Supporting Information

Ruthenium-Catalyzed [2+2] Cycloadditions between Norbornene and Propargylic Alcohols or their Derivatives

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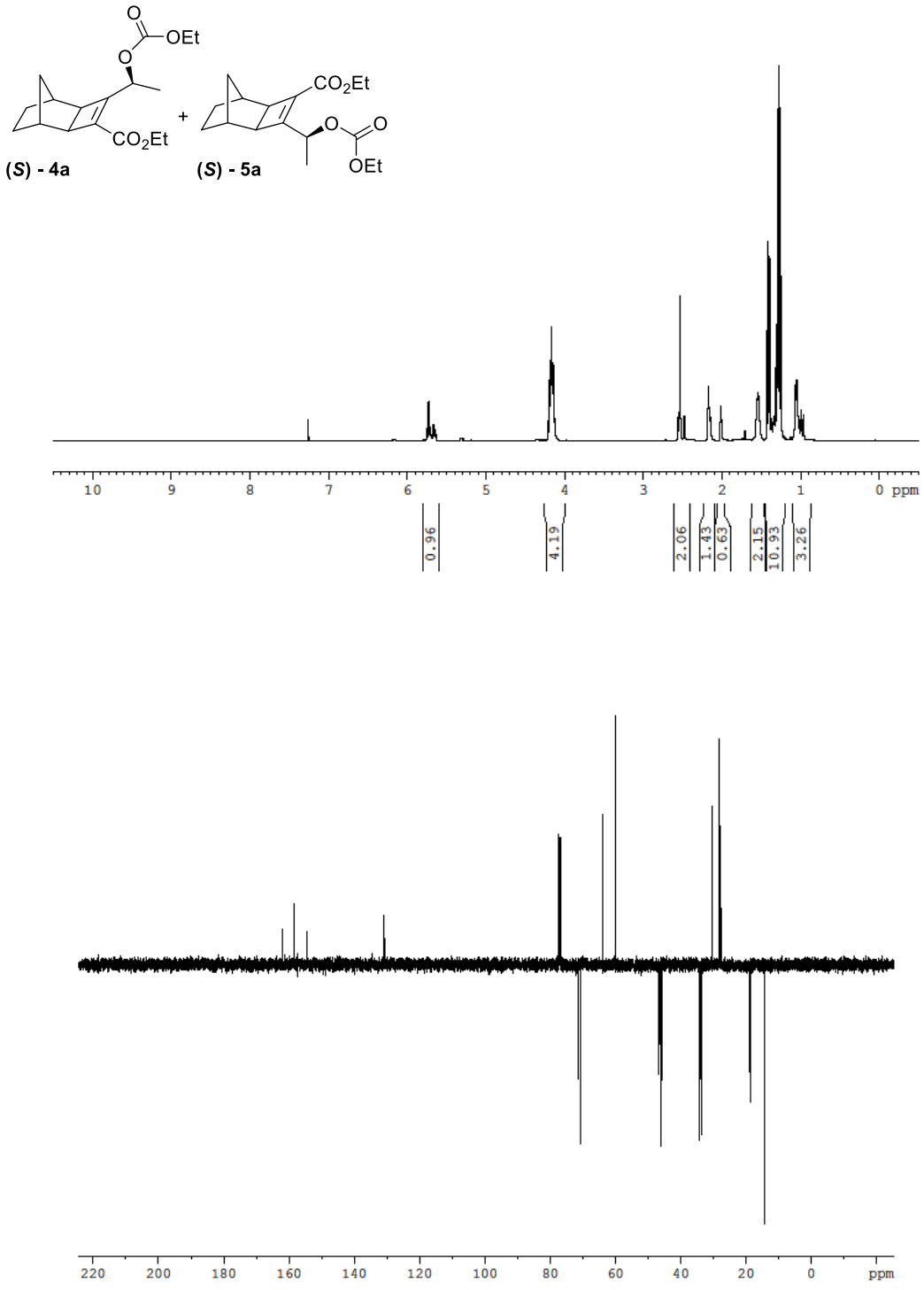
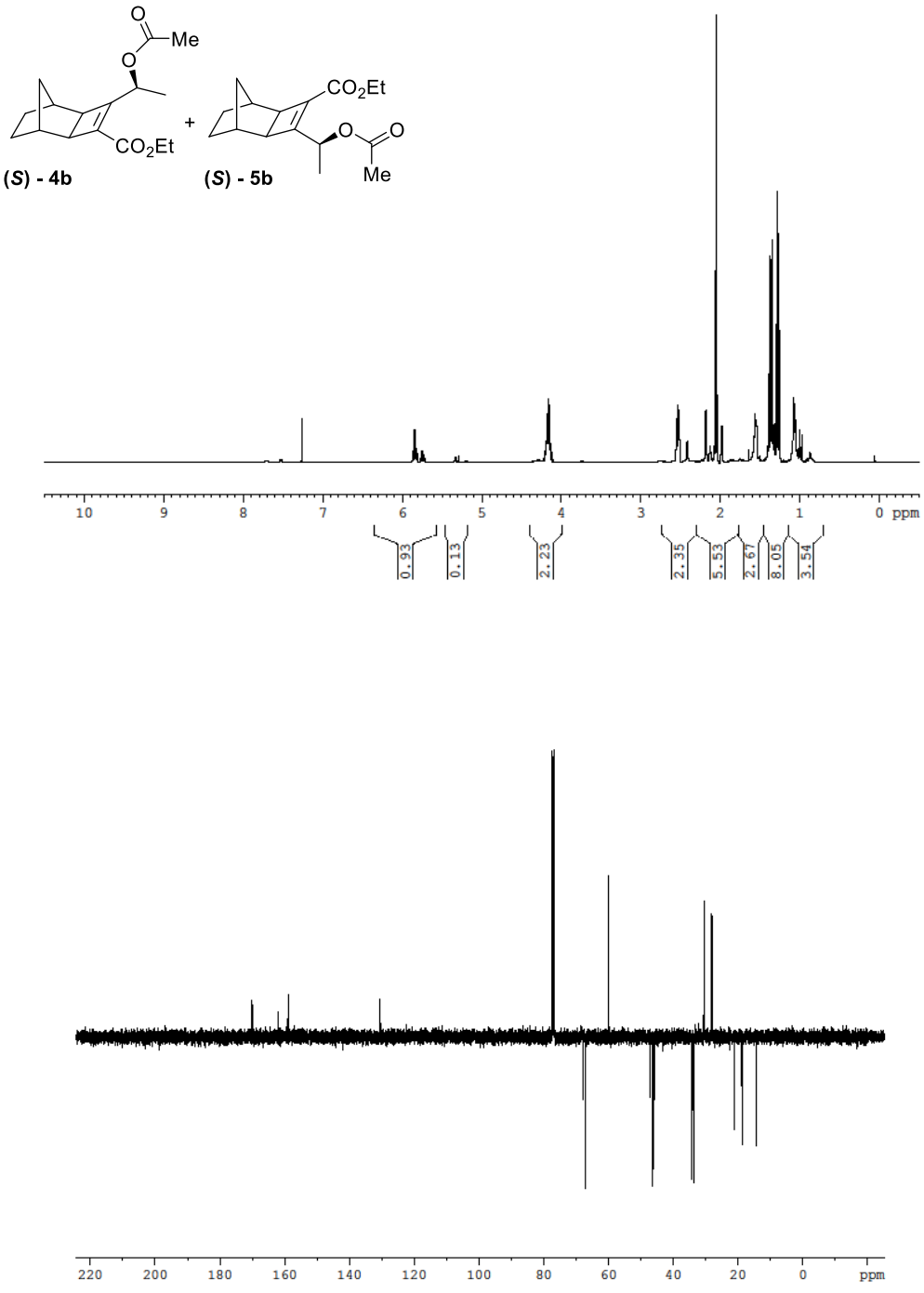


^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of 4/5a in $CDCl_3$



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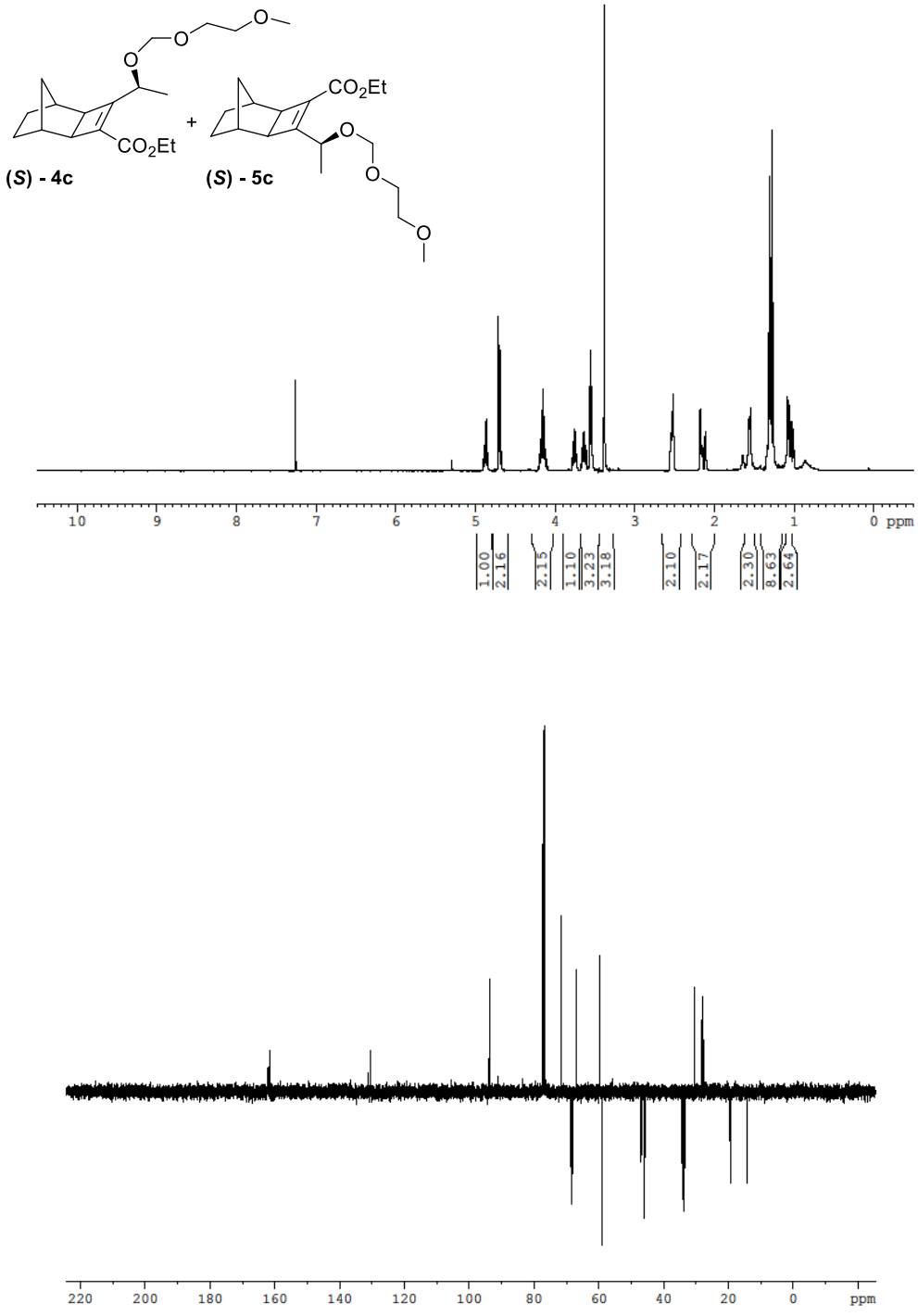

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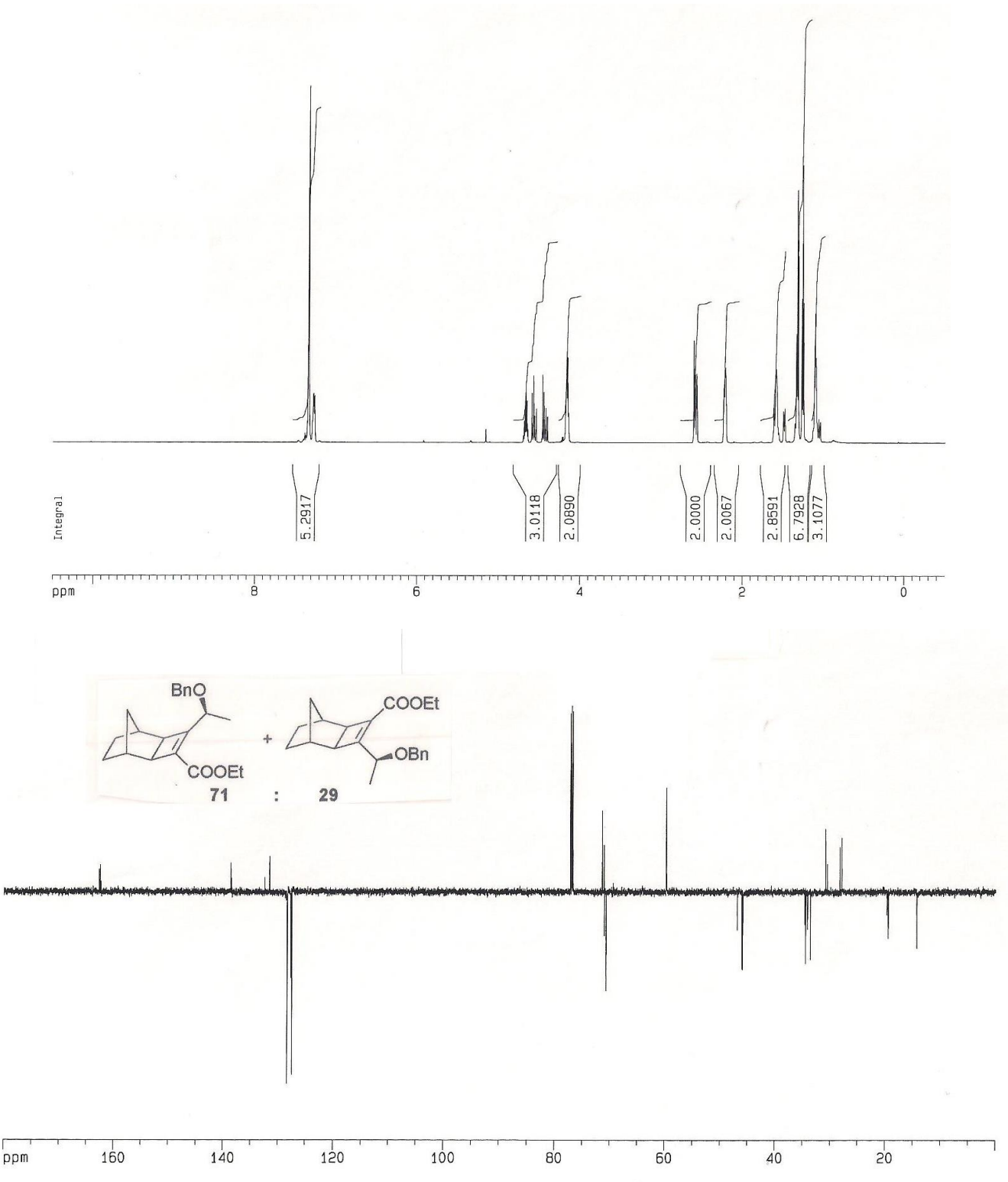

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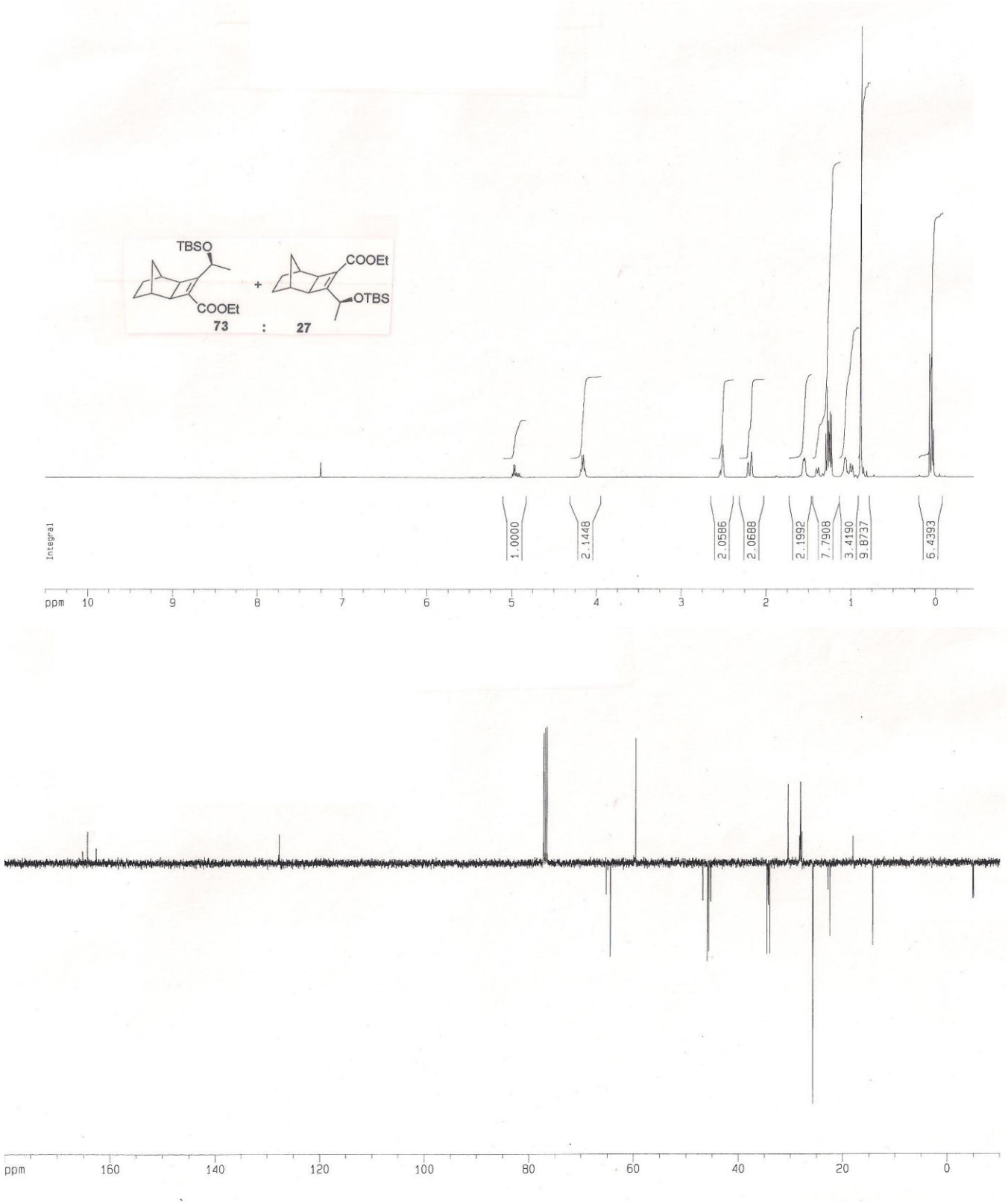

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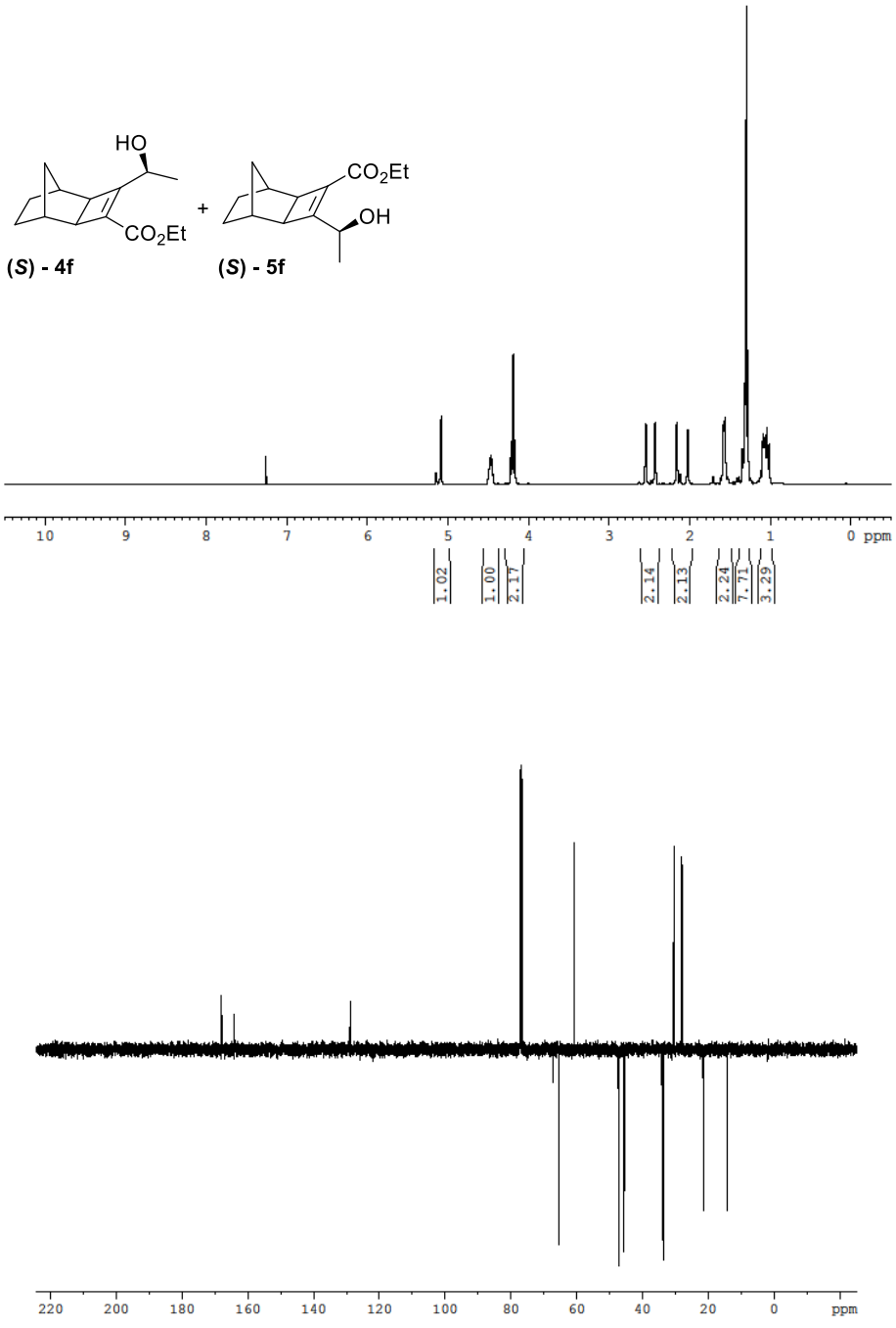

