Synlett

Accounts and Rapid Communications in Chemical Synthesis

Supporting Information

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Thieme

Supporting Information

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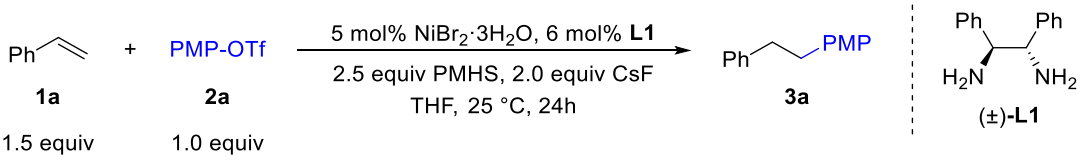
I. General Information

General reagent information. $NiBr_2$▪$3H_2O$ (CAS: 7789-49-3, Alfa Aesar), $NiCl_2$▪gylme (CAS: 29046-78-4, Aldrich Chemical), (±)-**L1** [a 1:1 mixture of (*1S,2S*)-(-)-1,2-diphenyl-1,2-ethanediamine (CAS: 5700-60-7, Bide Pharmatech Ltd) and (*1R,2R*)-(-)-1,2-diphenyl-1,2-ethanediamine (CAS: 35132-20-8, Bide Pharmatech Ltd)]. Polymethylhydrosiloxanes (PMHS, CAS: 9004-73-3, Acros) and styrene (CAS: 100-42-5, TCI) were stored under nitrogen at –25 °C in glove box. K_3PO_4▪H_2O (CAS: 27176-10-9, Adamas-beta®) and CsF (CAS: 13400-13-0, TCI) were stored under nitrogen in glove box. Methanol (CAS: 67-56-1, Energy Chemical, 99.8%, Extra Dry, with molecular sieves, Water≤50 ppm(by K.F.), EnergySeal) used as received. Et_2O (CAS: 60-29-7) and toluene (CAS: 108-88-3) were purchased from Nanjing Reagent and were dried by passage through alumina and Q5 reactant-packed columns on a solvent purification system. Other commercial reagents were purchased from Aldrich Chemical, Alfa Aesar, Acros, TCI, J&K, Energy Chemical, and Bide Pharmatech Ltd. were used as received. Other solvents were purified and dried by passage through alumina and Q5 reactant-packed columns on a solvent purification system. Flash chromatography was performed using glass columns with Silica Gel (Huanghai, 300-400 mesh).

General analytical information. ^{1}H NMR spectra ^{11}B NMR spectra and ^{19}F NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer. Data for ^{1}H NMR were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, td = triplet of doublets, dd = doublet of doublets, m = multiplet), integration, and coupling constant (Hz). ^{13}C NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer and are referenced to $CDCl_3$ at δ 77.16 ppm or CD_3OD at δ 45.00 ppm. Data for ^{13}C NMR were reported in terms of chemical shift and multiplicity where appropriate. IR spectra were recorded

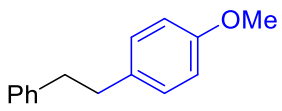
on a Bruker ALPHA FT-IR spectrometer and reported in terms of frequency of absorption (cm^{-1}). Low Resolution Mass spectra were obtained from on an Agilent 5977A GC-MS. rr refers to regioisomeric ratio, representing the ratio of the target coupling product to the sum of all other isomers as determined by GC and GC-MS analysis. High Resolution Mass spectra were obtained from on an Agilent 6540 Q-TOF mass spectrometer, operating electrospray ionization (ESI) mode. High performance liquid chromatography (HPLC) was performed on Agilent 1260 Series chromatographs using Daicel Chiralcel columns (25 cm). Optical rotations were measured on a S3 Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm pathlength cell at 589 nm with [α]D values reported in degrees; concentration (c) is in g/100 mL.

II. NiH-Catalyzed anti-Markovnikov Hydroarylation of Styrenes



General procedure (A) for the NiH-catalyzed anti-Markovnikov hydroarylation of styrenes : In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added $NiBr_2 \cdot 3H_2O$ (2.73 mg, 0.010 mmol, 5 mol%), **L1** (2.55 mg, 0.012 mmol, 6 mol%), CsF (60.8 mg, 0.40 mmol, 2.0 equiv), 0.40 mL anhydrous THF, and the mixture was stirred for 5 min, at which time PMHS (30 μL, 0.50 mmol, 2.5 equiv) was added and the stirring was continued for another 5 min at room temperature. Styrene (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv) and 4-methoxyphenyl trifluoromethanesulfonate (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and stirred at 25 °C for up to 24 h. After the

reaction was complete, the reaction was quenched upon the addition of H_2O, and the mixture was extracted with ethyl acetate for three times. The organic layer was concentrated to give the crude product. Dodecane (20 μL) was added as an internal standard for GC analysis. The product was purified by chromatography on silica gel for each substrate.

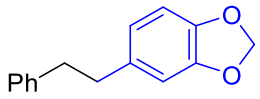


1-Methoxy-4-phenethylbenzene (Scheme 3, 3a)[1]**.** Prepared following general procedure **A** using **styrene** (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv), **4-methoxyphenyl trifluoromethanesulfonate** (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv) and anhydrous THF (0.40 mL, 0.5M). The reaction mixture was stirred for 12 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a white solid in 85% yield (36.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.24 – 7.13 (m, 3H), 7.13 – 7.07 (m, 2H), 6.86 – 6.80 (m, 2H), 3.80 (s, 3H), 2.92 – 2.84 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 142.0, 134.0, 129.5, 128.6, 128.4, 126.0, 113.9, 55.4, 38.4, 37.2.

MS (EI) calcd. for $C_{15}H_{16}O$ $[M]^+$ m/z 212.1, found 212.1.



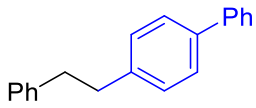
5-Phenethylbenzo[*d*][1,3]dioxole (Scheme 3, 3b)[1]**.** Prepared following general procedure **A** using **styrene** (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv), **benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate** (**2b**, 54.0 mg, 0.20 mmol, 1.0 equiv) and anhydrous THF (0.40 mL, 0.5M). The reaction mixture was stirred for 12 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the

title compound as a white solid in 92% yield (41.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.14 – 7.07 (m, 3H), 6.67 – 6.59 (m, 2H), 6.56 – 6.51 (m, 1H), 5.85 (s, 2H), 2.85 – 2.71 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.8, 141.8, 135.8, 128.6, 128.5, 126.1, 121.3, 109.1, 108.2, 100.9, 38.4, 37.8.

MS (EI) calcd. for $C_{15}H_{14}O_2$ $[M]^+$ m/z 226.1, found 226.1.

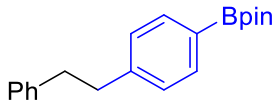


4-Phenethyl-1,1'-biphenyl (Scheme 3, 3c)[2]**.** Prepared following general procedure **A** using **styrene** (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv), **[1,1'-biphenyl]-4-yl trifluoromethanesulfonate** (**2c**, 60.4 mg, 0.20 mmol, 1.0 equiv) and anhydrous THF (0.40 mL, 0.5M). The reaction mixture was stirred for 18 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a white solid in 82% yield (42.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.47 – 7.41 (m, 2H), 7.40 – 7.31 (m, 2H), 7.29 – 7.09 (m, 8H), 2.90 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 141.2, 141.1, 139.0, 129.0, 128.9, 128.6, 128.5, 127.2, 127.2, 127.1, 126.1, 38.0, 37.7.

MS (EI) calcd. for $C_{20}H_{18}$ $[M]^+$ m/z 258.1, found 258.1.



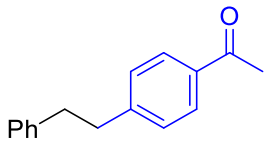
4,4,5,5-Tetramethyl-2-(4-phenethylphenyl)-1,3,2-dioxaborolane (Scheme 3, 3d)[3]**.** Prepared following general procedure **A** using **styrene** (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv), **4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl**

trifluoromethanesulfonate (**2d**, 70.4 mg, 0.20 mmol, 1.0 equiv) and anhydrous THF (0.40 mL, 0.5M). The reaction mixture was stirred for 12 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a white solid in 64% yield (39.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.07 (m, 7H), 2.89 – 2.82 (m, 4H), 1.27 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 141.8, 135.0, 128.6, 128.5, 128.1, 126.1, 83.8, 38.3, 37.9, 25.0.

MS (EI) calcd. for $C_{20}H_{25}BO_2$ $[M]^+$ m/z 308.2, found 308.2.

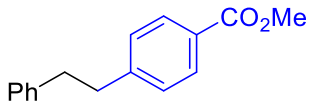


1-(4-Phenethylphenyl)ethan-1-one (Scheme 3, 3e)[1]**.** Prepared following general procedure **A** using **styrene** (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv), **4-acetylphenyl trifluoromethanesulfonate** (**2e**, 53.6 mg, 0.20 mmol, 1.0 equiv) and anhydrous THF (0.40 mL, 0.5M). The reaction mixture was stirred for 12 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 15:1) to provide the title compound as a white solid in 65% yield (29.2 mg), 94:6 rr.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 2H), 7.23 – 7.06 (m, 7H), 2.94 – 2.83 (m, 4H), 2.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 147.6, 141.2, 135.3, 128.8, 128.6, 128.6, 128.5, 126.2, 38.0, 37.6, 26.7.

MS (EI) calcd. for $C_{16}H_{16}O$ $[M]^+$ m/z 224.1, found 224.1.

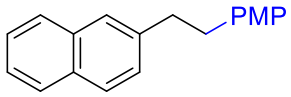


Methyl 4-phenethylbenzoate (Scheme 3, 3f)[4]**.** Prepared following general procedure **A** using styrene (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv), **methyl 4-(((trifluoromethyl)sulfonyl)oxy)benzoate** (**2f**, 56.8 mg, 0.20 mmol, 1.0 equiv) and anhydrous THF (0.4 mL, 0.5M). The reaction mixture was stirred for 12 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 20:1) to provide the title compound as a colorless oil in 69% yield (33.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.81 (m, 2H), 7.24 – 7.04 (m, 7H), 3.83 (s, 3H), 2.92 – 2.83 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 147.3, 141.3, 129.8, 128.7, 128.6, 128.5, 128.1, 126.2, 52.1, 38.0, 37.6.

MS (EI) calcd. for $C_{16}H_{16}O_2$ $[M]^+$ m/z 240.1, found 240.1.



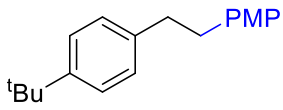
2-(4-Methoxyphenethyl)naphthalene (Scheme 3, 3g)[4]**.** Prepared following general procedure **A** using **2-vinylnaphthalene** (**1e**, 46.2 mg, 0.30 mmol, 1.5 equiv), **4-methoxyphenyl trifluoromethanesulfonate** (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv) and anhydrous THF (0.40 mL, 0.5M). The reaction mixture was stirred for 24 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a white solid in 75% yield (39.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 3H), 7.53 (s, 1H), 7.40 – 7.32 (m, 2H), 7.25 (dd, J = 8.4, 1.7 Hz, 1H), 7.07 – 7.01 (m, 2H), 6.78 – 6.72 (m, 2H), 3.71 (s, 3H), 3.01 – 2.86 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 139.5, 134.0, 133.8, 132.2, 129.5, 128.0, 127.8,

127.6, 127.5, 126.6, 126.0, 125.3, 113.9, 55.4, 38.5, 37.1.

MS (EI) calcd. for $C_{19}H_{18}O$ $[M]^+$ m/z 262.1, found 262.1.

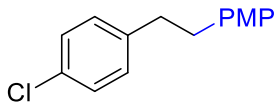


1-(*tert*-Butyl)-4-(4-methoxyphenethyl)benzene (Scheme 3, 3h)[4]**.** Prepared following general procedure **A** using **1-(*tert*-butyl)-4-vinylbenzene** (**1f**, 48.0 mg, 0.30 mmol, 1.5 equiv), **4-methoxyphenyl trifluoromethanesulfonate** (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv) and anhydrous THF (0.40 mL, 0.5M). The reaction mixture was stirred for 24 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a white solid in 79% yield (42.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 7.09 – 7.03 (m, 4H), 6.78 – 6.73 (m, 2H), 3.72 (s, 3H), 2.78 (s, 4H), 1.24 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 148.8, 139.0, 134.3, 129.4, 128.2, 125.4, 113.9, 55.4, 37.8, 37.1, 34.5, 31.6.

MS (EI) calcd. for $C_{19}H_{24}O$ $[M]^+$ m/z 268.2, found 268.2.

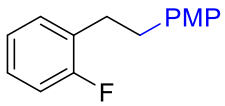


1-Chloro-4-(4-methoxyphenethyl)benzene (Scheme 3, 3i)[5]**.** Prepared following general procedure **A** using **1-chloro-4-vinylbenzene** (**1g**, 41.4 mg, 0.30 mmol, 1.5 equiv), **4-methoxyphenyl trifluoromethanesulfonate** (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv) and anhydrous THF (0.40 mL, 0.5M). The reaction mixture was stirred for 24 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a white solid in 51% yield (25.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.14 (m, 2H), 7.09 – 6.94 (m, 4H), 6.76 – 6.72 (m, 2H), 3.71 (s, 3H), 2.84 – 2.69 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 140.3, 133.5, 131.7, 130.0, 129.5, 128.5, 113.9, 55.4, 37.6, 37.0.

MS (EI) calcd. for $C_{15}H_{15}ClO$ $[M]^+$ m/z 246.1, found 246.1.



1-Fluoro-2-(4-methoxyphenethyl)benzene (Scheme 3, 3j). Prepared following general procedure **A** using **1-fluoro-2-vinylbenzene** (**1h**, 36.6 mg, 0.30 mmol, 1.5 equiv), **4-methoxyphenyl trifluoromethanesulfonate** (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv) and anhydrous THF (0.40 mL, 0.5M). The reaction mixture was stirred for 24 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a white solid in 73% yield (33.5 mg).

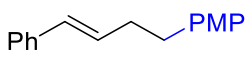
IR (neat, cm^{-1}) 1513.42, 1493.07, 1246.62, 1178.90, 828.37, 759.70.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 6.96 (m, 2H), 6.99 – 6.89 (m, 1H), 6.79 – 6.70 (m, 1H), 3.71 (s, 1H), 2.88 – 2.73 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, J = 245.5 Hz), 158.0, 133.8, 130.9 (d, J = 5.5 Hz), 129.5, 128.7 (d, J = 16.1 Hz), 127.7 (d, J = 8.0 Hz), 124.0 (d, J = 3.3 Hz), 115.3 (d, J = 22.2 Hz), 113.9, 55.4, 35.7, 31.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.0;

HRMS (ESI) calcd. for $C_{15}H_{16}OF$ $[M+H]^+$ m/z 231.1180 , found 231.1177.



1-Methoxy-4-(4-phenylbut-3-en-1-yl)benzene (Scheme 3, 3k)[6]. Prepared following

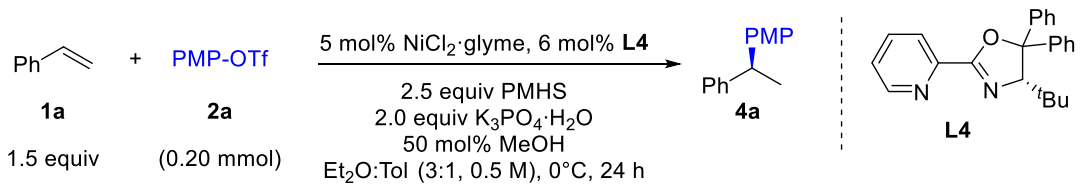
general procedure **A** using **buta-1,3-dien-1-ylbenzene** (**1k**, 39.0 mg, 0.30 mmol, 1.5 equiv), **4-methoxyphenyl trifluoromethanesulfonate** (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv) and anhydrous THF (0.40 mL, 0.5M). The reaction mixture was stirred for 24 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a white solid in 21% yield (10.0 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 7.22 – 7.13 (m, 3H), 6.87 – 6.83 (m, 2H), 6.41 (d, J = 15.8 Hz, 1H), 6.31 – 6.21 (m, 1H), 3.80 (s, 3H), 2.74 (t, 2H), 2.55 – 2.46 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 137.9, 134.0, 130.4, 130.2, 129.5, 128.6, 127.0, 126.1, 113.9, 55.4, 35.3, 35.1.

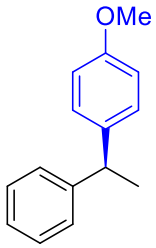
MS (EI) calcd. for $C_{17}H_{18}O$ $[M]^+$ m/z 238.1, found 238.1.

III. NiH-Catalyzed Enantioselective Markovnikov Hydroarylation of Styrenes



General procedure (B) for the NiH-catalyzed enantioselective Markovnikov hydroarylation of styrenes: In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added $NiCl_2$·glyme (2.20 mg, 0.010 mmol, 5 mol%), **L4** (4.27 mg, 0.012 mmol, 6 mol%), K_3PO_4·H_2O (92.1 mg, 0.40 mmol, 2.0 equiv), methanol (3.2 mg, 0.10 mmol, 50mol%), and mixed solvent (Et_2O:Tol = 3:1, 0.40 mL). The reaction mixture was stirred for 5 min, at which time PMHS (30 μL, 0.50 mmol, 2.5 equiv) was added and the stirring was continued for another 5 min at room temperature. Styrene (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv) and 4-methoxyphenyl trifluoromethanesulfonate (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv) were

added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and stirred at 0 °C for up to 24 h. After the reaction was complete, the reaction was quenched upon the addition of H_2O, and the mixture was extracted with ethyl acetate for three times. The organic layer was concentrated to give the crude product. *n*-Dodecane (20 μL) was added as an internal standard for GC analysis. The product was purified by chromatography on silica gel for each substrate.



(*S*)-1-Methoxy-4-(1-phenylethyl)benzene (Scheme 3, 4a)[7]**.** Prepared following general procedure **B** using **styrene** (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv), **4-methoxyphenyl trifluoromethanesulfonate** (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv). The reaction mixture was stirred for 24 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless oil in 55% yield (23.3 mg), 94:6 rr.

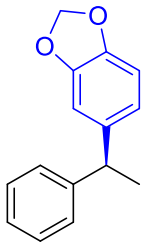
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.03 (m, 7H), 6.81 – 6.72 (m, 2H), 4.03 (q, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 1.54 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 146.9, 138.7, 128.6, 128.5, 127.7, 126.1, 113.9, 55.4, 44.1, 22.2.

MS (EI) calcd. for $C_{15}H_{16}O$ $[M]^+$ m/z 212.1, found 212.1.

$[\alpha]_D^{25}$ = +7.5 (c = 0.8, $CHCl_3$).

HPLC analysis (OJ-H, 5% IPA/hexane, 1.0 mL/min, 220nm) indicated 95% ee, t_R (major) = 16.9 min, t_R (minor) = 18.1 min.



(*S*)-5-(1-Phenylethyl)benzo[*d*][1,3]dioxole (Scheme 3, 4b)[8]. Prepared following general procedure **B** using styrene (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv), **Benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate** (**2b**, 54.0 mg, 0.20 mmol, 1.0 equiv). The reaction mixture was stirred for 24 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless oil in 40% yield (18.3 mg), 93:7 rr.

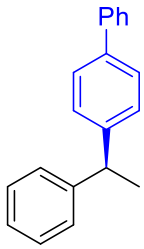
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.17 – 7.07 (m, 3H), 6.71 – 6.59 (m, 3H), 5.83 (s, 2H), 4.00 (q, J = 7.2 Hz, 1H), 1.52 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 146.5, 145.8, 140.6, 128.5, 127.6, 126.2, 120.5, 108.4, 108.2, 101.0, 44.6, 22.2.

MS (EI) calcd. for $C_{15}H_{14}O_2$ $[M]^+$ m/z 226.1, found 226.1.

$[\alpha]_D^{25}$ = +8.0 (c = 0.6, $CHCl_3$).

HPLC analysis (OJ-H, 8% EtOH/hexane, 0.8 mL/min, 220nm) indicated 87% ee, t_R (major) = 15.7 min, t_R (minor) = 16.6 min.



(*S*)-4-(1-Phenylethyl)-1,1'-biphenyl (Scheme 3, 4c). Prepared following general

procedure **B** using **styrene** (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv), **[1,1'-biphenyl]-4-yl trifluoromethanesulfonate** (**2c**, 60.4 mg, 0.20 mmol, 1.0 equiv). The reaction mixture was stirred for 24 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless oil in 58% yield (30.0 mg), 93:7 rr.

IR (neat, cm^{-1}) 1487.23, 1263.87, 731.28, 670.52

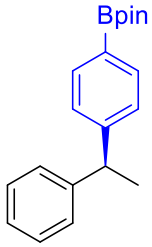
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 4H), 7.49 – 7.43 (m, 2H), 7.39 – 7.28 (m, 7H), 7.27 – 7.21 (m, 1H), 4.24 (q, J = 7.2 Hz, 1H), 1.72 (d, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 145.6, 141.1, 139.1, 128.8, 128.6, 128.2, 127.8, 127.2, 127.2, 127.2, 126.2, 44.6, 22.0.

HRMS (ESI) calcd. for $C_{20}H_{18}Na$ $[M+Na]^+$ m/z 281.13007, found 281.12946.

$[\alpha]_D^{25}$ = +10.9 (c = 0.4, $CHCl_3$).

HPLC analysis (OJ-H, 10% EtOH/hexane, 1.0 mL/min, 220nm) indicated 85% ee, t_R (major) = 11.4 min, t_R (minor) = 12.8 min.



(*S*)-4,4,5,5-Tetramethyl-2-(4-(1-phenylethyl)phenyl)-1,3,2-dioxaborolane (Scheme 3, 4d). Prepared following general procedure **B** using **styrene** (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv), **4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate** (**2d**, 70.4 mg, 0.20 mmol, 1.0 equiv). The reaction mixture was stirred for 24 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a

colorless oil in 53% yield (32.7 mg), 91:9 rr.

IR (neat, cm^{-1}) 2976.85, 1610.59, 1359.22, 1090.04, 734.47, 699.74.

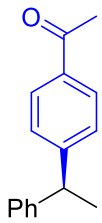
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.33 – 7.16 (m, 7H), 4.19 (q, *J* = 7.2 Hz, 1H), 1.67 (d, *J* = 7.2 Hz, 3H), 1.35 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 146.2, 135.1, 128.5, 127.8, 127.2, 126.2, 83.8, 45.1, 25.0, 21.8.

HRMS (ESI) calcd. for $C_{20}H_{26}BO_2$ $[M+H]^+$ m/z 309.20204, found 308.20177.

$[\alpha]_D^{25}$ = +5.1 (c = 0.6, $CHCl_3$).

HPLC analysis (two collected AD columns, 1% EtOH/hexane, 0.5 mL/min, 220nm) indicated 99% ee, t_R (major) = 15.3 min, t_R (minor) = 16.2 min.



(S)-1-(4-(1-phenylethyl)phenyl)ethan-1-one (Scheme 3, 4e)[9]. Prepared following general procedure **B** using **styrene** (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv), **4-acetylphenyl trifluoromethanesulfonate** (**2e**, 53.6 mg, 0.20 mmol, 1.0 equiv). The reaction mixture was stirred for 24 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 15:1) to provide the title compound as a colorless oil in 66% yield (29.6 mg), 92:8 rr.

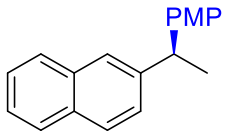
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 2H), 7.34 – 7.27 (m, 4H), 7.23 – 7.18 (m, 3H), 4.21 (q, *J* = 7.2 Hz, 1H), 2.57 (s, 3H), 1.66 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.0, 152.2, 145.4, 135.3, 128.7, 128.7, 128.0, 127.7, 126.5, 45.0, 26.7, 21.7.

MS (EI) calcd. for $C_{16}H_{16}O$ $[M]^+$ m/z 224.1, found 224.1.

$[\alpha]_D^{25}$ =+4.8 (c = 0.2, $CHCl_3$).

HPLC analysis (IF-3, 2% IPA/hexane, 1.0 mL/min, 220nm) indicated 75% ee, t_R (major) = 9.2 min, t_R (minor) = 10.8 min.



(*R*)-2-(1-(4-Methoxyphenyl)ethyl)naphthalene (Scheme 3, 4g)[10]**.** Prepared following general procedure **B** using **2-vinylnaphthalene** (**1e**, 46.2 mg, 0.30 mmol, 1.5 equiv), **4-methoxyphenyl trifluoromethanesulfonate** (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv). The reaction mixture was stirred for 24 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless oil in 40% yield (36.0 mg), 94:6 rr.

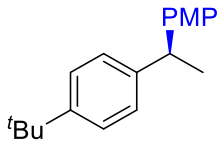
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.58 (m, 4H), 7.40 – 7.30 (m, 2H), 7.21 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.78 – 6.71 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 1H), 3.69 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 144.3, 138.5, 133.7, 132.2, 128.8, 128.0, 127.8, 127.7, 126.9, 126.0, 125.4, 125.3, 113.9, 55.4, 44.2, 22.1.

MS (EI) calcd. for $C_{19}H_{18}O$ $[M]^+$ m/z 262.1, found 262.1.

$[\alpha]_D^{25}$ = -26.8 (c = 1.2, $CHCl_3$).

HPLC analysis (OJ-H, 5% IPA/hexane, 1.0 mL/min, 220nm) indicated 97% ee, t_R (major) = 22.6 min, t_R (minor) = 26.6 min.



(*S*)-1-(*tert*-Butyl)-4-(1-(4-methoxyphenyl)ethyl)benzene (Scheme 3, 4h). Prepared following general procedure **B** using**1-(*tert*-butyl)-4-vinylbenzene** (**1f**, 48.0 mg, 0.30 mmol, 1.5 equiv), **4-methoxyphenyl trifluoromethanesulfonate** (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv). The reaction mixture was stirred for 24 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless oil in 65% yield (35.0 mg), 93:7 rr.

IR (neat, cm^{-1}) 2960.11, 1510.14, 1244.56, 1201.87, 827.55, 578.81.

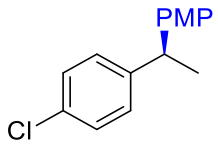
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 2H), 7.09 – 7.04 (m, 4H), 6.78 – 6.72 (m, 2H), 4.00 (q, *J* = 7.2 Hz, 1H), 3.69 (s, 3H), 1.53 (d, *J* = 7.2 Hz, 3H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 148.7, 143.8, 138.9, 128.6, 127.2, 125.3, 113.9, 113.8, 55.4, 43.6, 34.5, 31.5, 22.2.

HRMS (ESI) calcd. for $C_{19}H_{24}OK$ $[M+K]^+$ m/z 307.14587, found 307.14589.

$[\alpha]_D^{25}$ = -1.6 (c = 1.5, $CHCl_3$).

HPLC analysis (OJ-H, 5% IPA/hexane, 1.0 mL/min, 220nm) indicated 87% ee, t_R (major) = 6.0 min, t_R (minor) = 9.3 min.



(*R*)-1-Chloro-4-(1-(4-methoxyphenyl)ethyl)benzene (Scheme 3, 4i)[11]**.** Prepared following general procedure **B** using **1-chloro-4-vinylbenzene** (**1g**, 41.4 mg, 0.30 mmol, 1.5 equiv), **4-methoxyphenyl trifluoromethanesulfonate** (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv). The reaction mixture was stirred for 24 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless oil in 80% yield (39.6 mg), 94:6 rr.

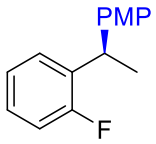
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 2H), 7.08 – 7.00 (m, 4H), 6.79 – 6.72 (m, 2H), 4.00 (q, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 1.51 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 145.4, 138.1, 131.8, 129.0, 128.6, 114.0, 55.4, 43.5, 22.1.

MS (EI) calcd. for $C_{15}H_{15}ClO$ $[M]^+$ m/z 246.1, found 246.1.

$[\alpha]_D^{25}$ = -2.1 (c = 0.3, $CHCl_3$).

HPLC analysis (two collected AD columns, 0.5% IPA/hexane, 0.5 mL/min, 220nm) indicated 96% ee, t_R (major) = 24.6 min, t_R (minor) = 25.6 min.



(*R*)-1-Fluoro-2-(1-(4-methoxyphenyl)ethyl)benzene (Scheme 3, 4j). Prepared following general procedure **B** using **1-fluoro-2-vinylbenzene** (**1h**, 36.6 mg, 0.30 mmol, 1.5 equiv), **4-methoxyphenyl trifluoromethanesulfonate** (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv). The reaction mixture was stirred for 24 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless oil in 67% yield (31.0 mg), 91:9 rr.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.05 (m, 4H), 7.01 – 6.86 (m, 2H), 6.80 – 6.72 (m, 2H), 4.35 (q, *J* = 7.3 Hz, 1H), 3.70 (s, 3H), 1.53 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7 (d, J = 173.2 Hz), 158.1, 137.3, 133.8 (d, J = 14.4), 128.6, 128.5, 127.7 (d, J = 8.3 Hz), 124.1 (d, J = 3.6 Hz), 115.5 (d, J = 22.6 Hz), 113.9, 55.4, 36.9, 21.0.

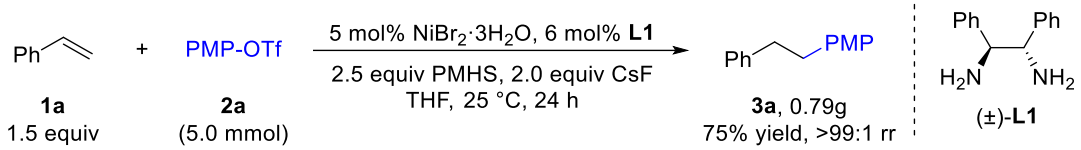
^{19}F NMR (376 MHz, $CDCl_3$) δ -118.09.

MS (EI) calcd. for $C_{15}H_{15}FO$ $[M]^+$ m/z 230.1, found 230.1.

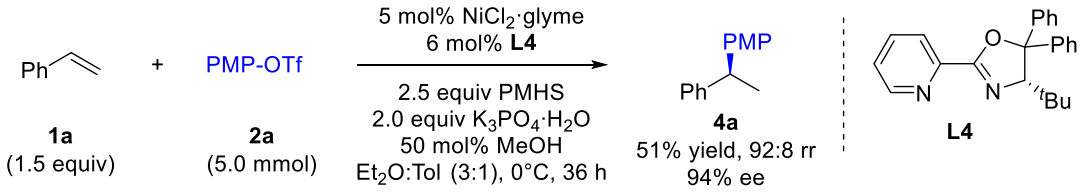
$[\alpha]_D^{25}$ = +10.4 (c = 0.9, $CHCl_3$).

HPLC analysis (OJ-H, 10% IPA/hexane, 0.8 mL/min, 220nm) indicated 96% ee, t_R (major) = 45.7 min, t_R (minor) = 22.6 min.

IV. 5 mmol-Scale Synthesis



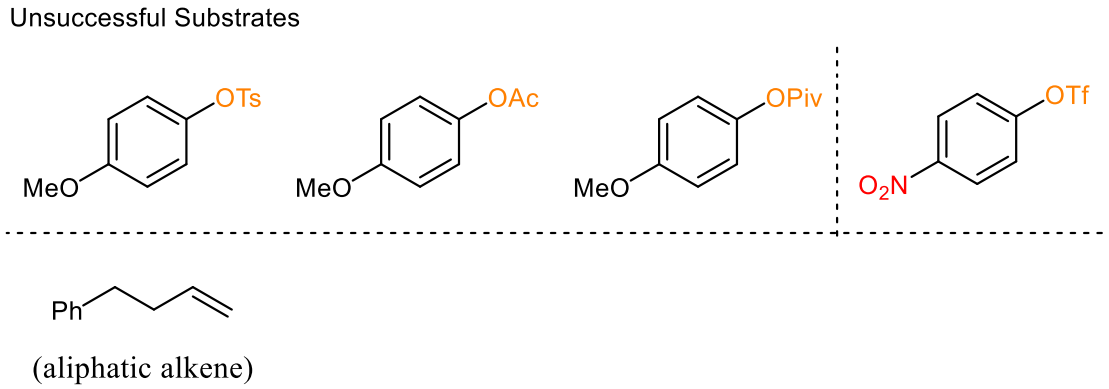
To an oven-dried 100 mL round bottom flask equipped with a magnetic stir bar was added **L1** (63.7 mg, 0.30 mmol, 6 mol%). The flask was introduced in a nitrogen-filled glove box, $NiBr_2 \cdot 3H_2O$ (68.1 mg, 0.25 mmol, 5 mol%), CsF (1.52 g, 10.0 mmol, 2.0 equiv) were added. The flask was sealed with a rubber stopper, removed from the glove box. Anhydrous THF (0.5 M, 10.0 mL) was added via syringe and the mixture was stirred for 10 min at room temperature, at which time PMHS (1.50 mL, 12.5 mmol, 2.5 equiv) was added dropwise. The stirring was continued for another 10 min at room temperature. Styrene (**1a**, 0.86 mL, 7.5 mmol, 1.5 equiv) and 4-methoxyphenyl trifluoromethanesulfonate (**2a**, 1.28 g, 5.0 mmol, 1.0 equiv) were added to the resulting mixture in this order. The resulted mixture was stirred at 25 °C for 36 h. The reaction was quenched upon the addition of water (20 mL). The mixture was extracted with EtOAc (30 mL×3). The organic layer was combined and concentrated. The crude product was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide **3a** as a white solid in 75% yield (0.79 g), >99:1 rr.



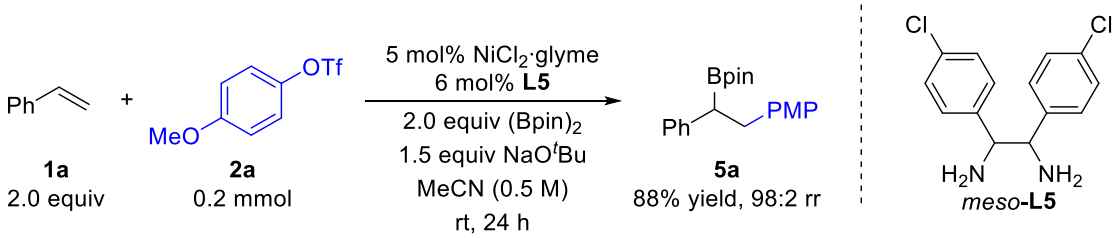
To an oven-dried 100 mL round bottom flask equipped with a magnetic stir bar was added **L4** (107 mg, 0.30 mmol, 6 mol%). The flask was introduced in a nitrogen-filled glove box, $NiCl_2 \cdot dme$ (54.9 mg, 0.25 mmol, 5 mol%), $K_3PO_4 \cdot H_2O$ (2.30 g, 10.0 mmol, 2.0 equiv) were added. The flask was sealed with a rubber stopper, removed from the glove box. A mixed solvent (Et_2O: Tol = 3: 1, a total of 10.0 mL) was added via syringe and the mixture was stirred for 10 min at room temperature, at which time PMHS (1.50

mL, 12.5 mmol, 2.5 equiv) was added dropwise. The stirring was continued for another 10 min at room temperature. Styrene (**1a**, 0.86 mL, 7.5 mmol, 1.5 equiv), 4-methoxyphenyl trifluoromethanesulfonate (**2a**, 1.28 g, 5.0 mmol, 1.0 equiv), and methanol (0.10 mL, 2.5 mmol, 50 mol%) were added to the resulting mixture in this order. The resulted mixture was stirred at 0 °C for 24 h. The reaction was quenched upon the addition of water (20 mL). The mixture was extracted with EtOAc (30 mL×3). The organic layer was combined and concentrated. The crude product was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide **4a** as a colorless oil in 51% yield (0.54 g), 92:8 rr. HPLC analysis indicated 94% ee.

