Enantioselective 1,1-Arylborylation of Alkenes: Merging Chiral Anion Phase-Transfer with Pd-Catalysis

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Supporting Information

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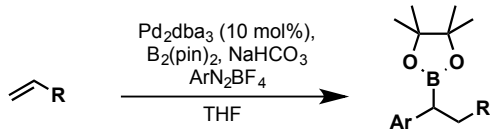
I. General Information

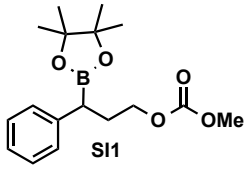
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Chiral anion phase-transfer (CAPT) reactions were performed in 1-dram (0.5" X 1.75") vials equipped with a screw cap and stirred using a magnetic Teflon stir bar (1/2" X 5/16"), placed on the surface of a magnetic stir plate. Due to the heterogeneous nature of these reactions, it is important that fast and efficient stirring be maintained over the course of the reaction in order to obtain optimal results. Diethyl ether (Et_2O) was used as purchased from Fischer Scientific. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Merck silica gel 60 F254 TLC plates, and visualized under UV or by staining with ceric ammonium molybdate or $KMnO_4$. Column chromatography was performed on Merck Silica Gel 60 Å, 230 X 400 mesh. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker AV-600, AV-500, DRX-500, AVQ-400, AVB-400 and AV-300 spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak ($CHCl_3$, δH = 7.27 ppm and δC = 77.23 ppm; DMSO, δH = 2.50 and δC = 39.5 ppm; CH_2Cl_2, δH = 5.32 and δC = 53.8 ppm). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, app t = apparent triplet, m = multiplet, br = broad resonance. Solvent abbreviations are reported as follows: B_2pin_2 = bis(pinicaloato)diboron, MTBE = Methyl *tert*-butyl ether, EtOAc = ethyl acetate, hex = hexanes, DCM = dichloromethane, Et_2O = diethyl ether, MeOH = methanol, *i*PrOH = isopropanol, THF = tetrahydrofuran, DMF = N,N-dimethylformamide, Et_3N = triethylamine. Mass spectral data were obtained from the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley or by usage of an Agilent Time of Flight (Q-TOF) mass spectrometer in ESI mode. Enantiomeric excesses were measured on a Shimadzu VP Series Chiral HPLC using Chiralpak IA, IB, or IC columns. The syntheses of TRIP, H8-TRIP, TCYP, and STRIP, have been previously reported. **Caution:** Although we have not experienced any problems during the preparation and handling of the aryldiazounium tetrafluoroborates reported herein, appropriate safety precautions should be taken due to the explosive nature of diazonium salts, including the use of a blast shield. Racemic CAPT products were synthesized utilizing homogeneous conditions in the absence of phase-transfer catalyst with THF as a solvent.

I. Experimental

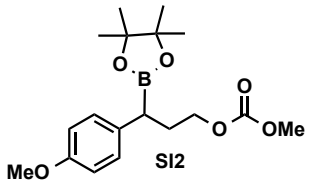
General procedure A: Racemic three-component 1,1-arylborylation reaction for the synthesis of substrates (S1-S)



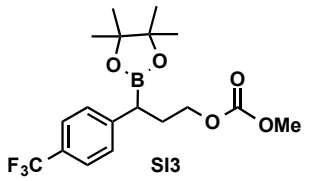
A 1 dram vial was charged with $B_2(pin)_2$ (1.2 equiv.), Pd_2dba_3 (5 mol%), $NaHCO_3$ (1.2 equiv.), the ArN_2BF_4 (1 equiv.). To the solid reagents was added a solution of the appropriate olefin (1 equiv.) in THF (0.086 M). The headspace of the reaction vessel was sparged with N_2 for ca. 0.5 min., and then the vial was capped and the heterogeneous reaction mixture was stirred vigorously. The reaction progress monitored *via* TLC analysis. Upon completion the reaction was concentrated *in vacuo* and the crude reactions were purified by flash column chromatography (EtOAc/Hexanes) to provide pure boronic esters.



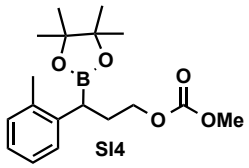
Following the general procedure A, **SI1** was obtained in 72% yield.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29-7.23 (m, 2H), 7.23-7.17 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 4.14 (dt, *J* = 10.6, 6.3 Hz, 1H), 4.05 (dt, *J* = 10.7, 6.9 Hz, 1H), 3.77 (s, 3H), 2.44 (t, *J* = 7.9 Hz, 1H), 2.24 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.02 (tt, *J* = 14.1, 6.4 Hz, 1H), 1.20 (d, *J* = 13.5 Hz, 12H).^{13}C NMR (151 MHz, $CDCl_3$) 156.02, 142.05, 128.69, 128.56, 125.76, 83.74, 67.62, 54.80, 31.43, 24.77. HRMS (ESI) *m/z* $[M+K]^+$ calcd for $C_{17}H_{25}BKO_5$ 359.1427, found 359.1429.



Following the general procedure A, **SI2** was obtained in 90% yield.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.17 – 7.05 (m, 2H), 6.87 – 6.75 (m, 2H), 4.13 (ddd, *J* = 10.6, 6.8, 5.8 Hz, 1H), 4.04 (dt, *J* = 10.6, 7.0 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 2.38 (t, *J* = 7.9 Hz, 1H), 2.19 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.96 (ddt, *J* = 14.2, 8.5, 6.2 Hz, 1H), 1.20 (d, *J* = 10.7 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.75, 156.02, 133.91, 129.46, 114.13, 83.68, 67.58, 55.39, 54.82, 31.63, 24.82, 24.78. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{27}BNaO_6$ 373.1793, found 373.1797.

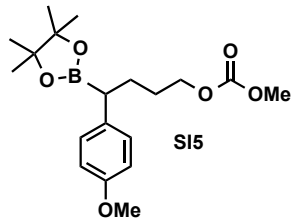


Following the general procedure A, **SI3** was obtained in 71% yield.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 4.14 (dt, *J* = 10.8, 6.2 Hz, 1H), 4.03 (ddd, *J* = 10.7, 7.3, 6.2 Hz, 1H), 3.76 (s, 3H), 2.52 (t, *J* = 7.9 Hz, 1H), 2.25 (dq, *J* = 14.2, 7.2 Hz, 1H), 2.02 (ddd, *J* = 14.0, 8.1, 6.0 Hz, 1H), 1.20 (d, *J* = 10.5 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.96, 146.52, 128.80, 128.24, 128.03, 125.61 (q, *J* = 7.5 Hz), 123.71, 84.05, 67.29, 54.87, 31.18, 24.83, 24.79. HRMS (EI) *m/z* $[M]^+$ calcd for $C_{18}H_{24}BF_3O_5$ 388.1669, found 388.1665.



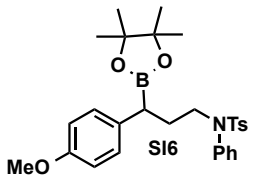
SI4

Following the general procedure A, **SI4** was obtained in 89% yield.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.20 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.15 (tt, *J* = 5.5, 1.5 Hz, 2H), 7.08 (td, *J* = 7.2, 1.5 Hz, 1H), 4.18 (dt, *J* = 10.7, 6.3 Hz, 1H), 4.07 (dt, *J* = 10.5, 6.9 Hz, 1H), 3.79 (s, 3H), 2.66 (t, *J* = 7.8 Hz, 1H), 2.35 (s, 3H), 2.27 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.02 (ddt, *J* = 14.0, 7.9, 6.2 Hz, 1H), 1.22 (d, *J* = 12.1 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.03, 140.49, 136.31, 130.54, 127.95, 126.27, 125.60, 83.65, 67.75, 54.82, 31.01, 24.88, 24.77, 20.29. HRMS (ESI) *m/z* $[M+K]^+$ calcd for $C_{18}H_{27}BKO_5$ 373.1583, 373.1584.



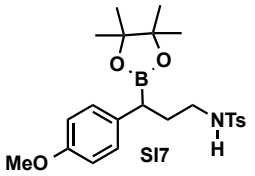
SI5

Following the general procedure A, **SI5** was obtained in 74% yield.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.17 – 7.02 (m, 2H), 6.88 – 6.73 (m, 2H), 4.12 (td, *J* = 6.6, 1.8 Hz, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 2.26 (t, *J* = 7.7 Hz, 1H), 1.96 – 1.83 (m, 1H), 1.76 – 1.57 (m, 3H), 1.22 (d, *J* = 11.4 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.61, 156.01, 134.72, 129.43, 114.01, 83.54, 68.43, 55.37, 54.82, 28.95, 28.33, 24.84, 24.79. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{29}BNaO_6$ 387.1949, found 387.1951.



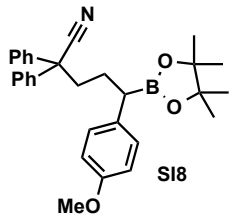
SI6

Following the general procedure A, utilizing deoxygenated THF, **SI6** was obtained in 84% yield.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 – 7.38 (m, 2H), 7.27 (dt, *J* = 4.5, 3.1 Hz, 3H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.06 – 6.93 (m, 4H), 6.81 – 6.67 (m, 2H), 3.75 (s, 3H), 3.48 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 2.32 (t, *J* = 7.9 Hz, 1H), 1.94 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.71 (dq, *J* = 13.6, 7.6 Hz, 1H), 1.17 (d, *J* = 18.5 Hz, 12H).^{13}C NMR (151 MHz, $CDCl_3$) δ 157.61, 143.32, 139.51, 135.50, 134.18, 129.46, 129.38, 129.05, 128.95, 127.90, 127.84, 113.99, 83.61, 55.36, 50.11, 31.41, 24.85, 24.73, 21.73. HRMS (EI) *m/z* $[M]^+$ calcd for $C_{29}H_{36}BNO_5S$ 521.2407, found 521.2399.



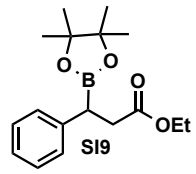
SI7

Following the general procedure A, utilizing deoxygenated THF, **SI6** was obtained in 91% yield.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 9.8 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 4.63 (t, *J* = 6.2 Hz, 1H), 3.79 (d, *J* = 2.5 Hz, 3H), 2.99 – 2.76 (m, 2H), 2.44 (d, *J* = 2.5 Hz, 3H), 2.26 (t, *J* = 7.7 Hz, 1H), 1.95 (dq, *J* = 14.6, 7.4 Hz, 1H), 1.79 (dq, *J* = 14.1, 7.0 Hz, 1H), 1.20 (dd, *J* = 12.8, 2.6 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.75, 143.40, 137.05, 133.81, 129.81, 129.41, 127.34, 114.14, 83.85, 83.34, 55.37, 42.73, 32.43, 24.81, 24.76, 21.71. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{23}H_{32}BNNaO_5S$ 468.1986, found 468.1985.



SI8

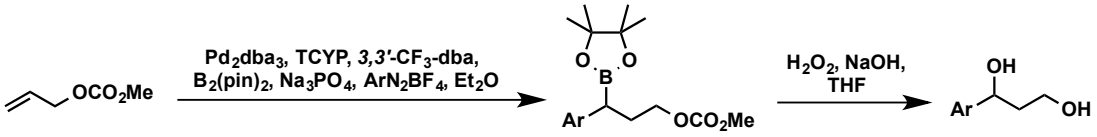
Following the general procedure A, **SI8** was obtained in 99% yield.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.23 (m, 10H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 2.41 – 2.30 (m, 2H), 2.28 (dd, *J* = 8.8, 6.7 Hz, 1H), 2.02 (ddd, *J* = 16.8, 13.7, 7.3 Hz, 1H), 1.87 – 1.73 (m, 1H), 1.21 (d, *J* = 10.4 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.67, 140.72, 140.06, 134.10, 129.47, 128.97, 128.96, 127.88, 127.05, 127.01, 122.63, 114.01, 83.60, 55.37, 51.85, 39.13, 28.43, 24.86, 24.76. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{30}H_{34}BNNaO_3$ 490.2524, found 490.2524.



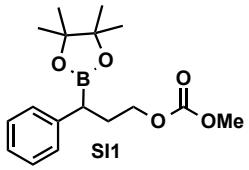
SI9

Following the general procedure A, **SI9** was obtained in 46% yield.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 – 7.23 (m, 4H), 7.22 – 7.16 (m, 1H), 4.24 – 4.06 (m, 2H), 2.92 (dd, *J* = 16.4, 10.2 Hz, 1H), 2.78 (dd, *J* = 10.2, 6.1 Hz, 1H), 2.70 (dd, *J* = 16.4, 6.1 Hz, 1H), 1.29 – 1.19 (m, 15H).^{13}C NMR (151 MHz, $CDCl_3$) δ 173.60, 141.60, 128.65, 128.40, 125.84, 83.74, 60.54, 37.53, 24.79, 24.70, 14.45. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{17}H_{25}BNaO_4$ 343.1477, found 343.1479.

General procedure B: Enantioselective three-component 1,1-arylborylation reaction for the synthesis of substrates (S1, S10-S22)

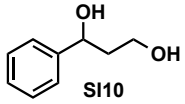


A 1 dram vial was charged with $B_2(pin)_2$ (2.4 equiv.), Pd_2dba_3 (5 mol%), TCYP (10 mol%), m-CF_3-dba (16 mol%), Na_3PO_4 (2.4 equiv.), the ArN_2BF_4 (2 equiv). To the solid reagents was added a solution of allyl methyl carbonate (1 equiv.) in Et_2O (0.043 M in allyl methyl carbonate). The headspace of the reaction vessel was sparged with N_2 for ca. 10 seconds then the vial was capped and the heterogeneous reaction mixture was stirred vigorously. The reaction progress was monitored *via* TLC analysis. Upon completion the reaction was filtered through a plug of cotton to remove solid particulates and then concentrated *in vacuo*.
^{1}H NMR yield: The crude reaction mixture was dissolved in a solution of CD_2Cl_2 and dimethyl sulfone (1 equiv.) to obtain the NMR yield.
Isolated yield of diol (over two steps): The crude reaction mixture was concentrated and purified *via* column chromatograph (EtOAc/Hexanes) to obtain the boronic ester product contaminated with residual B_2pin_2. To this mixture was added THF (1.0 mL), 1 M NaOH (0.50 mL), and 30 % aq. H_2O_2 (0.25 mL) and then reaction mixture was stirred under a N_2 atmosphere. Reaction progress was monitored *via* TLC analysis. Upon complete conversion to the diol, the reaction was quenched with sat. aq. $Na_2S_2O_3$ (5 mL) and extracted with EtOAc (3 X 10 mL). The organic layers were combined, dried with Na_2SO_4, concentrated, and then purified *via* column chromatography (40-60% EtOAc/Hexanes) to provide pure diol.
The amounts of THF, 1M NaOH and hydrogen peroxide are representative of those used in a reaction with 0.043 mmol allyl methyl carbonate.



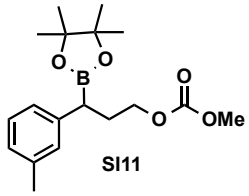
SI1

Following the general procedure B, **SI1** was provided in 36% yield (*via* ^{1}H NMR analysis).
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29-7.23 (m, 2H), 7.23-7.17 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 4.14 (dt, *J* = 10.6, 6.3 Hz, 1H), 4.05 (dt, *J* = 10.7, 6.9 Hz, 1H), 3.77 (s, 3H), 2.44 (t, *J* = 7.9 Hz, 1H), 2.24 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.02 (tt, *J* = 14.1, 6.4 Hz, 1H), 1.20 (d, *J* = 13.5 Hz, 12H).^{13}C NMR (151 MHz, $CDCl_3$) 156.02, 142.05, 128.69, 128.56, 125.76, 83.74, 67.62, 54.80, 31.43, 24.77. HRMS (ESI) *m/z* $[M+K]^+$ calcd for $C_{17}H_{25}BKO_5$ 359.1427, found 359.1429. 92% ee



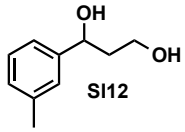
SI10

Following the general procedure B, **SI10** was isolated in 23% yield over two steps. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 6.5 Hz, 3H), 7.33 – 7.22 (m, 2H), 4.98 (dd, *J* = 9.0, 3.6 Hz, 1H), 3.88 (t, *J* = 5.5 Hz, 2H), 2.80 (s, 1H), 2.35 (s, 1H), 2.10 – 1.98 (m, 1H), 1.96 (dq, *J* = 14.2, 4.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.52, 128.76, 127.84, 125.86, 74.63, 61.73, 40.75. Spectra matches previously reported spectra: Borowiecki, P.; Wawro, A. M.; Winska, P.; Wielechowska, M.; Bretner, M. *Eur. J. Med. Chem.* **2014**, *84*, 364. HPLC (ChiralPak IC column) 90:10 (hexane/iPrOH) 1mL/min; T_{major} (15.4 min), T_{minor} (11.8 min); 92% ee



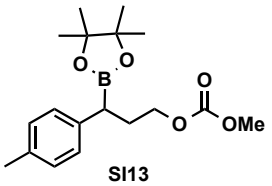
SI11

Following the general procedure B, **SI11** was provided in 50% yield (*via* ^{1}H NMR analysis).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.15 (t, *J* = 7.5 Hz, 1H), 7.03 – 6.94 (m, 3H), 4.14 (ddd, *J* = 10.6, 6.8, 5.8 Hz, 1H), 4.05 (dt, *J* = 10.6, 6.9 Hz, 1H), 3.77 (s, 3H), 2.39 (t, *J* = 7.9 Hz, 1H), 2.31 (s, 3H), 2.22 (dq, *J* = 14.4, 7.3 Hz, 1H), 1.99 (ddt, *J* = 14.1, 8.2, 6.2 Hz, 1H), 1.20 (d, *J* = 11.0 Hz, 12H).^{13}C NMR (126 MHz, $CDCl_3$) δ 156.02, 141.90, 138.16, 129.43, 128.55, 126.55, 125.50, 83.70, 67.69, 54.81, 31.49, 24.79, 21.66. HRMS (ESI) *m/z* $[M+K]^+$ calcd for $C_{18}H_{27}BKO_5$ 373.1583, found 373.1582.



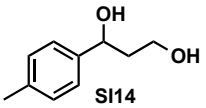
SI12

Following the general procedure B, **SI12** was isolated in 30% yield over two steps. ^{1}H NMR (500 MHz, Chloroform-*d*) 7.27 (d, *J* = 7.6 Hz, 1H), 7.23 (s, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 4.97 (dd, *J* = 8.9, 3.6 Hz, 1H), 3.90 (dd, *J* = 6.5, 4.6 Hz, 2H), 2.77 (s, 1H), 2.39 (s, 4H), 2.11-2.01 (m, 1H), 1.96 (dtd, *J* = 14.6, 5.2, 3.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) 144.44, 138.44, 128.65, 128.58, 126.54, 122.89, 74.75, 61.82, 40.65, 21.69. Spectra matches previously reported spectra: Boyer, S. H.; Sun, Z.; Jiang, H.; Esterbrook, J.; Gómez-Galeno, J. E.; Craigo, W.; Reddy, K. R.; Ugarkar, B. G.; MacKenna, D. A.; Erion, M. D. *J. Med. Chem.* **2006**, *49*, 7711. HPLC (ChiralPak IC column) 90:10 (hexane/iPrOH) 1mL/min; T_{major} (18.2 min), T_{minor} (12.3 min); 88% ee



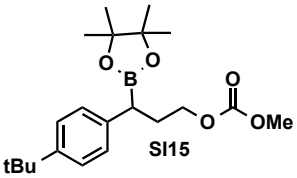
SI13

Following the general procedure B, **SI13** was provided in 46% yield (*via* ^{1}H NMR analysis).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.16 – 7.02 (m, 4H), 4.15 (ddd, *J* = 10.6, 6.8, 5.8 Hz, 1H), 4.06 (dt, *J* = 10.7, 7.0 Hz, 1H), 3.78 (s, 3H), 2.42 (t, *J* = 7.9 Hz, 1H), 2.32 (s, 3H), 2.23 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.00 (ddt, *J* = 14.2, 8.4, 6.2 Hz, 1H), 1.22 (d, *J* = 10.6 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.02, 138.83, 135.13, 129.41, 128.44, 83.67, 67.62, 54.80, 31.56, 24.82, 24.79, 21.20. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{27}BNaO_5$ 357.1844, found 357.1844.



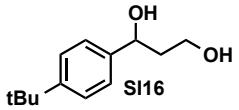
SI14

Following the general procedure B, **SI14** was isolated in 35% yield over two steps. ^{1}H NMR (500 MHz, Chloroform-*d*) = 7.29 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 4.97 (dd, *J* = 9.0, 3.6 Hz, 1H), 3.89 (t, *J* = 5.5 Hz, 2H), 2.72 (s, 1H), 2.38 (s, 4H), 2.11-2.00 (m, 1H), 2.00-1.90 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) = 141.52, 137.55, 129.41, 125.80, 74.59, 61.80, 40.65, 21.33. Spectra matches previously reported spectra: Kim, J.; De Castro, K. A.; Lim, M.; Rhee, H. *Tetrahedron,* **2010**, *66*, 3995. HPLC (ChiralPak IC column) 90:10 (hexane/iPrOH) 1mL/min; T_{major} (18.9 min), T_{minor} (14.2 min); 90% ee



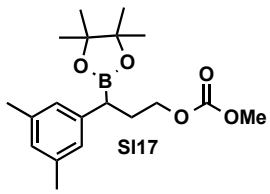
SI15

Following the general procedure B, **SI15** was provided in 32% yield (*via* ^{1}H NMR analysis).
^{1}H NMR (600 MHz, Chloroform-*d*) 7.26 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 4.14 (dt, *J* = 10.6, 6.3 Hz, 1H), 4.05 (dt, *J* = 10.6, 6.9 Hz, 1H), 3.76 (s, 3H), 2.41 (t, *J* = 7.9 Hz, 1H), 2.25-2.14 (m, 1H), 1.99 (dq, *J* = 13.9, 6.3 Hz, 1H), 1.28 (s, 9H), 1.21 (d, *J* = 12.4 Hz, 12H).^{13}C NMR (151 MHz, $CDCl_3$) 156.06, 148.38, 138.77, 128.20, 125.58, 83.69, 67.73, 54.79, 34.51, 31.66, 31.62, 24.84. HRMS (ESI) *m/z* $[M+K]^+$ calcd for $C_{21}H_{33}BKO_5$ 415.2053, found 415.2051.



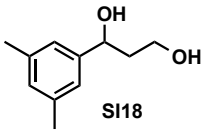
SI16

Following the general procedure B, **SI16** was isolated in 32% yield over two steps. ^{1}H NMR (500 MHz, Chloroform-*d*) 7.42 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 4.99 (dd, *J* = 9.1, 3.6 Hz, 1H), 3.91 (s, 2H), 2.59 (s, 1H), 2.36 (s, 1H), 2.11-2.05 (m, 1H), 2.01-1.92 (m, 1H), 1.35 (s, 10H), 1.29 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) 150.87, 141.47, 125.68, 125.61, 74.58, 61.87, 40.56, 34.75, 31.57. Spectra matches previously reported spectra: Reddy, K. R.; Matelich, M. C.; Ugarkar, B. G.; Gómez-Galeno, J. E.; DaRe, J.; Ollis, K.; Sun, Z.; Craigo, W.; Colby, T. J.; Fujitaki, J. M.; Boyer, S. H.; van Poelje, P. D.; Erion, M. D. *J. Med. Chem.* **2008**, *51*, 666. HPLC (ChiralPak IC column) 90:10 (hexane/iPrOH) 1mL/min; T_{major} (14.9 min), T_{minor} (11.4 min); 96% ee



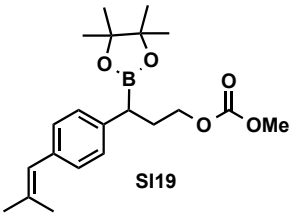
SI17

Following the general procedure B, **SI17** was provided in a 60% yield (*via* ^{1}H NMR analysis).
^{1}H NMR (500 MHz, Chloroform-*d*) = 6.71 (s, 2H), 6.69 (s, 1H), 4.04 (ddd, *J* = 10.8, 6.9, 5.9 Hz, 1H), 3.96 (dt, *J* = 10.5, 6.9 Hz, 1H), 3.67 (s, 3H), 2.25 (t, *J* = 7.9 Hz, 1H), 2.17 (s, 6H), 2.11 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.91-1.83 (m, 1H), 1.11 (d, *J* = 10.6 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) 156.01, 141.80, 137.97, 128.51, 127.48, 126.38, 83.64, 67.74, 54.77, 31.56, 24.74, 21.51. HRMS (ESI) *m/z* $[M+K]^+$ calcd for $C_{19}H_{29}BKO_5$ 387.1740, found 387.1739.



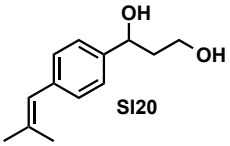
SI18

Following the general procedure B, **SI18** was isolated in a 42% yield over two steps. ^{1}H NMR (600 MHz, Chloroform-*d*) = 6.99 (s, 2H), 6.94 (s, 1H), 4.91 (dd, *J* = 7.7, 4.5 Hz, 1H), 3.99-3.80 (m, 2H), 2.61 (s, 1H), 2.33 (s, 6H), 2.10-1.98 (m, 1H), 1.98-1.88 (m, 1H), 1.60 (s, 2H), 1.25 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) 144.50, 138.37, 129.48, 123.64, 74.74, 61.82, 40.74, 25.09, 21.55. Spectra matches previously reported spectra: Reddy, K. R.; Matelich, M. C.; Ugarkar, B. G.; Gómez-Galeno, J. E.; DaRe, J.; Ollis, K.; Sun, Z.; Craigo, W.; Colby, T. J.; Fujitaki, J. M.; Boyer, S. H.; van Poelje, P. D.; Erion, M. D. *J. Med. Chem.* **2008**, *51*, 666. HPLC (ChiralPak IC column) 90:10 (hexane/iPrOH) 1mL/min; T_{major} (18.1 min), T_{minor} (11.9 min); 85% ee



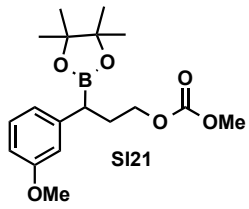
SI19

Following the general procedure B, **SI19** was provided in a 40% yield (*via* ^{1}H NMR analysis).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.14 (s, 4H), 6.22 (t, *J* = 1.6 Hz, 1H), 4.14 (dt, *J* = 10.8, 6.3 Hz, 1H), 4.06 (dt, *J* = 10.6, 6.9 Hz, 1H), 3.76 (d, *J* = 0.8 Hz, 3H), 2.42 (t, *J* = 7.9 Hz, 1H), 2.22 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.89 (d, *J* = 1.3 Hz, 3H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.20 (d, *J* = 10.9 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.02, 139.42, 136.13, 134.99, 129.05, 128.22, 125.13, 83.72, 67.66, 54.81, 31.41, 27.18, 24.82, 24.77, 19.68. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{21}H_{31}BNaO_5$ 397.2157, found 397.2160.



SI20

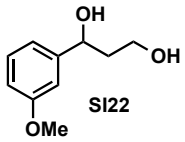
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.26 (s, 1H), 5.04 – 4.87 (m, 1H), 3.89 (q, *J* = 5.3, 4.8 Hz, 2H), 2.65 (d, *J* = 2.7 Hz, 1H), 2.30 (s, 1H), 2.11 – 2.00 (m, 1H), 2.00 – 1.94 (m, 1H), 1.91 (d, *J* = 1.4 Hz, 3H), 1.87 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.82, 138.35, 135.97, 129.08, 125.59, 124.87, 74.63, 61.84, 40.59, 27.14, 19.65. HRMS (EI) *m/z* $[M]^+$ calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1310. HPLC (ChiralPak IC column) 90:10 (hexane/iPrOH) 1mL/min; T_{major} (min), T_{minor} (min); 98% ee



SI21

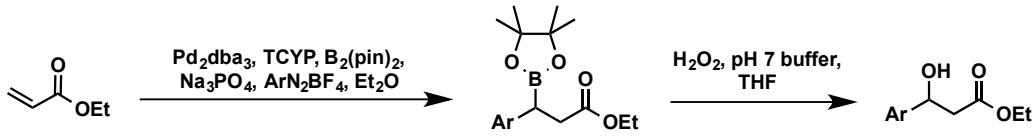
Following the general procedure B, **SI21** was provided in a 58% yield (*via* ^{1}H NMR analysis).
^{1}H NMR (600 MHz, Chloroform-*d*) 7.18 (t, *J* = 7.9 Hz, 1H), 6.79 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.76 (t, *J* = 2.2 Hz, 1H), 6.70 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 4.21 ? 4.09 (m, 1H), 4.05 (dt, *J* = 10.7, 6.9 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 2.42 (t, *J* = 7.9 Hz, 1H), 2.22 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.00 (ddt, *J* = 14.2, 8.5, 6.2 Hz,

1H), 1.20 (d, J = 12.5 Hz, 12H).[13]C NMR (151 MHz, $CDCl_3$) 159.87, 156.01, 143.66, 129.59, 121.04, 114.18, 111.30, 83.76, 67.60, 55.29, 54.80, 31.42, 24.80. **HRMS**



Following the general procedure B, **SI22** was isolated in a 37% yield over two steps. [1]H NMR (500 MHz, Chloroform-*d*) 7.33-7.21 (m, 1H), 7.01-6.91 (m, 2H), 6.87-6.77 (m, 1H), 4.96 (dd, J = 8.8, 3.7 Hz, 1H), 3.88 (dd, J = 6.6, 4.4 Hz, 2H), 3.83 (s, 3H), 2.82 (s, 1H), 2.33 (s, 1H), 2.10-1.99 (m, 1H), 1.99-1.88 (m, 1H). [13]C NMR (126 MHz, $CDCl_3$) 159.99, 146.23, 129.78, 118.11, 113.24, 111.32, 74.58, 61.76, 55.46, 40.64. Spectra matches previously reported spectra: Borowiecki, P.; Wawro, A. M.; Winska, P.; Wielechowska, M.; Bretner, M. *Eur. J. Med. Chem.* **2014**, *84*, 364. HPLC (ChiralPak IC column) 90:10 (hexane/iPrOH) 1mL/min; T_{major} (19.6 min), T_{minor} (11.1 min); 87% ee

General procedure C: Enantioselective three-component 1,1-arylborylation reaction for the synthesis of substrates (SI9, SI23-S28)

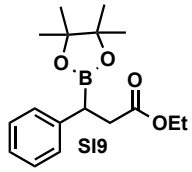


A 1 dram vial was charged with $B_2(pin)_2$ (2.2 equiv.), Pd_2dba_3 (4 mol%), TCYP (10 mol%), Na_3PO_4 (2.4 equiv.), the ArN_2BF_4 (1 equiv). To the solid reagents was added a solution of ethyl acrylate (1 equiv.) in Et_2O (0.1 M). The vial was capped and the heterogeneous reaction mixture was stirred vigorously. The reaction progress monitored *via* TLC analysis. Upon completion the reaction was filtered through a plug of Celite, and then concentrated *in vacuo*.

[1]H NMR yield: The NMR yield was assessed by dissolving the crude reaction mixture in a solution of CD_2Cl_2 with dimethyl sulfone (1 equiv.) as the internal standard.

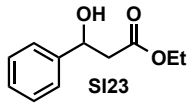
Isolated yield of alcohol (over two steps): The crude reaction mixture (containing dimethyl sulfone) was purified *via* flash column chromatography (EtOAc/Hexanes) to provide the boronic ester product that was contaminated with residual B_2pin_2. The mixture of product and byproduct was treated with THF (1 ml), pH 7 phosphate buffer solution (0.5 mL) was added, followed by the dropwise addition of 30% aq. hydrogen peroxide (0.25 mL). After 0.5 hr, stirring under a N_2 atmosphere, the reaction mixture was cautiously quenched with sat. aq. $Na_2S_2O_3$ (2 mL), and then diluted with H_2O. The aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The crude reaction mixture was purified *via* flash column chromatography (EtOAc/Hexanes) to afford pure hydroxy ethyl esters as yellow oils.

The amounts of THF, pH 7 buffer and hydrogen peroxide are representative of those used in a reaction with 0.09 mmol ethyl acrylate.