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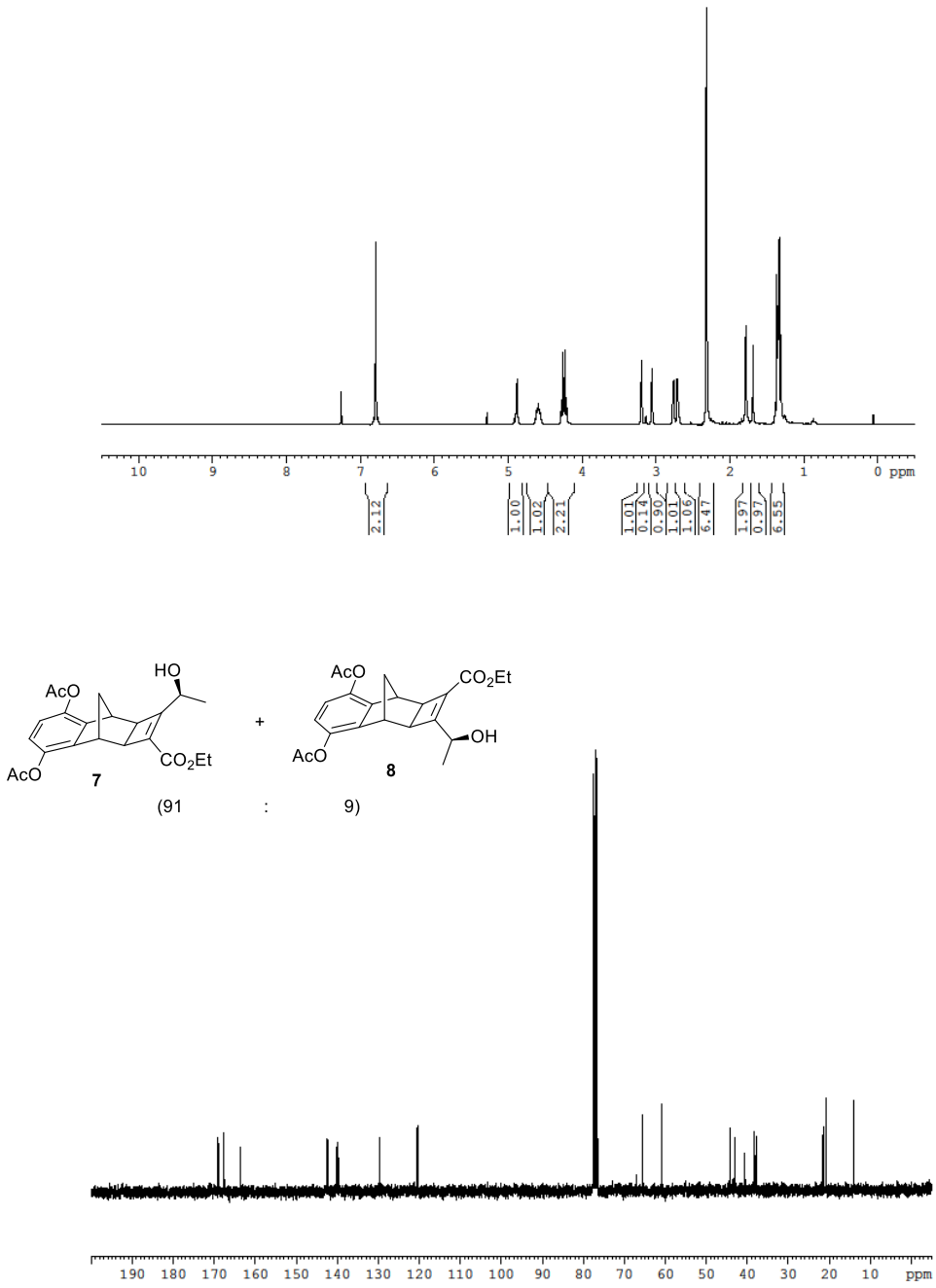

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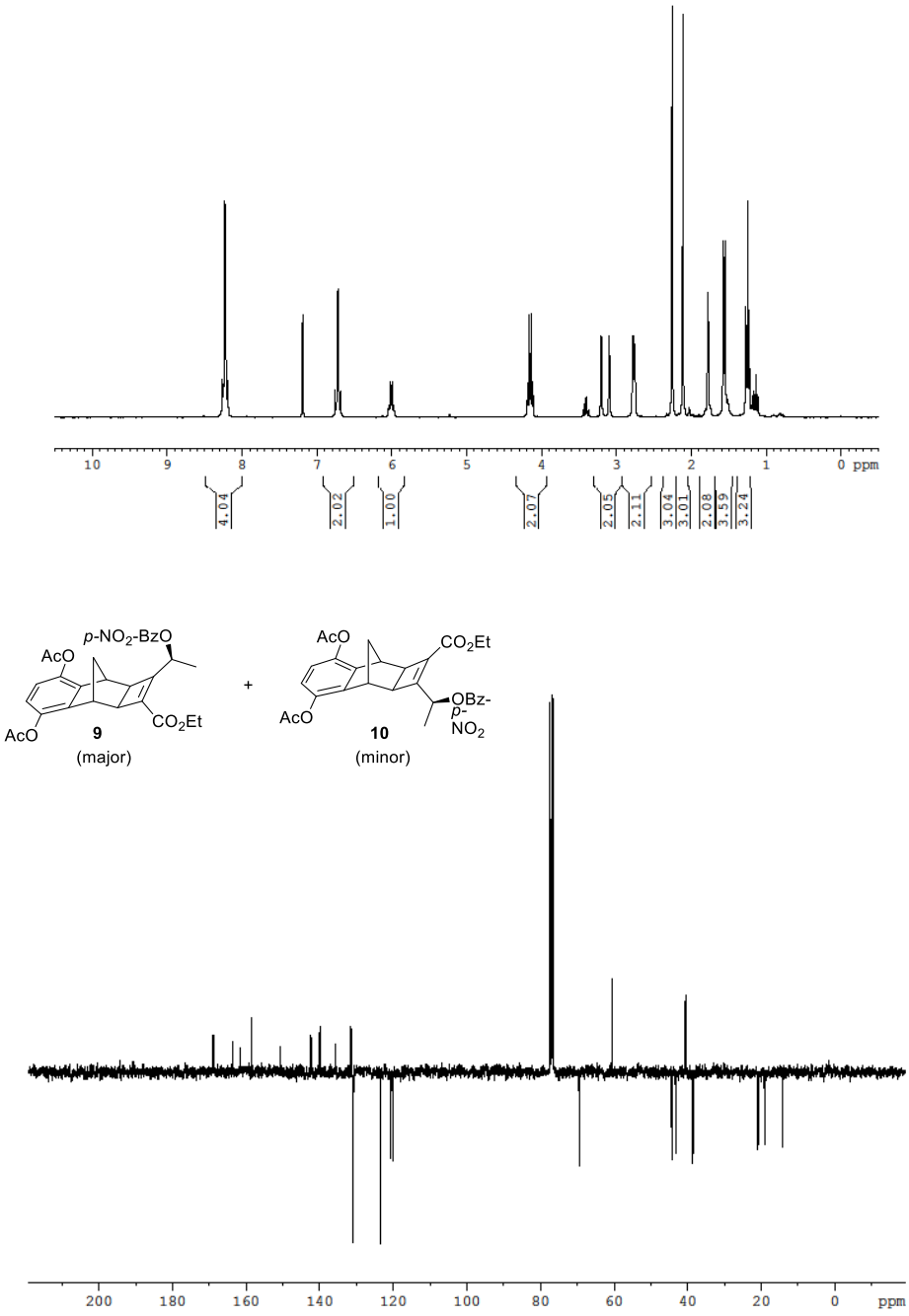

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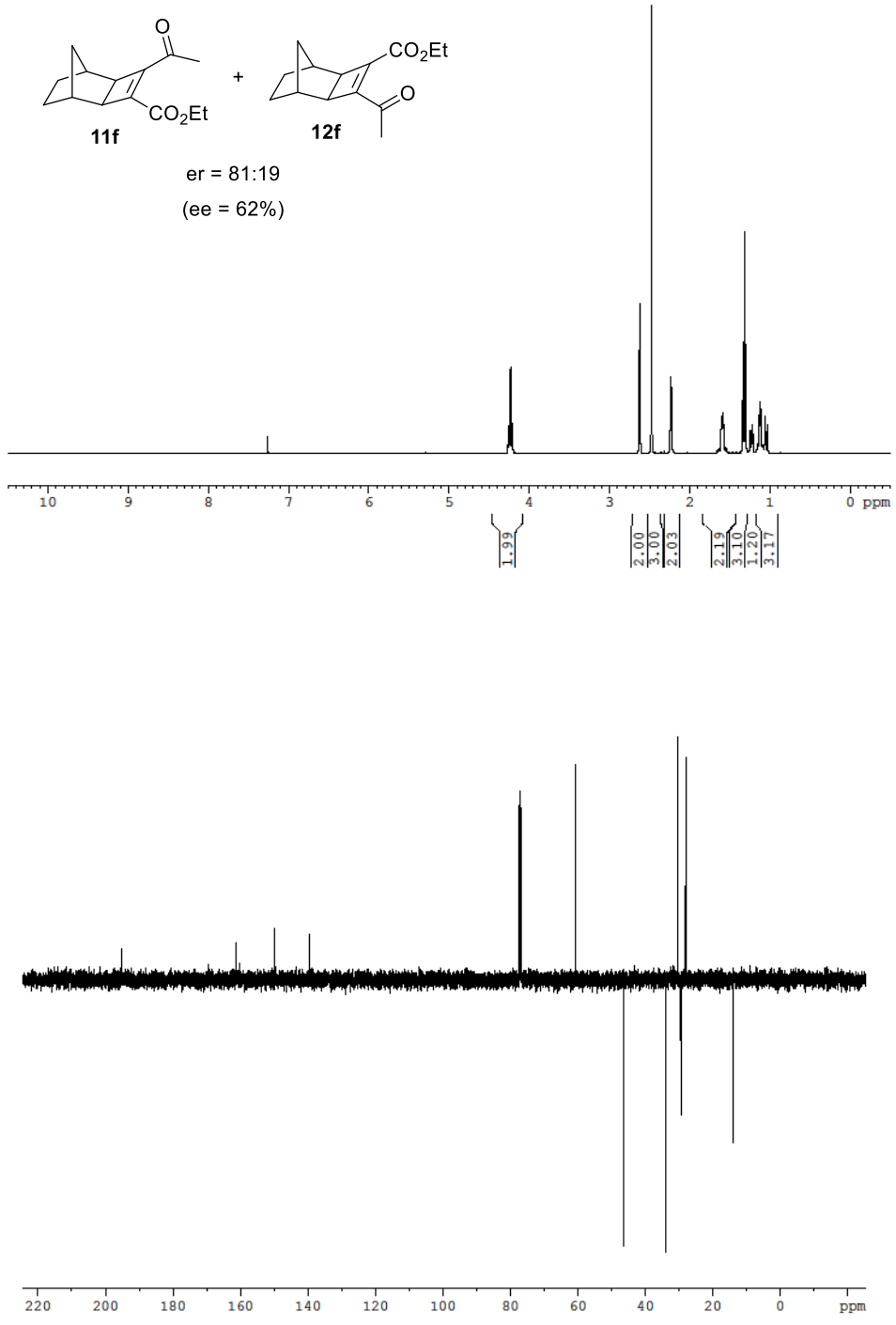

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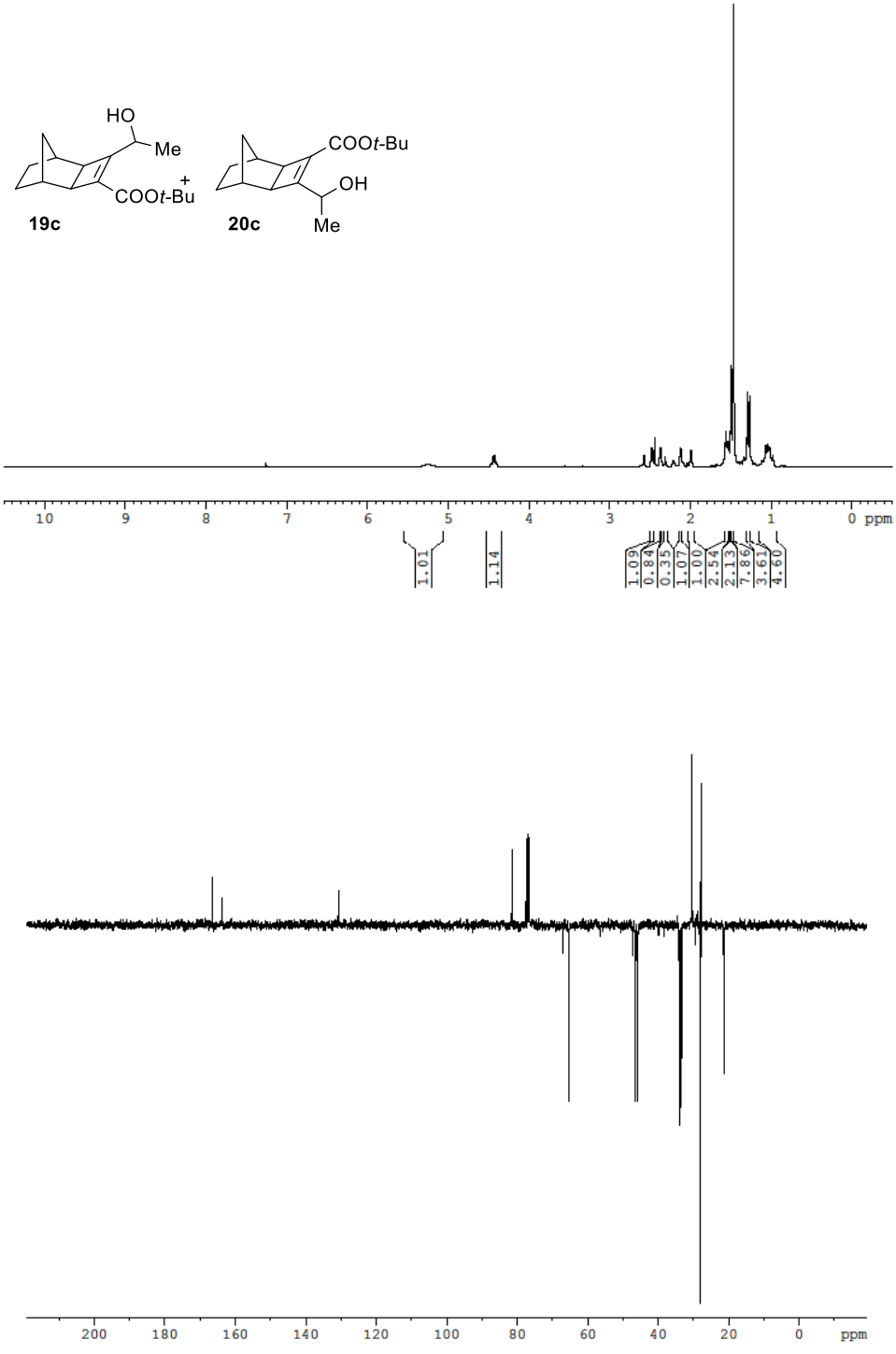

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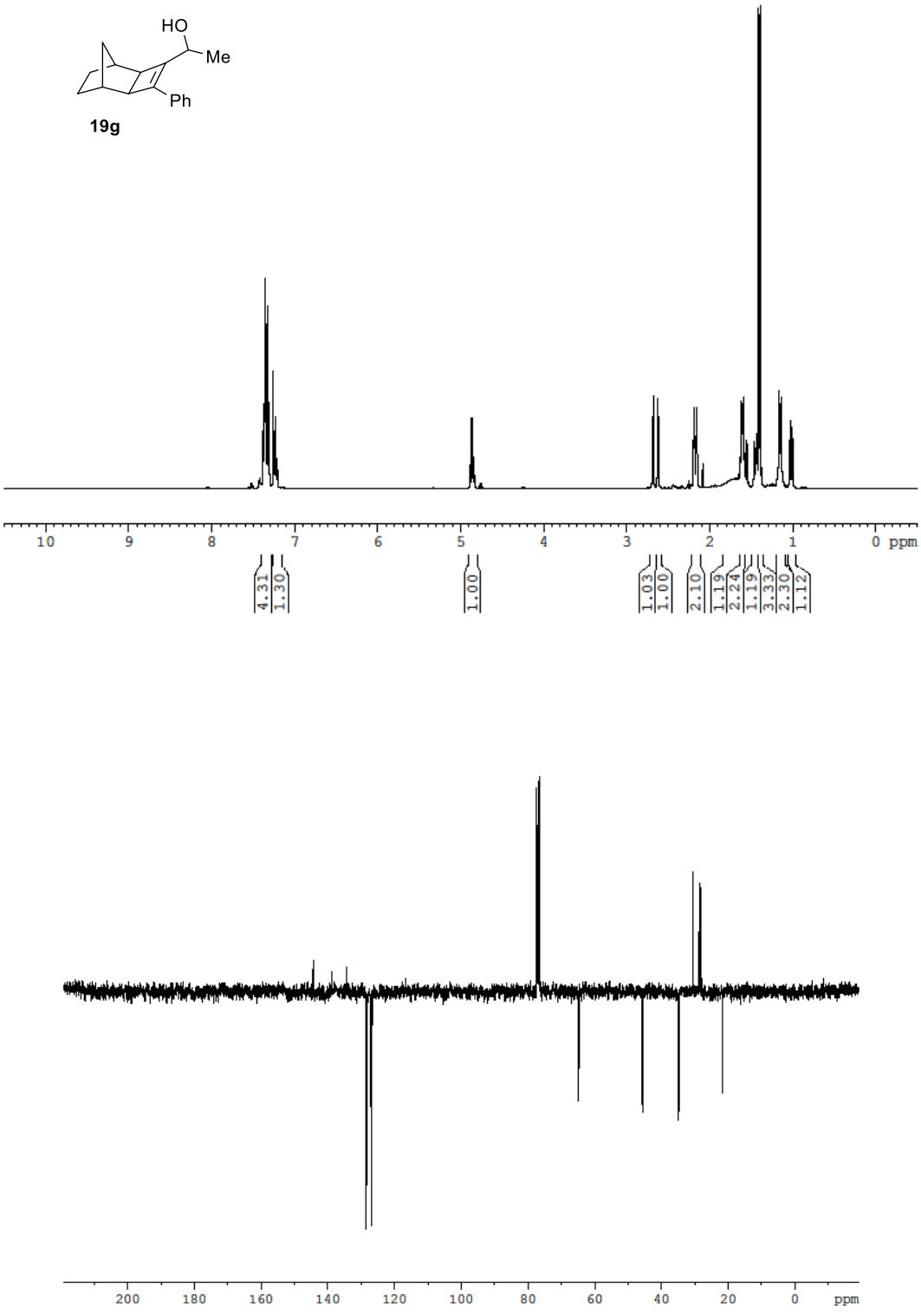

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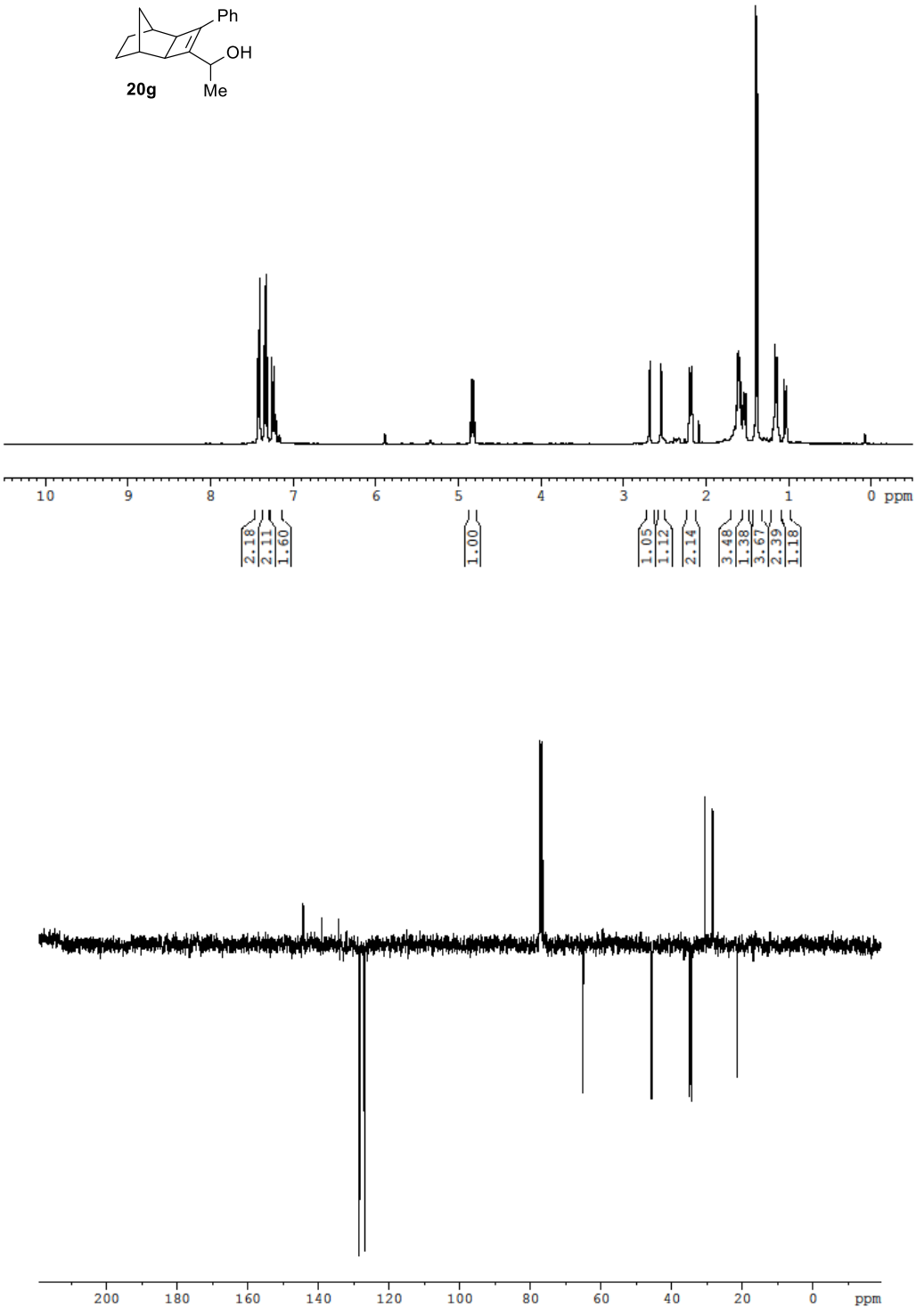

