Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper-Catalyzed Enantioselective Synthesis of Bridged Bicyclic Ketals from 1,1-Disubstituted-4-methylene-1,6-hexanediols and Related Alkenols

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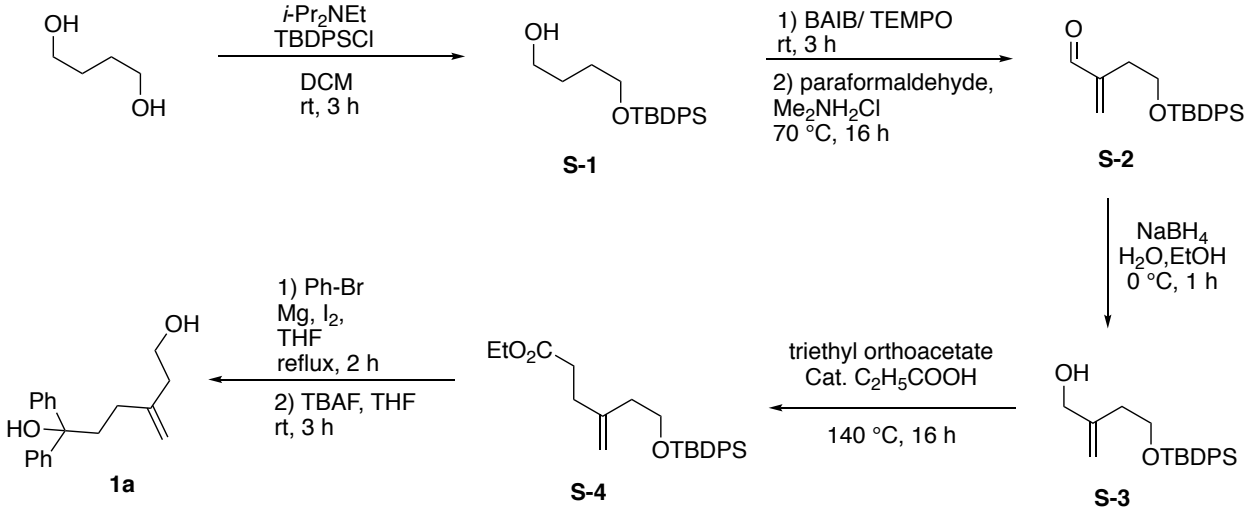
General Information: All reagents were used out of the bottle as purchased from the supplier without further purification unless otherwise noted. Achiral bis(oxazoline) ligand 4, 5-dihydro-2-(2-(4,5-dihydrooxazol-2-yl)propan-2-yl)oxazole, (achiral box) was used to generate racemic samples for HPLC analysis for % ee determination. It was synthesized using our previously reported procedure.[1] Chiral bisoxazoline ligands, (*S*)-*t*-Bu-Box and (*S*)-*i*-Pr-Box, were obtained from Acros chemicals and used directly from the bottle. The MnO_2 used was obtained from Aldrich as an activated, <5 μm powder of 85% purity and used out of the bottle as supplied. All other reagents were purchased from Sigma-Aldrich, Acros or TCI. Solvents were purified using a solvent filtration system purchased from Contour Glass Co (Irvine, California). $PhCF_3$ was purchased from Acros and distilled from P_2O_5 and stored under argon with molecular sieves prior to use. ^1H NMR spectra were recorded at 300 or 400 MHz using Varian instruments. ^{13}C NMR data were recorded at 75 MHz or 101 MHz. Coupling constants (J) are in hertz. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, ABq = AB quartet, and br = broad. IR spectra were taken neat using a Perkin-Elmer FTIR. Wave numbers in cm^{-1} are reported for characteristic peaks. High resolution mass spectra were obtained at the University at Buffalo's mass spectrometry facility. Melting points were obtained on an electrothermal melting point apparatus and are reported uncorrected. X-ray structures were obtained by Dr. Jason Benedict and co-workers at the University of Buffalo. Optical rotations were obtained using a Rudolph Autopol I Polarimeter fitted with a micro cell with a 1 dm path length. Enantiomeric excess was determined by high performance liquid chromatography (HPLC) on a Agilent 1200 instrument using Chiralpak AD-RH analytical column and UV detection.

Substrate Synthesis

The diol substrates **1a** to **1e** were made from 1,4-butanediol, following the route shown below. An oxidation[2] and Mannich[3] protocol was used to install the 1,1-disubstituted alkene. Following this a $NaBH_4$ reduction followed by a Johnson-Claisen reaction and a Grignard addition was used to install the α,α-disubstituted diol. The compounds **S-1**, **S-2** and **S-3** were made and their identity ascertained by comparison of their ^1H NMR to literature data.[4–6]



4-((tert-Butyldiphenylsilyl)oxy)-2-methylenebutanal (S-2)

Following a literature procedure,[2] 4-((tert-butyldiphenylsilyl)oxy)butan-1-ol (2.5 g, 7.6 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (8.0 mL). To this mixture iodobenzene diacetate (2.7 g, 8.4 mmol, 1.1 equiv) and TEMPO radical (0.13 g , 0.80 mmol, 0.10 equiv) was added. The resulting mixture was stirred at rt for about 3 h. The reaction was followed by TLC. On completion the reaction was quenched by addition of saturated $Na_2S_2O_3$ (aq). The aqueous layer was extracted with dichloromethane (3 X 15 mL) and the combined aqueous extract was washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated in vacuo to yield the aldehyde whose ^1H NMR matched literature.[7] The obtained crude aldehyde was used without further purification for the Mannich reaction.

Following a literature procedure,[3] the crude aldehyde was dissolved in dichloroethane (10 mL). To this mixture dimethylamine hydrochloride (3.0 g, 38 mmol, 5.0 equiv) and paraformaldehyde (2.2 g, 76 mmol, 10 equiv) were added. The resulting mixture was stirred at 70 °C overnight. The resulting mixture was then cooled to rt, filtered and the residue washed with CH_2Cl_2 (2x20 mL). The resulting organic solution was concentrated in vacuo to yield the Mannich product **S-2.** The crude mixture was purified by column chromatography (silica gel, 100:0 to 50:50 hexanes: EtOAc) to yield the pure α,β-unsaturated aldehyde **S-2** (2.0 g, 77% yield). ^{1}H NMR of the product is consistent with literature data.[5]

^{1}H NMR (300 MHz, $CDCl_3$); δ 9.49 (s, 1H), 7.64 (d, *J* = 7.0 Hz, 4H), 7.30 - 7.49 (m, 6H), 6.35 (s, 1H), 6.05 (s, 1H), 3.77 (t, *J* = 6.2 Hz, 2H), 2.51 (t, *J* = 6.2 Hz, 2H), 1.03 (s, 9H).

Ethyl 6-((tert-butyldiphenylsilyl)oxy)-4-methylenehexanoate (S-4)

Following a literature procedure,[8] 4-((tert-butyldiphenylsilyl)oxy)-2-methylenebutan-1-ol **S-3** (850 mg, 2.49 mmol, 1.0 equiv) was dissolved in triethyl orthoacetate (4.6 mL, 24.9 mmol, 10 equiv). To this solution propionic acid (0.20 mL, 0.24 mmol, 0.1 equiv) was added and the resulting reaction mixture was refluxed overnight. It was then cooled to rt and further to 0 °C. It was then quenched by addition of saturated NH_4Cl (aq) and extracted with EtOAc (3x10 mL). The organic extracts were combined dried with Na_2SO_4 and then concentrated in vacuo. The crude ester was purified by flash column chromatography (silica gel, 0:100 to 40:60 Et_2O /hexanes) to yield the ester **S-4** as a colourless oil (890 mg, 87 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.71 (m, 4H), 7.48-7.40 (m, 6H), 4.81 (s, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.81 (t, *J* = 6.8 Hz, 2H), 2.46-2.42 (m, 2H), 2.37-2.32 (m, 4H), 1. 28 (t, *J* = 7.2 Hz, 3H), 1.10(s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 145.0, 135.5, 133.8, 129.5, 127.5, 111.2, 62.8,

60.2, 39.2, 32.6, 31.1, 26.8, 19.1, 14.2; IR (neat, thin film) ν 2931, 2857, 1735, 1427, 1105 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{35}NaO_3Si$ $[M+H]^+$: 411.2349, found 411.2349.

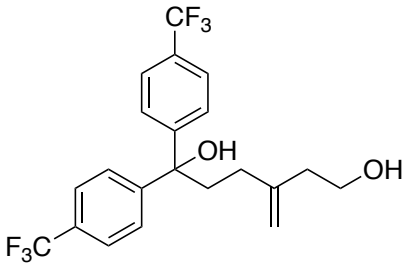
4-Methylene-1,1-diphenylhexane-1,6-diol (1a)

In a vacuum flushed dry round-bottomed flask equipped with a magnetic stir bar, Mg filings (197 mg, 8.2 mmol, 4.4 equiv) and a crystal of iodine were suspended in THF (8 mL). This suspension was colled to 0 °C and then a solution of bromobenzene (0.80 mL, 7.44 mmol, 4.0 equiv), in 2.0 mL THF was added. The resultant mixture was allowed to warm to rt following which it was refluxed for 30 min. The solution was then cooled to rt. and a solution of **S-4** (760 mg, 1.86 mmol, 1 equiv) dissolved in THF (10 mL) was added dropwise. The resulting mixture was refluxed for 2 h with TLC monitoring. The reaction was then quenched by addition of 1 M HCl and extracted into Et_2O (5x10 mL). The combined organic layers were then washed with brine, dried with Na_2SO_4 and then concentrated in vacuo to yield the crude alcohol which was deprotected without further purification.

Deprotection of the protected diol was performed following a literature procedure.[9] A solution of TBAF (1.0 M in THF, 2.3 mL, 1.2 equiv) was added to a solution of the crude alcohol in THF (5.0 mL) at 0 °C. The reaction was allowed to warm to rt and was stirred for 2 h. The reaction was quenched with sat. aq. NH_4Cl and extracted with EtOAc (3x10 mL). The organic extracts were combined, dried with Na_2SO_4 and concentrated in vacuo. The crude alcohol was then purified by flash column chromatography (silica gel, 0:100 to 50:50 EtOAc/hexanes) to yield **5a** (400 mg, 77 % yield) as a white wax.

^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 4H), 7.20 (t, *J* = 6.0 Hz, 4H), 7.14-7.09 (m, 2H), 4.76 (s, 1H), 4.70 (s, 1H), 3.50 (t, *J* = 6.0 Hz, 2H), 2.55 (bs, 1H), 2.36-2.30 (m, 2H), 2.15 (t,

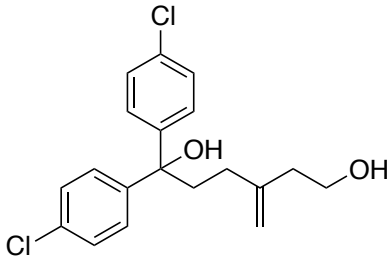
J = 6.0 Hz, 2H), 1.92 (t, *J* = 7.5 Hz, 2H), 1.81 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8, 146.4, 128.1,126.8, 125.9, 111.5, 78.1, 60.3, 39.8, 39.3, 30.0; IR (neat, thin film) ν 3365, 2935, 1644, 1492, 1446, 1044 cm^{-1}; HRMS (FTCIR) calcd for $C_{19}H_{22}O_2Na$ $[M+Na]^+$: 305.1512, found 305.1516.



4-Methylene-1,1-bis(4-(trifluoromethyl)phenyl)hexane-1,6-diol (1d)

The diol **1d** was prepared from the ester **S-4** (500 mg, 1.2 mmol, 1 equiv) using the same procedure as diol **1a** using 1-bromo-4-(trifluoromethyl)benzene (1.3 g, 4.8 mmol, 4 equiv) instead of bromobenzene for the Grignard addition. The resulting crude product was not purified before deprotection. Crude diol **1d** was purified by flash column chromatography (silica gel, 100:0 to 20:80 hexanes:EtOAc) to isolate the purified product (360 mg, 73%) as a white wax.

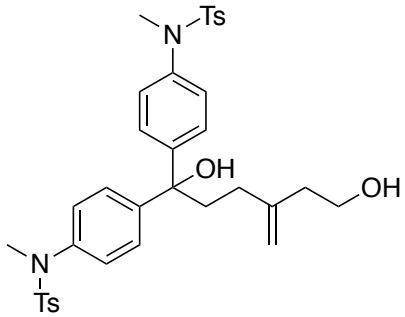
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.5 Hz, 4 H), 7.54 (d, *J* = 8.5 Hz, 4 H), 4.87 (s, 1 H), 4.85 (s, 1H), 3.66 (t, *J* = 8 Hz, 2 H), 2.89 (bs, 1 H), 2.50-2.486 (m, 2 H), 2.28 (t, *J* = 6 Hz, 2 H), 2.06-2.02 (m, 2 H), 1.72 (bs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 145.9, 129.4 (q, *J* = 32.0 Hz), 126.2, 125.3 (q, *J* = 3.0 Hz), 124.0 (q, *J* = 271.0 Hz), 112.1, 77.7, 60.6, 39.5, 39.1, 29.8; ^{19}F NMR (282 MHz, $CDCl_3$, CF_3COOH as internal standard) δ -62.83; IR (neat, thin film) ν 3379, 2945, 1616, 1322, 1068; HRMS (FTICR) calcd for $C_{21}H_{20}F_6O_2Na$ $[M+Na]^+$: 441.1260, found 441.1280.



1,1-Bis(4-chlorophenyl)-4-methylenehexane-1,6-diol (1f)

The diol **1f** was prepared from ester **S-4** (500mg, 1.2 mmol, 1 equiv) using the same procedure as diol **1a** using 4-chloro-1-iodobenzene (1.15 g, 4.8 mmol, 4 equiv) instead of bromobenzene for the grignard step. Purification was done by flash column chromatography (silica gel, 100:0 to 50:50 hexanes:EtOAc) to isolate the pure diol **1f** (277 mg, 62%) as a white wax.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.6 Hz , 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 4.86 (s, 1H), 4.84 (s, 1H), 3.66 (t, *J* = 6.3 Hz, 2H), 2.43 – 2.34 (m, 2H), 2.28 (t, *J* = 6.2 Hz, 2H), 2.06 – 1.97 (bs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0,144.9, 133.0, 128.4, 127.3, 111.9,77.6, 60.5, 39.7, 39.2, 30.0; FT-IR (neat, thin film) ν 3384, 3078, 2938, 1645, 1591, 1489, 1093, 822 cm^{-1} ; HRMS HRMS (EI) calcd for $C_{19}H_{20}Cl_2NaO_2$ $[M+Na]^+$: 373.0732, found 373.0738.

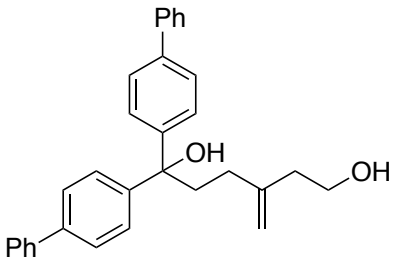


N,N'-((1,6-dihydroxy-4-methylenehexane-1,1-diyl)bis(4,1-phenylene))bis(N,4-dimethylbenzenesulfonamide) (1h)

The diol **1h** was prepared from the ester **S-4** (500mg, 1.2 mmol, 1 equiv) using the same procedure as diol **1a** using N-(4-bromophenyl)-N,4-dimethylbenzenesulfonamide (1.62 g, 4.8 mmol, 4 equiv)

instead of bromobenzene for the Grignard step. Purification was done by flash column chromatography (silica gel, 70:30 to 0:100 hexanes:EtOAc) to isolate the pure diol **1h** (560 mg, 71%) as a brown waxy solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J*=8.2 Hz, 4 H), 7.31 (d, *J*=9.0 Hz, 4 H), 7.18 - 7.27 (m, 5 H), 6.98 - 7.12 (m, 5 H), 4.85 (d, *J* = 4.3 Hz, 2 H), 3.66 (t, *J*=6.4 Hz, 2 H), 3.09 - 3.20 (m, 7 H), 2.34 - 2.45 (m, 9 H), 2.29 (t, *J*=5.9 Hz, 2 H), 1.97 - 2.04 (m, 2 H); ^{13}C NMR(101 MHz, $CDCl_3$) δ 146.2, 145.5, 143.6, 140.2, 133.4, 133.4, 129.3, 127.7, 126.4, 126.1, 111.7, 77.6, 60.5, 39.8, 39.2, 37.9, 30.0, 21.4; FTIR (neat, thin film) v 3509, 2931, 1644, 1598, 1504, 1343, 1170, 1153; HRMS (EI) calcd for $C_{35}H_{40}N_2NaO_6S_2$ $[M+Na]^+$: 671.2220, found 671.2219.



1,1-Di([1,1'-biphenyl]-4-yl)-4-methylenehexane-1,6-diol (1i)

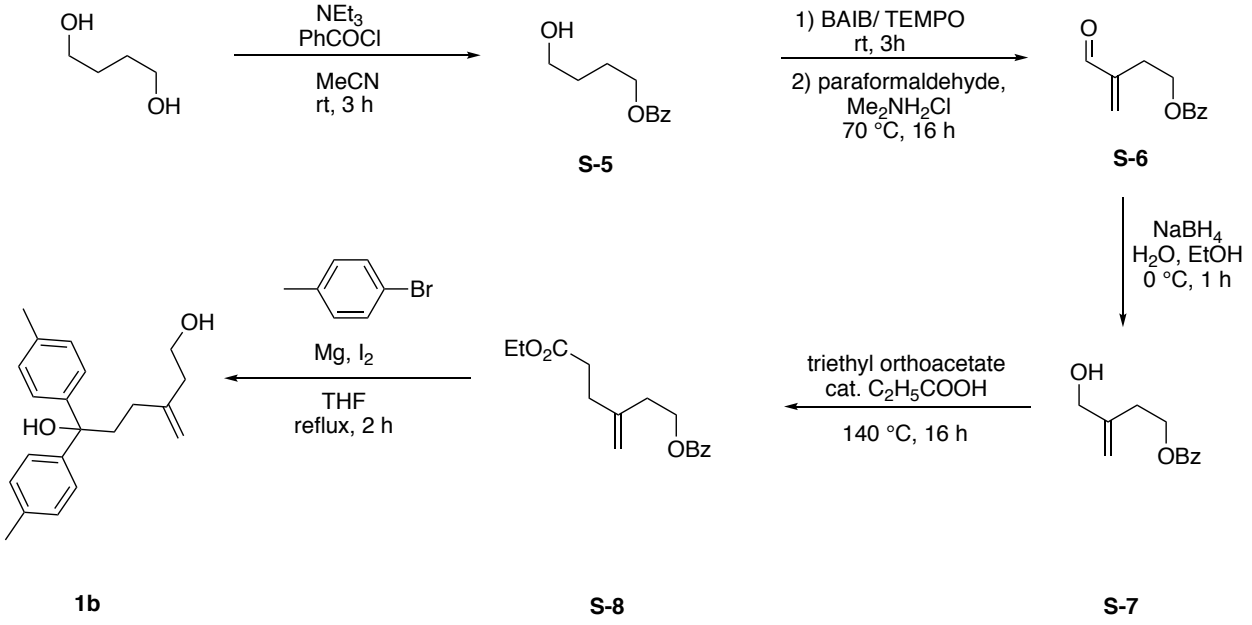
The diol **1i** was prepared was prepared from the ester **S-4** (500 mg, 1.2 mmol, 1.0 equiv) using the same procedure as diol **1a** using 4-bromobiphenyl (1.1 g, 4.8 mol, 4.0 equiv) instead of bromobenzene for the Grignard addition. The resulting product was used crude for the deprotection step. The diol **1i** was purified by flash column chromatography (silica gel, 90:10 to 40:60 hexanes:EtOAc) to isolate the pure diol (410 mg, 81%) as a white waxy solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 - 7.49 (m, 12H), 7.43 (t, *J* = 8 Hz, 4H), 7.34 (t, *J* = 8 Hz, 2H), 4.94 (s, 1H), 4.87 (s, 1 H), 3.69 (t, *J* = 6.0 Hz, 2H), 2.53 (t, *J* = 8 Hz, 2H), 2.38 (bs, 1H), 2.33 (t, *J* = 6.0 Hz, 2H), 2.13 (t, *J* = 8 Hz, 2H), 1.58 (bs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 145.7, 140.6, 139.8, 128.7, 127.3, 127.0, 126.9, 126.4, 111.8, 78.1, 60.4, 40.0, 39.4, 30.1; FTIR (neat,

thin film) ν 3374 (br.), 3056, 3029, 2933, 1644, 1599, 1485, 1041, 1006; HRMS (EI) calcd for $C_{31}H_{30}O_2Na$ $[M+Na]^+$: 457.2138, found 457.2138.

Modified protocol for synthesis of substrates 1b to 1d, 1g

Substrates **1b to 1d and 1g** were synthesized via a modified scheme using a benzoyl ester instead of a silyl ether as the protecting group. A modified protocol was necessary since the presence of electron donating groups on the benzene rings led to acid catalyzed eliminations in during the TBAF deprotection step. **S-5b**, **S-6** and **S-7** were synthesized using literature procedures and their identities ascertained by comparing their ^{1}H NMRs with literature data.[10,11]



6-Ethoxy-3-methylene-6-oxohexyl benzoate (S-8)

The ester **S-8** was made from the protected diol 1,4-butanediol **(**2.1 g, 23.1 mmol, 1.5 eq) using steps similar to the synthesis of ester **S-4.** The crude ester **S-8** was purified by flash column

chromatography (silica gel, 100:0 to 40:60 hexanes:EtOAc) to furnish the ester **S-8** as a clear oil (2.3 g, 54% over 4 steps).

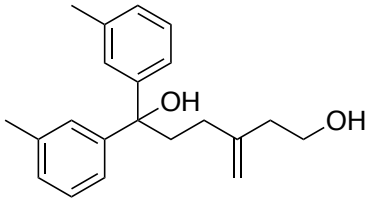
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.97 (m, 2H), 7.57-7.53 (m, 1H), 7.48 – 7.37 (m, 2H), 4.89 (s, 1H), 4.86 (s, 1H), 4.43 (t, *J* = 7.7, 2H), 4.12 (q, *J* = 7.2, 2H), 2.69 – 2.46 (m, 4H), 2.43 (t, *J* = 7.7 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 166.0, 143.7, 132.5, 130.0, 129.2, 128.0, 111.4, 109.8, 62.8, 59.9, 35.0, 32.3, 30.6, 13.9; FTIR (neat , thin film) ν 2981, 1717, 1602, 1271, 1112 cm^{-1}, HRMS (EI) calcd for $C_{16}H_{20}NaO_4$ $[M+Na]^+$ 299.1253, found 299.1260.

4-Methylene-1,1-di-*p*-tolylhexane-1,6-diol (1b)

In a vacuum flushed dry round-bottomed flask equipped with a magnetic stir bar, Mg filings (268 mg, 11.0 mmol, 6.1 equiv) and a crystal of iodine were suspended in THF (10 mL). This suspension was cooled to 0 °C and then a solution of 4-bromotoluene (1.9 g, 10.9 mmol, 6 equiv), in 3 mL THF was added. The resultant mixture was allowed to warm to rt following which it was refluxed for 30 min. The solution was then cooled to rt and a solution of **S-8** (500 mg, 1.8 mmol, 1 equiv) dissolved in THF (10 mL) was added dropwise. The resulting mixture was refluxed for 20 minutes with TLC monitoring. The reaction was then quenched by addition of sat. NH_4Cl and extracted into Et_2O (5X10 mL). The combined organic layers were then washed with brine, dried with Na_2SO_4 and then concentrated in vacuo to yield the crude diol **1b.** This was further purified by column chromatography (silica gel, 90:10 to 60:40 hexanes:EtOAc) to furnish the diol **1b** as a pale yellow oil (432 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.3 Hz, 4H), 7.09 (d, *J* = 8.6 Hz, 4H), 4.85 (s, 1H), 4.79 (s, 1H), 3.60 (t, *J* = 6.2 Hz, 2H), 2.48 (bs, 1H), 2.42 – 2.34 (m, 2H), 2.30 (s, 6H), 2.25 (t, *J* = 6.3

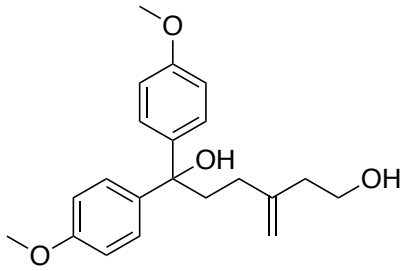
Hz, 2H), 2.04-1.98 (m, 2H), 1.77 (bs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 144.0, 136.3, 128.8, 125.8, 111.3, 77.9, 60.3, 39.9, 39.3, 30.0, 20.9; FTIR (neat, thin film) ν 3300 (bs), 2894, 1604, 1504, 1215, 1089 cm^{-1}; HRMS (EI) calcd. for $C_{21}H_{26}NaO_2$ $[M+Na]^+$ 333.1825, found 333.1832.



4-Methylene-1,1-di-*m*-tolylhexane-1,6-diol (1c)

Diol **1c** was prepared from ester **S-8** (500 mg, 1.8 mmol, 1 equiv) in the same manner as **1b** using 3-bromotoluene (1.9 g, 10.9 mmol, 6.0 equiv) as the source of the Grignard reagent. The crude reaction mixture was purified using flash column chromatography (silica gel, 90:10 to 60:40 hexanes:EtOAc) to yield the diol **1c** as a white wax (350 mg, 62%).