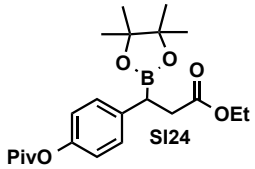
Following the general procedure C, **SI9** was provided in a 47% yield (*via* [1]H NMR analysis).

[1]H NMR (600 MHz, Chloroform-*d*) δ 7.33 – 7.23 (m, 4H), 7.22 – 7.16 (m, 1H), 4.24 – 4.06 (m, 2H), 2.92 (dd, J = 16.4, 10.2 Hz, 1H), 2.78 (dd, J = 10.2, 6.1 Hz, 1H), 2.70 (dd, J = 16.4, 6.1 Hz, 1H), 1.29 – 1.19 (m, 15H).[13]C NMR (151 MHz, $CDCl_3$) δ 173.60, 141.60, 128.65, 128.40, 125.84, 83.74, 60.54, 37.53, 24.79, 24.70, 14.45. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{17}H_{25}BNaO_4$ 343.1477, found 343.1479.



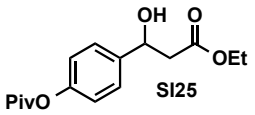
SI23

Following the general procedure C, **SI23** was isolated in a 46% yield over two steps. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.37 (dd, *J* = 13.5, 6.2 Hz, 4H), 7.30 (t, *J* = 7.0 Hz, 1H), 5.15 (dt, *J* = 9.1, 3.3 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.28 (d, *J* = 3.4 Hz, 1H), 2.83 – 2.64 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.63, 142.72, 128.77, 128.02, 125.89, 70.56, 61.10, 43.55, 14.37. Spectra matches previously reported spectra: Wolf, C.; Moskowitz, M. *J. Org. Chem.* **2011**, *76*, 6372. HPLC (ChiralPak column) (hexane/iPrOH) 1mL/min; T_{major} (9.0 min), T_{minor} (8.2 min); 86% ee



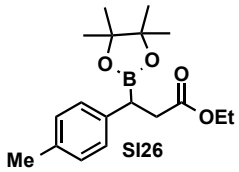
SI24

Following the general procedure C, **SI24** was provided in a 40% yield (*via* ^{1}H NMR analysis).
^{1}H NMR (500 MHz, Chloroform-*d*) 7.26-7.18 (m, 2H), 7.02-6.87 (m, 2H), 4.11 (qq, *J* = 10.8, 7.1 Hz, 2H), 2.86 (dd, *J* = 16.3, 10.0 Hz, 1H), 2.74 (dd, *J* = 10.0, 6.0 Hz, 1H), 2.65 (dd, *J* = 16.3, 6.0 Hz, 1H), 1.34 (s, 9H), 1.28-1.22 (m, 3H), 1.20 (app d, *J* = 20.4 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) 177.41, 173.52, 149.25, 138.84, 129.24, 121.57, 83.82, 60.65, 39.24, 37.57, 27.35, 24.79, 24.71, 14.46. HRMS (ESI) *m/z* $[M+K]^+$ calcd for $C_{22}H_{33}BKO_6$ 427.2262, found 427.2266.



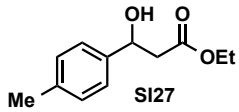
SI25

Following the general procedure C, **SI25** was isolated in a 37% yield over two steps. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 5.15 (dt, *J* = 7.9, 3.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.33 (d, *J* = 3.3 Hz, 1H), 2.81 – 2.63 (m, 2H), 1.36 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.34, 172.61, 150.76, 140.00, 126.92, 121.79, 70.04, 61.18, 43.50, 39.28, 27.34, 14.37. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{16}H_{22}NaO_5$ 317.1359, found 317.1357. 92% ee



SI26

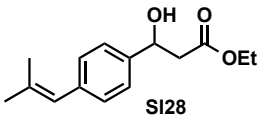
Following the general procedure C, **SI26** was provided in a 44% yield (*via* ^{1}H NMR analysis).
^{1}H NMR (600 MHz, Chloroform-*d*) 7.12 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 4.21-4.01 (m, 2H), 2.86 (dd, *J* = 16.3, 10.1 Hz, 1H), 2.70 (dd, *J* = 10.1, 6.1 Hz, 1H), 2.63 (dd, *J* = 16.4, 6.1 Hz, 1H), 2.30 (s, 3H), 1.24-1.13 (m, 15H). ^{13}C NMR (151 MHz, $CDCl_3$) 173.66, 138.47, 135.22, 129.37, 128.29, 83.69, 60.50, 37.73, 24.81, 24.73, 21.18, 14.46. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{18}H_{27}BNaO_4$ 341.1895, found 341.1894.



SI27

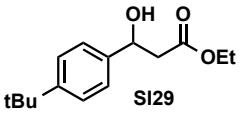
Following the general procedure C, **SI27** was isolated in a 44% yield over two steps. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 – 7.22 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 5.11 (dd, *J* = 9.6, 3.4 Hz, 1H), 4.19 (qd, *J* = 7.1, 1.1 Hz, 2H), 3.21 (s, 1H), 2.76 (ddd, *J* = 16.3, 9.4, 1.1 Hz, 1H), 2.70 (ddd, *J* = 16.3, 3.7, 1.1 Hz, 1H), 2.35 (s, 3H), 1.28 (td, *J* = 7.2, 1.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.63, 139.80, 137.70, 129.41, 125.83, 70.41, 61.04, 43.55, 21.31, 14.37. Spectra matches previously reported spectra: Wolf, C.;

Moskowitz, M. *J. Org. Chem.* **2011**, *76*, 6372. HPLC (ChiralPak column) (hexane/iPrOH) 1mL/min; T_{major} (9.0 min), T_{minor} (8.2 min); 84% ee



SI28

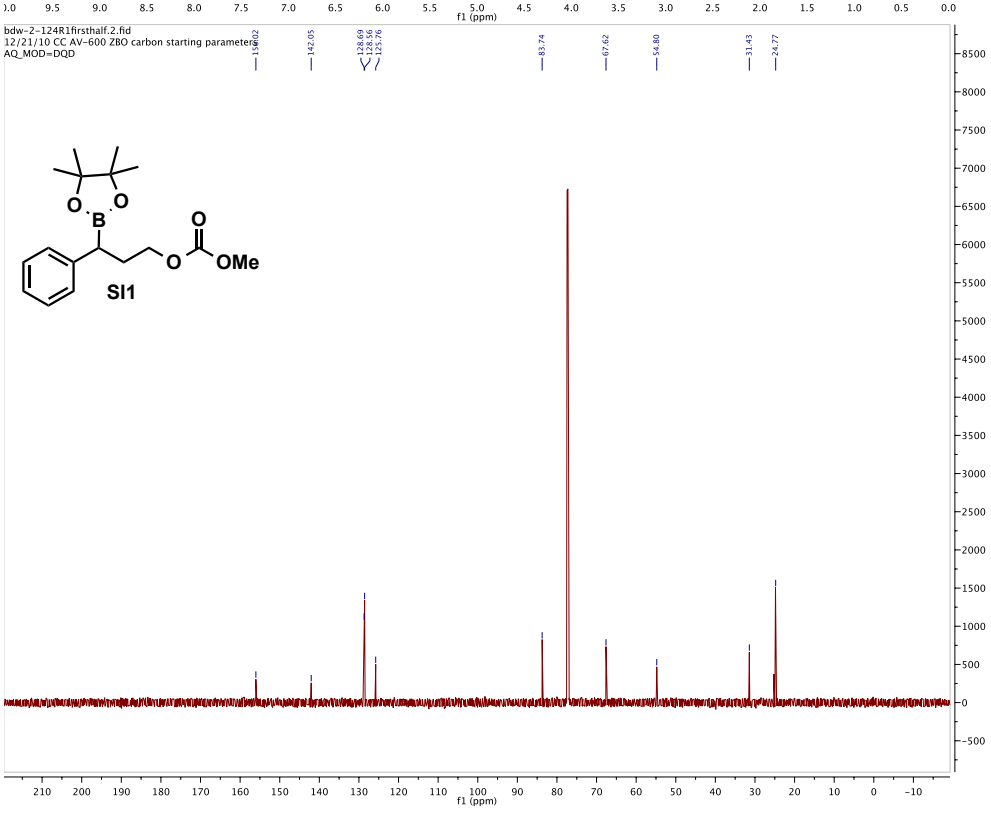
Following the general procedure C, **SI28** was isolated in a 27% yield over two steps. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.26 (s, 1H), 5.13 (dt, *J* = 9.3, 3.2 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.24 (d, *J* = 3.4 Hz, 1H), 2.84 – 2.64 (m, 2H), 1.91 (d, *J* = 1.4 Hz, 3H), 1.86 (d, *J* = 1.4 Hz, 3H), 1.27 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.72, 140.00, 138.50, 136.03, 129.08, 125.62, 124.86, 70.42, 61.10, 43.42, 27.13, 19.63, 14.38. HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{15}H_{20}NaO_3$ 271.1305, found 271.1306. HPLC (ChiralPak column) (hexane/iPrOH) 1mL/min; T_{major} (21.0 min), T_{minor} (22.3 min); 96% ee



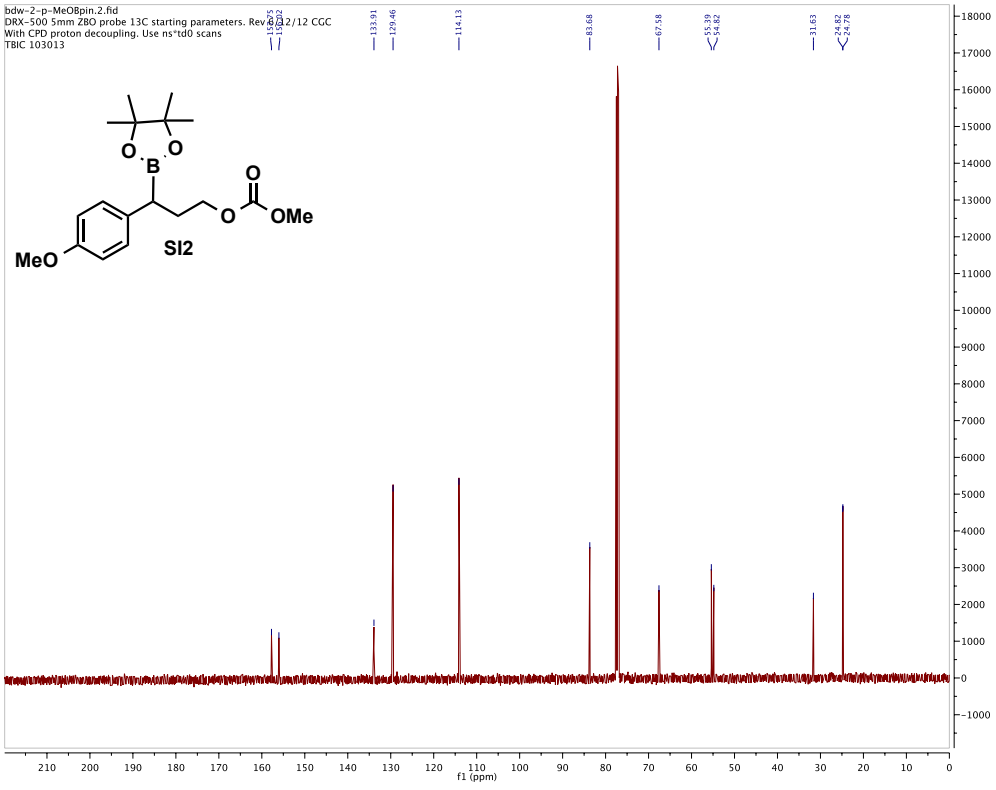
SI29

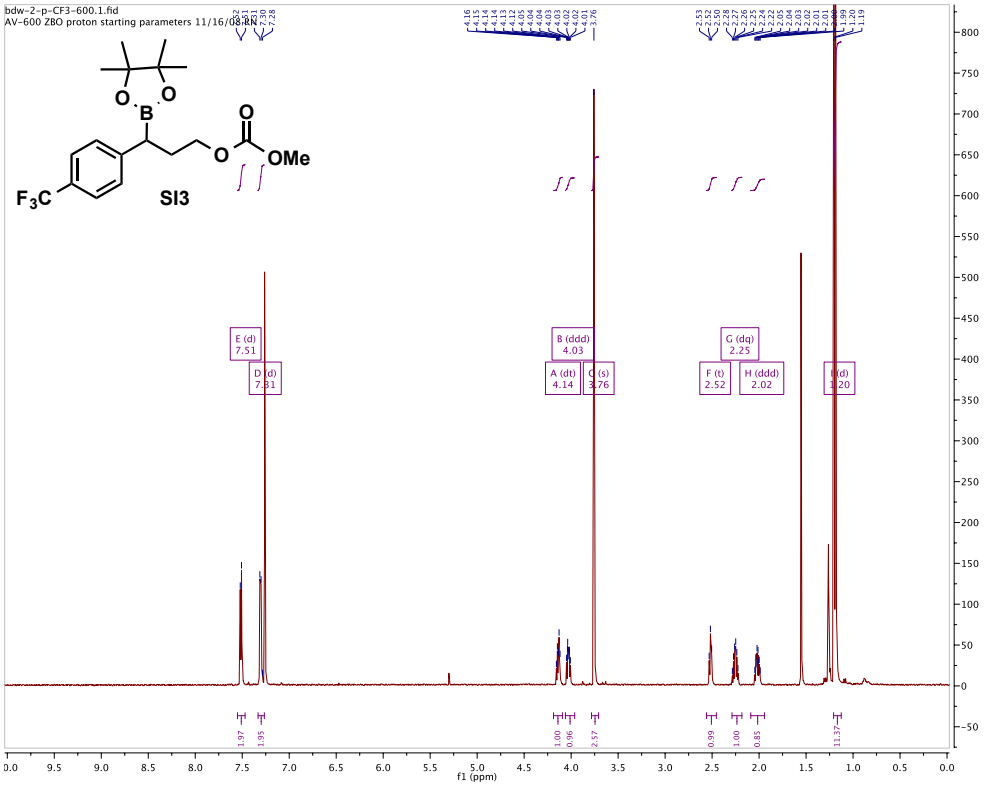
^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 5.12 (dt, *J* = 7.3, 3.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.25 – 3.09 (bs, 1H), 2.80 – 2.66 (m, 2H), 1.35 (s, 8H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 172.65, 151.05, 140.17, 125.73, 125.68, 70.34, 61.10, 43.59, 34.74, 31.40, 14.30. Spectra matches previously reported spectra: Wolf, C.; Moskowitz, M. *J. Org. Chem.* **2011**, *76*, 6372. HPLC (ChiralPak column) (hexane/iPrOH) 1mL/min; T_{major} (21.4 min), T_{minor} (23.0 min); 98 % ee

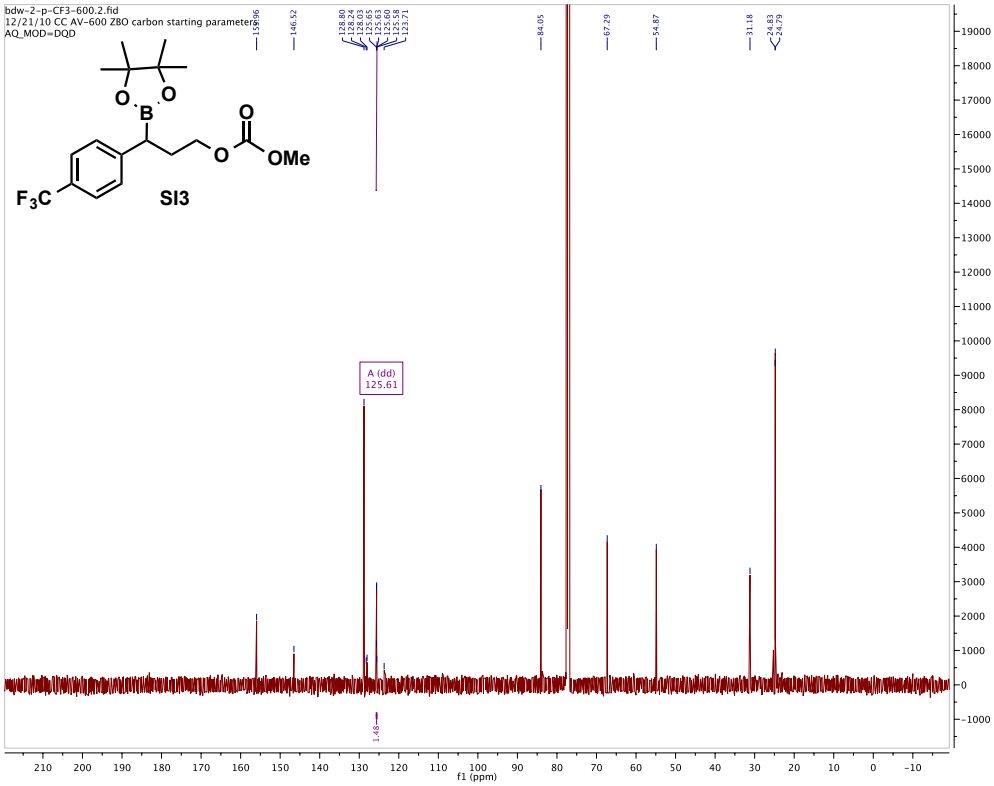

bdw-2-124R1firsthalf.1.fid
AV-600 ZBO proton starting parameters 11/15/08 RN
SI1
E (m) 7.26
D (m) 7.20
J (t) 7.15
B (dt) 4.05
A (dd) 4.14
C (d) 3.77
G (dq) 2.24
F (t) 2.44
H (tt) 2.02
I (d) 1.20
f1 (ppm)

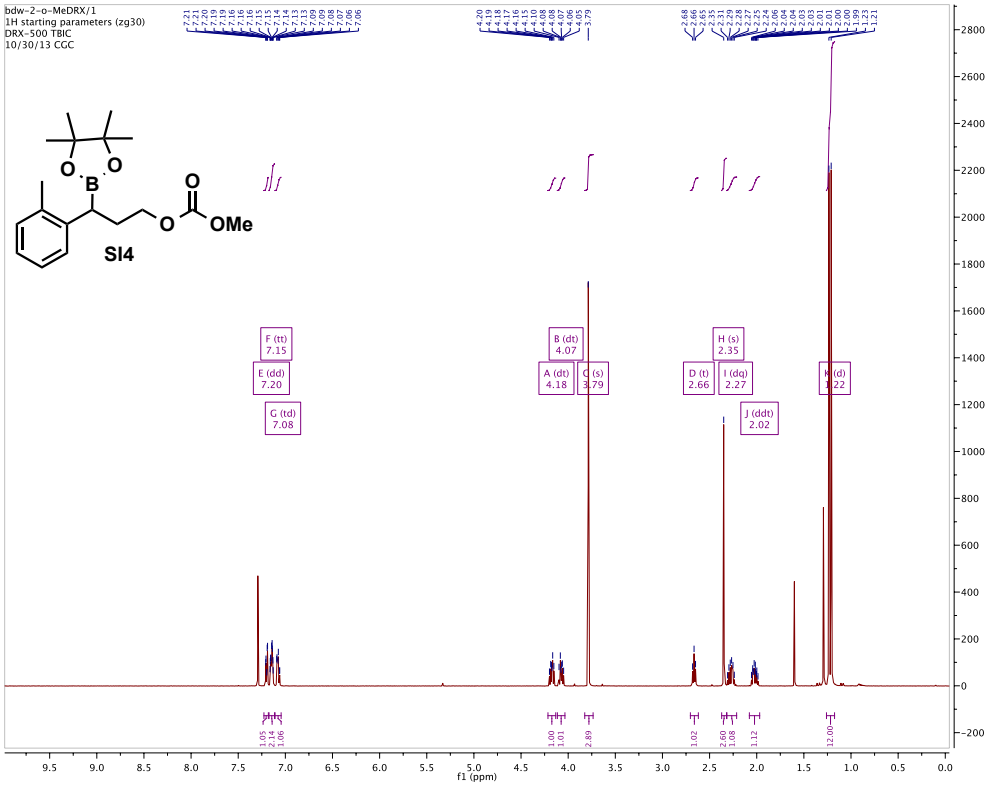

bdw-2-124R1firsthalf.2.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
SI1
f1 (ppm)

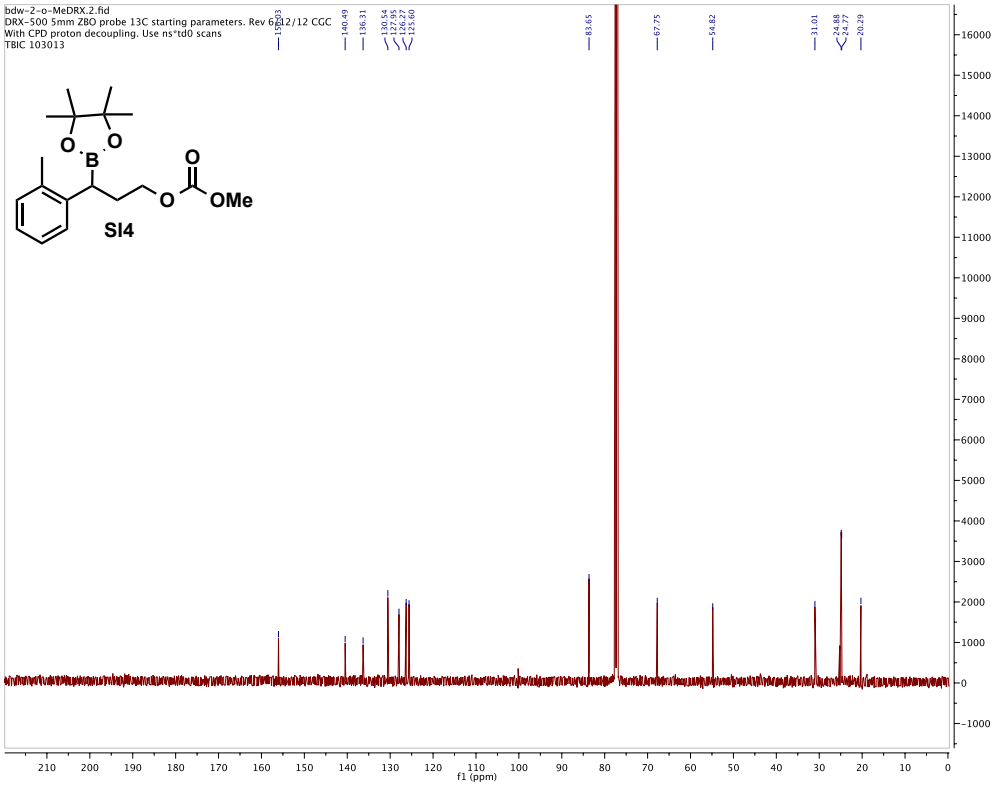

bdw-2-p-MeOBpin.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
MeO
SI2
OMe
D (s) 3.78
B (dt) 4.04
F (m) 6.82
E (m) 7.11
A (ddd) 4.13
C (s) 3.76
H (dq) 2.19
G (t) 2.38
I (ddt) 1.96
J (d) 1.20
f1 (ppm)

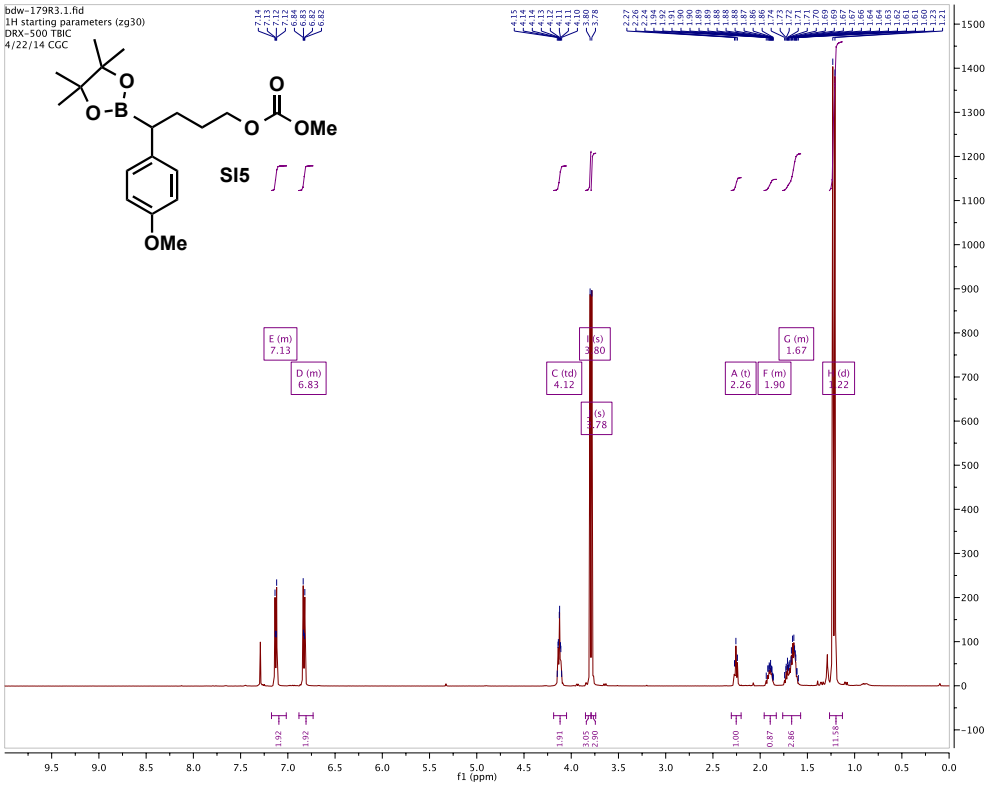

bdw-2-p-MeOBpin.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
MeO
SI2
OMe
f1 (ppm)

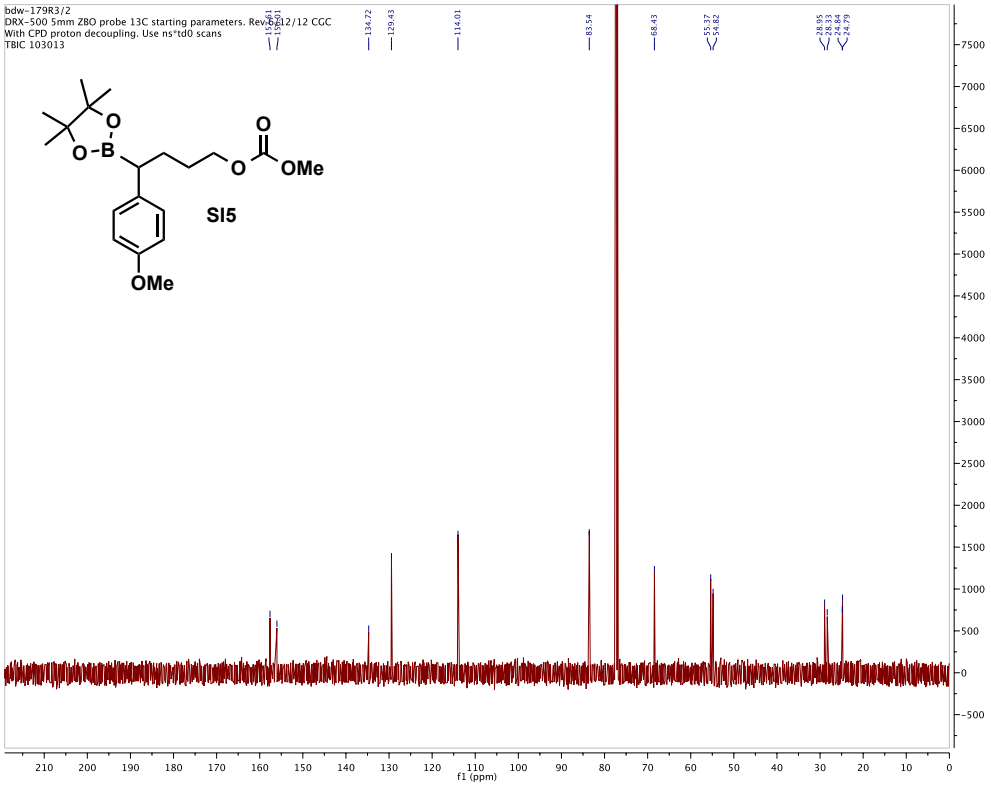

bdw-2-p-CF3-600.1.fid
AV-600 ZBO proton starting parameters 11/16/08 RZ
SI3
E (d) 7.51
D (d) 7.31
B (ddd) 4.03
A (dt) 4.14
C (s) 3.76
G (dq) 2.25
F (t) 2.52
H (dddd) 2.02
I (d) 1.20
f1 (ppm)

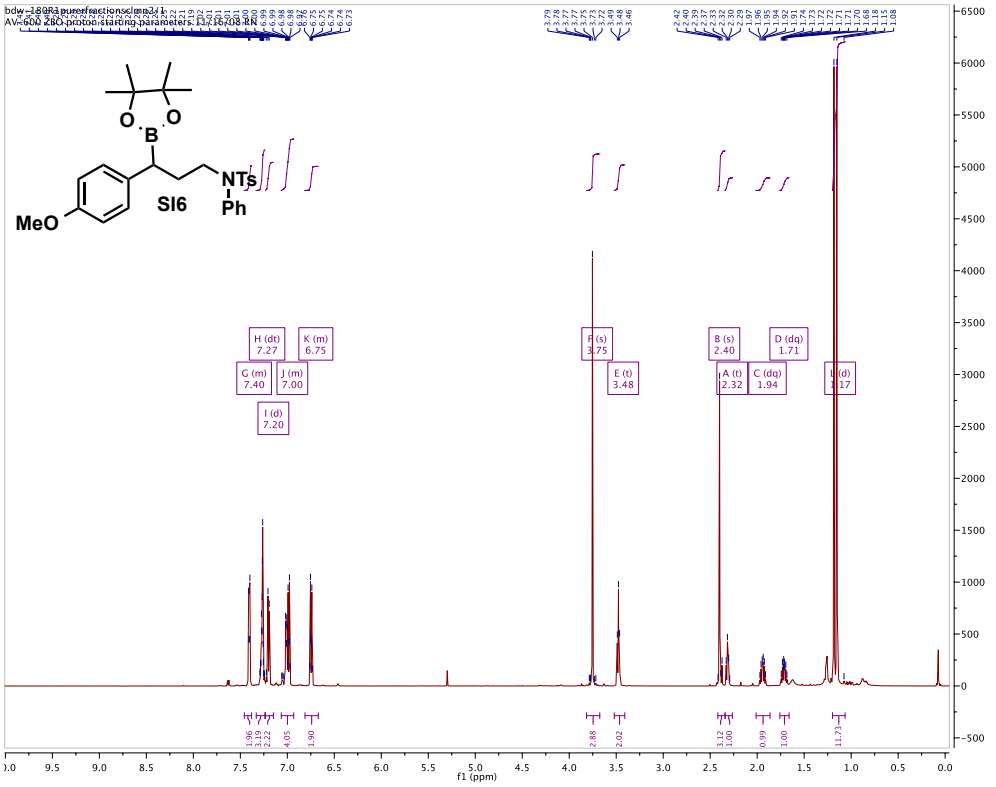

bdw-2-p-CF3-600.2.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
SI3
A (dd) 125.61
f1 (ppm)

