Supporting information for

Catalyst Controlled Formal [4+3] Cycloaddition Applied to the Total Synthesis of (+)-Barekoxide and (-)-Barekol

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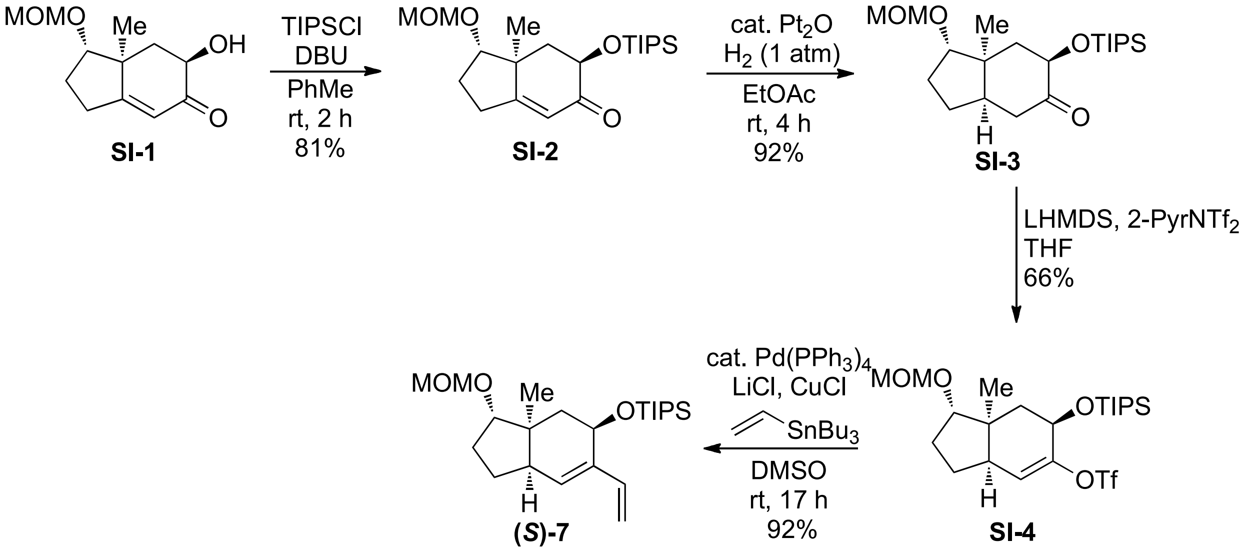
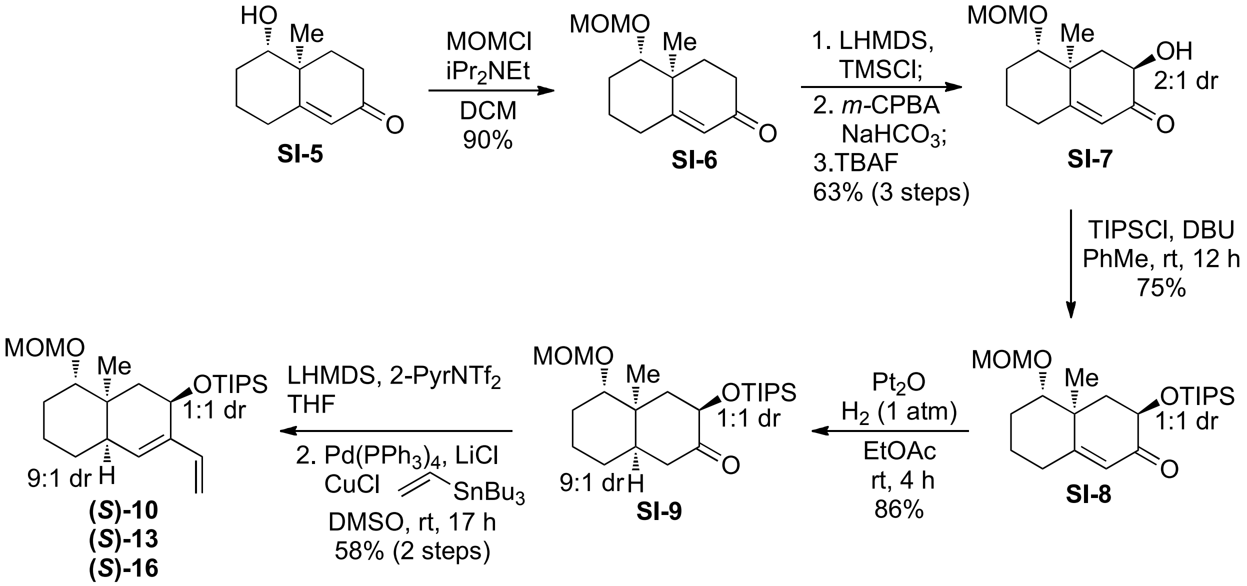
Supporting Information

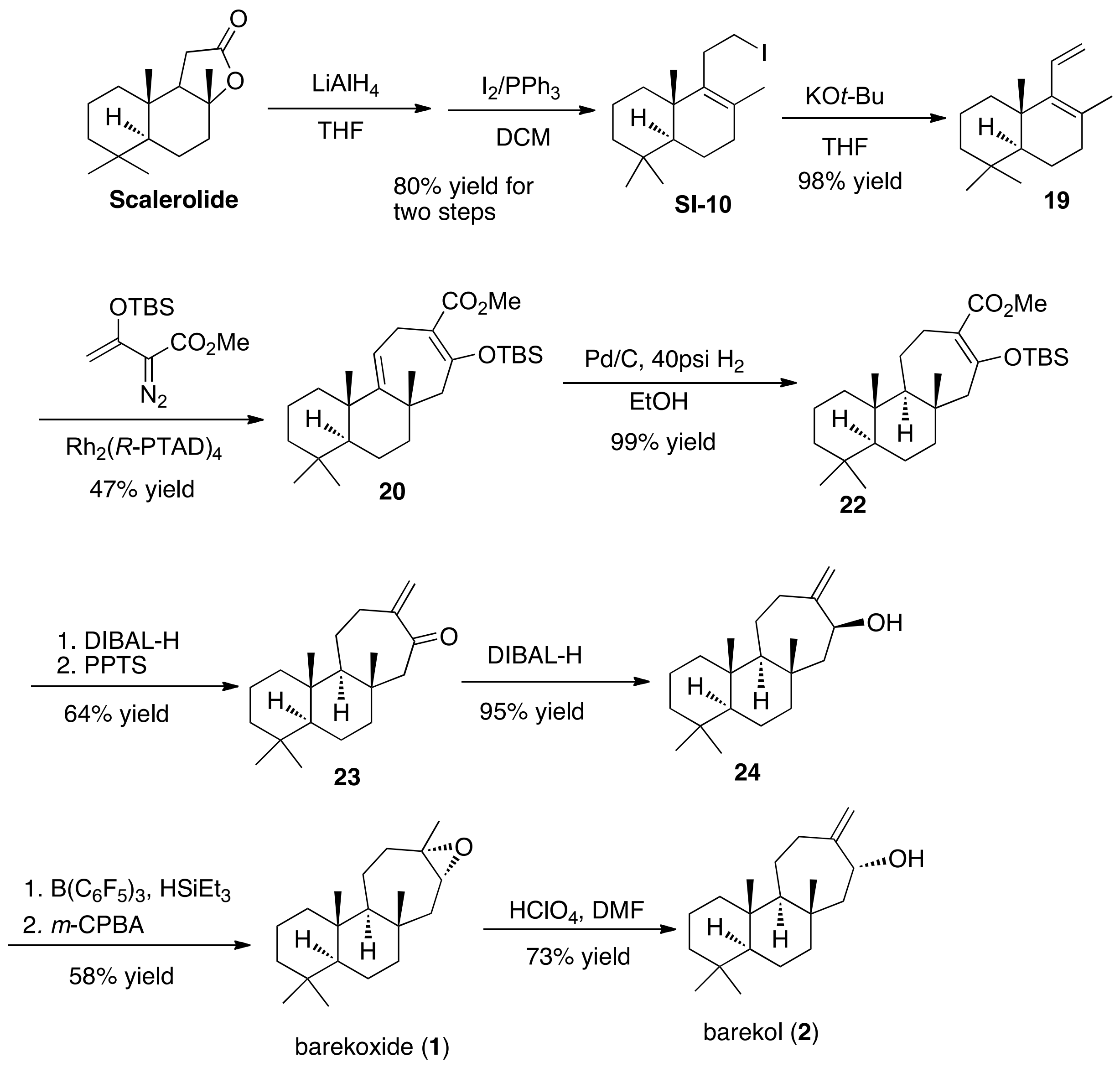
Scheme S1: The synthetic route to *cis*-[4.3.0] bicyclic diene (*S*)-7



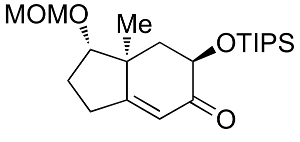
Scheme S2: The synthetic route to *cis*-[4.4.0] bicyclic diene (*S*)-10, (*S*)-13, (*S*)-16



Scheme S3: The complete synthetic route to Barekoxide and Barekol

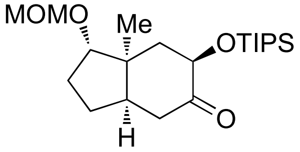


General Methods: All experiments were performed under anhydrous conditions in an atmosphere of argon except where stated, using flame-dried glassware. Toluene and hexane were dried by a solvent purification system (passed through activated alumina columns). Unless otherwise noted, all other reagents were obtained from commercial sources and used as received. ^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded at 400 or 600 MHz. Data are presented as follows: chemical shift (in ppm on the δ scale relative to δH 7.26 for the residual protons in $CDCl_3$ and δH 7.15 for the residual protons in C_6D_6), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J*/Hz), integration. Coupling constants were taken directly from the spectra and are uncorrected. ^{13}C NMR spectra were recorded at 100 or 150 MHz, and all chemical shift values are reported in ppm on the δ scale, with an internal reference of δC 77.0 for $CDCl_3$ and δC 128.02 for C_6D_6. Mass spectral determinations were carried out by using APCI as ionization source. Melting points are uncorrected. Infrared spectral data are reported in units of cm^{-1}. Analytical TLC was performed on silica gel plates using UV light or potassium permanganate stain if stated. Flash column chromatography was performed on silica gel 60A (230-400 mesh). Optical rotations were measured on Jasco polarimeters. Analytical enantioselective chromatographies were measured on Varian Prostar instrument and used isopropanol/hexane as gradient.



SI-2

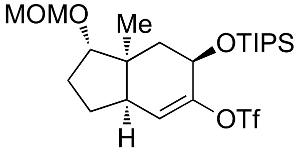
(1*S*,6*R*,7a*S*)-1-(methoxymethoxy)-7a-methyl-6-((triisopropylsilyl)oxy)-2,3,7,7a-tetrahydro-1*H*-inden-5(6*H*)-one SI-2: *α*-Hydroxy Enone **SI-1** (3.33 g, 14.58 mmol) was dissolved in PhMe (40 mL) at rt. TIPSCl (2.95 ml, 17.64 mmol) and DBU (2.61 mL, 17.64 mmol) were added sequentially. After stirring overnight (ca. 12 h), water (60 mL) was added, and the aqueous layer was separated and extracted with EtOAc (3 x 40 mL). The organic layers were combined, dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography (4:1 hexanes/EtOAc) to give 3.20 g of **SI-2** as a clear oil in 81% yield (BRSM). R_f 0.59 (2:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (t, *J* = 1.2 Hz, 1H), 4.67 (d, *J* = 6.7 Hz, 1H), 4.65 (d, *J* = 6.5 Hz, 1H), 4.49 (dd, *J* = 13.0, 5.5 Hz, 1H), 3.67 (dd, *J* = 10.0, 8.0 Hz, 1H), 3.37 (s, 3H), 2.68 (dd, *J* = 19.0, 12.0 Hz, 1H), 2.40-2.33 (m, 2H), 2.18-2.13 (m, 1H), 1.92-1.78 (m, 2H), 1.24 (s, 3H), 1.17-1.06 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 171.6, 122.2, 96.2, 85.3, 70.6, 55.3, 46.4, 45.2, 26.8, 26.3, 17.99, 17.95, 16.6, 12.4; IR (film) νmax 2942, 2866, 16898, 1464, 1210, 1151, 1090, 1048 cm^{-1}; HRMS (ESI$^+$) calcd for $[C_{21}H_{38}NaO_4Si]^+$ $(M+Na)^+$: m/z 405.2437, found 405.2440.



SI-3

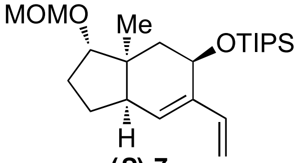
(1*S*,3a*R*,6*R*,7a*S*)-1-(methoxymethoxy)-7a-methyl-6-((triisopropylsilyl)oxy)hexahydro-1*H*-inden-5(6*H*)-one SI-3: Enone **SI-2** (3.18 g, 8.30 mmol) and PtO_2 (57 mg, 0.25 mmol) were combined in 66 mL EtOAc. The flask was evacuated and backfilled with hydrogen (3x) and stirred under an atmosphere of hydrogen for 1 h. The solution was filtered through Celite and concentrated. The crude product was purified by flash chromatography (gradient of 9:1 hexanes/EtOAc to 4:1 hexanes/EtOAc) to give 2.93 g of ketone **SI-3** as a clear oil in a 92% yield. R_f 0.48 (5:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 (d, *J* = 6.8 Hz, 1H), 4.56 (d, *J* = 6.8, 1H), 4.47 (dd, *J* = 11.6, 6.4 Hz, 1H), 3.67 (d, *J* = 4.4 Hz, 1H), 3.36 (s, 3H), 2.51 (dd, *J* = 14.8, 6.8 Hz, 1H), 2.35-2.29 (m, 2H), 2.11-2.02 (m, 1H), 1.94-1.82 (m, 2H), 1.69-1.59 (m, 2H), 1.32 (s, 3H), 1.40-1.28 (m, 1H), 1.12-1.03 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 95.1, 84.7, 73.2, 55.5, 46.0, 45.0, 43.6, 40.2, 28.9, 27.8, 19.2, 17.89, 17.87, 12.2; IR (film) νmax

2943, 2866, 1733, 1465, 1180, 1147, 1117, 1047 cm^{-1}; HRMS (ESI$^+$) calcd for $[C_{21}H_{40}NaO_4Si]^+$(M+Na)$^+$: m/z 407.2594, found 407.2603.



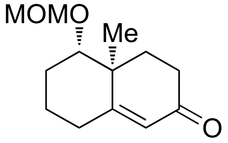
SI-4

(1*S*,3a*R*,6*R*,7a*S*)-1-(methoxymethoxy)-7a-methyl-6-((triisopropylsilyl)oxy)-2,3,3a,6,7,7a-hexahydro-1*H*-inden-5-yl trifluoromethanesulfonate SI-4: HMDS (1.8 mL, 8.53 mmol) was dissolved in THF (68 mL) and cooled to - 78 °C. *n*-BuLi (4.1 mL, 1.9 M in hexanes, 7.76 mmol) was added dropwise. After 40 min. at -78 °C, ketone **SI-3** (2.71 g, 7.05 mmol) in THF (5 mL) was added dropwise. The reaction was maintained at -78 °C for 1.5 h, after which 2-pyrNTf$_2$ (2.78 g, 7.76 mmol) in THF (5 mL) was added. After an additional 30 min at -78 °C, the cold bath was removed, and the reaction mixture was stirred at rt for 30 min. The reaction mixture was quenched by the addition of sat. aq. NH_4Cl (30 mL). The solution was separated and extracted with EtOAc (3 x 35 mL). The combined organic layers were dried over $MgSO_4$ and concentrated to give a golden orange oil. Flash chromatography (gradient of 20:1 hexanes/EtOAc to 4:1 hexanes/EtOAc) gave enol triflate **SI-4** (2.39 g, 66% yield) as a clear oil. R_f 0.35 (9:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (d, J = 5.2 Hz, 1H), 4.65 (d, J = 6.4 Hz, 1H), 4.60 (t, J = 6.0 Hz, 1H), 4.58 (d, J = 6.8 Hz, 1H), 3.77 (t, J = 4.0 Hz, 1H), 3.36 (s, 3H), 2.41 (dd, J = 13.6, 8.4 Hz, 1H), 2.18-2.07 (m, 2H), 1.82 (dd, J = 13.2, 6.0 Hz, 1H), 1.77-1.69 (m, 2H), 1.57-1.50 (m, 1H), 1.11-1.05 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 122.2, 95.7, 84.6, 66.0, 55.4, 44.6, 43.7, 41.5, 30.3, 28.8, 19.8, 18.1, 12.7; IR (film) νmax 1645, 1420, 1208, 1145 cm^{-1}; HRMS (ESI$^+$) calcd for $[C_{22}H_{39}F_3NaO_6SSi]^+$ (M+Na)$^+$: m/z 539.2086, found 539.3951.



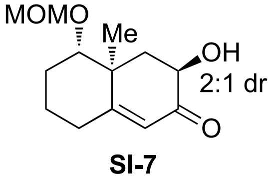
(*S*)-7

triisopropyl(((3*S*,3a*S*,5*R*,7a*R*)-3-(methoxymethoxy)-3a-methyl-6-vinyl-2,3,3a,4,5,7a-hexahydro-1*H*-inden-5-yl)oxy)silane (*S*)-7: Anhydrous LiCl (1.06 g, 25.08 mmol) was added to a Schlenk flask, which was heated to 120 °C under vacuum for 18 h. After cooling to rt and backfilling with N_2, $Pd(PPh_3)_4$ (0.483 g, 0.418 mmol) and CuCl (2.184 g, 22.07 mmol) were added. The Schlenk flask was evacuated and backfilled with N_2 (4x). A solution of enol triflate **SI-4** (2.16 g, 4.18 mmol) and vinyl tributylstannane (1.99 g, 6.27 mmol) in DMSO (35 mL) was added to the Schlenk flask, and then the mixture was sparged with N_2 for 15 min. The dark red-brown solution was stirred at rt for 17 h, before it was diluted with Et_2O (40 mL) and washed with a 5:1 brine/5% NH_4OH solution (40 mL). The aqueous layer was extracted with Et_2O (40 mL), and the combined organic layers were washed sequentially with H_2O (2 x 40 mL) and brine (2 x 40 mL). After drying over Na_2SO_4 and concentrating, the crude product was purified by flash chromatography (gradient of 20:1 hexanes/EtOAc) to afford diene **(*S*)-7** (1.52 g) as a clear oil in 92% yield. R_f 0.64 (20:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 (dd, *J* = 16.0, 8.0 Hz, 1H), 5.89 (d, *J* = 4.0 Hz, 1H), 5.36 (d, *J* = 16.0 Hz, 1H), 4.97 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 4.0 Hz, 1H), 4.60 (d, *J* = 8.0 Hz, 1H), 4.58-4.55 (m, 1H), 3.70 (t, *J* = 4.0 Hz, 1H), 3.37 (s, 3H), 2.26-2.21 (m, 1H), 2.11-2.04 (m, 2H), 1.73-1.60 (m, 3H), 1.54-1.28 (m, 4H), 1.09 (s, 21H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 136.2, 128.0, 112.5, 95.5, 86.2, 67.5, 55.3, 44.6, 44.3, 41.7, 30.5, 29.6, 20.3, 18.33, 18.28, 12.9; IR (film) *v*max 2945, 2868, 1641, 1464, 1421, 1383, 1247, 1209, 1147, 1096, 1042 cm^{-1}; HRMS (ESI$^+$) calcd for $[C_{23}H_{42}NaO_3Si]^+$ $(M+Na)^+$: m/z 417.2801, found 417.2805.



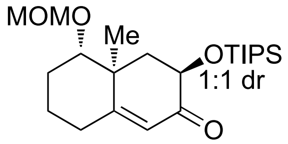
SI-6

(4a*S*,5*S*)-5-(methoxymethoxy)-4a-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one SI-6: To a solution of alcohol **SI-5** (22.78 g, 126.4 mmol) in DCM (316 ml, 0.4M) at 0 °C was added MOMCl (19.20 ml, 258.8 mmol) and i-Pr_2NEt (28.20 ml, 158.0 mmol) dropwise, and allowed to warm to room temperature. Upon completion (5 h), the reaction was quenched with sat. NH_4Cl and stirred vigorously for 15 min. The organic phase was separated, and the aqueous extracted three times with DCM. The combined organics were washed with brine, dried over $MgSO_4$, concentrated, and purified by flash chromatography (2:1 hexanes/EtOAc) to give MOM ether **SI-6** (25.50 g) as a clear oil in 90% yield. R_f 0.75 (1:1 hexanes/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (d, *J* = 1.4 Hz, 1H), 4.72 (d, *J* = 5.2 Hz, 1H), 4.61 (d, *J* = 6.8, 1H), 3.37 (s, 3H), 3.30 (dd, *J* = 8.8, 4.4 Hz, 1H), 2.48-2.29 (m, 3H), 2.23-2.16 (m, 2H), 2.03-1.94 (m, 1H), 1.92-1.78 (m, 2H), 1.65 (qd, *J* = 13.2, 3.6 Hz, 1H), 1.36 (qt, *J* = 13.6, 4.4 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 168.2, 125.3, 95.6, 83.6, 55.6, 41.2, 34.3, 33.7, 32.0, 27.1, 23.0, 16.2; IR (film) vmax 3446, 2945, 1668, 1143, 1105, 1034 cm^{-1}; HRMS (ESI^{+}) calcd for [$C_{13}H_{20}NaO_3$]$^{+}$ (M+Na)$^{+}$: m/z 247.1310, found 247.1316.



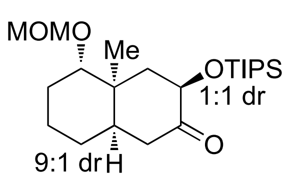
SI-7

(3*R*,4a*S*,5*S*)-3-hydroxy-5-(methoxymethoxy)-4a-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one SI-7: To a solution of hexamethyldisilazane (HMDS) (14.0 mL, 67.44 mmol) in THF (200 mL) at -78 °C was added n-BuLi (24.5 mL, 2.5 M in hexanes, 61.31 mmol) dropwise. After 40 min. at -78 °C, a solution of **SI-6** (12.5 g, 55.74 mmol) in 20 mL THF was added dropwise. The resulting orange solution was stirred at -78 °C for 2 h. TMSCl (10.6 mL, 83.61 mmol) was then added dropwise, and the pale yellow solution was stirred at -78 °C for an additional 0.5 h, and then allowed to warm to rt. The mixture was quenched with sat. aq. $NaHCO_3$ (100 mL). The aqueous layer was quickly extracted with EtOAc (3 x 75 mL). The combined organic layers were brine washed, dried over $MgSO_4$ and concentrated to give a dark yellow oil. The crude product was dissolved in DCM (200 mL) and the reaction mixture was cooled to -42 °C. To the mixture was added $KHCO_3$ (27.90 g, 278.7 mmol) and *m*-CPBA (~75%, 19.24 g, 83.61 mmol). The reaction mixture was stirred at -42 °C for 2 h and then allowed to warm to rt. H_2O (100 mL) was added, and the resulting mixture was extracted with EtOAc (3 x 75 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The crude pale yellow solid was dissolved in THF (200 mL) and the mixture was cooled to 0 °C. TBAF (56 mL, 1.0 M in THF, 56.0 mmol) was added. After 15 min, the cold bath was removed, and following 15 min of stirring at rt, the reaction mixture was quenched with sat. aq. NH_4Cl (100 mL). After extraction with EtOAc (3 x 75 mL), the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to give an orange oil. Flash chromatography (4:1 hexanes/EtOAc to 2:1 to 1:1) gave **SI-7** (8.41 g) as a light yellow oil in 63% yield (2:1 dr). R_f 0.20 (1:1 hexanes/EtOAc); ^{1}H NMR (* denotes major diastereomer) (400 MHz, $CDCl_3$) δ 5.84* + 5.82 (d, *J* = 1.6 & 1.6 Hz, 1H), 4.76*, 4.71 (d, *J* = 7.2 & 6.8 Hz, 1H), 4.66* + 4.58 (d, *J* = 6.8 & 6.8 Hz, 1H), 4.29-4.21 (m, 1H), 3.68* + 3.25 (dd, *J* = 13.2, 5.5 Hz & *J* = 11.6, 4.0 Hz, 1H), 3.41* + 3.36 (s, 3H), 2.68* + 2.55 (dd, *J* = 19.6, 12.1 Hz & *J* = 12.8, 6.0 Hz, 1H), 2.47-2.39* + 2.35-2.27 (m, 1H), 2.02-1.86 (m, 2H), 1.75-1.58 (m, 2H), 1.51* (t, *J* = 13.6 Hz, 1H), 1.30 + 1.17* (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) Major diastereomer: δ 199.7, 170.3, 120.7, 95.9, 78.1, 68.6, 55.8, 43.7, 38.1, 32.0, 27.2, 25.2, 21.5; Minor diastereomer: δ 199.7, 170.0, 121.8, 95.6, 83.8, 69.4, 55.7, 43.0, 42.7, 31.9, 26.6, 22.6, 16.7; IR (film) νmax 3455, 2946, 1682, 1621, 1447, 1228, 1144, 1108, 1035 cm^{-1}; HRMS (ESI$^+$) calcd for $[C_{13}H_{20}NaO_4]^+$ (M+Na)$^+$: m/z 263.1259, found 263.1258.



SI-8

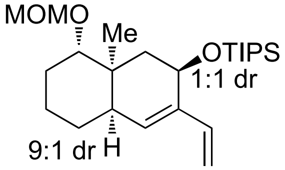
(3*R*,4a*S*,5*S*)-5-(methoxymethoxy)-4a-methyl-3-((triisopropylsilyl)oxy)-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one SI-8: *α*-Hydroxy Enone **SI-7** (4.0 g, 16.65 mmol) was dissolved in PhMe (66 mL) at rt. TIPSCl (4.23 ml, 19.98 mmol) and DBU (3.0 mL, 19.98 mmol) were added sequentially. After stirring overnight (ca. 12 h), water (40 mL) was added, and the aqueous layer was separated and extracted with EtOAc (3 x 50 mL). The organic layers were combined, washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography (4:1 hexanes/EtOAc) to give 4.938 g of **SI-8** as a clear oil in 92% yield. R_f 0.75 (2:1 hexanes/EtOAc); ^{1}H NMR (* denotes major diastereomer) (400 MHz, $CDCl_3$) δ 5.76* + 5.71 (d, *J* = 1.4 & 1.4 Hz, 1H), 4.75* + 4.65 & 4.59 (dd, *J* = 6.8, 2.0 Hz, 1H + d, *J* = 6.8 Hz & d, *J* = 6.8 Hz, 1H), 4.43* + 4.27 (dd, *J* = 13.2, 5.2 Hz, 1H + dd, *J* = 8.0, 4.8 Hz, 1H), 3.39* + 3.38 (s, 3H), 3.47-3.35* + 3.26 (m + dd, *J* = 12.0, 4.4 Hz, 1H), 2.43-2.35 (m, 1H), 2.30-2.05 (m, 3H), 2.01-1.84 (m, 2H), 1.76-1.56 (m, 2H), 1.30* + 1.29 (s, 3H), 1.14-1.04 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) Major diastereomer: δ 197.7, 167.3, 122.8, 96.3, 82.7, 71.1, 55.7, 43.1, 41.5, 32.0, 27.4, 24.2, 20.7, 18.1, 18.0, 12.4, Minor diastereomer: δ 198.6, 166.0, 123.7, 95.5, 83.9, 71.1, 55.7, 44.8, 42.6, 31.4, 26.6, 22.9, 18.0, 17.7, 16.9, 12.4; IR (film) νmax 2943, 2866, 1698, 1465, 1147, 1106, 1036 cm^{-1}; HRMS (FAB$^+$) calcd for $[C_{22}H_{40}NaO_4Si]^+$ (M+Na)$^+$: m/z 419.2594, found 419.2601.



SI-9

Ketone SI-9: Conjugated ketone **SI-8** (4.92 g, 12.40 mmol) and PtO_2 (84 mg, 0.37 mmol) were combined in 100 mL EtOAc. The flask was evacuated and backfilled with hydrogen (3x) and stirred under an atmosphere of hydrogen for 1 h. The solution was filtered through Celite and concentrated. The crude product was purified by flash chromatography (gradient of 9:1

hexanes/EtOAc to 4:1 hexanes/EtOAc) to give 4.20 g of the ketone **SI-9** as a clear oil in a 91% yield. R_f 0.60 (5:1 hexanes/EtOAc); ^{1}H NMR (* denotes major diastereomer) (600 MHz, $CDCl_3$) δ 4.69* + 4.59 & 4.54 (dd, *J* = 6.6, 1.8 Hz + d, *J* = 6.6 Hz & d, J = 6.6 Hz, 2H), 4.47* + 4.16 (dd, *J* = 11.4, 7.2 Hz + t, *J* = 3.6, 1H), 3.39* + 3.35 (s, 3H), 3.09* + 2.80 (dd, *J* = 13.8, 5.4 Hz + t, *J* = 13.8 Hz, 1H), 2.11-1.96 (m, 3H), 1.77-1.43 (m, 7H), 1.32* + 1.20 (s, 3H), 1.09-1.01 (m, 21H); ^{13}C NMR (150 MHz, $CDCl_3$) Major diastereomer: δ 210.3, 95.4, 79.8, 75.4, 55.5, 45.2, 42.1, 40.4, 38.7, 27.9, 26.5, 23.3, 19.8, 17.9, 12.3. Minor diastereomer: δ 209.1, 95.9, 85.1, 73.8, 55.8, 46.3, 39.7, 38.6, 28.1, 25.3, 24.0, 19.6, 17.8, 12.0; IR (film) νmax 2942, 2866, 1731, 1147, 1044 cm^{-1}; HRMS (ESI$^+$) calcd for $[C_{22}H_{42}NaO_4Si]^+(M+Na)^+$: m/z 421.2750, found 421.2753.

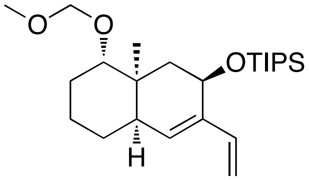


(*S*)-10
(*S*)-13
(*S*)-16

(*S*)-10, (*S*)-13, (*S*)-16: HMDS (2.65 mL, 12.68 mmol) was dissolved in THF (95 mL) and cooled to - 78 °C. *n*-BuLi (4.60 mL, 2.5 M in hexanes, 11.50 mmol) was added dropwise. After 40 min. at -78 °C, the ketone **SI-9** (4.18 g, 10.49 mmol) in THF (5 mL) was added dropwise. The reaction was maintained at -78 °C for 1 h, after which 2-pyrNTf$_2$ (4.13 g, 11.53 mmol) in THF (5 mL) was added. After an additional 30 min at -78 °C, the cold bath was removed, and the reaction mixture warmed to rt for 30 min. The reaction mixture was quenched by the addition of sat. aq. NH_4Cl (60 mL). The solution was separated and extracted with EtOAc (3 x 40 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to give a golden-orange oil. Upon dilution with 9:1 hexane:EtOAc, the solution was filtered and concentrated. Due to the lability of the enol triflate on silica, the crude material was immediately carried on into the subsequent reaction without purification. R_f 0.35 (9:1 hexanes/EtOAc).

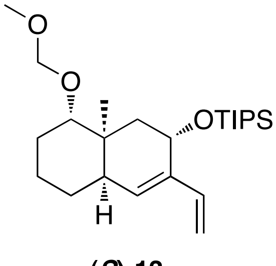
Anhydrous LiCl (2.67 g, 62.91 mmol) was added to a Schlenk flask, which was heated to 120 °C under vacuum for 18 h. After cooling to rt and backfilling with N_2, $Pd(PPh_3)_4$ (1.21 g, 1.05 mmol) and CuCl (5.48 g, 55.36 mmol) were added. The Schlenk flask was evacuated and backfilled with N_2 (4x). A solution of enol triflate (5.56 g, 10.49 mmol) and vinyl tributylstannane (4.60 ml, 15.73 mmol) in DMSO (87 mL) was added to the Schlenk flask, and then the mixture was sparged with N_2 for 15 min. The dark red-brown solution was stirred at rt for 17 h, before it was diluted with Et_2O (100 mL) and washed with a 5:1 brine/5% NH_4OH

solution (60 mL). The aqueous layer was extracted with Et_2O (40 mL), and the combined organic layers were washed sequentially with H_2O (2 x 60 mL) and brine (2 x 60 mL). In order to remove the organotin impurities, KF/Celite was added and allowed to stir for 1 h, which upon filtering, drying over Na_2SO_4 and concentrating, the crude product was purified by flash chromatography (gradient of 20:1 hexanes/EtOAc) to afford the diene (2.50 g) as as a mixture of three isomers in 58% yield (2 steps). R_f 0.64 (20:1 hexanes/EtOAc). The ratio of (*S*)-**10**/(*S*)-**13**/(*S*)-**16** was 5/4/1. Careful column chromatograpgy on silica gel (20:1 pentane/Et_2O, $R_f = 0.54$ for (*S*)-**13**; $R_f = 0.41$ for (*S*)-**10**; $R_f = 0.39$ for (*S*)-**16**) provided (*S*)-**13** as a pure colorless oil and a mixture of (*S*)-**10** and (*S*)-**16**, which were further purified on silica gel (3:1 pentane/methylene chloride, $R_f = 0.47$ for (*S*)-**10**; $R_f = 0.43$ for (*S*)-**16**).



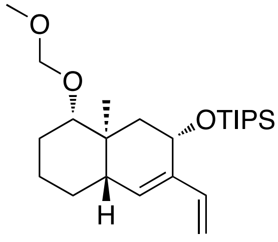
(*S*)-10

triisopropyl(((2*R*,4a*R*,8*S*,8a*S*)-8-(methoxymethoxy)-8a-methyl-3-vinyl-1,2,4a,5,6,7,8,8a-octahydronaphthalen-2-yl)oxy)silane (*S*)-10: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.35 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.82 (d, *J* = 5.5 Hz, 1H), 5.36 (dd, *J* = 17.6, 1.8 Hz, 1H), 4.97 (dd, *J* = 11.0, 1.8 Hz, 1H), 4.70 (d, *J* = 7.0 Hz, 1H), 4.61 (d, *J* = 7.0 Hz, 1H), 4.57-4.62 (m, 1H), 3.39 (s, 3H), 3.32-3.35 (m, 1H), 1.92-1.03 (m, 2H), 1.67-1.77 (m, 2H), 1.55-1.66 (m, 2H), 1.41-1.53 (m, 2H), 1.22-1.34 (m, 1H), 1.06-1.12 (m, 21H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.9, 136.8, 130.7, 112.7, 96.0, 80.4, 68.5, 55.7, 39.0, 38.5, 37.5, 29.8, 26.0, 21.7, 19.8, 18.4, 18.3, 13.0; IR (neat): 2939, 2865, 1436, 1097, 1036, 1011, 917, 883, 679 cm^{-1}; HRMS (ESI) calc. for $C_{24}H_{44}O_3NaSi$ $(M+Na)^+$ 431.2952 found 431.2953; $[\alpha]^{25}_D$ 16.3 (*c* = 2.07, $CHCl_3$).



(*S*)-13

triisopropyl(((2*S*,4a*R*,8*S*,8a*S*)-8-(methoxymethoxy)-8a-methyl-3-vinyl-1,2,4a,5,6,7,8,8a-octahydronaphthalen-2-yl)oxy)silane (*S*)-13: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.33 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.57 (t, *J* = 0.9 Hz, 1H), 5.35 (dm, *J* = 17.7 Hz, 1H), 4.97 (d, *J* = 11.3 Hz, 1H), 4.64-4.69 (m, 2H), 4.56-4.63 (m, 1H), 3.35 (s, 3H), 3.34-3.39 (m, 1H), 2.39 (dd, *J* = 12.8, 6.4 Hz, 1H), 2.32 (br, 1H), 1.67-1.85 (m, 2H), 1.18-1.58 (m, 5H), 1.07-1.11 (m, 21H), 1.02 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.4, 136.5, 131.4, 113.0, 96.9, 77.9, 67.6, 55.3, 43.3, 43.0, 39.2, 28.3, 27.2, 21.2, 20.7, 18.4, 18.3, 13.0; IR (neat): 2941, 2866, 1465, 1105, 1045, 918, 883, 678 cm^{-1}; HRMS (ESI) calc. for $C_{24}H_{44}O_3NaSi$ $(M+Na)^+$ 431.2952 found 431.2953; $[\alpha]^{25}_{D}$ -5.3 (*c* = 1.51, $CHCl_3$).

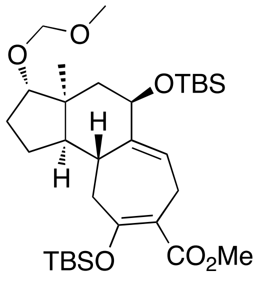


(*S*)-16

triisopropyl(((2*S*,4a*S*,8*S*,8a*S*)-8-(methoxymethoxy)-8a-methyl-3-vinyl-1,2,4a,5,6,7,8,8a-octahydronaphthalen-2-yl)oxy)silane (*S*)-16: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.35 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.57 (s, 1H), 5.38 (dm, *J* = 17.7 Hz, 1H), 4.99 (d, *J* = 11.2 Hz, 1H), 4.72 (d, *J* = 7.0 Hz, 1H), 4.59 (d, *J* = 6.7 Hz, 1H), 4.53 (d, *J* = 5.2 Hz, 1H), 3.40 (s, 3H), 3.16 (dd, *J* = 11.0, 4.3 Hz, 1H), 2.35 (d, *J* = 13.7 Hz, 1H), 1.72-1.82 (m, 3H), 1.52-1.62 (m, 1H), 1.30-1.50 (m, 4H), 1.06-1.12 (m, 21H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.65, 137.59, 129.2, 112.4, 95.5, 83.6, 66.2, 55.43, 55.41, 44.4, 43.8, 36.98, 26.9, 26.3, 24.4, 18.3, 13.1, 11.5; IR (neat): 2941, 2865, 1465, 1142, 1038, 931, 882, 771, 675 cm^{-1}; HRMS (ESI) calc. for $C_{24}H_{44}O_3NaSi$ $(M+Na)^+$ 431.2952 found 431.2953; $[\alpha]^{25}_{D}$ -8.0 (*c* = 2.33, $CHCl_3$).

General procedure for the enantiodivergent [4 + 3] cycloadditions

A solution of methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**4**) (46.7 mg, 0.18 mmol, 3.0 equiv.) in dried toluene (3 mL) was added dropwise to a stirred solution of diene and $Rh_2(PTAD)_4$ (1.9 mg, 2 mol %) in toluene (3 mL) at 0 °C or room temperature under argon atmosphere over 3 h by syringe pump. The contents were stirred for additional 1 h and then heated to 60 °C for 1 h. The solution was then cooled to room temperature and concentrated *in vacuo*. The residue was then purified by flash chromatography to give product as a colorless oil.



5b

(3*S*,3a*S*,5*R*,10a*R*,10b*R*)-methyl 5,9-bis((*tert*-butyldimethylsilyl)oxy)-3-(methoxymethoxy)-3a-methyl-1,2,3,3a,4,5,7,10,10a,10b-decahydrocyclohepta[*e*]indene-8-carboxylate (5b): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**4**) (46.7 mg, 0.18 mmol, 3.0 equiv.) and diene ***S*-3**[1] (21.2 mg, 0.06 mmol, 1.0 equiv.) with Rh_2(*R*-PTAD)$_4$ (1.9 mg, 2 mol %) at 0 °C, and purified by flash chromatography (10:1 pentane/Et_2O, $R_f = 0.38$) to give product **(5b)** (28.3 mg, 81% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 5.70 (t, J = 6.0 Hz, 1H), 4.70 (d, J = 6.4 Hz, 1H), 4.64 (d, J = 6.4 Hz, 1H), 4.41 (t, J = 8.3 Hz, 1H), 4.08 (t, J = 4.0 Hz, 1H), 3.67 (s, 3H), 3.34 (s, 3H), 3.00 (dd, J = 6.4, 1.6 Hz, 2H), 2.61 (dd, J = 13.3, 3.2 Hz, 1H), 2.35-2.48 (m, 2H), 1.94-2.06 (m, 3H), 1.57-1.64 (m, 1H), 1.40-1.52 (m, 3H), 0.95 (s, 9H), 0.87 (s, 3H), 0.85 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H), 0.01 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 161.9, 143.4, 122.5, 113.1, 97.0, 83.9, 75.8, 55.2, 51.0, 50.5, 43.5, 41.5, 37.7, 34.8, 28.4, 25.9, 25.7, 25.1 (2C), 23.6, 18.3, 18.1, -3.6, -3.9, -4.6, -4.7; IR (neat): 2951, 2928, 1691, 1201, 1147, 1044, 886, 827, 775 cm^{-1}; HRMS (APCI) calc. for $C_{31}H_{57}O_6Si_2$ $(M+H)^+$ 581.3688 found 581.3696; $[\alpha]^{25}_D$ -15.0 (c = 1.34, $CHCl_3$). For the reaction beginning with racemic diene **3** in the presence of Rh_2(*R*-PTAD)$_4$, HPLC of product **5b**: (AD-H, 0.3% isopropanol in hexane, 0.7 mL/min) retention times of 6.1 min (minor) and 6.9 min (major), 90% ee.

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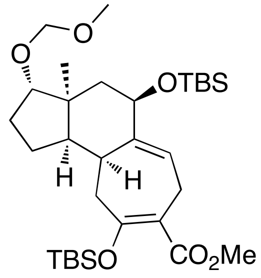
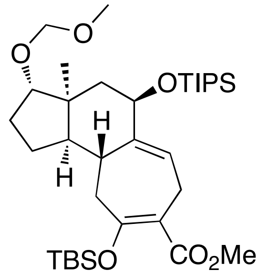
[1] Miller, L. C.; Ndungu, J. M.; Sarpong, R. *Angew. Chem. Int. Ed.* **2009**, *48*, 2398.



