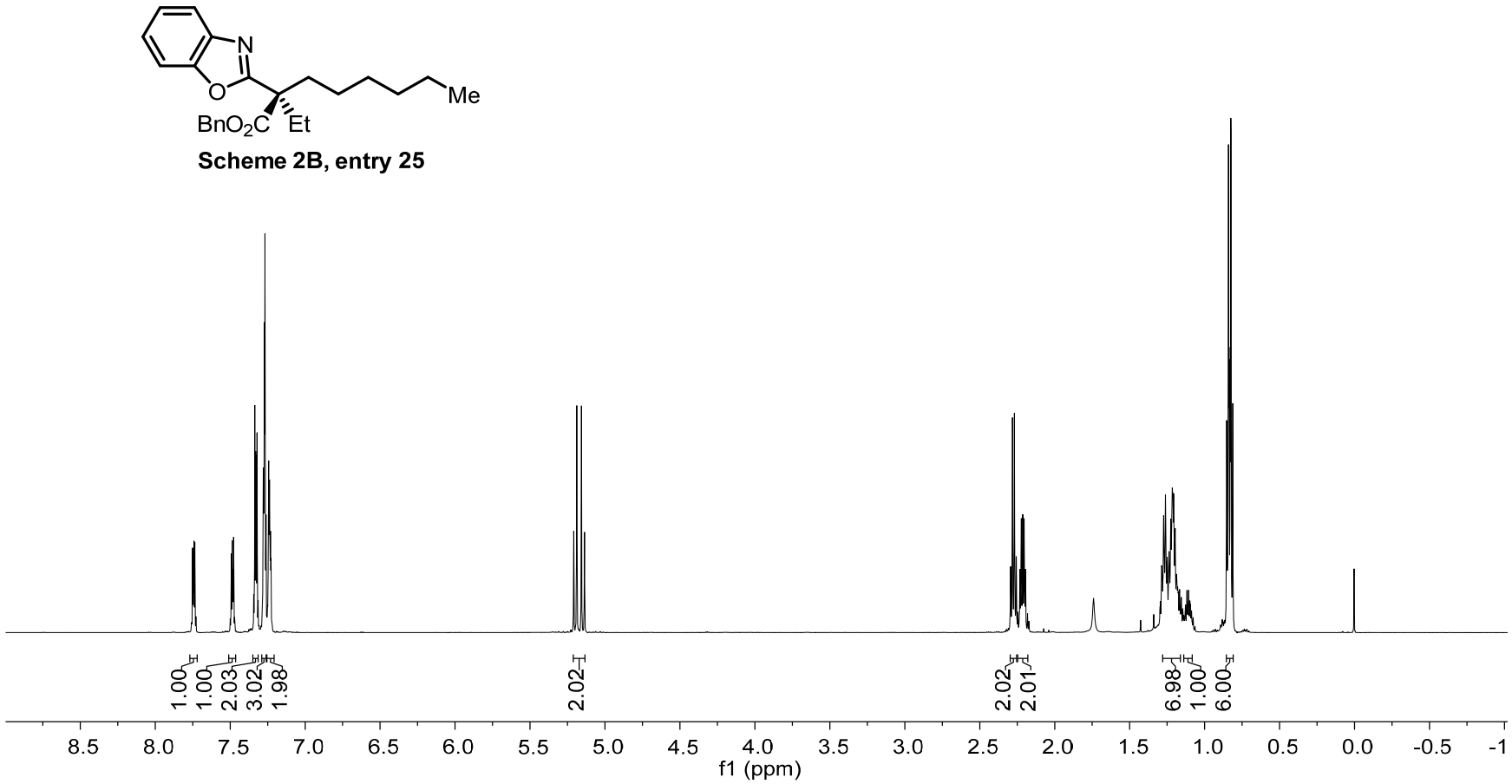


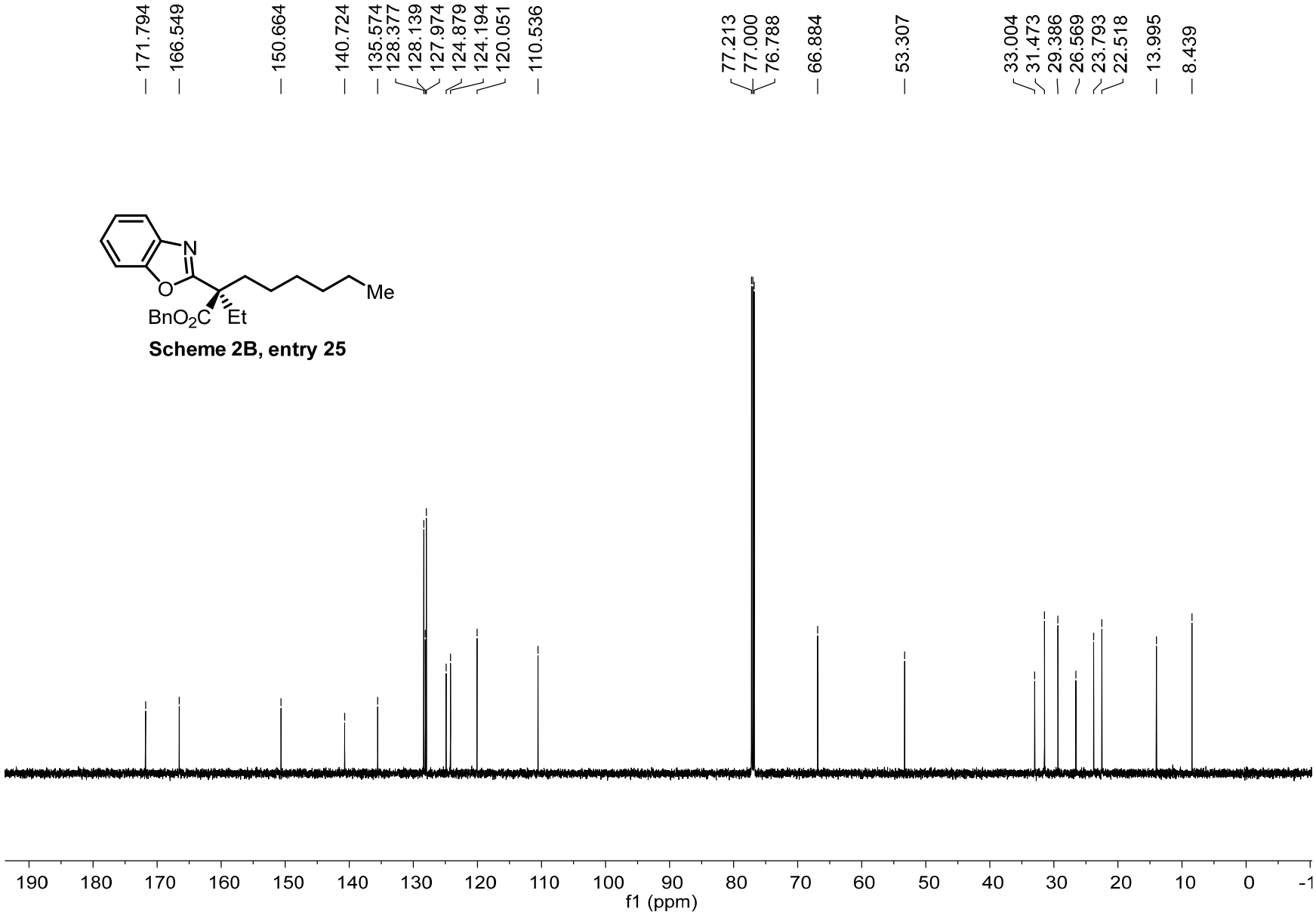
Scheme 2B, entry 23

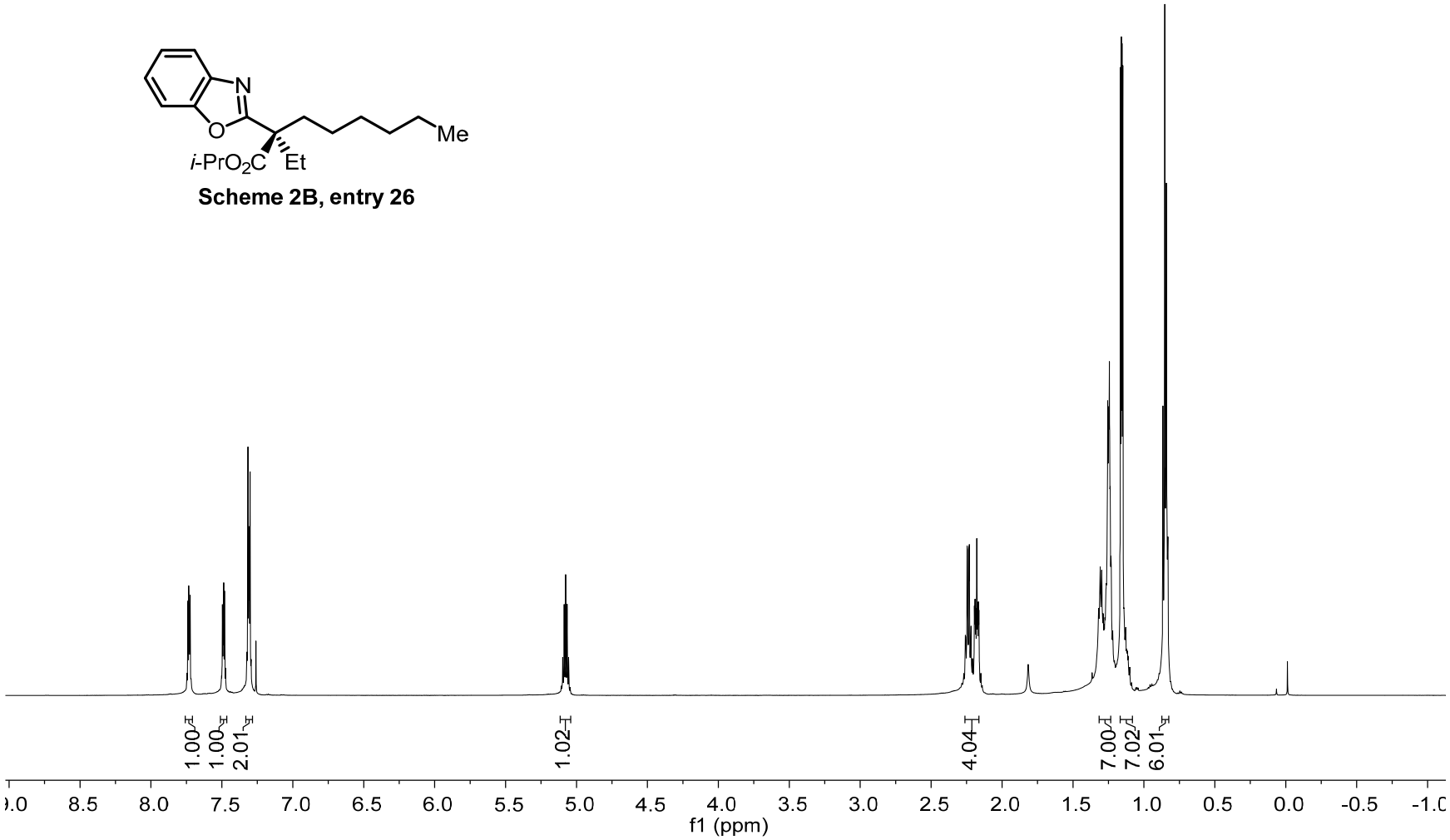


Scheme 2B, entry 24

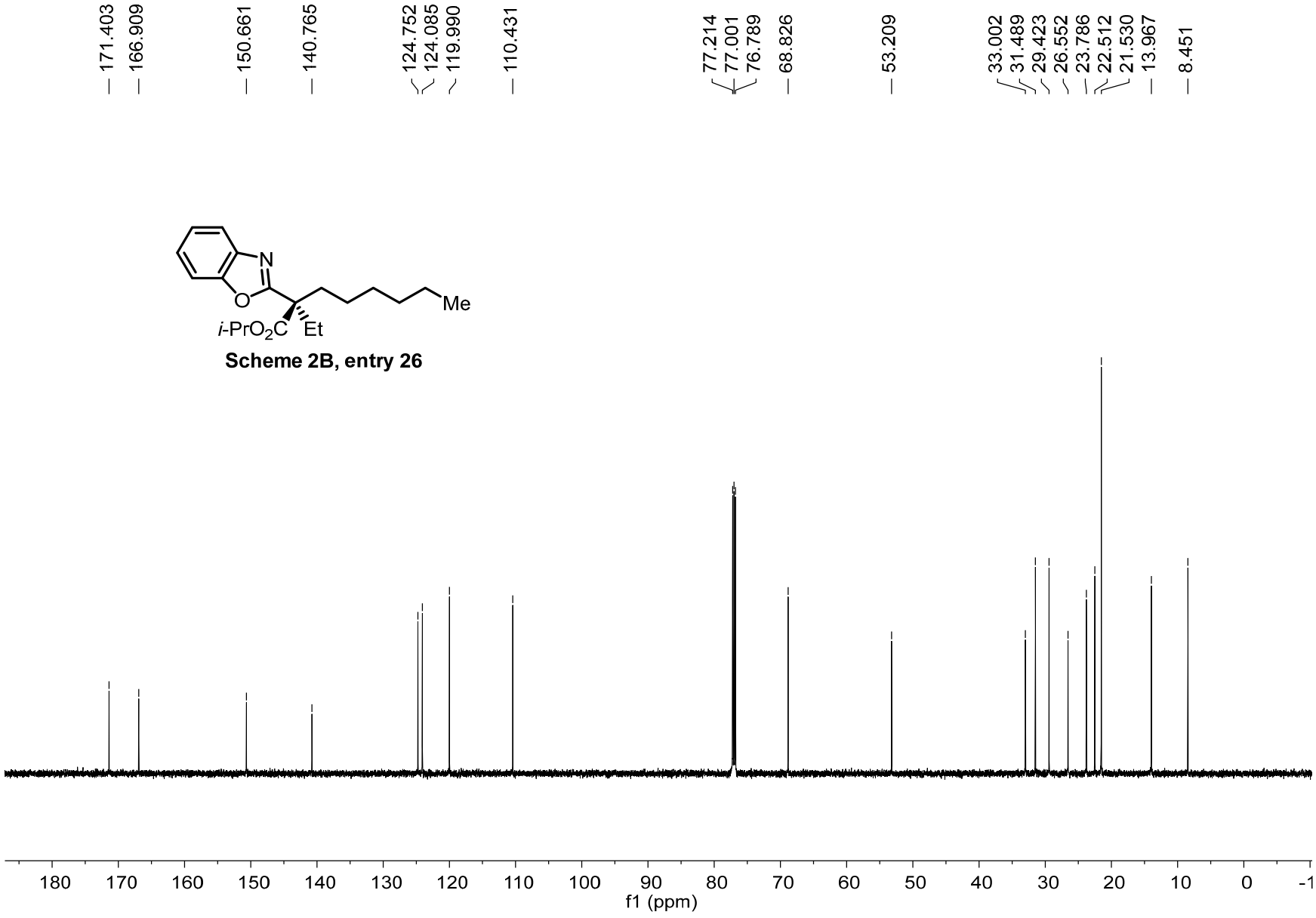

173.411
172.282
152.372
135.403
125.565
124.587
122.825
121.272
81.727
77.210
76.998
76.789
57.916
41.144
37.624
36.112
31.497
31.075
30.812
29.493
24.391
22.534
14.007
8.953
N
S
Me
Ad-1O2C
Et
Scheme 2B, entry 24
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
Me
BnO2C
Et
Scheme 2B, entry 25
1.00
1.00
2.03
3.02
1.98
2.02
2.02
2.01
6.98
1.00
6.00
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)

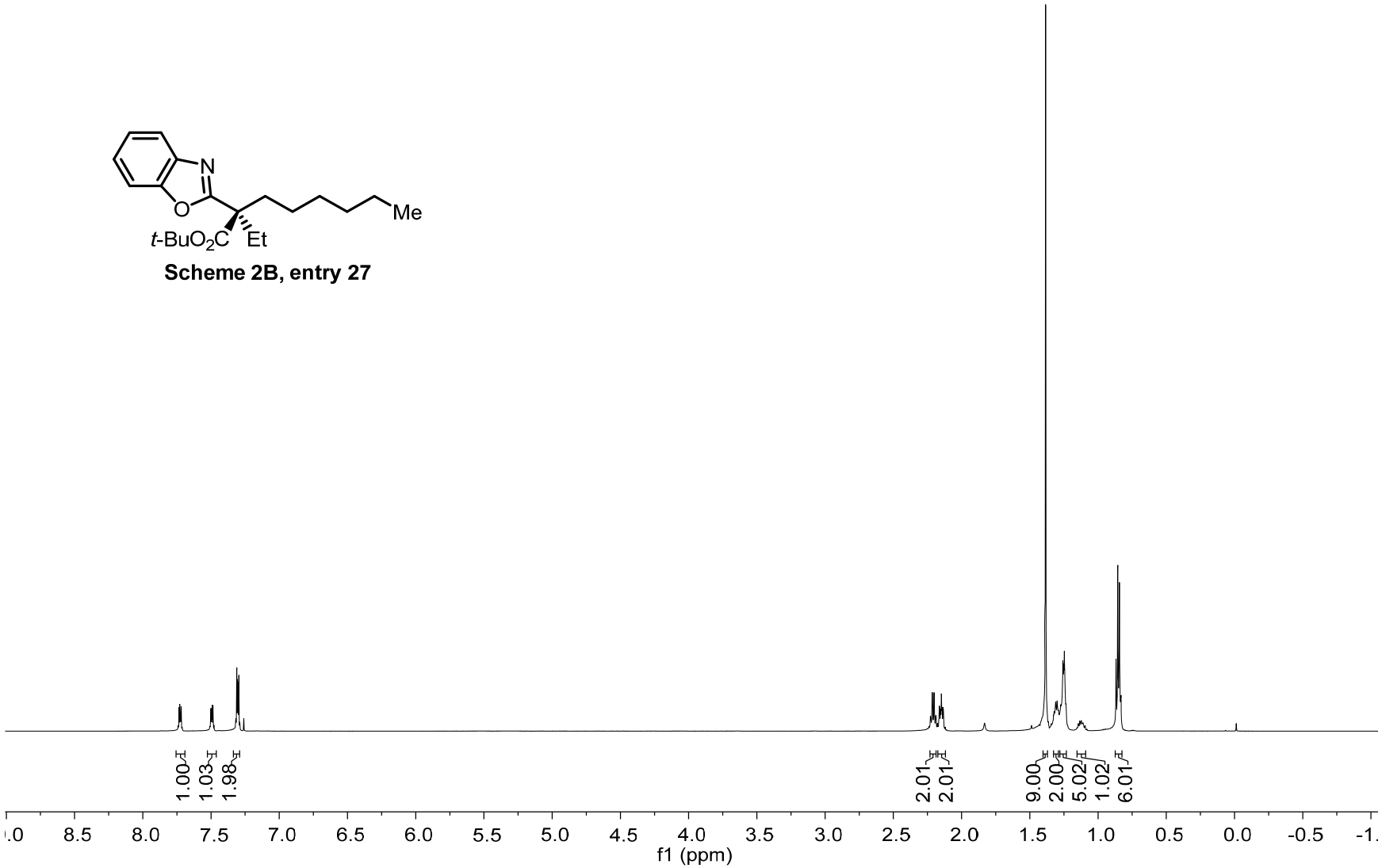

171.794
166.549
150.664
140.724
135.574
128.377
128.139
127.974
124.879
124.194
120.051
110.536
77.213
77.000
76.788
66.884
53.307
33.004
31.473
29.386
26.569
23.793
22.518
13.995
8.439
N
O
Me
BnO2C
Et
Scheme 2B, entry 25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



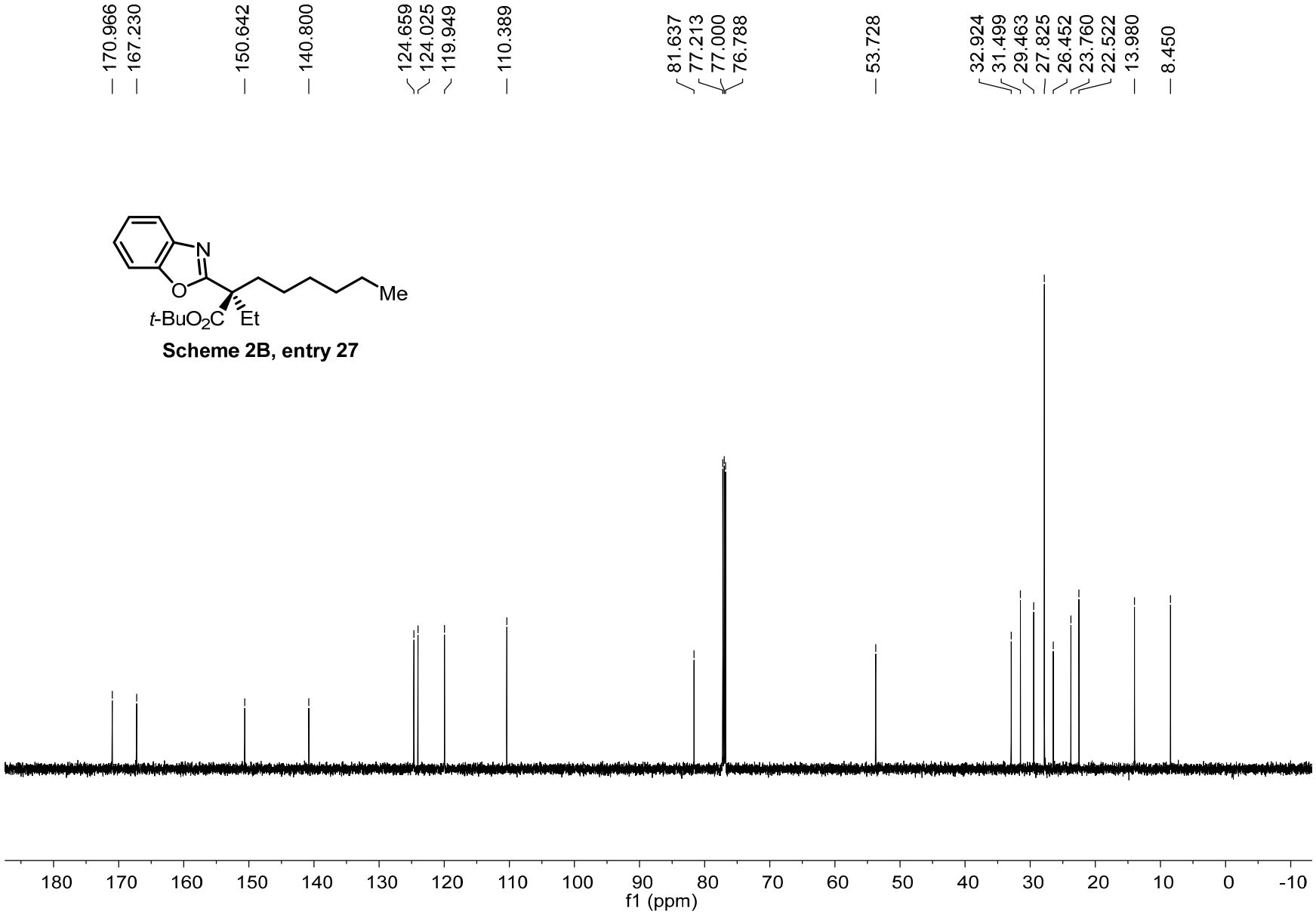
Scheme 2B, entry 26



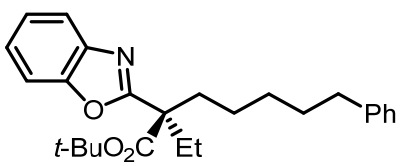
Scheme 2B, entry 26



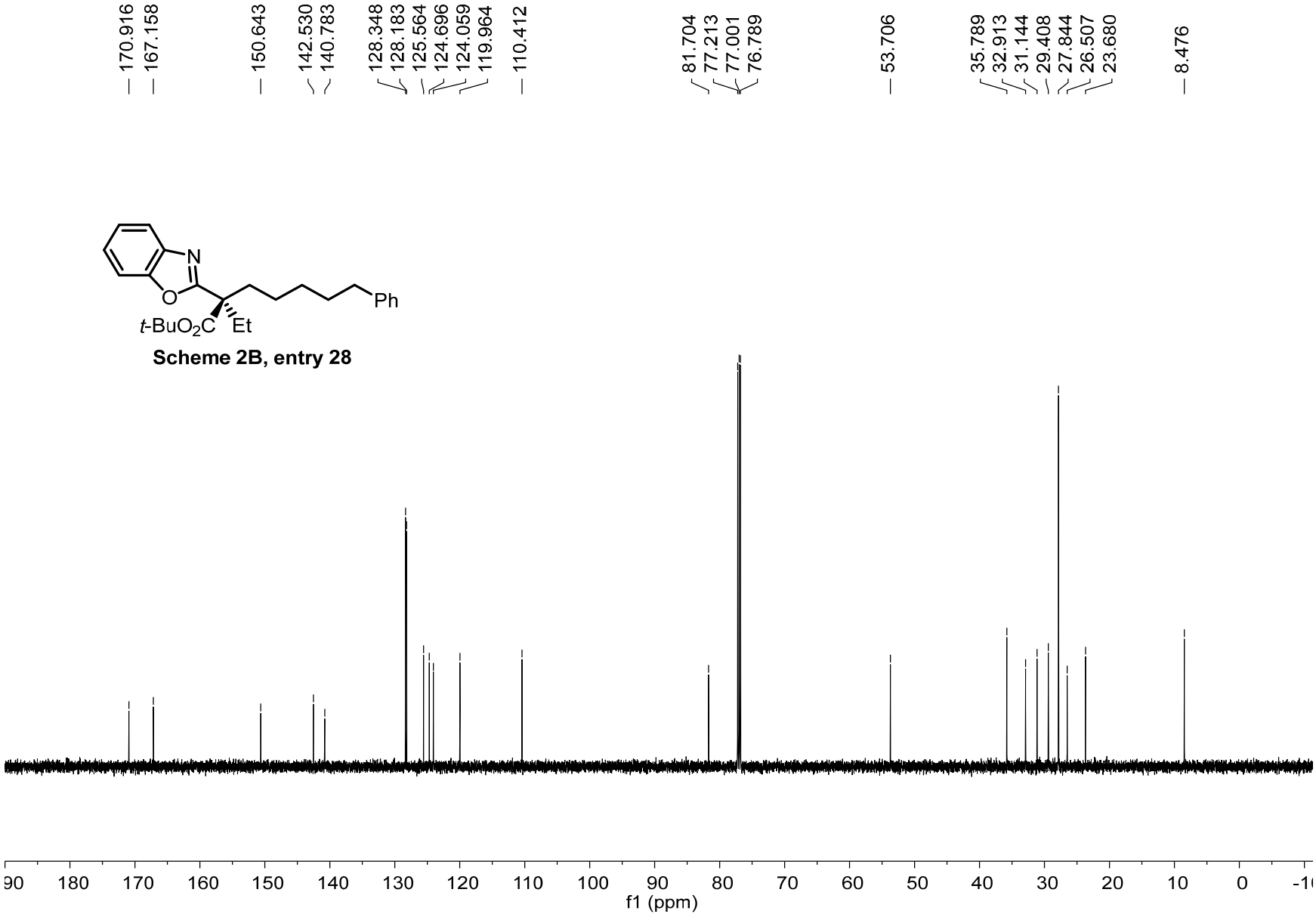
Scheme 2B, entry 27

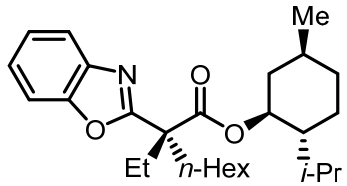


Scheme 2B, entry 27

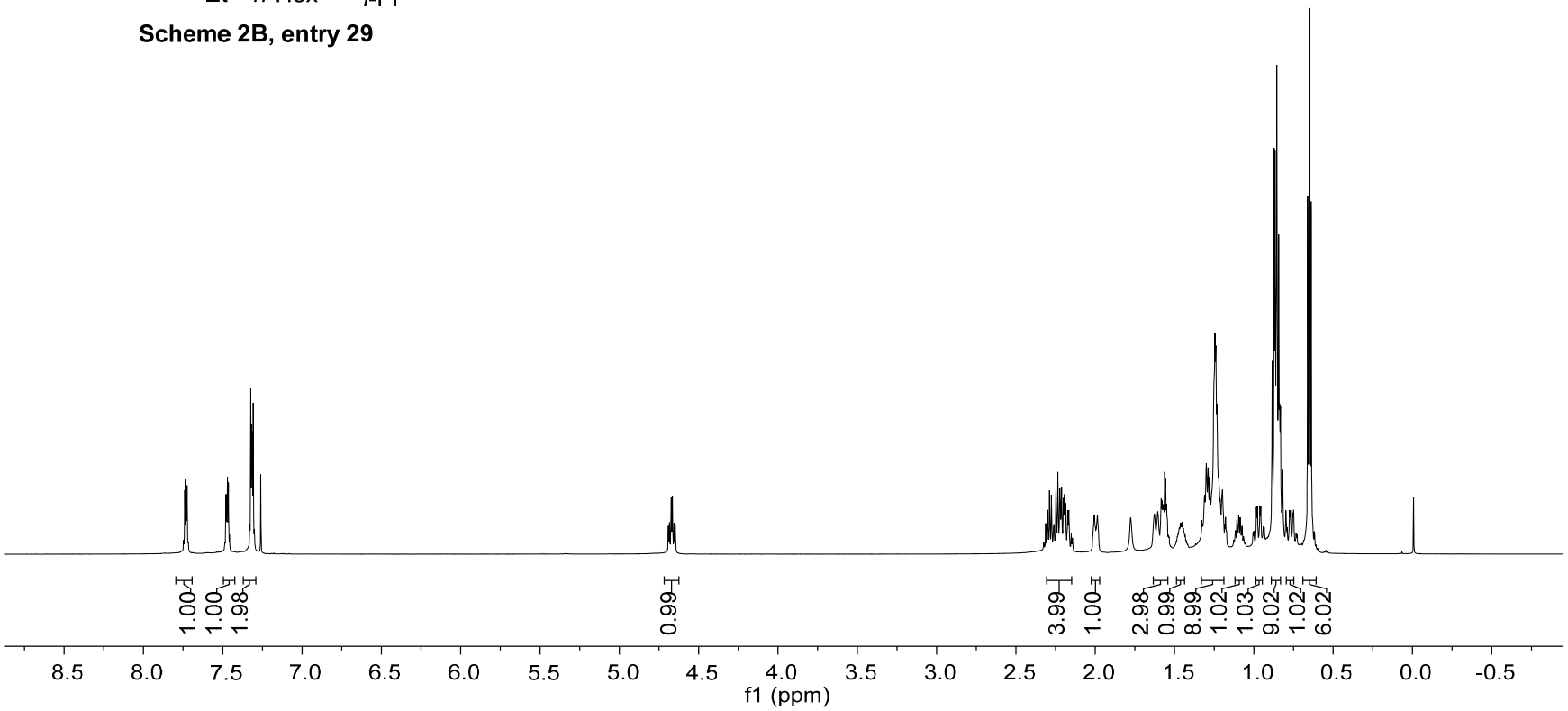


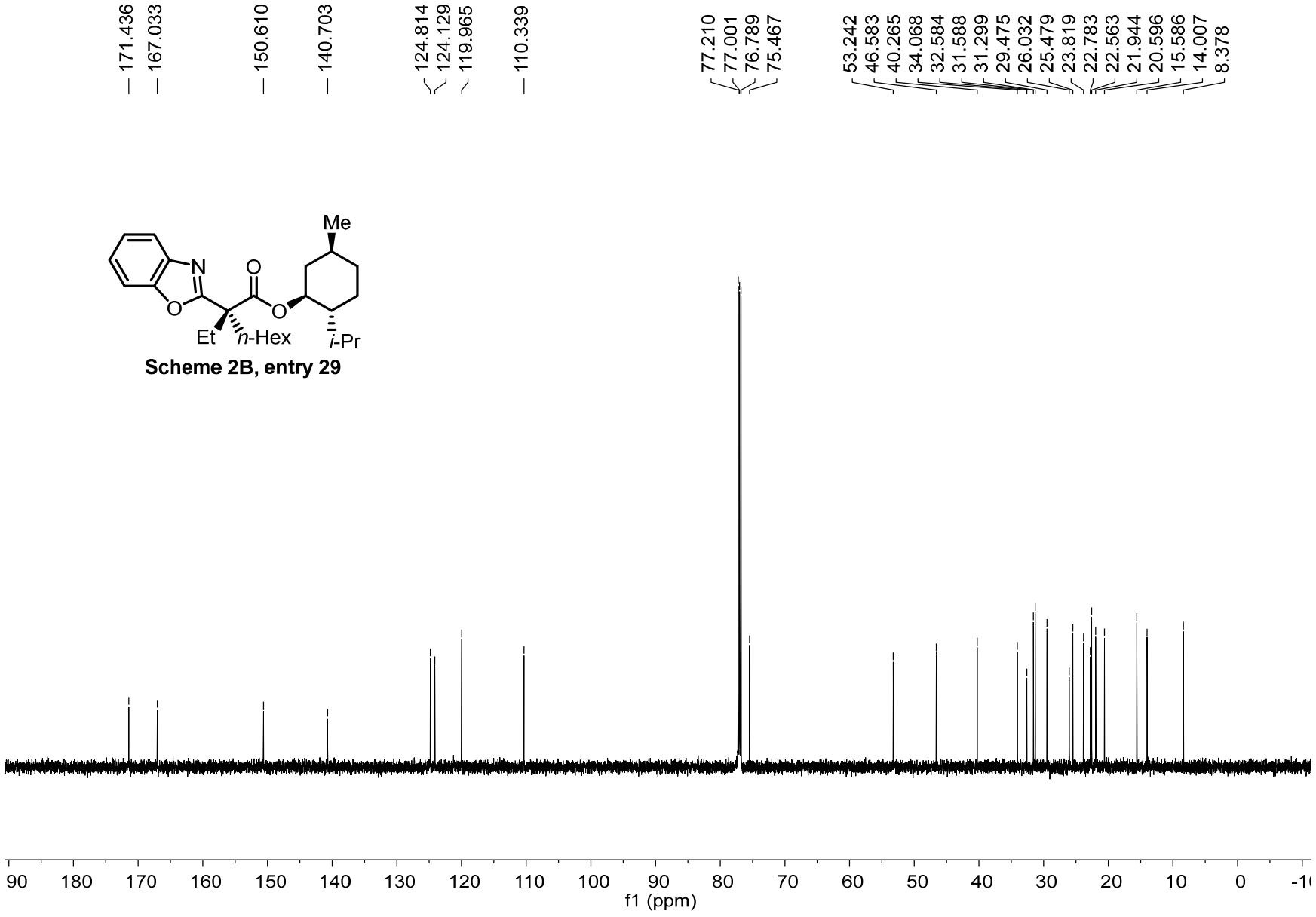
Scheme 2B, entry 28


170.916
167.158
150.643
142.530
140.783
128.348
128.183
125.564
124.696
124.059
119.964
110.412
81.704
77.213
77.001
76.789
53.706
35.789
32.913
31.144
29.408
27.844
26.507
23.680
8.476
N
O
Ph
t-BuO2C
Et
Scheme 2B, entry 28
f1 (ppm)