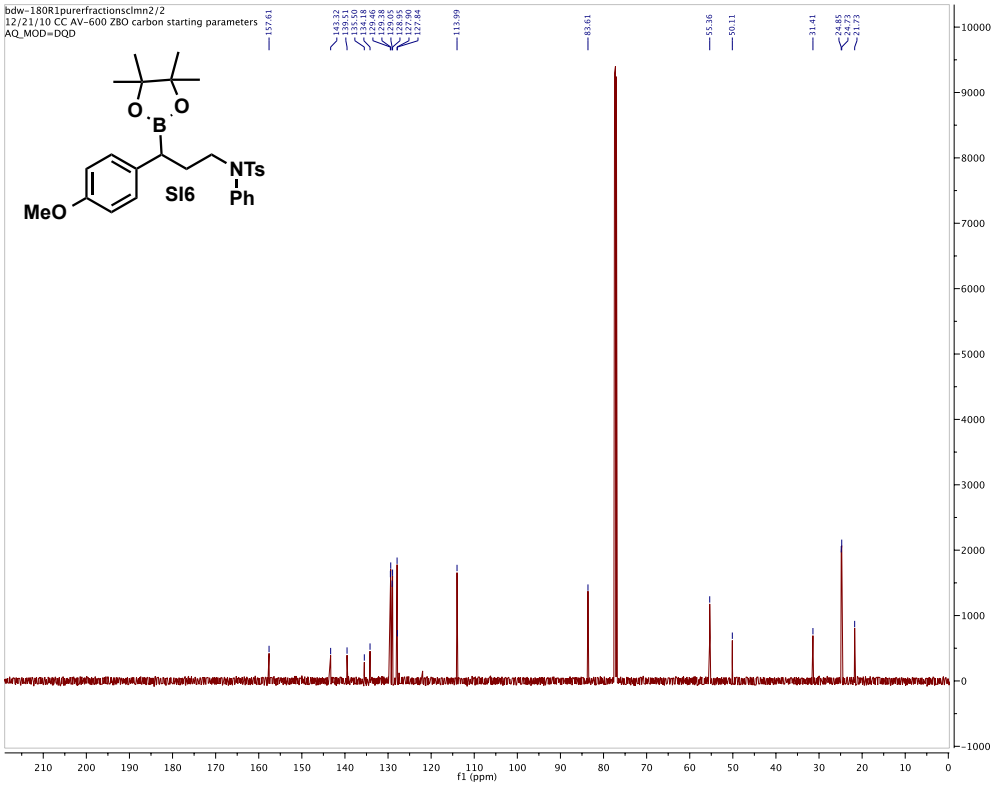

bdw-2-o-MeDRX/1
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
SI4
F (tt) 7.15
E (dd) 7.20
G (td) 7.08
B (dt) 4.07
A (dt) 4.18
C (s) 3.79
H (s) 2.35
D (t) 2.66
I (dq) 2.27
J (ddt) 2.02
K (d) 1.22
f1 (ppm)

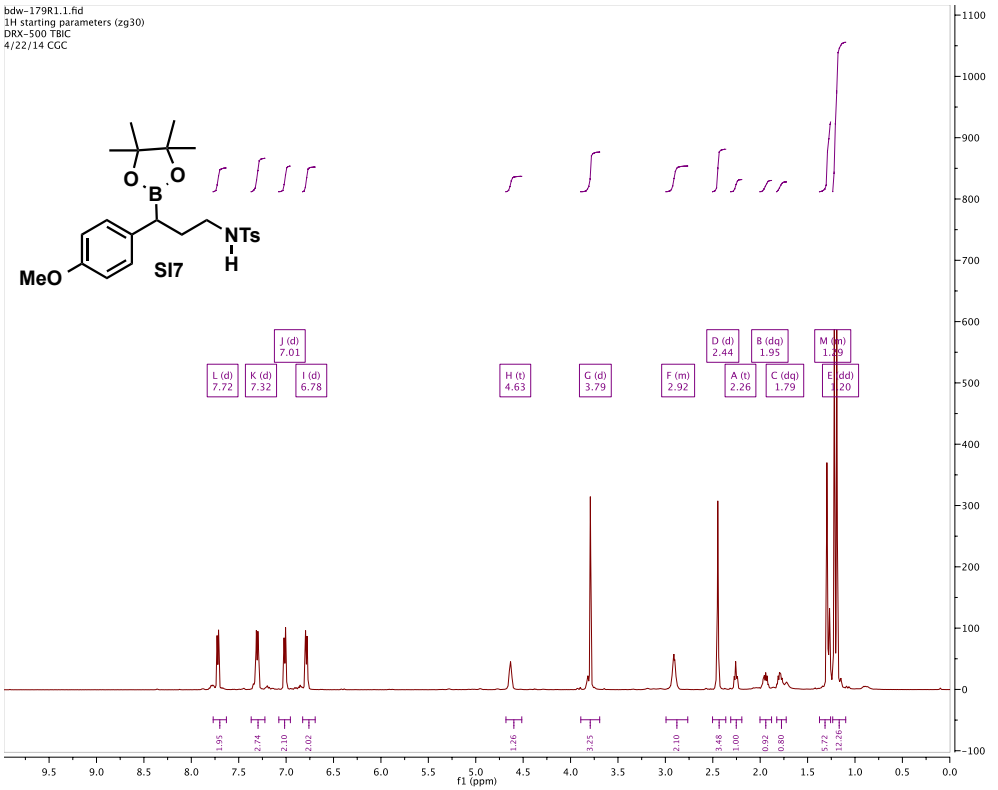

bdw-2-o-MeDRX.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
SI4
f1 (ppm)

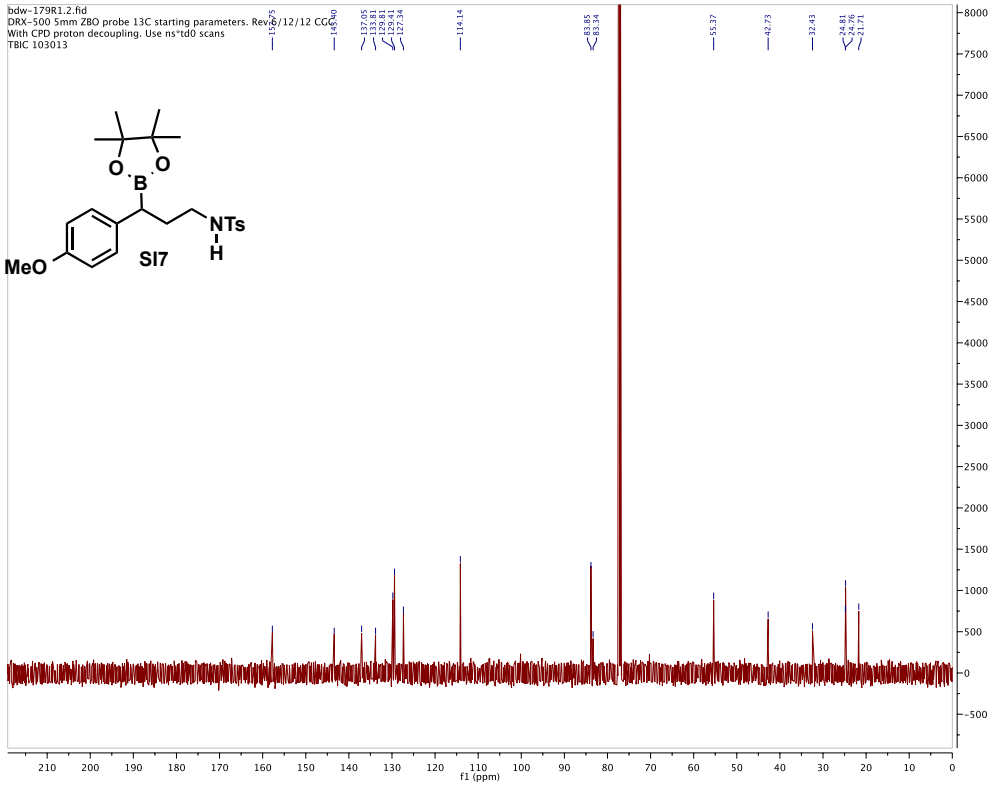

bdw-179R3.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
4/22/14 CGC
SI5
OMe
E (m) 7.13
D (m) 6.83
C (td) 4.12
B (s) 3.80
A (t) 2.26
F (m) 1.90
G (m) 1.67
f1 (ppm)

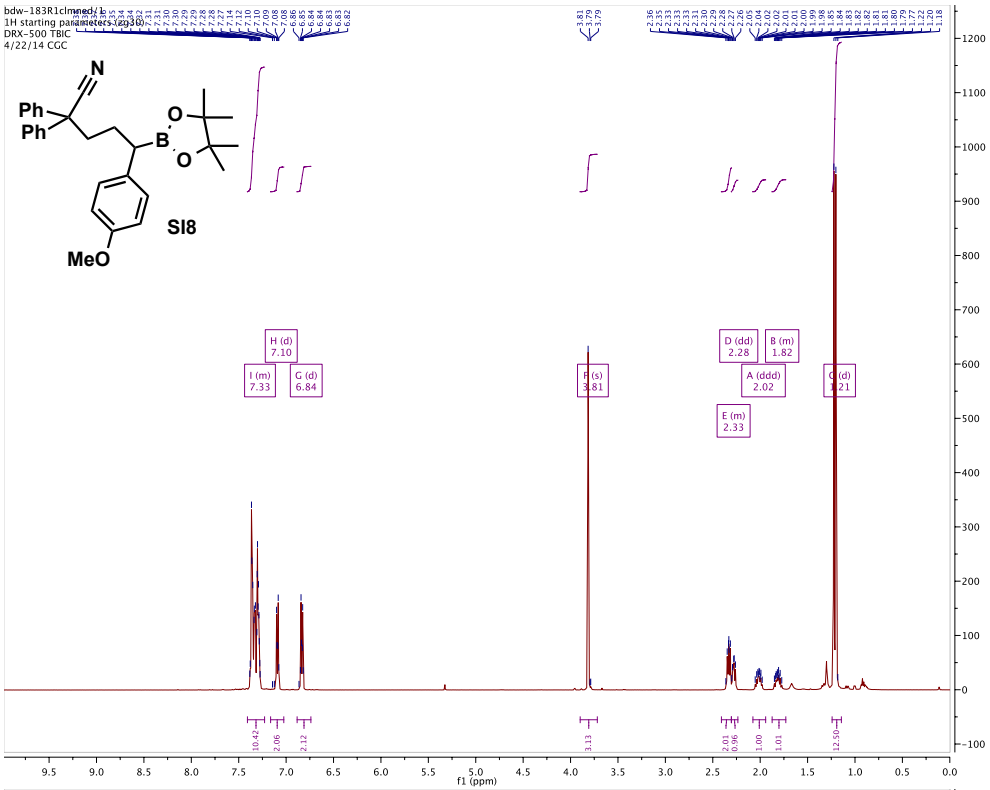

bdw-179R3/2
DRX-500 5mm ZBO probe 13C starting parameters. Rev. 12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
SI5
OMe
f1 (ppm)

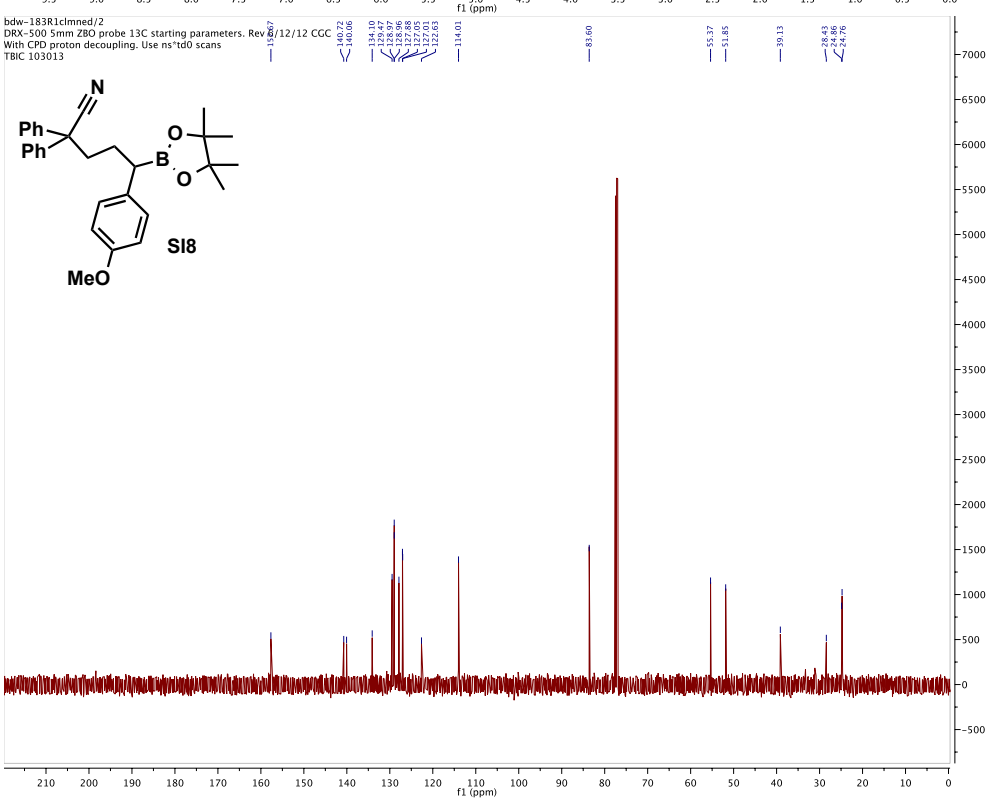

bdw-180R1purerfractionsclmn2/1
AV-600 ZBO proton starting parameters 12/16/08 RR
O
B
O
NTs
Ph
MeO
SI6
H (dt) 7.27
K (m) 6.75
G (m) 7.40
J (m) 7.00
I (d) 7.20
F (s) 3.75
E (t) 3.48
B (s) 2.40
D (dq) 1.71
A (t) 2.32
C (dq) 1.94
L (d) 1.17
f1 (ppm)

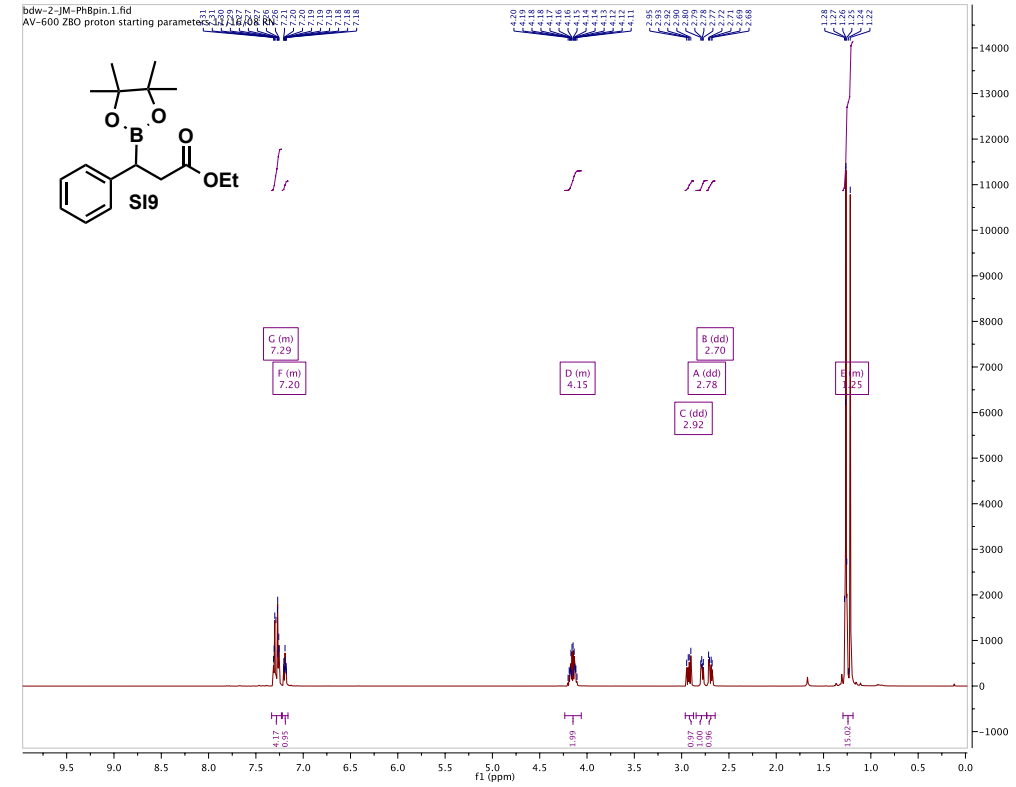

bdw-180R1purerfractionsclmn2/2
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
O
B
O
NTs
Ph
MeO
SI6
157.61
143.32
135.51
135.50
134.48
129.49
129.38
128.95
128.95
127.90
127.84
113.99
83.61
55.36
50.11
31.41
24.85
24.73
21.73
f1 (ppm)

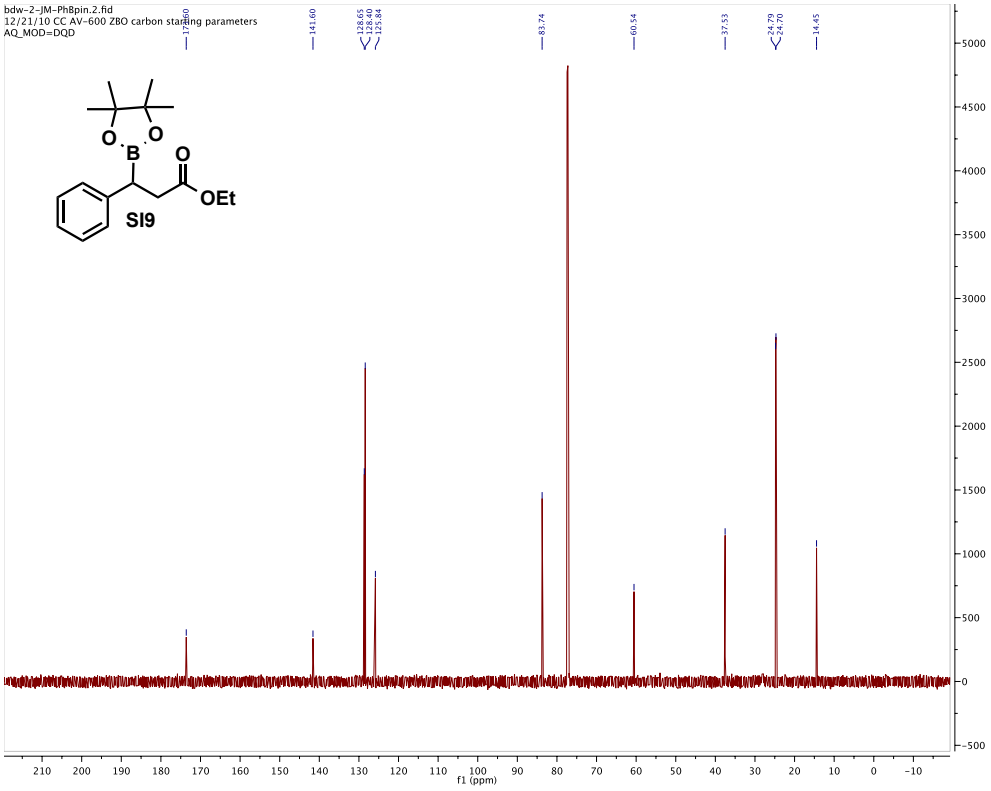

bdw-179R1.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
4/22/14 CGC
O
O
B
NTs
H
MeO
SI7
L (d) 7.72
K (d) 7.32
J (d) 7.01
I (d) 6.78
H (t) 4.63
G (d) 3.79
F (m) 2.92
D (d) 2.44
A (t) 2.26
B (dq) 1.95
C (dq) 1.79
M (m) 1.29
E (dd) 1.20
1.95
2.74
2.10
2.02
1.26
3.25
2.10
3.48
1.00
0.92
0.80
5.72
12.26
f1 (ppm)

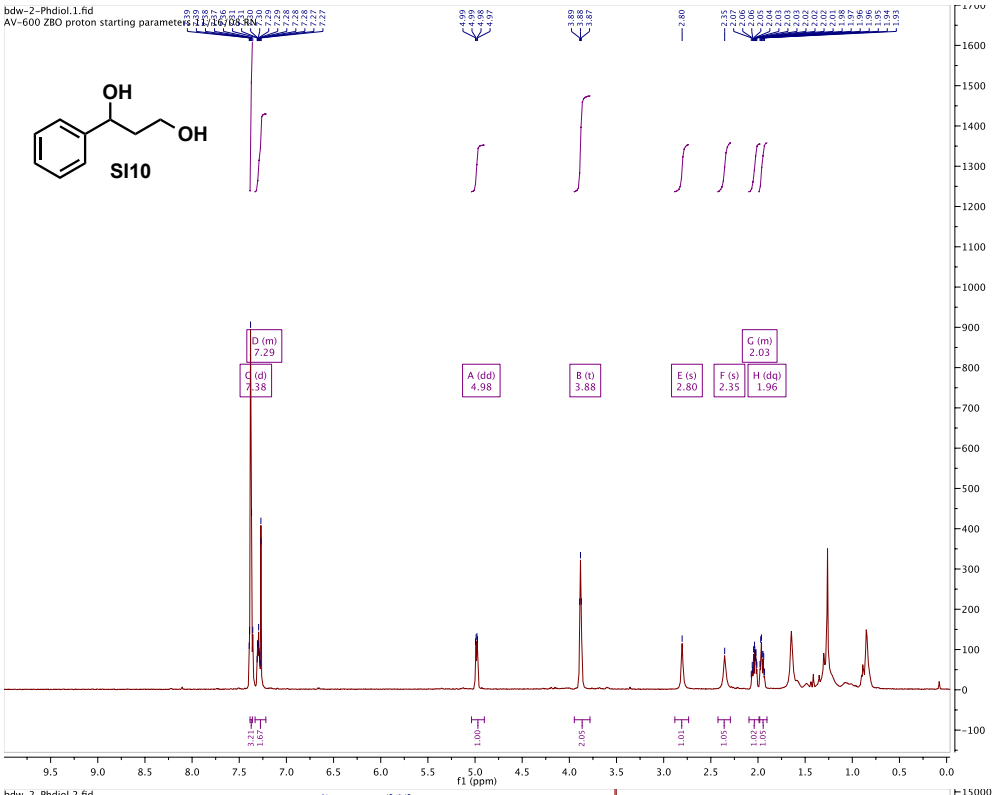

bdw-179R1.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev. 7/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
155.75
144.40
137.05
133.81
129.81
129.34
127.34
114.14
83.85
83.34
55.37
42.73
32.43
24.81
24.26
21.71
O
O
B
NTs
H
MeO
SI7
f1 (ppm)

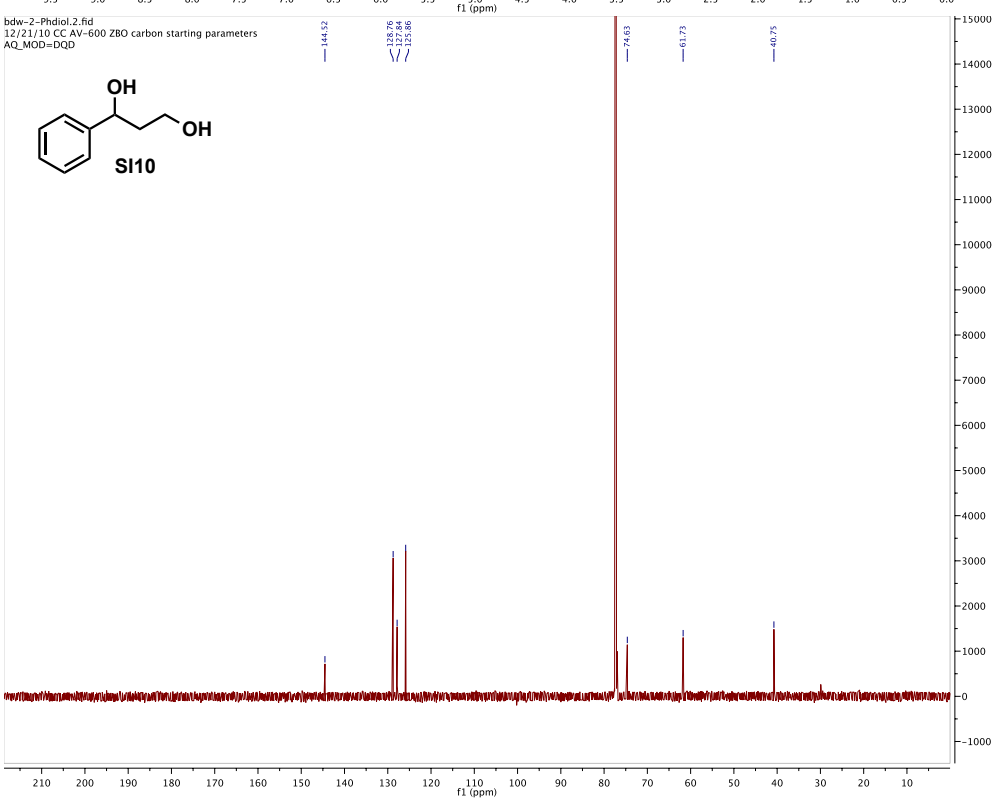

bdw-183R1clmned/1
1H starting parameters (zg30)
DRX-500 TBIC
4/22/14 CGC
N
Ph
Ph
O
B
O
MeO
SI8
H (d) 7.10
I (m) 7.33
G (d) 6.84
F (s) 3.81
D (dd) 2.28
B (m) 1.82
A (ddd) 2.02
C (d) 1.21
E (m) 2.33
f1 (ppm)

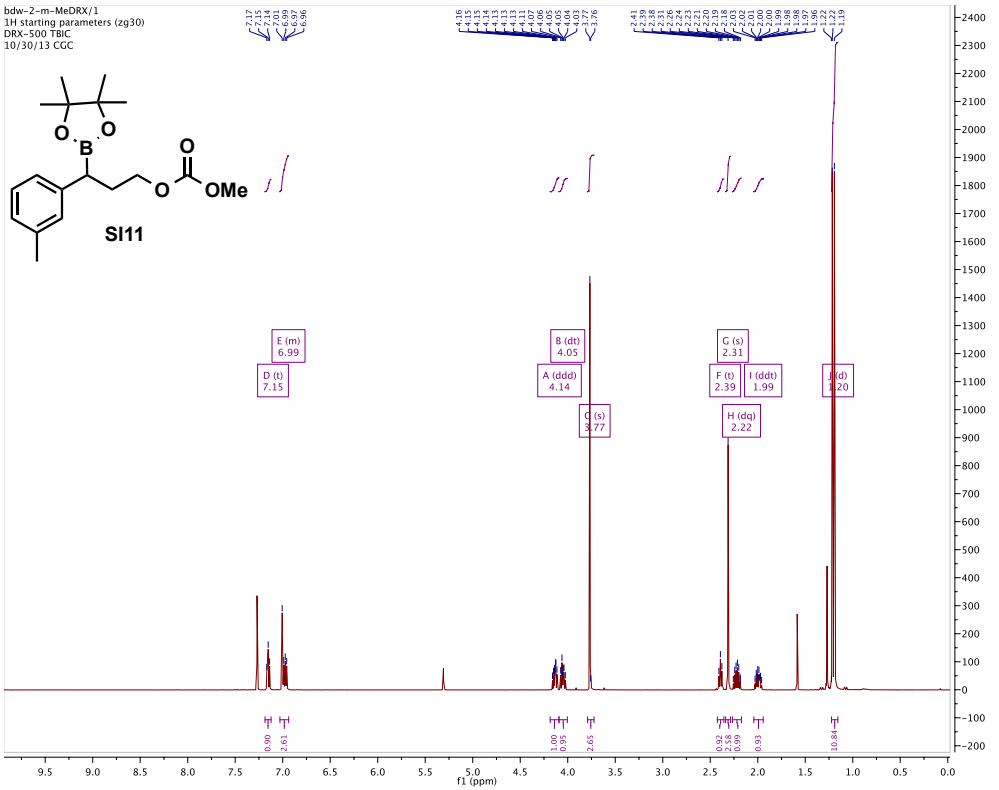

bdw-183R1clmned/2
DRX-500 5mm ZBO probe 13C starting parameters. Rev 12/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
N
Ph
Ph
O
B
O
MeO
SI8
f1 (ppm)

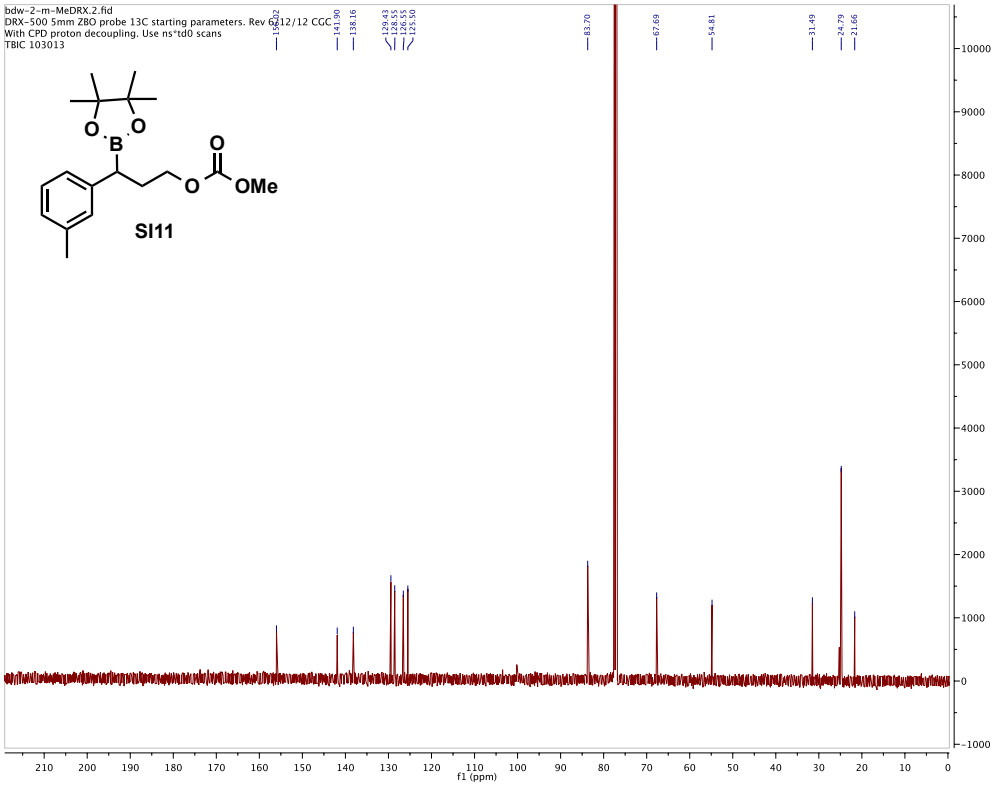

bdw-2-JM-PhBpin.1.fid
AV-600 ZBO proton starting parameters 12/16/08 RK
SI9
G (m) 7.29
F (m) 7.20
D (m) 4.15
B (dd) 2.70
A (dd) 2.78
C (dd) 2.92
E (m) 1.25
f1 (ppm)

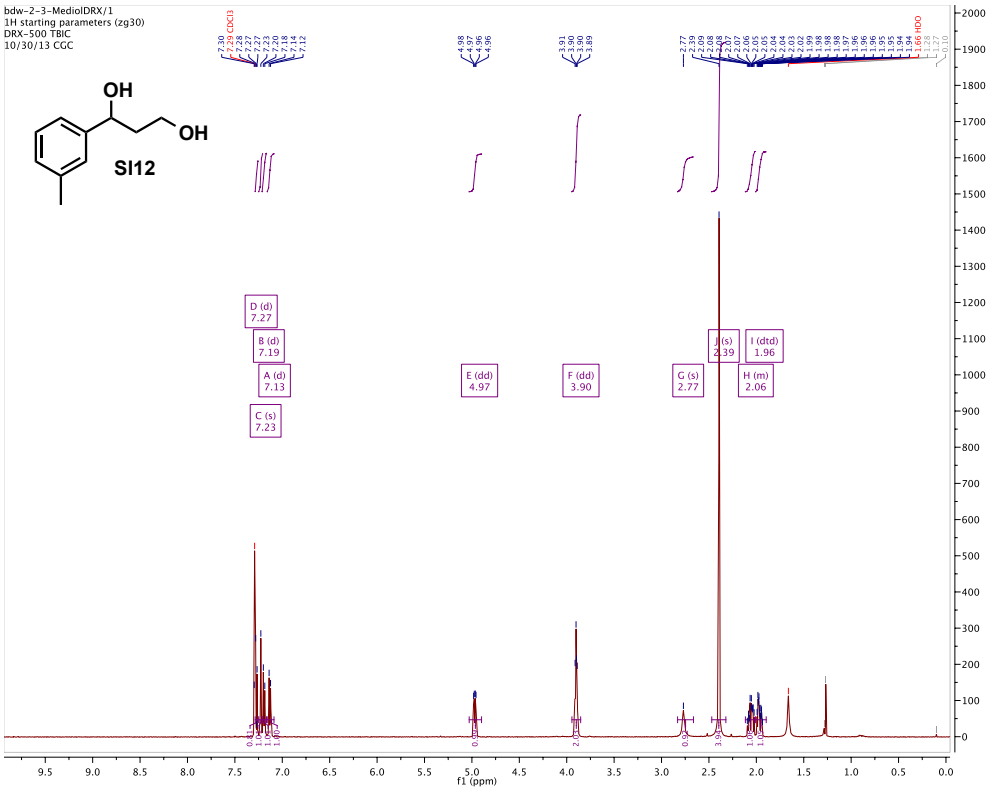

bdw-2-JM-PhBpin.2.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
SI9
f1 (ppm)