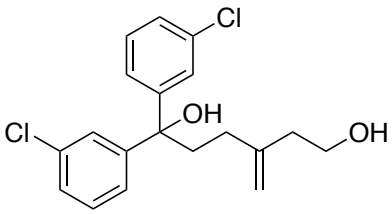
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.23 (m, 2H), 7.22 – 7.12 (m, 4H), 7.06-7.02 (m, 2H), 4.89 (s, 1H), 4.83 (s, 1H), 3.64 (t, *J* = 6.3 Hz, 2H), 2.56 – 2.39 (m, 2H), 2.33 (s, 6H), 2.28 (m, 3H), 2.03 (m,, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.78, 146.47, 137.76, 128.03, 127.60, 126.54, 122.98, 111.59, 78.13, 77.31, 76.99, 76.68, 60.36, 40.02, 39.40, 30.04, 21.63. FTIR (neat, thin film) ν 3379 (br), 2922, 1644, 1604, 1456, 1042 cm^{-1}, HRMS (EI) calcd. for $C_{21}H_{26}NaO_2$ $[M+Na]^+$ 333.1825, found 333.1832.



1,1-Bis(4-methoxyphenyl)-4-methylenehexane-1,6-diol (1e)

Diol **1e** was prepared from ester **S-8** (500 mg, 1.8 mmol, 1.0 equiv) in the same manner as **1b** using 3-bromotoluene (1.9 g, 10.9 mmol, 6.0 equiv) as the source of the Grignard reagent. The crude reaction mixture was purified using flash column chromatography (silica gel, 90:10 to 20:80 hexanes:EtOAc) to yield the diol **1e** as a yellowish oil (510 mg, 82 %).

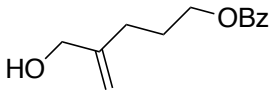
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.9 Hz, 4H), 6.83 (d, *J* = 8.9 Hz, 4H), 4.87 (s, 1H), 4.82 (s, 1H), 3.78 (s, 6H), 3.64 (t, *J* = 6.2 Hz, 2H), 2.49-2.45 (m, 1H), 2.38 (t, *J* = 8 Hz, 2H), 2.28 (t, *J* = 6Hz, 2H), 2.01 (t, *J* = 8 Hz, 2H), 1.71 (bs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 146.4, 139.3, 127.2, 113.4, 111.5, 77.7, 60.4, 55.2, 40.2, 39.4, 30.2; FTIR (neat, thin film) ν 3401(br.), 2931, 1608, 1508, 1246, 1176, 1033 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{26}NaO_4$ $[M+Na]^+$: 365.1723, found 365.1710



1,1-bis(3-chlorophenyl)-4-methylenehexane-1,6-diol (1g)

Diol **1g** was prepared from ester **S-8** (500 mg, 1.8 mmol, 1.0 equiv) in the same manner as **1b** using 3-bromochlorobenzene (2.1 g, 10.9 mmol, 6.0 equiv) as the source of the Grignard reagent. The crude reaction mixture was purified using flash column chromatography (silica gel, 90:10 to 20:80 hexanes:EtOAc) to yield the diol **1g** as a yellowish oil (490 mg, 77 %).

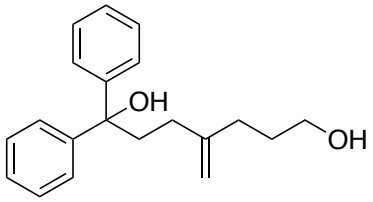
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 2H), 7.28 – 7.17 (m, 6H), 4.87 (s, 1H), 4.84 (s, 1H), 3.66 (m, 2H), 2.43 – 2.35 (m, 2H), 2.28 (t, *J* = 5.6 Hz, 2H), 2.21 (br. s, 1H), 2.01 (t, *J* = 5.6 Hz, 2H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 145.9, 134.3, 129.6, 129.4, 127.3, 127.0, 126.2, 126.1, 124.2, 124.0, 111.9, 77.5, 60.5, 39.5, 39.1, 29.8; FTIR (neat, thin film) FTIR (neat, thin film) ν 3379, 3072, 2941, 1645, 1592, 1572, 1473, 1422, 1044 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{19}O_2Cl_2$ $[M-H]^-$ 349.0762; found 349.0763.



3-(Hydroxymethyl)pent-4-en-1-yl benzoate (S-9)

The allyl alcohol **S-9** was made from 1,5-pentanediol (1.2 g, 11.4 mmol, 1.5 eq) using the same protocol as alcohol **S-7.** The crude ester **S-9** was purified by flash column chromatography (silica gel, 90:10 to 40:60 hexanes:EtOAc) to furnish the ester **S-9** as a clear oil (1.01 g, 60% over 3 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 7.94 (m, 2H), 7.65 – 7.49 (m, 2H), 7.51 – 7.36 (m, 2H), 5.08 (s, 1H), 4.93 (s, 1H), 4.34 (t, *J* = 6.5 Hz, 2H), 4.10 (s, 2H), 2.23 (t, *J* = 7.7 Hz, 2H), 1.96 (m, 2H), 1.90 – 1.65 (bs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 147.7, 132.8, 130.2, 129.5, 128.3, 110.0, 77.3, 76.9, 76.7, 65.8, 64.4, 29.2, 26.7; FTIR (neat, thin film) ν 3423, 2923, 1717, 1602, 1275, 1116, 1033, 712 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{16}NaO_3$ $[M+Na]^+$ 243.0992, found 243.0997.



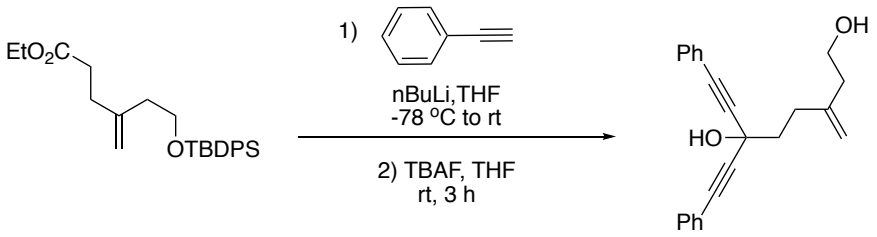
4-Methylene-1,1-diphenylheptane-1,7-diol (1j)

The diol **1j** was prepared from the allyl alcohol **S-9 (**900 mg, 4.09 mmol, 1 eq**),** using the same synthetic protocol as used for diol **1b**. The intermediate ester arising from the Johnson-Claisen was not isolated and used crude for the subsequent grignard reaction. Purification was done by flash column chromatography (silica gel, 90:10 to 50:50 hexanes:EtOAc) to isolate the pure diol **1j** (710 mg, 65% over 2 steps) as a white wax.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.45 (m, 4 H), 7.24 - 7.32 (m, 4 H), 7.15 - 7.23 (m, 2 H), 4.74 (bs, 2 H), 3.57 (t, *J* = 6.2 Hz, 2 H), 2.35 - 2.45 (m, 2 H), 2.15 (s, 1H), 1.95 - 2.10 (m, 4 H), 1.71 (d, *J*=6.2 Hz, 1 H), 1.52 - 1.65 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 146.8, 128.1, 126.8, 126.0, 109.3, 78.2, 62.5, 40.0, 32.5, 30.6, 30.2; FTIR (neat, thin film) υ 3379, 3025, 2940, 1704, 1643, 1598, 1446, 1058 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{24}NaO_2$ $[M+Na]^+$: 319.1668, found 319.1668.

Synthesis of alkyne containing substrates

Substrates **1k and 1l** were prepared from the ester **S-4** via the addition of an organolithium followed by deprotection of the intermediate using a suitable fluoride source.



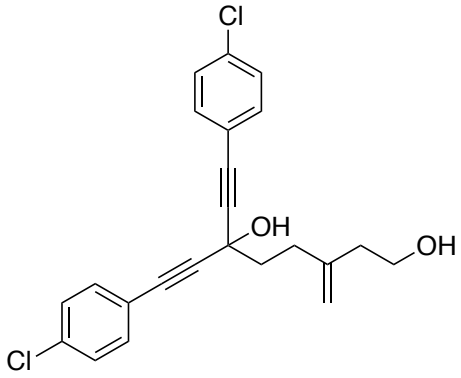
S-4 **1k**

3-Methylene-8-phenyl-6-(phenylethynyl)oct-7-yne-1,6-diol (1k)

To a washed, dried and argon cooled round-bottomed flask equipped with a stir bar, a solution phenylacetylene (500 mg, 4.8 mmol, 4.0 equiv) in THF (2.0 mL) was added. The solution was then cooled to -78 °C, following which, *n*-BuLi (2.5 M in THF, 2.0 mL, 5.0 mmol, 4.1 equiv) was added. The red coloured solution was stirred vigourously at -78 °C for 1 h. Following this, a solution of ester **S-4** (500 mg, 1.2 mmol, 1.0 equiv) was added dropwise at -78 °C. Once the addition was complete the reaction mixture was gradually allowed to warm to rt where it was spun for an additional 30 min. The reaction was then quenched by the addition of 1M HCl and extracted into Et_2O (5 X 10 mL). The organic layers were combined, dried over Na_2SO_4 and then evaporated to yield the protected diol which was used crude for the deprotection.

Deprotection of the protected diol to **1k** was afforded following the same protocol used for substrate **1a**. The crude diol was purified by flash column chromatography (silica gel, 90:10 to 50:50 hexanes:EtOAc) to isolate the pure diol **1k** (210 mg, 52%)as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7.56 (m, 4 H), 7.28 - 7.38 (m, 6 H), 4.97 (s, 1 H), 4.89 (s, 1 H), 3.78 (t, *J*=6.4 Hz, 2 H), 3.14 - 3.33 (bs, 1 H), 2.50 (t, *J* = 8 Hz, 2 H), 2.39 (t, *J* = 6.4 Hz, 2 H), 2.18 - 2.32 (m, 2 H), 1.66 - 1.85 (bs, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 131.8, 128.7, 128.2, 122.0, 112.0, 89.0, 83.7, 64.1, 60.3, 42.1, 60.3, 42.1, 39.3, 30.8; FTIR (neat, thin film) v 3335, 3080, 2928, 2229, 1645, 1597, 1489, 1046 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{22}NaO_2$ [M+Na]: 353.1512, found 353.1511.



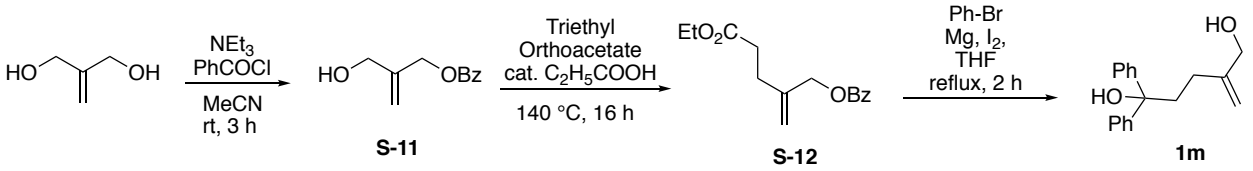
8-(4-Chlorophenyl)-6-((4-chlorophenyl)ethynyl)-3-methyleneoct-7-yne-1,6-diol (1l)

The diol **1l** was made by a similar protocol as **1k** using 4-chlorophenylacetylene (652 mg, 4.8 mmol, 4.0 equiv) for the ester addition step. Deprotection was afforded as per the previously described protocol. The compound was purified using flash column chromatograpy to yield the diol as a white waxy solid (362 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 4.97 (s, 1H), 4.90 (s, 1H), 3.77 (t, *J* = 6.3 Hz, 2H), 2.94 (bs, 1H), 2.46 (t, *J* = 8.0 Hz, 2H), 2.38 (t, *J* = 6.3 Hz, 2H), 2.24 (t, *J* = 8.0 Hz, 2H),; ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 134.9, 133.0, 128.7, 120.3, 112.2, 89.6, 82.9, 64.1, 60.4, 41.9, 39.4, 30.8 ; IR (neat,thin film) v 3513, 3323, 2933, 2229, 1649, 1489, 1312, 1015, 980, 833 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{20}Cl_2NaO_2$ $[M+Na]^+$: 421.0732, found 421.0725.

Modified Scheme for allyl alcohol substrates

The allyl alcohol substrates were made from 2-methylene-1,3-propanediol using a benzoyl protecting group for one of the alcohol groups following which a Johnson-Claisen and Grignard protocol were used to obtain the final diols.



2-(Hydroxymethyl)allyl benzoate (S-11)

To a stirred solution of 2-methylene-1,3-propanediol (4.00 g, 45.0 mmol,. 1.5 equiv) in CH_3CN (20 mL) was added NEt_3 (6.3 mL, 45.0 mmol, 1.5 eq). The resulting solution was cooled in ice following which benzoyl chloride (3.5 mL, 30.0 mmol, 1 eq) was added dropwise. The solution was then allowed to warm up to rt and stirred for 3h. The solvent was then evaporated in vacuo and product isolated by flash column chromatography (silica gel, 90:10 to 40:60, hexanes:EtOAc) as a colourless oil. (4.9 g, 86%).

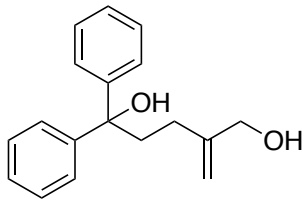
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 7.57 – 7.50 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 5.28 (s, 1H), 5.24 (s, 1H), 4.87 (s, 2H), 4.20 (s, 2H), 2.74 (bs, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 143.3, 133.1, 129.7, 129.5, 128.3, 113.9, 109.9, 77.2, 76.9, 76.7, 65.0, 63.4; FTIR (neat, thin film) ν 3422, 2935, 1719, 1601, 1272, 1113, 710 cm^{-1}; HRMS (EI) calcd. for $C_{11}H_{12}NaO_3$ $[M+Na]^+$ 215.0678, found 215.0673.

5-Ethoxy-2-methylene-5-oxopentyl benzoate (S-12)

The ester **S-12** was made from the protected alcohol **S-11** (2.50 g, 13.0 mmol, 1.0 equiv**)** using the protocol used for **S-4.** The product was isolated by flash column chromatography (silica gel, 100:0 to 60:40 hexanes:EtOAc) as a colourless oil (2.34 g, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.1 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 5.18 (s, 1H), 5.02 (s, 1H), 4.79 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.63 – 2.41 (m, 5H), 1.24 (t, *J* = 7.2 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 166.1, 142.4, 133.0, 130.0, 129.6, 128.4, 113.2,

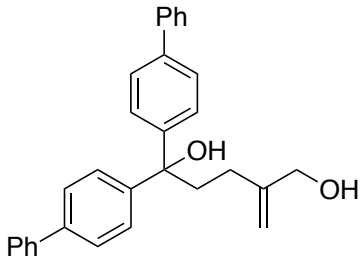
77.3, 77.0, 76.7, 67.2, 60.4, 32.4, 28.2, 14.2; FTIR (neat, thin film) υ 2981, 2933, 1719, 1655, 1601, 1584, 1451, 1267, 1109, 709 cm^{-1}; HRMS (EI) calcd. for $C_{15}H_{18}NaO_4$ $[M+Na]^+$: 2815.1097, found 285.1098.



4-Methylene-1,1-diphenylpentane-1,5-diol (1m)

The diol **1m** was prepared from 2-methylene-1,3-propanediol (500 mg, 1.92 mmol, 1.0 equiv)**,** using the same procedure as the one used for diol **1b**. Purification was performed by flash column chromatography (silica gel, 90:10 to 20:80 hexanes:EtOAc) to isolate the pure diol **1m** (310 mg, 59%) as a white solid.

mp = 79-81 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.42 (d, *J* = 7.4 Hz, 4 H), 7.32 (t, *J* = 7.6 Hz, 4 H), 7.18 - 7.25 (m, 2 H), 5.02 (s, 1 H), 4.89 (s, 1 H), 4.06 (s, 2 H), 2.39 - 2.55 (m, 3 H), 2.07 (t, *J* = 8 Hz, 2 H), 1.66 (bs, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 146.7, 128.1, 126.9, 125.9, 109.6, 78.1, 66.0, 39.9, 27.2; FTIR (neat, thin film) υ 3390, 3059, 2970, 1739, 1648, 1492, 1446, 1061 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{20}NaO_2$ $[M+Na]^+$: 291.1355, found 291.1353.

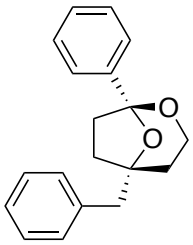


1,1-Di([1,1'-biphenyl]-4-yl)-4-methylenepentane-1,5-diol (1n)

Diol **1n** was prepared in a similar manner as diol **1m** using 4'-bromobiphenyl for the Grignard addition step. The product was purified using flash column chromatography (silica gel, 90:10 to 20:80 hexanes:EtOAc) which yielded the pure diol **1n** as a white solid (350 mg, 61% over 3 steps). Mp = 105-108 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (m, 12H), 7.43 (t, *J* = 7.6 Hz, 4H), 7.36 – 7.30 (m, 2H), 5.06 (s, 1H), 4.93 (s, 1H), 4.10 (s, 2H), 2.55 (t, *J* = 5.9 Hz, 2H), 2.16 (t, *J* = 6.0 Hz, 2H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 145.7, 140.6, 139.8, 128.7, 127.2, 127.0, 126.9, 126.4, 109.7, 78.1, 77.3, 76.9, 76.7, 66.1, 40.0, 27.3; IR (neat, thin film) ν 3380, 3029, 2925, 1599, 1486, 1007, 740, 696 cm^{-1}; HRMS (EI) calcd. for $C_{30}H_{28}NaO_2$ $[M+Na]^+$ 438.1981, found 438.1990.

General Procedure for Copper-Catalyzed Group Transfer Reactions

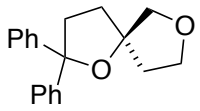
A clean and dry, argon cooled glass reaction tube equipped with a microstir bar was charged with $Cu(OTf)_2$ (7.1 mg, 0.02 mmol, 20 mol%). The $Cu(OTf)_2$ was flame dried lightly under vacuum and the tube then back flushed with argon gas. To this (*S*)-*t*-Bu-Box (7.0 mg, 0.025 mmol, 25 mol%) was added with 0.5 mL of $PhCF_3$ and 4 Å molecular sieves (20 mg, flame dried). The tube was sealed and the mixture was stirred at 60 °C for 2 h. It was then allowed to cool to rt after which substrate (0.1 mmol) was added along with 0.5 mL of $PhCF_3$, MnO_2 (26.1 mg, 0.26 mmol, 260 mol%) and K_2CO_3 (13.8 mg, 0.1 mmol, 100 mol%). The tube was then re-sealed under argon and the reaction mixture stirred at 120 °C. Following this the reaction was cooled to rt, diluted with EtOAc and then filtered through a celite plug. The plug was washed with 3 X 10 mL of EtOAc. The filtrate was then concentrated in vacuo to furnish the crude product which was then purified by flash column chromatography on silica gel and/or preparative TLC.



(1*R*,5*S*)-5-Benzyl-1-phenyl-2,8-dioxabicyclo[3.2.1]octane (2a)

Following the general procedure, diol **1a** (30 mg, 0.1 mmol) was converted to the bridged ketal **2a**. Reaction was run for 60 h. The product **2a** was isolated by flash chromatography (silica gel, 100:0-80-20 gradient hexanes/EtOAc) to give a colourless oil (19 mg, 64% yield).

$[\alpha]_{21.7}^{D}$ = -11.5 (c 0.97, $CHCl_3$); ee = 92% determined by HPLC [Chiralpak AD-RH, 23 : 77 Water:MeOH, 0.8 mL/min, λ= 210 nm, t(major)= 12.5 min, t(minor) = 19.6 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.8, 1.6 Hz, 2H), 7.38-7.29 (m, 7H), 7.28-7.24 (m, 1H), 4.12-4.08 (m, 2H), 3.04 (ABq, J_{AB} = 13.6 Hz, $\Delta\nu_{AB}$ = 34.4 Hz, 2H), 2.48-2.41 (m, 1H), 2.15-1.97 (m, 3H), 1.89-1.83 (m,1H), 1.38-1.33 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 136.8, 130.4, 128.1, 128.0, 127.9,126.4, 125.0, 106.1, 83.4, 60.4, 45.8, 37.3, 34.8, 32.5; IR (neat, thin film) υ 2960, 1496, 1448,1333, 1259 1010 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{20}O_2$ $[M]^+$: 280.1458, found 280.1468.

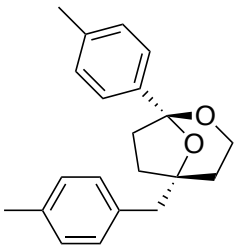


(R)-2,2-Diphenyl-1,7-dioxaspiro[4.4]nonane (3a)

The dioxaspirocycle **3a** was obtained as the minor product during the conversion of the diol **1a** to the bridged ketal **2a**, when 25 mol% $Cu(OTf)_2$ and 31 mol% (S)-*t*-Bu-Box were used. It was

isolated by flash chromatography (silica gel, 100:0-80:20 gradient hexanes/EtOAc) as a colorless oil (4 mg, 14% yield). The products ^{1}H NMR spectrum matched the literature data.[12]

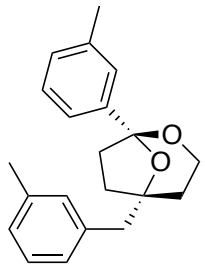
$[\alpha]_{21.7}^{D}$ = -7.3 (c 0.1, $CHCl_3$); ee= 86% determined by HPLC [Chiralpak AD-RH, 99 : 1 hexanes:*i*PrOH, 0.3 mL/min, , λ= 254 nm, t(minor) = 31.5 min, t(major) = 33.7 min) ;. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J*=8.2 Hz, 4 H), 7.26 - 7.33 (m, 3 H), 7.26 (s, 3 H), 7.14 - 7.22 (m, 2 H), 4.06 (q, *J* = 7.6 Hz, 1 H), 3.85 - 3.96 (m, 2 H), 3.61 (d, *J* = 9.0 Hz, 1 H), 2.63 - 2.71 (m, 2 H), 2.19 - 2.29 (m, 1 H), 1.96 - 2.11 (m, 2 H), 1.88 (dt, *J* = 12.5, 8.0 Hz, 1 H).



(1*R*,5*S*)-5-(4-methylbenzyl)-1-(*p*-tolyl)-2,8-dioxabicyclo[3.2.1]octane (2b)

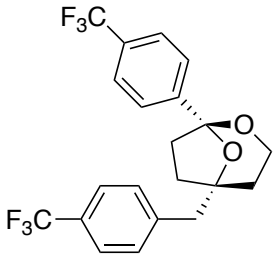
Following the representative procedure, diol **1b** (31 mg, 0.1 mmol) was converted to the bridged ketal **2b**. The reaction was run for 24 h. The product was isolated by flash chromatography (silica gel, 100:0-80:20 gradient hexanes/EtOAc) to give a colourless oil (12 mg, 40% yield).

$[\alpha]_{21.7}^{D}$ = -10.8 (c 0.125, $CHCl_3$); ee = 88% determined by HPLC [Chiralpak AD-RH, 77: 23 CH_3CN/water, 1 mL/min, λ= 250 nm, t(major) = 3.4 min, t(minor) = 4.6 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.22-7.08 (m, 6H), 4.14 – 4.03 (m, 2H), 3.02 (ABq, J_{AB} = 16.0 Hz, $\Delta\nu_{AB}$ = 27.7 Hz, 2H) , 2.41 (ddd, *J* = 13.3, 9.5, 4.5 Hz, 1H), 2.34 (s, 6H), 2.15 – 1.92 (m, 3H), 1.82 (ddd, *J* = 12.6, 9.6, 4.2 Hz, 1H), 1.38 – 1.24 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 137.5, 135.9, 133.8, 130.3, 128.7, 128.6, 124.9, 106.1, 83.4, 60.4, 45.4, 37.2, 34.8, 32.5, 21.2, 21.0; FTIR (neat, thin film) ν 2949, 2868, 1515, 1334, 1078, 813 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{24}O_2$ $[M]^+$ 308.1776, found 308.1774.



(1*R*,5*S*)-5-(3-methylbenzyl)-1-(*m*-tolyl)-2,8-dioxabicyclo[3.2.1]octane (2c)

Following the representative procedure, diol **1c** (31 mg, 0.1 mmol) was converted to the bridged ketal **2c**. The reaction was run for 48 h. The product was isolated by flash chromatography (silica gel, 100:0-80:20 gradient hexanes/EtOAc) to give a pale yellow solid (13 mg, 43% yield). $[\alpha]_{21.7}^{D}$ = -56.7 (c 0.2, $CHCl_3$); ee = 92% determined by HPLC [Chiralpak AD-RH, 60:40 CH_3CN /water, 2 mL/min, λ= 220 nm, t(major) = 26.7 min, t(minor) = 29.7 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 2H), 7.29 – 7.17 (m, 2H), 7.16-7.03 (m, 4H), 4.09 (m, 2H), 3.03 (ABq, J_{ABq} = 13.6 Hz, Δv_{AB} = 35.3 Hz, 2H), 2.48 – 2.38 (m, 1H), 2.36 (s, 6H), 2.16 – 1.93 (m, 3H), 1.88 – 1.77 (m, 1H), 1.40 – 1.31 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 137.6, 137.5, 136.7, 131.3, 128.6, 128.0, 127.9, 127.4, 127.1, 125.6, 122.0, 106.1, 83.4, 60.5, 45.7, 37.3,34.9, 32.4, 21.5, 21.4; FTIR (neat, thin film) ν 3027, 2950, 2922, 2887, 1609, 1585, 1355, 1078 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{25}O_2$ $[M+H]^+$ 309.1849, found 309.1848.

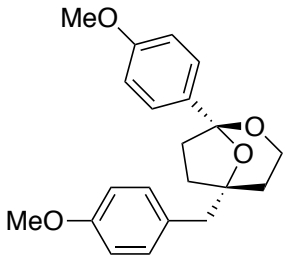


(1R,5S)-5-(4-(Trifluoromethyl)benzyl)-1-(4-(trifluoromethyl)phenyl)-2,8-dioxabicyclo[3.2.1]octane(2d)

Diol **1d** (42 mg, 0.1 mmol) was converted to the bridged ketal **2d** using the general procedure except for $Cu(OTf)_2$ (9.0 mg, 0.025 mmol, 25 mol%) and (*S*)-*t*-Bu-Box (9.1 mg, 0.031 mmol, 31 mol%) were used. The reaction was run for 72 h. The ketal **2d** isolated by flash chromatography (silica gel, 100:0-80:20 gradient hexanes/EtOAc) to give a colorless oil (30 mg, 72% yield).