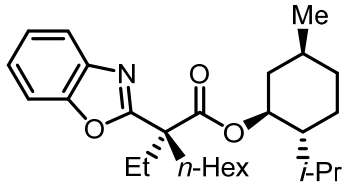


Scheme 2B, entry 29

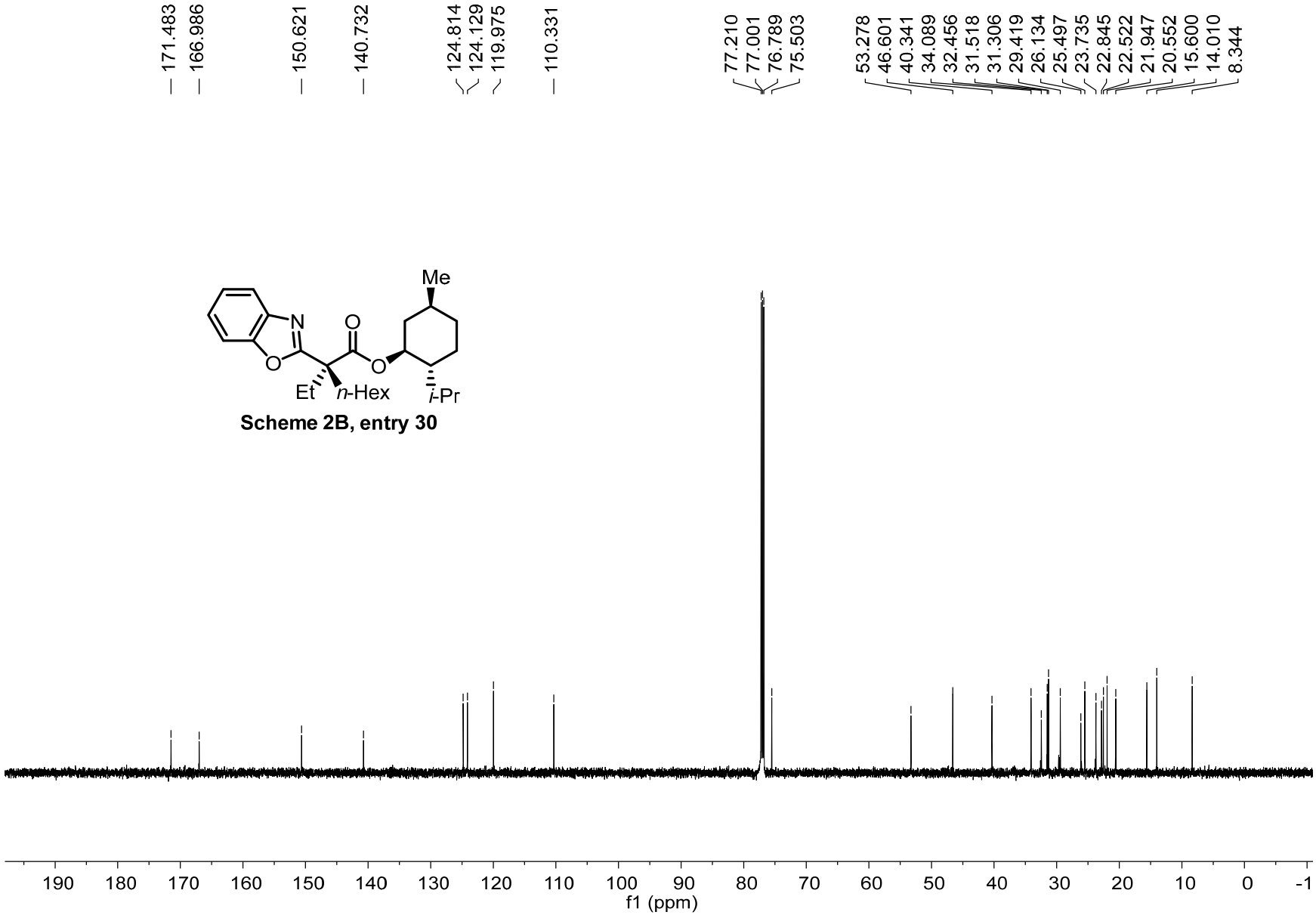




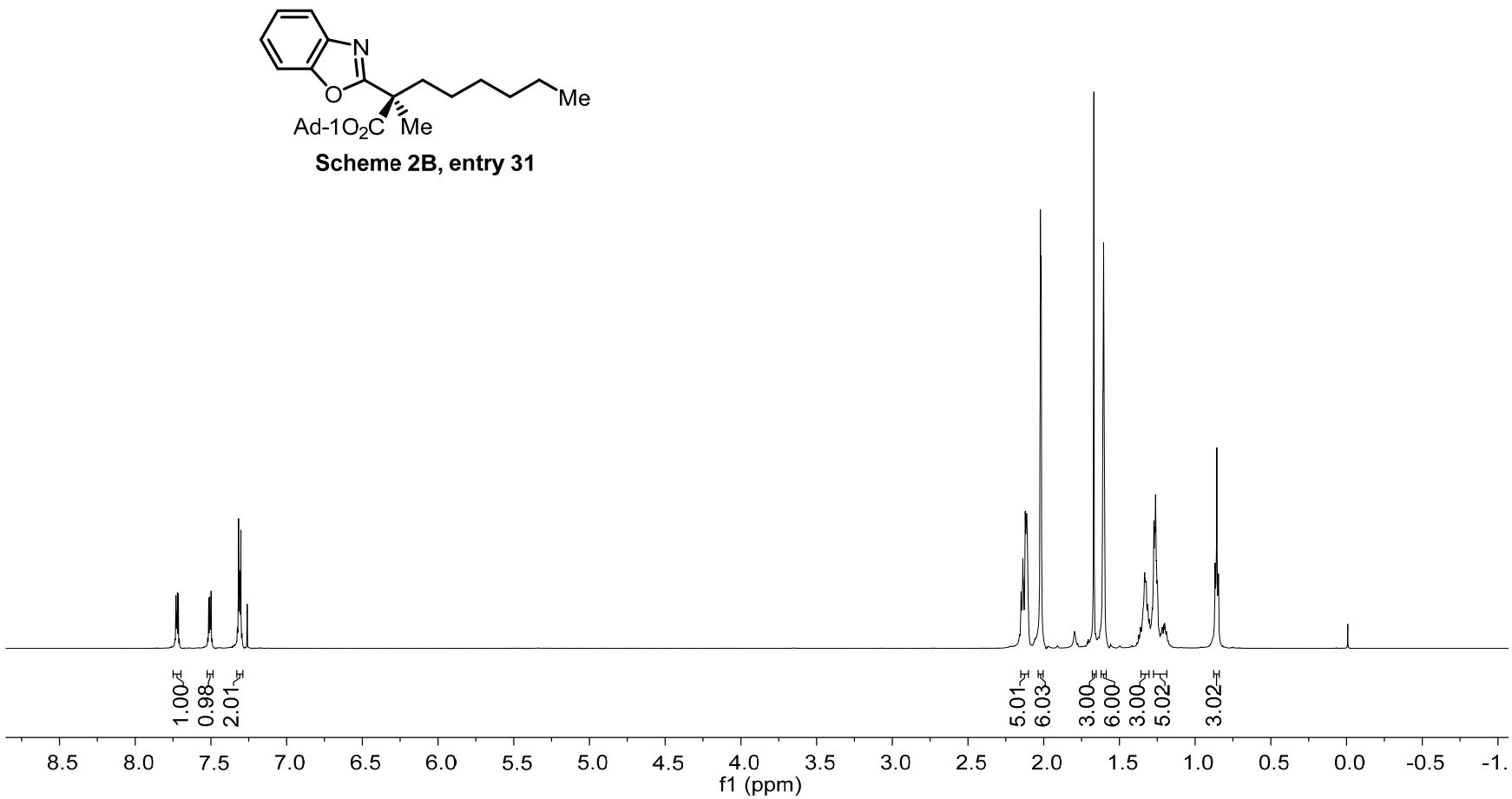
Scheme 2B, entry 29

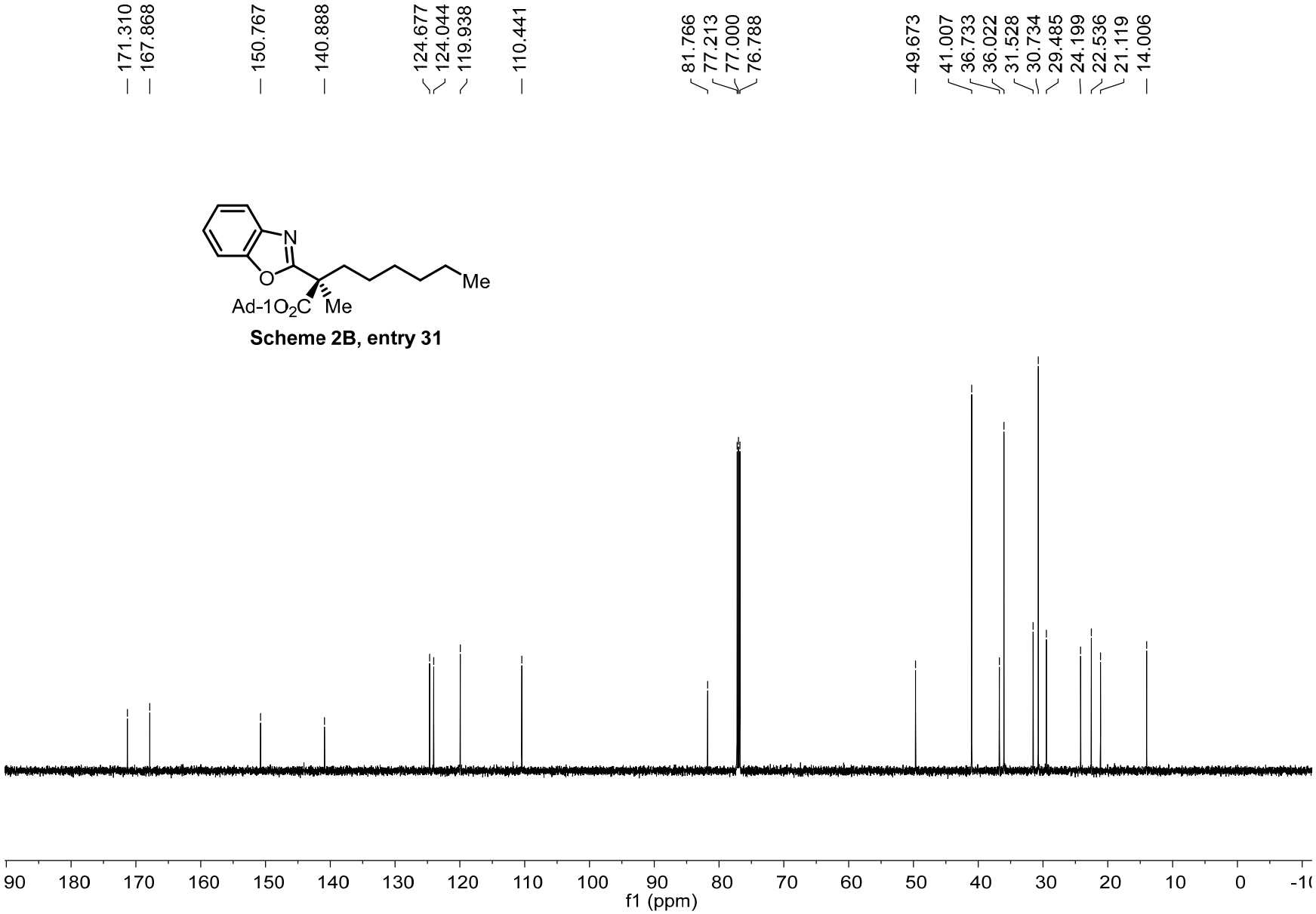


Scheme 2B, entry 30

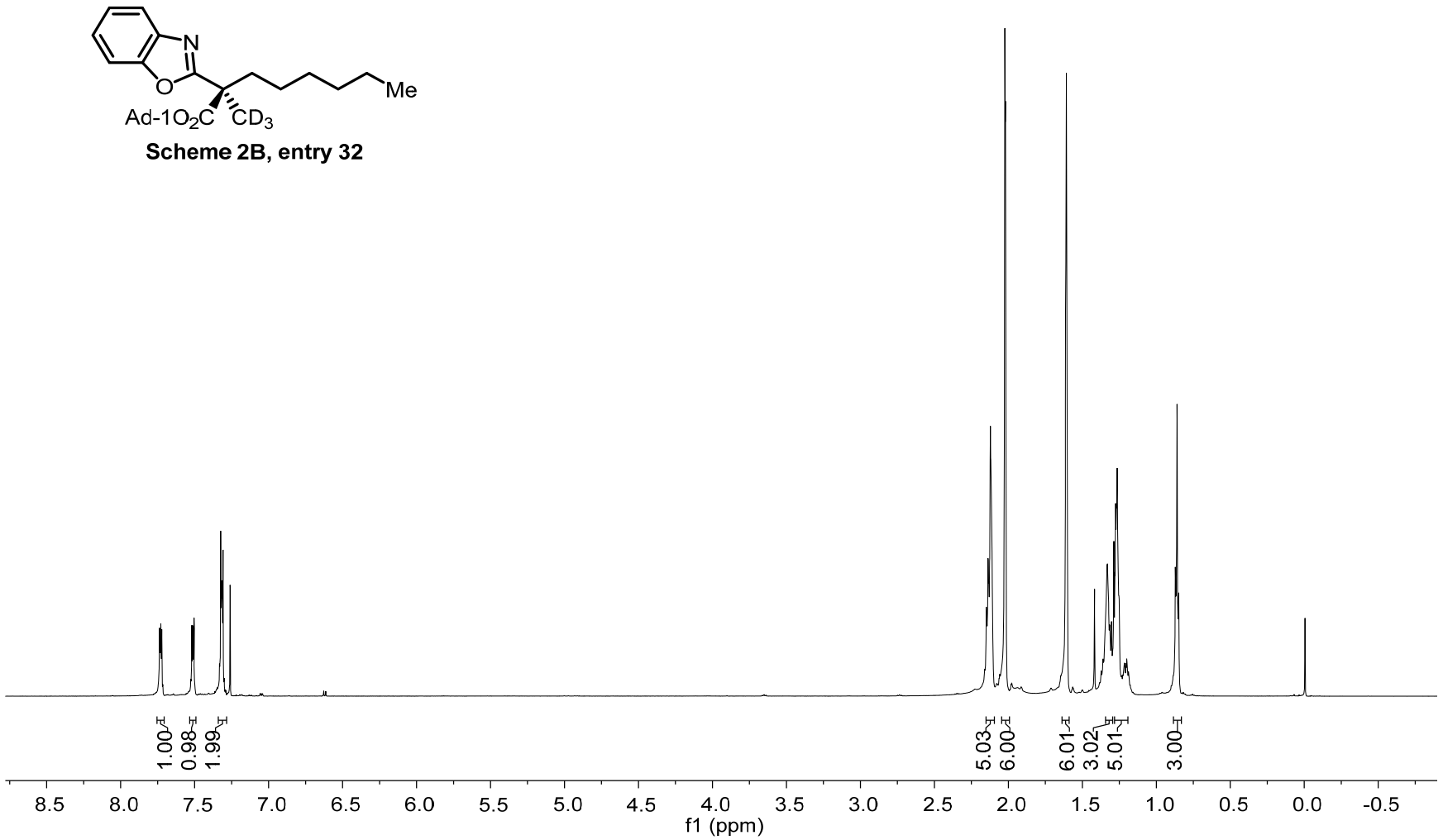


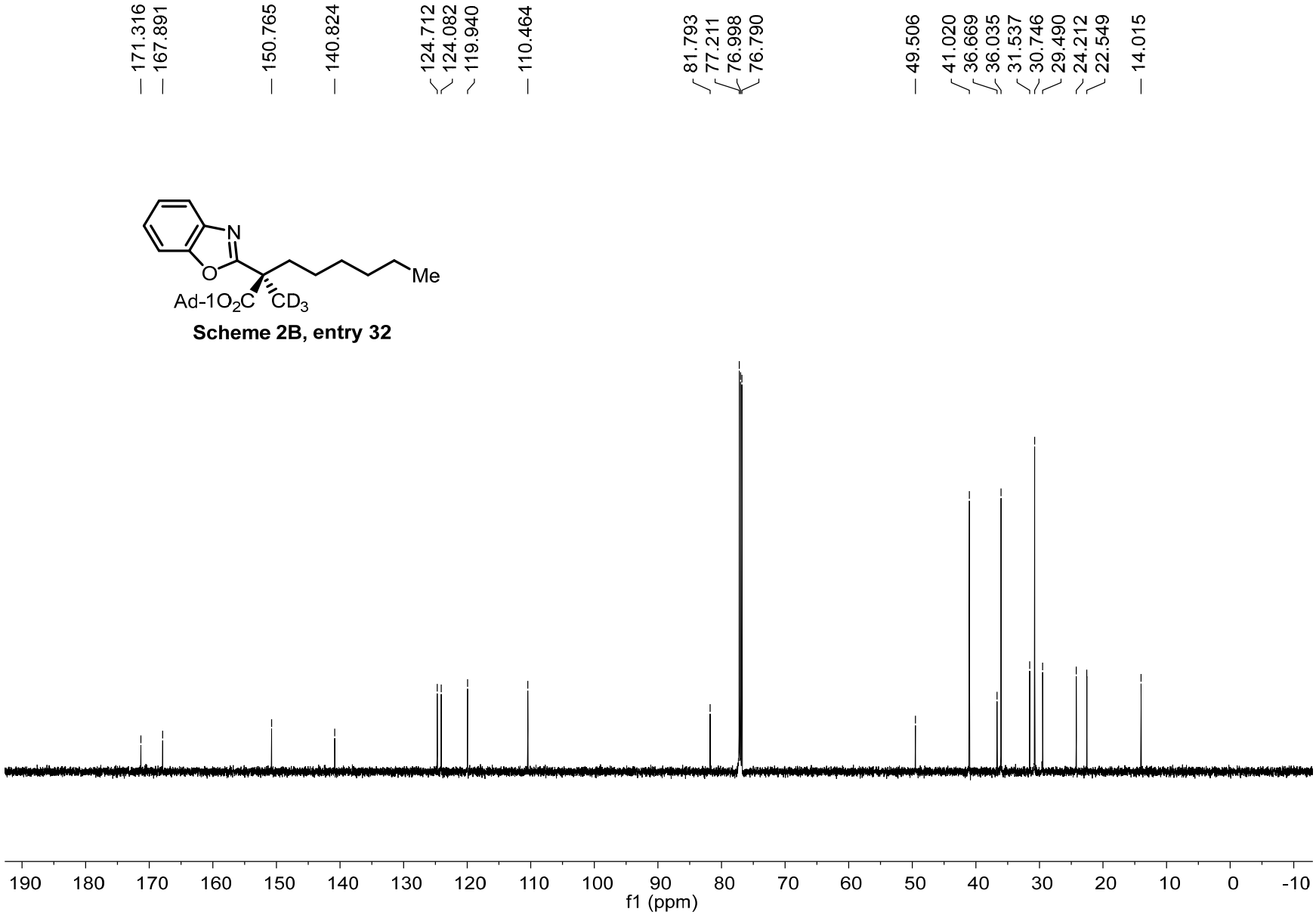
Scheme 2B, entry 30


N
O
Me
Ad-1O2C Me
Scheme 2B, entry 31
1.00
0.98
2.01
5.01
6.03
3.00
6.00
3.00
5.02
3.02
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)

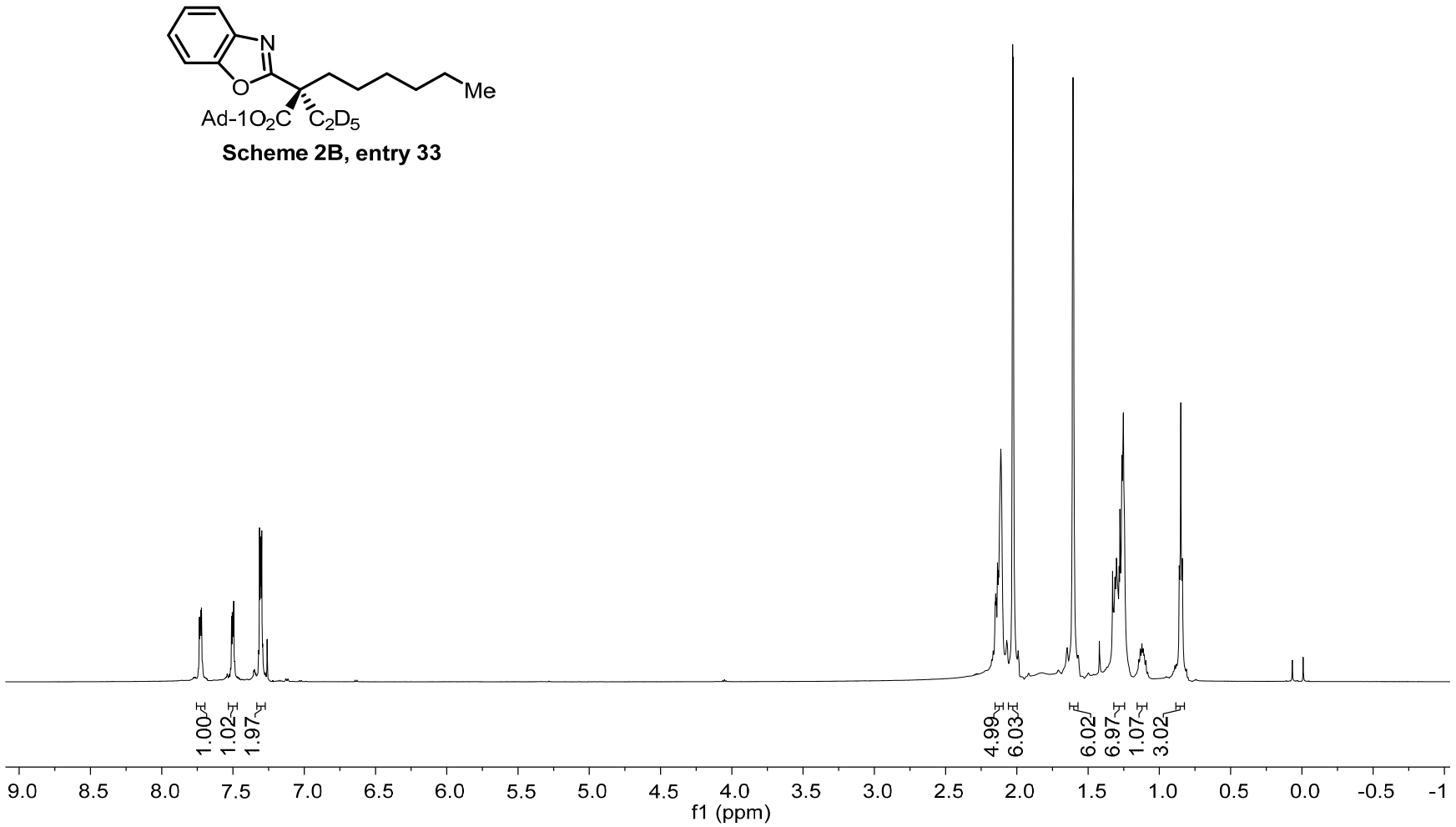


Scheme 2B, entry 31

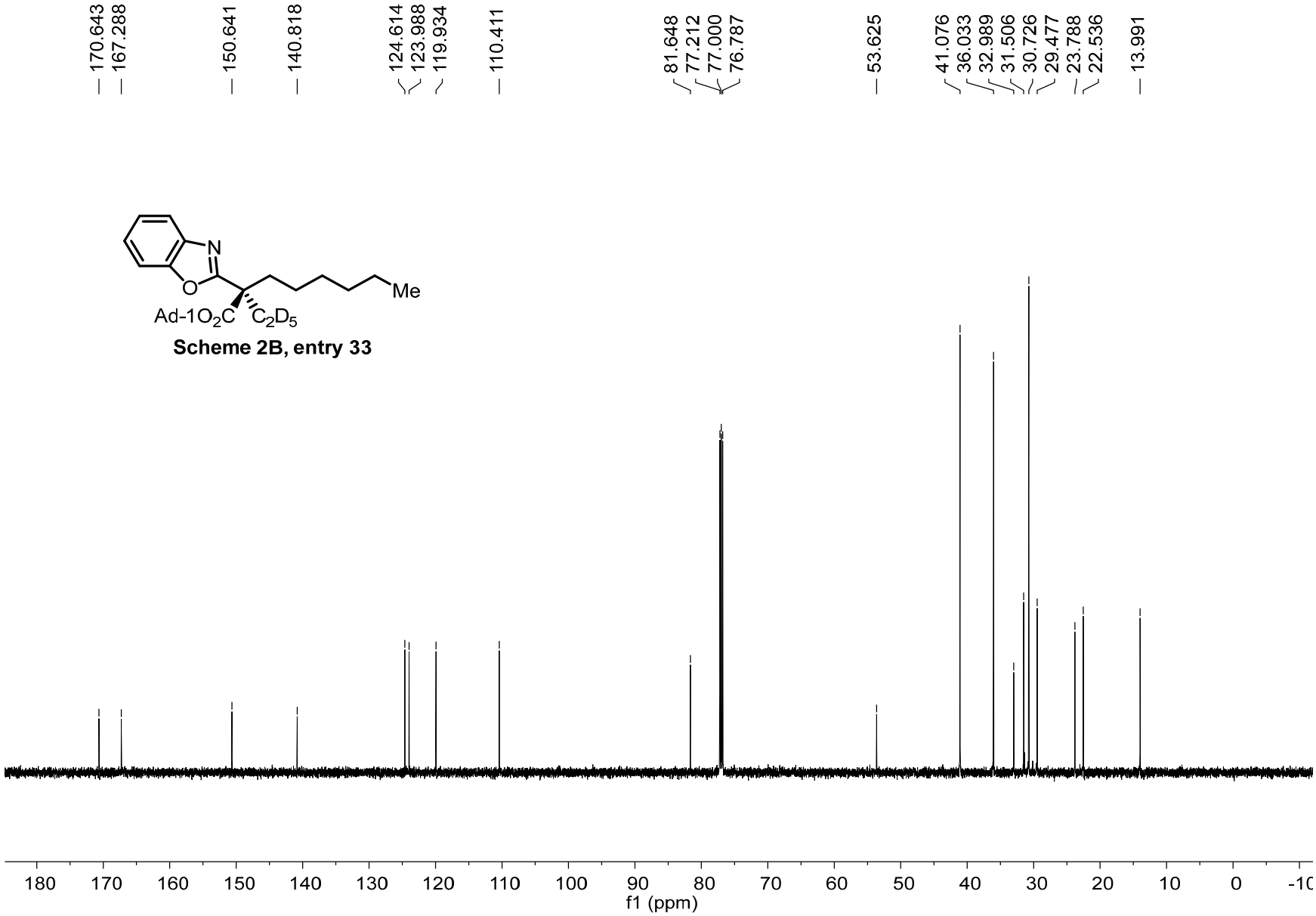

N
O
Me
Ad-1O2C CD3
Scheme 2B, entry 32
1.00
0.98
1.99
5.03
6.00
6.01
3.02
5.01
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

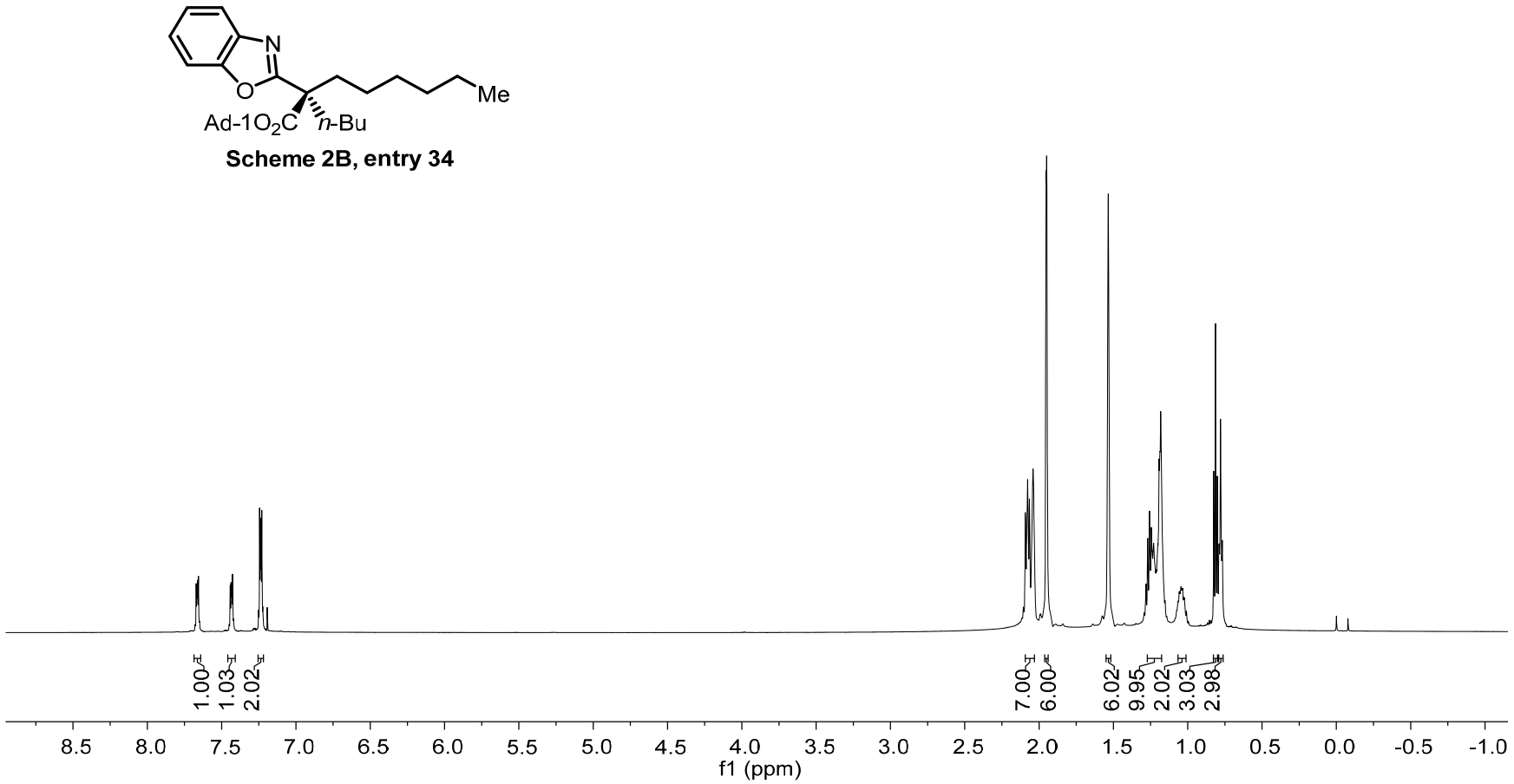


Scheme 2B, entry 32

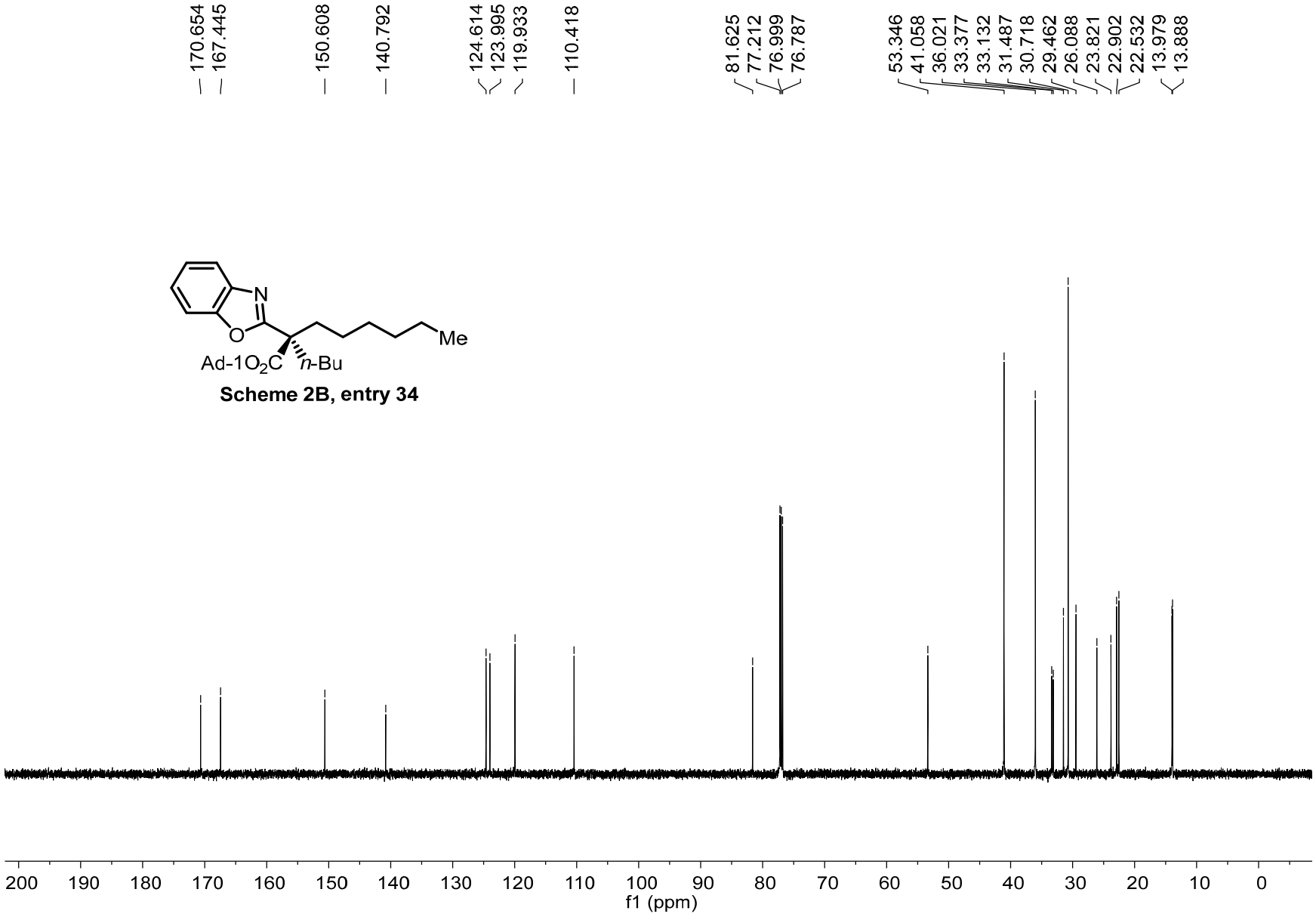


Scheme 2B, entry 33

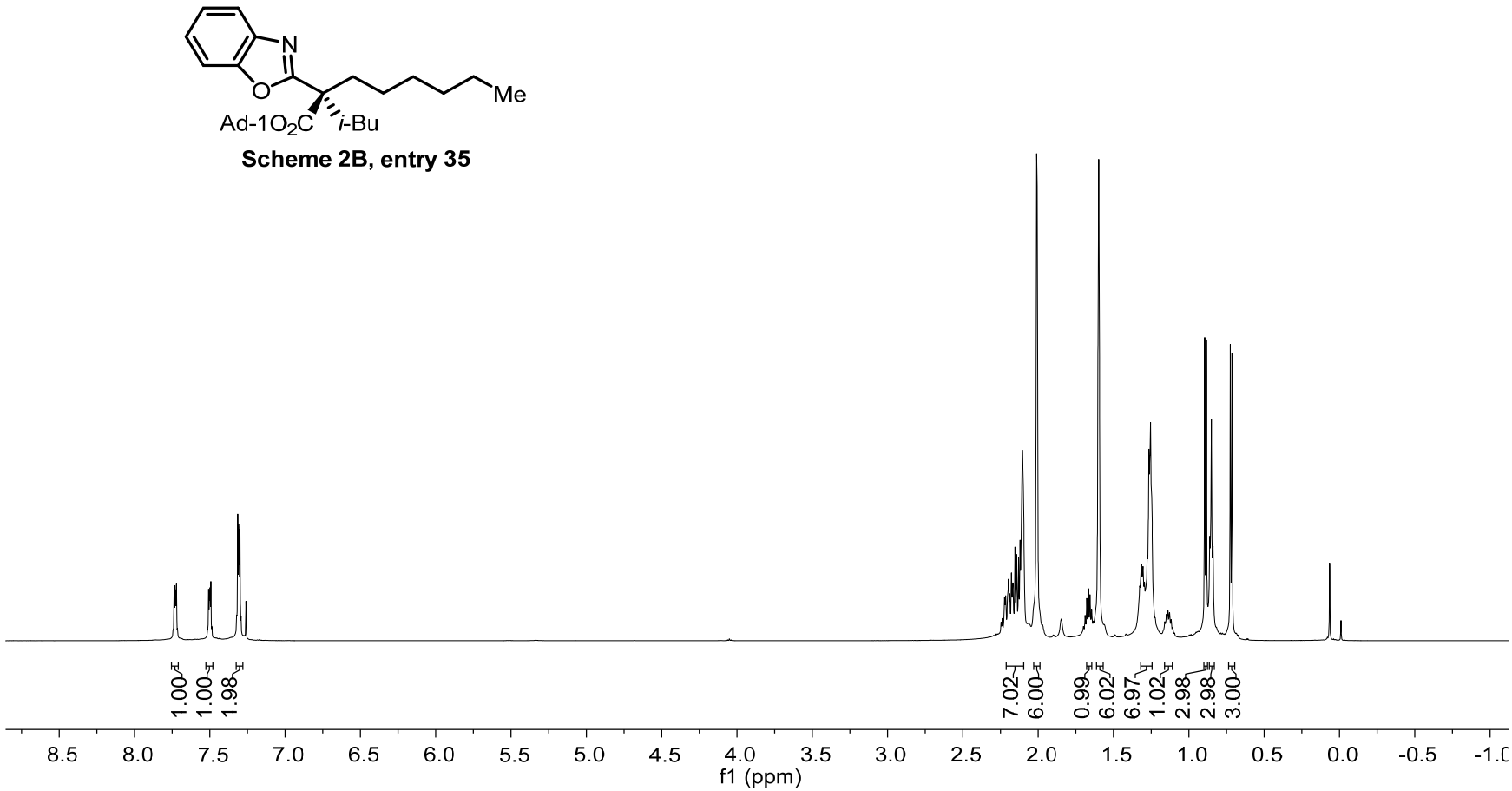

170.643
167.288
150.641
140.818
124.614
123.988
119.934
110.411
81.648
77.212
77.000
76.787
53.625
41.076
36.033
32.989
31.506
30.726
29.477
23.788
22.536
13.991
N
O
Me
Ad-1O2C
C2D5
Scheme 2B, entry 33
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



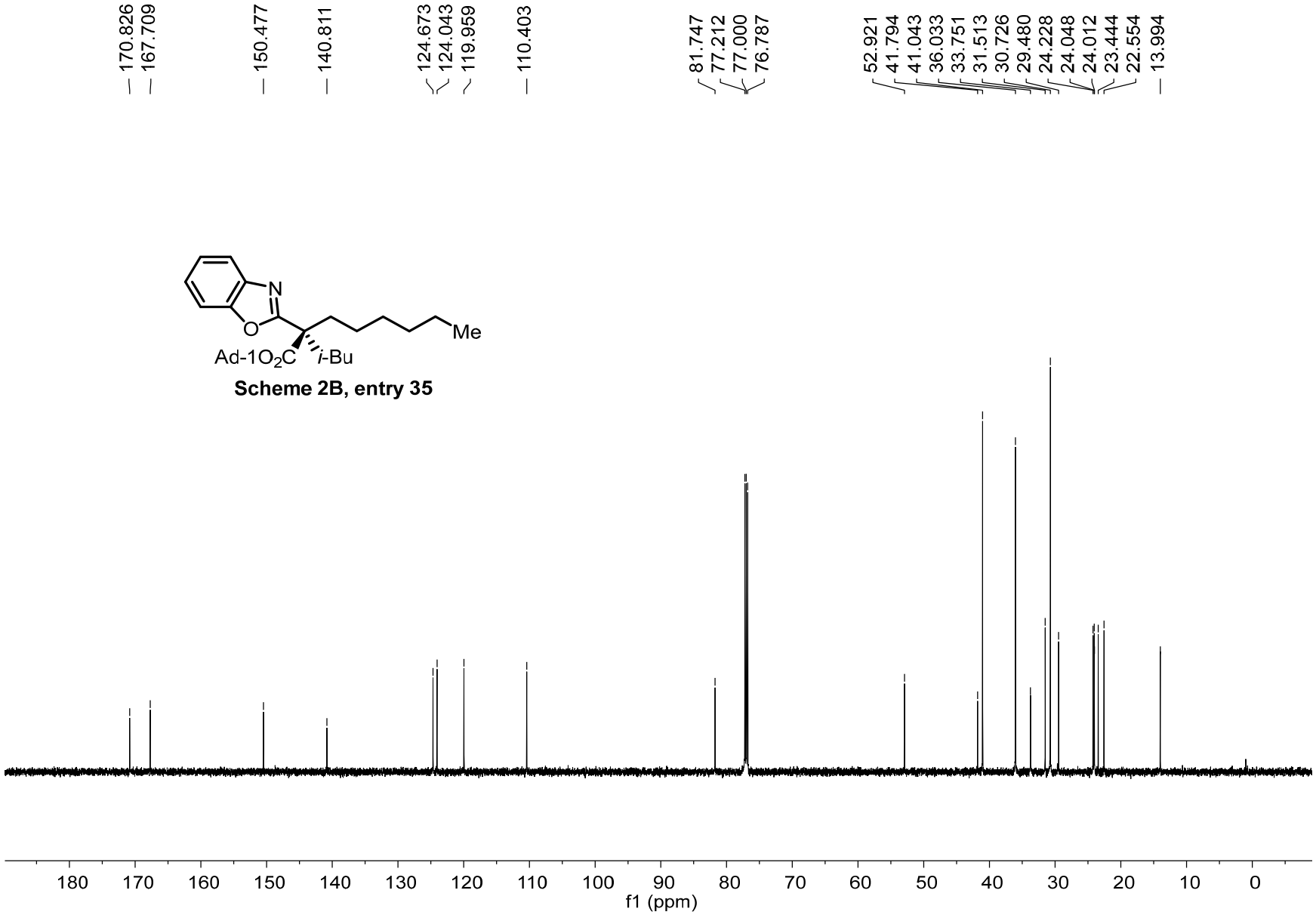
Scheme 2B, entry 34

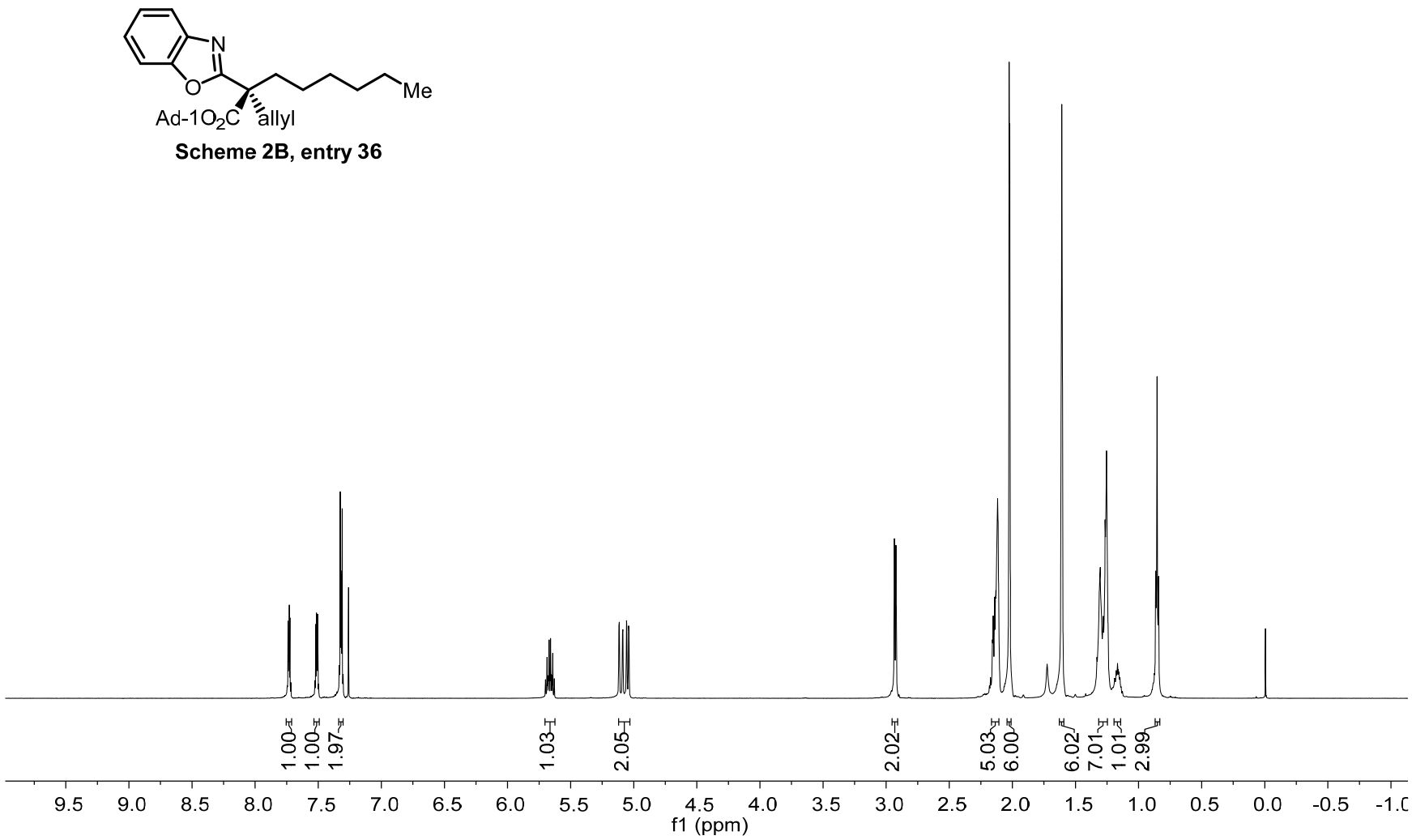


Scheme 2B, entry 34

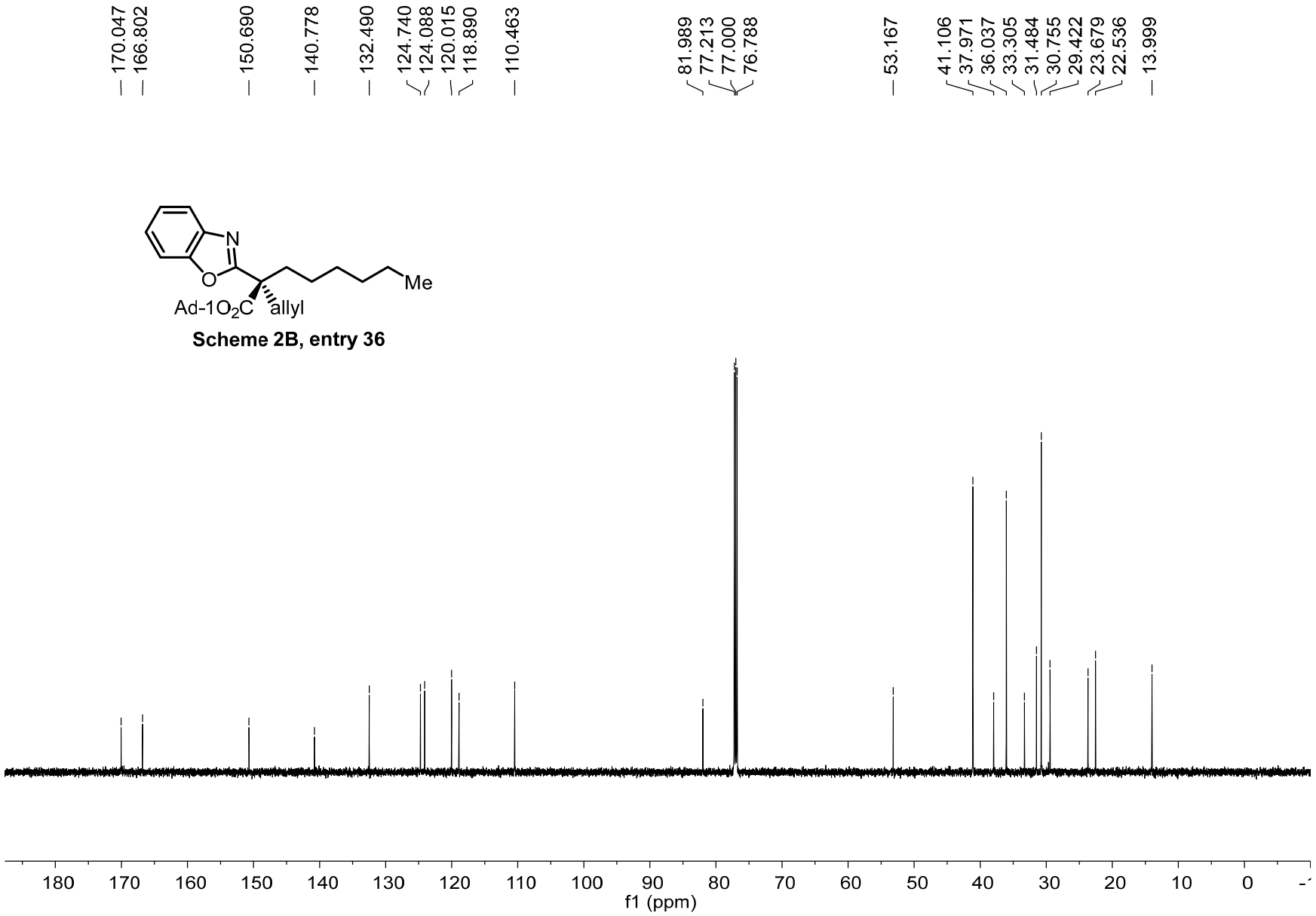


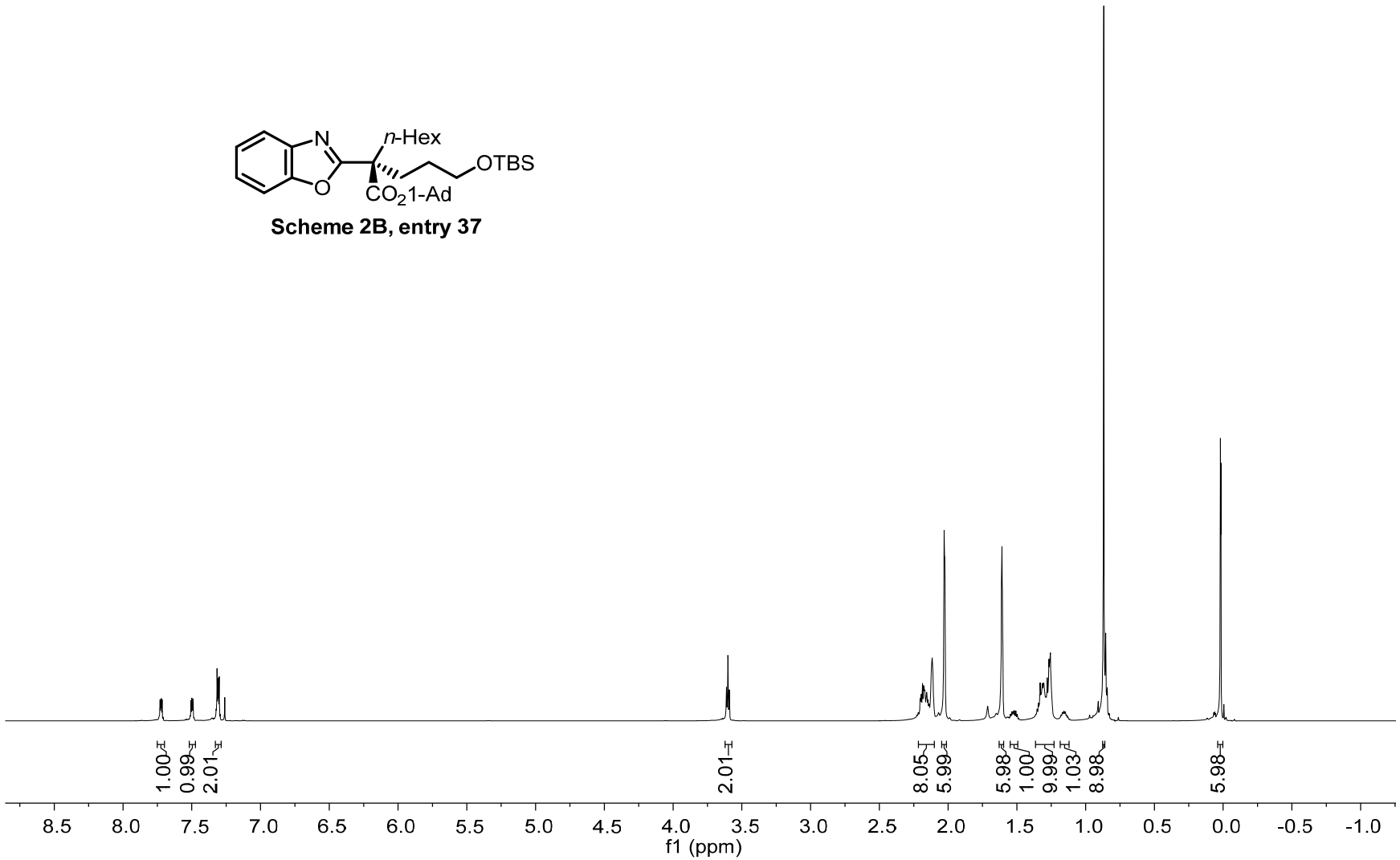
Scheme 2B, entry 35


170.826
167.709
150.477
140.811
124.673
124.043
119.959
110.403
81.747
77.212
77.000
76.787
52.921
41.794
41.043
36.033
33.751
31.513
30.726
29.480
24.228
24.048
24.012
23.444
22.554
13.994
N
O
Me
Ad-1O2C
i-Bu
Scheme 2B, entry 35
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

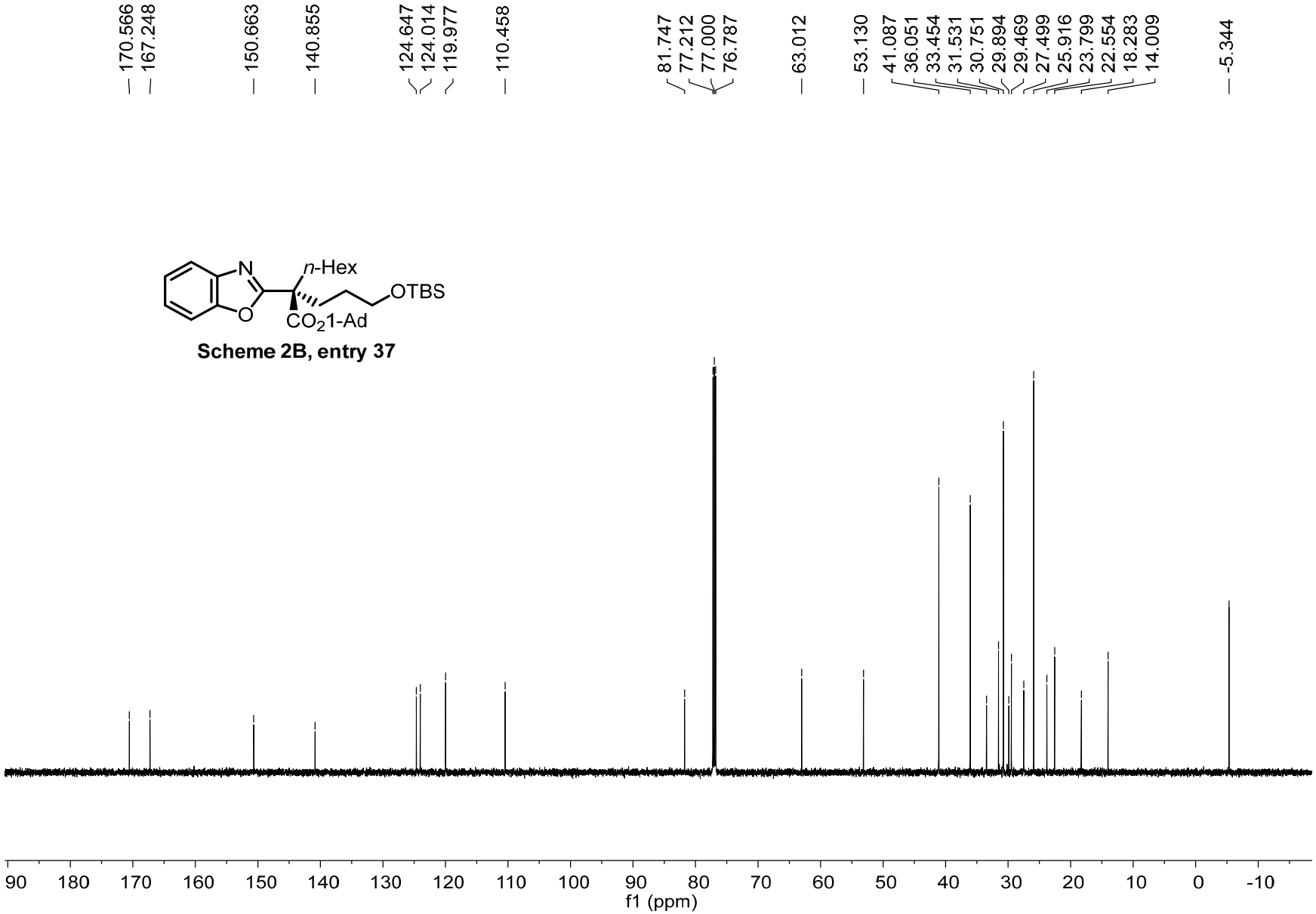


Scheme 2B, entry 36

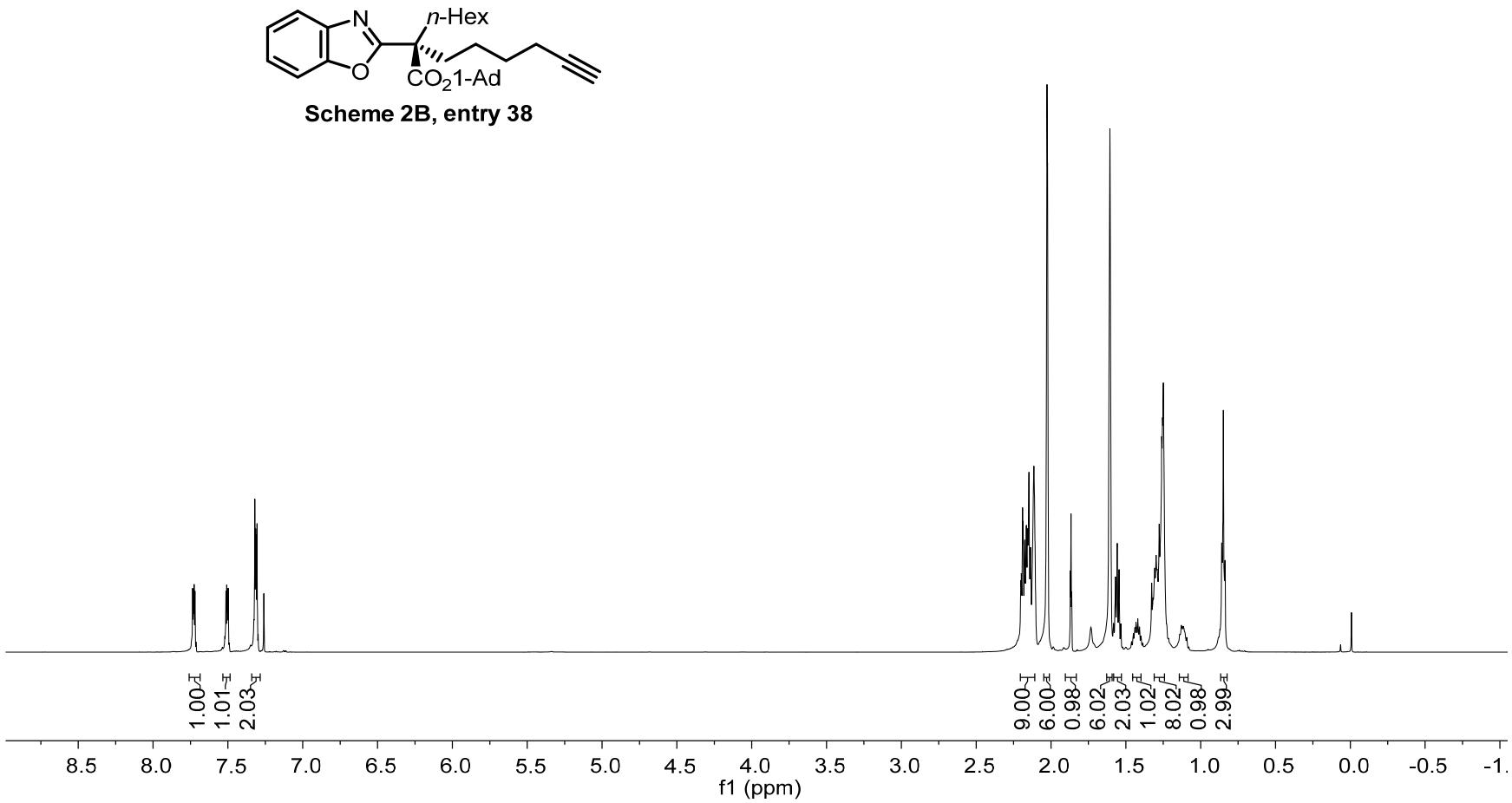

170.047
166.802
150.690
140.778
132.490
124.740
124.088
120.015
118.890
110.463
81.989
77.213
77.000
76.788
53.167
41.106
37.971
36.037
33.305
31.484
30.755
29.422
23.679
22.536
13.999
N
O
Me
Ad-1O2C
allyl
Scheme 2B, entry 36
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