V. Unsuccessful substrates

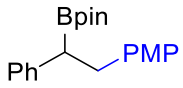


VI. Mechanistic Studies



In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a

magnetic stir bar was added $NiCl_2$·glyme (2.2 mg, 0.010 mmol, 5 mol%), **L5** (3.4 mg, 0.012 mmol, 6 mol%, CAS: 86212-34-2), 0.40 mL anhydrous MeCN, and the mixture was stirred for 5 min, at which time styrene (**1a**, 41.6 mg, 0.40 mmol, 2.0 equiv), 4-methoxyphenyl trifluoromethanesulfonate (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv), NaO^{t}Bu (28.8 mg, 0.30 mmol, 1.5 equiv), and $(Bpin)_2$ (102.0 mg, 0.40 mmol, 2.0 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and stirred at 25 °C for up to 24 h. After the reaction was complete, the reaction was quenched upon the addition of H_2O, and the mixture was extracted with ethyl acetate for three times. The organic layer was concentrated to give the crude product. Dodecane (20 μL) was added as an internal standard for GC analysis. The product was purified by chromatography on silica gel (petroleum ether/EtOAc = 50:1).

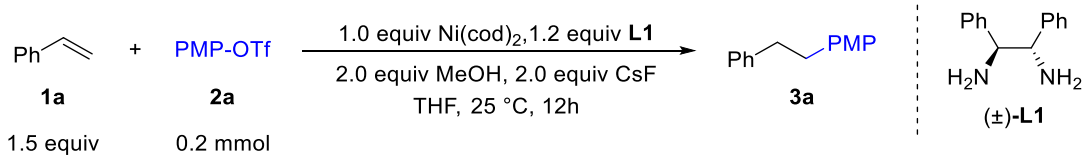


2-(2-(4-Ethoxyphenyl)-1-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[12]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 4H), 7.19 – 7.15 (m, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 3.13 (dd, *J* = 13.6, 9.7 Hz, 1H), 2.94 (dd, *J* = 13.6, 6.9 Hz, 1H), 2.68 (dd, *J* = 9.7, 6.9 Hz, 1H), 1.15 (s, 6H), 1.15 (s, 6H).

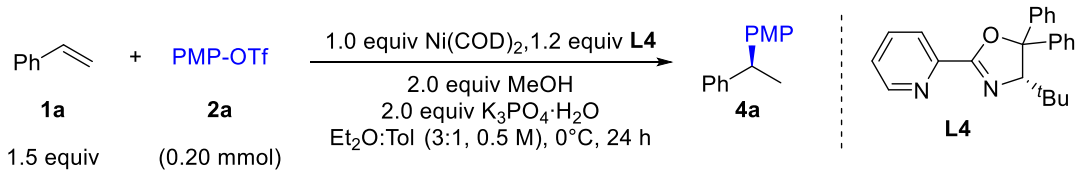
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 142.6, 133.9, 129.8, 128.4, 128.3, 125.3, 113.4, 83.4, 55.2, 37.9, 24.6, 24.5.

MS (EI) calcd. for $C_{19}H_{24}O$ $[M]^+$ m/z 338.2, found 338.2.



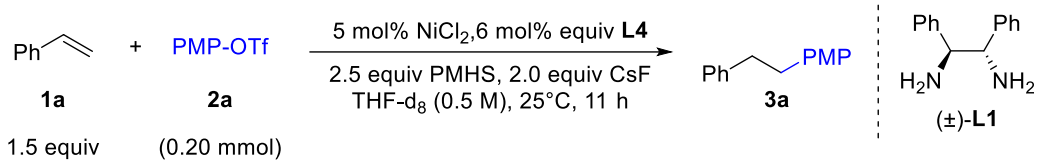
In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added $Ni(cod)_2$ (55.0 mg, 0.20 mmol, 1.0 equiv), **L1** (50.9 mg,

0.24 mmol, 1.2 equiv), CsF (60.8 mg, 0.40 mmol, 2.0 equiv), 0.40 mL anhydrous THF, and the mixture was stirred for 5 min at room temperature. Styrene (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv), 4-methoxyphenyl trifluoromethanesulfonate (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv) and methanol (12.8 mg, 0.4 mmol, 2.0 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and stirred at 25 °C for 12 h. After the reaction was complete, the reaction was quenched upon the addition of H_2O, and the mixture was extracted with ethyl acetate for three times. The organic layer was concentrated to give the crude product. Dodecane (20 μL) was added as an internal standard for GC analysis. The product was purified by chromatography on silica gel (petroleum ether/EtOAc = 50:1) to provide **3a** as a white solid in 20% yield (8.5 mg).



In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added $Ni(cod)_2$ (55.0 mg, 0.20 mmol, 1.0 equiv), **L4** (85.5 mg, 0.24 mmol, 1.2 equiv), $K_3PO_4·H_2O$ (92.1 mg, 0.40 mmol, 2.0 equiv) and mixed solvent (Et_2O:Tol = 3:1, 0.40 mL). The reaction mixture was stirred for 5 min at room temperature. Styrene (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv), 4-methoxyphenyl trifluoromethanesulfonate (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv) and methanol (12.8 mg, 0.40 mmol, 2.0 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and stirred at 0 °C for 24 h. After the reaction was complete, the reaction was quenched upon the addition of H_2O, and the mixture was extracted with ethyl acetate for three times. The organic layer was concentrated to give the crude product. *n*-Dodecane (20 μL) was added as an internal standard for GC analysis. The product was purified by chromatography on

silica gel (petroleum ether/EtOAc = 50:1) to provide **4a** as a colorless oil in 20% yield (8.5 mg). HPLC analysis indicated 89% ee.



Isotopic Experiment: In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar was added $NiCl_2$ (1.3 mg, 0.010 mmol, 5 mol%), **L1** (2.55 mg, 0.012 mmol, 6 mol%), CsF (60.8 mg, 0.40 mmol, 2.0 equiv), 0.40 mL THF-d_8, and the mixture was stirred for 5 min, at which time PMHS (30 μL, 0.50 mmol, 2.5 equiv) was added and the stirring was continued for another 5 min at room temperature. Styrene (**1a**, 31.2 mg, 0.30 mmol, 1.5 equiv) and 4-methoxyphenyl trifluoromethanesulfonate (**2a**, 51.2 mg, 0.20 mmol, 1.0 equiv) were added to the resulting mixture in this order. The tube was sealed with a teflon-lined screw cap, removed from the glove box and stirred at 25 °C for 11 h. After the reaction was complete, the reaction was quenched upon the addition of H_2O, and the mixture was extracted with ethyl acetate for three times. The organic layer was concentrated to give the crude product. *n*-Dodecane (20 μL) was added as an internal standard for GC analysis. The product was purified by chromatography on silica gel (petroleum ether/EtOAc = 50:1) to provide **3a** as a white solid in 60% yield (25.4 mg). No ^2H NMR signal was observed. The spectrum data is consistent with that of **3a** in Scheme 3. No D incorporation into the product (**3a**) indicated that the hydride of the product was not from the solvent.

VII. References

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VIII. GC Trace

Note:

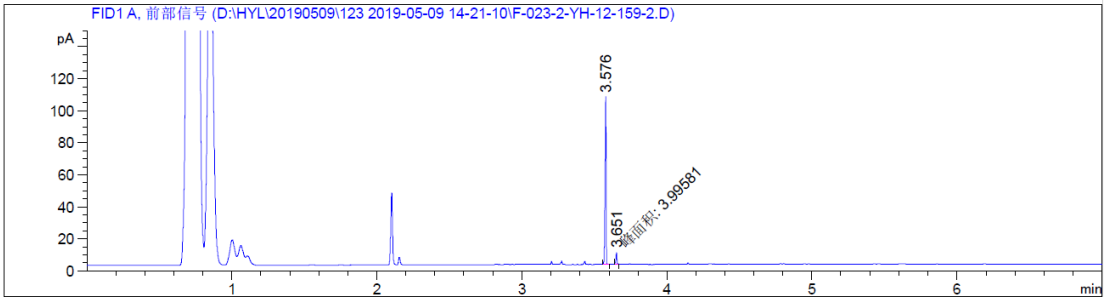
1) Dodecane (tr=2.00 min) was used as internal standard for GC yield.

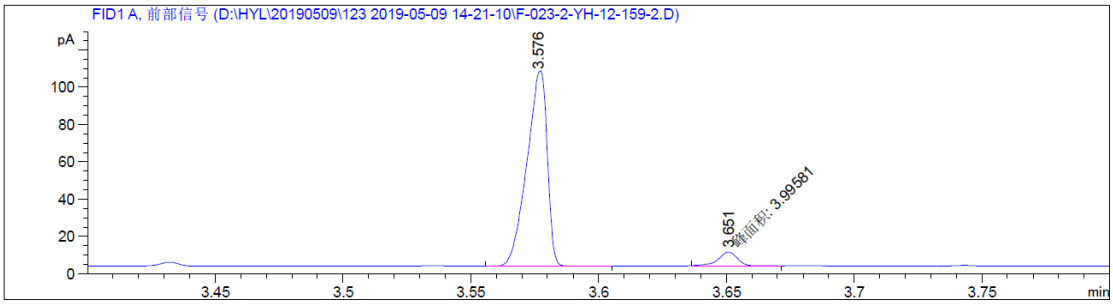
2) GC analysis was performed on Agilent 7890B gas chromatograph or Agilent 8890B gas chromatograph with an FID detector using a J & W DB-1 column (10 m, 0.1 mm I.D.).

3) GC method: 100 method starts at 100 °C holds the oven at this temperature for 1 minute, then ramp of 50 °C/min till 250 °C and hold the oven at this temperature for 3 minutes (or 5 minutes for 100B method, or 16 minutes for 100C method).

4) rr refers to regioisomeric ratio, represents the ratio of major (1,1-diarylalkane) product to the sum of all other isomers as determined by GC, all isomers' peaks were confirmed by GC-MS analysis.

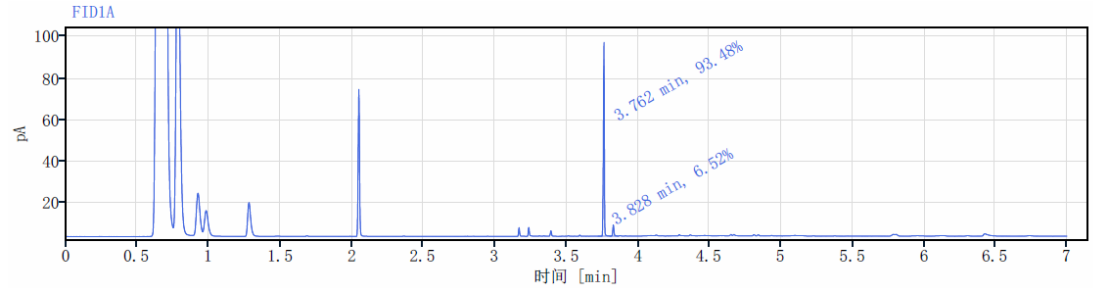
4a: GC trace

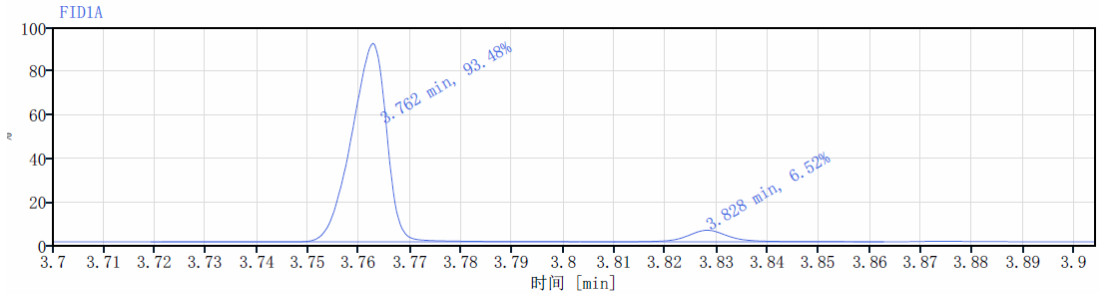




Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.576	BB	9.64e-3	57.83543	104.84646	93.53756
2	3.651	FM	8.70e-3	3.99581	7.65909	6.46244

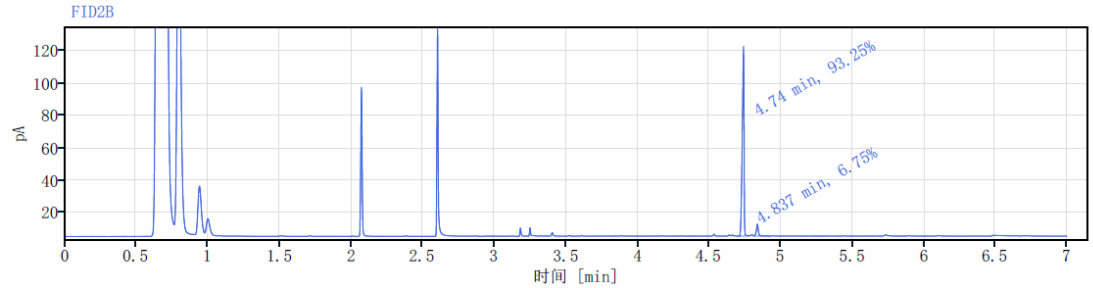
4b: GC trace

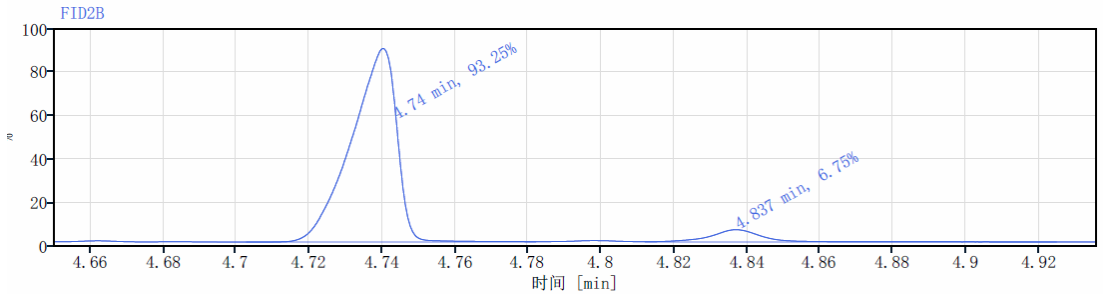




RetTime	Signal	Width(min)	Area	Height	Area%
3.762	FID1A	0.091	44.7	89.7	93.48
3.828	FID1A	0.053	3.1	5.4	6.52

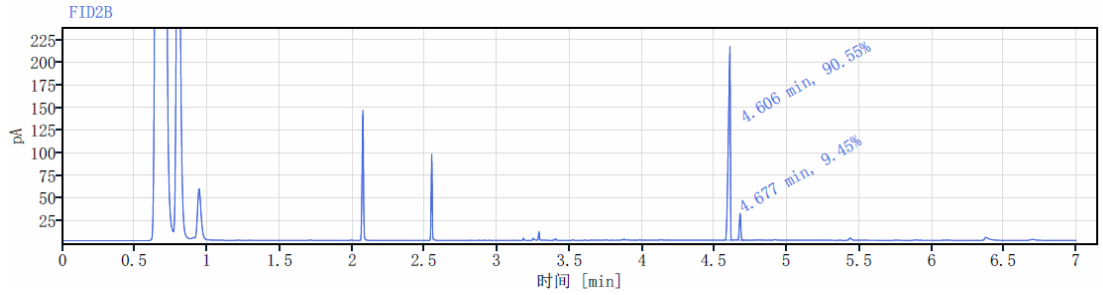
4c: GC trace

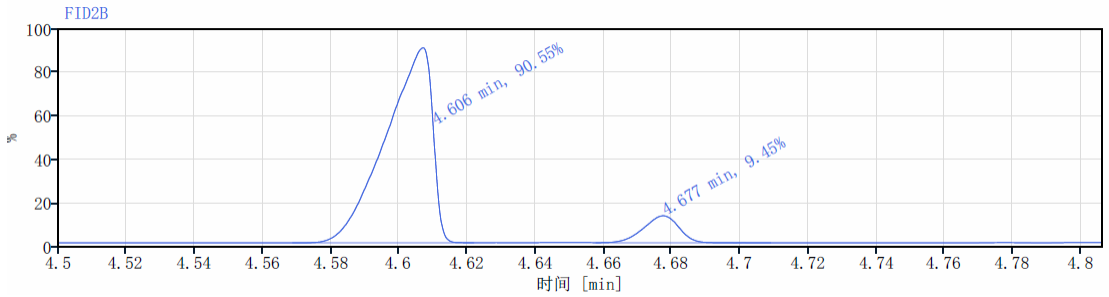




RetTime	Signal	Width(min)	Area	Height	Area%
4.740	FID2B	0.079	101.6	117.6	93.25
4.837	FID2B	0.113	7.4	7.4	6.75

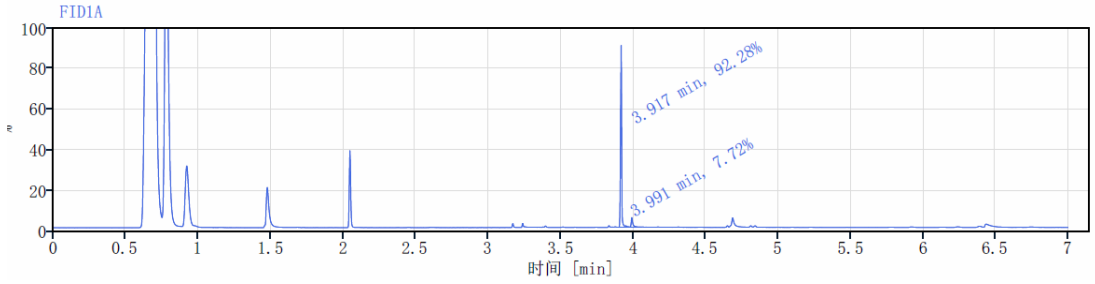
4d: GC trace

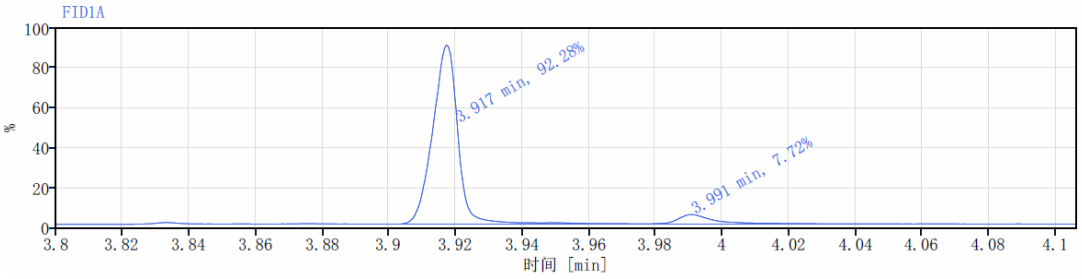




RetTime	Signal	Width(min)	Area	Height	Area%
4.606	FID2B	0.053	203.5	209.9	90.55
4.677	FID2B	0.051	21.2	29.4	9.45

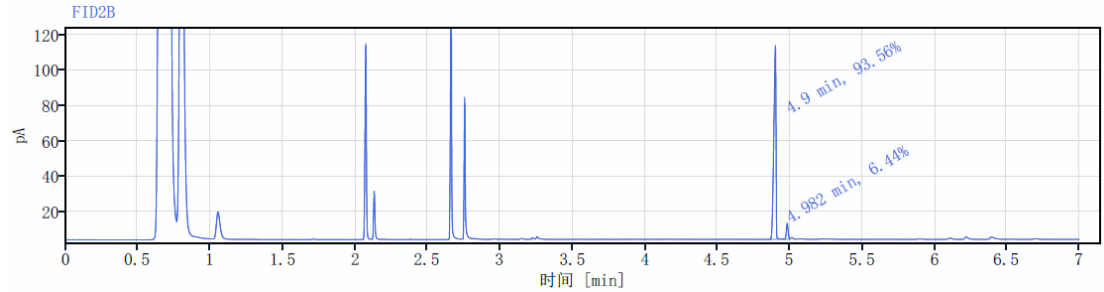
4e: GC trace

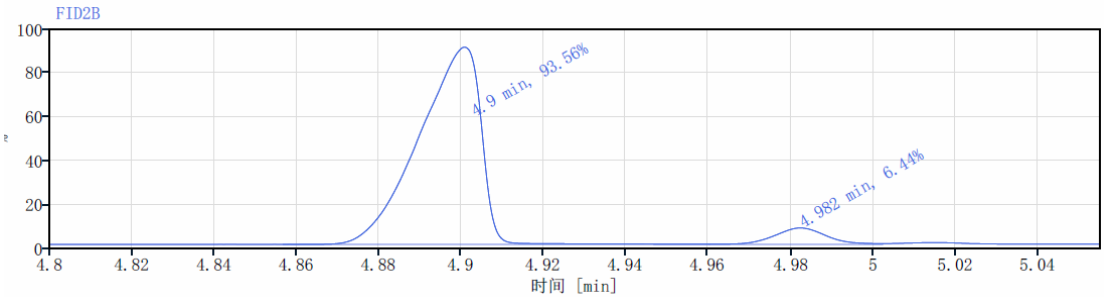




RetTime	Signal	Width(min)	Area	Height	Area%
3.917	FID1A	0.077	40.7	74.7	92.28
3.991	FID1A	0.082	3.4	4.1	7.72

4g: GC trace





RetTime	Signal	Width(min)	Area	Height	Area%
4.900	FID2B	0.104	114.4	107.0	93.56
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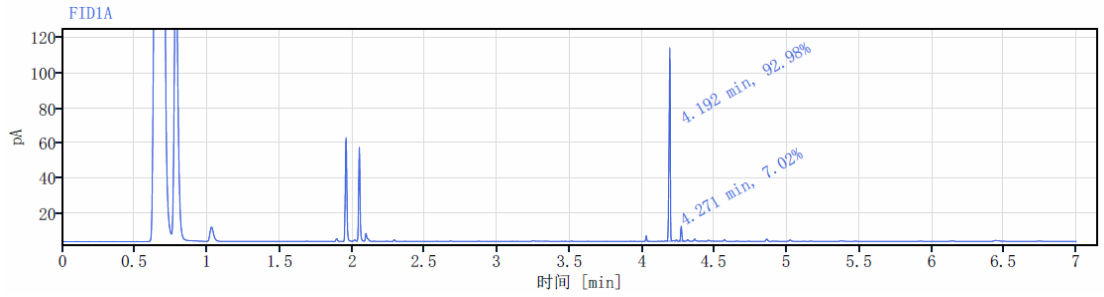
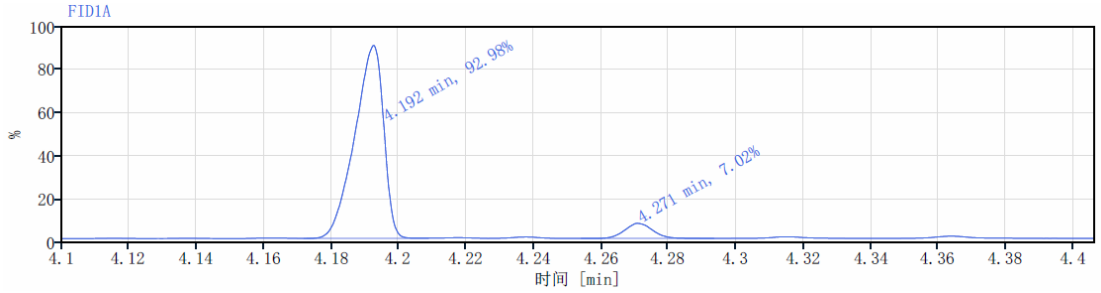
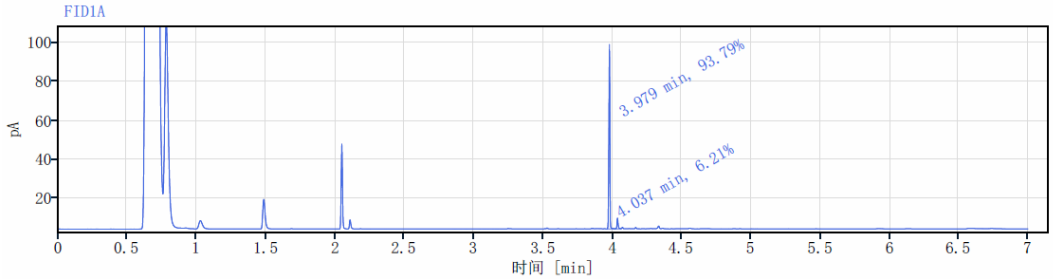
4h: GC trace

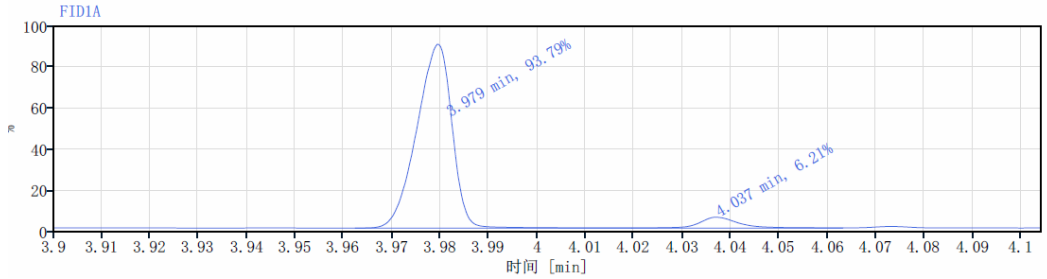




RetTime	Signal	Width(min)	Area	Height	Area%
4.192	FID1A	0.037	66.1	110.6	92.98
4.271	FID1A	0.039	5.0	8.6	7.02

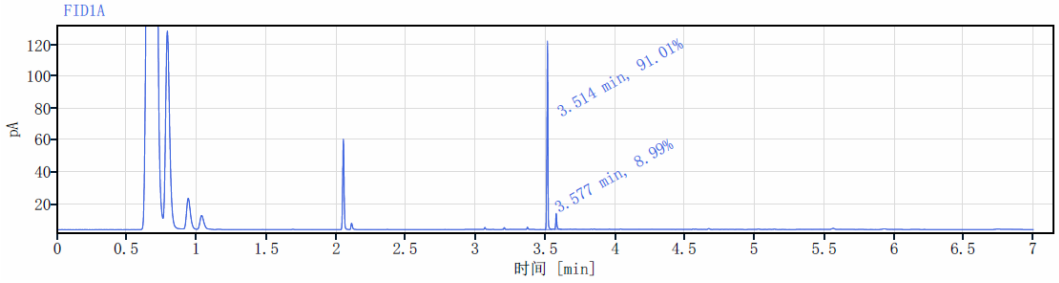
4i: GC trace

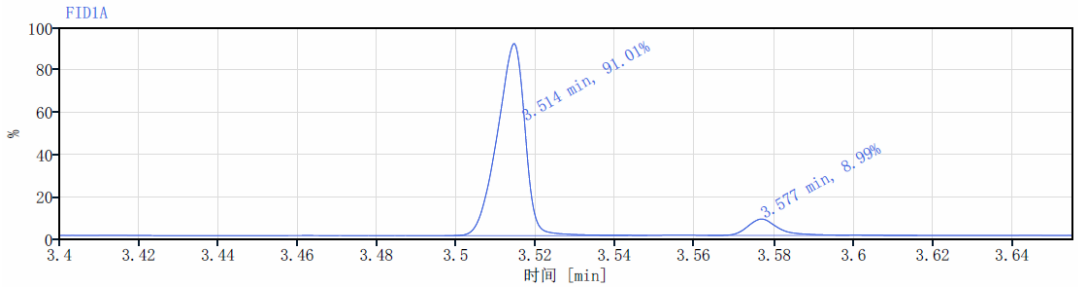




RetTime	Signal	Width(min)	Area	Height	Area%
3.979	FID1A	0.057	48.2	94.4	93.79
4.037	FID1A	0.044	3.2	5.6	6.21

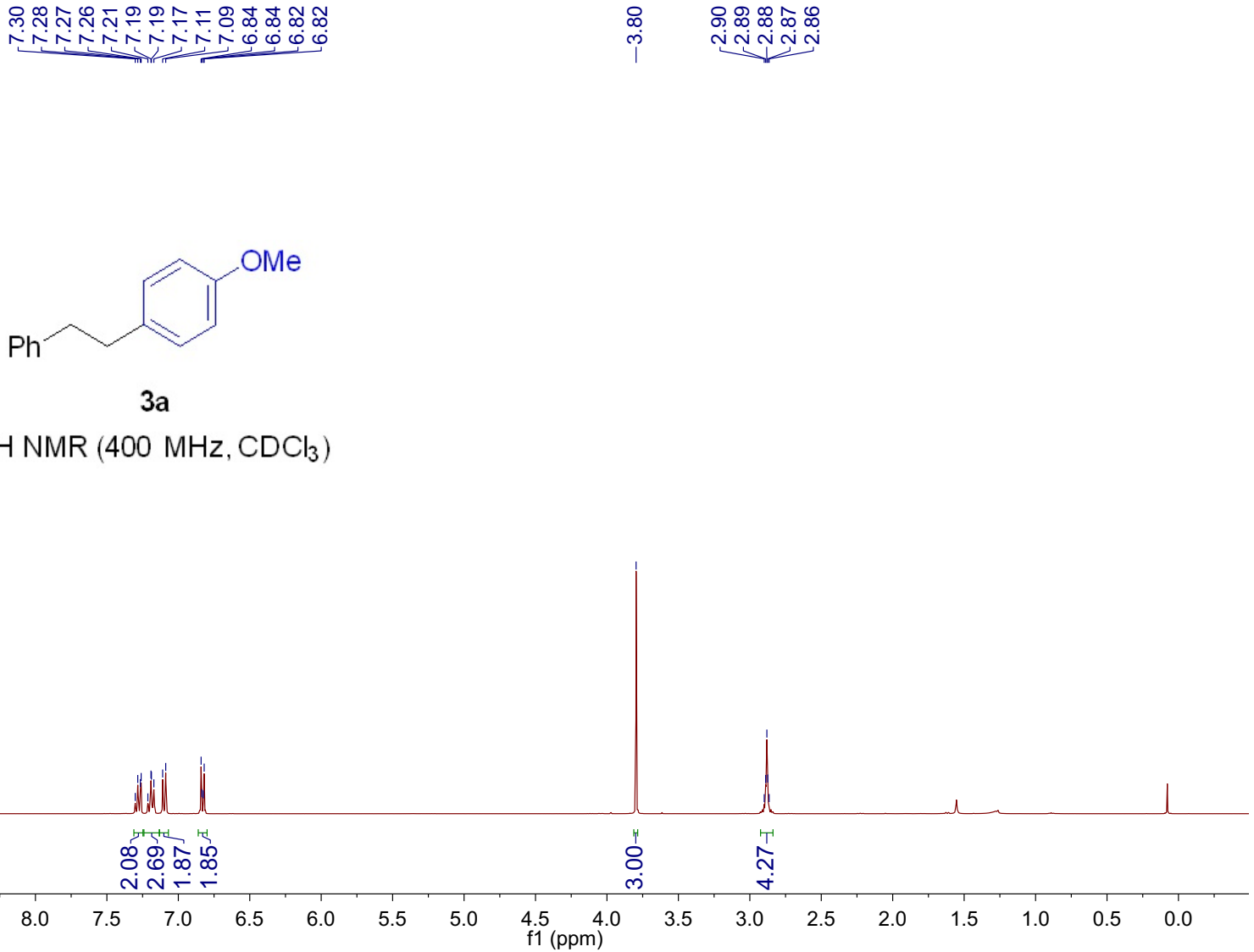
4j: GC trace





RetTime	Signal	Width(min)	Area	Height	Area%
3.514	FID1A	0.051	57.6	114.7	91.01
3.577	FID1A	0.053	5.7	10.1	8.99