[**Note:** This substrate was demonstrated at 1 mmol scale. 44% yield, 85% ee was recorded. 34% of the substrate was also recovered.]

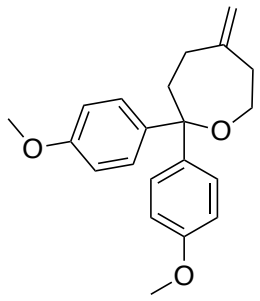
$[\alpha]_{21}^{D}$ = -6.6 (c 0.17, $CHCl_3$); ee >95% determined by HPLC [Chiralpak AD-RH, 75 : 25 acetonitrile/water, 1 mL/min, λ = 254 nm, t(major) = 3.3 min, t(minor) = 4.1 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 - 7.70 (m, 6 H), 7.41 (d, *J* = 8.2 Hz, 2 H), 4.03 - 4.22 (m, 2 H), 3.11 (ABq J_{ABq} = 16.0 Hz, $\Delta\nu_{AB}$ = 36.6, 2 H), 2.37 - 2.50 (m, 1 H), 1.84 - 2.10 (m, 4 H), 1.30 - 1.41 (m, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 140.7, 130.8, 130.2 (q, *J* = 32.0 Hz), 129.0 (q, *J* = 32.0 Hz), 125.5, 125.0 (m), 124.2 (q, *J* = 271.0 Hz), 105.6, 83.3, 60.3, 45.2, 37.3, 34.7, 32.5; ^{19}F NMR (282 MHz, $CDCl_3$, CF_3CO_2H as internal standard) δ -62.83, -62.67; IR (neat, thin film) υ 2960, 1519, 1487,1323, 1091, 1067, 1008 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{18}F_6O_2Na$ $[M+H]^+$: 439.1103, found 439.1101.



(1*R*,5*S*)-5-(4-methoxybenzyl)-1-(4-methoxyphenyl)-2,8-dioxabicyclo[3.2.1]octane (2e)

Diol **1e** (33 mg, 0.1 mmol) was converted to the bridged ketal **2e** using a modified version of the representative procedure in which $Cu(NTf_2)_2$ (12.8 mg, 0.02 mmol, 20 mol%) was used instead of $Cu(OTf)_2$. The reaction was run for 48 h. The product was isolated by flash chromatography (silica gel, 100:0-80:20 gradient hexanes/EtOAc) to give a white solid (13 mg, 40% yield).

$[\alpha]_{22.2}^{D}$ = +6.57 (c 0.1, $CHCl_3$) ; mp = 128-130 °C; ee = 69% determined by HPLC [Chiralpak AD-RH, 85 : 15 CH_3CN/water, 0.5 mL/min, λ= 230 nm, t(major)= 2.7 min, t(minor)= 5.1 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, J = 8.6Hz, 2H), 7.30 – 7.16 (m, 2H), 6.92 – 6.81 (m, 4H), 4.25 – 4.00 (m, 2H), 3.80 (s, 6H), 2.99 (ABq, J_{ABq} = 13.8 Hz, $\Delta\nu_{AB}$ = 25.0 Hz, 2H), 2.40 (m, 1H), 2.00 (m, 3H), 1.83 (m, 1H), 1.46 – 1.25 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 158.2, 134.2, 131.3, 129.0, 126.3, 113.5, 113.3, 106.0, 83.4, 60.4, 55.3, 55.2, 44.8, 37.2, 34.7, 32.4; FTIR (neat, thin film) ν 2993, 2854, 2871, 2838, 1613, 1585, 1514, 1247, 1077 cm^{-1}; HRMS (EI) calcd. for $C_{21}H_{24}NaO_4$ $[M+Na]^+$: 363.1567, found 363.1575.

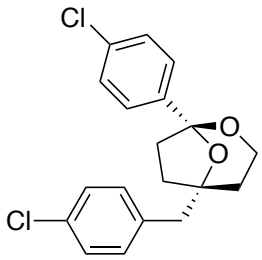


2,2-bis(4-methoxyphenyl)-5-methyleneoxepane (4e)

The cyclic ether **4d** was obtained as the major product when the standard optimized conditions were used. The product was isolated using flash column chromatography (silica gel, 95:4.5:0.5 hexanes:EtOAc:NEt_3) as a colourless oil (20 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.8 Hz, 4H), 6.81 (d, J = 8.8 Hz, 4H), 4.69 (s, 1H), 4.65 (s, 1H), 3.77 (s, 6H), 3.61 (t, J = 5.3 Hz, 2H), 2.56 – 2.44 (m, 4H), 2.30 – 2.22 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 149.9, 139.7, 127.5, 113.2, 110.3, 82.7, 77.3, 76.9, 76.7, 62.6, 55.1,

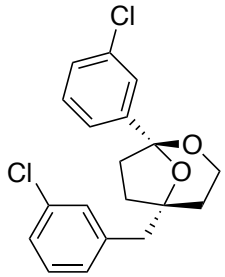
39.4, 39.1, 30.9; FTIR (neat, thin film) ν 2934, 1608, 1508, 1248, 1175, 1033, 826 cm^{-1}; HRMS (EI) calcd. for $C_{21}H_{24}NaO_3$ $[M+Na]^+$ 347.1617, found 347.1625.



(1*R*,5*S*)-5-(4-chlorobenzyl)-1-(4-chlorophenyl)-2,8-dioxabicyclo[3.2.1]octane (2f)

Following the representative procedure, diol **1f** (35 mg, 0.1 mmol) was converted to the bridged ketal **2f**. The reaction was run for 48 h. The product was isolated by flash chromatography (silica gel, 100:0-80:20 gradient hexanes/EtOAc) to give a pale yellow solid (18 mg, 52 % yield).

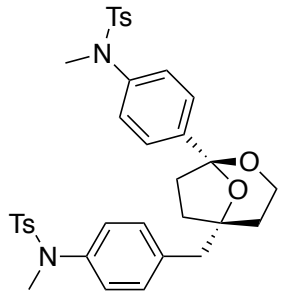
Mp = 112-114 °C; $[\alpha]_{21.7}^{D}$ = -9.31 (c 0.075, $CHCl_3$) ; ee = 88% determined by HPLC [Chiralpak AD-RH, 77 : 23 CH_3CN/water, 1 mL/min, λ= 210 nm, t(major)= 5.4 min, t(minor)= 6.4 min]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 2H), 7.33 – 7.19 (m, 6H), 4.15 - 4.05 (m, 2H), 3.03 (ABq, J_{AB} = 14.0 Hz, $\Delta\nu_{AB}$ = 35.5 Hz, 2 H), 2.46 – 2.32 (m, 1H), 2.10 – 1.78 (m, 4H), 1.37 – 1.28 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 135.1, 133.8, 132.5, 131.8, 128.2, 128.1, 126.5, 1, 105.7, 83.3, 60.4, 45.0, 37.4, 34.7, 32.5; FTIR (neat, thin film) ν 2955, 2932, 2873, 1602, 1492, 1408, 1372, 1228, 1181, 1068 cm^{-1}; HRMS (EI) calcd. for $C_{19}H_{18}Cl_2NaO_2$ $[M+Na]^+$: 371.0576, found 371.0583.



(1*R*,5*S*)-5-(3-chlorobenzyl)-1-(*m*-chlorophenyl)-2,8-dioxabicyclo[3.2.1]octane (2g)

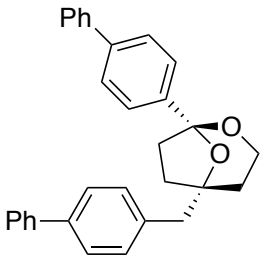
Diol **1g** (35 mg, 0.1 mmol) was converted to the bridged ketal **2g** using a modified version of the representative procedure in which $Cu(NTf_2)_2$ (12.8 mg, 0.02 mmol, 20 mol%) was used instead of $Cu(OTf)_2$. The reaction was run for 48 h. The product was isolated by flash chromatography (silica gel, 100:0-80:20 gradient hexanes/EtOAc) to give a colourless oil (20 mg, 58 % yield).

$[\alpha]_{21.7}^{D}$ = +7.35 (c 0.1, CH_2Cl_2) ; ee = 94% determined by HPLC [Chiralpak AD-RH, 55 : 20: 25 CH_3CN/EtOH/water, 1 mL/min, λ= 210 nm, t(major)= 5.0min, t(minor)= 6.0 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.52 (m, 1H), 7.41-7.38 (m, 1H), 7.33 – 7.22 (m, 5H), 7.25 – 7.15 (m, 1H), 4.16 – 4.04 (m, 2H), 3.04 (ABq, J_{ABq} = 15 Hz, ν_{ABq} = 52.9 Hz), 2.43-2.38 (m, 1H), 2.09 – 1.98 (m, 2H), 197-1.91 (m, 1H), 1.90-1.84 (m, 1H), 1.35 (ddd, *J* = 12.9, 3.2, 1.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 138.5, 134.0, 133.8, 130.5, 130.4, 129.4, 129.4, 129.32, 125.5, 125.5, 123.2, 105.5, 83.2, 60.3, 45.1, 45.1, 37.4, 37.4, 34.8, 32.3; FTIR (neat, thin film) ν 2952, 2873, 1599, 1547, 1477, 1330, 1227, 1161, 1082 cm^{-1}; HRMS (EI) calcd. for $C_{19}H_{19}Cl_2O_2$ $[M+H]^+$: 349.0742, found 349.0742.



N-(4-((1R,5S)-5-(4-((N,4-Dimethylphenyl)sulfonamido)benzyl)-2,8-dioxabicyclo[3.2.1]octan-1-yl)phenyl)-N,4-dimethylbenzenesulfonamide (2h)

Diol **1h** (42 mg, 0.1 mmol) was converted to the bridged ketal **2h** using the general procedure except for $Cu(OTf)_2$ (9.0 mg, 0.025 mmol, 25 mol%) and (*S*)-*t*-Bu-Box (9.1 mg, 0.031 mmol, 31 mol%) were used. The reaction was run for 72 h. Product was isolated by flash chromatography (silica gel, 100:0-80:20 gradient hexanes/EtOAc) to give a pale yellow wax (71 mg, 72 % yield). $[\alpha]_{22.7}^{D}$ = -18.31 (c 0.05, $CHCl_3$); ee = 84% determined by HPLC [Chiralpak AD-RH, 80 : 20 EtOH/water, 0.5 mL/min, λ= 254 nm, t(major) = 24.1 min, t(minor) = 27.1 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J*=8.20 Hz, 6 H), 7.29 - 7.16 (m, 9 H), 7.05 (dd, *J* = 15.4, 8.40 Hz, 5 H), 4.16 - 4.01 (m, 2 H), 3.15 (s, 3 H), 3.12 (s, 3 H), 3.02 (ABq, J_{AB} = 12.0 Hz, $\Delta\nu_{AB}$ = 38.1 Hz, 2 H), 2.40 (s, 6 H), 1.81 - 2.08 (m, 5 H), 1.36-1.30 (m, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 141.3, 140.4, 140.1, 135.8, 133.5, 130.9, 129.3, 127.9, 126.2, 126.1, 125.6, 105.8, 83.3, 60.4, 45.0, 38.0, 37.4, 34.7, 32.5, 21.5; FTIR (neat, thin film) υ 3095, 2970,1597, 1508, 1347, 1170, 1069 cm^{-1}; HRMS (EI) calcd for $C_{35}H_{39}N_2O_6S_2$ $[M+Na]^+$: 647.2244, found 647.2248.

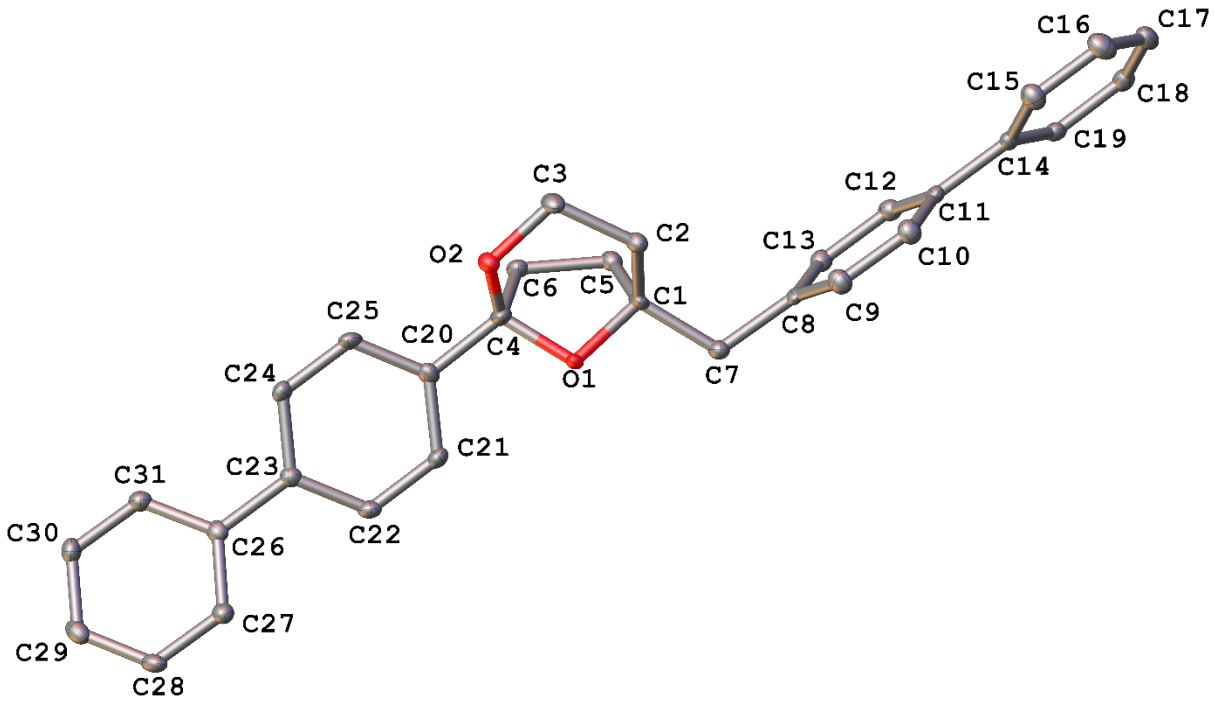


(1*R*,5*S*)-1-([1,1'-Biphenyl]-4-yl)-5-([1,1'-biphenyl]-4-ylmethyl)-2,8-dioxabicyclo[3.2.1]octane (2i)

The diol **1i** (42 mg, 0.1 mmol) was converted to the bridged ketal **2i** following the representative procedure except that $Cu(OTf)_2$ (9.0 mg, 0.025 mmol, 25 mol%), (*S*)-*i*-Pr-Box (8.2 mg, 0.031 mmol, 31 mol%) was used in place of (*S*)-*t*-Bu-Box. Reaction was run for 72 h. The product was purified by flash chromatography (silica gel, 100:0-60:40 gradient hexanes/EtOAc) to yield the product as a white solid (24 mg, 56 % yield).

mp = 192 – 194 °C; $[\alpha]_{21.7}^{D}$ = -12.3 (c 0.1, $CHCl_3$); ee = 60 % (20% with (S)-*t*-Bu-Box) determined by HPLC [Chiralpak AD-RH, 95 : 5 acetonitrile/water, 1.3 mL/min, λ= 250 nm, t(major)= 5-7 min, t(minor)= 8-10 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 - 7.52 (m, 10 H), 7.50 - 7.29 (m, 8 H), 4.22 - 4.03 (m, 2 H), 3.13 (ABq, J_{AB} = 14.0 Hz, $\Delta\nu_{AB}$ = 31.0 Hz, 2 H), 2.49 (m, 1 H), 2.24 – 1.99 (m, 3 H), 1.41 (dd, *J*=12.9, 2.3 Hz, 1 H), 1.96 - 1.85 (m, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 140.9, 140.8, 140.7, 139.4, 135.9, 130.8, 128.8, 128.7, 127.2, 127.1, 127.0, 126.9, 126.8, 125.5, 110.0, 106.1, 83.5, 60.51, 45.4, 37.3, 34.8, 32.6; FTIR (neat, thin film) υ 3027, 2944, 2881, 1599, 1487, 1091, 1076 ; MS (EI) calcd for $C_{31}H_{29}O_2$ $[M+H]^+$ 433.2162, found 433.2157.

X-ray structure of 2i (CDCC- 2020673) – Displayed at 50% ellipsoid contour probability level

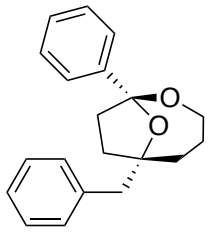


The compound has crystallized in the centrosymmetric space group P21/n, with one complex in the asymmetric unit. The structure contains the mirror image of the of the center rings in proportion of 88:12. The hydrogen atoms were removed from the image above for clarity. The restraint EADP was applied to the five member ring to make C7b have the thermal ellipsoid consistent with the rest of the atoms in the ring.

Table 1 Crystal data and structure refinement for EDS_111703_0m.

Identification code	EDS_111703_0m
Empirical formula	$C_{31}H_{28}O_2$
Formula weight	432.53
Temperature/K	90.0
Crystal system	monoclinic
Space group	$P2_1/n$

a/Å	14.015(2)
b/Å	9.4761(9)
c/Å	17.0238(18)
α/°	90
β/°	95.826(6)
γ/°	90
Volume/Å^3	2249.2(5)
Z	4
ρ_{calc}g/cm^3	1.277
μ/mm^{-1}	0.078
F(000)	920.0
Crystal size/mm^3	0.04 × 0.03 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.59 to 52.806
Index ranges	-17 ≤ h ≤ 17, -11 ≤ k ≤ 11, -21 ≤ l ≤ 20
Reflections collected	21398
Independent reflections	4604 [R_{int} = 0.1985, R_{sigma} = 0.1030]
Data/restraints/parameters	4604/15/320
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0593, wR_2 = 0.1585
Final R indexes [all data]	R_1 = 0.0726, wR_2 = 0.1658
Largest diff. peak/hole / e Å^{-3}	0.32/-0.37

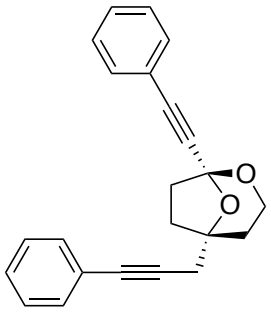


(1*R*,6*S*)-6-Benzyl-1-phenyl-2,9-dioxabicyclo[4.2.1]nonane (2j)

Diol **1j** (42 mg, 0.1 mmol) was converted to the bridged ketal **2j** using the general procedure except for $Cu(OTf)_2$ (9.0 mg, 0.025 mmol, 25 mol%) and (*S*)-*t*-Bu-Box (9.1 mg, 0.031 mmol, 31 mol%) were used. The reaction was run for 72 h. The product was isolated by flash chromatography (silica

gel, 100:0-50:500 gradient hexanes/EtOAc) to yield the product as a colorless oil (20 mg, 67 % yield).

$[\alpha]_{22}^{D}$ = -19.8 (c 0.1, $CHCl_3$); ee = 93% determined by HPLC [Chiralpak AD-RH, 70 : 30 ethanol/water, 1 mL/min, λ= 254 nm, t(major)= 5.5 min, t(minor)= 6.6 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.52 (m, 2 H), 7.21 - 7.36 (m, 8 H), 3.81 - 3.92 (m, 1 H), 3.69 (d, *J*=12.1 Hz, 1 H), 2.98 (ABq, J_{AB} = 14.0 Hz, $\Delta\nu_{ABq}$ = 43.8 Hz, 2 H), 1.62 - 2.19 (m, 7 H), 1.46 - 1.59 (m, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 137.5, 130.9, 127.8, 127.6, 126.4, 125.9, 107.6, 88.0, 61.9, 47.8, 42.1, 37.1, 29.7, 27.6; FTIR (neat, thin film) υ 3029, , 2928, 2859, 1426, 1449, 1356, 1089, 1010 cm^{-1}; HRMS (EI) calcd. for $C_{20}H_{22}O_2$ $[M]^+$: 294.1625, found 294.1616.

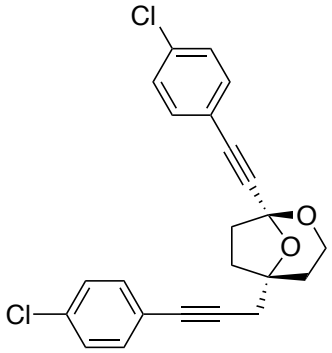


(1*R*,5*S*)-1-(Phenylethynyl)-5-(3-phenylprop-2-yn-1-yl)-2,8-dioxabicyclo[3.2.1]octane (2k)

Following the representative procedure, diol **1k** (31 mg, 0.1 mmol) was converted to the bridged ketal **2k**. The reaction was run for 24 h. The product was isolated by flash chromatography (silica gel, 100:0-80:20 gradient hexanes/EtOAc) furnished the product as a waxy solid. (22 mg, 71 % yield).

$[\alpha]_{22}^{D}$ = -19.6 (c 0.1, $CHCl_3$); ee= 87% determined by HPLC [Chiralpak AD-RH, 86 : 14 ethanol : water, 1 mL/min, λ = 230 nm, t(major) = 4.8 min, t(minor) = 3.7 min] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J*=6.2 Hz, 2 H), 7.40 (d, *J*=2.7 Hz, 2 H), 7.27 - 7.36 (m, 6 H), 4.01 - 4.16 (m, 2 H), 2.86 (ABq, J_{AB} = 18.0 Hz, $\Delta\nu_{ABq}$ = 24.0 Hz, 2 H), 2.55 (m, 2 H), 2.06 - 2.21 (m, 3 H), 1.69 (dd, *J*=12.9,

2.7 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.1, 131.6, 128.9, 128.2, 128.2, 127.9, 123.3, 121.5, 100.1, 85.6, 84.7,83.7, 83.1, 82.9, 60.7, 37.5, 34.0, 32.6, 30.7; IR (neat, thin film) υ 2962, 2247, 2189, 1599, 1540, 1491, 1081, 1026 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{21}O_2$ $[M+H]^+$: 329.1536, found 329.1537.



(1*R*,5*S*)-1-((4-chlorophenyl)ethynyl)-5-(3-(4-chlorophenyl)prop-2-yn-1-yl)-2,8-dioxabicyclo[3.2.1]octane (2l)

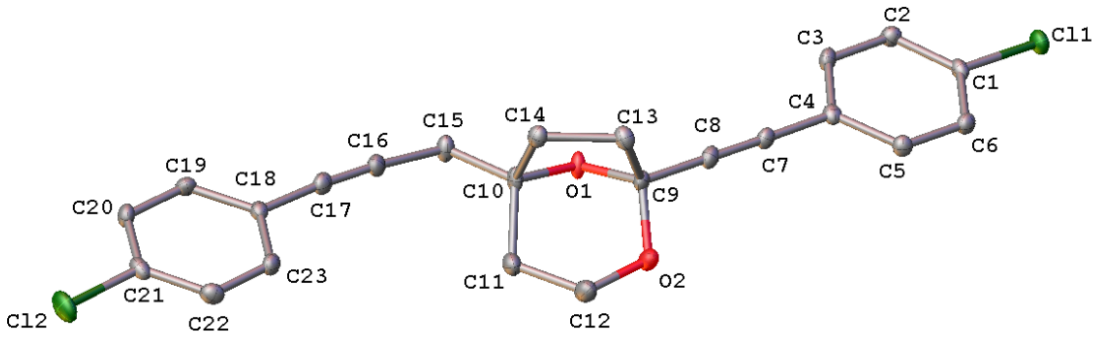
Following the representative procedure, diol **1l** (39 mg, 0.1 mmol) was converted to the bridged ketal **2l**. The reaction was run for 48 h. The product was isolated by flash chromatography (silica gel, 100:0-80:20 gradient hexanes/EtOAc) furnished the product as a white solid. (24 mg, 62% yield).

mp = 130-132 °C; $[\alpha]_{21.7}^{D}$ = -15.3 (c 0.1, $CHCl_3$); ee = 92% determined by HPLC [Chiralpak AD-RH, 77 : 23 CH_3CN/water, 0.8 mL/min, λ= 254 nm, t(major) = 9.1 min, t(minor) = 8.0 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 2H), 7.29 – 7.14 (m, 6H), 4.00 (m, 2H), 2.76 (ABq, J_{AB} = 16.0 Hz, $\Delta\nu_{ABq}$ = 22.9 Hz, 2 H), 2.50 – 2.39 (m, 2H), 2.14 – 1.97 (m, 3H), 1.56 (dd, J = 13.0, 3.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 133.9, 133.3, 132.8, 128.6, 128.5, 121.8, 120.0, 100.0, 86.4, 85.7, 82.9, 82.6, 81.9, 60.7, 37.4, 34.0, 32.5, 30.6; FTIR (neat, thin film) ν 2958, 2930, 2878,

2248, 1592, 1485, 1357, 1082 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{18}Cl_2NaO_2$ $[M+Na]^+$ 419.0576, found 419.0584.

X-ray structure of Compound 2l (CDCC No – 1978089) - Displayed at 50% ellipsoid contour probability level

Using this X-ray structure the (1R, 5S) stereochemistry of the bridged ketal products were ascertained.

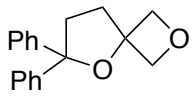


The compound has crystallized in the chiral space group $P2_12_12_1$ with one molecule in the asymmetric unit, and therefore this is the only enantiomer present in the lattice. The hydrogen atoms in the image above were removed for visual clarity.

