Exploitation of Rh (I)-Rh (III) Cycles in Enantioselective C-C Bond Cleavages: Access to β-Tetralones and Benzobicyclo[2.2.2]octenones

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Supplementary Information

Table of Content:

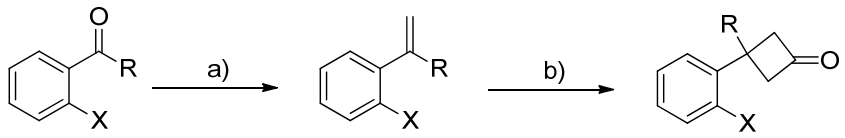
General Methods:

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring, unless otherwise indicated. Toluene, THF, diethyl ether, DCM were purified by a Innovative Technology Solvent Delivery System. All other reagents were used as obtained from the suppliers. Flash Chromatography was performed with Fluka silica gel 60 (0.040-0.063 µm grade). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were visualized by UV-light at 254 nm and by dipping the plates in an ethanolic vanillin/sulfuric acid solution or an aqueous potassium permanganate solution followed by heating. Proton nuclear magnetic resonance (^{1}H-NMR) data were acquired on a Bruker AV400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet, br, broad. Proton decoupled Carbon-13 nuclear magnetic resonance (^{13}C-NMR) data were acquired at 100 MHz on a Bruker AV400 spectrometer, at 125 MHz on a Bruker AV500, at 150 MHz on a Bruker DRX600. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-*d.* Infrared (IR) data were recorded on an Alpha-P Bruker FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). High resolution mass spectra were performed by a Agilent LC-MS TOF and are given in *m/z*. Optical rotations were measured on a Polartronic M polarimeter using a 0.5 cm cell with a Na 589 nm filter. The specific solvents and concentrations (in g/100 mL) are indicated.

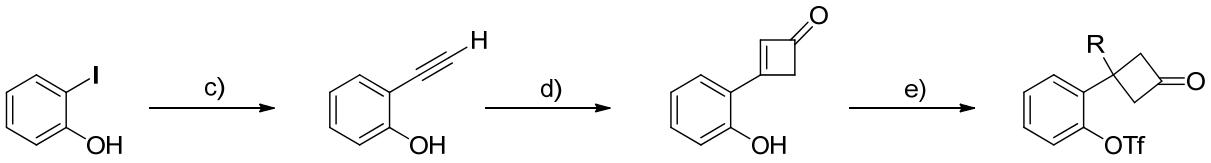
Experimental Section

General procedure for substrates synthesis:

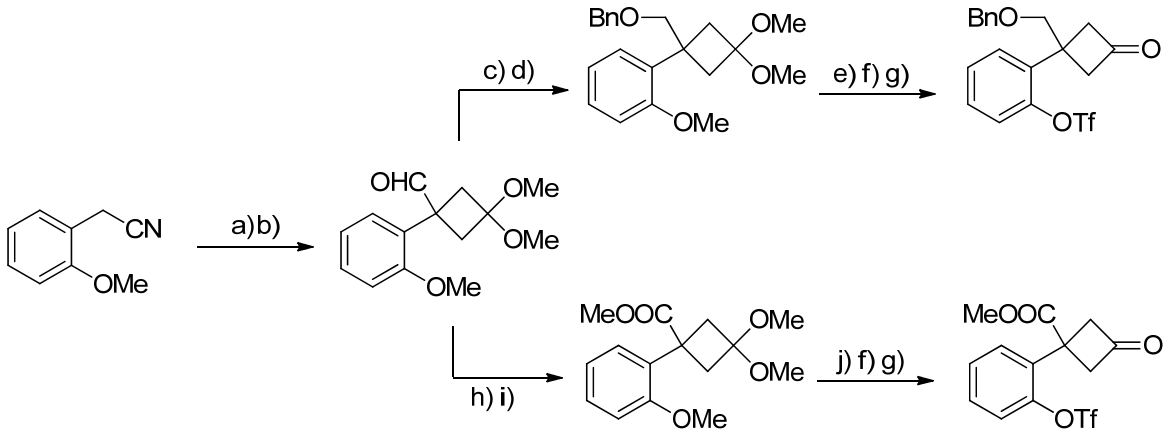
Cyclobutanones Syntheses: The required cyclobutanones were prepared according to: a) L. R. Krepski, A. Hassner *J. Org. Chem.* **1978**, *43*, 2879–2882; b) B. D. Johnston, E. Czyzewska, A. C. Oehlschlager *J. Org. Chem.*, **1987**, *52*, 3693-3697; c) P. P. Shao, F. Ye *Tetrahedron Lett.* **2008**, *49*, 3554–3557; d) W. Cao, I. Erden, R. H. Grow, J. R. Keeffe, J. Song, M. B. Trudell, T. L. Wadsworth, F. Xu, J. Zheng *Can. J. Chem.* **1999**, *77*, 1009; e) R. R. Galucci, R. Going *J. Org. Chem.* **1981**, *46*, 2532; f) K. Sugimoto, R. Hayashi, H. Nemoto, N. Toyooka, Y. Matsuya, *Org. Lett.* **2012**, *14*, 3510-3513.



Reaction conditions:
if X= Br, I: a) 1.2eq. NaH, 1.2eq. $MePPh_3Br$, DMSO. 60°C, 6h; b) i) 6eq. Zn/Cu, 1.5eq. $POCl_3$, 1.5eq. trichloroacetyl chloride, Et_2O, 40°C, sonication; ii) 6eq. Zn/Cu, 3eq. NH_4Cl, MeOH, 23°C; if X = OH: a) i) 1.1eq. BnBr, 1.2eq. K_2CO_3, 0.1eq. KI, acetone, 50°C; ii) 1.2eq. NaH, 1.2eq. $MePPh_3Br$, DMSO. 60°C, 6h; b) i) 6eq. Zn/Cu, 1.5eq. $POCl_3$, 1.5eq. trichloroacetyl chloride, Et_2O, 40°C, sonication; ii) 6eq. Zn/Cu, 3eq. NH_4Cl, MeOH, 23°C; iii) 1.2eq. ethylene glycol,0.1eq. p-TsOH, toluene, 120°C, 3h; iv) 0.1eq. Pd/C, H_2 1atm, MeOH; v) 1.2eq. NaH, 1.2eq. $PhNTf_2$,THF, 23°C, 4h; vi) 5eq. 2M H_2SO_4, THF/water, 60°C, 4h.

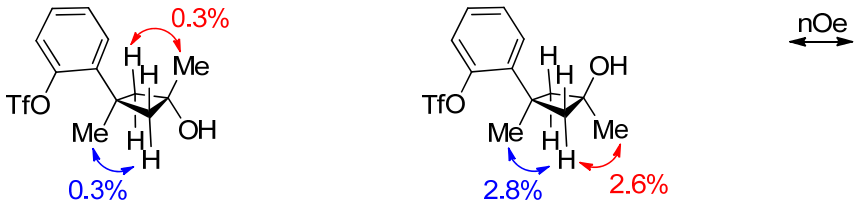


Reaction conditions:
c) i) 10mol% $[Pd(PPh_3)Cl_2]$, 20mol% CuI, 3eq. TMS-acetylene, THF/Et_3N 1:1, 24h, 23°C ; ii) 1.5eq. K_2CO_3, MeOH, 23°C, 1h; d) i) 5eq. Zn/Cu, 2.5eq. trichloroacetyl chloride, Et_2O/DME, 23°C, 2h, ii) 6eq. Zn/Cu, 3eq. NH_4Cl, MeOH, 23°C; e) i) 1.2eq. NaH, 1.1eq. $PhNTf_2$, THF, 23°C, 4h, ii) 10mol% CuI, 1.5 eq. RMgX, THF, -78°C, 2h.

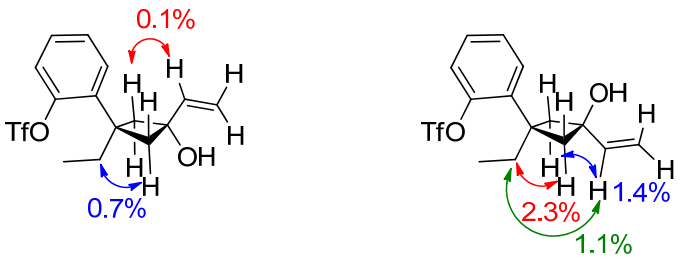


Reaction conditions:
a) 2.5eq. NaH, 1.2eq. 1,3-dibromo-2,2-dimethoxypropane, DMSO, 70°C, 40h; b) 1.1eq. DIBAL-H, DCM, 1h, 0°C; c) 1.1eq. $NaBH_4$, MeOH, 0°C, 15min; d) 1.1eq. BnBr, 1.1eq. NaH, DMF, 2h, 23°C; e) 5eq. NaCN, DMSO, 180°C, 8h; f) 1.2eq. NaH, 1.1eq. $PhNTf_2$, THF, 23°C, 1h; g) 3eq. 2N HCl, acetone, 23°C, 1h; h) $NaClO_2$, H_2O_2, NaH_2PO_4, ACN/water, 1h, 23°C; i) 1.1eq. MeI, 1.1eq. K_2CO_3, DMF, 23°C, 24h; j) 1.1eq. BBr_3, DCM, -78°C, 1h.

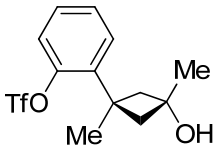
Cyclobutanol Syntheses: To a 0°C cold solution of the Grignard reagent (1.5 equiv.) in dry THF (1 mL / mmol) was added the cyclobutanone (1 equiv.) as solution in dry THF (1 mL / mmol). The reaction was stirred for 4 h at 0°C. The reaction was quenched with sat. aq. NH_4Cl and extracted with EtOAc. The organic layer was washed with water and brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified on a short silica gel plug to give a mixture of *cis* / *trans* isomers of the *tert*-cyclobutanol in 50–95% yield.The cis and trans isomers of the cyclobutanols were separated by preparative HPLC and assigned by nOe analysis (see examples on scheme below).



1a **cis-1a**



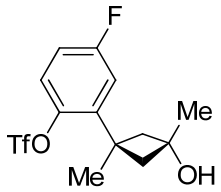
1l **cis-1l**



1a

***trans*-2-(3-hydroxy-1,3-dimethylcyclobutyl)phenyl trifluoromethane sulfonate (1a):**

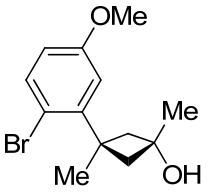
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.18 (m, 4H), 2.62 – 2.53 (m, 2H), 2.48 – 2.35 (m, 2H), 1.65 (s, 1H), 1.64 (s, 3H), 1.29 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 148.0 , 142.8 , 129.1 , 128.2 , 128.0 , 121.6 – 120.8 (q, *J* = 1.4 Hz), 118.6 (q, *J* = 319.6 Hz), 70.1 , 49.1 , 34.6 , 31.2 , 30.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.4; **IR (ATR)** $\tilde{\nu}$ = 3366, 2970, 2932, 2872, 1443, 1204 1136, 1059, 892, 764, 651, 630, 959, 507 cm^{-1}; **HRMS (ESI)** calculated for $[C_{13}H_{16}F_3O_4S - H_2O]^+$: 307.0610, found: 307.0607; R_f = 0.30 (Pentane/Ethyl Acetate 6:1).



1b

***trans*-4-fluoro-2-(3-hydroxy-1,3-dimethylcyclobutyl)phenyl trifluoro methanesulfonate (1b):**

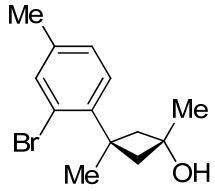
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.19 (dd, *J* = 8.6, 6.3 Hz, 2H), 7.13 – 6.87 (m, 2H), 2.60 – 2.45 (m, 1H), 2.45 – 2.31 (m, 2H), 1.68 (s, 1H), 1.62 (s, 3H), 1.28 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 161.0 (d, *J* = 249.2 Hz), 147.2 (d, *J* = 10.4 Hz), 139.9 (d, *J* = 4.0 Hz), 129.6 (d, *J* = 8.7 Hz), 118.6 (q, *J* = 319.8 Hz), 115.4 (d, *J* = 20.5 Hz), 109.3 (d, *J* = 26.6 Hz), 68.8, 50.3, 31.2, 30.0, 30.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.3, -112.5; **IR (ATR)** $\tilde{\nu}$ = 3375, 2971, 2931, 2901, 1409, 1248, 1215, 1141, 1055, 970, 858, 847, 601 cm^{-1}; **HRMS (ESI)** calculated for $[C_{13}H_{15}F_4O_4S - H_2O]^+$: 325.0516, found: 325.0521; R_f = 0.46 (Pentane/Ethyl Acetate 5:1).



1c

***trans*-3-(2-bromo-5-methoxyphenyl)-3-methyl-1-methylcyclobutanol (1c):**

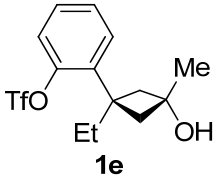
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.39 (d, *J* = 8.7 Hz, 1H), 6.72 (d, *J* = 3.0 Hz, 1H), 6.60 (dd, *J* = 8.7, 3.0 Hz, 1H), 3.79 (s, 3H), 2.69 – 2.56 (m, 2H), 2.47 – 2.32 (m, 2H), 1.65 (s, 3H), 1.27 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 158.8, 149.8, 134.8, 114.3, 112.5, 112.2, 69.4, 55.4, 49.1, 37.8, 30.4, 29.5; **IR (ATR)** $\tilde{\nu}$ = 2962, 2929, 2867, 2836, 1591, 1568, 1466, 1408, 1374, 1295, 1246, 1228, 1196, 1066, 1047, 1017, 933, 802, 602 cm^{-1}; **HRMS (ESI)** calculated for $[C_{13}H_{17}BrO_2 - H_2O]^+$: 267.0379, found: 267.0374; R_f = 0.19 (Pentane/Ethyl Acetate).



1d

***trans*-3-(2-bromo-4-methylphenyl)-1,3-dimethylcyclobutanol (1d):**

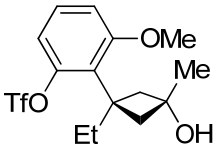
^{1}H-NMR (400 MHz, $CDCl_3$) δ =7.35 (s, 1H), 7.06 (m, 2H), 2.69 – 2.58 (m, 2H), 2.45 – 2.35 (m, 2H), 2.29 (s, 3H), 1.64 (s, 3H), 1.60 (s,1H), 1.26 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 145.6, 137.3, 134.6, 128.0, 127.5, 121.8, 69.6, 49.2, 37.3, 30.4, 29.7, 20.4; **IR (ATR)** $\tilde{\nu}$ = 3376, 2968, 2926, 2866, 1487, 1451, 1417, 1372, 1245, 1197, 1091, 1034, 952, 931, 819, 672, 564 cm^{-1}; **HRMS (ESI)** calculated for $[C_{13}H_{17}BrO - H_2O]^+$: 251.0430, found: 251.0429; R_f = 0.25 (Pentane/Ethyl Acetate 10:1).



1e

***trans*-2-(1-ethyl-3-hydroxy-3-methylcyclobutyl)phenyl trifluoromethane sulfonate (1e):**

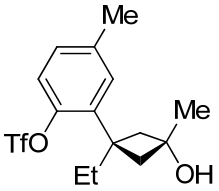
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.26 (m, 3H), 7.19 – 7.15 (m, 1H), 2.58 – 2.50 (m, 2H),, 2.44 – 2.36 (m, 2H), 2.05 (q, *J* = 7.4 Hz, 2H), 1.60 (s, 1H), 1.26 (s, 3H), 0.62 (t, *J* = 7.4 Hz, 3H);**^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 148.3, 139.4, 130.5, 127.9, 127.2, 120.8, 118.4 (q, *J* = 319.6 Hz), 69.6, 47.5, 38.1, 34.7, 30.7, 8.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.4; **IR (ATR)** $\tilde{\nu}$ = 3342, 2967, 2935, 2877, 1416, 1207, 1137, 1068, 893, 764, 652, 630, 596 cm^{-1}; **HRMS (ESI)** calculated for $[C_{14}H_{18}F_3O_4S - H_2O]^+$: 321.0767, found: 321.0765; R_f = 0.32 (Pentane/Ethyl Acetate 6:1).



1f

***trans*-3-methoxy-2-(3-hydroxy-1-ethyl-3-methylcyclobutyl)phenyl trifluoromethanesulfonate (1f):**

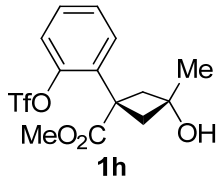
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.20 (t, J = 8.4 Hz, 1H), 6.94 (dd, J = 8.4, 1.0 Hz, 1H), 6.82 (dd, J = 8.4, 1.0 Hz, 1H), 3.78 (s, 3H), 2.57 - 2.38 (m, 4H), 2.29 - 2.15 (m, 1H), 2.15 - 2.00 (m, 1H), 1.60 (s, 1H), 1.29 (s, 3H), 0.77 (t, J = 7.5 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 159.7 , 149.1 , 128.8 , 127.8 , 118.7 (q, *J* = 319.8 Hz), 112.8, 110.6 , 71.6 , 55.9 , 48.3, 48.3, 38.6, 34.2, 31.2, 9.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.3; **IR (ATR)** $\tilde{\nu}$ = 3348, 2958, 2916, 2849, 1605, 1575, 1466, 1438, 1417, 1266, 1251, 1213, 1142, 1083, 1057, 933, 843, 827, 730, 605, 512 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{20}F_3O_5S- H_2O]^+$: 351.0872, found: 351.0870; R_f = 0.35 (Pentane/Ethyl Acetate 10:1).



1g

***trans*-4-methyl-2-(3-hydroxy-1-ethyl-3-methylcyclobutyl)phenyl trifluoromethanesulfonate (1g):**

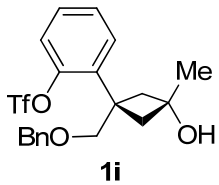
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.18 (d, J = 8.4 Hz, 1H), 7.05 (dd, J = 8.4, 2.2 Hz, 1H), 6.93 (s, 1H), 2.55 – 2.48 (m, 2H), 2.44 – 2.32 (m, 5H), 2.03 (q, J = 7.4 Hz, 2H), 1.57 (s, 1H), 1.27 (s, 3H), 0.63 (t, J = 7.4 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 146.4, 139.3, 137.3, 131.2, 128.6, 120.7, 118.7 (q, *J* = 319.7 Hz), 70.1, 47.8, 38.3, 34.8, 30.9, 21.4, 9.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.2 ; **IR (ATR)** $\tilde{\nu}$ = 3345, 2967, 2934, 2877, 1488, 1416, 1378, 1247, 1207, 1140, 1065, 905, 879, 813, 705, 646, 623, 593, 584, 502 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{20}F_3O_4S- H_2O]^+$: 335.0923, found: 335.0920; R_f = 0.52 (Pentane/Ethyl Acetate 10:1).



1h

***cis*-methyl 3-hydroxy-3-methyl-1-(2-(((trifluoromethyl)sulfonyl)oxy) phenyl)cyclobutanecarboxylate (1h):**

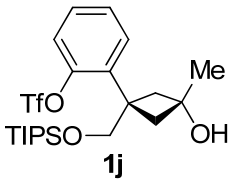
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 – 7.35 (m, 2H), 7.32 – 7.28 (m, 2H), 4.23 (s, 1H), 3.67 (s, 3H), 3.01 – 2.92 (m, 2H), 2.72 – 2.63 (m, 2H), 1.30 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 177.7, 148.2, 135.2 , 129.4, 129.1, 127.8, 120.9 (q, *J* = 1.5 Hz), 118.3 (q, *J* = 319.5 Hz), 69.8, 53.3, 47.4, 43.2, 28.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.7; **IR (ATR)** $\tilde{\nu}$ = 3412, 2958, 2925, 2855, 1734, 1716, 1420, 1249, 1212, 1140, 1084, 1050, 895, 767, 591 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{16}F_3O_6S - H_2O]^+$: 351. 0509, found: 351.0515; R_f = 0.15 (Pentane/Ethyl Acetate 5:1)



1i

***trans*-2-(1-((benzyloxy)methyl)3-hydroxy-3-methylcyclobutyl)phenyl trifluoromethanesulfonate (1i):**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.28 (m, 8H), 7.22 – 7.16 (m, 1H), 4.64 (s, 2H), 4.37 (s, 1H), 3.53 (s, 2H), 2.78 – 2.66 (m, 2H), 2.65 – 2.51 (m, 2H), 1.27 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 148.2, 138.3, 137.3, 130.5, 129.0, 128.4, 128.3, 128.2, 121.2, 118.6 (q, *J* = 319.7 Hz), 76.6, 74.2, 68.6, 46.8, 39.0, 29.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.4; **IR (ATR)** $\tilde{\nu}$ = 3297, 2959, 2927, 2859, 1450, 1516, 1370, 1255, 1206, 1070, 752, 698 cm^{-1}; **HRMS (ESI)** calculated for $[C_{20}H_{22}F_3O_5S - H_2O]^+$: 413.1029, found: 413.1032; R_f = 0.34 (Pentane/Ethyl Acetate 6:1)

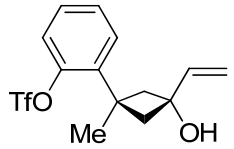


1j

***trans*-2-(3-hydroxy-3-methyl-1-(((triisopropylsilyl)oxy)methyl) cyclobutyl)phenyl trifluoromethanesulfonate (1j):**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.12 (m, 4H), 4.44 (s, 1H), 3.67 (s, 2H), 2.74 – 2.62 (m, 2H), 2.61 – 2.48 (m, 2H), 1.24 (s, 3H), 1.15 – 1.05 (m, 3H), 1.03 (d, *J* = 6.2 Hz, 18H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 148.3, 138.5, 130.7, 128.9, 128.2, 121.23, 118.6 (q, *J* = 319.7 Hz), 70.1, 68.7, 46.4, 40.4, 28.9, 18.2, 12.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.3; **IR (ATR)** $\tilde{\nu}$ = 3448,

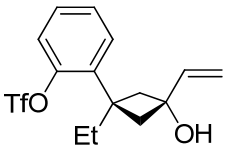
2944, 2894, 2868, 1420, 1248, 1213, 1141, 1094, 1056, 893, 791, 765, 684, 652, 597 cm^{-1}; **HRMS (ESI)** calculated for $[C_{23}H_{35}F_3O_5SSi - H_2O]^+$: 479.1894, found: 479.1899; R_f = 0.47 (Pentane/Dichloromethane 2:1)



1k

***trans*-2-(3-hydroxy-1-methyl-3-vinylcyclobutyl)phenyltrifluoromethane sulfonate (1k):**

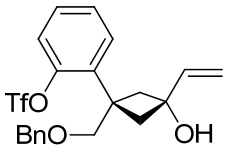
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.22 (m, 3H), 7.21 (ddd, *J* = 7.1, 2.0, 0.8 Hz, 1H), 5.94 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.16 (dd, *J* = 17.3, 1.0 Hz, 1H), 4.99 (dd, *J* = 10.6, 1.0 Hz, 1H), 2.75 – 2.66 (m, 2H), 2.49 – 2.39 (m, 2H), 1.75 (s, 1H), 1.72 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 147.8, 144.6, 143.0, 128.9, 128.3, 128.1, 118.6 (q, *J* = 319.5 Hz), 121.1 (q, *J* = 1.5 Hz), 111.9, 72.3, 47.5, 35.6, 30.7.; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.4; **IR (ATR)** $\tilde{\nu}$ = 3359, 2982, 2933, 1486, 1417, 1247, 1211, 1140, 1059, 920, 894, 851, 765, 650, 630, 596, 524 cm^{-1}; **HRMS (ESI)** calculated for $[C_{14}H_{16}F_3O_4S - H_2O]^+$: 319.0610, found: 319.0608; R_f = 0.28 (Pentane/Ethyl Acetate 6:1).



1l

***trans*-2-(1-ethyl-3-hydroxy-3-vinylcyclobutyl)phenyl trifluoromethane sulfonate (1l):**

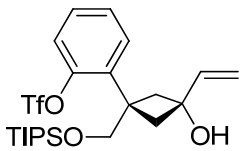
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.26 (m, 3H), 7.22 – 7.13 (m, 1H), 5.97 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.17 (dd, *J* = 17.2, 1.0 Hz, 1H), 5.00 (dd, *J* = 10.6, 1.0 Hz, 1H), 2.74 – 2.65 (m, 2H), 2.54 – 2.45 (m, 2H), 2.19 (q, *J* = 7.4 Hz, 2H), 1.95 (s, 1H), 0.67 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR** δ = 148.3, 144.7, 139.7, 130.6, 128.2, 127.4, 121.0, 118.6 (q, *J* = 319.7 Hz), 111.9, 72.3, 46.2, 39.3, 34.2, 9.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.4; **IR (ATR)** $\tilde{\nu}$ = 3340, 2968, 2936, 1444, 1416, 1206, 1136, 1068, 993, 889, 864, 763, 650, 628, 595, 522 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{18}F_3O_4S - H_2O]^+$: 333.0767, found: 333.0765; R_f = 0.53 (Pentane/Dichloromethane 1:1).



1m

***trans*-2-(3-hydroxy-1-phenethyl-3-vinylcyclobutyl)phenyl trifluoro methanesulfonate (1m):**

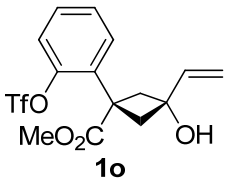
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.27 (m, 8H), 7.22 – 7.19 (m, 1H), 5.92 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.21 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.01 (dd, *J* = 10.6, 1.4 Hz, 1H), 4.65 (s, 2H), 4.54 (s, 1H), 3.59 (s, 2H), 2.90 – 2.68 (m, 4H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 148.1, 143.4, 138.1, 137.2, 130.4, 129.0, 129.0, 128.4, 128.3, 128.3, 121. , 118.5 (q, *J* = 319.7 Hz), 112.3, 76.3, 74.1, 70.6, 45.9, 39.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.4; ; **IR (ATR)** $\tilde{\nu}$ = 3426, 2927, 2857, 1417, 1363, 1247, 1207, 1137, 1120, 1075, 892, 747, 698, 629, 594, 524 cm^{-1}; **HRMS (ESI)** calculated for $[C_{21}H_{22}F_3O_5S - H_2O]^+$: 425.1029, found: 425.1032; R_f = 0.44 (Pentane/Ethyl Acetate 6:1).



1n

***trans*-2-(3-hydroxy-1-phenethyl-3-vinylcyclobutyl)phenyl trifluoromethane sulfonate (1n):**

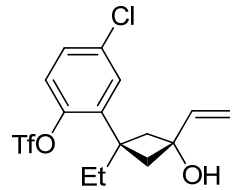
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.29 (m, 3H), 7.24 – 7.20 (m, 1H), 5.95 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.21 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.02 (dd, *J* = 10.7, 1.3 Hz, 1H), 3.82 (s, 2H), 2.80 – 2.70 (m, 4H), 1.22 – 1.12 (m, 3H), 1.10 – 1.05 (m, 18H).; **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 148.2, 143.5, 138.4, 130.8, 128.9, 128.2, 121.2, 118.7 (q, *J* = 319.5 Hz), 112.4, 70.7, 70.0, 45.3, 40.8, 18.2, 12.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.3; **IR (ATR)** $\tilde{\nu}$ = 3428, 2944, 2893, 2867, 1463, 1445, 1420, 1248, 1213, 1140, 1101, 1065, 920, 886, 791, 765, 682, 650, 597, 524 cm^{-1}; **HRMS (ESI)** calculated for $[C_{23}H_{35}F_3O_5SSi - H_2O]^+$: 491.1894, found: 491.1892; R_f = 0.33 (Pentane/Dichloromethane 3:1).



1o

***cis*-methyl 3-hydroxy-1-(2-(((trifluoromethyl)sulfonyl)oxy)phenyl)-3-vinylcyclobutanecarboxylate (1o):**

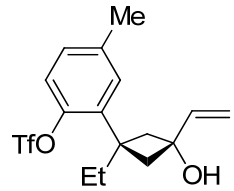
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 – 7.36 (m, 2H), 7.32 (m, 2H), 5.93 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.25 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.07 (dd, *J* = 10.7, 1.2 Hz, 1H), 4.30 (s, 1H), 3.70 (s, 3H), 3.09 – 2.98 (m, 2H), 2.93 – 2.81 (m, 2H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 177.7, 148.3, 142.6, 135.3, 129.7, 129.3, 128.2 , 121.3 (d, *J* = 1.5 Hz), 118.6 (q, *J* = 319.6 Hz), 113.5 , 72.0 , 53.7 , 46.8 , 44.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.7; **IR (ATR)** $\tilde{\nu}$ = 3448, 2988, 2956, 2925, 1734, 1715, 1487, 1420, 1248, 1210, 1139, 893, 767, 629, 592, 523 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{16}F_3O_6S - H_2O]^+$: 363.0509, found: 363.0509; ***R*$_f$** = 0.29 (Dichloromethane).



1p

***trans*-4-chloro-2-(3-hydroxy-1-ethyl-3-vinylcyclobutyl)phenyl trifluoro methanesulfonate (1p):**

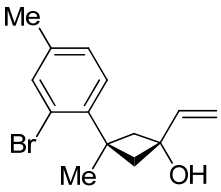
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.26 - 7.24 (m, 2H), 7.10 (dd, J = 1.9, 1.0 Hz, 1H), 5.95 (dd, J = 17.2, 10.6 Hz, 1H), 5.15 (dd, J = 17.2, 1.0 Hz, 1H), 5.01 (dd, J = 10.6, 1.0 Hz, 1H), 2.73 - 2.56 (m, 2H), 2.54 - 2.35 (m, 2H), 2.16 (q, J = 7.4 Hz, 2H), 1.61 (s, 1H), 0.67 (t, J = 7.4 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 146.6, 144.5, 142.0, 133.3, 130.5, 128.1 , 122.3, 118.6 (q, J = 319.8 Hz), 112.2, 72.2, 46.1, 39.6, 33.9, 9.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.2; **IR (ATR)** $\tilde{\nu}$ = 3333, 2970, 2936, 1469, 1421, 1248, 1214, 1140, 1105, 1082, 1070, 920, 897, 870, 818, 762, 666, 618, 580 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{17}ClF_3O_4S - H_2O]^+$: 367.0377, found: 367.0378; ***R*$_f$** = 0.63 (Pentane/Ethyl Acetate 10:1).



1q

***trans*-4-methyl-2-(3-hydroxy-1-ethyl-3-vinylcyclobutyl)phenyl trifluoro methanesulfonate (1q):**

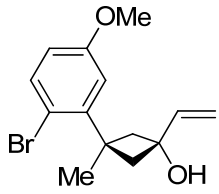
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.18 (d, J = 8.4 Hz, 1H), 7.05 (dd, J = 8.4, 2.2 Hz, 1H), 6.90 (d, J = 2.2 Hz, 1H), 5.95 (dd, J = 17.2, 10.6 Hz, 1H), 5.14 (dd, J = 17.2, 1.0 Hz, 1H), 4.98 (dd, J = 10.6, 1.0 Hz, 1H), 2.76 - 2.59 (m, 2H), 2.51 - 2.40 (m, 2H), 2.35 (s, 3H), 2.14 (q, J = 7.4 Hz, 2H), 1.65 (s, 1H), 0.65 (t, J = 7.4 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 146.3, 144.8, 139.4, 137.3, 131.0, 128.6, 120.7, 118.7 (q, *J* = 319.6 Hz), 111.8, 72.3, 46.2, 39.2, 34.2, 21.3, 9.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.4; **IR (ATR)** $\tilde{\nu}$ = 3447, 2980, 2936, 2878, 1739, 1488, 1417, 1401, 1374, 1243, 1207, 1140, 1065, 1045, 901, 877, 813, 704, 645, 621, 583, 501 cm^{-1}; **HRMS (ESI)** calculated for $[C_{16}H_{20}F_3O_4S - H_2O]^+$: 347.0923, found: 347.0918; ***R*$_f$** = 0.61 (Pentane/Ethyl Acetate 10:1).



1r

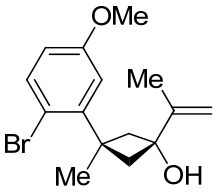
***trans*-3-(2-bromo-4-methylphenyl)-3-methyl-1-vinylcyclobutanol (1r):**

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.38 – 7.31 (m, 1H), 7.11 – 7.03 (m, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 5.93 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.14 (dd, *J* = 17.2, 1.1 Hz, 1H), 4.96 (dd, *J* = 10.6, 1.1 Hz, 1H), 2.80 – 2.69 (m, 2H), 2.52 – 2.41 (m, 2H), 2.29 (s, 3H), 1.71 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 146.0, 144.8, 137.5, 134.6, 128.2, 127.6, 121.6, 111.3, 71.9, 47.9, 38.5, 29.3, 20.5; **IR (ATR)** $\tilde{\nu}$ = 3385, 2977, 2926, 2867, 1488, 1451, 1415, 1381, 1369, 1261,1238, 1063, 1034, 994, 957, 918, 819, 676, 569 cm^{-1}; **HRMS (ESI)** calculated for $[C_{14}H_{17}BrO - H_2O]^+$: 263.0430, found: 263.0432; ***R*$_f$** = 0.32 (Pentane/Ethyl Acetate 10:1).



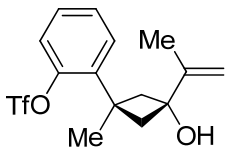
1s

***trans*- 3-(2-bromo-5-methoxyphenyl)-3-methyl-1-vinylcyclobutanol (1s):**
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.39 (d, *J* = 8.7 Hz, 1H), 6.69 (d, *J* = 3.0 Hz, 1H), 6.60 (dd, *J* = 8.7, 3.0 Hz, 1H), 5.94 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.15 (dd, *J* = 17.3, 1.1 Hz, 1H), 4.98 (dd, *J* = 10.6, 1.1 Hz, 1H), 3.79 (s, 3H), 2.78 – 2.69 (m, 2H), 2.51 – 2.39 (m, 2H), 1.72 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 159.2, 150.4, 144.9, 135.0, 114.5, 112.6, 112.5, 111.7, 72.0, 55.8, 48.0, 39.2, 29.3; **IR (ATR)** $\tilde{\nu}$ = 3401, 2960, 2925, 2855, 1466, 1407, 1394, 1290, 1229, 1049 cm^{-1}; **HRMS (ESI)** calculated for $[C_{14}H_{18}BrO_2 - H_2O]^+$: 279.0379, found: 279.0381; R_f = 0.35 (Pentane/Ethyl Acetate 10:1).



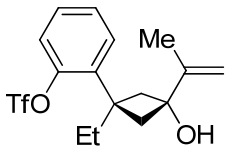
1t

***trans*-3-(2-bromo-5-methoxyphenyl)-1-(prop-1-en-2-yl)-3-methyl cyclobutanol (1t):**
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 8.6 Hz, 1H), 6.69 (d, *J* = 3.0 Hz, 1H), 6.59 (dd, *J* = 8.6, 3.0 Hz, 1H), 4.95 – 4.71 (m, 2H), 3.78 (s, 3H), 2.88 – 2.71 (m, 2H), 2.5 – 2.4 (m, 2H), 1.6 (s, 1H), 1.73 (m, 6H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 159.0, 150.6, 149.6, 134.7, 114.3, 112.3, 112.2, 109.6, 74.0, 55.6, 45.9, 38.5, 28.7, 17.5; **IR (ATR)** $\tilde{\nu}$ = 3435, 2966, 2934, 1593, 1568, 1466, 1408, 1296, 1233, 1173, 1048, 1016, 902, 800, 603, 446 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{20}BrO_2 - H_2O]^+$: 293.0536, found: 293.0534; R_f = 0.58 (Pentane/Ethyl Acetate 5:1).



1u

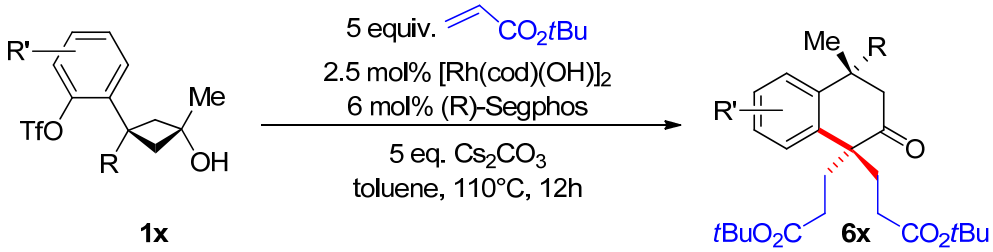
***trans*-2-(3-hydroxy-1-methyl-3-(prop-1-en-2-yl)cyclobutyl)phenyltrifluoro methanesulfonate (1u):**
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.21 (m, 4H), 4.89 (dd, *J* = 1.4, 0.8 Hz, 1H), 4.79 (p, *J* = 1.4 Hz, 1H), 2.83 – 2.73 (m, 2H), 2.48 – 2.38 (m, 2H), 1.76 (s, 3H), 1.75 (dd, *J* = 1.5, 0.8 Hz, 3H), 1.73 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 149.6, 147.8, 143.4, 128.9, 128.3, 128.0, 121.1 (q, J = 1.8 Hz), 118.4 (q, J = 319.5 Hz), 110.0, 74.6, 45.6, 35.0, 30.4, 17.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.4; **IR (ATR)** $\tilde{\nu}$ = 3377, 2980, 2933, 1486, 1443, 1418, 1248, 1212, 1140, 1075, 1056, 900, 850, 765, 650, 630, 959, 520 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{18}F_3O_4S - H_2O]^+$: 333.0767, found: 333.0764; R_f = 0.50 (Pentane/Dichloromethane 3:1).



1v

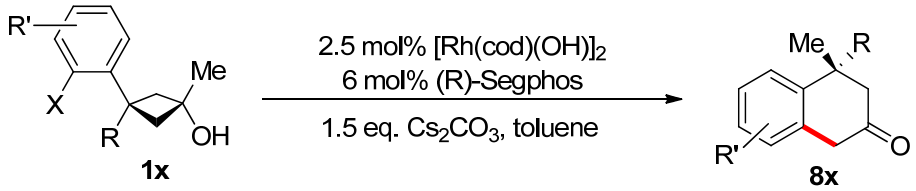
***trans*-2-(1-ethyl-3-hydroxy-3-(prop-1-en-2-yl)cyclobutyl)phenyl trifluoro methanesulfonate (1v):**
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.20 (m, 3H), 7.18 – 7.04 (m, 1H), 4.87 – 4.85 (m, 1H), 4.76 (p, *J* = 1.4 Hz, 1H), 2.77 – 2.64 (m, 2H), 2.53 – 2.34 (m, 2H), 2.18 (q, *J* = 7.4 Hz, 2H), 1.72 (q, *J* = 0.9 Hz, 3H), 1.70 (s, 1H), 0.64 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 149.6, 148.3, 140.1, 130.6, 128.0, 127.4, 120.8 (q, *J* = 1.7 Hz), 118.6 (q, *J* = 319.5 Hz), 110.0, 74.7, 44.3, 38.9, 33.6, 17.6, 9.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -74.4; **IR (ATR)** $\tilde{\nu}$ = 3385, 2970, 2937, 2878, 1738, 1444, 1246, 1212, 1139, 1069, 1046, 898, 765, 735, 596 cm^{-1}; **HRMS (ESI)** calculated for $[C_{16}H_{20}F_3O_4S - H_2O]^+$: 347.0923, found: 347.0920; R_f = 0.49 (Pentane/Dichloromethane 3:1).

General Procedure for the Synthesis of β-Tetralones 6:



The *tert*-cyclobutanol (0.100 mmol), $[Rh(cod)(OH)]_2$ (1.14 mg, 2.50 µmol), (*R*)-Segphos (6.00 µmol), *tert*-butyl acrylate (87 µL,0.500 mmol) and cesium carbonate (162.50 mg, 0.500 mmol) were weighted into an oven-dried vial equipped with a magnetic stir bar, capped with a septum and purged with nitrogen. Dry toluene (0.5 mL) was added and the mixture was degassed with three freeze-pump-thaw cycles. The mixture was stirred for 20 min at 23°C and subsequently immersed in a preheated oil bath at the indicated temperature (110°C or 125°C). After no more starting material was detected by TLC (12 h), the reaction mixture was cooled to 23°C and purified on a silica gel column. The product was eluted with Pentane/Ethyl Acetate (10:1 to 40:1) to give the β-Tetralones **6** as colorless oils in 66–74% yield.

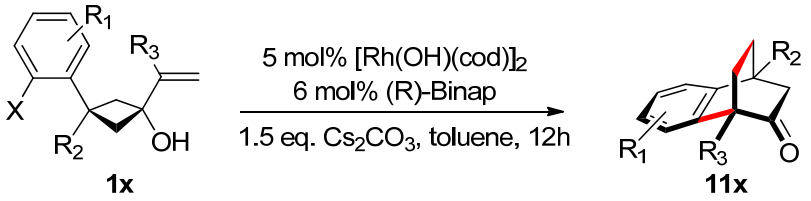
General Procedure for the Synthesis of β-Tetralones 8:



X = OTf: The *tert*-cyclobutanol (0.100 mmol), $[Rh(cod)(OH)]_2$ (1.14 mg, 2.50 µmol), (*R*)-Segphos (6.00 µmol), and cesium carbonate (48.90 mg, 0.150 mmol) were weighted into an oven-dried vial equipped with a magnetic stir bar, capped with a septum and purged with nitrogen. Dry toluene (0.5 mL) was added and the mixture was degassed with three freeze-pump-thaw cycles.

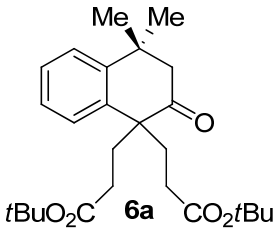
X = Br: The *tert*-cyclobutanol (0.100 mmol), $[Rh(cod)(OH)]_2$ (1.14 mg, 2.50 µmol), (*R*)-Segphos (6.00 µmol), silver acetate (16.70 mg, 0.100 mmol), triphenylphosphine (26.20 mg, 0.100 mmol) and cesium carbonate (48.90 mg, 0.150 mmol) were weighted into an oven-dried vial equipped with a magnetic stir bar, capped with a septum and purged with nitrogen. Dry toluene (0.5 mL) was added and the mixture was degassed with three freeze-pump-thaw cycles.
In both cases, the mixture was stirred for 20 min at 23°C and subsequently immersed in a preheated oil bath at the indicated temperature (110°C or 125°C). After no more starting material was detected by TLC (12 h), the reaction mixture was cooled to 23°C and purified on a silica gel column. The product was eluted with Pentane/Ethyl Acetate (10:1 to 40:1) to give the β-Tetralones **8** as colorless oils in 63–89% yield.

General Procedure for the Synthesis of benzobicyclo[2.2.2]octenones 11 :

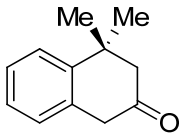


X = OTf: The *tert*-cyclobutanol (0.100 mmol), $[Rh(cod)(OH)]_2$ (1.14 mg, 2.50 µmol), (*R*)-Segphos (6.00 µmol), and cesium carbonate (48.90 mg, 0.150 mmol) were weighted into an oven-dried vial equipped with a magnetic stir bar, capped with a septum and purged with nitrogen. Dry toluene (0.1 mL) was added and the mixture was degassed with three freeze-pump-thaw cycles.

X = Br: The *tert*-cyclobutanol (0.100 mmol), $[Rh(cod)(OH)]_2$ (1.14 mg, 2.50 µmol), (*R*)-Segphos (6.00 µmol), silver acetate (16.70 mg, 0.100 mmol), triphenylphosphine (26.20 mg, 0.100 mmol) and cesium carbonate (48.90 mg, 0.150 mmol) were weighted into an oven-dried vial equipped with a magnetic stir bar, capped with a septum and purged with nitrogen. Dry toluene (0.1 mL) was added and the mixture was degassed with three freeze-pump-thaw cycles.
In both cases, the mixture was stirred for 20 min at 23°C and subsequently immersed in a preheated oil bath at the indicated temperature (110°C or 125°C). After no more starting material was detected by TLC (12 h), the reaction mixture was cooled to 23°C and purified on a silica gel column. The product was eluted with Pentane/Ethyl Acetate (10:1 to 40:1) to give the benzobicyclo[2.2.2]octenones **11** as colorless oils in 48–67% yield.

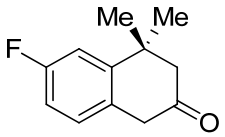


di-tert-butyl 3,3'-(4,4-dimethyl-2-oxo-1,2,3,4-tetrahydronaphthalene-1,1-diyl)dipropanoate (6a):
Synthesized according to the general procedure on a 0.100 mmol scale, 67% (29.1 mg) isolated as a colorless oil.
^{1}H-NMR (101 MHz, $CDCl_3$) δ = 7.42 – 7.38 (m, 1H), 7.30 – 7.26 (m, 3H), 2.64 (s, 2H), 2.37 (ddd, *J* = 13.7, 11.5, 4.7 Hz, 2H), 2.22 – 1.98 (m, 4H), 1.80 (ddd, *J* = 15.3, 11.5, 4.1 Hz, 2H), 1.39 (s, 18H), 1.32 (s, 6H); **^{13}C-NMR** (400 MHz, $CDCl_3$) δ = 211.9, 172.7, 145.0, 139.7, 127.9, 127.4, 127.3, 125.6, 80.7, 55.0, 52.3, 39.2, 35.0, 31.8, 31.4, 28.4; **IR (ATR)** $\tilde{\nu}$ = 2974, 2932, 2871, 1725, 1486, 1445, 1422, 1366, 1303, 1287, 1256, 1213, 1147, 847, 761, 552; **HRMS (ESI)** calculated for $[C_{26}H_{39}O_5]^+$: 431.2792, found: 431.2787; R_f = 0.36 (Pentane/Ethyl Acetate 10:1).



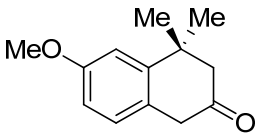
8a

4,4-dimethyl-3,4-dihydronaphthalen-2(1H)-one (8a):
Synthesized according to the general procedure on a 0.100 mmol scale, 88% (15.3 mg) isolated as a colorless oil.
^{1}H-NMR (101 MHz, $CDCl_3$) δ = 7.42 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.22 (td, *J* = 7.4, 1.5 Hz, 1H), 7.14 – 7.09 (m, 1H), 3.67 (s, 2H), 2.53 (s, 2H), 1.34 (s, 6H); **^{13}C-NMR** (400 MHz, $CDCl_3$) δ = 210.3, 144.8, 132.8, 129.2, 127.4, 127.1, 124.8, 54.2, 44.2, 37.3, 29.6; **IR (ATR)** $\tilde{\nu}$ = 2962, 2886, 2867, 1721, 1490, 1450, 1308, 1239, 762; **HRMS (ESI)** calculated for $[C_{12}H_{15}O]^+$: 175.1117, found: 175.1110; R_f = 0.30 (Pentane/Ethyl Acetate 10:1).



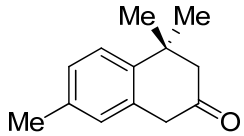
8b

6-fluoro-4,4-dimethyl-3,4-dihydronaphthalen-2(1H)-one (8b):
Synthesized according to the general procedure on a 0.080 mmol scale, 72% (10.1 mg) isolated as a colorless oil.
^{1}H-NMR (101 MHz, $CDCl_3$) δ = 7.37 (dd, *J* = 8.7, 5.6 Hz, 1H), 6.95 (td, *J* = 8.7, 2.8 Hz, 1H), 6.82 (dt, *J* = 8.7, 1.7 Hz, 1H), 3.64 (s, 2H), 2.52 (s, 2H), 1.32 (s, 6H); **^{13}C-NMR** (400 MHz, $CDCl_3$) δ = 209.0, 160.8 (d, *J* = 361.2 Hz), 155.0 (d, *J* = 10.7 Hz), 140.6 (d, *J* = 62.0 Hz), 126.1 (d, *J* = 8.3 Hz), 115.2 (d, *J* = 21.3 Hz), 113.9 (d, *J* = 20.9 Hz), 53.8, 43.8, 36.6, 29.4;**^{19}F-NMR** (376 MHz, $CDCl_3$) δ = -116.6; **IR (ATR)** $\tilde{\nu}$ = 2959, 2936, 2877, 2837, 1720, 1597, 1578, 1467, 1438, 1379, 1311, 1283, 1250, 1132, 1080, 1050, 777, 741; **HRMS (ESI)** calculated for $[C_{12}H_{14}FO]^+$: 193.1023, found: 193.1021; R_f = 0.61 (Pentane/Ethyl Acetate 5:1).



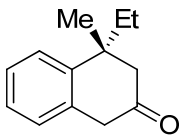
8c

4,4,7-trimethyl-3,4-dihydronaphthalen-2(1H)-one (8c):
Synthesized according to the general procedure on a 0.040 mmol scale, 74% (6.1 mg) isolated as a colorless oil.
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.04 (d, *J* = 8.3 Hz, 1H), 6.97 (d, *J* = 2.6 Hz, 1H), 6.77 (dd, *J* = 8.3, 2.6 Hz, 1H), 3.83 (s, 3H), 3.61 (s, 2H), 2.50 (s, 2H), 1.33 (s, 6H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 210.4, 158.8, 146.0, 129.8, 124.6, 111.8, 110.9, 55.5, 53.9, 43.3, 37.2, 29.3; **IR (ATR)** $\tilde{\nu}$ = 2961, 2874, 1717, 1611, 1577, 1494, 1464, 1424, 1291, 1235, 1191, 1166, 1077, 1043, 816, 471 cm^{-1}; **HRMS (ESI)** calculated for $[C_{13}H_{17}O_2]^+$: 205.1223, found: 205.1217; R_f = 0.42 (Pentane/Ethyl Acetate 8:1).