IX. Spectroscopic Data (NMR and HPLC Spectrum)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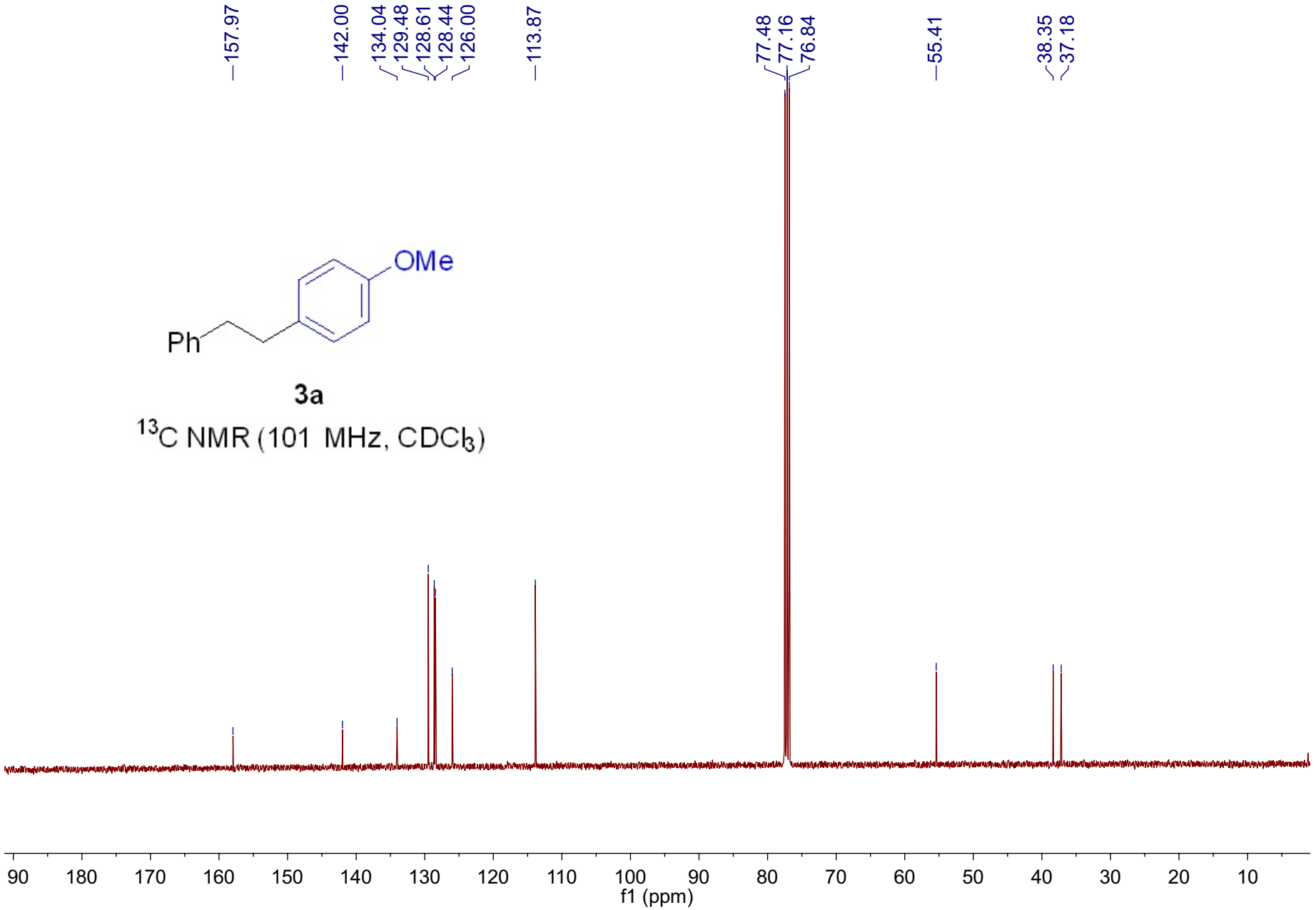
7.28
7.27
7.26
7.21
7.19
7.19
7.17
7.11
7.09
6.84
6.84
6.82
6.82
3.80
2.90
2.89
2.88
2.87
2.86
OMe
Ph
3a
1H NMR (400 MHz, CDCl3)
2.08
2.69
1.87
1.85
3.00
4.27
f1 (ppm)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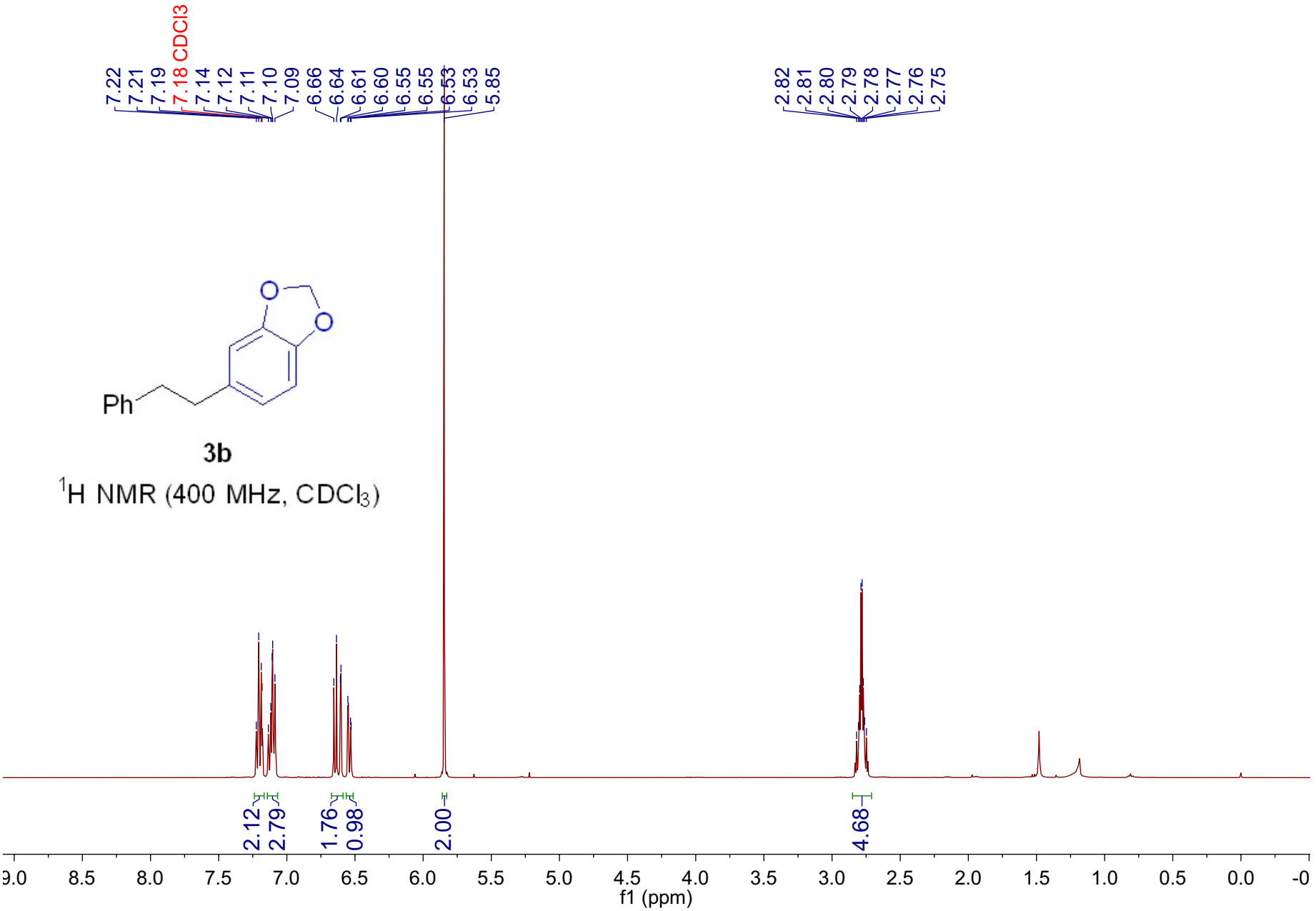
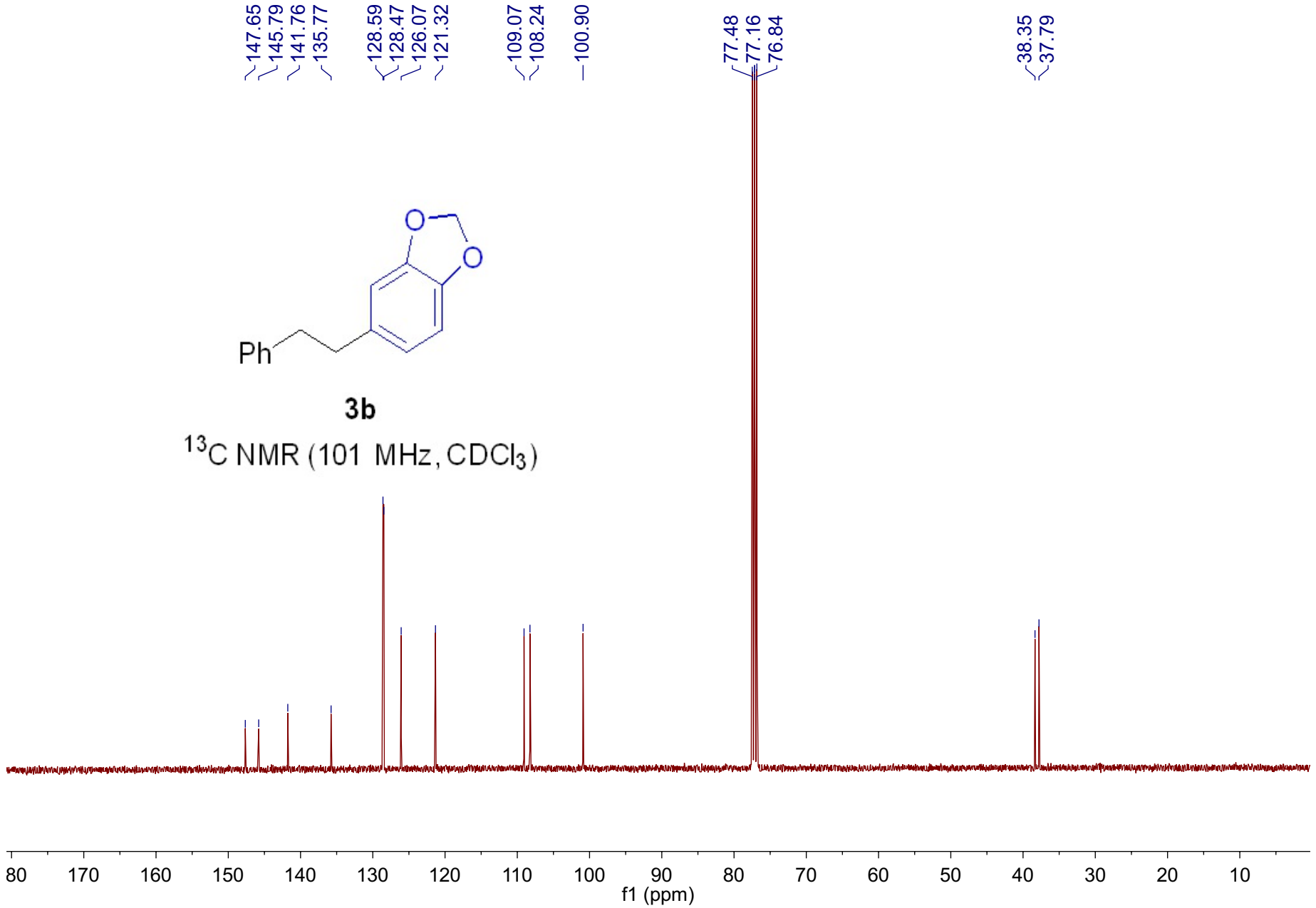
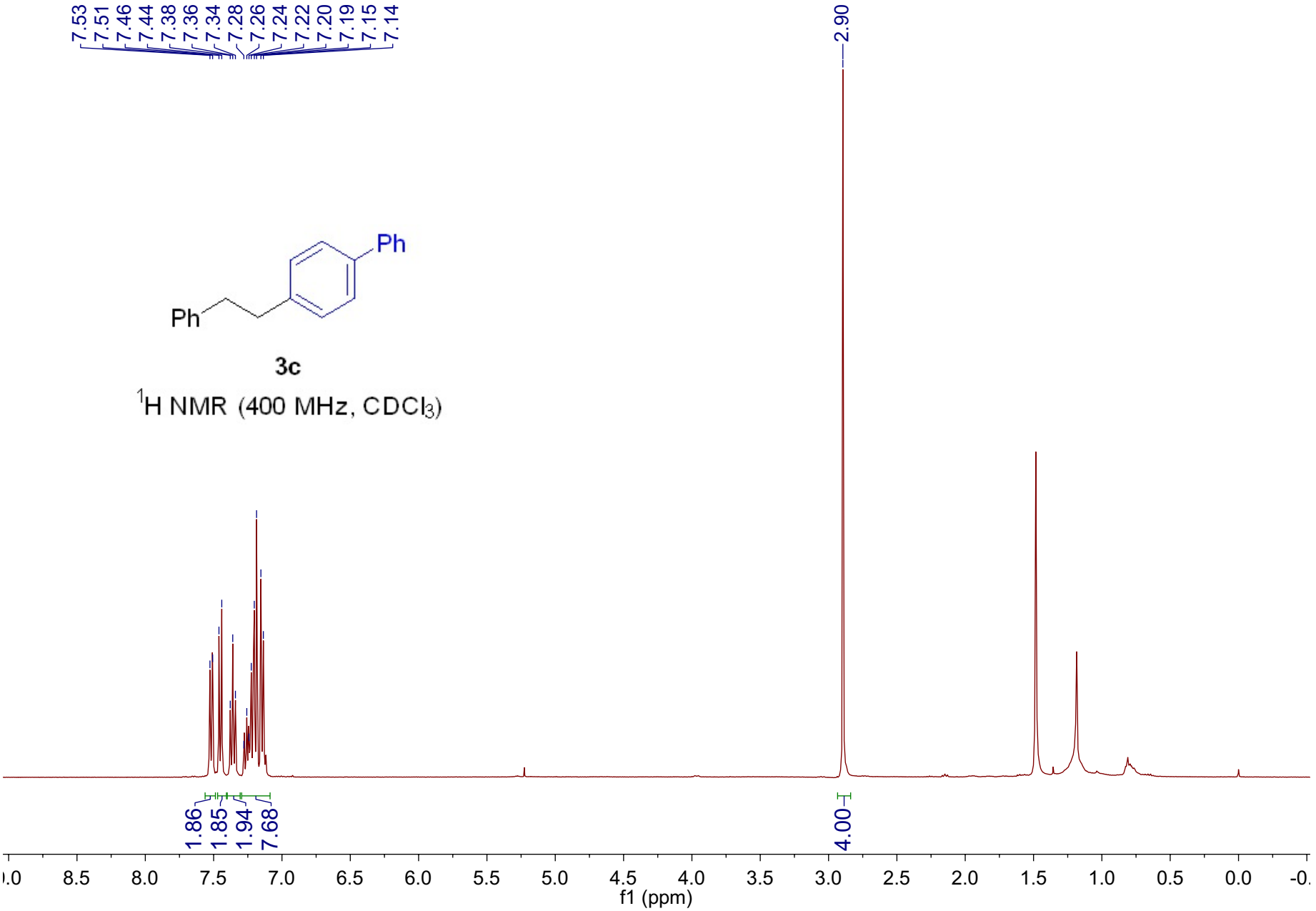
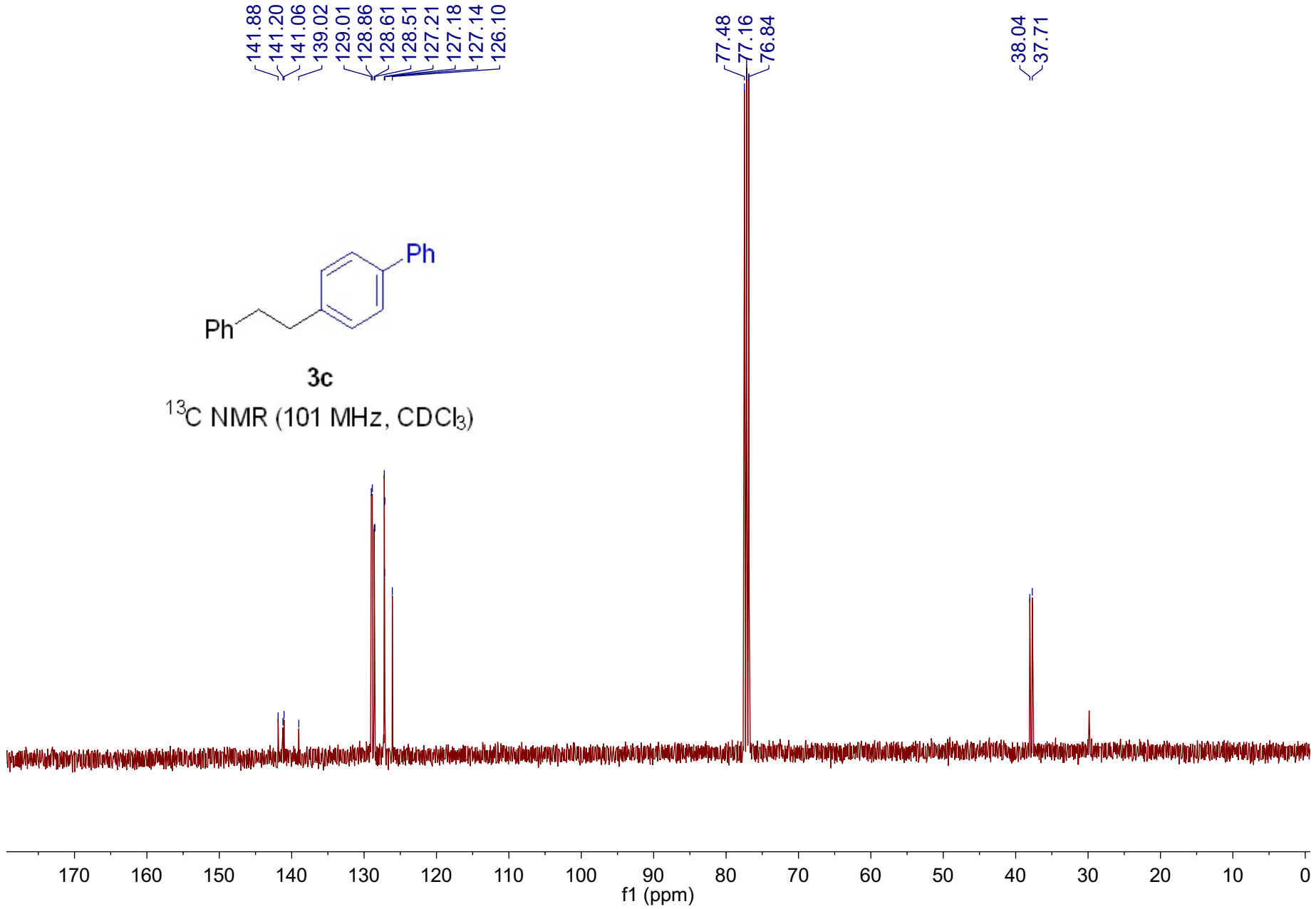
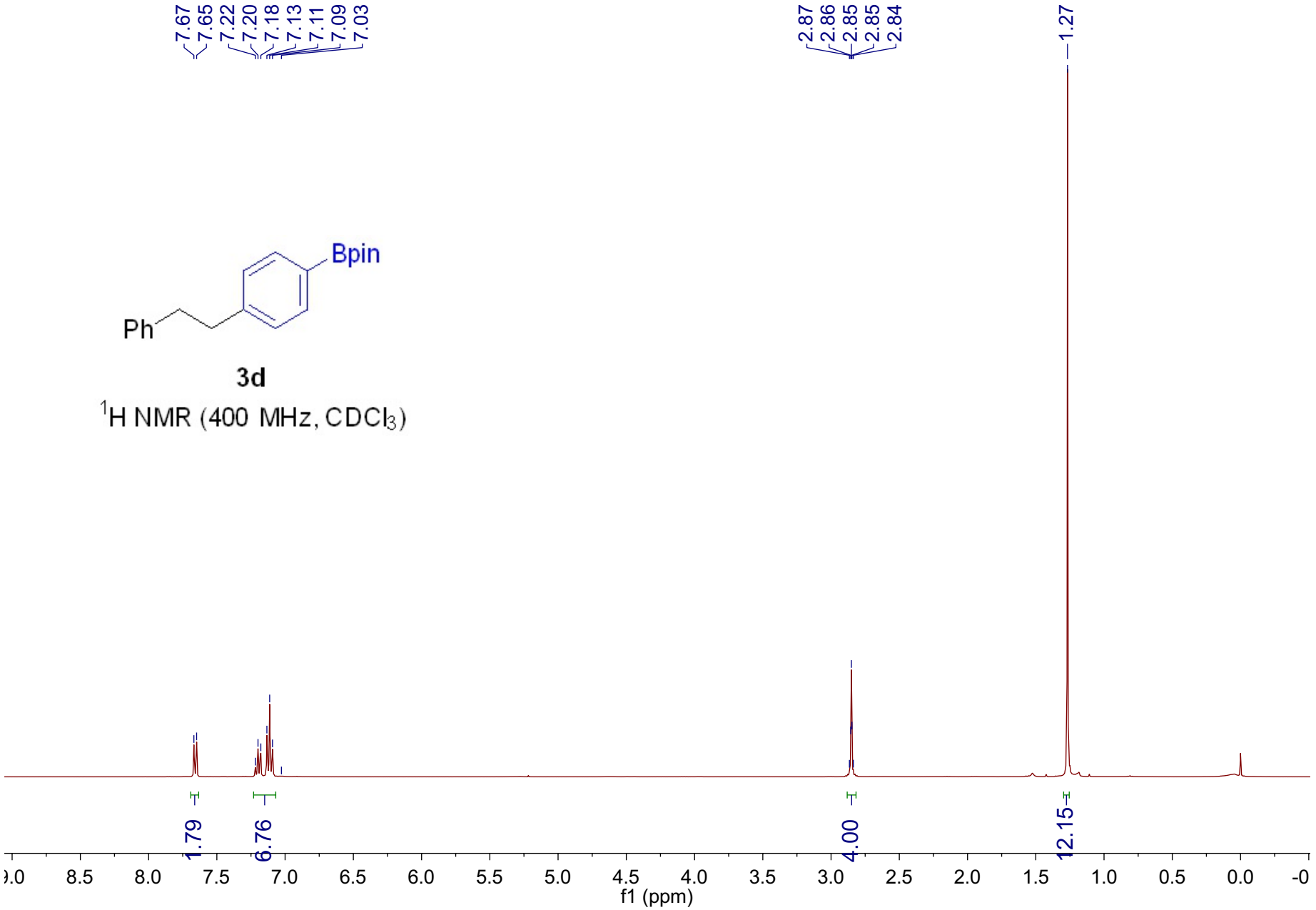
142.00
134.04
129.48
128.61
128.44
126.00
113.87
77.48
77.16
76.84
55.41
38.35
37.18
OMe
Ph
3a
13C NMR (101 MHz, CDCl3)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

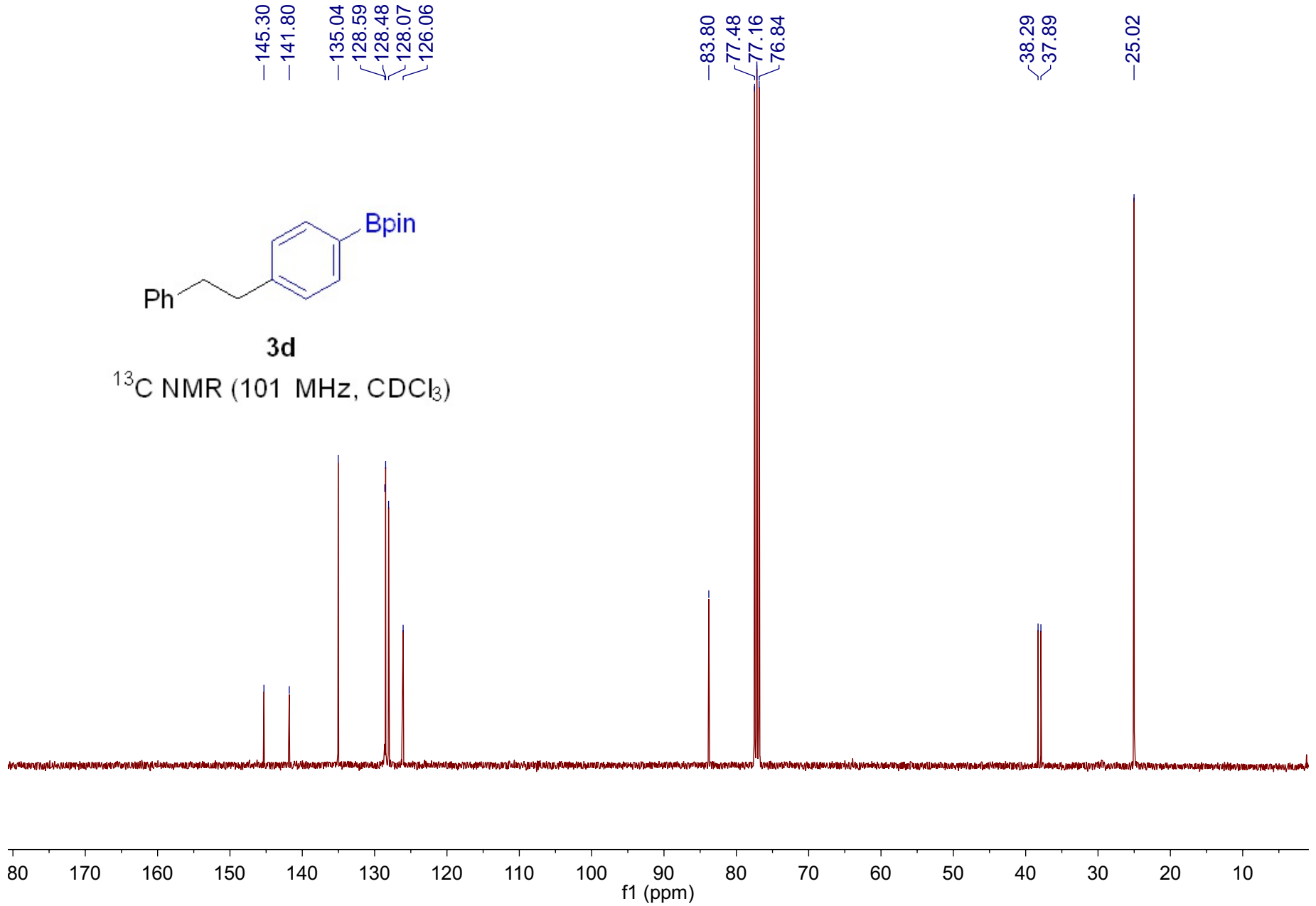

7.22
7.21
7.19
7.18 CDCl3
7.14
7.12
7.11
7.10
7.09
6.66
6.64
6.61
6.60
6.55
6.55
6.53
6.53
5.85
2.82
2.81
2.80
2.79
2.78
2.77
2.76
2.75
O
O
Ph
3b
1H NMR (400 MHz, CDCl3)
2.12
2.79
1.76
0.98
2.00
4.68
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


147.65
145.79
141.76
135.77
128.59
128.47
126.07
121.32
109.07
108.24
100.90
77.48
77.16
76.84
38.35
37.79
O
O
Ph
3b
^{13}C NMR (101 MHz, $CDCl_3$)
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.53
7.51
7.46
7.44
7.38
7.36
7.34
7.28
7.26
7.24
7.22
7.20
7.19
7.15
7.14
2.90
Ph
Ph
3c
1H NMR (400 MHz, CDCl3)
1.86
1.85
1.94
7.68
4.00
f1 (ppm)


141.88
141.20
141.06
139.02
129.01
128.86
128.61
128.51
127.21
127.18
127.14
126.10
77.48
77.16
76.84
38.04
37.71
Ph
Ph
3c
13C NMR (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.67
7.65
7.22
7.20
7.18
7.13
7.11
7.09
7.03
2.87
2.86
2.85
2.85
2.84
1.27
Bpin
Ph
3d
^{1}H NMR (400 MHz, $CDCl_3$)
1.79
6.76
4.00
12.15
f1 (ppm)


145.30
141.80
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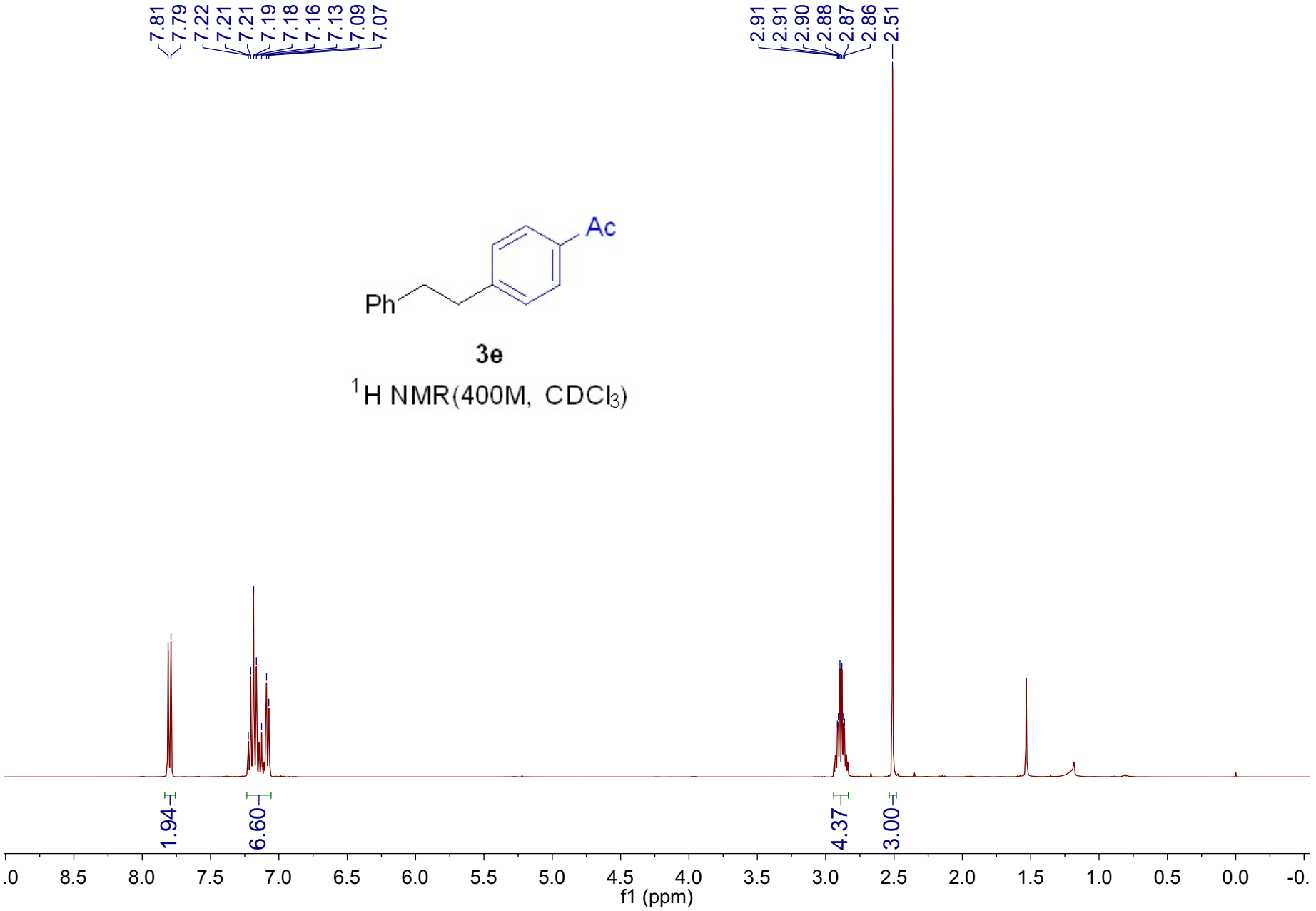
128.59
128.48
128.07
126.06
83.80
77.48
77.16
76.84
38.29
37.89
25.02
Bpin
Ph
3d
13C NMR (101 MHz, CDCl3)
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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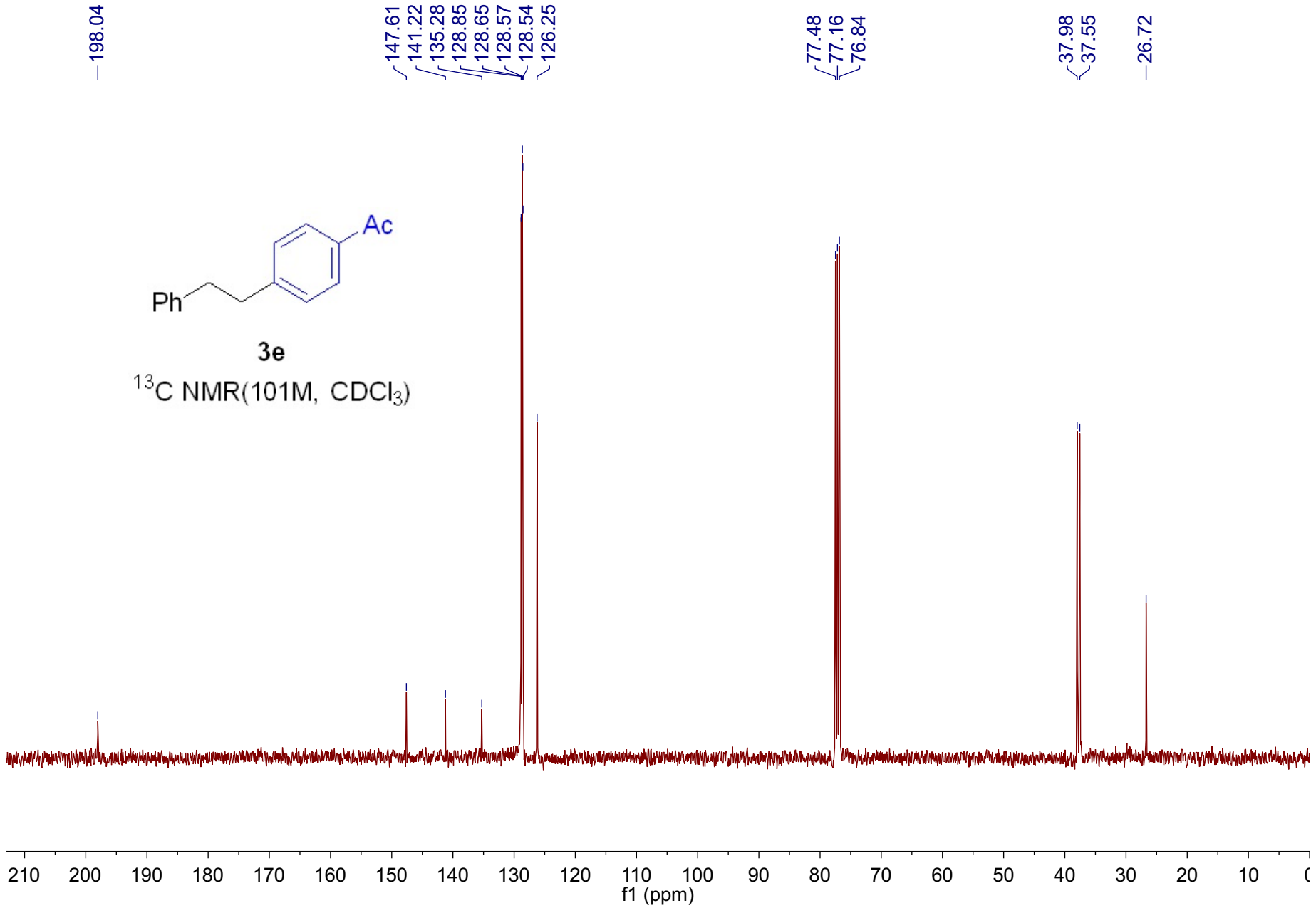
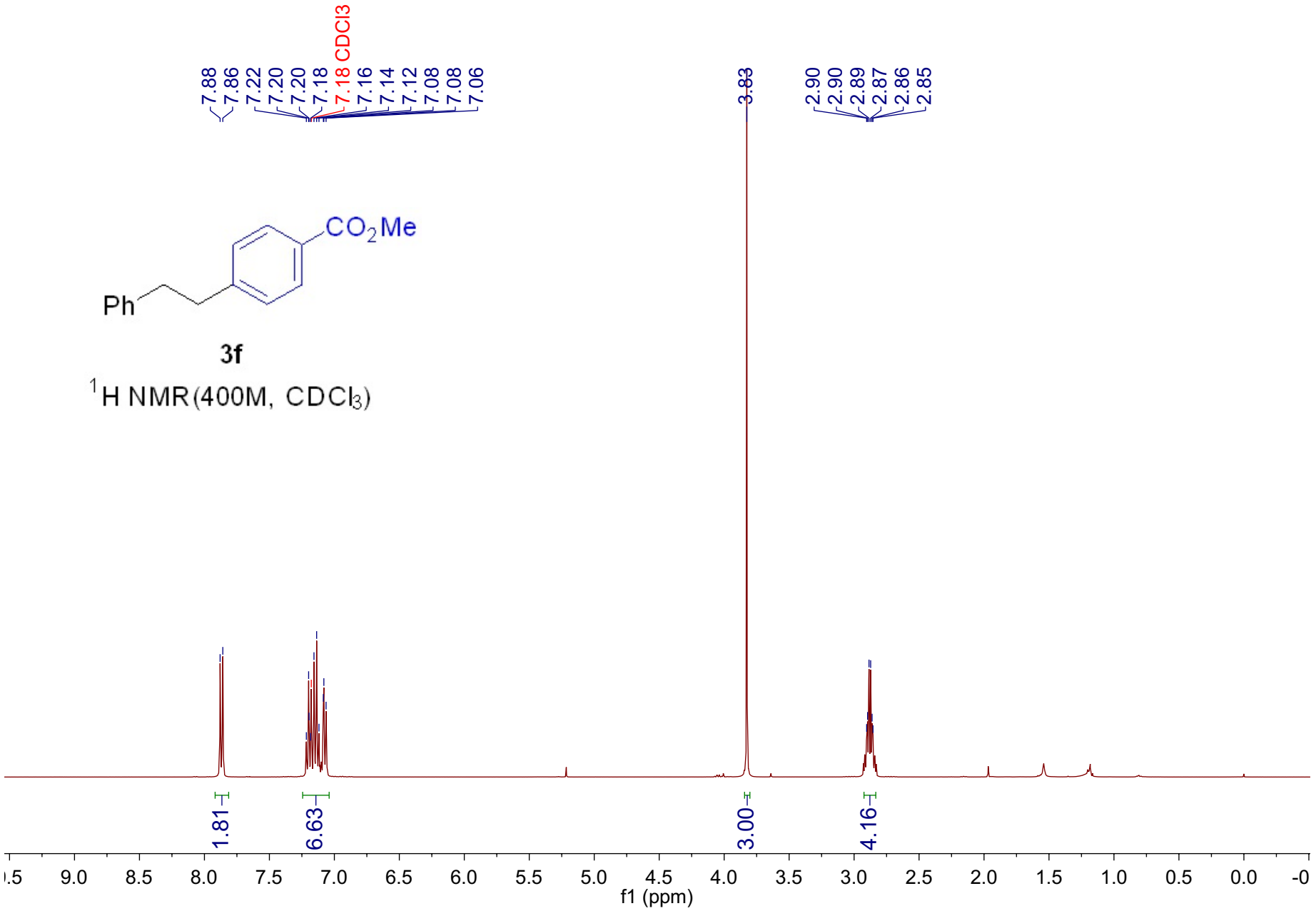
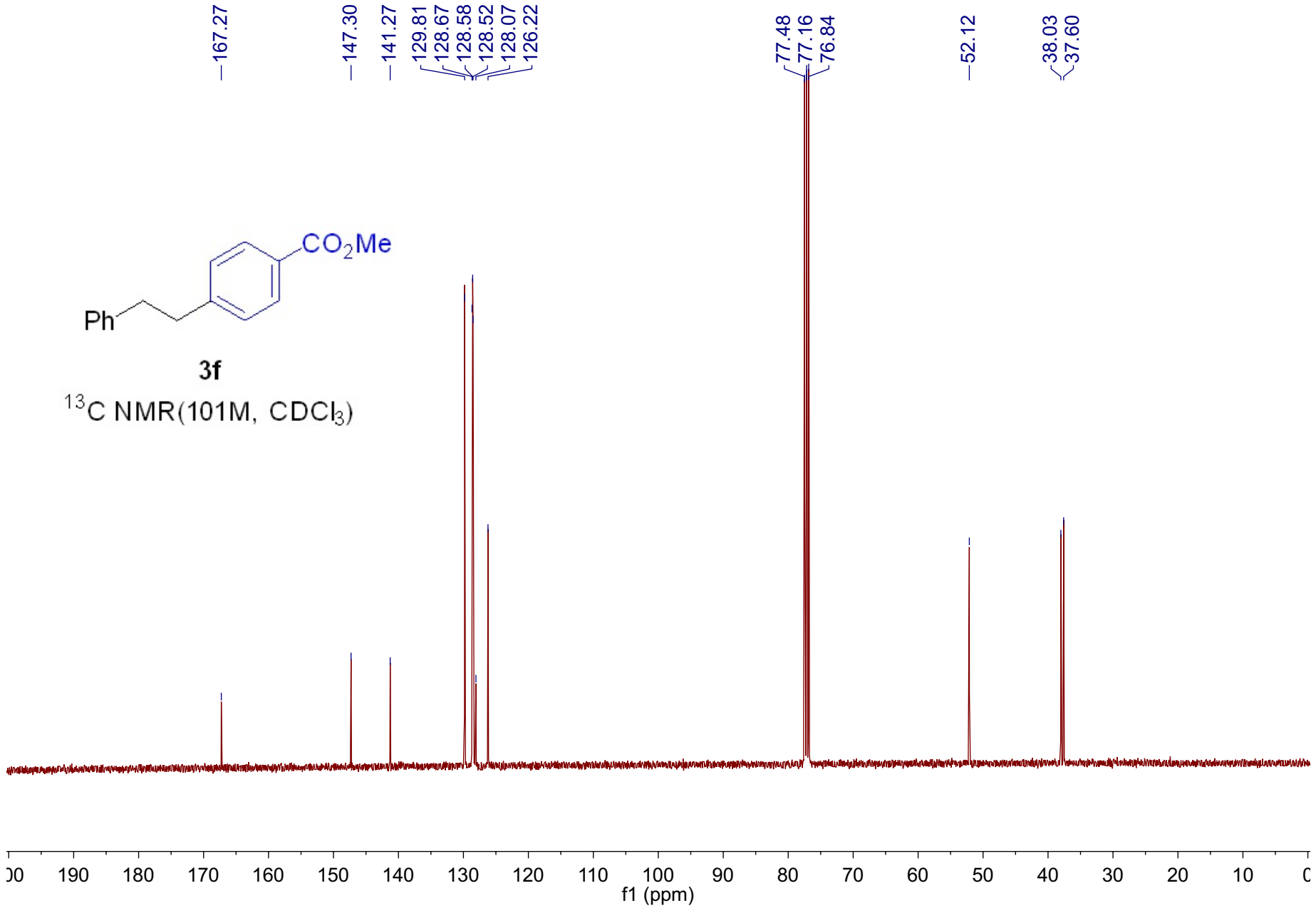
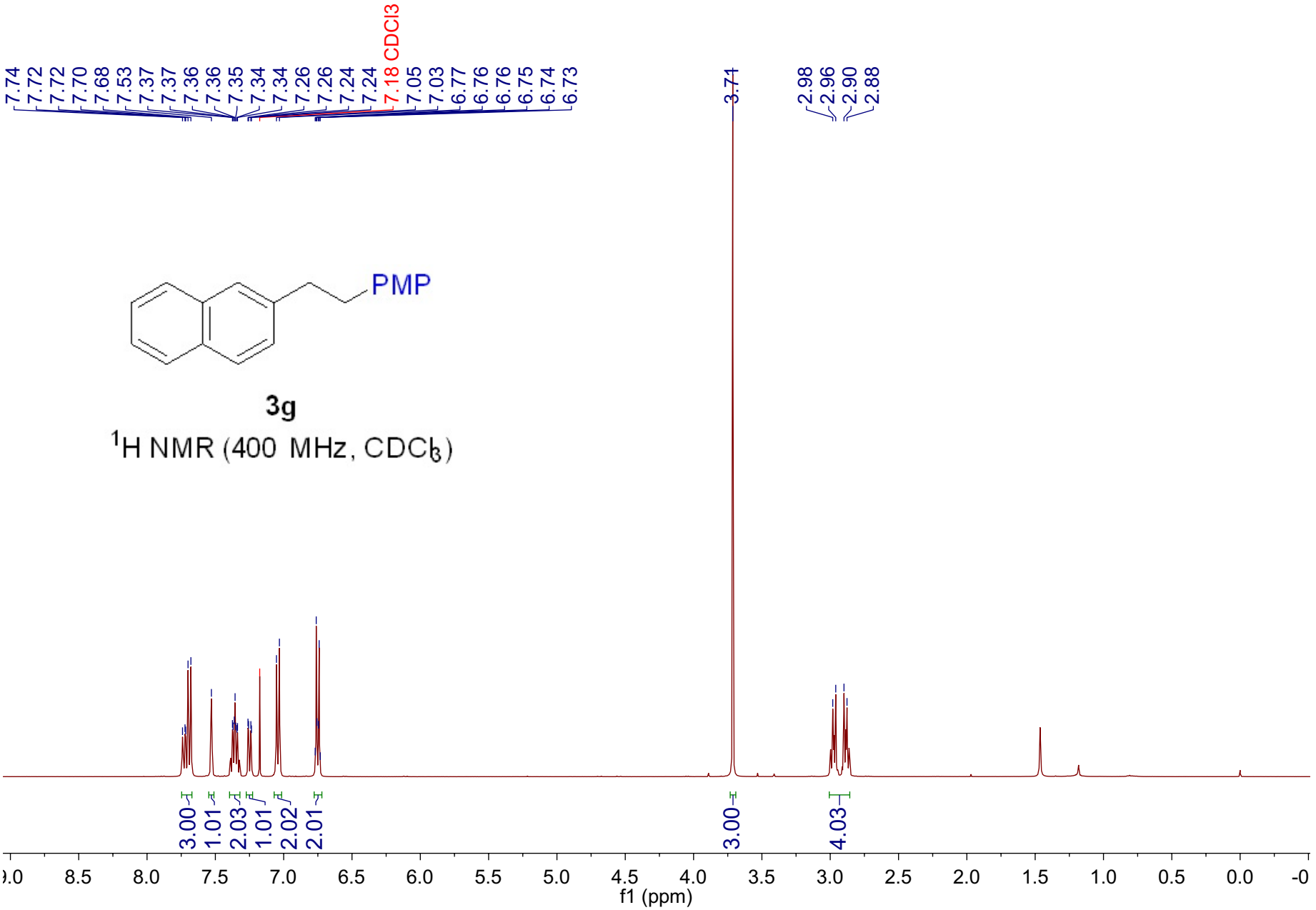
7.79
7.22
7.21
7.21
7.19
7.18
7.16
7.13
7.09
7.07
2.91
2.91
2.90
2.88
2.87
2.86
2.51
Ac
Ph
3e
1H NMR(400M, CDCl3)
1.94
6.60
4.37
3.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