The Flack parameter is the standard method for estimating the absolute configuration of a molecular structure determined by X-ray diffraction. For this model, the Flack parameter was found not to deviate significantly from zero (0.03). Therefore the current model is an accurate representation of the absolute configuration.

Table 1 Crystal data and structure refinement for EDS_071903_0m.

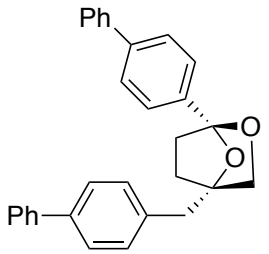
Identification code	EDS_071903_0m
Empirical formula	$C_{23}H_{18}Cl_2O_2$
Formula weight	397.27
Temperature/K	90
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.4867(5)
b/Å	12.1391(11)
c/Å	28.047(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1868.0(3)
Z	4
ρ_{calc}g/cm^3	1.413
μ/mm^{-1}	0.363
F(000)	824.0
Crystal size/mm^3	0.2 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.656 to 52.774
Index ranges	$-6 \le h \le 6$, $-15 \le k \le 14$, $-35 \le l \le 34$
Reflections collected	19753
Independent reflections	3809 [R_{int} = 0.0573, R_{sigma} = 0.0421]
Data/restraints/parameters	3809/0/244
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0304, wR_2 = 0.0685
Final R indexes [all data]	R_1 = 0.0371, wR_2 = 0.0704
Largest diff. peak/hole / e Å^{-3}	0.21/-0.20
Flack parameter	0.03(3)



6,6-diphenyl-2,5-dioxaspiro[3.4]octane (3m)

The diol **1m** (25 mg, 0.1 mmol) was converted to the dioxaspirocycle **3m**, using the representative procedure. Achiral Box **(L1)** (5.4 mg, 0.031 mol, 0.31 equiv) was used as the ligand instead of (S)-*t*-Bu-Box. The reaction was run for 24 h. The product was purified by flash chromatography (silica gel, 100:0:0.5-50:49.5:0.5 gradient hexanes:EtOAc:NEt_3) to yield the product as a colorless oil (13 mg, 54 %)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 - 7.44 (m, 4H), 7.25 - 7.33 (m, 5H), 7.14 - 7.22 (m, 2H), 4.98 (d, *J*=7.0 Hz, 2H), 4.51 (d, *J*=7.6 Hz, 2H), 2.52 - 2.61 (m, 2H), 2.24 - 2.34 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 128.1, 126.9, 125.6, 89.3, 84.7, 82.4, 38.2, 35.6; FTIR (neat, thin film) v 3103, 2941, 2887, 1734, 1697, 1595, 1490, 1143, 1010 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{18}NaO_2$ $[M+Na]^+$ 289.1199, found 289.1197.

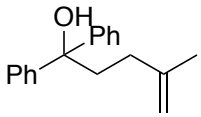


(1*R*,4*S*)-1-([1,1'-biphenyl]-4-yl)-4-([1,1'-biphenyl]-4-ylmethyl)-2,7-dioxabicyclo[2.2.1]heptane (2n)

The diol **1n** (42 mg, 0.1 mmol) was converted to the bridged ketal **2n**, using the representative procedure. The reaction was run for 48 h. The product was purified by flash chromatography (silica gel, 99.5:0:0.5-50:49.5:0.5 gradient hexanes:EtOAc:NEt_3) to yield the product as a white solid (24 mg, 57% yield). [ee was not determined since the product decomposes on the HPLC/ GC column.] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.59 (dt, *J* = 17.0, 8.4 Hz, 8H), 7.49 – 7.30 (m, 8H), 3.83 (d, *J* = 6.1 Hz, 1H), 3.75 – 3.68 (m, 1H), 3.40 – 3.27 (m, 2H), 2.43 – 2.31 (m, 1H),

2.18 (ddd, *J* = 12.2, 9.8, 6.3 Hz, 1H), 1.93 (dt, *J* = 7.9, 5.0 Hz, 2H); ^{13}C NMR (101 Hz, $CDCl_3$) δ 141.7, 140.8, 140.7, 139.7, 135.5, 135.4, 130.1, 128.8, 127.4, 127.2, 127.1, 127.1, 127.0, 126.5, 109.1, 87.1, 74.7, 38.3, 30.0, 32.8; HRMS (EI) calcd. for $C_{30}H_{26}NaO_2$ $[M+Na]^+$ 441.1825, found 441.1816.

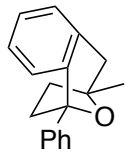
Mechanistic Probe experiment



4-Methyl-1,1-diphenylpent-4-en-1-ol (5b)

The substrate **5b** was synthesized according to literature procedures. The ^{1}H NMR of the synthesized compounde matches literature data.[13]

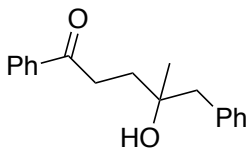
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 4H), 7.32 – 7.25 (m, 4H), 7.23 – 7.17 (m, 2H), 4.70 (s, 1H), 4.68 (s, 1H), 2.46 – 2.37 (m, 2H), 2.29 (s, 1H), 2.04 – 1.95 (m, 2H), 1.71 (s, 3H).



8-Methyl-5-phenyl-6,7,8,9-tetrahydro-5*H*-5,8-epoxybenzo[7]annulene (6b)

The alcohol **5b** (50 mg, 0.2mmol) was converted to the bridged bicyclic ether **6b,** using the standard group transfer conditions. Achiral box (9 mg, 0.025 mmol, 25 mol%) was used as the ligand. Reaction was run for 24 hours. Product was isolated using preparative thin-layer chromatography (silica gel plate, 85:15 hexanes:EtOAc mobile phase), as a colorless oil (25 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.9 Hz, 2H), 7.43 – 7.23 (m, 3H), 7.16 – 7.05 (m, 2H), 7.00 – 6.91 (m, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 3.26 (d, *J* = 16.3 Hz, 1H), 2.76 (d, *J* = 16.2 Hz, 1H), 2.62 – 2.40 (m, 2H), 2.09 – 1.88 (m, 2H), 1.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 142.9, 133.1, 128.7, 128.2, 128.1, 127.5, 127.5, 126.6, 125.6, 124.9, 86.7, 79.8, 77.3, 77.0, 76.6, 43.5, 41.2, 35.6, 27.4; FTIR (neat,thinfilm) υ 3062, 3028, 2970, 1601, 1485, 1451, 1289, 1157, 1090 cm^{-1}; HRMS (EI) calcd. for C18H18NaO [M+Na]+ 273.1249, found 273.1248.



4-Hydroxy-4-methyl-1,5-diphenylpentan-1-one (7)

The ketone **7** was obtained as a side product during the conversion of alcohol **5b** to the ether **6b**. Product was isolated using preparative thin-layer chromatography (silica gel plate, 85:15 hexanes:EtOAc mobile phase), as a pale yellow oil (7 mg, 14 %). [**Note** : This compound is highly acid sensitive and decomposes in $CDCl_3$. NMRs were hence recorded in C_6D_6 Characterization of compound was done on a sample of approximately 90% purity as repeated attempts towards purifying the compound led to decomposition of the sample].

^{1}H NMR (400 MHz, C_6D_6) δ 7.88 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.25 – 7.01 (m, 8H), 2.84 (td, *J* = 9.0, 6.2 Hz, 2H), 2.70 – 2.36 (ABq, J_{AB} = 14.0 Hz, $\Delta\nu_{ABq}$ = 39.5 Hz, 2H), 1.96 – 1.73 (m, 2H), 0.93 (s, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 199.8, 138.2, 137.8, 132.9, 131.1, 128.8, 128.4, 128.2, 128.0, 126.9, 126.4, 126.3, 71.8, 49.3, 35.9, 33.5, 26.7; FTIR (neat,thinfilm) υ 3410 (br.), 3061, 3028, 2929, 1716,1681, 1600, 1449, 1274, 1113, 700 cm^{-1}; HRMS (EI) calcd. for C18H20NaO2 [M+Na]+ 291.1355, found 291.1355.

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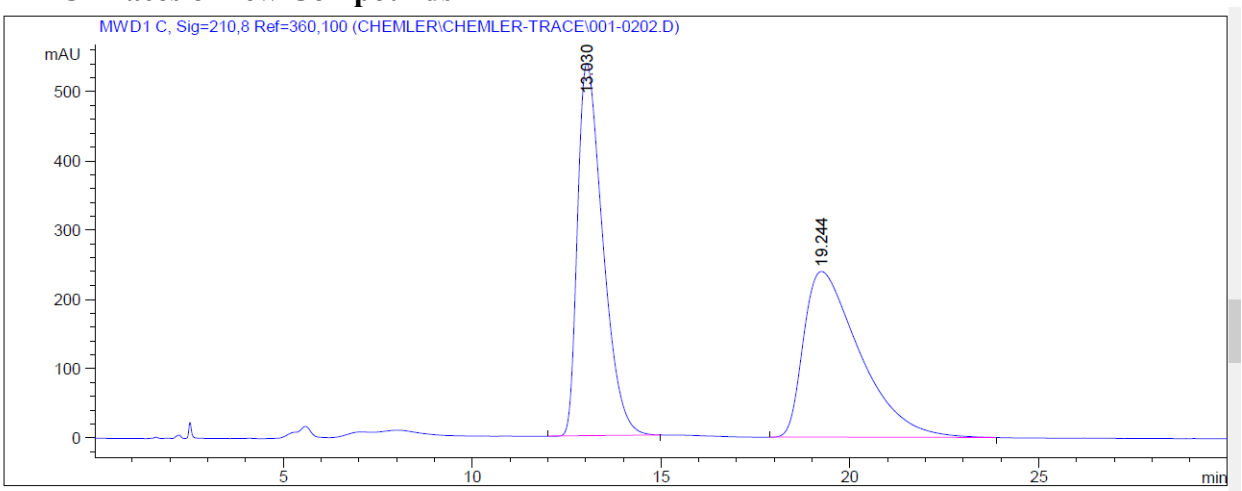
HPLC Traces of new Compounds



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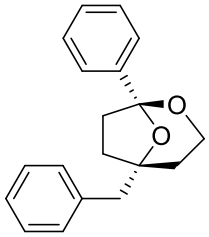

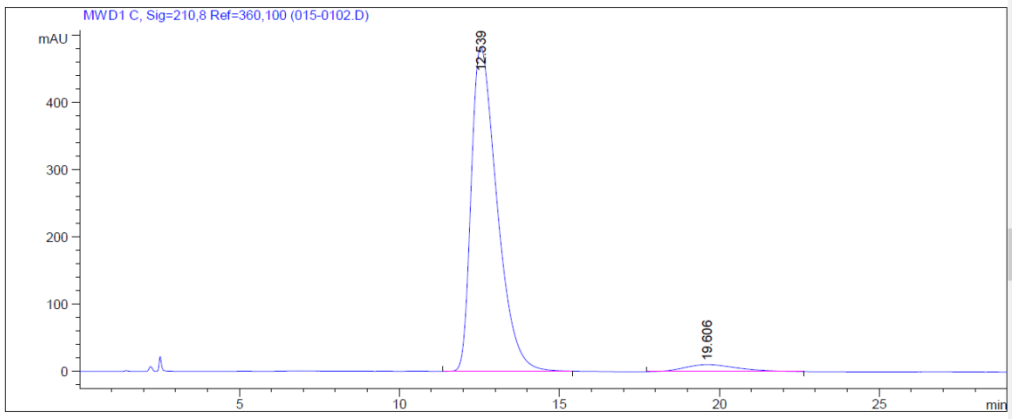

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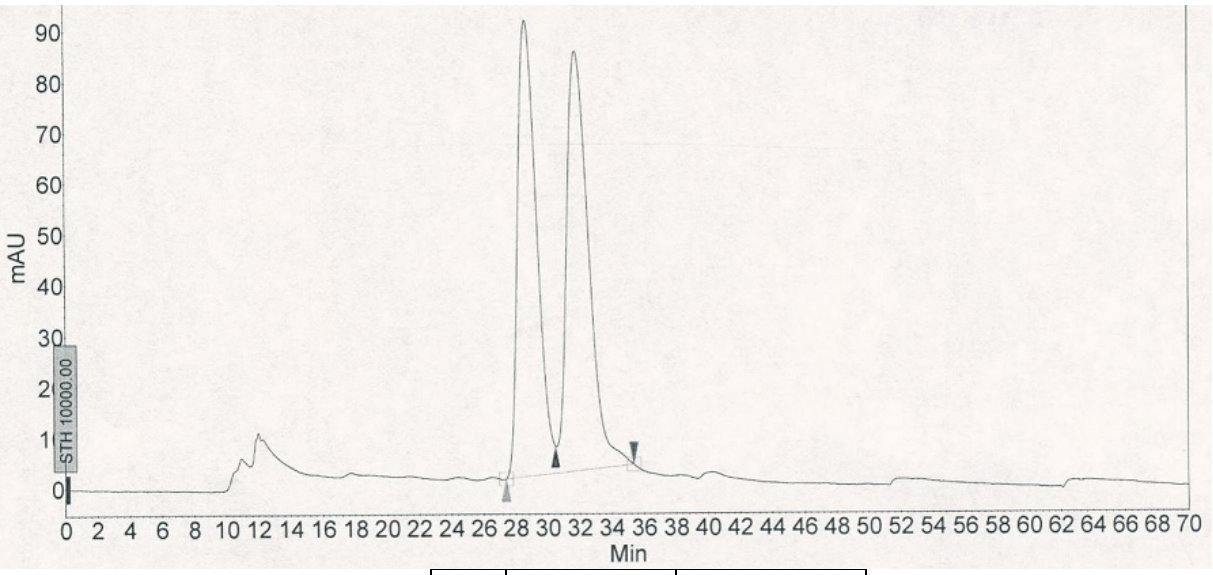

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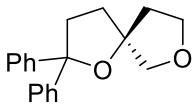

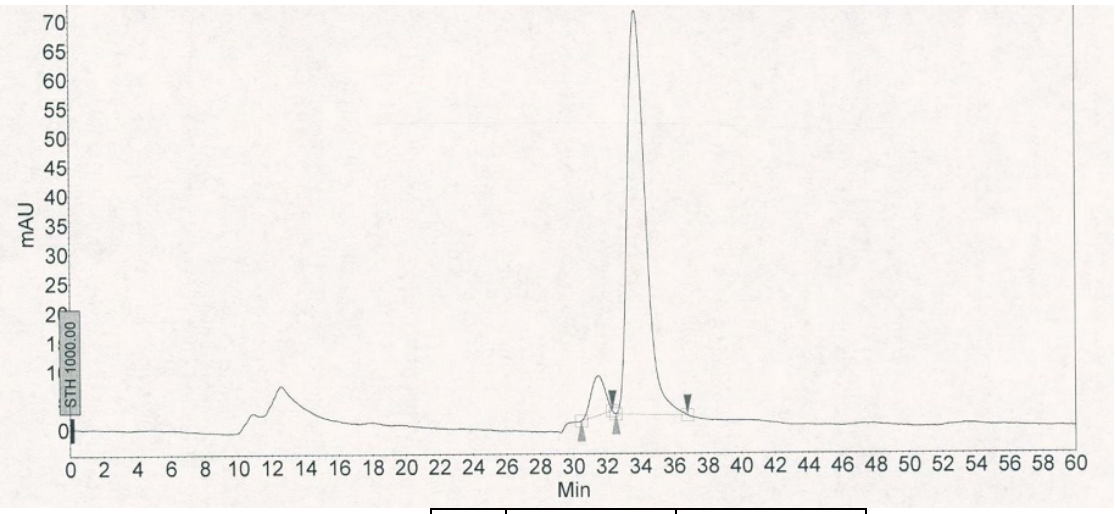

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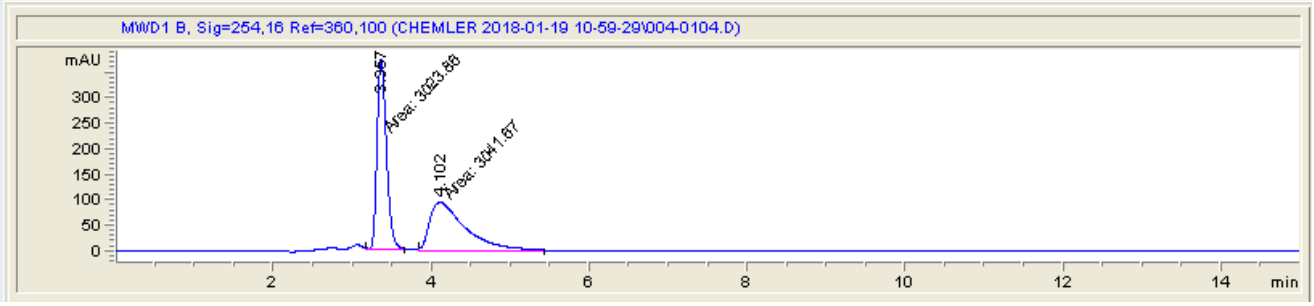

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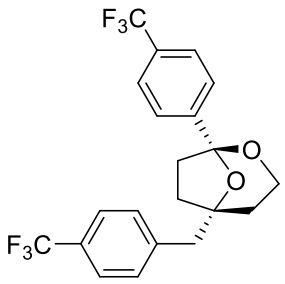

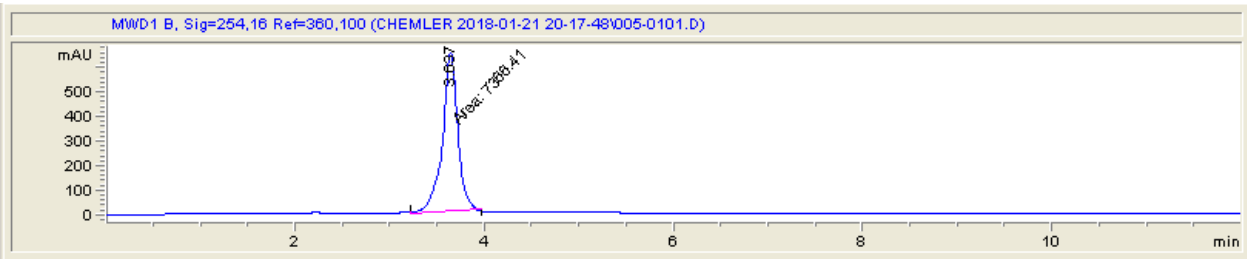

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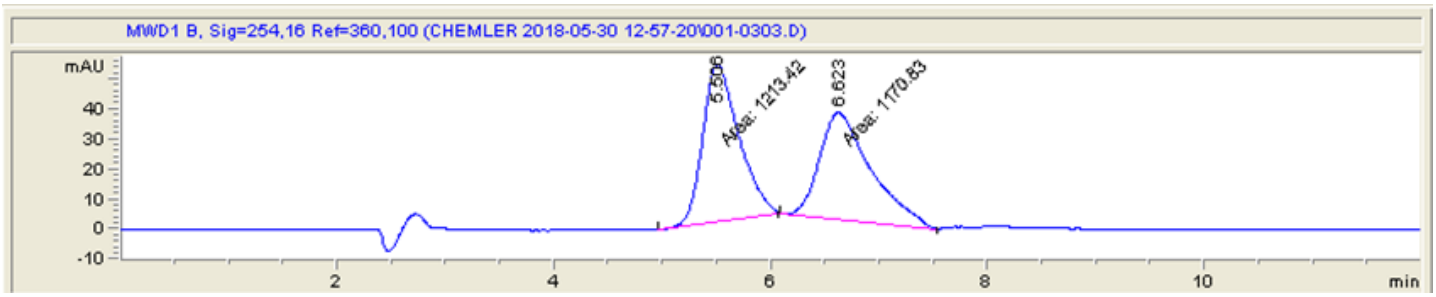

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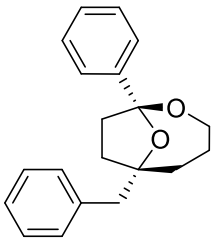

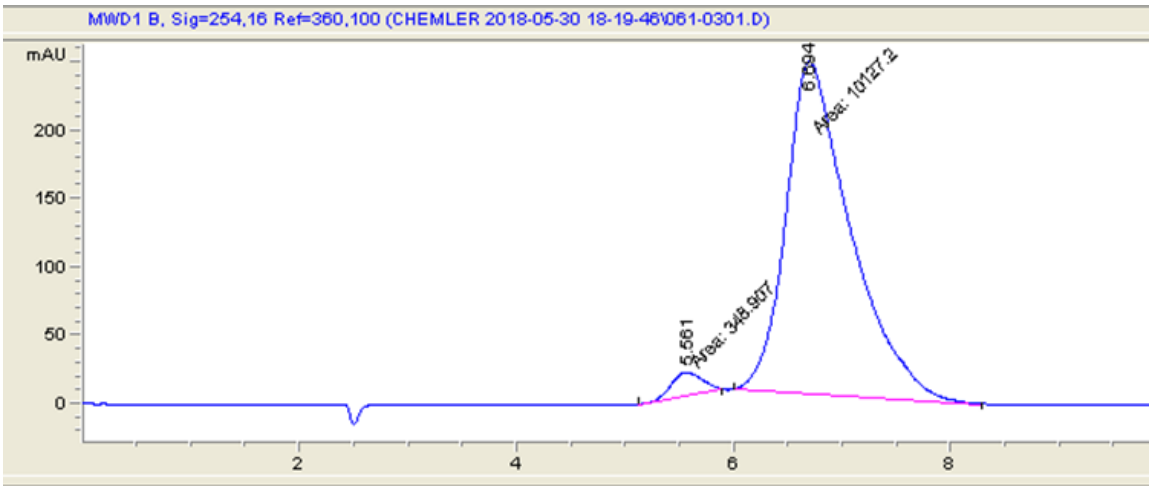

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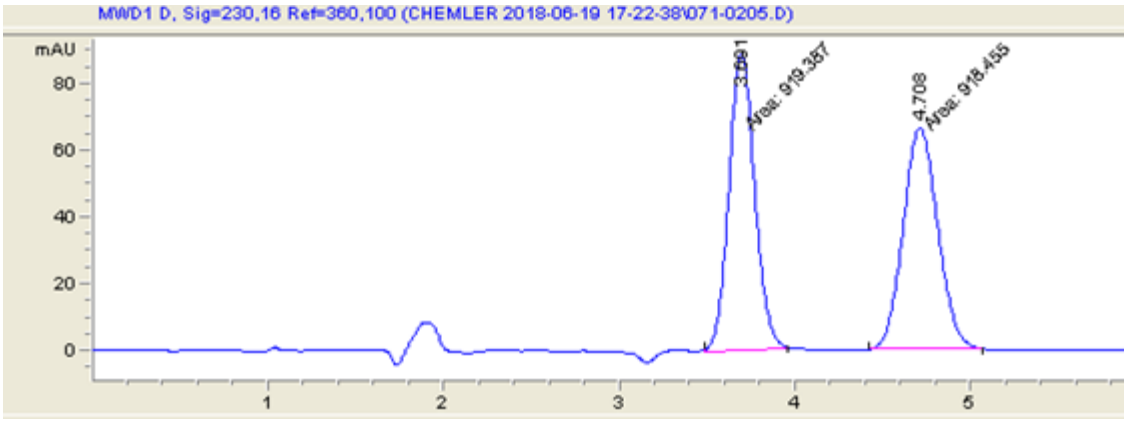

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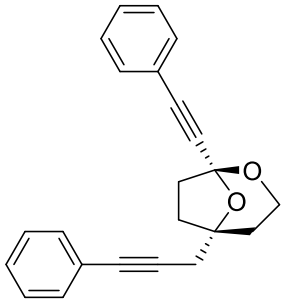

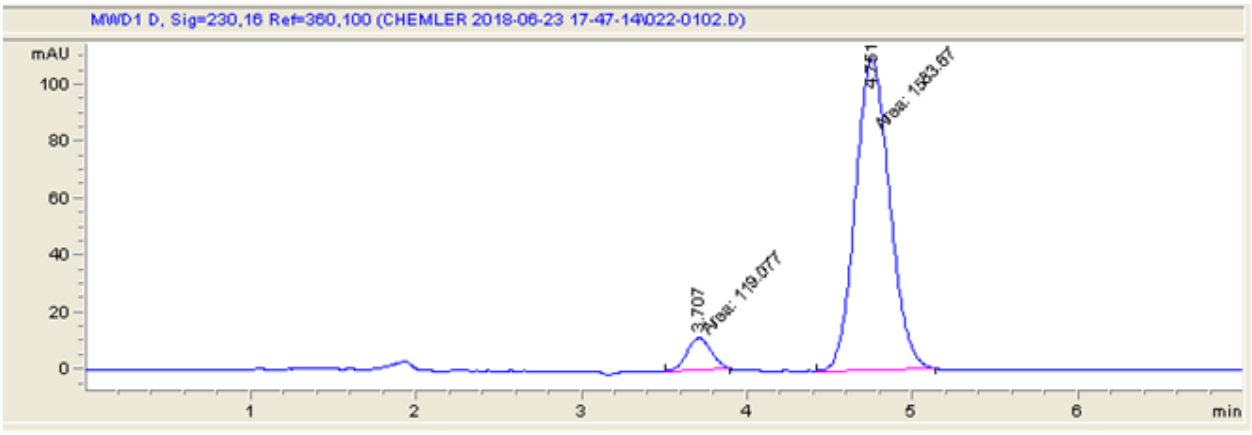

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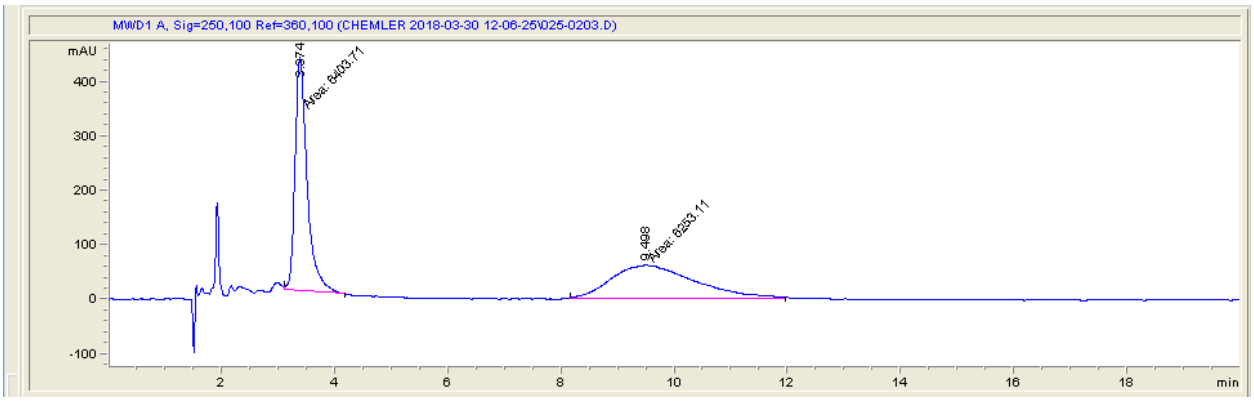

