A Catalytic Enantiotopic-Group-Selective Suzuki Reaction for the Construction of Chiral Organoboronates

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I. General Information

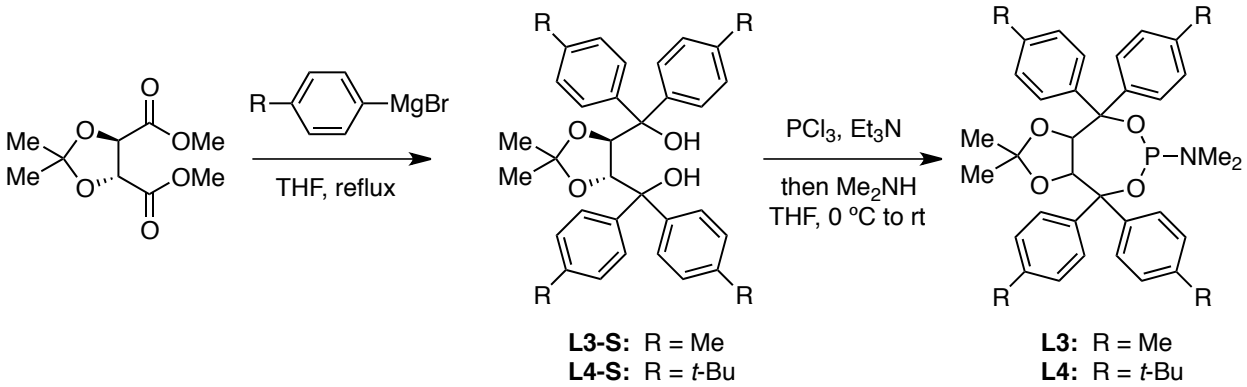
^{1}H NMR spectra were recorded on either a Varian Gemini-500 (500 MHz), or a Varian Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on either a Varian Gemini-500 (125 MHz), or a Varian Inova-500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). ^{31}P NMR spectra were recorded on a Varian Gemini-500 (202 MHz) spectrometer. ^{11}B NMR spectra were recorded on a Varian Gemini-500 (128 MHz) spectrometer. Infrared (IR) spectra were recorded on a Bruker alpha-P Spectrometer. Frequencies are reported in wavenumbers (cm^{-1}) as follows: strong (s), broad (br), medium (m), and weak (w). High-resolution mass spectrometry (ESI+) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230 x 450 Mesh) purchased from Silicycle. Thin layer chromatography (TLC) was performed on 25 μm silica gel glass backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm) and ceric ammonium molybdate (CAM) in ethanol.

Analytical chiral supercritical fluid chromatography (SFC) was performed on a TharSFC Method Station II equipped with Waters 2998 Photodiode Array Detector. Optical rotations were measured on a ATAGO AP-300 Polarimeter.

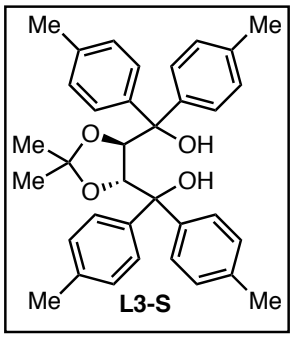
All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (DCM) and toluene were purified using Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after purging with argon. Bis(pinacolato)diboron was generously donated by Allychem Co., Ltd. and used without further purification Phosphorous trichloride and palladium acetate were purchased from Strem Chemicals, Inc. and used without further purification. Triethylamine was purchased from Alfa Aesar and distilled over calcium hydride prior to use. All other reagents were purchased from either Aldrich, Alfa Aesar or Acros and used without further purification.

II. Ligand Synthesis and Characterization

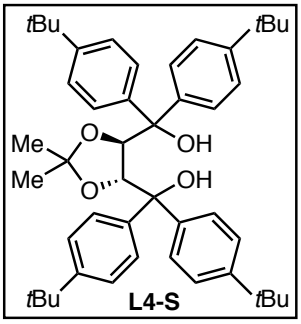


Procedure for preparation of L3-S and L4-S. Dimethyl ketal *para*-methylphenyl-TADDOL was prepared according to the literature procedure[1] with slight modification. To a flame dried 250 mL 2-neck round-bottom flask equipped with a magnetic stir bar and reflux condenser was added freshly crushed magnesium turnings (4.37 g, 179.9 mmol) under N_2. The apparatus was flame-dried, and a single crystal of I_2 was added as a solution in THF (180 mL). 4-Bromotoluene (30.76 g, 179.9 mmol) was slowly added to the magnesium mixture at room temperature *via* syringe. The reaction was cautiously allowed to reflux at 80 °C in an oil bath for 2 h, at which time the reaction was cooled to 0 °C, and a solution of (4*R*,5*R*)-dimethyl 2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (8.53 g, 39.10 mmol) in tetrahydrofuran (20 mL) was added slowly *via* syringe. The reaction was allowed to reflux for 12 h, after which it was cooled to 0 °C and quenched with sat. $NH_4Cl_{(aq)}$ (100 mL). The organic and aqueous layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organics were dried over $Na_2SO_{4(s)}$, filtered, and concentrated *in vacuo*. The crude material was recrystallized from hot methanol. The crystallized solid was isolated by filtration, washed with cold methanol, and dried under vacuum to afford the product as a white solid (17.0 g, 83% yield).

(1) Sieber, J. D.; Morken, J. P. *J. Am. Chem. Soc.* **2008**, *130*, 4978.

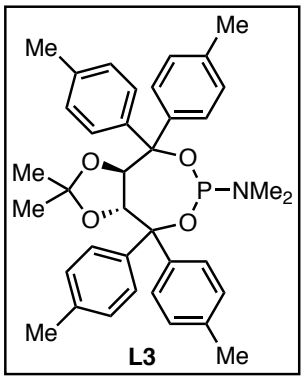


((4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(bis(4-methylphenyl)methanol) (L3-S). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.2 Hz, 4H), 7.24 (d, *J* = 8.2 Hz, 4H), 7.15 (d, *J* = 8.0 Hz, 4H), 7.07 (d, *J* = 8.1 Hz, 4H), 4.59 (s, 2H), 3.97 (s, 2H), 2.39 (s, 6H), 2.31 (s, 6H), 1.09 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.20, 139.99, 137.04, 136.59, 128.72, 128.44, 127.97, 127.50, 109.31, 81.03, 77.88, 27.26, 21.11, 21.05. IR (neat) ν_{max} 3326 (br), 3026 (w), 2983 (w), 2918 (w), 2881 (w), 1509 (m), 1449 (m), 1406 (w), 1376 (m), 1263 (m), 1240 (m), 1216 (m), 1167 (s), 1037 (s), 1019 (s), 885 (s), 813 (s), 750 (s), 611 (m), 563 (m) cm^{-1}. HRMS (ESI+) for $C_{41}H_{47}O_2$ [M+H-2H_2O]: calculated: 545.2662, found: 545.2673; $[\alpha]^{20}_D$: -42.27 (c = 1.00, $CHCl_3$, *l* = 50 mm). Melting point: 101-104 °C.

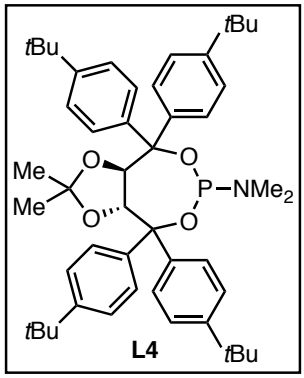


((4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(bis(4-(*tert*-butyl)phenyl)methanol) (L4-S). The reaction was performed *as shown above* with *para*-*t*-butyl bromobenzene. The crude reaction mixture was purified by recrystallization from methanol to afford a white solid (2.95 g, 85% yield). R_f = 0.3 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45-7.43 (m, 4H), 7.33-7.31 (m, 4H), 7.29 (s, 8H), 4.56 (s, 2H), 3.89 (s, 2H), 1.33 (s, 18H), 1.27 (d, *J* = 2.1 Hz, 18H), 1.01 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.99, 149.76, 143.32, 139.67, 128.22, 127.29, 124.92, 124.04, 109.27, 81.15, 77.77, 34.46, 34.42, 31.46, 31.32, 27.04. IR (neat) ν_{max} 3292 (br), 2961 (s), 2903 (w), 2867 (w), 1510 (m), 1460 (m), 1403 (m), 1377 (m), 1268 (m), 1263 (m), 1241 (w), 1169 (w), 1052 (s), 1015 (s), 888 (m), 838 (s), 777 (w), 707 (m), 676 (m), 582 (m) cm^{-1}. HRMS (ESI+) for $C_{47}H_{62}O_4Na$ $[M+Na]^+$: calculated: 713.4540, found: 713.4557; $[\alpha]^{20}_D$: -56.07 (c = 1.00, $CHCl_3$, *l* = 50 mm). Melting point: 211-213 °C.

Procedure for preparation of L3 and L4. To a flame-dried 150 mL round-bottom flask equipped with a magnetic star bar was added TADDOL derivative **L3-S** (2.61 g, 5.0 mmol) and THF (50 mL, 0.1 M) under N_2. Triethylamine (2.37 mL, 17.0 mmol) was added *via* syringe and the reaction mixture was cooled to 0 °C in an ice bath. Phosphorous trichloride (523 μL, 6.0 mmol) was added dropwise *via* syringe at 0 °C and the reaction was brought to room temperature and allowed to stir for 2 h. Then the reaction was cooled back to 0 °C and dimethylamine (25.0 mL, 2.0 M in THF solution, 50.0 mmol) was added *via* syringe. The reaction was allowed to warm to room temperature and stir overnight. The reaction was diluted with Et_2O, filtered through Celite and concentrated *in vacuo*. The crude material was purified by rapid silica gel chromatography (hexanes: ethyl acetate = 20:1), or by recrystallization from hot acetonitrile, to afford the title compound as a white solid (2.65 g, 89% yield).



(3a*R*,8a*R*)-*N*,*N*,2,2-tetramethyl-4,4,8,8-tetra-*p*-tolyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine (L3). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.14-7.11 (m, 6H), 7.08 (d, *J* = 8.2 Hz, 2H), 5.16 (dd, *J* = 8.5, 3.1 Hz, 1H), 4.81 (d, *J* = 8.4 Hz, 1H), 2.77 (s, 3H), 2.76 (d, *J* = 10.7 Hz, 4H), 2.34 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H), 1.34 (s, 3H), 0.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.44, 144.03, 139.37, 139.31, 136.94, 136.78, 136.59, 129.01, 128.88, 128.70, 128.49, 128.32, 127.90, 127.12, 127.05, 111.59, 82.89, 82.86, 82.73, 82.58, 81.67, 81.16, 81.10, 35.52, 35.37, 27.73, 25.54, 21.25, 21.19, 21.17, 21.11. ^{31}P NMR (202 MHz, $CDCl_3$) δ 139.59. IR (neat) ν_{max} 2993 (w), 2921 (w), 2894 (w), 1509 (m), 1448 (m), 1371 (m), 1296 (m), 1198 (m), 1161 (m), 1095 (m), 1033 (m), 976 (s), 876 (s), 811 (s), 783 (s), 756 (s), 705 (s), 614 (m), 496 (m) cm^{-1}. HRMS (ESI) calc. for $C_{37}H_{42}NO_4NaP$ $[M+Na]^+$ 618.2744, found 618.2750. $[\alpha]^{20}_D$: -131.46 (c = 1.00, $CHCl_3$, *l* = 50 mm). Melting point: 200-202 °C.



(3a*R*,8a*R*)-4,4,8,8-tetrakis(4-(*tert*-butyl)phenyl)-*N*,*N*,2,2-tetramethyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine (L4). The reaction was performed *as shown above.* The crude reaction mixture was purified by rapid silica gel chromatography (96:4 hexanes/ethyl acetate) to afford a white solid (1.38 g, 90% yield). R_f = 0.2 in 98:2 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.39-7.26 (m, 12H), 5.18 (dd, *J* = 8.5, 3.1 Hz, 1H), 4.78 (d, *J* = 8.5 Hz, 1H), 2.79 (s, 3H), 2.77 (s, 3H), 1.36 (s, 3H), 1.32 (s, 9H), 1.32 (s, 9H), 1.31 (s, 9H), 1.27 (s, 9H), 0.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.94, 149.91, 149.79, 149.45, 144.01, 143.90, 139.29, 139.23, 128.83, 128.29, 128.27, 126.83, 126.04, 125.04, 124.61, 124.56, 124.04, 111.47, 83.25, 83.23, 82.80, 82.67, 81.27, 81.23, 35.62, 35.49, 34.55, 34.52, 34.47, 31.51, 31.46, 27.76, 25.08. ^{31}P NMR (202 MHz, $CDCl_3$) δ 138.89. IR (neat) ν_{max} 2960 (m), 2903 (w), 2867 (w), 1509 (m), 1459 (w), 1363 (m), 1251 (m), 1212 (m), 1165 (m), 1089 (s), 1054 (s), 962 (s), 881 (s), 840 (s), 777 (s), 708 (s), 582 (w) cm^{-1}. HRMS (ESI) calc. for $C_{49}H_{66}NO_4NaP$ $[M+Na]^+$ 786.4622, found 786.4634. $[\alpha]^{20}_D$: -97.34 (c = 1.00, $CHCl_3$, *l* = 50 mm). Melting point: 177-180 °C.

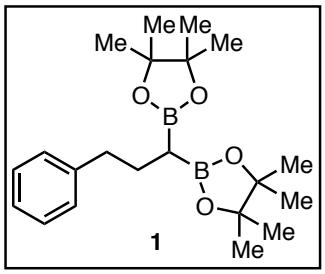
III. Representative Procedure for Preparation of 1,1-Diborylalkanes

Method A.[2] In the glove box, an oven-dried 2-dram vial with magnetic stir bar was charged with CuI (9.6 mg, 0.05 mmol), $B_2(pin)_2$ (266.8 mg, 0.10 mmol), PPh_3 (17.2 mg, 0.065 mmol) and LiOMe (57.0 mg, 1.5 mmol). The vial was sealed with a polypropylene open-top cap with PTFE/silicone septum, and removed from the glove box. A solution of 1,1-dibromoalkane (prepared according to the literature procedure[3]) (0.50 mmol) in DMF (1.0 mL) was added *via* syringe. The reaction was allowed to stir at room temperature for 24 hours. Upon completion, the reaction mixture was diluted with diethyl ether (3 mL) and filtered through a short plug of Celite. The filtrate was washed with water (3 mL), dried over $MgSO_{4(s)}$ and concentrated *in vacuo*. The crude mixture was purified on silica gel (hexanes/ethyl acetate, stain in CAM) to give the desired product.

(2) Ito, H.; Kubota, K. *Org. Lett*. **2012**, *14*, 890
(3) Zhou, Q.; Chen, X.; Ma, D. *Angew. Chem., Int. Eng.* **2010**, *49*, 3513.

Method B.[4] In the glove box, an oven-dried 25-mL round bottom flask with magnetic stir bar was charged with lithium 2,2,6,6-tetramethylpiperidide (328.2 mg, 2.2 mmol). The flask was sealed with a rubber septum, removed from the glove box. THF (5 mL) was added and the reaction was cooled to 0 °C in an ice/water bath. A solution of bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (536.0 mg, 2.0 mmol) in THF (3 mL) was added *via* syringe and the mixture was allowed to stir at 0 °C for 5 minutes. Then a solution of the corresponding alkyl bromide (2.2 mmol) in THF (2 mL) was added and the reaction mixture was allowed to warm to room temperature and stirred for 2 hours. Upon completion, the reaction mixture was cooled to 0 °C and quenched by the addition of sat. $NH_4Cl_{(aq)}$ (0.5 mL). The resulting solution was dried over $MgSO_{4(s)}$, filtered and concentrated *in vacuo*. The crude mixture was purified on silica gel (hexanes/ethyl acetate, stain in CAM) to give the desired product.

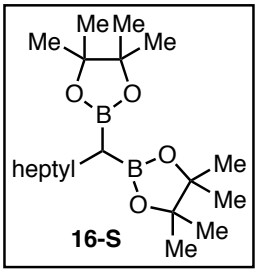
IV. Characterization of 1,1-Diborylalkanes



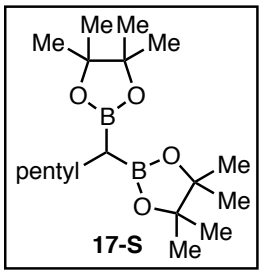
1

2,2'-(3-phenylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1) The reaction was performed according to *Representative Procedure (Method A)*. The crude reaction mixture was purified by column chromatography on SiO_2 (92:8 hexanes/ethyl acetate, stain in CAM) to afford a white solid (83% yield). R_f = 0.3 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.22 (m, 3H), 7.18-7.12 (m, 2H), 2.59 (t, *J* = 8.0 Hz, 2H), 1.85 (q, *J* = 8.0 Hz, 2H), 1.23 (s, 12H), 1.23 (s, 12H), 0.81 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.05, 128.68, 128.21, 125.58, 83.07, 38.84, 28.11, 25.02, 24.64. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.60. IR (neat) ν_{max} 2975 (m), 2928 (w), 2862 (w), 1453 (w), 1358 (m), 1306 (s), 1260 (m), 1216 (m), 1108 (s), 966 (m), 847 (m), 750 (m), 702 (m), 670 (m), 578 (w) cm^{-1}. HRMS (ESI) calc. for $C_{21}H_{35}B_2O_4$ $[M+H]^+$ 373.2721, found 373.2725. Melting point: 79-82 °C.

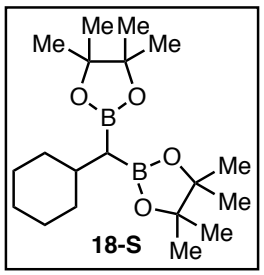
(4) Matteson, D. S.; Moody, R. J. *Organometallics*, **1982**, *1*, 20.



2,2'-(octane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (16-S) The reaction was performed according to *Representative Procedure (Method A)* . The crude reaction mixture was purified by column chromatography on SiO_2 (95:5 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (71% yield). R_f = 0.5 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55-1.51 (m, 2H), 1.28-1.24 (m, 8H), 1.23 (s, 12H), 1.22 (s, 12H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.71 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.94, 32.69, 31.95, 29.68, 29.32, 25.79, 24.96, 24.62, 22.77, 14.23. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.71. IR (neat) ν_{max} 2977 (w), 2924 (w), 2854 (w), 1466 (w), 1355 (m), 1308 (s), 1266 (m), 1214 (w), 1139 (s), 968 (m), 908 (w), 849 (m), 732 (m), 699 (w), 578 (w) cm^{-1}. HRMS (ESI) calc. for $C_{20}H_{41}B_2O_4$ $[M+H]^+$ 367.3191, found 367.3193.

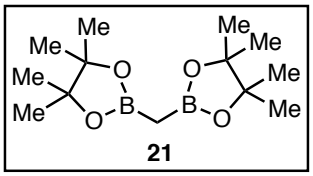


2,2'-(hexane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (17-S) The reaction was performed according to *Representative Procedure (Method A).* The crude reaction mixture was purified by column chromatography on SiO_2 (90:10 hexanes/ethyl acetate, stain in CAM) to afford a white solid (79% yield). R_f = 0.4 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55-1.51 (m, 2H), 1.31-1.24 (m, 6H), 1.23 (s, 12H), 1.22 (s, 12H), 0.85 (t, *J* = 7.0 Hz, 3H), 0.71 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.05, 82.94, 32.33, 31.93, 25.74, 24.96, 24.63, 22.64, 14.14. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.03. IR (neat) ν_{max} 2977 (m), 2926 (m), 2859 (w), 1466 (w), 1357 (m), 1309 (s), 1265 (m), 1215 (m), 1139 (s), 967 (m), 906 (m), 849 (m), 731 (s), 647 (m), 578 (w) cm^{-1}. HRMS (ESI) calc. for $C_{18}H_{37}B_2O_4$ $[M+H]^+$ 339.2878, found 339.2887.

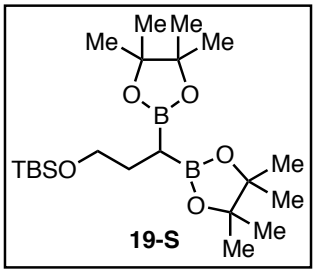


2,2'-(cyclohexylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (18-S) The reaction was performed according to *Representative Procedure (Method A).* The crude reaction mixture was purified by column chromatography on SiO_2 (95:5 hexanes/ethyl acetate, stain in CAM) to afford a white solid (81% yield). R_f = 0.5 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.79-1.76 (m, 2H), 1.70 (dt, *J* = 10.9, 3.4 Hz, 1H), 1.66-1.56 (m, 3H), 1.31-1.24 (m, 1H), 1.23 (s, 12H),

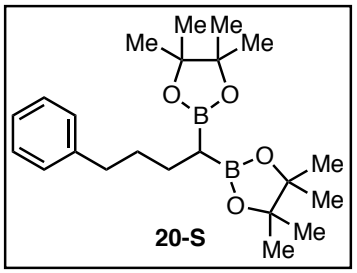
1.22 (s, 12H), 1.13-1.04 (m, 1H), 0.91 (qd, J = 12.0, 3.1 Hz, 2H), 0.64 (d, J = 10.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.90, 36.09, 36.02, 26.87, 26.44, 24.98, 24.68. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.57. IR (neat) ν_{max} 2977 (m), 2922 (m), 2851 (w), 1446 (w), 1378 (m), 1343 (s), 1312 (s), 1295 (s), 1265 (w), 1213 (w), 1135 (s), 968 (m), 885 (w), 848 (m), 665 (w), 577 (w) cm^{-1}. HRMS (ESI) calc. for $C_{19}H_{37}B_2O_4$ $[M+H]^+$ 351.2878, found 351.2894. Melting point: 82-84 °C.