198.04
147.61
141.22
135.28
128.85
128.65
128.57
128.54
126.25
77.48
77.16
76.84
37.98
37.55
26.72
Ac
Ph
3e
13C NMR(101M, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

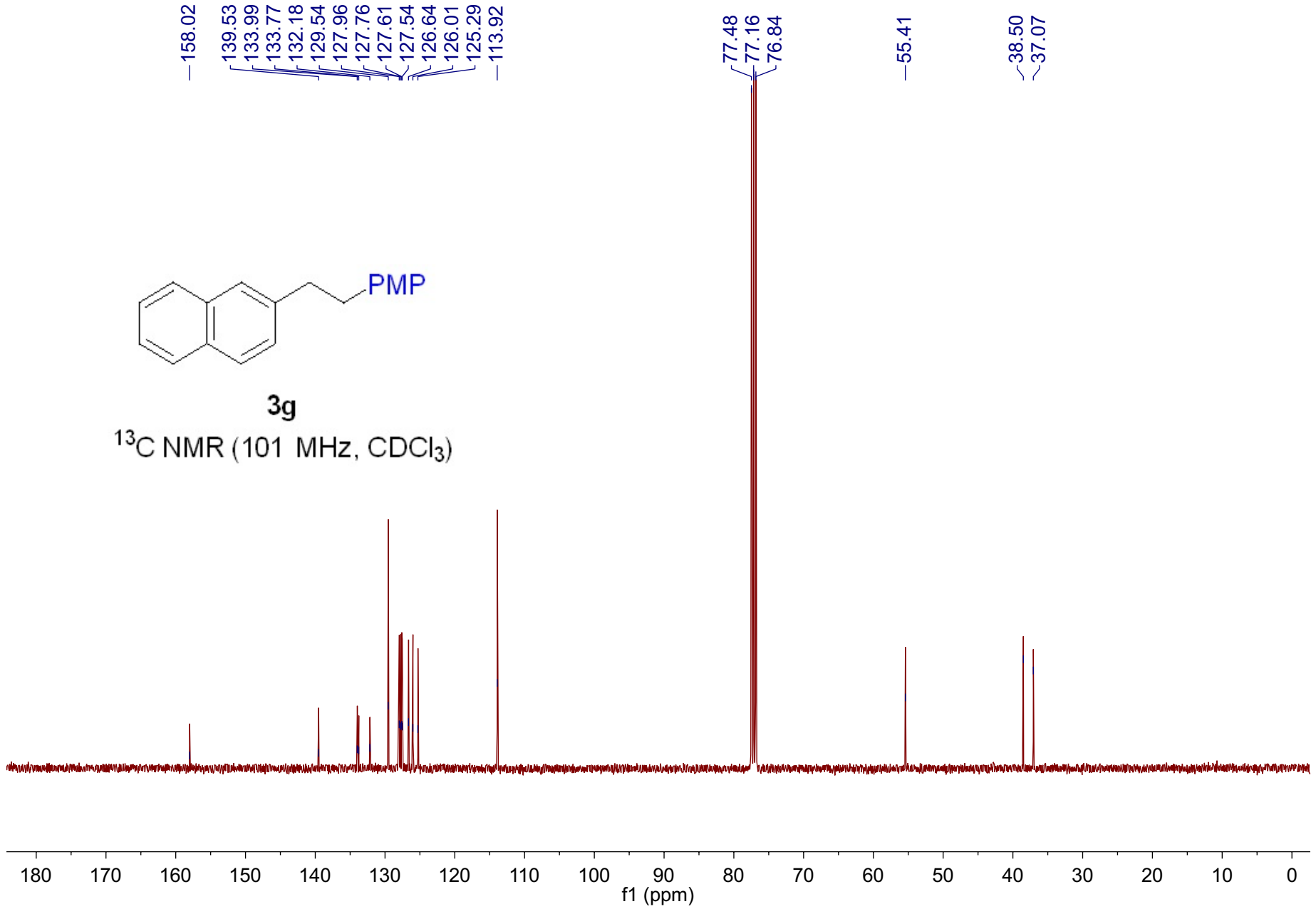

7.88
7.86
7.22
7.20
7.20
7.18
7.18 CDCl3
7.16
7.14
7.12
7.08
7.08
7.06
3.83
2.90
2.90
2.89
2.87
2.86
2.85
CO2Me
Ph
3f
1H NMR(400M, CDCl3)
1.81
6.63
3.00
4.16
f1 (ppm)

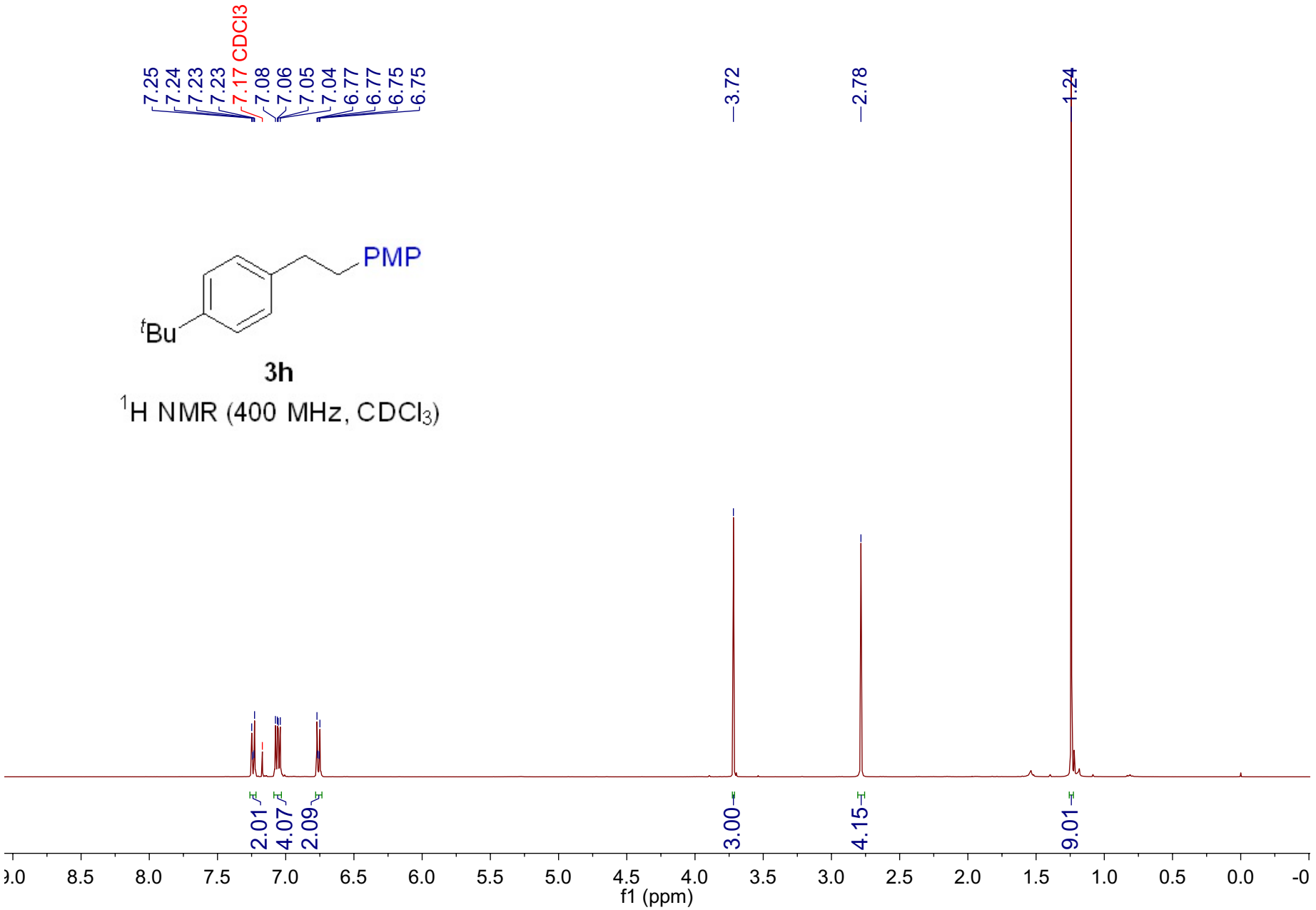

167.27
147.30
141.27
129.81
128.67
128.58
128.52
128.07
126.22
77.48
77.16
76.84
52.12
38.03
37.60
CO2Me
Ph
3f
13C NMR(101M, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

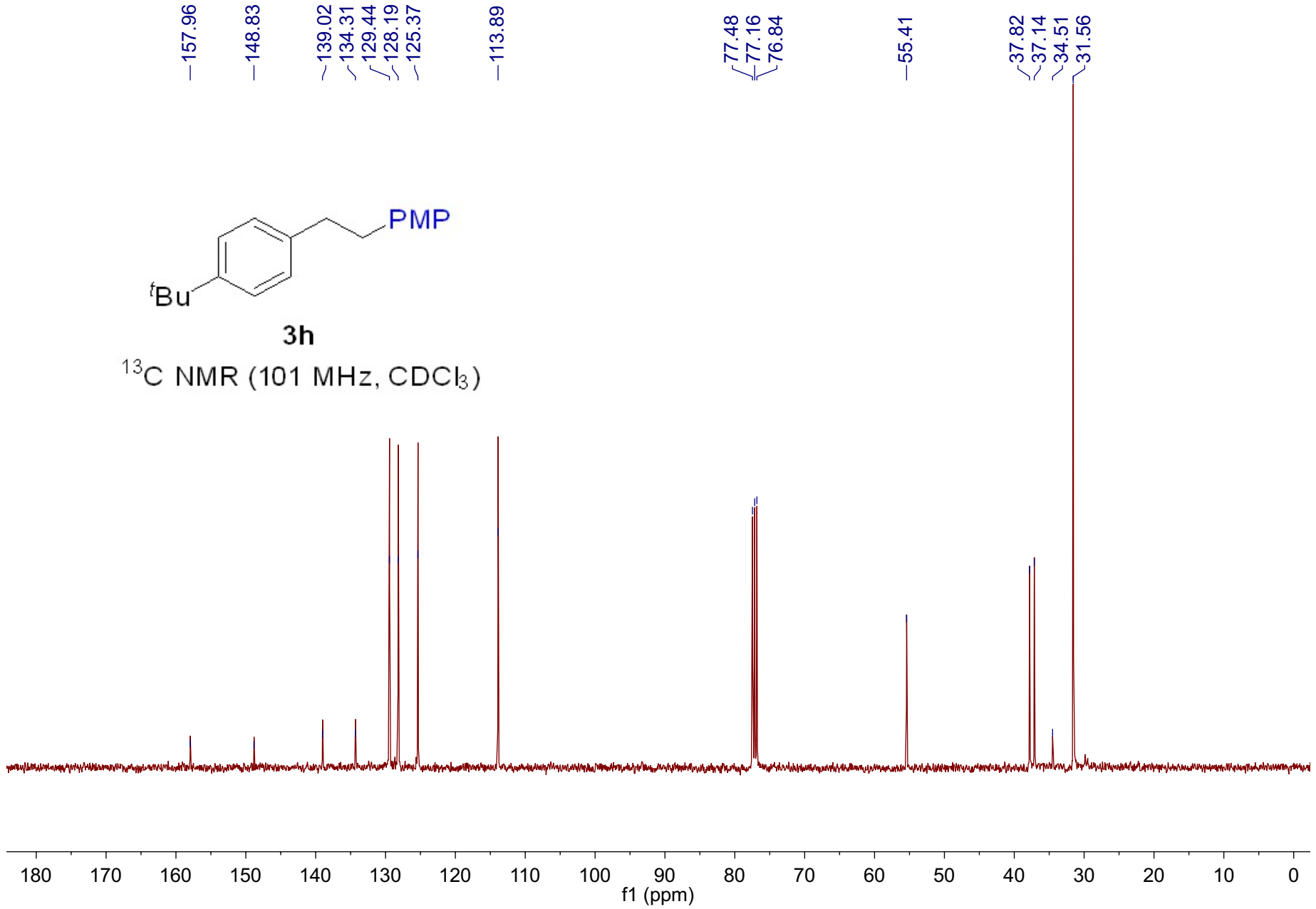


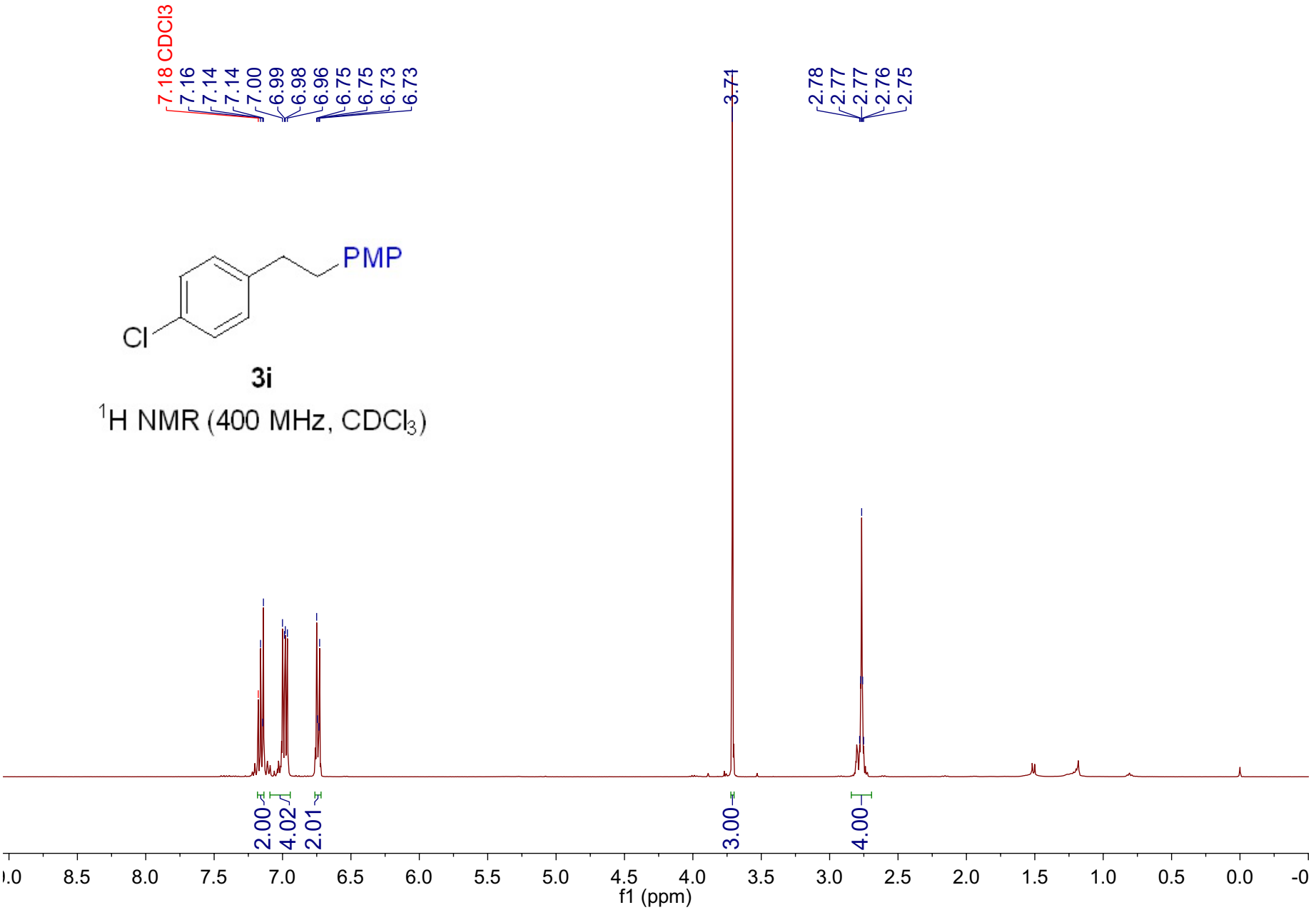
3g

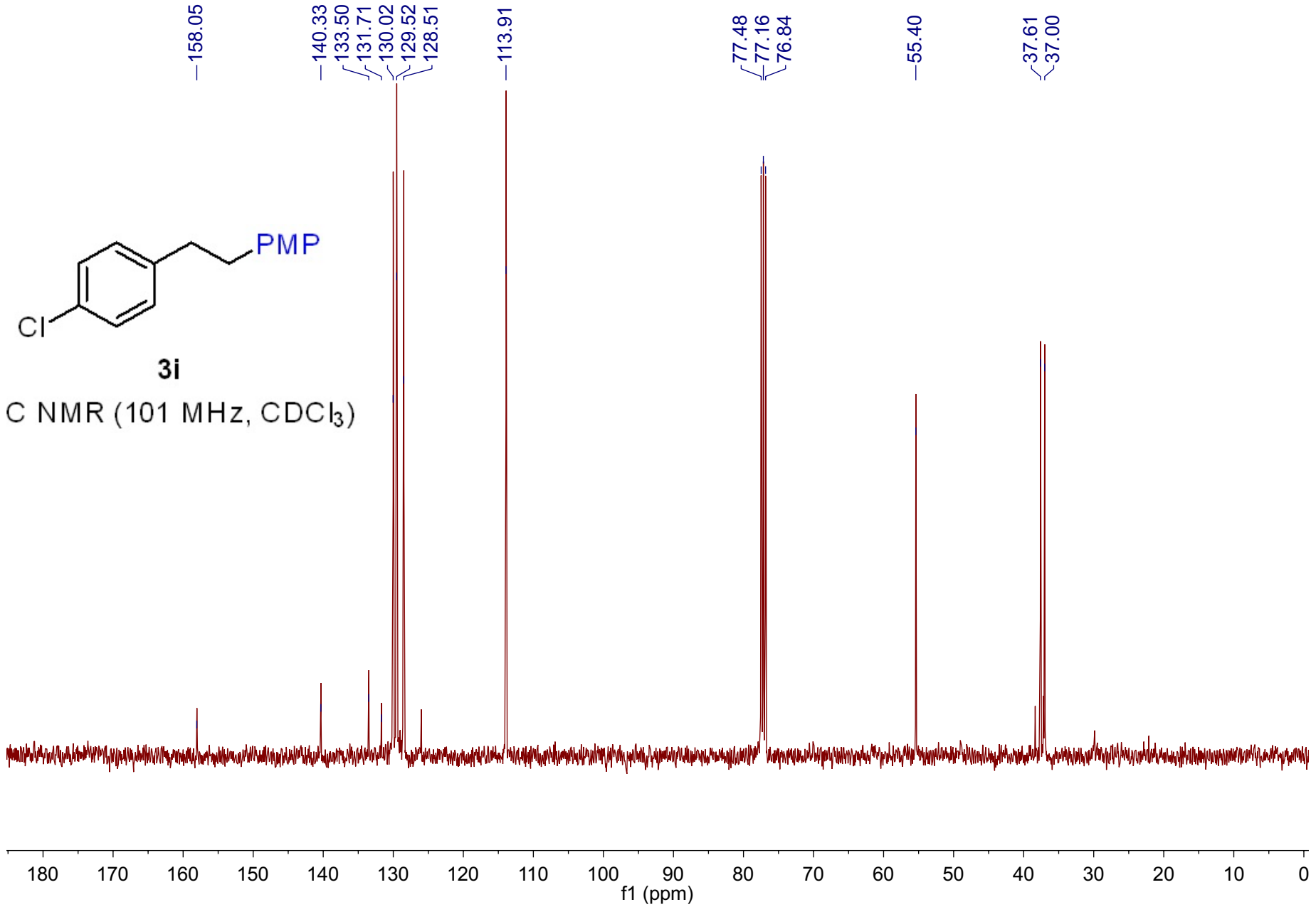
^{1}H NMR (400 MHz, $CDCl_3$)

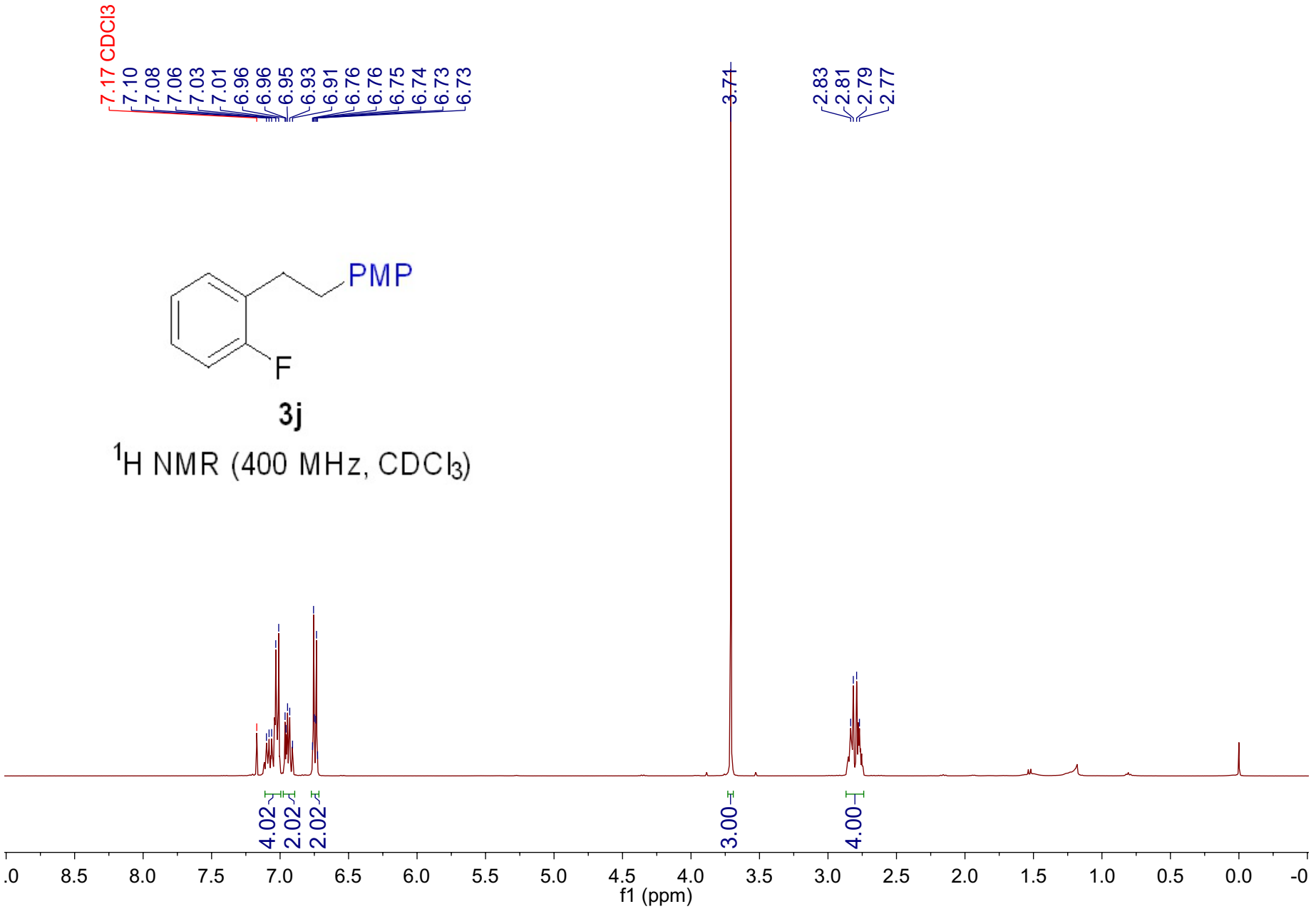

158.02
139.53
133.99
133.77
132.18
129.54
127.96
127.76
127.61
127.54
126.64
126.01
125.29
113.92
77.48
77.16
76.84
55.41
38.50
37.07
PMP
3g
13C NMR (101 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

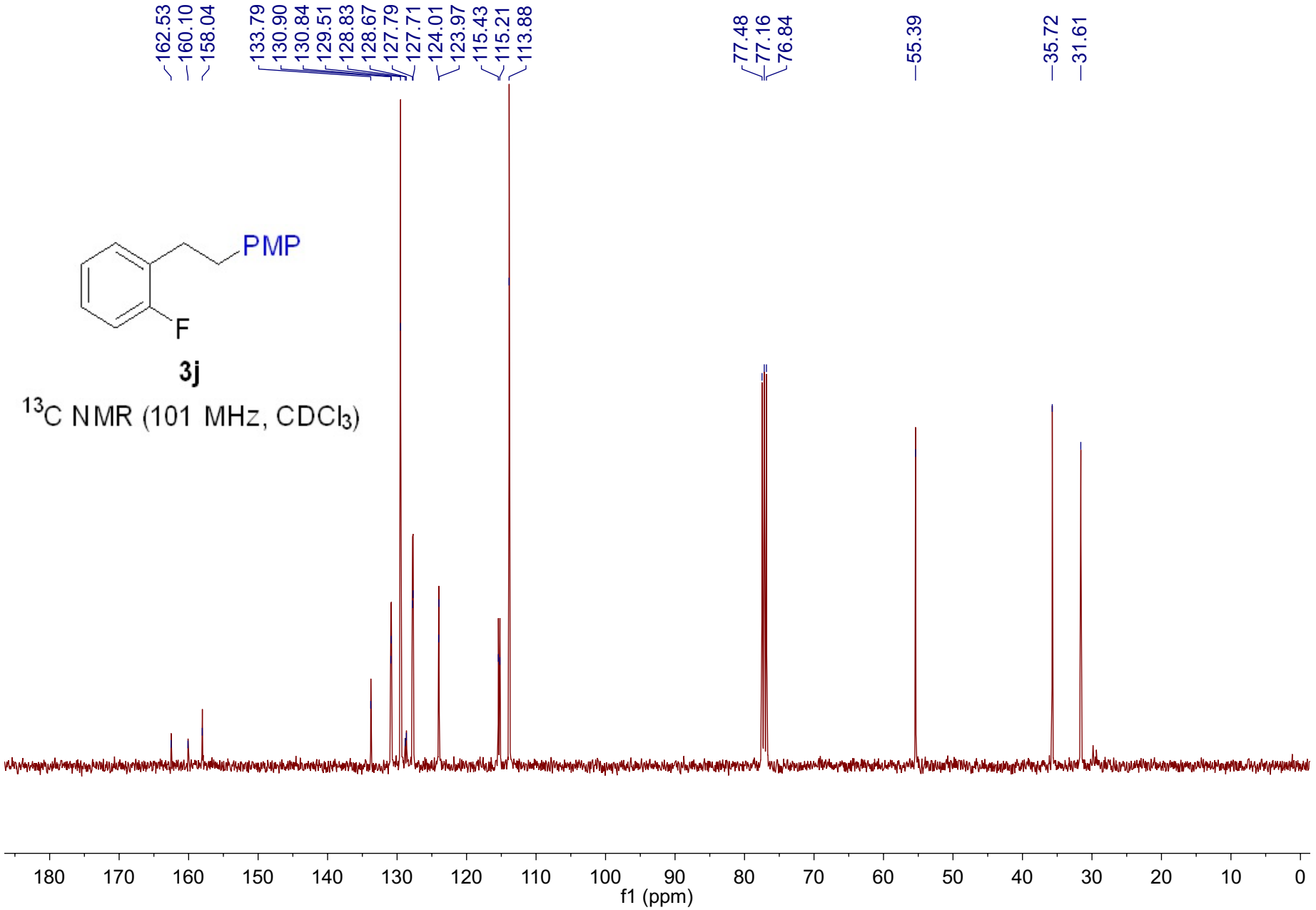

7.25
7.24
7.23
7.23
7.17 CDCl3
7.08
7.06
7.05
7.04
6.77
6.77
6.75
6.75
3.72
2.78
1.24
PMP
tBu
3h
1H NMR (400 MHz, CDCl3)
2.01
4.07
2.09
3.00
4.15
9.01
f1 (ppm)