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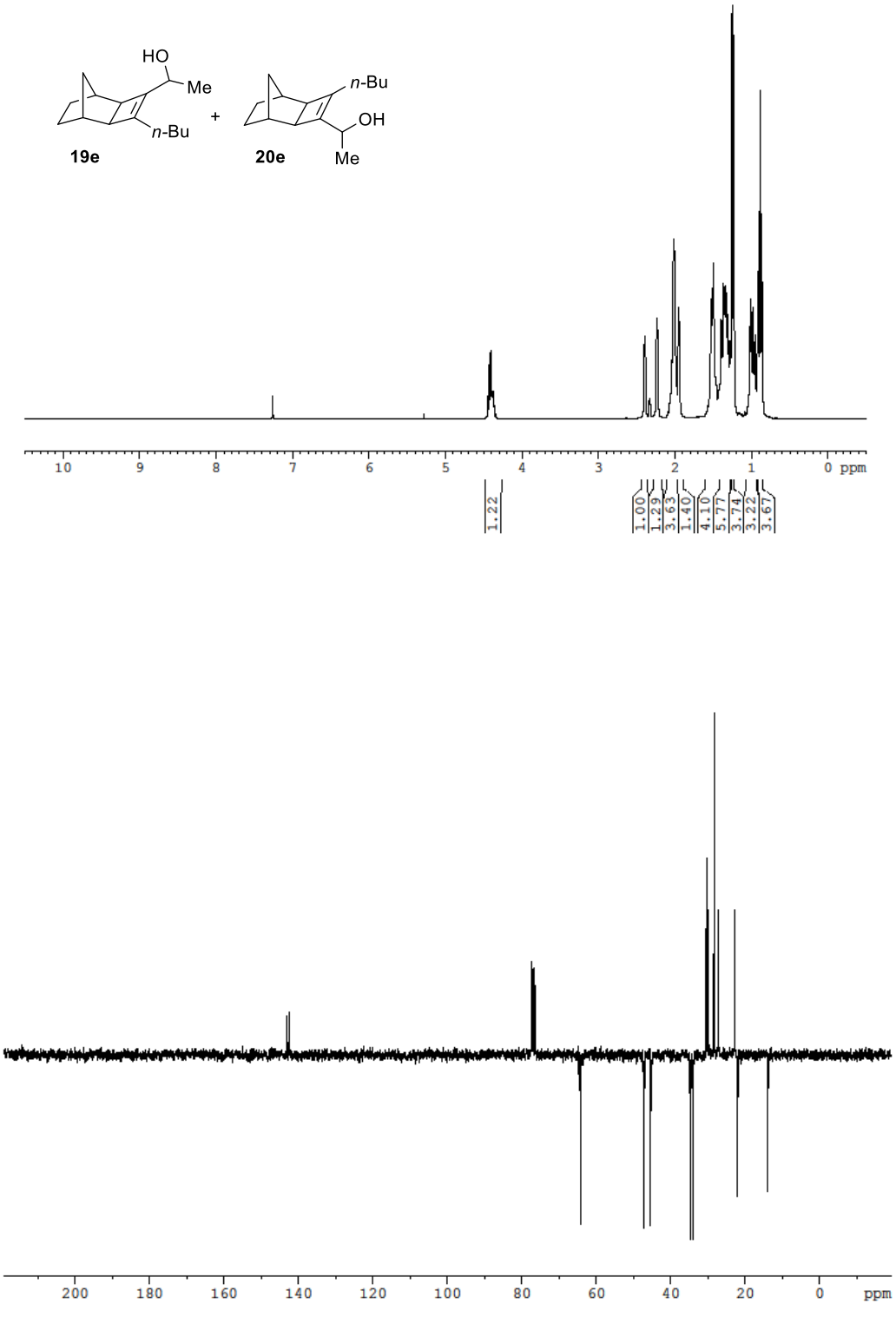

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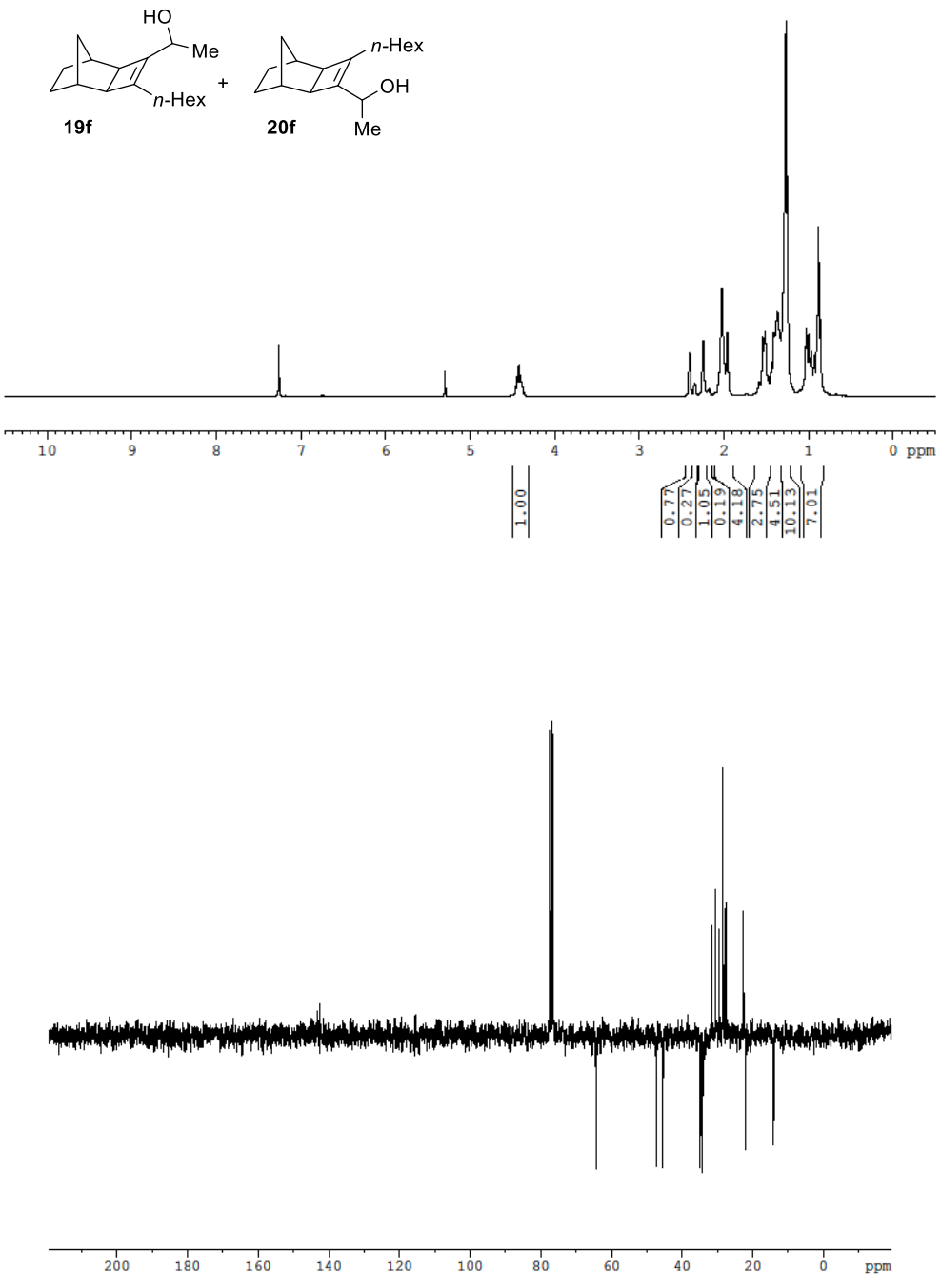

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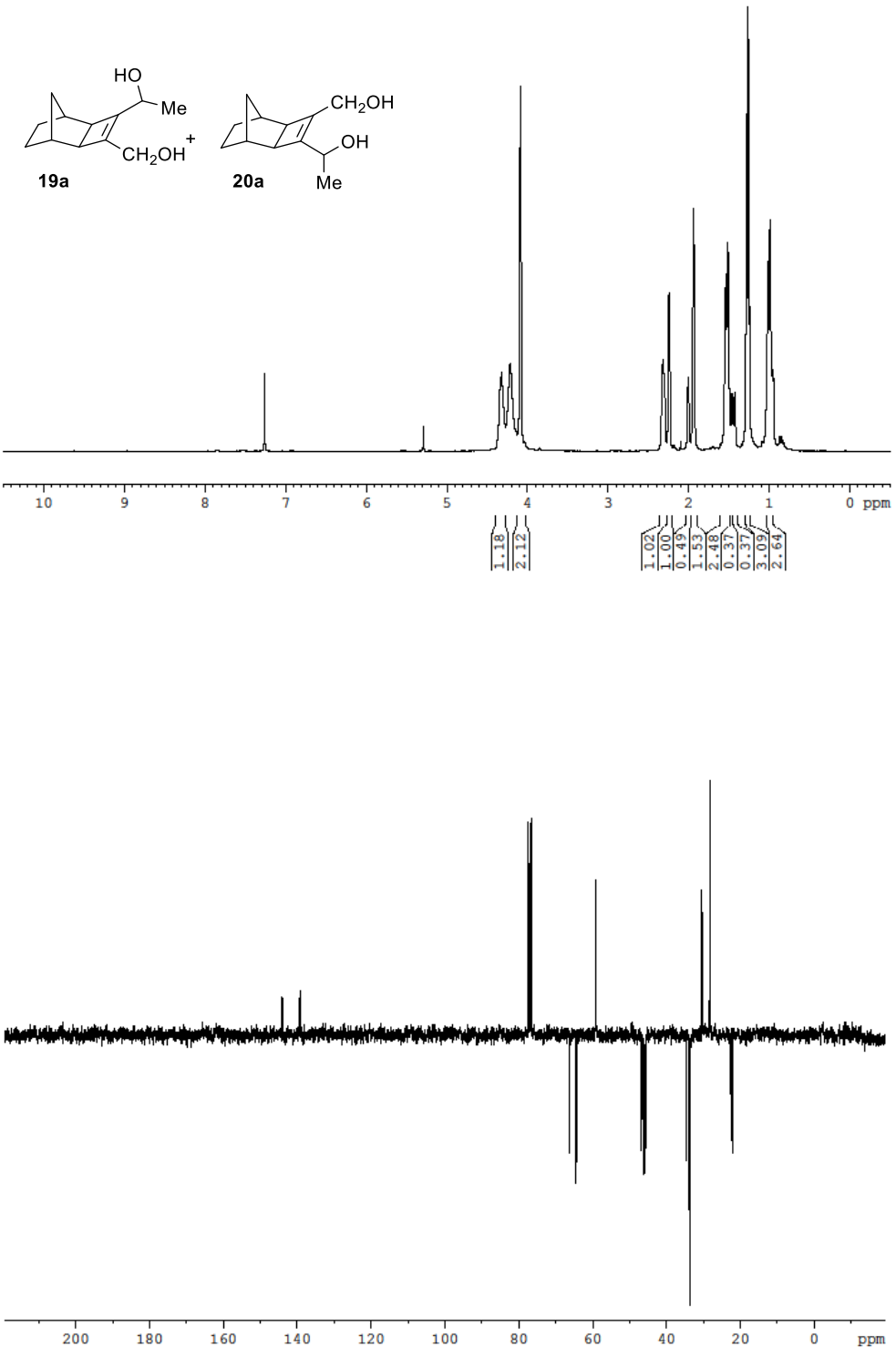

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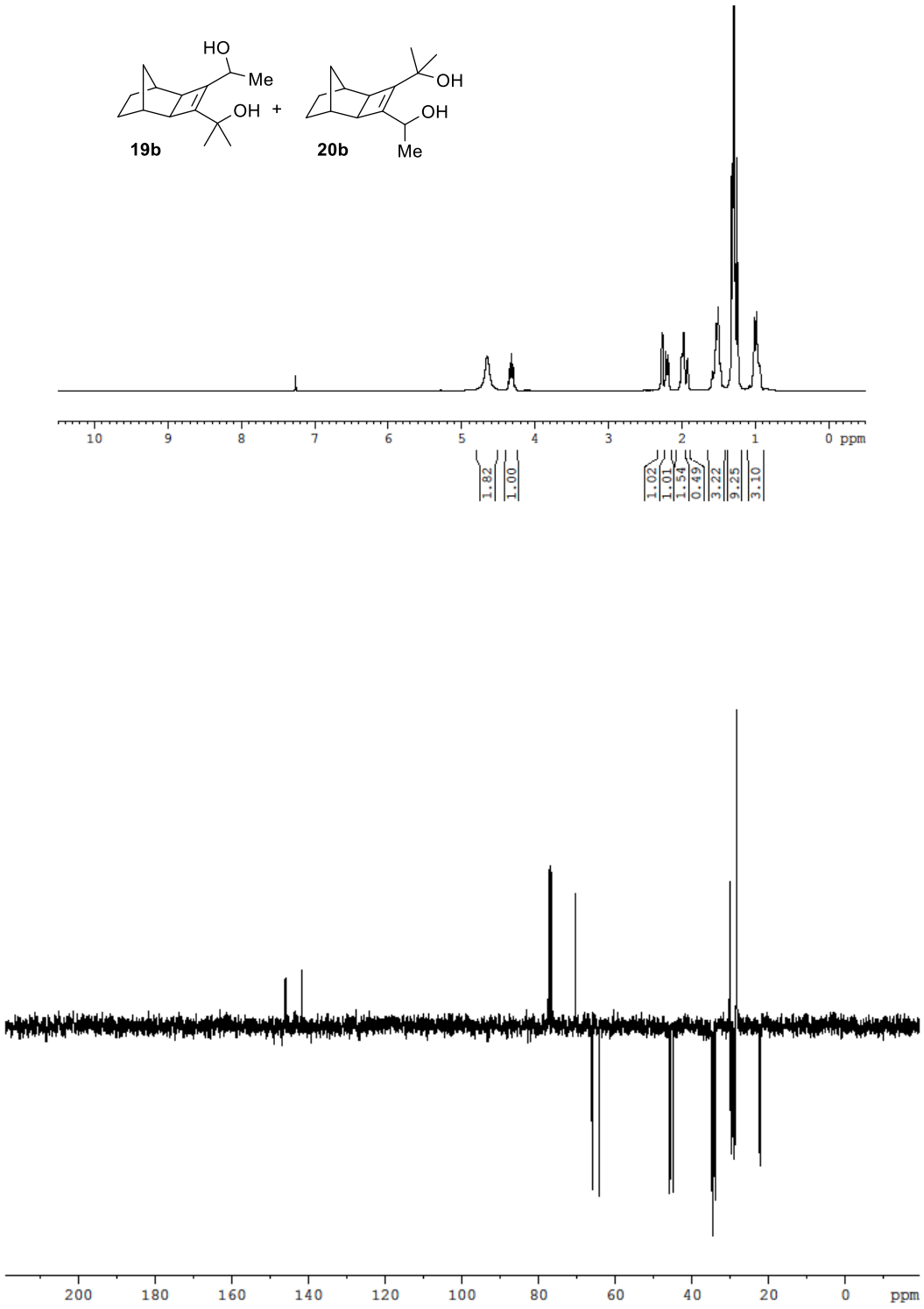

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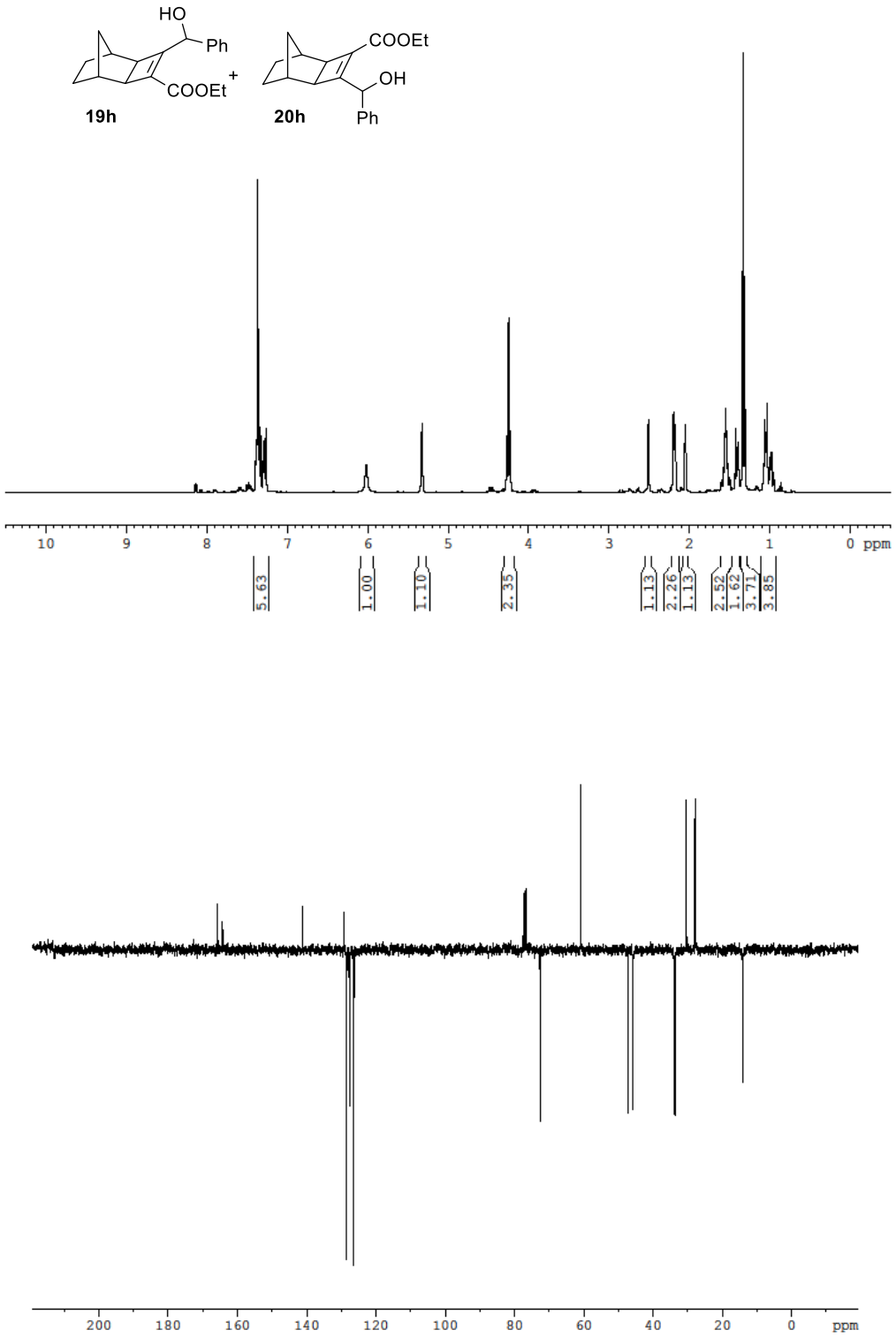

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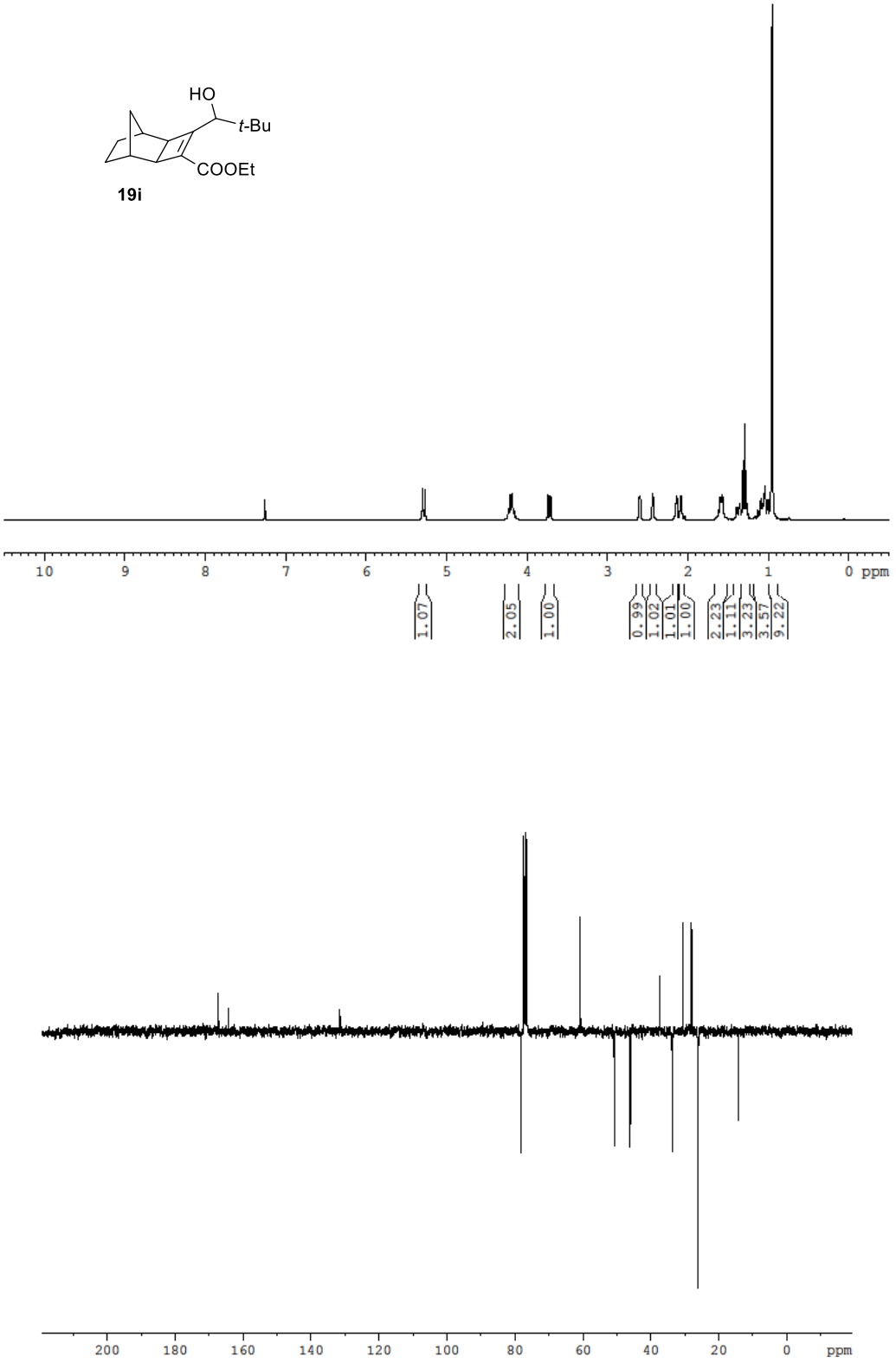