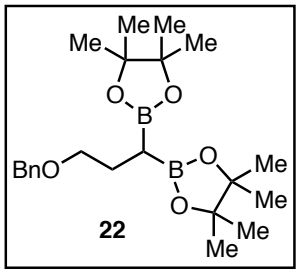
bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (21). The reaction was performed according to *Representative Procedure (Method A)*. The crude reaction mixture was purified by sublimation to afford a white solid (62%) or by column chromatography on SiO_2 (85:15 hexanes/ethyl acetate, stain in CAM) to afford a white solid (79% yield). R_f = 0.3 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (s, 24H), 0.35 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 83.04, 24.79. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.40. IR (neat) ν_{max} 2976 (m), 2932 (w), 1448 (w), 1370 (w), 1304 (s), 1266 (s), 1214 (m), 1137 (s), 1090 (m), 966 (s), 895 (m), 844 (s), 674 (m), 578 (w) cm^{-1}. HRMS (ESI) calc. for $C_{13}H_{27}B_2O_4$ $[M+H]^+$ 269.2095, found 269.2101. Melting point: 44-48 °C.



(3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)(*tert*-butyl)dimethylsilane (19-S) The reaction was performed according to *Representative Procedure (Method A)*. The crude reaction mixture was purified by column chromatography on SiO_2 (90:10 hexanes/ethyl acetate, stain in CAM) to afford a white solid (82% yield). R_f = 0.3 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.53 (t, J = 7.2 Hz, 2H), 1.75 (q, J = 7.4 Hz, 2H), 1.21 (s, 12H), 1.20 (s, 12H), 0.87 (s, 9H), 0.76 (t, J = 7.7 Hz, 1H), 0.02 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 83.06, 65.16, 28.82, 26.17, 25.02, 24.62, 18.53, -5.10. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.68. IR (neat) ν_{max} 2976 (m), 2928 (m), 2896 (w), 2856 (w), 1472 (w), 1358 (m), 1313 (s), 1290 (m), 1244 (w), 1213 (m), 1137 (s), 1112 (m), 1070 (m), 967 (m), 902 (w), 834 (s), 767 (s), 665 (m), 578 (w), 532 (w) cm^{-1}. HRMS (ESI) calc. for $C_{21}H_{45}B_2O_5Si$ $[M+H]^+$ 427.3225, found 427.3222. Melting point: 29-32 °C.



2,2'-(4-phenylbutane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (20-S) The reaction was performed according to *Representative Procedure (Method B)*. The crude reaction mixture was purified by column chromatography on SiO_2 (90:10 hexanes/ethyl acetate, stain in CAM) to afford a colorless oil (94% yield). R_f = 0.3 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.23 (m, 2H), 7.17-7.13 (m, 3H), 2.59 (t, *J* = 7.1 Hz, 2H), 1.65-1.59 (m, 4H), 1.23 (s, 12H), 1.22 (s, 12H), 0.76 (t, *J* = 5.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.11, 128.42, 128.24, 125.50, 83.01, 36.14, 34.44, 25.67, 24.98, 24.63. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.87. IR (neat) ν_{max} 3026 (w), 2977 (w), 2929 (w), 2851 (w), 1454 (w), 1359 (m), 1308 (s), 1265 (m), 1213 (w), 1136 (s), 968 (m), 908 (m), 849 (m), 730 (s), 698 (s), 669 (m), 578 (w) cm^{-1}. HRMS (ESI) calc. for $C_{22}H_{37}B_2O_4$ $[M+H]^+$ 387.2878, found 387.2870.



(*R*)-2-(1-(benzofuran-5-yl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22). The reaction was performed according to *Representative Procedure (Method B)*. The crude reaction mixture was purified by column chromatography on SiO_2 (90:10 hexanes/ethyl acetate, stain in CAM) to afford a colorless oil (70% yield). R_f = 0.5 in 80:20 hexanes/ethyl acetate on TLC.^{1}H NMR (500 MHz, $CDCl_3$) 7.35-7.29 (m, 4H), 7.24 (t, *J* = 7.0 Hz, 1H), 4.49 (s, 2H), 3.41 (t, *J* = 6.7 Hz, 2H), 1.87 (q, *J* = 7.1 Hz, 2H), 1.21 (s, 12H), 1.19 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.94, 128.21, 127.56, 127.23, 82.93, 72.46, 71.83, 25.68, 24.82, 24.47. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.43. IR (neat) ν_{max} 2976 (m), 2930 (w), 2855 (m), 1454 (w), 1356 (s), 1308 (s), 1267 (m), 1214 (w), 1138 (s), 1102 (m), 968 (m), 901 (w), 848 (s), 734 (m), 697 (m), 699 (m) cm^{-1}. HRMS (ESI) calc. for $C_{22}H_{36}B_2O_5$ $[M+H]^+$ 403.2827, found 403.2833.

V. Procedures for Enantiotopic-Group-Selective Suzuki-Miyaura Coupling

For Aryl Iodides (Method C; Conditions A of Main Text):

In the glove box, an oven-dried 1-dram vial equipped with magnetic stir bar was charged with 1,1-diborylalkane (0.11 mmol), aryl iodide (0.1 mmol), and (*R,R*)-TADDOL-derived phosphoramide ligand (**L3**) (6.0 mg, 0.01 mmol). The vial was sealed with rubber septum, removed from the glove box. A stock solution of $Pd(OAc)_2$ in 1,4-dioxane (0.2 mL, 0.024 M, 5 μmol) was added *via* syringe followed by the addition of freshly degassed $KOH_{(aq)}$[5] (188 μL, 8.0 M, 1.5 mmol) and the mixture was allowed to stir at room temperature for 12 hours. Upon completion, the reaction mixture was diluted with diethyl ether (2 mL) and filtered through a short plug of silica gel. The filtrate was concentrated under vacuum and purified on silica gel (hexanes/ethyl acetate or hexanes/dichloromethane, stain in CAM) to give the desired product.

Note that the reaction can also be performed without the need for a glove box, which leads to the same yields and enantioselectivities. A 1-dram vial with magnetic stir bar was charged with 1,1-diborylalkane (0.11 mmol), aryl iodide (0.1 mmol), and (*R,R*)-TADDOL-derived phosphoramide ligand (**L3**) (6.0 mg, 0.01 mmol). The vial was sealed with rubber septum, and purged with N_2 for 10 minutes. A solution of $Pd(OAc)_2$ in 1,4-dioxane stock solution (0.2 mL, 0.024 M, 5 μmol) was added *via* syringe followed by the addition of freshly degassed $KOH_{(aq)}$ (188 μL, 8.0 M, 1.5 mmol) and the mixture was allowed to stir at room temperature for 12 hours. Upon completion, the reaction mixture was diluted with diethyl ether (2 mL) and filtered through a short plug of silica gel. The filtrate was concentrated under vacuum and purified on silica gel (hexanes/ethyl acetate or hexanes/dichloromethane, stain in CAM) to give the desired product.

For Aryl Bromides (Method D; Conditions B of Main Text):

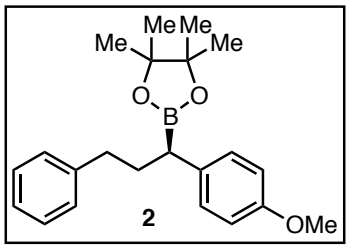
In the glove box, an oven-dried 1-dram vial with magnetic stir bar was charged with 1,1-diborylalkane (0.11 mmol), aryl bromide (0.1 mmol), NaI (16.5 mg, 0.11 mmol) and (*R,R*)-TADDOL-derived phosphoramide ligand (**L3**) (6.0 mg, 0.01 mmol). The vial was sealed with rubber septum, removed from the glove box. A solution of $Pd(OAc)_2$ in 1,4-dioxane stock solution (0.2 mL, 0.024 M, 5 μmol) was added *via* syringe followed by the addition of freshly degassed $KOH_{(aq)}$ (188 μL, 8.0 M, 1.5 mmol) and the mixture was allowed to stir at room

(5) $KOH_{(aq.)}$ was sparged with N_2 for 30 min at room temperature before using.

temperature for 12 hours. Upon completion, the reaction mixture was diluted with diethyl ether (2 mL) and filtered through a short plug of silica gel. The filtrate was concentrated under vacuum and purified on silica gel (hexanes/ethyl acetate or hexanes/dichloromethane, stain in CAM) to give the desired product.

Note that the reaction can also be performed without need for a glove box, which leads to the same yields and enantioselectivities. A 1-dram vial with magnetic stir bar was charged with 1,1-diborylalkane (0.11 mmol), aryl bromide (0.1 mmol), NaI (16.5 mg, 0.11 mmol) and (*R,R*)-TADDOL-derived phosphoramide ligand (**L3**) (6.0 mg, 0.01 mmol). The vial was sealed with rubber septum, and purged with N_2 for 10 min. A solution of $Pd(OAc)_2$ in 1,4-dioxane stock solution (0.2 mL, 0.024 M, 5 μmol) was added *via* syringe followed by the addition of freshly degassed $KOH_{(aq)}$ (188 μL, 8.0 M, 1.5 mmol) and the mixture was allowed to stir at room temperature for 12 hours. Upon completion, the reaction mixture was diluted with diethyl ether (2 mL) and filtered through a short plug of silica gel. The filtrate was concentrated under vacuum and purified on silica gel (hexanes/ethyl acetate or hexanes/dichloromethane, stain in CAM) to give the desired product.

VI. Characterization of Reaction Products and Analysis of Stereochemistry

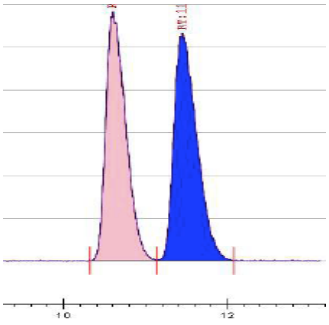


(*R*)-2-(1-(4-methoxyphenyl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2). The reaction was performed according to *Representative Procedure (Method C).* The crude reaction mixture was purified by column chromatography on SiO_2 (97:3 hexanes/diethyl ether, stain in CAM) to afford a yellow oil (29.0 mg, 82% yield). R_f = 0.4 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.27-7.24 (m, 2H), 7.17-7.13 (m, 5H), 6.84-6.81 (m, 2H), 3.79 (s, 3H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.30 (t, *J* = 7.9 Hz, 1H), 2.17-2.09 (m, 1H), 1.98-1.91 (m, 1H), 1.22 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.51, 142.77, 135.02, 129.41, 128.62, 128.34, 125.72, 113.92, 83.40, 55.32, 35.48, 34.73, 24.83, 24.74. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.29. IR (neat) ν_{max} 3061 (w), 3026 (w), 2976 (m), 2929 (m), 2857 (w), 2834 (w), 1607 (m), 1508 (s), 1454 (m), 1359 (s), 1321 (s), 1322 (s), 1244 (s), 1141 (s), 1037 (m), 967 (m), 850 (m), 828 (m), 749 (m), 699 (m), 529 (w) cm^{-1}. HRMS (ESI) calc. for $C_{22}H_{30}BO_3$ $[M+H]^+$ 353.2288, found 353.2277. $[\alpha]^{20}_D$: -16.97 (c = 0.85, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute configuration was assigned by comparing the optical rotation of the corresponding alcohol after the oxidation with the reported value in the literature.[6]

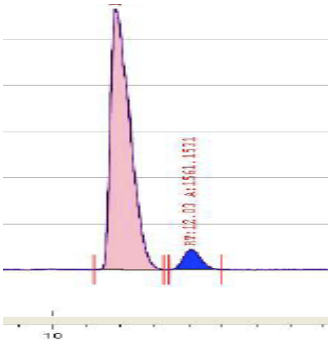
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 2% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	48.9245	9833.2521	10.6	582.9338
2	51.0755	10265.576	11.45	532.1942
Total:	100	20098.8281		

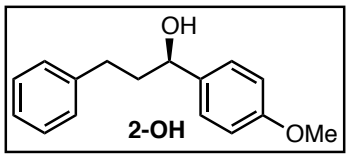
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	93.4672	22336.07	10.92	1129.4131
2	6.5328	1561.1531	12.03	88.5124
Total:	100	23897.2231		

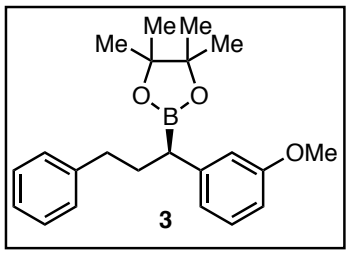
Reaction product



(*R*)-1-(4-methoxyphenyl)-3-phenylpropan-1-ol (2-OH). Prepared by oxidation of the boronate with $NaOH/H_2O_2$ in THF. The crude reaction mixture was purified by column chromatography on SiO_2 (80:20 hexanes/ethyl acetate, stain in CAM) to afford a colorless oil. R*f* = 0.5 in 75:25 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.30-7.26 (m, 4H), 7.20-7.17 (m, 3H), 6.91-6.88 (m, 2H), 4.64 (t, *J* = 6.0 Hz, 1H), 3.79 (s, 3H), 2.73 (ddd, *J* = 14.3,

(6) Liu, Y.; Da, C.-S.; Yu, S.-L.; Yin, X.-G.; Wang, J.-R.; Fan, X.-Y.; Li, W.-P.; Wang, R. *J. Org. Chem.* **2010**, *75*, 6869.

9.4, 5.4 Hz, 1H), 2.68-2.61 (m, 1H), 2.14 (dddd, *J* = 13.6, 9.6, 7.7, 5.9 Hz, 1H), 2.01 (ddt, *J* = 13.6, 9.7, 6.0 Hz, 1H), 1.83 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.09, 141.80, 136.67, 128.40, 128.34, 127.17, 125.79, 113.87 73.47, 55.27, 40.32, 32.11. IR (neat) ν_{max} 3258 (br), 3024 (w), 3000 (w), 2948 (m), 2926 (m), 2880 (w), 2834 (w), 1608 (m), 1510 (s), 1445 (m), 1341 (w), 1301 (m), 1243 (s), 1176 (m), 1023 (m), 1002 (m), 833 (m), 820 (m), 701 (m) cm^{-1}. HRMS (ESI) calc. for $C_{16}H_{17}O$ $[M+H-H_2O]^+$ 225.1279, found 225.1284. $[\alpha]^{20}_D$: 10.34 (c = 0.86, $CHCl_3$, *l* =50 mm). The absolute stereochemistry was assigned by comparing the optical rotation with the reported value in the literature (for (*S*)-**2-OH**, $[\alpha]^{20}_D$: -26 (c = 1.0, CH_3OH)).[6]



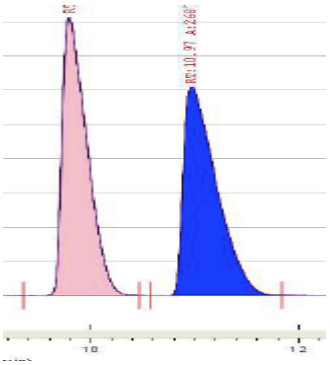
3

(*R*)-2-(1-(3-methoxyphenyl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3). The reaction was performed according to *Representative Procedure (Method C)*. The crude reaction mixture was purified by column chromatography on SiO_2 (98:2 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (21.8 mg, 62% yield). R_f = 0.4 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2H), 7.20-7.16 (m, 4H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.79 (t, *J* = 2.0 Hz, 1H), 6.70 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.80 (s, 3H), 2.57 (quintet, *J* = 7.7 Hz, 2H), 2.34 (t, *J* = 7.9 Hz, 1H), 2.19-2.11 (m, 1H), 2.02-1.95 (m, 1H), 1.22 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.58, 144.55, 142.51, 129.16, 128.47, 128.19, 125.59, 120.92, 113.98, 110.76, 83.32, 55.07, 35.37, 34.28, 24.66, 24.60. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.19. IR (neat) ν_{max} 3083 (w), 3061 (w), 3025 (m), 2976 (m), 2930 (w), 2858 (m), 1599 (m), 1581 (m), 1487 (m), 1454 (m), 1359 (m), 1322 (m), 1259 (m), 1141 (s), 1047 (m), 967 (w), 864 (w), 778 (w), 749 (w), 699 (m) cm^{-1}. HRMS (ESI) calc. for $C_{22}H_{30}BO_3$ $[M+H]^+$ 353.2288, found 353.2298. $[\alpha]^{20}_D$: -6.05 (c = 0.71, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by analogy.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 2% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

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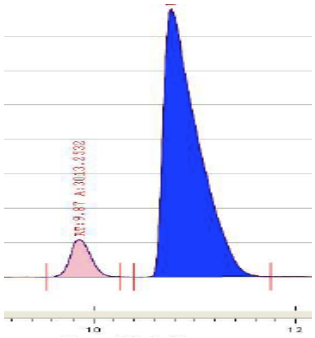
Total:	100	53409.5541		

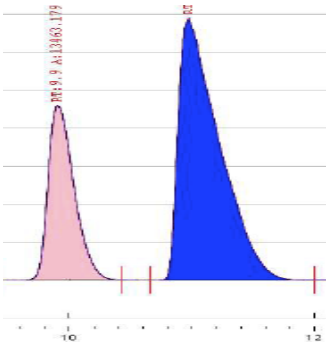
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	7.7208	3013.2532	9.87	216.0845
2	92.2792	36014.6454	10.77	1561.4805
Total:	100	39027.8986		

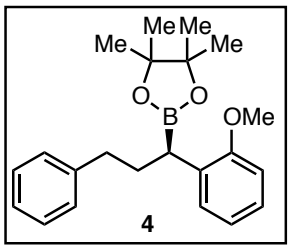
Reaction product



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	29.819	13463.179	9.9	918.8884
2	70.181	31686.5253	10.97	1380.2182
Total:	100	45149.7043		

Co-injection of product + racemic

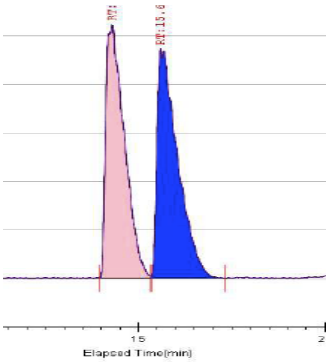


(*R*)-2-(1-(2-methoxyphenyl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4). The reaction was performed according to *Representative Procedure (Method C)*. The crude reaction mixture was purified by column chromatography on SiO_2 (98:2 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (19.3mg, 55% yield). R_f = 0.4 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.22 (m, 2H), 7.17-7.12 (m, 4H), 6.88 (td, *J* = 7.4, 1.1 Hz, 1H), 6.81 (dd, *J* = 8.1, 0.8 Hz, 1H), 3,78 (s, 3H), 2.57 (t, *J* = 8.2 Hz, 2H), 2.48 (dd, *J* = 8.4, 6.9 Hz, 1H), 2.17-2.09 (m, 1H), 2.00-1.92 (m, 1H), 1.23 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.06, 143.00, 131.89, 129.79, 128.50, 128.10, 126.34, 125.43, 120.51, 83.01, 55.02, 35.38, 32.52, 24.80, 24.67. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.75. IR (neat) ν_{max} 3061 (w), 3024 (w), 2977 (m), 2931 (s), 2859 (w), 2834 (w), 1491 (s), 1456 (m), 1437 (w), 1359 (s), 1317 (m), 1268 (w), 1240 (s), 1143 (s), 1111 (w), 1030 (w), 967 (w), 852 (w), 750 (m), 699 (w) cm^{-1}. HRMS (ESI) calc. for $C_{22}H_{30}BO_3$ $[M+H]^+$ 353.2288, found 353.2298. $[\alpha]^{20}_D$: -17.44 (c = 0.47, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by analogy.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 1% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

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1	49.8537	35972.3101	14.28	1043.7349
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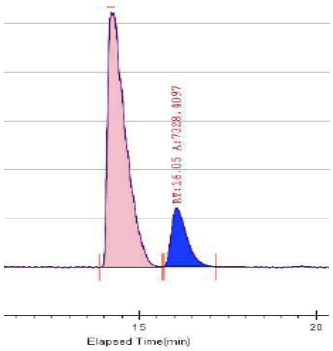
Total:	100	72155.7558		