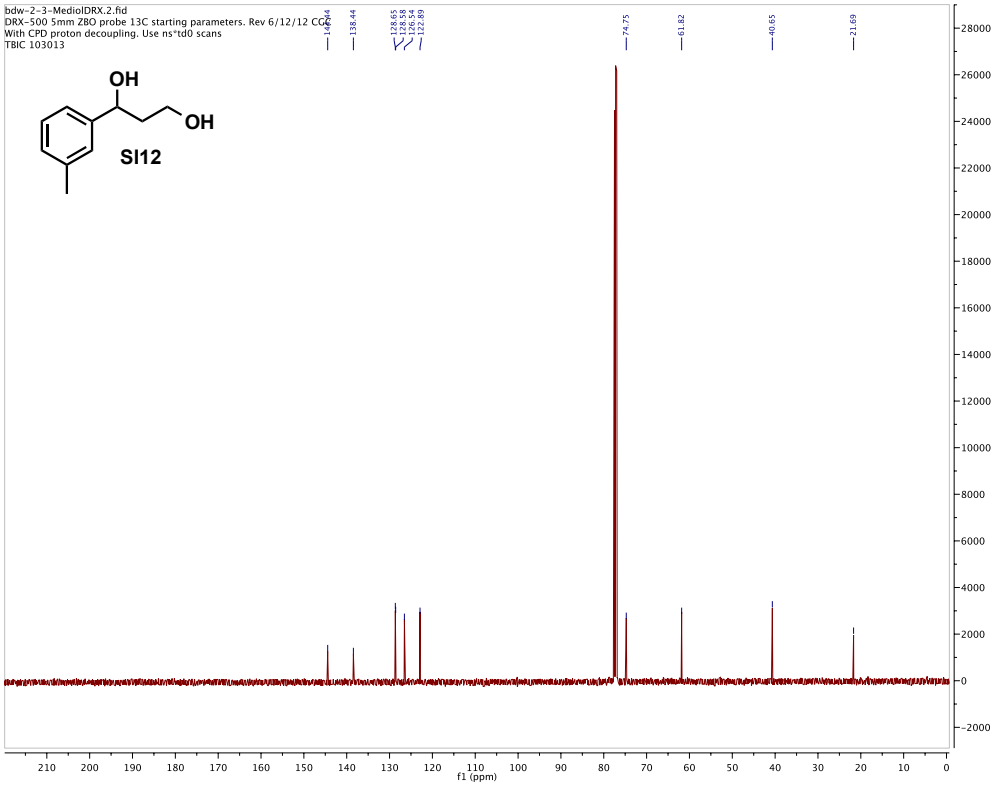

bdw-2-Phdiol.1.fid
AV-600 ZBO proton starting parameters 11/16/08
OH
OH
SI10
D (m) 7.29
C (d) 7.38
A (dd) 4.98
B (t) 3.88
E (s) 2.80
F (s) 2.35
G (m) 2.03
H (dq) 1.96
f1 (ppm)

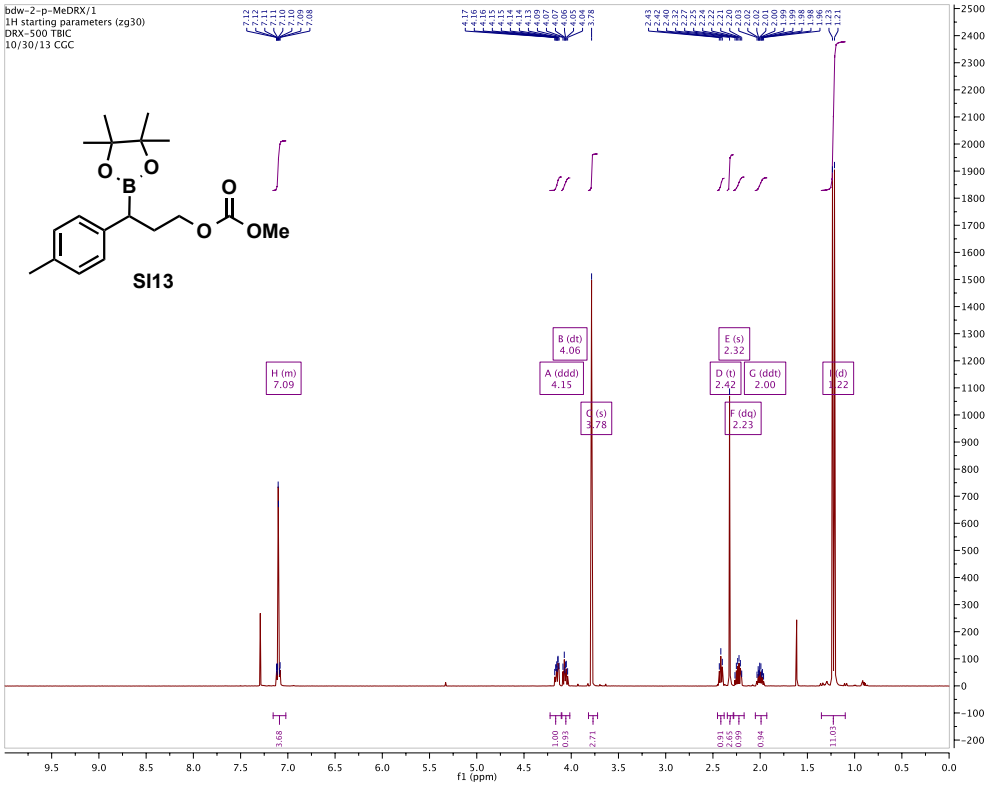

bdw-2-Phdiol.2.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
OH
OH
SI10
144.52
128.76
127.84
125.86
74.63
61.73
40.75
f1 (ppm)

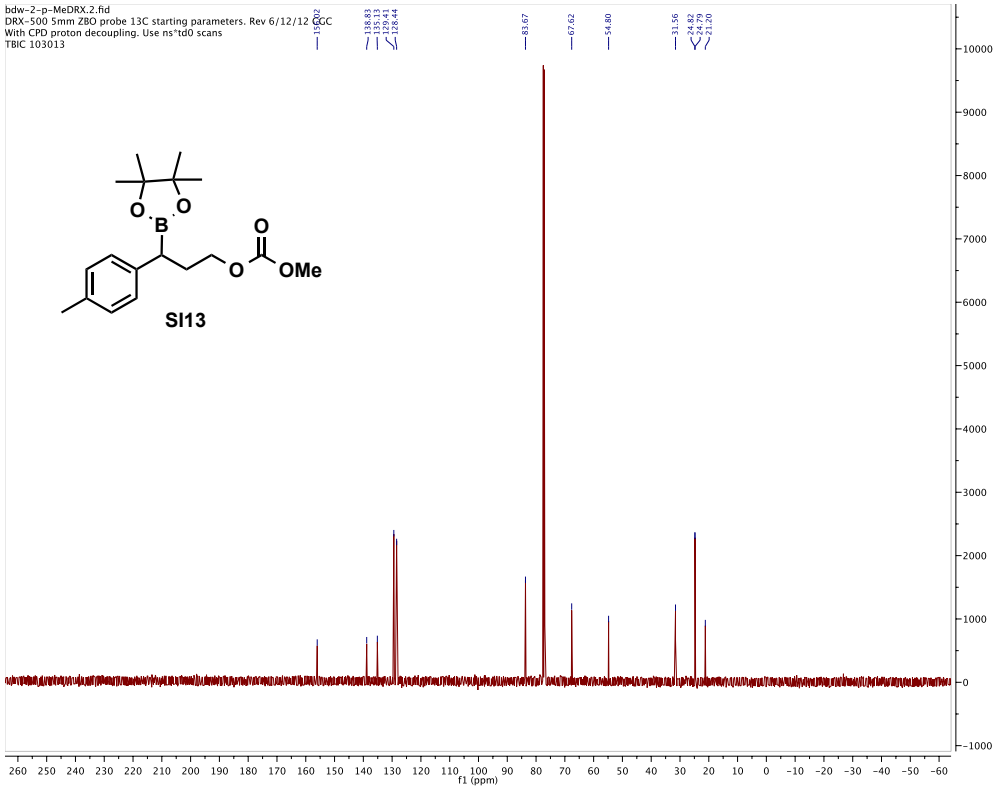

bdw-2-m-MeDRX/1
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
SI11
E (m) 6.99
D (t) 7.15
B (dt) 4.05
A (ddd) 4.14
C (s) 3.77
G (s) 2.31
F (t) 2.39
I (ddt) 1.99
H (dq) 2.22
J (d) 1.20
f1 (ppm)

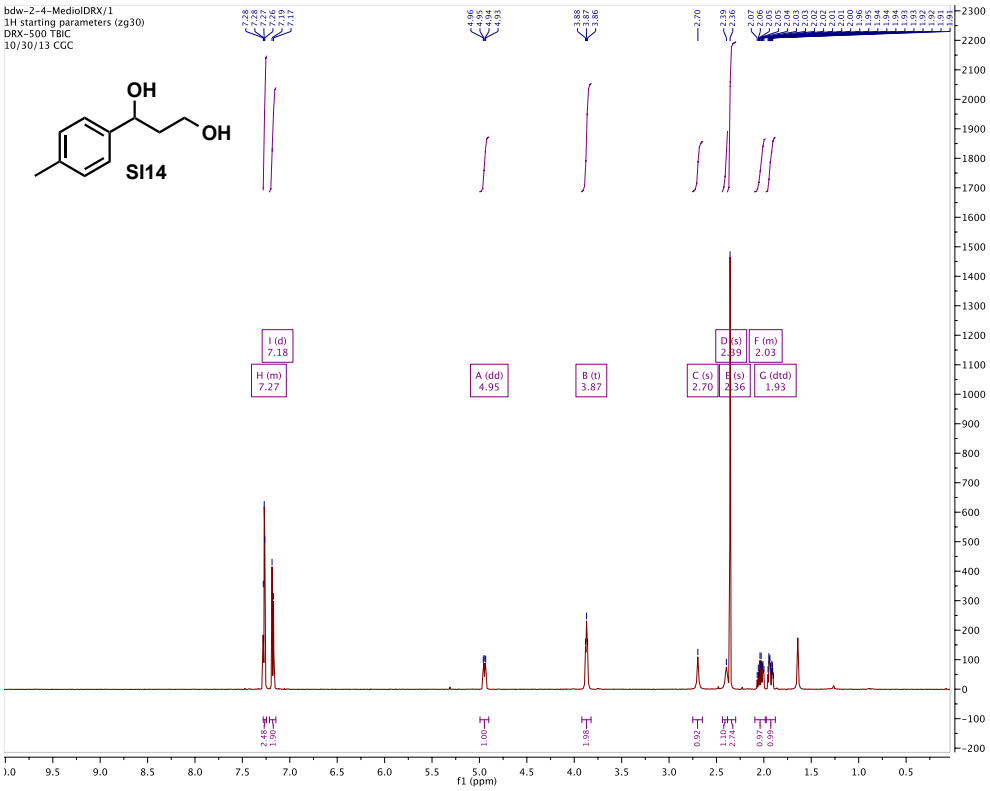

bdw-2-m-MeDRX.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
SI11
83.70
67.69
54.81
31.49
24.79
21.66
f1 (ppm)

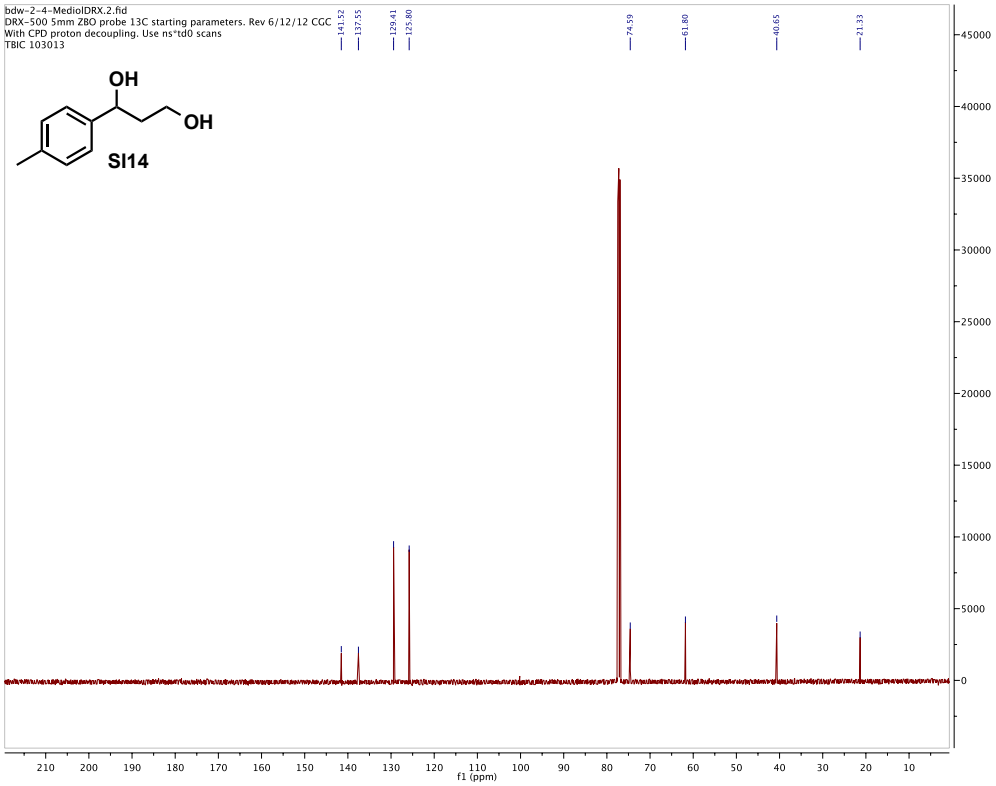

bdw-2-3-MediolDRX/1
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
OH
OH
SI12
D (d) 7.27
B (d) 7.19
A (d) 7.13
C (s) 7.23
E (dd) 4.97
F (dd) 3.90
G (s) 2.77
J (s) 2.39
I (dtd) 1.96
H (m) 2.06
f1 (ppm)

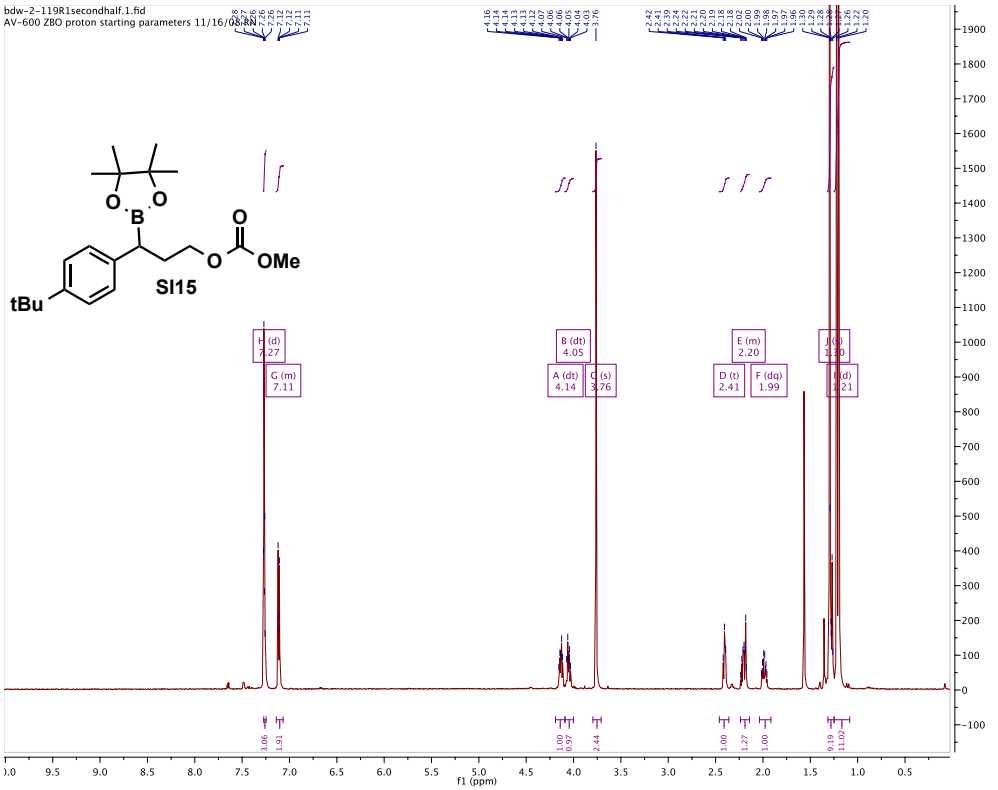

bdw-2-3-MediolDRX.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
OH
OH
SI12
146.44
138.44
128.65
128.58
126.54
122.89
74.75
61.82
40.65
21.69
f1 (ppm)

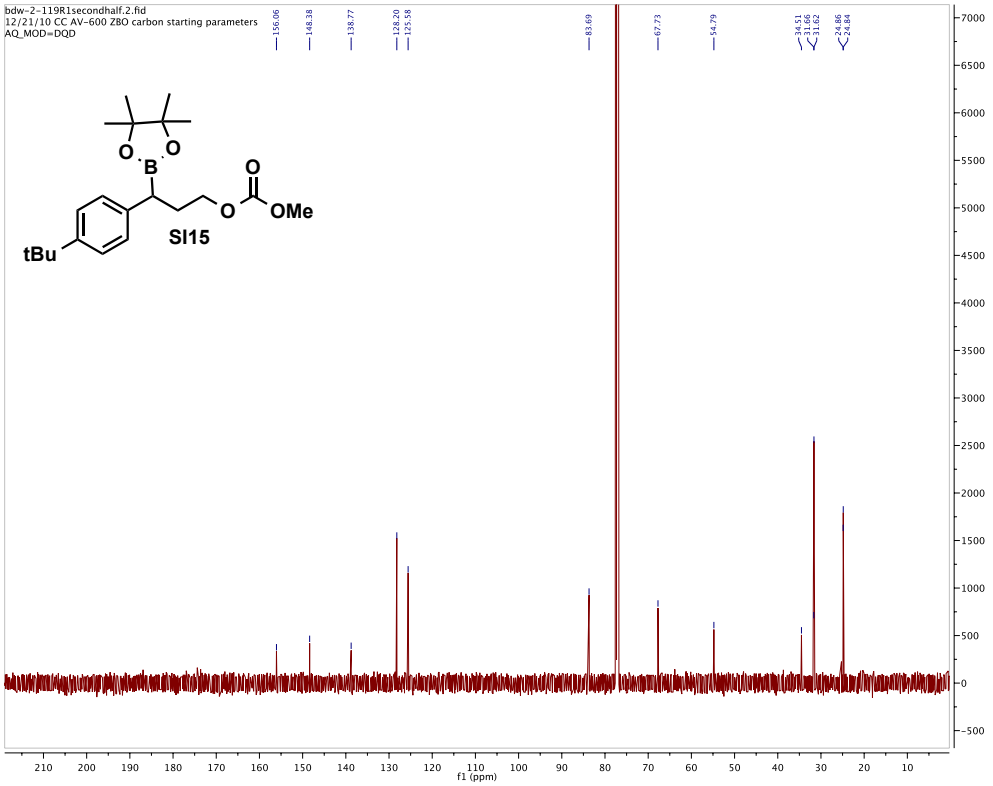

bdw-2-p-MeDRX/1
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
SI13
H (m) 7.09
A (ddd) 4.15
B (dt) 4.06
C (s) 3.78
D (t) 2.42
E (s) 2.32
F (dq) 2.23
G (ddt) 2.00
I (dd) 1.22
f1 (ppm)

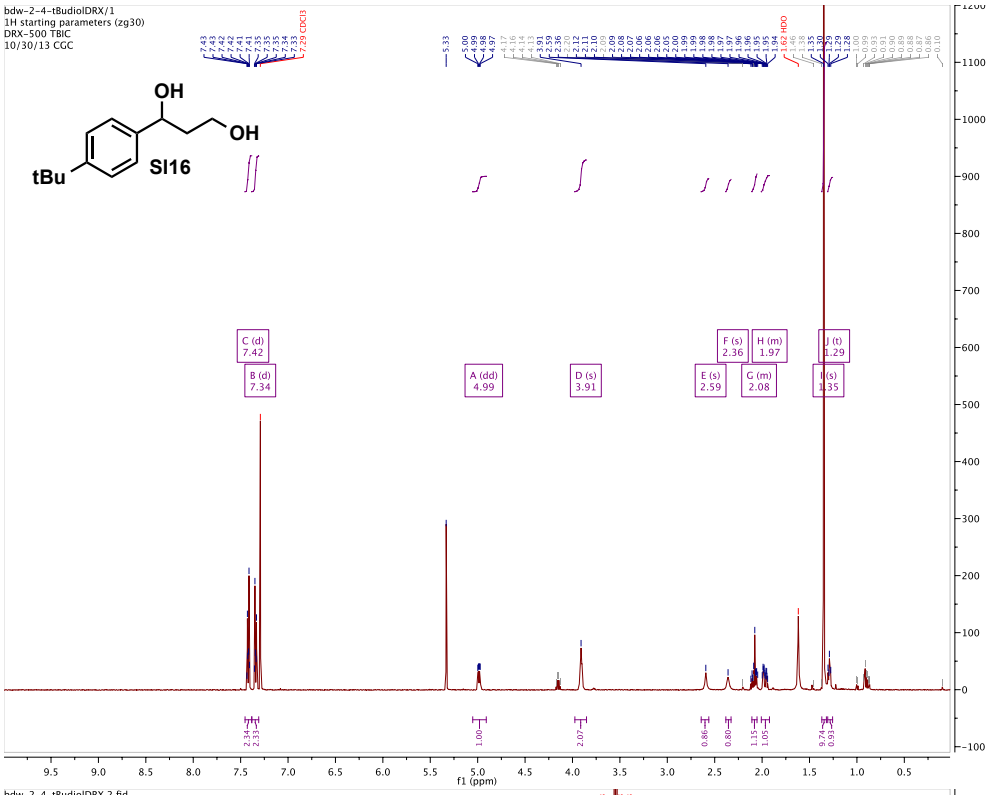

bdw-2-p-MeDRX.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
SI13
f1 (ppm)

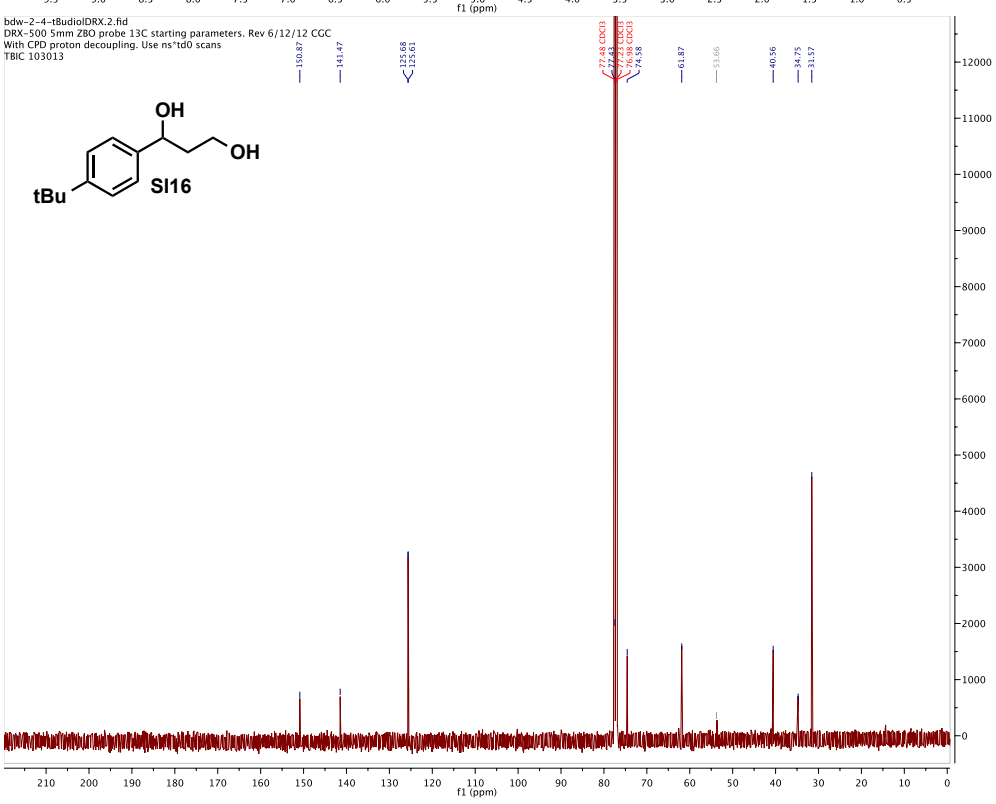

bdw-2-4-MediolDRX/1
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
OH
OH
SI14
I (d) 7.18
H (m) 7.27
A (dd) 4.95
B (t) 3.87
C (s) 2.70
D (s) 2.39
E (s) 2.36
F (m) 2.03
G (dtd) 1.93
f1 (ppm)

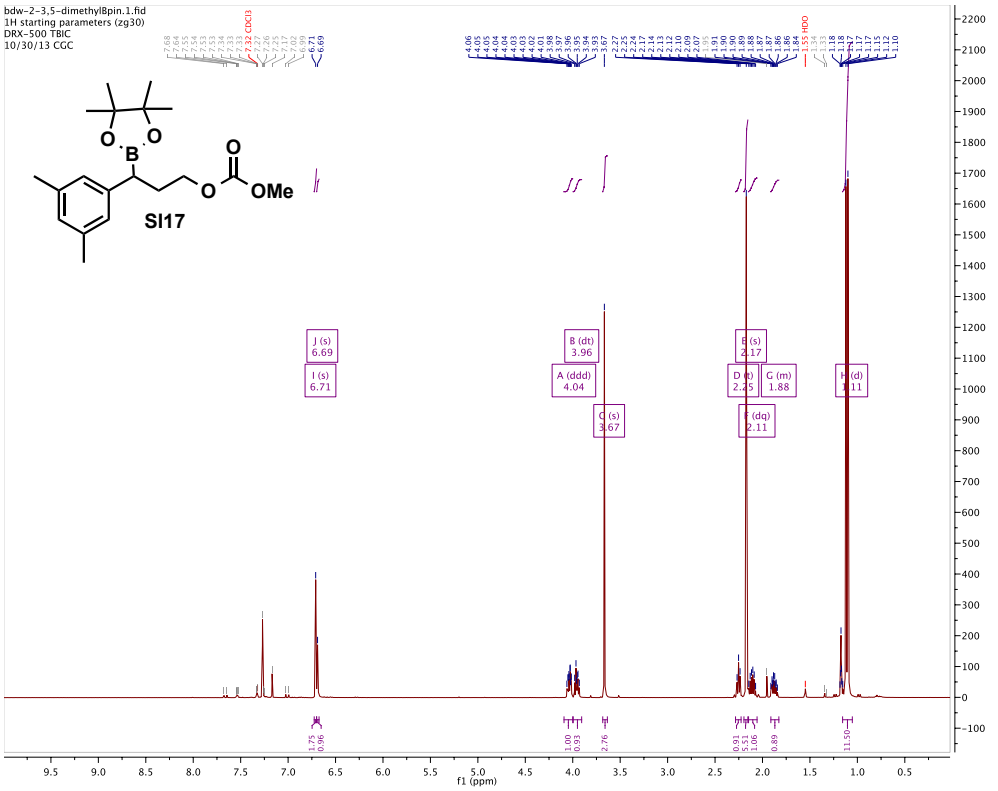

bdw-2-4-MediolDRX.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
OH
OH
SI14
141.52
137.55
129.41
125.80
74.59
61.80
40.65
21.33
f1 (ppm)

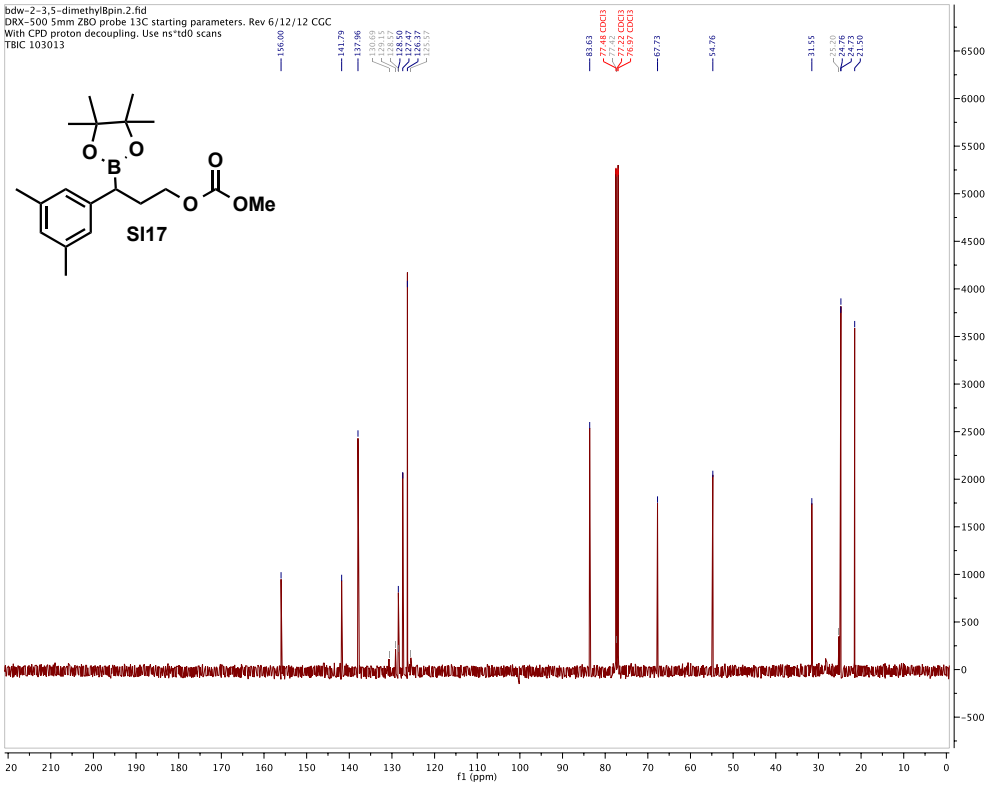

bdw-2-119R1secondhalf.1.fid
AV-600 ZBO proton starting parameters 11/16/0
SI15
tBu
OMe
f1 (ppm)

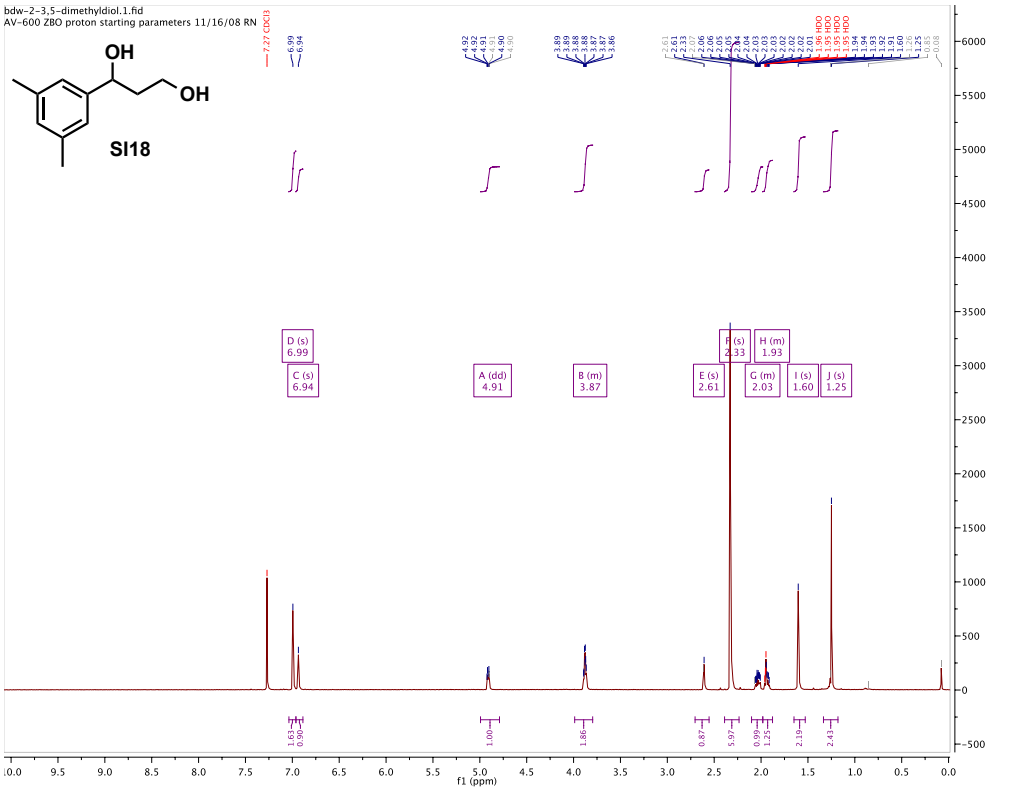

bdw-2-119R1secondhalf.2.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
SI15
tBu
OMe
f1 (ppm)