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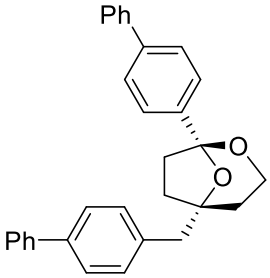

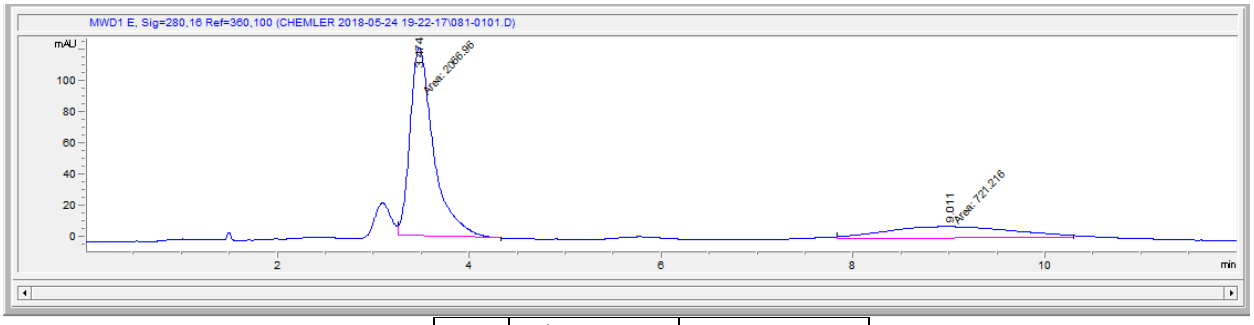

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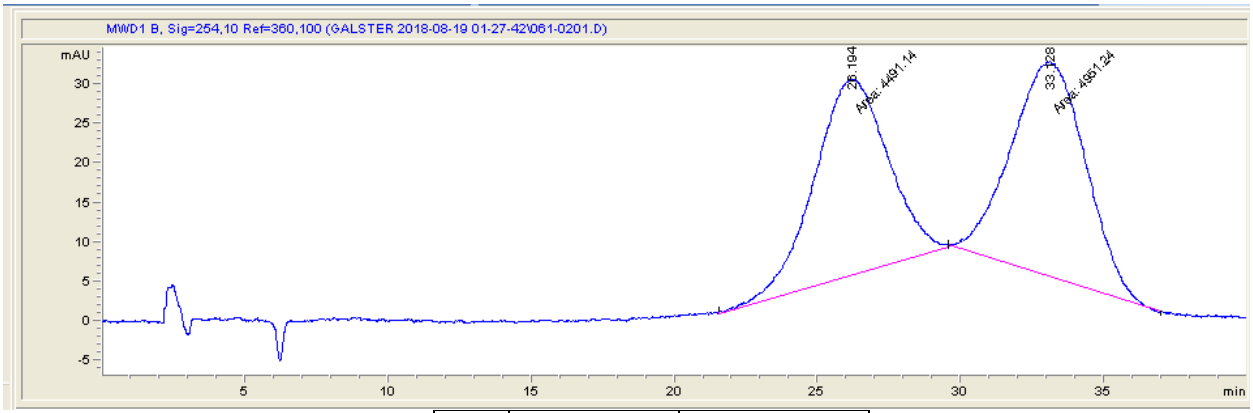

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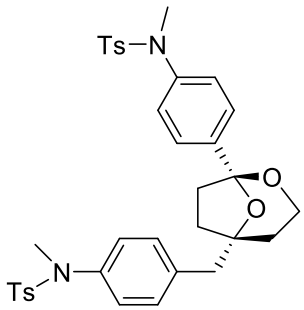

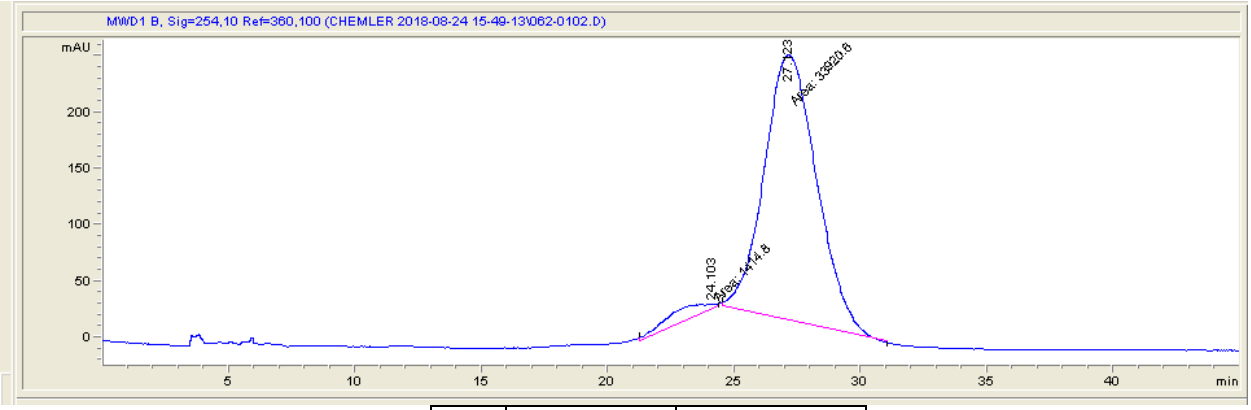

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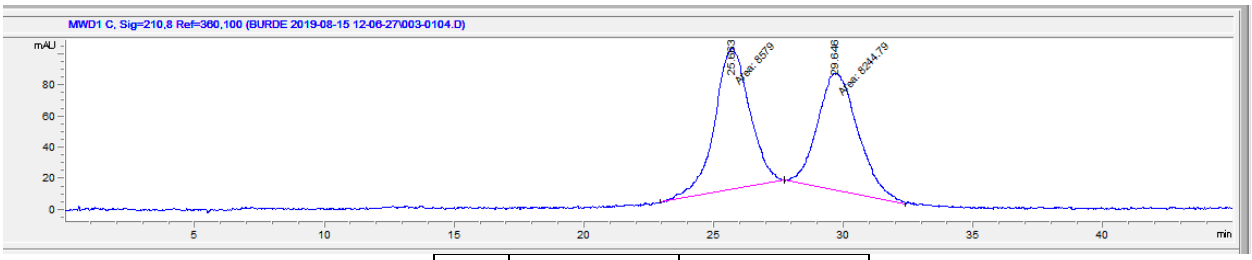

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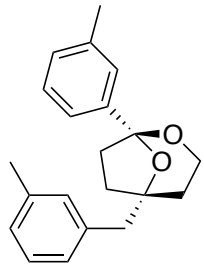
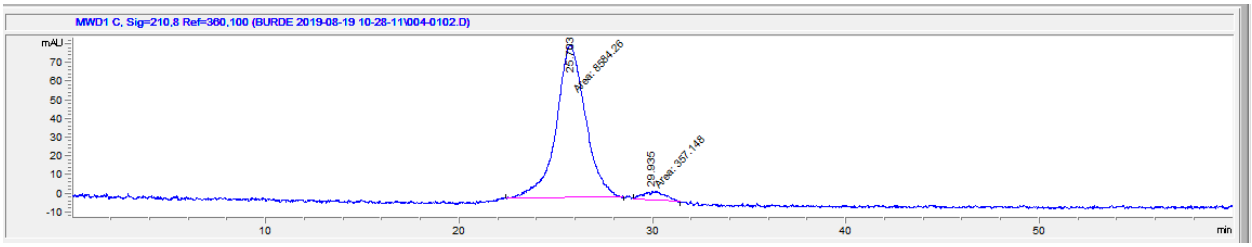
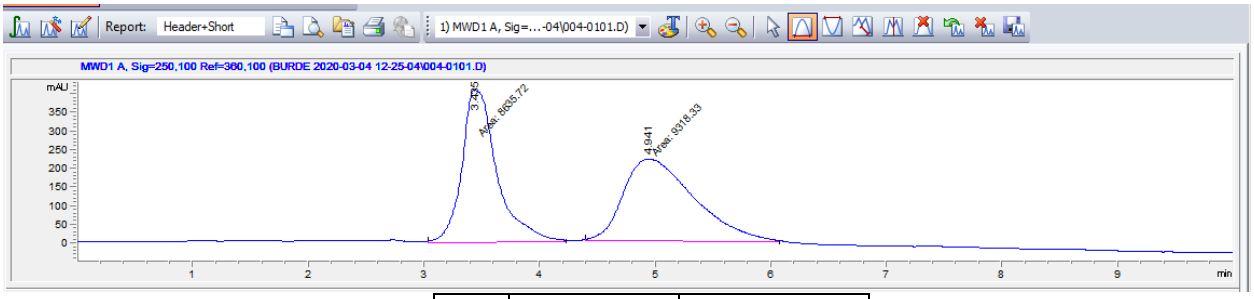
2	29.6	49.1

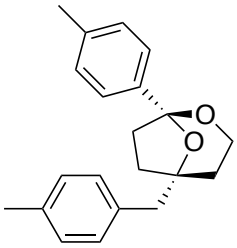


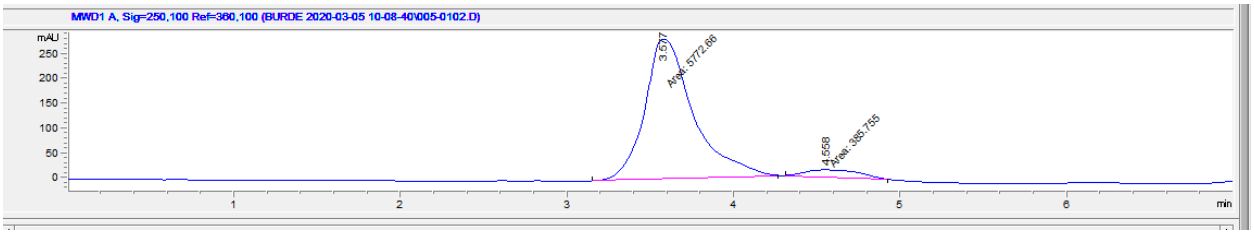


#	Time [min]	Area [%]
1	25.8	96.0
2	29.7	4.0

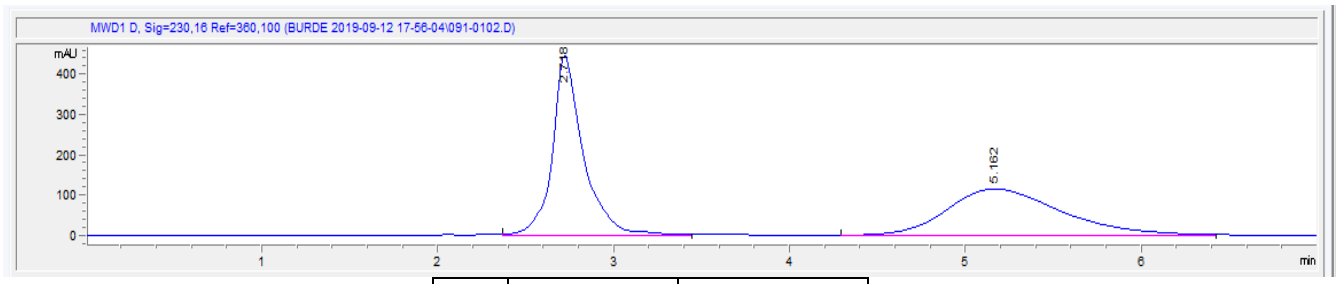


#	Time [min]	Area [%]
1	3.4	48.1
2	4.9	51.9

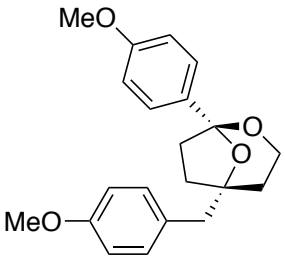


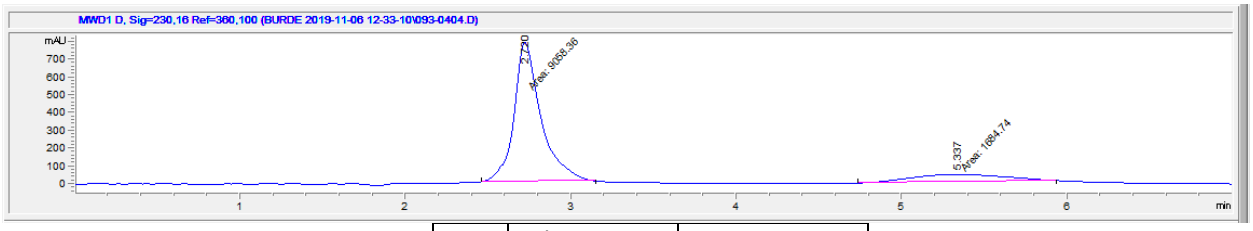


#	Time [min]	Area [%]
1	3.4	93.7
2	4.9	6.3

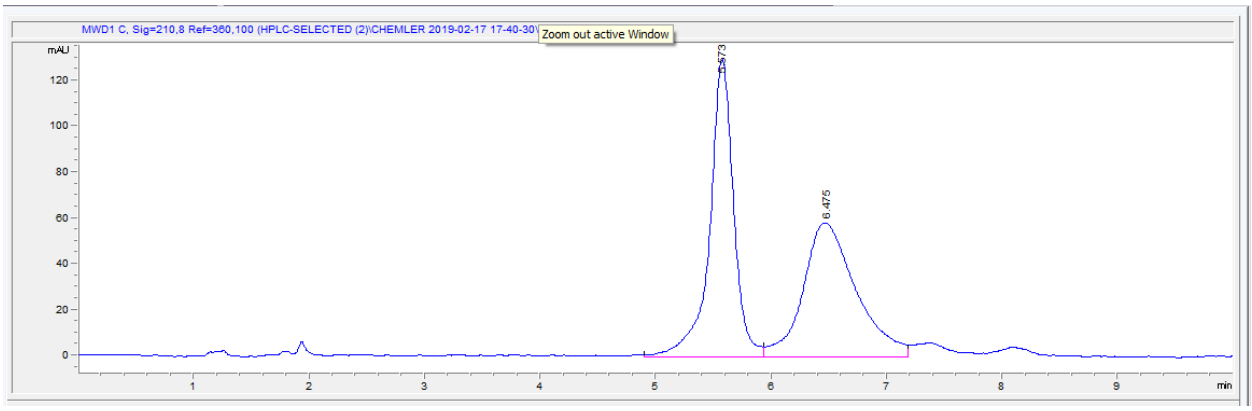


#	Time [min]	Area [%]
1	2.7	50.9
2	5.1	49.1

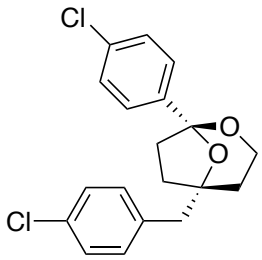


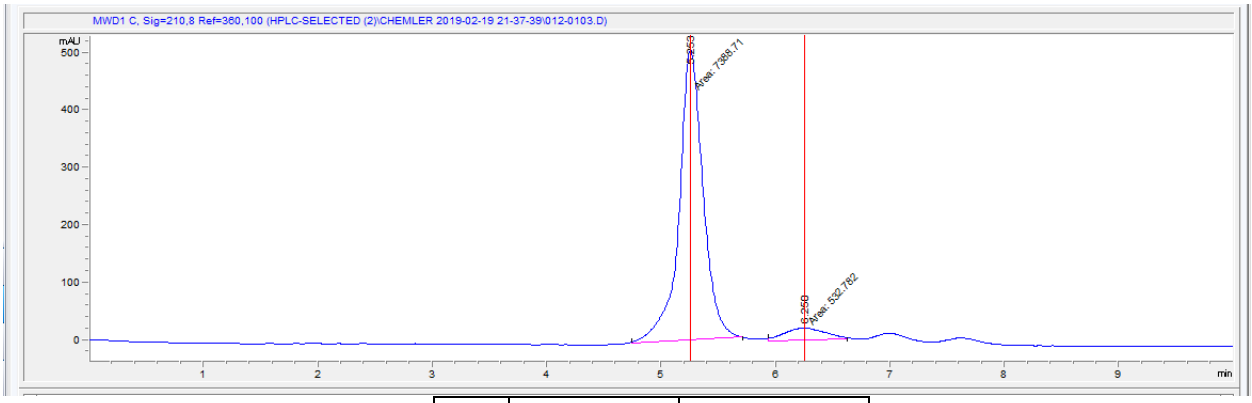


#	Time [min]	Area [%]
1	2.7	84.3
2	5.1	15.7

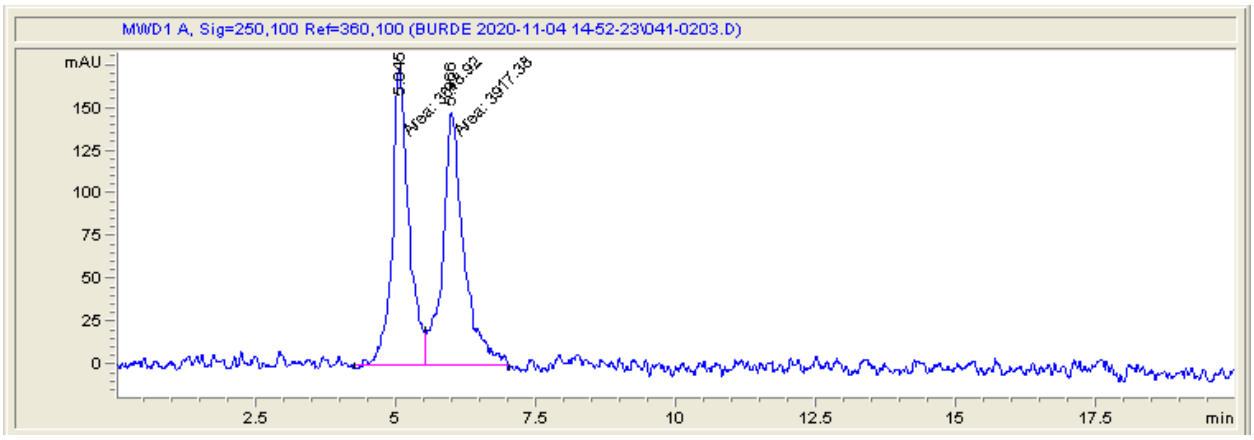


#	Time [min]	Area [%]
1	5.4	49.8
2	6.4	50.2

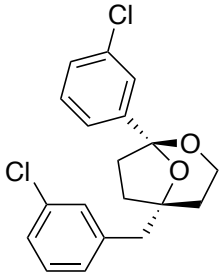


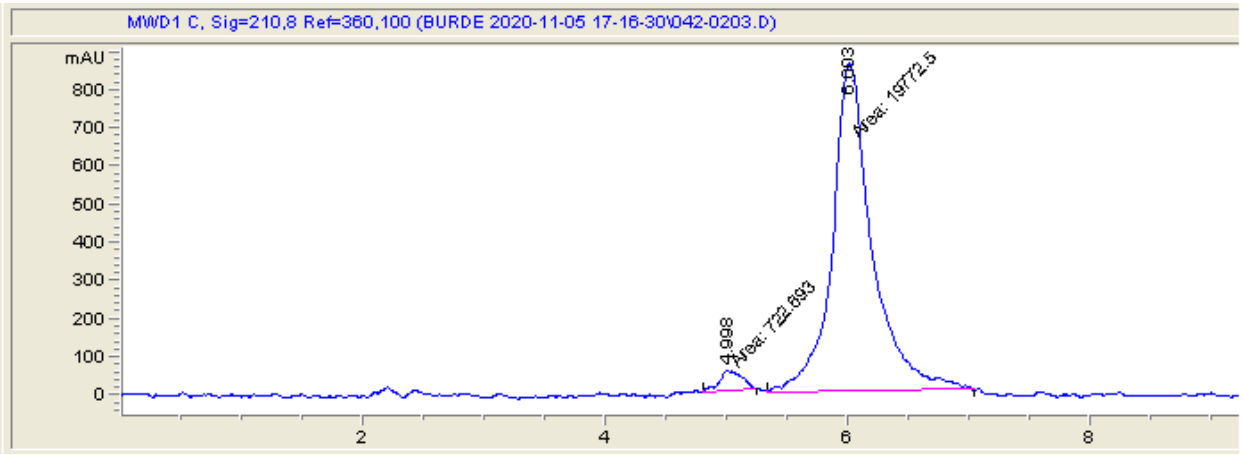


#	Time [min]	Area [%]
1	5.2	93.2
2	6.2	6.8

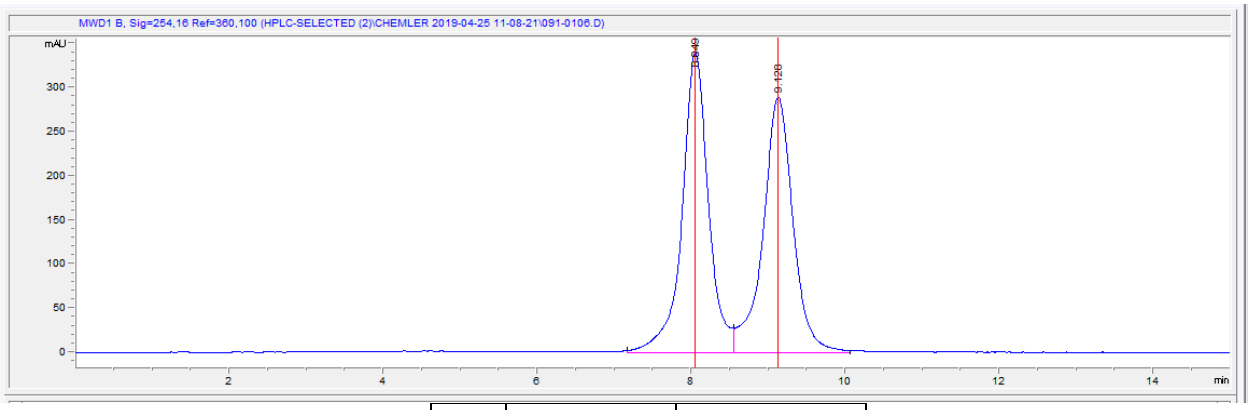


#	Time [min]	Area [%]
1	5.0	48.3
2	6.0	51.7

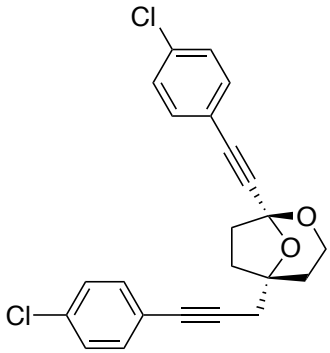


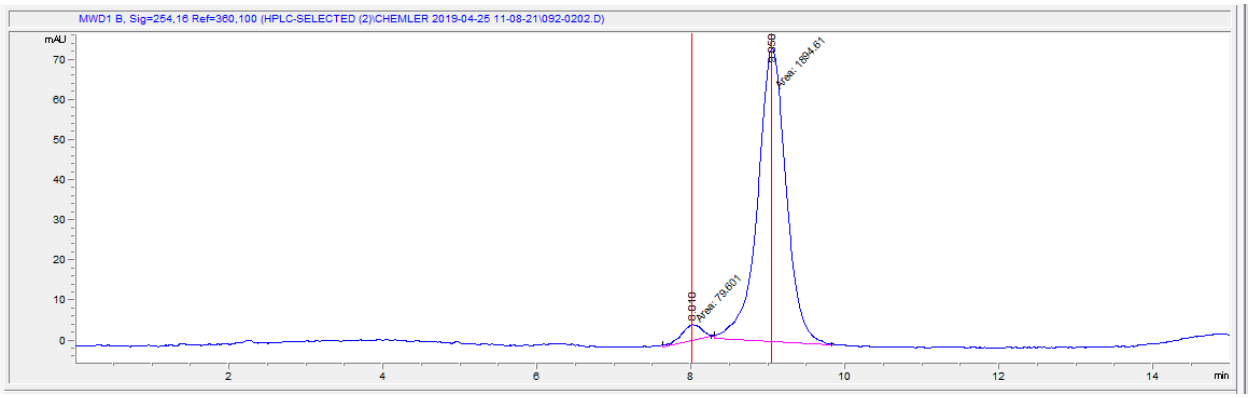


#	Time [min]	Area [%]
1	5.0	96.6
2	6.0	3.4

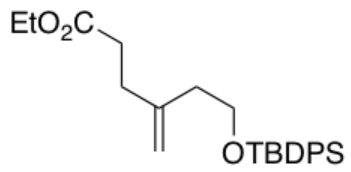


#	Time [min]	Area [%]
1	8.0	50.6
2	9.1	49.4



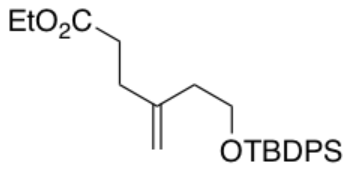


#	Time [min]	Area [%]
1	8.0	4.1
2	9.1	95.9



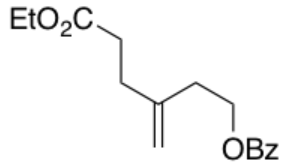
(S-4)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	18
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-794.7
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