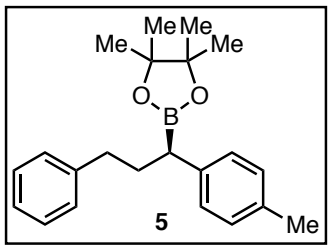
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	83.3269	36625.0376	14.21	1046.7348
2	16.6731	7328.4097	16.05	243.4293
Total:	100	43953.4473		

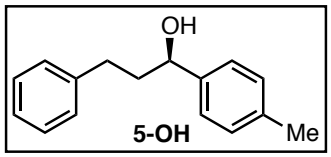
Reaction product



(*R*)-4,4,5,5-tetramethyl-2-(3-phenyl-1-(*p*-tolyl)propyl)-1,3,2-dioxaborolane (5). The reaction was performed according to *Representative Procedure (Method C)*. The crude reaction mixture was purified by column chromatography on SiO_2 (99:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (24.0 mg, 72% yield). R_f = 0.4 in 95:5 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.28-7.25 (m, 2H), 7.18-7.15 (m, 3H), 7.14-7.08 (m, 4H), 2.58 (t, *J* = 8.0 Hz, 2H), 2.33 (t, *J* = 7.8 Hz, 1H), 2.32 (s, 3H), 2.19-2.12 (m, 1H), 2.01-1.94 (m, 1H), 1.23 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.62, 139.73, 134.52, 129.03, 128.48, 128.27, 128.17, 125.56, 83.25, 35.39, 34.48, 24.68, 24.60, 20.99. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.39. IR (neat) ν_{max} 3024 (w), 2976 (m), 2925 (m), 2860 (w), 1603 (w), 1510 (m), 1495 (m), 1453 (m), 1358 (s), 1319 (s), 1267 (m), 1232 (m), 1214 (s), 1140 (s), 1109 (m), 966 (m), 849(m), 815 (s), 749 (s), 698 (s) cm^{-1}. HRMS (ESI) calc. for $C_{21}H_{36}BO_3$ $[M+H]^+$ 337.2339, found 337.2344. $[\alpha]^{20}_D$: -13.20 (c = 1.24, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the oxidized reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction followed by oxidation. The absolute stereochemistry was assigned by comparing the optical rotation of the corresponding alcohol with the reported value in the literature.[6]

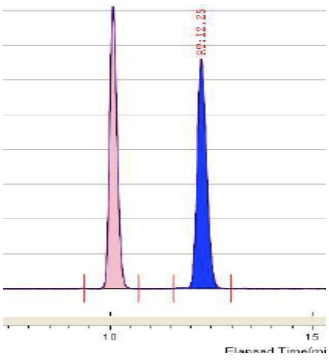


(*R*)-3-phenyl-1-(*p*-tolyl)propan-1-ol (5-OH). Prepared by oxidation of the boronate with $NaOH/H_2O_2$ in THF. The crude reaction mixture was purified by column chromatography on SiO_2 (85:15 hexanes/ethyl acetate, stain in CAM) to afford a colorless oil. R_f = 0.5 in 80:20 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.30-7.24 (m, 4H), 7.21-7.16 (m, 5H), 4.66 (t, *J* = 6.5 Hz 1H), 2.78-2.70 (m, 1H), 2.70-2.63 (m, 1H), 2.36 (s, 3H), 2.18-2.09 (m, 1H), 2.08-1.99 (m, 1H), 1.85 (br, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.83, 141.56, 137.31, 129.17, 128.42, 128.35, 125.88, 125.80, 73.72, 40.35, 32.09, 21.10. IR (neat) ν_{max} 3386 (br), 3060 (w), 3025 (w), 2922 (m), 2859 (w), 1603 (w), 1513 (m), 1495 (m), 1453 (s), 1060 (s), 1032 (s), 1301 (m), 924 (m), 818 (s), 749 (m), 699 (s) cm^{-1}. HRMS (ESI) calc. for $C_{15}H_{23}O_1$ $[M+H-H_2O]^+$ 225.1279, found 225.1285. $[\alpha]^{20}_D$: 19.43 (c = 0.68, $CHCl_3$, *l* =50 mm).

Proof of Stereochemistry:

The absolute stereochemistry was assigned by comparing the optical rotation with the reported value in the literature (for (*S*)-**5-OH**, $[\alpha]^{20}_D$: -16 (c = 2.2, CH_3OH)).[6]

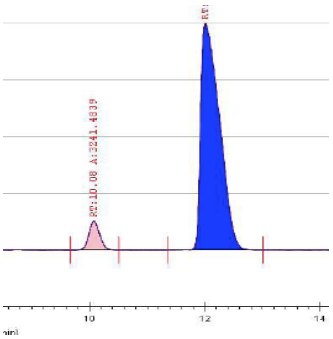
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 10% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	49.8362	10610.3082	10.07	810.2659
2	50.1638	10680.0578	12.25	659.1737
Total:	100	21290.366		

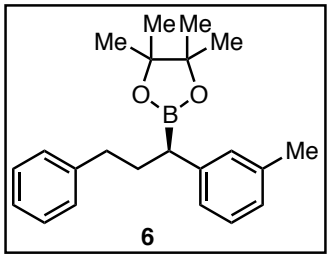
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	6.7024	3241.4839	10.08	252.9248
2	93.2976	45121.4182	12.01	1992.2415
Total:	100	48362.9021		

Reaction product



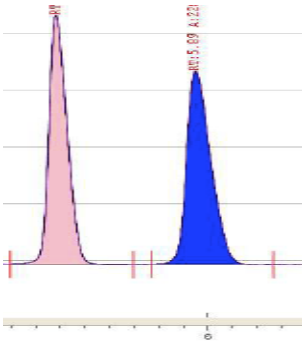
6

(*R*)-4,4,5,5-tetramethyl-2-(3-phenyl-1-(*m*-tolyl)propyl)-1,3,2-dioxaborolane (6). The reaction was performed according to *Representative Procedure (Method C).* The crude reaction mixture was purified by column chromatography on SiO_2 (99:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (28.1 mg, 84% yield). R_f = 0.4 in 95:5 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.28-7.25 (m, 2H), 7.18-7.15 (m, 4H), 7.04 (s, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 2.58 (t, *J* = 8.0 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 1H), 2.33 (s, 3H), 2.16 (dq, *J* = 13.4, 7.9 Hz, 1H), 1.98 (dq, *J* = 13.4, 8.0 Hz, 1H), 1.23 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.80, 142.61, 137.71, 129.26, 128.47, 128.18, 128.16, 126.00, 125.57, 125.35, 83.27, 35.47, 34.40, 24.66, 24.59, 21.47. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.31. IR (neat) ν_{max} 3061 (w), 3025 (w), 2977 (m), 2927 (m), 2859 (w), 1455 (w), 1360 (s), 1322 (s), 1268 (w), 1165 (w), 1142 (s), 989 (w), 871 (w), 850 (w), 786 (w), 748 (w), 699 (w) cm^{-1}. HRMS (ESI) calc. for $C_{22}H_{30}BO_2$ $[M+H]^+$ 337.2339, found 337.2343. $[\alpha]^{20}_D$: -12.53 (c = 1.21, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

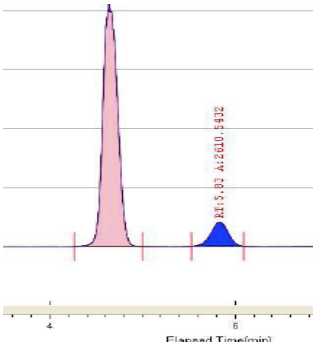
The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by analogy.

Chiral SFC (OJ-H, Chiraldex, 2 mL/min, 2% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



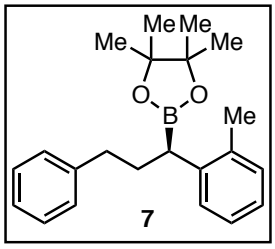
Peak Info				
Peak No	% Area	Area	RT (min)	Height (mV)
1	49.4553	2231.9923	4.76	218.8439
2	50.5447	2281.1584	5.89	169.9129
Total:	100	4513.1507		

Racemic



Peak Info				
Peak No	% Area	Area	RT (min)	Height (mV)
1	89.4825	22210.3197	4.64	2053.4226
2	10.5175	2610.5432	5.83	204.4704
Total:	100	24820.8629		

Reaction product



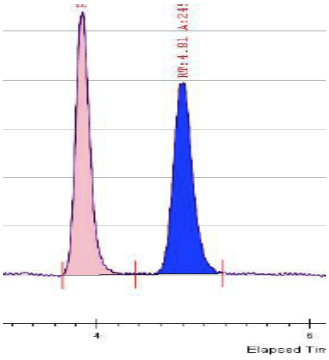
7

(*R*)-4,4,5,5-tetramethyl-2-(3-phenyl-1-(*o*-tolyl)propyl)-1,3,2-dioxaborolane (7). The reaction was performed according to *Representative Procedure (Method C).* The crude reaction mixture was purified by column chromatography on SiO_2 (99:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (22.3 mg, 67% yield). R_f = 0.4 in 95:5 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.27-7.24 (m, 4H), 7.14-7.11 (m, 5H), 7.06-7.03 (m, 1H), 2.63-2.57 (m, 1H), 2.55 (t, *J* = 7.9 Hz, 1H), 2.26 (s, 3H), 2.19 (td, *J* = 14.5, 8.8 Hz, 1H), 1.97 (ddt, *J* = 13.7, 9.7, 6.9 Hz, 1H), 1.22 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.58, 141.30, 136.04, 130.11, 128.46, 128.20, 127.62, 125.92, 125.60, 124.99, 83.22, 35.50, 33.83, 24.73, 24.58, 20.07. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.39. IR (neat) ν_{max} 3061 (w), 3025 (w), 2977 (m), 2929 (m), 2860 (w), 1506 (w), 1489 (w), 1455 (w), 1370 (s), 1357 (s), 1321 (s), 1322 (s), 1268 (s), 1234 (w), 1165 (w), 1142 (s), 966 (w), 850 (m), 748 (m), 730 (m), 699 (m) cm^{-1}. HRMS (ESI) calc. for $C_{22}H_{30}BO_2$ $[M+H]^+$ 337.2339, found 337.2332. $[\alpha]^{20}_D$: 3.68 (c = 1.07, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by analogy.

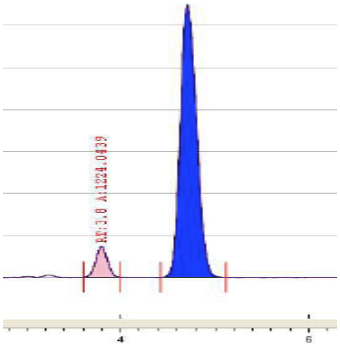
Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 2% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	50.4156	2492.1234	3.86	269.8622
2	49.5844	2451.0366	4.81	196.9501
Total:	100	4943.16		

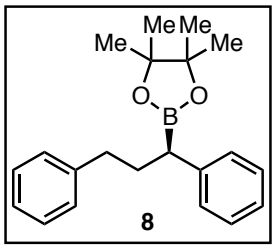
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	7.3327	1224.0439	3.8	145.8525
2	92.6673	15468.8226	4.71	1299.3587
Total:	100	16692.8665		

Reaction product



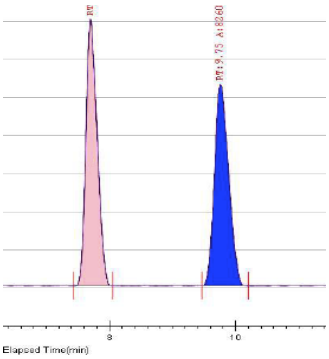
(*R*)-2-(1,3-diphenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8). The reaction was performed according to *Representative Procedure (Method C)*. The crude reaction mixture was purified by column chromatography on SiO_2 (99:1 hexanes/diethyl ether, stain in CAM) to afford a brown oil (28.5 mg, 88% yield). R_f = 0.4 in 95:5 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.23 (m, 6H), 7.18-7.14 (m, 4H), 2.59 (t, *J* = 8.0 Hz, 2H), 2.38 (t, *J* = 7.9 Hz, 1H), 2.22-2.14 (m, 1H), 2.00 (dq, *J* = 13.4, 8.0 Hz, 1H), 1.23 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.91, 142.54, 128.48, 128.40, 128.30,

128.21, 125.60, 125.22, 83.31, 35.40, 34.33, 24.68, 24.58. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.26. IR (neat) ν_{max} 3083 (w), 3061 (w), 3025 (m), 2977 (m), 2929 (m), 2858 (w), 1494 (m), 1453 (m), 1361 (s), 1322 (s), 1269 (w), 1233 (w), 1142 (s), 966 (m), 850 (w), 748 (m), 699 (s) cm^{-1}. HRMS (ESI) calc. for $C_{21}H_{28}BO_2$ $[M+H]^+$ 323.2182, found 323.2184. $[\alpha]^{20}_D$: -7.34 (c = 1.10, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by analogy.

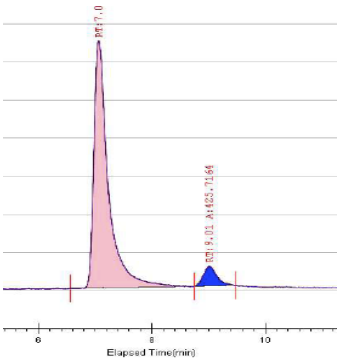
Chiral SFC (OJ-H, Chiraldex, 2 mL/min, 2% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	51.0629	8619.1212	7.7	701.1641
2	48.9371	8260.2857	9.75	529.6317
Total:	100	16879.4069		

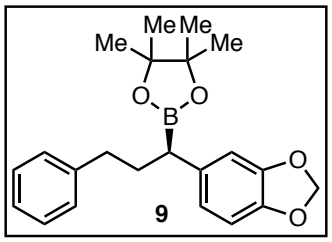
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	93.1428	5782.5575	7.07	325.3719
2	6.8572	425.7164	9.01	26.7913
Total:	100	6208.2739		

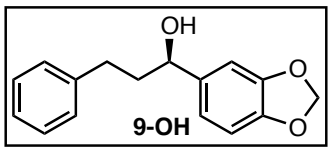
Reaction product



(*R*)-2-(1-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9). The reaction was performed according to *Representative Procedure (Method C).* The crude reaction mixture was purified by column chromatography on SiO_2 (98:2 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (32.0 mg, 88% yield). R_f = 0.4 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.24 (m, 2H), 7.17-7.14 (m, 3H), 6.75 (d, *J* = 1.7 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.66 (dd, *J* = 8.0, 1.7 Hz, 1H), 5.92 (q, *J* = 1.6 Hz, 2H), 2.56 (ddd, *J* = 9.6, 6.3, 3.4 Hz, 2H), 2.28 (t, *J* = 7.9 Hz, 1H), 2.10 (ddt, *J* = 13.7, 9.3, 6.8 Hz, 1H), 1.92 (dtd, *J* = 13.5, 8.8, 6.6 Hz, 1H), 1.22 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.52, 145.18, 142.72, 128.46, 128.20, 125.60, 121.21, 108.82, 108.13, 83.33, 35.24, 34.65, 24.68, 24.59. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.20. IR (neat) ν_{max} 3062 (w), 3025 (w), 2976 (m), 2927 (m), 1502 (m), 1486 (s), 1439 (m), 1370 (m), 1321 (s), 1241 (s), 1142 (s), 1039 (s), 967 (m), 938 (m), 859 (m), 809 (m), 749 (m), 699 (m) cm^{-1}. HRMS (ESI) calc. for $C_{22}H_{28}BO_4$ $[M+H]^+$ 367.2081, found 367.2076. $[\alpha]^{20}_D$: -16.79 (c = 1.41, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the corresponding alcohol after the oxidation. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction followed by oxidation. The absolute stereochemistry was assigned by analogy.



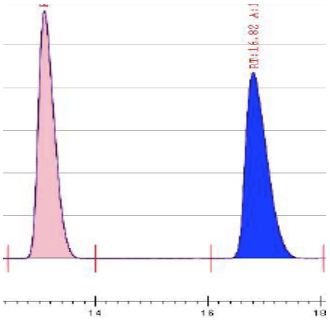
(*R*)-1-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylpropan-1-ol (9-OH). Prepared by oxidation of the boronate with $NaOH/H_2O_2$ in THF. The crude reaction mixture was purified by column chromatography on SiO_2 (85:15 hexanes/ethyl acetate, stain in CAM) to afford a colorless oil. R*f* = 0.5 in 80:20 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.29-7.25 (m, 2H), 7.19-7.18 (m, 3H), 6.87 (s, 1H), 6.81-6.76 (m, 2H), 5.95 (t, *J* = 1.4 Hz, 2H), 4.60 (t, *J* = 6.4 Hz, 1H), 2.72 (ddd, *J* = 14.2, 8.9, 5.7 Hz, 1H), 2.64 (dd, *J* = 14.6, 7.9 Hz, 1H), 2.15-2.07 (m, 1H), 2.02-1.95 (m, 1H), 1.85-1.77 (br, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 147.882, 146.98, 141.68, 138.61, 128.39, 128.36, 125.83, 119.36, 108.07, 106.37, 100.98, 73.73, 40.38, 32.05. IR (neat) ν_{max} 3395 (br),

3062 (w), 3026 (m), 2923 (m), 2857 (w), 2279 (w), 1051 (m), 1487 (s), 1442 (m), 1245 (s), 1187 (w), 1095 (w), 1039 (s), 934 (m), 865 (w), 812 (w), 699 (m) cm^{-1}. HRMS (ESI) calc. for $C_{16}H_{16}O_3$ $[M+H]^+$ 256.1099, found 256.1093. $[\alpha]^{20}_D$: 5.56 (c = 0.41, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The absolute stereochemistry was assigned by analogy.

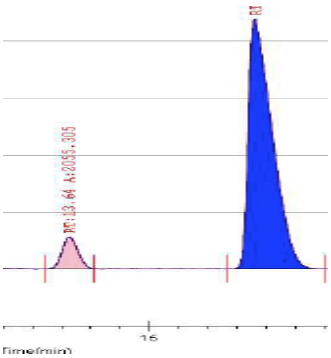
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 10% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	49.9949	11391.4243	13.09	580.2795
2	50.0051	11393.726	16.82	435.4981
Total:	100	22785.1503		

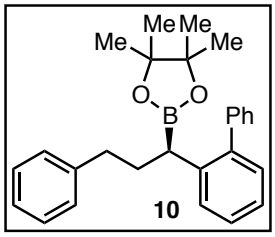
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	7.7484	2055.305	13.64	113.0891
2	92.2516	24470.169	16.81	874.8253
Total:	100	26525.474		

Reaction product

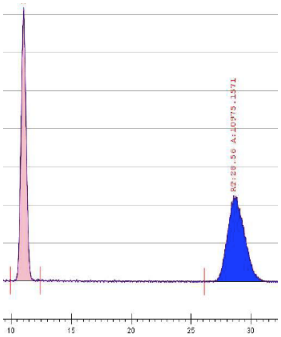


(*R*)-2-(1-([1,1'-biphenyl]-2-yl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10). The reaction was performed according to *Representative Procedure (Method C)* with 6 hours at room temperature. The crude reaction mixture was purified by column chromatography on SiO_2 (80:20 hexanes/dichloromethane, stain in CAM) to afford a brown oil (21.0 mg, 53% yield). R_f= 0.4 in 67:50 hexanes/dichloromethane on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.39 (m, 1H), 7.37 (dd, *J* = 13.0, 6.2 Hz, 2H), 7.33-7.29 (m, 4H), 7.23 (d, *J* = 2.3 Hz, 4H), 7.12-7.09 (m, 1H), 6.99 (d, *J* = 0.5 Hz, 2H), 2.61 (t, *J* = 7.8 Hz, 1H), 2.41-2.31 (m, 2H), 2.09-2.02 (m, 1H), 1.93-1.86 (m, 1H), 1.23 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.66, 142.34, 142.12, 140.82, 129.96, 129.69, 128.28, 128.12, 128.08, 127.87, 127.34, 126.53, 125.42, 124.79, 83.19, 35.36, 35.33, 24.71, 24.64. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.40. IR (neat) ν_{max} 3059 (w), 3023 (w), 2977 (s), 2928 (m), 2858 (w), 1496 (m), 1478 (m), 1358 (s), 1320 (s), 1265 (m), 1232 (w), 1142 (s), 966 (w), 748 (s), 700 (s) cm^{-1}. HRMS (ESI) calc. for $C_{27}H_{32}BO_2$ $[M+H]^+$ 399.2495, found 399.2498. $[\alpha]^{20}_D$: -7.86 (c = 0.85, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by analogy.

