

SUPPORTING INFORMATION

General Method for the Synthesis of Phenyliodonium Ylides from Malonate Esters: Easy Access to 1,1-Cyclopropane Diesters

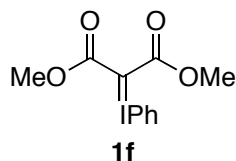
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General: All non-aqueous reactions were run under an inert atmosphere (nitrogen or argon) using standard techniques for manipulating air-sensitive compounds.¹ Anhydrous solvents were obtained either by filtration through drying columns (THF, ether, CH₂Cl₂, benzene, DMF, CH₃CN, toluene, hexane, methanol). Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel. Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, or aqueous potassium permanganate. Flash column chromatography was performed using 230-400 mesh silica of the indicated solvent system according to standard technique.² Melting points were obtained on a melting point apparatus and are uncorrected. Infrared spectra were taken on a FTIR apparatus and are reported in reciprocal centimeters (cm⁻¹). Nuclear magnetic resonance spectra (¹H, ¹³C, DEPT 135, COSY, HMQC, NOESY) were recorded either on a 300 or 400 MHz spectrometer. Chemical shifts for ¹H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, integration. Chemical shifts for ¹³C NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of deuteriochloroform (77.00 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. When ambiguous, proton and carbon assignments were established using COSY, HMQC and DEPT experiments.

Reagents: Unless otherwise stated, commercial reagents were used without purification. PhI(OAc)₂, malonate esters, alkenes, Rh₂(OAc)₄, Rh₂(esp)₂, (CuOTf)₂·C₆H₆ were commercially available. PhI=O was synthesized according to a previously reported procedure.³ Diazomethyl malonate (**1h**) and diazodiisopropyl malonate (**1i**) were synthesized according to a previously reported procedure.⁴



Synthesis of Bis(methoxycarbonyl)(phenyliodinio)methanide (**1f**)

In a 50-mL flask under argon were added KOH (2.00 g, 36.0 mmol), MeCN (20 mL) and dimethyl malonate (693 μL, 6.00 mmol). The heterogeneous mixture was cooled at 0 °C (ice/water bath) and was stirred vigorously for 5 min to produce a milky white suspension. PhI(OAc)₂ (2.13 g, 6.60 mmol) was then added in one portion and the reaction mixture was stirred vigorously for 2.0 h at 0 °C. The reaction mixture gradually became a thick creamy mixture. Water (10 mL) was then added and the mixture was stirred for 1 min. The beige/yellow biphasic solution containing a fluffy white suspension was filtered. The solid was washed with water (2 x 5 mL). It is important that the solvent be completely removed between each wash. The solid was finally washed with Et₂O (10 mL) then dried under high vacuum to yield **1f** as an off-white solid (1.56 g, 78%): mp 100 °C (decomposition); ¹H NMR (300 MHz, CDCl₃) δ 7.77-7.72 (m, 2H), 7.56-7.50 (m, 1H), 7.44-7.37 (m, 2H), 3.74 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 166.3 (2), 131.6 (2), 131.5 (2), 131.3, 114.3, 52.4 (2); IR (neat) 3081, 2982, 2948, 2899, 1668, 1585, 1575, 1562, 1435, 1425, 1320, 1060, 990 cm⁻¹; Anal. calcd for C₁₁H₁₁IO₄: C, 39.54; H, 3.35; found: C, 39.05; H, 3.34. The spectral data were consistent with that previously reported.⁵ The product partially degraded during the preparation of the NMR sample.

¹ Shriver, D. F.; Drezdson, M. A. *The manipulation of air-sensitive compounds*; 2nd Edition ed.; Wiley: New York, 1986.

² Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

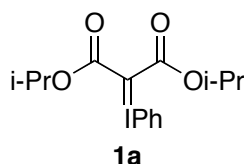
³ Saltzman, H.; Sharefkin, J. G. *Org. Synth.* **1973**, *5*, 658; **1963**, *43*, 60.

⁴ Tallis, J. S.; Helquist, P. *Org. Synth.* **1998**, *74*, 229.

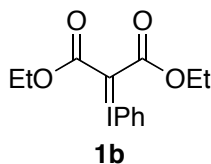
⁵ Müller, P.; Fernández, D. *Helv. Chim. Acta* **1995**, *78*, 947.

General procedure for the synthesis of iodonium ylides:

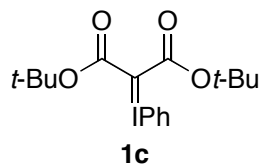
In a 100 mL flask under argon were added KOH (2.00 g, 36.0 mmol), CH₂Cl₂ (20 mL) and the malonate (7.20 mmol). The heterogeneous mixture was put in a room temperature water bath (20 °C) and was stirred vigorously for 5 min to produce a milky white suspension. PhI(OAc)₂ (1.93 g, 6.00 mmol) was then added in one portion and the reaction mixture was stirred vigorously for 2.0 h at room temperature. The reaction mixture gradually became yellow. The heterogeneous mixture was then filtered on a cotton plug and the flask was washed five times with CH₂Cl₂ (5 mL). The yellow solution was then concentrated under reduced pressure at room temperature (20 °C) and then put under high vacuum for 1 h.



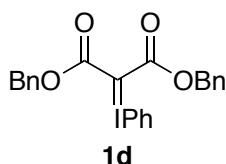
Bis(isopropoxycarbonyl)(phenyliodinio)methanide (1a). Purification: dissolved in a minimum of CH₂Cl₂, crystallized by adding hexane, filtered on Büchner and washed with hexane to yield 1.78 g (76% yield) of a white solid: mp 105 °C (decomposition); ¹H NMR (300 MHz, CDCl₃) δ 7.76-7.71 (m, 2H), 7.53-7.47 (m, 1H), 7.41-7.34 (m, 2H), 4.99 (septet, *J* = 6.2 Hz, 2H), 1.22 (d, *J* = 6.2 Hz, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 165.3 (2), 131.6 (2), 131.0 (2), 130.2, 114.6, 67.7 (2), 22.3 (4); IR (neat) 3043, 2979, 2936, 1599, 1568, 1366, 1301, 1054, 1000, 992 cm⁻¹; Anal. calcd for C₁₅H₁₉IO₄: C, 46.17; H, 4.91; found: C, 46.16; H, 4.81. The product partially degraded during the preparation of the NMR sample.



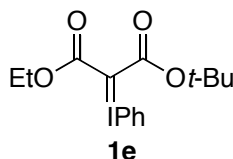
Bis(ethoxycarbonyl)(phenyliodinio)methanide (1b). Purification: dissolved in a minimum of CH₂Cl₂, crystallized by adding hexane, filtered on Büchner and washed with hexane to yield 826 mg (38% yield) of a white solid: mp 72 °C (decomposition); ¹H NMR (300 MHz, CDCl₃) δ 7.75-7.70 (m, 2H), 7.53-7.47 (m, 1H), 7.41-7.34 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 4H), 1.25 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 165.9 (2), 131.6 (2), 131.4 (2), 131.2, 114.4, 60.8 (2), 14.7 (2); IR (neat) 3581, 3515, 3042, 2980, 1600, 1566, 1364, 1321, 1295, 1223, 1163, 1069, 1038, 991 cm⁻¹; Anal. calcd for C₁₃H₁₅IO₄: C, 43.11; H, 4.17; found: C, 42.68; H, 4.24. The product partially degraded during the preparation of the NMR sample.



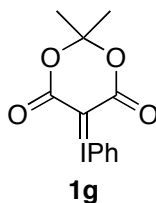
Bis(tert-butoxycarbonyl)(phenyliodinio)methanide (1c). Purification: triturated in hexane, filtered on Büchner and washed with hexane to yield 1.88 g (75% yield) of a beige solid: mp 94 °C (decomposition); ¹H NMR (300 MHz, CDCl₃) δ 7.65-7.60 (m, 2H), 7.43-7.37 (m, 1H), 7.33-7.26 (m, 2H), 1.36 (s, 18H); ¹³C NMR (75 MHz, CDCl₃) δ 165.1 (2), 131.0 (2), 130.7 (2), 130.6, 114.5, 79.5 (2), 28.5 (6); IR (neat) 2982, 2937, 1750, 1738, 1368, 1272, 1255, 1146 cm⁻¹; Anal. calcd for C₁₇H₂₃IO₄: C, 48.82; H, 5.54; found: C, 49.21; H, 5.63. The product partially degraded during the preparation of the NMR sample.



Bis(benzyloxy)(phenyliodonio)methanide (1d). Unable to isolate this ylide analytically pure. Trimethoxybenzene was added as internal standard before concentration to determine the yield (determined from the pic at 3.78 ppm (trimethoxybenzene) and the pic at 5.21 ppm (**1d**)). Crude brown oil (53% yield) was obtained: ^1H NMR (400 MHz, CDCl_3) δ 7.68-7.64 (m, 2H), 7.53-7.49 (m, 1H), 7.40-7.21 (m, 12H), 5.21 (s, 4H).



(tert-Butoxycarbonyl)(ethoxycarbonyl)(phenyliodonio)methanide (1e). Purification: triturated in hexane, filtered on Büchner and washed with hexane to yield 1.71 g (73% yield) of a beige solid: mp 105 °C (decomposition); ^1H NMR (400 MHz, CDCl_3) δ 7.71-7.65 (m, 2H), 7.47-7.42 (m, 1H), 7.36-7.31 (m, 2H), 4.12 (q, $J = 7.1$ Hz, 2H), 1.40 (s, 9H), 1.21 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 164.8, 131.2 (2), 131.1 (2), 130.8, 114.5, 79.7, 60.6, 28.4 (3), 14.6; IR (neat) 3058, 2991, 2971, 2927, 1618, 1325, 1215, 1162, 1059, 1045, 1011, 989 cm^{-1} ; Anal. calcd for $\text{C}_{15}\text{H}_{19}\text{IO}_4$: C, 46.17; H, 4.91; found: C, 46.39; H, 4.86. The product partially degraded during the preparation of the NMR sample.

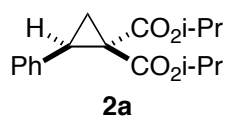


2-Phenyliodonio-5,5-dimethyl-4,6-dioxo-1,3-dioxocyclohexane methylide (1g). Purification: triturated in hexane, filtered on Büchner and washed with hexane to yield 1.46 g (70% yield) of a white solid: mp 92 °C (decomposition), [lit.⁶ 97 °C (decomposition)]; ^1H NMR (300 MHz, CDCl_3) δ 7.92-7.86 (m, 2H), 7.60-7.54 (m, 1H), 7.46-7.38 (m, 2H), 1.70 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 163.7 (2), 132.9 (2), 131.5, 131.4 (2), 114.6, 104.3, 56.1, 25.6 (2); IR (neat) 2982, 2844, 1622, 1283, 1192, 1026, 991, 908 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{11}\text{IO}_4$ $[\text{M}+\text{H}]^+$: 346.9778, found 346.9775. The spectral data were consistent with that previously reported.⁷

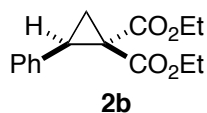
General procedure for the cyclopropanation of styrene with iodonium ylides or diazomalonates catalyzed by rhodium or copper: Cyclopropanes **2a-f** were prepared according to the following general procedure. In a 10 mL flask was added styrene (573 μL , 5.00 mmol), CH_2Cl_2 (2.0 mL) and the catalyst (5.0 μmol , 0.5 mol %). The iodonium ylide or the diazomalonate (1.00 mmol) was then added in one portion (iodonium ylide) or over 1 h (diazomalonate) at room temperature. Reaction mixture was stirred for 3 h. The solution was then concentrated and purified by flash chromatography on silica gel.

⁶ Schank, K.; Lick, C. *Synthesis* **1983**, 392.

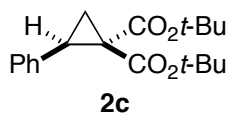
⁷ Müller, P.; Allenbach, Y.; Robert, E. *Tetrahedron: Asymmetry* **2003**, 14, 779.



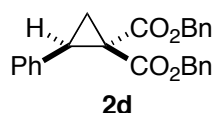
Diisopropyl 2-phenylcyclopropane-1,1-dicarboxylate (2a). Iodonium ylide **1a** and (CuOTf)•C₆H₆ was used. Purified by chromatography on silica gel (5% EtOAc/hexane) to yield 177 mg (61% yield) of colorless oil: *R_f* 0.38 (10% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.17 (m, 5H), 5.09 (septet, *J* = 6.3 Hz, 1H), 4.72 (septet, *J* = 6.3 Hz, 1H), 2.13 (dd, *J* = 8.0, 5.2 Hz, 1H), 1.64 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.26 (d, *J* = 6.3 Hz, 3H), 1.05 (d, *J* = 6.3 Hz, 3H), 0.68 (d, *J* = 6.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.5, 166.2, 134.7, 128.5 (2), 128.0 (2), 127.1, 69.2, 68.5, 37.8, 31.7, 21.7, 21.6, 21.2, 21.0, 18.3; IR (neat) 2980, 2937, 1717, 1374, 1315, 1275, 1215, 1099 cm⁻¹; HRMS (ESI) calcd for C₁₇H₂₂O₄ [M+Na]⁺: 313.1410, found 313.1413.



Diethyl 2-phenylcyclopropane-1,1-dicarboxylate (2b). Iodonium ylide **1b** (0.85 mmol) and Rh₂(OAc)₄ was used. Purified by chromatography on silica gel (5% EtOAc/hexane) to yield 108 mg (49% yield) of colorless oil: *R_f* 0.34 (10% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.19 (m, 5H), 4.32-4.18 (m, 2H), 3.85 (qd, *J* = 7.2, 0.4 Hz, 2H), 3.22 (t, *J* = 8.6 Hz, 1H), 2.18 (dd, *J* = 8.0, 5.2 Hz, 1H), 1.71 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 166.6, 134.6, 128.5 (2), 128.1 (2), 127.3, 61.7, 61.1, 37.4, 32.1, 18.7, 14.1, 13.6; IR (neat) 2982, 1720, 1321, 1273, 1213, 1188, 1129 cm⁻¹. The spectral data were consistent with that previously reported.⁸



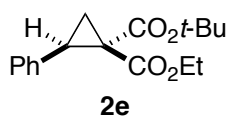
Di-tert-butyl 2-phenylcyclopropane-1,1-dicarboxylate (2c). Iodonium ylide **1c** and Rh₂(OAc)₄ was used. Purified by chromatography on silica gel (5% EtOAc/hexane) to yield 74.7 mg (47% yield) of a white solid: mp 101-103 °C; *R_f* 0.47 (10% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.18 (m, 5H), 3.10 (t, *J* = 8.6 Hz, 1H), 2.03 (dd, *J* = 7.8, 5.0 Hz, 1H), 1.53 (dd, *J* = 9.0, 5.0 Hz, 1H), 1.51 (s, 9H), 1.10 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 169.2, 165.8, 134.9, 128.7 (2), 127.9 (2), 126.9, 81.6, 80.8, 39.2, 30.8, 28.0 (3), 27.4 (3), 17.6; IR (neat) 2977, 2932, 1715, 1367, 1333, 1289, 1165, 1126 cm⁻¹. The spectral data were consistent with that previously reported.⁹



Dibenzyl 2-phenylcyclopropane-1,1-dicarboxylate (2d). Iodonium ylide **1d** (crude mixture) and (CuOTf)•C₆H₆ was used. Purified by chromatography on silica gel (10% EtOAc/hexane) to yield 97 mg (25% yield, 2 steps) of a white solid: mp 67-69 °C (lit.⁸ 67-69 °C); *R_f* 0.30 (10% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.18 (m, 13H), 6.97-6.92 (m, 2H), 5.28 (d, *J* = 12.4 Hz, 1H), 5.17 (d, *J* = 12.4 Hz, 1H), 4.76 (s, 2H), 3.29 (t, *J* = 8.6 Hz, 1H), 2.24 (dd, *J* = 8.1, 5.2 Hz, 1H), 1.78 (dd, *J* = 9.2, 5.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 169.5, 166.3, 135.3, 135.0, 134.3, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.3, 67.2, 67.1, 37.4, 32.6, 19.1; IR (neat) 3032, 2952, 1721, 1320, 1270, 1212, 1178, 1125 cm⁻¹. The spectral data were consistent with that previously reported.⁸

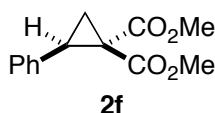
⁸ Watanabe, S.; Nakayama, I.; Kataoka, T. *Eur. J. Org. Chem.* **2005**, 1493.

⁹ Doyle, M. P.; Hu, W. *ARKIVOC* **2003**, 7, 15.

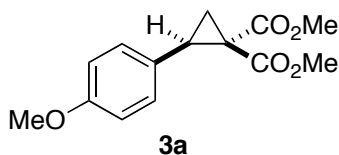


1-tert-Butyl 1-ethyl (1*S,2*R**)-2-phenylcyclopropane-1,1-dicarboxylate (2e).** Purified by chromatography on silica gel (5% EtOAc/hexane) to yield 58.0 mg (40% yield) of colorless oil: R_f 0.43 (10% EtOAc/hexane); ^1H NMR (300 MHz, CDCl_3) δ 7.31-7.18 (m, 5H), 3.94-3.77 (m, 2H), 3.15 (t, J = 8.6 Hz, 1H), 2.11 (dd, J = 7.9, 5.1 Hz, 1H), 1.64 (dd, J = 9.2, 5.1 Hz, 1H), 1.51 (s, 9H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.7, 166.9, 134.9, 128.4 (2), 128.0 (2), 127.0, 81.9, 60.8, 38.4, 31.3, 27.9 (3), 18.2, 13.7; IR (neat) 2979, 2934, 1716, 1368, 1288, 1165, 1126 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{22}\text{O}_4$ $[\text{M}+\text{Na}]^+$: 313.1410, found 313.1411.

General procedure for the synthesis of 1,1-cyclopropanediester using $\text{Rh}_2(\text{esp})_2$: Cyclopropanes **2f**, **3a-g** were prepared according to the following general procedure. In a 25 mL flask under argon were added $\text{Rh}_2(\text{esp})_2$ (2.0 mg, 2.5 μmol), CH_2Cl_2 (5.0 mL) and the alkene (2.50 mmol). The reaction mixture was cooled at 0 $^\circ\text{C}$ (ice/water bath) and the iodonium ylide **1f** (1.09 g, 3.25 mmol) was added in one portion (or in small portions if it reacts too quickly). Reaction mixture was stirred for 15 min at 0 $^\circ\text{C}$ and then 2 h at room temperature. The solution was then concentrated and purified by chromatography on silica gel.

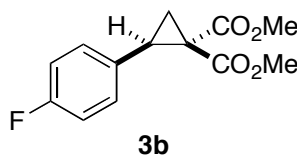


Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (2f). 0.005 mol % of $\text{Rh}_2(\text{esp})_2$ was used and the reaction was performed on a 5 mmol scale. Purified by chromatography on silica gel (10% EtOAc/hexane) to yield 1.07 g (91% yield) of a colorless oil: R_f 0.53 (20% EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.17 (m, 5H), 3.77 (s, 3H), 3.34 (s, 3H), 3.23 (t, J = 8.6 Hz, 1H), 2.19 (dd, J = 8.0, 5.2 Hz, 1H), 1.73 (dd, J = 9.2, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.1, 166.9, 134.5, 128.3 (2), 128.0 (2), 127.3, 52.6, 52.0, 37.1, 32.4, 19.0; IR (neat) 2953, 1726, 1436, 1332, 1277, 1217, 1130 cm^{-1} . The spectral data were consistent with that previously reported.¹⁰

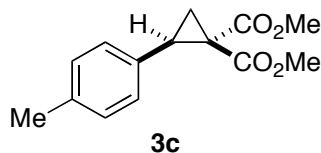


Dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (3a). Purified by chromatography on silica gel (10% EtOAc/hexane) to yield 515 mg (78% yield) of a colorless oil: R_f 0.41 (20% EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.12-7.09 (m, 2H), 6.81-6.77 (m, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.38 (s, 3H), 3.17 (t, J = 8.8 Hz, 1H), 2.14 (dd, J = 8.0, 5.2 Hz, 1H), 1.71 (dd, J = 9.2, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 167.1, 158.8, 129.5 (2), 126.3, 113.5 (2), 55.1, 52.7, 52.2, 37.0, 32.1, 19.2; IR (neat) 3002, 2953, 2838, 1721, 1612, 1516, 1435, 1276, 1247, 1216, 1174, 1128 cm^{-1} . The spectral data were consistent with that previously reported.¹⁰

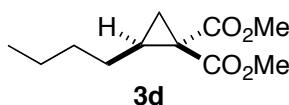
¹⁰ Perreault, C.; Goudreau, S. R.; Zimmer, L. E.; Charette, A. B. *Org. Lett.* **2008**, *10*, 689.



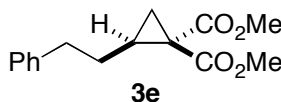
Dimethyl 2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate (3b). Purified by chromatography on silica gel (10% EtOAc/hexane) to yield 600 mg (95% yield) of colorless oil: R_f 0.25 (10% EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.19-7.14 (m, 2H), 6.99-6.93 (m, 2H), 3.79 (s, 3H), 3.39 (s, 3H), 3.19 (t, J = 8.8 Hz, 1H), 2.15 (dd, J = 8.0, 5.6 Hz, 1H), 1.74 (dd, J = 9.2, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.1, 166.9, 162.1 (d, J = 240 Hz), 130.3, 130.2 (d, J = 10 Hz, 2C), 115.1 (d, J = 20 Hz, 2C), 52.8, 52.3, 37.0, 31.7, 19.2; IR (neat) 2954, 1723, 1514, 1436, 1277, 1217, 1129 cm^{-1} ; HRMS(ESI) calcd for $\text{C}_{13}\text{H}_{13}\text{FO}_4$ $[\text{M}+\text{Na}]^+$: 275.0690, found 275.0695. The spectral data were consistent with that previously reported.¹⁰



Dimethyl 2-(4-methylphenyl)cyclopropane-1,1-dicarboxylate (3c). Purified by chromatography on silica gel (10% EtOAc/hexane) to yield 589 mg (95% yield) of colorless oil: R_f 0.41 (20% EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.07 (s, 4H), 3.78 (s, 3H), 3.38 (s, 3H), 3.20 (t, J = 8.6 Hz, 1H), 2.30 (s, 3H), 2.17 (dd, J = 8.0, 5.1 Hz, 1H), 1.72 (dd, J = 9.3, 5.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 167.0, 136.9, 131.3, 128.8 (2), 128.2 (2), 52.6, 52.1, 37.0, 32.3, 20.9, 19.0; IR (neat) 2952, 2866, 2844, 1722, 1435, 1331, 1274, 1213, 1127 cm^{-1} . The spectral data were consistent with that previously reported.¹¹



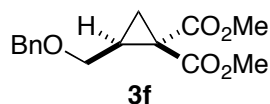
Dimethyl 2-butylcyclopropane-1,1-dicarboxylate (3d). Purified by chromatography on silica gel (10% EtOAc/hexane) to yield 504 mg (94% yield) of a colorless oil: R_f 0.52 (20% EtOAc/hexane); ^1H NMR (300 MHz, CDCl_3) δ 3.74 (s, 3H), 3.71 (s, 3H), 1.94-1.83 (m, 1H), 1.51-1.24 (m, 7H), 1.21-1.09 (m, 1H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.9, 168.7, 52.5, 52.4, 33.8, 30.9, 28.7, 28.3, 22.2, 21.3, 13.9; IR (neat) 2955, 2932, 2862, 1723, 1435, 1278, 1209, 1129 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{18}\text{O}_4$ $[\text{M}+\text{Na}]^+$: 237.1097, found 237.1093.