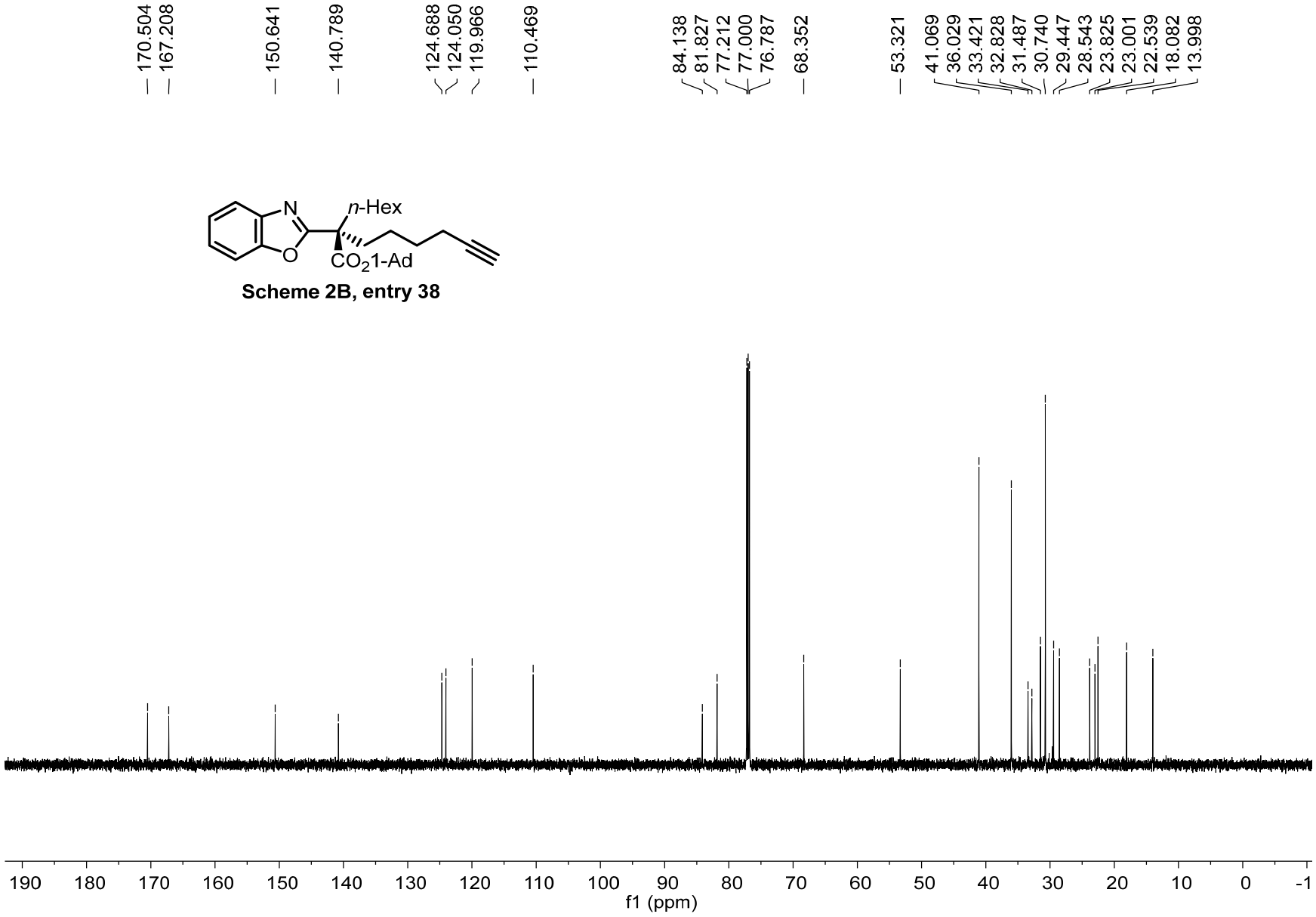
Scheme 2B, entry 37



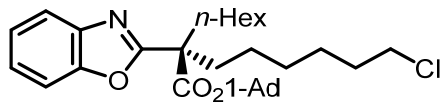
Scheme 2B, entry 37



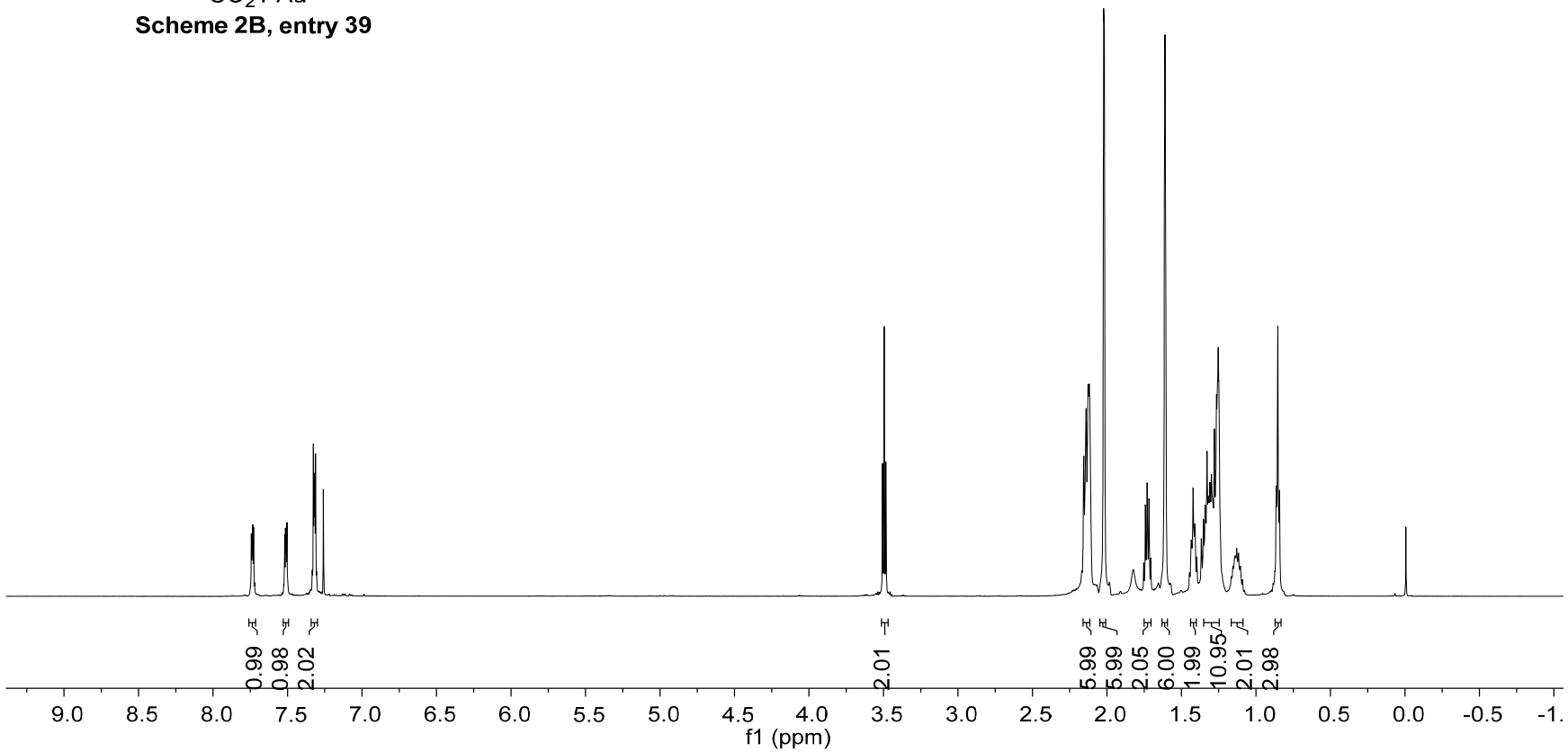
Scheme 2B, entry 38

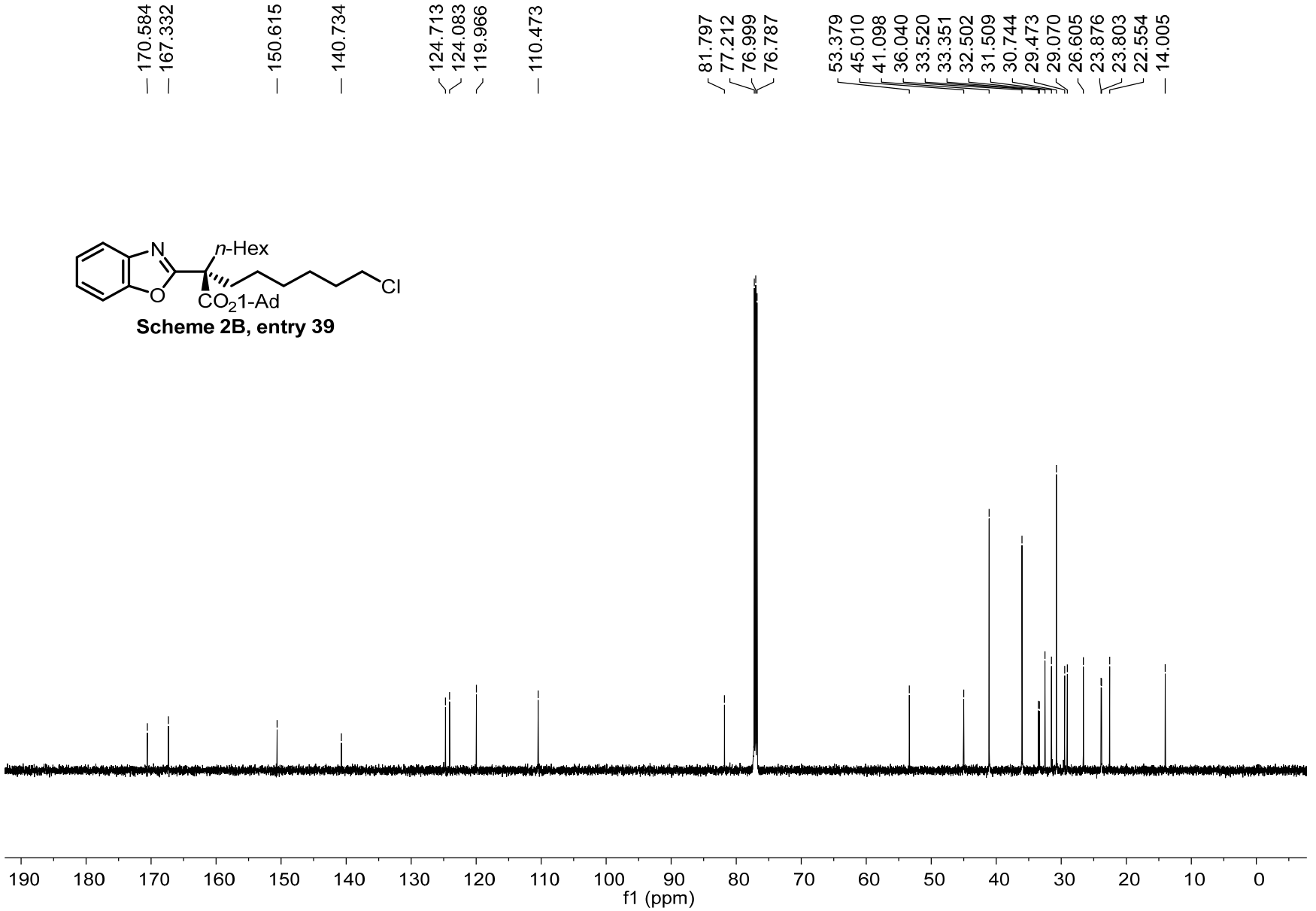


Scheme 2B, entry 38

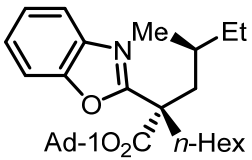


Scheme 2B, entry 39

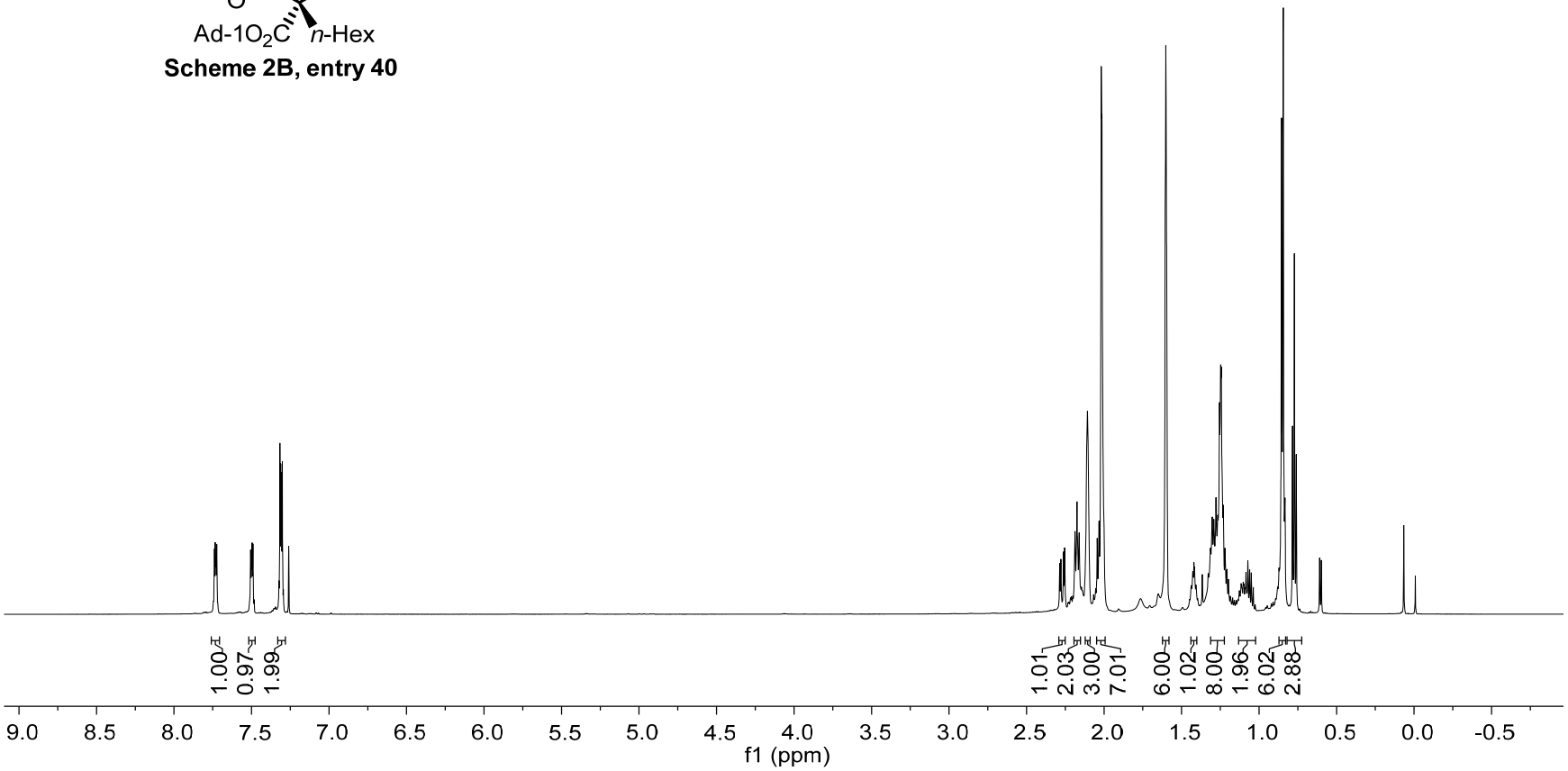


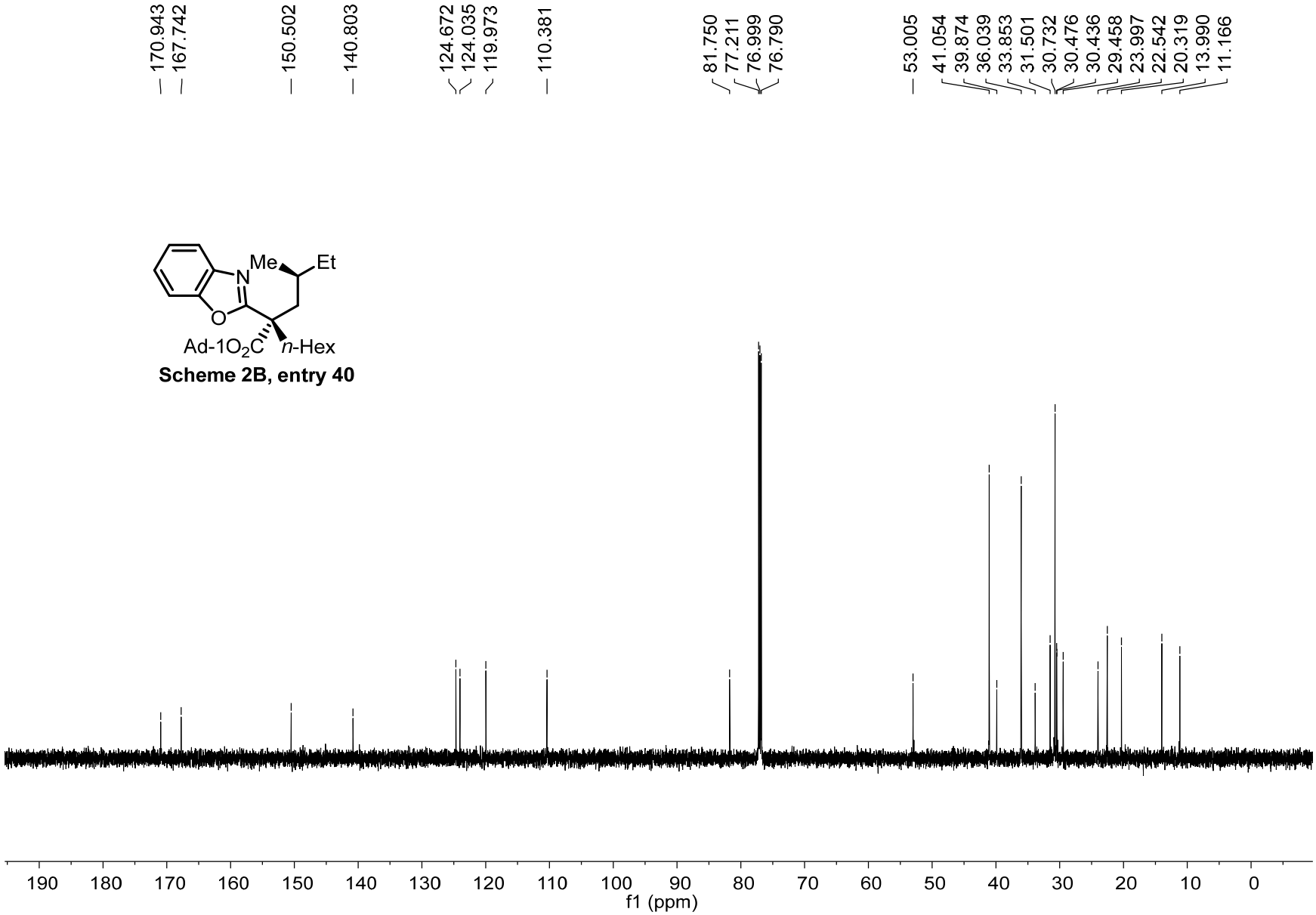


Scheme 2B, entry 39

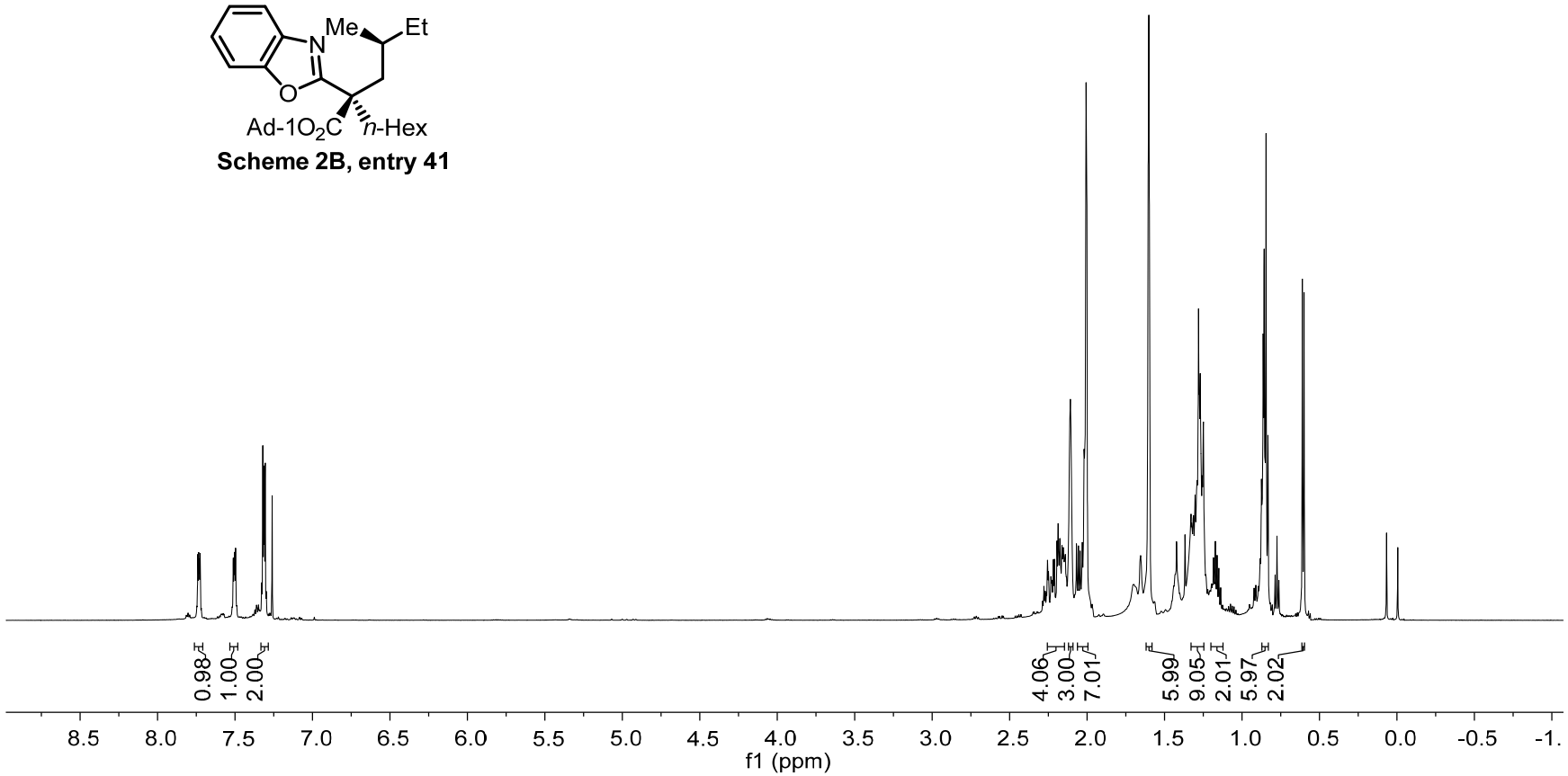


Scheme 2B, entry 40

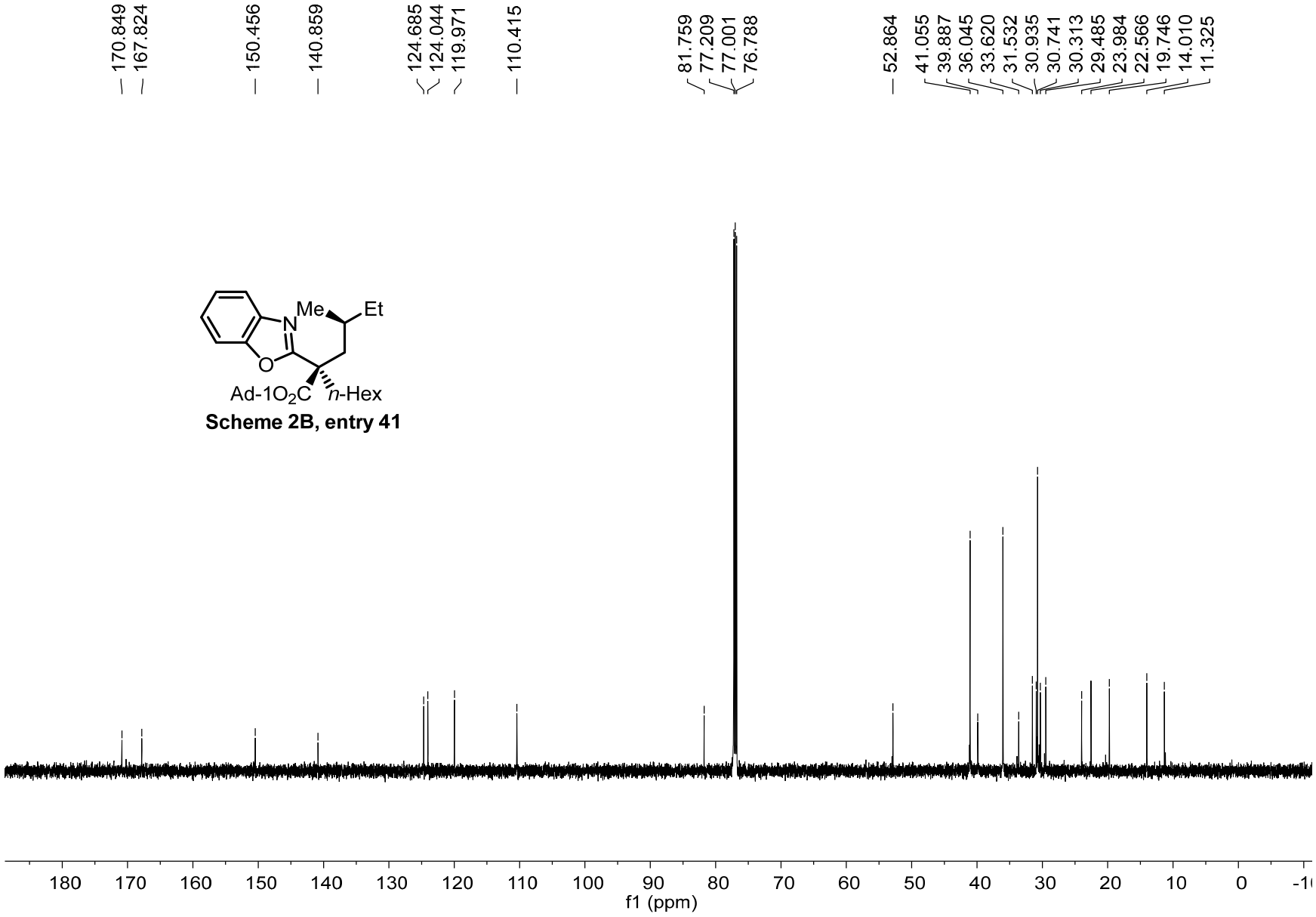




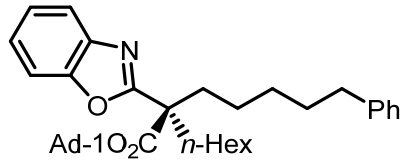
Scheme 2B, entry 40



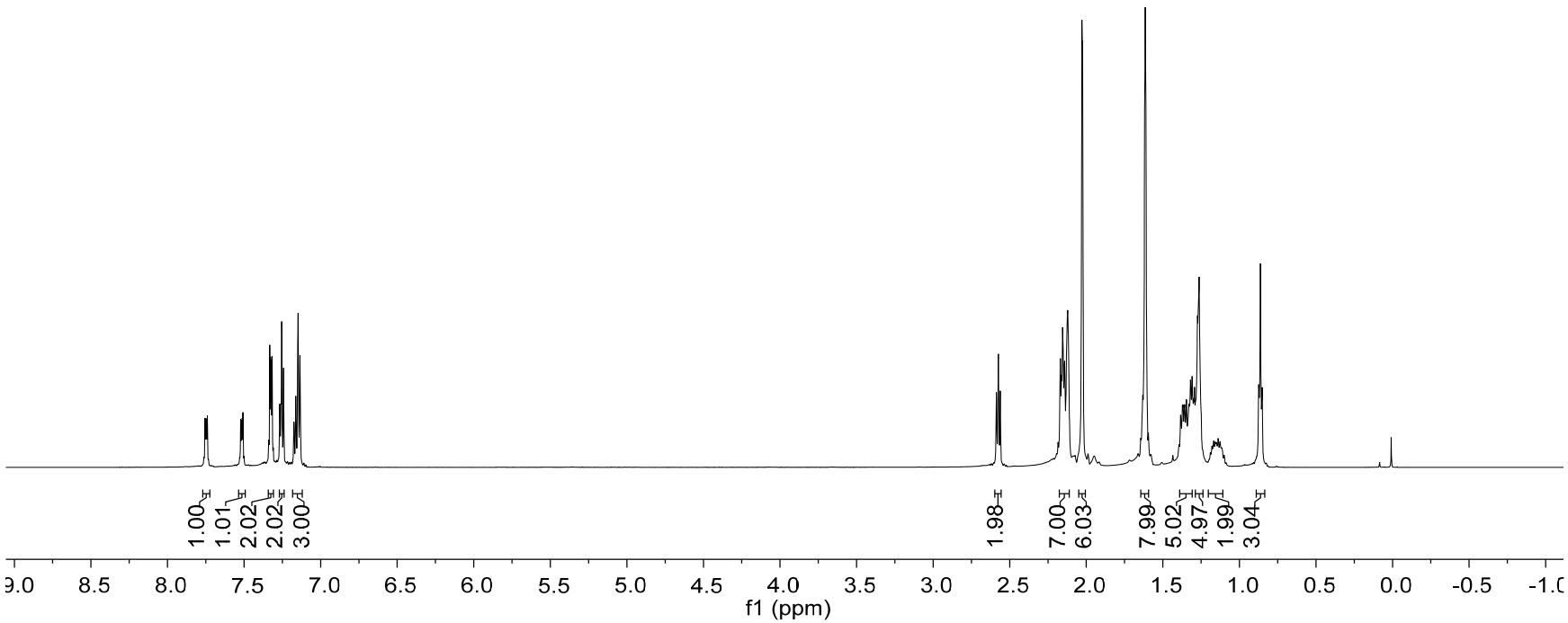
Scheme 2B, entry 41

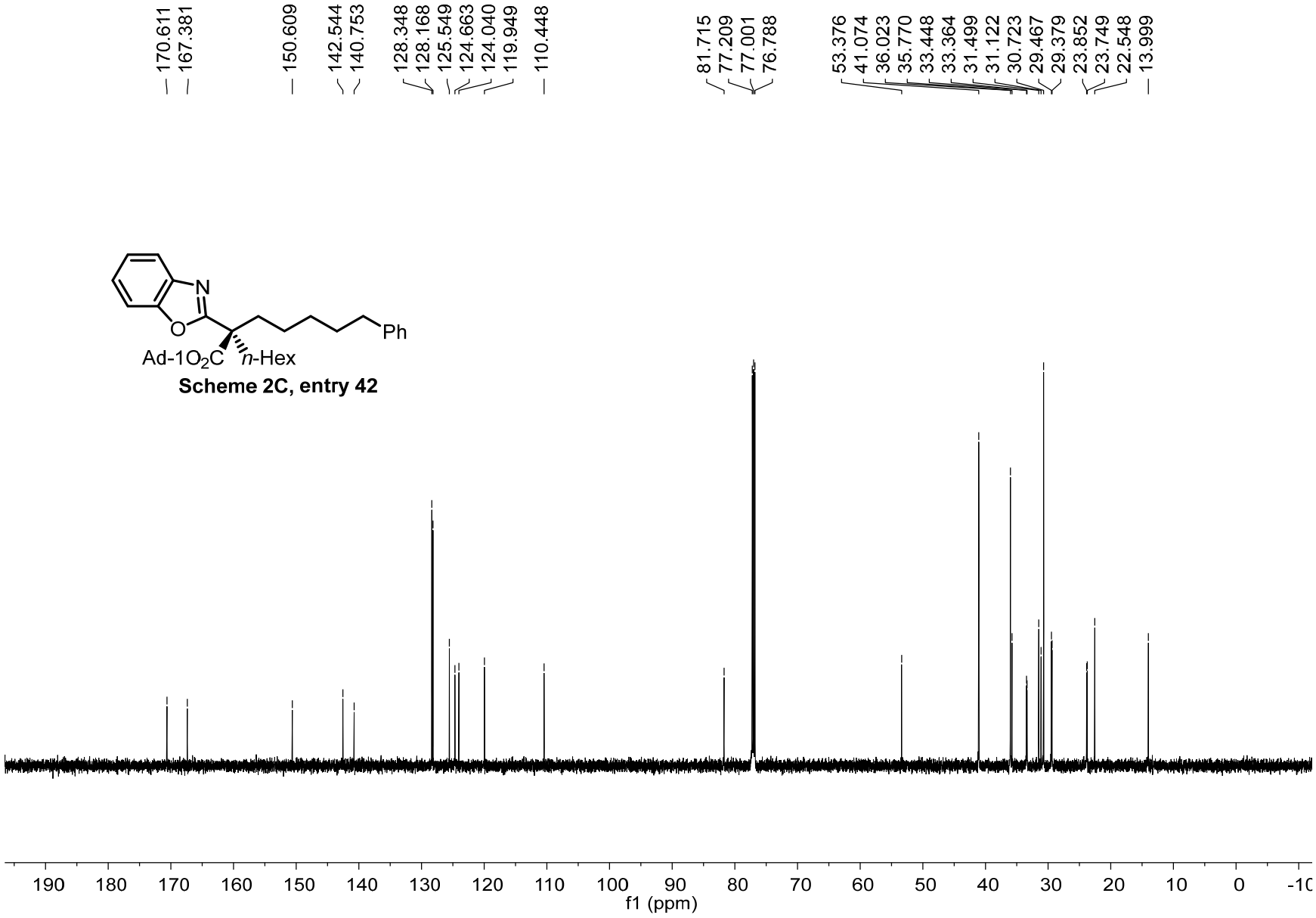


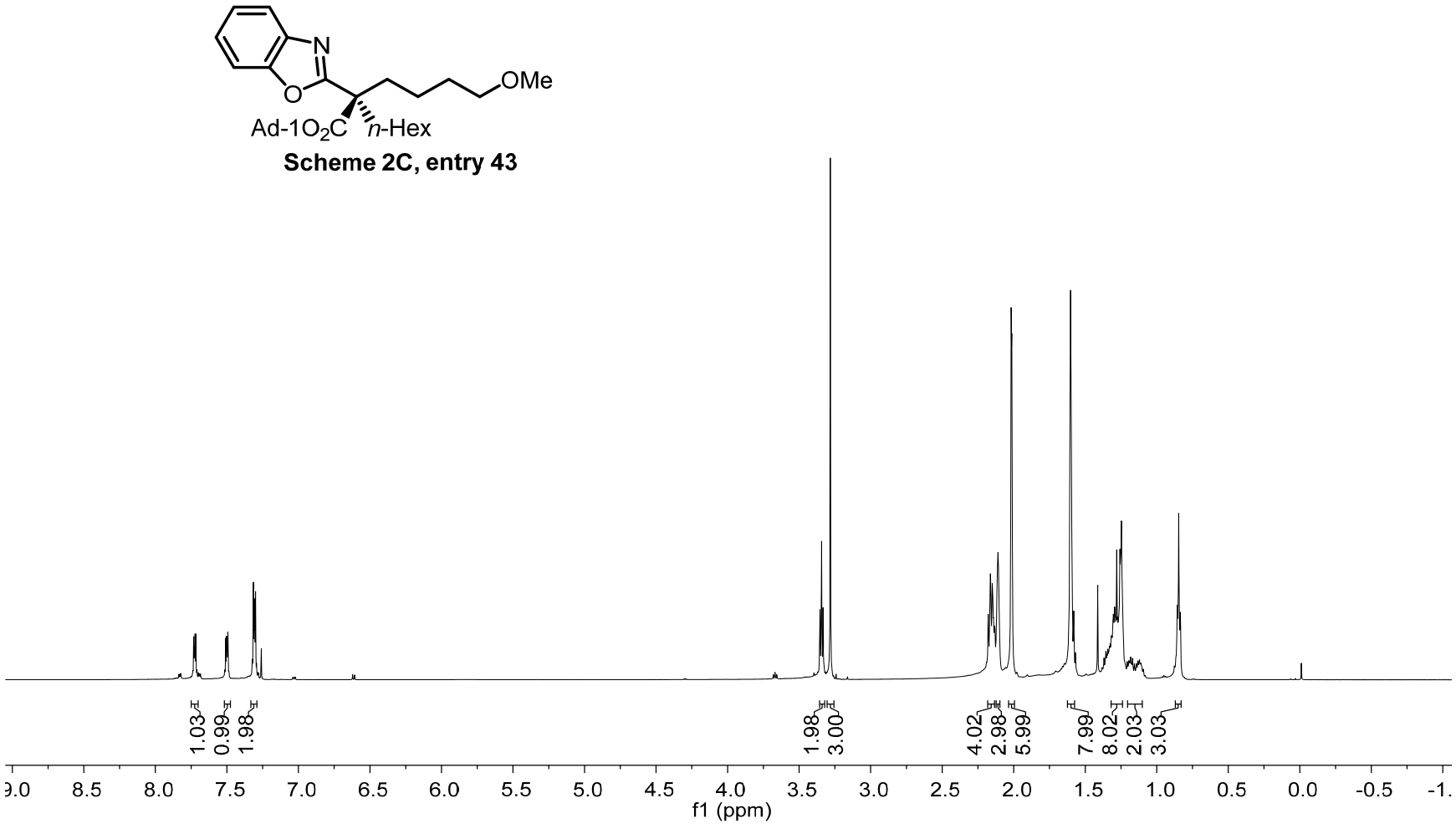
Scheme 2B, entry 41



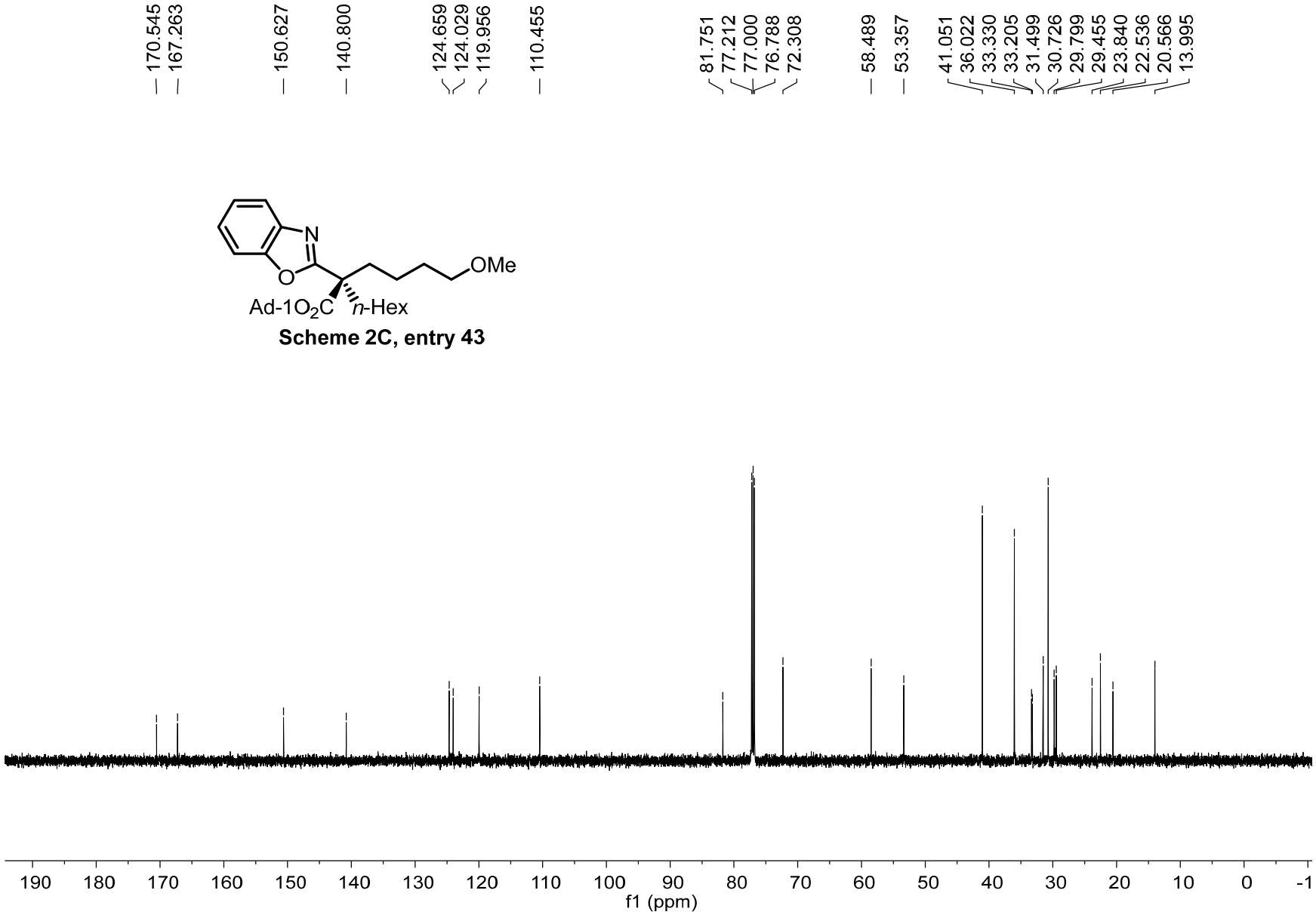
Scheme 2C, entry 42



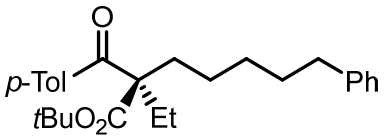

170.611
167.381
150.609
142.544
140.753
128.348
128.168
125.549
124.663
124.040
119.949
110.448
81.715
77.209
77.001
76.788
53.376
41.074
36.023
35.770
33.448
33.364
31.499
31.122
30.723
29.467
29.379
23.852
23.749
22.548
13.999
N
O
Ph
Ad-1O2C
n-Hex
Scheme 2C, entry 42
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