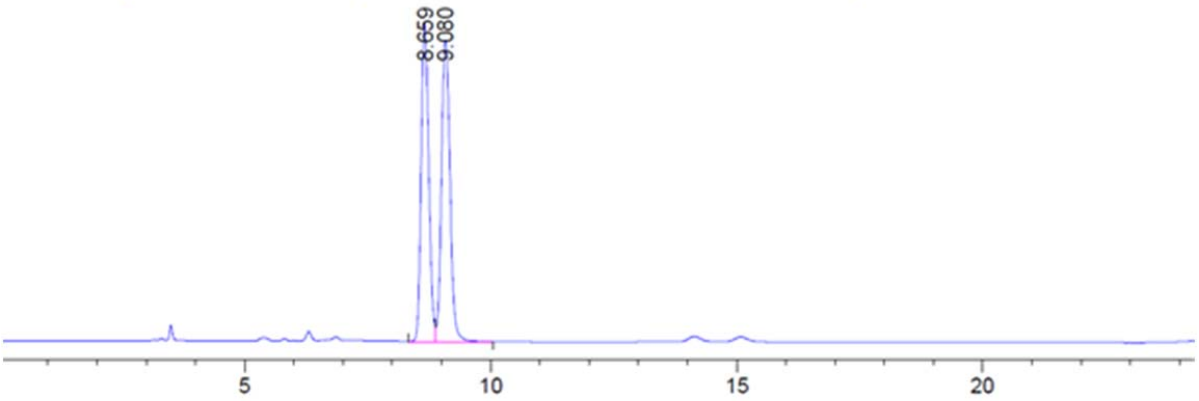
8d

4,4,7-trimethyl-3,4-dihydronaphthalen-2(1H)-one (8d):
Synthesized according to the general procedure on a 0.100 mmol scale, 77% (14.6 mg) isolated as a colorless oil.
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.03 (m, 1H), 6.94 (d, *J* = 1.6 Hz, 1H), 3.63 (s, 2H), 2.51 (s, 2H), 2.32 (s, 3H), 1.32 (s, 6H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 210.3, 141.7, 136.6, 132.5, 129.6, 128.0, 124.5, 54.2, 44.0, 36.9, 29.5, 21.0; **IR (ATR)** $\tilde{\nu}$ = 2961, 2929, 2887, 2872, 1720, 1502, 1459, 1386, 1305, 1257, 1242, 718, 545 cm^{-1}; **HRMS (ESI)** calculated for $[C_{13}H_{17}O]^+$: 189.1274, found: 189.1271; R_f = 0.27 (Pentane/Ethyl Acetate 10:1).

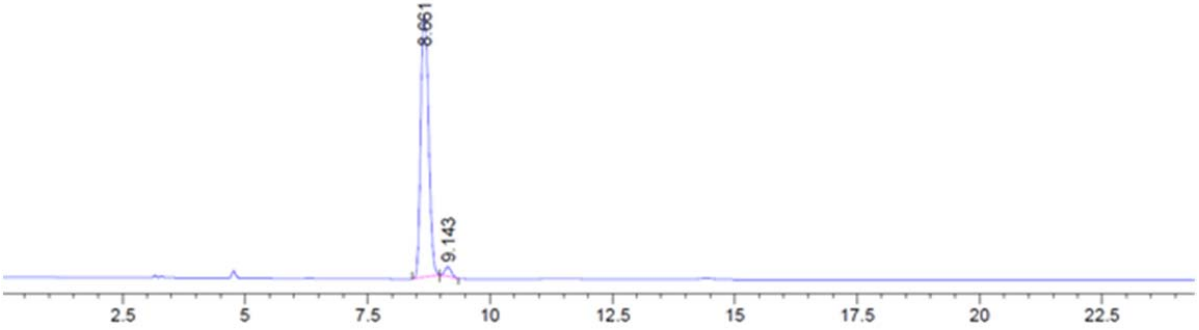


8e

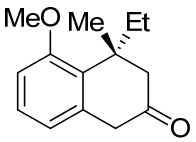
4-ethyl-4-methyl-3,4-dihydronaphthalen-2(1H)-one (8e):
Synthesized according to the general procedure on a 0.100 mmol scale, 85% (16.0 mg) isolated as a colorless oil.
^{1}H-NMR (101 MHz, $CDCl_3$) δ = 7.35 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.21 (td, *J* = 7.3, 1.4 Hz, 1H), 7.16 – 7.08 (m, 1H), 3.69 (d, *J* = 21.6 Hz, 1H), 3.62 (d, *J* = 21.6 Hz, 1H), 2.61 (d, *J* = 15.2 Hz, 1H), 2.46 (d, *J* = 15.2 Hz, 1H), 1.73 – 1.48 (m, 2H), 1.33 (s, 3H), 0.81 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR** (400 MHz, $CDCl_3$) δ = 210.4, 143.2, 133.1, 129.1, 126.9, 126.8, 125.7, 51.7, 44.0, 40.5, 33.9, 26.6, 8.9; **IR (ATR)** $\tilde{\nu}$ = 3064, 3023, 2965, 2937, 2879, 1717, 1489, 1460, 1395, 1382, 1299, 1253, 1230, 759, 734, 460; **HRMS (ESI)** calculated for $[C_{13}H_{17}O]^+$: 189.1274, found: 189.1268; **$[\alpha]_D^{20}$** = +60 (*c* = 3 mg/ml, $CHCl_3$); ***R*$_f$** = 0.50 (Pentane/Ethyl Acetate 10:1); HPLC separation (column AZH Hexane/Isopropanol 98:2 30min), 94% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.659	BV	0.1731	1.85730e4	1704.80933	49.0560
2	9.080	VB	0.1874	1.92878e4	1613.94116	50.9440

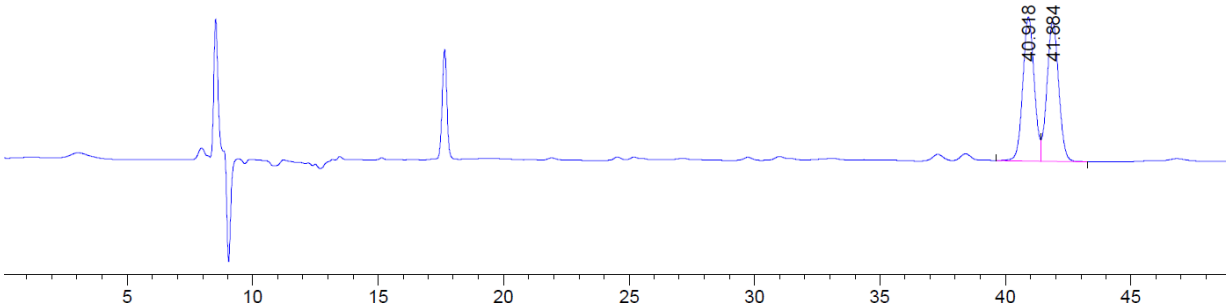


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.661	MM	0.1879	2.45364e4	2175.86035	97.1594
2	9.143	MM	0.1528	717.34888	78.24854	2.8406

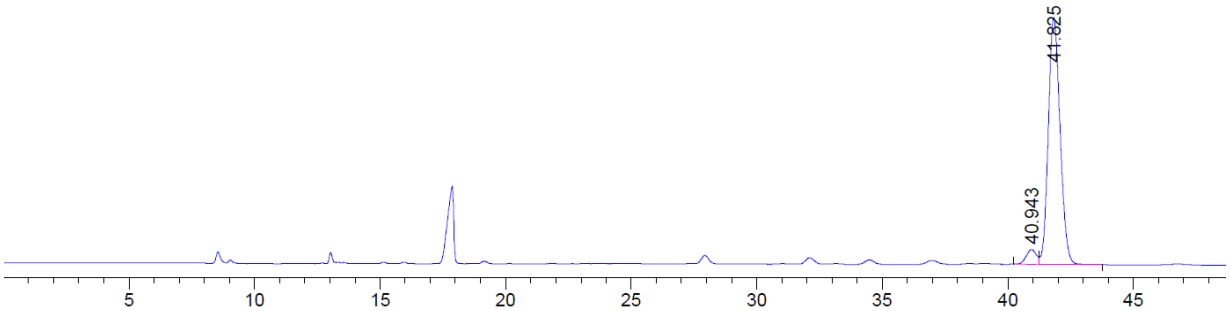


8f

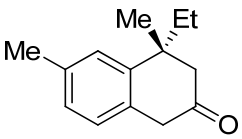
4-ethyl-5-methoxy-4-methyl-3,4-dihydronaphthalen-2(1H)-one (8f): Synthesized according to the general procedure on a 0.060 mmol scale, 74% (4.8 mg) isolated as a colorless oil. **^{1}H-NMR** (101 MHz, $CDCl_3$) δ = 7.16 (t, J = 7.9 Hz, 1H), 6.77 (d, J = 7.9 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 3.82 (s, 3H), 3.66 (d, *J* = 20.6 Hz, 1H), 3.57 (d, *J* = 20.6 Hz, 1H), 2.73 (d, *J* = 14.2 Hz, 1H), 2.35 (d, *J* = 14.2 Hz, 1H), 2.16 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.49 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.40 (s, 3H), 0.75 (t, J = 7.4 Hz, 3H); **^{13}C-NMR** (400 MHz, $CDCl_3$) δ = 210.7, 158.8, 135.7, 131.0, 127.8, 121.9, 110.0, 55.5, 53.4, 44.6, 43.8, 33.9, 27.8, 9.7; **IR (ATR)** $\tilde{\nu}$ = 2959, 2936, 2877, 2837, 1720, 1598, 1578, 1467, 1438, 1379, 1311, 1283, 1250, 1080, 1050, 777, 741; **HRMS (ESI)** calculated for $[C_{14}H_{19}O_2]^+$: 219.1380, found: 219.1370; **$[\alpha]_D^{20}$** = -22 (*c* = 2.5 mg/ml, $CHCl_3$); ***R*$_f$** = 0.44 (Pentane/Ethyl Acetate 10:1); HPLC separation (two IC column connected in series, Hexane/Isopropanol 99:1 50 min), 90% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.918	BV	0.4906	3315.64526	104.95827	50.1638
2	41.884	VB	0.5032	3293.99854	101.88778	49.8362

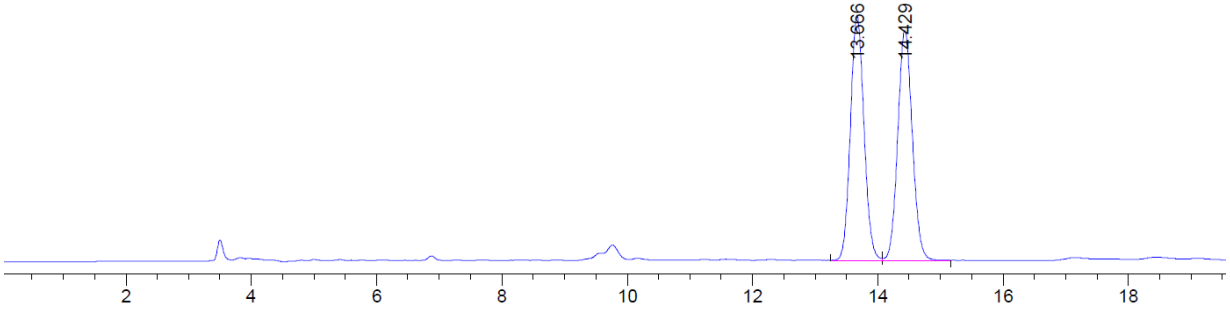


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.943	BV	0.4292	213.40939	7.51782	4.9232
2	41.825	VB	0.5059	4121.35400	126.57719	95.0768

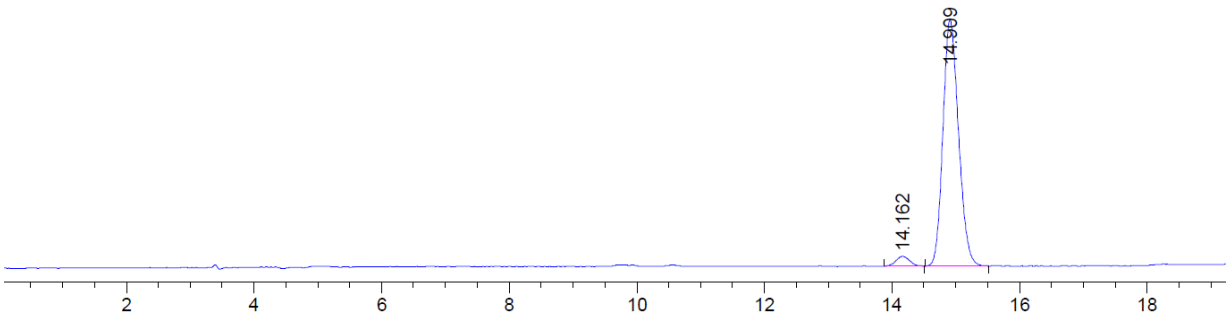


8g

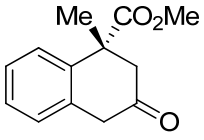
4-ethyl-4,6-dimethyl-3,4-dihydronaphthalen-2(1H)-one (8g): Synthesized according to the general procedure on a 0.080 mmol scale, 74% (14.0 mg) isolated as a colorless oil. **^{1}H-NMR** (101 MHz, $CDCl_3$) δ = 7.14 (s, 1H), 7.08 - 6.91 (m, 2H), 3.64 (d, *J* = 21.8 Hz, 1H), 3.58 (d, *J* = 21.8 Hz, 1H), 2.59 (d, *J* = 15.1 Hz, 1H), 2.44 (d, *J* = 15.1 Hz, 1H), 2.36 (s, 3H), 1.77 - 1.44 (m, 2H), 1.31 (s, 3H), 0.81 (t, J = 7.4 Hz, 3H); **^{13}C-NMR** (400 MHz, $CDCl_3$) δ = 211.0, 143.3, 136.5, 130.1, 129.1, 127.8, 126.4, 52.0, 43.8, 40.7, 34.2, 26.8, 21.7, 9.1; **IR (ATR)** $\tilde{\nu}$ = 2959, 2936, 2877, 2837, 1720, 1597, 1578, 1467, 1438, 1379, 1311, 1283, 1250, 1080, 1050, 777, 741; **HRMS (ESI)** calculated for $[C_{14}H_{19}O]^+$: 203.1430, found: 203.1427; **$[\alpha]_D^{20}$** = 62 (*c* = 8 mg/ml, $CHCl_3$); ***R*$_f$** = 0.72 (Pentane/Ethyl Acetate 10:1); HPLC separation (column IC Hexane/Isopropanol 99:1 20min), 93% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.666	BV	0.2338	4232.05029	280.86182	49.9008
2	14.429	VB	0.2500	4248.88086	263.61292	50.0992



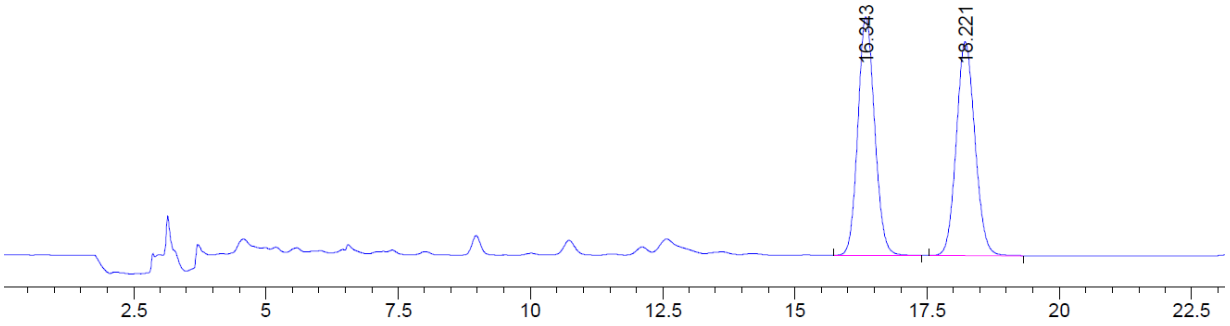
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.162	BB	0.2254	26.81332	1.78339	3.3699
2	14.909	BB	0.2623	768.84747	45.24350	96.6301



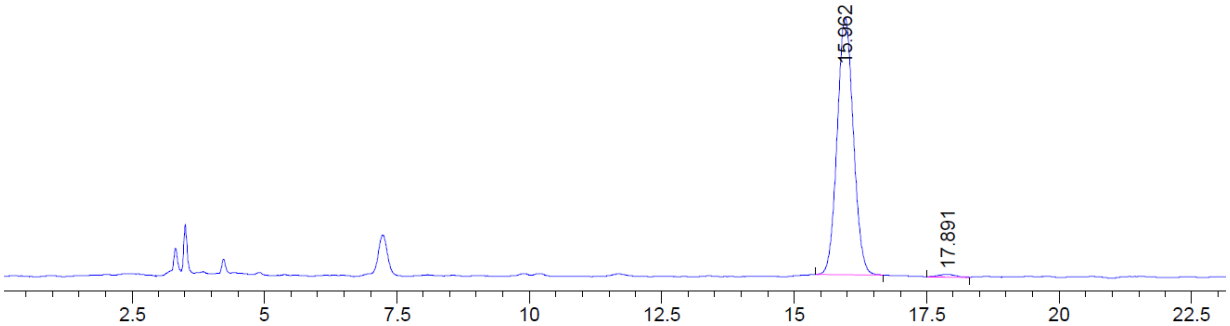
8h

methyl 1-methyl-3-oxo-1,2,3,4-tetrahydronaphthalene-1-carboxylate (8h): Synthesized according to the general procedure on a 0.100 mmol scale, 63% (13.8 mg) isolated as a colorless oil.

^{1}H-NMR (101 MHz, $CDCl_3$) δ = 7.46 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.16 – 7.12 (m, 1H), 3.75 (d, *J* = 21.0 Hz, 1H), 3.64 (s, 3H), 3.58 (d, *J* = 21.0 Hz, 1H), 3.03 (d, *J* = 16.5 Hz, 1H), 2.39 (d, *J* = 16.5 Hz, 1H), 1.70 (s, 3H); **^{13}C-NMR** (400 MHz, $CDCl_3$) δ = 207.5, 174.8, 137.9, 133.8, 129.1, 128.2, 127.5, 126.0, 52.9, 49.2, 43.9, 29.9, 24.0; **IR (ATR)** $\tilde{\nu}$ = 2942, 2891, 2866, 1723, 1492, 1463, 1388, 1368, 1146, 1105, 1068, 1013, 997, 882, 808, 759, 683, 660, 504, 457; **HRMS (ESI)** calculated for $[C_{13}H_{15}O_3]^+$: 219.1016, found: 219.1013; **$[\alpha]_D^{20}$** = +45 (*c* = 10 mg/ml, $CHCl_3$); ***R*$_f$** = 0.47 (Pentane/Ethyl Acetate 4:1); HPLC separation (column AZH Hexane/Isopropanol 90:10 30min), 98% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.343	BB	0.3407	4447.78369	202.13313	50.0076
2	18.221	BB	0.3802	4446.43848	181.24562	49.9924



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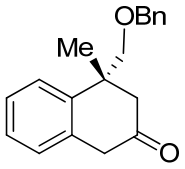
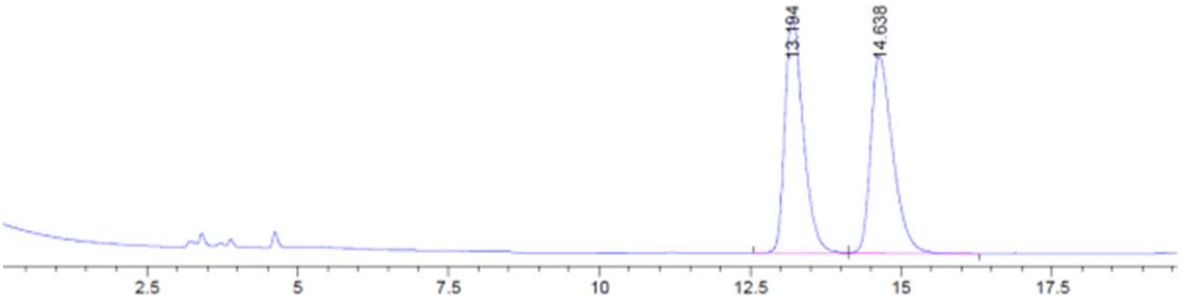
1	15.962	BB	0.3344	2974.32959	139.71382	98.8698
2	17.891	BB	0.2762	34.00116	1.46833	1.1302



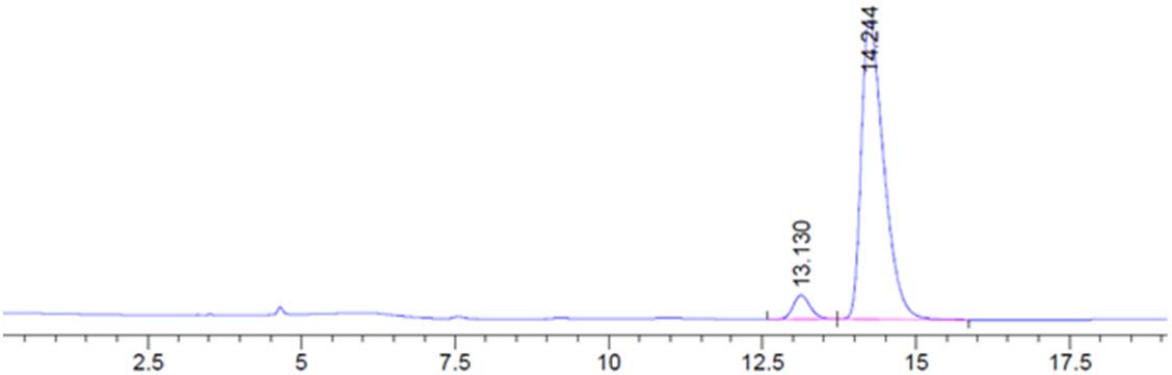
8i

4-((benzyloxy)methyl)-4-methyl-3,4-dihydronaphthalen-2(1H)-one (8i): Synthesized according to the general procedure on a 0.090 mmol scale, 89% (22.5 mg) isolated as a colorless oil.

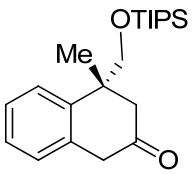
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.42 – 7.07 (m, 9H), 4.43 (d, *J* = 12.4 Hz, 1H), 4.38 (d, *J* = 12.4 Hz, 1H), 3.69 (d, *J* = 21.6 Hz, 1H), 3.58 (d, *J* = 21.6 Hz, 1H), 3.49 (d, *J* = 9.0 Hz, 1H), 3.38 (d, *J* = 9.0 Hz, 1H), 2.75 (d, *J* = 15.5 Hz, 1H), 2.48 (d, *J* = 15.5 Hz, 1H), 1.35 (s, 3H); **^{13}C-NMR** (400 MHz, $CDCl_3$) δ = 209.8, 141.2, 138.3, 134.6, 129.0, 128.6, 127.9 127.7, 127.4, 127.1, 125.7, 79.1, 73.6, 50.6, 44.3, 42.1, 24.8; **IR (ATR)** $\tilde{\nu}$ = 3063, 3029, 2963, 2935, 2858, 1718, 1493, 1460, 1099, 762, 738, 699, 456; **HRMS (ESI)** calculated for $[C_{19}H_{21}O_2]^+$: 281.1536, found: 281.1536; **$[\alpha]_D^{20}$** = +38 (*c* = 10 mg/ml, $CHCl_3$); ***R*$_f$** = 0.46 (Pentane/Ethyl Acetate 5:1); HPLC separation (column AYH Hexane/Isopropanol 95:2 20min), 89% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.194	BV	0.3248	1.33024e4	628.81769	49.8790
2	14.638	VB	0.3867	1.33669e4	525.52948	50.1210

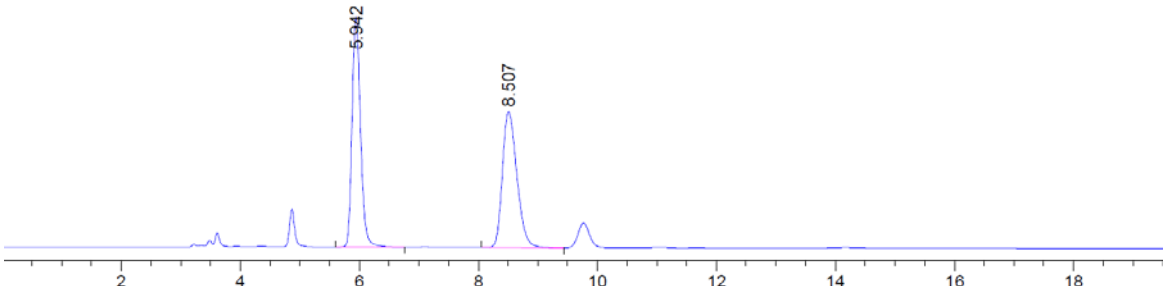


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.130	BB	0.2985	840.12158	43.28097	5.7564
2	14.244	BB	0.3874	1.37544e4	539.61145	94.2436

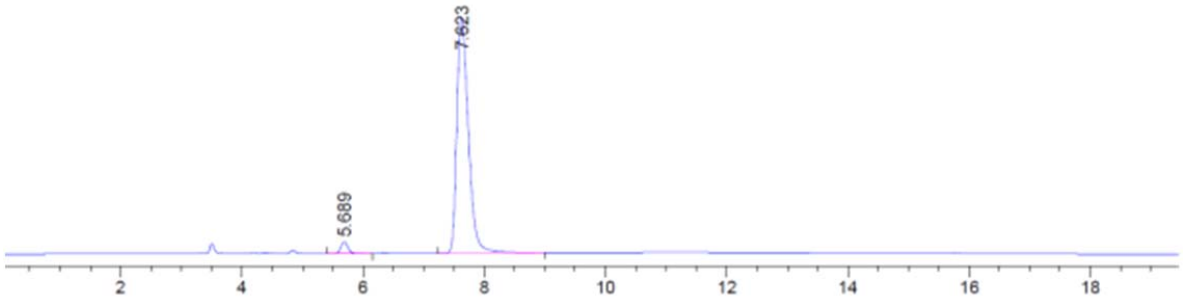


8j

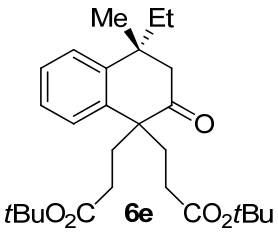
4-methyl-4-(((triisopropylsilyl)oxy)methyl)-3,4-dihydronaphthalen -2(1H)-one (8j):
Synthesized according to the general procedure on a 0.100 mmol scale, 72% (25.1 mg) isolated as a colorless oil.
^{1}H-NMR (101 MHz, $CDCl_3$) δ = 7.39 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.30 – 7.17 (m, 2H), 7.13 – 7.08 (m, 1H), 3.75 – 3.56 (m, 4H), 2.72 (d, *J* = 15.6 Hz, 1H), 2.47 (d, *J* = 15.6 Hz, 1H), 1.36 (s, 3H), 1.04 – 0.95 (m, 3H), 0.95 – 0.89 (m, 18H); **^{13}C-NMR** (400 MHz, $CDCl_3$) δ = 209.6, 141.2, 134.5, 128.9, 127.3, 127.1, 126.0, 72.8, 50.1, 44.3, 43.5, 24.4, 18.2, 12.2; **IR (ATR)** $\tilde{\nu}$ = 2942, 2891, 2866, 1723, 1492, 1463, 1388, 1368, 1146, 1105, 1068, 1013, 997, 882, 808, 759, 683, 660, 504, 457; **HRMS (ESI)** calculated for $[C_{21}H_{35}O_2Si]^+$: 347.2401, found: 347.2396; **$[\alpha]_D^{20}$** = +33 (*c* = 4 mg/ml, $CHCl_3$); ***R*$_f$** = 0.27 (Pentane/Ethyl Acetate 15:1); HPLC separation (column OZH Hexane/Isopropanol 99:1 20min), 94% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.942	BV	0.1515	1.27124e4	1284.39246	49.7873
2	8.507	BB	0.2609	1.28211e4	759.56738	50.2127



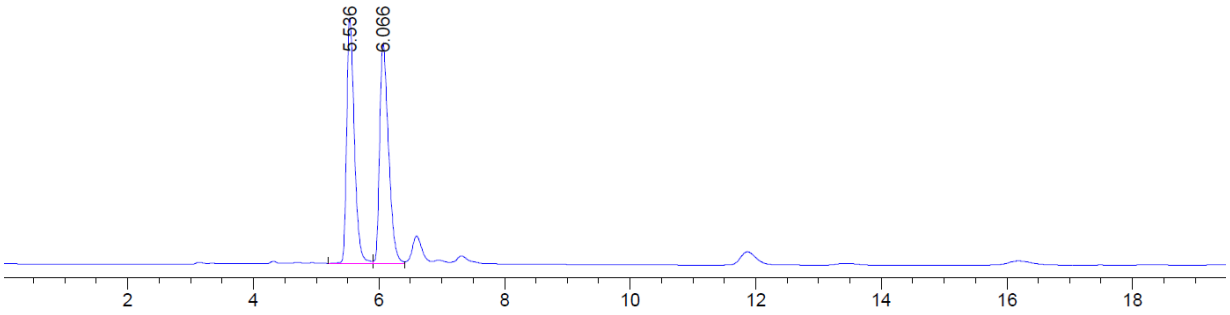
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.689	BB	0.1255	401.01086	49.00425	2.9477
2	7.623	BB	0.2046	1.32033e4	996.17072	97.0523



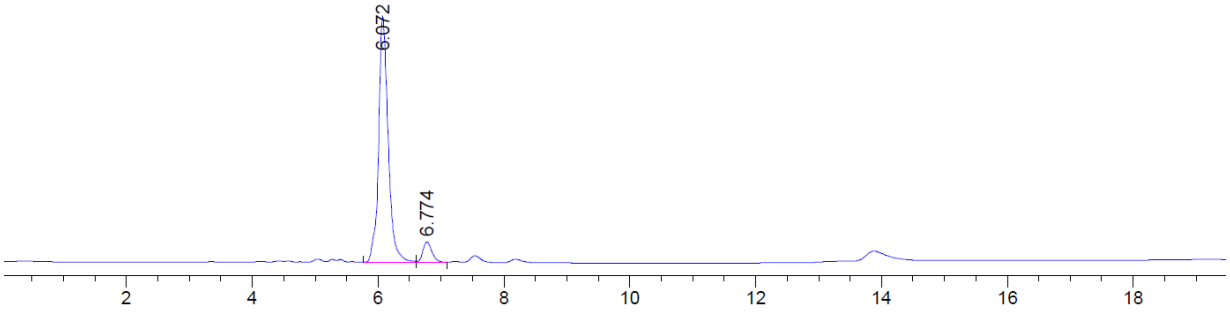
di-tert-butyl 3,3'-(4-ethyl-4-methyl-2-oxo-1,2,3,4-tetrahydro naphthalene-1,1-diyl)dipropanoate (6e):

Synthesized according to the general procedure on a 0.080 mmol scale, 67% (23.8 mg) isolated as a colorless oil.

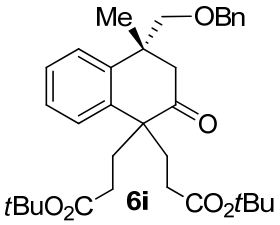
^{1}H-NMR (101 MHz, $CDCl_3$) δ = 7.37 – 7.19 (m, 4H), 2.73 (d, *J* = 13.1 Hz, 1H), 2.49 (d, *J* = 13.1 Hz, 1H), 2.42 – 2.27 (m, 2H), 2.20 – 2.07 (m, 2H), 2.07 – 1.96 (m, 2H), 1.85 – 1.72 (m, 2H), 1.68 (q, *J* = 7.4 Hz, 1H), 1.49 (q, *J* = 14.5, 7.5 Hz, 1H), 1.39 (s, 9H), 1.38 (s, 9H), 1.25 (s, 3H), 0.82 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR** (400 MHz, $CDCl_3$) δ = 212.0, 172.4, 172.4, 143.3, 140.0, 127.4, 127.0, 126.8, 126.0, 80.5, 80.5, 54.6, 48.5, 42.1, 35.5, 34.8, 34.5, 31.1, 31.0, 29.2, 28.1, 28.1, 8.7; **IR (ATR)** $\tilde{\nu}$ = 2974, 2934, 2879, 1727, 1455, 1422, 1367, 1300, 1283, 1249, 1213, 1150, 892, 848, 762, 591; **HRMS (ESI)** calculated for $[C_{27}H_{41}O_5]^+$: 445.2949, found: 445.2953; **$[\alpha]_D^{20}$** = +4 (*c* = 6 mg/ml, $CHCl_3$); ***R*$_f$** = 0.36 (Pentane/Ethyl Acetate 10:1); HPLC separation (column IB Hexane/Isopropanol 99:1 20min), 92% *ee*.



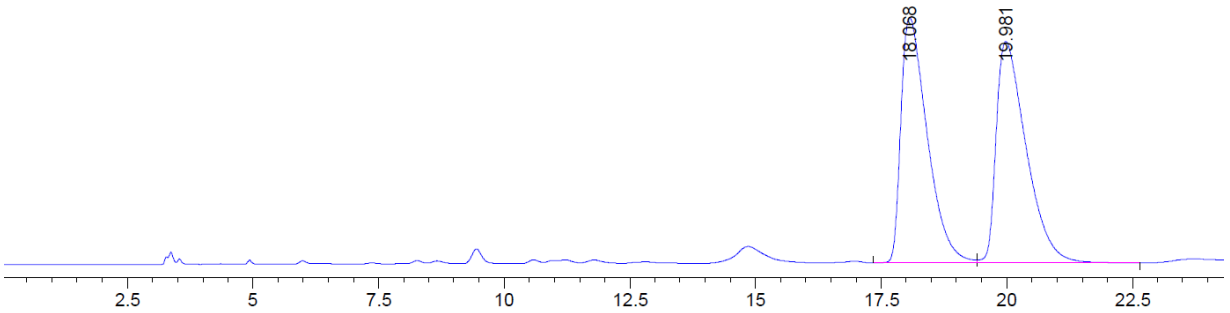
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.536	BV	0.1306	9790.19238	1158.60791	49.1103
2	6.066	VV	0.1480	1.01449e4	1037.95020	50.8897



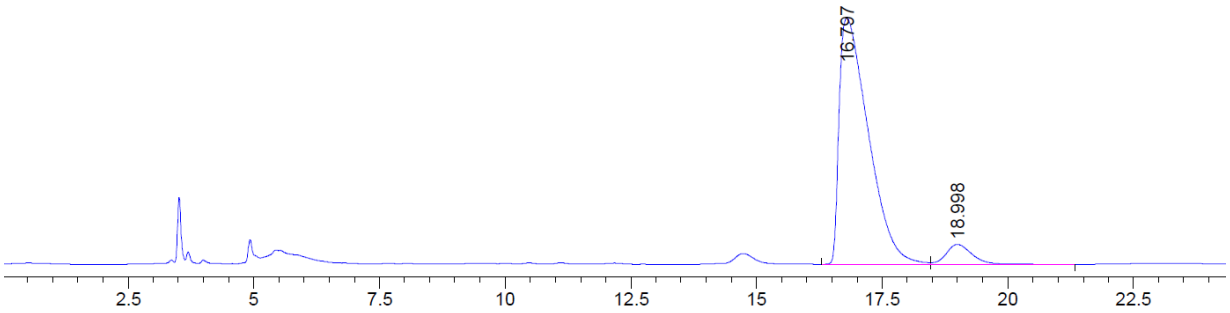
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.059	BV	0.1367	1241.19751	135.67790	96.2289
2	6.878	VB	0.1544	48.64160	4.71193	3.7711



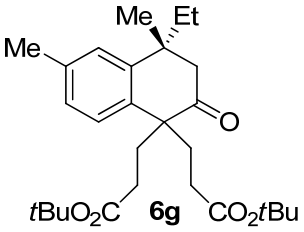
di-tert-butyl 3,3'-(4-((benzyloxy)methyl)-4-methyl-2-oxo-1,2,3,4-tetra hydronaphthalene-1,1-diyl)dipropanoate (6i):
Synthesized according to the general procedure on a 0. 800 mmol scale, 66% (28.5 mg) isolated as a colorless oil.
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.34 – 7.18 (m, 9H), 4.45 (s, 2H), 3.42 (d, *J* = 9.1 Hz, 1H), 3.28 (d, *J* = 9.1 Hz, 1H), 2.85 (d, *J* = 13.7 Hz, 1H), 2.59 (d, *J* = 13.7 Hz, 1H) 2.48 – 2.37 (m, 1H), 2.29 (ddd, *J* = 13.6, 11.4, 4.9 Hz, 1H), 2.22 – 1.95 (m, 4H), 1.84 (ddd, *J* = 15.6, 11.3, 4.4 Hz, 1H), 1.80 – 1.68 (m, 1H), 1.39 (s, 9H), 1.37 (s, 9H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 211.4, 173.0, 172.7, 141.3, 141.0, 138.4, 128.7, 128.2, 128.0, 127.9, 127.3, 127.2, 126.4, 80.8, 80.5, 78.8, 73.4, 54.8, 48.0, 43.5, 36.6, 33.6, 31.4, 31.4, 28.4, 27.0; **IR (ATR)** $\tilde{\nu}$ = 2976, 2931, 2856, 1725, 1454, 1418, 1392, 1367, 1245, 1213, 1145, 1097, 1053, 930, 847, 830, 751, 735, 698, 600, 506 cm^{-1}; **HRMS (ESI)** calculated for $[C_{33}H_{45}O_6]^+$: 537.3211, found: 537.3199; **$[\alpha]_D^{20}$** = 17 (*c* = 2.5 mg/ml, $CHCl_3$); ***R*$_f$** = 0.4 (Pentane/Ethyl Acetate 5:1); HPLC separation (column ID Hexane/Isopropanol 98:1 20min), 86% *ee*..



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.068	BV	0.5579	1.99082e4	545.33429	49.3424
2	19.981	VB	0.6268	2.04389e4	491.90790	50.6576



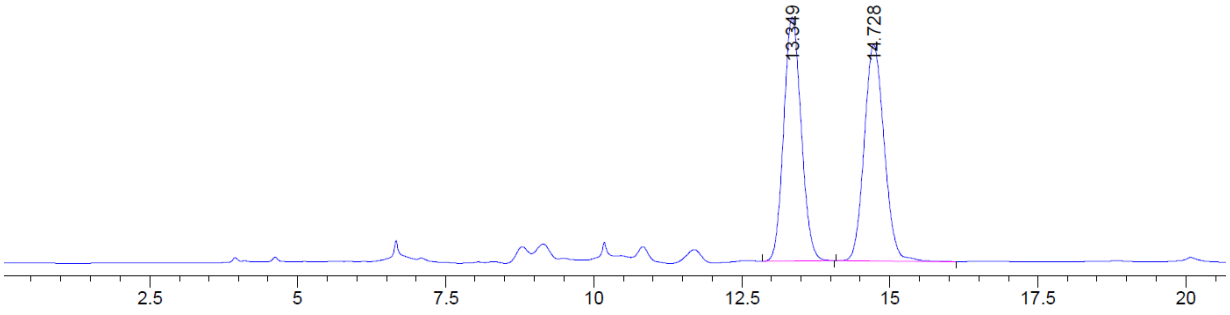
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.797	BV	0.6199	5.65845e4	1404.88757	93.2778
2	18.998	VB	0.5422	4077.83081	113.75439	6.7222



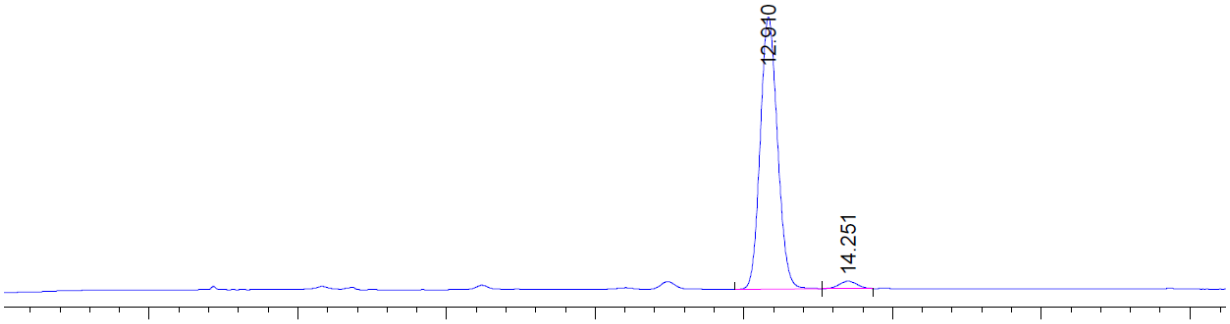
di-tert-butyl 3,3'-(4-ethyl-4,6-dimethyl-2-oxo-1,2,3,4-tetrahydro naphthalene-1,1-diyl)dipropanoate (6g):

Synthesized according to the general procedure on a 0.100 mmol scale, 74% (33.8 mg) isolated as a colorless oil.

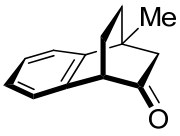
^{1}H-NMR (101 MHz, $CDCl_3$) δ = 7.16 (d, *J* = 8.6 Hz, 1H), 7.09 (m, 2H), 2.70 (d, *J* = 13.1 Hz, 1H), 2.48 (d, *J* = 13.1 Hz, 1H), 2.41 – 2.27 (m, 6H), 2.18 – 2.06 (m, 2H), 1.98 (ddd, *J* = 13.8, 11.6, 4.2 Hz, 2H), 1.86 – 1.74 (m, 2H), 1.67 (dt, *J* = 14.8, 7.4 Hz, 1H), 1.53 – 1.41 (m, 3H), 1.39 (s, 9H), 1.38 (s, 9H), 0.83 (t, *J* = 7.3 Hz, 3H); **^{13}C-NMR** (400 MHz, $CDCl_3$) δ = 212.6, 172.8, 172.8, 143.6, 137.3, 136.6, 128.7, 127.2, 126.8, 80.7, 54.7, 48.9, 42.4, 35.8, 35.3, 34.8, 31.5, 31.4, 29.5, 28.4, 28.4, 21.6, 9.1; **IR (ATR)** $\tilde{\nu}$ =; **HRMS (ESI)** calculated for $[C_{27}H_{41}O_5]^+$: 445.2949, found: 445.2953; **$[\alpha]_D^{20}$** = +1.7 (*c* = 15 mg/ml, $CHCl_3$); R_f = (Pentane/Ethyl Acetate 10:1); HPLC separation (column IB Hexane/Isopropanol 99:1 20min), 94% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.349	BB	0.3199	3517.76831	171.10526	49.7154
2	14.728	BB	0.3634	3558.04028	151.81424	50.2846

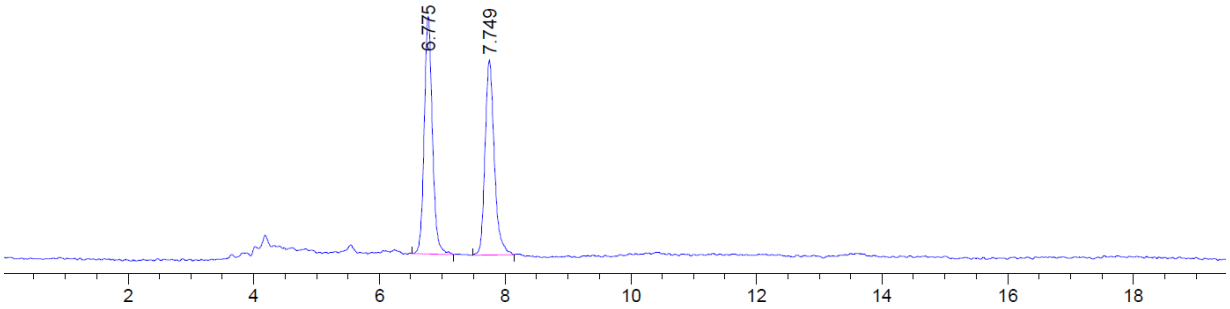


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.910	BB	0.3121	5558.96387	277.06329	97.3093
2	14.251	BB	0.3229	153.71170	7.44563	2.6907

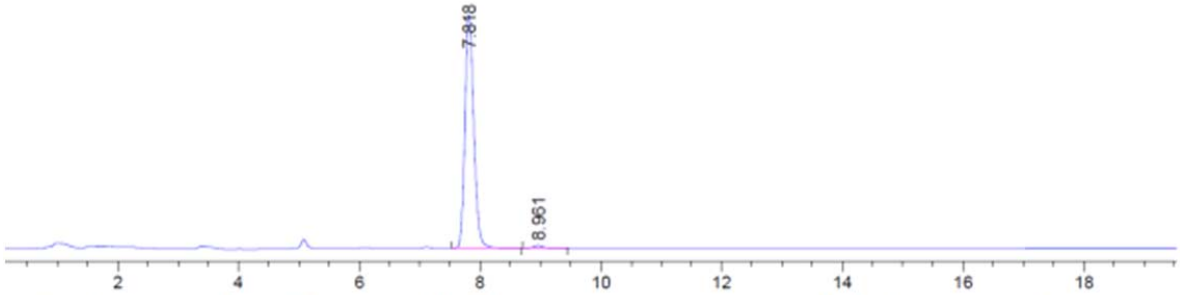


11k

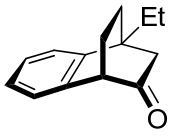
4-methyl-3,4-dihydro-1,4-ethanonaphthalen-2(1H)-one (11k): Synthesized according to the general procedure on a 0.100 mmol scale, 51% (9.5 mg) isolated as a colorless oil. **^{1}H-NMR** (400 MHz, Chloroform-d) δ = 7.34 – 7.27 (m, 2H), 7.22 (m, 2H), 3.61 (t, *J* = 2.8 Hz, 1H), 2.24 (d, *J* = 18.5 Hz, 1H), 2.19 – 2.08 (m, 1H), 2.02 (dd, *J* = 18.5, 3.3 Hz, 1H), 1.86 – 1.70 (m, 2H), 1.51 – 1.42 (m, 1H), 1.53(s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 212.2, 145.5, 137.0, 127.6, 127.2, 125.6, 121.5, 53.4, 48.6, 38.7, 32.9, 25.0, 22.2; **IR (ATR)** $\tilde{\nu}$ = 2926, 2927, 2871, 1734, 1481, 1455, 1402, 1379, 1184, 1090, 755, 489 cm^{-1}; **HRMS (ESI)** calculated for $[C_{13}H_{15}O]^+$: 187.1117, found: 187.1119; **$[\alpha]_D^{20}$** = -208.7 (*c* = 2.5 mg/ml, $CHCl_3$); ***R*$_f$** = 0.43 (Pentane/Ethyl Acetate 10:1); HPLC separation (column OZH Hexane/Isopropanol 98:2 20min), 97% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.775	BB	0.1357	29.85264	3.35709	51.3468
2	7.750	BB	0.1566	28.28655	2.73695	48.6532

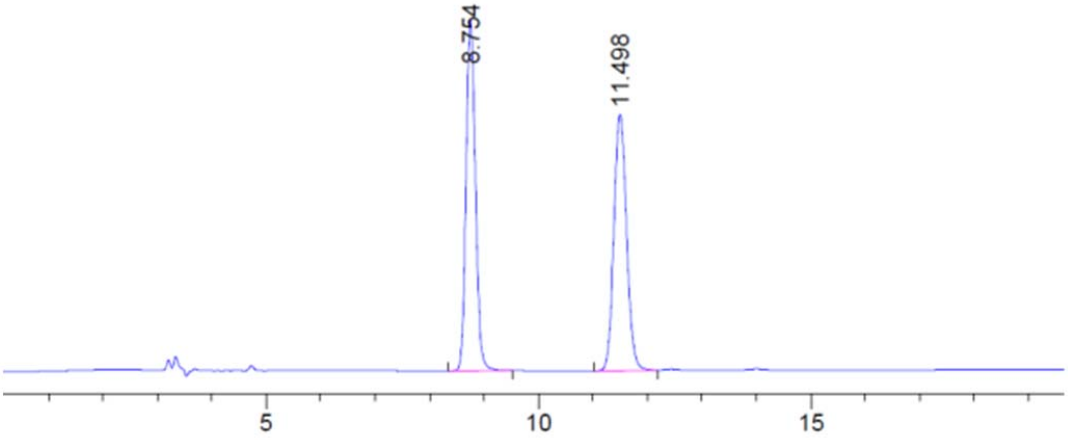


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.818	BB	0.1580	1.15784e4	1145.02502	98.6024
2	8.961	BB	0.1835	164.11662	13.92996	1.3976

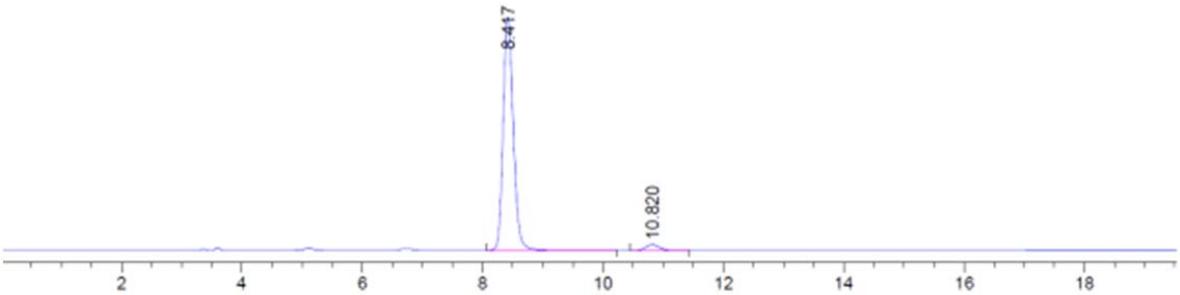


11l

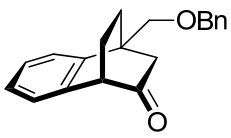
4-ethyl-3,4-dihydro-1,4-ethanonaphthalen-2(1H)-one (11l):
Synthesized according to the general procedure on a 0.100 mmol scale, 74% (11.1 mg) isolated as a colorless oil.
^{1}H-NMR (400 MHz, Chloroform-d) δ = 7.31 – 7.28 (m, 2H), 7.26 – 7.19 (m, 2H), 3.60 (t, *J* = 2.8 Hz, 1H), 2.27 (d, *J* = 18.5 Hz, 1H), 2.12 (dddd, *J* = 13.1, 10.6, 4.6, 2.4 Hz, 1H), 2.07 – 1.91 (m, 3H), 1.86 (ddd, *J* = 12.5, 10.5, 4.6 Hz, 1H), 1.81 – 1.71 (m, 1H), 1.38 (dddd, *J* = 12.4, 11.4, 4.6, 3.3 Hz, 1H), 1.11 (t, *J* = 7.5 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 212.4, 145.1, 137.5, 127.5, 127.0, 125.8, 122.0, 53.4, 45.4, 41.8, 29.6, 27.8, 24.7, 9.1; **IR (ATR)** $\tilde{\nu}$ = 2963, 2939, 2869, 1732, 1480, 1459, 1181, 755, 500; **HRMS (ESI)** calculated for $[C_{14}H_{17}O]^+$: 201.1274, found: 201.1273; **$[\alpha]_D^{20}$** = -338.7 (*c* = 2.5 mg/ml, $CHCl_3$); ***R*$_f$** = 0.46 (Pentane/Ethyl Acetate 10:1); HPLC separation (column OZH Hexane/Isopropanol 98:2 20min), 94% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.754	BB	0.1843	3487.48926	294.24561	50.0396
2	11.498	BB	0.2525	3481.96606	215.53912	49.9604



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.417	VB	0.1907	2.01702e4	1672.11877	97.0812
2	10.821	BB	0.2306	606.43213	40.98882	2.9188

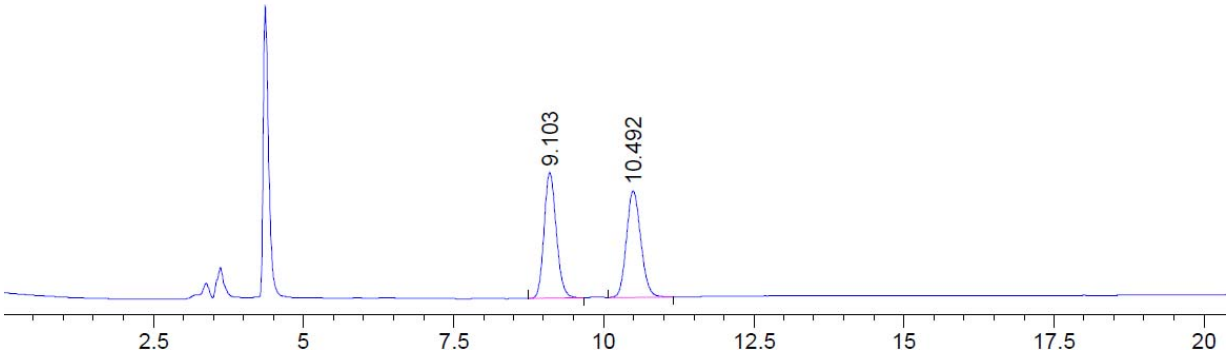


11m

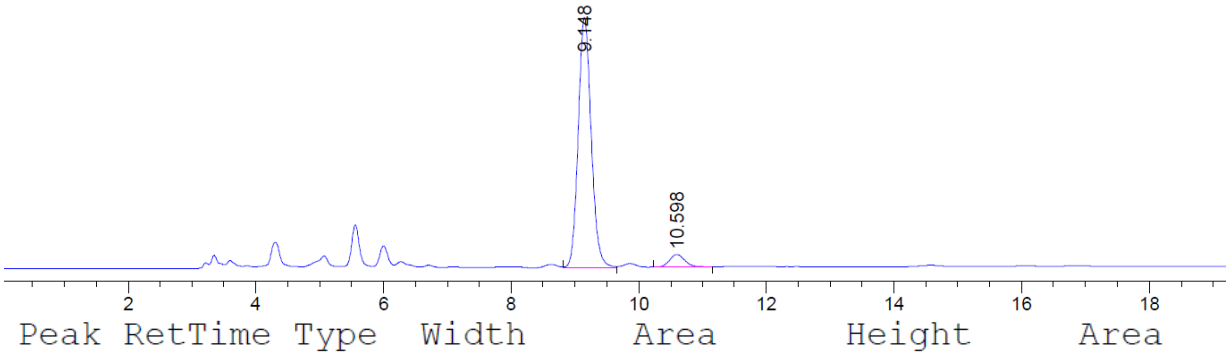
4-((benzyloxy)methyl)-3,4-dihydro-1,4-ethanonaphthalen-2(1H)-one (11m):

Synthesized according to the general procedure on a 0.060 mmol scale, 51% (9.0 mg) isolated as a colorless oil.