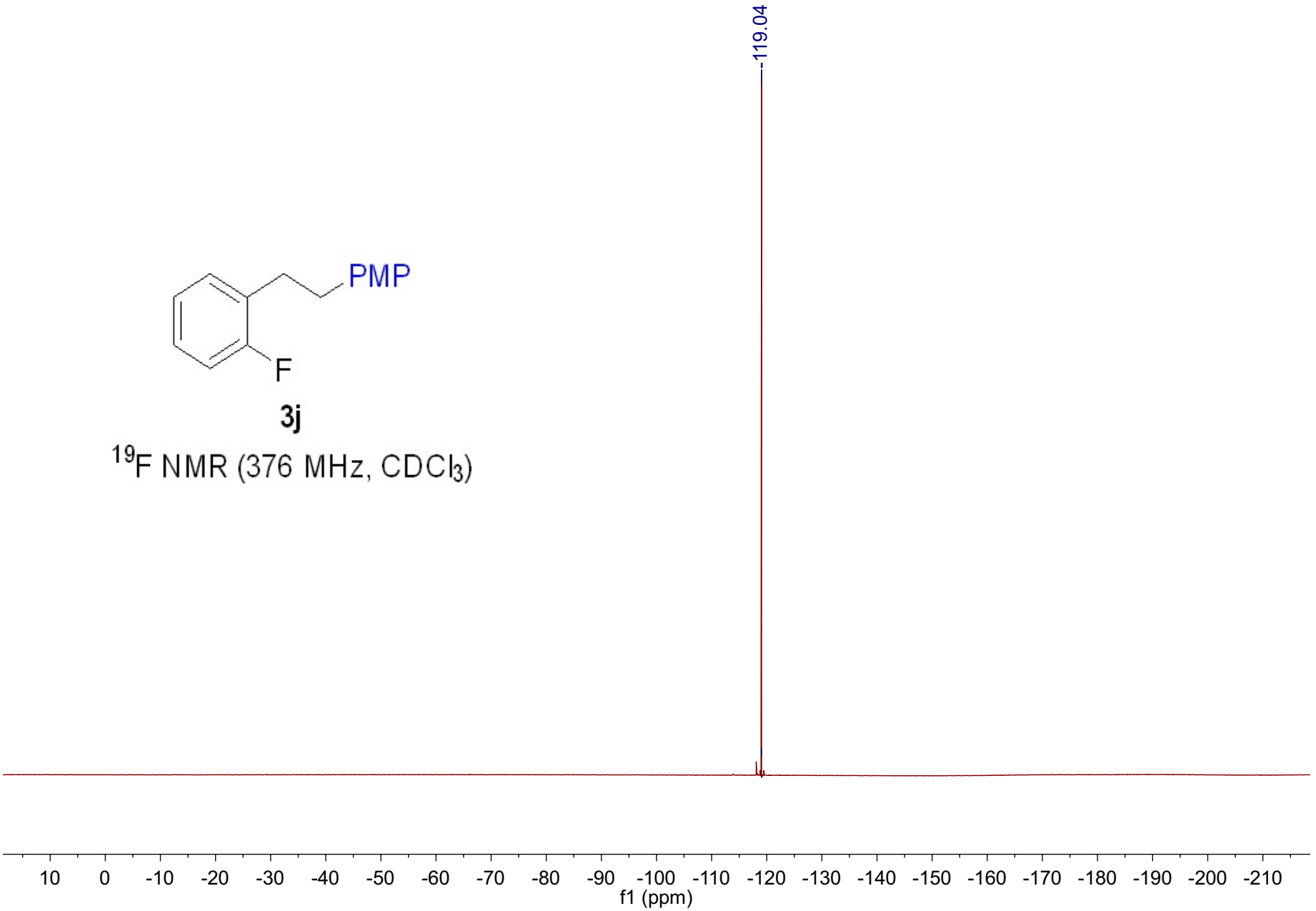

157.96
148.83
139.02
134.31
129.44
128.19
125.37
113.89
77.48
77.16
76.84
55.41
37.82
37.14
34.51
31.56
PMP
tBu
3h
13C NMR (101 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.18 CDCl3
7.16
7.14
7.14
7.00
6.99
6.98
6.96
6.75
6.75
6.73
6.73
3.74
2.78
2.77
2.77
2.76
2.75
PMP
Cl
3i
1H NMR (400 MHz, CDCl3)
2.00
4.02
2.01
3.00
4.00
f1 (ppm)


158.05
140.33
133.50
131.71
130.02
129.52
128.51
113.91
77.48
77.16
76.84
55.40
37.61
37.00
PMP
Cl
3i
C NMR (101 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

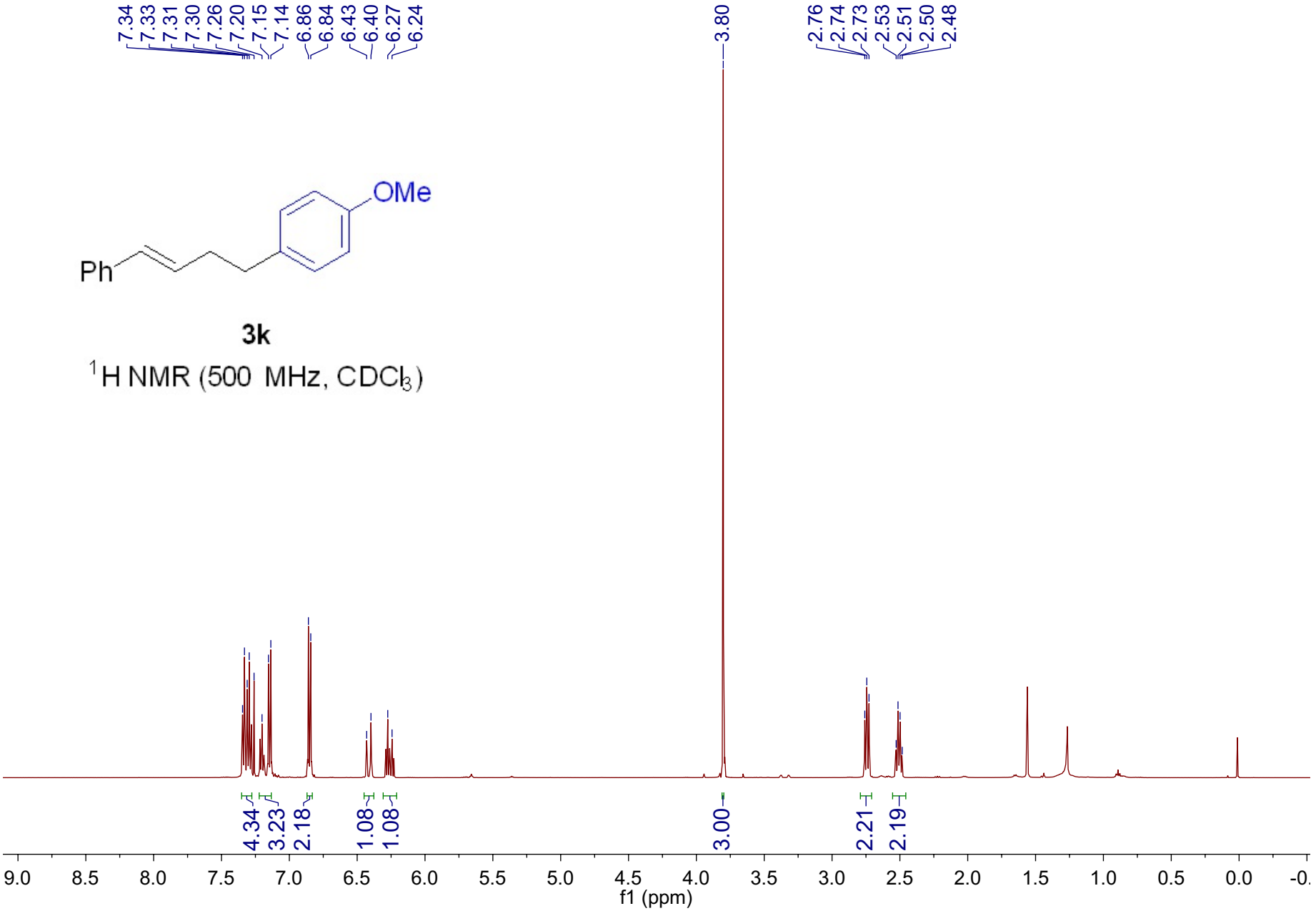

7.17 CDCl3
7.10
7.08
7.06
7.03
7.01
6.96
6.96
6.95
6.93
6.91
6.76
6.76
6.75
6.74
6.73
6.73
3.74
2.83
2.81
2.79
2.77
PMP
F
3j
1H NMR (400 MHz, CDCl3)
4.02
2.02
2.02
3.00
4.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

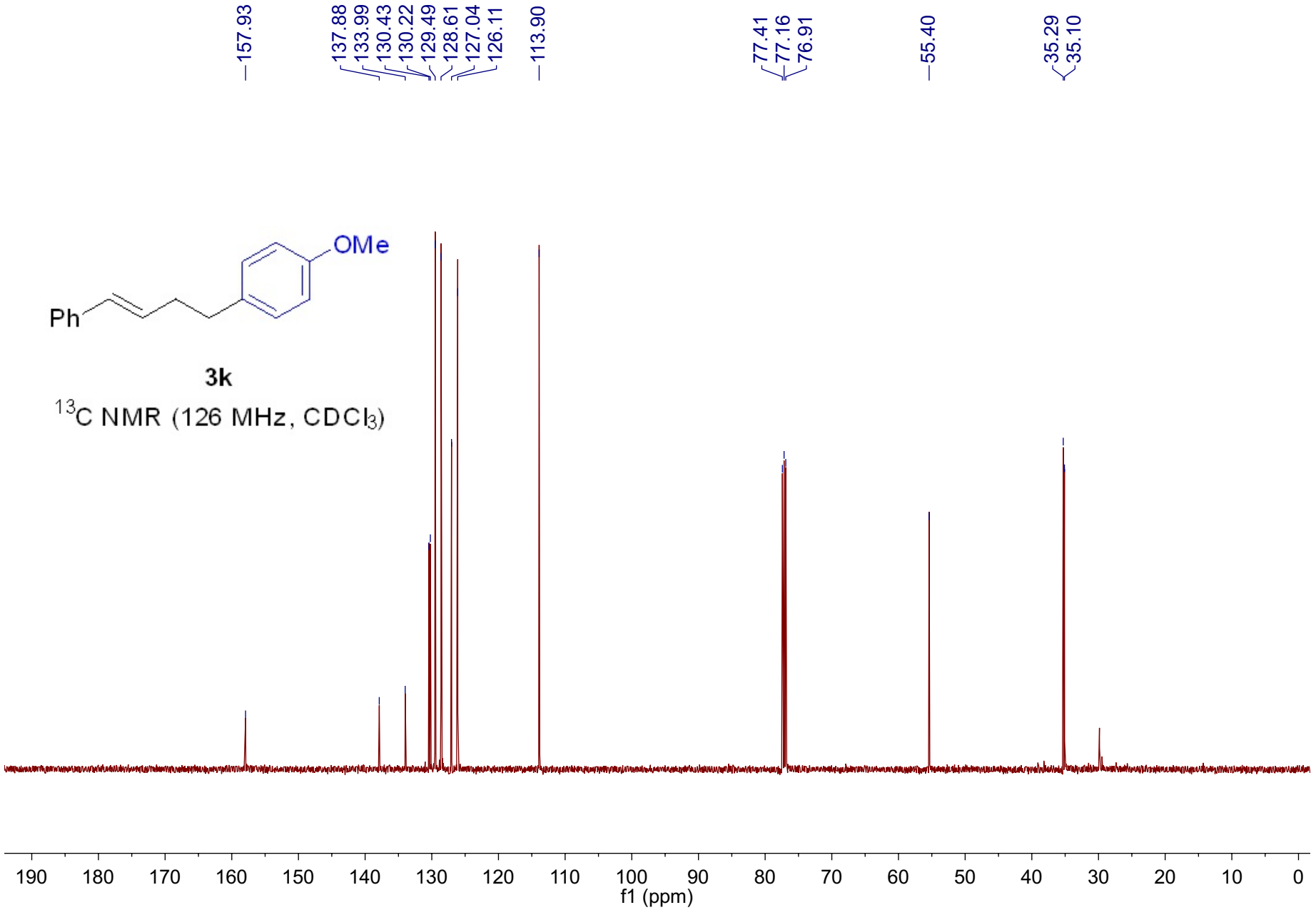

162.53
160.10
158.04
133.79
130.90
130.84
129.51
128.83
128.67
127.79
127.71
124.01
123.97
115.43
115.21
113.88
77.48
77.16
76.84
55.39
35.72
31.61
PMP
F
3j
13C NMR (101 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

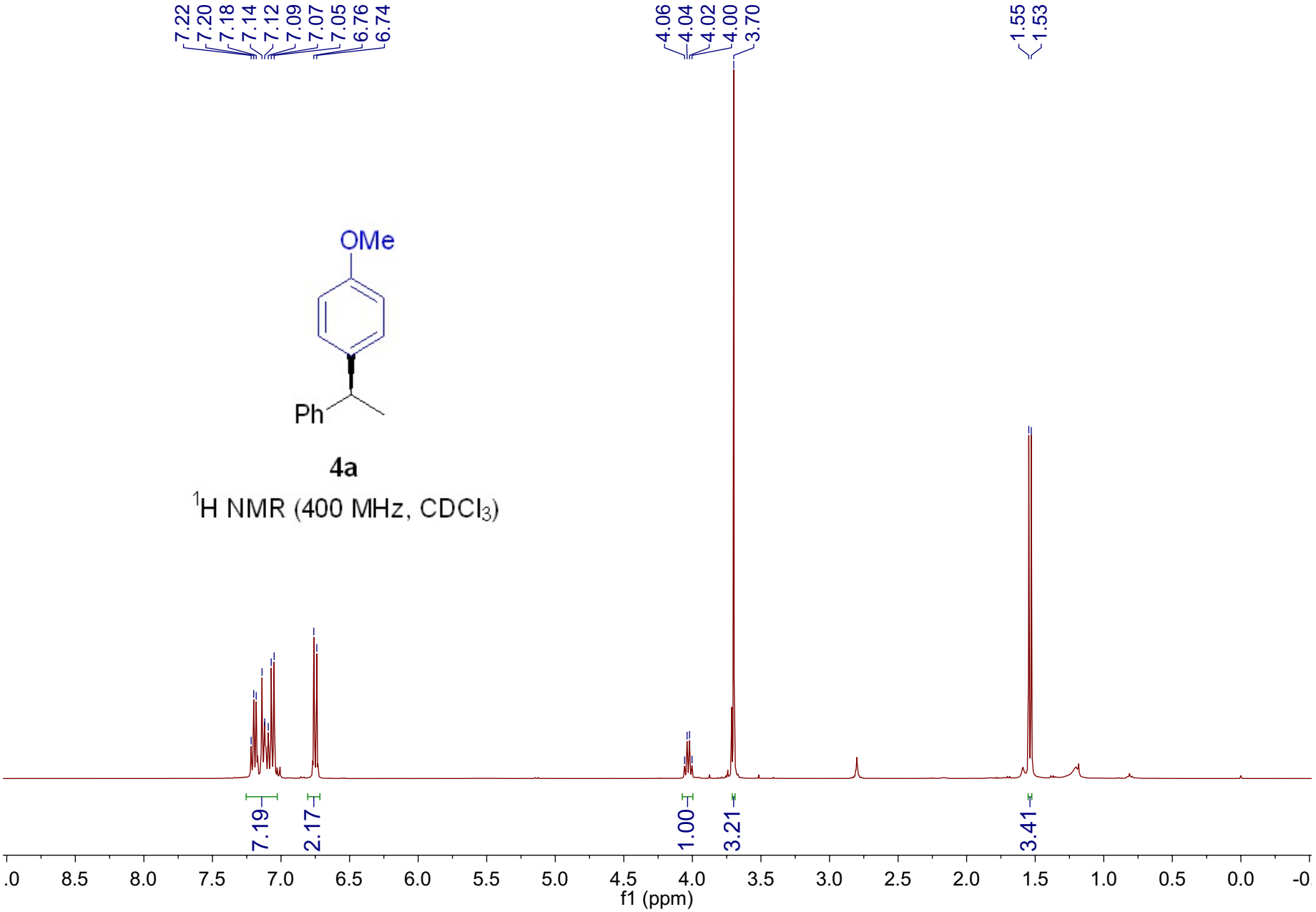


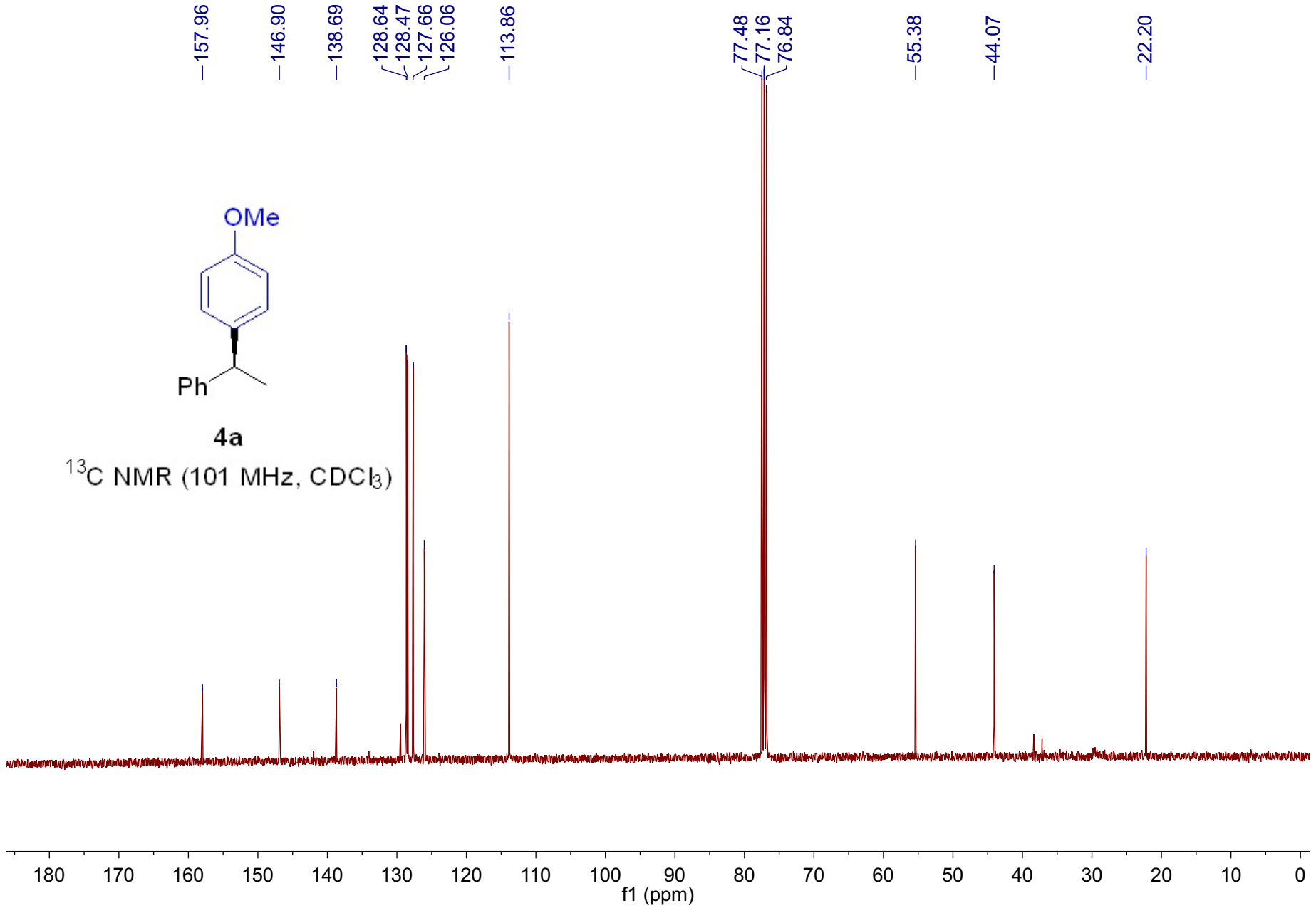
3j

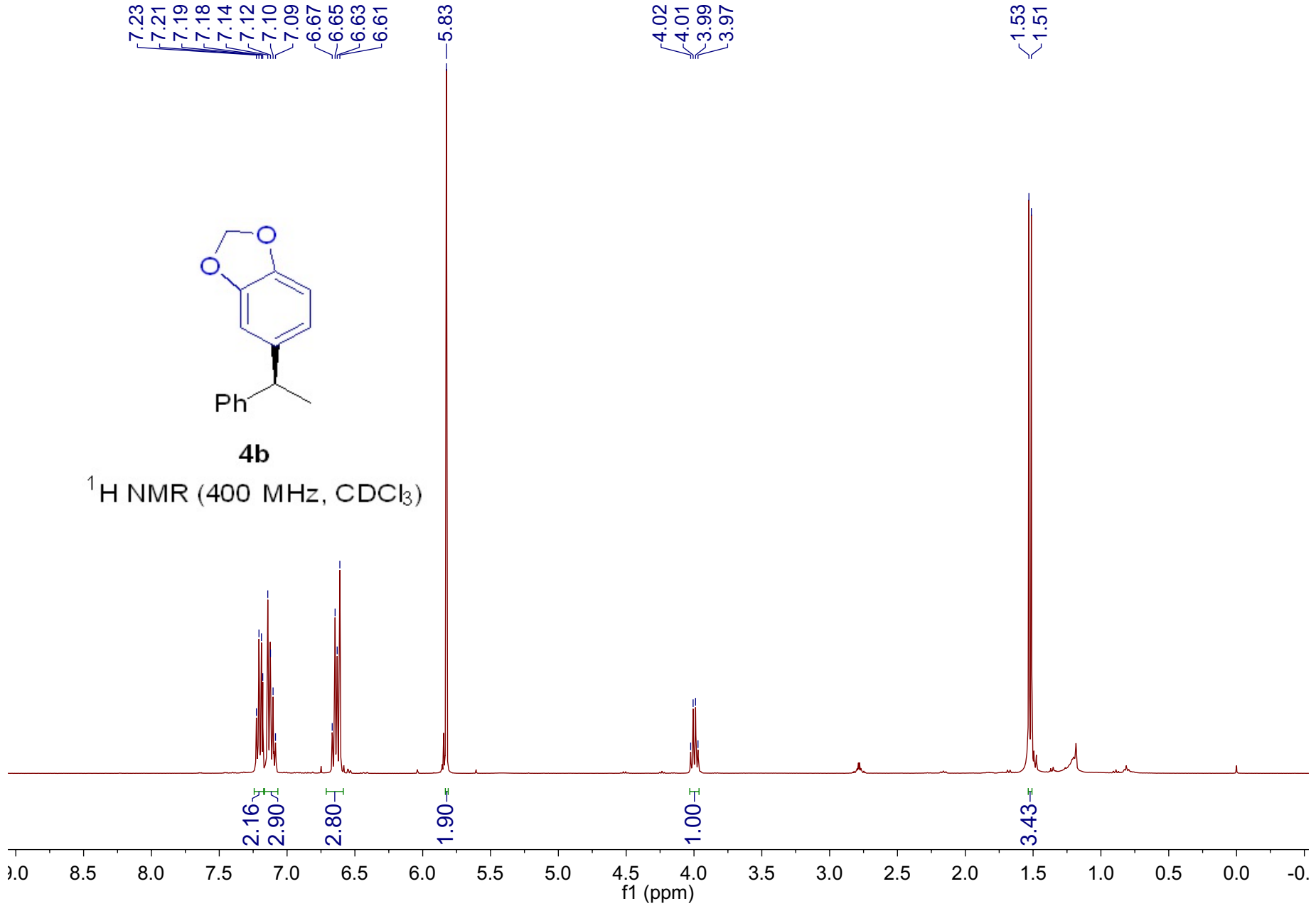
^{19}F NMR (376 MHz, $CDCl_3$)

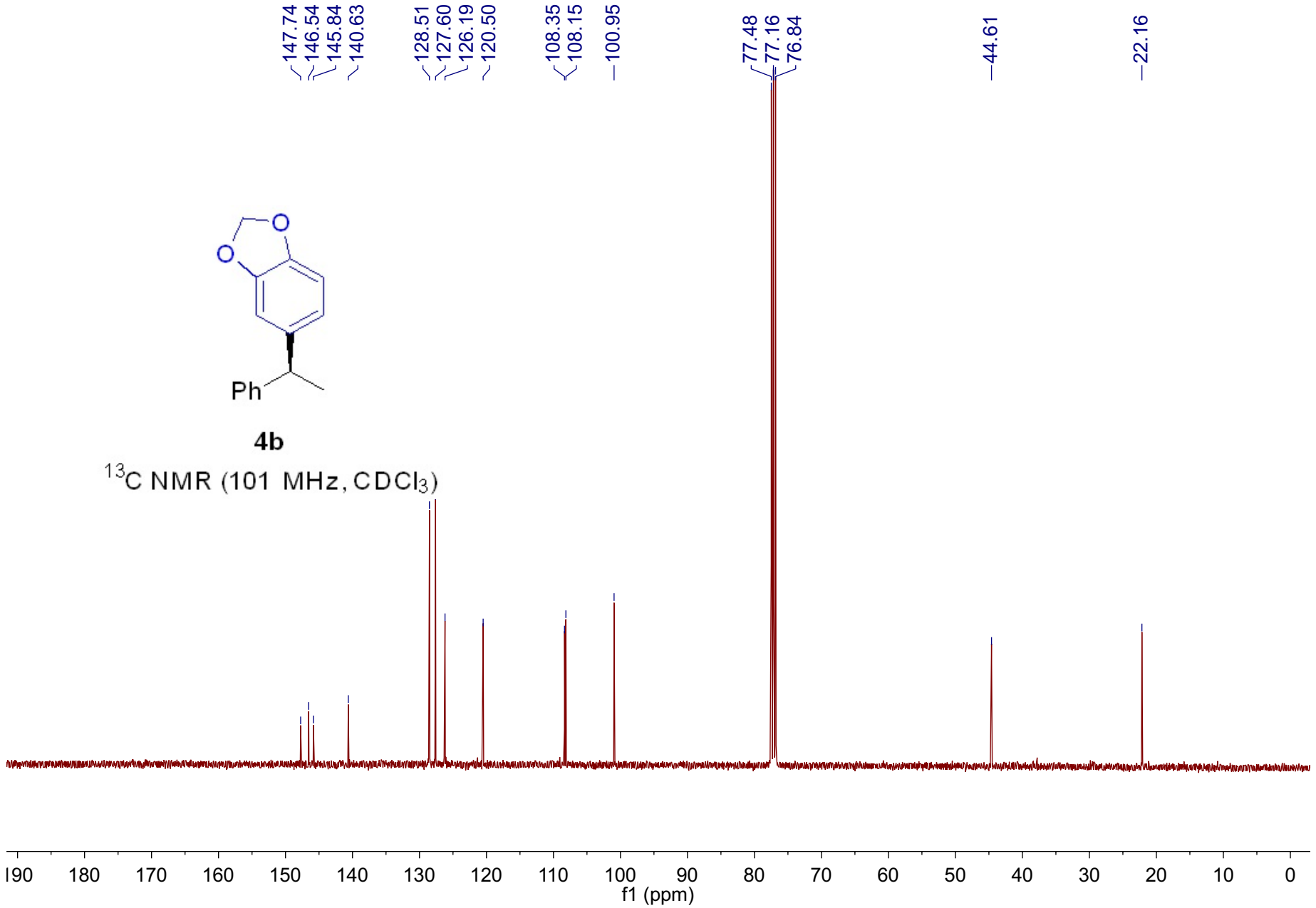

7.34
7.33
7.31
7.30
7.26
7.20
7.15
7.14
6.86
6.84
6.43
6.40
6.27
6.24
3.80
2.76
2.74
2.73
2.53
2.51
2.50
2.48
OMe
Ph
3k
1H NMR (500 MHz, CDCl3)
4.34
3.23
2.18
1.08
1.08
3.00
2.21
2.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

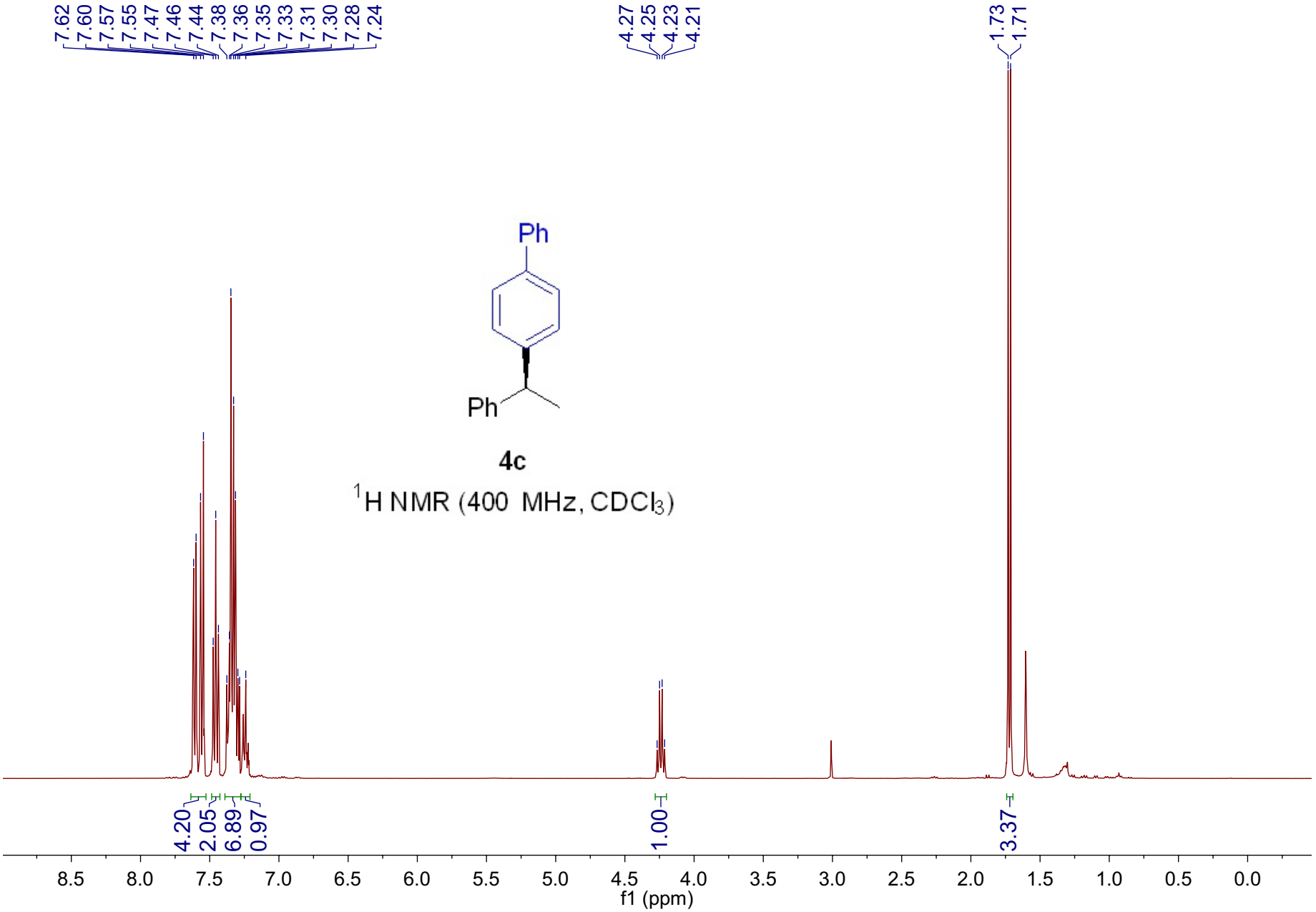

157.93
137.88
133.99
130.43
130.22
129.49
128.61
127.04
126.11
113.90
77.41
77.16
76.91
55.40
35.29
35.10
OMe
Ph
3k
13C NMR (126 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

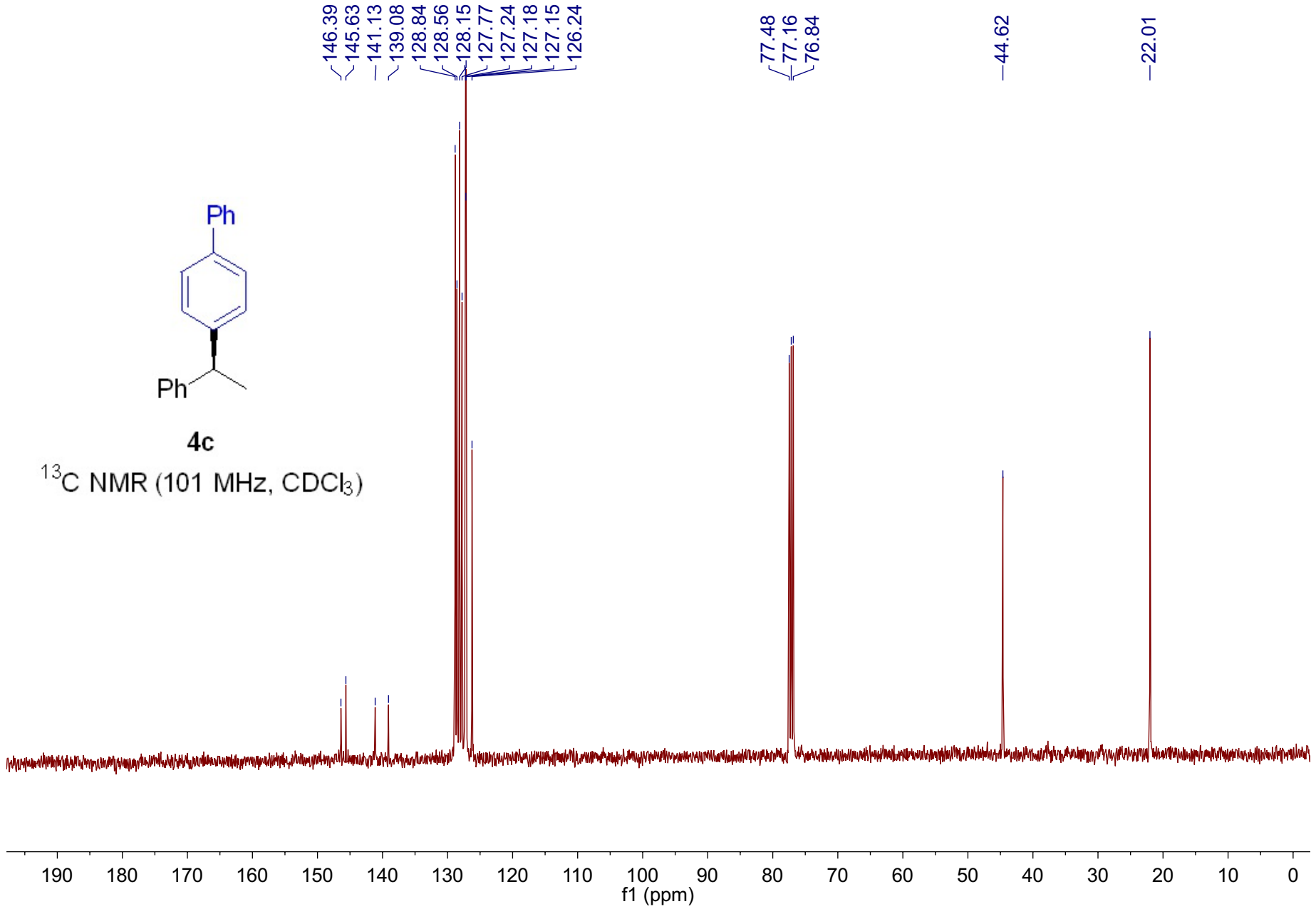

7.22
7.20
7.18
7.14
7.12
7.09
7.07
7.05
6.76
6.74
4.06
4.04
4.02
4.00
3.70
1.55
1.53
OMe
Ph
4a
1H NMR (400 MHz, CDCl3)
7.19
2.17
1.00
3.21
3.41
f1 (ppm)