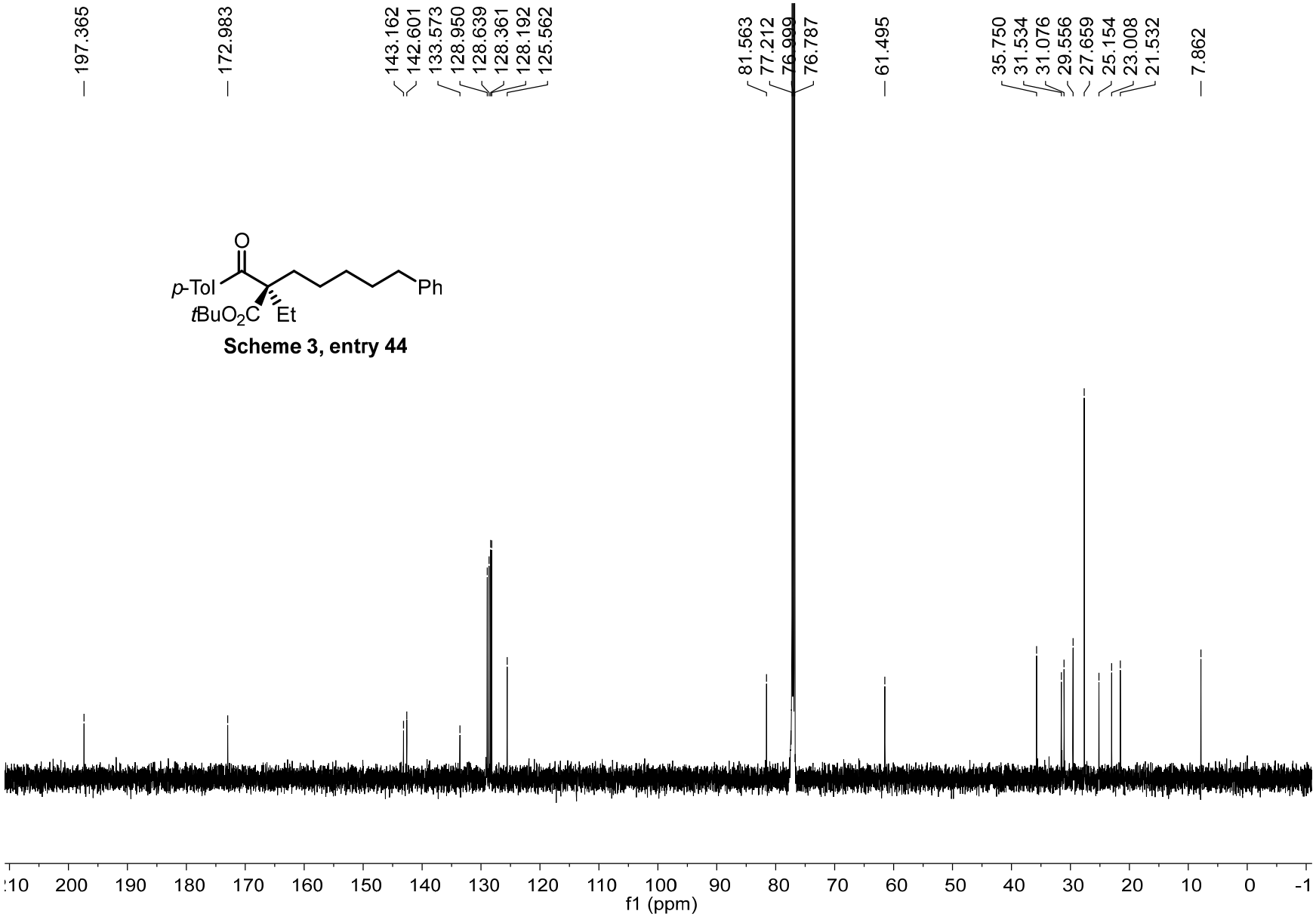
Scheme 2C, entry 43

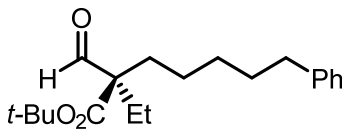


Scheme 2C, entry 43

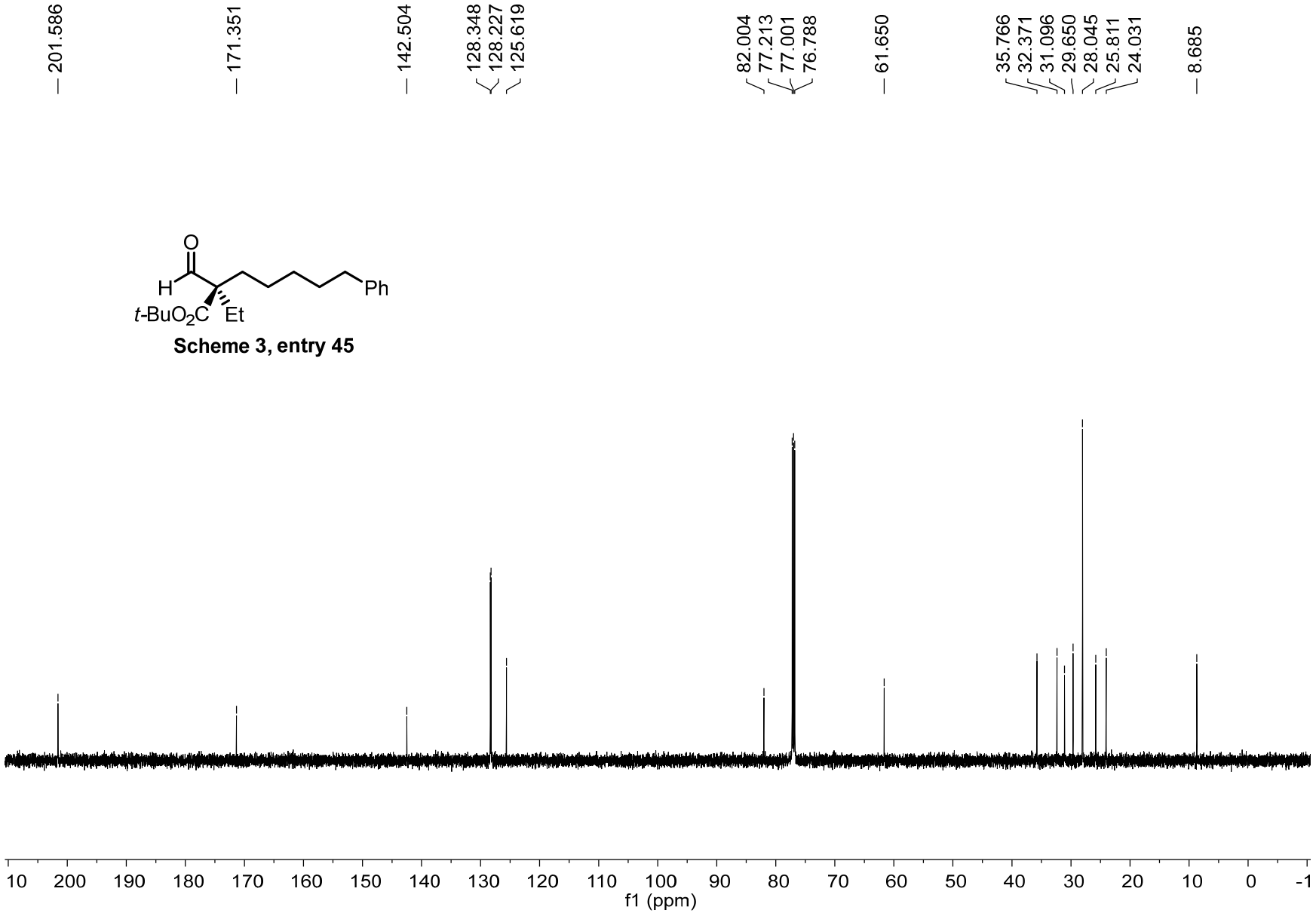


Scheme 3, entry 44

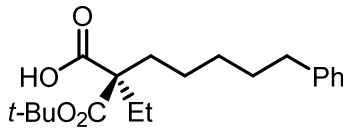

197.365
172.983
143.162
142.601
133.573
128.950
128.639
128.361
128.192
125.562
81.563
77.212
76.999
76.787
61.495
35.750
31.534
31.076
29.556
27.659
25.154
23.008
21.532
7.862
O
p-Tol
Ph
tBuO2C
Et
Scheme 3, entry 44
f1 (ppm)



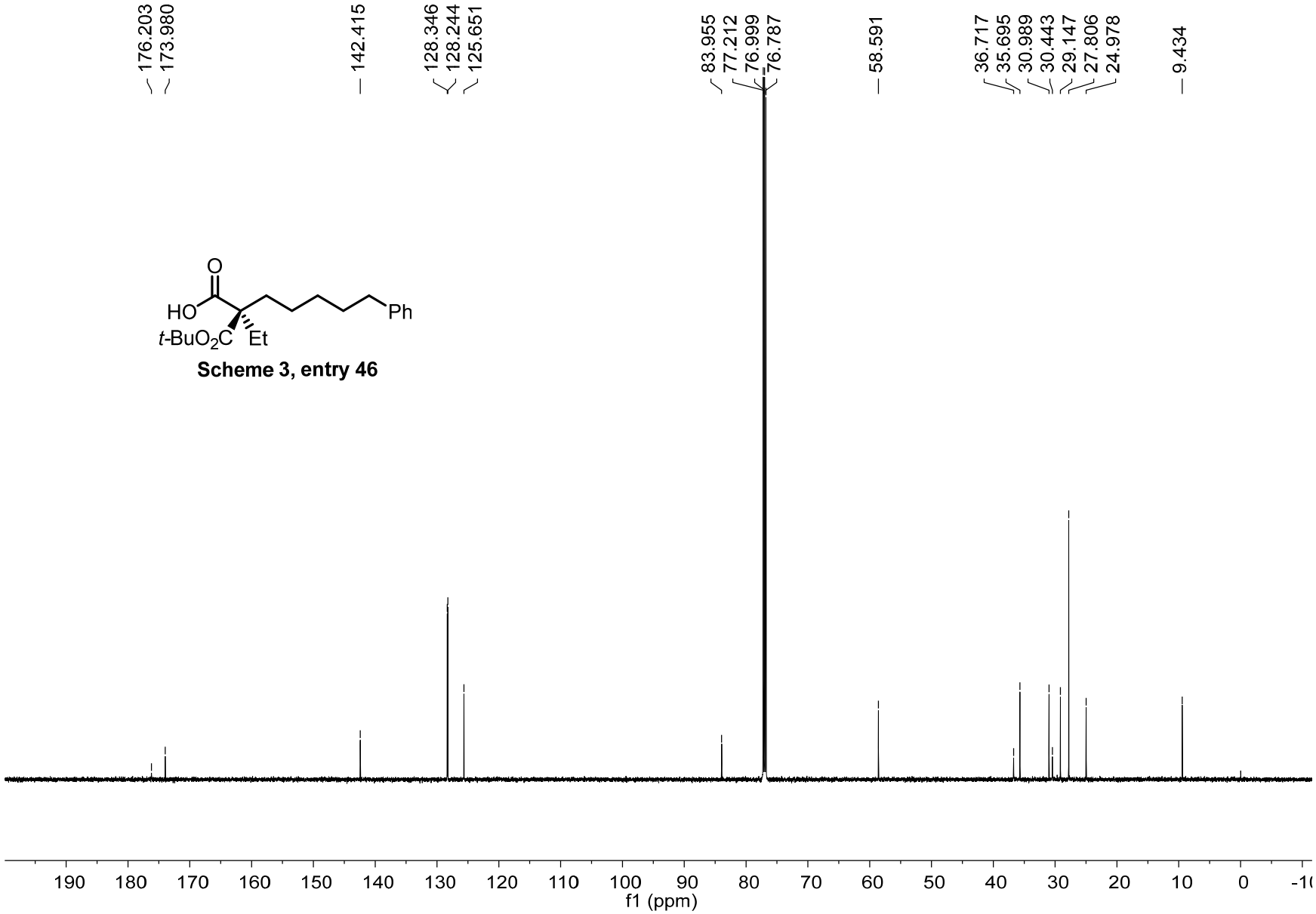
Scheme 3, entry 45



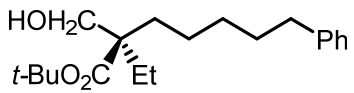
Scheme 3, entry 45



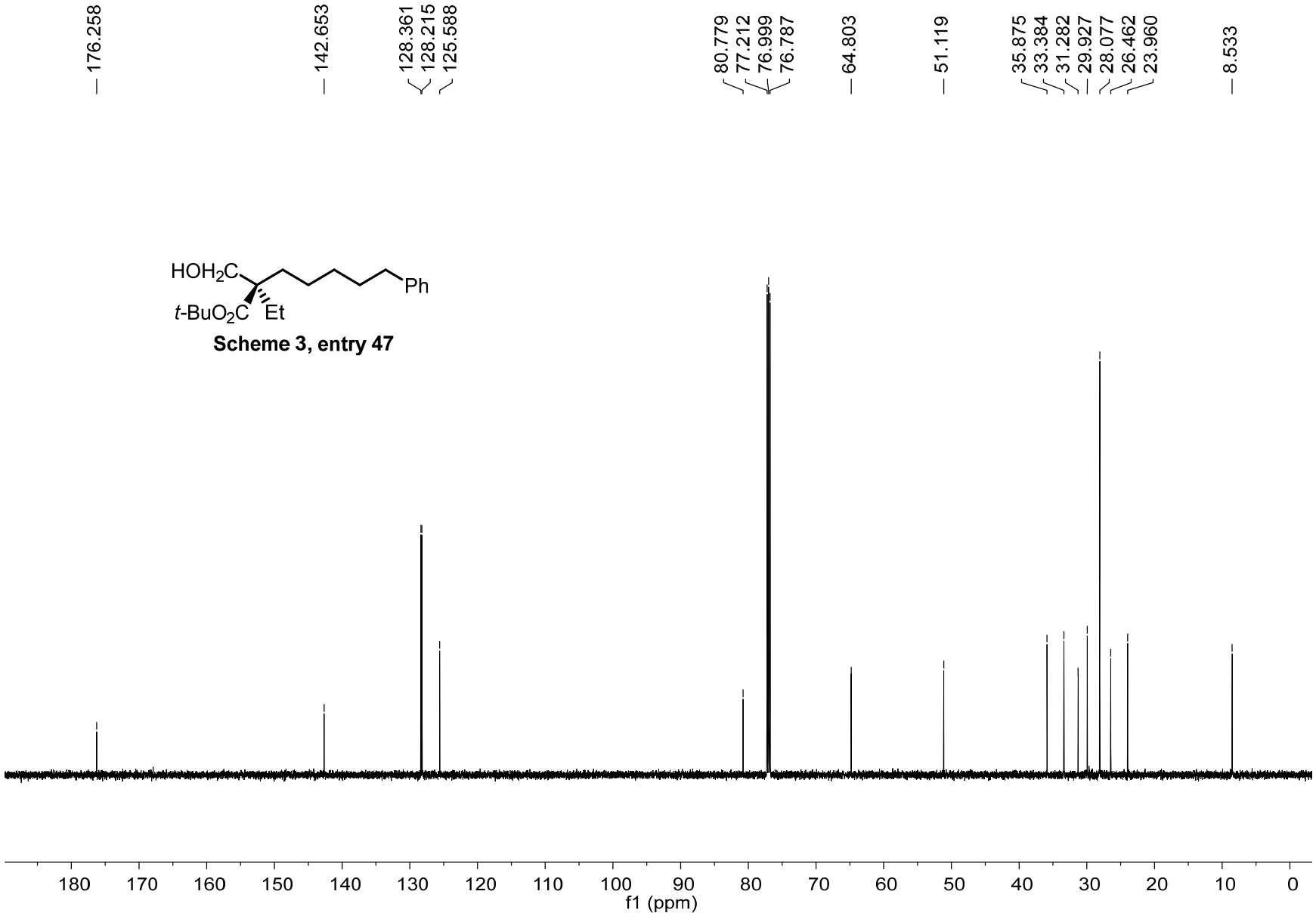
Scheme 3, entry 46

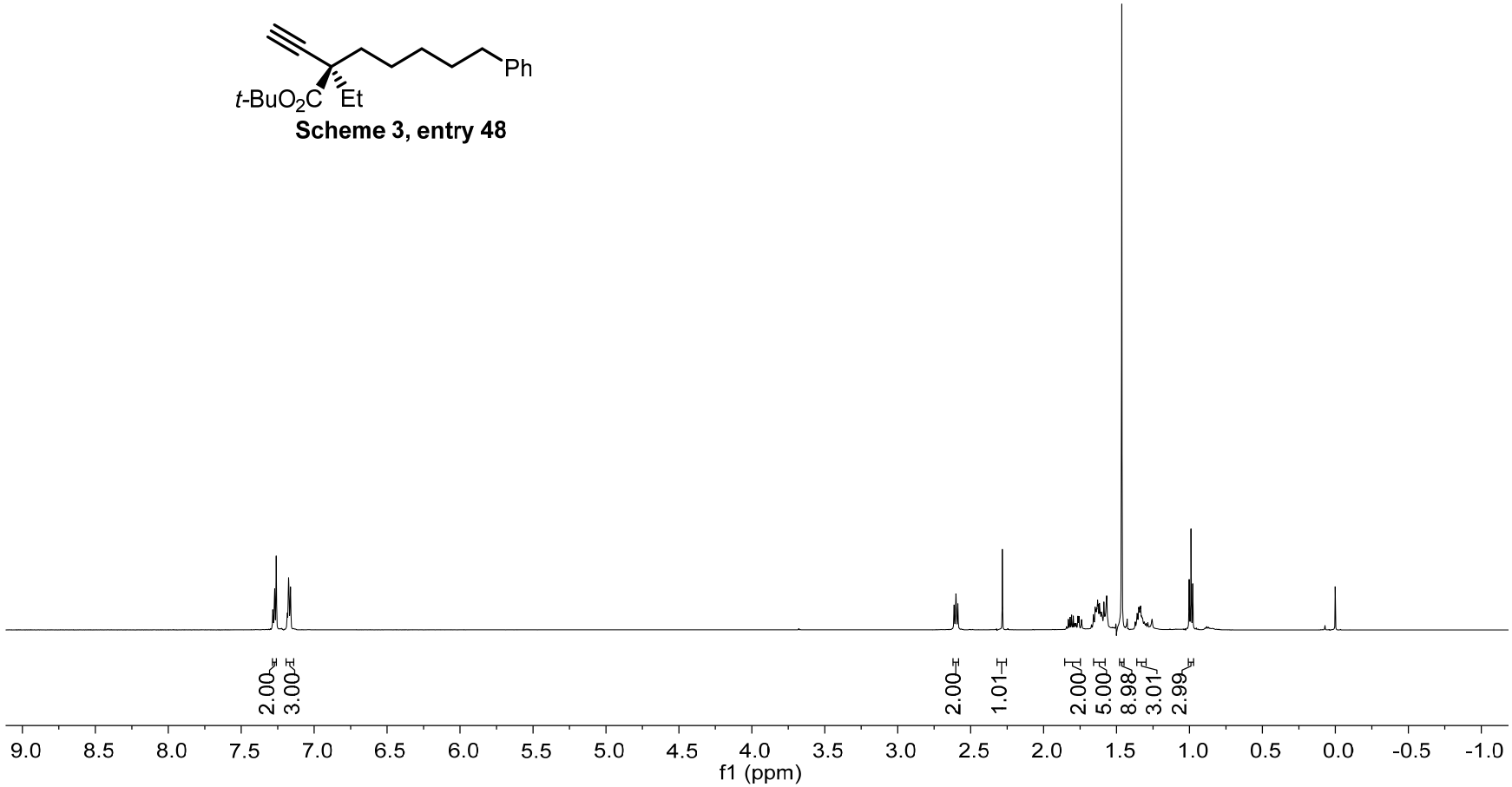


Scheme 3, entry 46

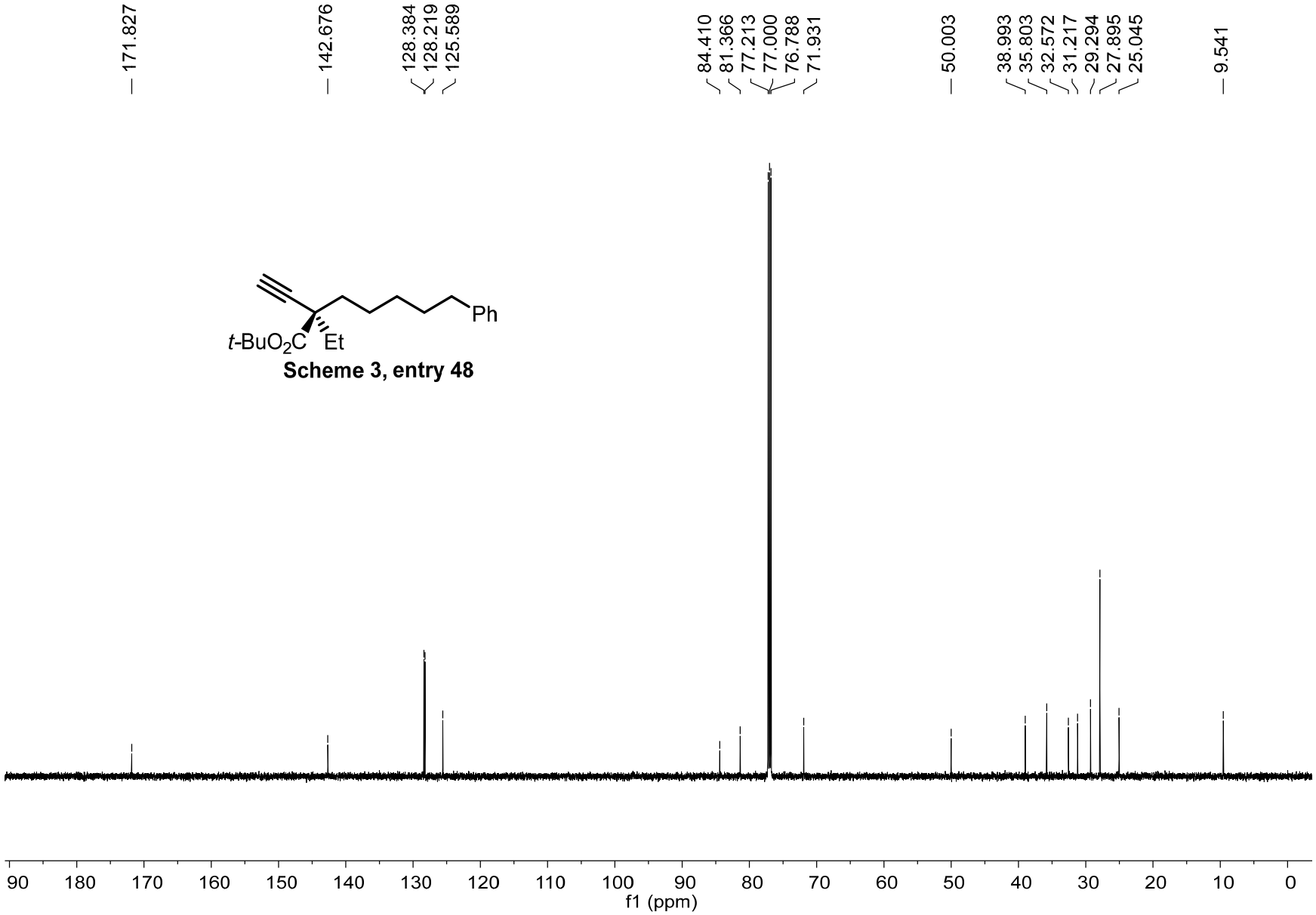


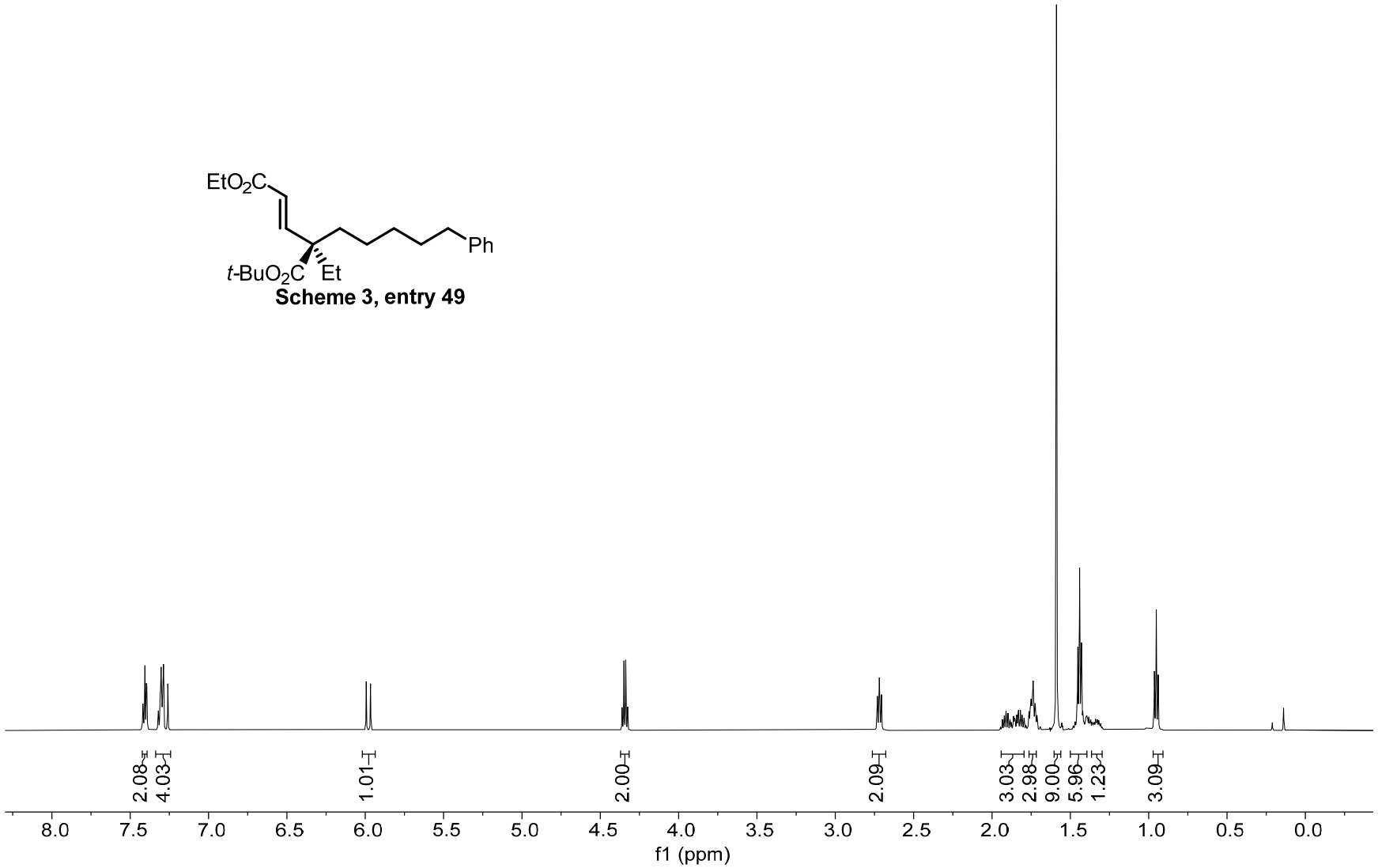
Scheme 3, entry 47


176.258
142.653
128.361
128.215
125.588
80.779
77.212
76.999
76.787
64.803
51.119
35.875
33.384
31.282
29.927
28.077
26.462
23.960
8.533
HOH2C
Ph
t-BuO2C
Et
Scheme 3, entry 47
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

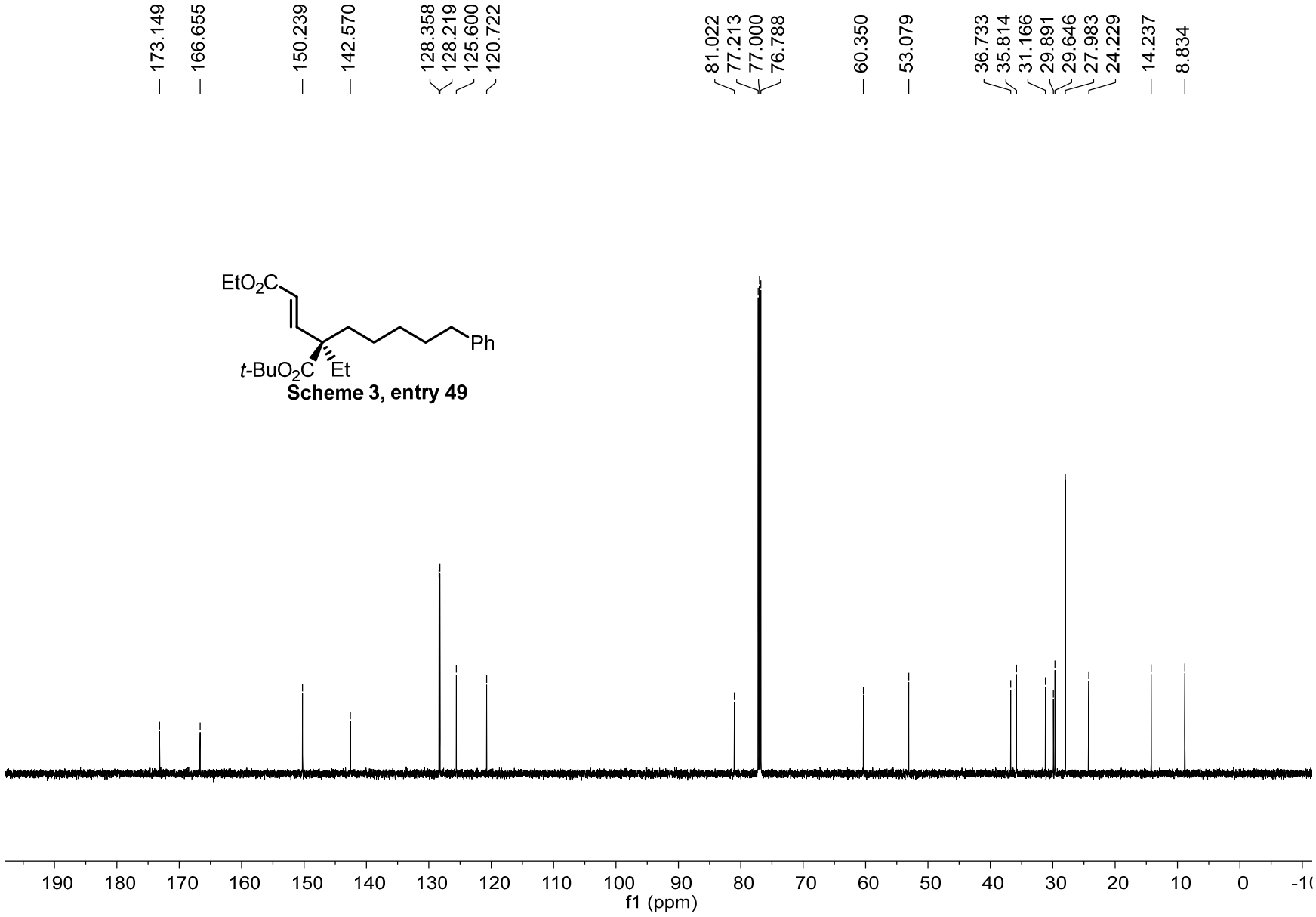


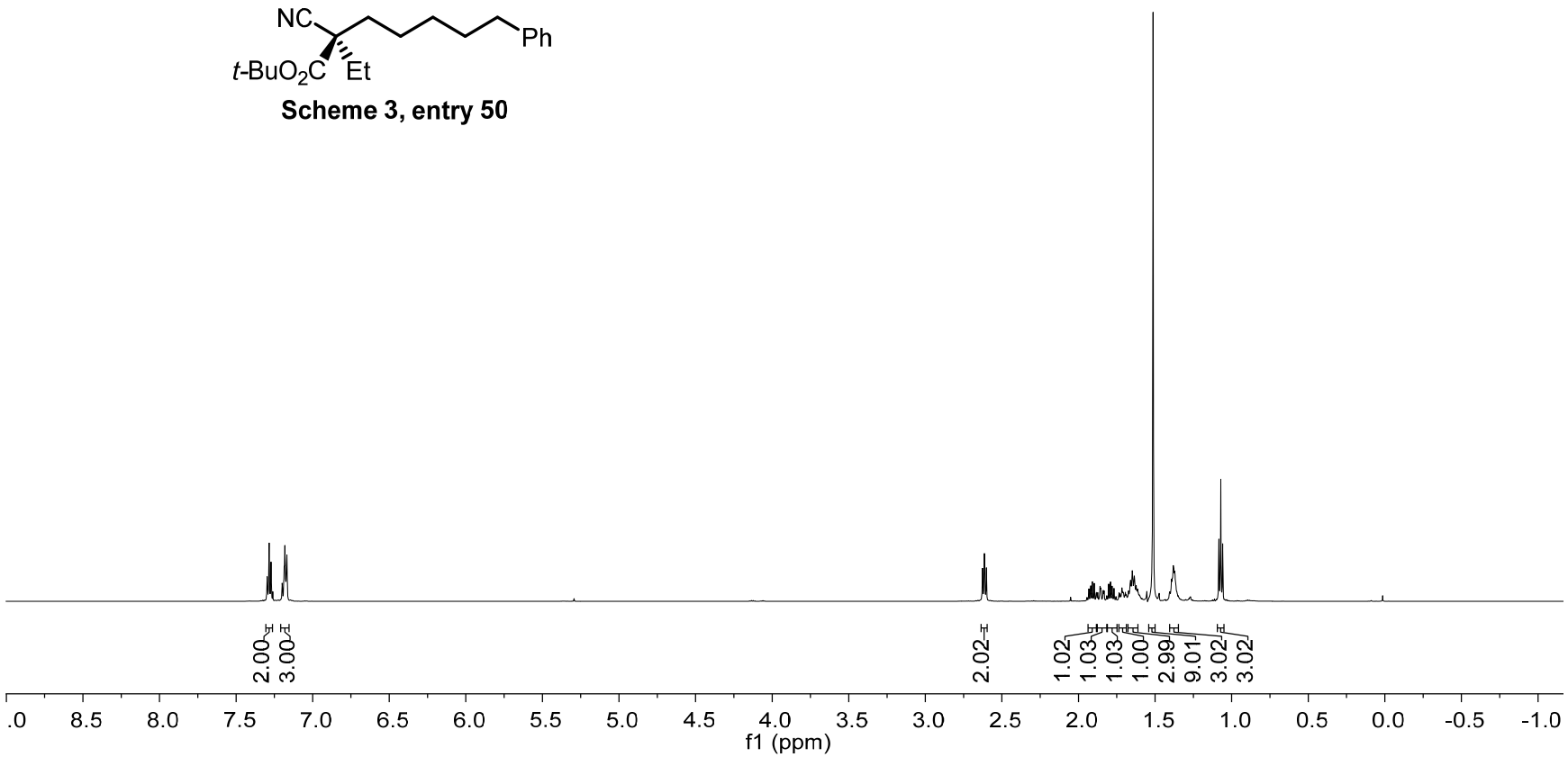
Scheme 3, entry 48


171.827
142.676
128.384
128.219
125.589
84.410
81.366
77.213
77.000
76.788
71.931
50.003
38.993
35.803
32.572
31.217
29.294
27.895
25.045
9.541
Ph
t-BuO2C
Et
Scheme 3, entry 48
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

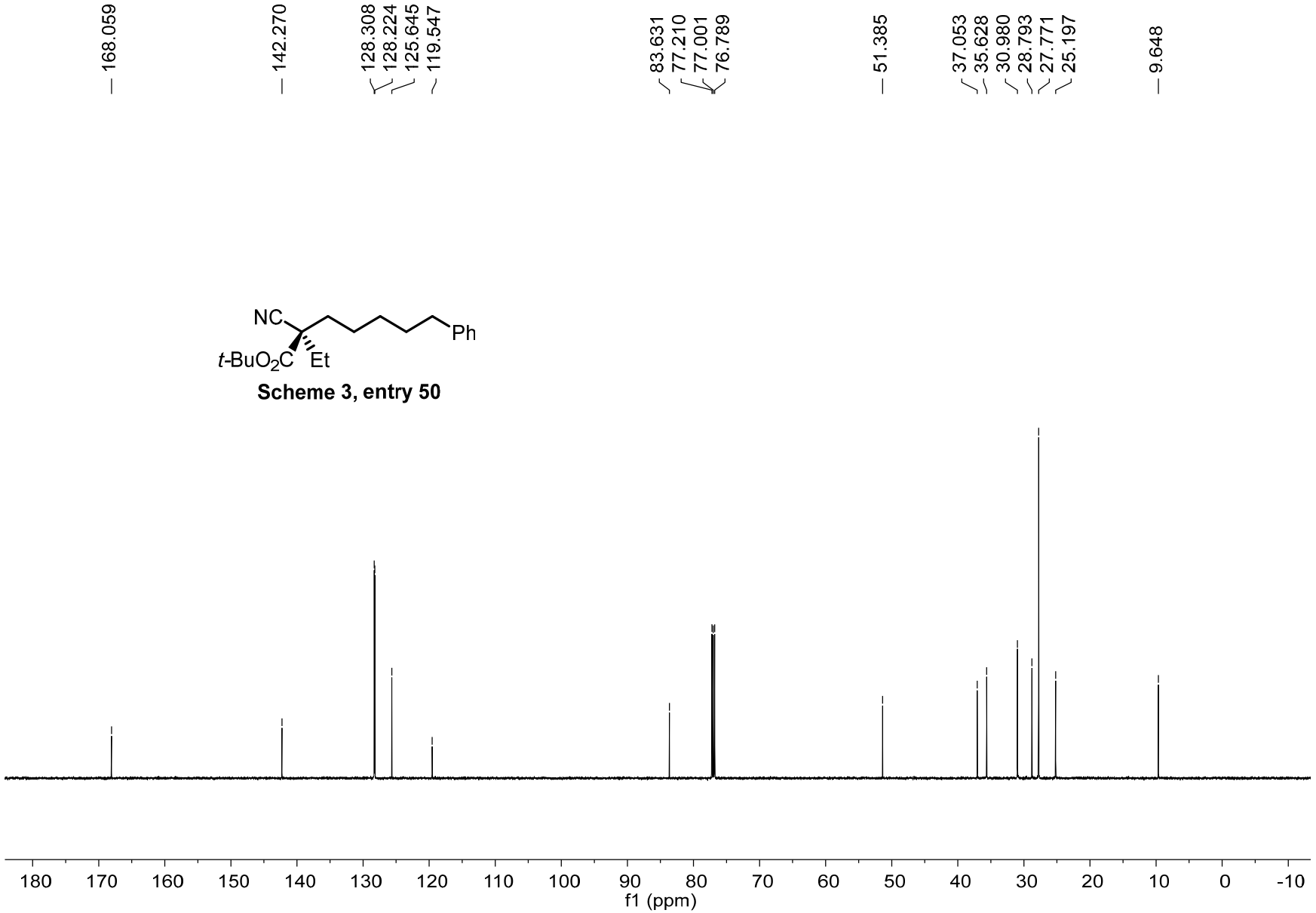


Scheme 3, entry 49

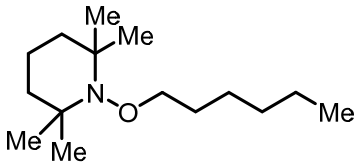

173.149
166.655
150.239
142.570
128.358
128.219
125.600
120.722
81.022
77.213
77.000
76.788
60.350
53.079
36.733
35.814
31.166
29.891
29.646
27.983
24.229
14.237
8.834
EtO2C
Ph
t-BuO2C
Et
Scheme 3, entry 49
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



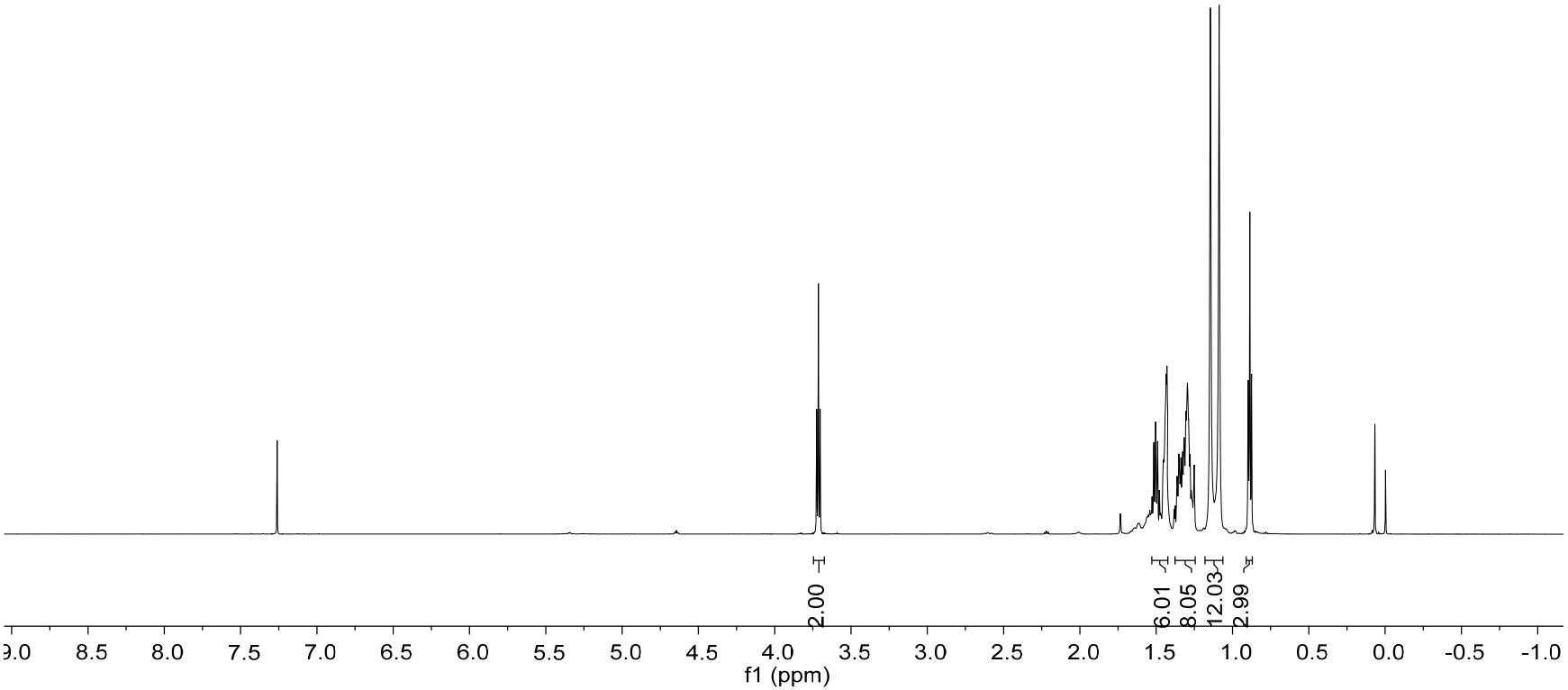
Scheme 3, entry 50

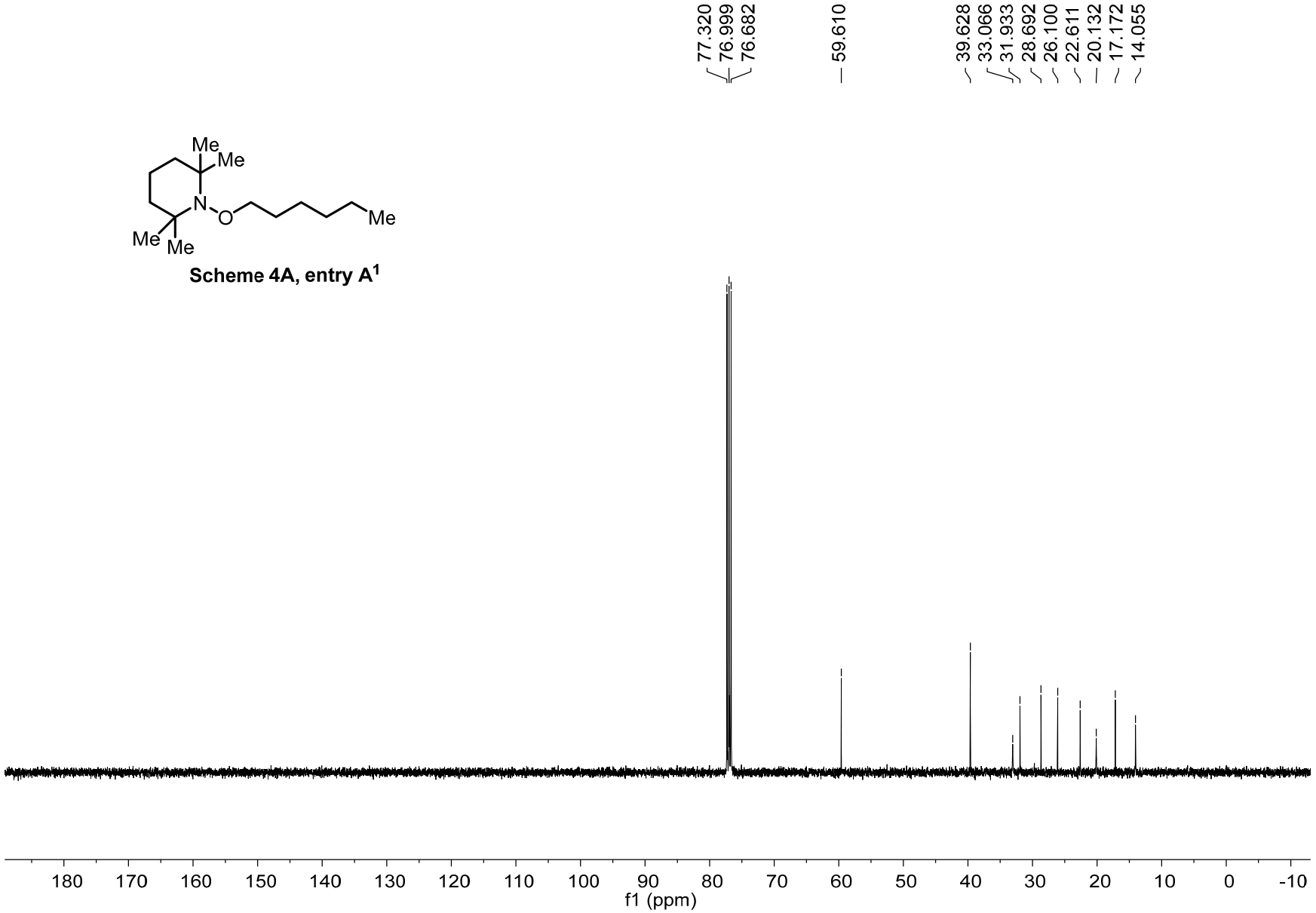


Scheme 3, entry 50



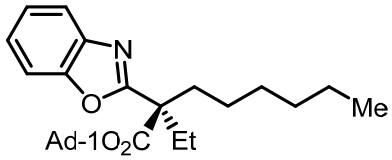
Scheme 4A, entry A[1]





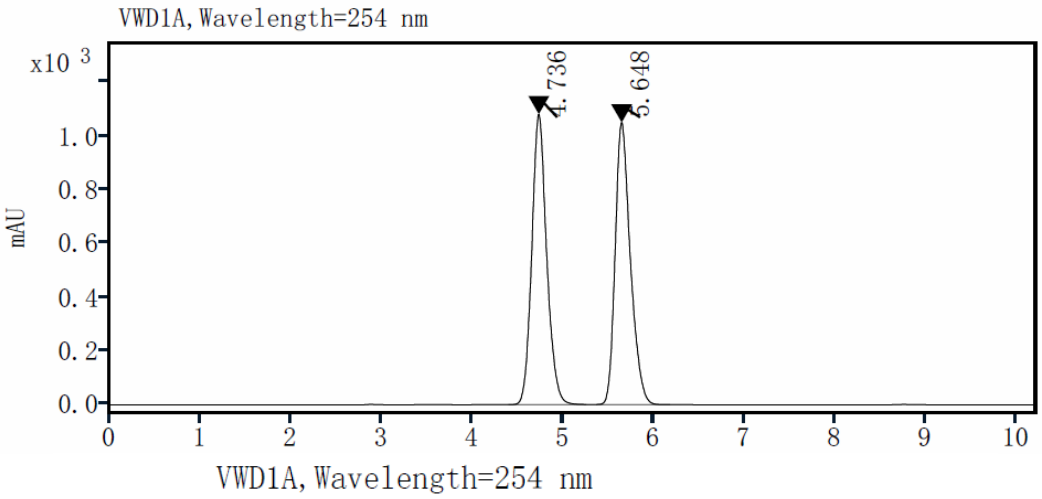
Scheme 4A, entry A[1]