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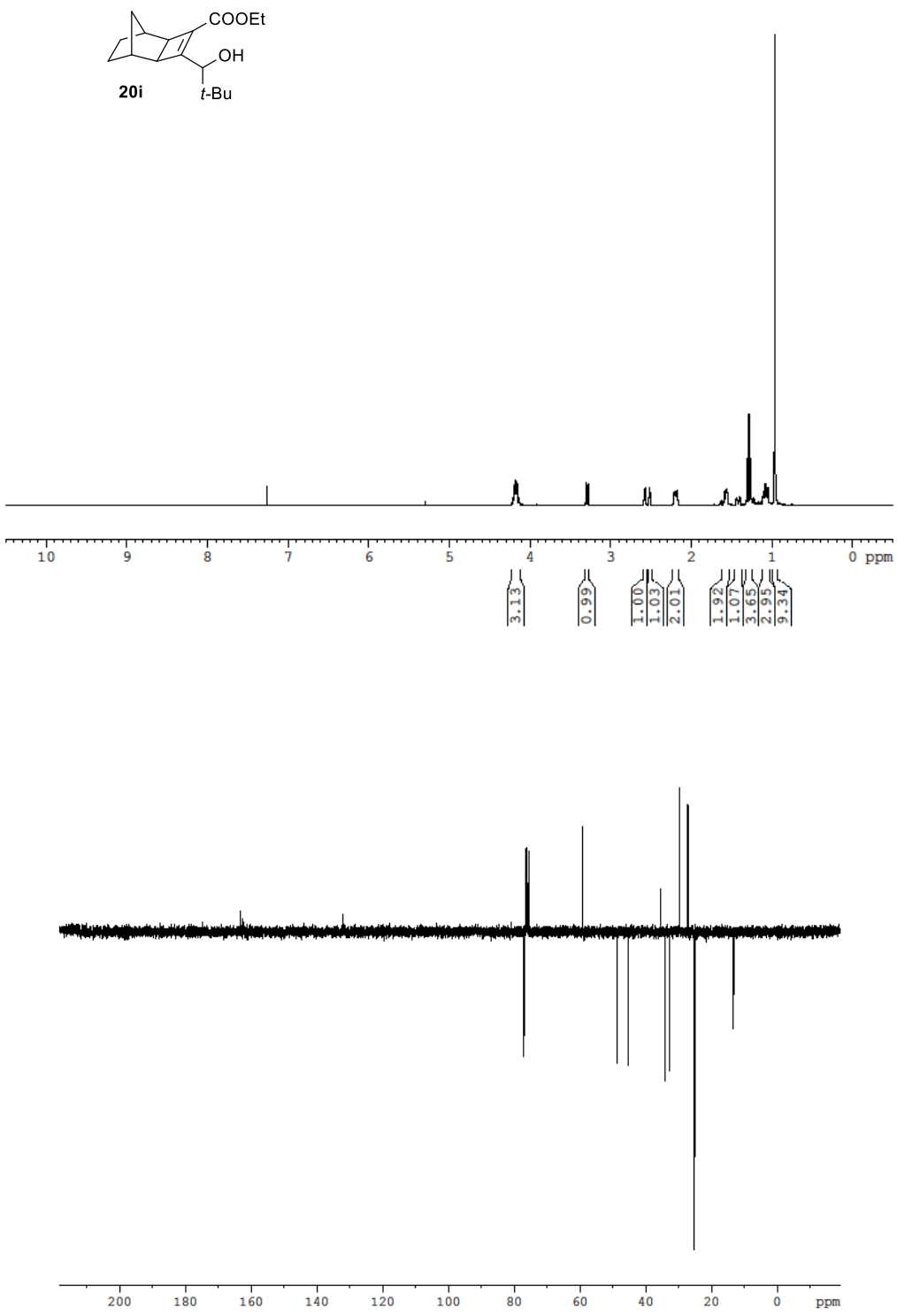

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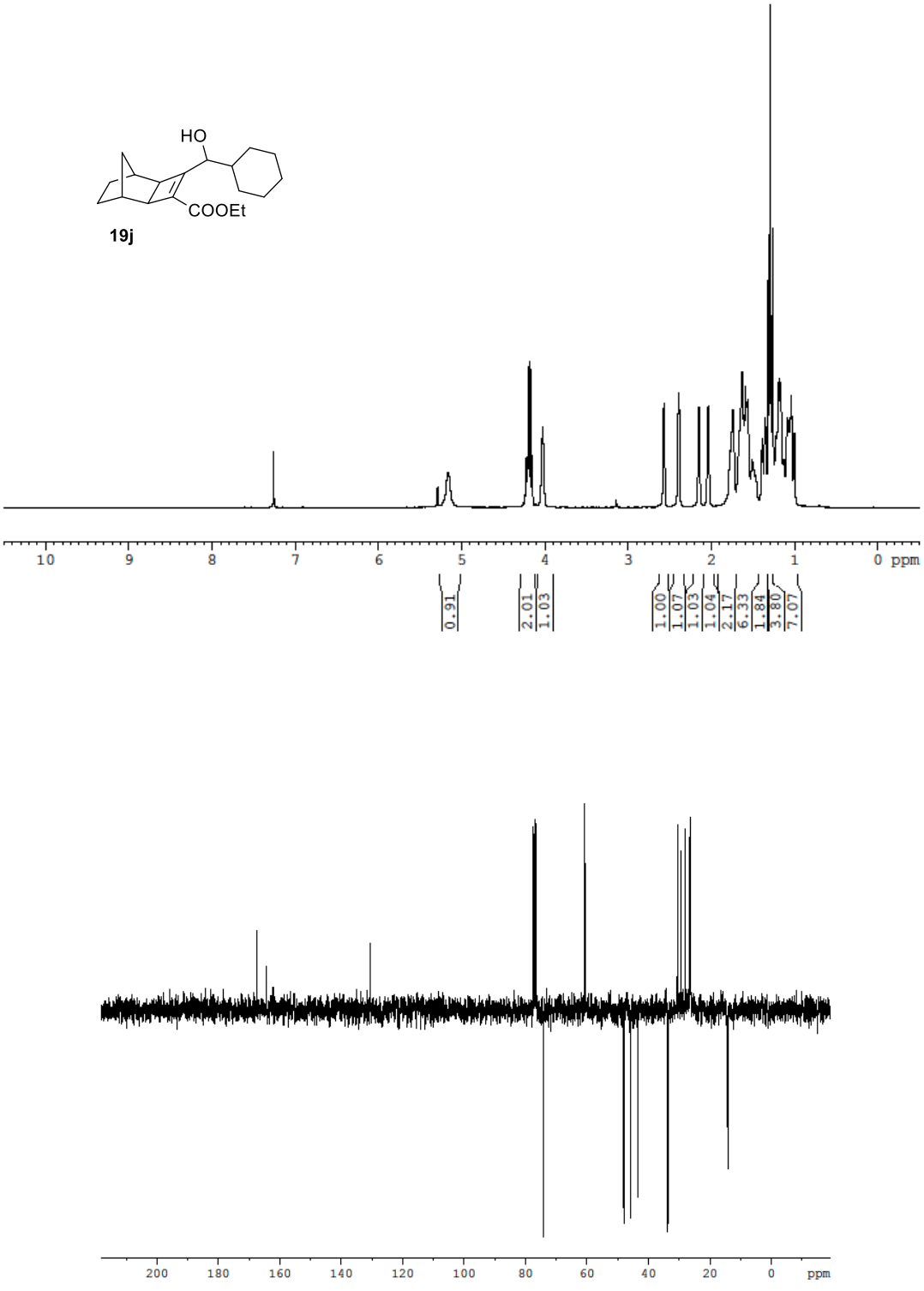

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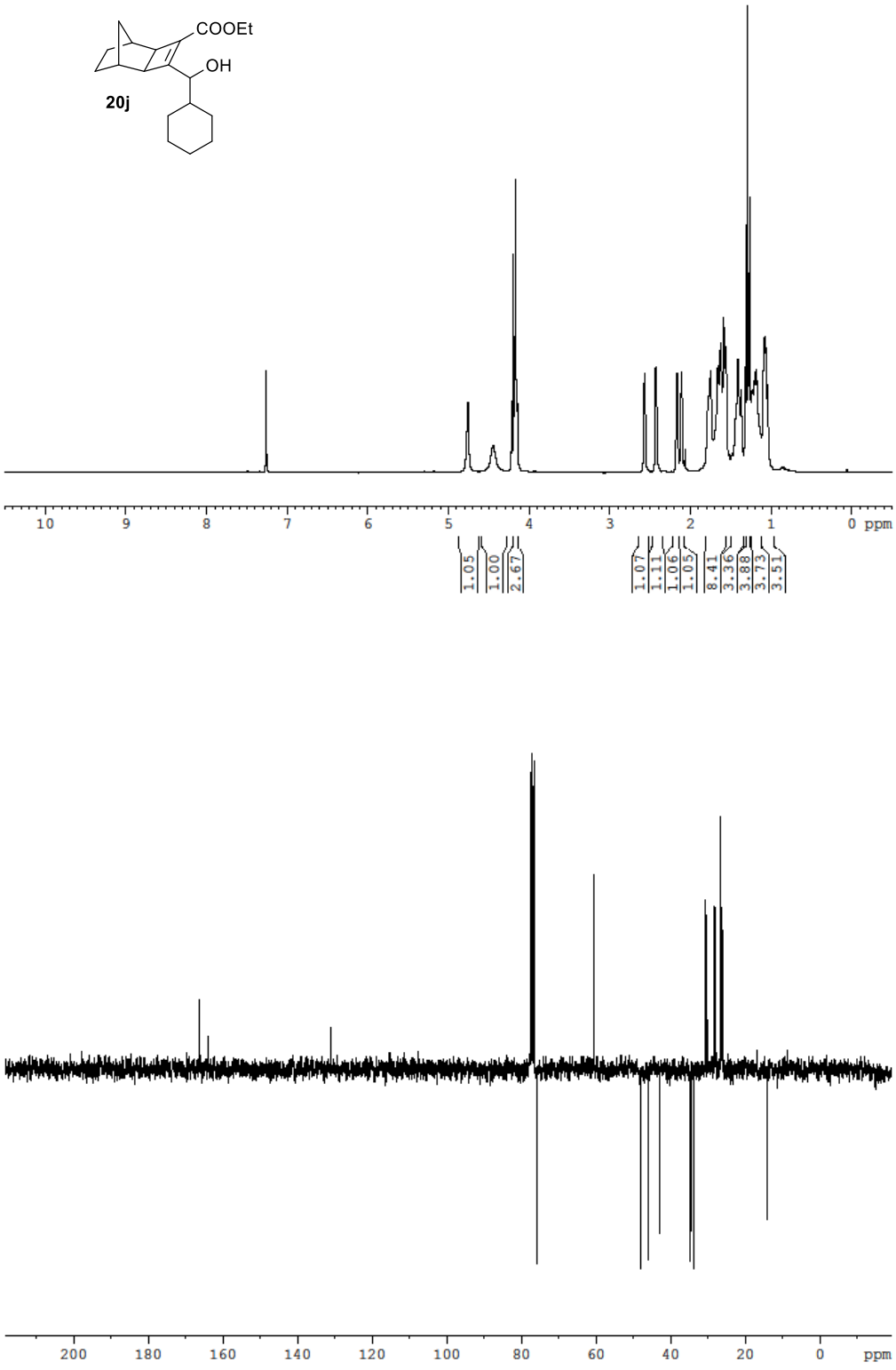

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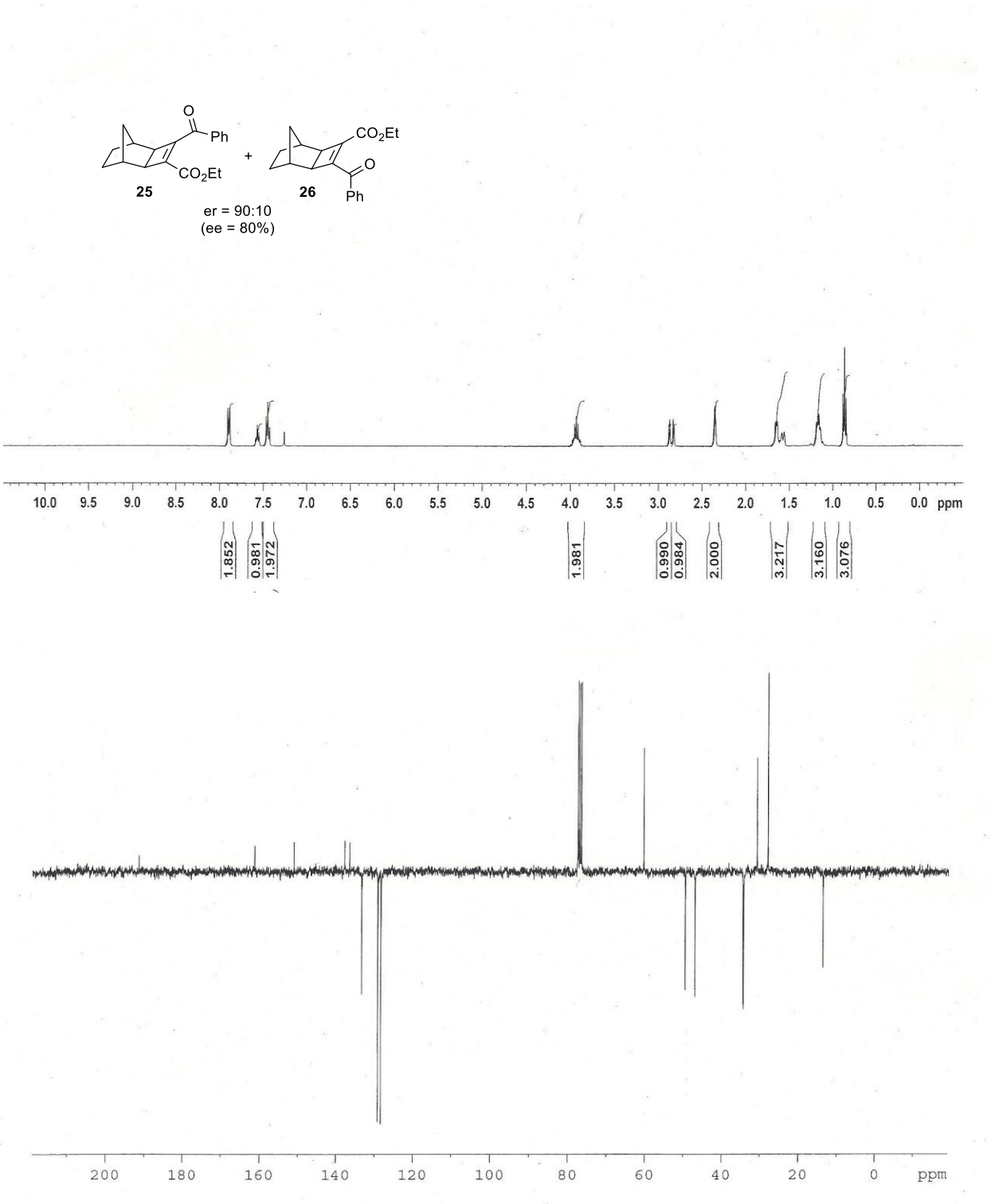

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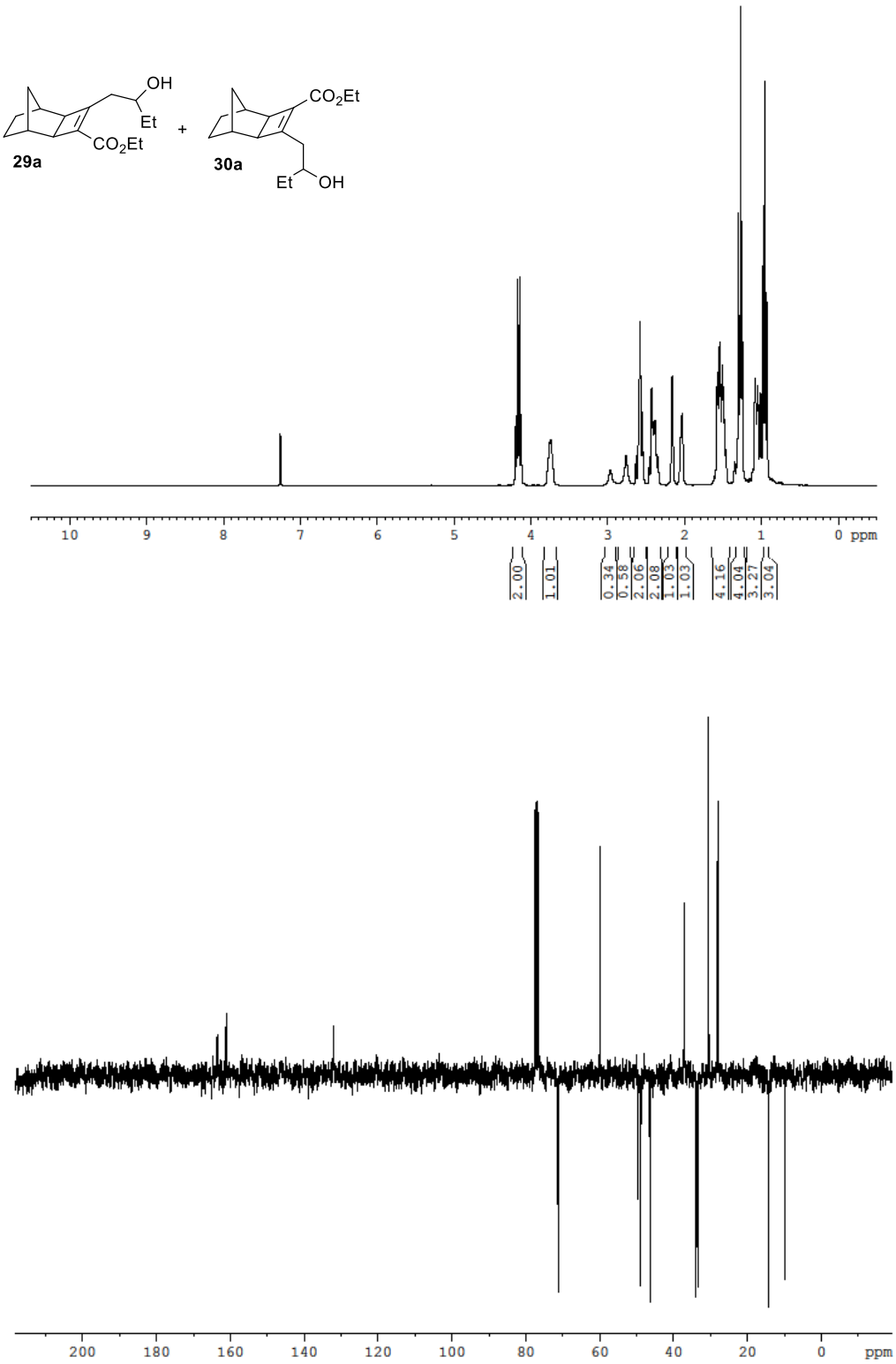

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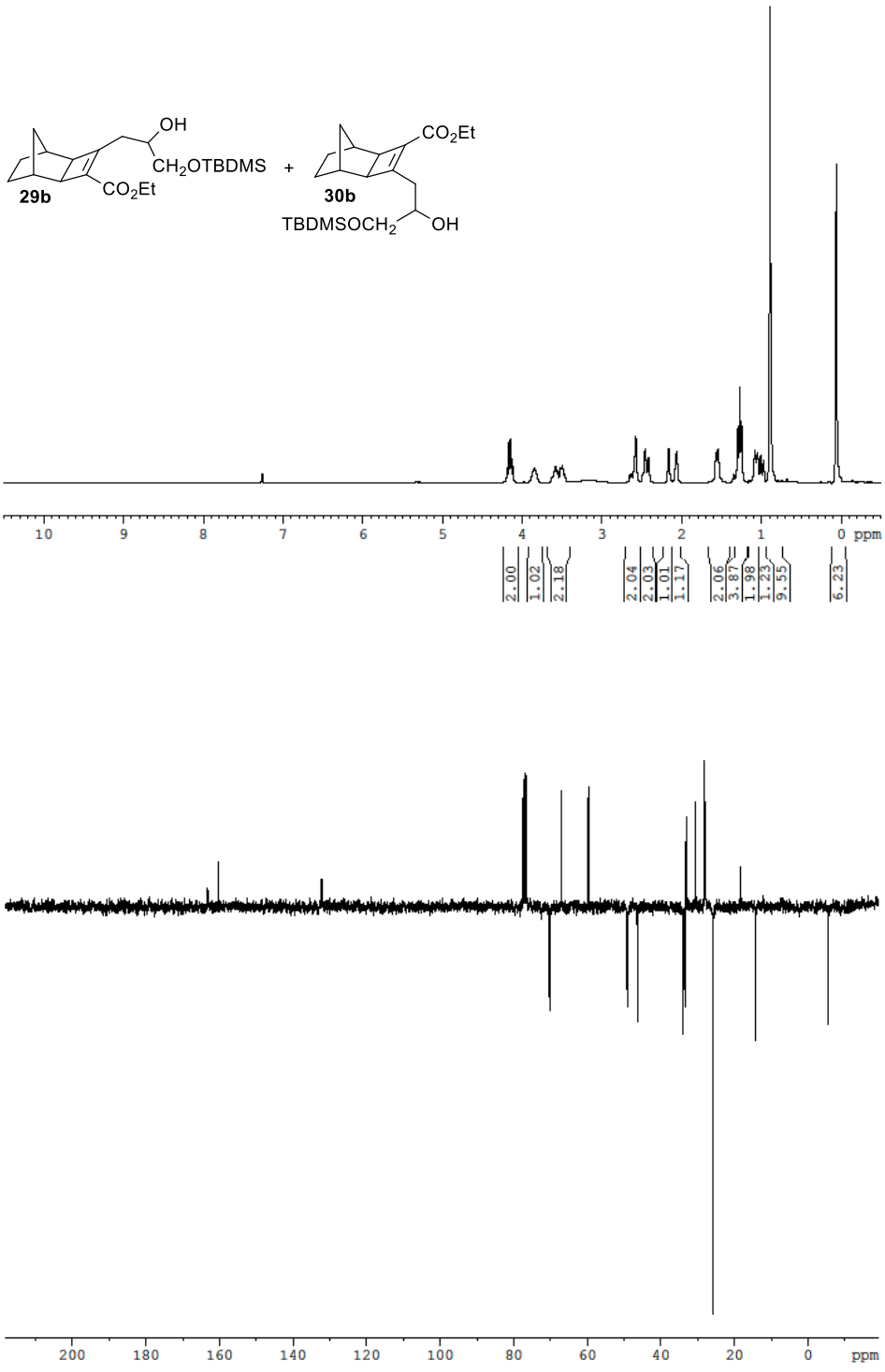

