Supporting Information

Synthesis of chiral cyclobutanes via rhodium/diene-catalyzed asymmetric 1,4-addition: dramatic ligand effect on the diasteroselectivity

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1. General.

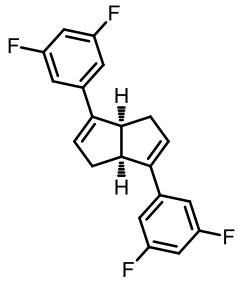
All reagents were obtained commercially unless otherwise noted. All reactions and manipulations were performed using standard schlenk techniques under predried argon. Air- and moisture-sensitive solvents were distilled from Na immediately before use and were transferred via syringe. Organic solutions were concentrated under reduced pressure (ca. 20 mm Hg) by rotary evaporation. Chromatographic purification of products was accomplished using forced flow chromatography on silica gel 60 (40-63 μm). Thin layer chromatography was performed on silica gel 60 F_{254} plates (250 μm). Visualization of the developed chromatogram was accomplished by fluorescence quenching and by staining with ethanolic anisaldehyde, aqueous potassium permanganate or aqueous ceric ammonium molybdate (CAM) solution. All chiral ligands were purchased from commercial sources or prepared according to the literature procedures[1]. All aryl boronic acid were purchased from commercial sources. Nuclear Magnetic Resonance (NMR) spectras were acquired on a Varian Mercury 400 operating at 400, 100 and 376 MHz for ^{1}H, ^{13}C, and ^{19}F, respectively. Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR, chloroform-d (δ 77.16) for ^{13}C NMR. ^{19}F NMR spectras are referenced internally using *α*,*α*,*α*-trifluorotoluene as a standard (–63.72 ppm). Datas for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br s, broad), integration and coupling constant (Hz). Datas for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm). Optical rotations were measured on a JASCOP-1030 polarimeter.

1 a) Wang, Z.-Q.; Feng, C.-G.; Xu, M.-H.; Lin, G.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 5336-5337. b) Feng, C.-G.; Wang, Z.-Q.; Tian, P.; Xu, M.-H.; Lin, G.-Q. *Chem. Asian J.* **2008**, *3*, 1511-1516. c) Zhang, S.-S.; Wang, Z.-Q.; Xu, M.-H.; Lin, G.-Q. *Org. Lett.* **2010**, *12*, 5546-5549.

2. Preparation of diene ligands

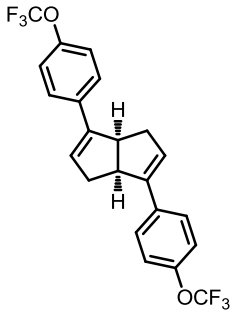
All diene-ligands were prepared according to the literature procedures[1]

(3a*S*,6a*S*)-3,6-bis(3,5-difluorophenyl)-1,3a,4,6a-tetrahydropentalene L7



$[\alpha]^{20}_{D}$ +287.9 (*c* 0.83, $CHCl_3$); m.p. 146-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92-6.91 (m, 4H), 6.71-6.66 (m, 2H), 6.06-6.05 (m, 2H), 3.99-3.96 (m, 2H), 2.97-2.89 (m, 2H), 2.41-2.36 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (dd, *J* = 13.1, 245.9 Hz), 143.5 (t, *J* = 2.7 Hz), 139.1 (t, *J* = 9.4 Hz), 127.3, 109.1 (dd, *J* = 6.8, 18.6 Hz), 102.4 (t, *J* = 25.5 Hz), 48.4, 38.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.3 ppm; IR(KBr): 3435, 3089, 2920, 2854, 1623, 1586, 1471, 1446, 1425, 1342, 1186, 1117, 989, 858, 838, 798, 680, 533; HRMS (EI): m/z Exact mass calcd for $C_{20}H_{14}F_4$ $[M]^+$: 330.1032, found: 330.1026.

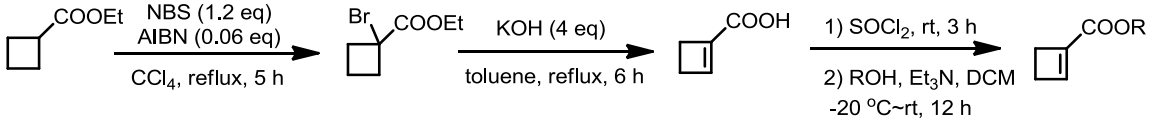
(3a*S*,6a*S*)-3,6-bis(4-(trifluoromethoxy)phenyl)-1,3a,4,6a-tetrahydropentalene L8



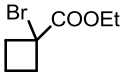
$[\alpha]^{20}_{D}$ +265.2 (*c* 0.12, $CHCl_3$); m.p. 125-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 4H), 7.18 (d, *J* = 8.0 Hz, 4H), 6.01-5.99 (m, 2H), 4.05-4.02 (m, 2H), 2.96-2.88 (m, 2H), 2.42-2.36 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2 (q, *J* = 1.8 Hz), 144.0, 134.6, 127.6, 125.4, 121.1, 120.7 (q, *J* = 255.7 Hz), 48.6, 38.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.9 ppm; IR(KBr): 3044, 2920, 2851, 1628, 1508, 1261, 1216, 1157, 1110, 1016, 911, 831, 805, 658; HRMS (EI): m/z Exact mass calcd for $C_{22}H_{16}O_2F_6$ $[M]^+$: 426.1054, found: 426.1057.

3. Preparation of cyclobut-1-enecarboxylic esters 1a-1h

Cyclobut-1-enecarboxylate esters were prepared from corresponding alcohols or phenols and cyclobut-1-enecarboxylic acid according to the procedures reported in the literatures.[2]



Ethyl 1-bromocyclobutanecarboxylate[2]

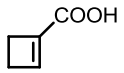


93% yield. Purified by chromatography on silica gel using 40/1 hexanes/ethyl acetate as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (q, *J* = 7.2 Hz, 2H), 2.88-2.81 (m, 2H), 2.59-2.52 (m, 2H),

2 a) Patent: US5849757 A1, **1998**. b) Song, A.; Parker, K. A.; Sampson, N. S. *J. Am. Chem. Soc.* **2009**, *131*, 3444-3445.

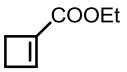
2.20-2.10 (m, 1H), 1.86-1.76 (m, 1H), 1.25 (t, J = 7.2 Hz, 3H) ppm; LRMS (EI): m/z 207.

Cyclobut-1-enecarboxylic acid[2]



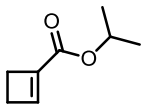
71% yield. Purified by chromatography on silica gel using 20/1 DCM/MeOH as eluent (colorless liquid): TLC R_f = 0.30 (5% DCM/MeOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (br s, 1H), 6.87 (s, 1H), 2.69 (t, J = 2.8 Hz, 2H), 2.44 (t, J = 2.8 Hz, 2H) ppm; LRMS (ESI): m/z 97.1 $[M-H]^+$.

Ethyl cyclobut-1-enecarboxylate 1a[2a]



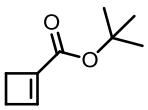
65% yield. Purified by chromatography on silica gel using 10% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76-6.75 (m, 1H), 4.18 (q, J = 6.8 Hz, 2H), 2.73-2.72 (m, 2H), 2.47-2.46 (m, 2H), 1.29 (t, J = 6.8 Hz, 3H) ppm; IR (film) ν 2963, 2922, 2850, 1412, 1261, 1093, 1020, 865, 800, 702; HRMS (EI): m/z Exact mass calcd for $C_7H_{10}O_2$ $[M]^+$: 126.0681, found: 126.0682.

Isopropyl cyclobut-1-enecarboxylate 1b



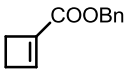
68% yield. Purified by chromatography on silica gel using 10% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74-6.73 (m, 1H), 5.10-5.01 (m, 1H), 2.72-2.71 (m, 2H), 2.46-2.44 (m, 2H), 1.26 (d, J = 6.4 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 146.0, 139.4, 67.5, 29.2, 27.0, 22.0 ppm; IR (film) ν 3459, 2983, 2941, 1725, 1456, 1376, 1262, 1215, 1183, 1164, 1105, 914, 804; HRMS (EI): m/z Exact mass calcd for $C_8H_{12}O_2$ $[M]^+$: 140.0837, found: 140.0840.

***Tert*-butyl cyclobut-1-enecarboxylate 1c**



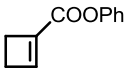
70% yield. Purified by chromatography on silica gel using 10% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58-6.57 (m, 1H), 2.60 (t, J = 3.2 Hz, 2H), 2.34-2.33 (m, 2H), 1.41 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 145.0, 140.5, 80.2, 29.2, 28.2, 26.5 ppm; IR (film) ν 3454, 2979, 1724, 1478, 1458, 1394, 1370, 1258, 1159, 844, 803, 738, 702, 473; HRMS (EI): m/z Exact mass calcd for $C_9H_{14}O_2$ $[M]^+$: 154.0994, found: 154.0998.

Benzyl cyclobut-1-enecarboxylate 1d[3]



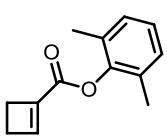
72% yield. Purified by chromatography on silica gel using 10% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.23 (m, 5H), 6.74-6.73 (m, 1H), 5.11 (s, 2H), 2.68 (t, *J* = 3.2 Hz, 2H), 2.41-2.39 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (1C), 147.2 (1C), 138.6 (1C), 136.2 (1C), 128.7 (2C), 128.3 (3C), 65.9 (1C), 29.9 (1C), 27.3 (1C) ppm; IR (film) ν 3439, 3090, 3033, 2952, 1721, 1498, 1455, 1378, 1272, 1217, 1116, 750, 714, 698, 587; HRMS (EI): m/z Exact mass calcd for $C_{12}H_{12}O_2$ $[M]^+$: 188.0837, found: 188.0840.

Phenyl cyclobut-1-enecarboxylate 1e[2b]



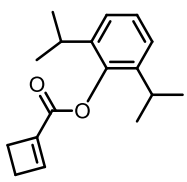
76% yield. Purified by chromatography on silica gel using 10% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.17-7.12 (m, 1H), 7.06-7.04 (m, 2H), 6.91 (t, *J* = 0.8 Hz, 1H), 2.77 (t, *J* = 3.2 Hz, 2H), 2.49-2.47 (m, 2H) ppm; IR (film) ν 3066, 2954, 1736, 1627, 1591, 1492, 1457, 1314, 1280, 1244, 1192, 1163, 1103, 1077, 1025, 1003, 906, 834, 742, 688, 501; HRMS (EI): m/z Exact mass calcd for $C_{11}H_{10}O_2$ $[M]^+$: 174.0681, found: 174.0685.

2,6-Dimethylphenyl cyclobut-1-enecarboxylate 1f



68% yield. Purified by chromatography on silica gel using 10% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08-7.05 (m, 3H), 7.01-7.00 (m, 1H), 2.89-2.87 (m, 2H), 2.58-2.57 (m, 2H), 2.16 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 149.0, 147.9, 137.9, 130.4, 128.6, 125.9, 29.5, 27.6, 16.4 ppm; IR (film) ν 3027, 2968, 2931, 1750, 1732, 1606, 1476, 1442, 1415, 1382, 1315, 1275, 1266, 1166, 1106, 922, 844, 790, 771, 762, 685, 534; HRMS (EI): m/z Exact mass calcd for $C_{13}H_{14}O_2$ $[M]^+$: 202.0994, found: 202.0997.

2,6-Diisopropylphenyl cyclobut-1-enecarboxylate 1g

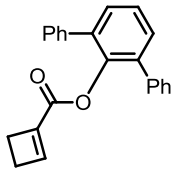


72% yield. Purified by chromatography on silica gel using 10% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.15 (m, 3H), 7.01-7.00 (m, 1H), 2.95-2.88 (m, 4H), 2.58-2.57 (m, 2H), 1.20 (d, *J* = 6.4 Hz,

3 a) Collon, S.; Kouklovsky, C.; Langlois, Y. *Eur. J. Org. Chem*. **2002**, 3566-3572; b) Xu, H.-D.; Zhang, W.; Shu, D.-X.; Werness, J. B.; Tang, W.-P. *Angew. Chem. Int. Ed.* **2008**, *47*, 8933-8936.

12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 149.0, 145.4, 140.6, 138.1, 126.6, 124.0, 29.6, 27.7, 27.6, 27.0 ppm; IR (film) ν 3065, 2964, 2930, 2870, 1735, 1602, 1466, 1442, 1384, 1362, 1310, 1240, 1185, 1167, 1098, 1081, 941, 907, 791, 734, 689; HRMS (EI): m/z Exact mass calcd for $C_{17}H_{22}O_2$ $[M]^+$: 258.1620, found: 258.1617.

2,6-Diphenylphenyl cyclobut-1-enecarboxylate 1h

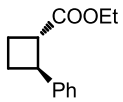


65% yield. Purified by chromatography on silica gel using 10% DCM/petroleum ether as eluent (white solid): TLC R_f = 0.35 (40% DCM/petroleum ether); m.p. 92-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.46 (m, 4H), 7.39-7.35 (m, 7H), 7.32-7.30 (m, 2H), 6.63-6.62 (m, 1H), 2.50 (t, *J* = 2.8 Hz, 2H), 2.32-2.28 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 148.4, 144.9, 137.9, 137.6, 136.0, 130.2, 129.2, 128.3, 127.5, 126.6, 29.1, 27.4 ppm; IR(KBr): 3053, 3031, 2971, 2931, 1729, 1603, 1496, 1455, 1418, 1309, 1245, 1178, 1093, 1082, 1062, 973, 906, 758, 702, 682, 604, 517; LRMS (ESI): m/z 327.2 $[M+H]^+$; HRMS (ESI): m/z Exact mass calcd for $C_{23}H_{18}NaO_2$ $[M+Na]^+$: 349.1199, found: 349.1200.

4. General procedure for the rhodium-catalyzed arylation of cyclobut-1-enecarboxylate esters

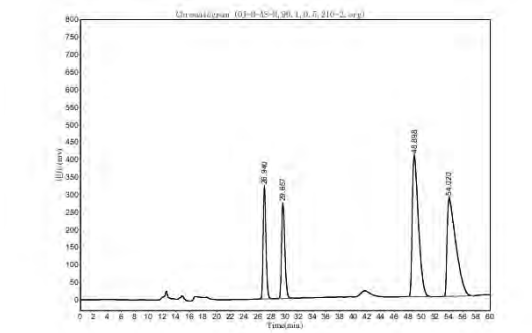
Under argon atmosphere, cyclobut-1-enecarboxylate esters (0.2 mmol), boron reagent (0.4 mmol, 2 equiv), and catalyst $[Rh(OH)(S,S)(\mathbf{L})]_2$ (0.003 mmol, 0.015 equiv) or $[Rh(C_2H_4)Cl]_2$ (0.003 mmol, 0.015 equiv) and diene ligand (0.0066 mmol, 0.033 equiv) were dissolved in 2 mL toluene in a schlenk tube. To this yellow solution was added 2M aqueous KOH (0.2 mL, 0.4 mmol, 2 equiv). The mixture was stirred at 30 °C or 50 °C for 1 d. Solvent was concentrated under reduced pressure. Purification of this residue by chromatography on silica gel furnished the desired product. The enantiomeric excess (ee) was determined by chiral HPLC analysis.

(1*S*, 2*S*)-Ethyl-2-phenylcyclobutanecarboxylate 3aa



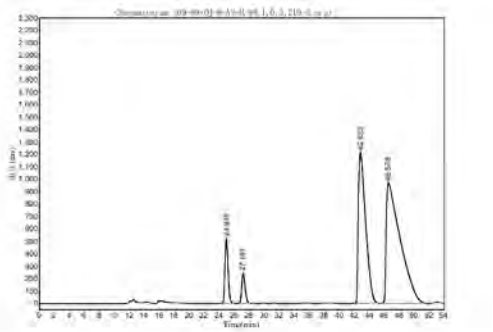
61% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.18 (m, 5H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.82-3.76 (m, 1H), 3.21-3.14 (m, 1H), 2.33-2.25 (m, 2H), 2.19-2.11 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 143.8, 128.5, 126.5, 126.4, 60.6, 45.6, 43.2, 25.4, 21.8, 14.4 ppm; IR (film) ν 3085, 3061, 3028, 2963, 2871, 1729, 1603, 1496, 1446, 1375, 1261, 1242, 1163, 1095, 1040, 861, 800, 753, 698, 536; HRMS (EI): m/z Exact mass calcd for $C_{13}H_{16}O_2$ $[M]^+$:

204.1150, found: 204.1148; enantiomeric excess was determined by HPLC with a Chiralcel OJ-H-AS-H column (*n*-hexane/*i*-propanol = 99/1, 0.5 mL/min, 210 nm, 25 °C); t_r (*R*, *S*) = 24.935 min, t_r (*S*, *R*) = 27.187 min, t_r (*R*, *R*) = 42.832 min, t_r (*S*, *S*) = 46.578 min; ee (trans) = 21%, ee (cis) = 34%.



Results

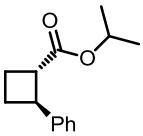
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.940	319151.969	9079802.000	13.2568
2		29.657	270806.938	9096525.000	13.2812
3		48.898	402390.906	25249846.000	36.8656
4		54.020	280595.219	25065494.000	36.5964
Total			1272945.031	68491667.000	100.0000



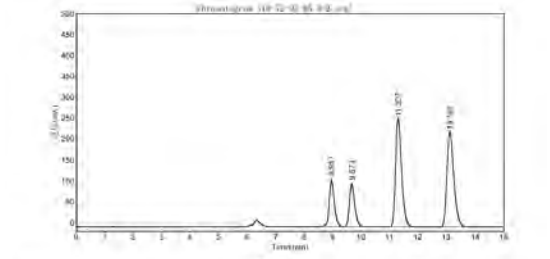
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.935	514756.719	15101109.000	6.5541
2		27.187	840687.647	7455652.000	3.2356
3		42.832	1211354.875	82097704.000	35.6314
4		46.578	965465.063	125754160.000	54.5788
Total			3532254.703	230408396.000	100.0000

(1*S*, 2*S*)-Isopropyl 2-phenylcyclobutanecarboxylate 3ba

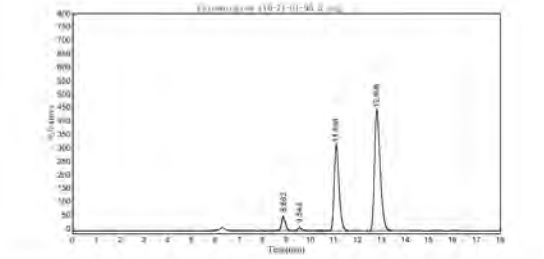


50% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 7.19-7.11 (m, 3H), 5.01-4.92 (m, 1H), 3.74-3.67 (m, 1H), 3.09-3.03 (m, 1H), 2.25-2.15 (m, 2H), 2.11-2.04 (m, 2H), 1.17 (d, *J* = 6.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 143.9, 128.4, 126.5, 126.4, 67.8, 45.9, 43.2, 25.2, 22.0, 21.99, 21.8 ppm; IR (film) ν 2963, 2917, 2849, 1732, 1413, 1261, 1020, 865, 800, 700; HRMS (EI): m/z Exact mass calcd for $C_{14}H_{18}O_2$ $[M]^+$: 218.1307, found: 218.1306; enantiomeric excess was determined by HPLC with a Chiralcel OJ-H column (*n*-hexane/*i*-propanol = 95/5, 0.5 mL/min, 214 nm, 25 °C); t_r (*R*, *S*) = 8.862 min, t_r (*S*, *R*) = 9.543 min, t_r (*R*, *R*) = 11.093 min, t_r (*S*, *S*) = 12.805 min; ee (trans) = 24%, ee (cis) = 62%.



Results

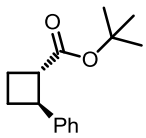
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.957	110512.109	1420028.750	13.4989
2		9.673	103176.805	1265121.500	12.0690
3		11.307	260009.688	3852125.500	36.5979
4		11.307	255358.359	3807467.750	36.0337
Total			697345.961	10525543.000	100.0000



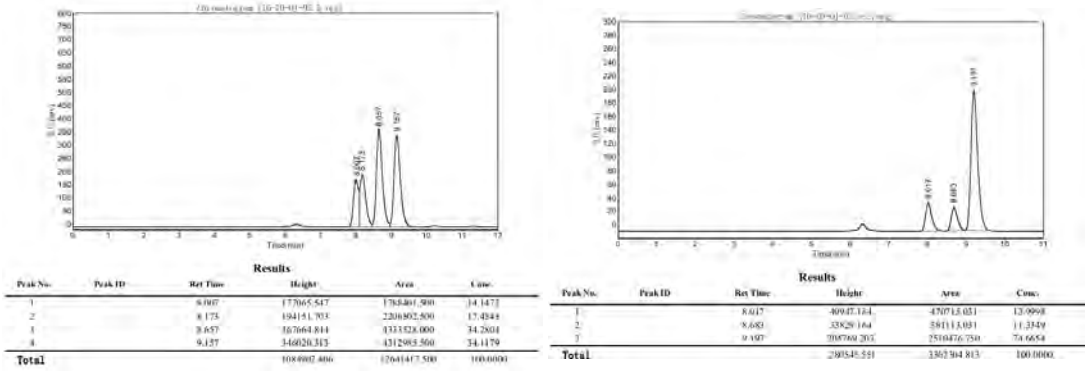
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.862	50462.613	617513.313	4.9970
2		9.543	11033.403	140555.688	1.1376
3		11.093	319433.813	4595867.500	37.1760
4		12.805	447933.063	7484288.000	56.2800
Total			829442.892	12346224.500	100.0000

(1*S*, 2*S*)-Tert-butyl 2-phenylcyclobutanecarboxylate 3ca



50% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); the trans diastereomer and cis diastereomer can't be separated by chromatography on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ peaks attributed to the trans diastereomer: 7.26-7.09 (m, 5H), 3.69-3.62 (m, 1H), 3.04-2.98 (m, 1H), 2.20-2.00 (m, 4H), 1.38 (s, 9H) ppm; peaks attributed to the cis diastereomer: 7.26-7.09 (m, 5H), 3.90-3.83 (m, 1H), 3.38-3.33 (m, 1H), 2.54-2.00 (m, 4H), 0.96 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ peaks attributed to the trans diastereomer: 174.0, 144.1, 128.4, 127.8, 126.5, 80.3, 46.8, 43.3, 28.3, 25.0, 21.7 ppm; peaks attributed to the cis diastereomer: 172.8, 141.4, 128.1, 126.4, 126.3, 79.9, 45.5, 42.6, 27.8, 24.2, 20.5 ppm; IR (film) ν 2962, 2920, 2851, 1261, 1093, 1020, 864, 800, 425, 418; LRMS (ESI): m/z 255.2 $[M+Na]^+$; HRMS (ESI): m/z Exact mass calcd for $C_{15}H_{20}NaO_2$ $[M+Na]^+$: 255.1356, found: 255.1360; enantiomeric excess was determined by HPLC with a Chiralcel OJ-H column (*n*-hexane/*i*-propanol = 95/5, 0.5 mL/min, 214 nm, 25 °C); t_r (*R*, *S*) = 8.007 min, t_r (*S*, *R*) = 8.173 min, t_r (*R*, *R*) = 8.657 min, t_r (*S*, *S*) = 9.157 min; ee (trans) = 74%.



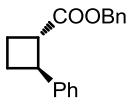
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.007	177065.547	4368461.500	34.1473
2		8.173	194151.703	4206802.500	17.4844
3		8.657	167664.844	4333528.000	34.2804
4		9.157	346026.313	4312985.500	34.1179
Total			1084902.406	12641417.500	100.0000

Results

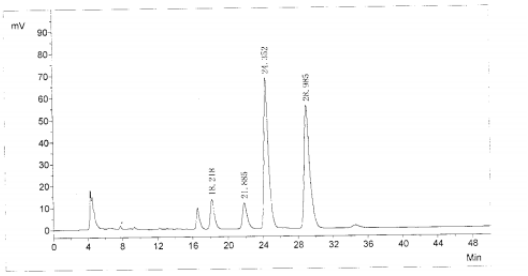
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.017	409417.124	4707153.031	13.0998
2		8.680	338291.164	5811133.031	11.3349
3		9.197	2007760.203	25104476.750	74.6654
Total			2805545.551	33623304.813	100.0000

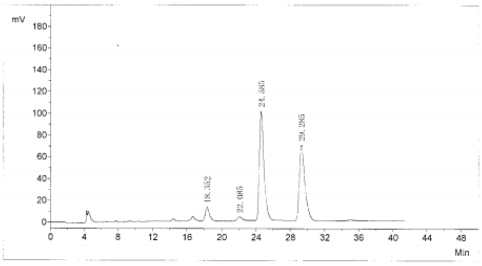
(1*S*, 2*S*)-Benzyl 2-phenylcyclobutanecarboxylate 3da



21% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.27 (m, 2H), 7.24-7.20 (m, 4H), 7.17-7.10 (m, 4H), 5.074-5.067 (m, 2H), 3.78-3.70 (m, 1H), 3.20-3.13 (m, 1H), 2.25-2.18 (m, 2H), 2.13-2.06 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 143.6, 136.2, 128.7, 128.5, 128.3, 128.2, 126.6, 126.5, 66.3, 45.6, 43.4, 25.4, 21.8 ppm; IR (film) ν 3063, 3030, 2962, 1731, 1603, 1497, 1455, 1261, 1242, 1162, 1093, 1028, 801, 752, 697; HRMS (EI): m/z Exact mass calcd for $C_{18}H_{18}O_2$ $[M]^+$:

266.1307, found: 266.1309; enantiomeric excess was determined by HPLC with a Chiralcel OJ-H column (*n*-hexane/*i*-propanol = 95/5, 0.7 mL/min, 214 nm, 25 °C); t_r (*R*, *S*) = 18.352 min, t_r (*S, R*) = 22.085 min, t_r (*S*, *S*) = 24.585 min, t_r (*R, R*) = 29.285 min, ee (trans) = 9.2%, ee (cis) = 46.7%.

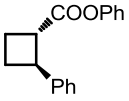




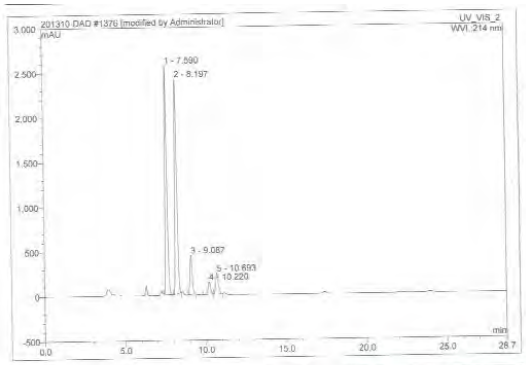
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		18.218	13357.0	426900.3	7.4166
2	2		21.885	11747.2	427027.5	7.4188
3	3		24.352	68268.3	2441916.9	42.4239
4	4		28.985	55776.1	2460150.4	42.7407
Total				149148.5	5755995.1	100.0000

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		18.352	12597.9	405794.3	5.4511
2	2		22.085	3799.4	147462.7	1.9809
3	3		24.585	99928.7	3762300.9	50.5394
4	4		29.285	69330.2	3128735.1	42.0286
Total				185656.3	7444293.1	100.0000

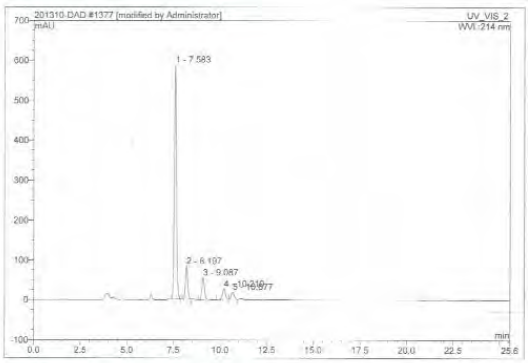
(1*S*, 2*S*)-Phenyl 2-phenylcyclobutanecarboxylate 3ea



25% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.19 (m, 5H), 7.11-7.08 (m, 2H), 7.02-6.97 (m, 1H), 6.24-6.22 (m, 2H), 4.10-4.03 (m, 1H), 3.74-3.69 (m, 1H), 2.68-2.58 (m, 1H), 2.47-2.40 (m, 1H), 2.34-2.19 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 150.6, 140.9, 129.2, 128.5, 127.8, 126.9, 125.6, 121.6, 45.1, 43.0, 24.4, 20.3 ppm; IR (film) ν 3061, 3028, 2962, 2850, 1749, 1493, 1456, 1360, 1344, 1261, 1195, 1162, 1131, 1025, 917, 865, 800, 756, 732, 698, 690, 498; HRMS (EI): m/z Exact mass calcd for $C_{17}H_{16}O_2$ $[M]^+$: 252.1150, found: 252.1149; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 95/5, 0.7 mL/min, 214 nm, 25 °C); t_r (*S*, *S*) = 7.58 min, t_r (*R, R*) = 8.20 min, t_r (*R*, *S*) = 9.09 min, t_r (*S, R*) = 10.68 min, ee (trans) = 74%, ee (cis) = 44%.

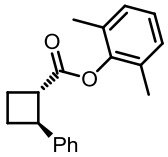


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.59	n.a.	2560.997	356.572	41.70	n.a.	BMB*
2	8.20	n.a.	2403.080	357.478	41.80	n.a.	BMB*
3	9.09	n.a.	440.974	70.251	8.21	n.a.	BMB*
4	10.22	n.a.	141.480	26.120	3.05	n.a.	BMB*
5	10.69	n.a.	235.027	44.756	5.23	n.a.	BMB*
Total:			5781.557	855.176	100.00	0.000	

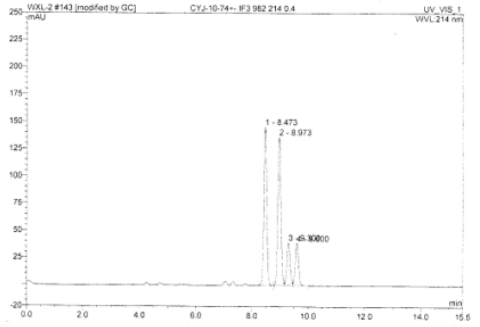


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.58	n.a.	587.504	77.355	72.79	n.a.	BMB*
2	8.20	n.a.	84.202	11.762	11.07	n.a.	BMB*
3	9.09	n.a.	58.030	8.759	8.24	n.a.	BMB*
4	10.21	n.a.	27.076	4.963	4.67	n.a.	BMB*
5	10.68	n.a.	19.171	3.434	3.23	n.a.	BMB*
Total:			773.984	106.273	100.00	0.000	

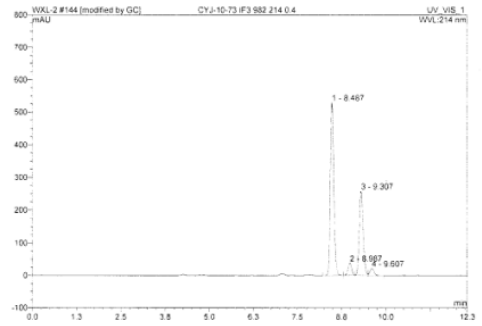
(1*S*, 2*S*)-2,6-Dimethylphenyl 2-phenylcyclobutanecarboxylate 3fa



80% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); the trans diastereomer and cis diastereomer can't be separated by chromatography on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ peaks attributed to the trans diastereomer: 7.27-7.11 (m, 5H), 7.00-6.94 (m, 3H), 3.95-3.88 (m, 1H), 3.47-3.41 (m, 1H), 2.43-2.15 (m, 4H), 2.05 (s, 6H) ppm; peaks attributed to the cis diastereomer: 7.27-7.11 (m, 5H), 6.87-6.81 (m, 3H), 4.08-4.01 (m, 1H), 3.81-3.75 (m, 1H), 2.76-2.15 (m, 4H), 1.57 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ peaks attributed to the trans diastereomer: 172.1, 148.2, 143.5, 130.2, 128.7, 128.60, 127.8, 126.5, 125.9, 45.4, 43.5, 25.8, 22.0, 16.5 ppm; peaks attributed to the cis diastereomer: 171.6, 148.3, 141.1, 130.4, 128.61, 128.5, 126.9, 126.6, 125.6, 44.9, 42.8, 25.0, 21.8, 16.0 ppm; IR (film) ν 3027, 2963, 2924, 2850, 1748, 1604, 1495, 1476, 1445, 1314, 1261, 1136, 1093, 1019, 943, 866, 800, 699; HRMS (EI): m/z Exact mass calcd for $C_{19}H_{20}O_2$ $[M]^+$: 280.1463, found: 280.1462; enantiomeric excess was determined by HPLC with a Chiralcel IF-3 column (*n*-hexane/*i*-propanol = 98/2, 0.4 mL/min, 214 nm, 25 °C); t_r (*S, S*) = 8.49 min, t_r (*R, R*) = 8.99 min, t_r (*R, S*) = 9.31 min, t_r (*S, R*) = 9.61 min, ee (trans) = 87%, ee (cis) = 84%。

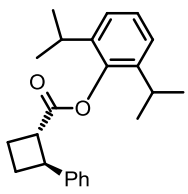


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.47	n.a.	146.052	17.108	38.34	n.a.	BMB
2	8.97	n.a.	136.741	17.071	38.26	n.a.	BM
3	9.30	n.a.	40.061	5.208	11.67	n.a.	M
4	9.60	n.a.	39.260	5.233	11.73	n.a.	MB
Total:			362.114	44.619	100.00	0.000	



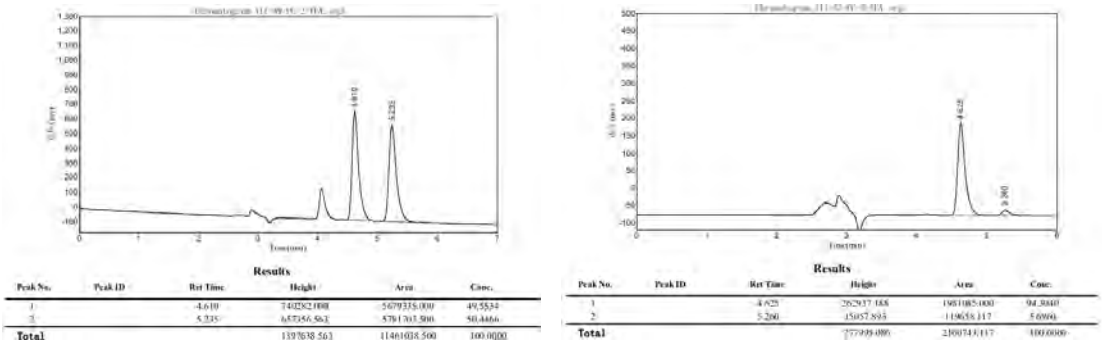
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.49	n.a.	529.544	60.899	60.38	n.a.	BMb*
2	8.99	n.a.	36.957	4.340	4.30	n.a.	bMB*
3	9.31	n.a.	257.272	32.715	32.44	n.a.	BM *
4	9.61	n.a.	21.743	2.906	2.88	n.a.	MB*
Total:			845.515	100.860	100.00	0.000	

(1*S*, 2*S*)-2,6-Diisopropylphenyl 2-phenylcyclobutanecarboxylate 3ga

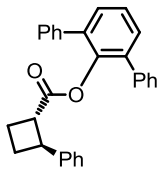


99% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); the trans diastereomer and cis diastereomer can't be separated by chromatography on silica gel. ^{1}H NMR (400 MHz, $CDCl_3$) δ peaks attributed to the trans diastereomer: 7.27-6.93 (m, 8H), 3.93-3.87 (m, 1H), 3.48-3.42 (m, 1H), 2.42-2.16 (m, 6H), 1.15-0.78 (m, 12H) ppm; peaks attributed to the cis diastereomer: 7.27-6.93 (m, 8H), 4.08- 4.01 (m, 1H), 3.84-3.78 (m, 1H), 2.86-2.70 (m, 6H),

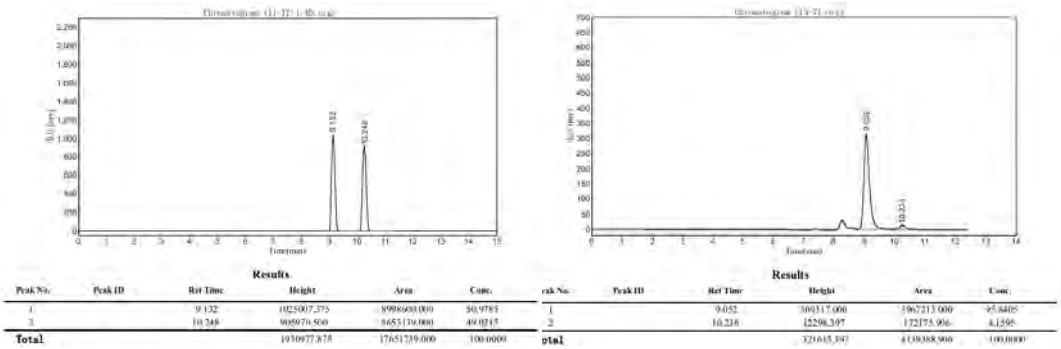
1.15-0.78 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ peaks attributed to the trans diastereomer: 172.9, 143.4, 140.4, 128.6, 127.6, 126.55, 126.54, 124.0, 123.9, 45.5, 43.8, 27.6, 25.9, 25.0, 22.8, 21.9 ppm; peaks attributed to the cis diastereomer: 172.4, 141.6, 141.0, 128.5, 126.9, 126.7, 126.3, 124.1, 123.8, 45.0, 42.9, 31.7, 27.0, 24.5, 23.7, 22.0 ppm; IR (film) ν 3028, 2964, 2869, 1750, 1459, 1443, 1363, 1237, 1164, 1138, 1096, 793, 698; LRMS (ESI): m/z 359.2 $[M+Na]^+$; HRMS (ESI): m/z Exact mass calcd for $C_{23}H_{29}O_2$ $[M+H]^+$: 337.2162, found: 337.2161; enantiomeric excess was determined through corresponding acid by HPLC with a Chiralcel PC-2 column (*n*-hexane/*i*-propanol/TFA = 90/10/0.1, 1.0 mL/min, 214 nm, 25 °C); t_r (major) = 4.625 min, t_r (minor) = 5.260 min, ee (trans) = 89% ee.



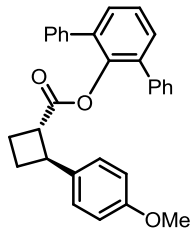
(1*S*, 2*S*)-[1,1':3',1''-Terphenyl]-2'-yl 2-phenylcyclobutanecarboxylate 3ha



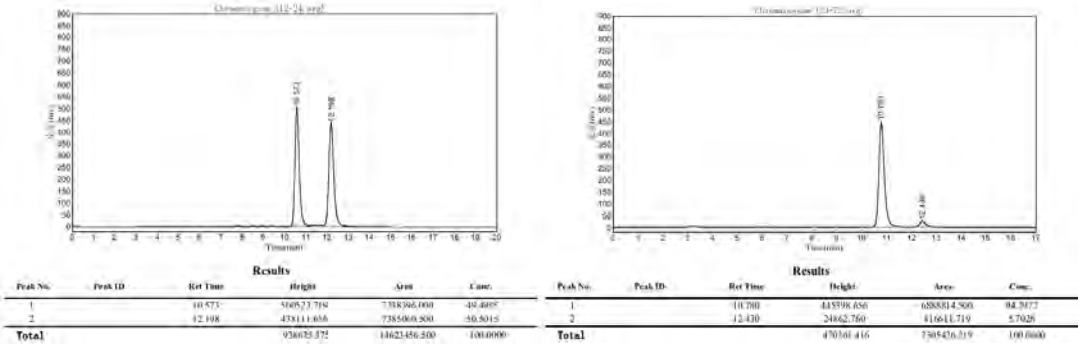
99% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); $[\alpha]^{20}_D$ +61.0 (*c* 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.31 (m, 13H), 7.22-7.13 (m, 3H), 6.84-6.82 (m, 2H), 3.52-3.45 (m, 1H), 2.99-2.92 (m, 1H), 2.14-2.07 (m, 1H), 1.97-1.81 (m, 2H), 1.75-1.63 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 145.2, 143.6, 137.9, 136.1, 130.2, 129.3, 128.30, 128.28, 127.5, 126.5, 126.14, 126.13, 44.6, 41.7, 25.1, 21.9 ppm; IR (film) ν 3058, 3028, 2987, 2948, 2869, 1752, 1597, 1576, 1496, 1463, 1443, 1421, 1372, 1338, 1315, 1239, 1185, 1134, 1073, 1030, 803, 756, 700, 612, 584, 516; HRMS (EI): m/z Exact mass calcd for $C_{29}H_{24}O_2$ $[M]^+$: 404.1776, found: 404.1780; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 254 nm, 25 °C); t_r (*S, S*) = 9.052 min, t_r (*R, R*) = 10.238 min, ee (trans) = 92%.



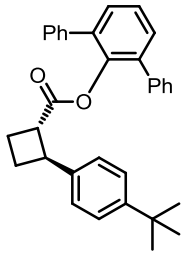
(1*S*, 2*S*)-[1,1':3',1''-Terphenyl]-2'-yl 2-(4-methoxyphenyl)cyclobutanecarboxylate 3hb



90% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); $[\alpha]^{20}_D$ +65.4 (*c* 0.98, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.31 (m, 13H), 6.77-6.72 (m, 4H), 3.77 (s, 3H), 3.44-3.37 (m, 1H), 2.92-2.86 (m, 1H), 2.09-2.01 (m, 1H), 1.92-1.79 (m, 2H), 1.73-1.62 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 158.0, 145.1, 137.9, 136.1, 135.8, 130.1, 129.2, 128.3, 127.5, 127.2, 126.4, 113.7, 55.4, 45.0, 41.2, 25.3, 21.7 ppm; IR (film) ν 3057, 3031, 2989, 2950, 2870, 2834, 1751, 1612, 1582, 1514, 1463, 1442, 1421, 1372, 1304, 1247, 1177, 1132, 1073, 1035, 1009, 918, 830, 803, 757, 701, 612, 583, 543, 531, 515; LRMS (ESI): m/z 457.2 $[M+Na]^+$; HRMS (ESI): m/z Exact mass calcd for $C_{30}H_{26}NaO_3$ $[M+Na]^+$: 457.1774, found: 457.1770; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 254 nm, 25 °C); t_r (*S, S*) = 10.780 min, t_r (*R, R*) = 12.430 min, ee (trans) = 89%.

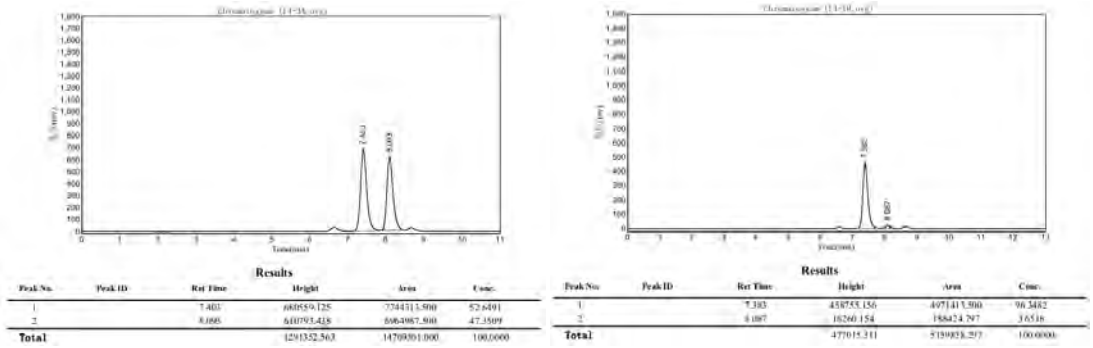


(1*S*, 2*S*)-[1,1':3',1''-Terphenyl]-2'-yl 2-(4-(tert-butyl)phenyl)cyclobutanecarboxylate 3hc

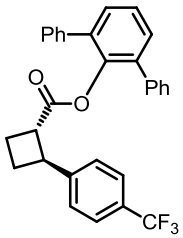


97% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); $[\alpha]^{20}_D$ +55.9 (*c* 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.39 (m, 4H), 7.37-7.34 (m, 3H), 7.33-7.29 (m, 6H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 3.49-3.42 (m, 1H), 2.97-2.91 (m, 1H), 2.10-2.03 (m, 1H), 1.96-1.79 (m, 2H), 1.71-1.61 (m, 1H), 1.31 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 148.9, 145.2, 140.5, 137.9, 136.1, 130.1, 129.2, 128.3, 127.5, 126.4, 125.9, 125.1, 44.8, 41.4, 34.5, 31.6, 25.2, 21.9 ppm; IR (film) ν 3057, 3030, 2962, 2904, 2867, 1753, 1597, 1500, 1463, 1420, 1363, 1268, 1239, 1185, 1134, 1073, 1021, 919, 831, 802, 756, 701, 613, 584, 567, 515; HRMS (EI): m/z Exact mass calcd for $C_{33}H_{32}O_2$ $[M]^+$: 460.2402, found: 460.2398;

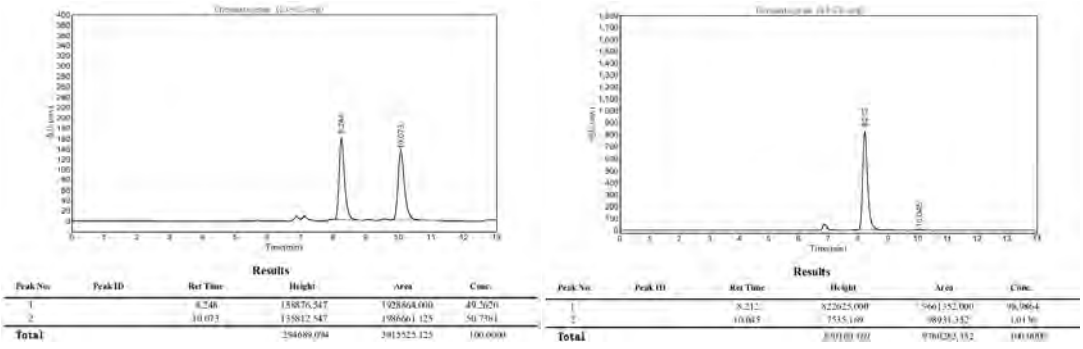
enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 254 nm, 25 °C); t_r (*S, S*) = 7.383 min, t_r (*R, R*) = 8.087 min, ee (trans) = 93%.



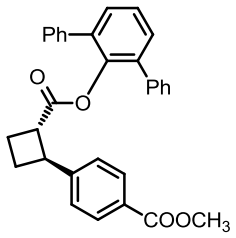
(1*S*, 2*S*)-[1,1':3',1''-Terphenyl]-2'-yl 2-(4-(trifluoromethyl)phenyl)cyclobutanecarboxylate 3hd



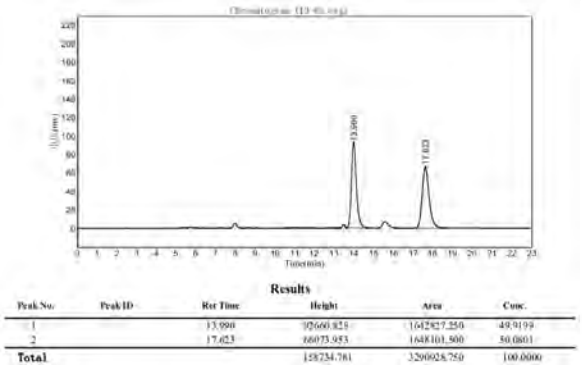
73% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); $[\alpha]^{20}_D$ +57.1 (*c* 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (m, 9H), 7.35-7.30 (m, 6H), 6.88 (d, *J* = 12.0 Hz, 2H), 3.54-3.47 (m, 1H), 2.97-2.91 (m, 1H), 2.16-2.08 (m, 1H), 1.98-1.84 (m, 2H), 1.77-1.67 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 147.5, 145.1, 137.9, 136.1, 130.2, 129.3, 128.3, 127.9 (q, *J* = 74.3 Hz), 127.6, 126.6, 126.5, 125.2 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 270.1 Hz), 44.6, 41.4, 24.9, 21.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4 ppm; IR (film) ν 3853, 3649, 3058, 3032, 2951, 2871, 1752, 1618, 1597, 1499, 1464, 1443, 1421, 1326, 1240, 1164, 1125, 1068, 1018, 920, 838, 802, 757, 701, 612, 602, 584, 515; LRMS (ESI): m/z 473.1 $[M+H]^+$; HRMS (ESI): m/z Exact mass calcd for $C_{30}H_{24}O_2F_3$ $[M+H]^+$: 473.1723, found: 473.1714; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 254 nm, 25 °C); t_r (*S, S*) = 8.212 min, t_r (*R, R*) = 10.045 min, ee (trans) = 98%.

