A Convergent Catalytic Asymmetric Synthesis of Esters of Chiral Dialkyl Carbinols

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Supporting Information

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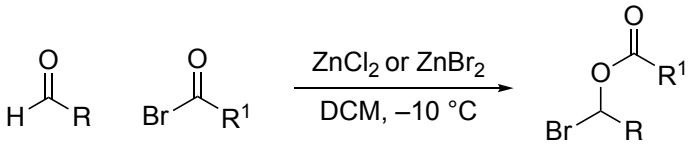
I. General Information

Unless otherwise noted, reagents received from commercial suppliers were used as received. Ligands (*S*,*S*)-**L*** and (*R*,*R*)-**L*** were prepared according to a literature procedure, and all analytical data matched that report.[1] $K_3PO_4 \cdot H_2O$ was purchased from Sigma-Aldrich; it is important that the mono-hydrate (1.0 equiv of water) is used. Anhydrous MTBE (methyl *tert*-butyl ether) and *i*-Pr_2O were purchased from Sigma-Aldrich and stored under nitrogen; other solvents were purified by passage through activated aluminum oxide in a solvent-purification system. Unless otherwise noted, all reactions were performed under an atmosphere of dry nitrogen. Flash column chromatography was performed using silica gel (SiliaFlash® P60, particle size 40-63 μm, Silicycle).

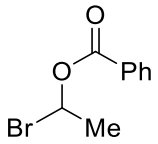
NMR spectra were collected on a Bruker 400 MHz or a Varian 500 MHz spectrometer at ambient temperature; chemical shifts (δ) are reported in ppm downfield from tertramethylsilane, using the solvent resonance as the internal standard. HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (4.6 × 250 mm, particle size 5 μm). SFC analyses were carried out on an Agilent 1260 Infinity II system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (4.6 × 250 mm, particle size 5 μm). FT-IR measurements were carried out on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD5 ATR accessory. HR-MS data were acquired on a Waters LCT Premier XE TOF MS in electrospray ionization (ESI+) mode. GC-MS data were obtained on an Agilent 7890A GC-MS system with an Agilent 5975C detector. Optical-rotation data were obtained with a Jasco P-2000 polarimeter at 589 nm, using a 100 mm pathlength cell in the solvent and at the concentration indicated. GC analyses were obtained on an Agilent 6890N GC.

II. Preparation of Electrophiles

The yields have not been optimized.



General Procedure 1 (GP-1): Preparation of the electrophile.[2] An oven-dried 100 mL round-bottom flask was charged with a magnetic stir bar and either $ZnCl_2$ or $ZnBr_2$ (0.050 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 DCM and the acyl bromide (1.2 equiv). The resulting solution was cooled to –10 °C, and the mixture was stirred for 10 min. At this temperature, the aldehyde (1.0 equiv) was added via syringe pump over 30 min, and the resulting mixture was stirred for 2 h. Then, the reaction mixture was filtered through a short column of neutral aluminium oxide, with a DCM washing. The filtrate was concentrated under reduced pressure. The residue was either purified by vacuum distillation to afford the pure product, or used directly after the determination of its purity by ^{1}H NMR (CH_2Br_2 as the internal standard).

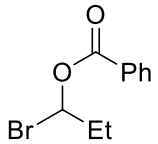


1-Bromoethyl benzoate. The title compound was synthesized according to **GP-1** from $ZnCl_2$ (544 mg, 4.0 mmol), BzBr (11.3 mL, 96.0 mmol), acetaldehyde (4.5 mL, 80 mmol), and DCM (10 mL). The product was purified by vacuum distillation (b.p. = 75–79 °C, 1.2 Torr). 9.6 g (42.1 mmol, 53% yield). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.04 (m, 2H), 7.65 – 7.56 (m, 1H), 7.52 – 7.42 (m, 2H), 6.97 (q, *J* = 5.9 Hz, 1H), 2.14 (d, *J* = 5.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 134.0, 130.2, 128.9, 128.7, 72.4, 27.0.

FT-IR (film): 2983, 1732, 1603, 1453, 1265, 1064, 898, 707 cm^{-1}.

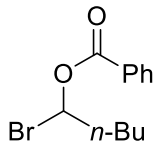


1-Bromopropyl benzoate. The title compound was synthesized according to **GP-1** from $ZnCl_2$ (870 mg, 6.4 mmol), BzBr (18.0 mL, 154 mmol), propionaldehyde (9.2 mL, 128 mmol), and DCM (20 mL). The product was purified by vacuum distillation (b.p. = 88–90 °C, 0.5 Torr). 22.4 g (92.6 mmol, 72% yield). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H), 7.65 – 7.58 (m, 1H), 7.50 – 7.43 (m, 2H), 6.85 (t, *J* = 5.7 Hz, 1H), 2.36 – 2.23 (m, 2H), 1.15 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 134.0, 130.1, 129.0, 128.7, 78.3, 32.9, 10.4.

FT-IR (film): 2980, 2941, 1732, 1602, 1453, 1261, 1066, 961, 908, 716 cm^{-1}.

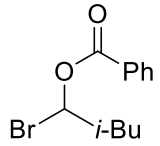


1-Bromopentyl benzoate. The title compound was synthesized according to **GP-1** from $ZnCl_2$ (544 mg, 4.0 mmol), BzBr (11.3 mL, 96.0 mmol), valeraldehyde (8.5 mL, 80 mmol), and DCM (10 mL). The product was purified by vacuum distillation (b.p. = 103–108 °C, 0.7 Torr). 8.4 g (31.1 mmol, 39% yield). Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 2H), 7.66 – 7.57 (m, 1H), 7.52 – 7.44 (m, 2H), 6.89 (t, *J* = 5.9 Hz, 1H), 2.37 – 2.21 (m, 2H), 1.61 – 1.49 (m, 2H), 1.48 – 1.35 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 134.0, 130.2, 129.0, 128.7, 76.8, 39.4, 28.1, 22.1, 14.0.

FT-IR (film): 2959, 1746, 1602, 1453, 1242, 1067, 989, 708 cm^{-1}.

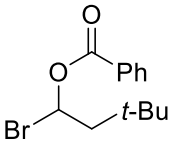


1-Bromo-3-methylbutyl benzoate. The title compound was synthesized according to **GP-1** from $ZnBr_2$ (888 mg, 4.0 mmol), BzBr (11.3 mL, 96.0 mmol), isovaleraldehyde (8.6 mL, 80 mmol), and DCM (10 mL). The product was purified by vacuum distillation (b.p. = 95–98 °C, 0.7 Torr). 14.3 g (53.0 mmol, 66% yield). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.04 (m, 2H), 7.65 – 7.57 (m, 1H), 7.53 – 7.42 (m, 2H), 6.95 (dd, *J* = 7.6, 5.6 Hz, 1H), 2.28 (ddd, *J* = 14.2, 7.6, 6.6 Hz, 1H), 2.16 (ddd, *J* = 14.3, 7.3, 5.6 Hz, 1H), 1.99 – 1.86 (m, 1H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 134.0, 130.2, 129.0, 128.7, 76.0, 48.4, 26.1, 22.4, 22.1.

FT-IR (film): 2962, 1735, 1602, 1452, 1260, 1067, 987, 716 cm^{-1}.



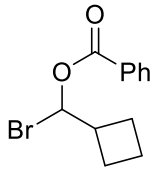
1-Bromo-3,3-dimethylbutyl benzoate. The title compound was synthesized according to **GP-1** from $ZnCl_2$ (340 mg, 2.5 mmol), BzBr (7.0 mL, 60 mmol), 3,3-dimethylbutyraldehyde (5.0

g, 50 mmol), and DCM (8 mL). The product was purified by vacuum distillation (b.p. = 102–103 °C, 0.9 Torr). 9.9 g (35 mmol, 70% yield). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.01 (m, 2H), 7.67 – 7.57 (m, 1H), 7.55 – 7.42 (m, 2H), 7.07 (dd, *J* = 10.1, 2.2 Hz, 1H), 2.54 (dd, *J* = 14.8, 10.1 Hz, 1H), 2.25 (dd, *J* = 14.8, 2.3 Hz, 1H), 0.98 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 134.1, 130.2, 128.9, 128.8, 74.9, 53.4, 32.1, 29.8.

FT-IR (film): 2956, 1738, 1602, 1454, 1246, 1063, 975, 714 cm^{-1}.

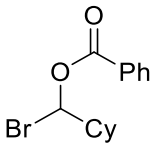


Bromo(cyclobutyl)methyl benzoate. The title compound was synthesized according to **GP-1** from $ZnBr_2$ (400 mg, 1.8 mmol), BzBr (5.0 mL, 43 mmol), cyclobutanecarbaldehyde (3.0 g, 36 mmol), and DCM (10 mL). The product was purified by vacuum distillation (b.p. = 103–104 °C, 0.6 Torr). 7.7 g (29 mmol, 80% yield). Yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.03 (m, 2H), 7.67 – 7.58 (m, 1H), 7.53 – 7.44 (m, 2H), 6.83 (d, *J* = 7.2 Hz, 1H), 3.19 – 3.07 (m, 1H), 2.17 (m, 2H), 2.10 – 1.81 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 134.0, 130.2, 129.0, 128.7, 80.2, 42.6, 25.3, 25.1, 16.8.

FT-IR (film): 2985, 1738, 1601, 1452, 1263, 1064, 994, 711 cm^{-1}.

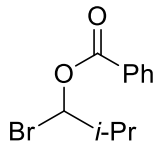


Bromo(cyclohexyl)methyl benzoate. The title compound was synthesized according to **GP-1** from $ZnBr_2$ (555 mg, 2.5 mmol), BzBr (7.0 mL, 60 mmol), cyclohexanecarbaldehyde (6.0 mL, 50 mmol), and DCM (5 mL). The product was used without further purification (98 wt.%). 14.3 g (47.3 mmol, 95% yield). Yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 2H), 7.65 – 7.58 (m, 1H), 7.51 – 7.44 (m, 2H), 6.77 (d, *J* = 4.7 Hz, 1H), 2.06 – 1.95 (m, 3H), 1.88 – 1.80 (m, 2H), 1.76 – 1.68 (m, 1H), 1.39 – 1.15 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 134.0, 130.1, 129.1, 128.7, 82.3, 45.6, 29.3, 28.6, 26.2, 25.73, 25.71.

FT-IR (film): 2932, 1732, 1602, 1452, 1258, 1064, 962, 708 cm^{-1}.

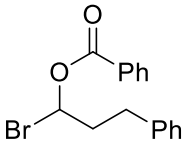


1-Bromo-2-methylpropyl benzoate. The title compound was synthesized according to **GP-1** from $ZnCl_2$ (544 mg, 4.0 mmol), BzBr (11.3 mL, 96.0 mmol), isobutyraldehyde (7.3 mL, 80 mmol), and DCM (10 mL). The product was purified by vacuum distillation (b.p. = 88–94 °C, 0.5 Torr). 11.9 g (46.5 mmol, 58% yield). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.02 (m, 2H), 7.66 – 7.58 (m, 1H), 7.53 – 7.43 (m, 2H), 6.81 (d, *J* = 4.2 Hz, 1H), 2.35 – 2.21 (m, 1H), 1.18 (t, *J* = 6.4 Hz, 3H), 1.16 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 134.0, 130.1, 129.1, 128.7, 83.3, 36.2, 18.5, 18.4.

FT-IR (film): 2973, 1746, 1602, 1456, 1255, 1064, 802, 680 cm^{-1}.



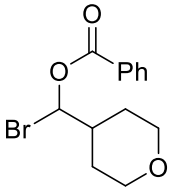
1-Bromo-3-phenylpropyl benzoate. The title compound was synthesized according to **GP-1** from $ZnBr_2$ (555 mg, 2.5 mmol), BzBr (7.0 mL, 60 mmol), 3-phenylpropionaldehyde (6.6 mL, 50 mmol), and DCM (10 mL). The product was used without further purification (95 wt.%). 13.6 g (40.6 mmol, 81% yield). Yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.67 – 7.59 (m, 1H), 7.52 – 7.44 (m, 2H), 7.37 – 7.28 (m, 2H), 7.26 – 7.19 (m, 3H), 6.87 (t, *J* = 5.8 Hz, 1H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.70 – 2.55 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 139.9, 134.1, 130.2, 128.9, 128.8, 128.7, 128.6, 126.5, 76.3, 41.0, 32.2.

FT-IR (film): 3027, 1738, 1602, 1453, 1245, 1065, 919, 711 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{16}H_{19}BrNO_2$: 336.0594, found: 336.0604.

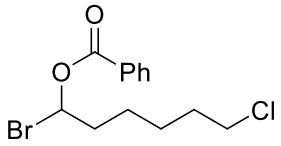


Bromo(tetrahydro-2*H*-pyran-4-yl)methyl benzoate. The title compound was synthesized according to **GP-1** from $ZnBr_2$ (235 mg, 1.1 mmol), BzBr (2.5 mL, 21 mmol), tetrahydro-2*H*-pyran-4-carbaldehyde (2.0 g, 18 mmol), and DCM (5 mL). The product was used without further purification (95 wt.%). 3.5 g (11.2 mmol, 64% yield). Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 2H), 7.66 – 7.58 (m, 1H), 7.53 – 7.43 (m, 2H), 6.77 (d, *J* = 5.4 Hz, 1H), 4.12 – 4.01 (m, 2H), 3.49 – 3.37 (m, 2H), 2.36 – 2.23 (m, 1H), 1.98 – 1.80 (m, 2H), 1.73 – 1.54 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 134.2, 130.2, 130.1, 128.8, 80.5, 67.42, 67.39*, 43.3, 29.5, 28.7.

FT-IR (film): 2951, 1732, 1602, 1451, 1258, 1064, 954, 711 cm^{-1}.

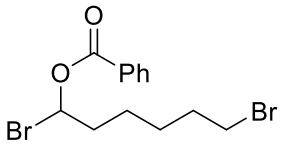


1-Bromo-6-chlorohexyl benzoate. The title compound was synthesized according to **GP-1** from $ZnBr_2$ (350 mg, 1.6 mmol), BzBr (4.5 mL, 38 mmol), 6-chlorohexanal (4.25 g, 31.6 mmol), and DCM (5 mL). The product was used without further purification (85 wt.%). 8.9 g (24 mmol, 75% yield). Brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.66 – 7.58 (m, 1H), 7.51 – 7.44 (m, 2H), 6.89 (t, *J* = 5.9 Hz, 1H), 3.55 (t, *J* = 6.6 Hz, 2H), 2.35 – 2.25 (m, 2H), 1.89 – 1.77 (m, 2H), 1.68 – 1.50 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 134.1, 130.2, 128.9, 128.7, 76.7, 44.9, 39.4, 32.4, 26.2, 25.3.

FT-IR (film): 2934, 1739, 1603, 1454, 1267, 1067, 996, 714 cm^{-1}.

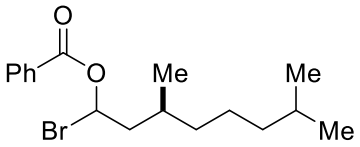


1,6-Dibromohexyl benzoate. The title compound was synthesized according to **GP-1** from $ZnBr_2$ (390 mg, 1.8 mmol), BzBr (4.9 mL, 42 mmol), 6-bromohexanal (6.2 g, 35 mmol), and DCM (5 mL). The product was used without further purification (89 wt.%). 8.9 g (22 mmol, 63% yield). Brown oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 2H), 7.65 – 7.59 (m, 1H), 7.50 – 7.45 (m, 2H), 6.89 (t, *J* = 5.8 Hz, 1H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.37 – 2.24 (m, 2H), 1.95 – 1.87 (m, 2H), 1.72 – 1.44 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 134.1, 130.1, 128.8, 128.7, 76.7, 39.3, 33.6, 32.5, 27.4, 25.2.

FT-IR (film): 2934, 1738, 1601, 1452, 1260, 1071, 980, 714 cm^{-1}.



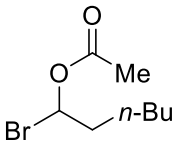
(3*S*)-1-Bromo-3,7-dimethyloctyl benzoate. The title compound was synthesized according to **GP-1** from $ZnBr_2$ (120 mg, 0.54 mmol), BzBr (1.6 mL, 13 mmol), (*S*)-3,7-dimethyloctanal (1.7 g, 11 mmol), and DCM (5 mL). The product was obtained as a mixture

of two diastereoisomers (~1:1) and used without further purification (62 wt.%). 3.7 g (6.7 mmol, 62% yield). Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.04 (m, 2H), 7.67 – 7.57 (m, 1H), 7.53 – 7.43 (m, 2H), 7.03 – 6.90 (m, 1H), 2.50 – 2.11 (m, 2H), 1.83 – 1.68 (m, 1H), 1.55 – 1.48 (m, 1H), 1.37 – 1.16 (m, 6H), 0.92 – 0.80 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.33, 164.26, 134.02, 134.00, 130.18, 130.15, 128.73, 128.71, 76.6, 75.7, 51.2, 47.0, 46.5, 39.2, 37.3, 37.0, 36.8, 30.8, 28.3, 28.1, 24.8, 24.6, 24.5, 22.8, 22.7, 20.1, 19.5, 19.3.

FT-IR (film): 2932, 1738, 1602, 1458, 1256, 1068, 993, 711 cm^{-1}.

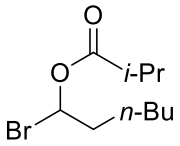


1-Bromohexyl acetate. The title compound was synthesized according to **GP-1** from $ZnCl_2$ (1.0 g, 7.5 mmol), AcBr (13.2 mL, 180 mmol), hexanal (18.4 mL, 150 mmol), and DCM (20 mL). The product was purified by vacuum distillation (b.p. = 58–59 °C, 1.0 Torr). 17.4 g (78.4 mmol, 52% yield). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (t, *J* = 6.1 Hz, 1H), 2.17 – 2.04 (m, 2H), 2.10 (s, 3H), 1.51 – 1.39 (m, 2H), 1.39 – 1.23 (m, 4H), 0.95 – 0.81 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 76.6, 39.4, 31.0, 25.6, 22.5, 21.1, 14.0.

FT-IR (film): 2956, 1767, 1449, 1375, 1211, 1027, 944, 687 cm^{-1}.

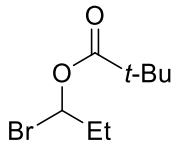


1-Bromohexyl isobutyrate. The title compound was synthesized according to **GP-1** from $ZnBr_2$ (555 mg, 2.5 mmol), isobutyryl bromide (6.4 mL, 60 mmol), hexanal (6.1 mL, 50 mmol), and DCM (10 mL). The product was purified by vacuum distillation (b.p. = 50–51 °C, 0.4 Torr). 7.2 g (29 mmol, 58% yield). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (t, *J* = 6.0 Hz, 1H), 2.69 – 2.49 (m, 1H), 2.22 – 2.06 (m, 2H), 1.51 – 1.41 (m, 2H), 1.36 – 1.28 (m, 4H), 1.19 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.8 Hz, 3H), 0.93 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 76.7, 39.5, 34.1, 31.0, 25.7, 22.5, 18.6, 18.5, 14.0.

FT-IR (film): 2960, 1760, 1467, 1388, 1230, 1108, 941, 680 cm^{-1}.



1-Bromopropyl pivalate. The title compound was synthesized according to **GP-1** from $ZnCl_2$ (480 mg, 3.6 mmol), pivaloyl bromide (14.0 g, 85.4 mmol), propionaldehyde (5.1 mL, 71 mmol), and DCM (10 mL). The product was purified by vacuum distillation (b.p. = 45–47 °C, 2.2 Torr). 6.6 g (30 mmol, 42% yield). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (t, *J* = 5.7 Hz, 1H), 2.22 – 2.08 (m, 2H), 1.21 (s, 9H), 1.04 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 78.0, 39.0, 32.8, 26.8, 10.4.

FT-IR (film): 2973, 1758, 1461, 1370, 1216, 1120, 969, 689 cm^{-1}.

III. Catalytic Enantioconvergent Couplings

General Procedure 2 (GP-2): MTBE as the solvent; electrophile is a liquid.

In the air, $NiBr_2$·diglyme (28.2 mg, 0.081 mmol, 0.10 equiv), (*S*,*S*)-**L*** (61.2 mg, 0.096 mmol, 0.12 equiv), and K_3PO_4·H_2O (552 mg, 2.4 mmol, 3.0 equiv) were added to an oven-dried 40 mL vial equipped with a cross stir bar. The vial was closed with a PTFE septum cap, the joint was wrapped with electrical tape, and the vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles). Anhydrous MTBE (8.0 mL) was added to the vial, and the mixture was stirred at room temperature for 30 min, at which time it was a pink heterogeneous solution. A balloon filled with nitrogen was attached to the reaction vial. Next, the electrophile (0.80 mmol, 1.0 equiv), olefin (2.4 mmol, 3.0 equiv), and triethoxysilane (440 μL, 2.4 mmol, 3.0 equiv) were added dropwise in turn to the reaction mixture. The balloon was removed, and the septum cap was sealed with vacuum grease. The mixture was stirred vigorously (1100 rpm) at room temperature for 20 h.

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 Et_2O. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.

General Procedure 3 (GP-3): MTBE as the solvent; electrophile is a solid.

In the air, $NiBr_2$·diglyme (28.2 mg, 0.081 mmol, 0.10 equiv), (*S*,*S*)-**L*** (61.2 mg, 0.096 mmol, 0.12 equiv), and K_3PO_4·H_2O (552 mg, 2.4 mmol, 3.0 equiv) were added to an oven-dried 40 mL vial equipped with a cross stir bar. The vial was closed with a PTFE septum cap, the joint was wrapped with electrical tape, and the vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles). Anhydrous MTBE (4.0 mL) was added to the vial, and the mixture was stirred at room temperature for 30 min, at which time it was a pink heterogeneous solution. A balloon filled with nitrogen was attached to the reaction vial.

Next, in the air, a separate oven-dried 20 mL vial was charged with the electrophile (0.80 mmol, 1.0 equiv). The vial was capped with a PTFE septum cap, and then it was evacuated and backfilled with nitrogen (three cycles). Anhydrous MTBE (4.0 mL) was added to this vial to dissolve the solid. Next, this solution of the electrophile was added in one portion via syringe to the catalyst solution, followed by the addition of olefin (2.4 mmol, 3.0 equiv) and triethoxysilane (440 μL, 2.4 mmol, 3.0 equiv). The balloon was removed, and the septum cap was sealed with vacuum grease. The mixture was stirred vigorously (1100 rpm) at room temperature for 20 h.

Work-up: Same as **GP-2**.

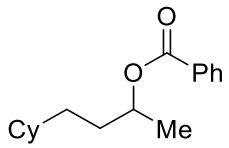
General Procedure 4 (GP-4): *i*-Pr_2O as the solvent; electrophile is a liquid.

In the air, $NiBr_2$·diglyme (28.2 mg, 0.081 mmol, 0.10 equiv), (*S*,*S*)-**L*** (61.2 mg, 0.096 mmol, 0.12 equiv), and K_3PO_4·H_2O (368 mg, 1.6 mmol, 2.0 equiv) were added to an oven-dried 40 mL vial equipped with a cross stir bar. The vial was closed with a PTFE septum cap, the joint was wrapped with electrical tape, and the vial was placed under a nitrogen atmosphere by

evacuating and backfilling the vial (three cycles). Anhydrous *i*-Pr_2O (4.0 mL) was added to the vial, and the mixture was stirred at room temperature for 30 min, at which time it was a yellow heterogeneous solution. A balloon filled with nitrogen was attached to the reaction vial. Next, the electrophile (0.80 mmol, 1.0 equiv), olefin (2.4 mmol, 3.0 equiv), and triethoxysilane (300 μL, 1.6 mmol, 2.0 equiv) were added dropwise in turn to the reaction mixture. The balloon was removed, and the septum cap was sealed with vacuum grease. The mixture was stirred vigorously (1100 rpm) at room temperature for 20 h.

Work-up: Same as **GP-2**.

General Procedure 5 (GP-5): Determination of enantioselectivity by converting the benzoate product to the corresponding phosphate. In the air, NaOH (48.0 mg, 1.2 mmol, 6.0 equiv) was added to a solution of the benzoate product (0.20 mmol, 1.0 equiv) in MeOH (6 mL). The reaction mixture was stirred at 50 °C for 24 h, and then the solvent was evaporated, and water (5 mL) was added to the residue. The reaction mixture was extracted with Et_2O (10 mL x 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to afford the alcohol, which was used directly without further purification. In the air, diphenyl phosphoryl chloride (83 μL, 0.38 mmol, 1.9 equiv) was added to a solution of the alcohol and DMAP (48.8 mg, 0.40 mmol, 2.0 equiv) in DCM (4 mL), and then the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was concentrated, and the residue was purified by flash chromatography on silica gel.



4-Cyclohexylbutan-2-yl benzoate (Figure 3, entry 1). The title compound was synthesized according to **GP-2** from 1-bromoethyl benzoate and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 169 mg, 81% yield, 92% ee; (*R*,*R*)-**L***: 171 mg, 82% yield, 93% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (0.5% *i*-PrOH in hexane, 0.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 12.5 min (major), 13.7 min (minor).

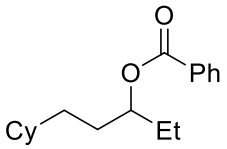
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.58 – 7.51 (m, 1H), 7.48 – 7.39 (m, 2H), 5.18 – 5.08 (m, 1H), 1.81 – 1.56 (m, 7H), 1.33 (d, *J* = 6.3 Hz, 3H), 1.32 – 1.06 (m, 6H), 0.95 – 0.80 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 132.8, 131.1, 129.6, 128.4, 72.2, 37.7, 33.52, 33.45, 33.2, 26.8, 26.5, 20.2.

FT-IR (film): 2929, 1716, 1603, 1451, 1276, 1110, 711 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{17}H_{28}NO_2$: 278.2115, found: 278.2114.

$[\alpha]^{23}_D$ = –28 (*c* 1.0, $CHCl_3$); 92% ee, from (*S*,*S*)-**L***.



1-Cyclohexylpentan-3-yl benzoate (Figure 3, entry 2). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 172 mg, 78% yield, 92% ee; (*R*,*R*)-**L***: 175 mg, 80% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (0.5% *i*-PrOH in hexane, 0.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 11.5 min (major), 12.7 min (minor).

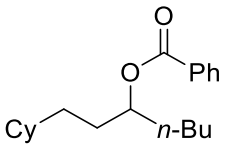
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 – 7.40 (m, 2H), 5.11 – 5.01 (m, 1H), 1.78 – 1.58 (m, 9H), 1.33 – 1.06 (m, 6H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.92 – 0.79 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 132.8, 131.0, 129.7, 128.4, 76.6, 37.8, 33.5, 33.4, 33.1, 31.1, 27.1, 26.8, 26.48, 26.46, 9.8.

FT-IR (film): 2920, 1716, 1602, 1450, 1276, 1111, 712 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{18}H_{30}NO_2$: 292.2271, found: 292.2275.

$[\alpha]^{23}_D$ = –8.4 (*c* 1.0, $CHCl_3$); 92% ee, from (*S*,*S*)-**L***.



1-Cyclohexylheptan-3-yl benzoate (Figure 3, entry 3). The title compound was synthesized according to **GP-2** from 1-bromopentyl benzoate and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 189 mg, 78% yield, 94% ee; (*R*,*R*)-**L***: 186 mg, 77% yield, 92% ee.

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

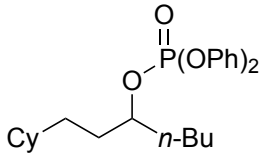
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.59 – 7.52 (m, 1H), 7.48 – 7.40 (m, 2H), 5.15 – 5.06 (m, 1H), 1.77 – 1.58 (m, 9H), 1.42 – 1.29 (m, 4H), 1.29 – 1.08 (m, 6H), 0.94 – 0.78 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 132.8, 131.0, 129.7, 128.4, 75.5, 37.8, 34.0, 33.5, 33.4, 33.1, 31.7, 27.7, 26.8, 26.49, 26.48, 22.8, 14.2.

FT-IR (film): 2921, 1715, 1603, 1453, 1274, 1114, 711 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{20}H_{34}NO_2$: 320.2584, found: 320.2583.

$[\alpha]^{23}_D$ = –2.2 (*c* 1.0, $CHCl_3$); 94% ee, from (*S*,*S*)-**L***.



1-Cyclohexylheptan-3-yl diphenyl phosphate. The title compound was synthesized according to **GP-5**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L***: 81.6 mg, 95% yield, 94% ee; (*R*,*R*)-**L***: 78.9 mg, 92% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 12.5 min (major), 13.8 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.28 – 7.22 (m, 4H), 7.18 (t, *J* = 7.3 Hz, 2H), 4.73 – 4.55 (m, 1H), 1.74 – 1.56 (m, 9H), 1.38 – 1.10 (m, 10H), 0.91 – 0.74 (m, 5H).

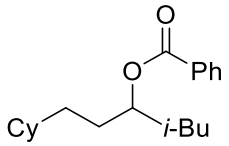
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (d, *J* = 7.1 Hz), 129.7, 125.2, 120.2 (d, *J* = 5.1 Hz), 82.8 (d, *J* = 7.1 Hz), 37.6, 34.7 (d, *J* = 5.1 Hz), 33.3, 33.2, 32.4, 32.33, 32.30, 26.9, 26.7, 26.4 (d, *J* = 1.0 Hz), 22.6, 14.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.4.

FT-IR (film): 2931, 1594, 1488, 1288, 1192, 1022, 768 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{25}H_{39}NO_4P$: 448.2611, found: 448.2621.

$[\alpha]^{23}_D$ = +1.9 (*c* 1.0, $CHCl_3$); 94% ee, from (*S*,*S*)-**L***.



1-Cyclohexyl-5-methylhexan-3-yl benzoate (Figure 3, entry 4). The title compound was synthesized according to **GP-2** from 1-bromo-3-methylbutyl benzoate and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 197 mg, 82% yield, 95% ee; (*R*,*R*)-**L***: 202 mg, 84% yield, 95% ee.

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

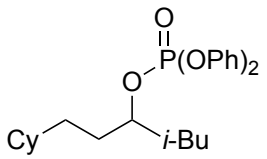
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.96 (m, 2H), 7.63 – 7.50 (m, 1H), 7.50 – 7.37 (m, 2H), 5.28 – 5.15 (m, 1H), 1.75 – 1.58 (m, 9H), 1.46 – 1.36 (m, 1H), 1.30 – 1.08 (m, 6H), 0.93 (d, *J* = 6.3 Hz, 6H), 0.91 – 0.79 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 132.8, 131.0, 129.7, 128.4, 73.9, 43.5, 37.8, 33.5, 33.4, 33.0, 32.3, 26.8, 26.49, 26.48, 24.0, 23.4, 22.4.

FT-IR (film): 2927, 1715, 1602, 1455, 1274, 1114, 713 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{20}H_{34}NO_2$: 320.2584, found: 320.2574.

$[\alpha]^{23}_D$ = +7.8 (*c* 1.0, $CHCl_3$); 95% ee, from (*S*,*S*)-**L***.



1-Cyclohexyl-5-methylhexan-3-yl diphenyl phosphate. The title compound was synthesized according to **GP-5**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L***: 79.0 mg, 92% yield, 95% ee; (*R*,*R*)-**L***: 79.0 mg, 92% yield, 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 11.9 min (minor), 15.2 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H), 7.27 – 7.20 (m, 4H), 7.20 – 7.13 (m, 2H), 4.74 – 4.63 (m, 1H), 1.74 – 1.56 (m, 9H), 1.41 – 1.30 (m, 1H), 1.25 – 1.05 (m, 6H), 0.94 – 0.74 (m, 8H).

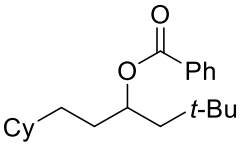
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (d, *J* = 7.1 Hz), 129.7 (d, *J* = 1.0 Hz), 125.2 (d, *J* = 1.0 Hz), 120.2 (d, *J* = 5.1 Hz), 81.2 (d, *J* = 6.1 Hz), 44.2 (d, *J* = 6.1 Hz), 37.6, 33.3, 33.2, 33.1, 33.0, 32.1, 26.7, 26.4 (d, *J* = 1.0 Hz), 24.4, 23.1, 22.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.4.

FT-IR (film): 2924, 1591, 1490, 1286, 1197, 1020, 762 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{25}H_{39}NO_4P$: 448.2611, found: 448.2619.

$[\alpha]^{23}_D$ = +10.8 (*c* 1.0, $CHCl_3$); 95% ee, from (*S*,*S*)-**L***.



1-Cyclohexyl-5,5-dimethylhexan-3-yl benzoate (Figure 3, entry 5). The title compound was synthesized according to **GP-2** from 1-bromo-3,3-dimethylbutyl benzoate and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 217 mg, 86% yield, 94% ee; (*R*,*R*)-**L***: 209 mg, 83% yield, 94% ee.

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

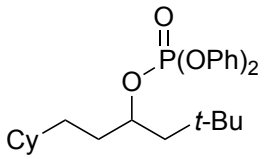
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.58 – 7.51 (m, 1H), 7.47 – 7.40 (m, 2H), 5.28 – 5.20 (m, 1H), 1.78 – 1.56 (m, 8H), 1.48 (dd, *J* = 14.8, 2.2 Hz, 1H), 1.27 – 1.07 (m, 6H), 0.93 (s, 9H), 0.90 – 0.79 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 132.8, 131.1, 129.7, 128.4, 73.2, 47.6, 37.9, 33.8, 33.5, 33.4, 32.8, 30.3, 30.1, 26.8, 26.5.

FT-IR (film): 2931, 1714, 1604, 1454, 1272, 1118, 709 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{21}H_{36}NO_2$: 334.2741, found: 334.2750.

$[\alpha]^{23}_D$ = +13.8 (*c* 1.0, $CHCl_3$); 94% ee, from (*S*,*S*)-**L***.



1-Cyclohexyl-5,5-dimethylhexan-3-yl diphenyl phosphate. The title compound was synthesized according to **GP-5**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L***: 69.6 mg, 78% yield, 94% ee; (*R*,*R*)-**L***: 74.4 mg, 83% yield, 94% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 11.2 min (minor), 15.6 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.27 – 7.22 (m, 4H), 7.22 – 7.14 (m, 2H), 4.85 – 4.69 (m, 1H), 1.78 – 1.58 (m, 8H), 1.53 – 1.44 (m, 1H), 1.31 – 1.06 (m, 6H), 0.95 (s, 9H), 0.89 – 0.74 (m, 2H).

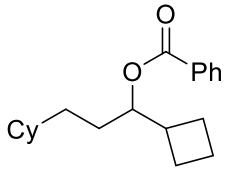
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8 (d, *J* = 7.1 Hz), 129.7 (d, *J* = 1.0 Hz), 125.1 (d, *J* = 2.0 Hz), 120.3 (d, *J* = 2.0 Hz), 120.2 (d, *J* = 2.0 Hz), 80.7 (d, *J* = 7.1 Hz), 48.4 (d, *J* = 7.1 Hz), 37.7, 34.7 (d, *J* = 2.0 Hz), 33.33, 33.26, 32.0, 30.1, 29.9, 26.7, 26.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.9.

FT-IR (film): 2938, 1596, 1495, 1288, 1202, 1010, 779 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{26}H_{41}NO_4P$: 462.2768, found: 462.2769.

$[\alpha]^{23}_D$ = +13.9 (*c* 1.0, $CHCl_3$); 94% ee, from (*S*,*S*)-**L***.



1-Cyclobutyl-3-cyclohexylpropyl benzoate (Figure 3, entry 6). The title compound was synthesized according to **GP-3** from bromo(cyclobutyl)methyl benzoate and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 195 mg, 81% yield, 98% ee; (*R*,*R*)-**L***: 190 mg, 79% yield, 98% ee.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 2H), 7.59 – 7.53 (m, 1H), 7.49 – 7.41 (m, 2H), 5.11 (q, *J* = 6.4 Hz, 1H), 2.68 – 2.54 (m, 1H), 2.07 – 1.91 (m, 3H), 1.91 – 1.73 (m, 3H), 1.73 – 1.50 (m, 7H), 1.29 – 1.02 (m, 6H), 0.93 – 0.76 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 132.8, 131.0, 129.7, 128.4, 78.1, 39.3, 37.8, 33.5, 33.4, 33.1, 29.5, 26.8, 26.49, 26.47, 24.7, 24.4, 18.2.

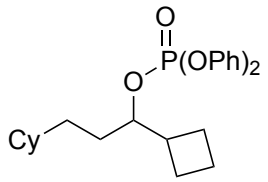
FT-IR (film): 2921, 1716, 1603, 1451, 1263, 1114, 708 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{20}H_{28}NaO_2$: 323.1982, found: 323.1966.

$[\alpha]^{23}_D$ = –4.0 (*c* 1.0, $CHCl_3$); 98% ee, from (*S*,*S*)-**L***.

Gram-scale reaction: In the air, $NiBr_2$·diglyme (176 mg, 0.50 mmol, 0.10 equiv), (*S*,*S*)-**L*** (383 mg, 0.60 mmol, 0.12 equiv), and K_3PO_4·H_2O (3.45 g, 15.0 mmol, 3.0 equiv) were added to an oven-dried 100 mL round-bottom flask equipped with a stir bar. The flask was closed with a rubber septum cap, the joint was wrapped with electrical tape, and the flask was placed under a nitrogen atmosphere by evacuating and backfilling the flask (three cycles). Anhydrous MTBE (20 mL) was added to the flask, and the mixture was stirred at room temperature for 30 min, at which time it was a pink heterogeneous solution. A balloon filled with nitrogen was attached to the reaction flask. In the air, a separate oven-dried 40 mL vial was charged with bromo(cyclobutyl)methyl benzoate (1.34 g, 5.0 mmol, 1.0 equiv). The vial was capped with a PTFE septum cap, and then it was evacuated and backfilled with nitrogen (three cycles). Anhydrous MTBE (20 mL) was added to the vial to dissolve the electrophile. Next, this solution of the electrophile was added in one portion via syringe to the catalyst solution, followed by the addition of vinyl cyclohexane (2.05 mL, 15.0 mmol, 3.0 equiv) and triethoxysilane (2.8 mL, 15.2 mmol, 3.0 equiv). The balloon was removed, and the septum was sealed with electrical tape. The reaction mixture was stirred vigorously (1100 rpm) at room temperature for 20 h. Next, the reaction mixture was passed through a 5 cm column of silica gel, and the flask, the septum, and the silica gel were rinsed with Et_2O. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 1.21 g, 81% yield, 99% ee.



1-Cyclobutyl-3-cyclohexylpropyl diphenyl phosphate. The title compound was synthesized according to **GP-5**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L***: 76.8 mg, 90% yield, 98% ee; (*R*,*R*)-**L***: 70.4 mg, 82% yield, 98% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 7.8 min (major), 8.7 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 7.26 – 7.20 (m, 4H), 7.20 – 7.13 (m, 2H), 4.60 – 4.49 (m, 1H), 2.65 – 2.50 (m, 1H), 2.03 – 1.76 (m, 5H), 1.72 – 1.48 (m, 8H), 1.24 – 1.04 (m, 6H), 0.86 – 0.69 (m, 2H).

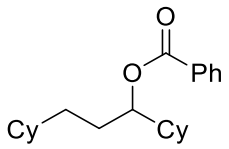
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.94 (d, *J* = 7.1 Hz), 150.93 (d, *J* = 7.1 Hz), 129.7, 125.2 (d, *J* = 1.0 Hz), 120.3 (d, *J* = 2.0 Hz), 120.2 (d, *J* = 1.0 Hz), 86.1 (d, *J* = 7.1 Hz), 39.5 (d, *J* = 5.1 Hz), 37.6, 33.4, 33.1, 32.2, 30.4, 30.3, 26.7, 26.4 (d, *J* = 2.0 Hz), 24.8, 24.4, 17.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.1.

FT-IR (film): 3483, 2922, 1596, 1488, 1286, 1204, 1016, 756 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{25}H_{37}NO_4P$: 446.2455, found: 446.2461.

$[\alpha]^{23}_D$ = +3.9 (*c* 1.0, $CHCl_3$); 98% ee, from (*S*,*S*)-**L***.



1,3-Dicyclohexylpropyl benzoate (Figure 3, entry 7). The title compound was synthesized according to **GP-3** from bromo(cyclohexyl)methyl benzoate and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 178 mg, 68% yield, 96% ee; (*R*,*R*)-**L***: 186 mg, 71% yield, 95% ee.

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

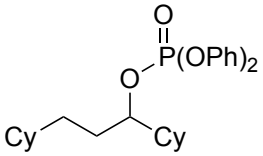
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.58 – 7.51 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.99 (q, *J* = 6.0 Hz, 1H), 1.84 – 1.58 (m, 13H), 1.29 – 1.05 (m, 11H), 0.94 – 0.76 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 132.8, 131.0, 129.7, 128.4, 79.1, 41.5, 37.8, 33.5, 33.3, 33.2, 29.3, 28.7, 28.2, 26.8, 26.6, 26.48, 26.46, 26.32, 26.26.

FT-IR (film): 2937, 1716, 1602, 1454, 1270, 713 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{22}H_{36}NO_2$: 346.2741, found: 346.2722.

$[\alpha]^{23}_D$ = –7.8 (*c* 1.0, $CHCl_3$); 96% ee, from (*S*,*S*)-**L***.



1,3-Dicyclohexylpropyl diphenyl phosphate. The title compound was synthesized according to **GP-5**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L***: 75.4 mg, 83% yield, 96% ee; (*R*,*R*)-**L***: 69.2 mg, 76% yield, 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AS column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 6.3 min (minor), 10.7 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.27 – 7.22 (m, 4H), 7.21 – 7.15 (m, 2H), 4.45 (ddd, *J* = 12.0, 7.2, 4.9 Hz, 1H), 1.79 – 1.56 (m, 13H), 1.29 – 1.00 (m, 11H), 0.89 – 0.72 (m, 2H).

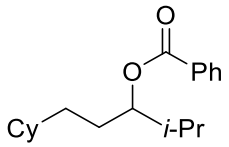
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0 (d, *J* = 7.1 Hz), 150.9 (d, *J* = 8.1 Hz), 129.7, 125.16 (d, *J* = 2.0 Hz), 125.15 (d, *J* = 1.0 Hz), 120.3 (d, *J* = 5.1 Hz), 120.2 (d, *J* = 5.1 Hz), 86.9 (d, *J* = 7.1 Hz), 41.7 (d, *J* = 5.1 Hz), 37.6, 33.4, 33.1, 32.5, 29.2 (d, *J* = 4.0 Hz), 28.4, 27.9, 26.7, 26.42, 26.40, 26.38, 26.2, 26.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.2.

FT-IR (film): 2925, 1592, 1494, 1292, 1191, 1010, 768 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{27}H_{41}NO_4P$: 474.2768, found: 474.2768.

$[\alpha]^{23}_D$ = –7.6 (*c* 1.0, $CHCl_3$); 96% ee, from (*S*,*S*)-**L***.



1-Cyclohexyl-4-methylpentan-3-yl benzoate (Figure 3, entry 8). The title compound was synthesized according to **GP-2** from 1-bromo-2-methylpropyl benzoate and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 161 mg, 70% yield, 94% ee; (*R*,*R*)-**L***: 154 mg, 67% yield, 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (0.5% *i*-PrOH in hexane, 0.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 10.2 min (major), 11.2 min (minor).

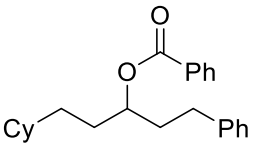
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 7.96 (m, 2H), 7.64 – 7.51 (m, 1H), 7.50 – 7.38 (m, 2H), 4.98 (dt, *J* = 7.1, 5.3 Hz, 1H), 2.05 – 1.88 (m, 1H), 1.78 – 1.55 (m, 7H), 1.27 – 1.07 (m, 6H), 0.97 (t, *J* = 7.0 Hz, 6H), 0.92 – 0.76 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 132.8, 131.0, 129.7, 128.4, 79.6, 37.8, 33.5, 33.4, 33.3, 31.6, 28.7, 26.8, 26.49, 26.47, 18.9, 17.7.

FT-IR (film): 2922, 1715, 1602, 1452, 1270, 1110, 709 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{19}H_{28}NaO_2$: 311.1982, found: 311.1984.

$[\alpha]^{23}_D$ = –8.1 (*c* 1.0, $CHCl_3$); 94% ee, from (*S*,*S*)-**L***.



1-Cyclohexyl-5-phenylpentan-3-yl benzoate (Figure 3, entry 9). The title compound was synthesized according to **GP-3** from 1-bromo-3-phenylpropyl benzoate and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 217 mg, 78% yield, 92% ee; (*R*,*R*)-**L***: 219 mg, 78% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 5.1 min (major), 5.8 min (minor).

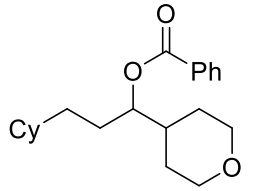
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 2H), 7.61 – 7.54 (m, 1H), 7.51 – 7.42 (m, 2H), 7.32 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 5.24 – 5.14 (m, 1H), 2.82 – 2.63 (m, 2H), 2.14 – 1.93 (m, 2H), 1.84 – 1.58 (m, 7H), 1.37 – 1.06 (m, 6H), 0.97 – 0.79 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 141.8, 132.9, 130.8, 129.7, 128.53, 128.45, 126.0, 75.0, 37.7, 36.1, 33.43, 33.40, 32.9, 31.9, 31.7, 26.8, 26.5.

FT-IR (film): 2928, 1716, 1603, 1455, 1276, 1111, 716 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{24}H_{34}NO_2$: 368.2584, found: 368.2584.

$[\alpha]^{23}_D$ = +5.6 (*c* 1.0, $CHCl_3$); 92% ee, from (*S*,*S*)-**L***.



3-Cyclohexyl-1-(tetrahydro-2*H*-pyran-4-yl)propyl benzoate (Figure 3, entry 10). The title compound was synthesized according to **GP-2** from bromo(tetrahydro-2*H*-pyran-4-yl)methyl benzoate and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:4 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 184 mg, 70% yield, 97% ee; (*R*,*R*)-**L***: 177 mg, 67% yield, 96% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 9.3 min (major), 12.1 min (minor).

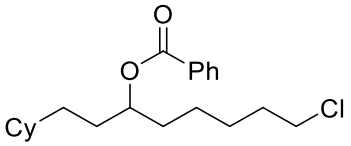
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 7.99 (m, 2H), 7.60 – 7.53 (m, 1H), 7.49 – 7.42 (m, 2H), 5.02 (q, *J* = 6.1 Hz, 1H), 4.09 – 3.90 (m, 2H), 3.45 – 3.28 (m, 2H), 1.96 – 1.82 (m, 1H), 1.73 – 1.42 (m, 11H), 1.31 – 1.04 (m, 6H), 0.93 – 0.77 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 133.0, 130.6, 129.7, 128.5, 78.0, 68.1, 67.9, 38.9, 37.8, 33.5, 33.3, 33.0, 29.3, 28.5, 28.2, 26.7, 26.5, 26.4.

FT-IR (film): 2920, 1715, 1602, 1454, 1274, 710 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+H]^+$ calcd for $C_{21}H_{31}O_3$: 331.2268, found: 331.2267.

$[\alpha]^{23}_D$ = –9.8 (*c* 1.0, $CHCl_3$); 97% ee, from (*S*,*S*)-**L***.



8-Chloro-1-cyclohexyloctan-3-yl benzoate (Figure 3, entry 11). The title compound was synthesized according to **GP-2** from 1-bromo-6-chlorohexyl benzoate and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 199 mg, 71% yield, 92% ee; (*R*,*R*)-**L***: 196 mg, 70% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 6.3 min (minor), 7.8 min (major).

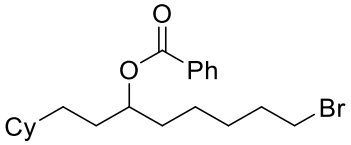
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 2H), 7.60 – 7.52 (m, 1H), 7.49 – 7.40 (m, 2H), 5.15 – 5.06 (m, 1H), 3.51 (t, *J* = 6.7 Hz, 2H), 1.81 – 1.60 (m, 11H), 1.53 – 1.33 (m, 4H), 1.30 – 1.09 (m, 6H), 0.96 – 0.78 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 132.9, 130.9, 129.7, 128.5, 75.3, 45.1, 37.7, 34.2, 33.5, 33.4, 33.1, 32.6, 31.7, 27.0, 26.8, 26.47, 26.46, 24.8.

FT-IR (film): 2922, 1716, 1603, 1450, 1278, 1114, 710 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{21}H_{35}ClNO_2$: 368.2351, found: 368.2353.

$[\alpha]^{23}_D$ = +0.86 (*c* 1.0, $CHCl_3$); 92% ee, from (*S*,*S*)-**L***.



8-Bromo-1-cyclohexyloctan-3-yl benzoate (Figure 3, entry 12). The title compound was synthesized according to **GP-2** from 1,6-dibromohexyl benzoate and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 204 mg, 65% yield, 94% ee; (*R*,*R*)-**L***: 204 mg, 65% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (0.5% *i*-PrOH in hexane, 0.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 14.4 min (major), 16.6 min (minor).

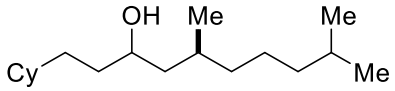
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.98 (m, 2H), 7.65 – 7.51 (m, 1H), 7.51 – 7.39 (m, 2H), 5.20 – 5.03 (m, 1H), 3.38 (t, *J* = 6.8 Hz, 2H), 1.91 – 1.80 (m, 2H), 1.76 – 1.57 (m, 9H), 1.52 – 1.32 (m, 4H), 1.32 – 1.05 (m, 6H), 0.94 – 0.78 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 132.9, 130.9, 129.7, 128.5, 75.3, 37.7, 34.1, 33.9, 33.5, 33.4, 33.1, 32.8, 31.7, 28.3, 26.8, 26.47, 26.46, 24.7.

FT-IR (film): 2930, 1715, 1602, 1449, 1272, 1113, 710 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{21}H_{35}BrNO_2$: 412.1846, found: 412.1845.

$[\alpha]^{23}_D$ = +1.1 (*c* 1.0, $CHCl_3$); 94% ee, from (*S*,*S*)-**L***.



(5*S*)-1-Cyclohexyl-5,9-dimethyldecan-3-ol (Figure 3, entries 13 and 14). The title compound was synthesized according to **GP-2** and **GP-5** (the benzoates could not be properly purified) from (3*S*)-1-bromo-3,7-dimethyloctyl benzoate and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:9 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 167 mg, 78% yield, 4:96 d.r.; (*R*,*R*)-**L***: 169 mg, 79% yield, 96:4 d.r.

HPLC analysis: The d.r. was determined after transforming the product to the corresponding phosphate.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 – 3.59 (m, 1H), 1.77 – 1.57 (m, 6H), 1.57 – 1.37 (m, 4H), 1.36 – 1.09 (m, 14H), 0.95 – 0.80 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 70.2, 45.2, 39.4, 38.3, 38.0, 35.8, 33.6, 33.54, 33.47, 29.4, 28.1, 26.8, 26.54, 26.52, 24.9, 22.84, 22.76, 19.4.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 – 3.58 (m, 1H), 1.76 – 1.42 (m, 8H), 1.39 – 1.11 (m, 15H), 1.10 – 1.01 (m, 1H), 0.96 – 0.79 (m, 11H).

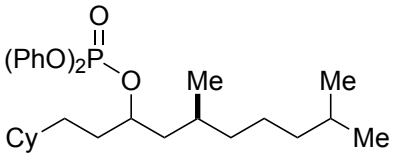
^{13}C NMR (101 MHz, $CDCl_3$) δ 70.5, 45.4, 39.5, 37.9, 37.0, 35.2, 33.7, 33.44, 33.36, 29.8, 28.1, 26.8, 26.54, 26.52, 24.7, 22.9, 22.7, 20.6.

FT-IR (film): 3341, 2920, 1717, 1456, 1070 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M-OH]^+$ calcd for $C_{18}H_{35}$: 251.2733, found: 251.2727.

$[\alpha]^{23}_D$ = +9.4 (*c* 1.0, $CHCl_3$); 4:96 d.r., from (*S*,*S*)-**L***.

$[\alpha]^{23}_D$ = –5.7 (*c* 1.0, $CHCl_3$); 96:4 d.r., from (*R*,*R*)-**L***.



(5*S*)-1-Cyclohexyl-5,9-dimethyldecan-3-yl diphenyl phosphate. The title compound was synthesized according to **GP-5**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L***: 102 mg, 99% yield, 4:96 d.r.; (*R*,*R*)-**L***: 99.4 mg, 99% yield, 96:4 d.r.

HPLC analysis: The d.r. was determined via HPLC on a CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 8.1 min (minor), 10.5 min (major).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.26 – 7.20 (m, 4H), 7.20 – 7.13 (m, 2H), 4.79 – 4.63 (m, 1H), 1.78 – 1.57 (m, 8H), 1.57 – 1.41 (m, 2H), 1.33 – 1.01 (m, 13H), 0.94 – 0.71 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.93 (d, *J* = 7.1 Hz), 150.92 (d, *J* = 7.1 Hz), 129.8, 125.2, 120.3 (d, *J* = 4.0 Hz), 120.2 (d, *J* = 5.1 Hz), 81.2 (d, *J* = 7.1 Hz), 42.7 (d, *J* = 6.1 Hz), 39.3, 37.8, 37.7, 33.50, 33.47, 33.34, 33.26, 32.3, 29.0, 28.1, 26.7, 26.4, 24.7, 22.8, 22.7, 19.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.4.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.26 – 7.20 (m, 4H), 7.20 – 7.13 (m, 2H), 4.77 – 4.64 (m, 1H), 1.73 – 1.57 (m, 7H), 1.57 – 1.42 (m, 4H), 1.37 – 1.00 (m, 12H), 0.92 – 0.77 (m, 11H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (d, *J* = 7.1 Hz), 129.8, 125.2 (d, *J* = 1.0 Hz), 120.2 (d, *J* = 5.1 Hz), 81.3 (d, *J* = 7.1 Hz), 42.5 (d, *J* = 5.1 Hz), 39.3, 37.6, 37.0, 33.4, 33.2, 32.64, 32.60, 32.0, 29.3, 28.1, 26.7, 26.4 (d, *J* = 2.0 Hz), 24.6, 22.8, 22.7, 20.0.

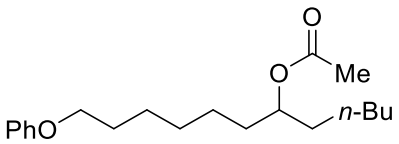
^{31}P NMR (162 MHz, $CDCl_3$) δ –12.4.

FT-IR (film): 2926, 2365, 1594, 1486, 1384, 1287, 1017, 770, 688 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{30}H_{49}NO_4P$: 518.3394, found: 518.3392.

$[\alpha]^{23}_D$ = +11.9 (*c* 1.0, $CHCl_3$); 4:96 d.r., from (*S*,*S*)-**L***.

$[\alpha]^{23}_D$ = –8.6 (*c* 1.0, $CHCl_3$); 96:4 d.r., from (*R*,*R*)-**L***.



12-Phenoxydodecan-6-yl acetate (Figure 3, entry 15). The title compound was synthesized according to **GP-4** from 1-bromohexyl acetate and (hex-5-en-1-yloxy)benzene. The product was purified by column chromatography on silica gel (1:9 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 162 mg, 63% yield, 93% ee; (*R*,*R*)-**L***: 167 mg, 65% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 10.8 min (minor), 14.0 min (major).

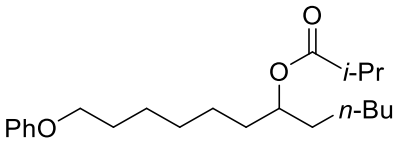
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 6.96 – 6.86 (m, 3H), 4.94 – 4.82 (m, 1H), 3.95 (t, *J* = 6.5 Hz, 2H), 2.04 (s, 3H), 1.83 – 1.71 (m, 2H), 1.59 – 1.41 (m, 6H), 1.40 – 1.18 (m, 10H), 0.95 – 0.81 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 159.2, 129.5, 120.6, 114.6, 74.5, 67.9, 34.21, 34.18, 31.9, 29.4, 29.3, 26.1, 25.4, 25.1, 22.7, 21.4, 14.2.

FT-IR (film): 2928, 1732, 1601, 1496, 1373, 1243, 754 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{20}H_{32}NaO_3$: 343.2244, found: 343.2245.

$[\alpha]^{23}_D$ = +1.5 (*c* 1.0, $CHCl_3$); 93% ee, from (*S*,*S*)-**L***.



12-Phenoxydodecan-6-yl isobutyrate (Figure 3, entry 16). The title compound was synthesized according to **GP-4** from 1-bromohexyl isobutyrate and (hex-5-en-1-yloxy)benzene. The product was purified by column chromatography on silica gel (1:25 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 166 mg, 60% yield, 94% ee; (*R*,*R*)-**L***: 170 mg, 61% yield, 95% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 8.5 min (major), 10.0 min (minor).

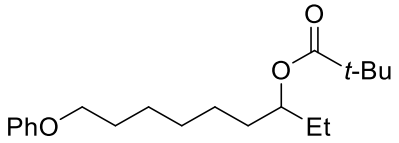
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 2H), 7.00 – 6.82 (m, 3H), 4.93 – 4.81 (m, 1H), 3.94 (t, *J* = 6.5 Hz, 2H), 2.52 (hept, *J* = 7.0 Hz, 1H), 1.86 – 1.72 (m, 2H), 1.57 – 1.41 (m, 6H), 1.39 – 1.23 (m, 10H), 1.16 (d, *J* = 7.0 Hz, 6H), 0.92 – 0.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 159.2, 129.5, 120.6, 114.6, 73.9, 67.9, 34.4, 34.24, 34.22, 31.8, 29.4, 29.3, 26.1, 25.4, 25.1, 22.7, 19.3, 14.1.

FT-IR (film): 2934, 1732, 1601, 1497, 1387, 1245, 751 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{22}H_{40}NO_3$: 366.3003, found: 366.3003.

$[\alpha]^{23}_D$ = +0.5 (*c* 1.0, $CHCl_3$); 94% ee, from (*S*,*S*)-**L***.



9-Phenoxynonan-3-yl pivalate (Figure 3, entry 17). The title compound was synthesized according to **GP-4** from 1-bromopropyl pivalate and (hex-5-en-1-yloxy)benzene. The product was purified by column chromatography on silica gel (1:9 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 106 mg, 41% yield, 91% ee; (*R*,*R*)-**L***: 105 mg, 41% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (0.5% *i*-PrOH in hexane, 0.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 11.7 min (major), 13.0 min (minor).

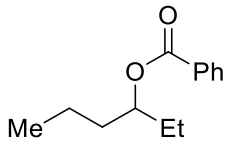
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.17 (m, 2H), 7.03 – 6.82 (m, 3H), 4.89 – 4.72 (m, 1H), 3.94 (t, *J* = 6.5 Hz, 2H), 1.83 – 1.72 (m, 2H), 1.63 – 1.49 (m, 4H), 1.49 – 1.28 (m, 6H), 1.20 (s, 9H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 159.2, 129.5, 120.6, 114.6, 75.0, 67.9, 39.0, 33.7, 29.4, 29.3, 27.4, 27.1, 26.1, 25.3, 9.7.

FT-IR (film): 2942, 1731, 1601, 1498, 1396, 1244, 754 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{20}H_{36}NO_3$: 338.2690, found: 338.2696.

$[\alpha]^{23}_D$ = +3.1 (*c* 1.0, $CHCl_3$); 91% ee, from (*S*,*S*)-**L***.



Hexan-3-yl benzoate (Figure 3, entry 18). In the air, $NiBr_2$·diglyme (28.2 mg, 0.081 mmol, 0.10 equiv), (*S*,*S*)-**L*** (61.2 mg, 0.096 mmol, 0.12 equiv), and K_3PO_4·H_2O (552 mg, 2.4 mmol, 3.0 equiv) were added to an oven-dried 25 mL side-armed Schlenk tube equipped with a stir bar. The tube was closed with two rubber septa, and it was placed under a nitrogen atmosphere by evacuating and backfilling the tube (three cycles). Anhydrous MTBE (8.0 mL) was added to the tube, and the mixture was stirred at room temperature for 30 min, at which time it was a pink heterogeneous solution. A balloon filled with nitrogen was attached to the side arm. Then 1-bromopropyl benzoate (194 mg, 0.80 mmol, 1.0 equiv) and triethoxysilane (440 μL, 2.4 mmol, 3.0 equiv) were added dropwise in turn to the reaction mixture. The top rubber septum was switched quickly to a Chem-Cap® valve, and the balloon attached to the side arm was removed. The side arm of the Schlenk tube was attached to a vacuum manifold. The solution was frozen in liquid nitrogen, and the tube was placed under vacuum. The flask was sealed under vacuum and separated from the vacuum manifold. Next, a balloon filled with propylene was attached to the side arm. The gas in the balloon was condensed into the Schlenk tube at 77 K (~1.0 mL), and the flask was resealed. The balloon was removed, and the mixture was stirred vigorously (1100 rpm) at room temperature for 20 h.

Work-up: Same as **GP-2**. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 139 mg, 84% yield, 89% ee; (*R*,*R*)-**L***: 130 mg, 79% yield, 87% ee.

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

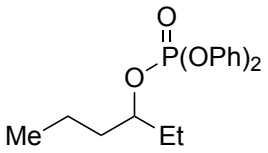
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.99 (m, 2H), 7.62 – 7.50 (m, 1H), 7.49 – 7.33 (m, 2H), 5.18 – 5.02 (m, 1H), 1.76 – 1.55 (m, 4H), 1.49 – 1.32 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 132.8, 131.0, 129.7, 128.4, 76.1, 36.0, 27.3, 18.8, 14.2, 9.8.

FT-IR (film): 2966, 1717, 1452, 1272, 1107, 712 cm^{-1}.

GC-MS (EI) m/z $[M]^+$ calcd for $C_{13}H_{18}O_2$: 206.1, found: 206.2.

$[\alpha]^{23}_D$ = –4.8 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L***.



Hexan-3-yl diphenyl phosphate. The title compound was synthesized according to **GP-5**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L***: 33.8 mg, 51% yield, 89% ee; (*R*,*R*)-**L***: 33.4 mg, 50% yield, 87% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 10.0 min (major), 11.9 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H), 7.25 – 7.20 (m, 4H), 7.20 – 7.14 (m, 2H), 4.69 – 4.52 (m, 1H), 1.78 – 1.51 (m, 4H), 1.46 – 1.27 (m, 2H), 0.91 (t, *J* = 7.6 Hz, 3H), 0.88 (t, *J* = 7.6 Hz, 3H).

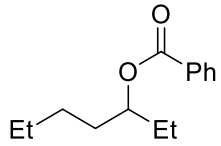
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (d, *J* = 7.1 Hz), 129.8, 125.2 (d, *J* = 1.0 Hz), 120.3 (d, *J* = 2.0 Hz), 120.2 (d, *J* = 2.0 Hz), 83.3 (d, *J* = 7.1 Hz), 36.6 (d, *J* = 5.1 Hz), 27.9 (d, *J* = 4.0 Hz), 18.2, 14.0, 9.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.3.

FT-IR (film): 2964, 2366, 1591, 1489, 1292, 1194, 1016, 772 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{18}H_{27}NO_4P$: 352.1672, found: 352.1680.

$[\alpha]^{23}_D$ = –5.0 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L***.



Heptan-3-yl benzoate (Figure 3, entry 19). A solution of the catalyst was prepared according to **GP-2**. After a balloon filled with nitrogen was attached to the reaction vial, 1-bromopropyl benzoate (194 mg, 0.80 mmol, 1.0 equiv), a solution of 1-butene in toluene (10 wt.%, 2.24 g, 4.0 mmol, 5.0 equiv), and triethoxysilane (440 μL, 2.4 mmol, 3.0 equiv) were added dropwise in turn to the reaction mixture. The balloon was removed, and the septum cap was sealed with vacuum grease. The mixture was stirred vigorously (1100 rpm) at room temperature for 20 h.

Work-up: Same as **GP-2**. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 146 mg, 83% yield, 91% ee; (*R*,*R*)-**L***: 150 mg, 85% yield, 90% ee.

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

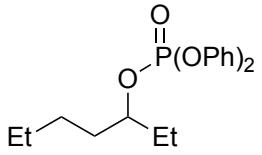
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.58 – 7.52 (m, 1H), 7.47 – 7.40 (m, 2H), 5.08 (tt, *J* = 7.4, 5.6 Hz, 1H), 1.77 – 1.61 (m, 4H), 1.42 – 1.28 (m, 4H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.92 – 0.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 132.8, 131.0, 129.7, 128.4, 76.3, 33.5, 27.7, 27.2, 22.8, 14.2, 9.8.

FT-IR (film): 2962, 1716, 1452, 1274, 1110, 711 cm^{-1}.

GC-MS (EI) m/z $[M]^+$ calcd for $C_{14}H_{20}O_2$: 220.1, found: 220.2.

$[\alpha]^{23}_D$ = –7.2 (*c* 1.0, $CHCl_3$); 91% ee, from (*S*,*S*)-**L***.



Heptan-3-yl diphenyl phosphate. The title compound was synthesized according to **GP-5**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L***: 48.4 mg, 70% yield, 91% ee; (*R*,*R*)-**L***: 49.2 mg, 71% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 9.5 min (major), 12.8 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 7.26 – 7.20 (m, 4H), 7.20 – 7.13 (m, 2H), 4.71 – 4.45 (m, 1H), 1.74 – 1.55 (m, 4H), 1.37 – 1.19 (m, 4H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.87 – 0.81 (m, 3H).

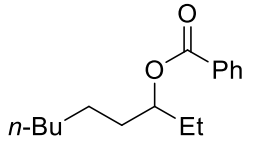
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (d, *J* = 7.1 Hz), 129.8, 125.2, 120.3 (d, *J* = 2.0 Hz), 120.2 (d, *J* = 1.0 Hz), 83.5 (d, *J* = 6.1 Hz), 34.2 (d, *J* = 5.1 Hz), 27.9 (d, *J* = 4.0 Hz), 27.0, 22.6, 14.0, 9.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.3.

FT-IR (film): 2955, 2361, 1593, 1488, 1292, 1199, 1014, 751 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{19}H_{29}NO_4P$: 366.1829, found: 366.1836.

$[\alpha]^{23}_D$ = –3.6 (*c* 1.0, $CHCl_3$); 91% ee, from (*S*,*S*)-**L***.



Nonan-3-yl benzoate (Figure 3, entry 20). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and 1-hexene. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 140 mg, 70% yield, 89% ee; (*R*,*R*)-**L***: 135 mg, 68% yield, 89% ee.

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

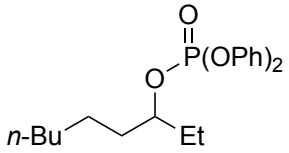
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H), 7.58 – 7.51 (m, 1H), 7.48 – 7.40 (m, 2H), 5.18 – 4.99 (m, 1H), 1.77 – 1.62 (m, 4H), 1.44 – 1.19 (m, 8H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.91 – 0.81 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 132.8, 131.0, 129.7, 128.4, 76.3, 33.8, 31.9, 29.4, 27.2, 25.5, 22.7, 14.2, 9.8.

FT-IR (film): 2931, 1716, 1603, 1452, 1272, 1109, 712 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{16}H_{28}NO_2$: 266.2115, found: 266.2117.

$[\alpha]^{23}_D$ = –8.9 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L***.



Nonan-3-yl diphenyl phosphate. The title compound was synthesized according to **GP-5**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L***: 56.5 mg, 75% yield, 89% ee; (*R*,*R*)-**L***: 52.9 mg, 70% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 8.6 min (major), 11.6 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.26 – 7.20 (m, 4H), 7.20 – 7.13 (m, 2H), 4.68 – 4.50 (m, 1H), 1.76 – 1.54 (m, 4H), 1.38 – 1.14 (m, 8H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 6.9 Hz, 3H).

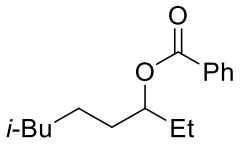
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (d, *J* = 7.1 Hz), 129.8, 125.2 (d, *J* = 1.0 Hz), 120.2 (d, *J* = 5.1 Hz), 83.5 (d, *J* = 6.1 Hz), 34.5 (d, *J* = 5.1 Hz), 31.8, 29.2, 27.9 (d, *J* = 4.0 Hz), 24.8, 22.6, 14.2, 9.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.3.

FT-IR (film): 2936, 1594, 1495, 1294, 1202, 1012, 764 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{21}H_{33}NO_4P$: 394.2142, found: 394.2147.

$[\alpha]^{23}_D$ = –3.3 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L***.



7-Methyloctan-3-yl benzoate (Figure 3, entry 21). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and 4-methylpent-1-ene. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 158 mg, 80% yield, 90% ee; (*R*,*R*)-**L***: 149 mg, 75% yield, 91% ee.

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

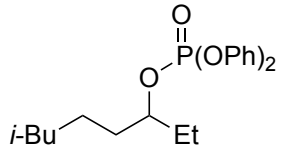
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H), 7.59 – 7.52 (m, 1H), 7.48 – 7.41 (m, 2H), 5.16 – 5.01 (m, 1H), 1.76 – 1.58 (m, 4H), 1.58 – 1.46 (m, 1H), 1.44 – 1.29 (m, 2H), 1.26 – 1.13 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 132.8, 131.0, 129.7, 128.4, 76.3, 39.0, 34.0, 27.9, 27.2, 23.3, 22.72, 22.65, 9.8.

FT-IR (film): 2953, 1716, 1603, 1453, 1274, 1111, 711 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{16}H_{24}NaO_2$: 271.1669, found: 271.1673.

$[\alpha]^{23}_D$ = –10.6 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L***.



7-Methyloctan-3-yl diphenyl phosphate. The title compound was synthesized according to **GP-5**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L***: 44.4 mg, 59% yield, 90% ee; (*R*,*R*)-**L***: 45.9 mg, 61% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 9.0 min (major), 12.2 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.26 – 7.20 (m, 4H), 7.20 – 7.14 (m, 2H), 4.67 – 4.53 (m, 1H), 1.77 – 1.52 (m, 4H), 1.51 – 1.40 (m, 1H), 1.39 – 1.20 (m, 2H), 1.19 – 1.04 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 6H).

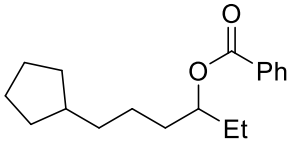
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (d, *J* = 8.1 Hz), 129.8, 125.2 (d, *J* = 1.0 Hz), 120.23 (d, *J* = 2.0 Hz), 120.19 (d, *J* = 2.0 Hz), 83.5 (d, *J* = 7.1 Hz), 38.8, 34.7 (d, *J* = 5.1 Hz), 28.0, 27.94, 27.91, 22.7, 22.6 (d, *J* = 2.0 Hz), 9.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.3.

FT-IR (film): 2956, 1593, 1488, 1290, 1199, 1012, 764 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{21}H_{33}NO_4P$: 394.2142, found: 394.2143.

$[\alpha]^{23}_D$ = –3.5 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L***.



6-Cyclopentylhexan-3-yl benzoate (Figure 3, entry 22). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and allylcyclopentane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 159 mg, 72% yield, 88% ee; (*R*,*R*)-**L***: 165 mg, 75% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (0.5% *i*-PrOH in hexane, 0.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 11.0 min (major), 11.9 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.00 (m, 2H), 7.58 – 7.52 (m, 1H), 7.47 – 7.40 (m, 2H), 5.19 – 5.00 (m, 1H), 1.76 – 1.27 (m, 15H), 1.12 – 0.98 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

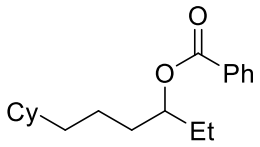
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 132.8, 131.0, 129.7, 128.4, 76.3, 40.1, 36.2, 34.1, 32.81, 32.76, 27.2, 25.3, 24.7, 9.8.

FT-IR (film): 2948, 1716, 1451, 1270, 1110, 710 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{18}H_{30}NO_2$: 292.2271, found: 292.2274.

$[\alpha]^{23}_D$ = –10.6 (*c* 1.0, $CHCl_3$); 88% ee, from (*S*,*S*)-**L***.

The title compound was also synthesized according to **GP-2**, using 2.0 equiv of the olefin: (*S*,*S*)-**L***: 160 mg, 73% yield, 89% ee; (*R*,*R*)-**L***: 158 mg, 72% yield, 90% ee.



6-Cyclohexylhexan-3-yl benzoate (Figure 3, entry 23). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and allylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 174 mg, 76% yield, 90% ee; (*R*,*R*)-**L***: 176 mg, 76% yield, 90% ee.

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

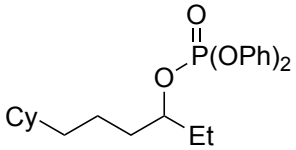
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 – 7.40 (m, 2H), 5.17 – 4.99 (m, 1H), 1.77 – 1.54 (m, 9H), 1.46 – 1.28 (m, 2H), 1.27 – 1.05 (m, 6H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.90 – 0.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 132.8, 131.0, 129.7, 128.4, 76.4, 37.6, 37.5, 34.1, 33.5, 33.4, 27.2, 26.8, 26.53, 26.52, 22.8, 9.8.

FT-IR (film): 2926, 1716, 1451, 1273, 1116, 712 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{19}H_{32}NO_2$: 306.2428, found: 306.2431.

$[\alpha]^{23}_D$ = –12.1 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L***.



6-Cyclohexylhexan-3-yl diphenyl phosphate. The title compound was synthesized according to **GP-5**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L***: 81.4 mg, 98% yield, 90% ee; (*R*,*R*)-**L***: 81.5 mg, 98% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 8.6 min (major), 10.2 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.27 – 7.20 (m, 4H), 7.20 – 7.10 (m, 2H), 4.68 – 4.50 (m, 1H), 1.75 – 1.50 (m, 9H), 1.40 – 1.02 (m, 8H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.87 – 0.70 (m, 2H).

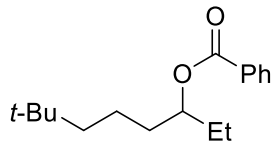
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (d, *J* = 7.1 Hz), 129.7, 125.2, 120.2 (d, *J* = 5.1 Hz), 83.5 (d, *J* = 6.1 Hz), 37.6, 37.3, 34.7 (d, *J* = 5.1 Hz), 33.38, 33.35, 28.0, 27.9, 26.8, 26.5, 22.2, 9.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.3.

FT-IR (film): 2920, 1596, 1488, 1286, 1195, 1022, 756 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{24}H_{37}NO_4P$: 434.2455, found: 434.2458.

$[\alpha]^{23}_D$ = –3.9 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L***.



7,7-Dimethyloctan-3-yl benzoate (Figure 3, entry 24). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and 4,4-dimethylpent-1-ene. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 165 mg, 79% yield, 88% ee; (*R*,*R*)-**L***: 162 mg, 77% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (0.5% *i*-PrOH in hexane, 0.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 10.3 min (minor), 11.1 min (major).

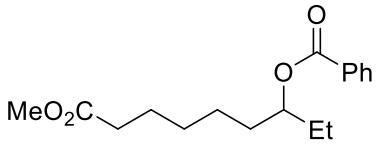
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.99 (m, 2H), 7.60 – 7.51 (m, 1H), 7.50 – 7.38 (m, 2H), 5.16 – 5.02 (m, 1H), 1.78 – 1.53 (m, 4H), 1.42 – 1.12 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.84 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 132.8, 131.0, 129.7, 128.4, 76.3, 44.2, 34.7, 30.4, 29.5, 27.2, 20.5, 9.8.

FT-IR (film): 2948, 1716, 1452, 1272, 1113, 711 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{17}H_{30}NO_2$: 280.2271, found: 280.2267.

$[\alpha]^{23}_D$ = –10.8 (*c* 1.0, $CHCl_3$); 88% ee, from (*S*,*S*)-**L***.



9-Methoxy-9-oxononan-3-yl benzoate (Figure 3, entry 25). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and methyl hex-5-enoate. The

product was purified by column chromatography on silica gel (1:4 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 146 mg, 62% yield, 86% ee; (*R*,*R*)-**L***: 148 mg, 63% yield, 88% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 8.6 min (major), 9.3 min (minor).

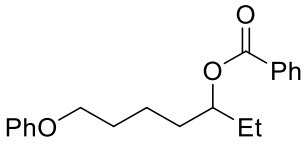
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.99 (m, 2H), 7.63 – 7.50 (m, 1H), 7.49 – 7.35 (m, 2H), 5.15 – 5.00 (m, 1H), 3.64 (s, 3H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.75 – 1.55 (m, 6H), 1.46 – 1.29 (m, 4H), 0.94 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 166.5, 132.9, 130.9, 129.7, 128.4, 76.1, 51.6, 34.1, 33.6, 29.2, 27.2, 25.2, 24.9, 9.8.

FT-IR (film): 2940, 1715, 1456, 1274, 1112, 715 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{17}H_{28}NO_4$: 310.2013, found: 310.2016.

$[\alpha]^{23}_D$ = –8.7 (*c* 1.0, $CHCl_3$); 86% ee, from (*S*,*S*)-**L***.



7-Phenoxyheptan-3-yl benzoate (Figure 3, entry 26). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and (but-3-en-1-yloxy)benzene. The product was purified by column chromatography on silica gel (1:10 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 171 mg, 69% yield, 89% ee; (*R*,*R*)-**L***: 179 mg, 72% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (1% *i*-PrOH in hexane, 0.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 7.0 min (major), 7.8 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.01 (m, 2H), 7.60 – 7.53 (m, 1H), 7.49 – 7.42 (m, 2H), 7.31 – 7.23 (m, 2H), 6.97 – 6.90 (m, 1H), 6.89 – 6.83 (m, 2H), 5.20 – 5.06 (m, 1H), 3.95 (t, *J* = 6.4 Hz, 2H), 1.93 – 1.67 (m, 6H), 1.66 – 1.47 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H).

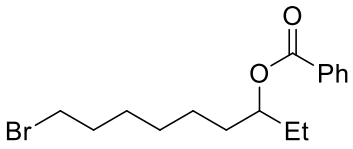
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 159.1, 132.9, 130.9, 129.7, 129.5, 128.5, 120.6, 114.6, 76.0, 67.6, 33.6, 29.3, 27.2, 22.1, 9.8.

FT-IR (film): 2948, 1715, 1601, 1495, 1272, 1110, 710 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{20}H_{24}NaO_3$: 335.1618, found: 335.1621.

$[\alpha]^{23}_D$ = –11.5 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L***.

The title compound was also synthesized according to **GP-2**, using 2.0 equiv of the olefin: (*S*,*S*)-**L***: 159 mg, 64% yield, 89% ee; (*R*,*R*)-**L***: 163 mg, 65% yield, 90% ee.



9-Bromononan-3-yl benzoate (Figure 3, entry 27). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and 6-bromohex-1-ene. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 165 mg, 63% yield, 92% ee; (*R*,*R*)-**L***: 171 mg, 66% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 8.2 min (major), 9.5 min (minor).

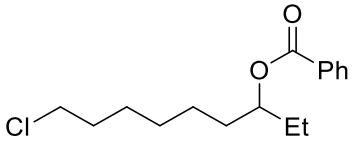
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.99 (m, 2H), 7.62 – 7.50 (m, 1H), 7.50 – 7.38 (m, 2H), 5.14 – 5.01 (m, 1H), 3.38 (t, *J* = 6.8 Hz, 2H), 1.89 – 1.79 (m, 2H), 1.75 – 1.62 (m, 4H), 1.48 – 1.30 (m, 6H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 132.9, 130.9, 129.7, 128.5, 76.1, 34.1, 33.7, 32.8, 28.8, 28.2, 27.2, 25.3, 9.8.

FT-IR (film): 2933, 2358, 1714, 1602, 1451, 1277, 1112, 710 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{16}H_{27}BrNO_2$: 344.1220, found: 344.1227.

$[\alpha]^{23}_D$ = –8.0 (*c* 1.0, $CHCl_3$); 92% ee, from (*S*,*S*)-**L***.



9-Chlorononan-3-yl benzoate (Figure 3, entry 28). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and 6-chlorohex-1-ene. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 157 mg, 70% yield, 88% ee; (*R*,*R*)-**L***: 147 mg, 65% yield, 87% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 5.8 min (major), 6.4 min (minor).

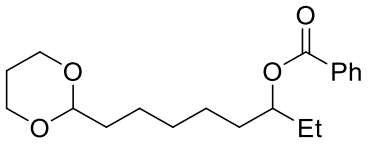
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.00 (m, 2H), 7.62 – 7.51 (m, 1H), 7.50 – 7.38 (m, 2H), 5.16 – 5.01 (m, 1H), 3.51 (t, *J* = 6.7 Hz, 2H), 1.80 – 1.62 (m, 6H), 1.48 – 1.30 (m, 6H), 0.95 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 132.9, 130.9, 129.7, 128.5, 76.2, 45.2, 33.7, 32.7, 28.9, 27.3, 26.9, 25.4, 9.8.

FT-IR (film): 2934, 2358, 1715, 1602, 1452, 1276, 1114, 717 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{16}H_{27}ClNO_2$: 300.1725, found: 300.1729.

$[\alpha]^{23}_D$ = –9.2 (*c* 1.0, $CHCl_3$); 88% ee, from (*S*,*S*)-**L***.



8-(1,3-Dioxan-2-yl)octan-3-yl benzoate (Figure 3, entry 29). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and 2-(pent-4-en-1-yl)-1,3-dioxane. The product was purified by column chromatography on silica gel (1:4 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 173 mg, 68% yield, 89% ee; (*R*,*R*)-**L***: 176 mg, 69% yield, 88% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 9.2 min (minor), 10.8 min (major).

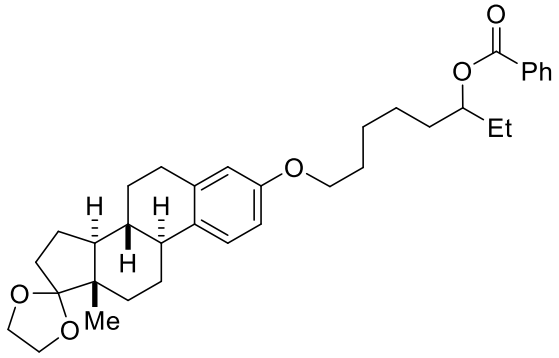
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.00 (m, 2H), 7.61 – 7.50 (m, 1H), 7.48 – 7.35 (m, 2H), 5.14 – 5.00 (m, 1H), 4.48 (t, *J* = 5.2 Hz, 1H), 4.14 – 4.02 (m, 2H), 3.78 – 3.65 (m, 2H), 2.16 – 1.96 (m, 1H), 1.77 – 1.51 (m, 6H), 1.46 – 1.27 (m, 7H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 132.8, 131.0, 129.7, 128.4, 102.4, 76.2, 67.0, 35.3, 33.7, 29.5, 27.2, 26.0, 25.4, 24.0, 9.8.

FT-IR (film): 2951, 1716, 1456, 1276, 1145, 714 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{19}H_{32}NO_4$: 338.2326, found: 338.2335.

$[\alpha]^{23}_D$ = –8.3 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L***.