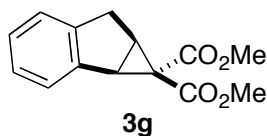
Dimethyl 2-(2-phenylethyl)cyclopropane-1,1-dicarboxylate (3e). Purified by chromatography on silica gel (10% EtOAc/hexane) to yield 610 mg (93% yield) of a colorless oil: R_f 0.43 (20% EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.27 (m, 2H), 7.24-7.16 (m, 3H), 3.79 (s, 3H), 3.75 (s, 3H), 2.82-2.69 (m, 2H), 1.97 (qn, J = 7.8 Hz, 1H), 1.84-1.74 (m, 1H), 1.61-1.51 (m, 1H), 1.47-1.38 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.7, 168.6, 141.3, 128.3 (4), 125.9, 52.5 (2), 35.1, 33.9, 30.7, 28.2, 21.2; IR (neat) 2951, 2863, 2844, 1722, 1436, 1327, 1285, 1210, 1132, 1032 cm^{-1} . The spectral data were consistent with that previously reported.¹²

¹¹ Müller, P.; Ghanem, A. *Org. Lett.* **2004**, *6*, 4347.

¹² González-Bobes, F.; Fenster, M. D. B.; Kiau, S.; Kolla, L.; Kolotuchin, S.; Soumeillant, M. *Adv. Synth. Catal.* **2008**, *350*, 813.

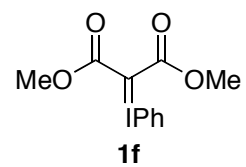


Dimethyl 2-[(benzyloxy)methyl]cyclopropane-1,1-dicarboxylate (3f). Purified by chromatography on silica gel (10% EtOAc/hexane) to yield 480 mg (69% yield) of colorless oil: R_f 0.29 (20% EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.20 (m, 5H), 4.48-4.38 (m, 2H), 3.69 (s, 3H), 3.64 (s, 3H), 3.55 (dd, $J = 10.5, 5.6$ Hz, 1H), 3.42 (dd, $J = 10.5, 7.1$ Hz, 1H), 2.28-2.18 (m, 1H), 1.55 (dd, $J = 7.6, 4.2$ Hz, 1H), 1.42 (dd, $J = 9.2, 4.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 168.1, 137.8, 128.2 (2), 127.5 (3), 72.7, 67.6, 52.6, 52.4, 32.6, 27.3, 18.7; IR (neat) 3030, 2953, 2861, 1723, 1436, 1330, 1274, 1210, 1128 cm^{-1} . The spectral data were consistent with that previously reported.¹²

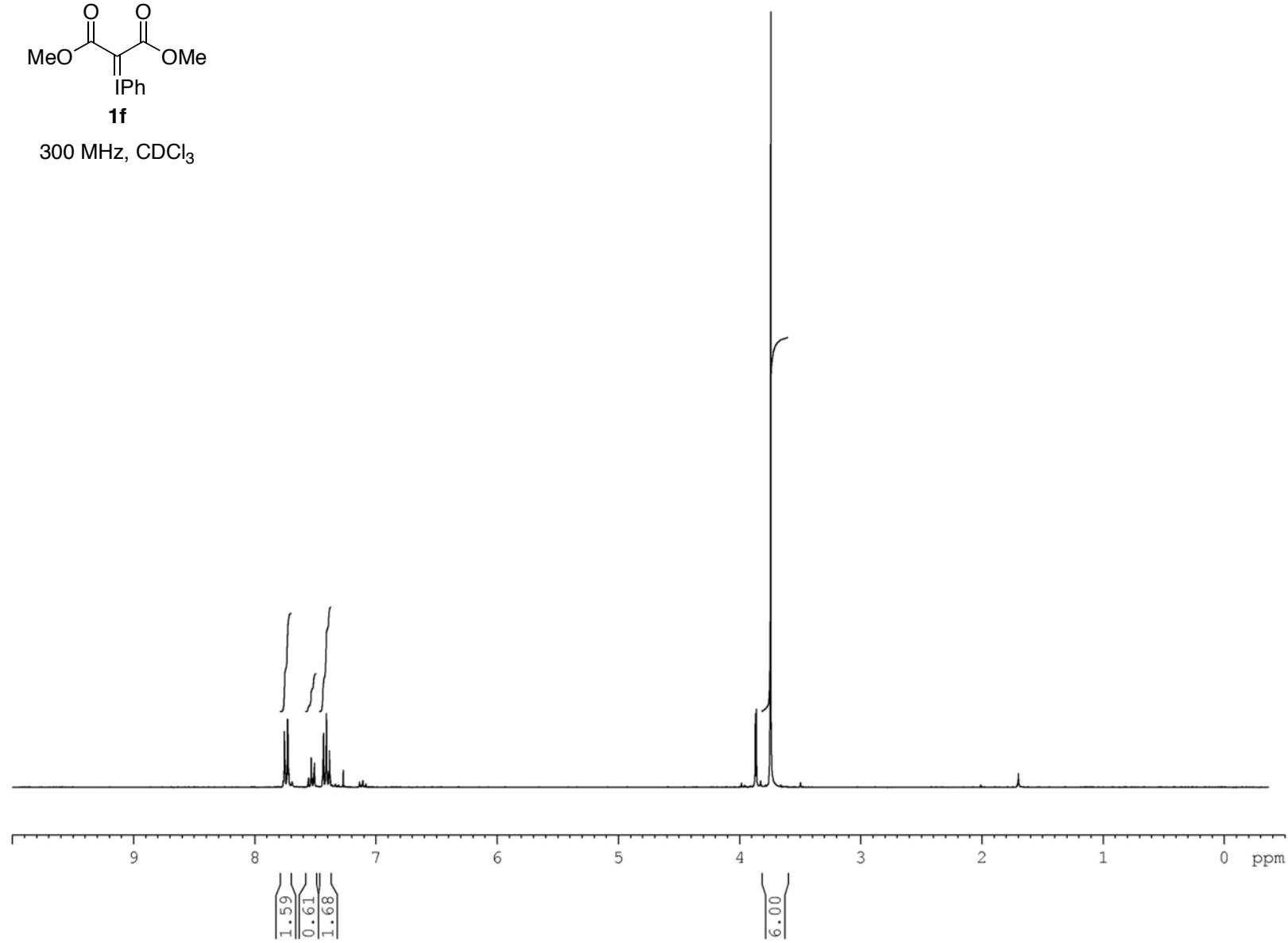


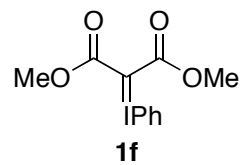
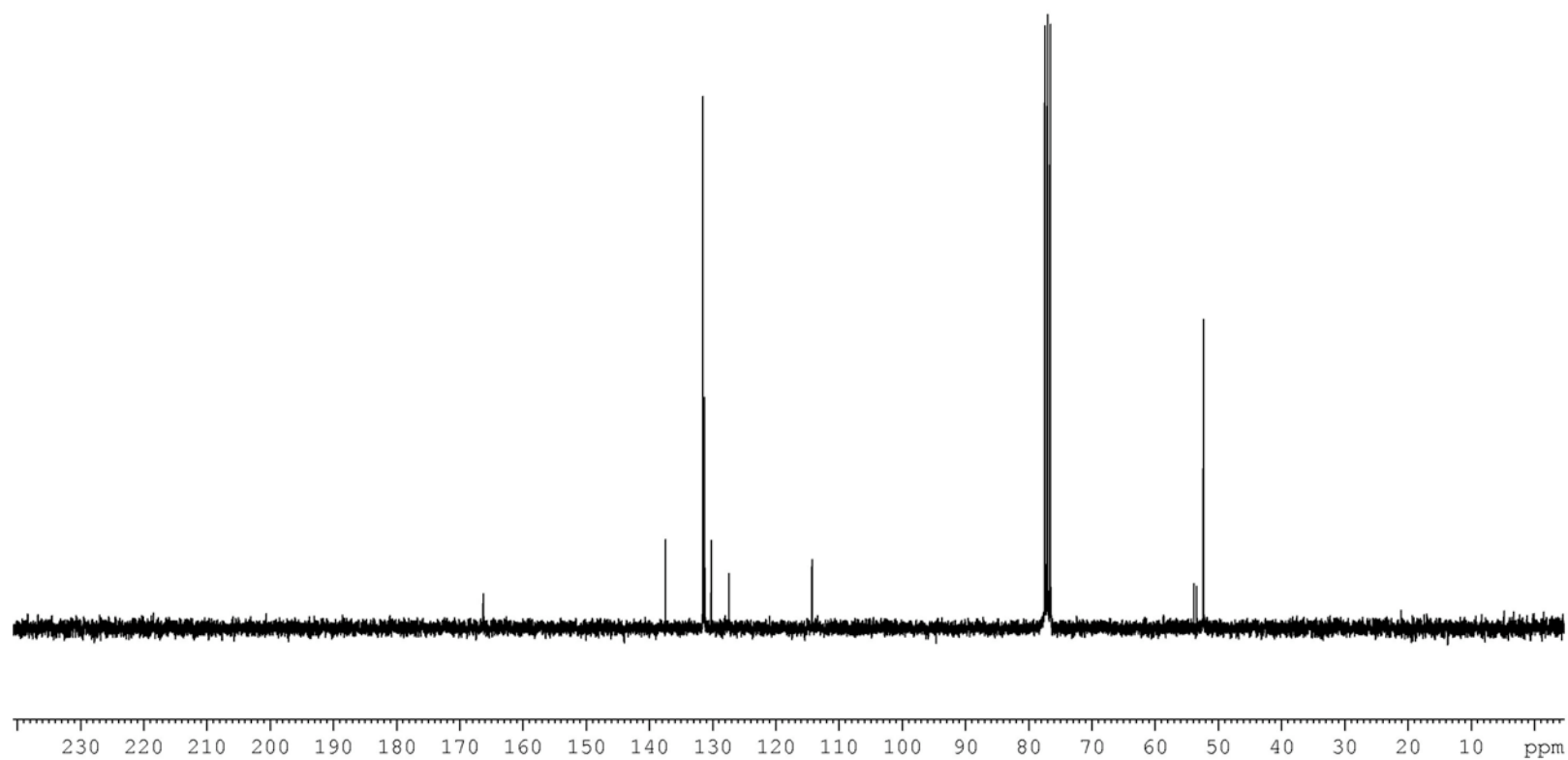
Dimethyl (1a*S,6a*S**)-6,6a-dihydrocyclopropa[*a*]indene-1,1(1a*H*)-dicarboxylate (3g).** Stirred for 16 h. Purified by chromatography on silica gel (10% EtOAc/hexane) to yield 517 mg (84% yield) of a colorless oil: R_f 0.38 (20% EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.35 (m, 1H), 7.20-7.12 (m, 3H), 3.76 (s, 3H), 3.40-3.23 (m, 6H), 2.68 (td, $J = 6.2, 1.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.8, 165.9, 141.5, 140.1, 127.0, 126.7, 125.4, 124.8, 52.7, 51.9, 39.5, 39.3, 33.4, 31.5; IR (neat) 2951, 2844, 1723, 1435, 1331, 1311, 1260, 1225, 1155 cm^{-1} . The spectral data were consistent with that previously reported.¹²

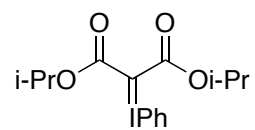
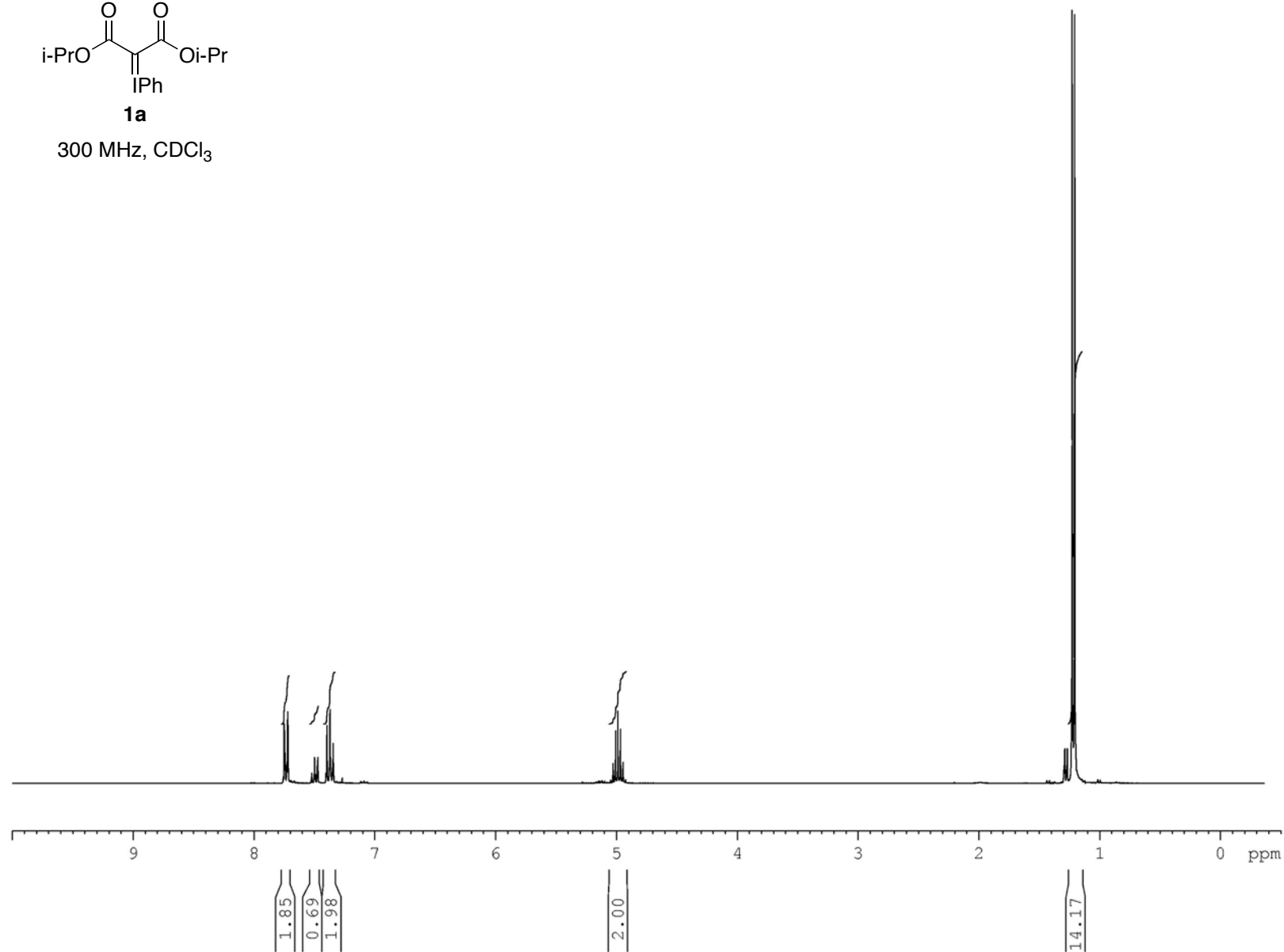
^1H and ^{13}C NMR Spectra of selected compounds

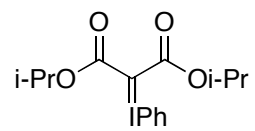
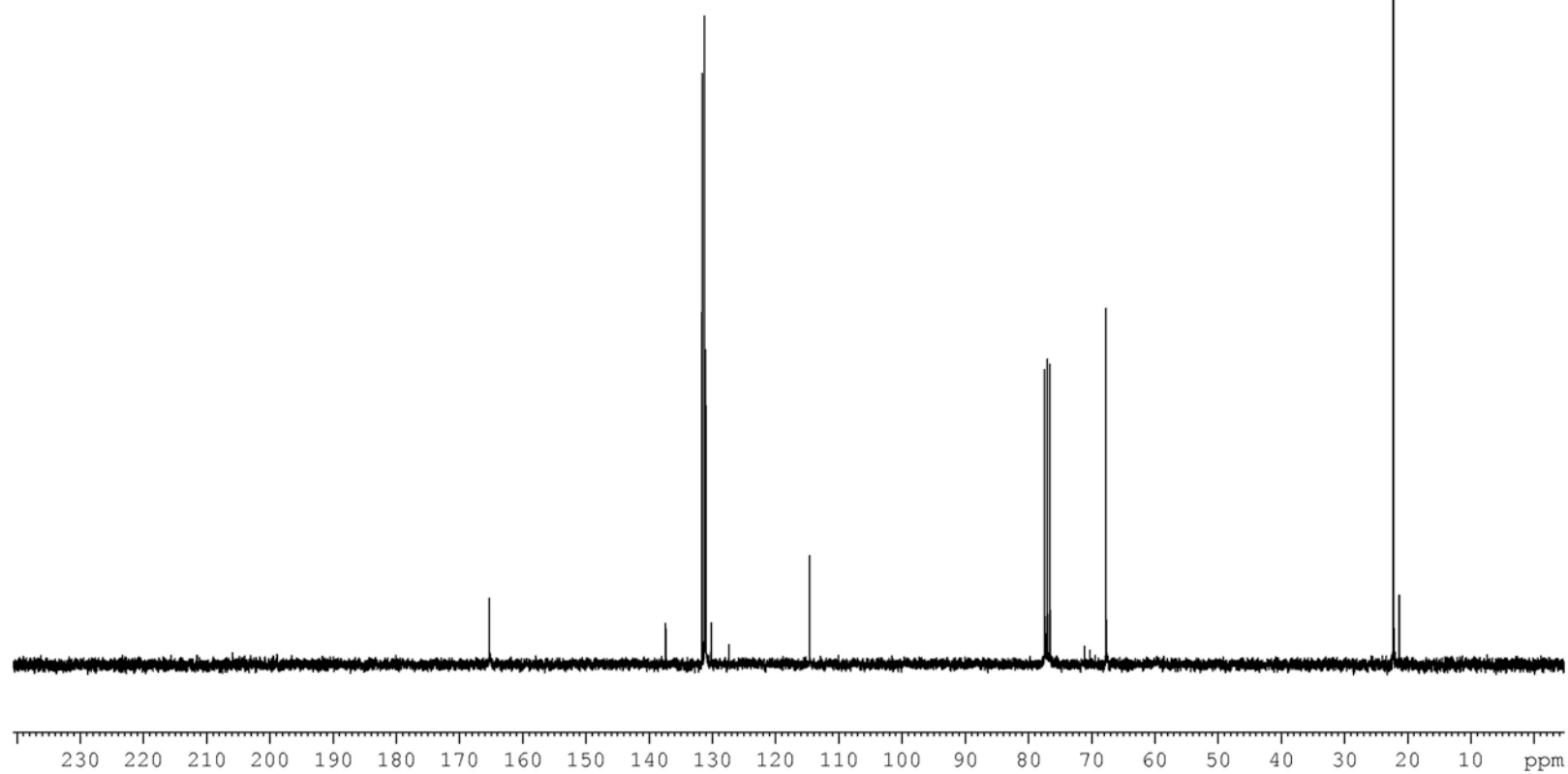


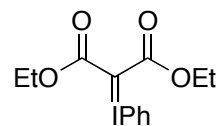
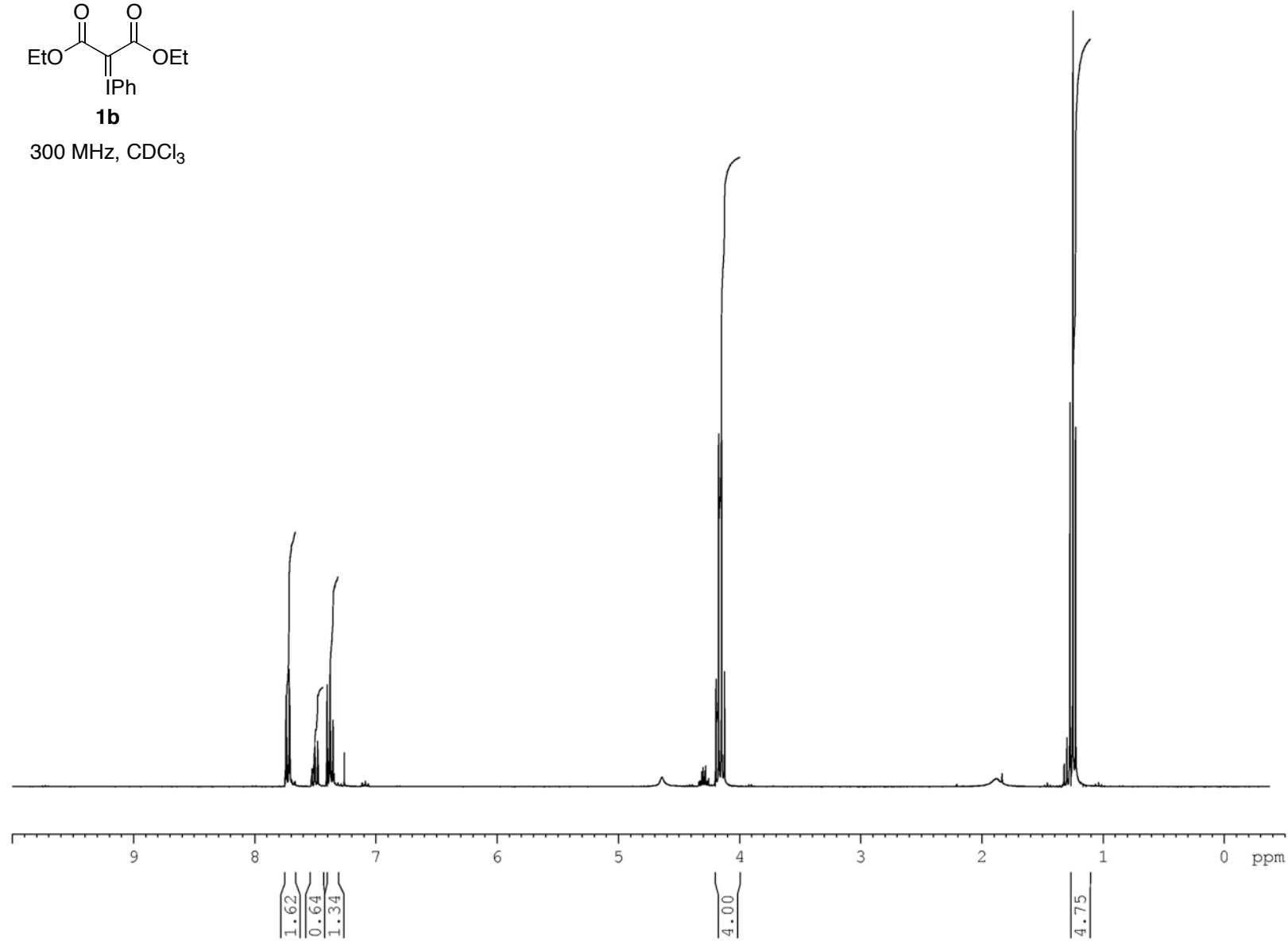
300 MHz, CDCl₃

