# Supporting Information

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## 1.0 Experimental Section

### 1.1 General Considerations

All experiments were performed in anhydrous conditions under an atmosphere of dry argon using flame-dried glassware. Solvents were dried by a Grubbs-type solvent purification system. Hexanes and pentanes were degassed with argon for 10 minutes prior to use. 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, 500 or 600 MHz. Data is presented as follows: chemical shift (in ppm on the δ scale relative to δH 7.26 for the residual protons in $CDCl_3$ or δH 7.16 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 75, 100, 125 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 $CDCl_3$ or δC 128.39 for $C_6D_6$. Mass spectral determinations were carried out using APCI, ESI, or NSI as ionization source. Melting points are uncorrected. Infrared spectral data are reported in units of $cm^{-1}$. Analytical TLC was performed on glass-backed silica gel F254 plates (EMD Chemicals). Visualization of developed plates was performed by fluorescence quenching or by staining with aqueous potassium permanganate ($KMnO_4$) or phosphomolybdic acid (PMA) in ethanol stain followed by heating. Flash column chromatography was performed on silica gel 60Å (230-400 mesh) according to the literature procedure described by Still.[1] Optical rotations were measured on a Jasco P-2000 polarimeter. Analytical chromatographies, using isopropanol/hexane as gradient, were measured on a Varian Prostar instrument. $Rh_2$(*S*-BTPCP)$_4$, $Rh_2$(*S*-PTAD)$_4$, and $Rh_2$(*S*-DOSP)$_4$ were

lyophilized prior to use using an SP VirTis BenchTop K freeze-dryer and were stored in a desiccator over Drierite™. Methyl 3-((tert-butyldimethylsilyl)oxy)-2-diazobut-3-enoate[2], (*Z*)-methyl 3-((tert-butyldimethylsilyl)oxy)-2-diazopent-3-enoate[3] and (((4*E*)-hexa-2,4-dien-3-yl)oxy)triisopropylsilane[4] were prepared according to published literature procedures.

## 1.2 General procedures

### *Diene synthesis*

To a round-bottom flask was added the ketone starting material (1.00 equiv), anhydrous DCM (0.2 M) and $Et_3N$ (1.40 equiv). The solution was cooled to 0 °C. Once cool, TBSOTf (1.15 equiv) was slowly added (over 1 minute). The reaction was allowed to stir overnight and gradually warm to room temperature. The reaction can be monitored by TLC using $Al_2O_3$ as the stationary phase. The reaction was stopped by diluting with pentane followed by saturated aqueous $NaHCO_3$. The mixture was transferred to a separation funnel and the two layers were separated. The aqueous layer was extracted with $Et_2O$ (2 times) and the organic layers were combined, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel using 99:1 pentane/$Et_3N$ as eluent to provide pure products.

*Procedure A*

***Enantioselective regioisomeric [4 + 3] cycloaddition***

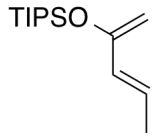
To a round-bottom flask was added the corresponding diene (1.51 mmol, 5.00 equiv), pentane (3.5 mL), and $Rh_2$(*S*-BTPCP)$_4$ (5.3 mg, 0.0030 mmol 0.010 equiv). A solution of methyl 3-((tert-butyldimethylsilyl)oxy)-2-diazobut-3-enoate (77.0 mg, 0.30, mmol, 1.00 equiv) in pentane (3.5 mL) was added by syringe pump over 1 h. Once the addition was complete, the reaction was allowed to stir at 23 °C for 0.5 h. The reaction was stopped by concentration under reduced pressure and purified by flash chromatography on silica gel to provide pure products.

*Procedure B*

***Enantioselective regioisomeric [4 + 3] cycloaddition***

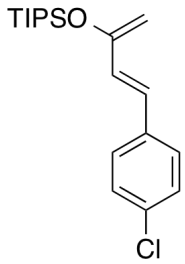
To a round-bottom flask was added the corresponding diene (0.187 mmol, 1.00 equiv), hexanes (2.0 mL), ad $Rh_2$(*S*-BTPCP)$_4$ (3.3 mg, 0.00187 mmol 0.010 equiv). The reaction vessel was equipped with a water-cooled reflux condenser and heated to reflux. A solution of (Z)-methyl 3-((tert-butyldimethylsilyl)oxy)-2-diazopent-3-enoate (101 mg, 0.374 mmol, 2.00 equiv) in hexanes (2.0 mL) was added by syringe pump over 1 h. Once the addition was complete, the reaction was allowed to stir at reflux for 0.5 h. The reaction was stopped by concentration under reduced pressure and purified by flash chromatography on silica gel to provide pure products.

## 2.0 Procedures and Characterization



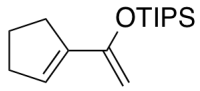

**(*E*)-triisopropyl(penta-1,3-dien-2-yloxy)silane:**

Derived from (*E*)-pent-3-en-2-one (10.2 mmol, 1.0 equiv) to provide the corresponding diene (2.5 g, 86% yield). $R_f$ = 0.8 (100% hexanes); $^1$H NMR (600 MHz; $C_6D_6$) δ 6.37 (dq, 1H, *J* = 13.8, 6.6 Hz), 5.99 (dd, *J* = 15, 1.8 Hz, 1H), 4.39 (s, 1H), 4.30 (s, 1H), 1.71 (d, *J* = 6.6 Hz, 3H), 1.31-1.26 (m, 3H), 1.24 (d, *J* = 6.6 Hz, 18H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 156.2, 130.3, 126.5, 93.1, 18.7, 17.9, 13.6; IR (neat): 2944, 2892, 2866, 1586, 1317; HRMS-(APCI) m/z 241.1988 [$(M+H)^+$ requires 241.1982].



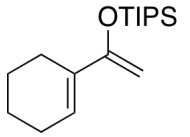

**(*E*)-((4-(4-chlorophenyl)buta-1,3-dien-2-yl)oxy)triisopropylsilane:**

Derived from (*E*)-4-(4-chlorophenyl)but-3-en-2-one (5.69 mmol, 1.0 equiv) to provide the corresponding diene (1.87 g, 97% yield). $R_f$ = 0.7 (100% hexanes); $^1$H NMR (600 MHz; $C_6D_6$) δ 7.30 (s, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 15 Hz, 1H), 4.61 (s, 1H), 4.51 (s, 1H), 1.37-1.34 (m, 3H), 1.29 (d, *J* = 6.6 Hz, 18H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 155.8, 135.8, 133.6, 129.1, 128.4, 128.3, 127.7, 96.4, 18.4, 13.2; IR (neat): 2943, 2891, 2865, 1321; HRMS-(APCI) m/z 337.1748 [$(M+H)^+$ requires 337.1749].



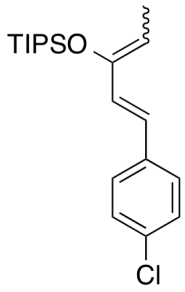

**((1-(cyclopent-1-en-1-yl)vinyl)oxy)triisopropylsilane:**

Derived from 1-(cyclopent-1-en-1-yl)ethan-1-one (9.08 mmol, 1.0 equiv) to provide the corresponding diene (2.4 g, 99% yield). $R_f$ = 0.8 (100% hexanes); $^1$H NMR (600 MHz; $C_6D_6$) δ 6.27 (s, 1H), 4.38 (s, 1H), 4.34 (s, 1H), 2.14-2.38 (m, 2H), 2.32-2.29 (m, 2H), 1.76 (p, *J* = 7.2 Hz, 2H), 1.27-1.19 (m, 3H), 1.16 (d, *J* = 6.6 Hz, 18H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 155.2, 142.1, 129, 92, 33.6, 32.9, 24.3, 18.7, 13.6; IR (neat): 2943, 2892, 2866, 1012; HRMS-(APCI) m/z 267.2143 [$(M+H)^+$ requires 267.2138].



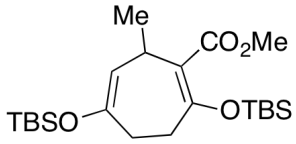

**((1-(cyclohex-1-en-1-yl)vinyl)oxy)triisopropylsilane:**

Derived from 1-(cyclohex-1-en-1-yl)ethan-1-one (7.78 mmol, 1.0 equiv) to provide the corresponding diene (2.0 g, 94% yield). $R_f$ = 0.8 (100% hexanes); $^1$H NMR (600 MHz; $C_6D_6$) δ 6.59 (t, 1H, *J* = 4.2 Hz), 4.43 (s, 1H), 4.32 (s, 1H), 2.15-2.12 (m, 2H), 2.06-2.04 (m, 2H), 1.53-1.49 (m, 2H), 1.43-1.39 (m, 2H), 1.25-1.22 (m, 3H), 1.16 (d, *J* = 6.6 Hz, 18H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 157.7, 134.1, 125.7, 89.9, 26.4, 26.1, 25.7, 23.4, 22.8, 18.6; IR (neat): 2928, 2857, 1256; HRMS-(APCI) m/z 281.2293 [$(M+H)^+$ requires 281.2295].



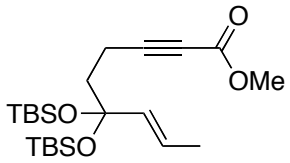

**(((1*E*)-1-(4-chlorophenyl)penta-1,3-dien-3-yl)oxy)triisopropylsilane:**

Derived from (*E*)-1-(4-chlorophenyl)pent-1-en-3-one to provide the corresponding diene as a 88:12 *Z,E:E,E* mixture of isomers which was determined by $^{1}$H NMR. $^{1}$H NMR (600 MHz; $C_6D_6$) δ 4.83 (q, *J* = 7.2 Hz, 1H (*Z,E*)), 5.01 (q, *J* = 7.2 Hz, 1H (*E,E*)) (507 mg, 91% yield). $R_f$ = 0.8 (100% hexanes); $^{1}$H NMR (600 MHz; $C_6D_6$) δ 7.08 (d, 2H, *J* = 8.4 Hz), 6.99 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 15.6 Hz, 1H), 6.43 (d, *J* = 16.2 Hz, 1H), 4.83 (q, *J* = 7.2 Hz, 1H), 1.72 (d, *J* = 7.2 Hz, 3H), 1.27-1.21 (m, 3H), 1.18-1.17 (m, 18H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 151.2, 136.4, 133.4, 129.5, 129.4, 128.2, 125.8, 110.3, 18.6, 14.6, 12.5; IR (neat): 2943, 2865, 1489; HRMS-(APCI) m/z 351.1904 [$(M+H)^+$ requires 351.1905].



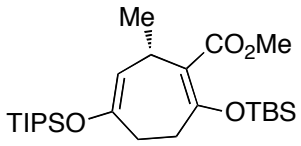

**Methyl 2,5-bis((tert-butyldimethylsilyl)oxy)-7-methylcyclohepta-1,dienecarboxylate(13a):**

Prepared *via* Procedure A. Derived from (*E*)-tert-butyldimethyl(penta-1,3-dien-2-yloxy)silane (300 mg, 1.51 mmol, 5.0 equiv) and purified by flash chromatography (98:2 pentane/$Et_2O$) on silica gel to provide the vinylogous [4+3] product as colorless oil (30 mg, 23% yield). $R_f$ = 0.10 (98:2 Pentane/$Et_2O$); $^1H$ NMR (600 MHz; $C_6D_6$) δ 5.07 (dd, 1H, *J* = 6.0, 12.0 Hz), 3.64 (p, *J* = 6 Hz, 1H), 3.46 (s, 3H), 2.69-2.64 (m, *J* = 1 Hz, 1H), 2.37-2.32 (m, 1H), 2.11-2.05 (m, 2H), 1.31 (d, *J* = 6 Hz, 3H), 0.98 (s, 9H), 0.97 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H), 0.11 (s, 3H), 0.09 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 169.3, 159.3, 150.7, 116.8, 111.9, 51.2, 32.5, 30, 25.7, 21.1, 18.2, 17.9, -3.9, -4.0, -4.3, -4.6; IR (neat): 2954, 2929, 2857, 1716, 1694, 836, 778; HRMS-(APCI) m/z 427.2694 [$(M+H)^+$ requires 427.2689]. HPLC analysis: (S,S-Whelk-O 1, 100 % hexanes, 0.5 ml/min), UV: 254 nm, retention time of 12.82 min (minor) and 16.35 min (major), 87 % ee.



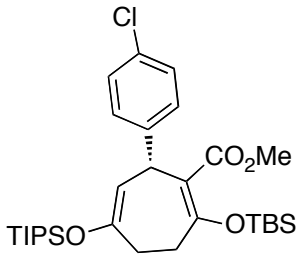

**(E)-methyl 6,6-bis((tert-butyldimethylsilyl)oxy)non-7-en-2-ynoate (14a):**

Prepared *via* procedure A. Derived from (*E*)-tert-butyldimethyl(penta-1,3-dien-2-yloxy)silane (300 mg, 1.51 mmol, 5.0 equiv) and purified by flash chromatography (98:2 pentane/$Et_2O$) on silica gel to provide the alkynoate product as colorless oil (54 mg, 42% yield). $R_f$ = 0.14 (98:2 Pentane:$Et_2O$); $^1$H NMR (600 MHz; $C_6D_6$) δ 5.67 (dq, 1H, *J* = 6.6, 13.2, 15.0 Hz), 5.40 (dd, *J* = 1.8.15.6 Hz, 1H), 3.27 (s, 3H), 2.38 (app dd, *J* = 8.4, 10.2 Hz, 2H), 1.93 (app dd, *J* = 6.6, 8.4 Hz, 2H), 1.47 (dd, *J* = 1.8, 6.6 Hz, 3H), 0.94 (s, 18H), 0.13 (s, 6H), 0.10 (s, 6H); $^{13}$C NMR (150 MHz, $C_6D_6$) δ 154.5, 135.4, 126.3, 98.6, 89.7, 74.2, 52.2, 42, 26.6, 18.8, 17.6, 14.6, 1.82, 2.04; IR (neat): 2954, 2929, 2857, 2240, 1718, 1247; HRMS-(APCI) m/z 427.2697 [$(M+H)^+$ requires 427.2694].



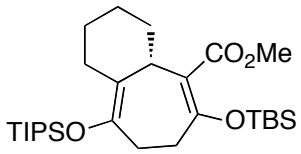

**Methyl2-((tert-butyldimethylsilyl)oxy)-7-methyl-5-((triisopropylsilyl)oxy)cyclohepta-1,5-dienecarboxylate (13c):**

Prepared *via* procedure A. Derived from (*E*)-triisopropyl(penta-1,3-dien-2-yloxy)silane (363 mg, 1.51 mmol, 5.0 equiv) and purified by flash chromatography (98:2 pentane/$Et_2O$) on silica gel to provide the vinylogous [4+3] product as colorless oil (84 mg, 59% yield). $R_f$ = 0.10 (98:2 Pentane:$Et_2O$); $[\alpha]_D^{20}$: 26.3 (*c*. 1.0, $CHCl_3$); $^1H$ NMR (600 MHz; $C_6D_6$) δ 5.10 (d, 1H, *J* = 7.8 Hz), 3.65 (p, *J* = 7.2 Hz, 1H), 3.46 (s, 3H), 2.68 (ddd, *J* = 15.0, 12.0, 3.0 Hz, 1H), 2.41 (ddd, *J* = 14.4, 14.4 Hz, 1H), 2.17 (m, 1H), 2.09 (ddd, *J* = 14.4, 6.6, 3.0 Hz, 1H), 1.32 (d, *J* = 7.2 Hz, 3H), 1.11 (bs, 21H), 0.98 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ 168.7, 159.6, 152, 117.7, 111.3, 51.1, 33.1, 30.8, 30.7, 26.3, 21.7, 18.9, 18.6, 13.4, -3.44; IR (neat): 2944, 2865, 1719, 1626, 1178; HRMS-(ESI) m/z 491.2986 [$(M+Na)^+$ requires 491.2983]. HPLC: (S,S-Whelk-O 1, 100 % hexane, 0.5 ml/min), UV: 254 nm, retention time of 12.24 min (minor) and 14.36 min (major), 96 % ee.



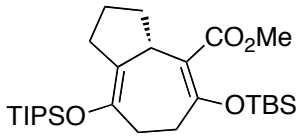

**Methyl 2-((tert-butyldimethylsilyl)oxy)-7-(4-chlorophenyl)-5-((triisopropylsilyl)oxy)cyclohepta-1,5-dienecarboxylate (16a):**

Prepared *via* procedure A. Derived from (*E*)-((4-(4-chlorophenyl)buta-1,3-dien-2-yl)oxy)triisopropylsilane (51.0 mg, 0.151 mmol, 1.00 equiv) and purified by flash chromatography (98:2 pentane/$Et_2O$) on silica gel to provide the vinylogous [4+3] product as colorless oil (66 mg, 77 % yield). $R_f$ = 0.10 (98:2 pentane/$Et_2O$); $[\alpha]_D^{20}$: 42.1 (*c*. 0.49, $CHCl_3$); $^1H$ NMR (600 MHz; $C_6D_6$) δ 7.78 (dd, 2H, *J* = 8.8, 2.4 Hz), 7.15 (m, 2H), 5.32 (d, *J* = 9.6 Hz, 1H), 5.05 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.50 (s, 3H), 2.50 (app t, *J* = 28, 13.8 Hz, 1H), 2.38 (app t, *J* = 16.8, 31.2 Hz, 1H), 2.12 (d, *J* = 17.4 Hz, 1H), 1.76 (app dt, *J* = 2.4, 2.4, 13.8 Hz, 1H), 1.09 (d, *J* = 8.4 Hz, 21H), 0.93 (s, 9H), 0.10 (d, *J* = 3.6 Hz, 6H); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ 168.7, 163.6, 154, 144.5, 132.3, 129.7, 128.7, 117.4, 107, 51.5, 38.7, 32.3, 30.6, 26.2, 18.9, 18.6, 13.33, 3.4, 3.3; IR (neat): 2945, 2864, 1687, 1185; HRMS-(APCI) m/z 565.2949 [$(M+H)^+$ requires 565.2930]. HPLC: (S,S-Whelk-O 1, 100 % hexane, 0.5 ml/min), UV: 254 nm, retention time of 28.14 min (minor) and 32.29 min (major), 95 % ee.



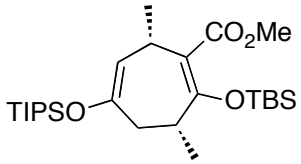

**Methyl 6-((*tert*-butyldimethylsilyl)oxy)-9-((triisopropylsilyl)oxy)-2,3,4,4a,7,8-hexahydro-1*H*-benzo[7]annulene-5-carboxylate (16b):**

Prepared *via* procedure A. Derived from ((1-(cyclohex-1-en-1-yl)vinyl)oxy)triisopropylsilane (423 mg, 1.51 mmol, 5.0 equiv) and purified by flash chromatography (98:2 pentane/$Et_2O$) on silica gel to provide the vinylogous [4+3] product as colorless oil (58 mg, 38 % yield). $R_f$ = 0.13 (98:2 Pentane/$Et_2O$); $[\alpha]_D^{20}$: 72.8 (*c*. 0.60, $CHCl_3$); $^1H$ NMR (600 MHz; $C_6D_6$) δ 3.5 (d, 1H, *J* = 10.2 Hz), 3.45 (s, 3H), 3.29-3.25 (m, 1H), 2.84 (ddd, *J* = 1.8, 12.6, 12.6 Hz, 1H), 2.71 (ddd, *J* = 2.4, 13.8, 13.8 Hz, 1H), 2.25 (dd, *J* = 6.0, 16.2 Hz, 1H), 2.11-2.05 (m, 2H), 1.77 (t, *J* = 9.6 Hz, 2H), 1.67-1.57 (m, 3H), 1.45-1.38 (m, 1H), 1.10-1.09 (m, 21H), 0.99 (s, 9H), 0.17 (d, *J* = 5.4 Hz, 6H); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ 168.9, 161.5, 143.2, 120.6, 115.9, 51.2, 42.7, 35.7, 34.9, 33.5, 31.9, 28.9, 28.7, 26.3, 18.9, 18.7, 13.9, -3.51; IR (neat): 2927, 2864, 1715, 1194; HRMS-(ESI) m/z 509.3476 $[(M+H)^+$ requires 509.3476]. HPLC: (S,S-Whelk-O 1, 100 % hexane, 0.25 ml/min), UV: 254 nm, retention time of 26.55 min (minor) and 29.51 min (major), 90 % ee.



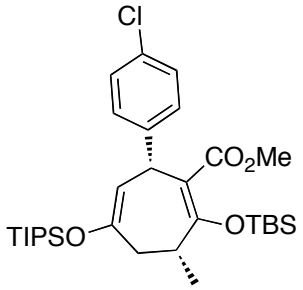

**Methyl 5-((tert-butyldimethylsilyl)oxy)-8-((triisopropylsilyl)oxy)-1,2,3,3a,6,7-hexahydroazulene-4-carboxylate (16c):**

Prepared *via* procedure A. Derived from ((1-(cyclopent-1-en-1-yl)vinyl)oxy)triisopropylsilane (402 mg, 1.51 mmol, 5.0 equiv) and purified by flash chromatography (98:2 pentane/$Et_2O$) on silica gel to provide the vinylogous [4+3] product as colorless oil (74 mg, 50 % yield). $R_f$ = 0.10 (98:2 Pentane:$Et_2O$); $[\alpha]_D^{20}$: 23.0 (*c*. 1.08, $CHCl_3$); $^1H$ NMR (600 MHz; $C_6D_6$) δ 3.49 (s, 3H), 2.61 (dd, *J* = 7.8, 16.8 Hz, 1H), 2.49-2.44 (m, 1H), 2.43-3.36 (m, 1H), 2.34-2.30 (m, 2H,), 2.18-2.13 (m, 1H), 2.10 (ddd, *J* = 5.4, 7.2, 24.6 Hz, 1H), 1.68-1.63 (m, 1H), 1.61-1.56 (m, 1H), 1.95 (dd, *J* = 4.2, 7.2 Hz, 2H), 1.35-1.08 (m, 21H), 0.97 (s, 9H), 0.18 (s, 3H), 0.15 (s, 3H); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ 169.2, 151.7, 143.6, 123.4, 119.4, 51, 39.4, 34.4, 31.9, 31.5, 31.2, 26.2, 25.4, 18.7, 14.1, -3.3, -3.5; IR (neat): 2945, 2864, 1723, 155; HRMS-(APCI) m/z 495.3321 $[(M+H)^+$ requires 495.3320. HPLC: (S,S-Whelk-O 1, 100 % hexane, 0.25 ml/min), UV:210 nm retention time of 20.68 min (minor) and 18.24 min (major), 92 % ee.



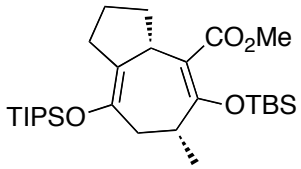

**(3*R*,7*S*)-methyl 2-((*tert*-butyldimethylsilyl)oxy)-3,7-dimethyl-5-((triisopropylsilyl)oxy)cyclohepta-1,5-dienecarboxylate (18a):**

Prepared *via* procedure B. Derived from ((1*E*)-1-(4-chlorophenyl)penta-1,3-dien-3-yl)oxy)triisopropylsilane (43 mg, 0.151 mmol, 1.0 equiv) and (*Z*)-methyl 3-((tert-butyldimethylsilyl)oxy)-2-diazopent-3-enoate. Purified by flash chromatography (98:2 pentane/$Et_2O$) on silica gel to provide the vinylogous [4+3] product as colorless oil (43 mg, 59 % yield). Rf = 0.15 (98:2 Pentane/$Et_2O$); $[\alpha]_D^{20}$: 21.9 (*c*. 0.7, $CHCl_3$); $^1H$ NMR (600 MHz; $C_6D_6$) δ 4.98 (dd, 1H, *J* = 5.4 Hz), 3.53-3.49 (m, 1H), 3.48 (s, 3H), 2.55 (d, *J* = 14.4 Hz, 1H), 2.51-2.48 (m, 1H), 2.19 (dd, *J* = 7.2, 15.6 Hz. 1H), 1.26 (d, *J* = 7.2 Hz, 3H), 1.22 (d, *J* = 6.6 Hz, 3H), 1.12 (s, 21H), 0.98 (s, 9H), 0.16 (d, *J* = 16.8 Hz, 6H); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ 170.5, 156.2, 150.9, 119.8, 111, 51.2, 38.2, 37, 30.7, 26.3, 21.5, 19.5, 18.8, 18.6, 13.3, -3.3, -3.5; IR (neat): 2945, 2865, 1720, 1251; HRMS-(APCI) m/z 483.3324 [$(M+H)^+$ requires 483.3320]. HPLC: (OD-H, 100 % hexane, 0.25 ml/min), UV: 254 nm, retention time of 17.66 min (minor) and 16.81 min (major), 99 % ee.