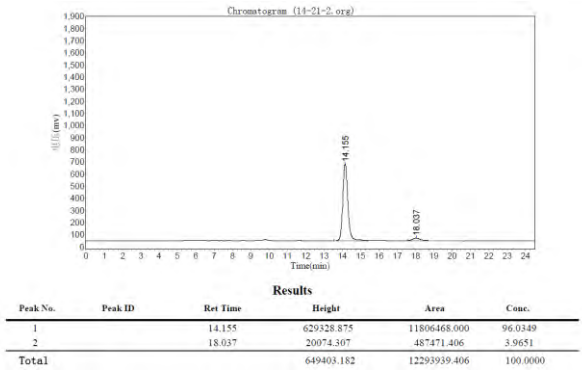


Methyl 4-((1*S*, 2*S*)-2-(([1,1':3',1''-terphenyl]-2'-yloxy)carbonyl)cyclobutyl)benzoate 3he

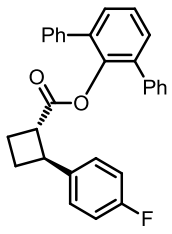


36% yield. Purified by chromatography on silica gel using 25% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (5% acetone/petroleum ether); $[\alpha]^{20}_D$ +74.1 (*c* 0.24, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.42-7.33 (m, 13H), 6.85 (d, *J* = 8.1 Hz, 2H), 3.92 (s, 3H), 3.54-3.47 (m, 1H), 2.99-2.92 (m, 1H), 2.17-2.09 (m, 1H), 1.98-1.84 (m, 2H), 1.77-1.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 167.2, 148.9, 145.1, 137.9, 136.1, 130.2, 129.7, 129.2, 128.3, 128.0, 127.6, 126.5, 126.1, 52.2, 44.4, 41.6, 25.0, 21.9 ppm; IR (film) ν 3853, 3675, 3057, 2950, 1752, 1720, 1609, 1492, 1435, 1420, 1279, 1184, 1136, 1110, 1019, 758, 701, 584; HRMS (EI): m/z Exact mass calcd for $C_{31}H_{26}O_4$ $[M]^+$: 462.1831, found: 462.1835; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 254 nm, 25 °C); t_r (*S, S*) = 14.155 min, t_r (*R, R*) = 18.037 min, ee (trans) = 92%.



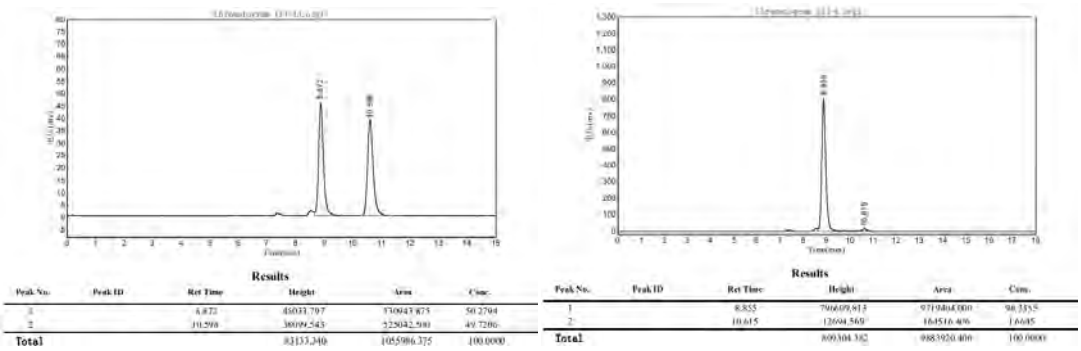


(1*S*, 2*S*)-[1,1':3',1''-Terphenyl]-2'-yl 2-(4-fluorophenyl)cyclobutanecarboxylate 3hf



78% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); $[\alpha]^{20}_D$ +67.5 (*c* 1.02, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.31 (m, 13H), 6.88-6.83 (m, 2H), 6.76-6.72 (m, 2H), 3.46-3.39 (m, 1H), 2.92-2.85 (m, 1H), 2.11-2.03 (m, 1H), 1.93-1.80 (m, 2H), 1.74-1.63 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 161.4 (d, *J* = 242.7 Hz), 145.1, 139.2 (d, *J* = 3.1 Hz), 137.9, 136.1, 130.2, 129.2, 128.3, 127.6 (d, *J* = 7.9 Hz), 127.5, 126.5, 115.0 (d, *J* = 21.1 Hz), 44.9, 41.0, 25.2, 21.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.2 ppm; IR (film) ν 3057, 3033, 2988, 2949, 2871, 1752, 1604, 1509, 1463, 1443, 1421, 1373, 1317, 1224, 1185, 1157, 1135, 1073, 1017, 833, 803, 757, 701, 613, 584, 530; LRMS (ESI): m/z 445.0 $[M+Na]^+$; HRMS (ESI): m/z Exact mass calcd for $C_{29}H_{23}FNaO_2$ $[M+Na]^+$: 445.1574, found: 445.1586; enantiomeric excess was determined by

HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 254 nm, 25 °C); t_r (*S*, *S*) = 8.855 min, t_r (*R, R*) = 10.615 min, ee (trans) = 97%.



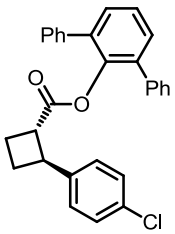
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.872	45033.797	730943.875	50.2794
2		10.598	38099.543	725042.500	49.7206
Total			83133.340	1455986.375	100.0000

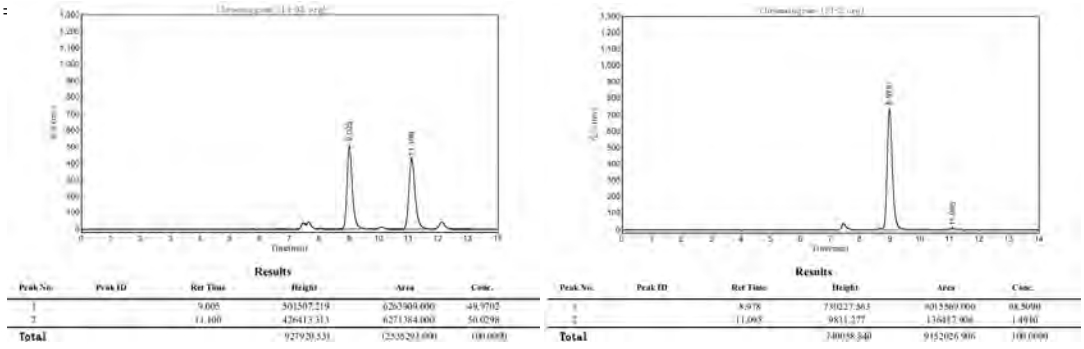
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.855	796609.813	9719464.000	98.3355
2		10.615	12694.569	164516.406	1.6645
Total			809304.382	9883920.406	100.0000

(1*S*, 2*S*)-[1,1':3',1''-Terphenyl]-2'-yl 2-(4-chlorophenyl)cyclobutanecarboxylate 3hg



96% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); $[\alpha]^{20}_D$ +70.5 (*c* 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 13H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 3.45-3.38 (m, 1H), 2.92-2.85 (m, 1H), 2.11-2.03 (m, 1H), 1.92-1.80 (m, 2H), 1.74-1.64 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 145.1, 142.0, 137.9, 136.1, 131.8, 130.2, 129.2, 128.32, 128.27, 127.6, 127.5, 126.5, 44.7, 41.1, 25.0, 21.8 ppm; IR (film) ν 3058, 3030, 2988, 2949, 1751, 1597, 1492, 1463, 1421, 1372, 1317, 1239, 1185, 1135, 1091, 1073, 1014, 826, 802, 757, 701, 612, 584, 510; HRMS (EI): m/z Exact mass calcd for $C_{29}H_{23}O_2Cl$ $[M]^+$: 438.1387, found: 438.1385; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 254 nm, 25 °C); t_r (*S*, *S*) = 8.978 min, t_r (*R, R*)



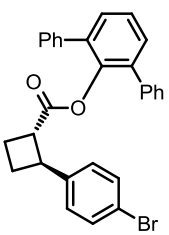
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.005	301507.219	6263909.000	49.9702
2		11.100	426413.313	6271384.000	50.0298
Total			727920.531	12535293.000	100.0000

Results

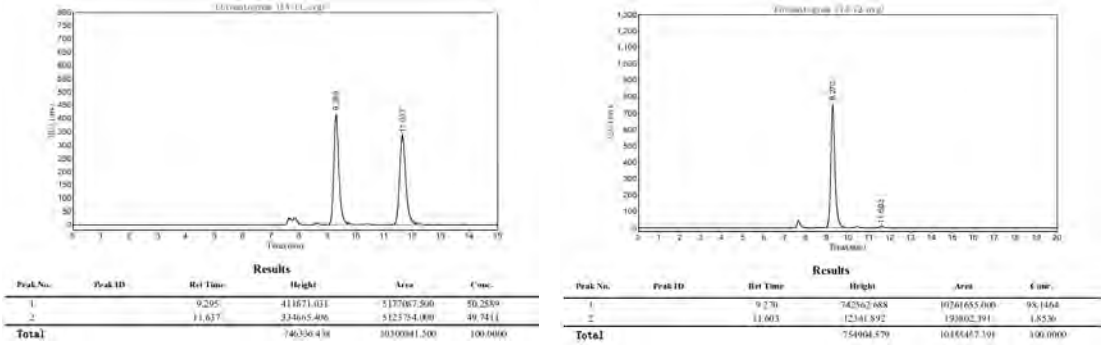
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.978	730227.563	8013560.000	88.5090
2		11.095	9831.277	136817.906	1.4910
Total			740058.840	9152026.906	100.0000

(1*S*, 2*S*)-[1,1':3',1''-Terphenyl]-2'-yl 2-(4-bromophenyl)cyclobutanecarboxylate 3hh



92% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether);

$[\alpha]^{20}_{D}$ +62.5 (*c* 1.00, $CHCl_3$); m.p. 102-105 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.28 (m, 15H), 6.65 (d, *J* = 8.4 Hz, 2H), 3.43-3.37 (m, 1H), 2.928-2.85 (m, 1H), 2.12-2.05 (m, 1H), 1.92-1.81 (m, 2H), 1.75-1.64 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 145.1, 142.5, 137.9, 136.1, 131.3, 130.2, 129.2, 128.3, 127.9, 127.6, 126.5, 119.9, 44.7, 41.1, 25.0, 21.8 ppm; IR (film) ν 3057, 3030, 2987, 2947, 1752, 1596, 1489, 1463, 1442, 1421, 1396, 1371, 1315, 1239, 1185, 1135, 1072, 1010, 820, 802, 758, 737, 710, 612, 584, 516; LRMS (ESI): m/z 505.0 $[M+Na]^{+}$; HRMS (ESI): m/z Exact mass calcd for $C_{29}H_{23}BrNaO_2$ $[M+Na]^{+}$: 505.0774, found: 505.0785; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 254 nm, 25 °C); t_r (*S, S*) = 9.270 min, t_r (*R, R*) = 11.603 min, ee (trans) = 96%.



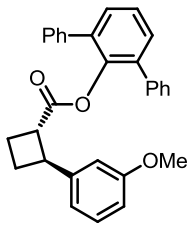
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.295	411671.031	5137087.500	50.2539
2		11.637	334665.406	5125794.000	49.7461
Total			746336.438	10300041.500	100.0000

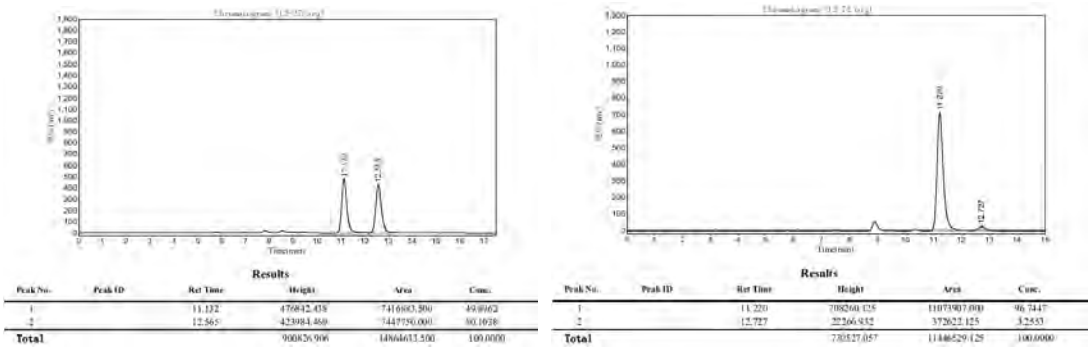
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.270	742562.688	10261655.000	95.1464
2		11.603	12341.892	193802.391	1.8536
Total			754904.579	10455457.391	100.0000

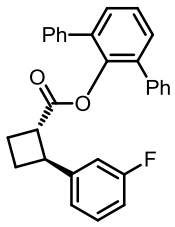
(1*S*, 2*S*)-[1,1':3',1''-Terphenyl]-2'-yl 2-(3-methoxyphenyl)cyclobutanecarboxylate 3hi



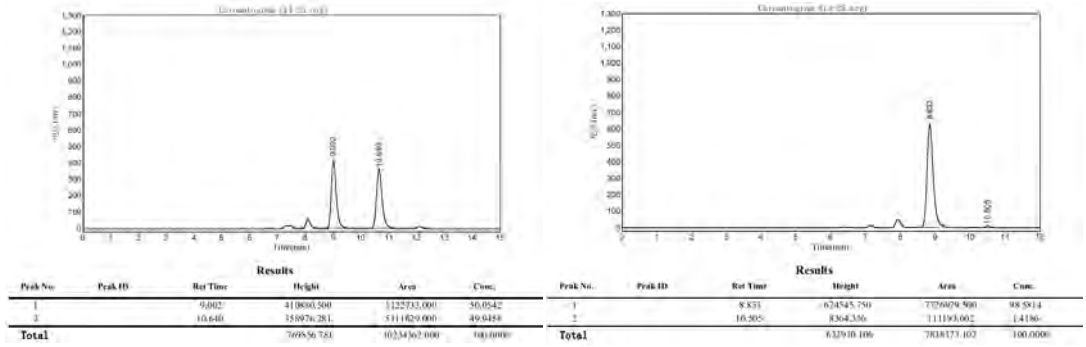
91% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); $[\alpha]^{20}_{D}$ +64.4 (*c* 0.69, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.29 (m, 13H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.71 (dd, *J* = 2.4, 8.0 Hz, 1H), 6.53 (s, 1H), 6.43 (d, *J* = 7.6 Hz, 1H), 3.74 (s, 3H), 3.46-3.39 (m, 1H), 2.99-2.93 (m, 1H), 2.12-2.03 (m, 1H), 1.96-1.81 (m, 2H), 1.74-1.63 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 159.6, 145.2, 145.1, 137.9, 136.1, 130.1, 129.3, 129.2, 128.3, 127.5, 126.5, 118.6, 112.0, 111.5, 55.3, 44.6, 41.9, 25.3, 21.7 ppm; IR (film) ν 3056, 3030, 2949, 2869, 2834, 1752, 1601, 1582, 1490, 1463, 1421, 1370, 1317, 1289, 1260, 1239, 1183, 1158, 1134, 1073, 1045, 916, 861, 803, 756, 700, 612, 583, 516; HRMS (EI): m/z Exact mass calcd for $C_{30}H_{26}O_3$ $[M]^{+}$: 434.1882, found: 434.1887; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 254 nm, 25 °C); t_r (*S, S*) = 11.220 min, t_r (*R, R*) = 12.727 min, ee (trans) = 93%.



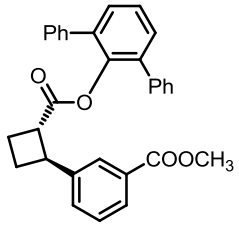
(1*S*, 2*S*)-[1,1':3',1''-Terphenyl]-2'-yl 2-(3-fluorophenyl)cyclobutanecarboxylate 3hj



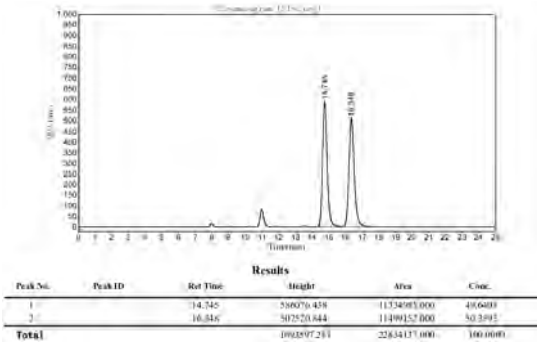
84% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); $[\alpha]^{20}_D$ +68.3 (*c* 0.37, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.29 (m, 13H), 7.18-7.12 (m, 1H), 6.87-6.82 (m, 1H), 6.60-6.55 (m, 2H), 3.48-3.41 (m, 1H), 2.96-2.89 (m, 1H), 2.13-2.05 (m, 1H), 1.95-1.82 (m, 2H), 1.75-1.64 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 162.9 (d, *J* = 244.3 Hz), 146.2 (d, *J* = 7.3 Hz), 145.1, 137.9, 136.1, 130.2, 129.7 (d, *J* = 8.2 Hz), 129.2, 128.3, 127.6, 126.5, 121.8 (d, *J* = 2.8 Hz), 113.2 (d, *J* = 21.1 Hz), 113.0 (d, *J* = 21.0 Hz), 44.6, 41.4, 25.1, 21.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.5 ppm; IR (film) ν 3058, 3032, 2950, 2870, 1752, 1614, 1588, 1490, 1463, 1442, 1421, 1371, 1316, 1272, 1240, 1207, 1184, 1136, 1073, 1027, 967, 866, 843, 802, 786, 757, 701, 612, 584; LRMS (ESI): m/z 423.2 $[M+H]^+$; HRMS (ESI): m/z Exact mass calcd for $C_{29}H_{24}O_2F$ $[M+H]^+$: 423.1755, found: 423.1751; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 254 nm, 25 °C); t_r (*S, S*) = 8.833 min, t_r (*R, R*) = 10.505 min, ee (trans) = 97%.



Methyl 3-((1*S*,2*S*)-2-(([1,1':3',1''-terphenyl]-2'-yloxy)carbonyl)cyclobutyl)benzoate 3hk

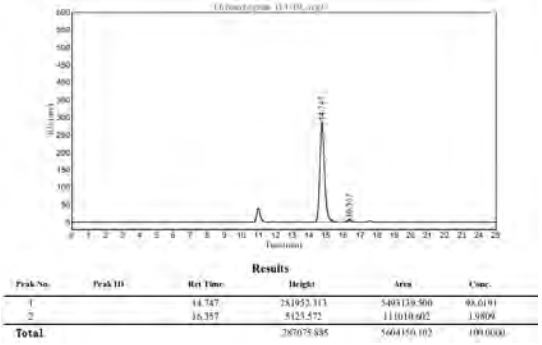


95% yield. Purified by chromatography on silica gel using 25% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (5% acetone/petroleum ether); $[\alpha]^{20}_D$ +55.2 (*c* 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.74 (s, 1H), 7.40-7.36 (m, 7H), 7.30-7.22 (m, 7H), 6.94 (d, *J* = 7.6 Hz, 1H), 3.90 (s, 3H), 3.48-3.41 (m, 1H), 3.00-2.94 (m, 1H), 2.15-2.09 (m, 1H), 1.98-1.83 (m, 2H), 1.79-1.70 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 167.2, 145.0, 143.8, 137.8, 136.0, 131.1, 130.11, 130.09, 129.2, 128.4, 128.2, 127.5, 127.2, 126.5, 52.2, 44.5, 41.7, 25.3, 21.6 ppm; IR (film) ν 3058, 3031, 2990, 2950, 1752, 1721, 1587, 1498, 1458, 1443, 1421, 1290, 1240, 1207, 1185, 1136, 1110, 1089, 1027, 914, 803, 755, 701, 612, 584, 514; HRMS (EI): m/z Exact mass calcd for $C_{31}H_{26}O_4$ $[M]^+$: 462.1831, found: 462.1832; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 254 nm, 25 °C); t_r (*S, S*) = 14.747 min, t_r (*R, R*) = 16.357 min, ee (trans) = 96%.



Results

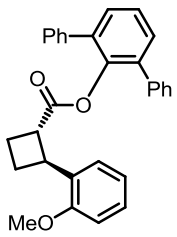
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.745	5869?0.438	11?34085.000	48.6403
2		16.346	5025?0.844	11499157.800	50.3595
Total			10?3597.283	22634137.000	100.0000



Results

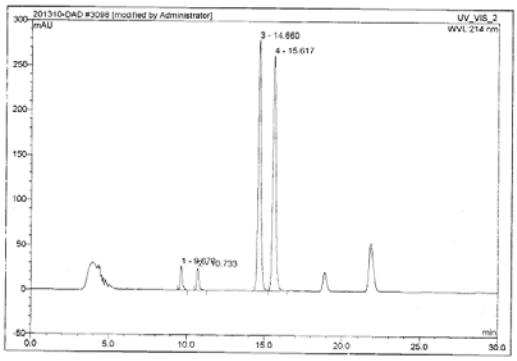
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.747	283952.313	5493139.500	98.0191
2		16.357	5125.572	110010.602	1.9809
Total			287078.885	5604150.102	100.0000

(1*S*, 2*S*)-[1,1':3',1''-Terphenyl]-2'-yl 2-(2-methoxyphenyl)cyclobutanecarboxylate 3hl

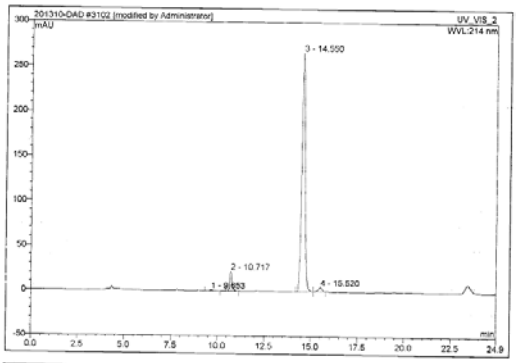


51% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); $[\alpha]^{20}_D$ +99.3 (*c* 0.76, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 7H), 7.29-7.28 (m, 6H),7.18-7.14 (m, 1H), 6.84-6.74 (m, 3H), 3.65-3.58 (m, 4H), 3.17-3.10 (m, 1H), 2.18-2.11 (m, 1H), 1.84-1.71 (m, 2H), 1.68-1.61 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 157.4, 145.2, 137.9, 136.1, 131.5, 130.1, 129.3, 128.2, 127.4, 127.3, 126.8, 126.4, 120.3, 110.1, 55.1, 42.4, 38.4, 26.1, 22.3 ppm; IR (film) ν 3058, 3030, 2990, 2950, 1754, 1600, 1586, 1493, 1463, 1437, 1420, 1375, 1243, 1185, 1131, 1029, 801, 754, 735, 701, 612, 583; HRMS (EI): m/z Exact mass calcd for $C_{30}H_{26}O_3$ $[M]^+$: 434.1882, found: 434.1879; enantiomeric excess was determined by HPLC with a Chiralcel IF-3 column

(*n*-hexane/*i*-propanol = 98/2, 0.7 mL/min, 214 nm, 25 °C); t_r (*S, S*) = 14.550 min, t_r (*R, R*) = 15.520 min, ee (trans) = 96%.

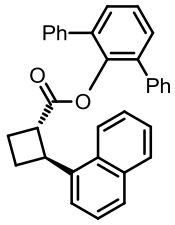


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.67	n.a.	26.811	4.145	3.24	n.a.	BMB
2	10.73	n.a.	24.479	4.171	3.26	n.a.	BMB
3	14.66	n.a.	278.996	59.915	46.76	n.a.	BM
4	15.62	n.a.	261.820	59.909	46.75	n.a.	MB
Total:			592.106	128.141	100.00	0.000	

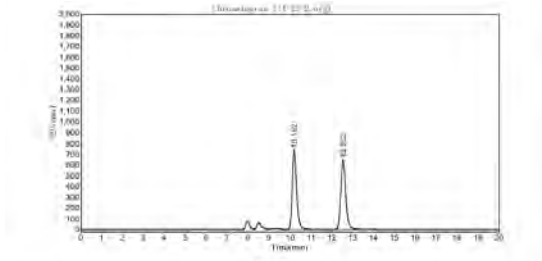


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.65	n.a.	0.720	0.123	0.21	n.a.	BMB*
2	10.72	n.a.	21.756	3.423	5.74	n.a.	BMB
3	14.55	n.a.	265.643	55.119	92.38	n.a.	BM
4	15.52	n.a.	4.406	0.998	1.67	n.a.	MB
Total:			292.524	59.663	100.00	0.000	

(1*S*, 2*S*)-[1,1':3',1''-Terphenyl]-2'-yl 2-(naphthalen-1-yl)cyclobutanecarboxylate 3hm

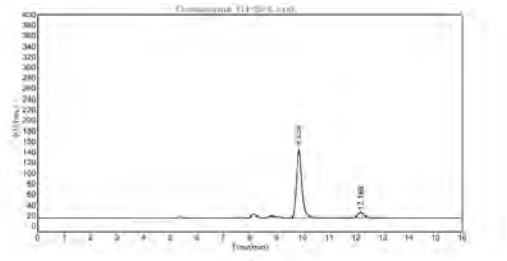


96% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); $[\alpha]^{20}_D$ +97.3 (*c* 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (m, 1H), 7.76-7.74 (m, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.46-7.34 (m, 10H), 7.29-7.20 (m, 6H), 6.99 (d, *J* = 6.8 Hz, 1H), 4.05-3.98 (m, 1H), 3.41-3.40 (m, 1H), 2.44-2.35 (m, 1H), 1.93-1.78 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 145.1, 139.0, 137.8, 136.1, 133.8, 131.3, 130.1, 129.2, 128.7, 128.2, 127.4, 126.9, 126.5, 125.8, 125.7, 125.5, 124.1, 122.6, 41.9, 40.2, 27.7, 22.1 ppm; IR (film) ν 3055, 2948, 2868, 1752, 1597, 1576, 1508, 1499, 1463, 1420, 1368, 1306, 1265, 1240, 1184, 1133, 1073, 798, 778, 756, 737, 701, 612, 584, 514, 448; LRMS (ESI): m/z 477.1 $[M+Na]^+$; HRMS (EI): m/z Exact mass calcd for $C_{33}H_{26}O_2$ $[M]^+$: 454.1927, found: 454.1922; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 254 nm, 25 °C); t_r (*S, S*) = 9.838 min, t_r (*R, R*) = 12.168 min, ee (trans) = 83%.



Results

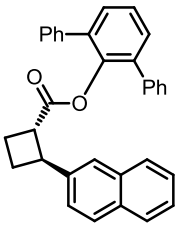
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.192	735613.250	10180729.000	50.2477
2		12.532	640007.875	10094237.000	49.7523
Total			1375621.125	21404918.000	100.0000



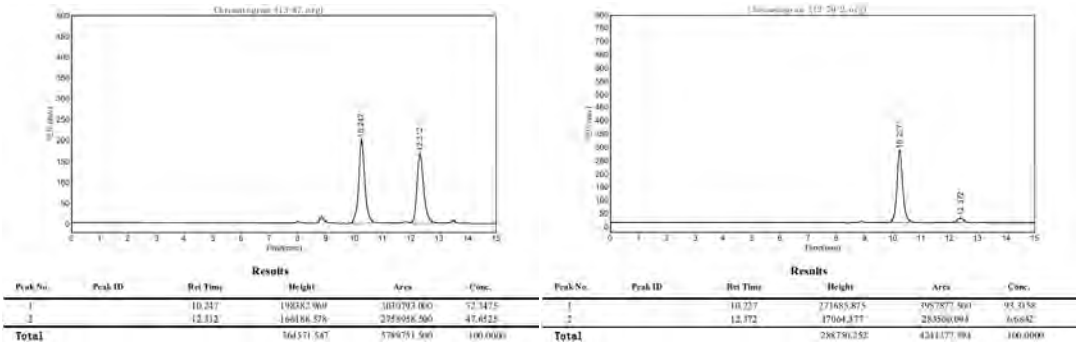
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.838	125094.375	1842096.000	91.7310
2		12.168	10857.109	166037.828	8.2682
Total			135951.484	2008133.828	100.0000

(1*S*, 2*S*)-[1,1':3',1''-Terphenyl]-2'-yl 2-(naphthalen-2-yl)cyclobutanecarboxylate 3hn



68% yield. Purified by chromatography on silica gel using 15% DCM/petroleum ether as eluent (colorless liquid): TLC R_f = 0.35 (40% DCM/petroleum ether); $[\alpha]^{20}_D$ +61.6 (*c* 0.98, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.71-7.65 (m, 2H), 7.42-7.25 (m, 16H), 7.04 (d, *J* = 8.0 Hz, 1H), 3.65-3.59 (m, 1H), 3.09-3.02 (m, 1H), 2.20-2.13 (m, 1H), 2.06-1.96 (m, 1H), 1.92-1.85 (m, 1H), 1.80-1.70 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 145.1, 141.0, 137.9, 136.1, 133.4, 132.2, 130.1, 129.2, 128.3, 128.0, 127.8, 127.7, 127.5, 126.5, 126.0, 125.4, 125.0, 124.3, 44.6, 42.0, 25.2, 21.8 ppm; IR (film) ν 3055, 2948, 2869, 1751, 1632, 1600, 1499, 1463, 1442, 1420, 1363, 1309, 1266, 1239, 1184, 1133, 1986, 1073, 1018, 856, 818, 802, 756, 701, 612, 477; LRMS (ESI): m/z 472.3 $[M+NH_4]^+$; HRMS (ESI): m/z Exact mass calcd for $C_{33}H_{30}O_2N$ $[M+NH_4]^+$: 472.2271, found: 472.2262; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 0.5 mL/min, 254 nm, 25 °C); t_r (*S, S*) = 10.227 min, t_r (*R, R*) = 12.372 min, ee (trans) = 87%;



Results

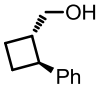
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.247	1983829.969	3810703.000	52.3475
2		12.312	1660186.578	2959958.500	47.6525
Total			3644371.547	5789751.500	100.0000

Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.227	2731685.875	5957877.500	93.0358
2		12.372	47064.377	283500.094	6.6642
Total			2887812.252	4241377.594	100.0000

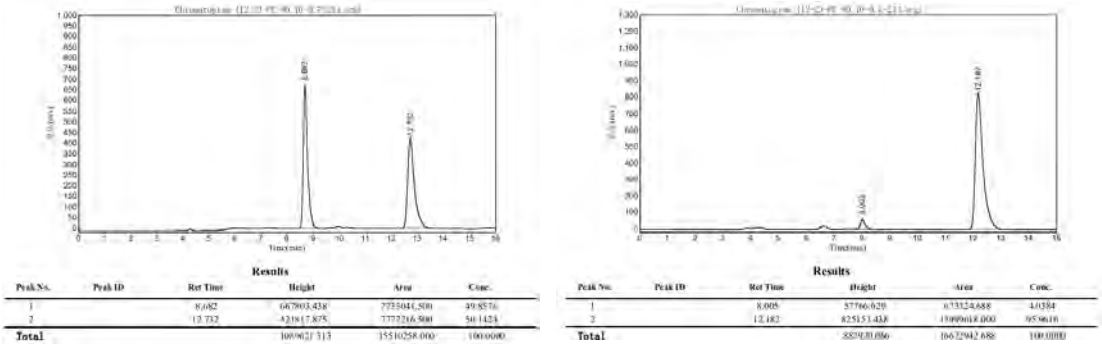
5. Reduction of compound 3ha

((1*S*, 2*S*)-2-Phenylcyclobutyl)methanol 5



To a suspension of lithium aluminum hydride (30 mg, 0.8 mmol) in THF (2 mL), a solution of (1*S*, 2*S*)-[1,1':3',1"-terphenyl]-2'-yl 2-phenylcyclobutanecarboxylate (80.8 mg, 0.2 mmol, 92% ee) in THF (2 mL) was added dropwise at 25℃. The mixture was reacted at 25℃ for 4 h and quenched with water. The aqueous layer was extracted with EtOAc three times, and the combined organic layer was dried and concentrated to provide the crude product. Flash chromatography on silica gel using 10% DCM/ petroleum ether as eluent gave the product as colorless oil 31.4 mg, 97% yield. TLC R_f = 0.35 (40% DCM/petroleum ether). $[\alpha]^{20}_D$ +52.7 (*c* 0.56, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.25-7.18 (m, 4H), 7.13-7.10 (m, 1H), 3.78-3.65 (m, 2H), 3.24-3.17 (m, 1H), 2.62-2.51 (m, 1H), 2.24-2.17 (m, 1H), 2.05-1.90 (m, 2H), 1.76-1.67 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 128.5, 126.8, 126.2, 66.5, 45.6,

43.1, 26.0, 21.2 ppm; IR (film) ν 3336, 3026, 2970, 2938, 2865, 1063, 1495, 1448, 1260, 1086, 1021, 747, 698; HRMS (EI): m/z Exact mass calcd for $C_{11}H_{14}O$ $[M]^+$: 162.1045, found: 162.1044; enantiomeric excess was determined by HPLC with a Chiralcel PC-2 column (*n*-hexane/*i*-propanol = 90/10, 0.7 mL/min, 214 nm, 25 °C); t_r (*R, R*) = 8.005 min, t_r (*S, S*) = 12.182 min, 92% ee.



Results

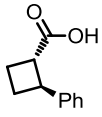
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.082	667803.438	7735041.500	49.8576
2		12.732	421817.875	7772216.500	50.1424
Total			1089621.313	15510258.000	100.0000

Results

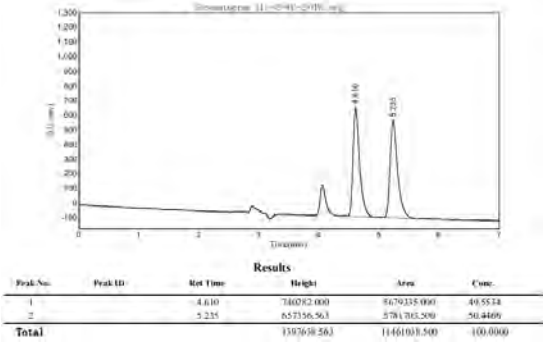
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.005	57766.020	673324.688	4.0384
2		12.182	825153.438	15990018.000	95.9616
Total			882919.086	16663342.688	100.0000

6. Hydrolysis of compound 3ha

(1*S*, 2*S*)-2-Phenylcyclobutanecarboxylic acid 6

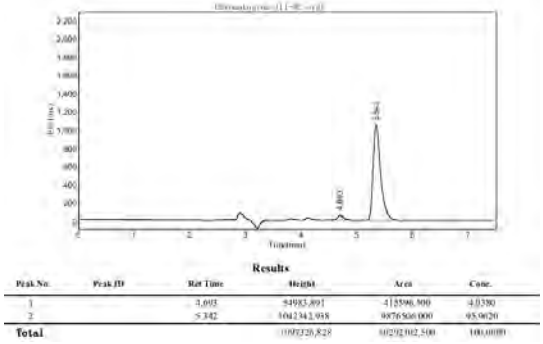


The adduct (1*S*, 2*S*)-[1,1':3',1''-terphenyl]-2'-yl 2-phenylcyclobutanecarboxylate (120 mg, 0.3 mmol, 92% ee) and potassium hydroxide (73 mg, 1.3 mmol) was dissolved in toluene (5 mL), and then the solution was heated to reflux for 2 h. After the mixture was cooled to 25° C, water (10 mL) was added, and the mixture was extracted with ethyl acetate (2× 10 mL). The aqueous phase was acidified with 1.0 M aqueous HCl to pH = 1. The acidified aqueous layer was extracted with ethyl acetate (3 × 10 mL), and the combined organic phase was washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by flash column chromatography on silica gel, eluting with 20/1 DCM/MeOH, TLC R_f = 0.30 (5% DCM/MeOH); gave the product (1*S*, 2*S*)-2-phenylcyclobutane-carboxylic acid 42 mg (colorless liquid, 89% yield). $[\alpha]^{20}_D$ +38.7 (*c* 1.83, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (br s, 1H), 7.18-7.03 (m, 5H), 3.70-3.63 (m, 1H), 3.11-3.04 (m, 1H), 2.21-2.10 (m, 2H), 2.07-1.95 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 143.4, 128.5, 126.6, 126.5, 45.1, 43.2, 25.4, 21.7 ppm; IR (film) ν 2947, 1694, 1495, 1421, 1260, 948, 743, 699, 552; HRMS (EI): m/z Exact mass calcd for $C_{11}H_{12}O_2$ $[M]^+$: 176.0837, found: 176.0833; enantiomeric excess was determined by HPLC with a Chiralcel PC-2 column (*n*-hexane/*i*-propanol/TFA = 90/10/0.1, 1.0 mL/min, 214 nm, 25 °C); t_r (*R, R*) = 4.693 min, t_r (*S, S*) = 5.342 min, 92% ee.



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		4.610	740082.000	5679335.000	49.5534
2		5.235	657356.563	5784305.500	50.4469
Total			1397438.563	11461013.500	100.0000

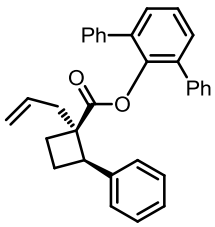


Results

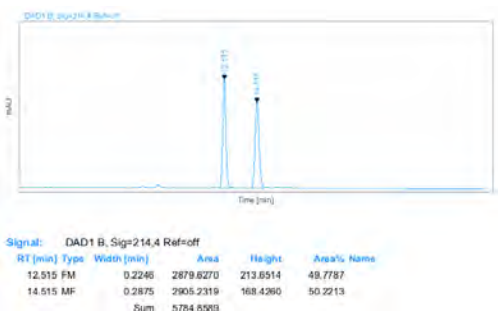
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		3.693	54983.891	4135590.500	4.0380
2		5.342	1042342.938	98276508.000	95.9620
Total			1097326.828	102412102.500	100.0000

7. Allylation of compound 3ha

(1*S*, 2*R*)-[1,1':3',1''-Terphenyl]-2'-yl 1-allyl-2-phenylcyclobutanecarboxylate 7

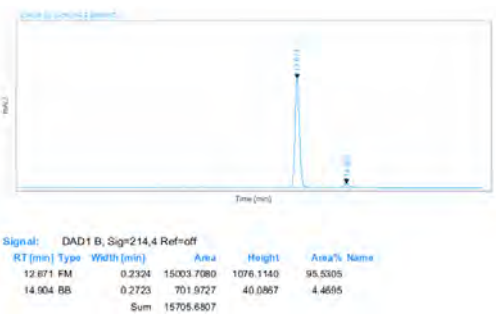


Under argon atmosphere, freshly distilled $^{i}Pr_2NH$ (84 μL, 0.598 mmol) was dissolved in 1 mL THF in a schlenk tube at -72 ° C, *n*-BuLi (2.5 M in hexane, 0.24 mL, 0.598 mmol) was added dropwised and the mixture was reacted for 20 min at -72 ° C. The solution of (1*S*, 2*S*)-[1,1':3',1"-terphenyl]-2'-yl 2-phenylcyclobutanecarboxylate (186 mg, 0.46 mmol) in 1 mL THF was added to the freshly prepared LDA-THF solution dropwised and then stirred for 1 h at -72 ° C. Then allyl iodide (63 μL, 0.69 mmol) was added to the mixture dropwised and was stirred for 1 h at -72 ° C, then removed the dry ice-ethonal bath. When the mixture was heated to 25℃ , the mixture was stirred for additional 1 h to accomplish the reaction. The solvent was evaporated and the residue was purified by flash column chromatography on silica gel (eluting with 10% DCM/petroleum ether, TLC R_f = 0.30 (25% DCM/ petroleum ether)) to get the product [1,1':3',1"-terphenyl]-2'-yl 1-allyl-2-phenylcyclo-butanecarboxylate (white solid, 202 mg, 99% yield). $[\alpha]^{20}_{D}$ -0.5 (*c* 0.70, $CHCl_3$); m.p. 83-85 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.26 (m, 13H), 7.00-6.98 (m, 3H), 6.55-6.53 (m, 2H), 5.31-5.21 (m, 1H), 4.95 (d, *J* = 13.6 Hz, 2H), 3.34 (t, *J* = 9.2 Hz, 1H), 2.17-2.00 (m, 3H), 1.92-1.72 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 145.0, 140.7, 138.2, 136.3, 134.2, 130.2, 129.7, 128.3, 127.8, 127.51, 127.47, 126.1, 125.8, 118.1, 54.4, 47.2, 42.5, 26.8, 21.9 ppm; IR(KBr): 3065, 3029, 2949, 1756, 1495, 1456, 1420, 1179, 1107, 1019, 918, 755, 700, 509; HRMS (EI): m/z Exact mass calcd for $C_{32}H_{28}O_2$ $[M]^+$: 444.2089, found: 444.2082. enantiomeric excess was determined by HPLC with a Chiralcel PC-4 column (*n*-hexane/*i*-propanol = 98/2, 0.4 mL/min, 214 nm, 25 °C); t_r (*S, R*) = 12.671 min, t_r (*R, S*) = 14.904 min, 91% ee. The absolute configuration was determined by ^{1}H NMR NOESY.