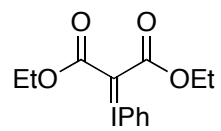
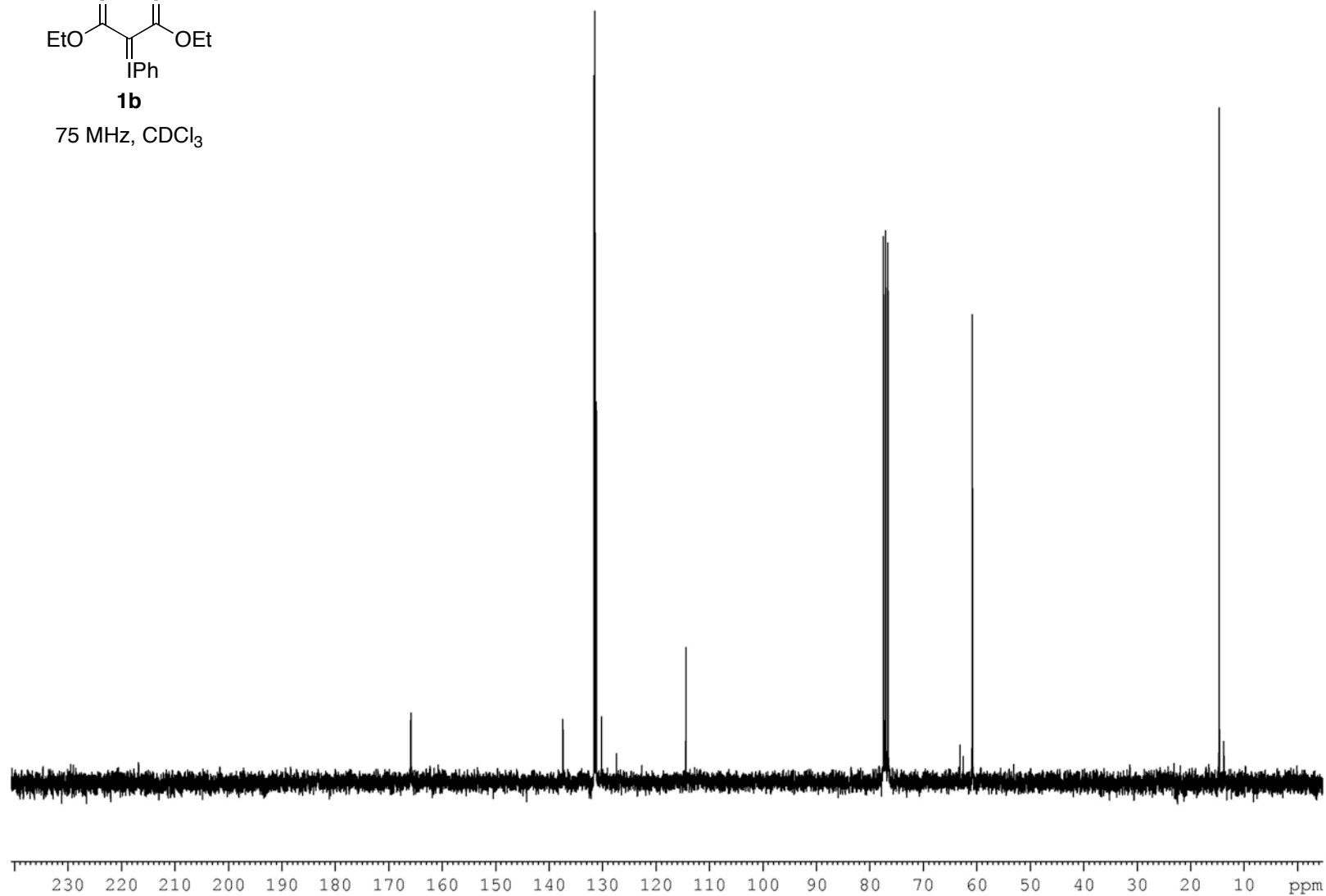


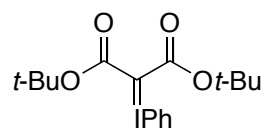
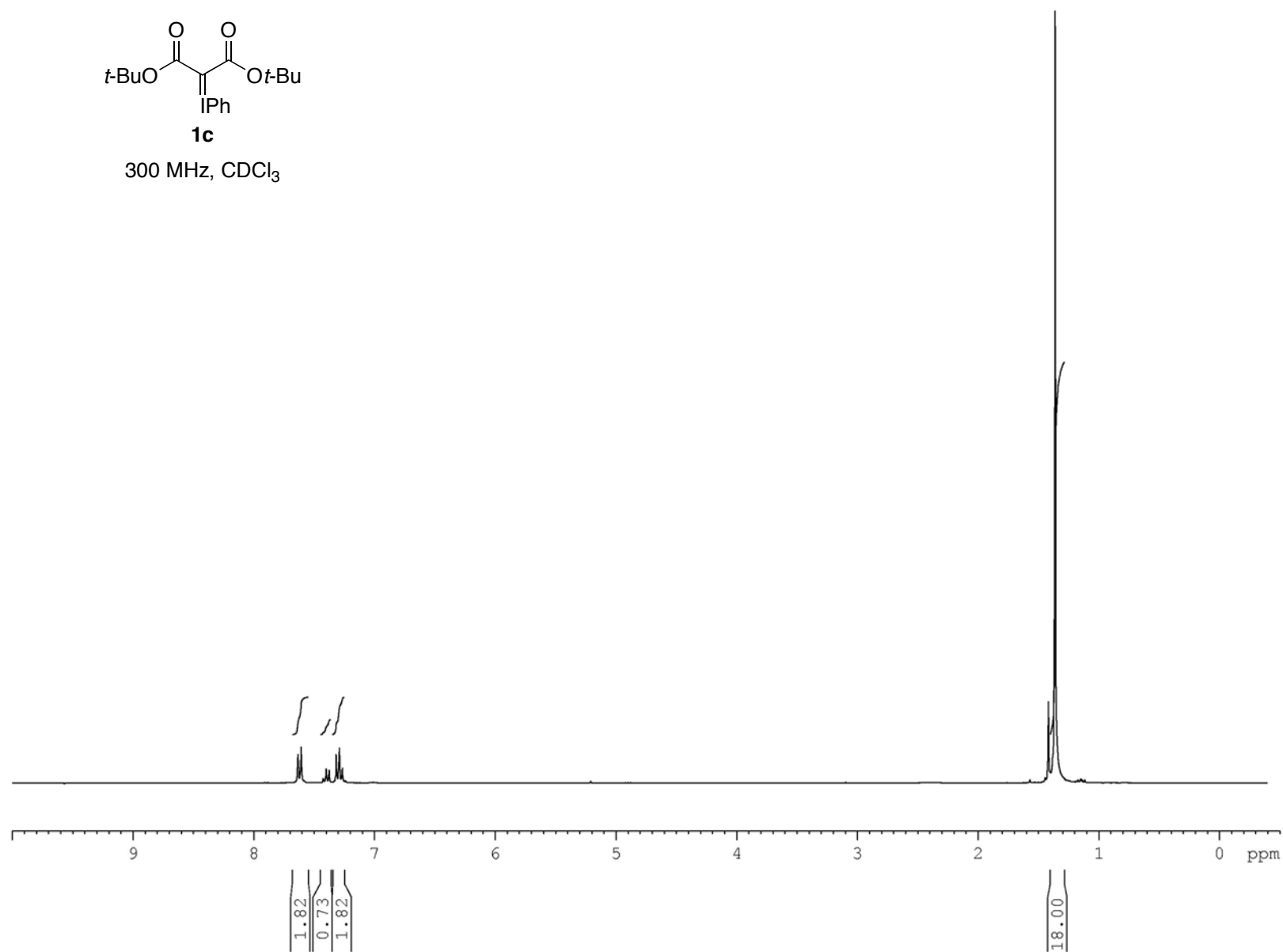
75 MHz, CDCl₃

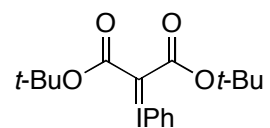
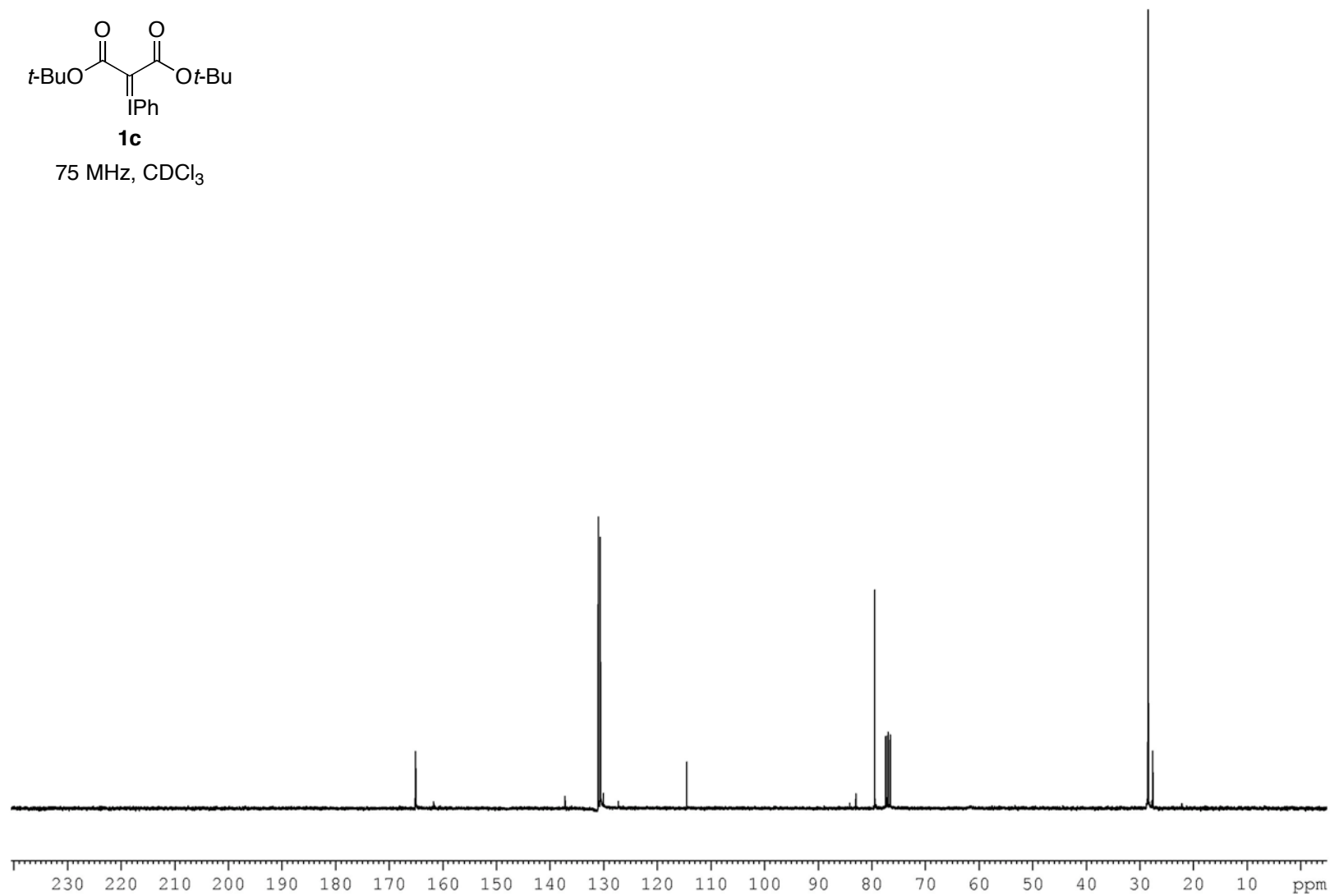
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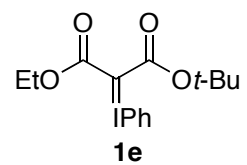
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**1b**300 MHz, CDCl₃

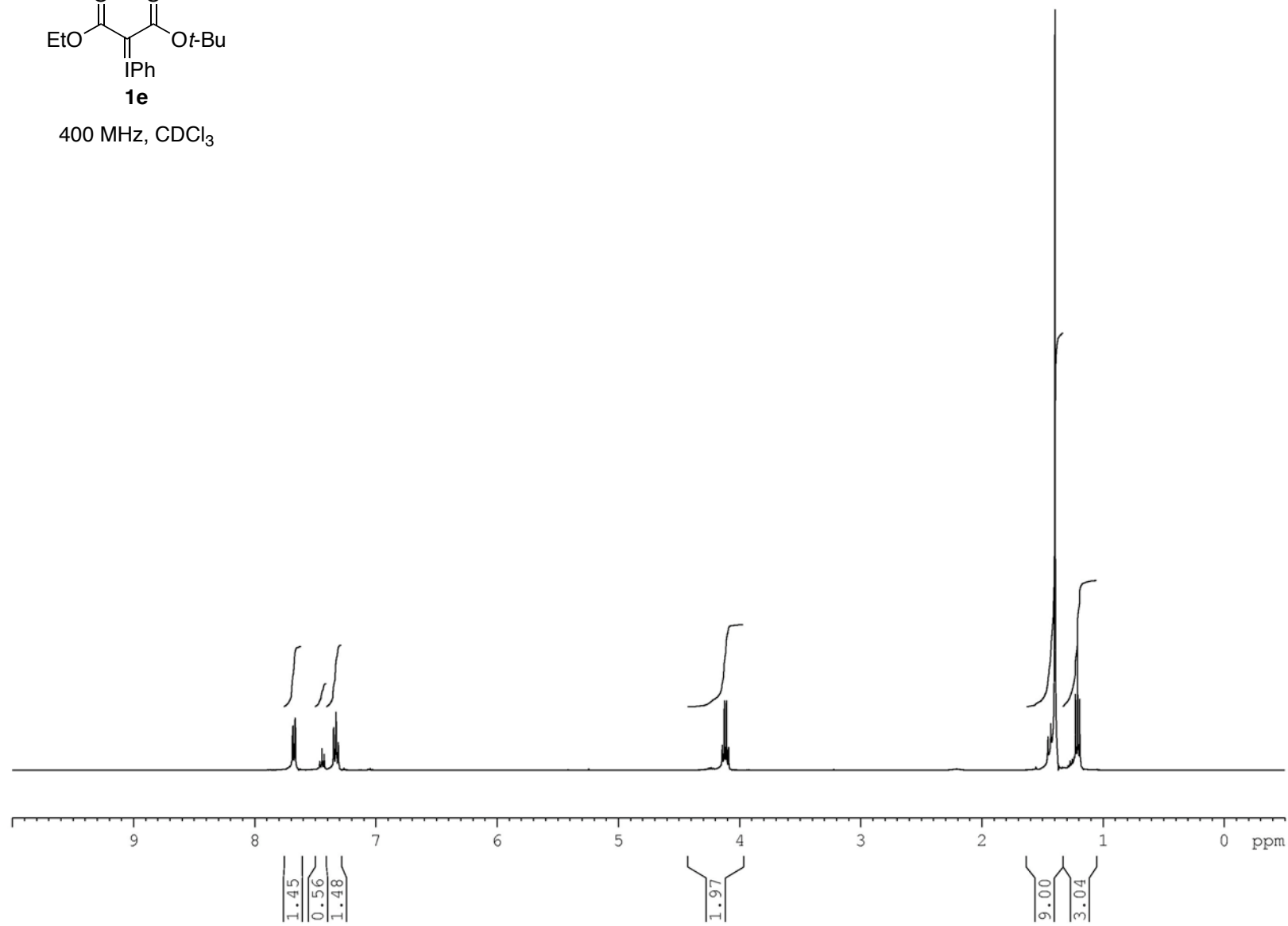
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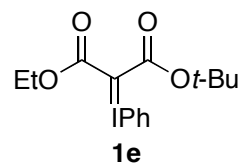
**1c**300 MHz, CDCl₃

**1c**75 MHz, CDCl_3 

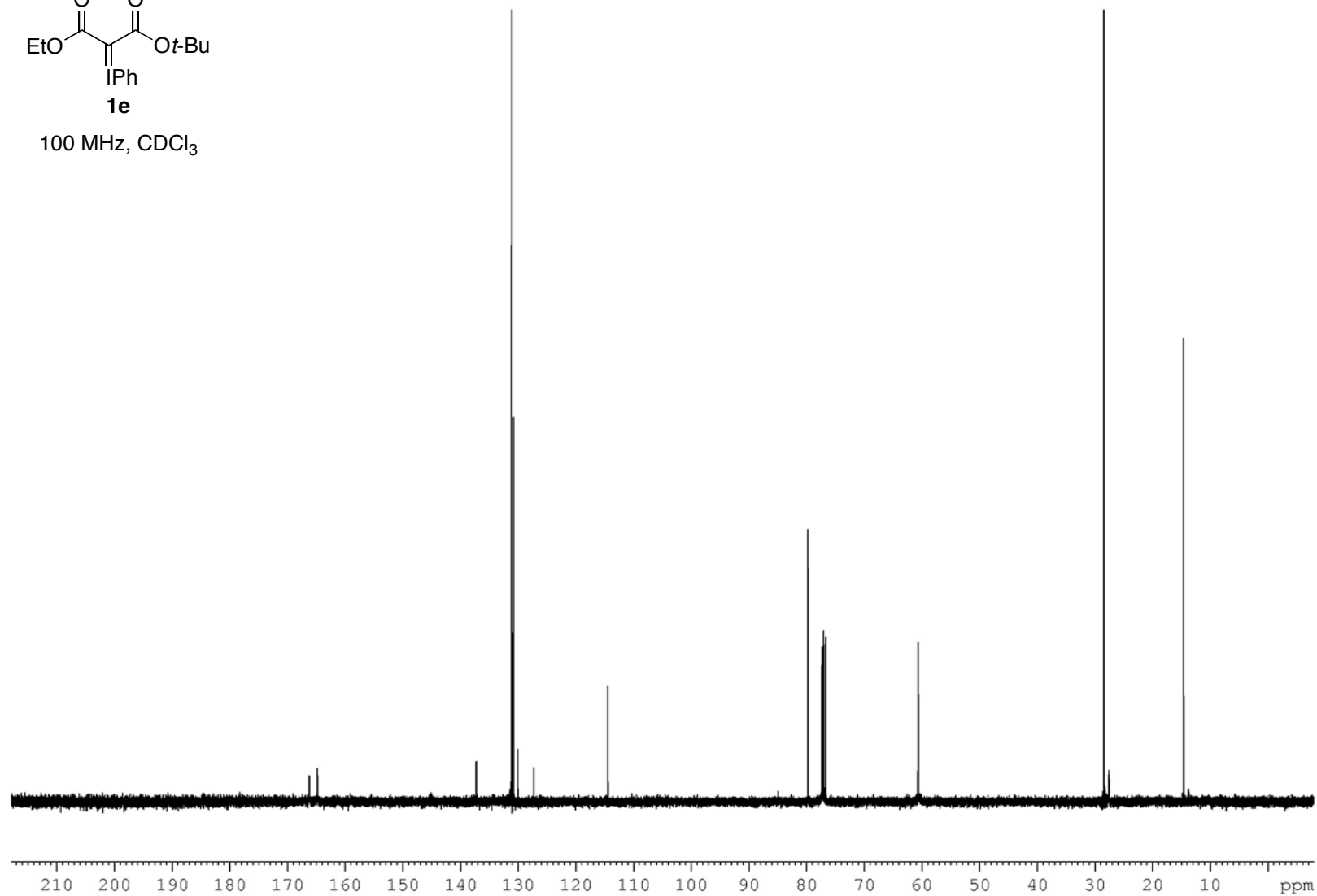


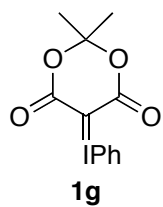
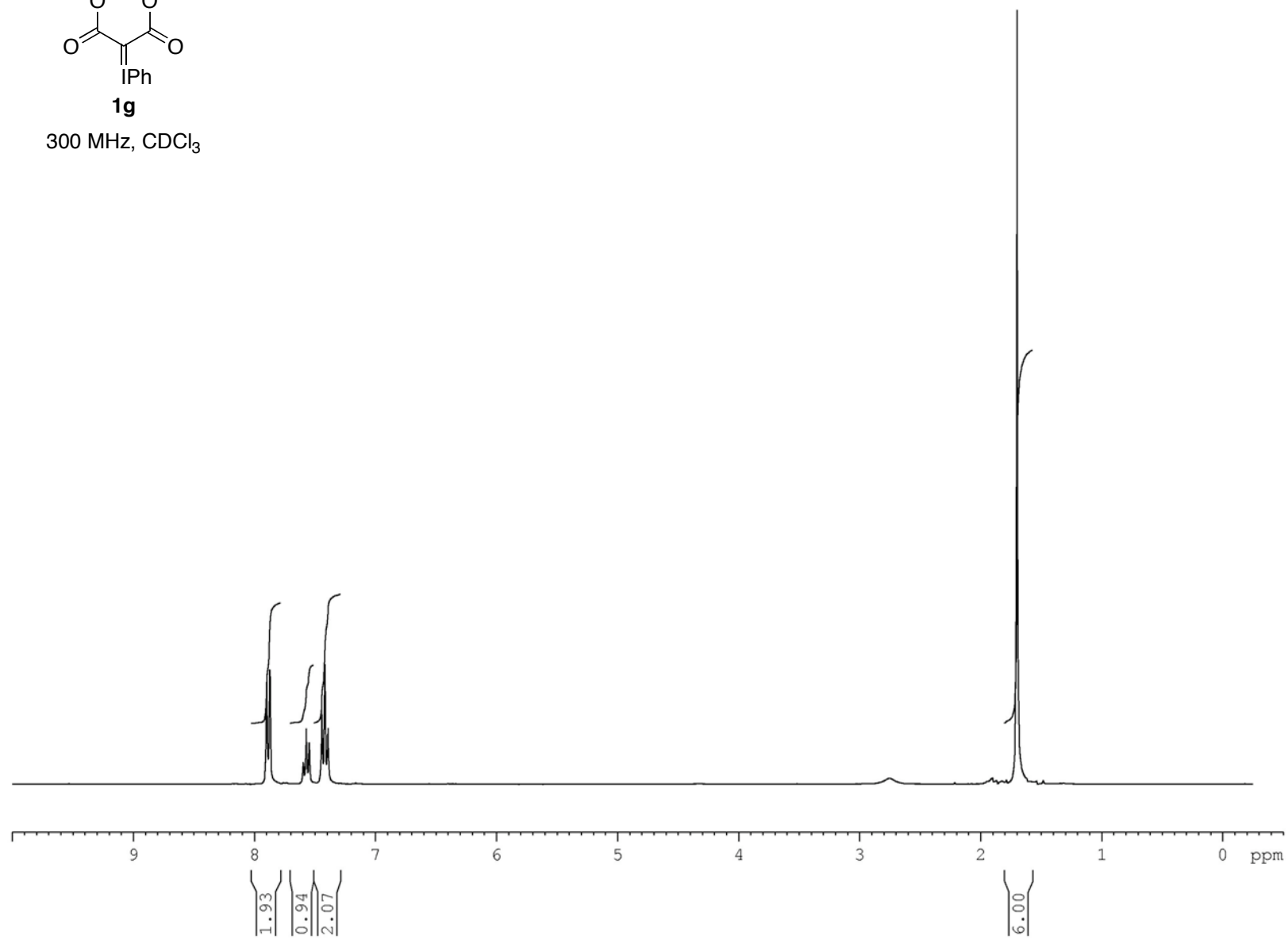
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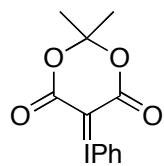