8-(((8*R*,9*S*,13*S*,14*S*)-13-Methyl-6,7,8,9,11,12,13,14,15,16 decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)oxy)octan-3-yl benzoate (Figure 3, entries 30 and 31). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(pent-4-en-1-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolane]. The product was purified by column chromatography on silica gel (1:4 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 354 mg, 81% yield, 95:5 d.r.; (*R*,*R*)-**L***: 344 mg, 79% yield, 7:93 d.r.

HPLC analysis: The d.r. was determined via HPLC on a CHIRALPAK IC column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 10.0 min (major), 10.9 min (minor).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.99 (m, 2H), 7.63 – 7.51 (m, 1H), 7.48 – 7.40 (m, 2H), 7.18 (d, *J* = 8.7 Hz, 1H), 6.67 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.60 (d, *J* = 2.7 Hz, 1H), 5.16 – 5.02 (m, 1H), 3.99 – 3.87 (m, 6H), 2.88 – 2.77 (m, 2H), 2.38 – 2.16 (m, 2H), 2.10 – 1.97 (m, 1H), 1.92 – 1.59 (m, 11H), 1.57 – 1.28 (m, 9H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 157.0, 138.1, 132.8, 132.7, 130.9, 129.7, 128.4, 126.4, 119.6, 114.5, 112.1, 76.2, 67.8, 65.4, 64.7, 49.5, 46.3, 43.8, 39.2, 34.4, 33.8, 30.9, 29.9, 29.4, 27.2, 27.1, 26.3, 26.2, 25.3, 22.5, 14.5, 9.8.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.99 (m, 2H), 7.59 – 7.52 (m, 1H), 7.48 – 7.41 (m, 2H), 7.18 (d, *J* = 8.6 Hz, 1H), 6.67 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.60 (d, *J* = 2.7 Hz, 1H), 5.16 – 5.02 (m, 1H), 4.02 – 3.87 (m, 6H), 2.87 – 2.78 (m, 2H), 2.37 – 2.17 (m, 2H), 2.10 – 1.98 (m, 1H), 1.92 – 1.61 (m, 11H), 1.57 – 1.28 (m, 9H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 157.0, 138.1, 132.9, 132.7, 130.9, 129.7, 128.4, 126.4, 119.6, 114.6, 112.1, 76.2, 67.8, 65.4, 64.7, 49.5, 46.3, 43.8, 39.2, 34.4, 33.8, 30.9, 29.9, 29.4, 27.2, 27.1, 26.3, 26.2, 25.3, 22.5, 14.5, 9.8.

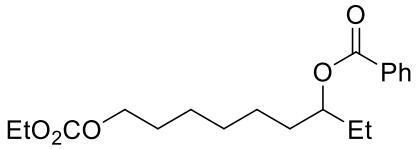
FT-IR (film): 3416, 2922, 1714, 1607, 1470, 1275, 717 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{35}H_{50}NO_5$: 564.3684, found: 564.3679.

$[\alpha]^{23}_D$ = +13.5 (*c* 1.0, $CHCl_3$); 95:5 d.r., from (*S*,*S*)-**L***.

$[\alpha]^{23}_D$ = +22.4 (*c* 1.0, $CHCl_3$); 7:93 d.r., from (*R*,*R*)-**L***.

The title compound was also synthesized according to **GP-2**, using 2.0 equiv of the olefin: (*S*,*S*)-**L***: 281 mg, 64% yield, 94:6 d.r.; (*R*,*R*)-**L***: 294 mg, 67% yield, 6:94 d.r.



9-((Ethoxycarbonyl)oxy)nonan-3-yl benzoate (Figure 3, entry 32). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and ethyl hex-5-en-1-yl carbonate. The product was purified by column chromatography on silica gel (1:5 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 169 mg, 63% yield, 91% ee; (*R*,*R*)-**L***: 175 mg, 65% yield, 91% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 8.8 min (major), 9.9 min (minor).

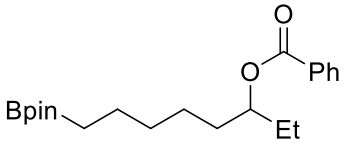
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.99 (m, 2H), 7.61 – 7.50 (m, 1H), 7.49 – 7.37 (m, 2H), 5.14 – 5.00 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.10 (t, *J* = 6.7 Hz, 2H), 1.77 – 1.57 (m, 6H), 1.44 – 1.22 (m, 9H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 155.4, 132.9, 130.9, 129.7, 128.4, 76.2, 68.0, 63.9, 33.7, 29.3, 28.7, 27.2, 25.8, 25.4, 14.4, 9.8.

FT-IR (film): 2939, 2357, 1716, 1603, 1455, 1269, 1109, 712 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{19}H_{28}NaO_5$: 359.1829, found: 359.1838.

$[\alpha]^{23}_D$ = –8.1 (*c* 1.0, $CHCl_3$); 91% ee, from (*S*,*S*)-**L***.



8-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)octan-3-yl benzoate (Figure 3, entry 33). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and 4,4,5,5-tetramethyl-2-(pent-4-en-1-yl)-1,3,2-dioxaborolane. The product was purified by column chromatography on silica gel (1:4 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 194 mg, 68% yield, 88% ee; (*R*,*R*)-**L***: 182 mg, 63% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 20.1 min (minor), 21.4 min (major).

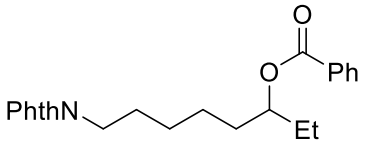
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.99 (m, 2H), 7.58 – 7.51 (m, 1H), 7.47 – 7.39 (m, 2H), 5.16 – 4.98 (m, 1H), 1.74 – 1.61 (m, 4H), 1.45 – 1.26 (m, 6H), 1.23 (s, 12H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.75 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 132.8, 131.0, 129.7, 128.4, 83.0, 76.3, 33.7, 32.5, 27.2, 25.3, 24.9, 24.0, 11.4, 9.8.

FT-IR (film): 2933, 1716, 1456, 1361, 1113, 717 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{21}H_{37}BNO_4$: 378.2810, found: 378.2817.

$[\alpha]^{23}_D$ = –8.5 (*c* 1.0, $CHCl_3$); 88% ee, from (*S*,*S*)-**L***.



8-(1,3-Dioxoisoindolin-2-yl)octan-3-yl benzoate (Figure 3, entry 34). The title compound was synthesized according to **GP-2** from 1-bromopropyl benzoate and 2-(pent-4-en-1-yl)isoindoline-1,3-dione. The product was purified by column chromatography on silica gel (1:3 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 223 mg, 74% yield, 89% ee; (*R*,*R*)-**L***: 234 mg, 77% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 13.4 min (major), 16.7 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.99 (m, 2H), 7.90 – 7.79 (m, 2H), 7.77 – 7.64 (m, 2H), 7.60 – 7.49 (m, 1H), 7.49 – 7.36 (m, 2H), 5.13 – 4.98 (m, 1H), 3.66 (t, *J* = 7.6 Hz, 2H), 1.79 – 1.55 (m, 6H), 1.50 – 1.27 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 166.5, 134.0, 132.8, 132.3, 130.9, 129.7, 128.4, 123.3, 76.1, 38.1, 33.7, 28.6, 27.2, 27.0, 25.1, 9.8.

FT-IR (film): 3470, 2922, 1714, 1277, 701 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{23}H_{25}NNaO_4$: 402.1676, found: 402.1677.

$[\alpha]^{23}_D$ = –4.4 (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L***.

The title compound was also synthesized according to **GP-2**, using 2.0 equiv of the olefin: (*S*,*S*)-**L***: 202 mg, 67% yield, 89% ee; (*R*,*R*)-**L***: 205 mg, 68% yield, 89% ee.

IV. Effect of Reaction Parameters

General Procedure 6 (GP-6).

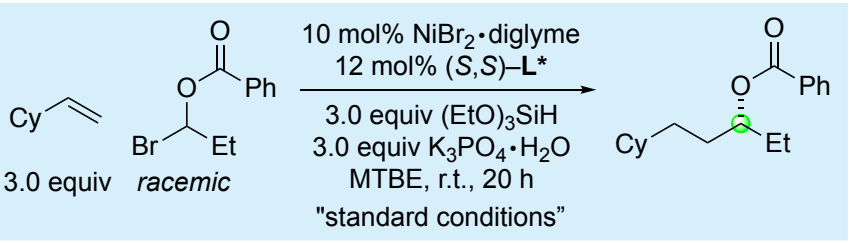
Preparation of a solution of the catalyst: In a nitrogen-filled glovebox, an oven-dried 4 mL vial that contained a magnetic stir bar was charged with $NiBr_2$·diglyme (3.5 mg, 0.010 mmol, 0.10 equiv), (*S*,*S*)-**L*** (7.7 mg, 0.012 mmol, 0.12 equiv), and $K_3PO_4·H_2O$ (69 mg, 0.30 mmol, 3.0 equiv). Next, anhydrous MTBE (1.0 mL) was added, the vial was capped with a PTFE septum cap, and the mixture was stirred at room temperature for 30 min, at which time it was a pink heterogeneous solution.

Coupling: In a nitrogen-filled glovebox, the electrophile (0.10 mmol, 1.0 equiv), olefin (0.30 mmol, 3.0 equiv), and triethoxysilane (55 μL, 0.30 mmol, 3.0 equiv) were added in turn dropwise to the reaction mixture. The vial was capped with a PTFE septum cap and taken out of the glovebox. The mixture was stirred vigorously (1100 rpm) at room temperature for 20 h.

Work-up: *n*-Dodecane (23 μL, 0.10 mmol, 1.0 equiv) was added via syringe. The reaction mixture was passed through a short pad of silica gel, with Et_2O as the eluent. The solvent was removed under reduced pressure, and the residue was purified by chromatography.

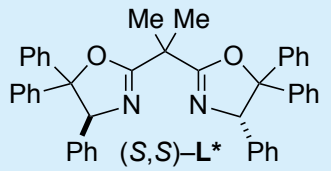
1-Bromopropyl benzoate was reacted with vinylcyclohexane according to **GP-6**. The yields were determined via GC analysis, with *n*-dodecane as the internal standard. The ee values were determined via HPLC analysis after purification by preparative thin-layer chromatography. All data are the average of two experiments.

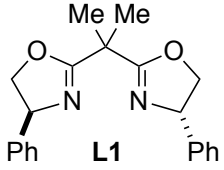
Table S-1. Effect of Reaction Parameters.

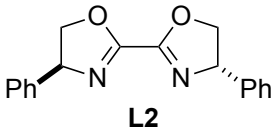


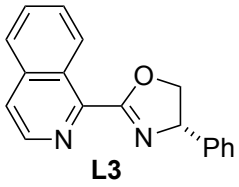
entry	variation from the "standard conditions"	yield (%)[a]	ee (%)[b]
1	none	78	92
2	no $NiBr_2$•diglyme	<1	–
3	no (*S*,*S*)–**L***	<1	–
4	**L1**, instead of (*S*,*S*)–**L***	31	19
5	**L2**, instead of (*S*,*S*)–**L***	8	<2
6	**L3**, instead of (*S*,*S*)–**L***	15	<2
7	**L4**, instead of (*S*,*S*)–**L***	7	51
8	**L5**, instead of (*S*,*S*)–**L***	10	<2
9	*i*-Pr_2O, instead of MTBE	74	92
10	Et_2O, instead of MTBE	64	90
11	5.0 mol% $NiBr_2$•diglyme, 6.0 mol% (*S*,*S*)–**L***	38	85
12	2.0 equiv vinylcyclohexane	59	89
13	1.5 equiv $(EtO)_3SiH$, 1.5 equiv K_3PO_4•H_2O	53	92
14	$(MeO)_3SiH$, instead of $(EtO)_3SiH$	74	92
15	$(EtO)_2MeSiH$, instead of $(EtO)_3SiH$	63	89
16	10, instead of 20, h	59	91
17	0.1 equiv H_2O added	76	92
18	under air in a closed vial	61	90

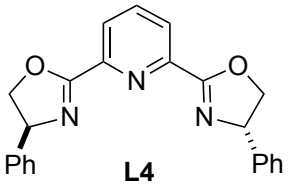
All data are the average of two experiments. [a] Determined through GC analysis. [b] Determined through HPLC analysis.

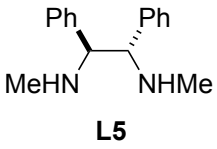










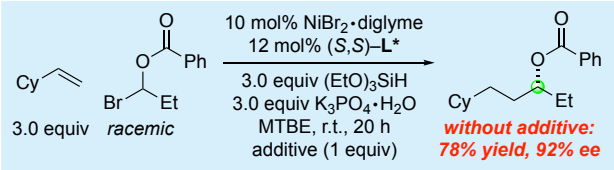


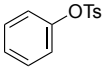
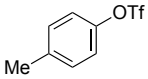
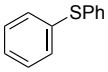
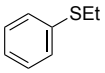
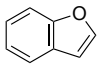
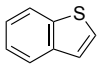
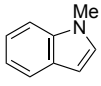
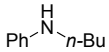
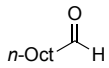
V. Functional-Group Compatibility

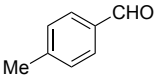
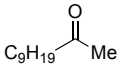
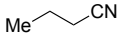
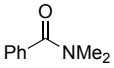
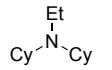
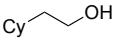
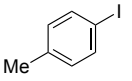
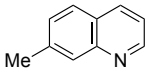
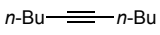
1-Bromopropyl benzoate was reacted with vinylcyclohexane according to **GP-6**, in the presence of 1.0 equiv of the additives shown below. The additive was added after the vinylcyclohexane.

The yield of the coupling product and the percent recovery of the additive were determined via GC analysis, with *n*-dodecane as the internal standard. The ee values were determined via HPLC analysis after purification by preparative thin-layer chromatography.

Table S-2. Functional-Group Compatibility.



entry	additive	recovery of additive (%)	yield (%)[a]	ee (%)[b]
1		>95	80	91
2		>95	78	91
3		>95	81	91
4		>95	79	89
5		>95	76	89
6		>95	80	89
7		>95	79	90
8		>95	78	90
9		>95	78	91
10		>95	79	87
11		>95	76	90
12		>95	81	91

entry	additive	recovery of additive (%)	yield (%)[a]	ee (%)[b]
13		>95	79	91
14		>95	77	90
15		>95	78	89
16		>95	78	91
17		>95	65	91
18		>95	72	89
19		>95	66	89
20		>95	54	84
21		64	76	90
22		94	43	92
23		88	18	52
24		59	20	66

[a] Analyzed via GC.
[b] Analyzed via HPLC.

VI. Four-Component Reactions

General Procedure 7 (GP-7): MTBE as the solvent.

Preparation of a solution of the electrophile: In the air, ZnF_2 (8.2 mg, 0.080 mmol, 0.10 equiv) was added to an oven-dried 4 mL vial equipped with a stir bar. The vial was closed with a PTFE septum cap, the joint was wrapped with electrical tape, and the vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles). Then, the acyl bromide (0.80 mmol, 1.0 equiv) and DCM (0.5 mL) were added. The resulting solution was cooled to –20 °C, and the resulting mixture was stirred for 10 min. At this temperature, the aldehyde (1.0 equiv) was added dropwise via microsyringe over 1 min, and the resulting mixture was stirred for 2 h.

Preparation of a solution of the catalyst: In the air, $NiBr_2$·diglyme (28.2 mg, 0.081 mmol, 0.10 equiv), (*S*,*S*)-**L*** (61.2 mg, 0.096 mmol, 0.12 equiv), and K_3PO_4·H_2O (552 mg, 2.4 mmol, 3.0 equiv) were added to a separate oven-dried 40 mL vial equipped with a cross stir bar. The vial was closed with a PTFE septum cap, the joint was wrapped with electrical tape, and the vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles). Anhydrous MTBE (4 mL) was added to the vial, and the mixture was stirred at room temperature for 30 min.

Coupling: A balloon filled with nitrogen was attached to a 40 mL vial. Then, the solution of the electrophile was added via syringe in one portion. The 4 mL vial was rinsed with MTBE, and the rinses (2 mL x 2) were added to the 40 mL vial. Next, the olefin (2.4 mmol, 3.0 equiv) and triethoxysilane (440 μL, 2.4 mmol, 3.0 equiv) were added in turn dropwise to the reaction mixture. The balloon was removed, and the septum cap was sealed with vacuum grease. The mixture was stirred vigorously (1100 rpm) at room temperature for 20 h.

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 Et_2O. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.

General Procedure 8 (GP-8): *i*-Pr_2O as the solvent.

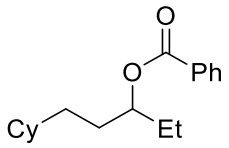
Preparation of the electrophile: Same as **GP-7**.

Preparation of a solution of the catalyst: In the air, $NiBr_2$·diglyme (28.2 mg, 0.081 mmol, 0.10 equiv), (*S*,*S*)-**L*** (61.2 mg, 0.096 mmol, 0.12 equiv), and K_3PO_4·H_2O (368 mg, 1.6 mmol, 2.0 equiv) were added to a separate oven-dried 40 mL vial equipped with a cross stir bar. The vial was closed with a PTFE septum cap, the joint was wrapped with electrical tape, and the vial was placed under a nitrogen atmosphere by evacuating and backfilling the vial (three cycles). Anhydrous *i*-Pr_2O (2 mL) was added to the vial, and the mixture was stirred at room temperature for 30 min.

Coupling: A balloon filled with nitrogen was attached to a 40 mL vial. Then, the solution of the electrophile was added via syringe in one portion. The 4 mL vial was rinsed with *i*-Pr_2O, and the rinses (1 mL x 2) were added to the 40 mL vial. Next, the olefin (2.4 mmol, 3.0

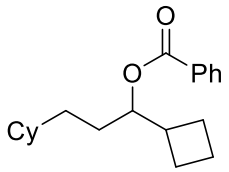
equiv) and triethoxysilane (300 μL, 1.6 mmol, 2.0 equiv) were added in turn dropwise to the reaction mixture. The balloon was removed, and the septum cap was sealed with vacuum grease. The mixture was stirred vigorously (1100 rpm) at room temperature for 20 h.

Work-up: Same as **GP-7**.



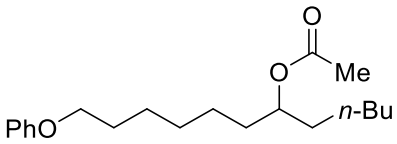
1-Cyclohexylpentan-3-yl benzoate (Figure 4, entry 35). The title compound was synthesized according to **GP-7** from benzoyl bromide, propionaldehyde, and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 151 mg, 69% yield, 92% ee; (*R*,*R*)-**L***: 158 mg, 72% yield, 90% ee.



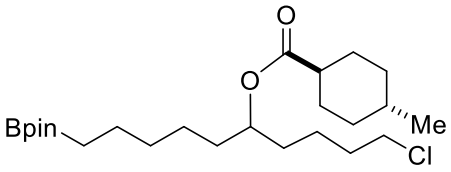
1-Cyclobutyl-3-cyclohexylpropyl benzoate (Figure 4, entry 36). The title compound was synthesized according to **GP-7** from benzoyl bromide, cyclobutanecarbaldehyde, and vinylcyclohexane. The product was purified by column chromatography on silica gel (1:40 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 170 mg, 71% yield, 95% ee; (*R*,*R*)-**L***: 169 mg, 70% yield, 96% ee.



12-Phenoxydodecan-6-yl acetate (Figure 4, entry 37). The title compound was synthesized according to **GP-8** from acetyl bromide, hexanal, and (hex-5-en-1-yloxy)benzene. The product was purified by column chromatography on silica gel (1:9 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 150 mg, 58% yield, 91% ee; (*R*,*R*)-**L***: 149 mg, 58% yield, 91% ee.



1-Chloro-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decan-5-yl (1*r*,4*r*)-4-methylcyclohexane-1-carboxylate (Figure 4, entry 38). The title compound was synthesized according to **GP-8** from (1*r*,4*r*)-4-methylcyclohexane-1-carbonyl bromide, 5-chloropentanal, and 4,4,5,5-tetramethyl-2-(pent-4-en-1-yl)-1,3,2-dioxaborolane. The product was purified by column chromatography on silica gel (1:5 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 234 mg, 66% yield, 92% ee; (*R*,*R*)-**L***: 229 mg, 65% yield, 92% ee.

HPLC analysis: The ee was determined after transforming the Bpin group to an OBz group (see below).

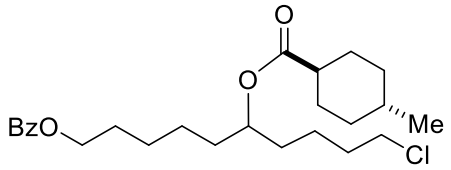
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 – 4.78 (m, 1H), 3.51 (t, *J* = 6.8 Hz, 2H), 2.17 (tt, *J* = 12.2, 3.6 Hz, 1H), 1.97 – 1.88 (m, 2H), 1.83 – 1.68 (m, 4H), 1.58 – 1.17 (m, 27H), 0.98 – 0.90 (m, 2H), 0.88 (d, *J* = 6.4 Hz, 3H), 0.75 (t, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 94.1, 83.0, 73.3, 45.0, 43.7, 34.4, 34.2, 33.5, 32.5, 32.4, 32.2, 29.3, 25.2, 25.0, 24.0, 22.71, 22.67, 11.6.

FT-IR (film): 3420, 2918, 1734, 1448, 1267, 1146, 850, 728 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{24}H_{48}BClNO_4$: 460.3359, found: 460.3352.

$[\alpha]^{23}_D$ = –3.7 (*c* 1.0, $CHCl_3$); 92% ee, from (*S*,*S*)-**L***.



10-Chloro-6-(((1*r*,4*r*)-4-methylcyclohexane-1-carbonyl)oxy)decyl benzoate. The purified product (44.2 mg, 0.10 mmol, 1.0 equiv) was oxidized with $NaBO_3 \cdot 4H_2O$ (73.8 mg, 0.48 mmol, 4.8 equiv) in THF/H_2O (1:1; 6 mL) at room temperature for 16 h. The mixture was extracted with Et_2O (5 mL x 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to afford the primary alcohol, which was used without further purification.

In the air, benzoyl chloride (24 uL, 0.21 mmol, 2.0 equiv) was added to a solution of the primary alcohol and pyridine (16 uL, 0.20 mmol, 2.0 equiv) in DCM (2 mL). The reaction mixture was stirred at room temperature for 3 h, and then it was concentrated. The product was purified by flash chromatography on silica gel (1:5 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 33.1 mg, 76% yield, 92% ee; (*R*,*R*)-**L***: 29.8 mg, 68% yield, 92% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OD column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 7.5 min (major), 8.9 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) 8.09 – 7.98 (m, 2H), 7.62 – 7.50 (m, 1H), 7.49 – 7.37 (m, 2H), 4.97 – 4.79 (m, 1H), 4.30 (t, *J* = 6.6 Hz, 2H), 3.51 (t, *J* = 6.6 Hz, 2H), 2.18 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.01 –

1.86 (m, 2H), 1.85 – 1.67 (m, 6H), 1.63 – 1.27 (m, 13H), 0.97 – 0.90 (m, 2H), 0.88 (d, J = 6.8 Hz, 3H).

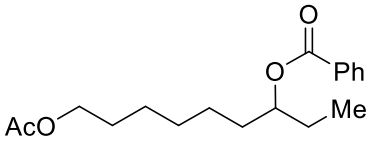
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 166.8, 133.0, 130.6, 129.7, 128.5, 73.1, 65.0, 45.0, 43.6, 34.4, 34.2, 33.5, 32.4, 32.1, 29.3, 28.8, 26.1, 25.1, 22.71, 22.65.

FT-IR (film): 3441, 2938, 2332, 1716, 1452, 1267, 1166, 1026, 718 cm^{-1}.

HRMS (ESI-MS) m/z $[M+Na]^+$ calcd for $C_{25}H_{37}ClNaO_4$: 459.2273, found: 459.2285.

$[\alpha]^{23}_D$ = –2.1 (c 0.35, $CHCl_3$); 92% ee, from (*S*,*S*)-**L***.

VII. Applications



9-Acetoxynonan-3-yl benzoate (Figure 4, entry 39). The title compound was synthesized according to **GP-7** from benzoyl bromide, propionaldehyde, and hex-5-en-1-yl acetate. The product was purified by column chromatography on silica gel (1:5 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 136 mg, 55% yield, 90% ee; (*R*,*R*)-**L***: 133 mg, 54% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (2% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 6.9 min (major), 7.6 min (minor).

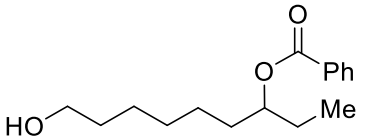
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 7.97 (m, 2H), 7.64 – 7.49 (m, 1H), 7.50 – 7.38 (m, 2H), 5.15 – 5.00 (m, 1H), 4.03 (t, *J* = 6.7 Hz, 2H), 2.03 (s, 3H), 1.79 – 1.54 (m, 6H), 1.47 – 1.27 (m, 6H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 166.5, 132.8, 130.9, 129.6, 128.4, 76.2, 64.7, 33.7, 29.3, 28.6, 27.2, 25.9, 25.4, 21.1, 9.8.

FT-IR (film): 3548, 2936, 1715, 1602, 1453, 1365, 1271, 1110, 711 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{18}H_{26}NaO_4$: 329.1723, found: 329.1731.

$[\alpha]^{23}_D$ = –8.5 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L***.



9-Hydroxynonan-3-yl benzoate (Figure 4, entry 40). In the air, $HBF_4{\cdot}Et_2O$ (0.10 mL) was added to a solution of the acetate (61.2 mg, 0.20 mmol, 1.0 equiv) in MeOH (2 mL) at room temperature, and the resulting reaction mixture was stirred at room temperature for 3 h. Next, the reaction mixture was concentrated, and then the residue was purified by flash chromatography on silica gel (1:2 Et_2O/hexanes). Colorless oil. The analytical data matched the literature report.[3a]

(*S*,*S*)-**L***: 50.4 mg, 95% yield, 90% ee; (*R*,*R*)-**L***: 49.7 mg, 94% yield, 89% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALCEL OJ column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 9.3 min (minor), 10.0 min (major).

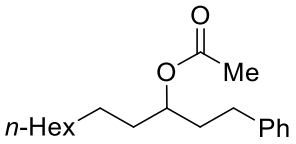
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.97 (m, 2H), 7.63 – 7.49 (m, 1H), 7.49 – 7.36 (m, 2H), 5.16 – 4.99 (m, 1H), 3.60 (t, *J* = 6.6 Hz, 2H), 1.77 – 1.59 (m, 5H), 1.58 – 1.47 (m, 2H), 1.44 – 1.27 (m, 6H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 132.8, 130.9, 129.6, 128.4, 76.2, 63.0, 33.7, 32.7, 29.4, 27.2, 25.7, 25.4, 9.8.

FT-IR (film): 3370, 2939, 2361, 1717, 1275, 1100, 713 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{16}H_{24}NaO_3$: 287.1618, found: 287.1623.

$[\alpha]^{23}_D$ = –9.5 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L***.



1-Phenylundecan-3-yl acetate (Figure 4, entry 41). The title compound was synthesized according to **GP-8** from acetyl bromide, 3-phenylpropanal, and 1-octene. The product was purified by column chromatography on silica gel (1:20 Et_2O/hexanes). Colorless oil. The analytical data matched the literature report.[4a]

(*S*,*S*)-**L***: 130 mg, 56% yield, 90% ee; (*R*,*R*)-**L***: 119 mg, 51% yield, 90% ee.

HPLC analysis: The ee was determined via HPLC on a CHIRALPAK AD column (0.5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 6.2 min (major), 7.0 min (minor).

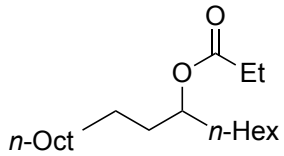
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 2H), 7.23 – 7.12 (m, 3H), 5.02 – 4.86 (m, 1H), 2.71 – 2.51 (m, 2H), 2.04 (s, 3H), 1.96 – 1.78 (m, 2H), 1.65 – 1.48 (m, 2H), 1.38 – 1.16 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 141.9, 128.5, 128.4, 126.0, 74.1, 36.0, 34.3, 32.0, 31.9, 29.7, 29.6, 29.4, 25.4, 22.8, 21.4, 14.3.

FT-IR (film): 2931, 1738, 1455, 1377, 1240, 1024, 740 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+Na]^+$ calcd for $C_{19}H_{30}NaO_2$: 313.2138, found: 313.2133.

$[\alpha]^{23}_D$ = –9.5 (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L***.



Heptadecan-7-yl propionate (Figure 4, entry 42). The title compound was synthesized according to **GP-8** from propionyl bromide, heptanal, and 1-decene. The product was purified by column chromatography on silica gel (1:20 Et_2O/hexanes). Colorless oil. The analytical data matched the literature report.[5]

(*S*,*S*)-**L***: 131 mg, 53% yield, 92% ee; (*R*,*R*)-**L***: 128 mg, 51% yield, 93% ee.

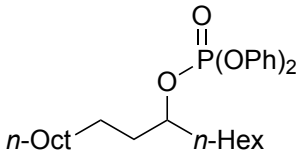
HPLC analysis: The ee was determined after transforming the product to the corresponding phosphate (see below).

^{1}H NMR (400 MHz, $CDCl_3$) 4.92 – 4.81 (m, 1H), 2.30 (q, *J* = 7.6 Hz, 2H), 1.56 – 1.44 (m, 4H), 1.36 – 1.18 (m, 24H), 1.14 (t, *J* = 7.6 Hz, 3H), 0.93 – 0.81 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 74.3, 34.3, 32.1, 31.9, 29.8, 29.72, 29.69, 29.5, 29.4, 28.1, 25.5, 25.4, 22.8, 22.7, 14.3, 14.2, 9.5.

FT-IR (film): 2926, 1738, 1463, 1379, 1275, 1192, 1082, 723 cm^{-1}.

$[\alpha]^{22}_D$ = +2.1 (*c* 1.0, $CHCl_3$); 92% ee, from (*S*,*S*)-**L***.



Heptadecan-7-yl diphenyl phosphate. The title compound was synthesized according to **GP-5**. The product was purified by column chromatography on silica gel (1:5 EtOAc/hexanes). Colorless oil.

(*S*,*S*)-**L***: 93.7 mg, 96% yield, 92% ee; (*R*,*R*)-**L***: 91.2 mg, 93% yield, 93% ee.

SFC analysis: The ee was determined via SFC on a CHIRALCEL OD column (4% CH_3CN in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**L***: 14.7 min (major), 15.7 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.26 – 7.20 (m, 4H), 7.20 – 7.13 (m, 2H), 4.74 – 4.54 (m, 1H), 1.71 – 1.52 (m, 4H), 1.36 – 1.14 (m, 24H), 0.93 – 0.81 (m, 6H).

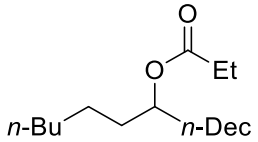
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (d, *J* = 7.1 Hz), 129.8, 125.2 (d, *J* = 1.0 Hz), 120.2 (d, *J* = 5.1 Hz), 82.5 (d, *J* = 7.1 Hz), 35.1 (d, *J* = 5.1 Hz), 32.0, 31.8, 29.71, 29.65, 29.6, 29.5, 29.4, 29.2, 24.9, 24.8, 22.8, 22.7, 14.24, 14.17.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.4.

FT-IR (film): 3485, 2916, 1592, 1495, 1296, 1198, 1020, 753 cm^{-1}.

HRMS (ESI-MS) *m*/*z* $[M+NH_4]^+$ calcd for $C_{29}H_{49}NO_4P$: 506.3394, found: 506.3399.

$[\alpha]^{22}_D$ = +3.6 (*c* 1.0, $CHCl_3$); 92% ee, from (*S*,*S*)-**L***.

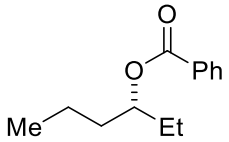


Heptadecan-7-yl propionate (Figure 4, entry 42). The title compound was synthesized according to **GP-8** from propionyl bromide, undecanal, and 1-hexene. The product was purified by column chromatography on silica gel (1:20 Et_2O/hexanes). Colorless oil.

(*S*,*S*)-**L***: 135 mg, 54% yield, 93% ee; (*R*,*R*)-**L***: 138 mg, 55% yield, 93% ee.

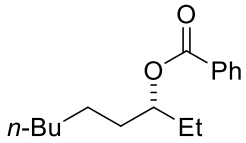
VIII. Assignment of Absolute Configuration

The configurations of the coupling products were assigned by comparison with published optical-rotation data.



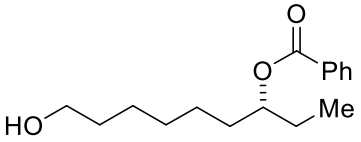
(*R*)-Hexan-3-yl benzoate (Figure 3, entry 18). The absolute configuration of this compound has been reported.[7] The material obtained with (*S*,*S*)-**L*** has the (*R*) configuration, by comparison with the sign of the published optical rotation.

Optical rotation: $[\alpha]^{23}_{D} = -4.8$ (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L***.
Lit.: $[\alpha]^{26}_{D} = -2.1$ (*c* 1.1, $CHCl_3$); 99% ee, (*R*) configuration.



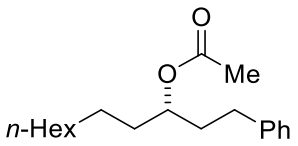
(*R*)-Nonan-3-yl benzoate (Figure 3, entry 20). The absolute configuration of this compound has been reported.[6] The material obtained with (*S*,*S*)-**L*** has the (*R*) configuration, by comparison with the sign of the published optical rotation.

Optical rotation: $[\alpha]^{23}_{D} = -8.9$ (*c* 1.0, $CHCl_3$); 89% ee, from (*S*,*S*)-**L***.
Lit.: $[\alpha]^{26}_{D} = -30$ (*c* 0.975, $CHCl_3$); 99% ee, (*R*) configuration.



(*R*)-9-Hydroxynonan-3-yl benzoate (Figure 4, entry 40). The absolute configuration of this compound has been reported.[3a] The material obtained with (*S*,*S*)-**L*** has the (*R*) configuration, by comparison with the published optical rotation.

Optical rotation: $[\alpha]^{23}_{D} = -9.5$ (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L***.
Lit.: $[\alpha]^{20}_{D} = -8.6$ (*c* 1.3, $CHCl_3$); 99% ee, (*R*) configuration.



(*S*)-1-Phenylundecan-3-yl acetate (Figure 4, entry 41). The absolute configuration of this compound has been reported.[4a] The material obtained with (*S*,*S*)-**L*** has the (*S*) configuration, by comparison with the sign of the published optical rotation.

Optical rotation: $[\alpha]^{23}_{D} = -9.5$ (*c* 1.0, $CHCl_3$); 90% ee, from (*S*,*S*)-**L***.

Lit.: $[\alpha]^{22}_{D} = +4.9$ (*c* 1.0, $CHCl_3$); ee not provided; (*R*) configuration.

IX. References

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X. NMR Spectra; ee Analysis

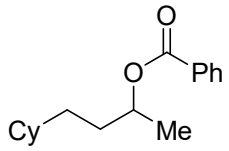


Fig. 3, entry 1
(400 MHz, $CDCl_3$)

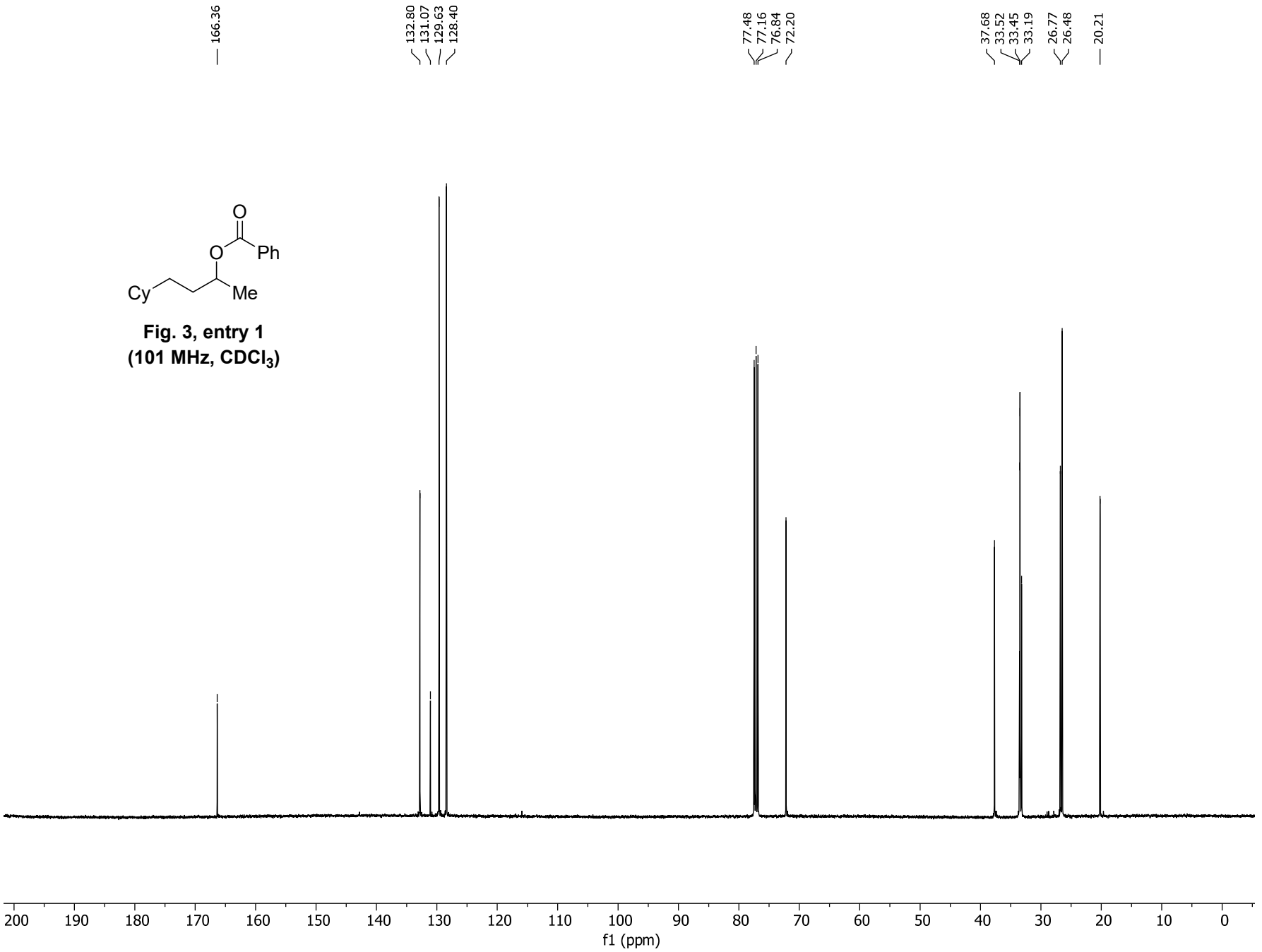


Fig. 3, entry 1
(101 MHz, $CDCl_3$)

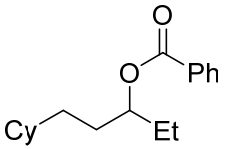


Fig. 3, entry 2
(400 MHz, $CDCl_3$)

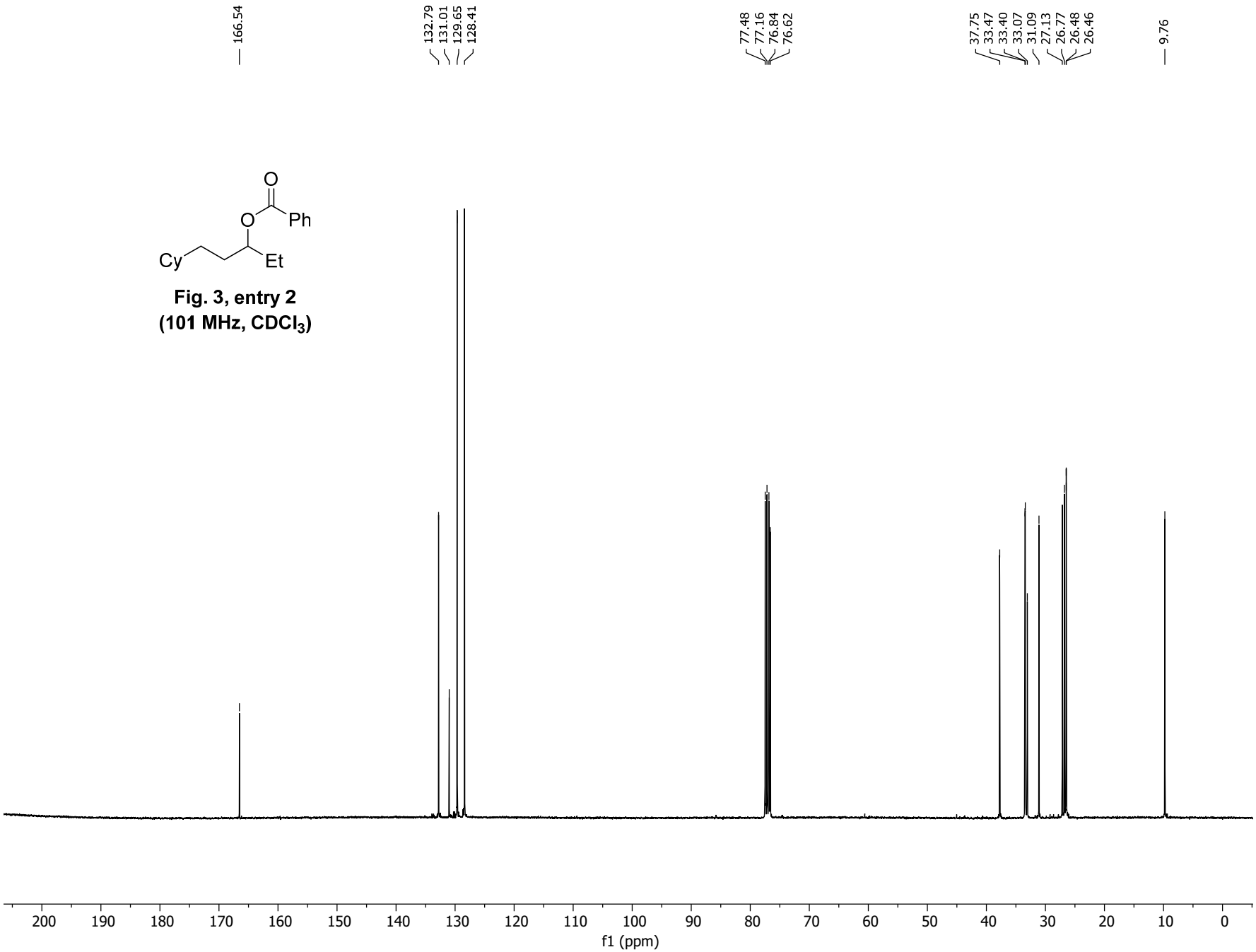


Fig. 3, entry 2
(101 MHz, $CDCl_3$)

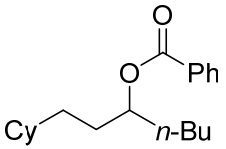
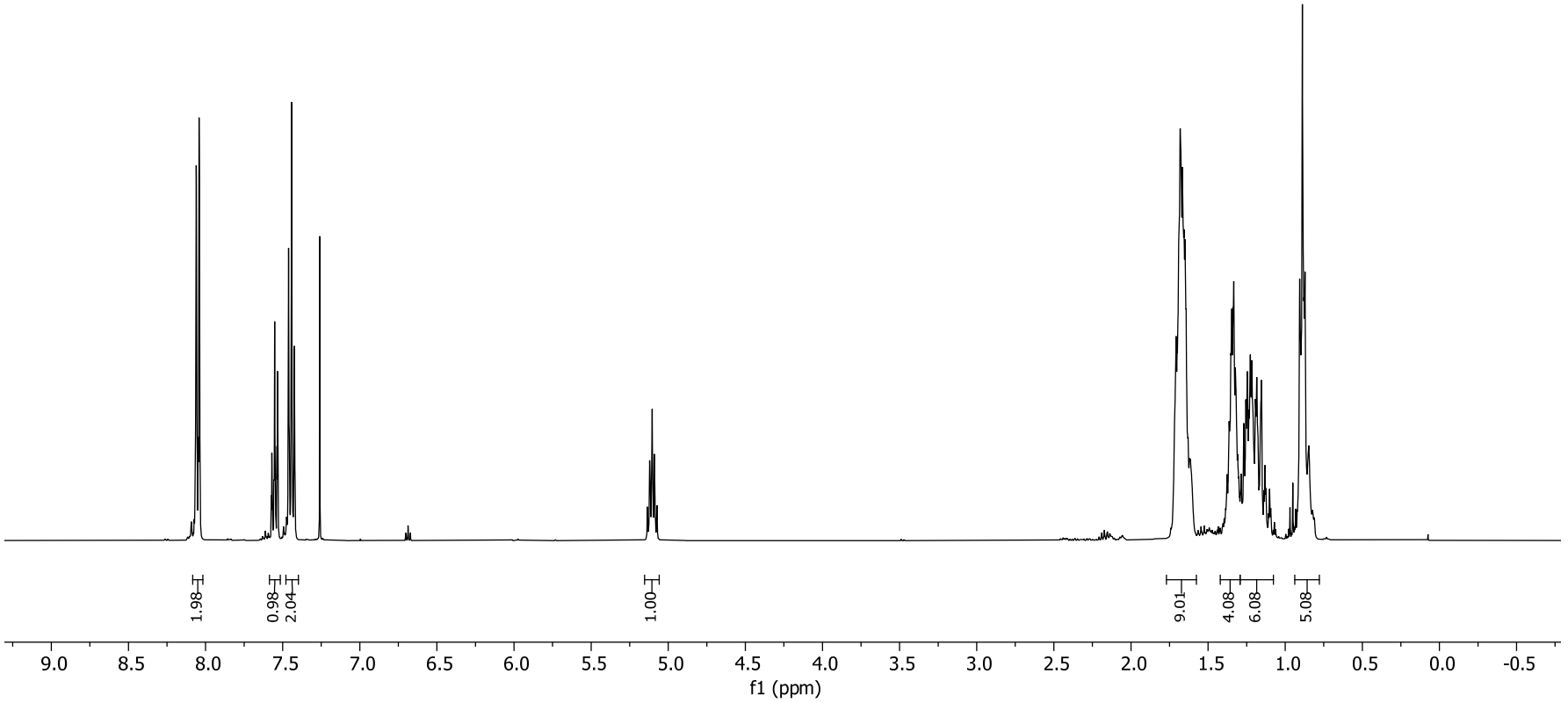


Fig. 3, entry 3
(400 MHz, $CDCl_3$)



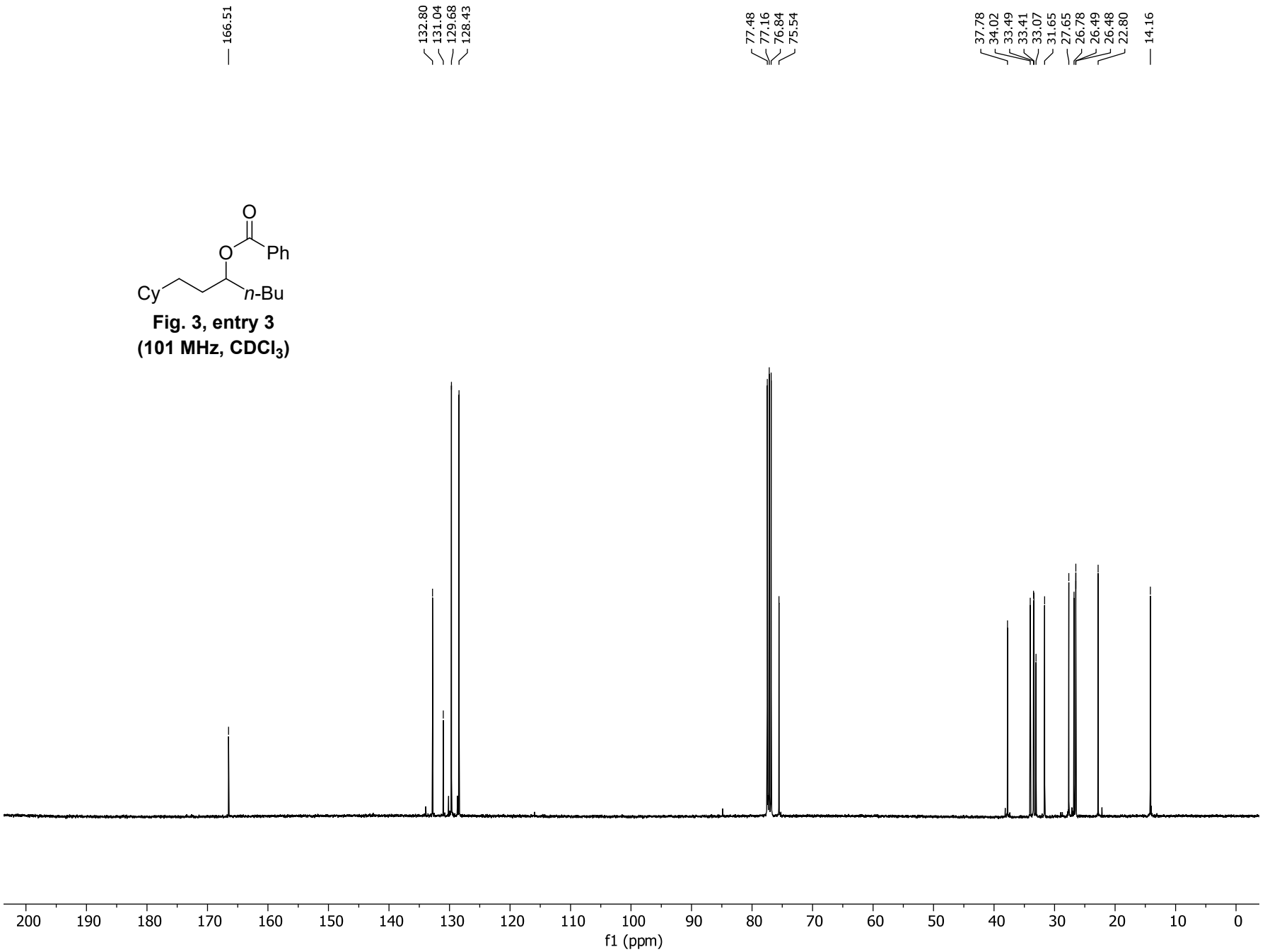
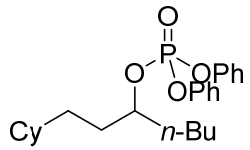
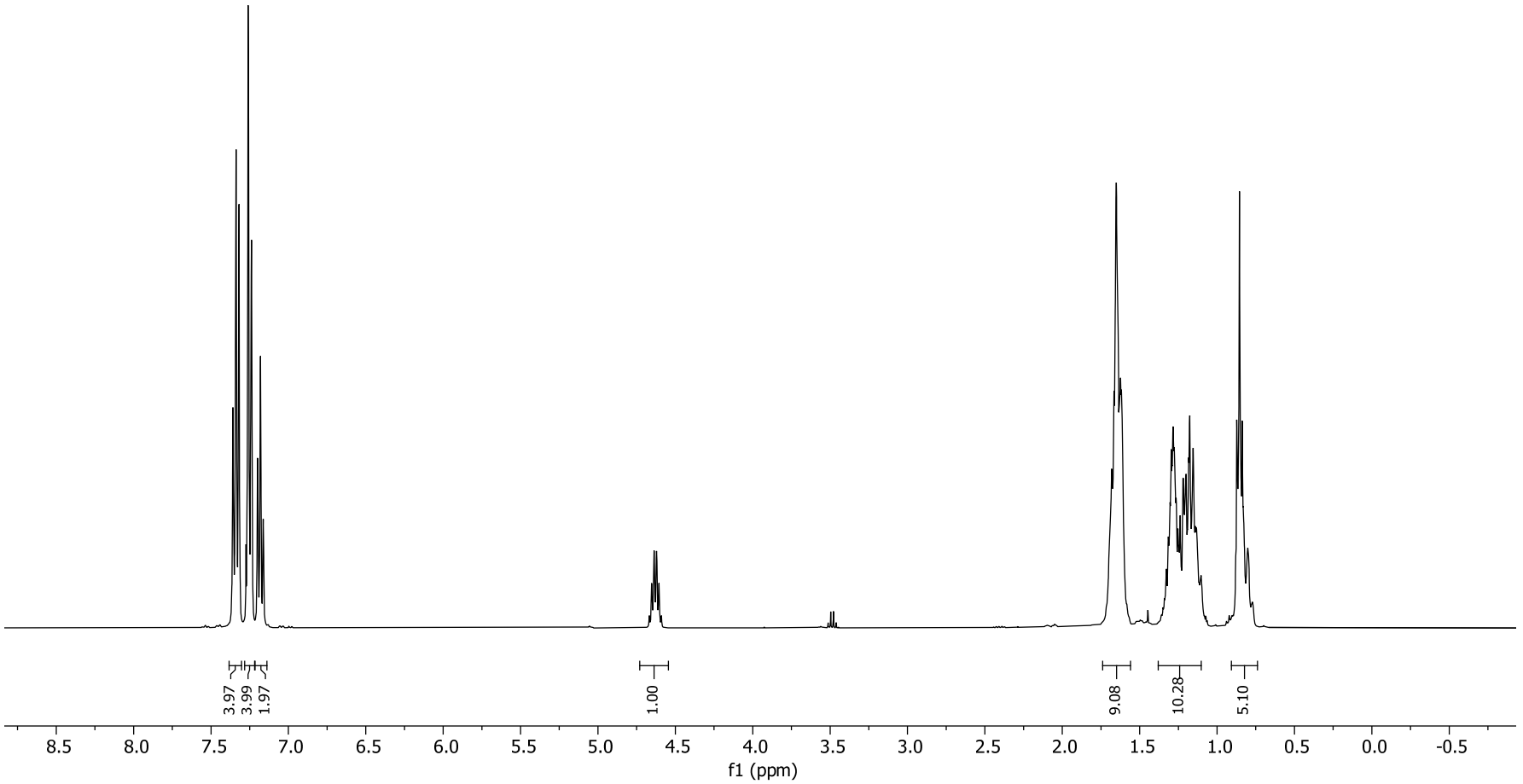
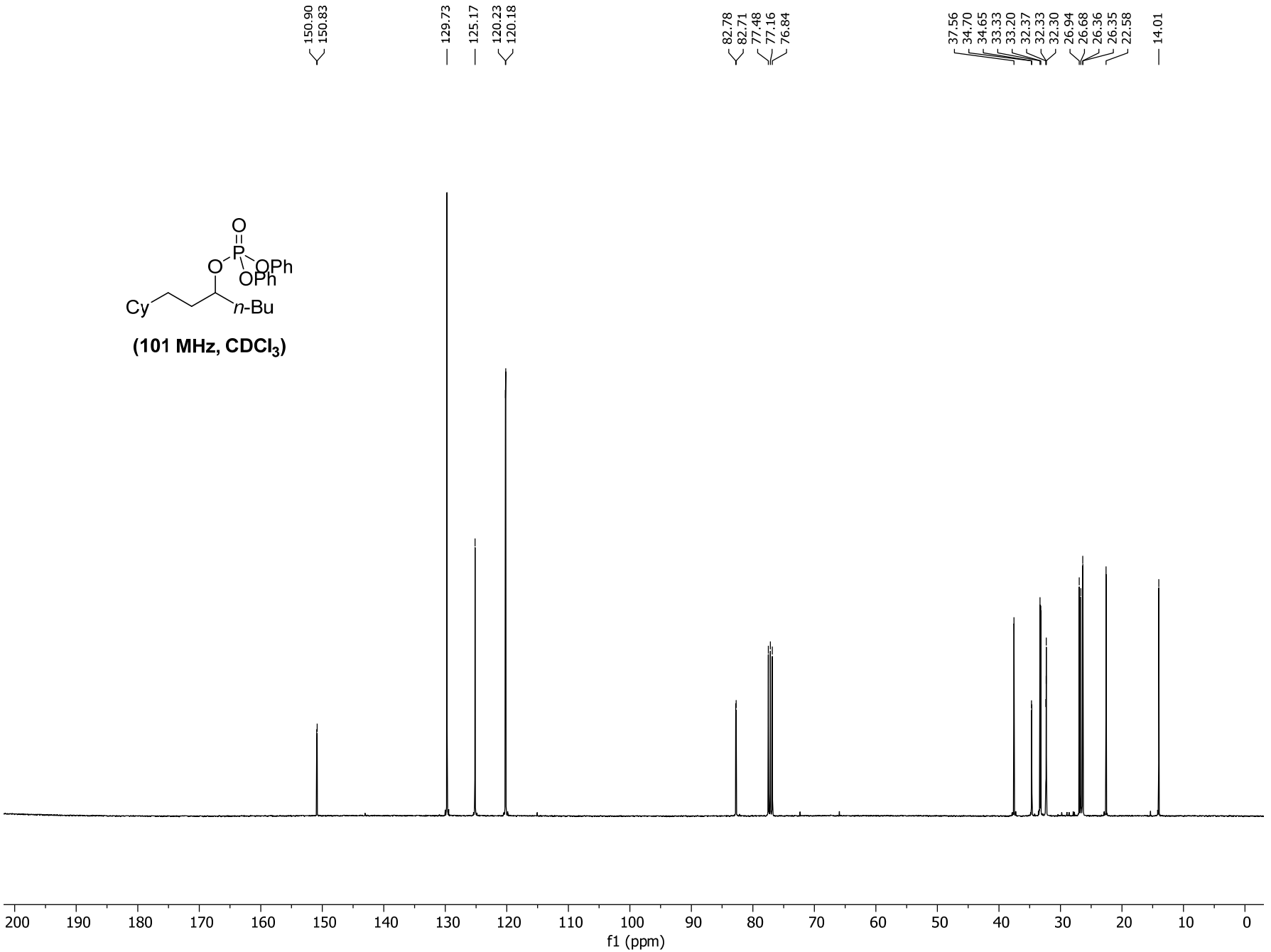


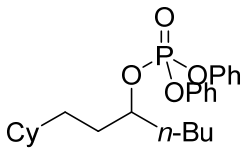
Fig. 3, entry 3
(101 MHz, $CDCl_3$)



(400 MHz, $CDCl_3$)




150.90
150.83
129.73
125.17
120.23
120.18
82.78
82.71
77.48
77.16
76.84
37.56
34.70
34.65
33.33
33.20
32.37
32.33
32.30
26.94
26.68
26.36
26.35
22.58
14.01
O
P
O
OPh
OPh
Cy
n-Bu
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



(162 MHz, $CDCl_3$)

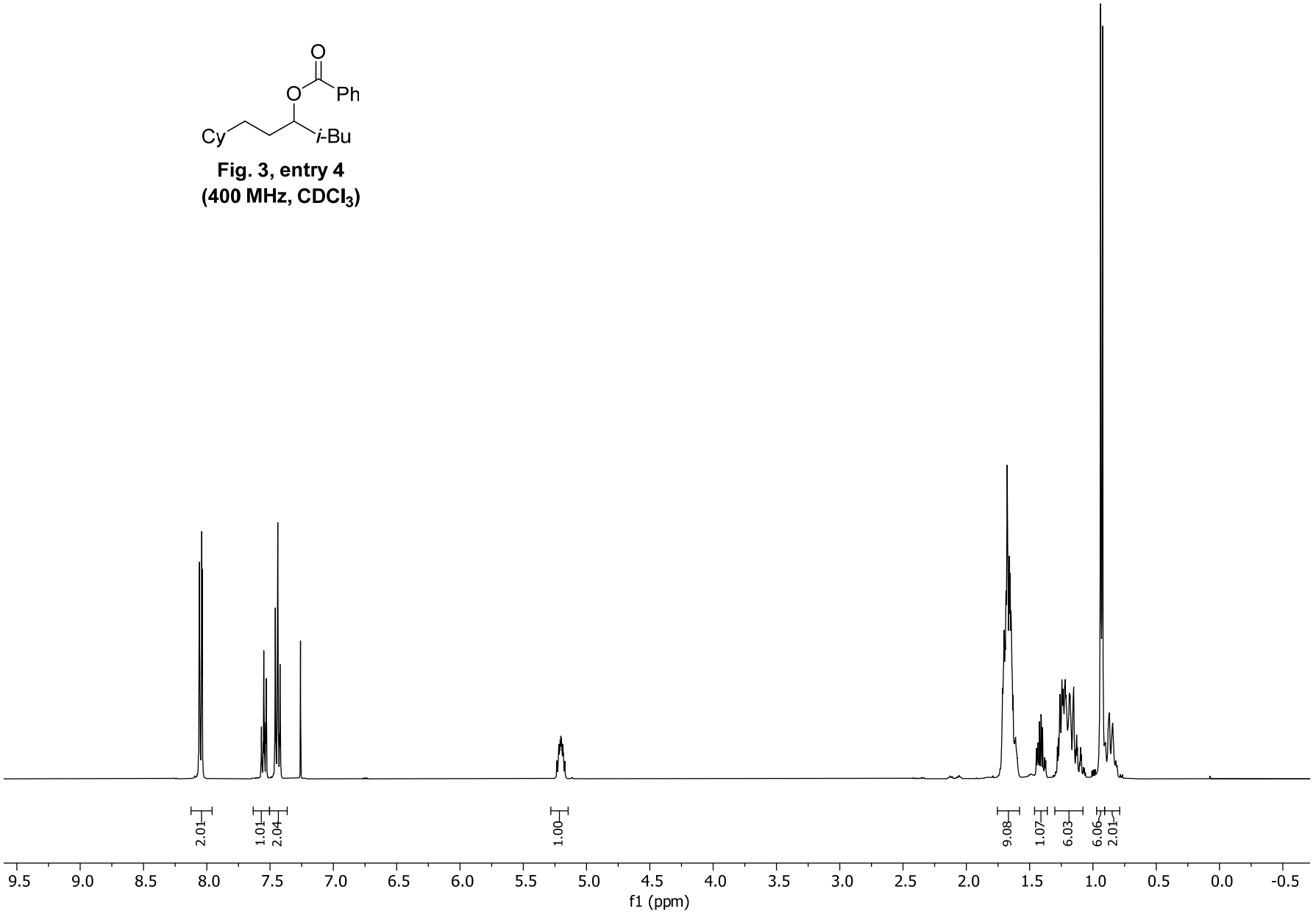


Fig. 3, entry 4
(400 MHz, $CDCl_3$)

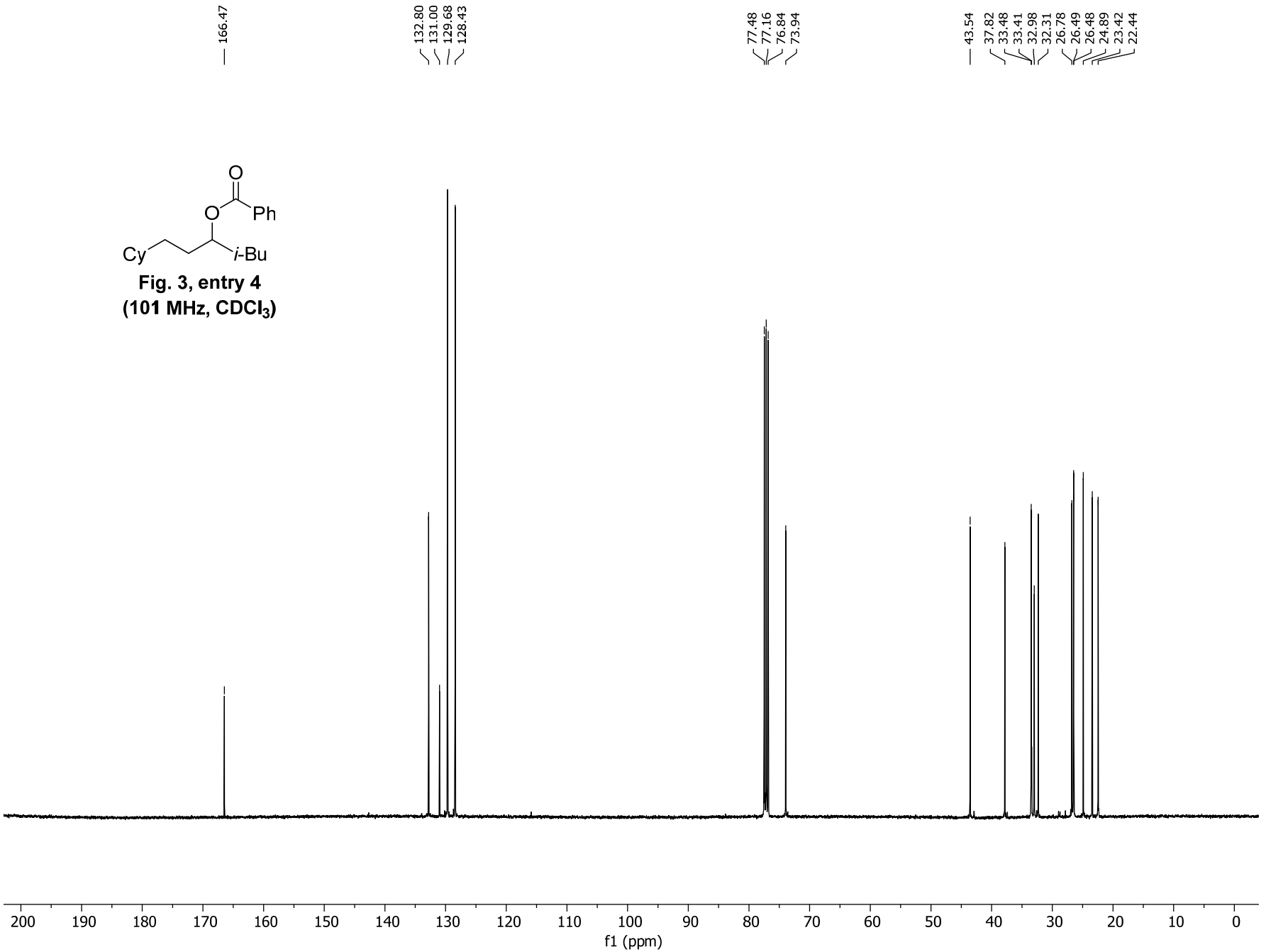
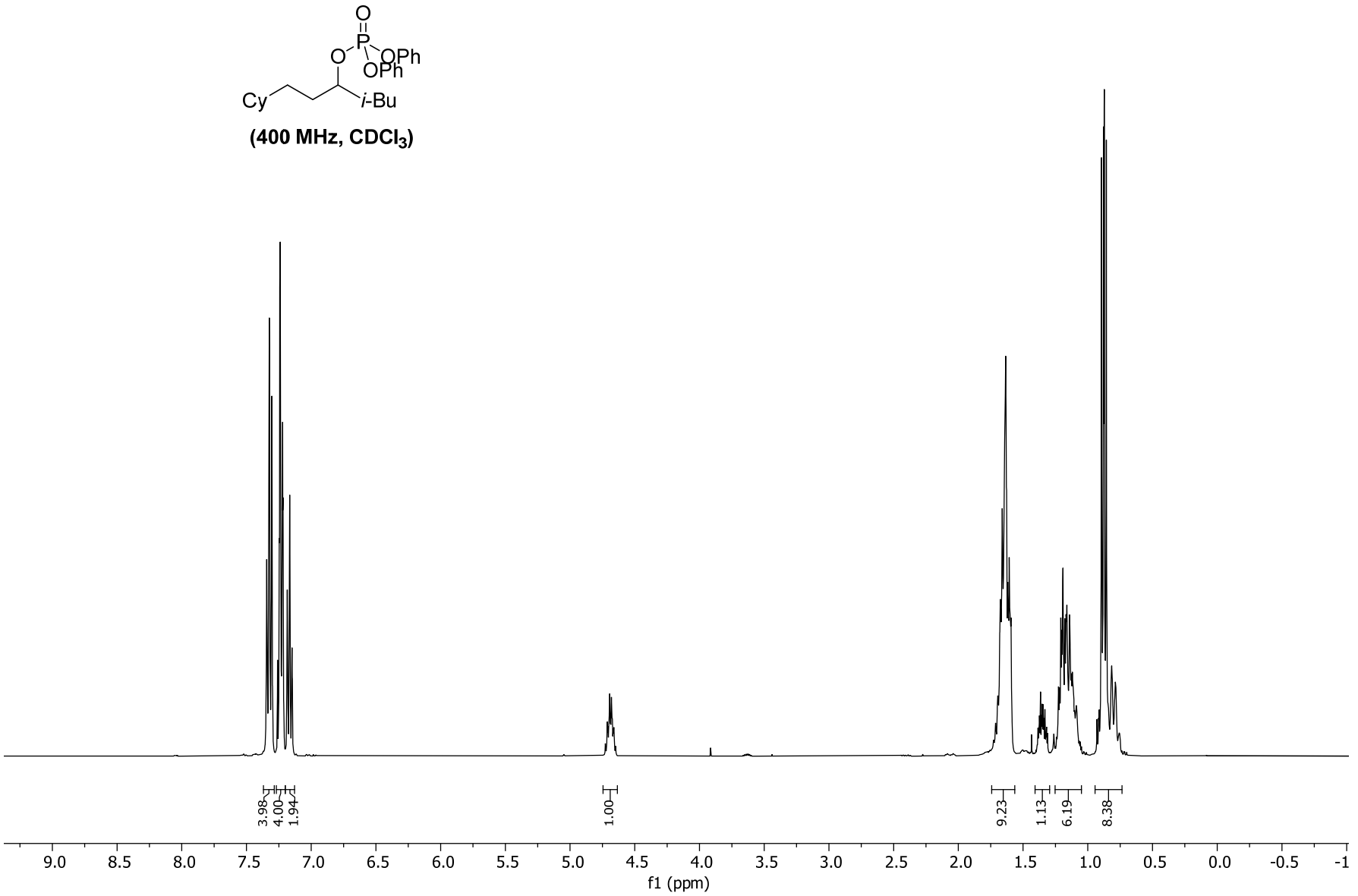
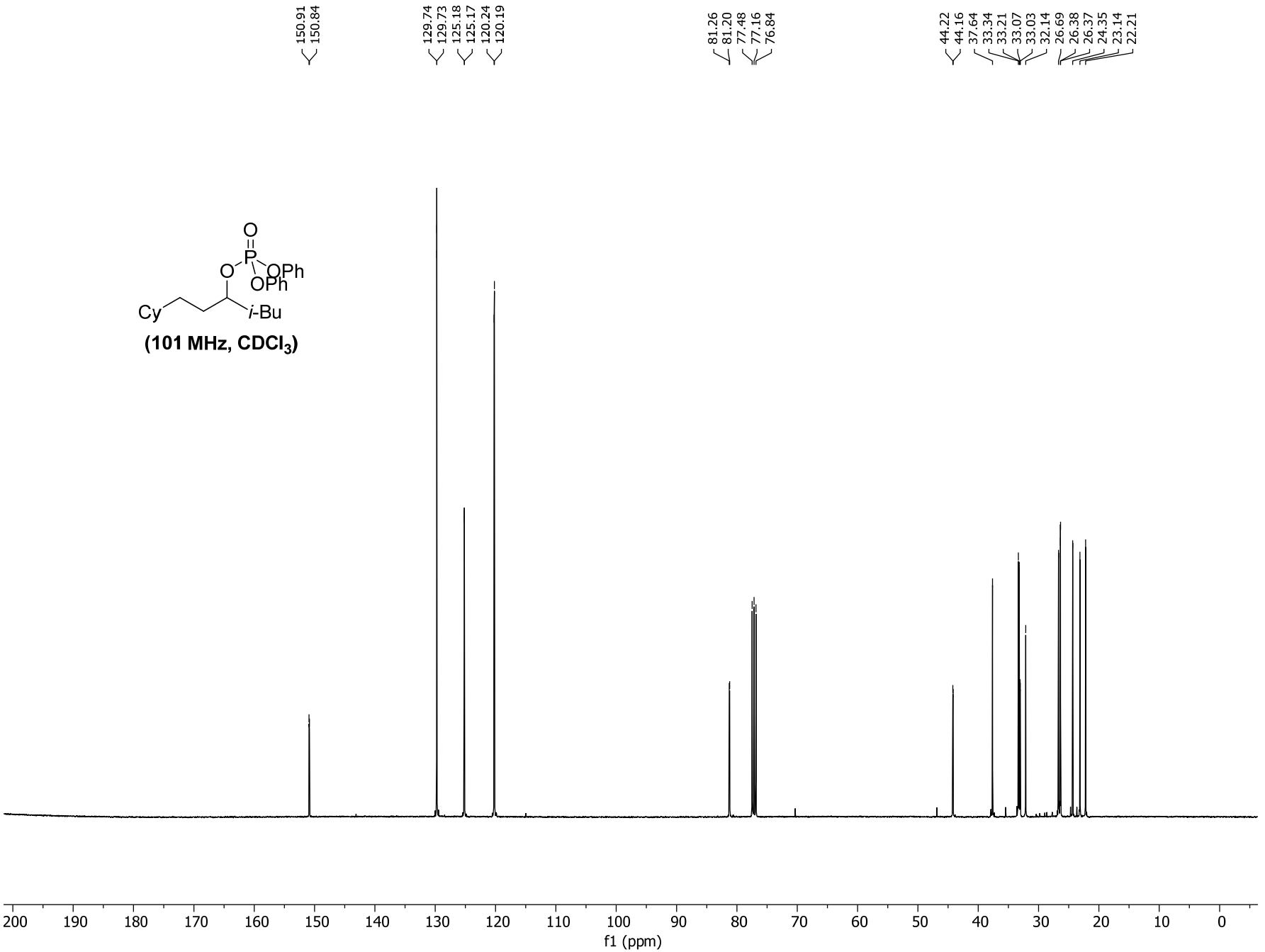
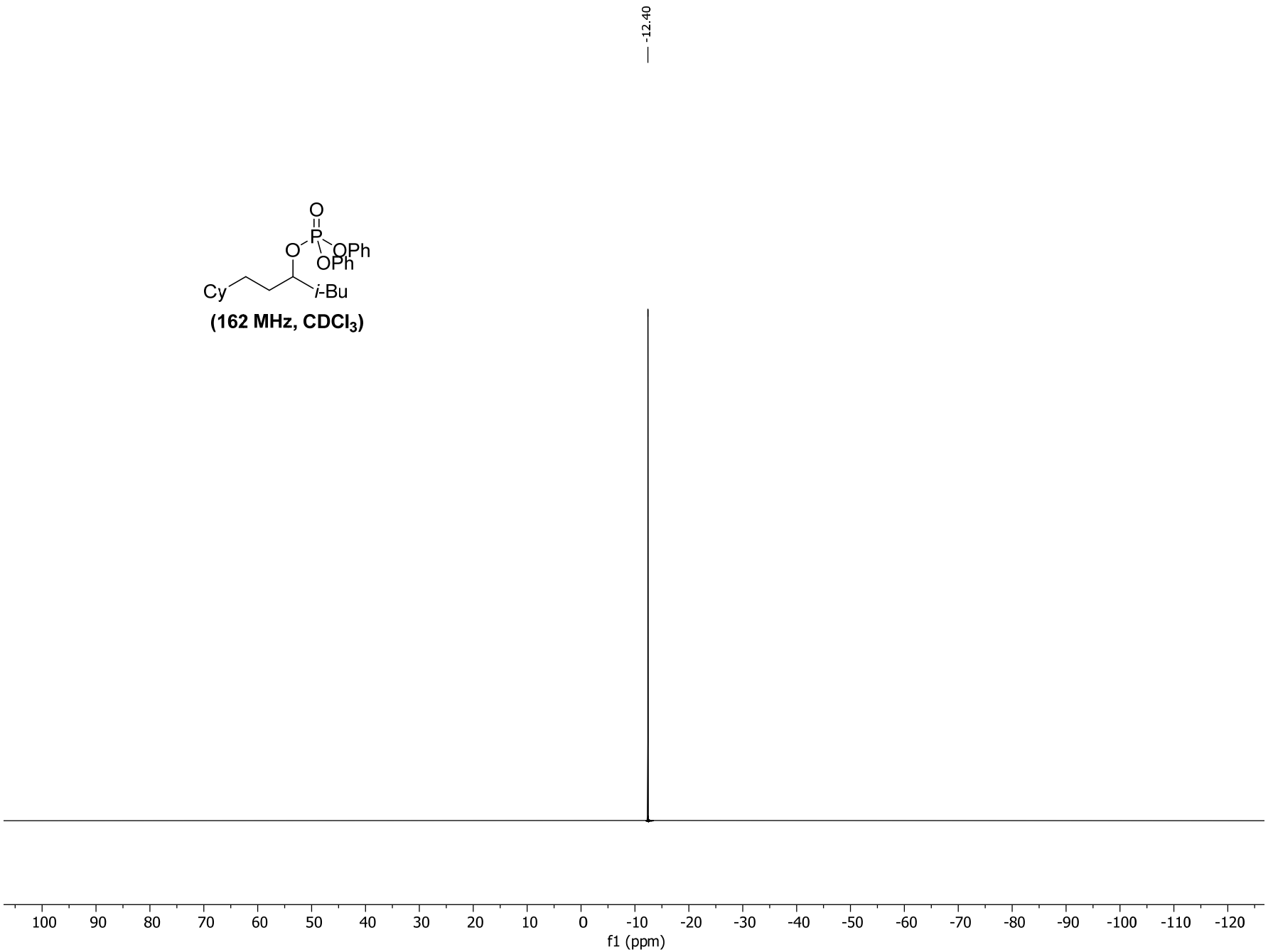


Fig. 3, entry 4
(101 MHz, $CDCl_3$)


O
P
O
OPh
OPh
Cy
i-Bu
(400 MHz, CDCl3)
3.98
4.00
1.94
1.00
9.23
1.13
6.19
8.38
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


150.91
150.84
129.74
129.73
125.18
125.17
120.24
120.19
81.26
81.20
77.48
77.16
76.84
44.22
44.16
37.64
33.34
33.21
33.07
33.03
32.14
26.69
26.38
26.37
24.35
23.14
22.21
O
P
O
OPh
OPh
Cy
i-Bu
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-12.40
O
P
O
OPh
OPh
Cy
i-Bu
(162 MHz, CDCl3)
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

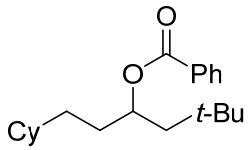


Fig. 3, entry 5
(400 MHz, $CDCl_3$)