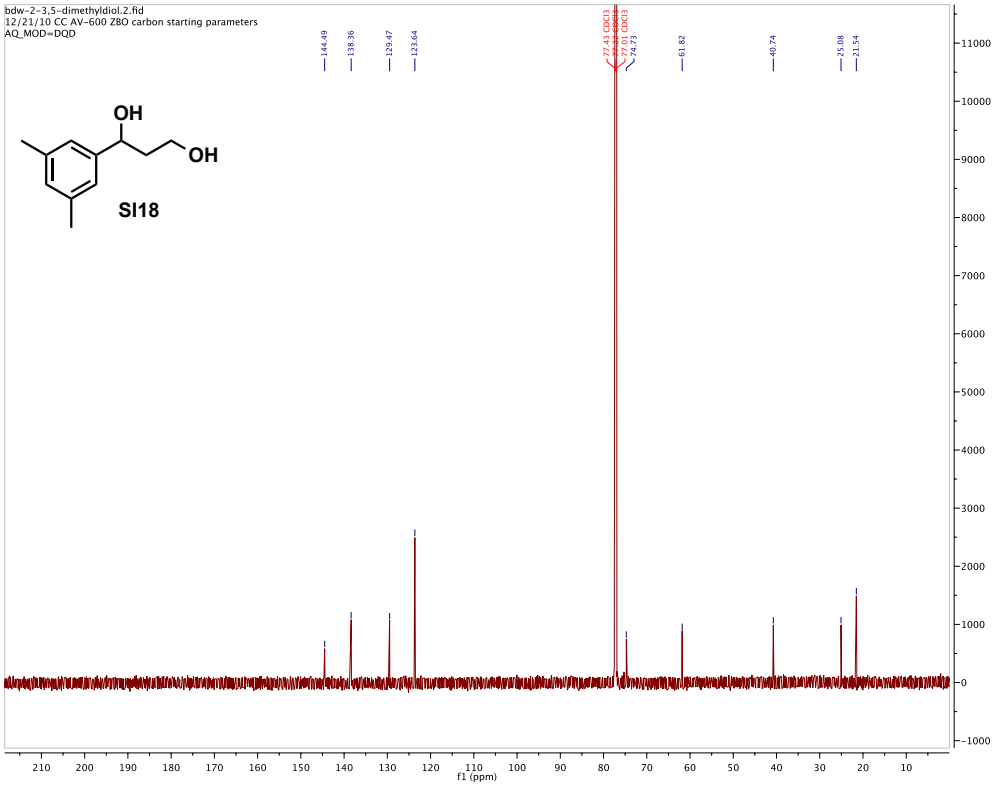

bdw-2-4-tBudiolDRX/1
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
OH
OH
tBu
SI16
C (d) 7.42
B (d) 7.34
A (dd) 4.99
D (s) 3.91
F (s) 2.36
H (m) 1.97
E (s) 2.59
G (m) 2.08
J (t) 1.29
I (s) 1.35
f1 (ppm)

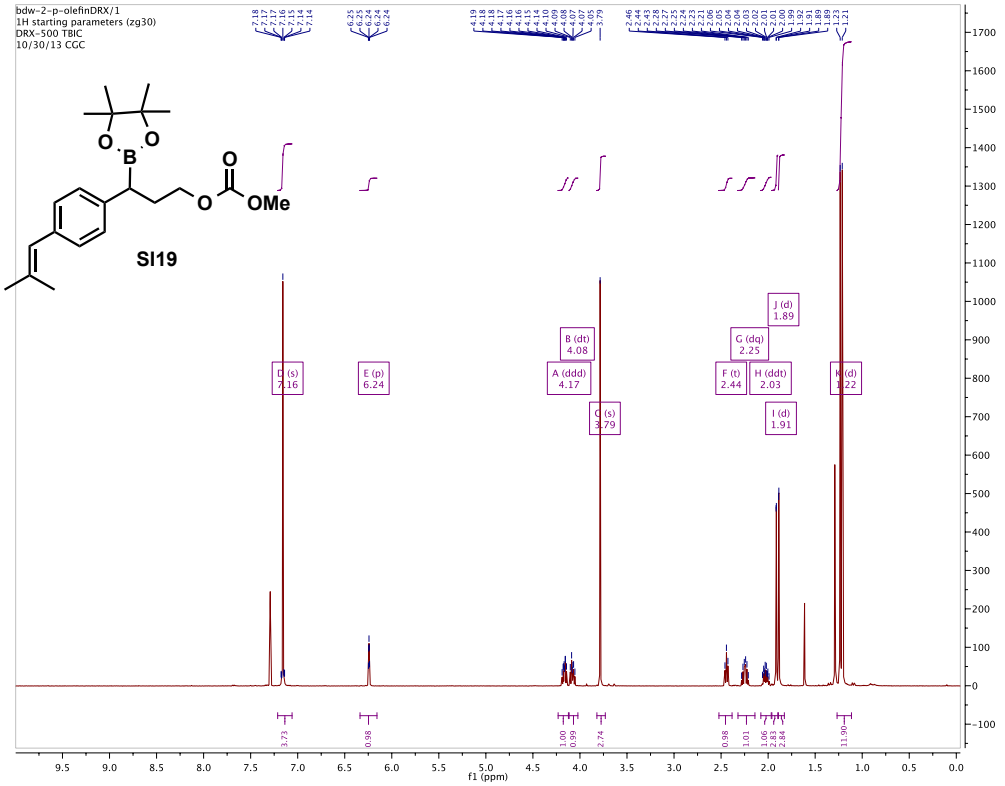

bdw-2-4-tBudiolDRX.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
OH
OH
tBu
SI16
150.87
141.47
125.68
125.61
77.48 CDCl3
77.03
76.58 CDCl3
74.58
61.87
53.66
40.56
34.75
31.57
f1 (ppm)

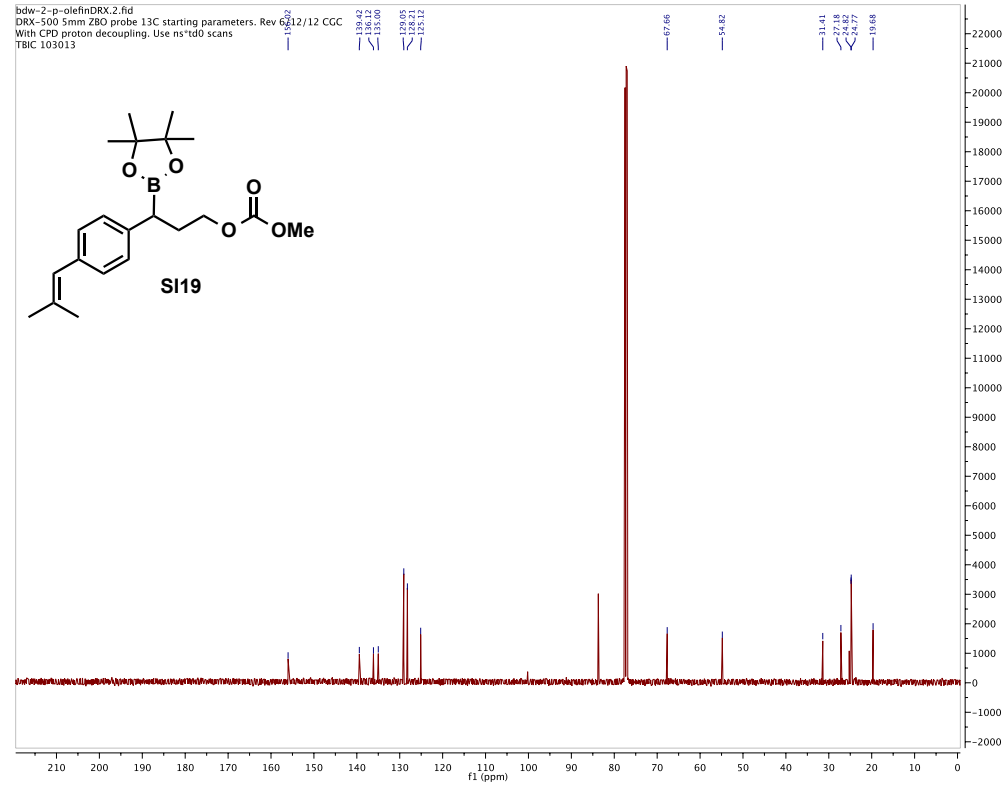

bdw-2-3,5-dimethylBpin.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
SI17
J (s) 6.69
I (s) 6.71
B (dt) 3.96
A (ddd) 4.04
C (s) 3.67
E (s) 2.17
D (t) 2.25
G (m) 1.88
F (dq) 2.11
H (d) 1.11
f1 (ppm)

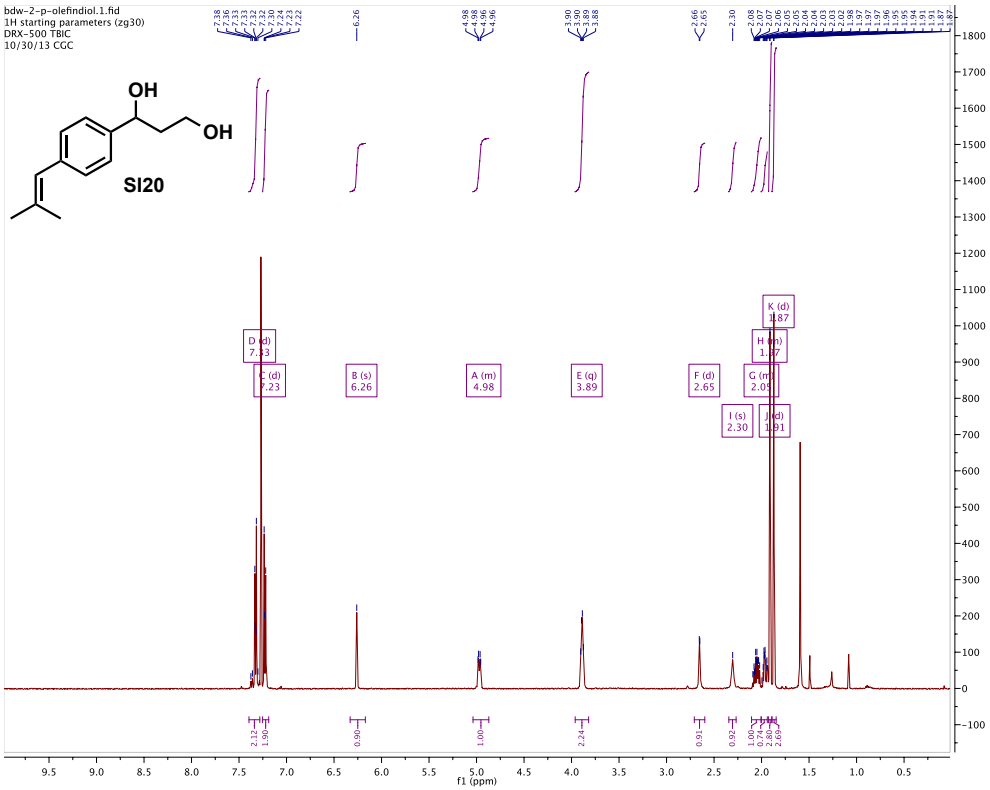

bdw-2-3,5-dimethylBpin.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
SI17
f1 (ppm)

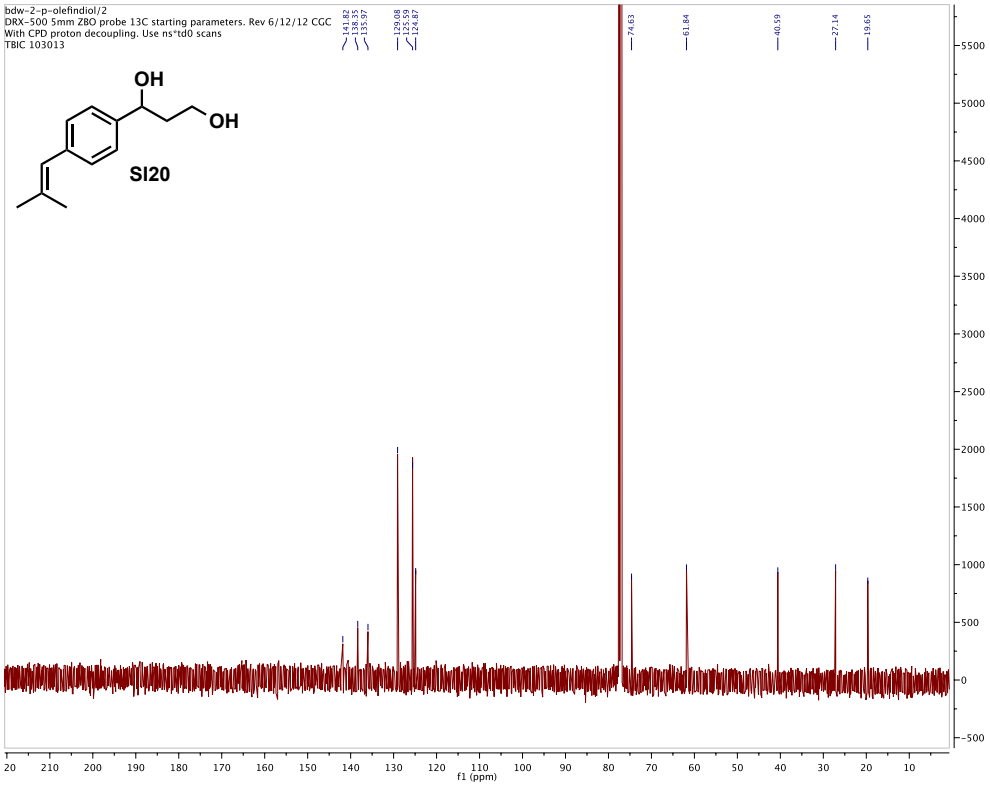

bdw-2-3,5-dimethyldiol.1.fid
AV-600 ZBO proton starting parameters 11/16/08 RN
OH
OH
SI18
D (s) 6.99
C (s) 6.94
A (dd) 4.91
B (m) 3.87
F (s) 2.33
H (m) 1.93
E (s) 2.61
G (m) 2.03
I (s) 1.60
J (s) 1.25
f1 (ppm)

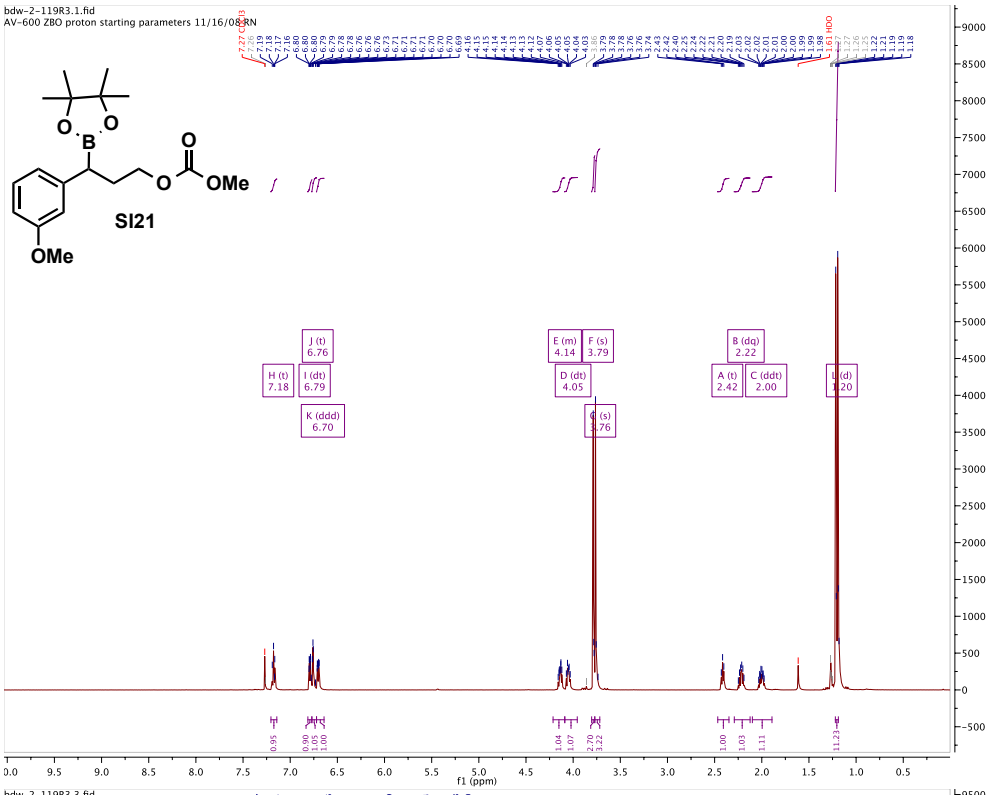

bdw-2-3,5-dimethyldiol.2.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
OH
OH
SI18
144.49
138.36
129.47
123.64
77.43 CDCl3
77.01 CDCl3
74.73
61.82
40.74
25.08
21.54
f1 (ppm)

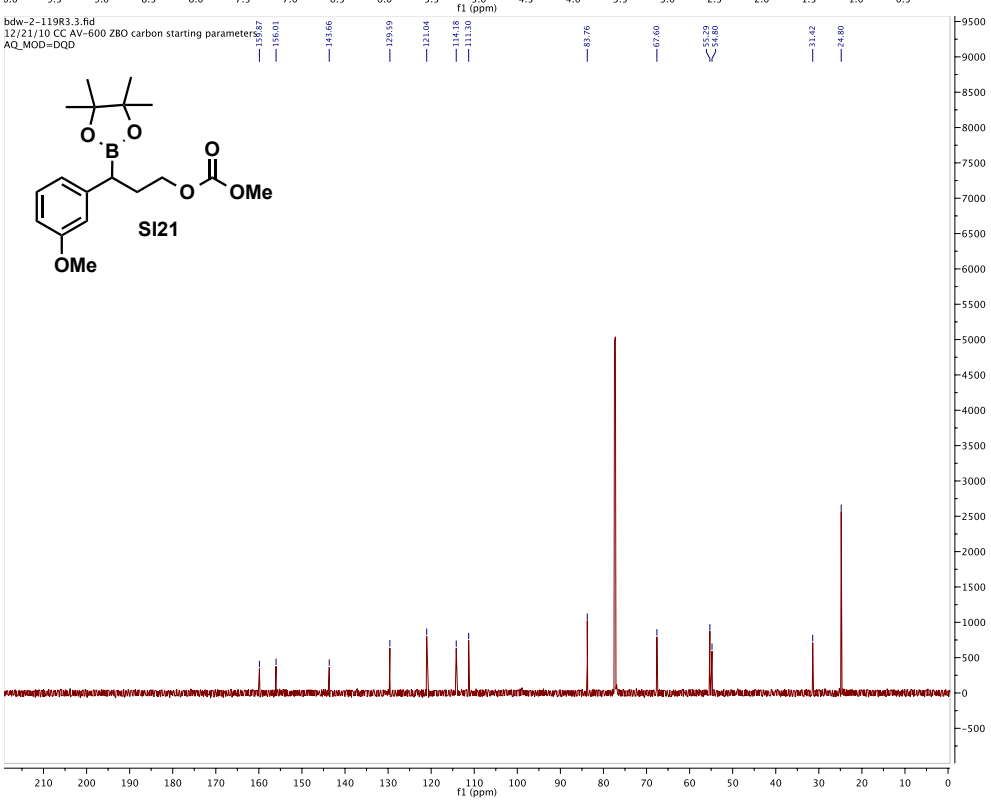

bdw-2-p-olefinDRX/1
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
SI19
D (s) 7.16
E (p) 6.24
A (ddd) 4.17
B (dt) 4.08
C (s) 3.79
F (t) 2.44
G (dq) 2.25
H (ddt) 2.03
I (d) 1.91
J (d) 1.89
K (d) 1.22
f1 (ppm)

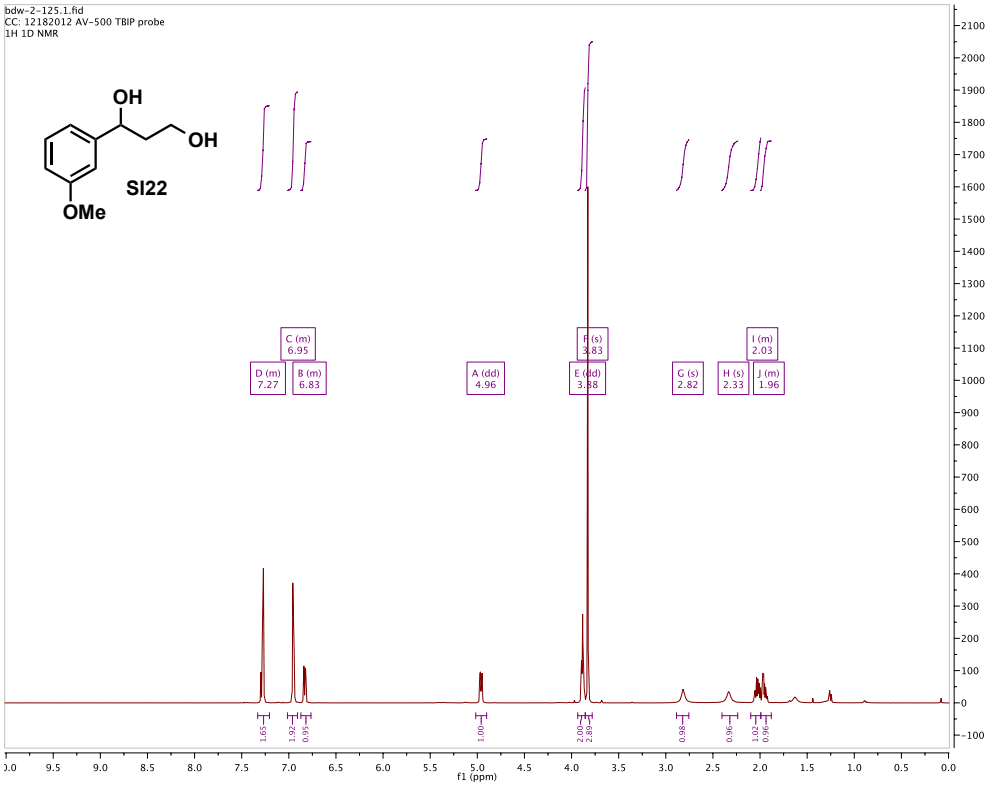

bdw-2-p-olefinDRX.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
SI19
f1 (ppm)

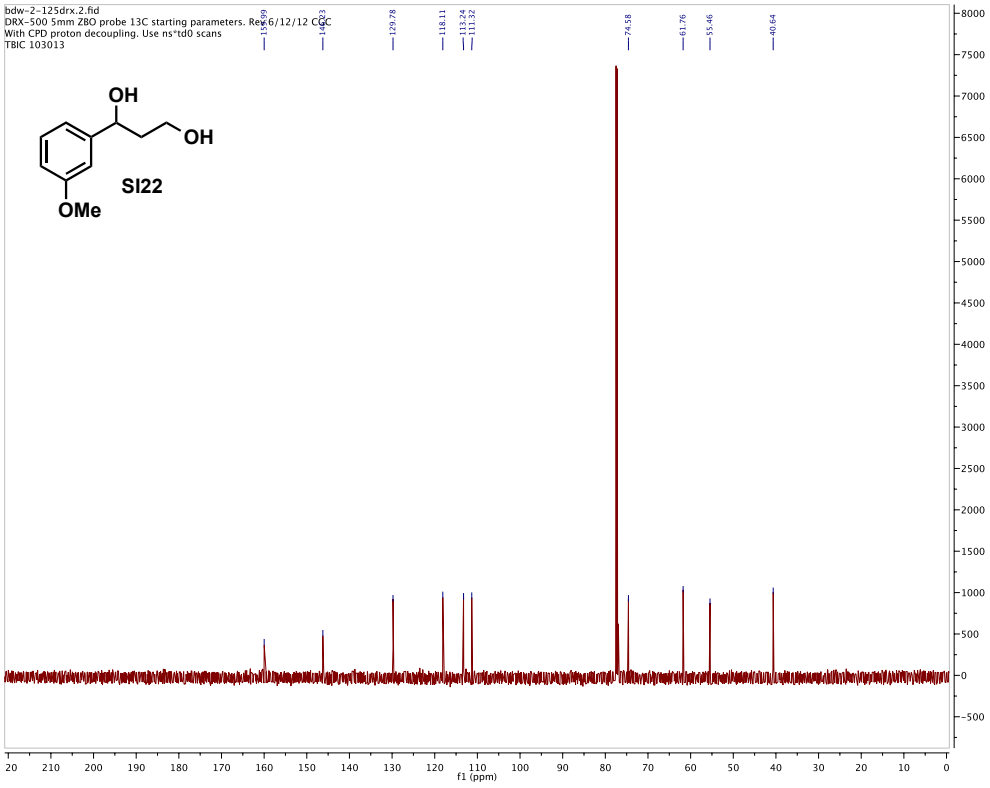

bdw-2-p-olefindiol.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
OH
OH
SI20
D (d) 7.33
C (d) 7.23
B (s) 6.26
A (m) 4.98
E (q) 3.89
F (d) 2.65
I (s) 2.30
K (d) 1.87
H (m) 1.37
J (d) 1.91
f1 (ppm)

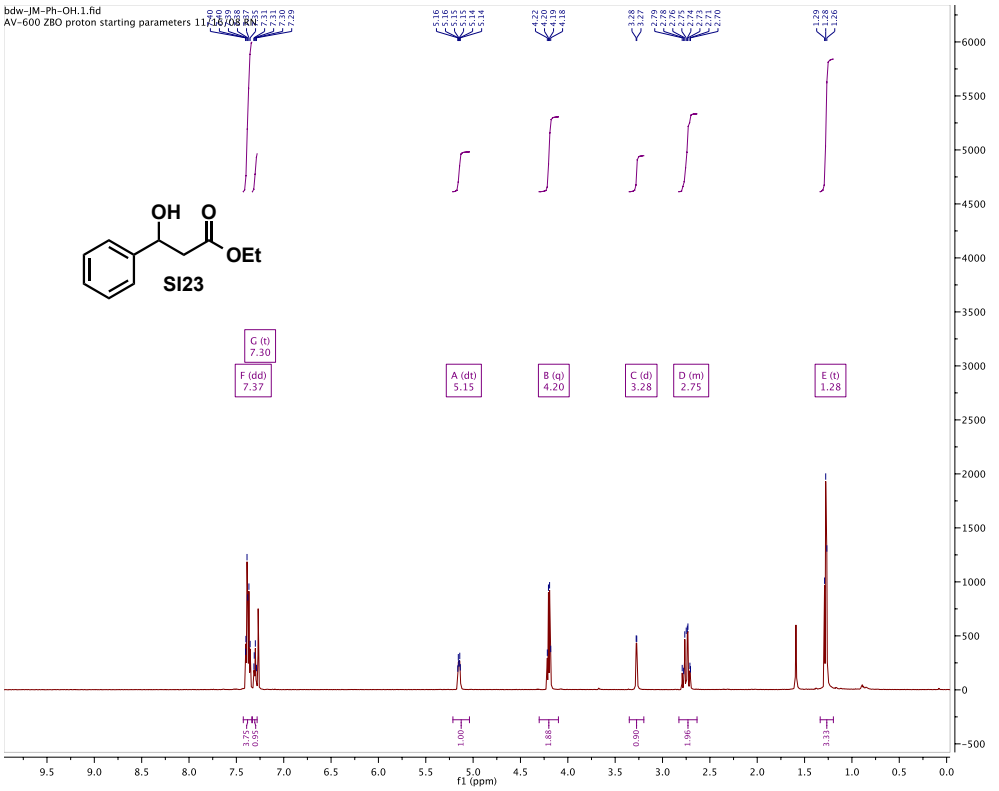

bdw-2-p-olefindiol/2
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
OH
OH
SI20
141.82
138.35
135.97
129.08
125.59
124.87
74.63
61.84
40.59
27.14
19.65
f1 (ppm)

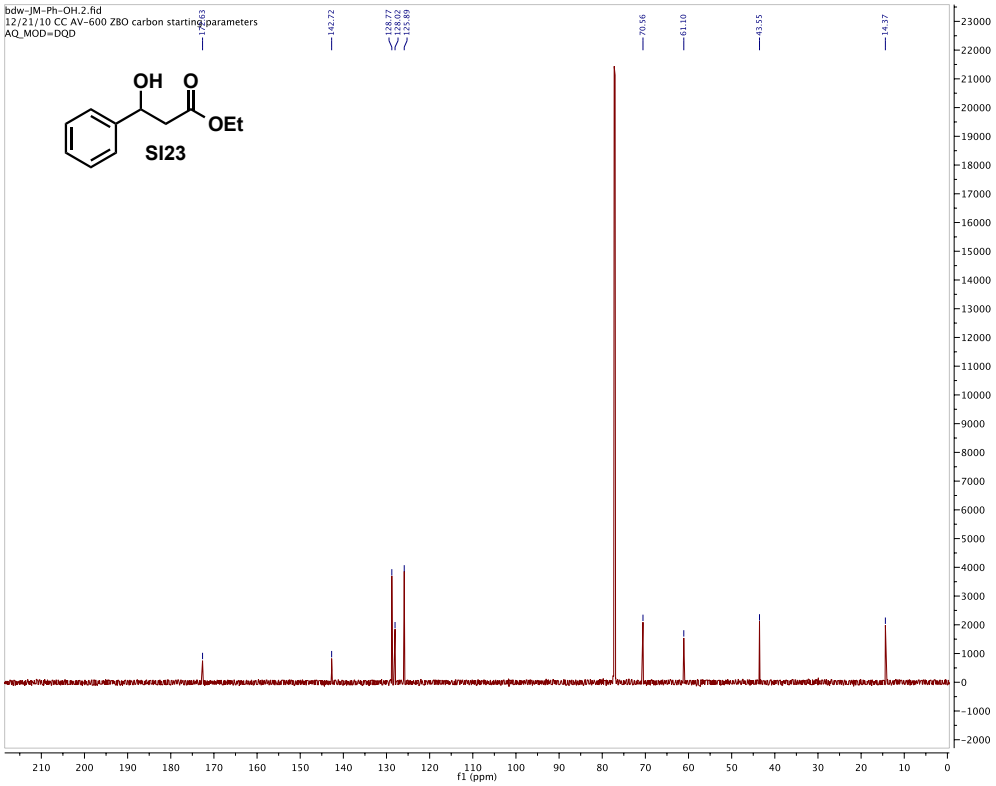

bdw-2-119R3.1.fid
AV-600 ZBO proton starting parameters 11/16/08 GN
SI21
OMe
OMe
J (t) 6.76
H (t) 7.18
I (dt) 6.79
K (ddd) 6.70
E (m) 4.14
F (s) 3.79
D (dt) 4.05
G (s) 3.76
B (dq) 2.22
A (t) 2.42
C (ddt) 2.00
L (d) 1.20
f1 (ppm)