100 MHz, CDCl₃

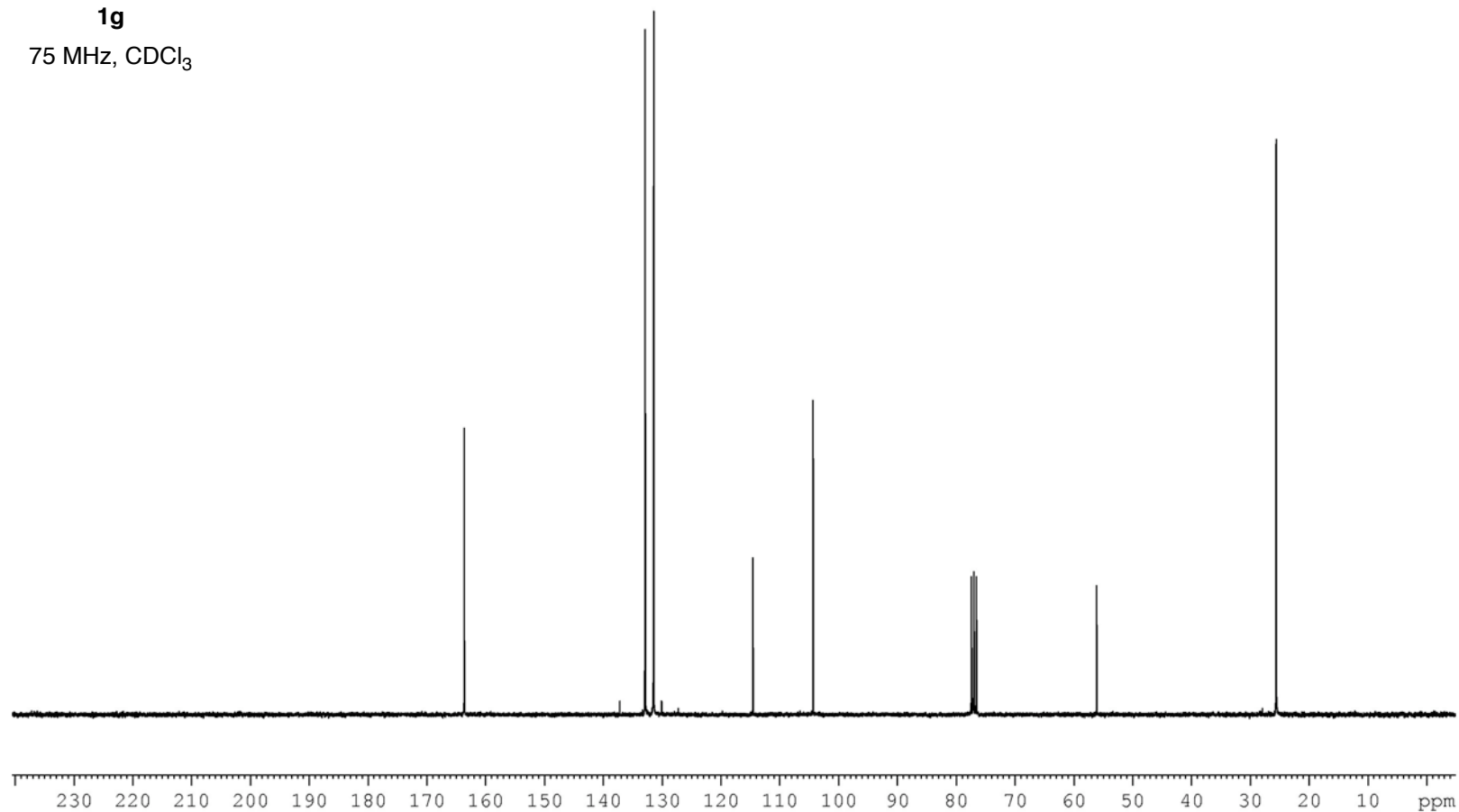


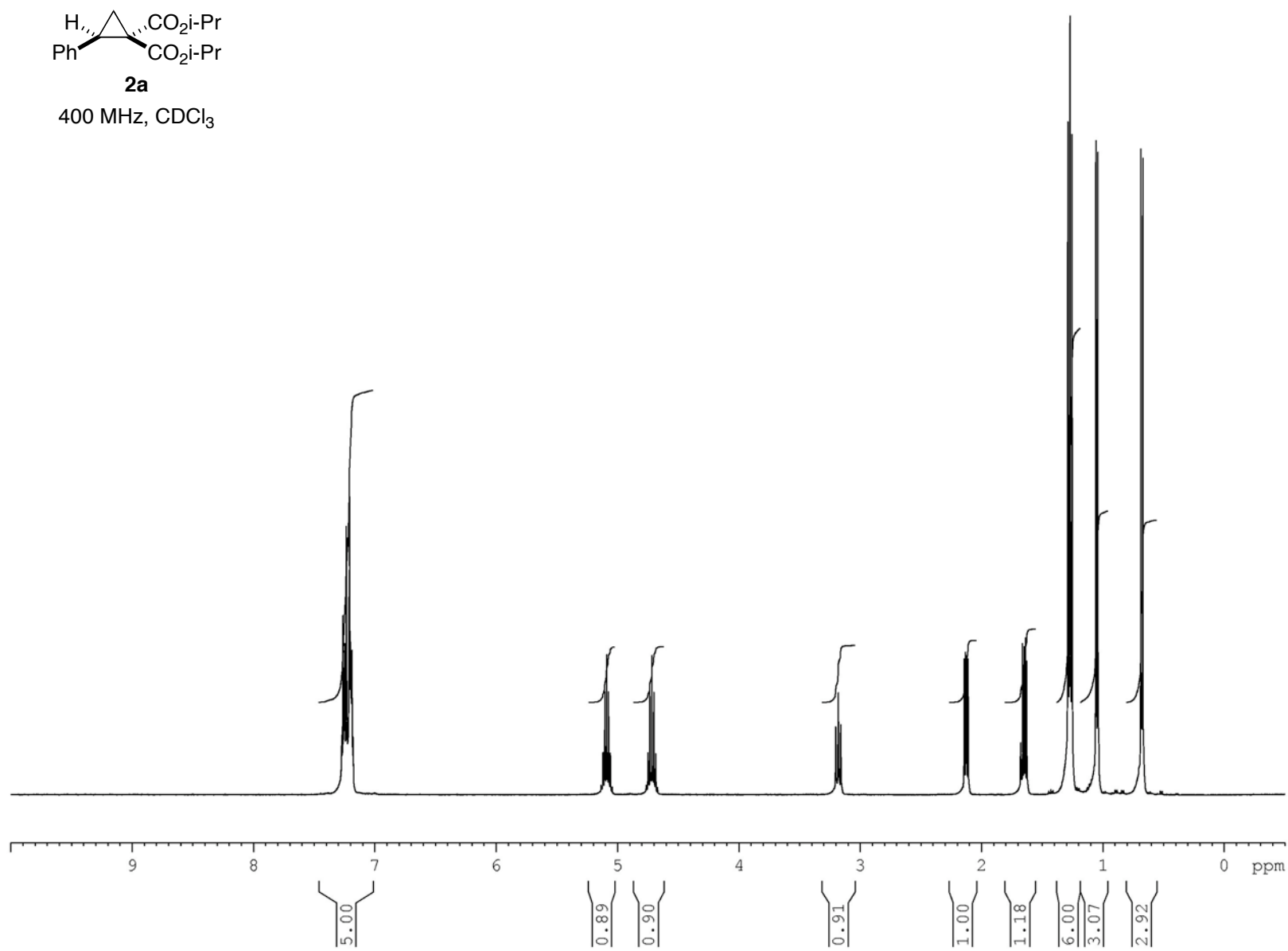
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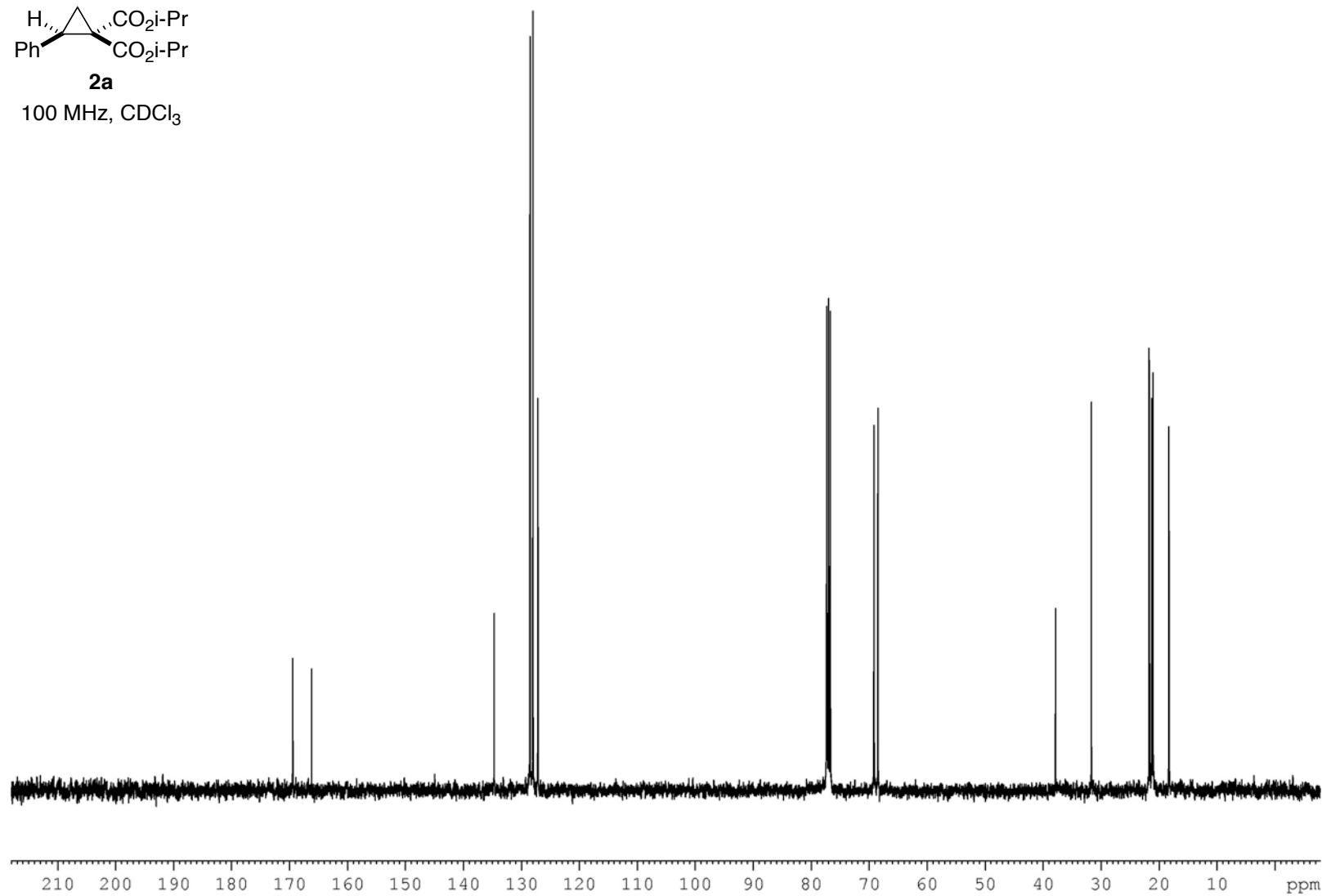
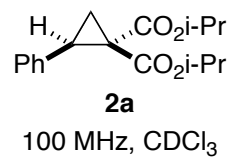


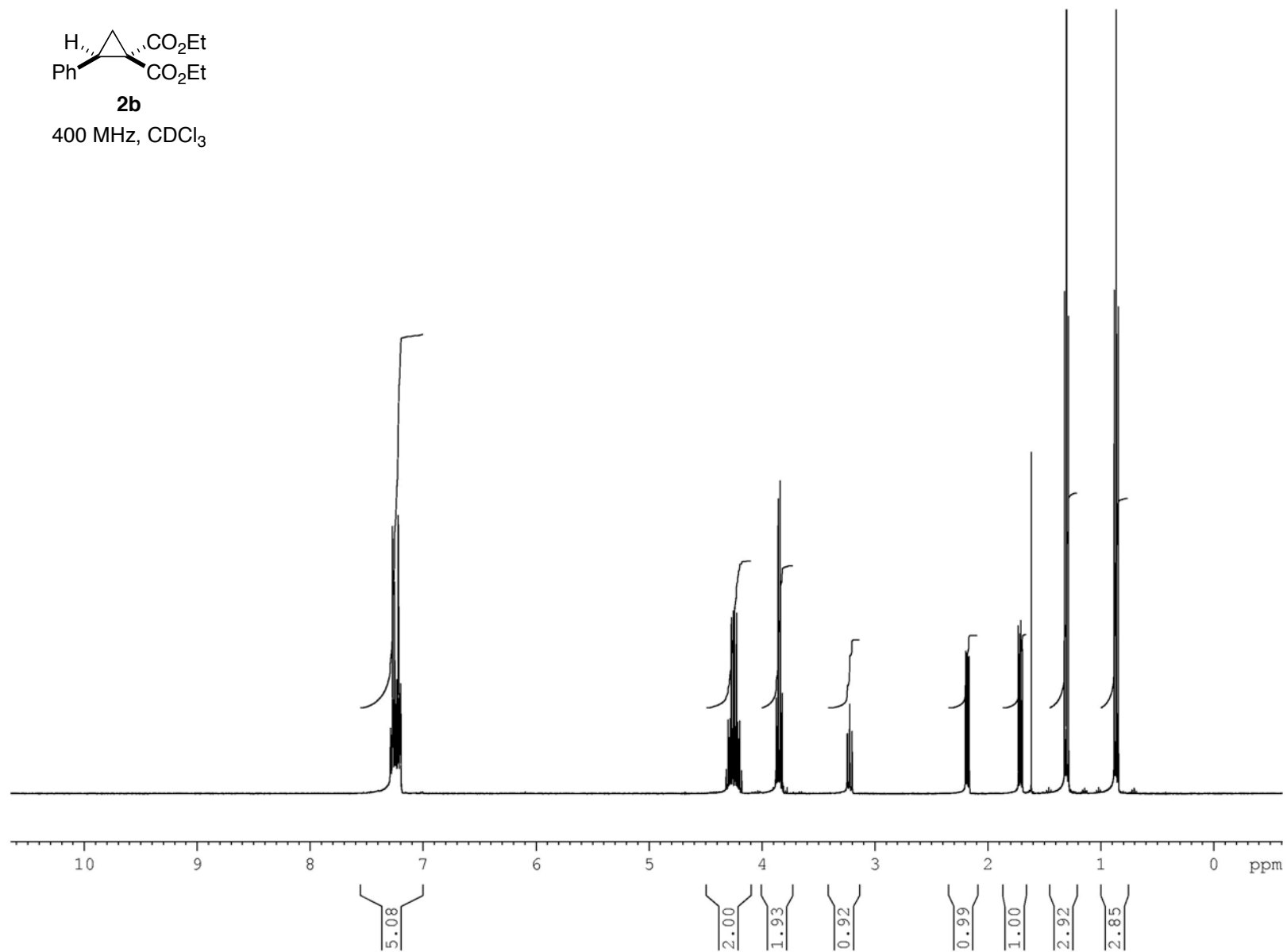
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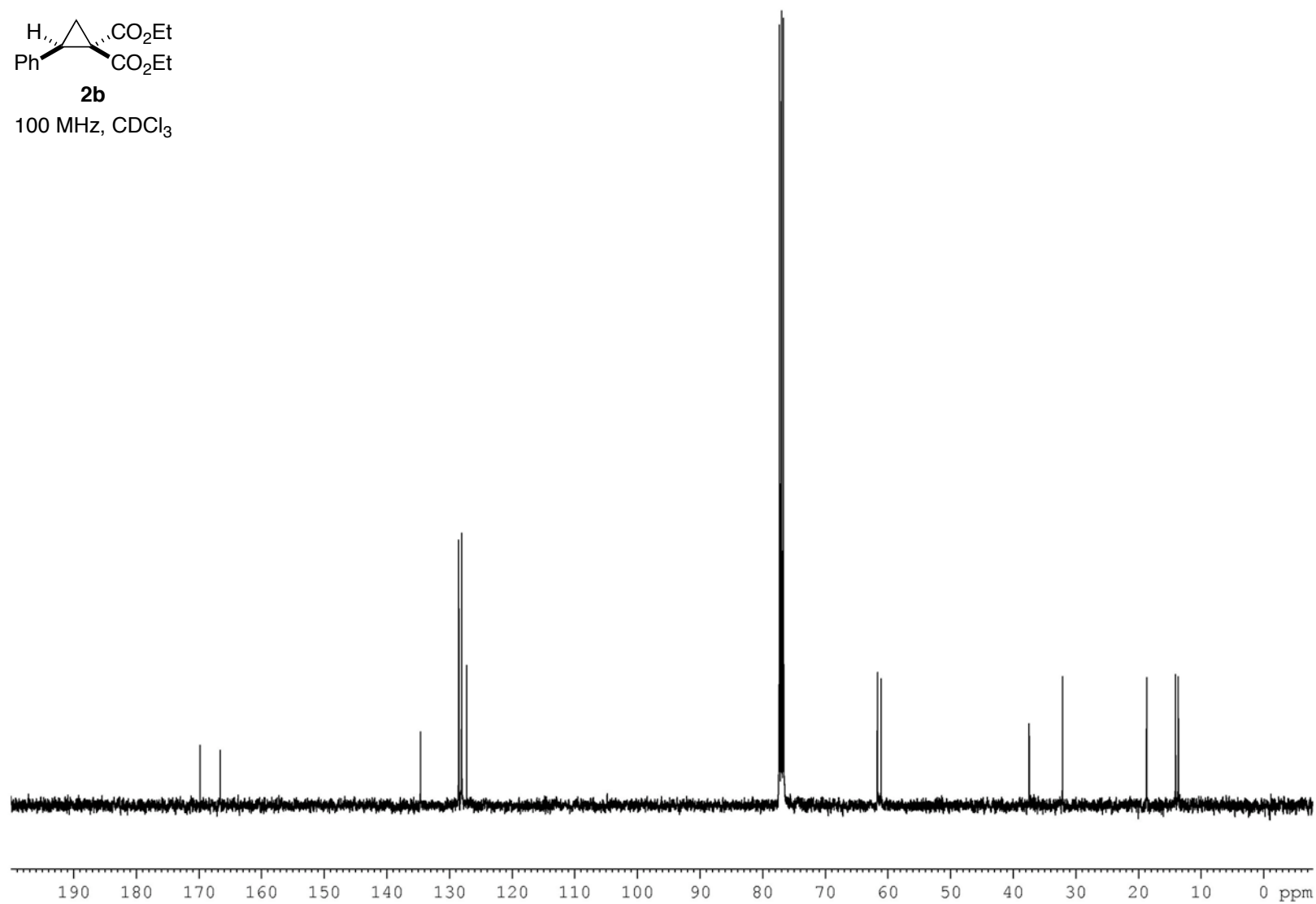
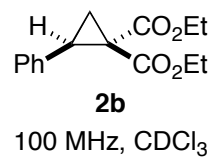
75 MHz, CDCl₃