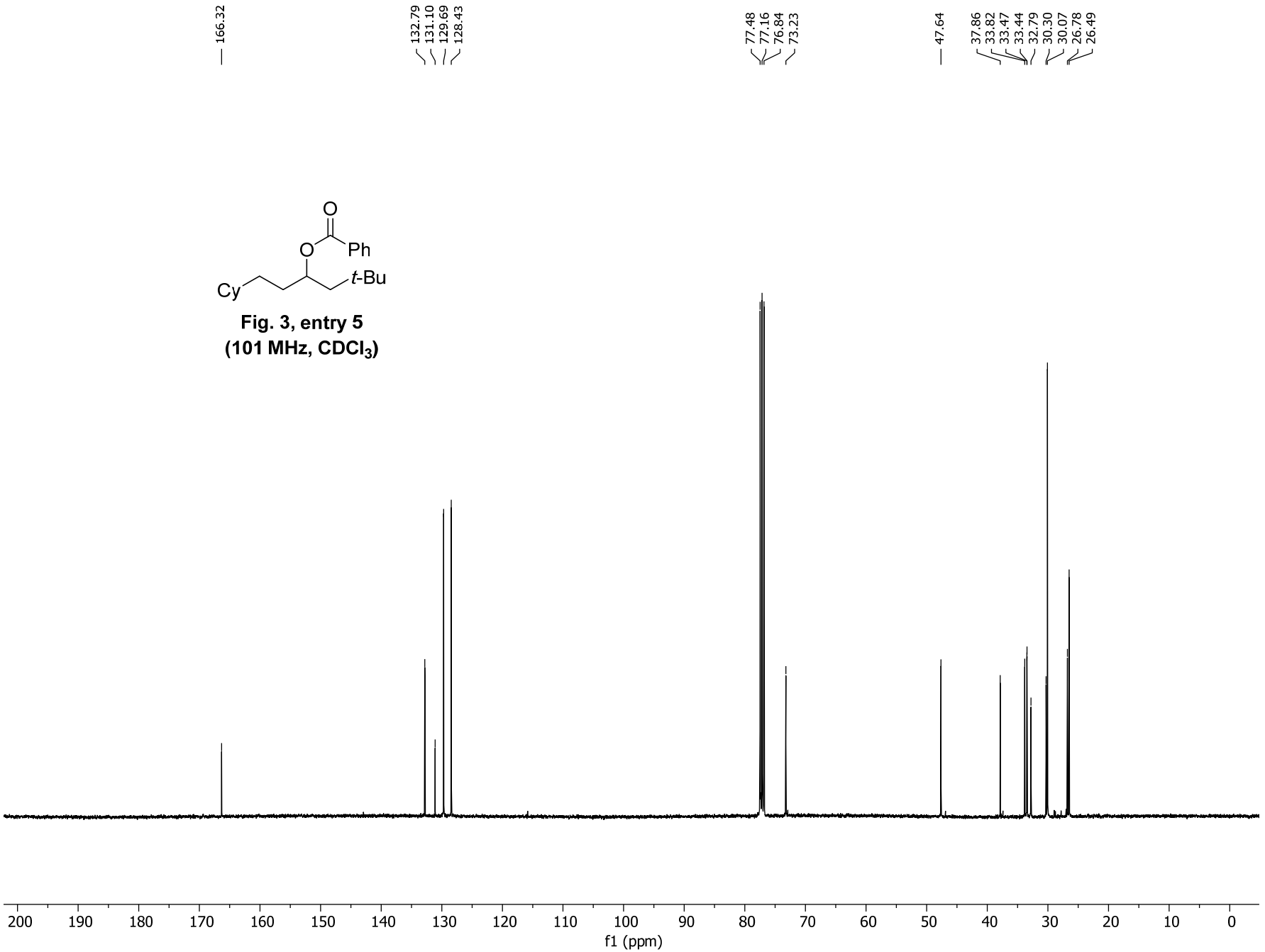
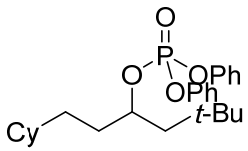
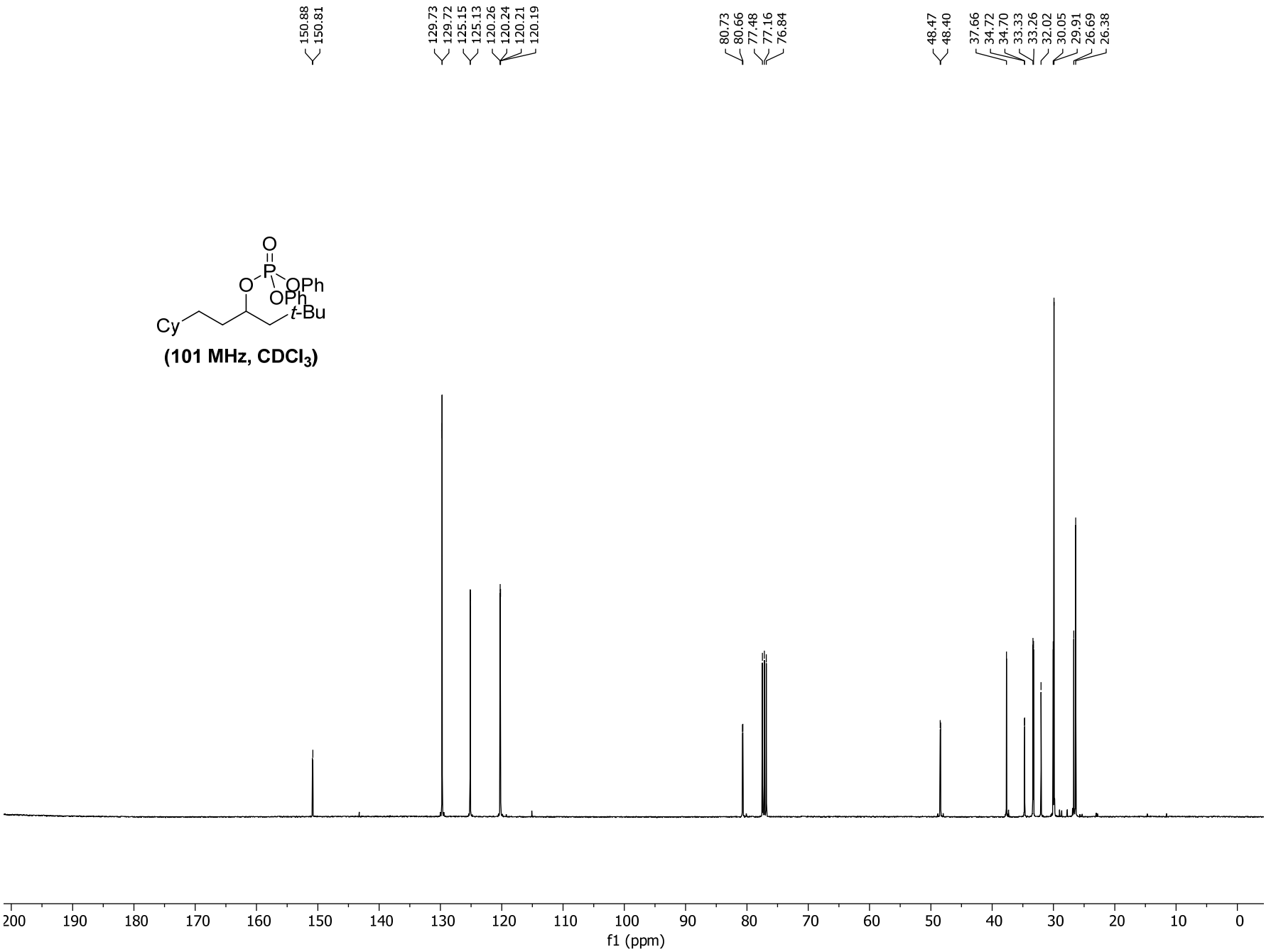
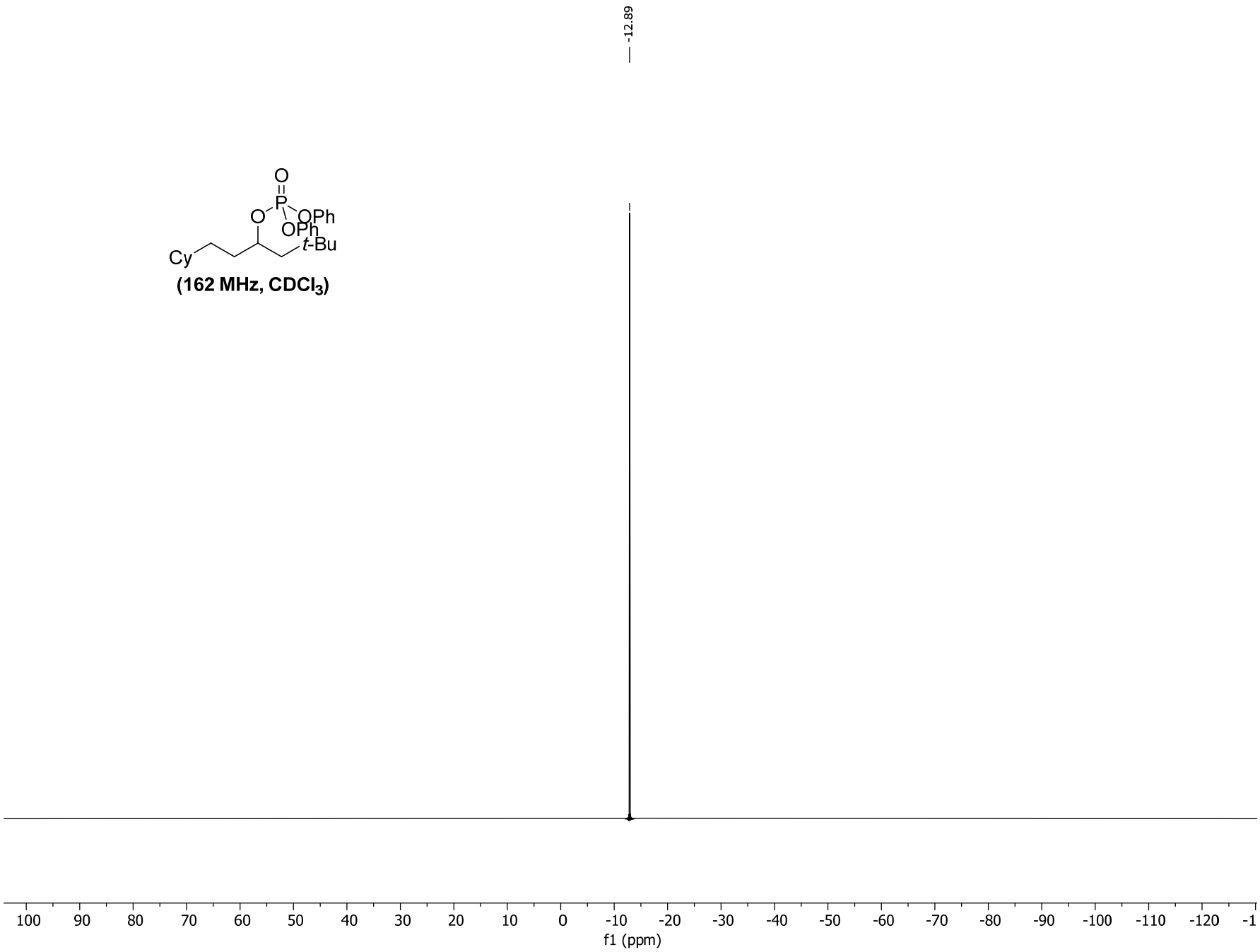


Fig. 3, entry 5
(101 MHz, $CDCl_3$)



(400 MHz, $CDCl_3$)


150.88
150.81
129.73
129.72
125.15
125.13
120.26
120.24
120.21
120.19
80.73
80.66
77.48
77.16
76.84
48.47
48.40
37.66
34.72
34.70
33.33
33.26
32.02
30.05
29.91
26.69
26.38
O
P
O
OPh
OPh
Cy
t-Bu
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-12.89
O
P
O
OPh
OPh
Cy
t-Bu
(162 MHz, CDCl3)
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -1
f1 (ppm)

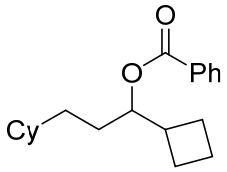
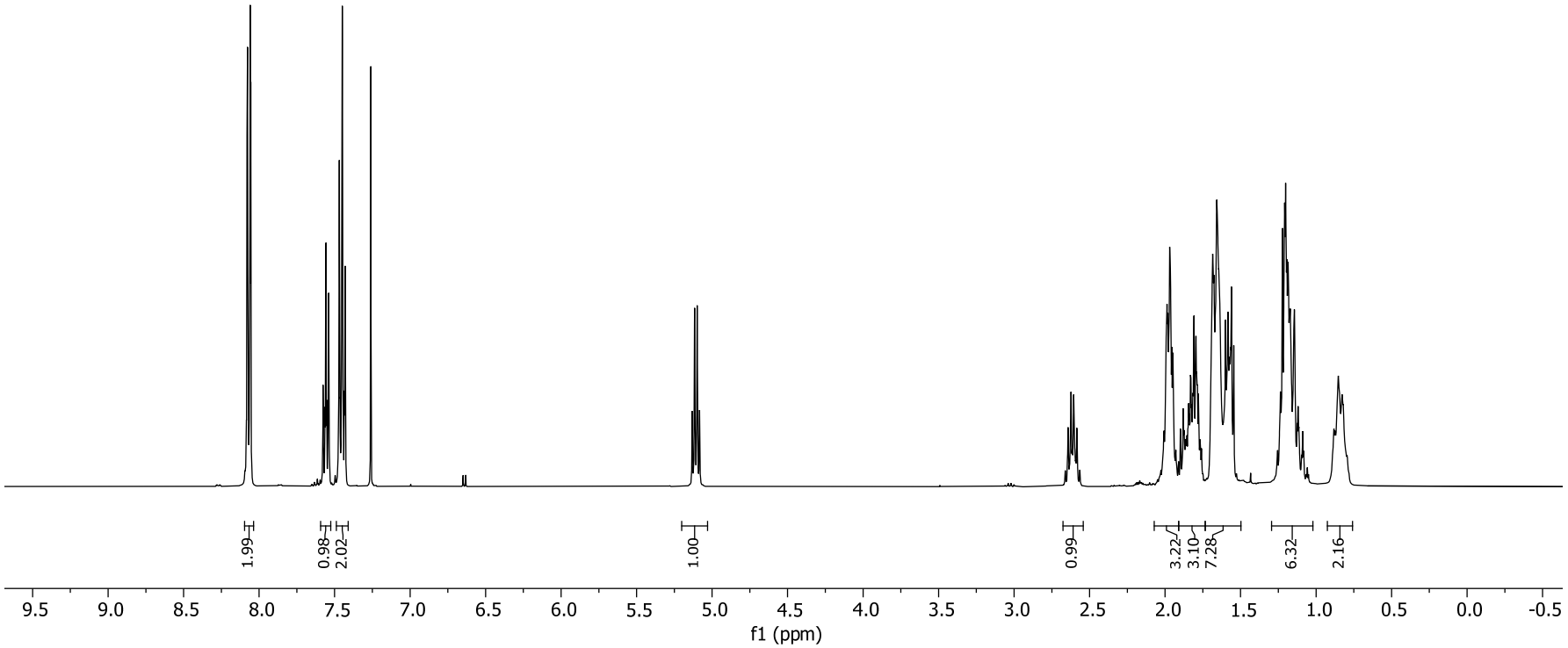


Fig. 3, entry 6
(400 MHz, $CDCl_3$)



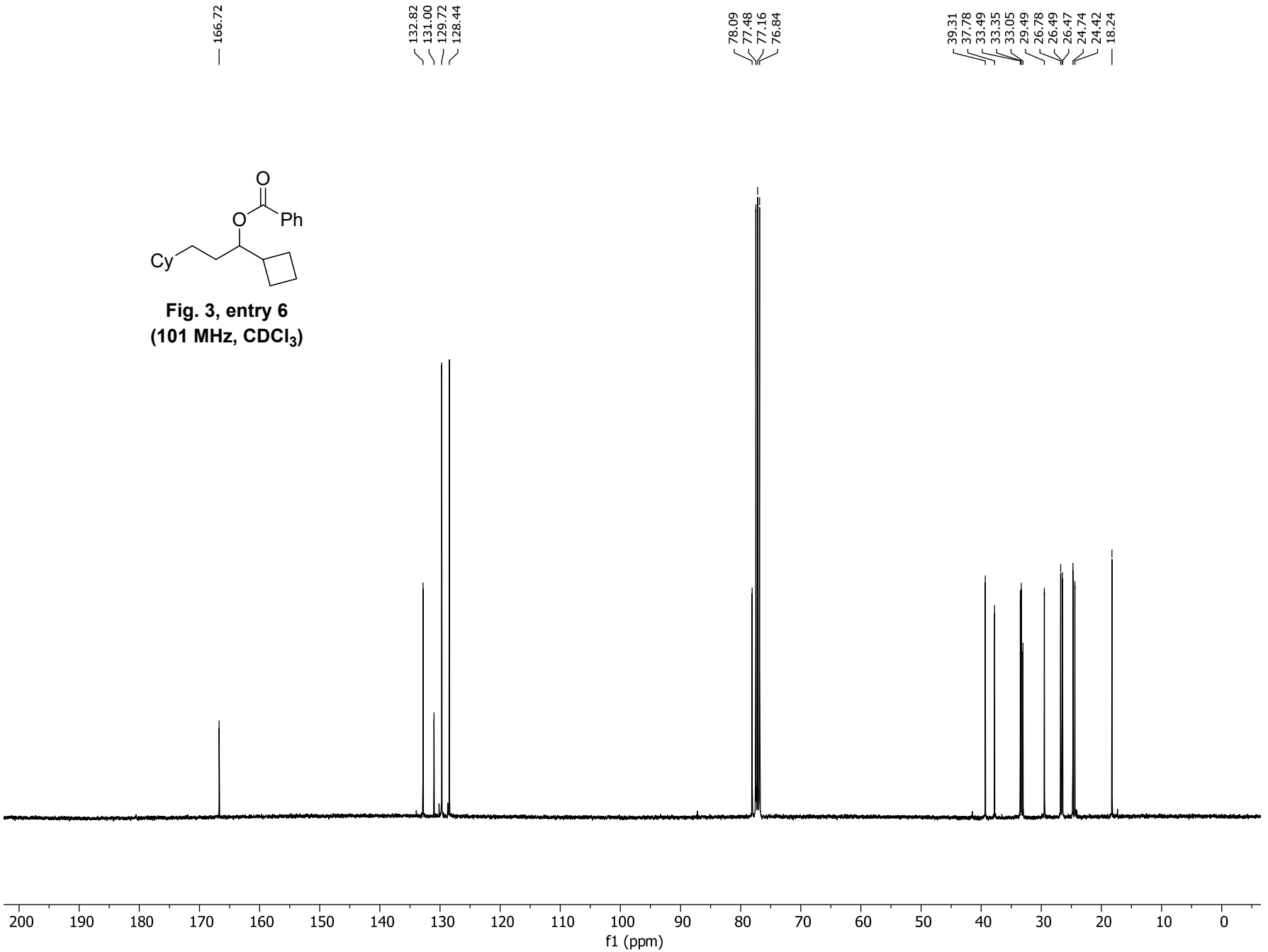
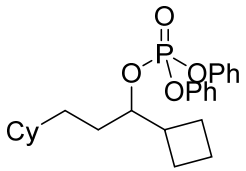
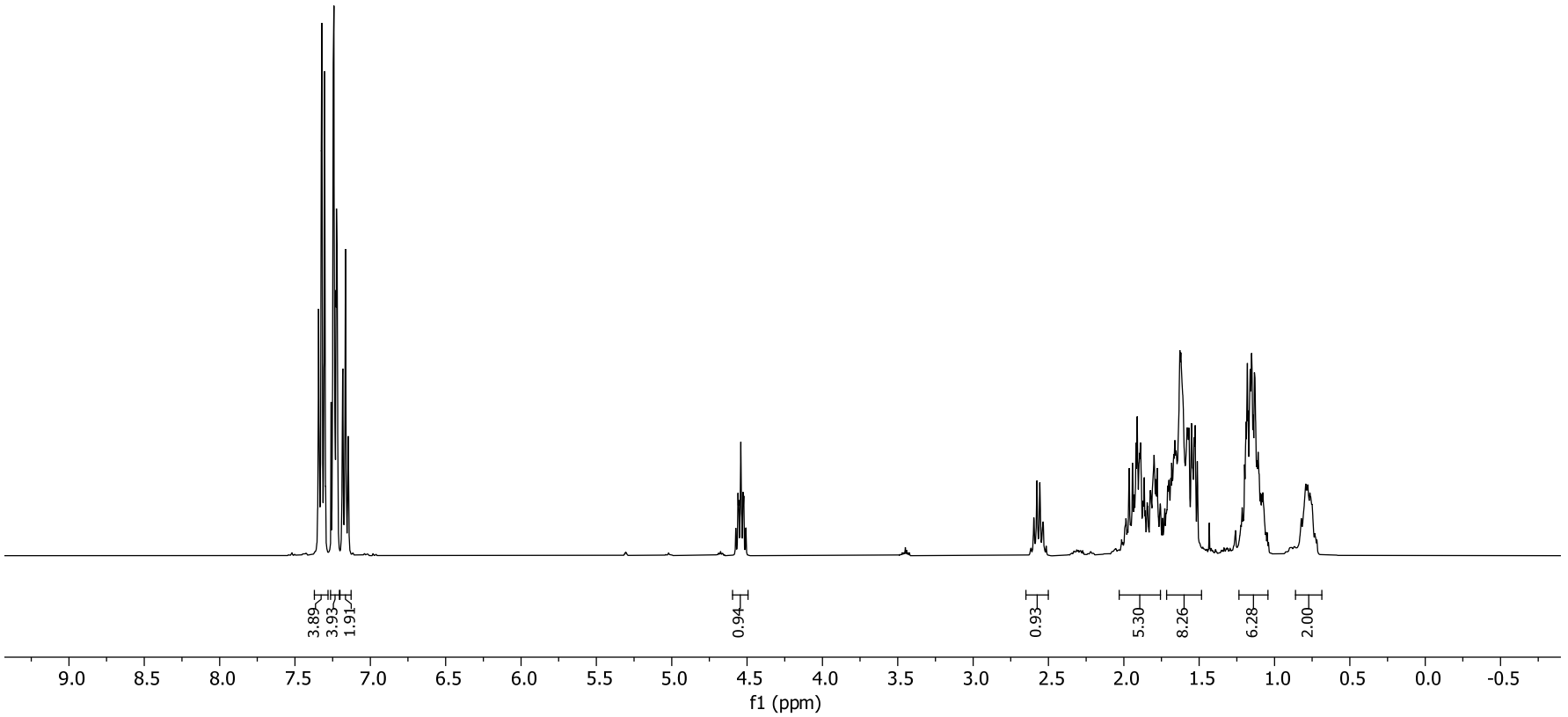
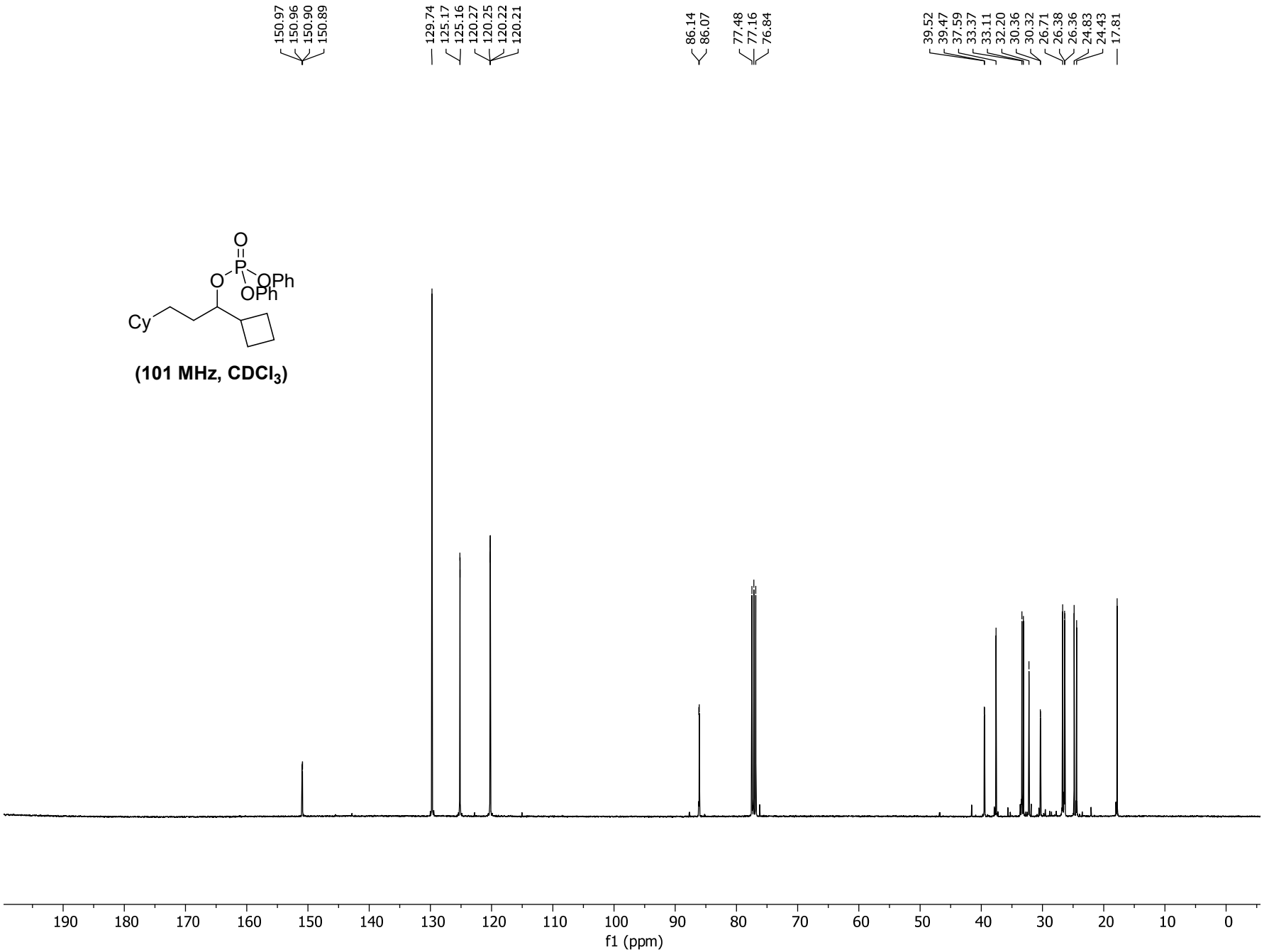


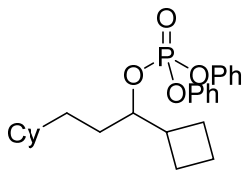
Fig. 3, entry 6
(101 MHz, $CDCl_3$)



(400 MHz, $CDCl_3$)




150.97
150.96
150.90
150.89
129.74
125.17
125.16
120.27
120.25
120.22
120.21
86.14
86.07
77.48
77.16
76.84
39.52
39.47
37.59
33.37
33.11
32.20
30.36
30.32
26.71
26.38
26.36
24.83
24.43
17.81
O
P
O
OPh
OPh
Cy
(101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



(162 MHz, $CDCl_3$)

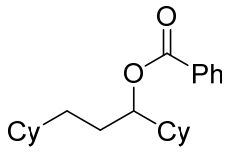
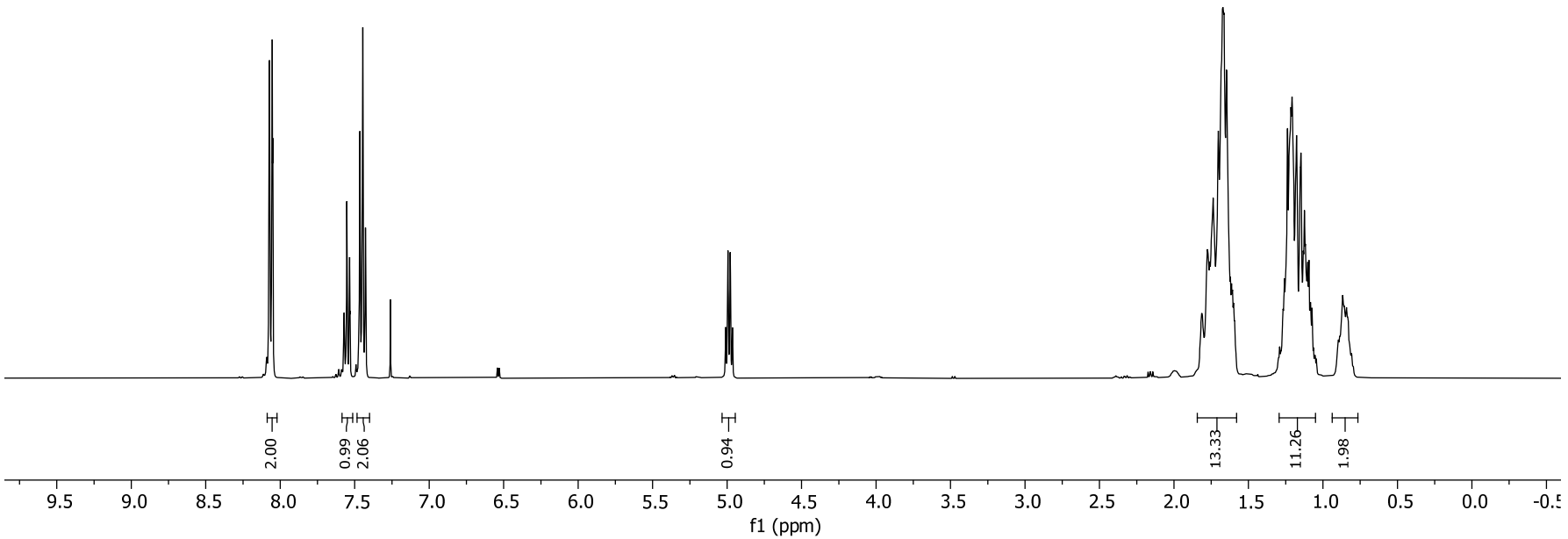


Fig. 3, entry 7
(400 MHz, $CDCl_3$)



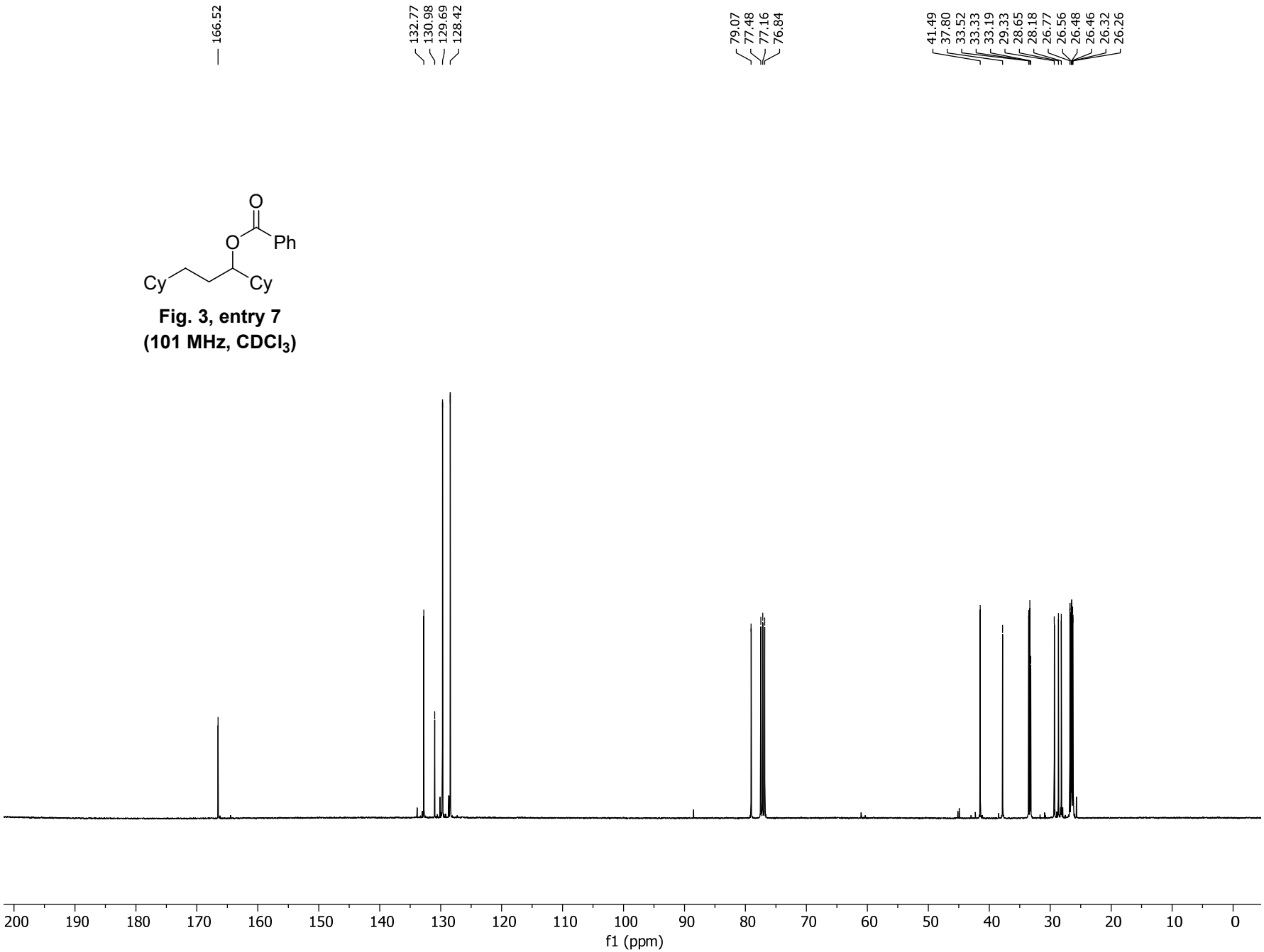
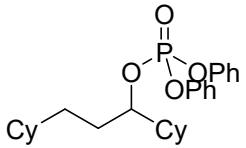
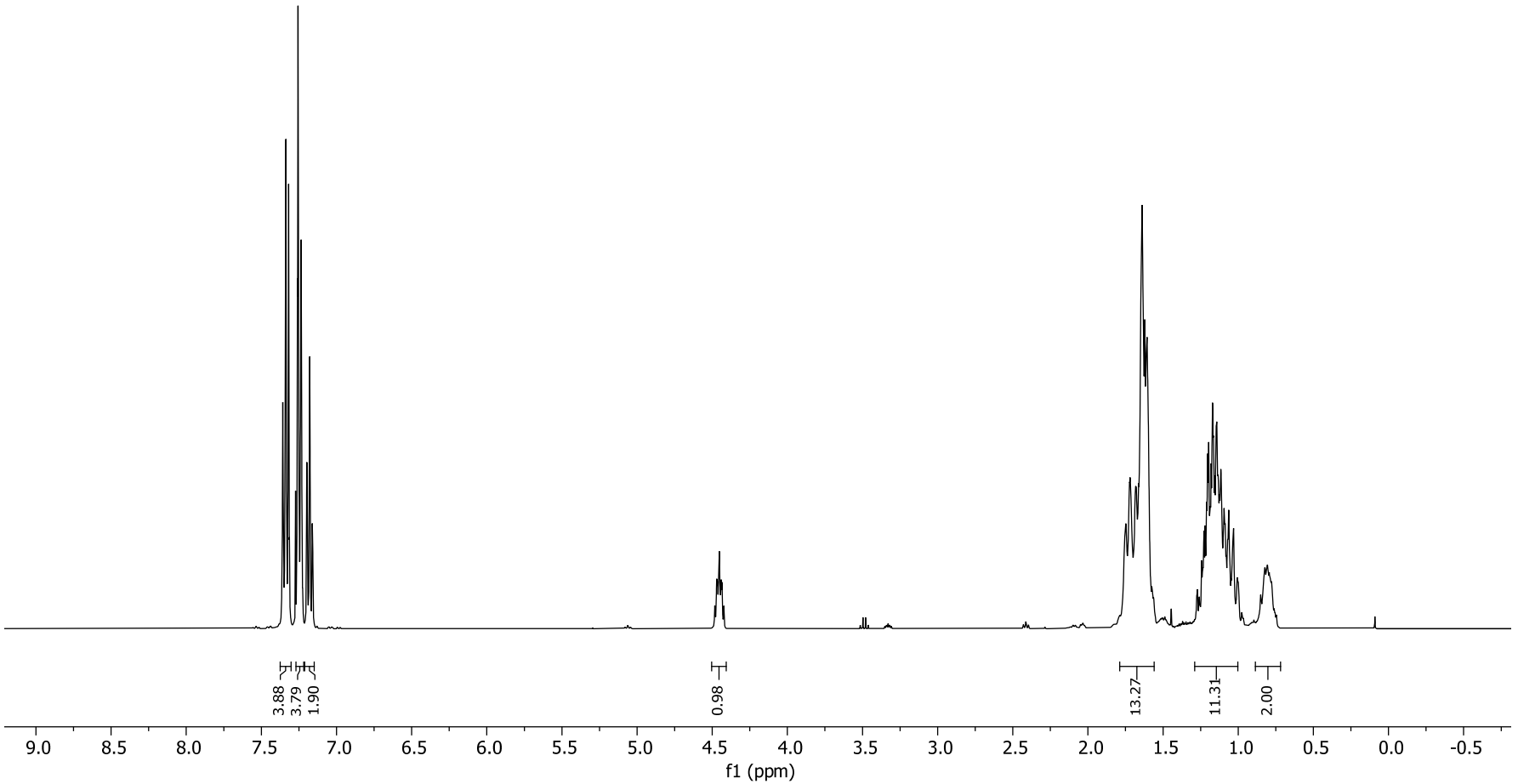
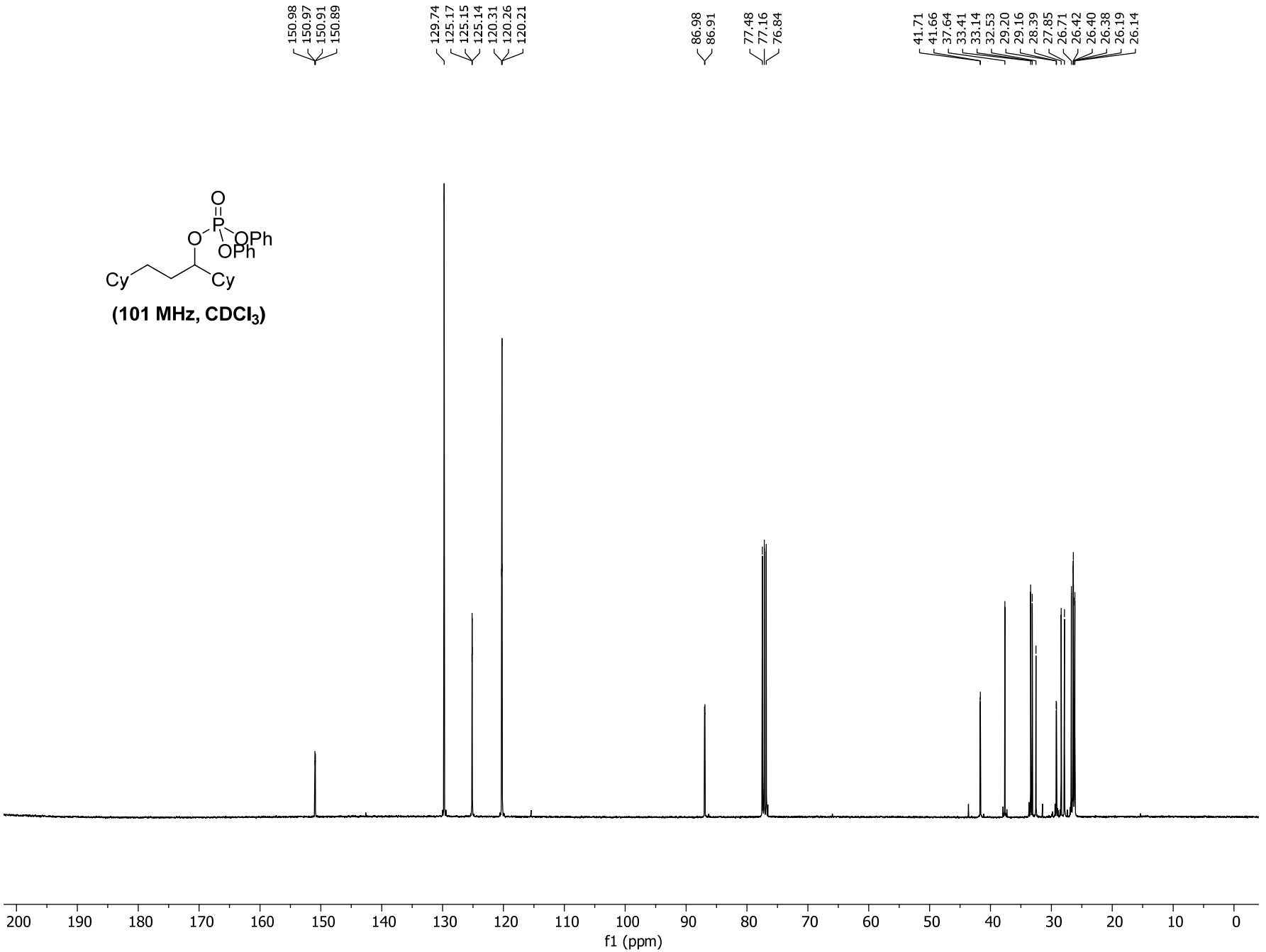


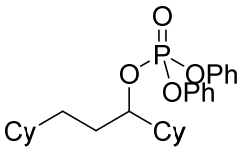
Fig. 3, entry 7
(101 MHz, $CDCl_3$)



(400 MHz, $CDCl_3$)




150.98
150.97
150.91
150.89
129.74
125.17
125.15
125.14
120.31
120.26
120.21
86.98
86.91
77.48
77.16
76.84
41.71
41.66
37.64
33.41
33.14
32.53
29.20
29.16
28.39
27.85
26.71
26.42
26.40
26.38
26.19
26.14
O
P
O
OPh
OPh
Cy
Cy
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



(162 MHz, $CDCl_3$)

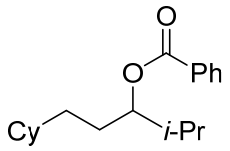
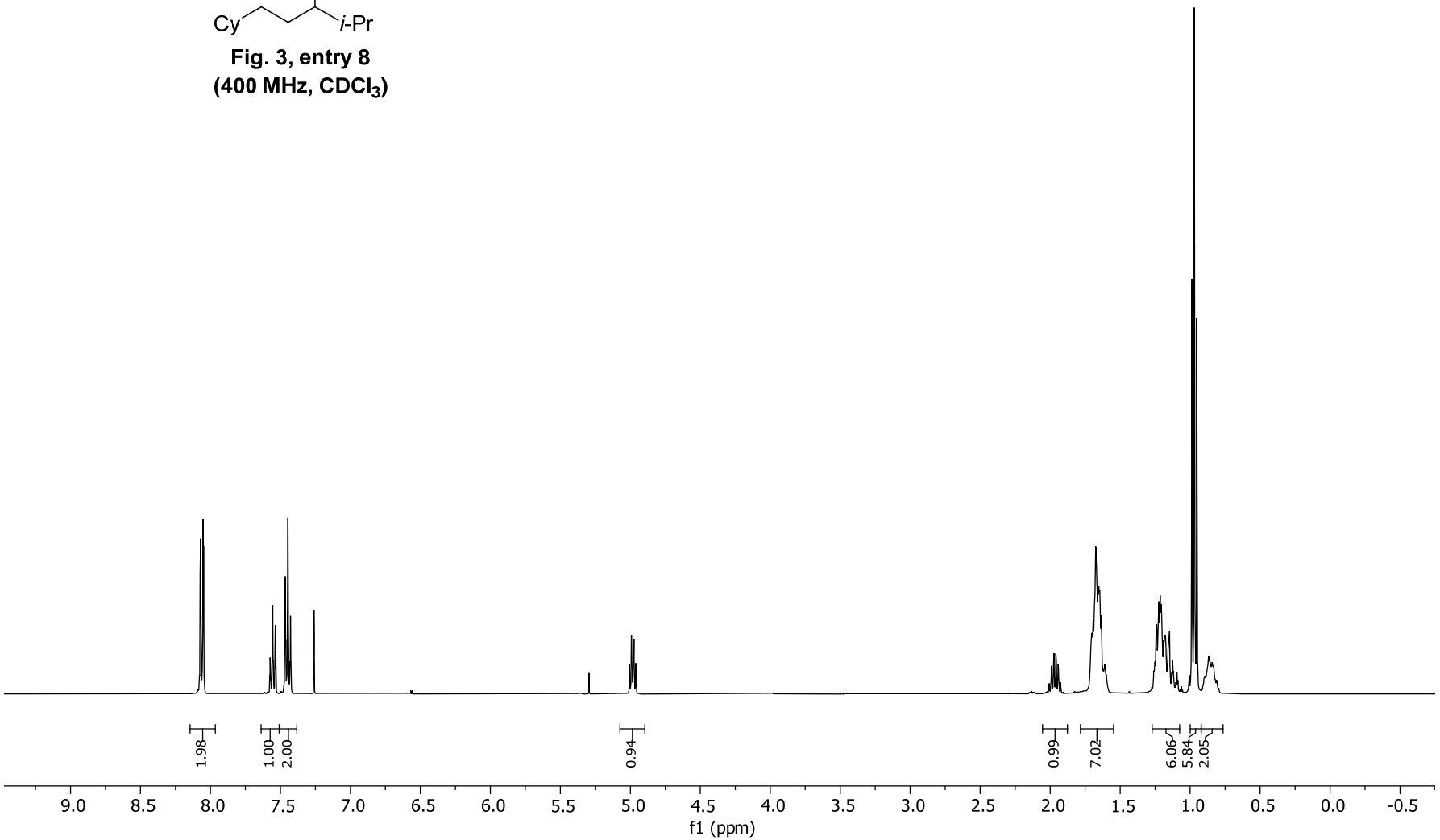


Fig. 3, entry 8
(400 MHz, $CDCl_3$)



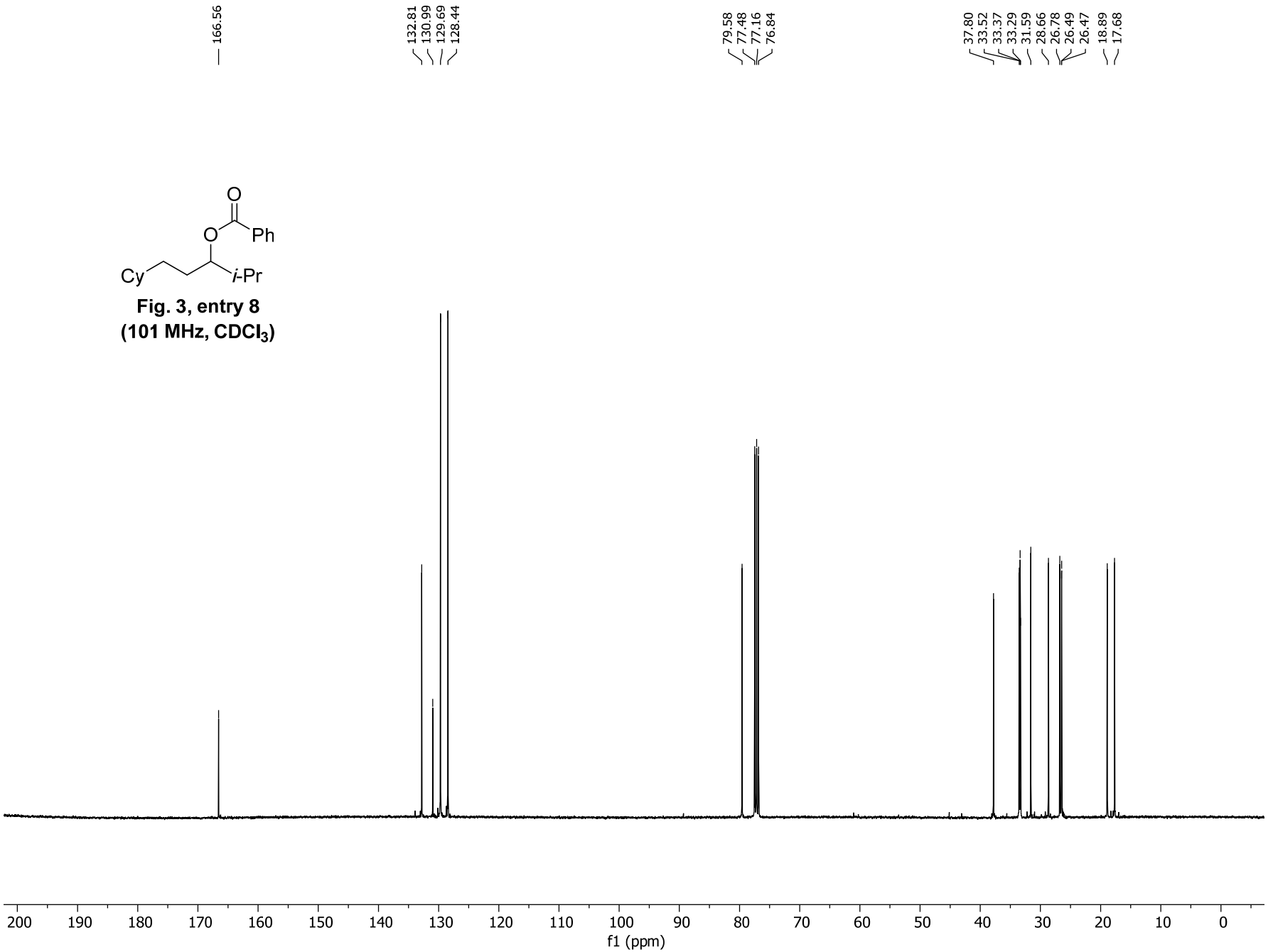


Fig. 3, entry 8
(101 MHz, $CDCl_3$)

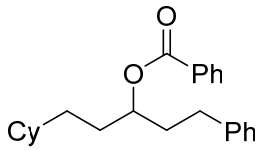
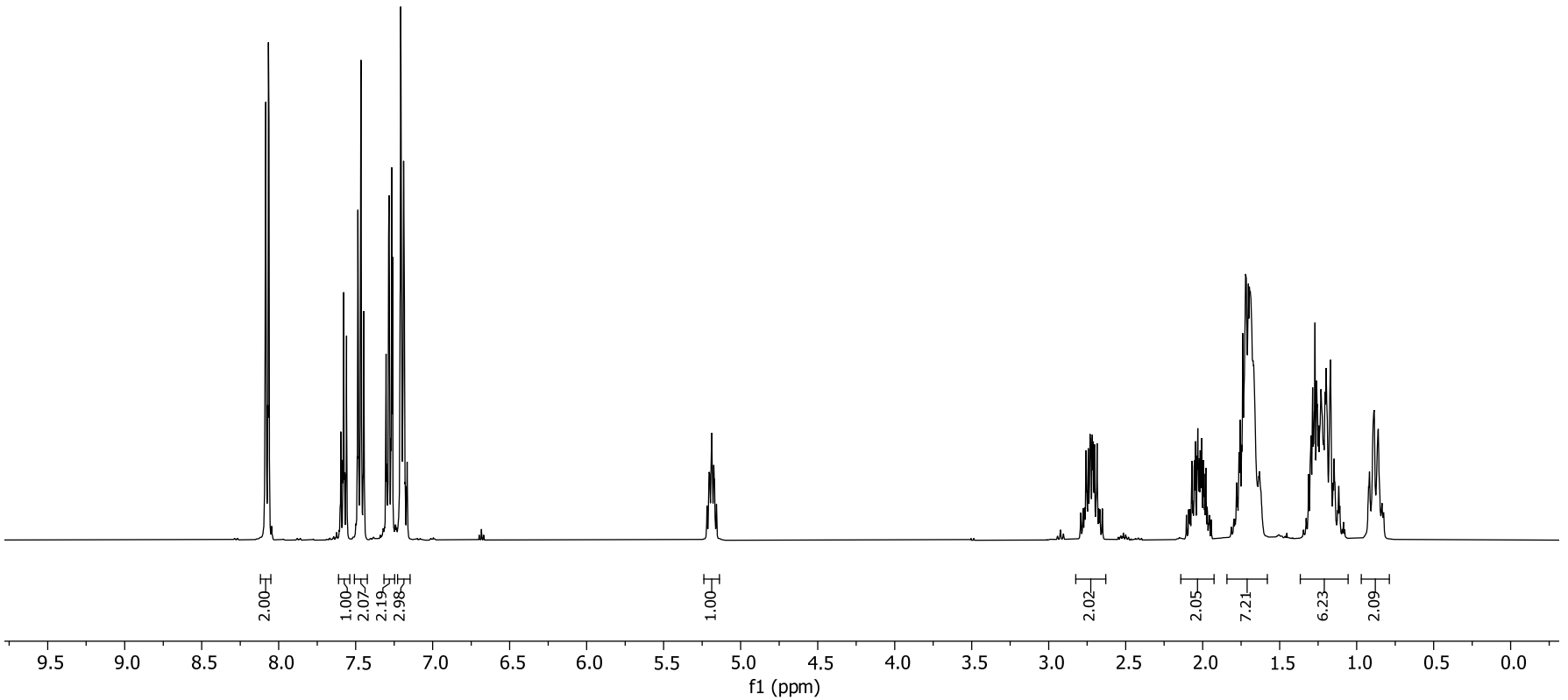


Fig. 3, entry 9
(400 MHz, $CDCl_3$)



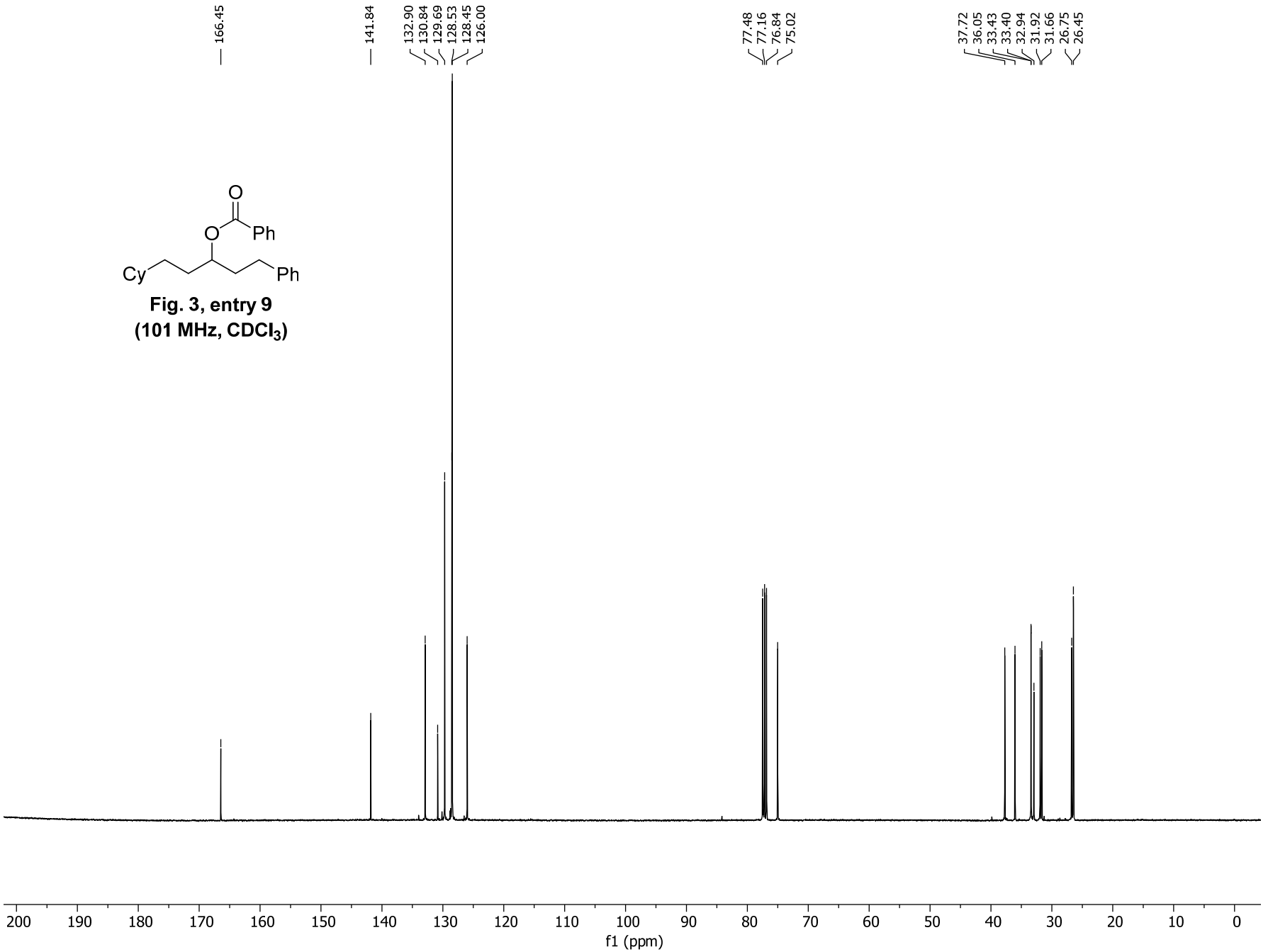


Fig. 3, entry 9
(101 MHz, $CDCl_3$)

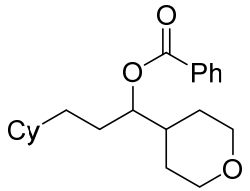
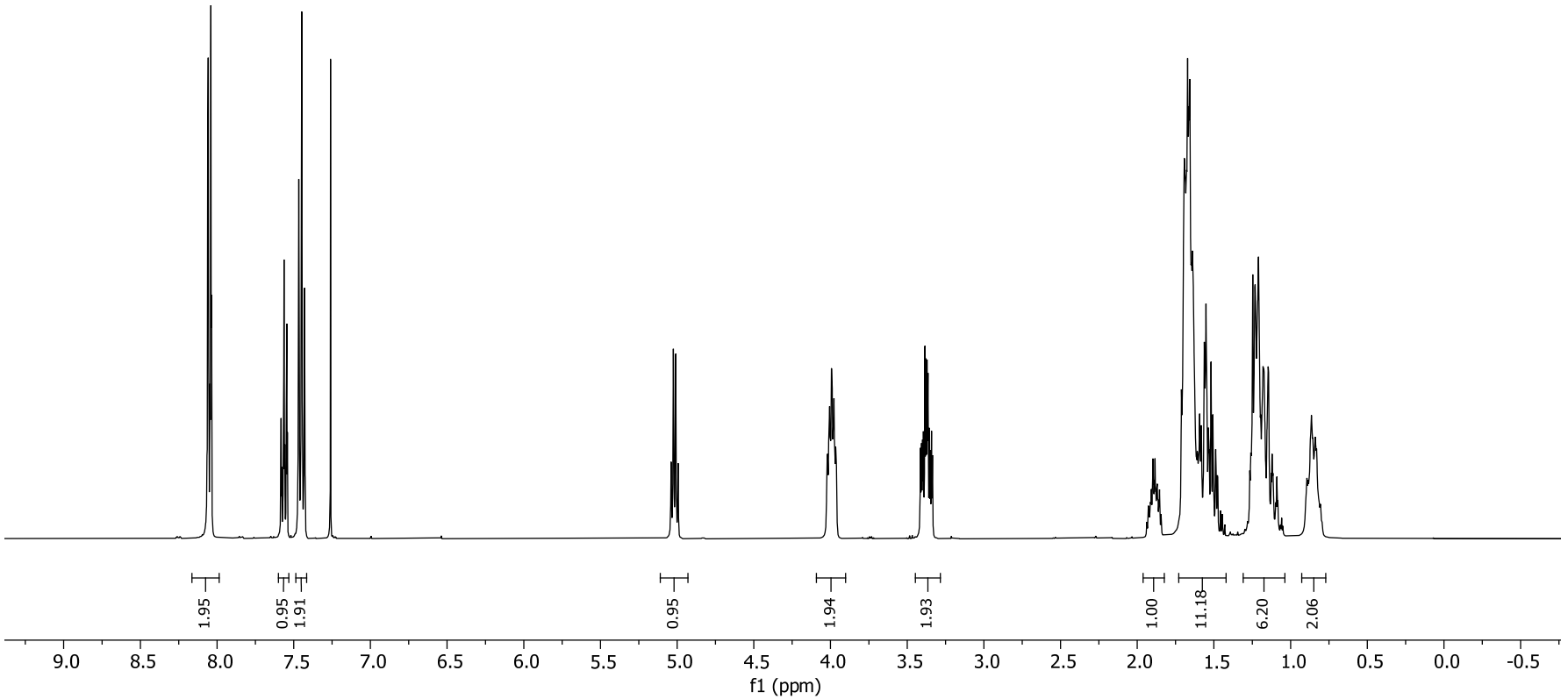


Fig. 3, entry 10
(400 MHz, $CDCl_3$)



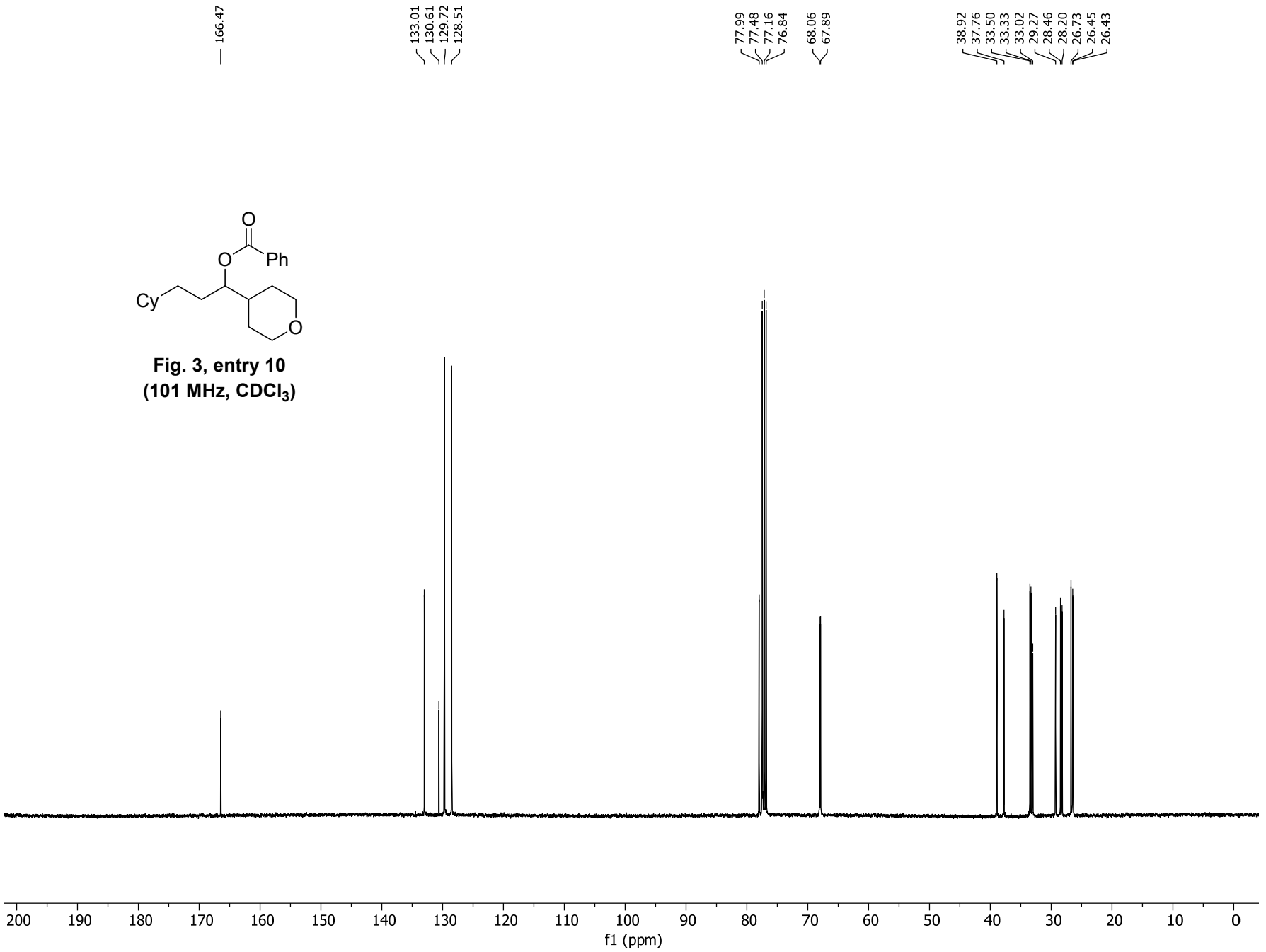


Fig. 3, entry 10
(101 MHz, $CDCl_3$)

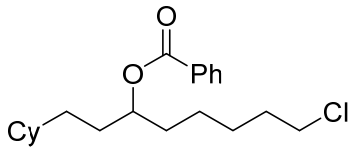
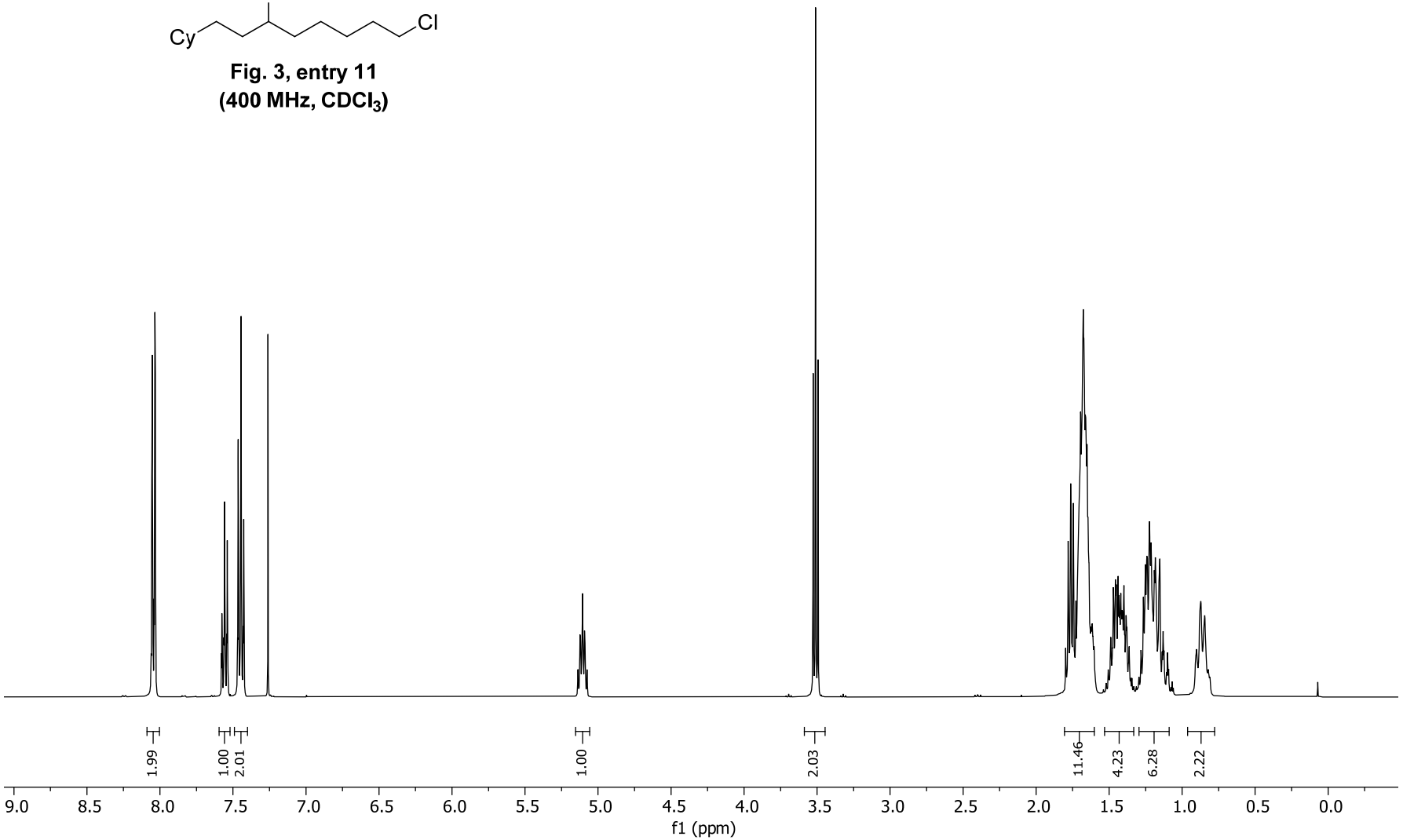


Fig. 3, entry 11
(400 MHz, $CDCl_3$)



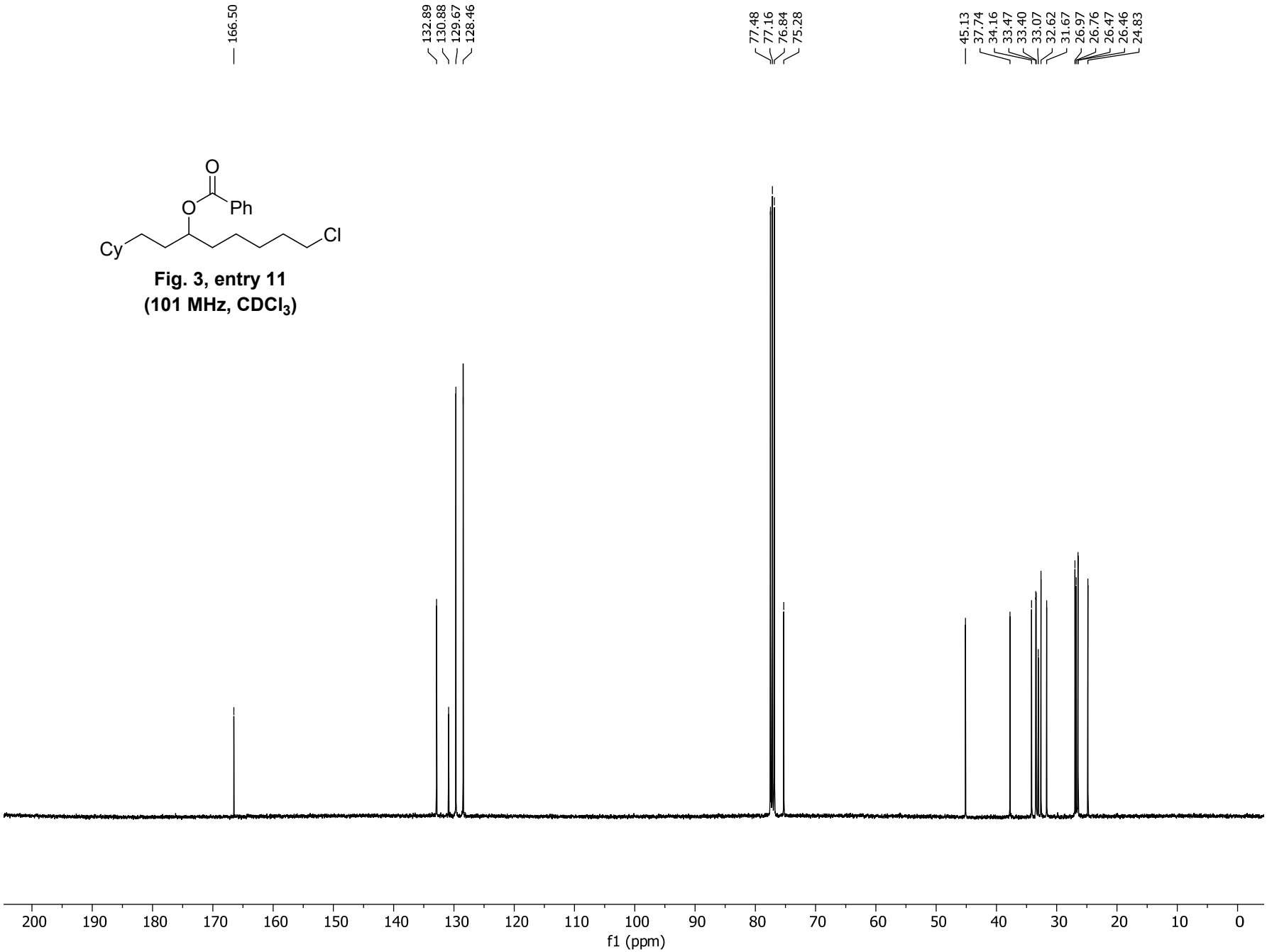


Fig. 3, entry 11
(101 MHz, $CDCl_3$)

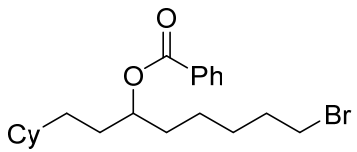


Fig. 3, entry 12
(400 MHz, $CDCl_3$)

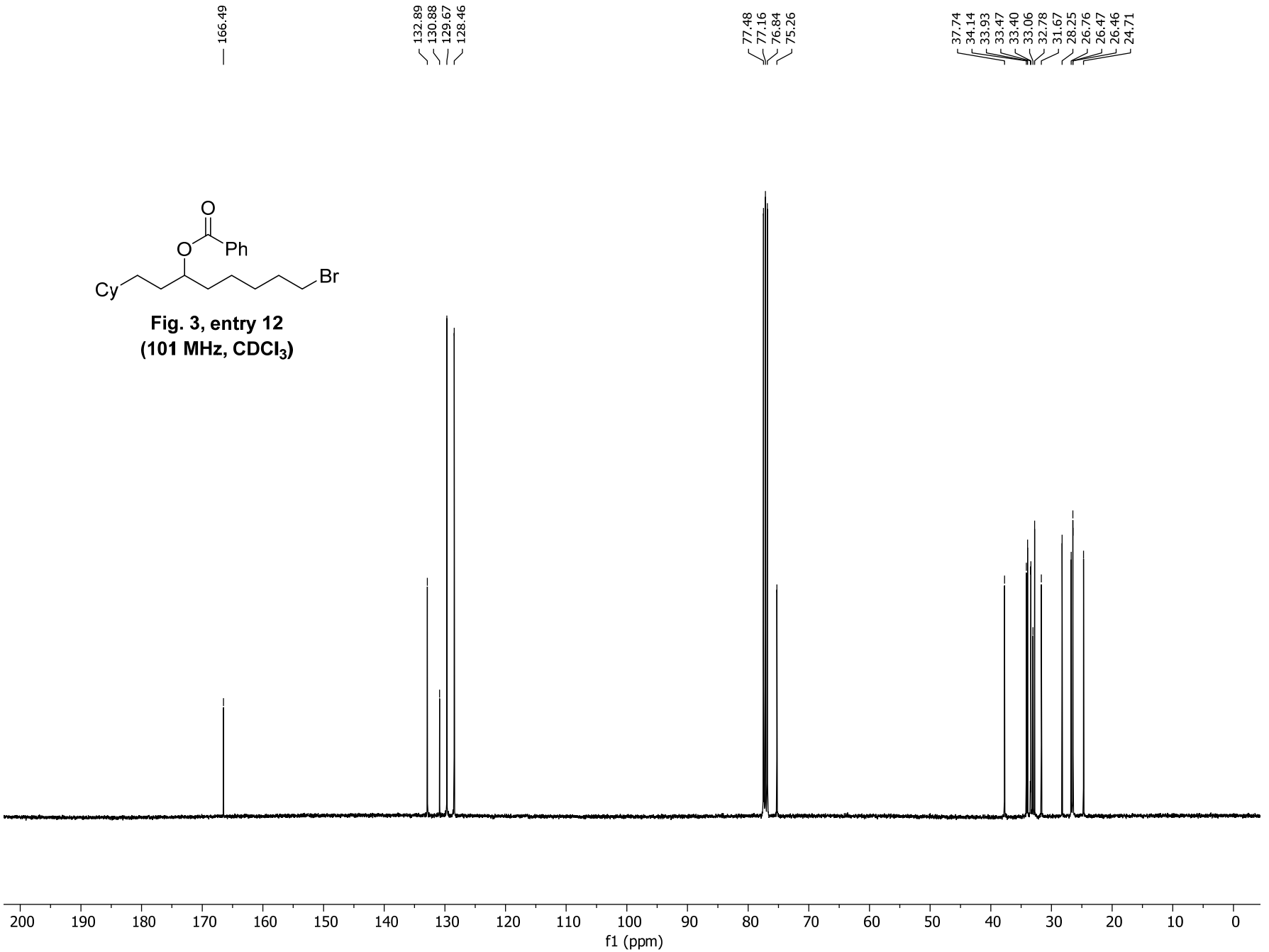


Fig. 3, entry 12
(101 MHz, $CDCl_3$)

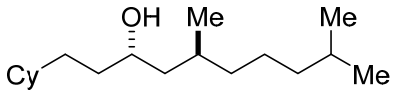


Fig. 3, entry 13
(400 MHz, $CDCl_3$)

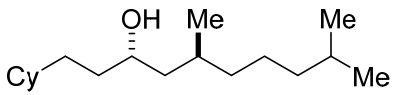


Fig. 3, entry 13
(101 MHz, $CDCl_3$)

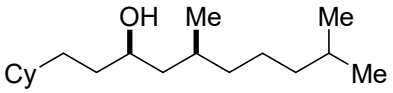


Fig. 3, entry 14
(400 MHz, $CDCl_3$)

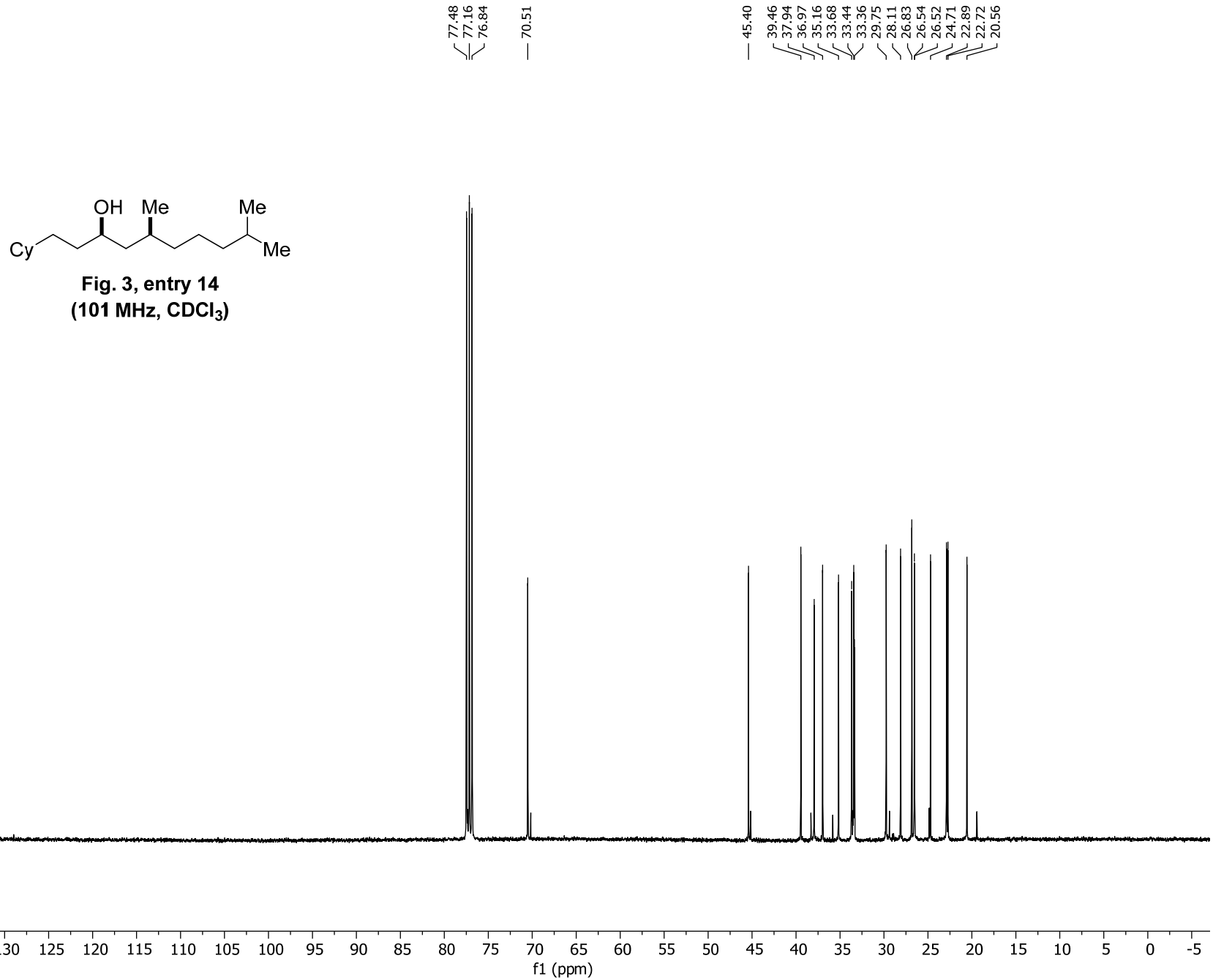
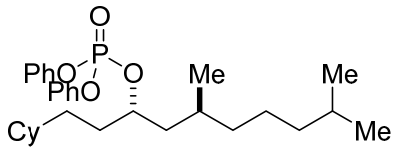
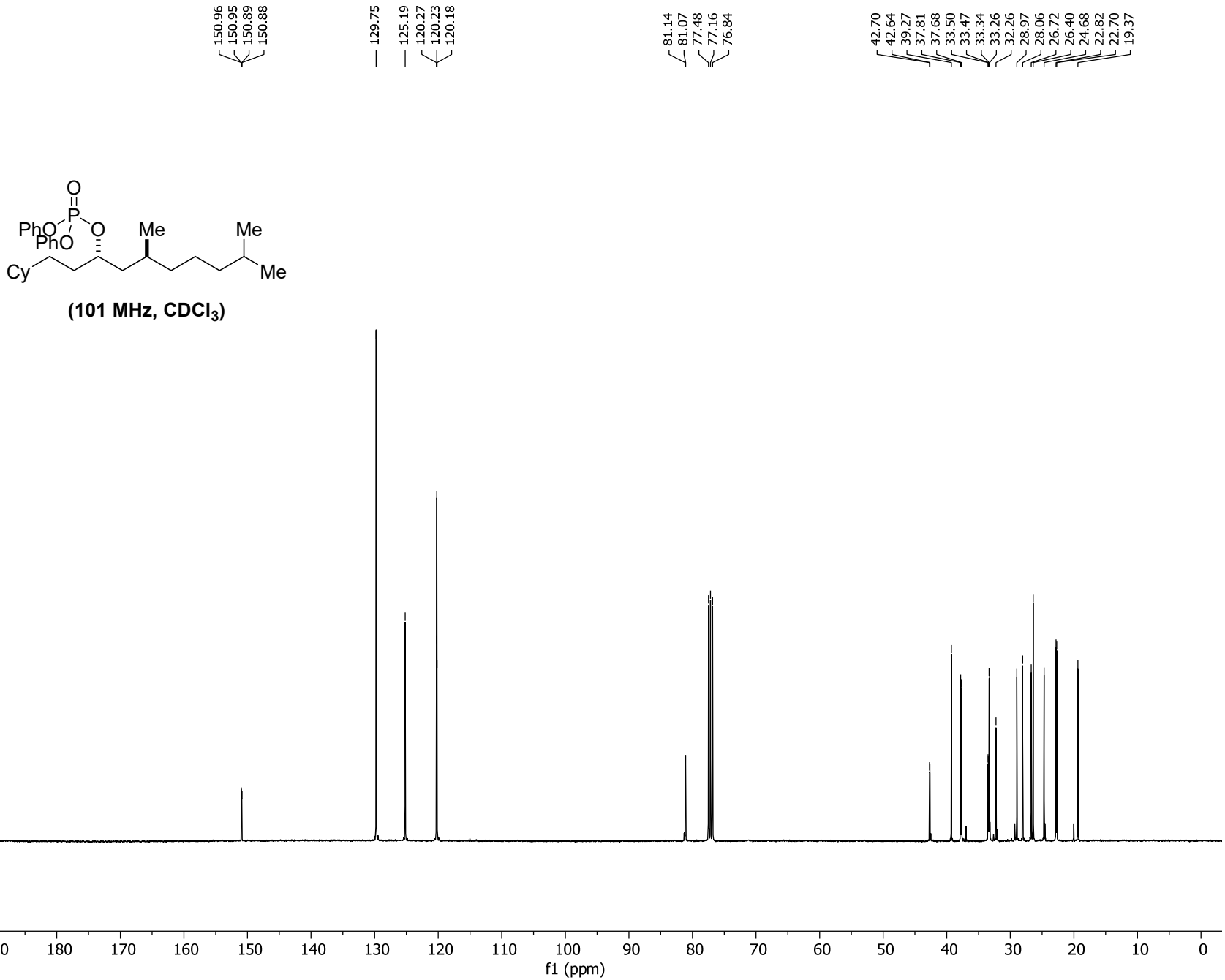
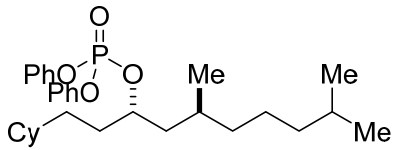


Fig. 3, entry 14
(101 MHz, $CDCl_3$)