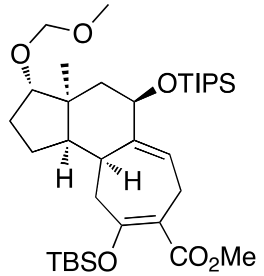
6b

(3*S*,3a*S*,5*R*,10a*S*,10b*R*)-methyl 5,9-bis((*tert*-butyldimethylsilyl)oxy)-3-(methoxymethoxy)-3a-methyl-1,2,3,3a,4,5,7,10,10a,10b-decahydrocyclohepta[*e*]indene-8-carboxylate (6b): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**4**) (46.7 mg, 0.18 mmol, 3.0 equiv.) and diene ***S*-3** (21.2 mg, 0.06 mmol, 1.0 equiv.) with Rh_2(*S*-PTAD)$_4$ (1.9 mg, 2 mol %) at 0 °C, and purified by flash chromatography (10:1 pentane/Et_2O, $R_f = 0.25$) to give product (**6b**) (27.8 mg, 80% yield) as a colorless oil.^{1}H NMR (400 MHz, $CDCl_3$): δ 6.03–6.07 (m, 1H), 4.66 (d, *J* = 6.7 Hz, 1H), 4.55 (d, *J* = 6.7 Hz, 1H), 3.95-3.99 (m, 1H), 3.69 (s, 3H), 3.56 (d, *J* = 5.4 Hz, 1H), 3.37 (s, 3H), 2.94-3.12 (m, 3H), 2.51-2.55 (m, 1H), 1.99-2.09 (m, 2H), 1.52-1.87 (m, 4H), 1.42-1.46 (m, 1H), 1.16 (s, 3H), 1.08-1.21 (m, 1H), 0.96 (s, 9H), 0.89 (s, 9H), 0.18 (s, 3H), 0.16 (s, 3H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 161.8, 139.9, 120.1, 113.5, 95.1, 85.8, 70.0, 55.5, 51.0, 49.6, 46.0, 42.6, 39.5, 34.8, 28.5, 25.9, 25.7, 24.4, 23.6, 19.0, 18.43, 18.41, -4.0, -4.1, -4.9, -5.0; IR (neat): 2951, 2929, 2857, 1714, 1692, 1361, 1252, 1189, 1148, 1097, 1033, 829, 776 cm^{-1}; HRMS (APCI) calc. for $C_{31}H_{57}O_6Si_2$ $(M+H)^+$ 581.3688 found 581.3692; $[\alpha]^{25}_D$ 39.8 (*c* = 1.43, $CHCl_3$). For the reaction beginning with racemic diene **3** in the presence of Rh_2(*R*-PTAD)$_4$, HPLC of product **6b**: ((*S*,*S*)-DACH DNB, 0.3% isopropanol in hexane, 0.7 mL/min) retention times of 15.0 min (major) and 16.7 min (minor), 99% ee.



8

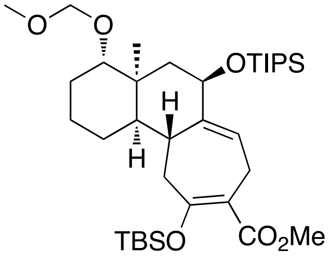
(3*S*,3a*S*,5*R*,10a*R*,10b*R*)-methyl 9-((*tert*-butyldimethylsilyl)oxy)-3-(methoxymethoxy)-3a-methyl-5-((triisopropylsilyl)oxy)-1,2,3,3a,4,5,7,10,10a,10b-decahydrocyclohepta[*e*]indene-8-carboxylate (8): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**4**) (46.7 mg, 0.18 mmol, 3.0 equiv.) and diene (***S***)**-7** (23.7 mg, 0.06 mmol, 1.0 equiv.) with Rh_2(*R*-PTAD)$_4$ (1.9 mg, 2 mol %) at 0 °C, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.55) to give product **8** (30.6 mg, 82% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.71 (t, *J* = 6.2 Hz, 1H), 4.68 (d, *J* = 6.2 Hz, 1H), 4.64 (d, *J* = 6.24 Hz, 1H), 4.47 (t, *J* = 8.1 Hz, 1H), 4.16 (t, *J* = 3.8 Hz, 1H), 3.67 (s, 3H), 3.34 (s, 3H), 3.00 (d, *J* = 5.7 Hz, 2H), 2.58-2.64 (m, 1H), 2.42-2.50 (m, 2H), 1.96-2.08 (m, 3H), 1.60-1.67 (m, 1H), 1.45-1.54 (m, 2H), 1.42 (dd, *J* = 14.3, 4.3 Hz, 1H), 0.99-1.06 (m, 21H), 0. 95 (s, 9H), 0.87 (s, 3H), 0.17 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 161.9, 143.4, 122.4, 113.1, 97.2, 84.2, 76.0, 55.3, 50.9, 50.7, 43.6, 41.6, 37.8, 34.6, 28.4, 25.7, 25.0, 24.9, 23.7, 18.3, 18.2, 18.1, 12.3, -3.6, -3.9; IR (neat): 2944, 2864, 1718, 1691, 1463, 1372, 1202, 1148, 1046, 883, 827 cm^{-1}; HRMS (APCI) calc. for $C_{34}H_{63}O_6Si_2$ $(M+H)^+$ 623.4163 found 623.4164; $[\alpha]^{25}_D$ -17.6 (*c* = 1.83, $CHCl_3$).



9

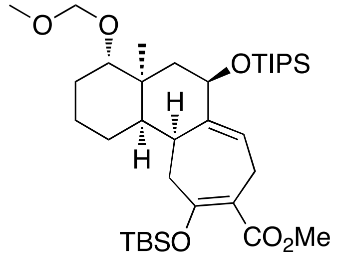
(3*S*,3a*S*,5*R*,10a*S*,10b*R*)-methyl 9-((*tert*-butyldimethylsilyl)oxy)-3-(methoxymethoxy)-3a-methyl-5-((triisopropylsilyl)oxy)-1,2,3,3a,4,5,7,10,10a,10b-decahydrocyclohepta[*e*]indene-8-carboxylate (9): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**4**) (46.7 mg, 0.18 mmol, 3.0 equiv.) and diene (***S***)**-7** (23.7 mg, 0.06 mmol, 1.0 equiv.) with Rh_2(*S*-PTAD)$_4$ (1.9 mg, 2 mol %) at 0 °C, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.42) to give product **9** (28.4 mg, 76% yield) as a colorless oil..^{1}H NMR (400 MHz, $CDCl_3$):

δ 6.13–6.19 (m, 1H), 4.66 (d, *J* = 6.7 Hz, 1H), 4.55 (d, *J* = 6.7 Hz, 1H), 4.03-4.10 (m, 1H), 3.67 (s, 3H), 3.56 (d, *J* = 5.5 Hz, 1H), 3.37 (s, 3H), 2.91-3.12 (m, 3H), 2.47-2.52 (m, 1H), 1.97-2.10 (m, 2H), 1.50-1.88 (m, 5H), 1.16 (s, 3H), 0.98-1.12 (m, 22H), 0.95 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.2, 161.6, 140.1, 120.4, 113.7, 95.1, 85.9, 70.1, 55.5, 50.9, 49.7, 46.1, 42.9, 39.4, 35.0, 28.5, 25.7, 24.3, 23.5, 19.1, 18.5, 18.12, 18.08, 12.4, -4.11, -4.14; IR (neat): 2943, 2865, 1714, 1694, 1463, 1252, 1220, 1189, 1147, 1098, 1034, 881, 830, 781 cm^{-1}; HRMS (APCI) calc. for $C_{34}H_{63}O_6Si_2$ $(M+H)^+$ 623.4163 found 623.4164; $[\alpha]^{25}_D$ 40.3 (*c* = 1.71, CHCl$_3$).



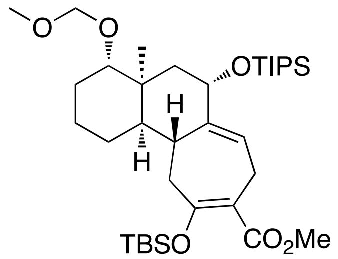
11

(4*S*,4a*S*,6*R*,11a*R*,11b*R*)-methyl 10-((*tert*-butyldimethylsilyl)oxy)-4-(methoxymethoxy)-4a-methyl-6-((triisopropylsilyl)oxy)-2,3,4,4a,5,6,8,11,11a,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (11): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**4**) (46.7 mg, 0.18 mmol, 3.0 equiv.) and diene (***S***)-**10** (24.5 mg, 0.06 mmol, 1.0 equiv.) with Rh$_2$(*R*-PTAD)$_4$ (1.9 mg, 2 mol %) at room temperature, and purified by flash chromatography (10:1 pentane/Et$_2$O, R_f = 0.41) to give product **11** (29.5 mg, 77% yield) as a colorless oil. ^{1}H NMR (600 MHz, CDCl$_3$): δ 5.68 (t, *J* = 6.2 Hz, 1H), 4.84 (d, *J* = 6.2 Hz, 1H), 4.63 (d, *J* = 6.2 Hz, 1H), 4.27 (dd, *J* = 11.4, 5.2 Hz, 1H), 4.17 (t, *J* = 3.3 Hz, 1H), 3.67 (s, 3H), 3.33 (s, 3H), 2.92-3.02 (m, 3H), 2.63-2.68 (m, 1H), 2.42 (dd, *J* = 13.8, 8.6 Hz, 1H), 2.29 (dd, *J* = 15.2, 3.3 Hz, 1H), 1.93-1.98 (m, 1H), 1.78-1.83 (m, 1H), 1.50-1.62 (m, 4H), 1.36-1.43 (m, 1H), 1.15 (dd, *J* = 14.3, 3.8 Hz, 1H), 1.00-1.10 (m, 21H), 0.952 (s, 3H), 0.949 (s, 9H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 167.6, 161.6, 144.8, 121.2, 113.4, 97.8, 80.0, 76.9, 55.0, 51.0, 49.4, 43.5, 38.8, 36.8, 30.2, 29.7, 25.7, 25.6, 24.9, 23.0, 22.0, 19.5, 18.3, 18.1, 12.5, -3.8, -4.0; IR (neat): 2934, 2864, 1719, 1691, 1463, 1253, 1212, 1193, 1146, 1045, 828 cm^{-1}; HRMS (ESI) calc. for $C_{35}H_{64}O_6NaSi_2$ $(M+Na)^+$ 659.4134 found 659.4131; $[\alpha]^{25}_D$ -48.1 (*c* = 0.71, CHCl$_3$).



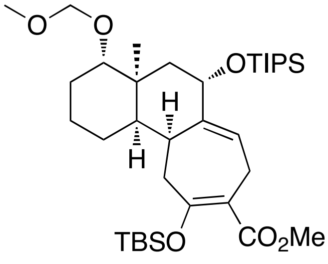
12

(4*S*,4a*S*,6*R*,11a*S*,11b*R*)-methyl 10-((*tert*-butyldimethylsilyl)oxy)-4-(methoxymethoxy)-4a-methyl-6-((triisopropylsilyl)oxy)-2,3,4,4a,5,6,8,11,11a,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (12): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**4**) (46.7 mg, 0.18 mmol, 3.0 equiv.) and diene (***S***)-**10** (24.5 mg, 0.06 mmol, 1.0 equiv.) with Rh_2(*S*-PTAD)$_4$ (1.9 mg, 2 mol %) at room temperature, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.36) to give product **11** (25.2 mg, 66% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.14–6.20 (m, 1H), 4.71 (d, *J* = 6.7 Hz, 1H), 4.59 (d, *J* = 6.7 Hz, 1H), 4.18-4.22 (m, 1H), 3.67 (s, 3H), 3.41 (s, 3H), 3.27 (t, *J* = 13.3 Hz, 1H), 3.22 (s, 1H), 3.05 (dd, *J* = 16.7, 9.5 Hz, 1H), 2.91 (dm, *J* = 16.7 Hz, 1H), 2.63 (d, *J* = 11.4 Hz, 1H), 1.80 (dd, *J* = 13.3, 3.8 Hz, 1H), 1.74 (t, *J* = 11.9 Hz, 1H), 1.51-1.68 (m, 6H), 1.40 (dd, *J* = 12.0, 5.2 Hz, 1H), 1.28-1.34 (m, 1H), 1.17 (s, 3H), 1.01-1.11 (m, 21H), 0.95 (s, 9H), 0.18 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.1, 162.2, 140.3, 120.5, 114.0, 95.8, 81.4, 70.3, 55.9, 50.9, 43.7, 41.0, 38.6, 37.9, 35.2, 25.8, 24.9, 24.4, 23.6, 21.7, 19.7, 18.5, 18.2, 18.1, 12.5, -4.05, -4.13; IR (neat): 2934, 2865, 1713, 1694, 1463, 1252, 1202, 1143, 1033, 829 cm^{-1}; HRMS (ESI) calc. for $C_{35}H_{64}O_6NaSi_2$ $(M+Na)^+$ 659.4134 found 659.4132; $[\alpha]^{25}_D$ 9.0 (*c* = 0.40, $CHCl_3$).



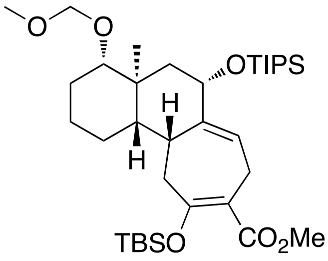
14

(4*S*,4a*S*,6*S*,11a*R*,11b*R*)-methyl 10-((*tert*-butyldimethylsilyl)oxy)-4-(methoxymethoxy)-4a-methyl-6-((triisopropylsilyl)oxy)-2,3,4,4a,5,6,8,11,11a,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (14): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**4**) (46.7 mg, 0.18 mmol, 3.0 equiv.) and diene (***S***)-**13** (24.5 mg, 0.06 mmol, 1.0 equiv.) with Rh_2(*R*-PTAD)$_4$ (1.9 mg, 2 mol %) at room temperature, and purified by flash chromatography (10:1 pentane/Et$_2$O, R$_f$ = 0.44) to give product **14** (24.1 mg, 63% yield) as a colorless oil. ^{1}H NMR (600 MHz, CDCl$_3$): δ 5.95 (t, *J* = 6.2 Hz, 1H), 4.69 (d, *J* = 6.7 Hz, 1H), 4.67 (d, *J* = 6.7 Hz, 1H), 4.09 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.65-3.71 (m, 4H), 3.35 (s, 3H), 3.04 (d, *J* = 6.2 Hz, 2H), 2.68 (d, *J* = 12.4 Hz, 1H), 2.33-2.43 (m, 3H), 1.97-2.01 (m, 1H), 1.75-1.80 (m, 1H), 1.47-1.64 (m, 4H), 1.28-1.38 (m, 1H), 1.01-1.10 (m, 21H), 0.99 (s, 3H), 0.95 (s, 9H), 0.86-0.90 (m, 1H), 0.14 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 167.5, 161.3, 144.7, 116.5, 114.5, 97.7, 79.1, 70.0, 55.2, 51.0, 49.0, 47.2, 39.5, 37.1, 34.3, 29.2, 25.8, 24.7, 22.5, 21.7, 19.3, 18.4, 18.2, 18.1, 12.5, -3.9, -4.3; IR (neat): 2941, 2864, 1714, 1694, 1626, 1212, 1146, 1043, 880, 827, 679 cm^{-1}; HRMS (ESI) calc. for $C_{35}H_{64}O_6NaSi_2$ (M+Na)$^+$ 659.4134 found 659.4132; $[\alpha]^{25}_D$ -66.6 (*c* = 0.57, CHCl$_3$).



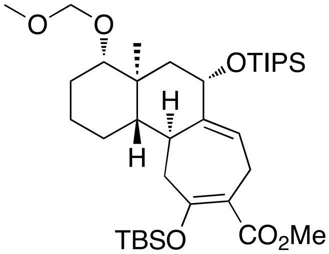
15

(4*S*,4a*S*,6*S*,11a*S*,11b*R*)-methyl 10-((*tert*-butyldimethylsilyl)oxy)-4-(methoxymethoxy)-4a-methyl-6-((triisopropylsilyl)oxy)-2,3,4,4a,5,6,8,11,11a,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (15): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**4**) (46.7 mg, 0.18 mmol, 3.0 equiv.) and diene (***S***)-**13** (24.5 mg, 0.06 mmol, 1.0 equiv.) with Rh$_2$(*S*-PTAD)$_4$ (1.9 mg, 2 mol %) at room temperature, and purified by flash chromatography (10:1 pentane/Et$_2$O, R$_f$ = 0.37) to give product **15** (26.4 mg, 69% yield) as a colorless oil. ^{1}H NMR (600 MHz, CDCl$_3$): δ 5.85 (dd, *J* = 9.1, 2.9 Hz, 1H), 4.70 (d, *J* = 6.7 Hz, 1H), 4.60 (d, *J* = 6.7 Hz, 1H), 4.17 (d, *J* = 2.4 Hz, 1H), 3.65 (s, 3H), 3.41 (s, 3H), 3.25 (t, *J* = 13.3 Hz, 1H), 3.17 (s, 1H), 3.10 (dm, *J* = 13.3 Hz, 1H), 3.00 (dd, *J* = 17.1, 9.1 Hz, 1H), 2.91 (dt, *J* = 17.1, 3.3 Hz, 1H), 1.87 (dd, *J* = 14.0, 4.2 Hz, 1H), 1.80 (dd, *J* = 14.0, 4.2 Hz, 1H), 1.50-1.68 (m, 6H), 1.39 (s, 3H), 1.33 (d, *J* = 13.8 Hz, 1H), 1.11-1.18 (m, 1H), 0.96-1.05 (m, 21H), 0.96 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 167.3, 162.7, 140.7, 126.8, 112.1, 96.1, 81.5, 75.8, 55.8, 50.8, 44.3, 38.3, 37.79, 37.76, 32.0, 25.5, 25.3, 25.0, 24.7, 21.6, 19.6, 18.23, 18.15, 12.2, -3.6, -3.7; IR (neat): 2941, 2864, 1716, 1689, 1621, 1462, 1372, 1226, 1202, 1148, 1036, 915, 839, 780 cm^{-1}; HRMS (ESI) calc. for $C_{35}H_{64}O_6NaSi_2$ (M+Na)$^+$ 659.4134 found 659.4137; $[\alpha]^{25}_D$ 20.8 (*c* = 1.32, CHCl$_3$).



17

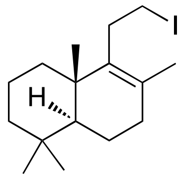
(4*S*,4a*S*,6*S*,11a*R*,11b*S*)-methyl 10-((*tert*-butyldimethylsilyl)oxy)-4-(methoxymethoxy)-4a-methyl-6-((triisopropylsilyl)oxy)-2,3,4,4a,5,6,8,11,11a,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (17): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**4**) (46.7 mg, 0.18 mmol, 3.0 equiv.) and diene (***S***)-**16** (24.5 mg, 0.06 mmol, 1.0 equiv.) with $Rh_2(R\text{-PTAD})_4$ (1.9 mg, 2 mol %) at room temperature, and purified by flash chromatography (10:1 pentane/Et_2O, R_f = 0.36) to give product **17** (21.0 mg, 55% yield) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ 5.89-5.91 (m, 1H), 4.72 (d, *J* = 7.1 Hz, 1H), 4.55 (d, *J* = 7.1 Hz, 1H), 4.38 (t, *J* = 8.1 Hz, 1H), 3.68 (s, 3H), 3.37 (s, 3H), 3.20 (dd, *J* = 18.1, 8.1 Hz, 1H), 3.12 (dd, *J* = 11.0, 4.3 Hz, 1H), 3.05 (dm, *J* = 18.1 Hz, 1H), 2.73-2.83 (m, 2H), 2.24 (d, *J* = 12.9 Hz, 1H), 1.98 (dd, *J* = 13.3, 7.1 Hz, 1H), 1.75-1.82 (m, 3H), 1.56 (dd, *J* = 13.2, 7.8 Hz, 1H), 1.18-1.40 (m, 4H), 1.01-1.11 (m, 21H), 0.99 (s, 3H), 0.94 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.5, 162.0, 143.4, 118.7, 111.7, 95.2, 85.8, 69.5, 55.6, 51.1, 48.3, 42.3, 38.8, 37.5, 36.9, 26.9, 25.8, 25.4, 25.1, 24.1, 18.4, 18.15, 18.14, 16.6, 12.3, -3.8, -3.9; IR (neat): 2941, 2864, 1717, 1695, 1630, 1366, 1212, 1042, 878, 839 cm^{-1}; HRMS (ESI) calc. for $C_{35}H_{64}O_6NaSi_2$ $(M+Na)^+$ 659.4134 found 659.4137; $[\alpha]^{25}_D$ 36.5 (*c* = 0.66, $CHCl_3$).



18

(4*S*,4a*S*,6*S*,11a*S*,11b*S*)-methyl 10-((*tert*-butyldimethylsilyl)oxy)-4-(methoxymethoxy)-4a-methyl-6-((triisopropylsilyl)oxy)-2,3,4,4a,5,6,8,11,11a,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (18): Derived from methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**4**) (46.7 mg, 0.18 mmol, 3.0 equiv.) and diene (***S***)-

16 (24.5 mg, 0.06 mmol, 1.0 equiv.) with Rh_2(*S*-PTAD)$_4$ (1.9 mg, 2 mol %) at room temperature, and purified by flash chromatography (10:1 pentane/Et_2O, $R_f = 0.28$) to give product **15** (31.0 mg, 81% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.71 (t, *J* = 6.2 Hz, 1H), 4.69 (d, *J* = 6.7 Hz, 1H), 4.54 (d, *J* = 6.7 Hz, 1H), 4.21 (t, *J* = 3.8 Hz, 1H), 3.66 (s, 3H), 3.35 (s, 3H), 3.06 (dd, *J* = 11.4, 4.3 Hz, 1H), 2.99 (dd, *J* = 17.1, 7.1 Hz, 1H), 2.93 (ddd, *J* = 17.1, 5.7, 1.4 Hz, 1H), 2.69 (q, *J* = 7.6 H, 1H), 2.50 (d, *J* = 6.7 Hz, 2H), 2.15 (dd, *J* = 13.8, 2.9 Hz, 1H), 1.66-1.80 (m, 3H), 1.45-1.52 (m, 1H), 1.37 (dd, *J* = 13.8, 4.2 Hz, 1H), 1.16-1.27 (m, 2H), 1.15 (s, 3H), 1.12-1.17 (m, 1H), 0.98-1.05 (m, 21H), 0.95 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.7, 161.4, 144.6, 122.1, 113.2, 95.6, 85.8, 75.6, 55.5, 50.9, 49.6, 46.1, 39.4, 36.9, 32.8, 26.3, 25.6, 25.5, 24.7, 23.9, 22.9, 18.21, 18.16, 14.0, 12.2, -3.6, -3.9; IR (neat): 2942, 2864, 1718, 1690, 1626, 1372, 1206, 1141, 1040, 920, 829, 780 cm^{-1}; HRMS (ESI) calc. for $C_{35}H_{64}O_6NaSi_2$ $(M+Na)^+$ 659.4134 found 659.4135; $[\alpha]^{25}_D$ 15.1 (*c* = 0.85, $CHCl_3$).



S1

(4a*S*,8a*S*)-8-(2-iodoethyl)-4,4,7,8a-tetramethyl-1,2,3,4,4a,5,6,8a-octahydro-naphthalene (S1): Prepared *via* a modified literature procedure.[2] To a solution of (+)-sclareolide (5.0 g, 20 mmol, 1.0 equiv.) in dried THF (50 mL) was added $LiAlH_4$ (20 mL of 1M solution in THF, 20 mmol, 1.0 equiv.) at 0 °C slowly. The solution was warmed up to room temperature and stirred for additional 3h. The mixture was quenched by saturated NH_4Cl solution and extracted by Et_2O (200 mL × 4). The organic layers were combined and dried ($MgSO_4$), concentrated under reduced pressure. The residue was then dissolved in 50 mL DCM and added to 50 mL DCM solution containing I_2 (5.6 g, 22.0 mmol, 1.1equiv.) and PPh_3 (5.8 g, 22.0 mmol, 1.1 equiv.) at 0 °C. The solution was warmed up to room temperature and stirred for additional 4h. Saturated $NaHSO_3$ aqueous solution (50 mL) was added and the mixture was stirred for 30 mins. The mixture was extracted by pentane (100 mL × 4) and dried ($MgSO_4$), concentrated. The residue was then purified by flash chromatography (pentane, $R_f = 0.76$) on silica gel to give product as a colorless solid with trace amount of isomer. The solid was recrystallized from EtOH to afford the

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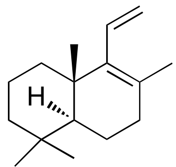
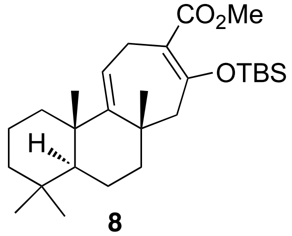
[2] Alvarez-Manzaneda, E.; Chahboun, R.; Cabrera, E.; Alvarez, E.; Haidour, A.; Ramos, J. M.; Alvarez-Manzaneda, R.; Hmamouchi, M.; Es-Samti, H. *Chem. Commun.*, **2009**, *592.*

pure product **S1** (5.55 g, 80% yield) as white crystals. ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.03–3.12 (m, 2H), 2.67 (td, *J* = 13.3, 5.1 Hz, 1H), 2.49 (td, *J* = 13.3, 5.1 Hz, 1H), 1.90-2.01 (m, 2H), 1.78-1.81 (m, 1H), 1.59-1.66 (m, 2H), 1.56 (s, 3H), 1.47-1.52 (m, 1H), 1.34-1.42 (m, 2H), 1.06-1.16 (m, 3H), 0.92 (s, 3H), 0.88 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 141.0, 129.1, 51.8, 41.7, 38.6, 37.1, 34.2, 33.6, 33.29, 33.26, 21.6, 20.0, 19.8, 19.0, 18.9, 5.2; IR (neat): 2924, 2865, 1458, 1387, 1162, 907, 733 cm^{-1}; M.p. 75-77 °C; HRMS (APCI) calc. for $C_{16}H_{28}{}^{127}I$ (M+H)$^+$ 347.1230 found 347.1233; $[\alpha]^{25}_D$ 28.3 (*c* = 1.15, CHCl$_3$).



7

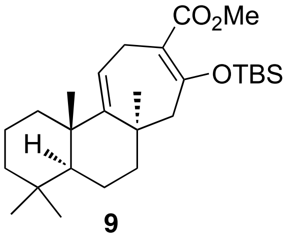
(4a*S*,8a*S*)-4,4,7,8a-tetramethyl-8-vinyl-1,2,3,4,4a,5,6,8a-octahydronaphthalene (7): To a solution of iodine **S1** (2.08g, 6.0 mmol, 1.0 equiv.) in THF (5 mL) was added a solution of KO*t*-Bu (1.35g, 12.0 mmol 2.0 equiv.) in THF (5 mL) slowly. The mixture was stirred for 6 h at room temperature and then quenched by saturated brine solution. The mixture was extracted by pentane (100 mL × 3) and dried (MgSO$_4$), concentrated under reduced pressure to afford the diene **7** (1.28 g, 98% yield) as colorless oil without further purification. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.08-6.16 (m, 1H), 5.23 (dd, *J* = 11.0, 2.7 Hz, 1H), 4.90 (dd, *J* = 17.7, 2.7 Hz, 1H), 2.03–2.10 (m, 2H), 1.63-1.71 (m, 5H), 1.37-1.61 (m, 4H), 1.06-1.19 (m, 3H), 1.00 (s, 3H), 0.89 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 142.0, 135.2, 126.8, 118.3, 51.2, 41.8, 38.1, 37.6, 33.5, 33.3, 33.2, 21.6, 21.1, 20.0, 19.0, 18.9; IR (neat): 2923, 2865, 1457, 1374, 1006, 914 cm^{-1}; HRMS (APCI) calc. for $C_{16}H_{27}$ (M+H)$^+$ 219.2107 found 219.2109; $[\alpha]^{25}_D$ 106.0 (*c* = 1.15, CHCl$_3$).



8

(4a*S*,6a*S*,11b*S*)-methyl8-((*tert*-butyldimethylsilyl)oxy)-4,4,6a,11b-tetramethyl-2,3,4,4a, 5,6,6a,7,10,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (8): A solution of methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**4**) (2.56 g, 10.0 mmol, 5.0 equiv.)

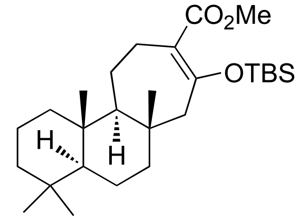
in dried hexane (6 mL) was added dropwise to a stirred solution of diene **7** (437 mg, 2.0 mmol, 1.0 equiv.) and Rh_2(*R*-PTAD)$_4$ (63 mg, 2 mol %) in refluxed hexane (6 mL) over 3 h by syringe pump under argon atmosphere. The solution was cooled to room temperature and concentrated under reduced pressure. The residue was then purified by flash chromatography (20:1 pentane/Et_2O, R_f = 0.60) on silica gel to give products (0.581 g, 65% combined yield) as a mixture of two diastereomers with 6/1 ratio favoring the product **8**. The mixture was carefully recrystallized from EtOH and the mother liquid was subsequently purified on silica gel impregnated with 5% $AgNO_3$ and followed by recrystallizing from EtOH again to afford the pure product **8** (0.43 g, 47% yield) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.48 (dd, *J* = 8.5, 3.4 Hz, 1H), 3.68 (s, 3H), 3.16 (dd, *J* = 18.3, 8.5 Hz, 1H), 3.05 (dd, *J* = 18.3, 3.4 Hz, 1H), 2.88 (d, *J* = 13.1 Hz, 1H), 1.78 (d, *J* = 13.4 Hz, 1H), 1.32-1.69 (m, 8H), 1.27 (s, 3H), 1.07-1.25 (m, 3H), 1.05 (s, 3H), 0.95 (s, 9H), 0.85 (s, 3H), 0.82 (s, 3H), 0.154 (s, 3H), 0.152 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.9, 162.7, 155.4, 116.5, 110.4, 54.2, 52.4, 51.0, 44.0, 41.9, 41.1, 39.4, 37.2, 34.0, 33.2, 27.3, 27.1, 25.8, 23.4, 21.6, 19.23, 19.19, 18.3, -3.6, -3.7; IR (neat): 2929, 1690, 1377, 1252, 1212, 1139, 1052, 829, 779, 732 cm^{-1}; M.p. 74-76 °C; HRMS (APCI) calc. for $C_{27}H_{47}O_3Si$ $(M+H)^+$ 447.3289 found 447.3284; $[\alpha]^{25}_D$ 24.5 (*c* = 1.64, $CHCl_3$).



9

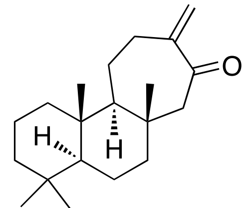
(4a*S*,6a*R*,11b*S*)-methyl 8-((*tert*-butyldimethylsilyl)oxy)-4,4,6a,11b-tetramethyl-2,3,4,4a,5,6,6a,7,10,11b-decahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (9): A solution of methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (**4**) (153 mg, 0.60 mmol, 3.0 equiv.) in dried hexane (3 mL) was added dropwise to a stirred solution of diene **7** (43.7 mg, 0.2 mmol, 1.0 equiv.) and Rh_2(*S*-PTAD)$_4$ (6.3 mg, 2 mol %) in refluxed hexane (3 mL) over 3 h by syringe pump under argon atmosphere. The solution was cooled to room temperature and concentrated under reduced pressure. The residue was then purified by flash chromatography (20:1 pentane/Et_2O, R_f = 0.60) on silica gel to give products (56.3 mg, 63% combined yield) as a mixture of two diastereomers with 9/1 ratio favoring the product **9**. The residue was carefully purified on silica gel impregnated with 5% $AgNO_3$ to afford the pure product **9** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.40 (t, *J* = 5.6 Hz, 1H), 3.69 (s, 3H), 3.20 (dd, *J* =

20.8, 5.6 Hz, 1H), 3.06 (ddd, *J* = 20.8, 5.6, 0.8 Hz, 1H), 2.65 (d, *J* = 14.8 Hz, 1H), 1.72-1.90 (m, 4H), 1.35-1.56 (m, 4H), 1.25-1.32 (m, 2H), 1.23 (s, 3H), 1.07-1.22 (m, 2H), 1.05 (s, 3H), 0.93 (s, 9H), 0.90 (s, 3H), 0.83 (s, 3H), 0.14 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 169.3, 158.8, 157.3, 117.5, 109.5, 52.3, 51.2, 43.9, 42.1, 41.0, 40.1, 36.4, 35.1, 34.1, 32.7, 28.4, 25.7, 25.5, 24.9, 21.3, 19.4, 18.3, 17.9, -3.7; IR (neat): 2928, 2858, 1719, 1693, 1434, 1378, 1252, 1199, 1047, 834, 779 cm^{-1}; HRMS (APCI) calc. for $C_{27}H_{47}O_3Si$ $(M+H)^+$ 447.3289 found 447.3284; $[\alpha]^{25}_{D}$ -2.5 (*c* = 2.66, CHCl$_3$).



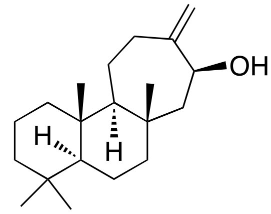
10

(4a*S*,6a*S*,11a*S*,11b*S*)-methyl 8-((*tert*-butyldimethylsilyl)oxy)-4,4,6a,11b-tetramethyl-2,3,4,4a,5,6,6a,7,10,11,11a,11b-dodecahydro-1*H*-cyclohepta[*a*]naphthalene-9-carboxylate (10): A solution of product **8** (0.267 g, 6.0 mmol, 1.0 equiv.) in EtOH (15 mL) containing Pd/C (62 mg of 10% palladium on activated carbon, 0.06 mmol, 0.1 equiv.) was shaken under H$_2$ atmosphere (45 psi) over-night. The mixture was filtrated through a celit pad to remove the catalyst and washed with EtOH (10 mL × 2). The filtrated solution was concentrated to afford the product **10** (0.268 g, 99% yield) as a colorless viscous oil without further purification. ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.68 (s, 3H), 2.84 (dd, *J* = 15.3, 7.3 Hz, 1H), 2.49 (d, *J* = 13.7 Hz, 1H), 1.94 (dd, *J* = 14.6, 11.0 Hz, 1H), 1.70-1.80 (m, 3H), 1.47-1.66 (m, 2H), 1.07-1.46 (m, 7H), 0.96-1.01 (m, 1H), 0.98 (s, 3H), 0.93 (s, 9H), 0.84 (s, 3H), 0.79 (s, 3H), 0.77 (s, 3H), 0.72-0.85 (m, 2H), 0.14 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$): δ 168.7, 162.5, 112.3, 64.6, 56.6, 55.2, 51.0, 44.6, 41.9, 39.7, 38.6, 35.4, 33.45, 33.36, 28.3, 25.8, 21.5, 21.2, 19.4, 19.1, 18.7, 18.3, 16.1, -3.6; IR (neat): 2930, 1715, 1688, 1435, 1363, 1249, 1206, 1149, 830, 779, 733 cm^{-1}; HRMS (APCI) calc. for $C_{27}H_{49}O_3Si$ $(M+H)^+$ 449.3446 found 449.3446; $[\alpha]^{25}_{D}$ -28.2 (*c* = 2.06, CHCl$_3$).



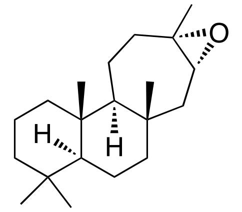
11

(4a*S*,6a*S*,11a*S*,11b*S*)-4,4,6a,11b-tetramethyl-9-methylenedodecahydro-1*H*-cyclohepta[*a*] naphthalen-8(11b*H*)-one (11): To a solution of ester **10** (0.494 g, 1.1 mmol, 1.0 equiv.) in THF (5 mL) was added 3.6 mL of DIBAL-H (1.0 M in THF, 3.6 mmol, 3.3 equiv.) at 0 °C dropwise. The mixture was stirred for 1h and quenched by 1M of NaOH aqueous solution. The solution was extracted by Et_2O (20 mL × 3) and dried ($MgSO_4$), concentrated under reduced pressure. The residue was dissolved in dried benzene (30 mL) containing PPTS (27.6 mg, 0.11 mmol, 0.1 equiv.) and the solution was heated under reflux with Dean Stark apparatus for 3h. The solution was then concentrated and purified by flash chromatography (85/15 pentane/ Et_2O, $R_f = 0.65$) on silica gel to give product **11** (0.203 g, 64% yield) as a white solid ^1H NMR (600 MHz, $CDCl_3$): 5.95 (d, $J = 1.1$ Hz, 1H), 5.19 (s, 1H), 2.68 (d, $J = 3.8$ Hz, 1H), 2.66 (d, $J = 4.8$ Hz, 1H), 2.34 (t, $J = 13.1$ Hz, 1H), 2.15 (d, $J = 12.4$ Hz, 1H), 2.09 (dd, $J = 14.3$, 7.6 Hz, 1H), 1.80 (dm, $J = 12.9$ Hz, 1H), 1.50-1.64 (m, 3H), 1.30-1.46 (m, 5H), 1.08-1.20 (m, 2H), 0.88 (s, 3H), 0.86 (s, 3H), 0.83-0.90 (m, 2H), 0.81 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.1, 147.3, 121.5, 63.5, 60.6, 56.5, 44.6, 41.8, 40.2, 38.8, 37.5, 34.4, 33.44, 33.40, 25.2, 21.5, 19.9, 18.9, 18.8, 16.0; IR (neat): 2934, 2851, 1683, 1611, 1455, 1386, 1288, 1198, 1092, 1037, 942, 899 cm^{-1}; M.p. 94-96 °C; HRMS (APCI) calc. for $C_{22}H_{33}O$ $(M+H)^+$ 289.2526 found 289.2526; $[\alpha]^{25}_D$ 135.3 (*c* = 0.80, $CHCl_3$).



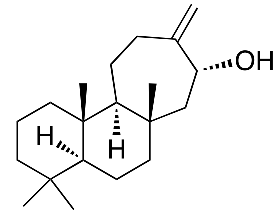
12

(4a*S*,6a*S*,8*S*,11a*S*,11b*S*)-4,4,6a,11b-tetramethyl-9-methylenetetradecahydro-1*H*-cyclohepta[*a*]naphthalen-8-ol (12): To a solution of conjugated ketone **11** (28.9 mg, 0.1 mmol, 1.0 equiv.) in THF (2 mL) was added 0.2 mL of DIBAL-H (1.0 M in THF, 0.2 mmol, 2.0 equiv.) at -78 °C dropwise. The mixture was warmed up to -30 °C over 1h and quenched by 1M of HCl aqueous solution. The mixture was extracted by Et_2O (10 mL × 3) and dried ($MgSO_4$), concentrated under reduced pressure to afford the allylic alcohol **12** (27.1 mg, 95% yield) as a white powder without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.01 (t, *J* = 1.5 Hz, 1H), 4.83 (s, 1H), 4.33-4.37 (m, 1H), 2.50 (ddd, *J* = 13.4, 5.5, 3.4 Hz, 1H), 1.92-2.01 (m, 1H), 1.70-1.82 (m, 2H), 1.65 (d, *J* = 5.2 Hz, 2H), 1.31-1.62 (m, 10H), 1.11 (td, *J* = 13.2, 4.4 Hz, 1H), 0.98 (s, 3H), 0.90 (dd, *J* = 10.4, 2.4 Hz, 1H), 0.85 (s, 3H), 0.80 (s, 3H), 0.79 (s, 3H), 0.74-0.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 108.2, 71.9, 59.3, 56.7, 53.0, 44.1, 42.0, 40.0, 38.6, 37.1, 34.9, 33.41, 33.38, 24.6, 22.1, 21.5, 18.8, 18.6, 16.2; IR (neat): 3396(br), 2920, 2843, 1462, 1387, 1039, 1012, 899, 757 cm^{-1}; M.p. 63-65 °C; HRMS (APCI) calc. for $C_{20}H_{35}O$ $(M+H)^+$ 291.2682 found 291.2684; $[\alpha]^{25}_D$ 10.5 (*c* = 0.95, $CHCl_3$).