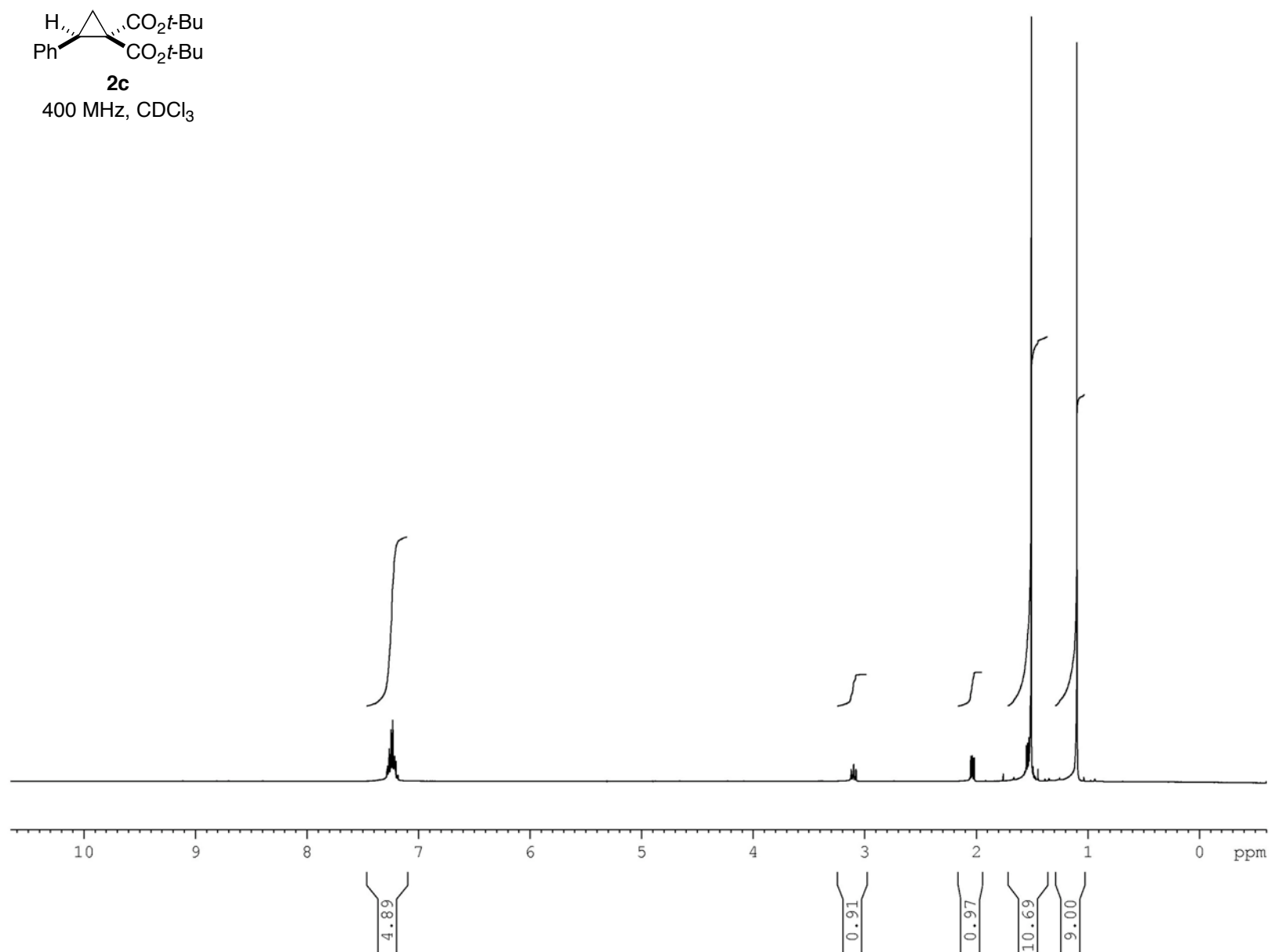


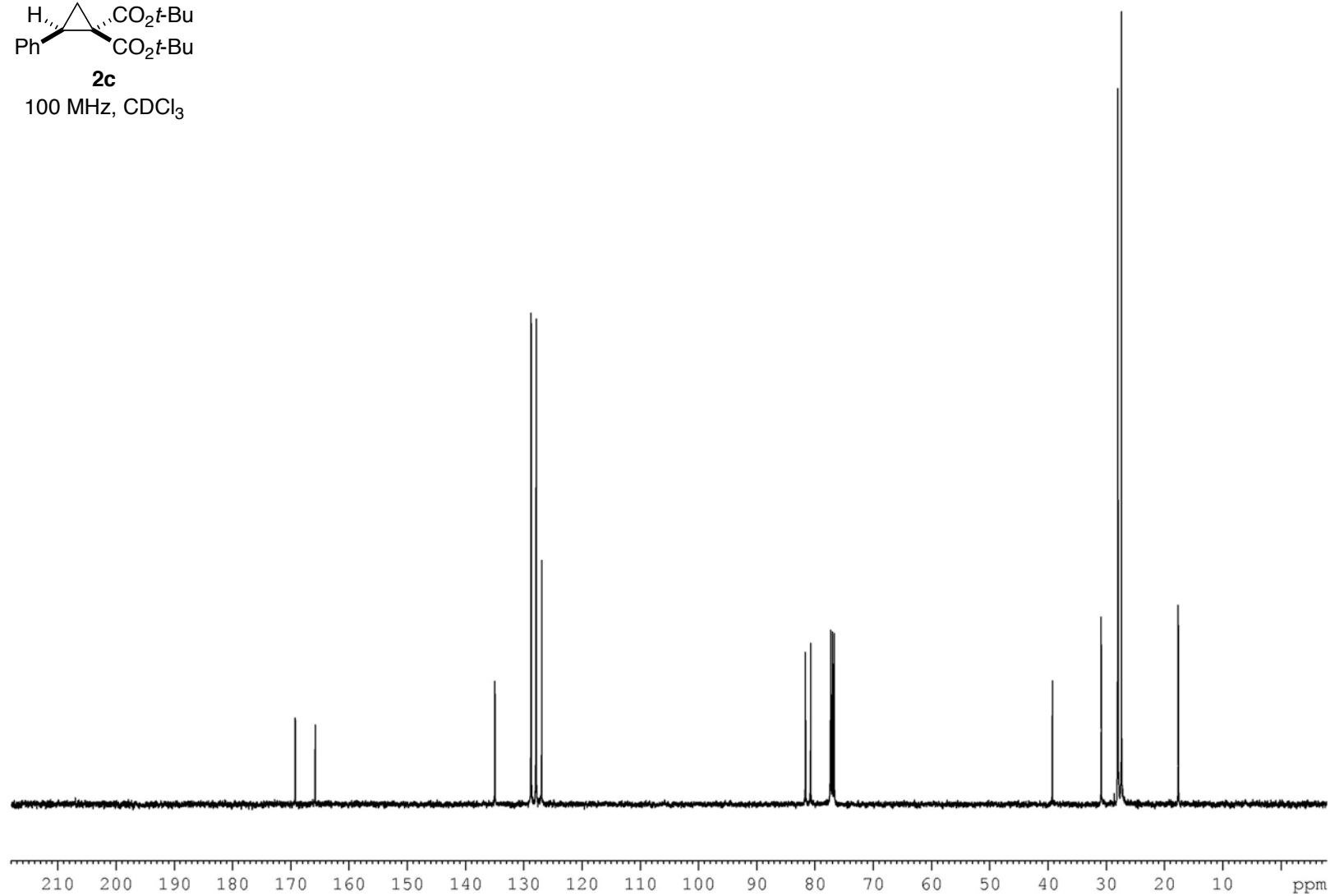
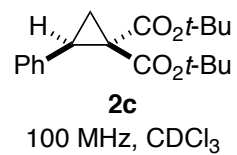


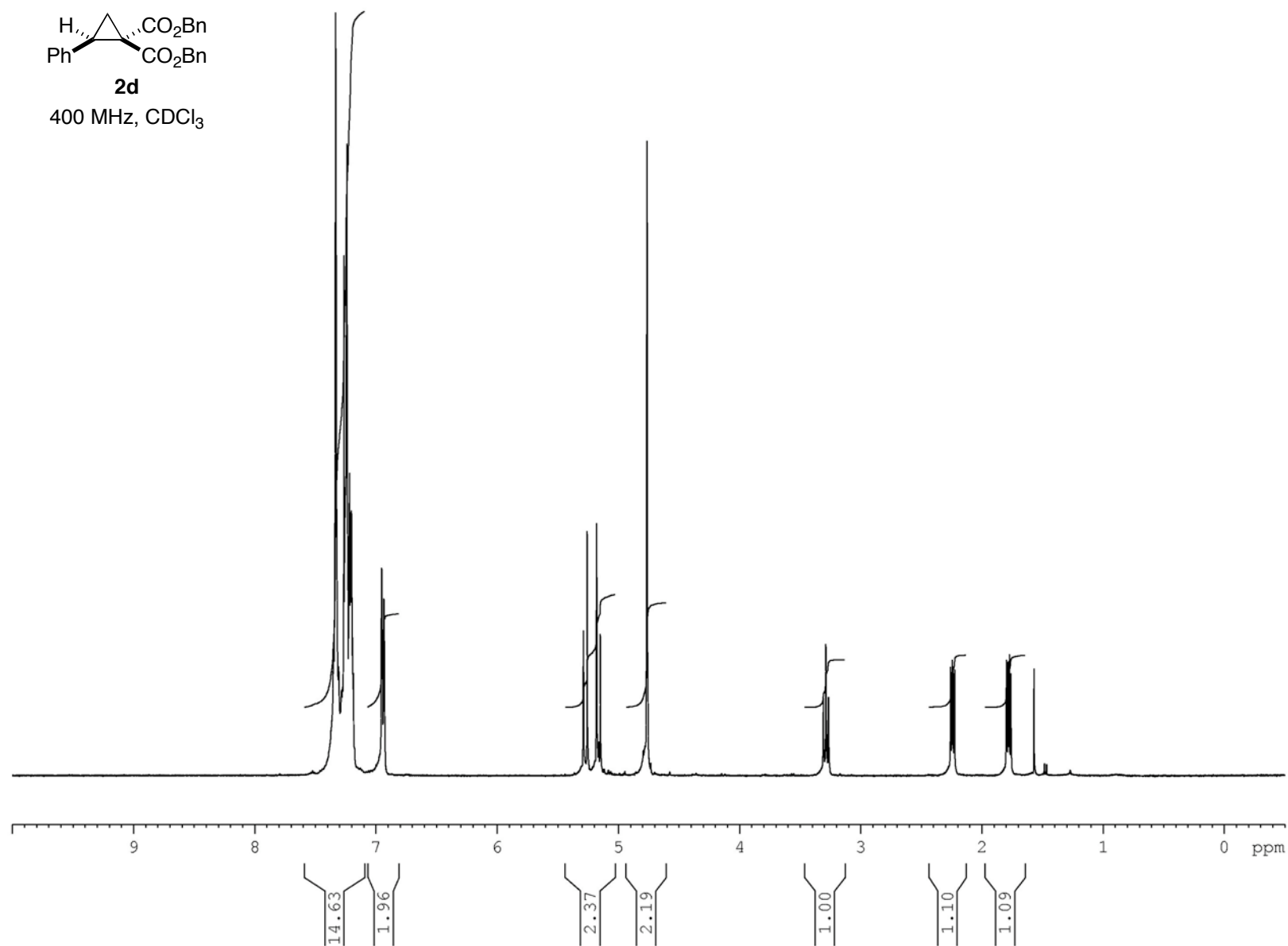


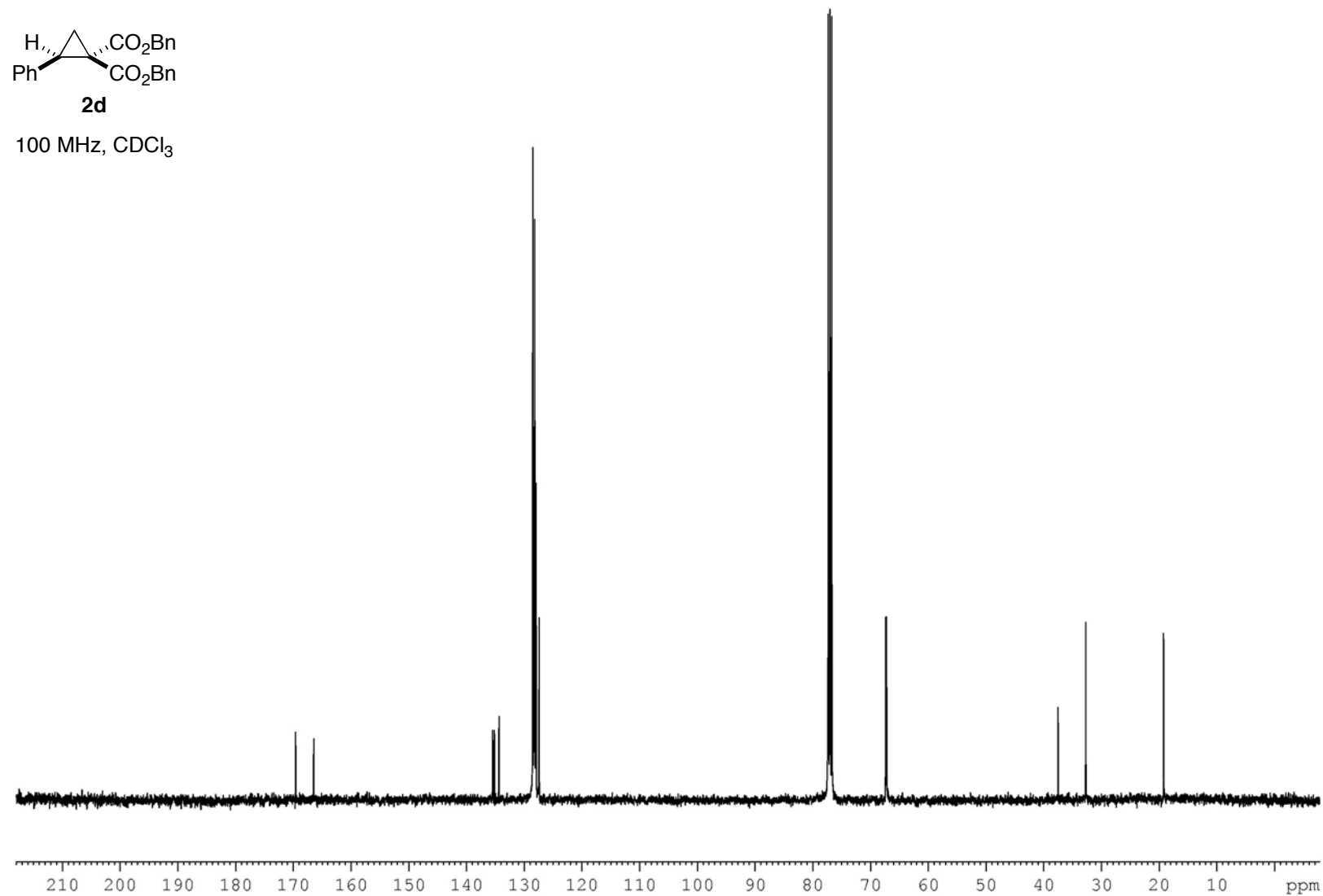


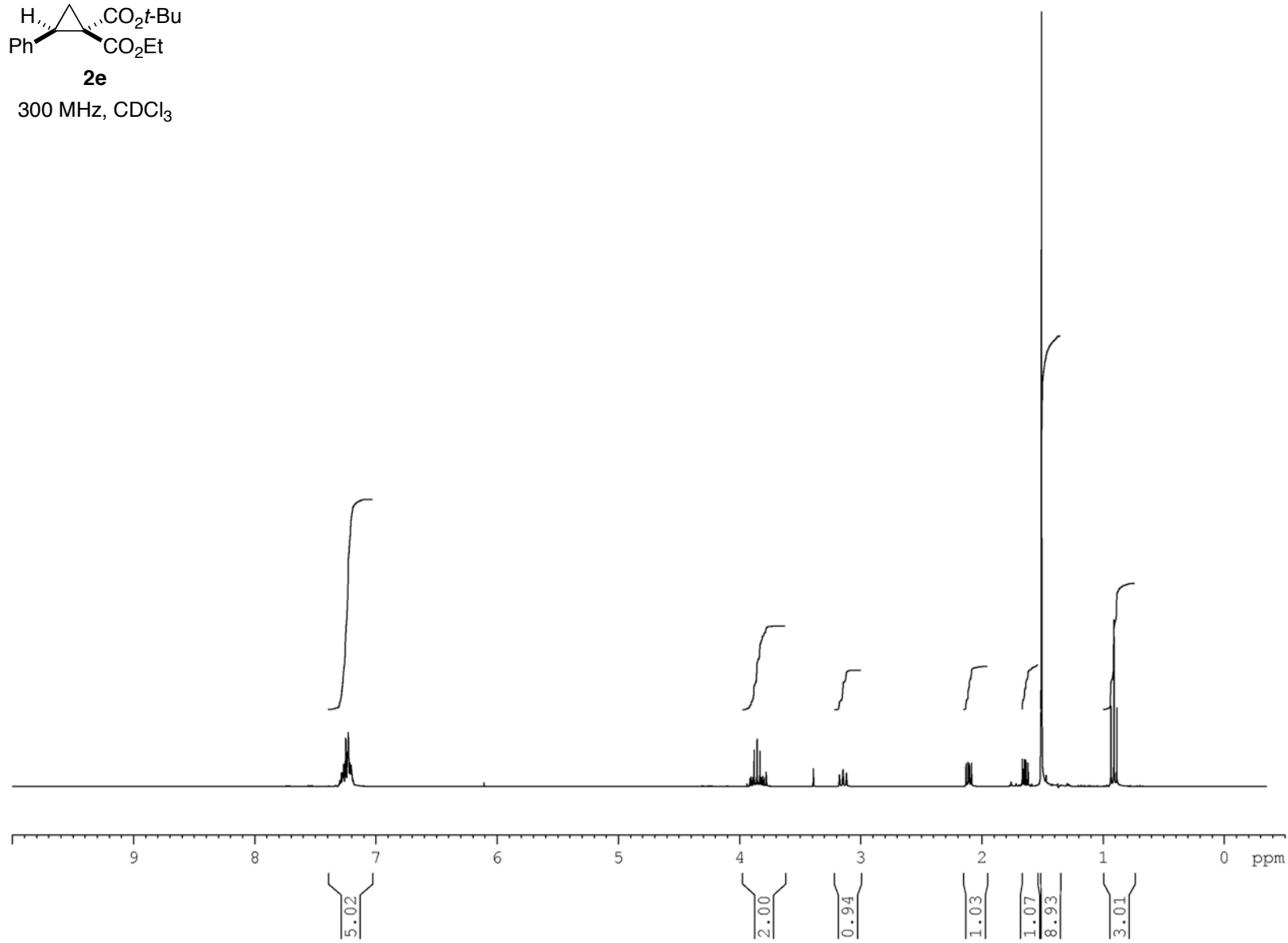
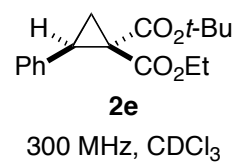


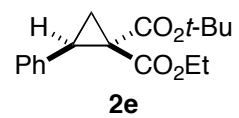
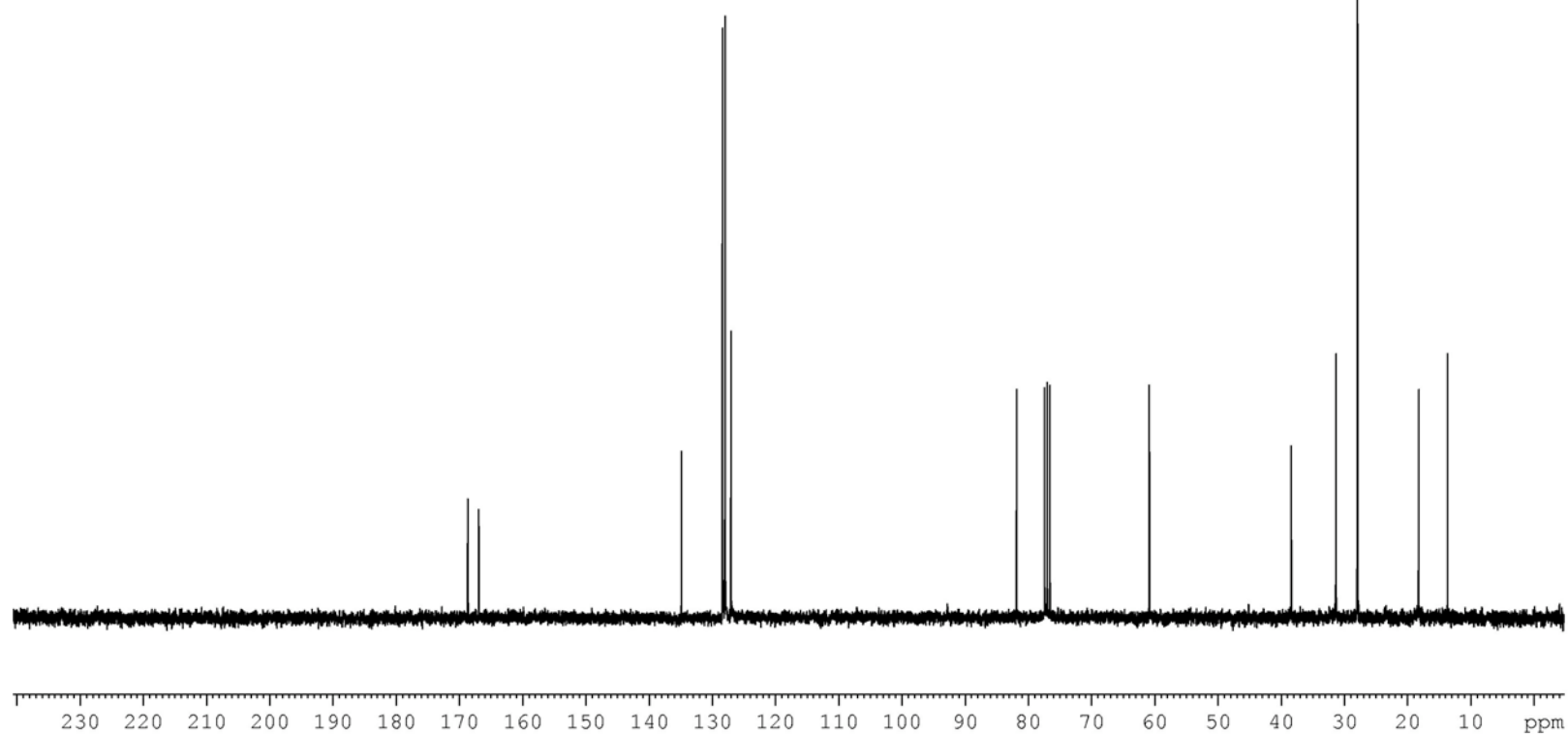