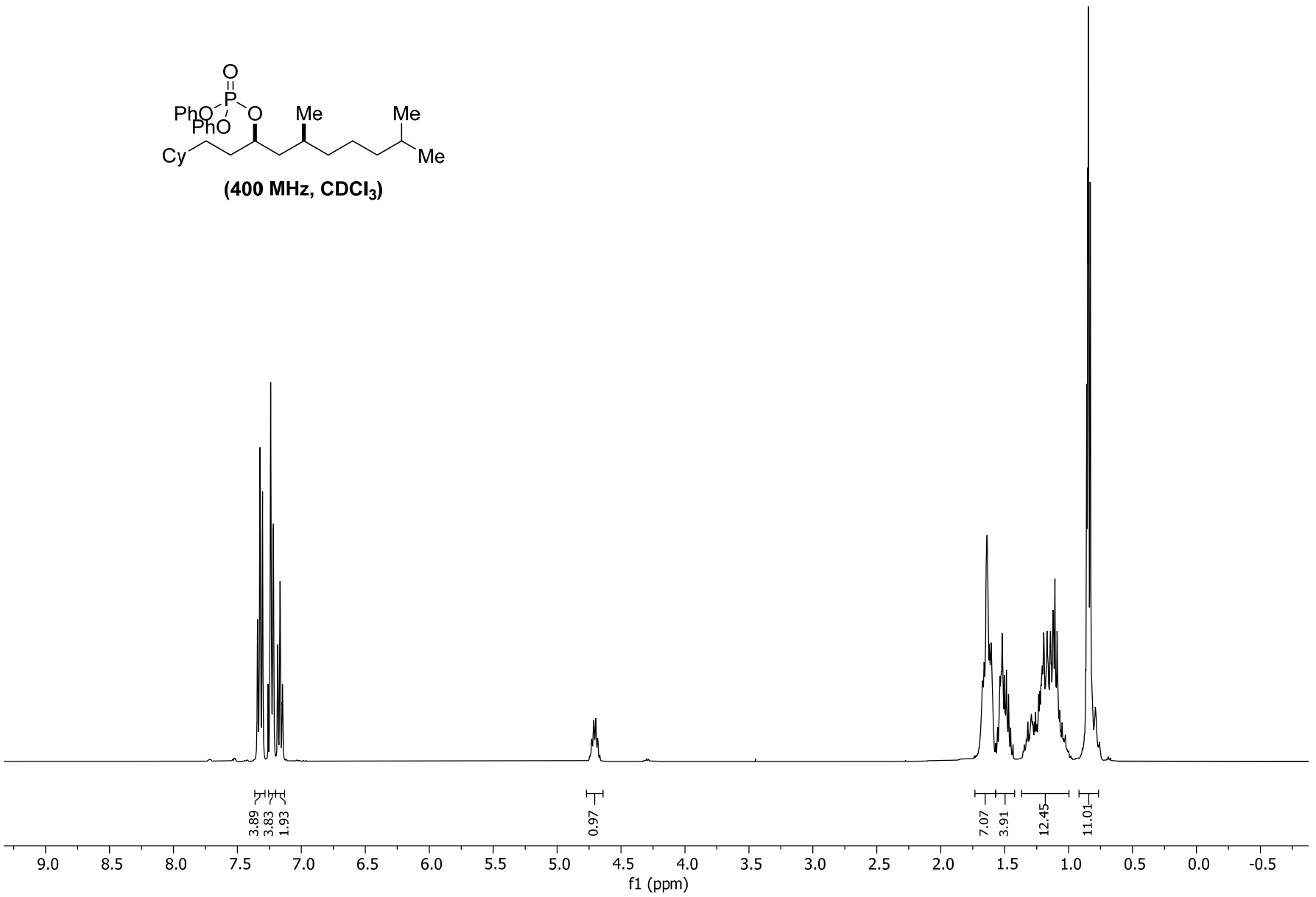


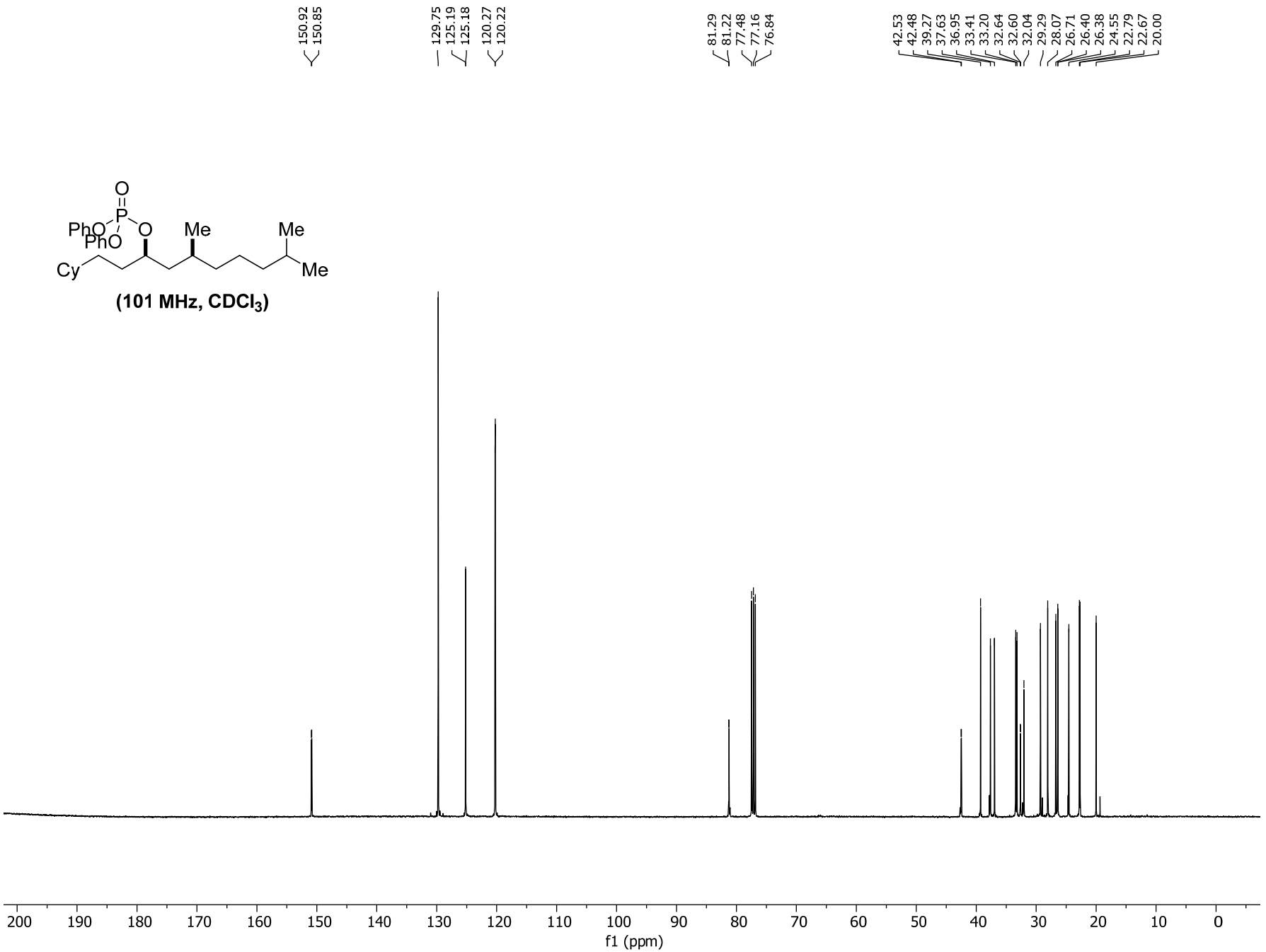
(400 MHz, $CDCl_3$)

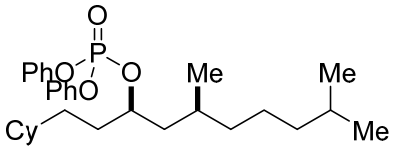

150.96
150.95
150.89
150.88
129.75
125.19
120.27
120.23
120.18
81.14
81.07
77.48
77.16
76.84
42.70
42.64
39.27
37.81
37.68
33.50
33.47
33.34
33.26
32.26
28.97
28.06
26.72
26.40
24.68
22.82
22.70
19.37
O
P
PhO
PhO
O
Me
Me
Cy
Me
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



(162 MHz, $CDCl_3$)


O
P
PhO
PhO
O
Me
Me
Cy
Me
(400 MHz, CDCl3)
3.89
3.83
1.93
0.97
7.07
3.91
12.45
11.01
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)


150.92
150.85
129.75
125.19
125.18
120.27
120.22
81.29
81.22
77.48
77.16
76.84
42.53
42.48
39.27
37.63
36.95
33.41
33.20
32.64
32.60
32.04
29.29
28.07
26.71
26.40
26.38
24.55
22.79
22.67
20.00
O
P
PhO
PhO
O
Me
Me
Cy
Me
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



(162 MHz, $CDCl_3$)

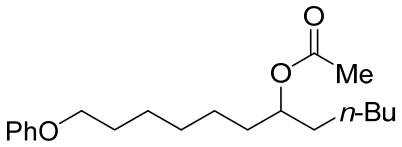


Fig. 3, entry 15
(400 MHz, $CDCl_3$)

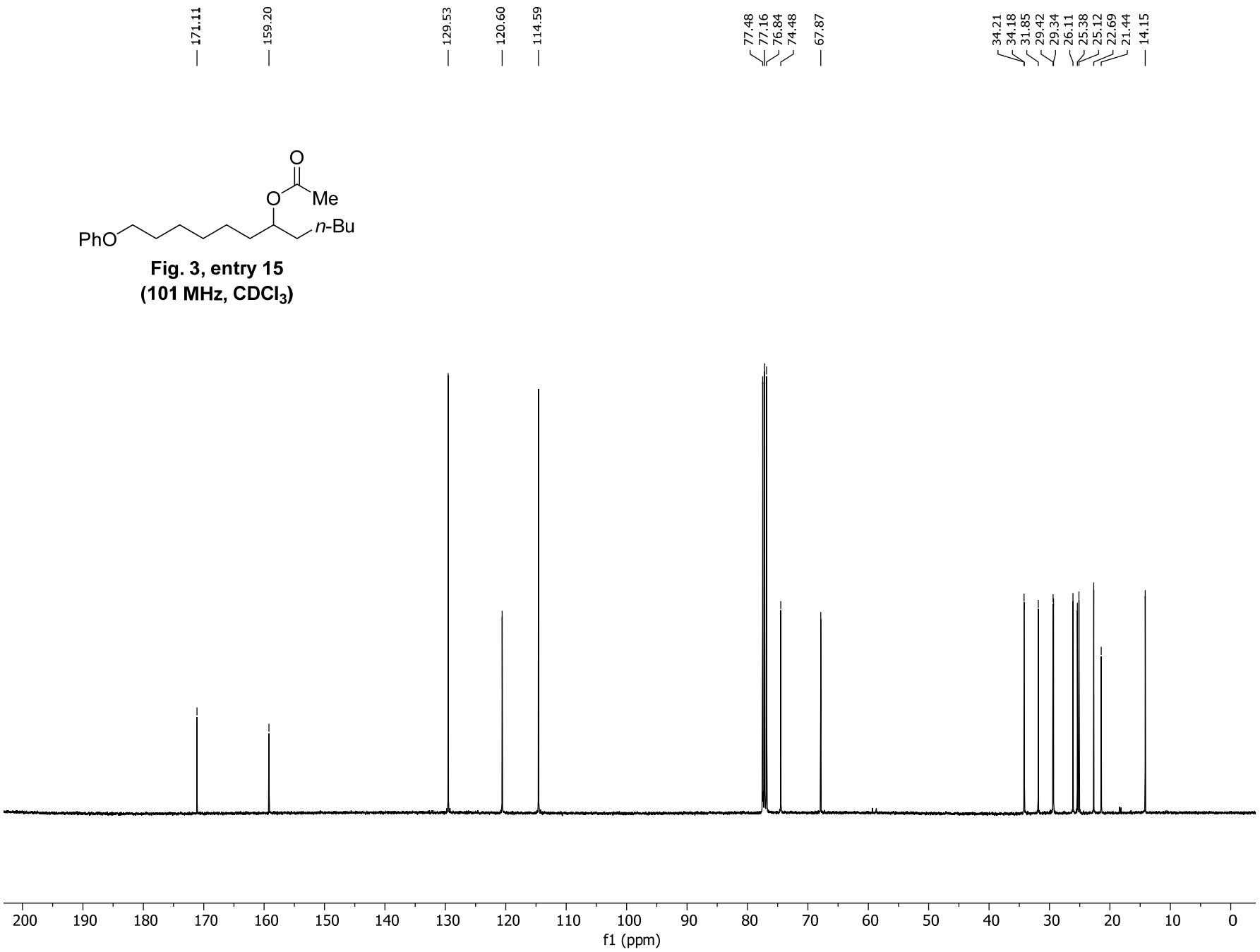


Fig. 3, entry 15
(101 MHz, $CDCl_3$)

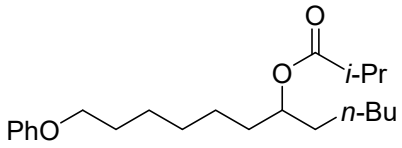


Fig. 3, entry 16
(400 MHz, $CDCl_3$)

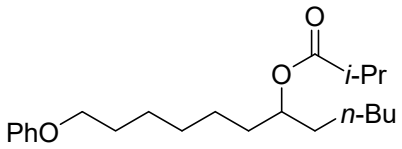


Fig. 3, entry 16
(101 MHz, $CDCl_3$)

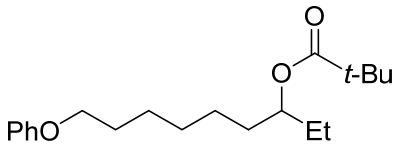


Fig. 3, entry 17
(400 MHz, $CDCl_3$)

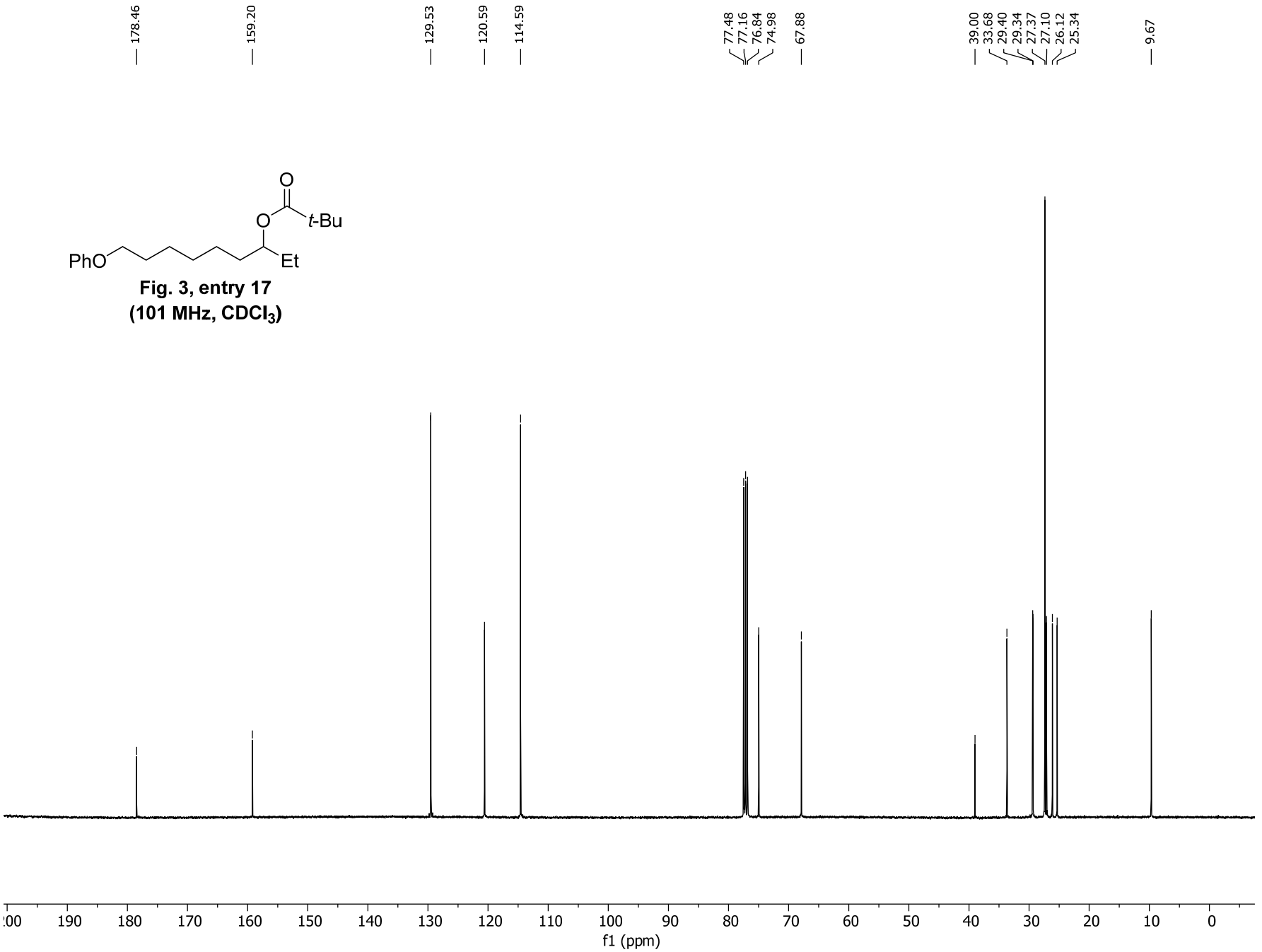


Fig. 3, entry 17
(101 MHz, $CDCl_3$)

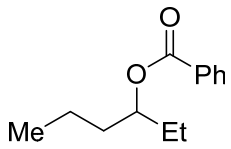


Fig. 3, entry 18
(400 MHz, $CDCl_3$)

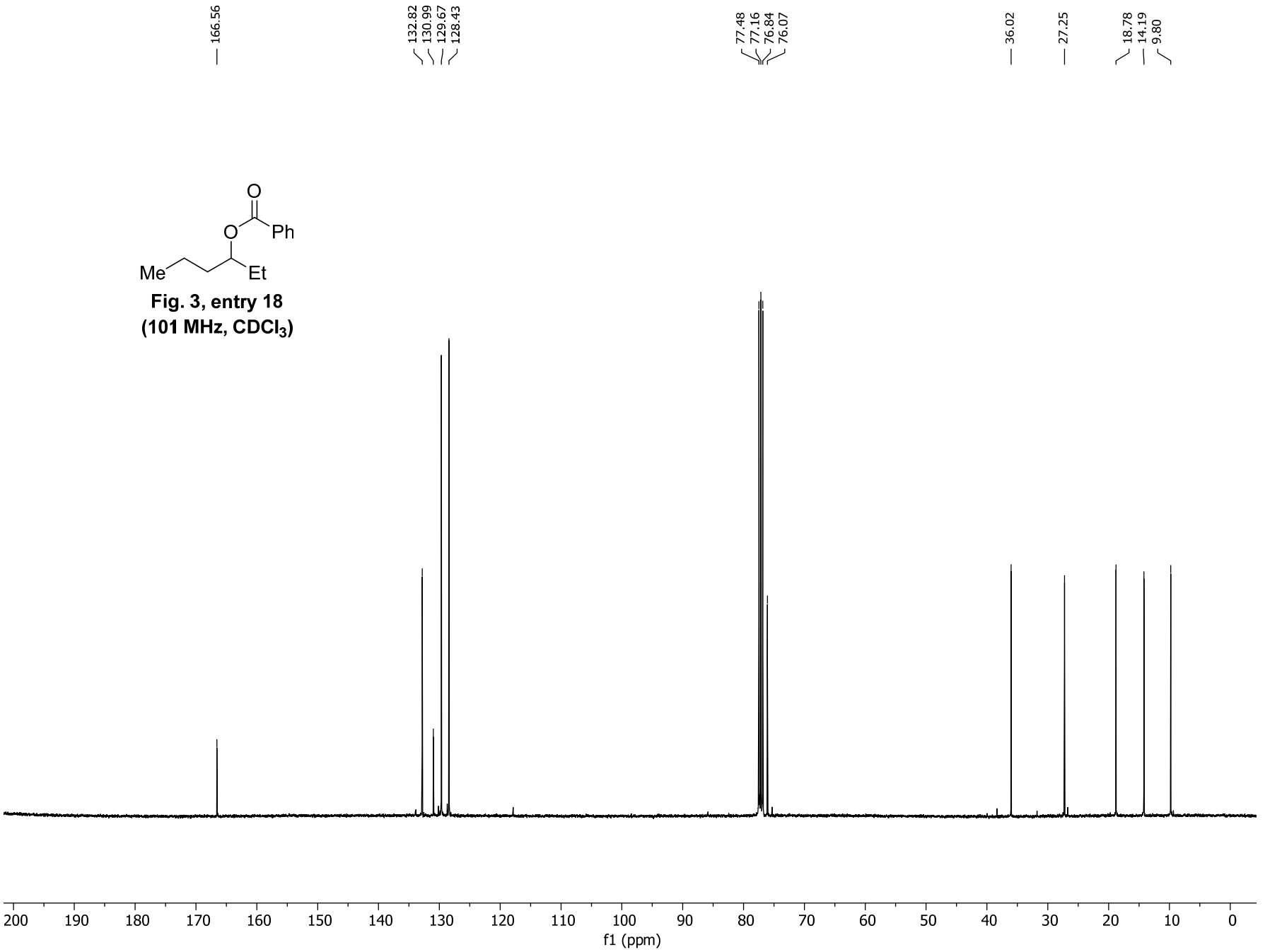
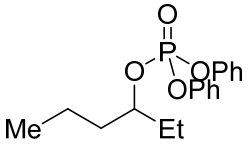
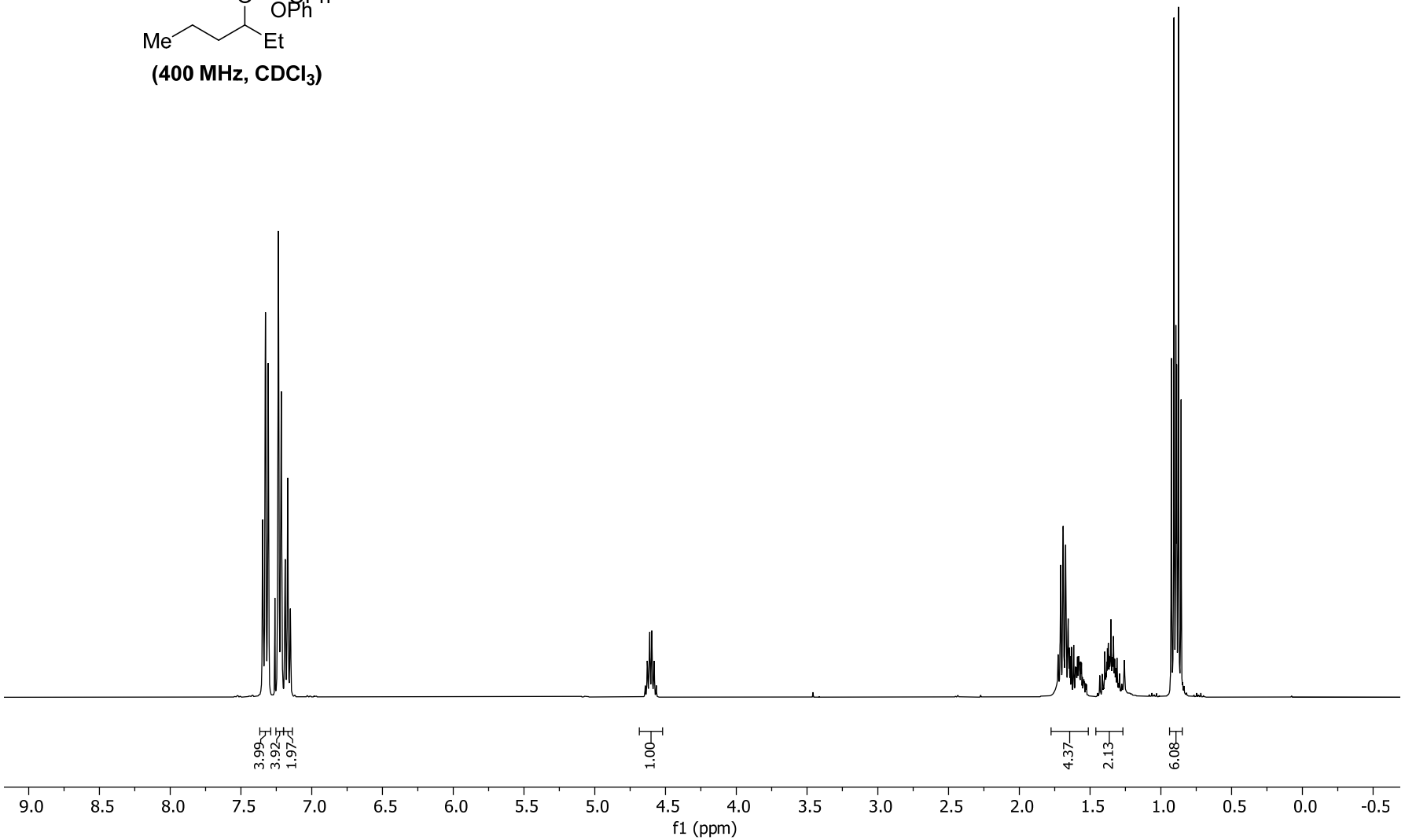
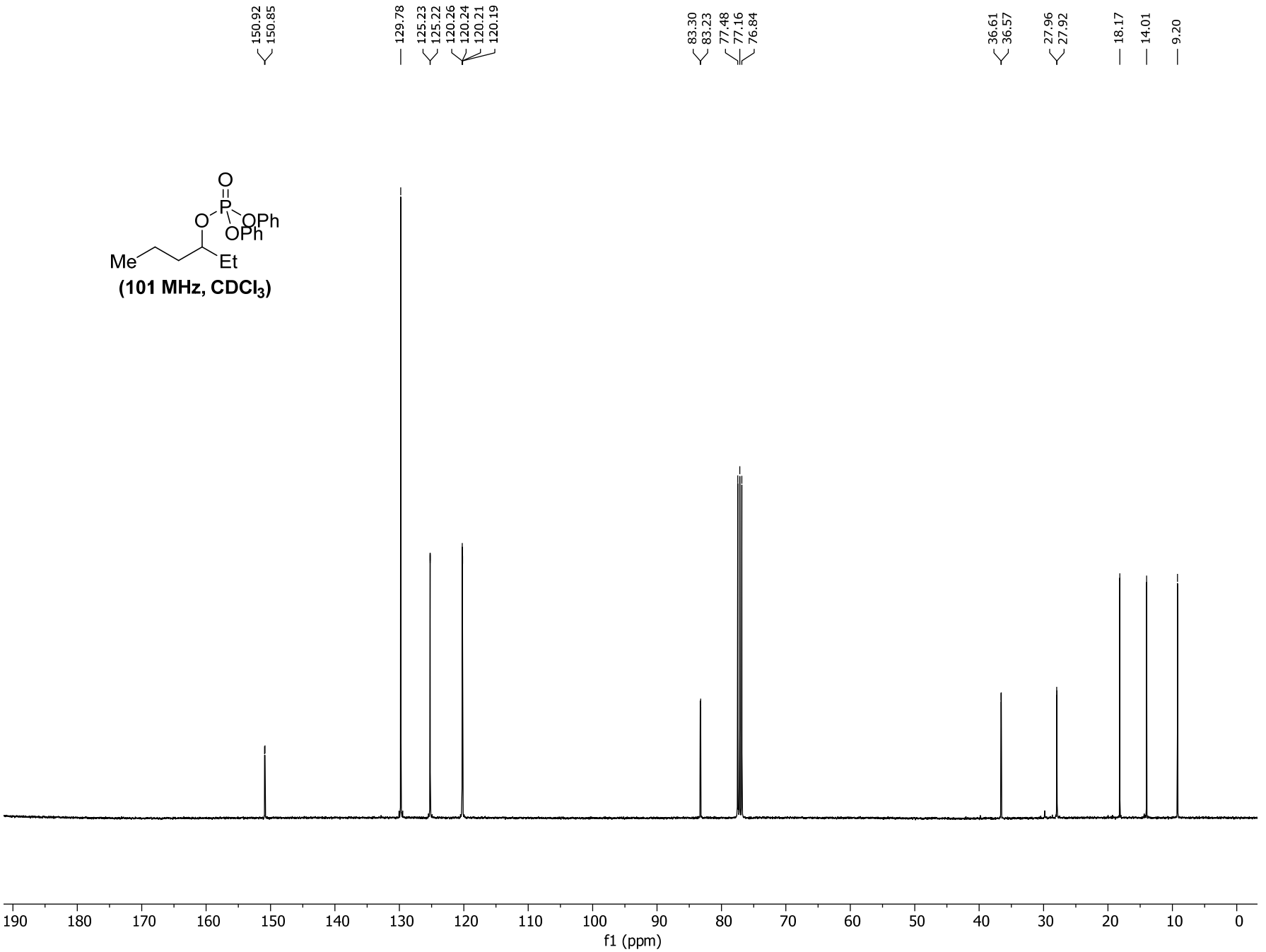


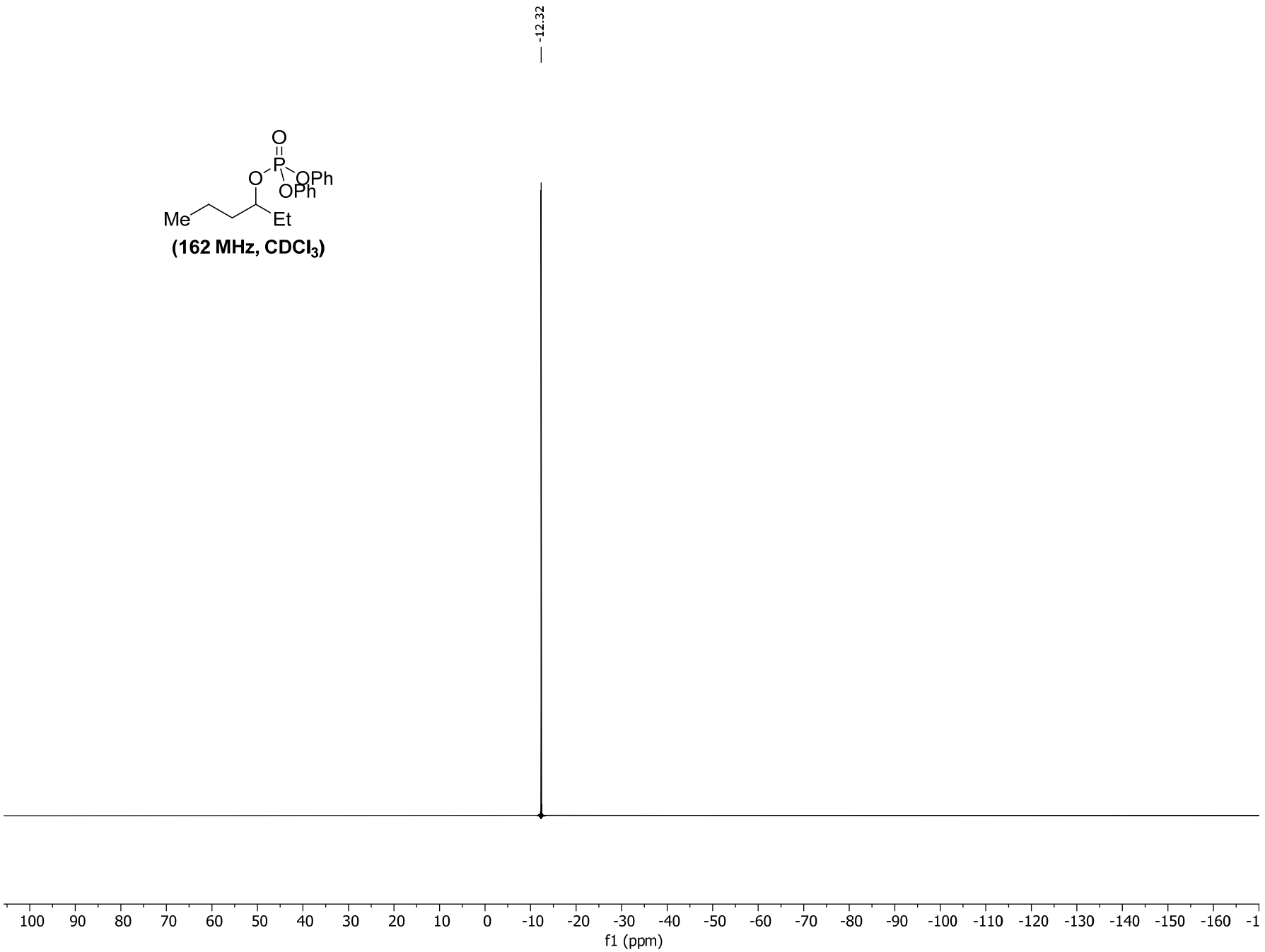
Fig. 3, entry 18
(101 MHz, $CDCl_3$)



(400 MHz, $CDCl_3$)




150.92
150.85
129.78
125.23
125.22
120.26
120.24
120.21
120.19
83.30
83.23
77.48
77.16
76.84
36.61
36.57
27.96
27.92
18.17
14.01
9.20
O
P
O
OPh
OPh
Me
Et
(101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-12.32
O
P
O
OPh
OPh
Me
Et
(162 MHz, CDCl3)
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -1
f1 (ppm)

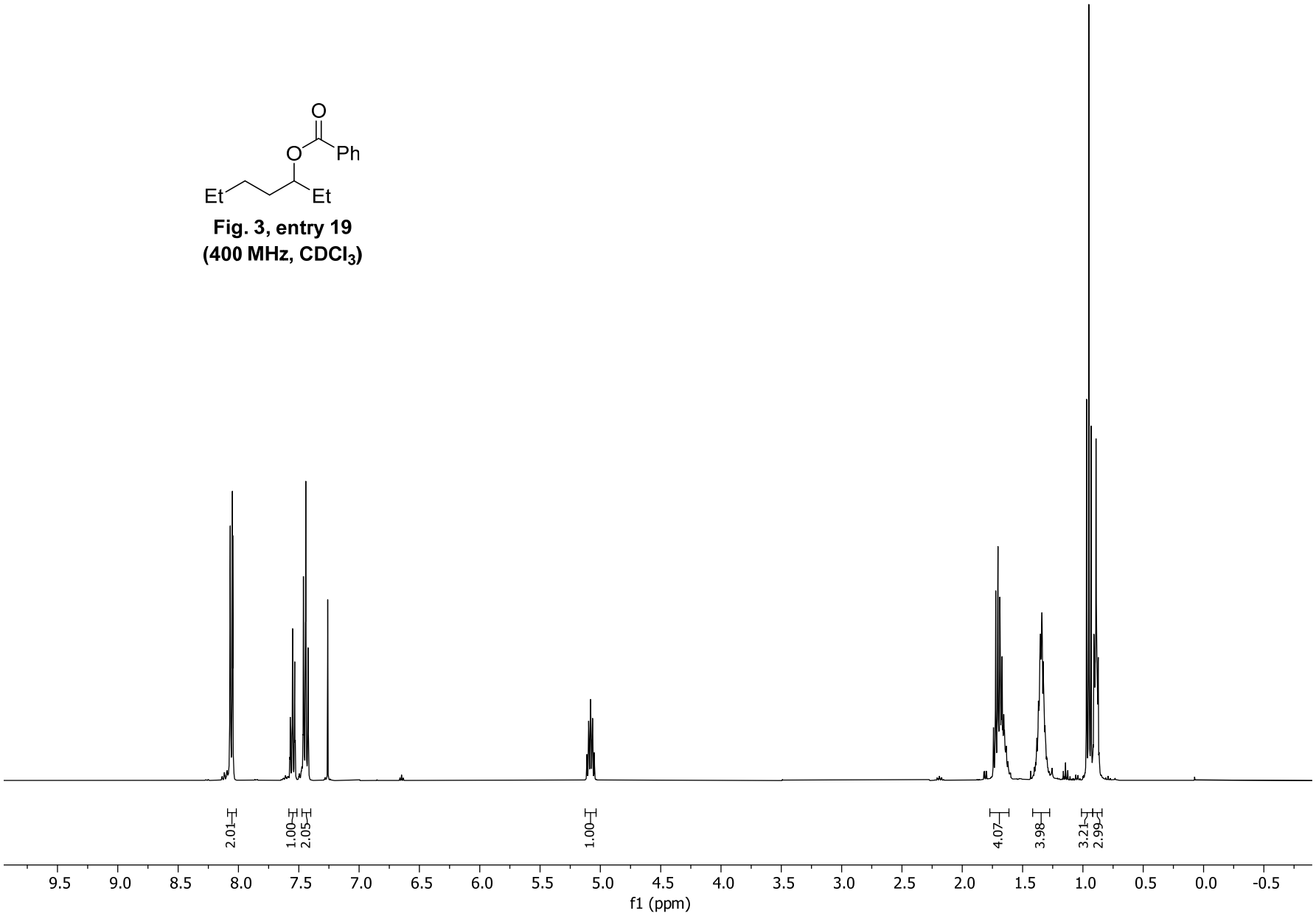


Fig. 3, entry 19
(400 MHz, $CDCl_3$)

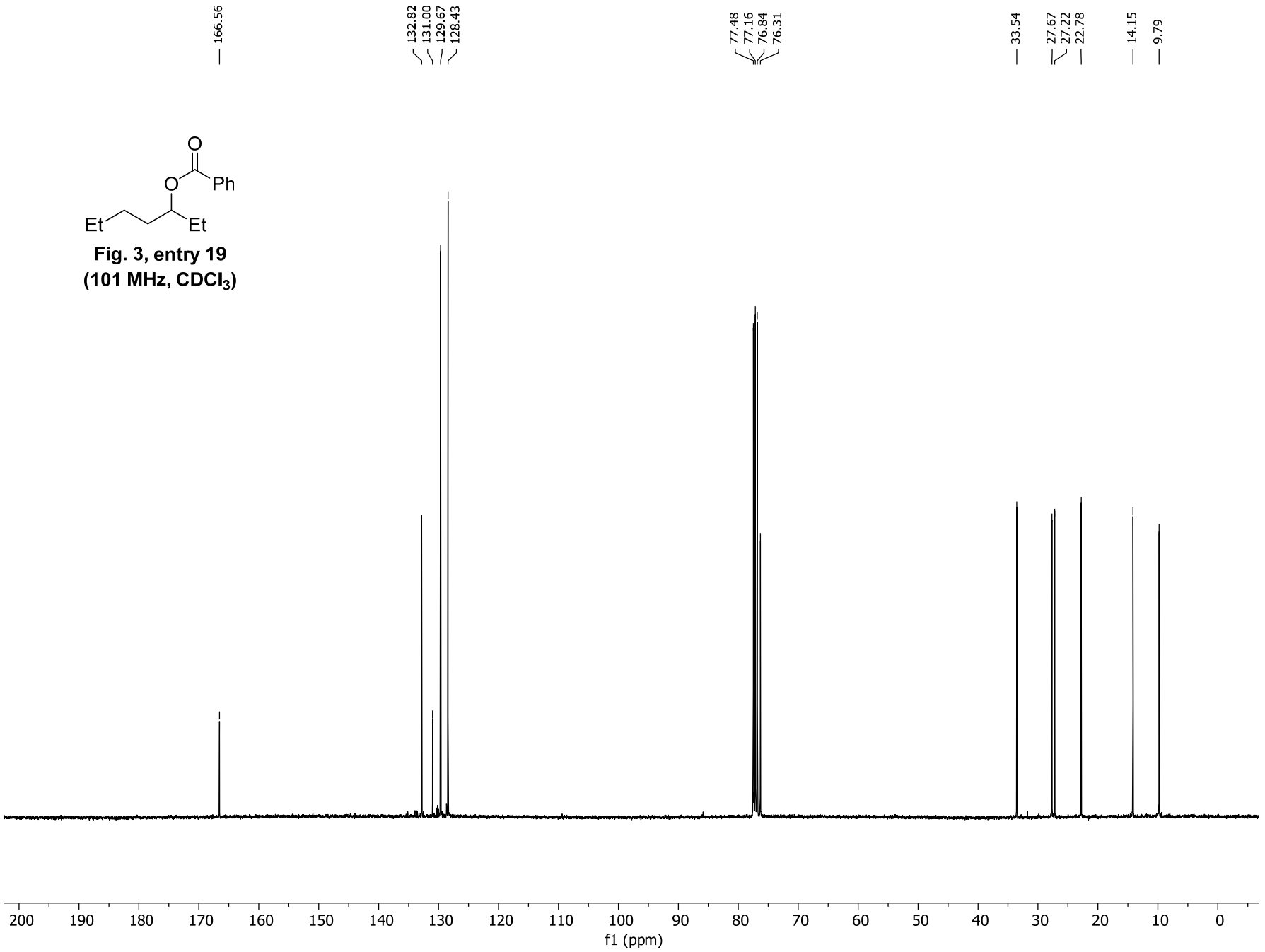
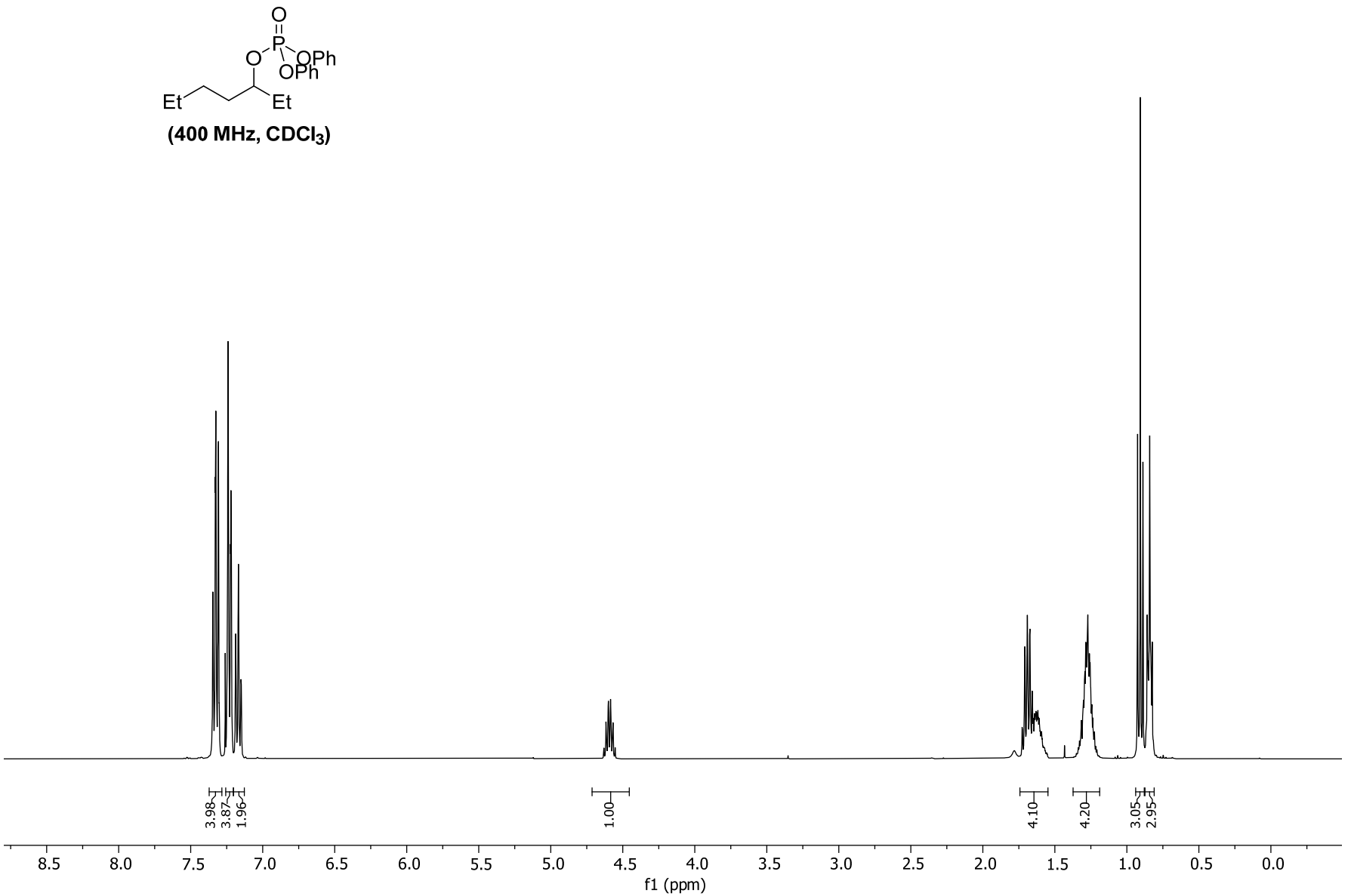
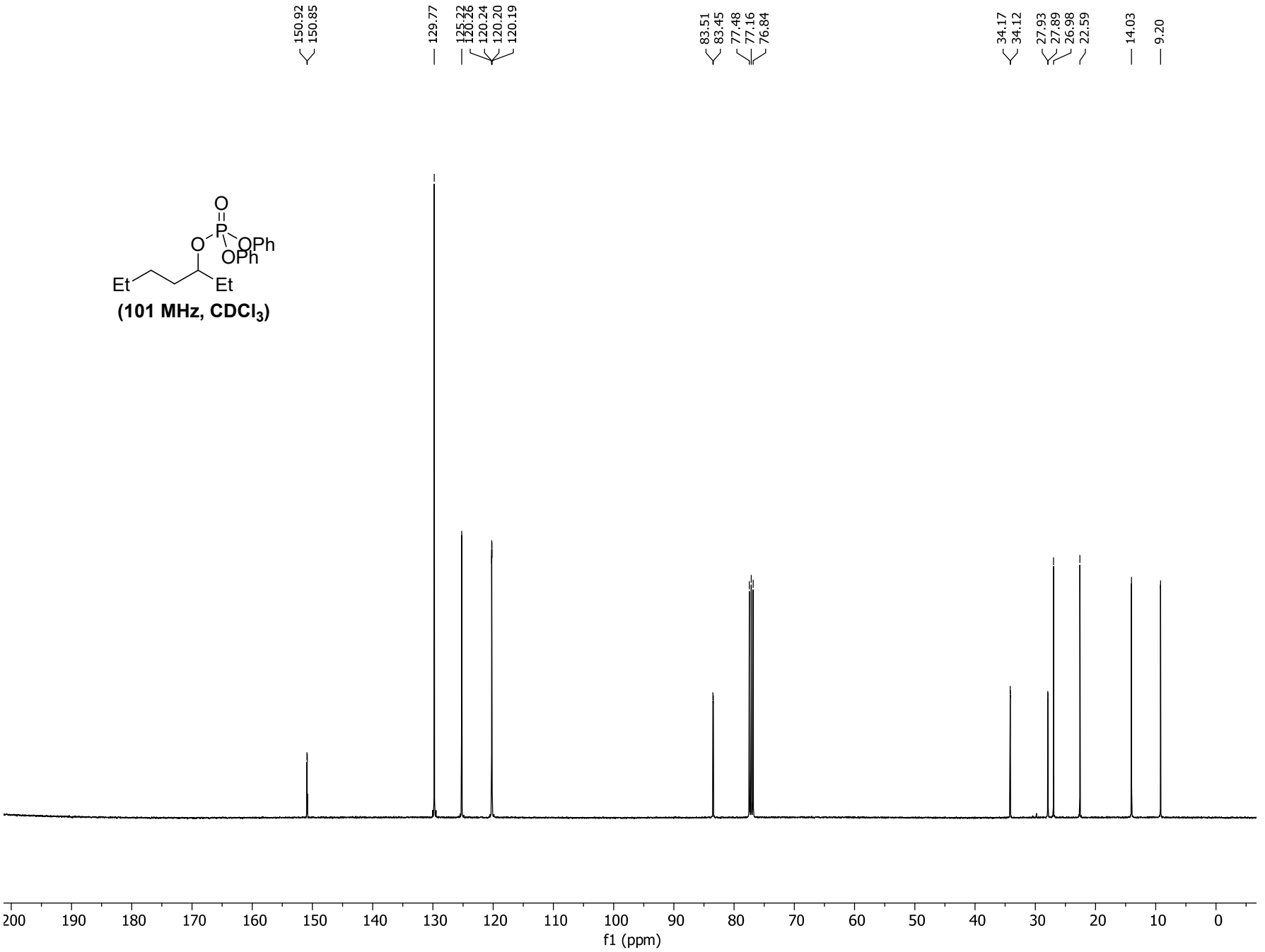
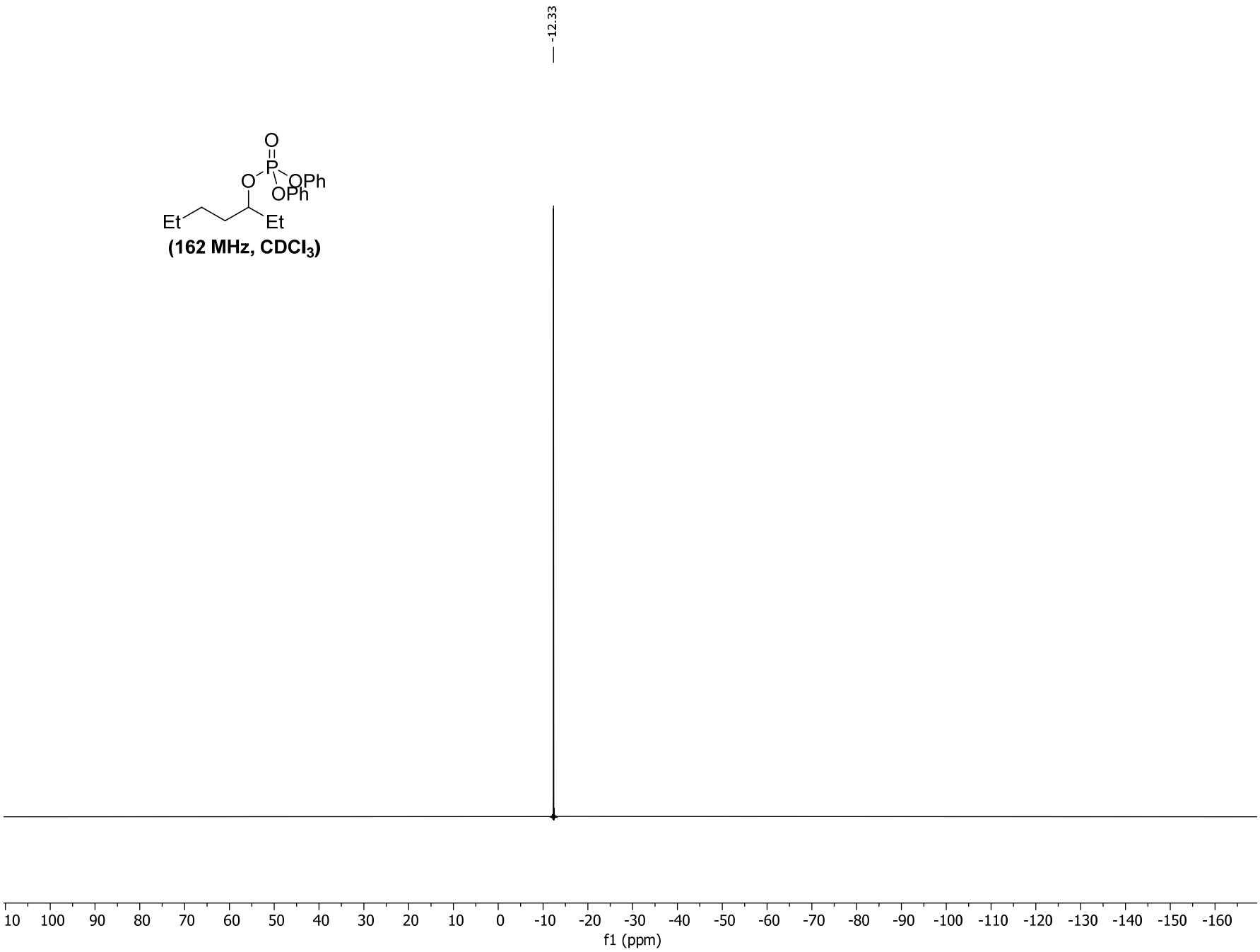


Fig. 3, entry 19
(101 MHz, $CDCl_3$)


O
P
O
OPh
OPh
Et
Et
(400 MHz, CDCl3)
3.98
3.87
1.96
1.00
4.10
4.20
3.05
2.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


150.92
150.85
129.77
125.22
120.26
120.24
120.20
120.19
83.51
83.45
77.48
77.16
76.84
34.17
34.12
27.93
27.89
26.98
22.59
14.03
9.20
O
P
O
OPh
OPh
Et
Et
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-12.33
O
P
O
OPh
OPh
Et
Et
(162 MHz, CDCl3)
10 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

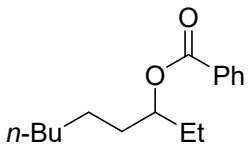


Fig. 3, entry 20
(400 MHz, $CDCl_3$)

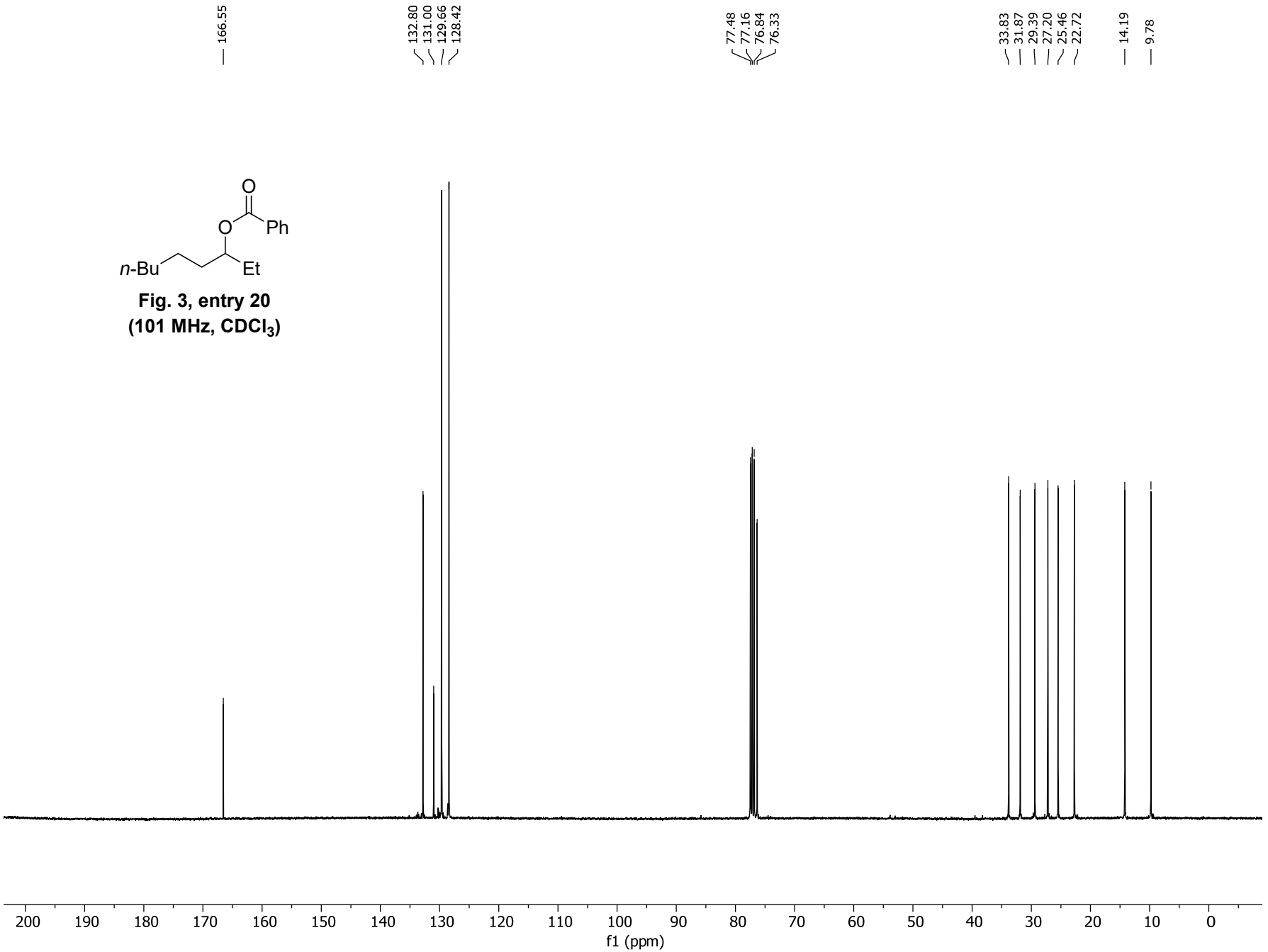
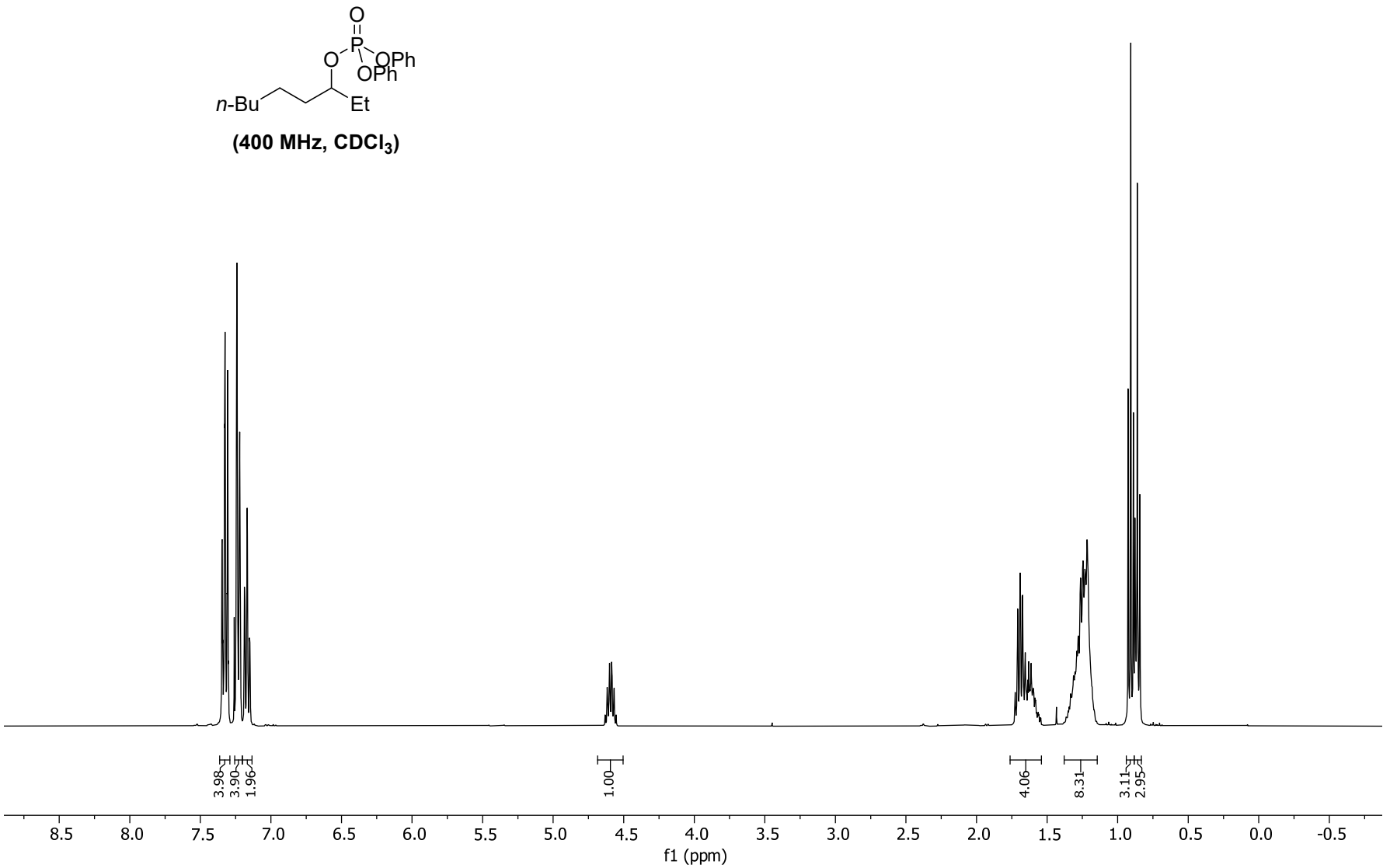
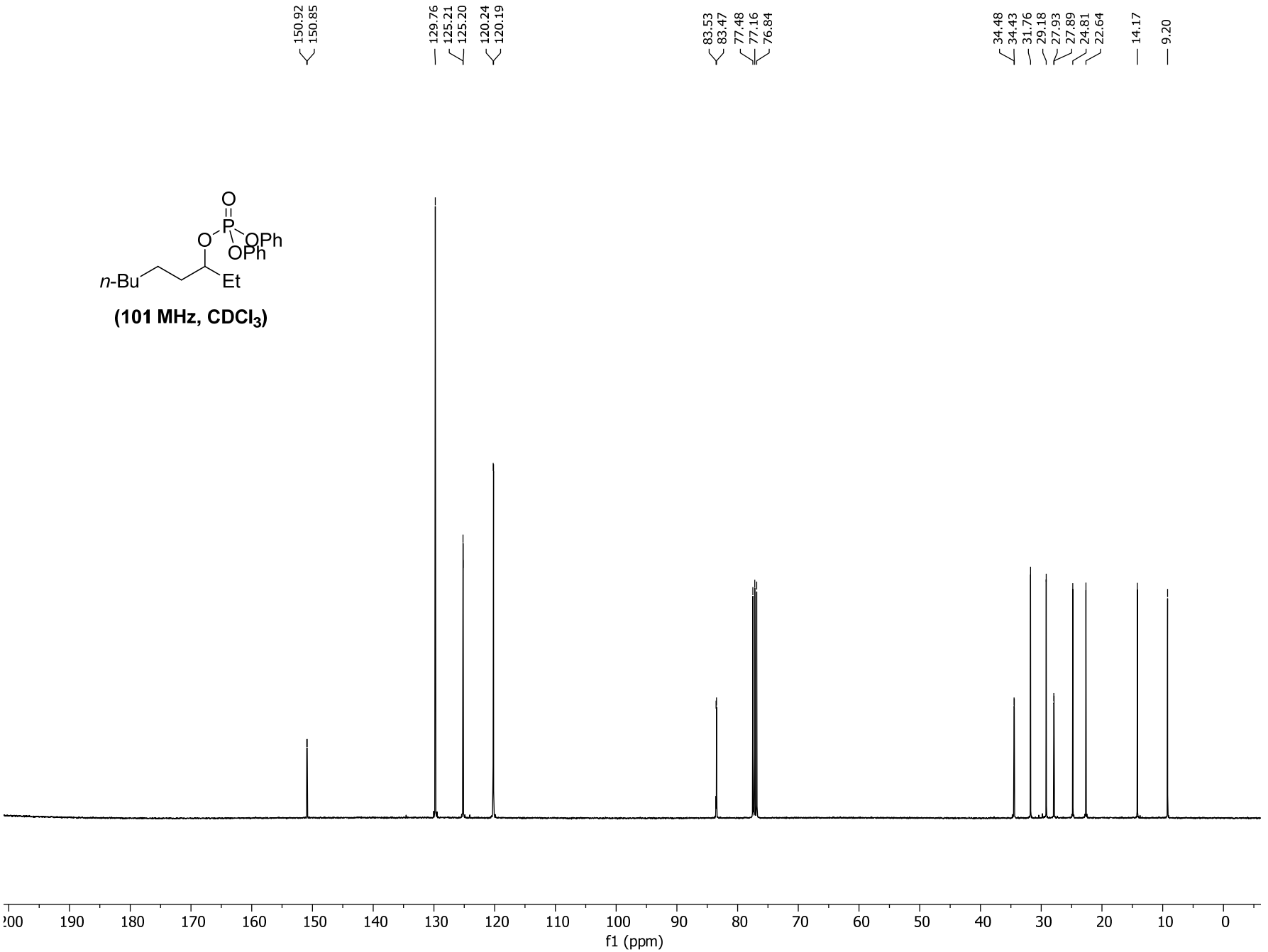
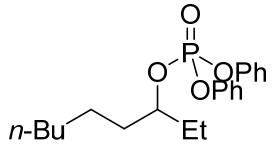


Fig. 3, entry 20
(101 MHz, $CDCl_3$)


O
P
O
OPh
OPh
n-Bu
Et
(400 MHz, CDCl3)
3.98
3.90
1.96
1.00
4.06
8.31
3.11
2.95
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)


150.92
150.85
129.76
125.21
125.20
120.24
120.19
83.53
83.47
77.48
77.16
76.84
34.48
34.43
31.76
29.18
27.93
27.89
24.81
22.64
14.17
9.20
O
P
O
OPh
OPh
n-Bu
Et
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



(162 MHz, $CDCl_3$)

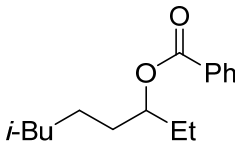


Fig. 3, entry 21
(400 MHz, $CDCl_3$)

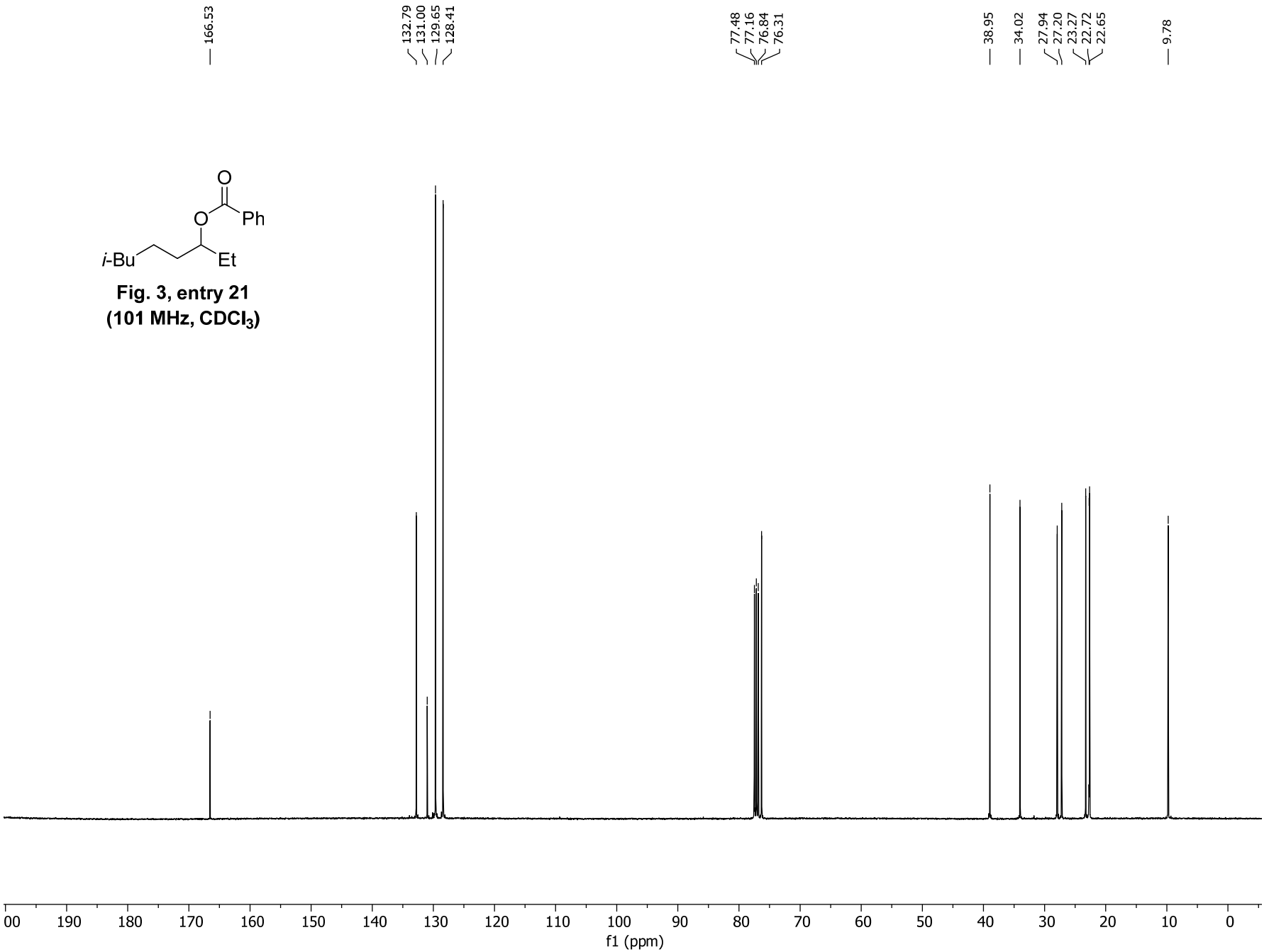
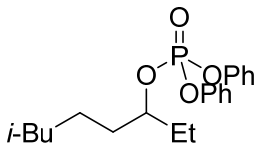
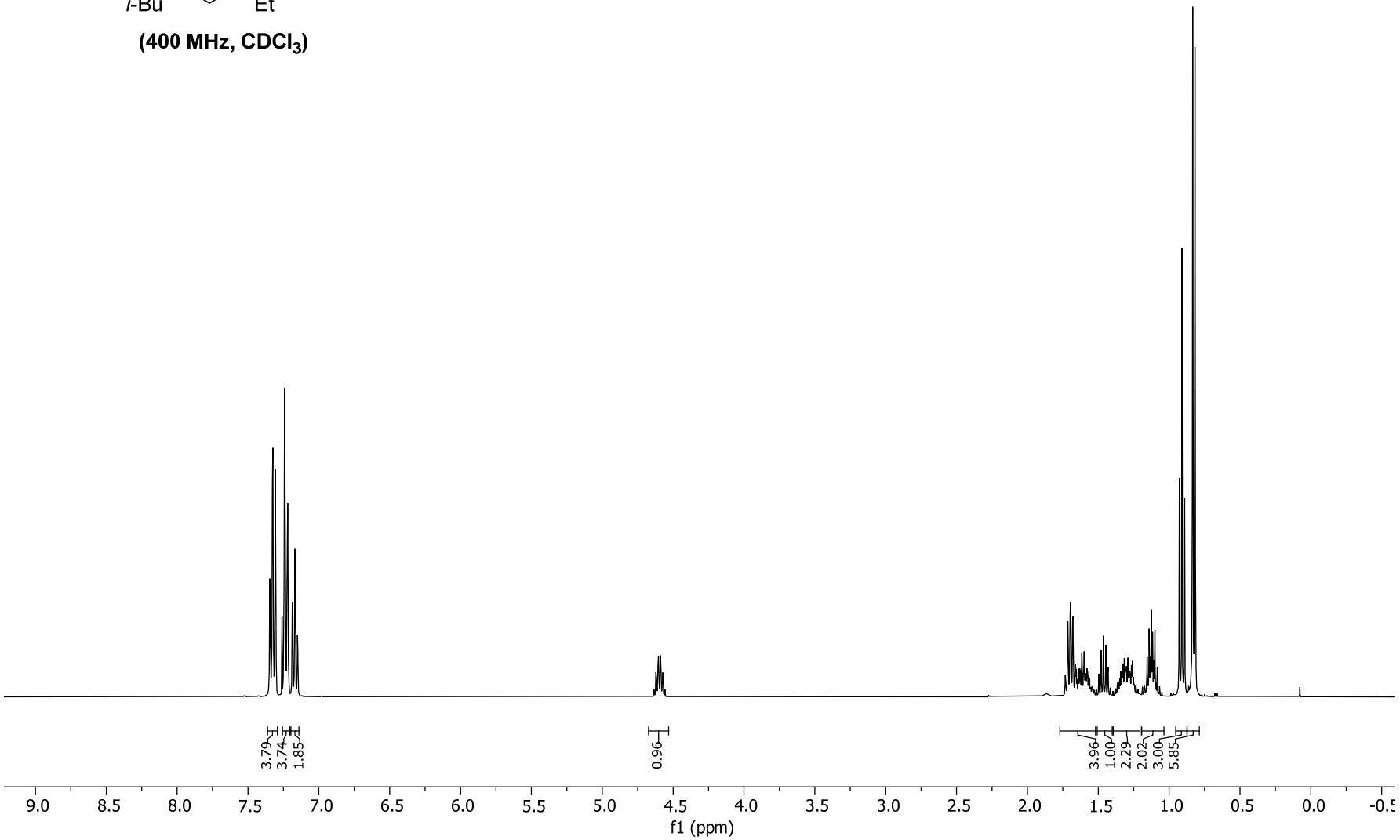
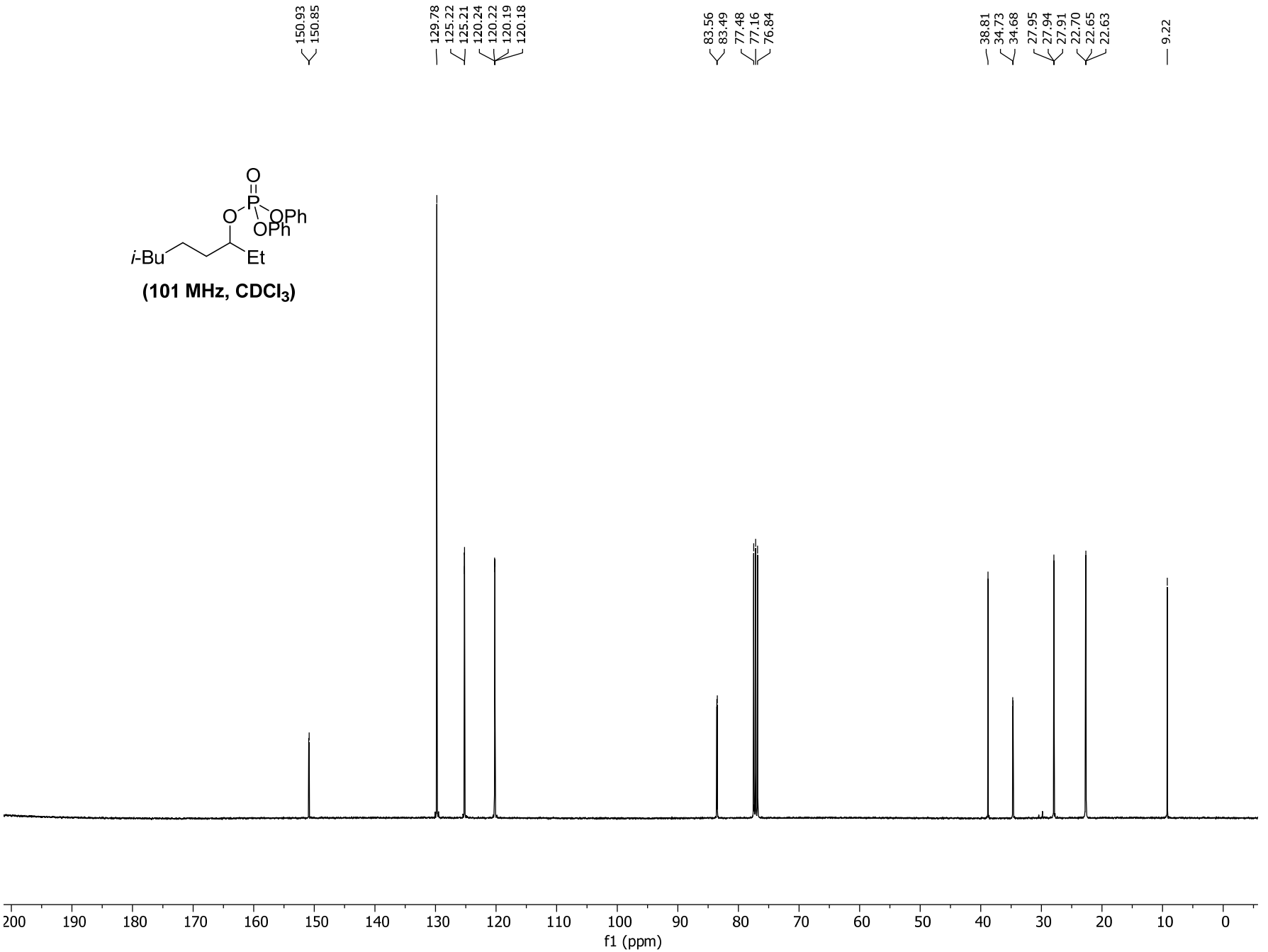


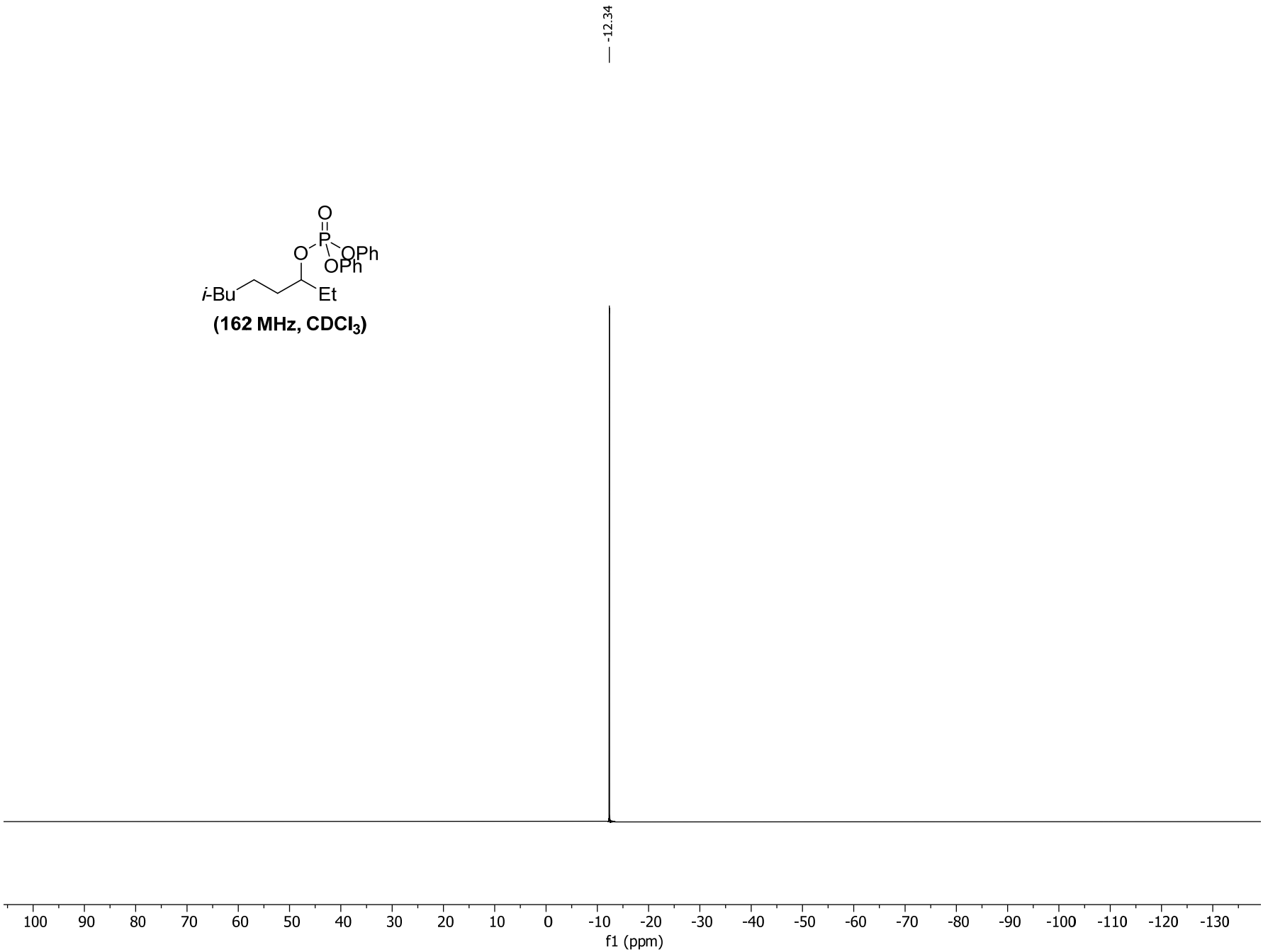
Fig. 3, entry 21
(101 MHz, $CDCl_3$)



(400 MHz, $CDCl_3$)




150.93
150.85
129.78
125.22
125.21
120.24
120.22
120.19
120.18
83.56
83.49
77.48
77.16
76.84
38.81
34.73
34.68
27.95
27.94
27.91
22.70
22.65
22.63
9.22
O
P
O
OPh
OPh
i-Bu
Et
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-12.34
O
P
O
OPh
OPh
i-Bu
Et
(162 MHz, CDCl3)
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

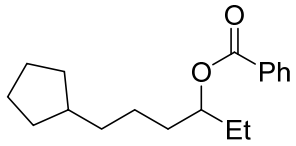


Fig. 3, entry 22
(400 MHz, $CDCl_3$)

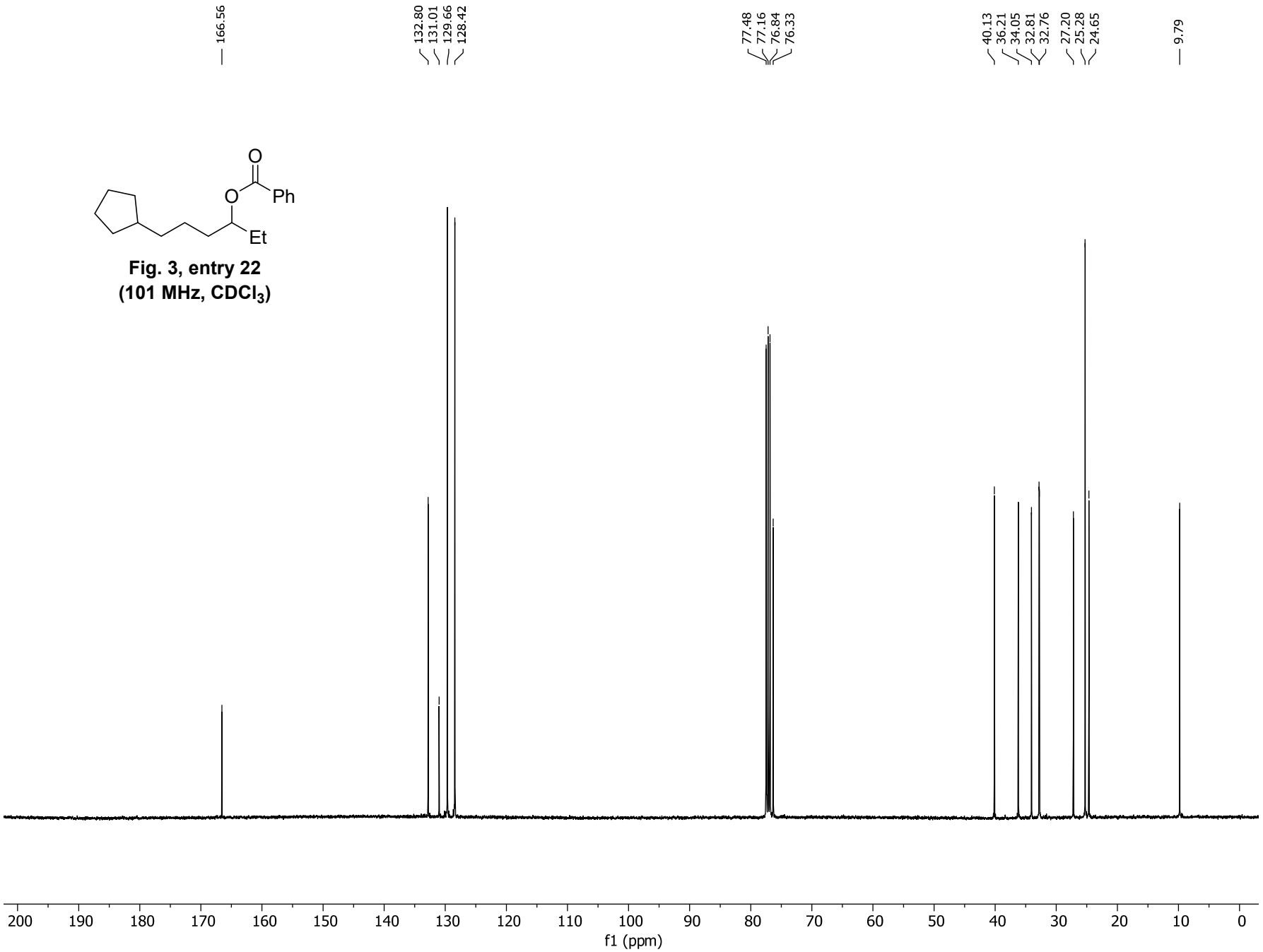


Fig. 3, entry 22
(101 MHz, $CDCl_3$)

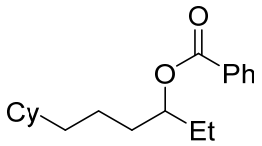


Fig. 3, entry 23
(400 MHz, $CDCl_3$)