Signal: DAD1 B, Sig=214,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.515	FM	0.2246	2879.6270	213.6514	49.7787	
14.515	MF	0.2875	2905.2319	168.4260	50.2213	
		Sum	5784.8589			



Signal: DAD1 B, Sig=214,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
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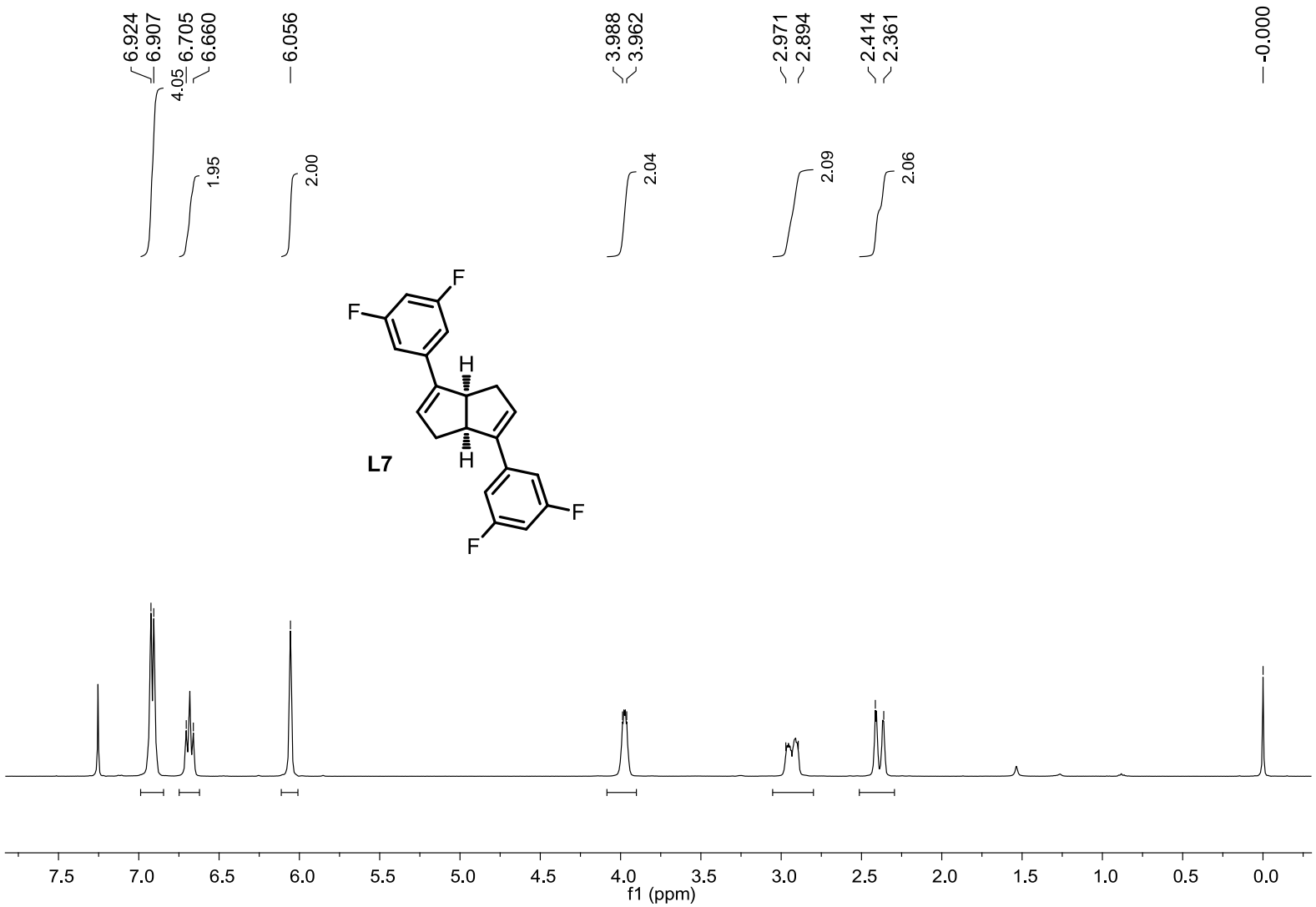
14.904	BB	0.2723	701.9727	40.0867	4.4695	
		Sum	15705.6807			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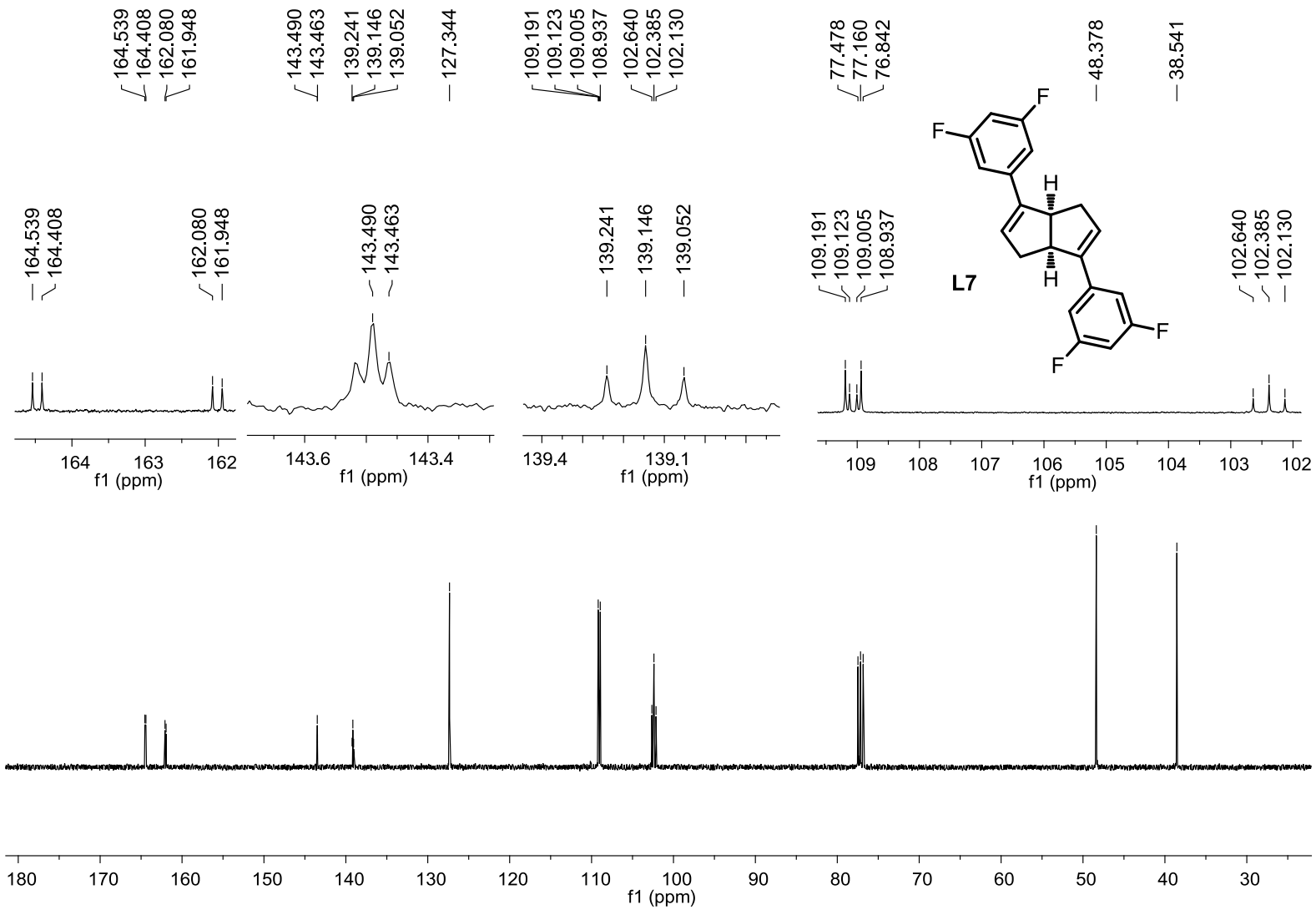
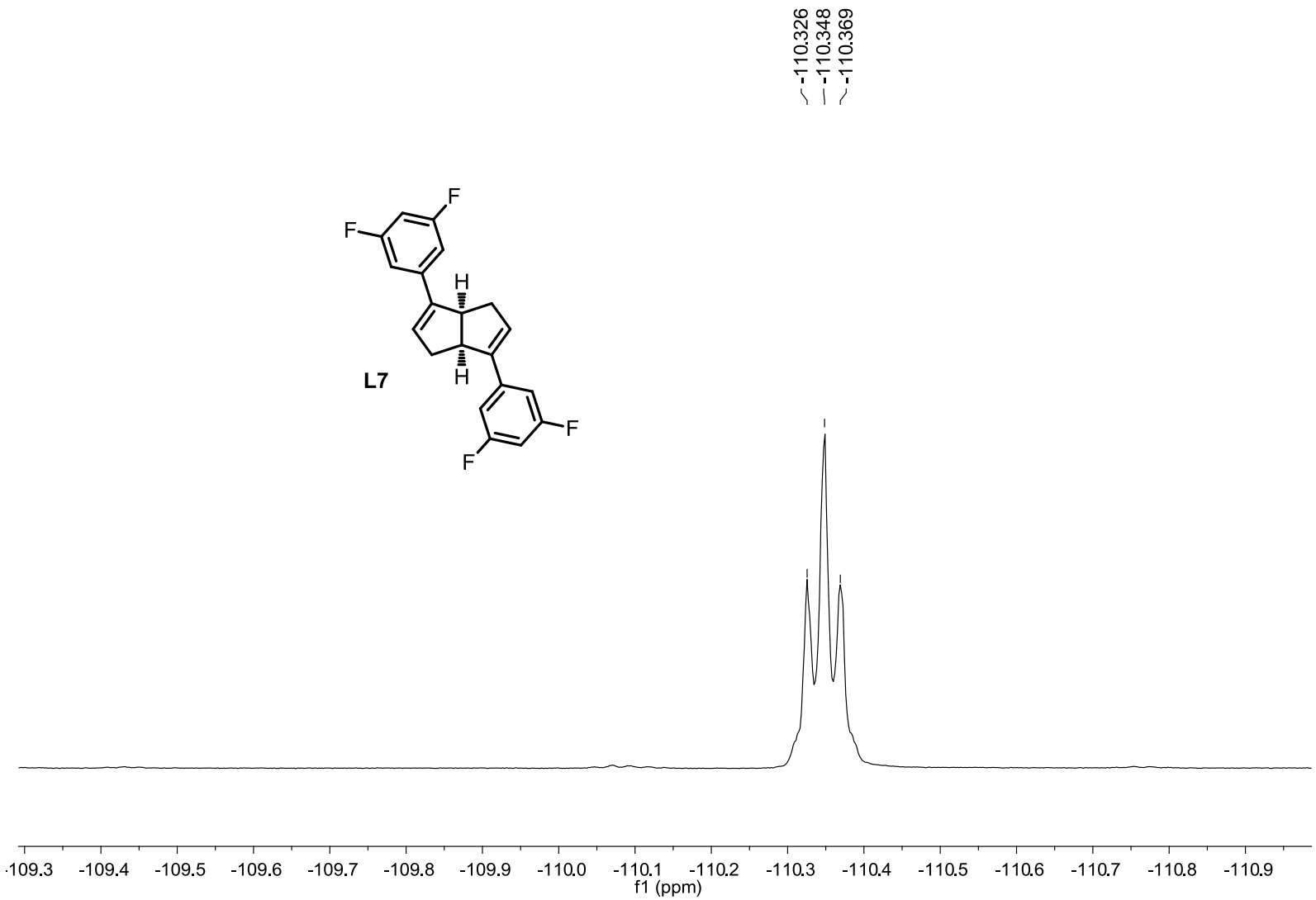
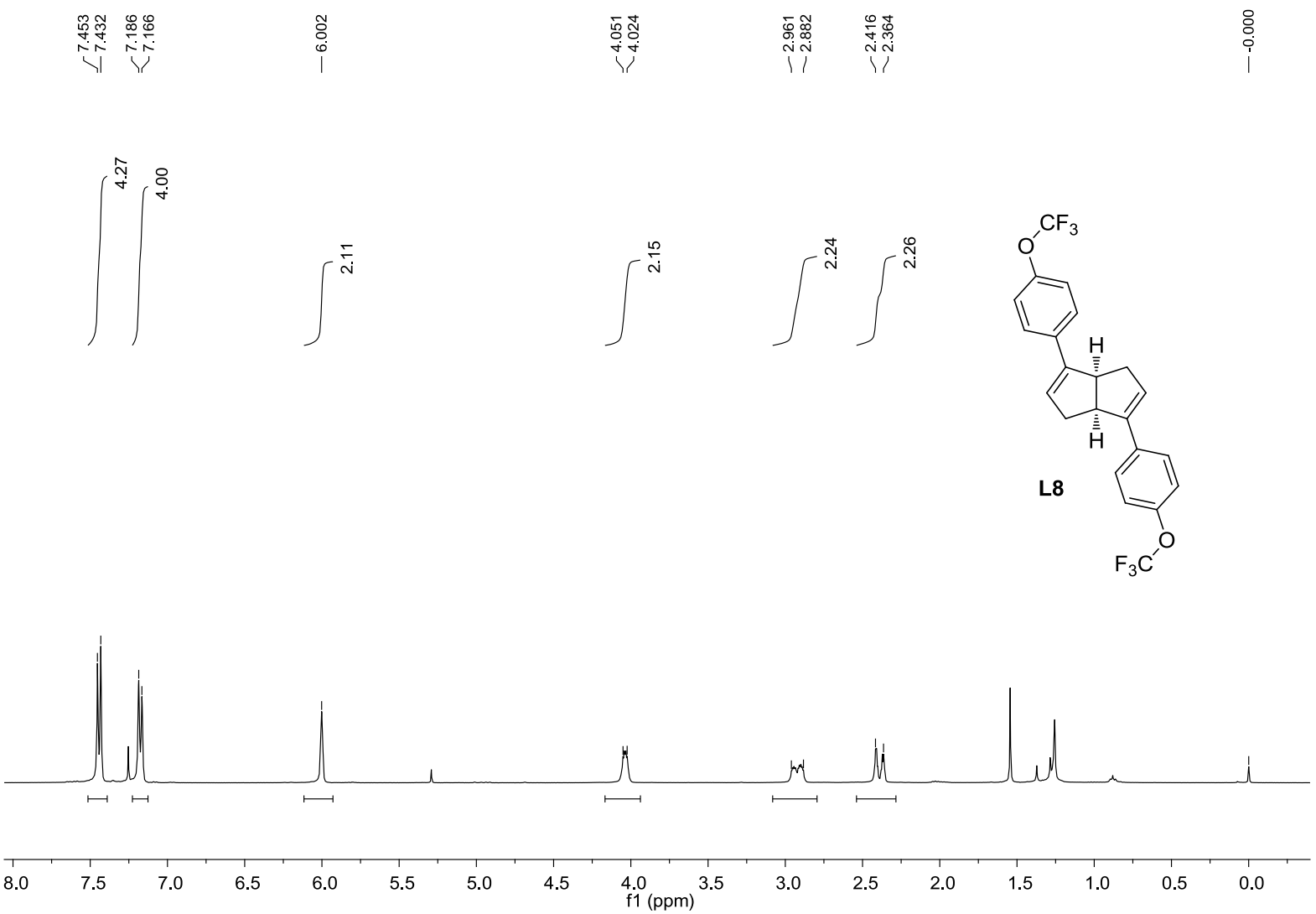
6.705
6.660
6.056
3.988
3.962
2.971
2.894
2.414
2.361
-0.000
4.05
1.95
2.00
2.04
2.09
2.06
F
F
H
H
F
F
L7
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.539
164.408
162.080
161.948
143.490
143.463
139.241
139.146
139.052
127.344
109.191
109.123
109.005
108.937
102.640
102.385
102.130
77.478
77.160
76.842
48.378
38.541
L7
f1 (ppm)


-110.326
-110.348
-110.369
F
F
H
H
L7
F
F
-109.3
-109.4
-109.5
-109.6
-109.7
-109.8
-109.9
-110.0
-110.1
-110.2
-110.3
-110.4
-110.5
-110.6
-110.7
-110.8
-110.9
f1 (ppm)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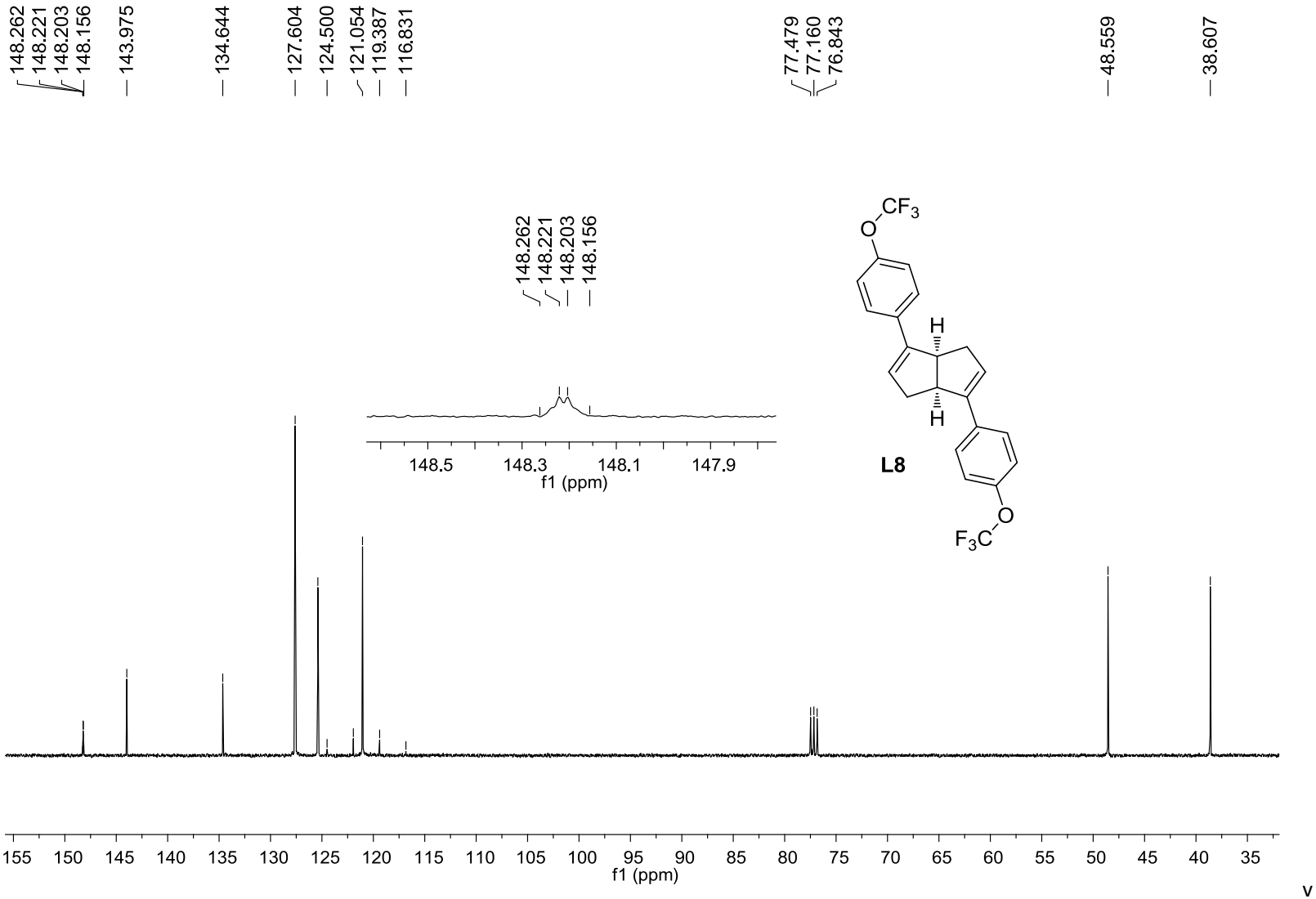
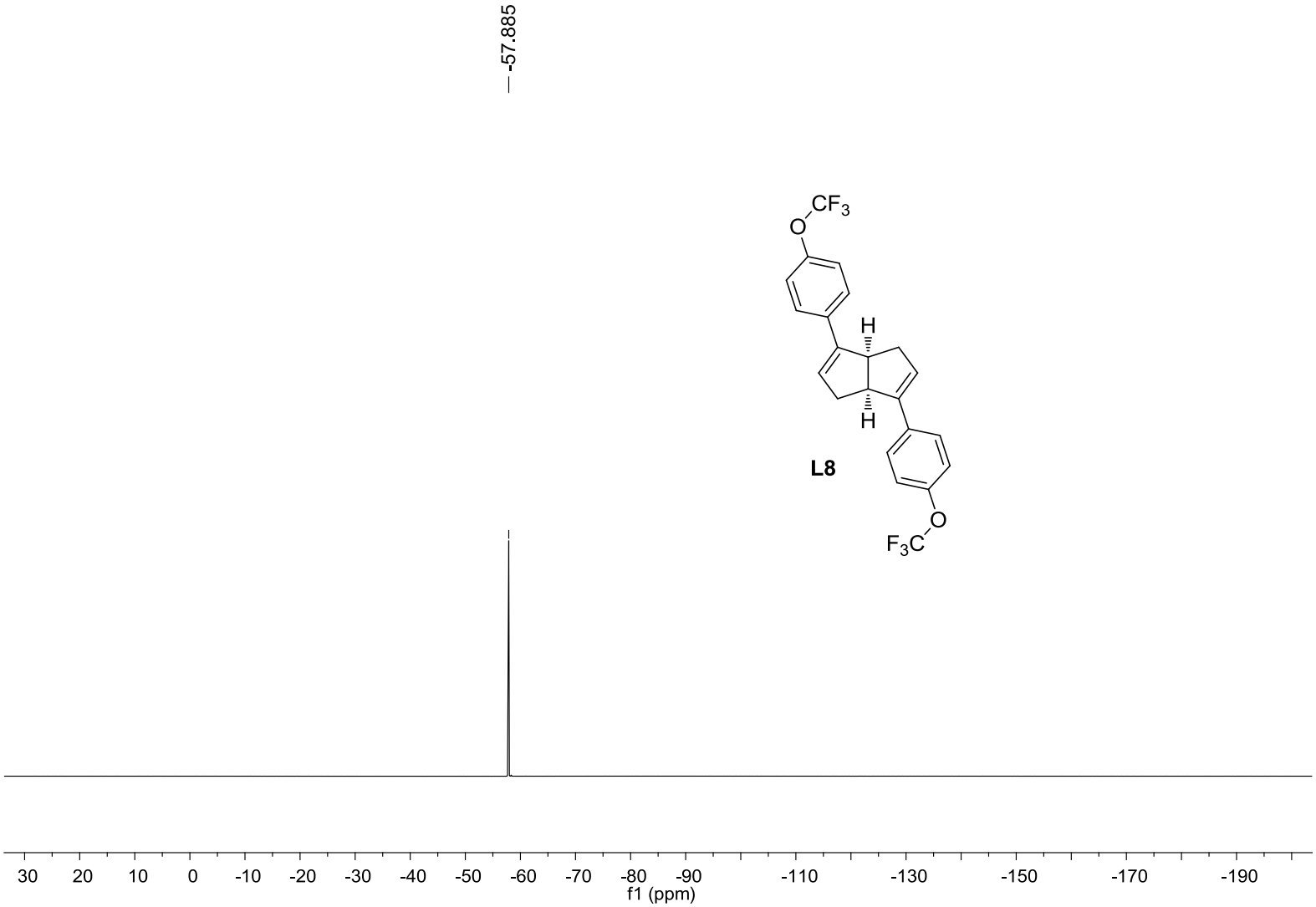
7.432
7.186
7.166
6.002
4.051
4.024
2.961
2.882
2.416
2.364
-0.000
4.27
4.00
2.11
2.15
2.24
2.26
CF3
O
H
H
L8
O
F3C
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


148.262
148.221
148.203
148.156
143.975
134.644
127.604
124.500
121.054
119.387
116.831
77.479
77.160
76.843
48.559
38.607
148.5
148.3
148.1
147.9
f1 (ppm)
CF3
O
H
H
L8
O
F3C
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)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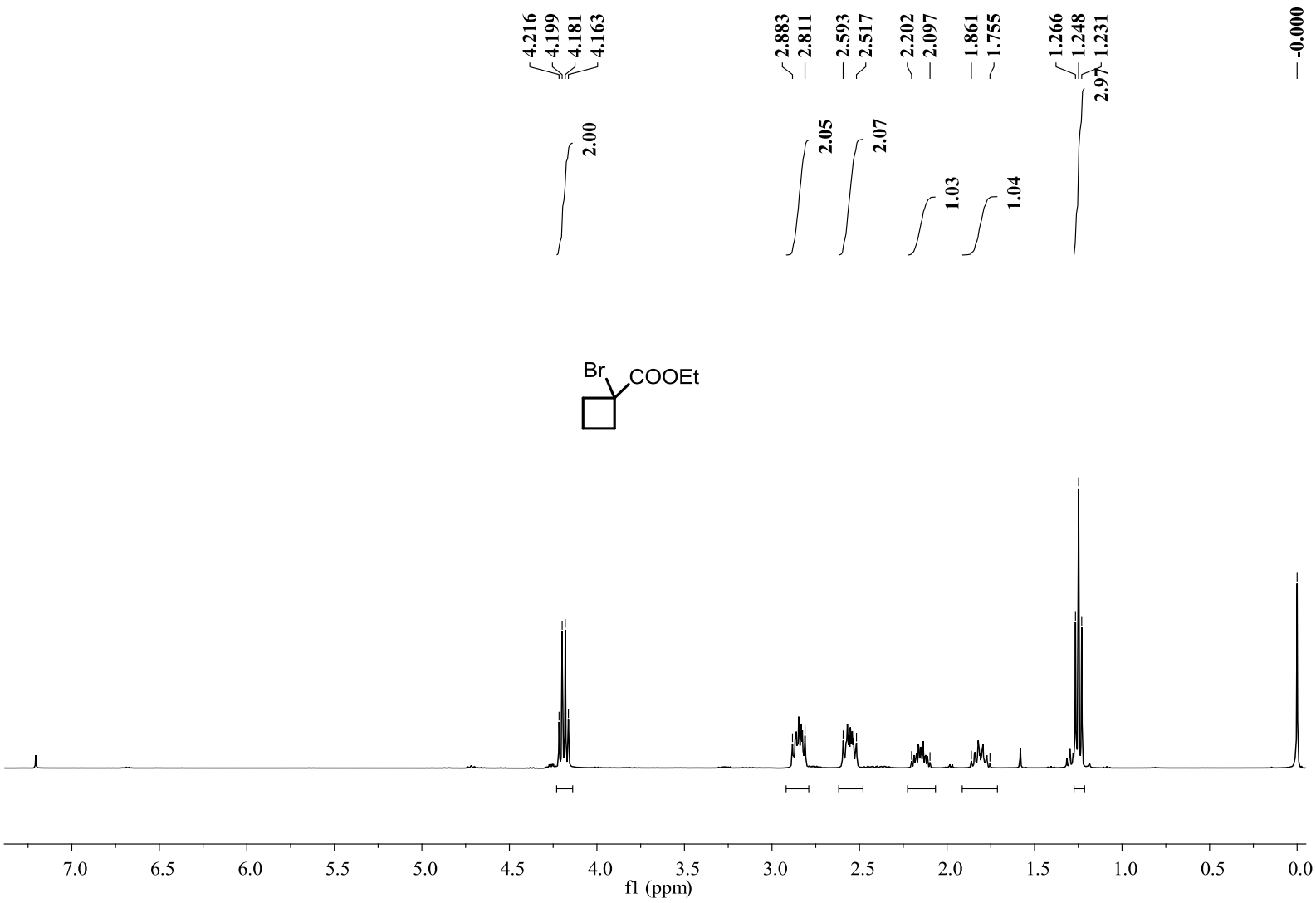
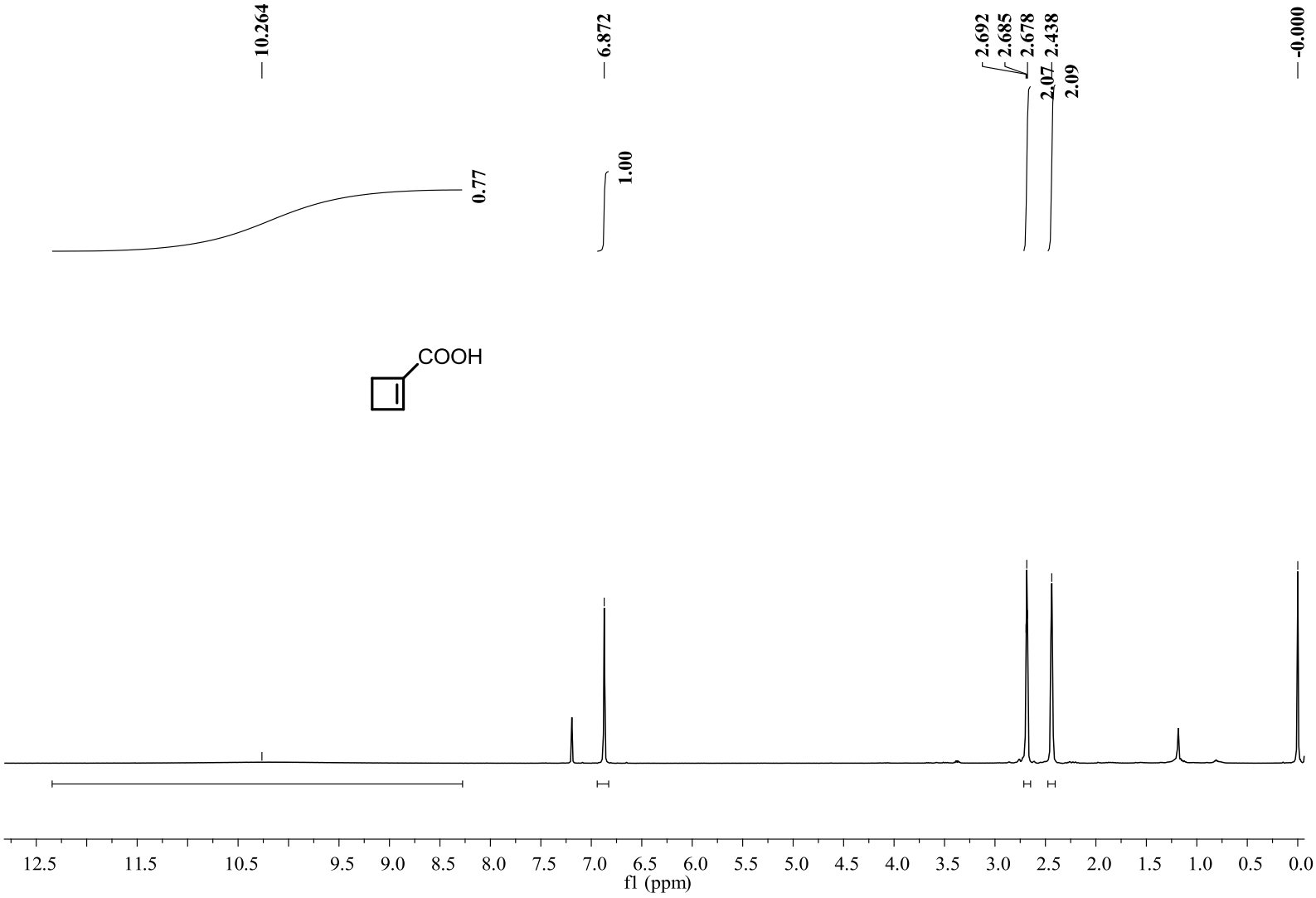
O
H
H
L8
O
F3C
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
f1 (ppm)


4.216
4.199
4.181
4.163
2.883
2.811
2.593
2.517
2.202
2.097
1.861
1.755
1.266
1.248
1.231
-0.000
2.00
2.05
2.07
1.03
1.04
2.97
Br
COOEt
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)


10.264
6.872
2.692
2.685
2.678
2.438
2.07
2.09
-0.000
0.77
1.00
COOH
12.5
11.5
10.5
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
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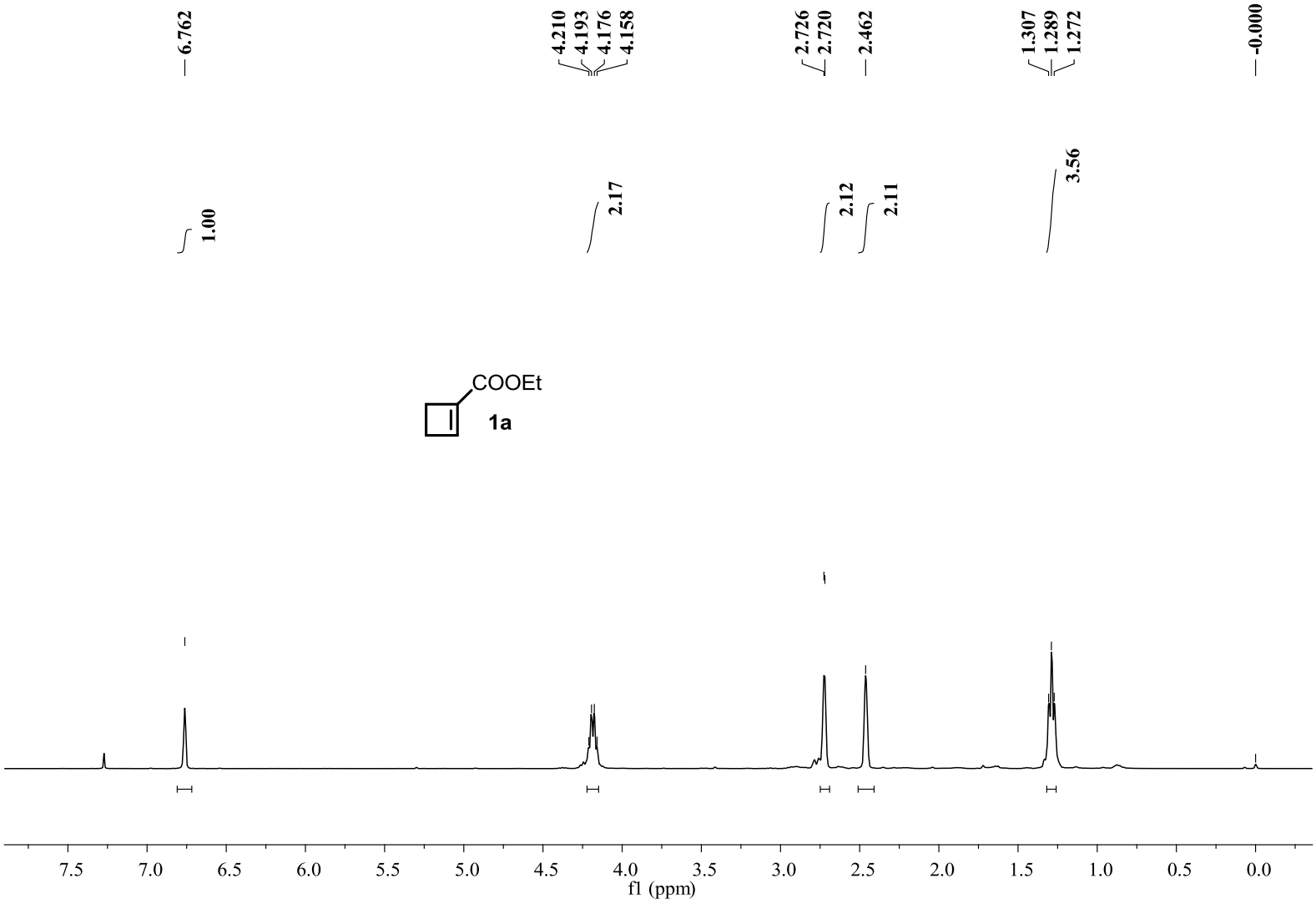
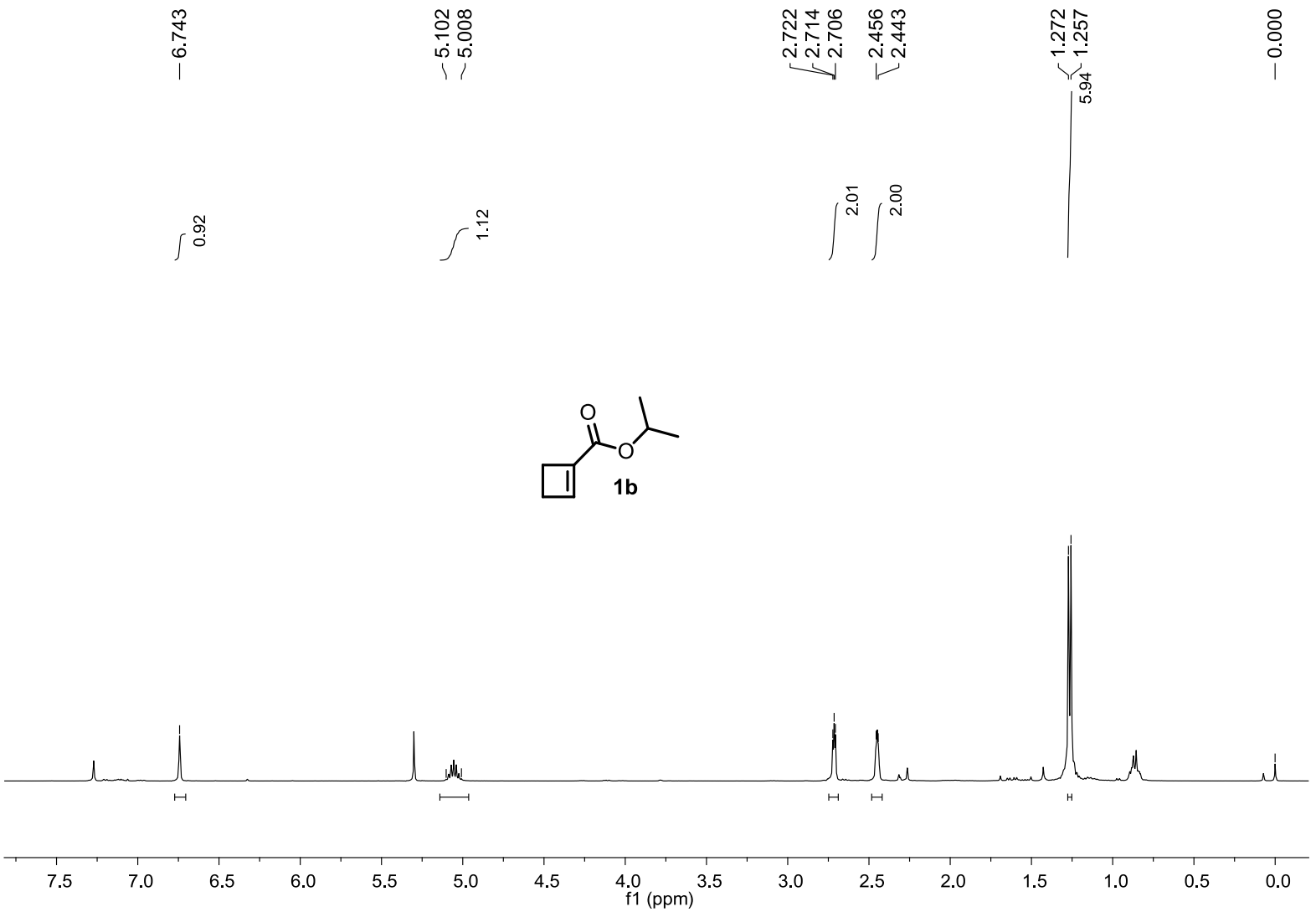
0.0
f1 (ppm)


6.762
4.210
4.193
4.176
4.158
2.726
2.720
2.462
1.307
1.289
1.272
-0.000
1.00
2.17
2.12
2.11
3.56
COOEt
1a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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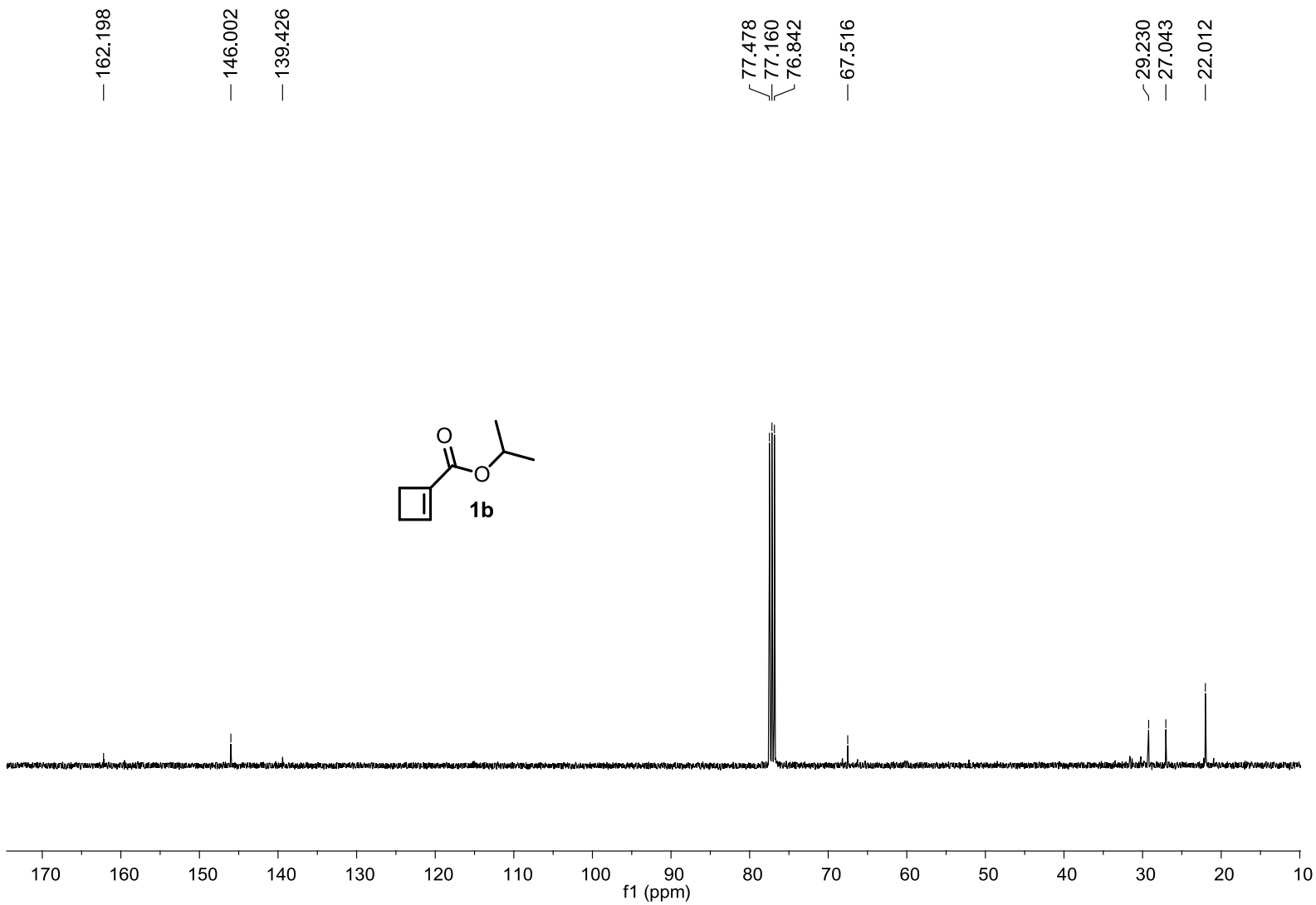
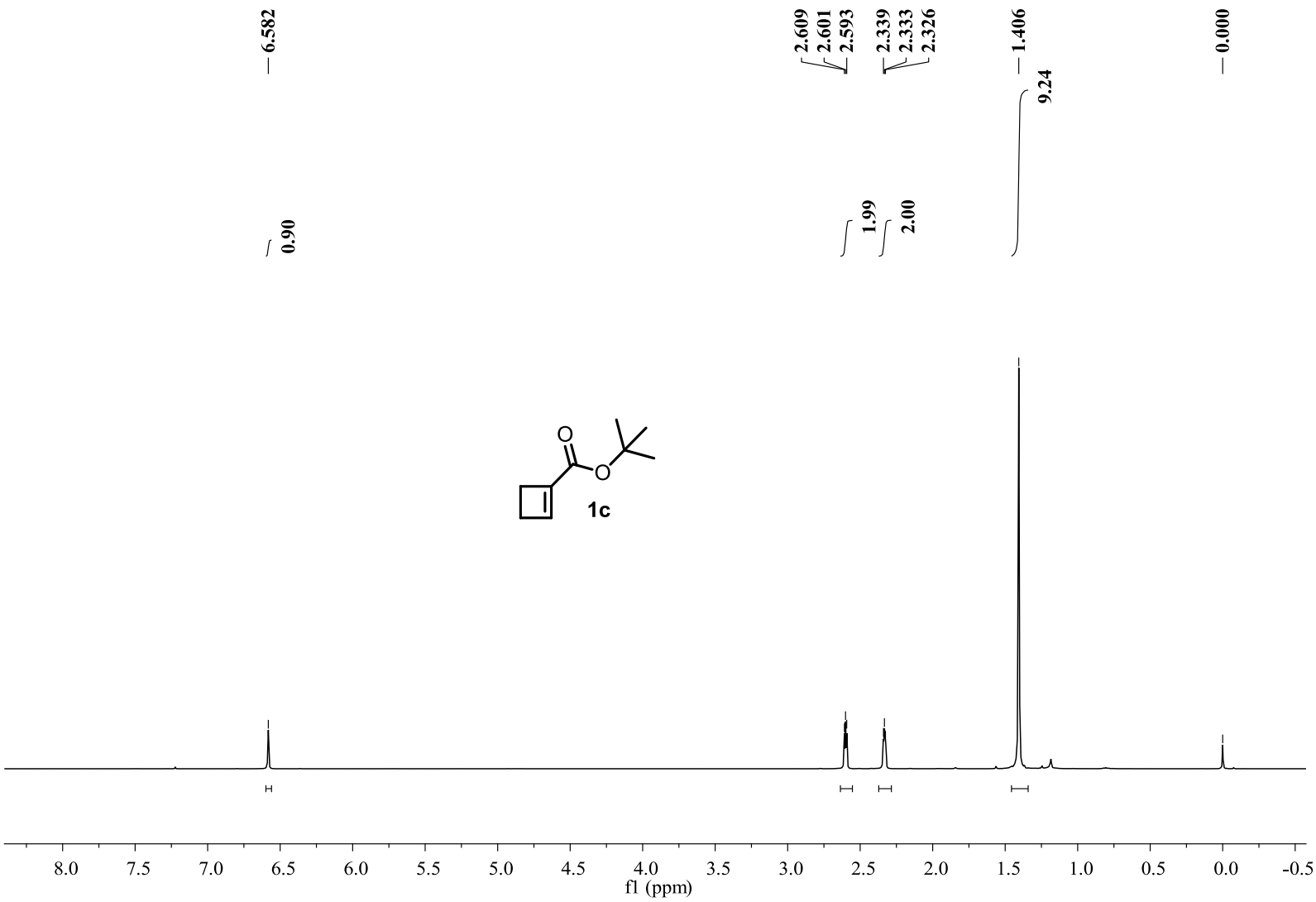
5.102
5.008
2.722
2.714
2.706
2.456
2.443
1.272
1.257
0.000
0.92
1.12
2.01
2.00
5.94
1b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


162.198
146.002
139.426
77.478
77.160
76.842
67.516
29.230
27.043
22.012
O
O
1b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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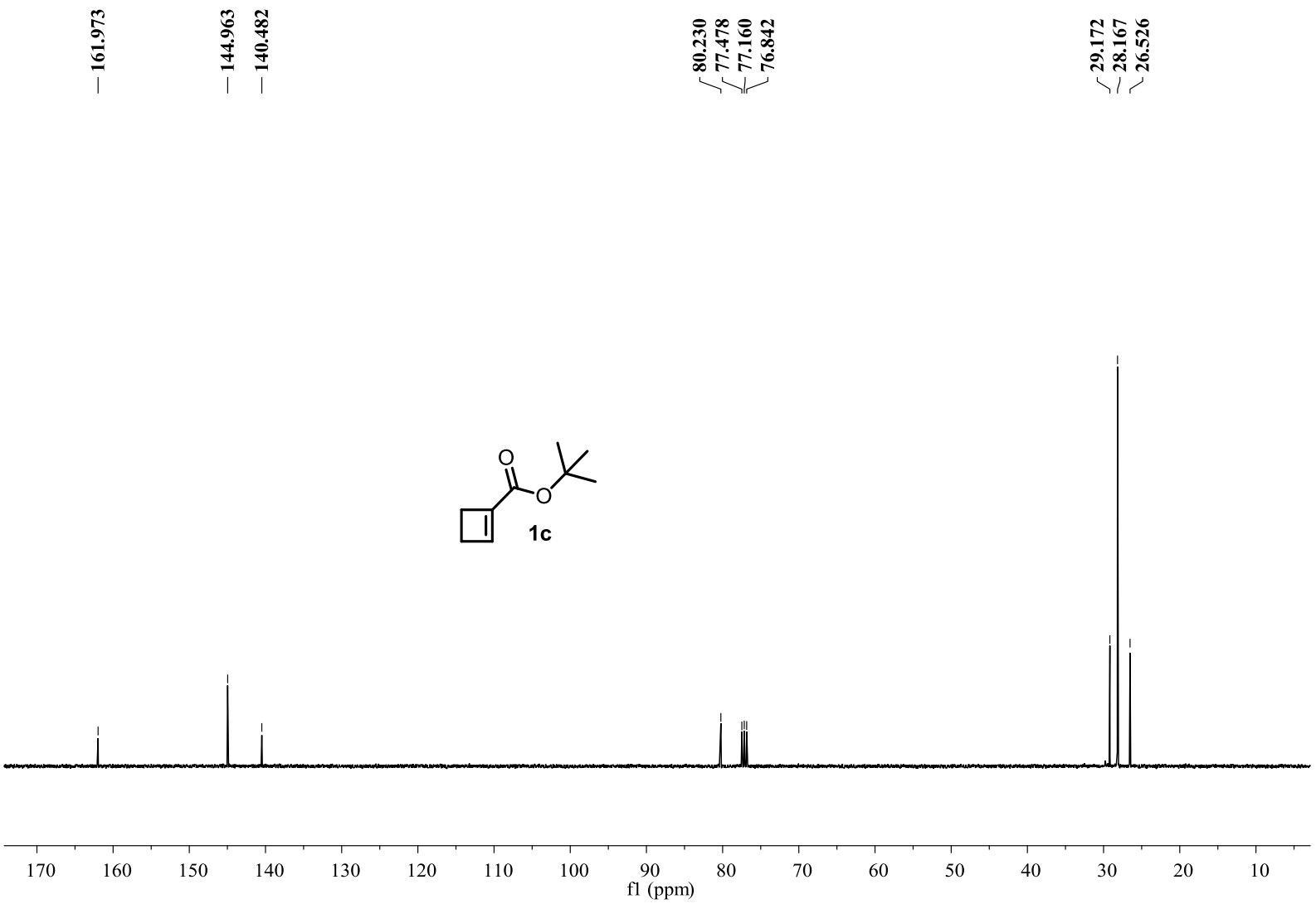
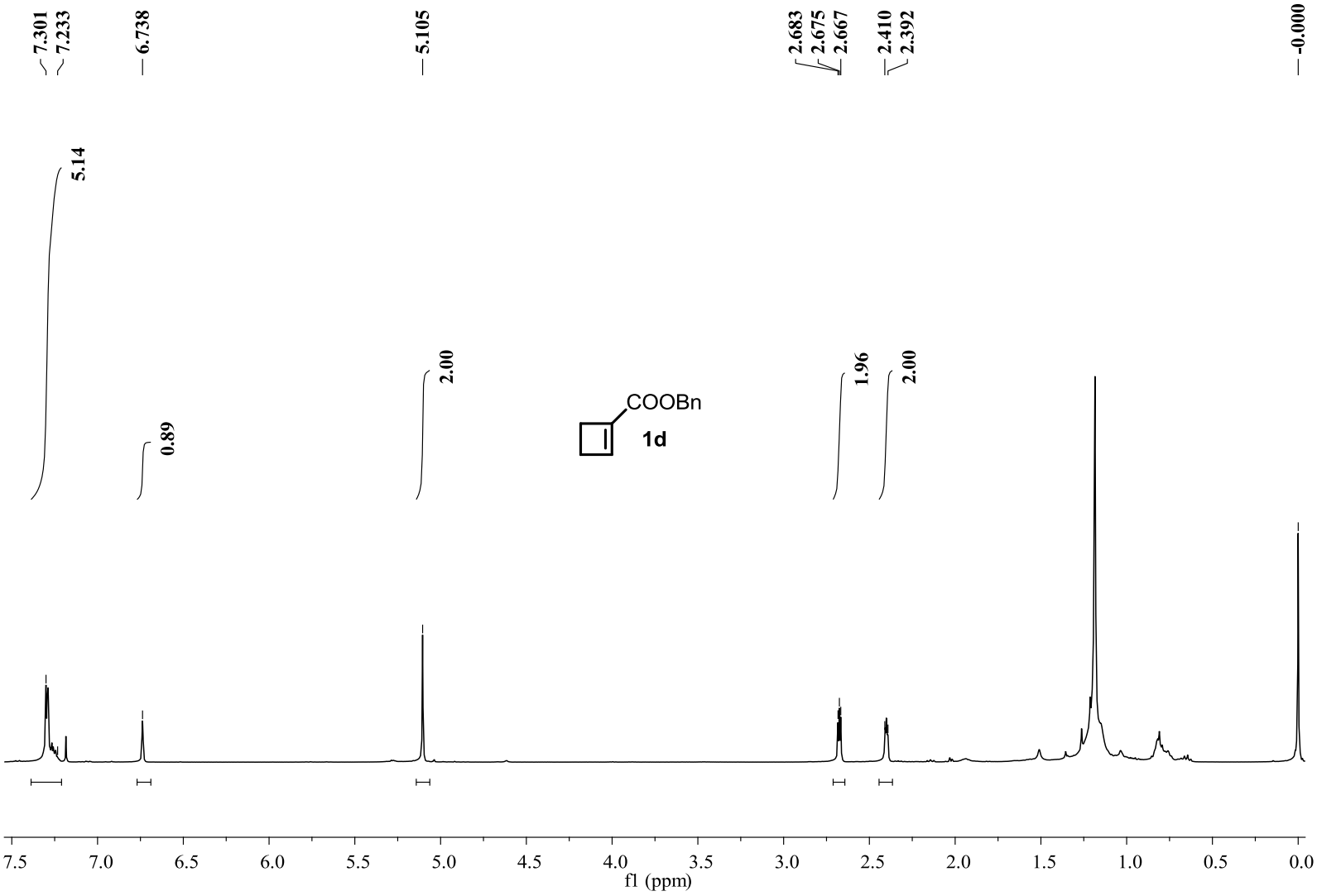
2.593
2.339
2.333
2.326
1.406
0.000
9.24
1.99
2.00
0.90
O
O
1c
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