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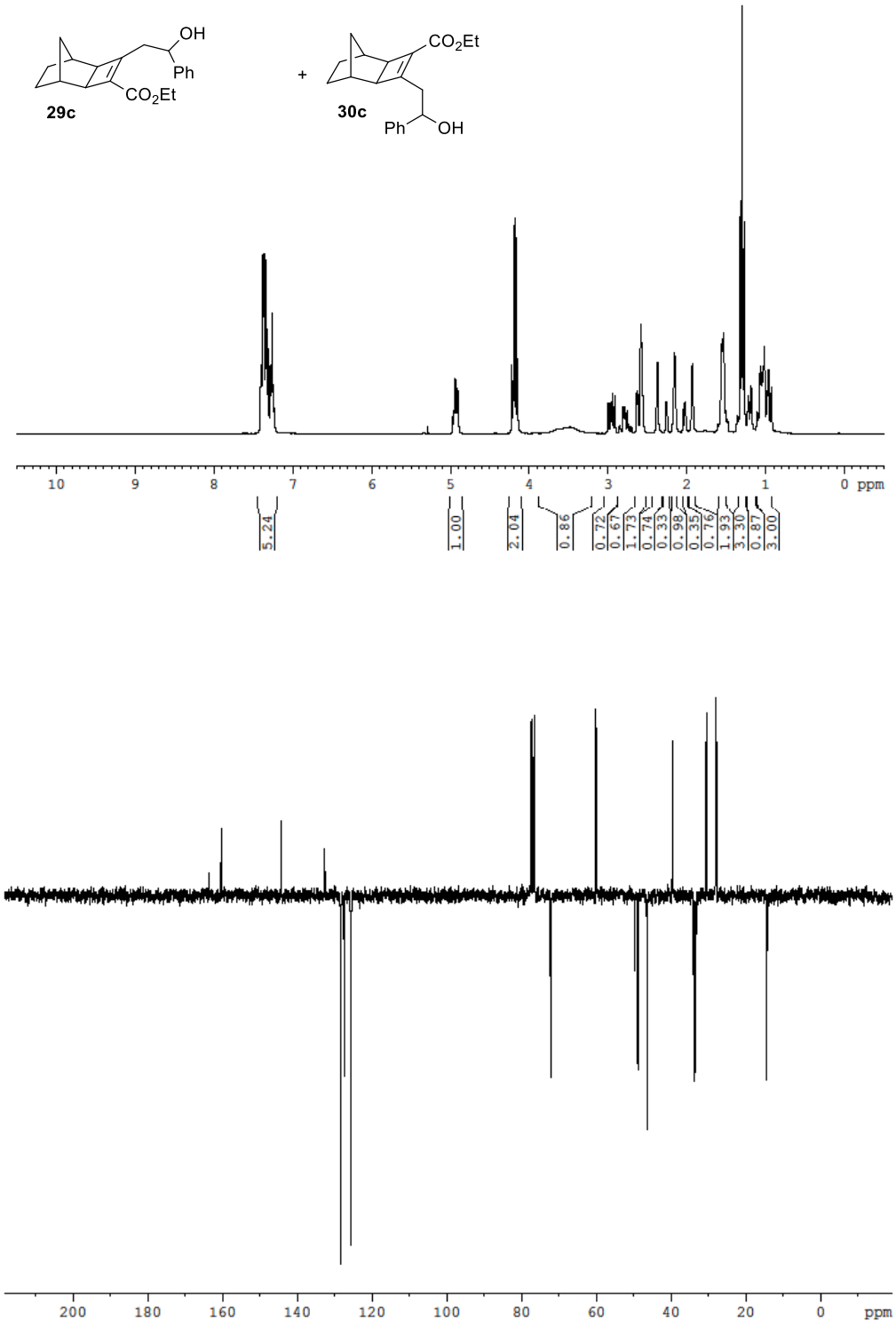

^{1}H (400 MHz) and ^{13}C (75 MHz) spectra of 29/30c in $CDCl_3$

Part II: Characterization of Alkynes

Unless otherwise stated, all alkynes were prepared according to general literature methods.[1,2,3]

Ethyl (*S*)-4-ethoxycarbonyloxy-pent-2-ynoate (2a): 0.194 g, 0.913 mmol, 73%; colorless oil. R_f 0.56 (EtOAc:hexanes=1:4); $[\alpha]_D^{22}$= -98.3 (c = 0.82, $CHCl_3$); IR (CH_2Cl_2) 2988, 2942, 2245, 1748, 1716, 1372, 1278, 1043 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.36 (q, 1H, *J*=6.8 Hz), 4.192 (q, 2H, *J*= 7.1 Hz), 4.189 (q, 2H, *J*= 7.1 Hz), 1.55 (d, 3H, *J*= 6.8 Hz), 1.28 (t, 3H, *J*= 7.1 Hz), 1.26 (t, 3H, *J*= 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.8, 152.8, 83.8, 76.8, 64.5, 63.0, 62.1, 20.3, 14.1, 13.8. HRMS calcd for $C_{10}H_{14}O_5$ $[M+H]^+$: 215.0919; found: 215.0944.

Ethyl (*S*)-4-acetoxy-pent-2-ynoate (2b): 204.7 mg, 1.110 mmol, 79%; colorless oil. R_f 0.45 (EtOAc:hexanes = 1:4); $[\alpha]_D^{22}$= -118.5 (c = 0.685, $CHCl_3$); IR (CH_2Cl_2) 2991, 2942, 2909, 2876, 2251, 1740, 1705, 1371, 1224 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.52 (q, 1H, *J*= 6.8 Hz), 4.23 (q, 2H, *J*= 7.1 Hz), 2.08 (s, 3H), 1.53 (d, 3H, *J*= 6.8 Hz), 1.30 (t, 3H, *J*= 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.6, 153.0, 84.7, 76.2, 62.2, 59.4, 20.8, 20.3, 14.0. Anal. calcd for $C_9H_{12}O_4$: C, 58.69%, H, 6.57%; found: C, 58.37%, H, 6.74%.

Ethyl (*S*)-4-(2-methoxy-ethoxymethoxy)-pent-2-ynoate (2c): 94.3 mg, 0.410 mmol, 65%; colorless oil. R_f 0.26 (EtOAc:hexanes = 1:4); $[\alpha]_D^{22}$= -158.1 (c = 0.43, $CHCl_3$); IR (CH_2Cl_2) 2986, 2944, 2887, 2815, 2242, 1717, 1452, 1251 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.93 (d, 1H, *J* =7.2 Hz), 4.72 (d, 1H, *J* = 7.2 Hz), 4.58 (q, 1H, *J* = 6.8 Hz), 4.22 (q, 2H, *J*= 7.1 Hz), 3.68-3.74 (m, 2H), 3.54-3.57 (m, 2H), 3.38 (s, 3H), 1.49 (d, 3H, *J* = 6.8 Hz), 1.29 (t, 3H, *J*= 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.3, 93.6, 86.5, 76.5, 71.6, 67.3, 62.0, 61.3, 59.0, 21.1, 14.0. Anal. calcd for $C_{11}H_{18}O_5$: C, 57.38%, H, 7.88%; found: C, 57.66%; H, 7.59%.

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[1] Villeneuve, K.; Tam, W. *Organometallics*. **2006**, *25*, 843.
[2] Villeneuve, K.; Tam, W. *Organometallics* **2007**, *26*, 6082.
[3] Miura, K.; Hondo, T.; Okajima, S.; Nakagawa, T.; Takahashi, T.; Hosomi, A. *J. Org. Chem.* **2002**, *67*, 6082.

(*S*)-4-(Phenylmethoxy)pent-2-ynoic acid ethyl ester (2d): 319 mg, 1.37 mmol, 70%; colourless liquid. R_f 0.36 (EtOAc:hexanes=1:9); $[\alpha]_D^{16}$ = –153.3 (c = 0.21, $CHCl_3$); IR (neat) 3033, 2988, 2938, 2869, 2241, 1717, 1497, 1455, 1392, 1367, 1329, 1301, 1253, 1136, 1103, 1073, 1040, 1017 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.33 (m, 5H), 4.80 (d, 1H, *J* = 11.6 Hz), 4.51 (d, 1H, *J* = 11.6 Hz), 4.33 (q, 1H, *J* = 6.7 Hz), 4.26 (q, 2H, *J* = 7.1 Hz), 1.52 (d, 3H, *J* = 6.7Hz), 1.33 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.3, 137.3, 128.5, 128.0, 127.9, 86.7, 77.1, 71.1, 64.1, 62.1, 21.2, 14.0. HRMS calcd. for $C_{14}H_{16}O_3$ $[M–H]^-$: 231.1022, found: 231.1021.

(*S*)-4-(*tert*-Butyldimethylsilyloxy)pent-2-ynoic acid ethyl ester (2e): 347 mg, 1.35 mmol, 87%; colourless liquid. R_f 0.51 (EtOAc:hexanes=1:19); $[\alpha]_D^{25}$ = –50.00 (c = 0.06, $CHCl_3$). IR (neat) 2988, 2958, 2932, 2244, 1717, 1244, 1102, 1074, 836 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.60 (q, 1H, 6.6 Hz), 4.22 (q, 2H, 7.1 Hz), 1.45 (d, 3H, 6.6 Hz), 1.30 (t, 3H, 7.1 Hz), 0.90 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 89.1, 75.2, 61.9, 58.6, 25.7, 24.4, 18.1, 14.0, -4.7, -5.1. **2e** was subsequently converted to **4/5e** which was fully characterized (see manuscript).

Ethyl (*S*)-4-hydroxy-pent-2-ynoate (2f): 635.8 mg, 4.473 mmol, 71%; colorless oil. R_f 0.28 (EtOAc:hexanes = 1:4); $[\alpha]_D^{22}$= -27.3 (c = 0.82, $CHCl_3$); IR (CH_2Cl_2) 3411, 2987, 2939, 2907, 2877, 2246, 1712, 1244 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.63 (q, 1H, *J* = 6.7 Hz), 4.23 (q, 2H, *J* = 7.1 Hz), 2.37 (br s, 1H), 1.51 (d, 3H, *J* = 6.7 Hz), 1.30 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.4, 88.4, 75.7, 62.2, 58.0, 23.2, 13.9. Anal. calcd for $C_7H_{10}O_3$: C, 59.14%, H, 7.09%; found: C, 59.01%, H, 7.27%. Spectral data are consistent with those of the literature.[4]

Pent-2-yne-1,4-diol (16a). 124.4 mg, 1.243 mmol, 76%; colourless oil. R_f 0.56 (EtOAc); IR (neat, NaCl) 3371, 2983, 2871, 1644, 1447, 1416, 1372, 1230 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.57 (q, 1H, *J* = 6.4 Hz), 4.29 (s, 2H), 3.43 (br s, 1H), 3.35 (br s, 1H), 1.45 (d, 3H, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 87.6, 82.2, 58.1, 50.7, 24.0; HRMS calcd. for $C_5H_8O_2$ $[M+H]^+$: 101.0603, found: 101.0610.

[4] Trost, B. M.; Müller, T. J. J.; Martinez, J. *J. Am. Chem. Soc.* **1995**, *117*, 1888.

2-Methyl-hex-3-yne-2,5-diol (16b). 175.7 mg, 1.371 mmol, 97%; colourless oil. R_f 0.29 (EtOAc:Hexanes = 4:6); IR (neat, NaCl) 3418, 2983, 2934, 2875, 1455, 1372, 1237, 1166, 1121, 1079 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.54-4.53 (m, 1H), 2.81 (s, 2H), 1.50 (s, 6H), 1.43 (d, 3H, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 88.7, 84.0, 65.0, 58.1, 31.3, 24.2; HRMS calcd. for $C_7H_{12}O_2$ $[M+H]^+$: 129.0916, found: 129.0921.

4-Hydroxy-pent-2-ynoic acid *tert*-butyl ester (16c). See our previous report.[2]

4-Bromo-but-3-yn-2-ol (16d). Prepared following literature methods.[5] 760.3 mg, 5.103 mmol, 80%; yellow oil. R_f 0.42 (EtOAc:Hexanes = 2:8); IR (neat, NaCl) 3355, 2985, 2934, 2877, 2211, 1710, 1451, 1373, 1329, 1123, 950, 853 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.54 (q, 1H, *J* = 6.6 Hz), 2.40 (br s, 1H), 1.45 (d, 3H, *J* = 6.6 Hz; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 81.8, 59.2, 44.5, 24.0; HRMS calcd. for C_4H_5OBr $[M+H]^+$: 148.9602, found: 148.9609.

Oct-3-yn-2-ol (16e). 224.6 mg, 1.780 mmol, 41%; colourless oil. R_f 0.22 (EtOAc:Hexanes = 1:9); ^1H NMR ($CDCl_3$, 300 MHz) δ 4.48 (tq, 1H, *J* = 6.5, 1.8 Hz), 2.23 (br s, 1H), 2.17 (dt, 2H, *J* = 6.9, 1.7 Hz), 1.39 (d, 3H, *J* = 6.6 Hz), 1.31-1.50 (m, 4H), 0.88 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 84.5, 82.2, 58.4, 30.6, 24.7, 21.8, 18.2, 13.5. Spectral data are consistent with that of the literature.[6]

Dec-3-yn-2-ol (16f). 36.8 mg, 0.238 mmol, 37 %; colourless oil. R_f 0.32 (EtOAc:Hexanes = 1:9); ^1H NMR ($CDCl_3$, 400 MHz) δ 4.51 (tq, 1H, *J* = 6.5, 1.9 Hz), 2.18 (dt, 2H, *J* = 7.1, 1.9 Hz), 1.77 (br s, 1H), 1.24-1.51 (m, 11H) including 1.42 (d, *J* = 6.5 Hz), 0.88 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 84.7, 82.2, 58.6, 31.3, 28.6, 28.5, 24.8, 22.5, 18.6, 14.0. Data are consistent with that of the literature.[7]

4-Phenyl-but-3-yn-2-ol (16g), **4-Hydroxy-4-phenyl-but-2-ynoic acid ethyl ester (16h), 4-Hydroxy-5,5-dimethyl-hex-2-ynoic acid ethyl ester (16i),** and **4-Cyclohexyl-4-hydroxy-but-2-ynoic acid ethyl ester (16j)**. See the Supplementary material of our former reports.[1,2]

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[5] Hofmeister, H.; Annen, K.; Laurent, H.; Wiechert, R. *Angew. Chem. Int. Ed. Engl.* **1984**, *9*, 727.
[6] Kalgutkar, A.S.; Kozak, K.R.; Crews, B.C.; Hochgesang, G.P.; Marnett, L.J. *J. Med. Chem.* **1998**, *41*, 4800.
[7] Miura, K.; Wang, D.; Matsumoto, Y.; Hosomi, A. *Org. Lett.* **2005**, *7*, 503.

(*R*)-4-Hydroxy-4-phenyl-but-2-ynoic acid ethyl ester (*R*)-21 (Scheme 7): 88.7 mg, 0.434 mmol, 79%; yellow oil. R_f 0.41 (EtOAc:Hexanes = 2:8); $[\alpha]^{24}_D$ = -2.33 (*c* 0.515, $CHCl_3$, 95%*ee* determined by HPLC); HPLC (OJ-H column, 0.50 mL/min, 50% ^{i}PrOH/Hexane, 215 nm): major enantiomer = 18.87 min, minor enantiomer = 11.94 min; The spectra are identical to those of the racemic ester **16b**.

5-Hydroxy-hept-2-ynoic acid ethyl ester, 27a. 772.3 mg, 4.537 mmol, 79%; brown oil. R_f 0.28 (EtOAc:Hexanes = 2:8); IR (NaCl) 3409, 2969, 2880, 2237, 1714, 1705, 1253 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.20 (q, 2H, *J* = 7.1 Hz), 3.76 (m, 1H), 2.43-2.59 (m, 2H), 2.25 (br s, 1H), 1.48-1.67 (m, 2H), 1.29 (t, 3H, *J* = 7.1 Hz), 0.96 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.6, 85.9, 74.9, 70.8, 61.9, 29.3, 27.1, 14.0, 9.8; HRMS calcd. for $C_9H_{14}O_3$: $[M+H]^+$ 171.1021, found: 171.1029.

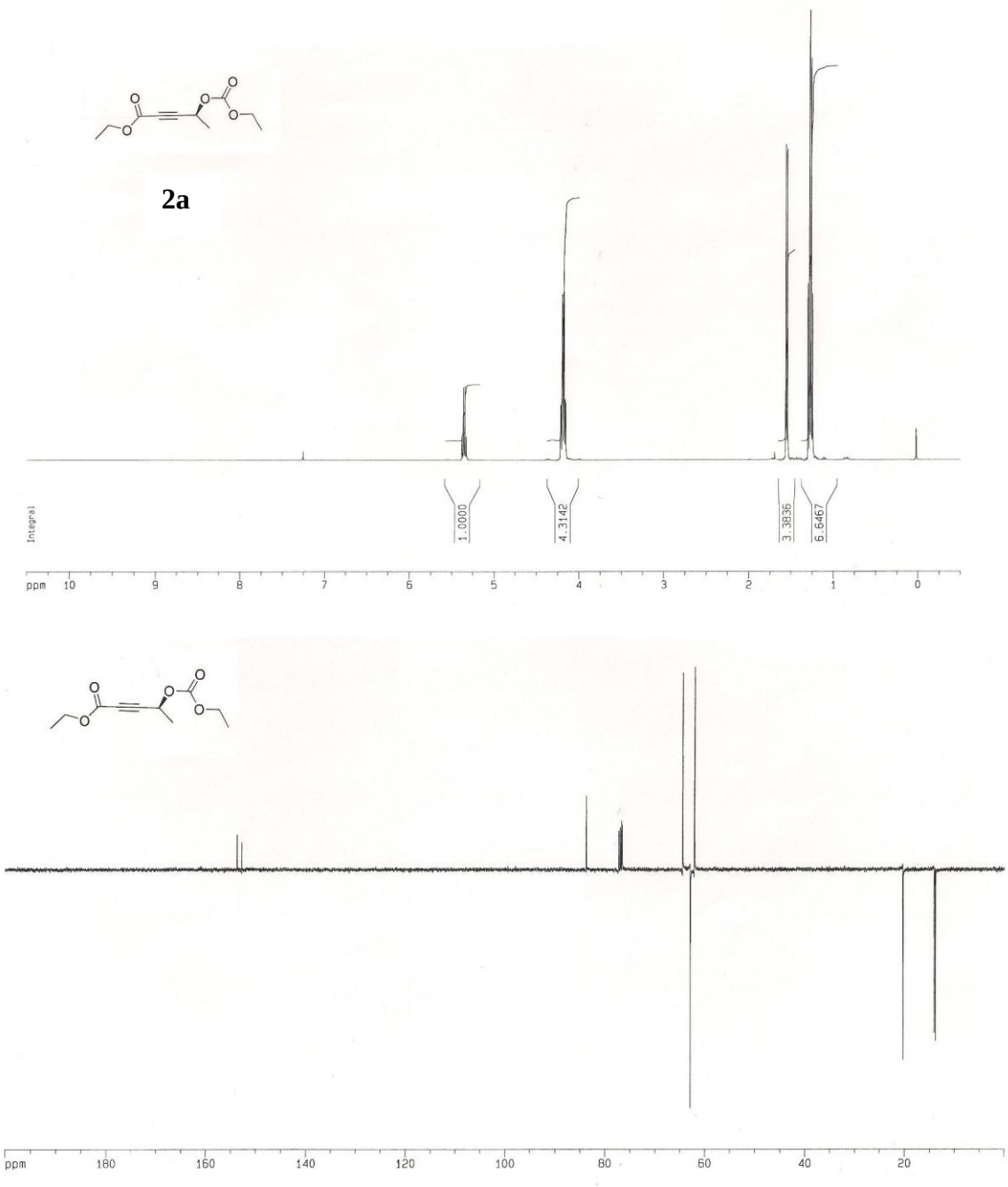
6-(*tert*-Butyl-dimethyl-silanyloxy)-5-hydroxy-hex-2-ynoic acid ethyl ester, 27b. 154.2 mg, 0.5383 mmol, 84%; pale yellow oil. R_f 0.39 (EtOAc:Hexanes = 2:8); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.21 (q, 2H, *J* = 7.1 Hz), 3.85-3.90 (m, 1H), 3.71 (dd, 1H, *J* = 10.1, 4.1 Hz), 3.62 (dd, 1H, *J* = 10.1, 5.4 Hz), 2.54 (dd, 2H, *J* = 15.7, 6.1 Hz), 1.30 (t, 3H, *J* = 7.1 Hz), 0.90 (s, 9H), 0.09 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.5, 85.1, 74.7, 69.5, 65.4, 61.9, 25.8, 23.4, 18.2, 14.0, -5.5. Spectral data are consistent with that of the literature.[8]

5-Hydroxy-5-phenyl-pent-2-ynoic acid ethyl ester, 27c. Prepared following literature methods.[9]

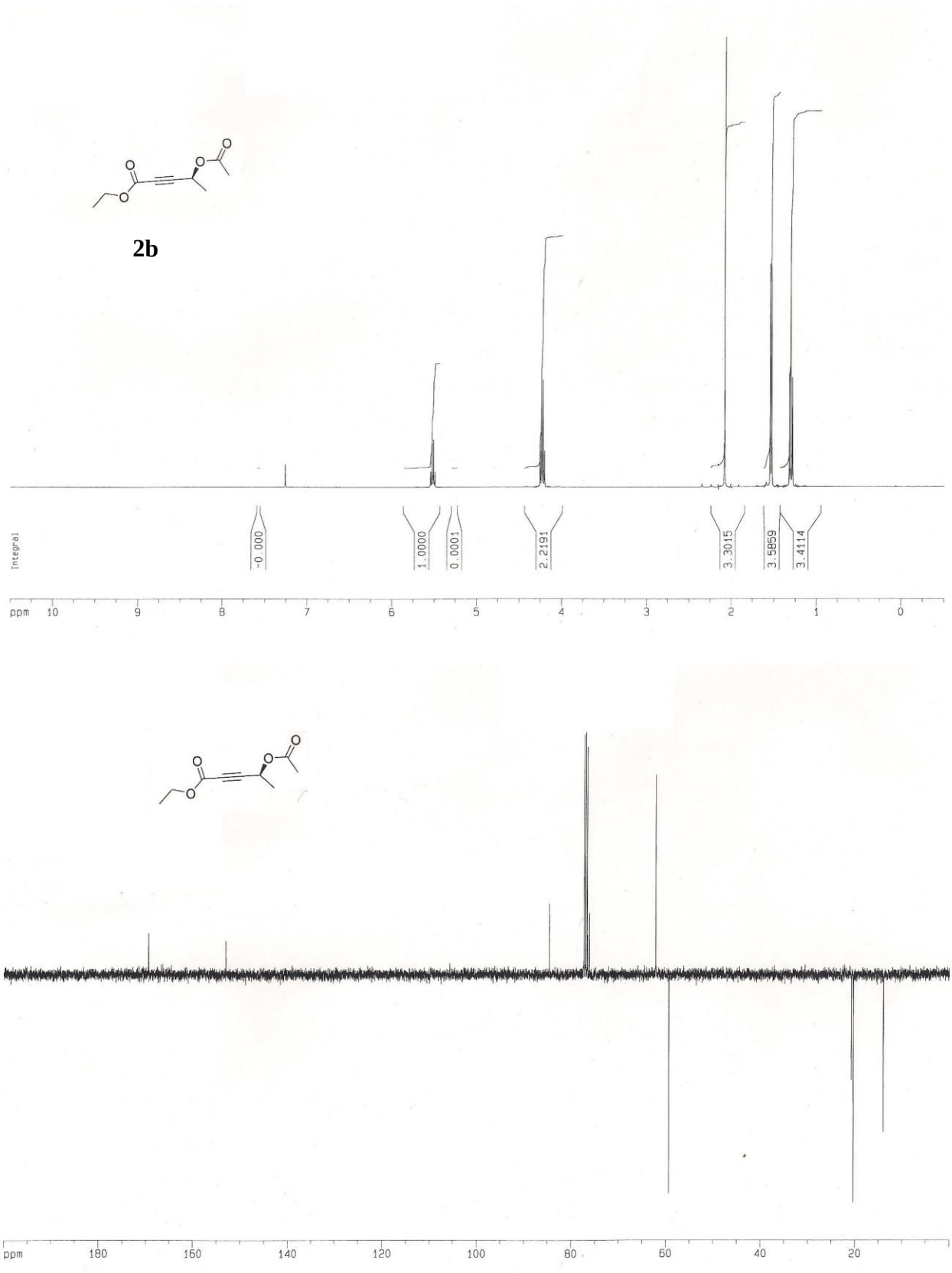
151.6 mg, 0.6946 mmol, 98%; pale yellow oil. R_f 0.28 (EtOAc:Hexanes = 2:8); IR (neat, NaCl) 3419, 2984, 2238, 1710, 1258, 1074 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.28-7.38 (m, 5H), 4.94 (t, 1H, *J* = 6.4 Hz), 4.20 (q, 2H, *J* = 7.1 Hz), 2.76 (dd, 2H, *J* = 6.3, 3.3 Hz), 2.63 (br s, 1H), 1.29 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.5, 142.0, 128.6, 128.2, 125.6, 85.4, 74.9, 71.9, 61.9, 29.5, 13.9; HRMS calcd. for $C_{13}H_{14}O_3$: $[M+H]^+$ 219.1017, found: 219.1021.