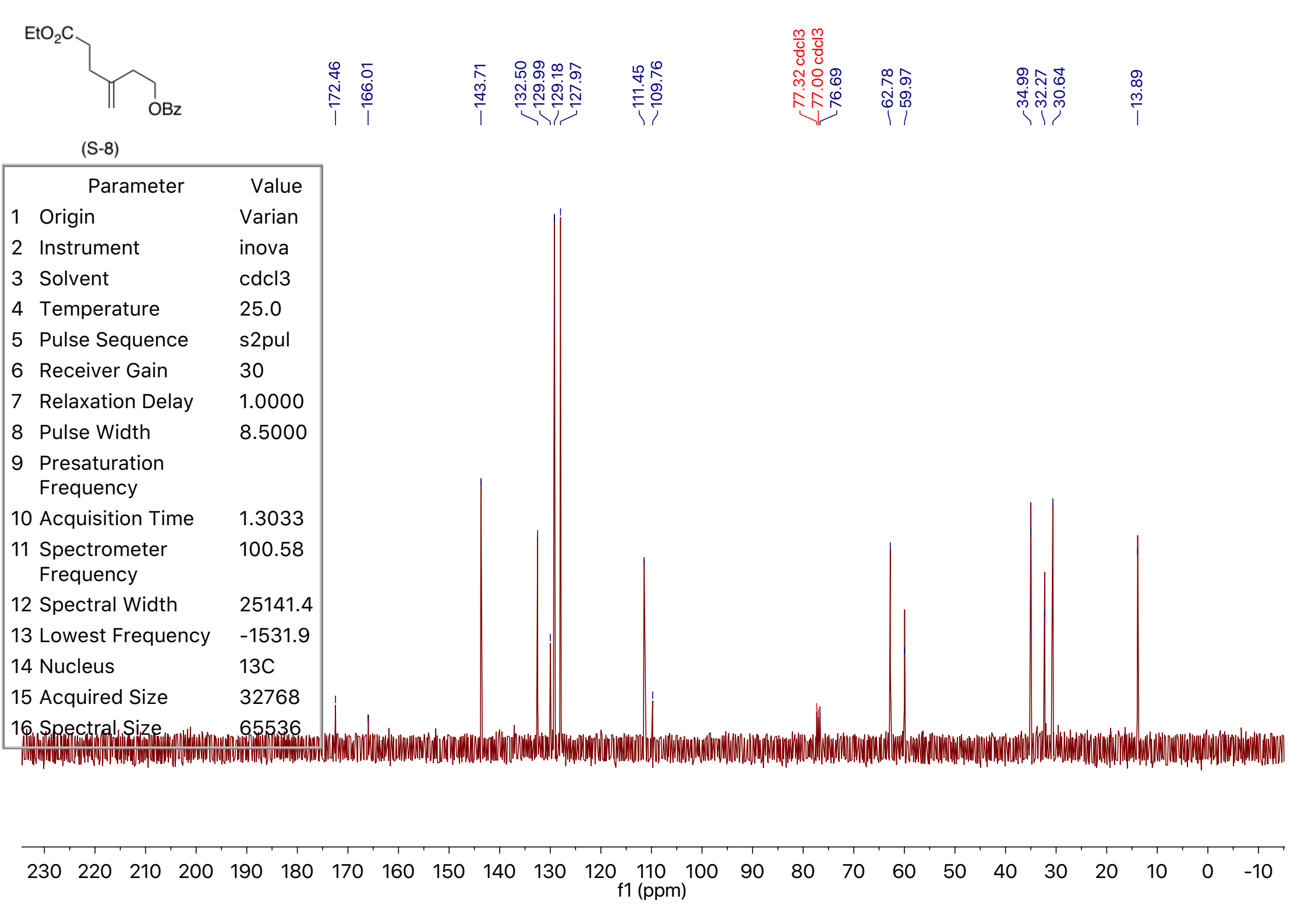
(S-4)

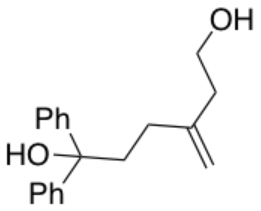
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.0500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1519.6
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



(S-8)

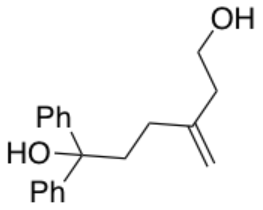
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	48
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-799.9
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536


EtO2C
OBz
(S-8)
172.46
166.01
143.71
132.50
129.99
129.18
127.97
111.45
109.76
77.32 cdcl3
77.00 cdcl3
76.69
62.78
59.97
34.99
32.27
30.64
13.89
Parameter Value
1 Origin Varian
2 Instrument inova
3 Solvent cdcl3
4 Temperature 25.0
5 Pulse Sequence s2pul
6 Receiver Gain 30
7 Relaxation Delay 1.0000
8 Pulse Width 8.5000
9 Presaturation Frequency
10 Acquisition Time 1.3033
11 Spectrometer Frequency 100.58
12 Spectral Width 25141.4
13 Lowest Frequency -1531.9
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



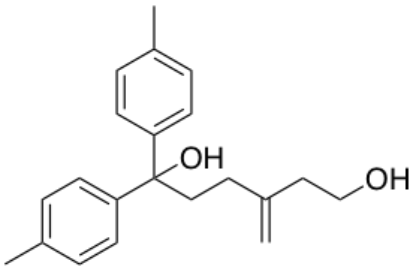
1a

	Parameter	Value
1	Origin	Varian
2	Instrument	mercury
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	12
7	Relaxation Delay	1.0000
8	Pulse Width	5.7000
9	Presaturation Frequency	
10	Acquisition Time	1.7064
11	Spectrometer Frequency	300.08
12	Spectral Width	4800.8
13	Lowest Frequency	-634.4
14	Nucleus	1H
15	Acquired Size	8192
16	Spectral Size	65536



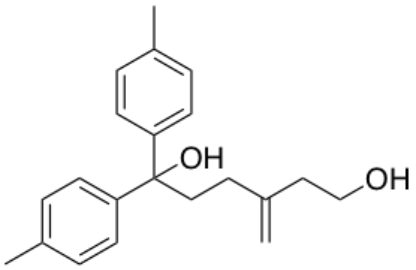
1a

	Parameter	Value
1	Origin	Varian
2	Instrument	mercury
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	6.5000
9	Presaturation Frequency	
10	Acquisition Time	0.8684
11	Spectrometer Frequency	75.46
12	Spectral Width	18867.9
13	Lowest Frequency	-1140.2
14	Nucleus	13C
15	Acquired Size	16384
16	Spectral Size	32768



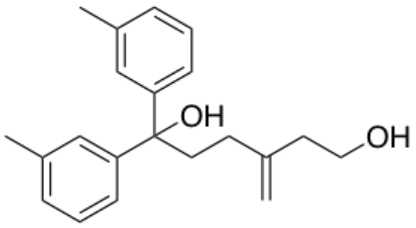
(1b)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	26
7	Relaxation Delay	1.0000
8	Pulse Width	2.6500
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-811.6
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



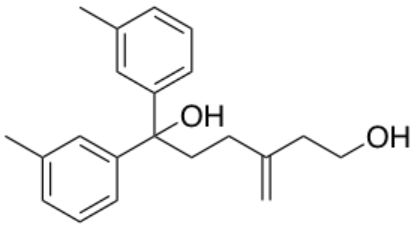
(1b)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5000
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1518.1
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



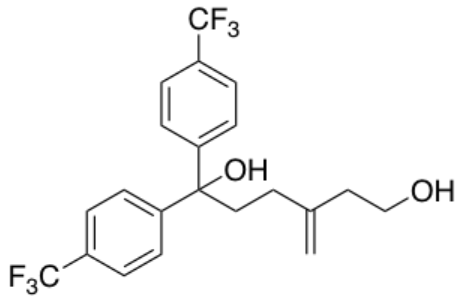
(1c)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	40
7	Relaxation Delay	1.0000
8	Pulse Width	2.6500
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-799.8
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



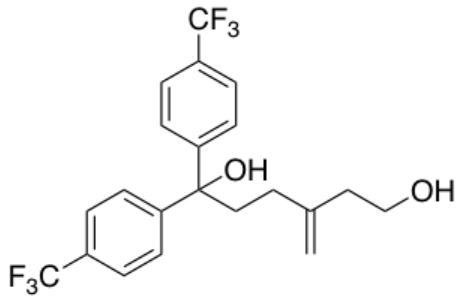
(1c)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5000
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1508.8
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



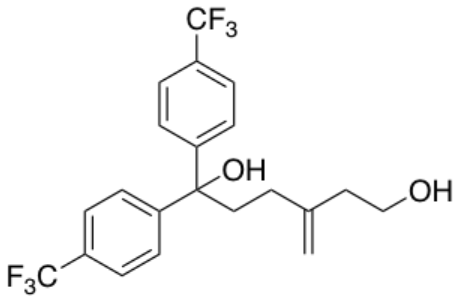
(1d)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	34
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-795.5
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



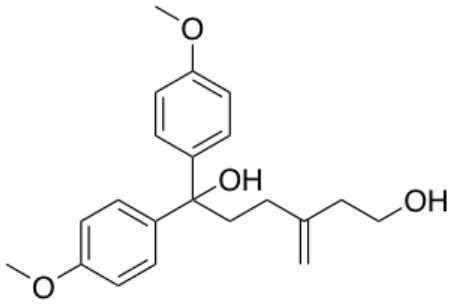
(1d)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.0500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1507.5
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



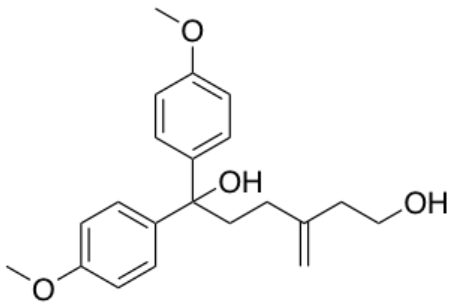
(1d)

	Parameter	Value
1	Origin	Varian
2	Instrument	mercury
3	Solvent	cdcl3
4	Temperature	24.0
5	Pulse Sequence	s2pul
6	Receiver Gain	38
7	Relaxation Delay	1.0000
8	Pulse Width	5.8667
9	Presaturation Frequency	
10	Acquisition Time	0.9856
11	Spectrometer Frequency	282.33
12	Spectral Width	64935.1
13	Lowest Frequency	-56537.8
14	Nucleus	19F
15	Acquired Size	64000
16	Spectral Size	131072



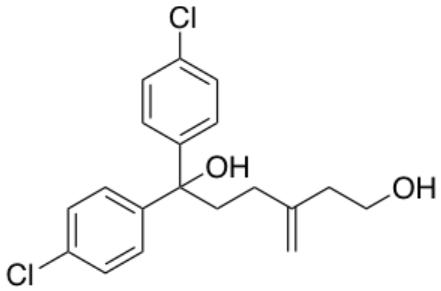
(1e)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	40
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-795.2
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



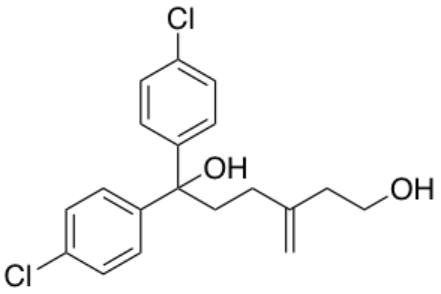
(1e)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5000
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1509.6
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



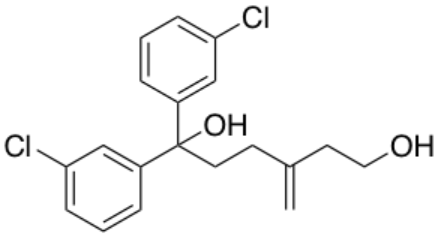
(1f)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	48
7	Relaxation Delay	1.0000
8	Pulse Width	2.6500
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-800.2
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



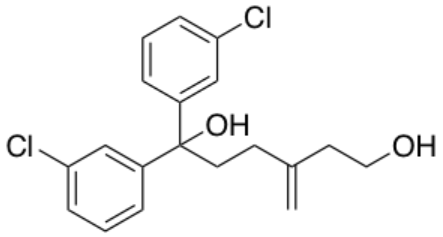
(1f)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	3.0000
8	Pulse Width	8.5000
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1507.1
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



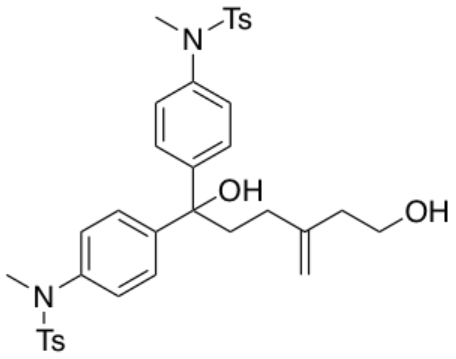
(1g)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	36
7	Relaxation Delay	1.0000
8	Pulse Width	2.7000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-787.1
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



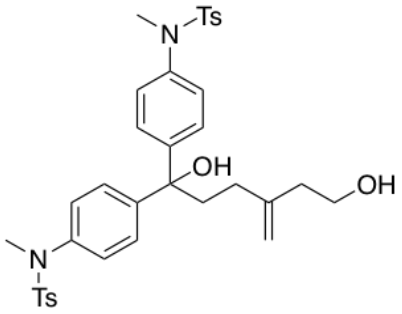
(1g)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1511.1
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



(1h)

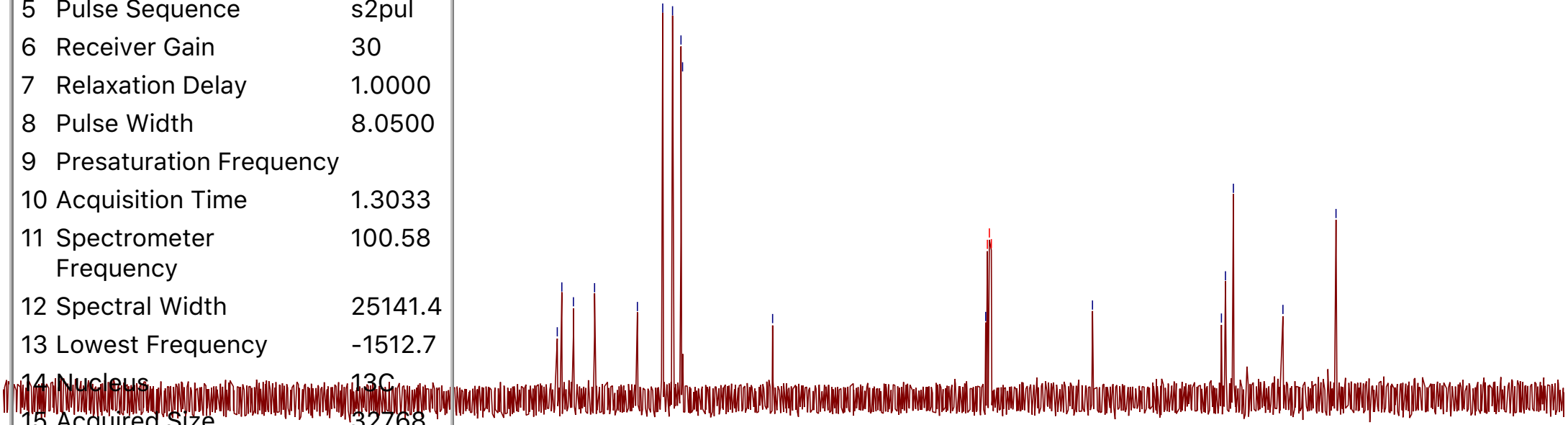
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	46
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-799.8
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536

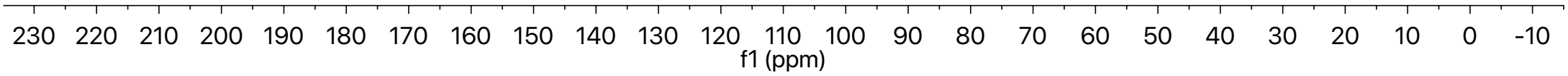


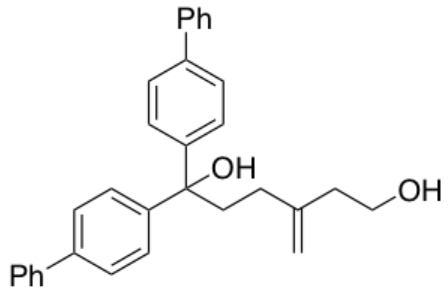
(1h)

146.21
145.47
143.62
140.23
133.37
129.32
127.74
126.39
126.14
111.71
77.58
77.31 cdcl3
77.00 cdcl3
76.68 cdcl3
60.47
39.82
39.18
37.91
29.97
21.47

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.0500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1512.7
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536

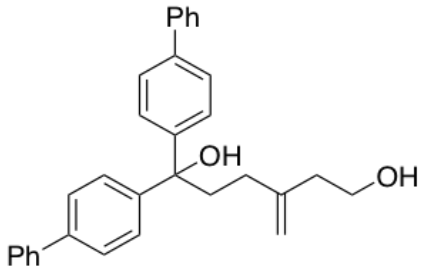






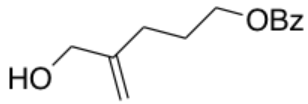
(1i)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	46
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-794.2
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



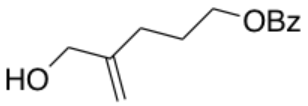
(1i)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.0500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1507.9
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



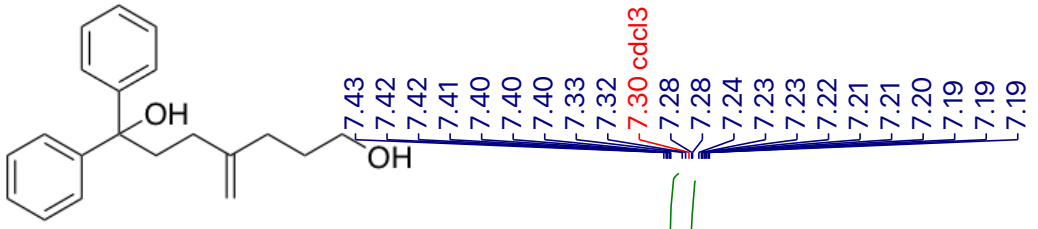
(S-9)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	36
7	Relaxation Delay	1.0000
8	Pulse Width	2.6500
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-794.3
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



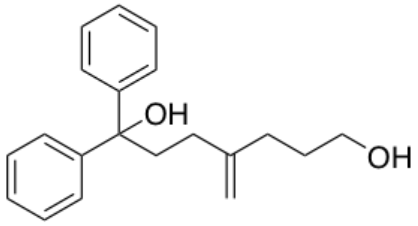
(S-9)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5000
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1512.7
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



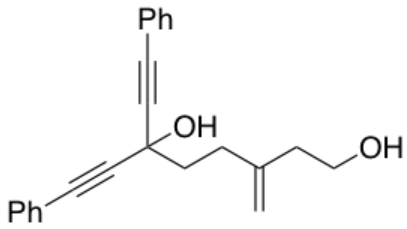
(1j)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-801.6
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



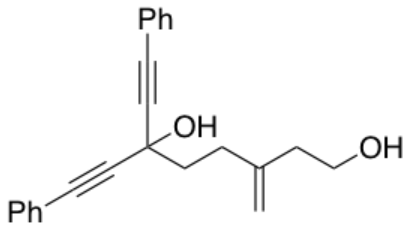
(1j)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.0500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1512.7
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



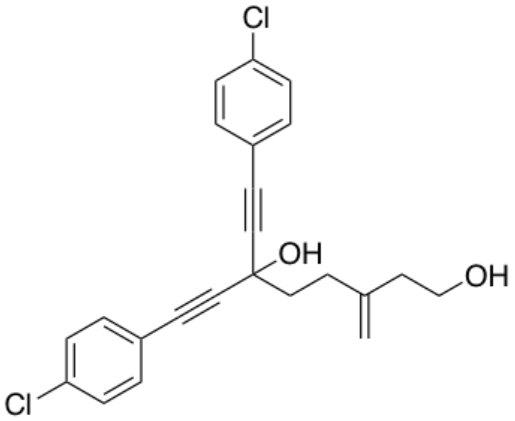
(1k)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	32
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-795.1
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



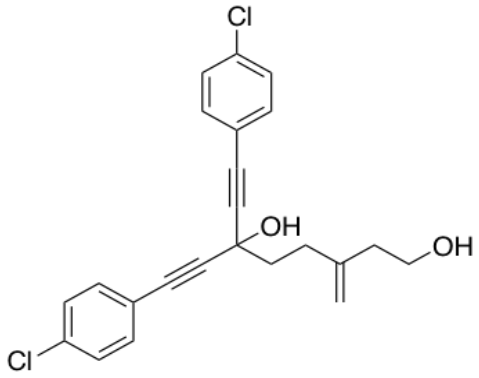
(1k)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.0500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1513.5
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



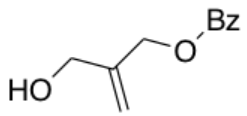
(1l)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	46
7	Relaxation Delay	1.0000
8	Pulse Width	2.6500
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-795.6
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



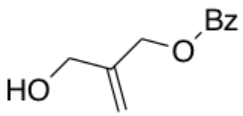
(1l)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5000
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1508.8
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



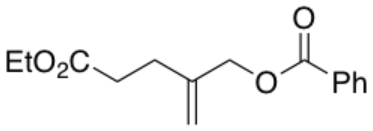
(S-11)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	42
7	Relaxation Delay	1.0000
8	Pulse Width	3.7000
9	Presaturation Frequency	
10	Acquisition Time	2.0484
11	Spectrometer Frequency	499.90
12	Spectral Width	7998.4
13	Lowest Frequency	-1006.2
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



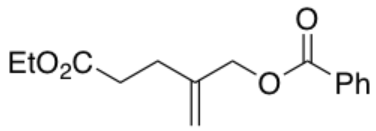
(S-11)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	7.2500
9	Presaturation Frequency	
10	Acquisition Time	1.0428
11	Spectrometer Frequency	125.71
12	Spectral Width	31421.8
13	Lowest Frequency	-1898.1
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



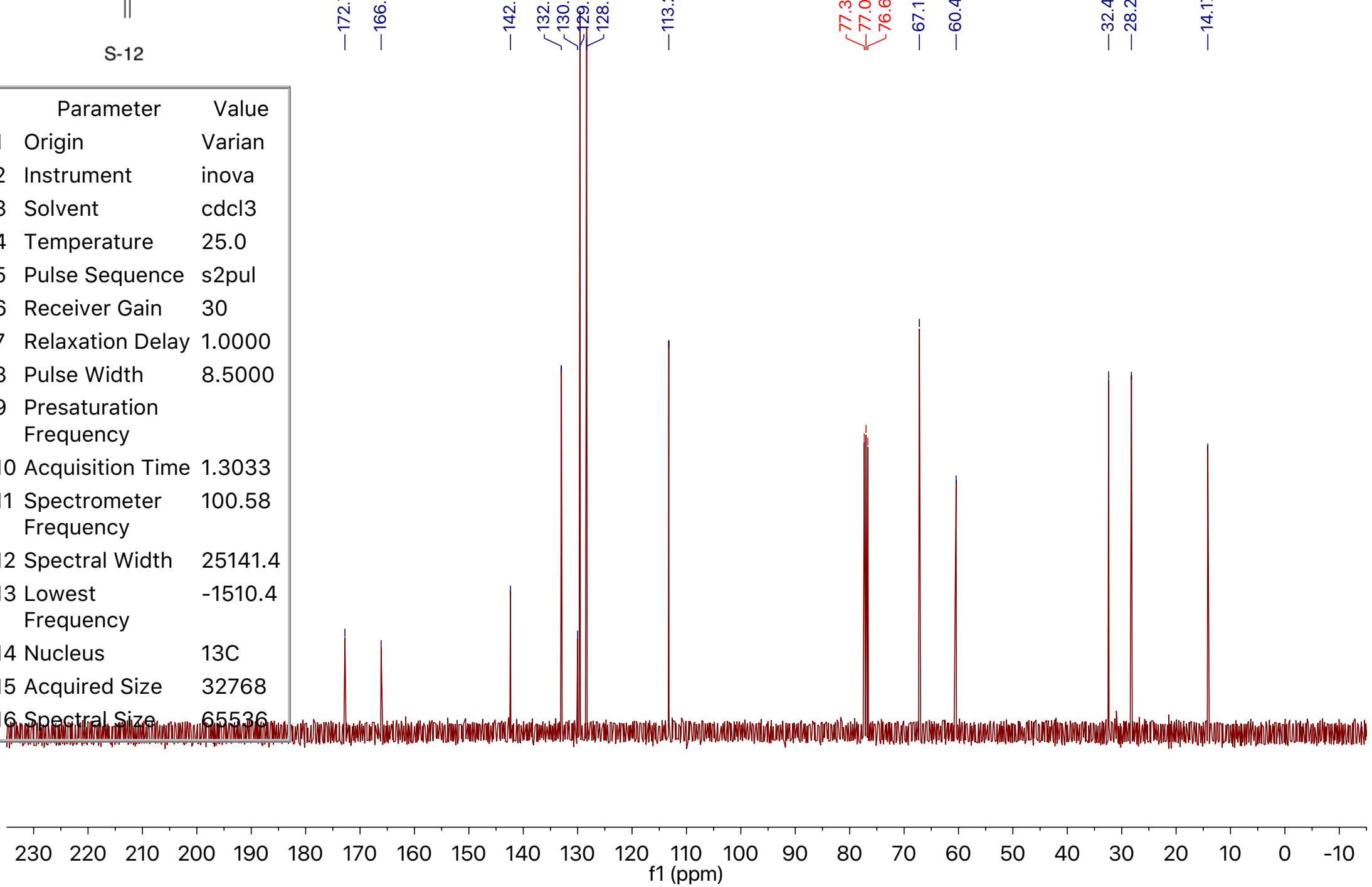
S-12

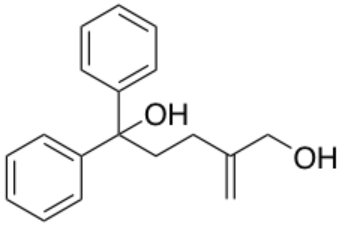
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	36
7	Relaxation Delay	1.0000
8	Pulse Width	2.6500
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-795.9
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