Determination of Stereoselectivity

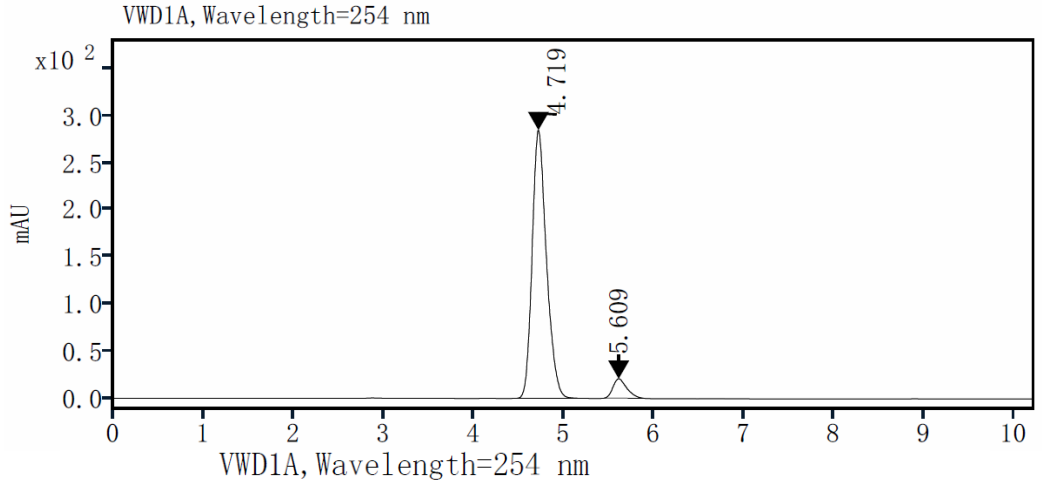


Scheme 2A, entry 1

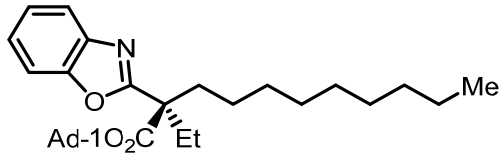
(*R,S*)-**L1**: 87% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.736	MM m	12302.71	50.24
	5.648	MM m	12186.79	49.76

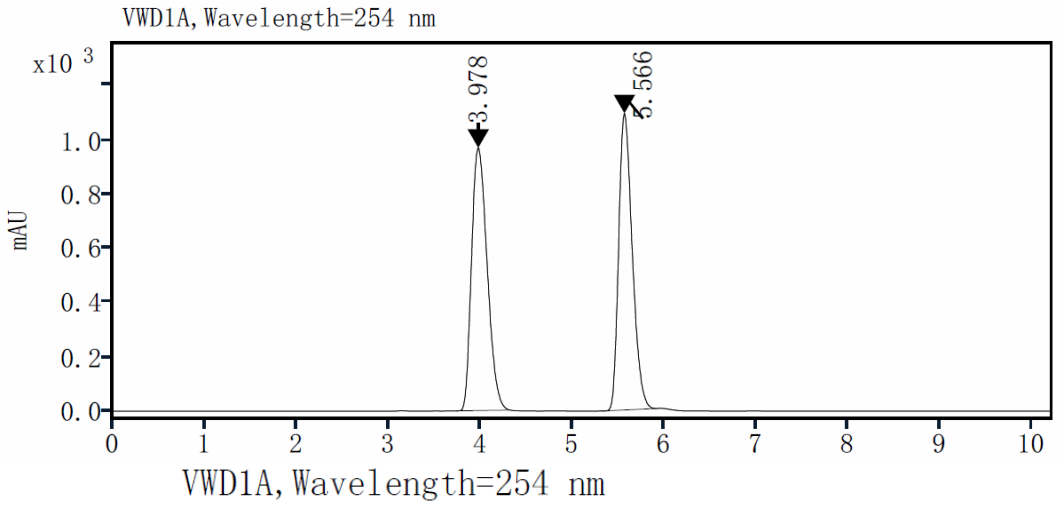


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.719	MM m	3137.27	93.48
	5.609	MM m	218.66	6.52



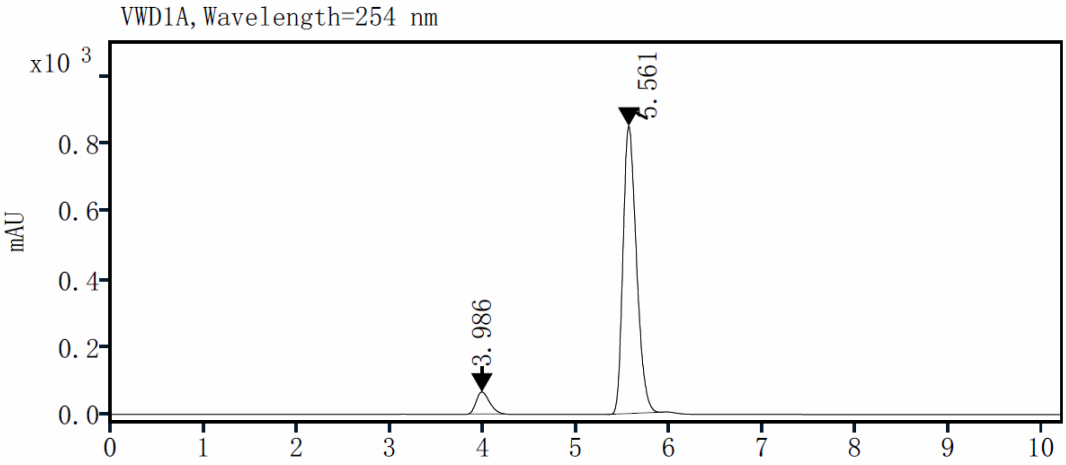
Scheme 2A, entry 2

(*R*,*S*)-**L1**: 86% ee



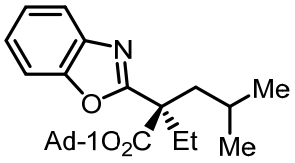
VWD1A,Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	3.978	MM m	11407.25	50.51
	5.566	MM m	11178.02	49.49

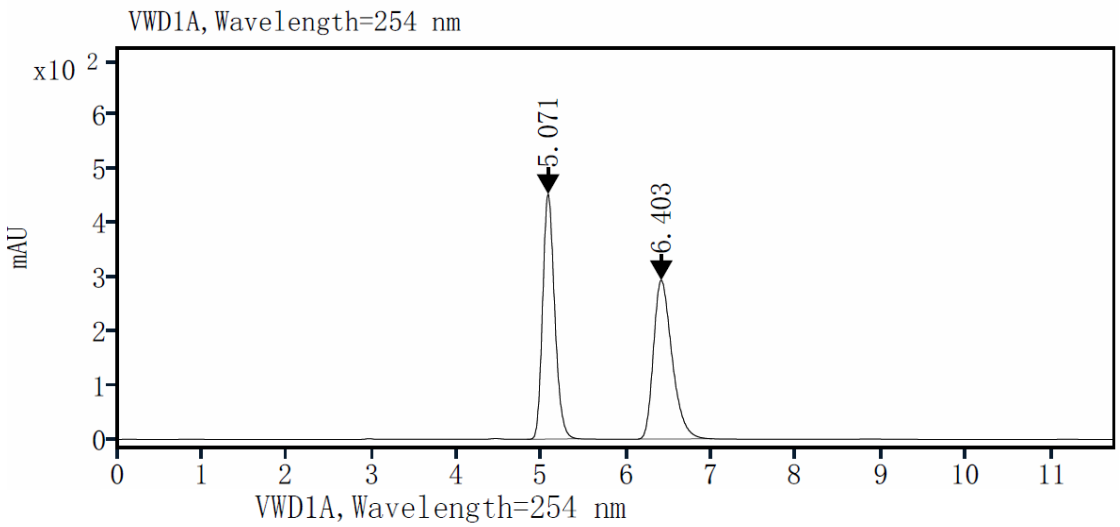


VWD1A,Wavelength=254 nm

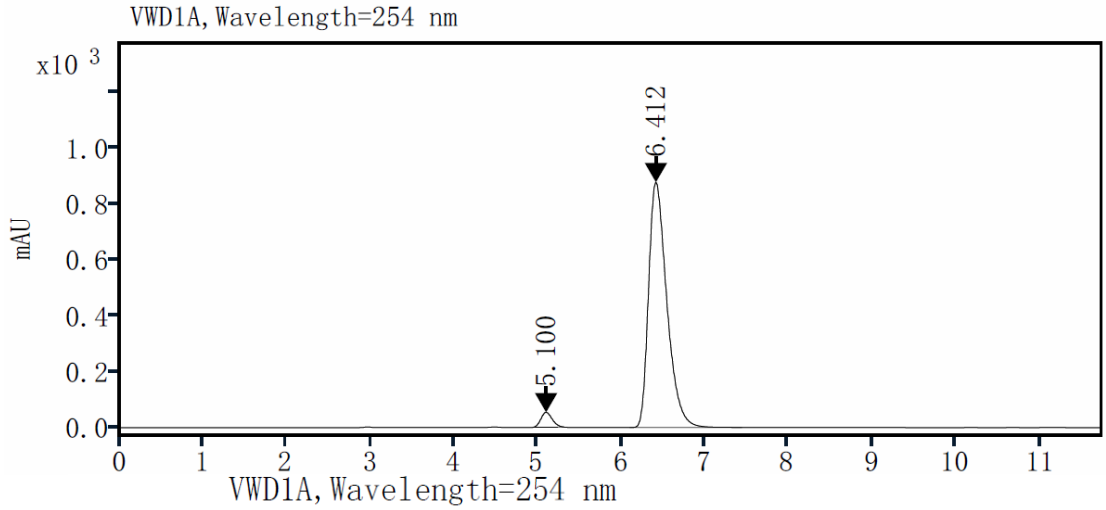
No.	RetTime[min]	Type	Area [mAu*s]	Area%
	3.986	MM m	641.85	6.99
	5.561	MM m	8541.33	93.01



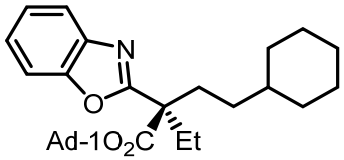
Scheme 2A, entry 3
(*R*,*S*)-**L1**: 93% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.071	MM m	4489.28	50.00
	6.403	MM m	4488.70	50.00

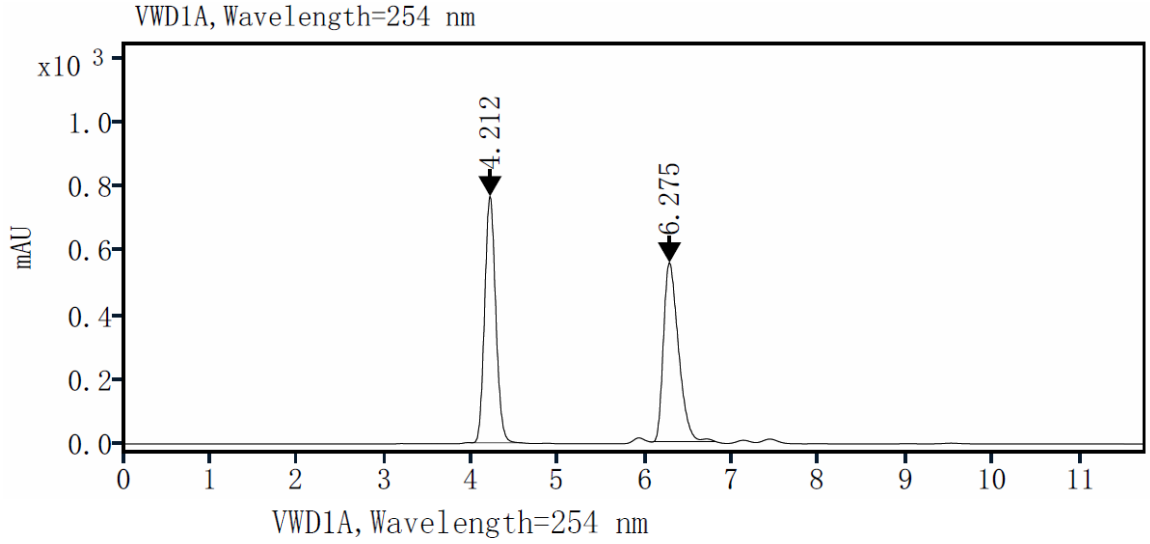


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.100	MM m	494.71	3.59
	6.412	MM m	13281.77	96.41

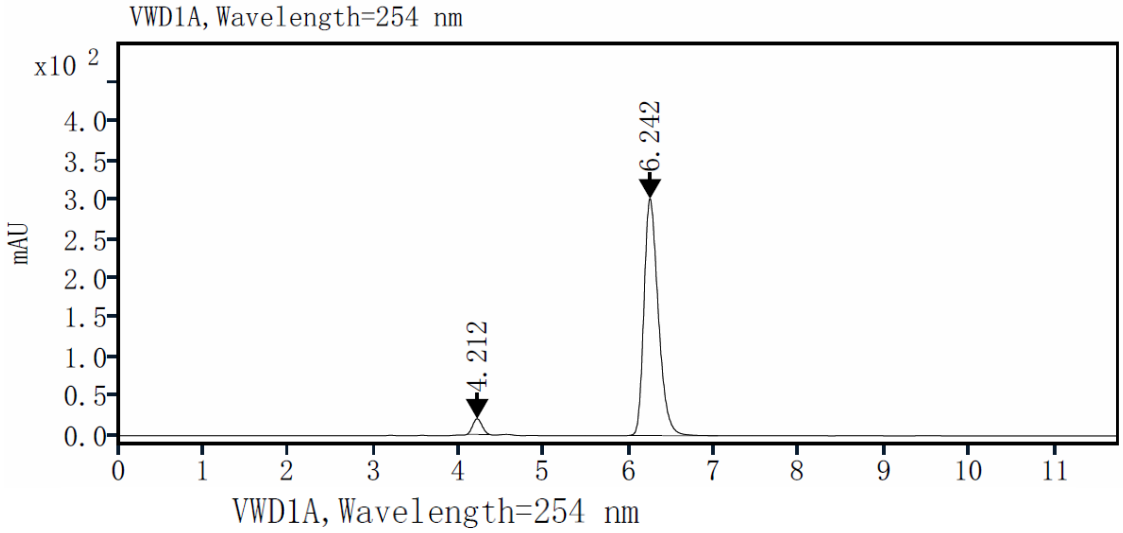


Scheme 2A, entry 4

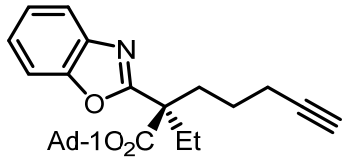
(*R,S*)-**L1**: 92% ee



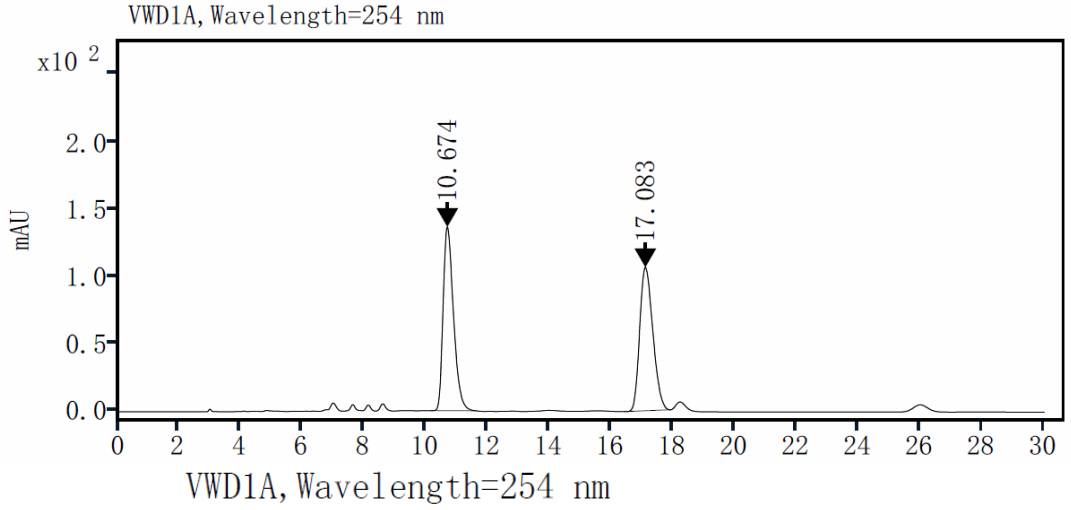
No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.212	MM m	6792.57	50.37
	6.275	MM m	6692.65	49.63



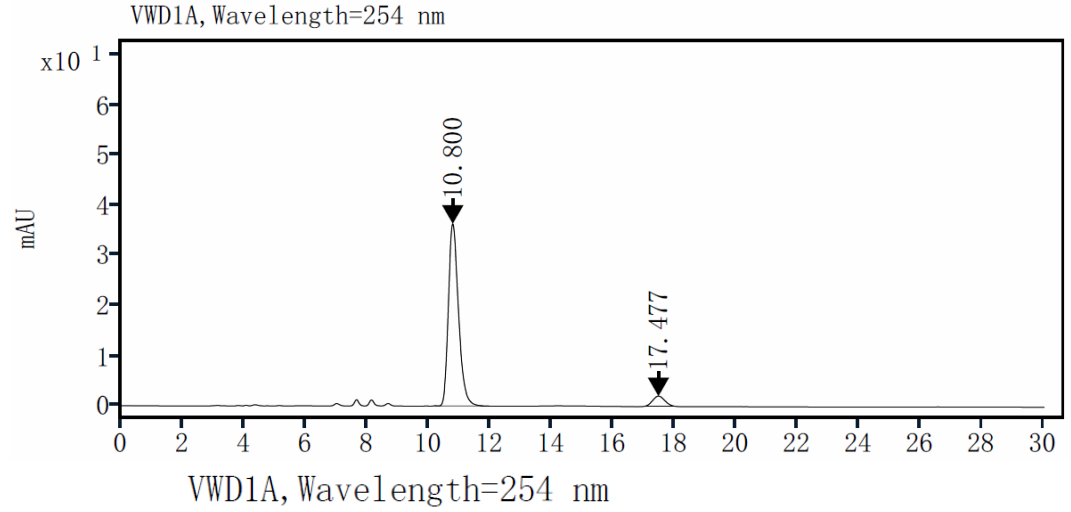
No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.212	MM m	151.40	4.11
	6.242	MM m	3529.78	95.89



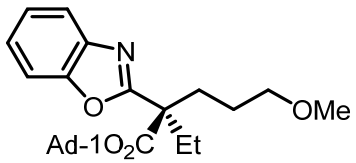
Scheme 2A, entry 5
(*R,S*)-**L1**: 88% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.674	MM m	3179.69	50.33
	17.083	MM m	3138.42	49.67

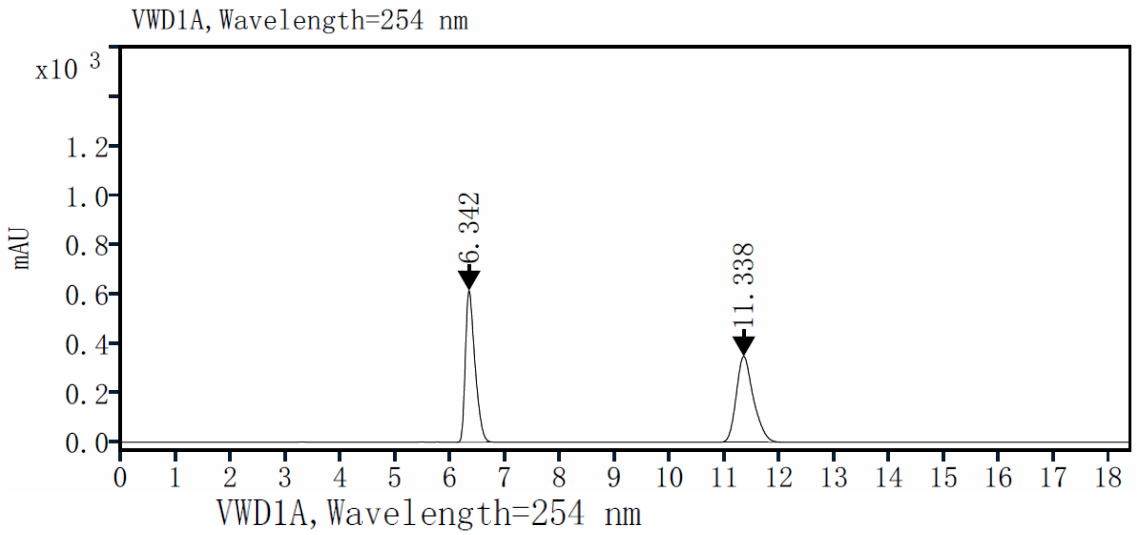


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.800	MM m	830.45	93.88
	17.477	MM m	54.13	6.12

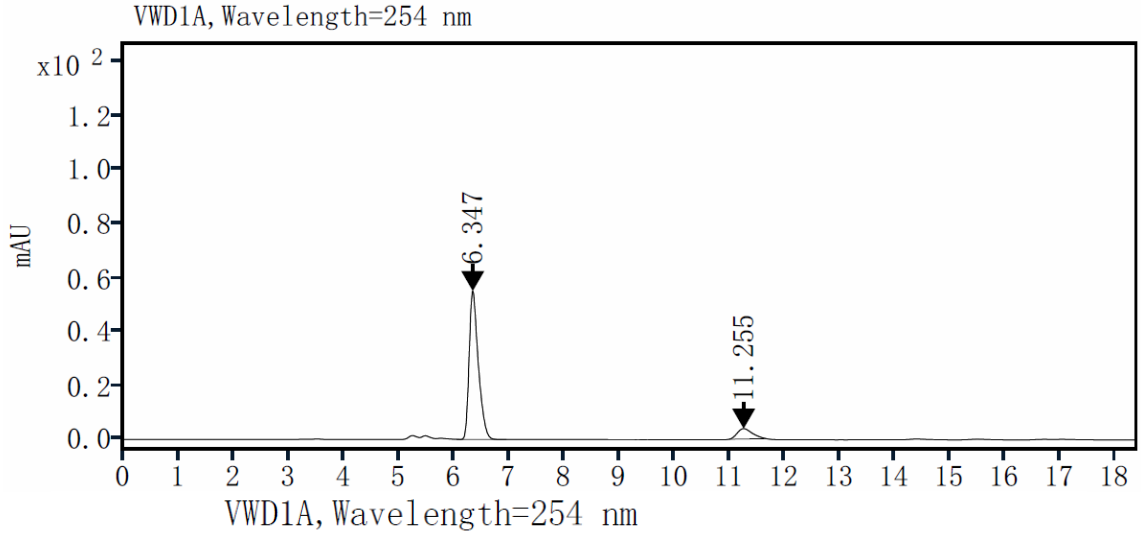


Scheme 2A, entry 6

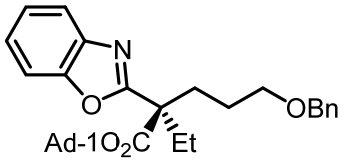
(*R*,*S*)-**L1**: 80% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.342	MM m	7451.91	49.92
	11.338	MM m	7477.07	50.08

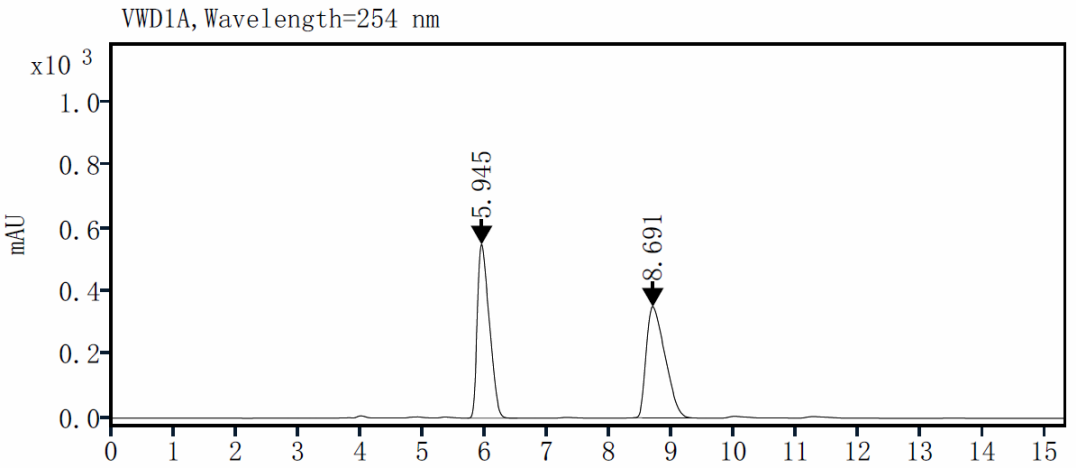


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.347	MM m	635.55	89.76
	11.255	MM m	72.53	10.24



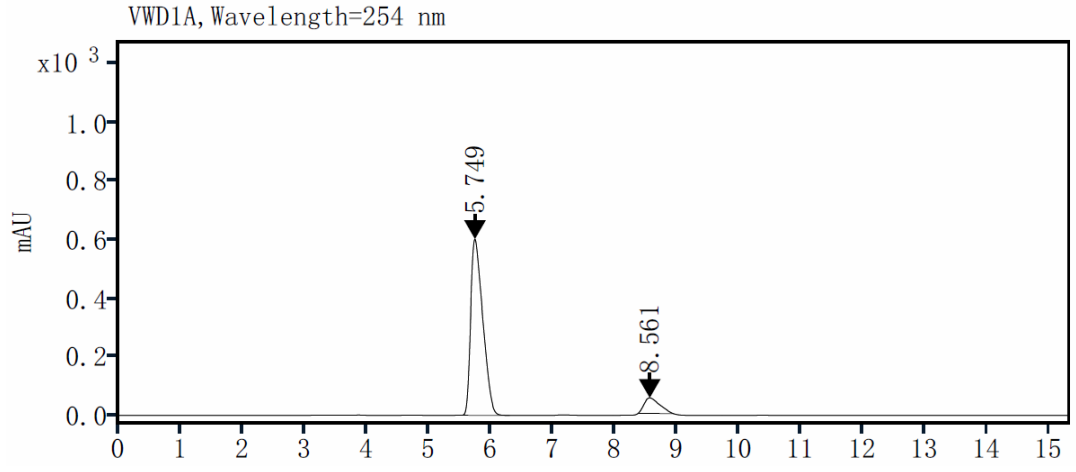
Scheme 2A, entry 7

(*R,S*)-**L1**: 80% ee



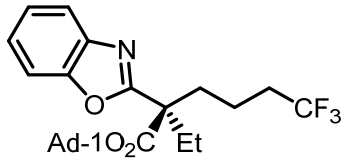
VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.945	MM m	7334.99	49.84
	8.691	MM m	7381.00	50.16



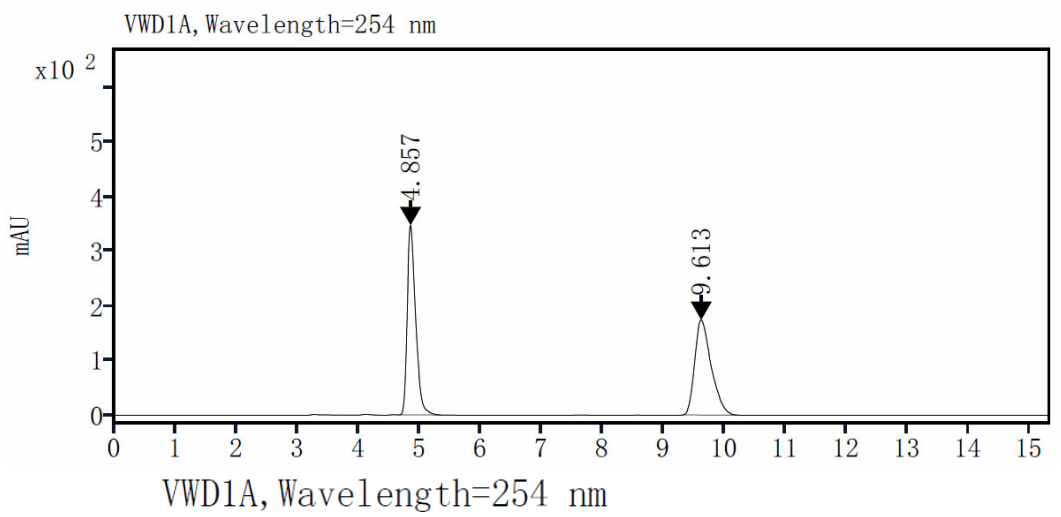
VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.749	MM m	8132.95	89.81
	8.561	MM m	922.90	10.19

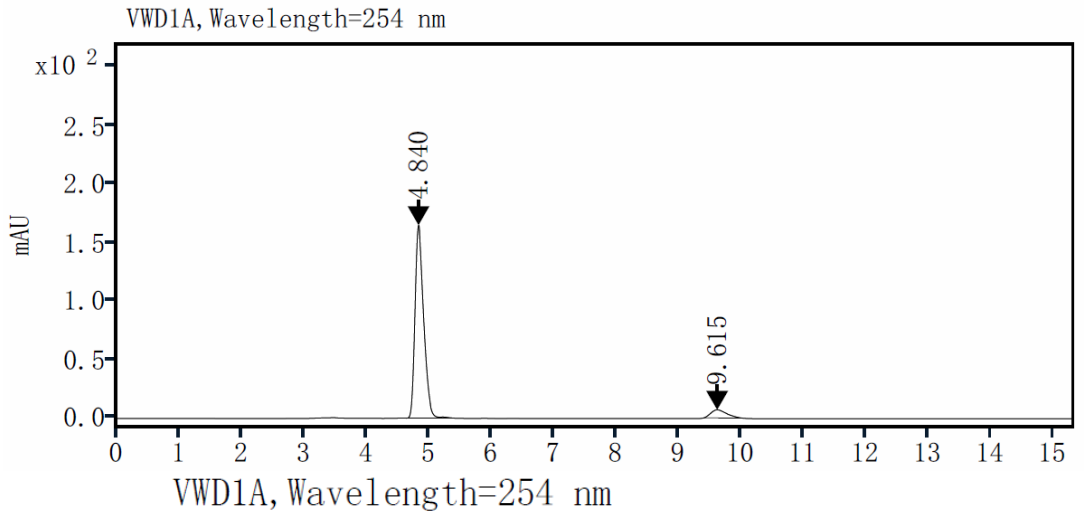


Scheme 2A, entry 8

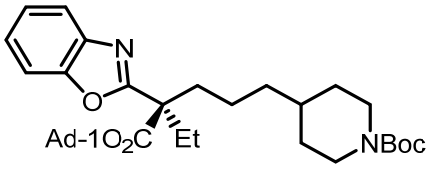
(*R,S*)-**L1**: 86% ee



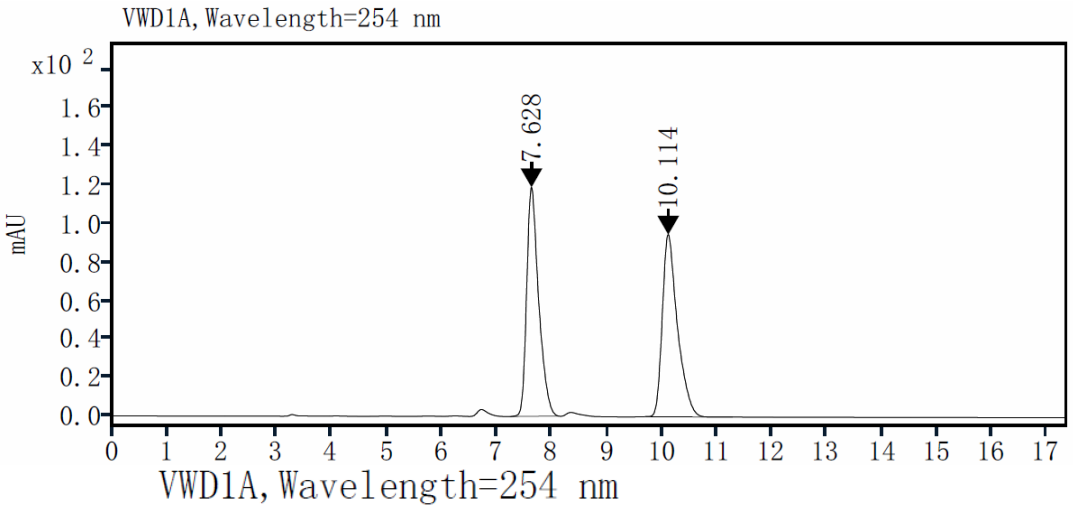
No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.857	MM m	3316.74	50.42
	9.613	MM m	3261.41	49.58



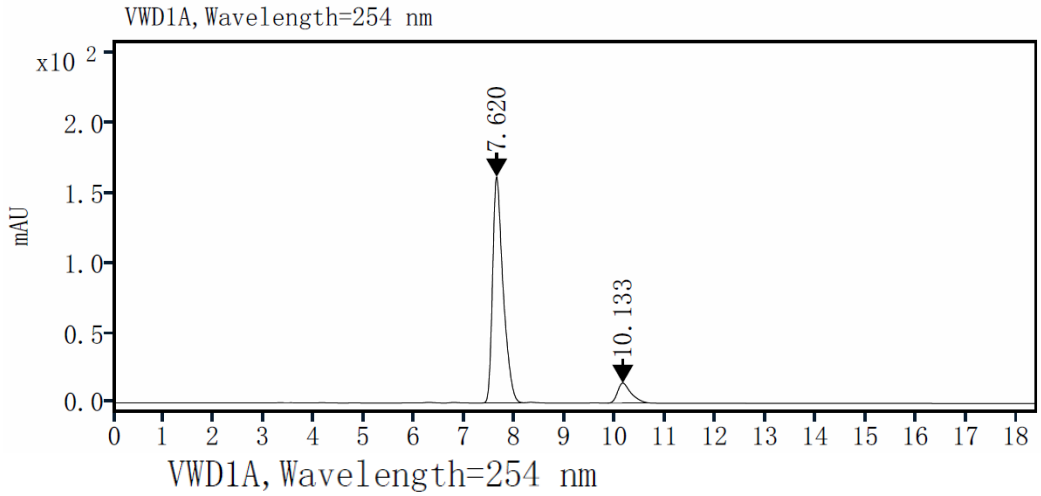
No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.840	MM m	1582.17	92.88
	9.615	MM m	121.28	7.12



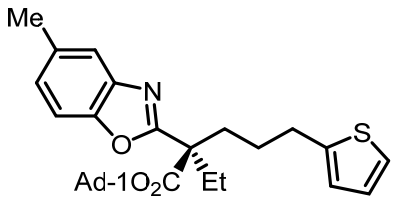
Scheme 2A, entry 9
(*R,S*)-**L1**: 80% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.628	MM m	1801.92	49.92
	10.114	MM m	1807.56	50.08

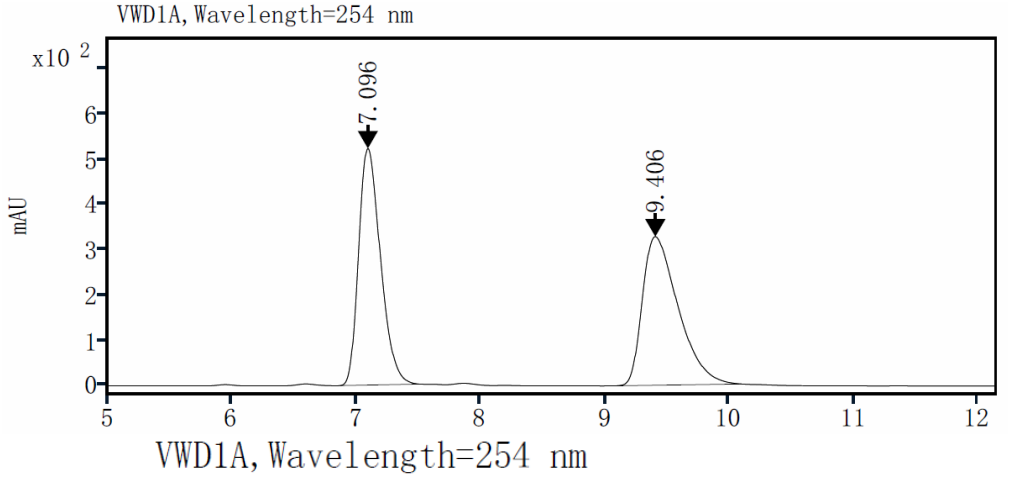


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.620	MM m	2362.06	89.99
	10.133	MM m	262.79	10.01



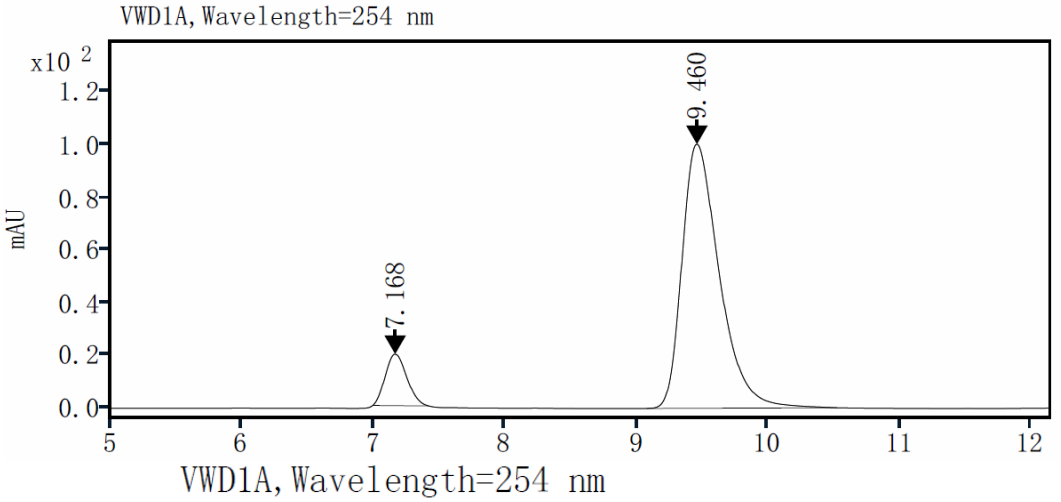
Scheme 2A, entry 10

(*R,S*)-**L1**: 80% ee



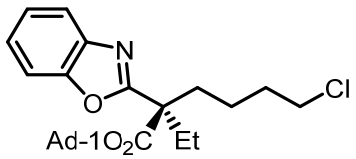
VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.096	MM m	6395.40	49.38
	9.406	MM m	6556.50	50.62

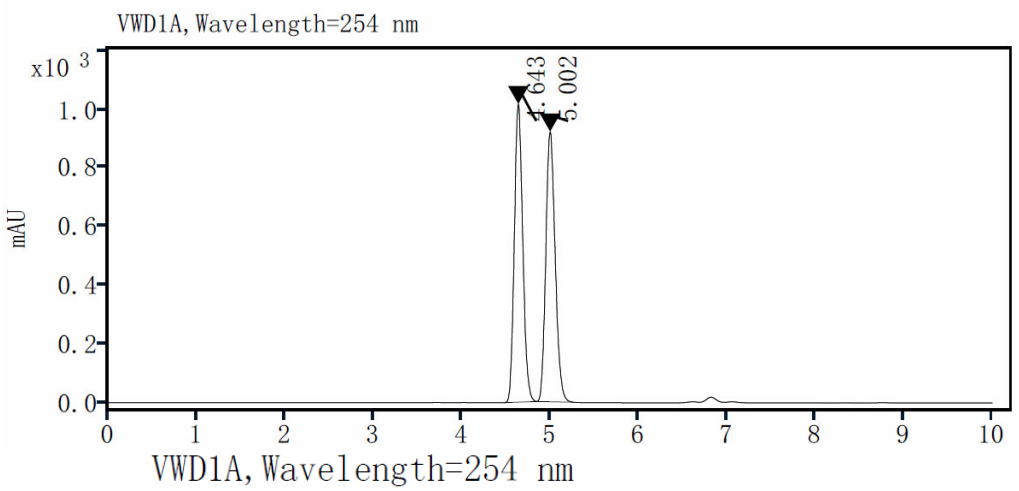


VWD1A, Wavelength=254 nm

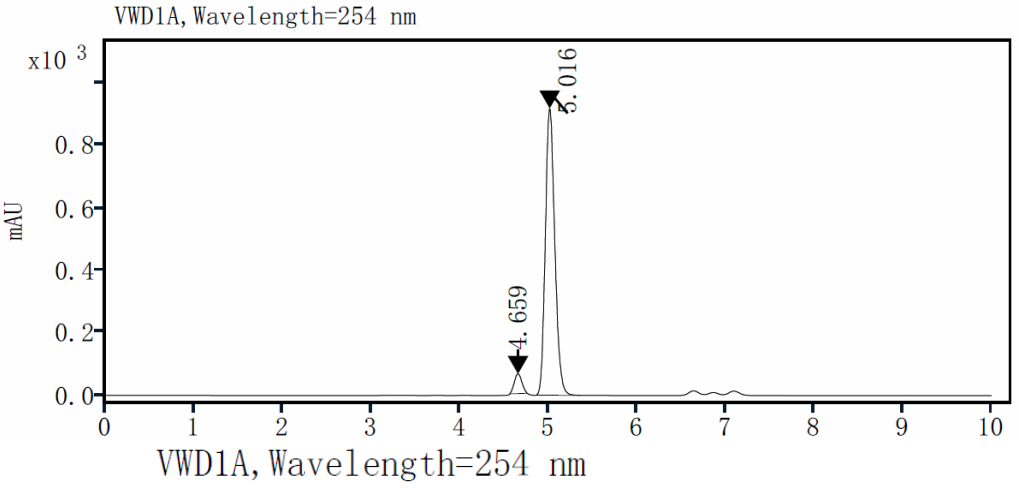
No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.168	MM m	221.68	10.07
	9.460	MM m	1979.58	89.93



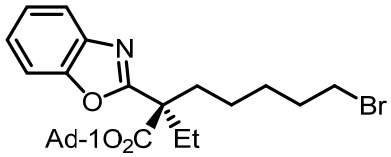
Scheme 2A, entry 11
(*R,S*)-**L1**: 90% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.643	MM m	6759.27	49.96
	5.002	MM m	6768.81	50.04

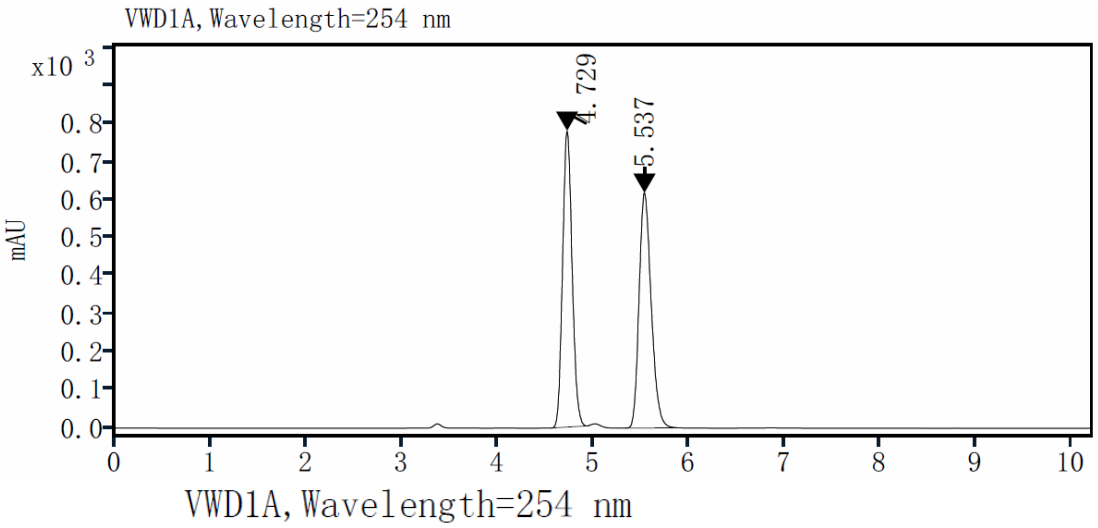


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.659	MM m	373.44	5.20
	5.016	MM m	6807.76	94.80



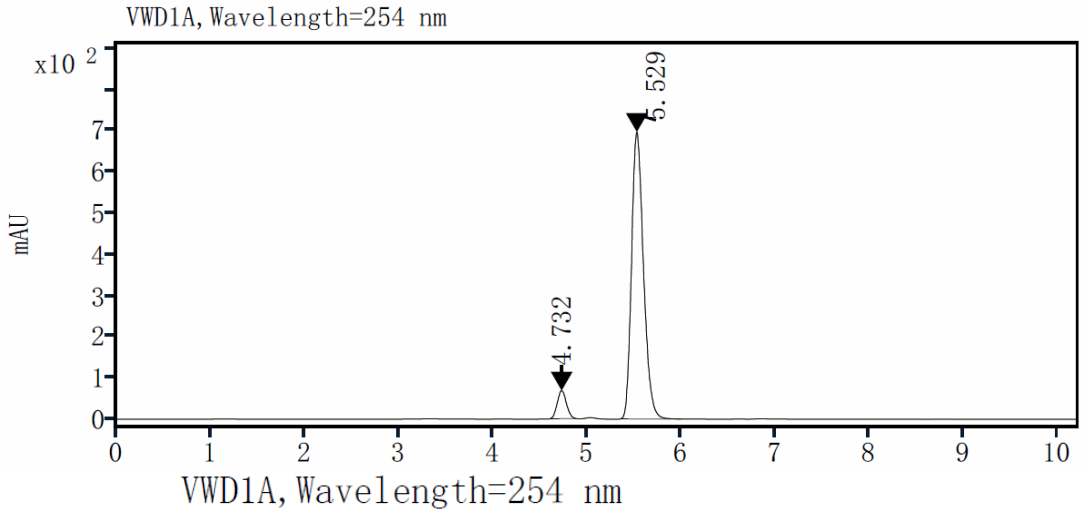
Scheme 2A, entry 12

(R,S)-**L1**: 86% ee



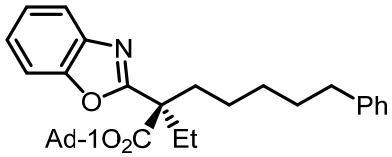
VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.729	MM m	5376.08	49.75
	5.537	MM m	5429.56	50.25