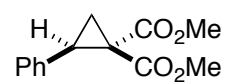
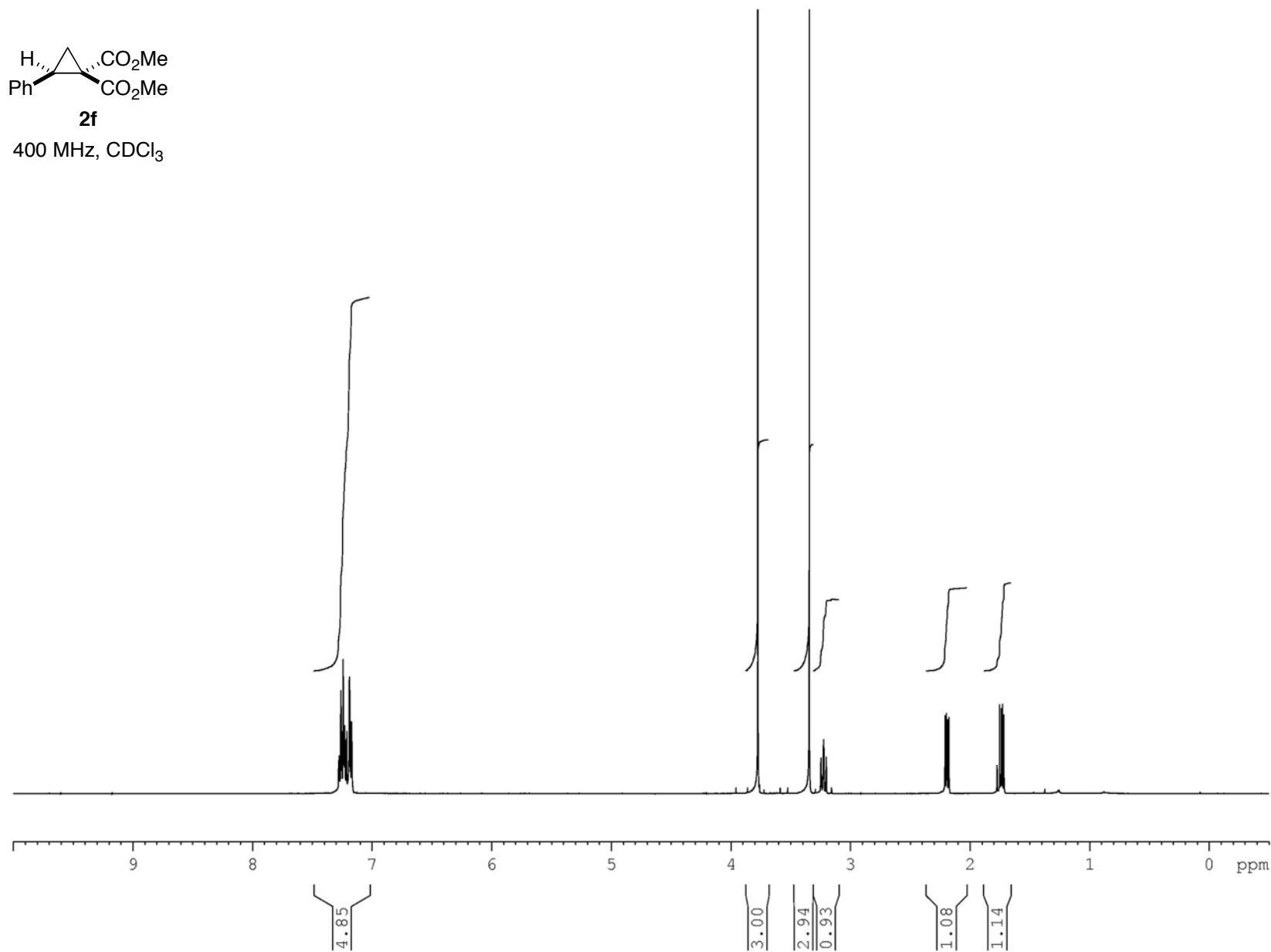


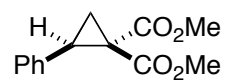
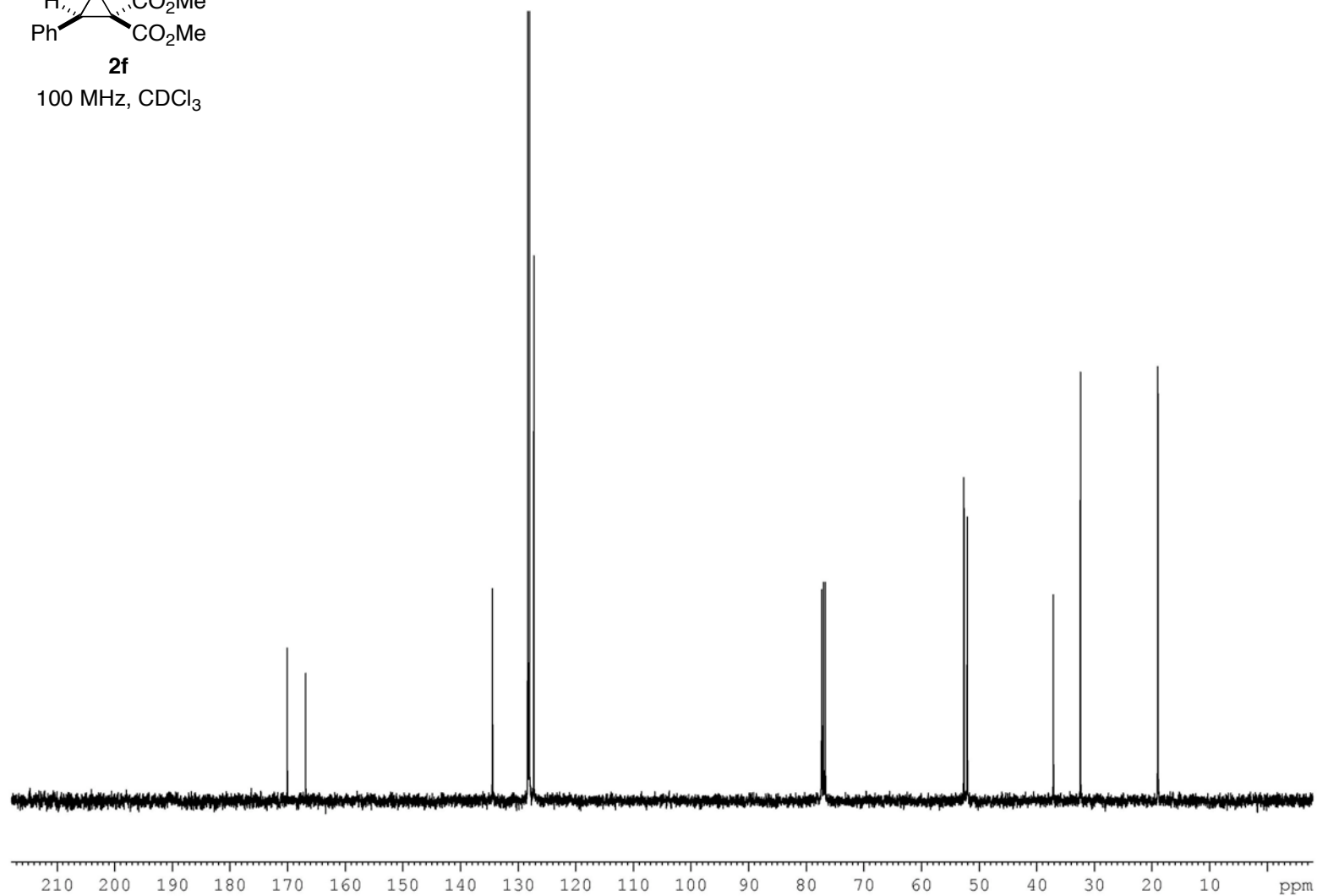


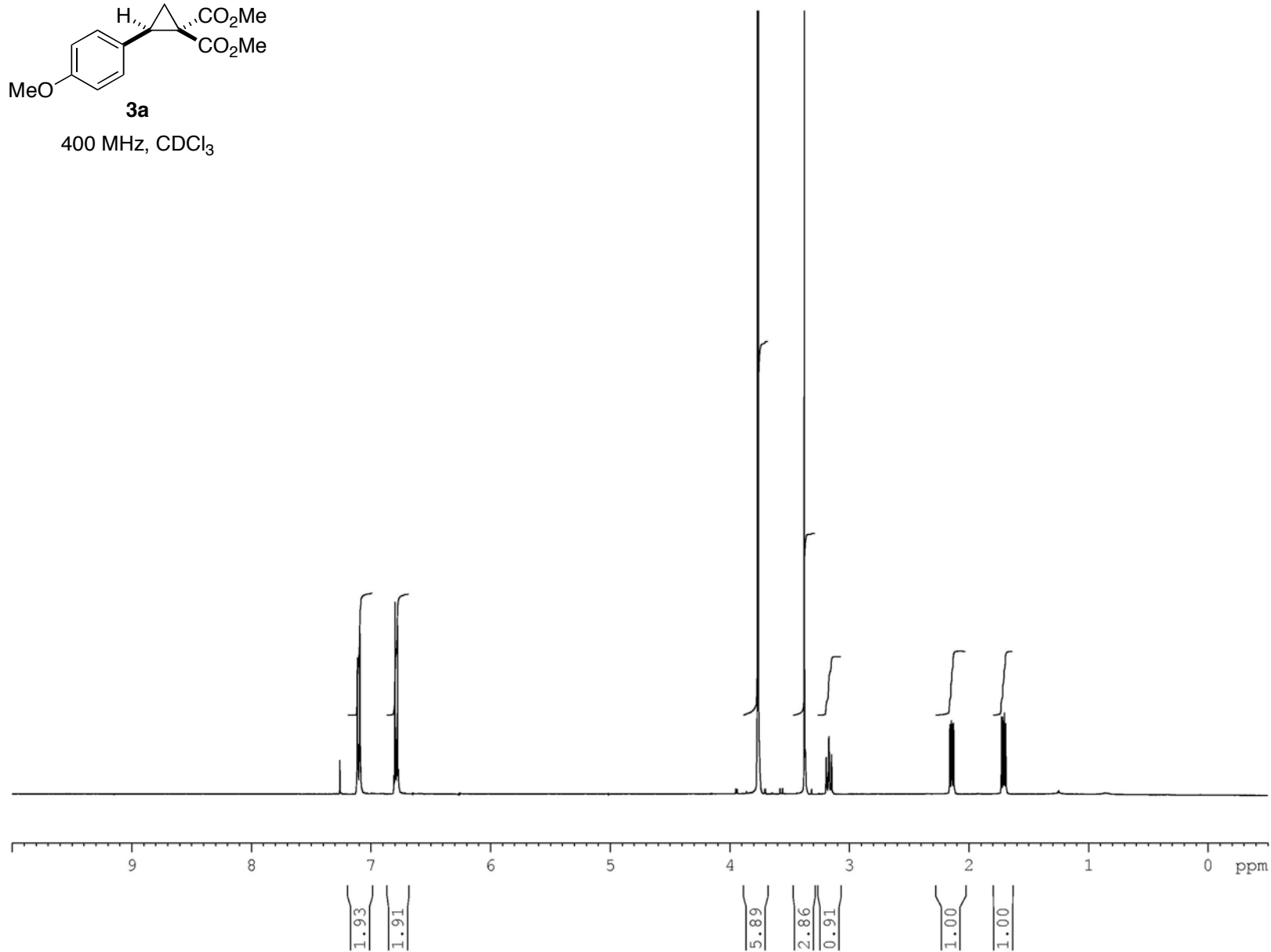
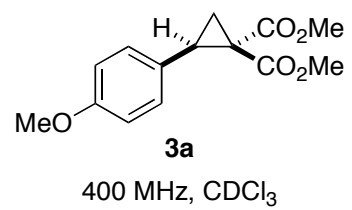


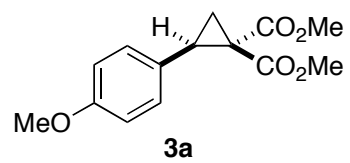
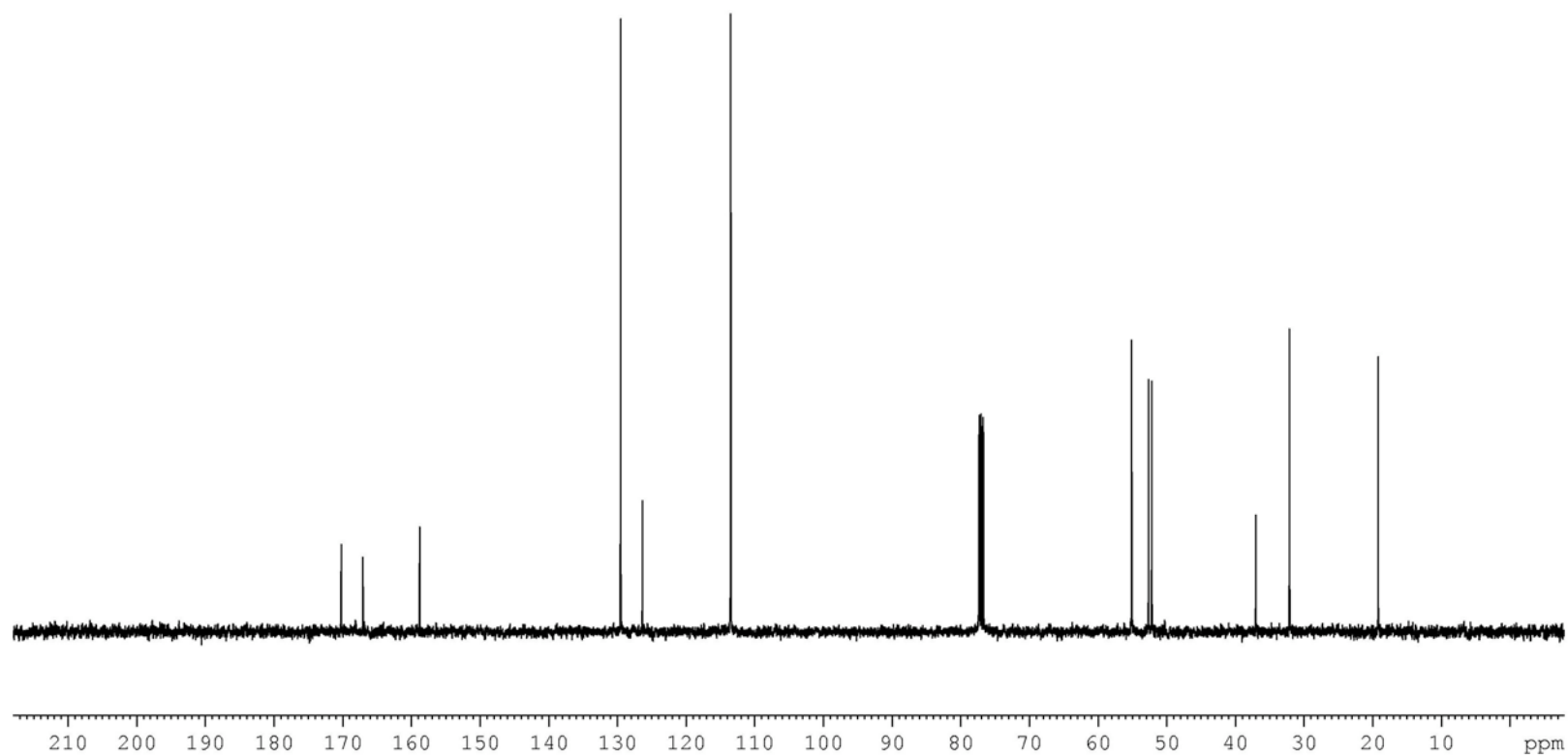


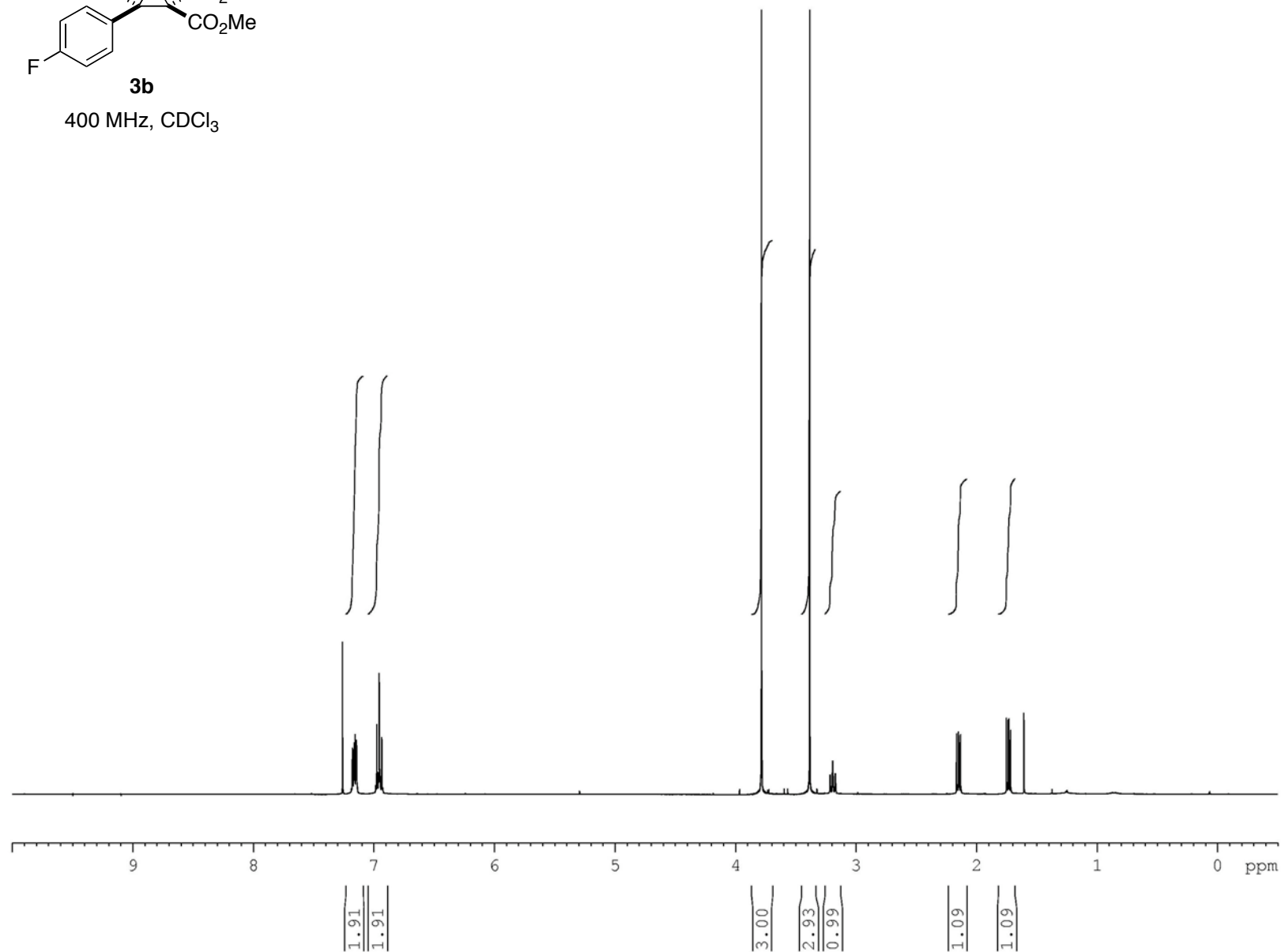
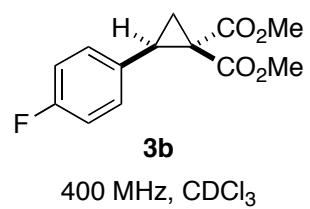
75 MHz, CDCl₃