S-12

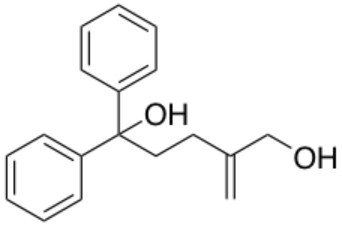
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5000
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1510.4
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536





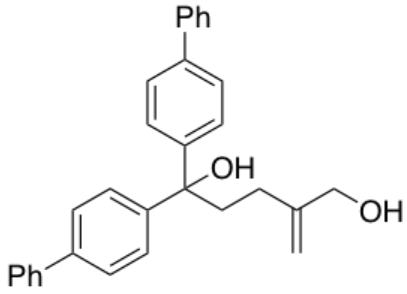
(1l)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	40
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-795.1
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



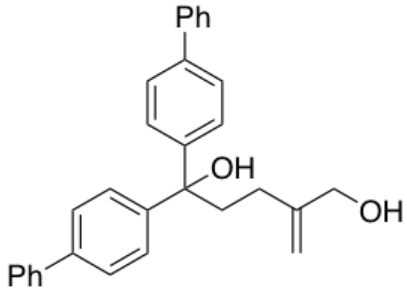
(1l)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.0500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1509.2
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



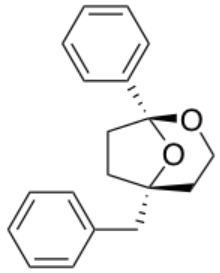
(1m)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	46
7	Relaxation Delay	1.0000
8	Pulse Width	2.6500
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-794.3
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



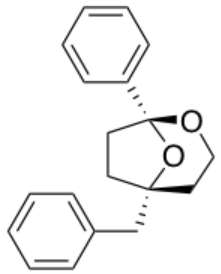
(1m)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5000
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1508.1
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



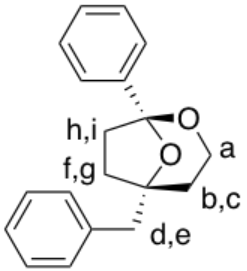
(2a)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	26
7	Relaxation Delay	2.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-817.5
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



(2a)

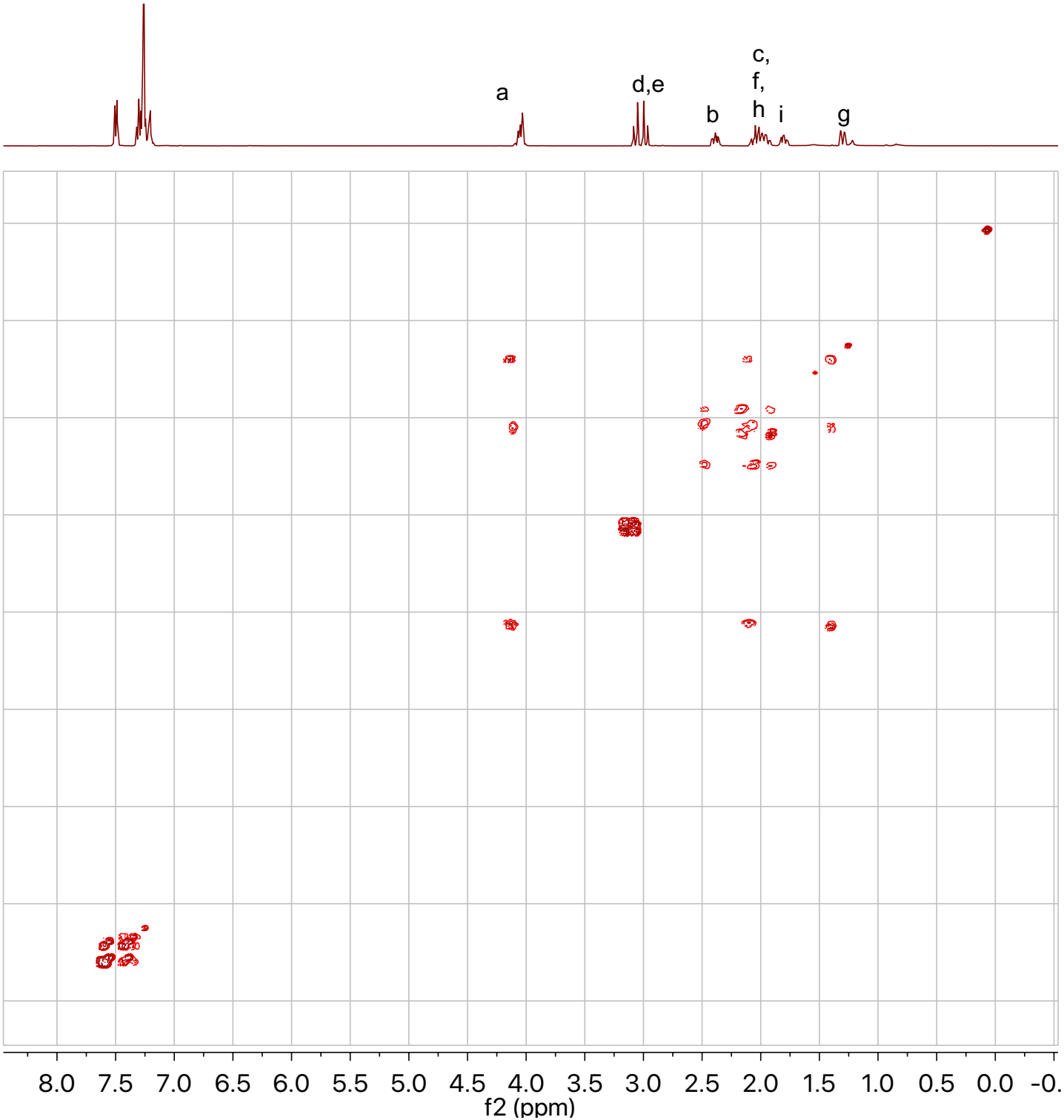
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.0500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1511.1
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536

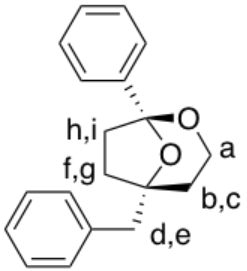


d and e are geminally coupled and not coupled to anything else in the molecule.

(2a)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	COSY
6	Receiver Gain	46
7	Relaxation Delay	1.0000
8	Pulse Width	6.6000
9	Presaturation Frequency	
10	Acquisition Time	0.1500
11	Spectrometer Frequency	(399.94, 399.94)
12	Spectral Width	(3599.9, 3599.9)
13	Lowest Frequency	(-217.6, -217.6)
14	Nucleus	(1H, 1H)
15	Acquired Size	(540, 860)
16	Spectral Size	(1024, 1024)

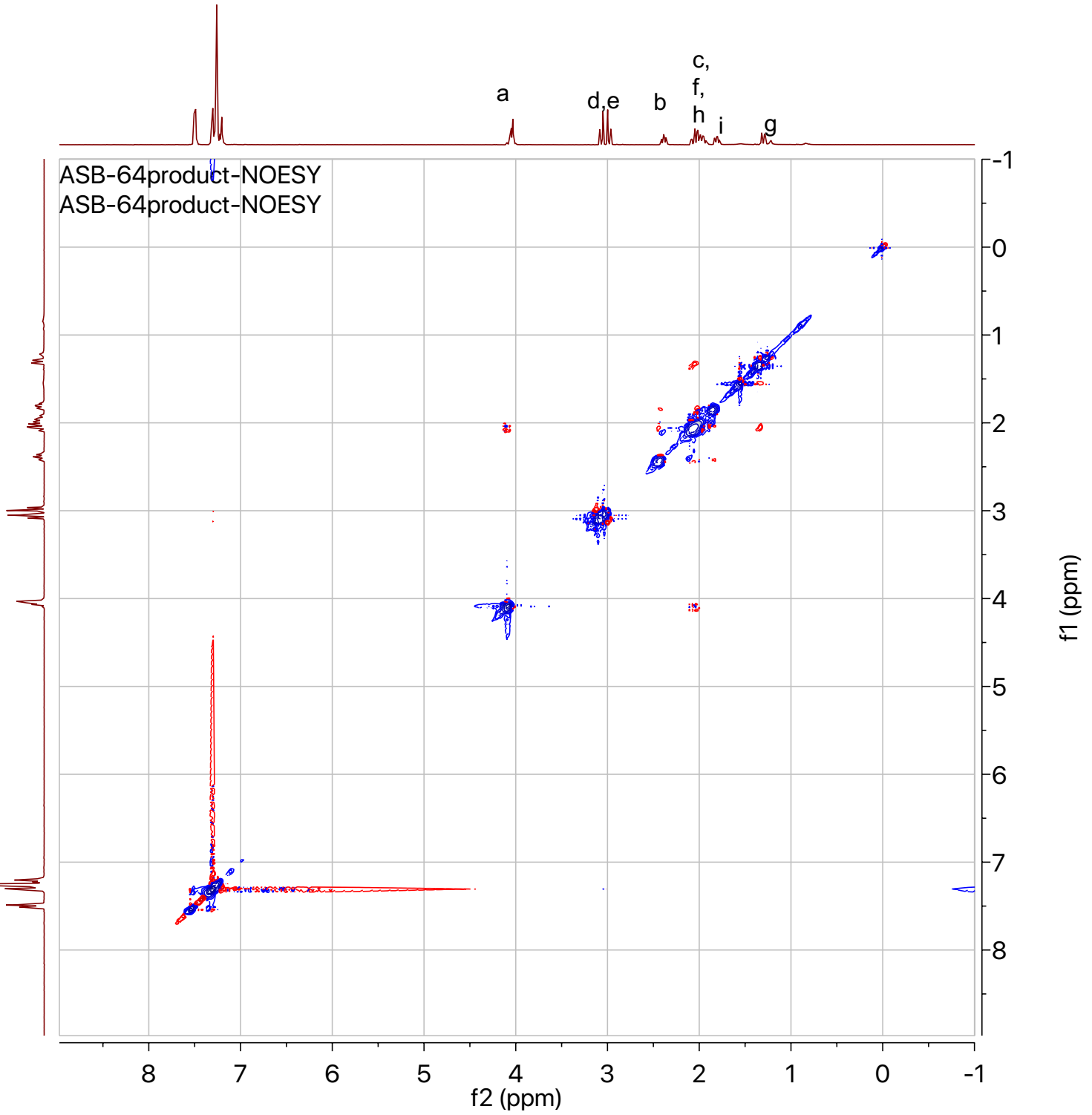


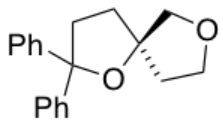


(2a)

d and e do not have any protons in close proximity.

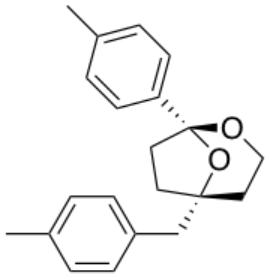
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	NOESY
6	Receiver Gain	40
7	Relaxation Delay	3.0000
8	Pulse Width	6.6000
9	Presaturation Frequency	
10	Acquisition Time	0.1499
11	Spectrometer Frequency	(399.94, 399.94)
12	Spectral Width	(3995.0, 3995.0)
13	Lowest Frequency	(-405.6, -405.6)
14	Nucleus	(1H, 1H)
15	Acquired Size	(599, 256)
16	Spectral Size	(1024, 1024)





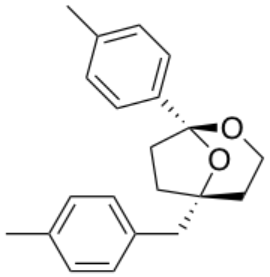
(3a)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	58
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-795.1
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



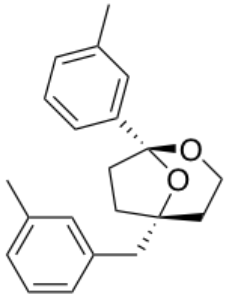
(2b)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	40
7	Relaxation Delay	1.0000
8	Pulse Width	2.6500
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-795.9
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



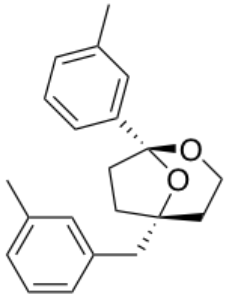
(2b)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5000
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1508.8
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



(2c)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	46
7	Relaxation Delay	1.0000
8	Pulse Width	2.6500
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-795.1
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



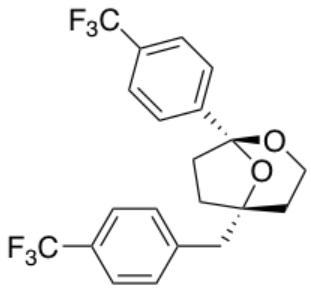
(2c)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5000
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1508.1
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536

141.57
137.57
137.52
136.72
131.29
128.61
127.94
127.92
127.44
127.15
125.63
122.05
106.10
83.44
77.31 cdcl3
76.99 cdcl3
76.67 cdcl3
60.46
45.68
37.29
34.89
32.44
21.50
21.42

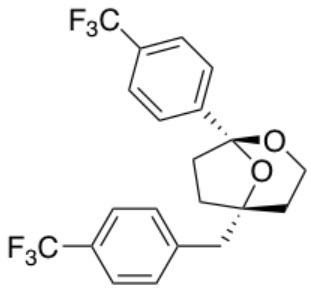
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



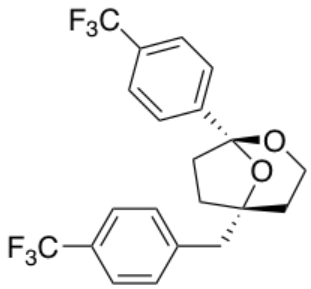
(2d)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	42
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-799.8
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



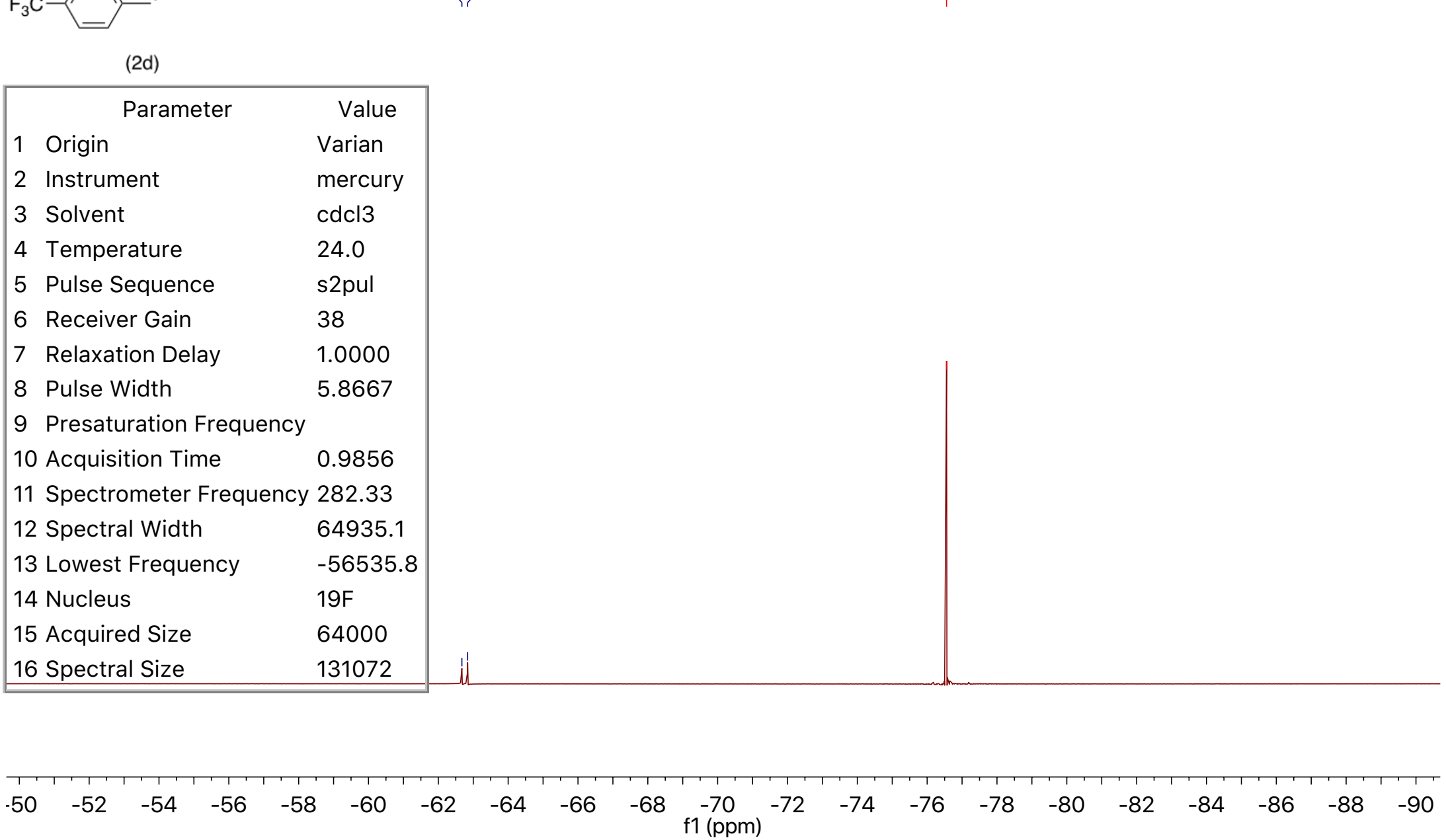
(2d)

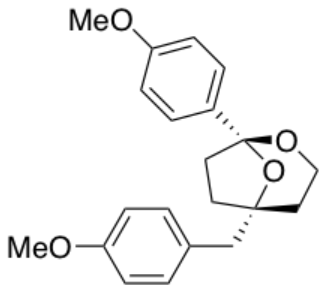
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	30.0000
8	Pulse Width	8.0500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1508.6
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



(2d)

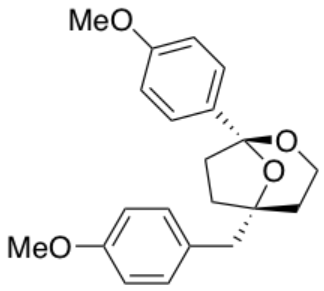
	Parameter	Value
1	Origin	Varian
2	Instrument	mercury
3	Solvent	cdcl3
4	Temperature	24.0
5	Pulse Sequence	s2pul
6	Receiver Gain	38
7	Relaxation Delay	1.0000
8	Pulse Width	5.8667
9	Presaturation Frequency	
10	Acquisition Time	0.9856
11	Spectrometer Frequency	282.33
12	Spectral Width	64935.1
13	Lowest Frequency	-56535.8
14	Nucleus	19F
15	Acquired Size	64000
16	Spectral Size	131072





(2e)

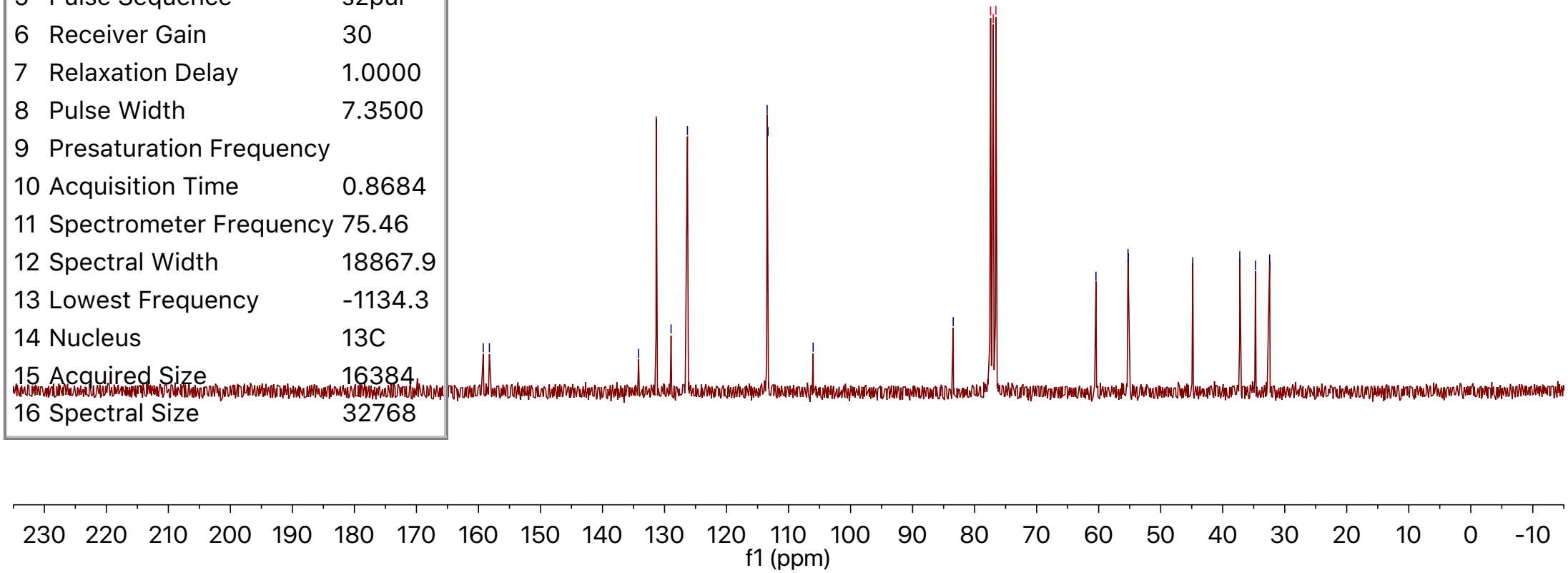
	Parameter	Value
1	Origin	Varian
2	Instrument	mercury
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	7.3000
9	Presaturation Frequency	
10	Acquisition Time	1.7064
11	Spectrometer Frequency	300.08
12	Spectral Width	4800.8
13	Lowest Frequency	-599.3
14	Nucleus	1H
15	Acquired Size	8192
16	Spectral Size	65536

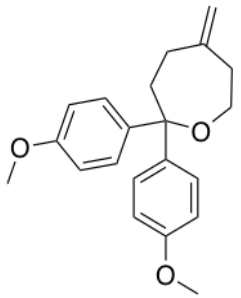


(2e)

159.24
158.24
134.18
131.34
128.95
126.31
113.46
113.32
106.04
83.45
77.42 cdcl3
77.00 cdcl3
76.57 cdcl3
60.44
55.27
55.21
44.82
37.25
34.72
32.43

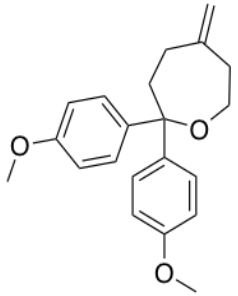
	Parameter	Value
1	Origin	Varian
2	Instrument	mercury
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	7.3500
9	Presaturation Frequency	
10	Acquisition Time	0.8684
11	Spectrometer Frequency	75.46
12	Spectral Width	18867.9
13	Lowest Frequency	-1134.3
14	Nucleus	13C
15	Acquired Size	16384
16	Spectral Size	32768





(4e)

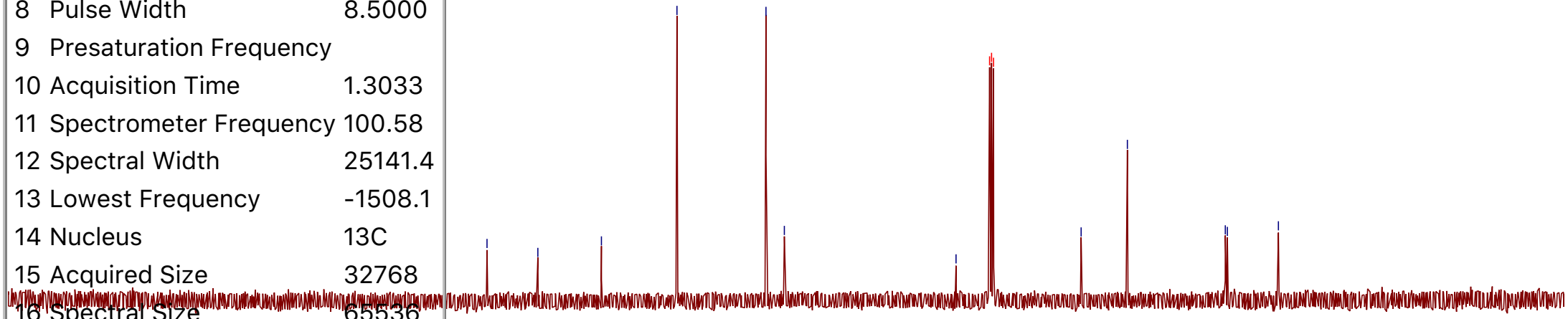
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	48
7	Relaxation Delay	1.0000
8	Pulse Width	2.6500
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-795.1
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



(4e)