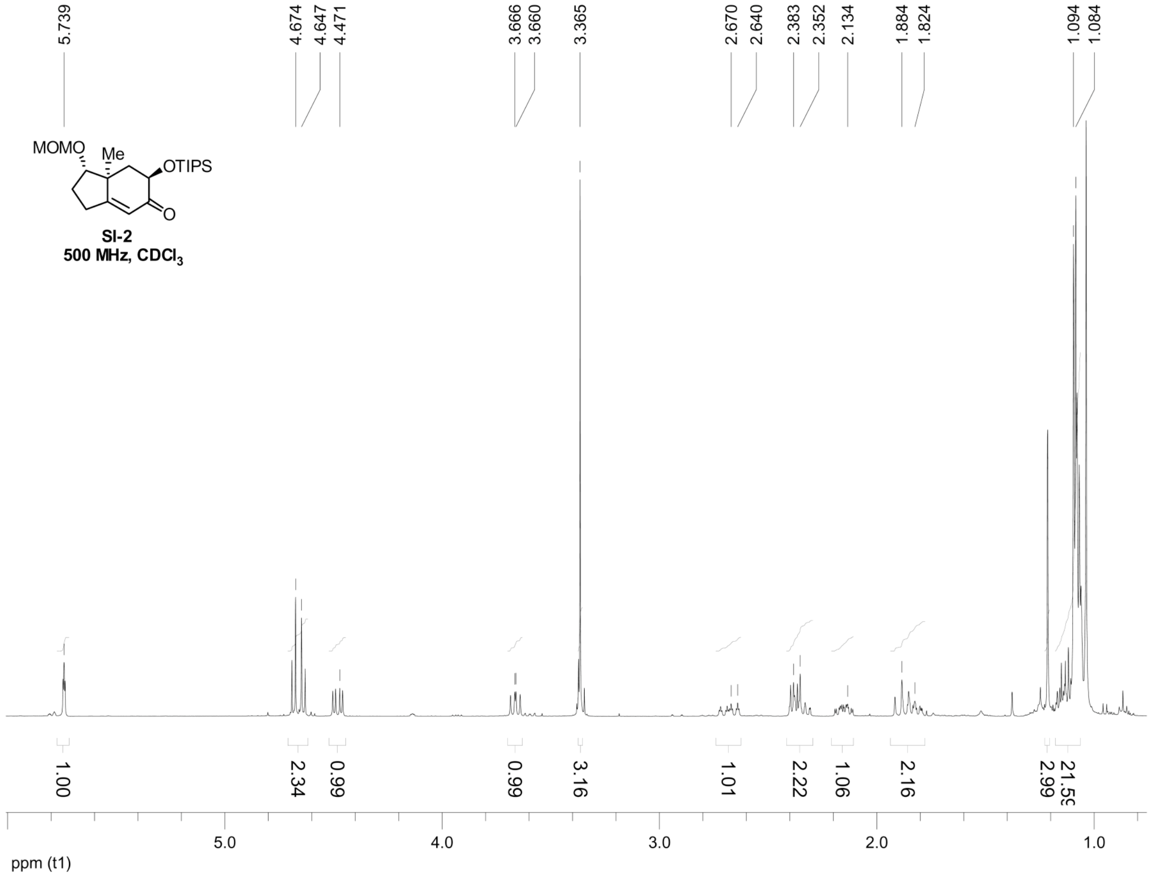
barekoxide (**1**)

Barekoxide (1): A DCE solution (4 mL) containing alcohol **12** (29.0 mg, 0.1 mmol, 1.0 equiv.), $B(C_6F_5)_3$ (4.1 mg, 0.008 mmol, 0.08 equiv.), $HSiEt_3$ (46.4 mg, 0.4 mmol, 4.0 equiv.) was heated under reflux for 14 h. The solution was concentrated and passed through a small pipet column on silica gel with pentane. The solvent was removed under reduced pressure and the residue was dissolved in DCM (5 mL). After cooling down to 0 °C, a DCM solution (5 mL) containing *m*-CPBA (50 mg, 0.2 mmol, 2.0 equiv.) was added to the olefin solution and the mixture was stirred for 1h. The solvent was quenched with saturated $Na_2S_2O_3$ aqueous solution. The mixture was extracted with Et_2O (10 mL × 3) and dried ($MgSO_4$), concentrated under reduced pressure. The residue was purified by flash chromatography (20/1 pentane/Et_2O, R_f = 0.26) on silica gel to afford barekoxide (**1**) (16.4 mg, 58% yield) as a white powder. ^{1}H NMR (400 MHz, C_6D_6): δ 2.59 (t, *J* = 7.3 Hz, 1H), 1.88 (dd, *J* = 13.7, 7.6 Hz, 1H), 1.70 (dd, *J* = 14.0, 6.4 Hz, 1H), 1.22-1.60 (m, 10H), 1.21 (s, 3H), 0.95-1.19 (m, 3H), 0.85 (s, 3H), 0.83 (s, 3H), 0.80 (s, 3H), 0.72 (s, 3H), 0.47-0.61 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 64.5, 60.0, 59.9, 56.2, 48.0, 44.2, 42.1, 40.2, 38.9, 37.7, 36.6, 33.6 (2C), 22.7, 21.8, 20.4, 19.8, 19.1, 18.8, 16.2; IR (neat): 2931, 2919, 2845, 1464, 1387, 873 cm^{-1}; M.p. 136-137 °C {lit. M.p. 140 °C}[6c]; HRMS (APCI) calc. for $C_{20}H_{35}O$ $(M+H)^+$ 291.2682 found 291.2682; $[\alpha]^{25}_D$ 1.73 (*c* = 0.59, $CHCl_3$) {lit. $[\alpha]^{22}_D$ 5.2 (*c* 0.256, $CHCl_3$)}[6c].

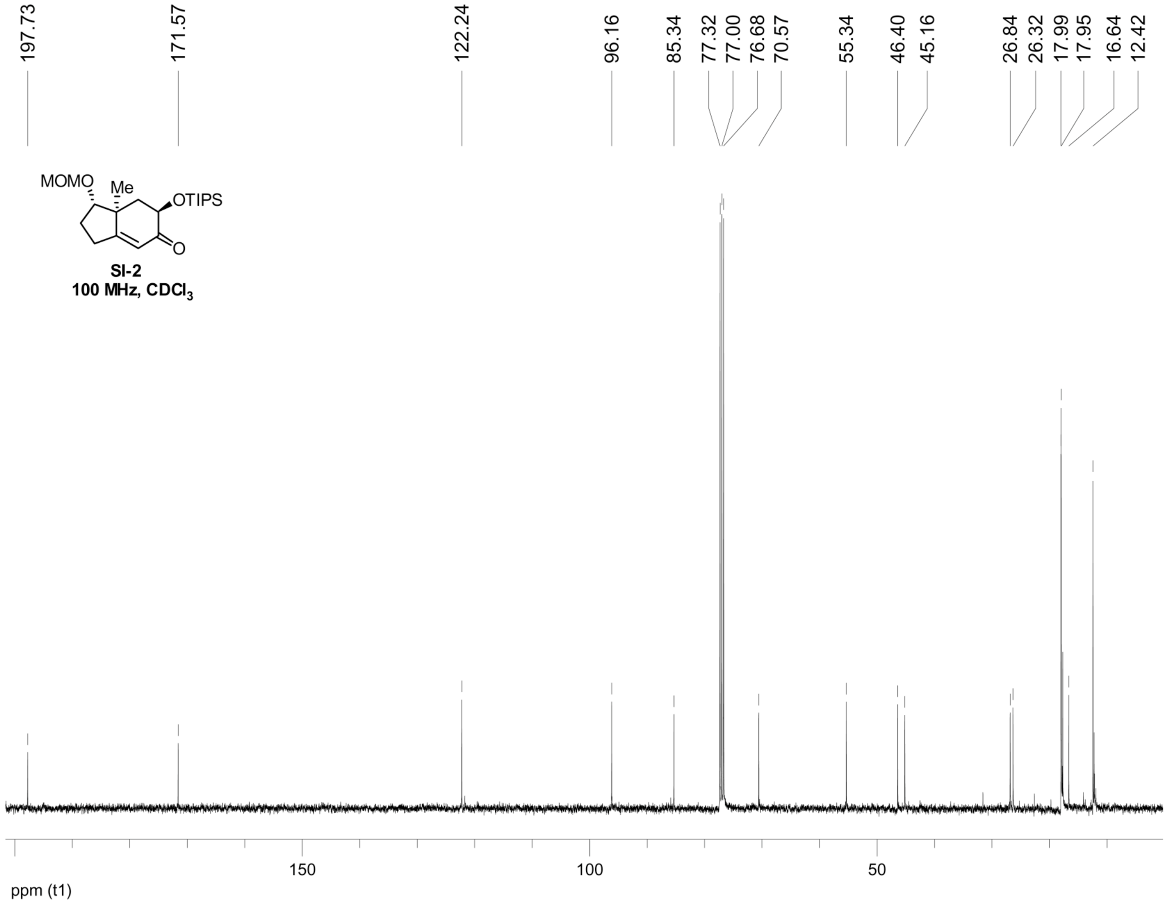


barekol (**2**)

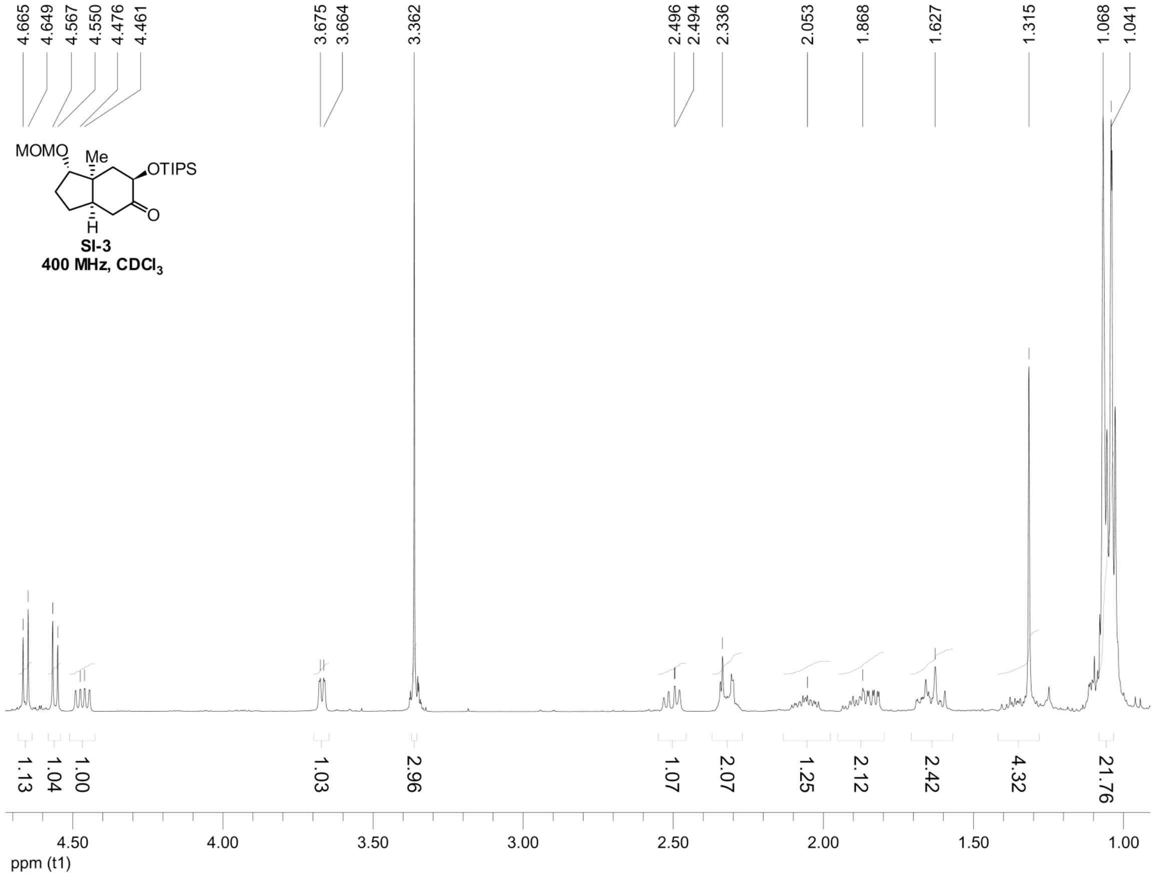
Barekol (2): To a solution of barekoxide (**1**) (25 mg, 0.09 mmol, 1.0 equiv.) in dried DMF (3 mL) was added 2 drop of $HClO_4$ (70% aqueous solution) and the solution was stirred at room temperature for 16h. The solution was quenched by saturated $NaHCO_3$ solution. The mixture was extracted by Et_2O (10 mL × 3) and dried ($MgSO_4$), concentrated under reduced pressure. The residue was purified by flash chromatography (85/15 pentane/ Et_2O , $R_f = 0.24$) on silica gel to afford the the barekol (**2**) (18.3 mg, 73% yield) as a white powder. Careful recrystallization from pentane afforded some crystals for X-ray crystallographic analysis. ^1H NMR (600 MHz, $CDCl_3$): δ 5.03 (s, 1H), 4.88 (s, 1H), 4.27 (dd, *J* = 11.0, 3.8 Hz, 1H), 2.42-2.47 (m, 1H), 2.15-2.21 (m, 1H), 1.72-1.83 (m, 2H), 1.67 (dd, *J* = 13.3, 4.3 Hz, 1H), 1.51-1.61 (m, 2H), 1.45-1.50 (m, 1H), 1.32-1.44 (m, 5H), 1.19-1.31(m, 2H), 1.12(td, *J* = 13.3, 4.2 Hz, 1H), 0.95 (s, 3H), 0.84-0.87 (m, 1H), 0.85 (s, 3H), 0.77-0.83 (m, 2H), 0.79 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 155.1, 110.5, 70.8, 60.3, 56.4, 55.4, 45.1, 41.9, 39.9, 38.6, 36.0, 33.4 (2C), 33.2, 24.1, 21.6, 20.3, 18.7, 18.6, 15.8; IR (neat): 3312(br), 2922, 2847, 1462, 1387, 1055, 1009, 897, 734 cm^{-1}; HRMS (APCI) calc. for $C_{20}H_{35}O$ $(M+H)^+$ 291.2682 found 291.2684; $[\alpha]^{25}_D$ –48.7 (*c* = 0.76, $CHCl_3$) {lit. $[\alpha]^{22}_D$ -29 (*c* 1.0, $CHCl_3$)}[6b].



SI-2
500 MHz, $CDCl_3$



SI-2
100 MHz, $CDCl_3$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3.664
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2.494
2.336
2.053
1.868
1.627
1.315
1.068
1.041
MOMO
Me
OTIPS
O
H
SI-3
400 MHz, CDCl$_3$
1.13
1.04
1.00
1.03
2.96
1.07
2.07
1.25
2.12
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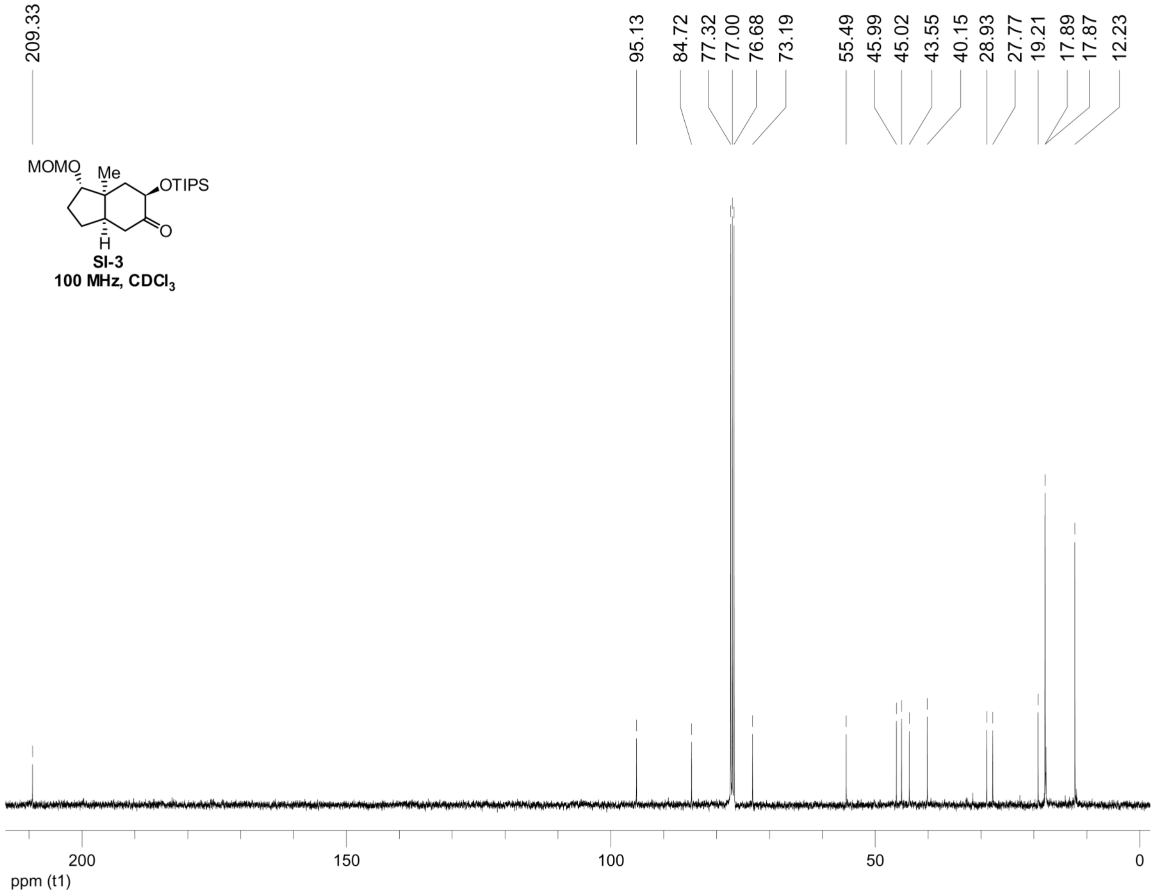
ppm (t1)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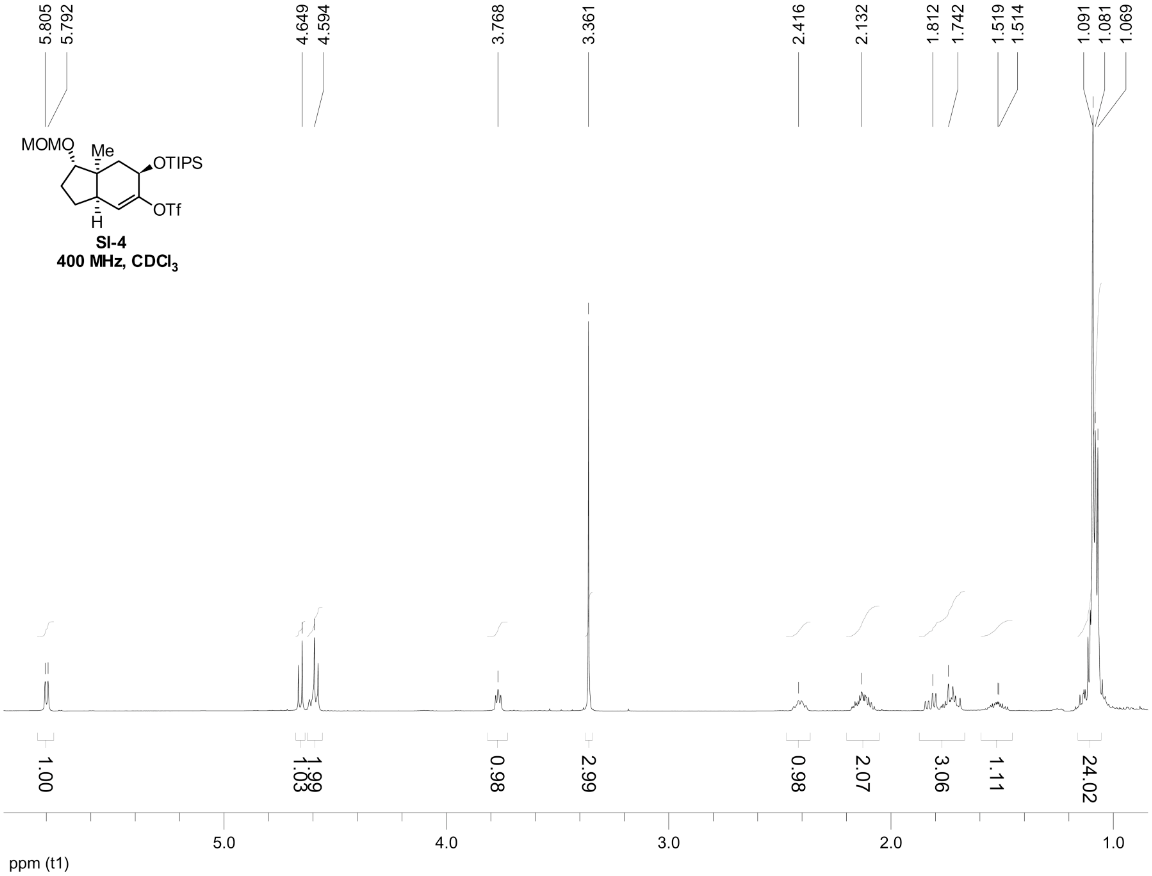
76.68
73.19
55.49
45.99
45.02
43.55
40.15
28.93
27.77
19.21
17.89
17.87
12.23
MOMO
Me
OTIPS
O
H
SI-3
100 MHz, CDCl$_3$
200
150
100
50
0
ppm (t1)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1.081
1.069
MOMO
Me
OTIPS
OTf
H
SI-4
400 MHz, $CDCl_3$
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1.03
1.99
0.98
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0.98
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24.02
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3.0
2.0
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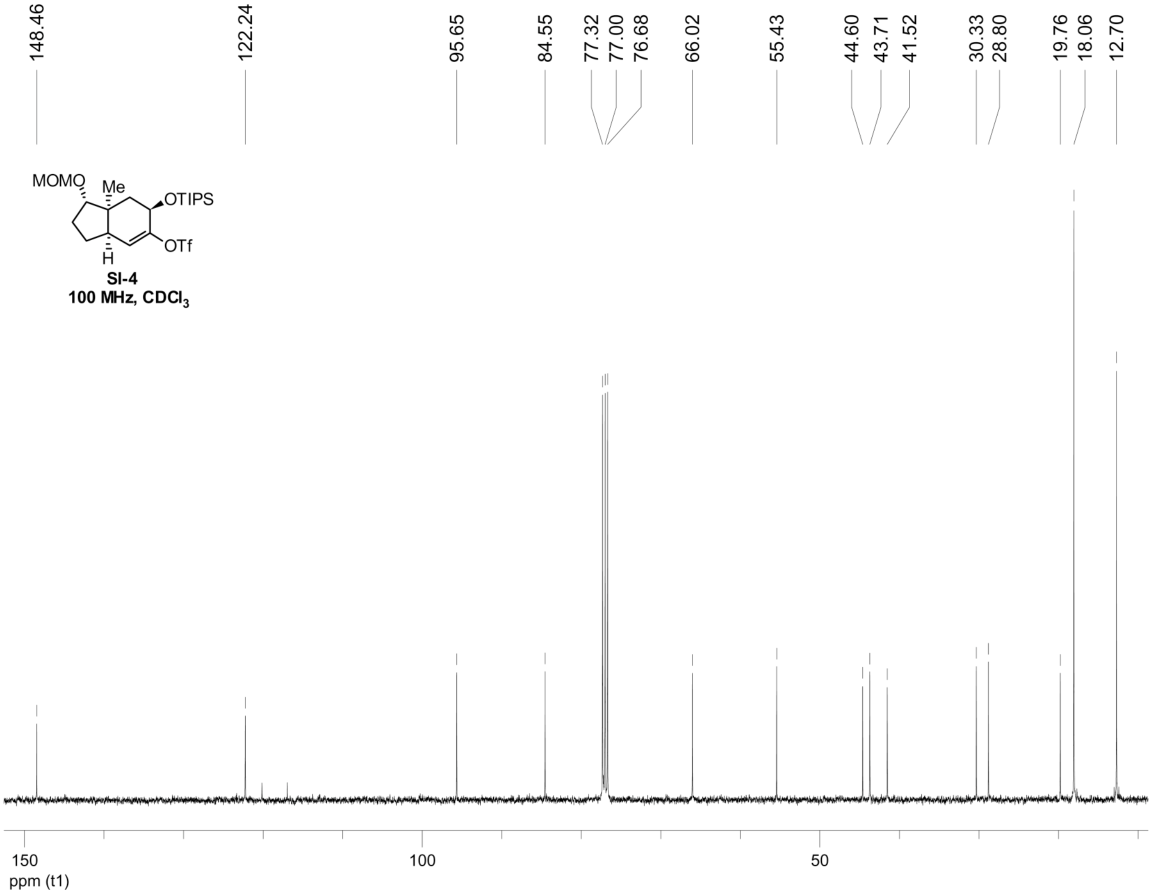
ppm (t1)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30.33
28.80
19.76
18.06
12.70
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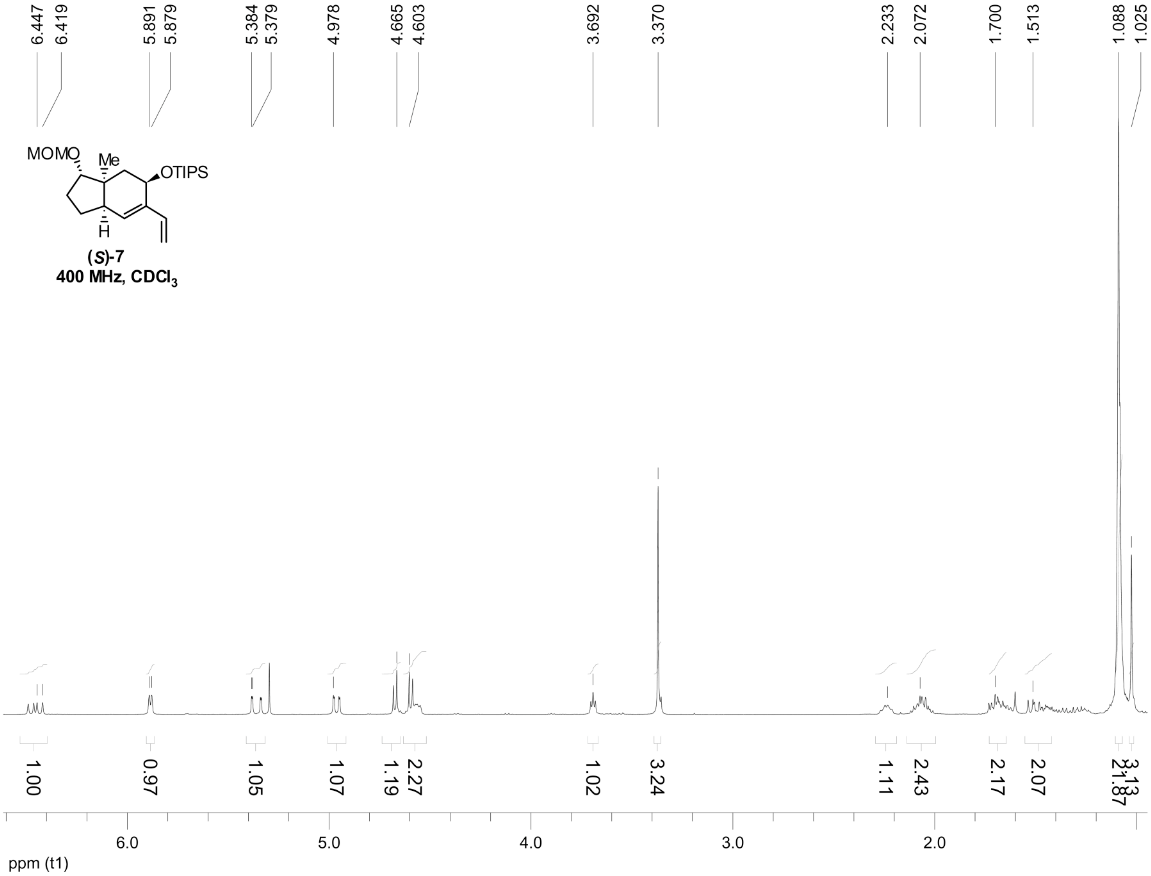
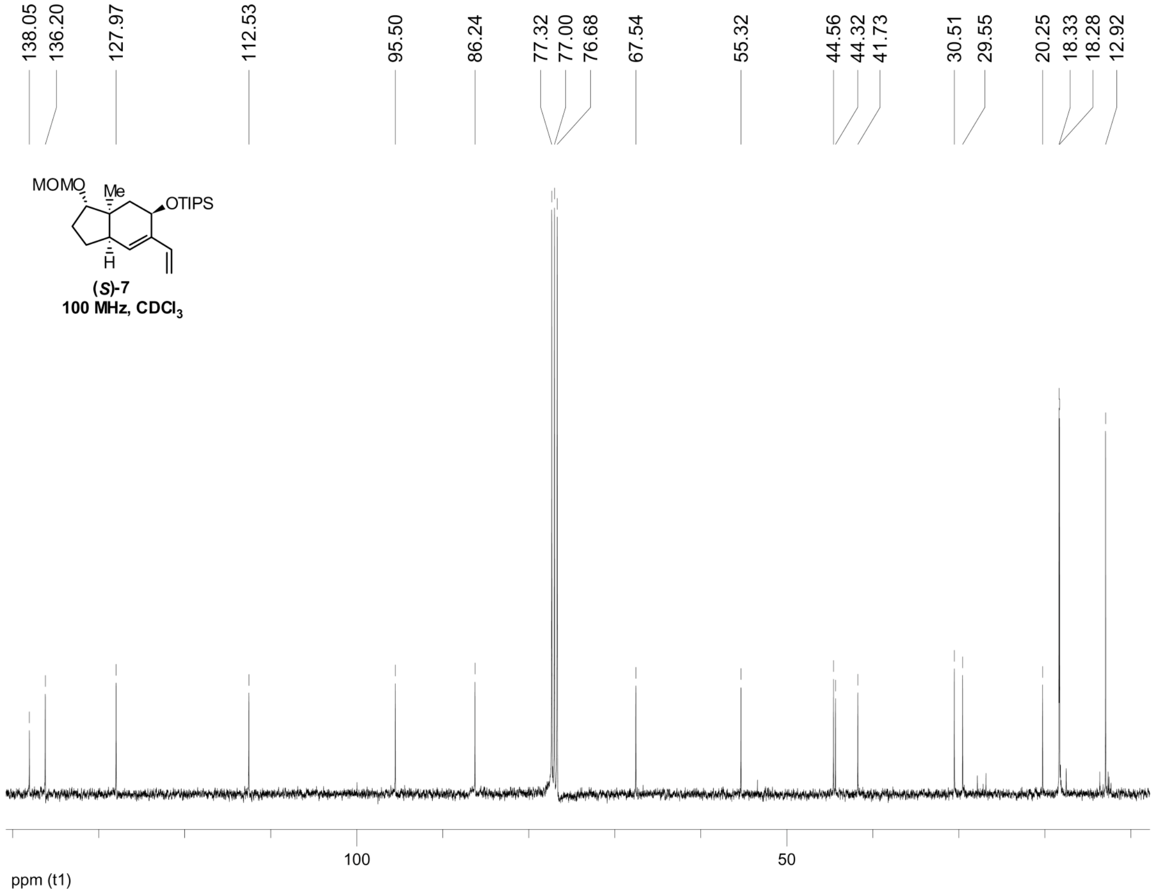
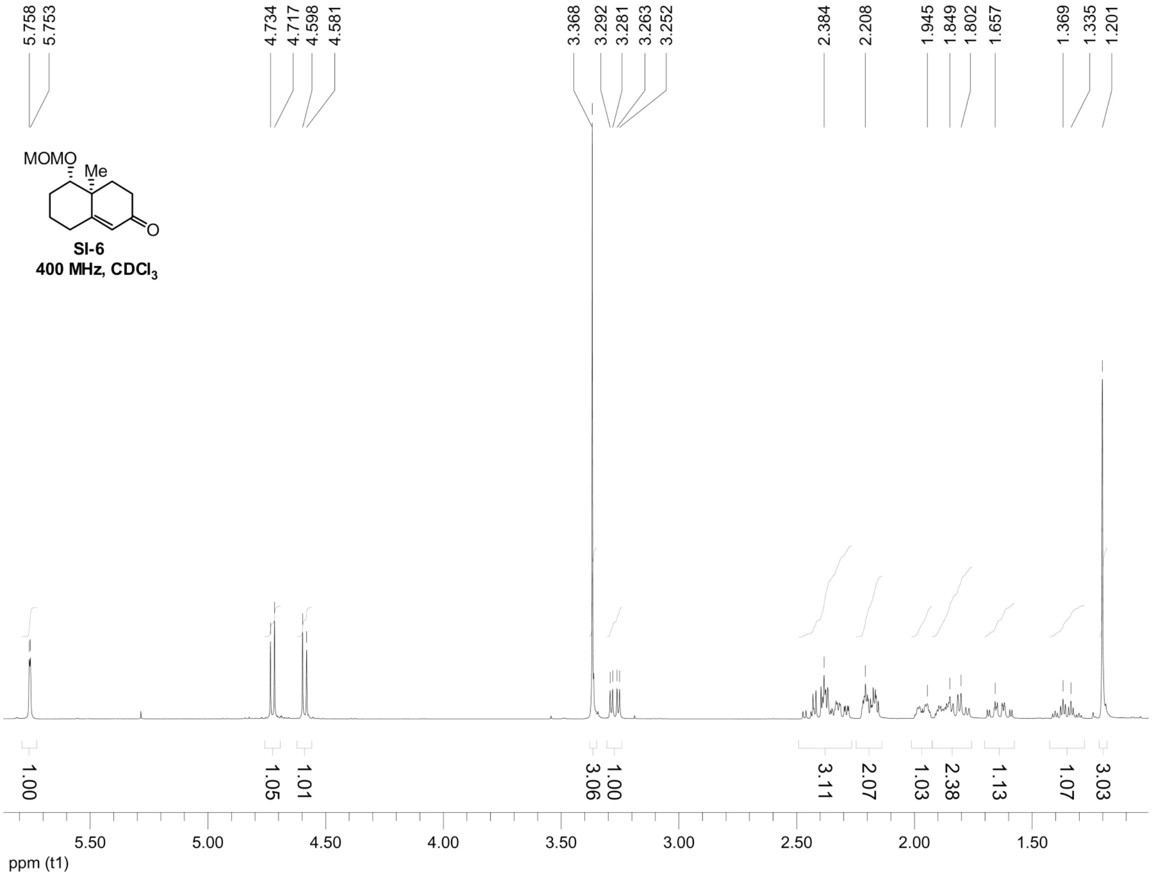
Me
OTIPS
OTf
H
SI-4
100 MHz, $CDCl_3$
150
100
50
ppm (t1)