161.973
144.963
140.482
80.230
77.478
77.160
76.842
29.172
28.167
26.526
O
O
1c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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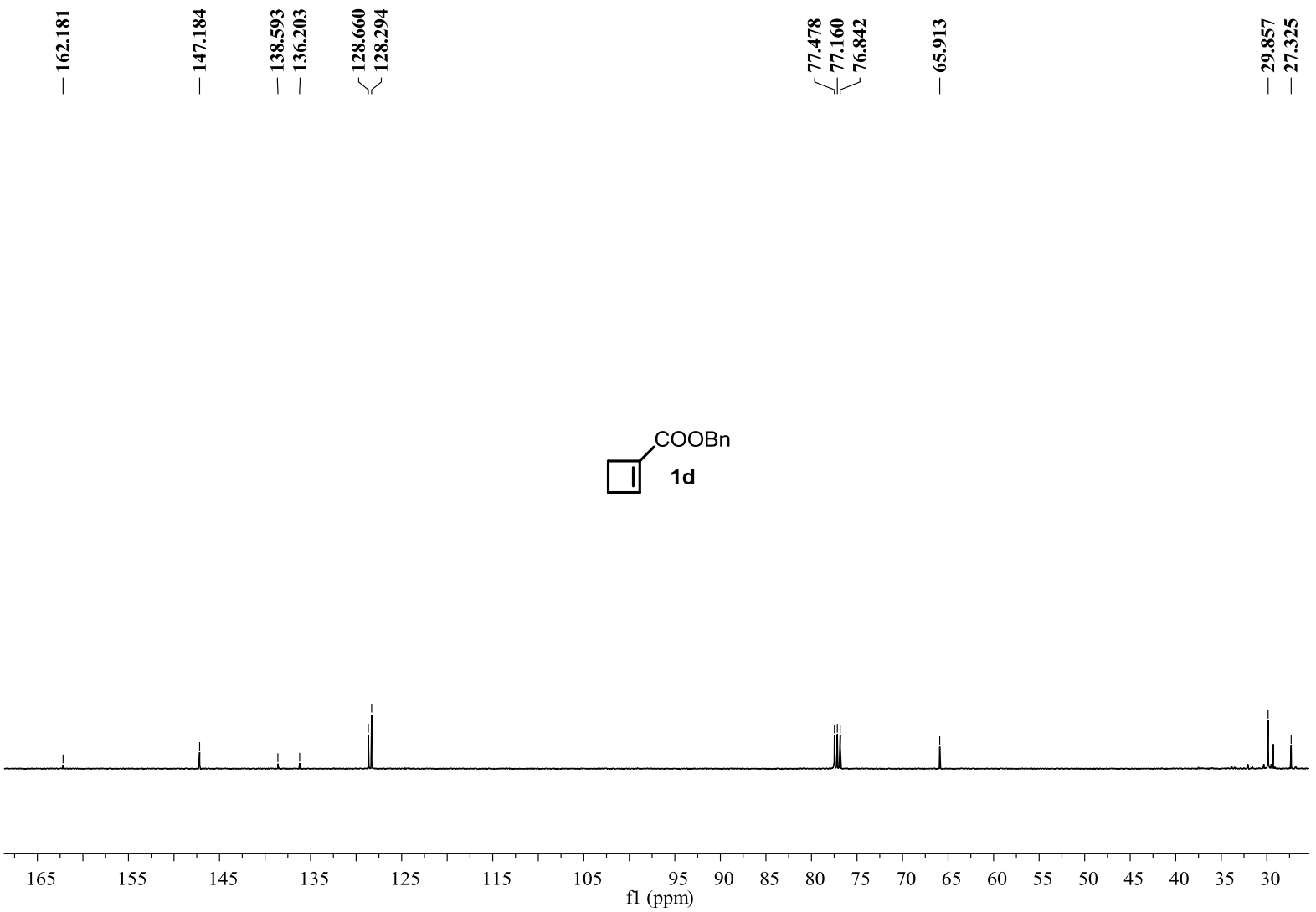
7.233
6.738
5.105
2.683
2.675
2.667
2.410
2.392
-0.000
5.14
0.89
2.00
1.96
2.00
COOBn
1d
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


162.181
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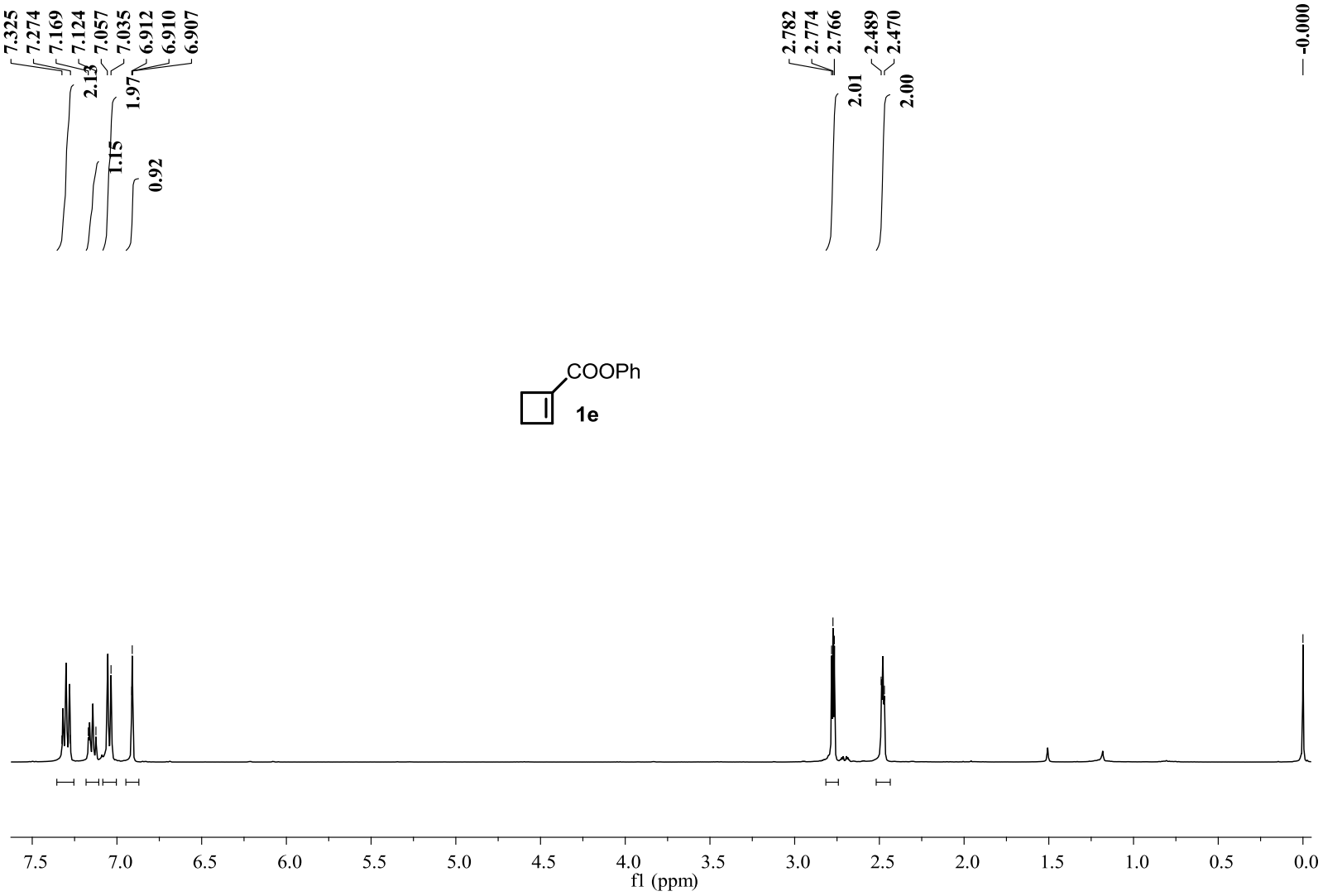
138.593
136.203
128.660
128.294
77.478
77.160
76.842
65.913
29.857
27.325
COOBn
1d
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)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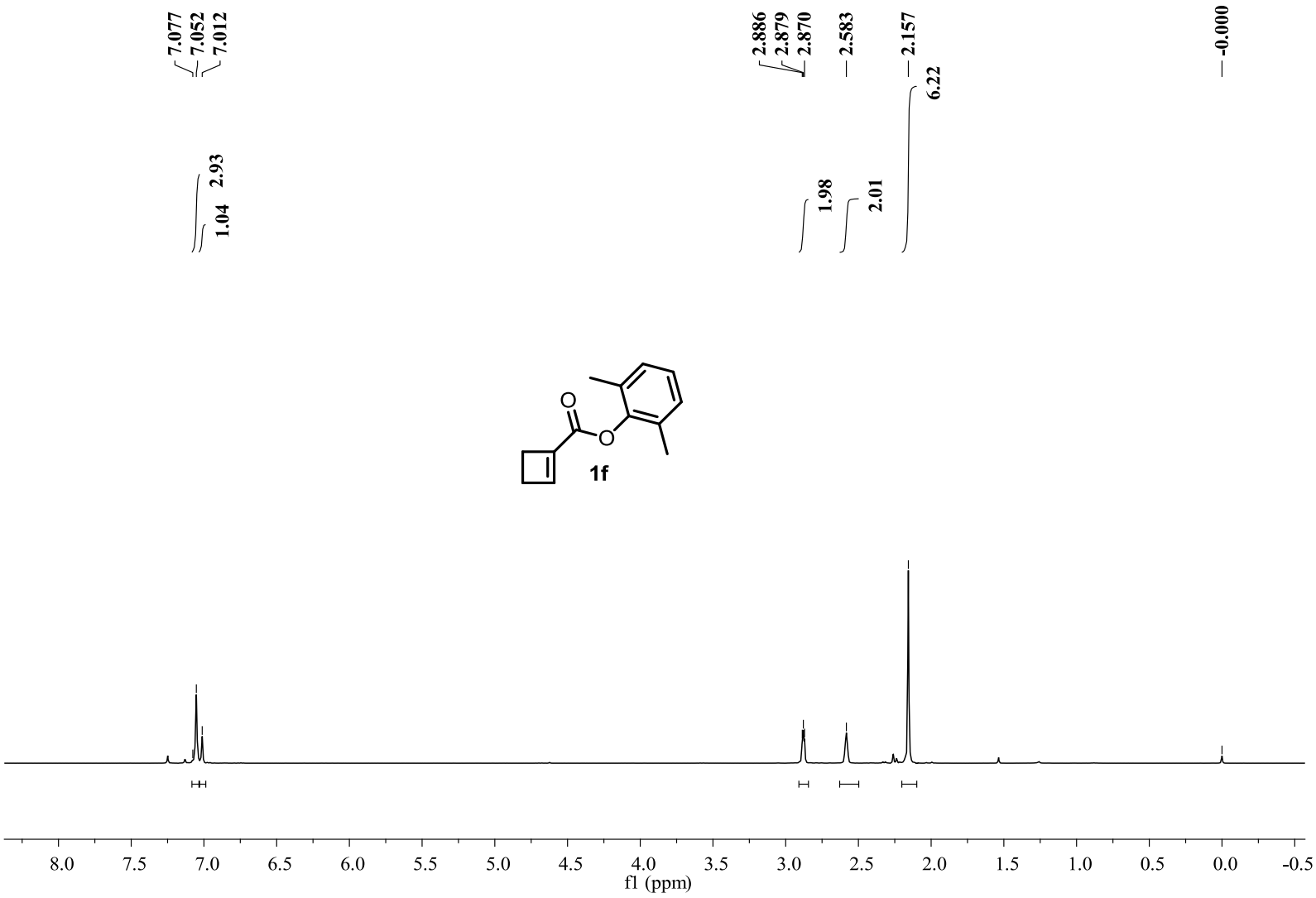
7.169
7.124
7.057
7.035
6.912
6.910
6.907
2.13
1.97
1.15
0.92
2.782
2.774
2.766
2.489
2.470
2.01
2.00
-0.000
COOPh
1e
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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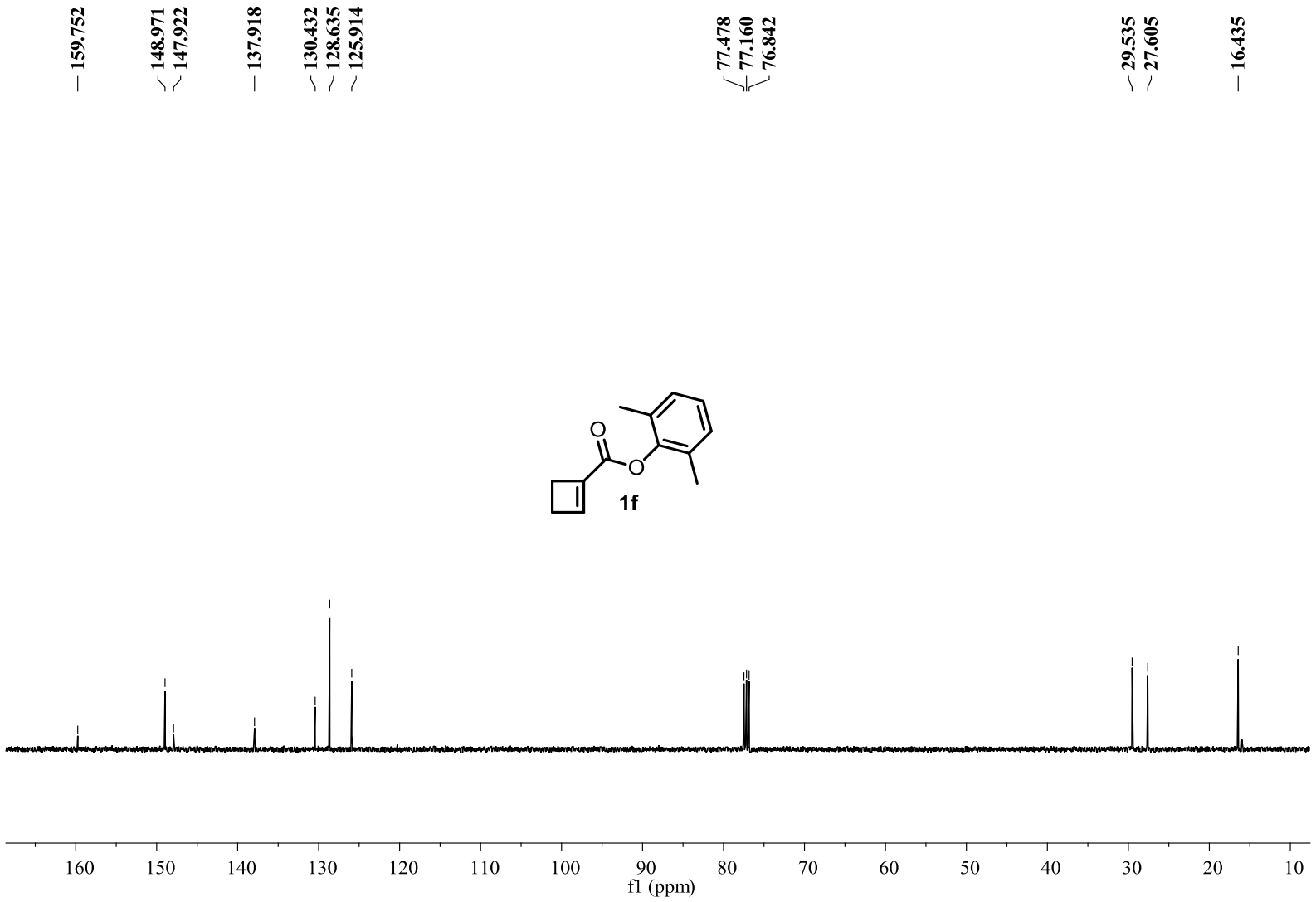
1.98
2.01
6.22
O
O
1f
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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147.922
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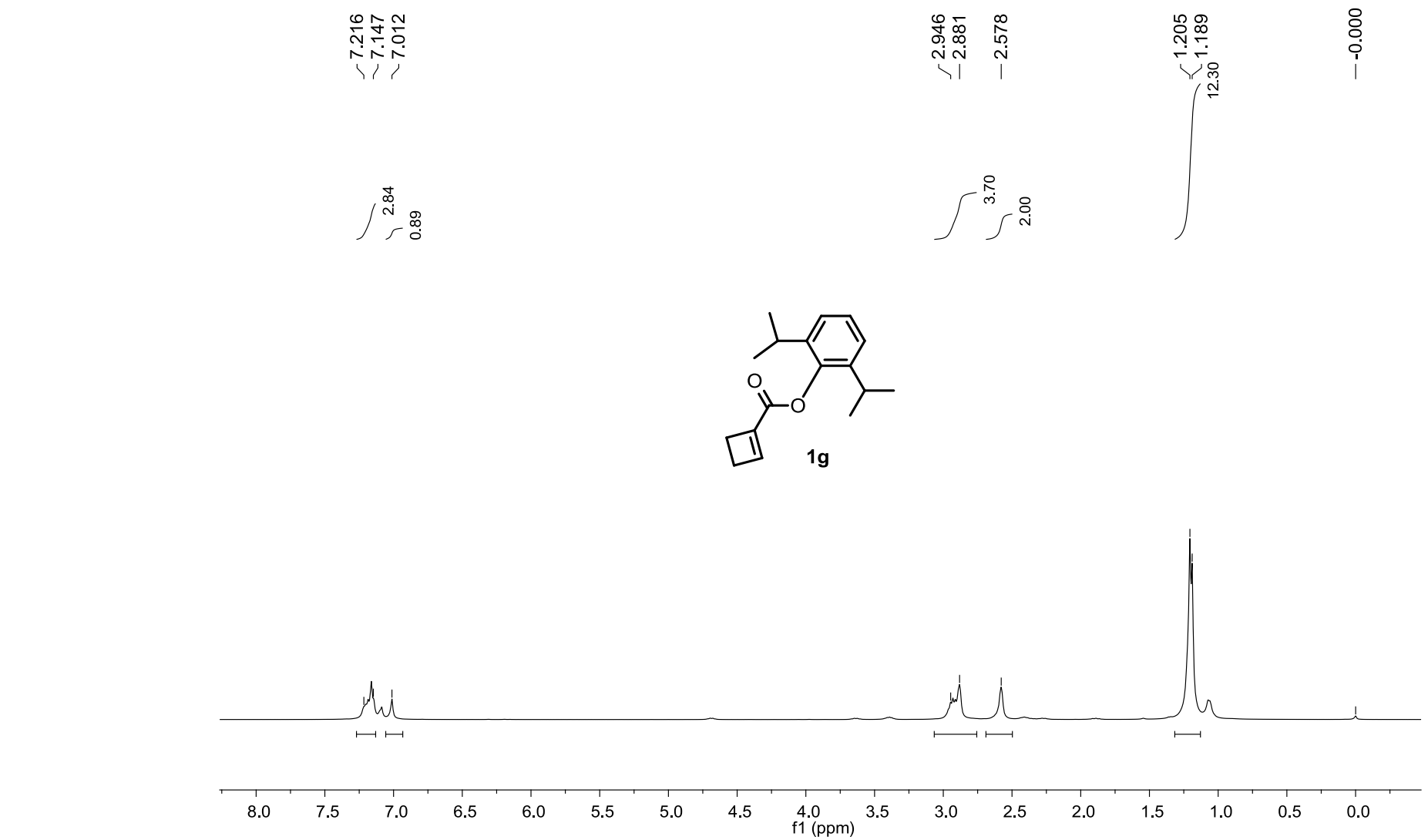
128.635
125.914
77.478
77.160
76.842
29.535
27.605
16.435
O
O
1f
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.147
7.012
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2.881
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1.189
-0.000
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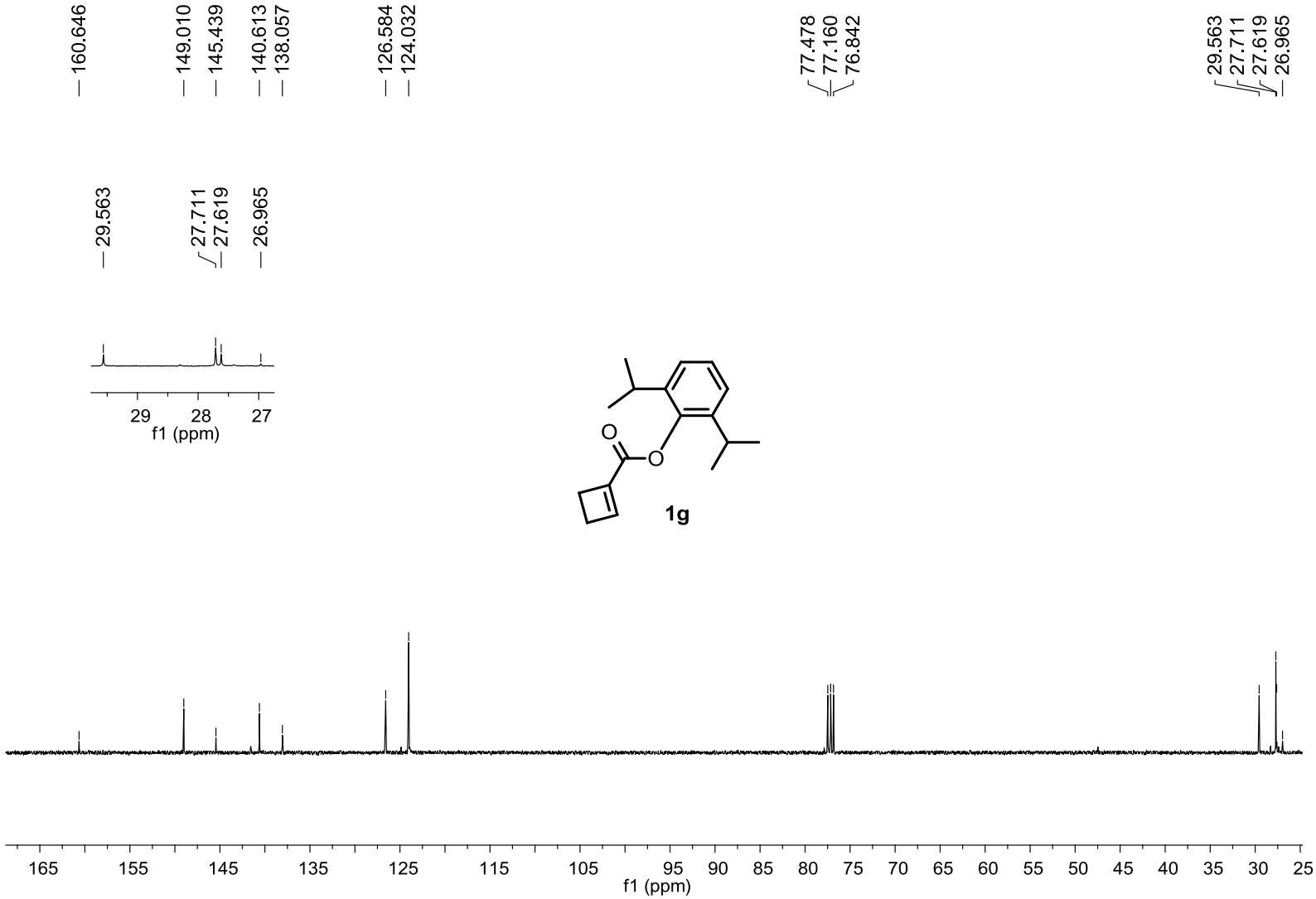
0.89
3.70
2.00
12.30
O
O
1g
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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145.439
140.613
138.057
126.584
124.032
77.478
77.160
76.842
29.563
27.711
27.619
26.965
29.563
27.711
27.619
26.965
29
28
27
f1 (ppm)
O
O
1g
165
155
145
135
125
115
105
95
90
85
80
75
70
65
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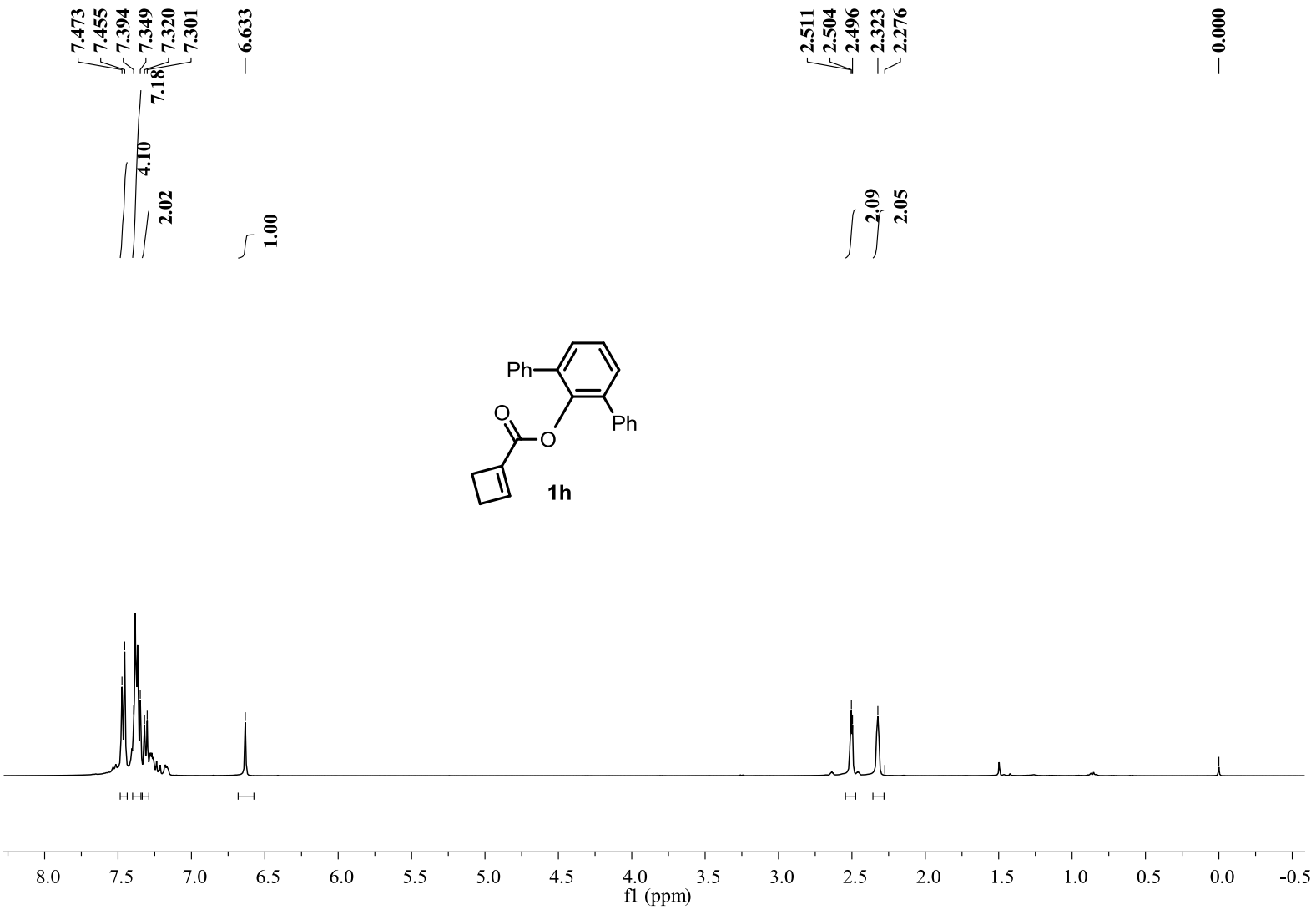
55
50
45
40
35
30
25
f1 (ppm)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7.320
7.301
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7.18
4.10
2.02
1.00
2.511
2.504
2.496
2.323
2.276
0.000
2.09
2.05
Ph
Ph
O
O
1h
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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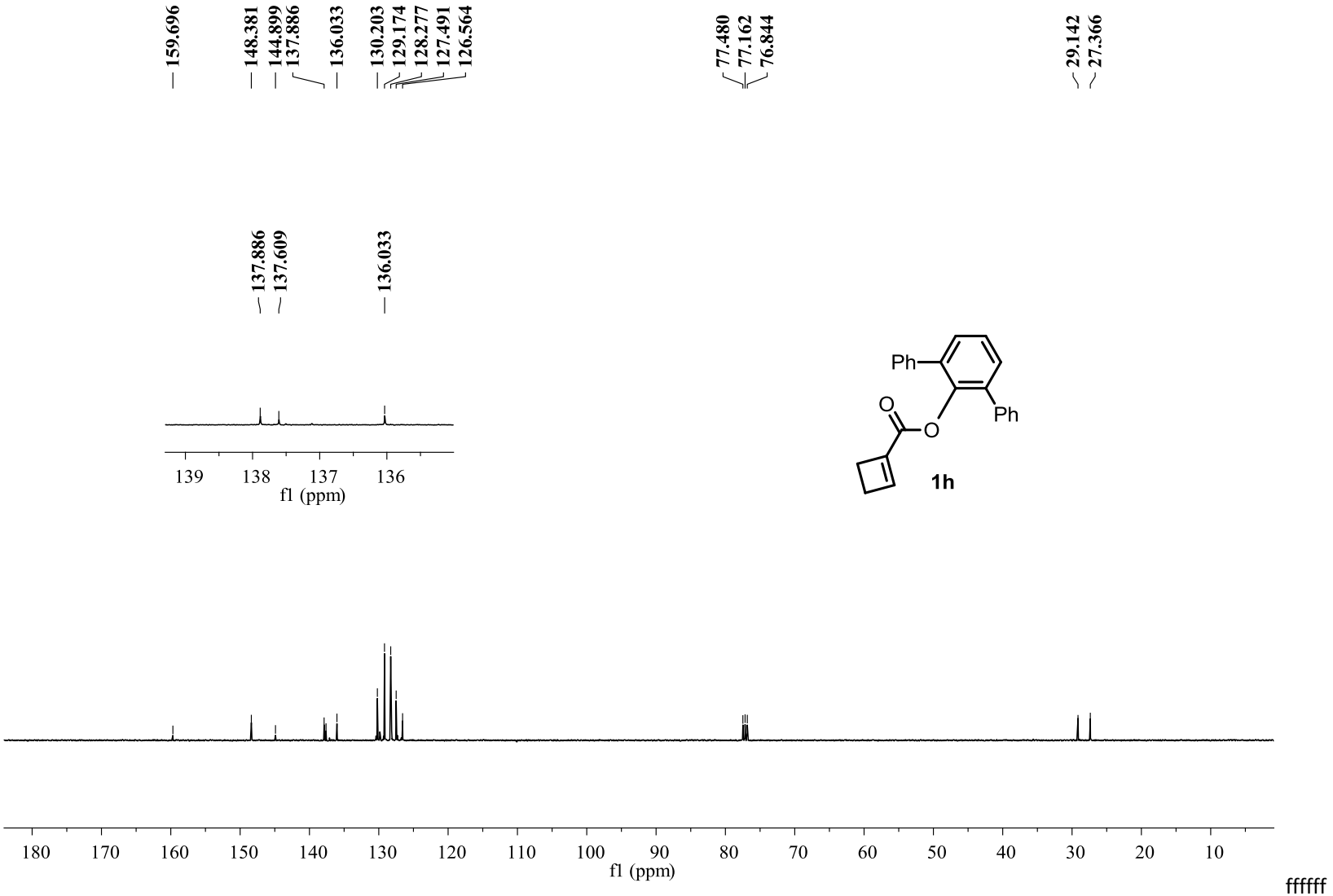
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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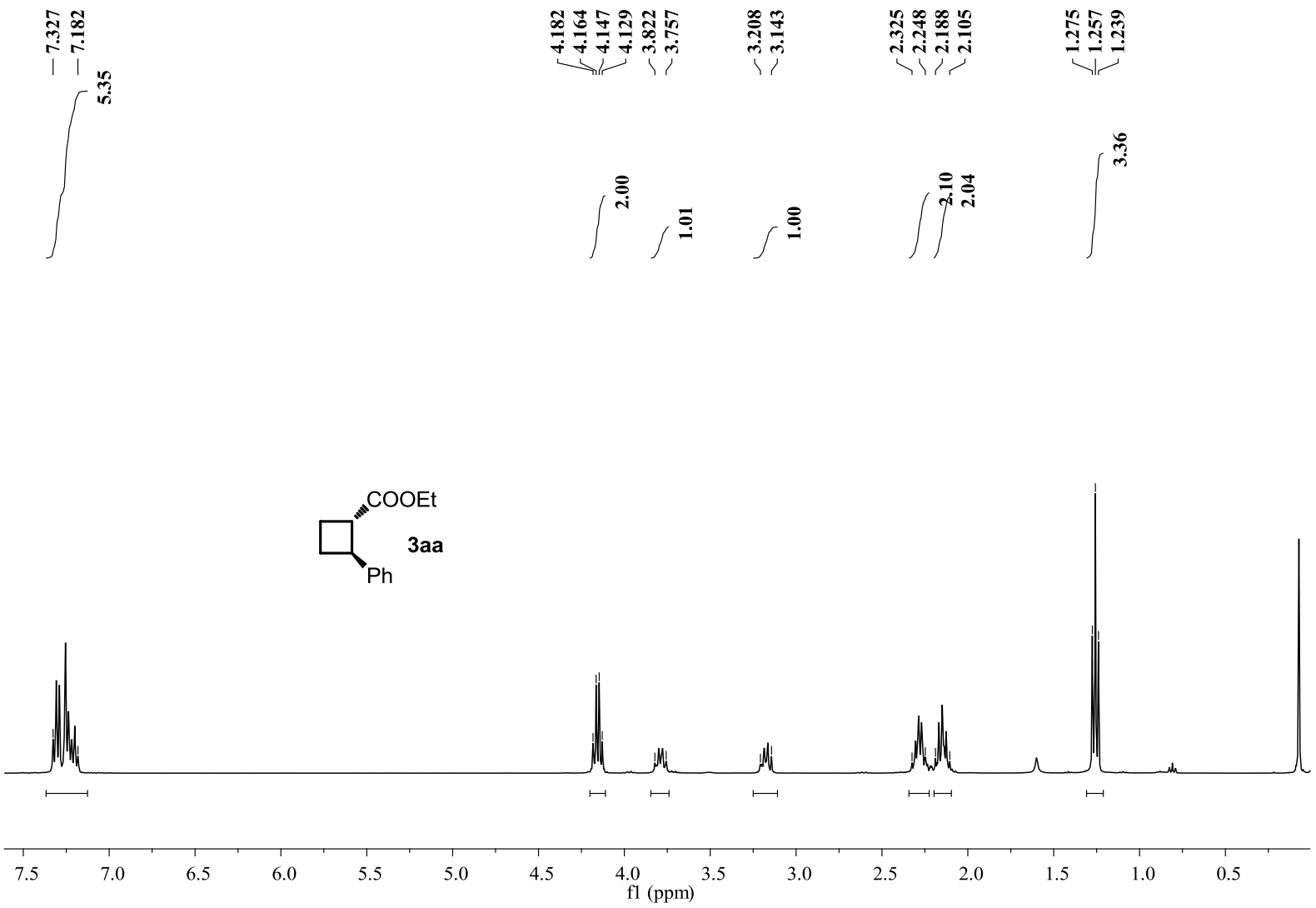
136.033
130.203
129.174
128.277
127.491
126.564
77.480
77.162
76.844
29.142
27.366
137.886
137.609
136.033
139
138
137
136
f1 (ppm)
Ph
Ph
O
O
1h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
ffffff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7.182
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3.208
3.143
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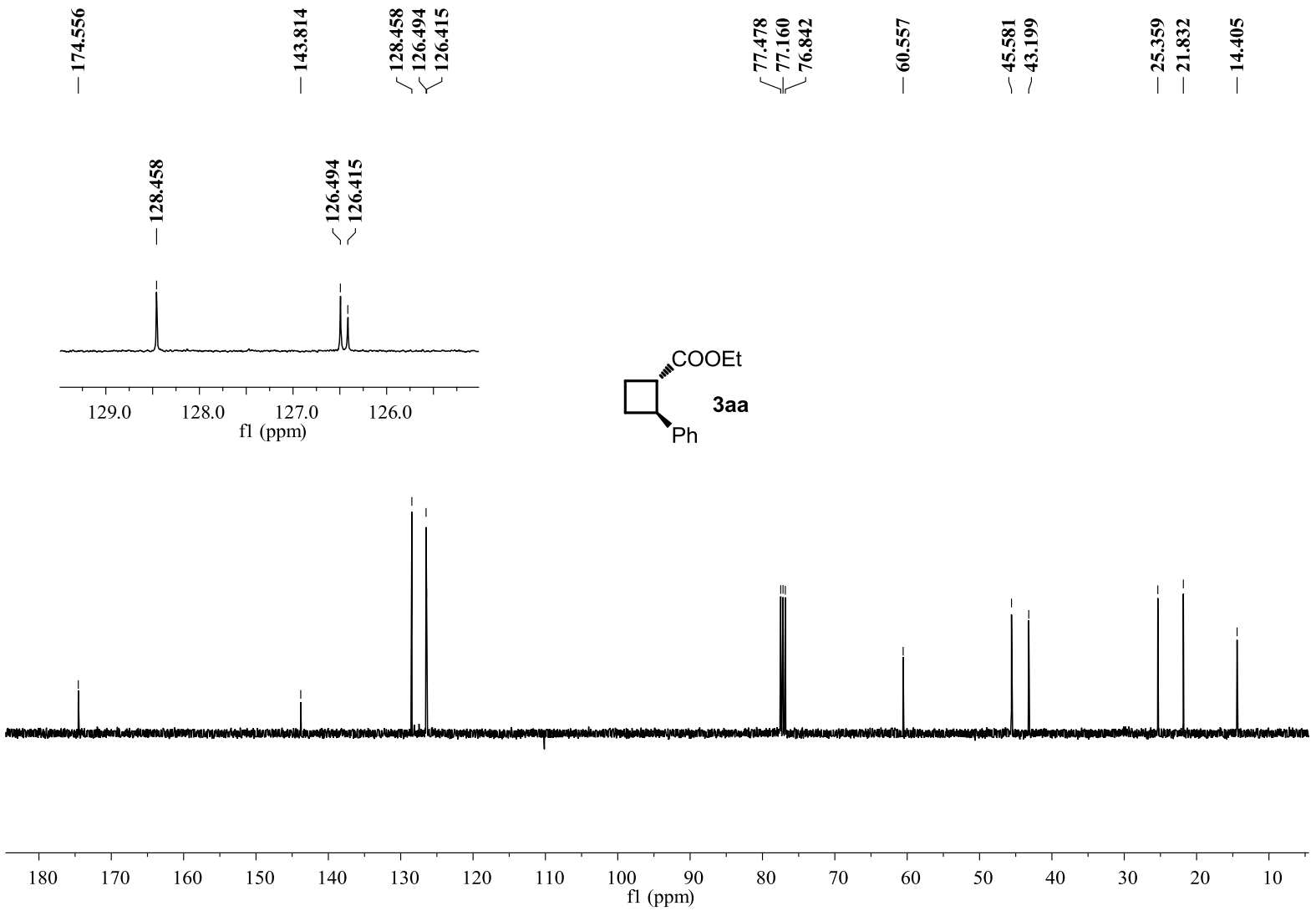
2.248
2.188
2.105
1.275
1.257
1.239
2.00
1.01
1.00
2.10
2.04
3.36
COOEt
3aa
Ph
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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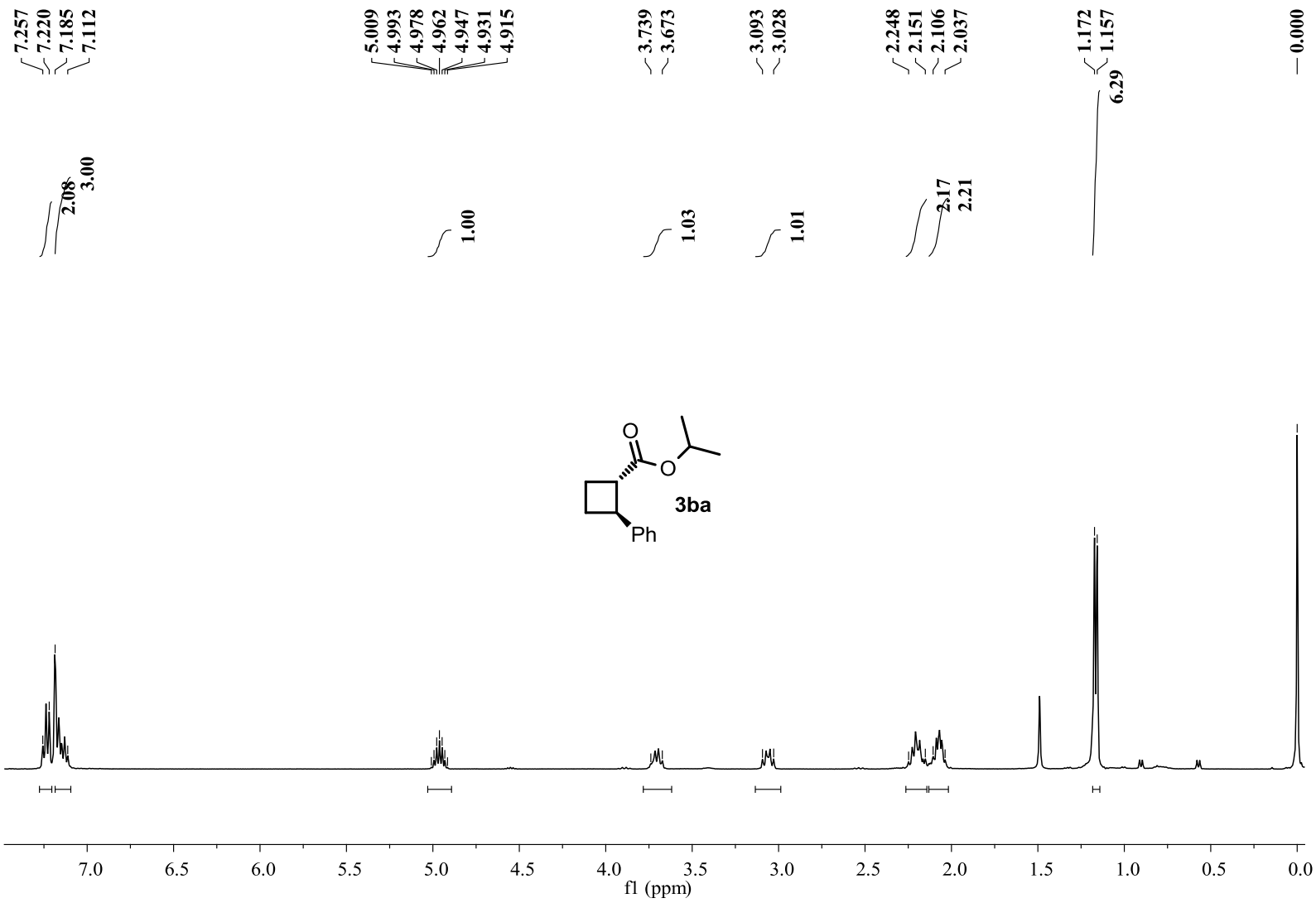
143.814
128.458
126.494
126.415
77.478
77.160
76.842
60.557
45.581
43.199
25.359
21.832
14.405
128.458
126.494
126.415
129.0
128.0
127.0
126.0
f1 (ppm)
COOEt
3aa
Ph
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.112
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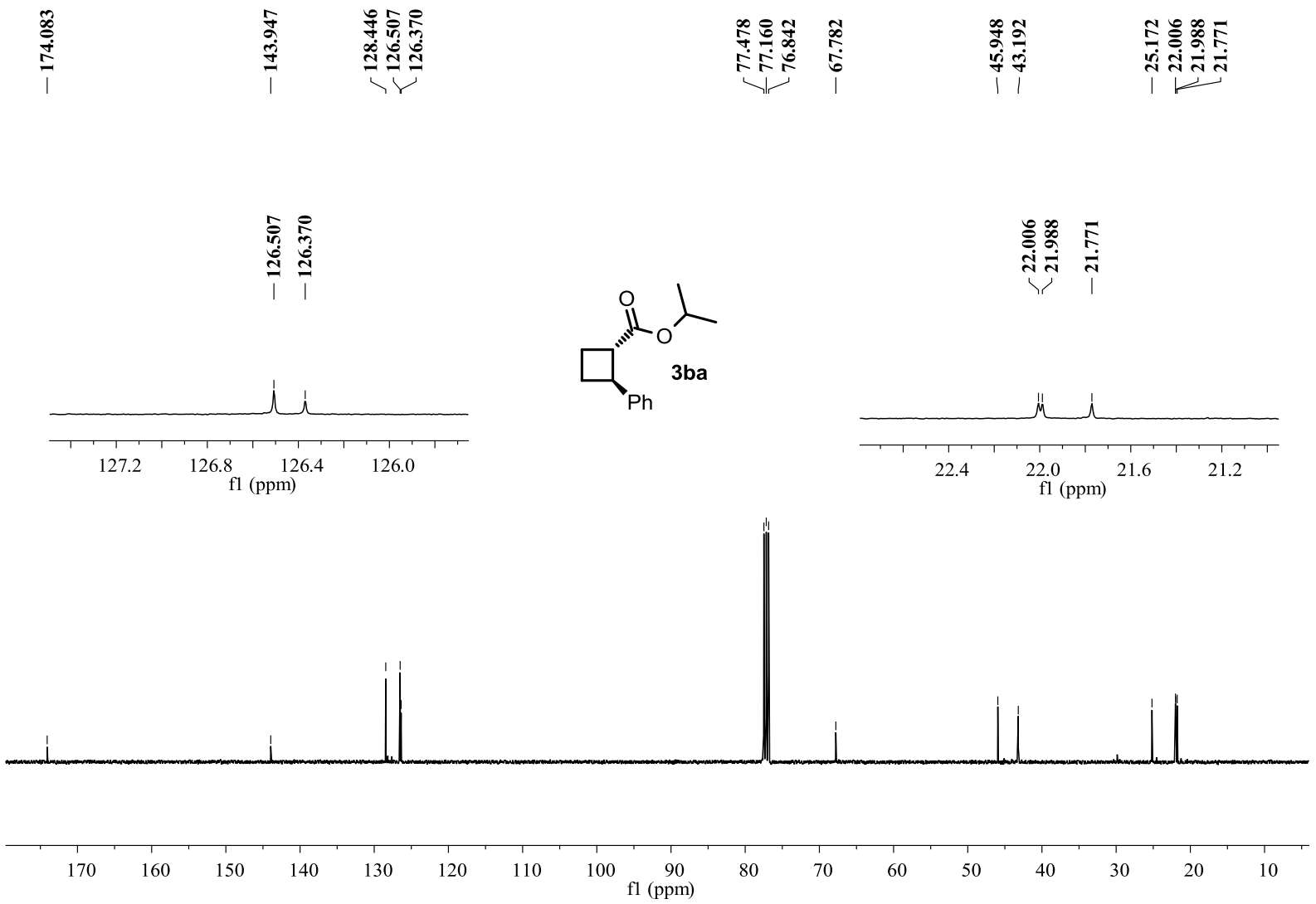
4.993
4.978
4.962
4.947
4.931
4.915
3.739
3.673
3.093
3.028
2.248
2.151
2.106
2.037
1.172
1.157
0.000
2.08
3.00
1.00
1.03
1.01
2.17
2.21
6.29
O
O
3ba
Ph
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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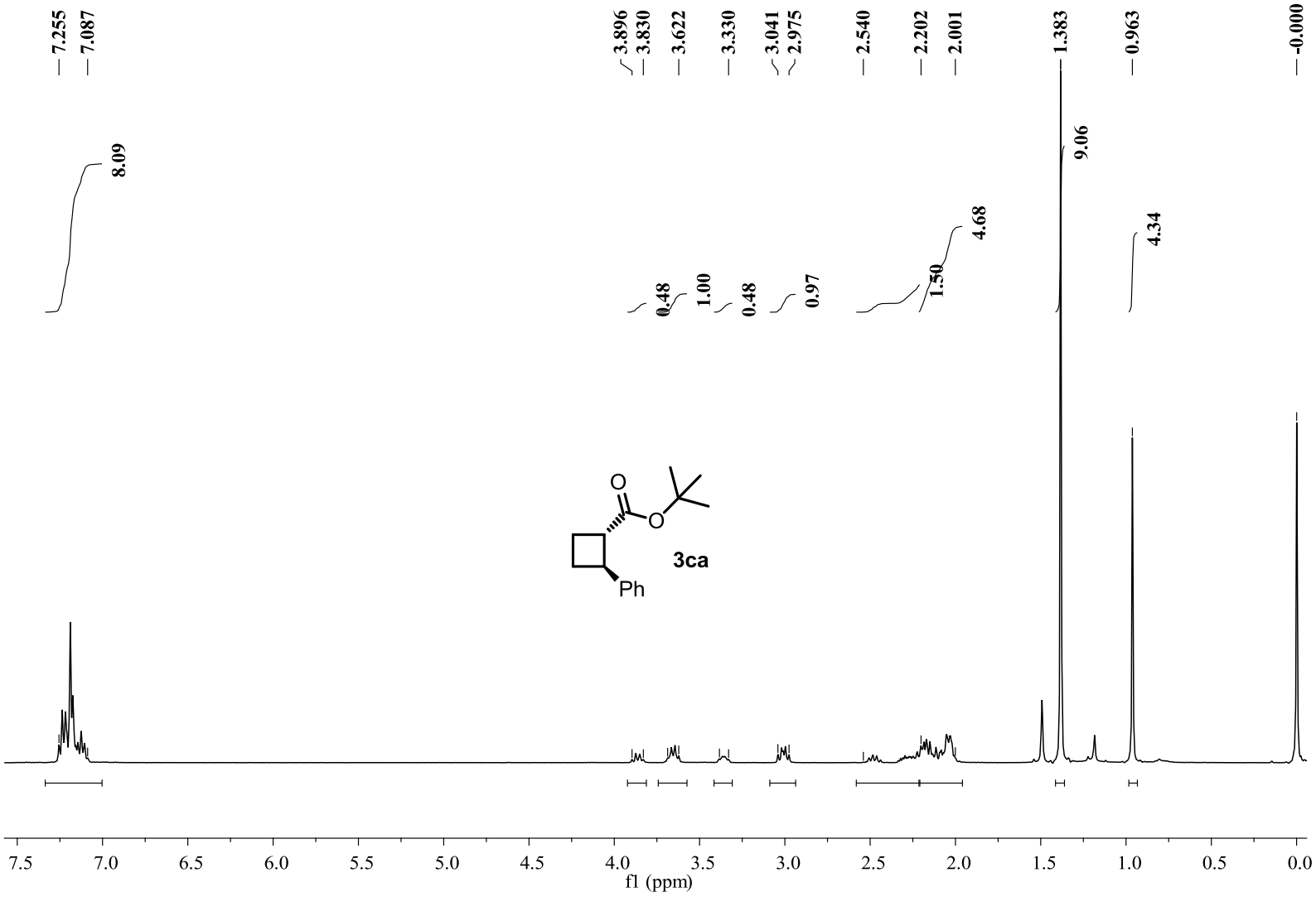
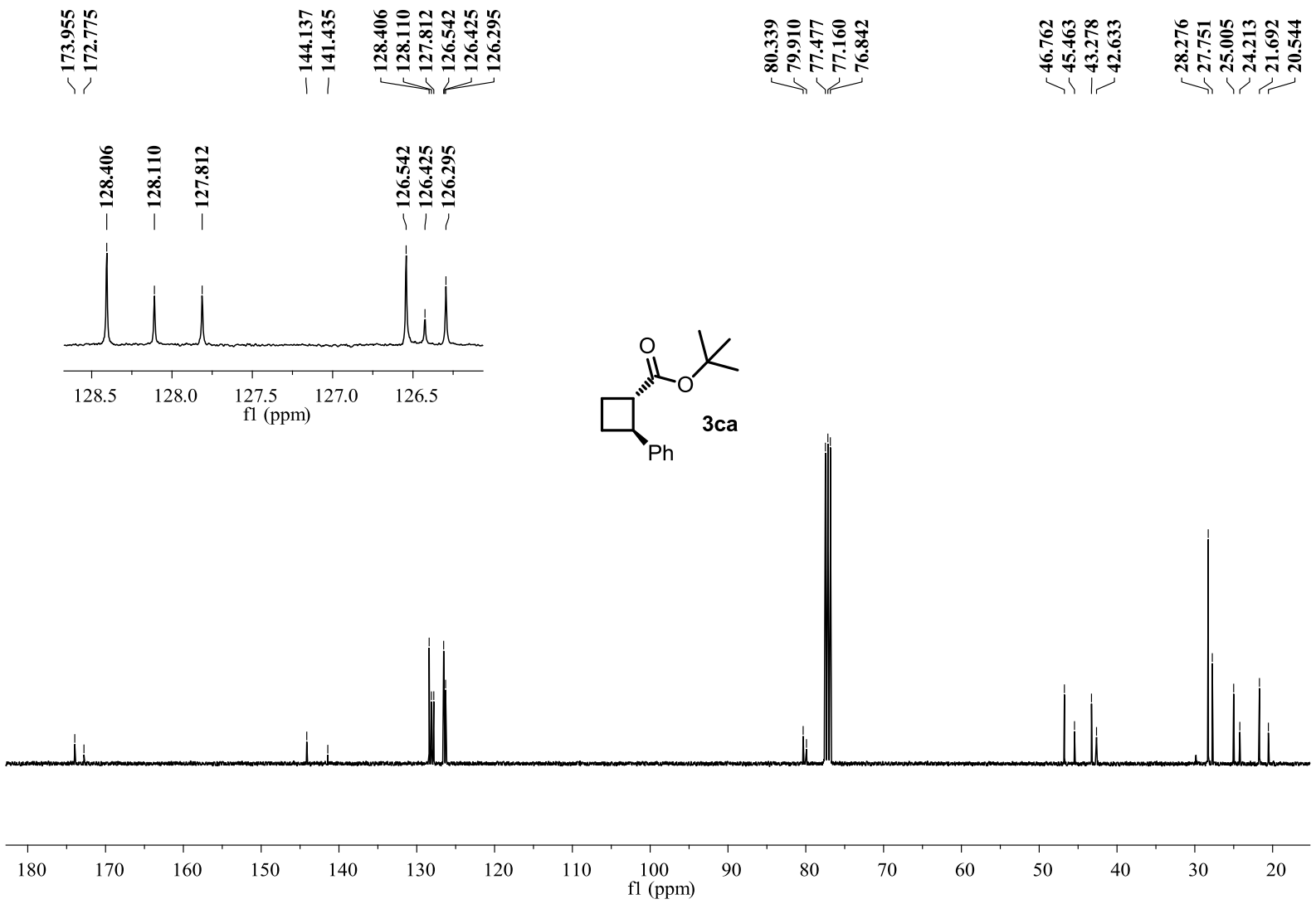
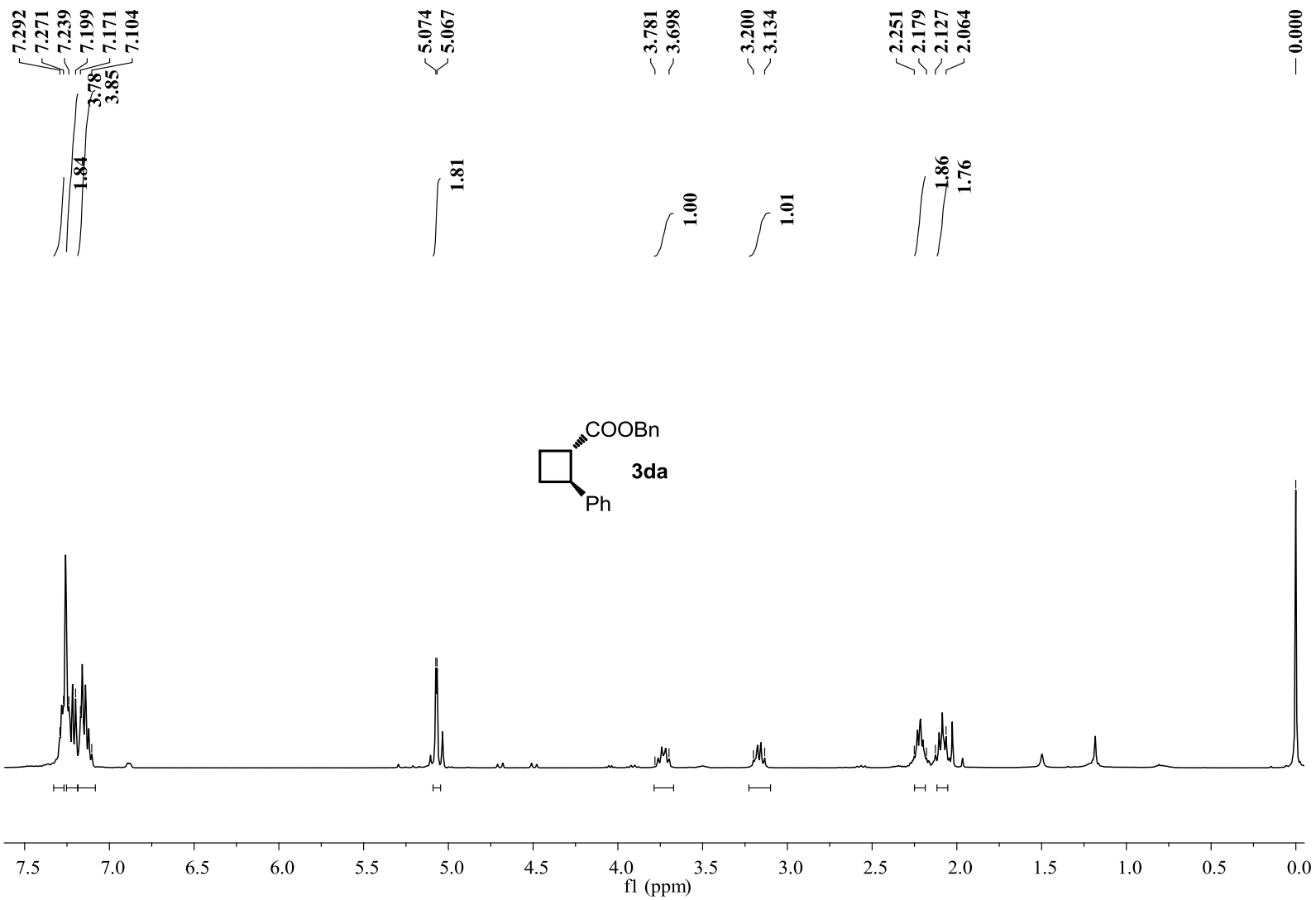
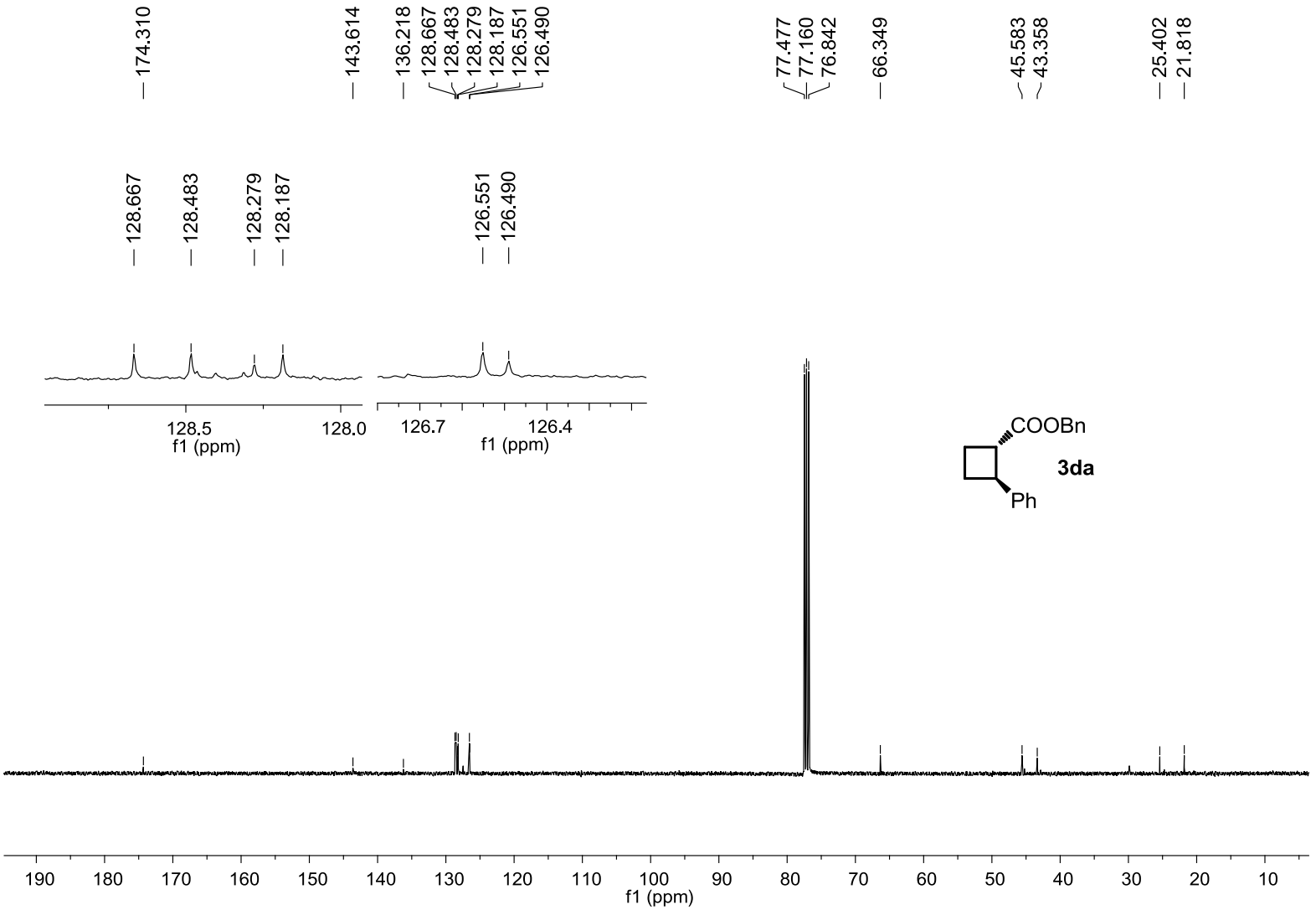
143.947
128.446
126.507
126.370
77.478
77.160
76.842
67.782
45.948
43.192
25.172
22.006
21.988
21.771
126.507
126.370
22.006
21.988
21.771
3ba
Ph
127.2
126.8
126.4
126.0
f1 (ppm)
22.4
22.0
21.6
21.2
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.255
7.087
3.896
3.830
3.622
3.330
3.041
2.975
2.540
2.202
2.001
1.383
0.963
-0.000
8.09
0.48
1.00
0.48
0.97
1.50
4.68
9.06
4.34
O
O
Ph
3ca
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)