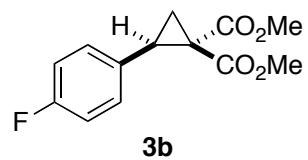
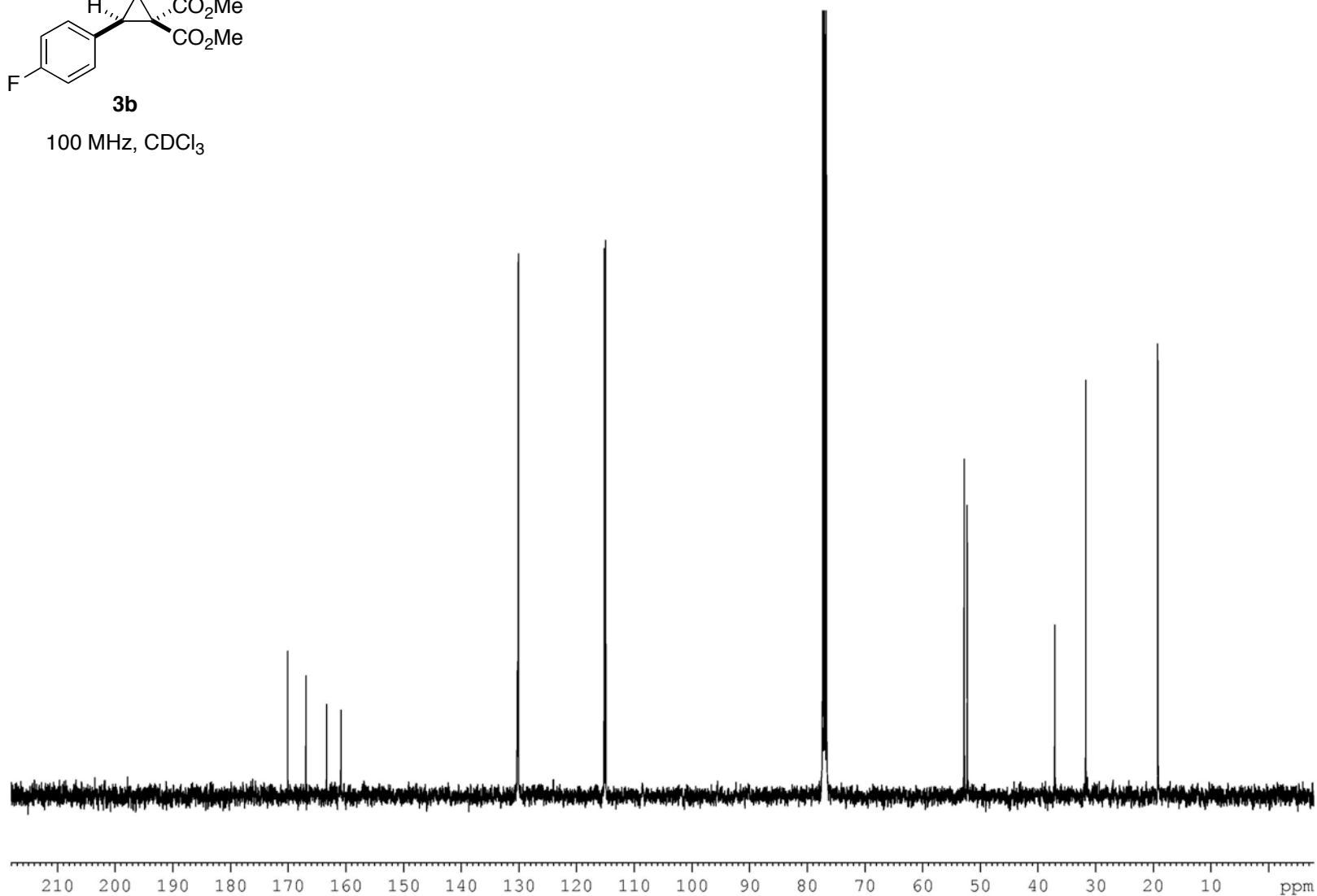
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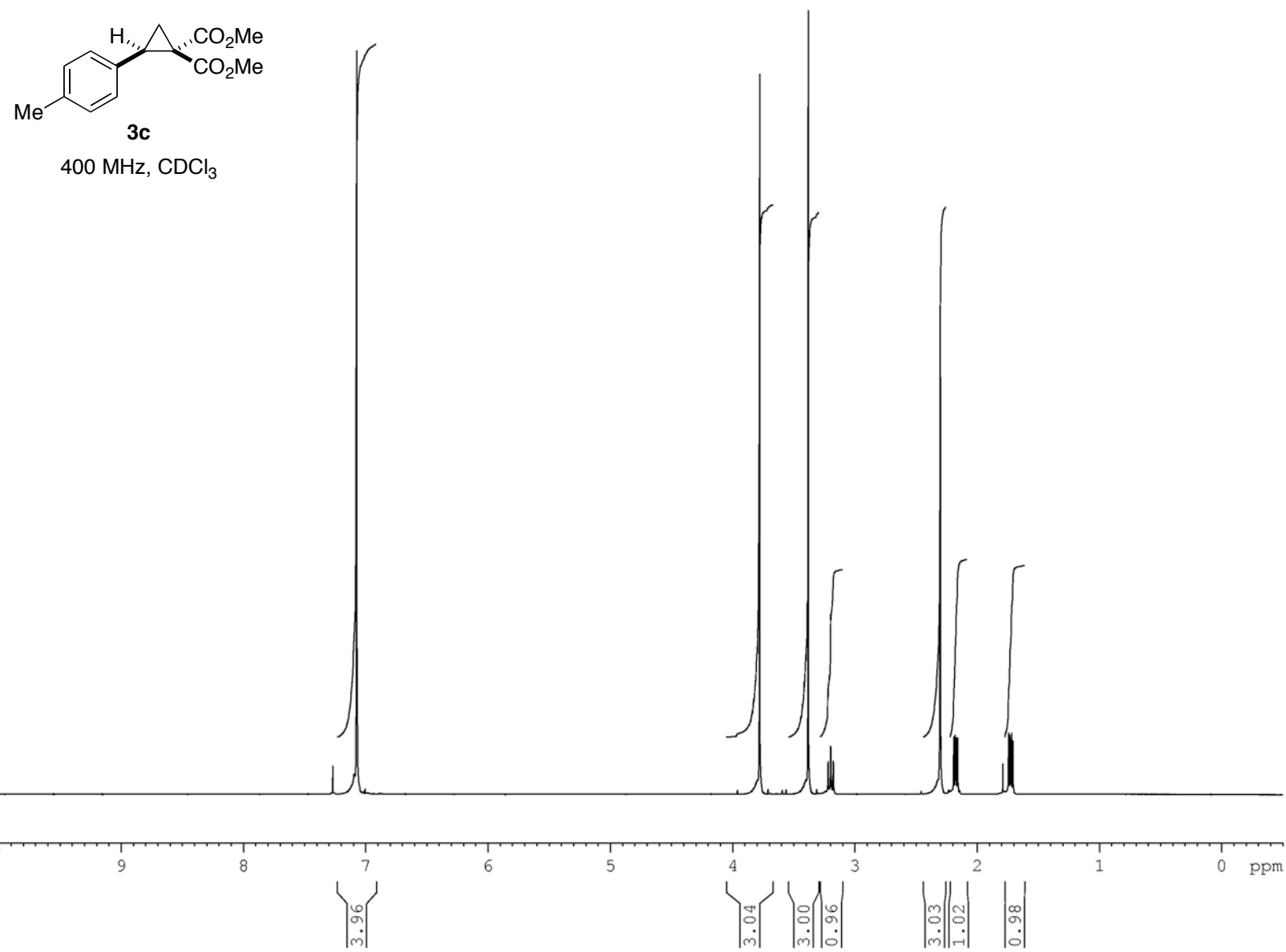
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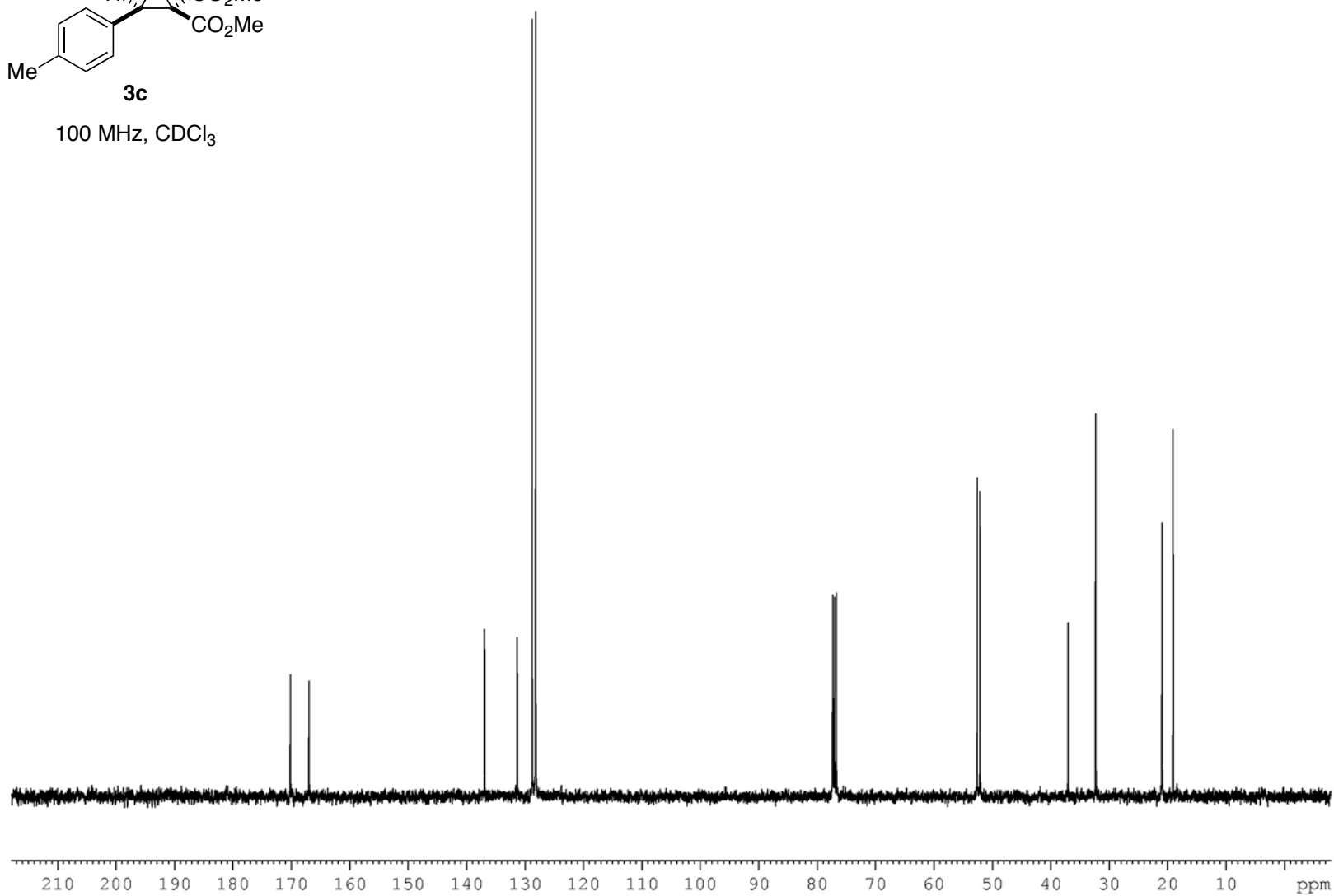
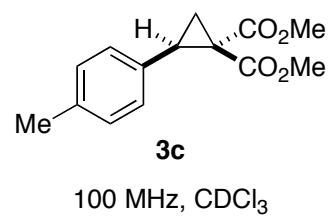


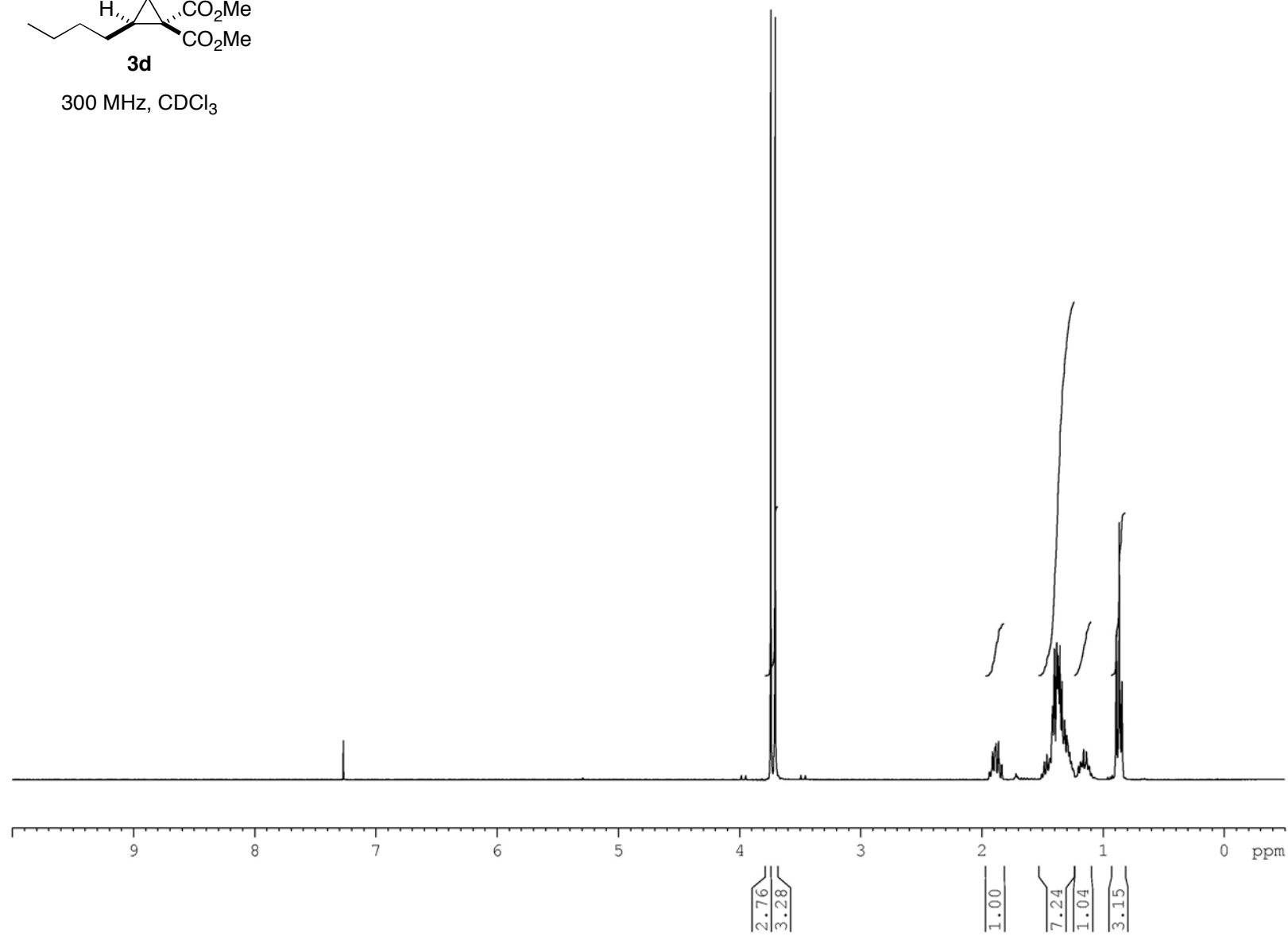
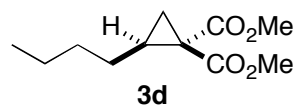
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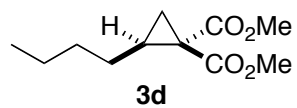


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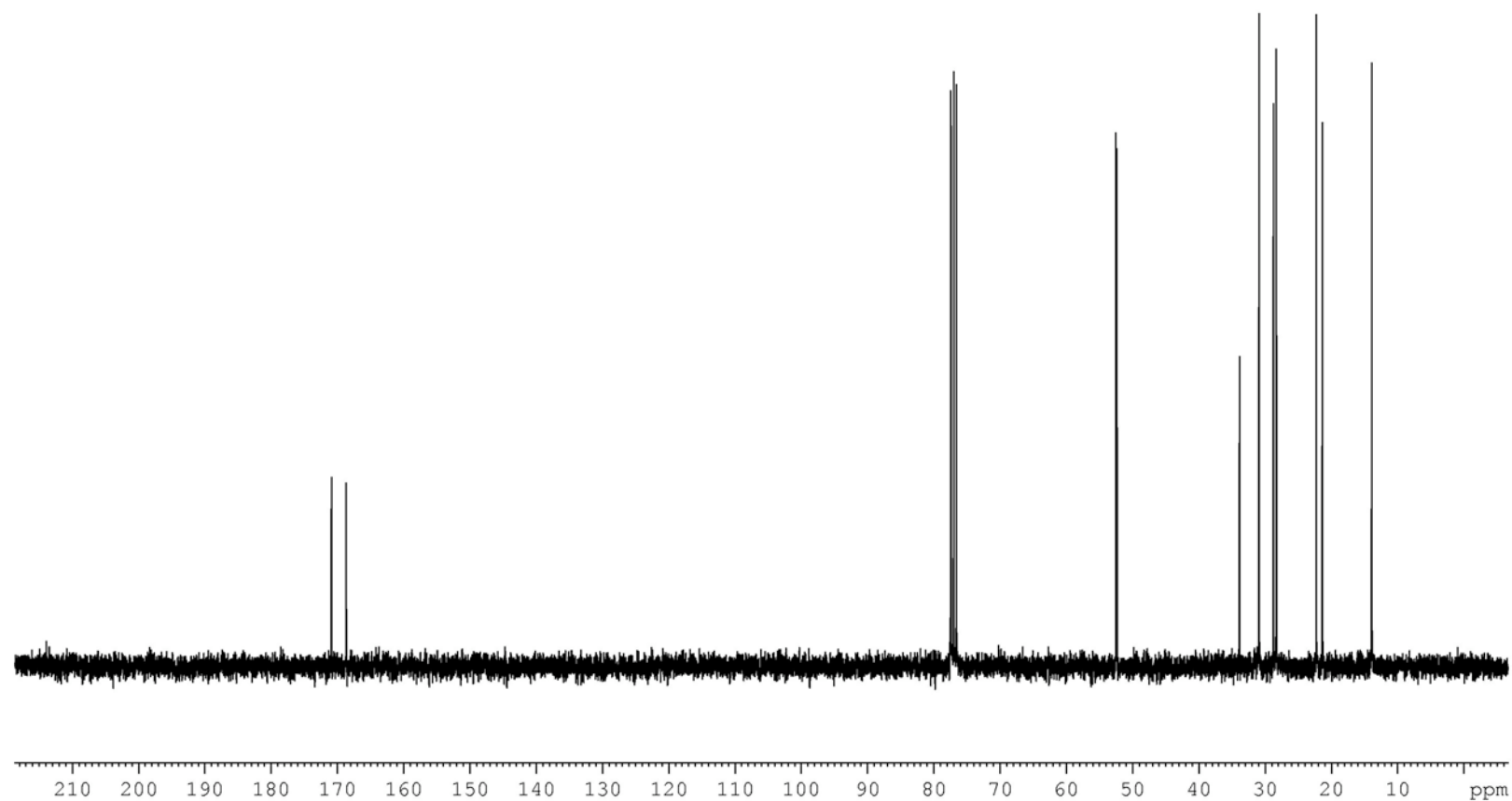


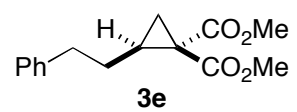




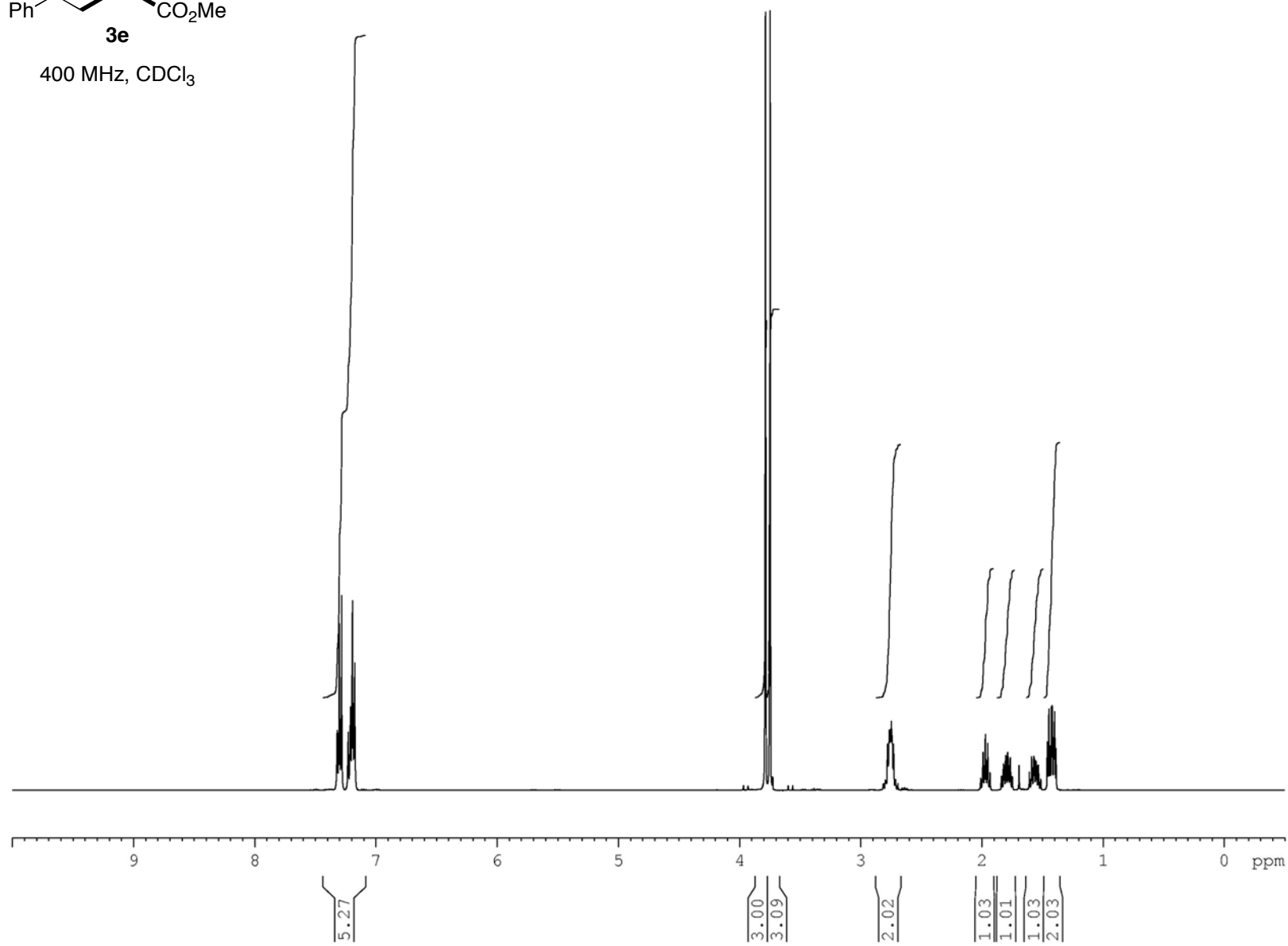


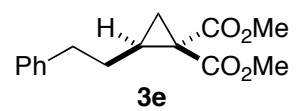
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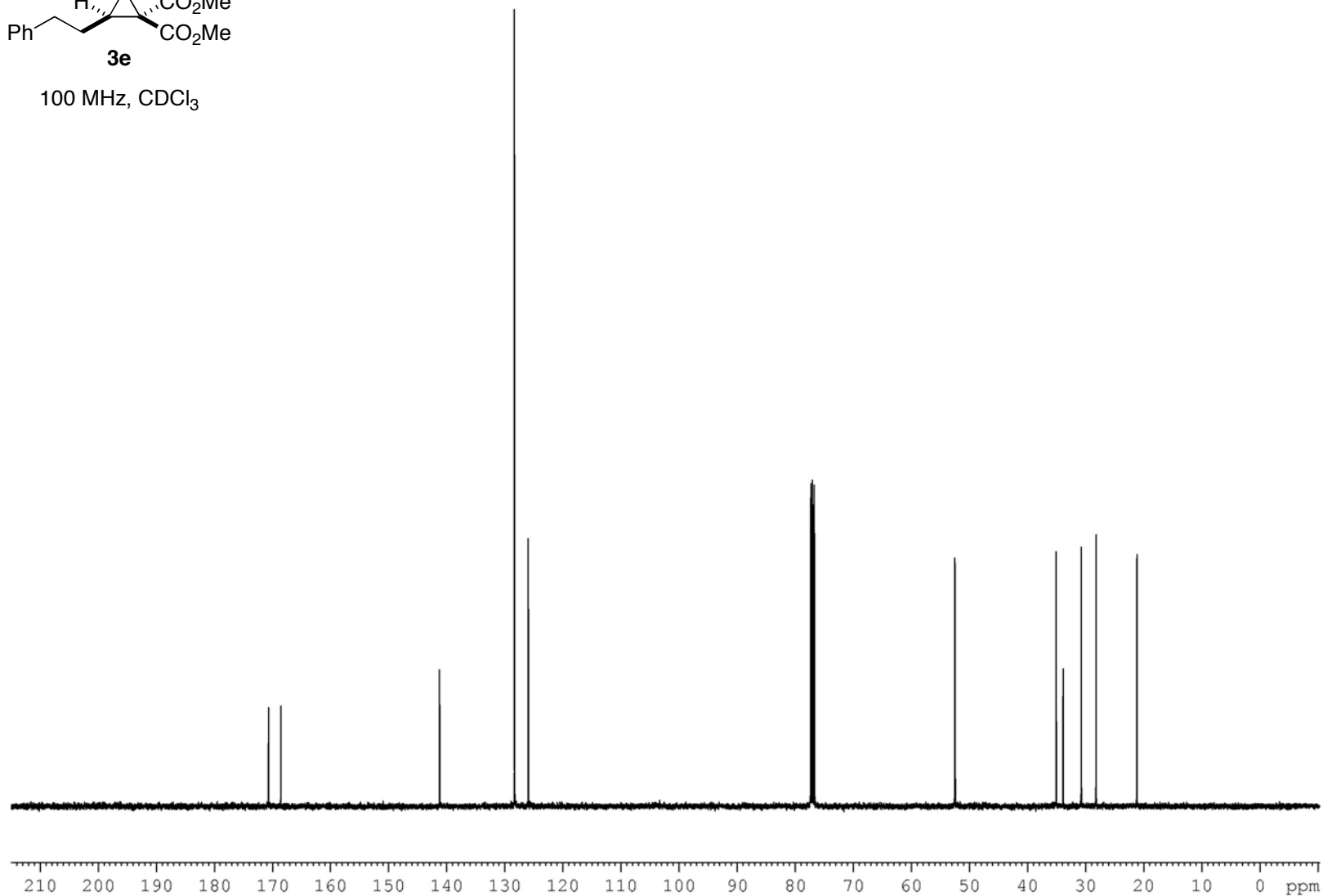