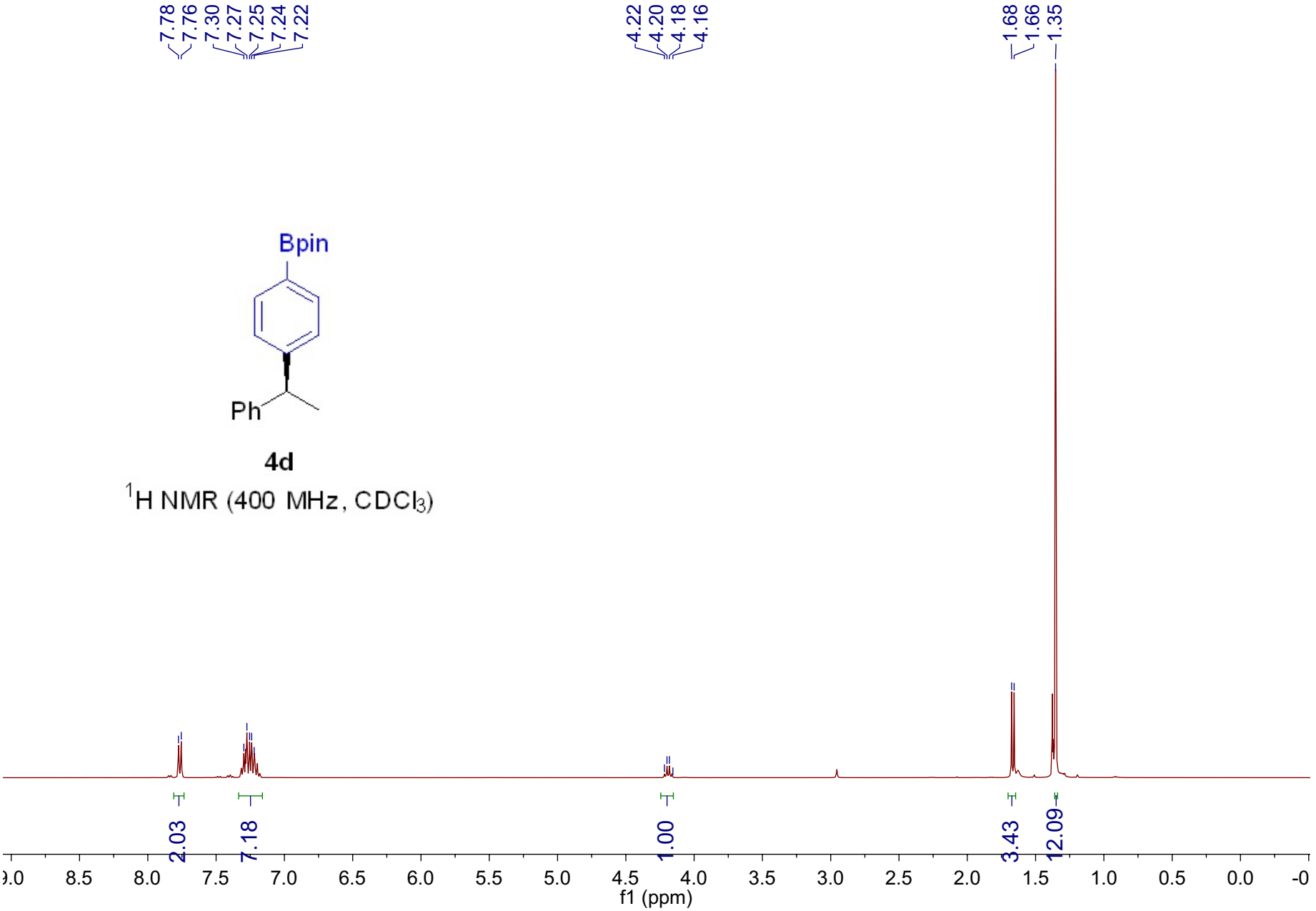

157.96
146.90
138.69
128.64
128.47
127.66
126.06
113.86
77.48
77.16
76.84
55.38
44.07
22.20
OMe
Ph
4a
13C NMR (101 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

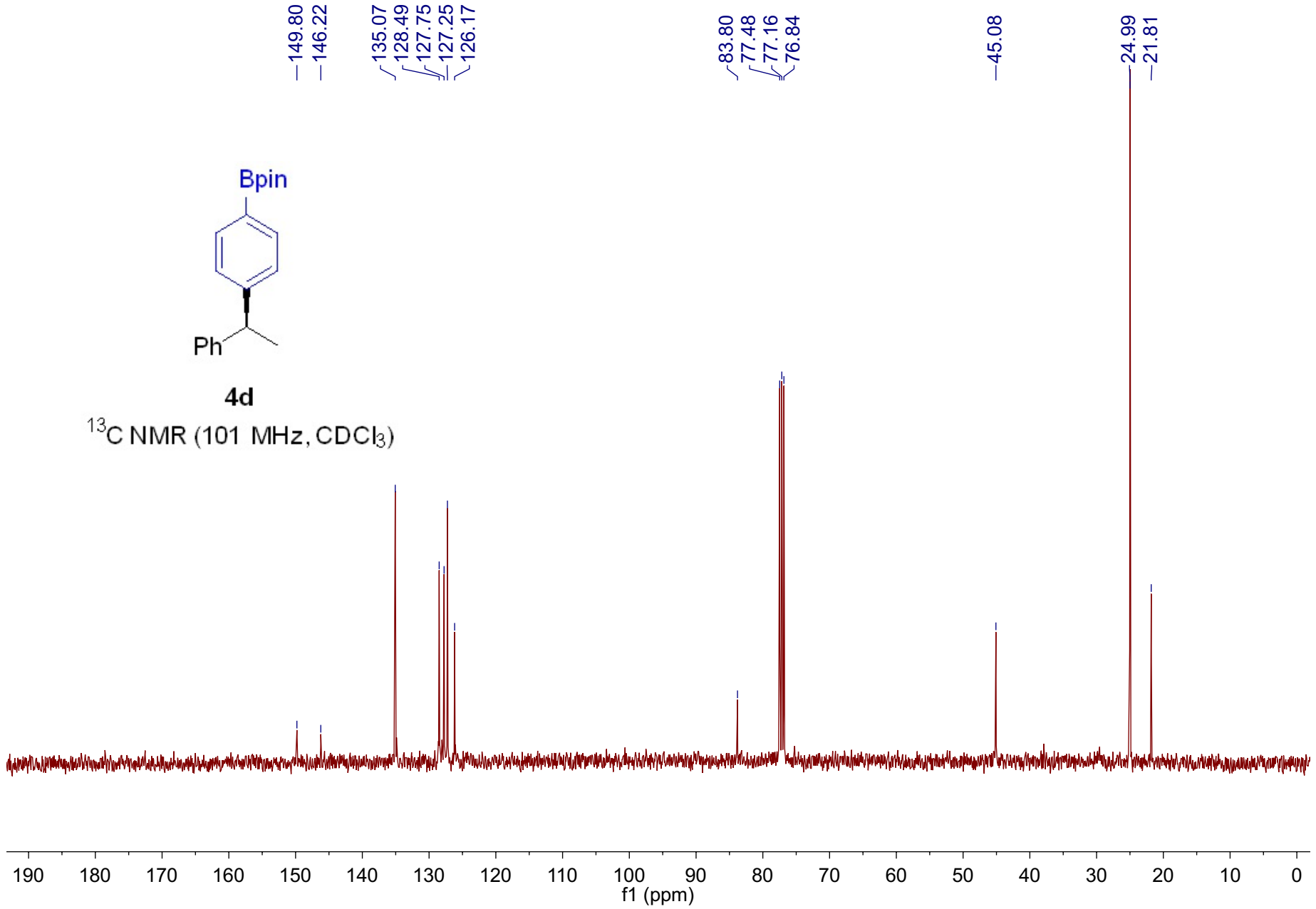

7.23
7.21
7.19
7.18
7.14
7.12
7.10
7.09
6.67
6.65
6.63
6.61
5.83
4.02
4.01
3.99
3.97
1.53
1.51
Ph
4b
1H NMR (400 MHz, CDCl3)
2.16
2.90
2.80
1.90
1.00
3.43
f1 (ppm)

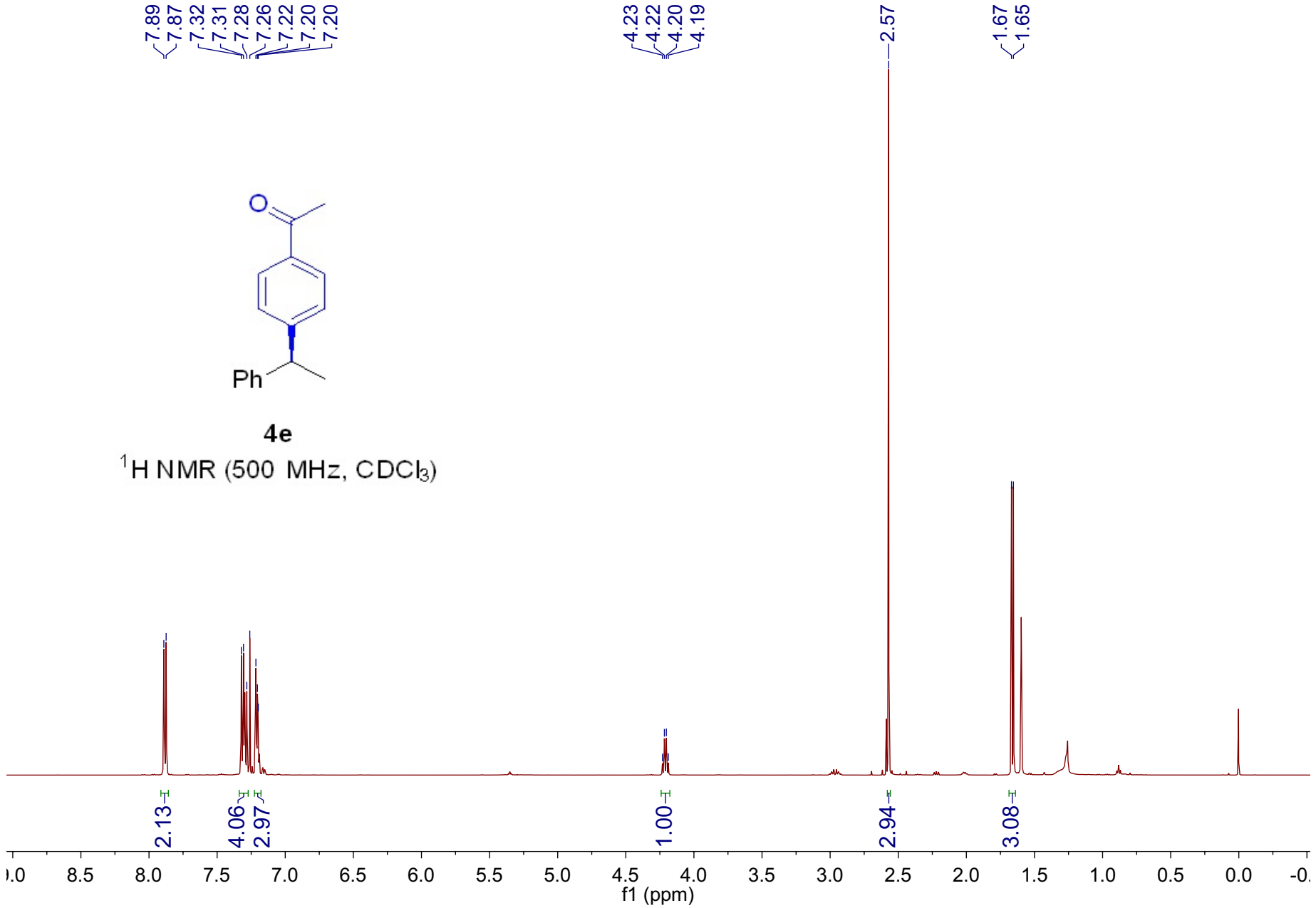

147.74
146.54
145.84
140.63
128.51
127.60
126.19
120.50
108.35
108.15
100.95
77.48
77.16
76.84
44.61
22.16
O
O
Ph
4b
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

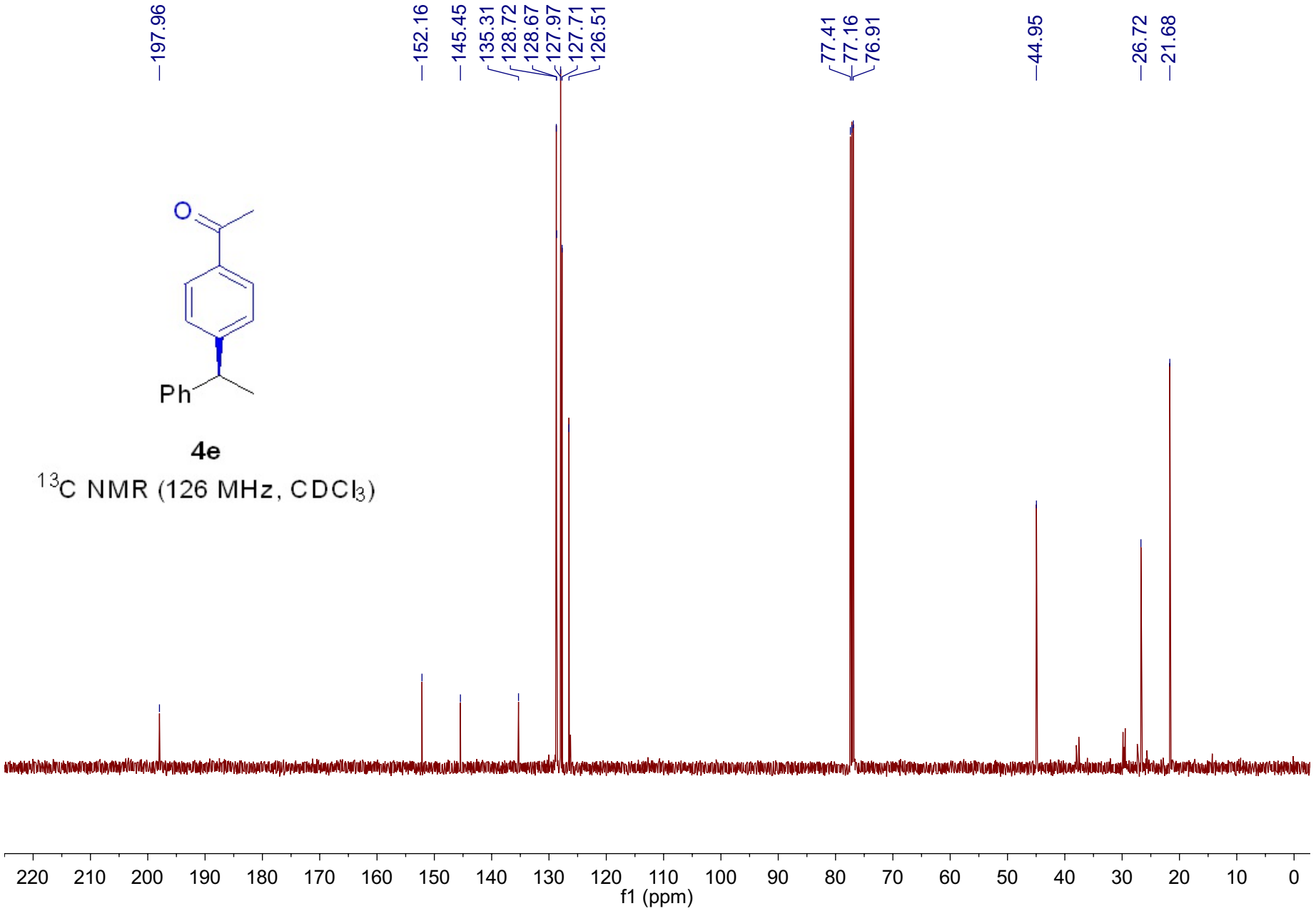

7.62
7.60
7.57
7.55
7.47
7.46
7.44
7.38
7.36
7.35
7.33
7.31
7.30
7.28
7.24
4.27
4.25
4.23
4.21
1.73
1.71
Ph
Ph
4c
1H NMR (400 MHz, CDCl3)
4.20
2.05
6.89
0.97
1.00
3.37
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

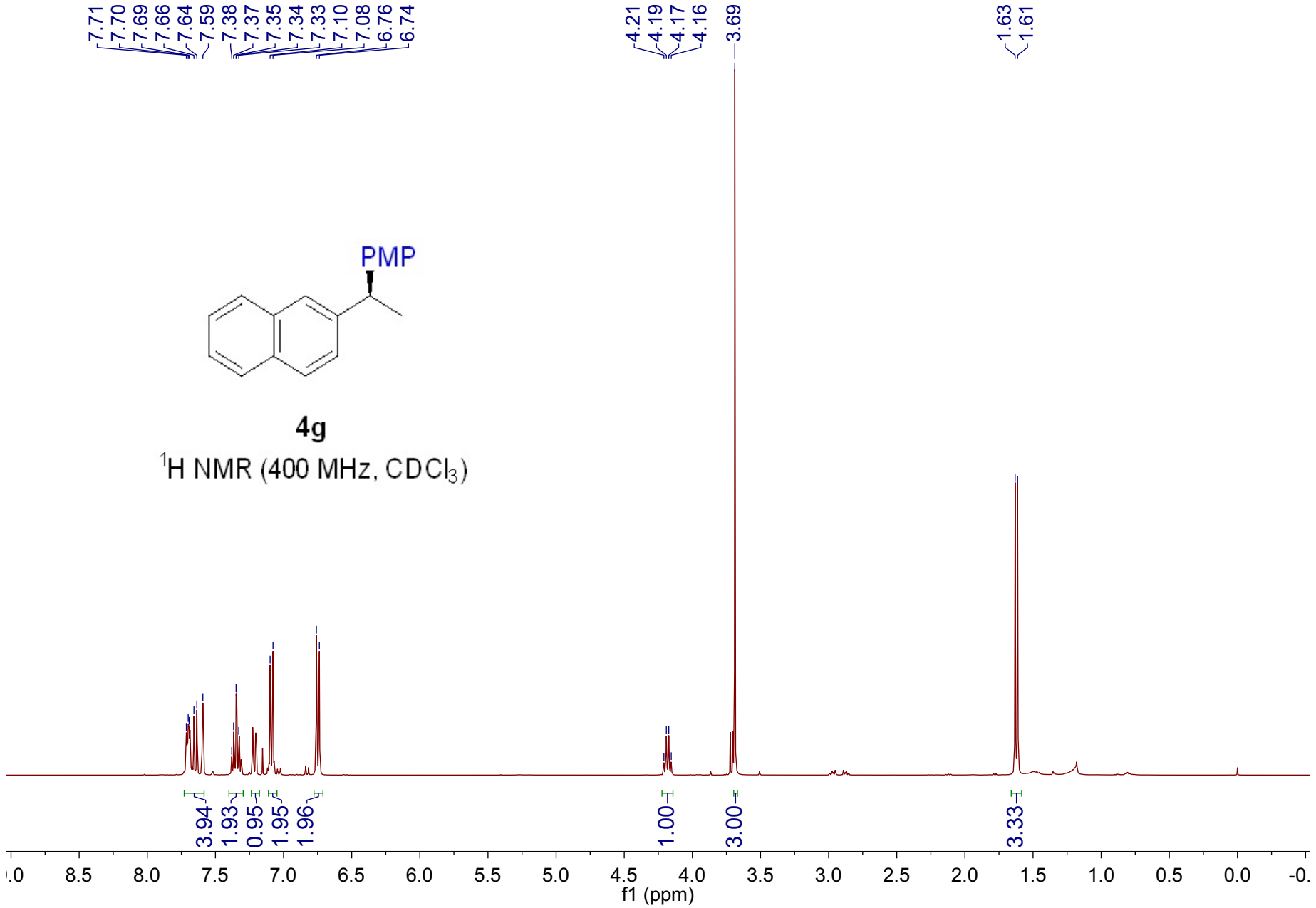

146.39
145.63
141.13
139.08
128.84
128.56
128.15
127.77
127.24
127.18
127.15
126.24
77.48
77.16
76.84
44.62
22.01
Ph
Ph
4c
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

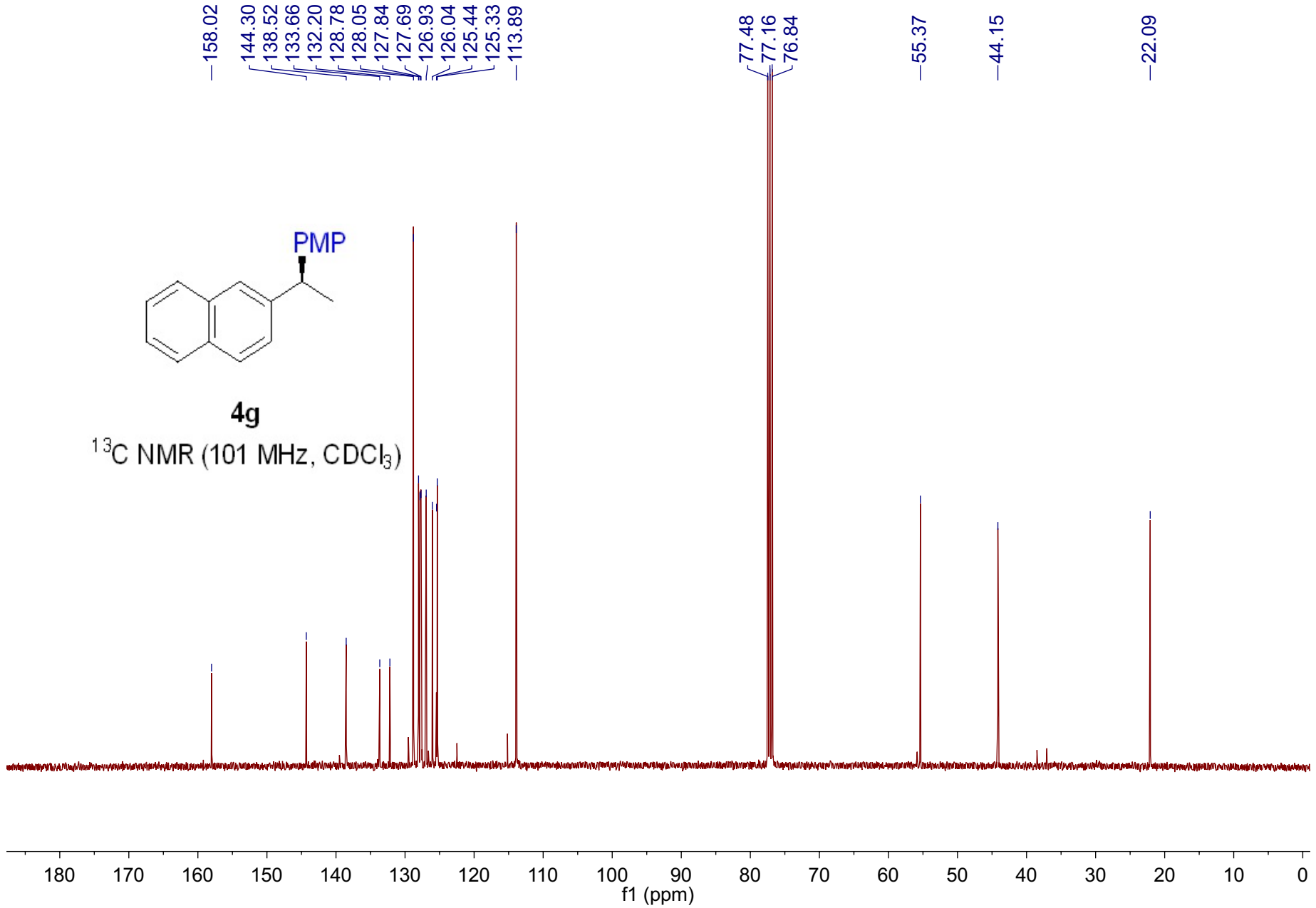

7.78
7.76
7.30
7.27
7.25
7.24
7.22
4.22
4.20
4.18
4.16
1.68
1.66
1.35
Bpin
Ph
4d
1H NMR (400 MHz, CDCl3)
2.03
7.18
1.00
3.43
12.09
f1 (ppm)

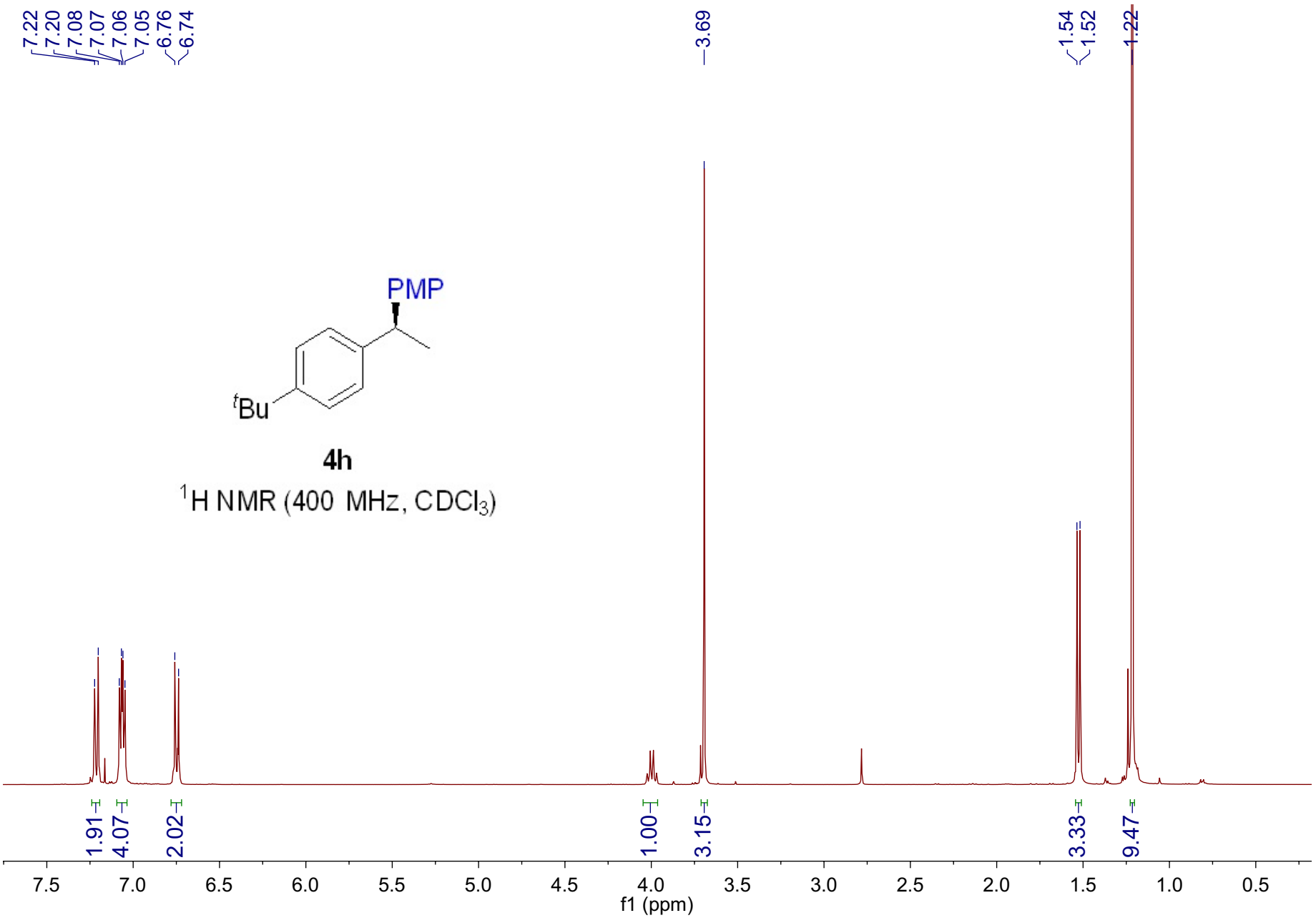

149.80
146.22
135.07
128.49
127.75
127.25
126.17
83.80
77.48
77.16
76.84
45.08
24.99
21.81
Bpin
Ph
4d
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

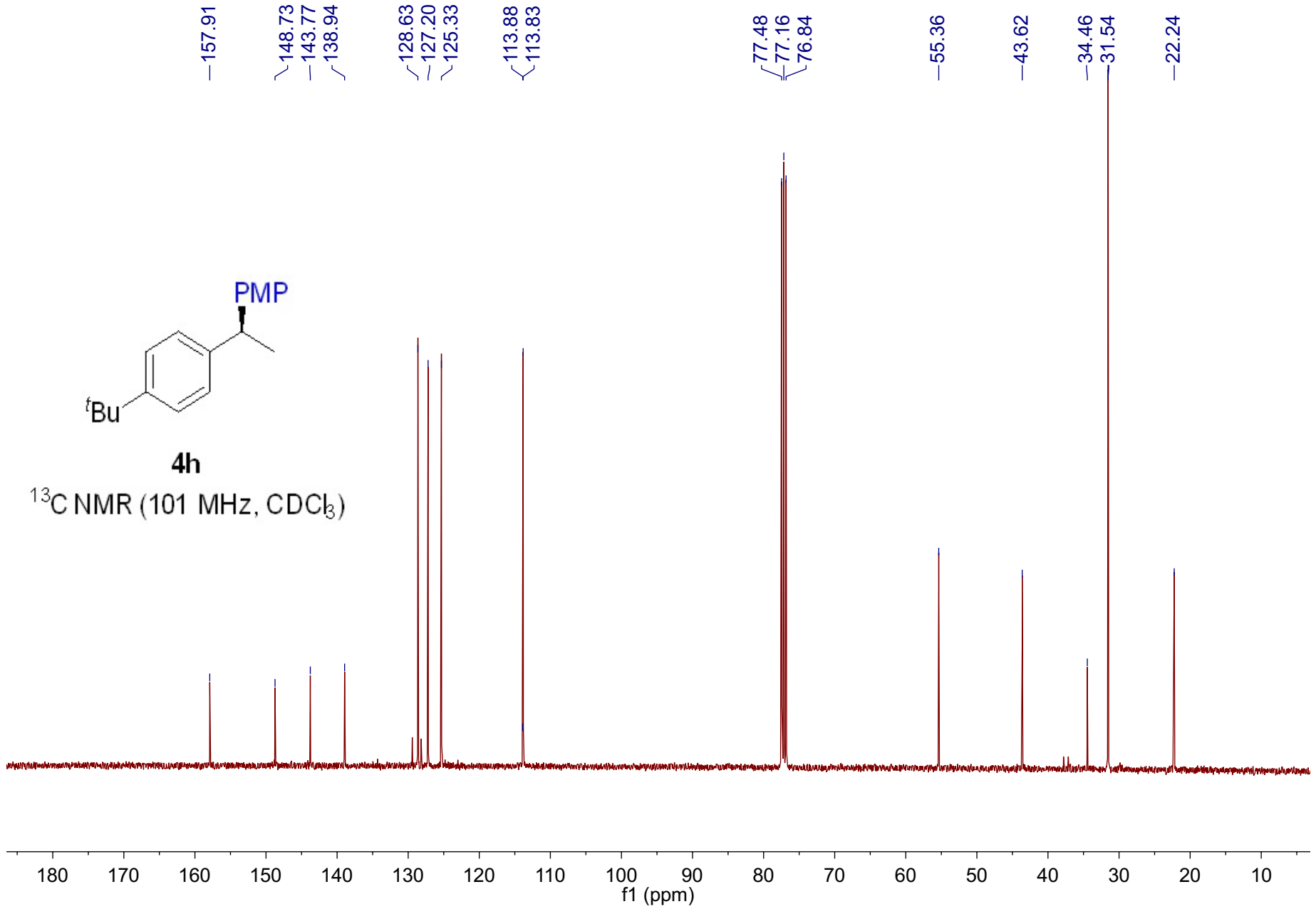

7.89
7.87
7.32
7.31
7.28
7.26
7.22
7.20
7.20
4.23
4.22
4.20
4.19
2.57
1.67
1.65
O
Ph
4e
1H NMR (500 MHz, CDCl3)
2.13
4.06
2.97
1.00
2.94
3.08
f1 (ppm)

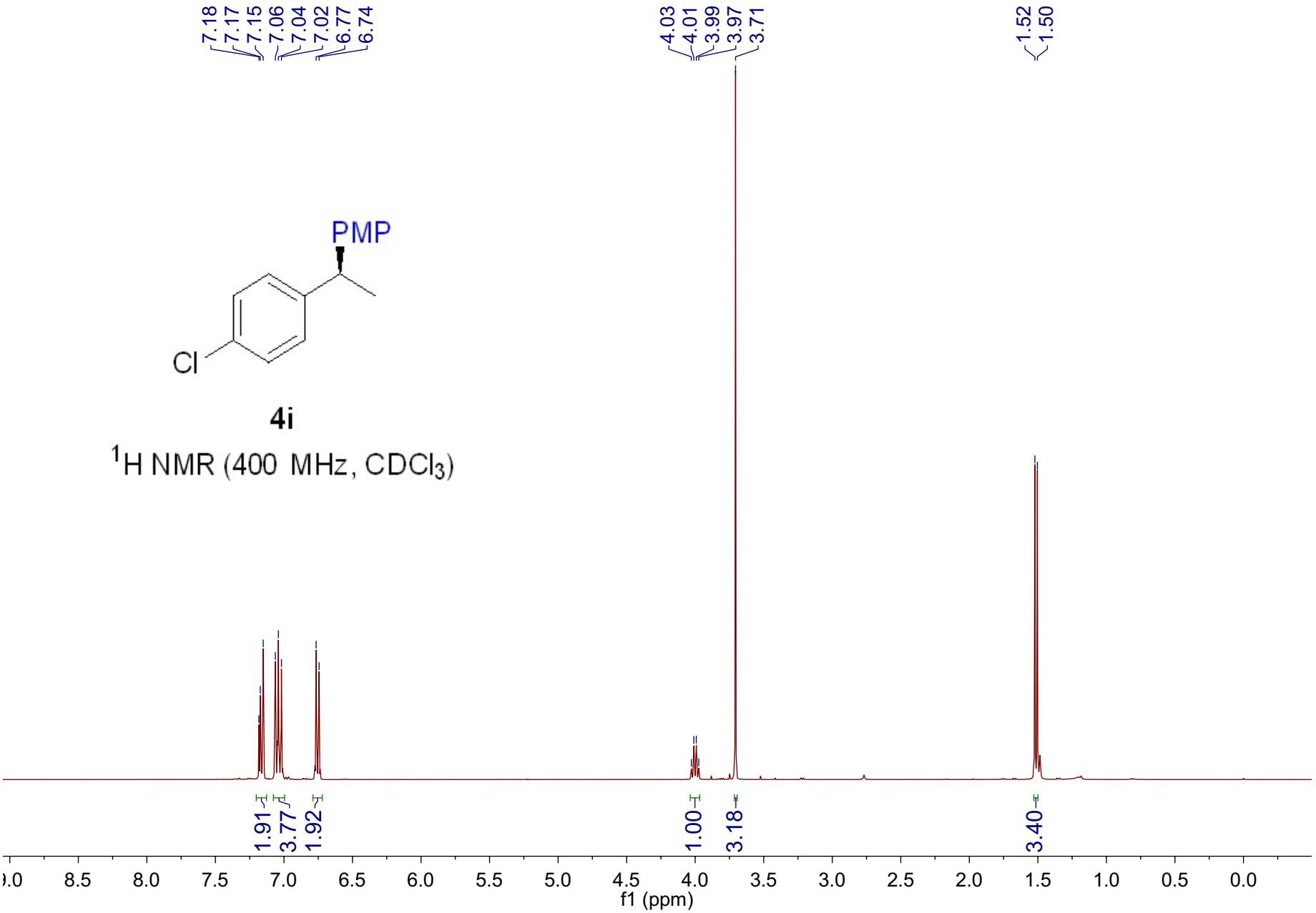

197.96
152.16
145.45
135.31
128.72
128.67
127.97
127.71
126.51
77.41
77.16
76.91
44.95
26.72
21.68
O
Ph
4e
13C NMR (126 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