173.955
172.775
144.137
141.435
128.406
128.110
127.812
126.542
126.425
126.295
80.339
79.910
77.477
77.160
76.842
46.762
45.463
43.278
42.633
28.276
27.751
25.005
24.213
21.692
20.544
128.406
128.110
127.812
126.542
126.425
126.295
128.5
128.0
127.5
127.0
126.5
f1 (ppm)
O
O
Ph
3ca
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


7.292
7.271
7.239
7.199
7.171
7.104
3.78
3.85
1.84
5.074
5.067
1.81
3.781
3.698
1.00
3.200
3.134
1.01
2.251
2.179
2.127
2.064
1.86
1.76
0.000
COOBn
3da
Ph
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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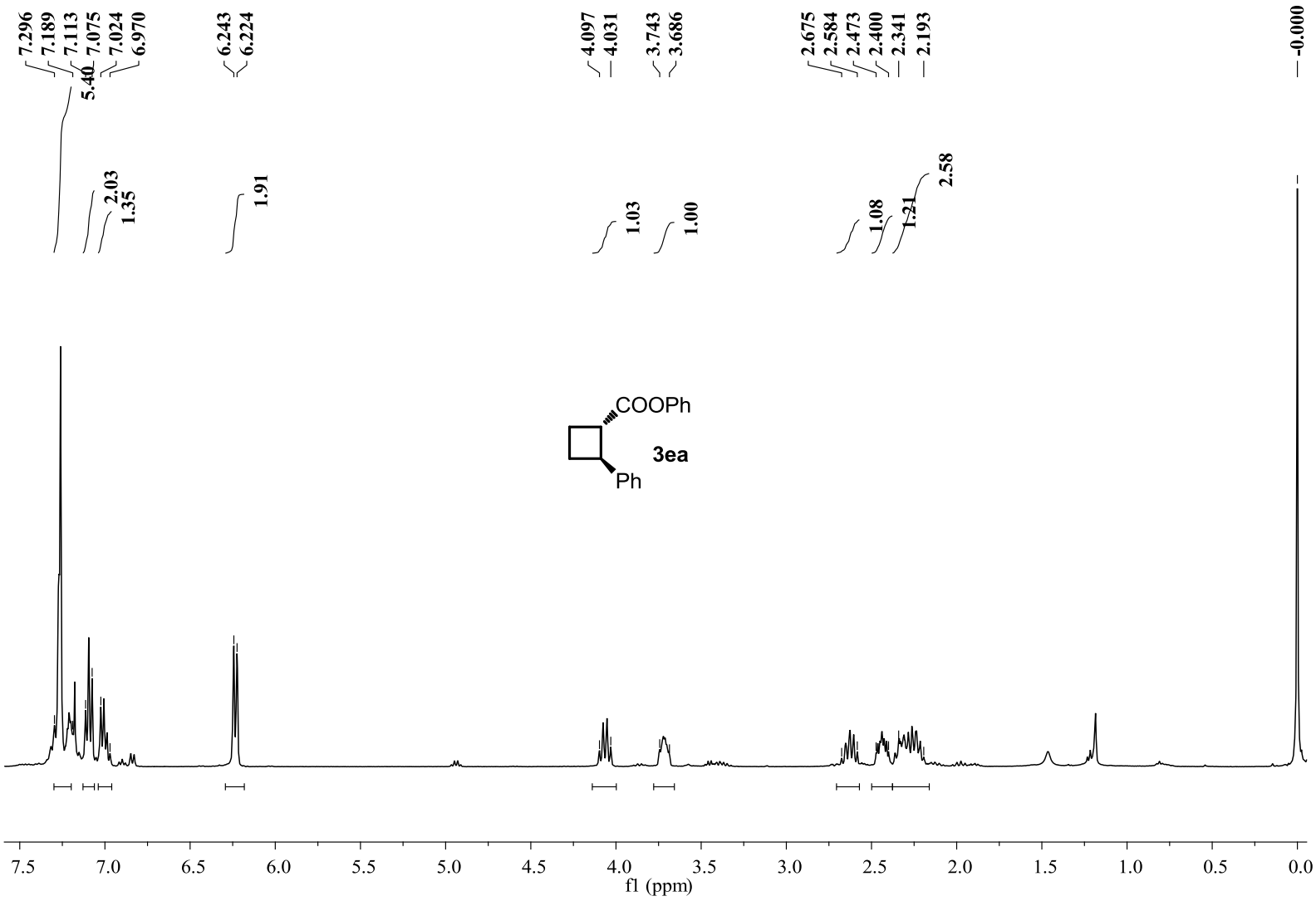
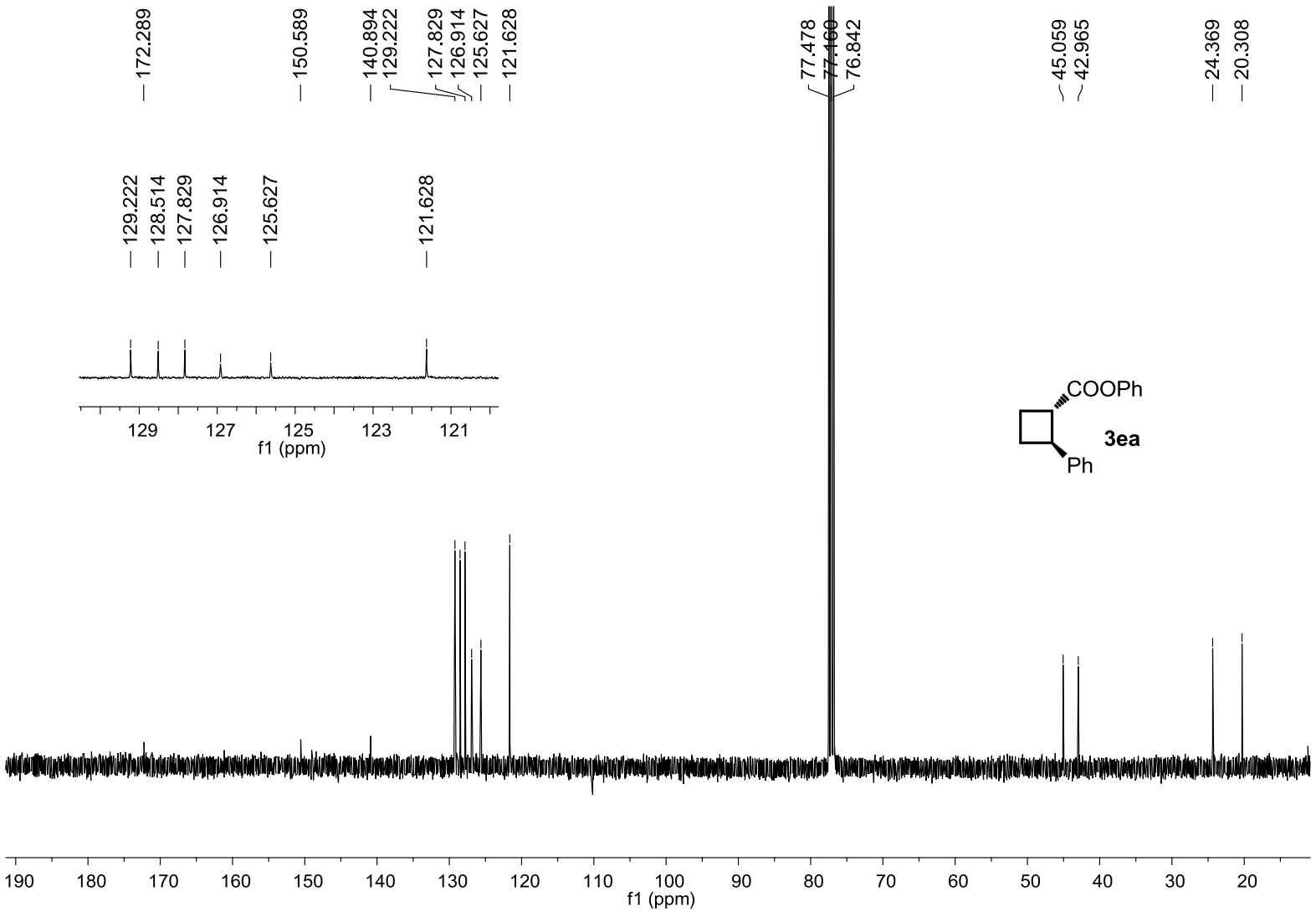
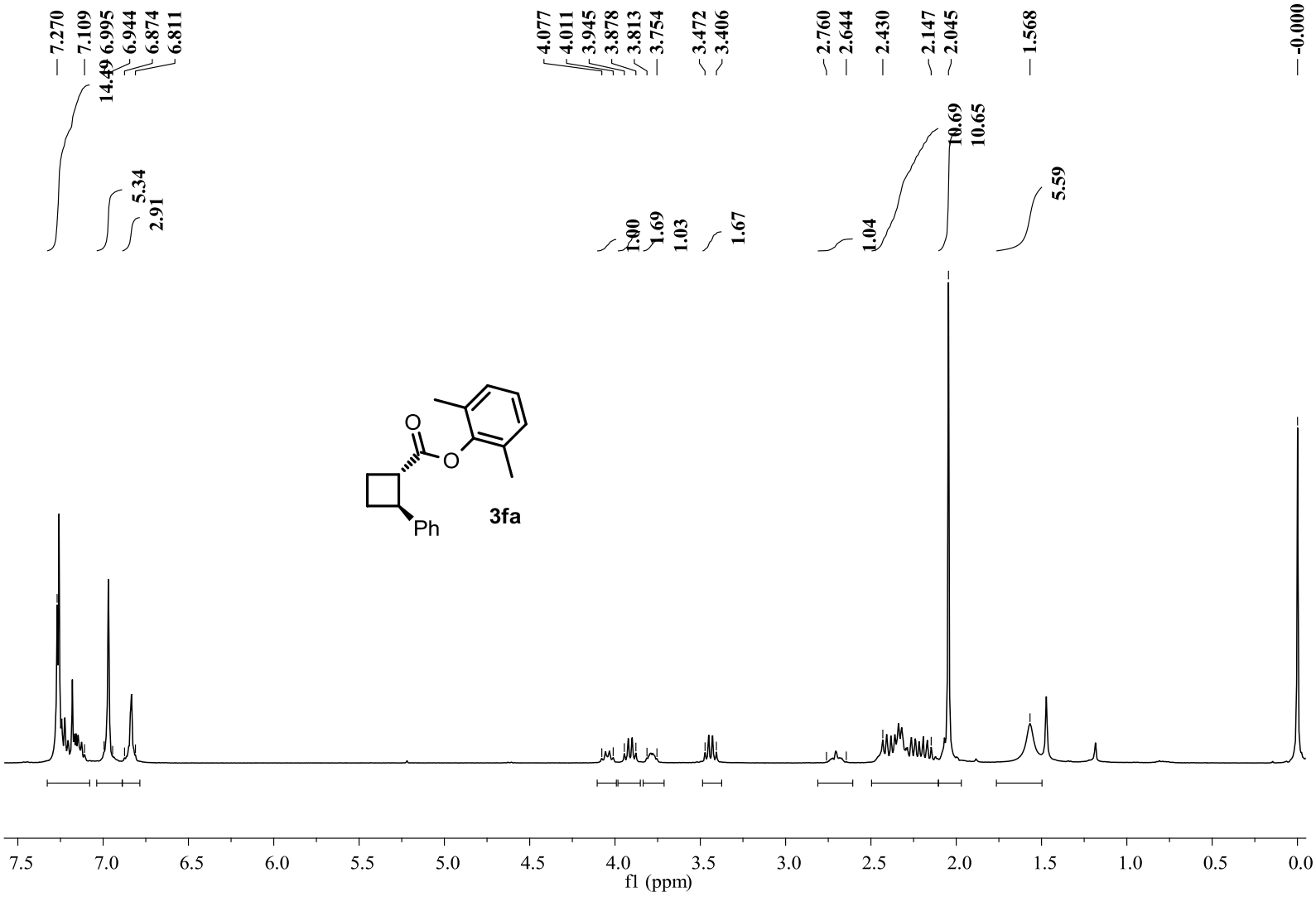
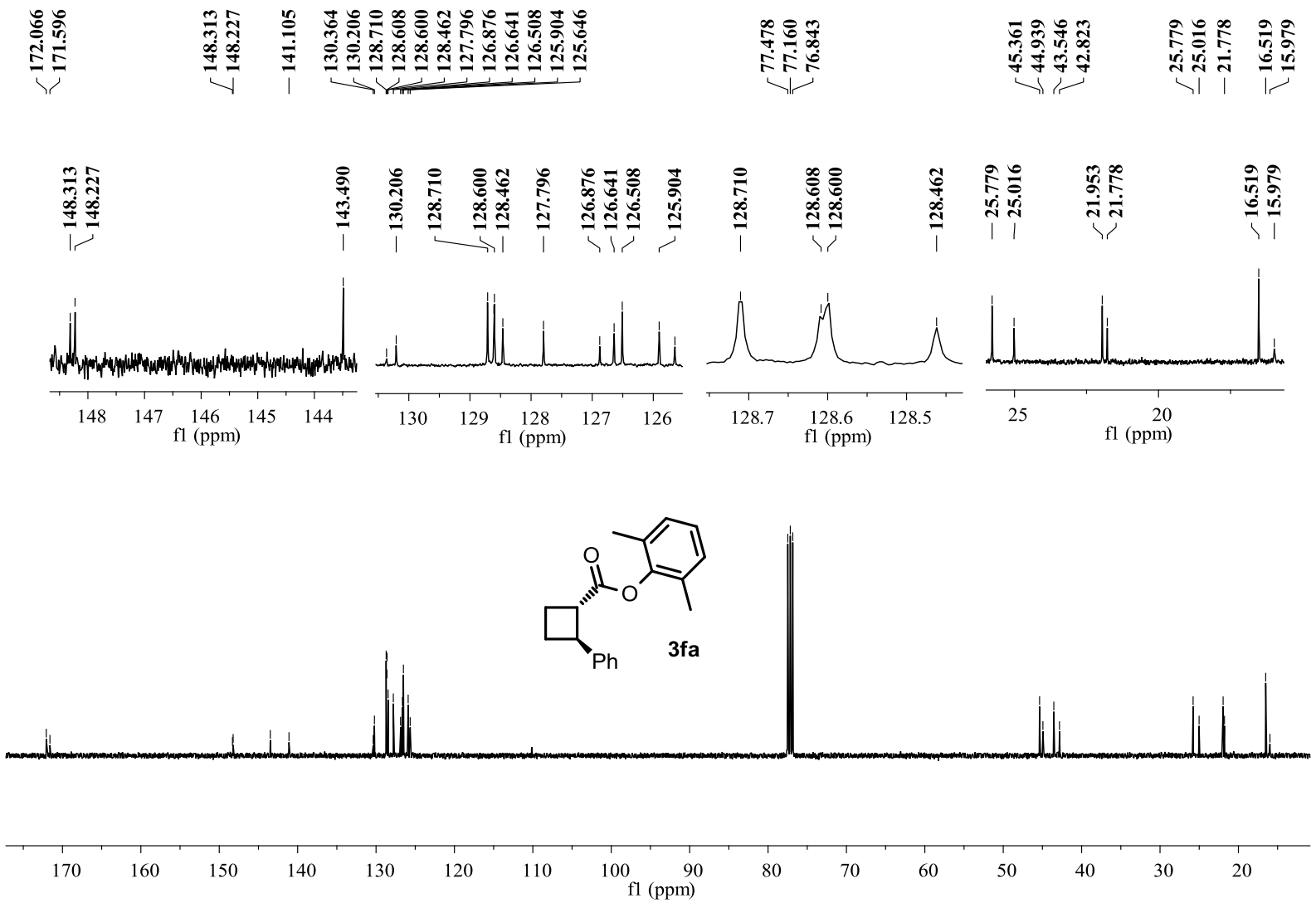
143.614
136.218
128.667
128.483
128.279
128.187
126.551
126.490
77.477
77.160
76.842
66.349
45.583
43.358
25.402
21.818
128.5
128.0
126.7
126.4
f1 (ppm)
COOBn
3da
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.296
7.189
7.113
5.40
7.075
7.024
6.970
6.243
6.224
4.097
4.031
3.743
3.686
2.675
2.584
2.473
2.400
2.341
2.193
-0.000
2.03
1.35
1.91
1.03
1.00
1.08
1.21
2.58
COOPh
3ea
Ph
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)


172.289
150.589
140.894
129.222
127.829
126.914
125.627
121.628
77.478
77.160
76.842
45.059
42.965
24.369
20.308
129.222
128.514
127.829
126.914
125.627
121.628
129
127
125
123
121
f1 (ppm)
COOPh
3ea
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


7.270
7.109
6.995
6.944
6.874
6.811
4.077
4.011
3.945
3.878
3.813
3.754
3.472
3.406
2.760
2.644
2.430
2.147
2.045
1.568
-0.000
14.49
5.34
2.91
1.00
1.69
1.03
1.67
1.04
10.69
10.65
5.59
O
O
Ph
3fa
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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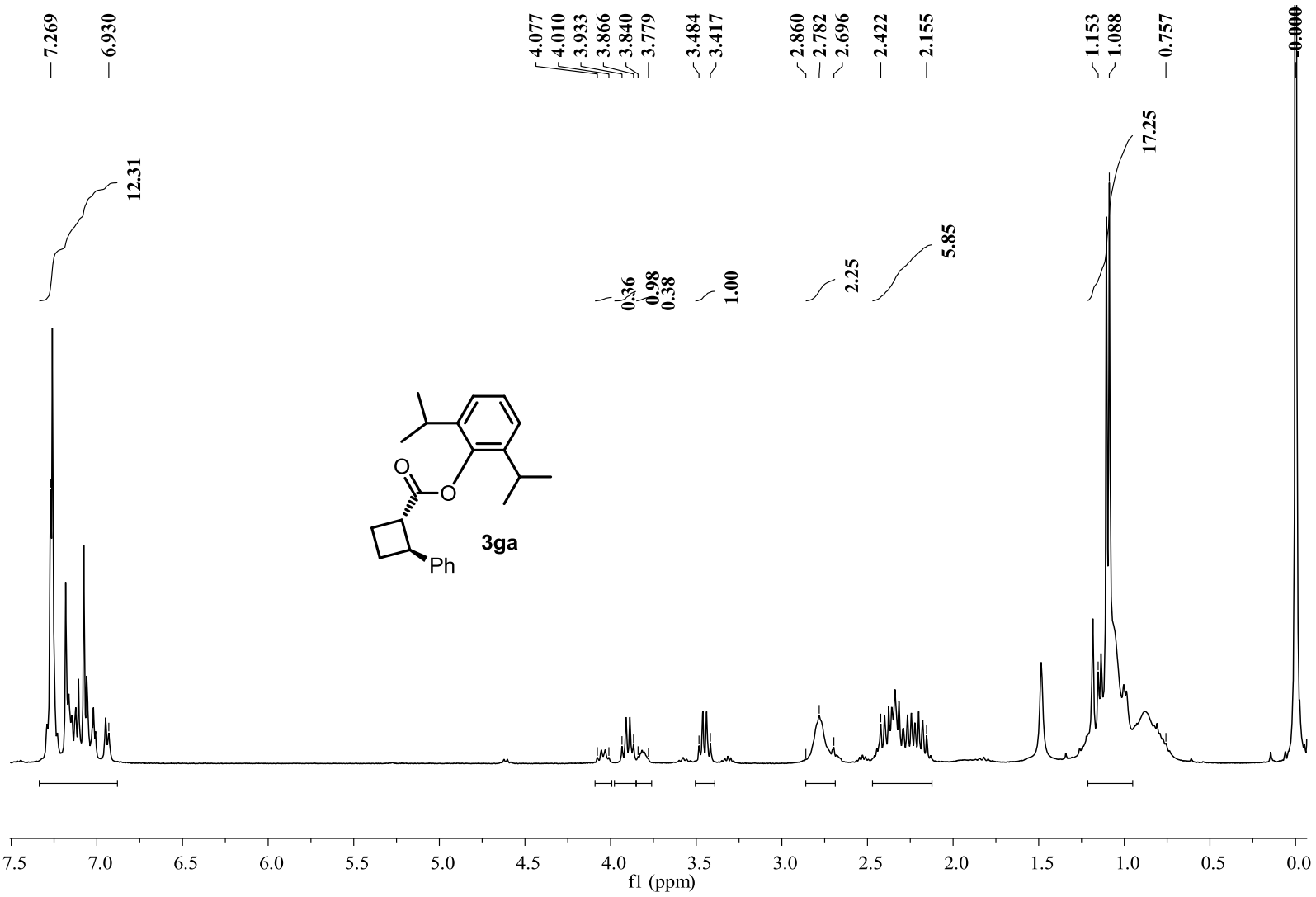
171.596
148.313
148.227
141.105
130.364
130.206
128.710
128.608
128.600
128.462
127.796
126.876
126.641
126.508
125.904
125.646
77.478
77.160
76.843
45.361
44.939
43.546
42.823
25.779
25.016
21.778
16.519
15.979
148.313
148.227
143.490
130.206
128.710
128.600
128.462
127.796
126.876
126.641
126.508
125.904
128.710
128.608
128.600
128.462
25.779
25.016
21.953
21.778
16.519
15.979
148 147 146 145 144
fl (ppm)
130 129 128 127 126
fl (ppm)
128.7 128.6 128.5
fl (ppm)
25 20
fl (ppm)
O
O
Ph
3fa
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
fl (ppm)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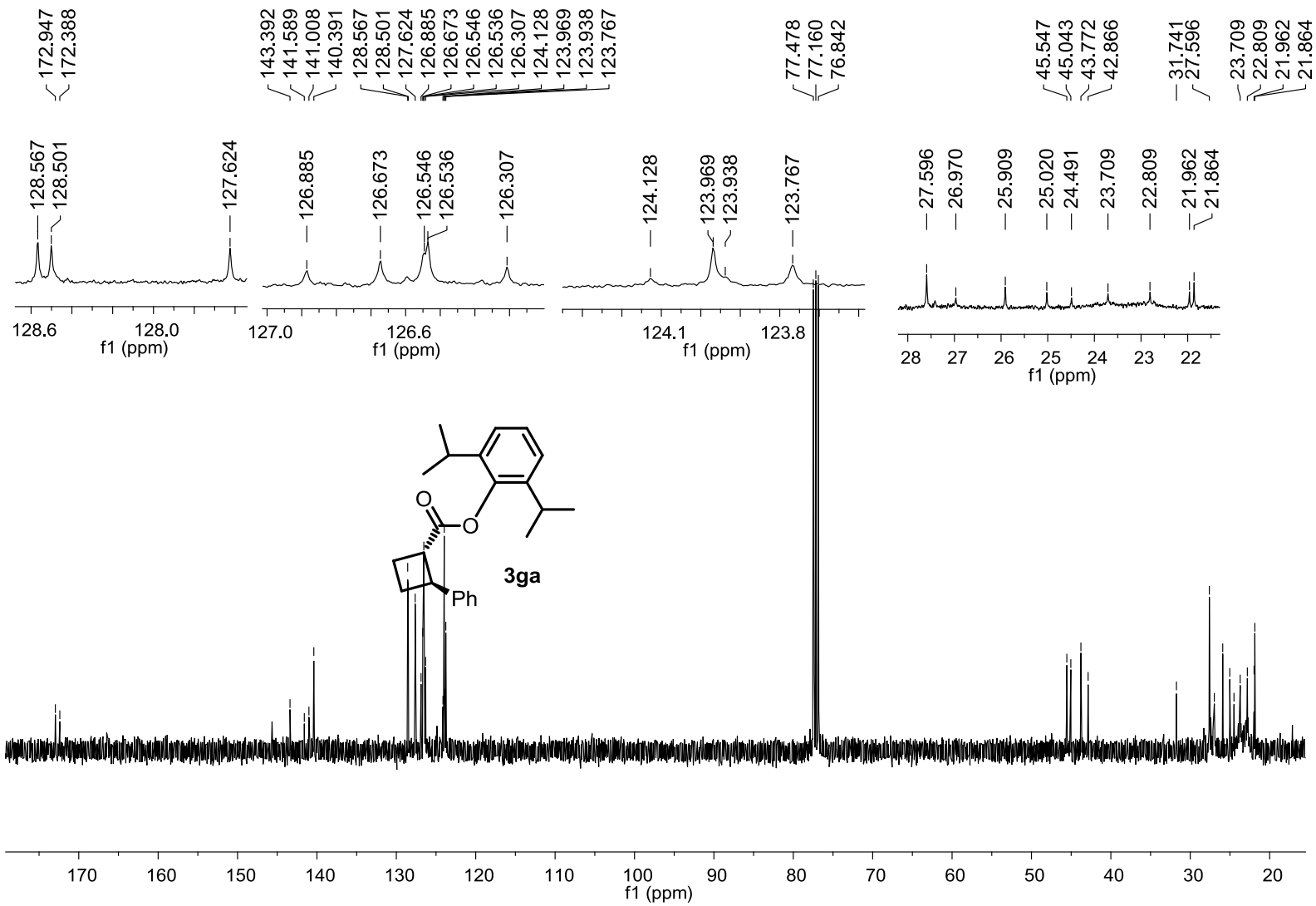
6.930
4.077
4.010
3.933
3.866
3.840
3.779
3.484
3.417
2.860
2.782
2.696
2.422
2.155
1.153
1.088
0.757
0.000
12.31
0.36
0.98
0.38
1.00
2.25
5.85
17.25
O
O
Ph
3ga
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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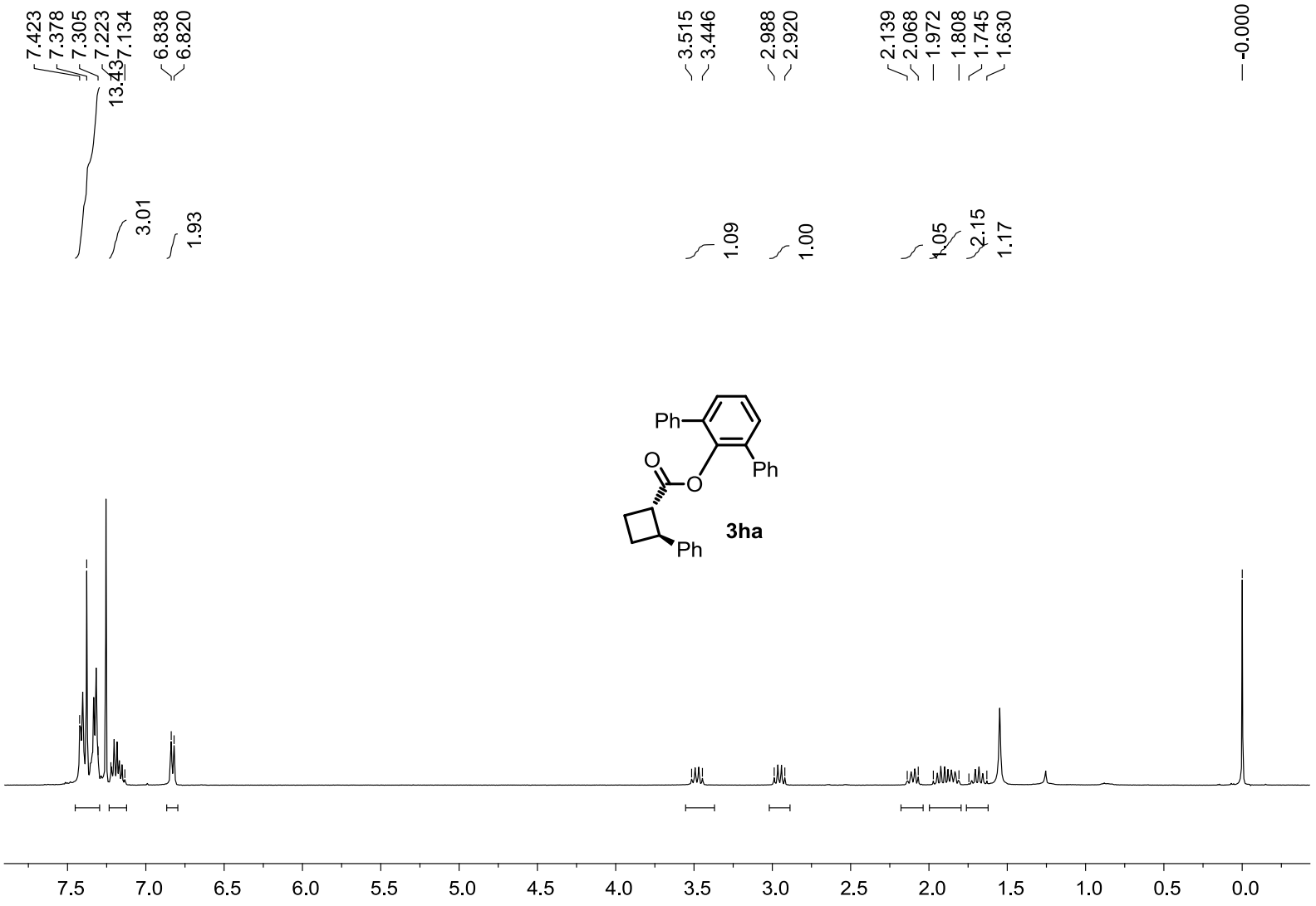
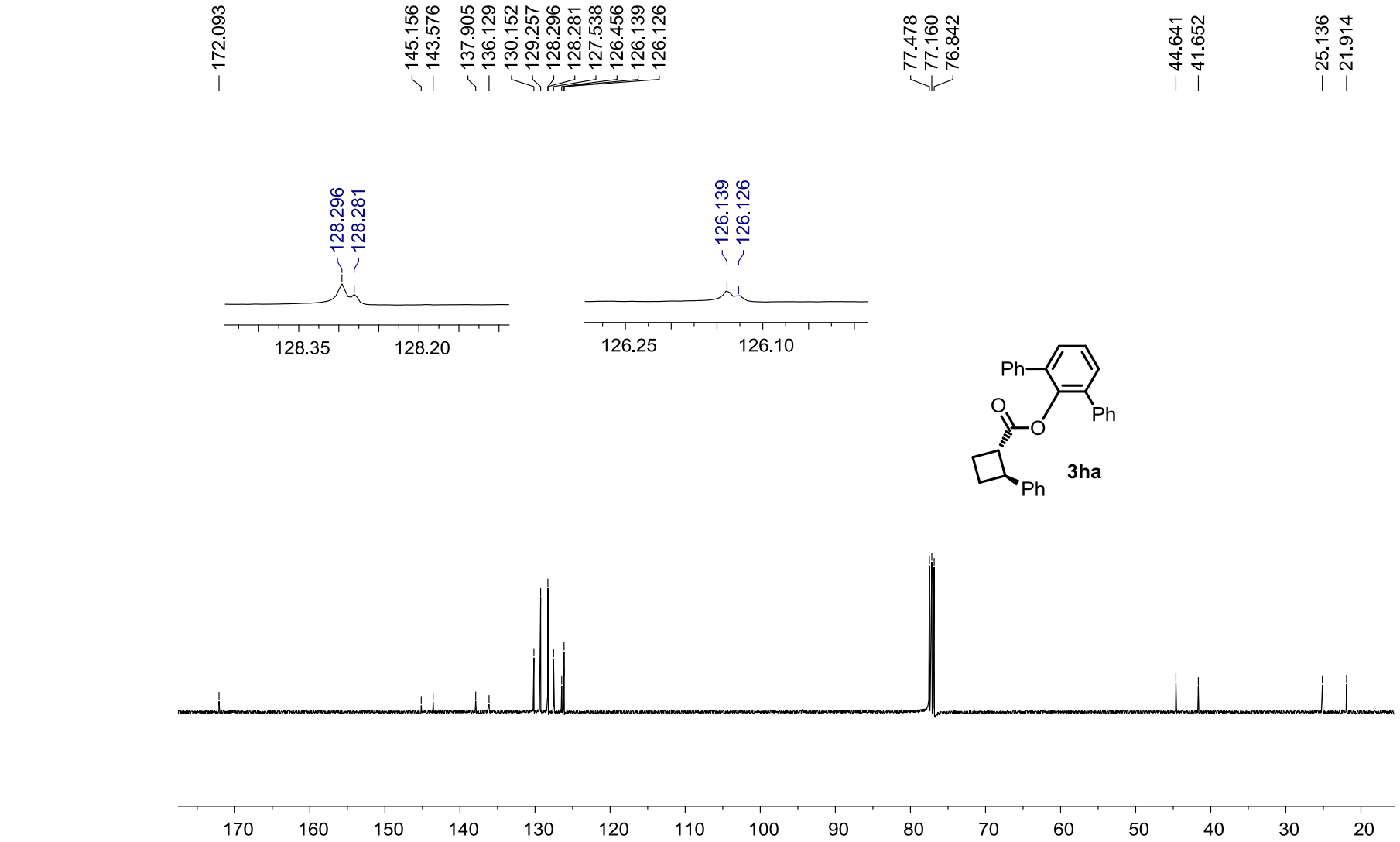
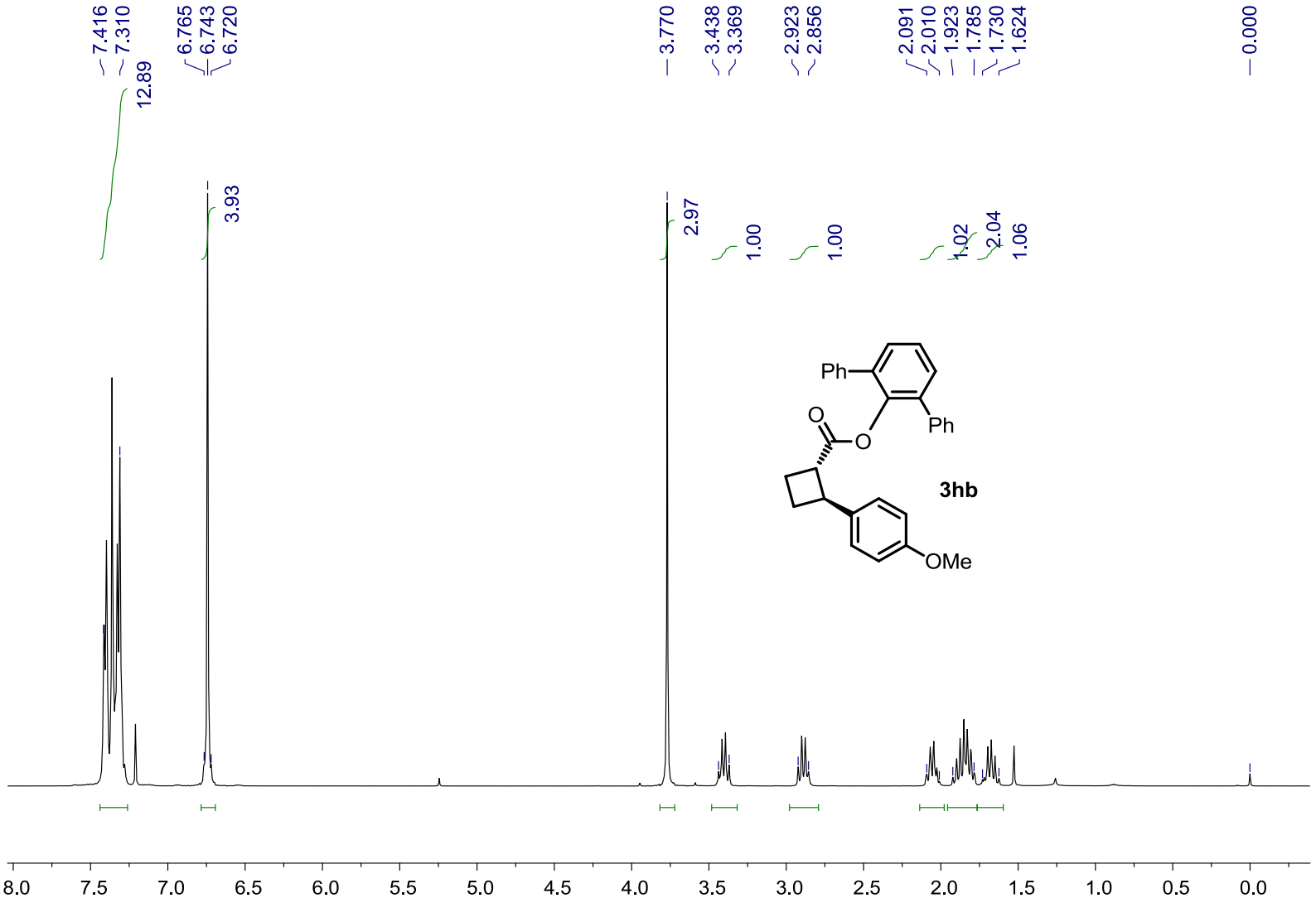
141.589
141.008
140.391
128.567
128.501
127.624
126.885
126.673
126.546
126.536
126.307
124.128
123.969
123.938
123.767
77.478
77.160
76.842
45.547
45.043
43.772
42.866
31.741
27.596
23.709
22.809
21.962
21.864
f1 (ppm)
O
O
Ph
3ga