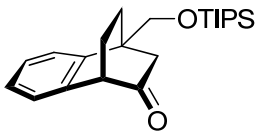
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.21 (m, 7H), 7.18 – 7.10 (m, 2H), 4.61 (s, 2H), 3.86 (d, *J* = 9.2 Hz, 1H), 3.78 (d, *J* = 9.2 Hz, 1H), 3.54 (t, *J* = 2.9 Hz, 1H), 2.28 (d, *J* = 18.6 Hz, 1H), 2.17 – 2.00 (m, 2H), 1.93 – 1.77 (m, 1H), 1.70 (m, 1H), 1.57 – 1.54 (m, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 211.5, 143.0, 138.3, 136.9, 128.6, 127.9, 127.7, 127.4, 127.1, 125.6, 122.1, 73.7, 73.2, 53.2, 44.2, 43.0, 28.0, 24.1.; **IR (ATR)** $\tilde{\nu}$ = 3064, 3029, 2955, 2925, 2855, 1732, 1456, 1404, 1364, 1287, 1261, 1233, 1214, 1180, 1094, 754, 699, 502 cm^{-1}; **HRMS (ESI)** calculated for $[C_{20}H_{21}O_2]^+$: 293.1536, found: 293.1532; **$[\alpha]_D^{20}$** = -14 (*c* = 2 mg/mL, $CHCl_3$); ***R*$_f$** = 0.17 (Pentane/Ethyl Acetate 6.1); HPLC separation (column OZH Hexane/Isopropanol 95:5 20min), 89% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.103	BV	0.2199	6658.54883	468.29340	50.3006
2	10.492	VB	0.2580	6578.96143	395.64740	49.6994

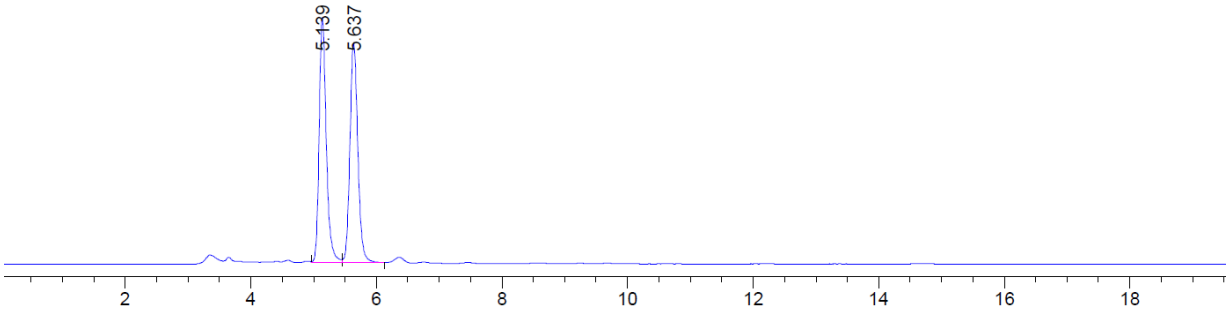


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.148	VV	0.2187	2530.64746	179.28632	94.4807
2	10.598	BB	0.2537	147.83240	8.99894	5.5193

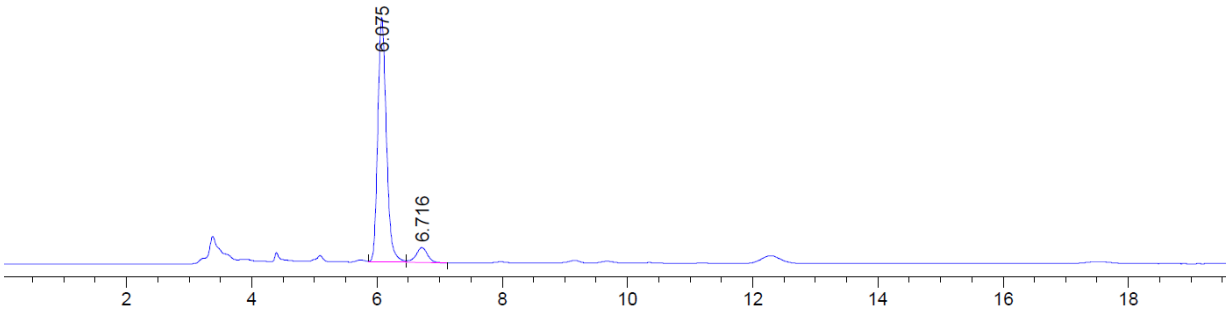


11n

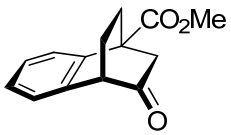
4-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-1,4-ethanonaphthalen-2(1H)-one (11n):
Synthesized according to the general procedure on a 0.060 mmol scale, 52% (11.2 mg) isolated as a colorless oil.
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.34 – 7.28 (m, 2H), 7.24 – 7.18 (m, 2H), 4.23 (d, *J* = 9.9 Hz, 1H), 4.13 (d, *J* = 9.9 Hz, 1H), 3.61 (t, *J* = 2.8 Hz, 1H), 2.39 (d, *J* = 18.6 Hz, 1H), 2.20 – 2.07 (m, 2H), 1.96 (ddd, *J* = 12.5, 10.6, 4.5 Hz, 1H), 1.78 (m, 1H), 1.51 – 1.41 (m, 1H), 1.23 – 1.13 (m, 3H), 1.11 (m, 18H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 212.0, 143.2, 137.2, 127.2, 126.9, 125.6, 122.0, 66.8, 53.3, 44.2, 43.9, 27.6, 24.1, 18.3, 12.1; **IR (ATR)** $\tilde{\nu}$ = 2943, 2866, 1734, 1717, 1541, 1507, 1457, 1405, 1109, 1093, 1067, 882, 800, 754, 684, 502; **HRMS (ESI)** calculated for $[C_{22}H_{35}O_2Si]^+$: 359.2401, found: 359.2397; **$[\alpha]_D^{20}$** = -30 (*c* = 3 mg/ml, $CHCl_3$); ***R*$_f$** = 0.4 (Pentane/Ethyl Acetate 15:1); HPLC separation (column OZH Hexane/Isopropanol 99:1 20 min), 93% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.139	VV	0.1227	2628.89624	331.02094	50.3895
2	5.637	VB	0.1360	2588.25610	295.89758	49.6105

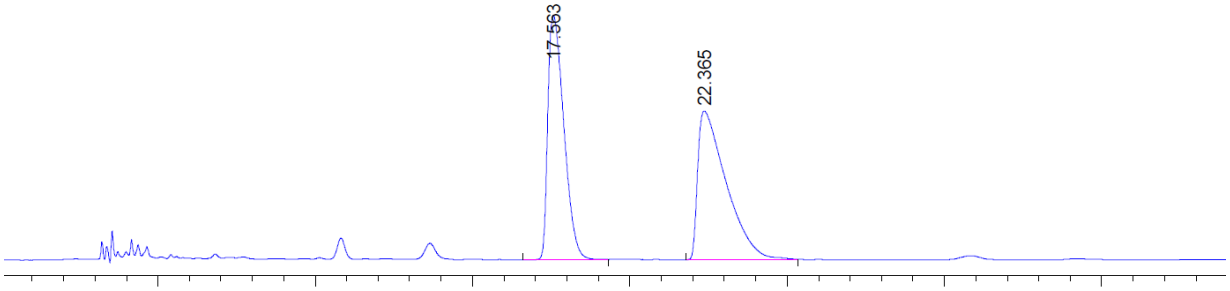


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.075	VV	0.1470	4773.97070	501.58017	92.3242
2	6.716	VB	0.1965	396.90613	30.75860	7.6758

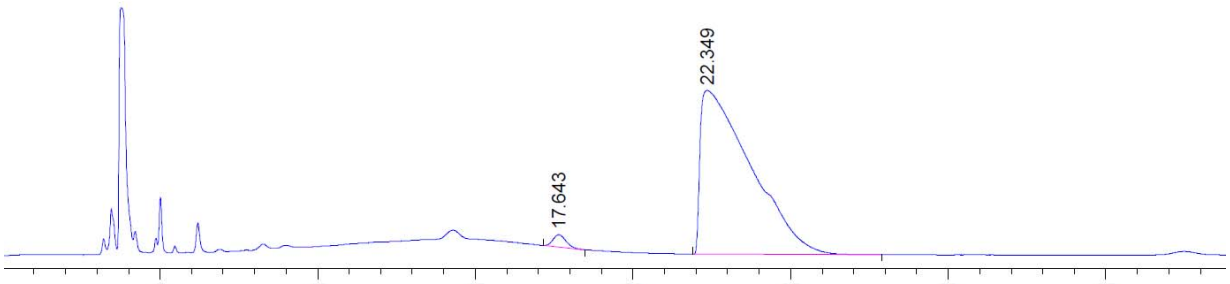


11o

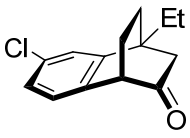
methyl 3-oxo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene-1-carboxylate (11o):
Synthesized according to the general procedure on a 0.100 mmol scale, 48% (11.1 mg) isolated as a colorless oil.
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.24 – 7.20 (m, 2H), 7.18 – 7.14 (m, 1H), 7.07 – 7.01 (m, 1H), 3.85 (s, 3H), 3.64 – 3.52 (m, 1H), 2.54 (dd, *J* = 18.6, 1.9 Hz, 1H), 2.45 (d, *J* = 18.6 Hz, 1H), 2.12 – 1.97 (m, 3H), 1.81 – 1.71 (m, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 209.2, 173.2, 140.8, 135.8, 127.9, 127.7, 126.0, 122.6, 52.8, 52.5, 50.2, 44.0, 28.4, 23.3; **IR (ATR)** $\tilde{\nu}$ = 2953, 2920, 2878, 1733, 1482, 1458, 1243, 1171, 1074, 755, 502; **HRMS (ESI)** calculated for $[C_{14}H_{15}O_3]^+$: 231.1016, found: 231.13013; **$[\alpha]_D^{20}$** = - 20 (*c* = 2 mg/ml, $CHCl_3$); ***R*$_f$** = 0.45 (Pentane/Ethyl Acetate 4:1); HPLC separation (column OZH Hexane/Isopropanol 90:10 40 min), 96 % *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.563	BB	0.5578	3.69762e4	1042.49194	48.0620
2	22.365	BV	0.8450	3.99583e4	634.29028	51.9380

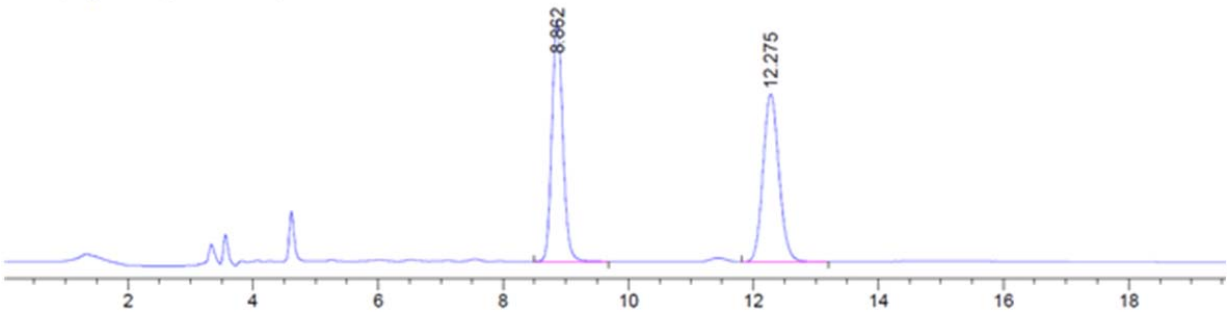


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.643	BB	0.4426	3795.93823	134.77057	1.8445
2	22.349	BB	1.4007	2.02004e5	1809.17224	98.1555

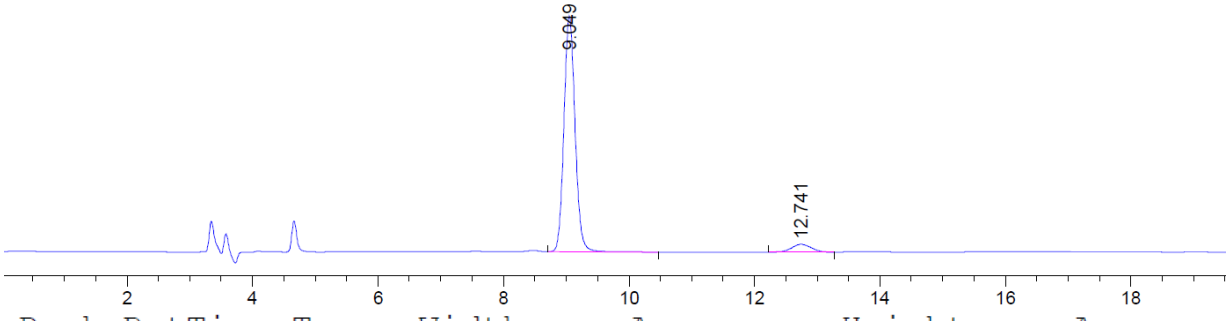


11p

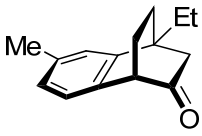
6-chloro-4-ethyl-3,4-dihydro-1,4-ethanonaphthalen-2(1H)-one (11p): Synthesized according to the general procedure on a 0.070 mmol scale, 63% (10.3 mg) isolated as a colorless oil. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.28 – 7.26 (m, 1H), 7.21 (dd, J = 7.9, 2.0 Hz, 1H), 7.13 (d, J = 7.9 Hz, 1H), 3.59 (t, J = 2.9 Hz, 1H), 2.28 (d, J = 18.5 Hz, 1H), 2.12 (dddd, J = 13.1, 10.6, 4.5, 2.4 Hz, 1H), 2.05 - 1.82 (m, 4H), 1.73 (tt, J = 12.8, 3.9 Hz, 1H), 1.44 - 1.30 (m, 1H), 1.25 (s, 3H), 1.11 (t, J = 7.5 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 211.2, 146.8, 135.7, 133.3, 126.9, 126.8, 122.6, 52.6, 44.8, 41.8, 29.1, 27.4, 24.3, 8.8 ; **IR (ATR)** $\tilde{\nu}$ = 2956, 2924, 2855, 1733, 1464, 1411, 1380, 1260, 1217, 1182, 1141, 1085, 970, 882, 821 cm^{-1}; **HRMS (ESI)** calculated for $[C_{14}H_{16}ClO]^+$:235.0884, found: 235.0888; ; **$[\alpha]_D^{20}$** = -103 (*c* = 2.5 mg/ml, $CHCl_3$); ***R*$_f$** = 0.48 (Pentane/Ethyl Acetate 20:1); HPLC separation (column OZH Hexane/Isopropanol 98:1 20 min) 89% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.862	BB	0.1869	8605.34961	712.37347	49.4328
2	12.275	BB	0.2776	8802.82617	494.81198	50.5672

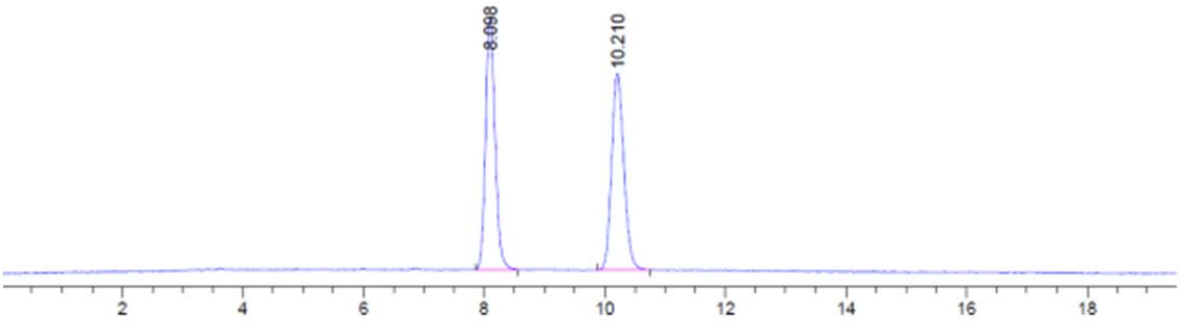


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.049	VB	0.1899	5598.67920	454.06497	94.4522
2	12.741	BB	0.3379	328.84674	15.11247	5.5478

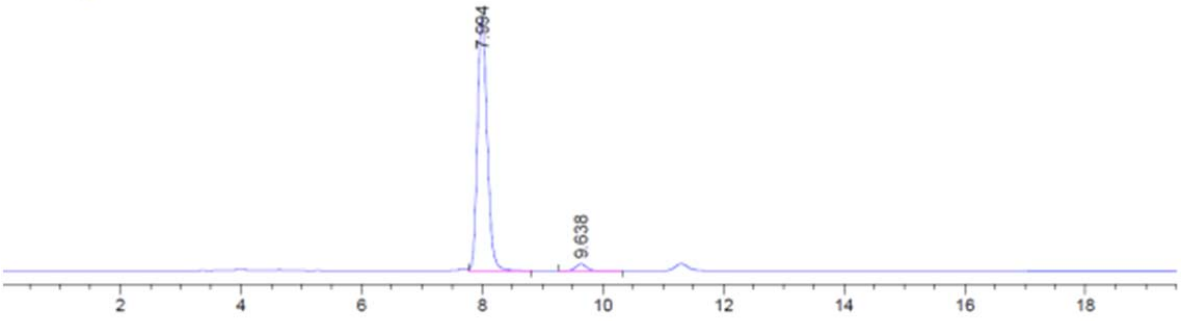


11q

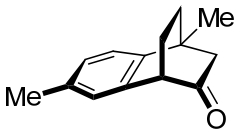
6-methyl-4-ethyl-3,4-dihydro-1,4-ethanonaphthalen-2(1H)-one (11q): Synthesized according to the general procedure on a 0.080 mmol scale, 67% (11.5 mg) isolated as a colorless oil. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.14 - 7.07 (m, 2H), 7.04 (dd, J = 8.0, 1.3 Hz, 1H), 3.56 (t, J = 2.9 Hz, 1H), 2.38 (s, 3H), 2.25 (d, J = 18.4 Hz, 1H), 2.10 (dddd, J = 13.0, 10.5, 4.6, 2.3 Hz, 1H), 2.05 - 1.90 (m, 3H), 1.85 (ddd, J = 12.5, 10.5, 4.6 Hz, 1H), 1.73 (m, 1H), 1.36 (m, 1H), 1.11 (t, J = 7.5 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 212.5, 145.1, 137.2, 134.5, 127.6, 125.6, 122.9, 53.0, 45.5, 41.7, 29.7, 27.8, 24.7, 22.0, 9.1; **IR (ATR)** $\tilde{\nu}$ = 2964, 2940, 2868, 1732, 1487, 1462, 1401, 1382, 1227, 1214, 1185, 829, 813, 4998 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{19}O]^+$: 215.1430, found: 215.1432; ; **$[\alpha]_D^{20}$** = -222 (*c* = 3 mg/ml, $CHCl_3$); ***R*$_f$** = 0.51 (Pentane/Ethyl Acetate 20:1); HPLC separation (column OZH Hexane/Isopropanol 98:1 20 min) 94% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.098	BB	0.1679	270.30295	24.66501	49.9411
2	10.210	BB	0.2183	270.94040	19.24385	50.0589

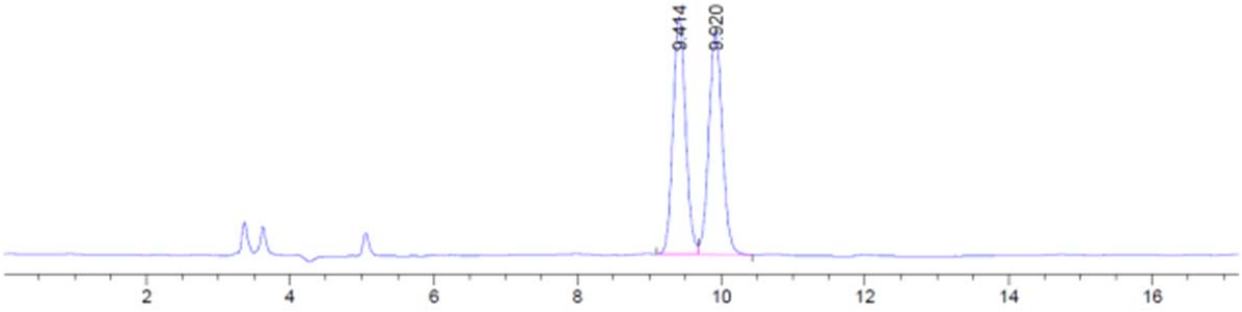


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.994	VB	0.1764	2.26521e4	1996.62061	96.9587
2	9.638	BB	0.2031	710.52313	54.86657	3.0413

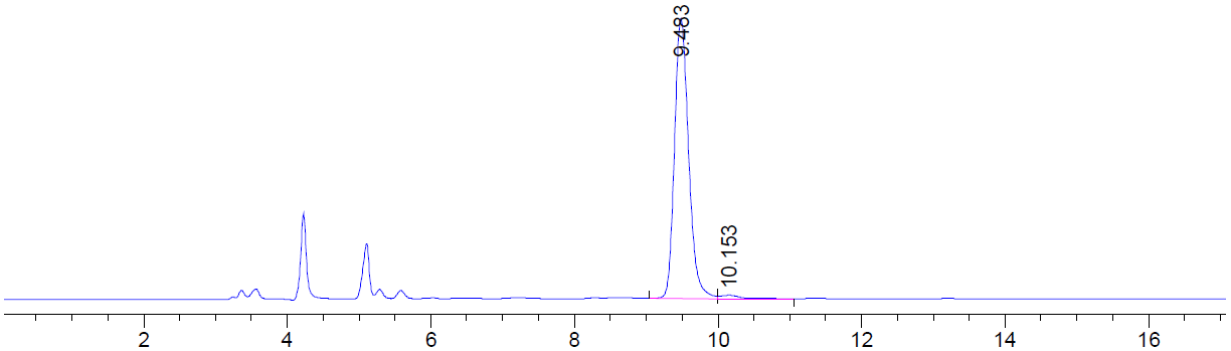


11r

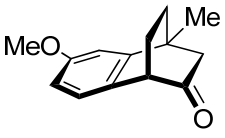
4,7-dimethyl-3,4-dihydro-1,4-ethanonaphthalen-2(1H)-one (11r): Synthesized according to the general procedure on a 0.100 mmol scale, 58% (11.6 mg) isolated as a colorless oil. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.16 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.03 (s, 1H), 3.56 (t, *J* = 2.8 Hz, 1H), 2.34 (s, 3H), 2.22 (d, *J* = 18.4 Hz, 1H), 2.15 – 2.07 (m, 1H), 2.00 (dd, *J* = 18.4, 3.3 Hz, 1H), 1.83 – 1.70 (m, 2H), 1.51 (s, 3H), 1.46 (m, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 212.2, 142.4, 136.7, 136.7, 127.9, 126.2, 121.2, 53.2, 48.6, 38.2, 32.9, 24.8, 22.0, 21.3; **IR (ATR)** $\tilde{\nu}$ = 2954, 2924, 2854, 1734, 1461, 1378, 1261, 1169, 1090, 815, 506, 418 cm^{-1}; **HRMS (ESI)** calculated for $[C_{14}H_{16}O_2]^+$: 201.1274, found: 201.1277; **$[\alpha]_D^{20}$** = -75 (*c* = 5 mg/ml, $CHCl_3$); ***R*$_f$** = 0.34 (Pentane/Ethyl Acetate 10:1); HPLC separation (column OZH Hexane/Isopropanol 99:1 20 min) 97% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.414	BV	0.1903	1196.74036	98.08430	49.7242
2	9.920	VB	0.2025	1210.01465	92.56657	50.2758

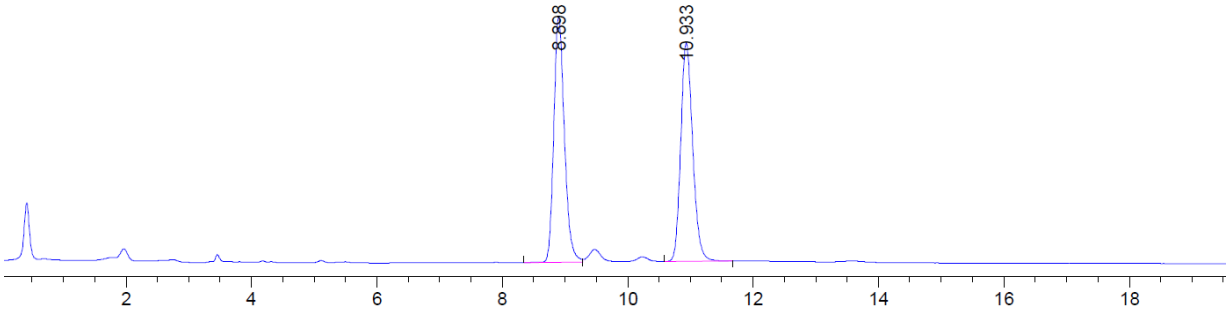


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.483	BV	0.2121	1.73977e4	1267.55713	98.3404
2	10.153	VB	0.2821	293.60269	15.56502	1.6596

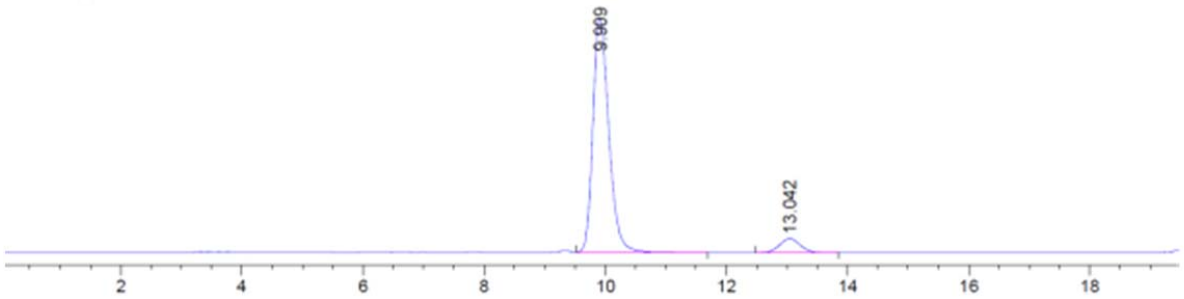


11s

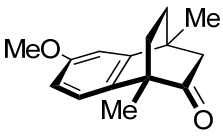
6-methoxy-4-methyl-3,4-dihydro-1,4-ethanonaphthalen-2(1H)-one (11s): Synthesized according to the general procedure on a 0.100 mmol scale, 60% (13.0 mg) isolated as a colorless oil. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.12 (d, *J* = 8.1 Hz, 1H), 6.86 (d, *J* = 2.6 Hz, 1H), 6.76 (dd, *J* = 8.1, 2.6 Hz, 1H), 3.82 (s, 3H), 3.56 (t, *J* = 2.8 Hz, 1H), 2.22 (d, *J* = 18.4 Hz, 1H), 2.16 – 2.05 (m, 1H), 2.05 – 1.97 (m, 1H), 1.83 – 1.67 (m, 2H), 1.50 (s, 3H), 1.48 – 1.40 (m, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 211.8, 159.4, 146.8, 128.9, 126.3, 111.2, 108.6, 55.5, 52.2, 48.4, 38.7, 32.7, 24.8, 22.0; **IR (ATR)** $\tilde{\nu}$ = 2955, 2937, 2870, 1731, 1610, 1584, 1486, 1462, 1294, 1265, 1229, 1040, 810, 496; **HRMS (ESI)** calculated for $[C_{14}H_{16}O_2]^+$: 217.1223, found: 217.1216; **$[\alpha]_D^{20}$** = - 20 (*c* = 2 mg/ml, $CHCl_3$); ***R*$_f$** = 0.35 (Pentane/Ethyl Acetate 10:1); HPLC separation (column OZH Hexane/Isopropanol 98:2 20 min), 86% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.898	BV	0.1809	2682.08936	228.62146	49.9473
2	10.933	BB	0.2043	2687.75415	203.17012	50.0527



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.909	VB	0.2813	5058.56396	276.67792	93.0379
2	13.042	BB	0.3567	378.53394	16.31306	6.9621

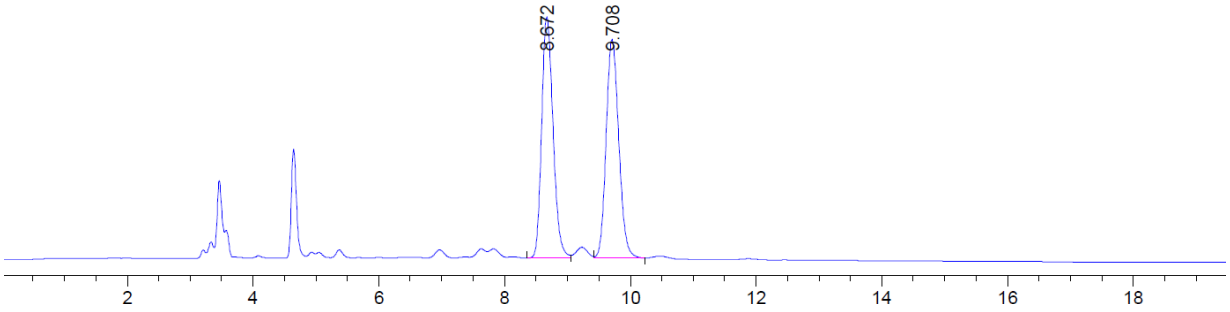


11t

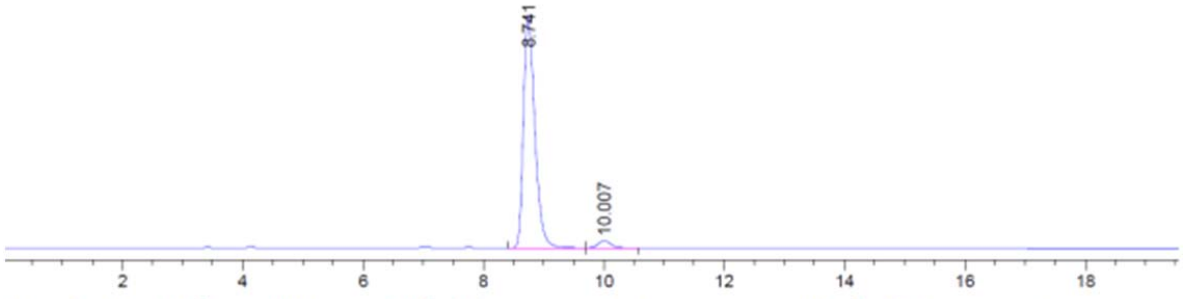
6-methoxy-1,4-dimethyl-3,4-dihydro-1,4-ethanonaphthalen-2(1H)-one (11t):

Synthesized according to the general procedure on a 0.050 mmol scale, 52% (6.1 mg) isolated as a colorless oil.

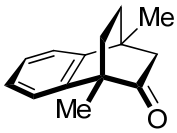
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.13 (d, *J* = 8.3 Hz, 1H), 6.86 (d, *J* = 2.6 Hz, 1H), 6.79 (dd, *J* = 8.3, 2.6 Hz, 1H), 3.83 (s, 3H), 2.26 (d, *J* = 18.5 Hz, 1H), 2.09 – 2.01 (m, 1H), 1.95 – 1.77 (m, 2H), 1.62 – 1.46 (m, 2H), 1.49 (s, 3H), 1.47 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 212.6, 159.1, 147.0, 131.5, 123.9, 110.9, 108.4, 55.5, 49.9, 48.4, 38.2, 33.9, 32.5, 22.2, 15.6; **IR (ATR)** $\tilde{\nu}$ = 2954, 2925, 2856, 1721, 1608, 1580, 1486, 1456, 1378, 1292, 1263, 1164, 1068, 1051, 1032, 877, 808, 501 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{18}O_2]^+$: 231.1380, found: 231.1384; **$[\alpha]_D^{20}$** = -253 (*c* = 5 mg/ml, $CHCl_3$); ***R*$_f$** = 0.45 (Pentane/Ethyl Acetate 5:1); HPLC separation (column OZH Hexane/Isopropanol 98:2 20 min), 93% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.672	BV	0.1950	1.00874e4	800.35242	49.8990
2	9.708	VB	0.2170	1.01283e4	725.02905	50.1010



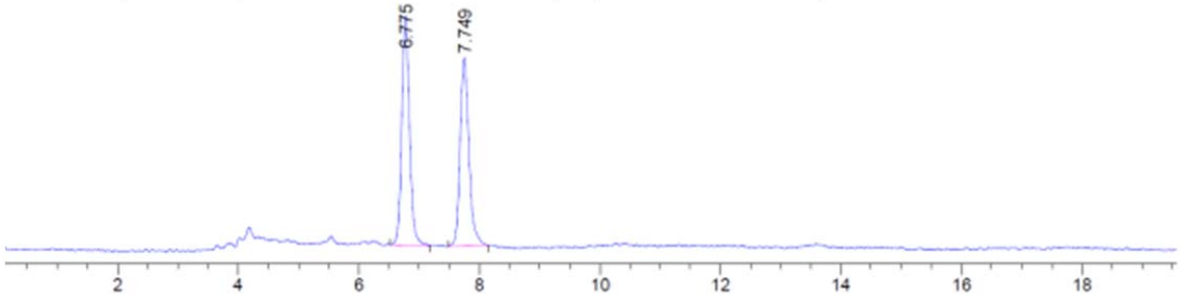
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.741	BV	0.2015	5169.31738	392.81650	96.7211
2	10.007	VB	0.2246	175.24162	11.98436	3.2789



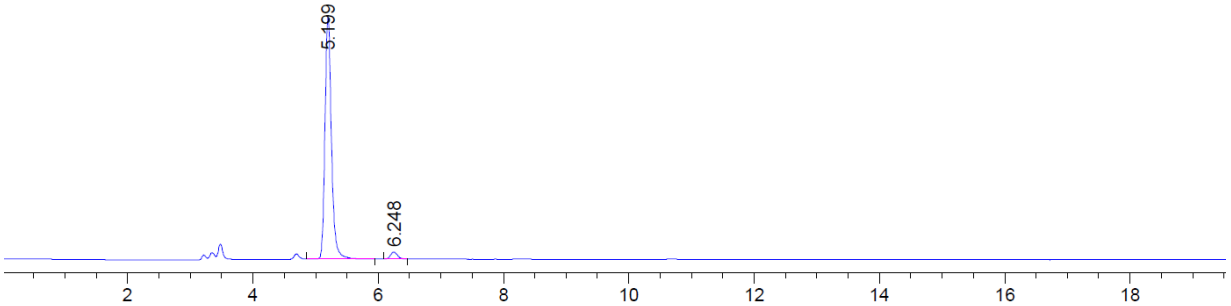
11u

1,4-dimethyl-3,4-dihydro-1,4-ethanonaphthalen-2(1H)-one (11u): Synthesized according to the general procedure on a 0.100 mmol scale, 52% (10.5 mg) isolated as a colorless oil.

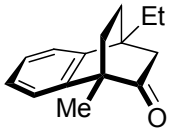
^{1}H-NMR (400 MHz, Chloroform-d) δ = 7.32 – 7.21 (m, 4H), 2.28 (d, *J* = 18.4 Hz, 1H), 2.10 – 2.01 (m, 2H), 1.94 (td, *J* = 11.7, 11.2, 3.4 Hz, 1H), 1.83 (td, *J* = 11.7, 11.2, 3.4 Hz, 1H), 1.60 (td, *J* = 11.9, 3.4 Hz, 1H), 1.53 (s, 3H), 1.50 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 206.1, 143.8, 136.7, 126.9, 126.7, 122.6, 121.0, 48.2, 37.8, 33.7, 32.3, 29.7, 22.1, 15.4 ; **IR (ATR)** $\tilde{\nu}$ = 2923, 2856, 1725, 1461, 1419, 1405, 1381, 1245, 1211, 1139, 1087, 1062, 898, 781, 755, 502 ; **HRMS (ESI)** calculated for $[C_{14}H_{17}O]^+$: 201.1274, found: 201.1271; **$[\alpha]_D^{20}$** = - 37 (*c* = 2.5 mg/ml, $CHCl_3$); ***R*$_f$** = 0.42 (Pentane/Ethyl Acetate 10:1); HPLC separation (column OZH Hexane/Isopropanol 98:2 20 min), 93% *ee*.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.775	BV	0.1343	1169.74475	133.45338	50.4007
2	7.749	VB	0.1576	1151.14490	112.25694	49.5993

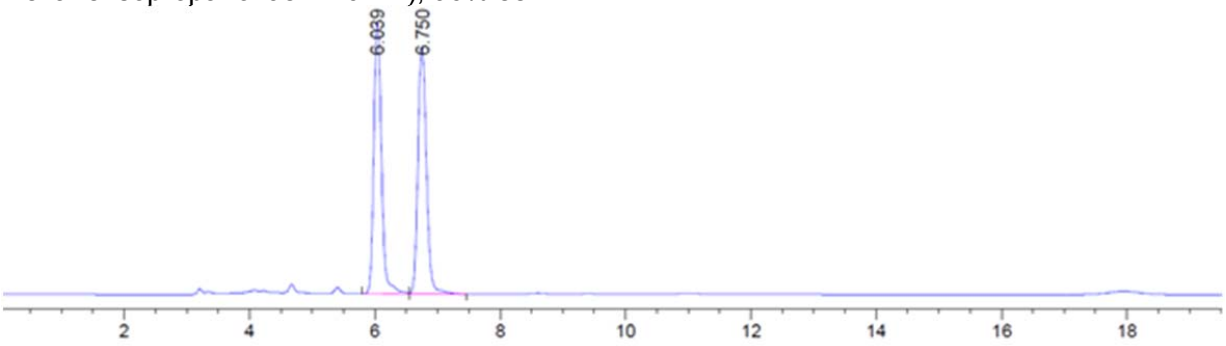


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.199	BB	0.1097	843.23071	117.50318	96.9902
2	6.248	BB	0.1180	26.16673	3.39272	3.0098

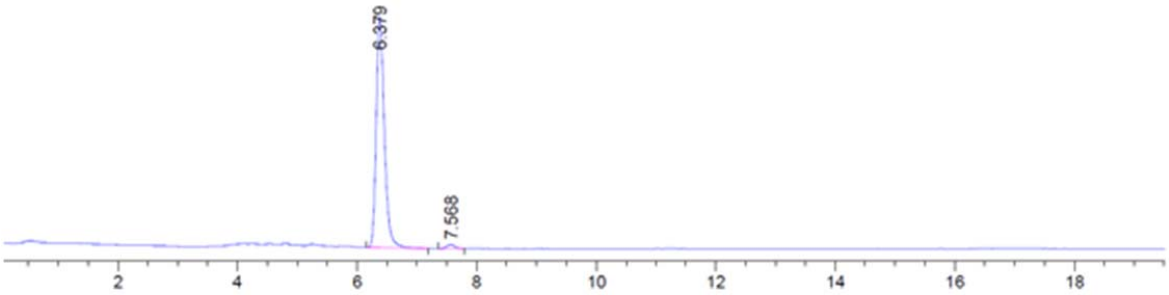


11v

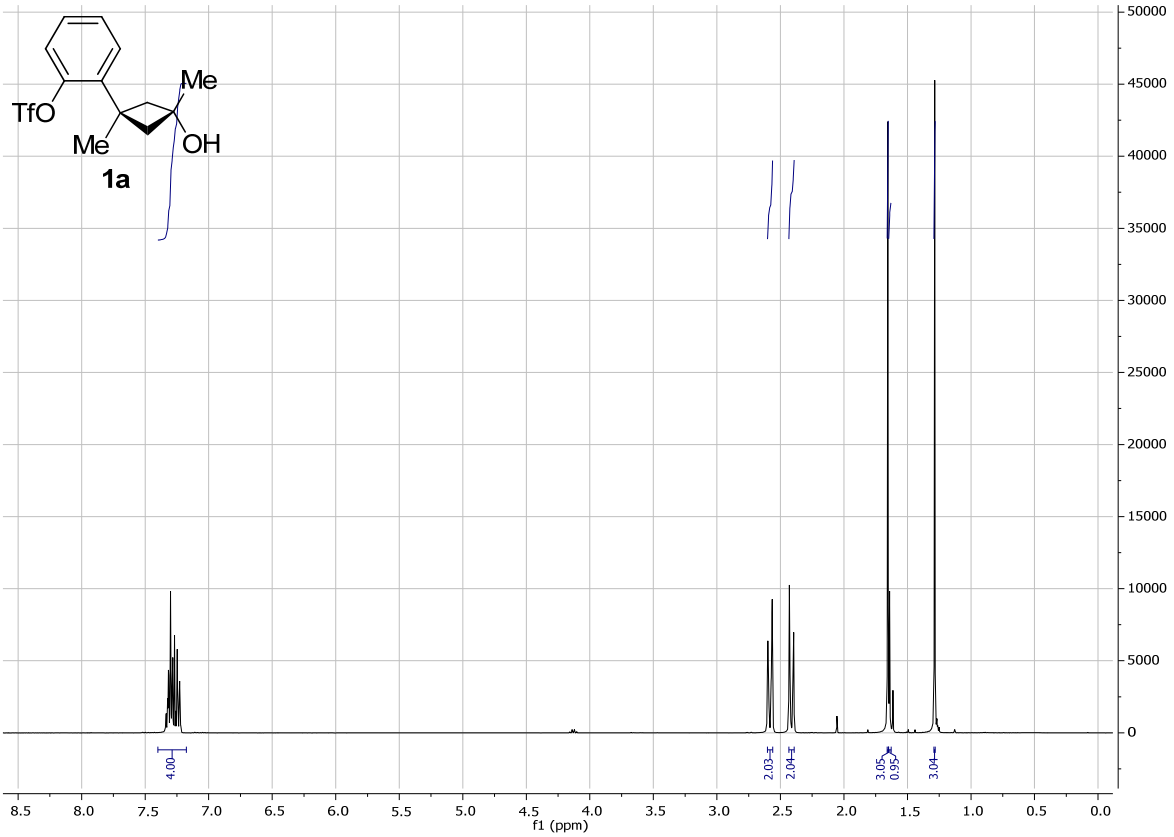
4-ethyl-1-methyl-3,4-dihydro-1,4-ethanonaphthalen-2(1H)-one (11v): Synthesized according to the general procedure on a 0.100 mmol scale, 51% (11.0 mg) isolated as a colorless oil. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.32 – 7.22 (m, 4H), 2.32 (d, *J* = 18.5 Hz, 1H), 2.08 – 1.86 (m, 6H), 1.49 (s, 3H), 1.44 (dt, *J* = 7.1, 3.5 Hz, 1H), 1.11 (t, *J* = 7.5 Hz, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 212.9, 145.2, 139.8, 126.9, 126.7, 122.9, 121.6, 50.6, 45.1, 40.9, 32.2, 30.5, 27.7, 15.5, 8.8; **IR (ATR)** $\tilde{\nu}$ = 2925, 2857, 1724, 1459, 1419, 1402, 1378, 1246, 1213, 1140, 1088, 1064, 898, 779, 754, 499; **HRMS (ESI)** calculated for $[C_{15}H_{19}O]^+$: 215.1430, found: 215.1428; **$[\alpha]_D^{20}$** = -30.5 (*c* = 1.5 mg/ml, $CHCl_3$); ***R*$_f$** = 0.35 (Pentane/Ethyl Acetate 15:1); HPLC separation (column OZH Hexane/Isopropanol 98:2 20min), 96% *ee*.