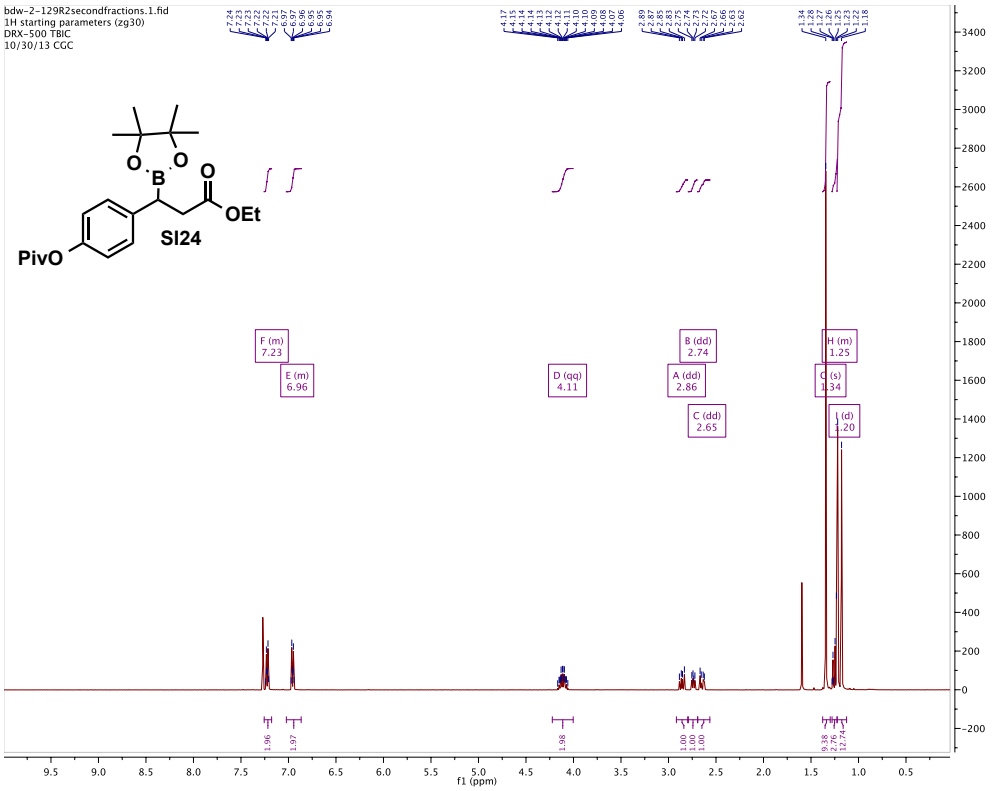

bdw-2-119R3.3.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
SI21
OMe
OMe
159.87
156.01
143.66
129.59
121.04
114.18
111.30
83.76
67.60
55.29
54.80
31.42
24.80
f1 (ppm)

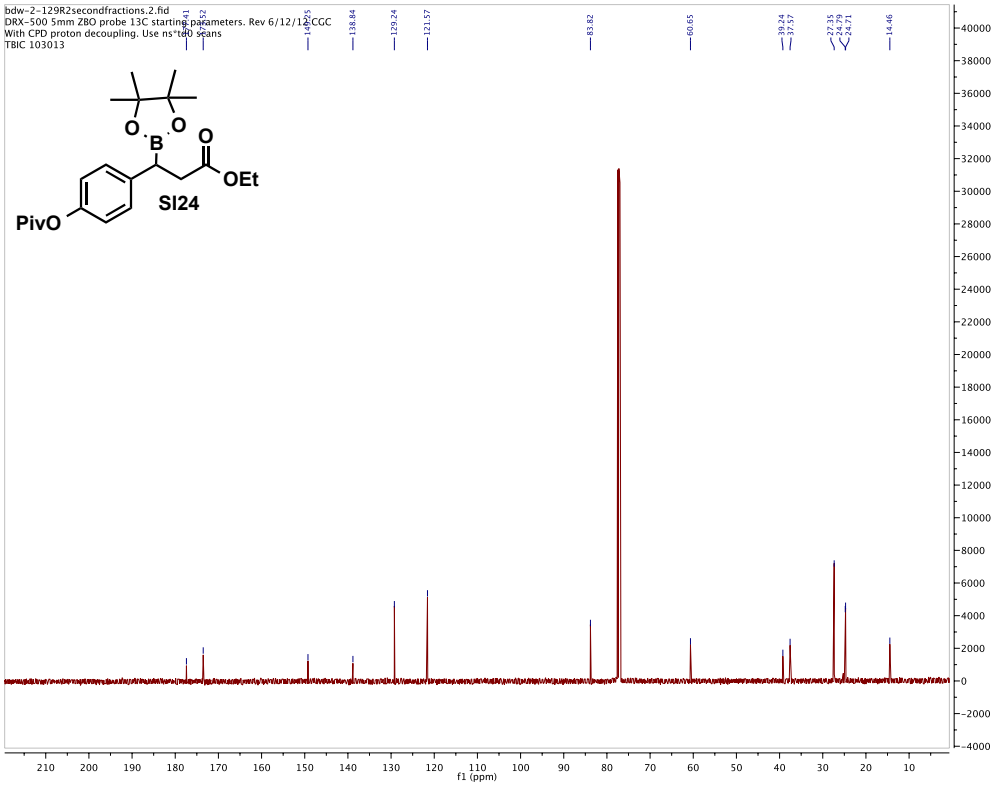

bdw-2-125.1.fid
CC: 12182012 AV-500 TBIP probe
1H 1D NMR
OH
OH
OMe
SI22
C (m) 6.95
D (m) 7.27
B (m) 6.83
A (dd) 4.96
F (s) 3.83
E (dd) 3.88
G (s) 2.82
I (m) 2.03
H (s) 2.33
J (m) 1.96
f1 (ppm)

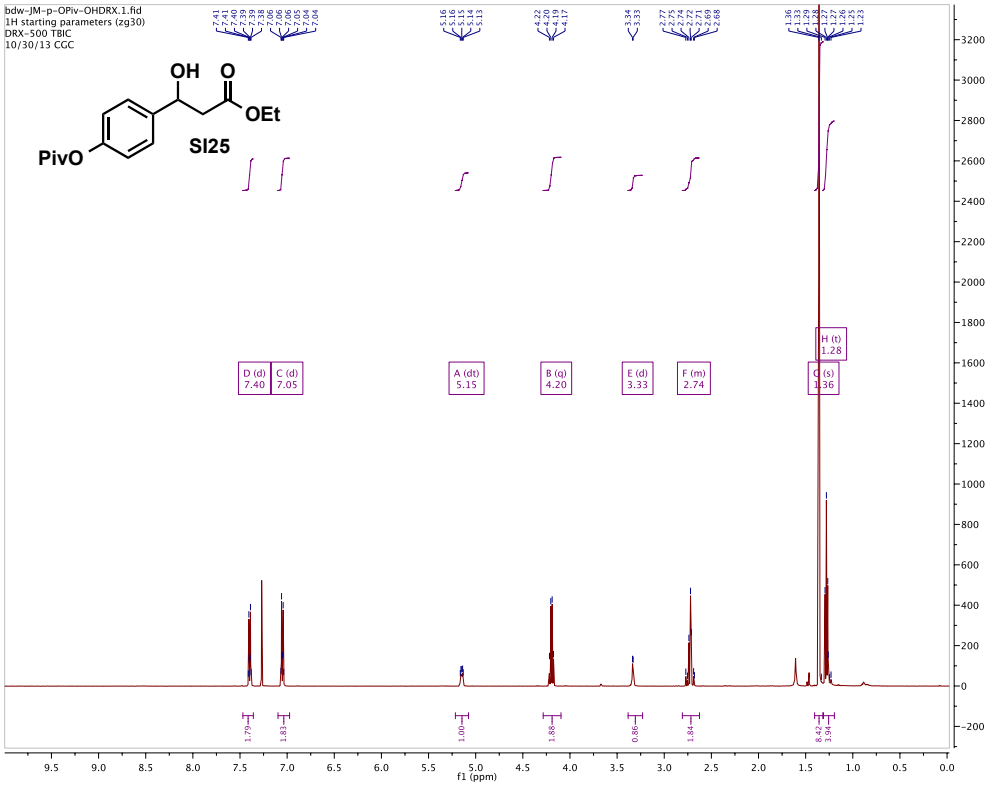

bdw-2-125drx.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CCC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
OH
OH
OMe
SI22
f1 (ppm)

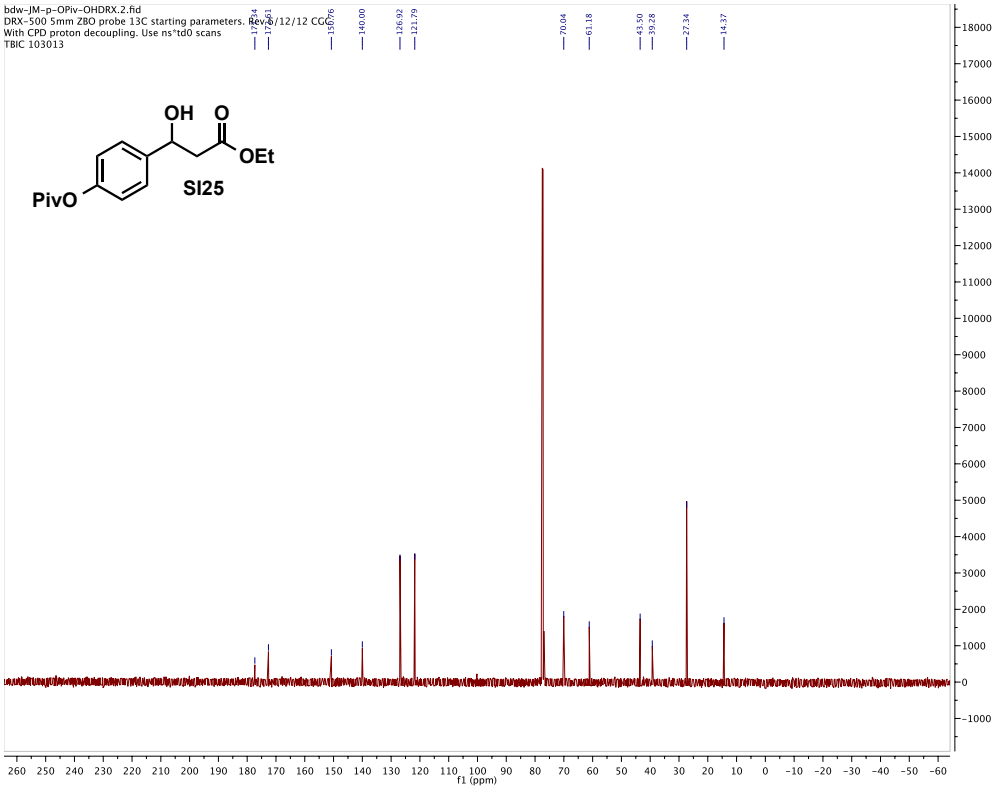

bdw-JM-Ph-OH.1.fid
OH
O
OEt
SI23
G (t) 7.30
F (dd) 7.37
A (dt) 5.15
B (q) 4.20
C (d) 3.28
D (m) 2.75
E (t) 1.28
f1 (ppm)

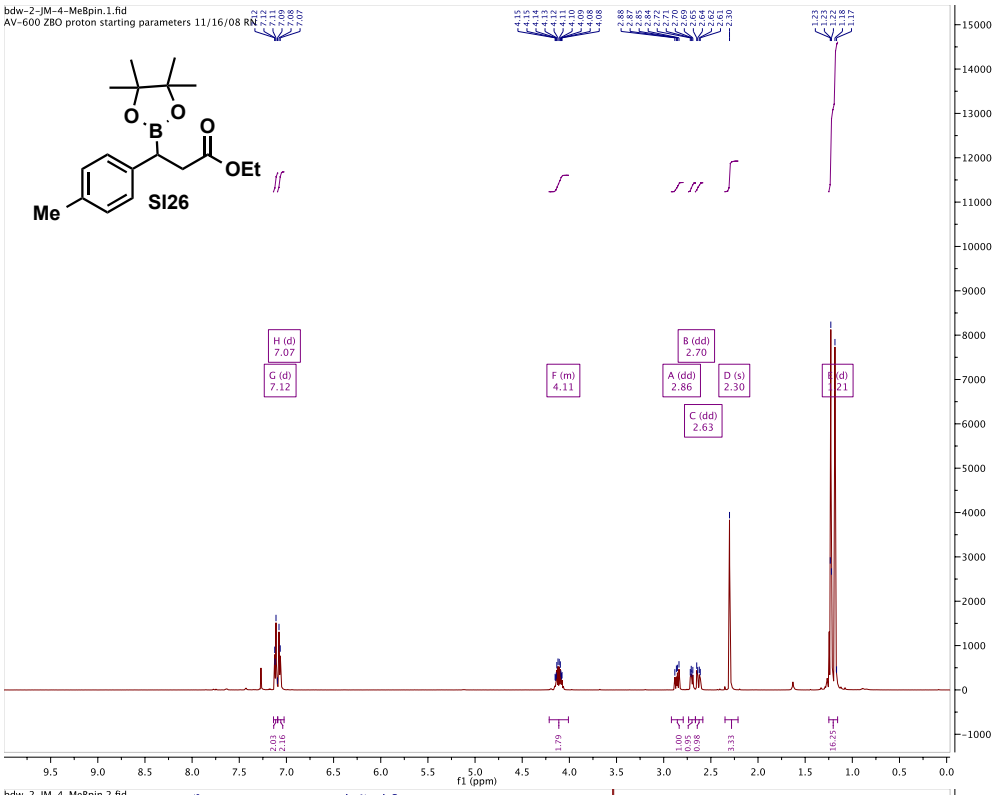

bdw-JM-Ph-OH.2.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
OH
O
OEt
SI23
142.72
128.77
128.02
125.89
70.56
61.10
43.55
14.37
f1 (ppm)

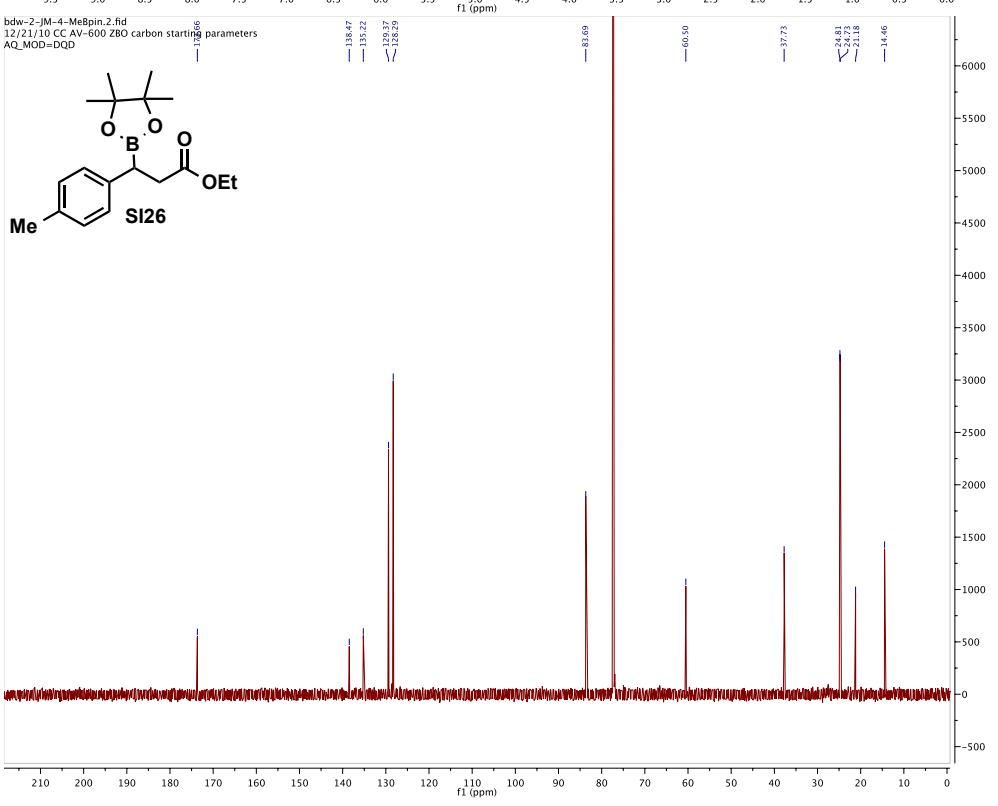

bdw-2-129R2secondfractions.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
O
B
O
O
OEt
PivO
Sl24
F (m)
7.23
E (m)
6.96
D (qq)
4.11
B (dd)
2.74
A (dd)
2.86
C (dd)
2.65
H (m)
1.25
G (s)
1.34
I (d)
1.20
f1 (ppm)

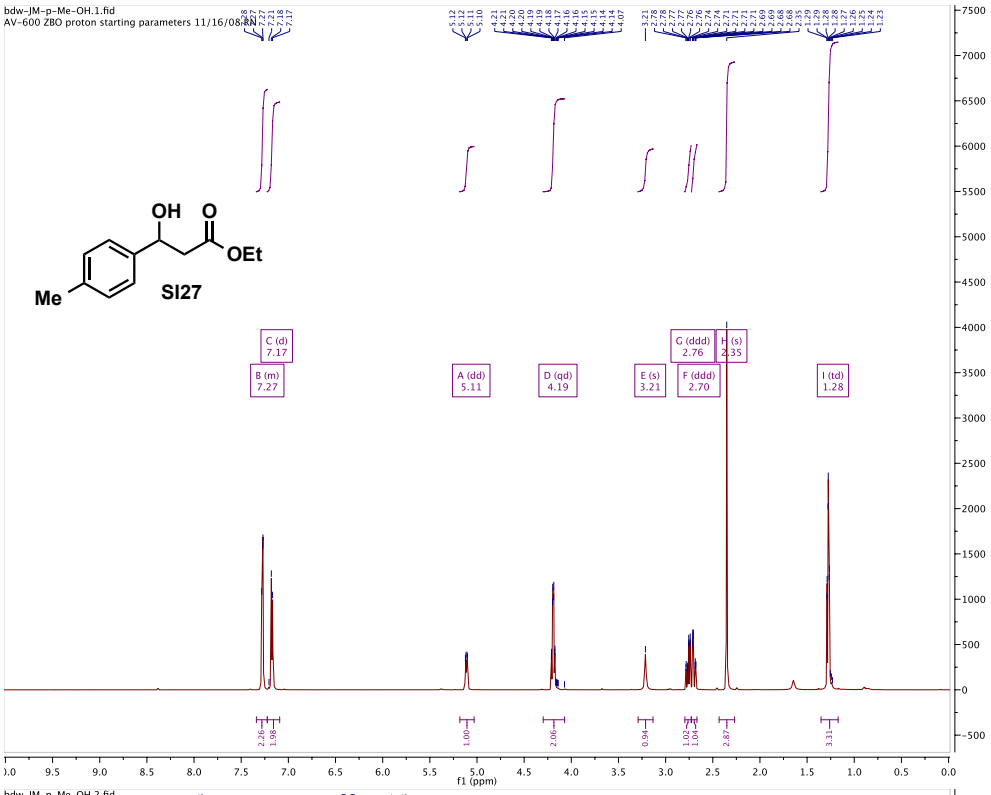

bdw-2-129R2secondfractions.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
O
B
O
O
OEt
PivO
Sl24
f1 (ppm)

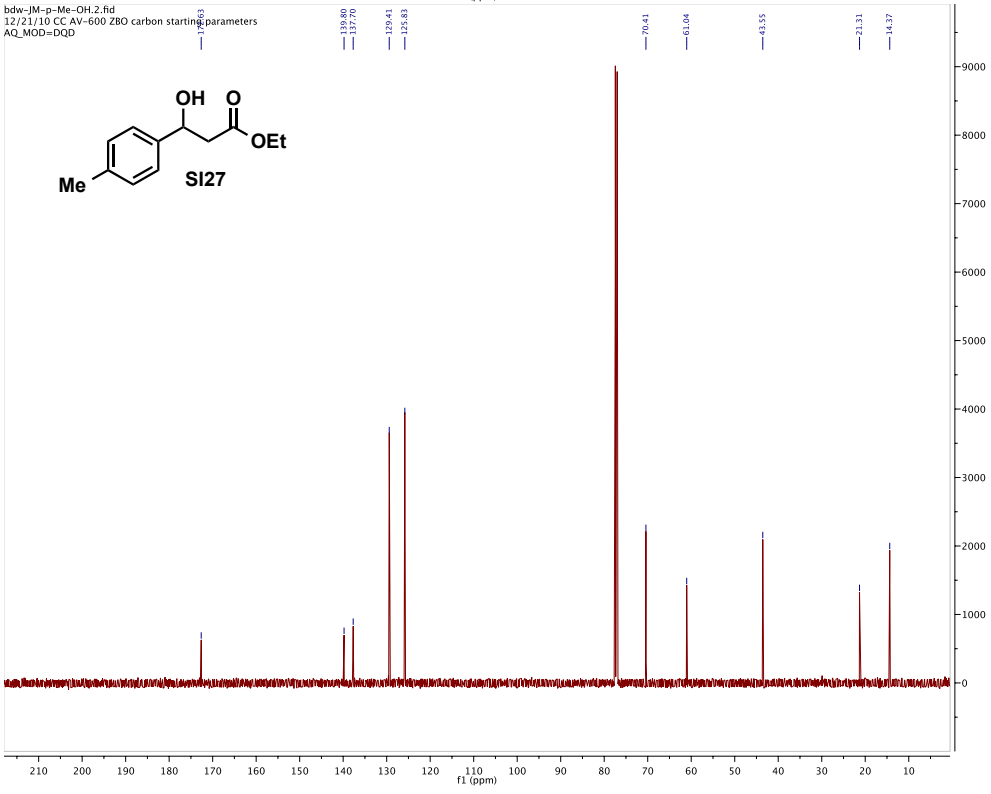

bdw-JM-p-OPiv-OHDRX.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
OH
O
OEt
PivO
Sl25
D (d) 7.40
C (d) 7.05
A (dt) 5.15
B (q) 4.20
E (d) 3.33
F (m) 2.74
H (t) 1.28
G (s) 1.36
f1 (ppm)


bdw-JM-p-OPiv-OHDRX.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev.6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
OH
O
OEt
PivO
Sl25
f1 (ppm)

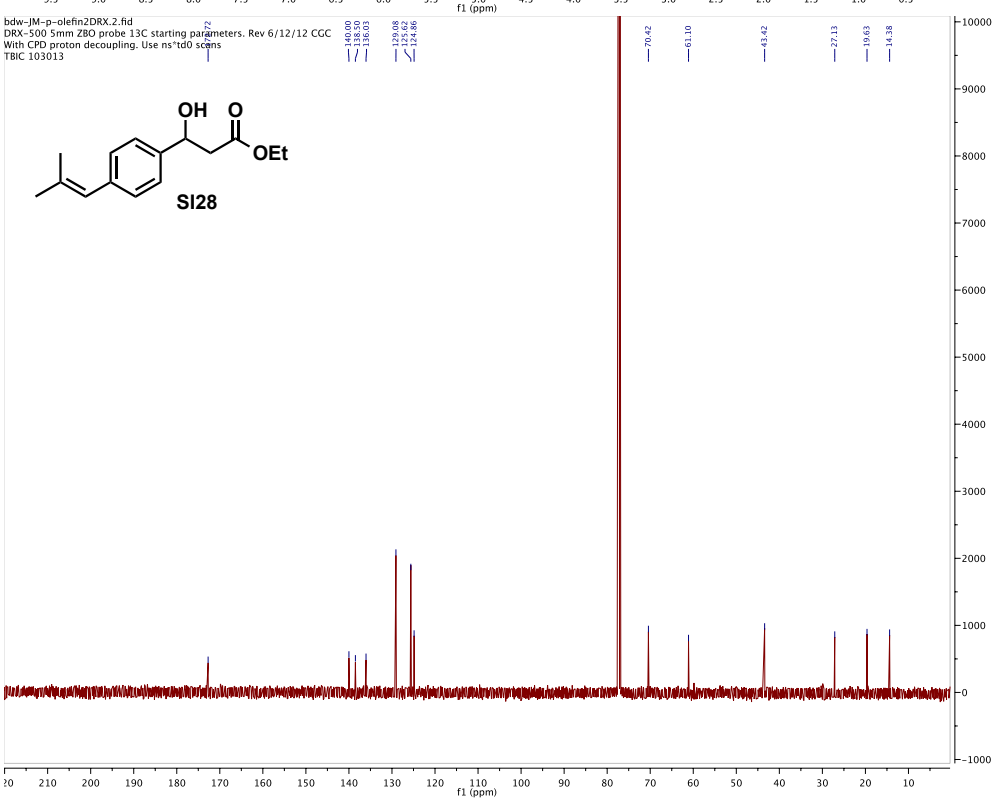

bdw-2-JM-4-MeBpin.1.fid
AV-600 ZBO proton starting parameters 11/16/08 RK
O
O
B
O
OEt
Me
SI26
H (d)
7.07
G (d)
7.12
F (m)
4.11
B (dd)
2.70
A (dd)
2.86
D (s)
2.30
C (dd)
2.63
E (d)
1.21
f1 (ppm)

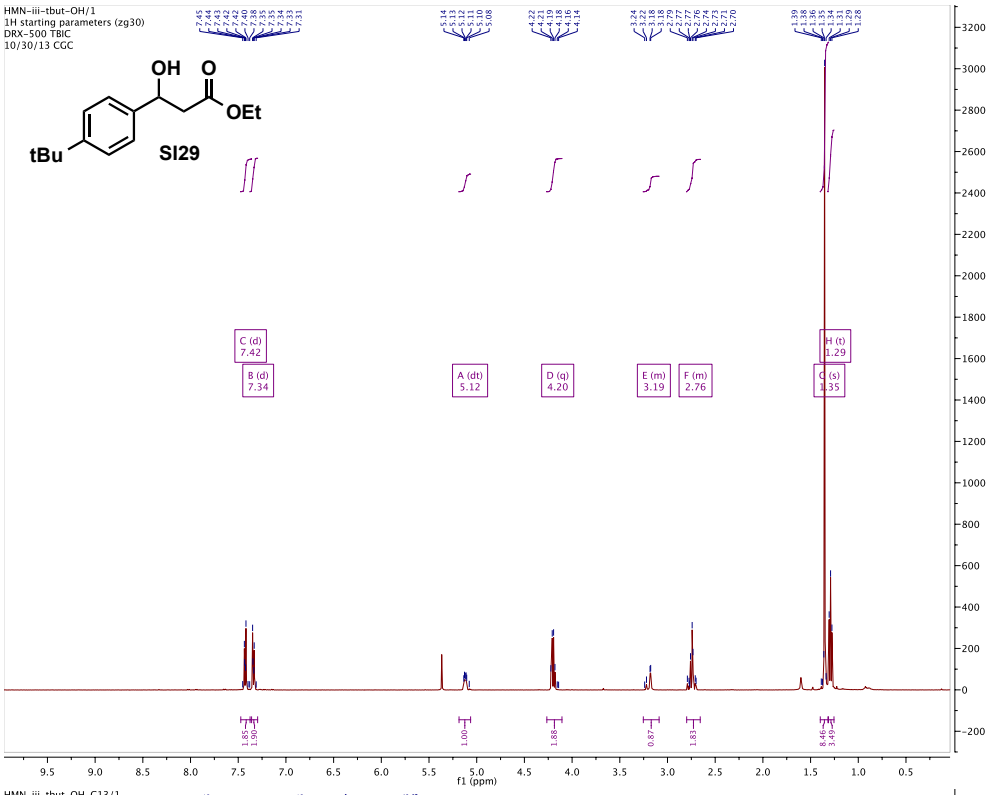

bdw-2-JM-4-MeBpin.2.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
O
O
B
O
OEt
Me
SI26
f1 (ppm)

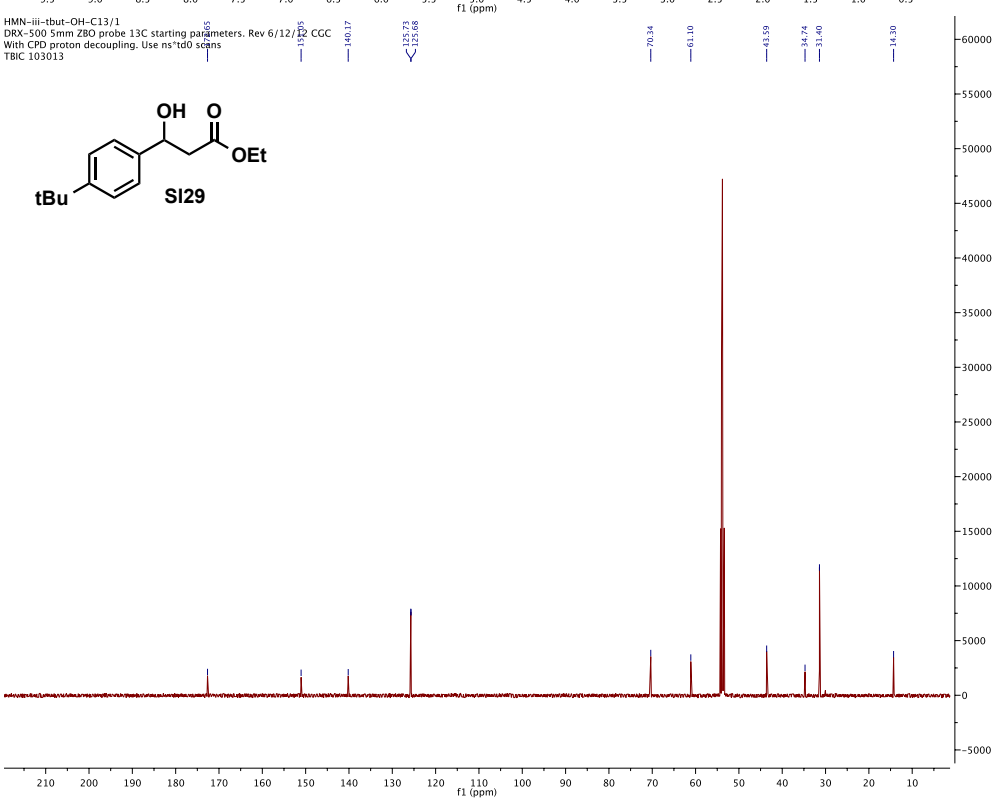

bdw-JM-p-Me-OH.1.fid
AV-600 ZBO proton starting parameters 11/16/08 AM
OH
O
OEt
Me
SI27
C (d) 7.17
B (m) 7.27
A (dd) 5.11
D (qd) 4.19
E (s) 3.21
F (ddd) 2.70
G (ddd) 2.76
H (s) 2.35
I (td) 1.28
f1 (ppm)

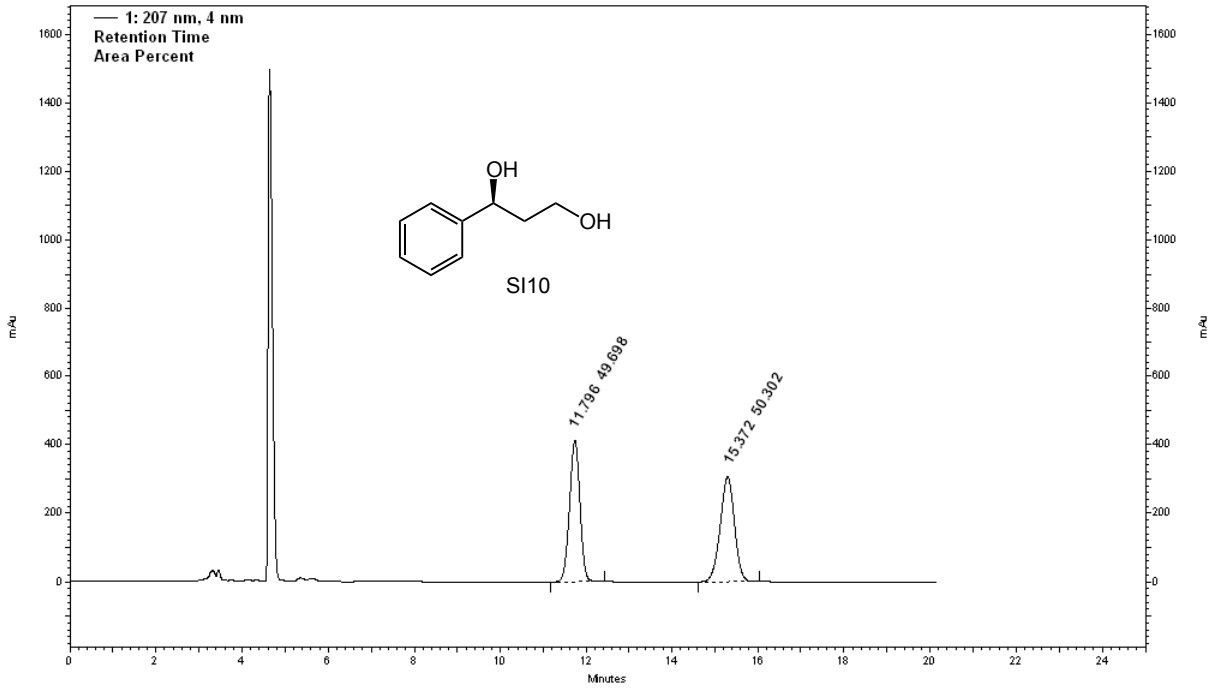

bdw-JM-p-Me-OH.2.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
OH
O
OEt
Me
SI27
139.80
137.70
129.41
125.83
70.41
61.04
43.55
21.31
14.37
f1 (ppm)