(*S*)-7
400 MHz, CDCl$_3$


(*S*)-7
100 MHz, CDCl$_3$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1.849
1.802
1.657
1.369
1.335
1.201
MOMO
Me
O
SI-6
400 MHz, $CDCl_3$
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1.05
1.01
3.06
1.00
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2.07
1.03
2.38
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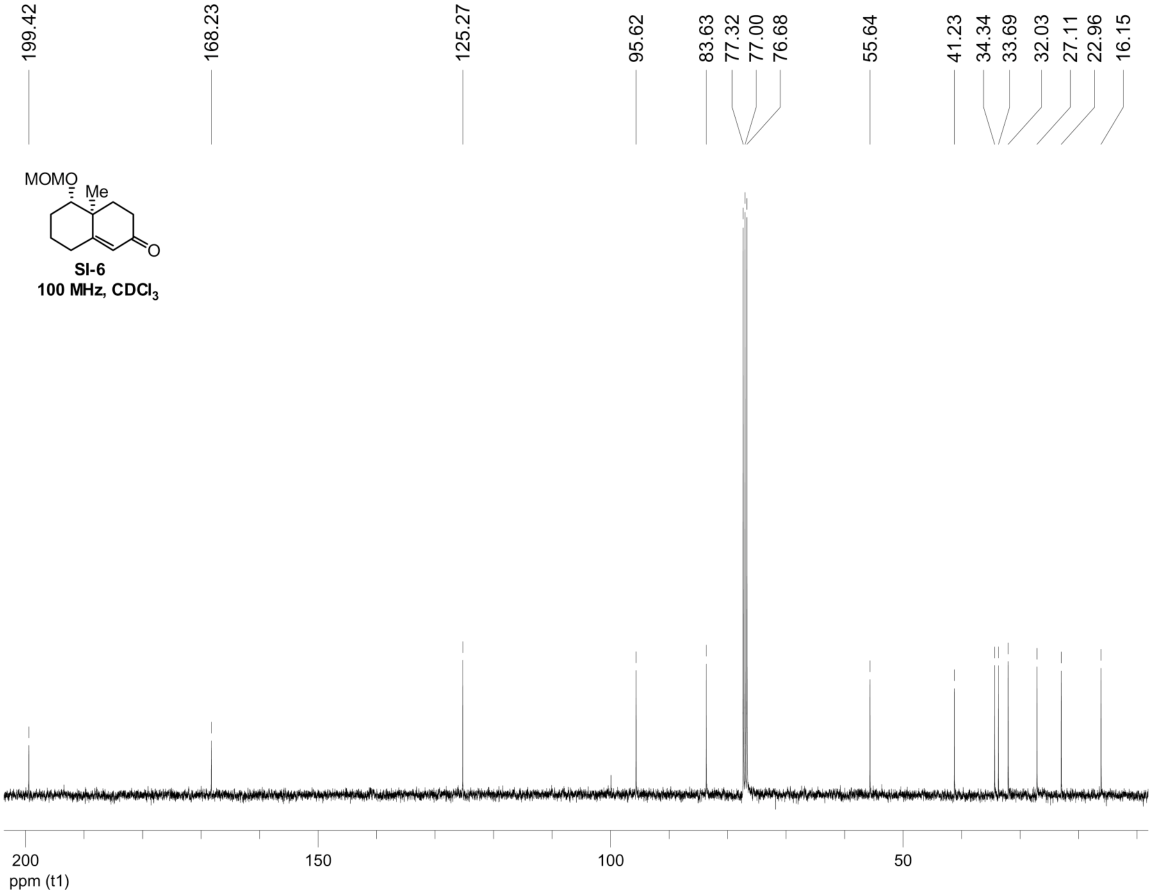
ppm (t1)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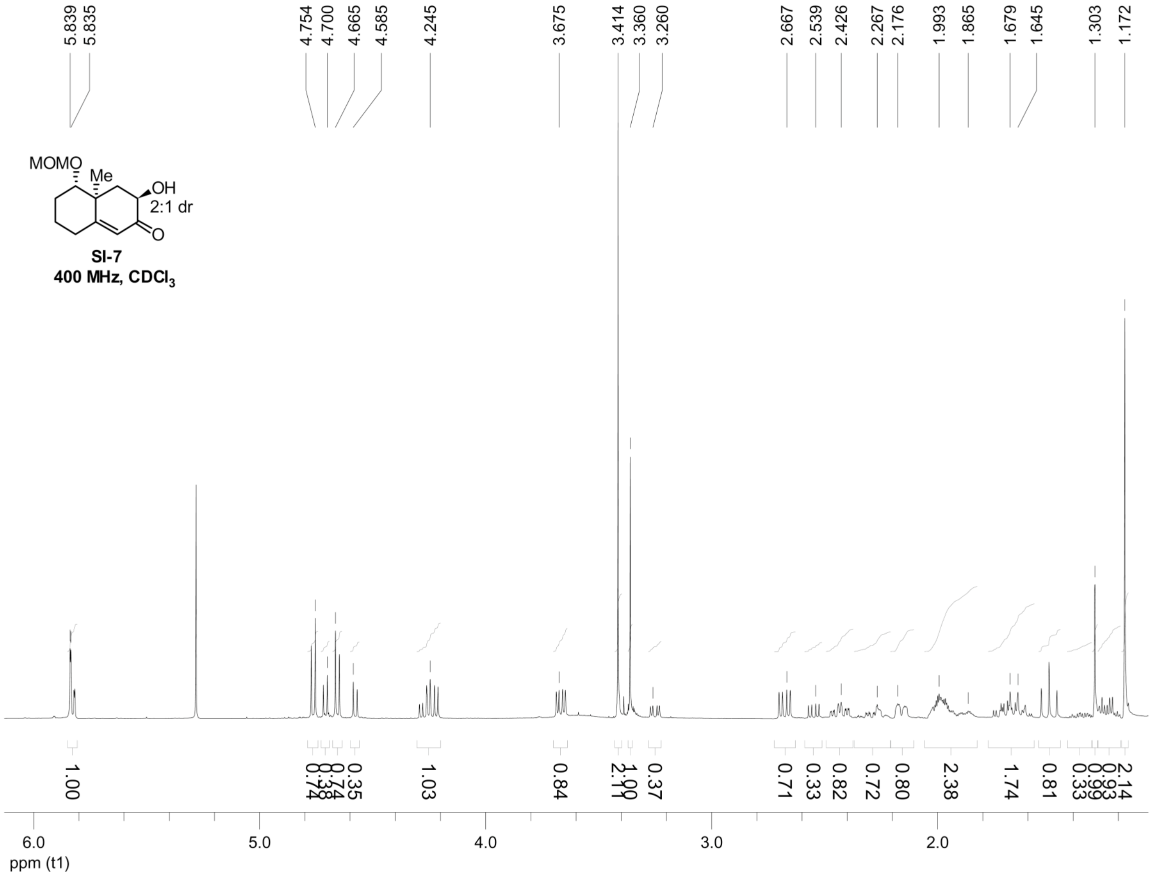
32.03
27.11
22.96
16.15
MOMO
Me
O
SI-6
100 MHz, $CDCl_3$
200
150
100
50
ppm (t1)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1.303
1.172
MOMO
Me
OH
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O
SI-7
400 MHz, CDCl3
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0.74
0.38
0.74
0.35
1.03
0.84
2.11
1.00
0.37
0.71
0.33
0.82
0.72
0.80
2.38
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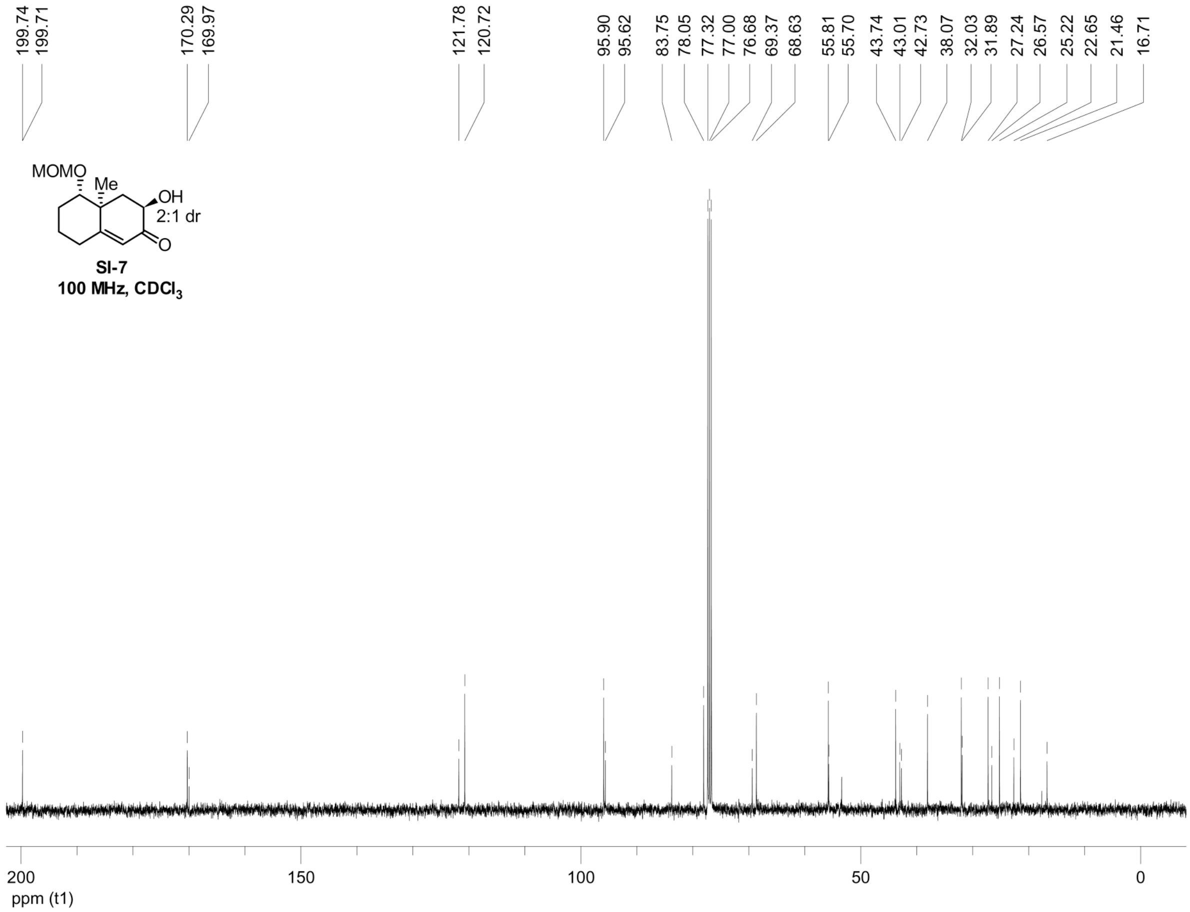
ppm (t1)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55.70
43.74
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42.73
38.07
32.03
31.89
27.24
26.57
25.22
22.65
21.46
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Me
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SI-7
100 MHz, CDCl3
200
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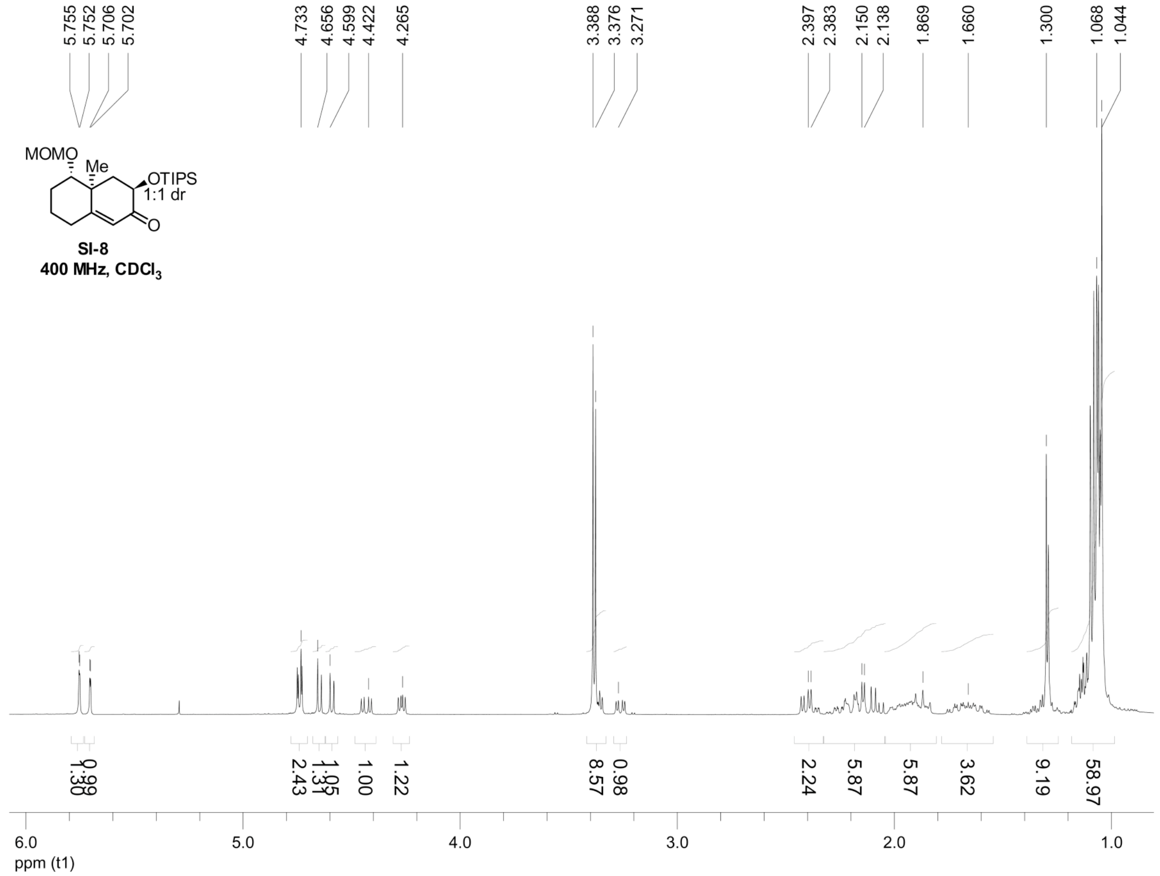
0
ppm (t1)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1.300
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1.044
MOMO
Me
OTIPS
1:1 dr
O
SI-8
400 MHz, $CDCl_3$
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0.99
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1.31
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1.00
1.22
8.57
0.98
2.24
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9.19
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3.0
2.0
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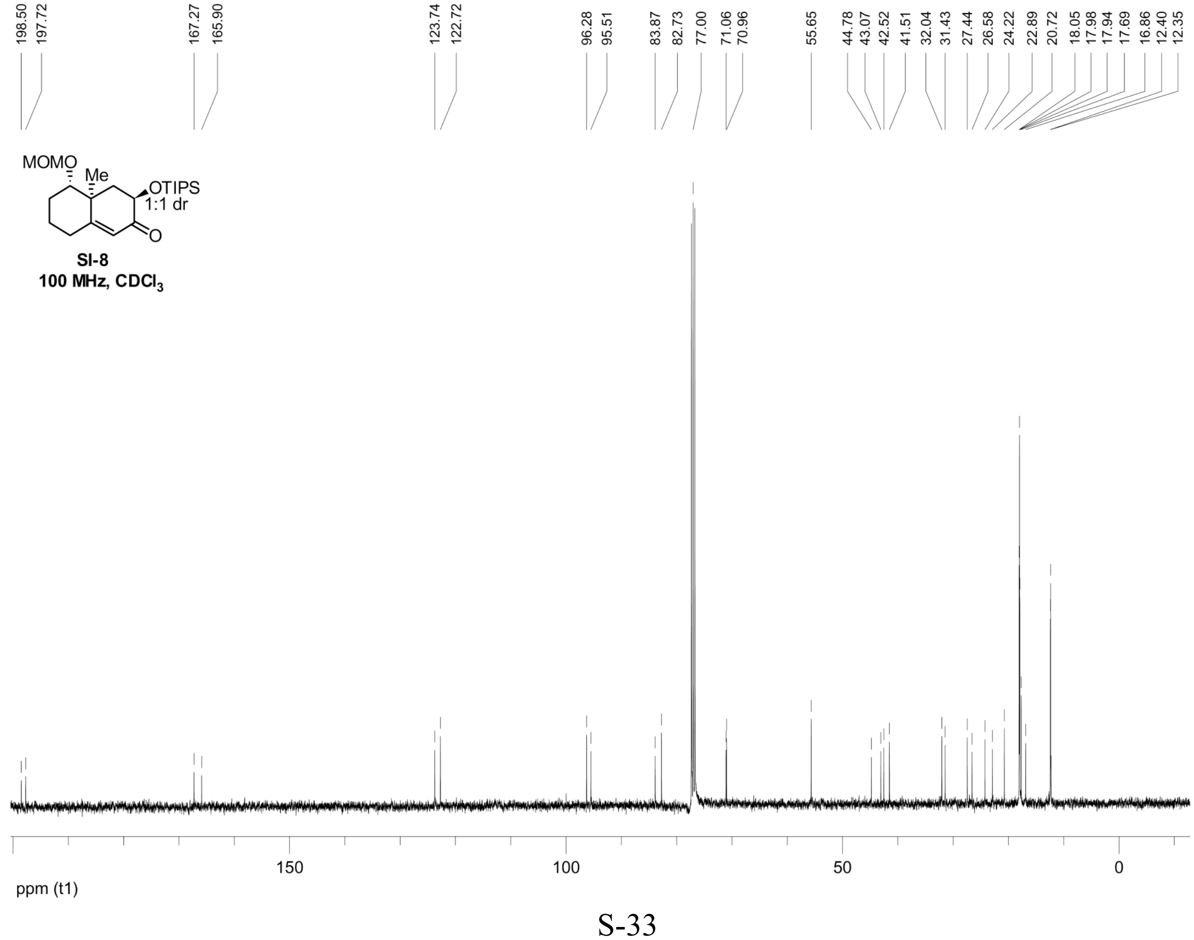
ppm (t1)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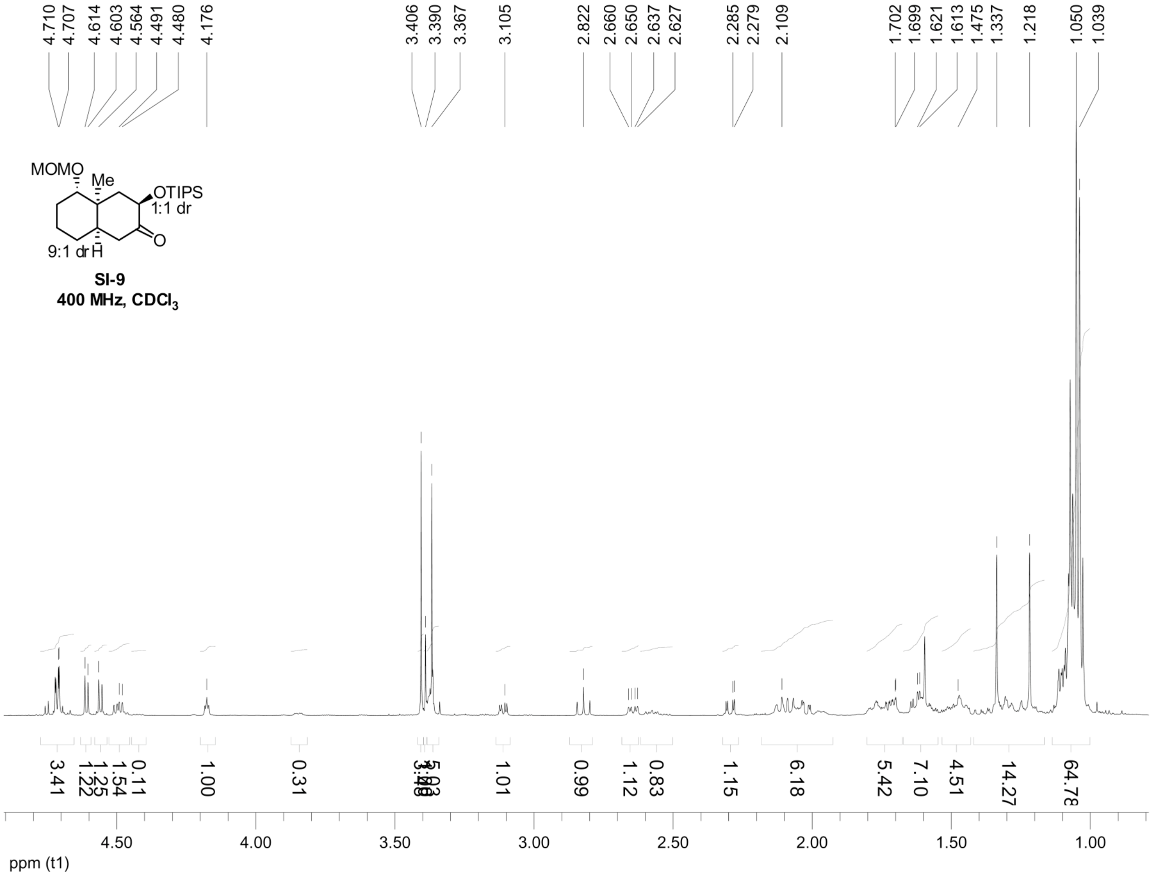
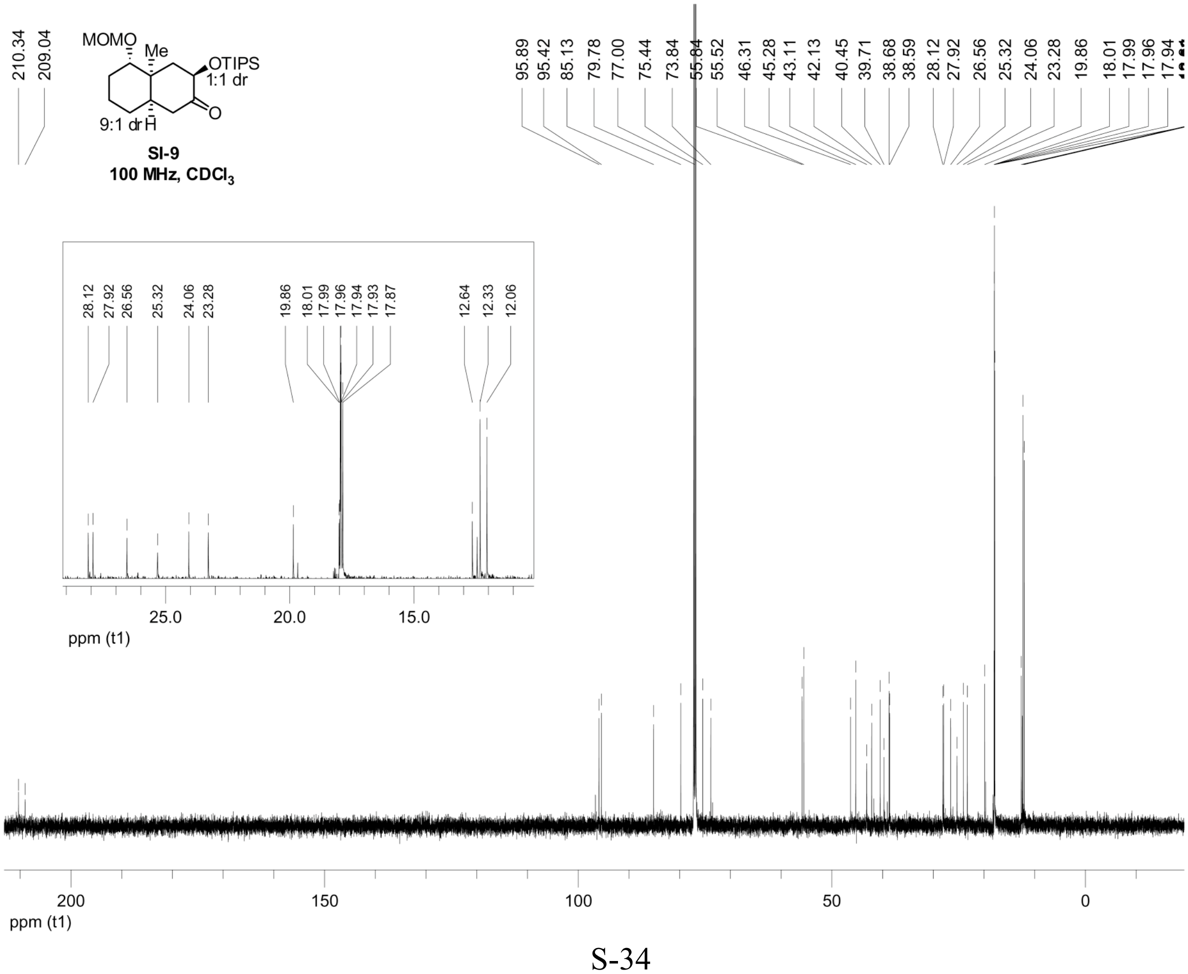
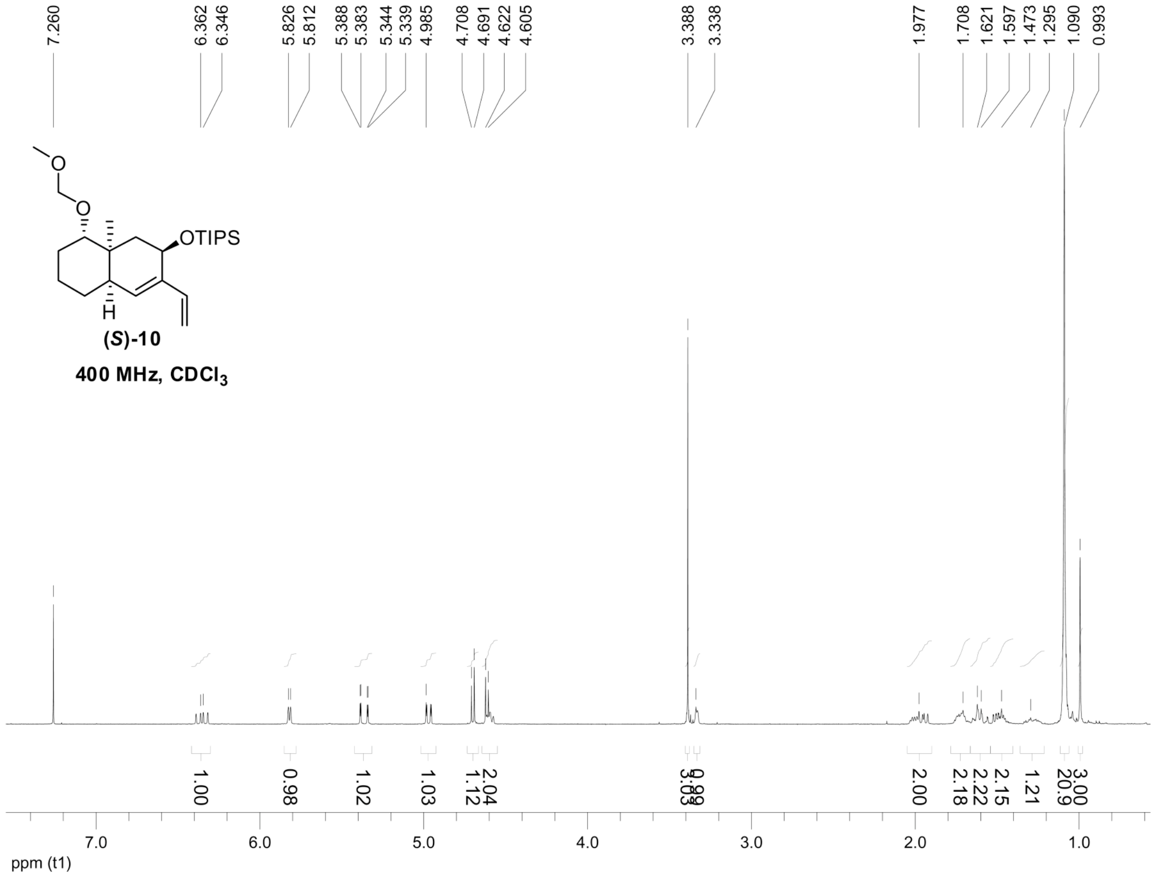
165.90
123.74
122.72
96.28
95.51
83.87
82.73
77.00
71.06
70.96
55.65
44.78
43.07
42.52
41.51
32.04
31.43
27.44
26.58
24.22
22.89
20.72
18.05
17.98
17.94
17.69
16.86
12.40
12.35
MOMO
Me
OTIPS
1:1 dr
O
SI-8
100 MHz, $CDCl_3$
150
100
50
0
ppm (t1)

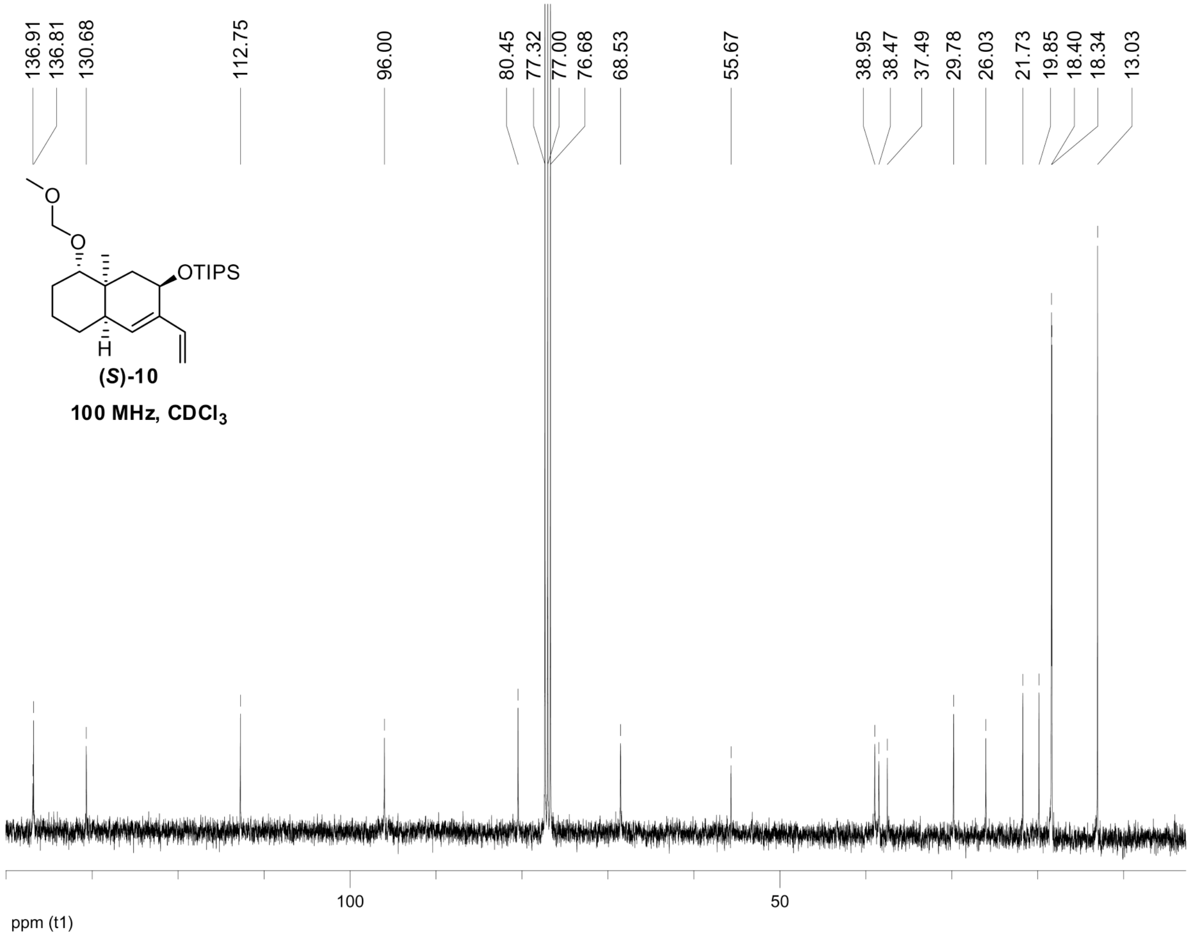


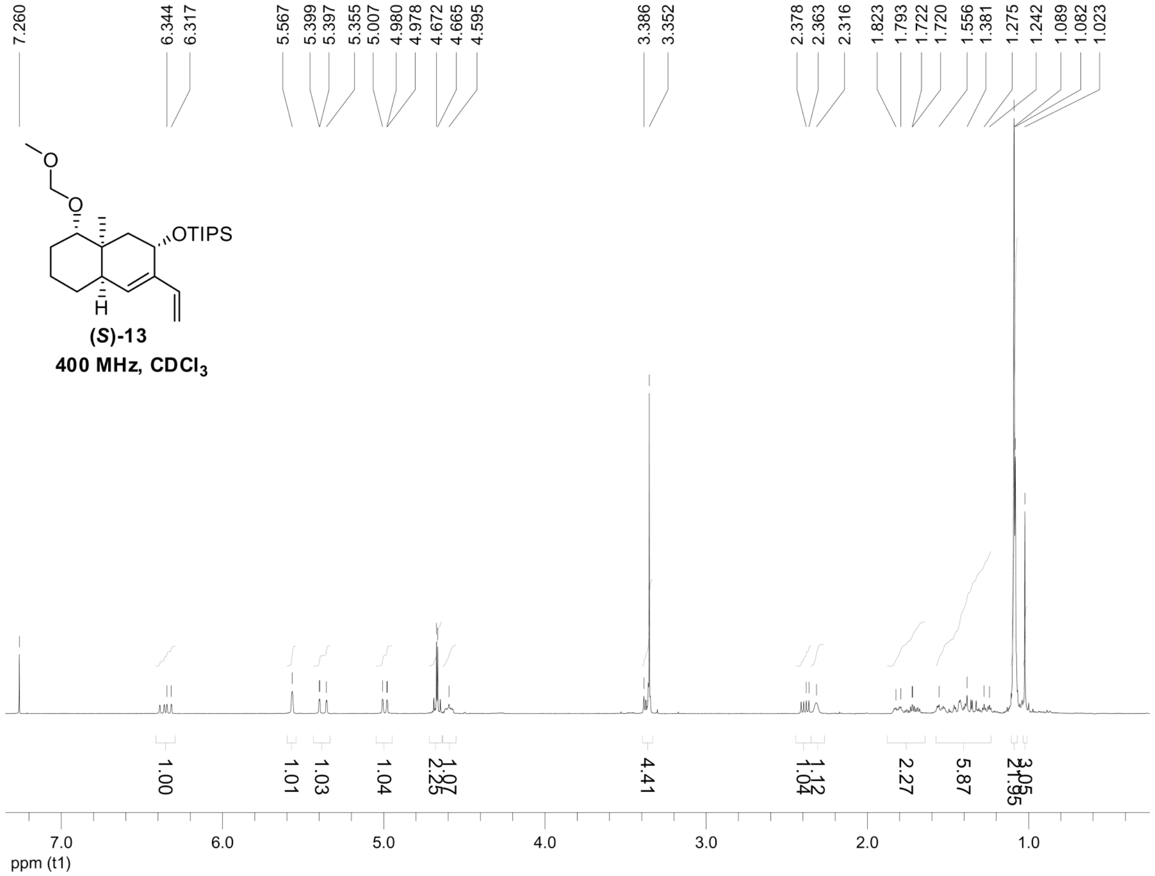
SI-9
400 MHz, $CDCl_3$

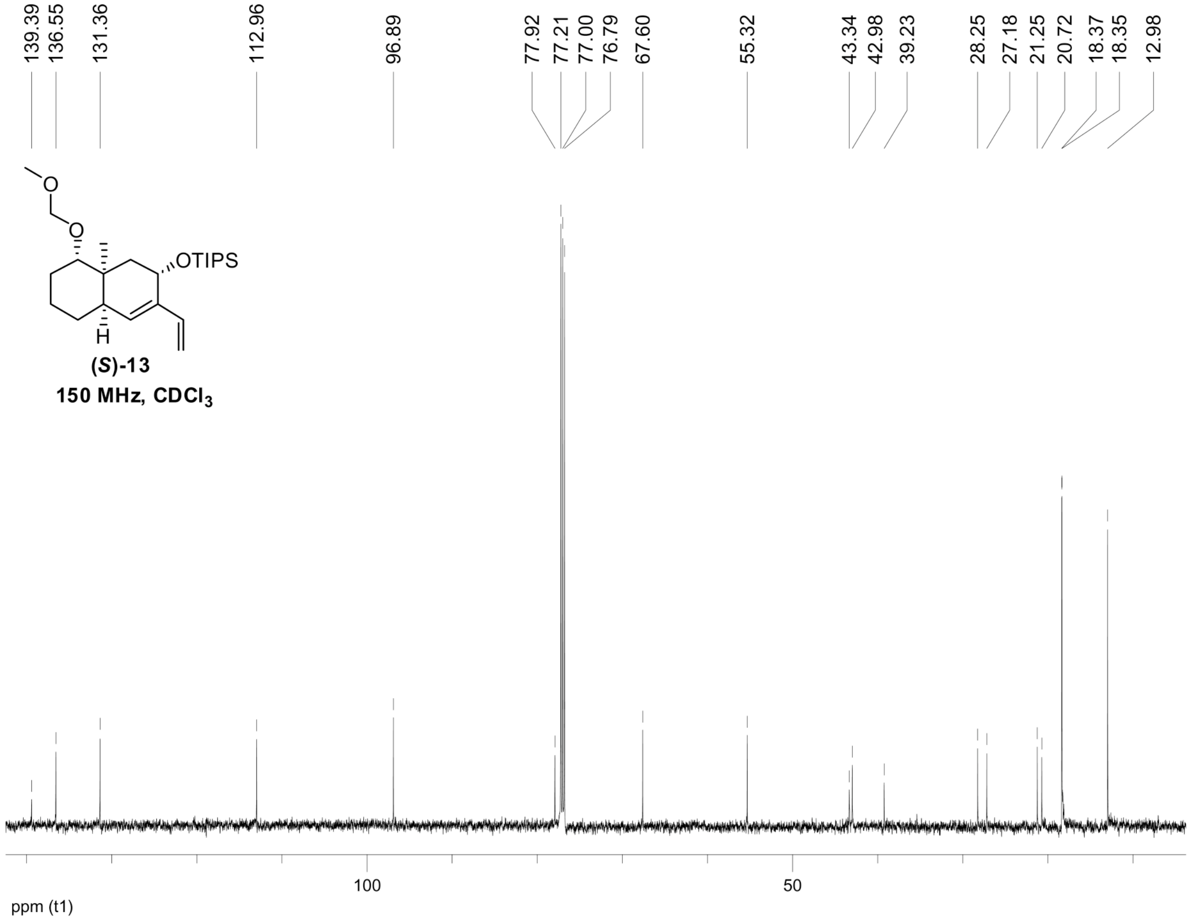


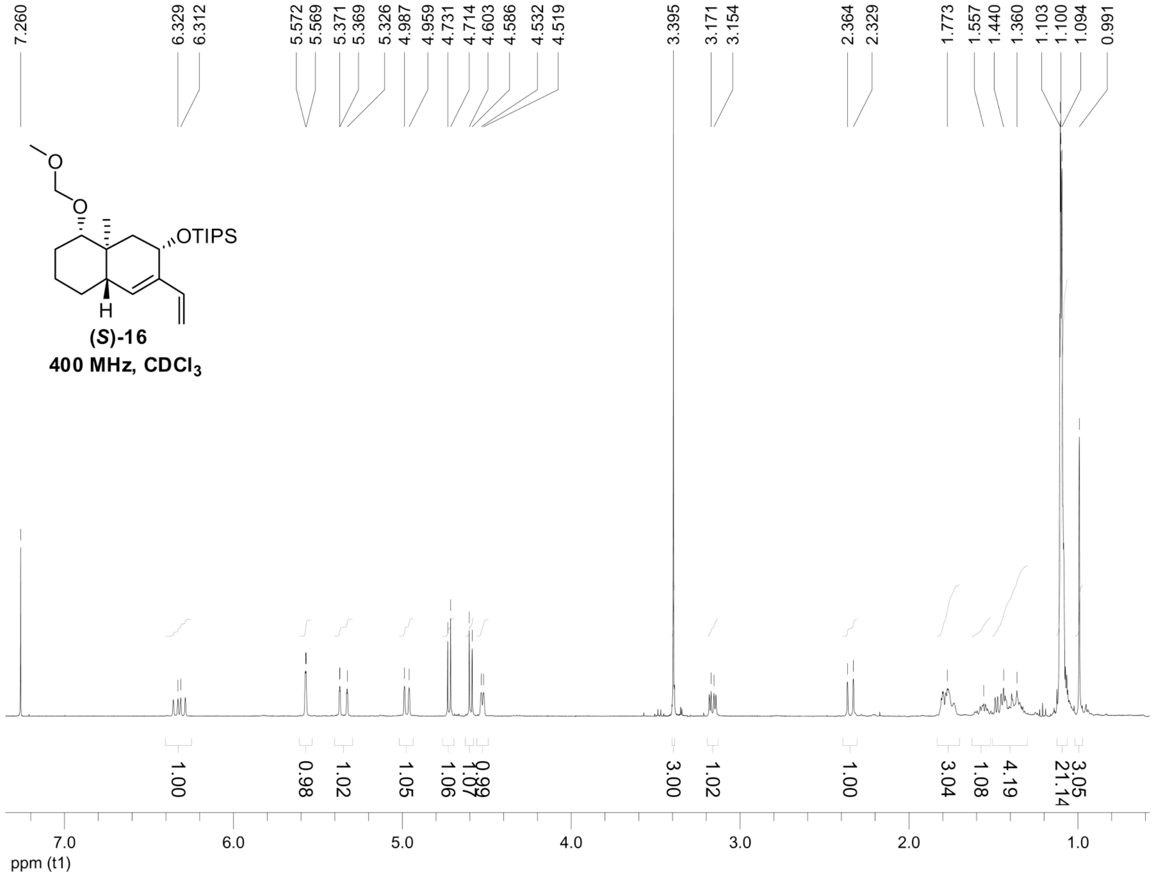
SI-9
100 MHz, $CDCl_3$

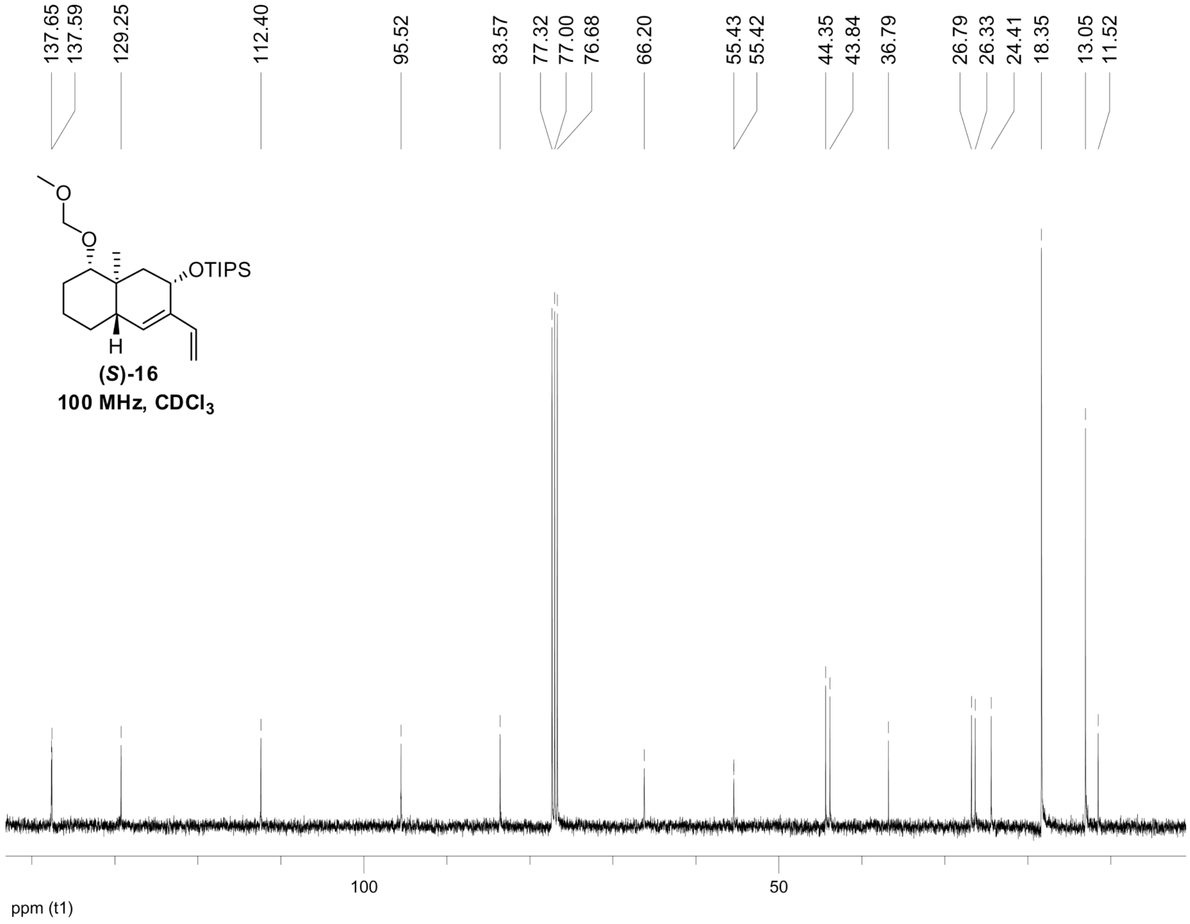

7.260
6.362
6.346
5.826
5.812
5.388
5.383
5.344
5.339
4.985
4.708
4.691
4.622
4.605
3.388
3.338
1.977
1.708
1.621
1.597
1.473
1.295
1.090
0.993
O
O
OTIPS
H
(S)-10
400 MHz, CDCl3
1.00
0.98
1.02
1.03
1.12
2.04
3.03
0.99
2.00
2.18
2.22
2.15
1.21
20.9
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

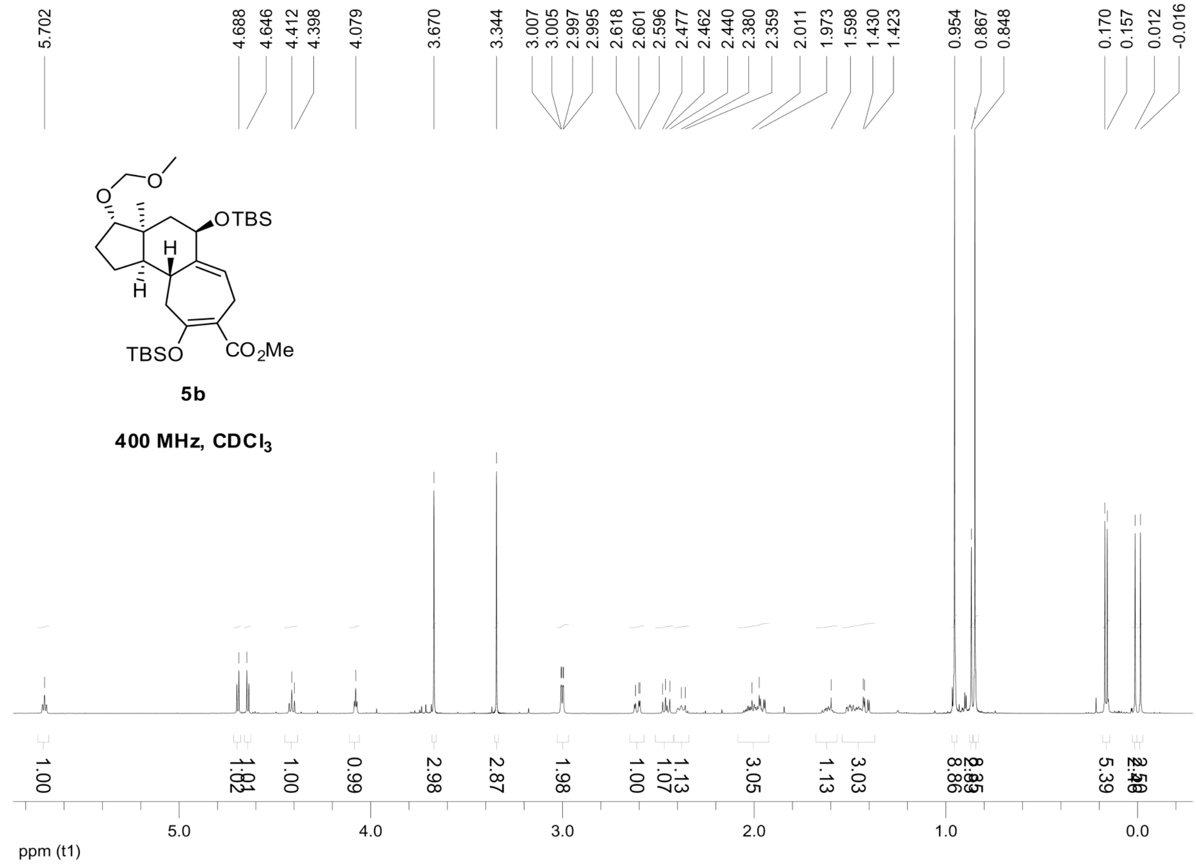

136.91
136.81
130.68
112.75
96.00
80.45
77.32
77.00
76.68
68.53
55.67
38.95
38.47
37.49
29.78
26.03
21.73
19.85
18.40
18.34
13.03
O
O
OTIPS
H
(S)-10
100 MHz, CDCl3
100
50
ppm (t1)


7.260
6.344
6.317
5.567
5.399
5.397
5.355
5.007
4.980
4.978
4.672
4.665
4.595
3.386
3.352
2.378
2.363
2.316
1.823
1.793
1.722
1.720
1.556
1.381
1.275
1.242
1.089
1.082
1.023
OTIPS
H
(S)-13
400 MHz, CDCl3
1.00
1.01
1.03
1.04
2.25
1.07
4.41
1.04
1.12
2.27
5.87
21.95
3.05
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


139.39
136.55
131.36
112.96
96.89
77.92
77.21
77.00
76.79
67.60
55.32
43.34
42.98
39.23
28.25
27.18
21.25
20.72
18.37
18.35
12.98
OTIPS
H
(S)-13
150 MHz, CDCl3
100
50
ppm (t1)

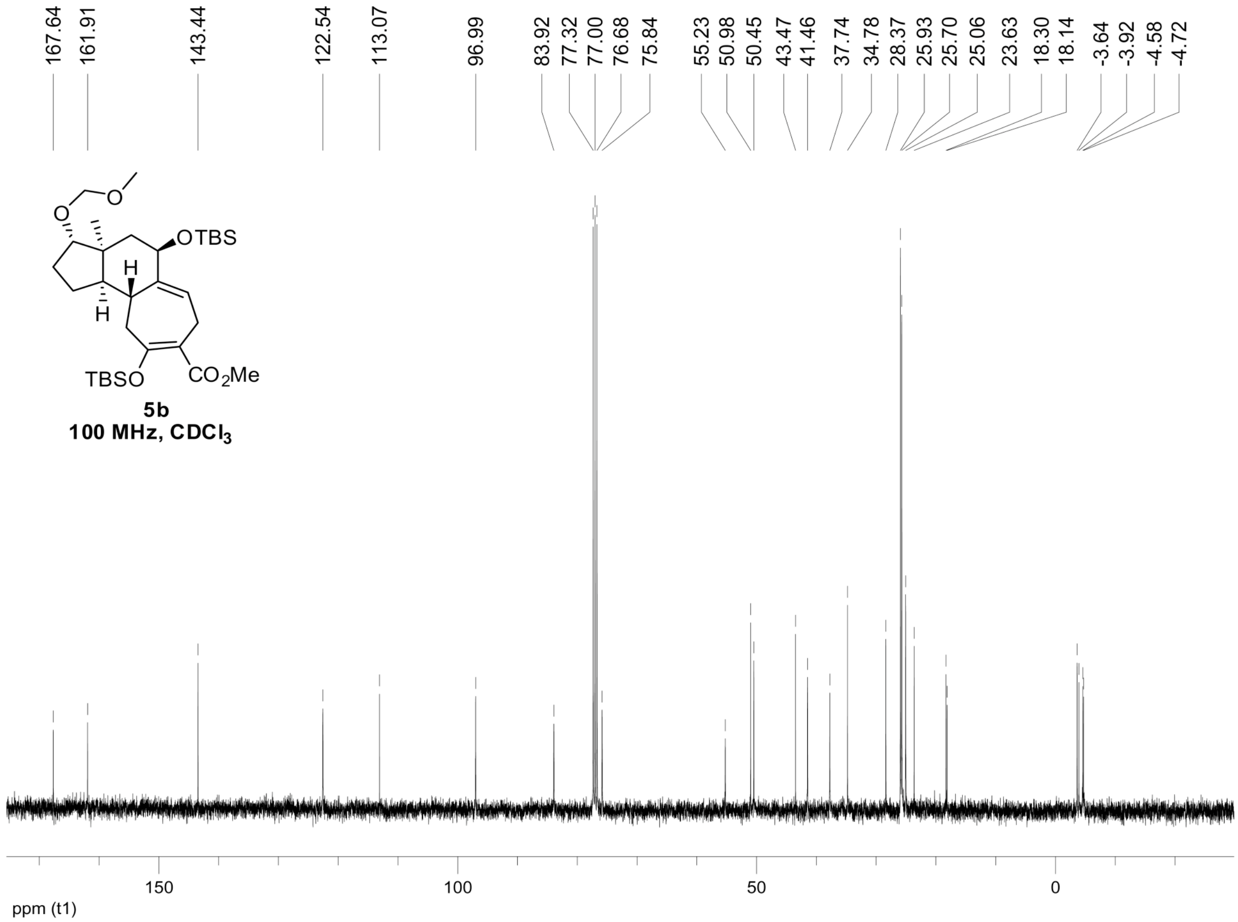

7.260
6.329
6.312
5.572
5.569
5.371
5.369
5.326
4.987
4.959
4.731
4.714
4.603
4.586
4.532
4.519
3.395
3.171
3.154
2.364
2.329
1.773
1.557
1.440
1.360
1.103
1.100
1.094
0.991
OTIPS
H
(S)-16
400 MHz, CDCl3
1.00
0.98
1.02
1.05
1.06
1.07
0.99
3.00
1.02
1.00
3.04
1.08
4.19
21.14
3.05
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