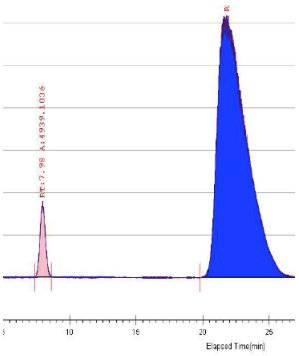
Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 1% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

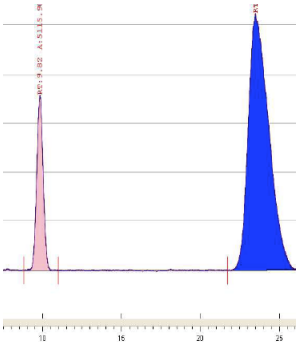
Peak No	% Area	Area	RT (min)	Height (mV)
1	49.1948	10627.277	11.02	359.7668
2	50.8052	10975.1571	28.56	113.1941
Total:	100	21602.4341		

Racemic



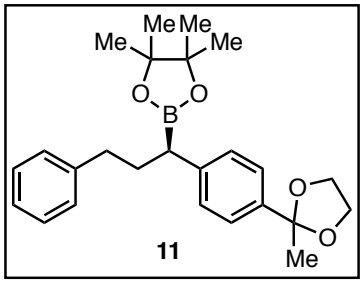
Peak Info				
Peak No	% Area	Area	RT (min)	Height (mV)
1	5.0777	4939.1036	7.98	177.8989
2	94.9223	92331.5416	21.79	616.5848
Total:	100	97270.6452		

Reaction product



Peak Info				
Peak No	% Area	Area	RT (min)	Height (mV)
1	17.7803	5115.9047	9.82	179.5886
2	82.2197	23656.9981	23.49	261.7358
Total:	100	28772.9028		

Co-injection of racemic + reaction product

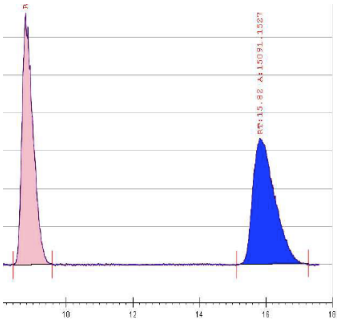


(*R*)-4,4,5,5-tetramethyl-2-(1-(4-(2-methyl-1,3-dioxolan-2-yl)phenyl)-3-phenylpropyl)-1,3,2-dioxaborolane (11). The reaction was performed according to *Representative Procedure (Method C)*. The crude reaction mixture was purified by column chromatography on SiO_2 (98:2 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (29.0 mg, 72% yield). R_f = 0.4 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.36 (d, *J* = 8.2 Hz, 2H), 7.27-7.24 (m, 2H), 7.19-7.14 (m, 5H), 4.04-4.01 (m, 1H), 3.84-3.76 (m, 1H), 2.57 (t, *J* = 8.0 Hz, 1H), 2.36 (t, *J* = 7.9 Hz, 1H), 2.15 (dq, *J* = 14.0, 7.3 Hz, 1H), 1.96 (dq, *J* = 14.0, 7.3 Hz, 1H), 1.65 (s, 3H), 1.22 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.65, 140.16, 128.59, 128.35, 128.28, 125.75, 125.37, 109.09, 83.49, 64.56, 35.57, 34.61, 29.84, 27.61, 24.83, 24.75. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.40. IR (neat) ν_{max} 3025 (w), 2977 (m), 2930 (m), 2887 (w), 1603(w), 1506 (w), 1454 (w), 1370 (s), 1321 (s), 1262 (m), 1197 (m), 1140 (s), 1095 (m), 1037 (s), 966 (w), 849 (s), 751 (m), 698 (m), 672 (s), 579 (w) cm^{-1}. HRMS (ESI) calc. for $C_{25}H_{34}BO_4$ $[M+H]^+$ 409.2550, found 409.2561. $[\alpha]^{20}_D$: 16.54 (c = 0.82, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by analogy.

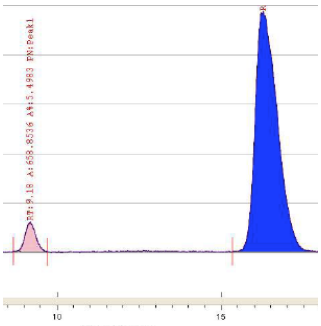
Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 2% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	50.213	15220.3067	8.77	665.39
2	49.787	15091.1527	15.82	331.7755
Total:	100	30311.4594		

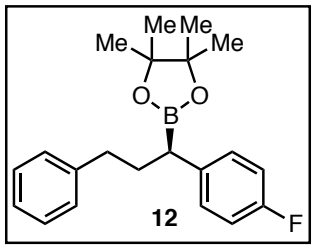
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	5.4983	658.8536	9.18	30.3287
2	94.5017	11324.0868	16.27	242.6981
Total:	100	11982.9404		

Reaction product

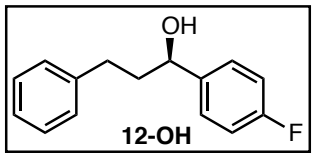


(*R*)-2-(1-(4-fluorophenyl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12). The reaction was performed according to *Representative Procedure (Method C)*. The crude reaction mixture was purified by column chromatography on SiO_2 (99:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (27.9 mg, 82% yield). R_f = 0.4 in 95:5 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.28-7.24 (m, 2H), 7.19-7.13 (m, 5H), 6.98-6.94 (m, 2H), 2.56 (t, *J* = 7.9 Hz, 2H), 2.34 (t, *J* = 7.9 Hz, 1H), 2.18-2.11 (m, 1H), 1.98-1.91 (m, 1H), 1.22 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (125 MHz,

$CDCl_3$) δ 161.92, 160.00, 142.34, 138.50 (d, J_{F-C} = 2.91 Hz), 129.60 (d, J_{F-C} = 7.66 Hz), 128.30 (d, J_{F-C} = 25.96 Hz), 125.67, 115.00 (d, J_{F-C} = 20.97 Hz), 83.39, 35.27, 34.44, 24.66, 24.56. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.46. IR (neat) ν_{max} 3026 (w), 2977 (m), 2929 (m), 2859 (w), 1602 (m), 1506 (s), 1454 (w), 1359 (s), 1321 (s), 1268 (m), 1218 (s), 1139 (s), 1107 (w), 966 (m), 849 (m), 831 (m), 748 (m), 698 (s), 512 (m) cm^{-1}. HRMS (ESI) calc. for $C_{21}H_{27}BFO_2$ $[M+H]^+$ 341.2088, found 341.2102. $[\alpha]^{20}_D$: -11.15 (c = 0.95, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the corresponding alcohol after the oxidation. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction followed by oxidation. The absolute stereochemistry was assigned by analogy.

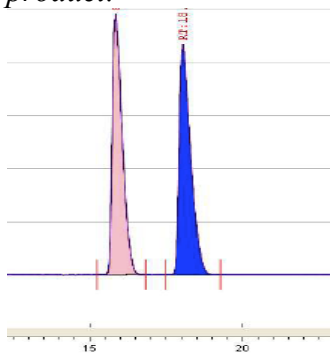


(*R*)-1-(4-fluorophenyl)-3-phenylpropan-1-ol (12-OH). Prepared by oxidation of the boronate with $NaOH/H_2O_2$ in THF. The crude reaction mixture was purified by column chromatography on SiO_2 (85:15 hexanes/ethyl acetate, stain in CAM) to afford a colorless oil. R_f = 0.5 in 80:20 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.34-7.26 (m, 4H), 7.21-7.18 (m, 3H), 7.06-7.02 (m, 2H), 4.68 (dt, *J* = 8.8, 3.9 Hz, 1H), 2.74 (ddd, *J* = 14.3, 9.3, 5.4 Hz, 1H), 2.66 (ddd, *J* = 14.4, 8.9, 6.0 Hz, 1H), 2.16-2.09 (m, 1H), 2.04-1.97 (m, 1H), 1.85 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.17, 161.22, 141.54, 140.27 (d, J_{F-C} = 3.6 Hz), 128.40 (d, J_{F-C} = 2.9 Hz), 127.53 (d, J_{F-C} = 8.0 Hz), 125.92, 115.31 (d, J_{F-C} = 21.4 Hz), 73.20, 40.55, 31.99. IR (neat) ν_{max} 3368 (br), 3084 (w), 3062 (w), 3027 (w), 2926 (w), 2860 (w), 2858 (w), 1603 (m), 1508 (s), 1454 (w), 1222 (s), 1156 (w), 1097 (m), 1061 (w), 1031 (w), 924 (w), 836 (w), 776 (m), 750 (w), 699 (m) cm^{-1}. HRMS (ESI) calc. for $C_{15}H_{14}F$ $[M+H-H_2O]^+$ 213.1080, found 213.1079. $[\alpha]^{20}_D$: 18.10 (c = 0.74, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The absolute stereochemistry was assigned by analogy.

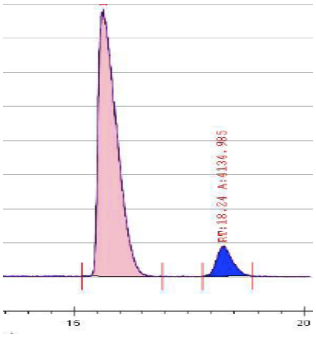
Chiral SFC (AD-H, Chiraldex, 3 mL/min, 6% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	49.9738	22648.4735	15.86	981.7129
2	50.0262	22672.2028	18.06	869.1424
Total:	100	45320.6763		

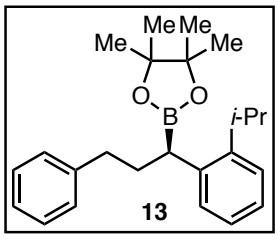
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	91.2675	43216.8039	15.65	1564.7897
2	8.7325	4134.985	18.24	176.2733
Total:	100	47351.7889		

Reaction product

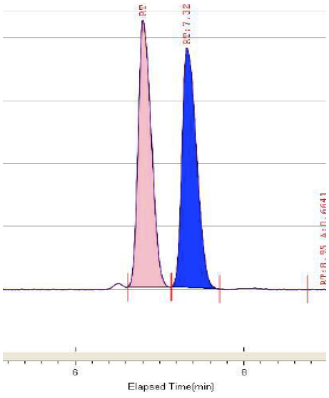


(*R*)-2-(1-(2-isopropylphenyl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13). The reaction was performed according to *Representative Procedure (Method D)*. The crude reaction mixture was purified by column chromatography on SiO_2 (99:1 hexanes/diethyl ether, stain in CAM) to afford a brown oil (39.2 mg, 53% yield). R_f = 0.4 in 95:5 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.24 (m, 4H), 7.18-7.11 (m, 5H), 3.13 (dt, *J* = 13.6, 6.8 Hz, 1H), 2.68-2.55 (m, 3H), 2.23 (ddd, *J* = 13.5, 9.7, 7.8 Hz, 1H), 1.95 (ddd, *J* = 13.5, 10.0, 7.4 Hz, 1H), 1.23 (s, 6H), 1.21 (s, 3H), 1.20 (s, 3H), 1.19 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.49, 142.60, 139.90, 128.46, 128.31, 128.18, 125.59, 125.49, 125.37, 125.13, 83.21, 35.59, 34.64, 28.70, 24.69, 24.65, 24.25, 23.70. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.42. IR (neat) ν_{max} 3061 (w), 3025 (w), 2974 (s), 2928 (m), 2865 (w), 1487 (m), 1453 (m), 1369 (s), 1320 (s), 1265 (m), 1267 (w), 1214 (w), 1106 (s), 966 (m), 850 (m), 748 (s), 700 (s) cm^{-1}. HRMS (ESI) calc. for $C_{24}H_{34}BO_2$ $[M+H]^+$ 365.2652, found 365.2642. $[\alpha]^{20}_D$: -5.58 (c = 1.84, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by analogy.

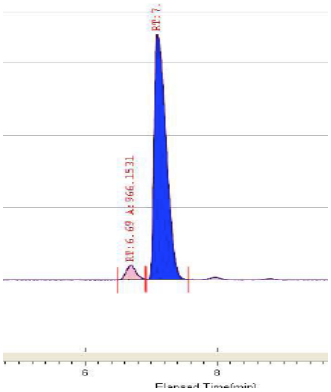
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 1% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	50.2084	9201.572	6.8	848.8586
2	49.788	9124.5245	7.32	761.5334
3	0.0036	0.6641	8.95	0.5059
Total:	100	18326.7606		

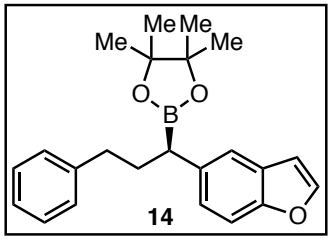
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	4.4742	966.1531	6.69	98.3626
2	95.5258	20627.498	7.09	1687.2565
Total:	100	21593.6511		

Reaction product



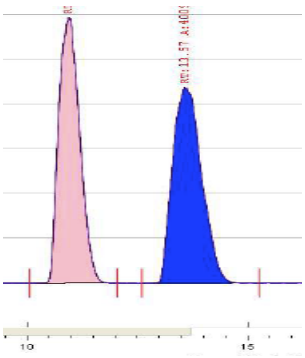
(*R*)-2-(1-(benzofuran-5-yl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14). The reaction was performed according to *Representative Procedure (Method D).* The crude reaction mixture was purified by column chromatography on SiO_2 (98:2 hexanes/diethyl ether, stain in CAM) to afford a brown oil (29.6 mg, 82% yield). R_f= 0.4 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.58 (d, *J* = 2.2 Hz, 1H), 7.44 (d, *J* = 1.7 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.28-7.24 (m, 2H), 7.18-7.15

(m, 4H), 6.71 (dd, J = 2.2, 0.9 Hz, 1H), 2.58 (t, J = 8.0 Hz, 1H), 2.45 (t, J = 7.9 Hz,), 2.20 (dq, J = 13.4, 7.9 Hz, 1H), 2.02 (dq, J = 13.4, 8.0 Hz, 1H), 1.22 (s, 6H), 1.95 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.36, 144.77, 142.58, 137.27, 128.47, 128.19, 127.54, 125.58, 124.93, 120.42, 110.99, 106.49, 83.31, 35.37, 34.86, 24.67, 24.58. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.40. IR (neat) ν_{max} 3061 (w), 3025 (w), 2977 (m), 2929 (m), 2859 (w), 1495 (m), 1465 (w), 1362 (s), 1321 (s), 1261 (w), 1142 (s), 1109 (w), 1031 (w), 967 (w), 874 (w), 849 (w), 812 (w), 748 (w), 767 (w), 739 (w) , 699 (w) cm^{-1}. HRMS (ESI) calc. for $C_{23}H_{28}BO_3$ $[M+H]^+$ 363.2132, found 363.2117. $[\alpha]^{20}_D$: -12.89 (c = 0.85, $CHCl_3$, l =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by analogy.

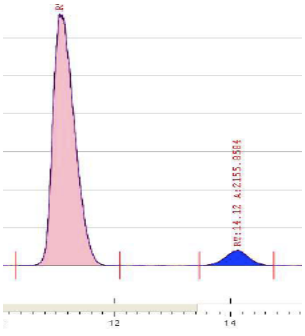
Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 2% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	49.5747	39423.261	10.94	1188.6344
2	50.4253	40099.6188	13.57	876.0553
Total:	100	79522.8798		

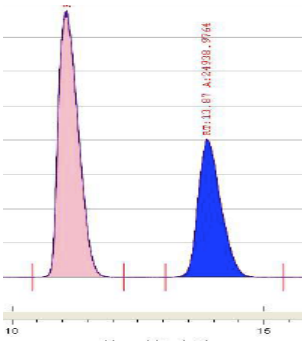
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	94.0405	34019.4669	11.06	1323.3229
2	5.9595	2155.8584	14.12	78.9807
Total:	100	36175.3253		

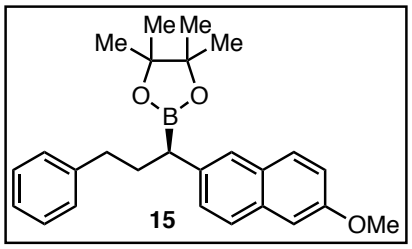
Reaction product



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	63.0043	42471.5296	11.09	1553.8149
2	36.9957	24938.9764	13.87	808.3331
Total:	100	67410.506		

Co-injection of racemic + reaction product

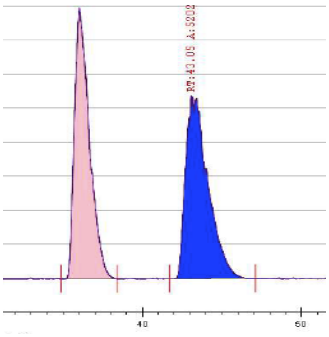


(*R*)-2-(1-(6-methoxynaphthalen-2-yl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15). The reaction was performed according to *Representative Procedure (Method D)*. The crude reaction mixture was purified by column chromatography on SiO_2 (98:2 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (37.9mg, 92% yield). R_f= 0.4 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.67 (dd, *J* = 8.1, 4.7 Hz, 2H), 7.59 (s, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.28-7.25 (m, 2H), 7.18-7.15 (m, 3H), 7.13-7.11 (m, 2H), 3.91 (s, 3H), 2.60 (t, *J* = 7.8 Hz, 2H), 2.50 (t, *J* = 7.8 Hz, 1H), 2.29-2.21 (m, 1H), 2.12-2.04 (m, 1H), 1.22 (s, 6H), 1.19 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.97, 142.56, 138.08, 132.72, 129.31, 128.94, 128.49, 128.21, 127.87, 126.67, 126.24, 125.60, 118.40, 105.61, 83.35, 55.28, 35.42, 34.20, 24.68, 24.59. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.48. IR (neat) ν_{max} 3058 (w), 3024 (w), 2976 (m), 2933 (m), 2858 (w), 1633 (m), 1604 (s), 1503 (w), 1481 (w), 1454 (w), 1358 (s), 1322 (s), 1265 (s), 1224 (s), 1141 (s), 1032 (m), 967 (m), 852 (m), 698 (m) cm^{-1}. HRMS (ESI) calc. for $C_{26}H_{32}BO_3$ $[M+H]^+$ 403.2445, found 403.2441. $[\alpha]^{20}_D$: -13.86 (c = 1.00, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by analogy.

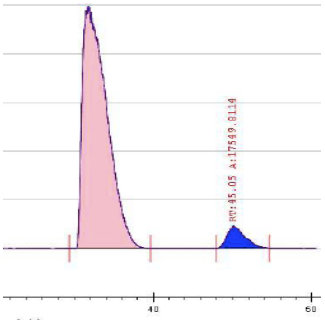
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 2% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	49.9048	51823.8941	36.05	797.401
2	50.0952	52021.5645	43.05	537.1204
Total:	100	103845.4586		

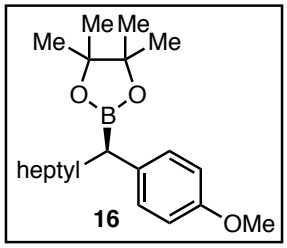
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	93.855	268046.6405	35.92	2489.4426
2	6.145	17549.8114	45.05	228.7655
Total:	100	285596.4519		

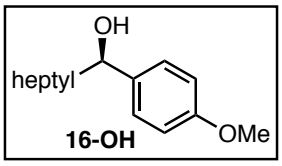
Reaction product



(*R*)-2-(1-(4-methoxyphenyl)octyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16). The reaction was performed according to *Representative Procedure (Method C).* The crude reaction mixture was flashed slowly by column chromatography on SiO_2 (2:1 hexanes/dichloromethane, stain in CAM) to afford a brown oil (26.8 mg, 78% yield). R_f = 0.4 in 2:1 hexanes/dichloromethane on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.13-7.10 (m, 2H), 6.81-6.78 (m, 2H), 3.77 (s, 3H), 2.23 (t, *J* = 7.9 Hz, 1H), 1.83-1.77 (m, 1H), 1.62-1.56 (m, 1H), 1.29-1.24 (m, 10H), 1.20 (s, 6H), 1.19 (s, 6H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.20, 135.49, 129.14, 113.64, 83.11, 55.13, 32.85, 31.83, 29.56, 29.19, 24.62, 24.57, 22.63, 14.07. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.53. IR (neat) ν_{max} 2976 (w), 2954 (w), 2023 (m), 2853 (m), 1508 (s), 1463 (m), 1359 (s), 1319 (s), 1243 (s), 1141 (s), 1038 (m), 966 (m), 850 (m), 827 (m), 530 (w) cm^{-1}. HRMS (ESI) calc. for $C_{21}H_{36}BO_3$ $[M+H]^+$ 347.2758, found 347.2756. $[\alpha]^{20}_D$: -13.71 (c = 1.15, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the corresponding alcohol after the oxidation. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction followed by oxidation. The absolute stereochemistry was assigned by analogy.