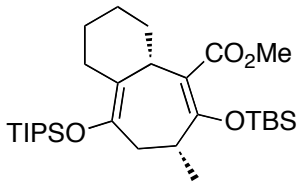

**(3*R*,7*R*)-methyl 2-((*tert*-butyldimethylsilyl)oxy)-7-(4-chlorophenyl)-3-methyl-5-((triisopropylsilyl)oxy)cyclohepta-1,5-dienecarboxylate (18b):**

Prepared *via* procedure B. Derived from (*E*)-((4-(4-chlorophenyl)buta-1,3-dien-2-yl)oxy)triisopropylsilane (51 mg, 0.151 mmol, 1.0 equiv) and (*Z*)-methyl 3-((tert-butyldimethylsilyl)oxy)-2-diazopent-3-enoate. Purified by flash chromatography (98:2 pentane/$Et_2O$) on silica gel to provide the vinylogous [4+3] product as colorless oil (49 mg, 57 % yield). $R_f$ = 0.11 (98:2 Pentane/$Et_2O$); $[\alpha]_D^{20}$: -18.5 (*c*. 0.9, $CHCl_3$); $^1H$ NMR (600 MHz; $C_6D_6$) δ 7.24 (d, 2H, *J* = 8.4 Hz), 7.12 (d, *J* = 8.4 Hz, 2H), 5.44 (d, *J* = 9 Hz, 1H), 4.79 (d, *J* = 8.4 Hz, 1H), 3.36 (s, 3H), 2.55-2.49 (m, 1H), 2.21 (dd, *J* = 11.4, 15.0 Hz, 1H), 1.99 (dd, *J* = 3.6, 15.0 Hz, 1H), 1.16 (d, *J* = 6.6 Hz, 3H), 1.09-1.07 (m, 21H), 0.99 (s, 9H), 0.165 (d, *J* = 31.2 Hz, 6H); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ 170.7, 160.8, 154.5, 143.8, 132.3, 130, 128.7, 117.3, 109.4, 51.6, 40.7, 38.1, 37.9, 26.3, 20.7, 18.8, 18.6, 13.2, -3.4, -3.8; IR (neat): 2945, 2864, 1716, 1175; HRMS-(ESI) m/z 579.3089 [$(M+H)^+$ requires 579.3087]. HPLC: (ADH, 100 % hexane, 0.25 ml/min), UV: 254 nm, retention time of 31.14 min (minor) and 24.86 min (major), 99 % ee.



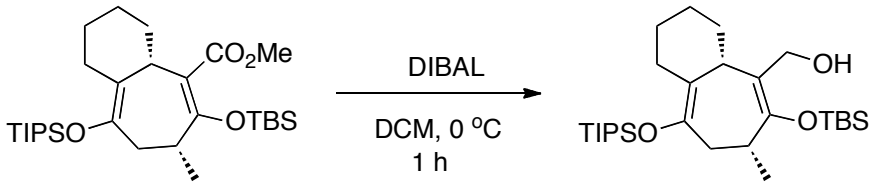

**(3aS,6R)-methyl 5-((tert-butyldimethylsilyl)oxy)-6-methyl-8-((triisopropylsilyl)oxy)-1,2,3,3a,6,7-hexahydroazulene-4-carboxylate (18c):**

Prepared *via* procedure B. Derived from ((1-(cyclopent-1-en-1-yl)vinyl)oxy)triisopropylsilane (51 mg, 0.151 mmol, 1.0 equiv) and (*Z*)-methyl 3-((tert-butyldimethylsilyl)oxy)-2-diazopent-3-enoate. Purified by flash chromatography (98:2 pentane/$Et_2O$) on silica gel to provide the vinylogous [4+3] product as colorless oil (49 mg, 52 % yield). $R_f$ = 0.11 (98:2 Pentane/$Et_2O$); $[\alpha]_D^{20}$: 68.9 (*c*. 1.4, $CHCl_3$); $^1$H NMR (600 MHz; $C_6D_6$) δ 3.47 (s, 3H), 3.39-3.36 (m, 1H), 3.30-3.27 (m, 1H), 3.03-3.00 (m, 1H), 2.55-2.51 (m, 1H), 2.17 (dd, *J* = 4.8, 15.6 Hz, 1H), 2.13 (d, *J* = 13.2 Hz, 1H), 1.71-1.68 (m, 3H), 1.63-1.57 (m, 1H), 1.39 (d, *J* = 7.2 Hz, 3H), 1.13-1.11 (m, 21H), 1.00 (s, 9H), 0.20 (d, *J* = 13.2 Hz, 6H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 170.5, 158.8, 139.3, 118.1, 117.9, 51.4, 42.1, 39.6, 39.4, 35.4, 30, 28, 27.6, 26.3, 18.7, 18.6, 14, -3.4; IR (neat): 2924, 2864, 1720, 1462, 1192; HRMS-(APCI) m/z 509.3479 [$(M+H)^+$ requires 509.3476]; HPLC: (DACHDNB, 100 % hexane, 0.25 ml/min), UV: 254 nm, retention time of 61.38 min (minor) and 50.81 min (major), 99 % ee.




**(4aS,7R)-methyl 6-((tert-butyldimethylsilyl)oxy)-7-methyl-9-((triisopropylsilyl)oxy)-2,3,4,4a,7,8-hexahydro-1H-benzo[7]annulene-5-carboxylate (18d):**

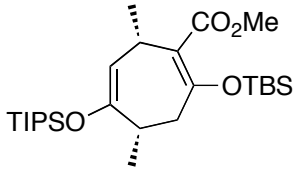
Prepared *via* procedure B. Derived from ((1-(cyclohex-1-en-1-yl)vinyl)oxy)triisopropylsilane (51 mg, 0.178 mmol, 1.0 equiv) and (*Z*)-methyl 3-((tert-butyldimethylsilyl)oxy)-2-diazopent-3-enoate. Purified by flash chromatography (98:2 pentane/$Et_2O$) on silica gel to provide the vinylogous [4+3] product as colorless oil (74 mg, 80 % yield). $R_f$ = 0.10 (98:2 Pentane/$Et_2O$); $^1H$ NMR (600 MHz; $C_6D_6$) δ 3.54-3.53 (m, 1H), 3.51 (s, 3H), 2.73 (d, *J* = 14.4 Hz, 1H), 2.54 (dd, *J* = 7.2, 16.2 Hz, 1H), 2.46-2.44 (m, 1H), 2.40-2.37 (m, 1H), 2.02-1.94 (m, 2H), 1.64-1.59 (m, 2H), 1.32-1.30 (m, 5H), 1.12-1.11 (m, 22H), 1.00 (s, 9H), 0.19 (d, *J* = 10.2 Hz, 6H); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ 170.5, 158.8, 139.3, 118.1, 117.9, 51.4, 42.1, 39.6, 39.4, 35.4, 30, 28, 27.6, 26.3, 18.7, 18.6, 14, -3.4; IR (neat): 2928, 2864, 1719, 1189; HRMS-(APCI) m/z 523.3636 [$(M+H)^+$ requires 523.3633].




**((4aS,7R)-6-((tert-butyldimethylsilyl)oxy)-7-methyl-9-((triisopropylsilyl)oxy)-2,3,4,4a,7,8-hexahydro-1H-benzo[7]annulen-5-yl)methanol:**

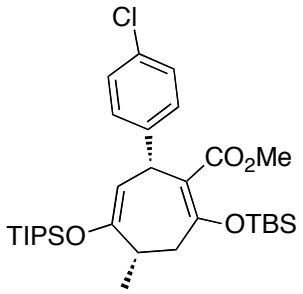
To a round-bottom flask was added (4aS,7R)-methyl 6-((tert-butyldimethylsilyl)oxy)-7-methyl-9-((triisopropylsilyl)oxy)-2,3,4,4a,7,8-hexahydro-1H-benzo[7]annulene-5-carboxylate (**18d**) (125 mg, 0.239 mmol, 1.0 eq) and DCM (14 mL). The solution was cooled to 0 °C. Once cool, DIBAL 1M in DCM (1.1 mL, 1.07 mmol, 4.5 eq) was slowly added to the reaction over 5 minutes. The reaction was allowed to stir, at 0 °C, for 1 hour. The reaction was then stopped by diluting with $Et_2O$ followed by addition of saturated aqueous solution of Rochelle's salt. The mixture was aggressively stirred for 1 h. The mixtures was then transferred to a separation funnel and diluted with $H_2O$ (100 mL). The two layers were separated and the aqueous layer was washed with $Et_2O$ (3 x 50 mL). The organic layers were combined, dried over $MgSO_4$, filtered through a glass frit and concentrated under reduced pressure. Purified by flash chromatography (95:5 hexanes/EtOAc) on silica gel to provide the reduced product as colorless oil (99 mg, 84 % yield). $R_f$ = 0.43 (90:10 Hexanes/EtOAc); $[\alpha]_D^{20}$: 88.7 (*c*. 0.81, $CHCl_3$); $^1H$ NMR (600 MHz; $C_6D_6$) δ 4.31 (dd, 1H, *J* = 4.8, 11.4 Hz), 3.99 (dd, *J* = 5.4, 11.4 Hz, 1H), 3.40 (d, *J* = 13.2 Hz, 1H), 3.06 (dd, *J* = 3.0, 15.6 Hz, 1H), 2.84 (d, J = 12 Hz, 1H), 2.53-2.48 (m, 1H), 2.22 (dd, *J* = 4.8, 16.2 Hz, 1H), 1.99 (d, *J* = 11.4 Hz, 1H), 1.79-1.73 (m, 2H), 1.64-1.59 (m, 1H), 1.48-1.42 (m, 2H), 1.38-1.37 (m, 5H), 1.16-1.13 (m, 21H), 0.98 (s, 9H), 0.13 (d, *J* = 29.4 Hz, 6H); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ 153.4, 138.9, 122.5, 118.4, 63.3, 44.2, 40.3, 38.7, 35.3, 30.7, 28.7, 28.3, 26.3, 18.8, 18.7, 14.1, -3.3, -3.6; IR (neat): 3440, 2927, 2864, 1169; HRMS-(NSI)

m/z 495.3687 [$(M+H)^+$ requires 495.3684]; HPLC: (S,S-Whelk, 100 % hexane, 0.5 ml/min), UV: 230 nm, retention time of 36.24 min (minor) and 43.36 min (major), 92 % ee.



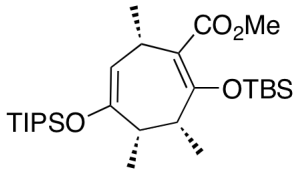

**Methyl 2-((tert-butyldimethylsilyl)oxy)-4,7-dimethyl-5-((triisopropylsilyl)oxy)cyclohepta-1,5-dienecarboxylate (20a):**

Prepared *via* procedure A. Derived from ((2*Z*,4*E*)-hexa-2,4-dien-3-yloxy)triisopropylsilane (384 mg, 1.51 mmol, 5.0 equiv) and purified by flash chromatography (98:2 pentane/$Et_2O$) on silica gel to provide the vinylogous [4+3] product as colorless oil (100 mg, 68 % yield). $R_f$ = 0.18 (98:2 Pentane:$Et_2O$); $[\alpha]_D^{20}$: 36.8 (*c*. 0.50, $CHCl_3$); $^1$H NMR (600 MHz; $C_6D_6$) δ 5.04 (dd, 1H, *J* = 7.8, 1.8 Hz), 3.69 (p, *J* = 1.2 Hz, 1H), 3.45 (s, 3H), 2.67 (dd, *J* = 11.4, 14.4 Hz, 1H), 2.60-2.54 (m, 1H), 2.15 (dd, *J* = 3.0, 14.4 Hz, 1H), 1.33 (d, *J* = 7.2 Hz, 3H), 1.21 (d, *J* = 7.2 Hz, 3H), 1.11-1.09 (m, 21H), 1.00 (s, 9H), 0.23 (s, 3H), 0.18 (s, 3H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 168.3, 158.7, 155.2, 117.7, 110.9, 51.1, 41.1, 34.9, 30.6, 26.4, 21.1, 20.5, 18.9, 18.7, 13.5, -3.4, -3.3; IR (neat): 2945, 2865, 1719, 1179; HRMS-(APCI) m/z 483.3334 [$(M+H)^+$ requires 483.3320]. HPLC: AD-H, 100 % hexane, 1.0 ml/min), UV: 254nm, retention time of 6.08 min (minor) and 5.26 min (major), 96 % ee.



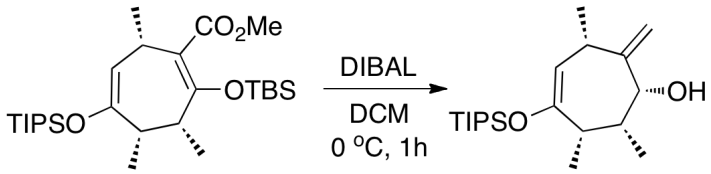

**(4S,7R)-methyl 2-((tert-butyldimethylsilyl)oxy)-7-(4-chlorophenyl)-4-methyl-5-((triisopropylsilyl)oxy)cyclohepta-1,5-dienecarboxylate (20b):**

Prepared *via* procedure A. Derived from ((1*E*)-1-(4-chlorophenyl)penta-1,3-dien-3-yl)oxy)triisopropylsilane (529 mg, 1.51 mmol, 5.0 equiv) and purified by flash chromatography (98:2 pentane/$Et_2O$) on silica gel to provide the vinylogous [4+3] product as colorless oil (124 mg, 71 % yield). $R_f$ = 0.16 (98:2 Pentane/$Et_2O$); $[\alpha]_D^{20}$: 43.4 (*c*. 0.58, $CHCl_3$); $^1H$ NMR (600 MHz; $C_6C_6$) δ 7.39 (d, 2H, *J* = 7.8 Hz), 7.14 (d, *J* = 8.4 Hz, 2H), 5.30 (dd, *J* = 1.2, 10.2 Hz, 1H), 5.06 (d, *J* = 10.2 Hz, 1H), 3.52 (s, 3H), 2.57-2.52 (m, 1H), 2.48 (app t, *J* = 13.2 Hz, 1H), 1.79 (dd, *J* = 3.0, 13.2 Hz, 1H), 1.17 (d, *J* = 6.6 Hz, 3H), 1.12-1.09 (m, 21H), 0.95 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H); $^{13}C$ NMR (100 MHz, $C_6C_6$) δ 167.9, 162.6, 156.7, 144, 131.8, 129.1, 128.2, 117.5, 105.8, 50.9, 40, 38.2, 34.9, 25.7, 20.1, 18.1, 12.9, 12.2, -3.8; IR (neat): 2945, 2865, 1687, 1184; HRMS-(APCI) m/z 579.3102 [$(M+H)^+$ requires 579.3087]. HPLC: (S,S-Whelk-O 1, 100 % hexane, 0.5 ml/min), UV: 254 nm, retention time of 20.70 min (minor) and 25.10 min (major), 96 % ee.



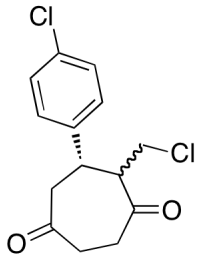

**(3R,4S,7S)-methyl 2-((tert-butyldimethylsilyl)oxy)-3,4,7-trimethyl-5-((triisopropylsilyl)oxy)cyclohepta-1,5-dienecarboxylate (21):**

Prepared *via* procedure B. Derived from ((2*Z*,4*E*)-hexa-2,4-dien-3-yloxy)triisopropylsilane (100 mg, 0.393 mmol, 1.0 equiv) and (*Z*)-methyl 3-((tert-butyldimethylsilyl)oxy)-2-diazopent-3-enoate (212 mg, 0.786, mmol, 2.00 equiv). Purified by flash chromatography (98:2 pentane/$Et_2O$) on silica gel to provide the vinylogous [4+3] product as colorless oil (141 mg, 72% yield). $R_f$ = 0.14 (98:2 pentane:diethyl ether); $[\alpha]_D^{20}$: 26.1 (*c*. 0.2, $CHCl_3$); $^1H$ NMR (600 MHz; $C_6D_6$) δ 4.73 (d, 1H, *J* = 3.6 Hz), 3.52-3.50 (m, 1H), 3.49 (s, 3H), 2.96 (app q, *J* = 7.2 Hz, 1H), 2.27-2.22 (m, 1H), 1.22 (t, *J* = 7.2 Hz, 6H), 1.12-1.10 (m, 21H), 1.05 (t, *J* = 9.6 Hz, 3H), 0.99 (s, 9H), 0.23 (s, 3H), 0.20 (s, 3H); $^{13}C$ NMR (100 MHz, $C_6D_6$) δ 169.3, 153.5, 152.8, 118.3, 108.5, 50, 41.9, 36.9, 28.1, 25.3, 20.5, 17.7, 14.8, 13.2, 12.5, -4.07, -4.6; IR (neat): 2944, 2865, 1721, 1158; HRMS- m/z 439.3432 $(M+H)^+$ requires 439.3422).




**(1R,2R,3S,6S)-2,3,6-trimethyl-7-methylene-4-((triisopropylsilyl)oxy)cyclohept-4-enol (22):**

To a round-bottom flask was added (3R,4S,7S)-methyl 2-((tert-butyldimethylsilyl)oxy)-3,4,7-trimethyl-5-((triisopropylsilyl)oxy)cyclohepta-1,5-dienecarboxylate (**21**) (132 mg, 0.266 mmol, 1.0 eq) and DCM (14 mL). The solution was cooled to 0 °C. Once cool, DIBAL 1M in DCM (1.1 mL, 1.07 mmol, 4.5 eq) was slowly added to the reaction over 5 minutes. The reaction was allowed to stir, at 0 °C, for 1 hour. The reaction was then stopped by diluting with $Et_2O$ followed by addition of saturated aqueous solution of Rochelle's salt and was aggressively stirred for 1 h. The mixtures was then transferred to a separation funnel and diluted with $H_2O$ (100 mL). The two layers were separated and the aqueous layer was washed with $Et_2O$ (3 x 50 mL). The organic layers were combined, dried over $MgSO_4$, filtered through a glass frit and concentrated under reduced pressure. Purified by flash chromatography (90:10 hexanes/EtOAc) on silica gel to provide the reduced product as colorless oil (19 mg, 21% yield). $R_f$ = 0.31 (90:10 hexanes:EtOAc); $^1$H NMR (400 MHz; $C_6D_6$) δ 5.11 (s, 1H), 4.91 (s, 1H), 4.53 (d, *J* = 4.8 Hz, 1H), 3.86 (s, 1H), 2.63 (q, *J* = 7.2 Hz, 1H), 2.55 (q, *J* = 6.6 Hz, 1H), 1.85 (q, *J* = 6 Hz, 1H), 1.19 (d, *J* = 7.2 Hz, 3H), 1.13 (s, *J* = 7.2 Hz, 3H), 1.12-1.11 (m, 21H), 0.92 (d, *J* = 7.2 Hz, 3H), 0.42 (bs, 1H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 153.4, 151.4, 108.3, 103.7, 79.8, 42.5, 38.7, 33, 19.5, 18.4, 16.3, 13.1, 7.5; IR (neat): 3384, 2964, 2943, 2866, 1645; HRMS- m/z 339.2716 [$(M+H)^+$ requires 339.2713]; HPLC: (S,S-Whelk, 100 % hexane, 0.25 ml/min), UV: 230 nm, retention time of 53.24 min (minor) and 56.11 min (major), 85 % ee.




**(6S)-5-(chloromethyl)-6-(4-chlorophenyl)cycloheptane-1,4-dione (derivative of 16a):**

To a round-bottom flask was added **16a** (1.00 g, 1.77 mmol, 1.0 eq) and DCM (70 mL). The solution was cooled to 0 °C. Once cool, DIBAL 1M in DCM (5.31 mL, 5.31 mmol, 3.0 eq) was slowly added to the reaction over 5 minutes. The reaction was allowed to stir, at 0 °C, for 1 hour. The reaction was then stopped by diluting with $Et_2O$ followed by addition of saturated aqueous solution of Rochelle's salt. The mixture was aggressively stirred for 1 h. The mixture was then transferred to a separation funnel and diluted with $H_2O$ (100 mL). The two layers were separated and the aqueous layer was washed with $Et_2O$ (3 x 50 mL). The organic layers were combined, dried over $MgSO_4$, filtered through a glass frit and concentrated under reduced pressure. To a round bottomed flask was added anhydrous THF (12 mL) and cooled to 10 °C. Once cool, 2 M HCl (4 mL) was added. The reaction was allowed to stir and gradually warm to room temperature overnight. The reaction was then cooled to 0 °C and quenched with saturated aqueous $NaHCO_3$ solution. The mixture was then transferred to a separation funnel and diluted with $Et_2O$. The two layers were separated and the aqueous layer was washed with $Et_2O$ (3 x 25 mL). The organic layers were combined, dried over $MgSO_4$, filtered through a glass frit and concentrated under reduced pressure to give a 64:36 mixture of diastereomers which was determined by $^1H$ NMR of the crude material. Purification by flash chromatography (75:25 hexanes/EtOAc) on silica gel provided the reduced product as white solid (22 mg, 5 % yield). $R_f$ = 0.17 (75:25 hexanes:EtOAc); $^1H$ NMR (600 MHz; $C_6D_6$) Selected chemical shifts for major

diastereomer: δ 6.995 (dd, *J* = 1.8, 8.4 Hz, 2H), 6.35 (dd, *J* = 1.8, 8.4 Hz, 2H), 3.25 (app t, *J* = 11.4 Hz, 1H), 2.95 (dd, *J* = 2.4, 10.8 Hz, 1H), 2.74-2.70 (m, 1H), 2.42 (m, 1H); $^{13}$C NMR (100 MHz, $C_6D_6$) chemical shifts for major diastereomer: δ 208.7, 207.6, 129.8, 129.6, 129.3, 128.5, 59.7, 49.7, 42.6, 41.8, 38.9, 38.5; IR (neat): 2959, 2920, 2852, 1700; HRMS- m/z 285.0437 [$(M+H)^+$ requires 285.0443].