[8] Trost, B.; Frontier, A. *J. Am. Chem. Soc.* **2000**, *122*, 11727.
[9] Lee, A. S.-Y.; Chu, S.-F.; Chang, Y.-T. ; Wang, S.-H. *Tetrahedron Lett.* **2004**, *45*, 1551.

Part III: ^{1}H and ^{13}C NMR Spectra of Alkynes



^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of 2a in $CDCl_3$



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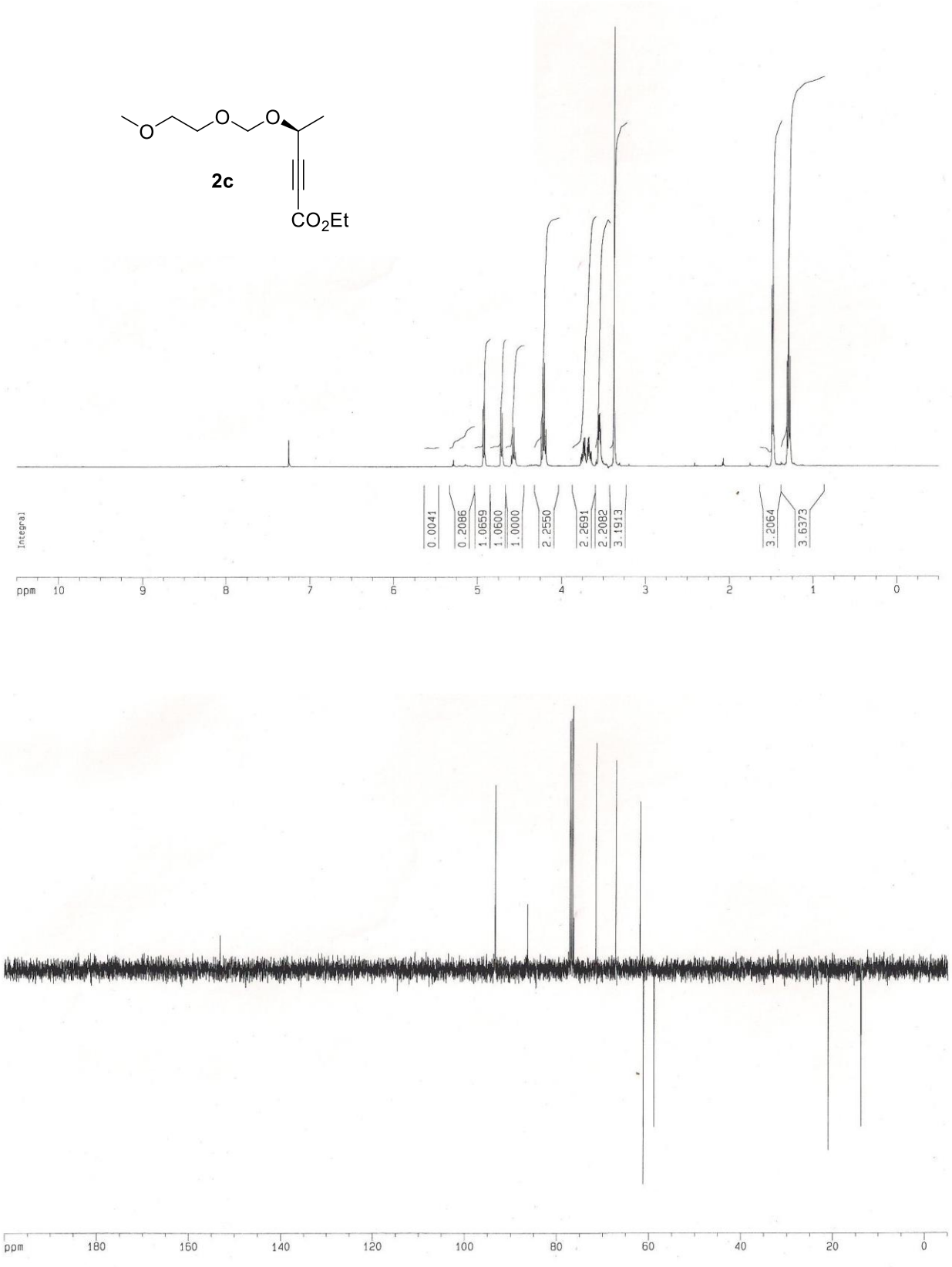

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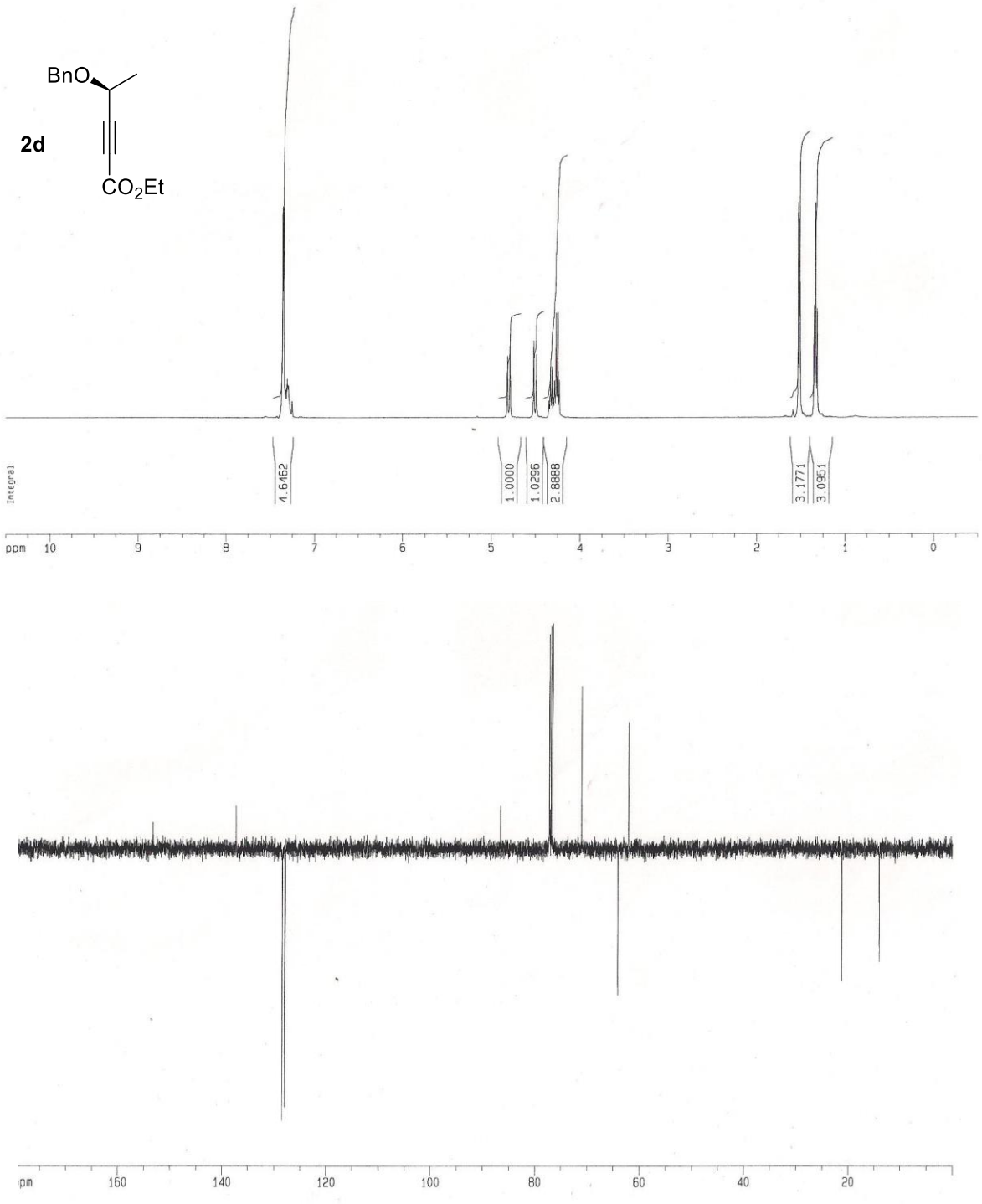
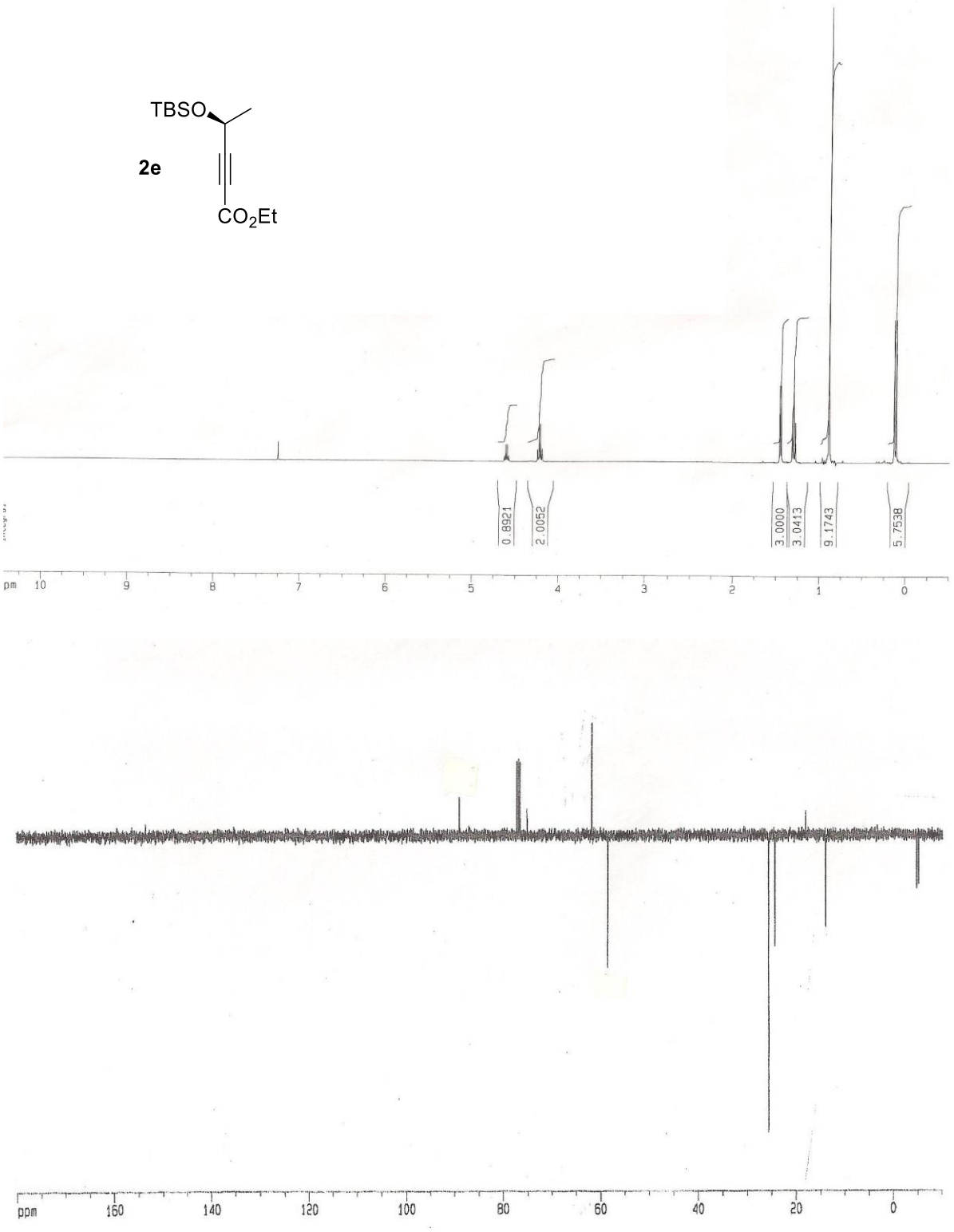


^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of 2d in $CDCl_3$



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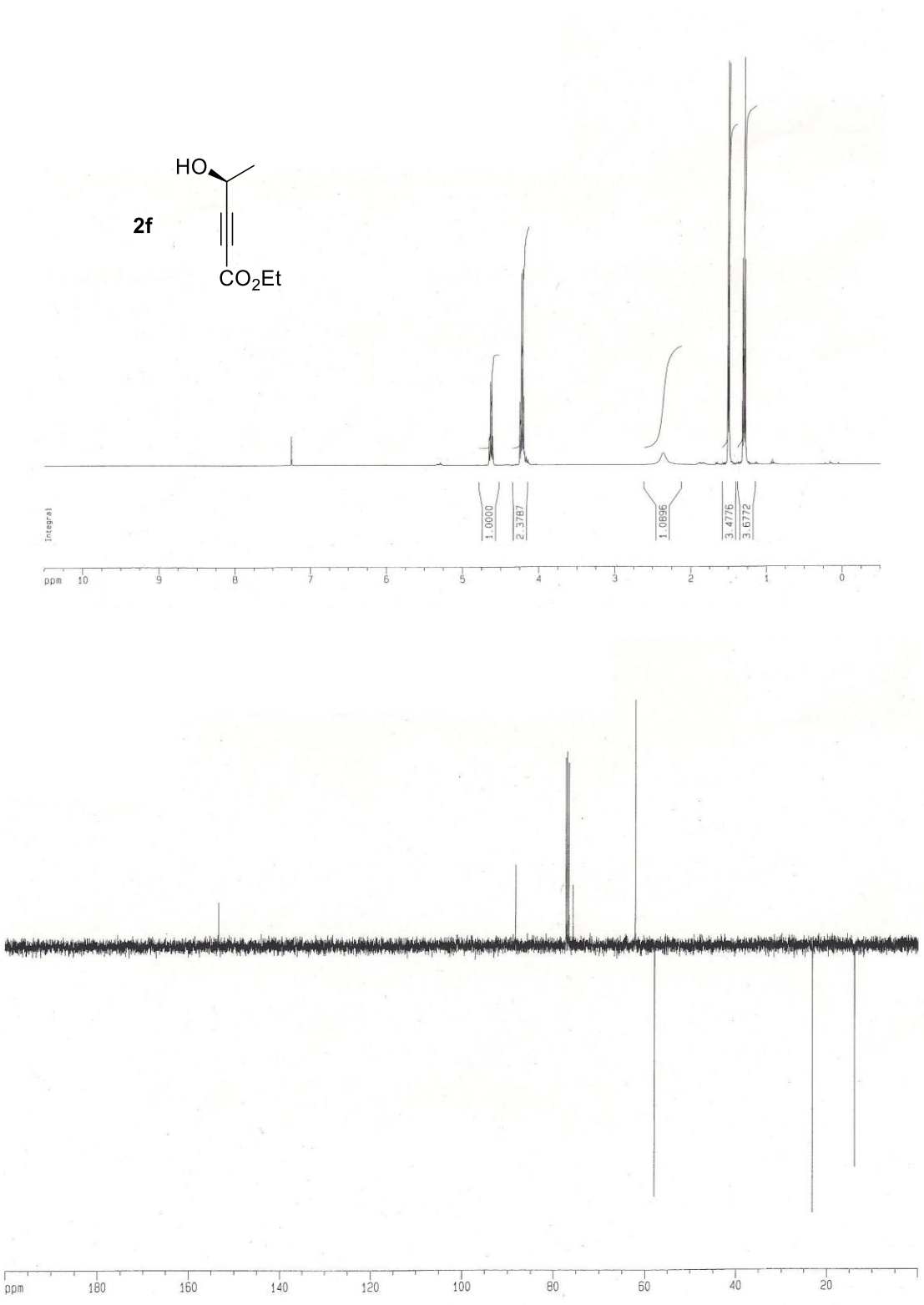
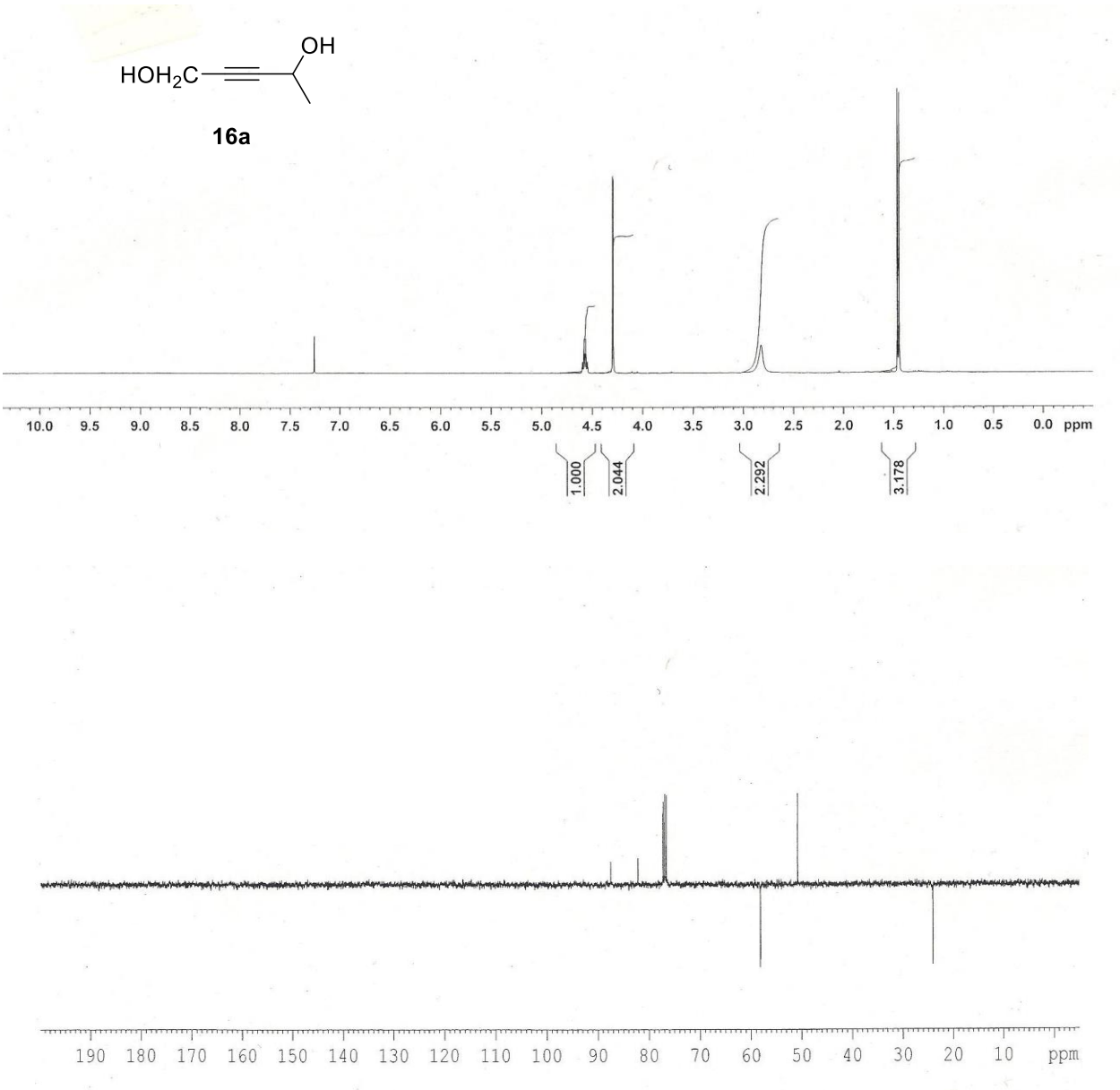
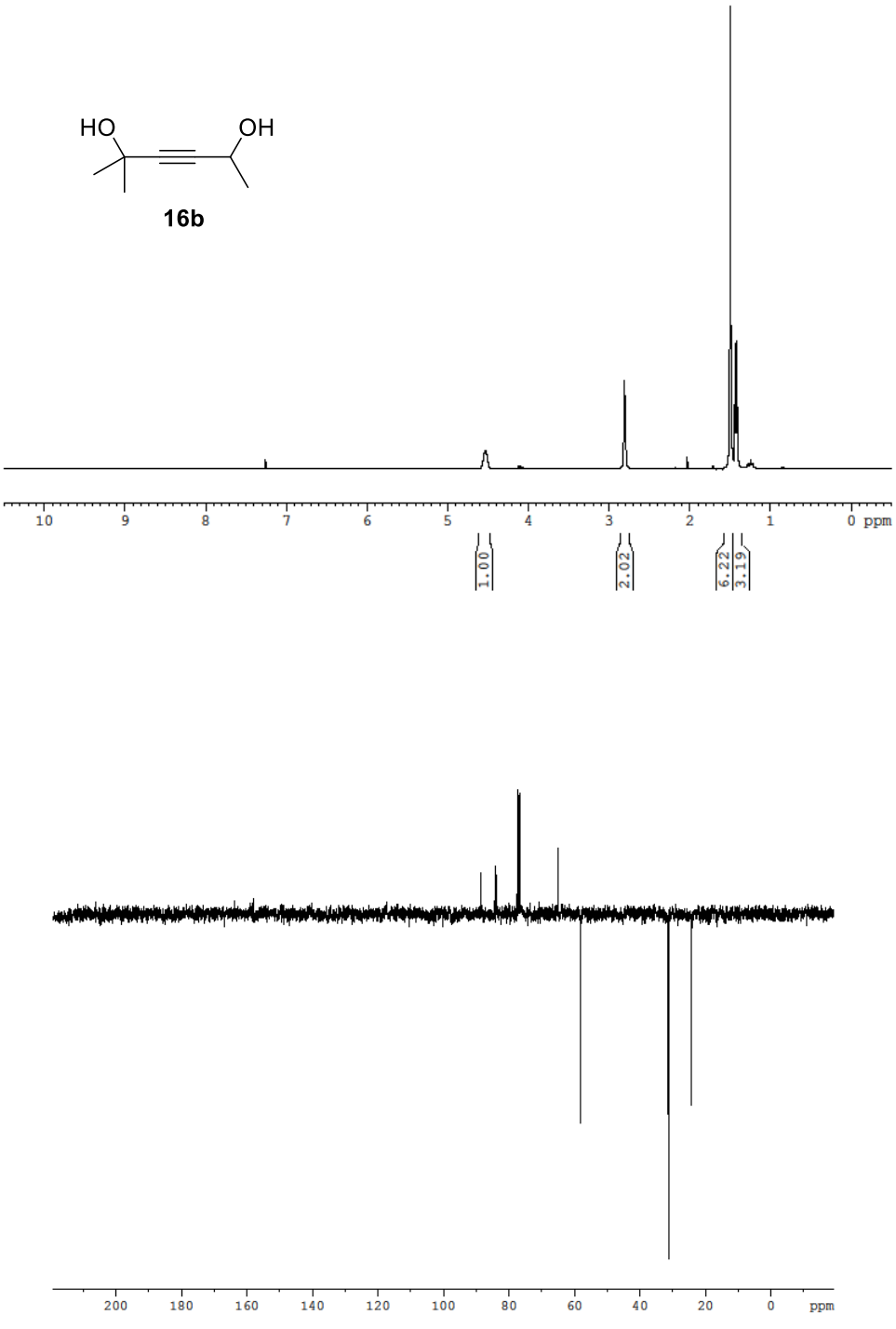