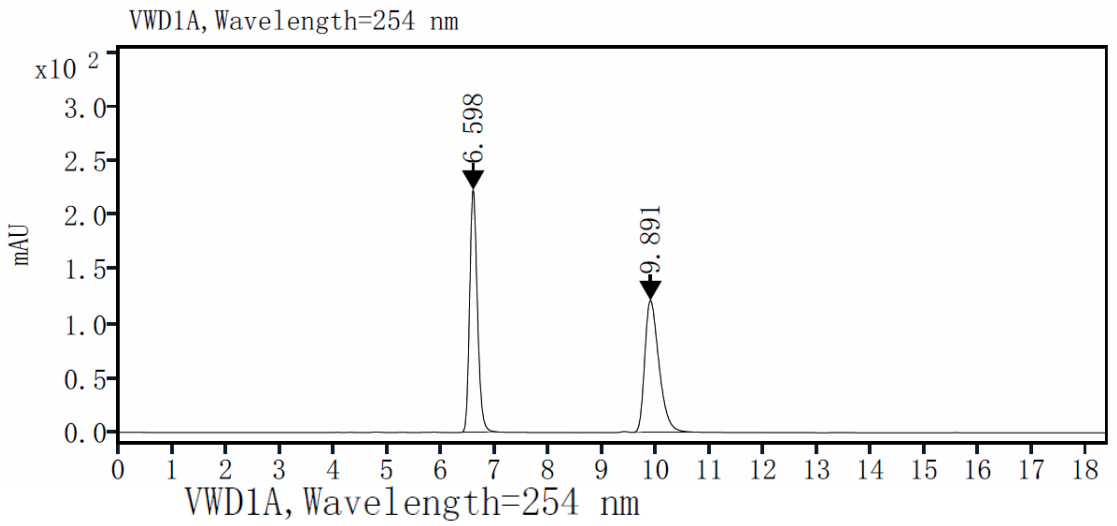
VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.732	MM m	457.92	6.93
	5.529	MM m	6151.32	93.07

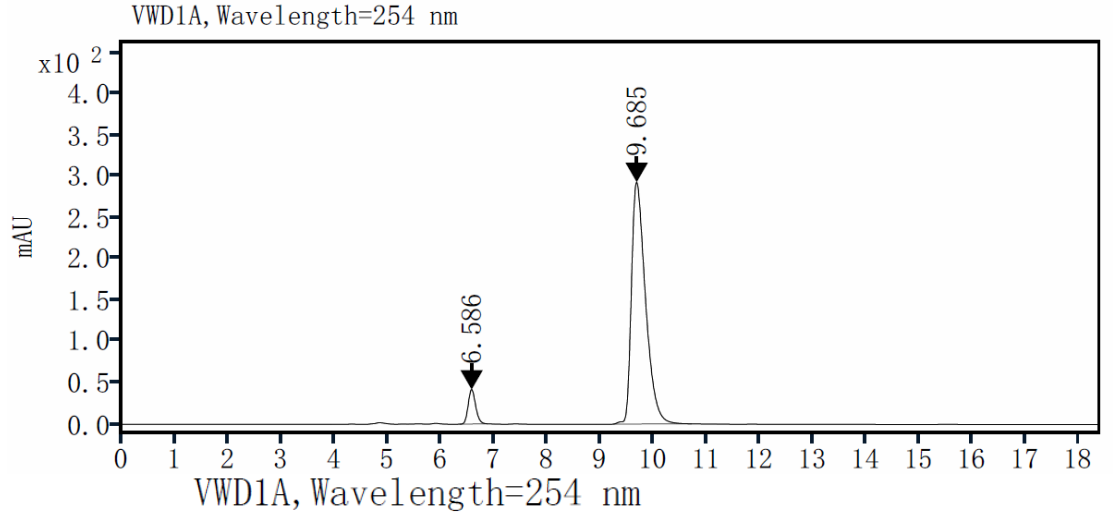


Scheme 2A, entry 13

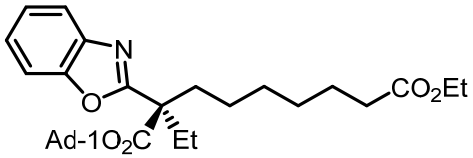
(*R,S*)-**L1**: 86% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.598	MM m	2233.84	50.14
	9.891	MM m	2221.51	49.86

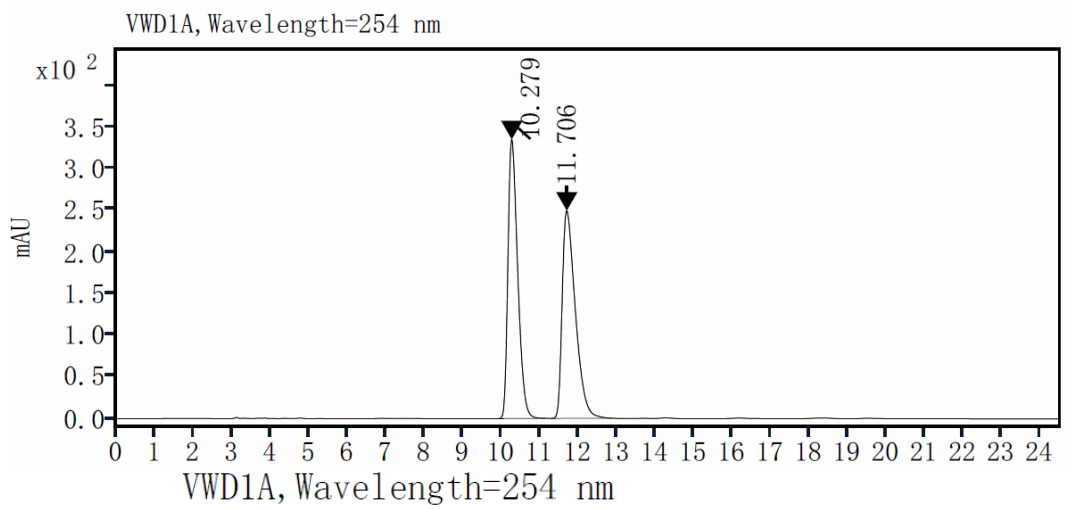


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.586	MM m	406.99	7.02
	9.685	MM m	5394.11	92.98

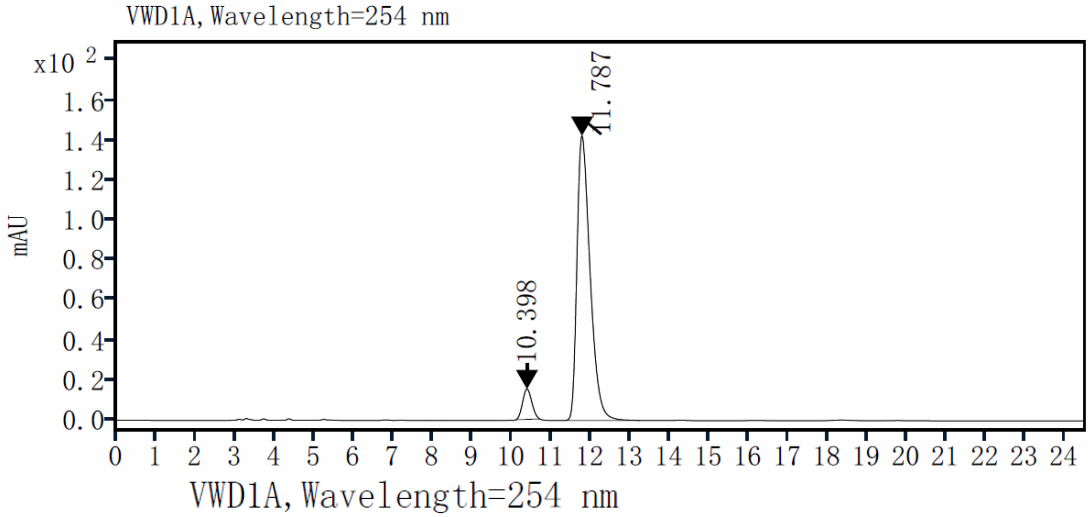


Scheme 2A, entry 14

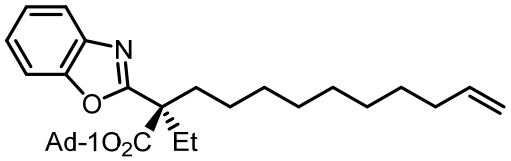
(*R,S*)-**L1**: 86% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.279	MM m	5885.59	50.02
	11.706	MM m	5881.25	49.98

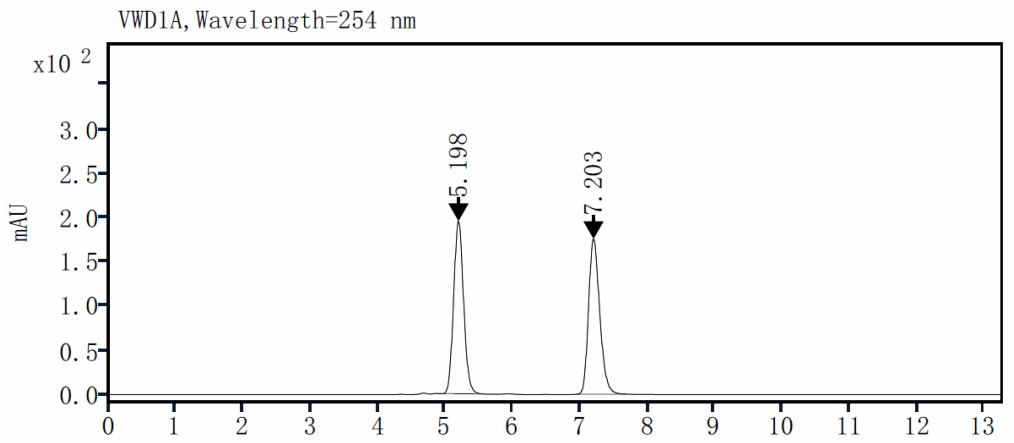


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.398	MM m	245.64	7.01
	11.787	MM m	3258.95	92.99



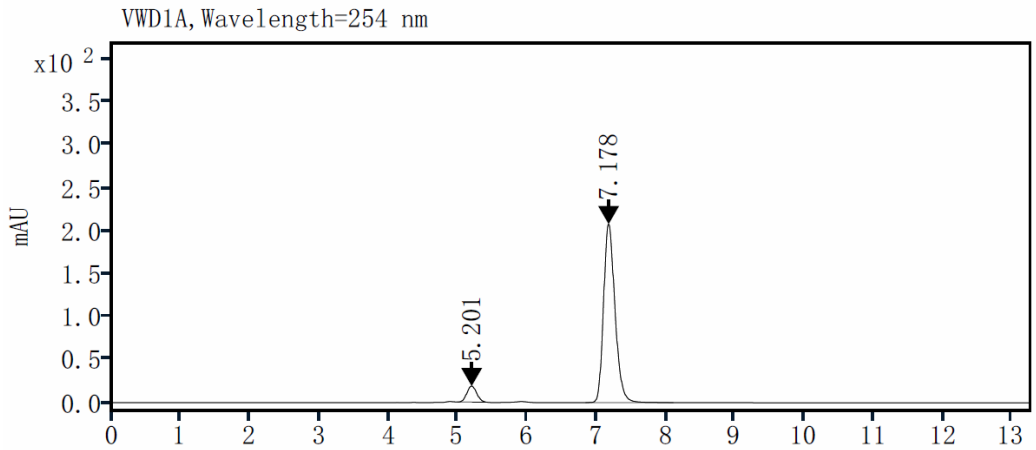
Scheme 2A, entry 15

(*R,S*)-**L1**: 86% ee



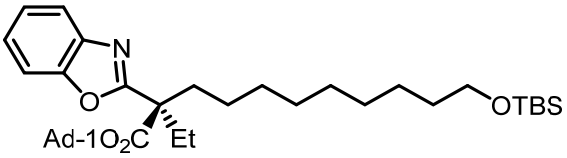
VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.198	MM m	2006.37	49.79
	7.203	MM m	2023.61	50.21



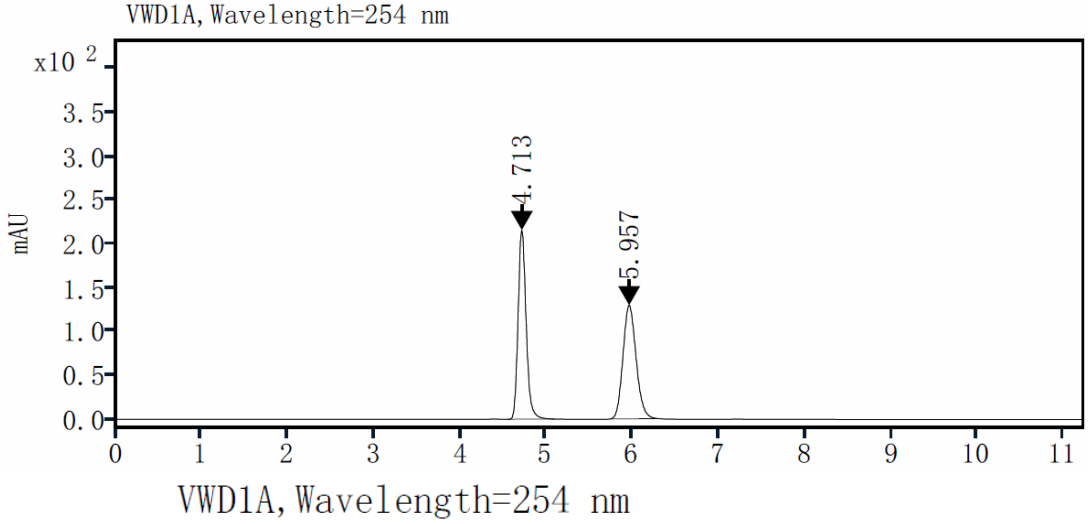
VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.201	MM m	183.07	7.08
	7.178	MM m	2401.06	92.92

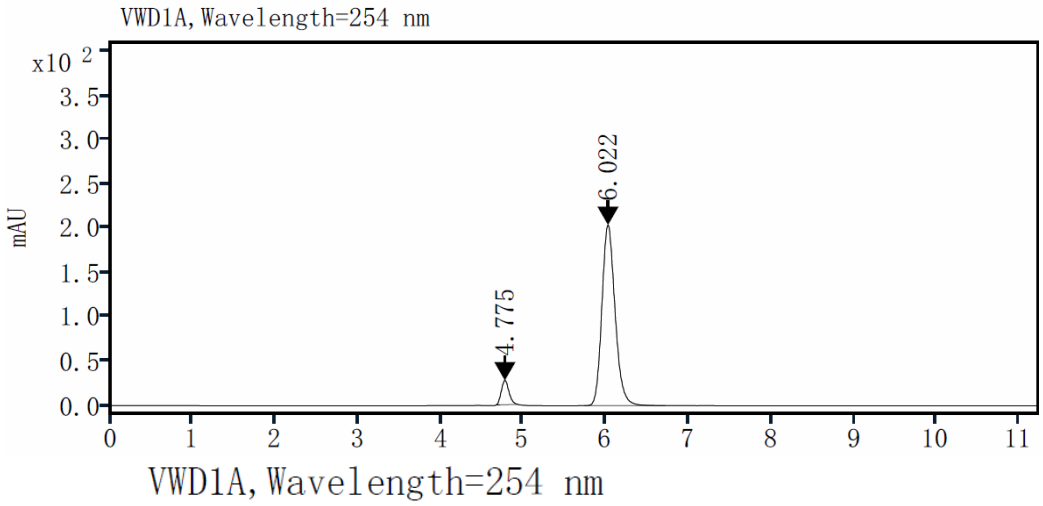


Scheme 2A, entry 16

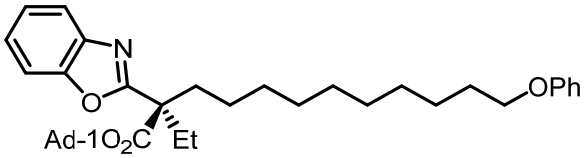
(*R,S*)-**L1**: 86% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.713	MM m	1396.14	50.47
	5.957	MM m	1370.35	49.53

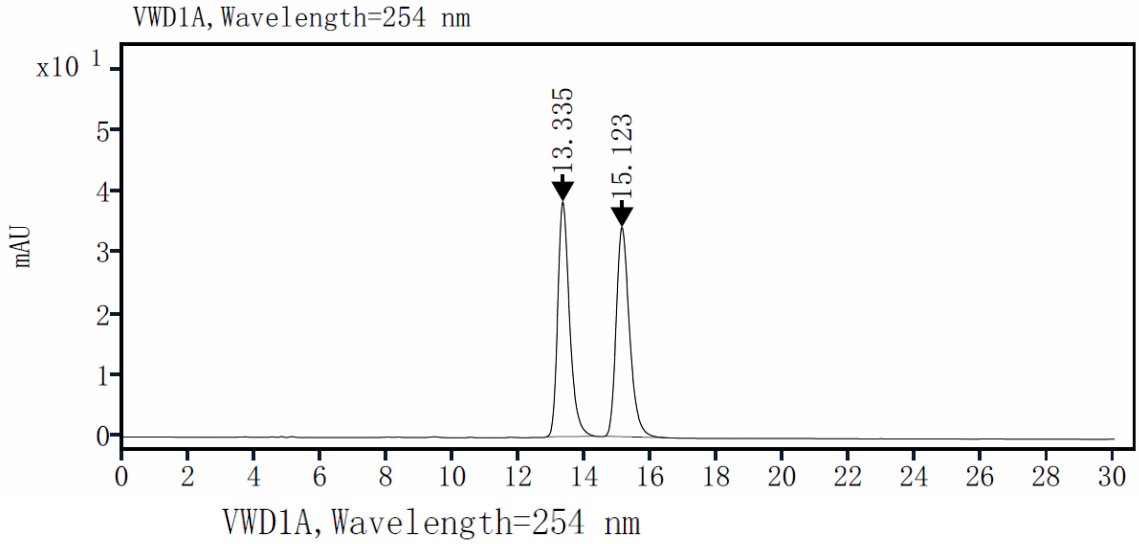


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.775	MM m	174.40	7.16
	6.022	MM m	2262.84	92.84

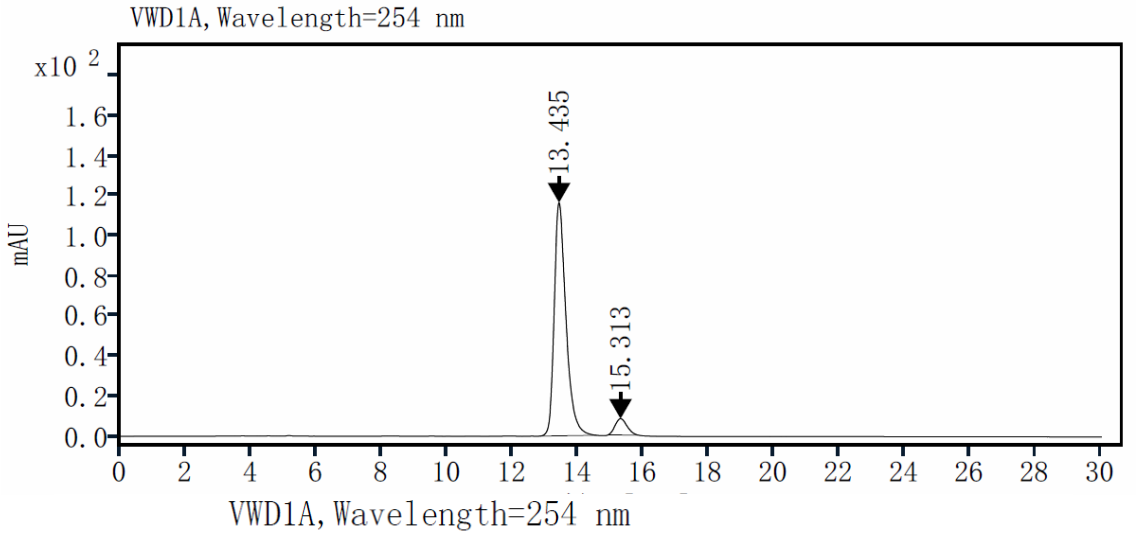


Scheme 2A, entry 17

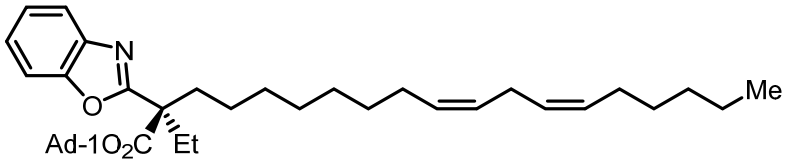
(*R,S*)-**L1**: 87% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	13.335	MM m	947.47	49.77
	15.123	MM m	956.26	50.23

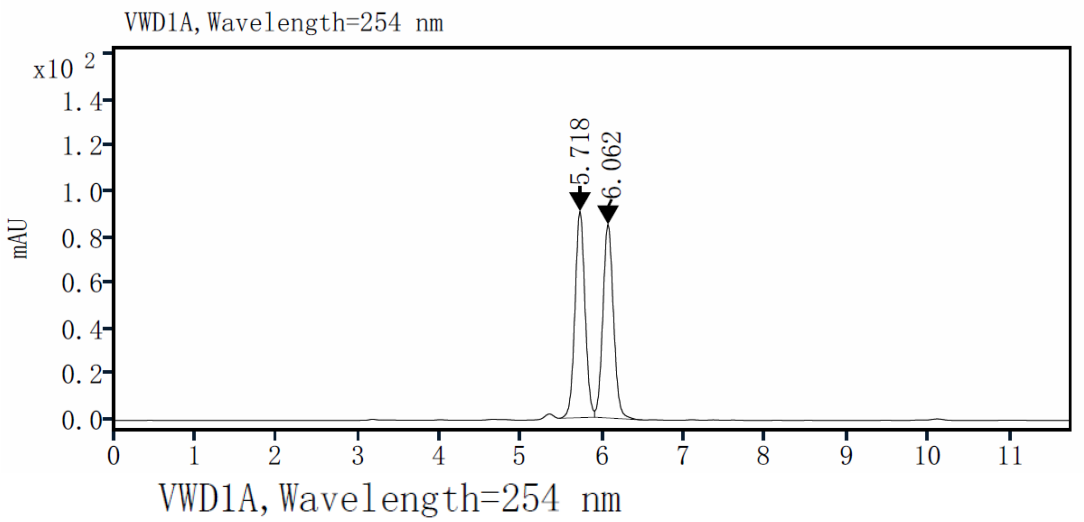


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	13.435	MM m	2913.96	93.42
	15.313	MM m	205.24	6.58

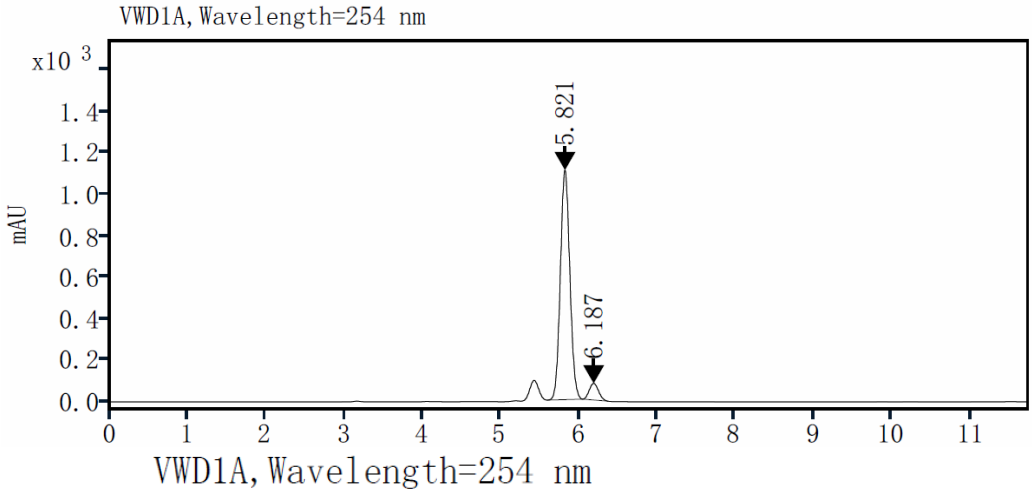


Scheme 2A, entry 18

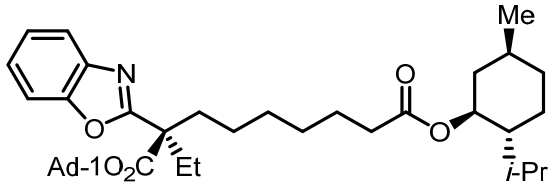
(*R,S*)-**L1**: 87% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.718	MM m	772.54	50.24
	6.062	MM m	765.04	49.76



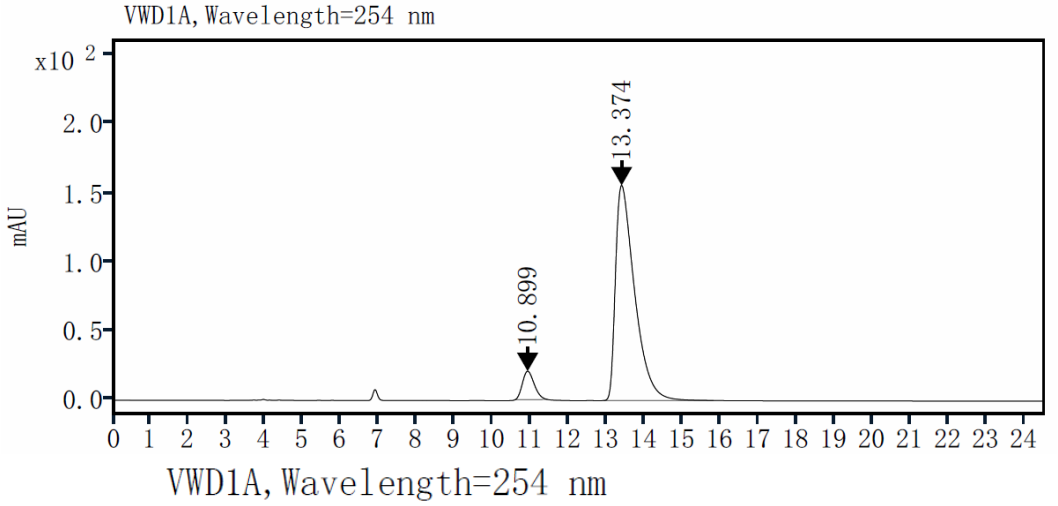
No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.821	MM m	9359.04	93.41
	6.187	MM m	660.02	6.59



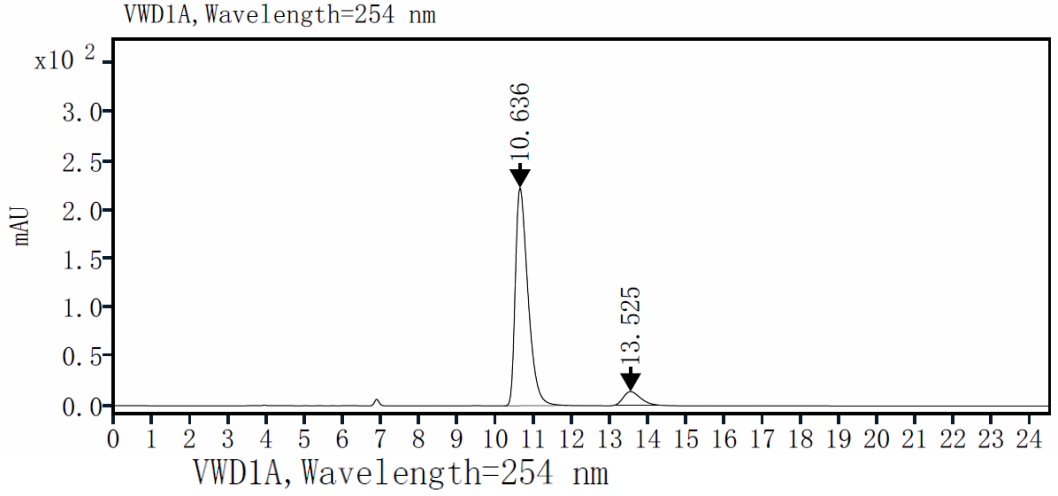
Scheme 2A, entries 19 and 20

(*R*,*S*)-**L1**: 92.5:7.5 dr

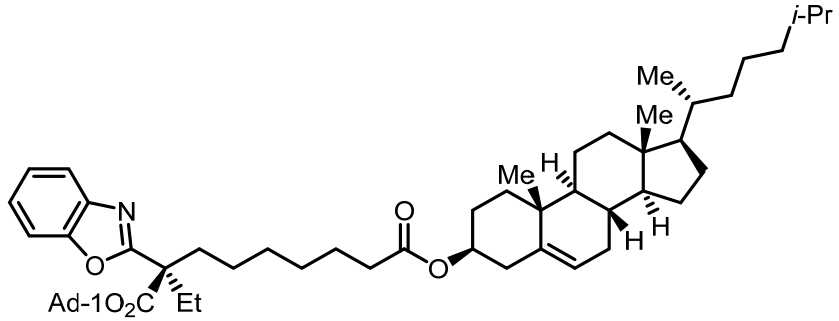
(*S*,*R*)-**L1**: 7.5:92.5 dr



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.899	MM m	442.85	7.51
	13.374	MM m	5454.71	92.49



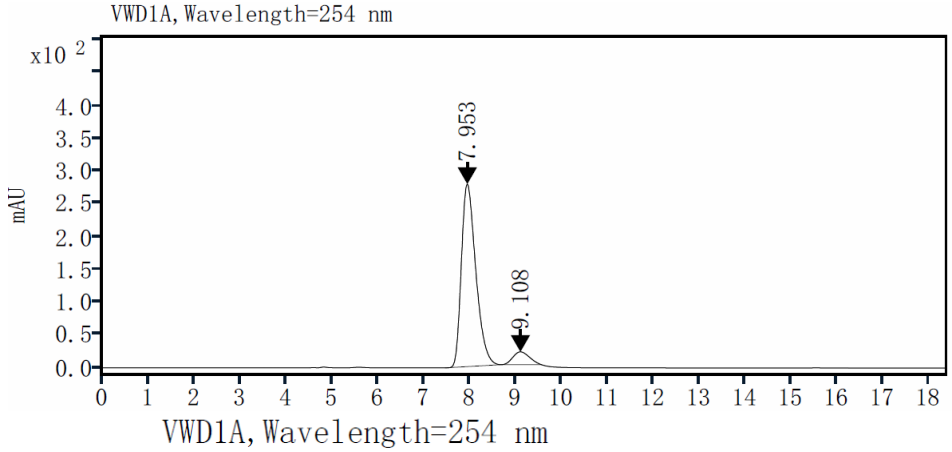
No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.636	MM m	5134.53	92.41
	13.525	MM m	421.80	7.59



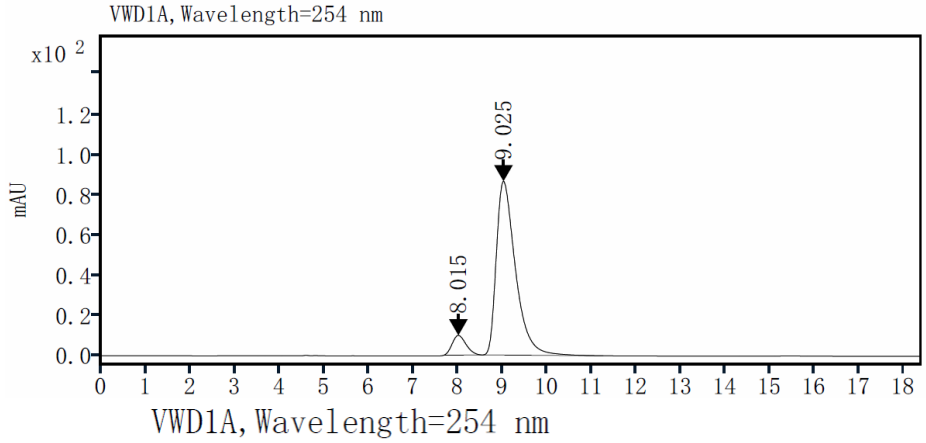
Scheme 2A, entries 21 and 22

(*R*,*S*)-**L1**: 92.5:7.5 dr

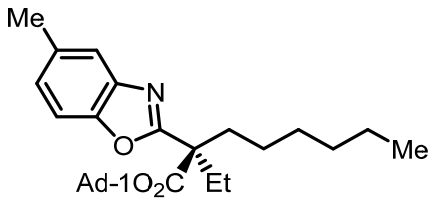
(*S*,*R*)-**L1**: 7.5:92.5 dr



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.953	MM m	6066.10	92.56
	9.108	MM m	487.81	7.44

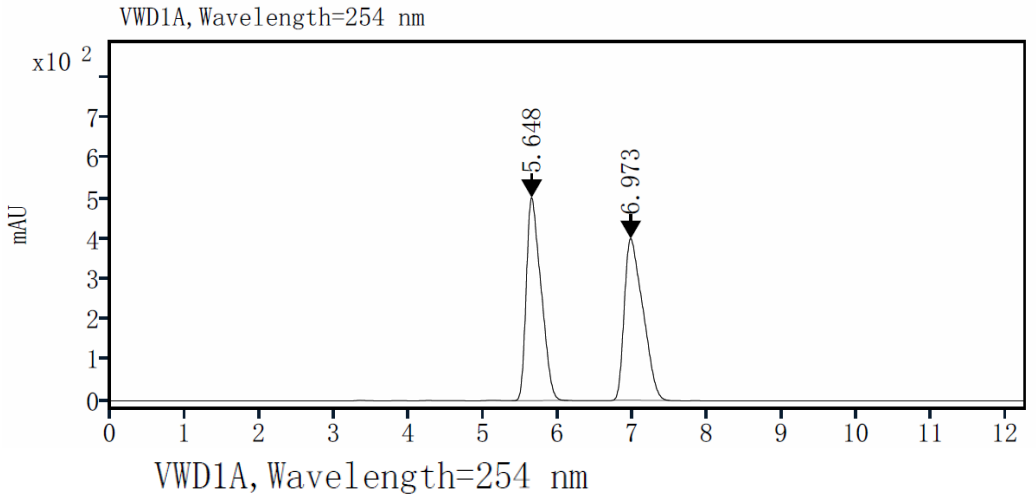


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	8.015	MM m	210.71	7.56
	9.025	MM m	2576.20	92.44



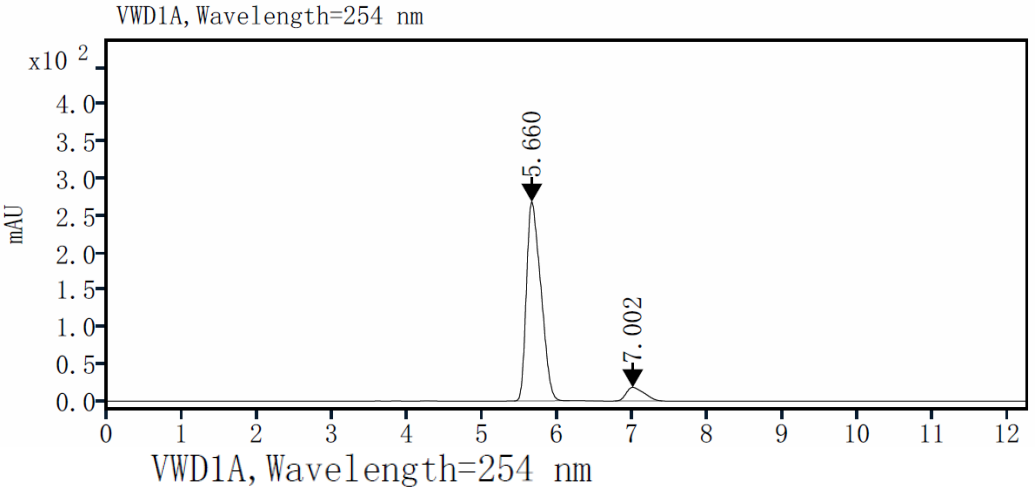
Scheme 2B, entry 23

(*R*,*S*)-**L1**: 85% ee



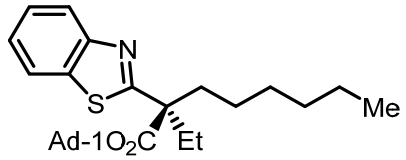
VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.648	MM m	6839.62	49.81
	6.973	MM m	6891.25	50.19



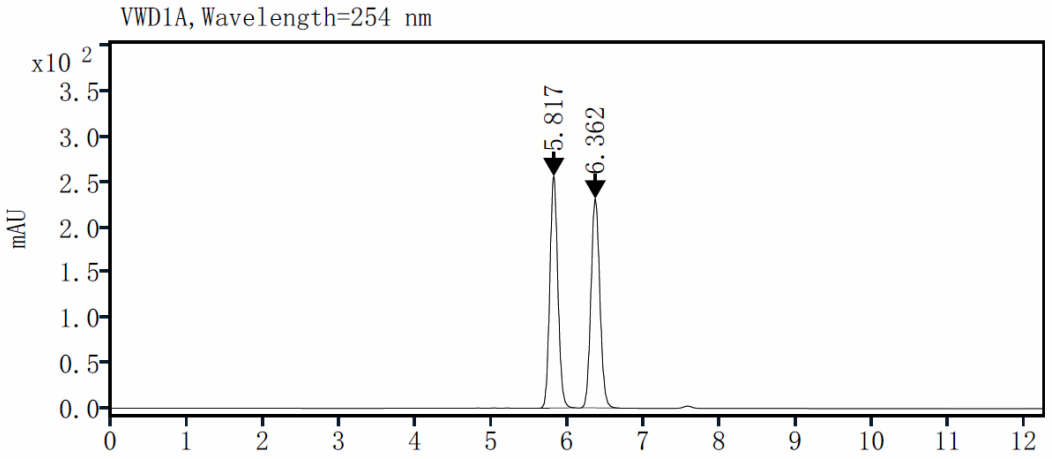
VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.660	MM m	3586.77	92.25
	7.002	MM m	301.50	7.75

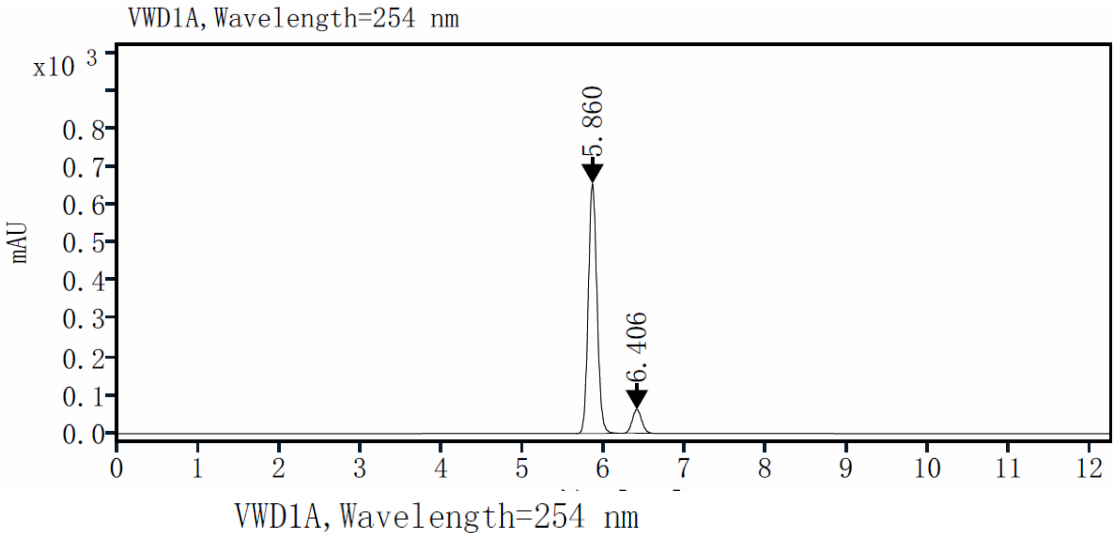


Scheme 2B, entry 24

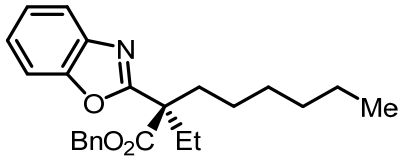
(*R,S*)-**L1**: 82% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.817	MM m	1878.57	50.06
	6.362	MM m	1873.81	49.94

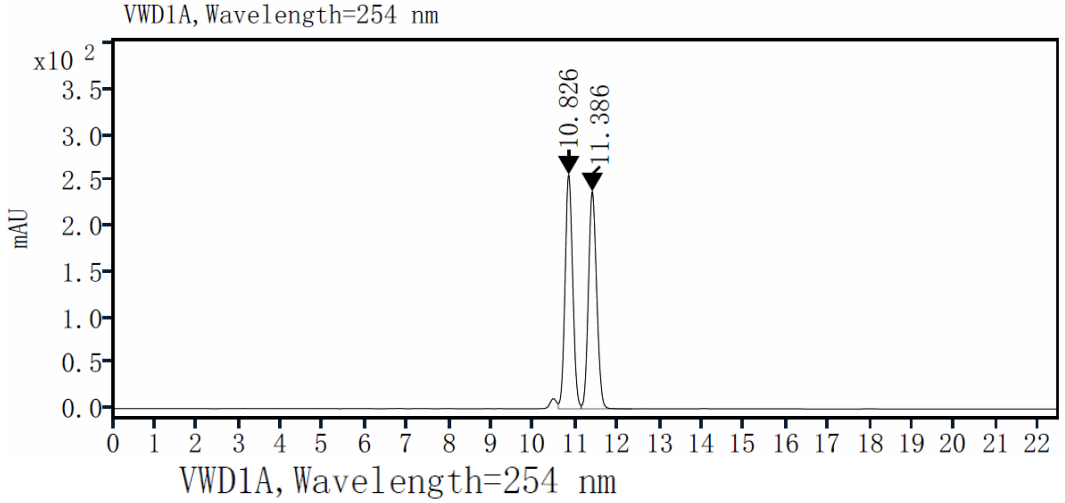


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.860	MM m	4857.48	90.76
	6.406	MM m	494.81	9.24

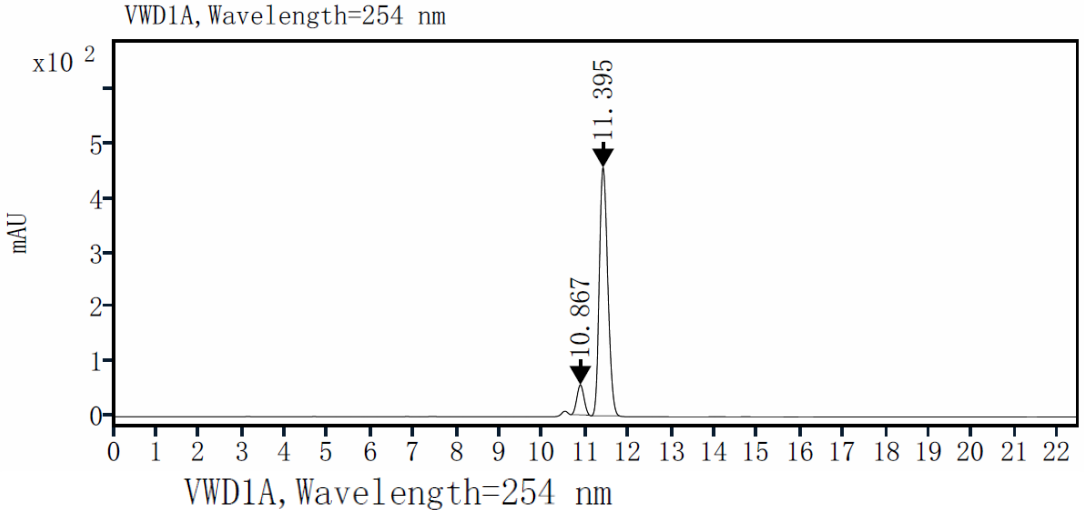


Scheme 2B, entry 25

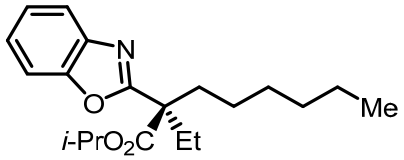
(*R*,*S*)-**L1**: 82% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.826	VV	3251.32	50.03
	11.386	VB	3247.47	49.97

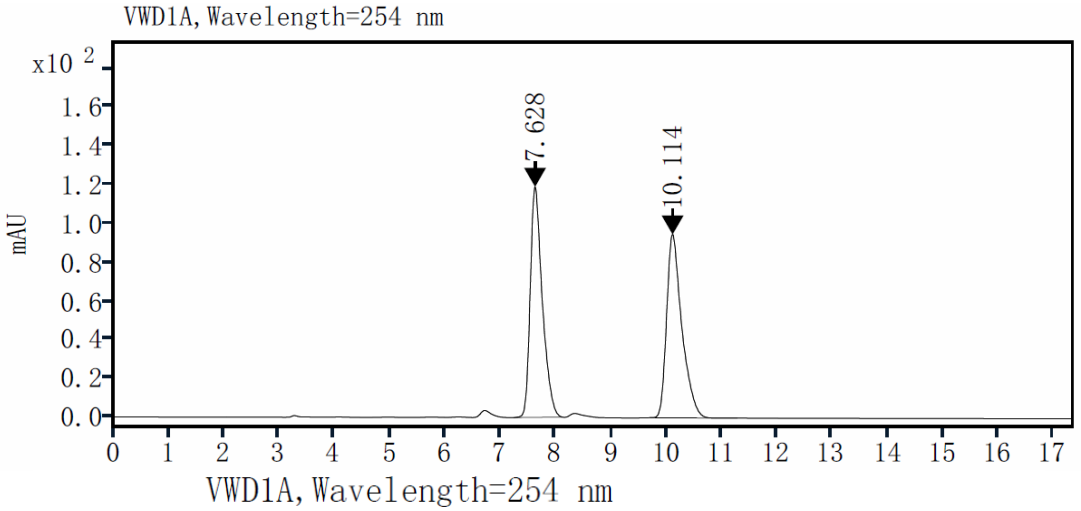


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.867	MM m	632.47	9.24
	11.395	MM m	6210.77	90.76

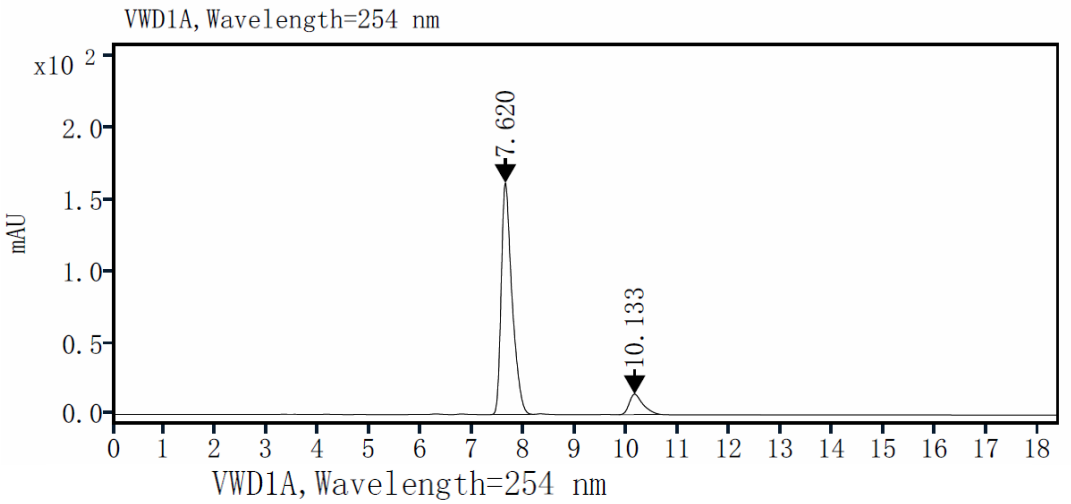


Scheme 2B, entry 26

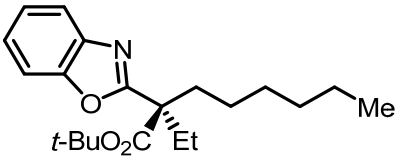
(*R,S*)-**L1**: 80% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.628	MM m	1801.92	49.92
	10.114	MM m	1807.56	50.08