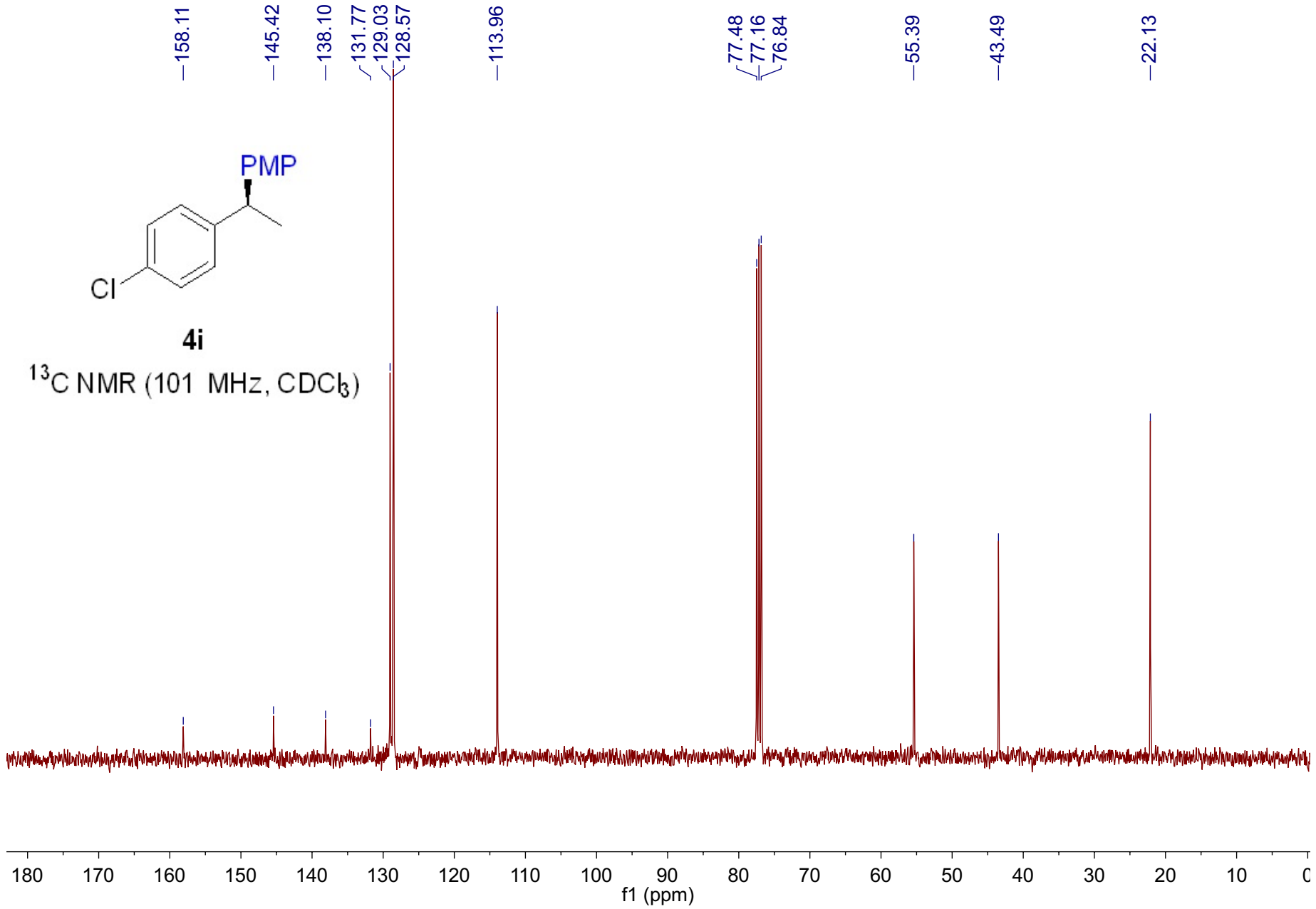

7.71
7.70
7.69
7.66
7.64
7.59
7.38
7.37
7.35
7.34
7.33
7.10
7.08
6.76
6.74
4.21
4.19
4.17
4.16
3.69
1.63
1.61
PMP
4g
1H NMR (400 MHz, CDCl3)
3.94
1.93
0.95
1.95
1.96
1.00
3.00
3.33
f1 (ppm)

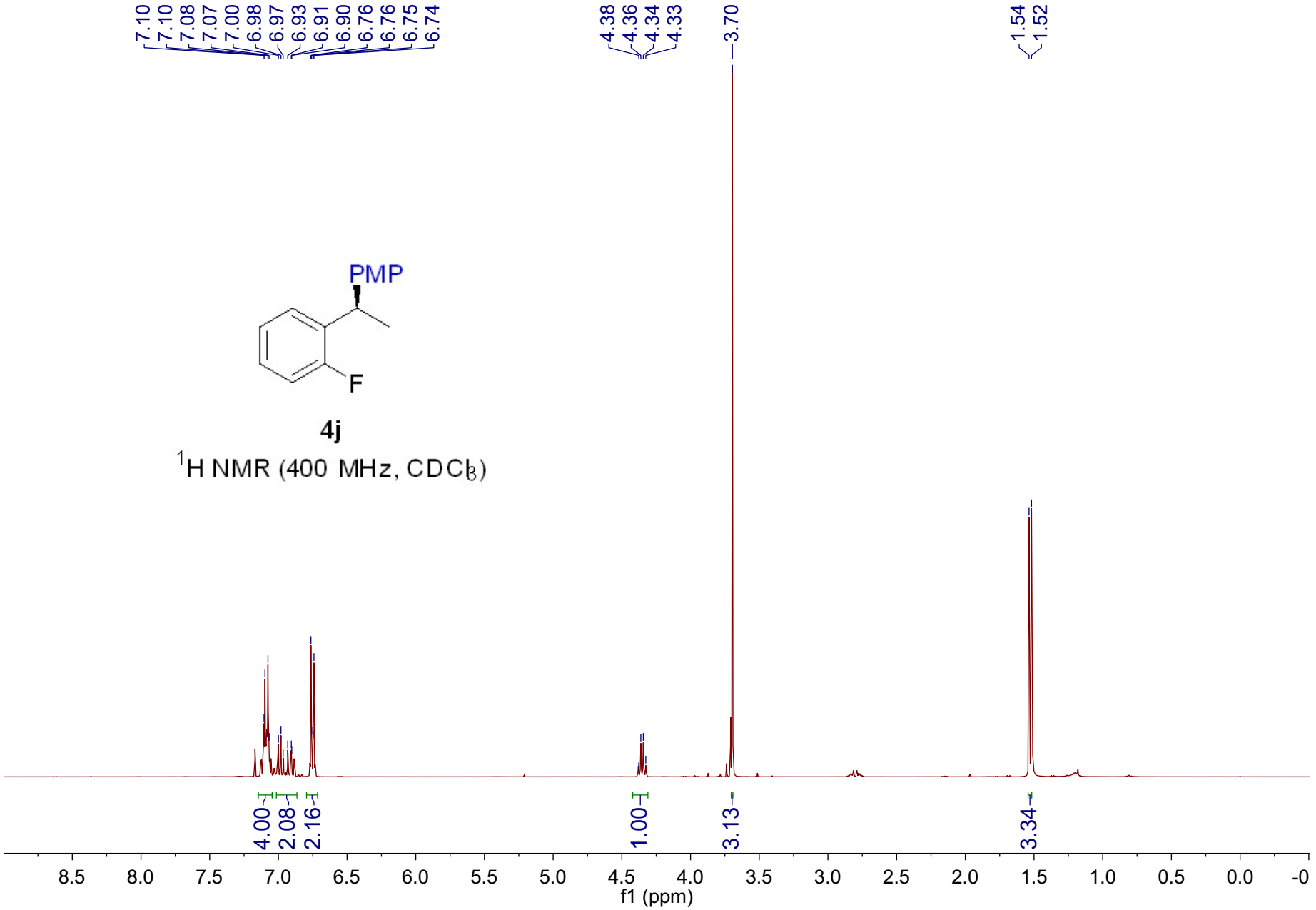

158.02
144.30
138.52
133.66
132.20
128.78
128.05
127.84
127.69
126.93
126.04
125.44
125.33
113.89
77.48
77.16
76.84
55.37
44.15
22.09
PMP
4g
13C NMR (101 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

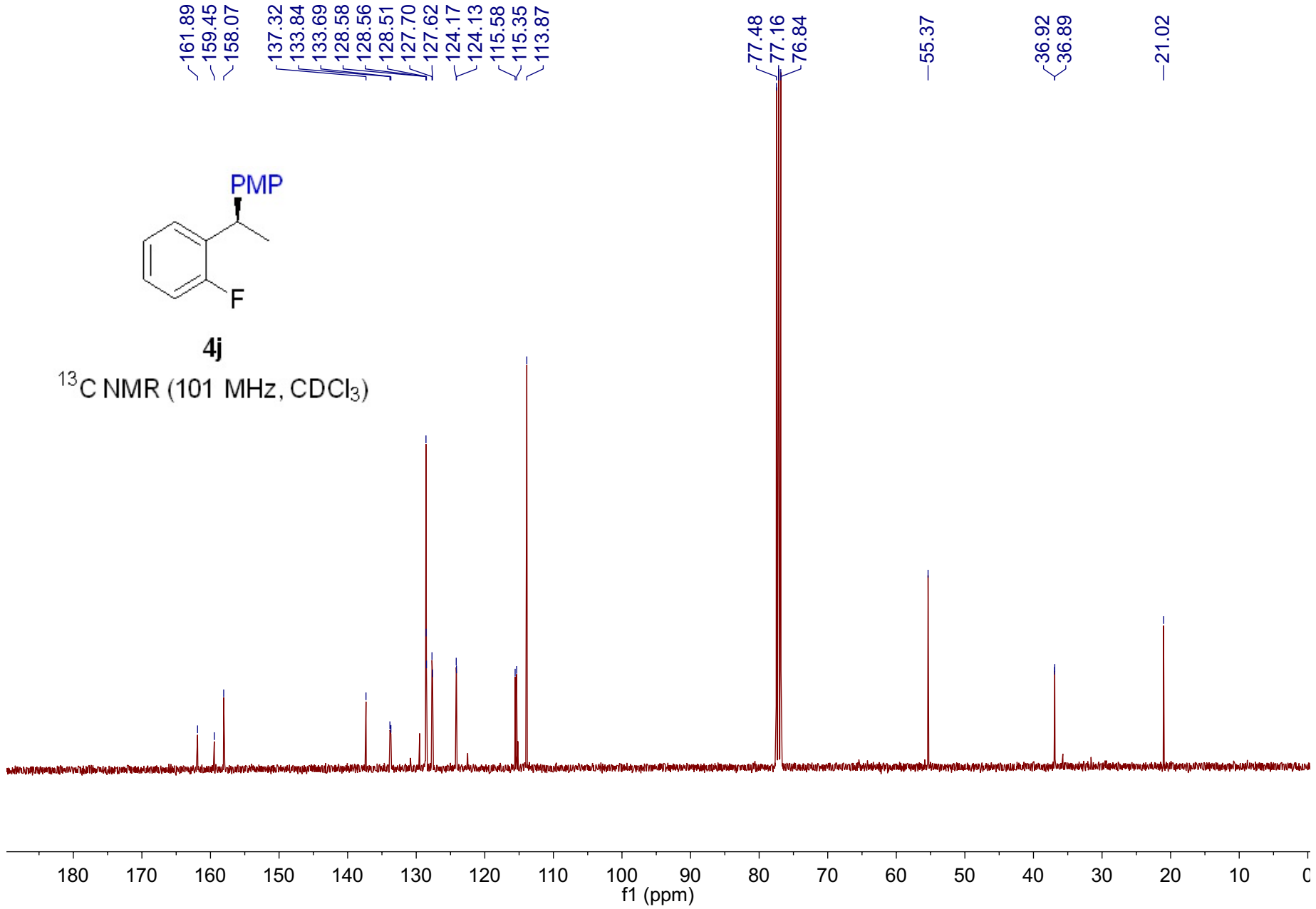

7.22
7.20
7.08
7.07
7.06
7.05
6.76
6.74
3.69
1.54
1.52
1.22
PMP
tBu
4h
1H NMR (400 MHz, CDCl3)
1.91
4.07
2.02
1.00
3.15
3.33
9.47
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

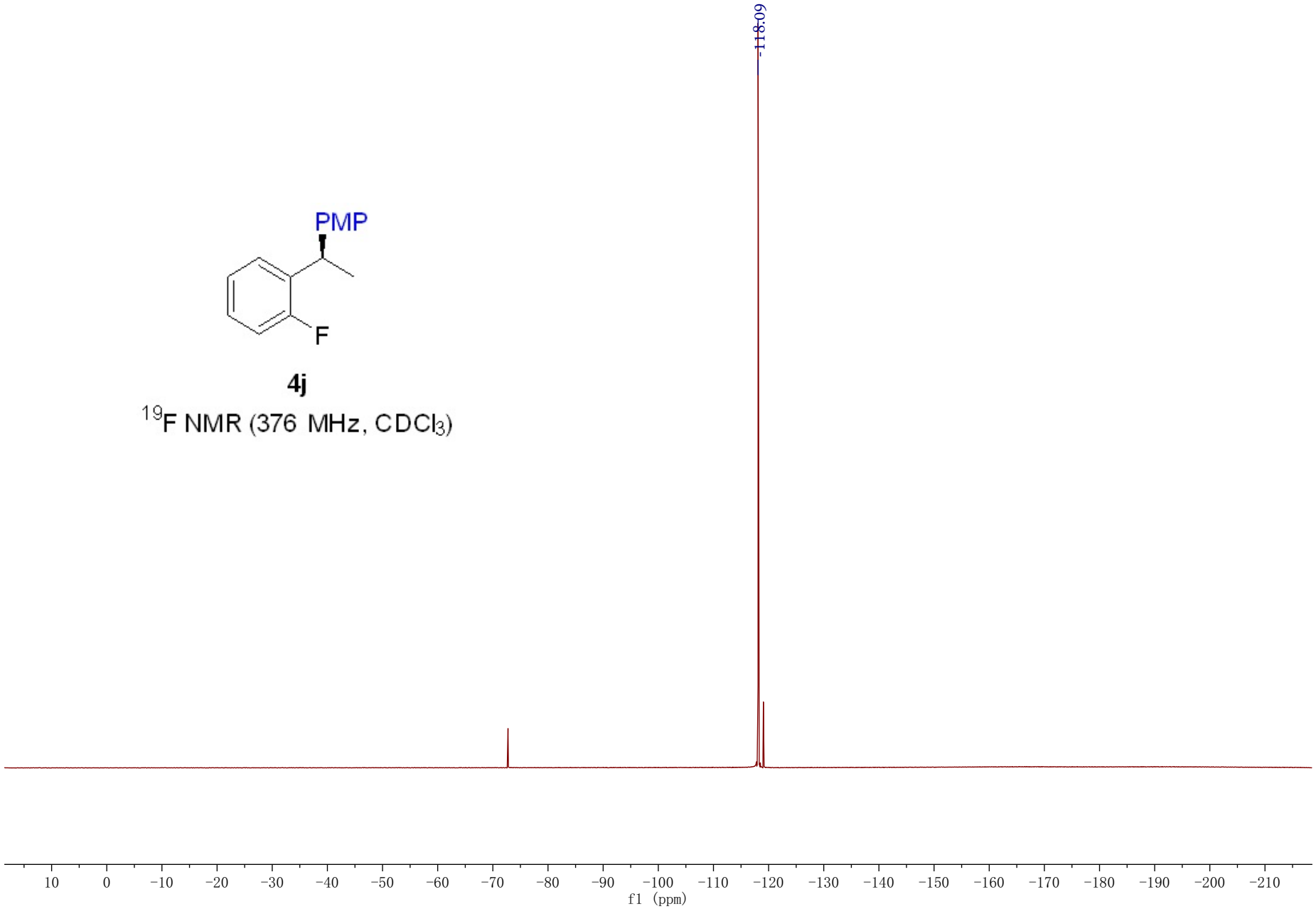

157.91
148.73
143.77
138.94
128.63
127.20
125.33
113.88
113.83
77.48
77.16
76.84
55.36
43.62
34.46
31.54
22.24
PMP
tBu
4h
13C NMR (101 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.18
7.17
7.15
7.06
7.04
7.02
6.77
6.74
4.03
4.01
3.99
3.97
3.71
1.52
1.50
PMP
Cl
4i
^{1}H NMR (400 MHz, $CDCl_3$)
1.91
3.77
1.92
1.00
3.18
3.40
f1 (ppm)


158.11
145.42
138.10
131.77
129.03
128.57
113.96
77.48
77.16
76.84
55.39
43.49
22.13
PMP
Cl
4i
13C NMR (101 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.10
7.10
7.08
7.07
7.00
6.98
6.97
6.93
6.91
6.90
6.76
6.76
6.75
6.74
4.38
4.36
4.34
4.33
3.70
1.54
1.52
PMP
F
4j
1H NMR (400 MHz, CDCl3)
4.00
2.08
2.16
1.00
3.13
3.34
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


161.89
159.45
158.07
137.32
133.84
133.69
128.58
128.56
128.51
127.70
127.62
124.17
124.13
115.58
115.35
113.87
77.48
77.16
76.84
55.37
36.92
36.89
21.02
PMP
F
4j
13C NMR (101 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

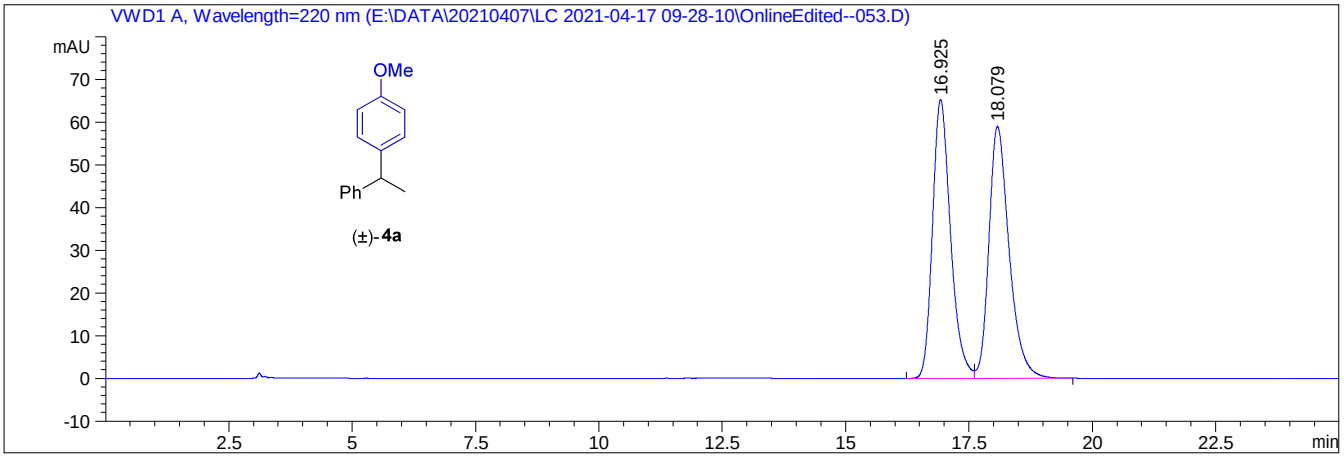


4j

^{19}F NMR (376 MHz, $CDCl_3$)

Data File E:\DATA\20210407\LC 2021-04-17 09-28-10\OnlineEdited--053.D
Sample Name: CJ-04-30-1

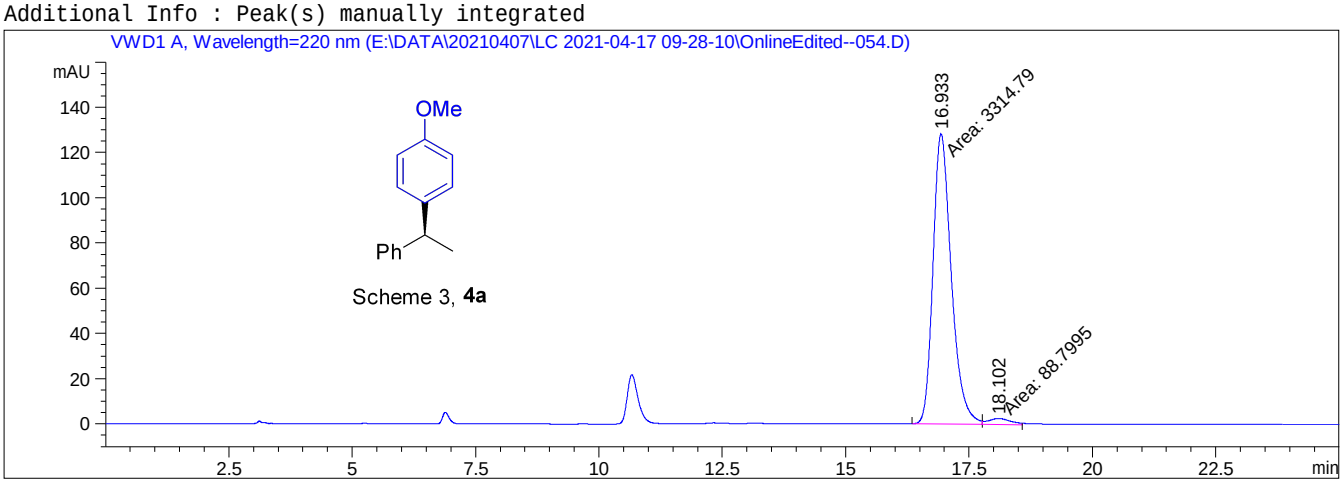
```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  53
    Acq. Instrument : HPLC1260                       Location :   P1-E3
    Injection Date  : 4/18/2021 4:05:40 AM               Inj :   1
                                                   Inj Volume : 3.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
    Acq. Method     : E:\DATA\20210407\LC 2021-04-17 09-28-10\5IPA_15_1_3.CJ.M
    Last changed    : 4/17/2021 11:10:37 PM by SYSTEM
    Analysis Method : E:\DATA\20210407\LC 2021-04-17 09-28-10\5IPA_15_1_3.CJ.M (Sequence Method)
    Last changed    : 4/27/2021 11:07:44 PM by SYSTEM
                      (modified after loading)
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=220 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.925 BV    0.3877 1658.44336   65.20196  49.6378
       2  18.079 VB    0.4319 1682.64856   58.96897  50.3622

    Totals :                  3341.09192  124.17093


    ======================================================================
                            *** End of Report ***
```

Data File E:\DATA\20210407\LC 2021-04-17 09-28-10\OnlineEdited--054.D
Sample Name: CJ-04-32-7

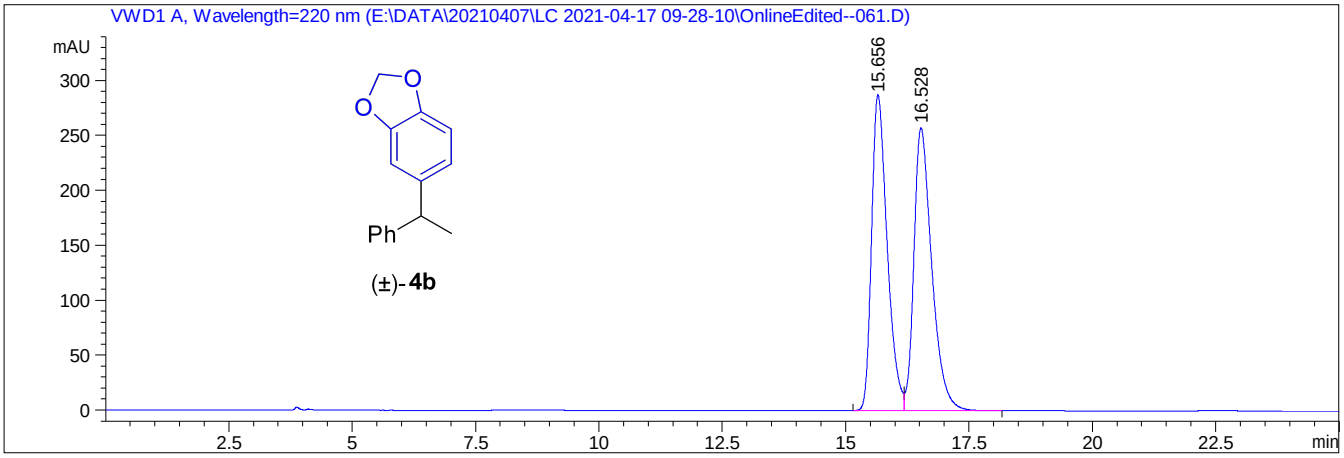
```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  54
Acq. Instrument : HPLC1260                       Location :   P1-F3
Injection Date  : 4/18/2021 4:31:28 AM                Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : E:\DATA\20210407\LC 2021-04-17 09-28-10\5IPA_15_1_3.CJ.M
Last changed    : 4/17/2021 11:10:37 PM by SYSTEM
Analysis Method : E:\DATA\20210407\LC 2021-04-17 09-28-10\5IPA_15_1_3.CJ.M (Sequence Method)
Last changed    : 4/27/2021 11:08:16 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.933 MF    0.4306 3314.79150  128.29298  97.3910
   2  18.102 FM    0.5348   88.79945    2.76713   2.6090

Totals :                  3403.59096  131.06011


=====================================================================
                        *** End of Report ***
```

Data File E:\DATA\20210407\LC 2021-04-17 09-28-10\OnlineEdited--061.D
Sample Name: CJ-04-26-5

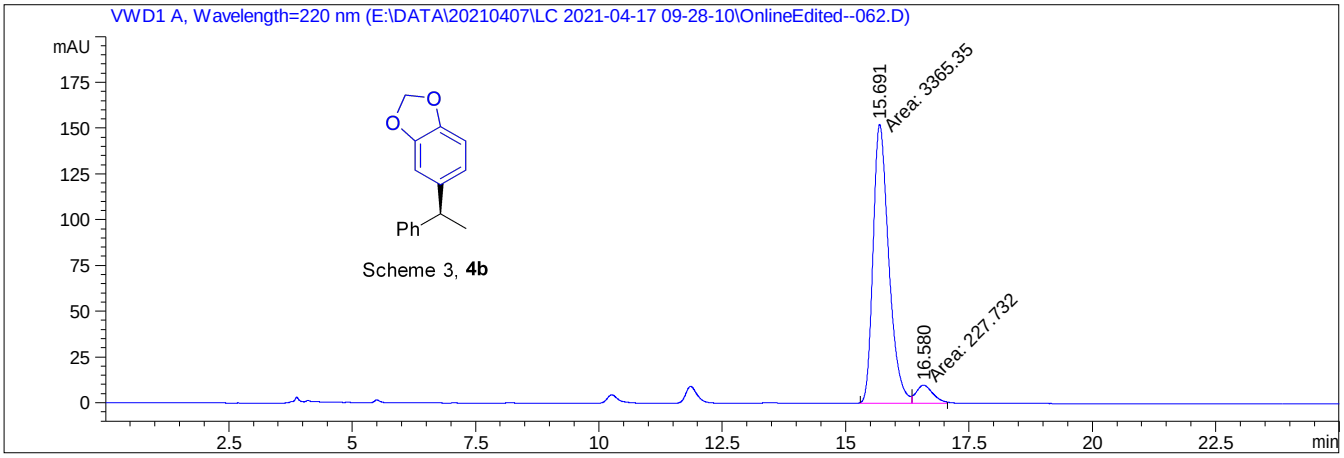
```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  61
Acq. Instrument : HPLC1260                       Location :   P1-E6
Injection Date  : 4/18/2021 7:47:38 AM                Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : E:\DATA\20210407\LC 2021-04-17 09-28-10\8EtOH_30_0.8_3-CJ.M
Last changed    : 4/17/2021 11:21:55 PM by SYSTEM
Analysis Method : E:\DATA\20210407\LC 2021-04-17 09-28-10\8EtOH_30_0.8_3-CJ.M (Sequence
                  Method)
Last changed    : 4/27/2021 11:12:40 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.656 BV    0.3332 6307.86084  287.22409  49.3121
   2  16.528 VB    0.3789 6483.84424  257.40140  50.6879

Totals :                  1.27917e4   544.62549

=====================================================================
                        *** End of Report ***
```

Data File E:\DATA\20210407\LC 2021-04-17 09-28-10\OnlineEdited--062.D
Sample Name: CJ-04-25-11

```
======================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  62
Acq. Instrument : HPLC1260                       Location :   P1-F6
Injection Date  : 4/18/2021 8:18:26 AM                Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : E:\DATA\20210407\LC 2021-04-17 09-28-10\8EtOH_30_0.8_3-CJ.M
Last changed    : 4/17/2021 11:21:55 PM by SYSTEM
Analysis Method : E:\DATA\20210407\LC 2021-04-17 09-28-10\8EtOH_30_0.8_3-CJ.M (Sequence
                  Method)
Last changed    : 4/27/2021 11:13:16 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

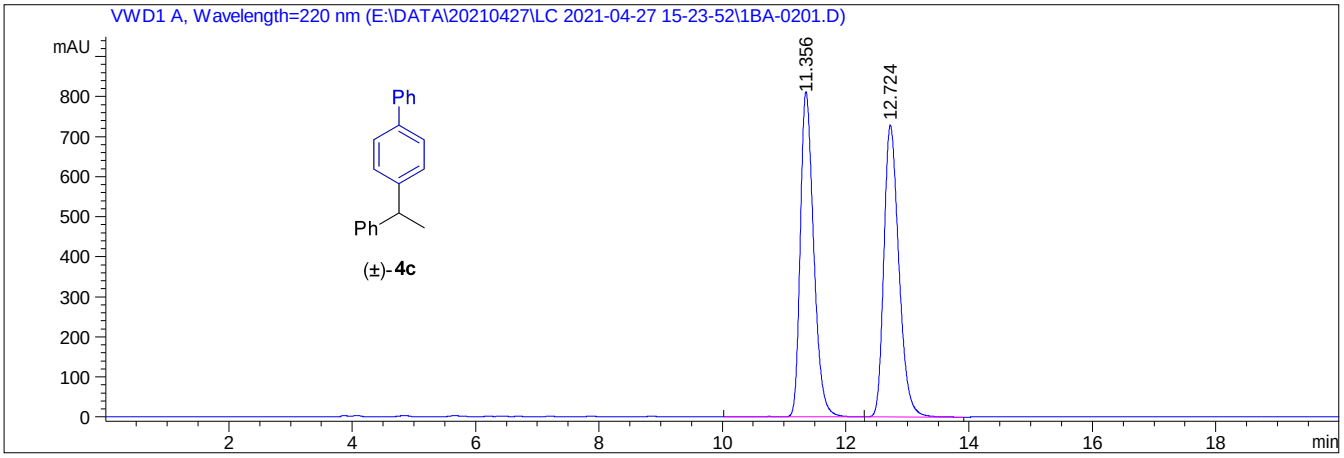


Scheme 3, **4b**

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.691 MF    0.3684 3365.34741  152.23299  93.6619
   2  16.580 FM    0.3873  227.73170    9.80064   6.3381

Totals :                  3593.07912  162.03363

======================================================================
                        *** End of Report ***
```

Data File E:\DATA\20210427\LC 2021-04-27 15-23-52\1BA-0201.D
Sample Name: CJ-04-49-2R

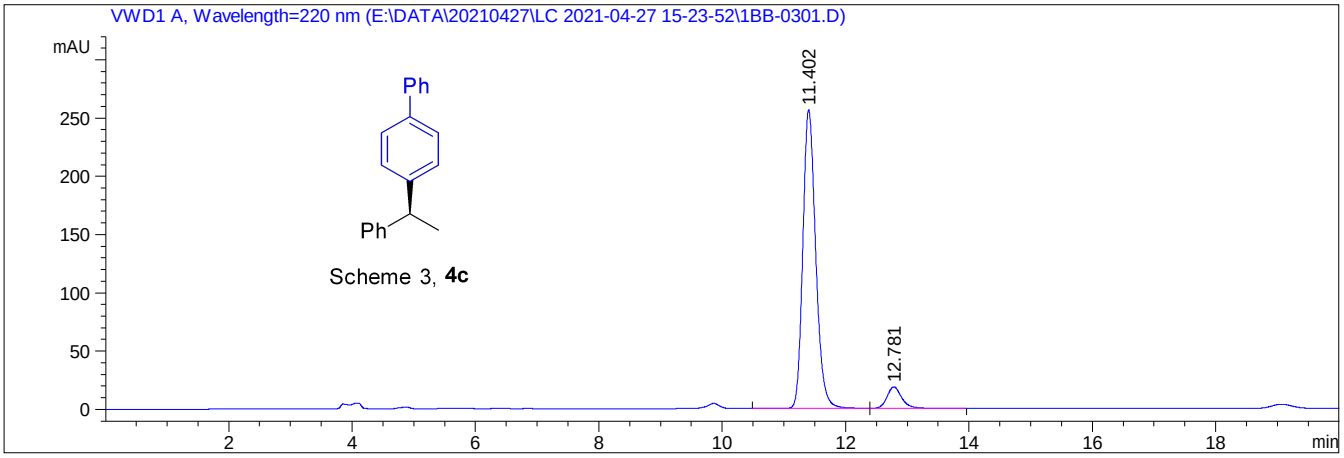
```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   2
Acq. Instrument : HPLC1260                       Location :   P1-B1
Injection Date  : 4/27/2021 3:46:49 PM                Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : E:\DATA\20210427\LC 2021-04-27 15-23-52\10EtOH_20_1.0_4.CJ.M
Last changed    : 4/27/2021 3:24:49 PM by SYSTEM
Analysis Method : E:\DATA\20210427\LC 2021-04-27 15-23-52\10EtOH_20_1.0_4.CJ.M (Sequence
                  Method)
Last changed    : 4/27/2021 11:15:39 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.356 VB R  0.2321 1.22495e4   811.64697  49.8674
   2  12.724 BB    0.2603 1.23146e4   728.36328  50.1326

Totals :                  2.45642e4  1540.01025


=====================================================================
                        *** End of Report ***
```