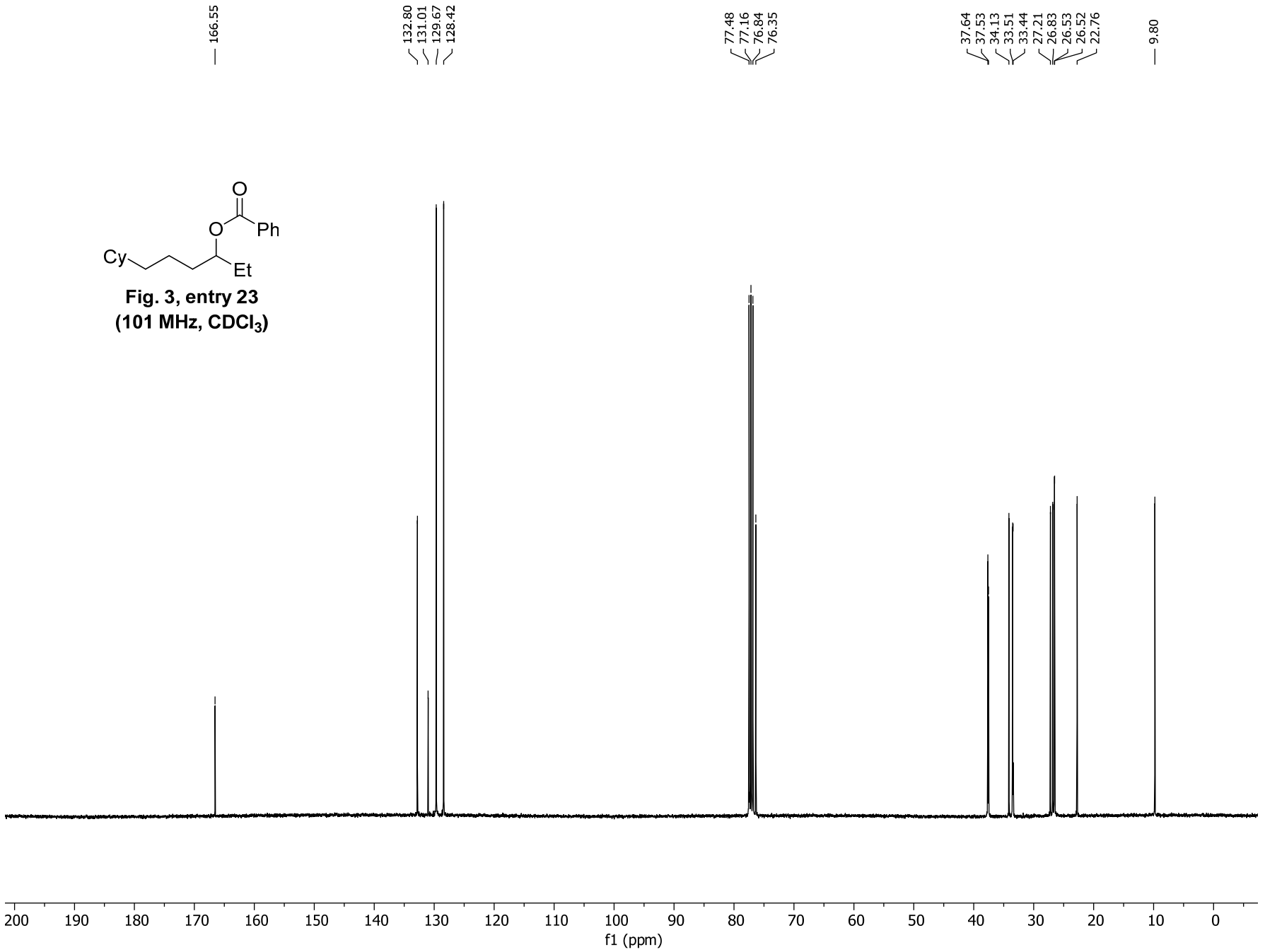
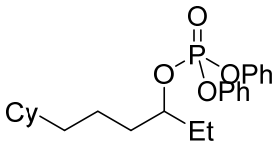
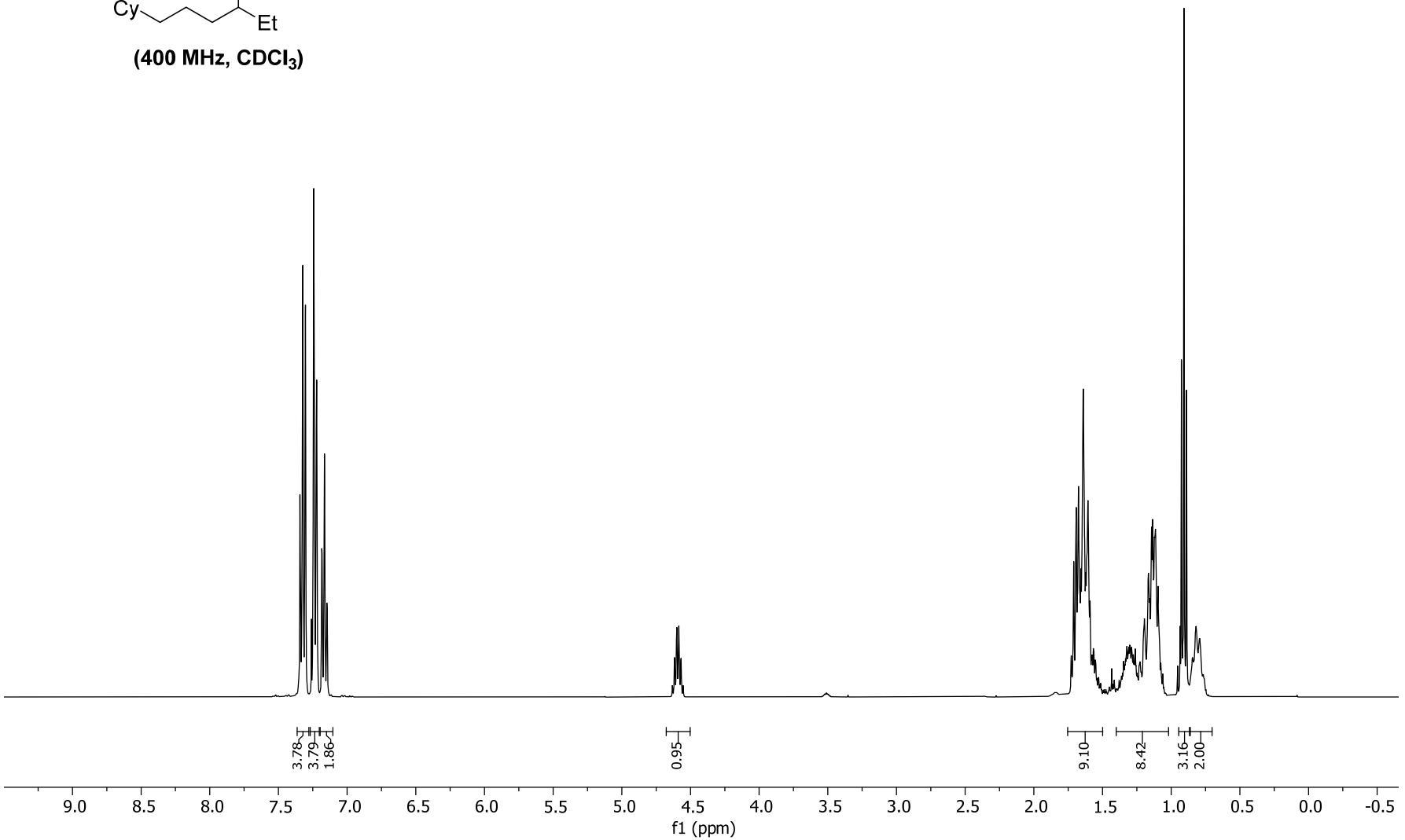
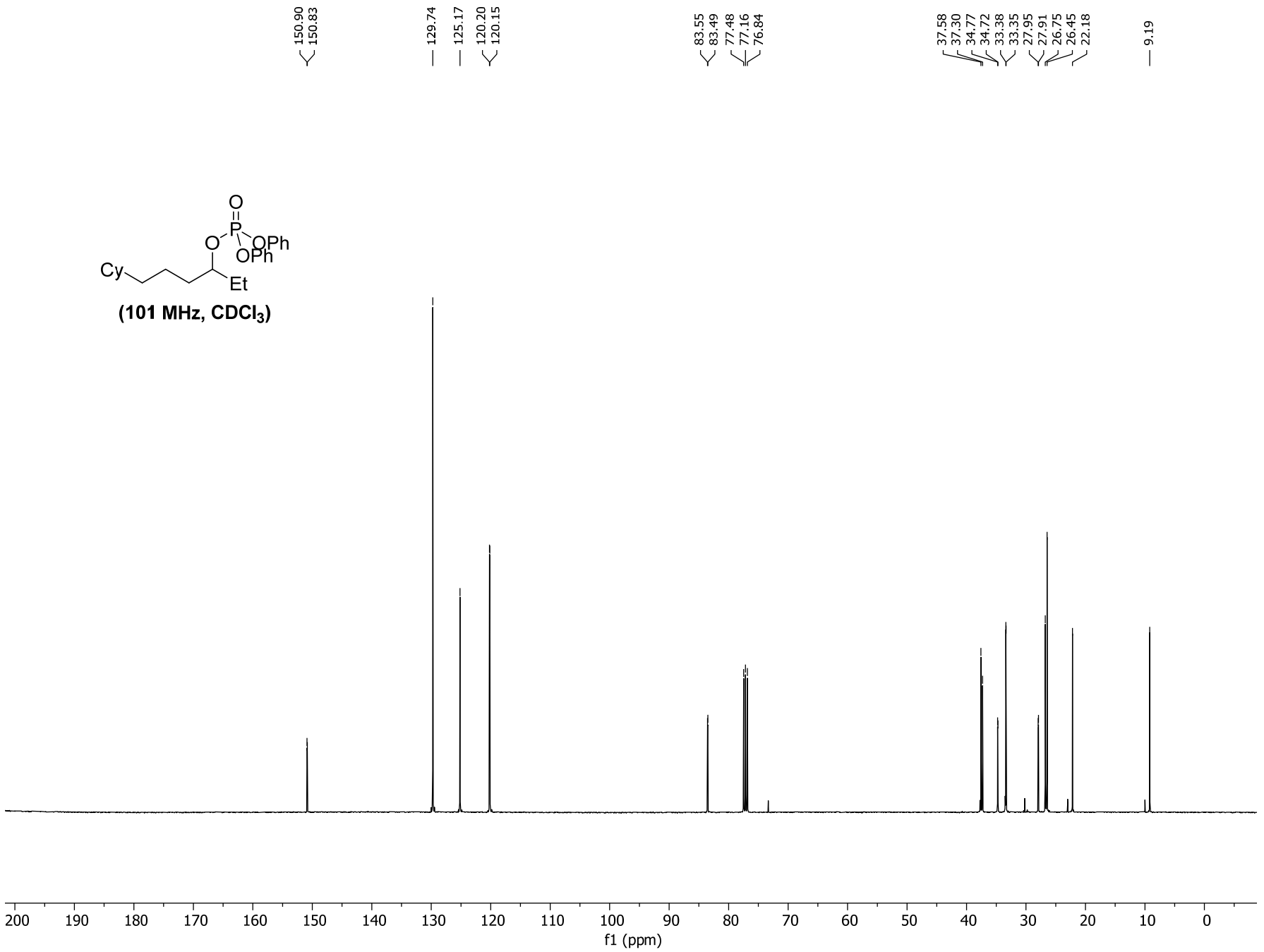


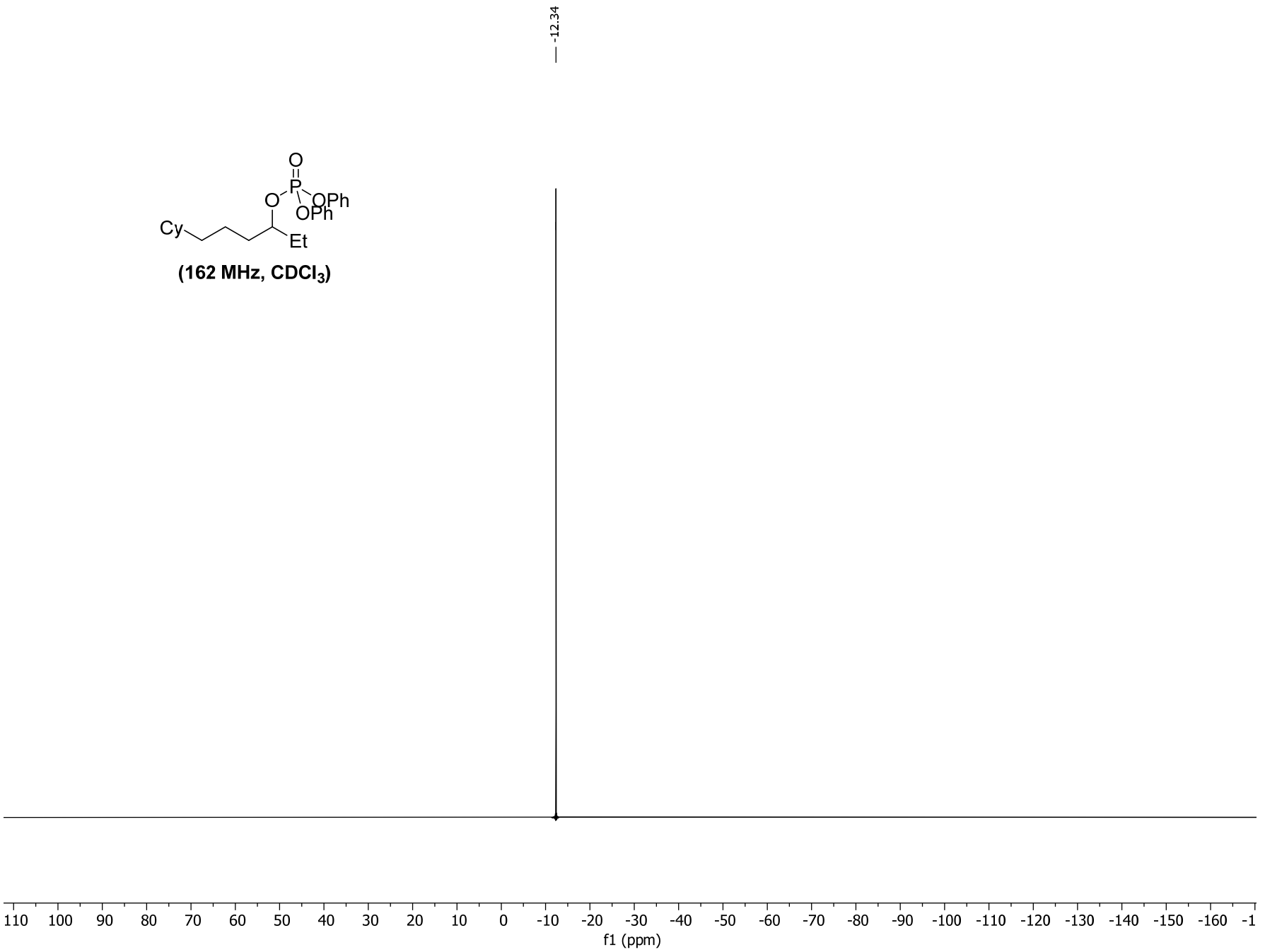
Fig. 3, entry 23
(101 MHz, $CDCl_3$)



(400 MHz, $CDCl_3$)




150.90
150.83
129.74
125.17
120.20
120.15
83.55
83.49
77.48
77.16
76.84
37.58
37.30
34.77
34.72
33.38
33.35
27.95
27.91
26.75
26.45
22.18
9.19
O
P
O
OPh
OPh
Cy
Et
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-12.34
O
P
O
OPh
OPh
Cy
Et
(162 MHz, CDCl3)
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -1
f1 (ppm)

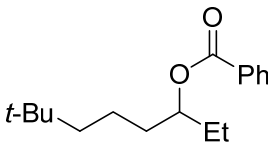


Fig. 3, entry 24
(400 MHz, $CDCl_3$)

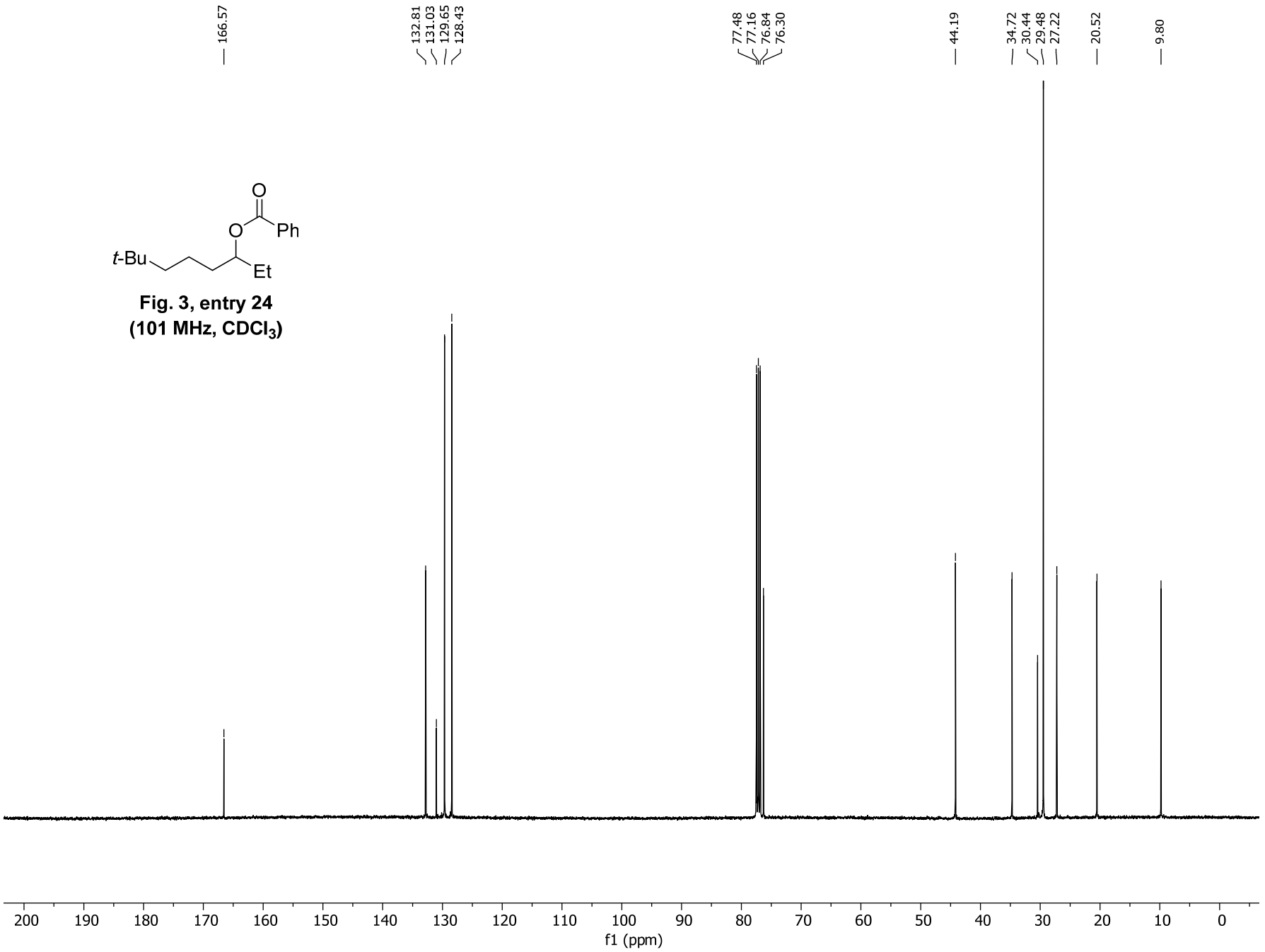


Fig. 3, entry 24
(101 MHz, $CDCl_3$)

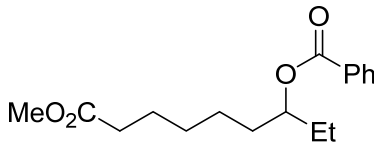


Fig. 3, entry 25
(400 MHz, $CDCl_3$)

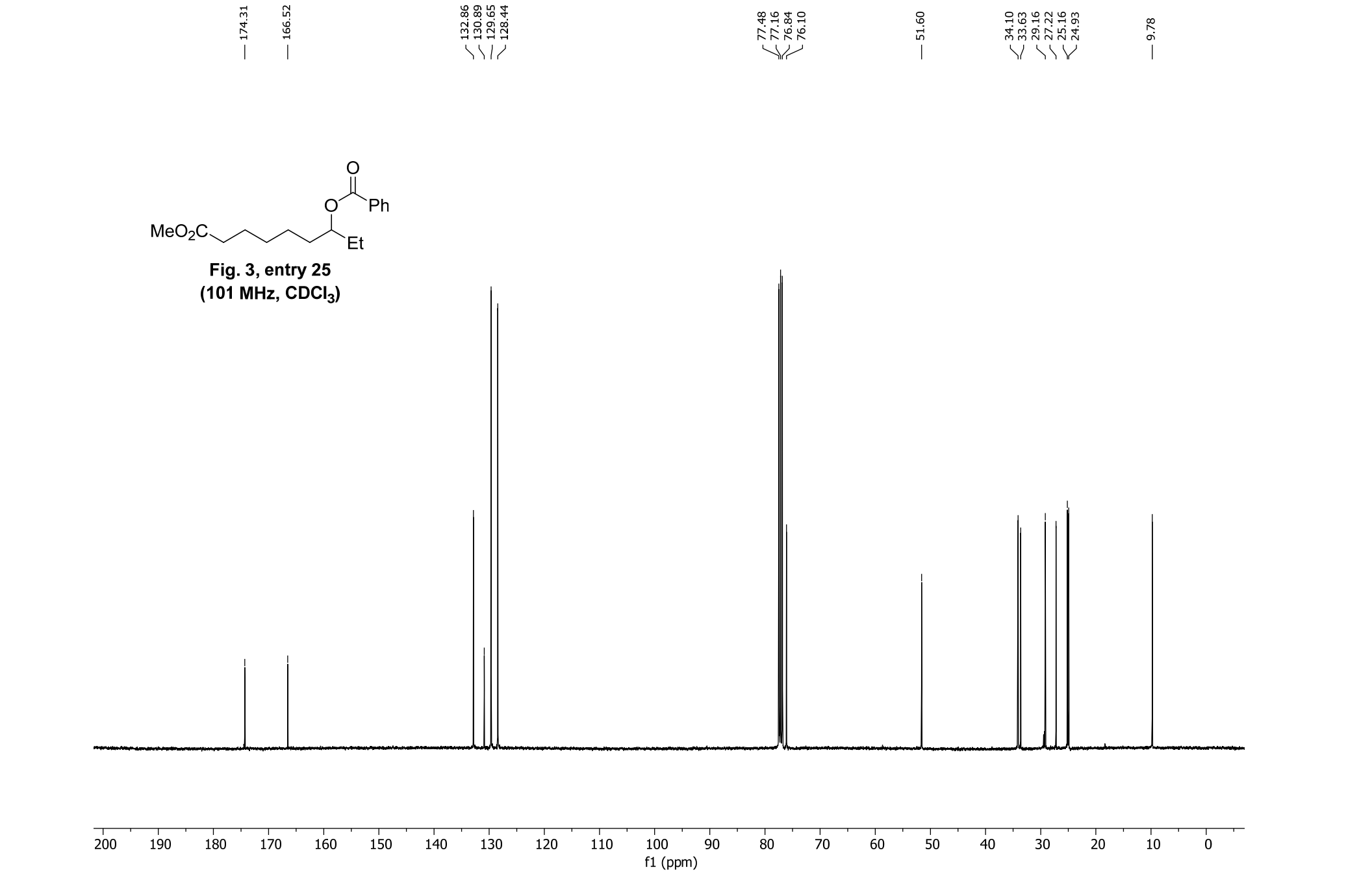


Fig. 3, entry 25
(101 MHz, $CDCl_3$)

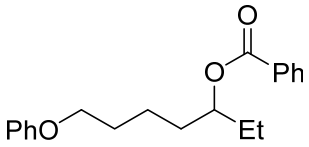


Fig. 3, entry 26
(400 MHz, $CDCl_3$)

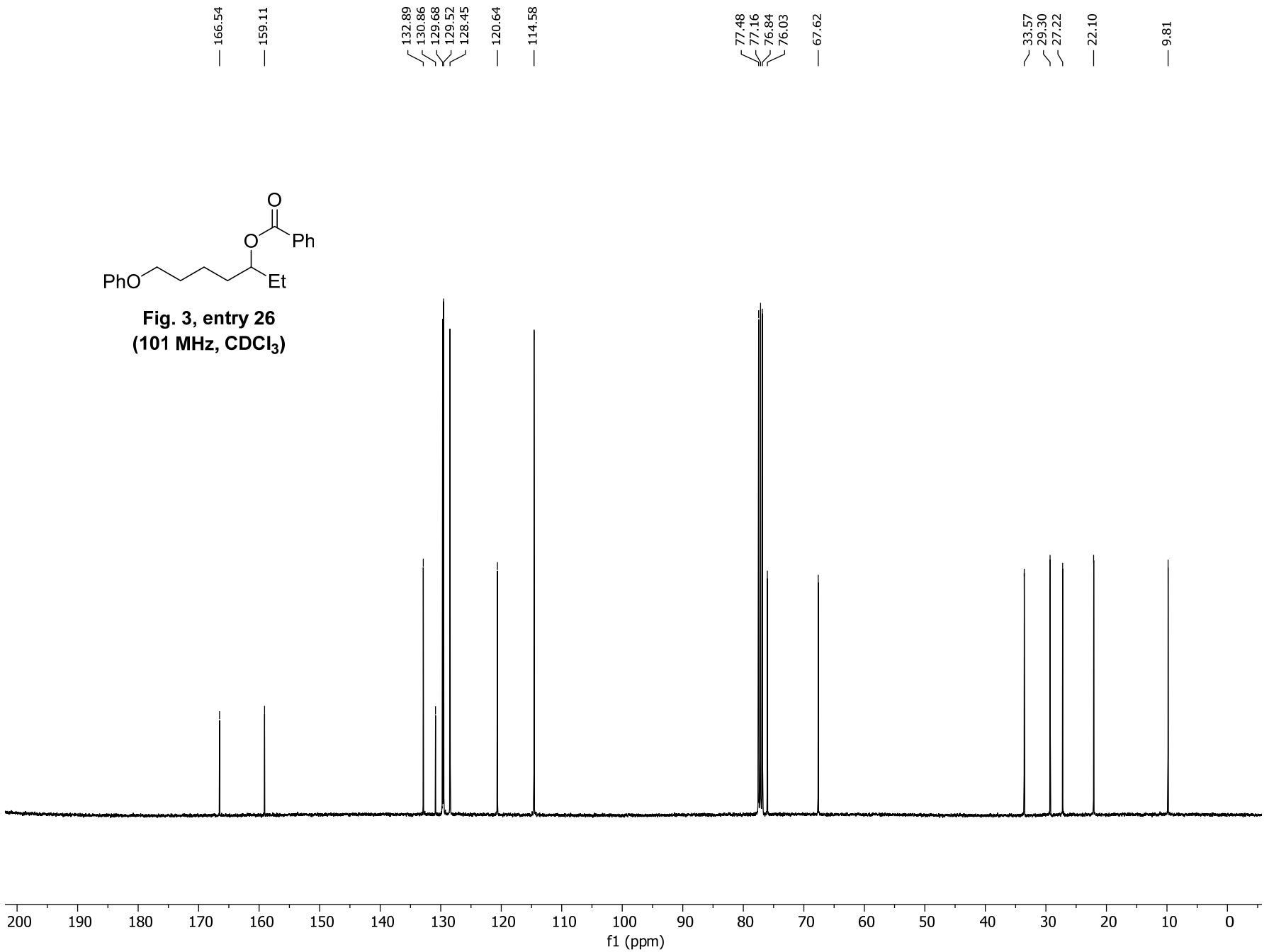


Fig. 3, entry 26
(101 MHz, $CDCl_3$)

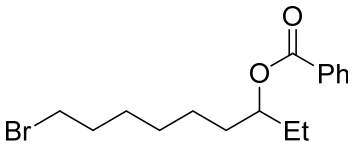


Fig. 3, entry 27
(400 MHz, $CDCl_3$)

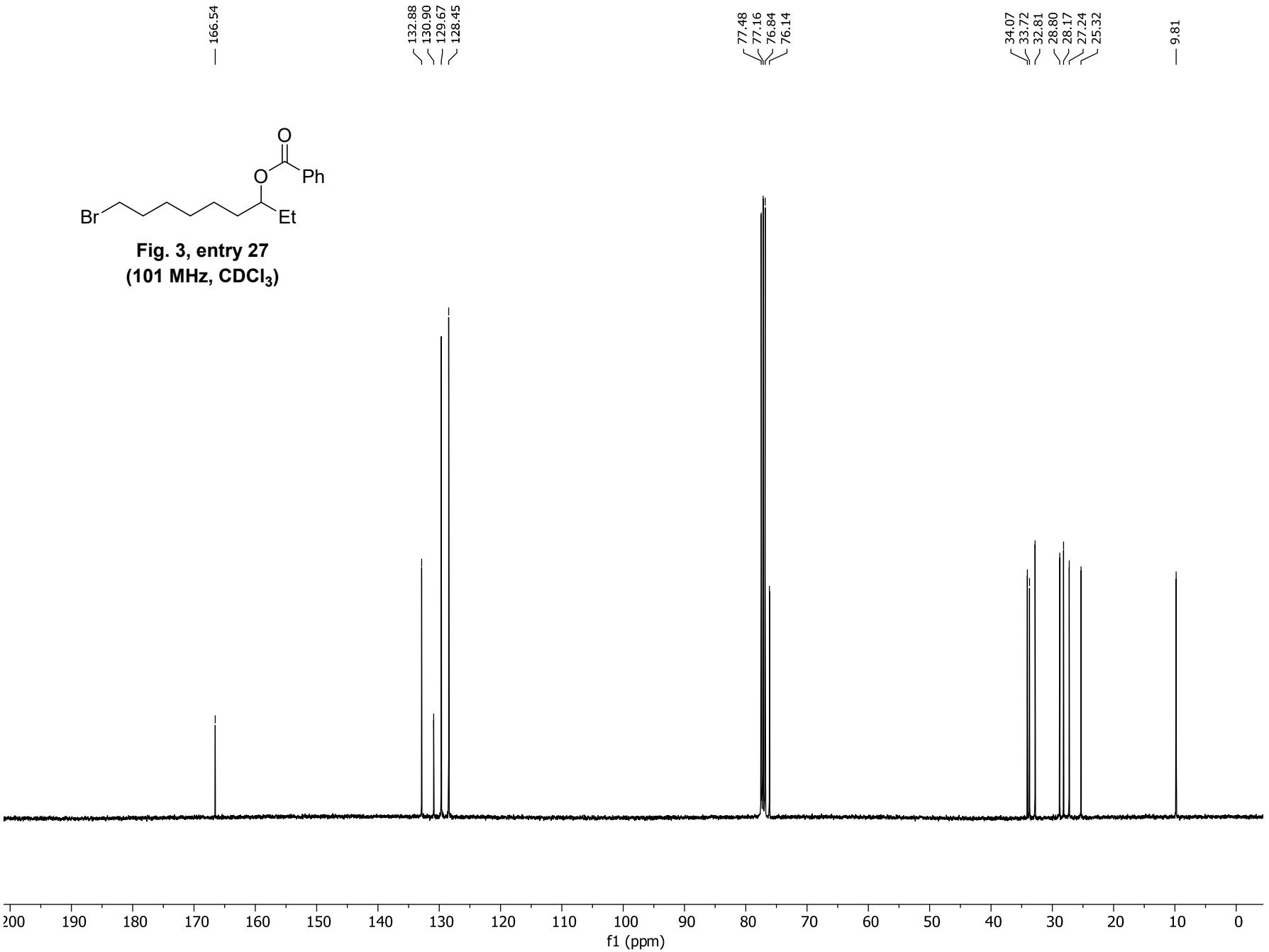


Fig. 3, entry 27
(101 MHz, $CDCl_3$)

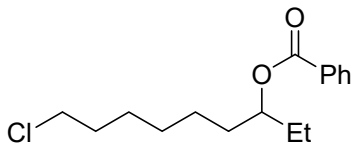


Fig. 3, entry 28
(400 MHz, $CDCl_3$)

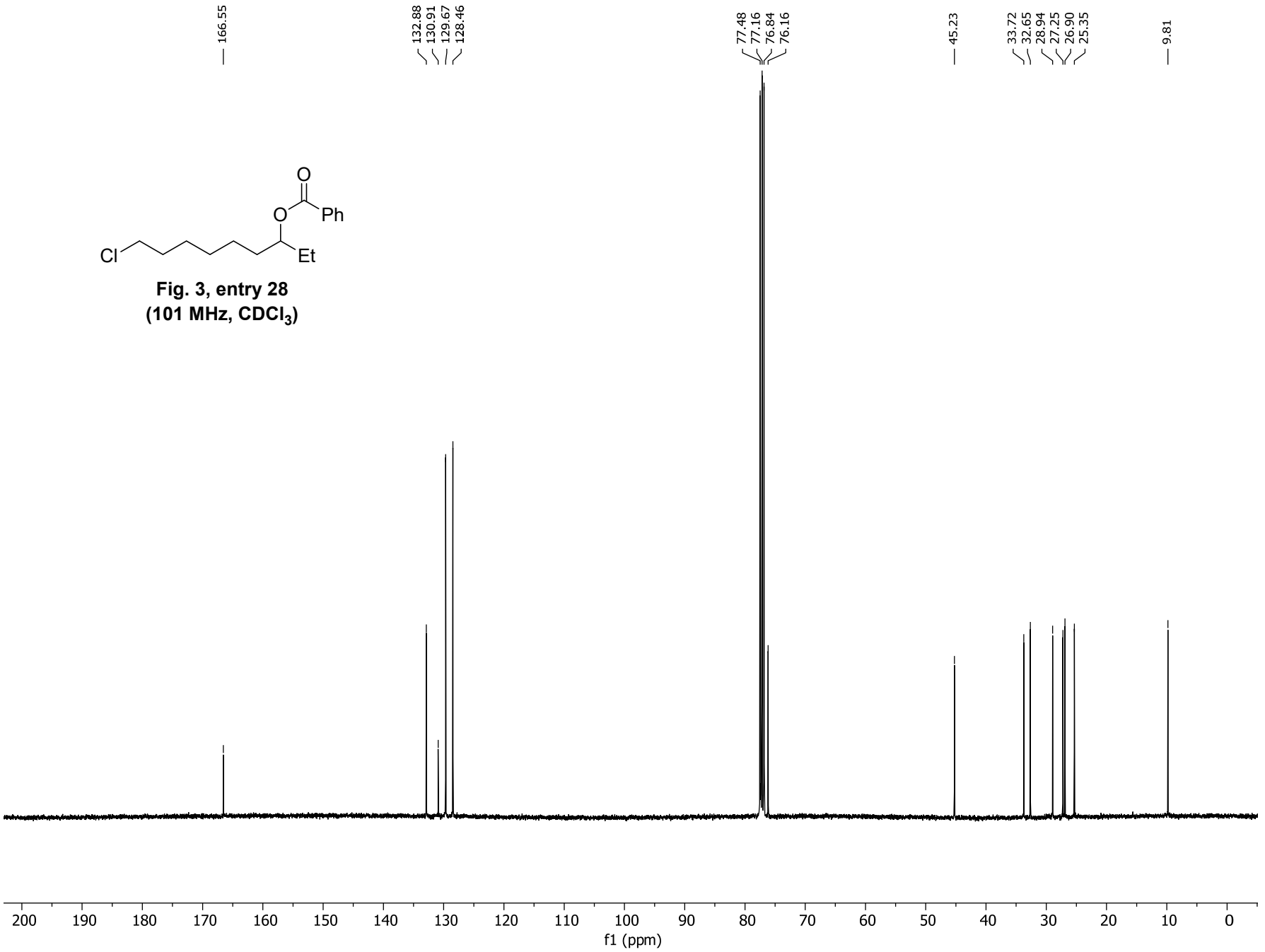


Fig. 3, entry 28
(101 MHz, $CDCl_3$)

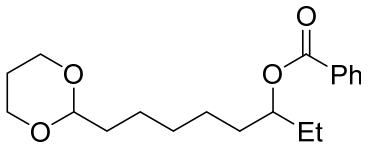


Fig. 3, entry 29
(400 MHz, $CDCl_3$)

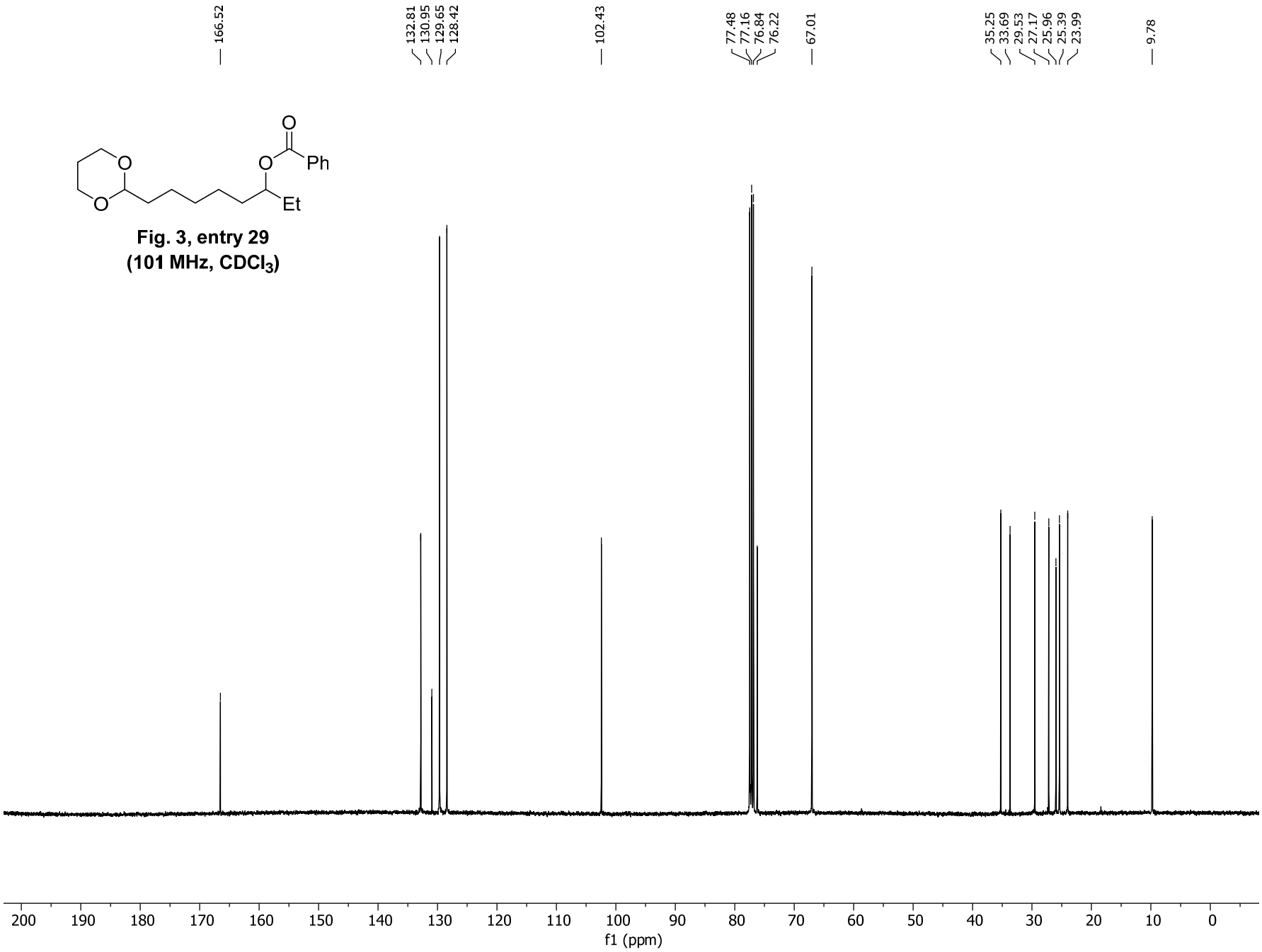


Fig. 3, entry 29
(101 MHz, $CDCl_3$)

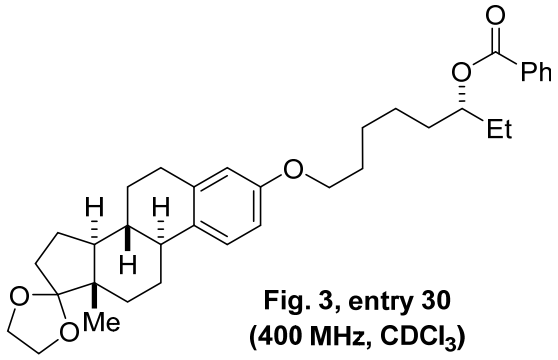


Fig. 3, entry 30
(400 MHz, $CDCl_3$)

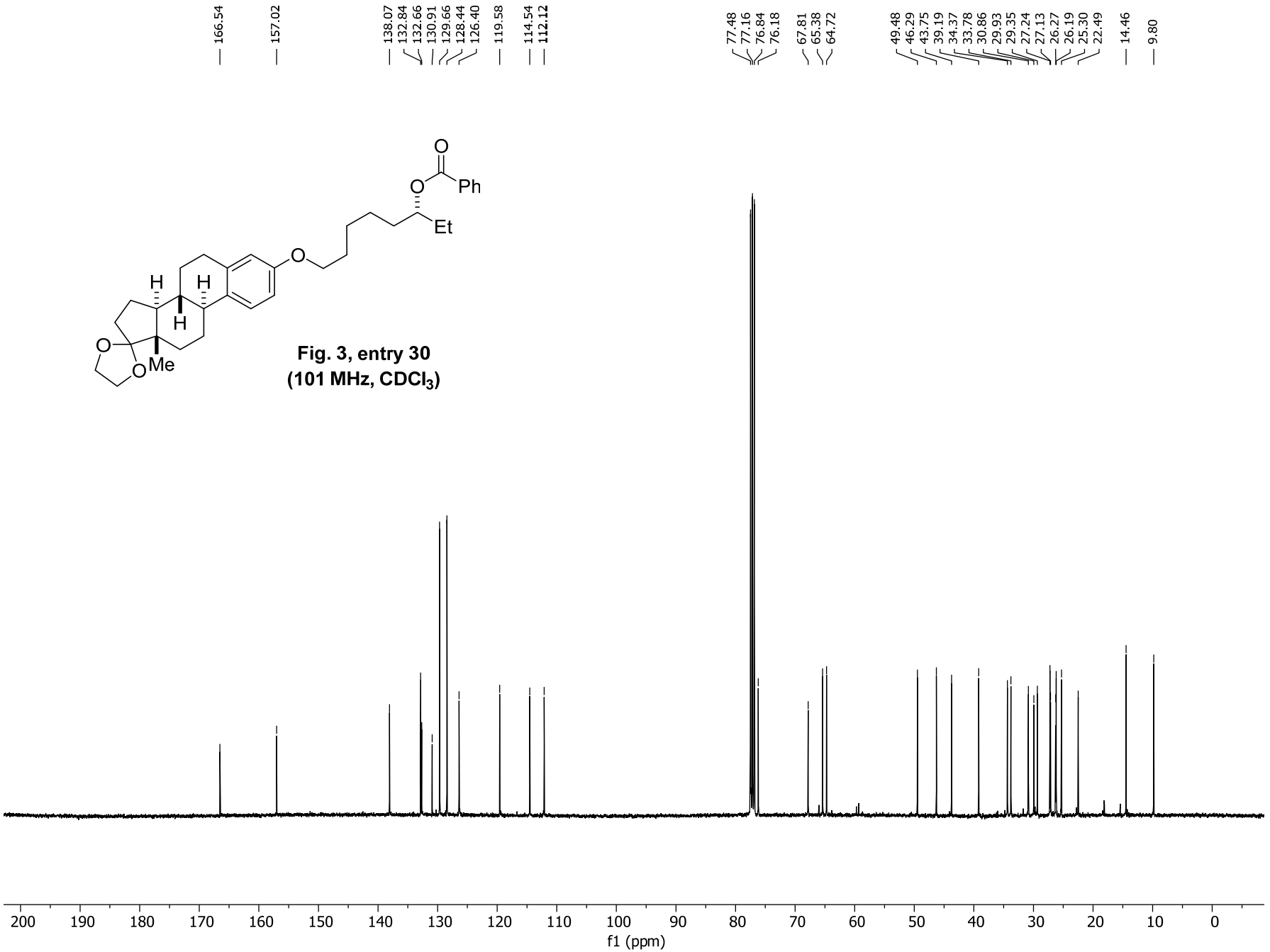


Fig. 3, entry 30
(101 MHz, $CDCl_3$)

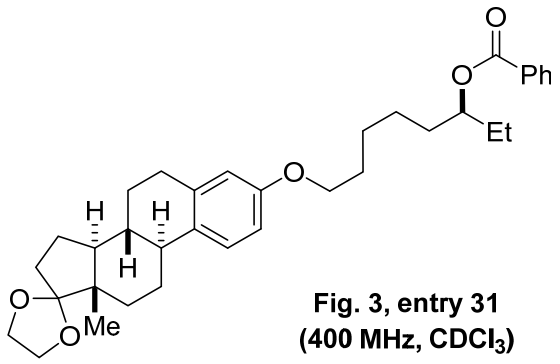


Fig. 3, entry 31
(400 MHz, $CDCl_3$)

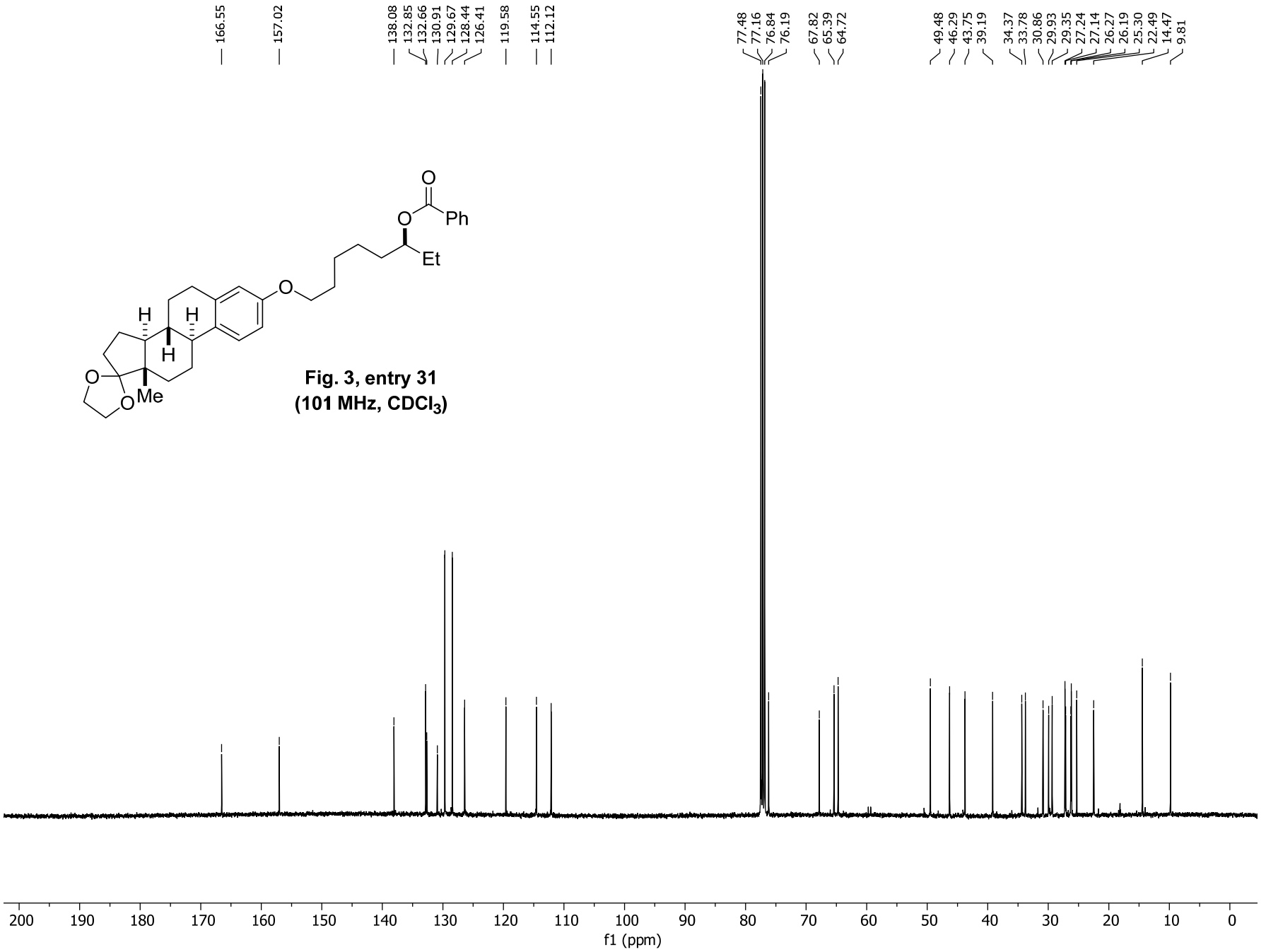


Fig. 3, entry 31
(101 MHz, $CDCl_3$)

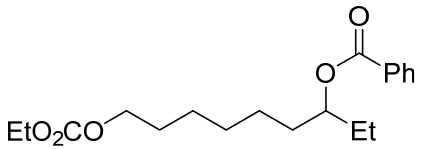


Fig. 3, entry 32
(400 MHz, $CDCl_3$)

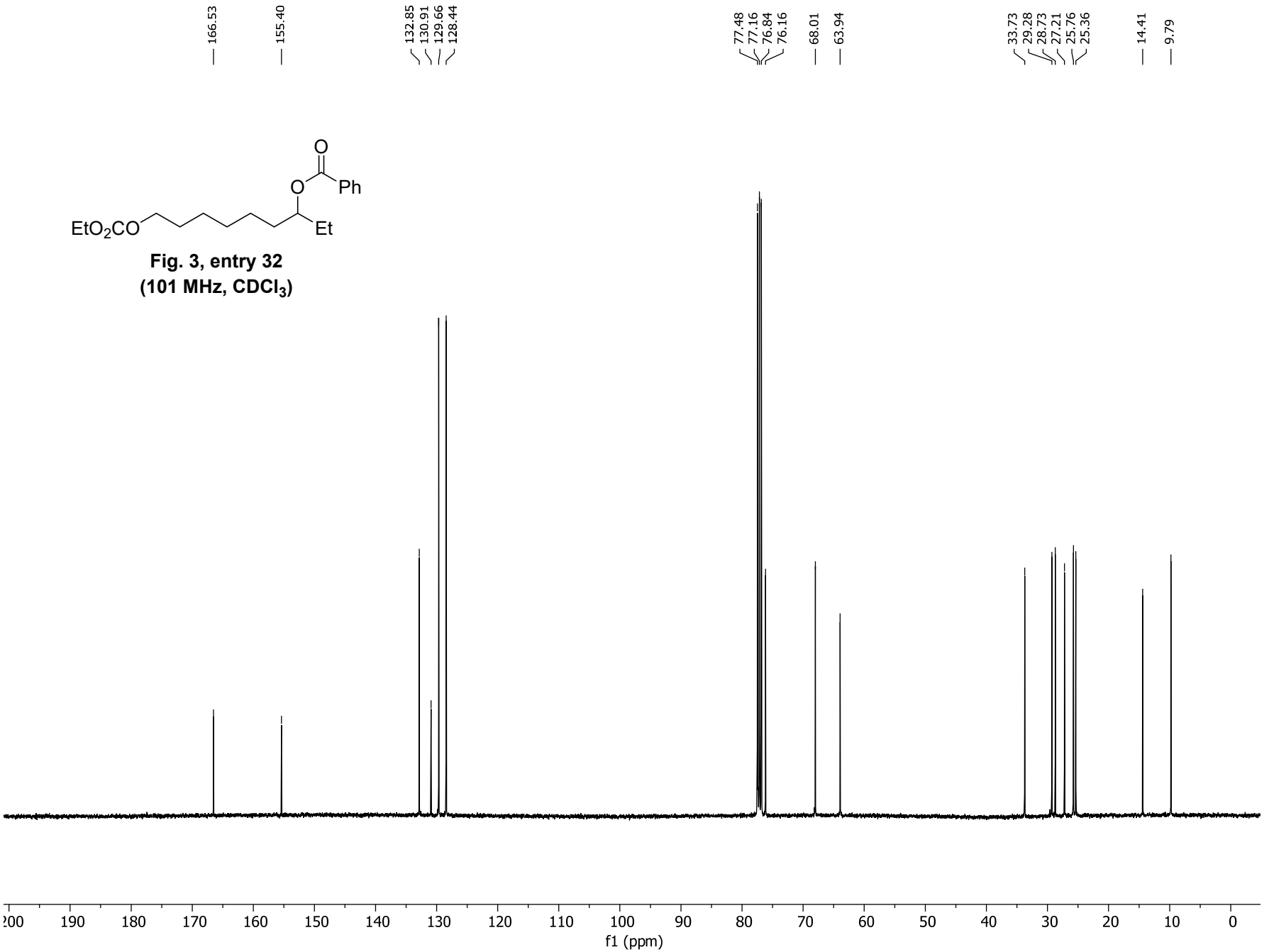


Fig. 3, entry 32
(101 MHz, $CDCl_3$)

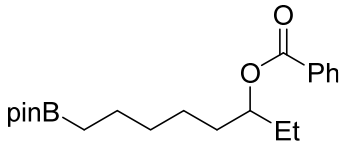


Fig. 3, entry 33
(400 MHz, $CDCl_3$)

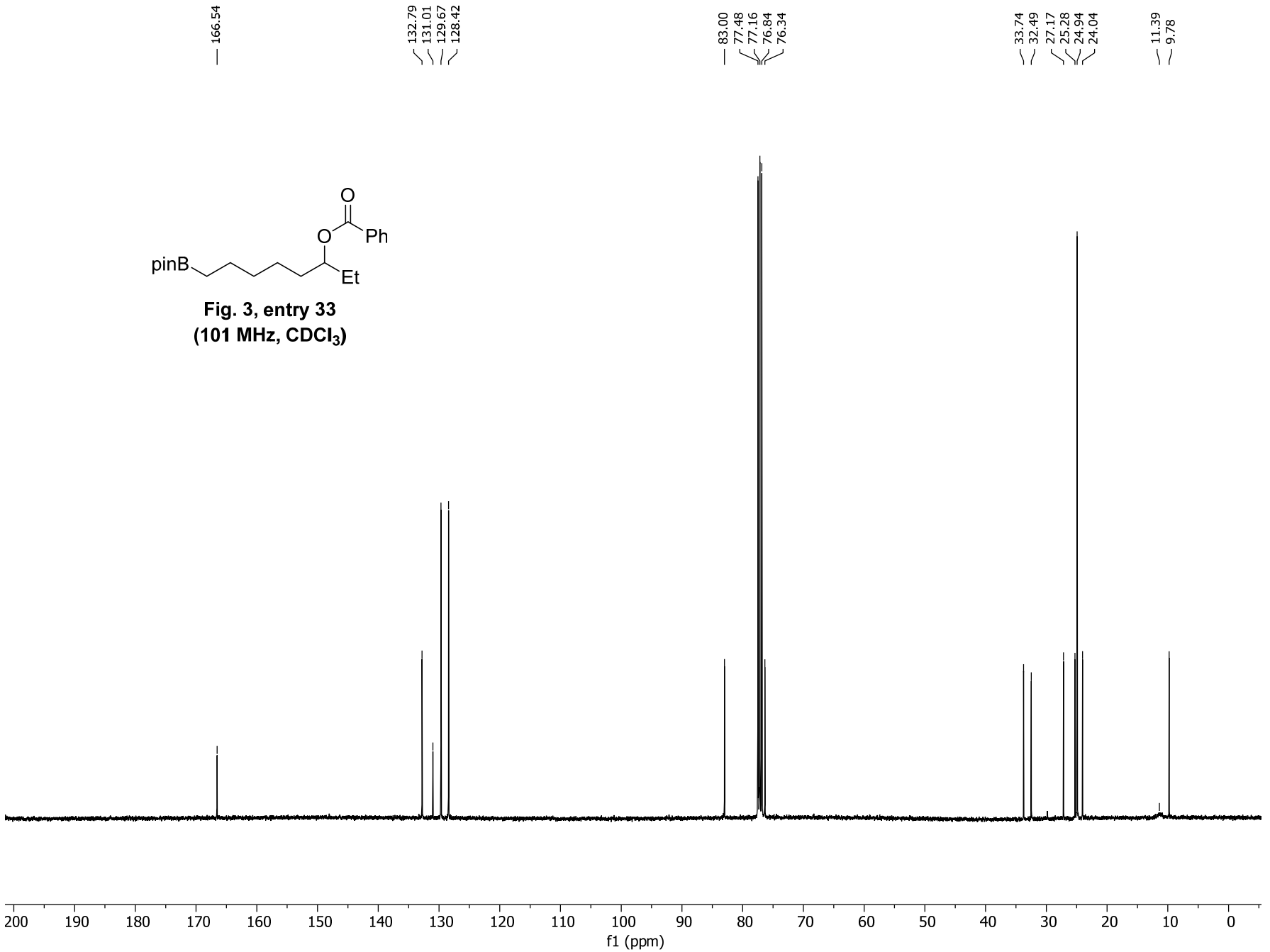


Fig. 3, entry 33
(101 MHz, $CDCl_3$)

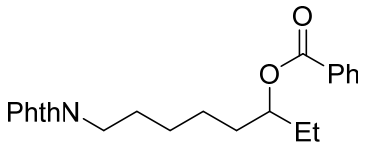


Fig. 3, entry 34
(400 MHz, $CDCl_3$)

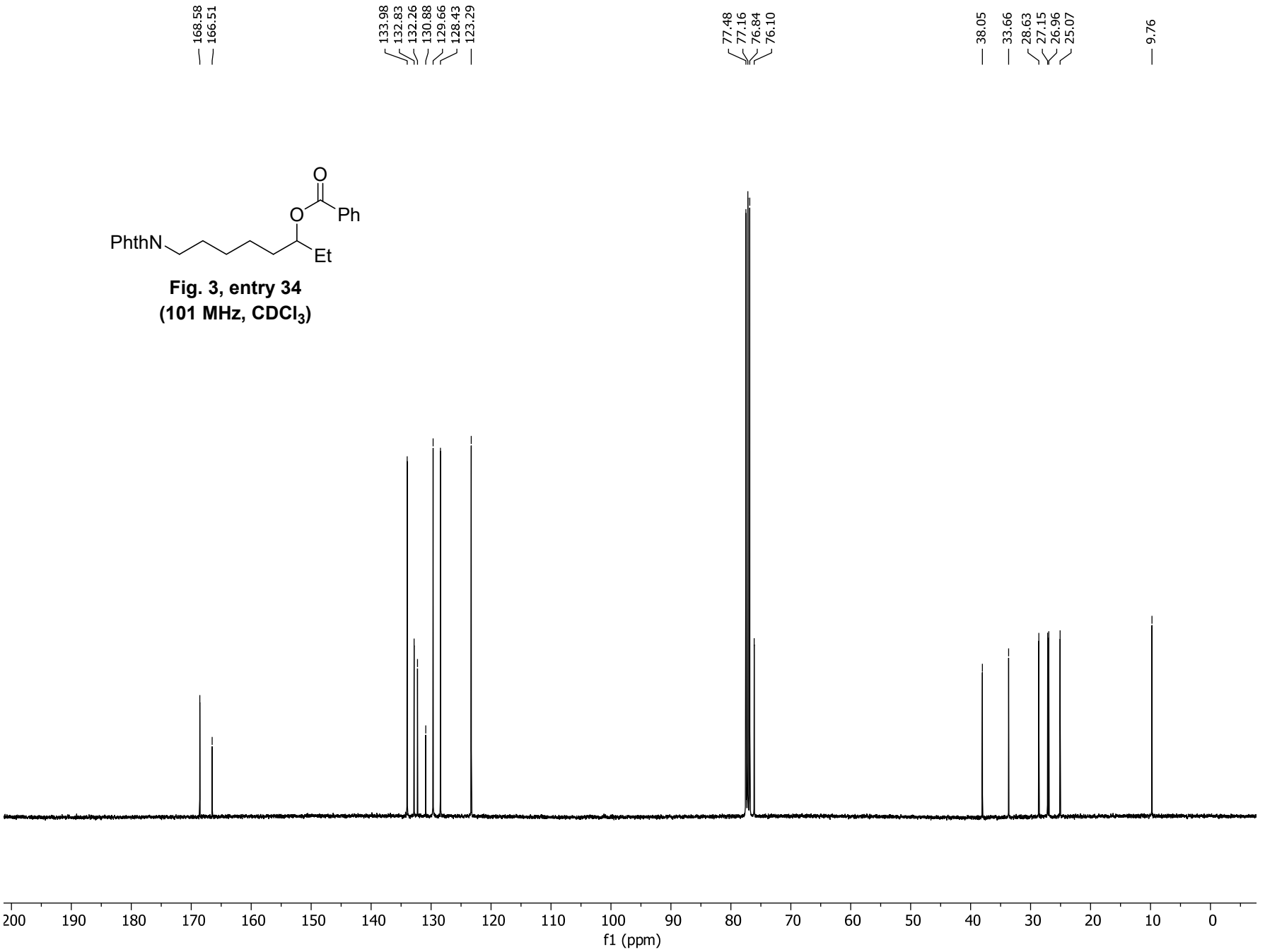


Fig. 3, entry 34
(101 MHz, $CDCl_3$)

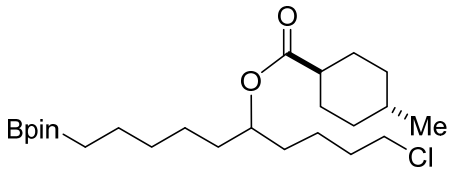


Fig. 4, entry 38
(400 MHz, $CDCl_3$)

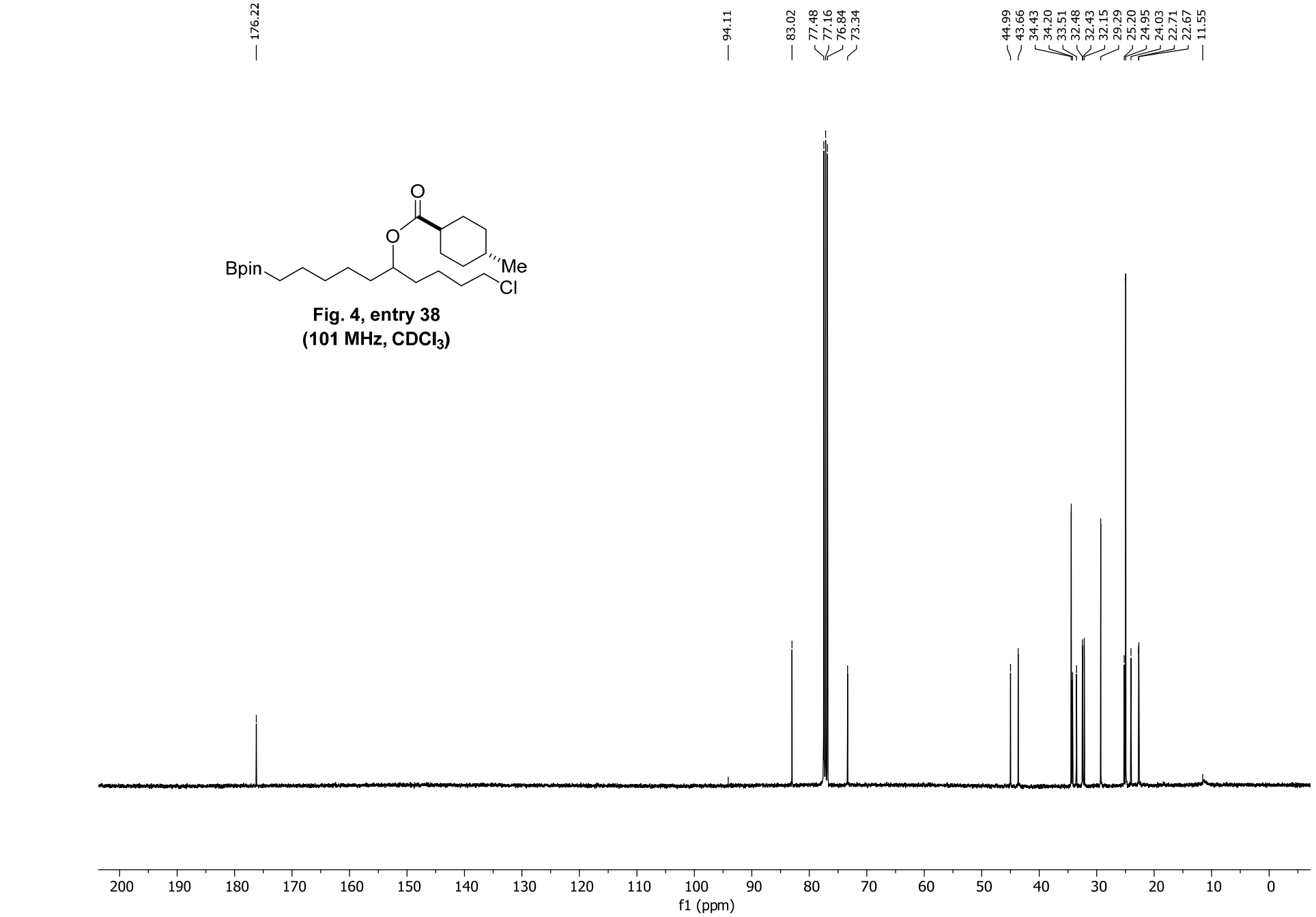
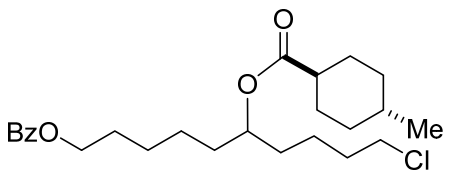
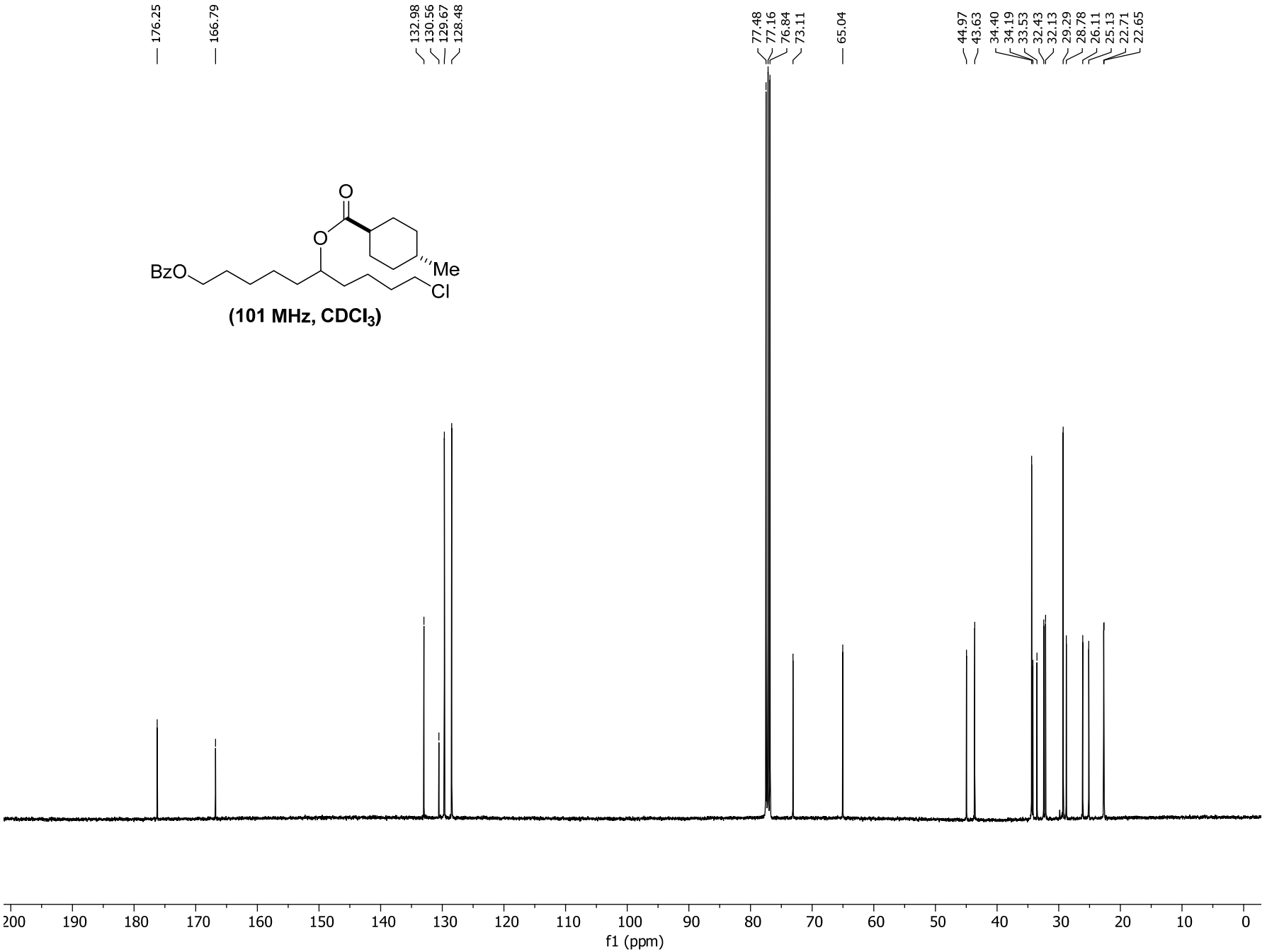


Fig. 4, entry 38
(101 MHz, $CDCl_3$)



(400 MHz, $CDCl_3$)


176.25
166.79
132.98
130.56
129.67
128.48
77.48
77.16
76.84
73.11
65.04
44.97
43.63
34.40
34.19
33.53
32.43
32.13
29.29
28.78
26.11
25.13
22.71
22.65
O
O
BzO
Me
Cl
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

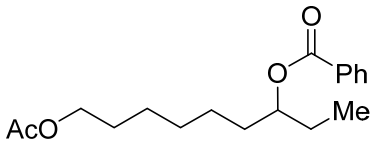


Fig. 4, entry 39
(400 MHz, $CDCl_3$)

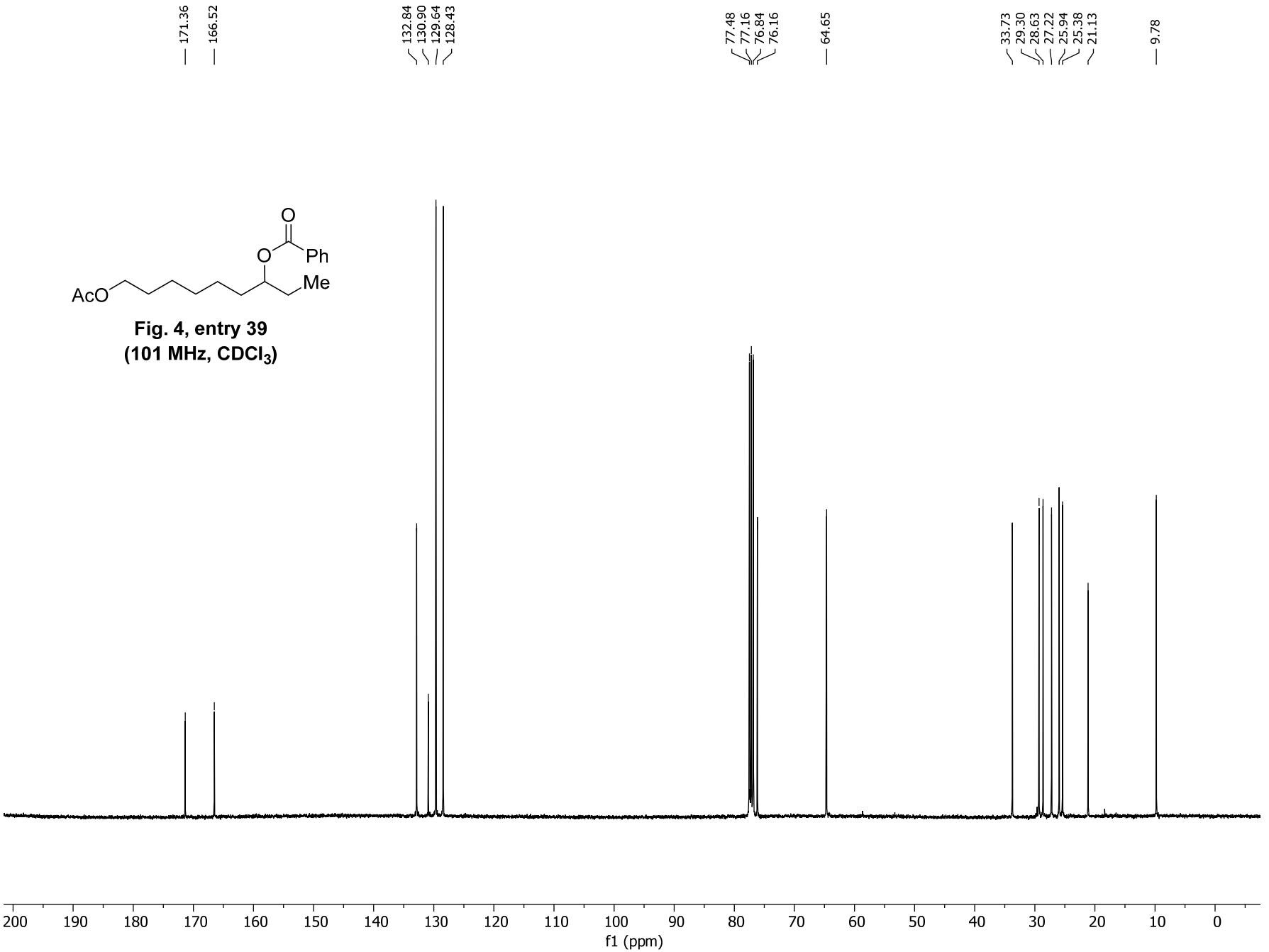


Fig. 4, entry 39
(101 MHz, $CDCl_3$)

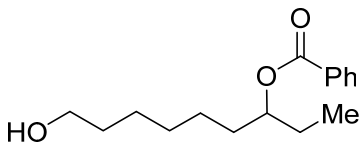


Fig. 4, entry 40
(400 MHz, $CDCl_3$)

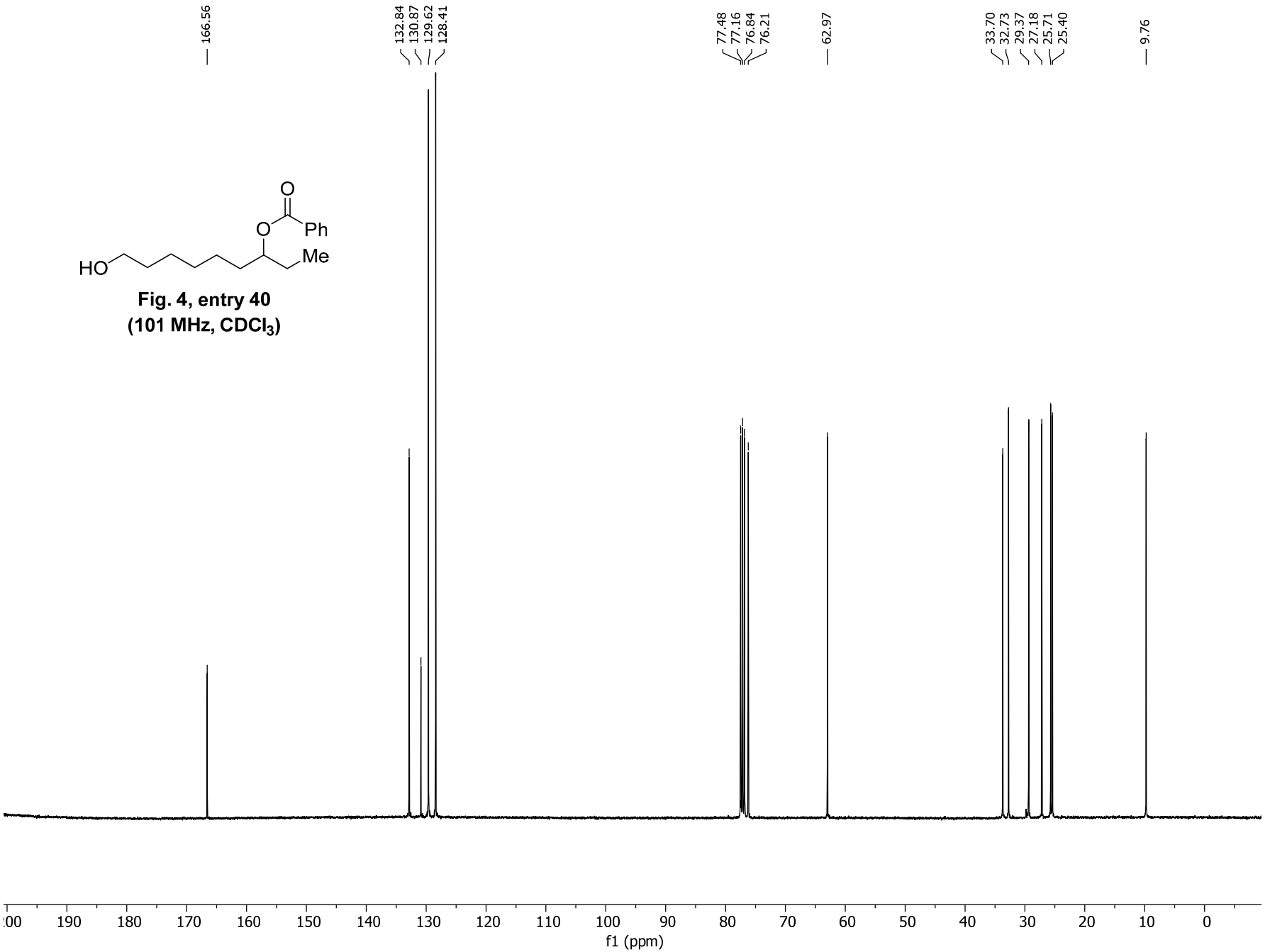


Fig. 4, entry 40
(101 MHz, $CDCl_3$)

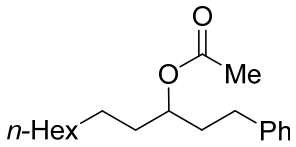


Fig. 4, entry 41
(400 MHz, $CDCl_3$)

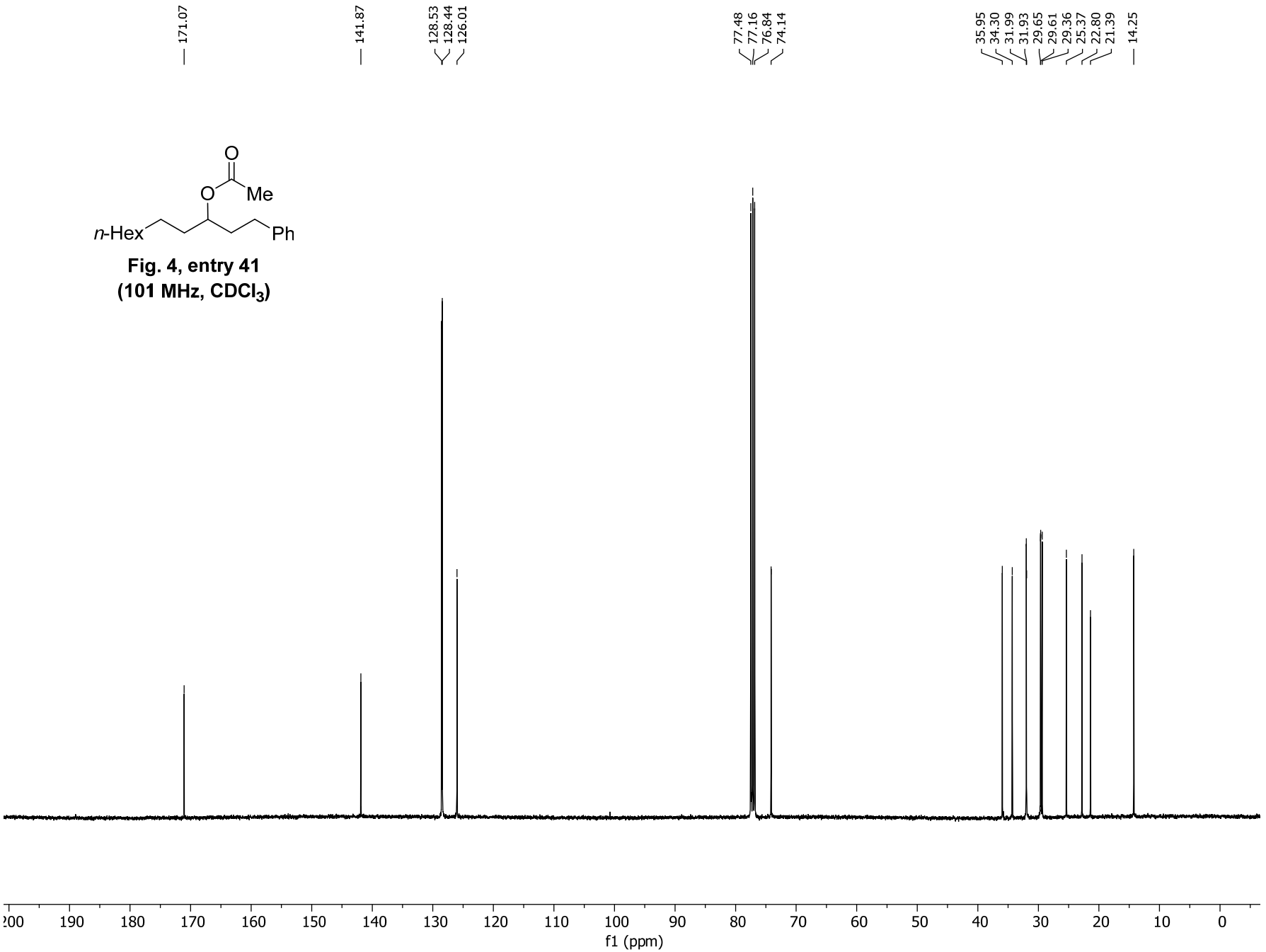


Fig. 4, entry 41
(101 MHz, $CDCl_3$)

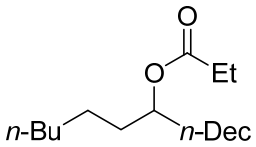


Fig. 4, entry 42
(400 MHz, $CDCl_3$)