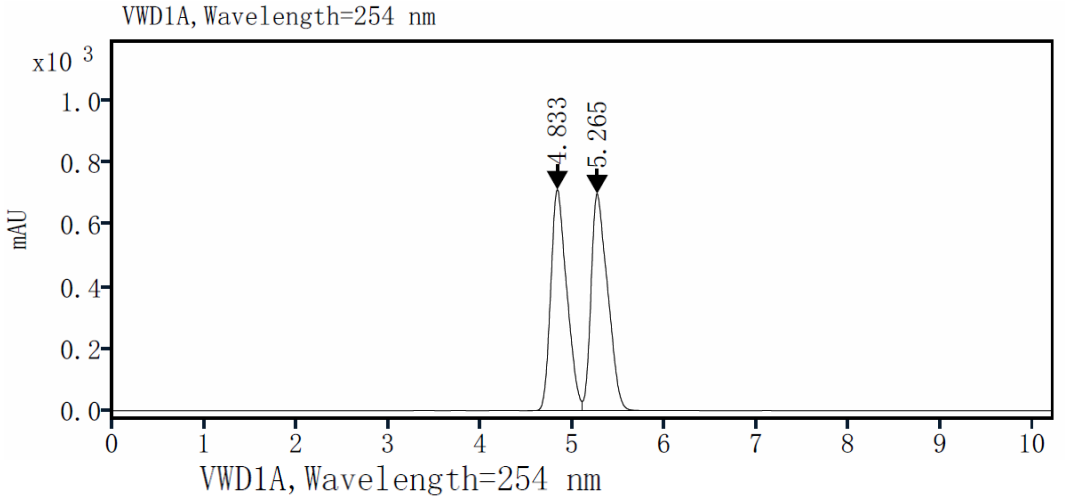


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	7.620	MM m	2362.06	89.99
	10.133	MM m	262.79	10.01

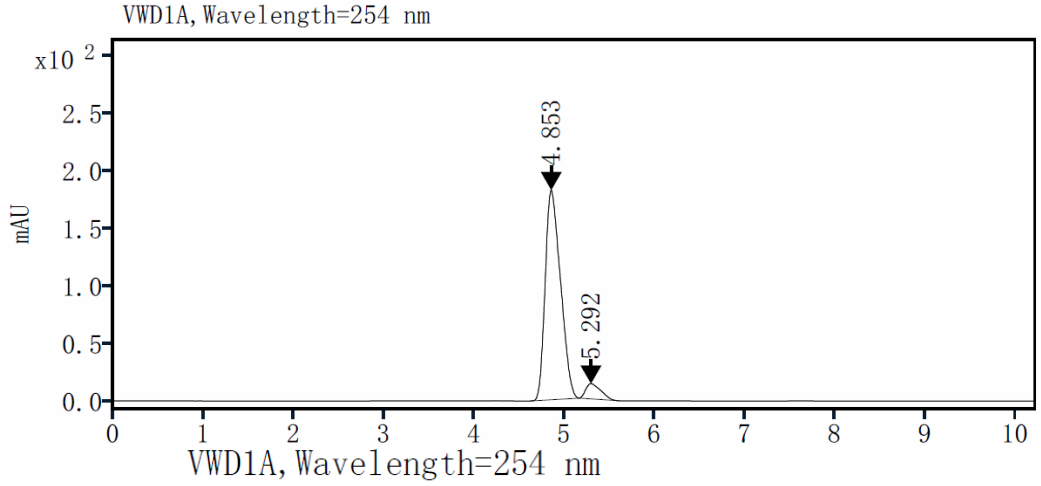


Scheme 2B, entry 27

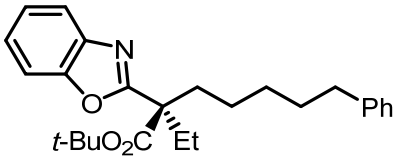
(*R*,*S*)-**L1**: 87% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.833	BV	8669.42	49.69
	5.265	VV	8776.96	50.31

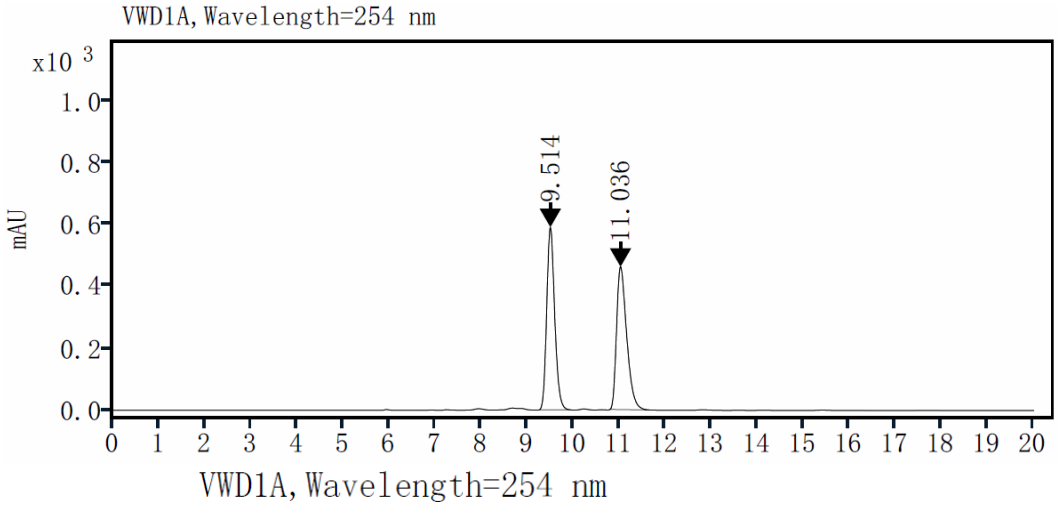


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.853	MM m	2144.11	93.32
	5.292	MM m	153.55	6.68

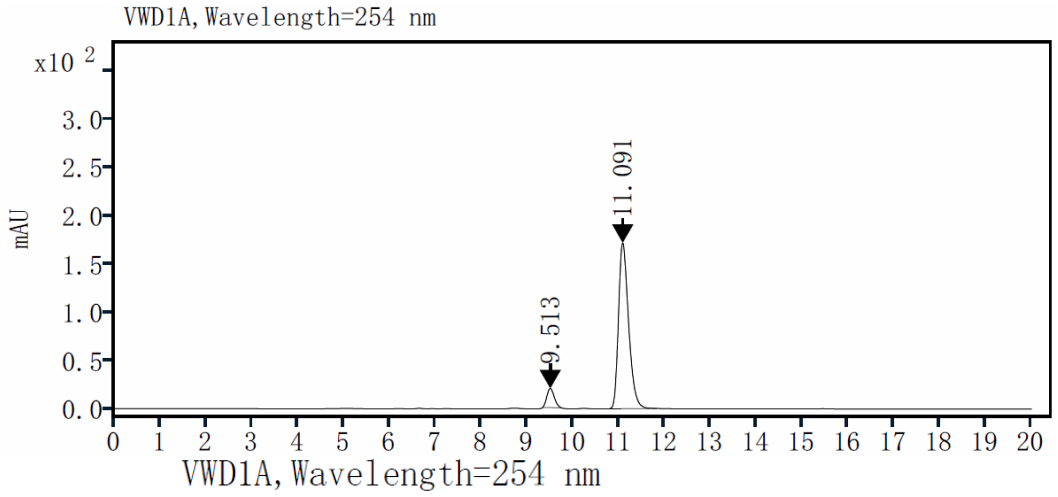


Scheme 2B, entry 28

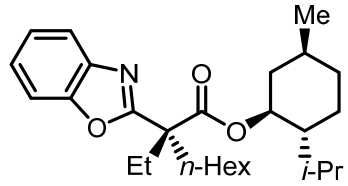
(*R*,*S*)-**L1**: 85% ee



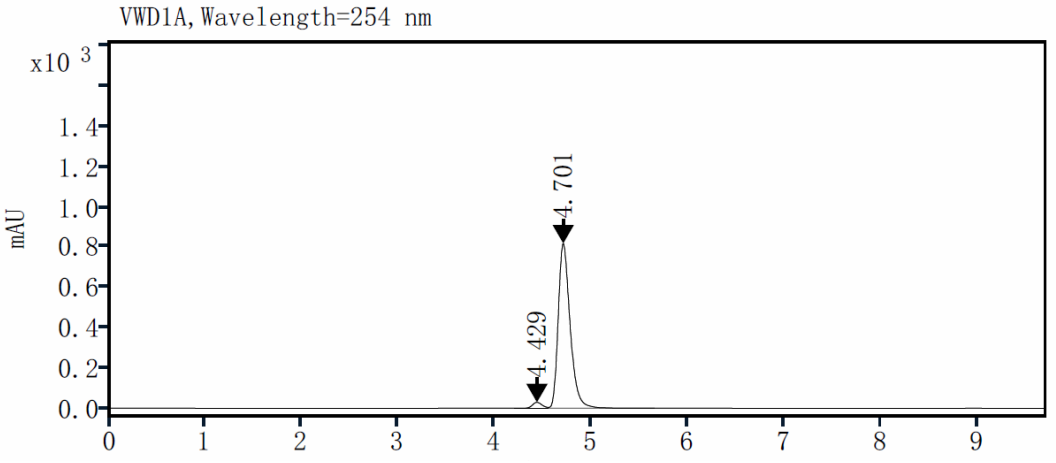
No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.514	MM m	7104.10	50.21
	11.036	MM m	7044.37	49.79



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	9.513	MM m	221.35	7.76
	11.091	MM m	2630.08	92.24

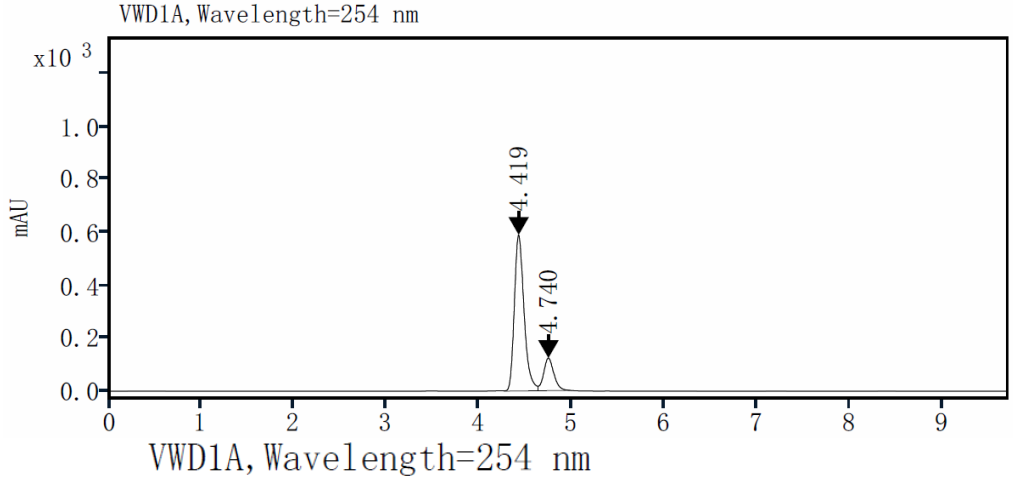


Scheme 2B, entries 29 and 30
(*R,S*)-**L1**: 3:97 dr
(*S,R*)-**L1**: 82:18 dr



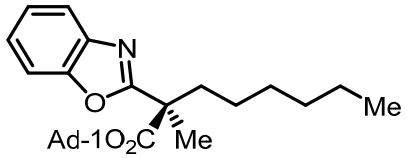
VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.429	VV	206.82	2.85
	4.701	VB	7041.07	97.15



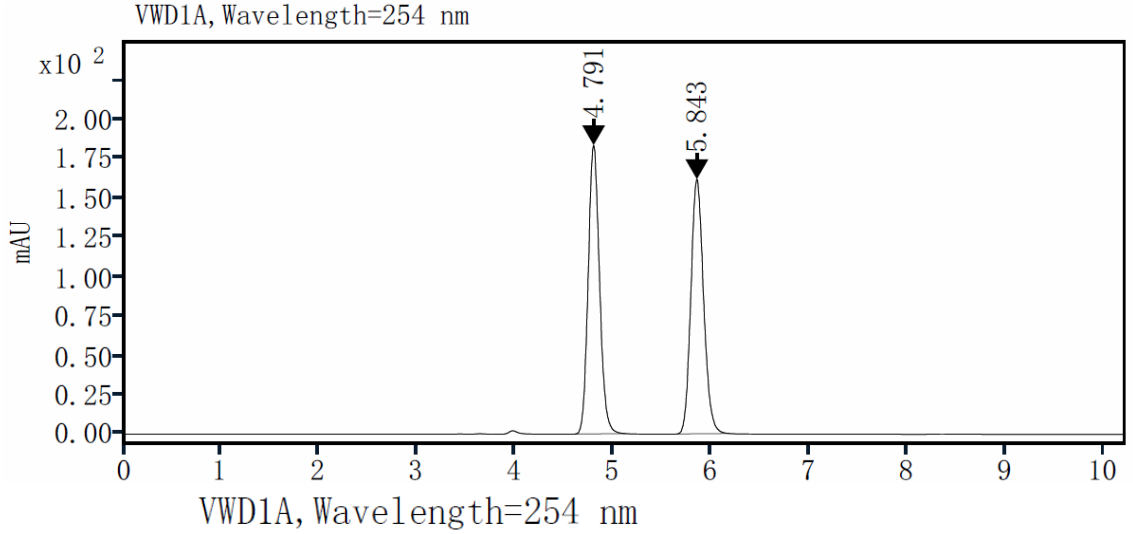
VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.419	VM m	4288.84	81.89
	4.740	MM m	948.18	18.11

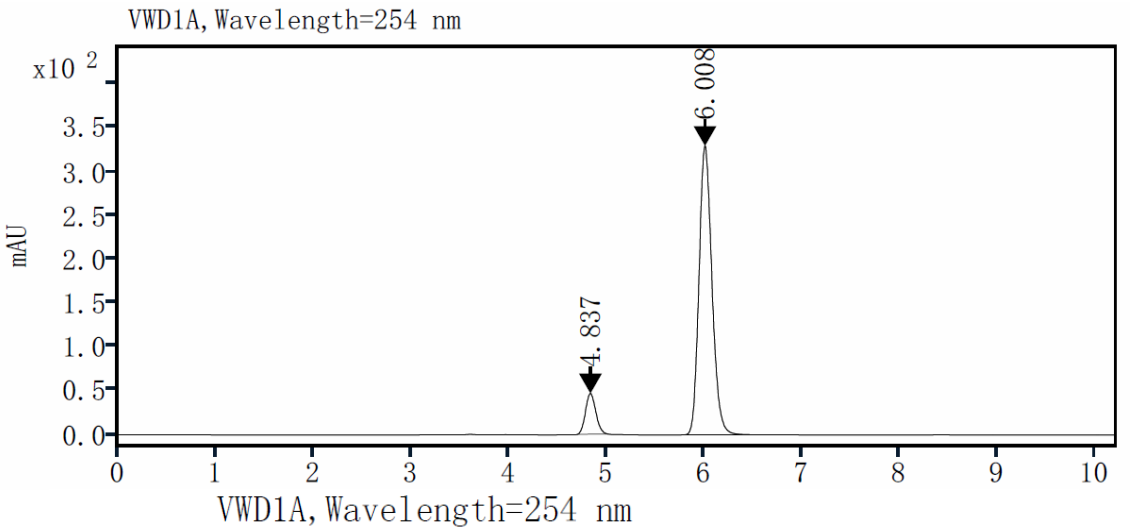


Scheme 2B, entry 31

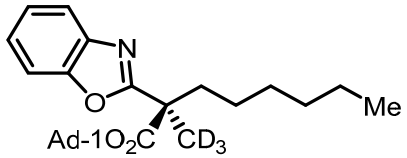
(*R*,*S*)-**L1**: 80% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.791	MM m	1469.81	50.11
	5.843	MM m	1463.55	49.89

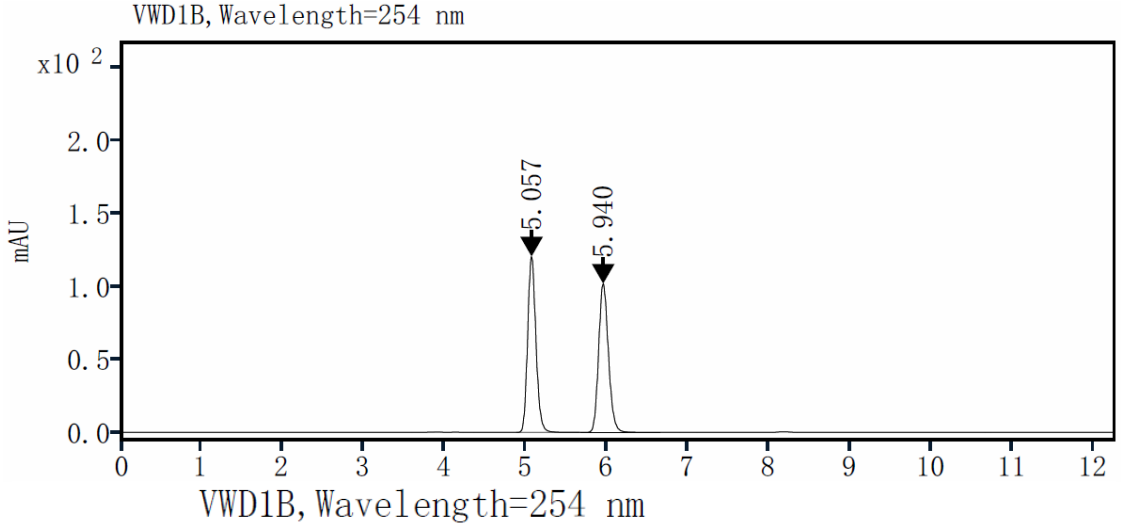


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.837	MM m	338.73	10.07
	6.008	MM m	3023.63	89.93

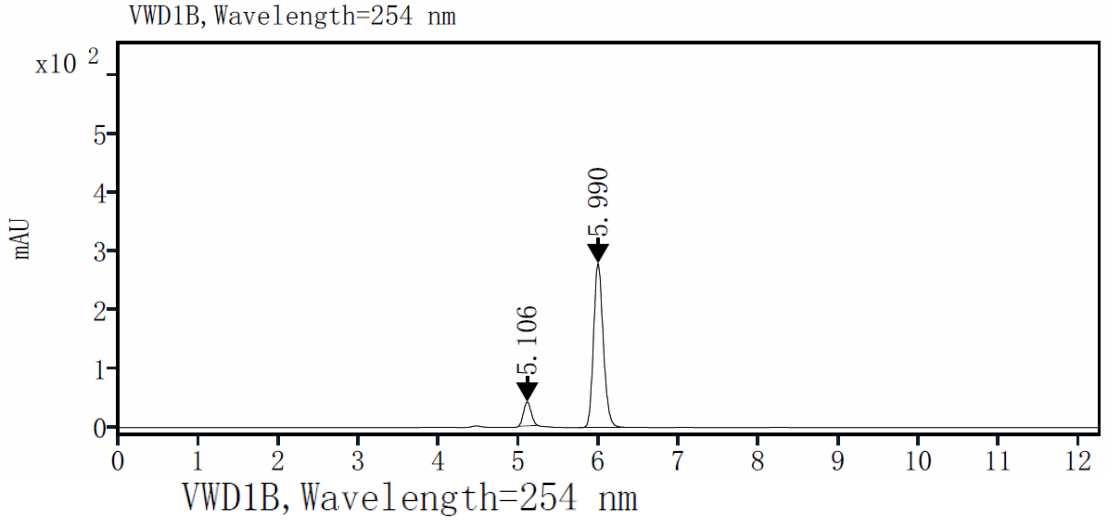


Scheme 2B, entry 32

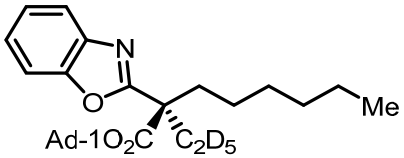
(*R*,*S*)-**L1**: 80% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.057	BB	858.34	50.01
	5.940	BB	857.91	49.99

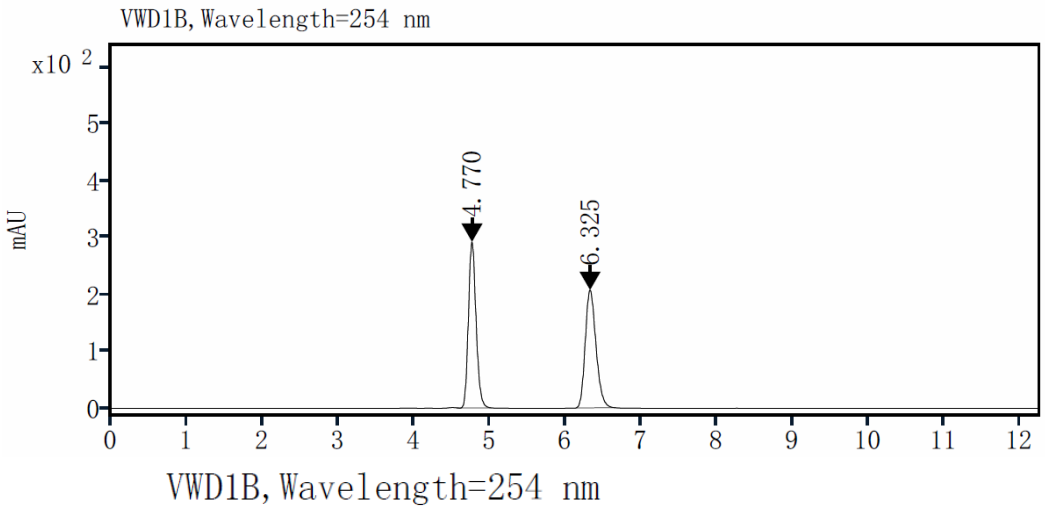


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.106	MM m	267.60	10.20
	5.990	MM m	2356.59	89.80



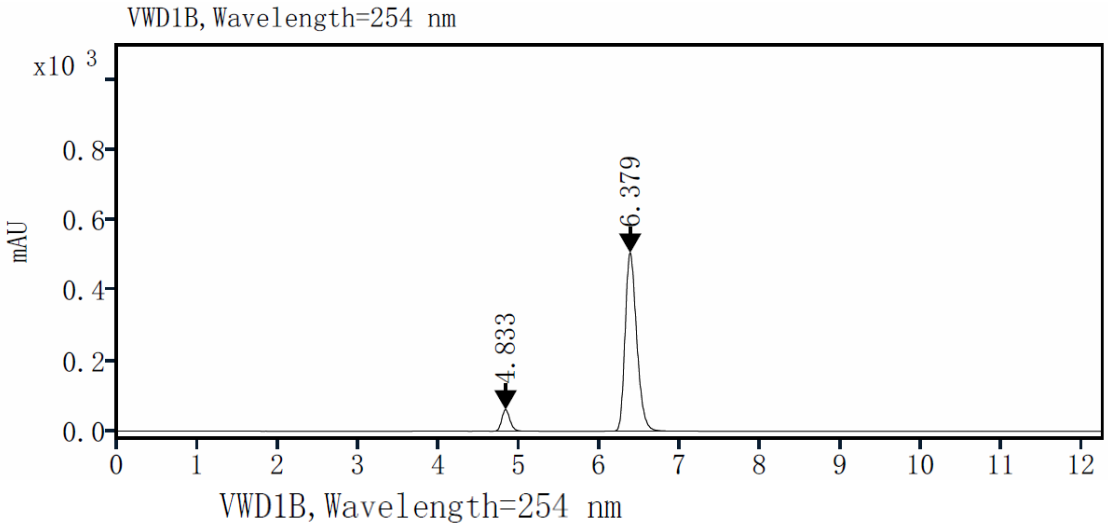
Scheme 2B, entry 33

(*R*,*S*)-**L1**: 85% ee



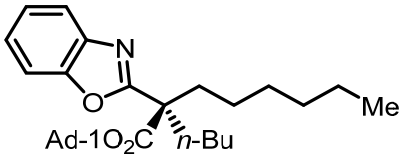
VWD1B, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.770	MM m	2036.18	50.08
	6.325	MM m	2029.57	49.92



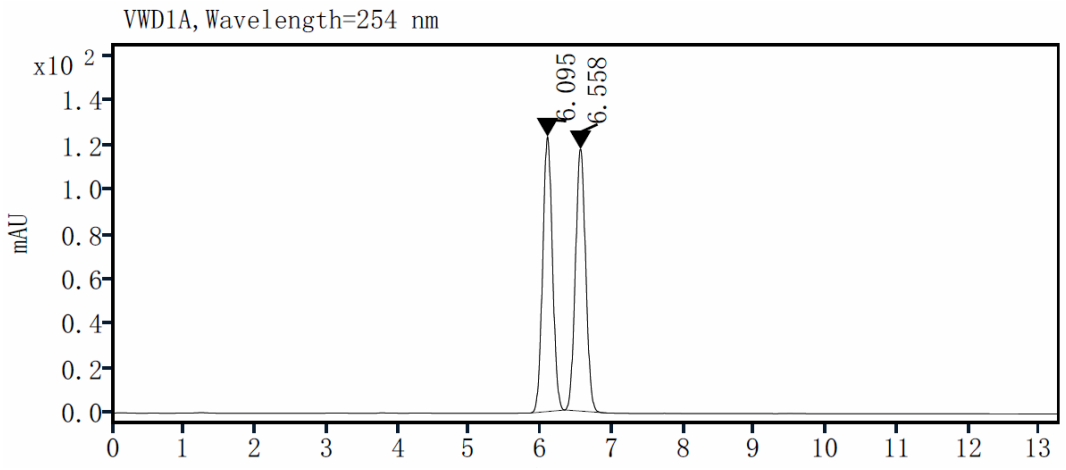
VWD1B, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.833	MM m	422.68	7.71
	6.379	MM m	5059.58	92.29

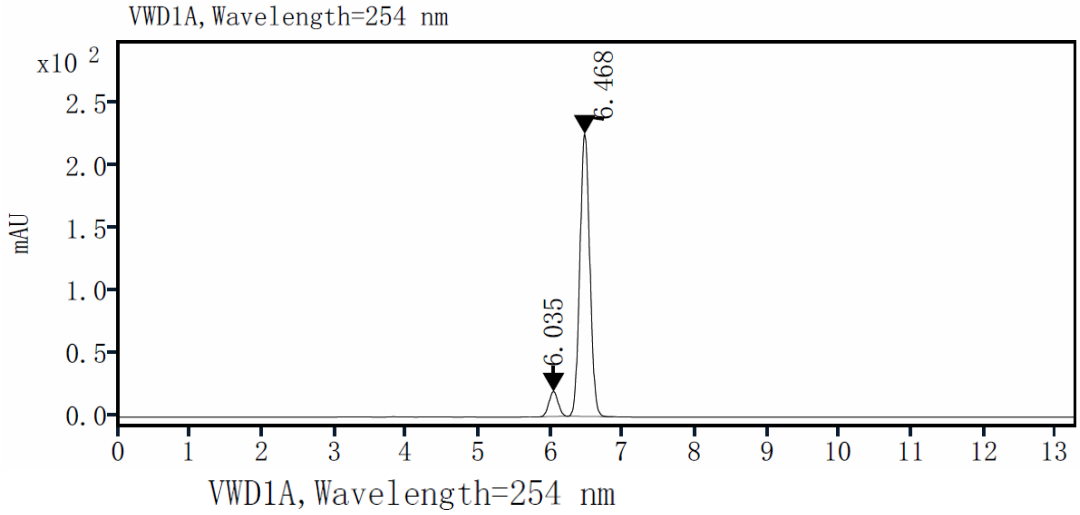


Scheme 2B, entry 34

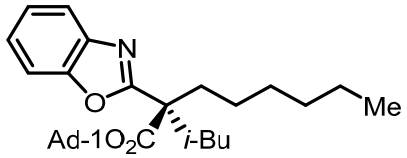
(*R*,*S*)-**L1**: 85% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.095	MM m	1175.07	50.04
	6.558	MM m	1172.99	49.96

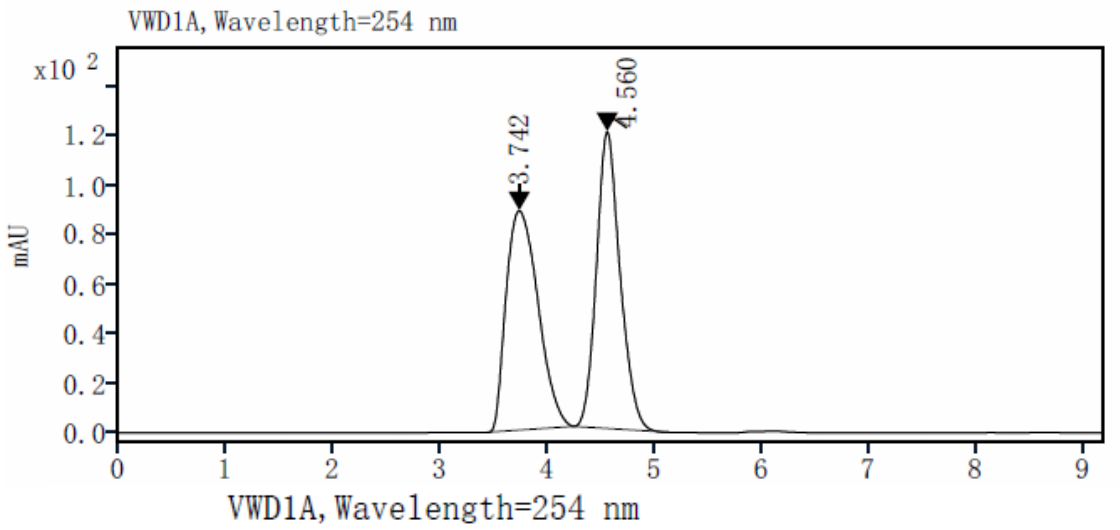


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.035	MM m	174.89	7.52
	6.468	MM m	2150.10	92.48

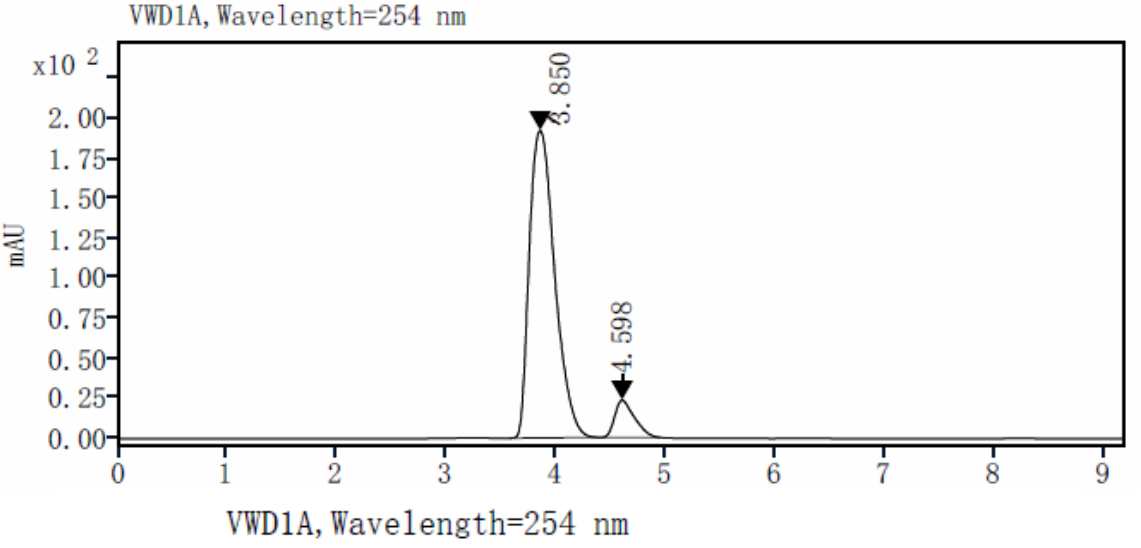


Scheme 2B, entry 35

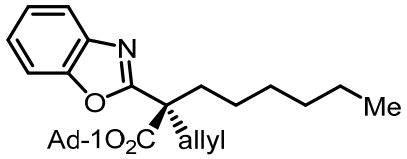
(*R*,*S*)-**L1**: 83% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	3.742	MM m	1836.24	50.07
	4.560	MM m	1831.03	49.93

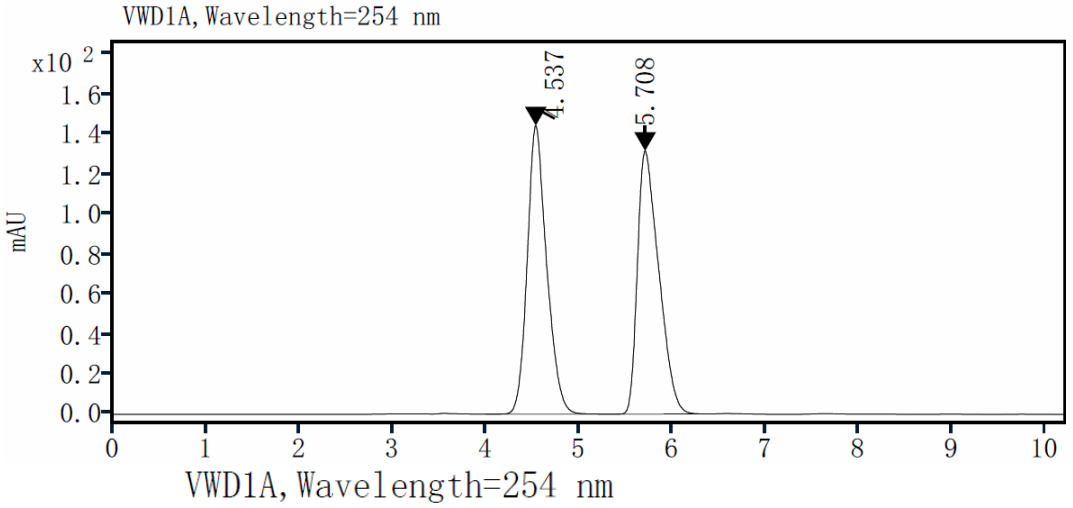


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	3.850	MM m	3086.28	91.41
	4.598	MM m	290.08	8.59

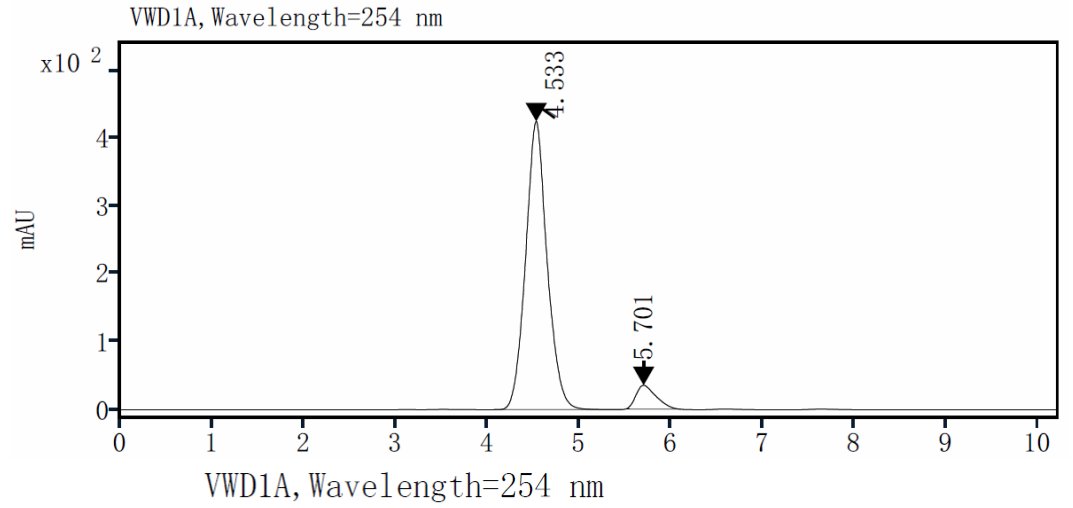


Scheme 2B, entry 36

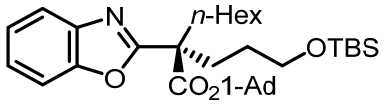
(*R*,*S*)-**L1**: 86% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.537	BB	2090.12	50.04
	5.708	BB	2086.52	49.96

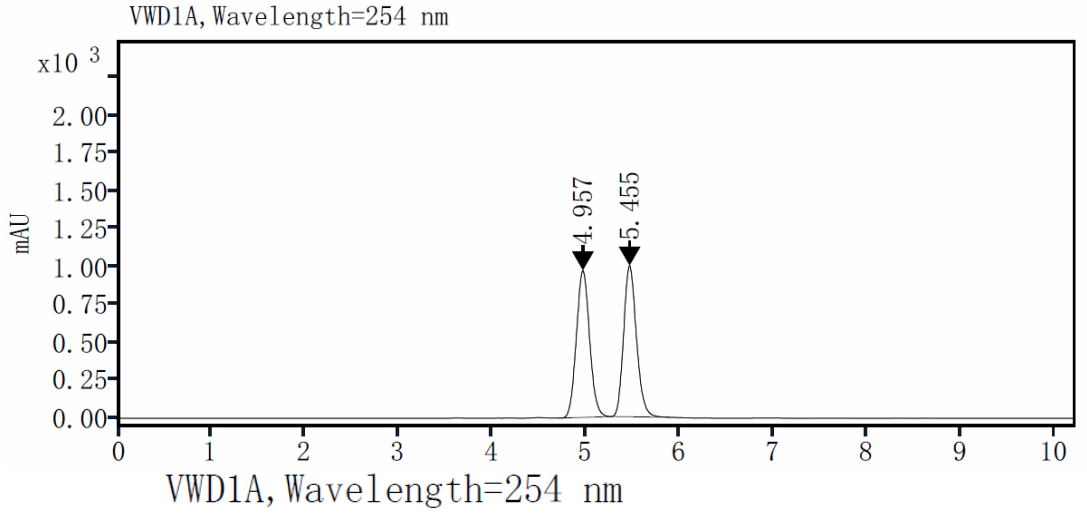


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.533	BM m	6924.45	92.87
	5.701	MM m	531.50	7.13

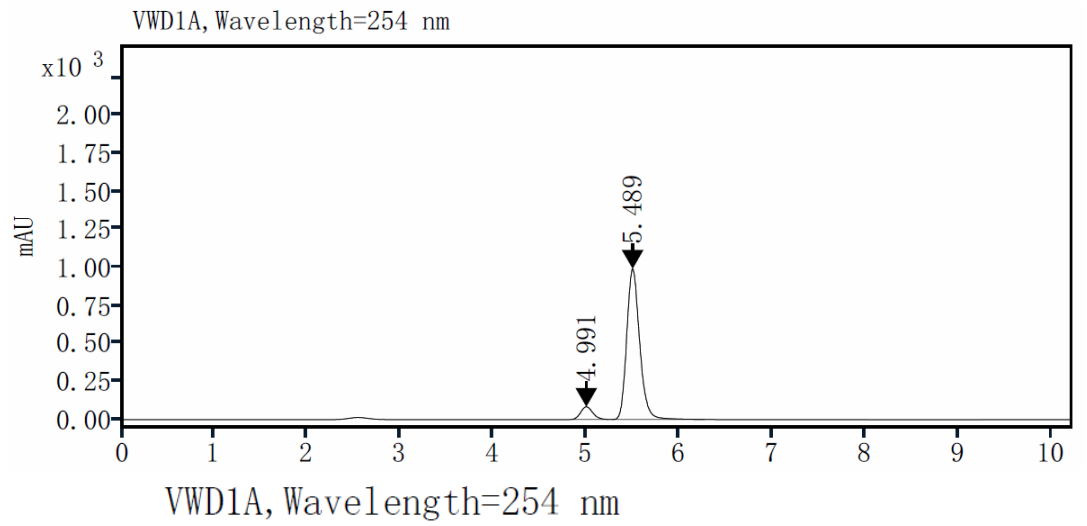


Scheme 2B, entry 37

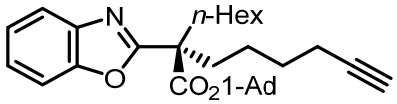
(*R,S*)-**L1**: 86% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.957	MM m	9532.43	50.06
	5.455	MM m	9509.30	49.94

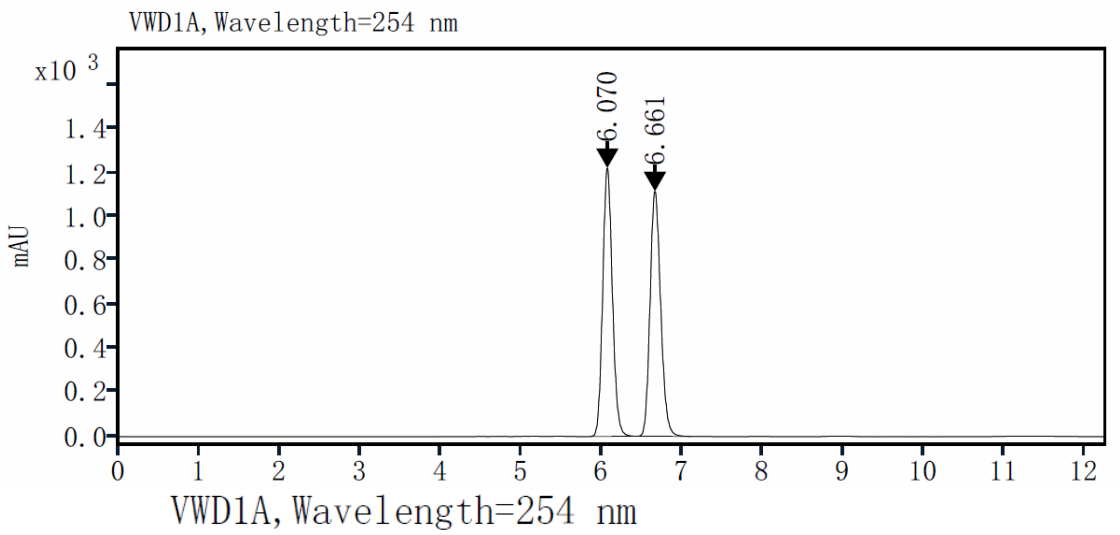


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.991	MM m	736.63	7.13
	5.489	MM m	9587.60	92.87

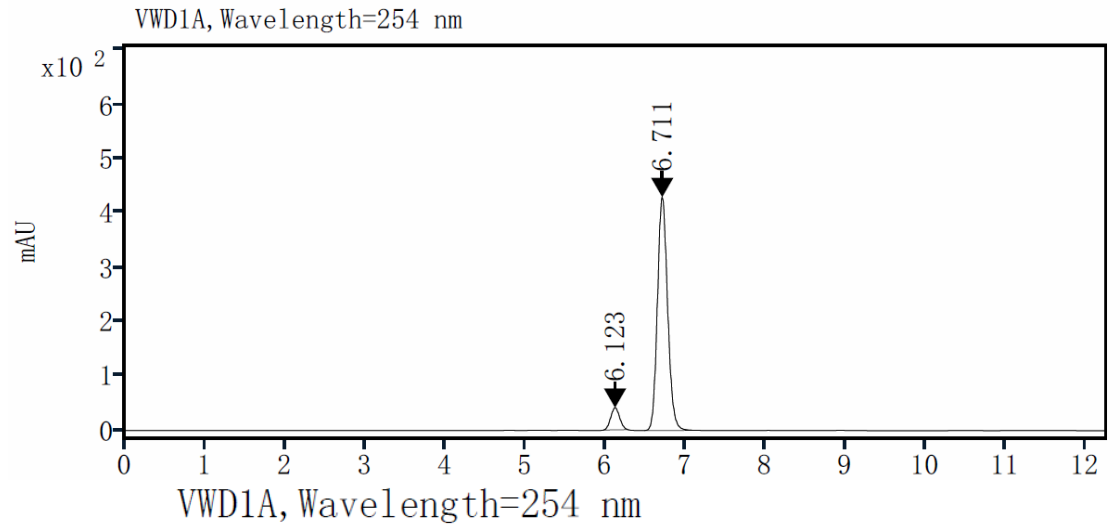


Scheme 2B, entry 38

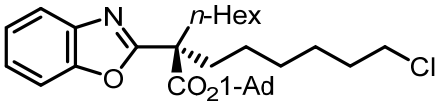
(*R*,*S*)-**L1**: 85% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.070	MM m	10204.96	49.99
	6.661	MM m	10207.99	50.01

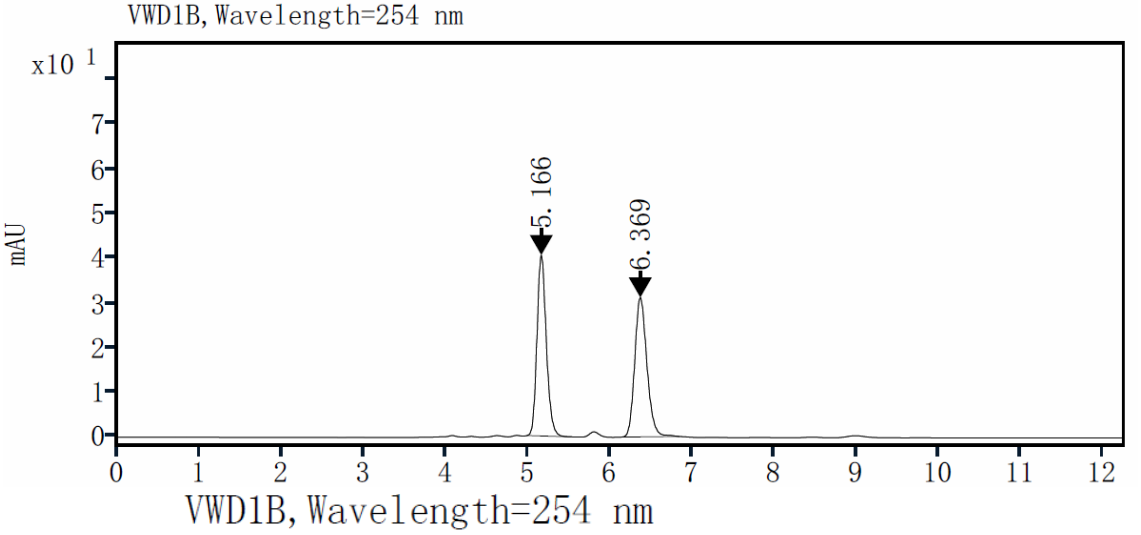


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.123	MM m	314.58	7.63
	6.711	MM m	3809.78	92.37