137.65
137.59
129.25
112.40
95.52
83.57
77.32
77.00
76.68
66.20
55.43
55.42
44.35
43.84
36.79
26.79
26.33
24.41
18.35
13.05
11.52
OTIPS
H
(S)-16
100 MHz, CDCl3
100
50
ppm (t1)



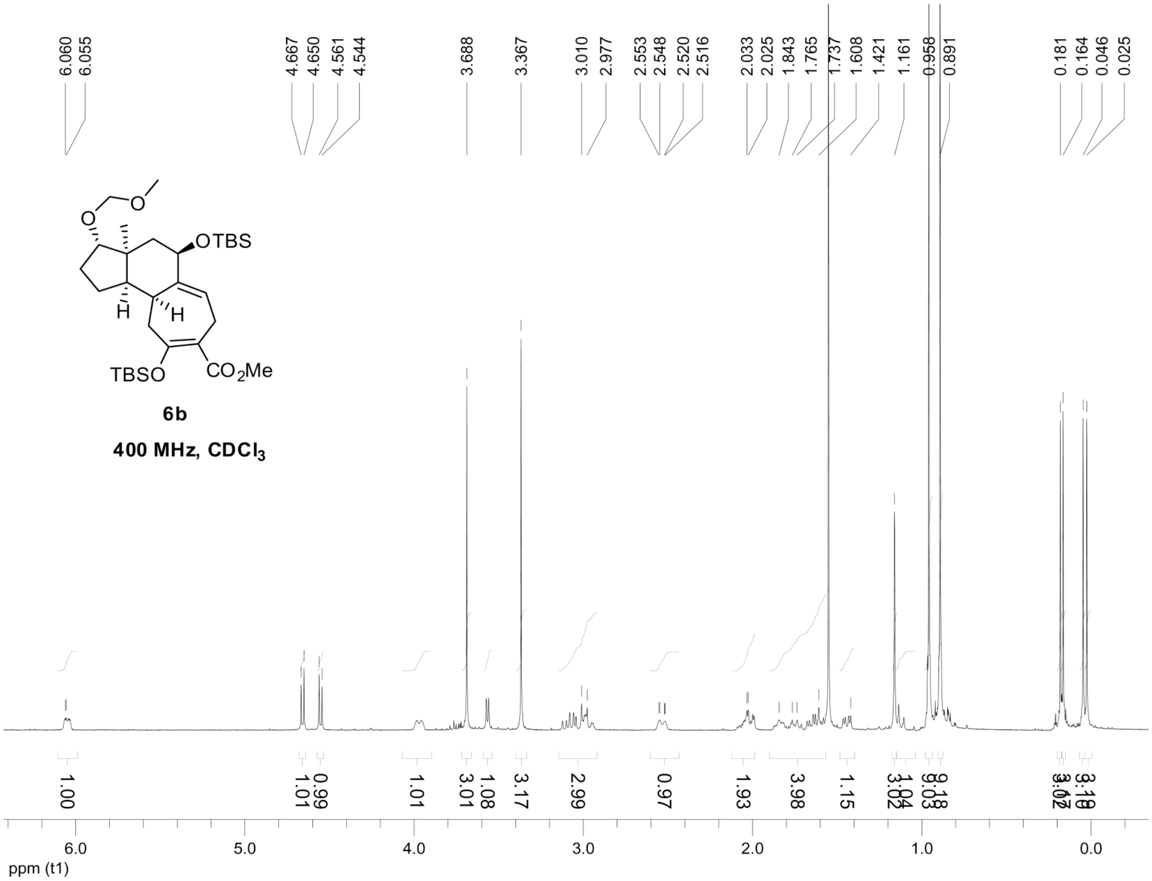
5b

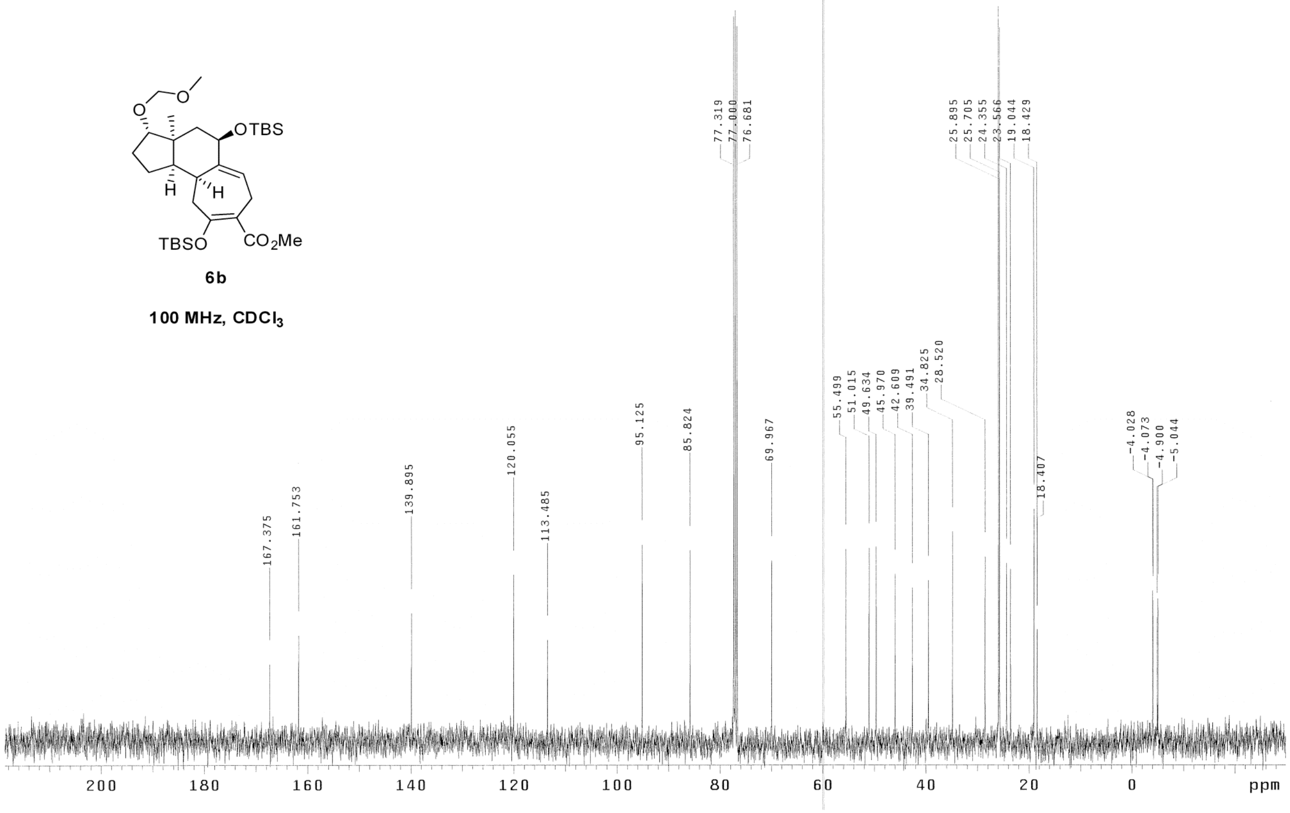
400 MHz, $CDCl_3$

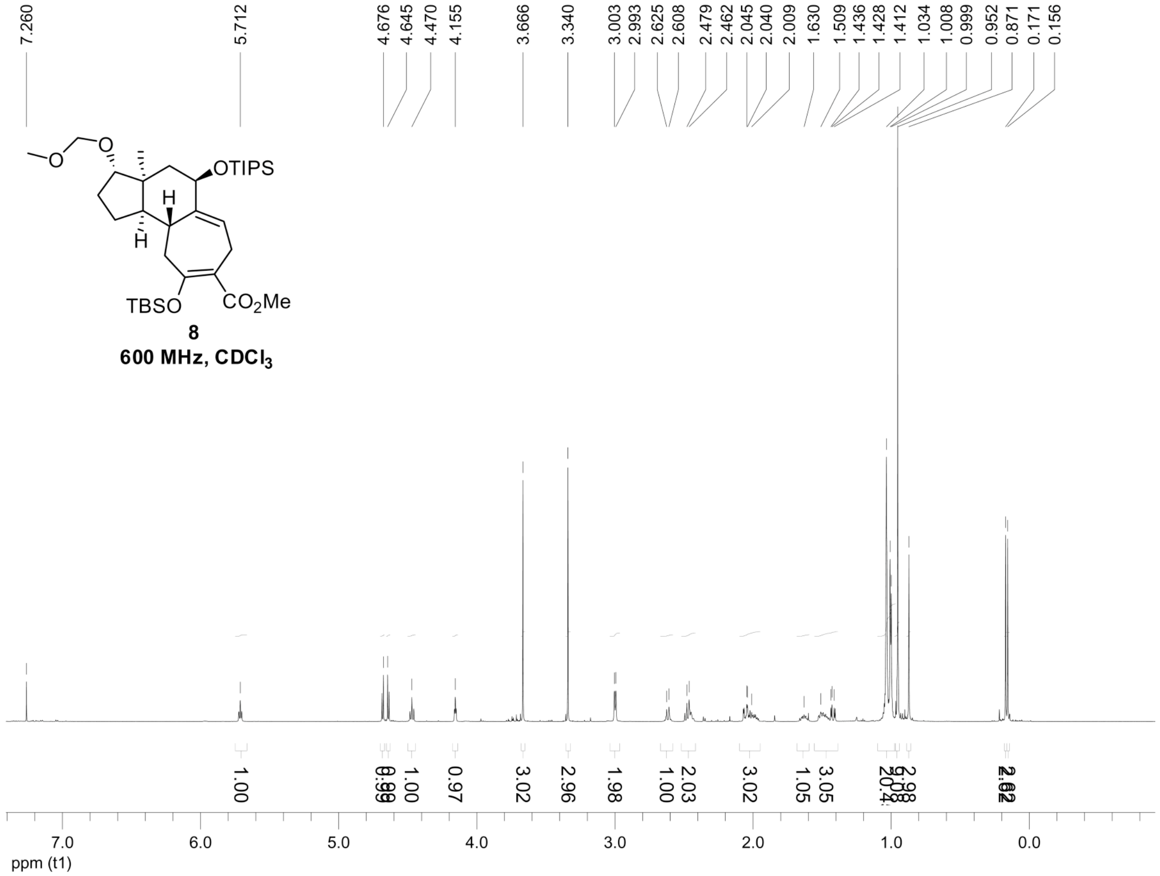


5b

100 MHz, $CDCl_3$

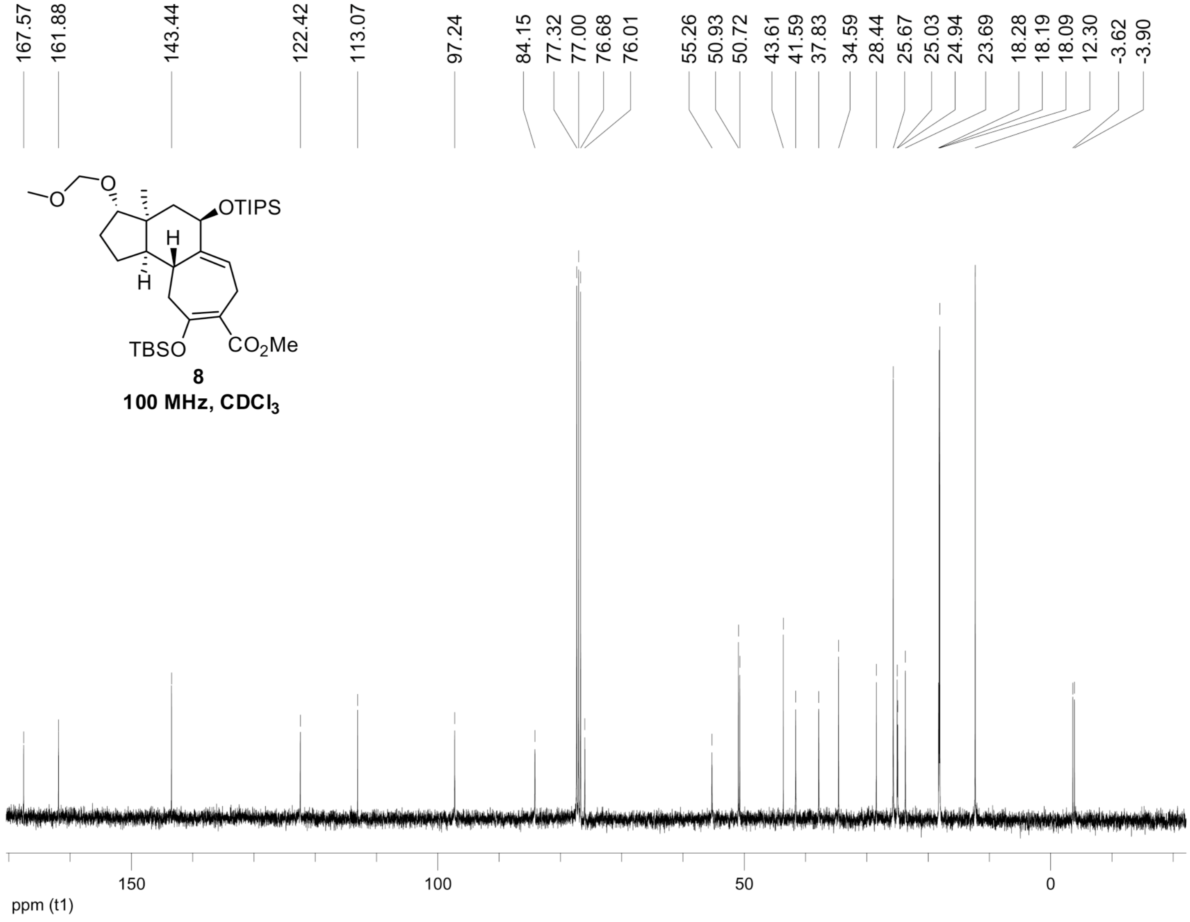

6.060
6.055
4.667
4.650
4.561
4.544
3.688
3.367
3.010
2.977
2.553
2.548
2.520
2.516
2.033
2.025
1.843
1.765
1.737
1.608
1.421
1.161
0.958
0.891
0.181
0.164
0.046
0.025
OTBS
H
H
TBSO
CO2Me
6b
400 MHz, CDCl3
1.00
1.01
0.99
1.01
3.01
1.08
3.17
2.99
0.97
1.93
3.98
1.15
3.02
1.04
9.03
9.18
3.02
3.07
3.19
3.10
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


77.319
77.000
76.681
25.895
25.705
24.355
23.566
19.044
18.429
OTBS
H
H
TBSO
CO2Me
6b
100 MHz, CDCl3
55.499
51.015
49.634
45.970
42.609
39.491
34.825
28.520
167.375
161.753
139.895
120.055
113.485
95.125
85.824
69.967
18.407
-4.028
-4.073
-4.900
-5.044
200
180
160
140
120
100
80
60
40
20
0
ppm



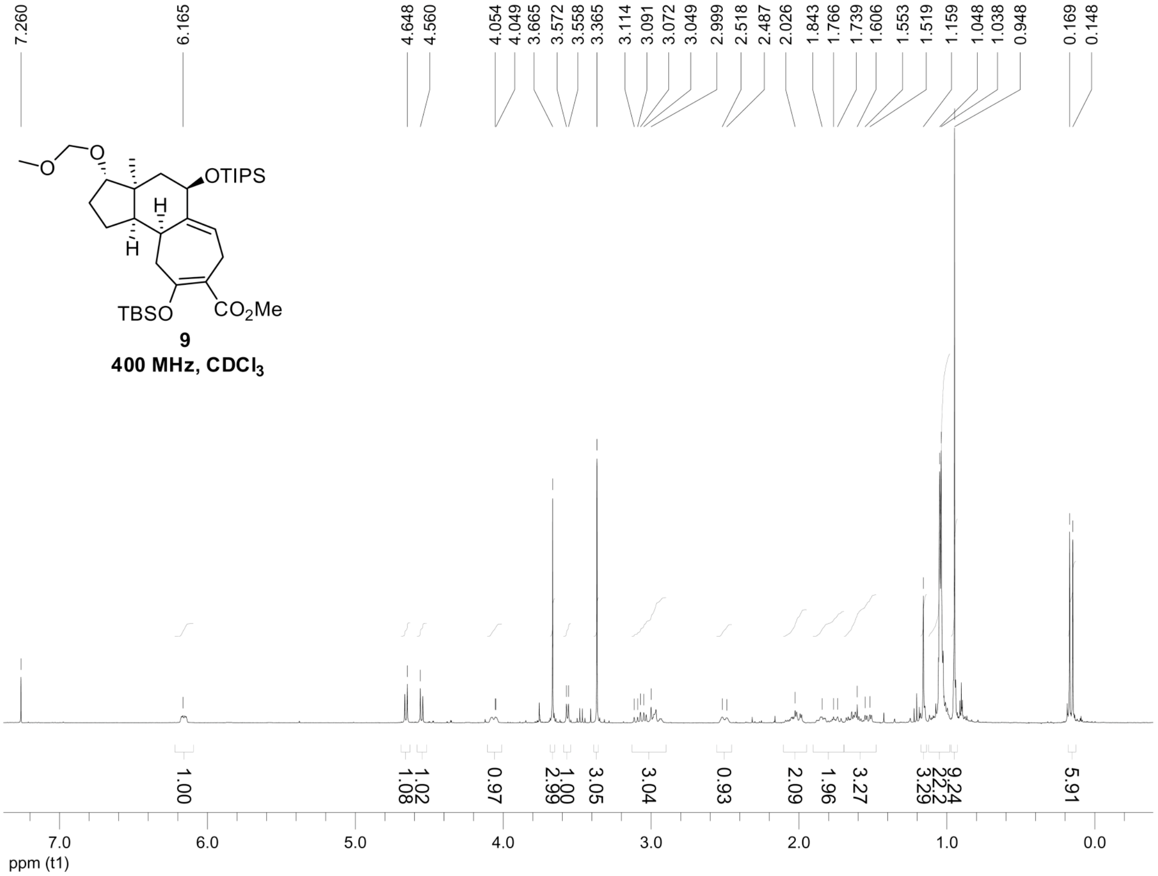
8

600 MHz, $CDCl_3$



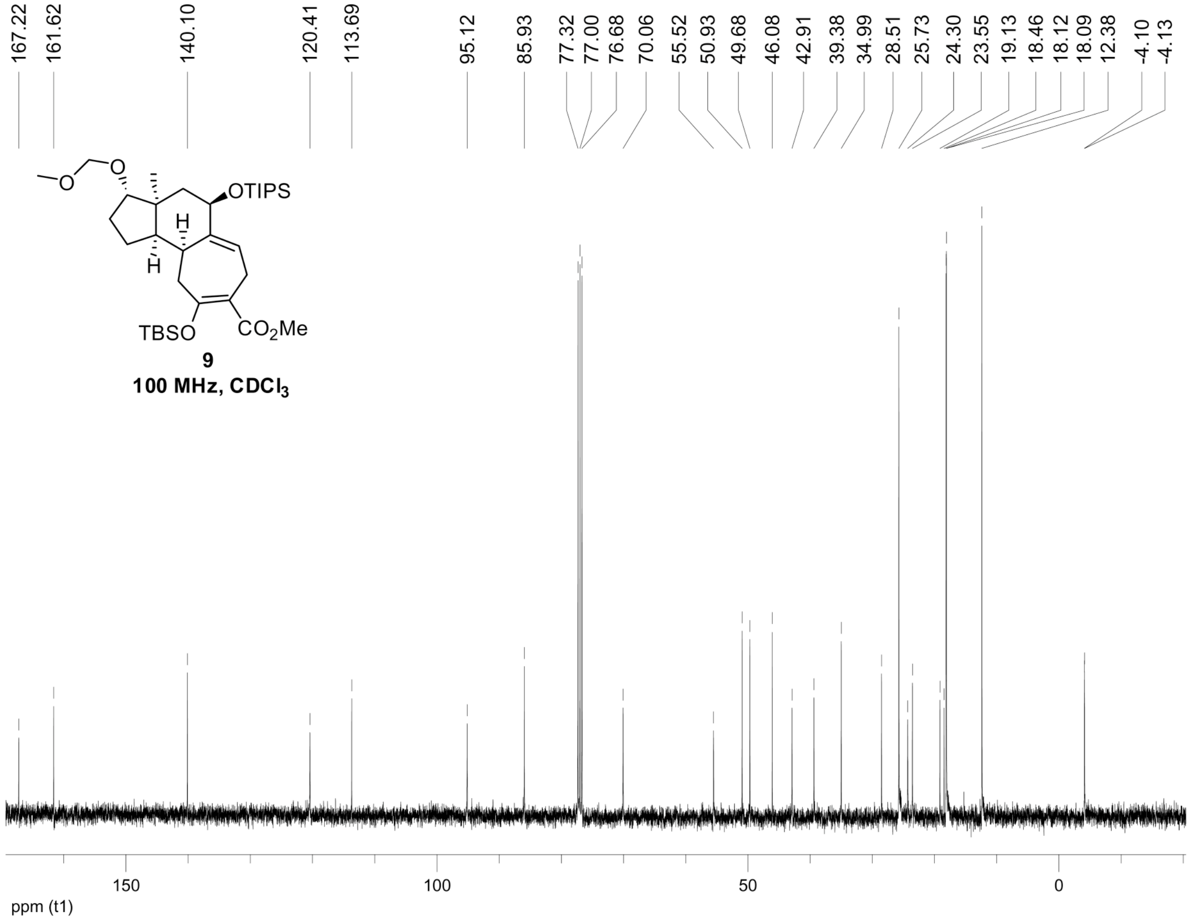
8

100 MHz, $CDCl_3$



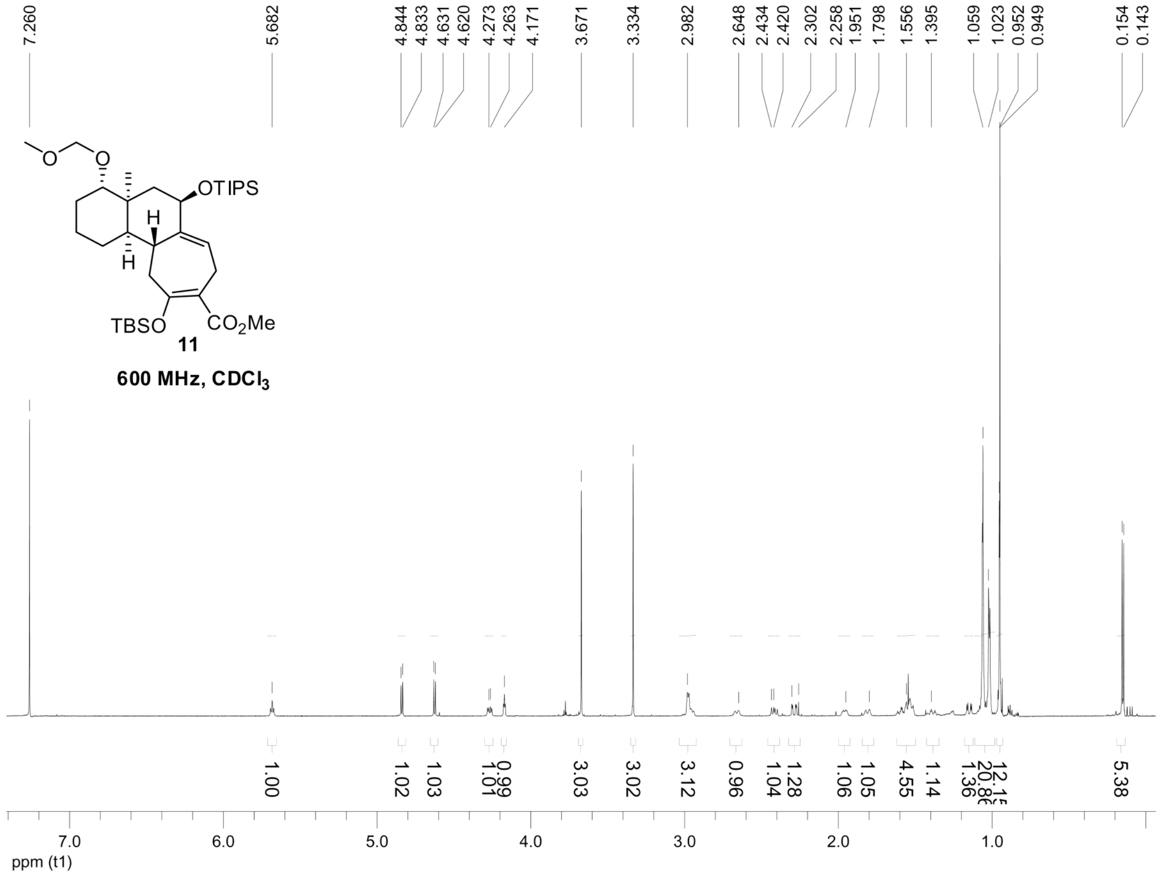
9

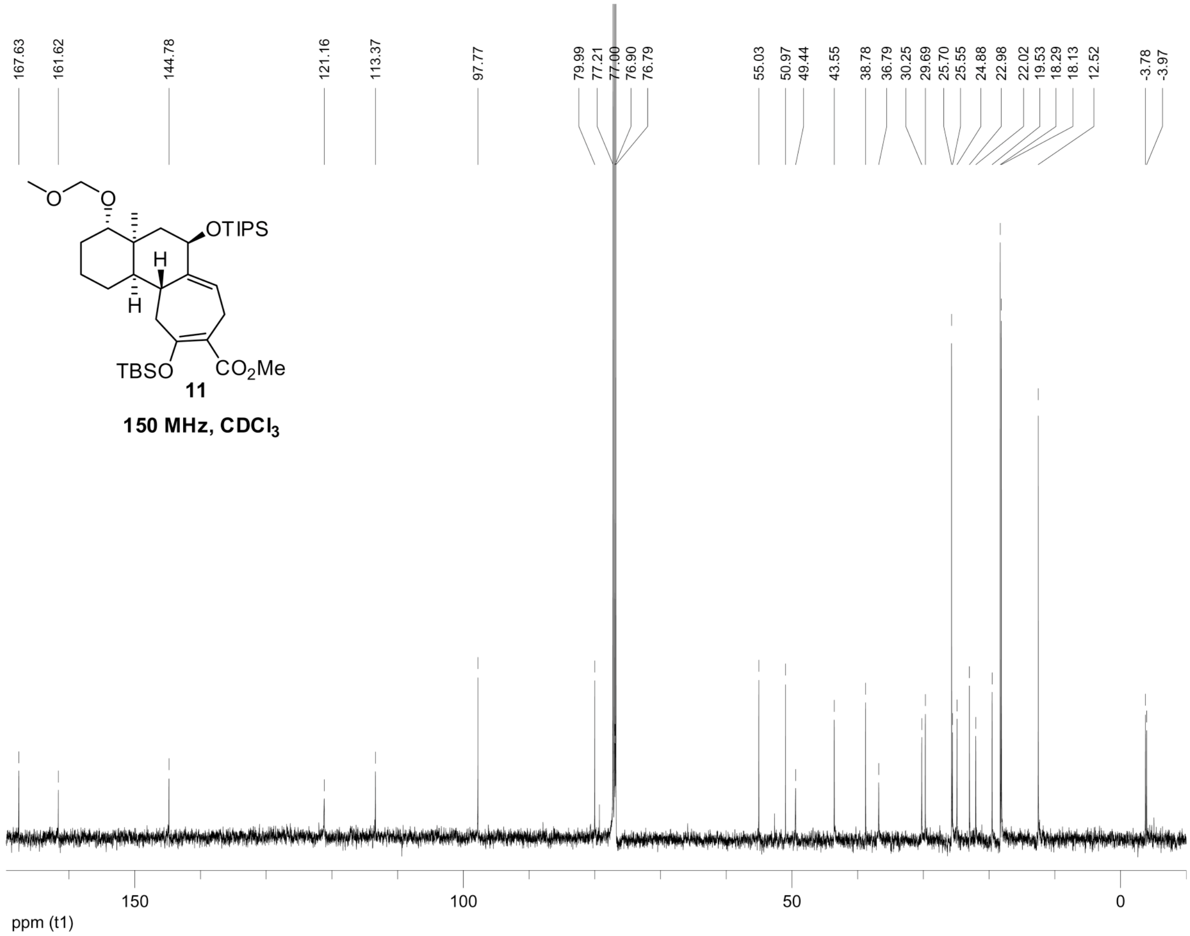
400 MHz, CDCl$_3$

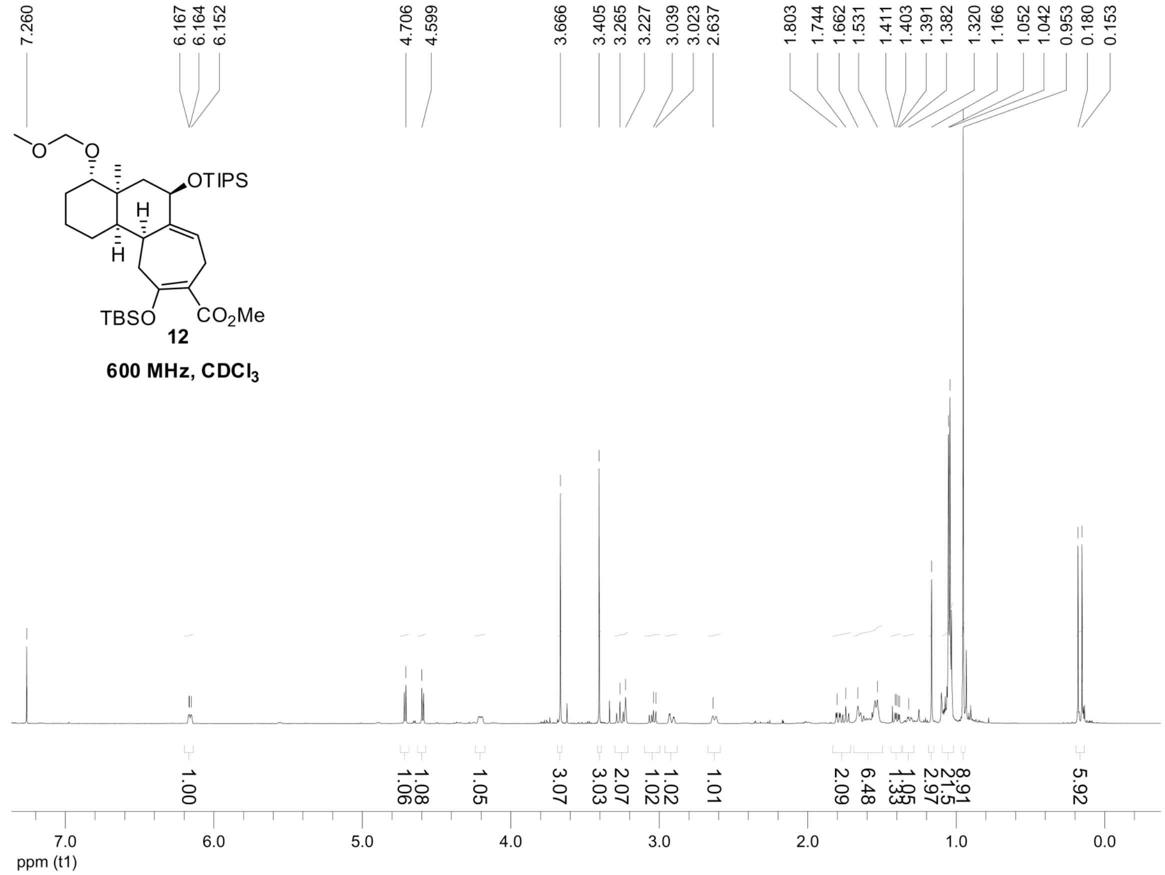


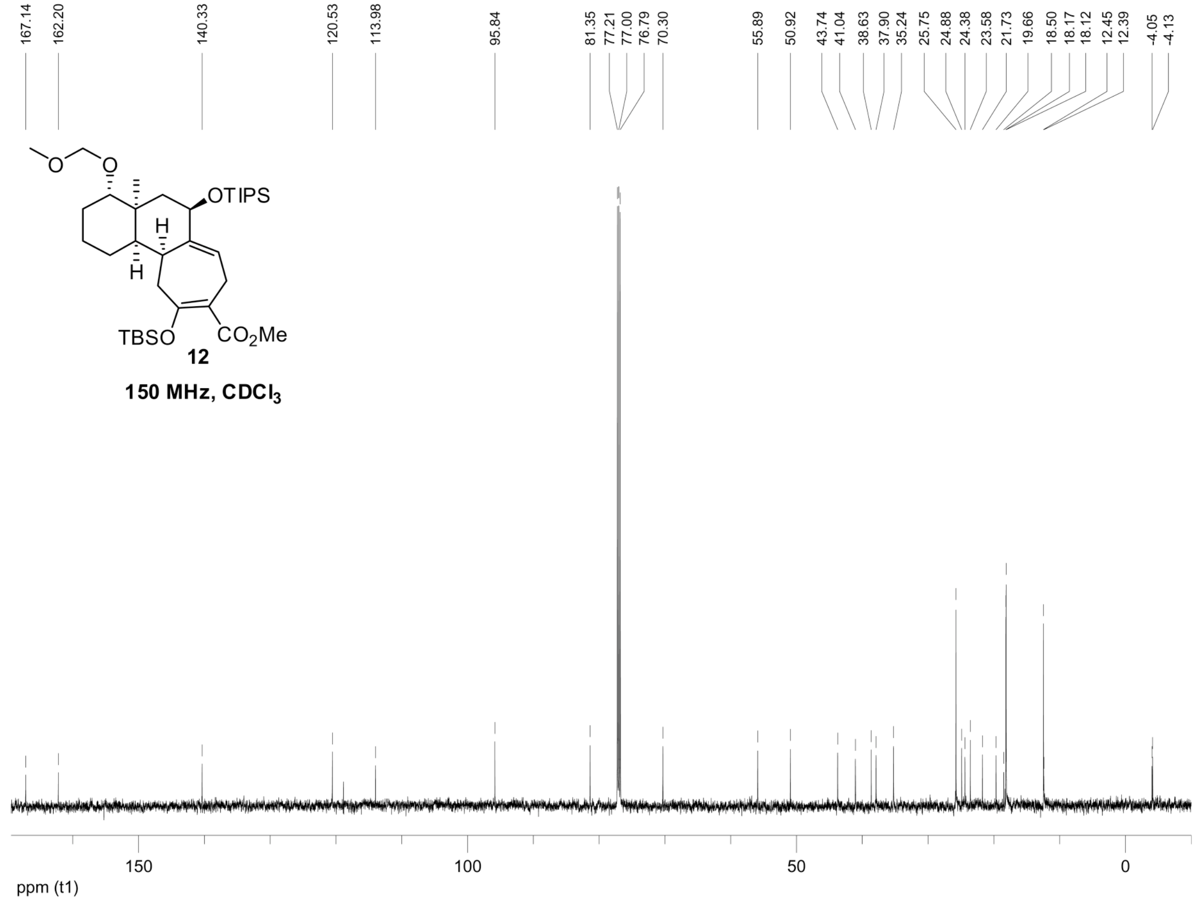
9

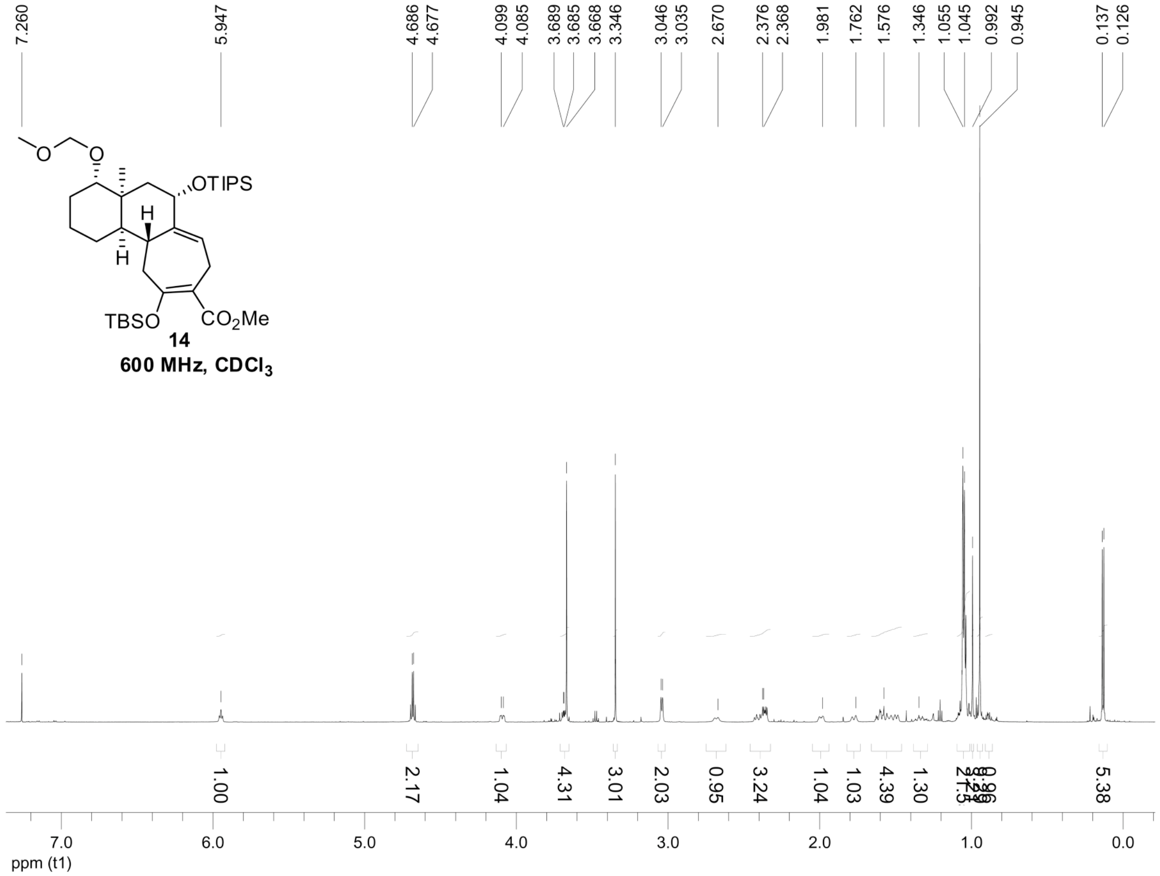
100 MHz, CDCl$_3$


7.260
5.682
4.844
4.833
4.631
4.620
4.273
4.263
4.171
3.671
3.334
2.982
2.648
2.434
2.420
2.302
2.258
1.951
1.798
1.556
1.395
1.059
1.023
0.952
0.949
0.154
0.143
OTIPS
H
H
TBSO
CO_2Me
11
600 MHz, $CDCl_3$
1.00
1.02
1.03
1.01
0.99
3.03
3.02
3.12
0.96
1.04
1.28
1.06
1.05
4.55
1.14
1.36
20.8
12.1
5.38
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


167.63
161.62
144.78
121.16
113.37
97.77
79.99
77.21
77.00
76.90
76.79
55.03
50.97
49.44
43.55
38.78
36.79
30.25
29.69
25.70
25.55
24.88
22.98
22.02
19.53
18.29
18.13
12.52
-3.78
-3.97
OTIPS
H
H
TBSO
CO_2Me
11
150 MHz, $CDCl_3$
150
100
50
0
ppm (t1)