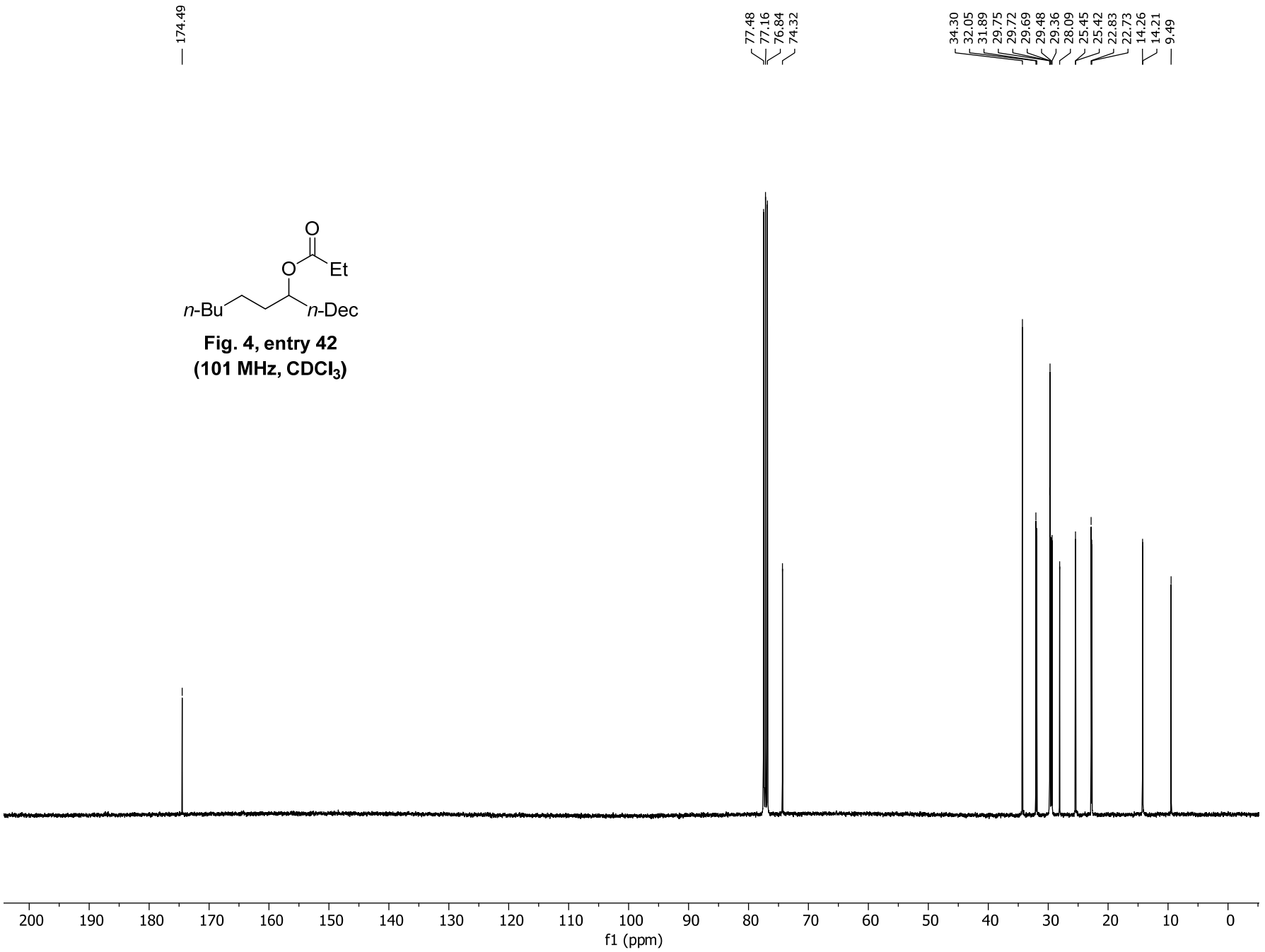
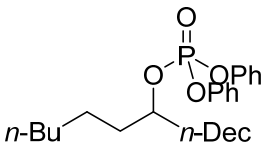
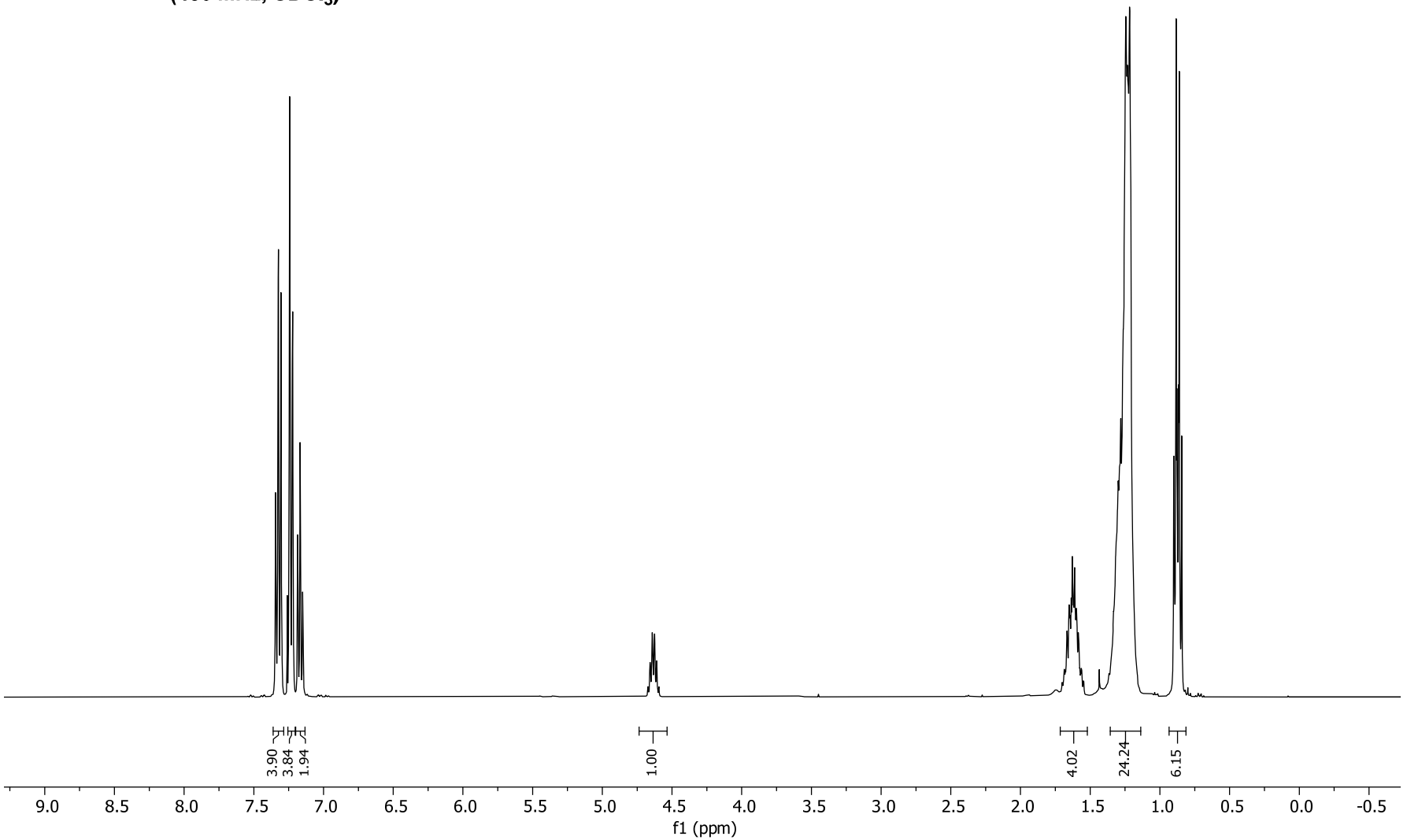
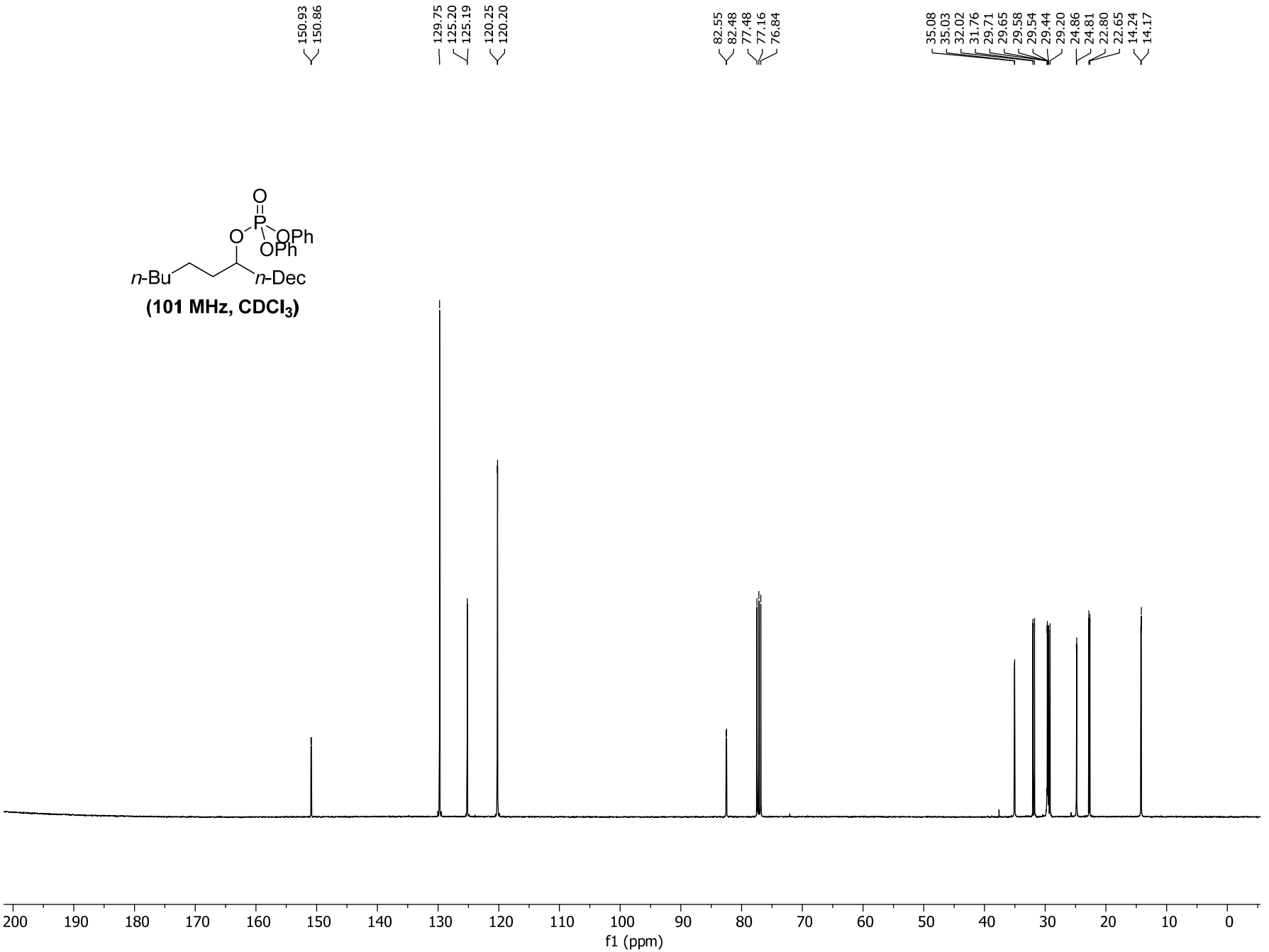


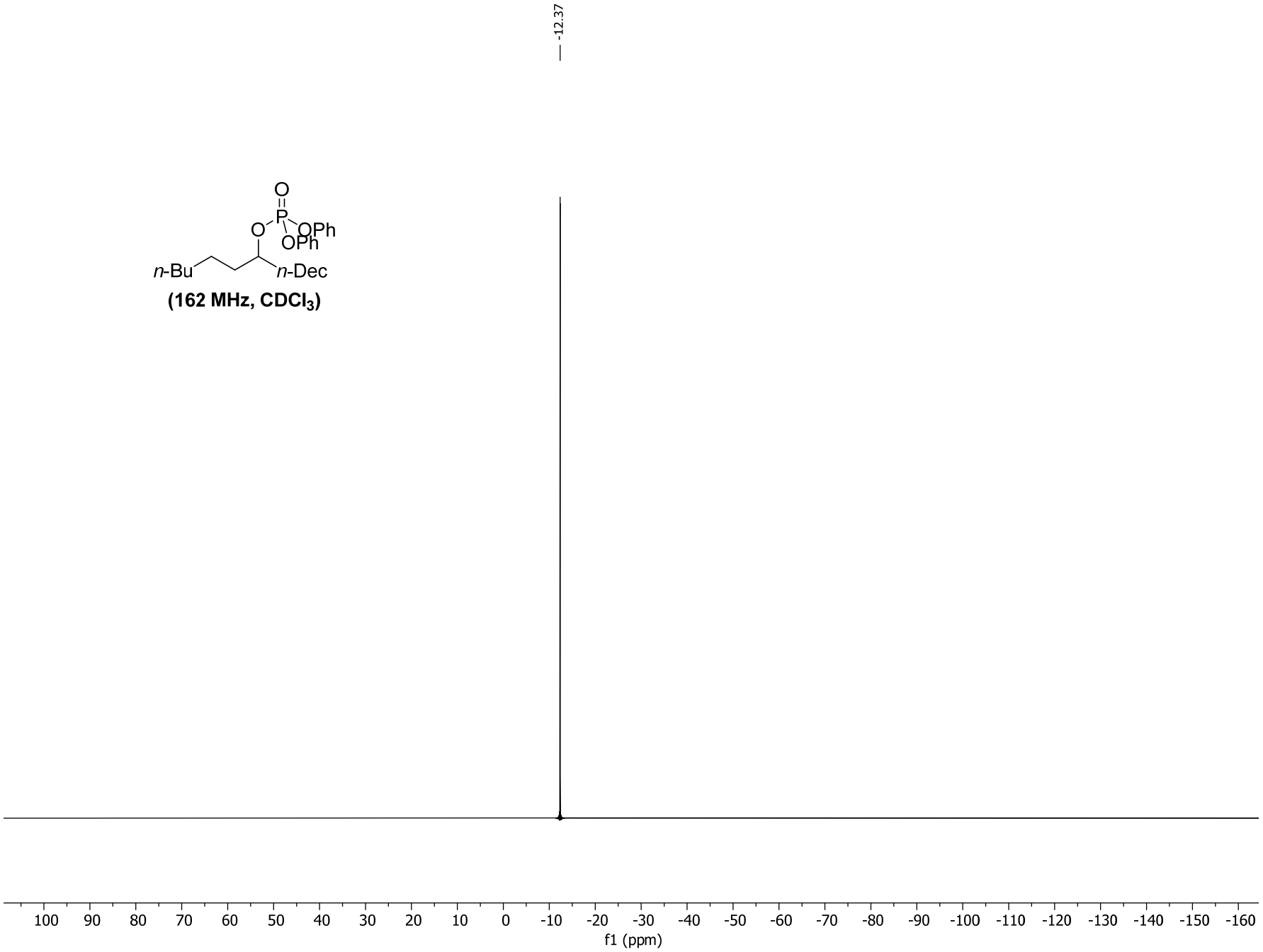
Fig. 4, entry 42
(101 MHz, $CDCl_3$)

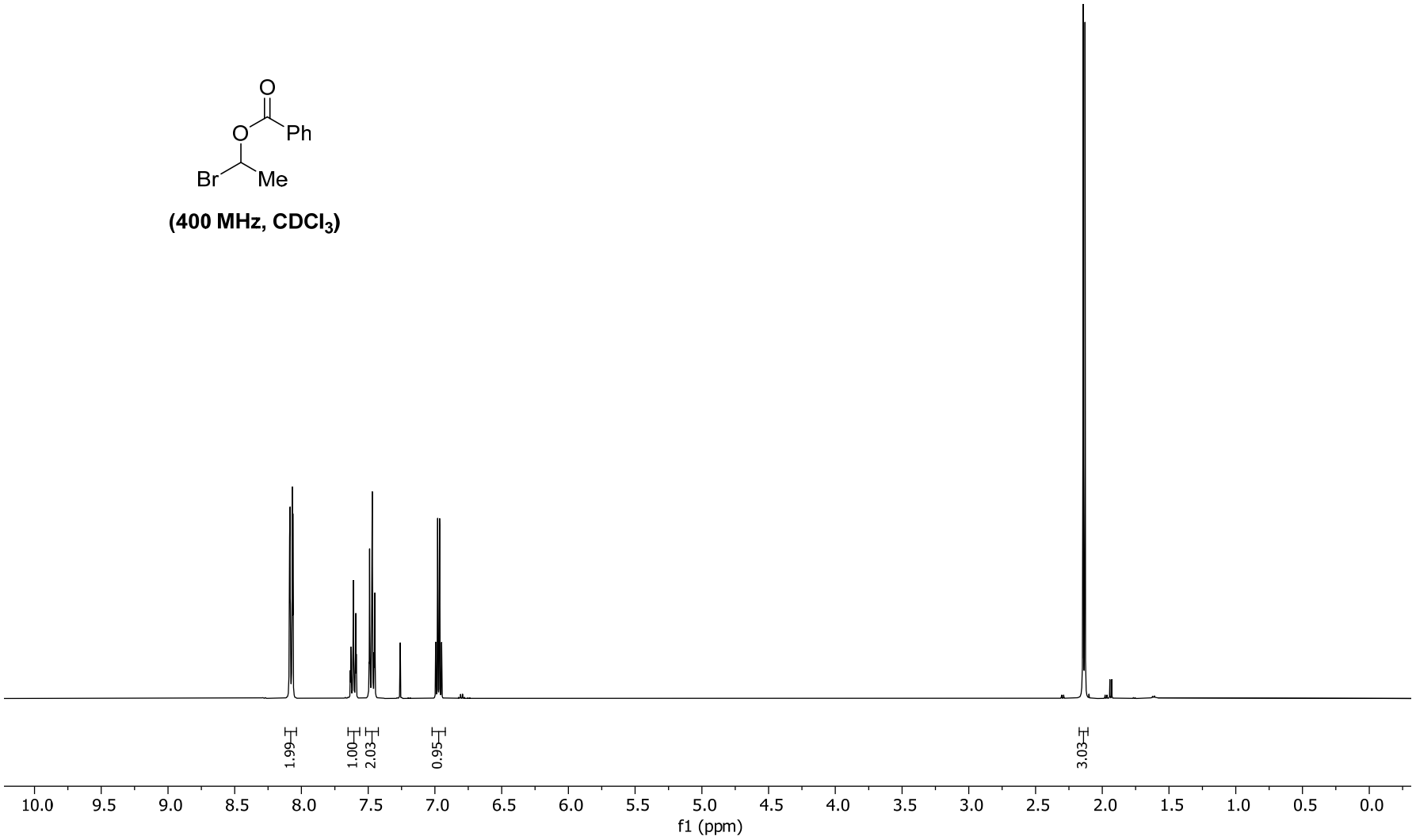


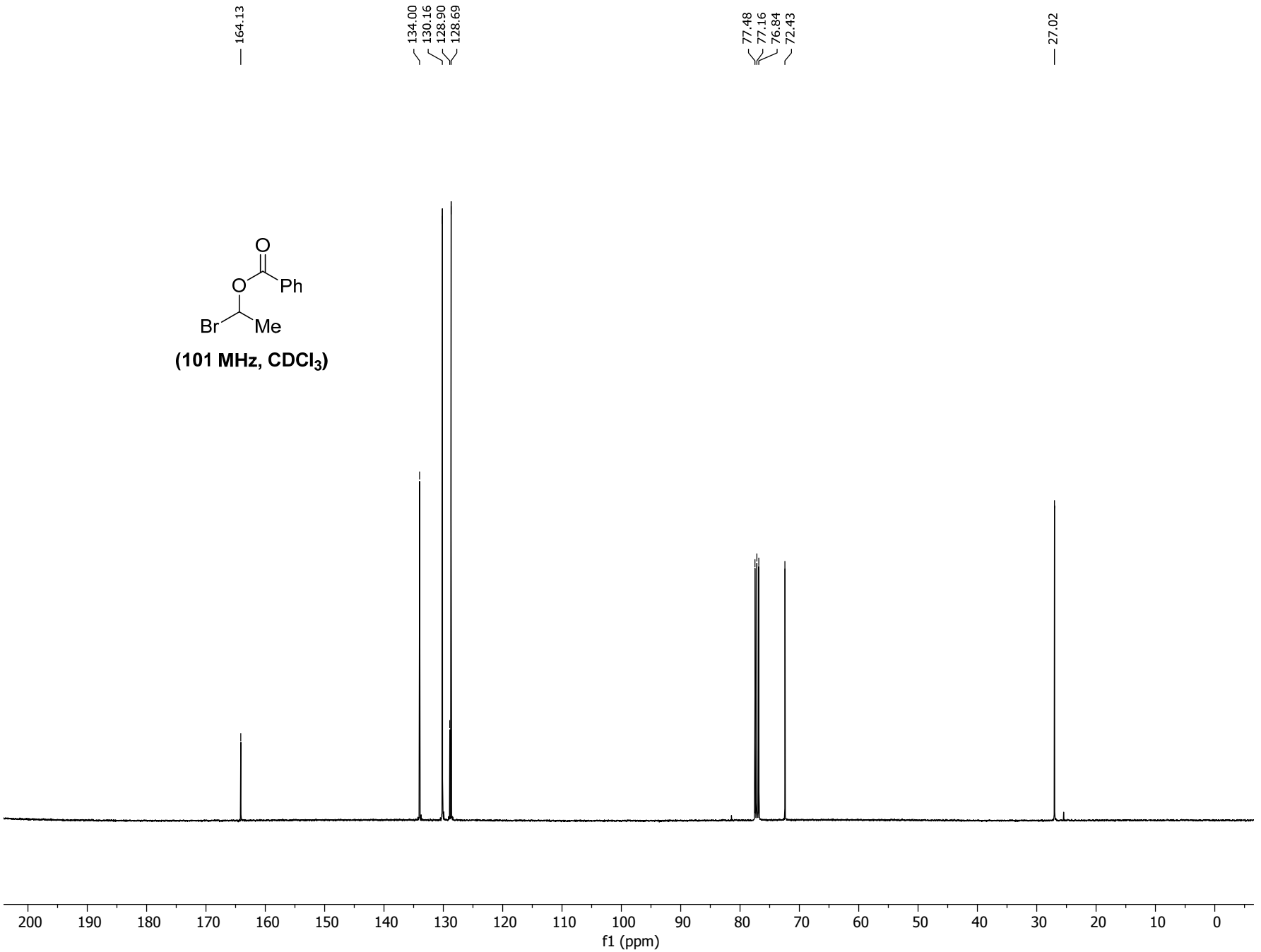
(400 MHz, $CDCl_3$)

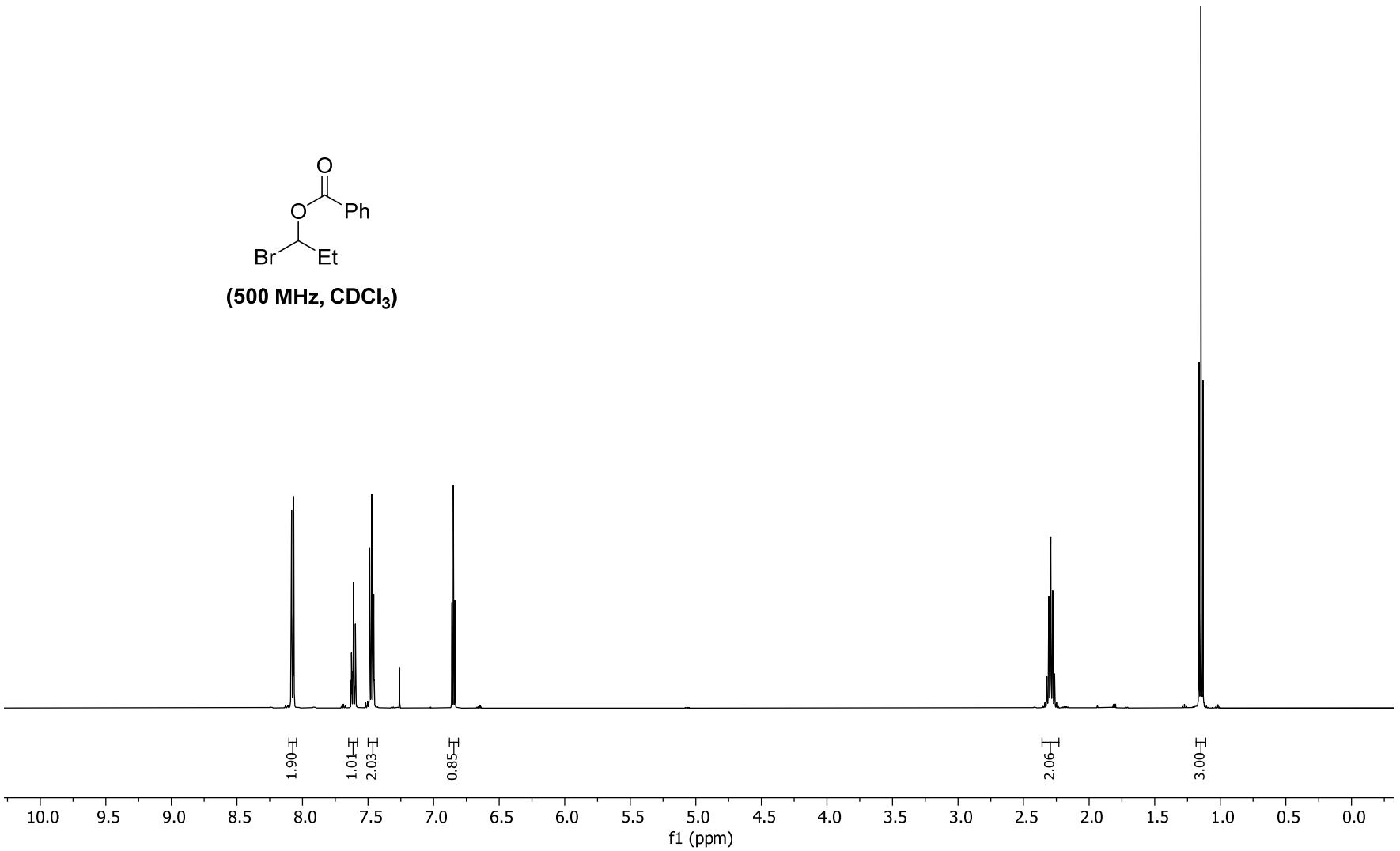


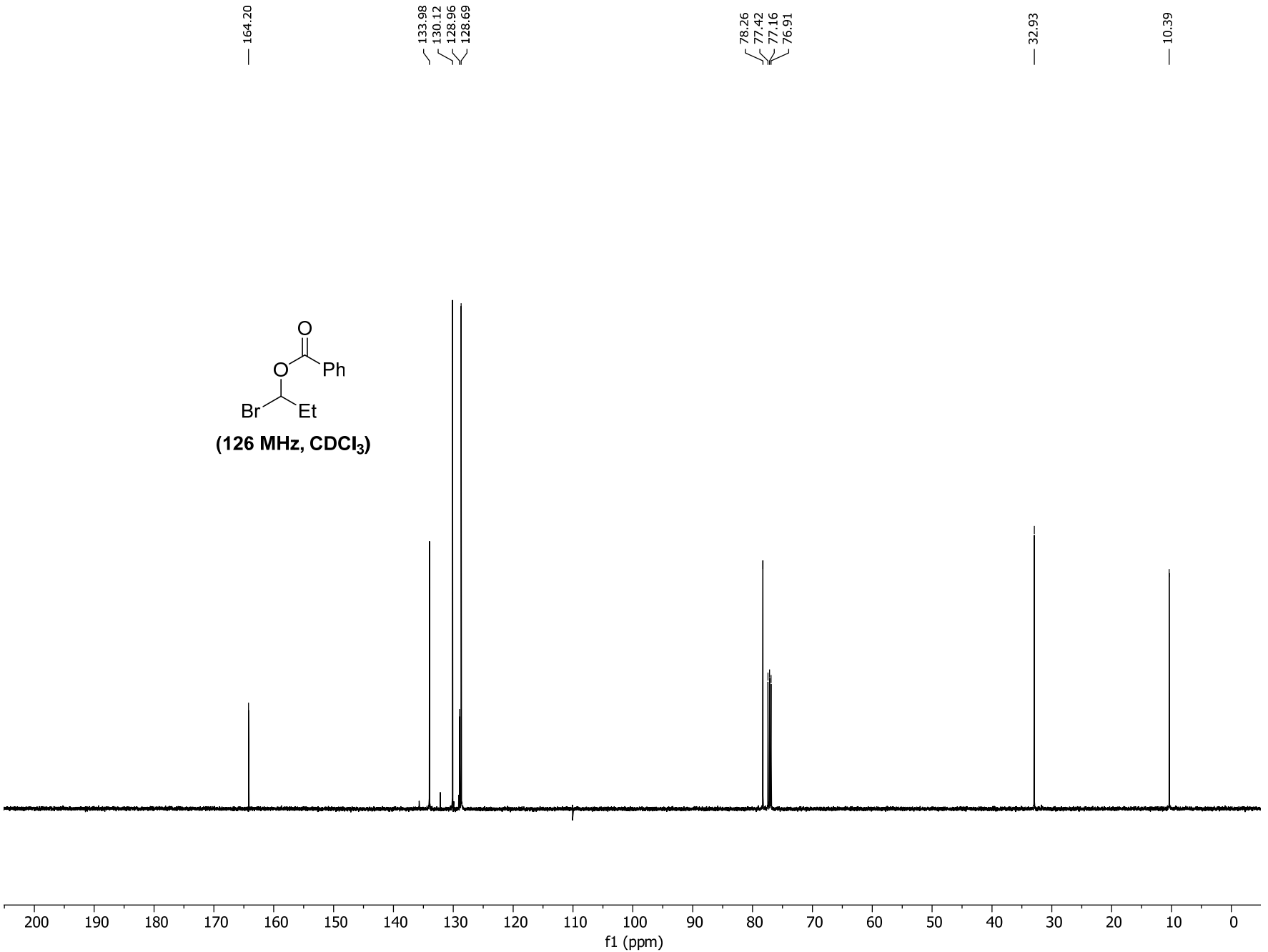

150.93
150.86
129.75
125.20
125.19
120.25
120.20
82.55
82.48
77.48
77.16
76.84
35.08
35.03
32.02
31.76
29.71
29.65
29.58
29.54
29.44
29.20
24.86
24.81
22.80
22.65
14.24
14.17
O
P
O
OPh
OPh
n-Bu
n-Dec
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

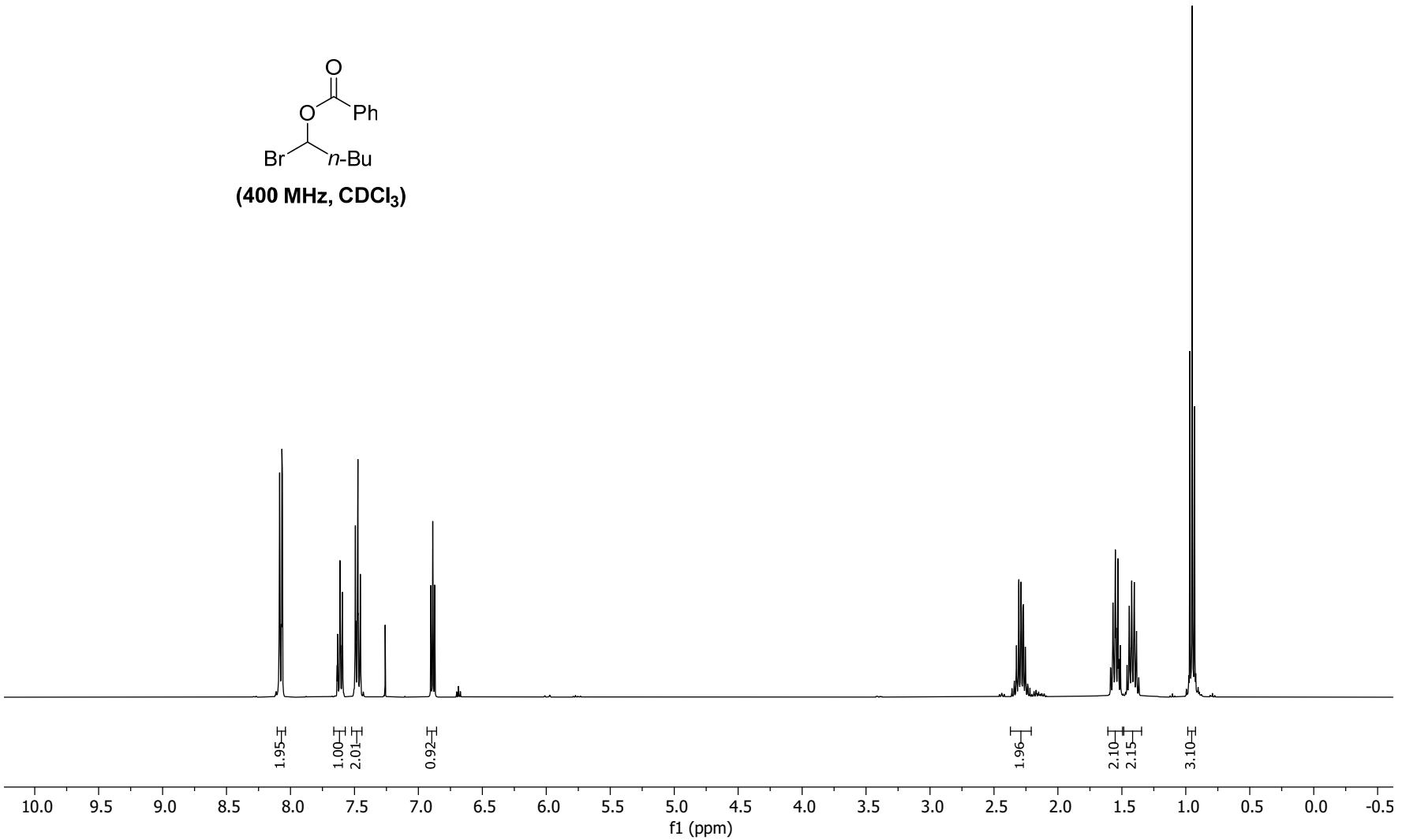

-12.37
O
P
O
OPh
OPh
n-Bu
n-Dec
(162 MHz, CDCl3)
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

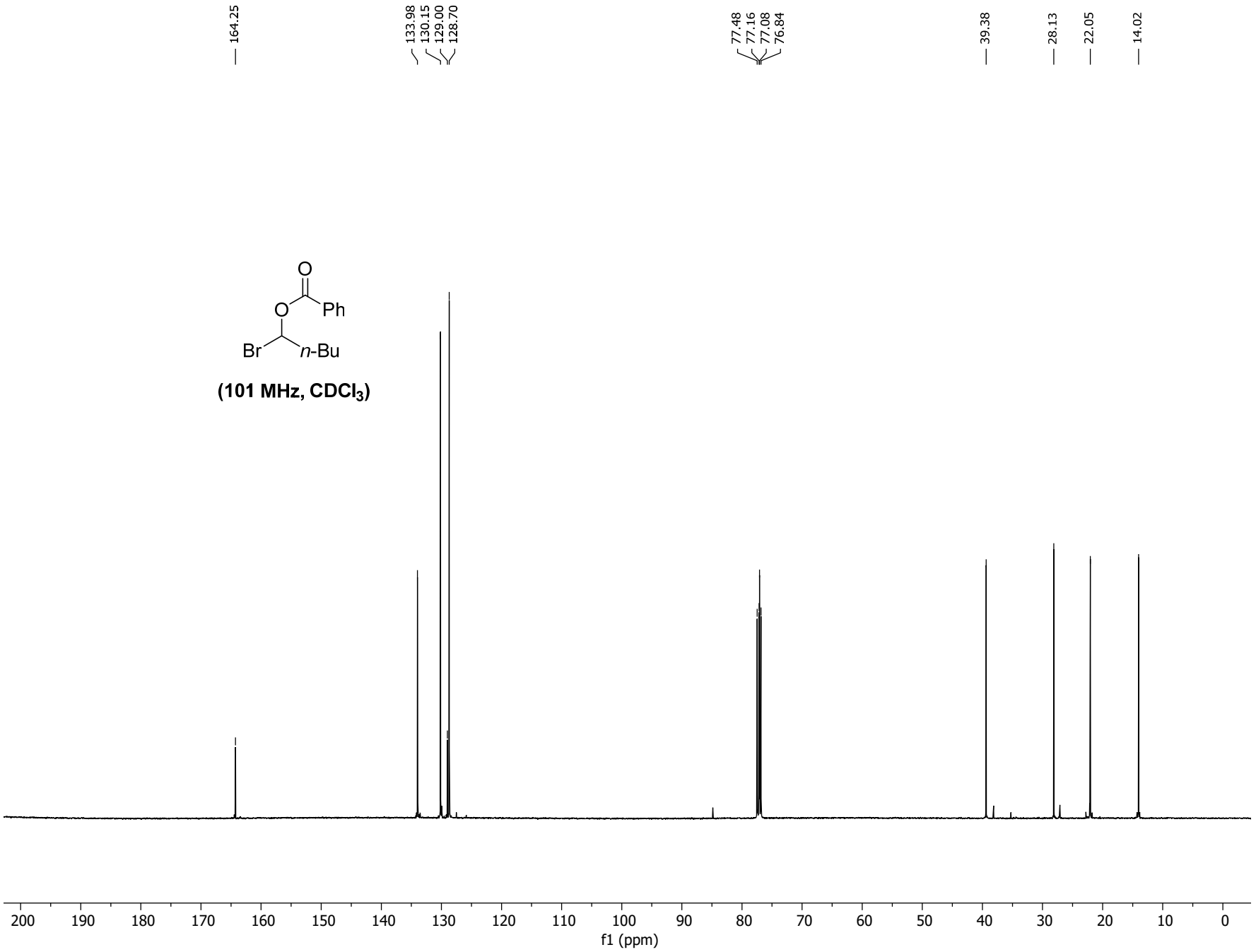

O
O
Ph
Br
Me
(400 MHz, CDCl3)
1.99
1.00
2.03
0.95
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

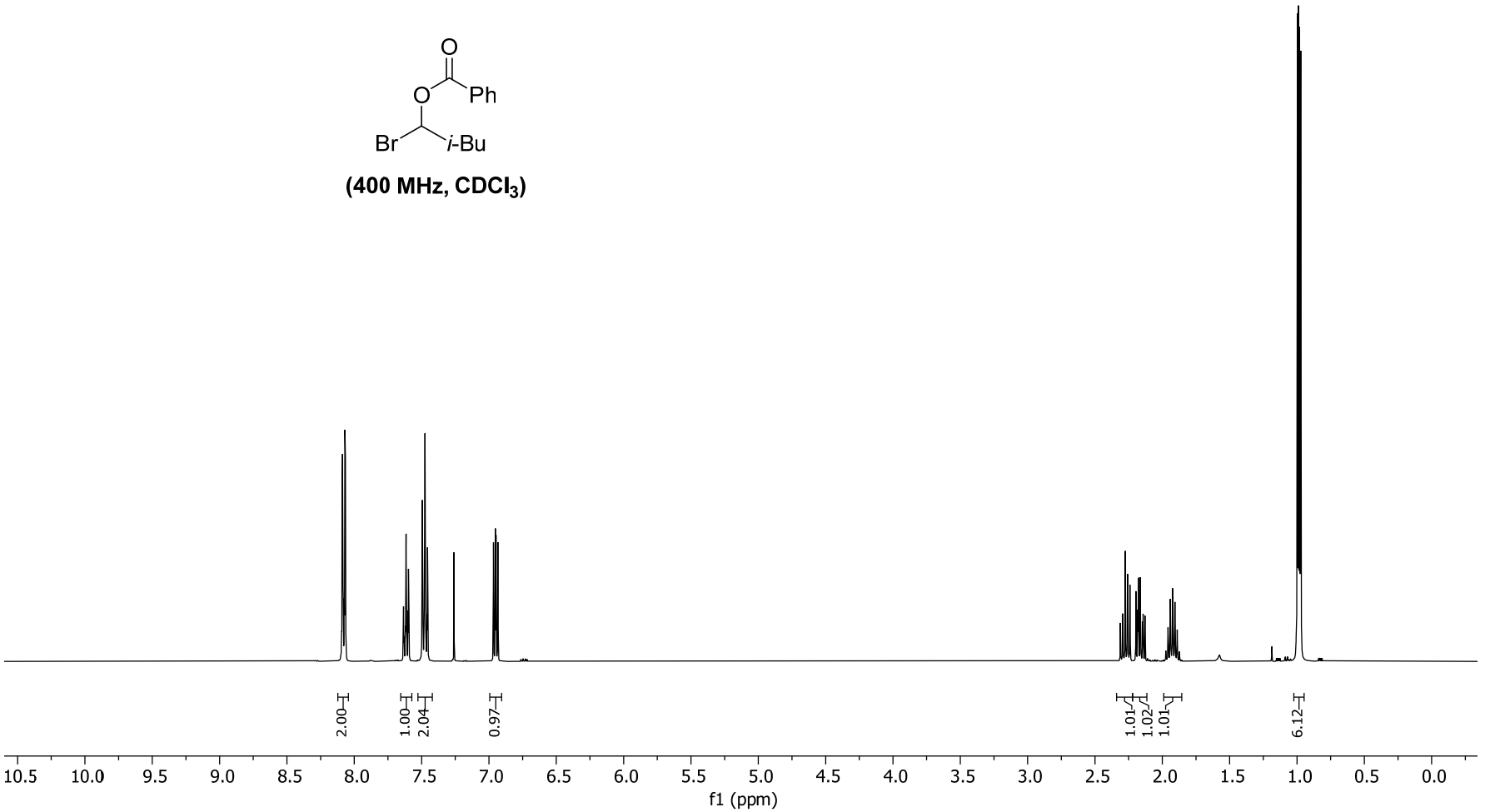

164.13
134.00
130.16
128.90
128.69
77.48
77.16
76.84
72.43
27.02
O
O
Ph
Br
Me
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

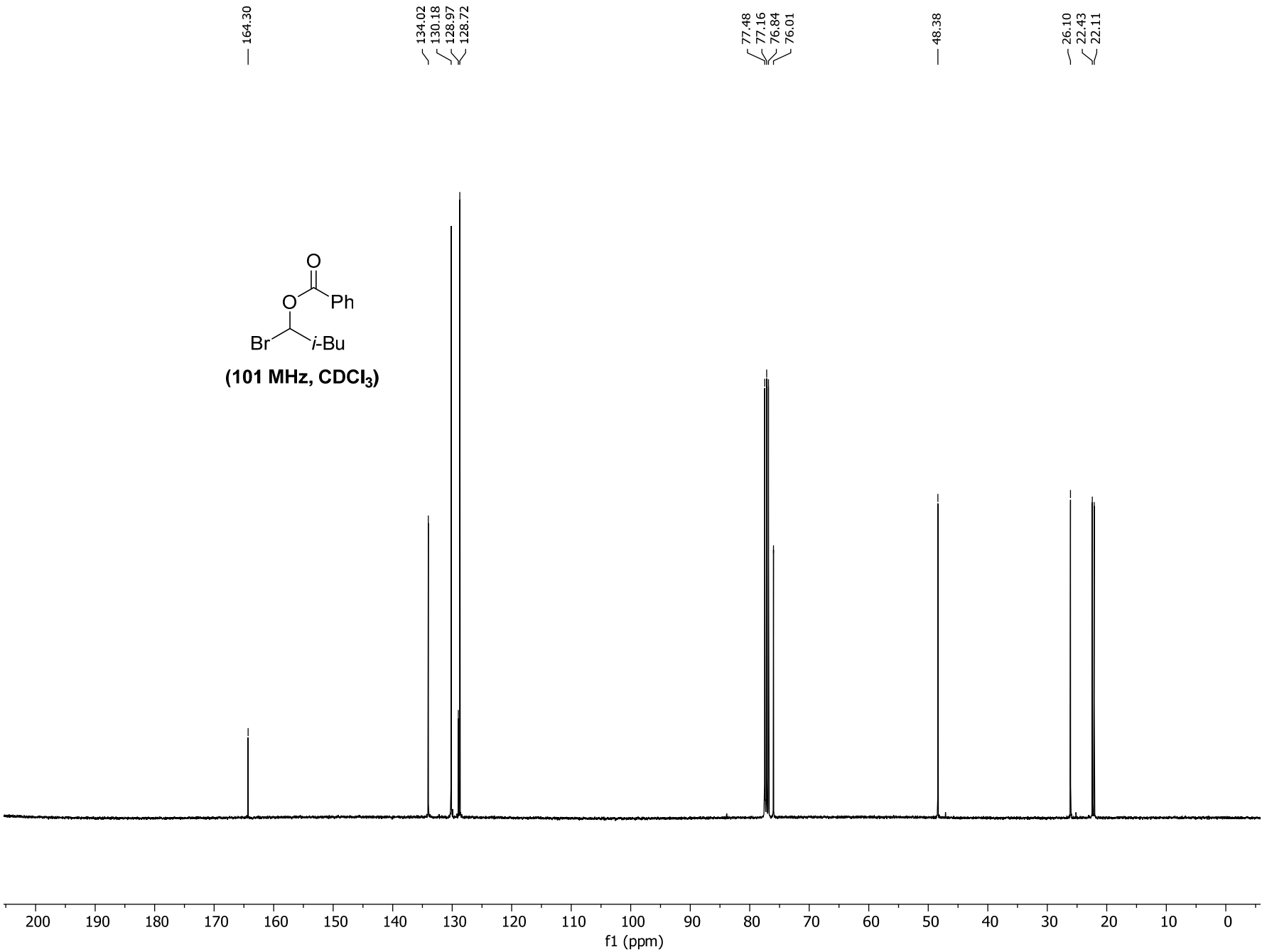

O
O
Ph
Br
Et
(500 MHz, CDCl3)
1.90
1.01
2.03
0.85
2.06
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

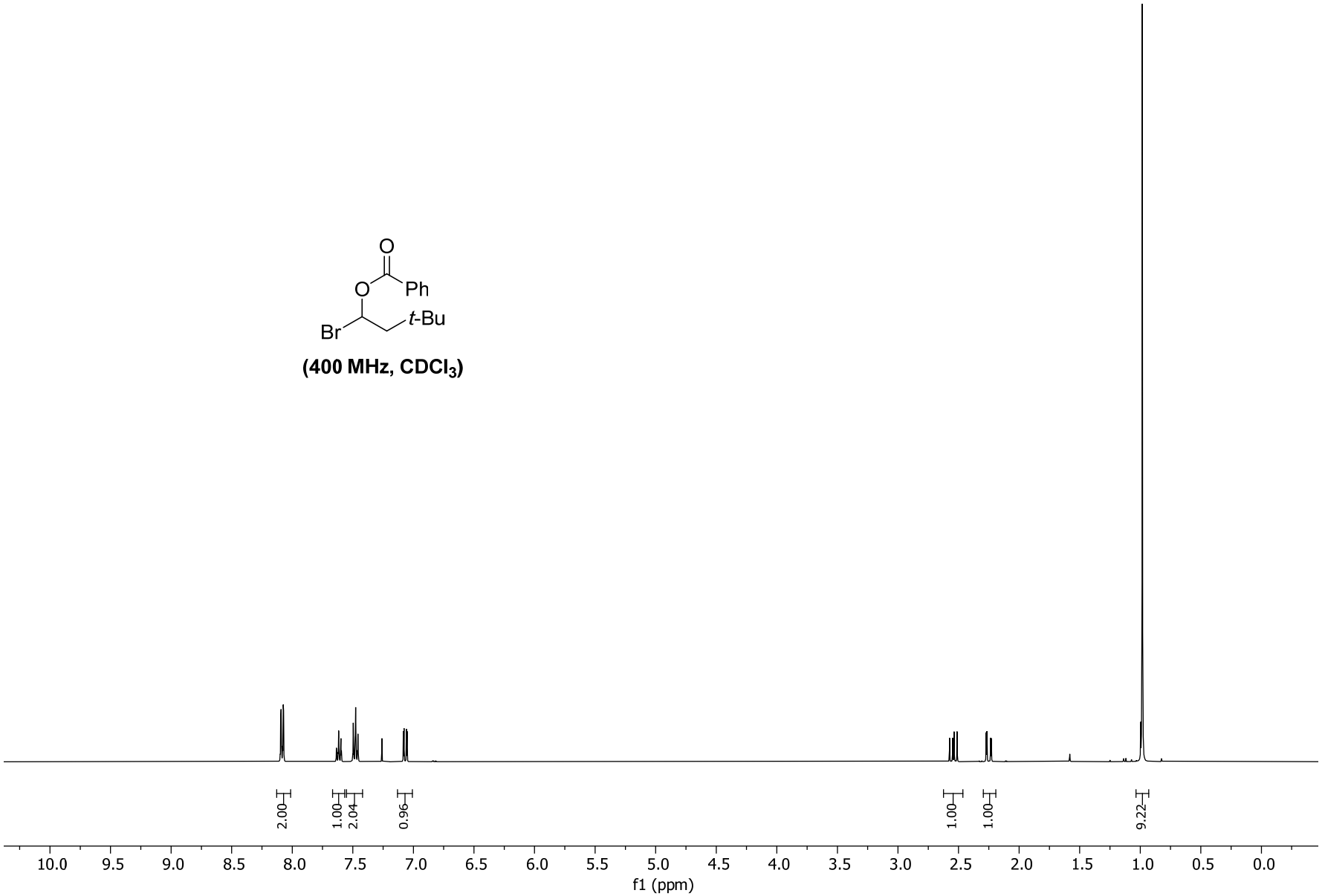

164.20
133.98
130.12
128.96
128.69
78.26
77.42
77.16
76.91
32.93
10.39
O
O
Ph
Br
Et
(126 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

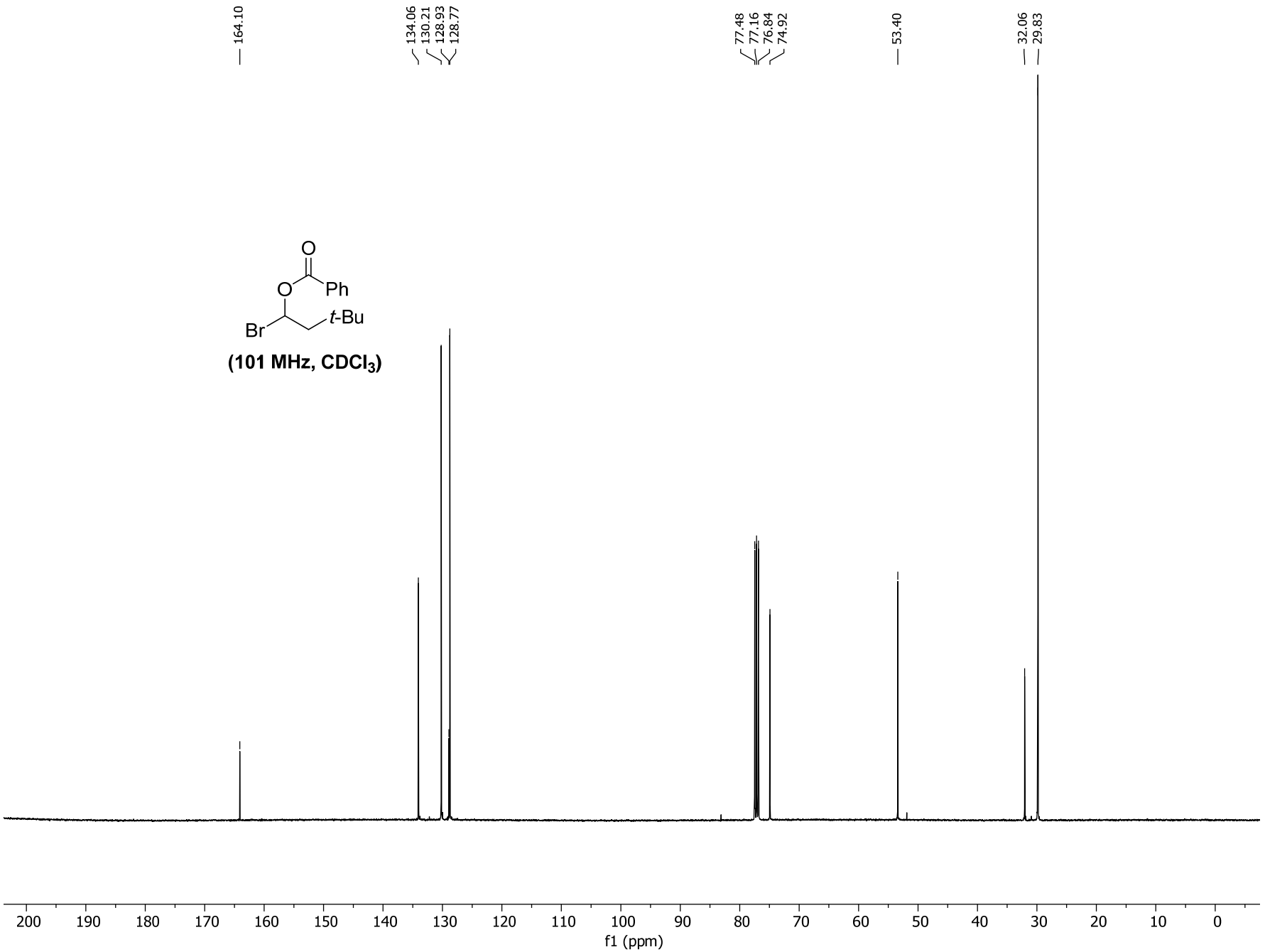

O
O
Ph
Br
n-Bu
(400 MHz, CDCl3)
1.95
1.00
2.01
0.92
1.96
2.10
2.15
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

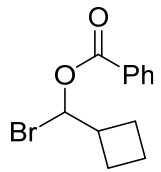

164.25
133.98
130.15
129.00
128.70
77.48
77.16
77.08
76.84
39.38
28.13
22.05
14.02
O
O
Ph
Br
n-Bu
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
Ph
Br
i-Bu
(400 MHz, CDCl3)
2.00
1.00
2.04
0.97
1.01
1.02
1.01
6.12
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

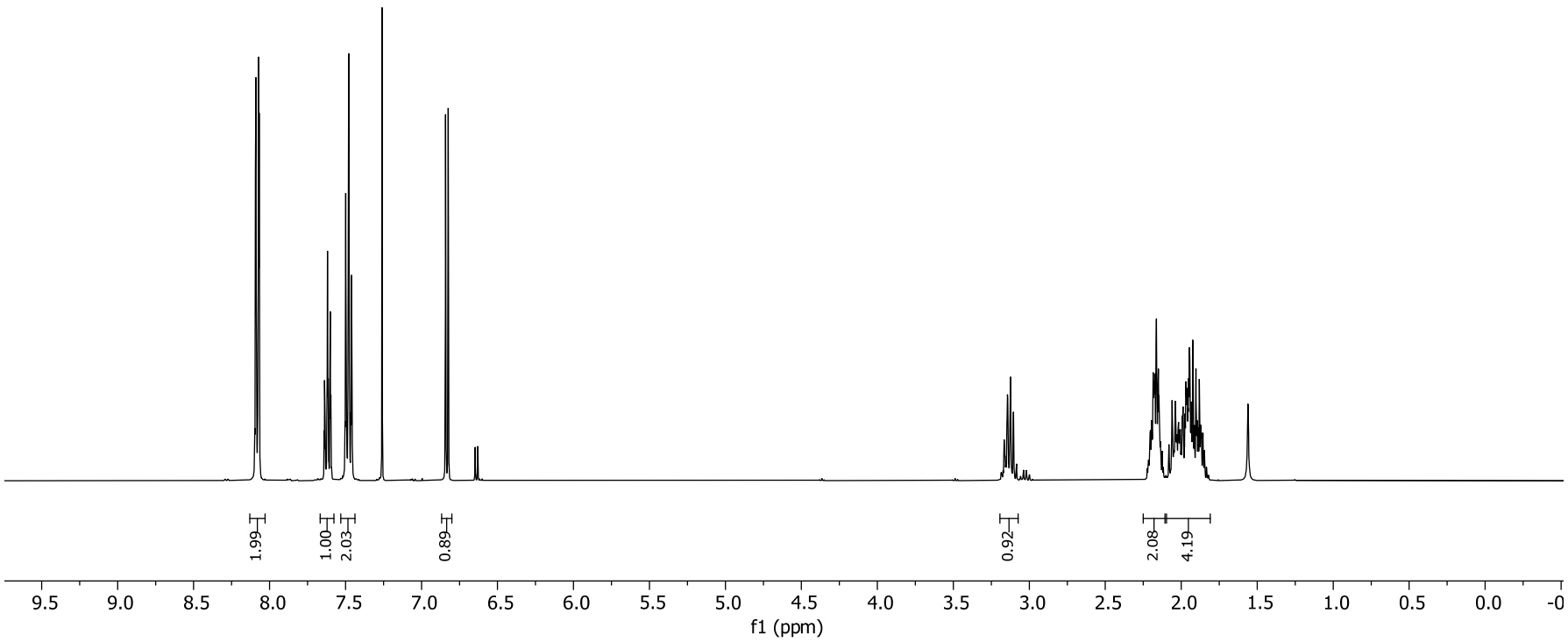

164.30
134.02
130.18
128.97
128.72
77.48
77.16
76.84
76.01
48.38
26.10
22.43
22.11
O
O
Ph
Br
i-Bu
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

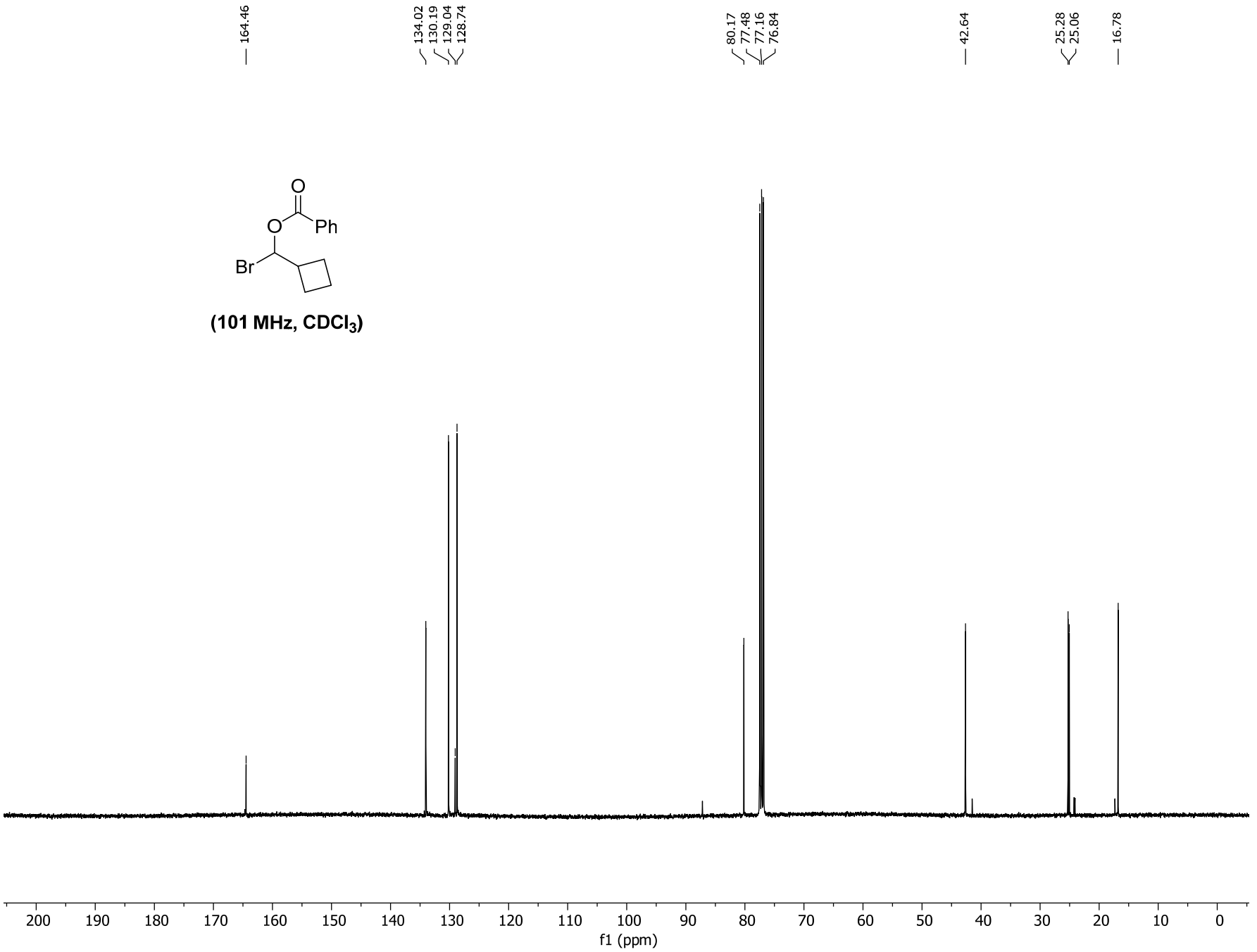

O
O
Ph
Br
t-Bu
(400 MHz, CDCl3)
2.00
1.00
2.04
0.96
1.00
1.00
9.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

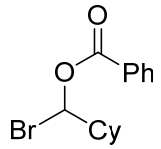

164.10
134.06
130.21
128.93
128.77
77.48
77.16
76.84
74.92
53.40
32.06
29.83
O
O
Ph
Br
t-Bu
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



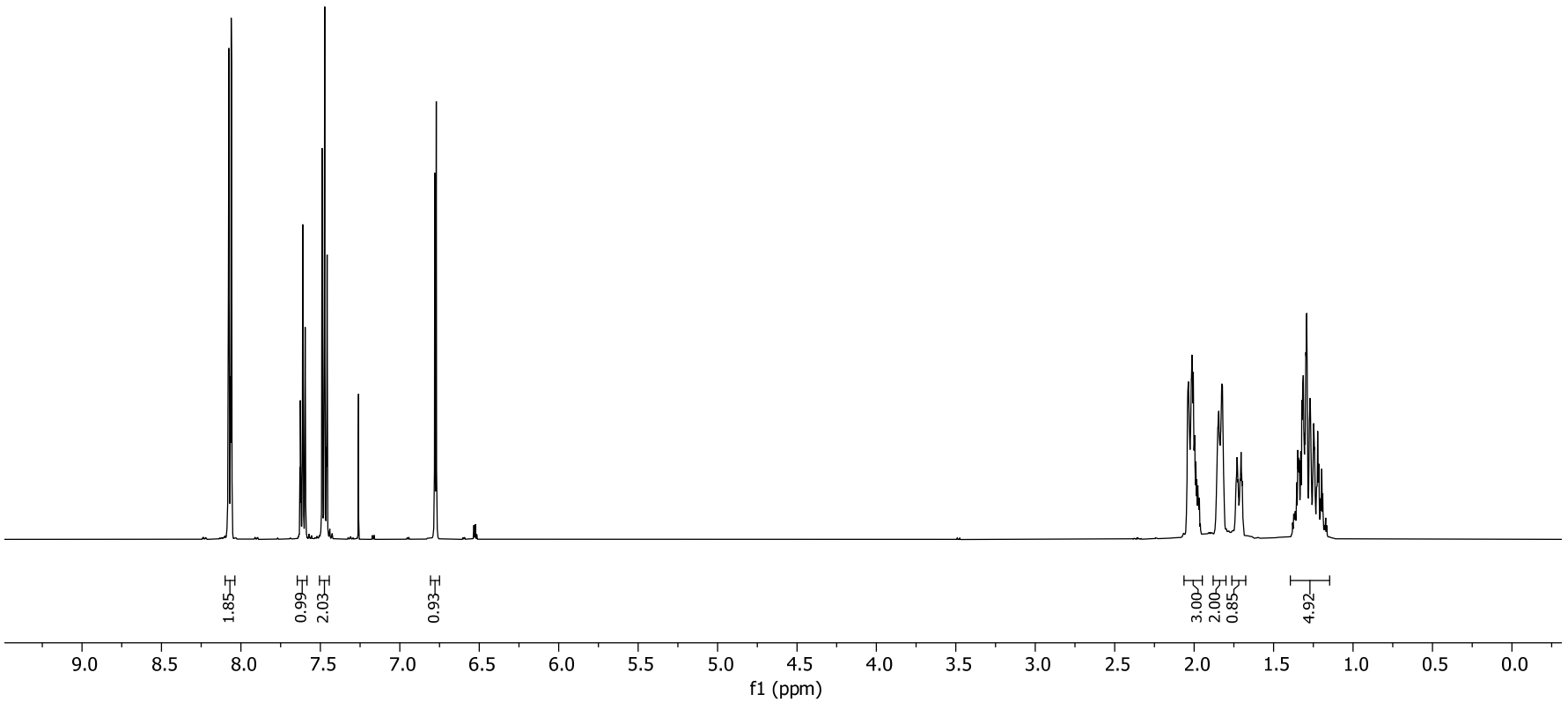
(400 MHz, $CDCl_3$)

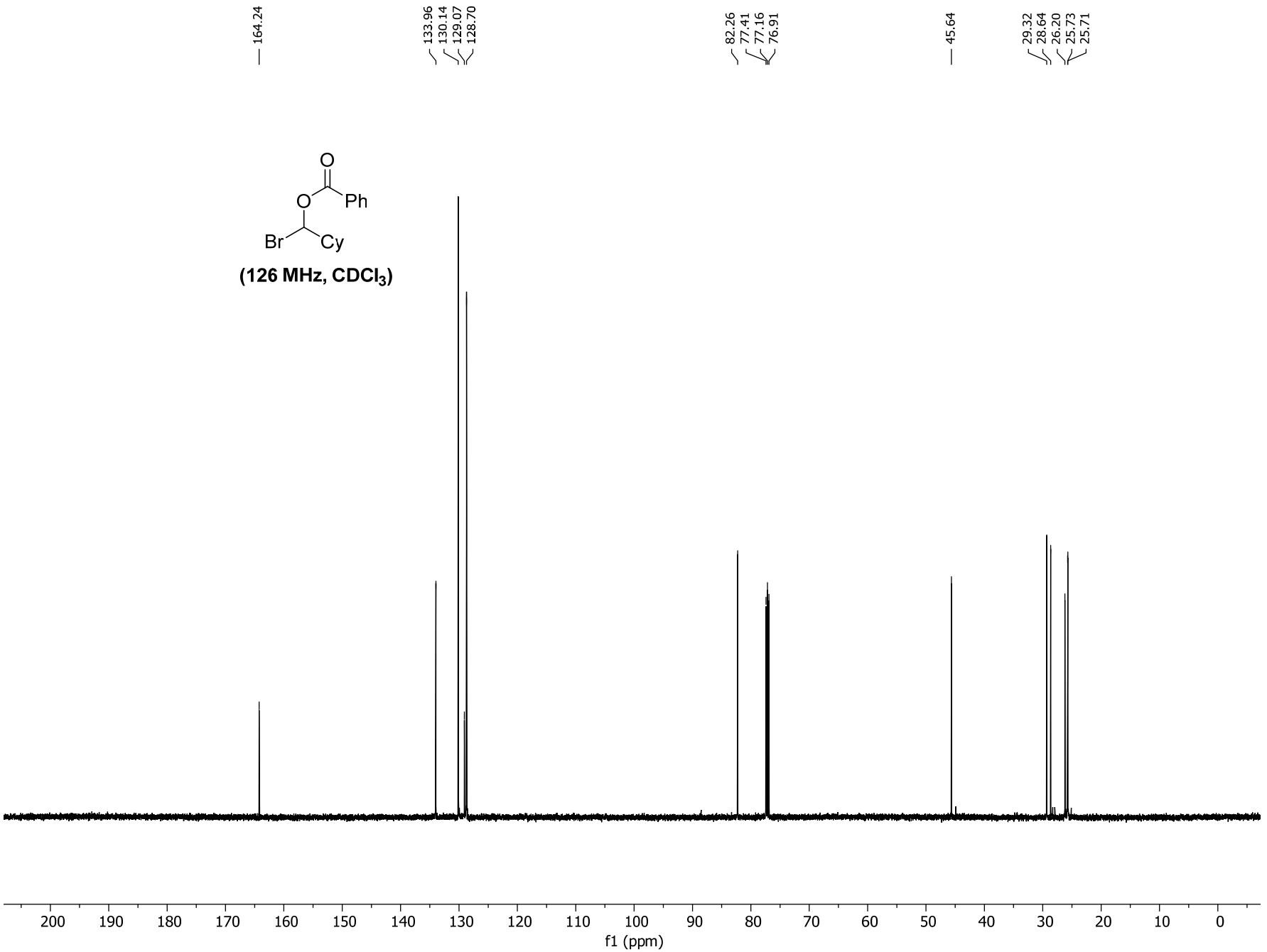


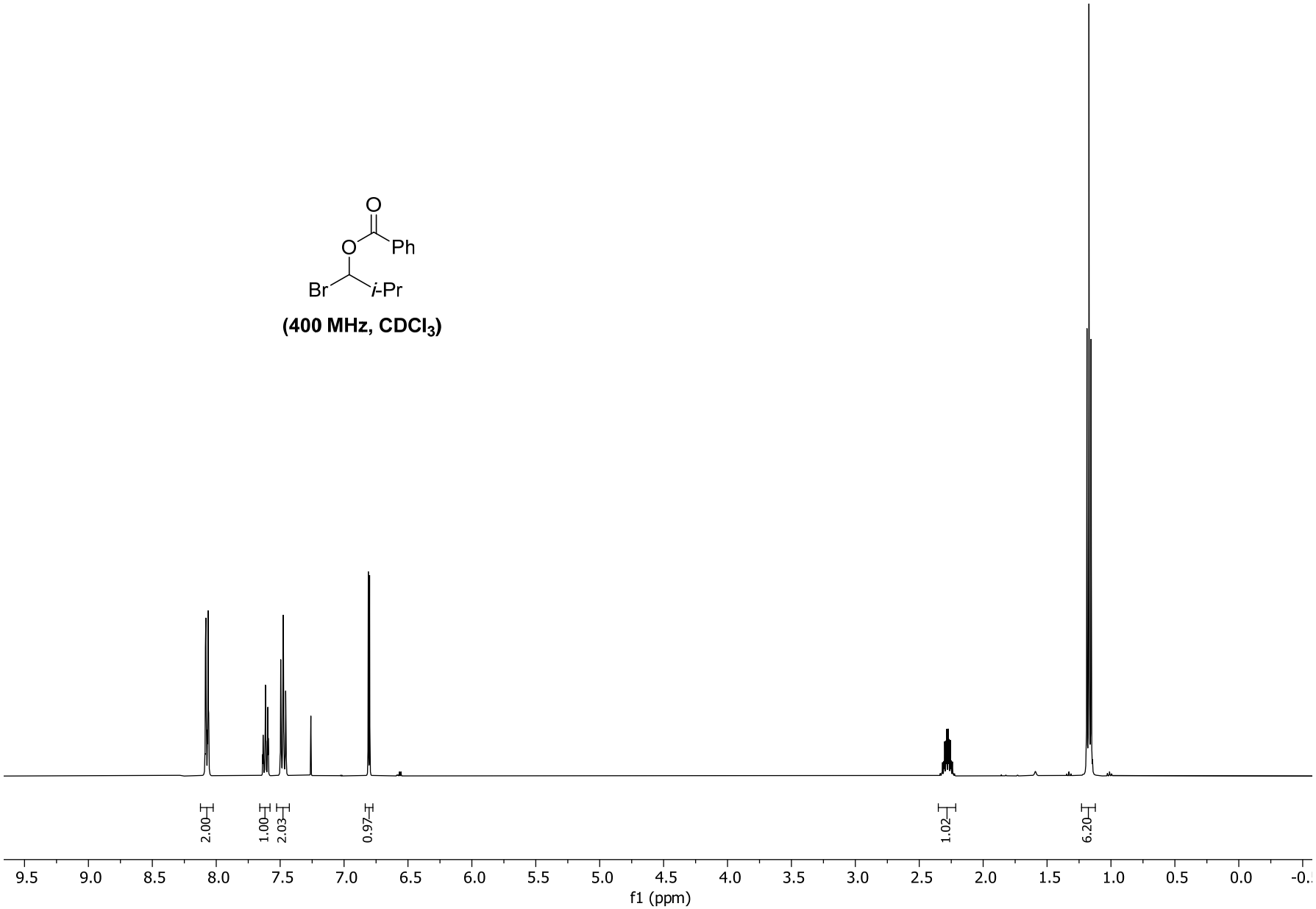

164.46
134.02
130.19
129.04
128.74
80.17
77.48
77.16
76.84
42.64
25.28
25.06
16.78
O
O
Ph
Br
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

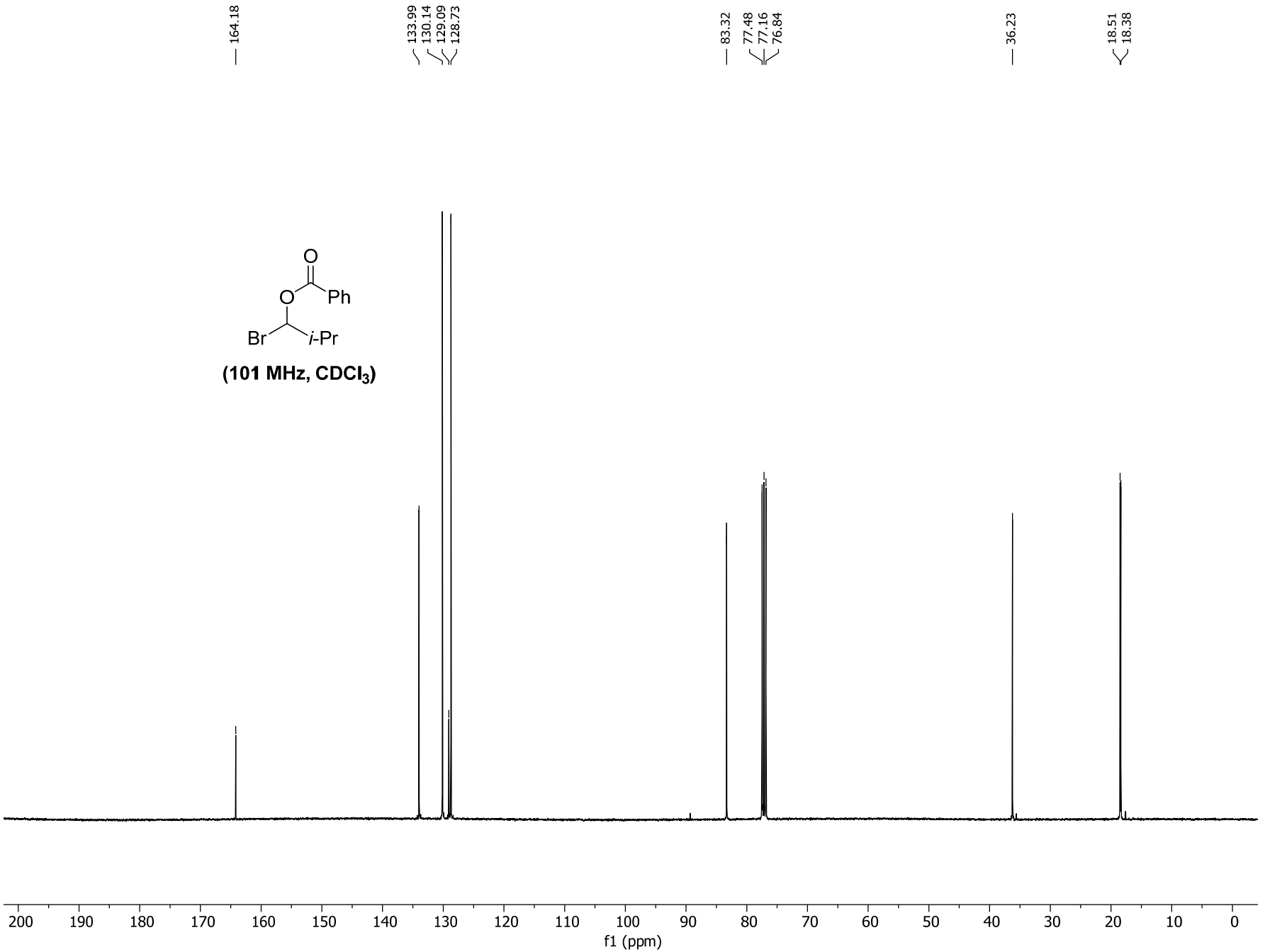


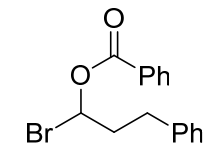
(500 MHz, $CDCl_3$)



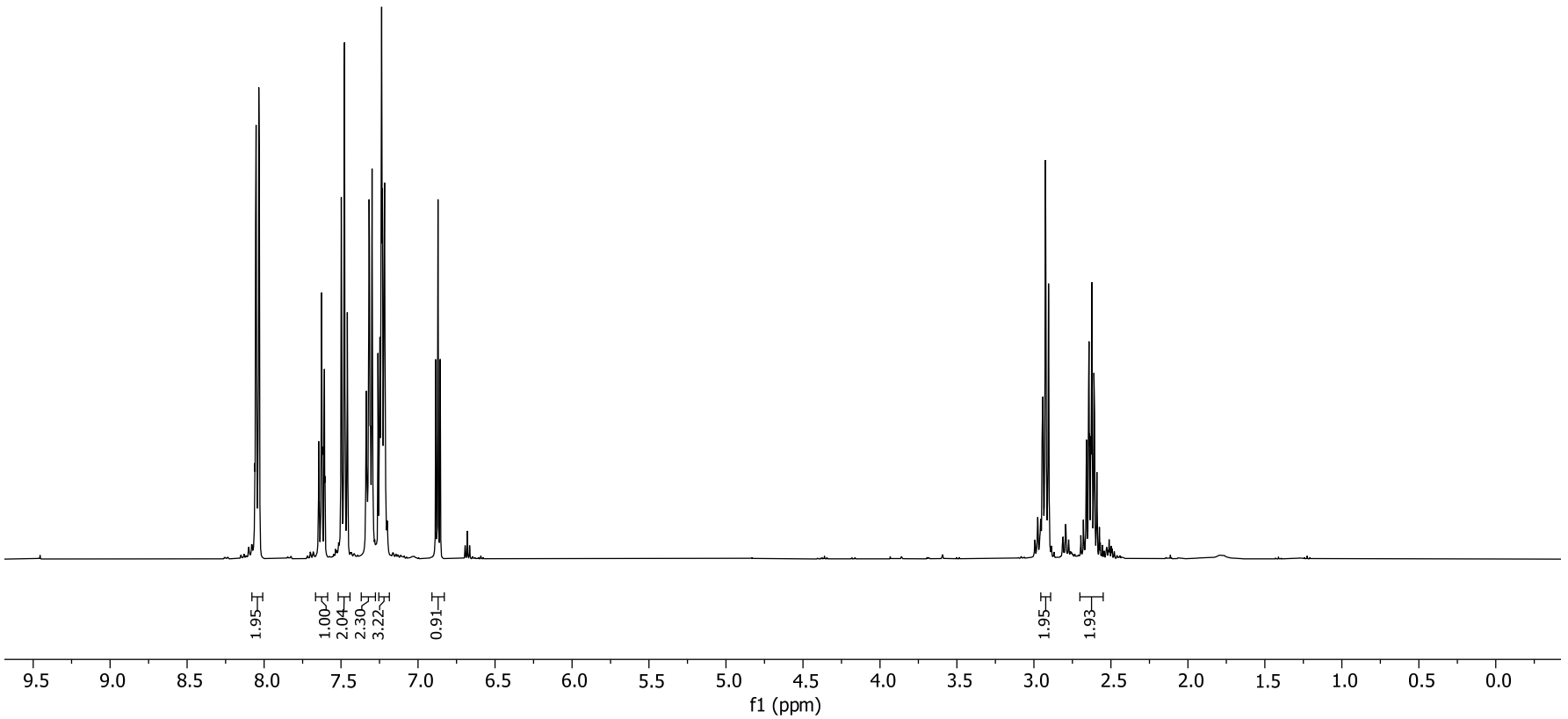

164.24
133.96
130.14
129.07
128.70
82.26
77.41
77.16
76.91
45.64
29.32
28.64
26.20
25.73
25.71
O
O
Ph
Br
Cy
(126 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

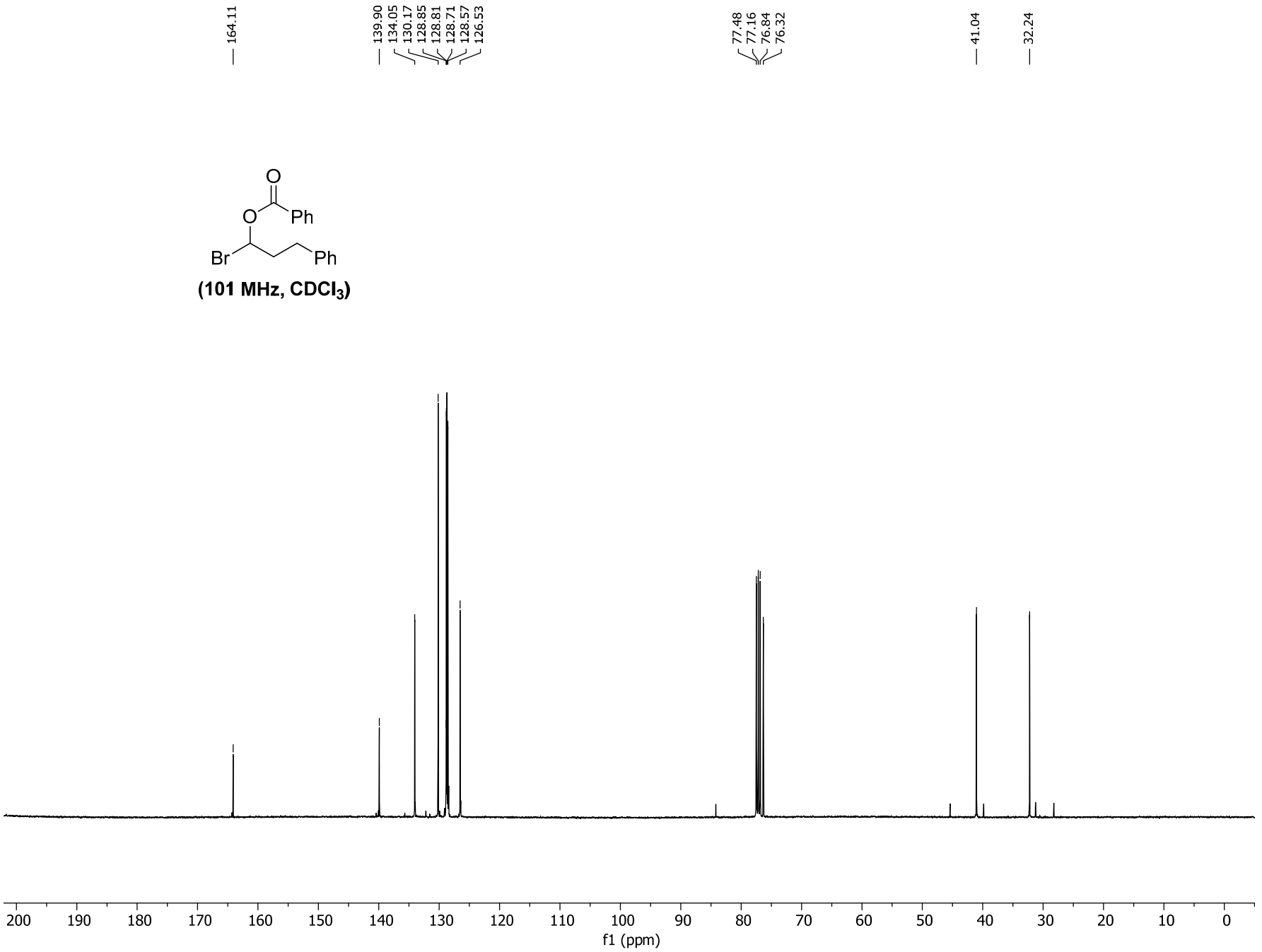

O
O
Ph
Br
i-Pr
(400 MHz, CDCl3)
2.00
1.00
2.03
0.97
1.02
6.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

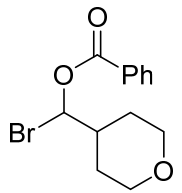

164.18
133.99
130.14
129.09
128.73
83.32
77.48
77.16
76.84
36.23
18.51
18.38
O
O
Ph
Br
i-Pr
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