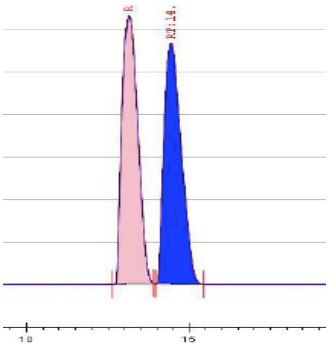


(*R*)-1-(4-methoxyphenyl)octan-1-ol (16-OH). Prepared by oxidation of the boronate with $NaOH/H_2O_2$ in THF. The crude reaction mixture was purified by column chromatography on SiO_2 (90:10 hexanes/ethyl acetate, stain in CAM) to afford a colorless solid. ^1H NMR (500 MHz, $CDCl_3$) 7.28-7.25 (m, 2H), 6.90-6.87 (m, 2H), 4.61 (t, J = 6.7 Hz, 1H), 3.81 (s, 3H), 1.83-1.76 (m, 1H), 1.71 (s, 1H), 1.71-1.64 (m, 1H), 1.43-1.36 (m, 1H), 1.31-1.21 (m, 9H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.97, 137.09, 127.11, 113.77, 74.28, 55.25, 38.98, 31.74, 29.47, 25.88, 22.61, 14.05. IR (neat) ν_{max} 3363 (br), 2953 (m), 2925 (s), 2854 (m), 1611 (m), 1585 (w), 1512 (s), 1464 (m), 1441 (w), 1301 (w), 1246 (s), 1174 (m), 1037 (w), 830 (m), 809 (w) cm^{-1}. HRMS (ESI) calc. for $C_{15}H_{23}O_1$ $[M+H-H_2O]^+$ 219.1749, found 219.1755. $[\alpha]^{20}_D$: 18.13 (c = 0.81, $CHCl_3$, l =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the corresponding alcohol after the oxidation. The absolute stereochemistry was assigned by analogy.

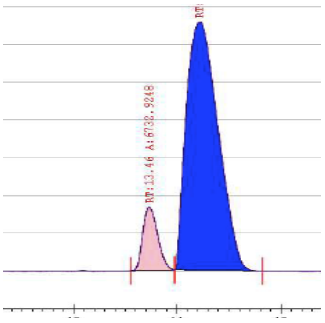
Chiral SFC (OJ-H, Chiraldex, 2 mL/min, 3% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	50.2548	42036.9534	13.15	1260.283
2	49.7452	41610.6857	14.44	1130.7105
Total:	100	83647.6391		

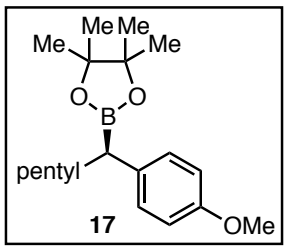
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	10.762	6732.9248	13.46	336.3644
2	89.238	55829.1037	14.43	1313.5301
Total:	100	62562.0285		

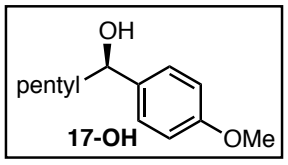
Reaction product



(*R*)-2-(1-(4-methoxyphenyl)hexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17). The reaction was performed according to *Representative Procedure (Method C)*. The crude reaction mixture was flashed slowly by column chromatography on SiO_2 (1:1 hexanes/dichloromethane, stain in CAM) to afford a brown oil (19.9 mg, 81% yield). R_f = 0.4 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.13-7.10 (m, 2H), 6.81-6.79 (m, 2H), 3.77 (s, 3H), 2.23 (t, *J* = 7.9 Hz, 1H), 1.81-1.76 (m, 1H), 1.62-1.55 (m, 1H), 1.29-1.23 (m, *J* = 7.1 Hz, 6H), 1.21 (s, 6H), 1.19 (s, 6H), 0.85 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.20, 135.48, 129.14, 113.64, 83.11, 55.13, 32.80, 31.81, 28.88, 24.62, 24.56, 22.53, 14.02. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.54. IR (neat) ν_{max} 3032 (w), 2976 (w), 2955 (w), 2926 (m), 2855 (w), 1609 (w), 1509 (s), 1464 (m), 1360 (s), 1320 (s), 1244 (s), 1142 (s), 1038 (m), 1140 (s), 967 (w), 851 (m), 808 (m) cm^{-1}. HRMS (ESI) calc. for $C_{19}H_{32}BO_3$ $[M+H]^+$ 319.2445, found 319.2437. $[\alpha]^{20}_D$: -15.18 (c = 0.93, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the corresponding alcohol after the oxidation. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction followed by oxidation. The absolute stereochemistry was assigned by analogy.



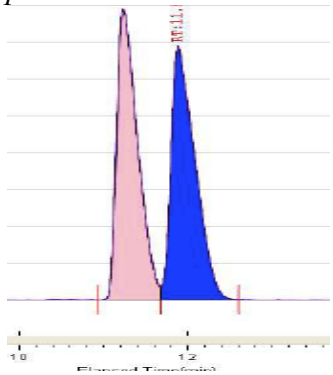
(*R*)-1-(4-methoxyphenyl)hexyl-1-ol (17-OH). Prepared by oxidation of the boronate with $NaOH/H_2O_2$ in THF. The crude reaction mixture was purified by column chromatography on SiO_2 (90:10 hexanes/ethyl

acetate, stain in CAM) to afford a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) 7.28-7.25 (m, 2H), 6.89-6.87 (m, 2H), 4.61 (t, *J* = 6.7 Hz, 1H), 3.80 (s, 3H), 1.82-1.77 (m, 1H), 1.71-1.64 (m, 1H), 1.43-1.34 (m, 1H), 1.34-1.21 (m, 5H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.12, 137.24, 127.26, 113.92, 74.43, 55.40, 39.10, 31.87, 25.71, 22.71, 14.15. IR (neat) ν_{max} 3363 (br), 2953 (m), 2925 (s), 2854 (m), 1611 (m), 1585 (w), 1512 (s), 1464 (m), 1441 (w), 1301 (w), 1246 (s), 1174 (m), 1037 (w), 830 (m), 809 (w) cm^{-1}. HRMS (ESI) calc. for $C_{13}H_{19}O_1$ $[M+H-H_2O]^+$ 191.1436, found 191.1438. $[\alpha]^{20}_D$: 18.88 (c = 0.38, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The absolute stereochemistry was assigned by analogy.

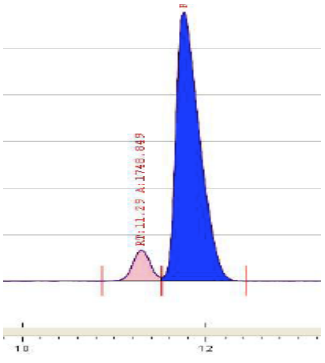
Chiral SFC (OJ-H, Chiraldex, 2 mL/min, 3% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	50.3181	27262.8807	11.22	1580.6507
2	49.6819	26918.1982	11.88	1379.6888
Total:	100	54181.0789		

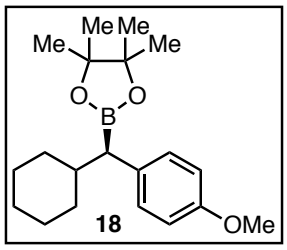
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	7.9606	1748.849	11.29	132.5783
2	92.0394	20220.0576	11.75	1151.8992
Total:	100	21968.9066		

Reaction product

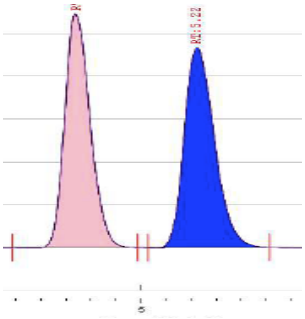


(*R*)-2-(cyclohexyl(4-methoxyphenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18). The reaction was performed according to *Representative Procedure (Method C)* with 48 hours at room temperature. The crude reaction mixture was purified by column chromatography on SiO_2 (60:40 hexanes/dichloromethane, stain in CAM) to afford a colorless oil (14.0 mg, 43% yield). R_f = 0.5in 50:50 hexanes/dichloromethane on TLC.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12-7.09 (m, 2H), 6.80-6.77 (m, 2H), 3.77 (s, 3H), 1.98 (d, *J* = 10.3 Hz, 1H), 1.82-1.79 (m, 1H), 1.76-1.68 (m, 2H), 1.62-1.56 (m, 2H), 1.48-1.45 (m, 1H), 1.35-1.24 (m, 1H), 1.19 (s, 6H), 1.17 (s, 6H), 1.11 (td, *J* = 10.0, 2.0 Hz, 2H), 1.07-0.97 (m, 1H), 0.70 (qd, *J* = 12.0, 3.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.26, 133.65, 129.98, 113.44, 83.05, 55.10, 40.39, 33.72, 32.38, 26.61, 26.54, 24.66, 24.53. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.20. IR (neat) ν_{max} 2976 (w), 2922 (s), 2850 (w), 1508 (s), 1447 (w), 1354 (m), 1319 (m), 1301 (w), 1224 (s), 1142 (s), 1038 (m), 973 (w), 884 (w), 851 (m), 764 (w) cm^{-1}. HRMS (ESI) calc. for $C_{20}H_{32}BO_3$ $[M+H]^+$ 331.2445, found 331.2440. $[\alpha]^{20}_D$: -13.22 (c = 0.50, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by analogy.

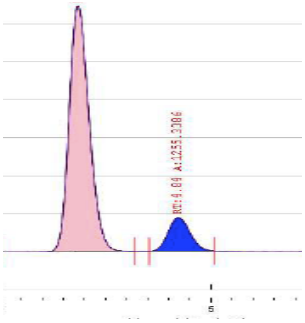
Chiral SFC (OD-H, Chiraldex, 5 mL/min, 3% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	49.7768	7700.4119	4.74	1093.7988
2	50.2232	7769.4558	5.22	935.1259
Total:	100	15469.8677		

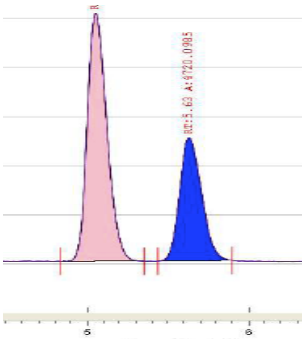
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	87.0548	8441.9985	4.37	1293.3652
2	12.9452	1255.3386	4.84	175.7446
Total:	100	9697.3371		

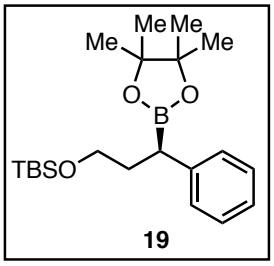
Reaction product



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	64.2219	8472.6176	5.05	1012.3464
2	35.7781	4720.0985	5.63	503.1541
Total:	100	13192.7161		

coinjection of racemic + reaction proudct

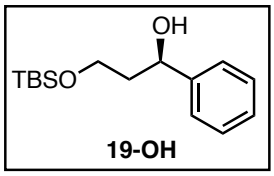


19

***(R)-tert*-Butyldimethyl(3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)silane (19).** The reaction was performed according to *Representative Procedure (Method C).* The crude reaction mixture was flashed slowly by column chromatography on SiO_2 (1:1 hexanes/dichloromethane, stain in CAM) to afford a brown oil (24.5 mg, 81% yield). R_f = 0.4 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.26-7.19 (m, 4H), 7.14-7.11 (m, 1H), 3.58-3.50 (m, 2H), 2.47 (t, *J* = 7.9 Hz, 1H), 2.07 (dq, *J* = 13.6, 6.9 Hz, 1H), 1.87 (td, *J* = 13.8, 7.5 Hz, 1H), 1.20 (s, 6H), 1.18 (s, 6H), 0.88 (s, 9H), 0.01 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.91, 128.59, 128.37, 125.28, 83.40, 62.33, 35.42, 26.14, 24.78, 24.70. 18.48, -5.12, -5.18. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.06. IR (neat) ν_{max} 2977 (w), 2953 (w), 2929 (m), 2886 (w), 2856 (m), 1471 (m), 1360 (s), 1322 (s), 1253 (s), 1142 (s), 1097 (s), 967 (w), 938 (w), 834 (s), 774 (s), 700 (s), 666 (w) cm^{-1}. $[\alpha]^{20}_D$: -6.37 (c = 0.93, $CHCl_3$, *l* =50 mm).

Analysis Stereochemistry:

The enantioselectivity was determined by SFC analysis of the corresponding alcohol after the oxidation. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by analogy.

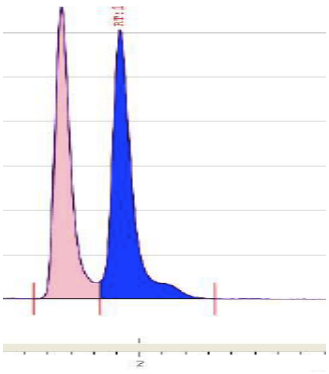


(*R*)-3-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpropan-1-ol (19-OH). Prepared by oxidation of the boronate with $NaOH/H_2O_2$ in THF. The crude reaction mixture was purified by column chromatography on SiO_2 (80:20 hexanes/ethyl acetate, stain in CAM) to afford a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) 7.43-7.31 (m, 4H), 7.30-7.22 (m, 1H), 4.96 (dt, *J* = 7.6, 3.6 Hz, 1H), 3.88-3.84 (m, 2H), 3.76 (d, *J* = 2.9 Hz, 1H), 1.98-1.93 (m, 2H), 0.93 (s, 9H), 0.10 (d, *J* = 2.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.67, 128.42, 127.29, 125.81, 74.23, 62.38, 40.73, 26.02, 18.30, -5.35, -5.39.

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The absolute stereochemistry was assigned by analogy.

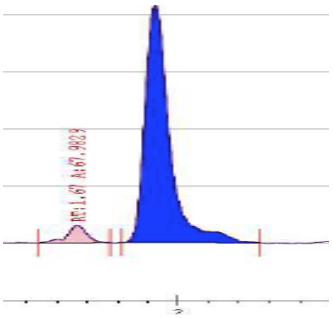
Chiral SFC (OJ-H, Chiraldex, 6 mL/min, 1% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	47.1201	3178.3797	1.66	657.16
2	52.8799	3566.8897	1.91	605.4309
Total:	100	6745.2694		

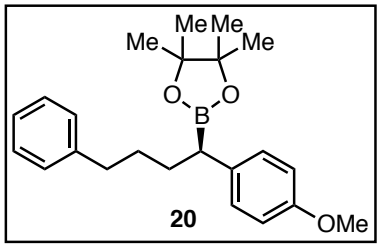
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	5.6486	67.9829	1.67	15.3696
2	94.3514	1135.5429	1.92	207.3589
Total:	100	1203.5258		

Reaction product

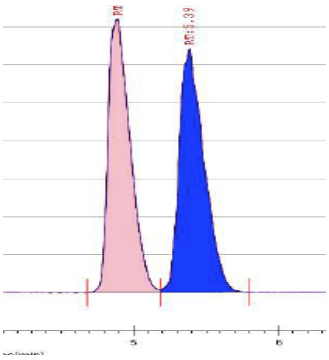


(*R*)-2-(1-(4-methoxyphenyl)-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20). The reaction was performed according to *Method C*. The crude reaction mixture was purified by column chromatography on SiO_2 (97:3 hexanes/ethyl acetate, stain in CAM) to afford a yellow oil (27.1 mg, 74% yield). R_f = 0.3 in 90:10 hexanes/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.27-7.24 (m, 2H), 7.17-7.11 (m, 5H), 6.82-6.79 (m, 2H), 3.78 (s, 1H), 2.61 (qt, *J* = 13.3, 7.5 Hz, 1H), 2.28 (t, *J* = 7.8 Hz,), 1.87 (dq, *J* = 13.0, 7.7 Hz,), 1.68 (td, *J* = 14.1, 7.7 Hz,), 1.63-1.58 (m, 1H), 1.21 (s, 6H), 1.19 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.43, 142.85, 135.28, 129.33, 128.48, 128.30, 125.64, 113.85, 83.34, 55.29, 36.08, 32.69, 31.14, 24.79, 24.73. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.45. IR (neat) ν_{max} 3061 (w), 3025 (w), 2977 (m), 2929 (m), 2856 (w), 1607 (w), 1509 (s), 1455 (w), 1369 (s), 1322 (s), 1245 (s), 1178 (s), 1143 (s), 1037 (w), 967 (w), 851 (w), 829 (w), 747 (w), 699 (m) cm^{-1}. HRMS (ESI) calc. for $C_{23}H_{32}BO_3$ $[M+H]^+$ 367.2445, found 367.2427. $[\alpha]^{20}_D$: -21.07 (c = 0.88, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

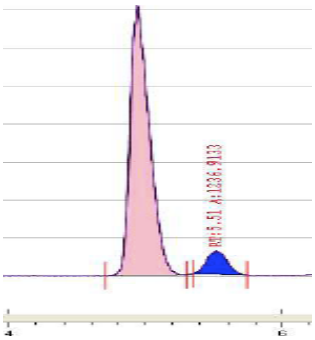
The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by analogy.

Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 4% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



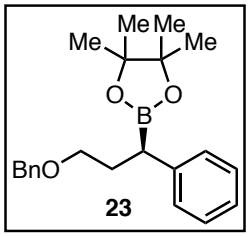
Peak Info				
Peak No	% Area	Area	RT (min)	Height (mV)
1	49.7511	15020.9032	4.89	1439.585
2	50.2489	15171.2223	5.39	1284.2012
Total:	100	30192.1255		

Racemic



Peak Info				
Peak No	% Area	Area	RT (min)	Height (mV)
1	91.779	13808.8353	4.94	1418.42
2	8.221	1236.9133	5.51	124.3644
Total:	100	15045.7486		

Reaction product



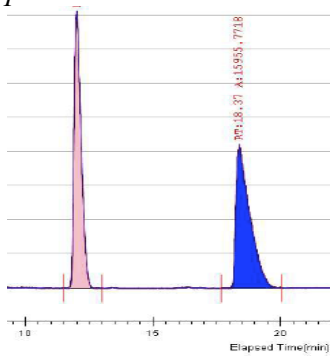
(*R*)-2-(3-(benzyloxy)-1-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23). The reaction was performed according to *Representative Procedure (Method C)*. The crude reaction mixture was purified by column chromatography on SiO_2 (50:50 to 25:75 hexanes/dichloromethane, stain in CAM) to afford a yellow oil (26.0 mg, 74% yield). R_f = 0.4 in 25:75 hexanes/dichloromethane on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.36-7.33 (m, 4H), 7.30-7.21 (m, 5H), 7.16-7.12 (m, 1H), 4.51-4.45 (m, 2H), 3.47 (ddd, *J* = 9.2, 6.4, 5.5 Hz, 1H), 3.40 (ddd, *J* = 9.2, 7.6, 6.3 Hz, 1H), 2.50 (t, *J* = 7.9 Hz, 1H), 2.26-2.19 (m, 1H), 1.98-1.91 (m, 1H), 1.18 (s, 6H), 1.16 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.80, 138.68, 128.40, 128.28, 128.27, 127.66, 127.40, 125.20, 83.26, 72.81, 69.40, 32.41, 24.58, 24.52. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.39. IR (neat) ν_{max} 3061 (w), 3026 (w), 2976 (m), 2930 (m), 2856 (m), 1600 (w), 1493 (w), 1453 (m), 1359 (s), 1323 (s), 1271 (w), 1214 (w), 1142 (s), 1103 (s),

1028 (m), 967 (m), 850 (m), 736 (m), 699 (s) cm^{-1}. HRMS (ESI) calc. for $C_{22}H_{30}BO_3$ $[M+H]^+$ 353.2288, found 353.2286. $[\alpha]^{20}_D$: -28.02 (c = 1.48, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using RuPhos as the achiral ligand in the cross coupling reaction. The absolute stereochemistry was assigned by comparing the optical rotation of the corresponding alcohol ($[\alpha]^{20}_D$: 23.12 (c = 0.64, $CHCl_3$, *l* =50 mm)) with the reported value in the literature.[7]

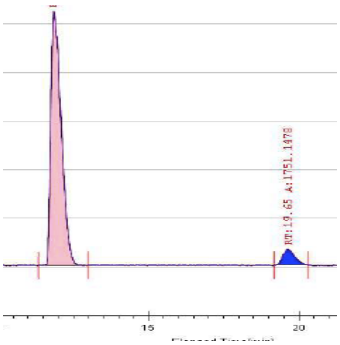
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 2% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	49.8498	15860.2246	12	812.9565
2	50.1502	15955.7718	18.37	422.6993
Total:	100	31815.9964		

Racemic

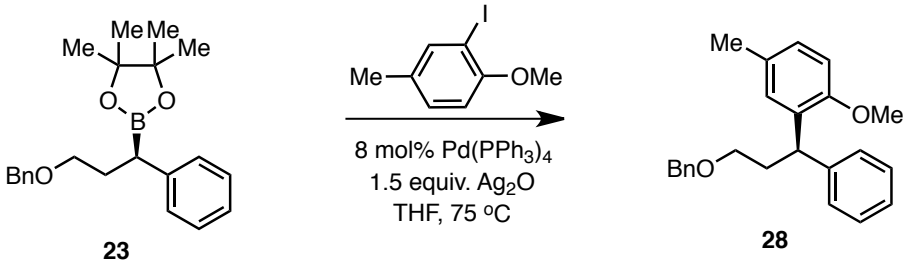


Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	93.4462	24968.3532	11.86	1043.9
2	6.5538	1751.1478	19.65	65.0213
Total:	100	26719.501		

Reaction product

[7] Uozumi, Y.; Kitayama, K.; Hayashi, T. *Tetrahedron: Asymmetry* **1993**, *4*, 2419.