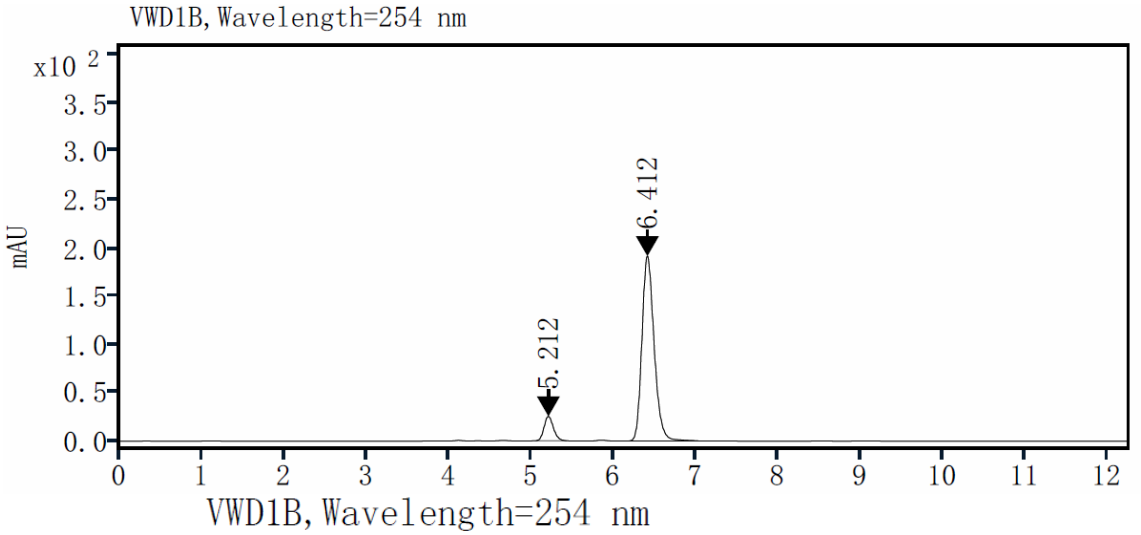


Scheme 2B, entry 39

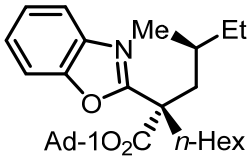
(*R*,*S*)-**L1**: 82% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.166	MM m	319.61	49.84
	6.369	MM m	321.73	50.16



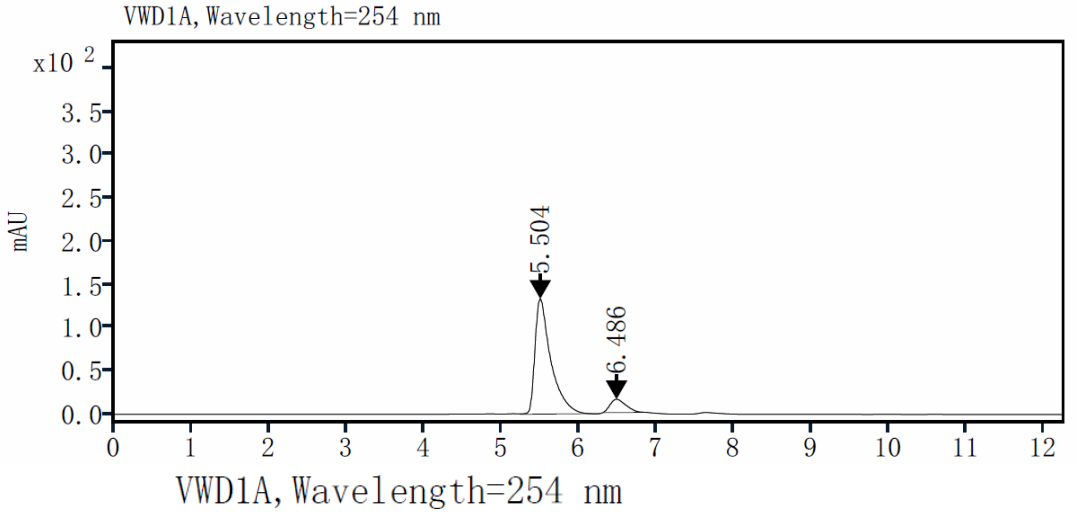
No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.212	MM m	197.87	9.09
	6.412	MM m	1979.95	90.91



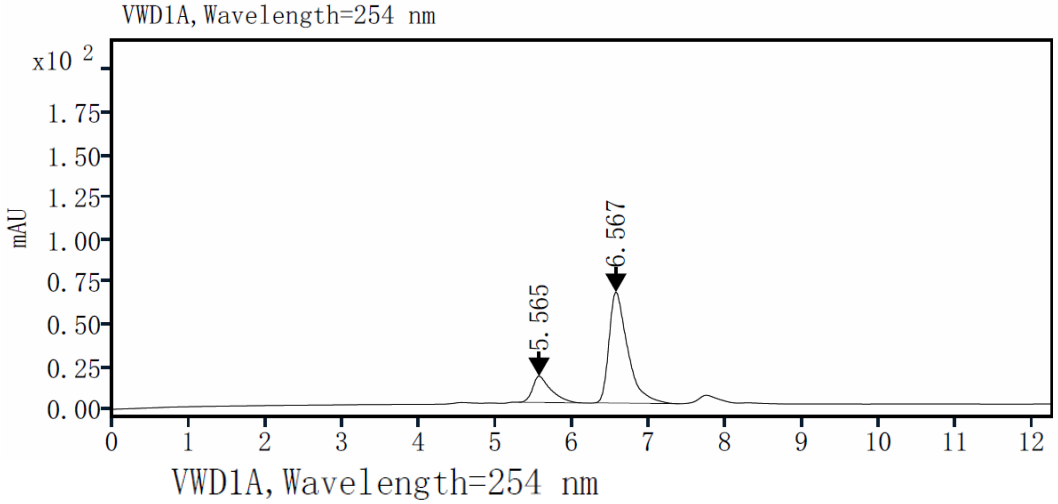
Scheme 2B, entries 40 and 41

(*R*,*S*)-**L1**: 90:10 dr

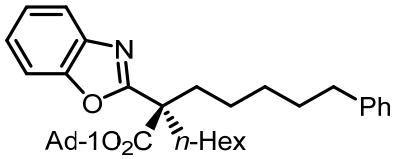
(*S*,*R*)-**L1**: 19:81 dr



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.504	VM m	1899.63	89.79
	6.486	MM m	215.94	10.21

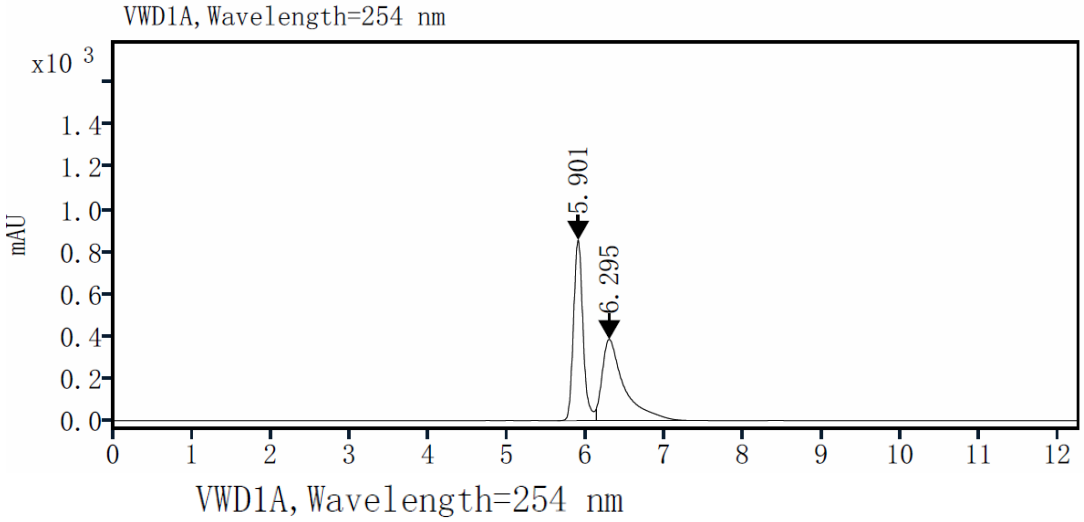


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.565	MM m	255.61	18.76
	6.567	MM m	1106.59	81.24

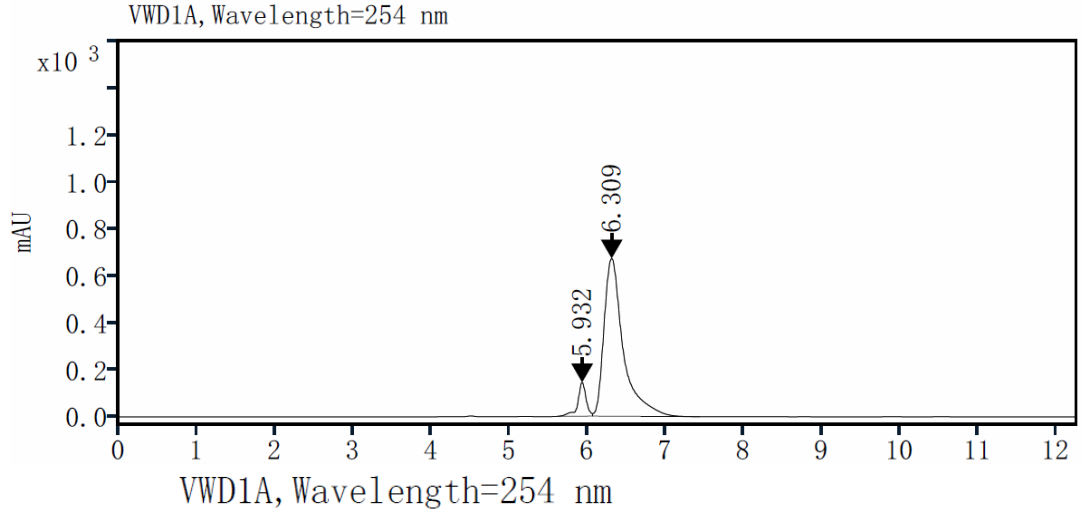


Scheme 2C, entry 42, *path a*

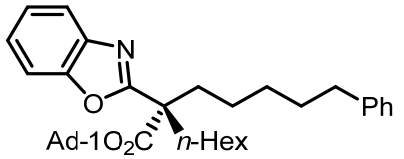
(*R*,*S*)-**L1**: 83% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.901	MM m	7202.92	49.09
	6.295	MM m	7469.39	50.91

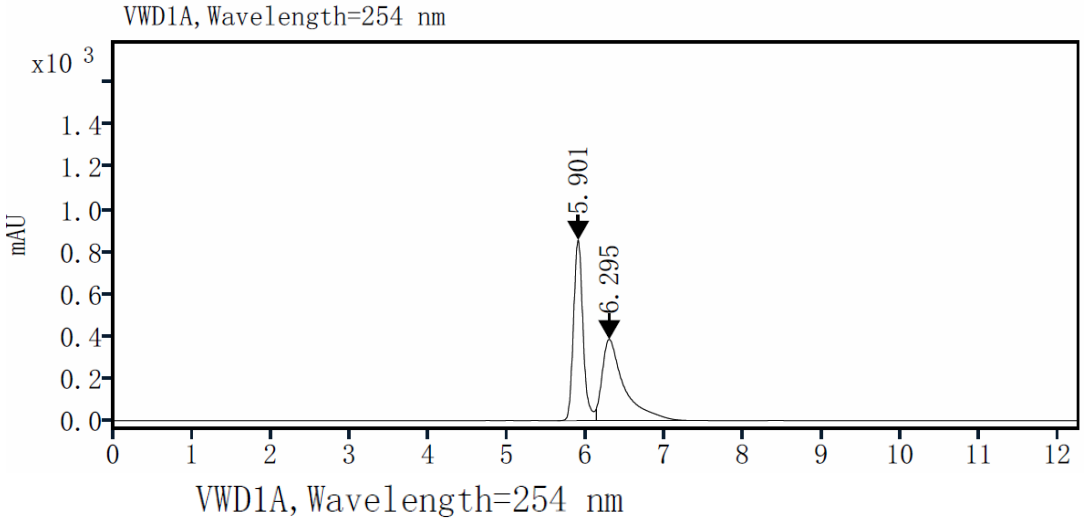


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.932	MM m	1064.99	8.44
	6.309	MM m	11547.44	91.56

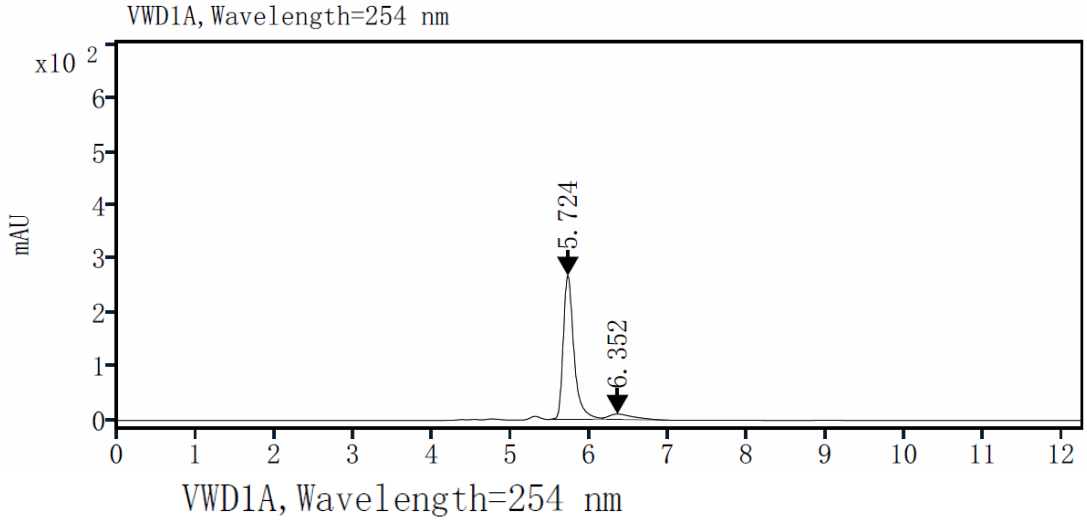


Scheme 2C, entry 42, *path b*

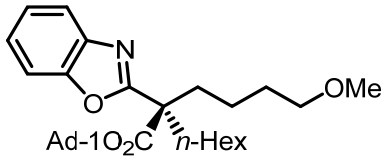
(*R,S*)-**L1**: -84% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.901	MM m	7202.92	49.09
	6.295	MM m	7469.39	50.91

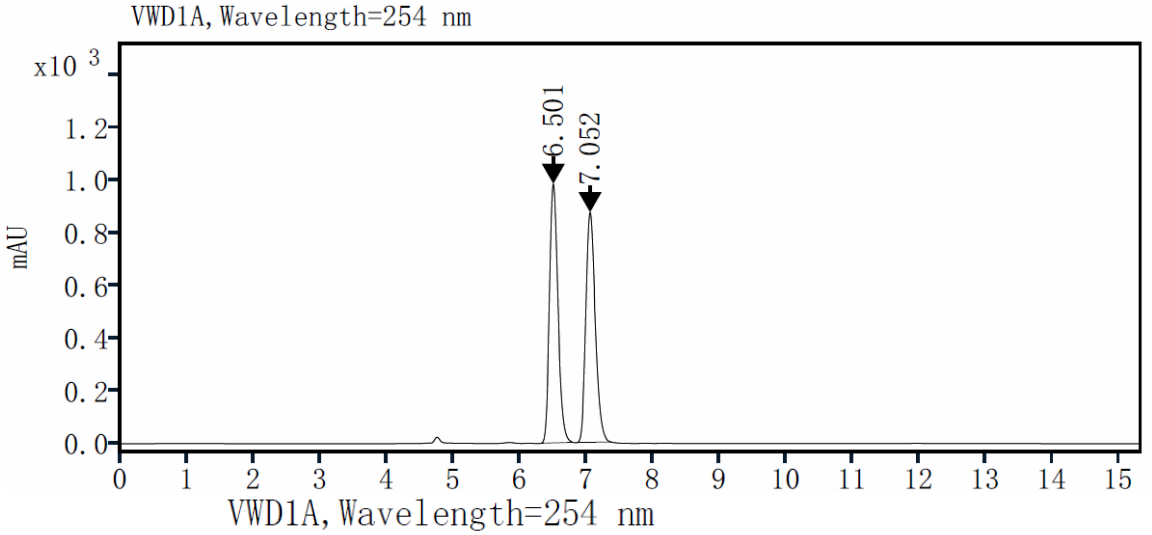


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.724	MM m	2544.27	92.05
	6.352	MM m	219.77	7.95

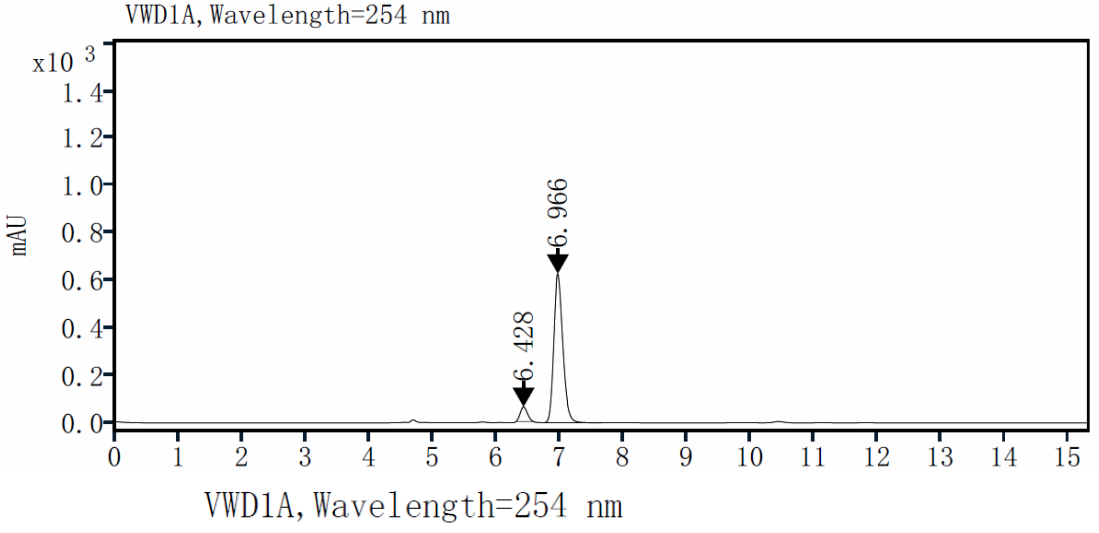


Scheme 2C, entry 43, *path a*

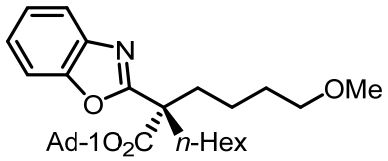
(*R*,*S*)-**L1**: 86% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.501	MM m	8682.60	50.21
	7.052	MM m	8610.26	49.79

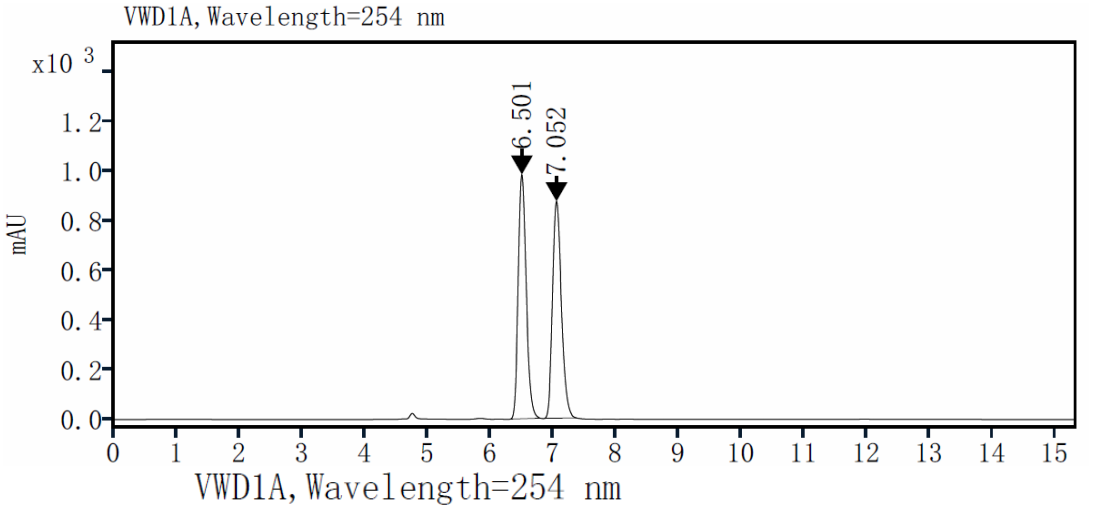


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.428	MM m	485.98	7.25
	6.966	VV	6221.06	92.75

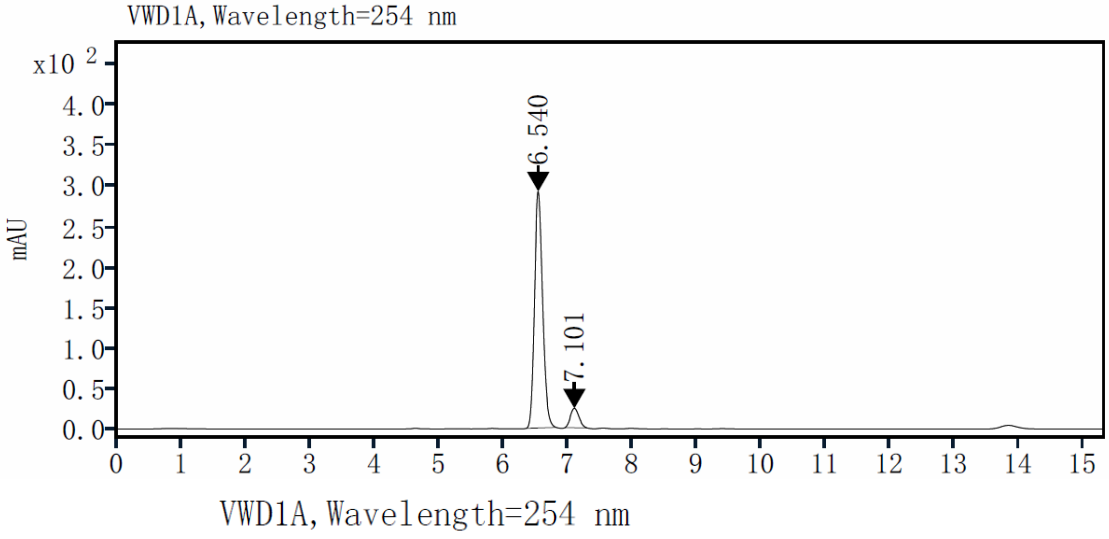


Scheme 2C, entry 43, *path b*

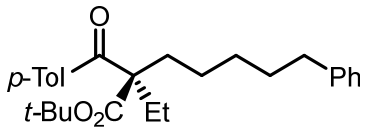
(*R*,*S*)-**L1**: -84% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.501	MM m	8682.60	50.21
	7.052	MM m	8610.26	49.79

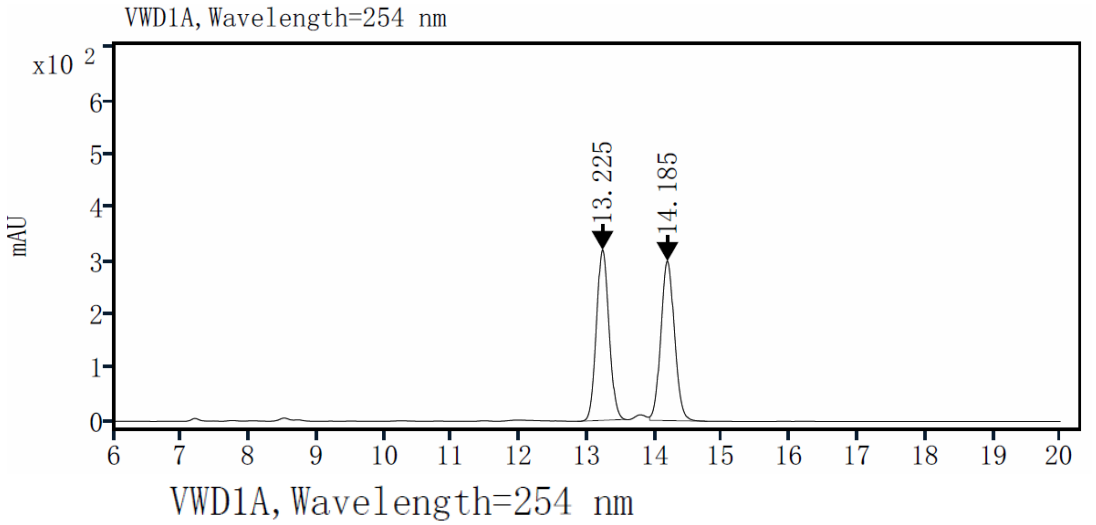


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	6.540	MM m	2571.02	92.07
	7.101	MM m	221.43	7.93

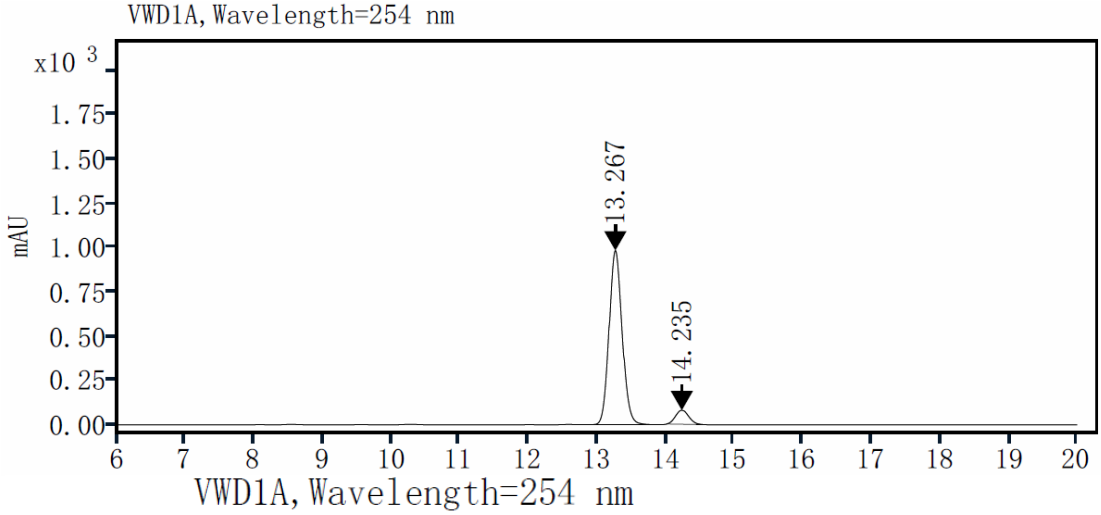


Scheme 3, entry 44

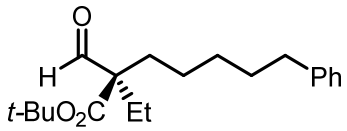
85% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	13.225	MM m	4155.86	49.65
	14.185	MM m	4215.11	50.35

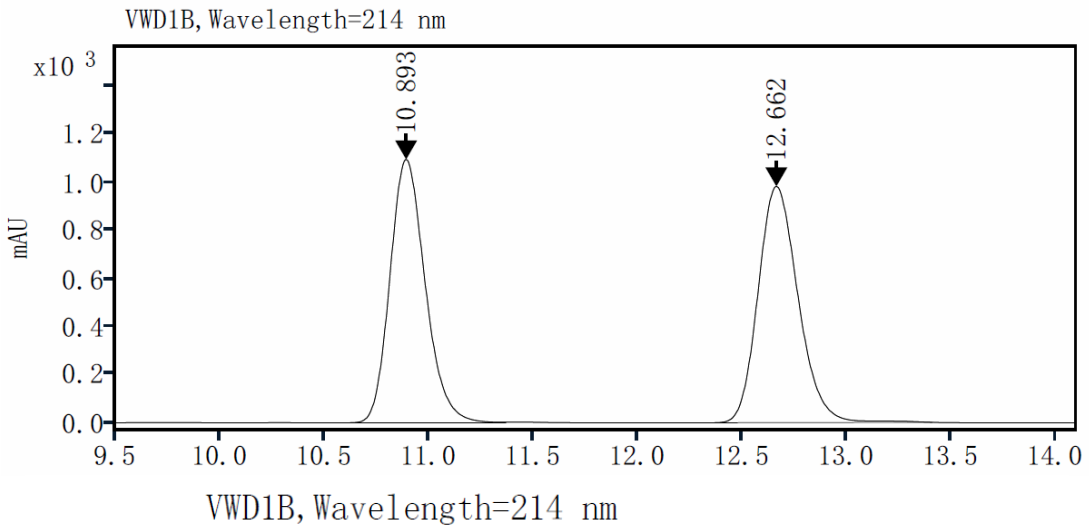


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	13.267	MM m	13058.29	92.46
	14.235	MM m	1064.83	7.54



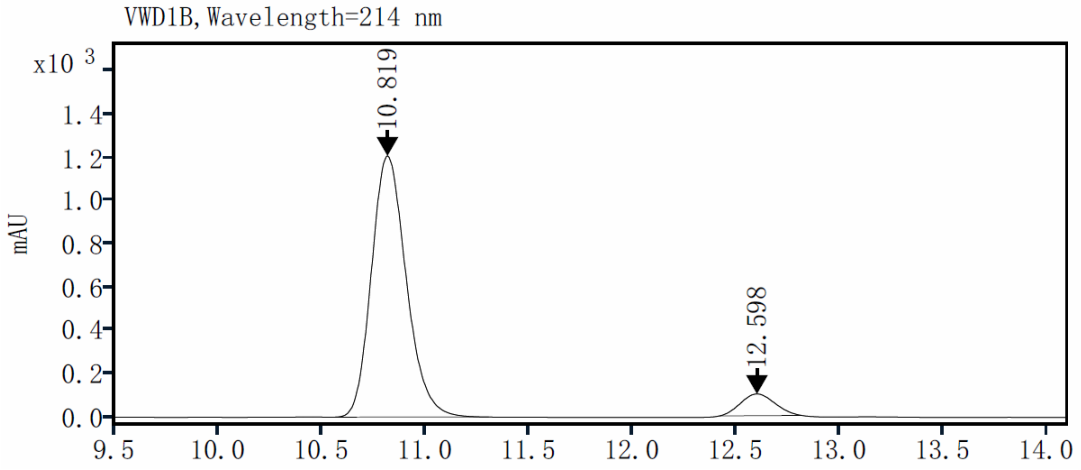
Scheme 3, entry 45

85% ee



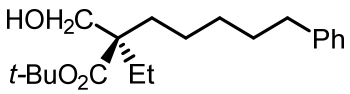
VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.893	BV	12835.75	49.53
	12.662	VM m	13080.99	50.47



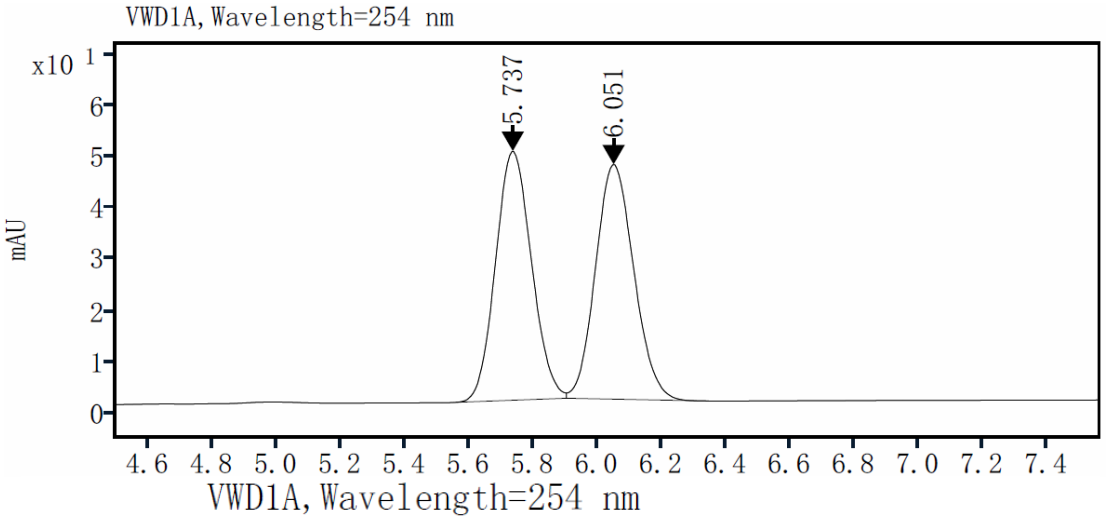
VWD1B, Wavelength=214 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	10.819	MM m	14095.63	92.47
	12.598	MM m	1147.24	7.53

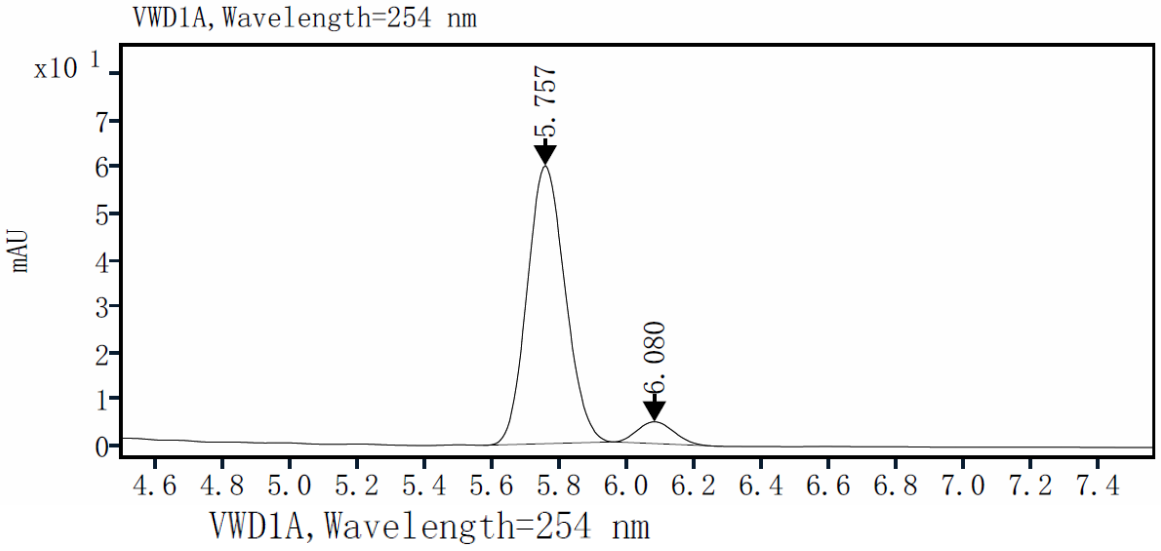


Scheme 3, entry 47

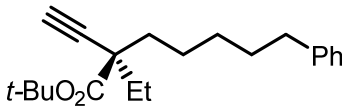
86% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.737	MM m	377.36	49.90
	6.051	MM m	378.85	50.10

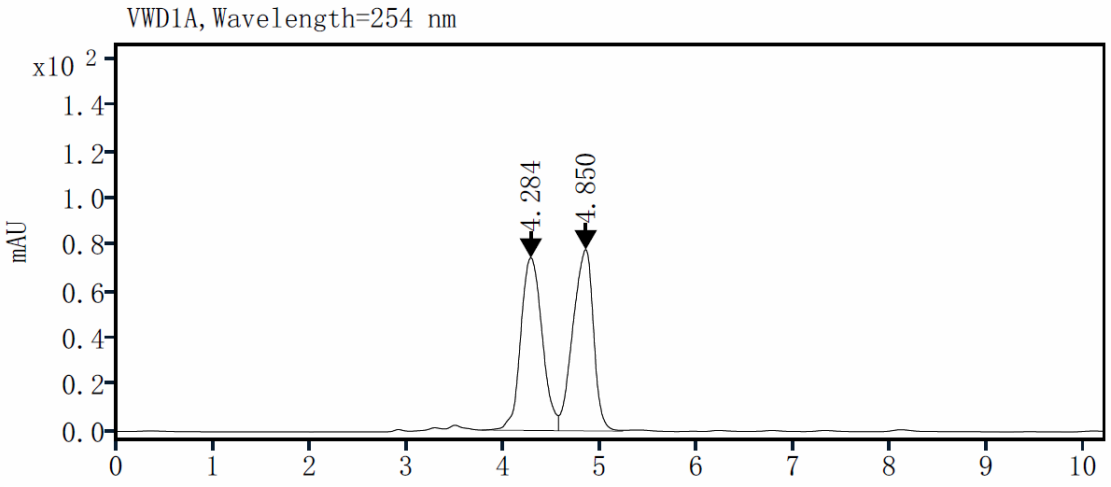


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.757	BM m	469.49	92.97
	6.080	MM m	35.48	7.03

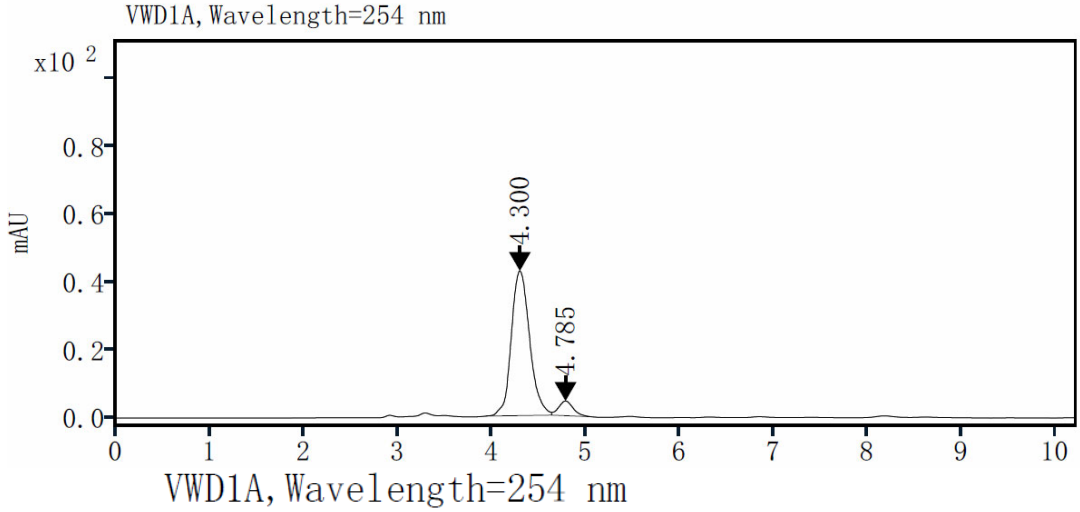


Scheme 3, entry 48

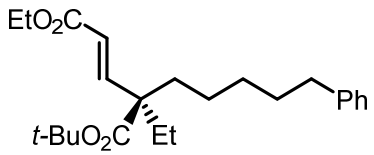
85% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.284	BV	1141.72	49.84
	4.850	VV	1149.11	50.16

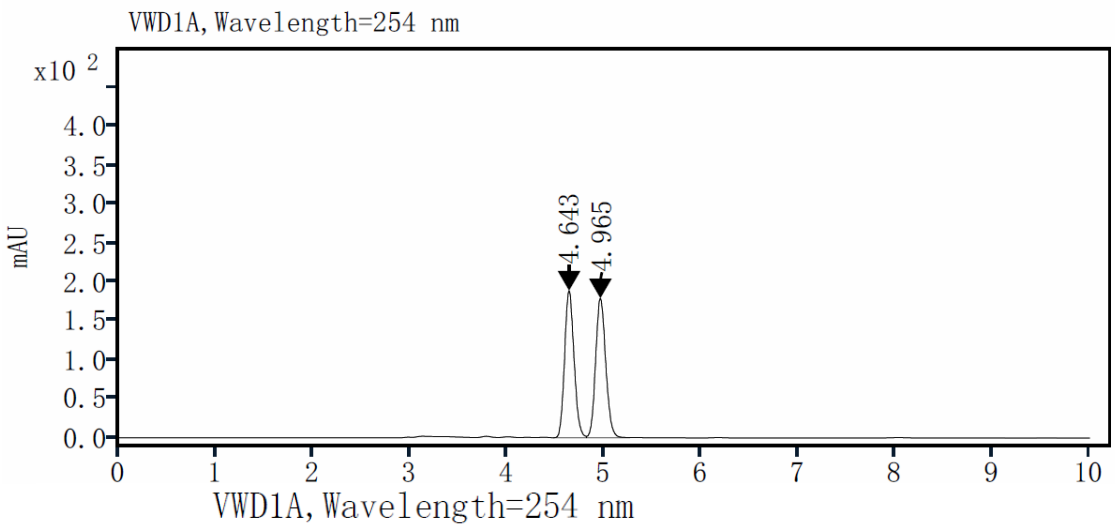


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.300	MM m	578.77	92.54
	4.785	MM m	46.64	7.46

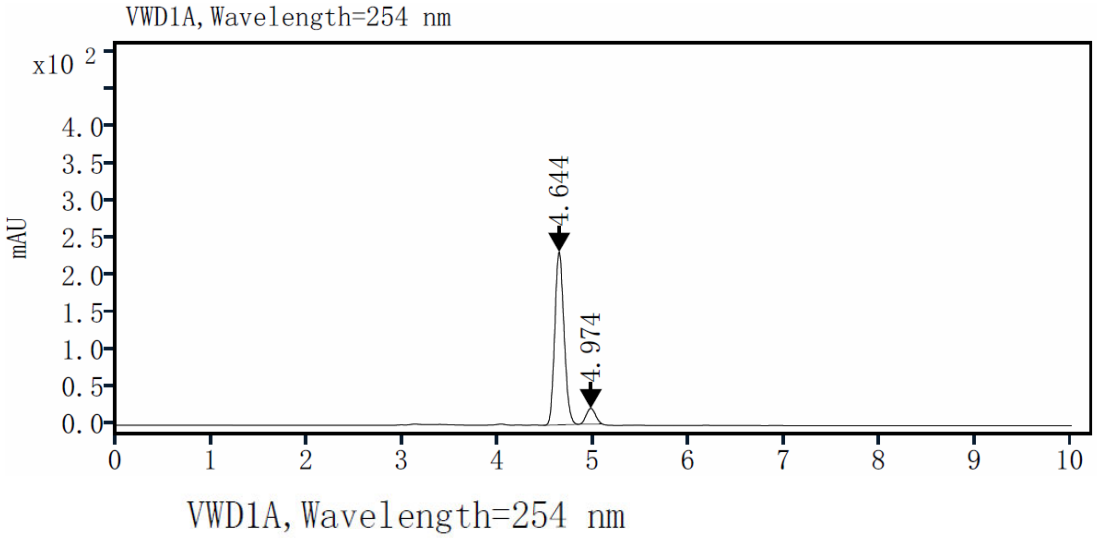


Scheme 3, entry 49

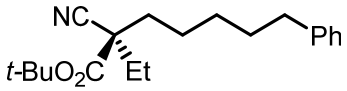
84% ee



No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.643	BV	1274.15	49.44
	4.965	VV	1303.16	50.56

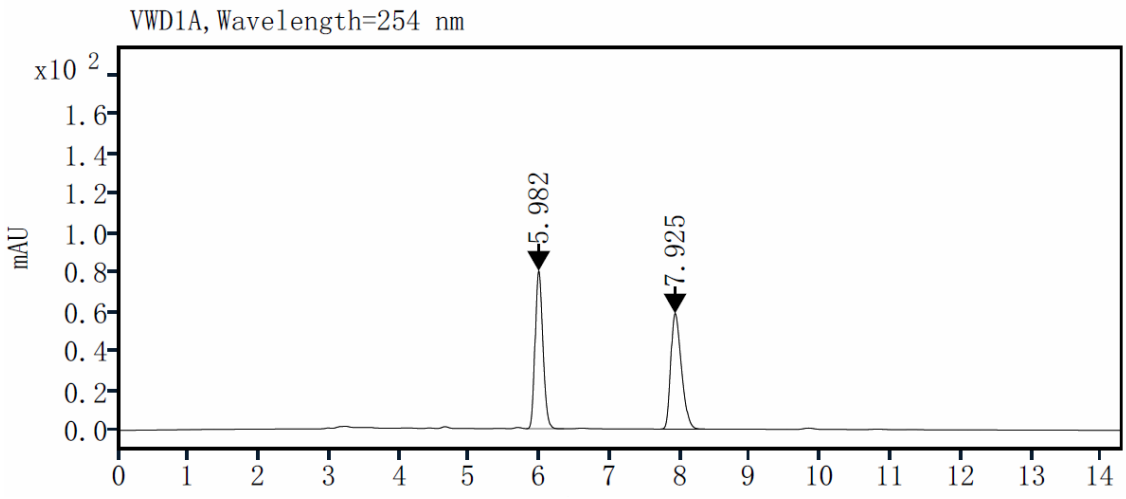


No.	RetTime[min]	Type	Area [mAu*s]	Area%
	4.644	BM m	1563.38	91.74
	4.974	MM m	140.70	8.26



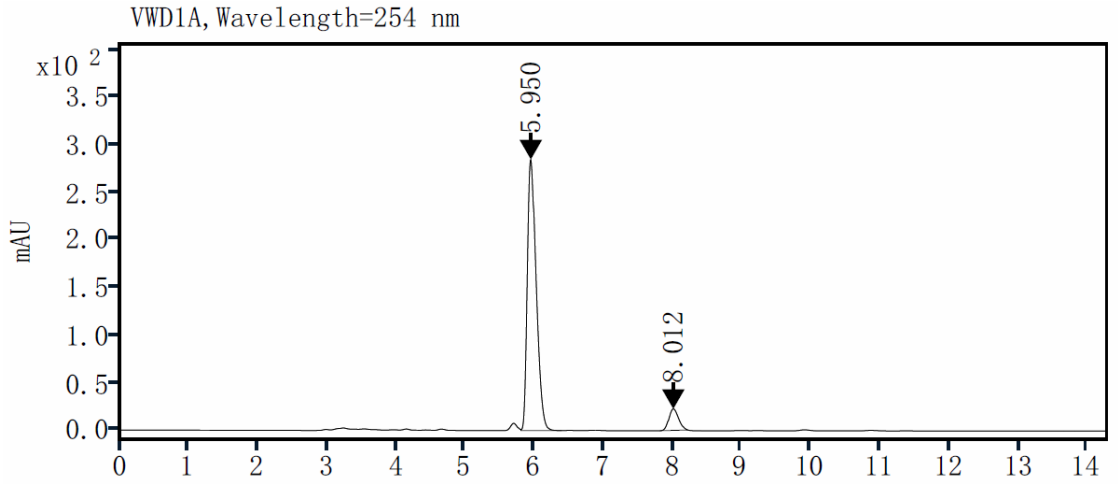
Scheme 3, entry 50

84% ee



VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.982	VB	618.43	49.90
	7.925	BB	620.81	50.10



VWD1A, Wavelength=254 nm

No.	RetTime[min]	Type	Area [mAu*s]	Area%
	5.950	VB	2548.92	92.01
	8.012	MM m	221.28	7.99