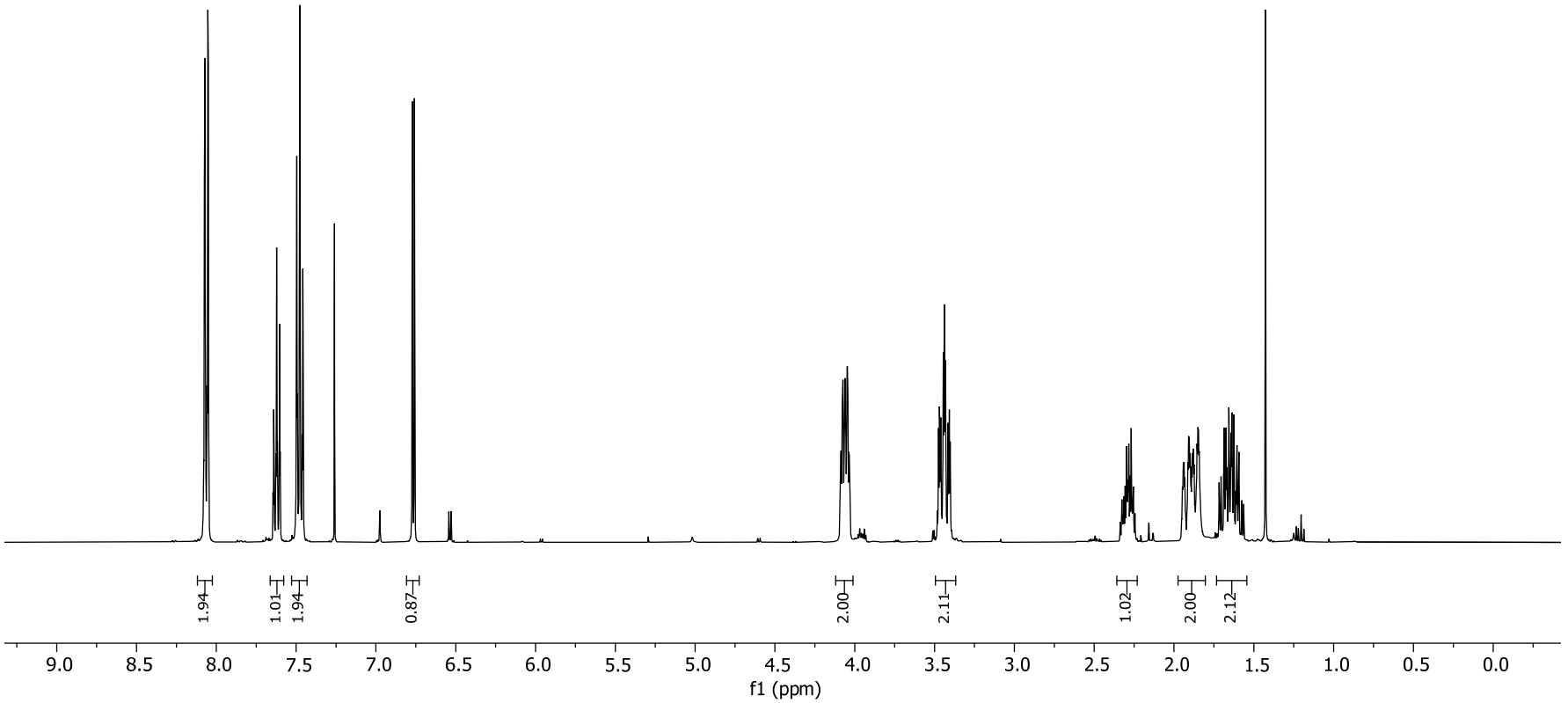
(400 MHz, $CDCl_3$)

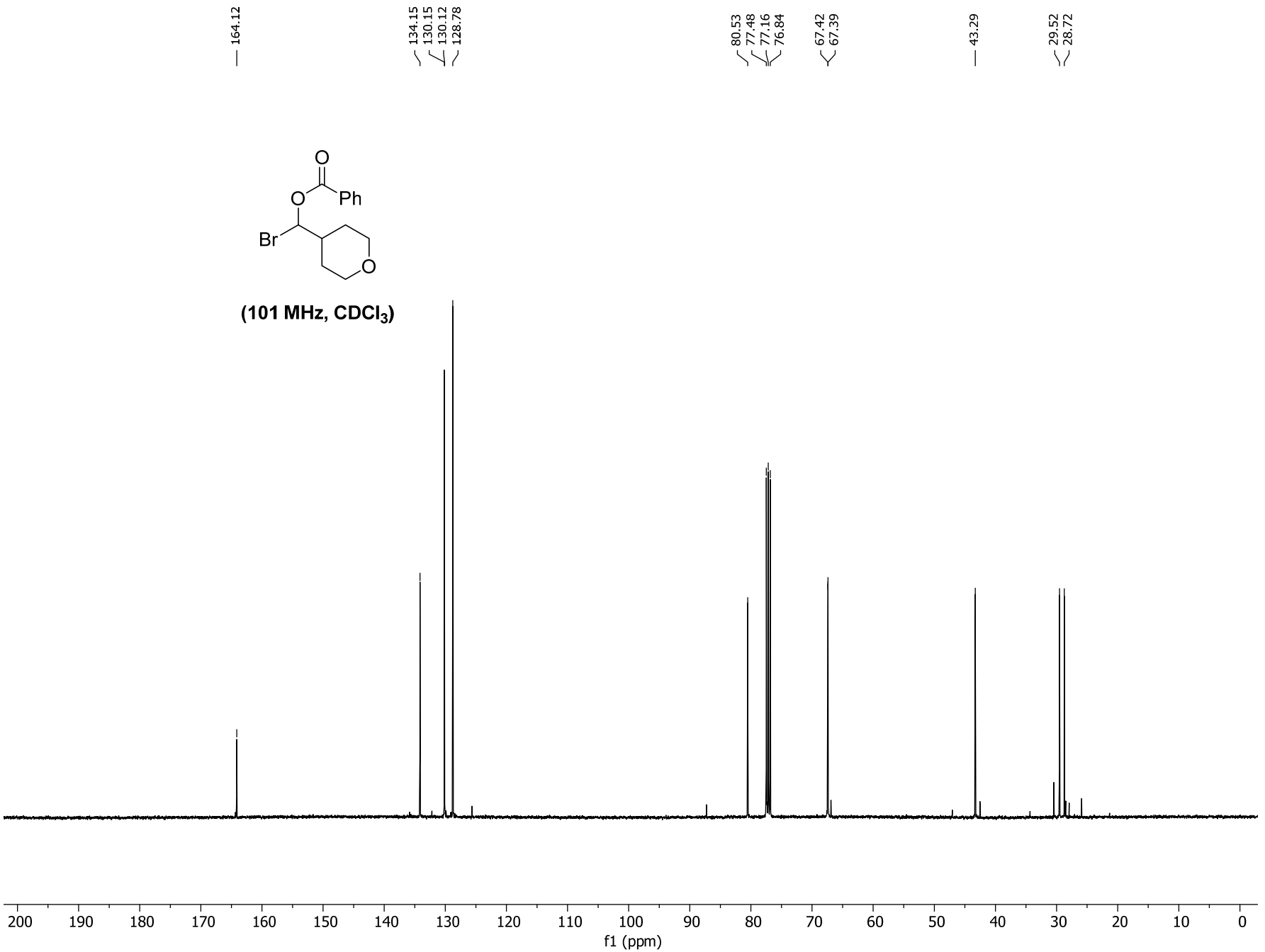


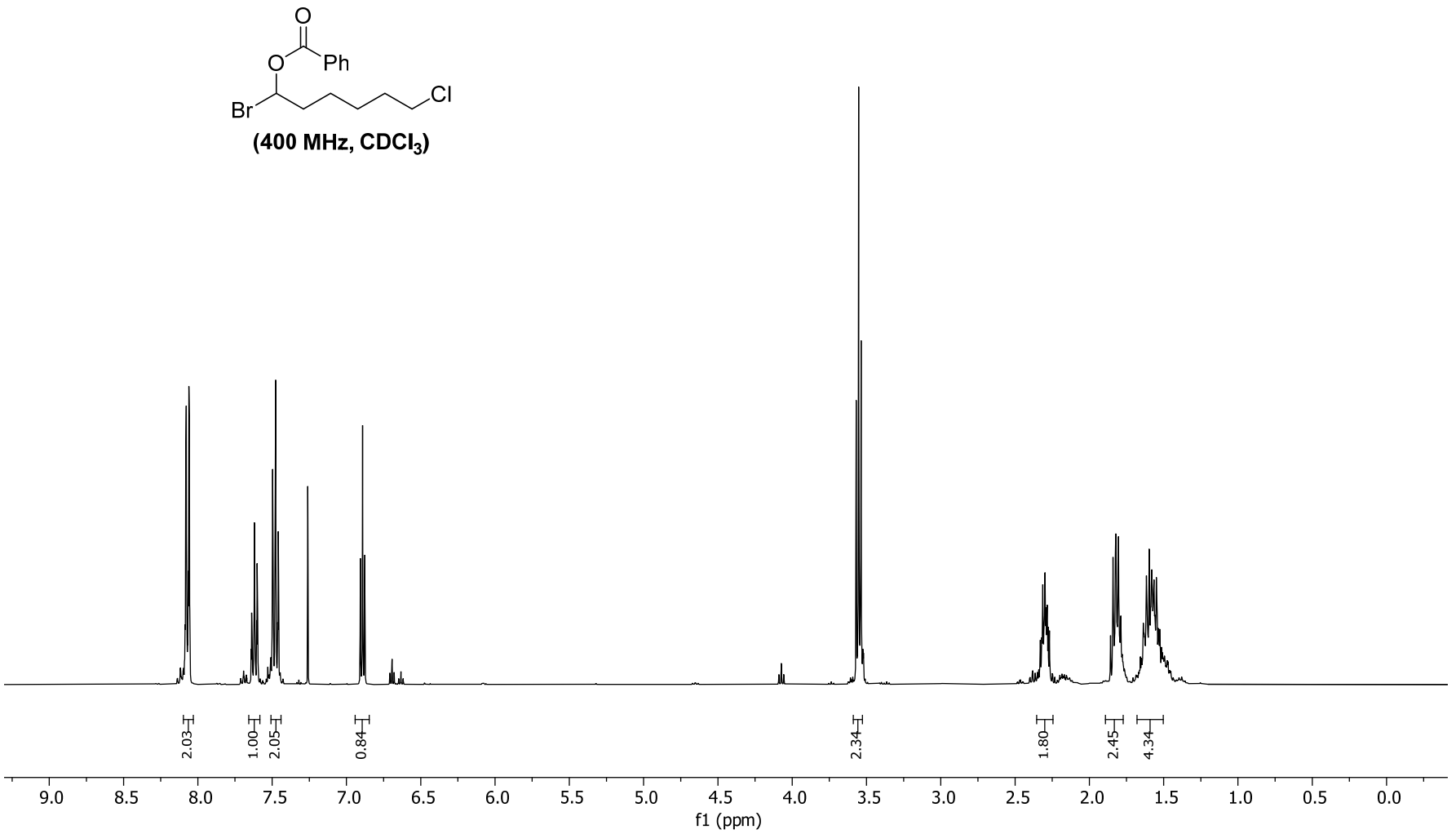

164.11
139.90
134.05
130.17
128.85
128.81
128.71
128.57
126.53
77.48
77.16
76.84
76.32
41.04
32.24
O
O
Ph
Br
Ph
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

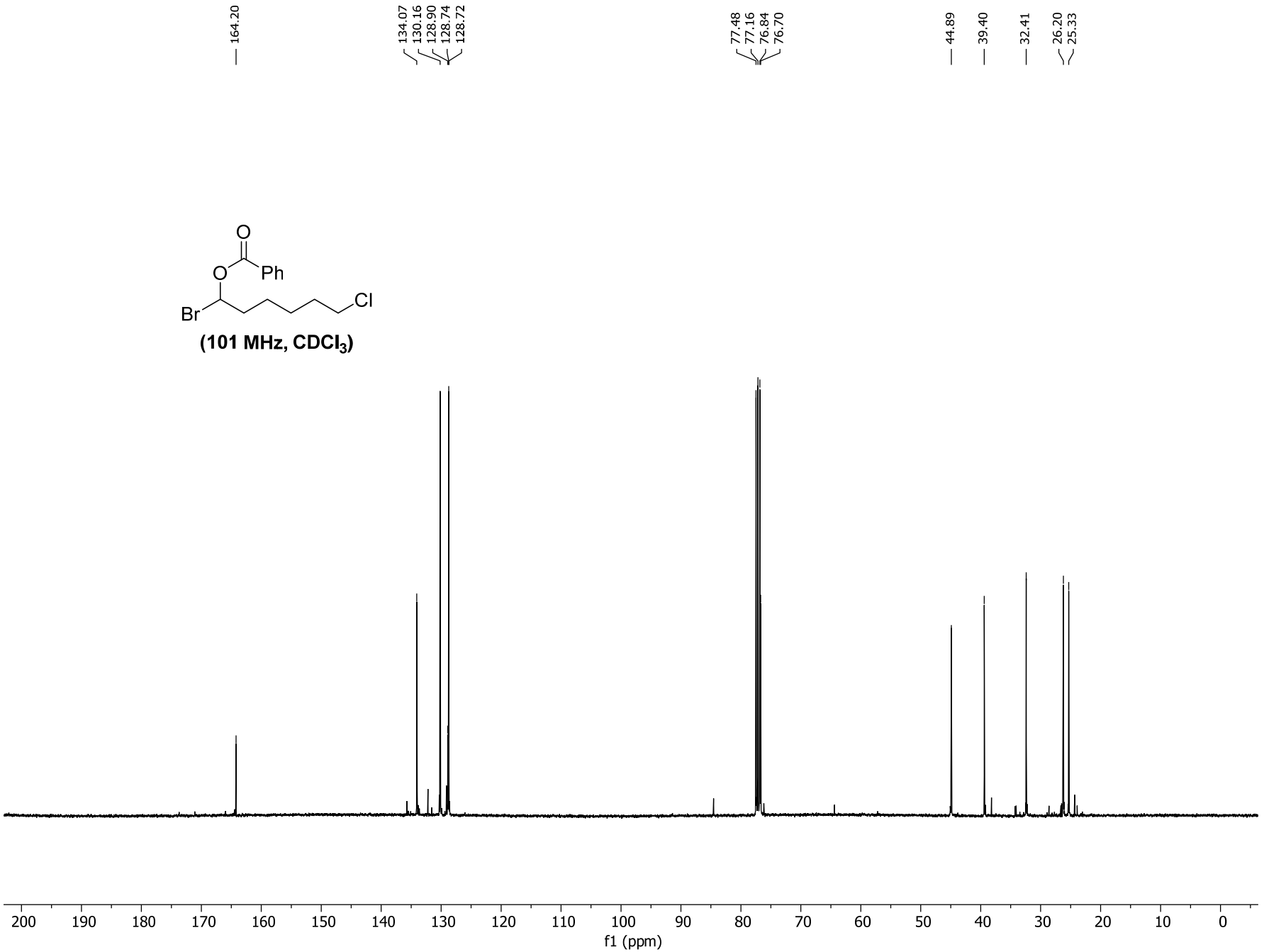


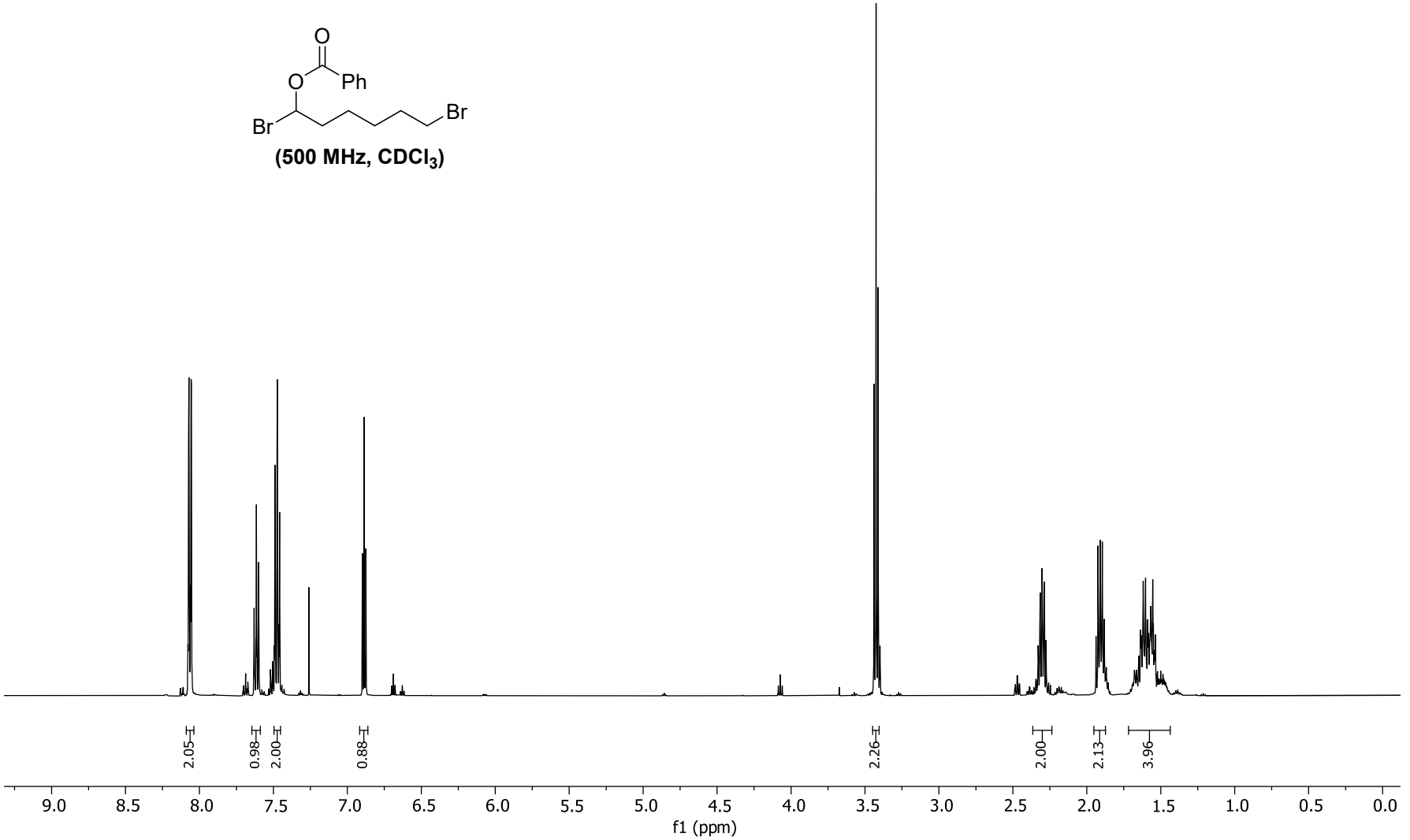
(400 MHz, $CDCl_3$)

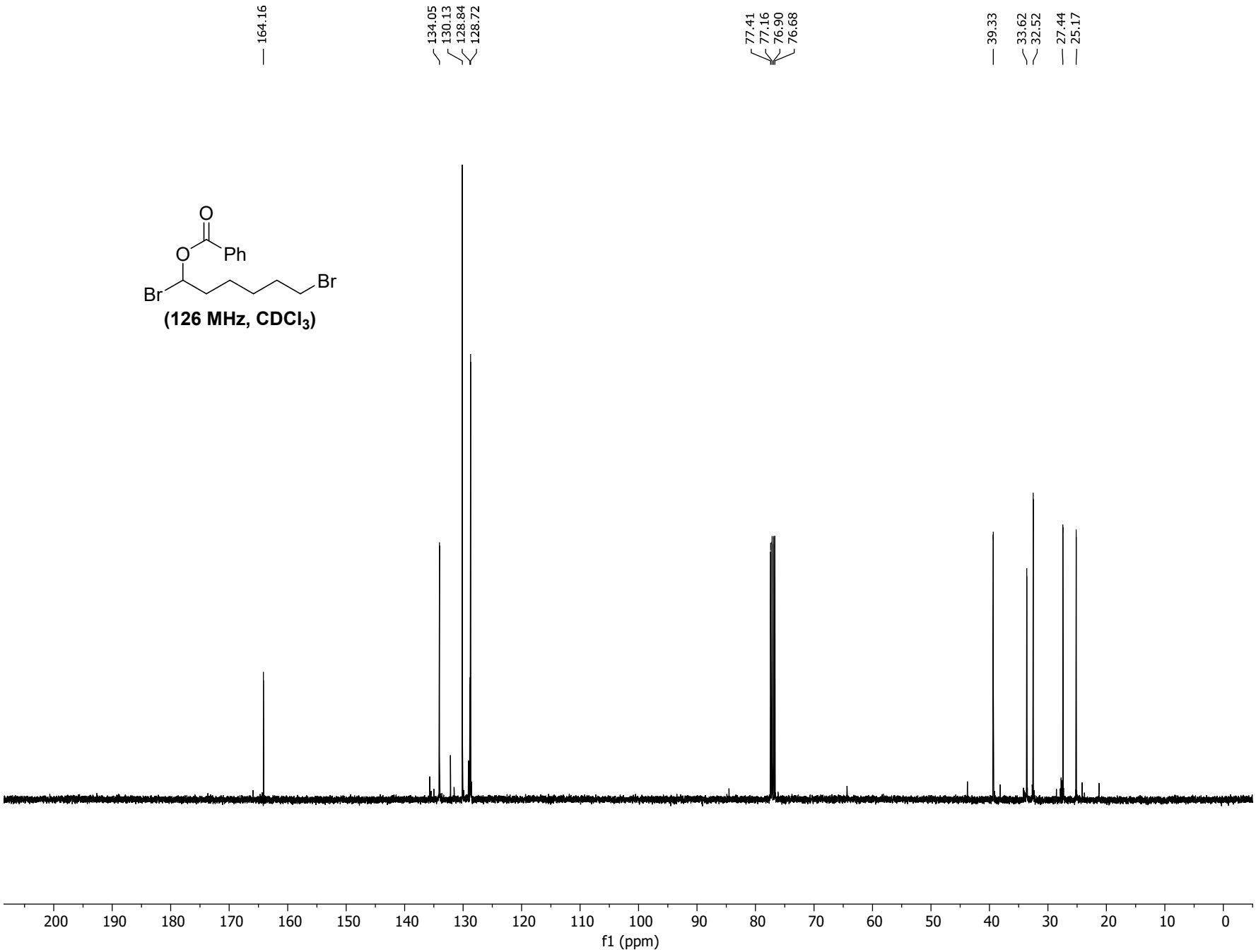


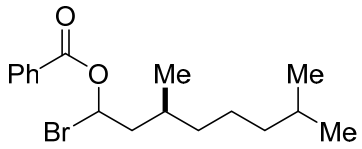

164.12
134.15
130.15
130.12
128.78
80.53
77.48
77.16
76.84
67.42
67.39
43.29
29.52
28.72
O
O
Ph
Br
O
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
Ph
Br
Cl
(400 MHz, CDCl3)
2.03
1.00
2.05
0.84
2.34
1.80
2.45
4.34
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

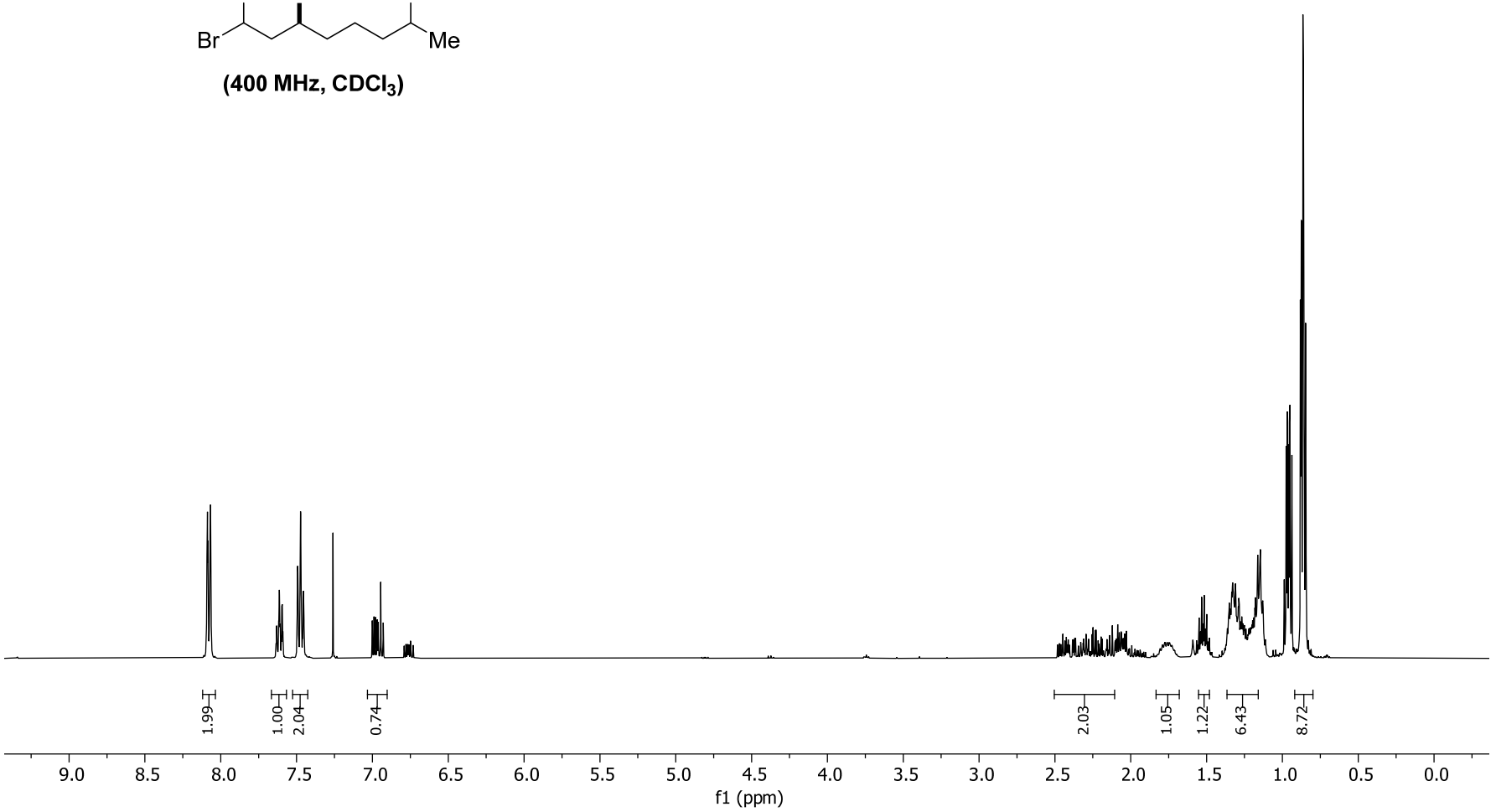

164.20
134.07
130.16
128.90
128.74
128.72
77.48
77.16
76.84
76.70
44.89
39.40
32.41
26.20
25.33
O
O
Ph
Br
Cl
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

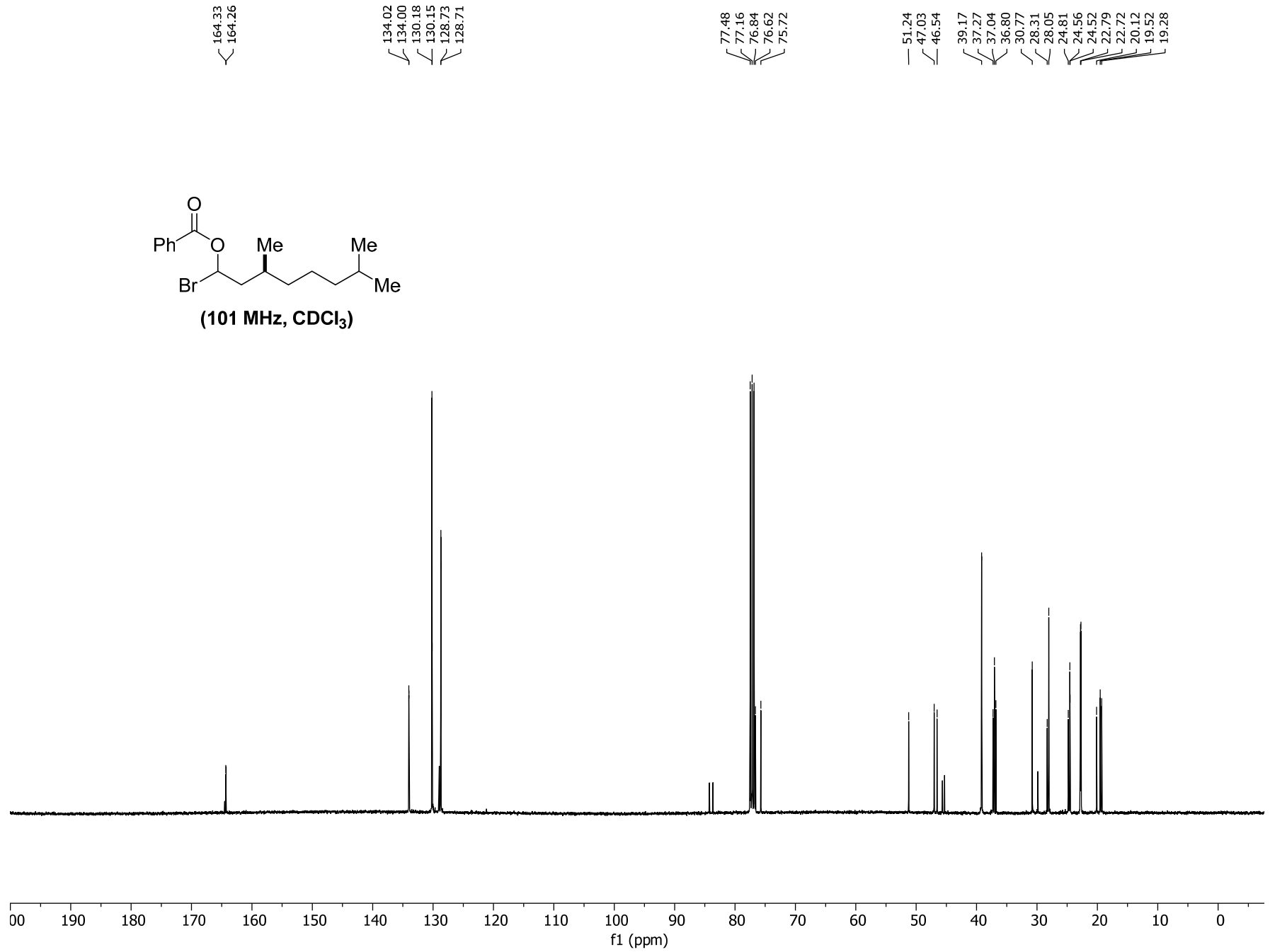

O
O
Ph
Br
Br
(500 MHz, CDCl3)
2.05
0.98
2.00
0.88
2.26
2.00
2.13
3.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

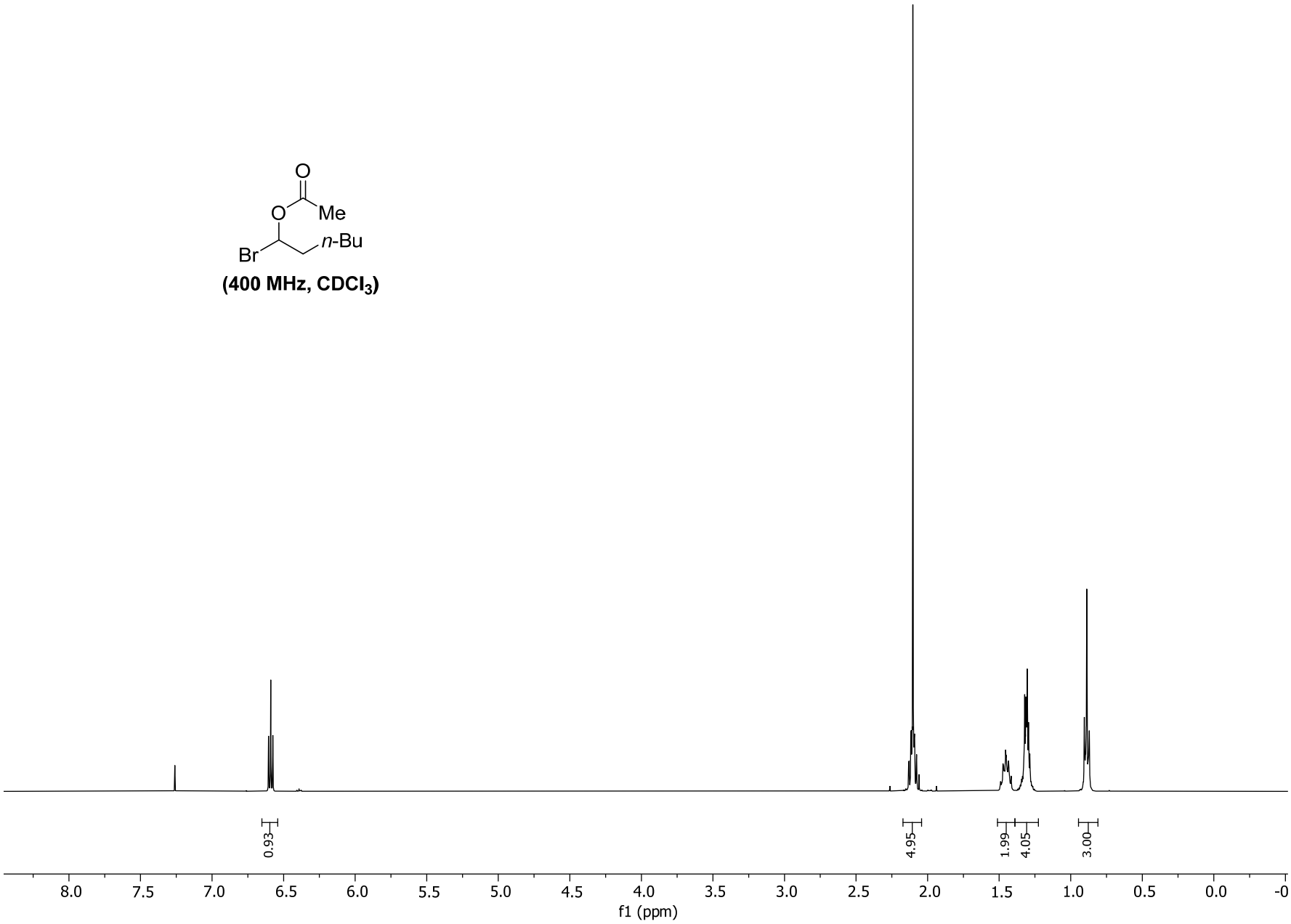

164.16
134.05
130.13
128.84
128.72
77.41
77.16
76.90
76.68
39.33
33.62
32.52
27.44
25.17
O
O
Ph
Br
Br
(126 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

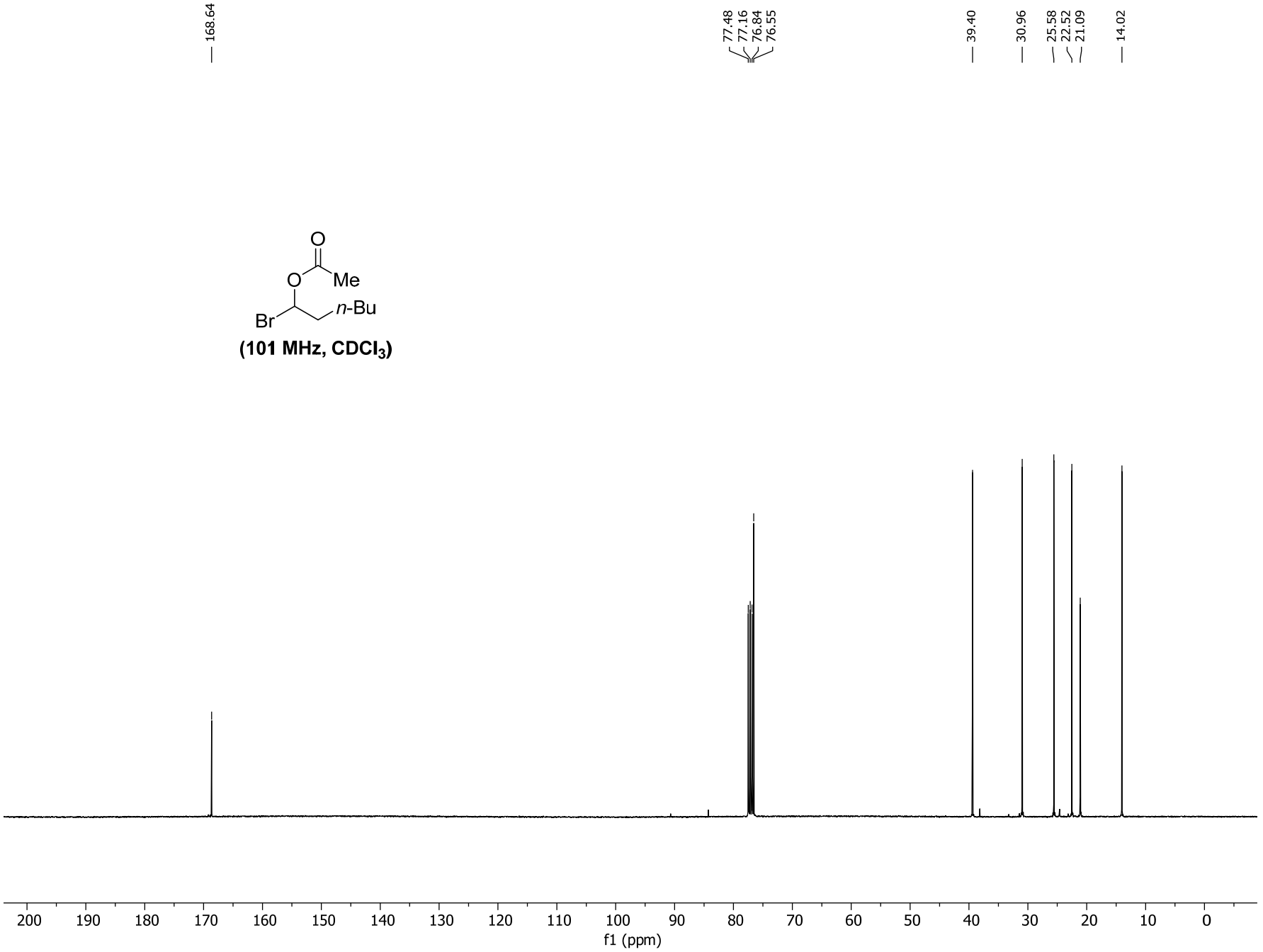


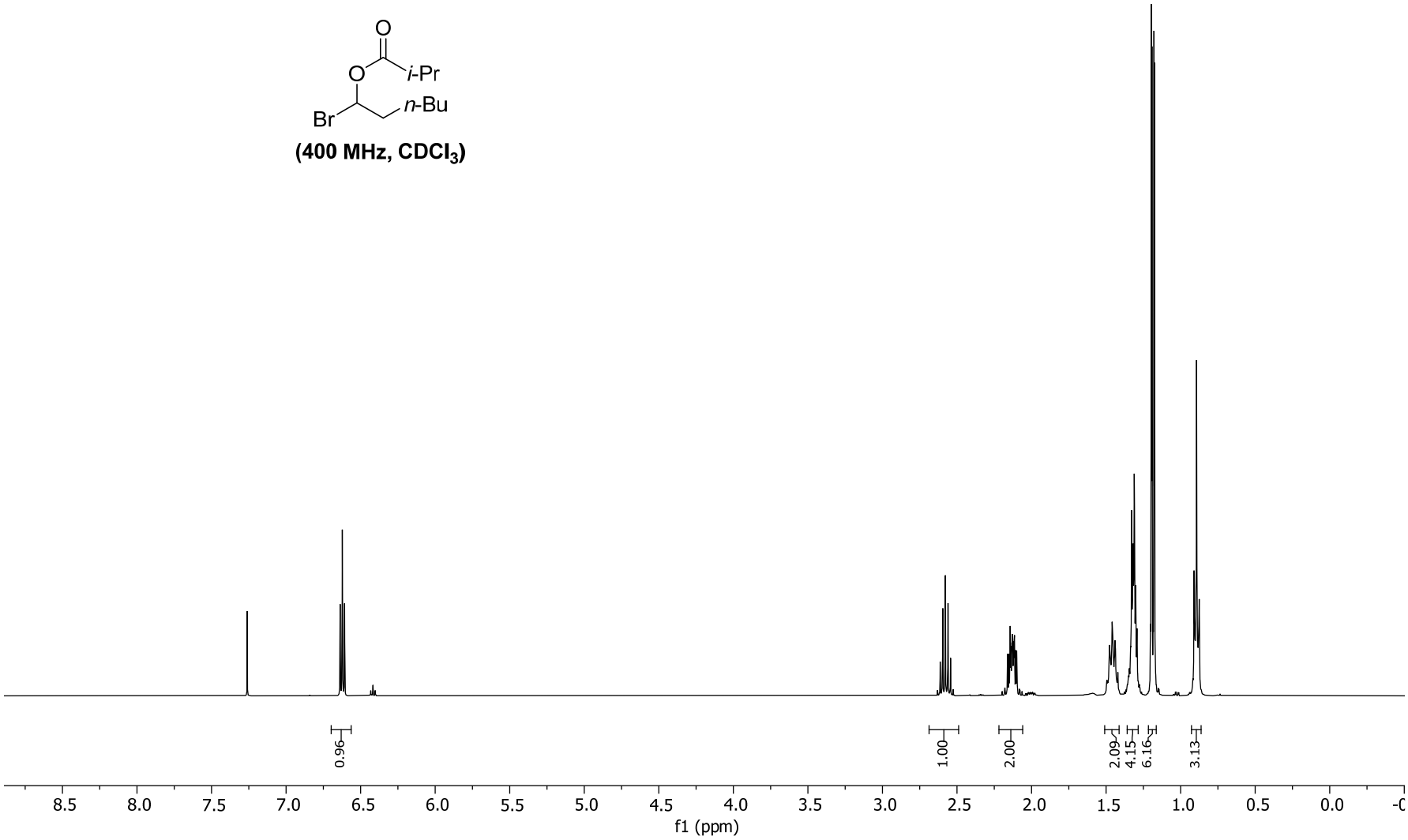
(400 MHz, $CDCl_3$)

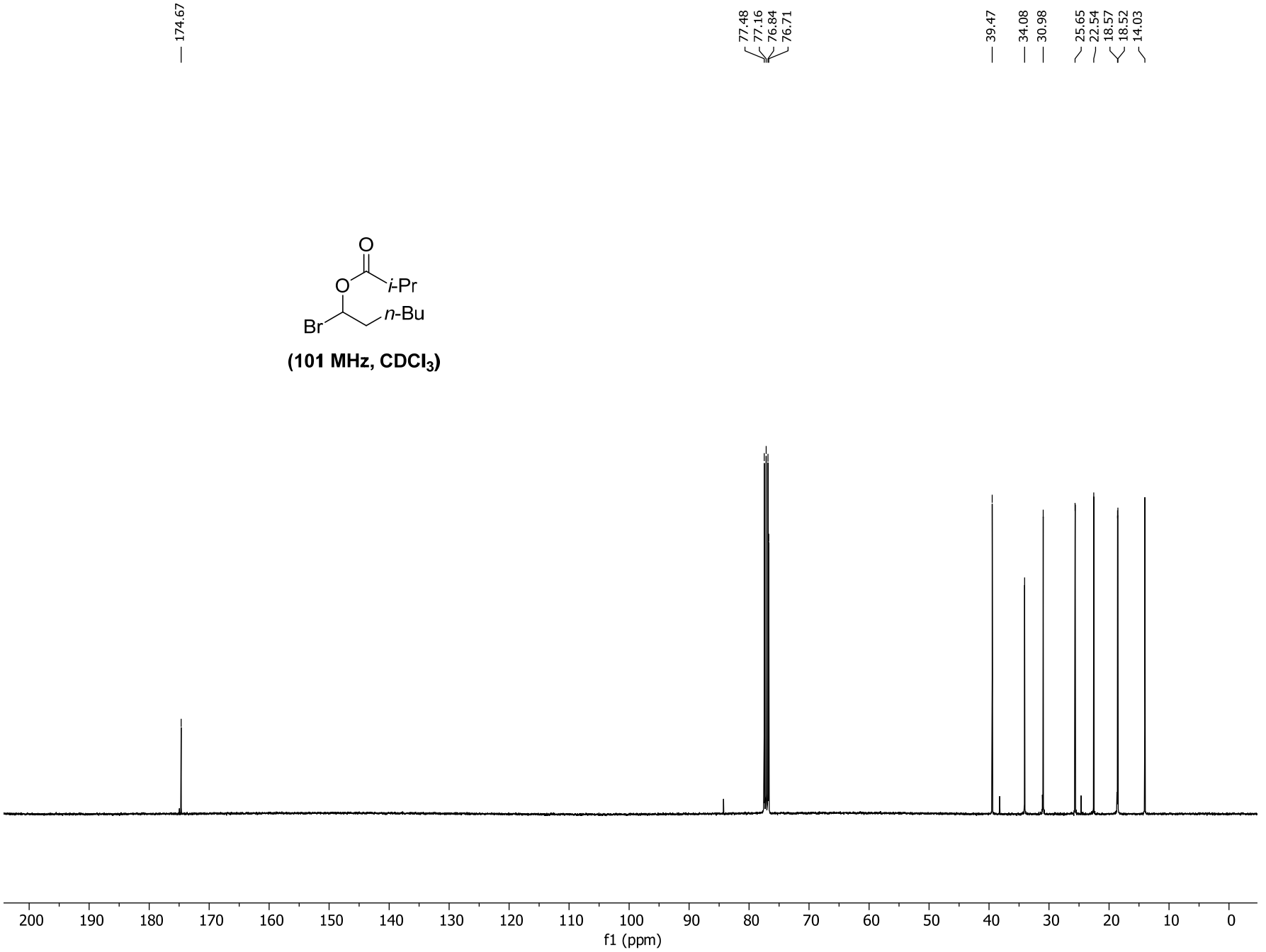


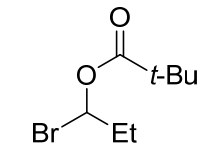

164.33
164.26
134.02
134.00
130.18
130.15
128.73
128.71
77.48
77.16
76.84
76.62
75.72
51.24
47.03
46.54
39.17
37.27
37.04
36.80
30.77
28.31
28.05
24.81
24.56
24.52
22.79
22.72
20.12
19.52
19.28
O
Ph
O
Me
Me
Br
Me
(101 MHz, CDCl3)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
Me
Br
n-Bu
(400 MHz, CDCl3)
0.93
4.95
1.99
4.05
3.00
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)

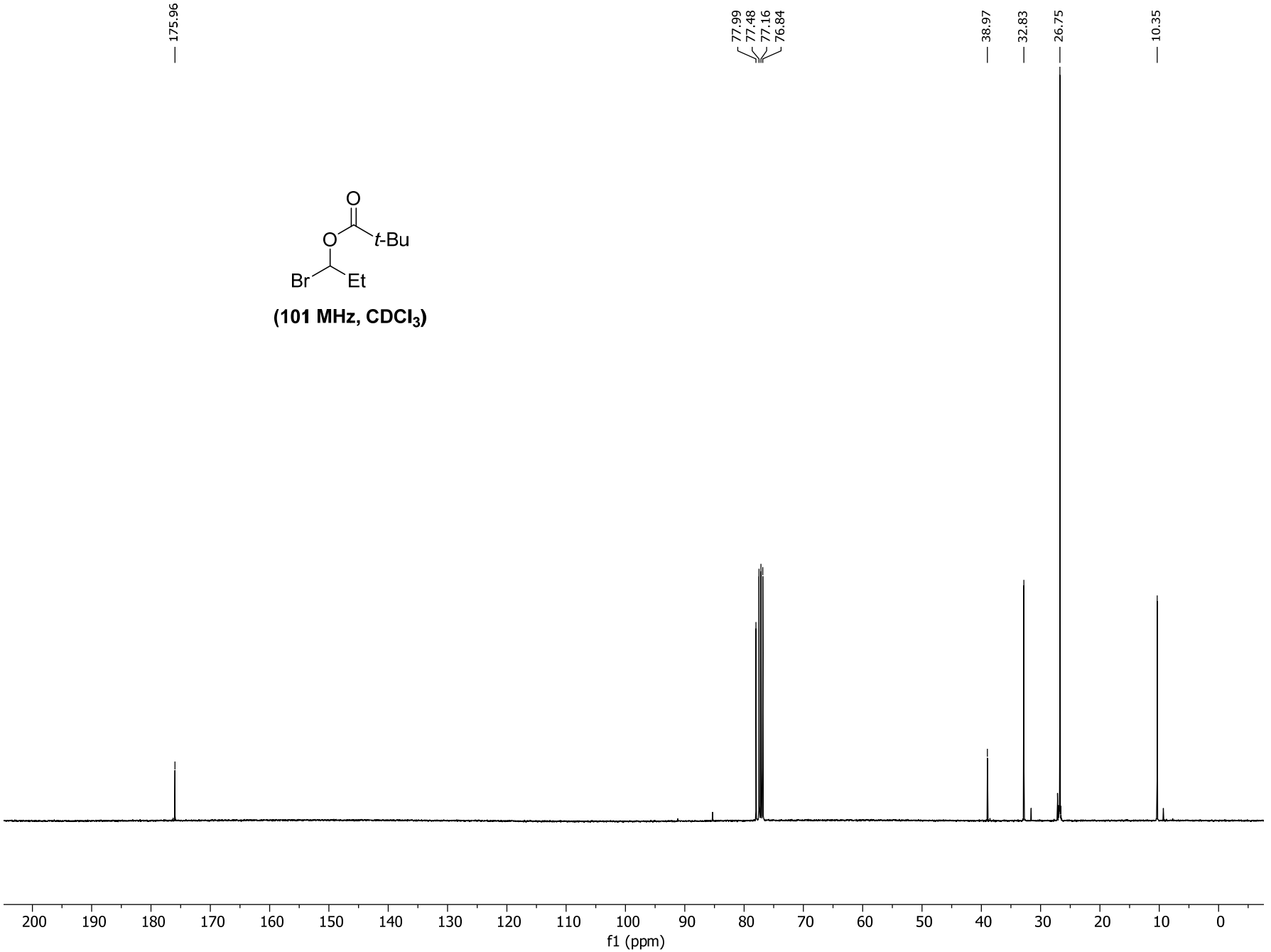

168.64
77.48
77.16
76.84
76.55
39.40
30.96
25.58
22.52
21.09
14.02
O
O
Me
n-Bu
Br
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
i-Pr
Br
n-Bu
(400 MHz, CDCl3)
0.96
1.00
2.00
2.09
4.15
6.16
3.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

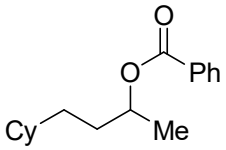

174.67
77.48
77.16
76.84
76.71
39.47
34.08
30.98
25.65
22.54
18.57
18.52
14.03
O
O
i-Pr
Br
n-Bu
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



(400 MHz, $CDCl_3$)


175.96
77.99
77.48
77.16
76.84
38.97
32.83
26.75
10.35
O
O
t-Bu
Br
Et
(101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

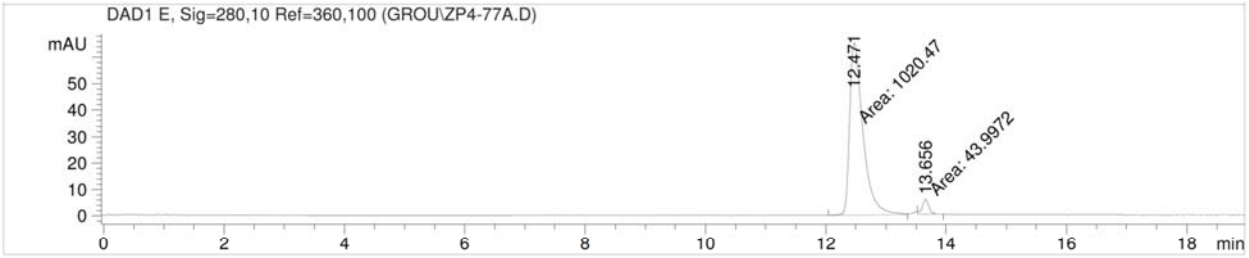
ee Analysis



4-Cyclohexylbutan-2-yl benzoate (Fig. 3, entry 1)

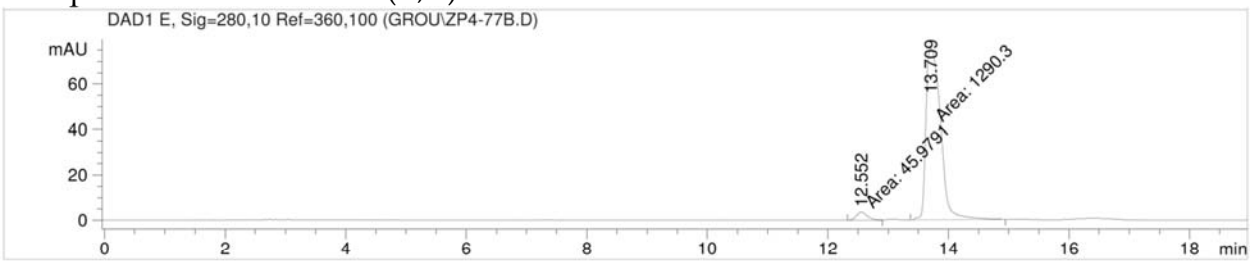
HPLC Analysis: CHIRALPAK IC column (0.5% *i*-PrOH in hexane, 0.5 mL/min).

Compound **1**: 92% ee from (*S*,*S*)-**L***

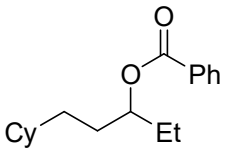


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.471	MM	0.2600	1020.46674	65.42083	95.8667
2	13.656	MM	0.1287	43.99716	5.69912	4.1333

Compound **1**: 93% ee from (*R*,*R*)-**L***



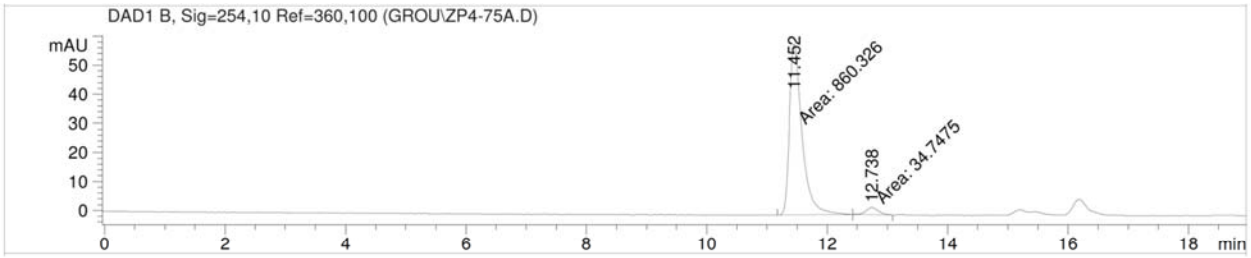
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.552	MM	0.2083	45.97911	3.67947	3.4408
2	13.709	MM	0.2834	1290.30188	75.88998	96.5592



1-Cyclohexylpentan-3-yl benzoate (Fig. 3, entry 2)

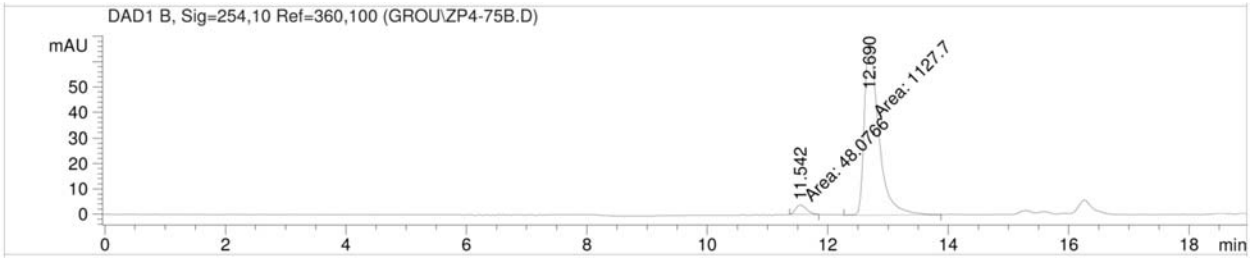
HPLC Analysis: CHIRALPAK IC column (0.5% *i*-PrOH in hexane, 0.5 mL/min).

Compound **2**: 92% ee from (*S*,*S*)-**L***

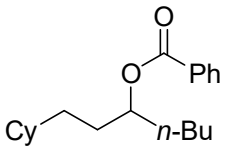


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.452	MM	0.2432	860.32556	58.95824	96.1179
2	12.738	MM	0.2300	34.74754	2.51796	3.8821

Compound **2**: 92% ee from (*R*,*R*)-**L***

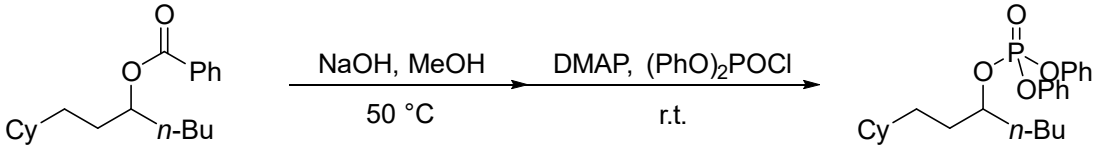


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.542	MM	0.2122	48.07655	3.77646	4.0889
2	12.690	MM	0.2791	1127.70300	67.35000	95.9111

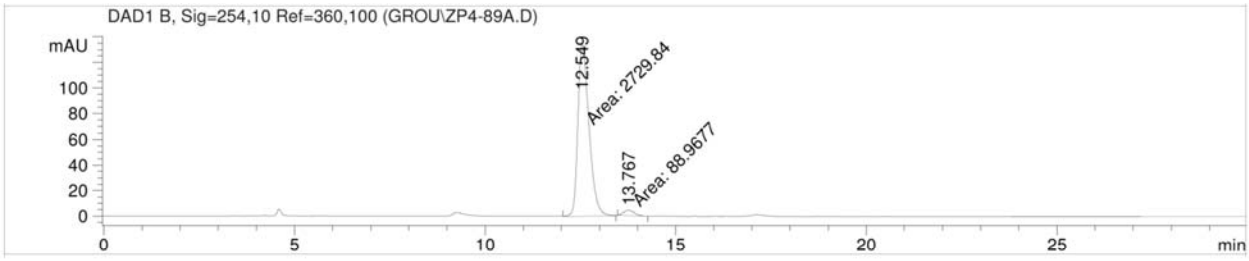


1-Cyclohexylpentan-3-yl benzoate (Fig. 3, entry 3)

Determination of the ee:

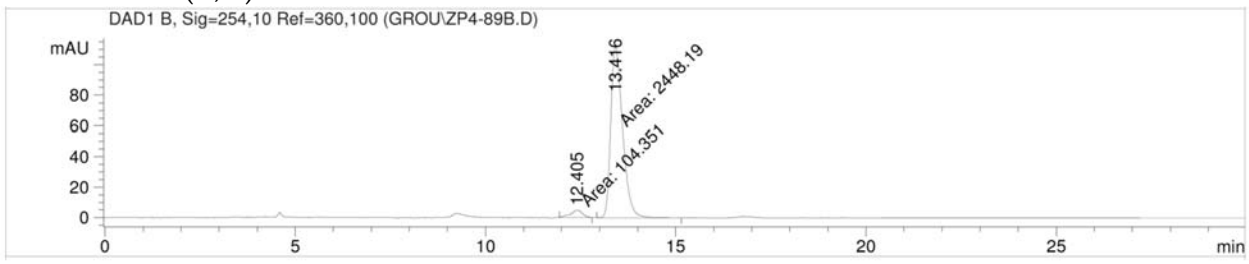


HPLC Analysis: CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min).
94% ee from (*S*,*S*)-**L***

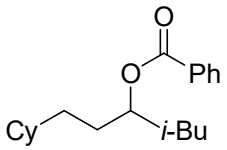


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.549	MM	0.3386	2729.84326	134.38257	96.8438
2	13.767	MM	0.3354	88.96774	4.42148	3.1562

92% ee from (*R*,*R*)-**L***

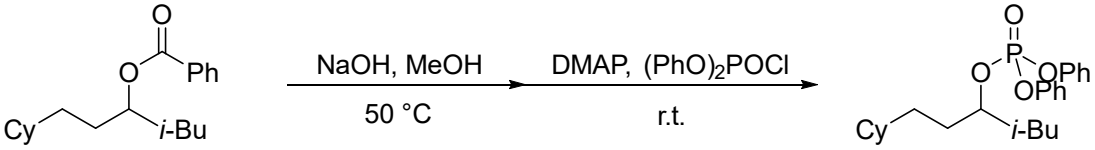


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.405	MM	0.3570	104.35123	4.87220	4.0881
2	13.416	MM	0.3641	2448.18970	112.07947	95.9119



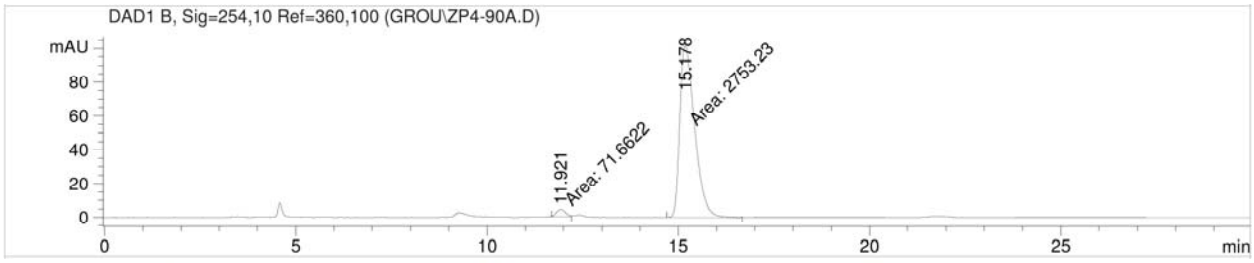
1-Cyclohexyl-5-methylhexan-3-yl benzoate (Fig. 3, entry 4)

Determination of the ee:



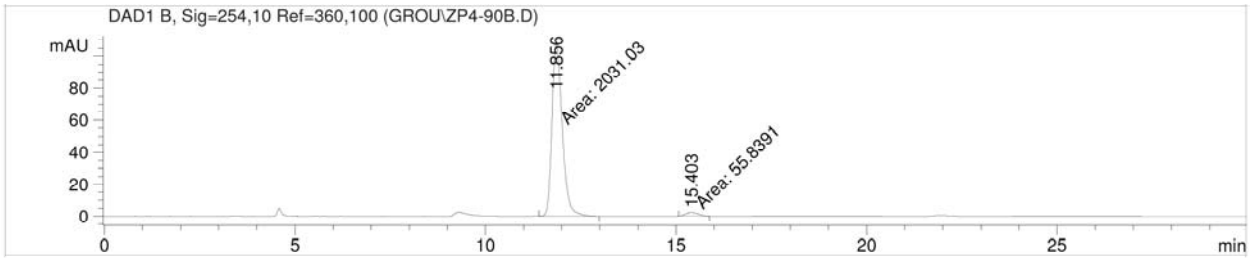
HPLC Analysis: CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min).

95% ee from (*S*,*S*)-**L***

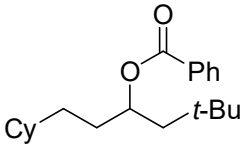


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.921	MM	0.2694	71.66221	4.43345	2.5368
2	15.178	MM	0.4493	2753.23022	102.12244	97.4632

95% ee from (*R*,*R*)-**L***

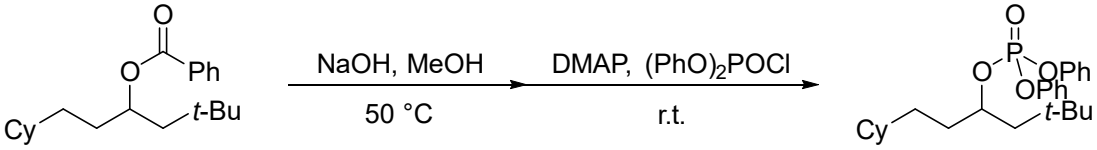


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.856	MM	0.3147	2031.03442	107.55618	97.3243
2	15.403	MM	0.3731	55.83907	2.49425	2.6757

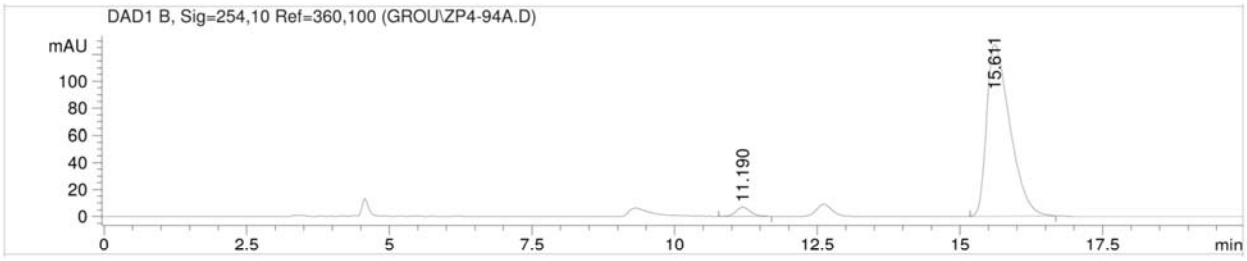


1-Cyclohexyl-5,5-dimethylhexan-3-yl benzoate (Fig. 3, entry 5)

Determination of the ee:

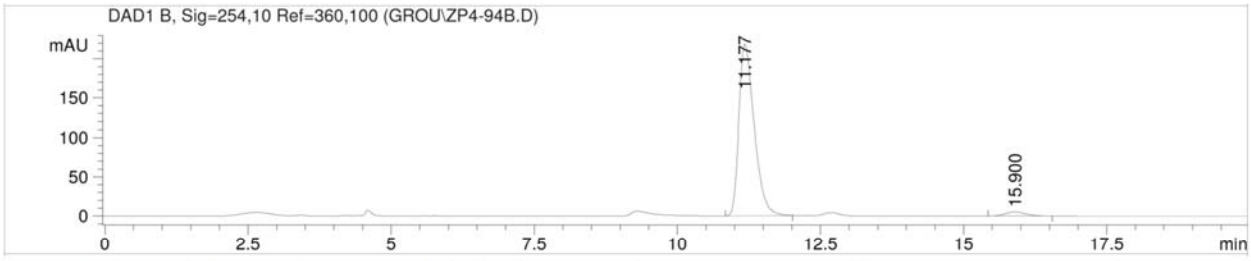


HPLC Analysis: CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min).
94% ee from (*S*,*S*)-**L***

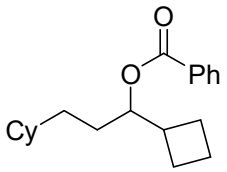


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.190	PP	0.2543	117.94586	6.80107	3.1592
2	15.611	BB	0.4117	3615.41064	127.15755	96.8408

94% ee from (*R*,*R*)-**L***

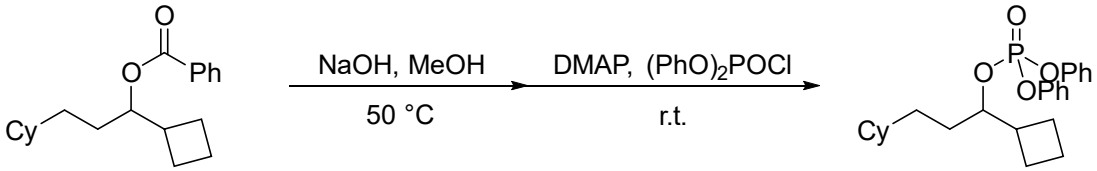


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.177	BB	0.2874	4078.64014	218.88083	97.0238
2	15.900	BB	0.3112	125.11219	5.11736	2.9762



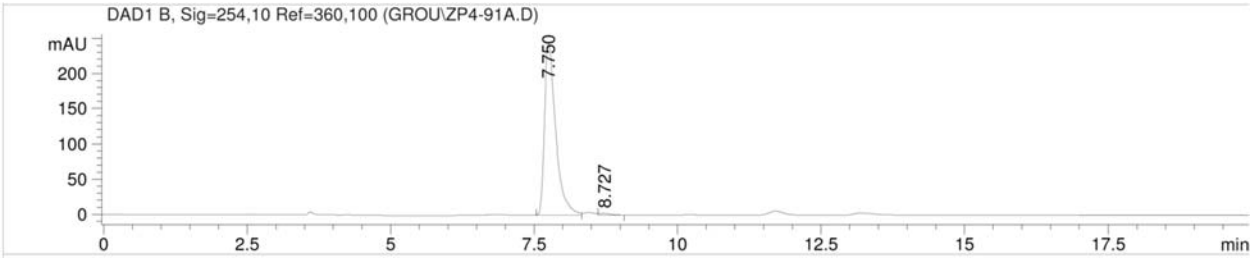
1-Cyclobutyl-3-cyclohexylpropyl benzoate (Fig. 3, entry 6)

Determination of the ee:



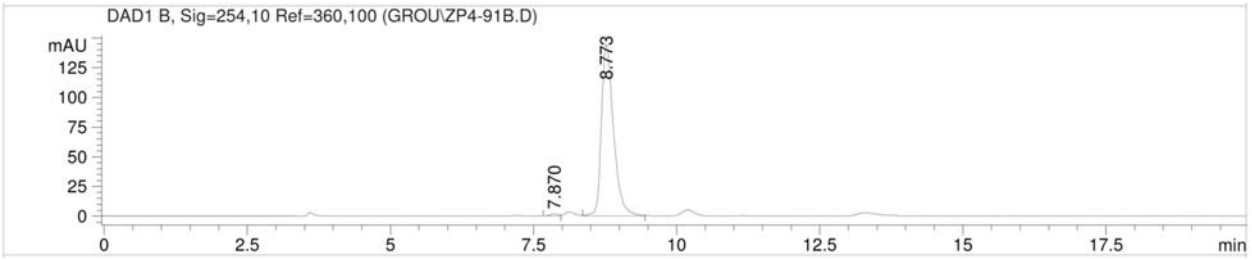
HPLC Analysis: CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min).

98% ee from (*S*,*S*)-**L***

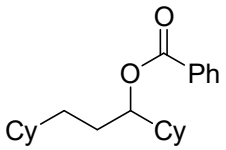


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.750	BV	0.2047	3332.25830	244.98424	98.9954
2	8.727	VP	0.2050	33.81463	2.51254	1.0046

98% ee from (*R*,*R*)-**L***

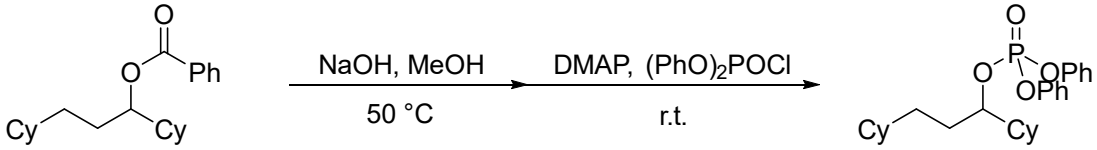


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.870	BV	0.1398	16.36773	1.59407	0.7649
2	8.773	VB	0.2213	2123.44824	144.64511	99.2351

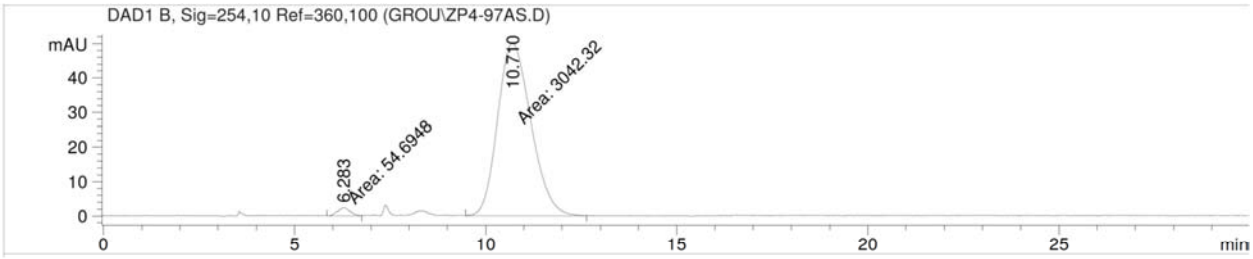


1,3-Dicyclohexylpropyl benzoate (Fig. 3, entry 7)

Determination of the ee:

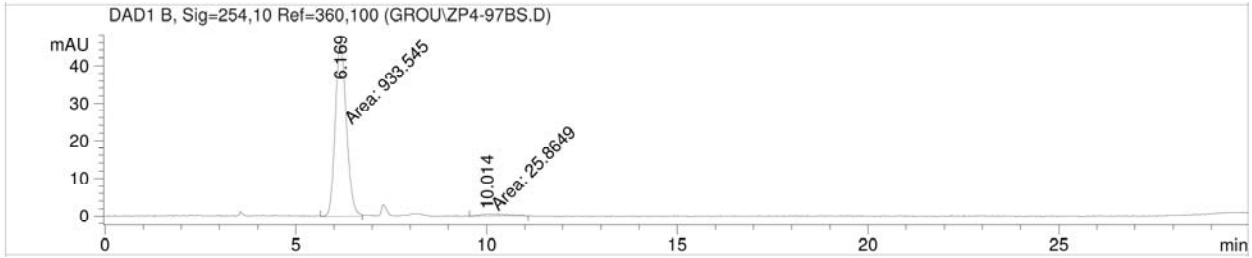


HPLC Analysis: CHIRALPAK AS column (5% *i*-PrOH in hexane, 1.0 mL/min).
96% ee from (*S*,*S*)-**L***

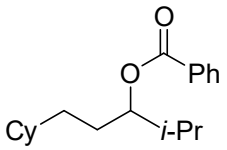


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.283	MM	0.3732	54.69480	2.44234	1.7660
2	10.710	MM	1.0137	3042.32031	50.02224	98.2340

95% ee from (*R*,*R*)-**L***



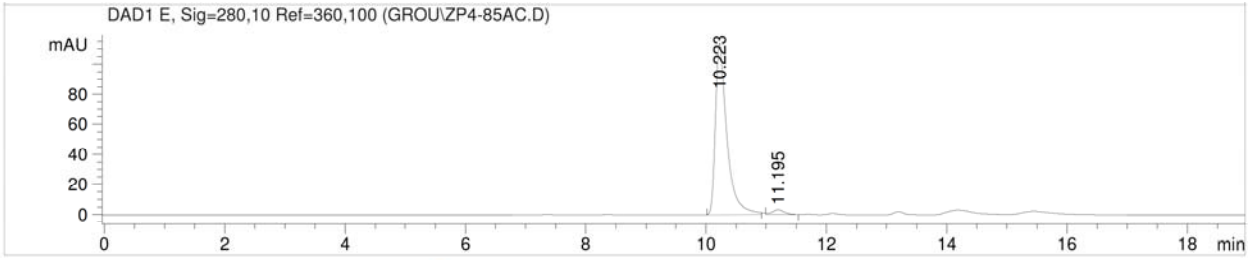
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.169	MM	0.3395	933.54541	45.82965	97.3041
2	10.014	MM	0.8480	25.86488	5.08327e-1	2.6959



1-Cyclohexyl-4-methylpentan-3-yl benzoate (Fig. 3, entry 8)

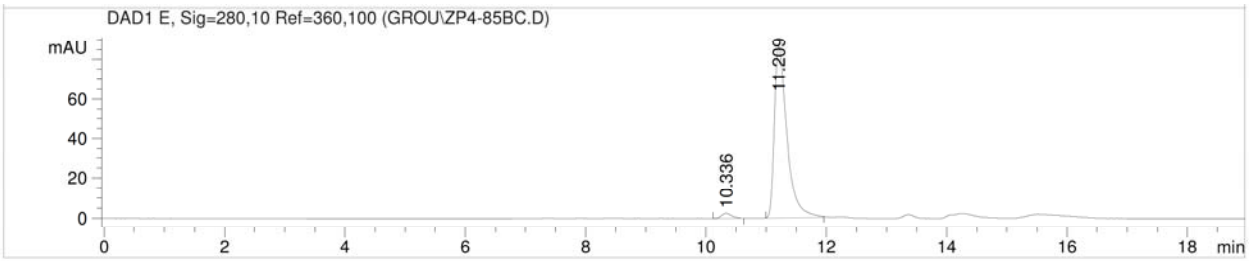
HPLC Analysis: CHIRALPAK IC column (0.5% *i*-PrOH in hexane, 0.5 mL/min).

Compound **8**: 94% ee from (*S*,*S*)-**L***

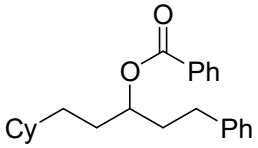


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.223	BB	0.2005	1527.53381	113.86597	97.2284
2	11.195	BP	0.2084	43.54475	3.12908	2.7716

Compound **8**: 95% ee from (*R*,*R*)-**L***



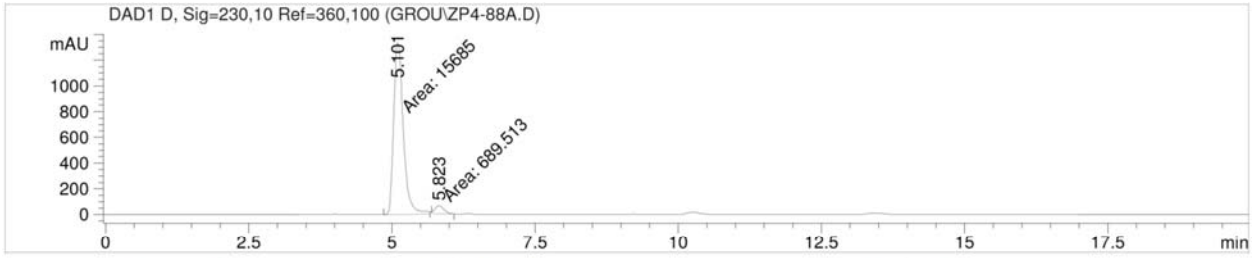
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.336	BB	0.1764	29.31732	2.50826	2.3050
2	11.209	BB	0.2175	1242.57068	86.55486	97.6950



1-Cyclohexyl-5-phenylpentan-3-yl benzoate (Fig. 3, entry 9)

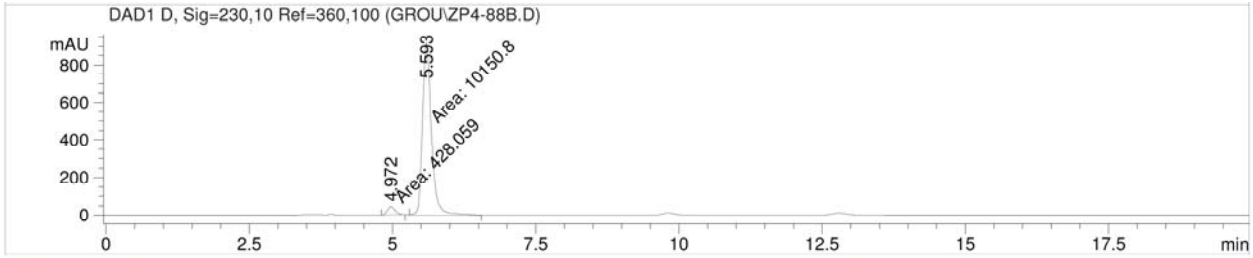
HPLC Analysis: CHIRALCEL OD column (1% *i*-PrOH in hexane, 1.0 mL/min).

Compound **9**: 92% ee from (*S*,*S*)-**L***

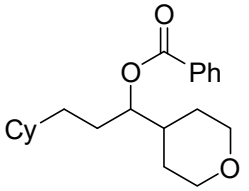


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.101	MM	0.1956	1.56850e4	1336.79956	95.7891
2	5.823	MM	0.1818	689.51324	63.22087	4.2109

Compound **9**: 92% ee from (*R*,*R*)-**L***



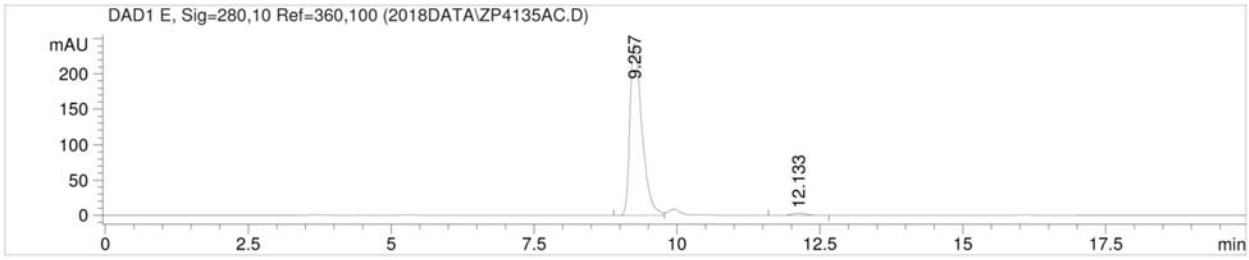
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.972	MM	0.1573	428.05896	45.36115	4.0464
2	5.593	MM	0.1837	1.01508e4	920.78693	95.9536



3-Cyclohexyl-1-(tetrahydro-2*H*-pyran-4-yl)propyl benzoate (Fig. 3, entry 10)

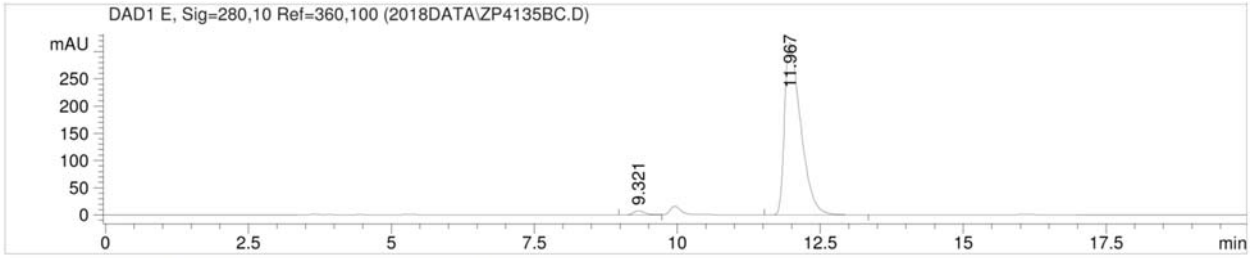
HPLC Analysis: CHIRALPAK IC column (3% *i*-PrOH in hexane, 1.0 mL/min).

Compound **10**: 97% ee from (*S*,*S*)-**L***

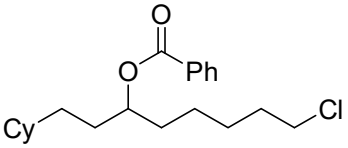


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.257	VV	0.2202	3556.41650	243.73369	98.3426
2	12.133	VV	0.2663	59.93850	3.23356	1.6574

Compound **10**: 96% ee from (*R*,*R*)-**L***



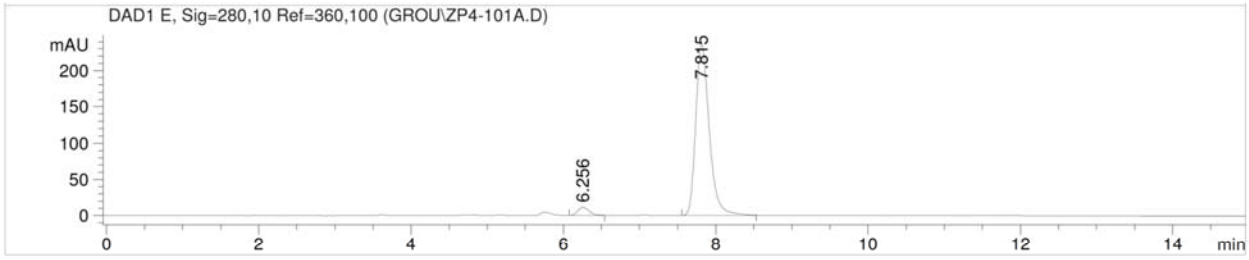
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.321	VV	0.2218	121.65885	8.16647	1.9065
2	11.967	VV	0.2984	6259.64893	316.97699	98.0935



8-Chloro-1-cyclohexyloctan-3-yl benzoate (Fig. 3, entry 11)

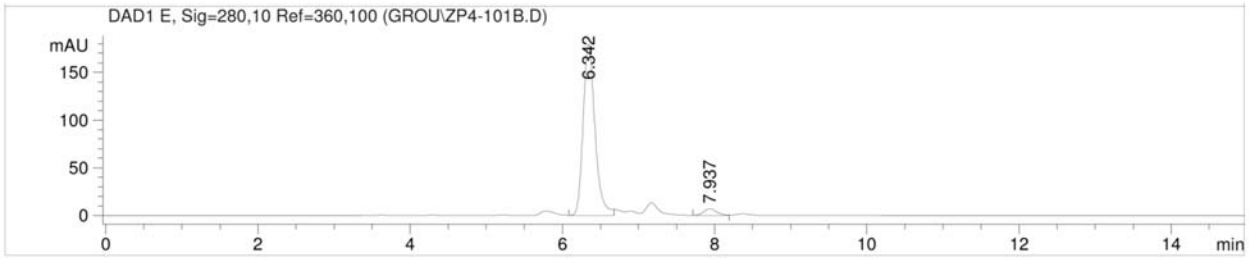
HPLC Analysis: CHIRALPAK AD column (1% *i*-PrOH in hexane, 1.0 mL/min).