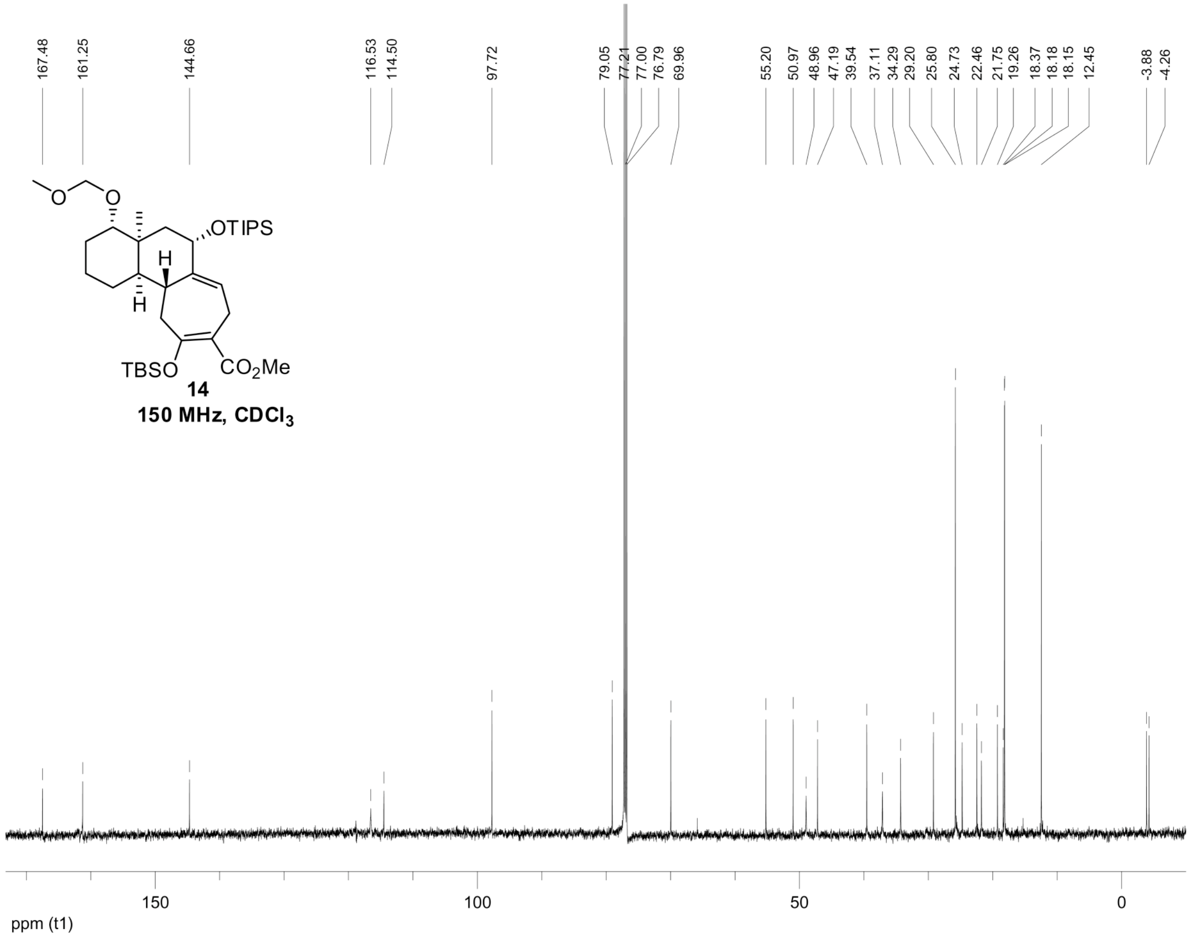

7.260
6.167
6.164
6.152
4.706
4.599
3.666
3.405
3.265
3.227
3.039
3.023
2.637
1.803
1.744
1.662
1.531
1.411
1.403
1.391
1.382
1.320
1.166
1.052
1.042
0.953
0.180
0.153
OTIPS
H
H
TBSO
CO2Me
12
600 MHz, CDCl3
1.00
1.06
1.08
1.05
3.07
3.03
2.07
1.02
1.02
1.01
2.09
6.48
1.33
1.05
2.97
21.5
8.91
5.92
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


167.14
162.20
140.33
120.53
113.98
95.84
81.35
77.21
77.00
76.79
70.30
55.89
50.92
43.74
41.04
38.63
37.90
35.24
25.75
24.88
24.38
23.58
21.73
19.66
18.50
18.17
18.12
12.45
12.39
-4.05
-4.13
OTIPS
H
H
TBSO
CO2Me
12
150 MHz, CDCl3
150
100
50
0
ppm (t1)



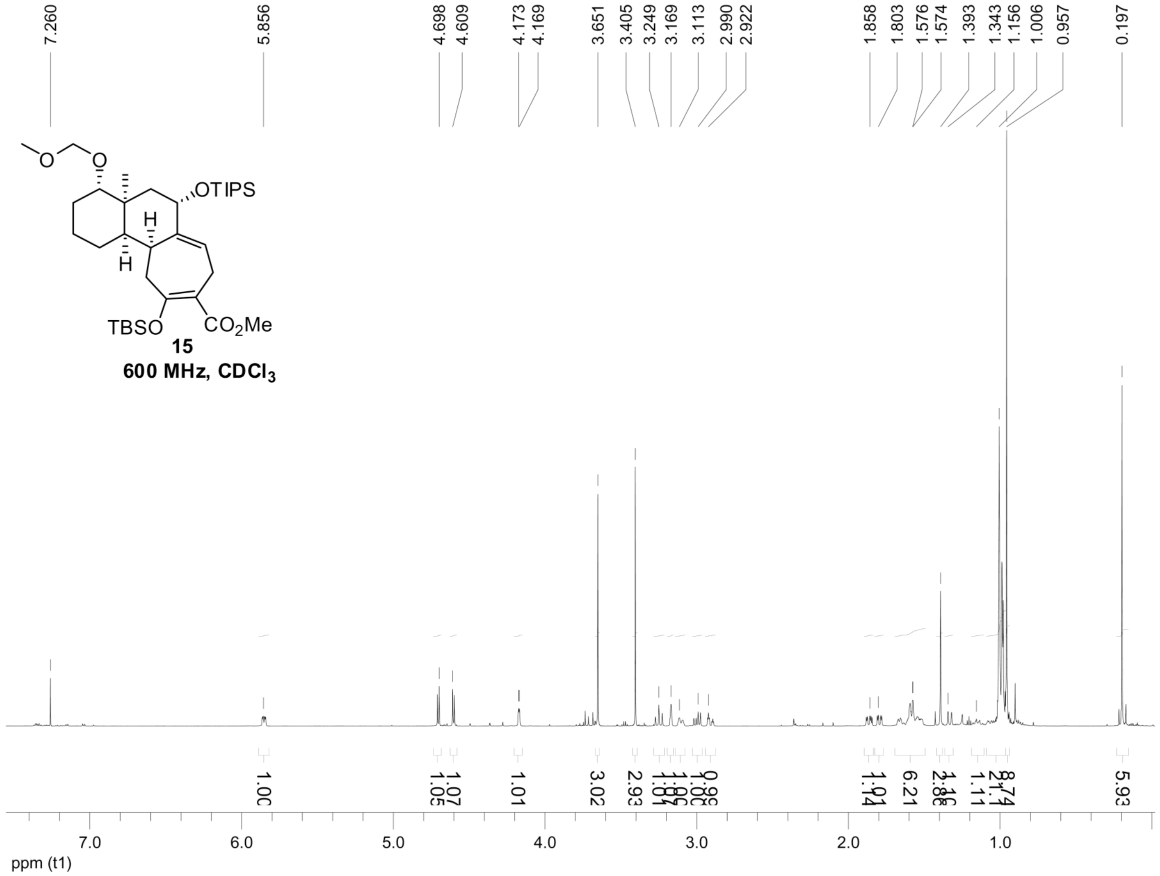
14

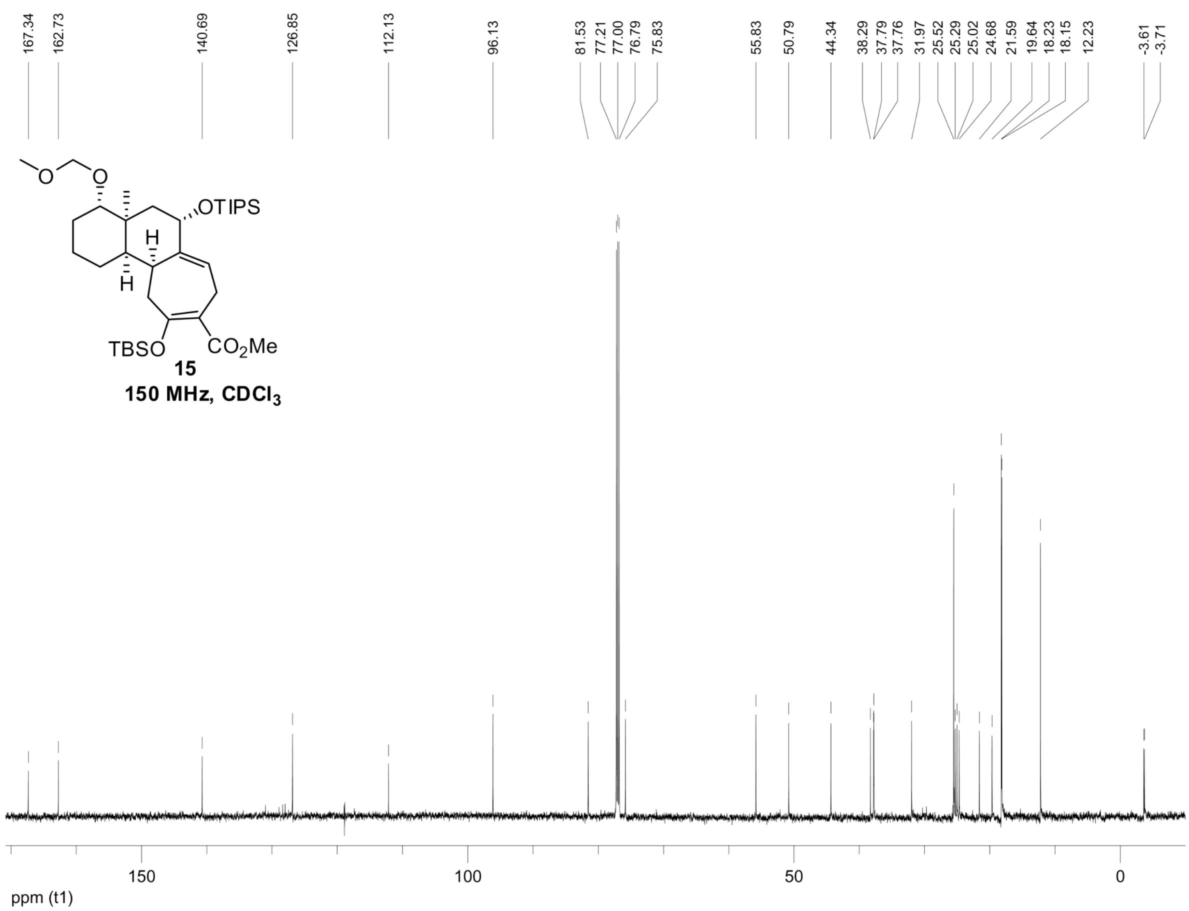
600 MHz, $CDCl_3$

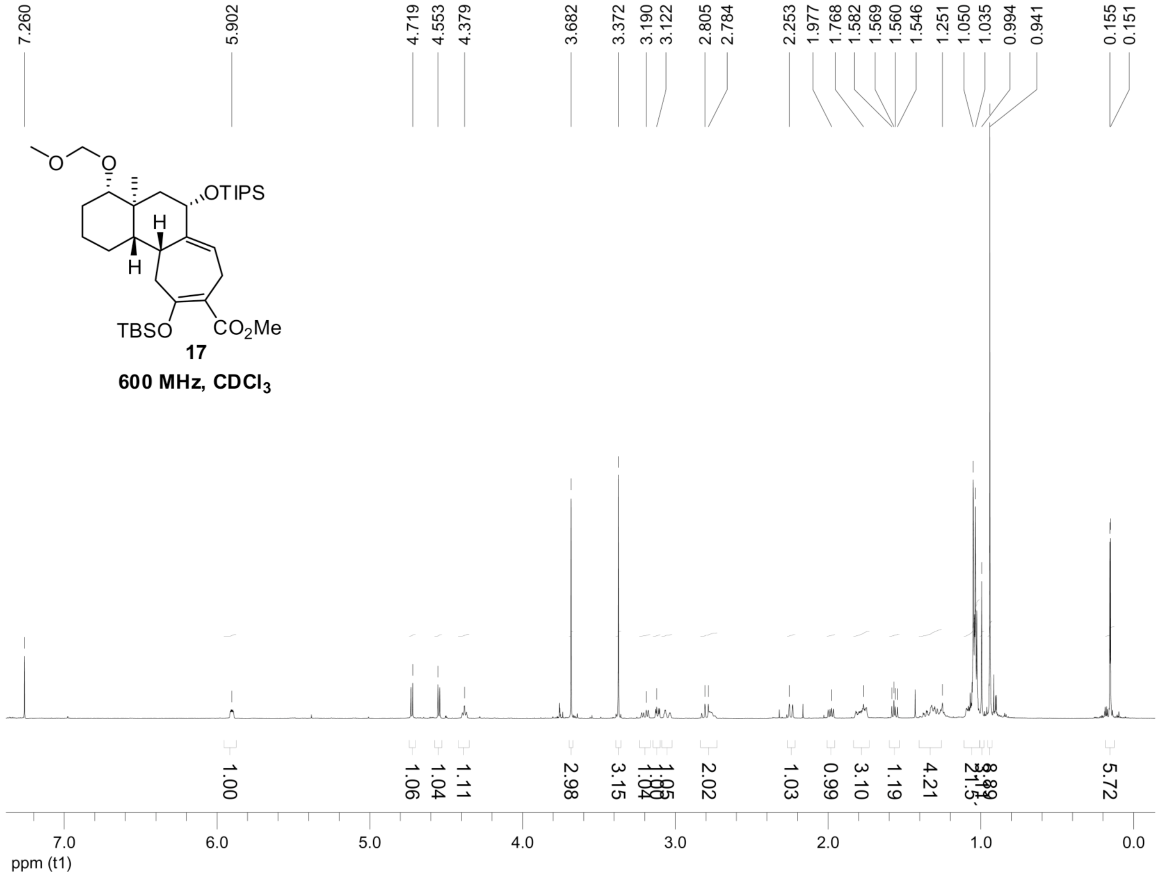


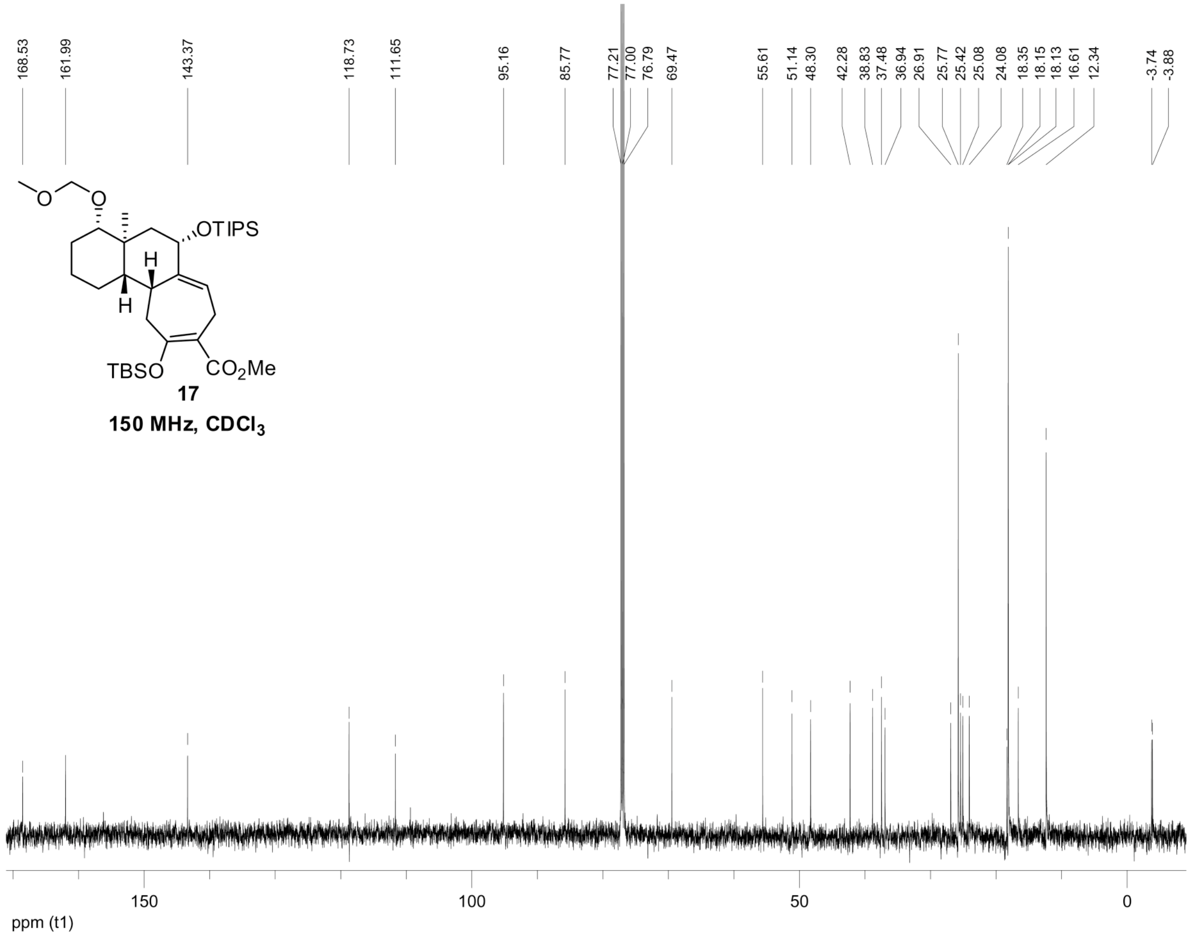
14

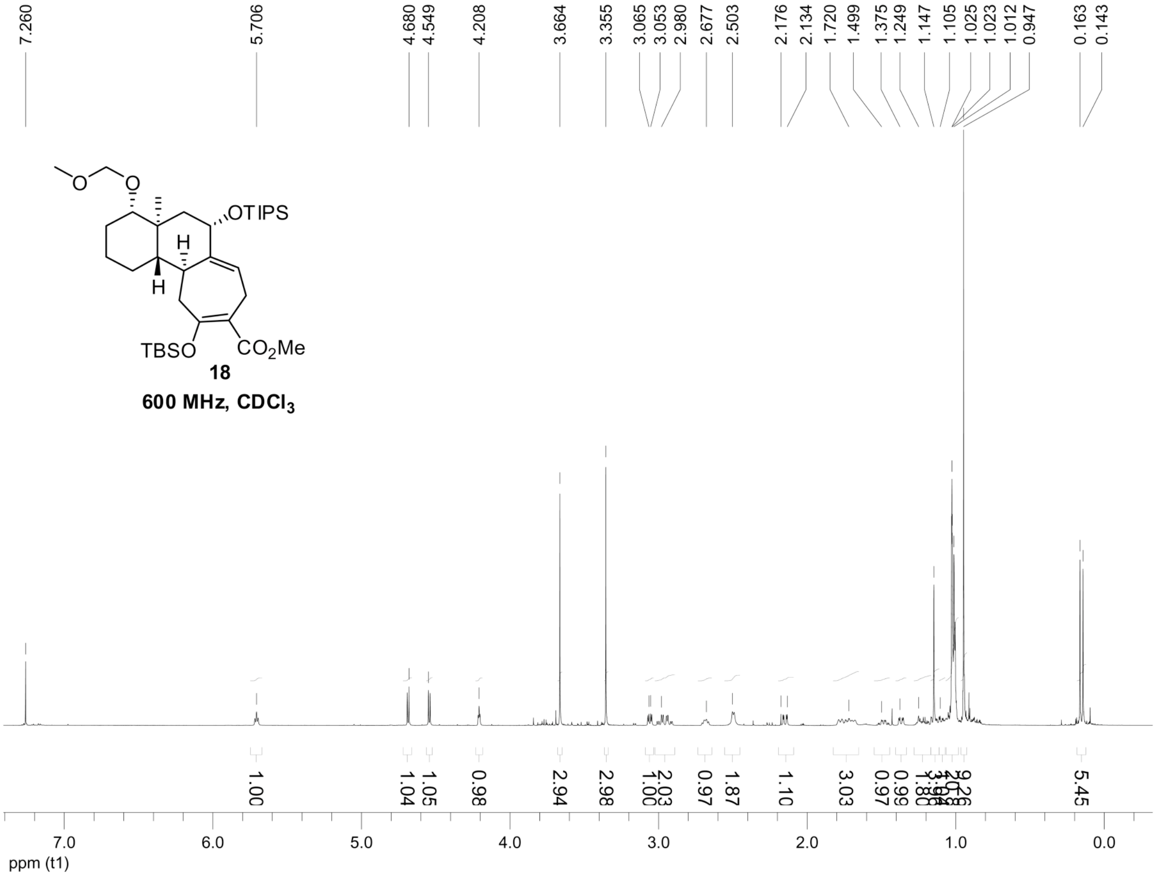
150 MHz, $CDCl_3$

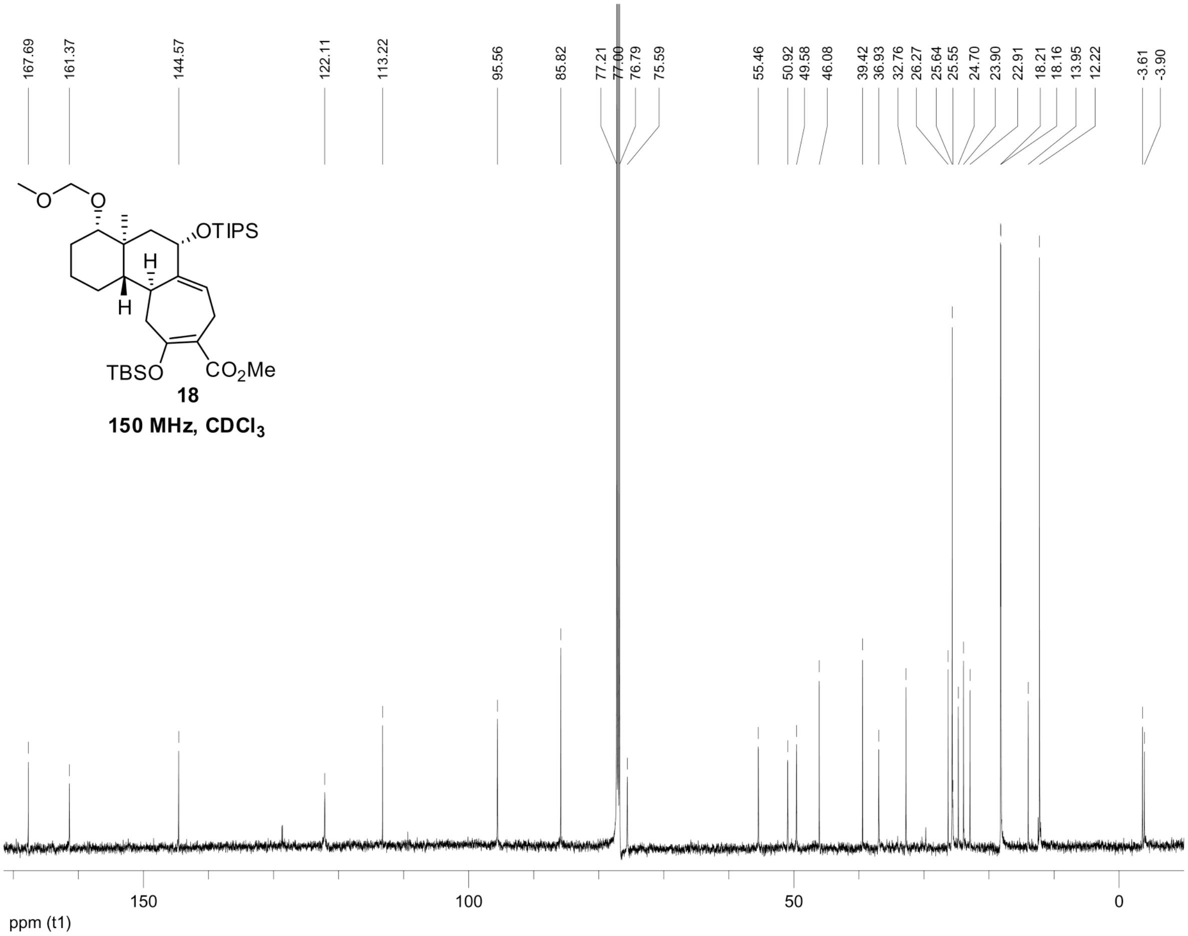

7.260
5.856
4.698
4.609
4.173
4.169
3.651
3.405
3.249
3.169
3.113
2.990
2.922
1.858
1.803
1.576
1.574
1.393
1.343
1.156
1.006
0.957
0.197
OTIPS
H
H
TBSO
CO2Me
15
600 MHz, CDCl3
1.00
1.05
1.07
1.01
3.02
2.93
1.07
1.05
1.00
0.98
1.01
1.14
6.21
2.86
1.16
1.11
21.1
8.74
5.93
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

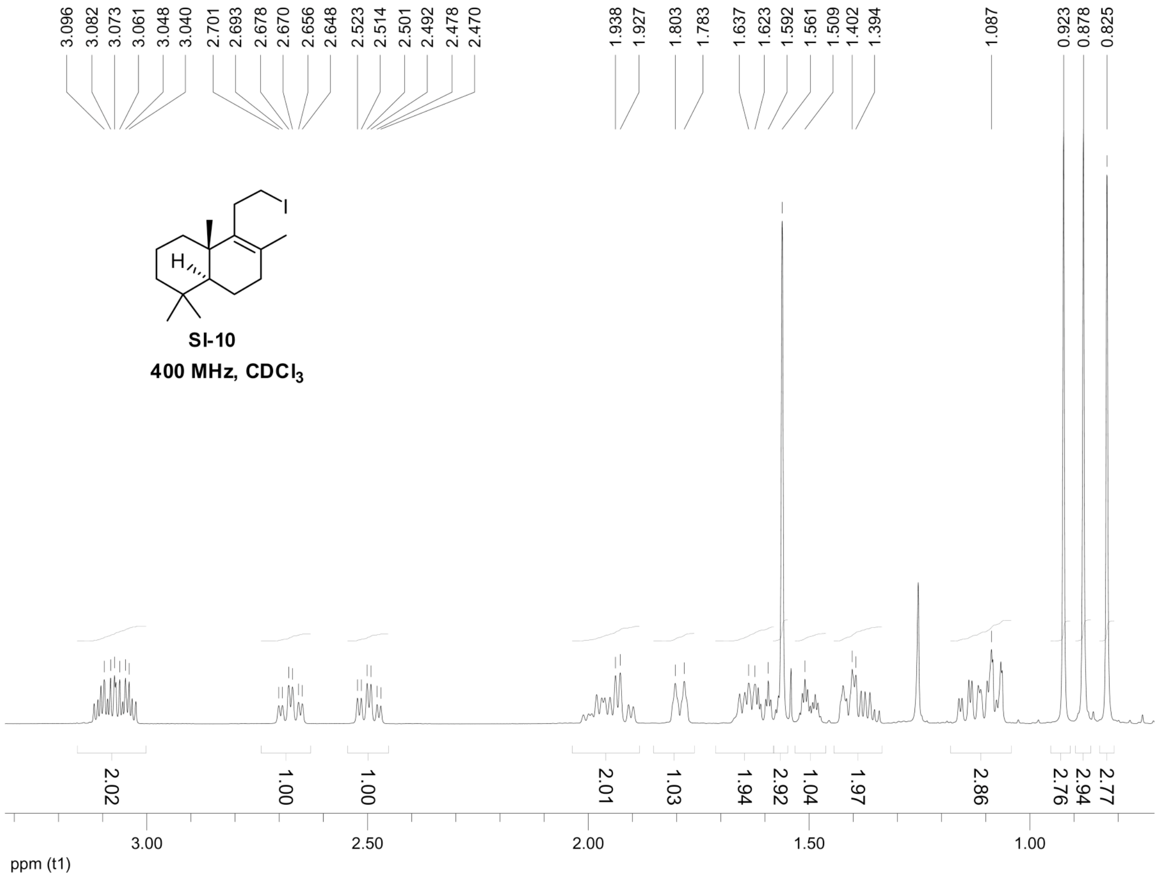

167.34
162.73
140.69
126.85
112.13
96.13
81.53
77.21
77.00
76.79
75.83
55.83
50.79
44.34
38.29
37.79
37.76
31.97
25.52
25.29
25.02
24.68
21.59
19.64
18.23
18.15
12.23
-3.61
-3.71
OTIPS
H
H
TBSO
CO2Me
15
150 MHz, CDCl3
150
100
50
0
ppm (t1)

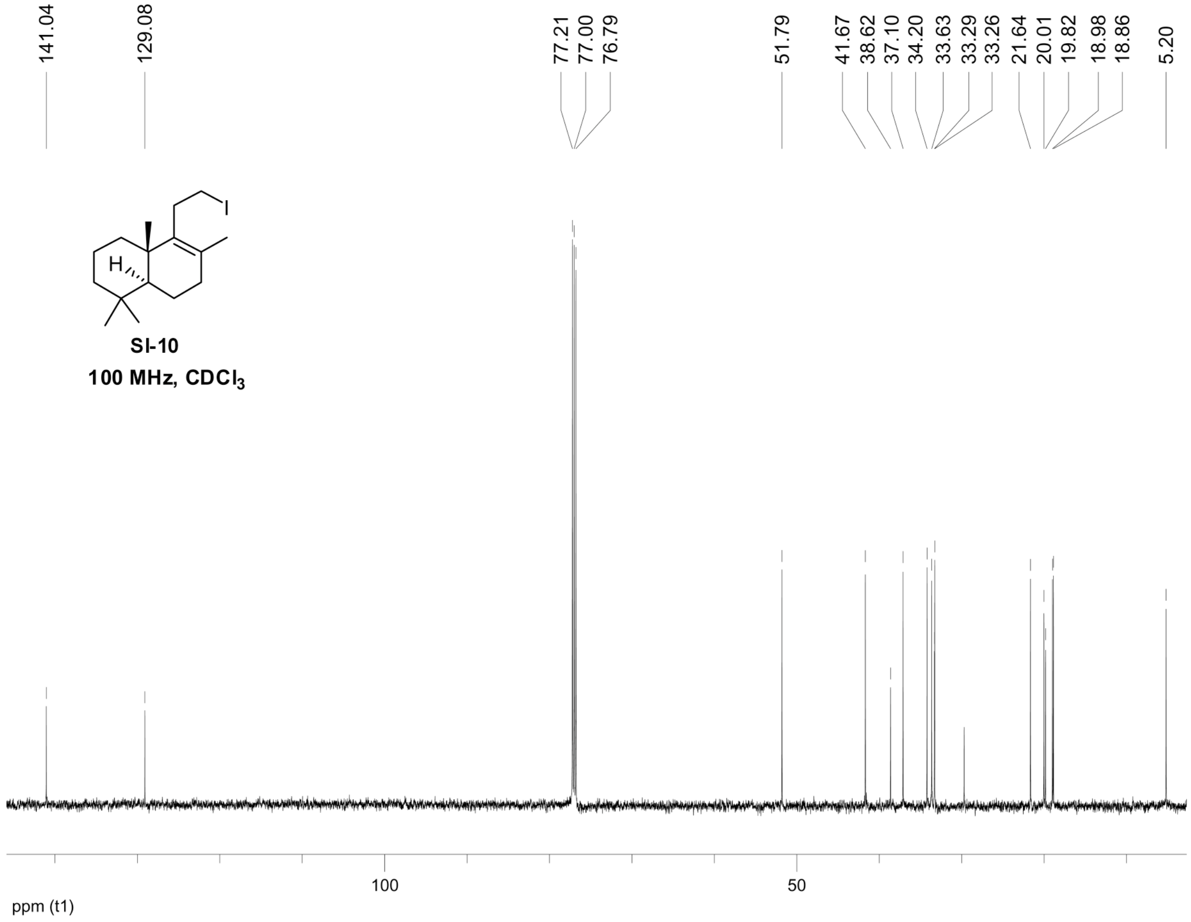

7.260
5.902
4.719
4.553
4.379
3.682
3.372
3.190
3.122
2.805
2.784
2.253
1.977
1.768
1.582
1.569
1.560
1.546
1.251
1.050
1.035
0.994
0.941
0.155
0.151
OTIPS
H
H
TBSO
CO2Me
17
600 MHz, CDCl3
1.00
1.06
1.04
1.11
2.98
3.15
1.04
1.05
2.02
1.03
0.99
3.10
1.19
4.21
21.5
8.89
5.72
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

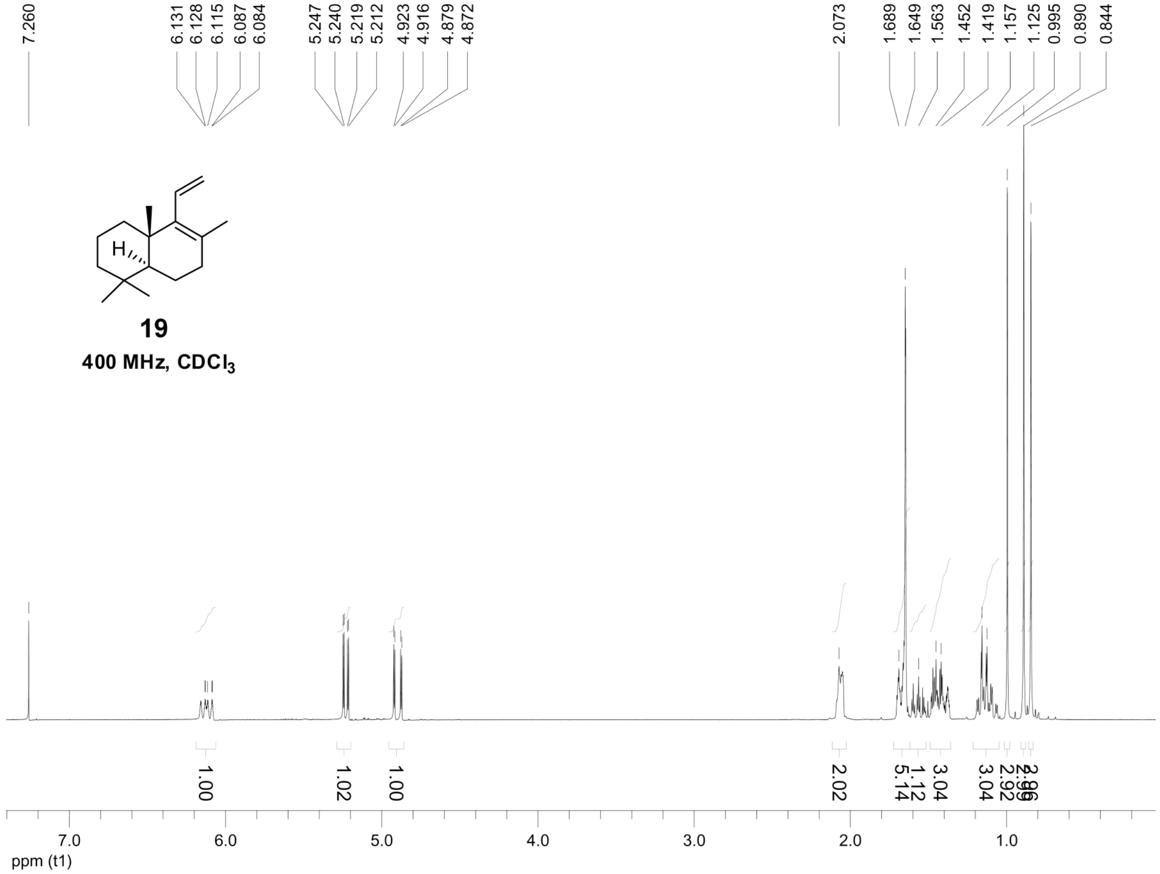

168.53
161.99
143.37
118.73
111.65
95.16
85.77
77.21
77.00
76.79
69.47
55.61
51.14
48.30
42.28
38.83
37.48
36.94
26.91
25.77
25.42
25.08
24.08
18.35
18.15
18.13
16.61
12.34
-3.74
-3.88
OTIPS
H
H
TBSO
CO2Me
17
150 MHz, CDCl3
150
100
50
0
ppm (t1)

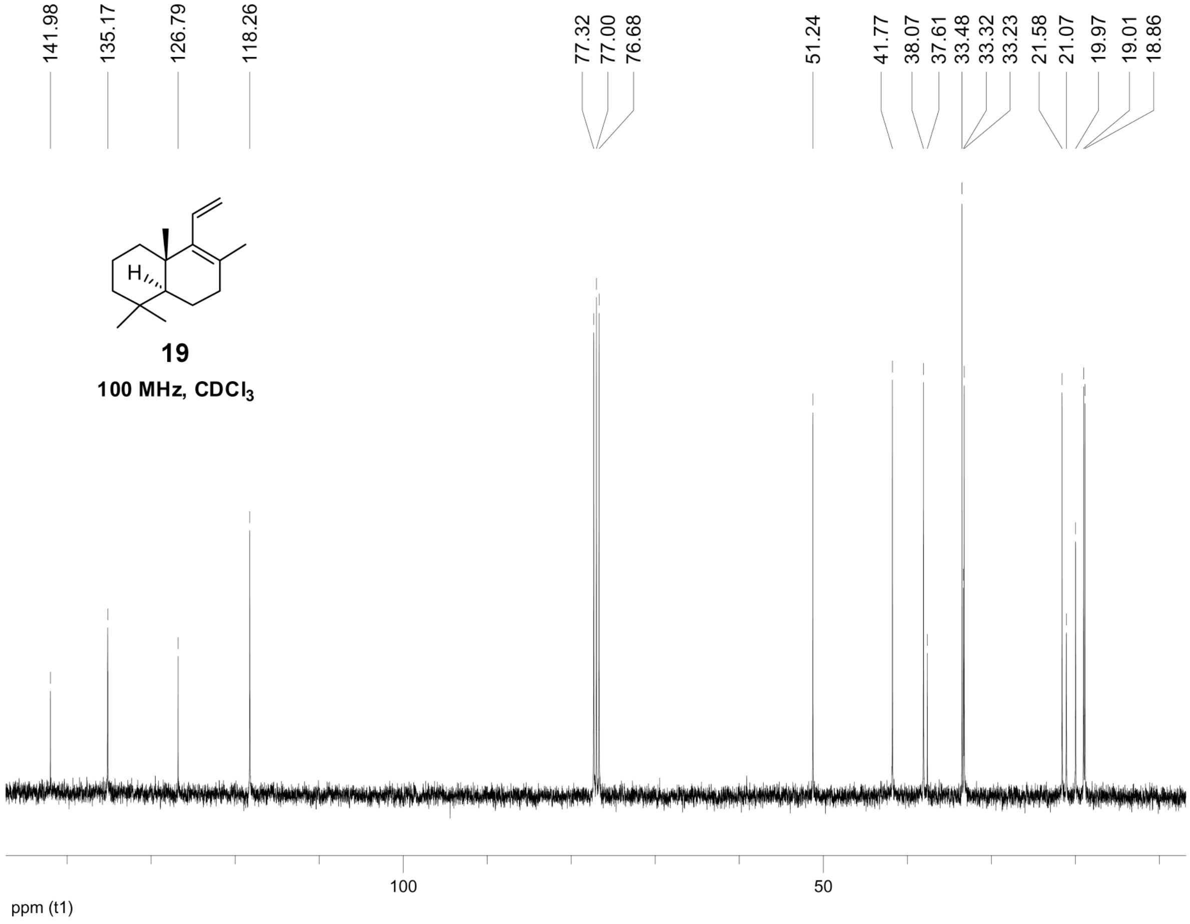

7.260
5.706
4.680
4.549
4.208
3.664
3.355
3.065
3.053
2.980
2.677
2.503
2.176
2.134
1.720
1.499
1.375
1.249
1.147
1.105
1.025
1.023
1.012
0.947
0.163
0.143
OTIPS
H
H
TBSO
CO$_2$Me
18
600 MHz, CDCl$_3$
1.00
1.04
1.05
0.98
2.94
2.98
1.00
2.03
0.97
1.87
1.10
3.03
0.97
0.99
1.80
9.26
5.45
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

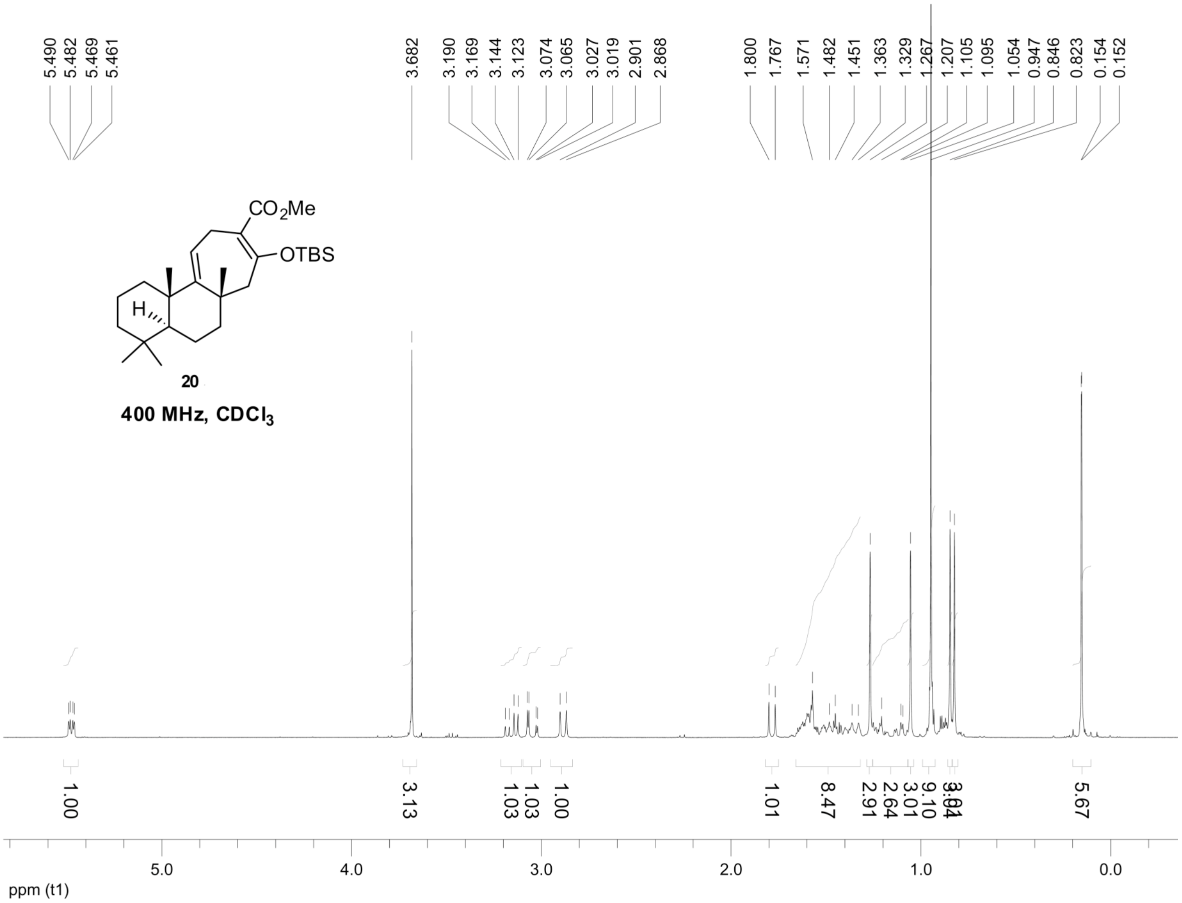

167.69
161.37
144.57
122.11
113.22
95.56
85.82
77.21
77.00
76.79
75.59
55.46
50.92
49.58
46.08
39.42
36.93
32.76
26.27
25.64
25.55
24.70
23.90
22.91
18.21
18.16
13.95
12.22
-3.61
-3.90
OTIPS
H
H
TBSO
CO$_2$Me
18
150 MHz, CDCl$_3$
150
100
50
0
ppm (t1)