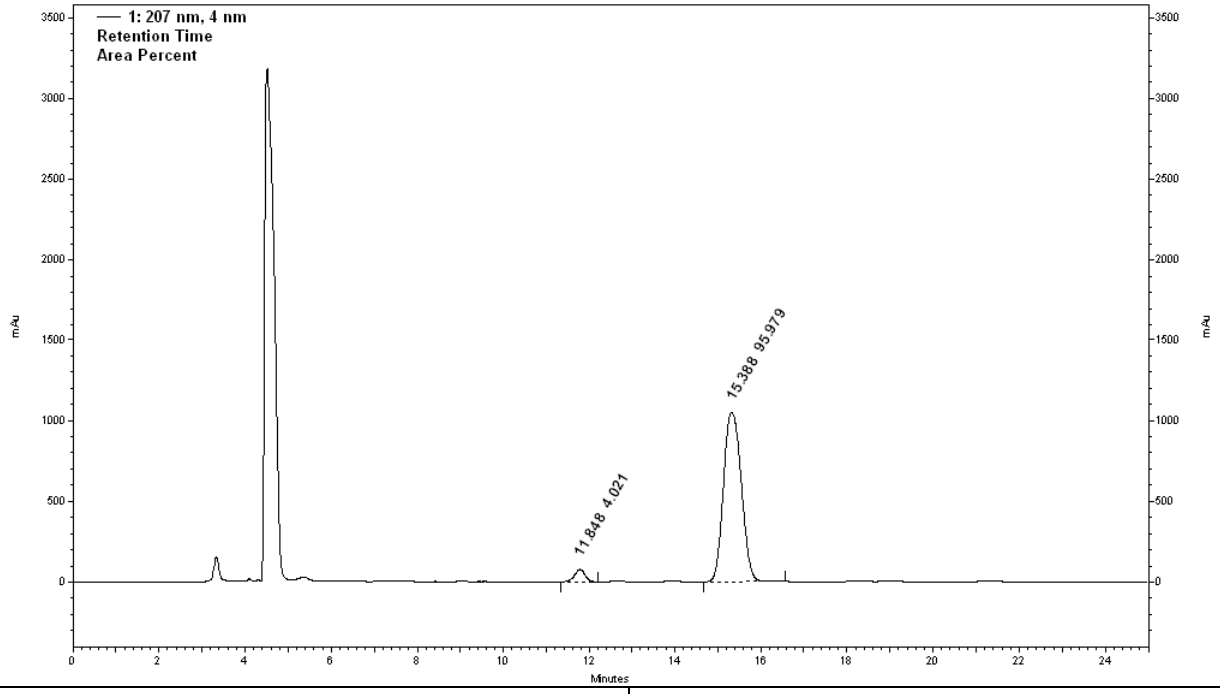

bdw-JM-p-olefin2DRX.1.fid
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
OH
O
OEt
SI28
D (d) 7.22
C (d) 7.33
B (s) 6.26
A (dt) 5.13
E (q) 4.20
F (d) 3.24
G (m) 2.75
I (d) 1.86
H (d) 1.91
J (d) 1.27
f1 (ppm)


bdw-JM-p-olefin2DRX.2.fid
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
OH
O
OEt
SI28
140.00
138.50
136.03
129.08
125.02
124.86
70.42
61.10
43.42
27.13
19.63
14.38
f1 (ppm)

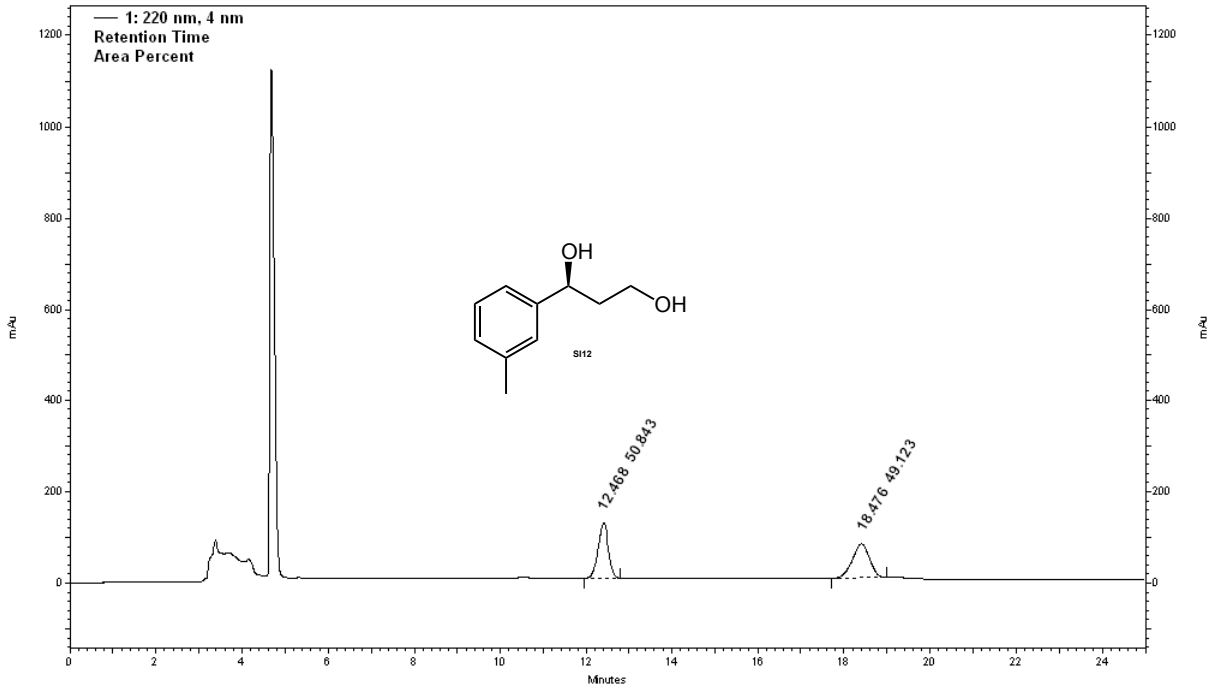

HMN-iii-tbut-OH/1
1H starting parameters (zg30)
DRX-500 TBIC
10/30/13 CGC
OH
O
OEt
tBu
SI29
C (d) 7.42
B (d) 7.34
A (dt) 5.12
D (q) 4.20
E (m) 3.19
F (m) 2.76
H (t) 1.29
G (s) 1.35
f1 (ppm)

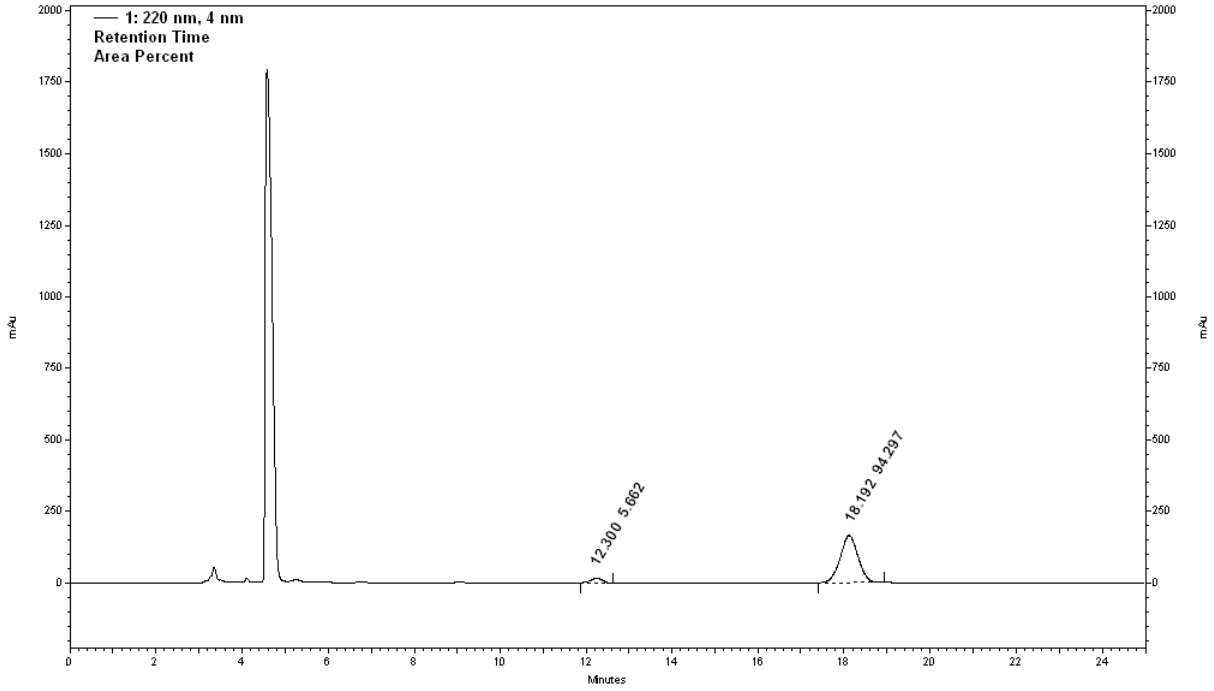

HMN-iii-tbut-OH-C13/1
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
OH
O
OEt
tBu
SI29
149.65
140.17
125.73
125.68
70.34
61.10
43.59
34.74
31.40
14.30
f1 (ppm)



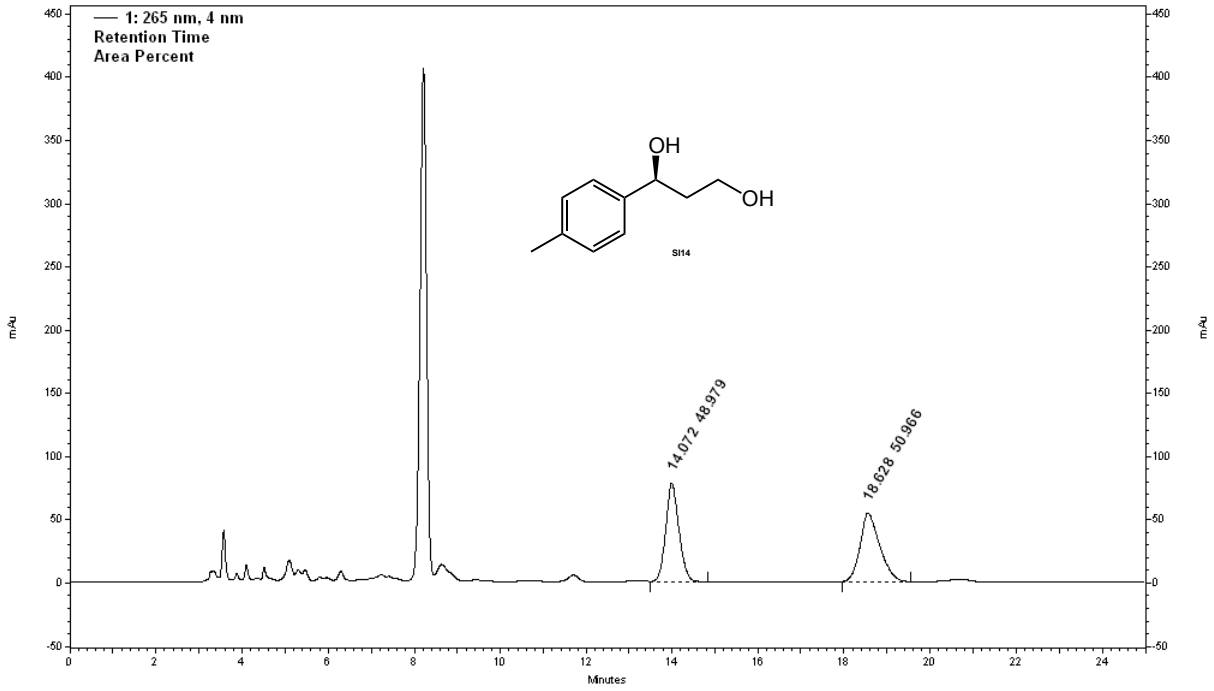


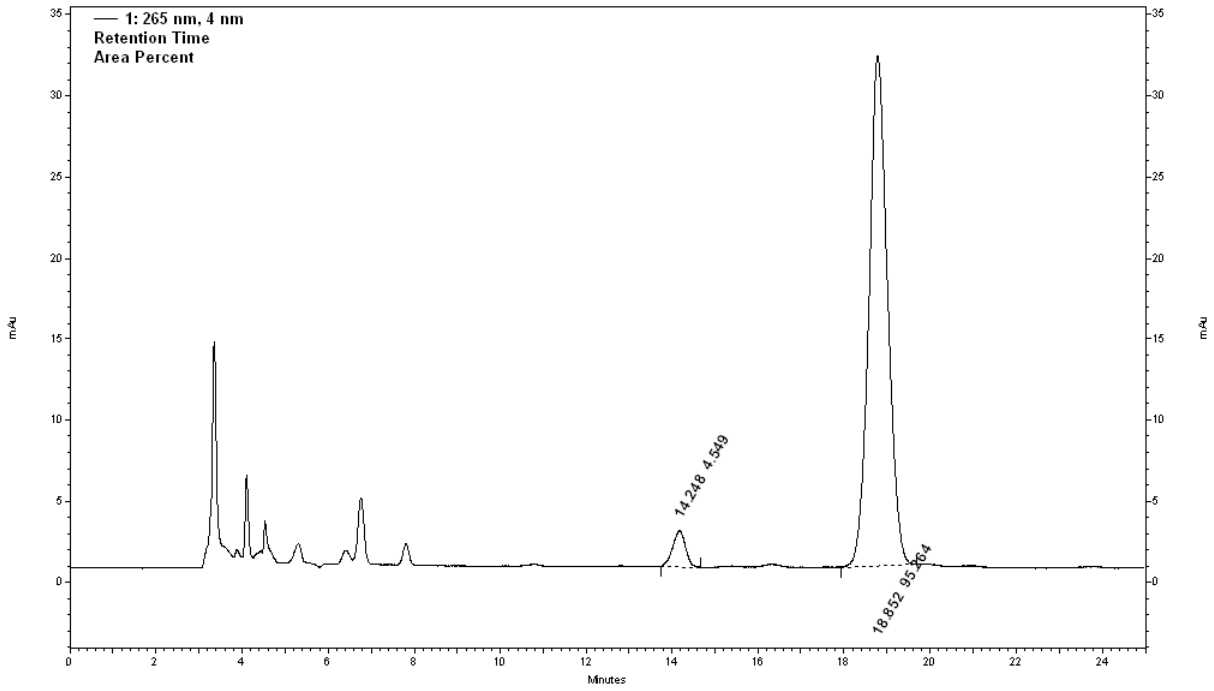
retention time (min)	area (%)
11.8	4.0
15.4	96.0



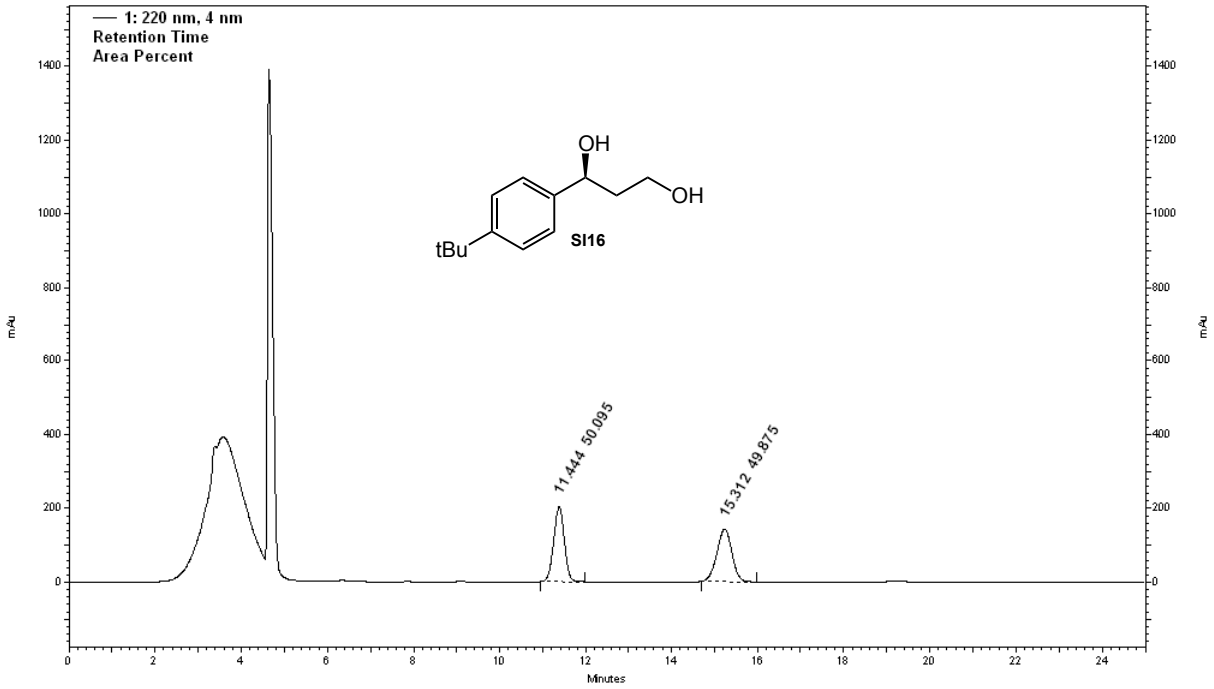


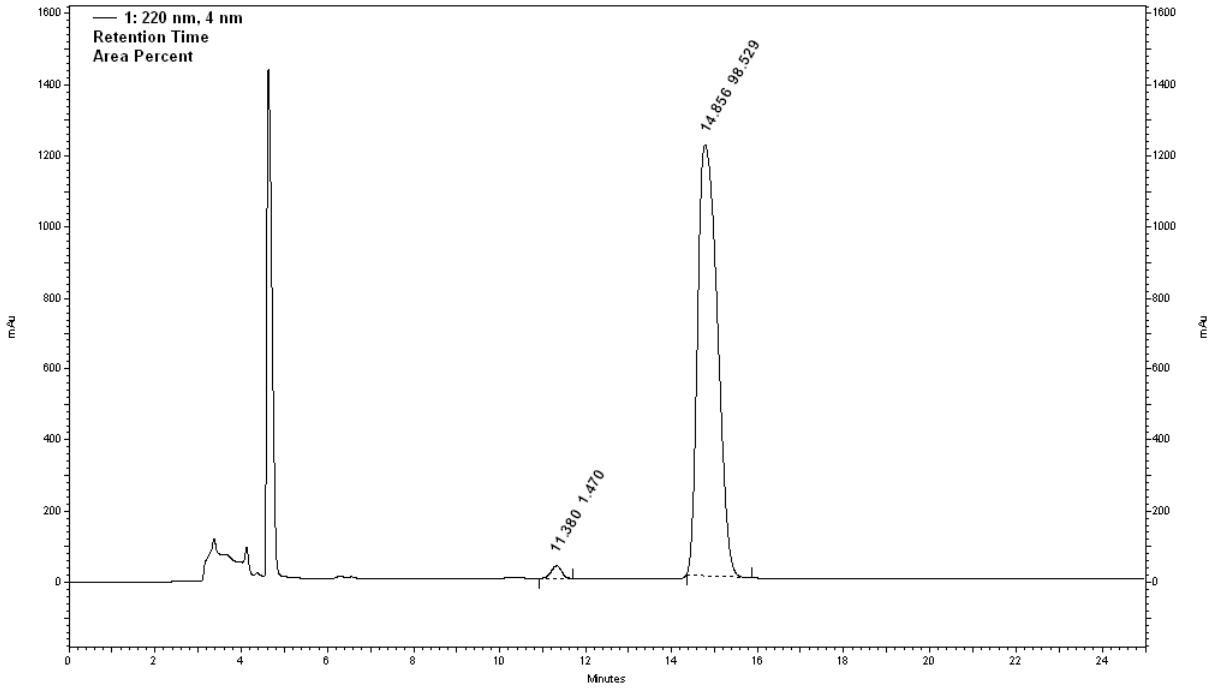
retention time (min)	area (%)
12.3	5.7
18.2	94.3



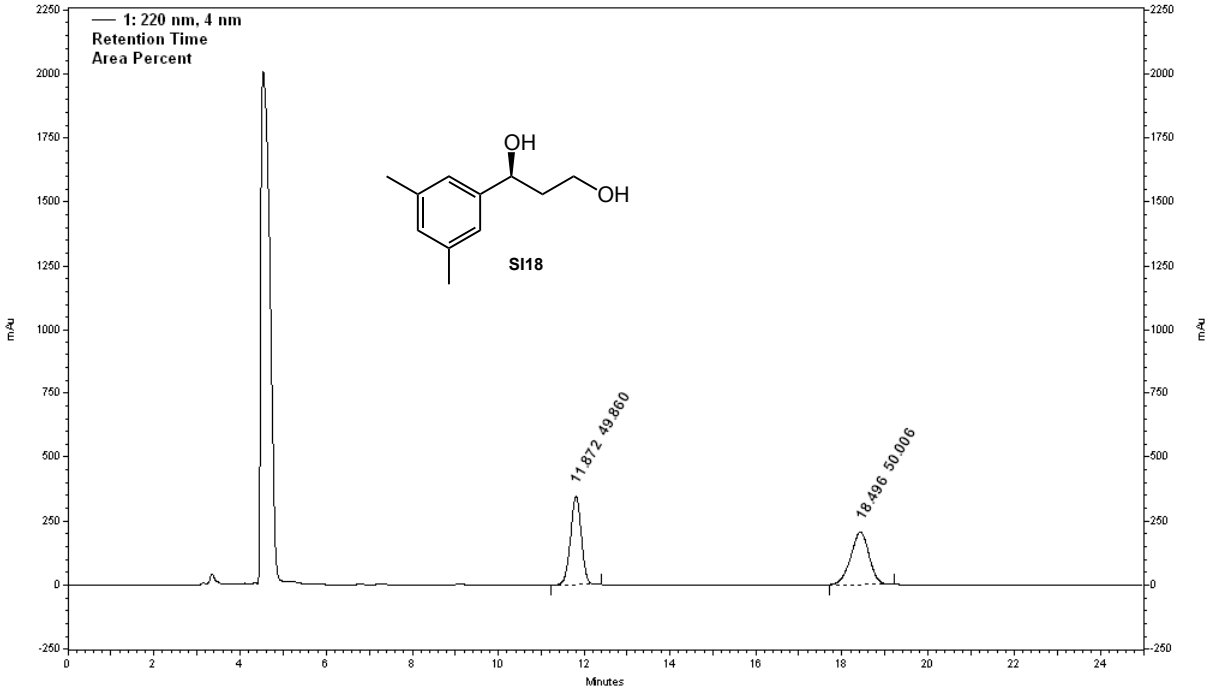


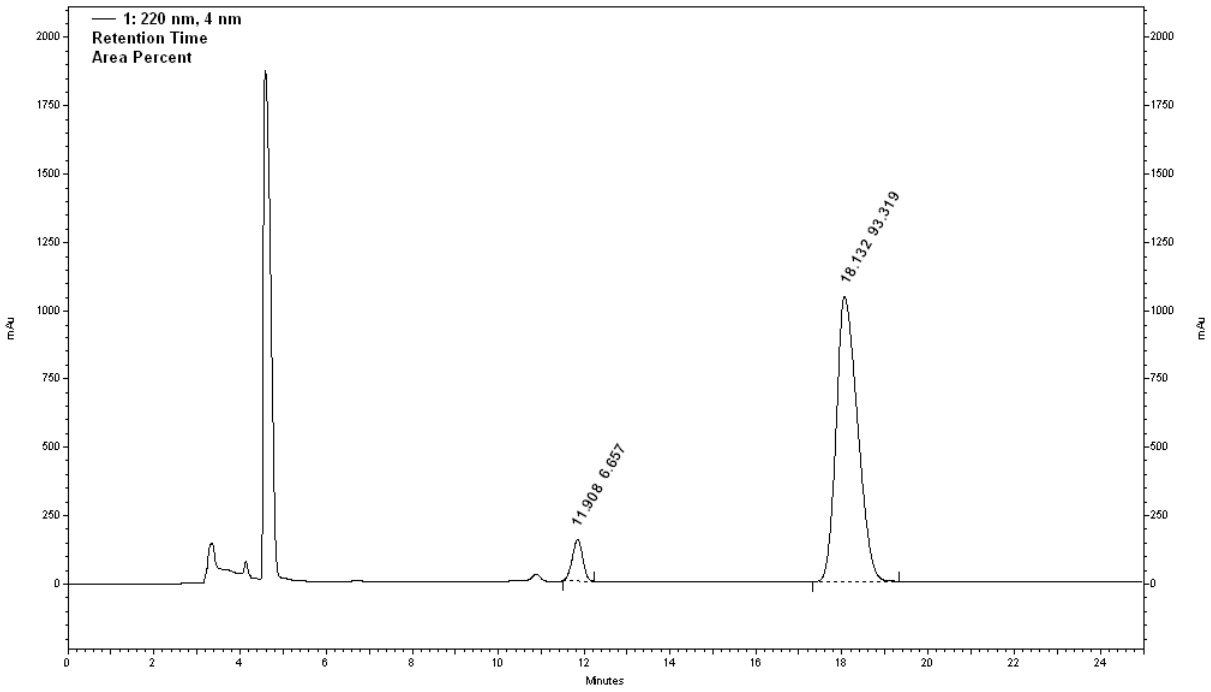
retention time (min)	area (%)
14.2	4.5
18.9	95.5



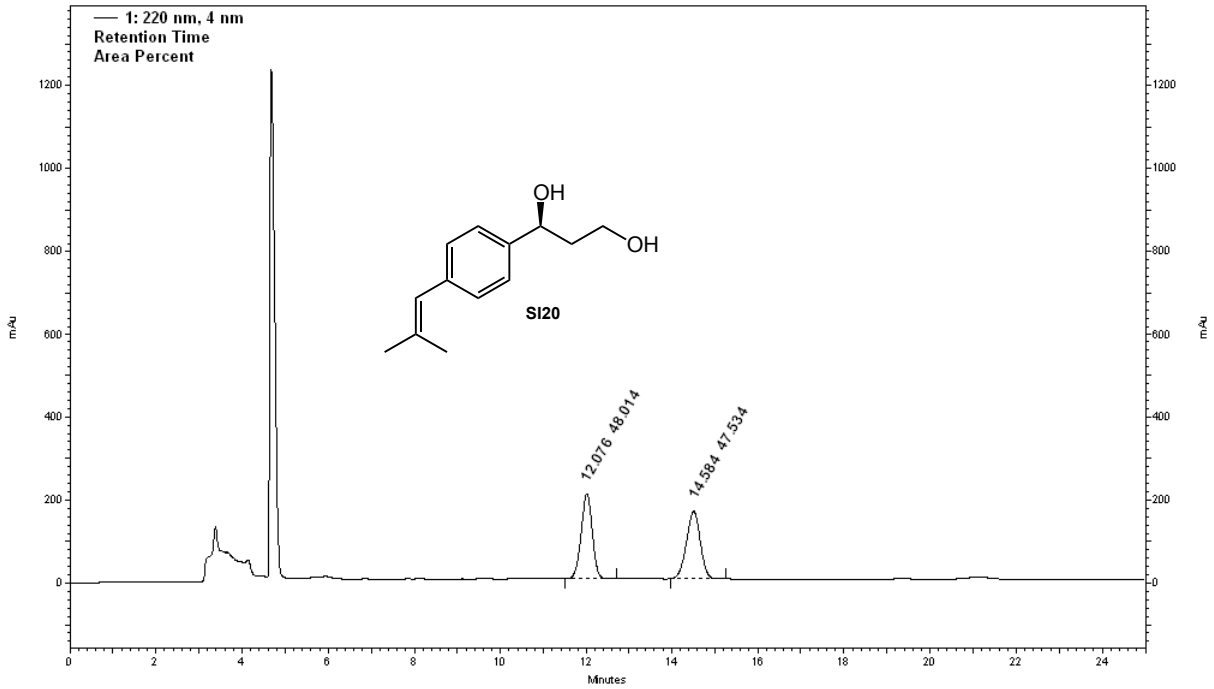


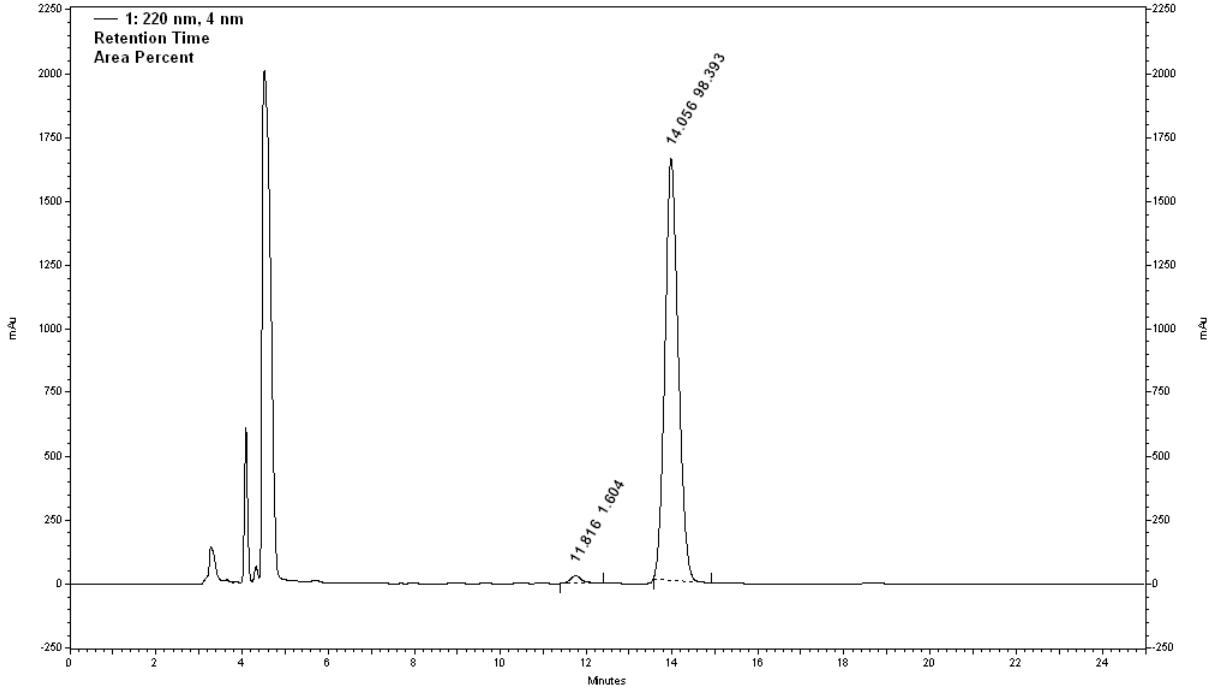
retention time (min)	area (%)
11.4	1.5
14.9	98.5