7.423
7.378
7.305
7.223
7.134
6.838
6.820
3.515
3.446
2.988
2.920
2.139
2.068
1.972
1.808
1.745
1.630
-0.000
3.01
1.93
1.09
1.00
1.05
2.15
1.17
Ph
Ph
O
O
Ph
3ha
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


172.093
145.156
143.576
137.905
136.129
130.152
129.257
128.296
128.281
127.538
126.456
126.139
126.126
77.478
77.160
76.842
44.641
41.652
25.136
21.914
128.296
128.281
128.35
128.20
126.139
126.126
126.25
126.10
Ph
Ph
O
O
Ph
3ha
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20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6.743
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3.770
2.97
3.438
3.369
1.00
2.923
2.856
1.00
2.091
2.010
1.923
1.785
1.730
1.624
1.02
2.04
1.06
0.000
Ph
Ph
O
O
3hb
OMe
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
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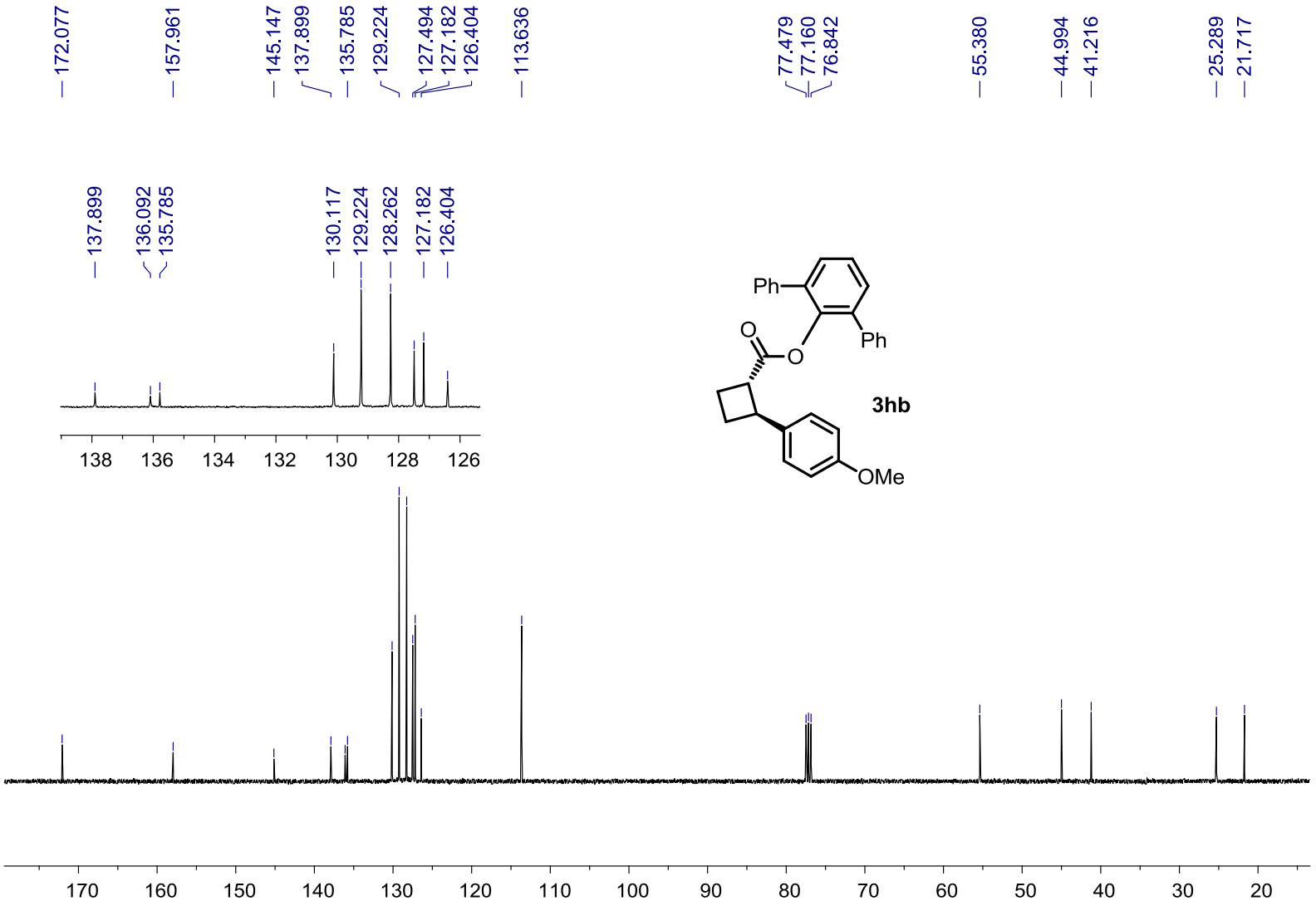
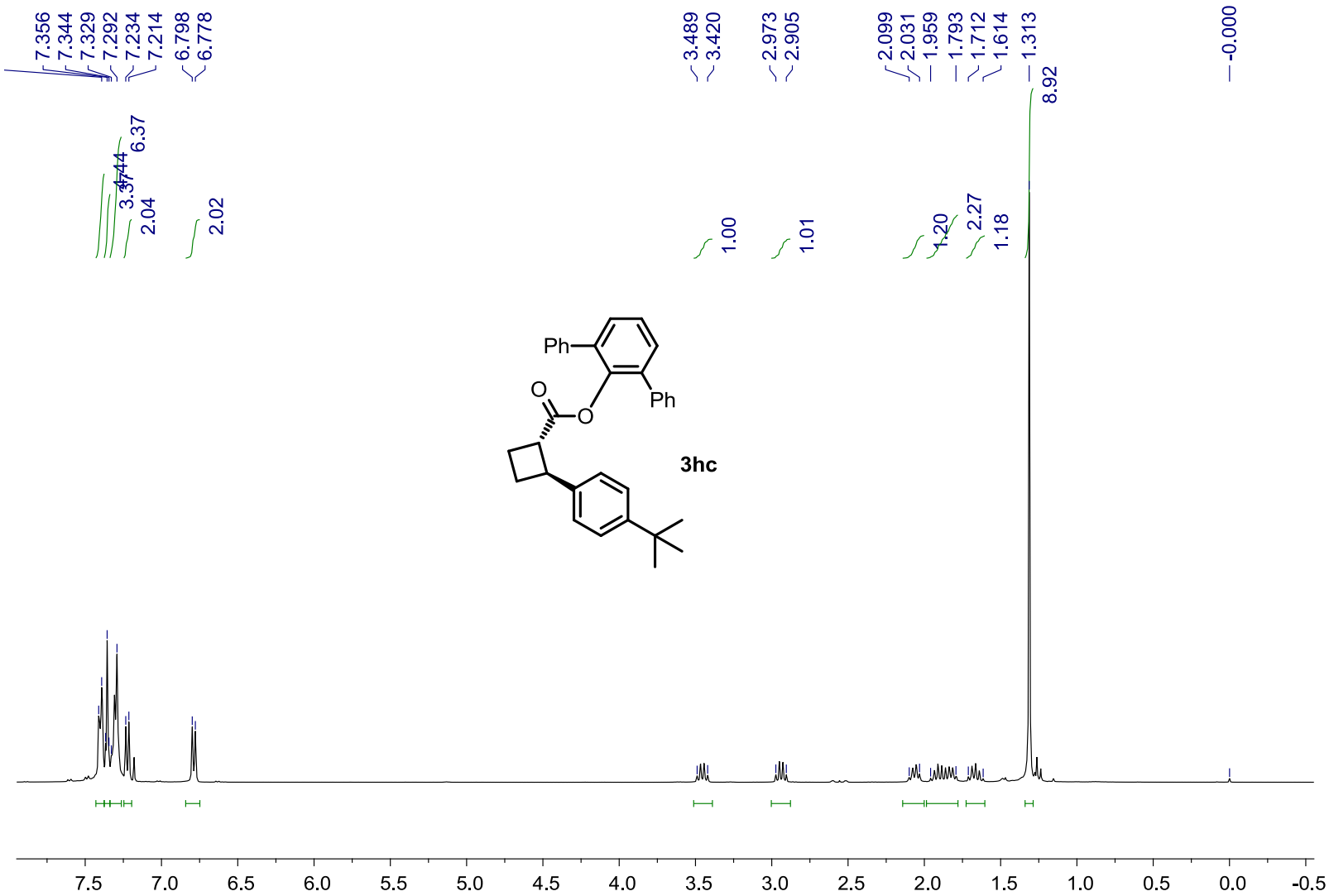

172.077
157.961
145.147
137.899
135.785
129.224
127.494
127.182
126.404
113.636
77.479
77.160
76.842
55.380
44.994
41.216
25.289
21.717
137.899
136.092
135.785
130.117
129.224
128.262
127.182
126.404
Ph
Ph
O
O
3hb
OMe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7.292
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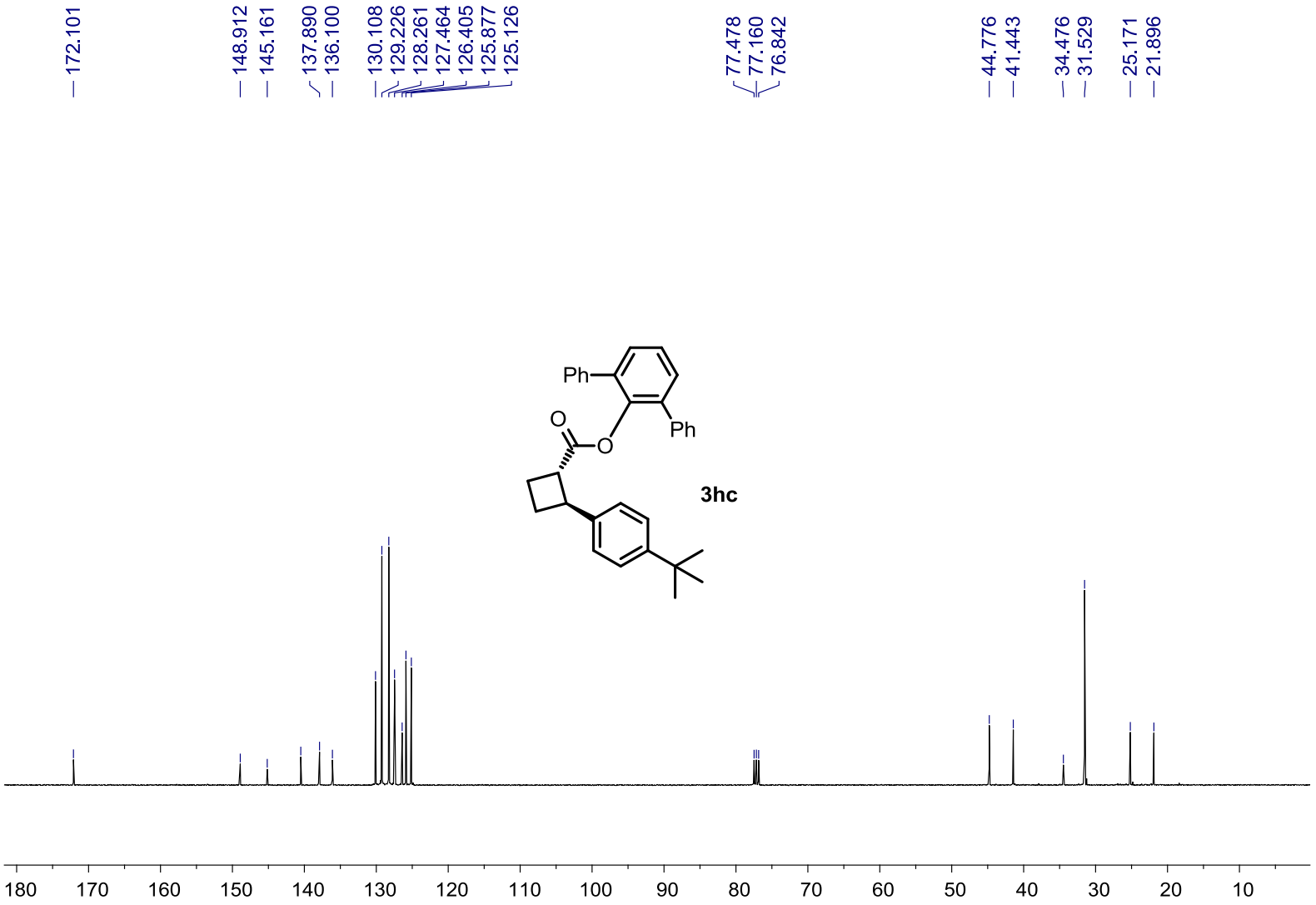
7.214
6.798
6.778
3.489
3.420
2.973
2.905
2.099
2.031
1.959
1.793
1.712
1.614
1.313
-0.000
8.92
6.37
3.44
3.37
2.04
2.02
1.00
1.01
1.20
2.27
1.18
Ph
Ph
O
O
3hc
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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145.161
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128.261
127.464
126.405
125.877
125.126
77.478
77.160
76.842
44.776
41.443
34.476
31.529
25.171
21.896
Ph
Ph
O
O
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160
150
140
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120
110
100
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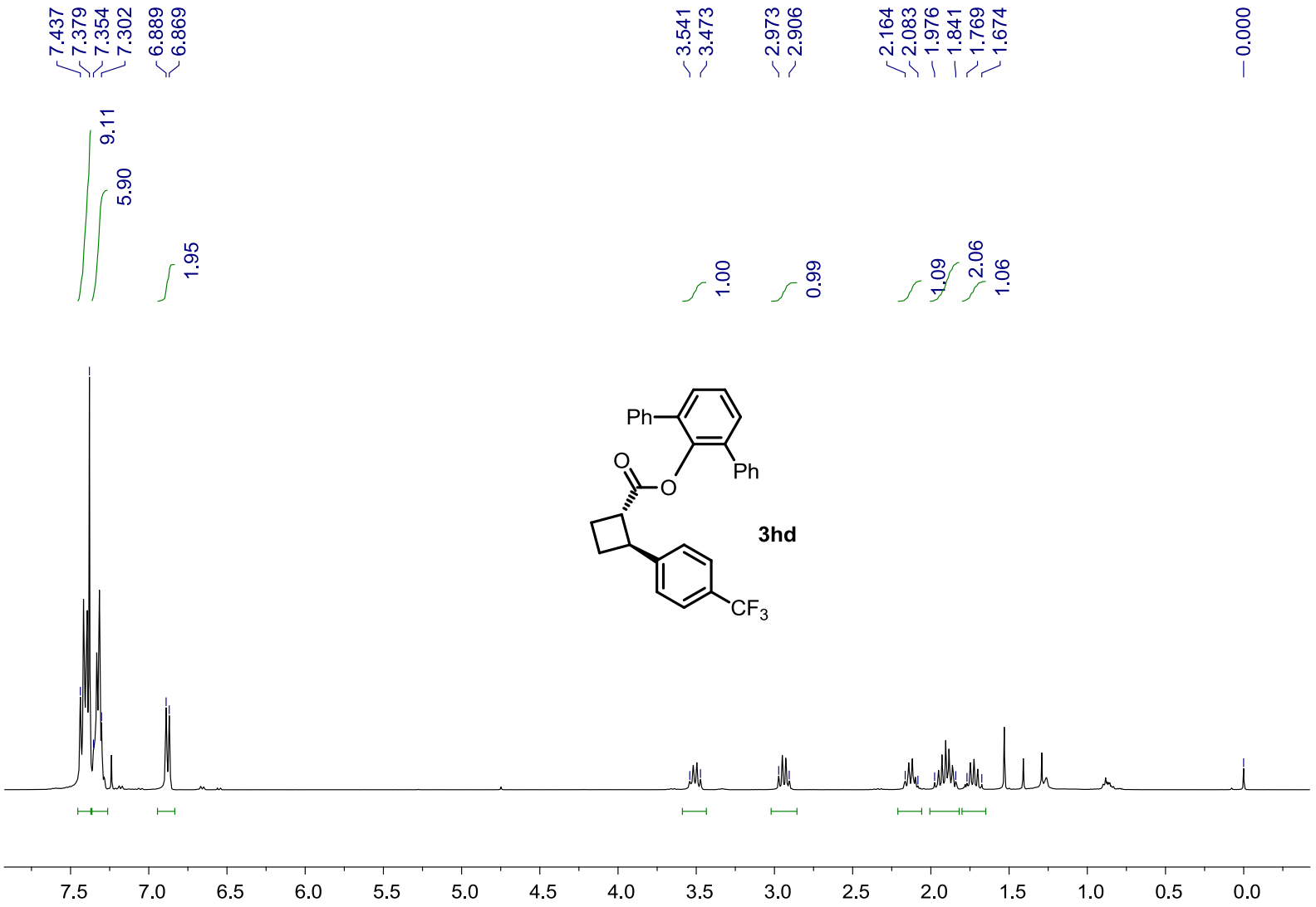
80
70
60
50
40
30
20
10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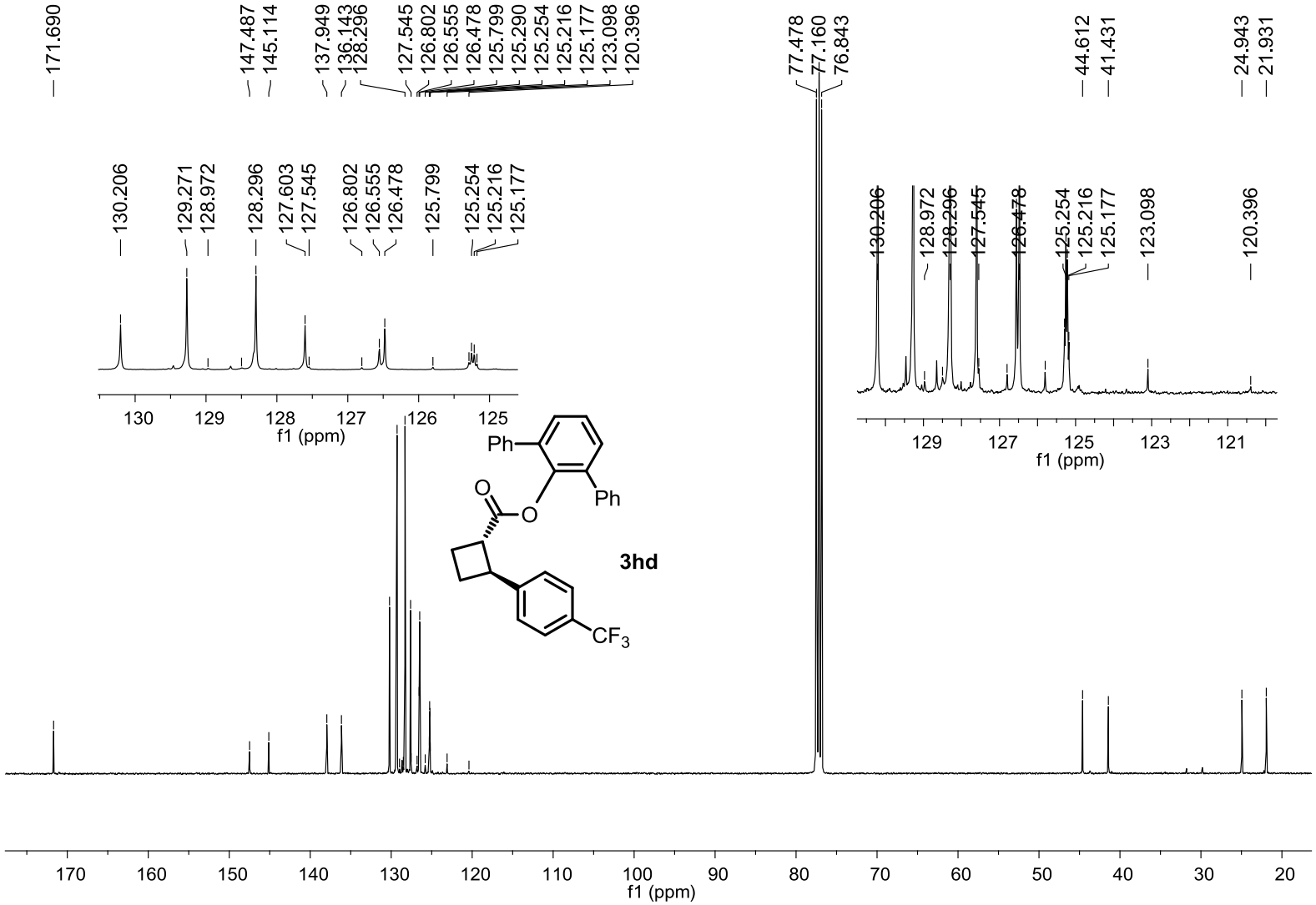
7.354
7.302
6.889
6.869
3.541
3.473
2.973
2.906
2.164
2.083
1.976
1.841
1.769
1.674
0.000
9.11
5.90
1.95
1.00
0.99
1.09
2.06
1.06
Ph
Ph
O
O
3hd
CF3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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136.143
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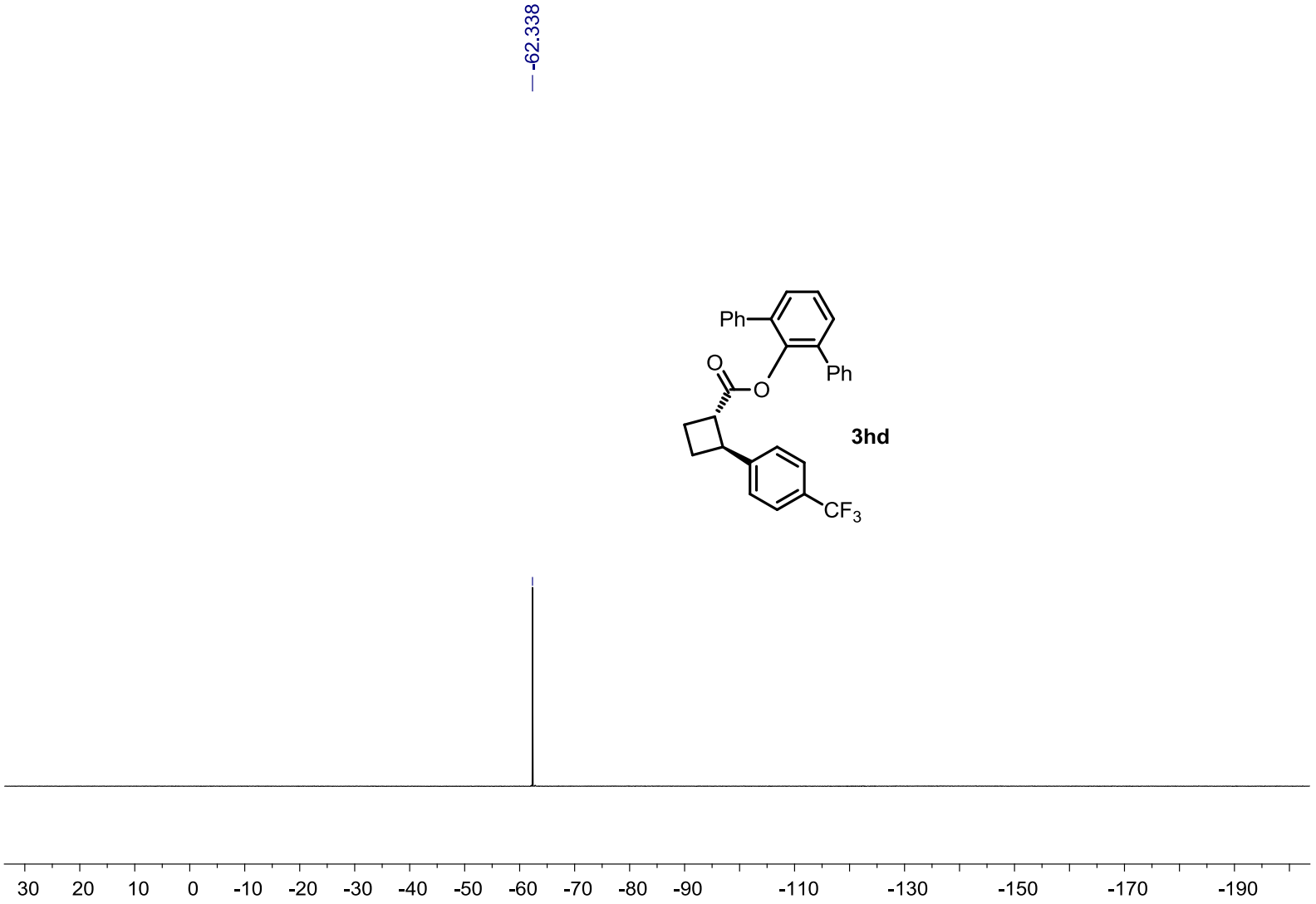
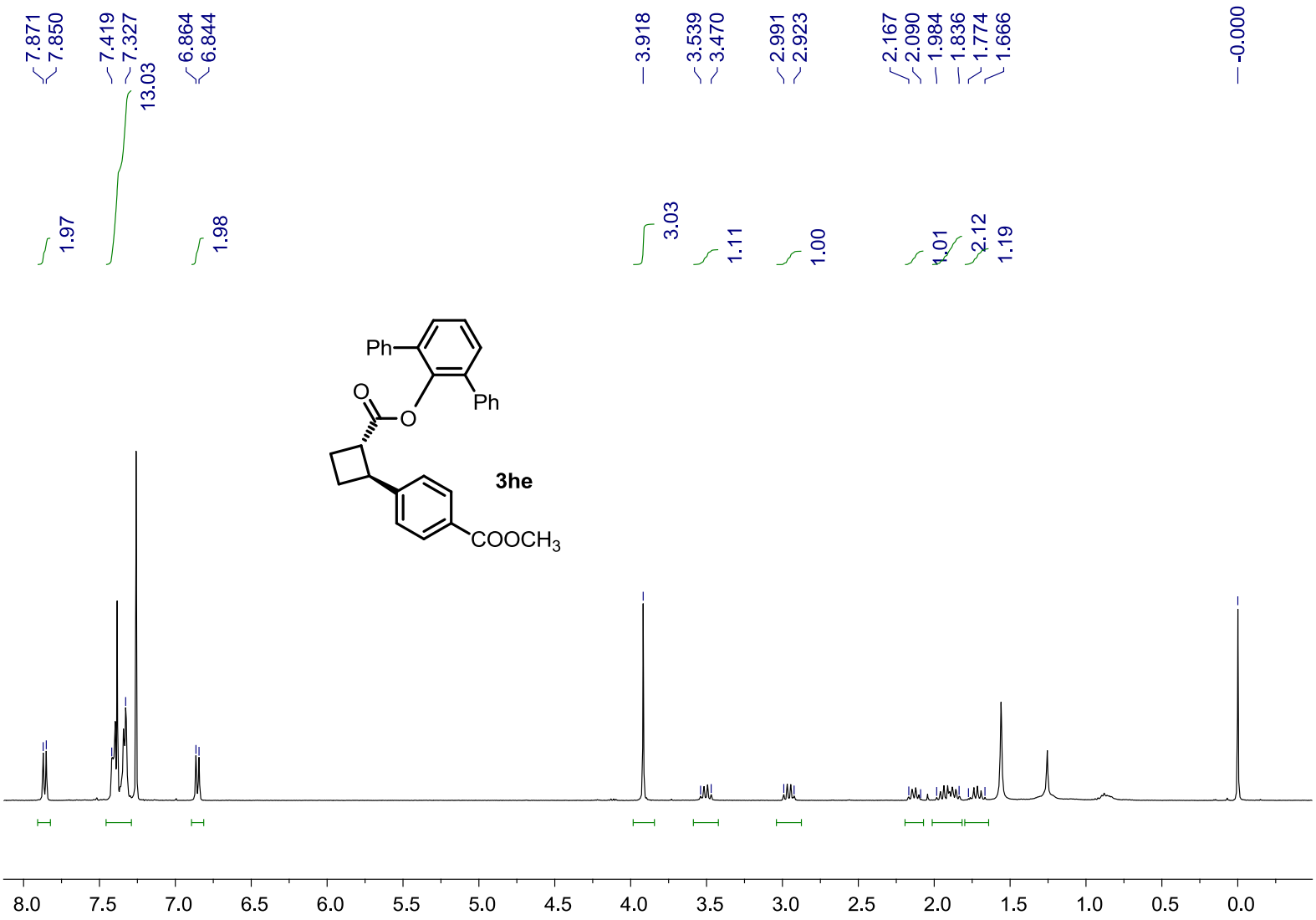
127.545
126.802
126.555
126.478
125.799
125.290
125.254
125.216
125.177
123.098
120.396
77.478
77.160
76.843
44.612
41.431
24.943
21.931
130.206
129.271
128.972
128.296
127.603
127.545
126.802
126.555
126.478
125.799
125.254
125.216
125.177
f1 (ppm)
130.206
128.972
128.296
127.545
126.478
125.254
125.216
125.177
123.098
120.396
f1 (ppm)
Ph
Ph
O
O
3hd
CF3
f1 (ppm)