SI-10
400 MHz, CDCl$_3$


SI-10
100 MHz, CDCl$_3$

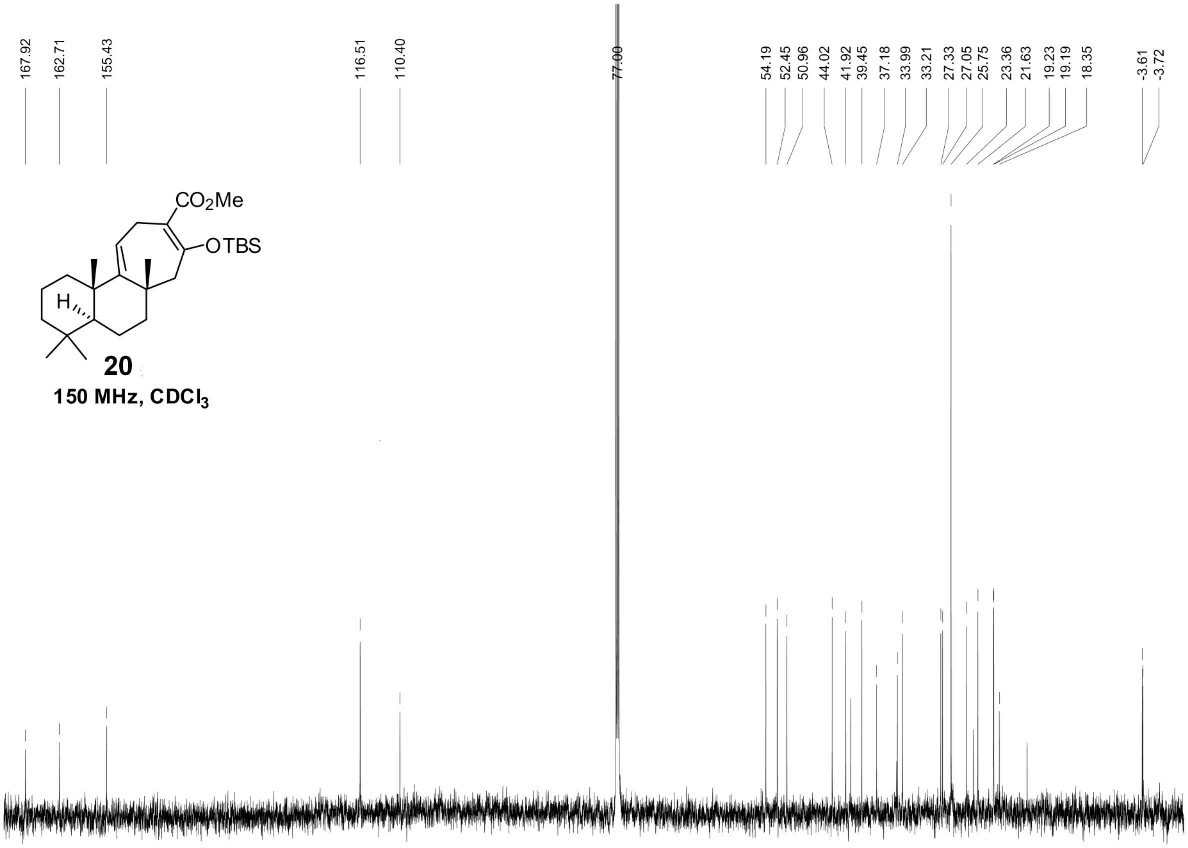

7.260
6.131
6.128
6.115
6.087
6.084
5.247
5.240
5.219
5.212
4.923
4.916
4.879
4.872
2.073
1.689
1.649
1.563
1.452
1.419
1.157
1.125
0.995
0.890
0.844
H
19
400 MHz, CDCl3
1.00
1.02
1.00
2.02
5.14
1.12
3.04
3.04
2.92
2.96
2.90
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


141.98
135.17
126.79
118.26
77.32
77.00
76.68
51.24
41.77
38.07
37.61
33.48
33.32
33.23
21.58
21.07
19.97
19.01
18.86
H
19
100 MHz, CDCl3
100
50
ppm (t1)



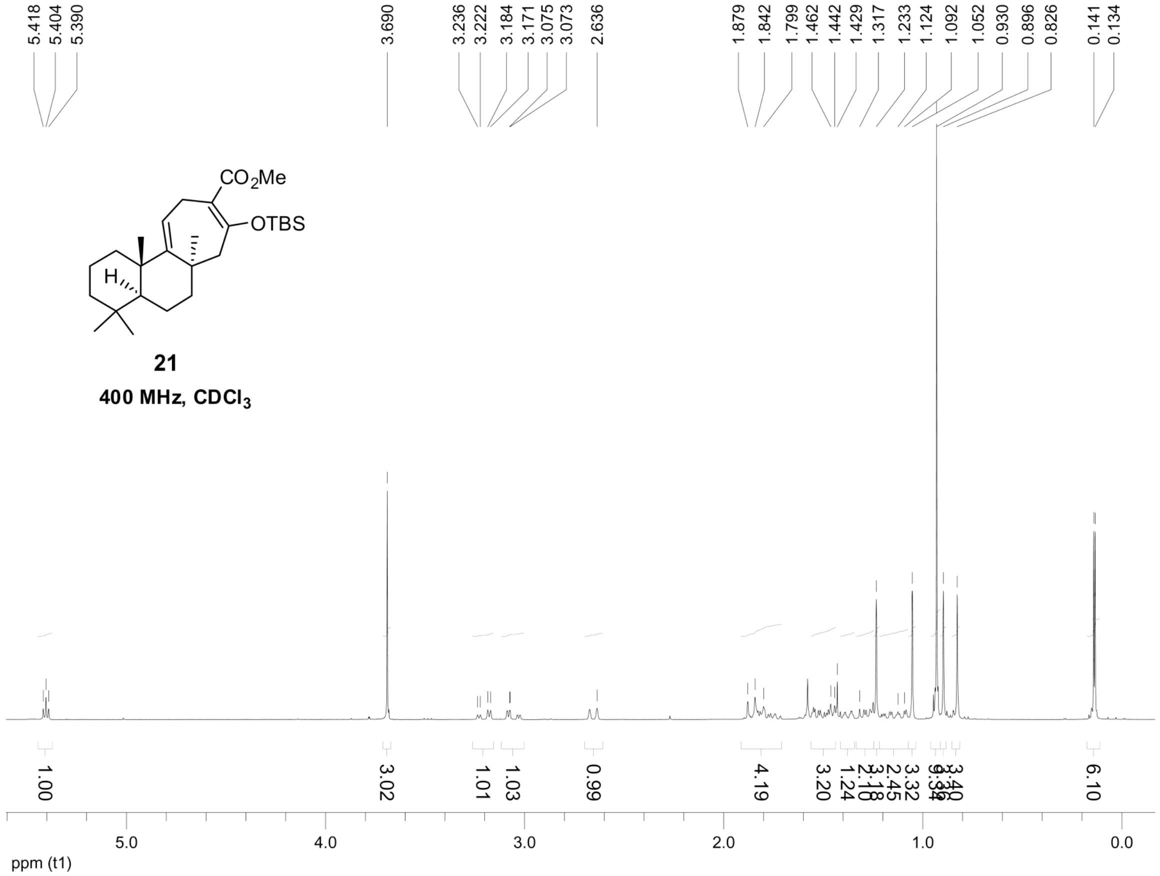
20

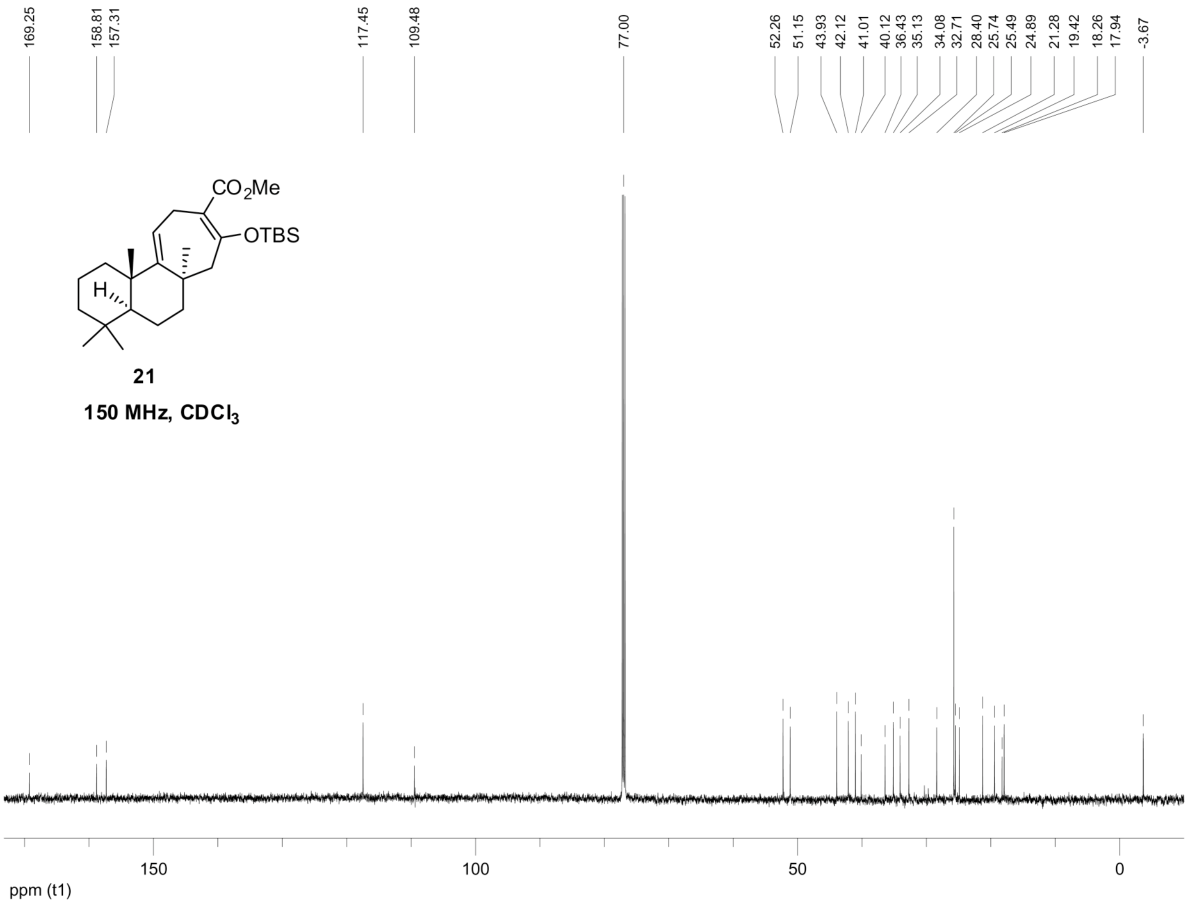
400 MHz, CDCl$_3$

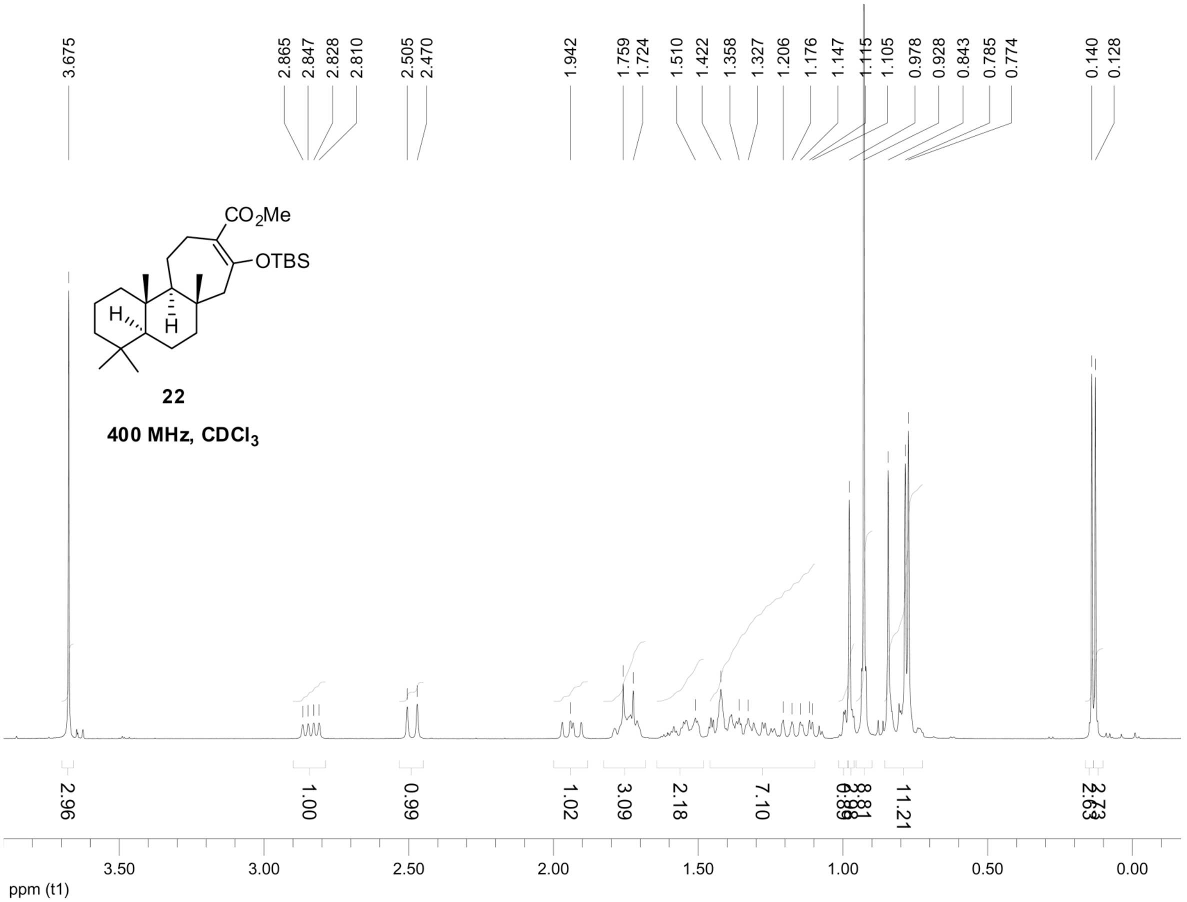


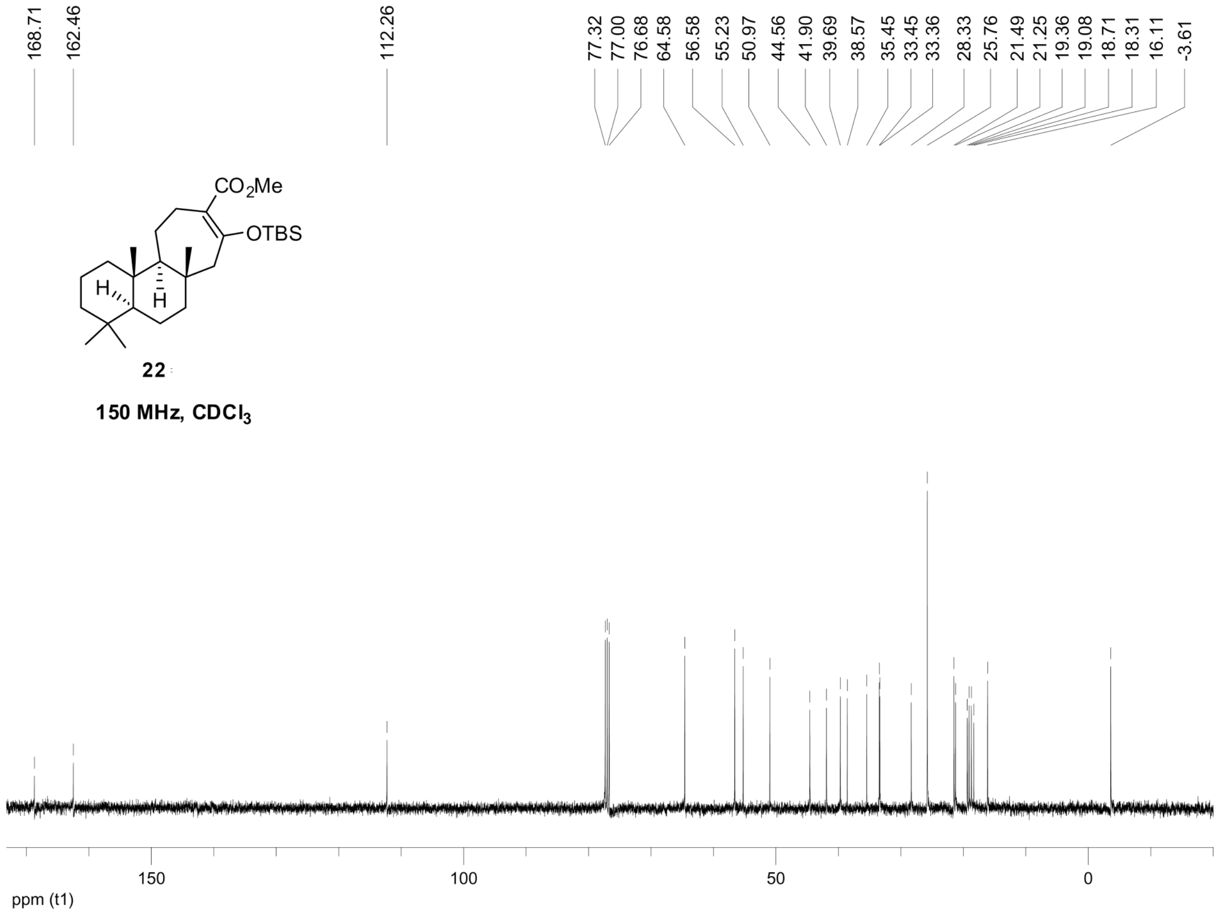
20

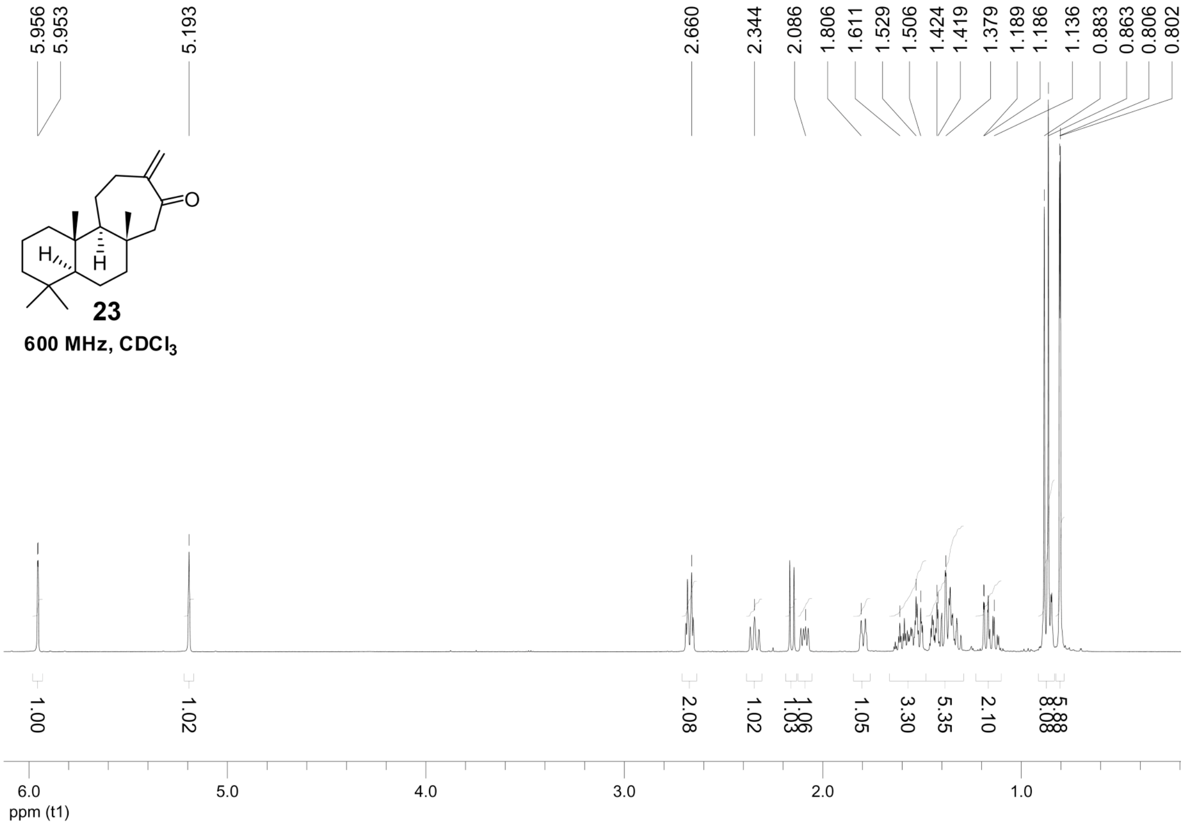
150 MHz, CDCl$_3$

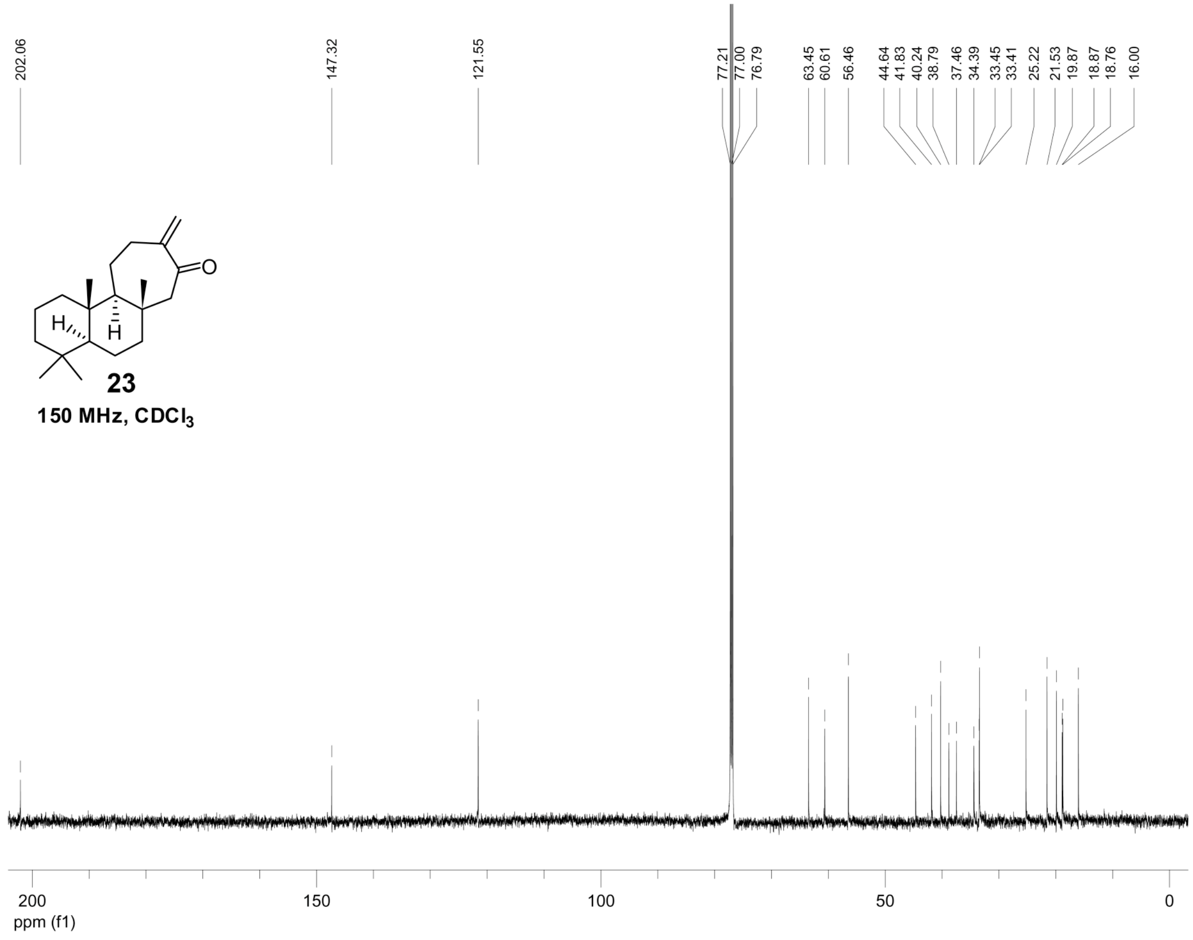

5.418
5.404
5.390
3.690
3.236
3.222
3.184
3.171
3.075
3.073
2.636
1.879
1.842
1.799
1.462
1.442
1.429
1.317
1.233
1.124
1.092
1.052
0.930
0.896
0.826
0.141
0.134
CO2Me
OTBS
H
21
400 MHz, CDCl3
1.00
3.02
1.01
1.03
0.99
4.19
3.20
1.24
2.10
3.18
2.45
3.32
9.34
3.36
3.40
6.10
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

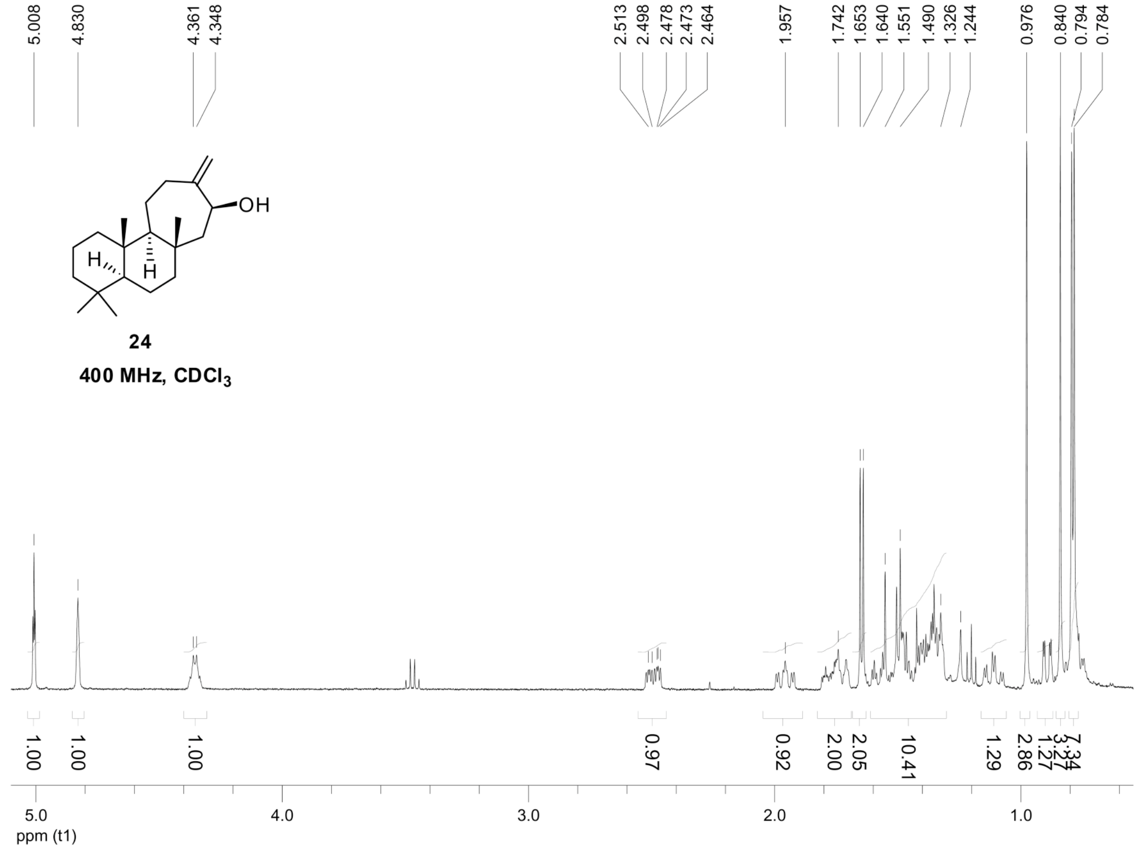

169.25
158.81
157.31
117.45
109.48
77.00
52.26
51.15
43.93
42.12
41.01
40.12
36.43
35.13
34.08
32.71
28.40
25.74
25.49
24.89
21.28
19.42
18.26
17.94
-3.67
CO2Me
OTBS
H
21
150 MHz, CDCl3
150
100
50
0
ppm (t1)


3.675
2.865
2.847
2.828
2.810
2.505
2.470
1.942
1.759
1.724
1.510
1.422
1.358
1.327
1.206
1.176
1.147
1.115
1.105
0.978
0.928
0.843
0.785
0.774
0.140
0.128
CO$_2$Me
OTBS
H
H
22
400 MHz, CDCl$_3$
2.96
1.00
0.99
1.02
3.09
2.18
7.10
0.89
6.88
8.81
11.21
2.63
2.73
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (t1)


168.71
162.46
112.26
77.32
77.00
76.68
64.58
56.58
55.23
50.97
44.56
41.90
39.69
38.57
35.45
33.45
33.36
28.33
25.76
21.49
21.25
19.36
19.08
18.71
18.31
16.11
-3.61
CO$_2$Me
OTBS
H
H
22
150 MHz, CDCl$_3$
150
100
50
0
ppm (t1)

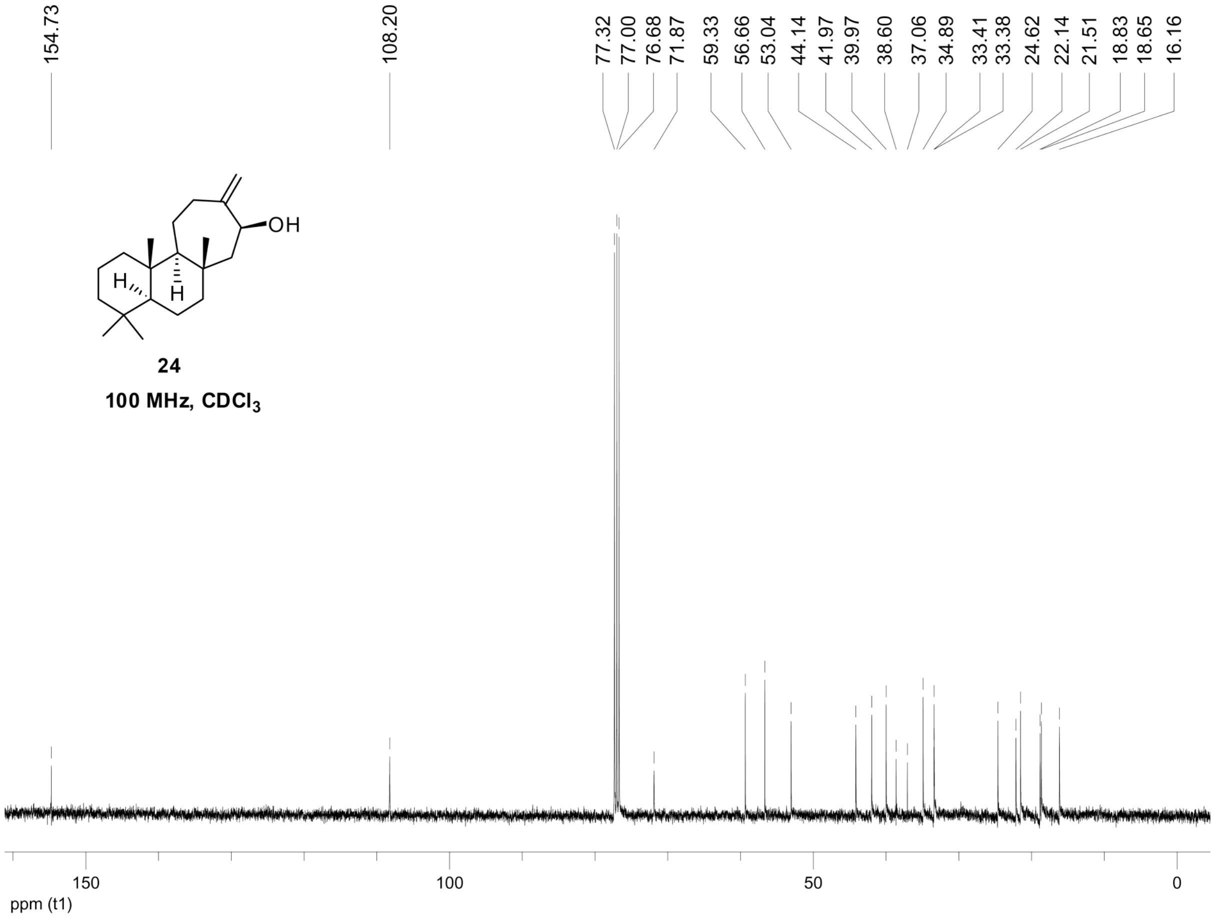

5.956
5.953
5.193
2.660
2.344
2.086
1.806
1.611
1.529
1.506
1.424
1.419
1.379
1.189
1.186
1.136
0.883
0.863
0.806
0.802
O
H
H
23
600 MHz, $CDCl_3$
1.00
1.02
2.08
1.02
1.06
1.03
1.05
3.30
5.35
2.10
8.08
5.88
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


202.06
147.32
121.55
77.21
77.00
76.79
63.45
60.61
56.46
44.64
41.83
40.24
38.79
37.46
34.39
33.45
33.41
25.22
21.53
19.87
18.87
18.76
16.00
O
H
H
23
150 MHz, $CDCl_3$
200
150
100
50
0
ppm (f1)



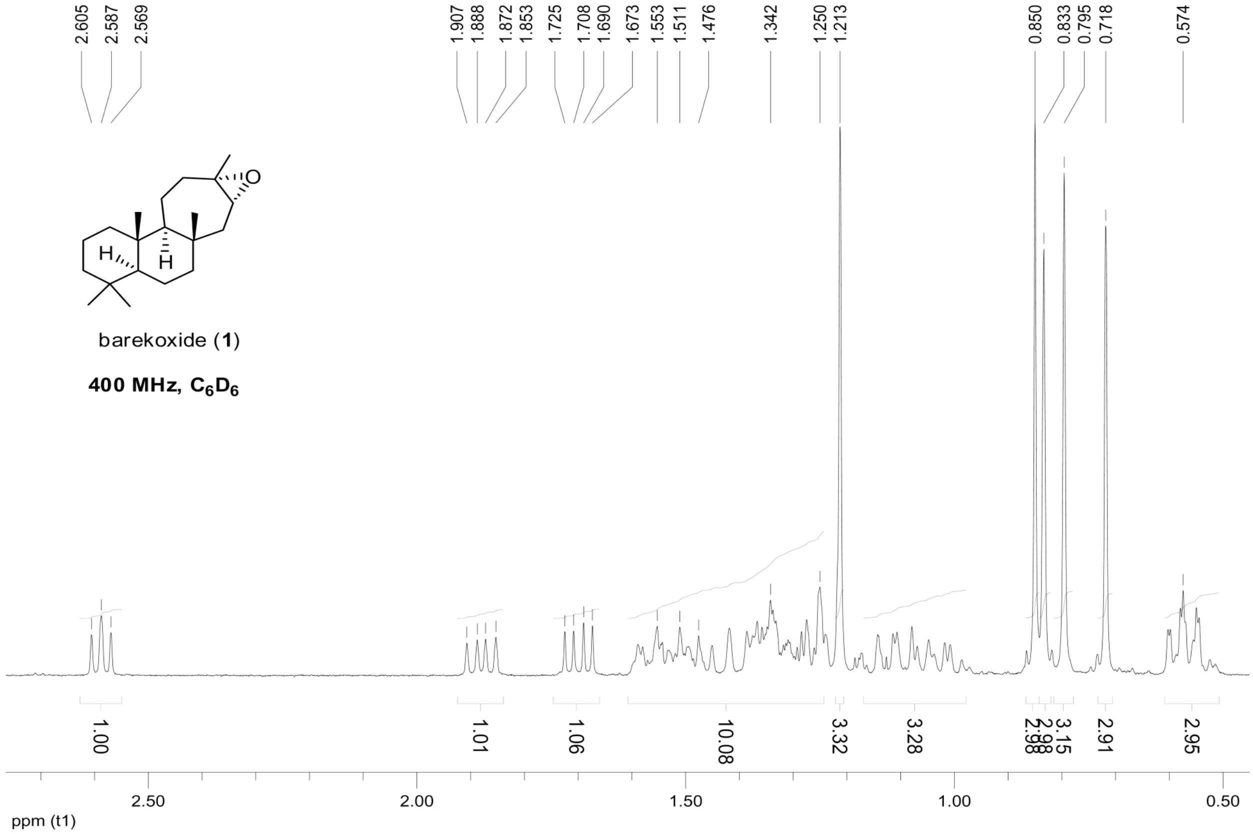
24

400 MHz, $CDCl_3$

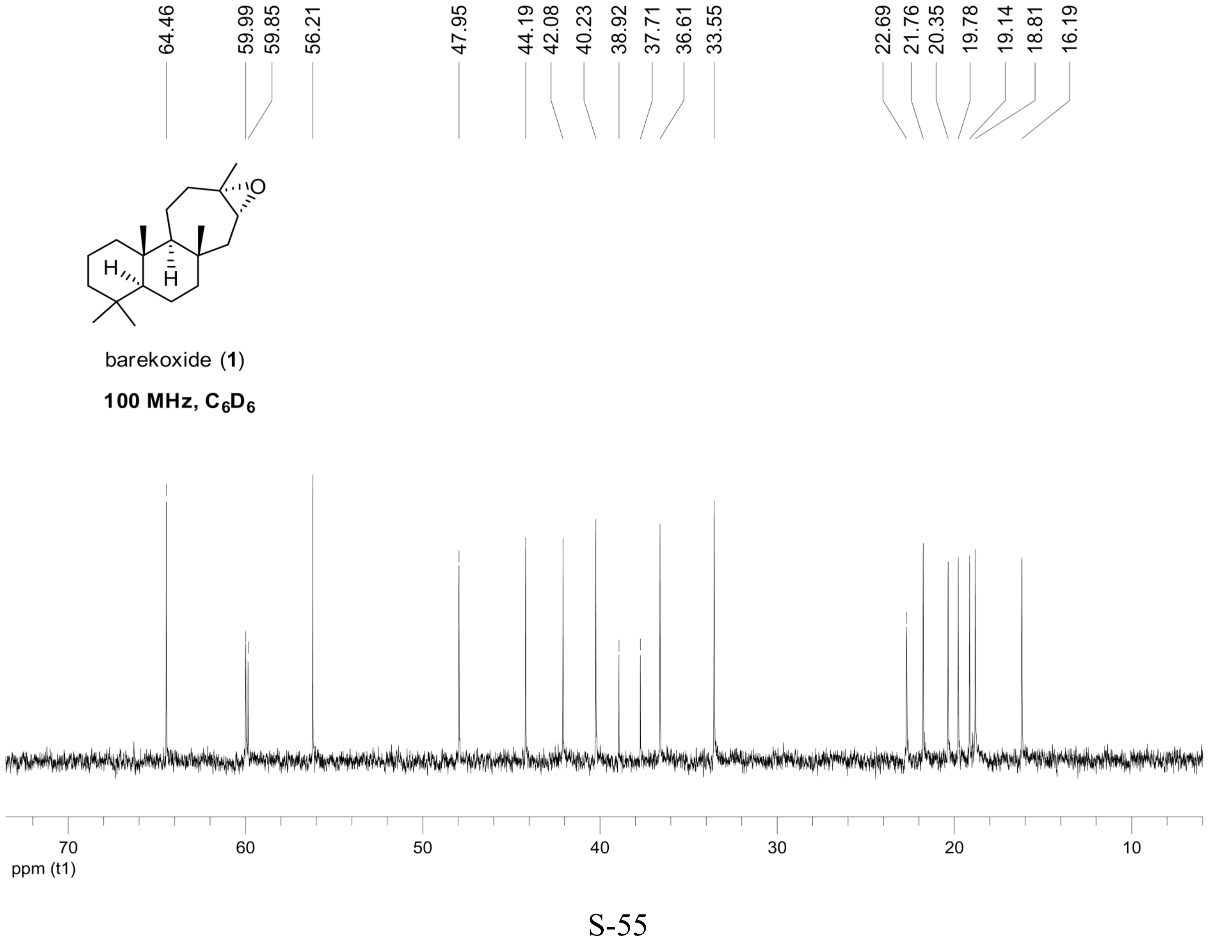


24

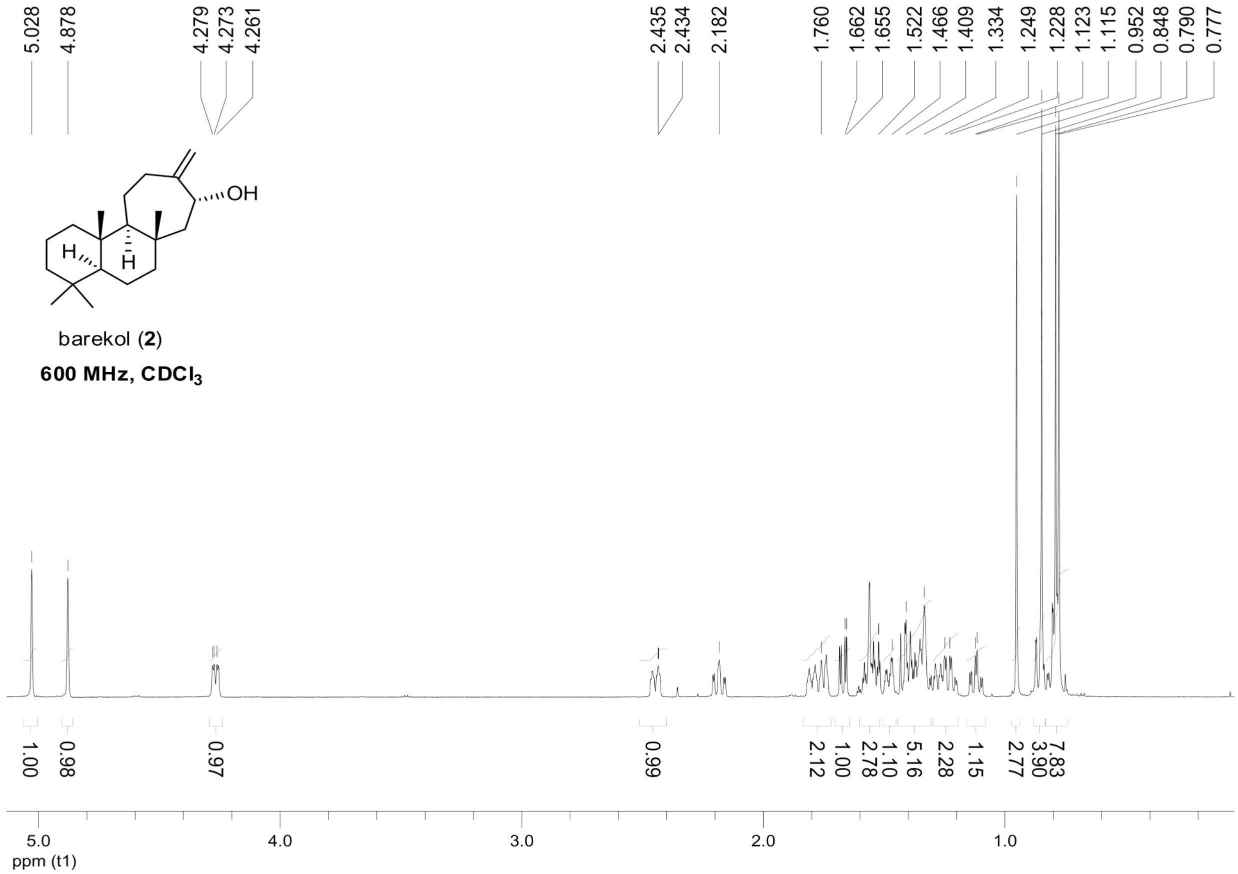
100 MHz, $CDCl_3$

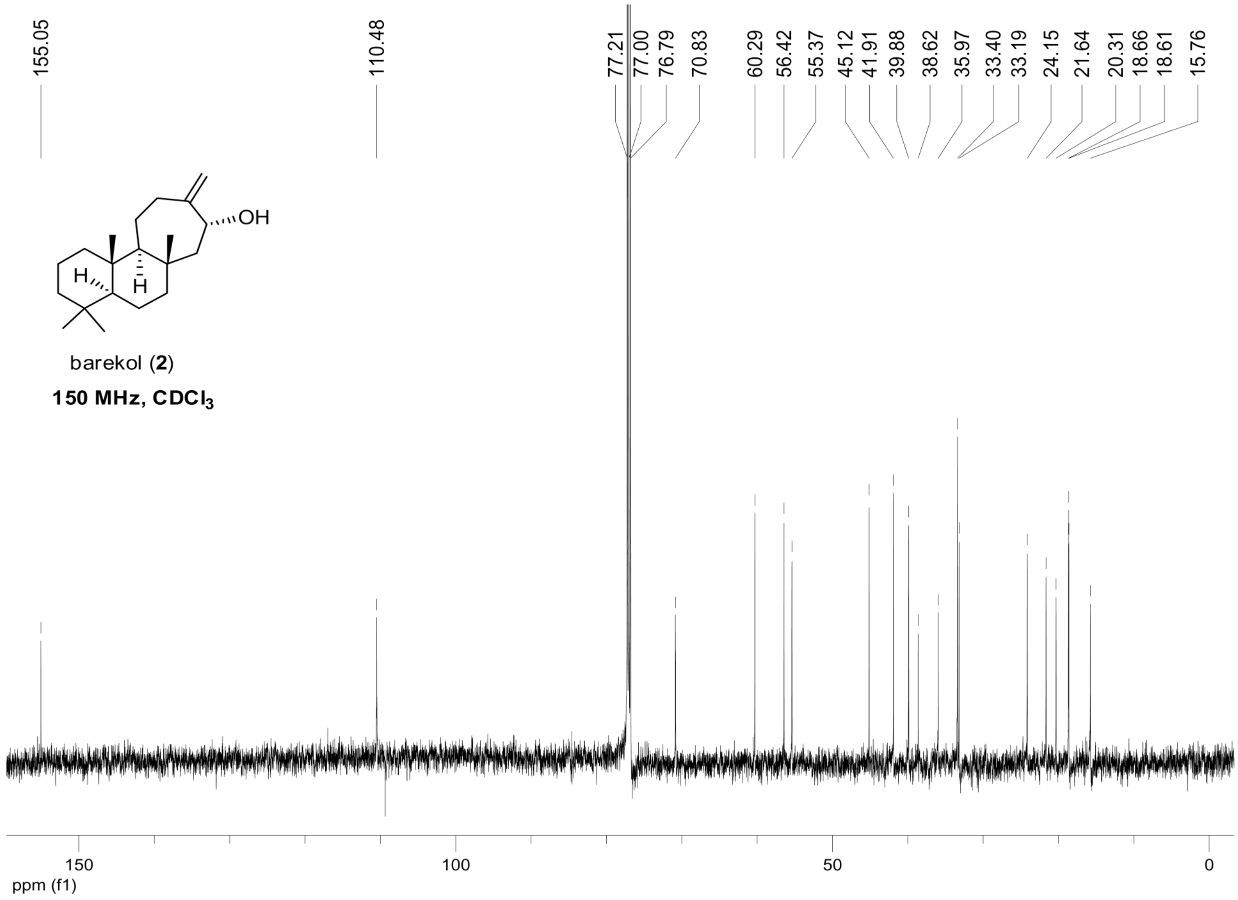

barekoxide (**1**)