Data File E:\DATA\20210427\LC 2021-04-27 15-23-52\1BB-0301.D
Sample Name: CJ-04-49-2EE

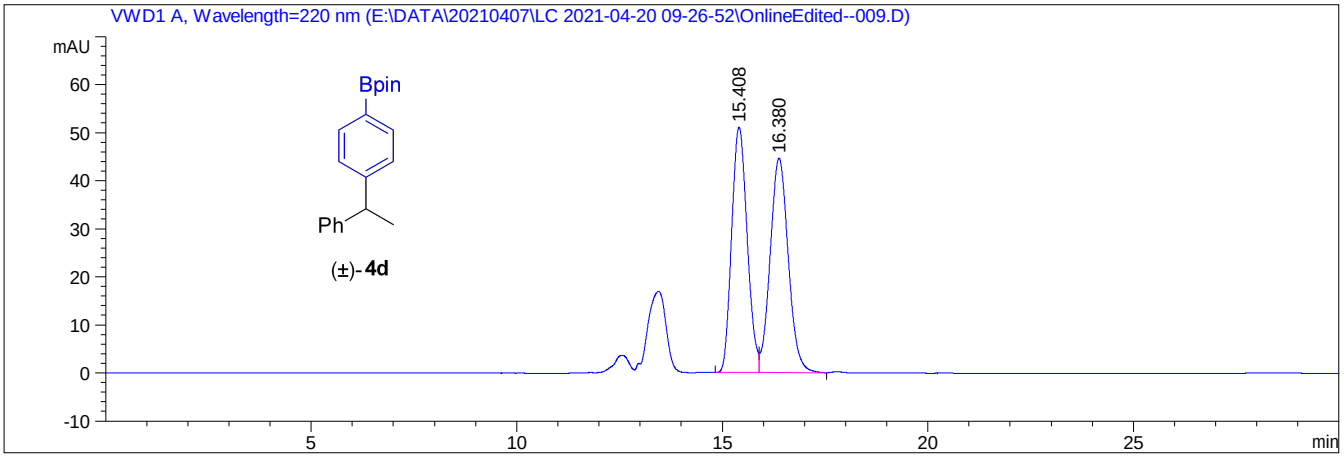
```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   3
Acq. Instrument : HPLC1260                       Location :   P1-B2
Injection Date  : 4/27/2021 4:07:36 PM                Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : E:\DATA\20210427\LC 2021-04-27 15-23-52\10EtOH_20_1.0_4.CJ.M
Last changed    : 4/27/2021 3:24:49 PM by SYSTEM
Analysis Method : E:\DATA\20210427\LC 2021-04-27 15-23-52\10EtOH_20_1.0_4.CJ.M (Sequence
                  Method)
Last changed    : 4/27/2021 11:16:34 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.402 BB    0.2230 3715.71143  256.43567  92.5222
   2  12.781 BB    0.2501  300.31174   18.33374   7.4778

Totals :                  4016.02316  274.76941


=====================================================================
                        *** End of Report ***
```

Data File E:\DATA\20210407\LC 2021-04-20 09-26-52\OnlineEdited--009.D
Sample Name: CJ-04-26-4R

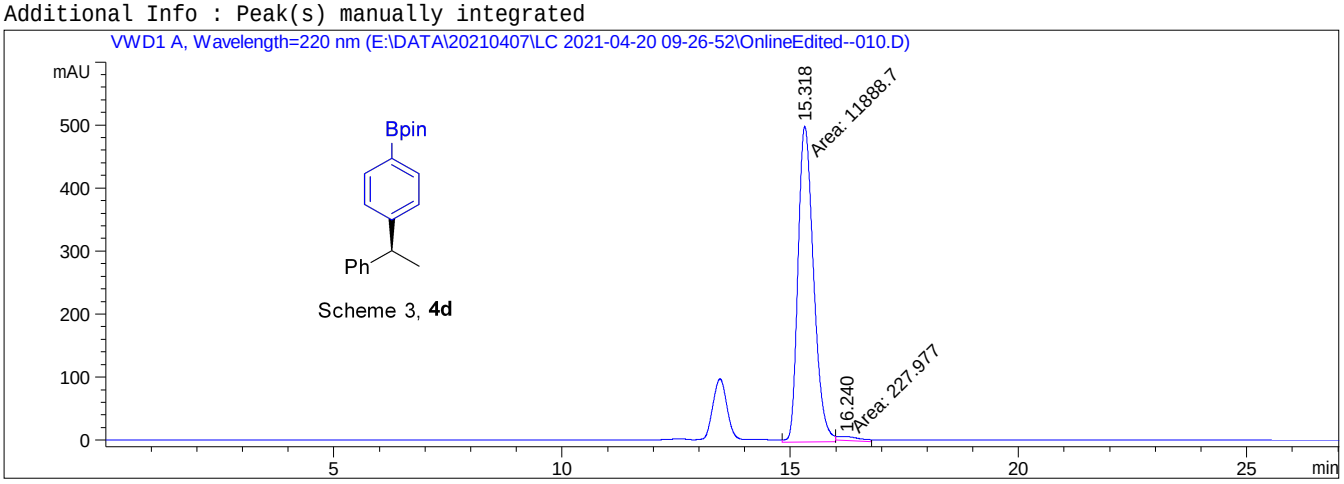
```
======================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   9
Acq. Instrument : HPLC1260                       Location :   P1-E3
Injection Date  : 4/20/2021 1:05:35 PM                Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : E:\DATA\20210407\LC 2021-04-20 09-26-52\1EtOH_30_0.5_1CJ.M
Last changed    : 4/20/2021 9:29:34 AM by SYSTEM
Analysis Method : E:\DATA\20210407\LC 2021-04-20 09-26-52\1EtOH_30_0.5_1CJ.M (Sequence Method
                  )
Last changed    : 4/27/2021 10:52:12 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.408 BV    0.4129 1342.29834   51.02207  49.5588
   2  16.380 VB    0.4751 1366.19971   44.63078  50.4412

Totals :                  2708.49805   95.65285


======================================================================
                        *** End of Report ***
```

Data File E:\DATA\20210407\LC 2021-04-20 09-26-52\OnlineEdited--010.D
Sample Name: CJ-04-25-10E

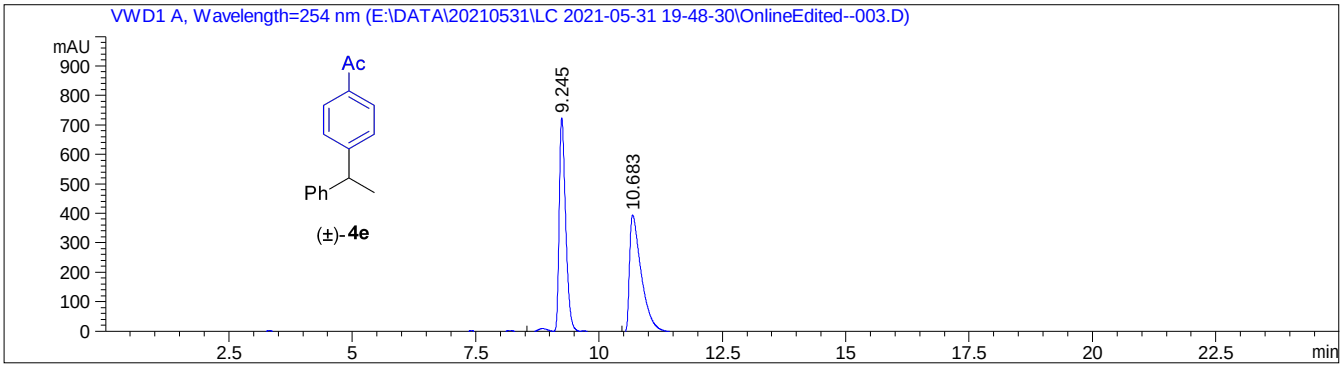
```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  10
Acq. Instrument : HPLC1260                       Location :   P1-E4
Injection Date  : 4/20/2021 1:36:23 PM                Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : E:\DATA\20210407\LC 2021-04-20 09-26-52\1EtOH_30_0.5_1CJ.M
Last changed    : 4/20/2021 2:03:25 PM by SYSTEM
                  (modified after loading)
Analysis Method : E:\DATA\20210407\LC 2021-04-20 09-26-52\1EtOH_30_0.5_1CJ.M (Sequence Method
                  )
Last changed    : 4/27/2021 10:52:50 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.318 MF    0.3958 1.18887e4   500.62378  98.1185
   2  16.240 MM    0.6010  227.97690    6.32201   1.8815

Totals :                  1.21167e4   506.94579


=====================================================================
                          *** End of Report ***
```

Data File E:\DATA\20210531\LC 2021-05-31 19-48-30\OnlineEdited--003.D
Sample Name: XYH-03-48-1

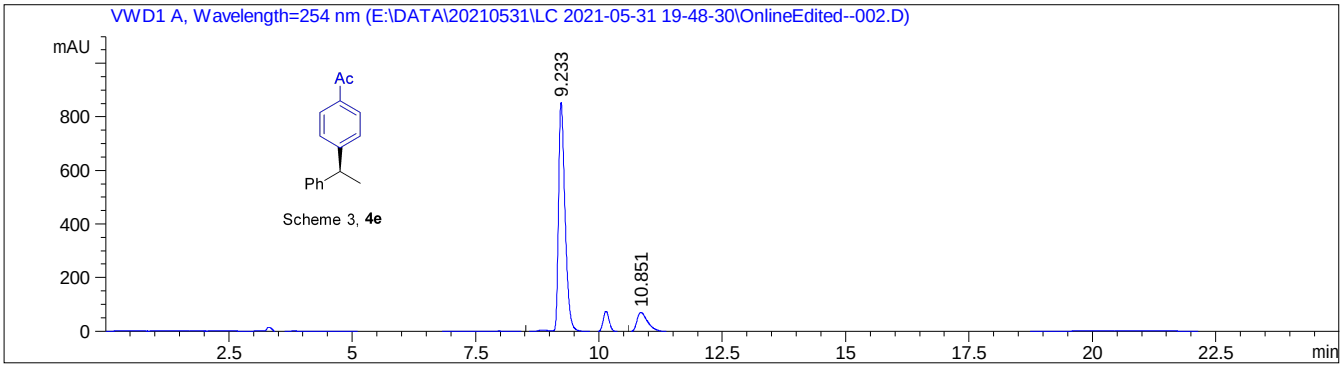
```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   3
Acq. Instrument : HPLC1260                       Location :   P2-D2
Injection Date  : 5/31/2021 8:30:37 PM                Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.400 µl
Acq. Method     : E:\DATA\20210531\LC 2021-05-31 19-48-30\2.0IPA-25-1.0-3-XYH.M
Last changed    : 5/31/2021 7:50:22 PM by SYSTEM
Analysis Method : E:\DATA\20210531\LC 2021-05-31 19-48-30\2.0IPA-25-1.0-3-XYH.M (Sequence
                  Method)
Last changed    : 5/31/2021 11:22:38 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.245 VV R  0.1399 6929.50684  729.13171  50.8662
   2  10.683 BB    0.2446 6693.51123  399.17273  49.1338

Totals :                  1.36230e4  1128.30444


=====================================================================
                        *** End of Report ***
```

Data File E:\DATA\20210531\LC 2021-05-31 19-48-30\OnlineEdited--002.D
Sample Name: XYH-03-11-3(IF)

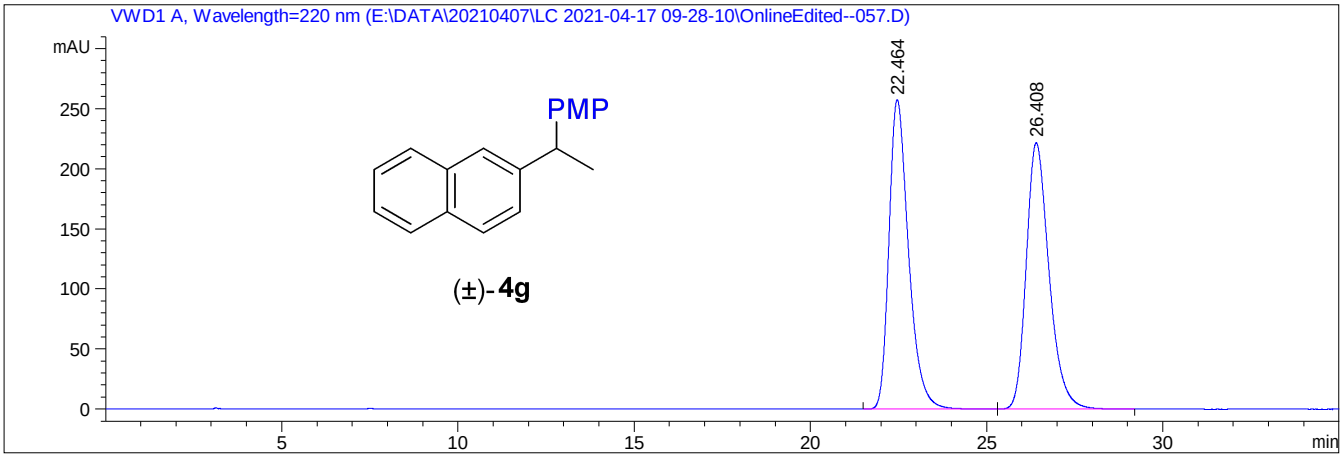
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   2
Acq. Instrument : HPLC1260                          Location :   P2-D1
Injection Date  : 5/31/2021 8:04:53 PM                   Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.400 µl
Acq. Method     : E:\DATA\20210531\LC 2021-05-31 19-48-30\2.0IPA-25-1.0-3-XYH.M
Last changed    : 5/31/2021 7:50:22 PM by SYSTEM
Analysis Method : E:\DATA\20210531\LC 2021-05-31 19-48-30\2.0IPA-25-1.0-3-XYH.M (Sequence
                  Method)
Last changed    : 5/31/2021 11:21:35 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.233 VV R  0.1404 7964.89111  855.36511  87.3591
   2  10.851 BB    0.2373 1152.52478   72.94921  12.6409

Totals :                  9117.41589  928.31432


==========================================================================
                          *** End of Report ***
```

Data File E:\DATA\20210407\LC 2021-04-17 09-28-10\OnlineEdited--057.D
Sample Name: CJ-04-30-2

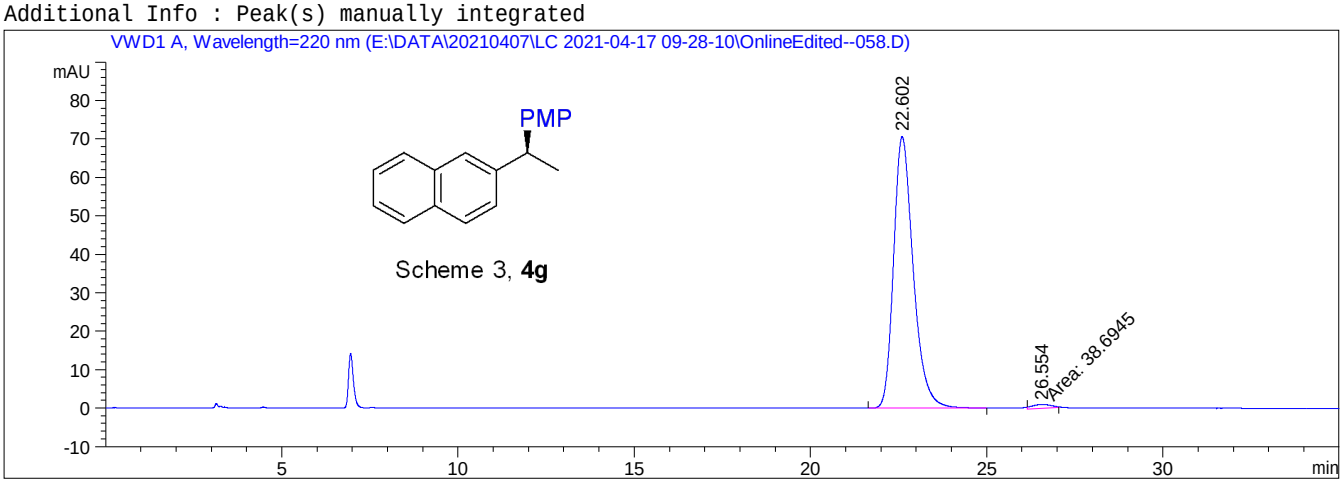
```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  57
Acq. Instrument : HPLC1260                       Location :   P1-E4
Injection Date  : 4/18/2021 5:48:56 AM                Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : E:\DATA\20210407\LC 2021-04-17 09-28-10\5IPA_35_1_3.CJ.M
Last changed    : 4/17/2021 11:15:34 PM by SYSTEM
Analysis Method : E:\DATA\20210407\LC 2021-04-17 09-28-10\5IPA_35_1_3.CJ.M (Sequence Method)
Last changed    : 4/27/2021 11:11:05 PM by SYSTEM
                  (modified after loading)
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.464 BB    0.5853 9943.07715  257.62805  49.9412
   2  26.408 BB    0.6866 9966.48145  221.64799  50.0588

Totals :                  1.99096e4   479.27605


=====================================================================
                        *** End of Report ***
```

Data File E:\DATA\20210407\LC 2021-04-17 09-28-10\OnlineEdited--058.D
Sample Name: CJ-04-29-2

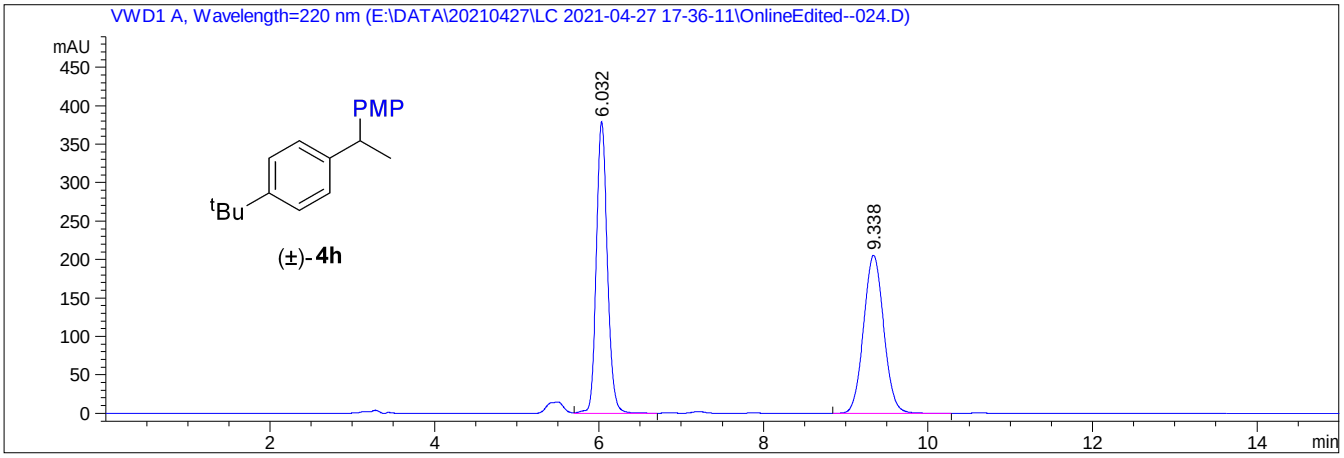
```
======================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  58
Acq. Instrument : HPLC1260                       Location :   P1-F4
Injection Date  : 4/18/2021 6:24:45 AM                Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : E:\DATA\20210407\LC 2021-04-17 09-28-10\5IPA_35_1_3.CJ.M
Last changed    : 4/17/2021 11:15:34 PM by SYSTEM
Analysis Method : E:\DATA\20210407\LC 2021-04-17 09-28-10\5IPA_35_1_3.CJ.M (Sequence Method)
Last changed    : 4/27/2021 11:11:33 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.602 BB    0.5902 2735.26685   70.56322  98.6051
   2  26.554 MM    0.6355   38.69446    1.01486   1.3949

Totals :                  2773.96131   71.57808


======================================================================
                        *** End of Report ***
```

Data File E:\DATA\20210427\LC 2021-04-27 17-36-11\OnlineEdited--024.D
Sample Name: cj-04-30-3r

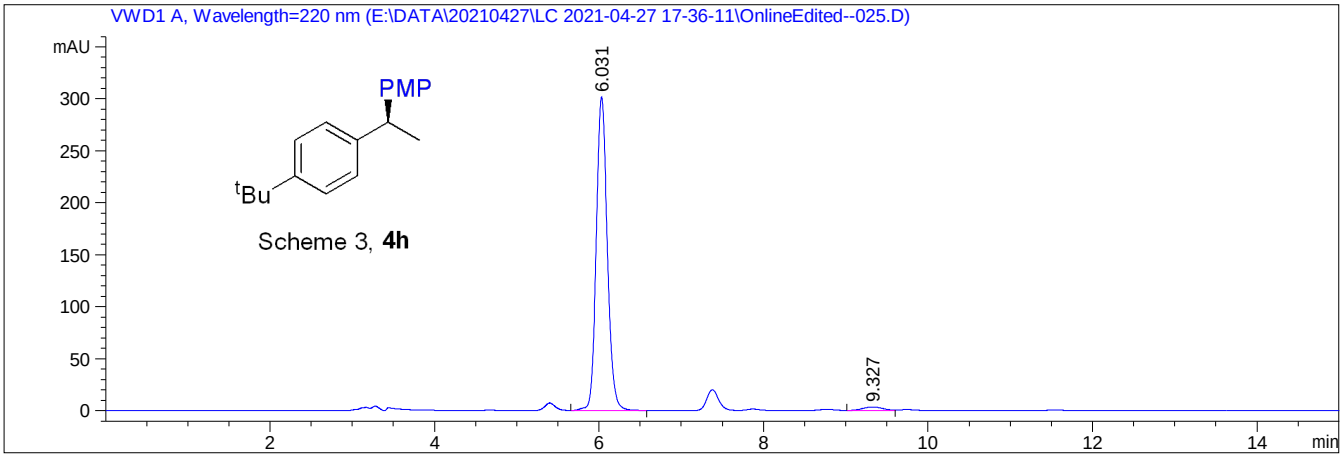
```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  24
Acq. Instrument : HPLC1260                       Location :   P1-C2
Injection Date  : 4/28/2021 4:41:48 AM                Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : E:\DATA\20210427\LC 2021-04-27 17-36-11\5IPA_20_1.0_4.CJM..M
Last changed    : 4/27/2021 11:29:19 PM by SYSTEM
Analysis Method : E:\DATA\20210427\LC 2021-04-27 17-36-11\5IPA_20_1.0_4.CJM..M (Sequence
                  Method)
Last changed    : 4/28/2021 9:17:15 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.032 VB    0.1434 3520.50366  378.95435  50.1762
   2   9.338 BB    0.2644 3495.77759  205.60980  49.8238

Totals :                  7016.28125  584.56415


=====================================================================
                        *** End of Report ***
```

Data File E:\DATA\20210427\LC 2021-04-27 17-36-11\OnlineEdited--025.D
Sample Name: cj-04-29-3e

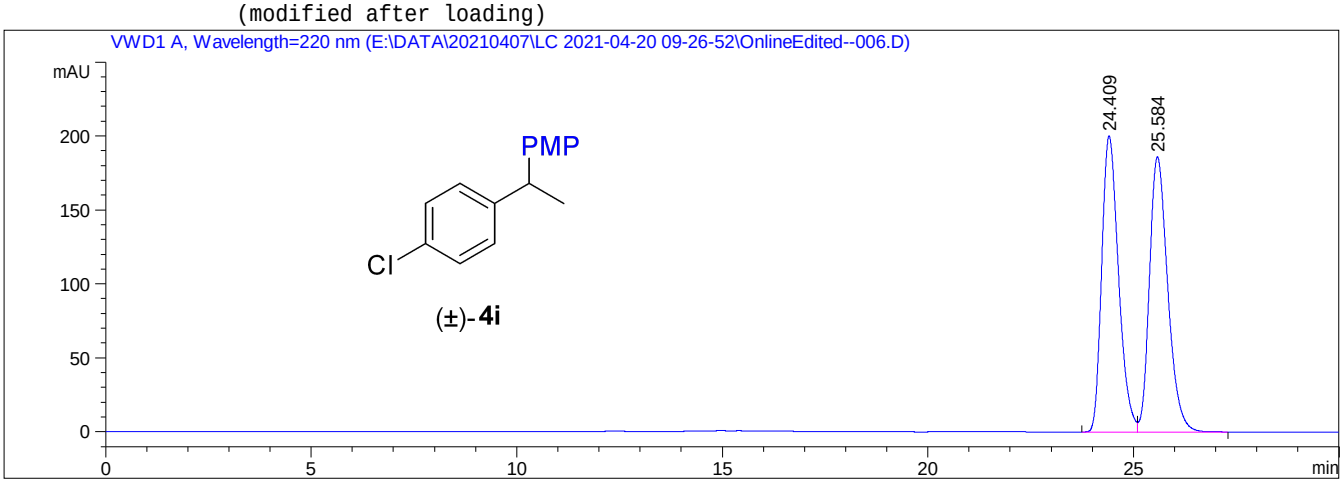
```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :  25
Acq. Instrument : HPLC1260                         Location :   P1-C3
Injection Date  : 4/28/2021 4:57:34 AM                  Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : E:\DATA\20210427\LC 2021-04-27 17-36-11\5IPA_20_1.0_4.CJM..M
Last changed    : 4/27/2021 11:29:19 PM by SYSTEM
Analysis Method : E:\DATA\20210427\LC 2021-04-27 17-36-11\5IPA_20_1.0_4.CJM..M (Sequence
                  Method)
Last changed    : 4/28/2021 9:18:47 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.031 VB    0.1438 2812.91113  301.75040  97.8716
   2   9.327 VV    0.2704   61.17134    3.52550   2.1284

Totals :                  2874.08247  305.27590

==========================================================================
                          *** End of Report ***
```

Data File E:\DATA\20210407\LC 2021-04-20 09-26-52\OnlineEdited--006.D
Sample Name: CJ-04-33-2R

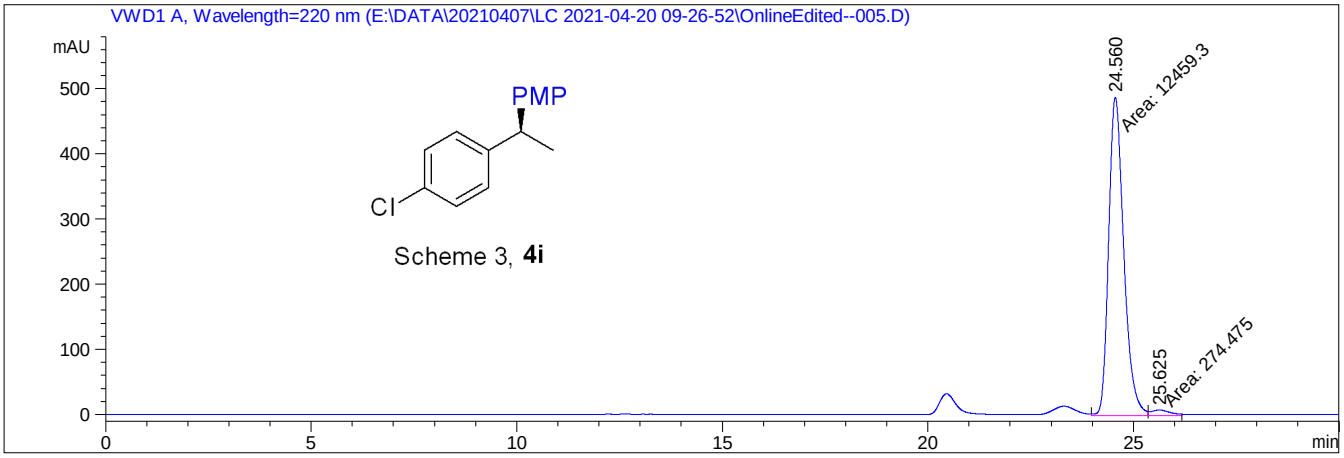
```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   6
Acq. Instrument : HPLC1260                       Location :   P1-E1
Injection Date  : 4/20/2021 11:48:06 AM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : E:\DATA\20210407\LC 2021-04-20 09-26-52\0.5IPA_30_0.5_1.CJ.M
Last changed    : 4/20/2021 9:27:13 AM by SYSTEM
Analysis Method : E:\DATA\20210407\LC 2021-04-20 09-26-52\0.5IPA_30_0.5_1.CJ.M (Sequence
                  Method)
Last changed    : 4/27/2021 11:04:14 PM by SYSTEM
                  (modified after loading)
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.409 BV    0.4405 5684.99561  200.05127  49.6654
   2  25.584 VB    0.4772 5761.59863  186.10242  50.3346

Totals :                  1.14466e4   386.15369


=====================================================================
                        *** End of Report ***
```

Data File E:\DATA\20210407\LC 2021-04-20 09-26-52\OnlineEdited--005.D
Sample Name: CJ-04-32-3E

```
======================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   5
Acq. Instrument : HPLC1260                       Location :   P1-E2
Injection Date  : 4/20/2021 11:17:19 AM               Inj :   2
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : E:\DATA\20210407\LC 2021-04-20 09-26-52\0.5IPA_30_0.5_1.CJ.M
Last changed    : 4/20/2021 9:27:13 AM by SYSTEM
Analysis Method : E:\DATA\20210407\LC 2021-04-20 09-26-52\0.5IPA_30_0.5_1.CJ.M (Sequence
                  Method)
Last changed    : 4/27/2021 11:03:43 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

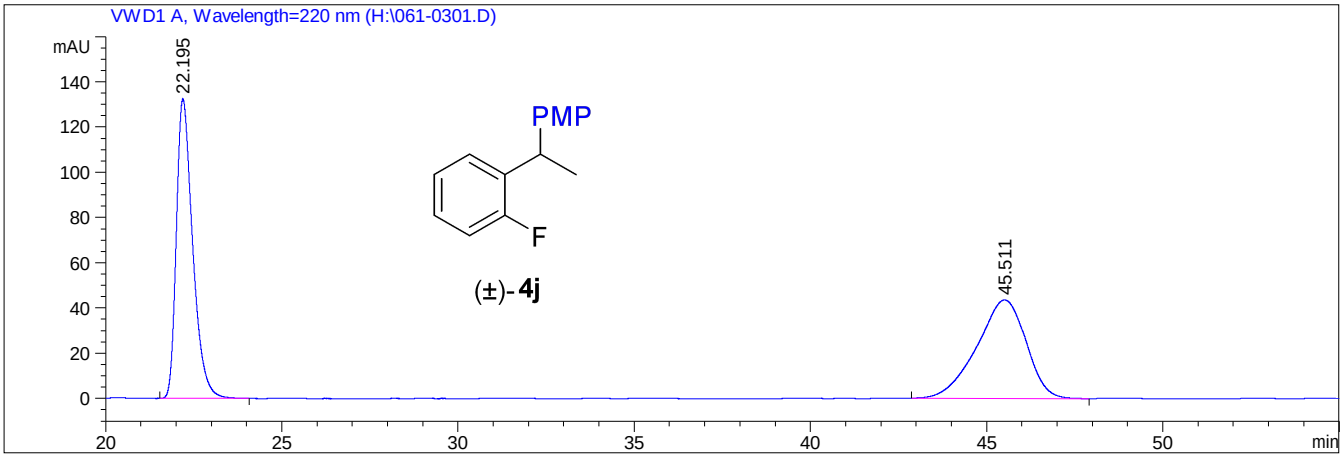


Scheme 3, **4i**

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.560 MF    0.4254 1.24593e4   488.12827  97.8445
   2  25.625 FM    0.5469  274.47507    8.36438   2.1555

Totals :                  1.27338e4   496.49264

======================================================================
                        *** End of Report ***
```

Data File H:\061-0301.D
Sample Name: CJ-04-36-2

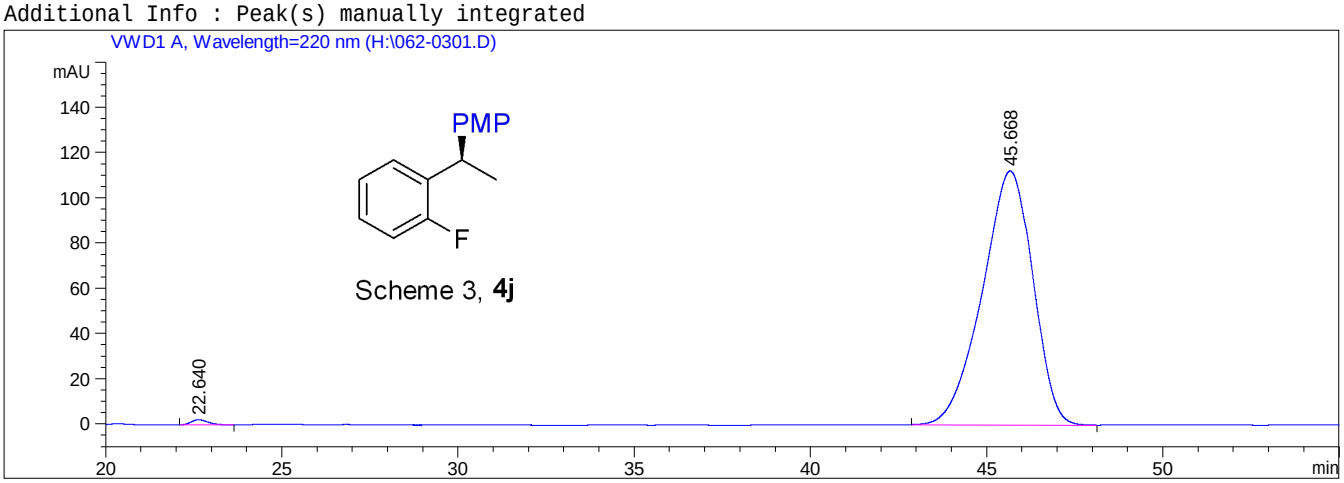
```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   3
Acq. Instrument : HPLC-1260                     Location :   61
Injection Date  : 4/20/2021 2:58:49 PM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\ZHH\20210417\YH 2021-04-20 13-49-35\0.5EtOH60_8-1-6-220CJ.M
Last changed    : 4/20/2021 1:50:33 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2021-01-12 20-07-38\10IPA_20_0.8_1.M (Sequence Method)
Last changed    : 4/27/2021 10:46:03 PM by SYSTEM
                  (modified after loading)
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.195 BB    0.4811 4266.07568  132.51329  50.1845
   2  45.511 BB    1.1500 4234.70752   43.53031  49.8155

Totals :                  8500.78320  176.04360


==========================================================================
                          *** End of Report ***
```

Data File H:\062-0301.D
Sample Name: CJ-04-35-3

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   3
Acq. Instrument : HPLC-1260                      Location :   62
Injection Date  : 4/20/2021 7:11:16 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 6.000 µl
Acq. Method     : D:\ZHH\20210417\YH 2021-04-20 18-41-58\0.5EtOH60_8-1-6-220CJ.M
Last changed    : 4/20/2021 6:41:59 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2021-01-12 20-07-38\10IPA_20_0.8_1.M (Sequence Method)
Last changed    : 4/27/2021 10:46:03 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.640 BB    0.3904   75.55983    2.27820   0.6697
   2  45.668 BB    1.2629 1.12078e4   112.29810  99.3303

Totals :                  1.12833e4   114.57631


==========================================================================
                          *** End of Report ***
```