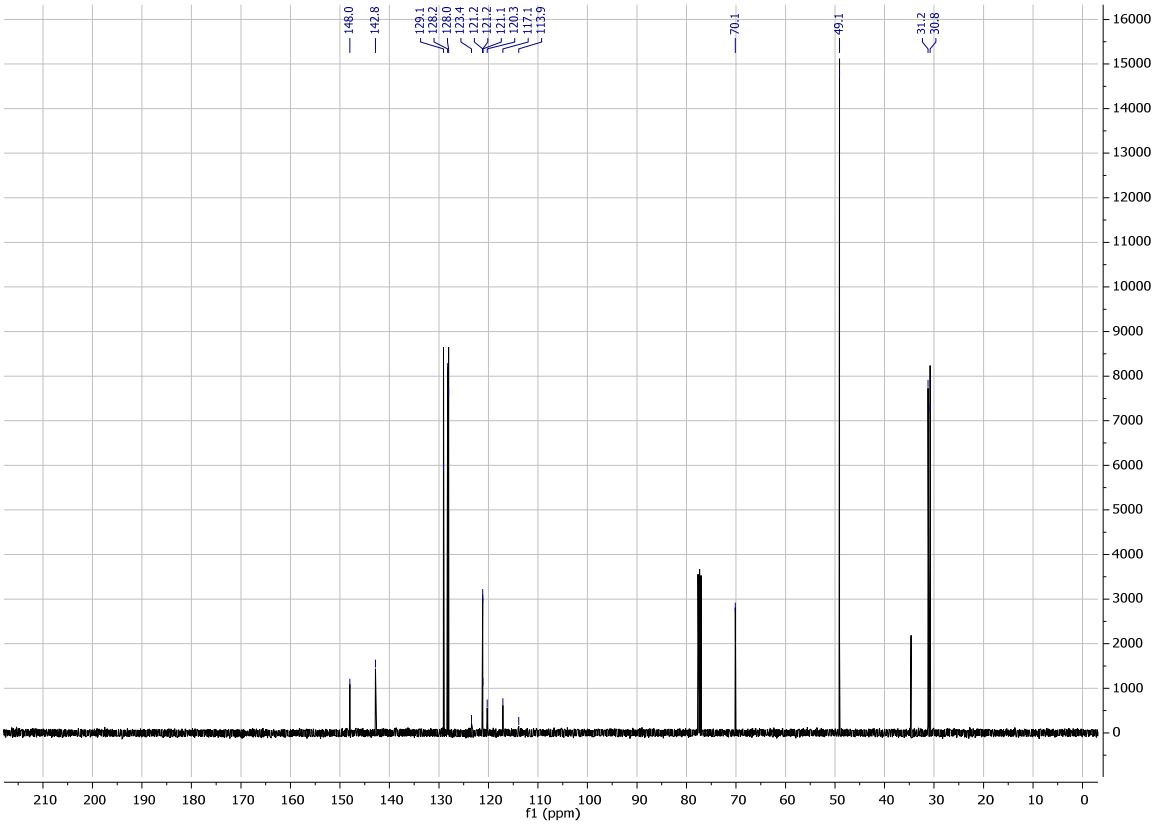


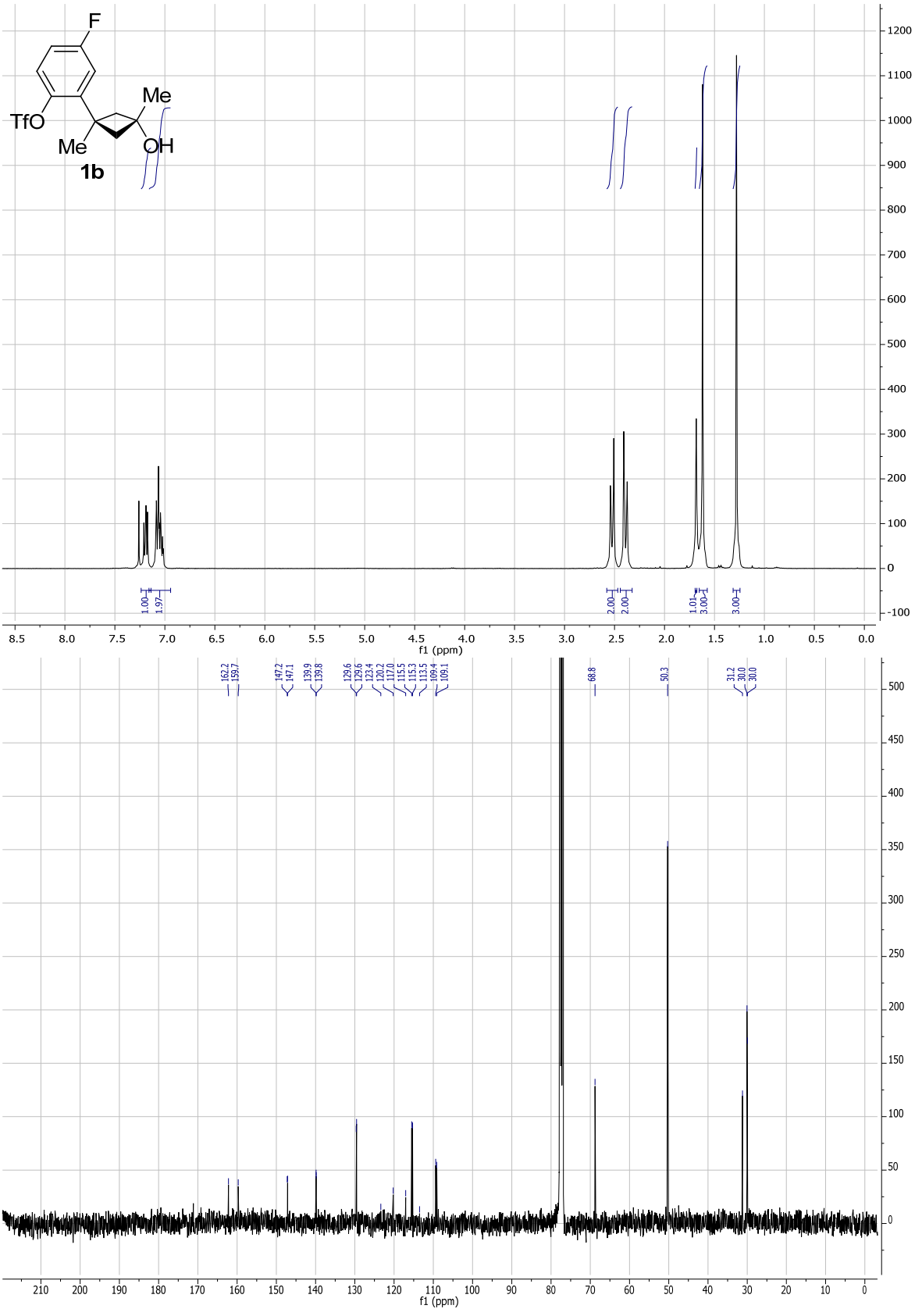
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.039	BV	0.1340	1.41063e4	1646.40063	49.9323
2	6.750	VB	0.1481	1.41446e4	1499.05383	50.0677

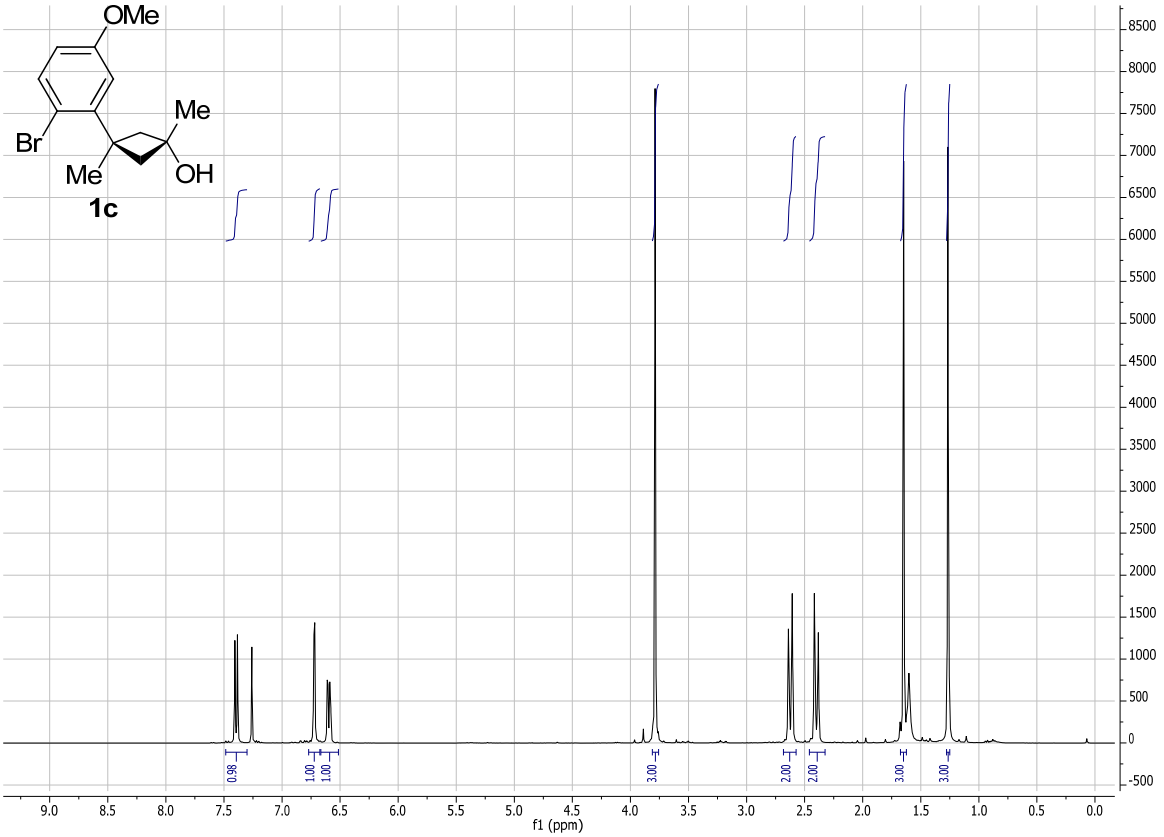


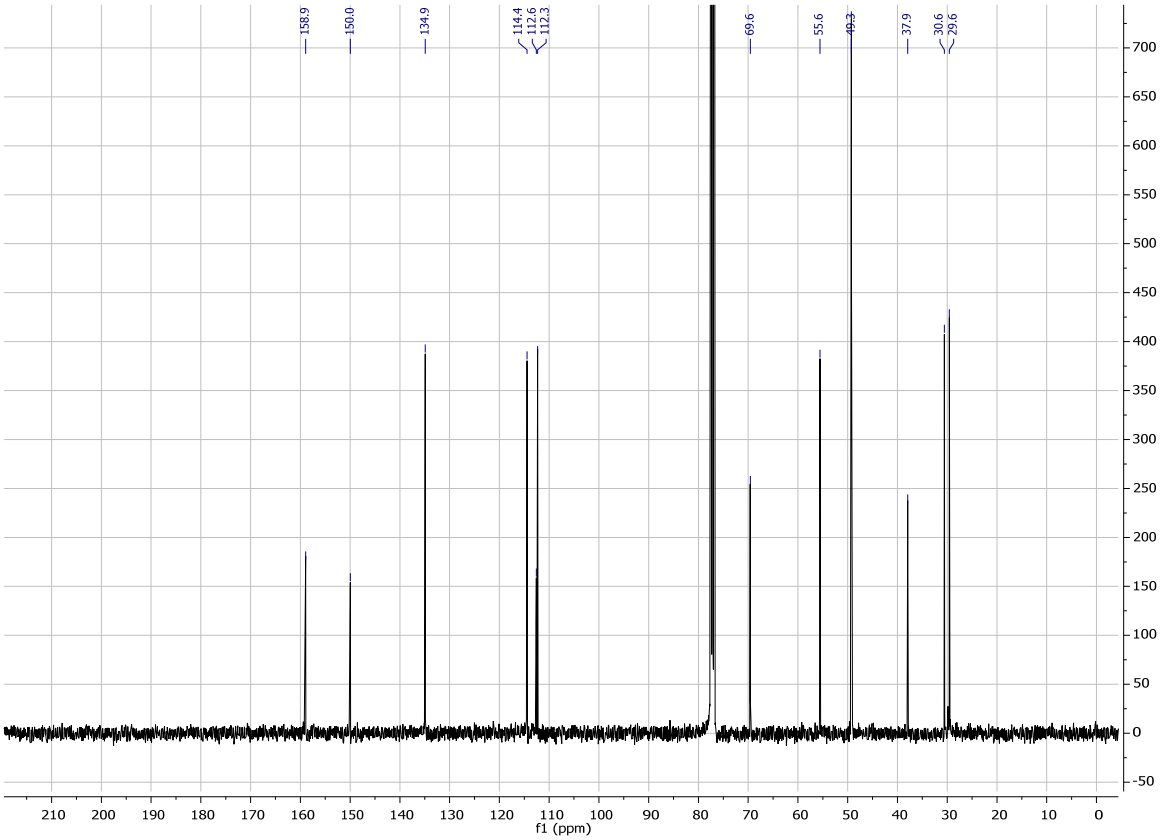
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.379	BB	0.1464	380.00031	40.16356	98.1199
2	7.568	MM	0.1803	7.28131	6.72997e-1	1.8801

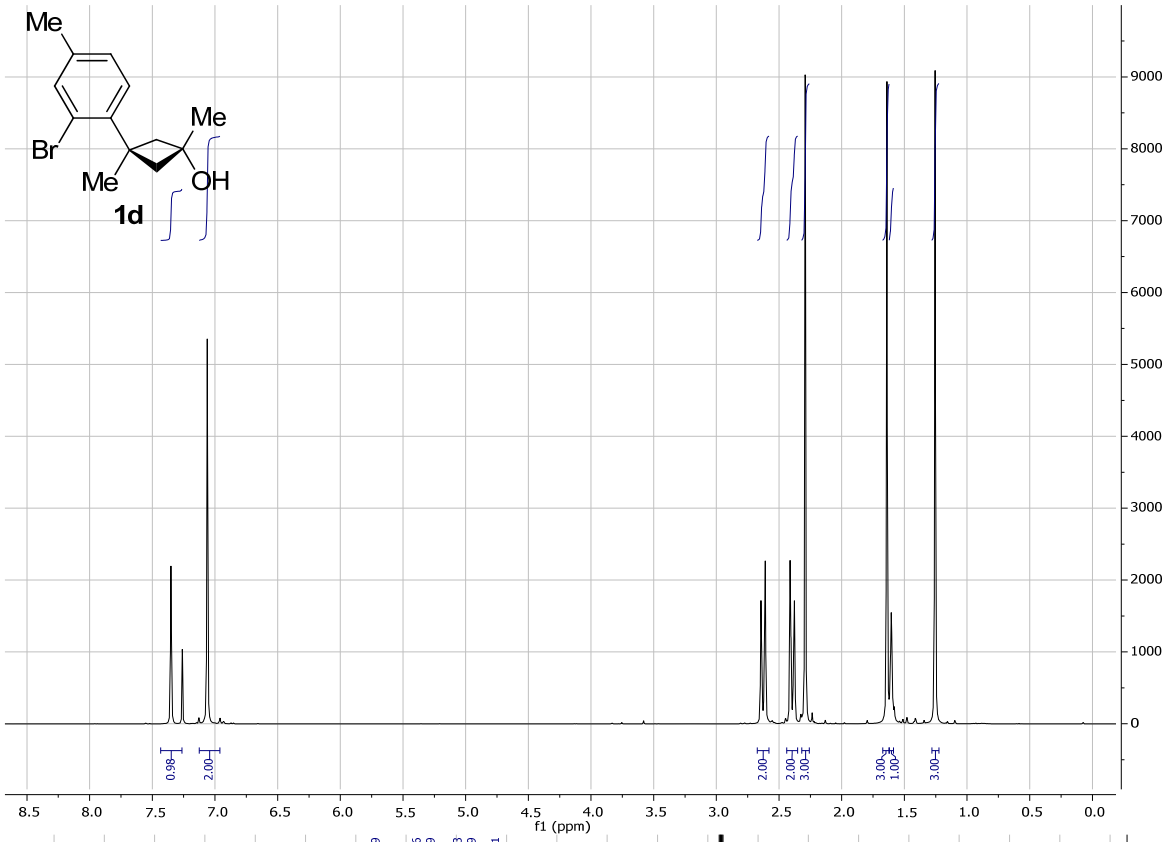

TfO
Me
Me
OH
1a
4.00
2.03
2.04
3.05
0.95
3.04
f1 (ppm)

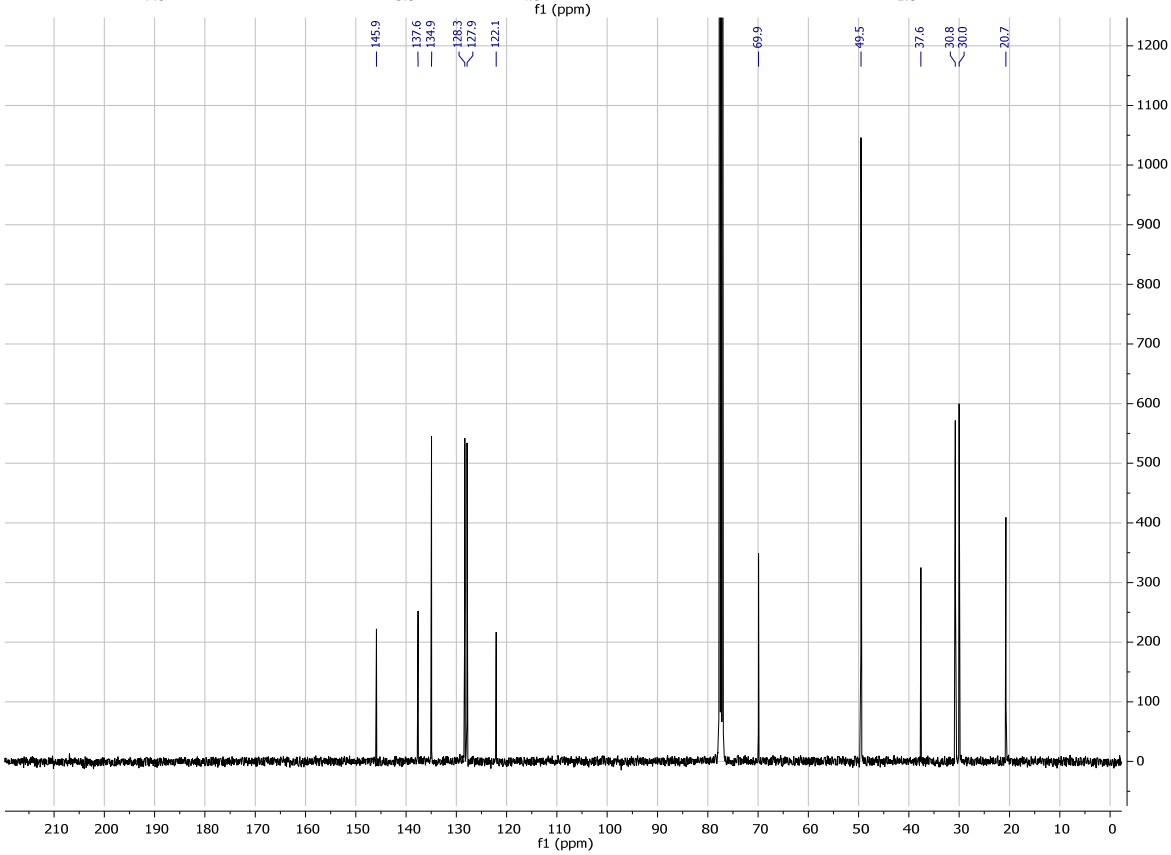

148.0
142.8
129.1
128.2
128.0
123.4
121.2
121.2
121.1
120.3
117.1
113.9
70.1
49.1
31.2
30.8
f1 (ppm)

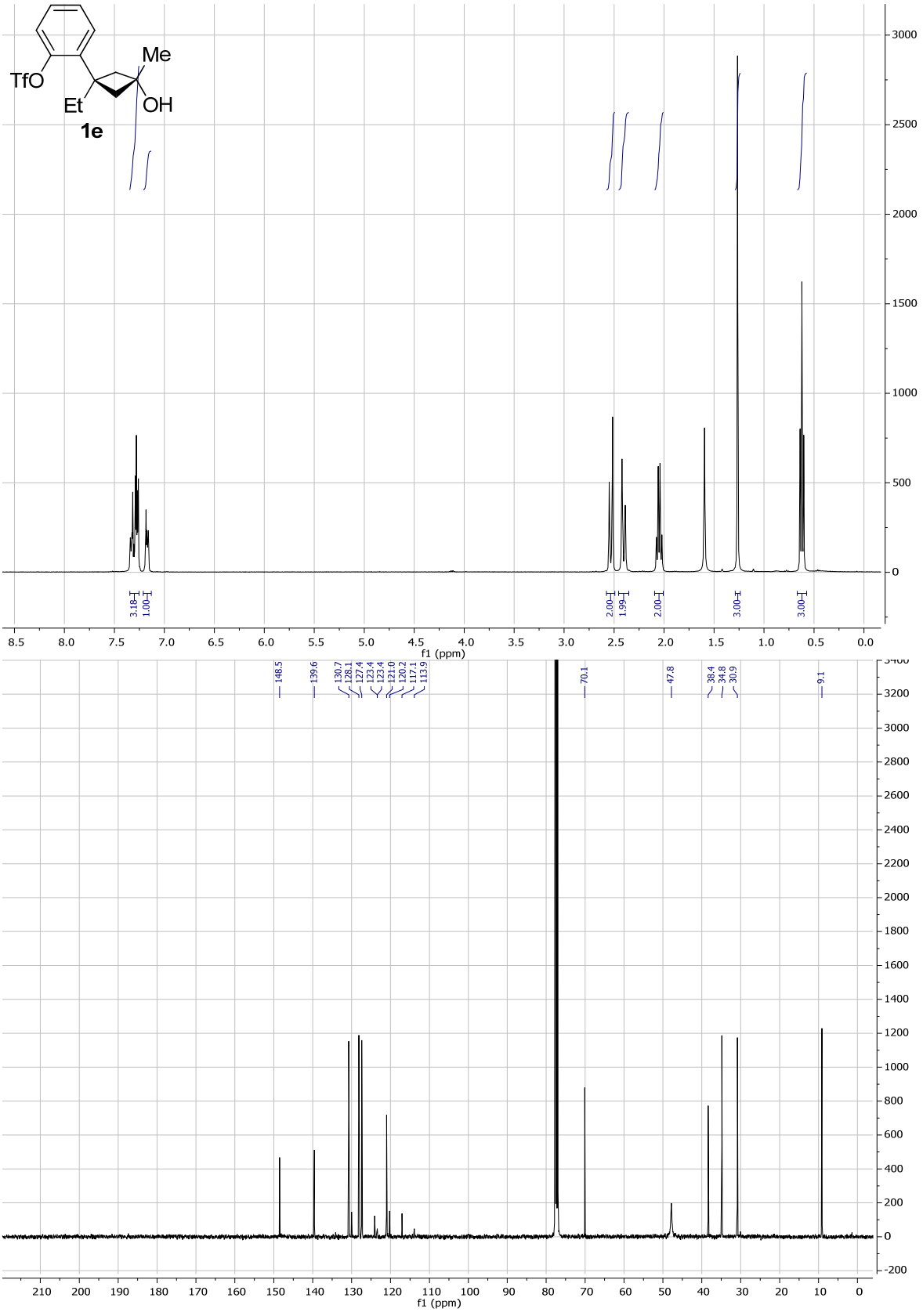

F
TfO
Me
Me
OH
1b
f1 (ppm)
f1 (ppm)

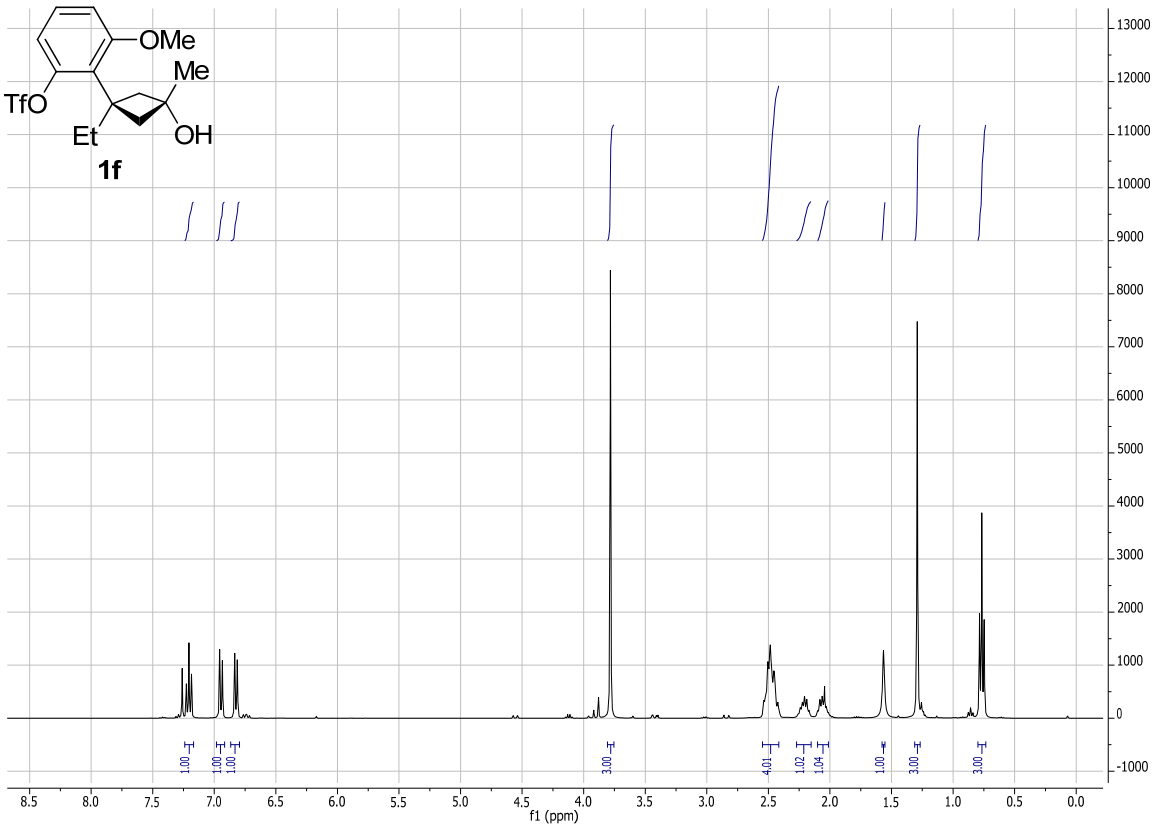

OMe
Br
Me
Me
OH
1c
f1 (ppm)

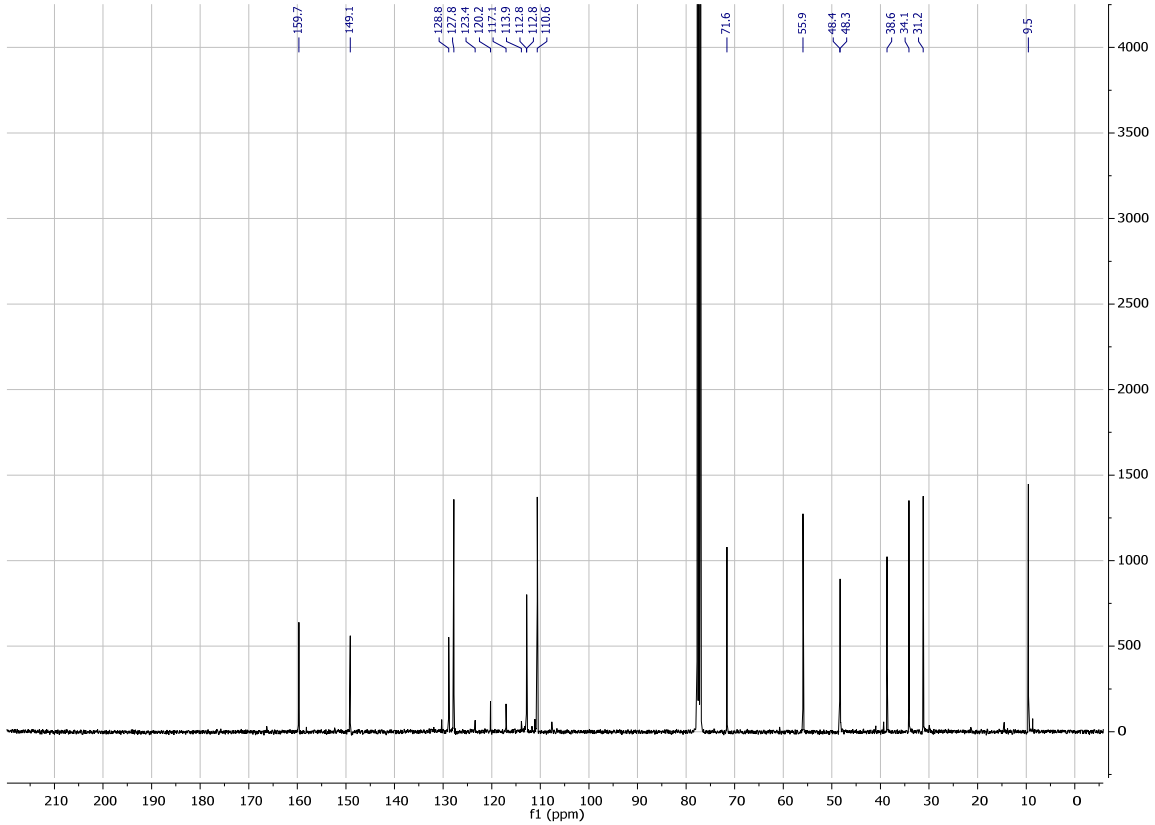

158.9
150.0
134.9
114.4
112.6
112.3
69.6
55.6
49.3
37.9
30.6
29.6
f1 (ppm)

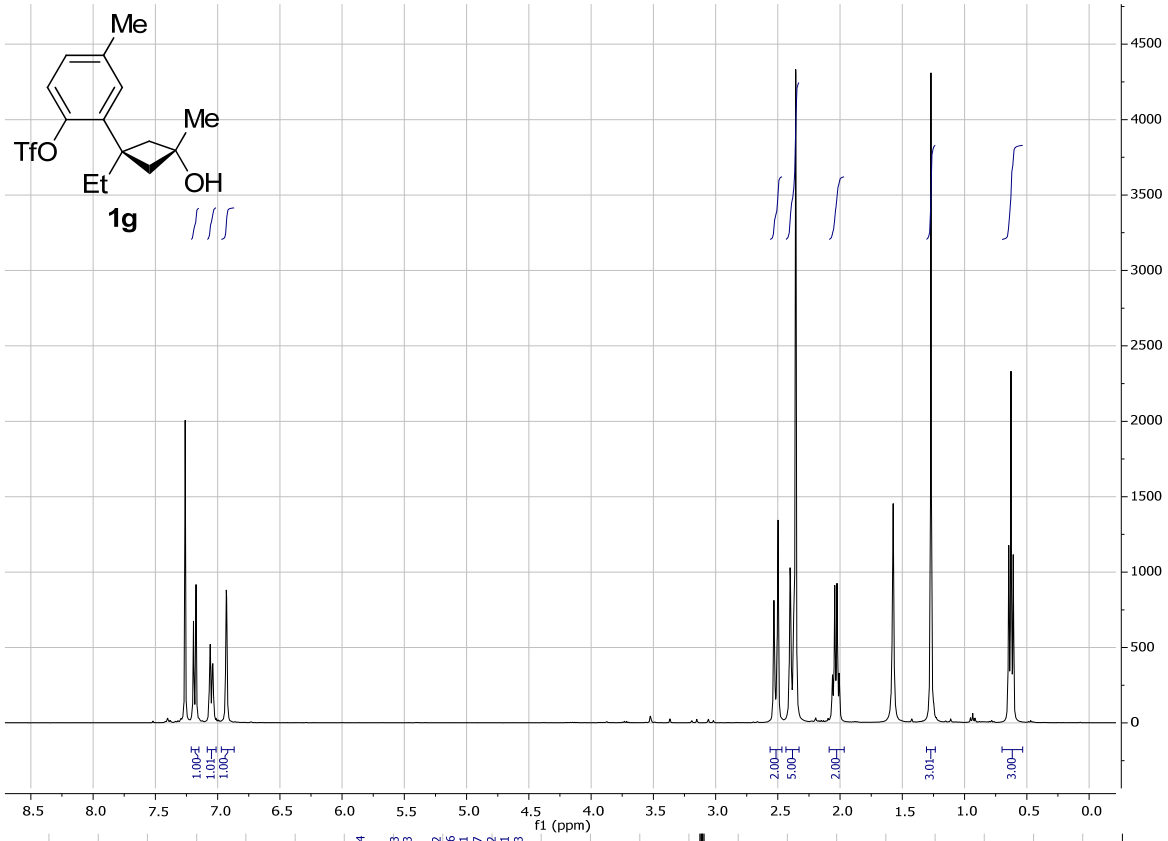

Me
Br
Me
Me
OH
1d
f1 (ppm)

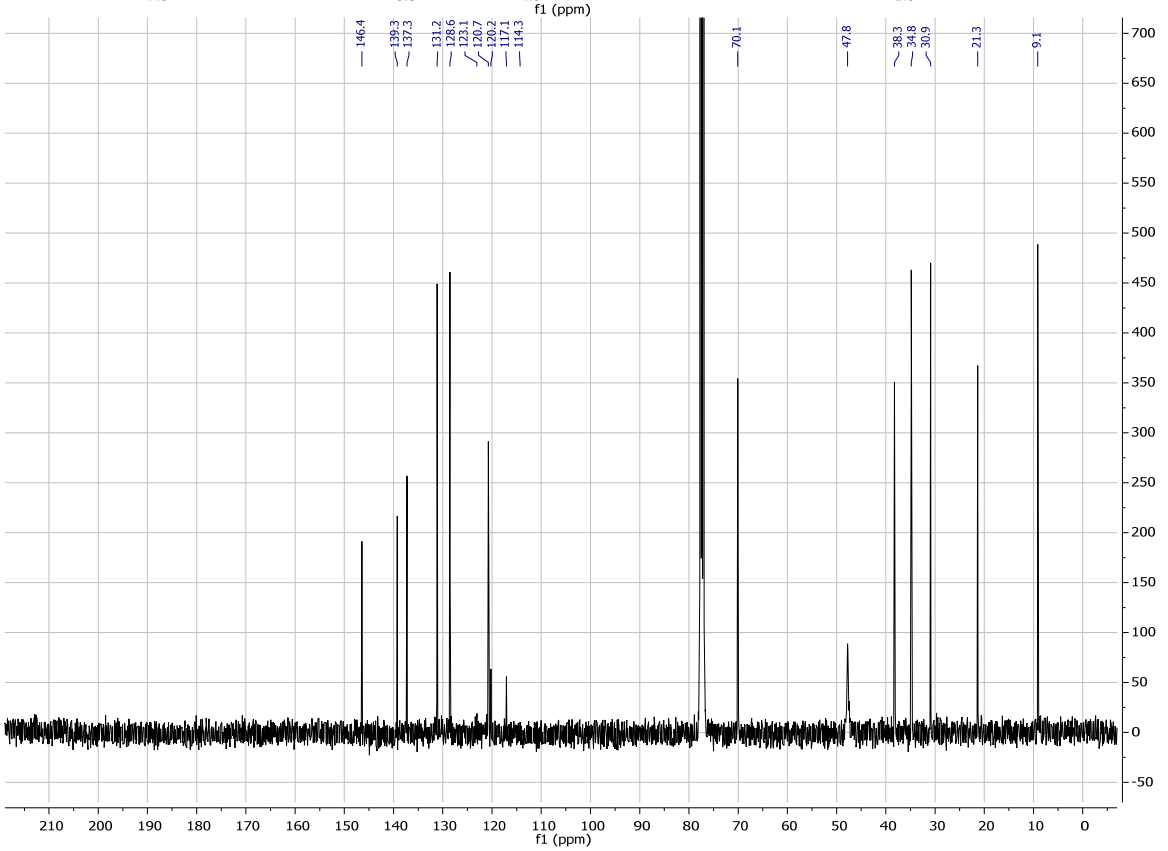

145.9
137.6
134.9
128.3
127.9
122.1
69.9
49.5
37.6
30.8
30.0
20.7
f1 (ppm)

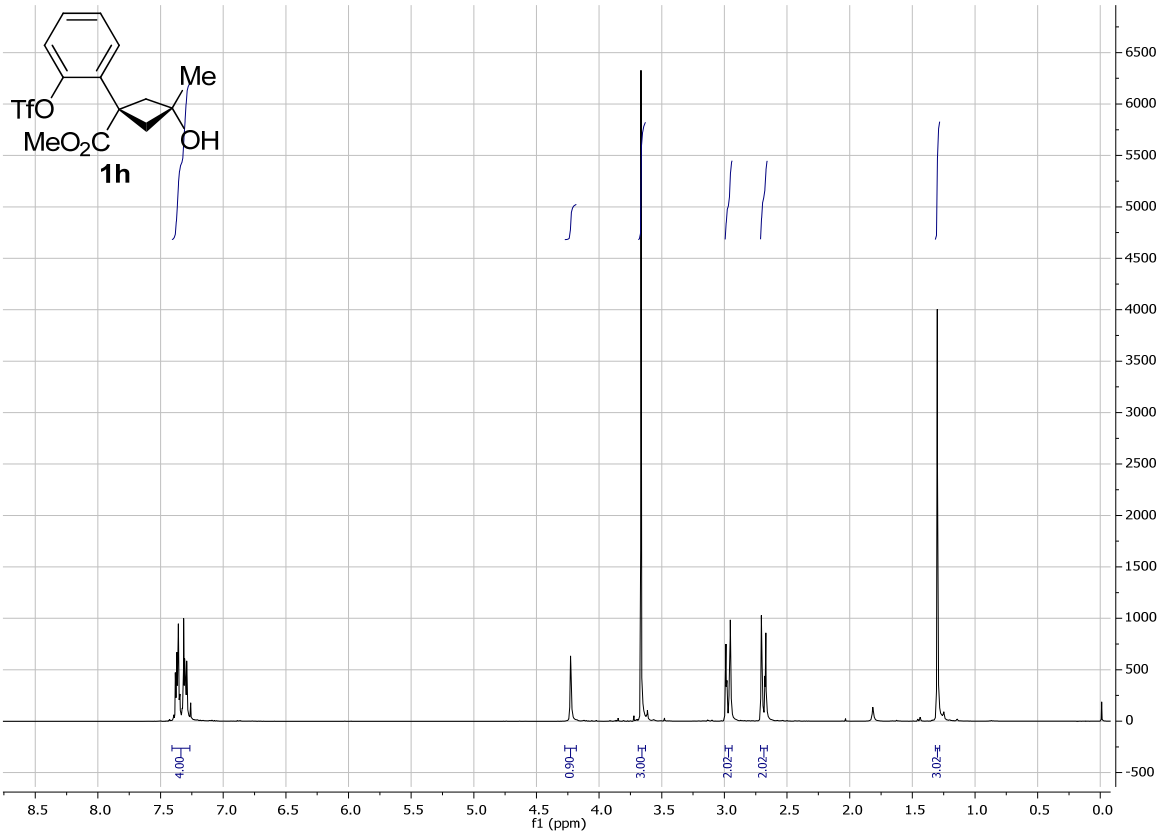


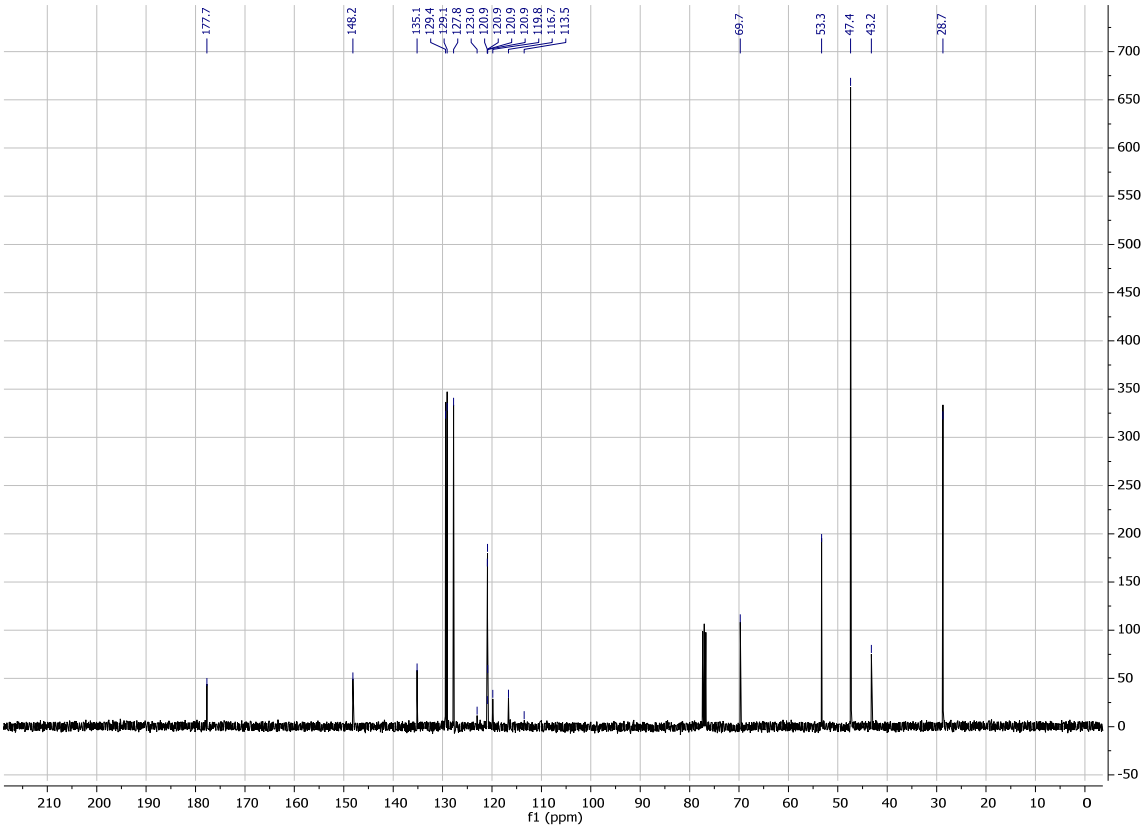





Me
TfO
Me
Et
OH
1g
f1 (ppm)


146.4
139.3
137.3
131.2
128.6
123.1
120.7
120.2
117.1
114.3
70.1
47.8
38.3
34.8
30.9
21.3
9.1
f1 (ppm)


Me
TfO
MeO2C
OH
1h
4.00
0.90
3.00
2.02
2.02
3.02
f1 (ppm)