## 3.0 References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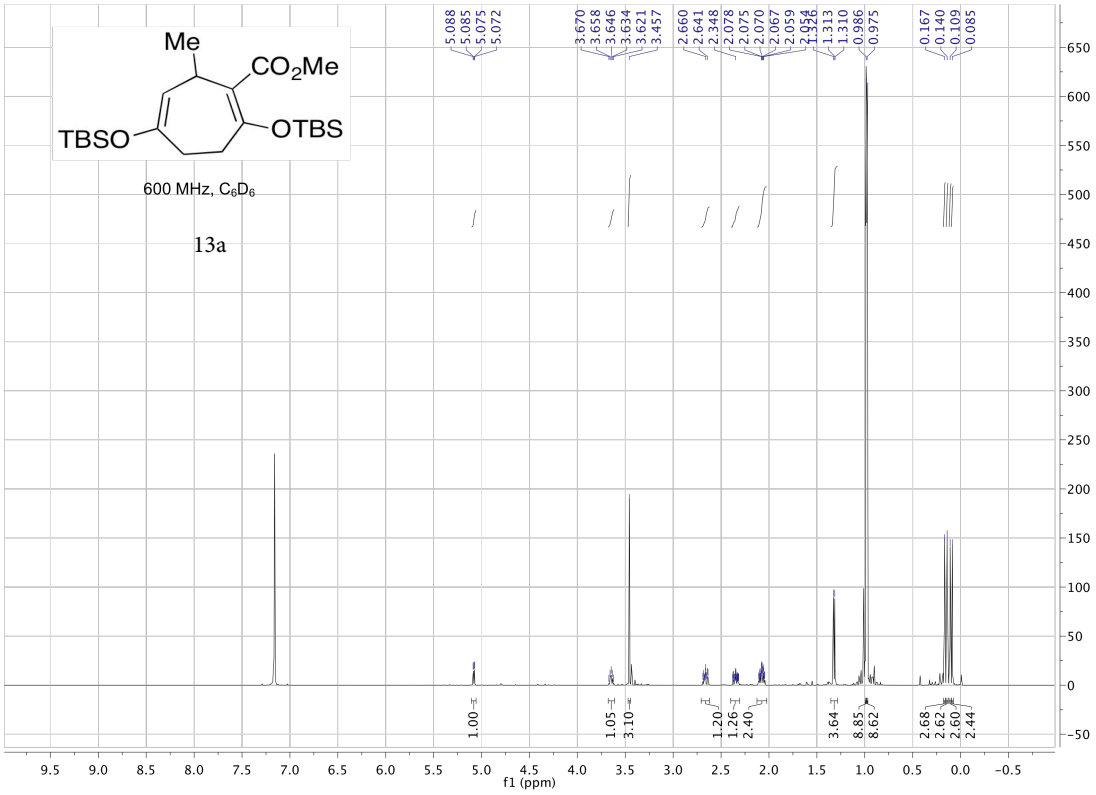
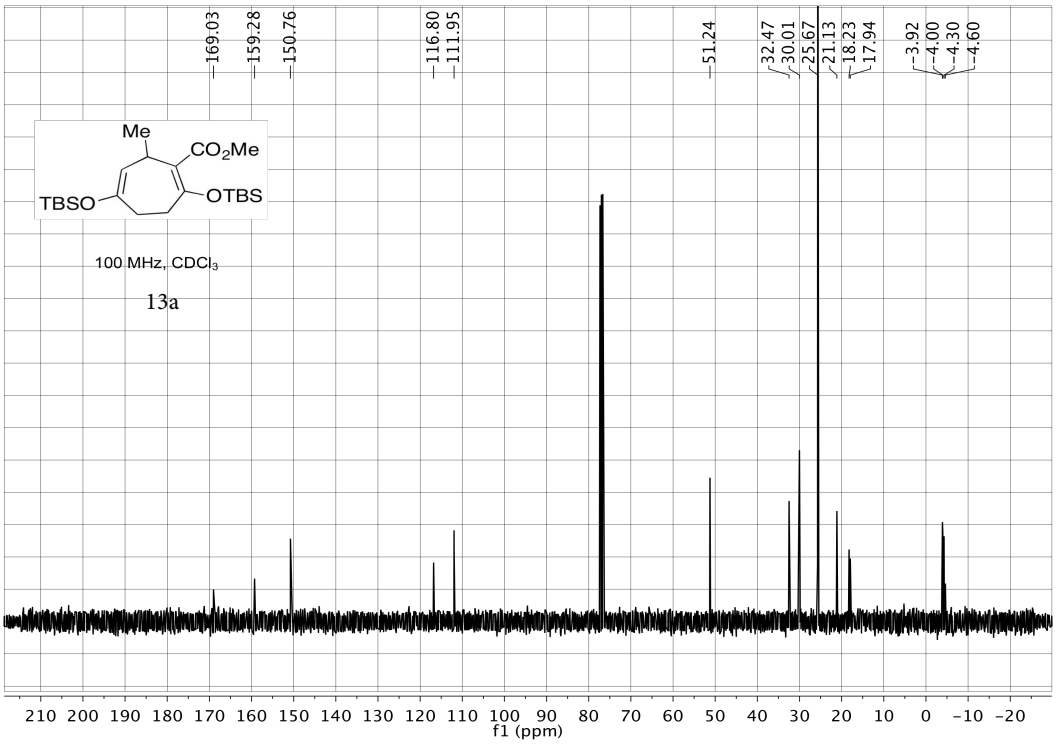
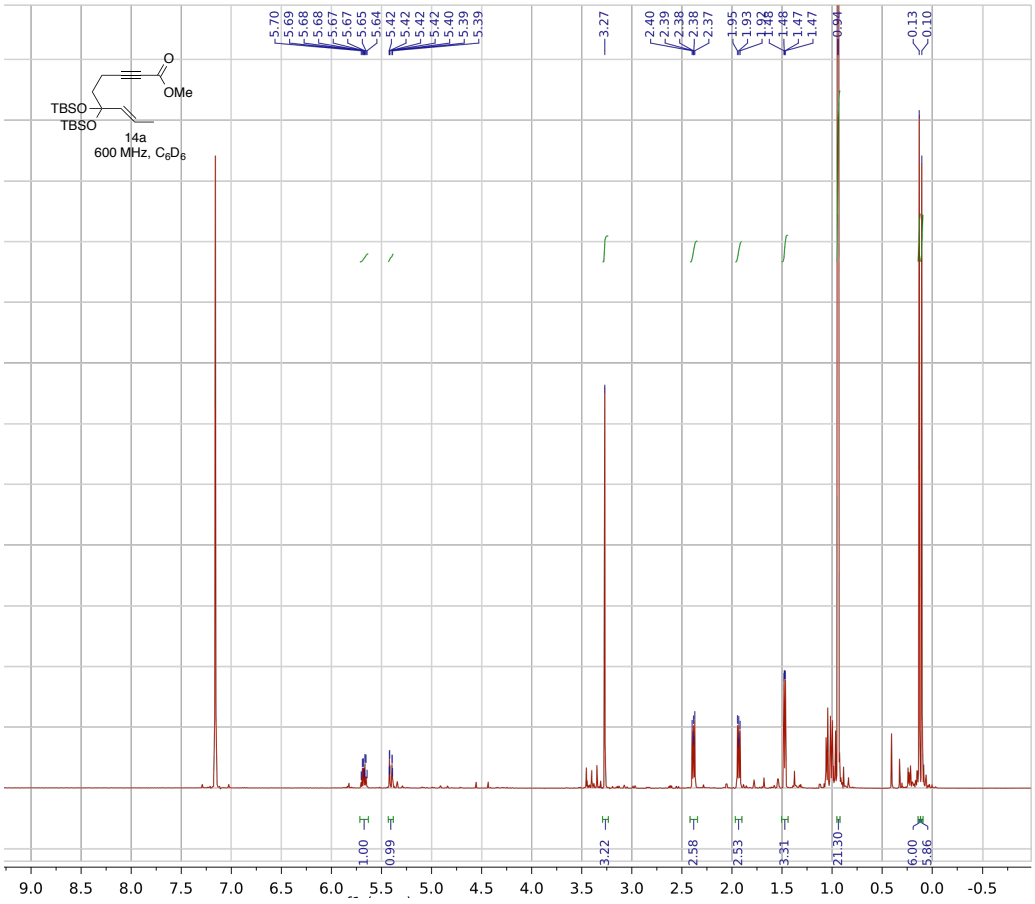
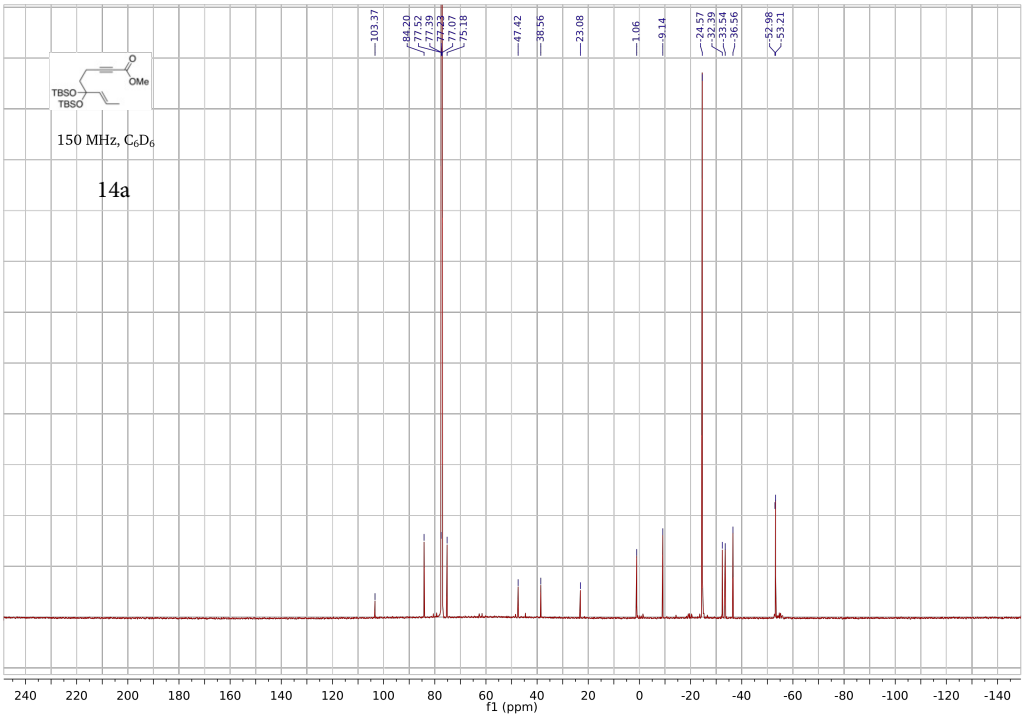
(4) Nakashima, D; Yamamoto, H. *J. Am. Chem. Soc.* **2006**, *128*, 9626-9627.

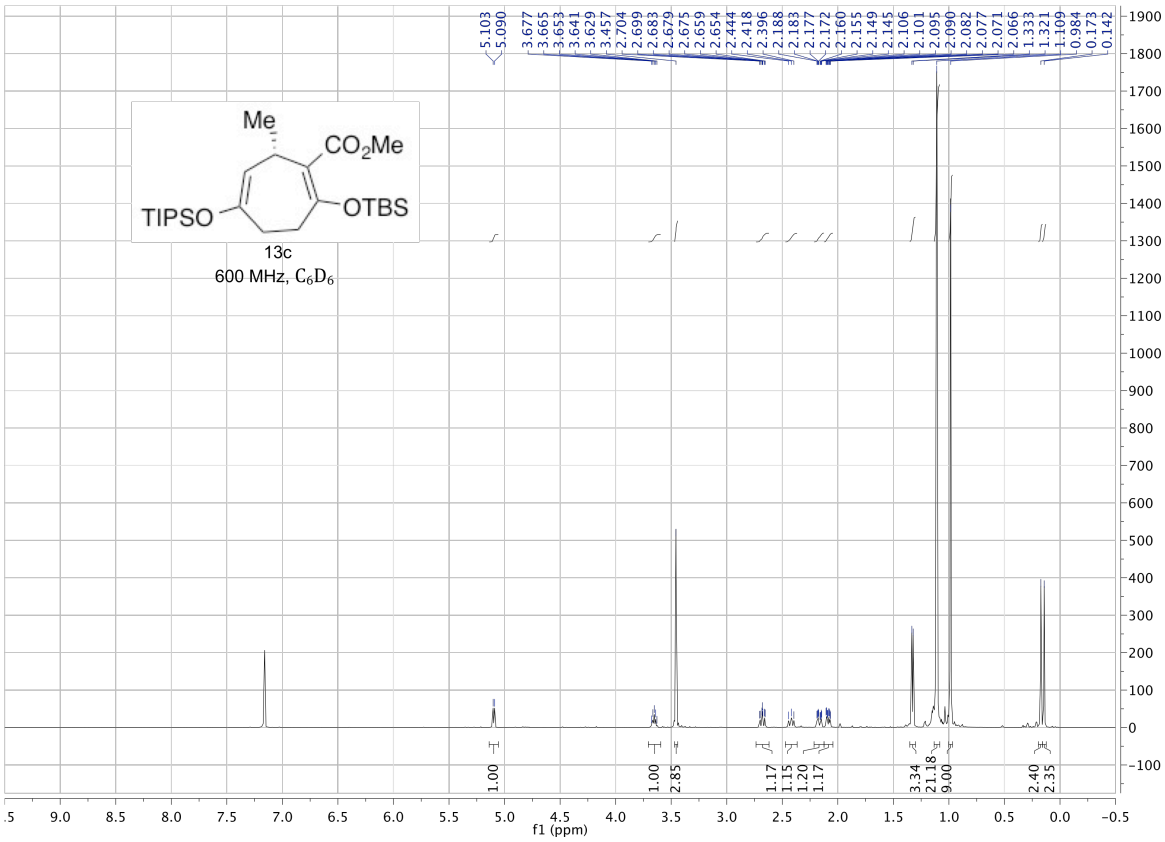
## 4.0 Proton and Carbon NMR Spectra

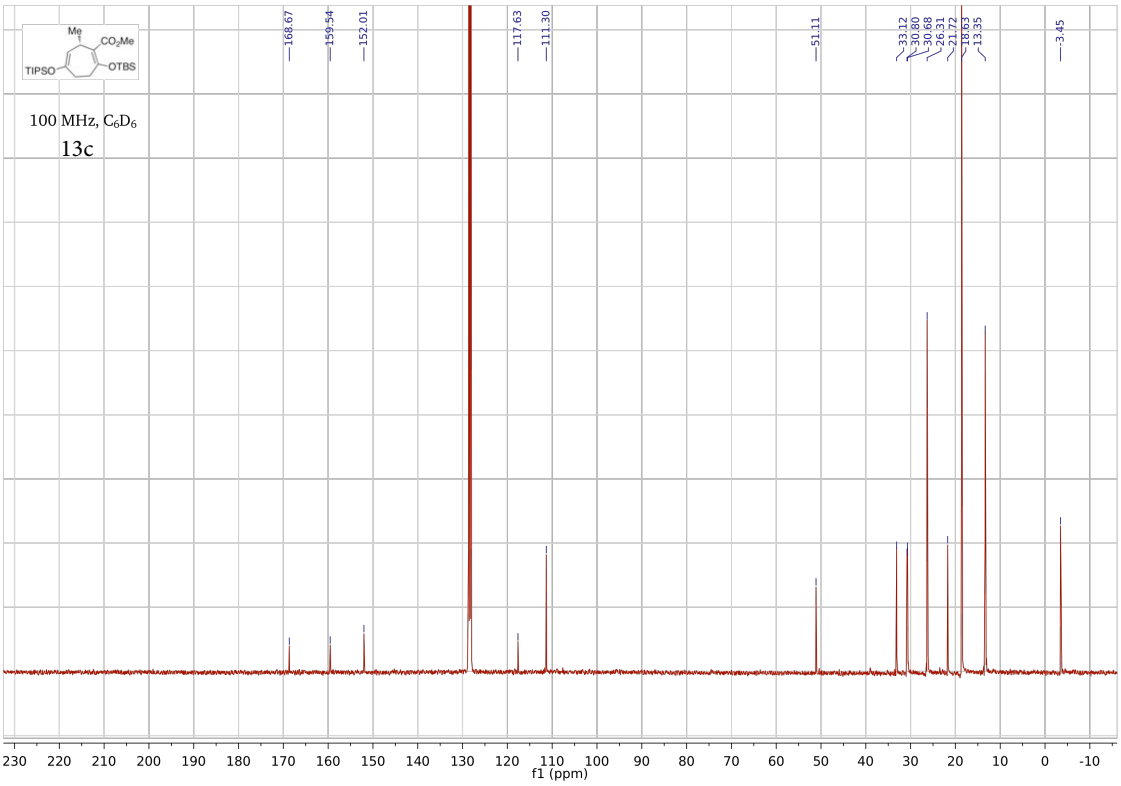


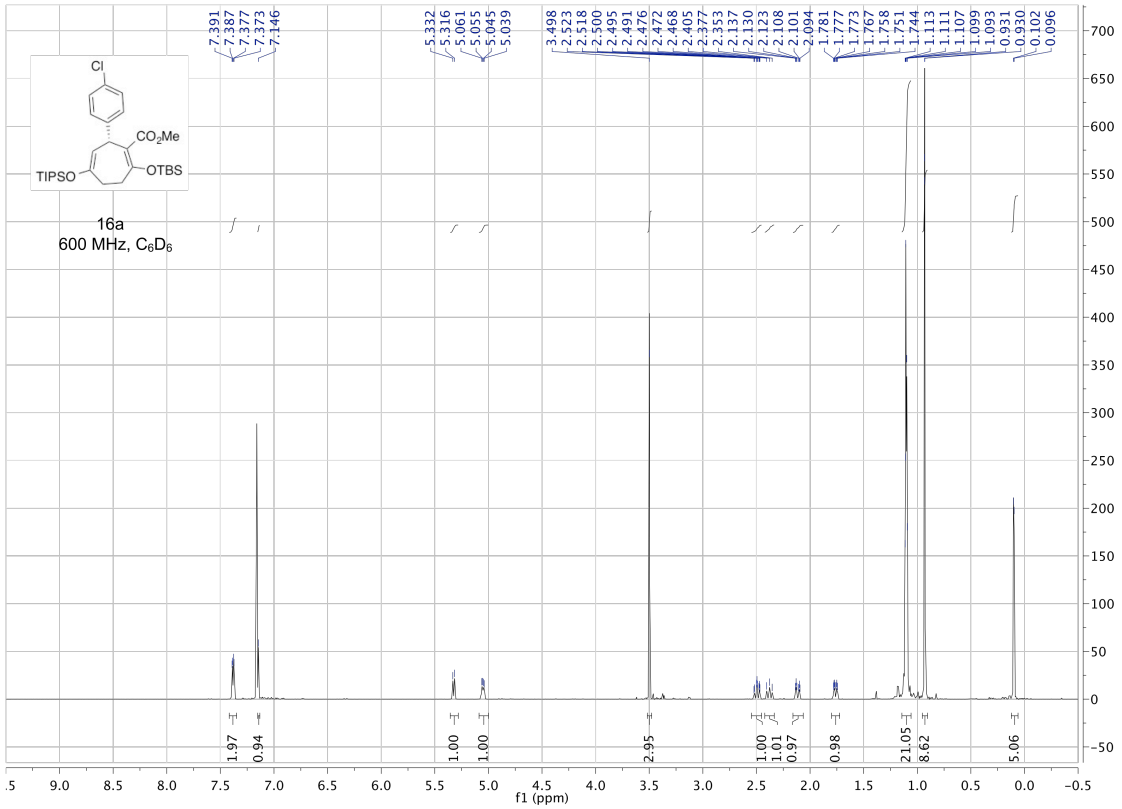



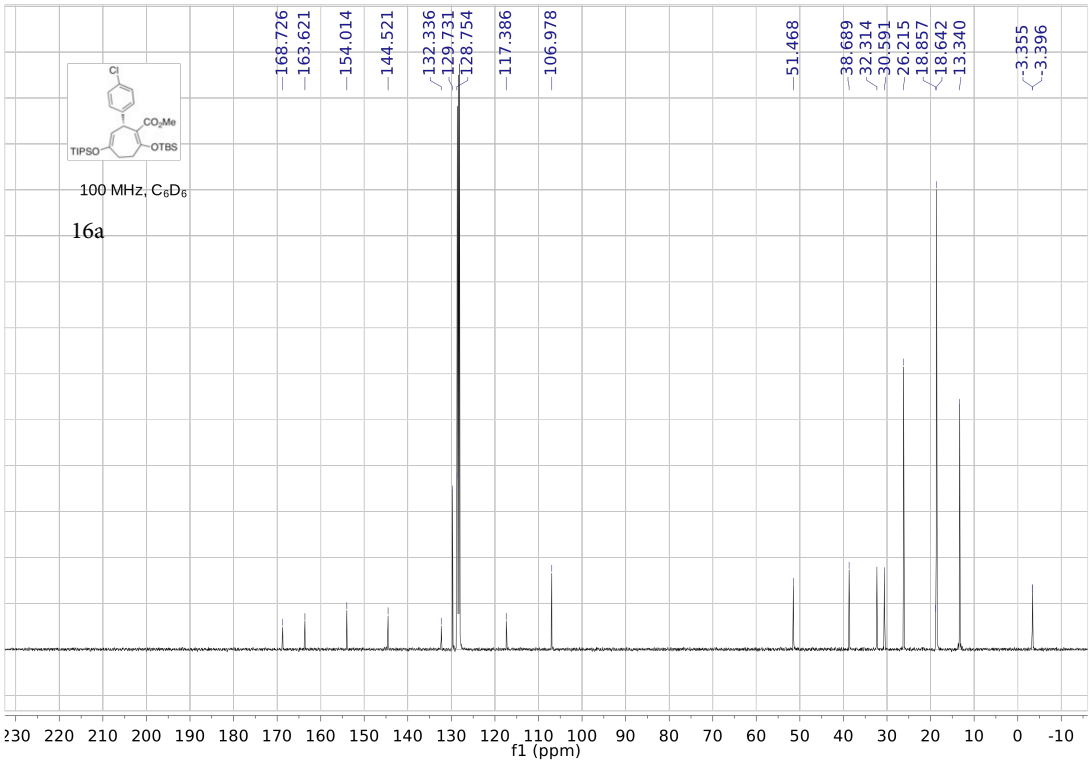

TBSO
TBSO
O
OMe
14a
600 MHz, C6D6
5.70
5.69
5.68
5.68
5.68
5.67
5.67
5.67
5.65
5.64
5.42
5.42
5.42
5.42
5.40
5.39
5.39
3.27
2.40
2.39
2.38
2.38
2.37
1.95
1.93
1.92
1.48
1.48
1.47
1.47
0.94
0.13
0.10
1.00
0.99
3.22
2.58
2.53
3.31
21.30
6.00
5.86
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

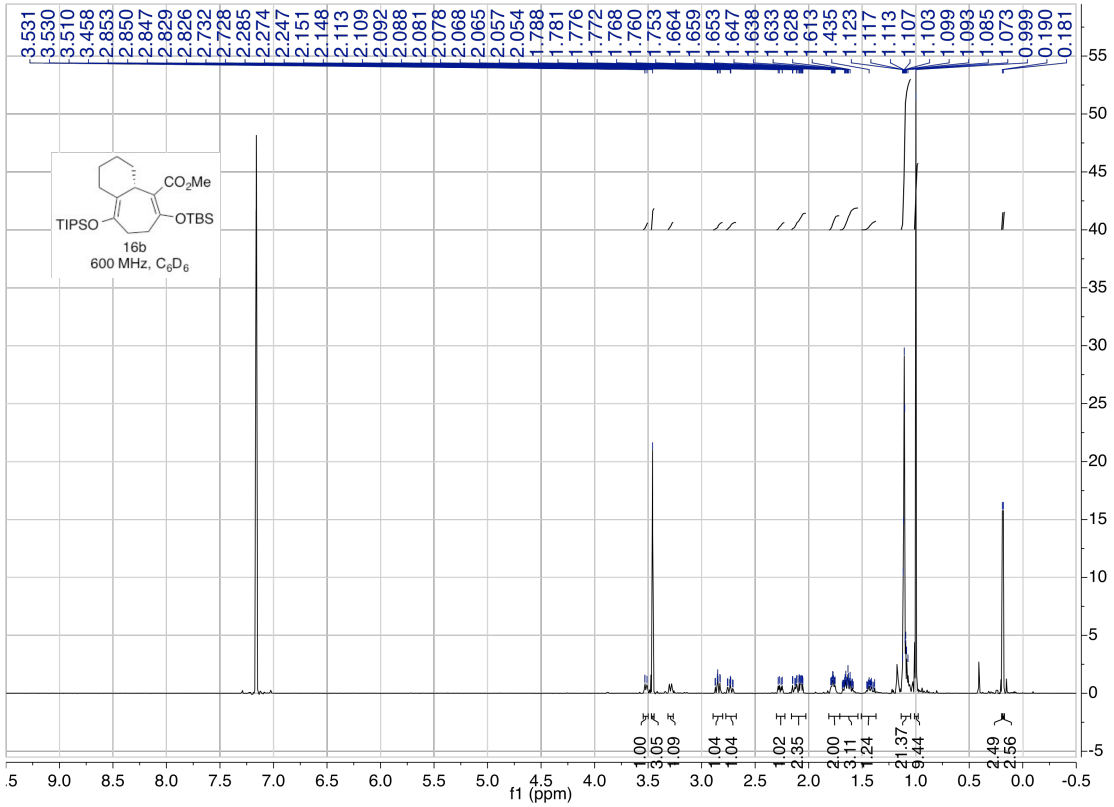

TBSO
TBSO
O
OMe
150 MHz, C6D6
14a
103.37
84.20
77.52
77.39
77.03
77.07
75.18
47.42
38.56
23.08
1.06
-9.14
24.57
23.39
33.54
36.56
52.06
53.21
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
f1 (ppm)