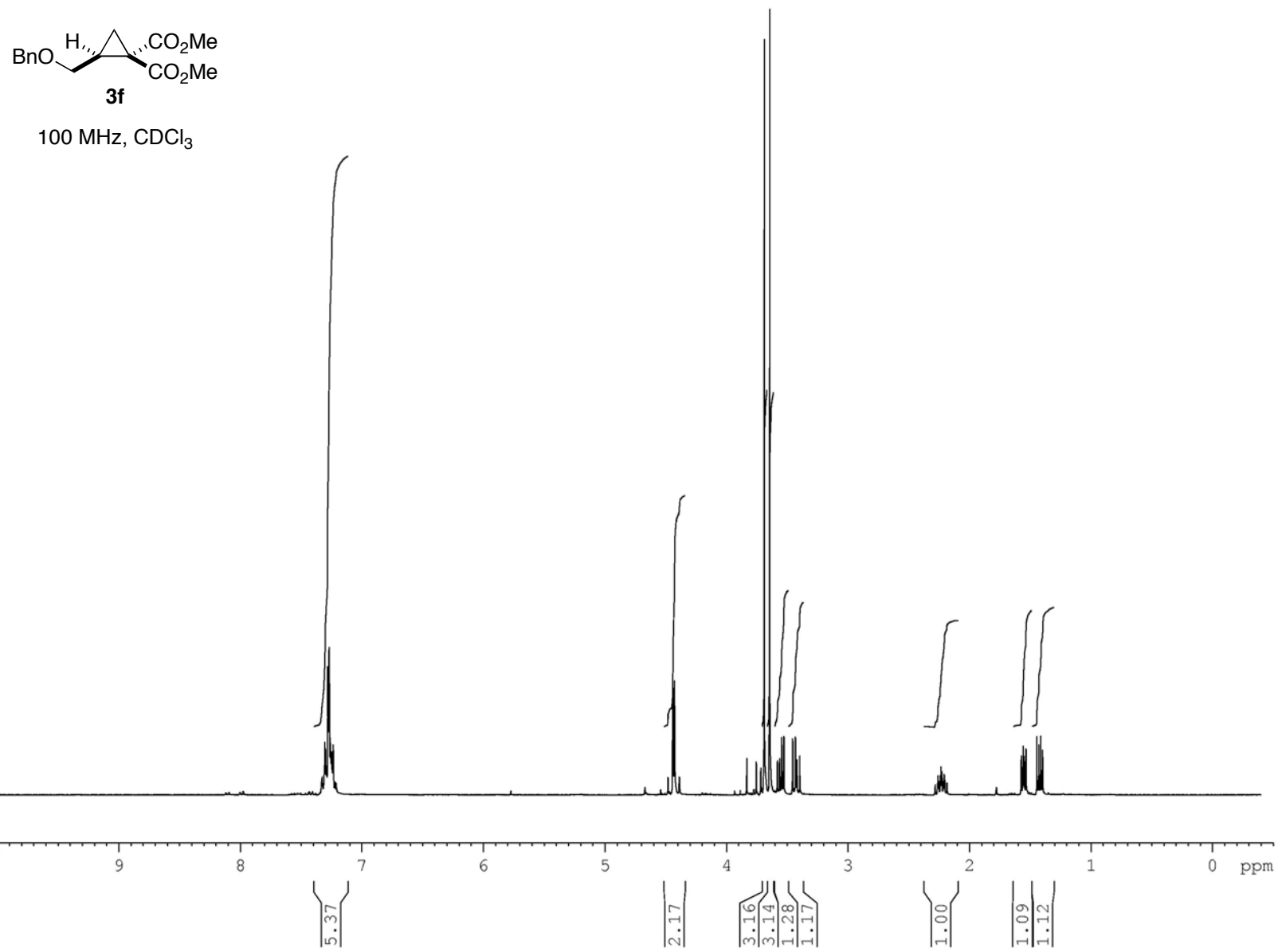
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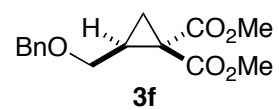




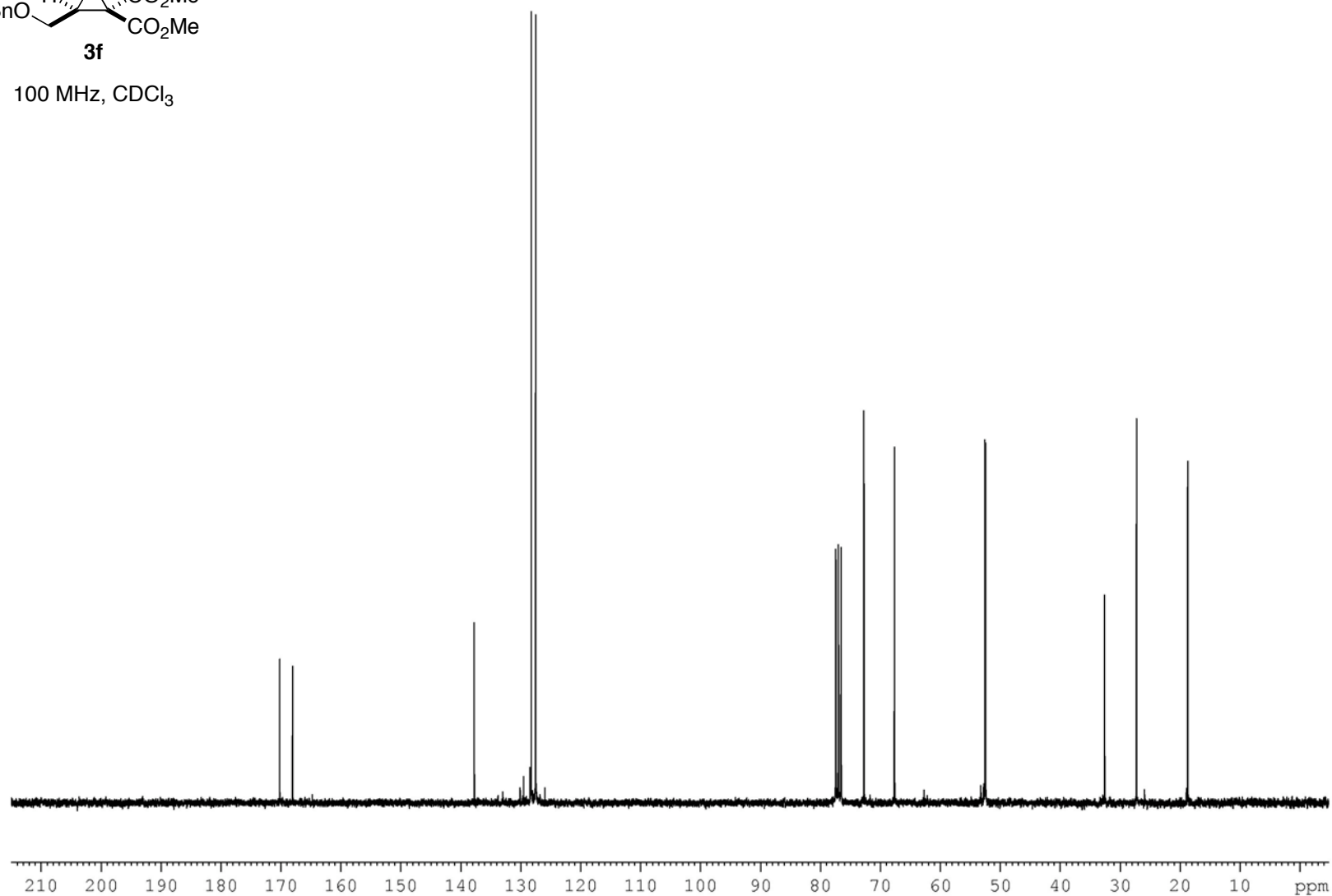
100 MHz, CDCl₃

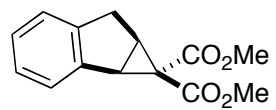
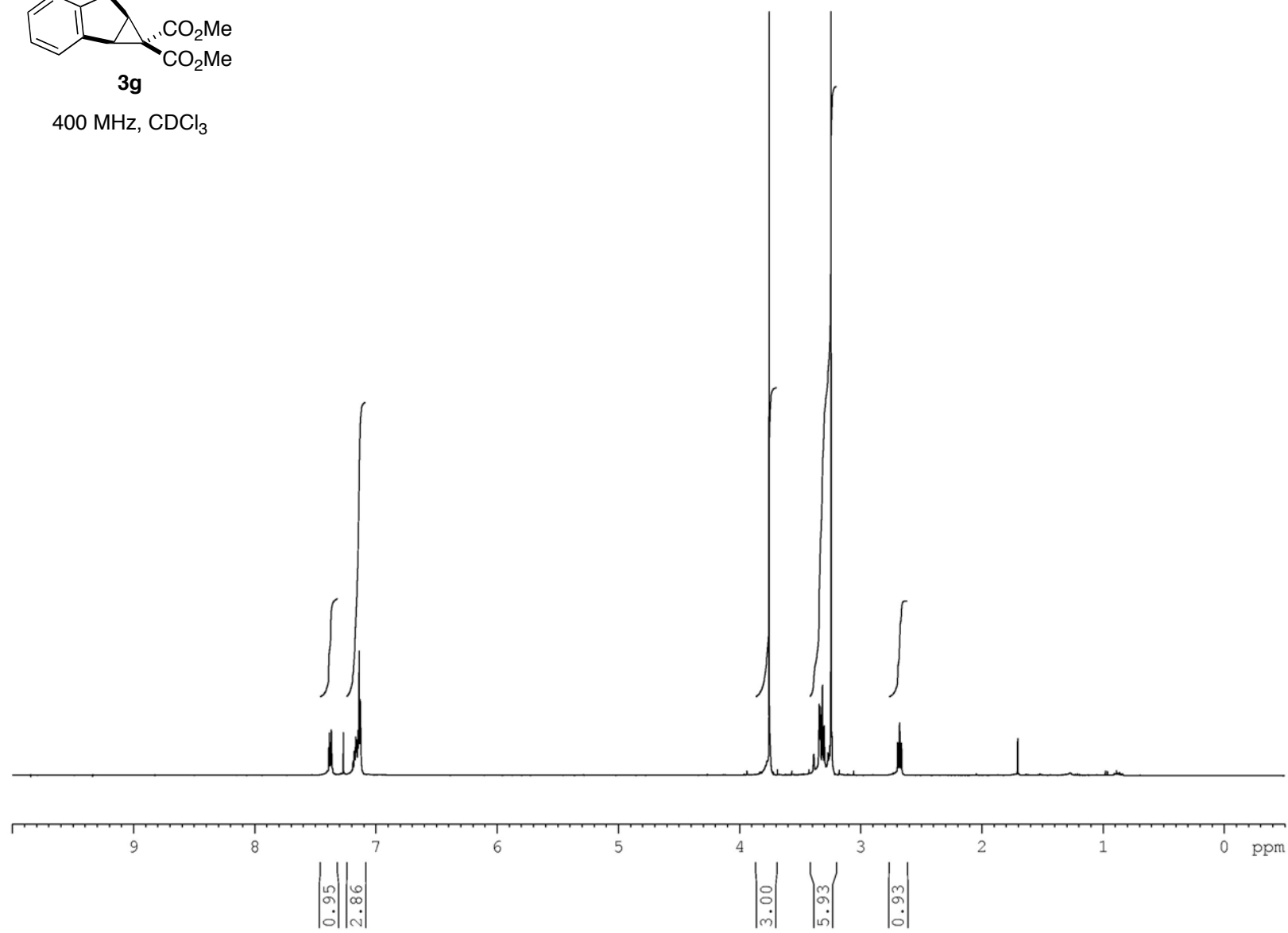


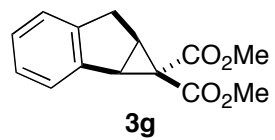




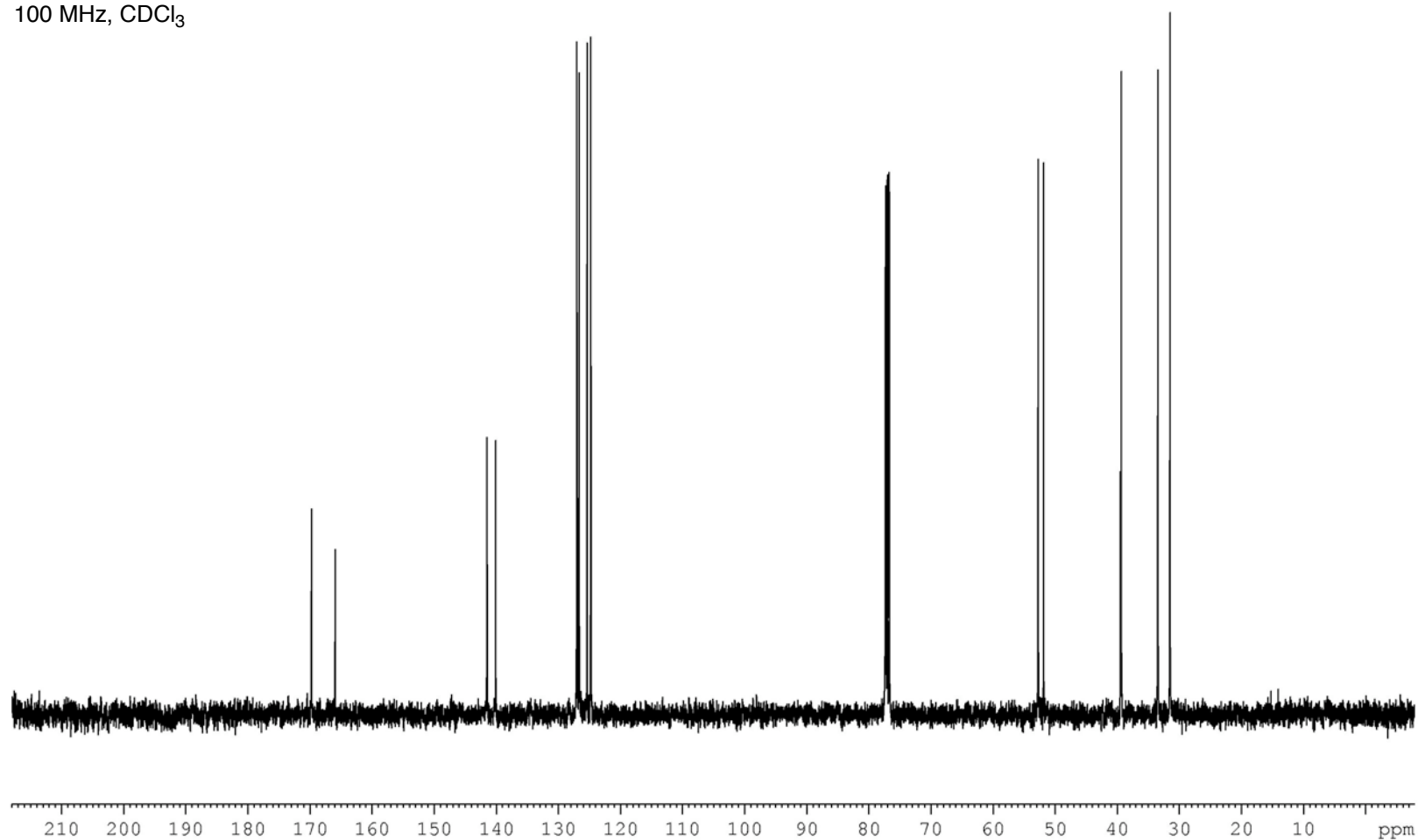
100 MHz, CDCl₃



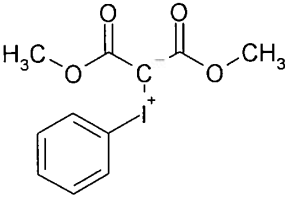
**3g**400 MHz, CDCl_3 

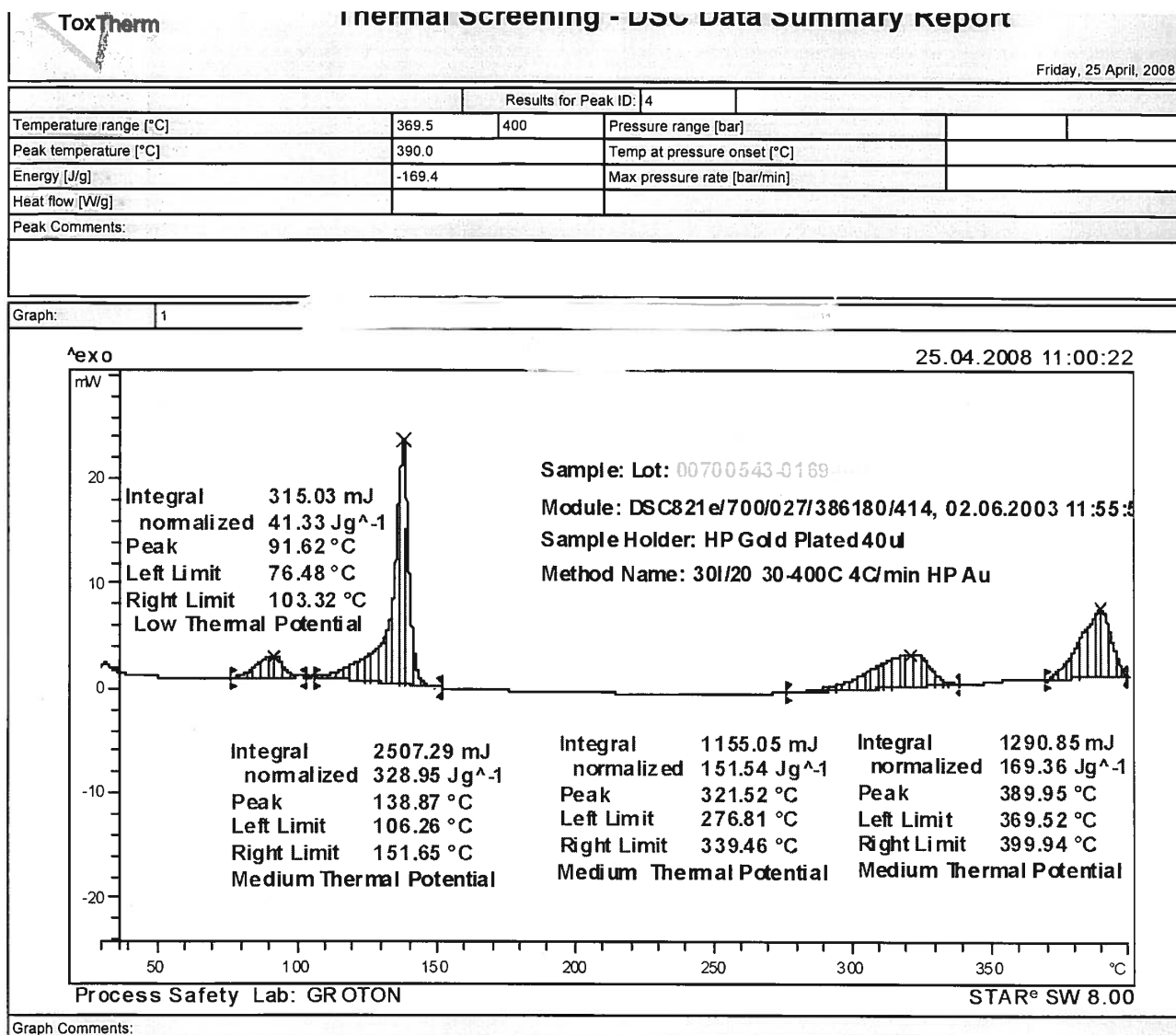


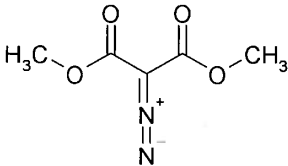
100 MHz, CDCl₃



DSC analyses

ToxTherm		Thermal Screening - DSC Data Summary Report				Friday, 25 April, 2008	
Project:	DEVELOPMENT GROTON					CI:	
SR:	2	Unassociated project work		Step:	1	Experiments for unassociated project work	
DB Ref:	111626-200-6	Author:	Boucher, Steven J	Location:	Groton CRD	Date:	24-Apr-08
Short Title:							
Name:							
Source:							
				Compound ID			
				Cell type		Au 40	
				Cell weight			
				Cell atmosphere			
				Initial cell pressure [bar]			
				Temperature [°C]		30	300
				Temperature rate [K/min]		4	
				Isothermal Temperature [°C]		30	
				Isothermal Time [min]		20	
				Stirrer speed [rpm]			
Sample mass		7.622	mg				
Weight loss							
Results for Experiment:							
Bomp Rupture [Yes/No]		N		Residual pressure [bar]			
Gas evolution onset [°C]				Thermal Hazard			
Permanent gas				Medium Thermal Hazard			
Maximum pressure [bar]				Melts [Yes/No]		N	
Max pressure rate [bar/min]				Decomposes [Yes/No]		N	
Comments:							
Results:							
Results for Peak ID: 1							
Temperature range [°C]		76.5	103.3	Pressure range [bar]			
Peak temperature [°C]		91.6		Temp at pressure onset [°C]			
Energy [J/g]		-41.3		Max pressure rate [bar/min]			
Heat flow [W/g]							
Peak Comments:							
Results for Peak ID: 2							
Temperature range [°C]		106.3	151.6	Pressure range [bar]			
Peak temperature [°C]		138.9		Temp at pressure onset [°C]			
Energy [J/g]		-329.0		Max pressure rate [bar/min]			
Heat flow [W/g]							
Peak Comments:							
Results for Peak ID: 3							
Temperature range [°C]		276.8	339.5	Pressure range [bar]			
Peak temperature [°C]		321.5		Temp at pressure onset [°C]			
Energy [J/g]		-151.5		Max pressure rate [bar/min]			
Heat flow [W/g]							
Peak Comments:							



ToxTherm		Thermal Screening - DSC Data Summary Report			
Wednesday, 26 March, 2008					
Project:	DEVELOPMENT GROTON				CI:
SR:	2	Unassociated project work		Step:	1
DB Ref:	111626-199-2	Author:	Boucher, Steven J	Location:	Groton CRD
Date:	25-Mar-08				
Short Title:					
Name:					
Source:					
				Compound ID Cell type Cell weight Cell atmosphere Initial cell pressure [bar] Temperature [°C] Temperature rate [K/min] Isothermal Temperature [°C] Isothermal Time [min] Stirrer speed [rpm] Sample mass Weight loss	
				Au 40 Air 30 300 4 30 20 22.3980 mg	
Results for Experiment:					
Bomp Rupture [Yes/No]		N		Residual pressure [bar]	
Gas evolution onset [°C]		Thermal Hazard			
Permanent gas		High Thermal Hazard			
Maximum pressure [bar]		Melts [Yes/No]		N	
Max pressure rate [bar/min]		Decomposes [Yes/No]		N	
Comments:					
Results:					
Results for Peak ID: 1					
Temperature range [°C]		103.3 211.7		Pressure range [bar]	
Peak temperature [°C]		170.9		Temp at pressure onset [°C]	
Energy [J/g]		-719.7		Max pressure rate [bar/min]	
Heat flow [W/g]					
Peak Comments:					
Results for Peak ID: 2					
Temperature range [°C]		215 300		Pressure range [bar]	
Peak temperature [°C]		272.6		Temp at pressure onset [°C]	
Energy [J/g]		-220.1		Max pressure rate [bar/min]	
Heat flow [W/g]					
Peak Comments:					