177.7
148.2
135.1
129.4
129.1
127.8
123.0
120.9
120.9
120.9
120.9
119.8
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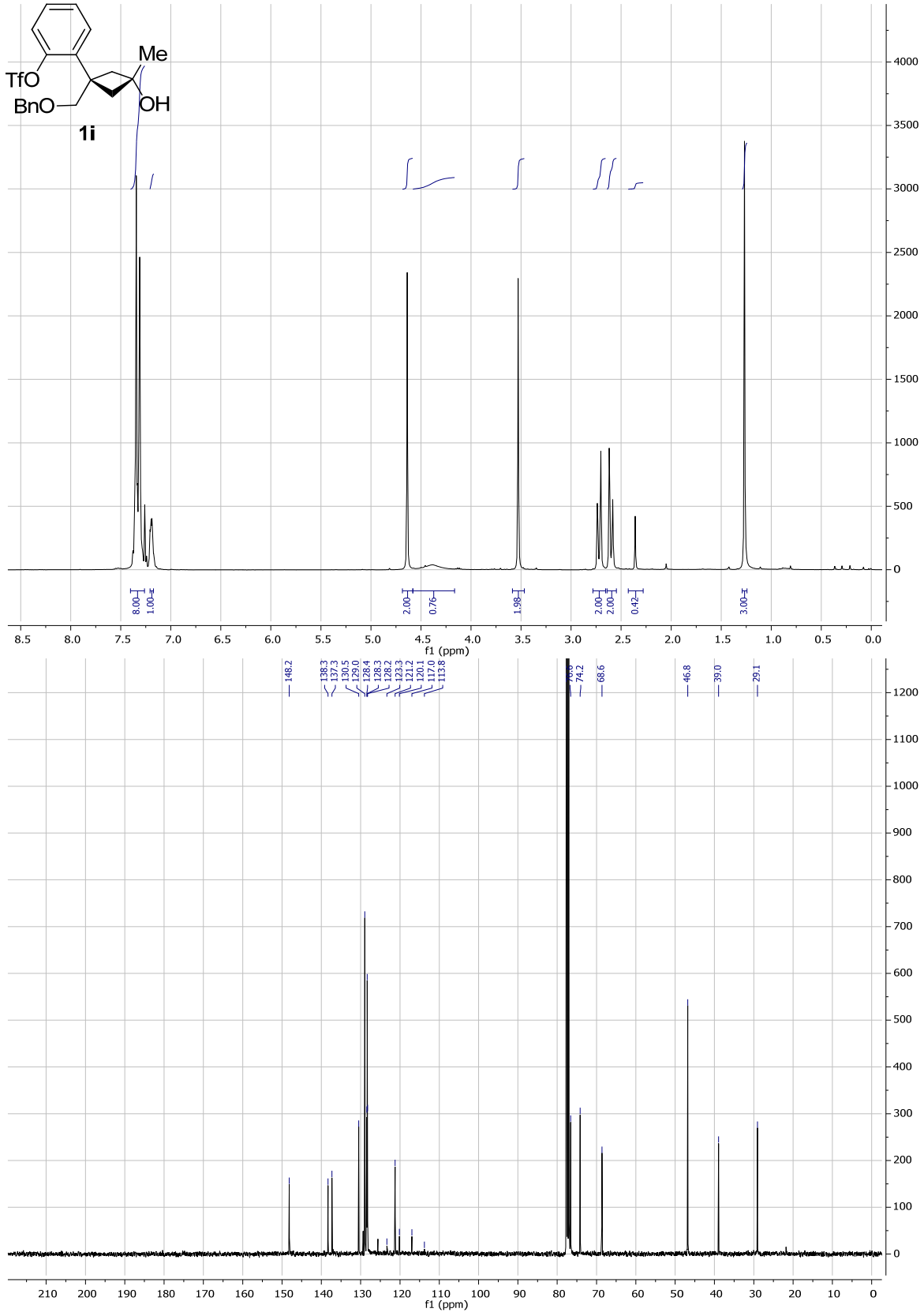
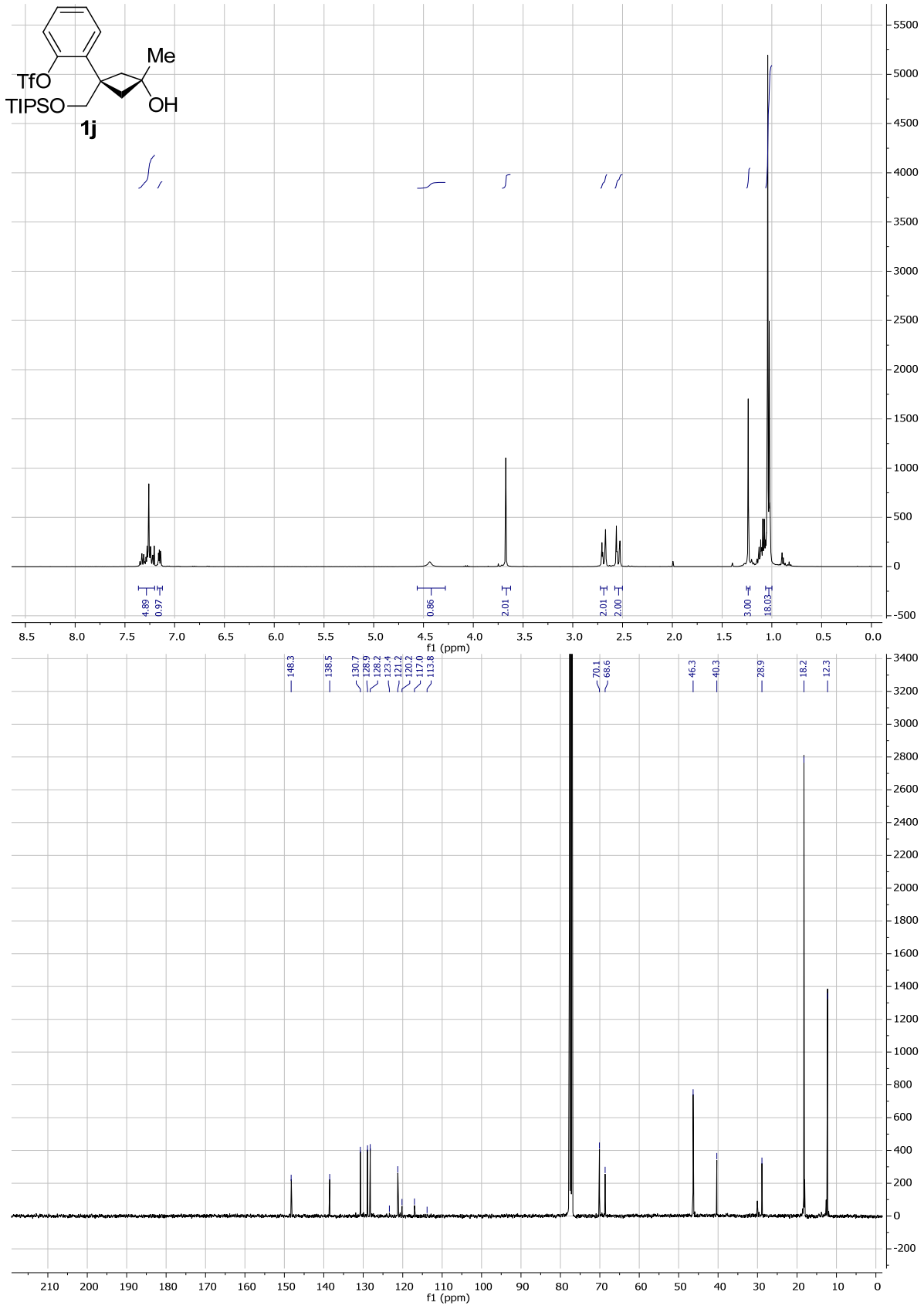
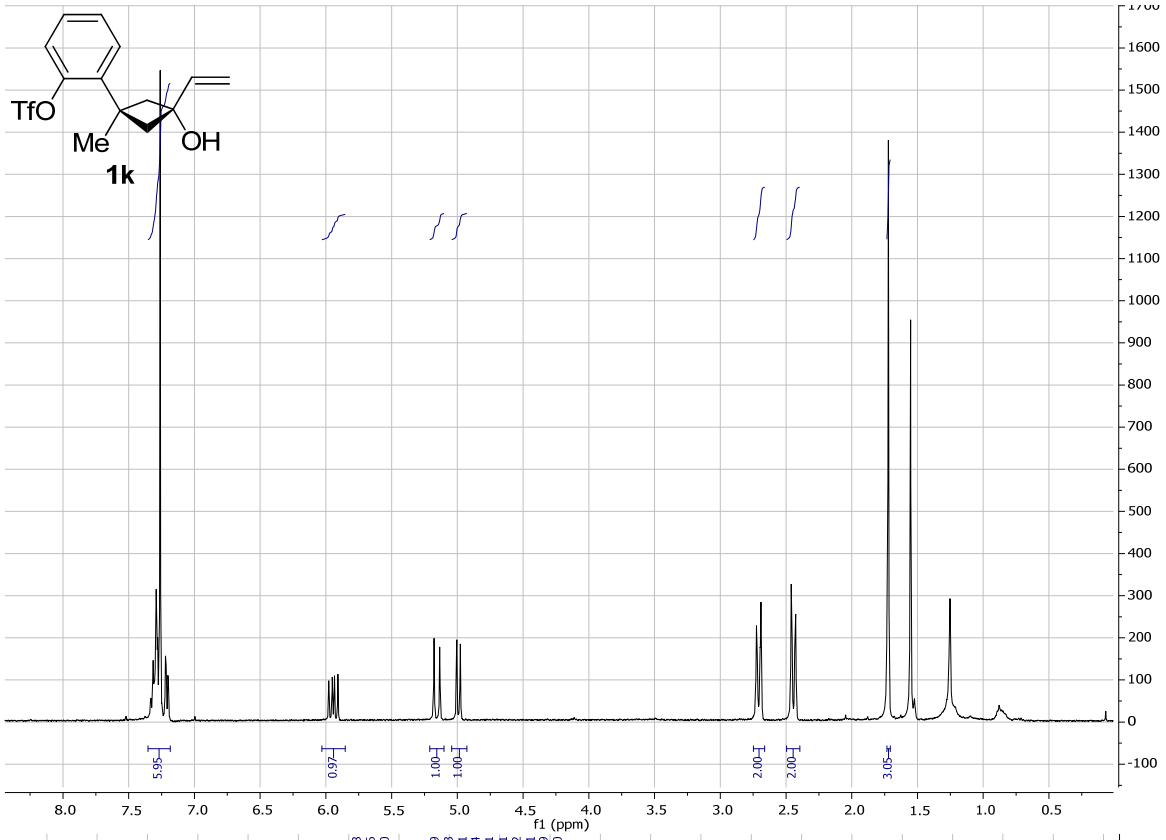
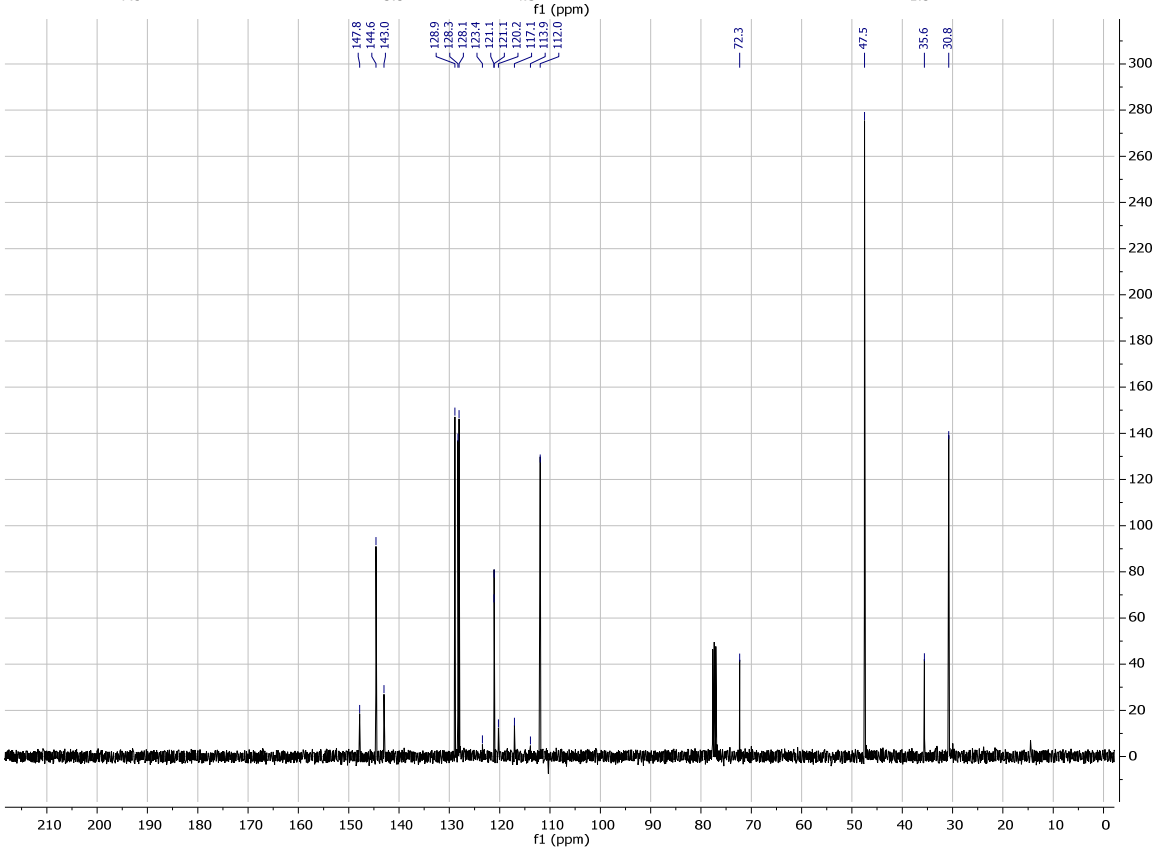
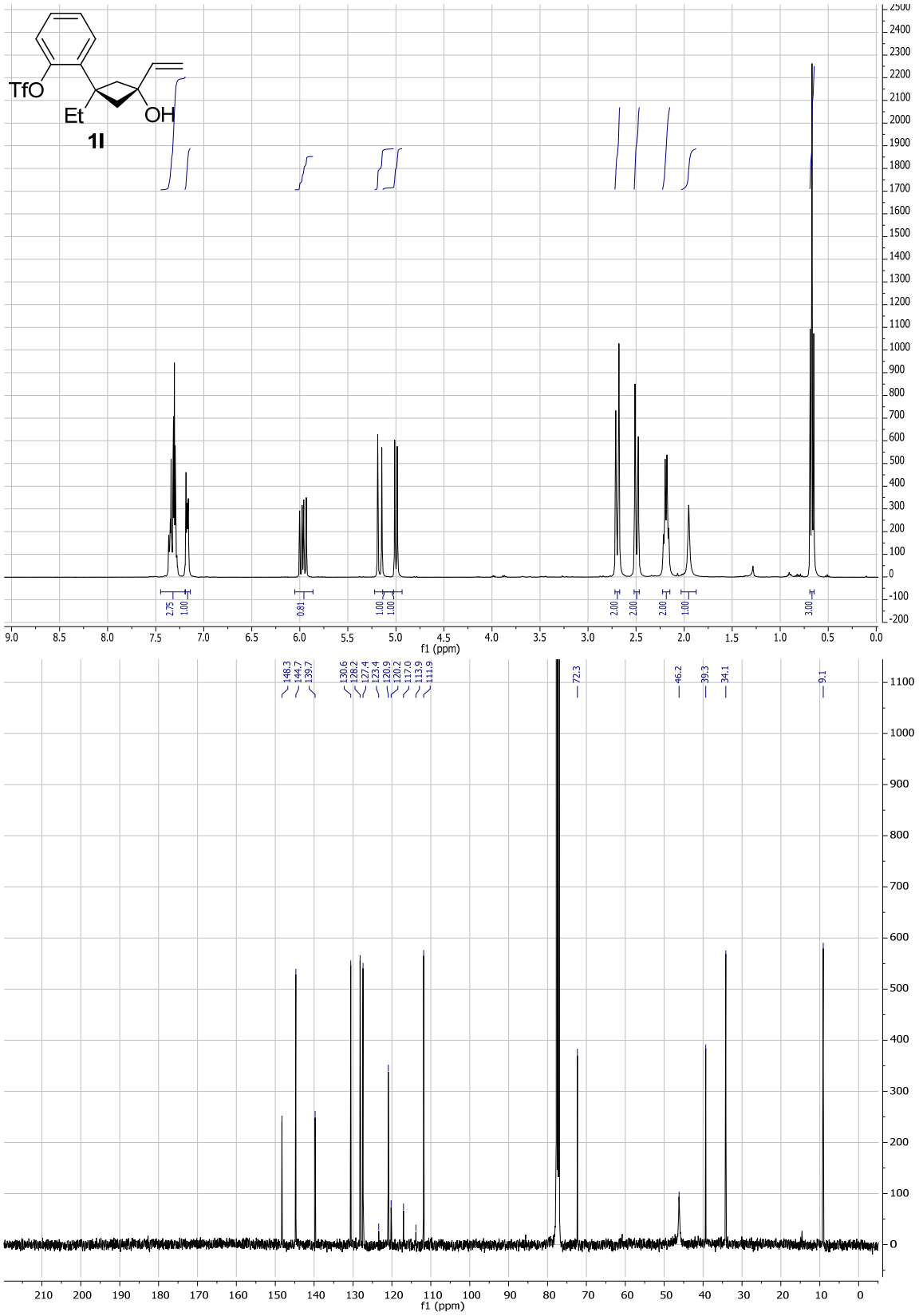
69.7
53.3
47.4
43.2
28.7
f1 (ppm)

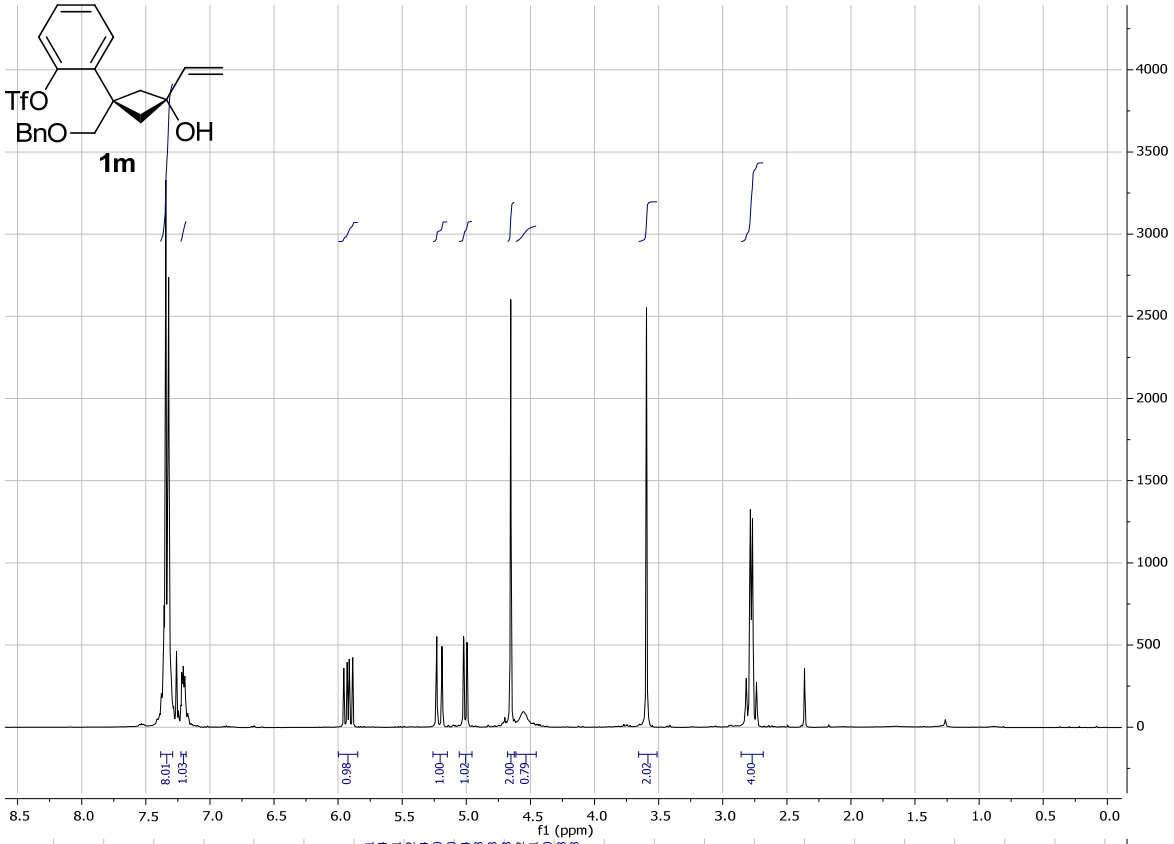

Me
TfO
BnO
OH
1i
8.00
1.00
2.00
0.76
1.98
2.00
2.00
0.42
3.00
f1 (ppm)
148.2
138.3
137.3
130.5
129.0
128.4
128.3
128.2
123.3
121.2
120.1
117.0
113.8
74.2
68.6
46.8
39.0
29.1
f1 (ppm)










TfO
BnO
OH
1m
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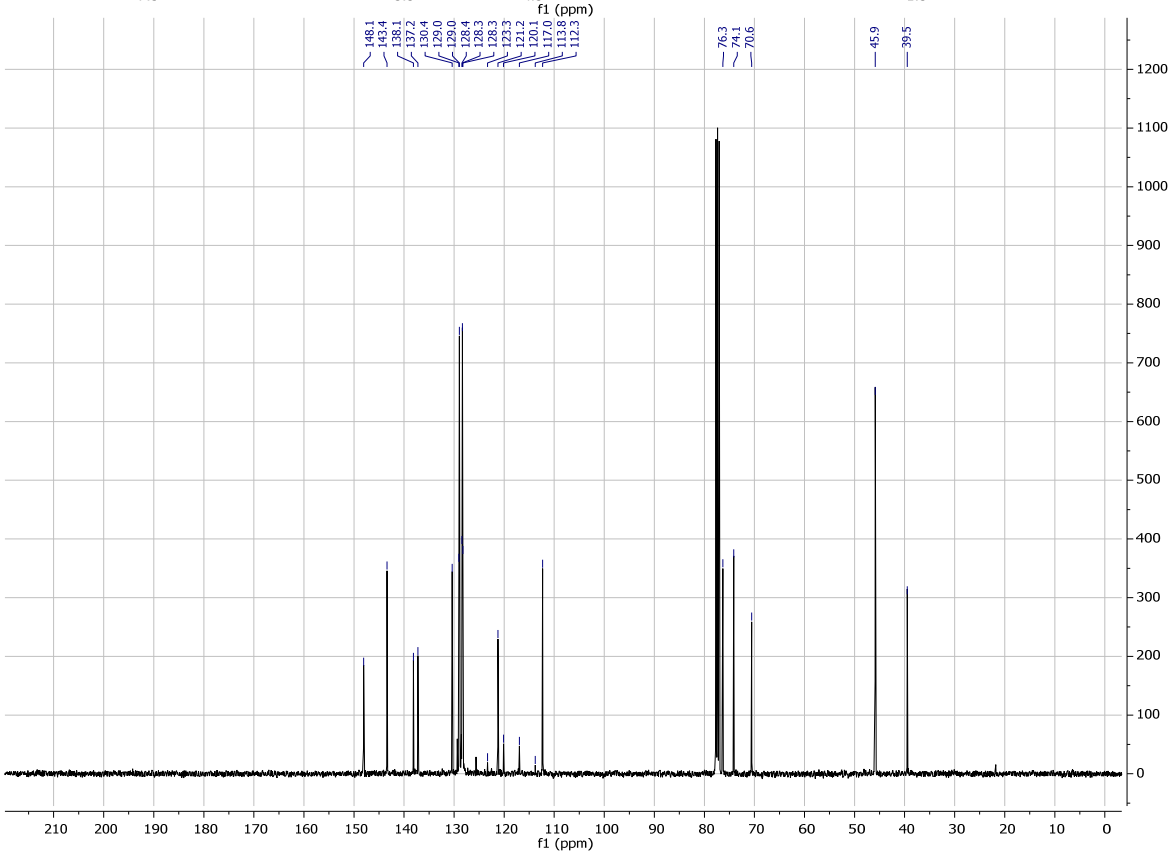
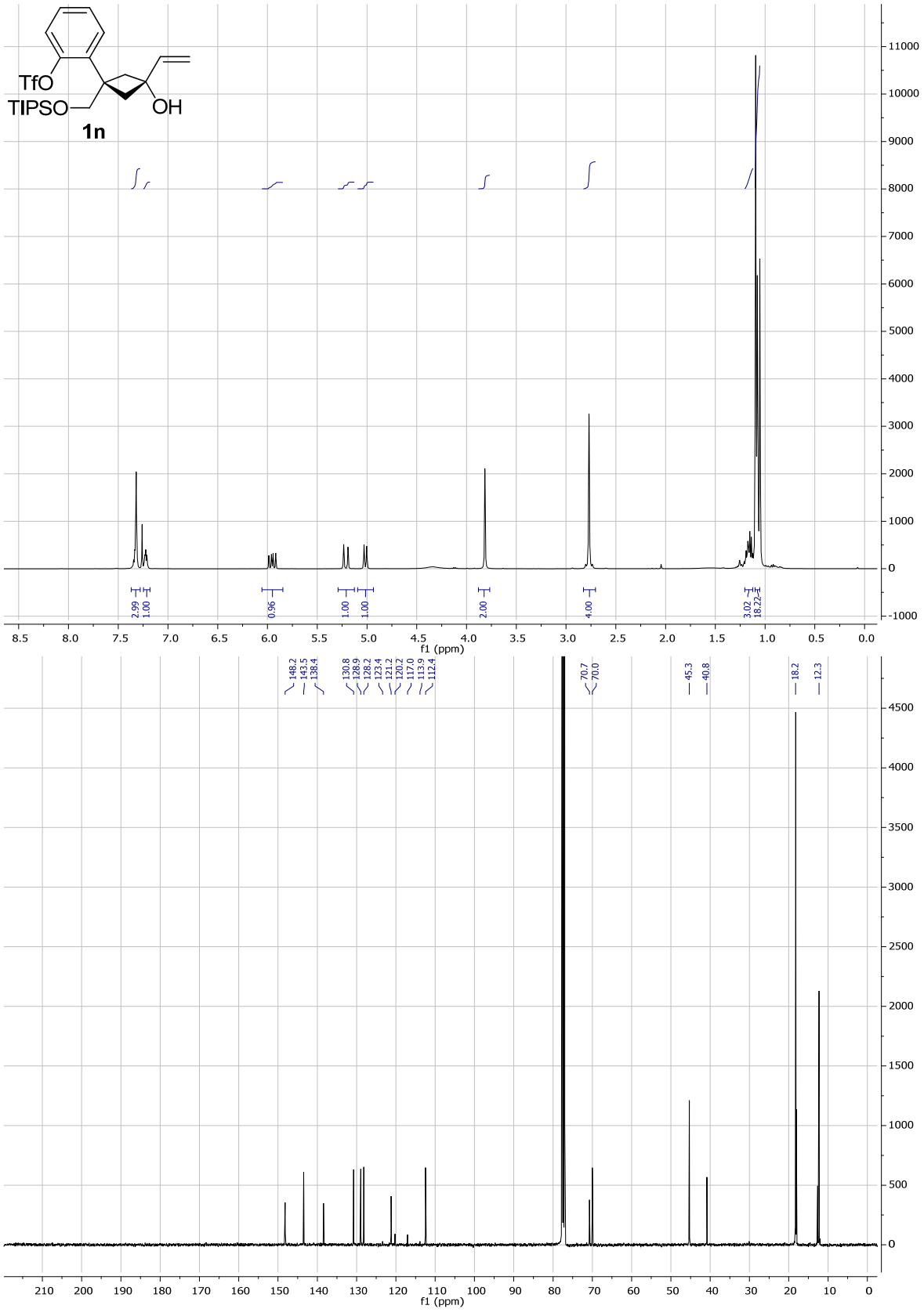
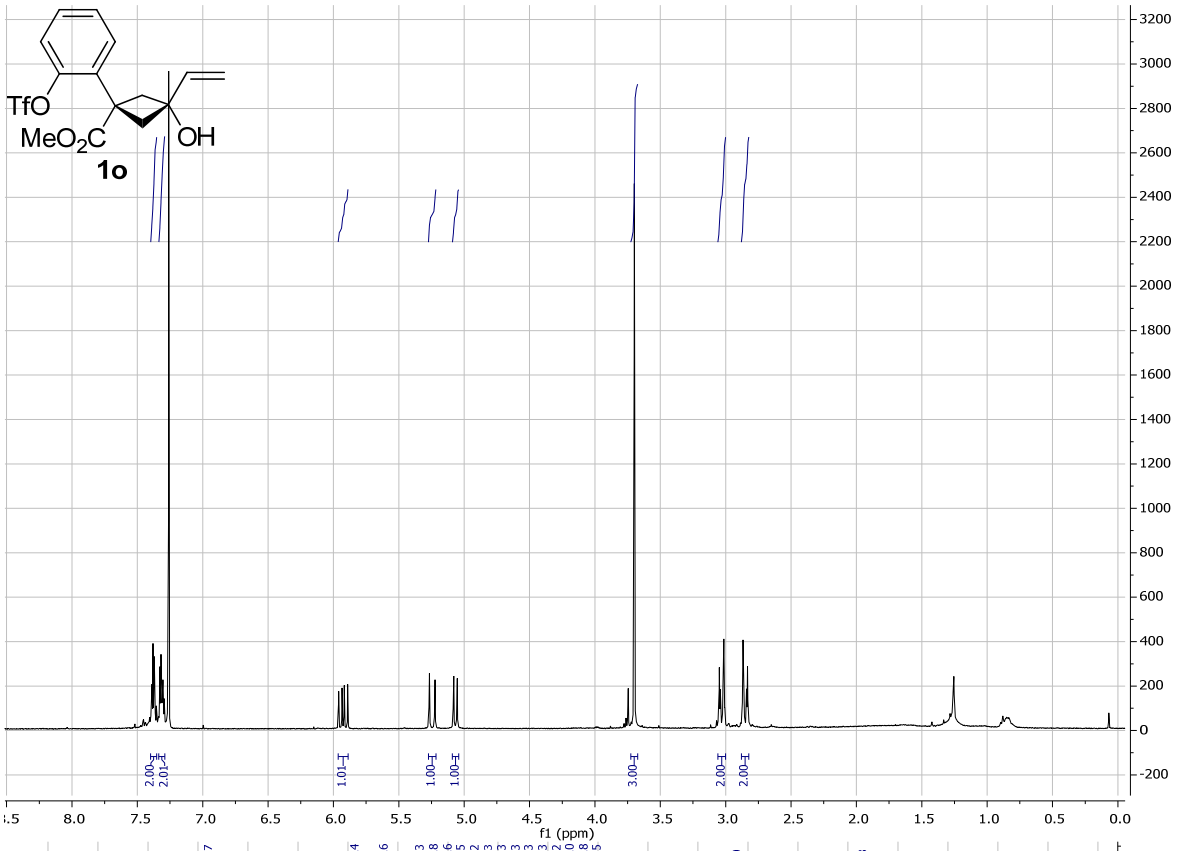
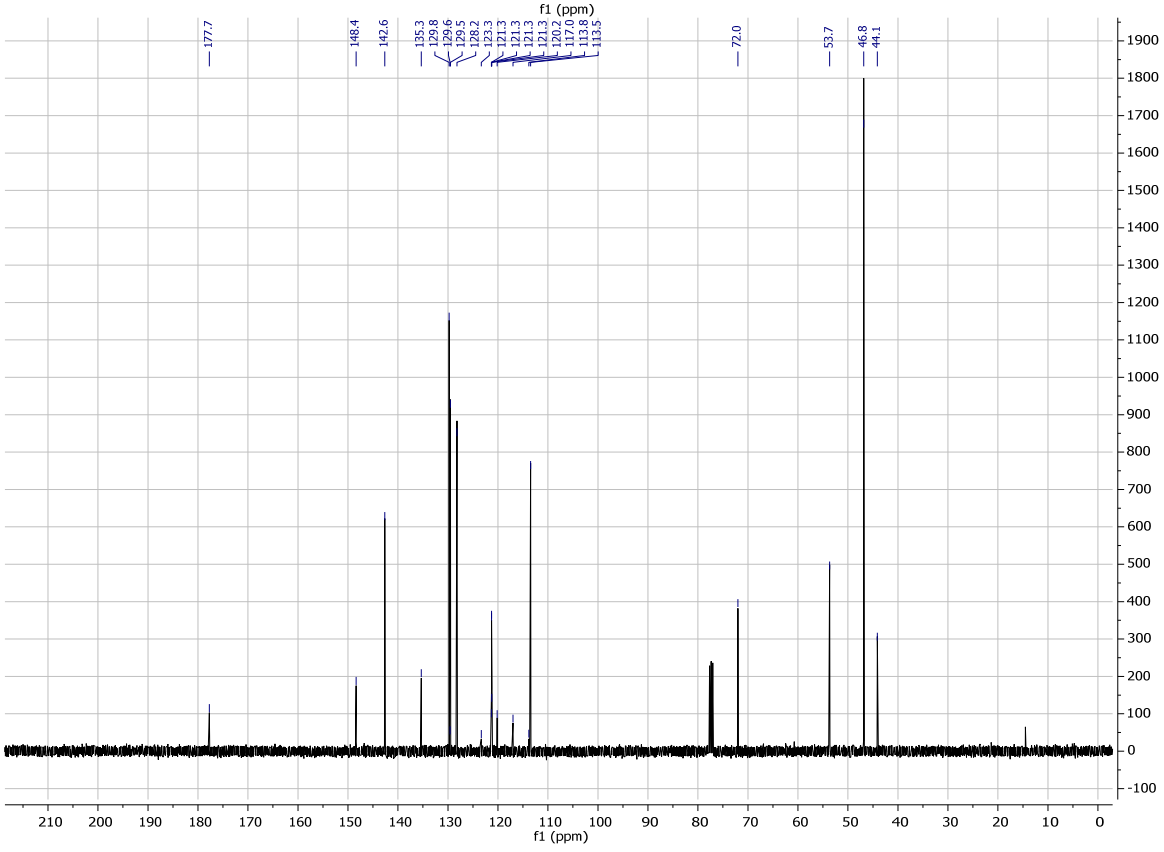
1.03
0.98
1.00
1.02
2.00
0.79
2.02
4.00
f1 (ppm)


148.1
143.4
138.1
137.2
130.4
129.0
129.0
128.4
128.3
123.3
121.2
120.1
117.0
113.8
112.3
76.3
74.1
70.6
45.9
39.5
f1 (ppm)




TfO
MeO2C
OH
1o
f1 (ppm)


177.7
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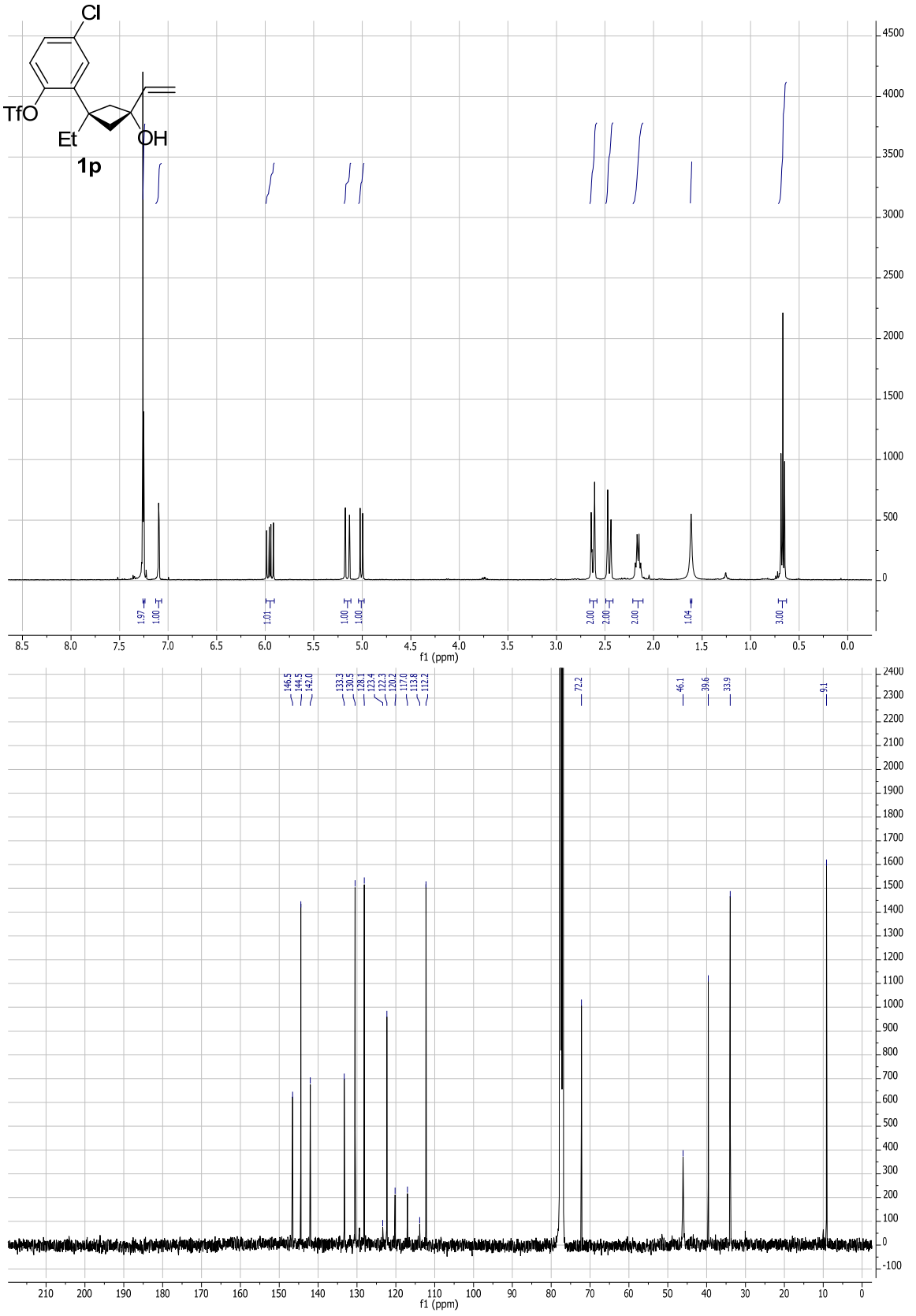
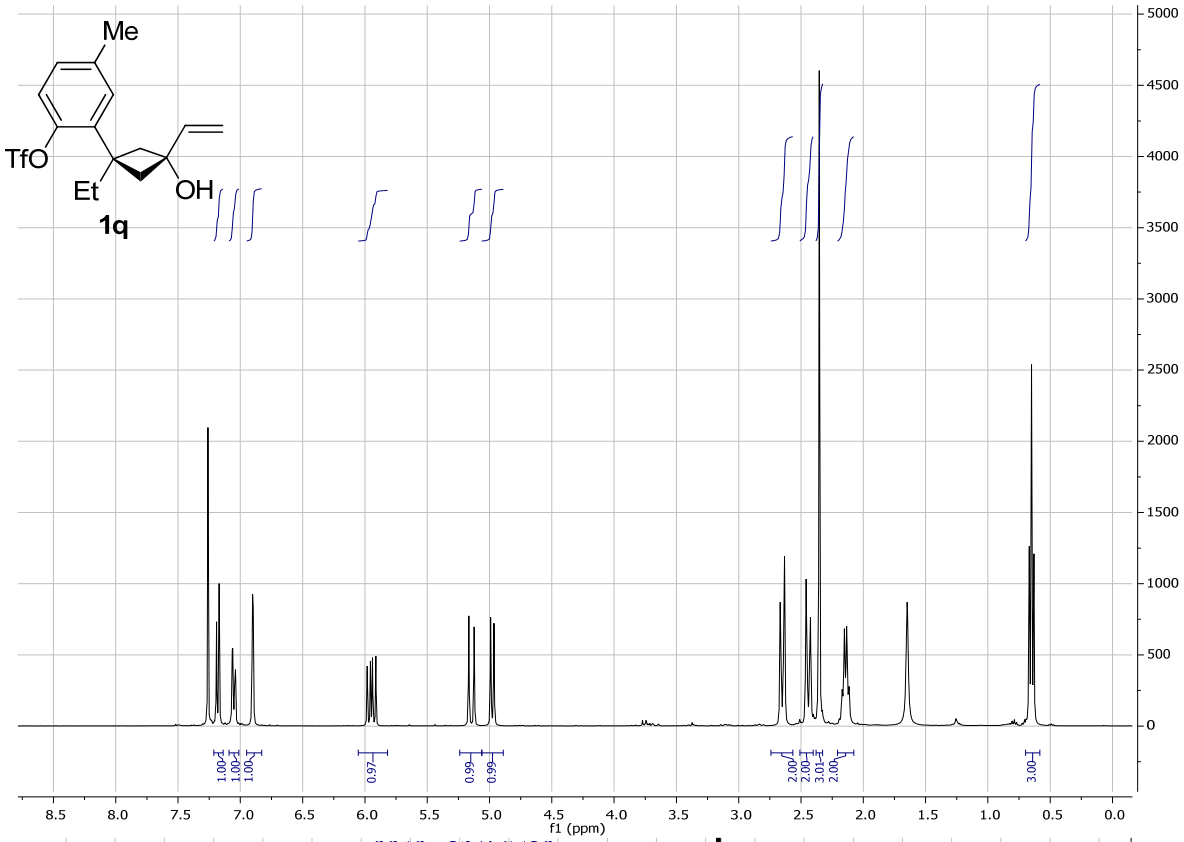
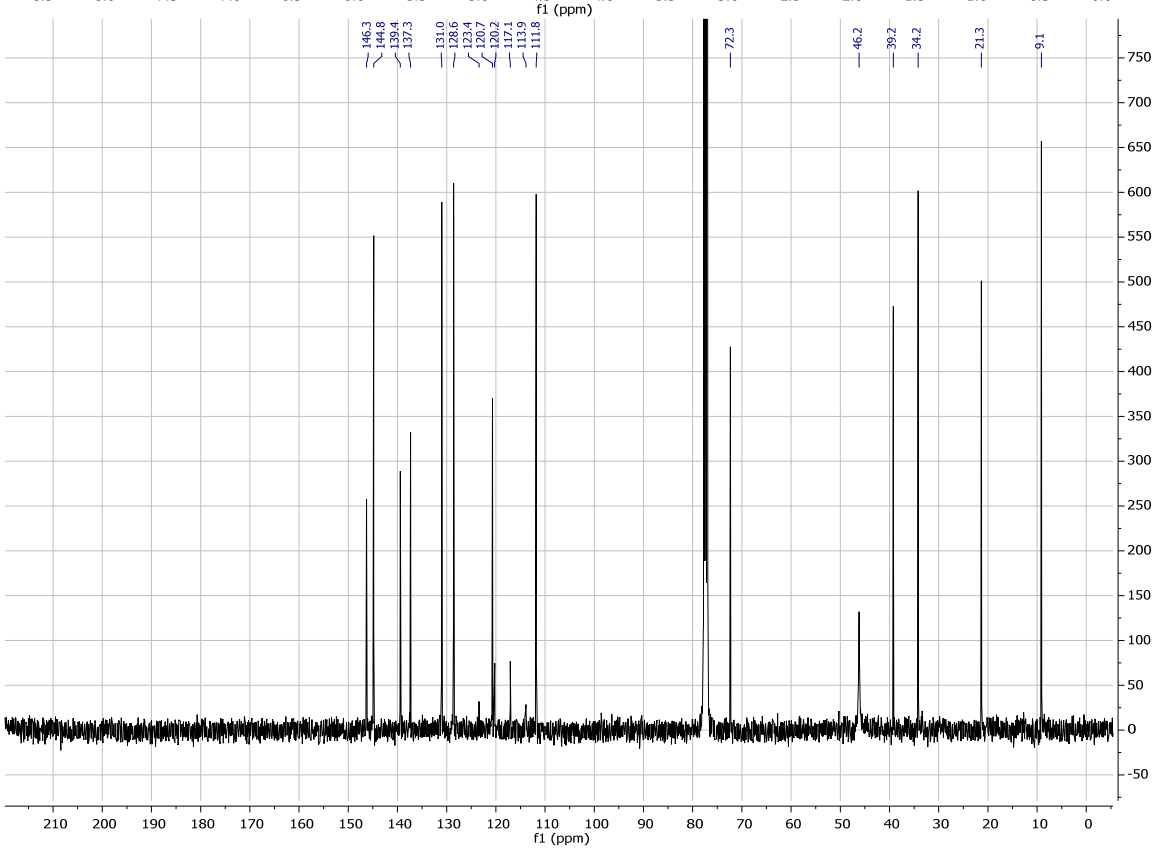
135.3
129.8
129.6
129.5
128.2
123.3
121.3
121.3
121.3
120.2
117.0
113.8
113.5
72.0
53.7
46.8
44.1
f1 (ppm)




Me
TfO
Et
OH
1q
f1 (ppm)


146.3
144.8
139.4
137.3
131.0
128.6
123.4
120.7
120.2
117.1
113.9
111.8
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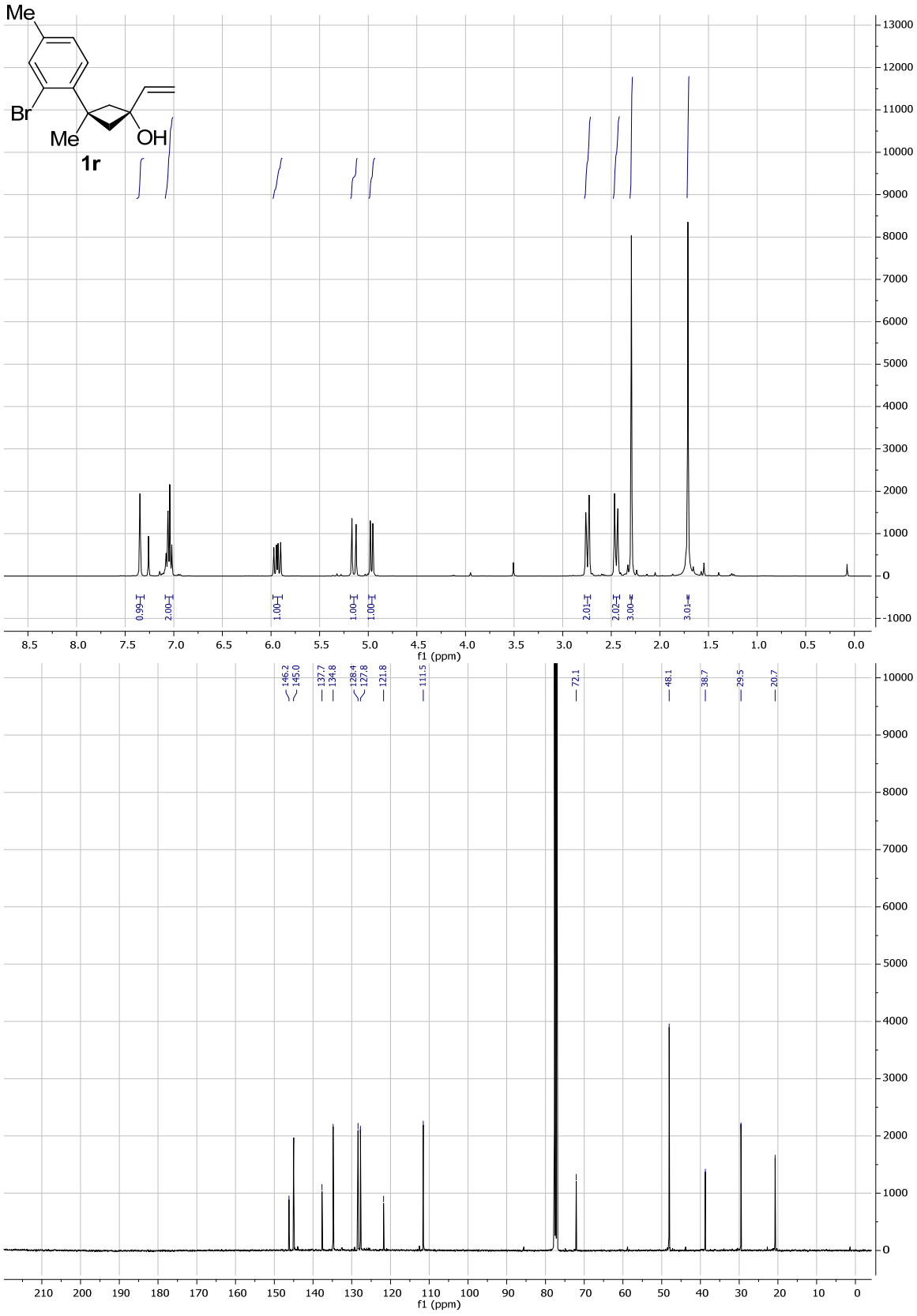
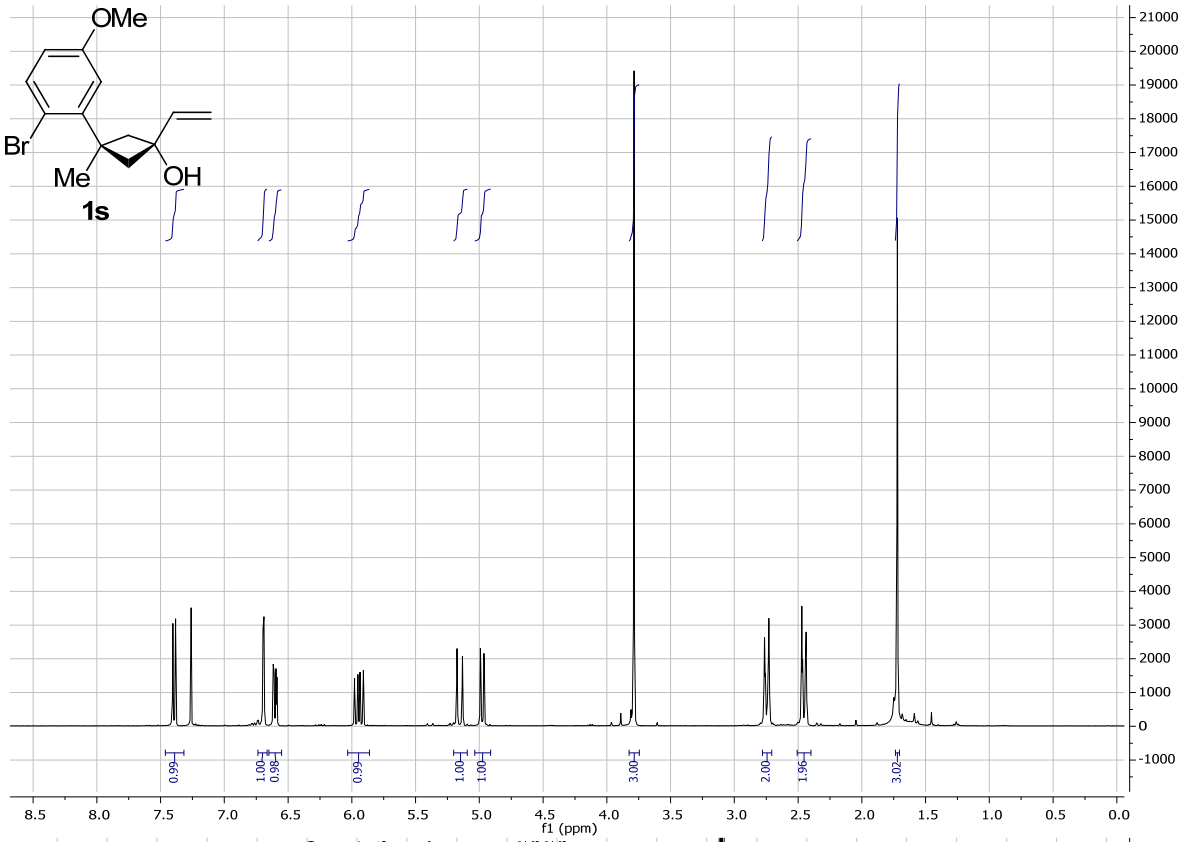
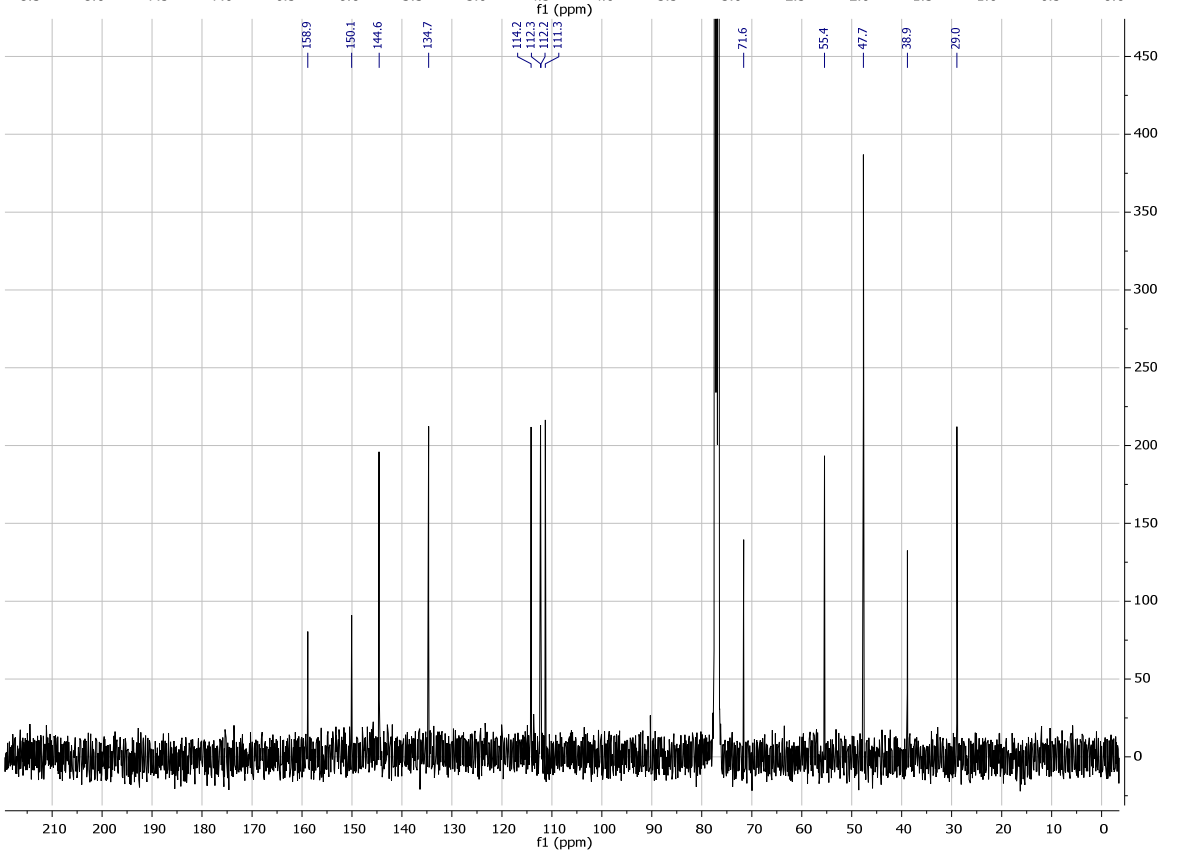
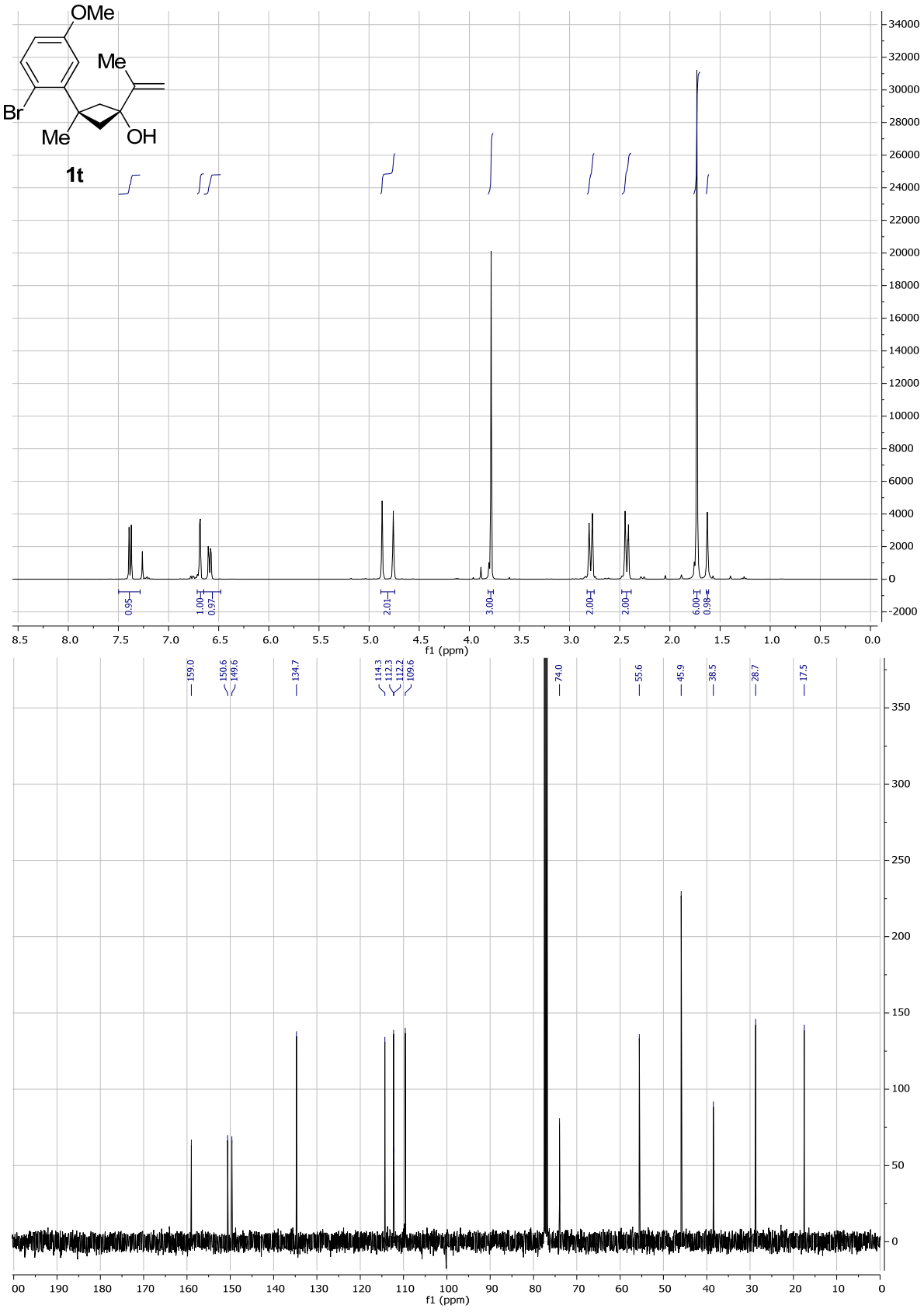
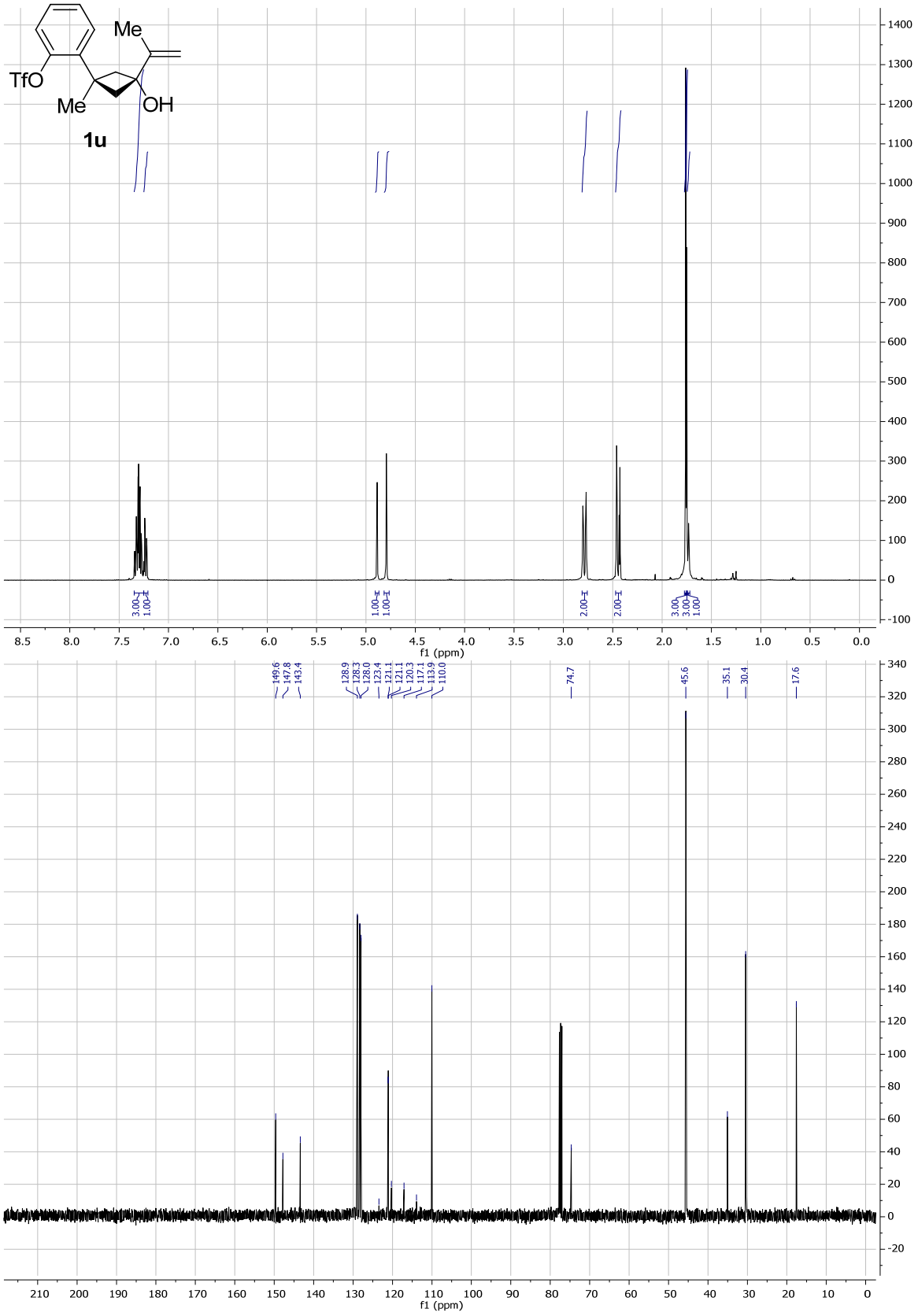
39.2
34.2
21.3
9.1
f1 (ppm)