-62.338
Ph
Ph
O
O
3hd
CF3
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190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6.844
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3.470
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2.923
2.167
2.090
1.984
1.836
1.774
1.666
-0.000
1.97
1.98
3.03
1.11
1.00
1.01
2.12
1.19
Ph
Ph
O
O
3he
COOCH3
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
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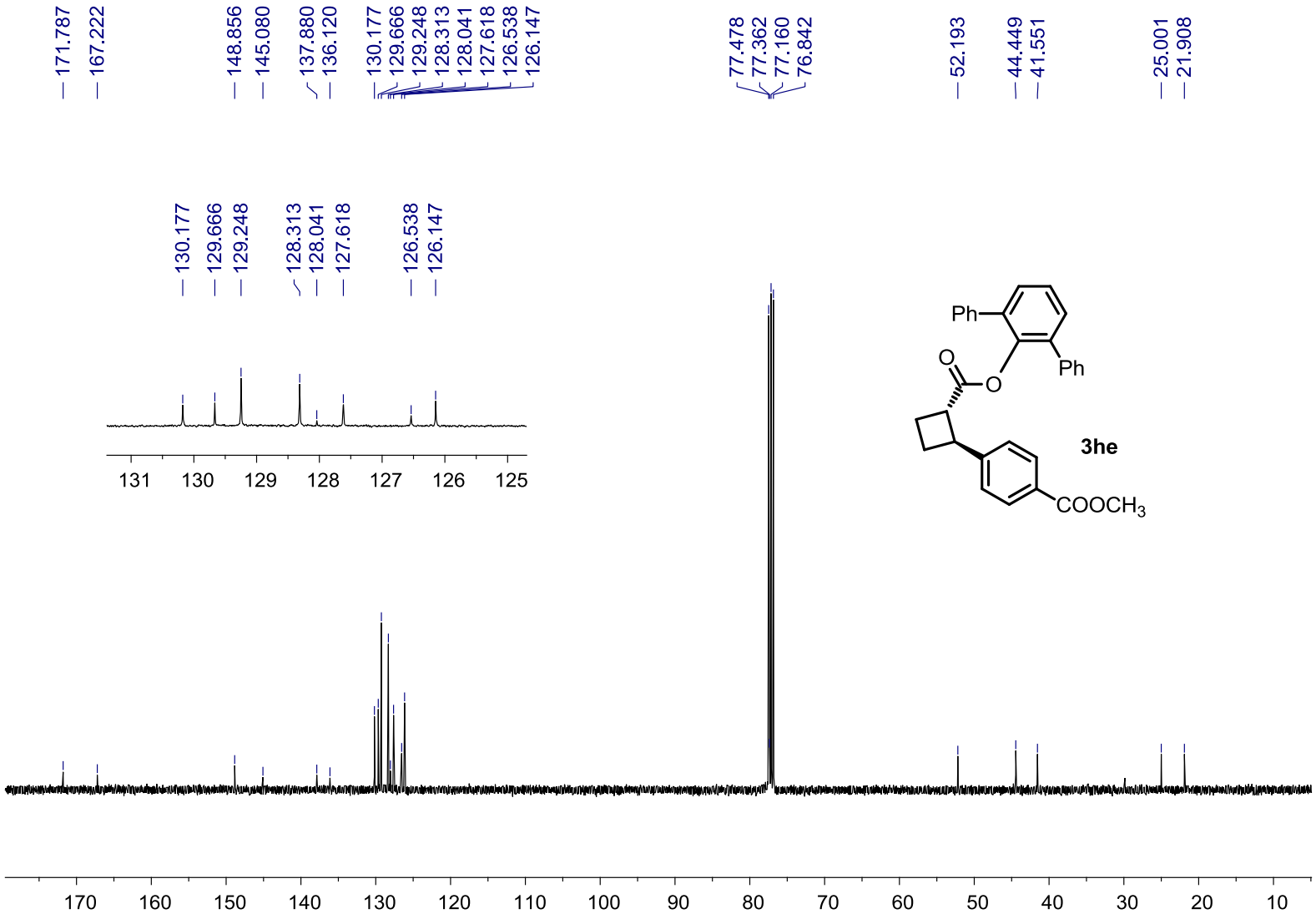
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O
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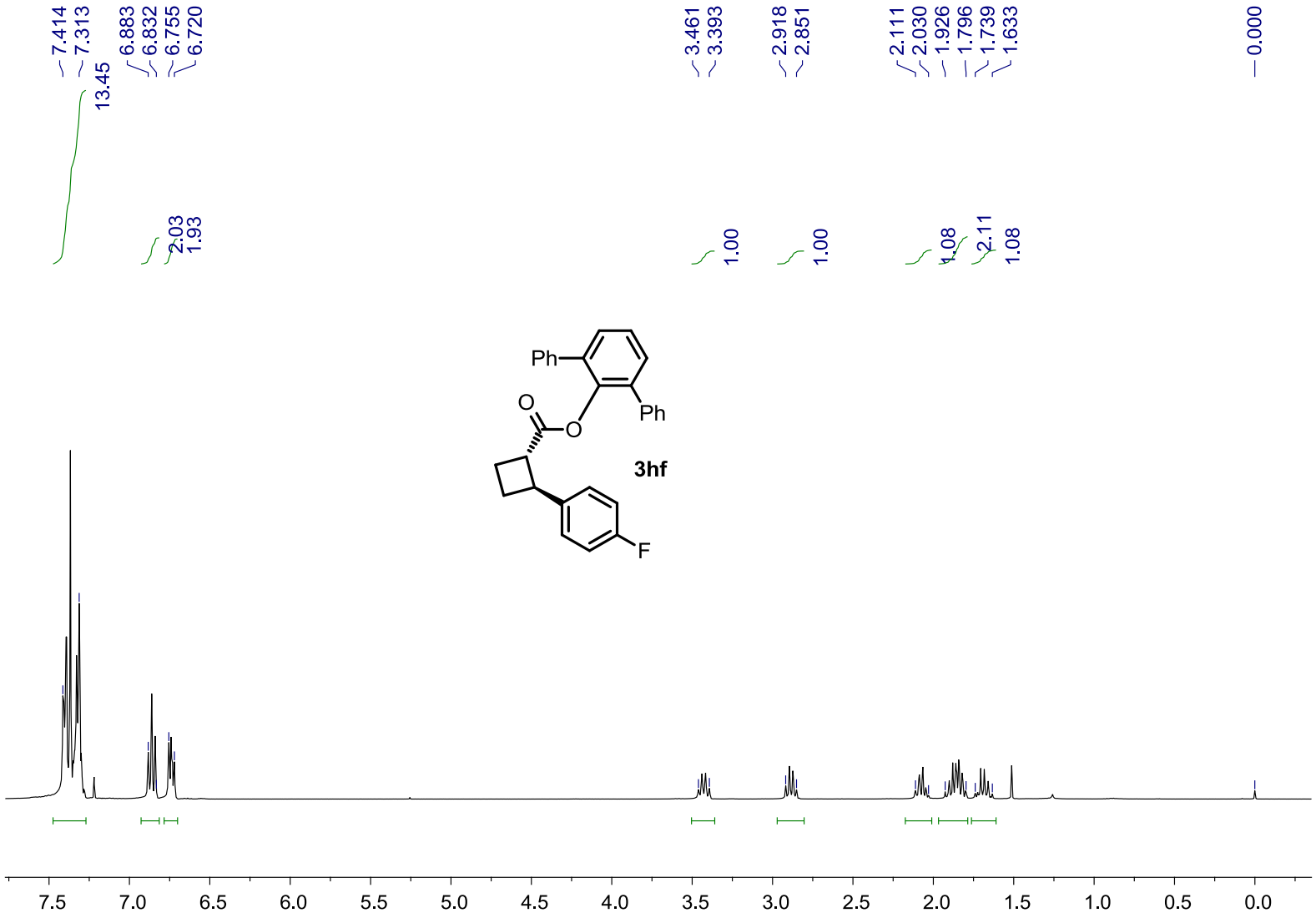
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Ph
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O
3hf
F
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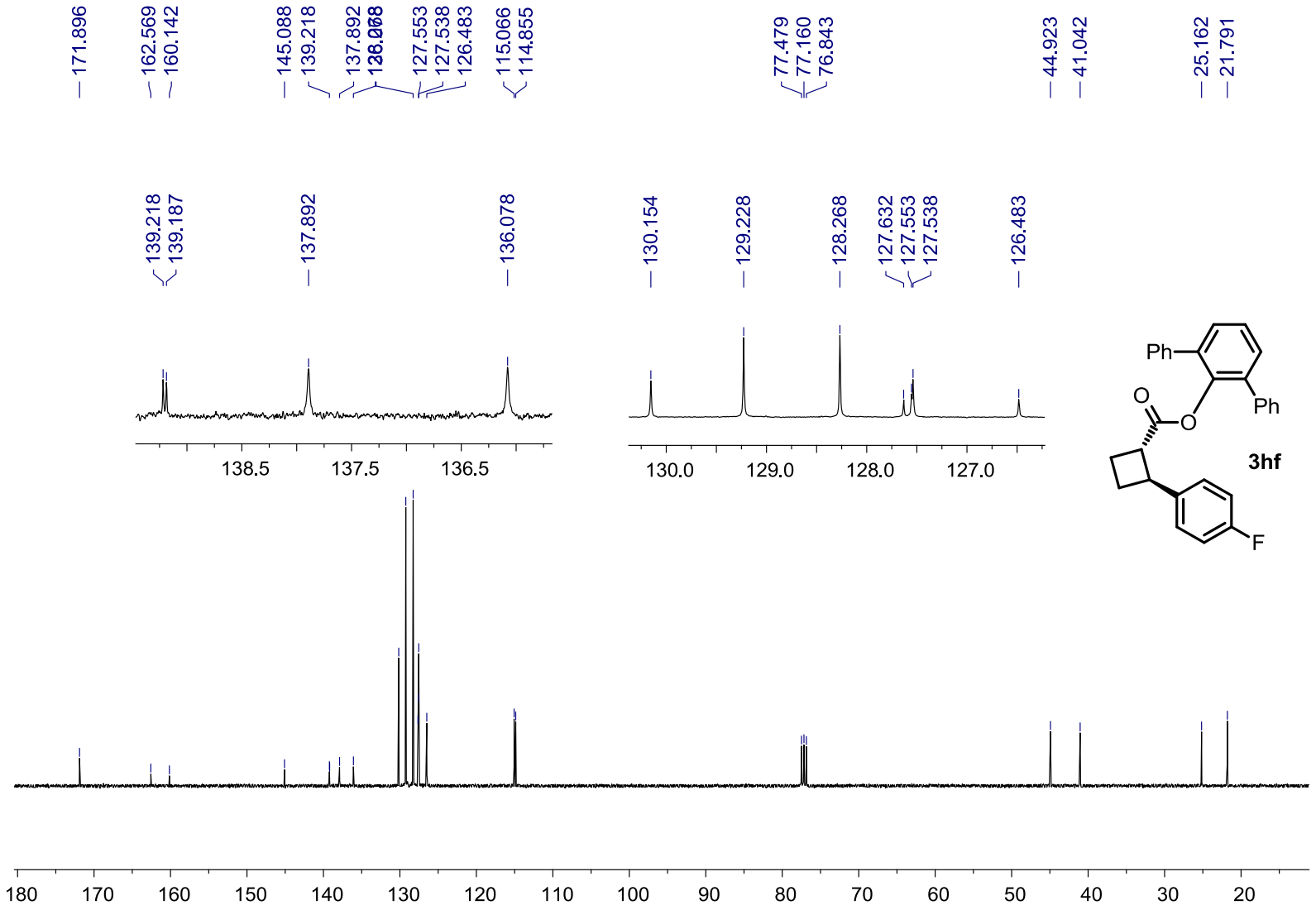
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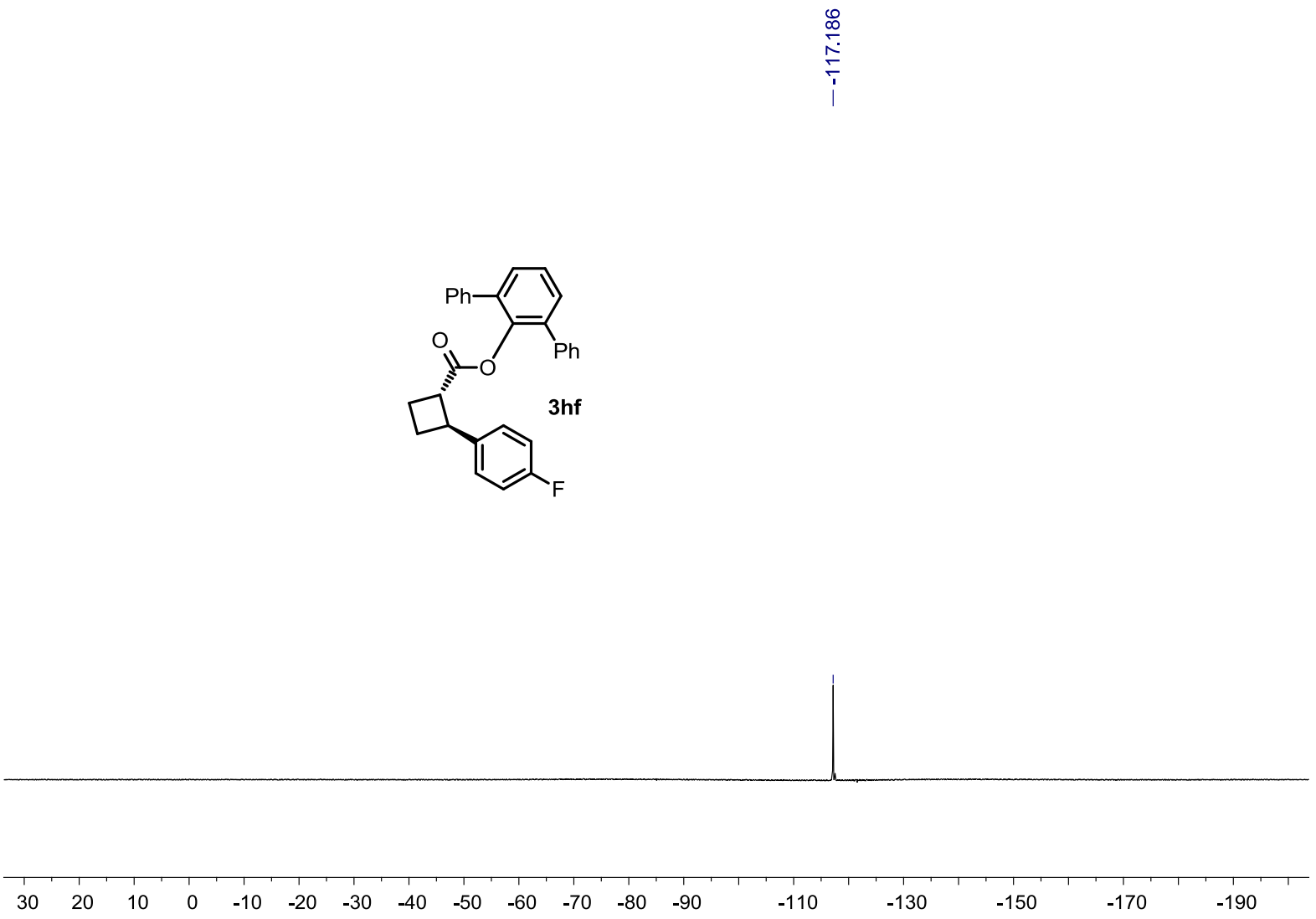
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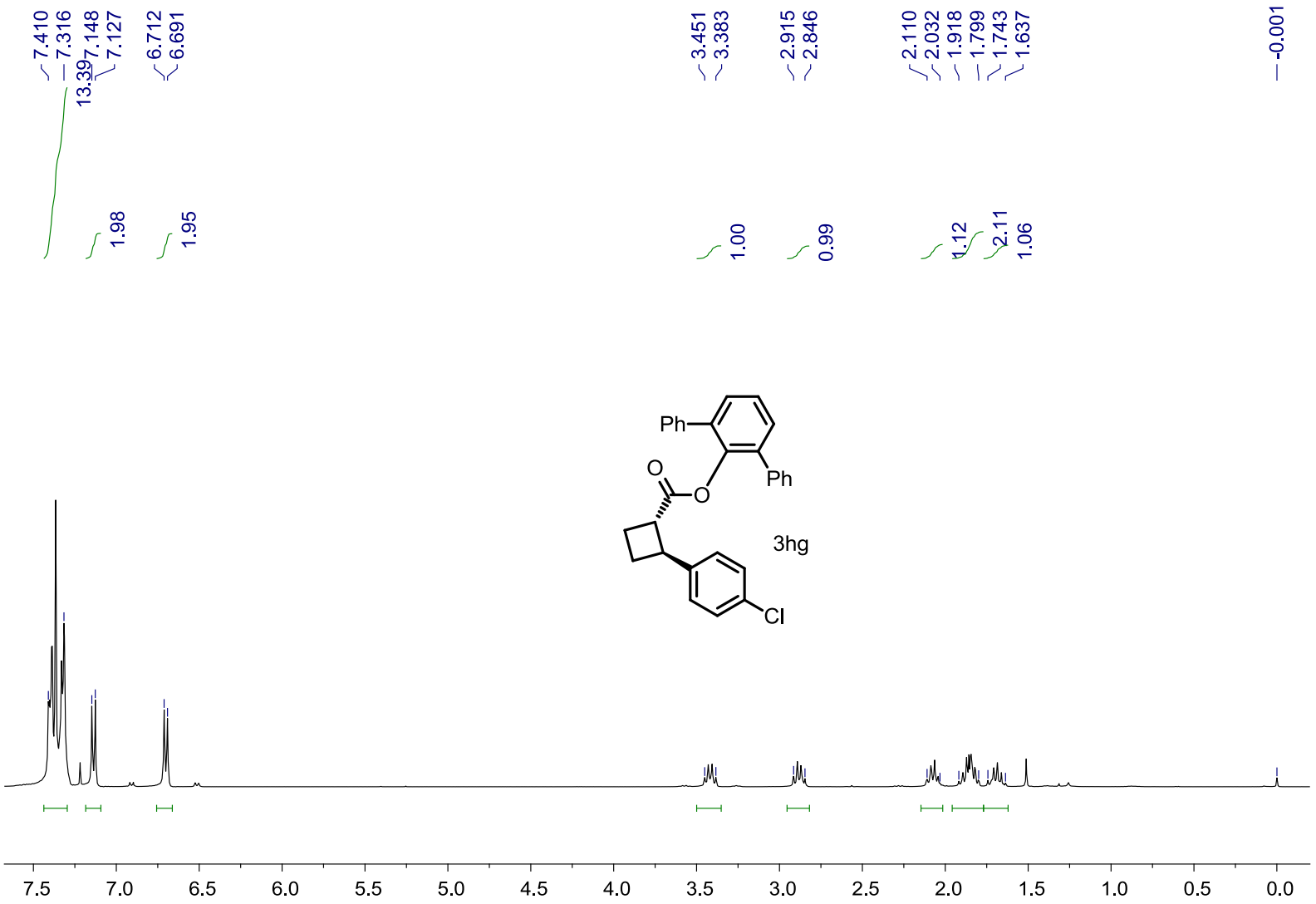
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0.99
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1.06
Ph
Ph
O
O
3hg
Cl
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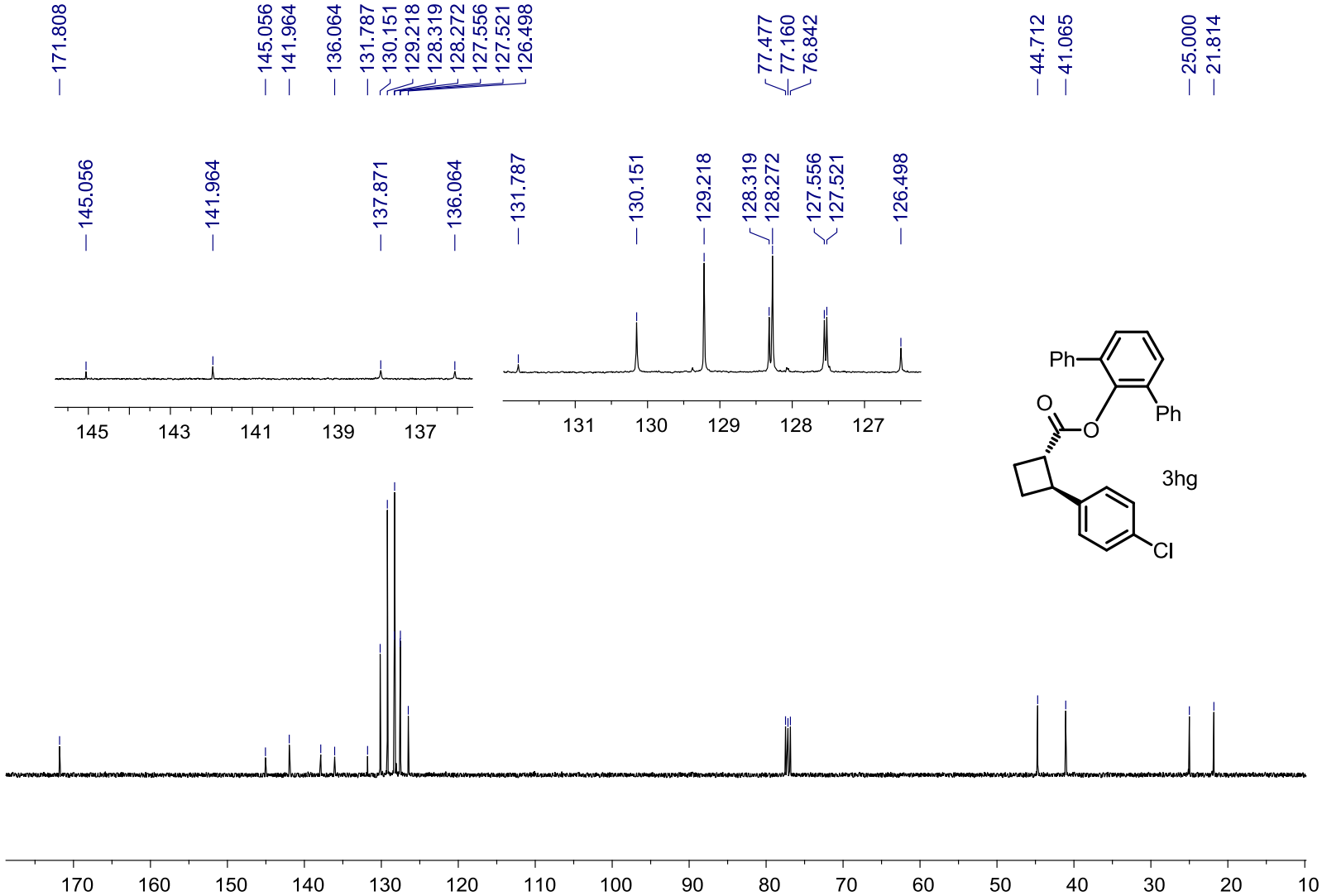
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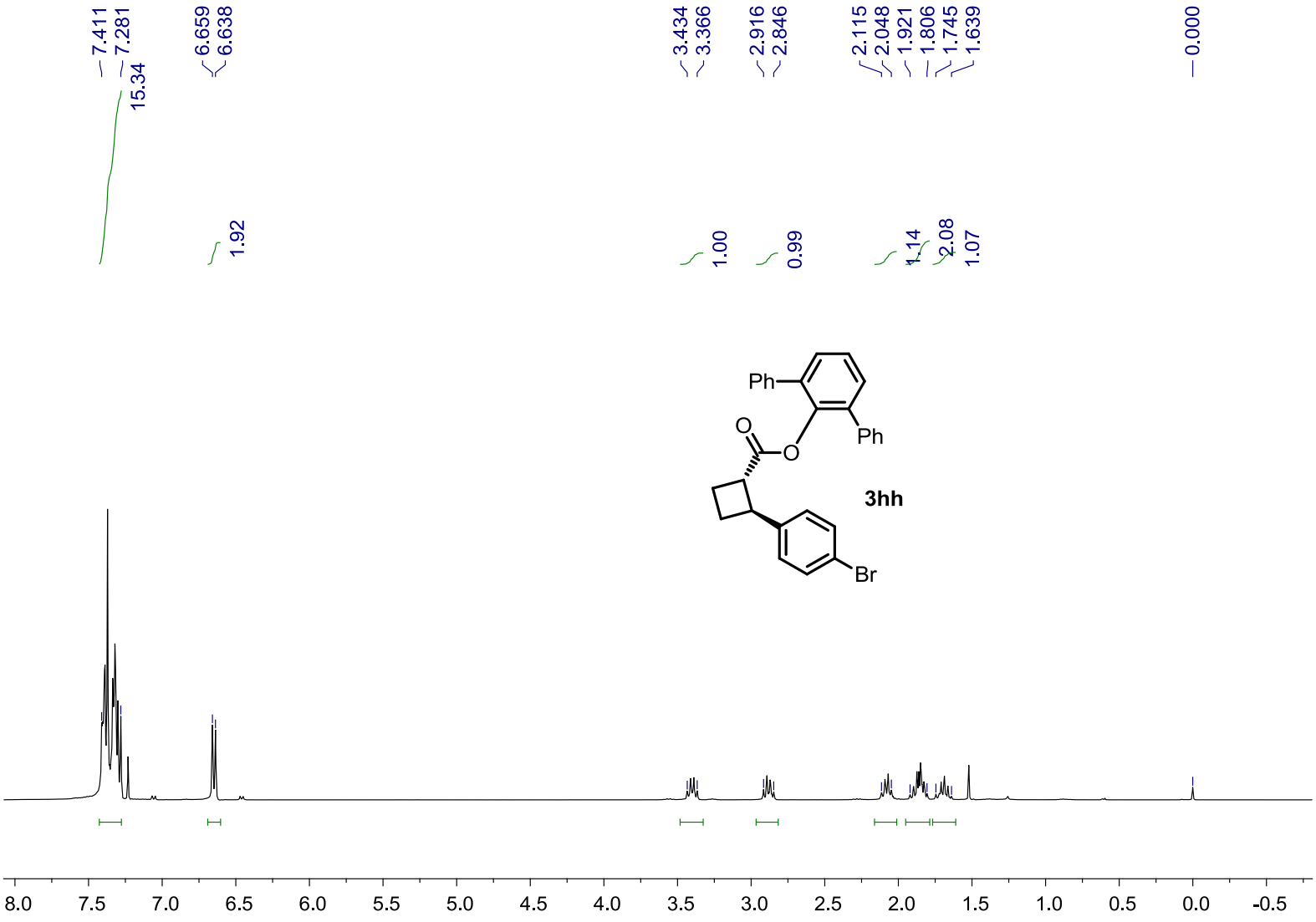
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1.745
1.639
1.14
2.08
1.07
0.000
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Ph
O
O
3hh
Br
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7.5
7.0
6.5
6.0
5.5
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2.5
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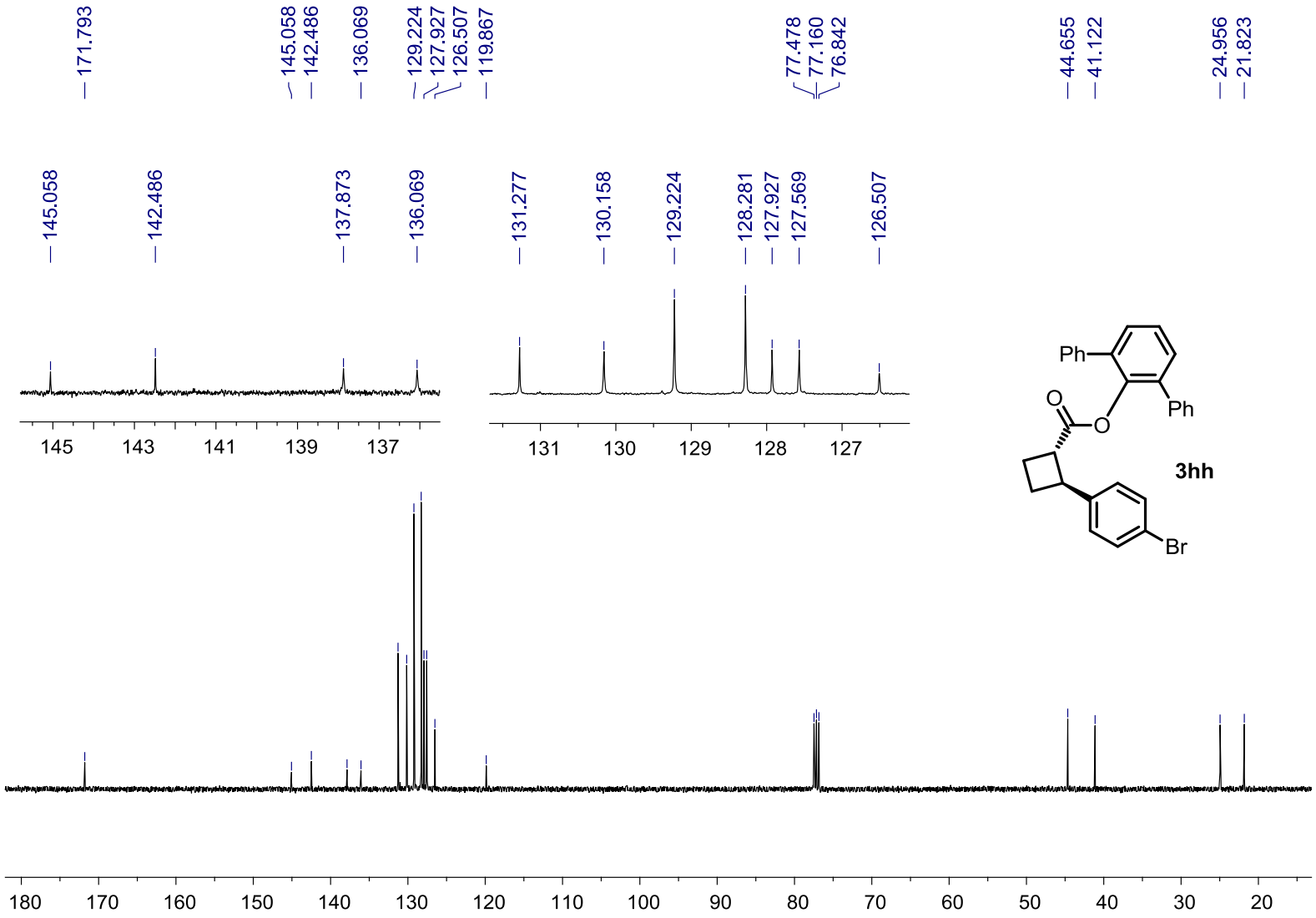
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143
141
139
137
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130
129
128
127
Ph
Ph
O
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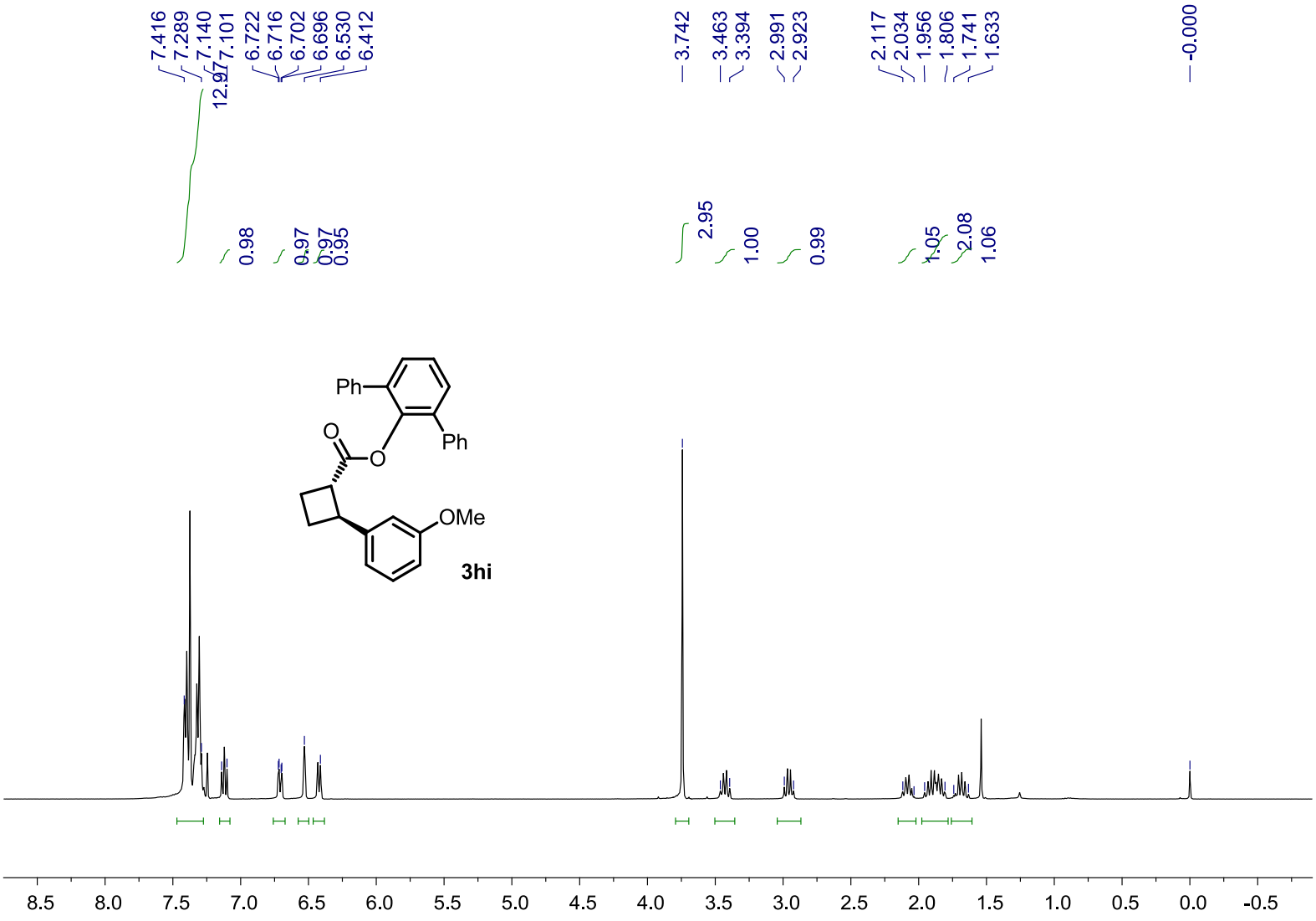
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2.117
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0.97
0.97
0.95
2.95
1.00
0.99
1.05
2.08
1.06
Ph
Ph
O
O
OMe
3hi
8.5
8.0
7.5
7.0
6.5
6.0
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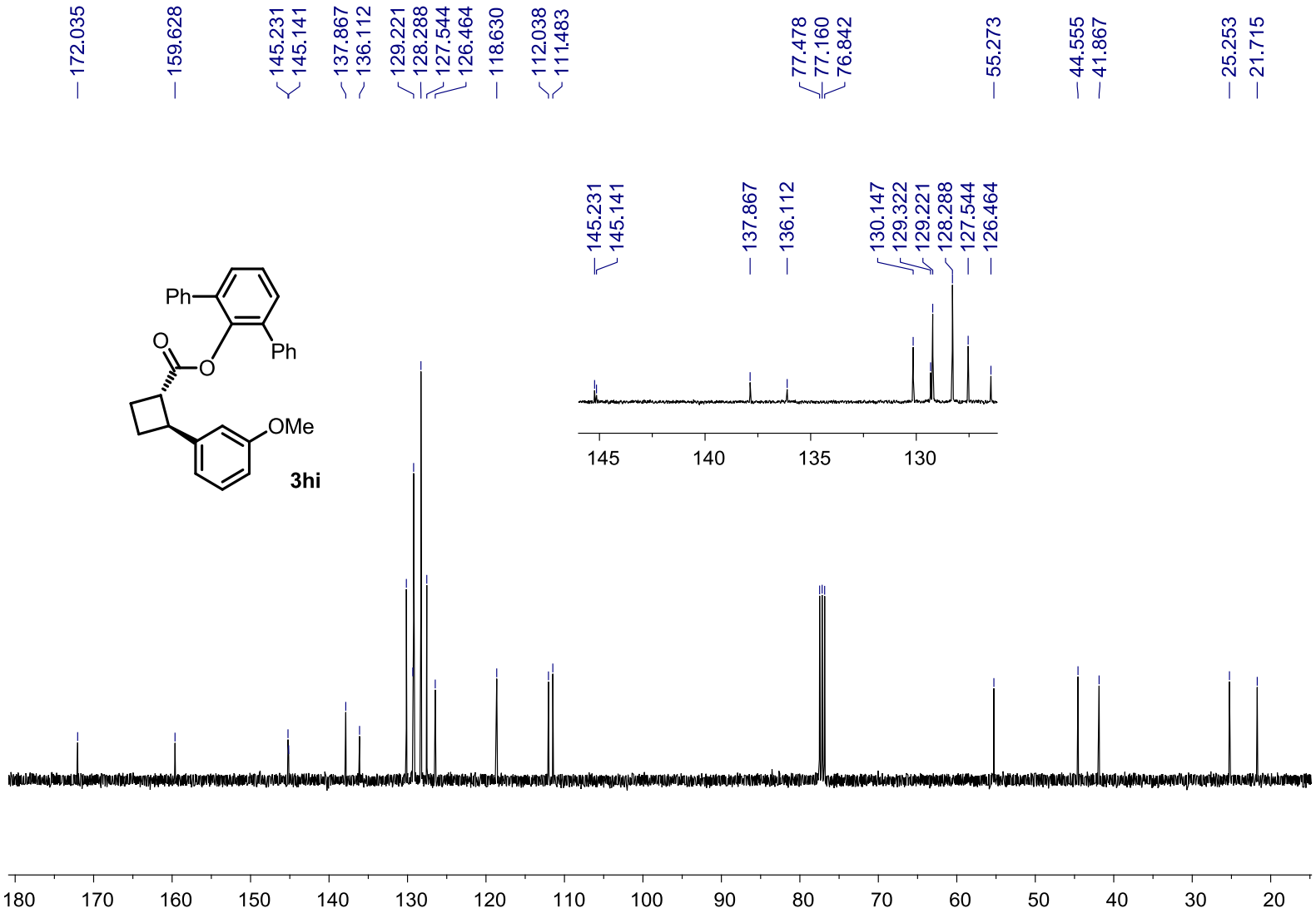
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55.273
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41.867
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O
Ph
OMe
3hi
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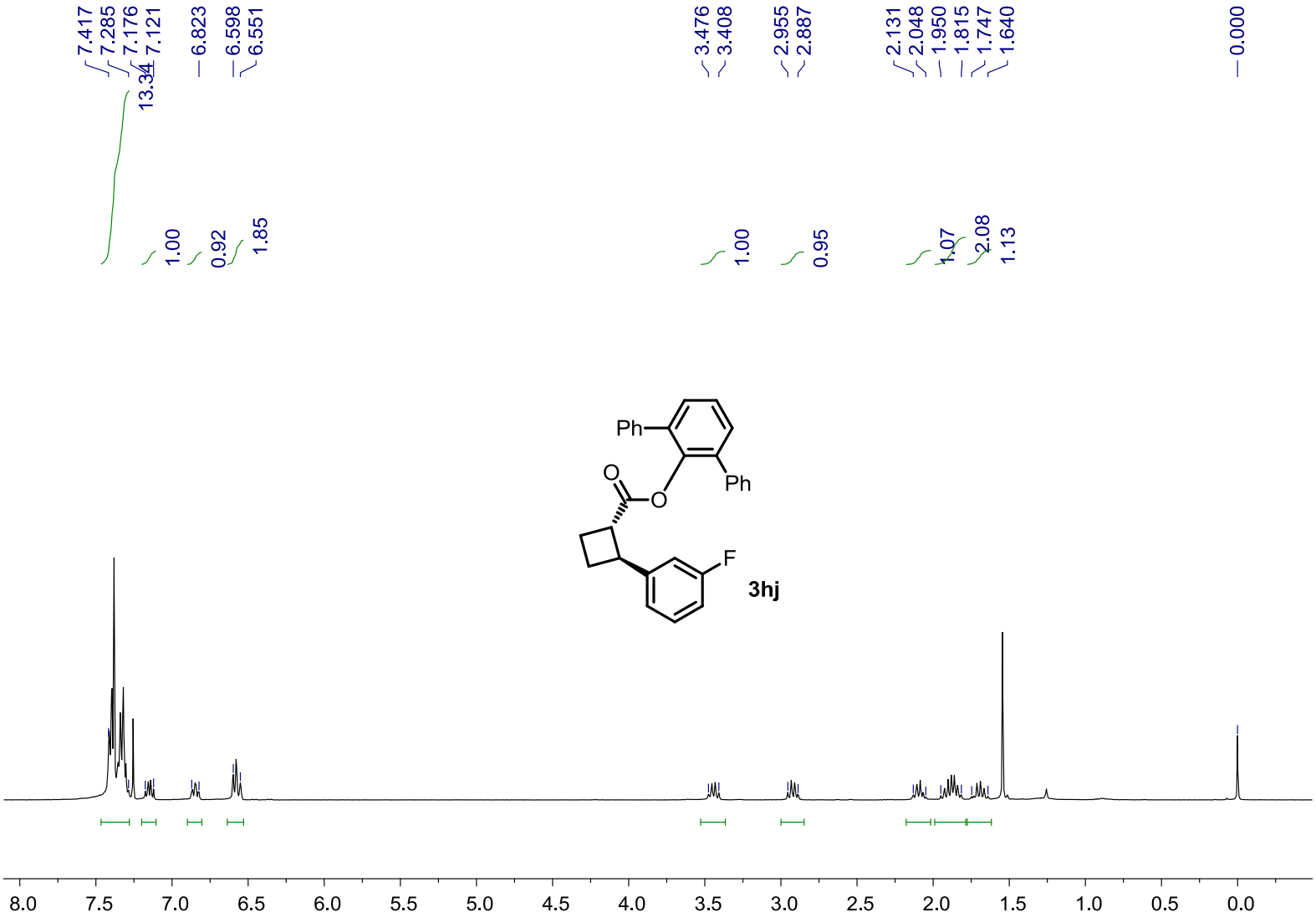
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0.000
1.00
0.95
1.07
2.08
1.13
Ph
Ph
O
O
F
3hj
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7.5
7.0
6.5
6.0
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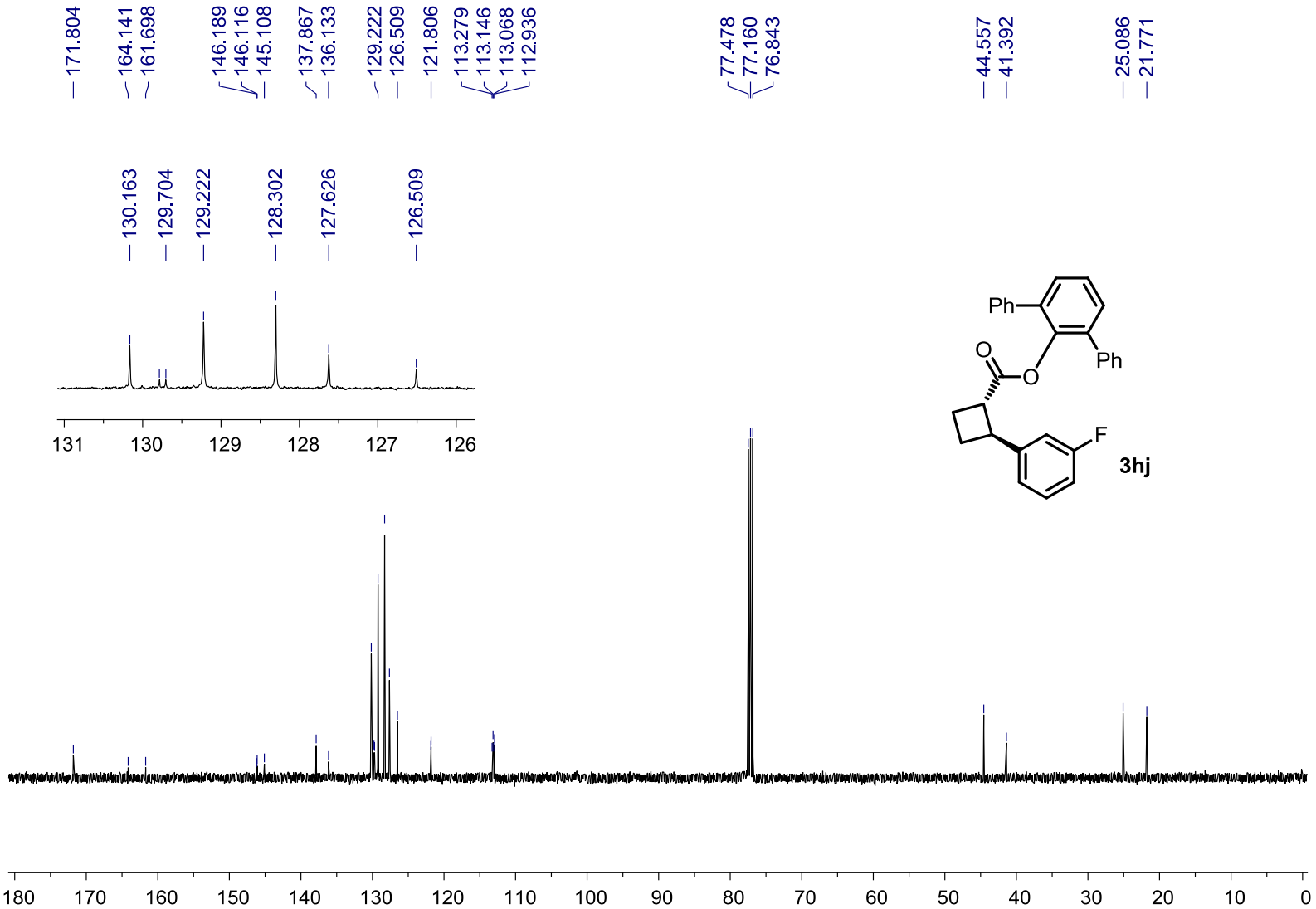
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O
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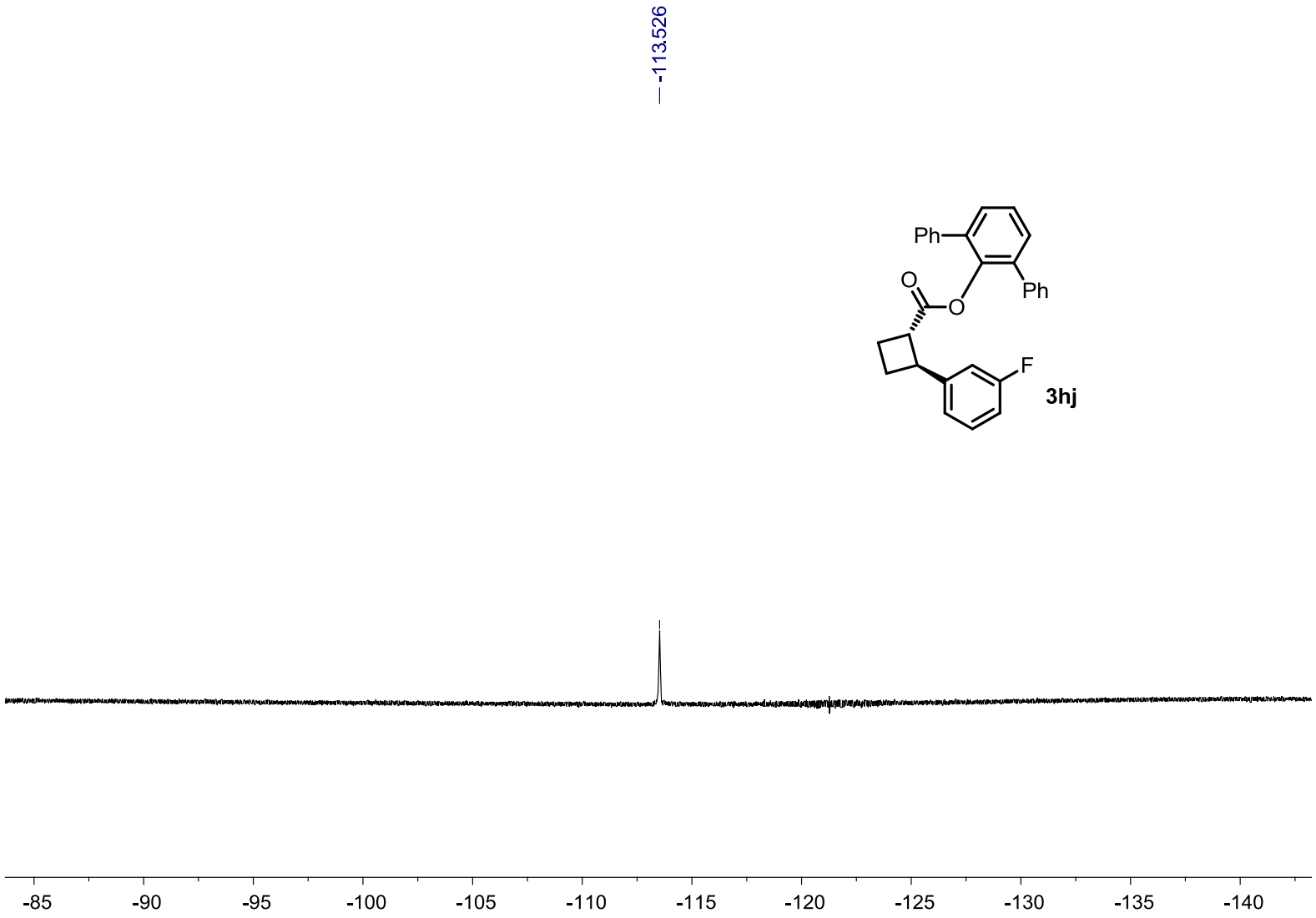
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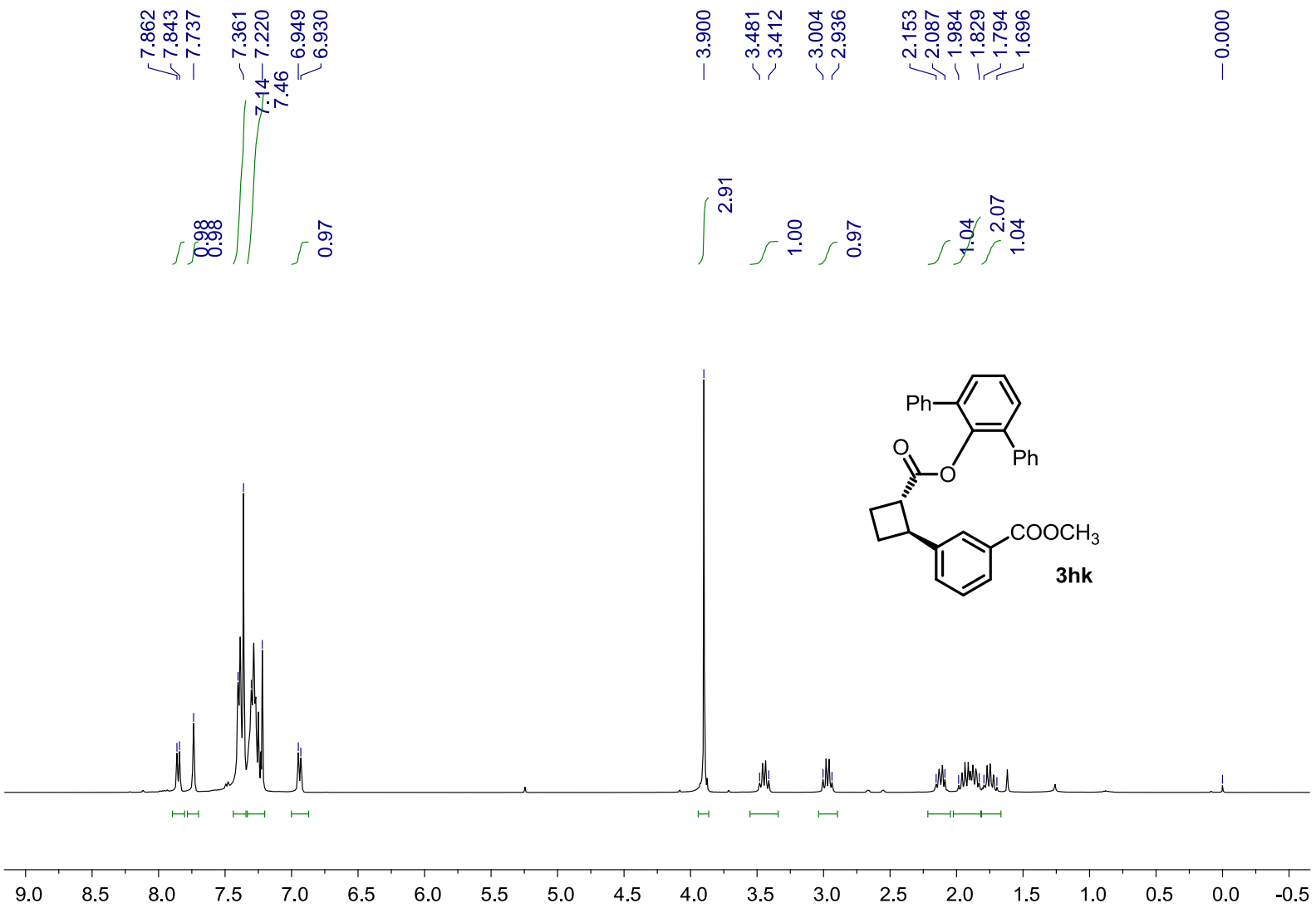
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0.97
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2.07
1.04
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Ph