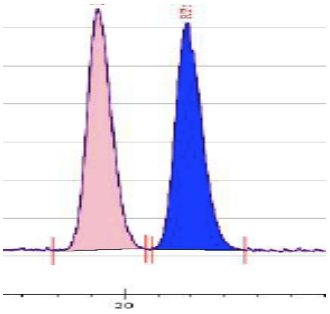
(*R*)-2-(3-(benzyloxy)-1-phenylpropyl)-1-methoxy-4-methylbenzene (28). The reaction was performed using the literature procedure[8] with slight modification. In the glove box, an oven-dried 2-dram vial with magnetic stir bar was charged with 2-iodo-1-methoxy-4-methylbenzene (15.1 mg, 0.06 mmol), $Pd(PPh_3)_4$ (5.6 mg, 0.005 mmol) and Ag_2O (21.1 mg, 0.091 mmol) followed by a solution of **23** (30.0 mg, 0.085 mmol) in THF (2.0 mL). The vial was sealed with a polypropylene cap, removed from the glove box, and heated to 75 °C in an oil bath for 16 hours. The vial was cooled to room temperature and diethyl ether (4.0 mL) was added. The resulting mixture was filtered through a short plug of silica gel. The filtrate was concentrated and purified on silica gel (hexanes: dichloromethane = 75:25) to afford colorless oil (18.2 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) 7.34-7.22 (m, 9H), 7.16-7.12 (m, 1H), 7.04 (d, J = 2.0 Hz, 1H), 6.95 (dd, J = 8.3, 1.8 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 4.53 (t, J = 7.9 Hz, 1H), 4.47-4.42 (m, 2H), 3.44 (t, J = 6.8 Hz, 2H), 2.35 (qd, J = 7.3, 2.2 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.44, 142.10, 136.11, 130.25, 127.00, 125.86, 125.68, 125.51, 124.95, 124.80, 124.79, 123.15, 108.23, 70.20, 66.28, 53.03, 37.31, 32.14, 18.15. IR (neat) ν_{max} 3060 (w), 3026 (w), 2922 (m), 2856 (m), 1585 (w), 1498 (s), 1453 (m), 1364 (w), 1289 (w), 1243 (s), 1103 (m), 1030 (m), 806 (m), 735 (m), 698 (s) cm^{-1}. HRMS (ESI) calc. for $C_{24}H_{27}O_2$ $[M+H]^+$ 347.2011, found 347.2017. $[\alpha]^{20}_D$: -10.86 (c = 0.60, $CHCl_3$, l =50 mm).

Proof of Stereochemistry:

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using the racemic benzyl boronate under the analogous reaction conditions. The absolute stereochemistry was assigned by comparison of the optical rotation of the corresponding aldehyde, which was obtained after benzyl deprotection and a subsequent oxidation, with the reported value in the literature (see below).

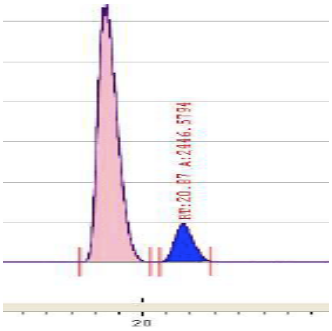
[8] Imao, D.; Glasspoole, B. W.; Laberge, V. S.; Crudden, C. M. *J. Am. Chem. Soc.* **2009**, *131*, 5024.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 5% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



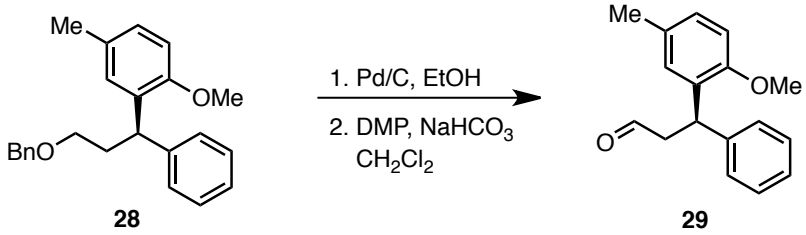
Peak Info				
Peak No	% Area	Area	RT (min)	Height (mV)
1	49.9676	3254.1781	19.62	127.0761
2	50.0324	3258.3953	20.95	119.6679
Total:	100	6512.5734		

Racemic



Peak Info				
Peak No	% Area	Area	RT (min)	Height (mV)
1	87.7347	17500.5112	19.24	644.3924
2	12.2653	2446.5794	20.87	94.9915
Total:	100	19947.0906		

Reaction product



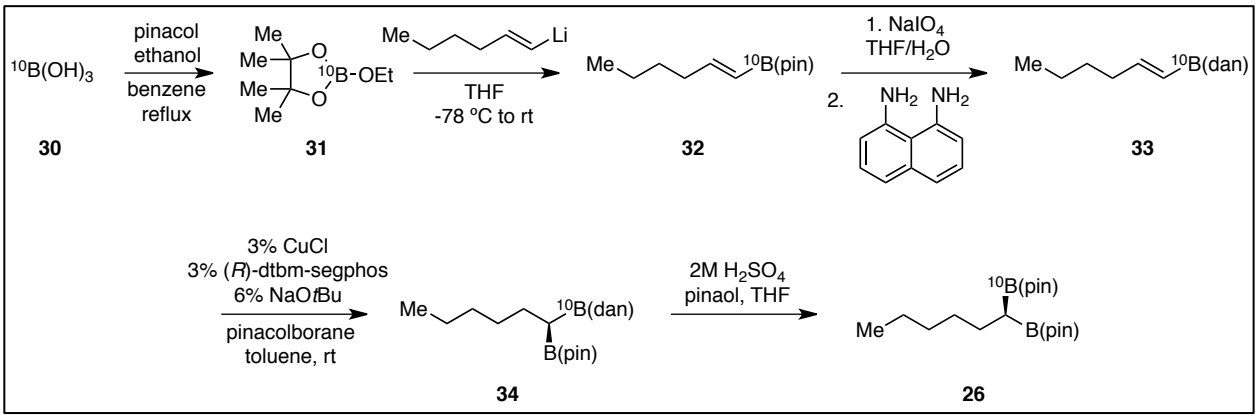
28 **29**

(*R*)-3-(2-methoxy-5-methylphenyl)-3-phenylpropanal (29). To a solution of **28** (37.0 mg, 0.107 mmol) in 2.0 mL of absolute ethanol was added Pd/C (10% wt on Pd basis) (11.7 mg, 0.011 mmol). The vial was sealed with a rubber septum and purged with N_2 for 3 times followed by purging with H_2 for 3 times. Then the reaction was allowed to stir at room temperature overnight. Upon the completion, the reaction mixture was filtered through a short pad of silica gel and concentrated under vacuum to give the crude alcohol, which was directly used for the next step without further purification. The crude alcohol was taken up in 2 mL CH_2Cl_2, and

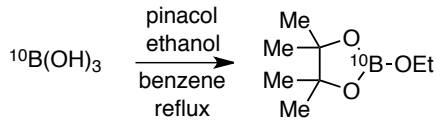
$NaHCO_3$ (10.8 mg, 0.128 mmol) and Dess-Martin periodinane (54.4 mg, 0.128 mmol) were added. The reaction was allowed to stir at room temperature for 3 hours before being diluted with diethyl ether (2 mL). The resulting mixture was filtered through a short plug of silica gel and concentrated *in vacuo*. The crude product was purified on silica gel (hexanes: ethyl acetate = 5:95) to afford colorless oil (24.0 mg, 88% yield over 2 steps). ^{1}H NMR (500 MHz, $CDCl_3$) 9.70 (t, *J* = 2.2 Hz, 1H), 7.31-7.26 (m, 4H), 7.21-7.18 (m, 1H), 6.99 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.88 (d, *J* = 2.0 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 5.01 (t, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 3.10 (dd, *J* = 7.9, 2.2 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.90, 154.57, 142.94, 131.32, 129.83, 128.83, 128.43, 128.05, 127.99, 126.35, 110.82, 55.53, 48.47, 38.29, 20.65. IR (neat) ν_{max} 3060 (w), 3027 (w), 3001 (w), 2945 (w), 2923 (w), 2834 (w), 2723 (w), 1721 (s), 1601 (w), 1498 (s), 1452 (m), 1412 (m), 1290 (w), 1242 (s), 1181 (w), 1126 (m), 1054 (m), 1031 (s), 807 (s), 735 (w), 699 (s), 539 (w) cm^{-1}. $[\alpha]^{20}_D$: 12.37 (c = 1.20, $CHCl_3$, *l* =50 mm). Lit.[9] (*S*) enantiomer = $[\alpha]^{20}_D$: -16.2 (c = 1.40, $CHCl_3$, *l* =50 mm).

VII. Preparation of Compound 26

Synthesis Summary:

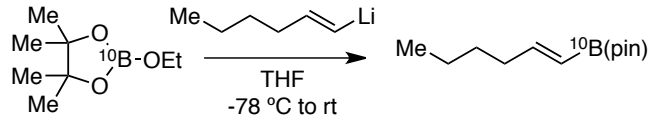


[9] Tokunaga, N.; Hayashi, T. *Tetrahedron: Asymmetry* **2006**, *17*, 607.



30 **31**

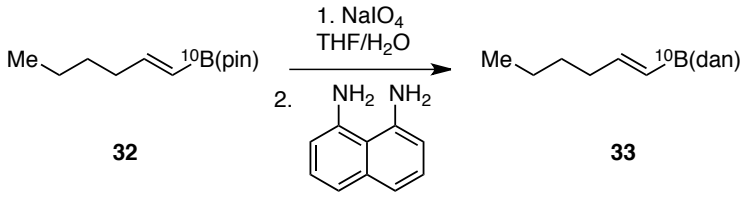
^{10}B-Labeled EtOB(pin) (**31**) was prepared from $^{10}B(OH)_3$ according to a literature procedure.[10] HRMS (ESI) calc. for $C_8H_{18}{}^{10}BO_3$ $[M+H]^+$ 172.1385, found 172.1385.



31 **32**

Preparation of ^{10}B-32. To a flame-dried 50 mL round bottom flask was added (E)-1-iodohex-1-ene[11] (731.3 mg, 3.5 mmol) as a solution in THF (15 mL). The reaction was cooled to -78 °C and *n*-BuLi (1.45 mL of a 2.5M solution in hexanes, 3.6 mmol) was added dropwise. ^{10}B-Ethyl pinacol borate (**31**, 655 mg, 3.83 mmol) was quickly added dropwise as a solution in THF (2 mL). The reaction was allowed to warm to room temperature and stirred for an hour. The reaction was poured into a mixture of water (40 mL) and ethyl acetate (40 mL). The layers were separated and the organic layer was washed with water (2 x 20 mL) and brine (20 mL). The organic layer was dried over $Na_2SO_{4(s)}$, filtered, and concentrated *in vacuo*. The title compound was purified by column chromatography on SiO_2 (90:10 hexanes/ethyl acetate, stain in CAM) to afford colorless oil (332 mg, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$) 6.63 (dt, J = 17.9, 6.4 Hz, 1H), 5.42 (d, J = 18.0 Hz, 1H), 2.15 (q, J = 6.6 Hz, 2H), 1.43-1.37 (m, 2H), 1.33 (dt, J = 14.8, 7.3 Hz, 2H), 1.26 (s, 12H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.75, 82.98, 35.56, 30.45, 24.84, 22.31, 13.97. IR (neat) ν_{max} 2977 (m), 2959 (w), 2928 (m), 2872 (w), 1639 (s), 1467 (w), 1396 (s), 1351 (s), 1144 (s), 997 (m), 970 (m), 849 (m), 663 (w) cm^{-1}. HRMS (ESI) calc. for $C_{12}H_{24}{}^{10}BO_2$ $[M+H]^+$ 210.1906, found 210.1908.

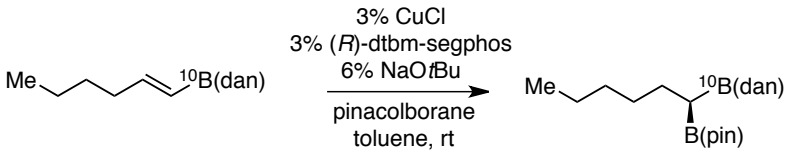
(10) Boudet, N.; Lachs, J. R.; Knochel, P. *Org. Lett.* **2007**, *9*, 5525.
(11) Cheung, L. W.; Yudin, A. K. *Org. Lett.* **2009**, *11*, 1281.



32 **33**

Preparation of ^{10}B-33. The reaction was performed according to a modified literature procedure.[12] To a 25 mL round bottom flask, **^{10}B-32** (332 mg, 1.6 mmol) was combined with sodium periodate (378.6 mg, 1.77 mmol) and stirred in a 1:1 mixture of THF/water (12 mL) for 30 minutes. Then $HCl_{(aq)}$ was added (1.12 mL, 1.0 M, 1.12 mmol). The reaction stirred for 12 hours at room temperature. Water (5 mL) and ethyl acetate (5 mL) were added, and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The organics were combined, dried over $Na_2SO_{4(s)}$, filtered, and concentrated *in vacuo*. 1,8-Diaminonaphthalene (240.5 mg, 1.52 mmol) and toluene (12 mL) were added and the flask was equipped with a Dean-Stark trap. The apparatus was purged with N_2, and the reaction was refluxed at 145^{o}C for 3 hours; the reaction was then cooled to room temperature and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on SiO_2 (70:25:5 hexanes/ethyl acetate/triethylamine, stain in CAM) to afford brown oil (231.1 mg, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$) 7.09 (t, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.37 (dt, *J* = 18.0, 6.4 Hz, 1H), 6.31 (d, *J* = 7.3 Hz, 2H), 5.70 (br, 2H), 5.56 (dt, *J* = 18.0, 1.5 Hz, 1H), 2.23-2.18 (m, 2H), 1.47-1.41 (m, 2H), 1.36 (dq, *J* = 14.9, 7.3 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.11, 141.36, 136.43, 127.63, 119.80, 117.43, 105.67, 35.64, 30.89, 22.37, 14.07. IR (neat) ν_{max} 3407 (br), 3052 (w), 2954 (m), 2924 (w), 2868 (w), 2855 (w), 1638 (m), 1596 (s), 1512 (s), 1414 (s), 1358 (s), 1261 (w), 1159 (s), 1054 (m), 985 (m), 817 (s), 757 (m), 645 (m) 588 (s) cm^{-1}. HRMS (ESI) calc. for $C_{12}H_{20}{}^{10}BN_2$ $[M+H]^+$ 250.1756, found 250.1759.

(12) Koyanagi, M.; Eichenauer, N.; Ihara, H.; Yamamoto, T.; Suginome, M. *Chem. Lett.* **2013**, *42*, 541.



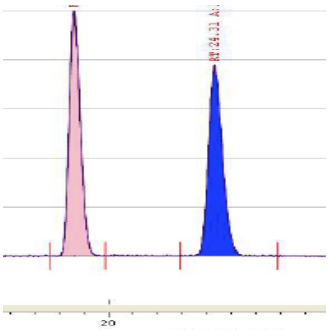
33 **34**

Preparation of (S)-^{10}B-34. The reaction was performed according to a literature procedure.[13] In the glove box, an oven-dried 2-dram vial with magnetic stir bar was charged with Cu(I)Cl (2.7 mg, 0.027 mmol), NaO*t*Bu (5.3 mg, 0.055 mmol), and (*R*)-(–)-dtbm-segphos (32.4 mg, 0.027 mmol). The vial was removed from the glove box, and toluene (1.5 mL) was added. The reaction stirred for 10 minutes at room temperature. Then pinacol borane (159.3 μL, 1.10 mmol) was added and stirred at room temperature for an additional 10 minutes. Substrate **33** (228.0 mg, 0.915 mmol) in toluene (1.2 mL) was added to the reaction mixture. The reaction was allowed to stir at room temperature for 20 hours. The reaction mixture was filtered through a pad of Celite with toluene (3 mL), and concentrated *in vacuo*. The product was purified by column chromatography on SiO_2 (90:10 hexanes/ethyl acetate) to afford white solid (300.2 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) 7.10 (t, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 7.7 Hz, 2H), 6.30 (d, *J* = 7.3 Hz, 2H), 5.80 (br, 2H), 1.69-1.61 (m, 1H), 1.56-1.48 (m, 1H), 1.41-1.30 (m, 6H), 1.27 (s, 6H), 1.26 (s, 6H), 0.91 (t, *J* = 6.8 Hz, 3H), 0.76 (dd, *J* = 9.4, 6.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.47, 136.40, 127.64, 119.60, 117.30, 105.51, 83.23, 32.16, 32.03, 26.49, 25.13, 24.60, 22.68, 14.19. ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.00. IR (neat) ν_{max} 3407 (br), 3055 (w), 2974 (w), 2957 (w), 1140 (s), 850 (w), 820 (m), 764 (s) cm^{-1}. HRMS (ESI) calc. for $C_{22}H_{33}{}^{10}B^{11}BN_2O_2$ $[M+H]^+$ 378.2764, found 378.2750. Melting point: 109-111 °C. $[\alpha]^{20}_D$: 12.72 (c = 1.54, $CHCl_3$, *l* =50 mm).

(13) Feng, X.; Jeon, H.; Yun, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 3989.

Analysis of Stereochemistry

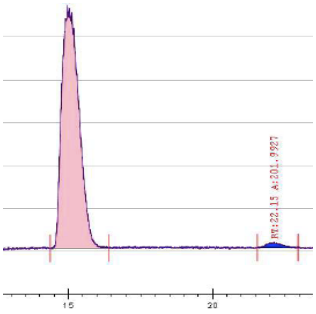
Chiral SFC (AD-H, Chiraldex, 3 mL/min, 5% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	50.1077	15421.6134	18.61	501.1748
2	49.8923	15355.3367	24.31	390.5567
Total:	100	30776.9501		

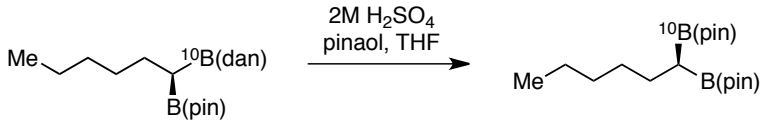
racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)
1	98.3028	11699.7533	14.97	283.5573
2	1.6972	201.9927	22.15	5.9155
Total:	100	11901.746		

reaction product



34 **26**

Preparation of (S)-^{10}B-26. The reaction was performed according to a literature procedure.[14] To a stirred solution of **^{10}B-34** (377 mg, 1.00 mmol) in THF (10 mL) was added 2 M $H_2SO_{4(aq)}$ (1.5 mL, 3.0 mmol) and pinacol (591 mg, 5.00 mmol) sequentially. The reaction was stirred for 24 h at room temperature before quenched by the addition of water (10 mL). The mixture was then extracted by diethyl ether (3 × 10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was then purified by flash column chromatography (1:3 hexanes/dichloromethane to 15% ethyl acetate/hexane) to give pure **26** as a brown oil (317 mg, 94% yield). ^{1}H NMR (500 MHz, $CDCl_3$) 1.56-1.51 (m, 2H), 1.31-1.24 (m, 6H), 1.23 (s, 12H),

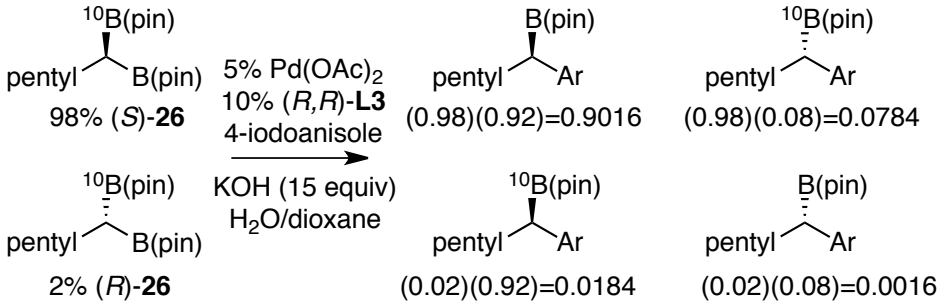
[14] Lee, J. C. H.; McDonald, R.; Hall, D. G. *Nature Chemistry*, **2011**, *3*, 894.