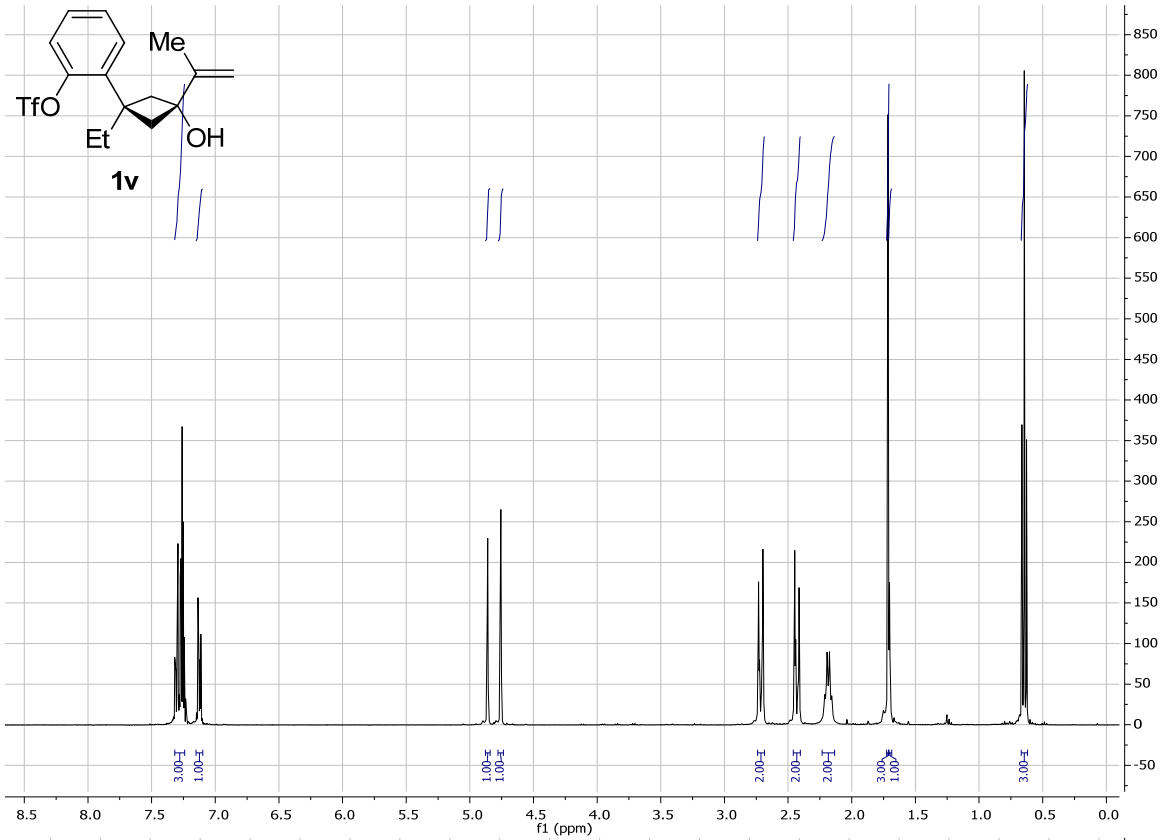

Me
Br
Me
OH
1r
f1 (ppm)
f1 (ppm)

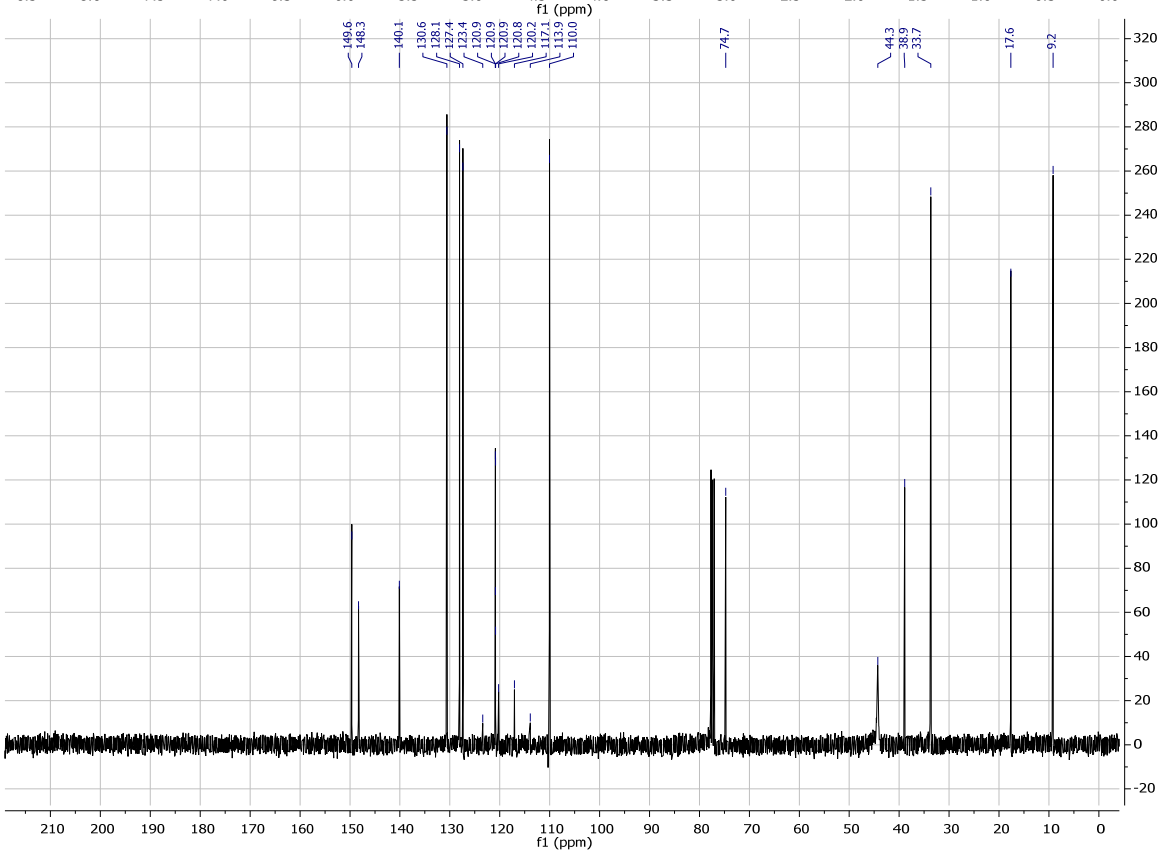


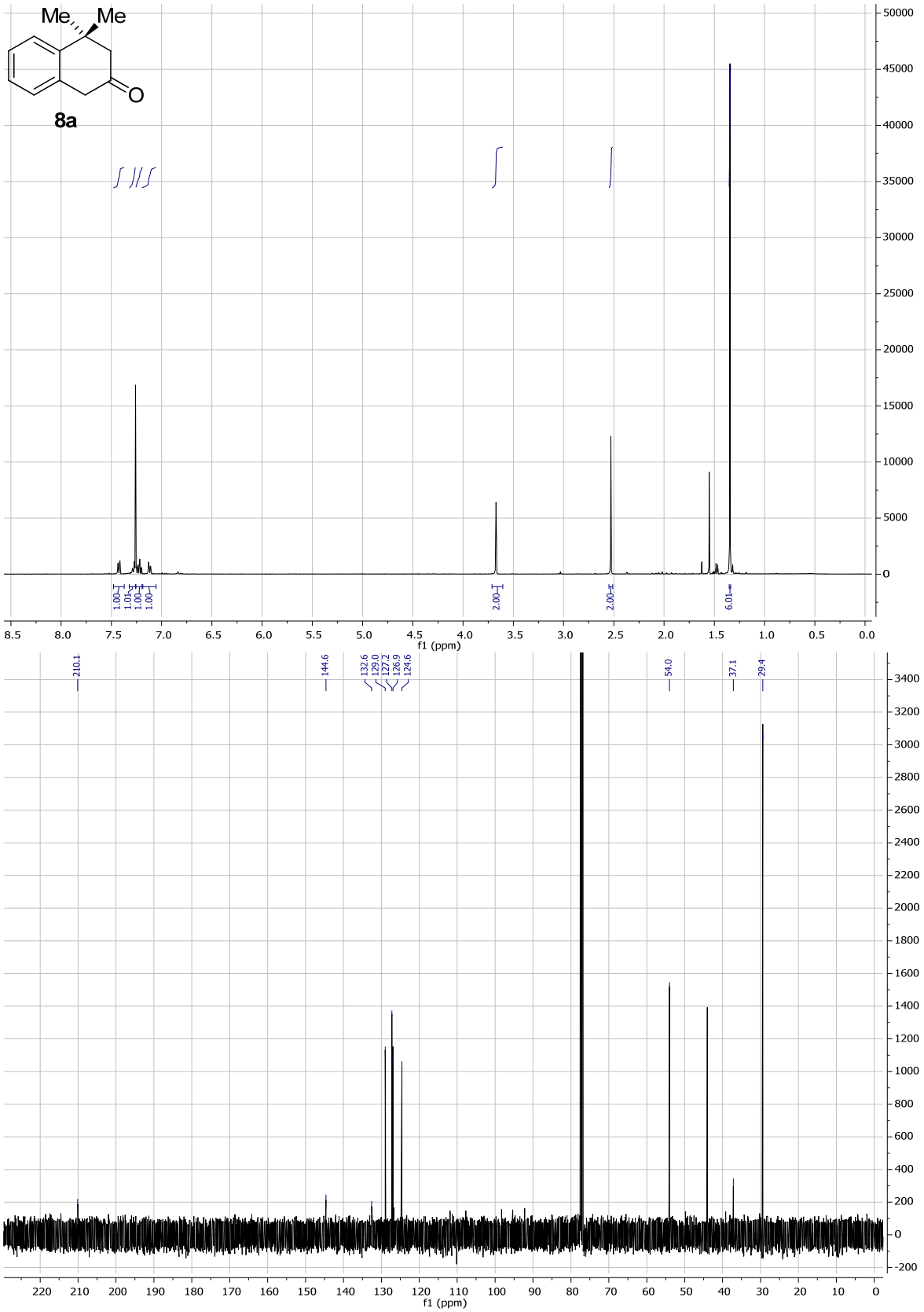


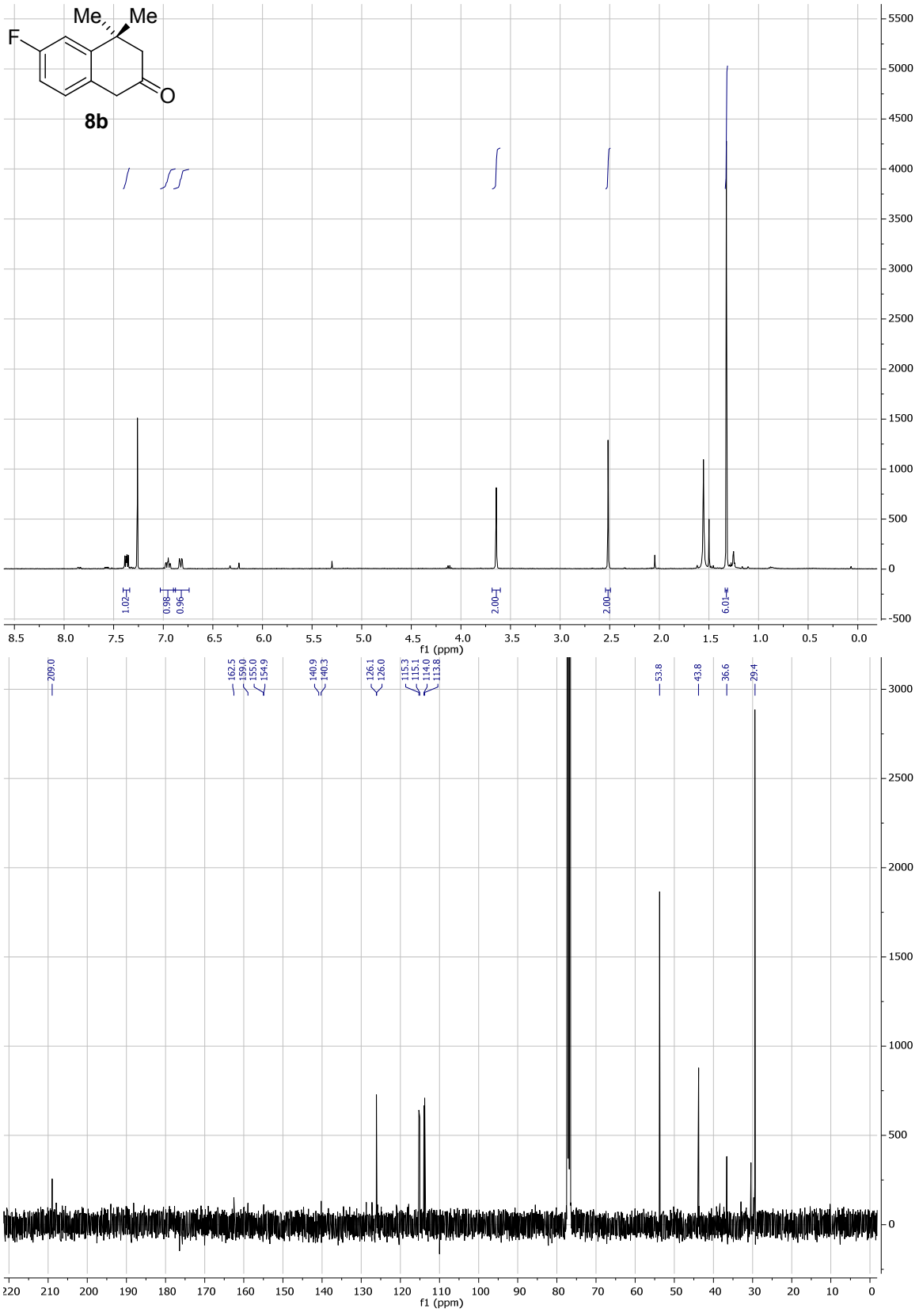


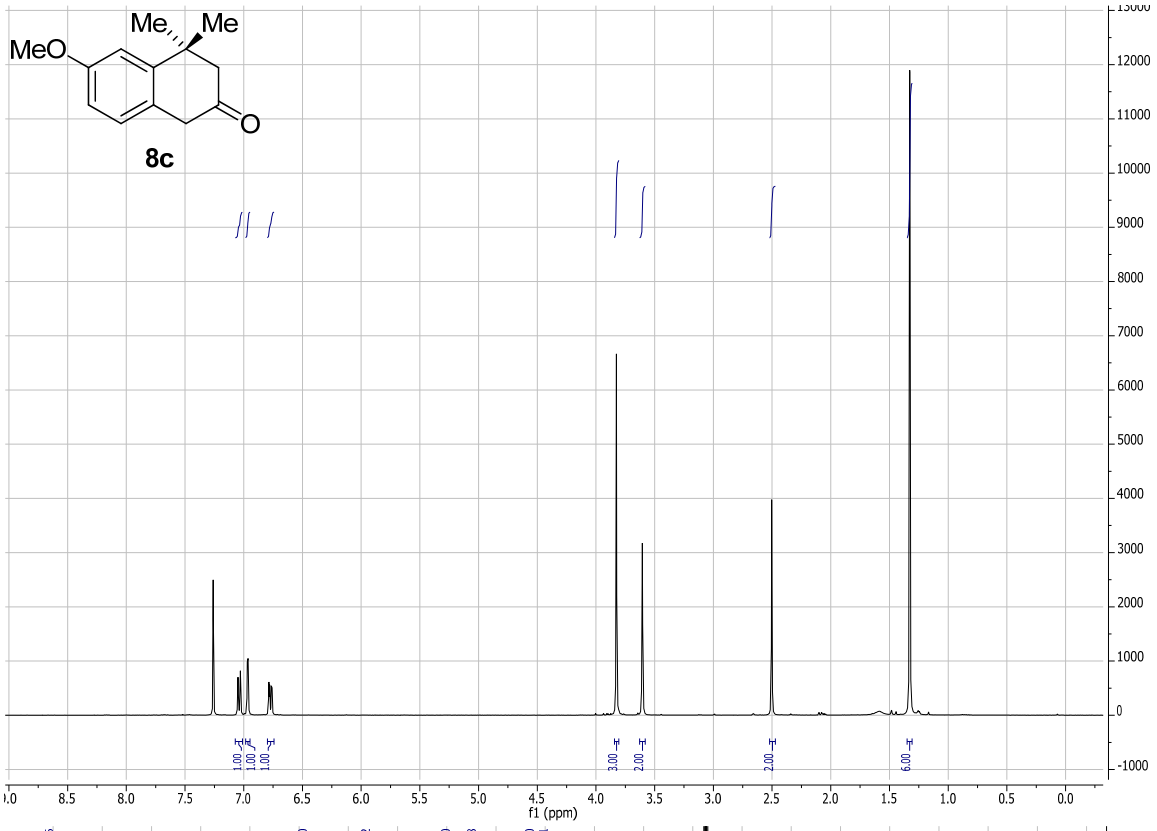


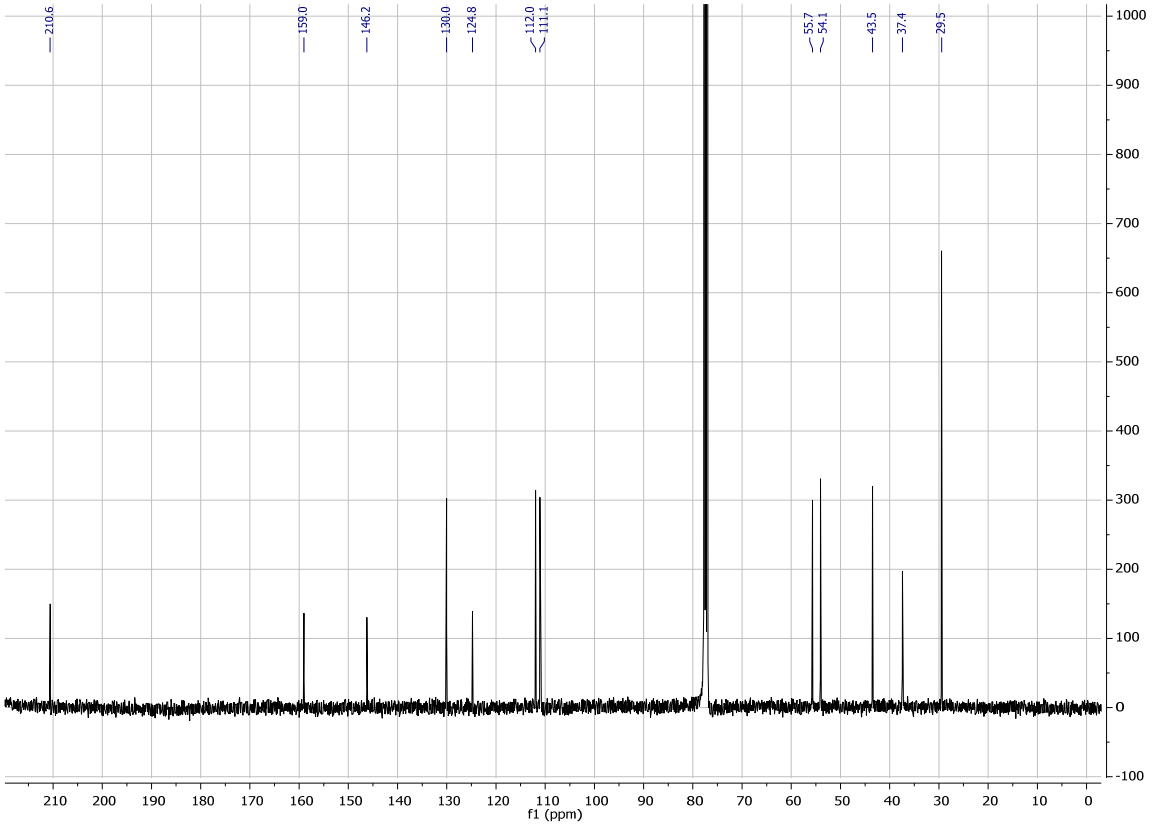

Me
TfO
Et
OH
1v
f1 (ppm)

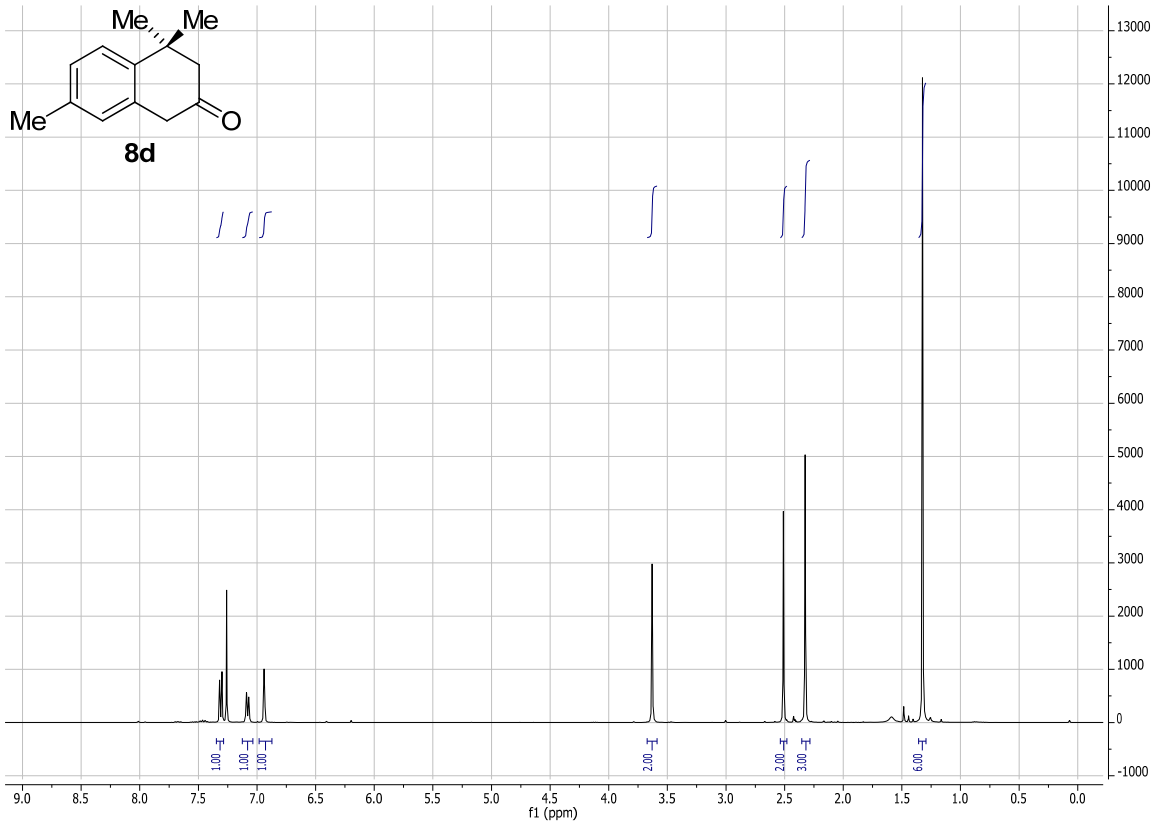

149.6
148.3
140.1
130.6
128.1
127.4
123.4
120.9
120.9
120.9
120.8
120.2
117.1
113.9
110.0
74.7
44.3
38.9
33.7
17.6
9.2
f1 (ppm)

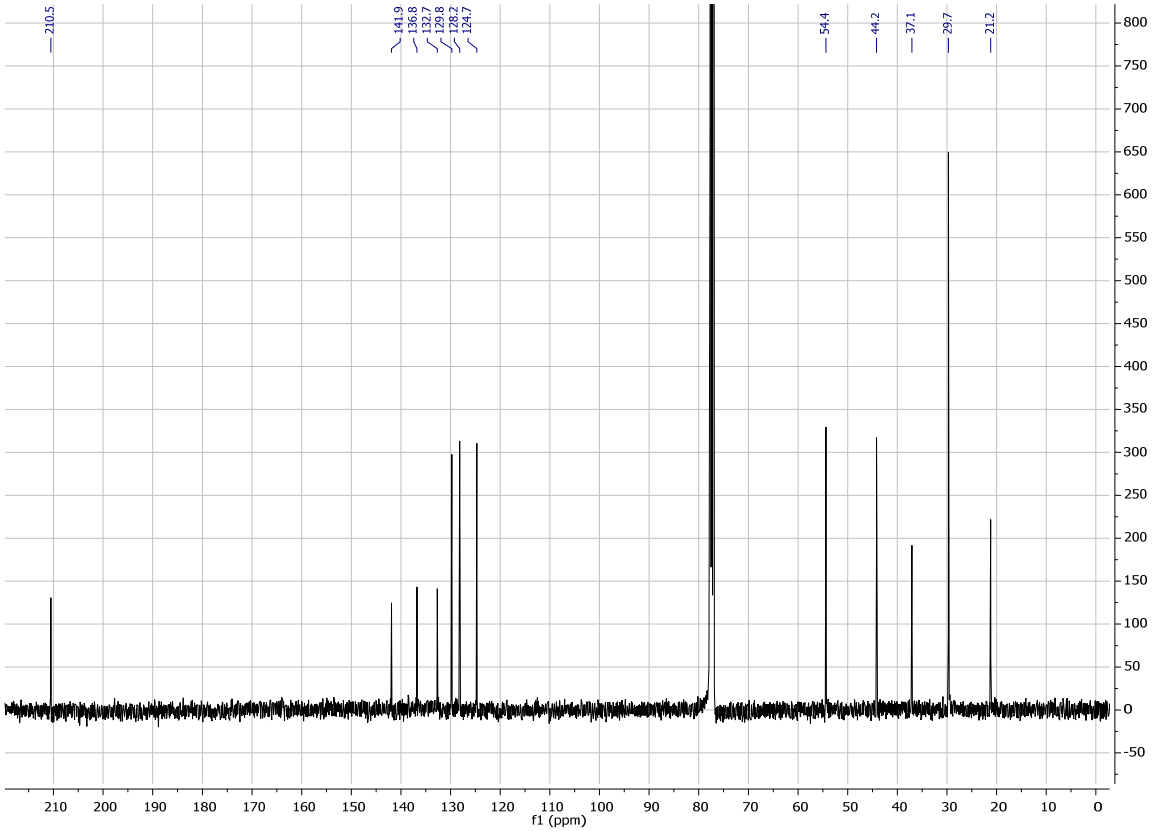


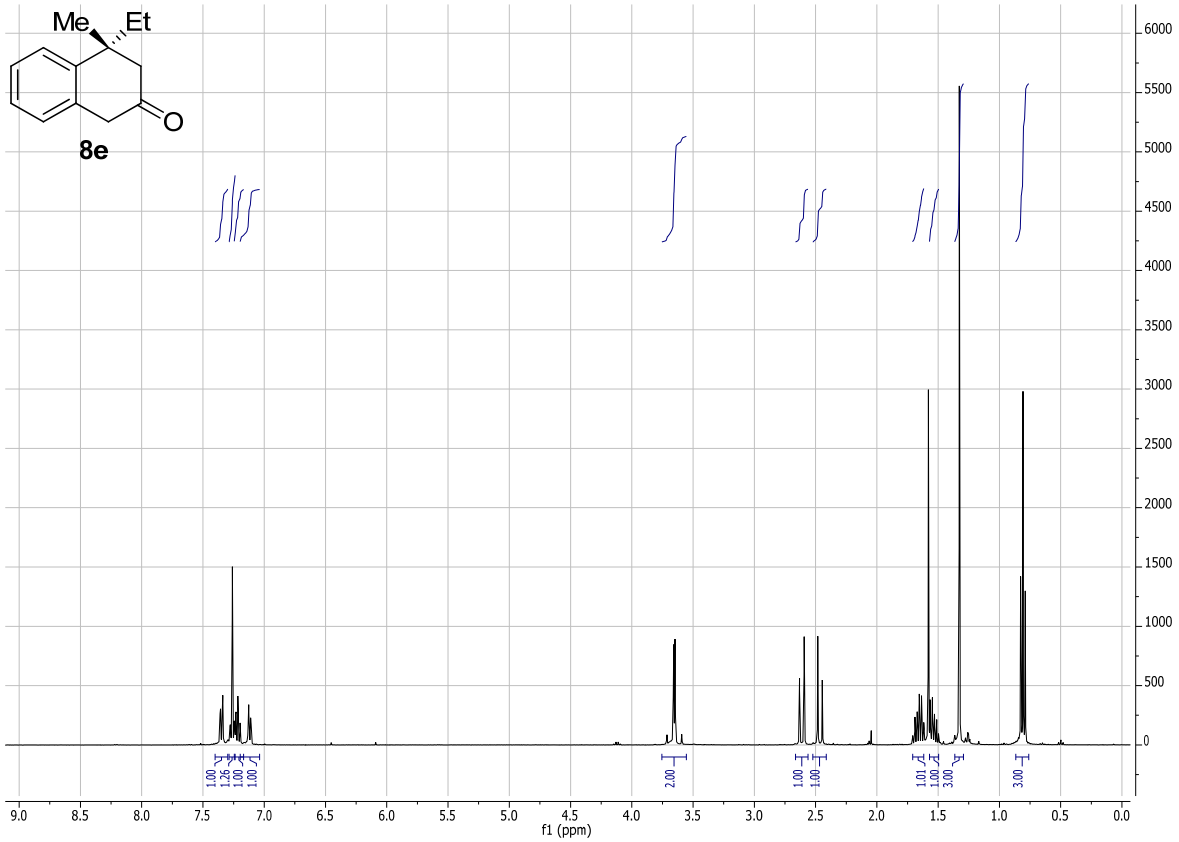


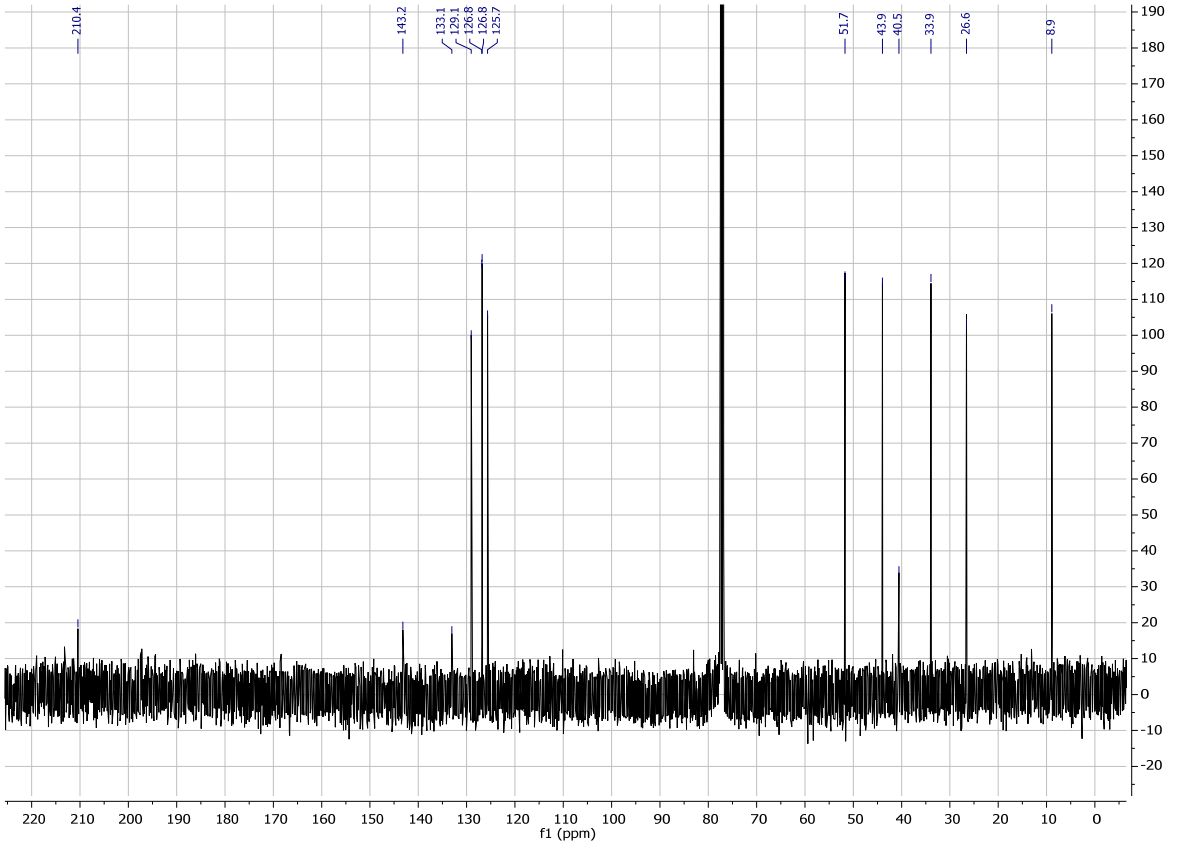

Me
Me
MeO
O
8c
f1 (ppm)

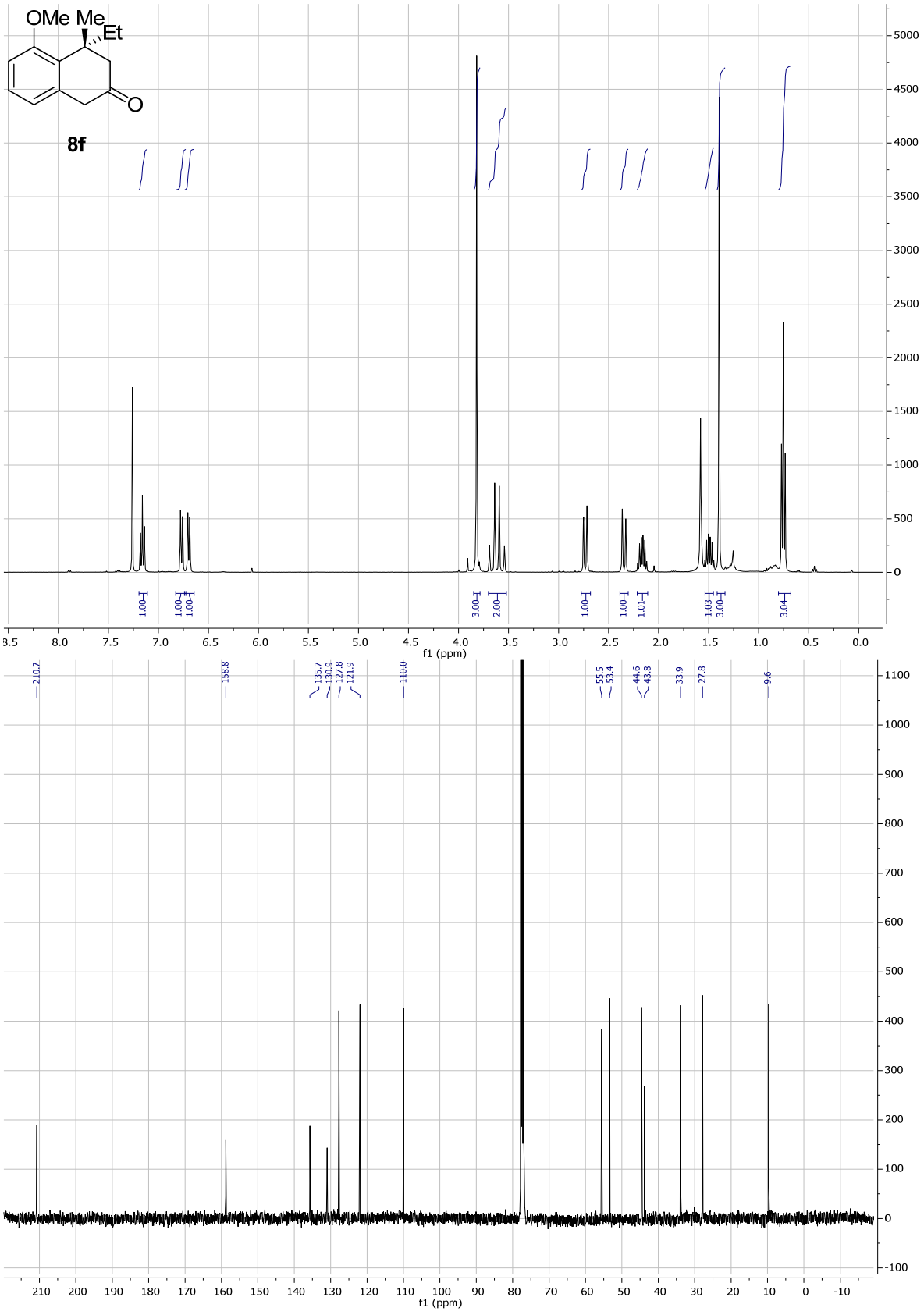

210.6
159.0
146.2
130.0
124.8
112.0
111.1
55.7
54.1
43.5
37.4
29.5
f1 (ppm)

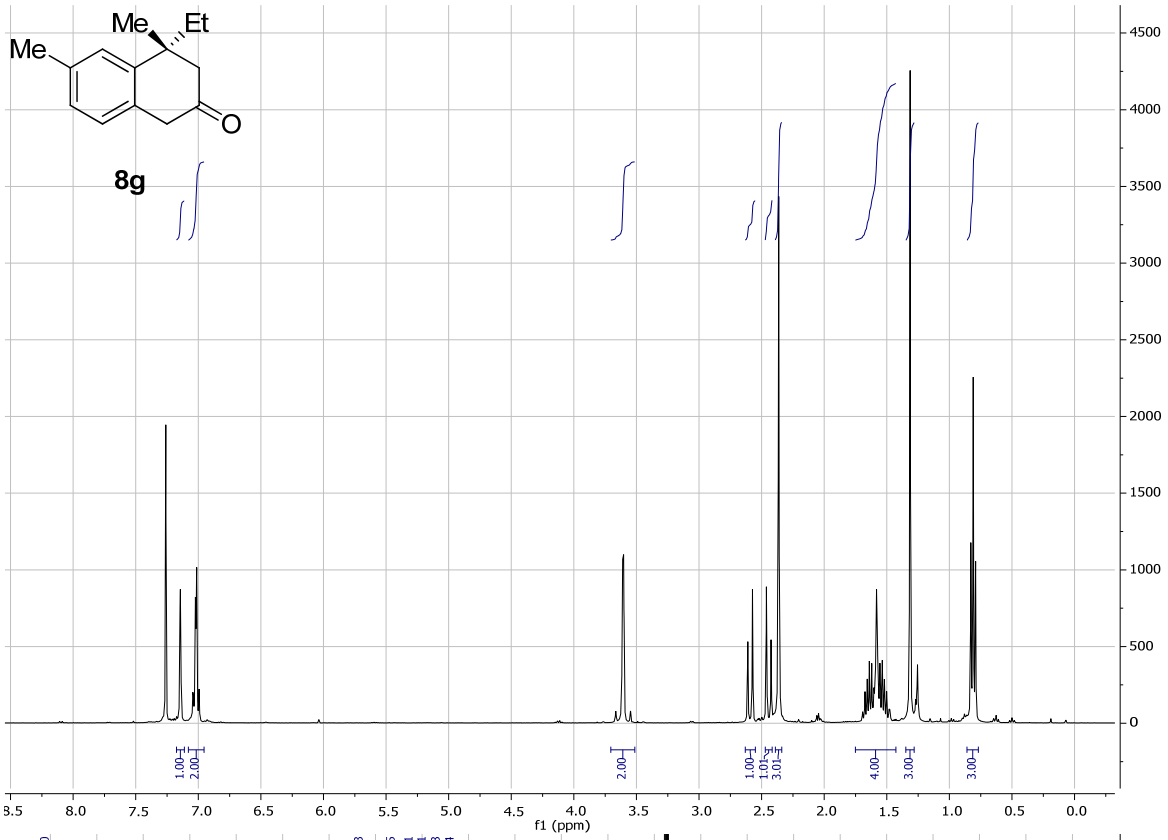

Me
Me
Me
O
8d
1.00
1.00
1.00
2.00
2.00
3.00
6.00
f1 (ppm)

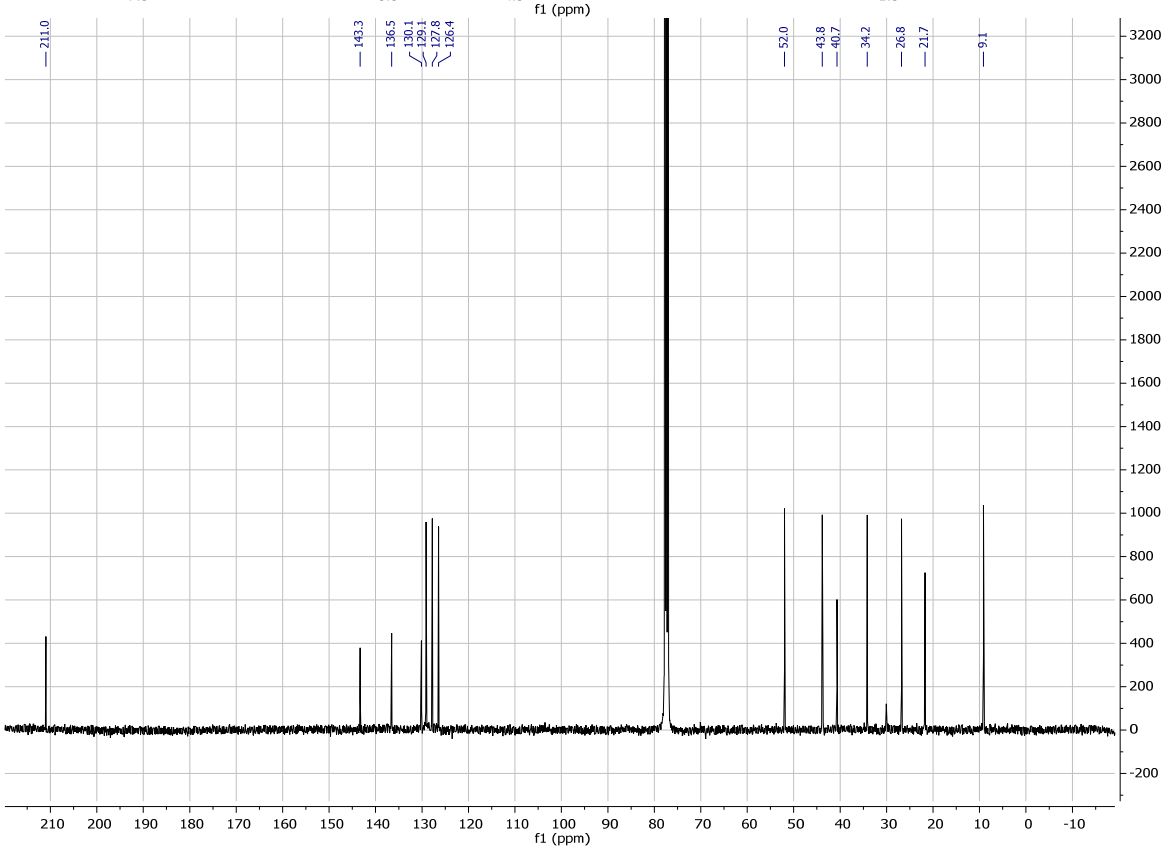

210.5
141.9
136.8
132.7
129.8
128.2
124.7
54.4
44.2
37.1
29.7
21.2
f1 (ppm)