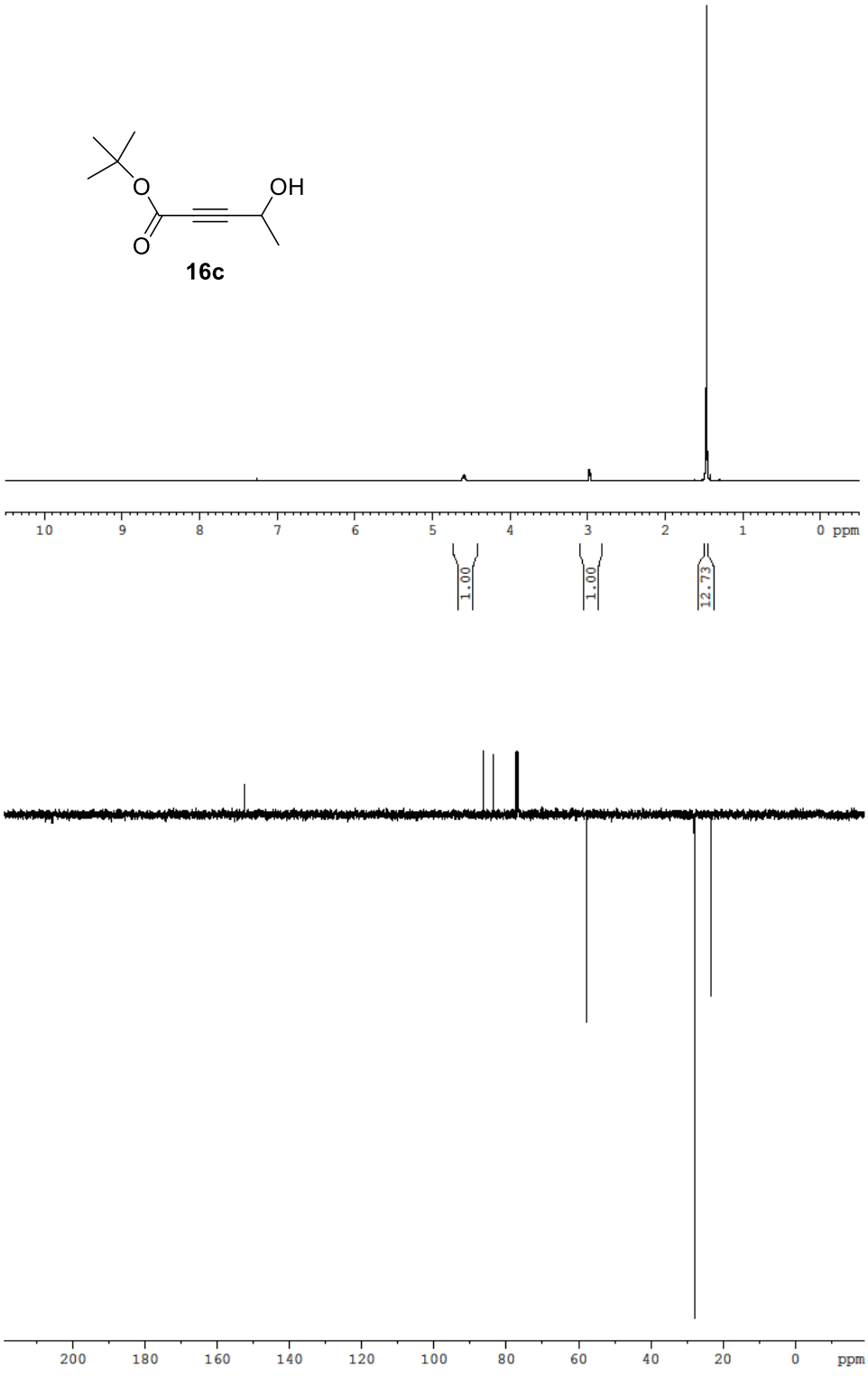
^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of 2f in $CDCl_3$



^{1}H (300 MHz) and ^{13}C (75 MHz) spectra of 16a in $CDCl_3$



^{1}H (300 MHz) and ^{13}C (75 MHz) spectra of 16b in $CDCl_3$



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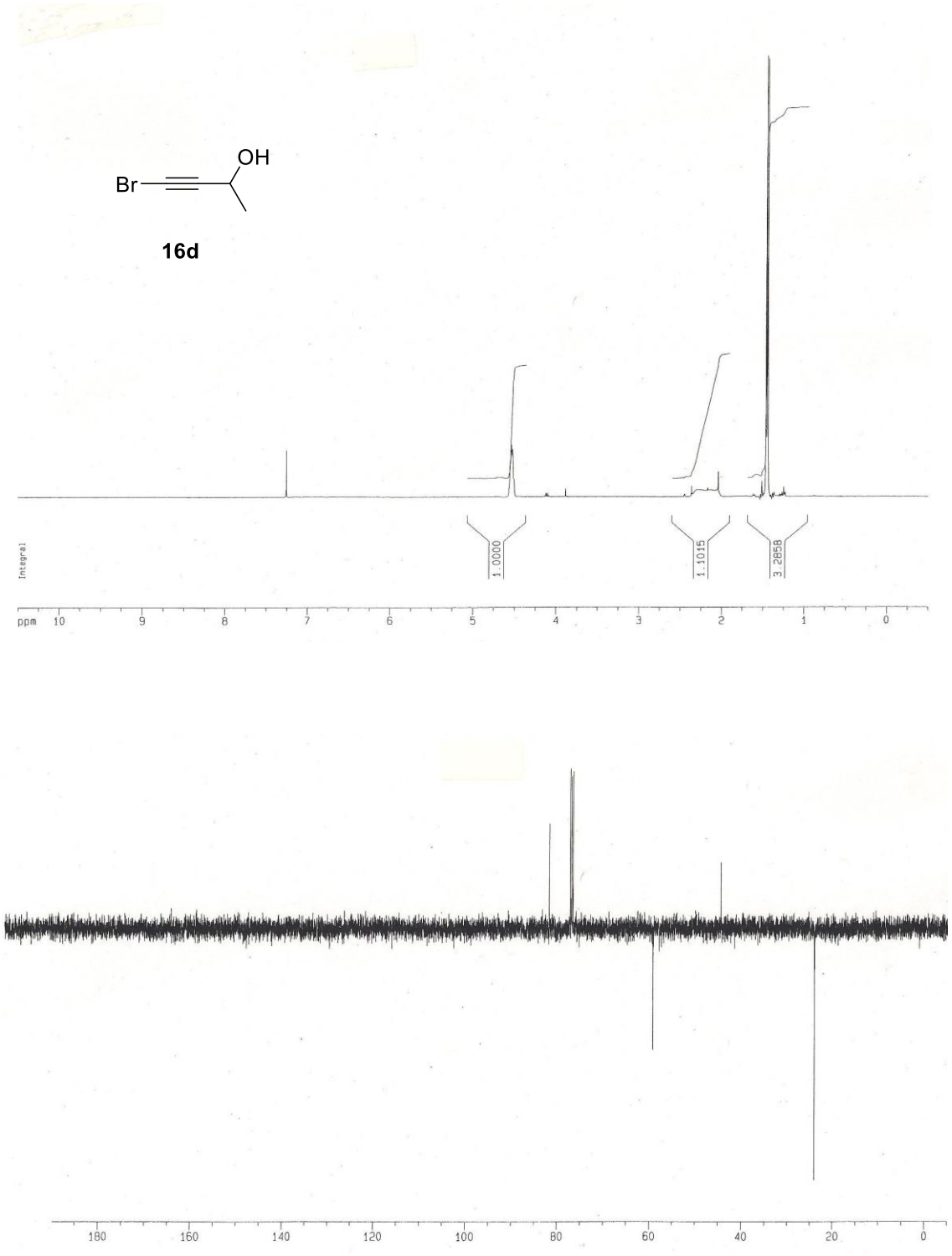
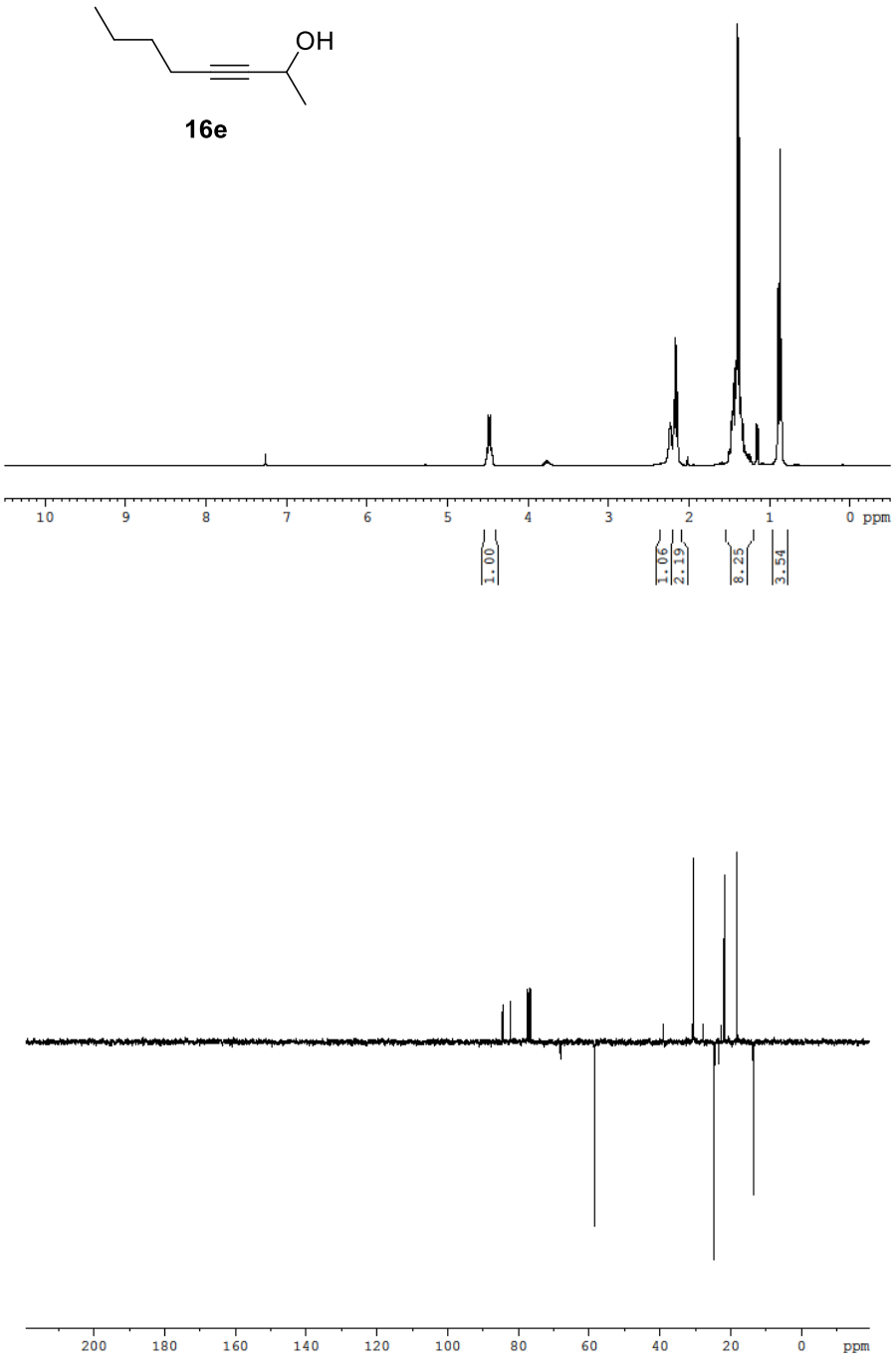
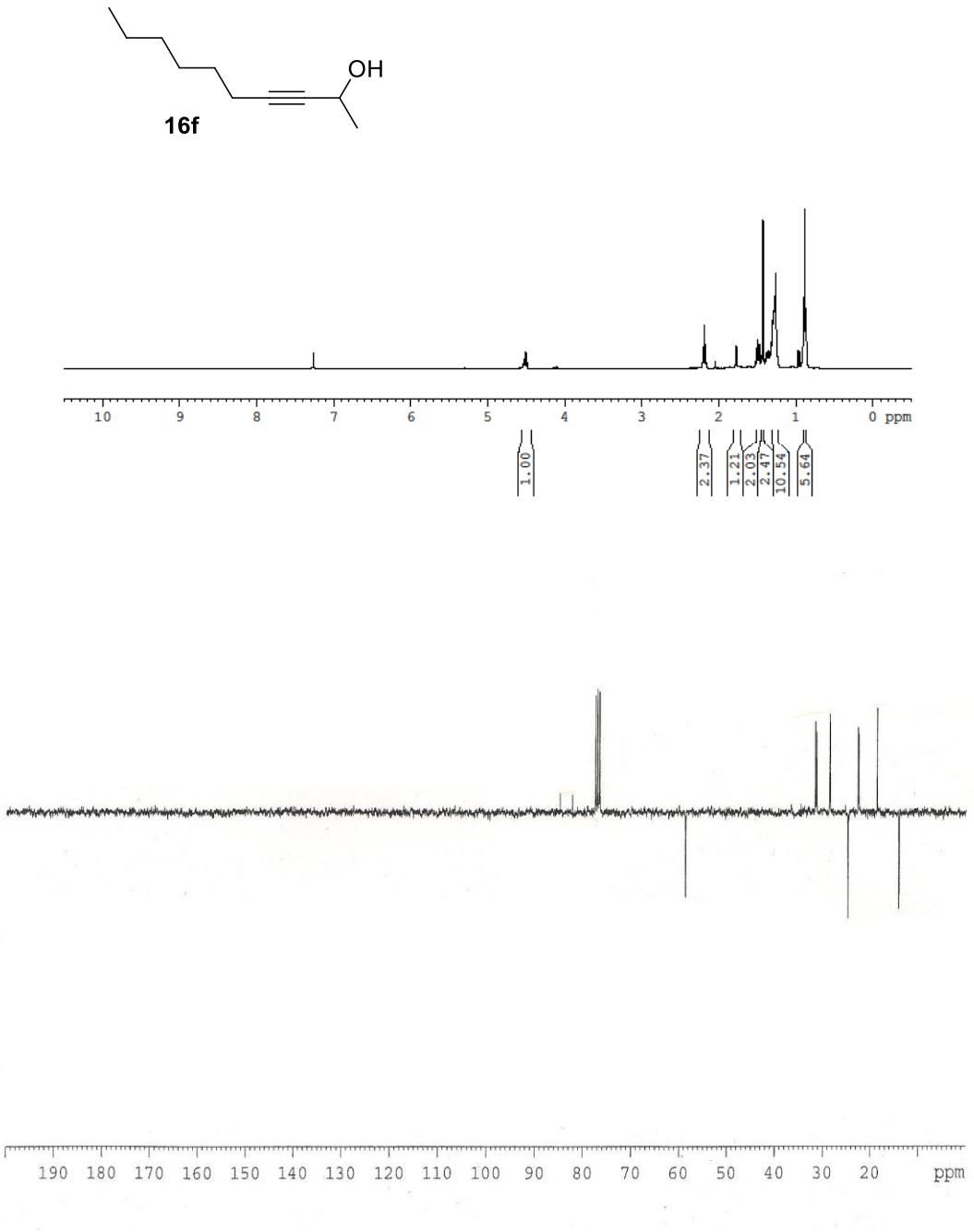