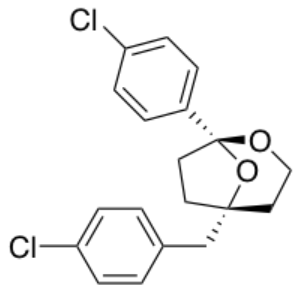
158.06
149.89
139.68
127.54
113.23
110.28
82.69
77.30 cdcl3
76.99 cdcl3
76.67 cdcl3
62.59
55.16
39.42
39.10
30.89

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5000
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1508.1
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



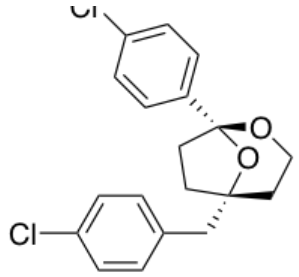
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



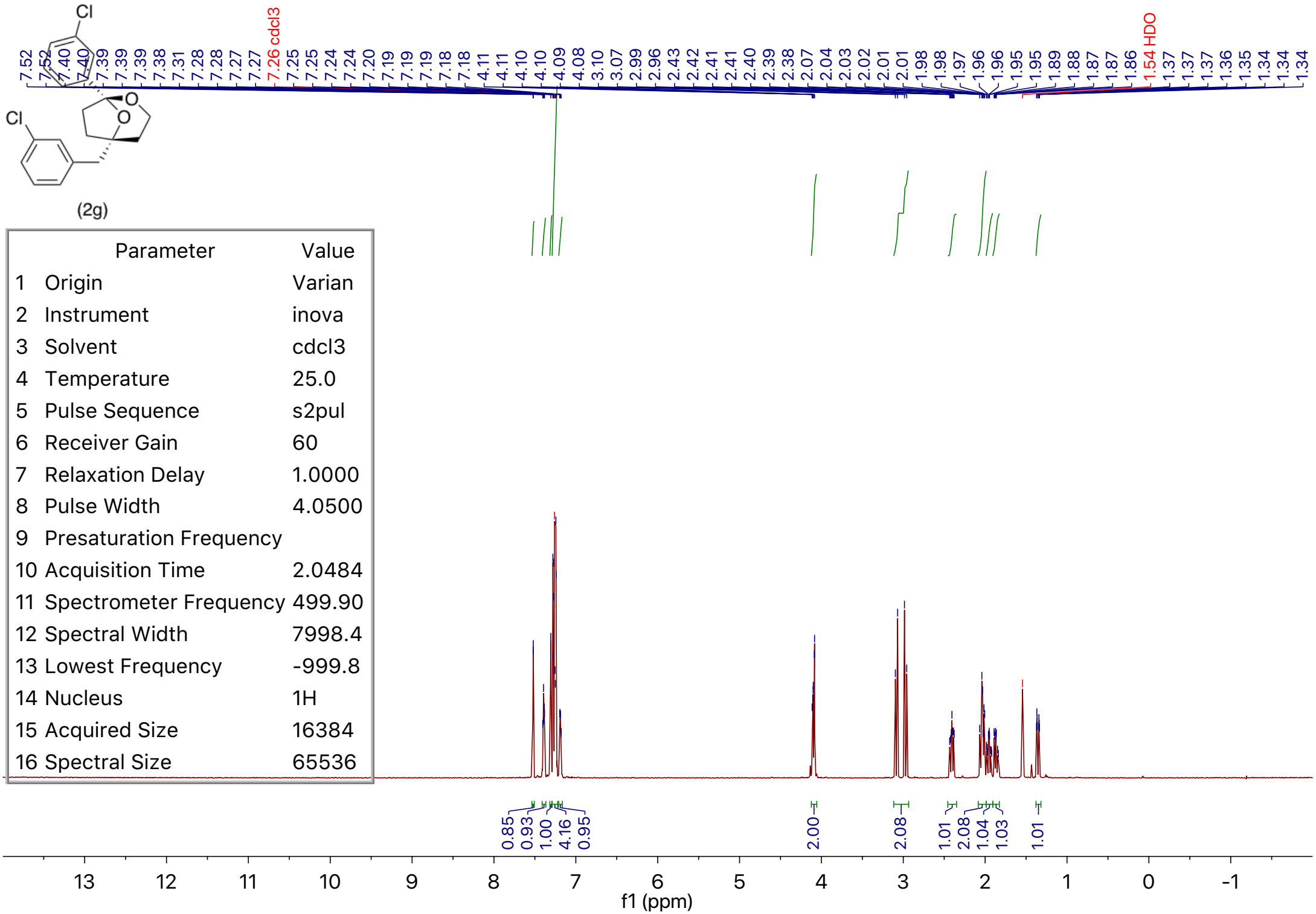
(2f)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	48
7	Relaxation Delay	1.0000
8	Pulse Width	2.6500
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-797.9
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536

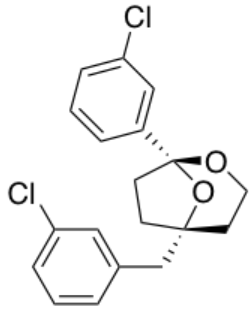


(2f)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5000
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1507.3
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536

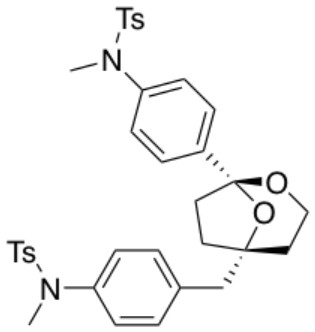


	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	60
7	Relaxation Delay	1.0000
8	Pulse Width	4.0500
9	Presaturation Frequency	
10	Acquisition Time	2.0484
11	Spectrometer Frequency	499.90
12	Spectral Width	7998.4
13	Lowest Frequency	-999.8
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



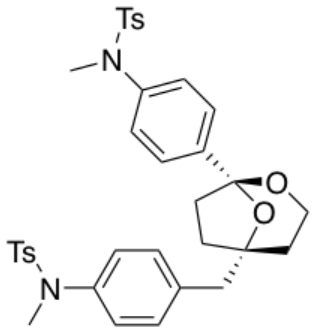
(2g)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	7.1500
9	Presaturation Frequency	
10	Acquisition Time	1.0428
11	Spectrometer Frequency	125.71
12	Spectral Width	31421.8
13	Lowest Frequency	-1884.7
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



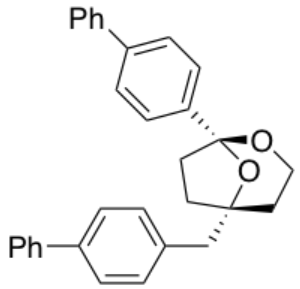
(2h)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	54
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-799.8
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



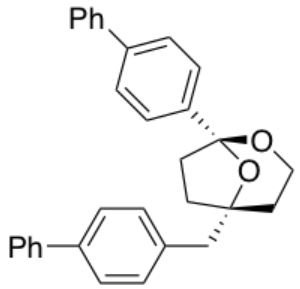
(2h)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.0500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1506.6
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



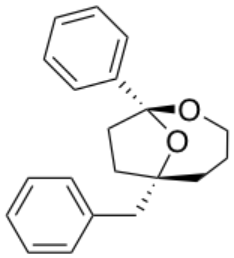
(2i)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	44
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-795.4
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



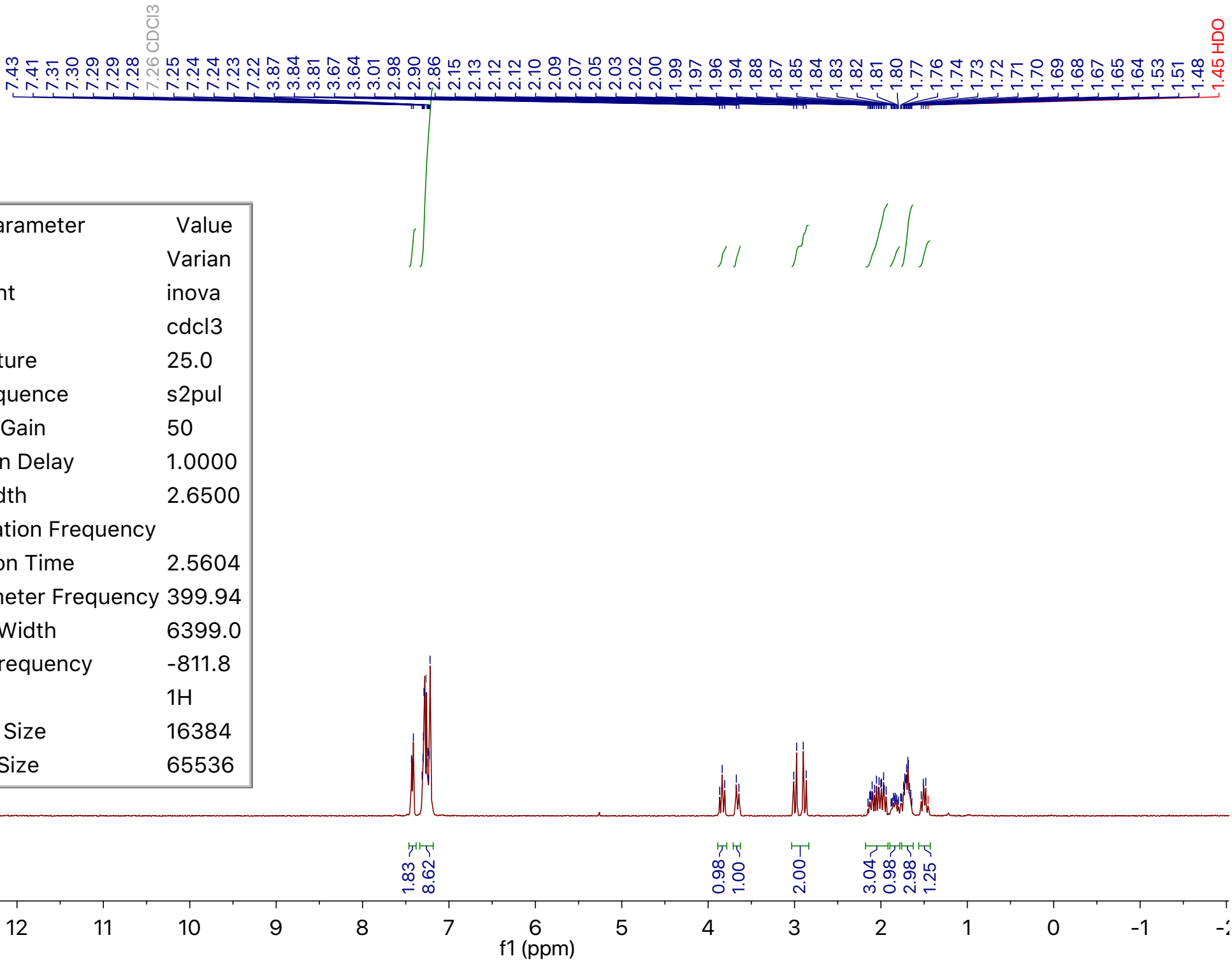
(2i)

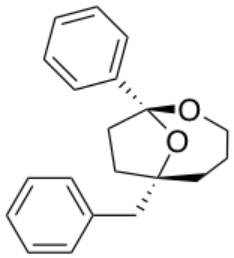
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	3.0000
8	Pulse Width	8.0500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1508.1
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



(2j)

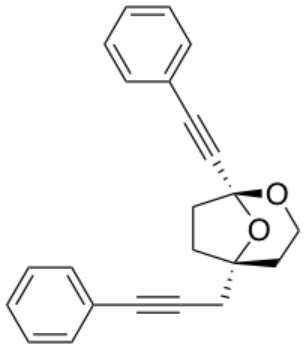
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	50
7	Relaxation Delay	1.0000
8	Pulse Width	2.6500
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-811.8
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536





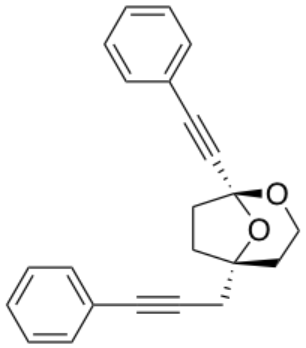
(2j)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5000
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1507.3
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



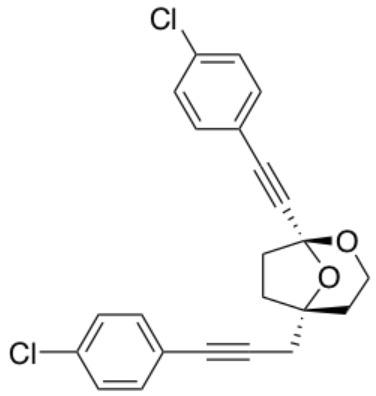
(2k)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	52
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-823.1
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



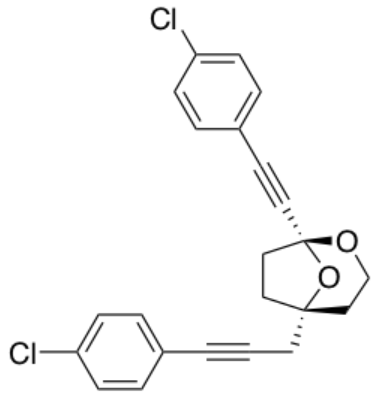
(2k)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	3.0000
8	Pulse Width	8.0500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1506.6
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



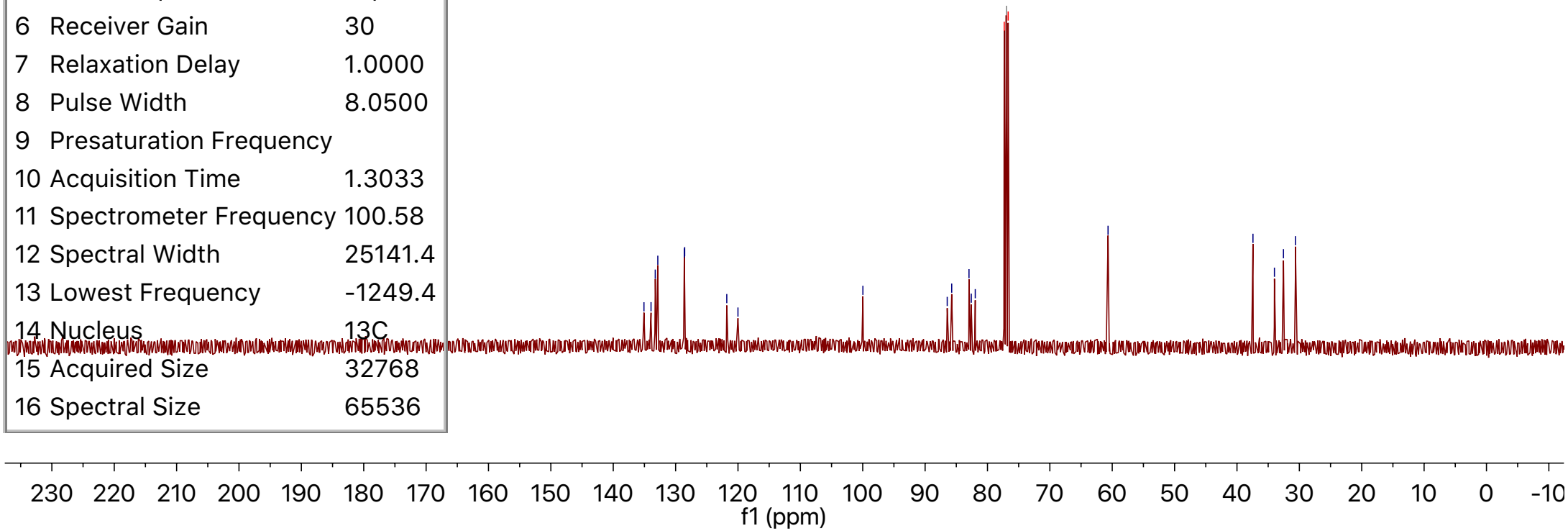
(2l)

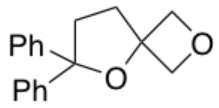
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	50
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-824.9
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



(2l)

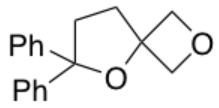
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	d2o
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.0500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1249.4
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536





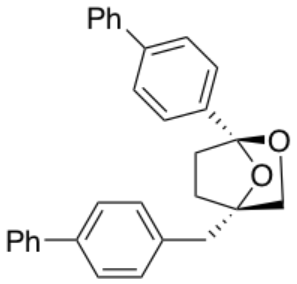
(3m)

	Parameter	Value
1	Origin	Varian
2	Instrument	mercury
3	Solvent	cdcl3
4	Temperature	24.0
5	Pulse Sequence	s2pul
6	Receiver Gain	38
7	Relaxation Delay	1.0000
8	Pulse Width	5.7000
9	Presaturation Frequency	
10	Acquisition Time	1.7064
11	Spectrometer Frequency	300.08
12	Spectral Width	4800.8
13	Lowest Frequency	-599.9
14	Nucleus	1H
15	Acquired Size	8192
16	Spectral Size	65536



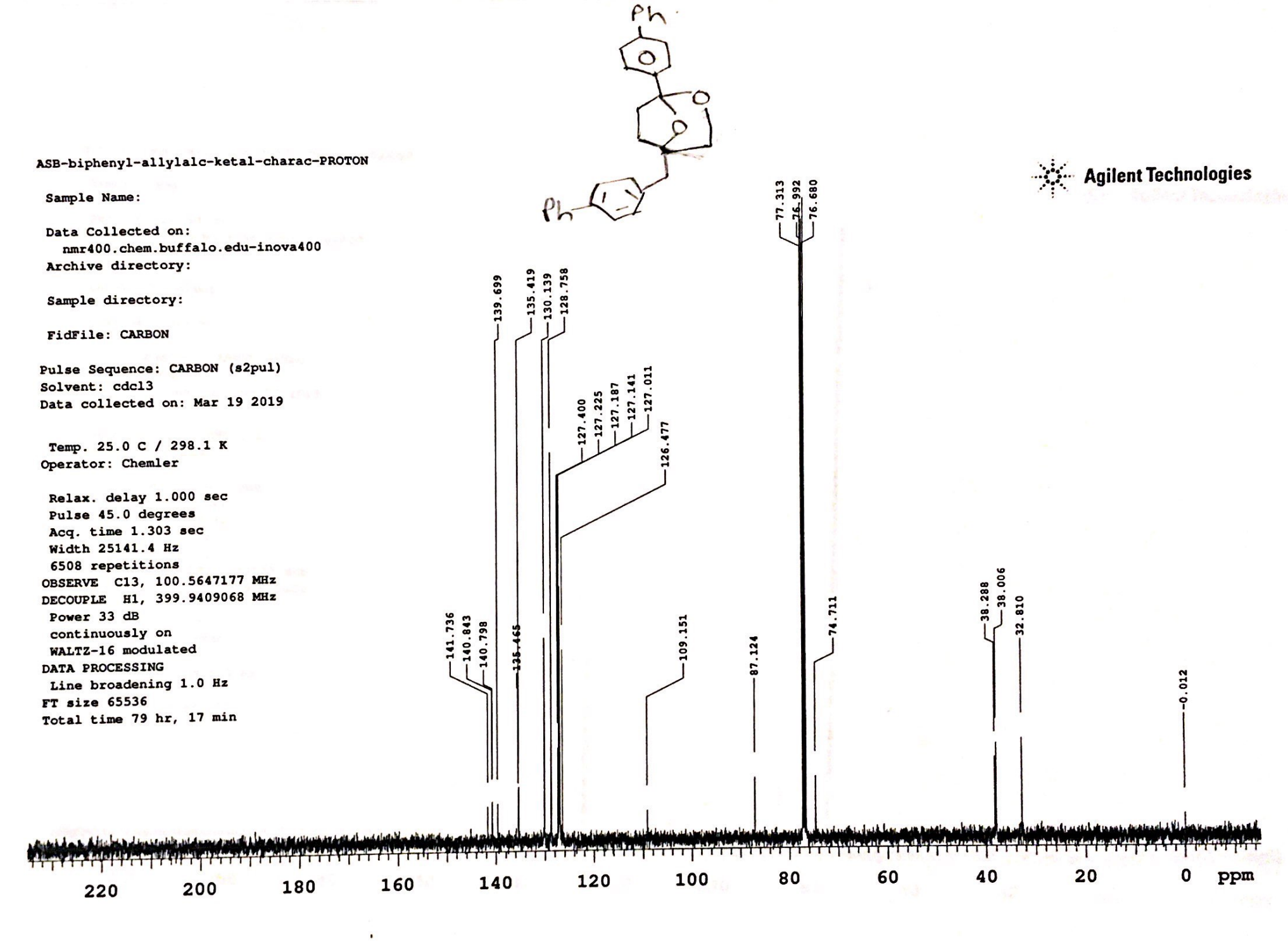
(3m)

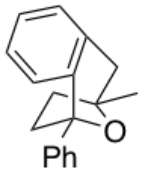
	Parameter	Value
1	Origin	Varian
2	Instrument	mercury
3	Solvent	cdcl3
4	Temperature	24.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	6.5000
9	Presaturation Frequency	
10	Acquisition Time	0.8684
11	Spectrometer Frequency	75.46
12	Spectral Width	18867.9
13	Lowest Frequency	-1121.3
14	Nucleus	13C
15	Acquired Size	16384
16	Spectral Size	32768



(2n)

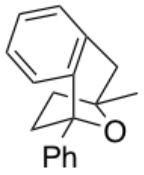
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	52
7	Relaxation Delay	1.0000
8	Pulse Width	3.3000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-795.1
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536


ASB-biphenyl-allylalc-ketal-charac-PROTON
Sample Name:
Data Collected on:
nmr400.chem.buffalo.edu-inova400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 19 2019
Temp. 25.0 C / 298.1 K
Operator: Chemler
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.303 sec
Width 25141.4 Hz
6508 repetitions
OBSERVE C13, 100.5647177 MHz
DECOUPLE H1, 399.9409068 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 79 hr, 17 min
Ph
O
O
O
Ph
Agilent Technologies
77.313
76.992
76.680
139.699
135.419
130.139
128.758
127.400
127.225
127.187
127.141
127.011
126.477
141.736
140.843
140.798
135.465
109.151
87.124
74.711
38.288
38.006
32.810
0.012
220
200
180
160
140
120
100
80
60
40
20
0
ppm



(6b)

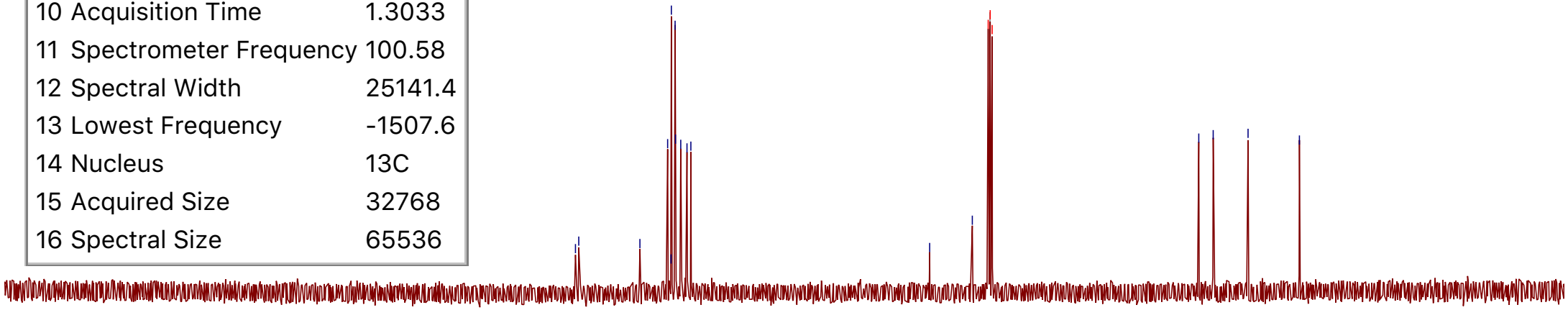
	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	42
7	Relaxation Delay	1.0000
8	Pulse Width	2.7000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-795.0
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536

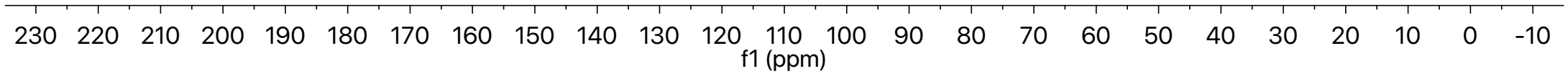


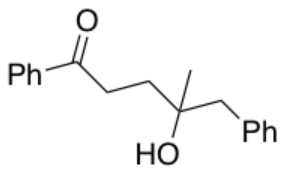
(6b)

143.49
142.96
133.16
128.71
128.17
128.12
127.51
127.45
126.61
125.61
124.99
86.70
79.86
77.32 cdcl3
77.00 cdcl3
77.00 CDCl3
76.68 cdcl3
43.56
41.25
35.66
27.42

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	cdcl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	8.5500
9	Presaturation Frequency	
10	Acquisition Time	1.3033
11	Spectrometer Frequency	100.58
12	Spectral Width	25141.4
13	Lowest Frequency	-1507.6
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536

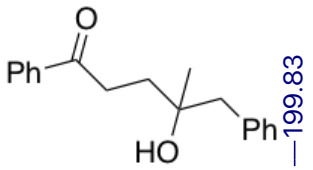






(7)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	c6d6
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	52
7	Relaxation Delay	1.0000
8	Pulse Width	2.7000
9	Presaturation Frequency	
10	Acquisition Time	2.5604
11	Spectrometer Frequency	399.94
12	Spectral Width	6399.0
13	Lowest Frequency	-778.3
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	65536



(7)

	Parameter	Value
1	Origin	Varian
2	Instrument	inova
3	Solvent	c6d6
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Receiver Gain	30
7	Relaxation Delay	1.0000
8	Pulse Width	7.1500
9	Presaturation Frequency	
10	Acquisition Time	1.0428
11	Spectrometer Frequency	125.71
12	Spectral Width	31421.8
13	Lowest Frequency	-1808.8
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536