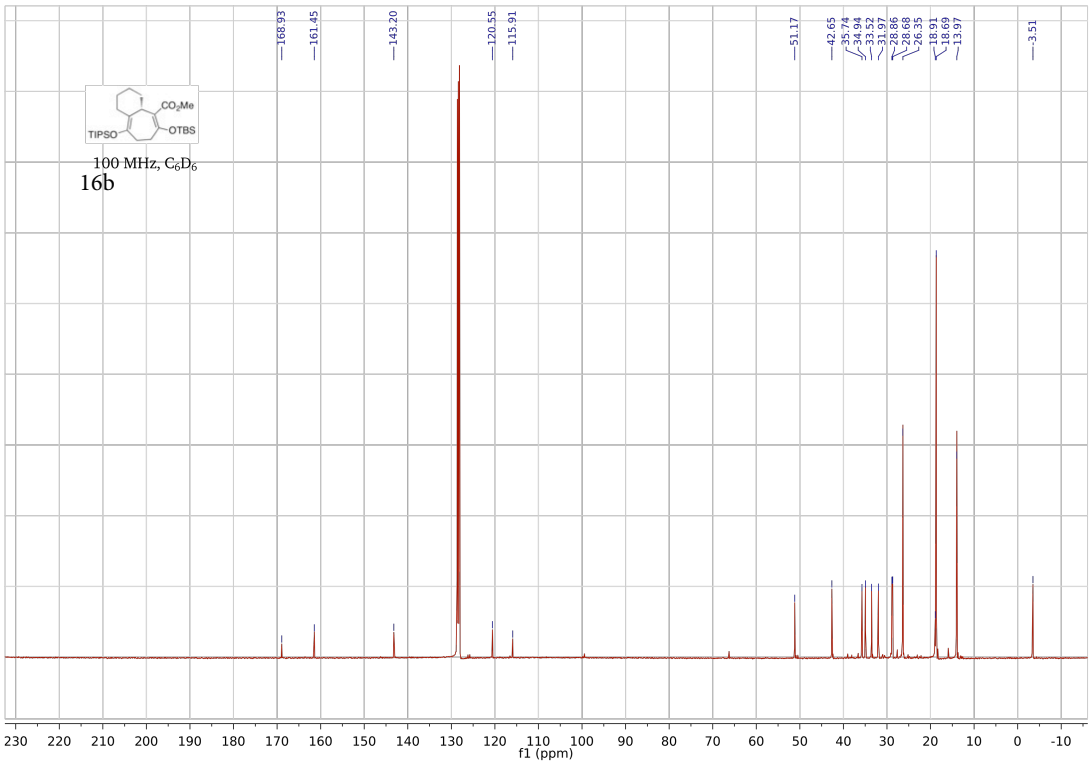

Me
CO2Me
TIPSO
OTBS
13c
600 MHz, C6D6
f1 (ppm)

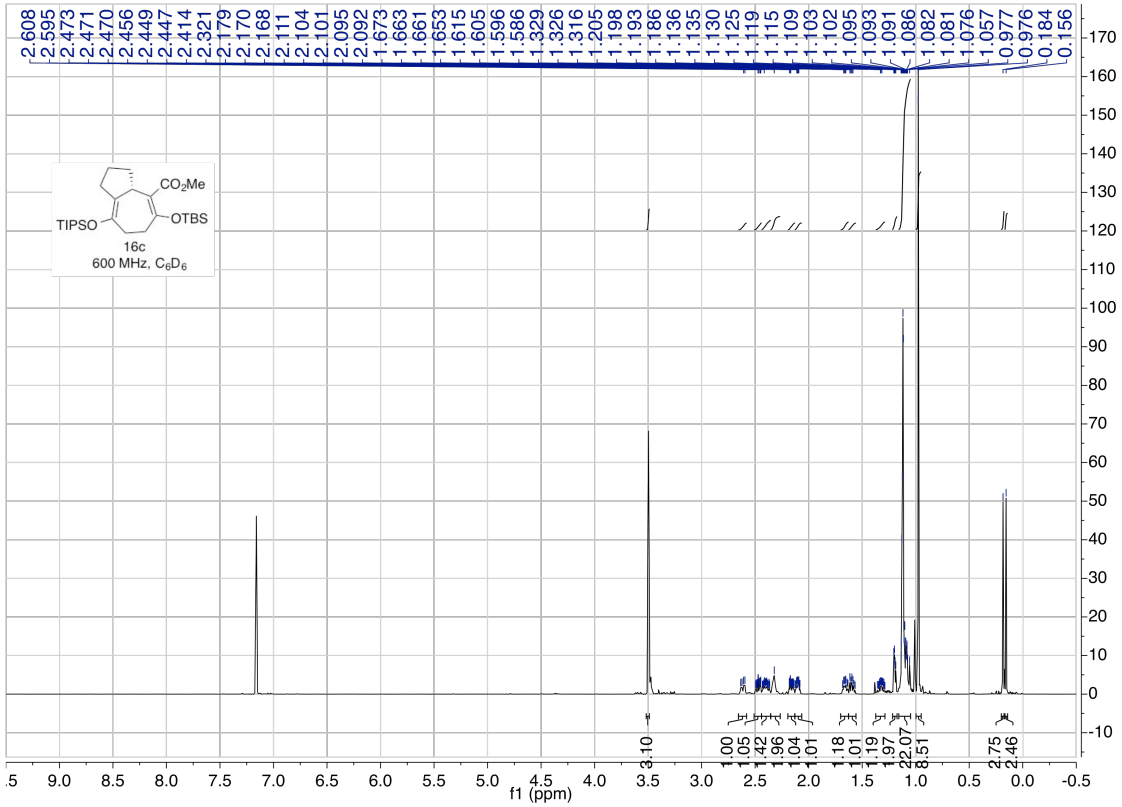

100 MHz, C6D6
13c
f1 (ppm)

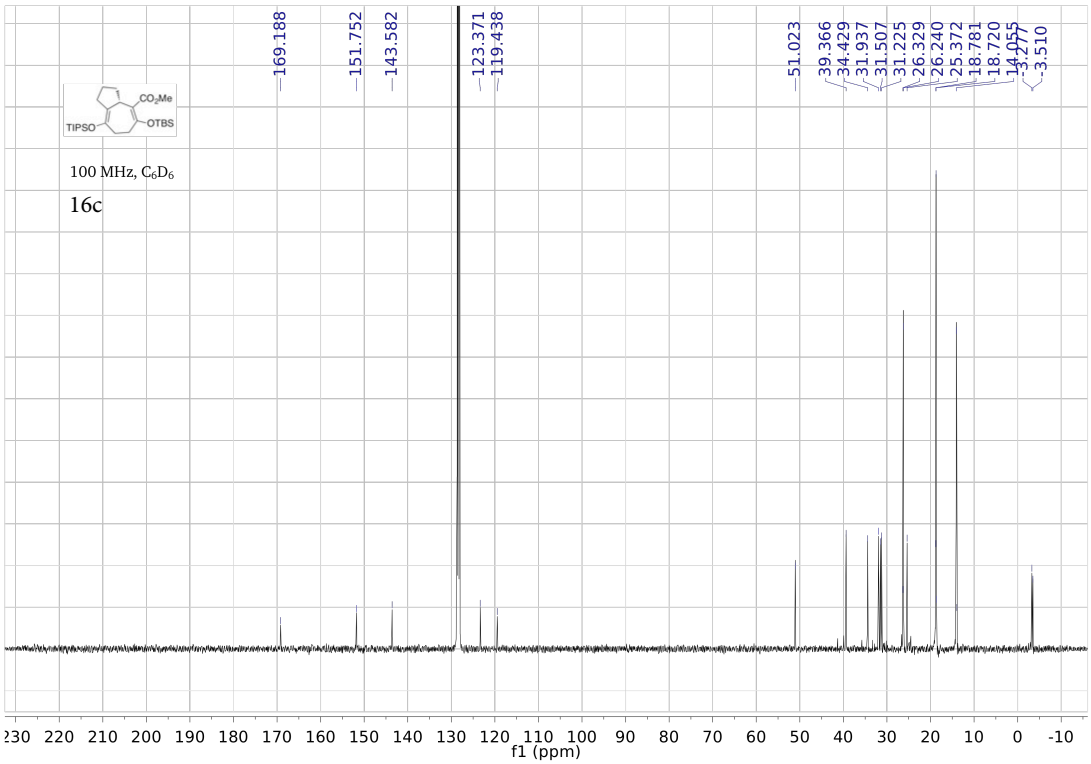

16a
600 MHz, C6D6
f1 (ppm)

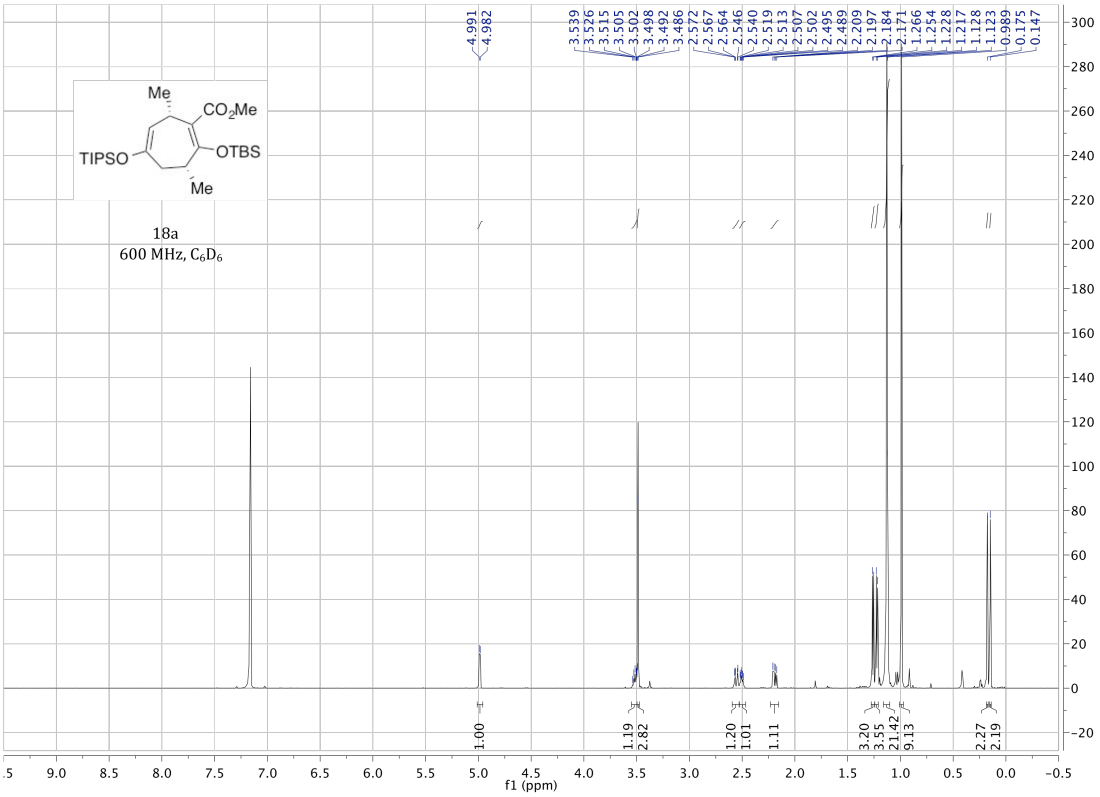

100 MHz, C6D6
16a
f1 (ppm)

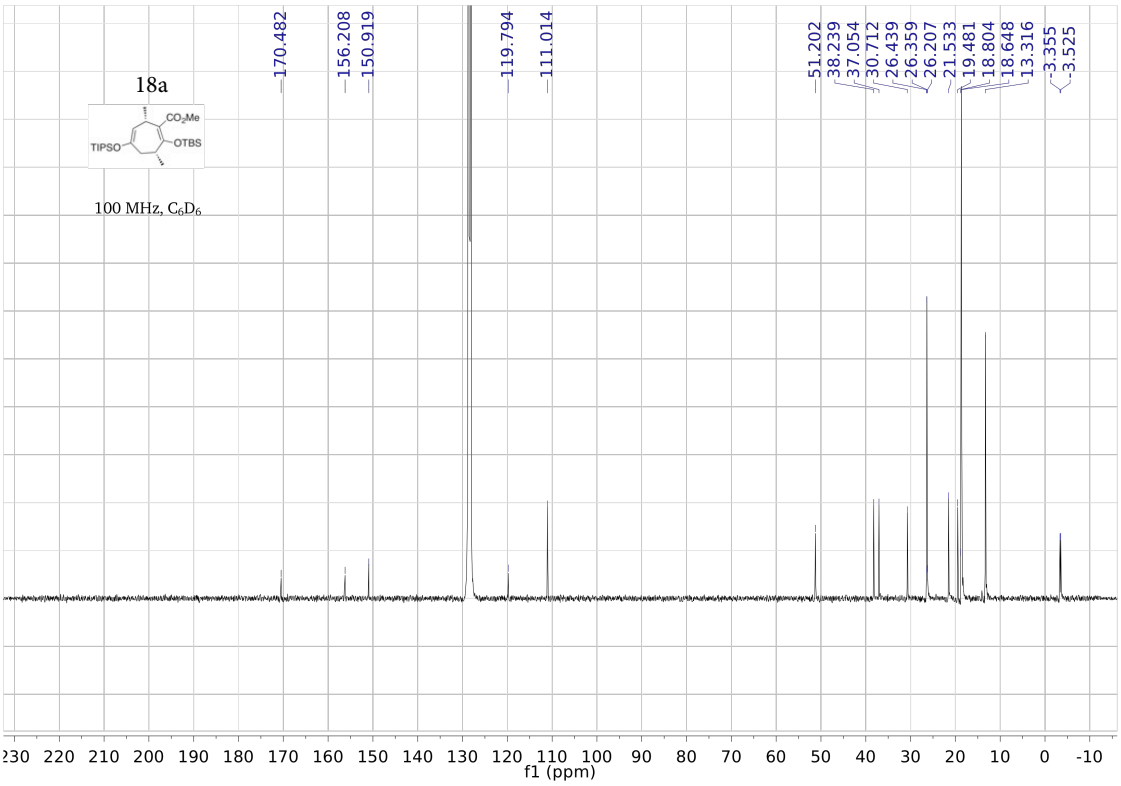

CO2Me
TIPSO
OTBS
16b
600 MHz, C6D6
f1 (ppm)

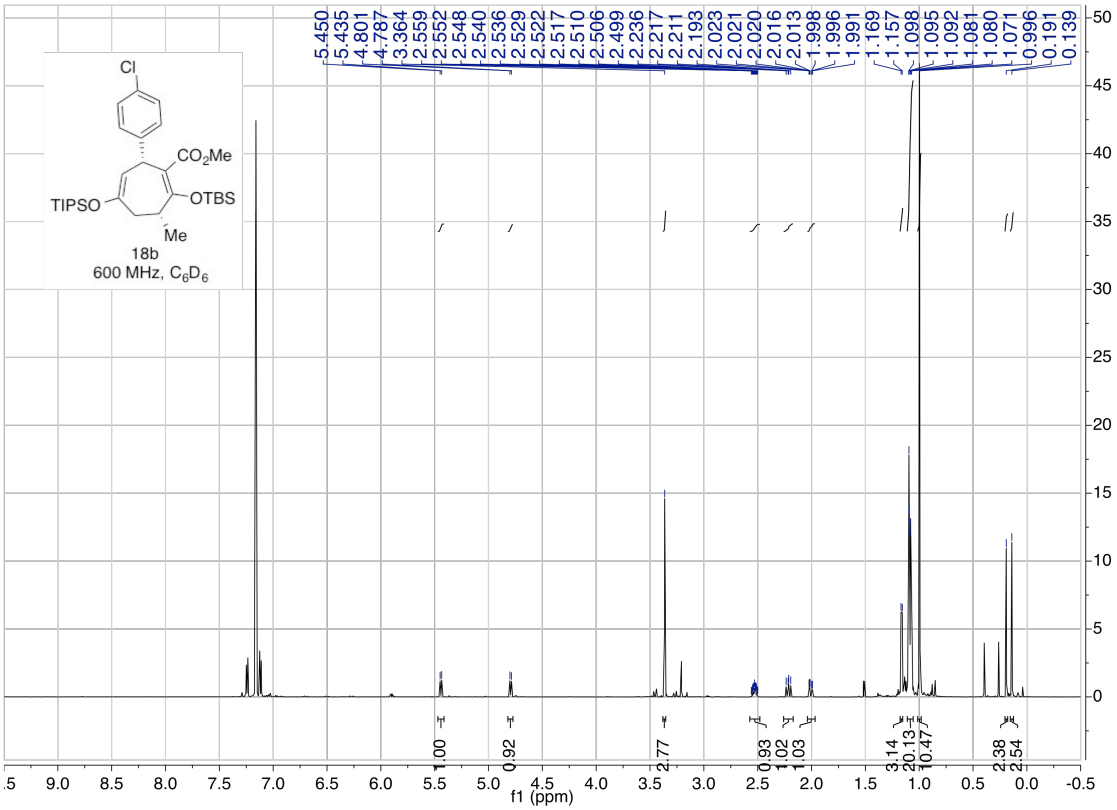

CO2Me
TIPSO
OTBS
100 MHz, C6D6
16b
f1 (ppm)

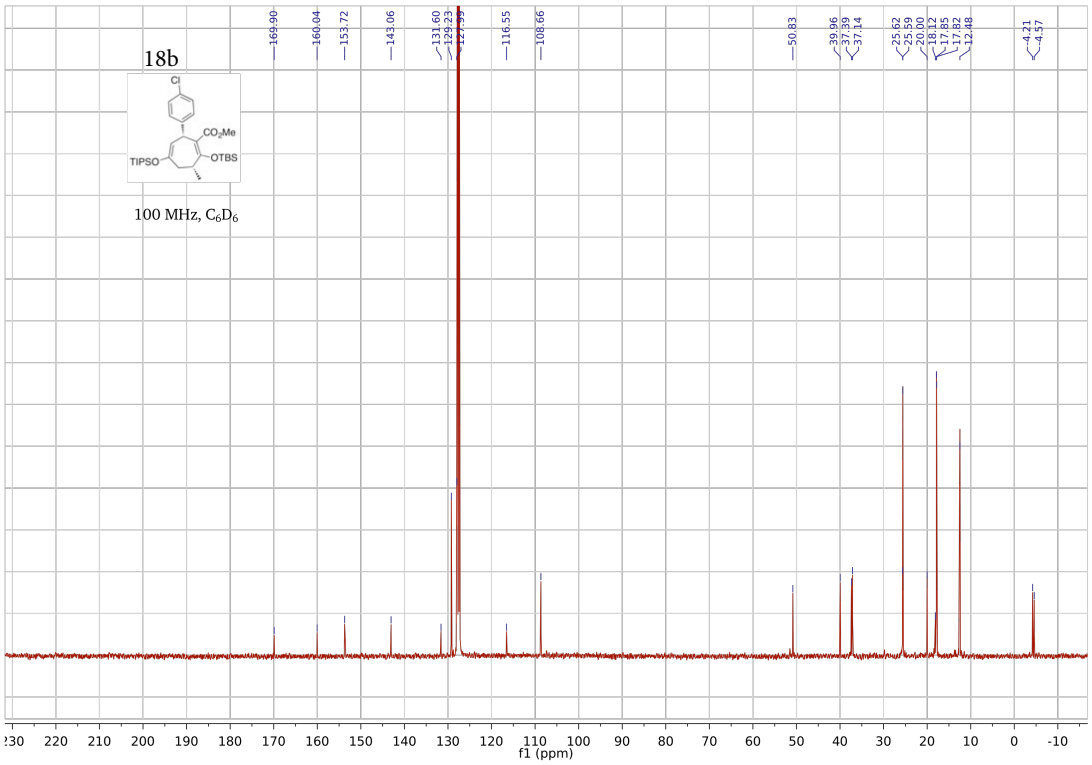

CO2Me
TIPSO
OTBS
16c
600 MHz, C6D6
f1 (ppm)

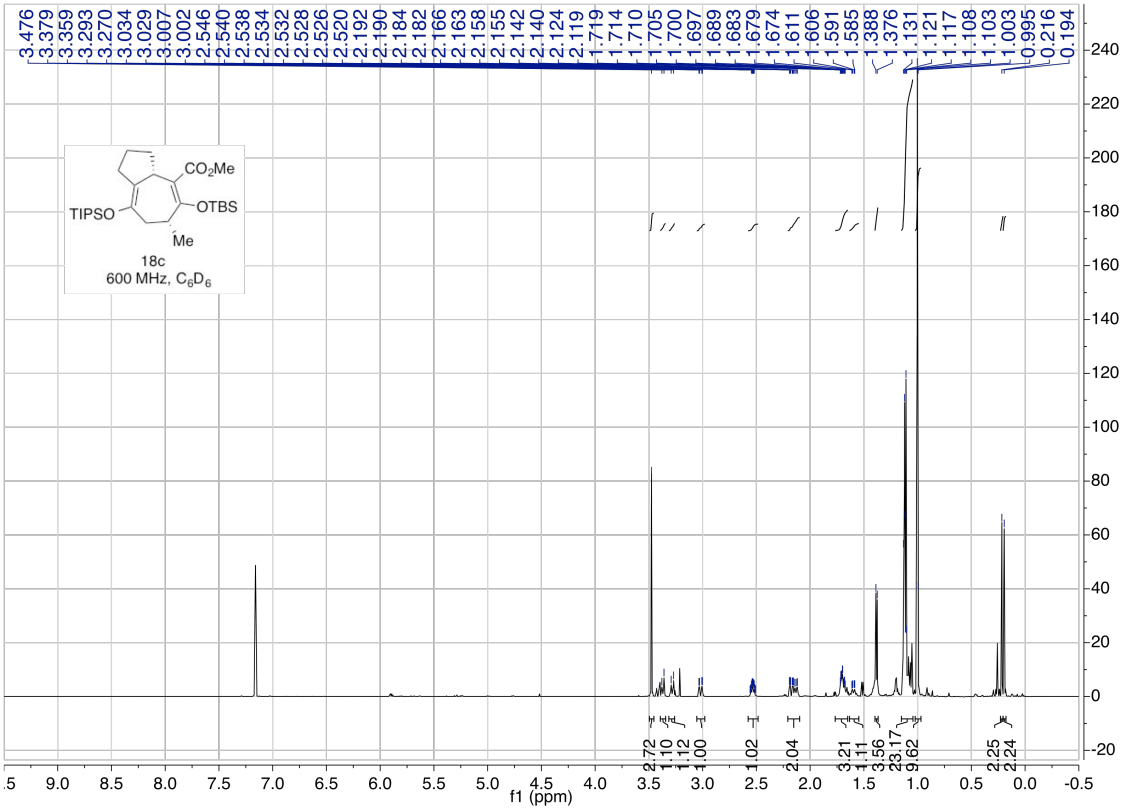

CO2Me
TIPSO
OTBS
100 MHz, C6D6
16c
f1 (ppm)