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O
COOCH3
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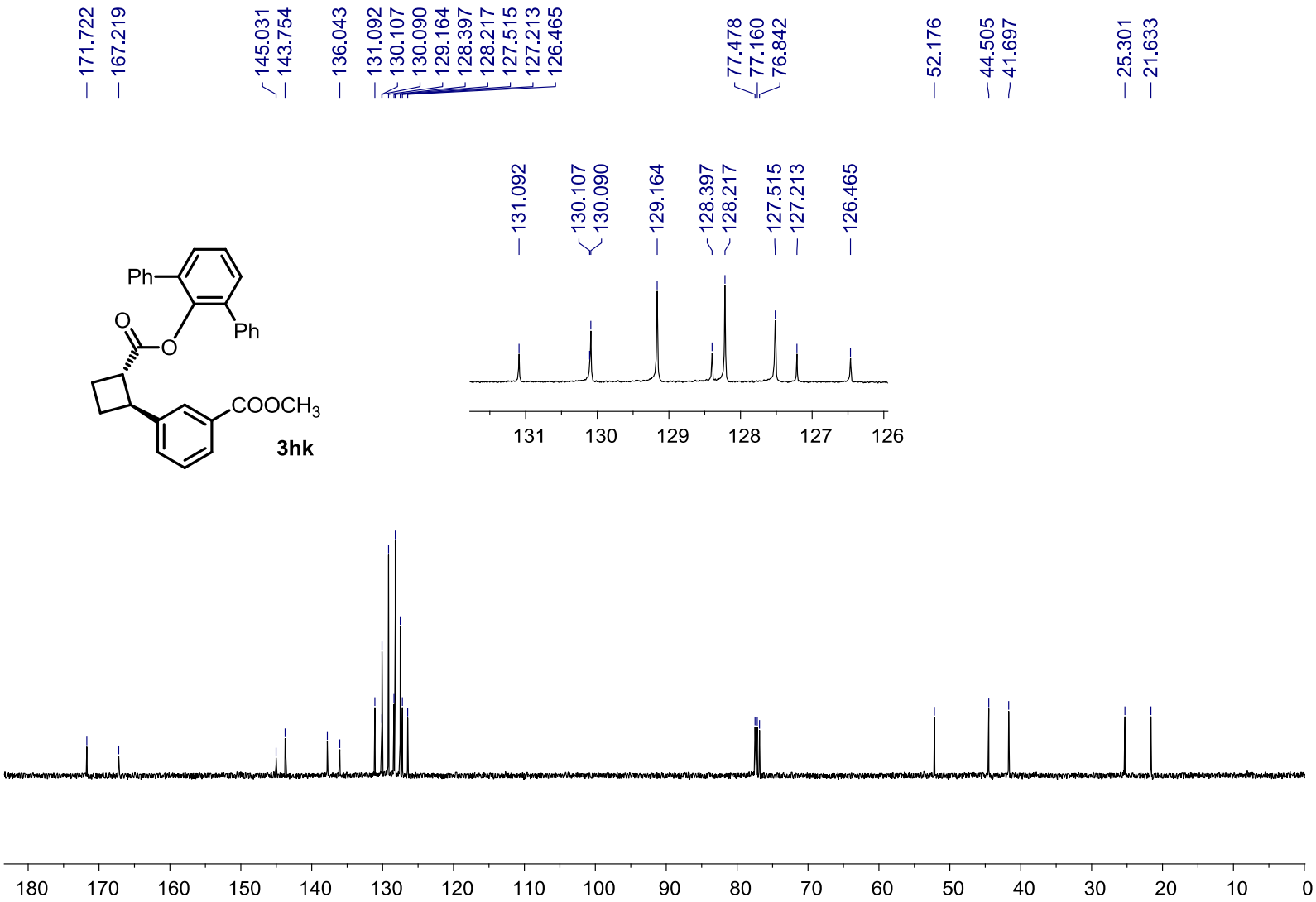
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77.160
76.842
52.176
44.505
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Ph
O
O
COOCH3
3hk
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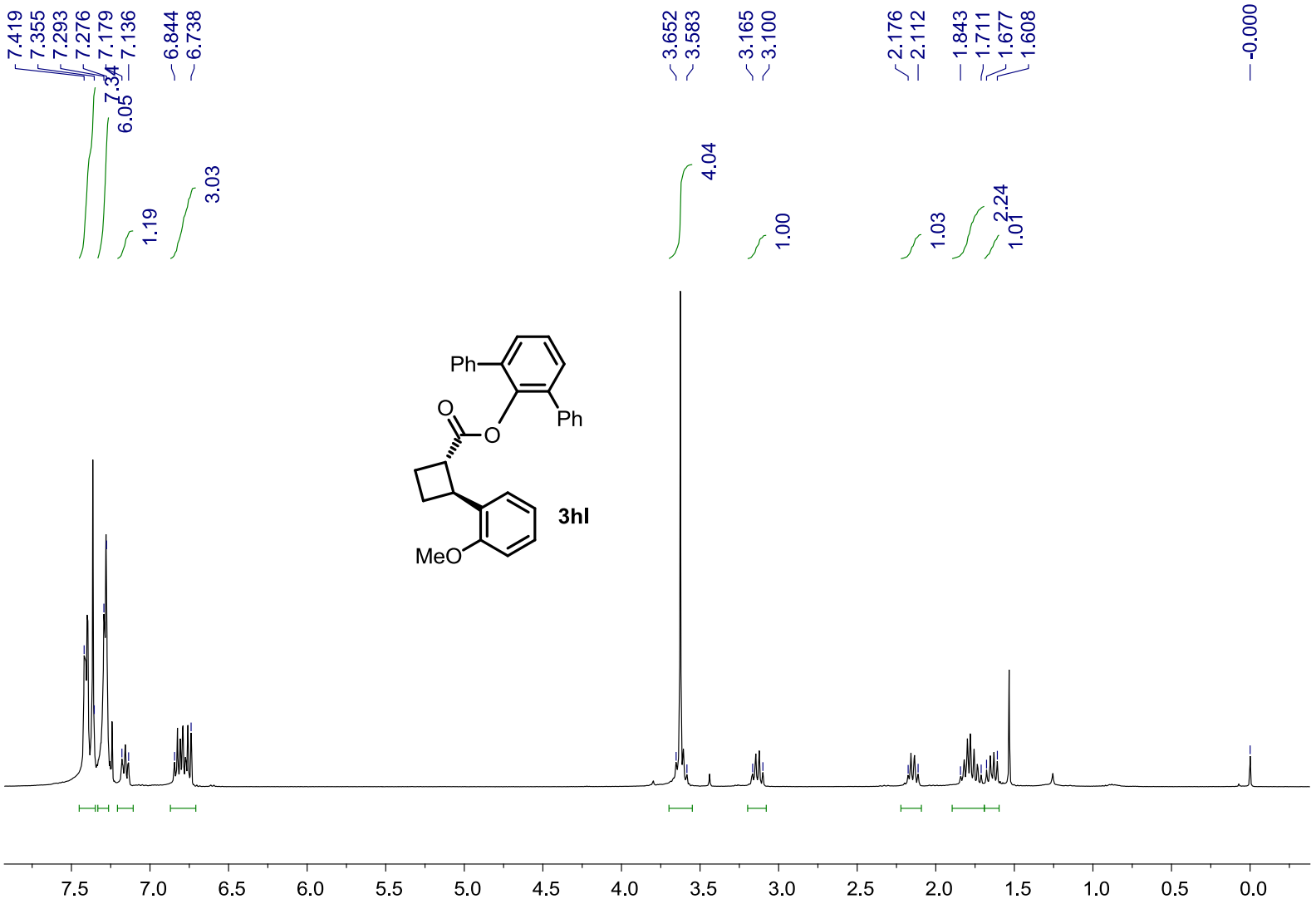
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4.04
1.00
1.03
2.24
1.01
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O
MeO
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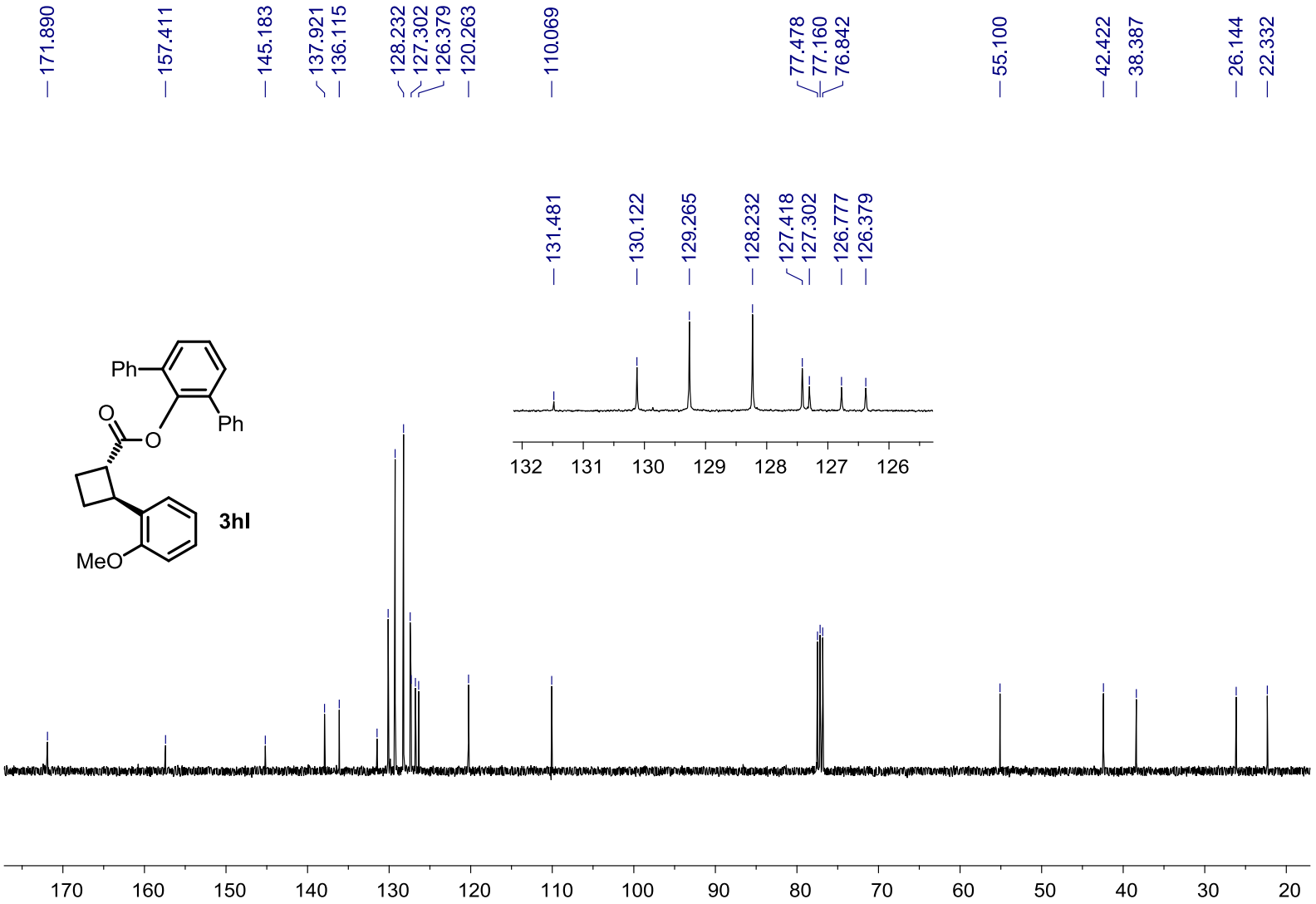
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Ph
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O
MeO
3hl
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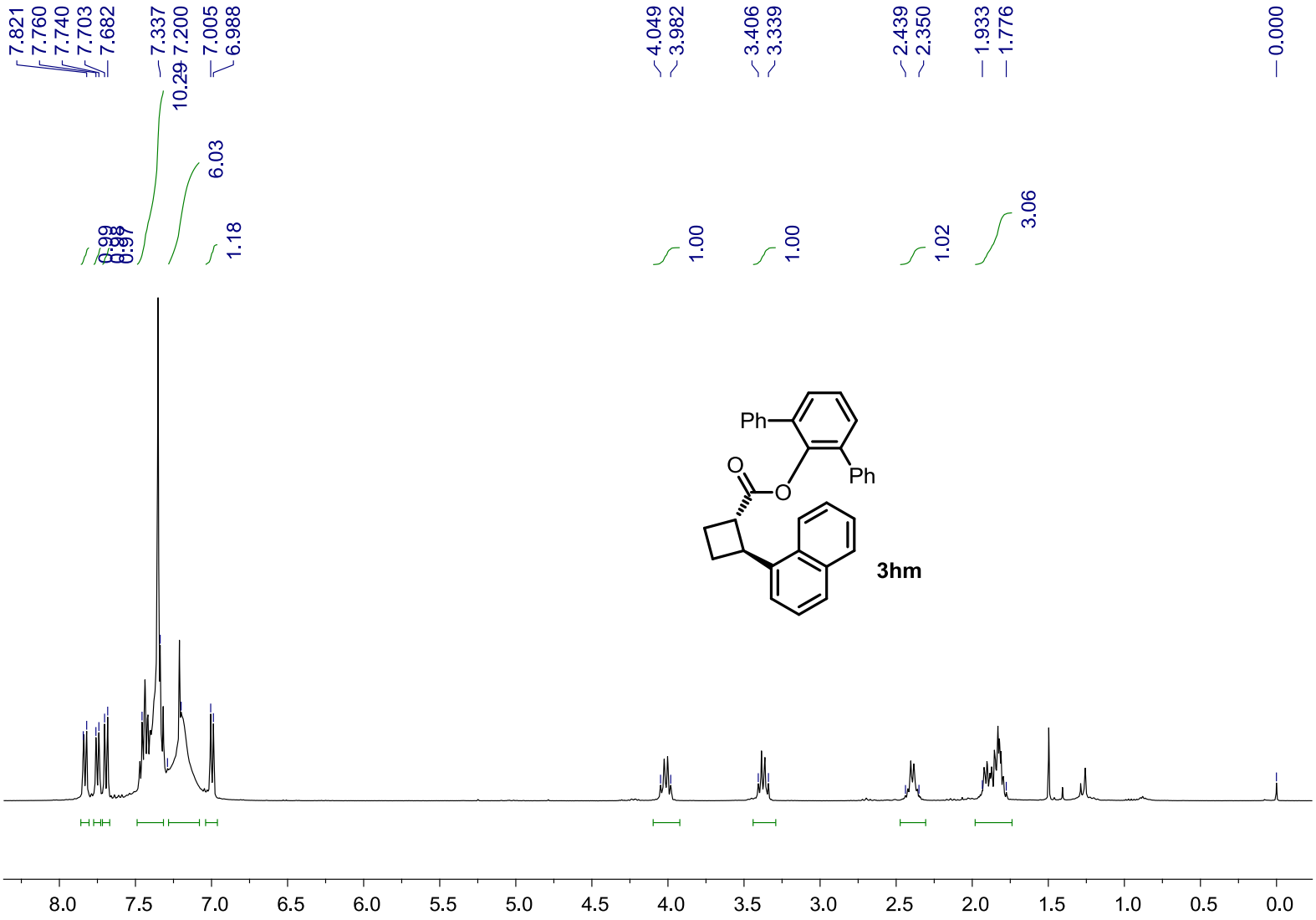
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1.00
1.02
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Ph
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O
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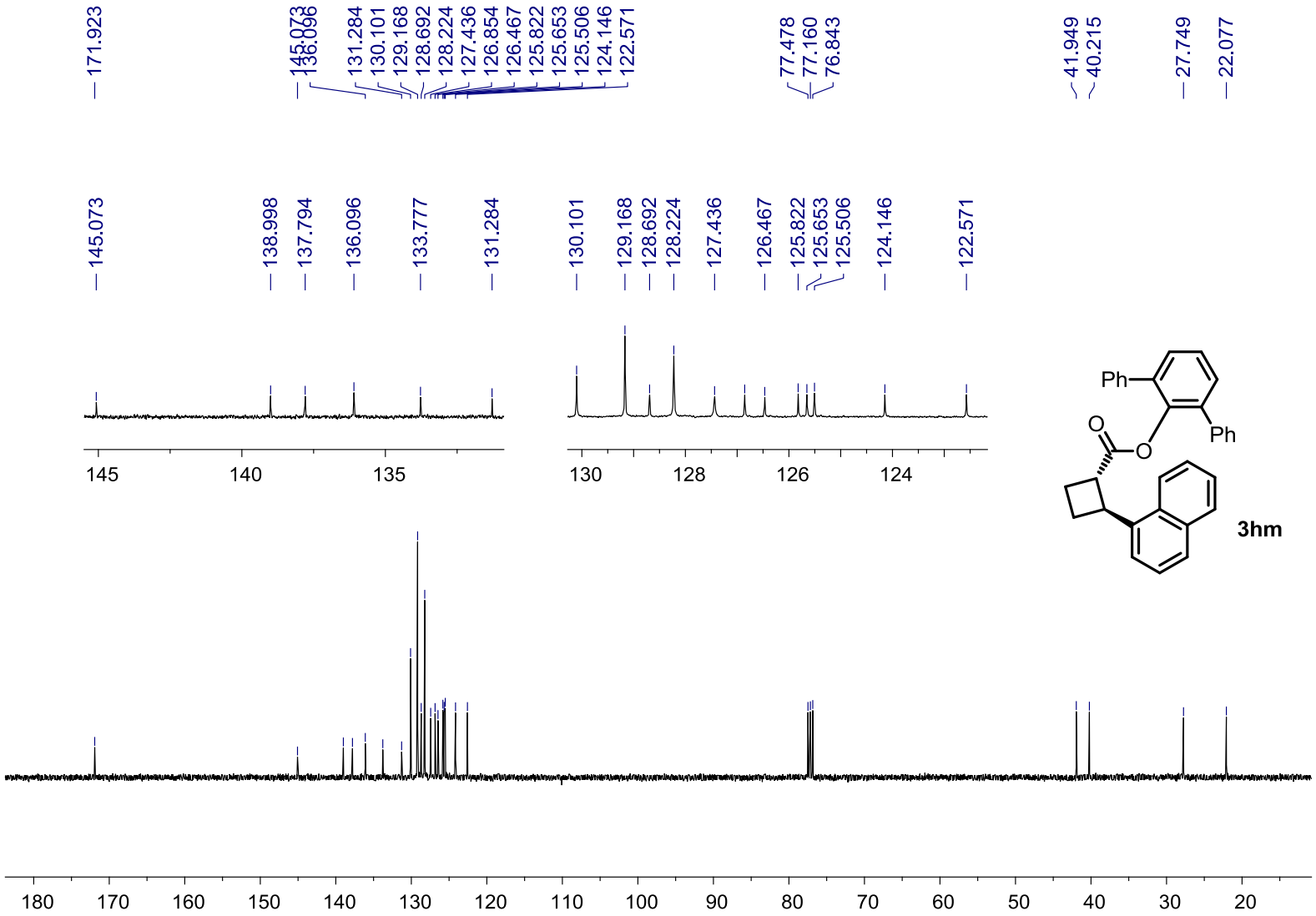
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126
124
Ph
Ph
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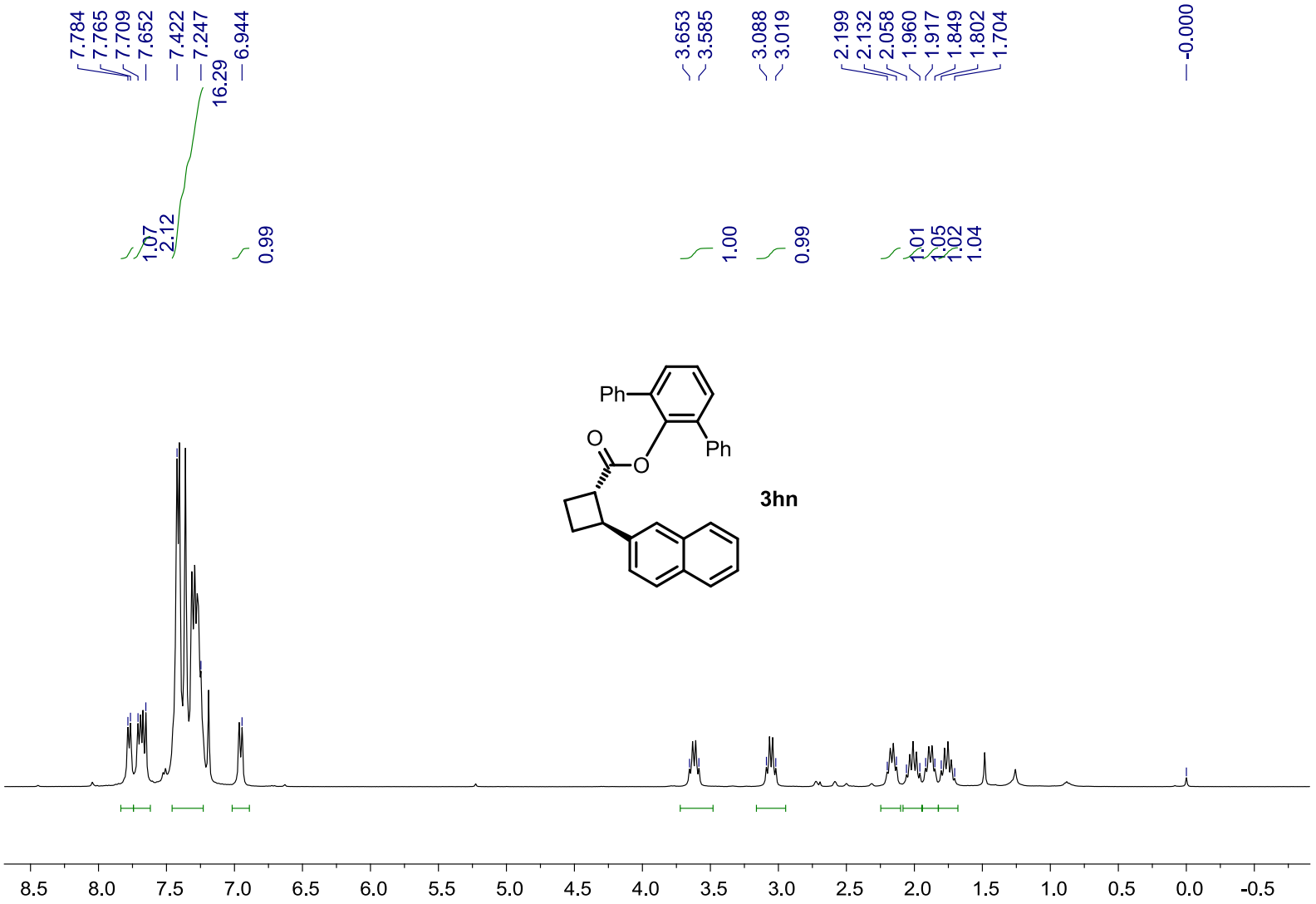
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1.802
1.704
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1.05
1.02
1.04
-0.000
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Ph
O
O
3hn
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8.0
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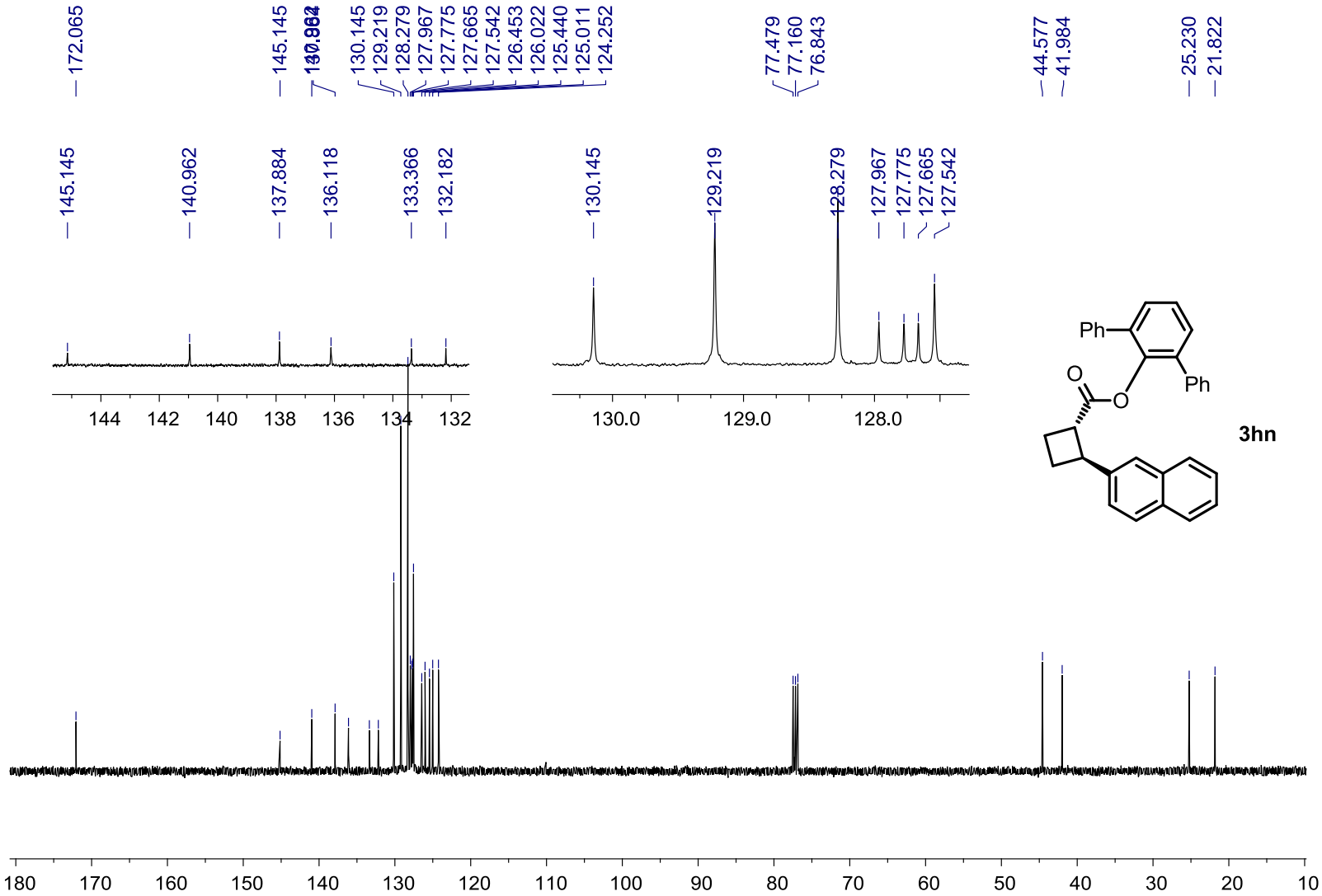
0.0
-0.5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Ph
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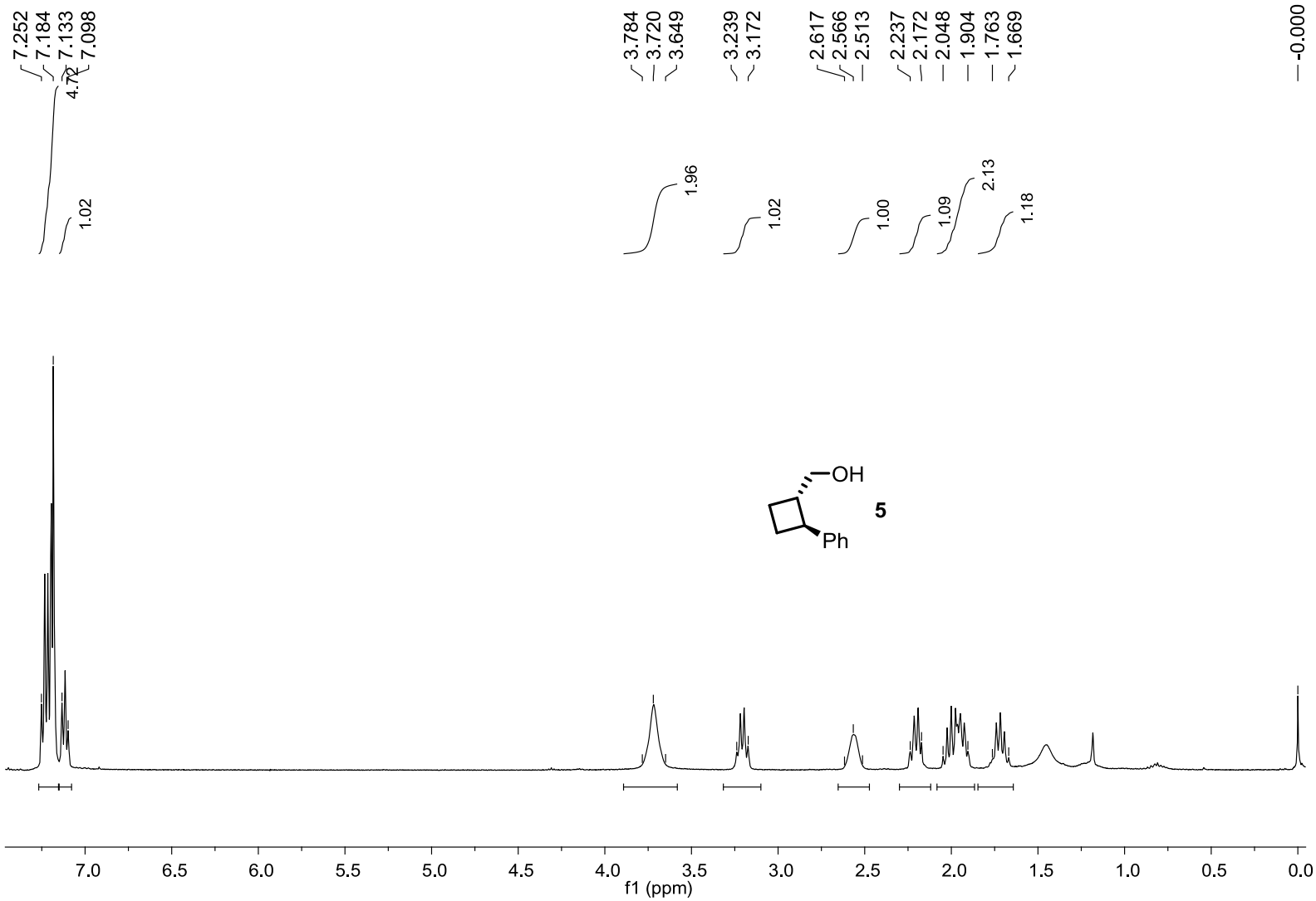
O
3hn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OH
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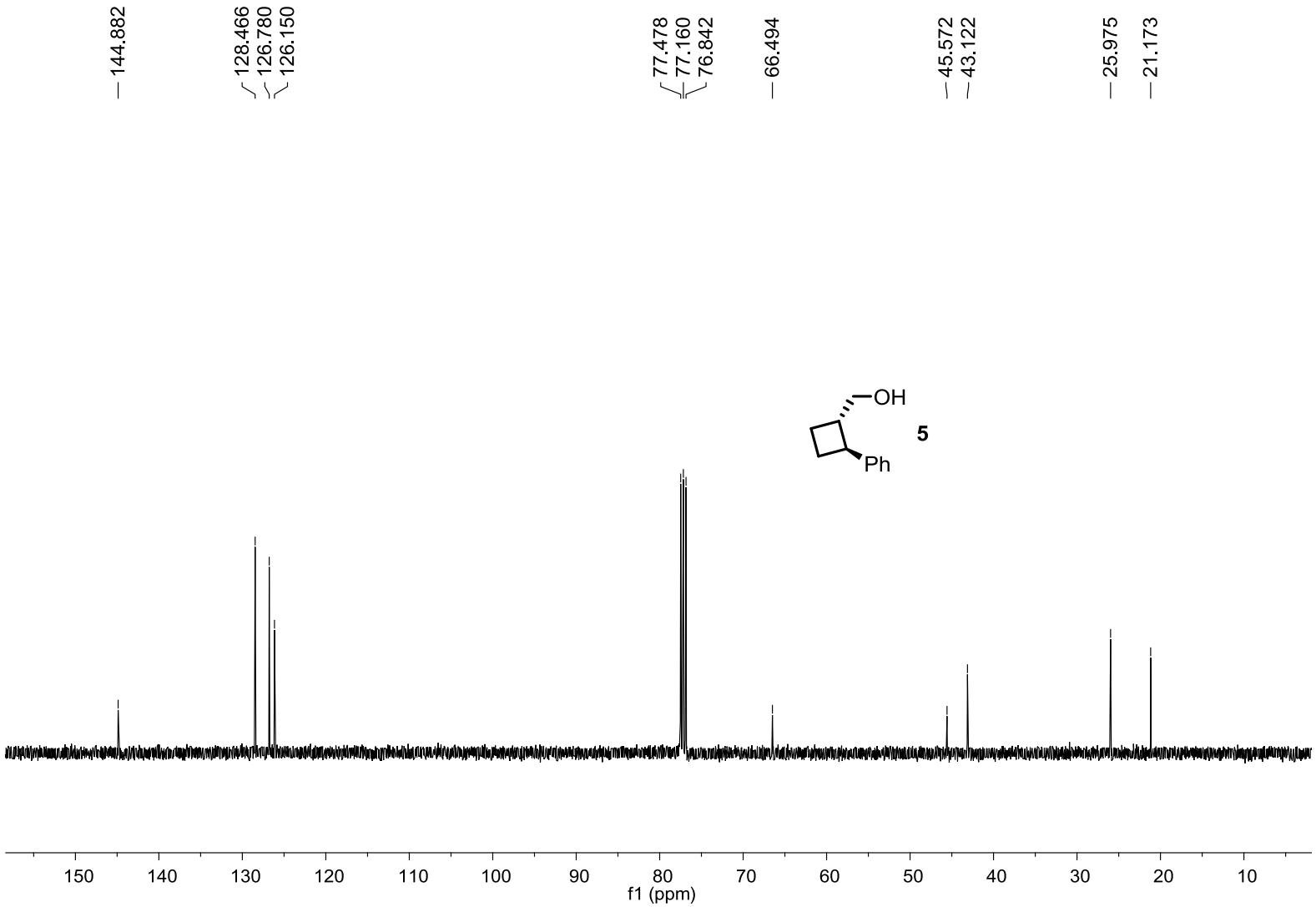
f1 (ppm)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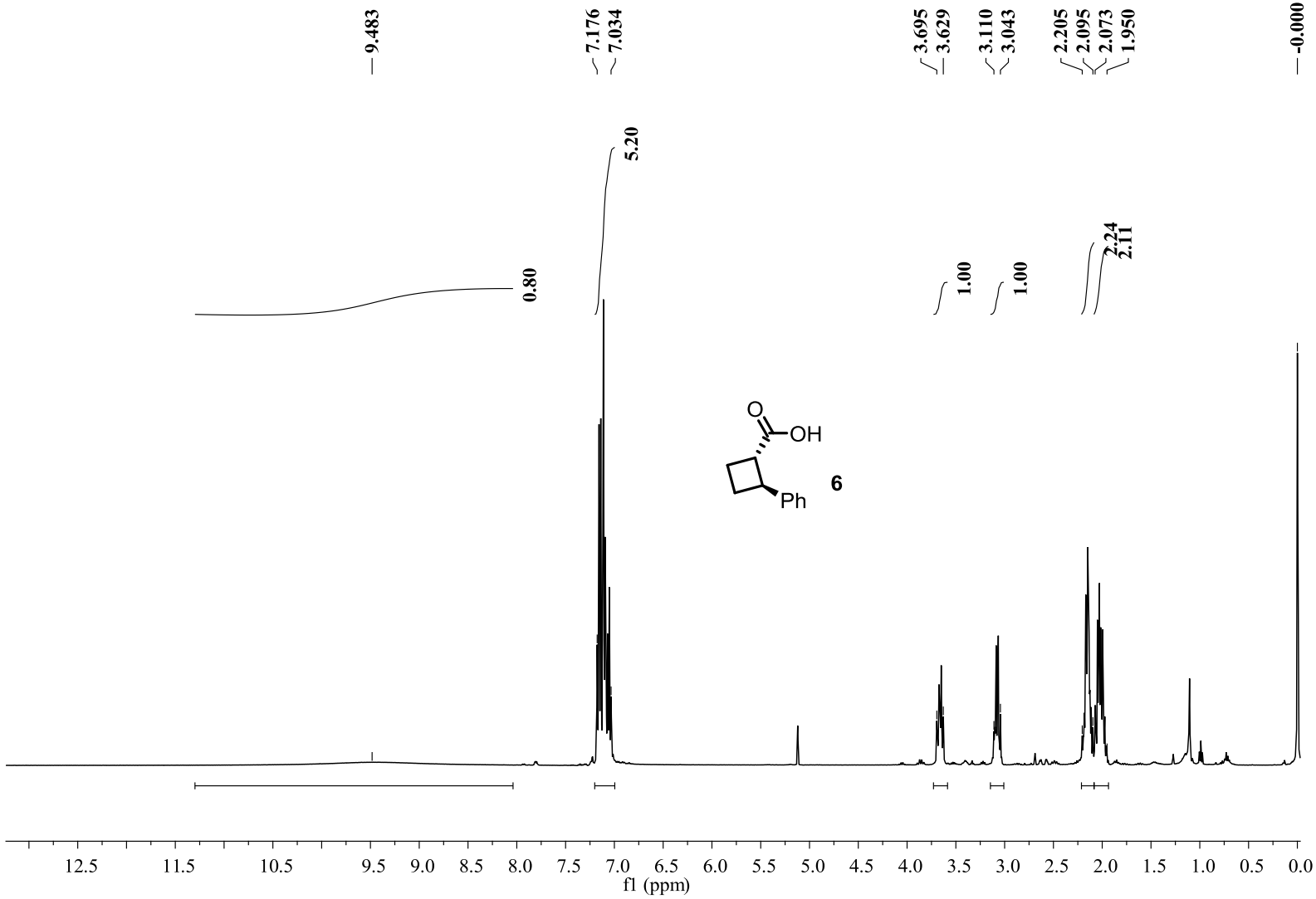
f1 (ppm)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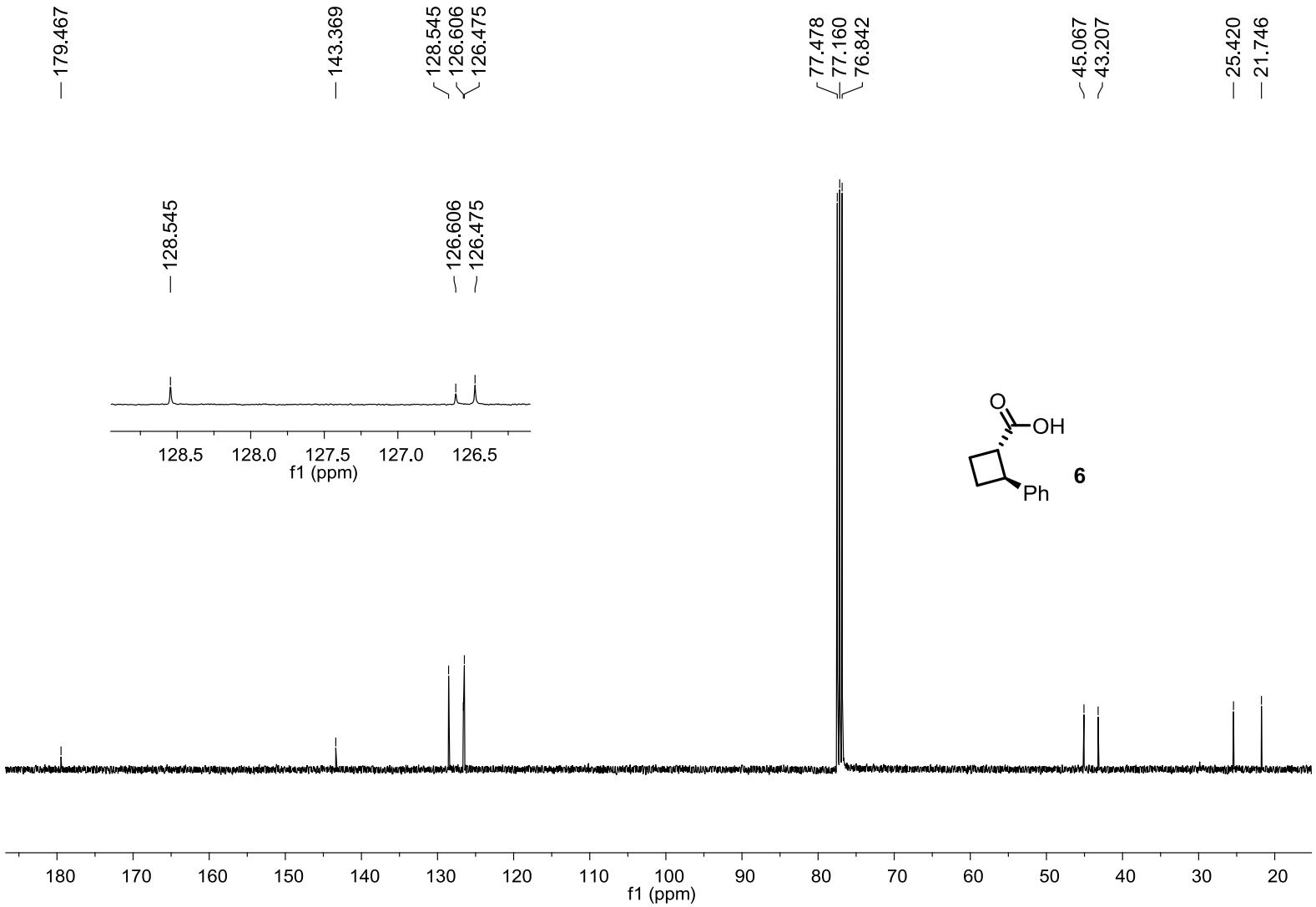
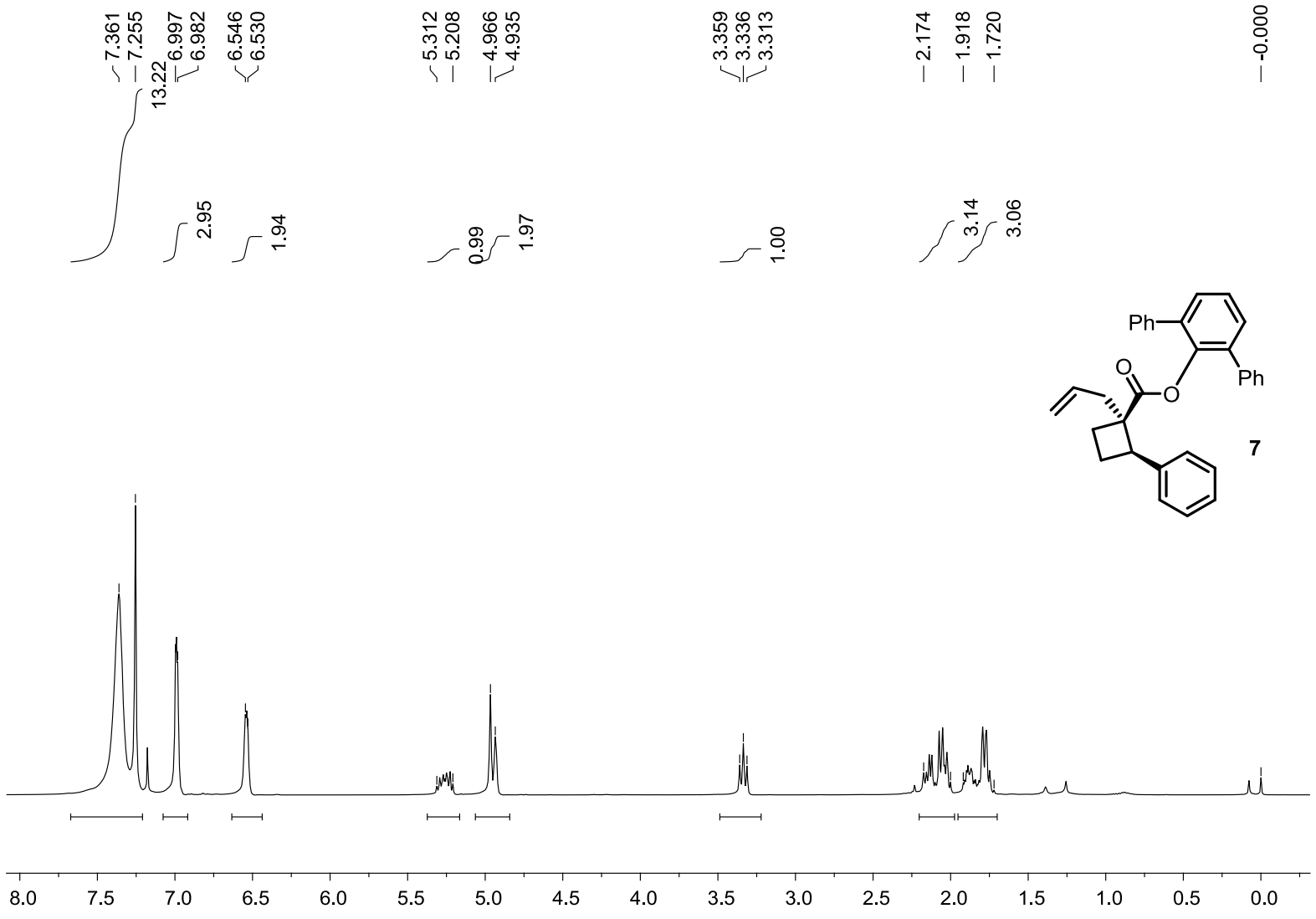
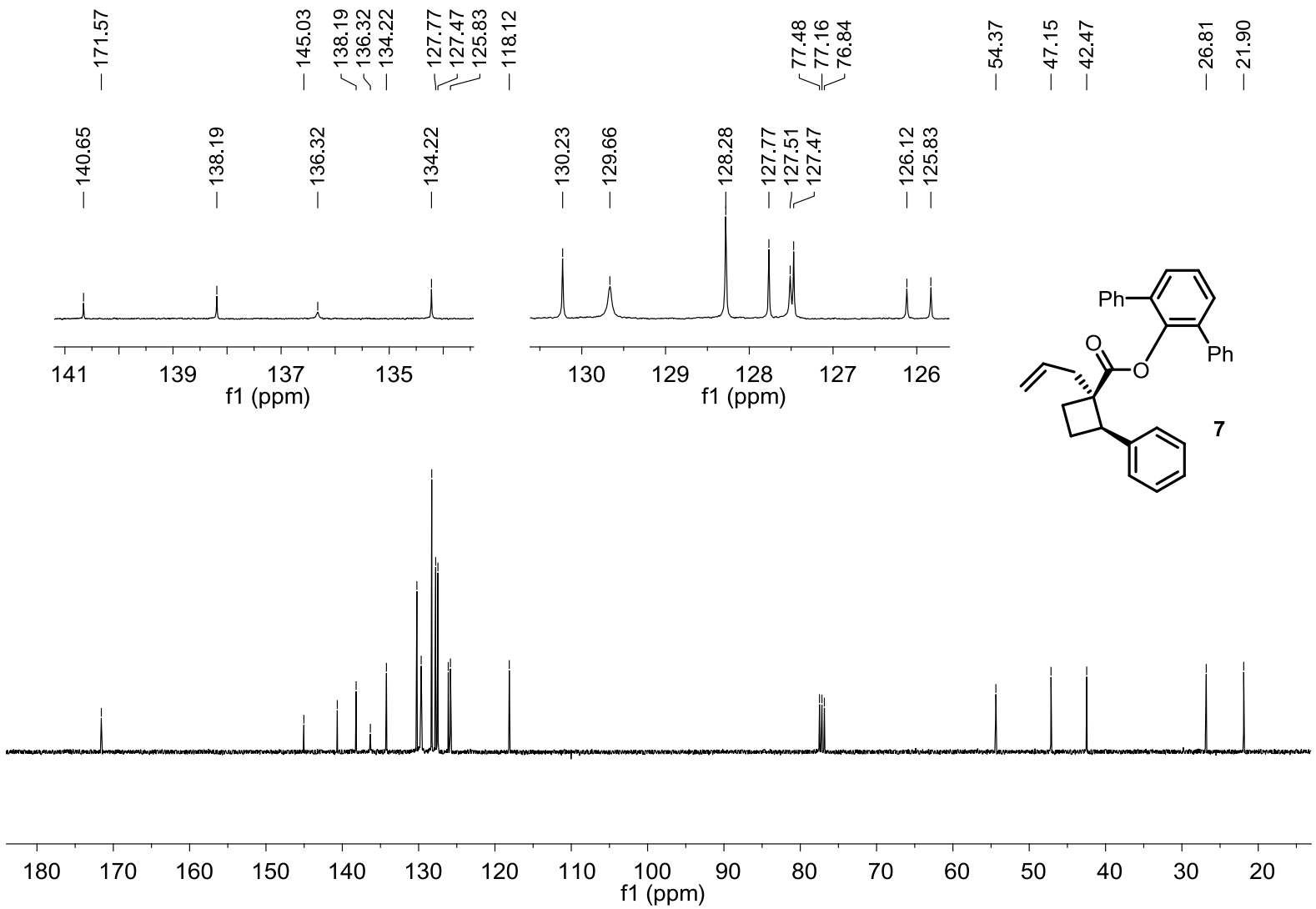
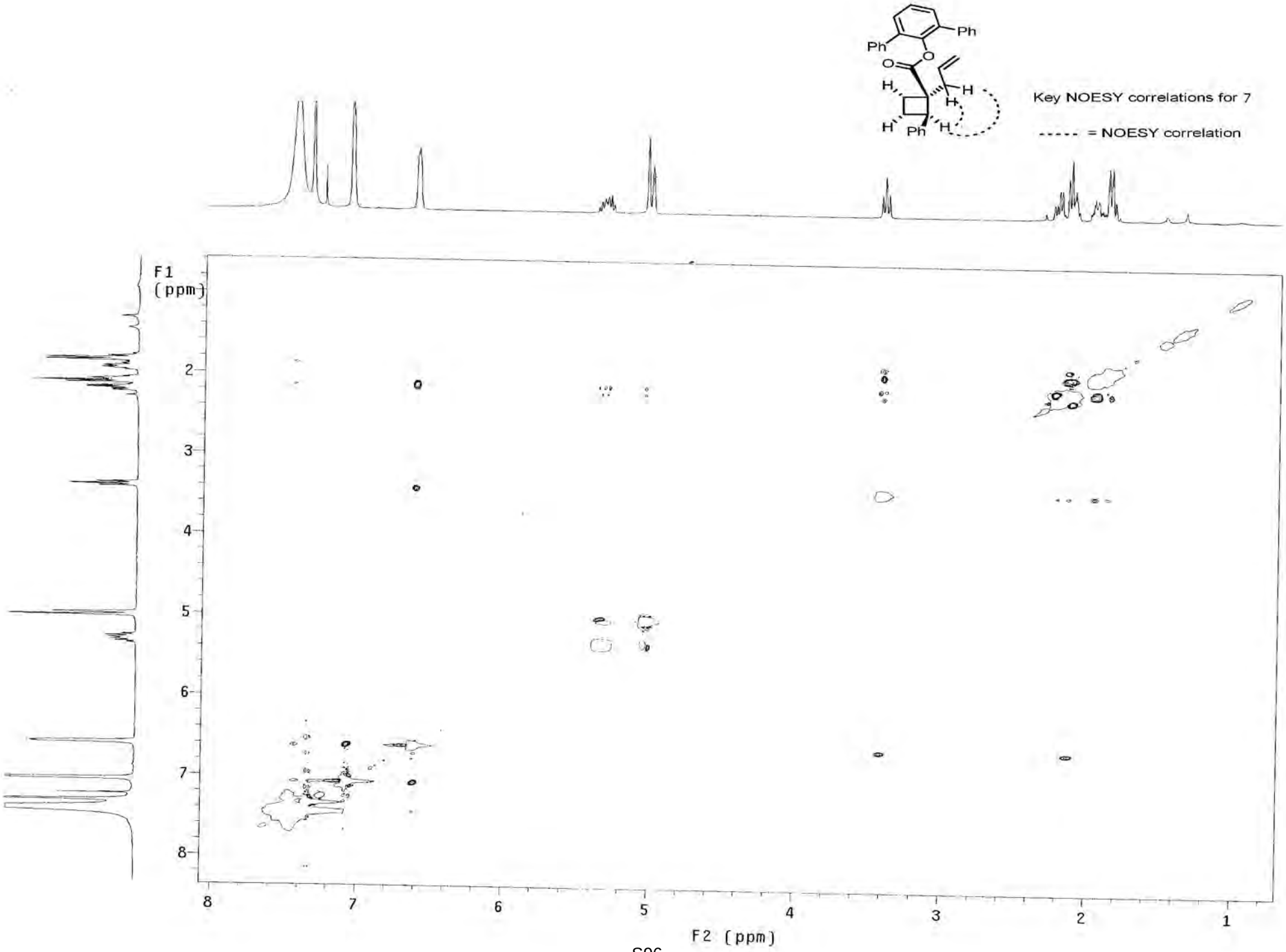
3.043
2.205
2.095
2.073
1.950
-0.000
0.80
5.20
1.00
1.00
2.24
2.11
OH
Ph
6
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


179.467
143.369
128.545
126.606
126.475
77.478
77.160
76.842
45.067
43.207
25.420
21.746
128.545
126.606
126.475
128.5
128.0
127.5
127.0
126.5
f1 (ppm)
O
OH
Ph
6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


7.361
7.255
13.22
6.997
6.982
6.546
6.530
5.312
5.208
4.966
4.935
3.359
3.336
3.313
2.174
1.918
1.720
-0.000
2.95
1.94
0.99
1.97
1.00
3.14
3.06
Ph
Ph
O
O
7
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


171.57
145.03
138.19
136.32
134.22
127.77
127.47
125.83
118.12
77.48
77.16
76.84
54.37
47.15
42.47
26.81
21.90
140.65
138.19
136.32
134.22
130.23
129.66
128.28
127.77
127.51
127.47
126.12
125.83
141
139
137
135
f1 (ppm)
130
129
128
127
126
f1 (ppm)
Ph
Ph
O
O
7
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


Ph
Ph
O
O
H
H
H
H
H
Ph
H
Key NOESY correlations for 7
----- = NOESY correlation
F1 (ppm)
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
F2 (ppm)