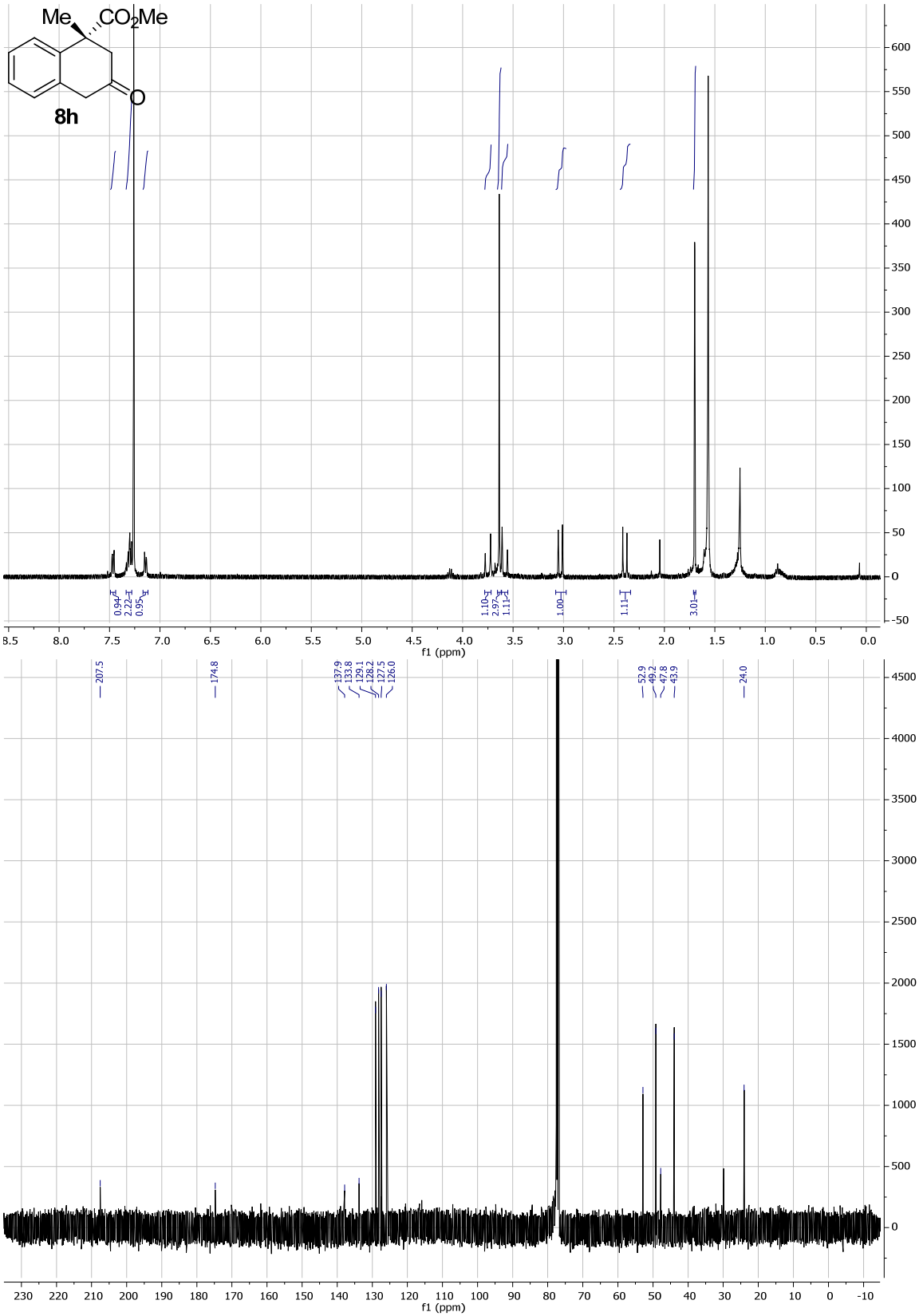

Me
Et
O
8e
f1 (ppm)

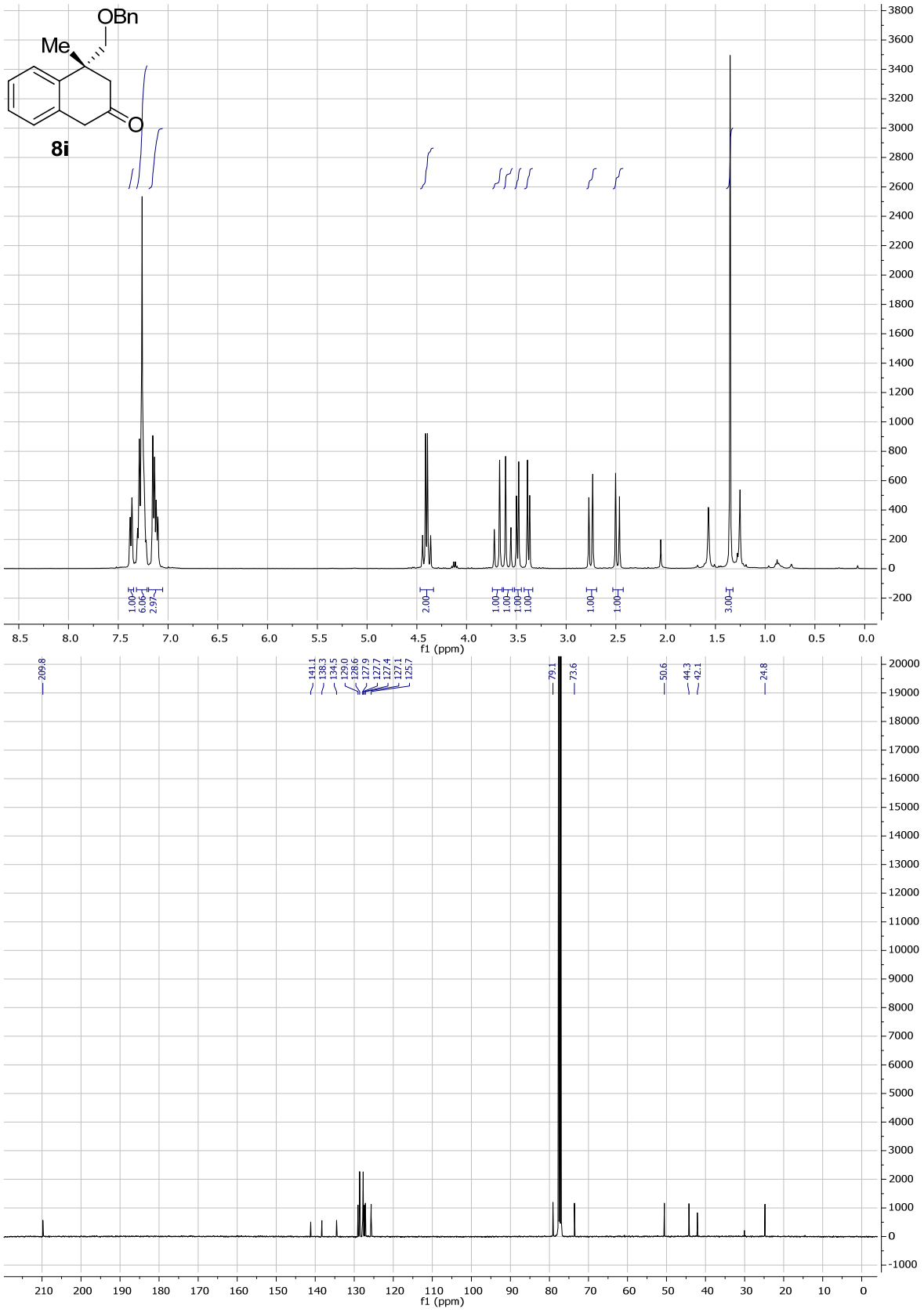

210.4
143.2
133.1
129.1
126.8
126.8
125.7
51.7
43.9
40.5
33.9
26.6
8.9
f1 (ppm)

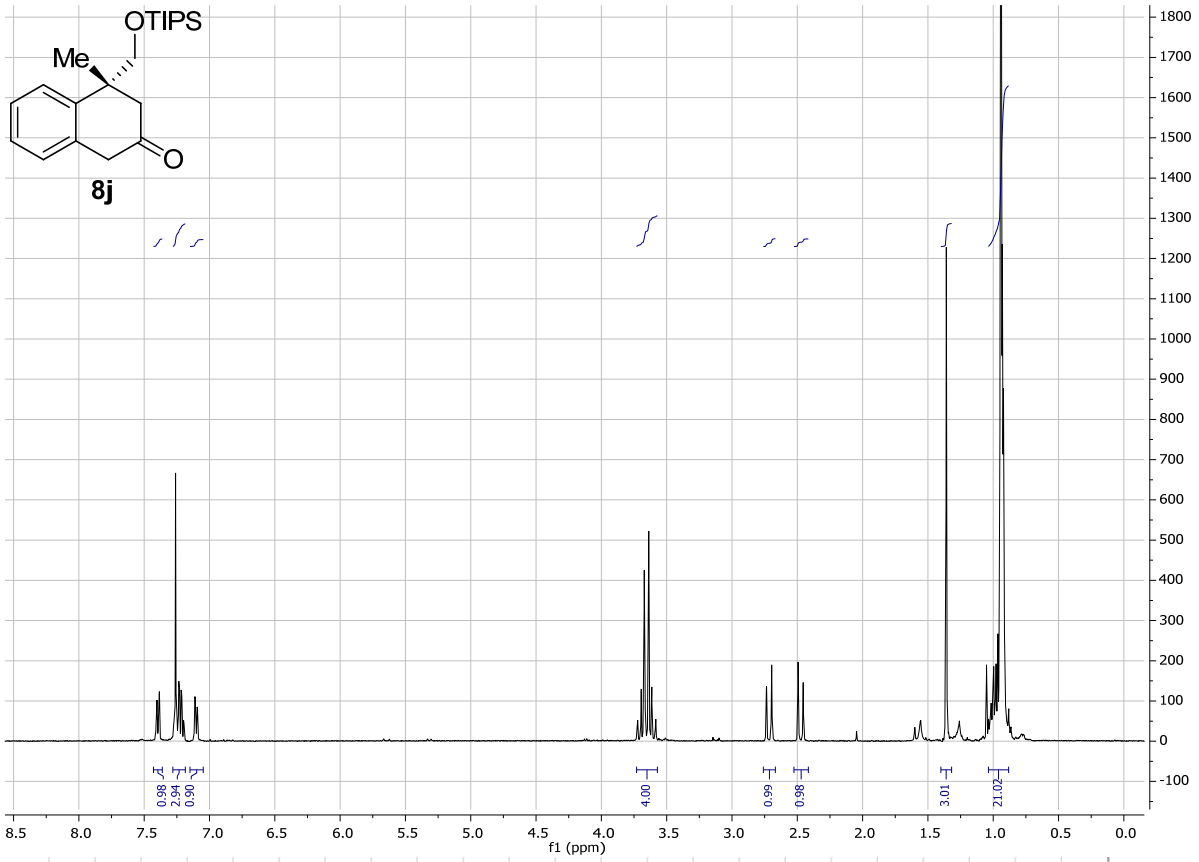

OMe Me
Et
O
8f
f1 (ppm)
210.7
158.8
135.7
130.9
127.8
121.9
110.0
55.5
53.4
44.6
43.8
33.9
27.8
9.6

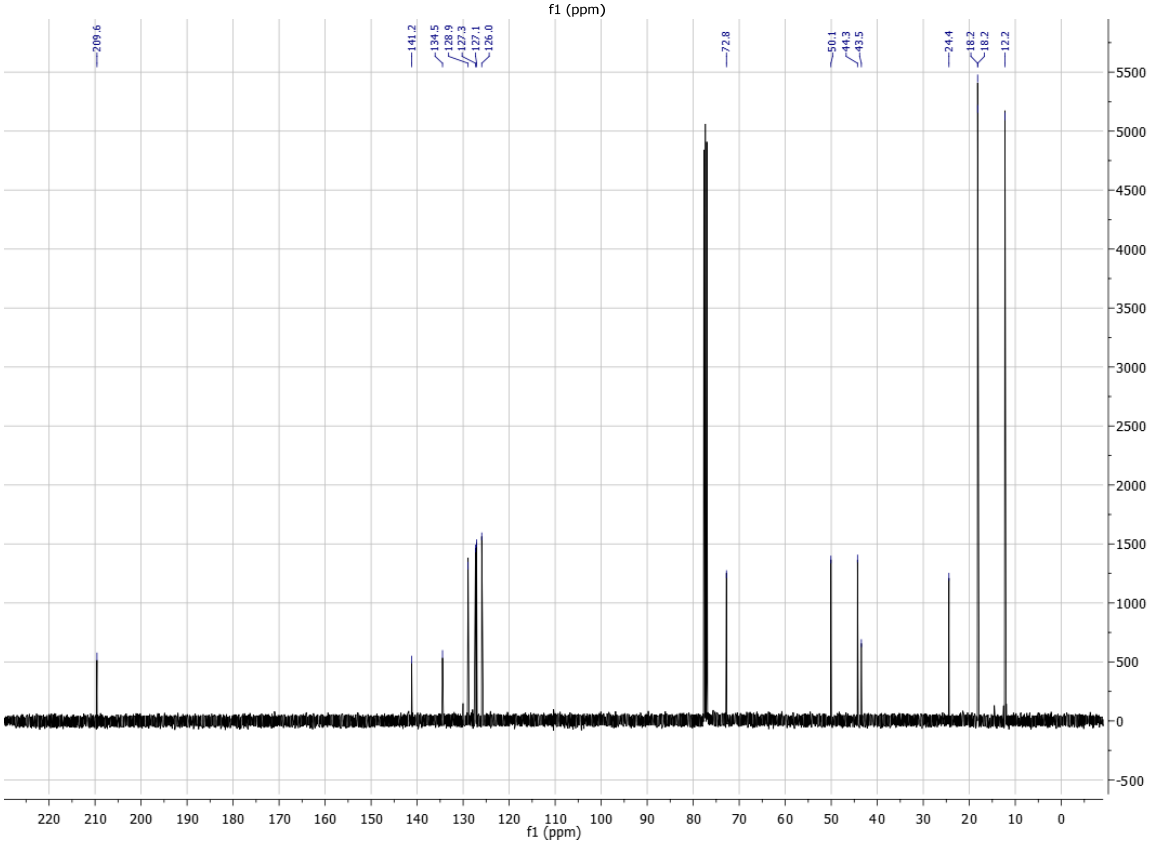

Me
Et
Me
O
8g
1.00
2.00
2.00
1.00
1.01
3.01
4.00
3.00
3.00
f1 (ppm)

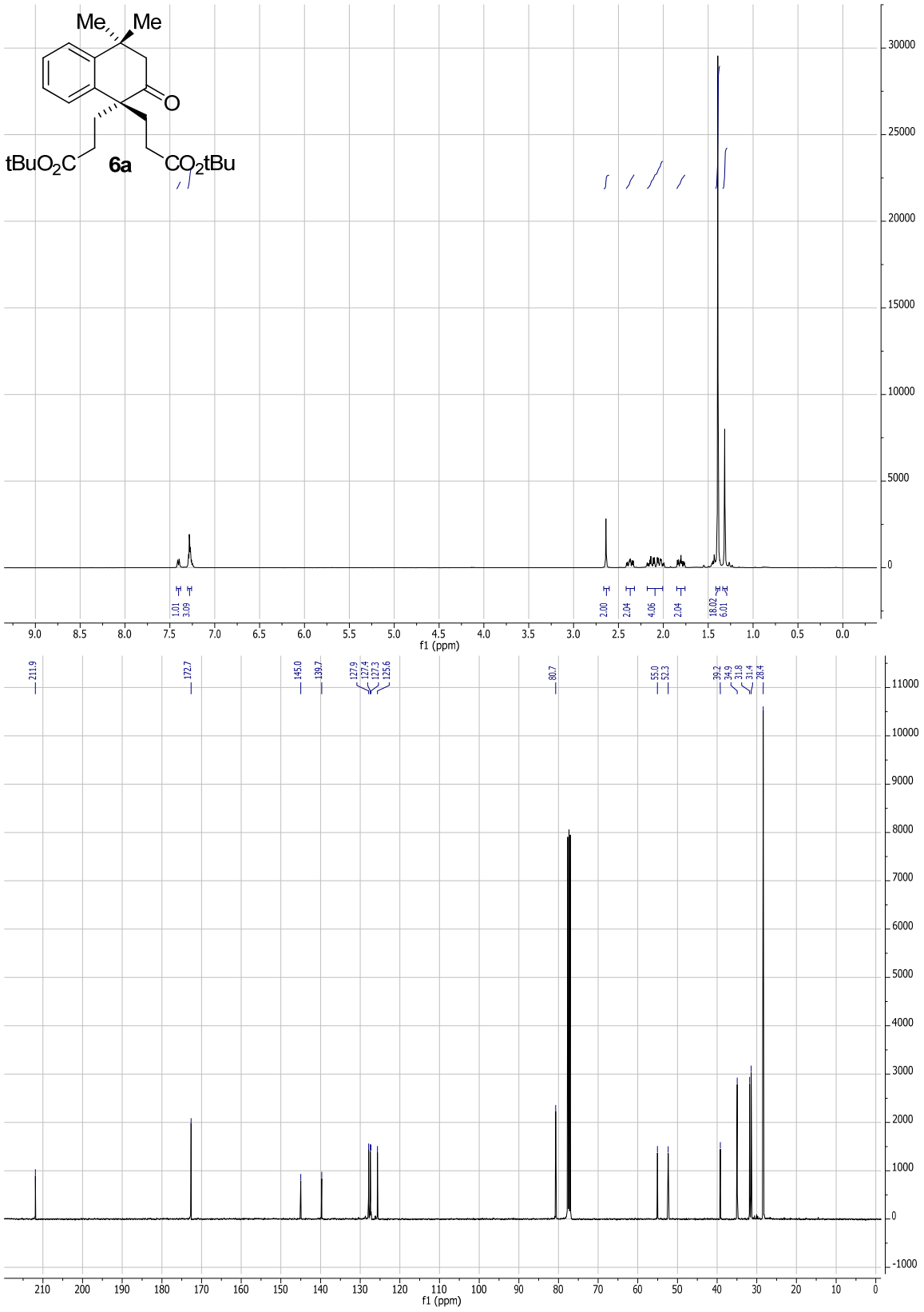

211.0
143.3
136.5
130.1
129.1
127.8
126.4
52.0
43.8
40.7
34.2
26.8
21.7
9.1
f1 (ppm)

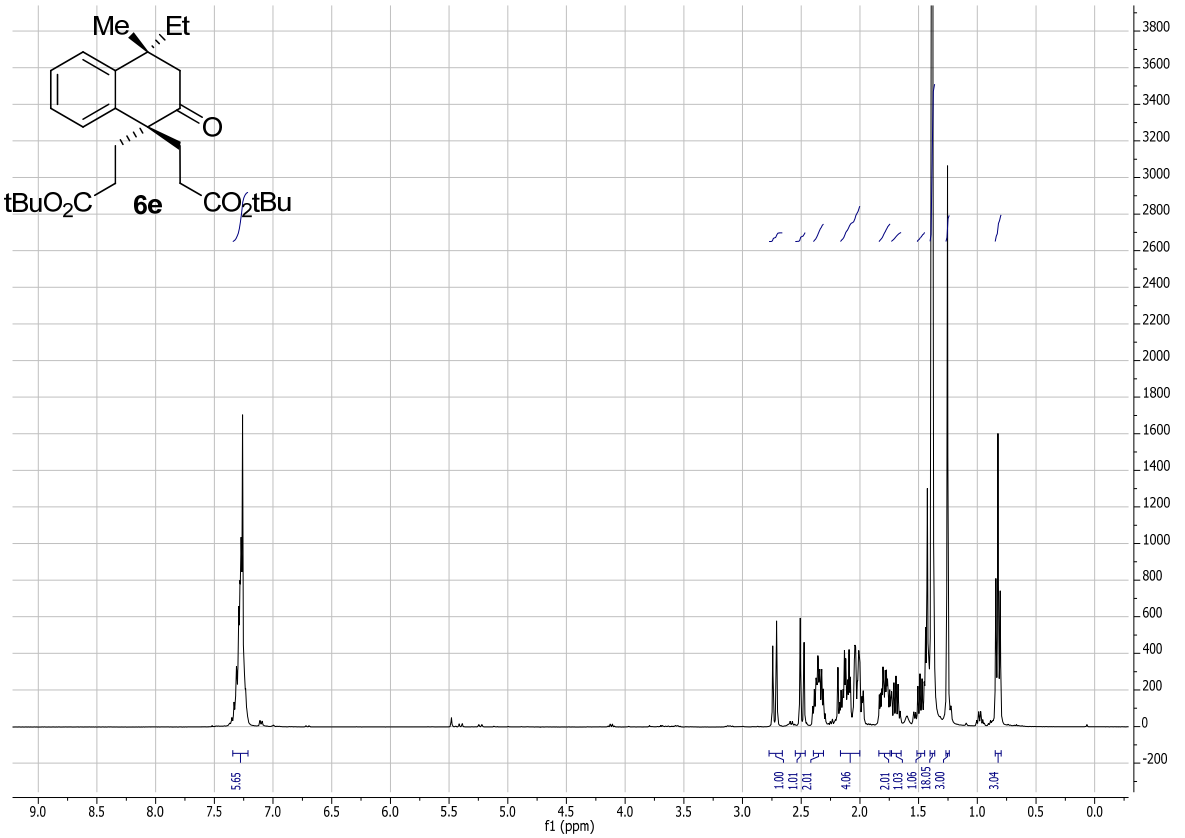


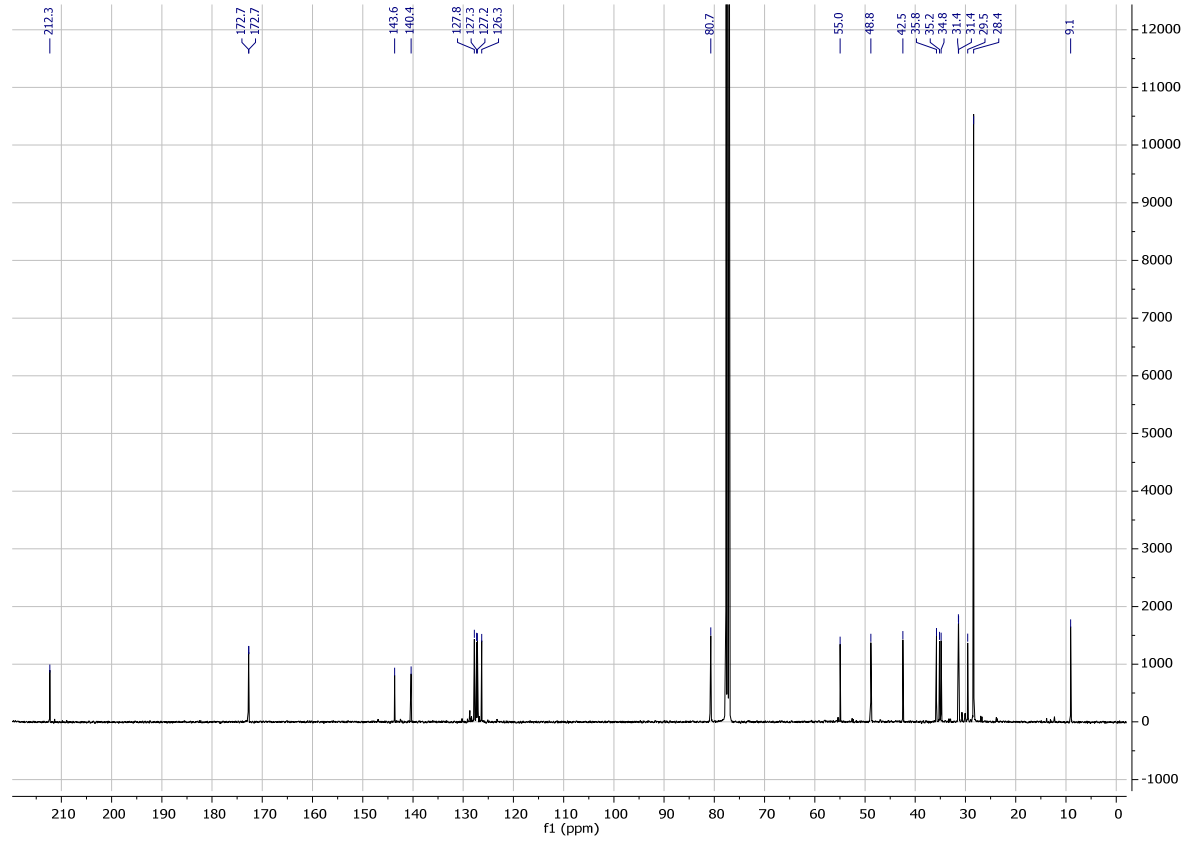

OBn
Me
O
8i
f1 (ppm)
209.8
141.1
138.3
134.5
129.0
128.6
127.9
127.7
127.4
127.1
125.7
79.1
73.6
50.6
44.3
42.1
24.8
f1 (ppm)

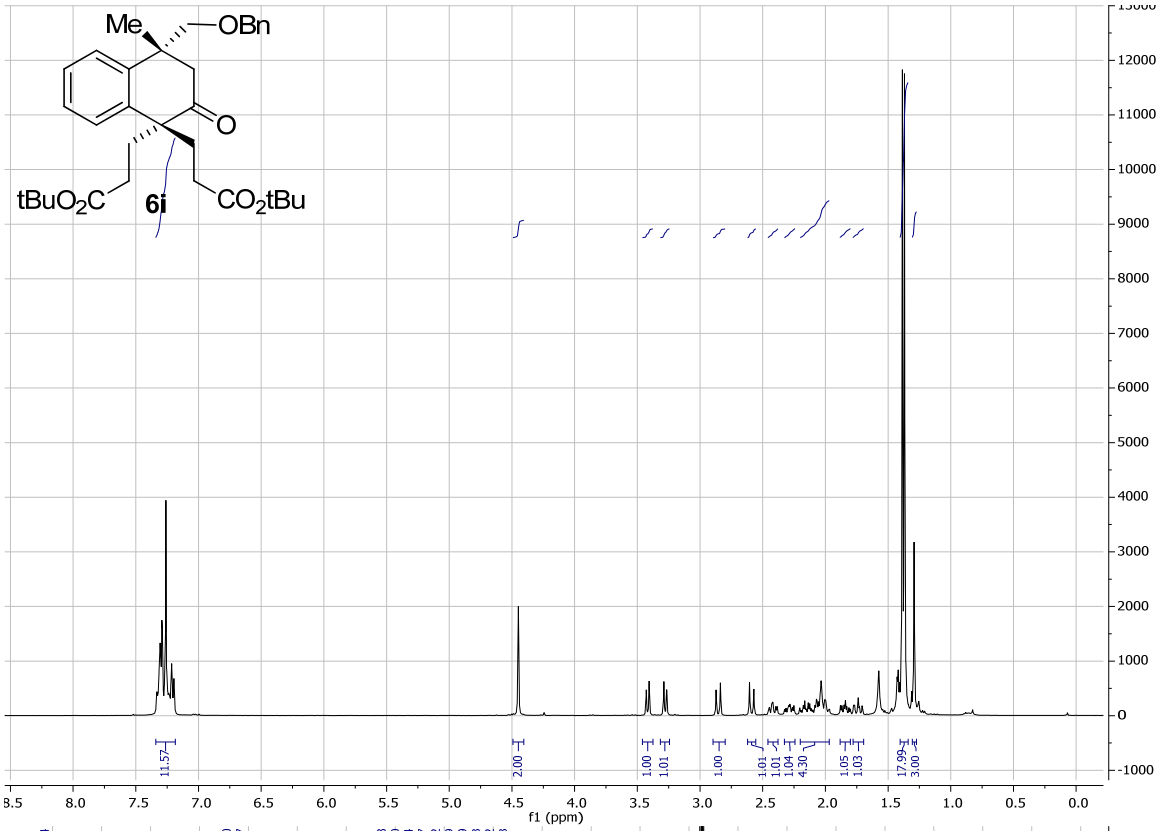

OTIPS
Me
O
8j
0.98
2.94
0.90
4.00
0.99
0.98
3.01
21.02
f1 (ppm)

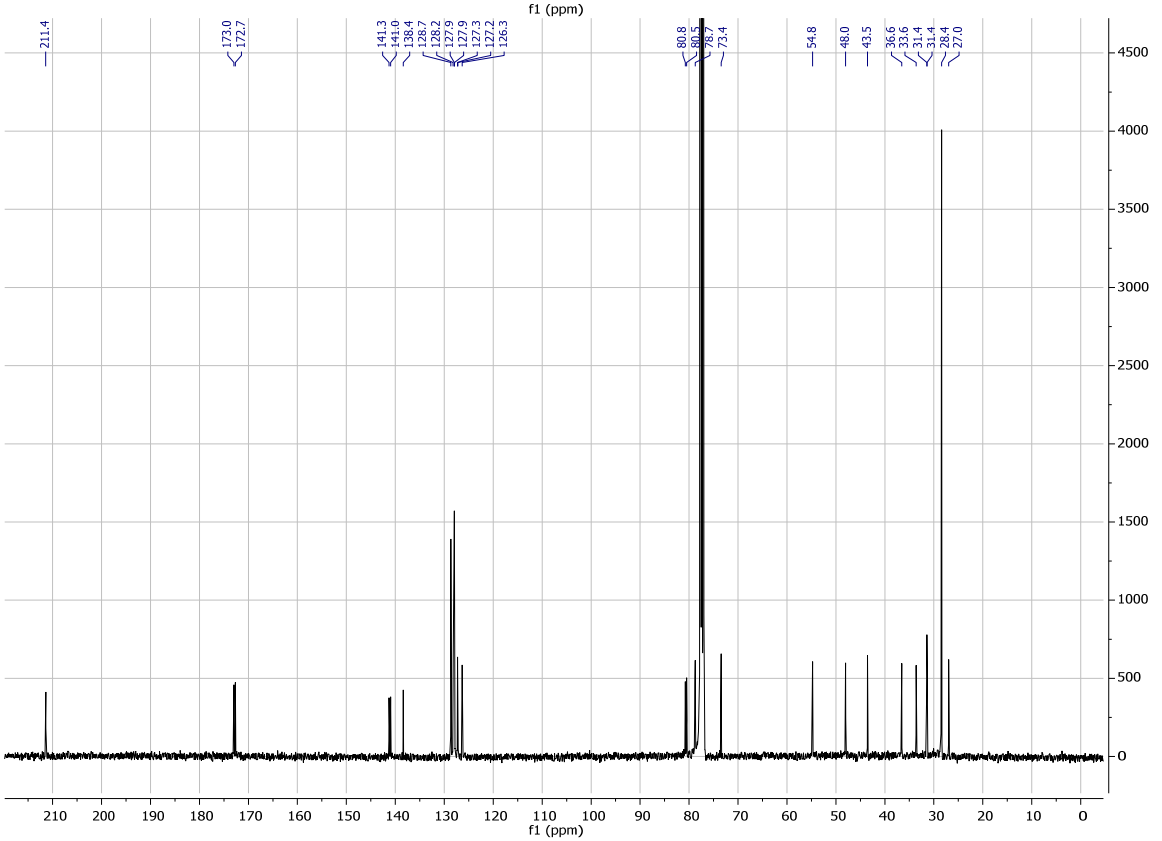

209.6
141.2
134.5
128.9
127.3
127.1
126.0
72.8
50.1
44.3
43.5
24.4
18.2
18.2
12.2
f1 (ppm)

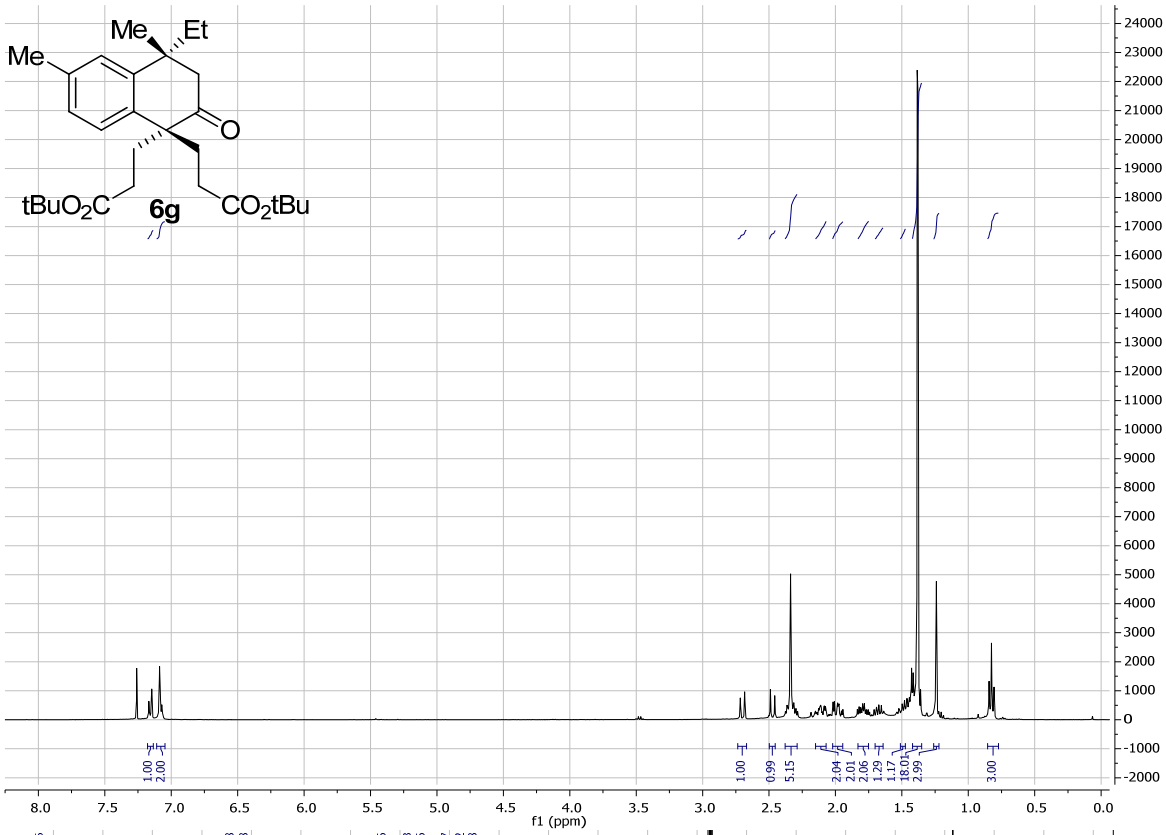

Me
Me
O
tBuO2C
6a
CO2tBu
f1 (ppm)
f1 (ppm)

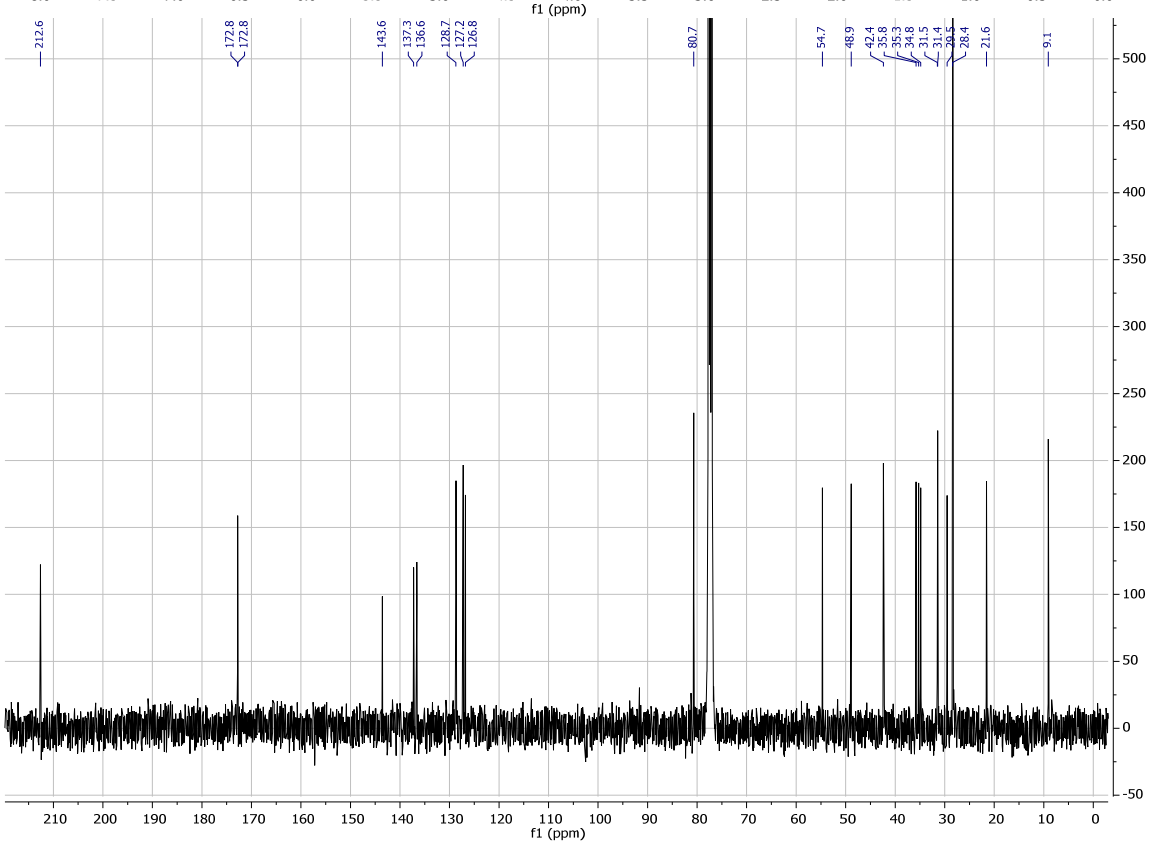

Me
Et
O
tBuO2C
6e
CO2tBu
f1 (ppm)

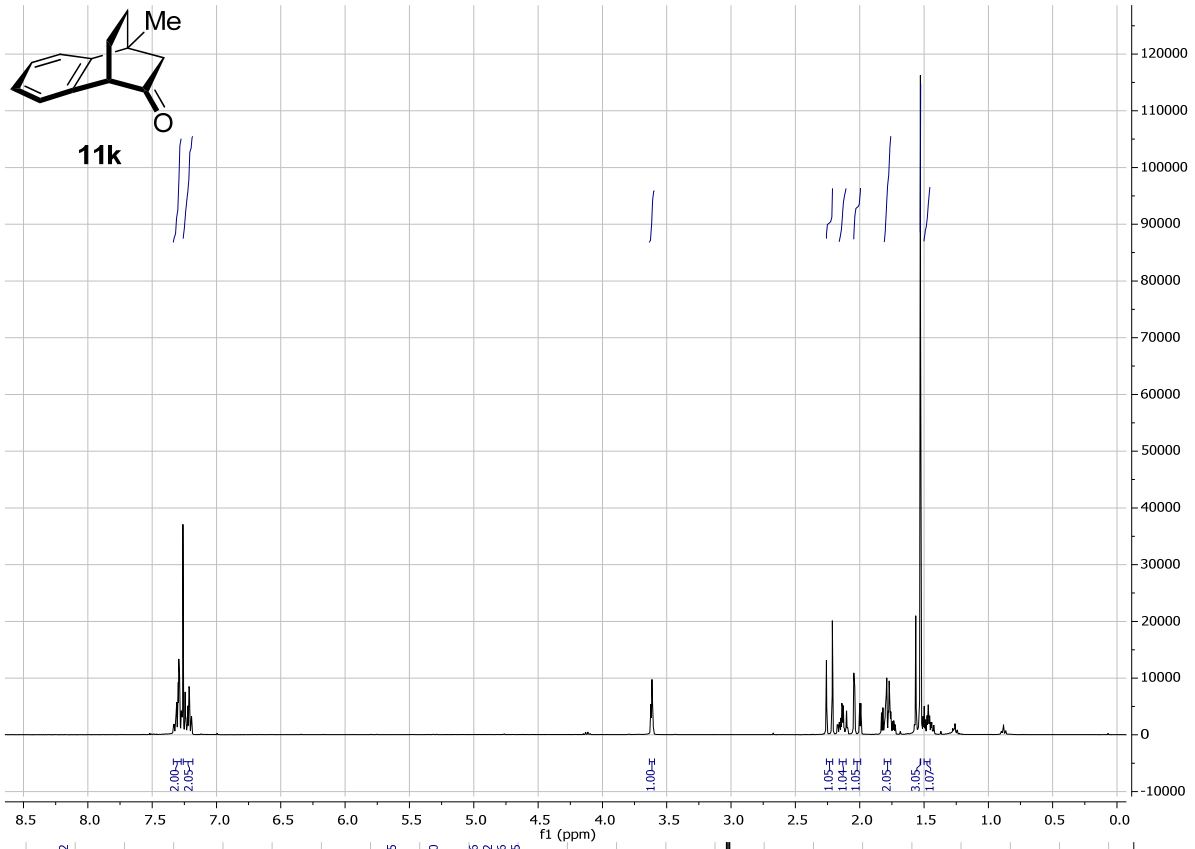

212.3
172.7
172.7
143.6
140.4
127.8
127.3
127.2
126.3
80.7
55.0
48.8
42.5
35.8
35.2
34.8
31.4
31.4
29.5
28.4
9.1
f1 (ppm)

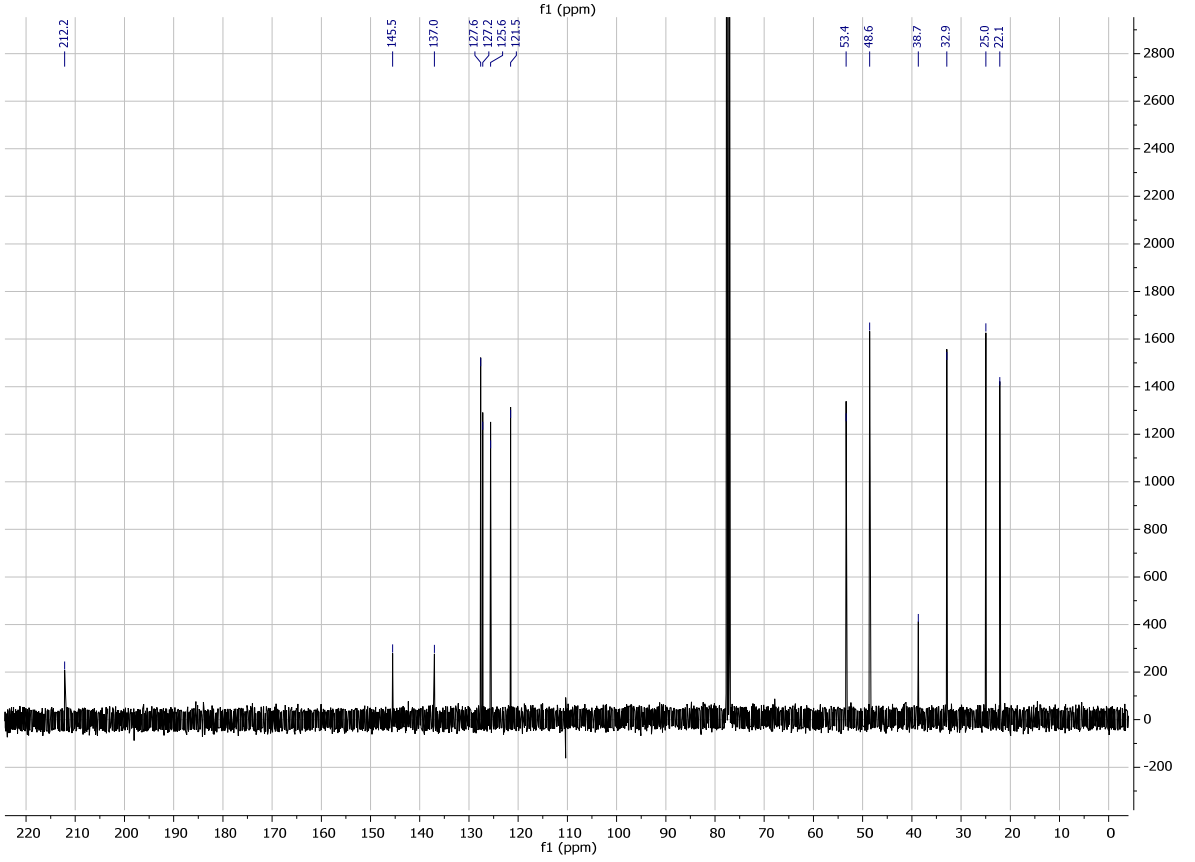

Me
OBn
O
tBuO2C
6i
CO2tBu
11.57
2.00
1.00
1.01
1.00
1.01
1.01
1.04
4.30
1.05
1.03
17.99
3.00
f1 (ppm)

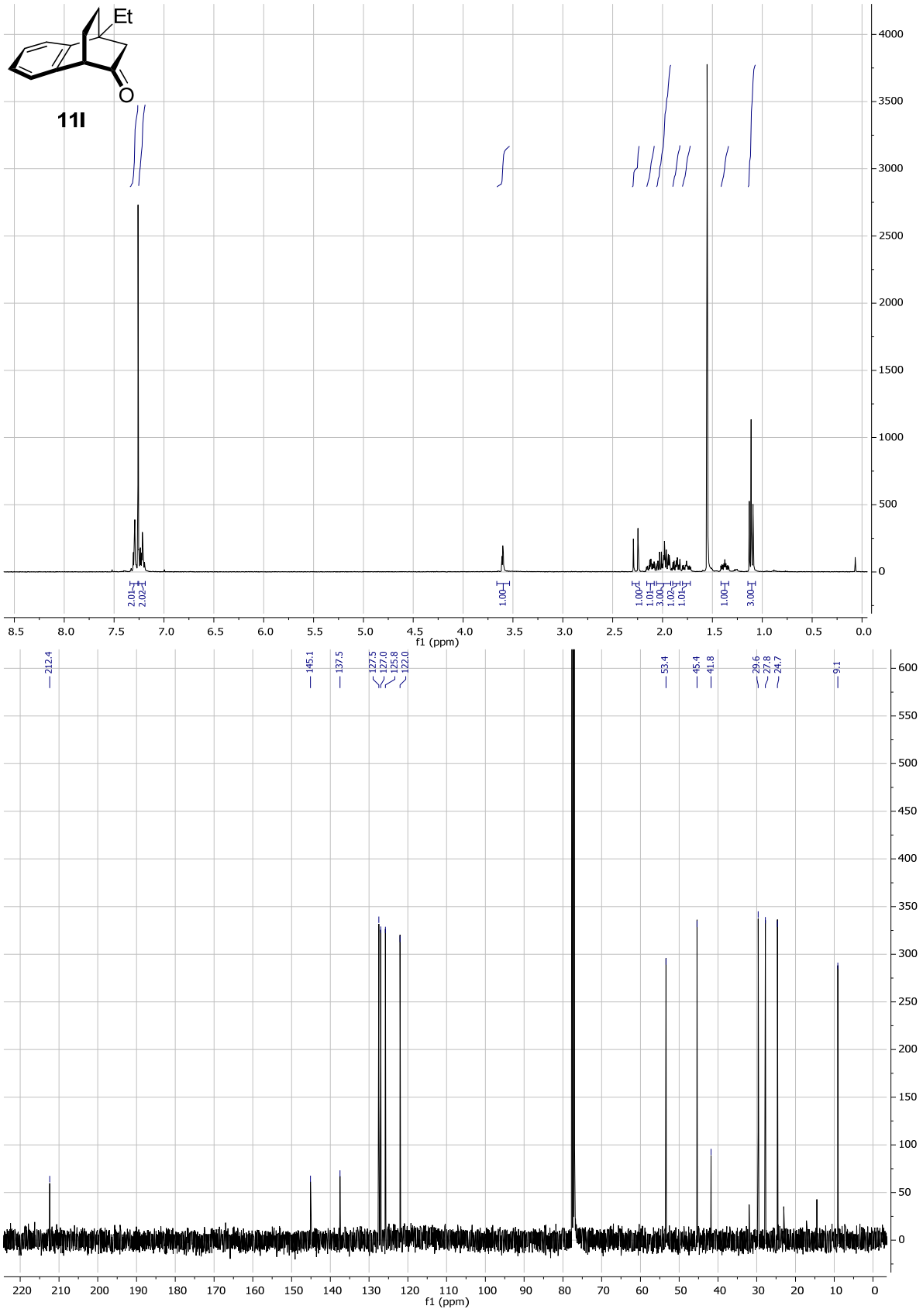

211.4
173.0
172.7
141.3
141.0
138.4
128.7
128.2
127.9
127.9
127.3
127.2
126.3
80.8
80.7
73.4
54.8
48.0
43.5
36.6
33.6
31.4
31.4
28.4
27.0
f1 (ppm)