^{1}H (300 MHz) and ^{13}C (75 MHz) spectra of 16d in $CDCl_3$



^{1}H (300 MHz) and ^{13}C (75 MHz) spectra of 16e in $CDCl_3$



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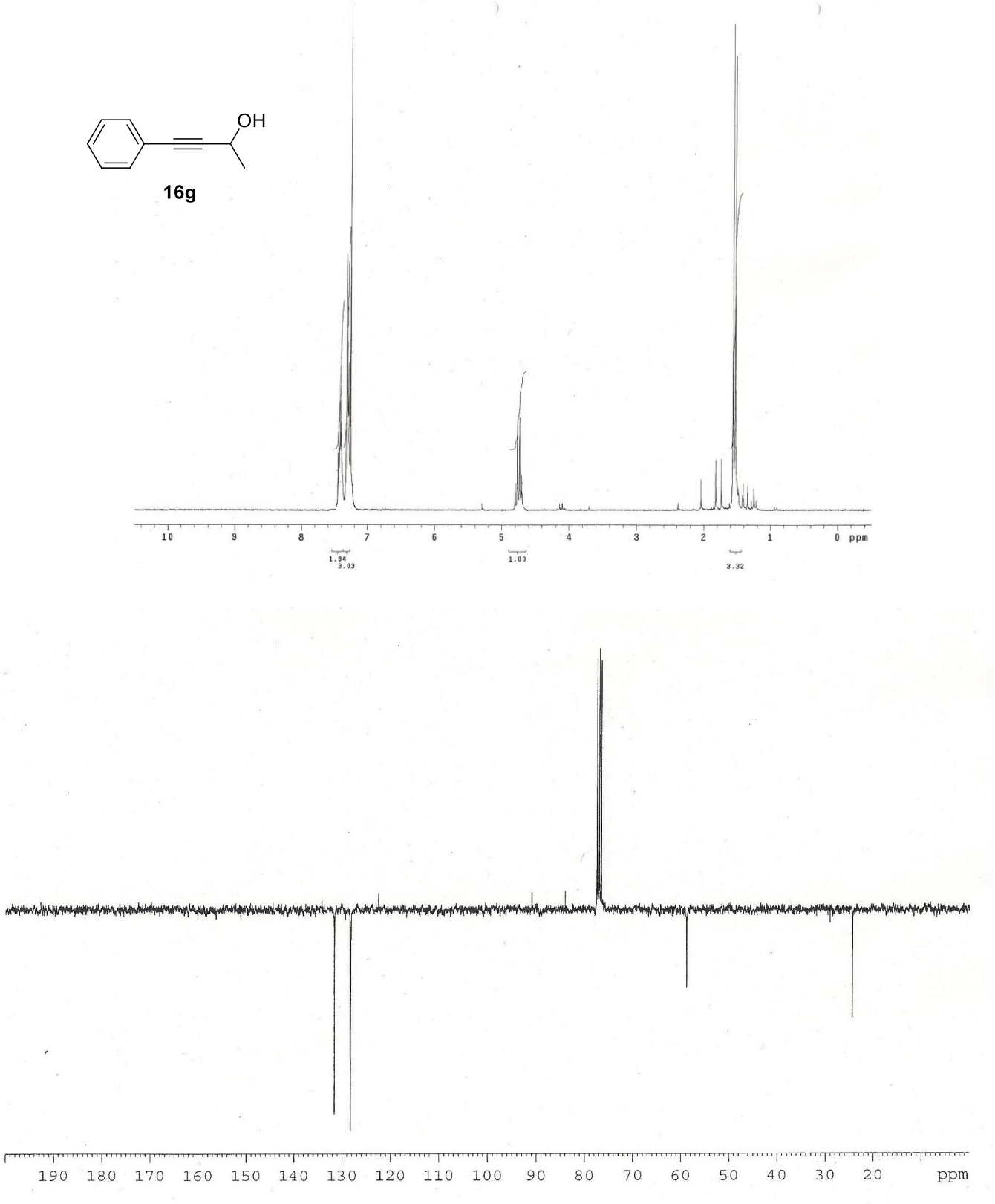
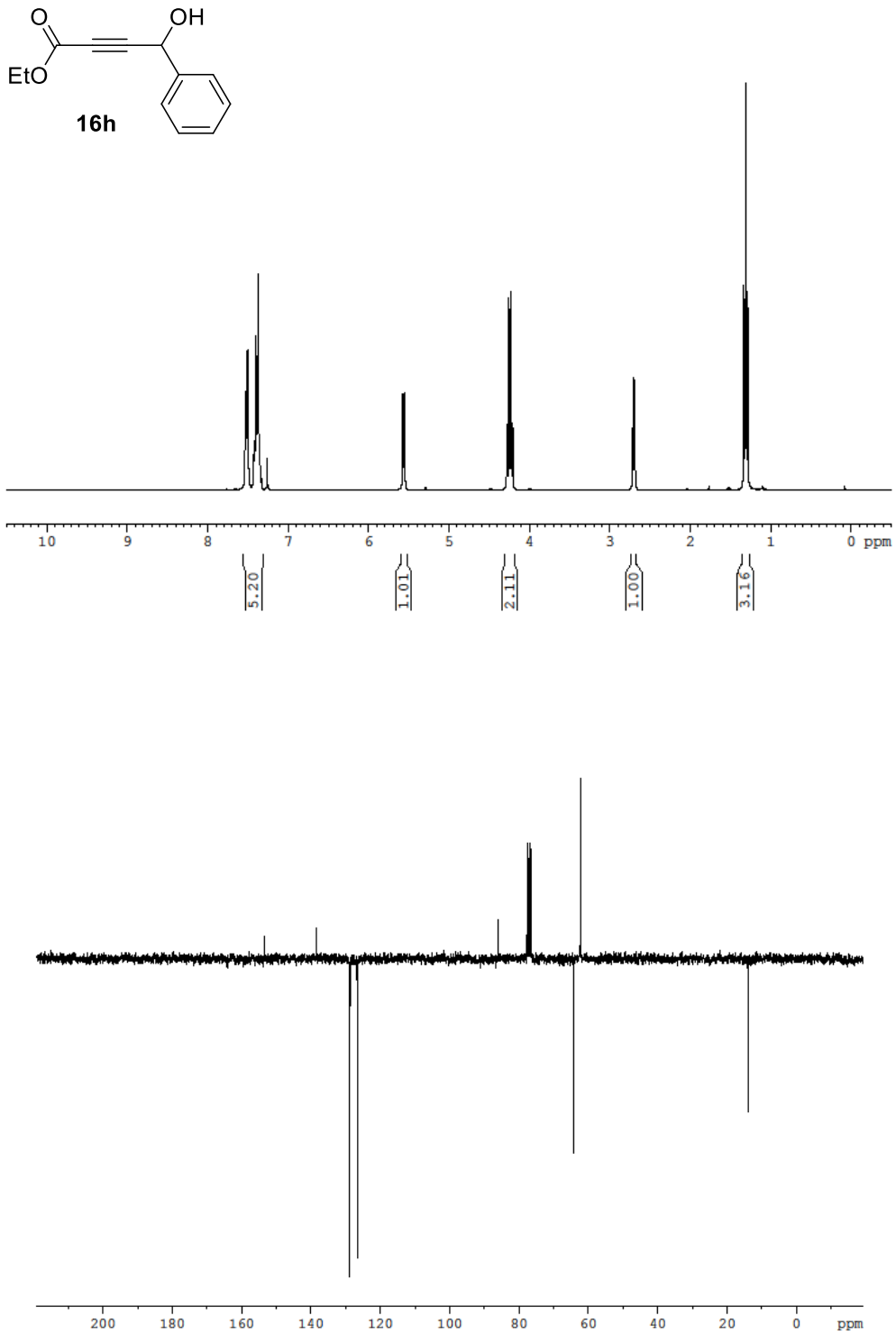
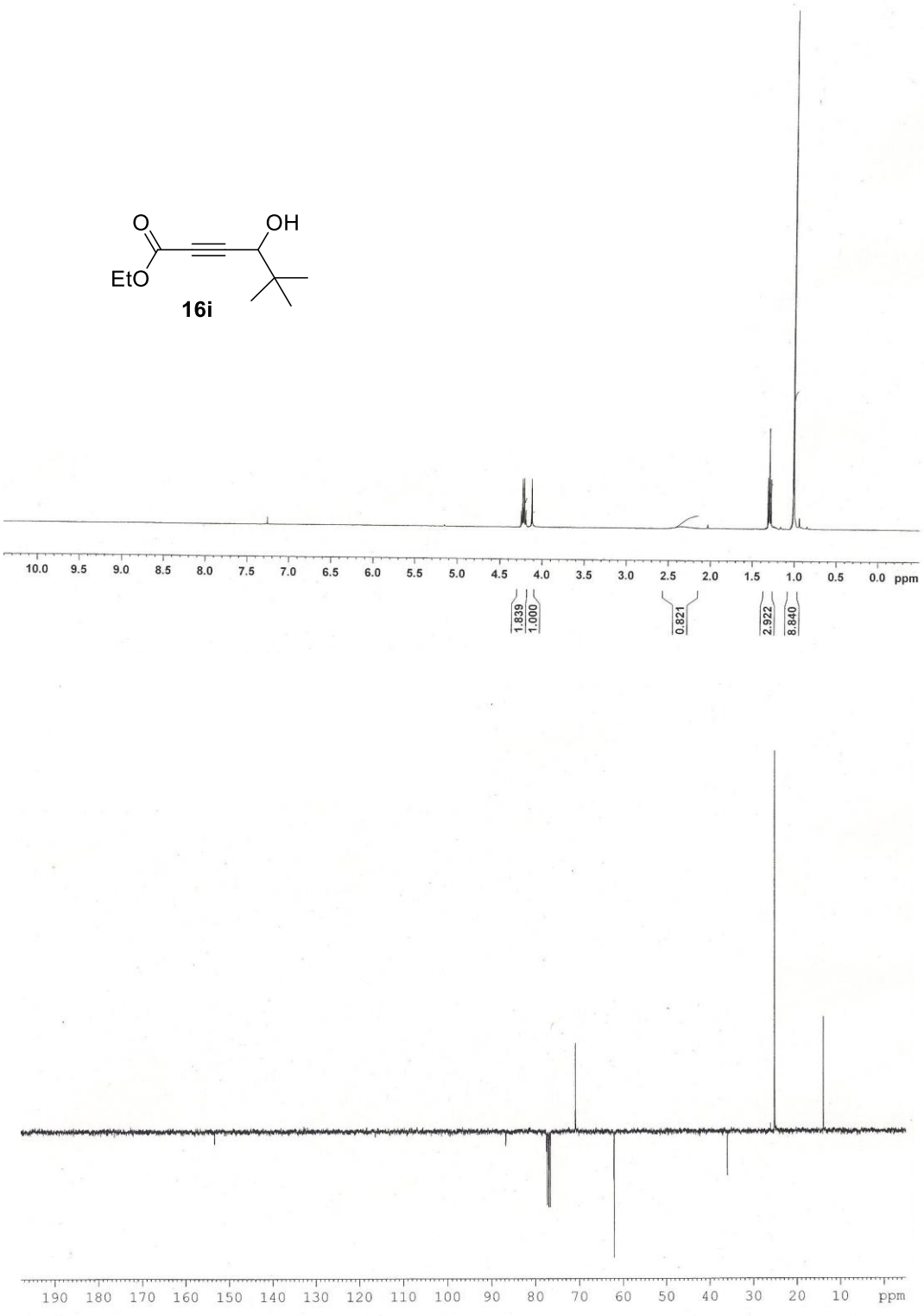


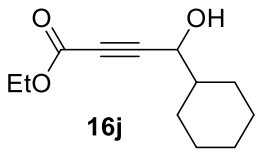
^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of 16g in $CDCl_3$



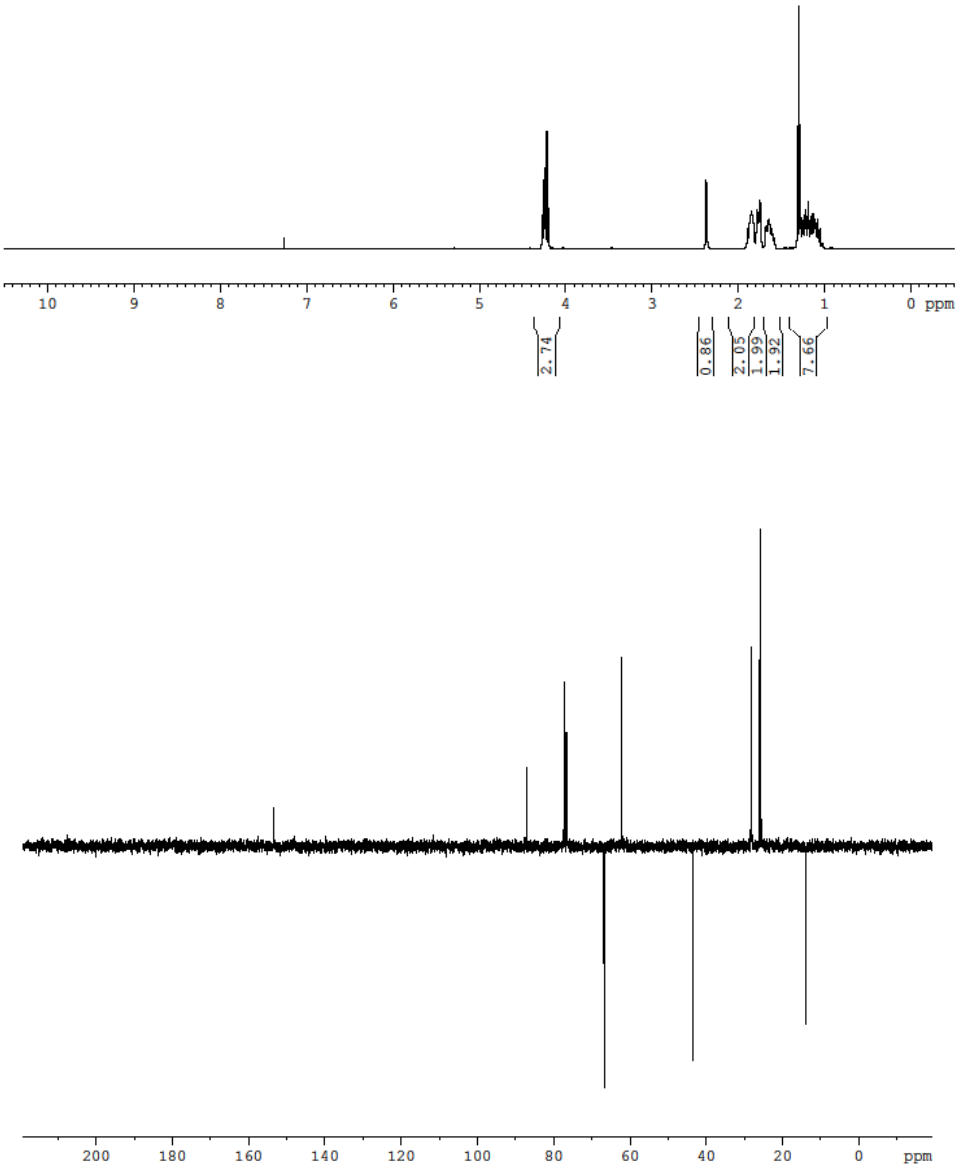
^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of 16h in $CDCl_3$



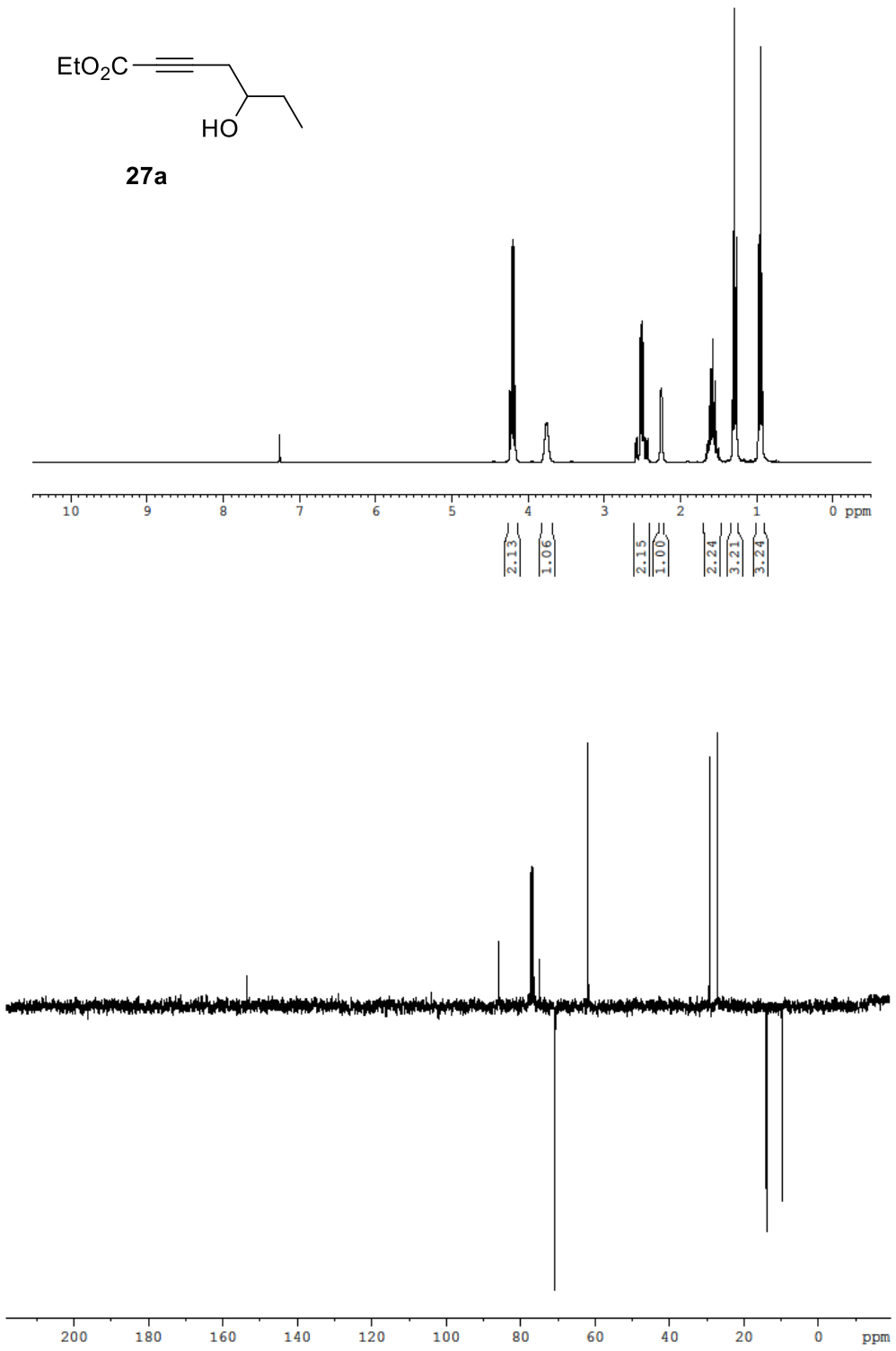
^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of 16i in $CDCl_3$



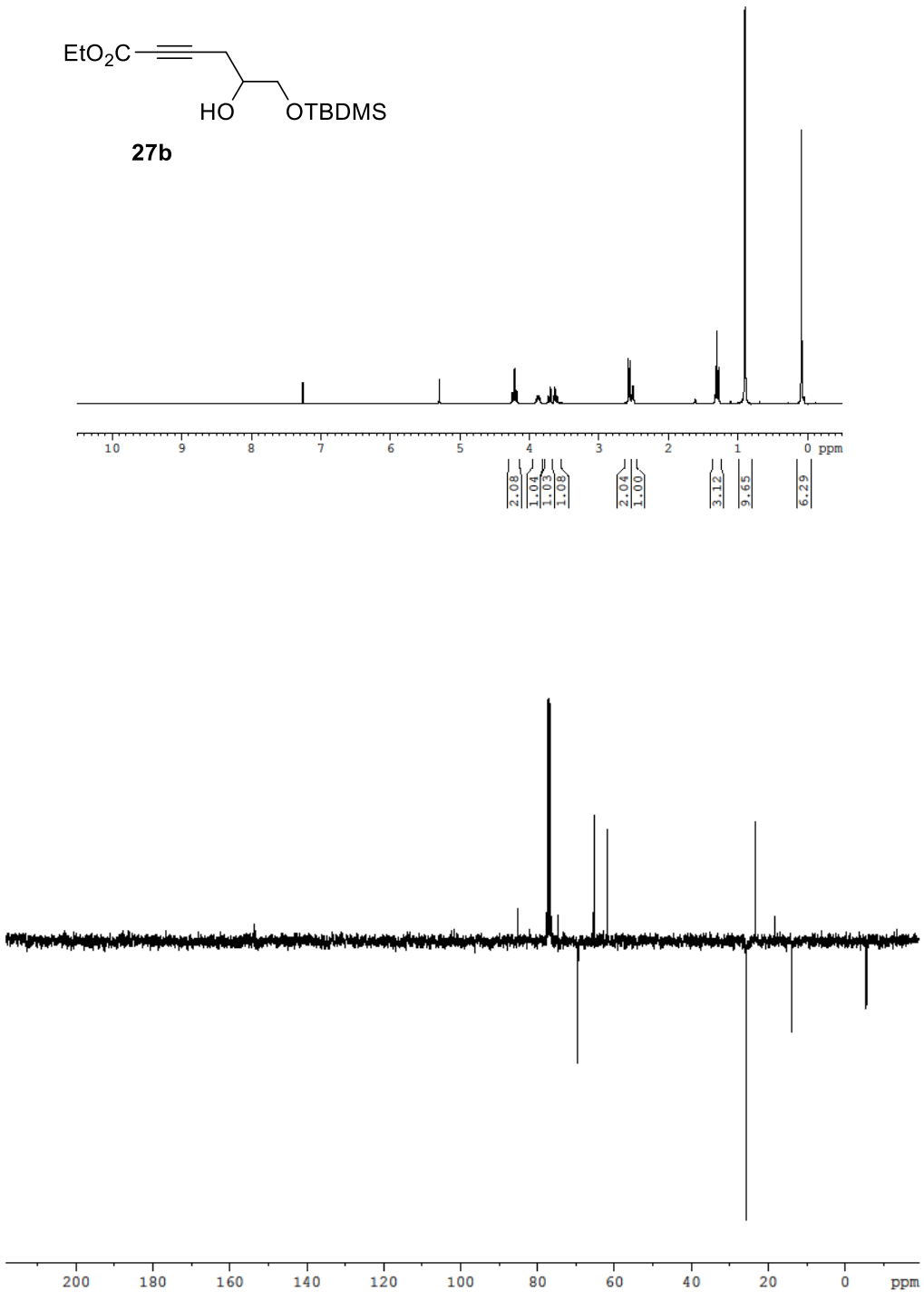
16j



^{1}H (400 MHz) and ^{13}C (100 MHz) spectra of 16j in $CDCl_3$



^{1}H (300 MHz) and ^{13}C (75 MHz) spectra of 27a in $CDCl_3$



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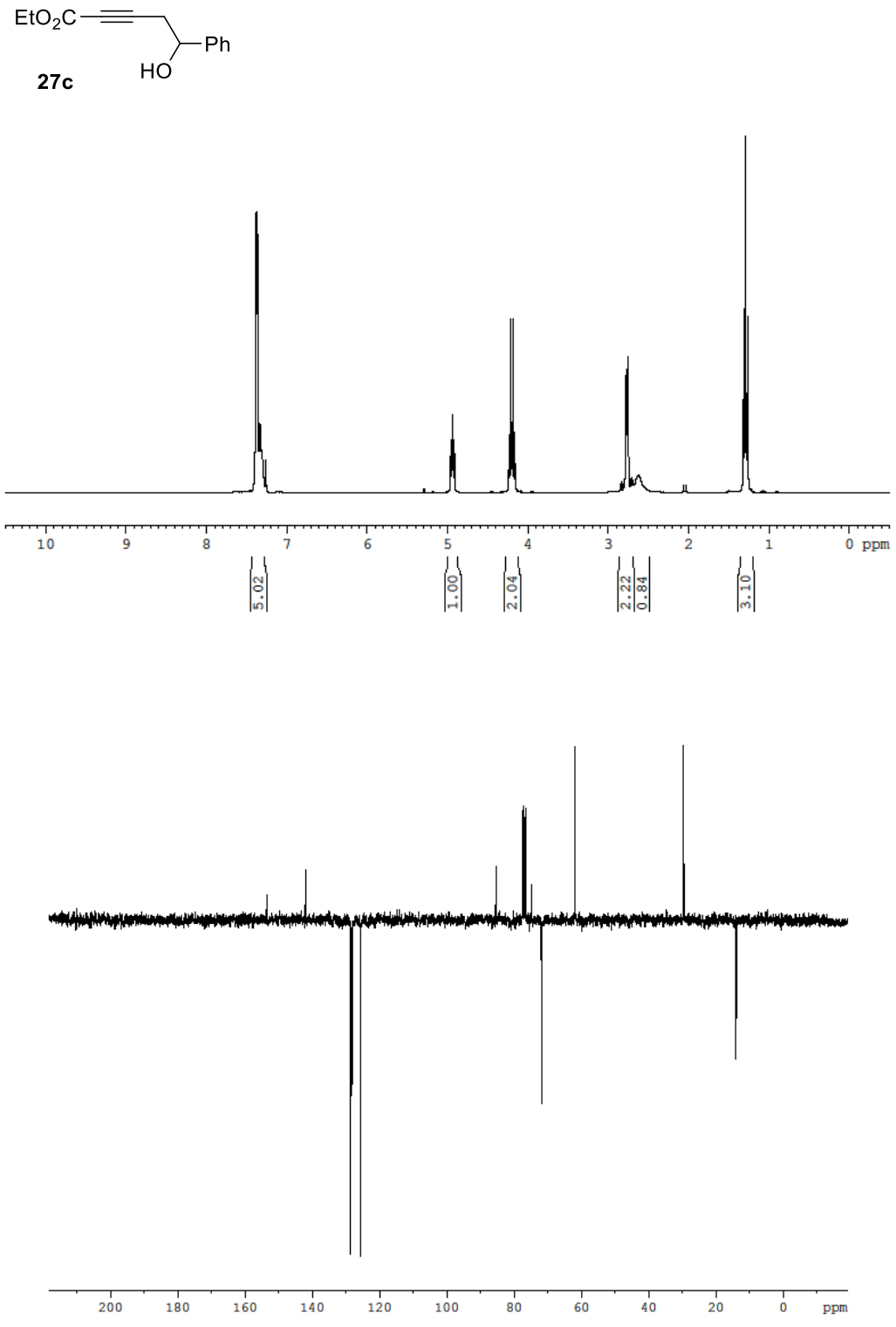

^{1}H (300 MHz) and ^{13}C (75 MHz) spectra of 27c in $CDCl_3$