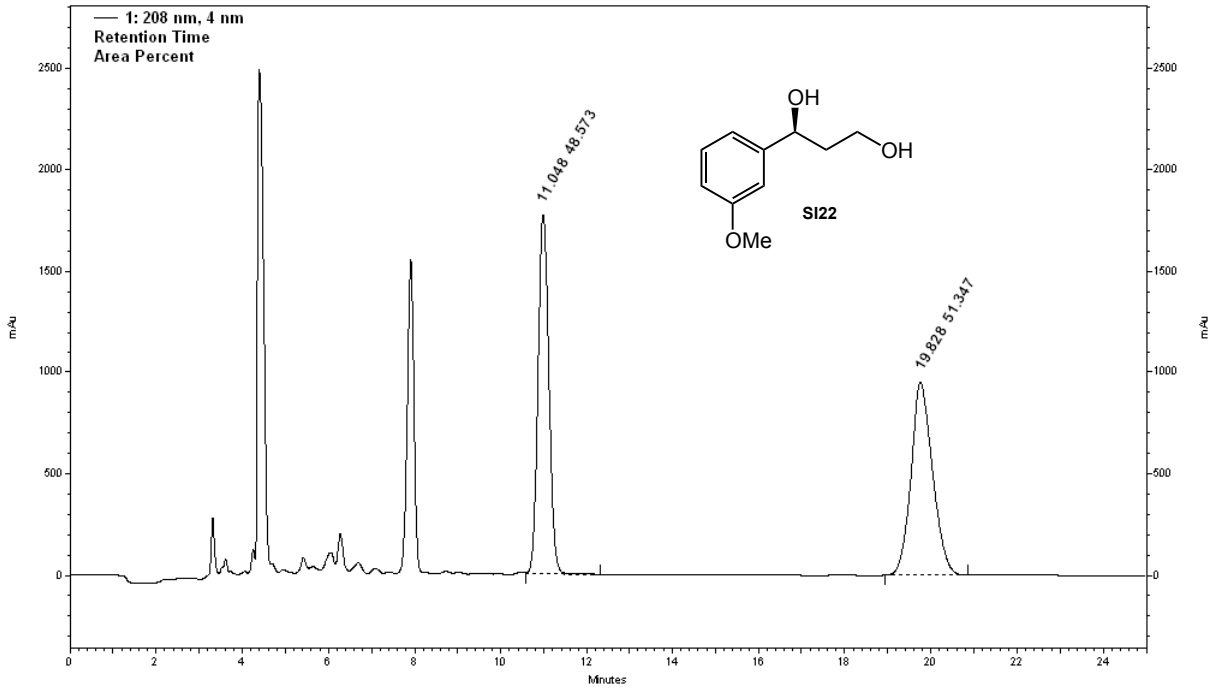


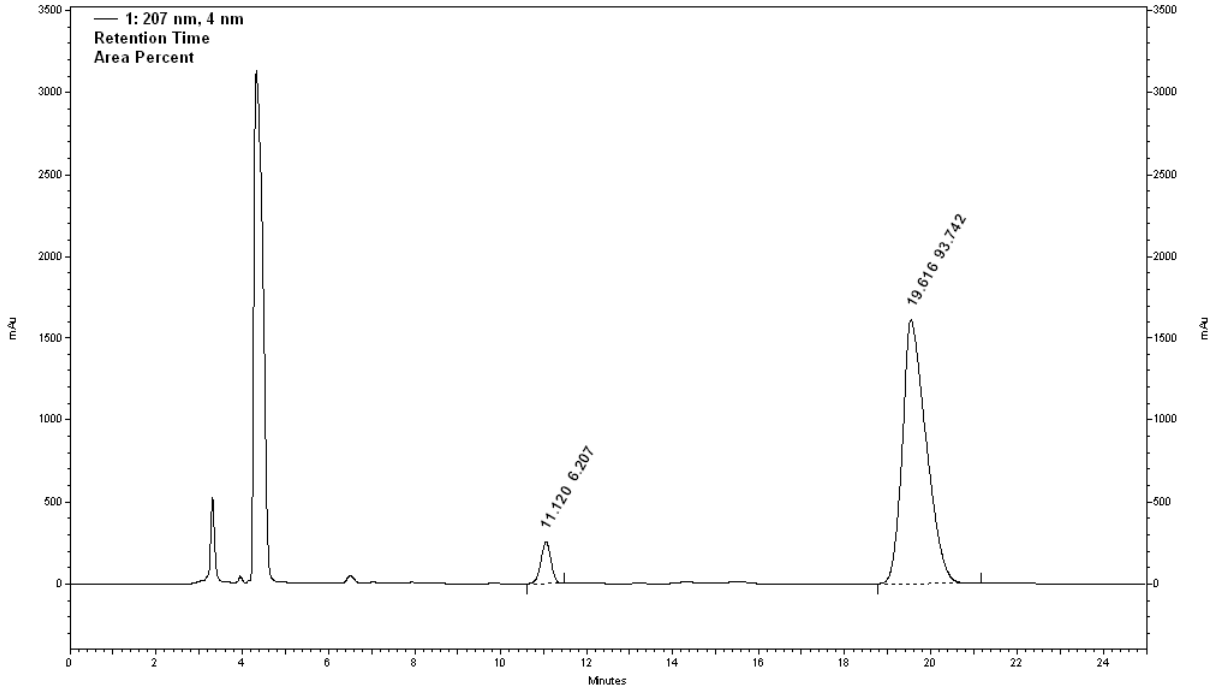
retention time (min)	area (%)
11.9	6.7
18.1	93.3



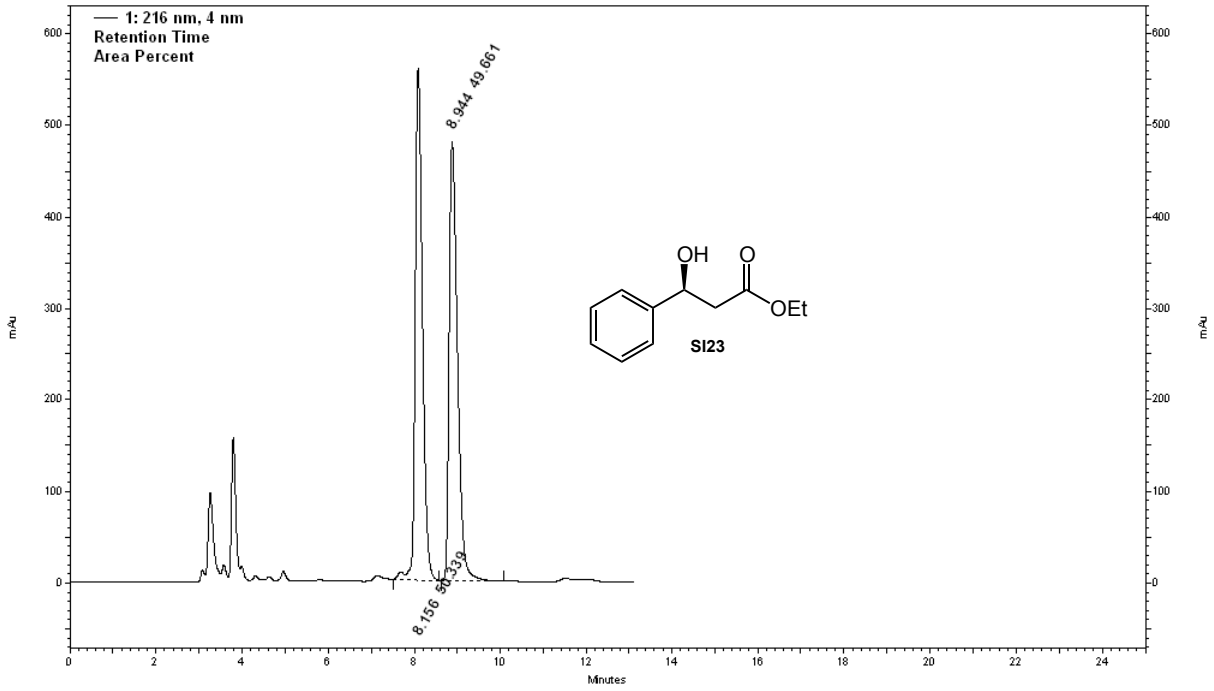


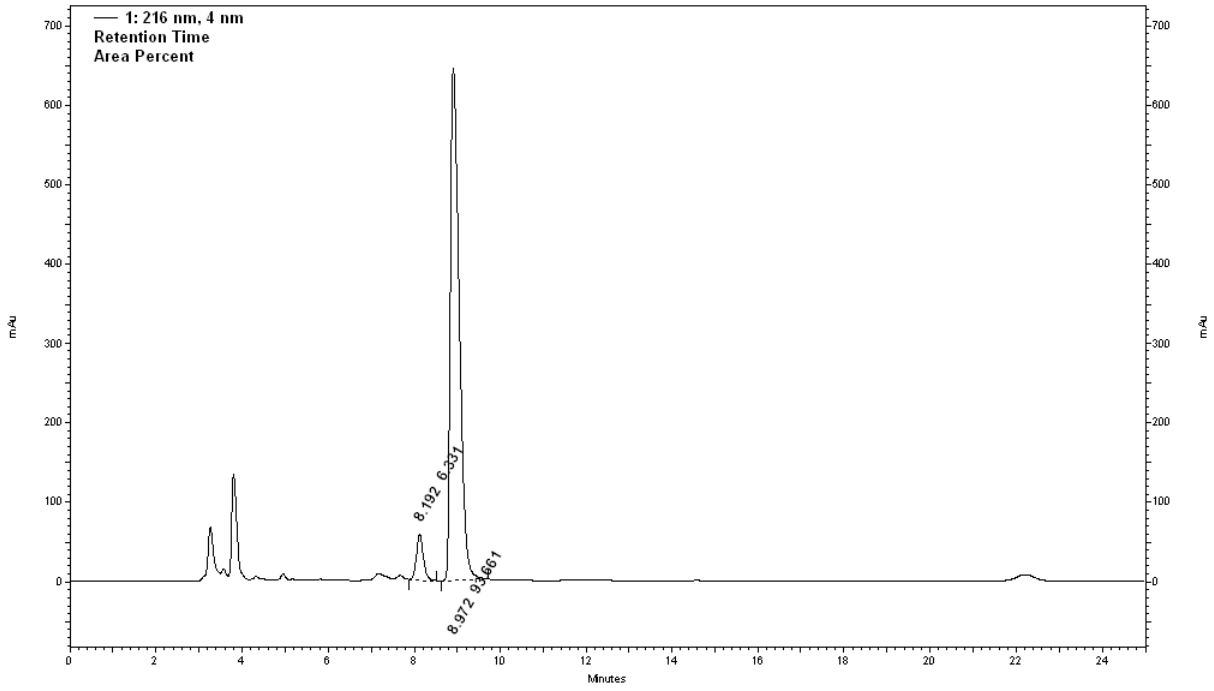
retention time (min)	area (%)
11.8	1.6
14.1	98.4



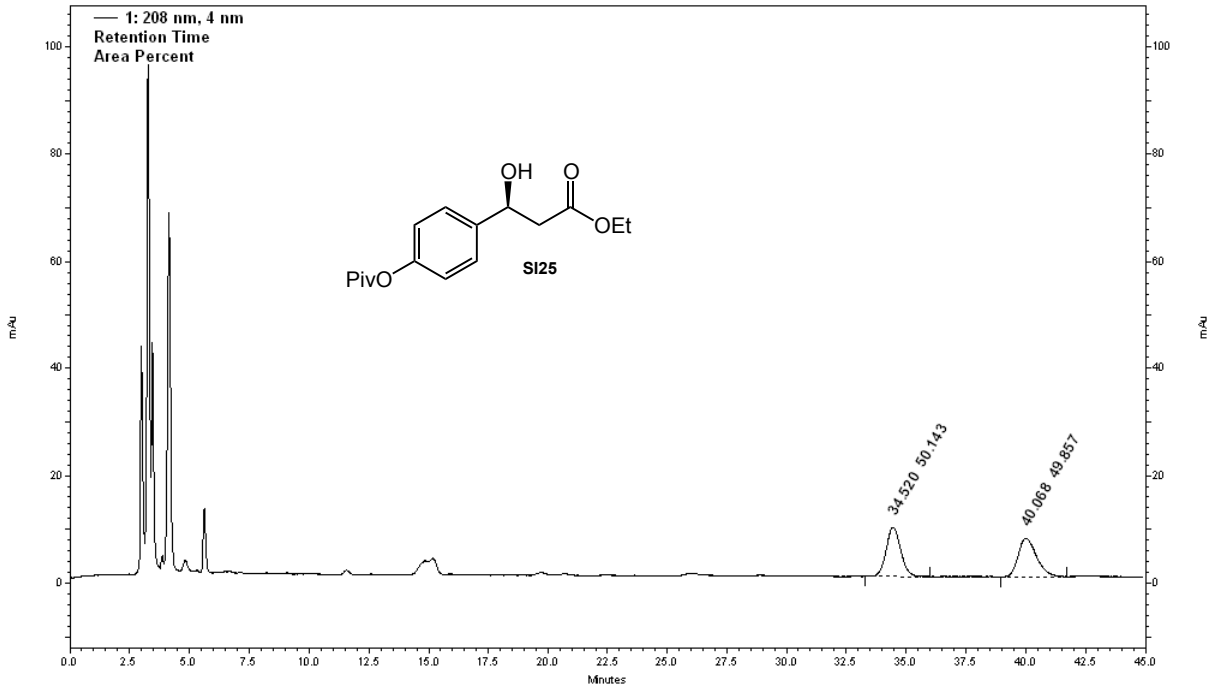


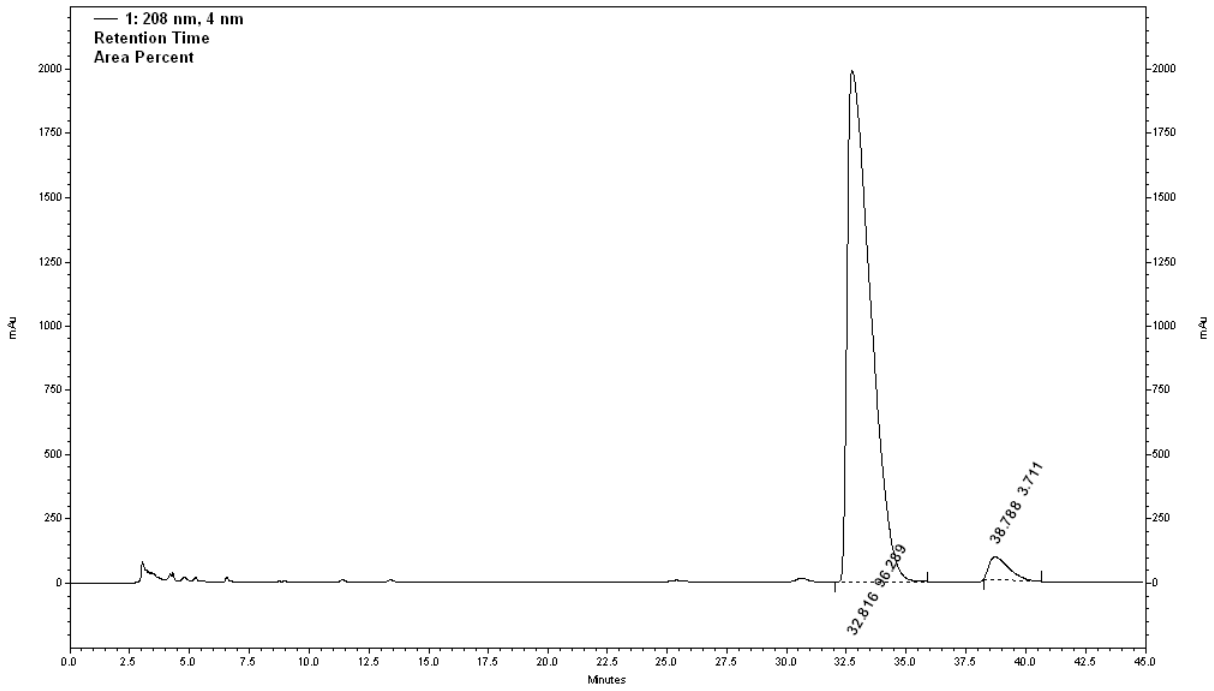
retention time (min)	area (%)
11.1	6.2
19.6	93.7



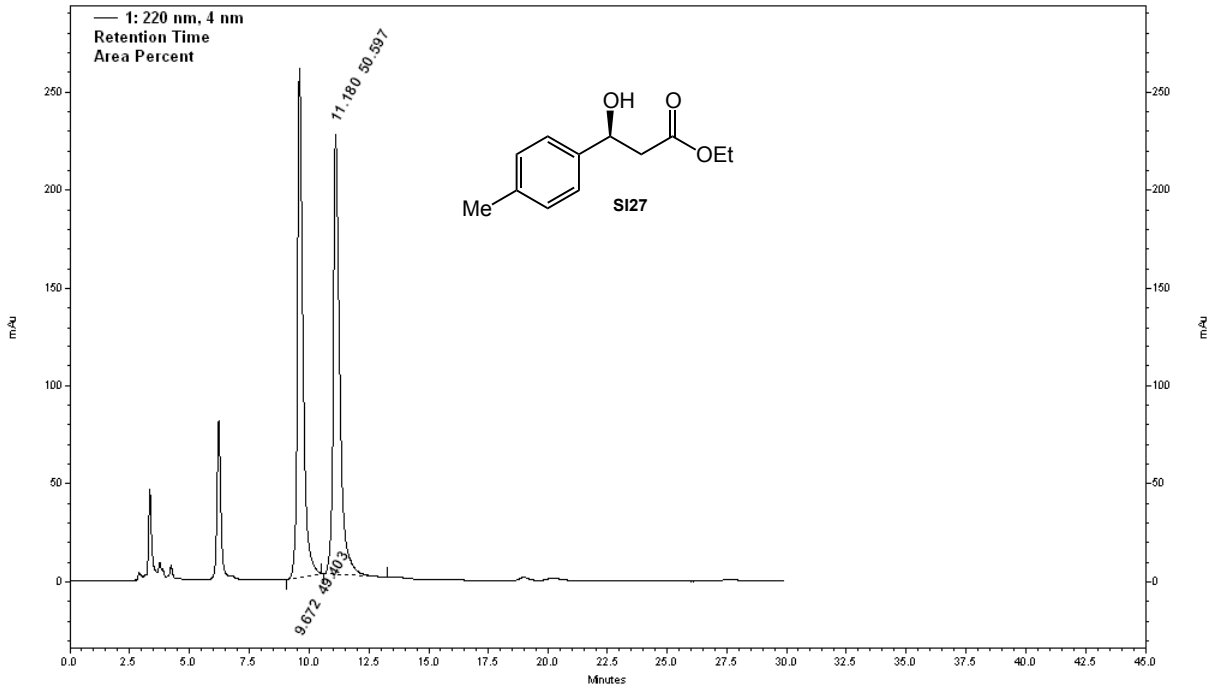


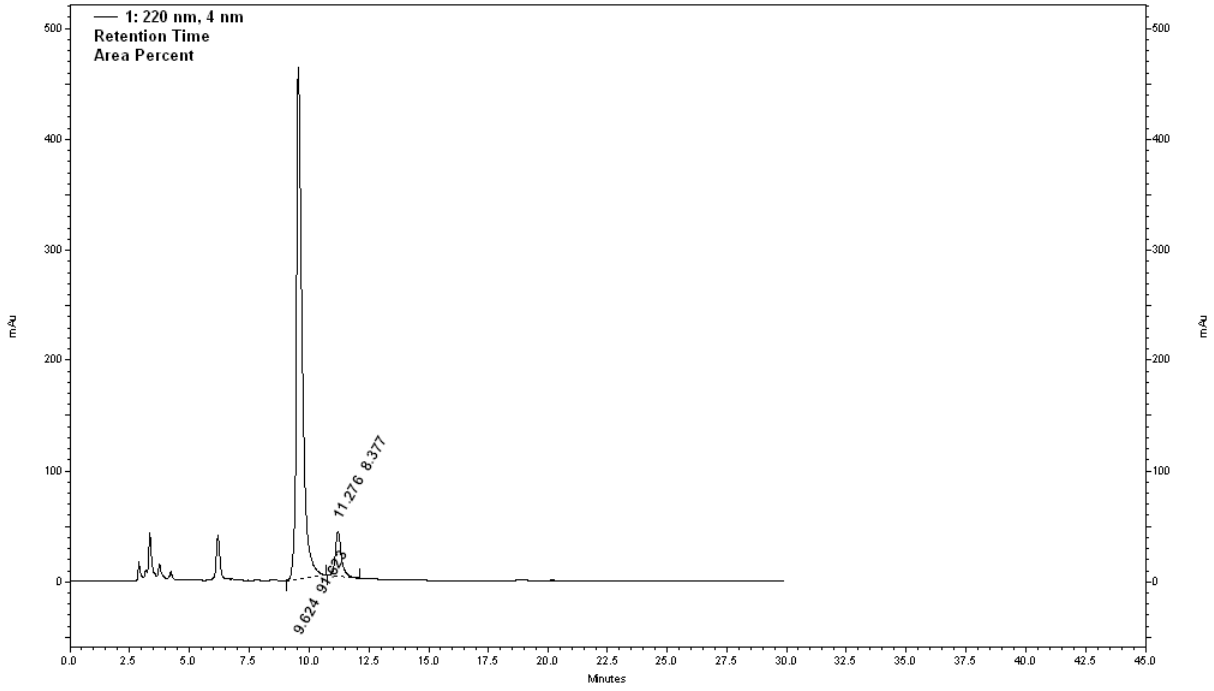
retention time (min)	area (%)
8.2	6.3
9.0	93.7



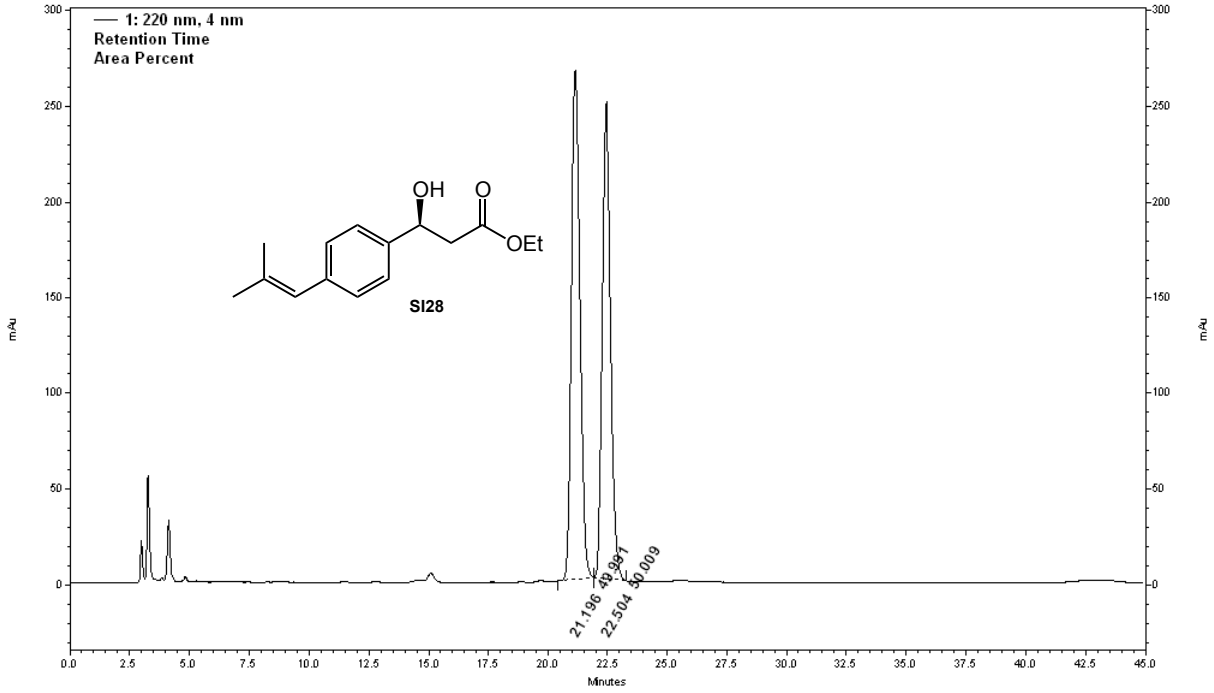


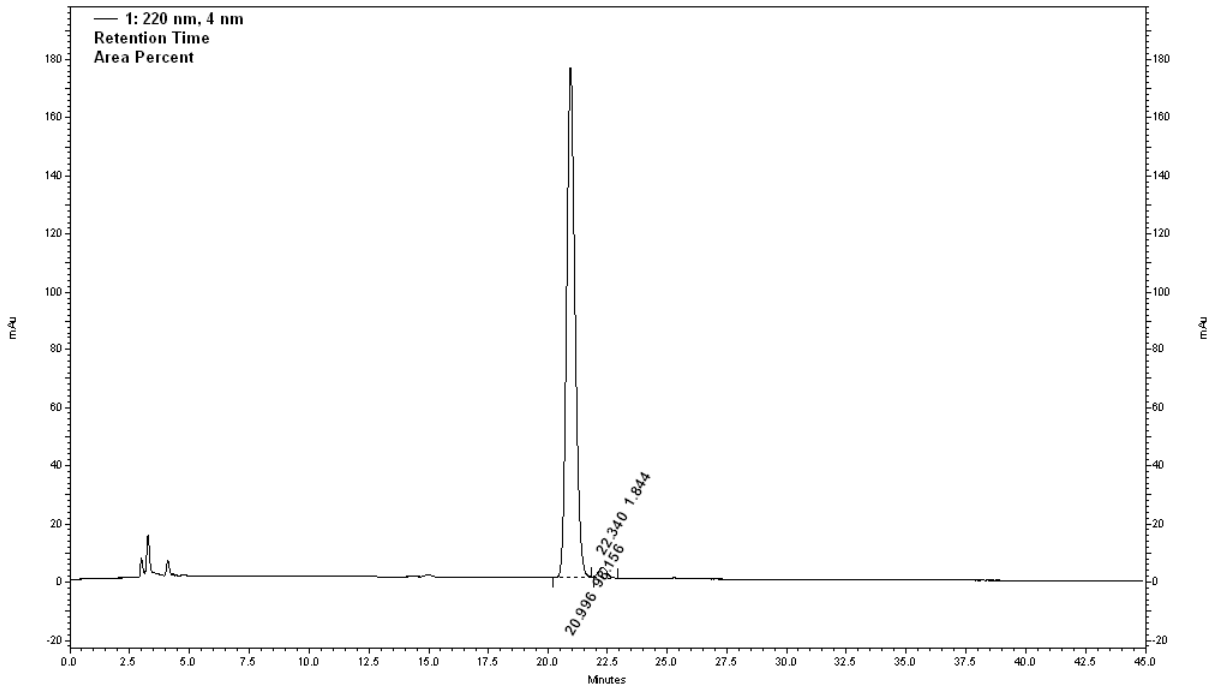
retention time (min)	area (%)
32.8	96.3
38.8	3.7



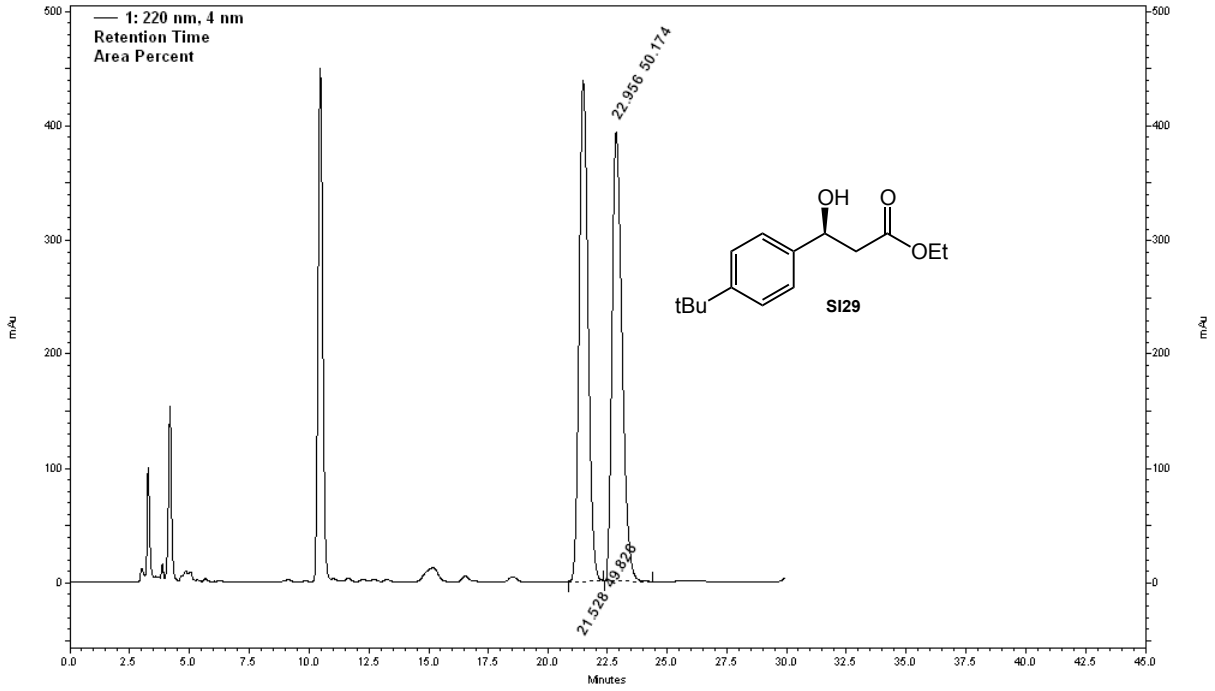


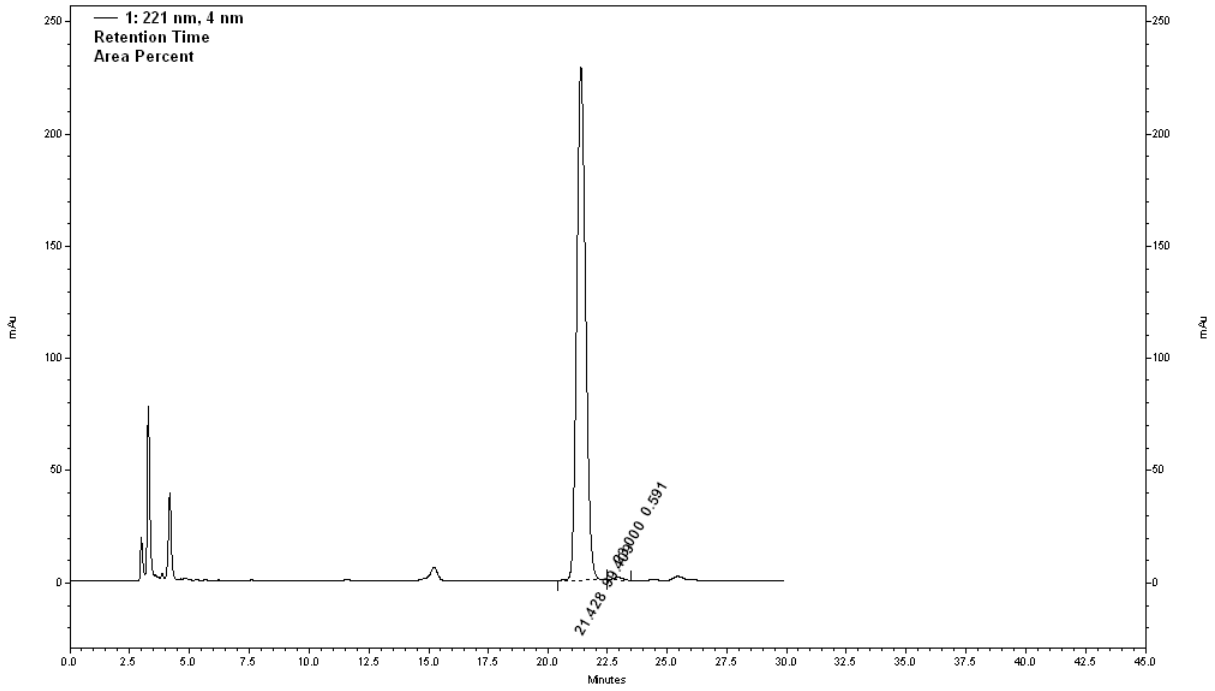
retention time (min)	area (%)
9.6	91.6
11.3	8.4





retention time (min)	area (%)
21.0	98.2
22.3	1.8





retention time (min)	area (%)
21.4	99.4
23.0	0.5