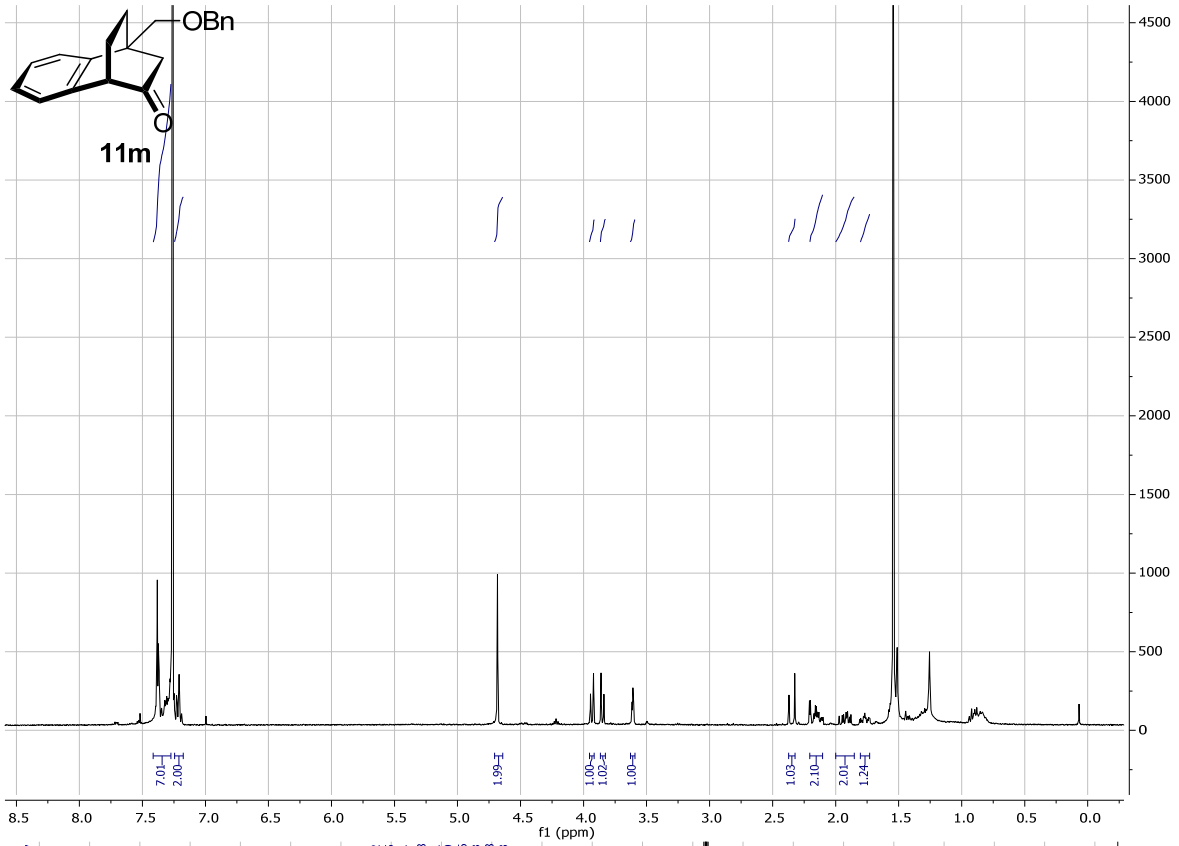

Me
Et
Me
O
tBuO2C
6g
CO2tBu
f1 (ppm)

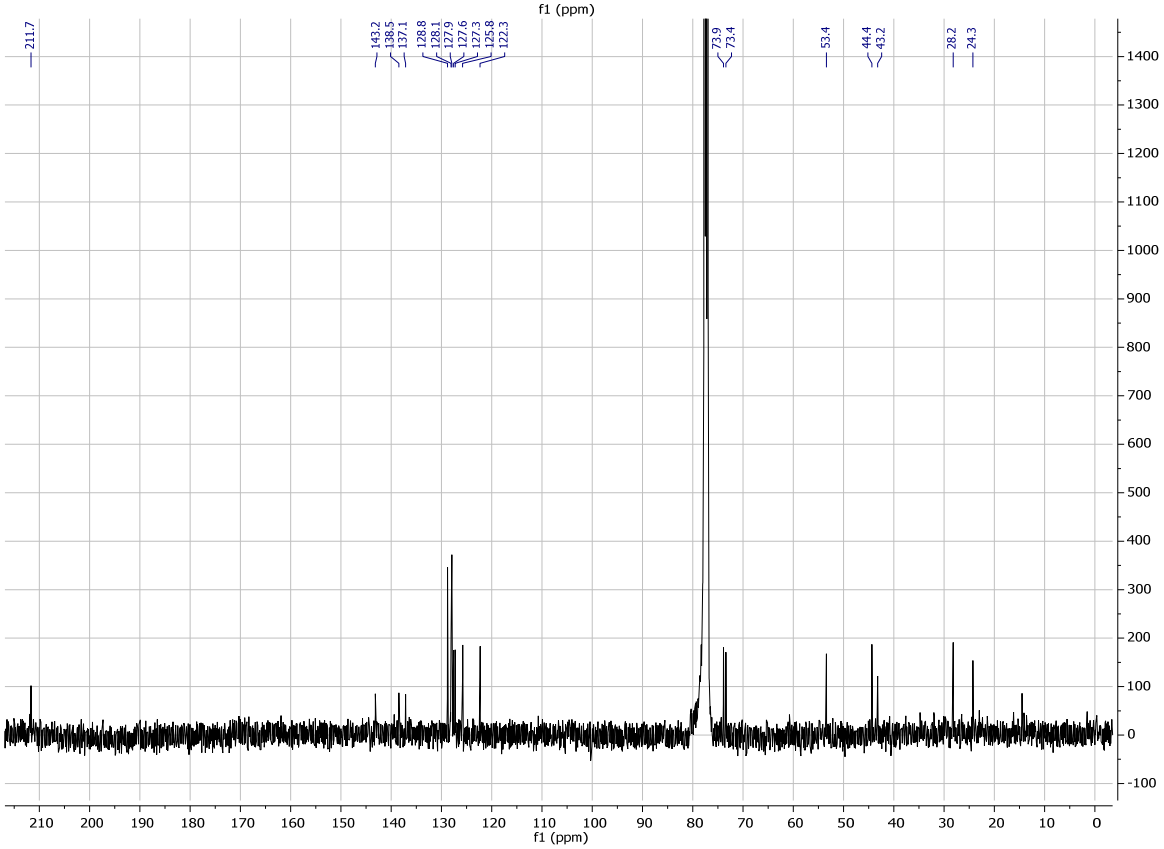

212.6
172.8
172.8
143.6
137.3
136.6
128.7
127.2
126.8
80.7
54.7
48.9
42.4
35.8
35.3
34.8
31.5
31.4
29.5
28.4
21.6
9.1
f1 (ppm)

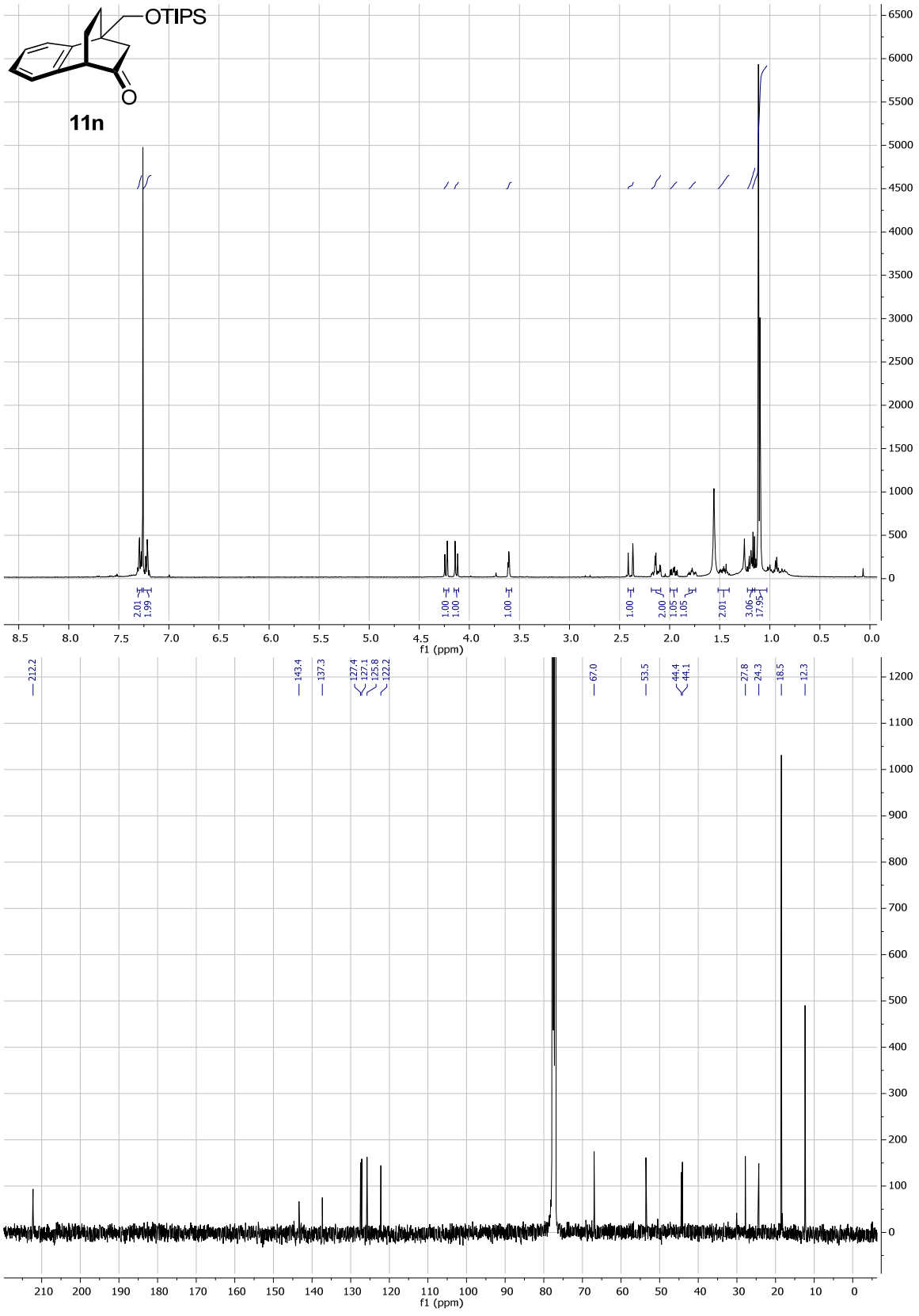

Me
O
11k
2.00
2.05
1.00
1.05
1.04
1.05
2.05
3.05
1.07
f1 (ppm)

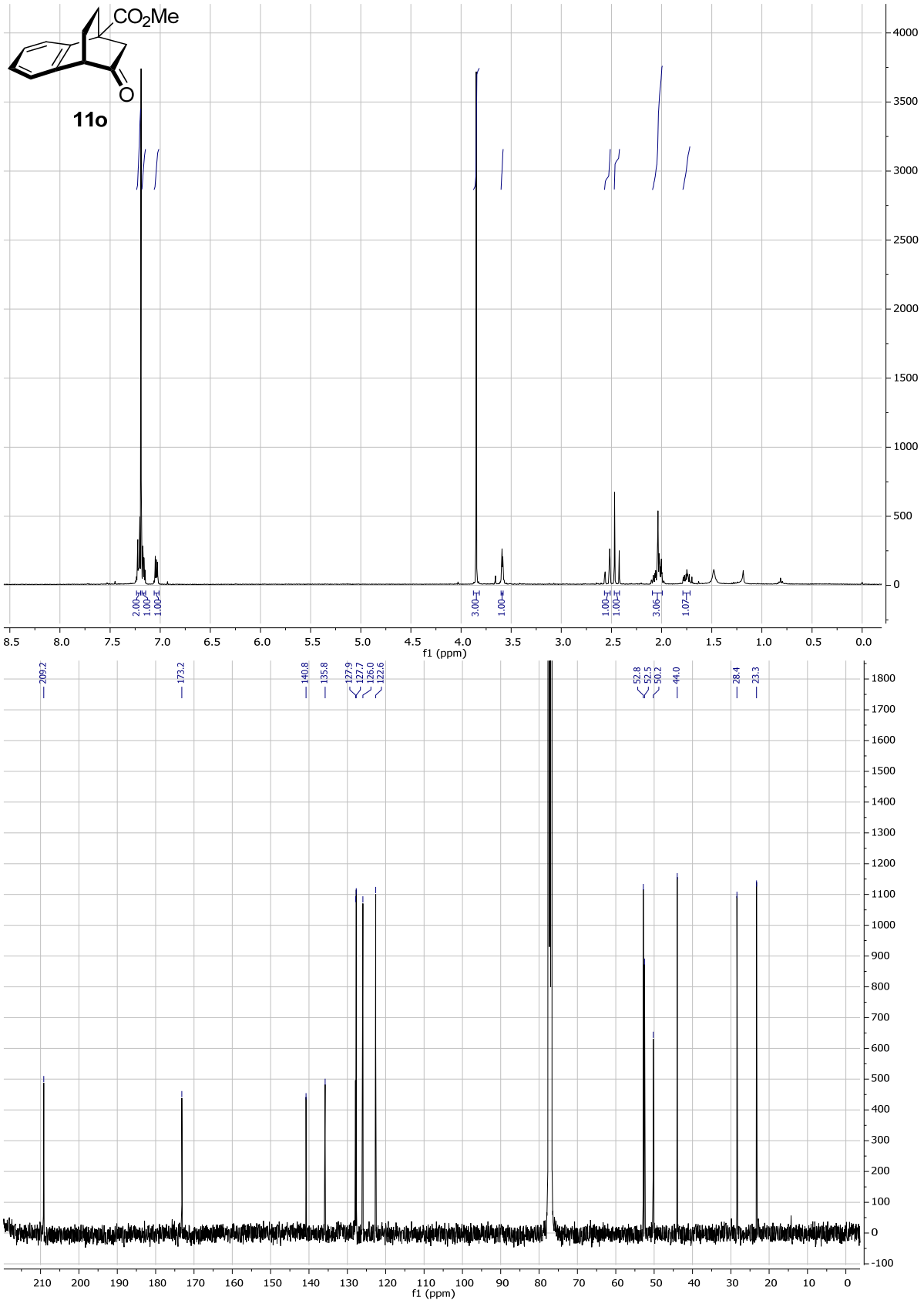

212.2
145.5
137.0
127.6
127.2
125.6
121.5
53.4
48.6
38.7
32.9
25.0
22.1
f1 (ppm)

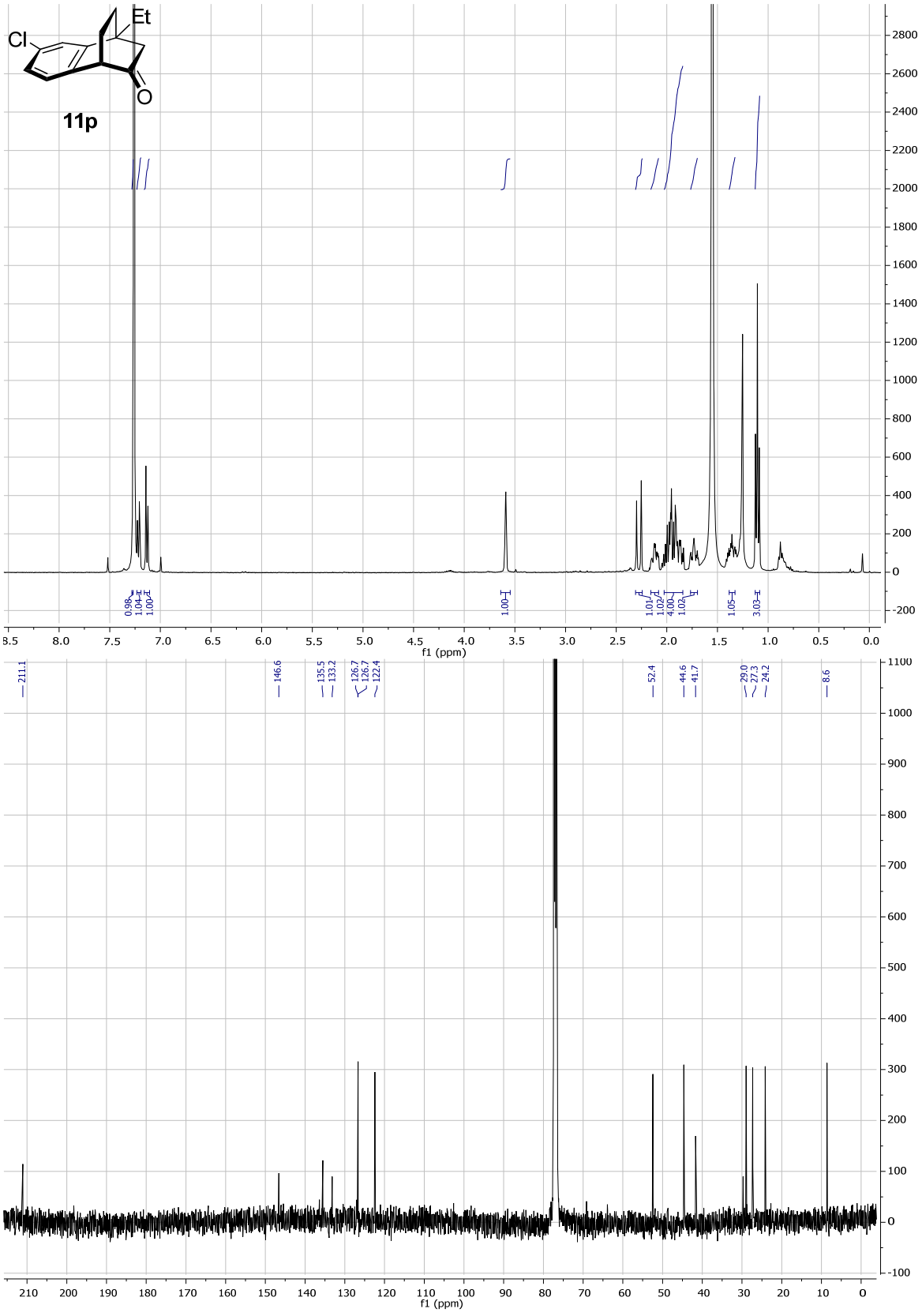

Et
O
11l
f1 (ppm)
212.4
145.1
137.5
127.5
127.0
125.8
122.0
53.4
45.4
41.8
29.6
27.8
24.7
9.1
f1 (ppm)

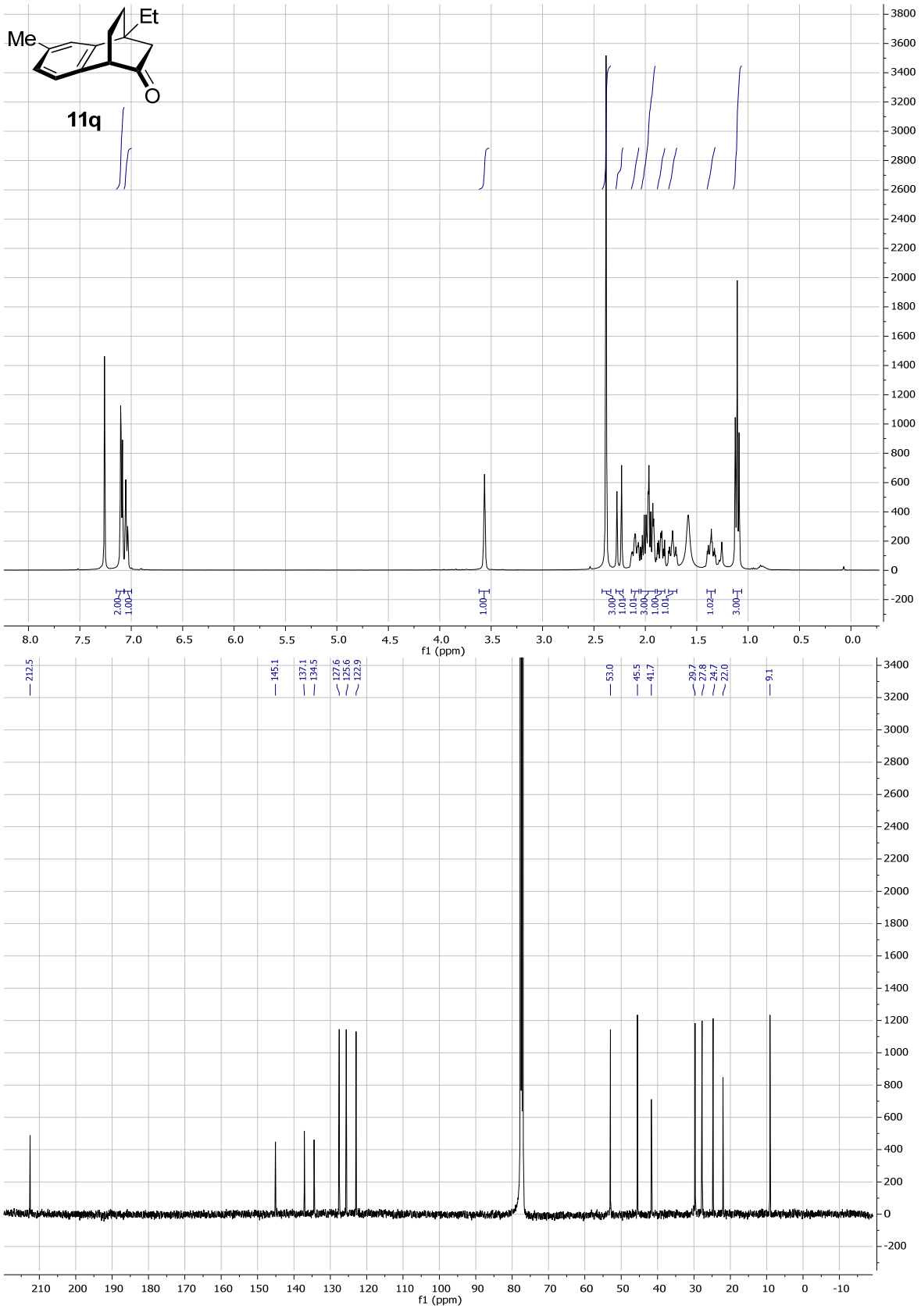

OBn
O
11m
7.01
2.00
1.99
1.00
1.02
1.00
1.03
2.10
2.01
1.24
f1 (ppm)

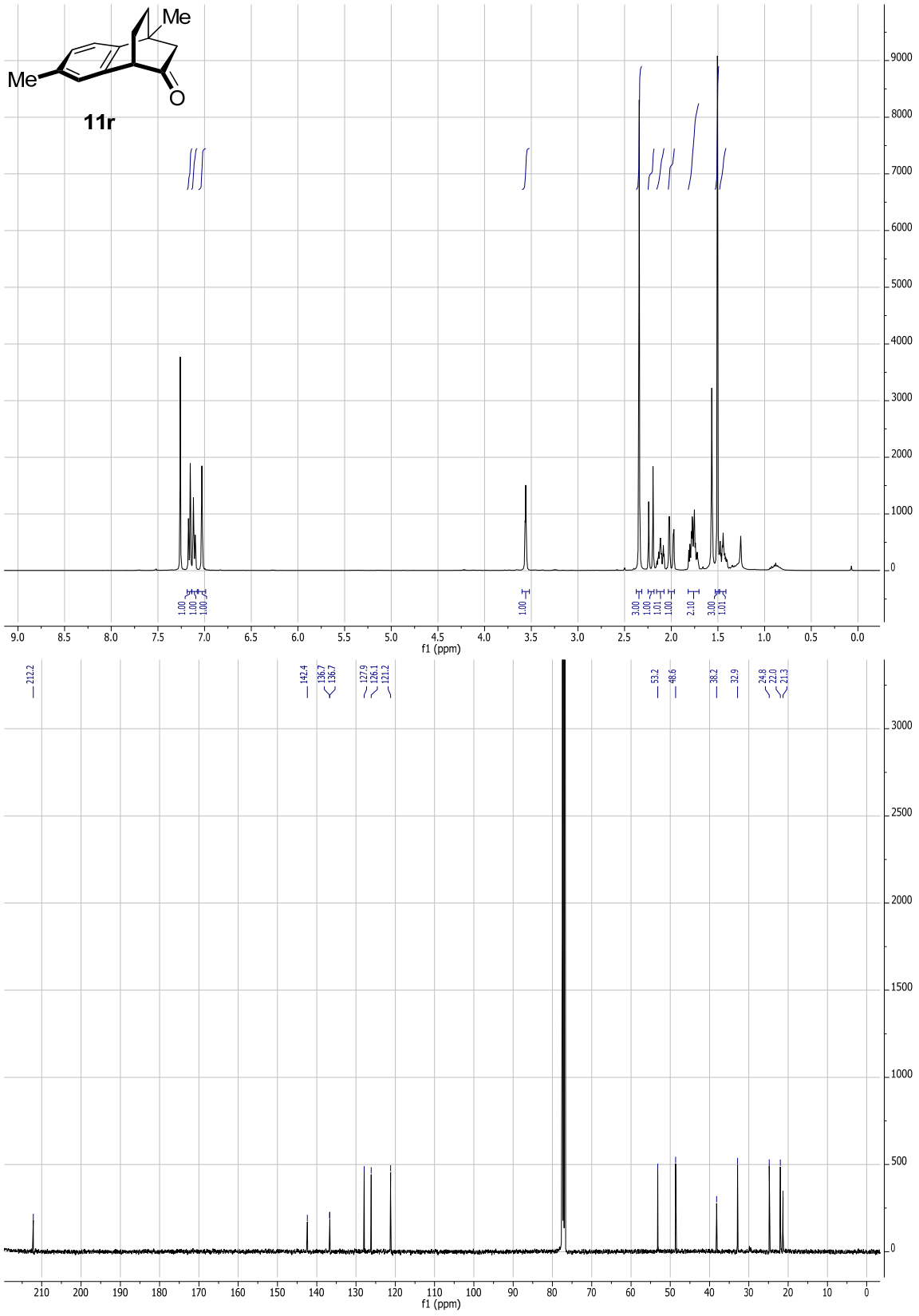

211.7
143.2
138.5
137.1
128.8
128.1
127.9
127.6
127.3
125.8
122.3
73.9
73.4
53.4
44.4
43.2
28.2
24.3
f1 (ppm)

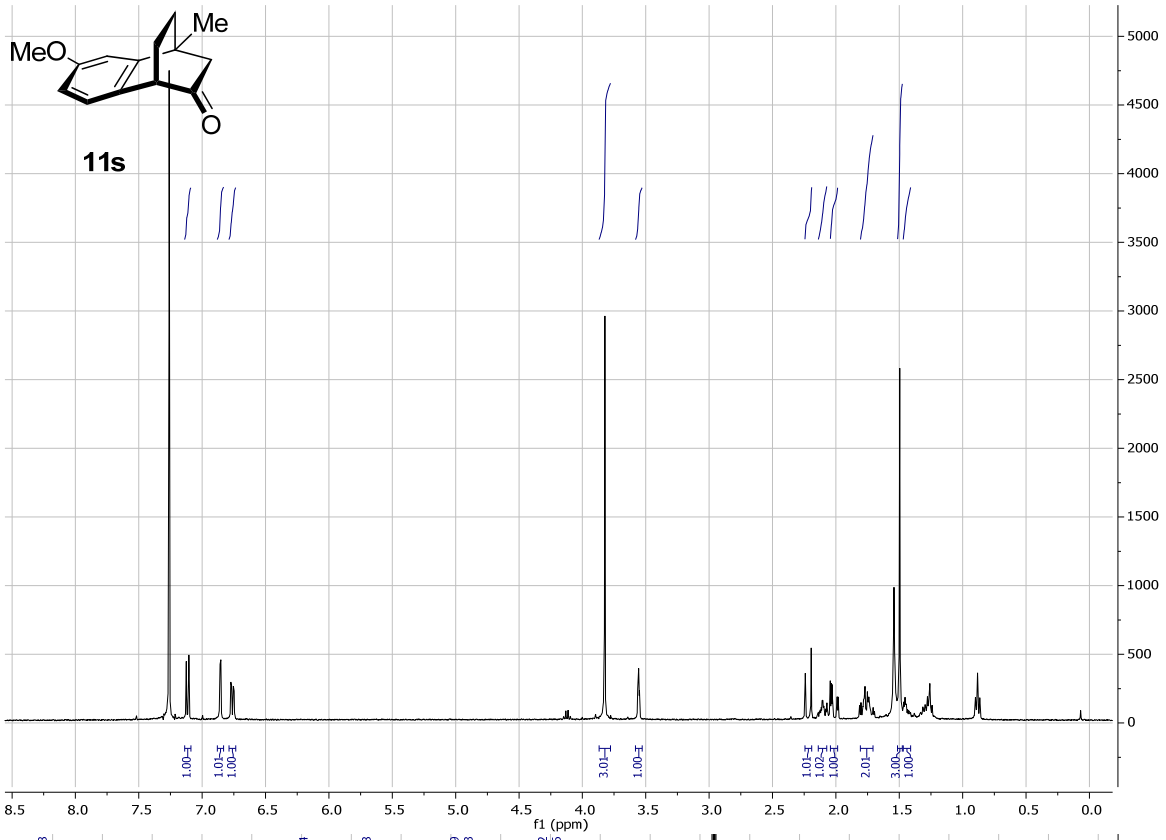

OTIPS
O
11n
f1 (ppm)
212.2
143.4
137.3
127.4
127.1
125.8
122.2
67.0
53.5
44.4
44.1
27.8
24.3
18.5
12.3
f1 (ppm)

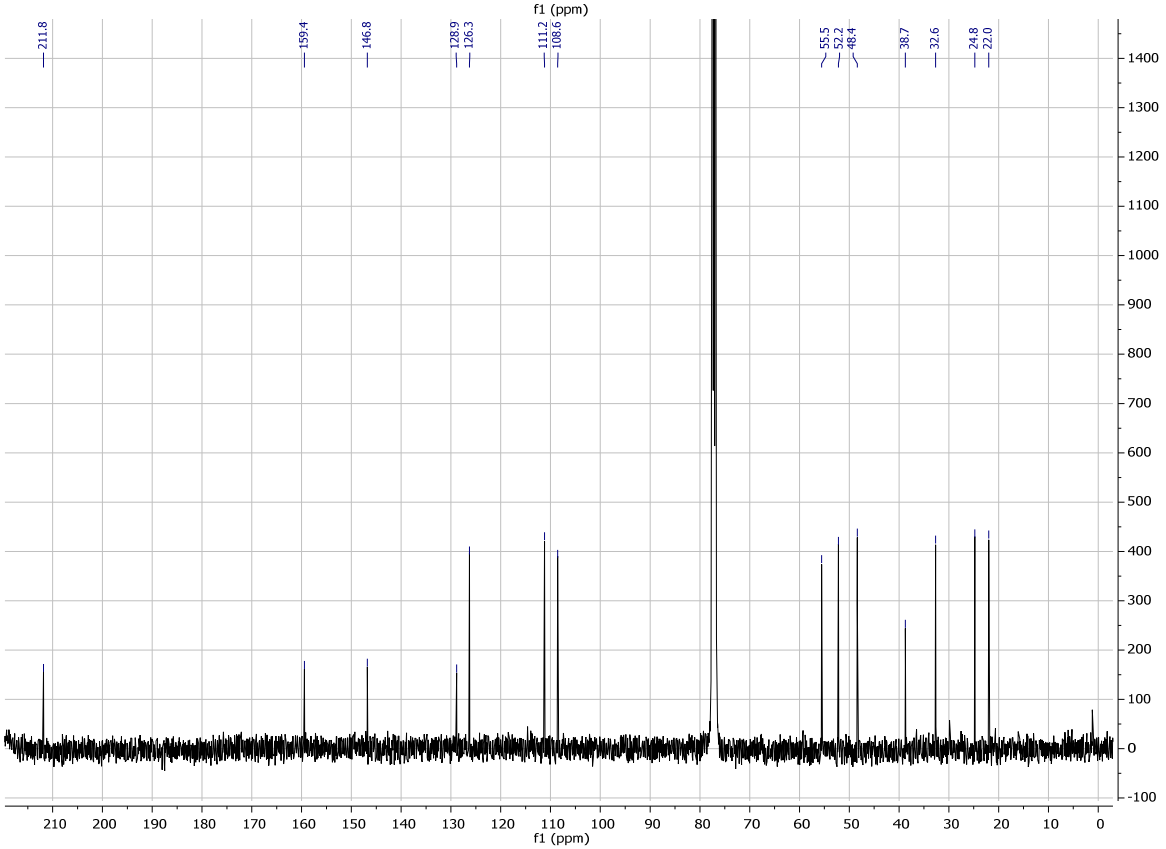

CO2Me
O
11o
f1 (ppm)
209.2
173.2
140.8
135.8
127.9
127.7
126.0
122.6
52.8
52.5
50.2
44.0
28.4
23.3
f1 (ppm)

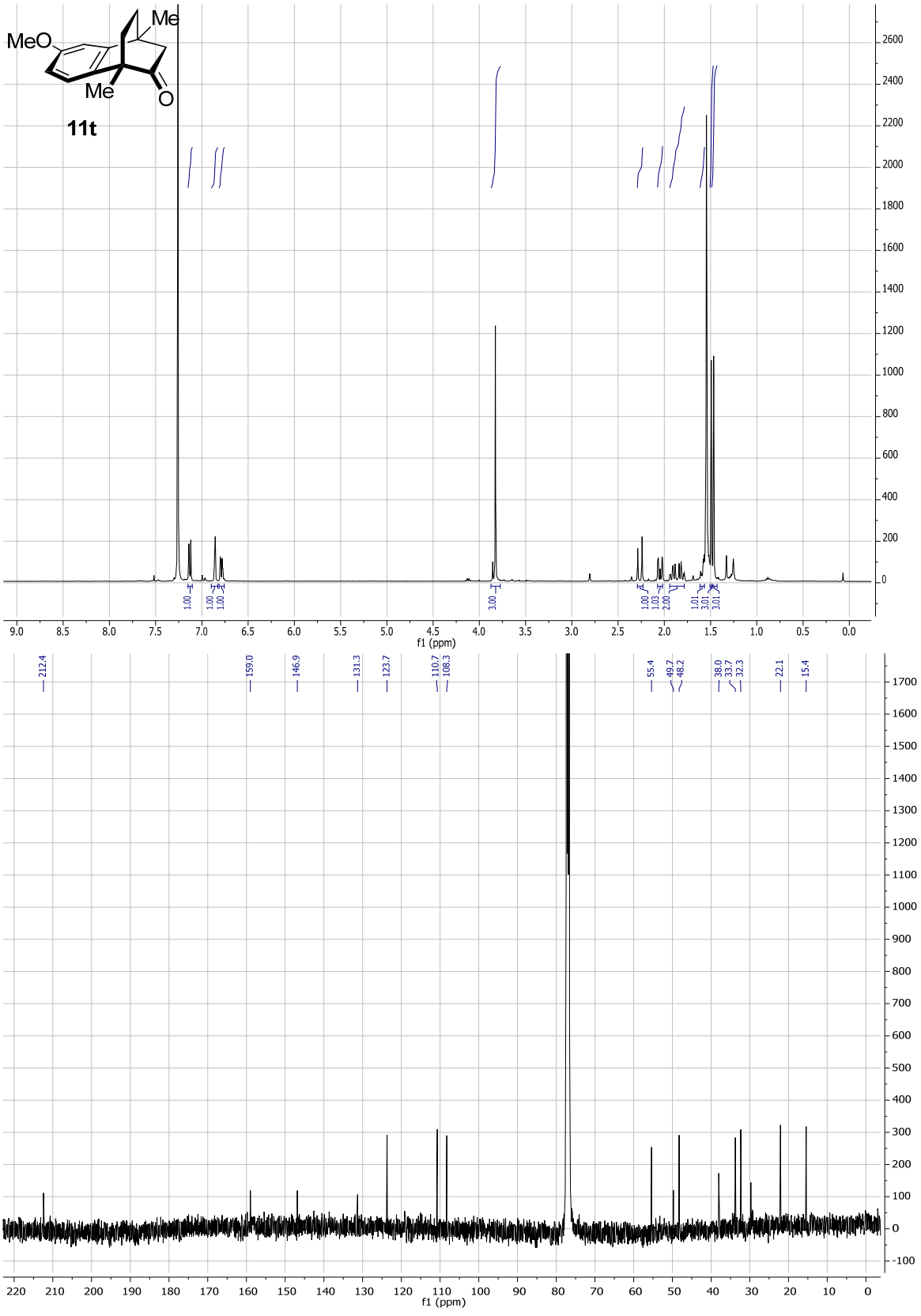

Cl
Et
O
11p
f1 (ppm)
211.1
146.6
135.5
133.2
126.7
126.7
122.4
52.4
44.6
41.7
29.0
27.3
24.2
8.6
f1 (ppm)

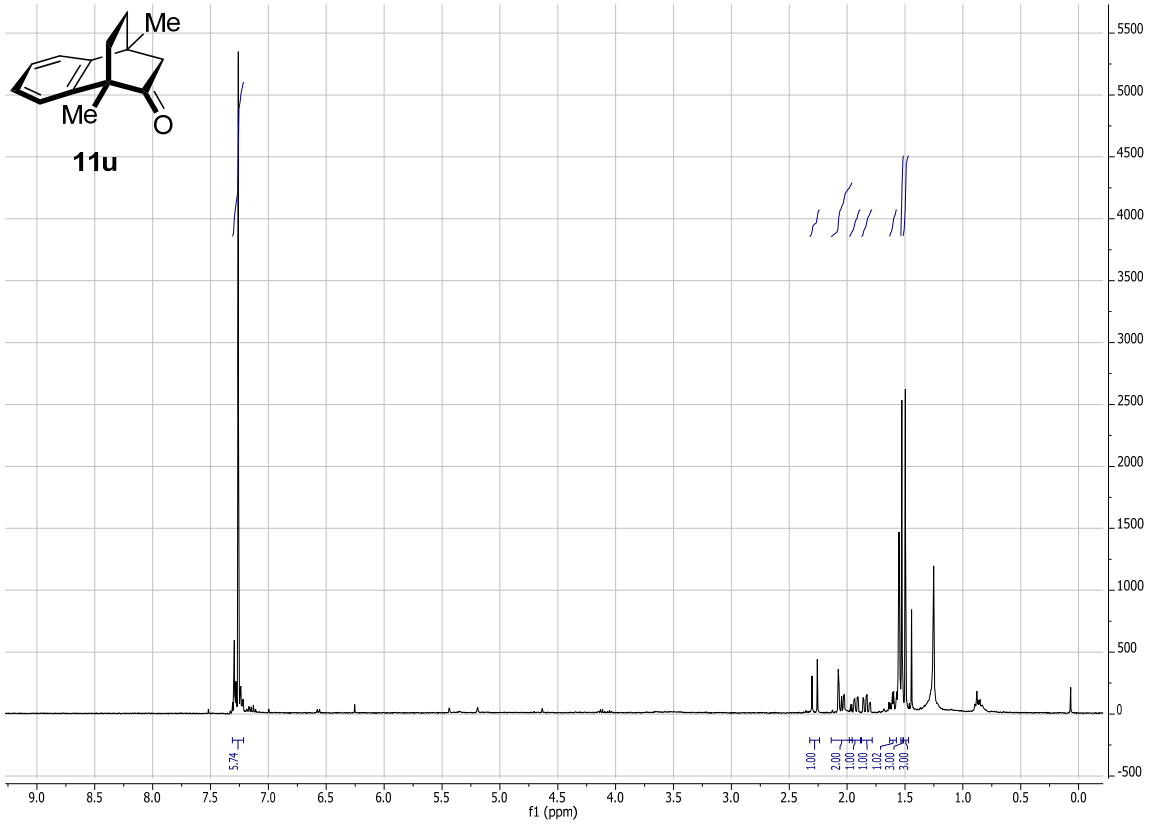

Me
Et
O
11q
f1 (ppm)
212.5
145.1
137.1
134.5
127.6
125.6
122.9
53.0
45.5
41.7
29.7
27.8
24.7
22.0
9.1

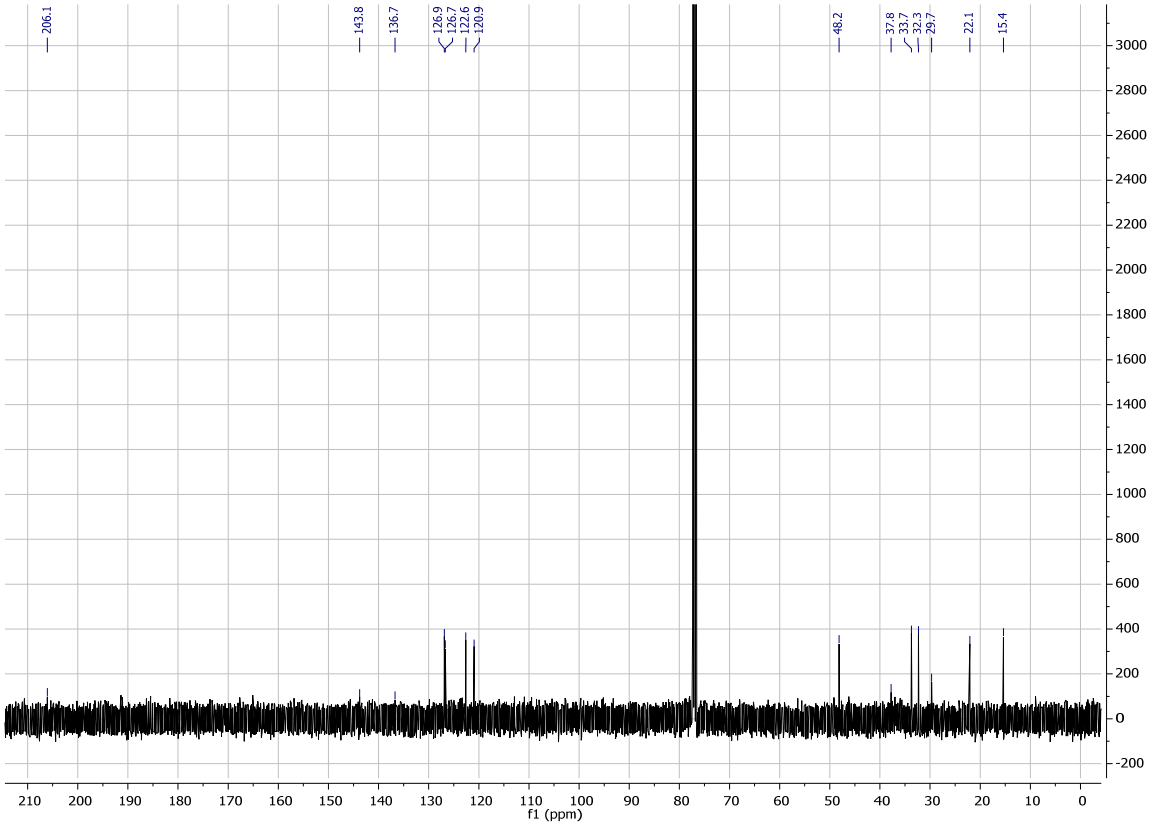

Me
Me
O
11r
f1 (ppm)
212.2
142.4
136.7
136.7
127.9
126.1
121.2
53.2
48.6
38.2
32.9
24.8
22.0
21.3
f1 (ppm)

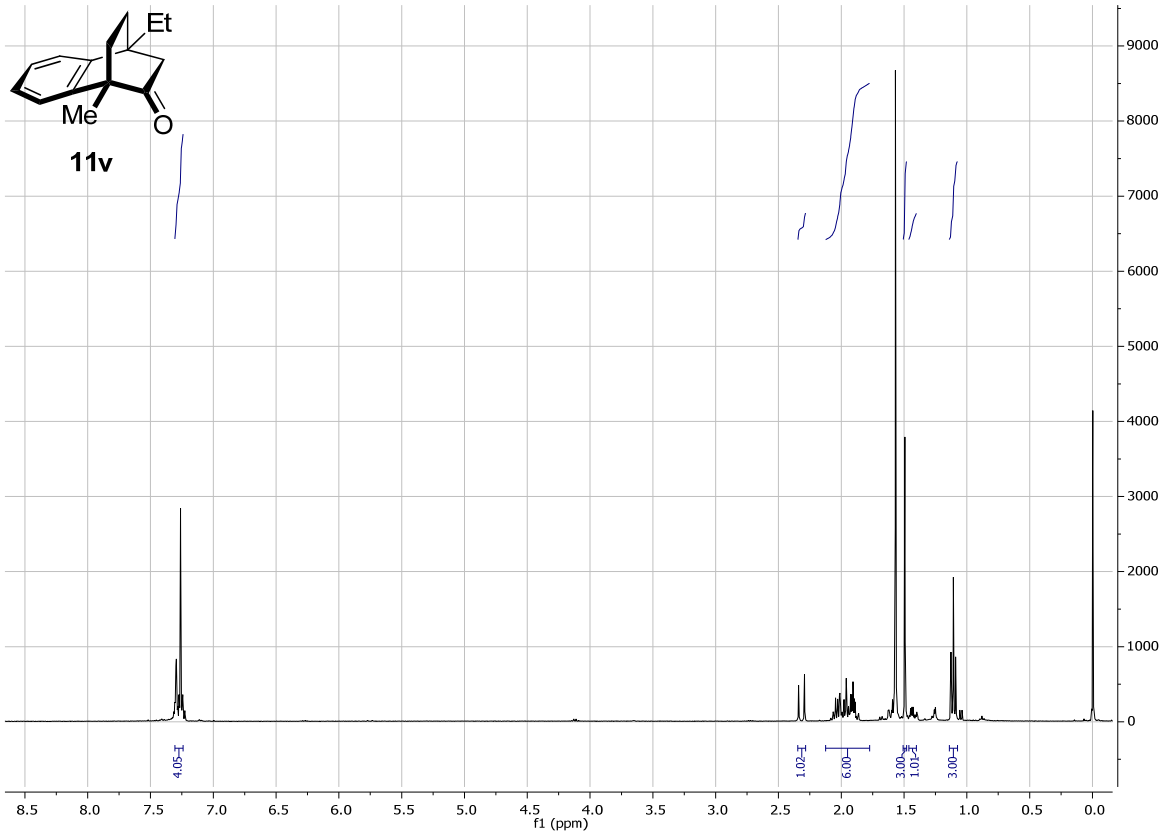

Me
MeO
O
11s
f1 (ppm)

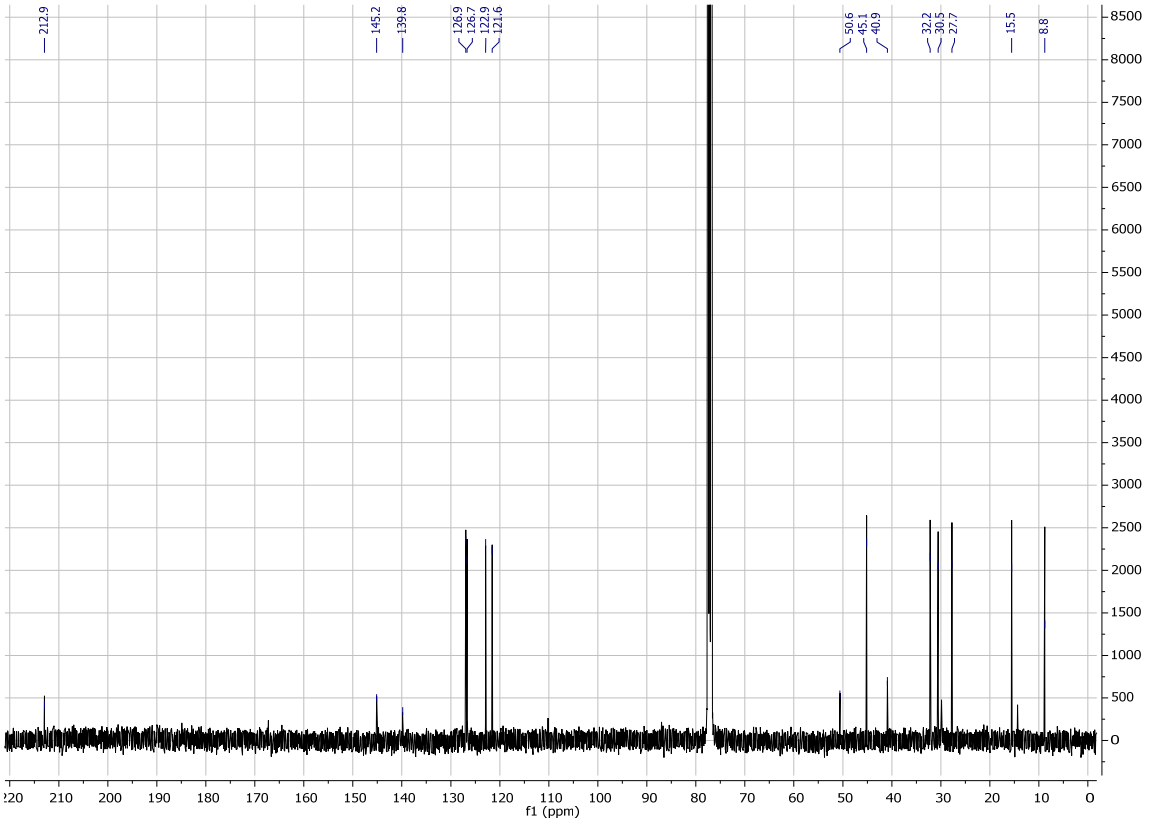

211.8
159.4
146.8
128.9
126.3
111.2
108.6
55.5
52.2
48.4
38.7
32.6
24.8
22.0
f1 (ppm)




Me
Me
O
11u
5.74
1.00
2.00
1.00
1.00
1.02
3.00
3.00
f1 (ppm)


206.1
143.8
136.7
126.9
126.7
125.6
120.9
48.2
37.8
33.7
32.3
29.7
22.1
15.4
f1 (ppm)


Et
Me
O
11v
4.05
1.02
6.00
3.00
1.01
3.00
f1 (ppm)


212.9
145.2
139.8
126.9
126.7
122.9
121.6
50.6
45.1
40.9
32.2
30.5
27.7
15.5
8.8
f1 (ppm)