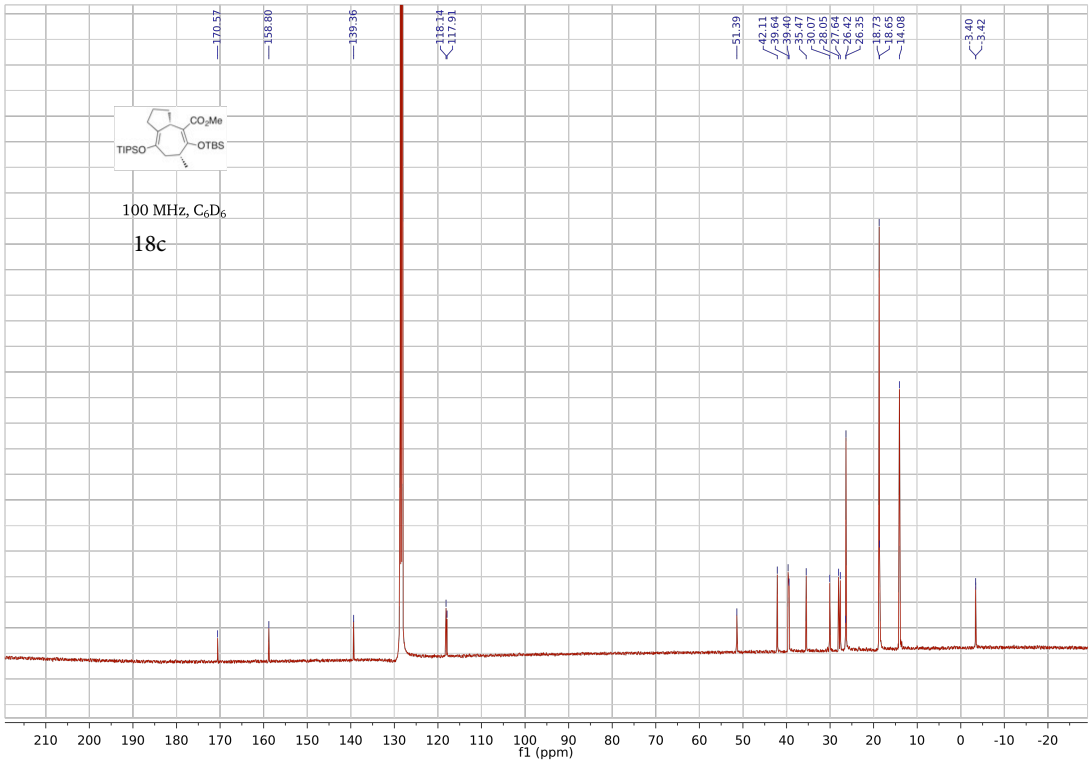

Me
CO2Me
TIPSO
OTBS
Me
18a
600 MHz, C6D6
f1 (ppm)

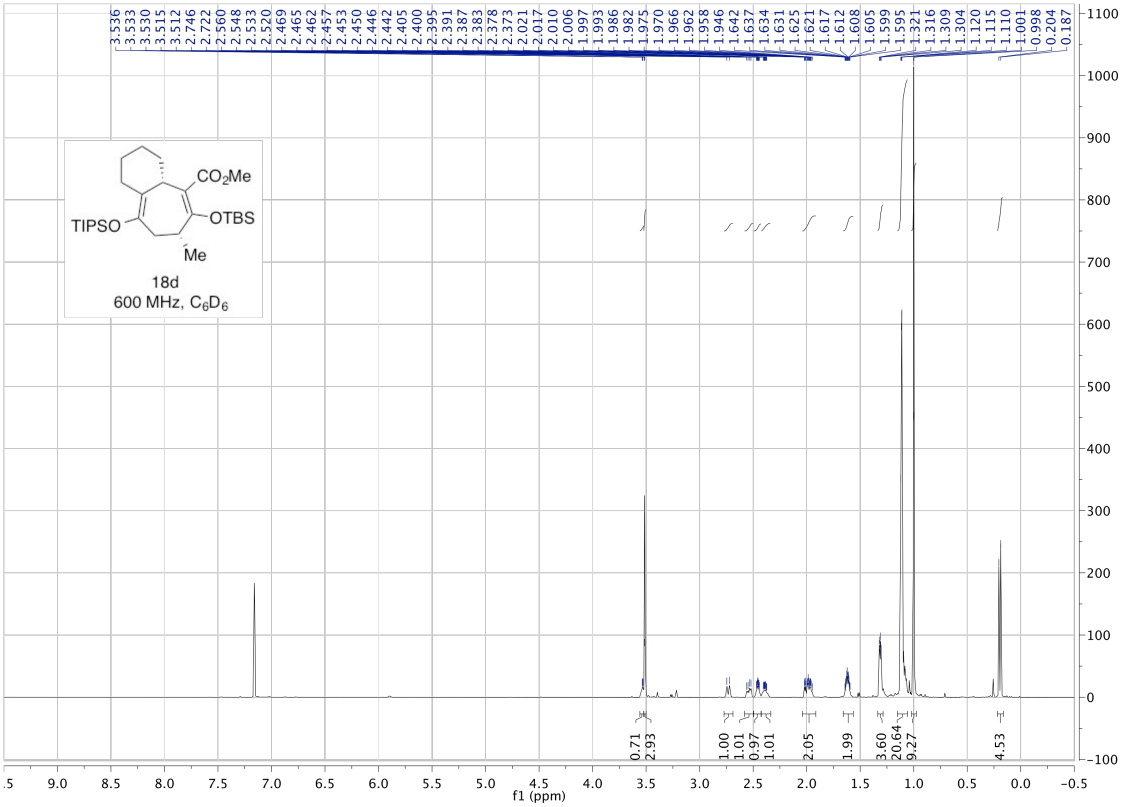

18a
CO2Me
TIPSO
OTBS
100 MHz, C6D6
f1 (ppm)

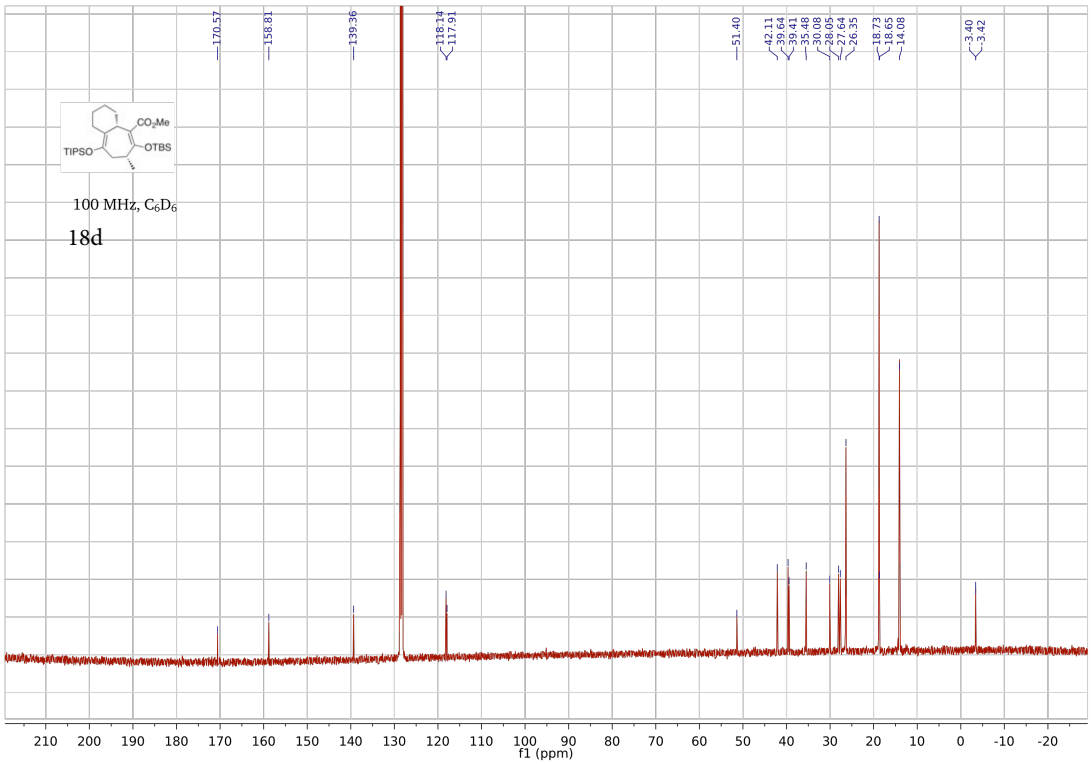

Cl
CO2Me
TIPSO
OTBS
Me
18b
600 MHz, C6D6
f1 (ppm)

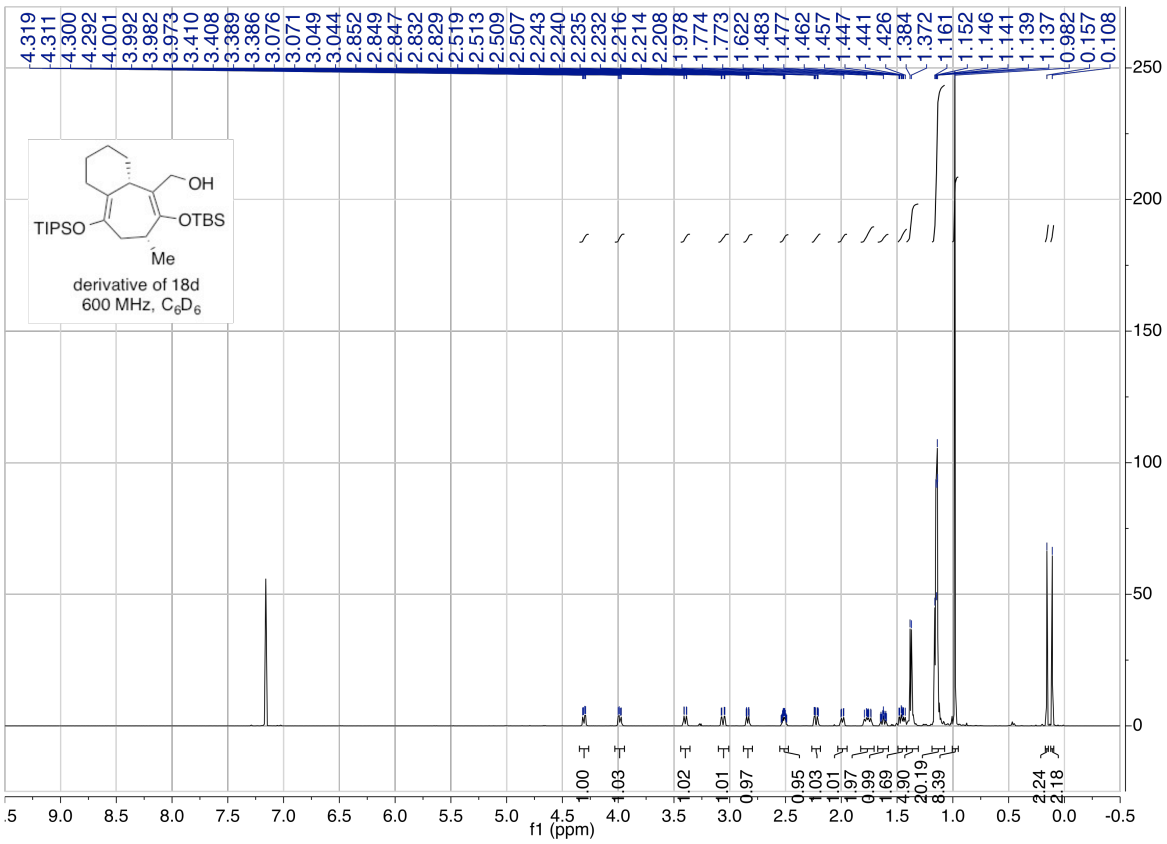

18b
100 MHz, C6D6
f1 (ppm)

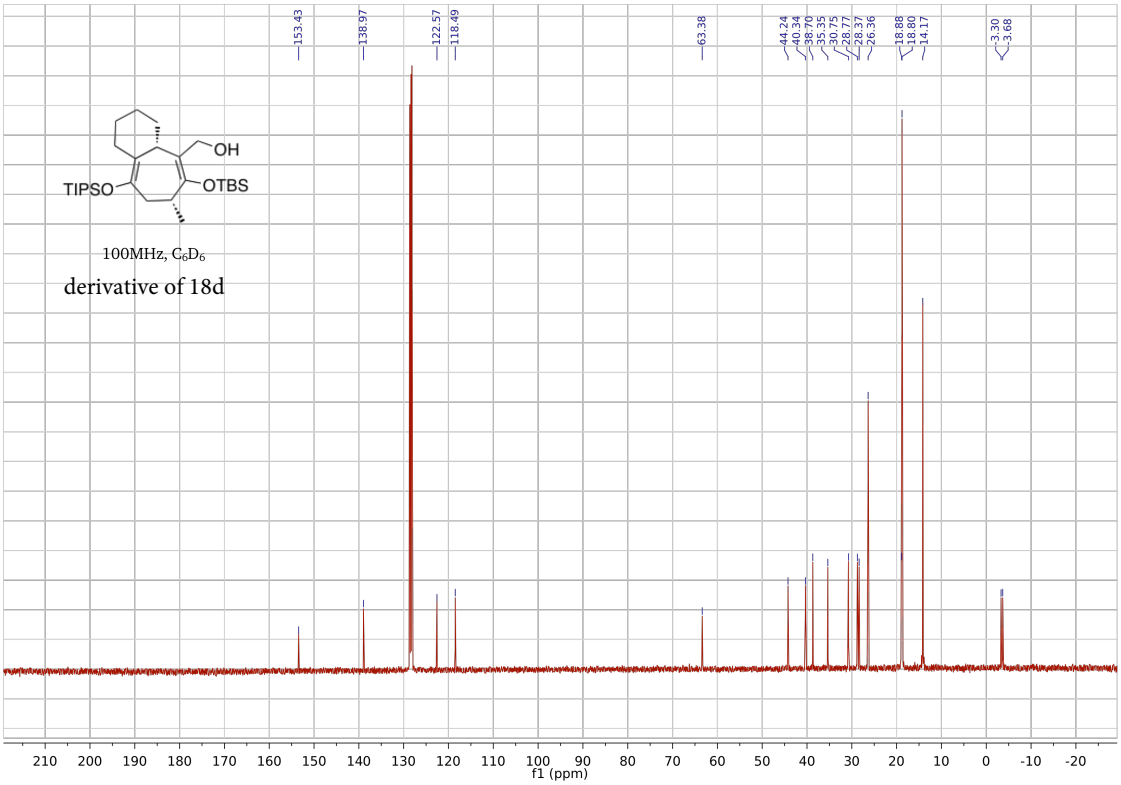

CO2Me
OTBS
TIPSO
Me
18c
600 MHz, C6D6
f1 (ppm)

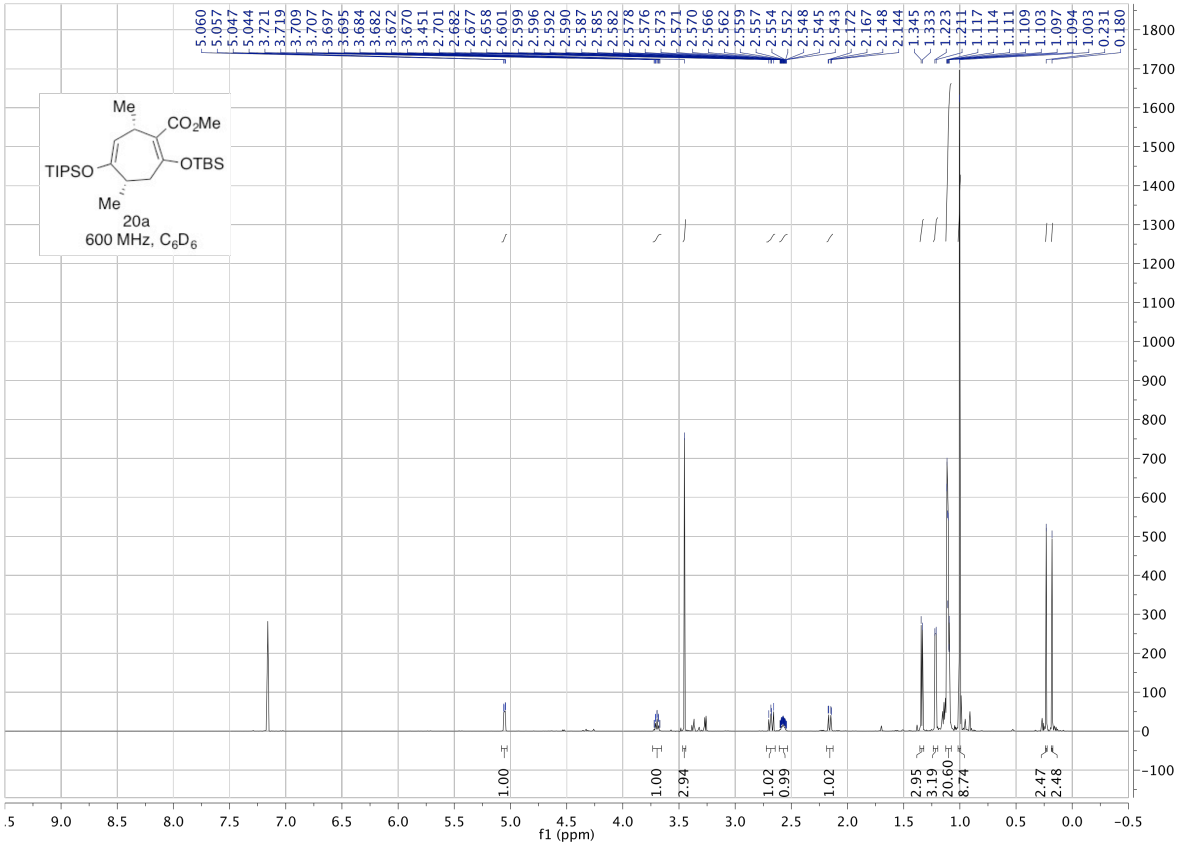

CO2Me
OTBS
TIPSO
100 MHz, C6D6
18c
f1 (ppm)

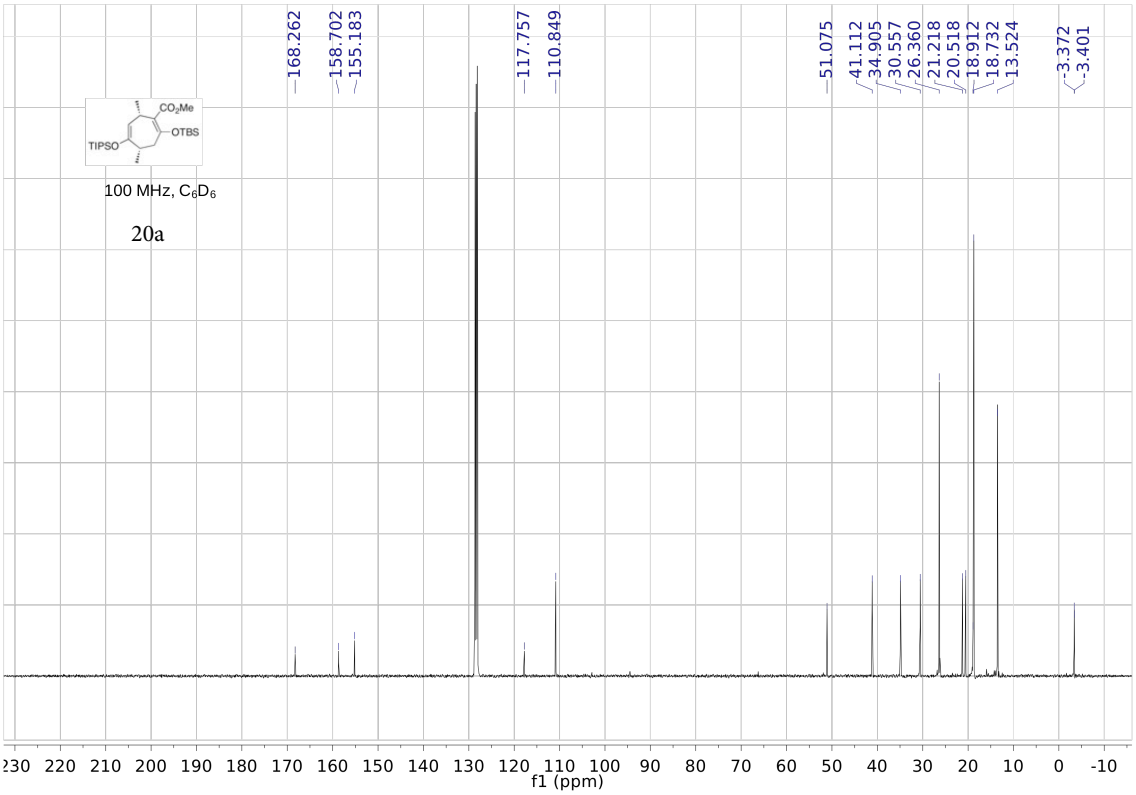

CO2Me
TIPSO
OTBS
Me
18d
600 MHz, C6D6
f1 (ppm)

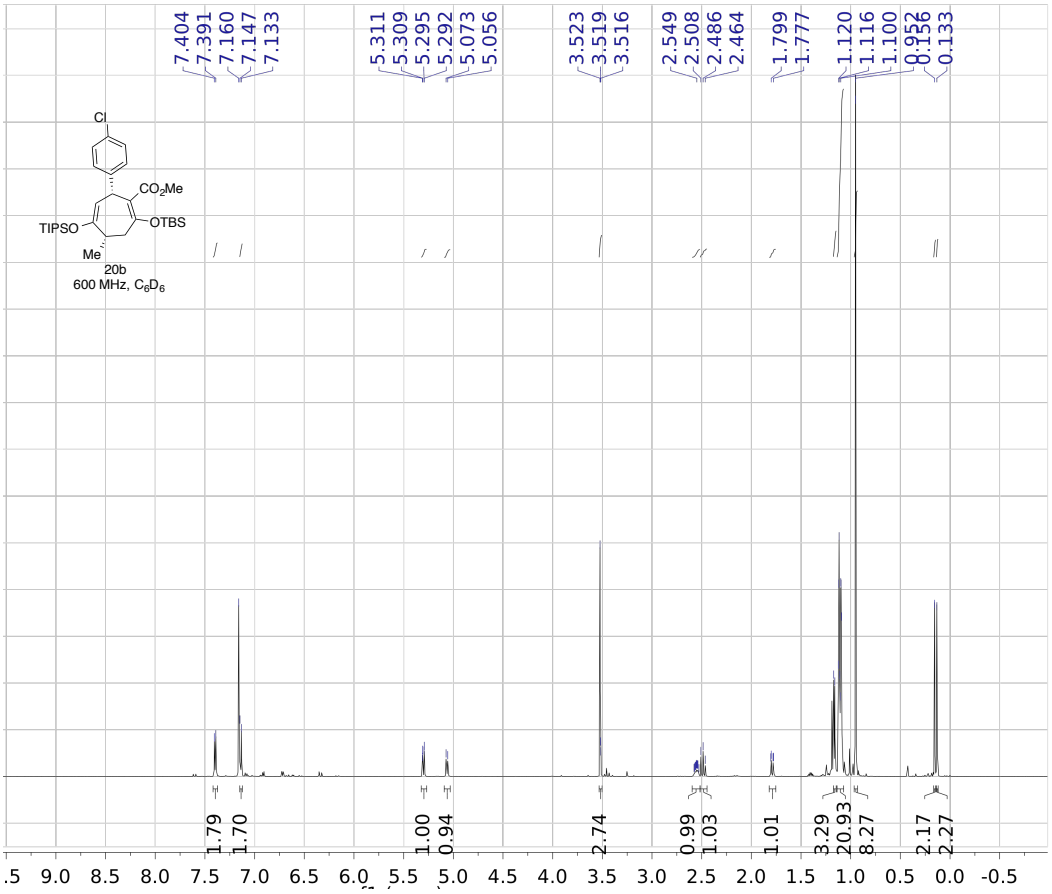

CO2Me
TIPSO
OTBS
100 MHz, C6D6
18d
f1 (ppm)