1.22 (s, 12H), 0.85 (t, J = 7.0 Hz, 3H), 0.71 (t, J = 7.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.94, 32.34, 31.93, 25.75, 24.96, 24.63, 22.64, 14.14. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.74. IR (neat) ν_{max} 2977 (m), 2926 (m), 2858 (w), 1467 (w), 1347 (s), 1308 (s), 1267 (s), 1215 (m), 1139 (s), 968 (m), 905 (w), 849 (m), 731 (m), 699 (w), 578 (w) cm^{-1}. HRMS (ESI) calc. for $C_{18}H_{37}{}^{10}B^{11}BO_4$ $[M+H]^+$ 338.2914, found 338.2912.

VIII. Cross-coupling of (S)-^{10}B-26.

A. Calculated isotope ratio in product 27 prepared using (R,R)-L3 ligand and assuming inversion during coupling:

note: bis(boronate) starting material (**26**) = 98:2 er
cross-coupling reaction selectivity = 92:8 er
natural abundance of boron is ^{10}B:^{11}B = 19.9:80.1



$^{10}B = (0.199)(.9016) + 0.0784 + 0.0184 + (0.199)(0.0016) = 0.276$

$^{11}B = (0.801)(.9016) + (0.801)(0.0016) = 0.723$

Relative [M+H] distributions for **^{10}B-27**		
$C_{19}H_{32}{}^{10}BO_3$ [M+H]:	318	0.816
$C_{18}{}^{13}CH_{32}{}^{10}BO_3$ [M+H]:	319	0.167
$C_{17}{}^{13}C_2H_{32}{}^{10}BO_3$ [M+H]:	320	0.016

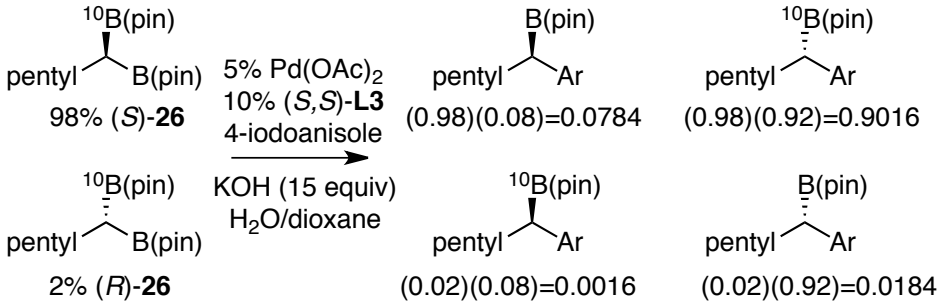
Relative [M+H] distributions for **^{11}B-27**		
$C_{19}H_{32}{}^{11}BO_3$ [M+H]:	319	0.816
$C_{18}{}^{13}CH_{32}{}^{11}BO_3$ [M+H]:	320	0.167
$C_{17}{}^{13}C_2H_{32}{}^{11}BO_3$ [M+H]:	321	0.016

Calculated Relative Intensities (27.6% of **^{10}B-27** + 72.3% **^{11}B-27**)

[M+H] for 318 amu = (0.276)(0.816) = 0.225	Found: 0.245
[M+H] for 319 amu = (0.276)(0.167) + (0.723)(0.816) = 0.636	Found: 0.638
[M+H] for 320 amu = (0.276)(0.016) + (0.723)(0.167) = 0.125	Found: 0.106
[M+H] for 321 amu = (0.723)(0.016) = 0.012	Found: 0.011

B. Calculated isotope ratio in product 27 prepared using (S,S)-L3 ligand and assuming inversion during coupling:

note: bis(boronate) starting material (**26**) = 98:2 er
cross-coupling reaction selectivity = 92:8 er
natural abundance of boron is ^{10}B:^{11}B = 19.9:80.1



^{10}B = (0.199)(.0784) + 0.9016 + 0.0016 + (0.199)(0.0184) = 0.922

^{11}B = (0.801)(.0784) + (0.801)(0.0184) = 0.077

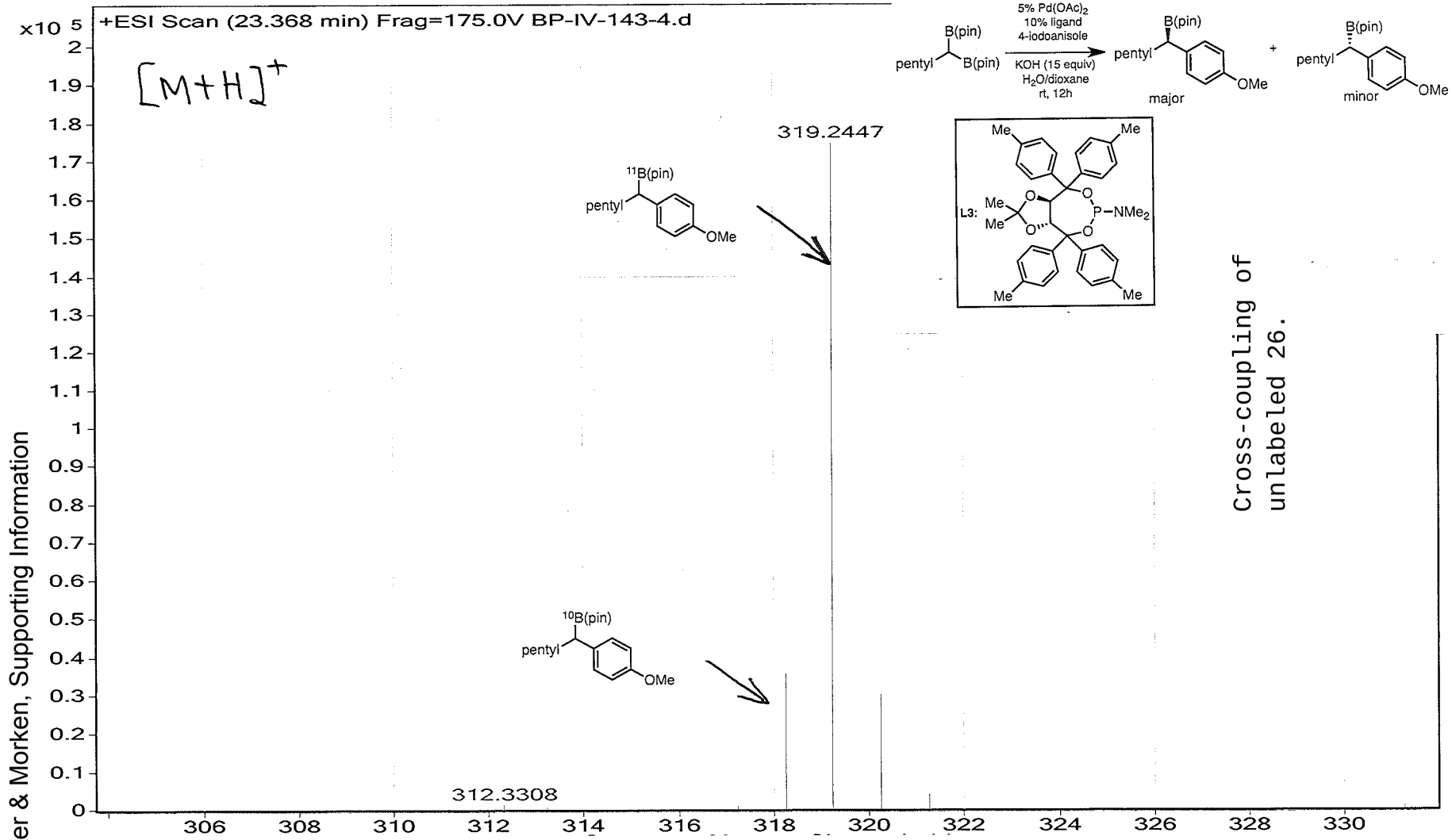
Relative [M+H] distributions for **^{10}B-27**		
$C_{19}H_{32}{}^{10}BO_3$ [M+H]:	318	0.816
$C_{18}{}^{13}CH_{32}{}^{10}BO_3$ [M+H]:	319	0.167
$C_{17}{}^{13}C_2H_{32}{}^{10}BO_3$ [M+H]:	320	0.016

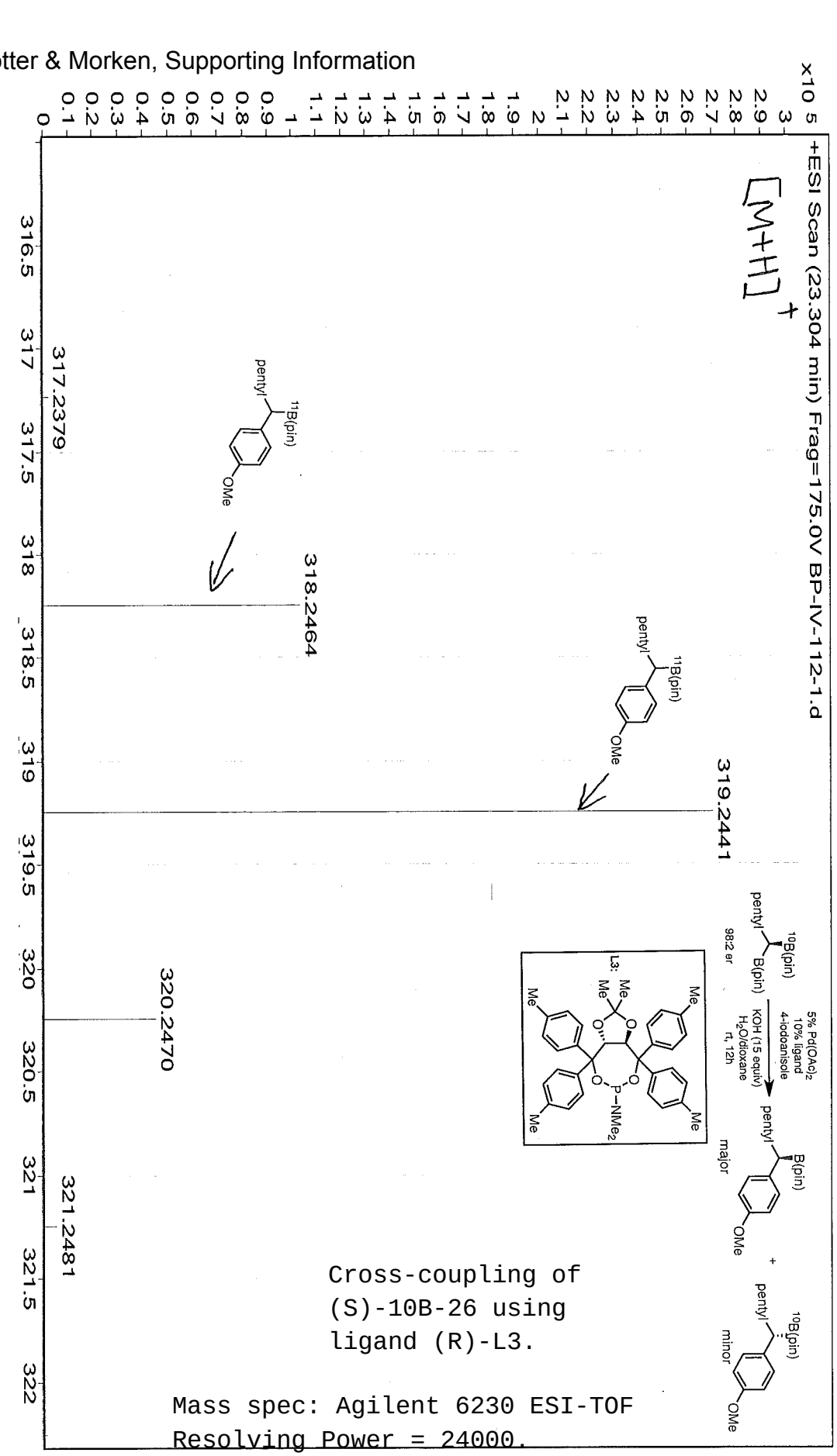
Relative [M+H] distributions for **^{11}B-27**		
$C_{19}H_{32}{}^{11}BO_3$ [M+H]:	319	0.816
$C_{18}{}^{13}CH_{32}{}^{11}BO_3$ [M+H]:	320	0.167
$C_{17}{}^{13}C_2H_{32}{}^{11}BO_3$ [M+H]:	321	0.016

Calculated Relative Intensities (92.2% of **^{10}B-27** + 7.7% **^{11}B-27**)

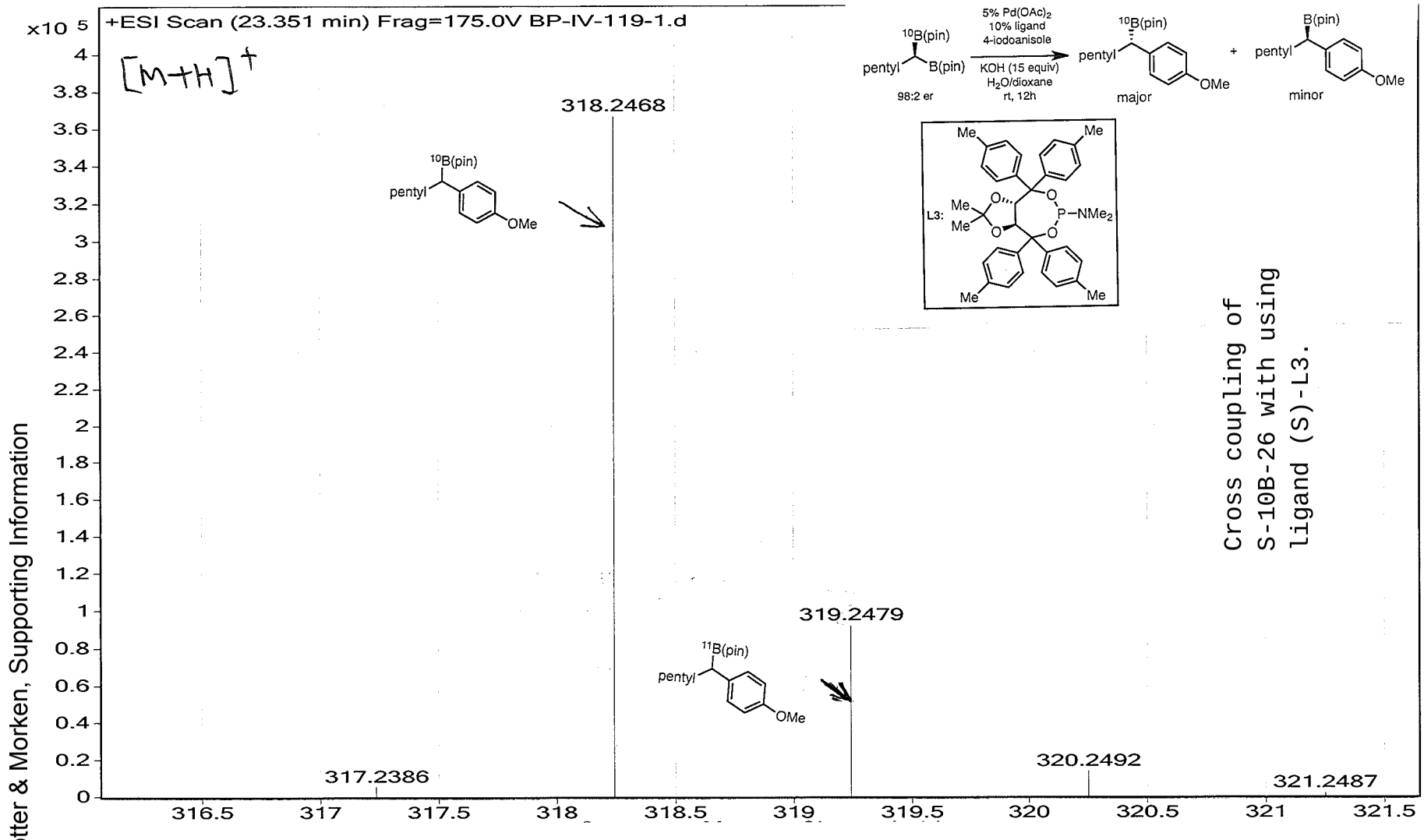
[M+H] for 318 amu = (0.922)(0.816) = 0.752	Found: 0.776
[M+H] for 319 amu = (0.922)(0.167) + (0.077)(0.816) = 0.217	Found: 0.194
[M+H] for 320 amu = (0.922)(0.016) + (0.077)(0.167) = 0.028	Found: 0.027
[M+H] for 321 amu = (0.077)(0.016) = 0.001	Found: 0.003

Sample Name	BP-IV-143-4	**Position**	Vial 41	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	5	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	BP-IV-143-4.d	**ACQ Method**	BP small molecule.m	**Comment**		**Acquired Time**	12/13/2013 8:00:56 PM




Sample Name
Inj Vol
Data Filename
Position
InjPosition
ACQ Method
Instrument Name
SampleType
Comment
User Name
IRM Calibration Status
Acquired Time
+ESI Scan (23.304 min) Frag=175.0V BP-IV-112-1.d
[M+H]+
317.2379
318.2464
319.2441
320.2470
321.2481
pentyl
10B(pin)
OMe
5% Pd(OAc)2
10% ligand
4-iodoanisole
KOH (15 equiv)
H2O/dioxane
rt, 12h
98:2 er
major
minor
L3:
P–NMe2
Me
Cross-coupling of
(S)-10B-26 using
ligand (R)-L3.
Mass spec: Agilent 6230 ESI-TOF
Resolving Power = 24000.

Sample Name	**Position**	**Instrument Name**	**User Name**
Inj Vol	**InjPosition**	**SampleType**	**IRM Calibration Status**
Data Filename	**ACQ Method**	**Comment**	**Acquired Time**

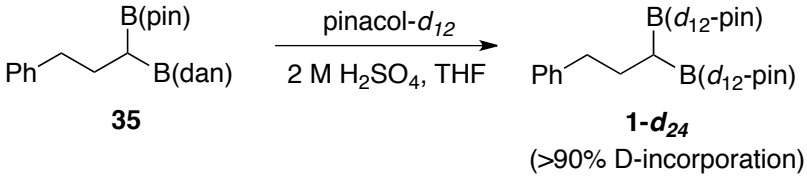


Cross coupling of S-10B-26 with using ligand (S)-L3.

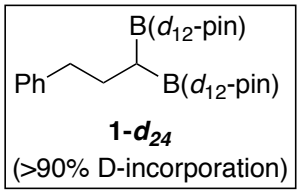
Sun, Potter & Morken, Supporting Information

IX. Cross-over Experiment (Equation 4)

Preparation 1-d_{24}.

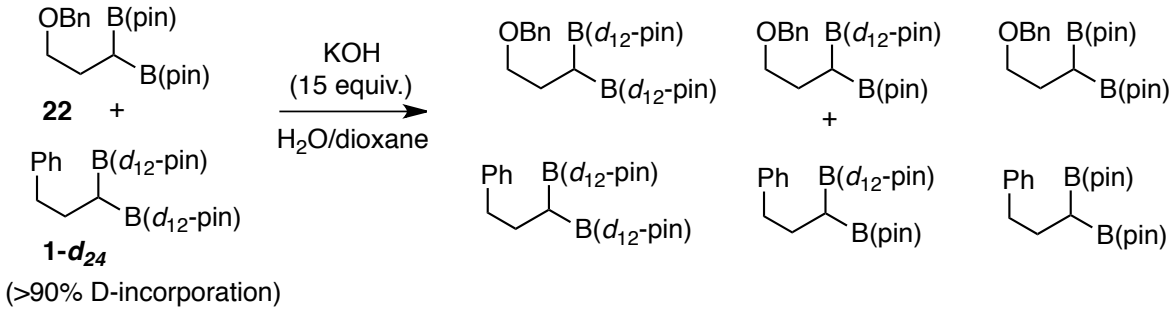


To a solution of **35** (124 mg, 0.30 mmol) in THF (0.6 mL) was added pinacol-d_{12} (392 mg, 3.0 mmol) follow by 2 M H_2SO_4 (0.35 mL, 0.90 mmol). The reaction was stirred at room temperature overnight and then filtered through a short pad of silica gel, concentrated and purified by column chromatography on SiO_2 (95:5 hexane/ethyl acetate, stain in CAM) to afford a colorless solid of 37 mg, yield 34%. R_f = 0.5 in 90:10 hexanes/ethyl acetate on TLC.

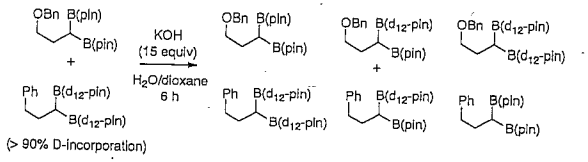


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.22 (m, 3H), 7.18-7.12 (m, 2H), 2.59 (t, *J* = 8.0 Hz, 2H), 1.85 (q, *J* = 8.0 Hz, 2H), 1.23 (s, 1H), 1.23 (s, 1H), 0.81 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.06, 128.68, 128.20, 125.56, 83.06, 82.72, 38.82, 25.02, 24.62. HRMS (ESI) calc. for $C_{21}H_{11}D_{24}B_2O_4$ $[M+H]^+$ 397.4150, found 397.4222.