Compound **11**: 92% ee from (*S*,*S*)-**L***

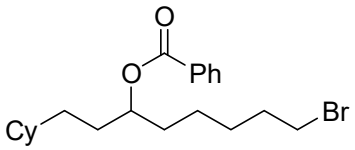


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.256	BB	0.1589	117.25640	11.31899	3.8425
2	7.815	BB	0.1903	2934.32153	237.18481	96.1575

Compound **11**: 92% ee from (*R*,*R*)-**L***



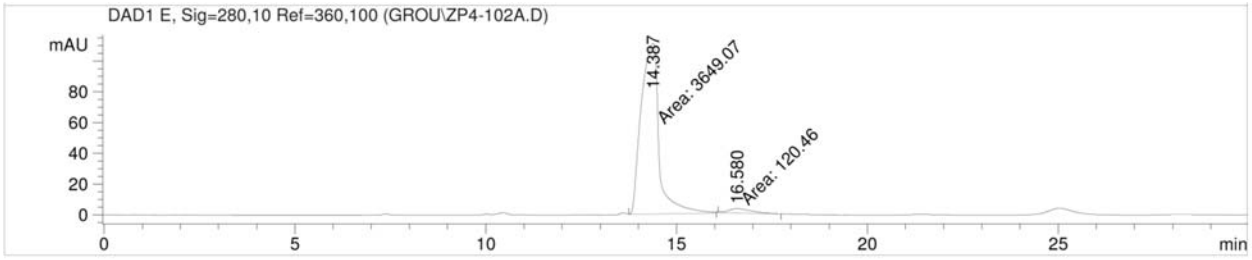
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.342	VB	0.1652	1960.16455	179.76314	95.8117
2	7.937	BV	0.1881	85.68716	7.13379	4.1883



8-Bromo-1-cyclohexyloctan-3-yl benzoate (Fig. 3, entry 12)

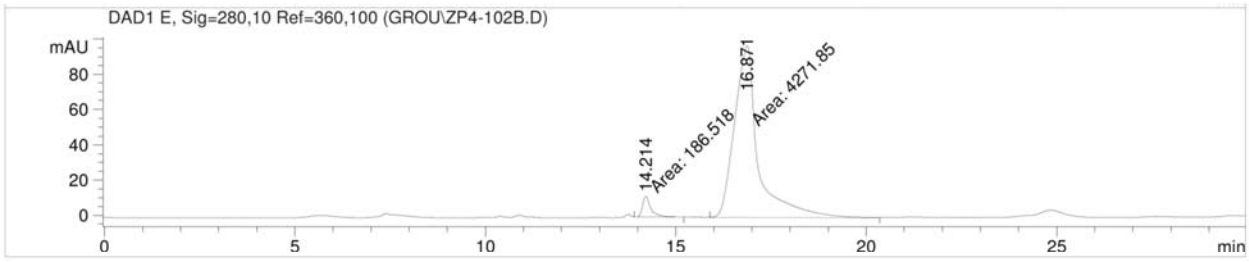
HPLC Analysis: CHIRALPAK IC column (0.5% *i*-PrOH in hexane, 0.5 mL/min).

Compound **12**: 94% ee from (*S*,*S*)-**L***

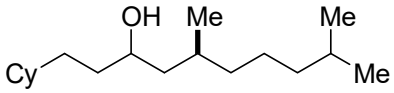


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.387	MM	0.5484	3649.07031	110.89110	96.8044
2	16.580	MM	0.6954	120.46003	2.88698	3.1956

Compound **12**: 92% ee from (*R*,*R*)-**L***

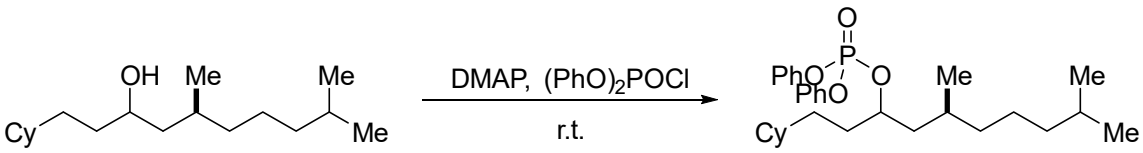


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.214	MM	0.2624	186.51799	11.84726	4.1835
2	16.871	MM	0.7293	4271.85449	97.62020	95.8165



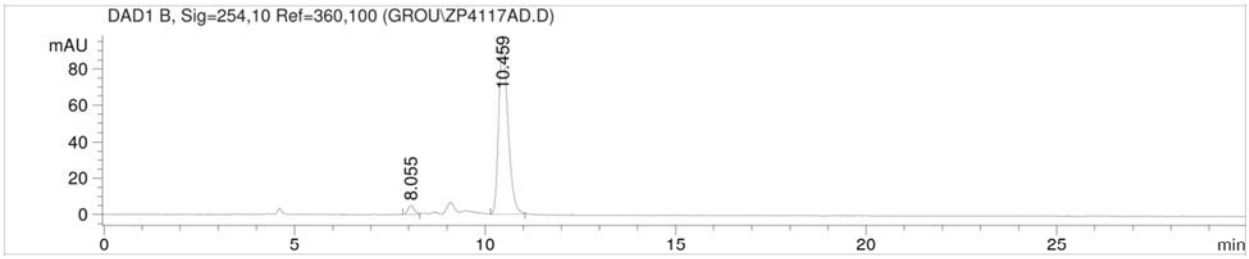
(5*S*)-1-Cyclohexyl-5,9-dimethyldecan-3-ol (Fig. 3, entries 13 and 14)

Determination of the ee:



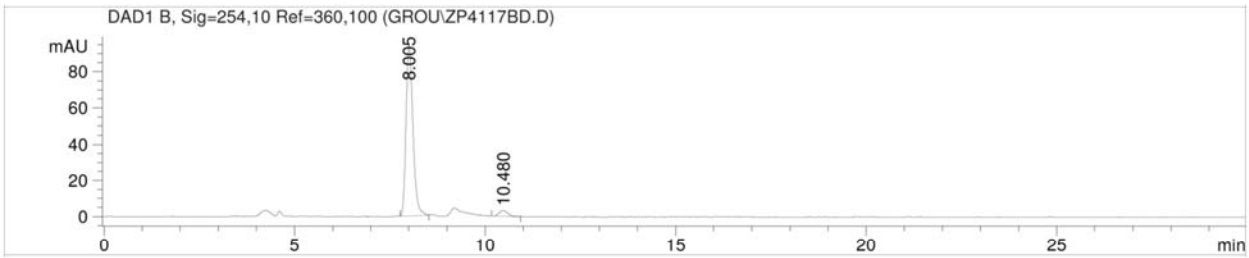
HPLC Analysis: AD column (10% *i*-PrOH in hexane, 1.0 mL/min).

4:96 d.r. ee from (*S*,*S*)-**L***

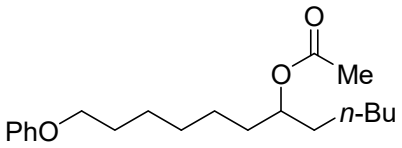


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.055	PV	0.1883	59.13276	4.91675	3.5444
2	10.459	BB	0.2646	1609.19922	93.58408	96.4556

96:4 d.r. from (*R*,*R*)-**L***



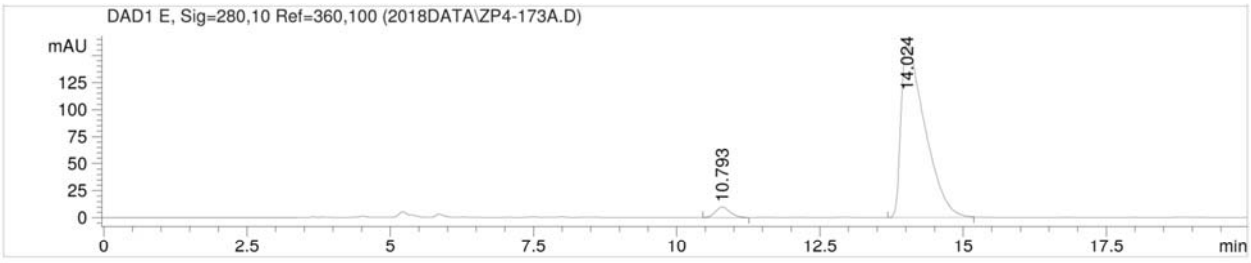
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.005	BB	0.1948	1189.57336	94.52553	95.8505
2	10.480	PB	0.2362	51.49876	3.15898	4.1495



12-Phenoxydodecan-6-yl acetate (Fig. 3, entry 15)

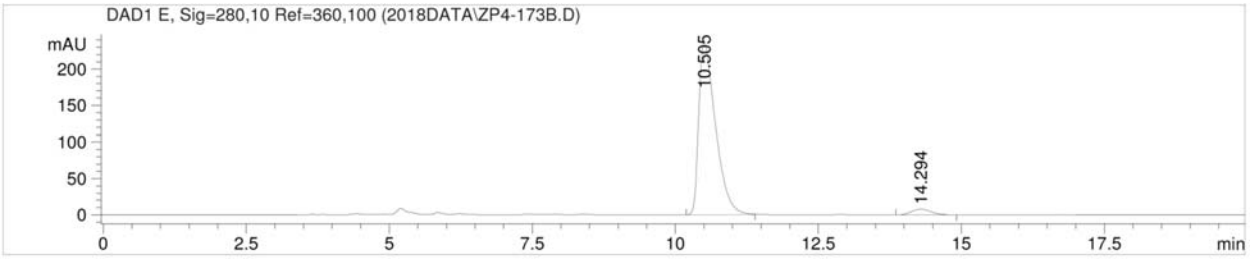
HPLC Analysis: CHIRALCEL OD column (2% *i*-PrOH in hexane, 1.0 mL/min).

Compound **15**: 93% ee from (*S*,*S*)-**L***

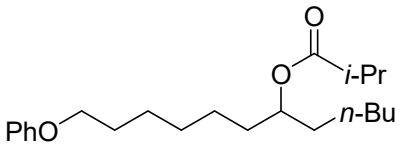


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.793	BP	0.2708	173.42961	9.78468	3.6057
2	14.024	BB	0.4243	4636.43018	159.88266	96.3943

Compound **15**: 92% ee from (*R*,*R*)-**L***



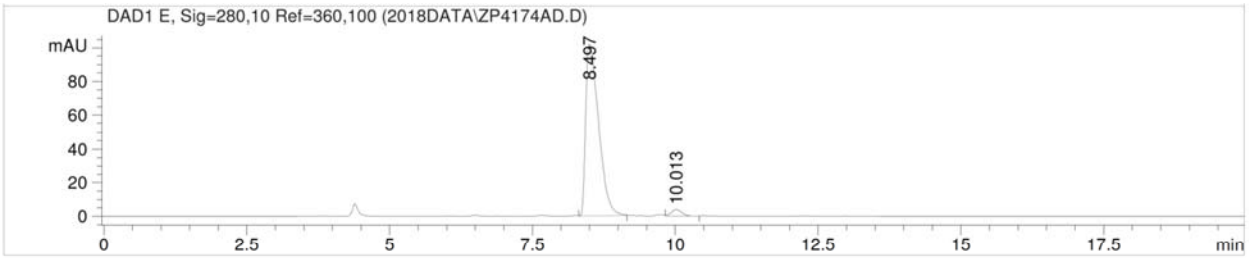
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.505	BB	0.3085	4817.05322	235.60921	96.1088
2	14.294	BB	0.3162	195.02824	8.11999	3.8912



12-Phenoxydodecan-6-yl isobutyrate (Fig. 3, entry 16)

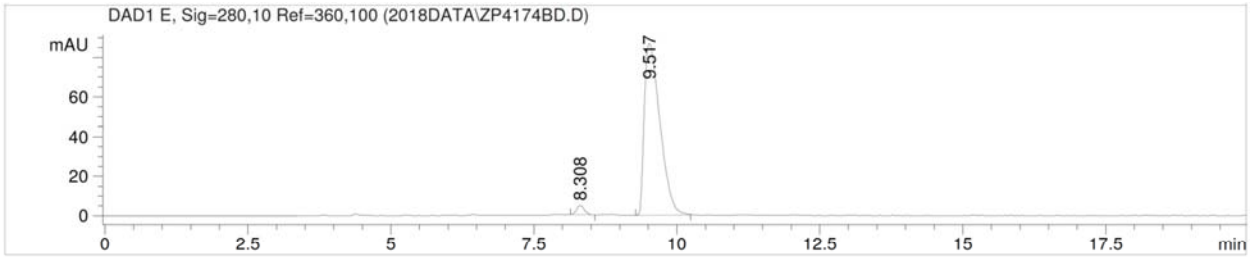
HPLC Analysis: CHIRALPAK AD column (0.5% *i*-PrOH in hexane, 1.0 mL/min).

Compound **16**: 94% ee from (*S*,*S*)-**L***

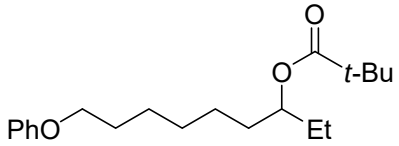


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.497	BB	0.2380	1606.96899	101.87103	97.1606
2	10.013	VP	0.1895	46.96135	3.87224	2.8394

Compound **16**: 95% ee from (*R*,*R*)-**L***



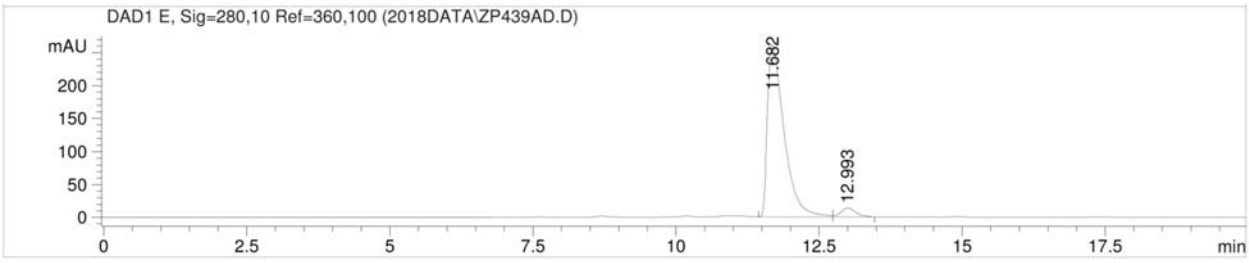
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.308	BP	0.1484	45.20425	4.69289	2.6562
2	9.517	BB	0.2985	1656.60596	86.87539	97.3438



9-Phenoxynonan-3-yl pivalate (Fig. 3, entry 17)

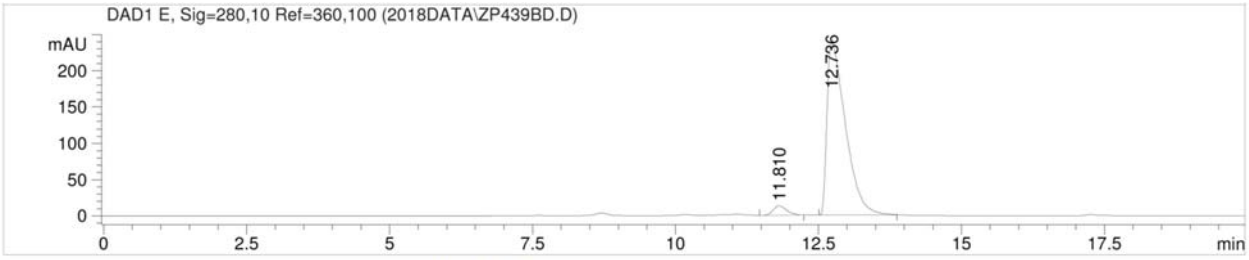
HPLC Analysis: CHIRALPAK AD column (0.5% *i*-PrOH in hexane, 0.5 mL/min).

Compound **17**: 91% ee from (*S*,*S*)-**L***

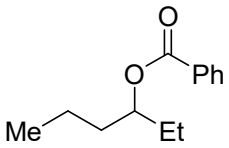


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.682	VB	0.3045	5305.00488	261.68567	95.4565
2	12.993	BB	0.2795	252.50493	13.79788	4.5435

Compound **17**: 92% ee from (*R*,*R*)-**L***

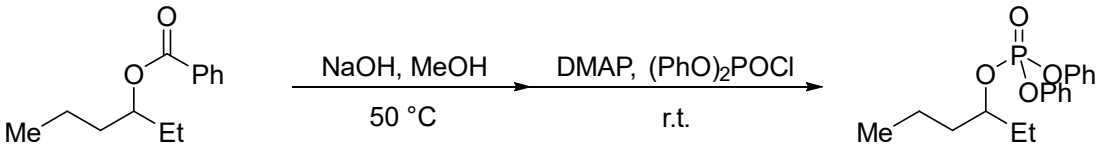


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.810	VB	0.2462	212.08485	13.00732	3.8034
2	12.736	PB	0.3378	5364.16016	237.23378	96.1966

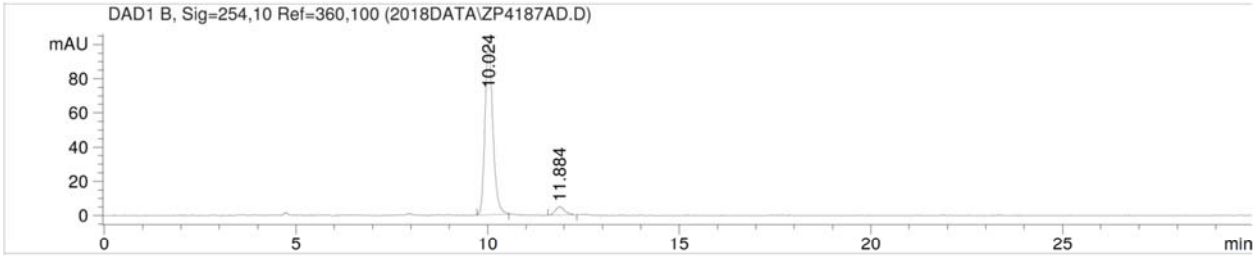


Hexan-3-yl benzoate (Fig. 3, entry 18)

Determination of the ee:

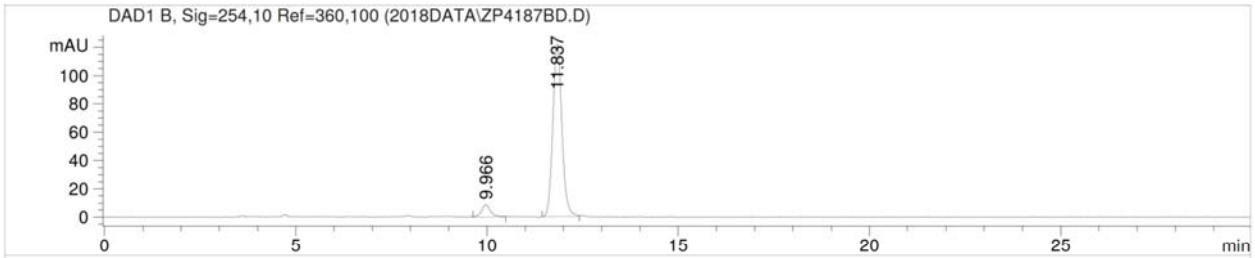


HPLC Analysis: CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min).
89% ee from (*S*,*S*)-**L***

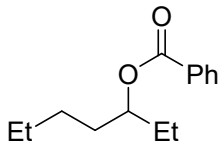


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.024	BB	0.2189	1442.60083	100.86459	94.4991
2	11.884	BP	0.2375	83.97512	4.96164	5.5009

87% ee from (*R*,*R*)-**L***

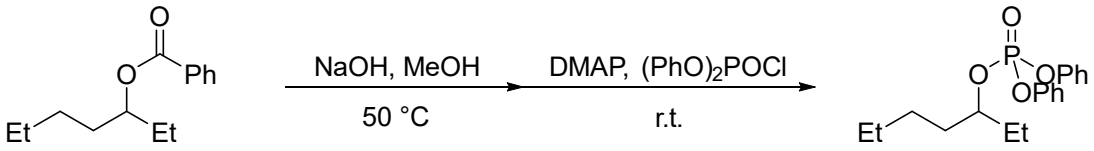


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.966	BB	0.2282	138.31622	8.66784	6.4281
2	11.837	BB	0.2546	2013.43555	121.95586	93.5719

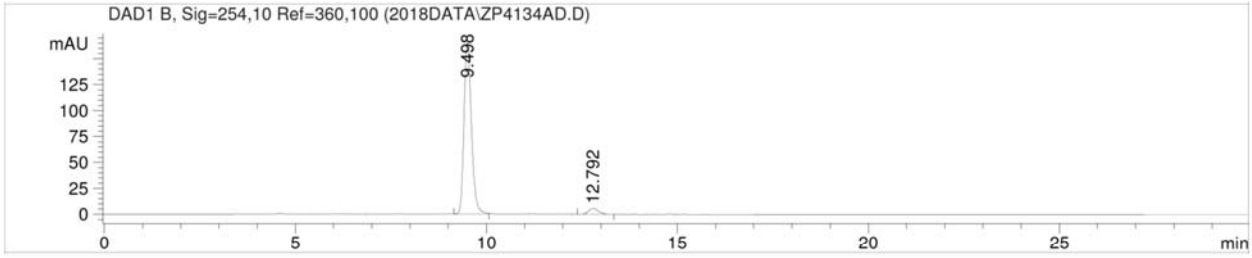


Heptan-3-yl benzoate (Fig. 3, entry 19)

Determination of the ee:

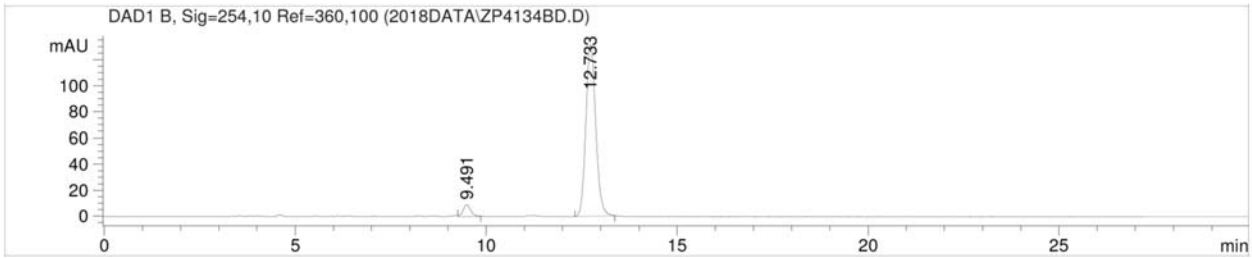


HPLC Analysis: CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min).
91% ee from (*S*,*S*)-**L***

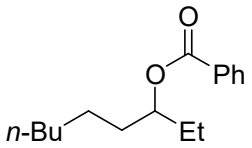


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.498	VB	0.2068	2226.49365	165.66118	95.3451
2	12.792	PB	0.2875	108.70207	5.77895	4.6549

90% ee from (*R*,*R*)-**L***

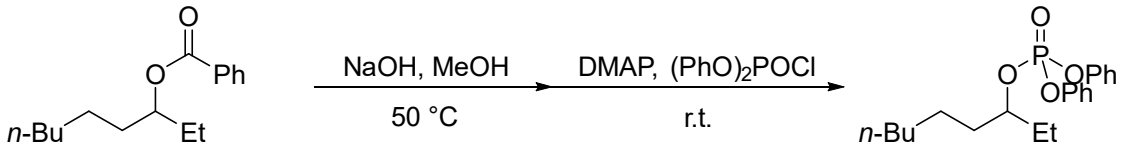


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.491	BB	0.2132	120.99550	8.86511	4.8546
2	12.733	BB	0.2778	2371.40942	131.85941	95.1454

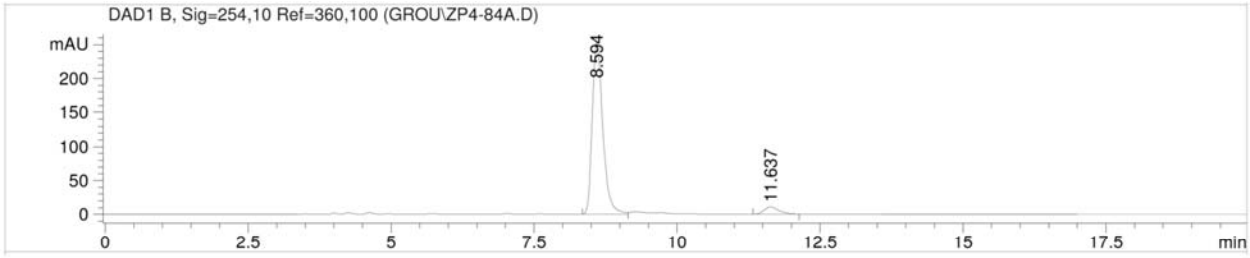


Nonan-3-yl benzoate (Fig. 3, entry 20)

Determination of the ee:

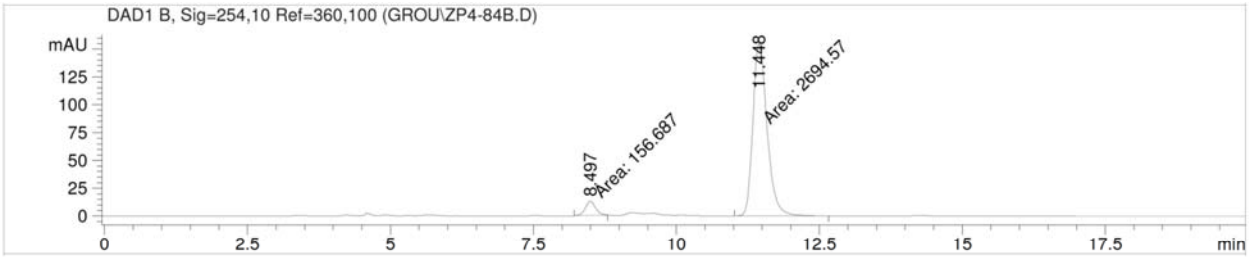


HPLC Analysis: AD column (10% *i*-PrOH in hexane, 1.0 mL/min).
89% ee from (*S*,*S*)-**L***

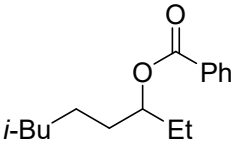


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.594	BB	0.1971	3276.86841	252.98671	94.2874
2	11.637	BB	0.2709	198.53766	10.87741	5.7126

89% ee from (*R*,*R*)-**L***

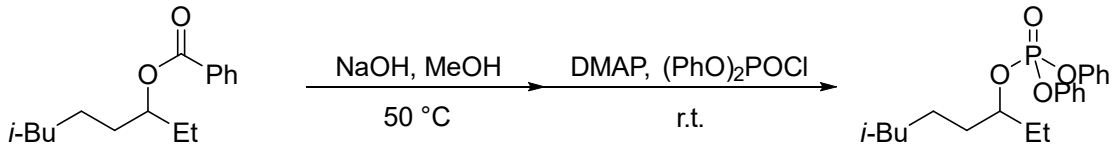


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.497	MM	0.2064	156.68736	12.65131	5.4954
2	11.448	MM	0.2893	2694.56665	155.21452	94.5046

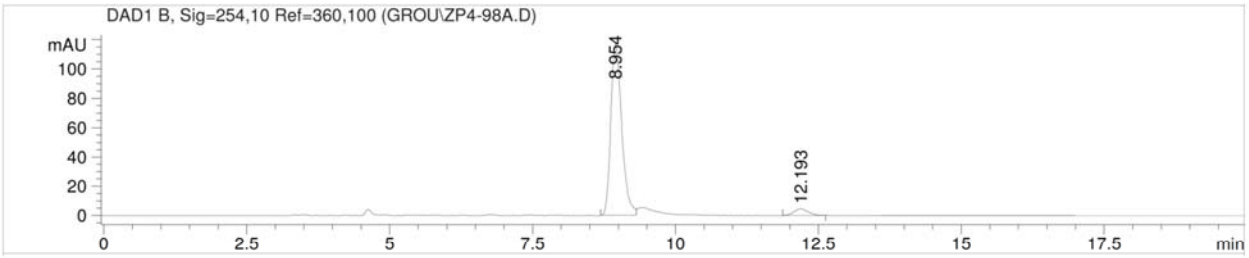


7-Methyloctan-3-yl benzoate (Fig. 3, entry 21)

Determination of the ee:

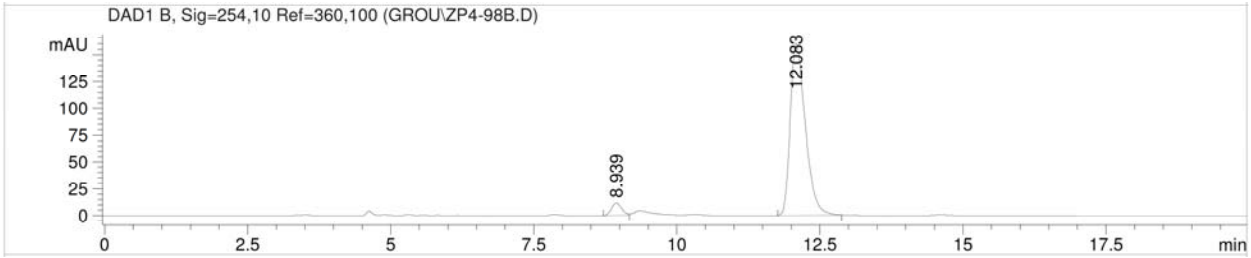


HPLC Analysis: CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min).
90% ee from (*S*,*S*)-**L***

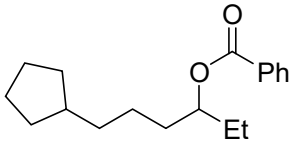


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.954	BV	0.2027	1554.69495	117.23003	95.2105
2	12.193	BB	0.2375	78.20767	4.57466	4.7895

91% ee from (*R*,*R*)-**L***



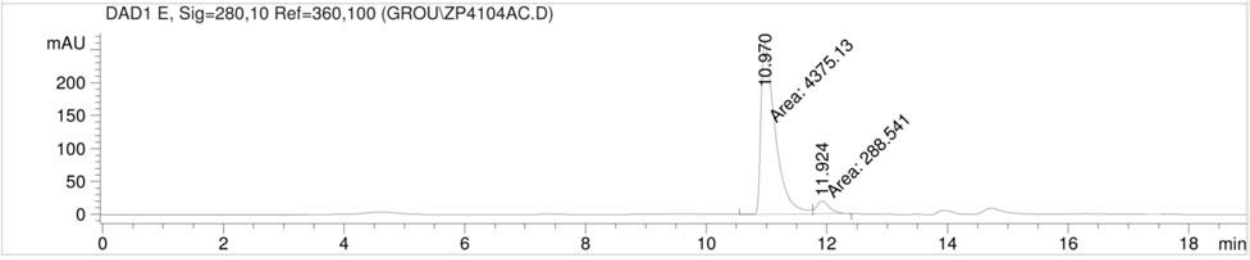
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.939	BV	0.1925	145.98038	11.62845	4.7152
2	12.083	BB	0.2805	2949.96094	160.47281	95.2848



6-Cyclopentylhexan-3-yl benzoate (Fig. 3, entry 22)

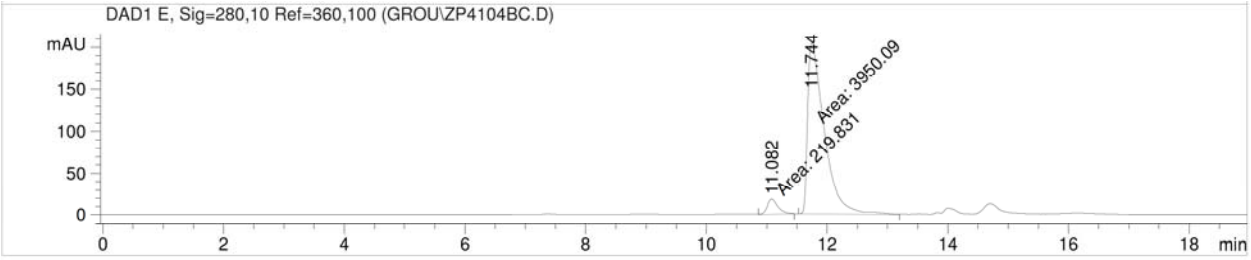
HPLC Analysis: CHIRALPAK IC column (0.5% *i*-PrOH in hexane, 0.5 mL/min).

Compound **22**: 88% ee from (*S*,*S*)-**L***

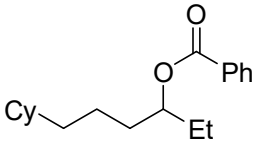


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.970	MF	0.2778	4375.12793	262.50116	93.8130
2	11.924	FM	0.2441	288.54120	19.70183	6.1870

Compound **22**: 89% ee from (*R*,*R*)-**L***

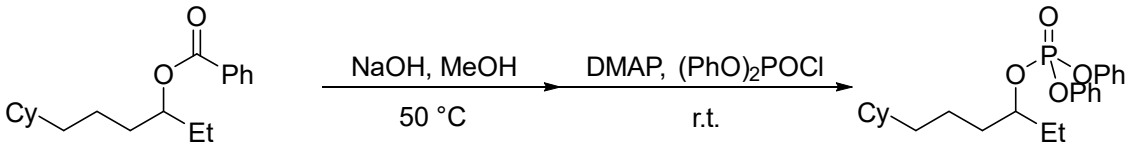


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.082	MM	0.2006	219.83051	18.26783	5.2718
2	11.744	MM	0.3219	3950.09253	204.48874	94.7282



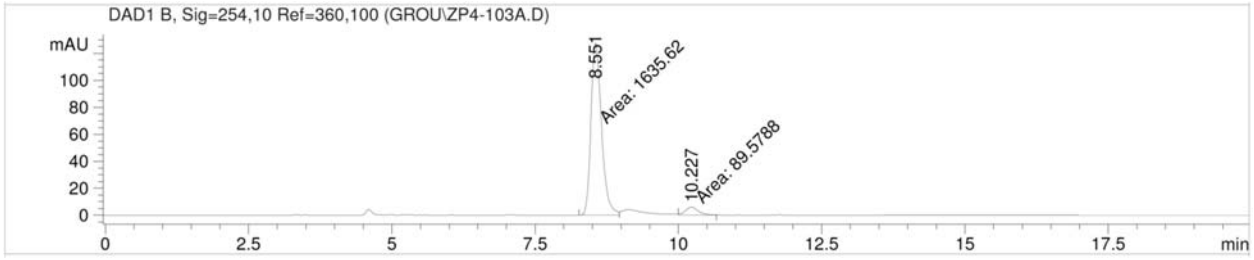
6-Cyclohexylhexan-3-yl benzoate (Fig. 3, entry 23)

Determination of the ee:



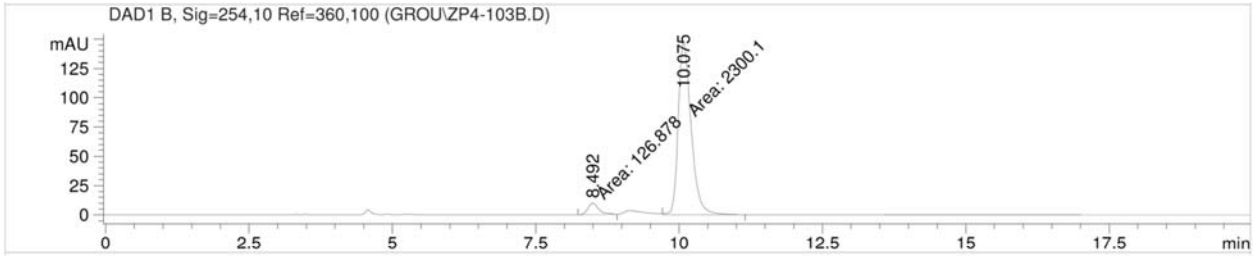
HPLC Analysis: CHIRALPAK AD column (10% *i*-PrOH in hexane, 1.0 mL/min).

90% ee from (*S*,*S*)-**L***

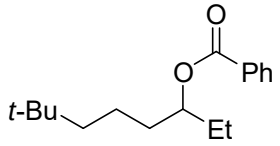


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.551	MM	0.2137	1635.61731	127.57049	94.8076
2	10.227	MM	0.2564	89.57881	5.82234	5.1924

90% ee from (*R*,*R*)-**L***



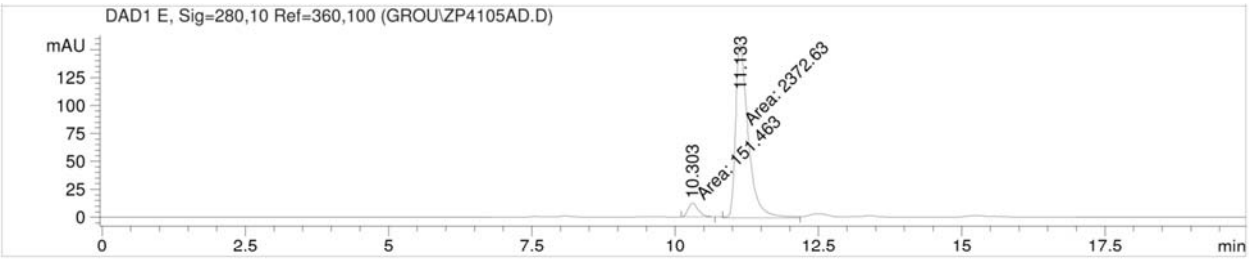
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.492	MM	0.2165	126.87782	9.76714	5.2278
2	10.075	MM	0.2609	2300.09668	146.90935	94.7722



7,7-Dimethyloctan-3-yl benzoate (Fig. 3, entry 24)

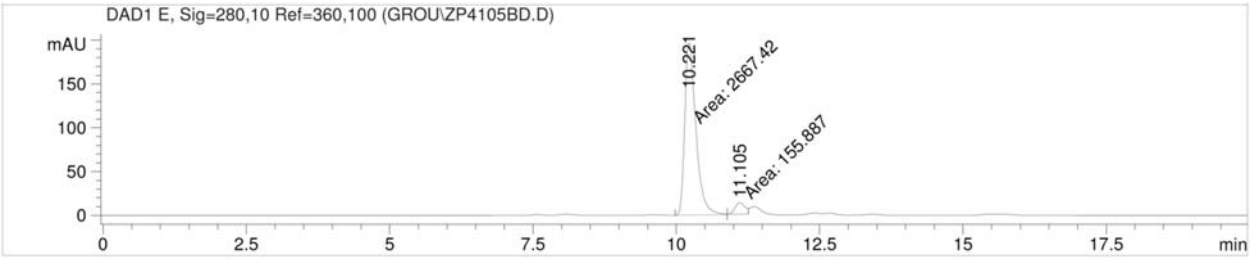
HPLC Analysis: CHIRALPAK AD column (0.5% *i*-PrOH in hexane, 0.5 mL/min).

Compound **24**: 88% ee from (*S*,*S*)-**L***

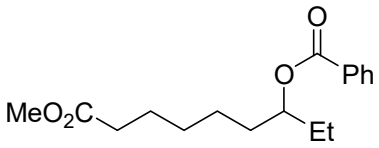


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.303	MM	0.2050	151.46315	12.31636	6.0007
2	11.133	MM	0.2550	2372.63062	155.06656	93.9993

Compound **24**: 89% ee from (*R*,*R*)-**L***



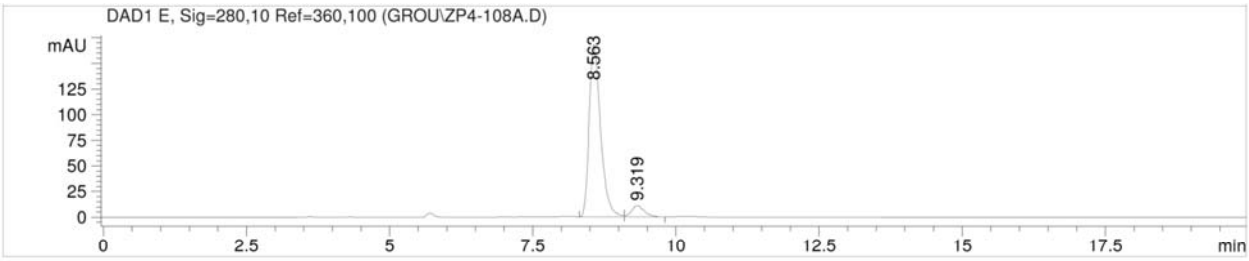
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.221	MM	0.2258	2667.42017	196.91032	94.4786
2	11.105	MM	0.2013	155.88695	12.90547	5.5214



9-Methoxy-9-oxononan-3-yl benzoate (Fig. 3, entry 25)

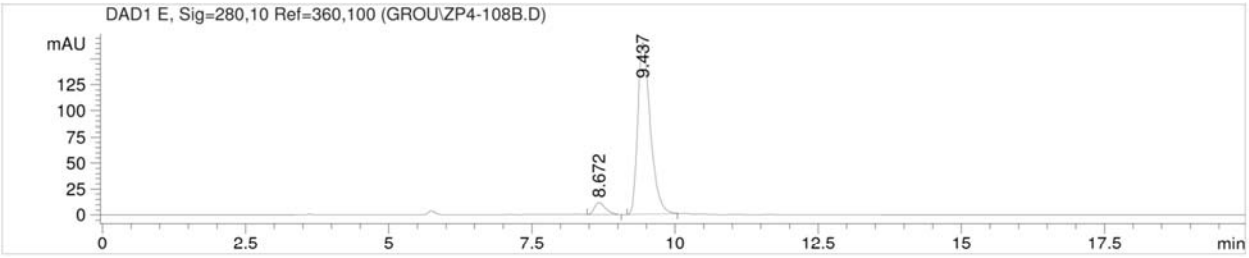
HPLC Analysis: CHIRALPAK AD column (1% *i*-PrOH in hexane, 1.0 mL/min).

Compound **25**: 86% ee from (*S,S*)-**L***

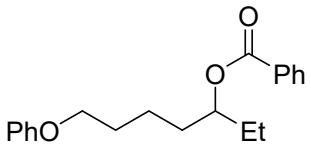


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.563	PV	0.2100	2336.60303	168.24300	93.1247
2	9.319	VP	0.2347	172.51022	11.01679	6.8753

Compound **25**: 88% ee from (*R,R*)-**L***



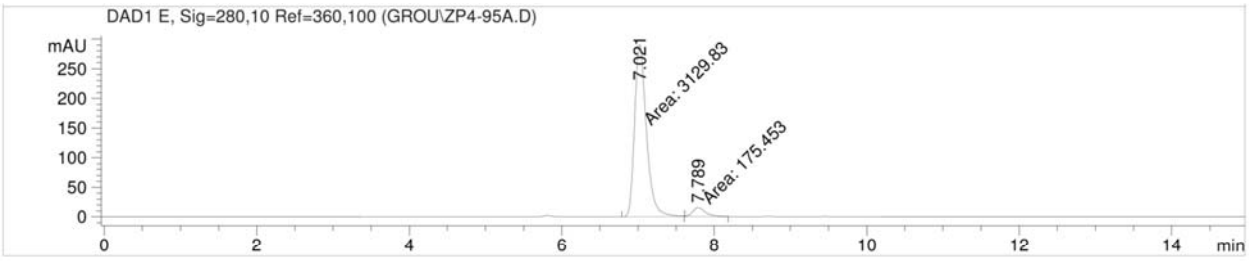
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.672	PP	0.2074	156.98535	11.63401	5.8282
2	9.437	PB	0.2332	2536.56519	165.13065	94.1718



7-Phenoxyheptan-3-yl benzoate (Fig. 3, entry 26)

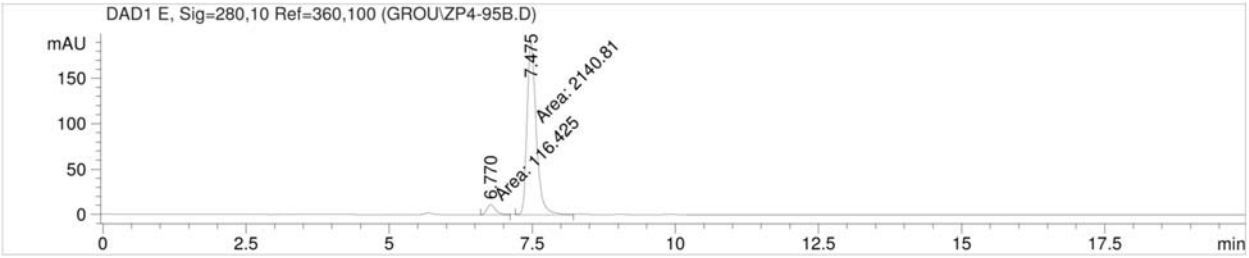
HPLC Analysis: CHIRALPAK AD column (1% *i*-PrOH in hexane, 0.5 mL/min).

Compound **26**: 89% ee from (*S*,*S*)-**L***

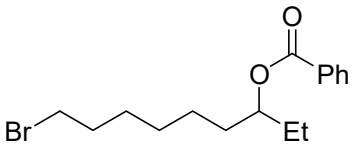


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.021	MM	0.1793	3129.83350	291.00714	94.6917
2	7.789	MM	0.1963	175.45293	14.89868	5.3083

Compound **26**: 90% ee from (*R*,*R*)-**L***



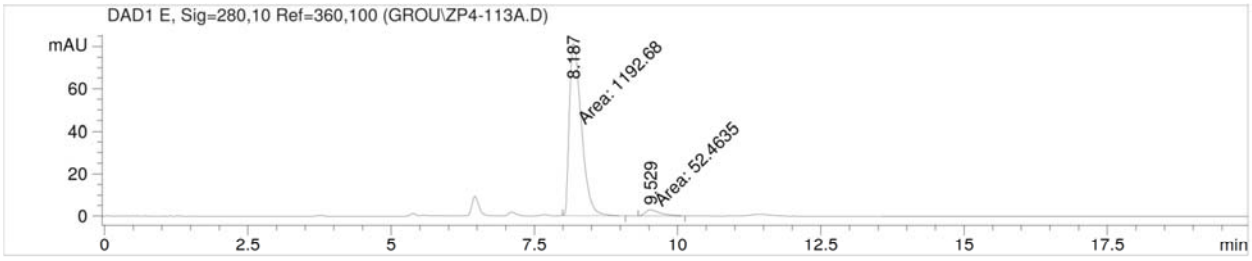
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.770	MM	0.1702	116.42479	11.40308	5.1578
2	7.475	MM	0.1872	2140.81152	190.56514	94.8422



9-Bromononan-3-yl benzoate (Fig. 3, entry 27)

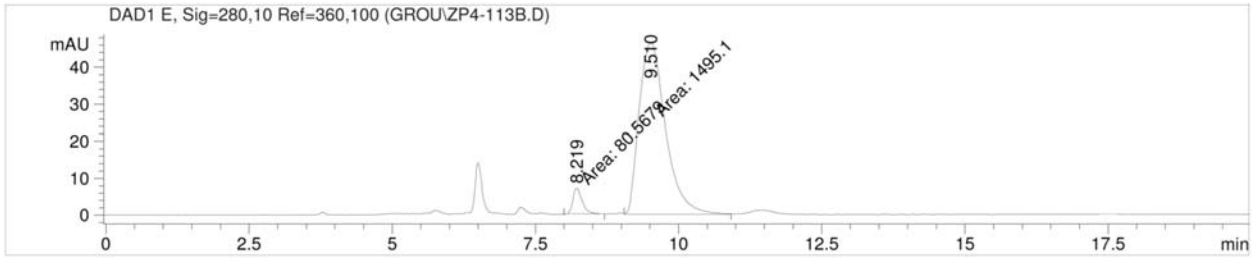
HPLC Analysis: CHIRALPAK AD column (0.5% *i*-PrOH in hexane, 1.0 mL/min).

Compound **27**: 92% ee from (*S,S*)-**L***

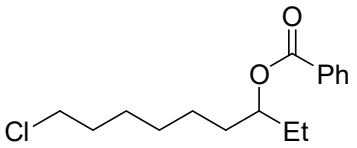


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.187	MM	0.2446	1192.67957	81.28077	95.7865
2	9.529	MM	0.3024	52.46350	2.89177	4.2135

Compound **27**: 90% ee from (*R,R*)-**L***



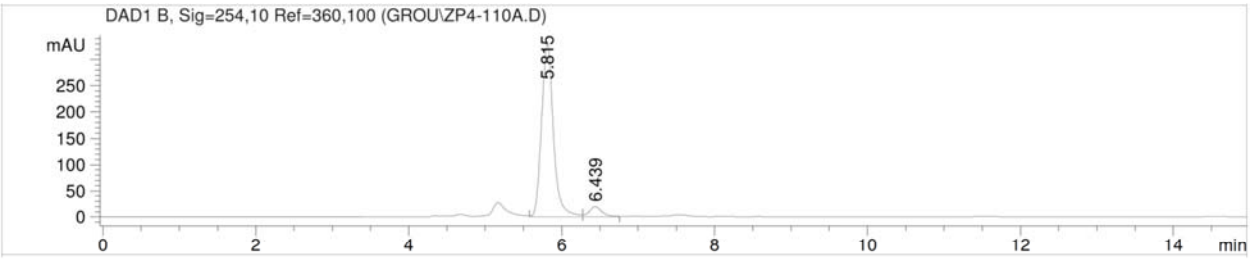
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.219	MM	0.1898	80.56791	7.07340	5.1132
2	9.510	MM	0.5371	1495.10229	46.39724	94.8868



9-Chlorononan-3-yl benzoate (Fig. 3, entry 28)

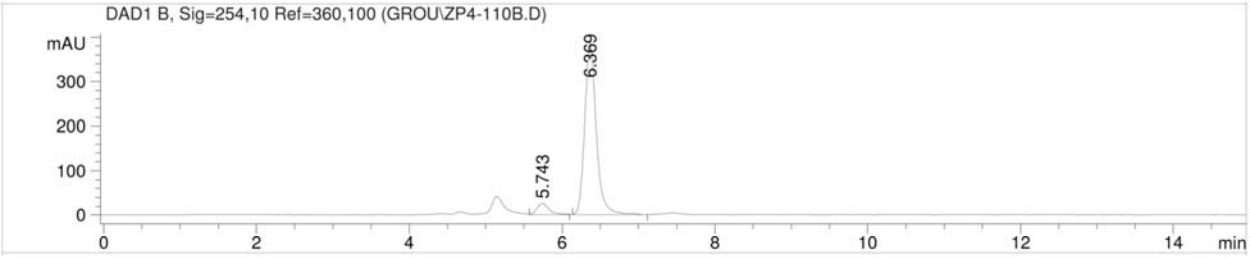
HPLC Analysis: CHIRALPAK AD column (1% *i*-PrOH in hexane, 1.0 mL/min).

Compound **28**: 88% ee from (*S,S*)-**L***

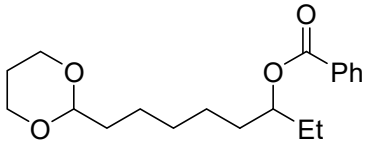


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.815	VV	0.1657	3555.25928	329.89691	94.0994
2	6.439	VB	0.1707	222.93671	19.30690	5.9006

Compound **28**: 87% ee from (*R,R*)-**L***



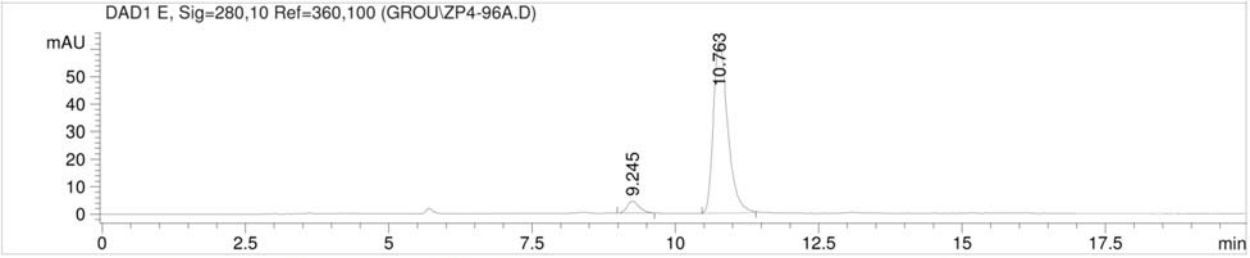
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.743	VB	0.1715	288.49451	25.59303	6.5798
2	6.369	BB	0.1611	4096.03564	388.16141	93.4202



8-(1,3-Dioxan-2-yl)octan-3-yl benzoate (Fig. 3, entry 29)

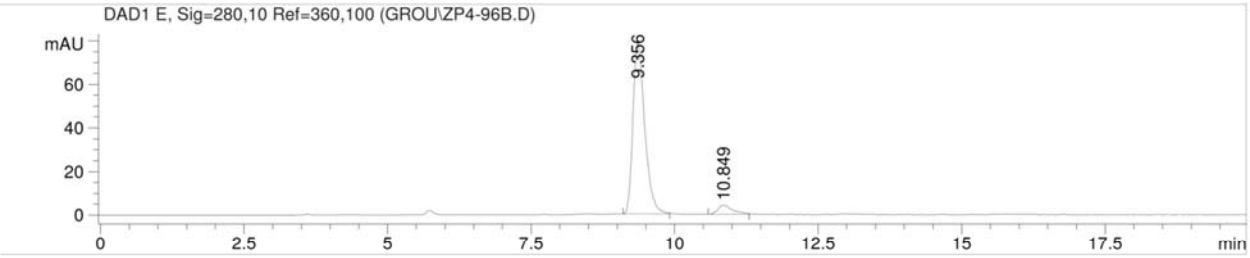
HPLC Analysis: CHIRALPAK AD column (1% *i*-PrOH in hexane, 1.0 mL/min).

Compound **29**: 89% ee from (*S*,*S*)-**L***

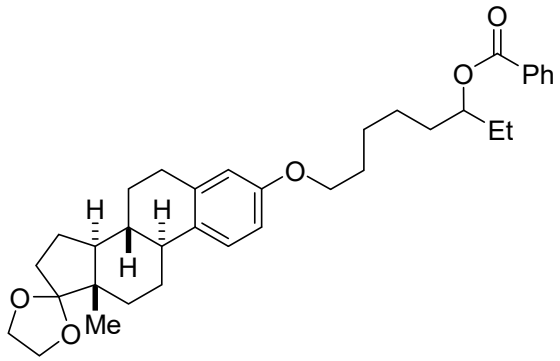


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.245	PB	0.2201	65.66151	4.40012	5.7182
2	10.763	BB	0.2615	1082.62769	62.68779	94.2818

Compound **29**: 88% ee from (*R*,*R*)-**L***



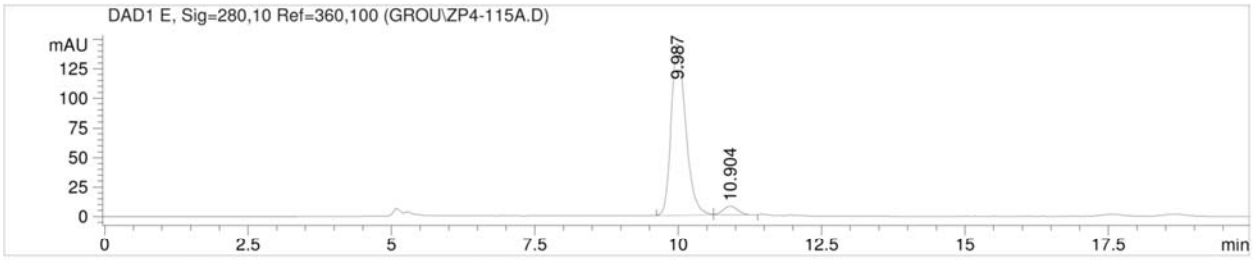
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.356	BB	0.2196	1129.05652	78.59576	93.7953
2	10.849	BB	0.2581	74.68848	4.18773	6.2047



8-(((8R,9S,13S,14S)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)oxy)octan-3-yl benzoate (Fig. 3, entries 30 and 31)

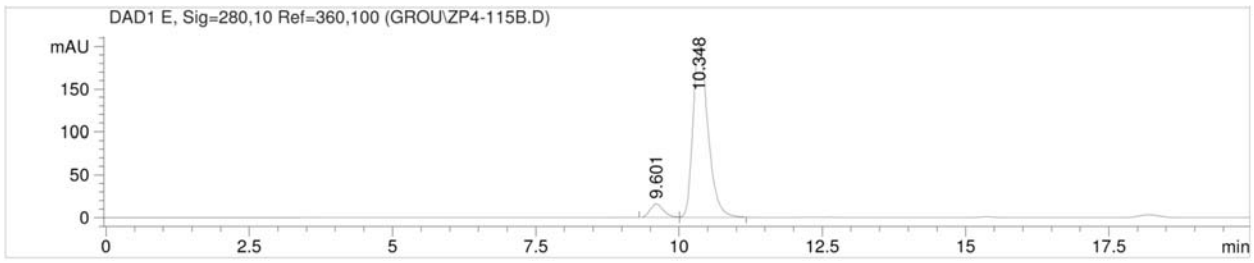
HPLC Analysis: CHIRALPAK IC column (5% *i*-PrOH in hexane, 1.0 mL/min).

Compound **30**: 95:5 d.r. from (*S*,*S*)-**L***

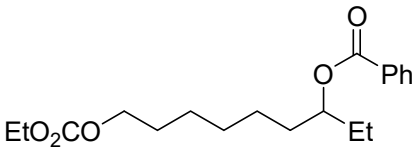


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.987	BB	0.2684	2571.91699	145.37537	95.1336
2	10.904	BP	0.2751	131.56252	7.48276	4.8664

Compound **31**: 7:93 d.r. from (*R*,*R*)-**L***



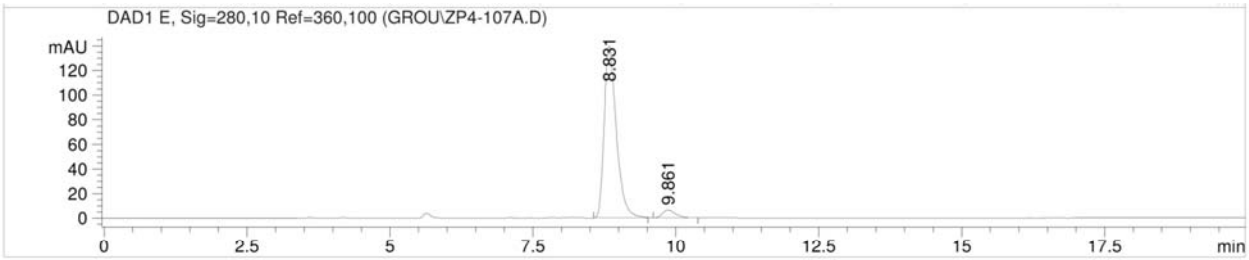
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.601	PV	0.2463	257.10187	15.76334	6.5533
2	10.348	VB	0.2793	3666.16821	200.56812	93.4467



9-((Ethoxycarbonyl)oxy)nonan-3-yl benzoate (Fig. 3, entry 32)

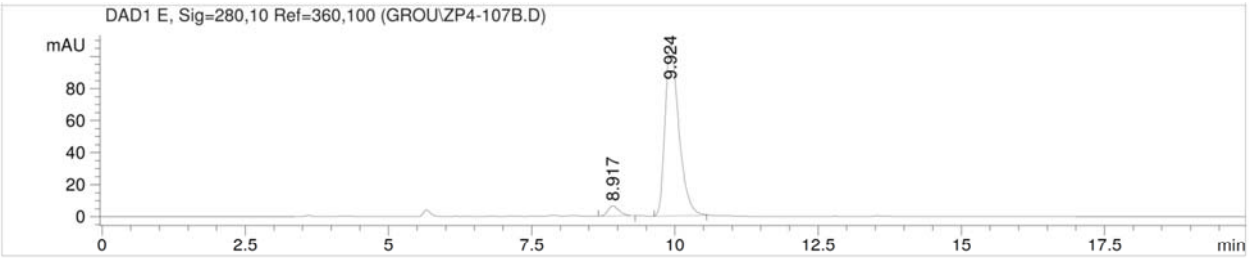
HPLC Analysis: CHIRALPAK AD column (1% *i*-PrOH in hexane, 1.0 mL/min).

Compound **32**: 91% ee from (*S*,*S*)-**L***

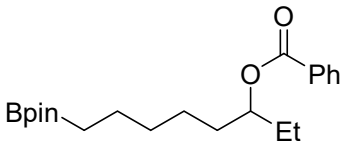


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.831	BB	0.2274	2080.28174	139.94989	95.2659
2	9.861	BP	0.2390	103.37729	6.38221	4.7341

Compound **32**: 91% ee from (*R*,*R*)-**L***



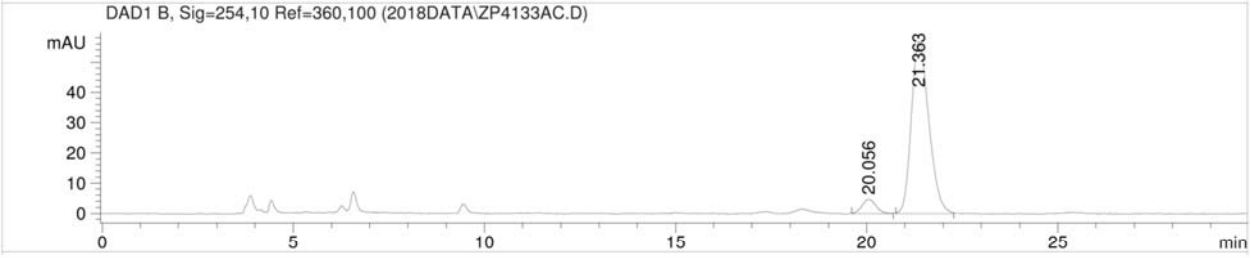
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.917	PB	0.2169	88.72775	6.35503	4.6915
2	9.924	BB	0.2556	1802.50647	107.52171	95.3085



8-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)octan-3-yl benzoate (Fig. 3, entry 33)

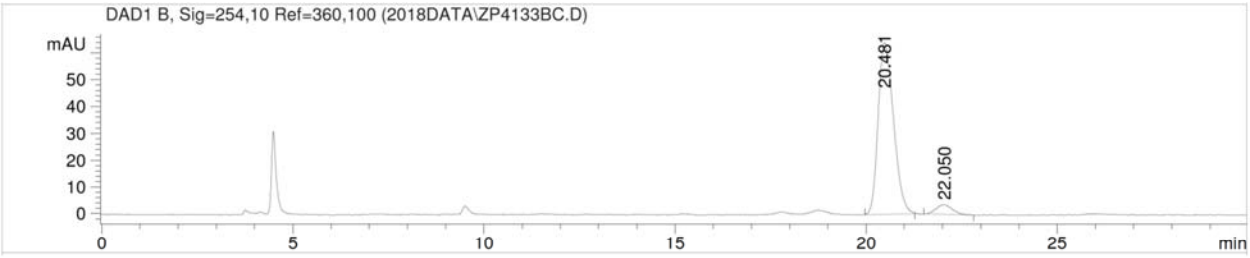
HPLC Analysis: CHIRALPAK IC column (5% *i*-PrOH in hexane, 1.0 mL/min).

Compound **33**: 88% ee from (*S*,*S*)-**L***

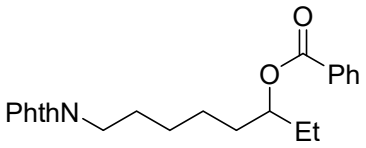


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.056	BB	0.3109	118.02908	4.63819	6.1224
2	21.363	BB	0.4849	1809.80981	56.92802	93.8776

Compound **33**: 89% ee from (*R*,*R*)-**L***



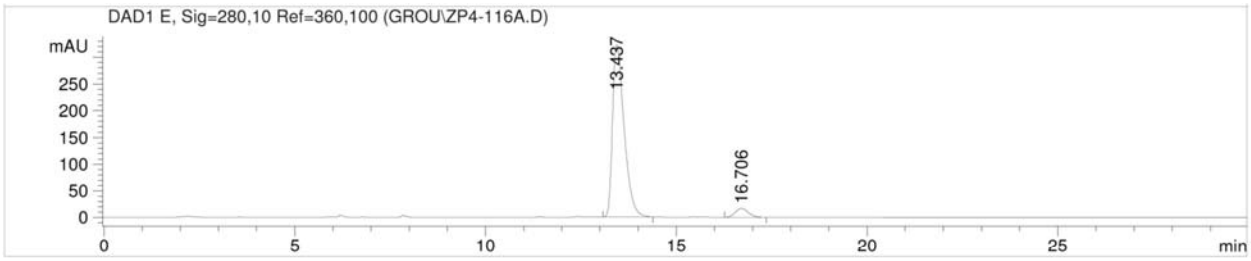
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.481	BB	0.4275	1801.49390	64.17296	94.3402
2	22.050	BP	0.3637	108.07824	3.60613	5.6598



8-(1,3-Dioxoisoindolin-2-yl)octan-3-yl benzoate (Fig. 3, entry 34)

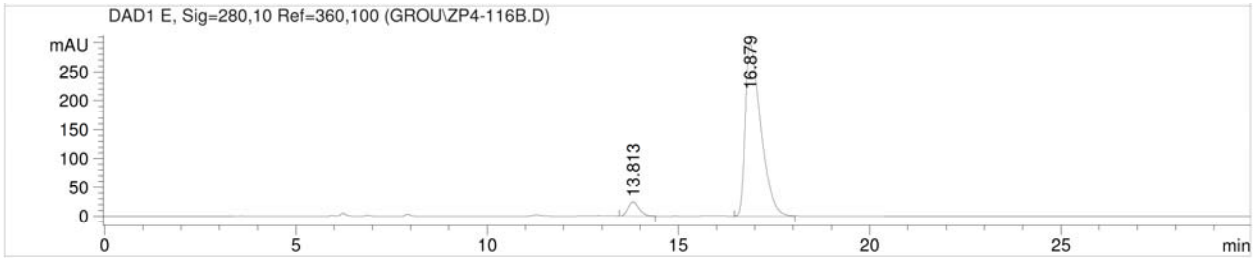
HPLC Analysis: CHIRALPAK IC column (10% *i*-PrOH in hexane, 1.0 mL/min).

Compound **34**: 89% ee from (*S*,*S*)-**L***

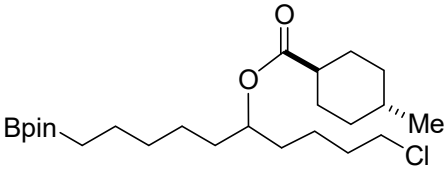


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.437	PB	0.3202	6822.78857	323.24841	94.3356
2	16.706	BB	0.3714	409.67432	16.98187	5.6644

Compound **34**: 89% ee from (*R*,*R*)-**L***

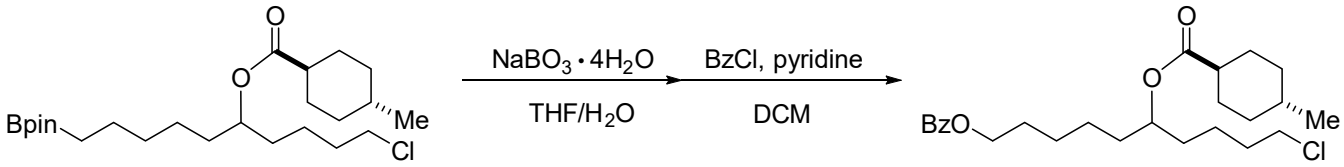


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.813	BB	0.3149	489.03201	24.28673	5.5302
2	16.879	BB	0.4155	8353.94922	297.56677	94.4698



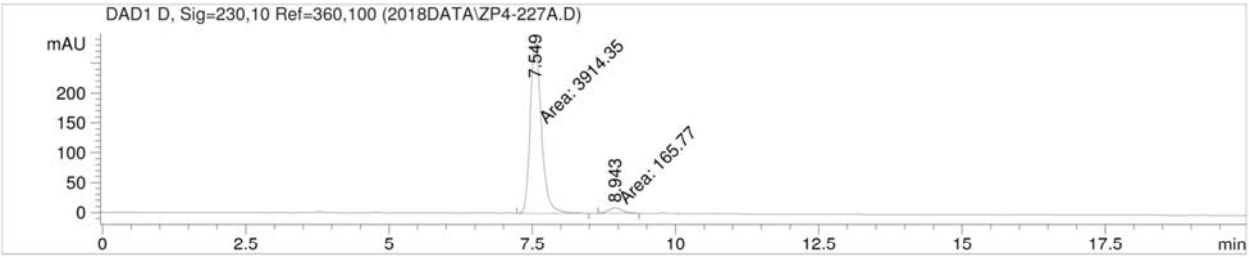
1-Chloro-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decan-5-yl (1r,4r)-4-methylcyclohexane-1-carboxylate (Fig. 4, entry 38)

Determination of the ee:



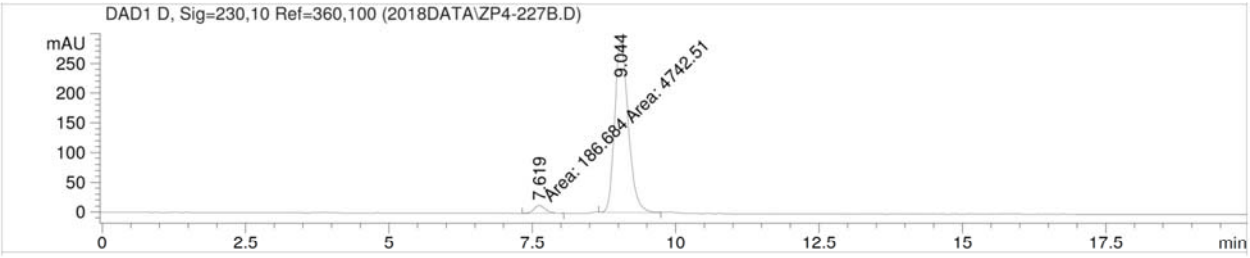
HPLC Analysis: CHIRALCEL OD column (3% *i*-PrOH in hexane, 1.0 mL/min).

92% ee from (*S*,*S*)-**L***

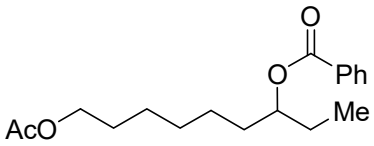


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.549	MM	0.2275	3914.35181	286.82129	95.9371
2	8.943	MM	0.2917	165.77034	9.47287	4.0629

92% ee from (*R*,*R*)-**L***



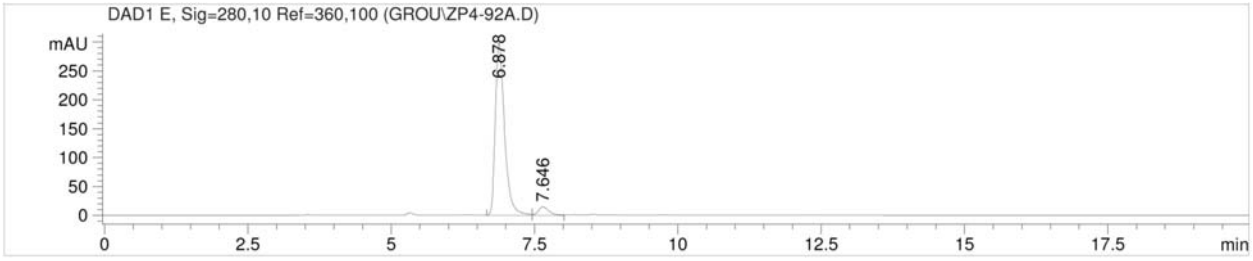
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.619	MM	0.2338	186.68445	13.30905	3.7873
2	9.044	MM	0.2760	4742.50830	286.38174	96.2127



9-Acetoxynonan-3-yl benzoate (Fig. 4, entry 39)

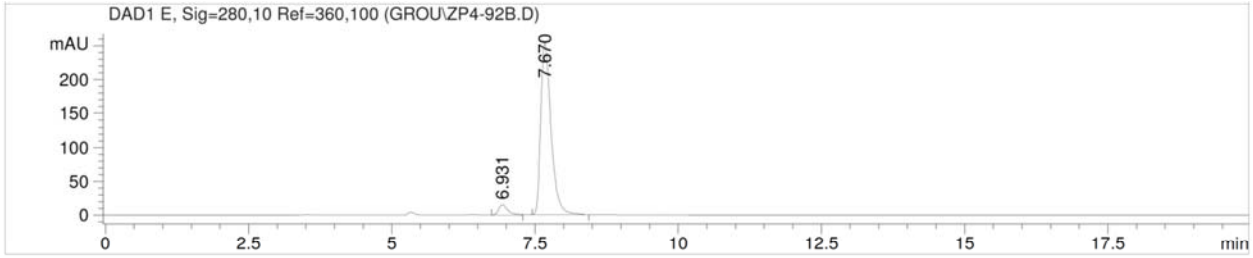
HPLC Analysis: CHIRALPAK AD column (2% *i*-PrOH in hexane, 1.0 mL/min).

Compound **39**: 90% ee from (*S,S*)-**L***

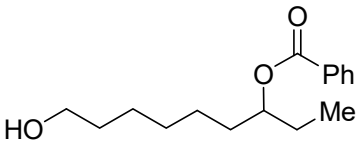


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.878	BV	0.1688	3349.00757	298.69806	94.8895
2	7.646	VB	0.1877	180.36739	14.44119	5.1105

Compound **39**: 89% ee from (*R,R*)-**L***



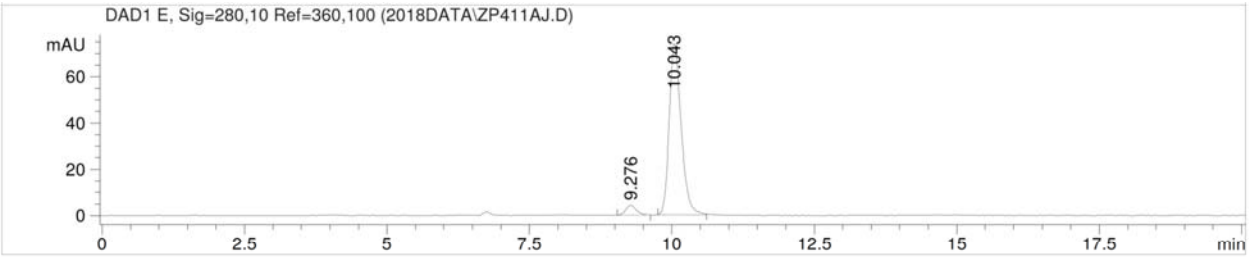
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.931	BB	0.1672	211.08757	19.05933	5.2665
2	7.670	BB	0.1900	3797.05566	303.41019	94.7335



9-Hydroxynonan-3-yl benzoate (Fig. 4, entry 40)

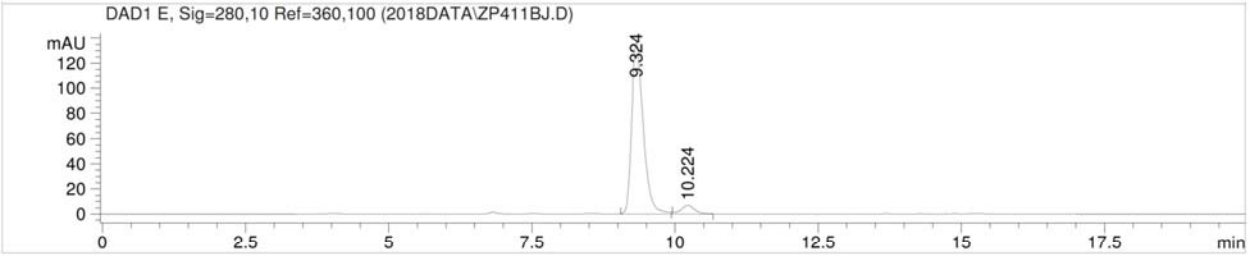
HPLC Analysis: CHIRALCEL OJ column (5% *i*-PrOH in hexane, 1.0 mL/min).

Compound **40**: 90% ee from (*S,S*)-**L***

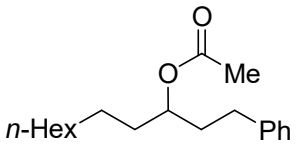


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.276	BB	0.1917	55.18505	4.24286	4.8447
2	10.043	BB	0.2247	1083.89282	74.09279	95.1553

Compound **40**: 89% ee from (*R,R*)-**L***



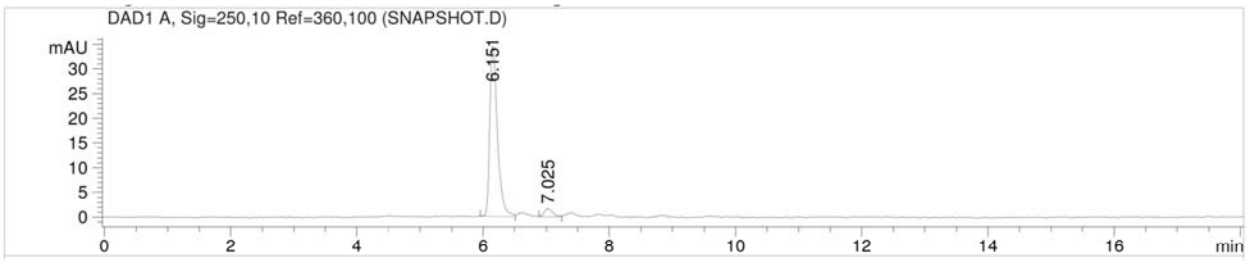
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.324	BB	0.2136	1921.59656	137.04965	94.3853
2	10.224	BB	0.2325	114.31011	6.92779	5.6147



1-Phenylundecan-3-yl acetate (Fig. 4, entry 41)

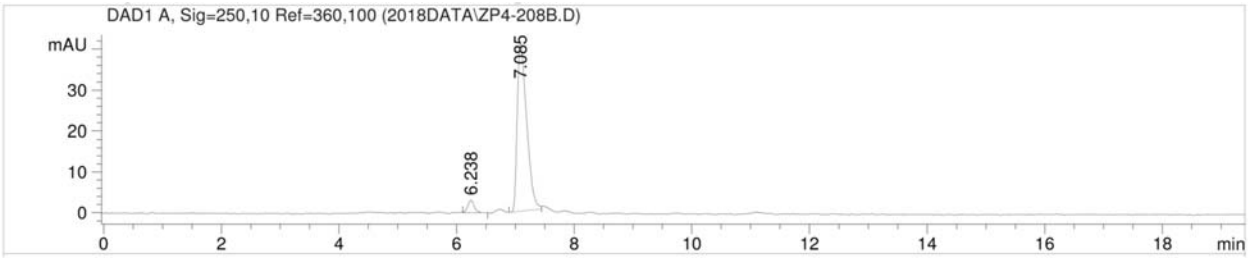
HPLC Analysis: CHIRALPAK AD column (0.5% *i*-PrOH in hexane, 1.0 mL/min).

Compound **41**: 90% ee from (*S,S*)-**L***

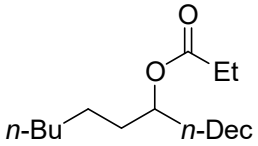


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.151	BB	0.1298	295.45636	34.54222	95.0634
2	7.025	BB	0.1391	15.34283	1.64067	4.9366

Compound **41**: 90% ee from (*R,R*)-**L***

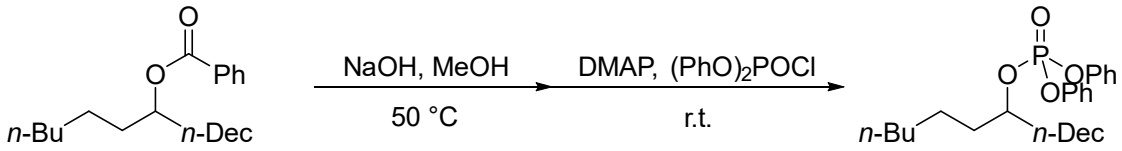


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.238	BB	0.1267	24.63585	3.10174	5.0885
2	7.085	VB	0.1705	459.51434	41.09470	94.9115

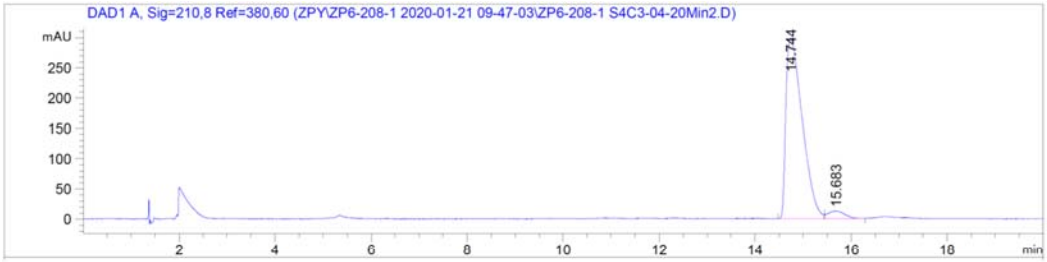


Heptadecan-7-yl propionate (Fig. 4, entry 42)

Determination of the ee:

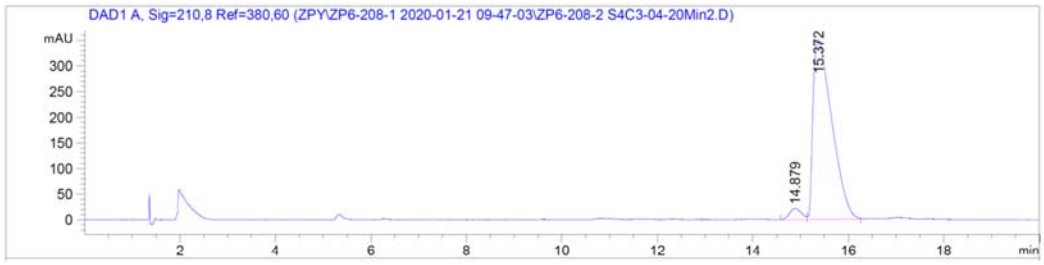


SFC Analysis: CHIRALCEL OD column (4% CH_3CN in supercritical CO_2, 2.5 mL/min).
Compound **42**: 92% ee from (*S*,*S*)-**L***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.744	BB	0.3318	7069.66699	299.04630	95.9326
2	15.683	BB	0.2841	299.74460	12.52983	4.0674

Compound **42**: 93% ee from (*R*,*R*)-**L***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.879	BV	0.2048	369.19495	21.56039	3.7224
2	15.372	VB	0.3734	9548.92773	349.88361	96.2776