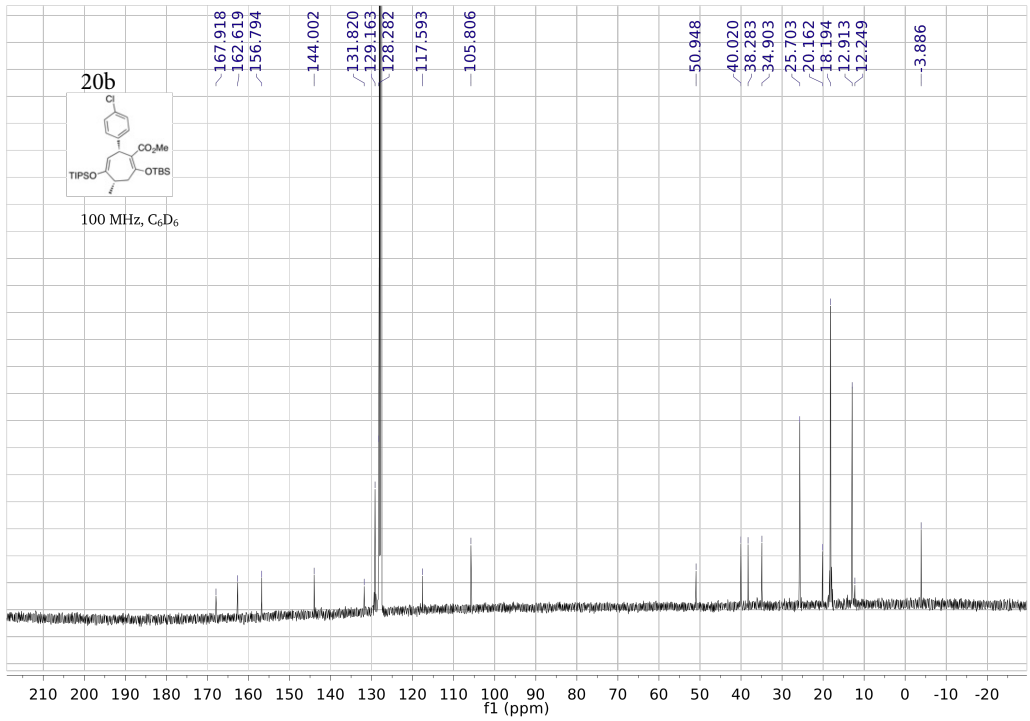

OH
TIPSO
OTBS
Me
derivative of 18d
600 MHz, C6D6
f1 (ppm)

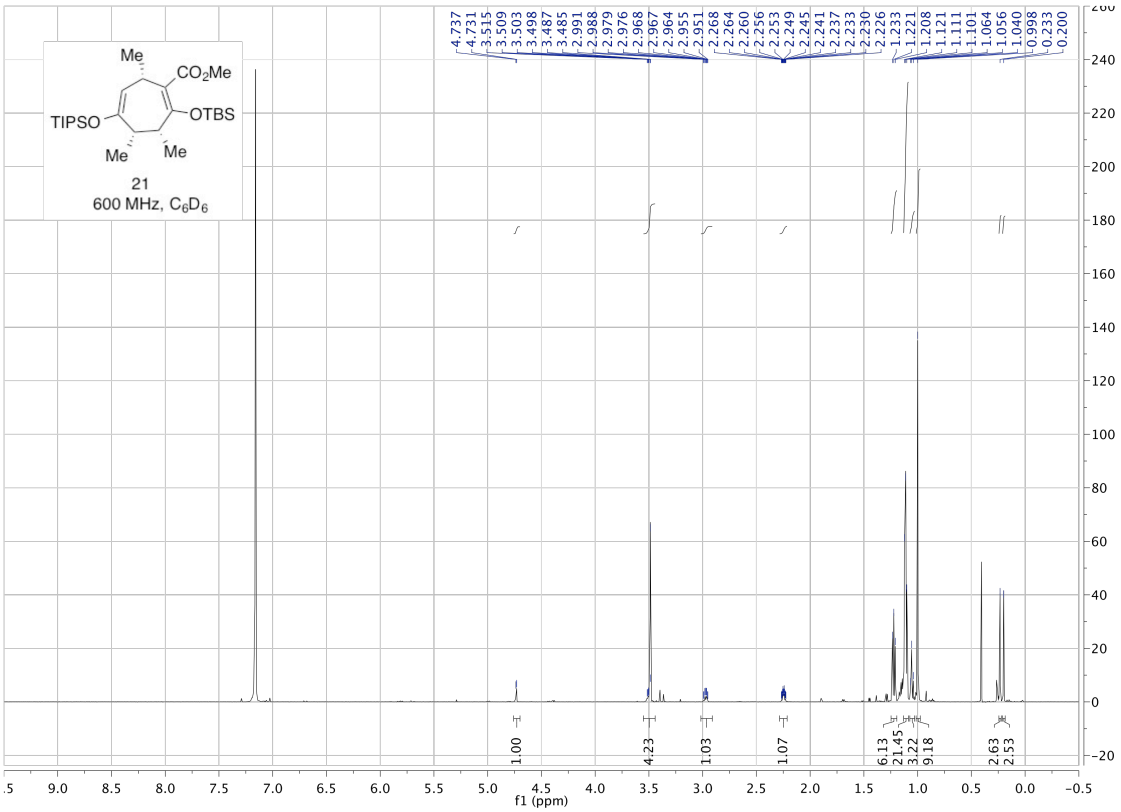

OH
TIPSO
OTBS
100MHz, C6D6
derivative of 18d
f1 (ppm)

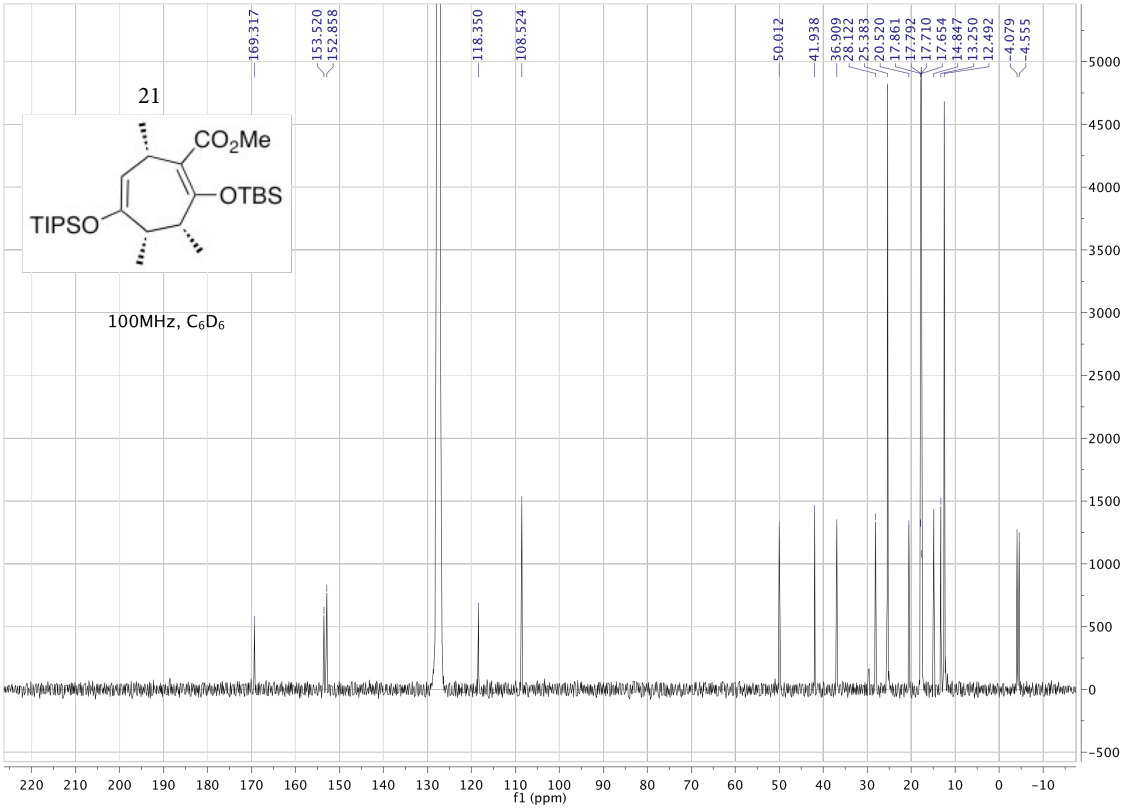

Me
CO2Me
TIPSO
OTBS
Me
20a
600 MHz, C6D6
f1 (ppm)

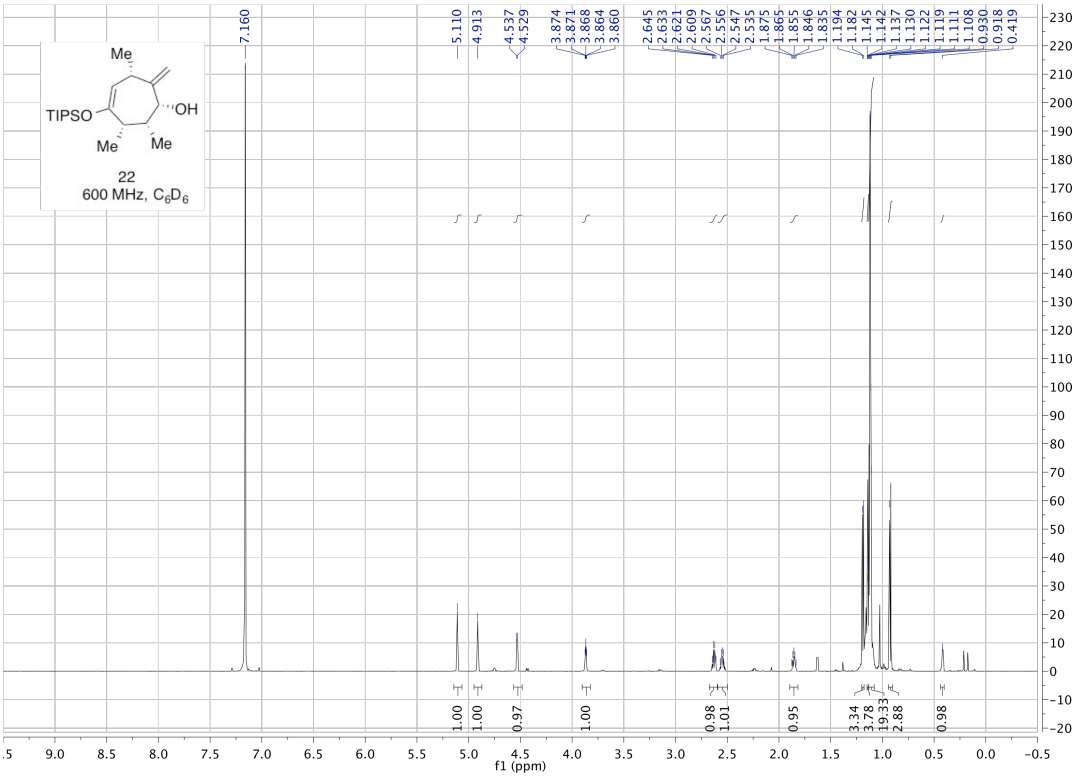

CO2Me
TIPSO
OTBS
100 MHz, C6D6
20a
f1 (ppm)

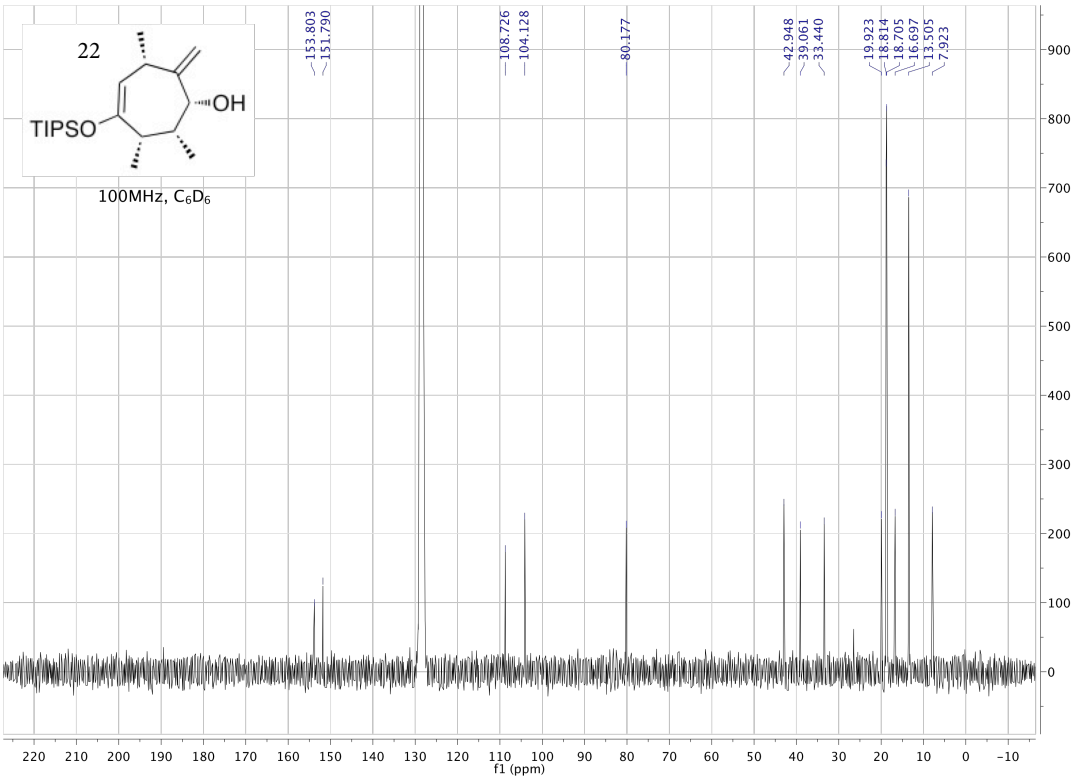

7.404
7.391
7.160
7.147
7.133
5.311
5.309
5.295
5.292
5.073
5.056
3.523
3.519
3.516
2.549
2.508
2.486
2.464
1.799
1.777
1.120
1.116
1.100
0.952
0.156
0.133
Cl
CO2Me
OTBS
TIPSO
Me
20b
600 MHz, C6D6
1.79
1.70
1.00
0.94
2.74
0.99
1.03
1.01
3.29
20.93
8.27
2.17
2.27
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

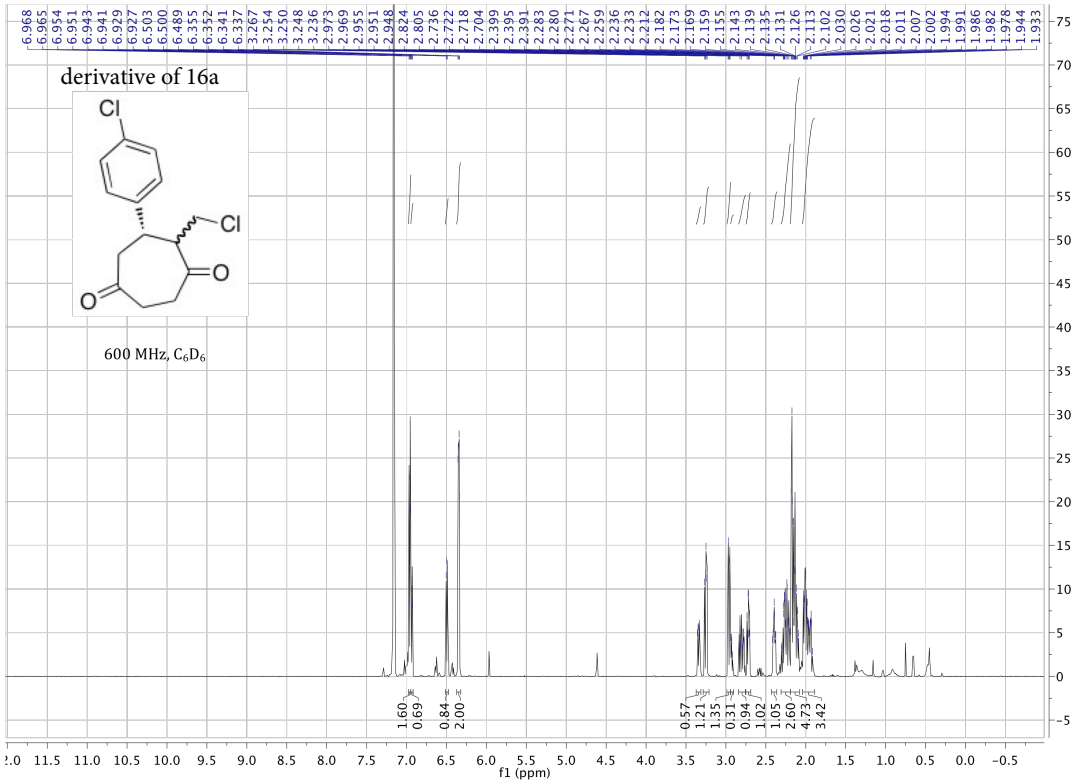

20b
100 MHz, C6D6
167.918
162.619
156.794
144.002
131.820
129.163
128.282
117.593
105.806
50.948
40.020
38.283
34.903
25.703
20.162
18.194
12.913
12.249
-3.886
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

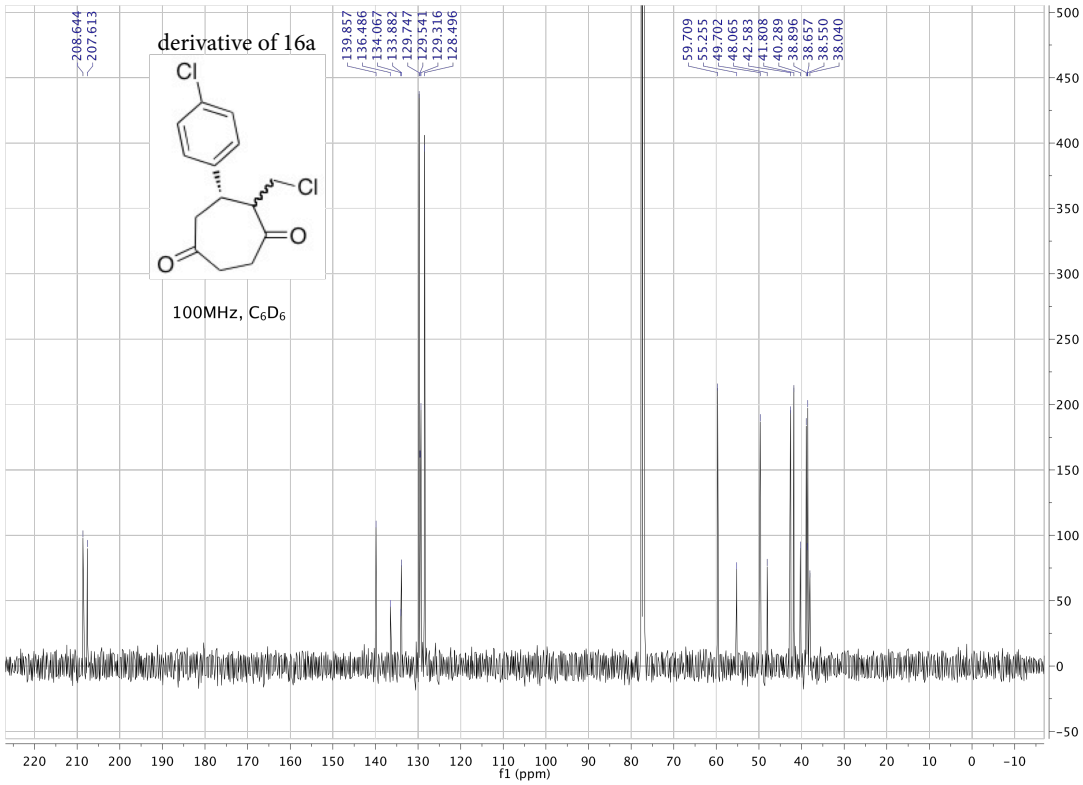

Me
CO2Me
TIPSO
OTBS
Me
Me
21
600 MHz, C6D6
f1 (ppm)


21
CO2Me
OTBS
TIPSO
100MHz, C6D6
f1 (ppm)

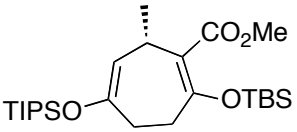

Me
TIPSO
OH
Me
Me
22
600 MHz, C6D6
7.160
5.110
4.913
4.537
4.529
3.874
3.871
3.868
3.864
3.860
2.645
2.633
2.621
2.609
2.567
2.556
2.547
2.535
1.875
1.865
1.855
1.846
1.835
1.194
1.182
1.145
1.142
1.137
1.130
1.122
1.119
1.111
1.108
0.930
0.918
0.419
1.00
1.00
0.97
1.00
0.98
1.01
0.95
3.34
3.78
19.33
2.88
0.98
f1 (ppm)


22
TIPSO
OH
100MHz, C6D6
153.803
151.790
108.726
104.128
80.177
42.948
39.061
33.440
19.923
18.814
18.705
16.697
13.505
7.923
f1 (ppm)

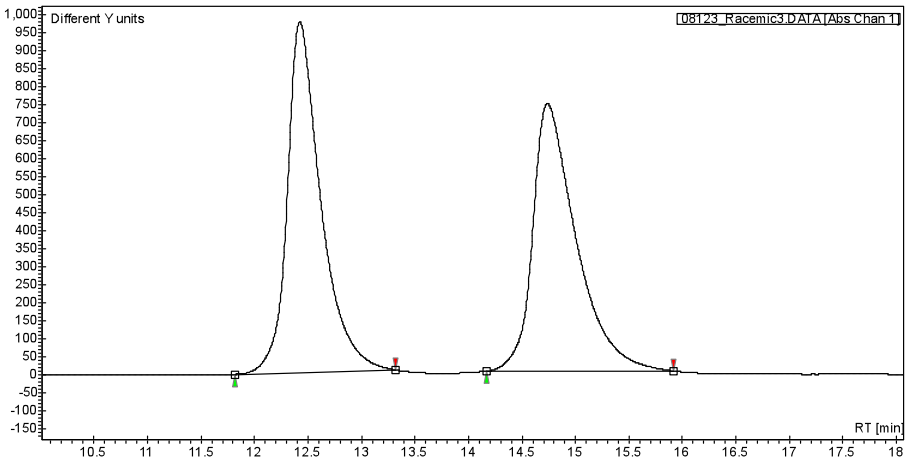

derivative of 16a
Cl
Cl
O
O
600 MHz, C6D6
f1 (ppm)


derivative of 16a
Cl
Cl
O
O
100MHz, C6D6
f1 (ppm)