400 MHz, C_6D_6

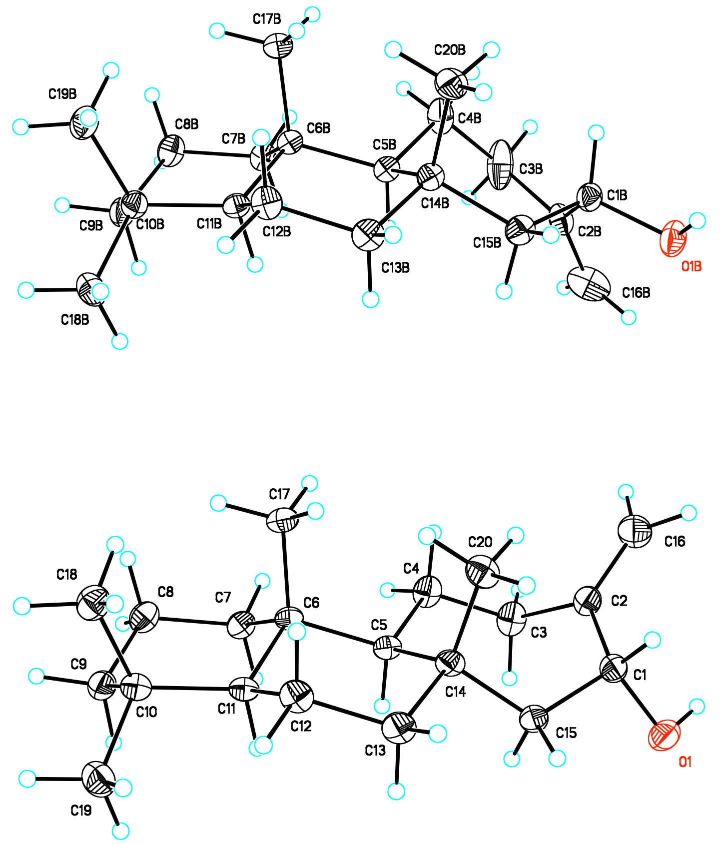

barekoxide (**1**)

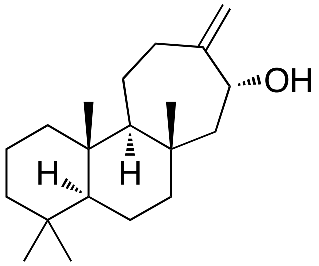
100 MHz, C_6D_6


5.028
4.878
4.279
4.273
4.261
2.435
2.434
2.182
1.760
1.662
1.655
1.522
1.466
1.409
1.334
1.249
1.228
1.123
1.115
0.952
0.848
0.790
0.777
OH
H
H
barekol (2)
600 MHz, CDCl3
1.00
0.98
0.97
0.99
2.12
1.00
2.78
1.10
5.16
2.28
1.15
2.77
3.90
7.83
5.0
4.0
3.0
2.0
1.0
ppm (t1)


155.05
110.48
77.21
77.00
76.79
70.83
60.29
56.42
55.37
45.12
41.91
39.88
38.62
35.97
33.40
33.19
24.15
21.64
20.31
18.66
18.61
15.76
OH
H
H
barekol (2)
150 MHz, CDCl3
150
100
50
0
ppm (f1)

Crystalgraphic Data of Barekol (2)





Barekol (**2**)

Table 1. Crystal data and structure refinement for Barekol (**2**).

Identification code	Barekol	
Empirical formula	$C_{20}H_{34}O$	
Formula weight	290.47	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 6.0927(2) Å	α= 80.027(2)°.
	b = 7.3057(3) Å	β= 86.454(2)°.
	c = 21.0808(8) Å	γ = 67.354(2)°.
Volume	852.89(6) Å^3	
Z	2	
Density (calculated)	1.131 Mg/m^3	
Absorption coefficient	0.498 mm^{-1}	
F(000)	324	
Crystal size	0.31 x 0.26 x 0.05 mm^3	
Theta range for data collection	2.13 to 65.87°.	
Index ranges	-6<=h<=7, -8<=k<=7, -24<=l<=24	
Reflections collected	5328	
Independent reflections	3290 [R(int) = 0.0131]	
Completeness to theta = 65.87°	84.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9755 and 0.8609	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3290 / 3 / 379	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.1081	
R indices (all data)	R1 = 0.0390, wR2 = 0.1082	
Absolute structure parameter	0.0(3)	
Largest diff. peak and hole	0.239 and -0.232 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for barekol (**2**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2486(5)	4224(4)	7135(1)	30(1)
C(2)	4132(5)	2290(3)	6930(1)	30(1)
C(3)	3246(5)	1522(4)	6428(1)	35(1)
C(4)	3619(5)	2463(3)	5737(1)	31(1)
C(5)	1968(4)	4662(3)	5497(1)	23(1)
C(6)	2320(4)	5295(3)	4755(1)	22(1)
C(7)	1808(5)	3857(3)	4377(1)	28(1)
C(8)	1580(5)	4571(4)	3650(1)	32(1)
C(9)	-330(5)	6644(4)	3482(1)	31(1)
C(10)	16(4)	8247(4)	3809(1)	27(1)
C(11)	395(4)	7445(3)	4544(1)	24(1)
C(12)	641(5)	8935(3)	4934(1)	29(1)
C(13)	256(5)	8310(3)	5646(1)	30(1)
C(14)	1968(4)	6195(3)	5939(1)	24(1)
C(15)	863(4)	5743(3)	6601(1)	28(1)
C(16)	6262(6)	1356(4)	7198(1)	43(1)
C(17)	4880(4)	5157(4)	4604(1)	29(1)
C(18)	2034(5)	8838(4)	3481(1)	34(1)
C(19)	-2278(5)	10127(4)	3703(1)	40(1)
C(20)	4433(5)	6231(4)	6037(1)	31(1)
O(1)	882(4)	3798(3)	7627(1)	44(1)
C(1B)	6142(4)	6942(4)	-1645(1)	28(1)
C(2B)	3762(5)	8572(4)	-1543(1)	31(1)
C(3B)	3732(7)	9873(5)	-1072(1)	53(1)
C(4B)	5579(6)	9036(4)	-542(1)	37(1)
C(5B)	5692(4)	7012(3)	-139(1)	23(1)
C(6B)	5963(4)	6939(3)	605(1)	22(1)
C(7B)	3733(4)	8628(3)	825(1)	27(1)
C(8B)	3524(5)	8448(4)	1563(1)	33(1)
C(9B)	3478(4)	6415(4)	1864(1)	31(1)
C(10B)	5645(4)	4618(3)	1700(1)	27(1)
C(11B)	5931(4)	4885(3)	951(1)	23(1)
C(12B)	7962(5)	3144(3)	712(1)	29(1)

C(13B)	7593(5)	3225(3)	-5(1)	29(1)
C(14B)	7509(4)	5184(3)	-430(1)	24(1)
C(15B)	6649(5)	5117(4)	-1101(1)	29(1)
C(16B)	1809(6)	8788(5)	-1840(2)	53(1)
C(17B)	8181(5)	7329(4)	748(1)	31(1)
C(18B)	5080(5)	2714(4)	1921(1)	37(1)
C(19B)	7847(5)	4367(4)	2071(1)	35(1)
C(20B)	10058(5)	5147(4)	-502(1)	33(1)
O(1B)	6087(3)	6318(3)	-2247(1)	37(1)

Table 3. Bond lengths [Å] and angles [°] for barekol (**2**).

C(1)-O(1)	1.457(3)
C(1)-C(2)	1.502(3)
C(1)-C(15)	1.529(3)
C(1)-H(1A)	1.0000
C(2)-C(16)	1.320(4)
C(2)-C(3)	1.497(4)
C(3)-C(4)	1.542(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.544(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(14)	1.575(3)
C(5)-C(6)	1.579(3)
C(5)-H(5A)	1.0000
C(6)-C(17)	1.540(3)
C(6)-C(7)	1.551(3)
C(6)-C(11)	1.563(3)
C(7)-C(8)	1.529(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.510(4)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.541(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(19)	1.531(4)
C(10)-C(18)	1.541(3)
C(10)-C(11)	1.557(3)
C(11)-C(12)	1.528(3)
C(11)-H(11A)	1.0000
C(12)-C(13)	1.522(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.538(3)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(20)	1.539(3)
C(14)-C(15)	1.551(3)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16)	0.9348
C(16)-H(16A)	1.0393
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800

C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
O(1)-H(1O)	0.8178
C(1B)-O(1B)	1.427(3)
C(1B)-C(2B)	1.512(3)
C(1B)-C(15B)	1.544(3)
C(1B)-H(1BA)	1.0000
C(2B)-C(16B)	1.320(5)
C(2B)-C(3B)	1.485(4)
C(3B)-C(4B)	1.509(4)
C(3B)-H(3B1)	0.9900
C(3B)-H(3B2)	0.9900
C(4B)-C(5B)	1.552(3)
C(4B)-H(4BA)	0.9900
C(4B)-H(4BB)	0.9900
C(5B)-C(14B)	1.564(3)
C(5B)-C(6B)	1.577(3)
C(5B)-H(5BA)	1.0000
C(6B)-C(17B)	1.540(3)
C(6B)-C(7B)	1.553(3)
C(6B)-C(11B)	1.557(3)
C(7B)-C(8B)	1.540(3)
C(7B)-H(7BA)	0.9900
C(7B)-H(7BB)	0.9900
C(8B)-C(9B)	1.521(4)
C(8B)-H(8BA)	0.9900
C(8B)-H(8BB)	0.9900
C(9B)-C(10B)	1.533(3)
C(9B)-H(9BA)	0.9900
C(9B)-H(9BB)	0.9900
C(10B)-C(19B)	1.528(4)
C(10B)-C(18B)	1.547(3)
C(10B)-C(11B)	1.564(3)
C(11B)-C(12B)	1.529(3)
C(11B)-H(11B)	1.0000
C(12B)-C(13B)	1.528(3)
C(12B)-H(12C)	0.9900
C(12B)-H(12D)	0.9900
C(13B)-C(14B)	1.536(3)
C(13B)-H(13C)	0.9900
C(13B)-H(13D)	0.9900
C(14B)-C(20B)	1.541(3)
C(14B)-C(15B)	1.554(3)
C(15B)-H(15C)	0.9900
C(15B)-H(15D)	0.9900
C(16B)-H(16B)	0.8774
C(16B)-H(16C)	0.9830
C(17B)-H(17D)	0.9800
C(17B)-H(17E)	0.9800
C(17B)-H(17F)	0.9800
C(18B)-H(18D)	0.9800
C(18B)-H(18E)	0.9800
C(18B)-H(18F)	0.9800
C(19B)-H(19D)	0.9800
C(19B)-H(19E)	0.9800
C(19B)-H(19F)	0.9800
C(20B)-H(20D)	0.9800
C(20B)-H(20E)	0.9800
C(20B)-H(20F)	0.9800
O(1B)-H(1BB)	0.8400

O(1)-C(1)-C(2)	109.14(19)
O(1)-C(1)-C(15)	105.1(2)
C(2)-C(1)-C(15)	114.6(2)
O(1)-C(1)-H(1A)	109.3
C(2)-C(1)-H(1A)	109.3
C(15)-C(1)-H(1A)	109.3
C(16)-C(2)-C(3)	123.4(2)

C(16)-C(2)-C(1)	119.2(2)
C(3)-C(2)-C(1)	117.4(2)
C(2)-C(3)-C(4)	112.70(19)
C(2)-C(3)-H(3A)	109.1
C(4)-C(3)-H(3A)	109.1
C(2)-C(3)-H(3B)	109.1
C(4)-C(3)-H(3B)	109.1
H(3A)-C(3)-H(3B)	107.8
C(3)-C(4)-C(5)	117.6(2)
C(3)-C(4)-H(4A)	107.9
C(5)-C(4)-H(4A)	107.9
C(3)-C(4)-H(4B)	107.9
C(5)-C(4)-H(4B)	107.9
H(4A)-C(4)-H(4B)	107.2
C(4)-C(5)-C(14)	114.24(18)
C(4)-C(5)-C(6)	111.28(17)
C(14)-C(5)-C(6)	115.33(16)
C(4)-C(5)-H(5A)	104.9
C(14)-C(5)-H(5A)	104.9
C(6)-C(5)-H(5A)	104.9
C(17)-C(6)-C(7)	108.19(17)
C(17)-C(6)-C(11)	113.40(17)
C(7)-C(6)-C(11)	107.15(19)
C(17)-C(6)-C(5)	111.74(19)
C(7)-C(6)-C(5)	108.83(16)
C(11)-C(6)-C(5)	107.35(16)
C(8)-C(7)-C(6)	113.65(18)
C(8)-C(7)-H(7A)	108.8
C(6)-C(7)-H(7A)	108.8
C(8)-C(7)-H(7B)	108.8
C(6)-C(7)-H(7B)	108.8
H(7A)-C(7)-H(7B)	107.7
C(9)-C(8)-C(7)	111.81(19)
C(9)-C(8)-H(8A)	109.3
C(7)-C(8)-H(8A)	109.3
C(9)-C(8)-H(8B)	109.3
C(7)-C(8)-H(8B)	109.3
H(8A)-C(8)-H(8B)	107.9
C(8)-C(9)-C(10)	113.8(2)
C(8)-C(9)-H(9A)	108.8
C(10)-C(9)-H(9A)	108.8
C(8)-C(9)-H(9B)	108.8
C(10)-C(9)-H(9B)	108.8
H(9A)-C(9)-H(9B)	107.7
C(19)-C(10)-C(9)	107.2(2)
C(19)-C(10)-C(18)	107.0(2)
C(9)-C(10)-C(18)	110.54(18)
C(19)-C(10)-C(11)	109.13(19)
C(9)-C(10)-C(11)	108.47(18)
C(18)-C(10)-C(11)	114.2(2)
C(12)-C(11)-C(10)	114.01(18)
C(12)-C(11)-C(6)	110.72(19)
C(10)-C(11)-C(6)	117.57(17)
C(12)-C(11)-H(11A)	104.3
C(10)-C(11)-H(11A)	104.3
C(6)-C(11)-H(11A)	104.3
C(13)-C(12)-C(11)	110.02(17)
C(13)-C(12)-H(12A)	109.7
C(11)-C(12)-H(12A)	109.7
C(13)-C(12)-H(12B)	109.7
C(11)-C(12)-H(12B)	109.7
H(12A)-C(12)-H(12B)	108.2
C(12)-C(13)-C(14)	114.79(18)
C(12)-C(13)-H(13A)	108.6
C(14)-C(13)-H(13A)	108.6
C(12)-C(13)-H(13B)	108.6
C(14)-C(13)-H(13B)	108.6
H(13A)-C(13)-H(13B)	107.5
C(20)-C(14)-C(13)	109.48(19)
C(20)-C(14)-C(15)	109.9(2)
C(13)-C(14)-C(15)	104.41(18)
C(20)-C(14)-C(5)	114.34(18)
C(13)-C(14)-C(5)	108.63(18)
C(15)-C(14)-C(5)	109.56(16)
C(1)-C(15)-C(14)	118.8(2)
C(1)-C(15)-H(15A)	107.6

C(14)-C(15)-H(15A)	107.6
C(1)-C(15)-H(15B)	107.6
C(14)-C(15)-H(15B)	107.6
H(15A)-C(15)-H(15B)	107.1
C(2)-C(16)-H(16)	125.5
C(2)-C(16)-H(16A)	124.1
H(16)-C(16)-H(16A)	110.4
C(6)-C(17)-H(17A)	109.5
C(6)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(6)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(10)-C(18)-H(18A)	109.5
C(10)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(10)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(10)-C(19)-H(19A)	109.5
C(10)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(10)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(14)-C(20)-H(20A)	109.5
C(14)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(14)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(1)-O(1)-H(1O)	102.9
O(1B)-C(1B)-C(2B)	108.7(2)
O(1B)-C(1B)-C(15B)	109.05(19)
C(2B)-C(1B)-C(15B)	110.45(18)
O(1B)-C(1B)-H(1BA)	109.5
C(2B)-C(1B)-H(1BA)	109.5
C(15B)-C(1B)-H(1BA)	109.5
C(16B)-C(2B)-C(3B)	121.8(3)
C(16B)-C(2B)-C(1B)	122.2(2)
C(3B)-C(2B)-C(1B)	116.0(3)
C(2B)-C(3B)-C(4B)	118.6(2)
C(2B)-C(3B)-H(3B1)	107.7
C(4B)-C(3B)-H(3B1)	107.7
C(2B)-C(3B)-H(3B2)	107.7
C(4B)-C(3B)-H(3B2)	107.7
H(3B1)-C(3B)-H(3B2)	107.1
C(3B)-C(4B)-C(5B)	114.3(2)
C(3B)-C(4B)-H(4BA)	108.7
C(5B)-C(4B)-H(4BA)	108.7
C(3B)-C(4B)-H(4BB)	108.7
C(5B)-C(4B)-H(4BB)	108.7
H(4BA)-C(4B)-H(4BB)	107.6
C(4B)-C(5B)-C(14B)	111.28(17)
C(4B)-C(5B)-C(6B)	112.40(17)
C(14B)-C(5B)-C(6B)	115.77(18)
C(4B)-C(5B)-H(5BA)	105.5
C(14B)-C(5B)-H(5BA)	105.5
C(6B)-C(5B)-H(5BA)	105.5
C(17B)-C(6B)-C(7B)	108.32(18)
C(17B)-C(6B)-C(11B)	114.60(19)
C(7B)-C(6B)-C(11B)	107.75(17)
C(17B)-C(6B)-C(5B)	111.23(18)
C(7B)-C(6B)-C(5B)	107.74(18)
C(11B)-C(6B)-C(5B)	106.96(15)
C(8B)-C(7B)-C(6B)	112.79(19)
C(8B)-C(7B)-H(7BA)	109.0
C(6B)-C(7B)-H(7BA)	109.0
C(8B)-C(7B)-H(7BB)	109.0
C(6B)-C(7B)-H(7BB)	109.0
H(7BA)-C(7B)-H(7BB)	107.8
C(9B)-C(8B)-C(7B)	110.93(18)
C(9B)-C(8B)-H(8BA)	109.5
C(7B)-C(8B)-H(8BA)	109.5
C(9B)-C(8B)-H(8BB)	109.5
C(7B)-C(8B)-H(8BB)	109.5

H(8BA)-C(8B)-H(8BB)	108.0
C(8B)-C(9B)-C(10B)	114.08(19)
C(8B)-C(9B)-H(9BA)	108.7
C(10B)-C(9B)-H(9BA)	108.7
C(8B)-C(9B)-H(9BB)	108.7
C(10B)-C(9B)-H(9BB)	108.7
H(9BA)-C(9B)-H(9BB)	107.6
C(19B)-C(10B)-C(9B)	111.0(2)
C(19B)-C(10B)-C(18B)	107.7(2)
C(9B)-C(10B)-C(18B)	107.21(19)
C(19B)-C(10B)-C(11B)	114.57(18)
C(9B)-C(10B)-C(11B)	108.05(18)
C(18B)-C(10B)-C(11B)	108.05(17)
C(12B)-C(11B)-C(6B)	110.60(17)
C(12B)-C(11B)-C(10B)	114.12(19)
C(6B)-C(11B)-C(10B)	116.98(17)
C(12B)-C(11B)-H(11B)	104.6
C(6B)-C(11B)-H(11B)	104.6
C(10B)-C(11B)-H(11B)	104.6
C(13B)-C(12B)-C(11B)	109.2(2)
C(13B)-C(12B)-H(12C)	109.8
C(11B)-C(12B)-H(12C)	109.8
C(13B)-C(12B)-H(12D)	109.8
C(11B)-C(12B)-H(12D)	109.8
H(12C)-C(12B)-H(12D)	108.3
C(12B)-C(13B)-C(14B)	114.10(18)
C(12B)-C(13B)-H(13C)	108.7
C(14B)-C(13B)-H(13C)	108.7
C(12B)-C(13B)-H(13D)	108.7
C(14B)-C(13B)-H(13D)	108.7
H(13C)-C(13B)-H(13D)	107.6
C(13B)-C(14B)-C(20B)	108.6(2)
C(13B)-C(14B)-C(15B)	105.24(17)
C(20B)-C(14B)-C(15B)	108.08(18)
C(13B)-C(14B)-C(5B)	109.09(17)
C(20B)-C(14B)-C(5B)	114.71(17)
C(15B)-C(14B)-C(5B)	110.64(19)
C(1B)-C(15B)-C(14B)	120.10(18)
C(1B)-C(15B)-H(15C)	107.3
C(14B)-C(15B)-H(15C)	107.3
C(1B)-C(15B)-H(15D)	107.3
C(14B)-C(15B)-H(15D)	107.3
H(15C)-C(15B)-H(15D)	106.9
C(2B)-C(16B)-H(16B)	126.2
C(2B)-C(16B)-H(16C)	112.2
H(16B)-C(16B)-H(16C)	121.4
C(6B)-C(17B)-H(17D)	109.5
C(6B)-C(17B)-H(17E)	109.5
H(17D)-C(17B)-H(17E)	109.5
C(6B)-C(17B)-H(17F)	109.5
H(17D)-C(17B)-H(17F)	109.5
H(17E)-C(17B)-H(17F)	109.5
C(10B)-C(18B)-H(18D)	109.5
C(10B)-C(18B)-H(18E)	109.5
H(18D)-C(18B)-H(18E)	109.5
C(10B)-C(18B)-H(18F)	109.5
H(18D)-C(18B)-H(18F)	109.5
H(18E)-C(18B)-H(18F)	109.5
C(10B)-C(19B)-H(19D)	109.5
C(10B)-C(19B)-H(19E)	109.5
H(19D)-C(19B)-H(19E)	109.5
C(10B)-C(19B)-H(19F)	109.5
H(19D)-C(19B)-H(19F)	109.5
H(19E)-C(19B)-H(19F)	109.5
C(14B)-C(20B)-H(20D)	109.5
C(14B)-C(20B)-H(20E)	109.5
H(20D)-C(20B)-H(20E)	109.5
C(14B)-C(20B)-H(20F)	109.5
H(20D)-C(20B)-H(20F)	109.5
H(20E)-C(20B)-H(20F)	109.5
C(1B)-O(1B)-H(1BB)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for barekol (**2**). The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	29(1)	31(1)	27(1)	-9(1)	-1(1)	-6(1)
C(2)	33(2)	24(1)	27(1)	-2(1)	1(1)	-8(1)
C(3)	48(2)	22(1)	34(1)	-6(1)	1(1)	-12(1)
C(4)	41(2)	19(1)	31(1)	-8(1)	2(1)	-8(1)
C(5)	21(1)	23(1)	29(1)	-9(1)	3(1)	-10(1)
C(6)	19(1)	19(1)	28(1)	-7(1)	3(1)	-6(1)
C(7)	30(1)	25(1)	29(1)	-8(1)	4(1)	-11(1)
C(8)	39(2)	31(1)	30(1)	-13(1)	6(1)	-15(1)
C(9)	30(1)	36(1)	27(1)	-6(1)	1(1)	-14(1)
C(10)	23(1)	27(1)	31(1)	-5(1)	0(1)	-8(1)
C(11)	19(1)	22(1)	29(1)	-6(1)	1(1)	-6(1)
C(12)	32(1)	18(1)	34(1)	-6(1)	-2(1)	-6(1)
C(13)	33(1)	19(1)	35(1)	-11(1)	0(1)	-3(1)
C(14)	22(1)	20(1)	29(1)	-10(1)	-1(1)	-4(1)
C(15)	26(1)	26(1)	28(1)	-9(1)	0(1)	-3(1)
C(16)	38(2)	36(1)	44(1)	-9(1)	-3(1)	0(1)
C(17)	22(1)	30(1)	33(1)	-6(1)	6(1)	-9(1)
C(18)	38(2)	32(1)	34(1)	-2(1)	3(1)	-16(1)
C(19)	40(2)	37(1)	35(1)	-3(1)	-5(1)	-5(1)
C(20)	31(1)	29(1)	37(1)	-9(1)	-4(1)	-14(1)
O(1)	38(1)	46(1)	30(1)	0(1)	5(1)	0(1)
C(1B)	24(1)	37(1)	25(1)	-10(1)	3(1)	-11(1)
C(2B)	33(2)	31(1)	24(1)	1(1)	4(1)	-9(1)
C(3B)	57(2)	44(2)	27(1)	0(1)	-1(1)	13(2)
C(4B)	56(2)	22(1)	28(1)	-5(1)	5(1)	-11(1)
C(5B)	23(1)	20(1)	25(1)	-4(1)	-2(1)	-6(1)
C(6B)	22(1)	22(1)	24(1)	-5(1)	-2(1)	-8(1)
C(7B)	29(1)	21(1)	27(1)	-5(1)	-3(1)	-5(1)
C(8B)	35(2)	30(1)	29(1)	-12(1)	2(1)	-5(1)
C(9B)	29(1)	39(1)	24(1)	-7(1)	2(1)	-12(1)
C(10B)	27(1)	28(1)	25(1)	-3(1)	-1(1)	-10(1)
C(11B)	21(1)	24(1)	26(1)	-5(1)	-2(1)	-8(1)
C(12B)	29(1)	21(1)	31(1)	-2(1)	-1(1)	-4(1)

C(13B)	30(1)	20(1)	34(1)	-9(1)	3(1)	-6(1)
C(14B)	22(1)	23(1)	25(1)	-7(1)	2(1)	-6(1)
C(15B)	26(1)	28(1)	31(1)	-10(1)	2(1)	-7(1)
C(16B)	34(2)	38(2)	77(2)	0(1)	3(2)	-8(1)
C(17B)	36(2)	34(1)	32(1)	-7(1)	-1(1)	-21(1)
C(18B)	43(2)	38(1)	31(1)	0(1)	5(1)	-20(1)
C(19B)	34(2)	38(1)	28(1)	-1(1)	-8(1)	-11(1)
C(20B)	25(1)	38(1)	36(1)	-11(1)	6(1)	-11(1)
O(1B)	34(1)	48(1)	26(1)	-14(1)	3(1)	-10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for barekol (**2**).

	x	y	z	U(eq)
H(1A)	3441	4857	7318	36
H(3A)	1529	1816	6496	42
H(3B)	4085	44	6477	42
H(4A)	3444	1621	5437	37
H(4B)	5281	2383	5703	37
H(5A)	324	4662	5533	27
H(7A)	3108	2514	4464	33
H(7B)	314	3711	4540	33
H(8A)	3122	4590	3478	39
H(8B)	1198	3612	3443	39
H(9A)	-1892	6579	3610	37
H(9B)	-359	7065	3009	37
H(11A)	-1140	7320	4693	29
H(12A)	2246	8976	4871	34
H(12B)	-545	10298	4782	34
H(13A)	-1395	8372	5704	36
H(13B)	422	9296	5888	36
H(15A)	79	7030	6766	34

H(15B)	-401	5267	6526	34
H(16)	7369	109	7123	52
H(16A)	6956	1937	7516	52
H(17A)	5033	5555	4140	43
H(17B)	5995	3772	4737	43
H(17C)	5240	6056	4838	43
H(18A)	1669	9328	3022	52
H(18B)	3533	7661	3532	52
H(18C)	2182	9899	3682	52
H(19A)	-2524	10640	3241	61
H(19B)	-2152	11160	3923	61
H(19C)	-3626	9786	3877	61
H(20A)	4286	7219	6314	46
H(20B)	5077	6599	5618	46
H(20C)	5506	4897	6240	46
H(1O)	1774	2822	7866	53
H(1BA)	7425	7480	-1651	34
H(3B1)	2147	10291	-866	64
H(3B2)	3884	11104	-1316	64
H(4BA)	5239	10036	-249	44
H(4BB)	7158	8844	-736	44
H(5BA)	4097	6964	-192	28
H(7BA)	3803	9949	645	32
H(7BB)	2292	8576	649	32
H(8BA)	4890	8620	1739	39
H(8BB)	2049	9529	1676	39
H(9BA)	2023	6314	1717	37
H(9BB)	3383	6340	2337	37
H(11B)	4455	4830	788	28
H(12C)	9502	3245	779	34
H(12D)	7992	1849	956	34
H(13C)	6085	3054	-61	34
H(13D)	8900	2082	-155	34
H(15C)	7858	3942	-1263	34
H(15D)	5172	4847	-1033	34
H(16B)	1727	8140	-2145	63
H(16C)	402	9877	-1708	63
H(17D)	8060	8647	515	47

H(17E)	9607	6283	609	47
H(17F)	8285	7304	1212	47
H(18D)	4882	2522	2389	55
H(18E)	6392	1541	1800	55
H(18F)	3610	2873	1712	55
H(19D)	7514	4231	2534	52
H(19E)	8258	5548	1937	52
H(19F)	9179	3161	1980	52
H(20D)	11073	3968	-691	49
H(20E)	10684	5081	-78	49
H(20F)	10036	6370	-785	49
H(1BB)	7456	5539	-2334	56

Table 6. Torsion angles [°] for barekol (**2**).

O(1)-C(1)-C(2)-C(16)	-96.0(3)
C(15)-C(1)-C(2)-C(16)	146.4(2)
O(1)-C(1)-C(2)-C(3)	83.9(2)
C(15)-C(1)-C(2)-C(3)	-33.7(3)
C(16)-C(2)-C(3)-C(4)	-95.5(3)
C(1)-C(2)-C(3)-C(4)	84.7(3)
C(2)-C(3)-C(4)-C(5)	-74.1(3)
C(3)-C(4)-C(5)-C(14)	55.6(3)
C(3)-C(4)-C(5)-C(6)	-171.6(2)
C(4)-C(5)-C(6)-C(17)	-61.1(2)
C(14)-C(5)-C(6)-C(17)	71.1(2)
C(4)-C(5)-C(6)-C(7)	58.3(2)
C(14)-C(5)-C(6)-C(7)	-169.49(19)
C(4)-C(5)-C(6)-C(11)	173.95(17)
C(14)-C(5)-C(6)-C(11)	-53.8(2)
C(17)-C(6)-C(7)-C(8)	-70.5(3)
C(11)-C(6)-C(7)-C(8)	52.1(2)
C(5)-C(6)-C(7)-C(8)	167.9(2)
C(6)-C(7)-C(8)-C(9)	-56.9(3)

C(7)-C(8)-C(9)-C(10)	55.9(3)
C(8)-C(9)-C(10)-C(19)	-168.87(19)
C(8)-C(9)-C(10)-C(18)	74.8(3)
C(8)-C(9)-C(10)-C(11)	-51.2(3)
C(19)-C(10)-C(11)-C(12)	-60.7(3)
C(9)-C(10)-C(11)-C(12)	-177.1(2)
C(18)-C(10)-C(11)-C(12)	59.1(3)
C(19)-C(10)-C(11)-C(6)	167.30(19)
C(9)-C(10)-C(11)-C(6)	50.8(3)
C(18)-C(10)-C(11)-C(6)	-72.9(2)
C(17)-C(6)-C(11)-C(12)	-65.3(2)
C(7)-C(6)-C(11)-C(12)	175.37(16)
C(5)-C(6)-C(11)-C(12)	58.6(2)
C(17)-C(6)-C(11)-C(10)	68.2(2)
C(7)-C(6)-C(11)-C(10)	-51.1(2)
C(5)-C(6)-C(11)-C(10)	-167.90(19)
C(10)-C(11)-C(12)-C(13)	163.0(2)
C(6)-C(11)-C(12)-C(13)	-61.7(2)
C(11)-C(12)-C(13)-C(14)	58.3(3)
C(12)-C(13)-C(14)-C(20)	74.9(2)
C(12)-C(13)-C(14)-C(15)	-167.4(2)
C(12)-C(13)-C(14)-C(5)	-50.6(3)
C(4)-C(5)-C(14)-C(20)	57.5(2)
C(6)-C(5)-C(14)-C(20)	-73.3(3)
C(4)-C(5)-C(14)-C(13)	-179.88(18)
C(6)-C(5)-C(14)-C(13)	49.3(2)
C(4)-C(5)-C(14)-C(15)	-66.4(2)
C(6)-C(5)-C(14)-C(15)	162.8(2)
O(1)-C(1)-C(15)-C(14)	-167.38(18)
C(2)-C(1)-C(15)-C(14)	-47.5(3)
C(20)-C(14)-C(15)-C(1)	-38.2(3)
C(13)-C(14)-C(15)-C(1)	-155.5(2)
C(5)-C(14)-C(15)-C(1)	88.3(2)
O(1B)-C(1B)-C(2B)-C(16B)	22.3(3)
C(15B)-C(1B)-C(2B)-C(16B)	-97.3(3)
O(1B)-C(1B)-C(2B)-C(3B)	-159.8(2)
C(15B)-C(1B)-C(2B)-C(3B)	80.6(3)
C(16B)-C(2B)-C(3B)-C(4B)	151.8(3)

C(1B)-C(2B)-C(3B)-C(4B)	-26.0(4)
C(2B)-C(3B)-C(4B)-C(5B)	-53.7(4)
C(3B)-C(4B)-C(5B)-C(14B)	90.7(3)
C(3B)-C(4B)-C(5B)-C(6B)	-137.6(2)
C(4B)-C(5B)-C(6B)-C(17B)	-56.9(3)
C(14B)-C(5B)-C(6B)-C(17B)	72.6(2)
C(4B)-C(5B)-C(6B)-C(7B)	61.7(2)
C(14B)-C(5B)-C(6B)-C(7B)	-168.87(16)
C(4B)-C(5B)-C(6B)-C(11B)	177.3(2)
C(14B)-C(5B)-C(6B)-C(11B)	-53.3(2)
C(17B)-C(6B)-C(7B)-C(8B)	-71.4(2)
C(11B)-C(6B)-C(7B)-C(8B)	53.1(2)
C(5B)-C(6B)-C(7B)-C(8B)	168.22(18)
C(6B)-C(7B)-C(8B)-C(9B)	-57.2(3)
C(7B)-C(8B)-C(9B)-C(10B)	57.1(3)
C(8B)-C(9B)-C(10B)-C(19B)	74.1(2)
C(8B)-C(9B)-C(10B)-C(18B)	-168.6(2)
C(8B)-C(9B)-C(10B)-C(11B)	-52.4(2)
C(17B)-C(6B)-C(11B)-C(12B)	-64.4(2)
C(7B)-C(6B)-C(11B)-C(12B)	174.94(18)
C(5B)-C(6B)-C(11B)-C(12B)	59.3(2)
C(17B)-C(6B)-C(11B)-C(10B)	68.5(3)
C(7B)-C(6B)-C(11B)-C(10B)	-52.1(3)
C(5B)-C(6B)-C(11B)-C(10B)	-167.72(18)
C(19B)-C(10B)-C(11B)-C(12B)	58.5(3)
C(9B)-C(10B)-C(11B)-C(12B)	-177.16(19)
C(18B)-C(10B)-C(11B)-C(12B)	-61.5(3)
C(19B)-C(10B)-C(11B)-C(6B)	-72.8(3)
C(9B)-C(10B)-C(11B)-C(6B)	51.5(2)
C(18B)-C(10B)-C(11B)-C(6B)	167.2(2)
C(6B)-C(11B)-C(12B)-C(13B)	-63.5(2)
C(10B)-C(11B)-C(12B)-C(13B)	162.15(18)
C(11B)-C(12B)-C(13B)-C(14B)	59.3(3)
C(12B)-C(13B)-C(14B)-C(20B)	75.0(2)
C(12B)-C(13B)-C(14B)-C(15B)	-169.4(2)
C(12B)-C(13B)-C(14B)-C(5B)	-50.7(3)
C(4B)-C(5B)-C(14B)-C(13B)	178.7(2)
C(6B)-C(5B)-C(14B)-C(13B)	48.7(2)

C(4B)-C(5B)-C(14B)-C(20B)	56.6(3)
C(6B)-C(5B)-C(14B)-C(20B)	-73.4(2)
C(4B)-C(5B)-C(14B)-C(15B)	-66.0(2)
C(6B)-C(5B)-C(14B)-C(15B)	164.06(17)
O(1B)-C(1B)-C(15B)-C(14B)	162.7(2)
C(2B)-C(1B)-C(15B)-C(14B)	-77.9(3)
C(13B)-C(14B)-C(15B)-C(1B)	174.8(2)
C(20B)-C(14B)-C(15B)-C(1B)	-69.2(3)
C(5B)-C(14B)-C(15B)-C(1B)	57.1(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for barekol (**2**) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1B)-H(1BB)...O(1)#1	0.84	1.99	2.816(3)	168.4

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z-1