## 5.0 Analytical HPLC Chromatograms

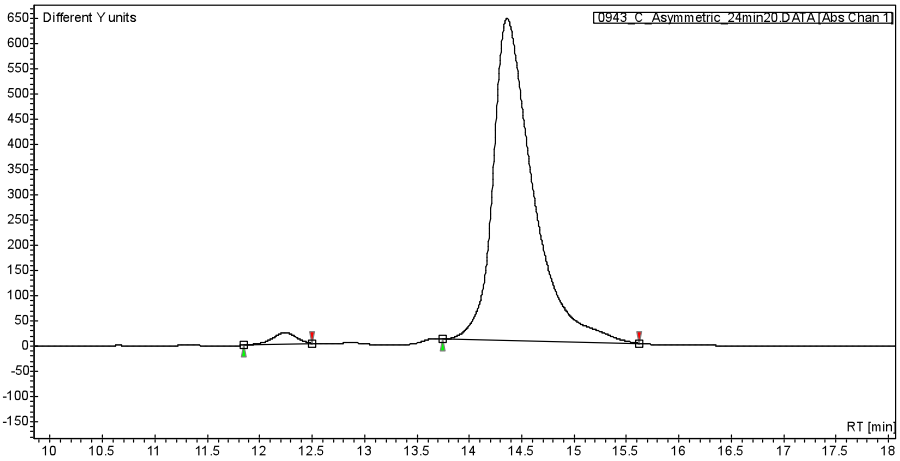



**13c Racemic**

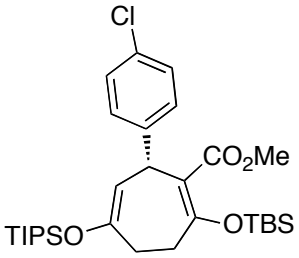



| # | Time [Min] | Area % |
|---|---|---|
| 1 | 12.42 | 50.335 |
| 2 | 14.74 | 49.665 |

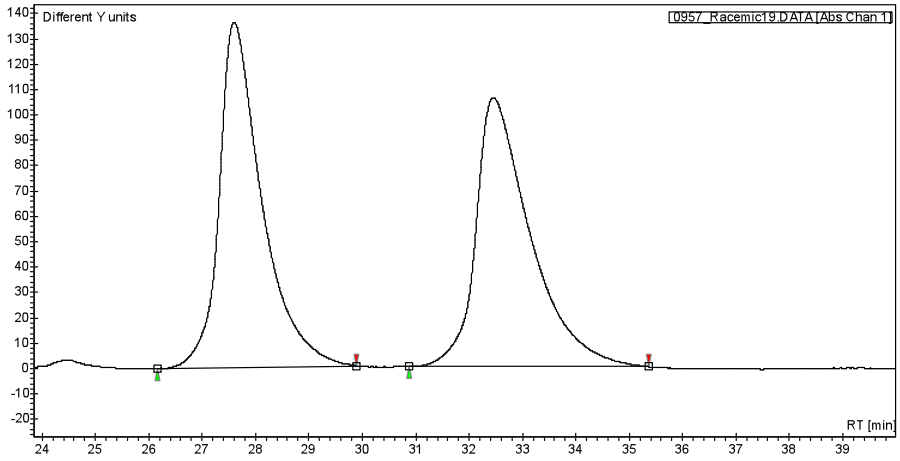
**13c Asymmetric**




| # | Time [Min] | Area % |
|---|---|---|
| 1 | 12.24 | 2.095 |
| 2 | 14.36 | 97.905 |

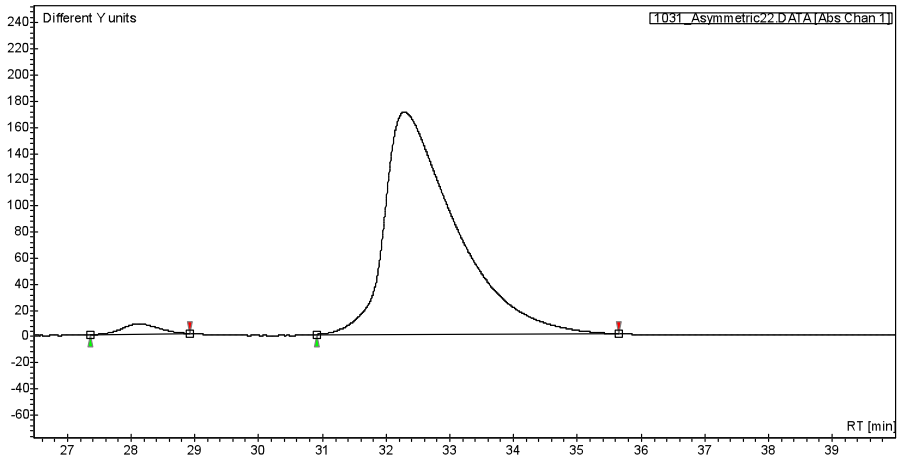



**16a Racemic**

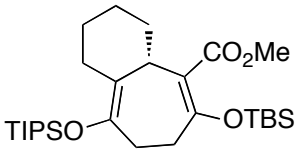



| # | Time [Min] | Area % |
|---|---|---|
| 1 | 27.60 | 50.172 |
| 2 | 32.45 | 49.828 |

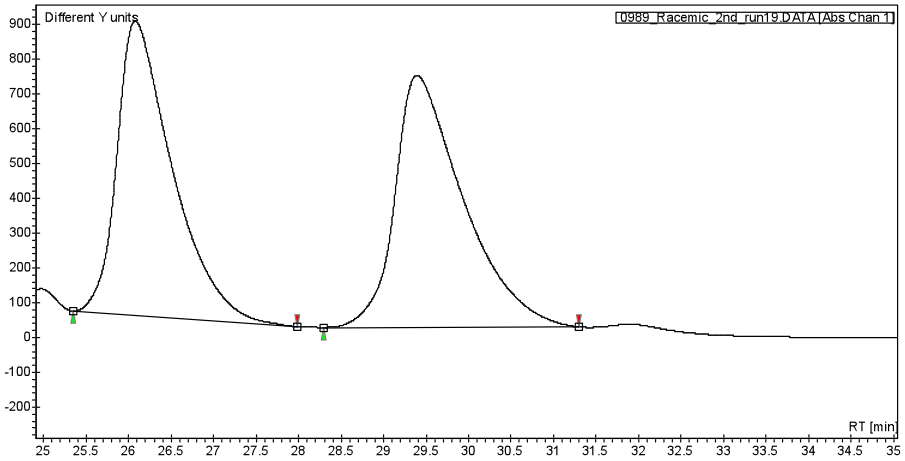
**16a Asymmetric**




| # | Time [Min] | Area % |
|---|---|---|
| 1 | 28.14 | 2.409 |
| 2 | 32.29 | 97.591 |

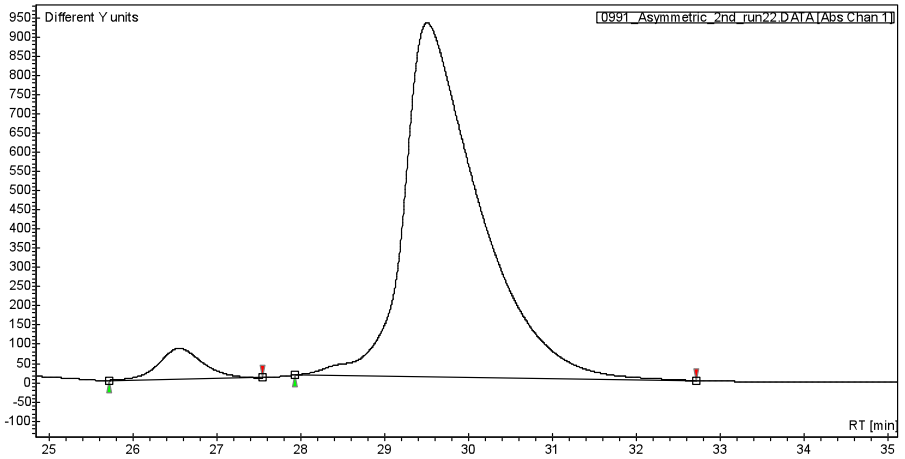



**16b Racemic**

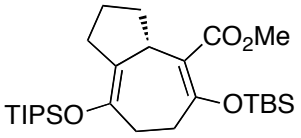



| # | Time [Min] | Area % |
|---|---|---|
| 1 | 26.08 | 48.802 |
| 2 | 29.39 | 51.198 |

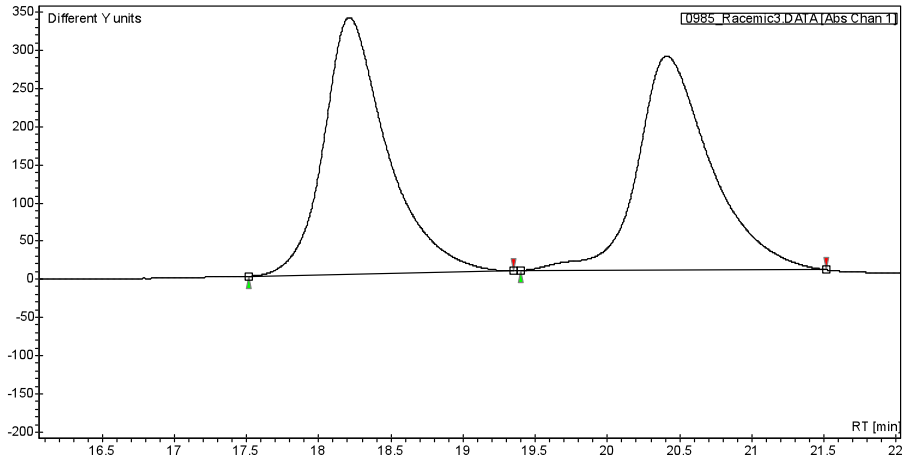
**16b Asymmetric**




| # | Time [Min] | Area % |
|---|---|---|
| 1 | 26.55 | 4.812 |
| 2 | 29.51 | 95.188 |

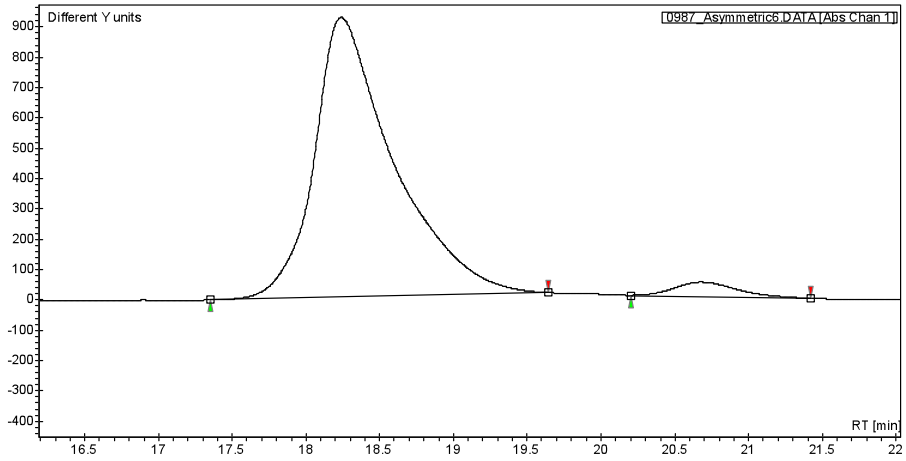



**16c Racemic**

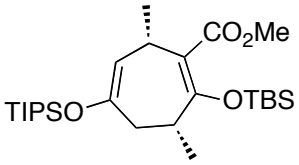



| # | Time [Min] | Area % |
|---|---|---|
| 1 | 18.21 | 50.868 |
| 2 | 20.41 | 49.132 |

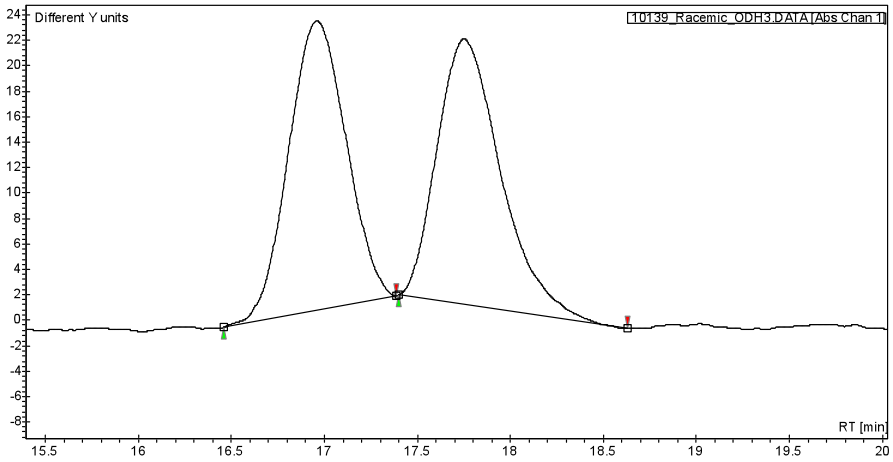
**16c Asymmetric**




| # | Time [Min] | Area % |
|---|---|---|
| 1 | 18.24 | 96.080 |
| 2 | 20.68 | 3.920 |

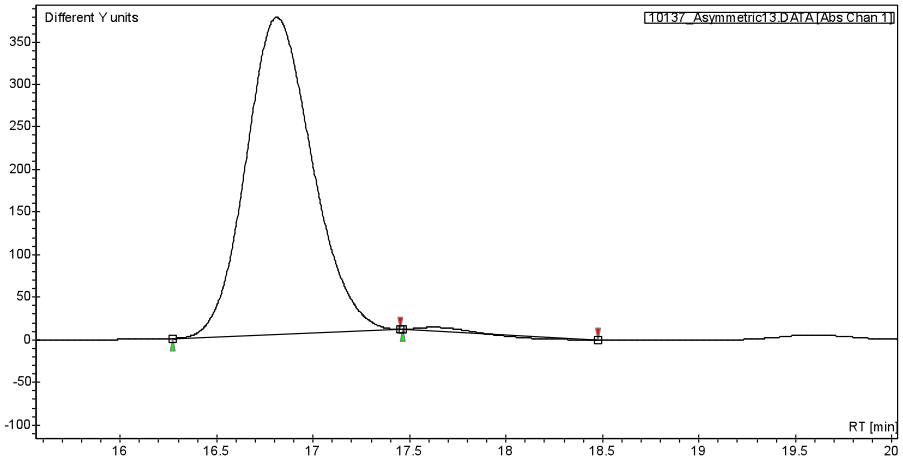



**18a Racemic**

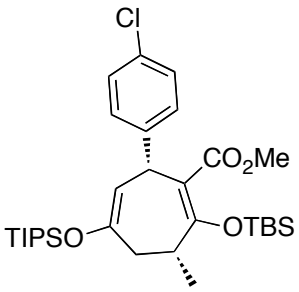



| # | Time [Min] | Area % |
|---|---|---|
| 1 | 16.96 | 49.617 |
| 2 | 17.75 | 50.383 |

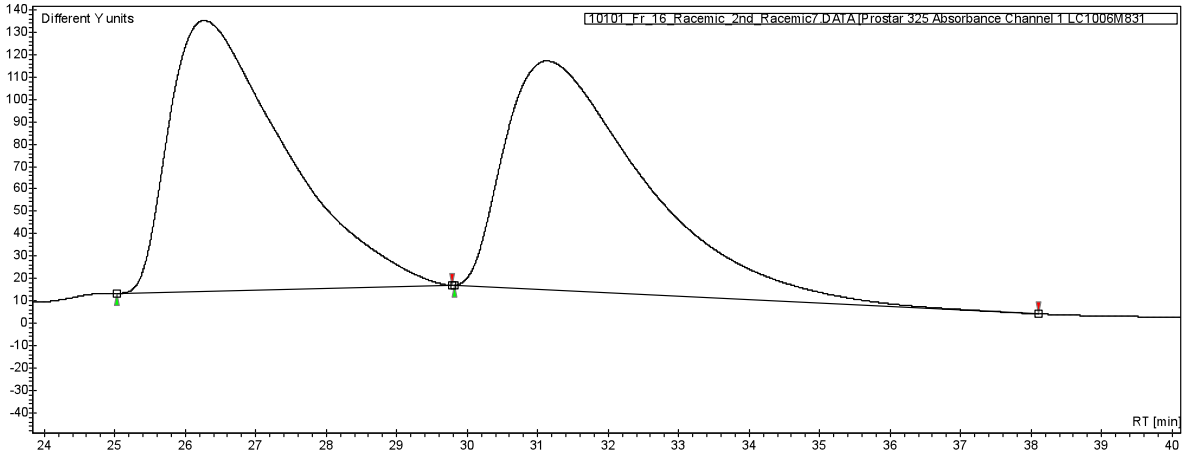
**18a Asymmetric**




| # | Time [Min] | Area % |
|---|---|---|
| 1 | 16.81 | 99.705 |
| 2 | 17.66 | 0.295 |

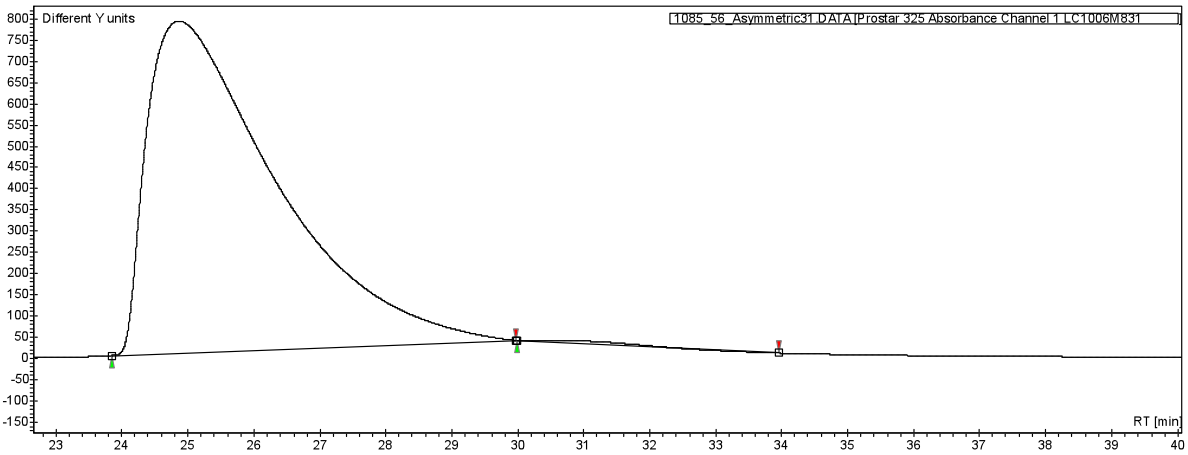



**18b Racemic**

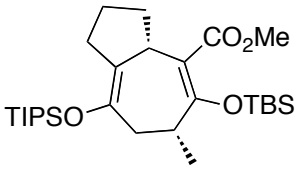



| # | Time [Min] | Area % |
|---|---|---|
| 1 | 26.27 | 49.499 |
| 2 | 31.14 | 50.501 |

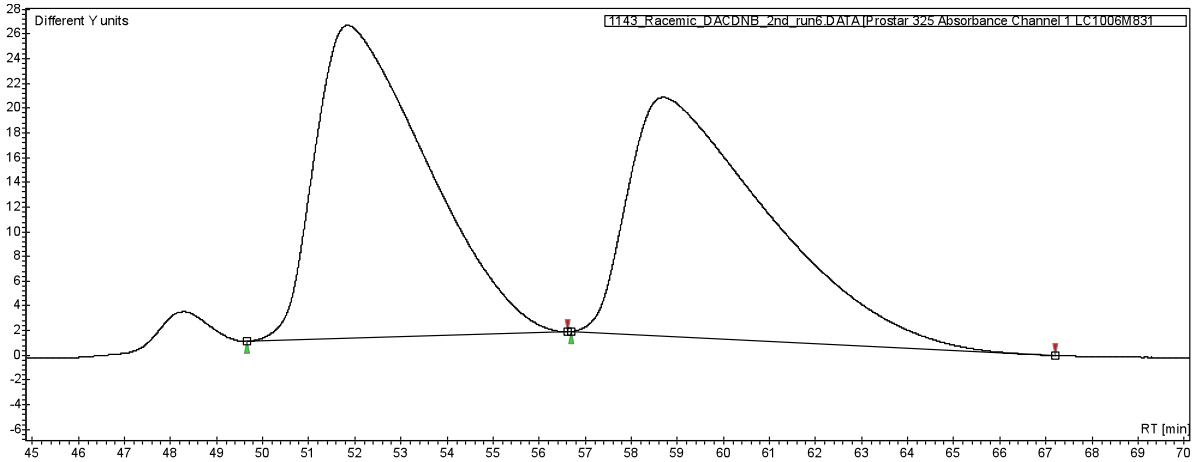
**18b Asymmetric**




| # | Time [Min] | Area % |
|---|---|---|
| 1 | 24.86 | 99.610 |
| 2 | 31.14 | 0.390 |

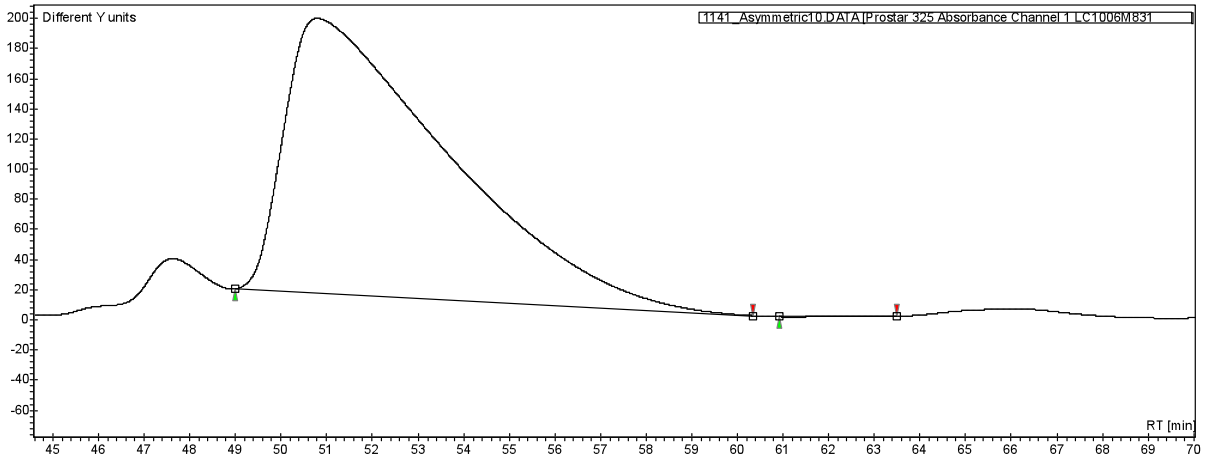



**18c Racemic**

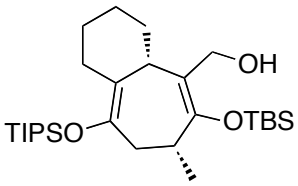



| # | Time [Min] | Area % |
|---|---|---|
| 1 | 51.84 | 50.839 |
| 2 | 58.70 | 49.161 |

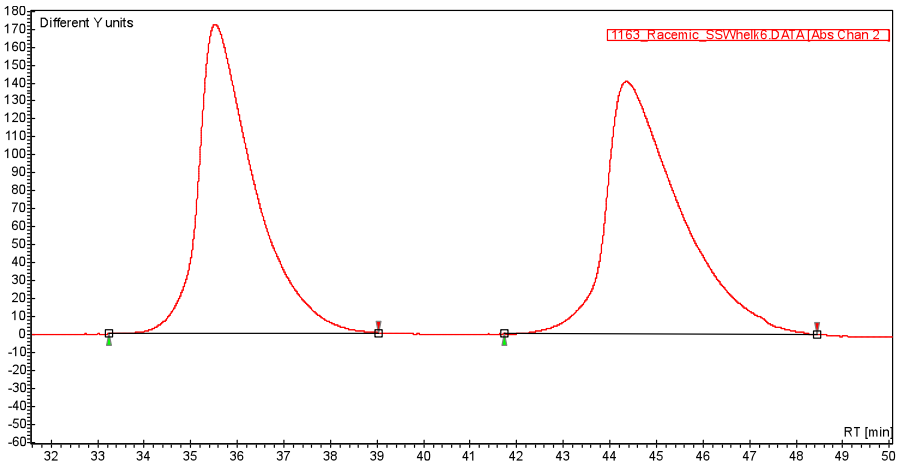
**18c Asymmetric**




| # | Time [Min] | Area % |
|---|---|---|
| 1 | 50.81 | 99.992 |
| 2 | 61.38 | 0.008 |

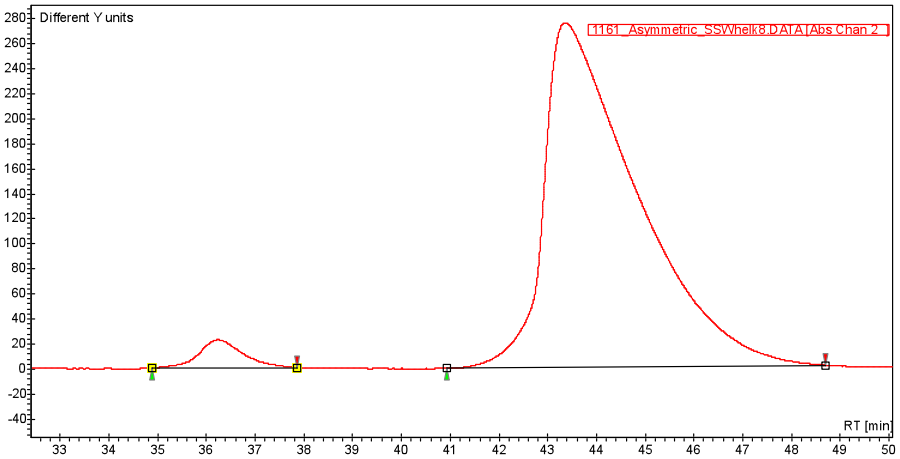



**Corresponding allylic alcohol of 18d Racemic**

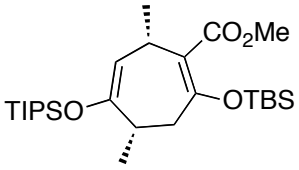



| # | Time [Min] | Area % |
|---|---|---|
| 1 | 35.52 | 48.035 |
| 2 | 44.35 | 51.965 |

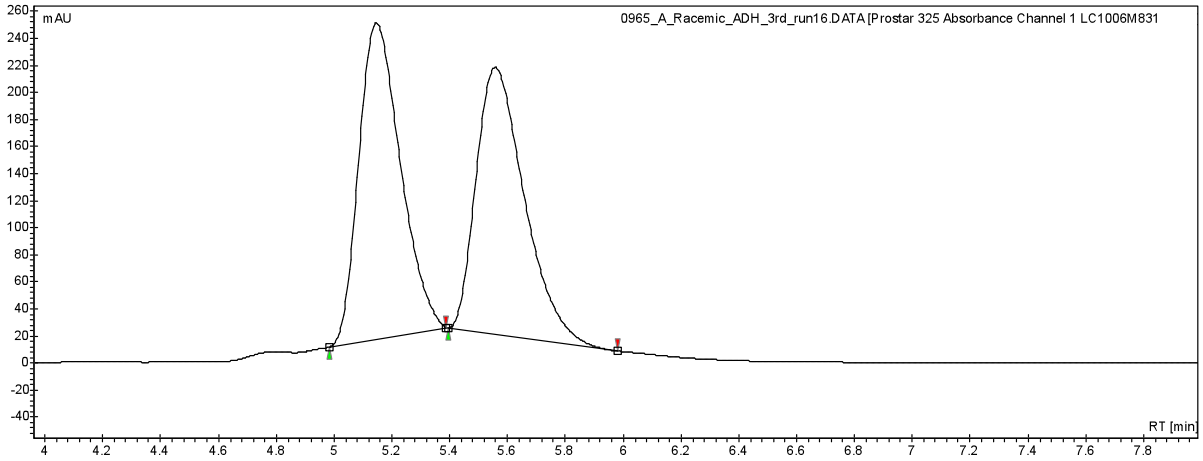
**Corresponding allylic alcohol of 18d Asymmetric**




| # | Time [Min] | Area % |
|---|---|---|
| 1 | 36.24 | 3.763 |
| 2 | 43.36 | 96.237 |

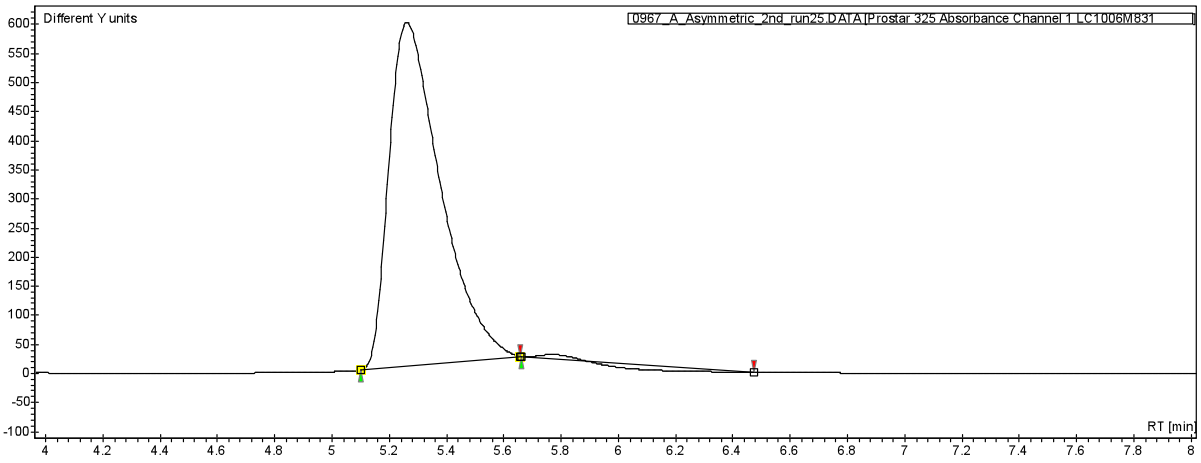



**20a Racemic**

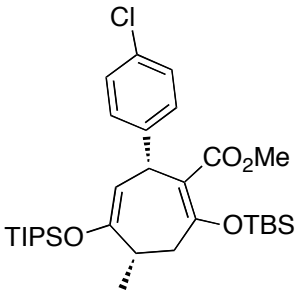



| # | Time [Min] | Area % |
|---|---|---|
| 1 | 5.15 | 50.629 |
| 2 | 5.56 | 49.371 |

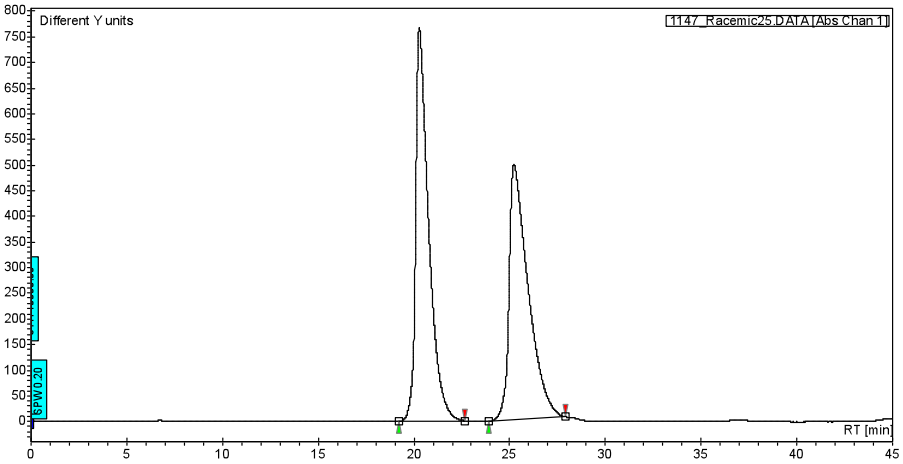
**20a Asymmetric**




| # | Time [Min] | Area % |
|---|---|---|
| 1 | 5.26 | 98.318 |
| 2 | 6.08 | 1.682 |

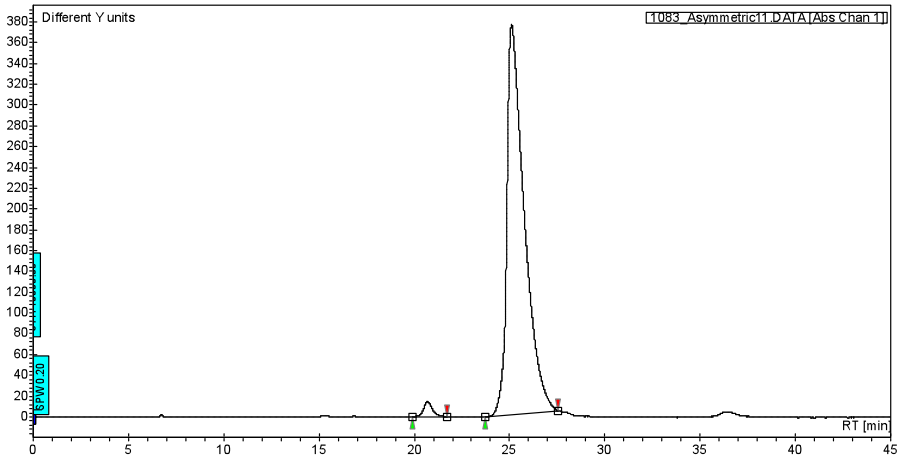



**20b Racemic**

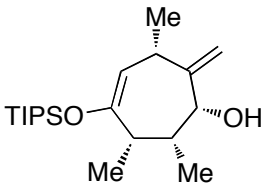



| # | Time [Min] | Area % |
|---|---|---|
| 1 | 20.28 | 51.235 |
| 2 | 25.22 | 48.765 |

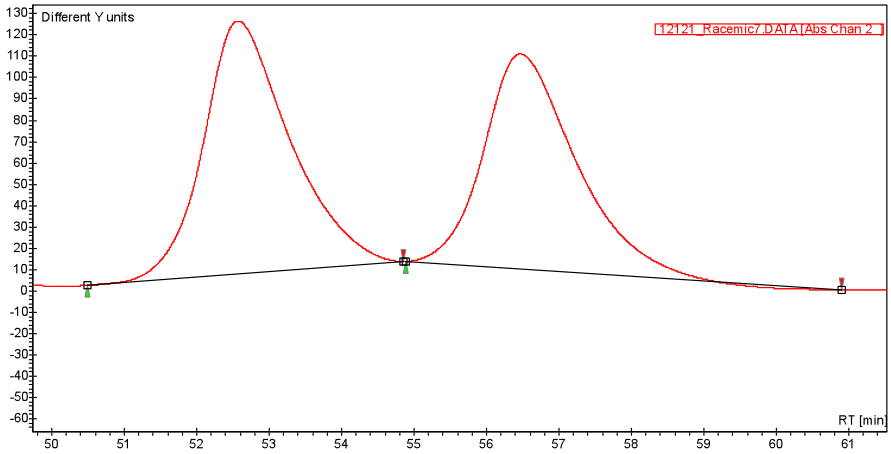
**20b Asymmetric**




| # | Time [Min] | Area % |
|---|---|---|
| 1 | 20.70 | 1.970 |
| 2 | 25.10 | 98.030 |

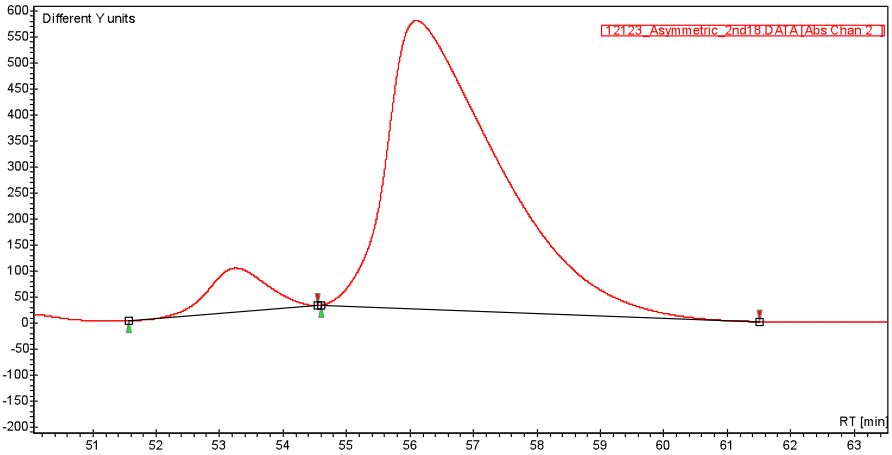



**22 Racemic**




| # | Time [Min] | Area % |
|---|---|---|
| 1 | 52.57 | 52.464 |
| 2 | 56.47 | 47.436 |

**22 Asymmetric**

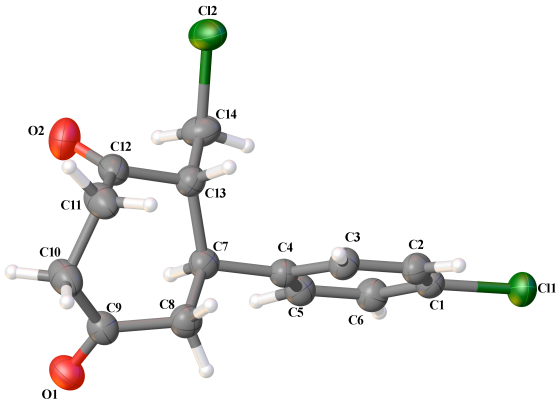



| # | Time [Min] | Area % |
|---|---|---|
| 1 | 53.24 | 7.424 |
| 2 | 56.11 | 92.576 |

## 6.0 X-Ray Crystallographic Data

## Crystal Data and Experimental

Crystal Submitted by: Pablo Guzman
Structure solved by: Kelly Kluge




**Crystal Data.** $C_{14}H_{14}Cl_2O_2$, M = 285.15, orthorhombic, $P2_12_12_1$ (No. 19), $a = 5.8584(3)$ Å, $b = 7.5562(4)$ Å, $c = 30.2791(16)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1340.37(12)Å^3$, $T = 173(2)$ K, $Z = 4$, $\mu$(Mo K$\alpha$) = 4.284, 7124 reflections measured, 2386 unique ($R_{int} = 0.0433$) which were used in all calculations. The final $wR_2$ was 0.1287 (all data) and $R_1$ was 0.0472 ($I > 2\sigma(I)$).

**Experimental.** Single crystals of $C_{14}H_{14}Cl_2O_2$ (**peg1121**) were recrystallised from a mixture of DCM and hexane.. A suitable crystal ($0.142 \times 0.140 \times 0.069 mm^3$) was selected and mounted on a loop paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173(2) K during data collection. Using Olex2 [1], the structure was solved with the XM [2] structure solution program, using the Dual Space solution method. The model was refined with the ShelXL [3] refinement package using Least Squares minimisation.

| **Compound** | peg1121 |
|---|---|
| CCDC | |
| Formula | $C_{14}H_{14}Cl_2O_2$ |
| $D_{calc.}$/ g cm$^{-3}$ | 1.413 |
| $\mu$/ mm$^{-1}$ | 4.284 |
| Formula Weight | 285.15 |
| Colour | colourless |
| Shape | prism |
| Size/$mm^3$ | $0.142 \times 0.140 \times 0.069$ |
| T/K | 173(2) |
| Crystal System | orthorhombic |
| Space Group | $P2_12_12_1$ |
| a/Å | 5.8584(3) |
| b/Å | 7.5562(4) |
| c/Å | 30.2791(16) |
| $\alpha$/° | 90 |
| $\beta$/° | 90 |
| $\gamma$/° | 90 |
| $V$/ Å$^3$ | 1340.37(12) |
| $Z$ | 4 |
| $\Theta_{min}$/° | 2.919 |
| $\Theta_{max}$/° | 68.931 |
| Measured Refl. | 7124 |
| Independent Refl. | 2386 |
| Reflections Used | 2135 |
| $R_{int}$ | 0.0433 |
| Parameters | 176 |
| Restraints | 4 |
| Largest Peak Largest Peak | 0.328 |
| Deepest Hole | -0.360 |
| GooF | 1.031 |
| $wR_2$(all data) | 0.1287 |
| $wR_2$ | 0.1237 |
| $R_1$(all data) | 0.0533 |
| $R_1$ | 0.0472 |

# References


[1] Olex2 (Dolomanov et al., 2009)

[2] SHELXS-97 (Sheldrick, 2008)

[3] SHELXL-97 (Sheldrick, 2008)

Table 1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\mathring{A}^2 \times 10^3$) for **peg1121**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| C1 | 7283(7) | −25(6) | 2436.7(12) | 42.1(8) |
| C2 | 6231(7) | 715(6) | 2803.2(15) | 44.8(9) |
| C3 | 7289(7) | 617(6) | 3210.2(14) | 42.9(9) |
| C4 | 9411(6) | −244(5) | 3256.3(13) | 38.7(8) |
| C5 | 10421(7) | −930(6) | 2879.9(15) | 43.9(9) |
| C6 | 9388(8) | −841(6) | 2470.4(14) | 45.6(9) |
| C7 | 10526(7) | −450(5) | 3705.0(14) | 41.9(8) |
| C8 | 11010(8) | 1404(6) | 3911.2(15) | 48.5(10) |
| C9 | 12672(8) | 1281(6) | 4291.9(15) | 46.1(9) |
| C10 | 11786(9) | 986(9) | 4750.2(17) | 60.0(13) |
| C11 | 9620(8) | −147(9) | 4761.1(15) | 59.5(12) |
| C12 | 9934(8) | −1769(7) | 4476.5(16) | 51.2(11) |
| C13 | 9033(7) | −1675(6) | 4002.4(14) | 43.8(9) |
| C14 | 8902(10) | −3492(7) | 3797.6(17) | 56.1(11) |
| Cl1 | 5931.1(18) | 89.3(15) | 1923.0(3) | 51.9(3) |
| Cl2 | 6699(2) | −4800.3(18) | 4051.4(4) | 62.9(4) |
| O1 | 14700(6) | 1390(5) | 4224.8(13) | 57.6(9) |
| O2 | 10896(8) | −3065(6) | 4610.1(15) | 74.4(12) |

Table 2: Anisotropic Displacement Parameters ($\times 10^4$) **peg1121**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*^2 U_{11} + ... + 2hka \times b \times U_{12}]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C1 | 45.9(18) | 41.5(18) | 38.9(18) | 4.4(17) | −4.4(14) | −5.9(18) |
| C2 | 39.1(19) | 47(2) | 48(2) | 5.8(17) | −0.2(16) | 3.2(17) |
| C3 | 41.9(19) | 47(2) | 39.4(19) | 2.9(16) | 3.0(16) | 4.7(16) |
| C4 | 38.5(17) | 38.5(18) | 39.1(18) | 1.4(16) | −0.2(14) | −2.0(16) |
| C5 | 39.6(19) | 45(2) | 47(2) | −2.1(18) | 1.6(16) | 3.7(17) |
| C6 | 50(2) | 46(2) | 41(2) | −4.3(17) | 1.1(17) | 2.6(19) |
| C7 | 38.1(17) | 44(2) | 43(2) | 0.8(17) | 1.4(15) | 2.2(15) |
| C8 | 50(2) | 46(2) | 49(2) | −0.4(18) | −2(2) | 2.0(19) |
| C9 | 43(2) | 49(2) | 47(2) | −5.4(18) | −0.7(17) | 1.4(17) |
| C10 | 48(2) | 86(4) | 46(2) | −7(3) | 0(2) | −10(3) |
| C11 | 51(2) | 87(4) | 41(2) | −5(3) | 4.2(17) | −14(3) |
| C12 | 41(2) | 64(3) | 48(3) | 10(2) | −2.7(18) | −8(2) |
| C13 | 44(2) | 48(2) | 40(2) | 3.6(17) | −1.3(17) | −0.7(17) |
| C14 | 65(3) | 54(2) | 50(2) | 3(2) | 12(2) | −8(2) |
| Cl1 | 57.3(5) | 56.8(6) | 41.7(5) | 3.8(5) | −11.9(4) | −5.6(5) |
| Cl2 | 76.7(7) | 63.0(7) | 49.1(6) | 5.9(5) | −2.5(5) | −22.7(6) |
| O1 | 45.3(18) | 68(2) | 60(2) | −0.4(17) | −0.8(15) | −7.2(15) |
| O2 | 68(2) | 83(3) | 72(3) | 19(2) | −21(2) | 4(2) |

Table 3: Bond Lengths in Å for **peg1121**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| C1 | C2 | 1.387(6) | C8 | C9 | 1.512(6) |
| C1 | C6 | 1.383(6) | C9 | C10 | 1.498(7) |
| C1 | Cl1 | 1.748(4) | C9 | O1 | 1.208(6) |
| C2 | C3 | 1.381(6) | C10 | C11 | 1.531(7) |
| C3 | C4 | 1.410(6) | C11 | C12 | 1.509(8) |
| C4 | C5 | 1.385(6) | C12 | C13 | 1.531(6) |
| C4 | C7 | 1.515(5) | C12 | O2 | 1.200(7) |
| C5 | C6 | 1.381(6) | C13 | C14 | 1.508(6) |
| C7 | C8 | 1.560(6) | C14 | Cl2 | 1.798(5) |
| C7 | C13 | 1.560(6) | | | |

Table 4: Bond Angles in ° for **peg1121**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C2 | C1 | Cl1 | 119.4(3) | C9 | C8 | C7 | 111.5(4) |
| C6 | C1 | C2 | 121.1(4) | C10 | C9 | C8 | 119.5(4) |
| C6 | C1 | Cl1 | 119.5(3) | O1 | C9 | C8 | 120.1(5) |
| C3 | C2 | C1 | 119.5(4) | O1 | C9 | C10 | 120.4(5) |
| C2 | C3 | C4 | 120.6(4) | C9 | C10 | C11 | 113.0(4) |
| C3 | C4 | C7 | 121.1(3) | C12 | C11 | C10 | 109.9(4) |
| C5 | C4 | C3 | 117.9(4) | C11 | C12 | C13 | 117.1(4) |
| C5 | C4 | C7 | 121.0(4) | O2 | C12 | C11 | 121.8(5) |
| C6 | C5 | C4 | 122.3(4) | O2 | C12 | C13 | 121.1(5) |
| C5 | C6 | C1 | 118.6(4) | C12 | C13 | C7 | 112.1(4) |
| C4 | C7 | C8 | 110.2(3) | C14 | C13 | C7 | 109.3(4) |
| C4 | C7 | C13 | 109.7(3) | C14 | C13 | C12 | 111.1(4) |
| C8 | C7 | C13 | 113.8(4) | C13 | C14 | Cl2 | 111.2(3) |

Table 5: Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **peg1121**.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H7 | 12028 | −1051 | 3660 | 50 |
| H8A | 11645 | 2197 | 3682 | 58 |
| H8B | 9560 | 1926 | 4017 | 58 |
| H10A | 11458 | 2147 | 4888 | 72 |
| H10B | 12984 | 399 | 4928 | 72 |
| H11A | 9289 | −509 | 5069 | 71 |
| H11B | 8309 | 553 | 4651 | 71 |
| H13 | 7454 | −1173 | 4012 | 53 |
| H14A | 10390 | −4097 | 3832 | 67 |
| H14B | 8586 | −3377 | 3478 | 67 |
| H2 | 4810(50) | 1370(70) | 2765(18) | 52(7) |
| H5 | 11960(40) | −1390(70) | 2922(18) | 52(7) |
| H3 | 6480(90) | 1190(70) | 3451(12) | 52(7) |
| H6 | 10270(80) | −1240(70) | 2215(12) | 52(7) |