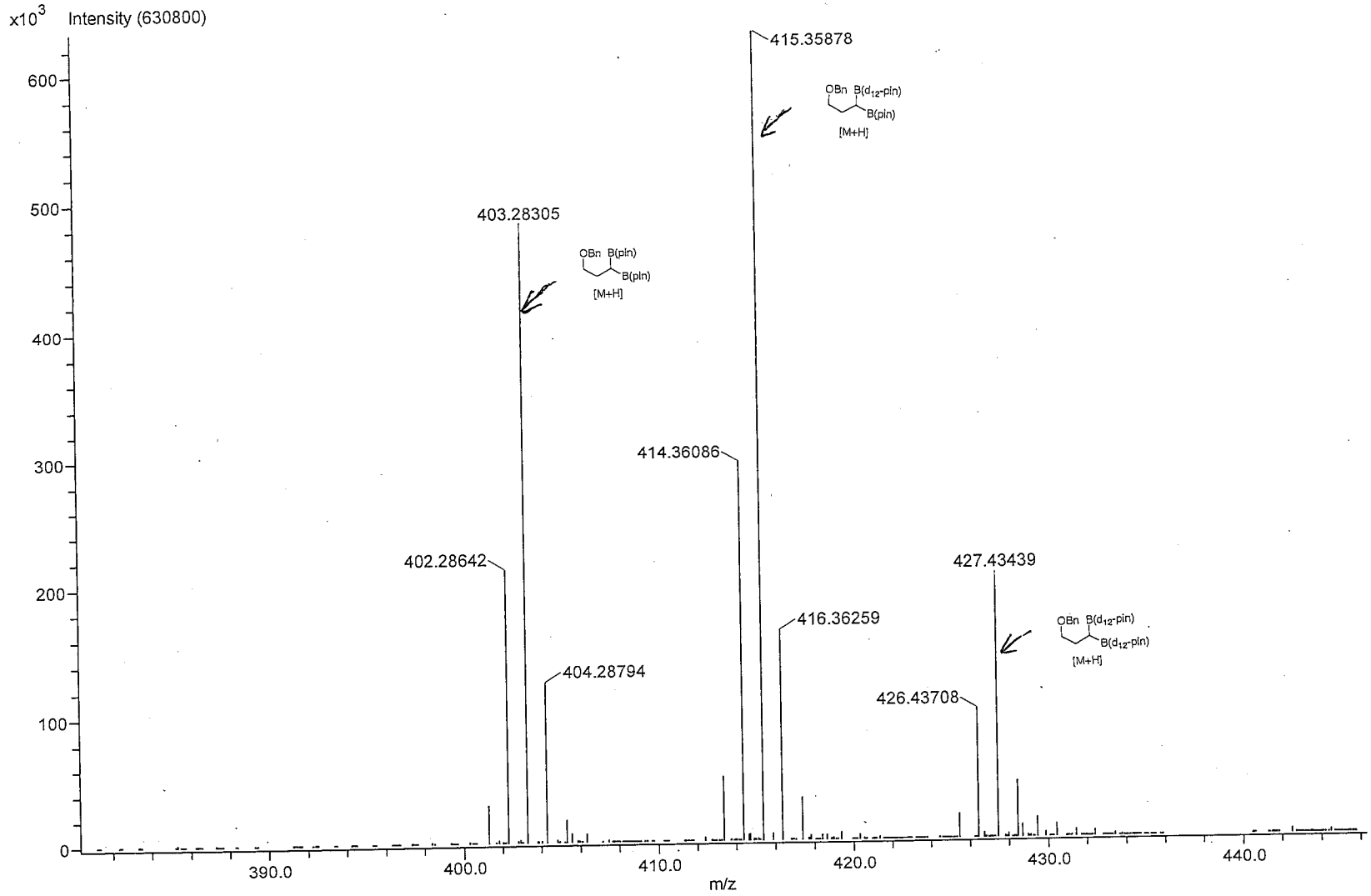
A. Cross-over Experiment of germinal bis(boronates) under basic condition:

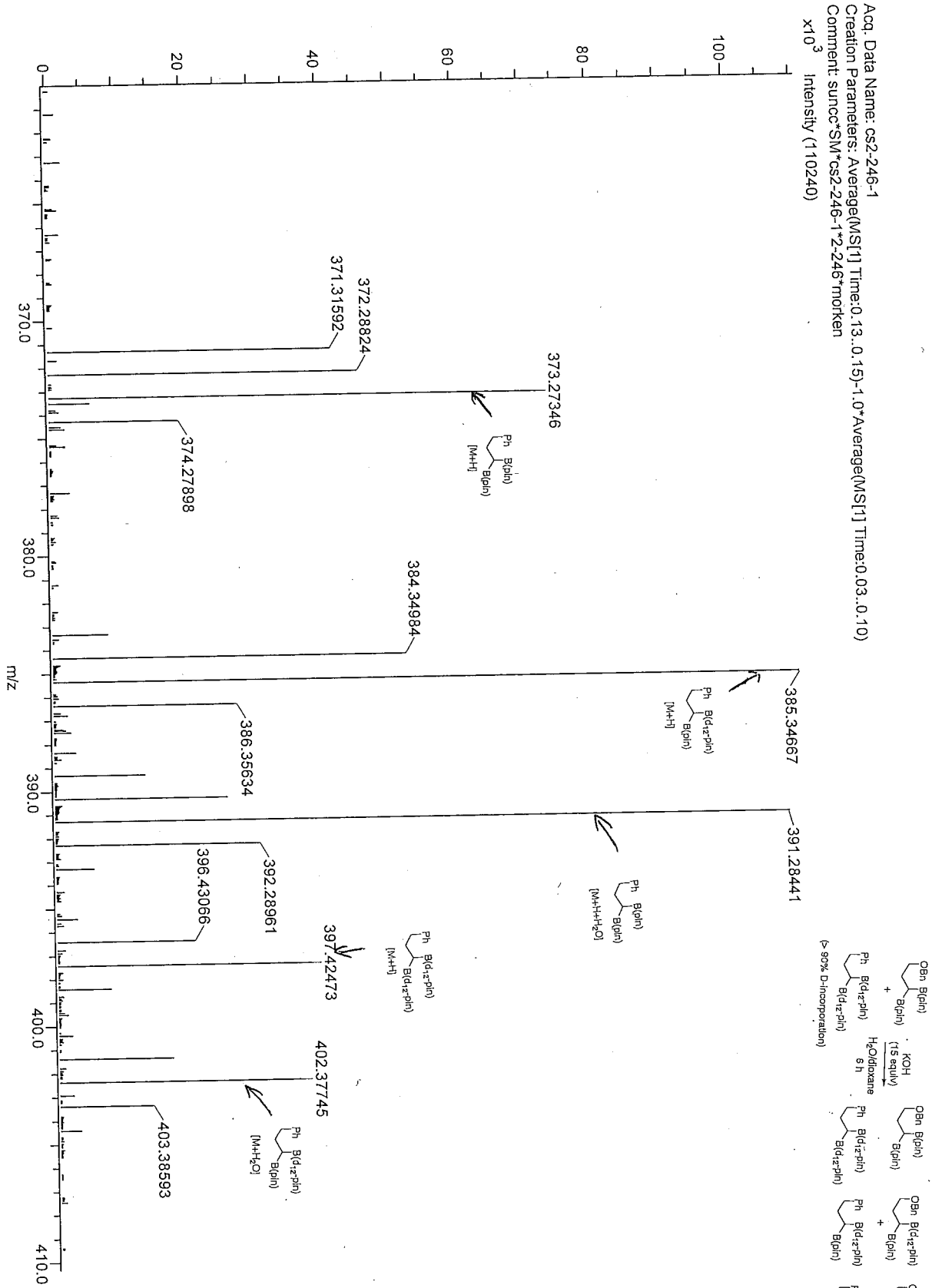


Boronate **22**(40.2 mg, 0.1 mmol) was mixed with **1-d_{24}** (36.2 mg, 0.1 mmol) in 0.4 mL dioxane and 0.38 mL of KOH (8M) and stirred for 6 hours. Then ether was added and the mixture filtered through silica gel prior to purification by silica gel chromatography to furnish labeled **1** (18 mg) and labeled **22** (10 mg).

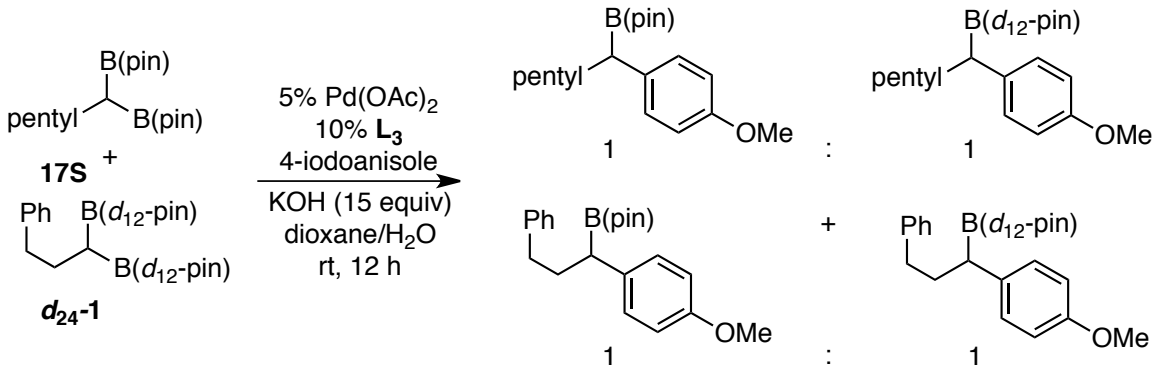


Acq. Data Name: cs2-246-2
Creation Parameters: Average(MS[1] Time:0.11..0.12)-1.0*Average(MS[1] Time:0.03..0.10)
Comment: suncc*SM*cs2-246-2*2-246*morken

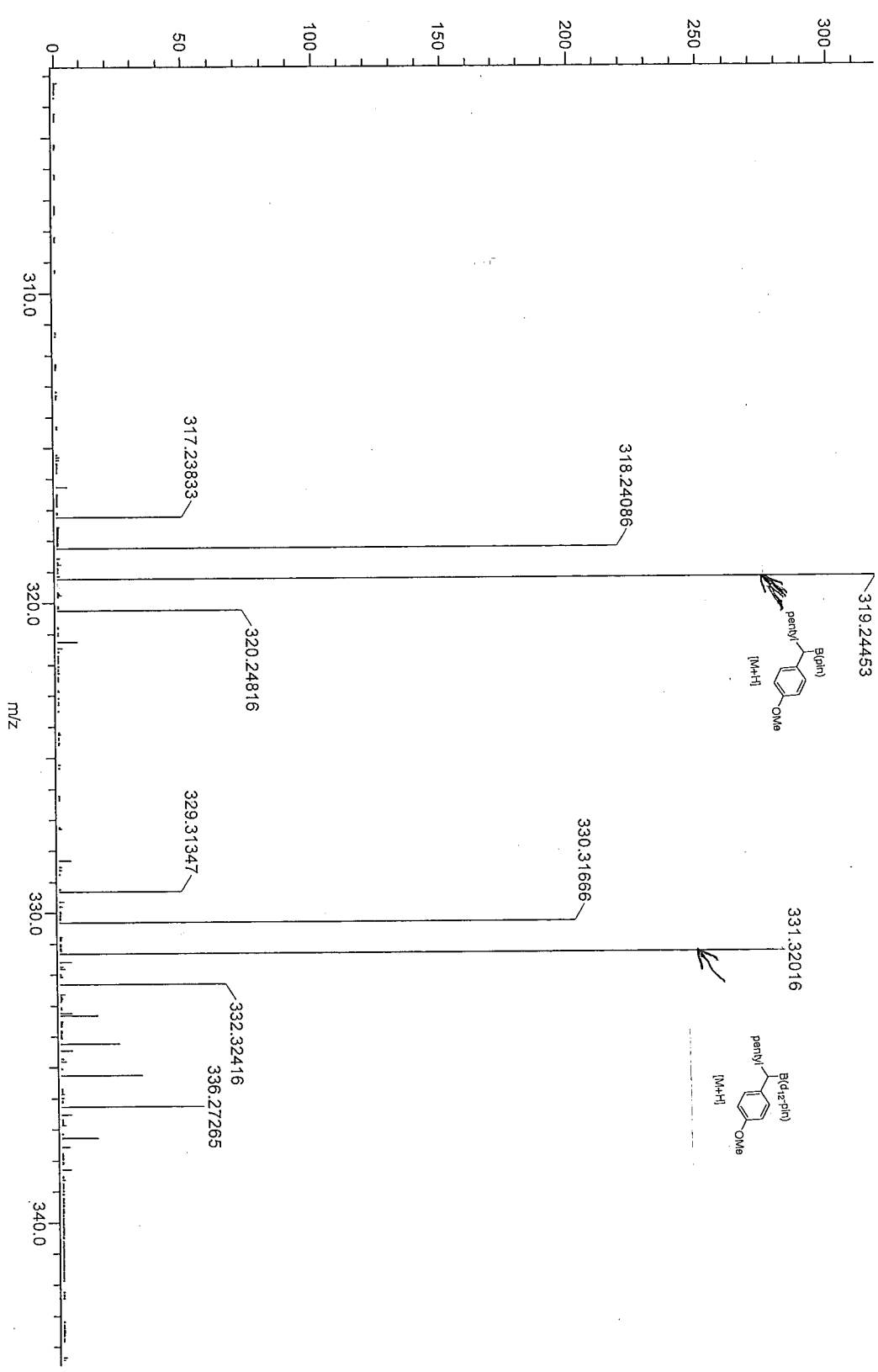



Acq. Data Name: cs2-246-1
Creation Parameters: Average(MS[1] Time:0.13..0.15)-1.0*Average(MS[1] Time:0.03..0.10)
Comment: suncc*SM*cs2-246-1*2-246*morken
x10^3 Intensity (110240)
m/z
371.31592
372.28824
373.27346
374.27898
384.34984
385.34667
386.35634
391.28441
392.28961
396.43066
397.42473
402.37745
403.38593
[M+H]
[M+H+H2O]
(15 equiv)
H2O/dioxane
6 h
KOH
(> 90% D-incorporation)

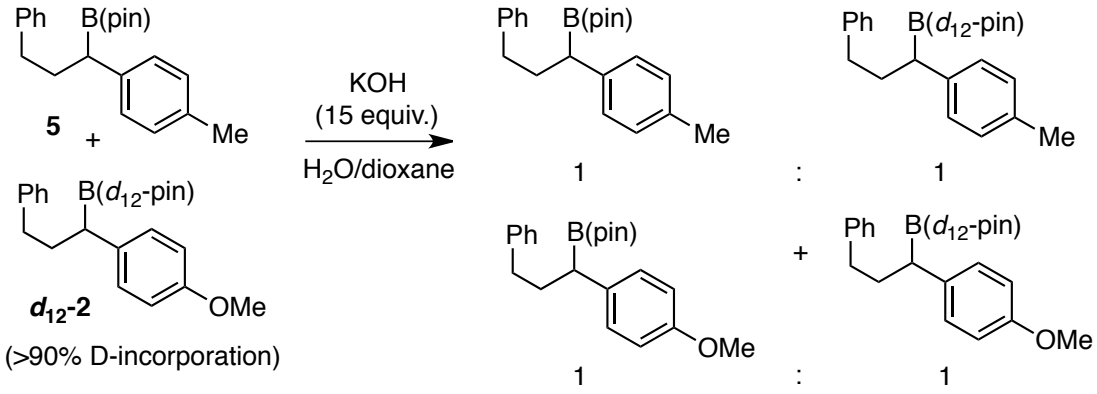
B. Cross-over Experiment of germinal bis(boronates) under catalytic cross-coupling condition with 4-iodoanisole:



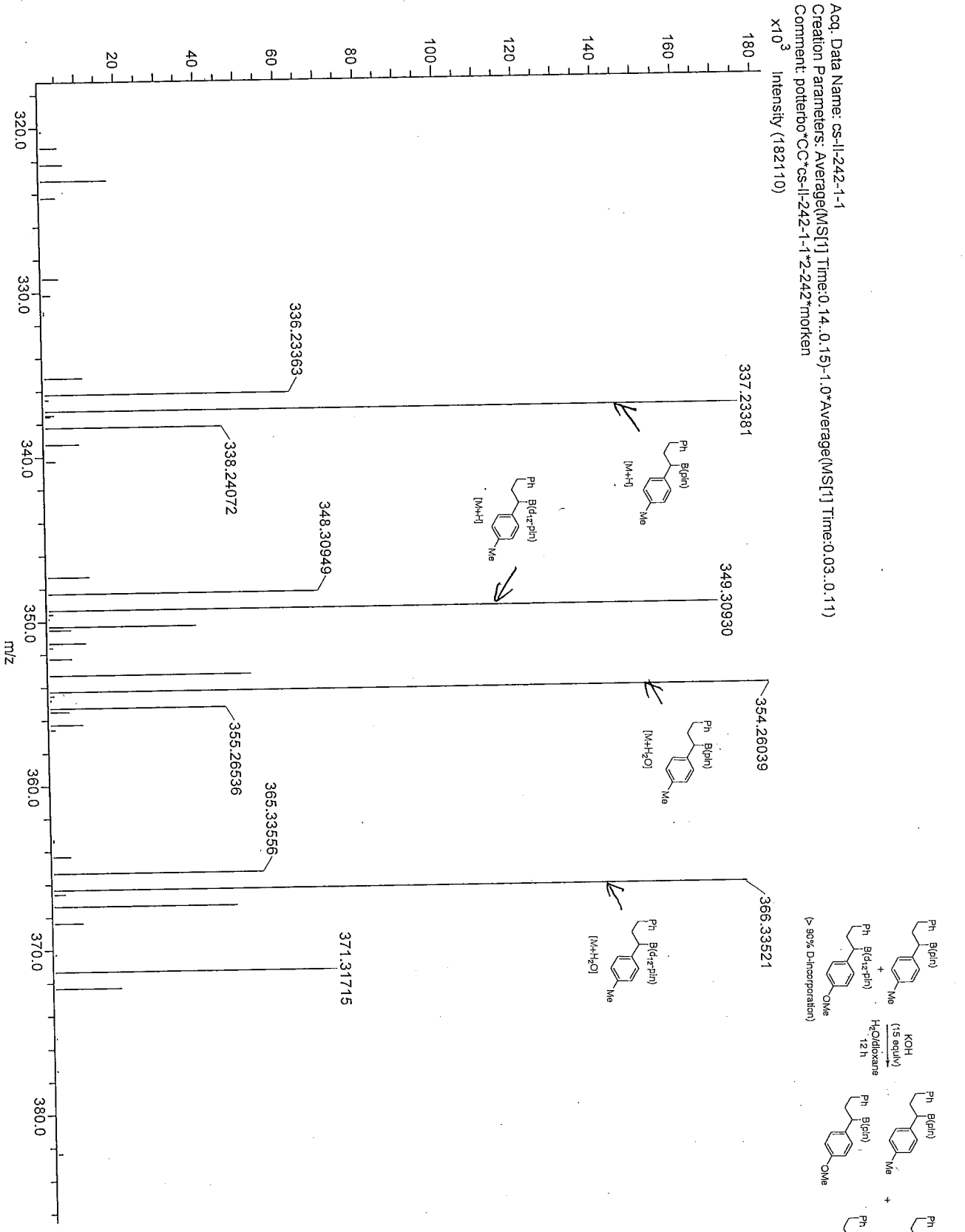
The standard cross-coupling procedure was followed with a mixture of boronates ***d*$_{24}$-1** and **17S** and the mixture purified on silica gel with hexane/CH_2Cl_2.

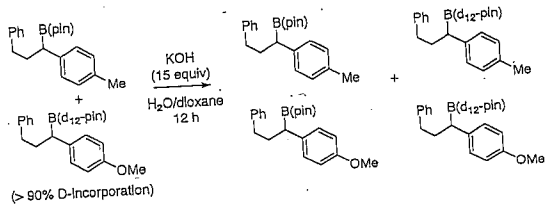

Acq. Data Name: cs2-249
Creation Parameters: Average(MS[1] Time:0.14..0.15)-1.0*Average(MS[1] Time:0.03..0.12)
Comment: sunoc*SM*cs2-249*2-249*morken
x10^3 Intensity (317590)
300
250
200
150
100
50
0
310.0
320.0
330.0
340.0
m/z
317.23833
318.24086
319.24453
320.24816
329.31347
330.31666
331.32016
332.32416
336.27265
pentyl
B(pin)
[M+H]
OMe
B(d12-pin)

C. Cross-over of benzyl boronate products under basic condition:

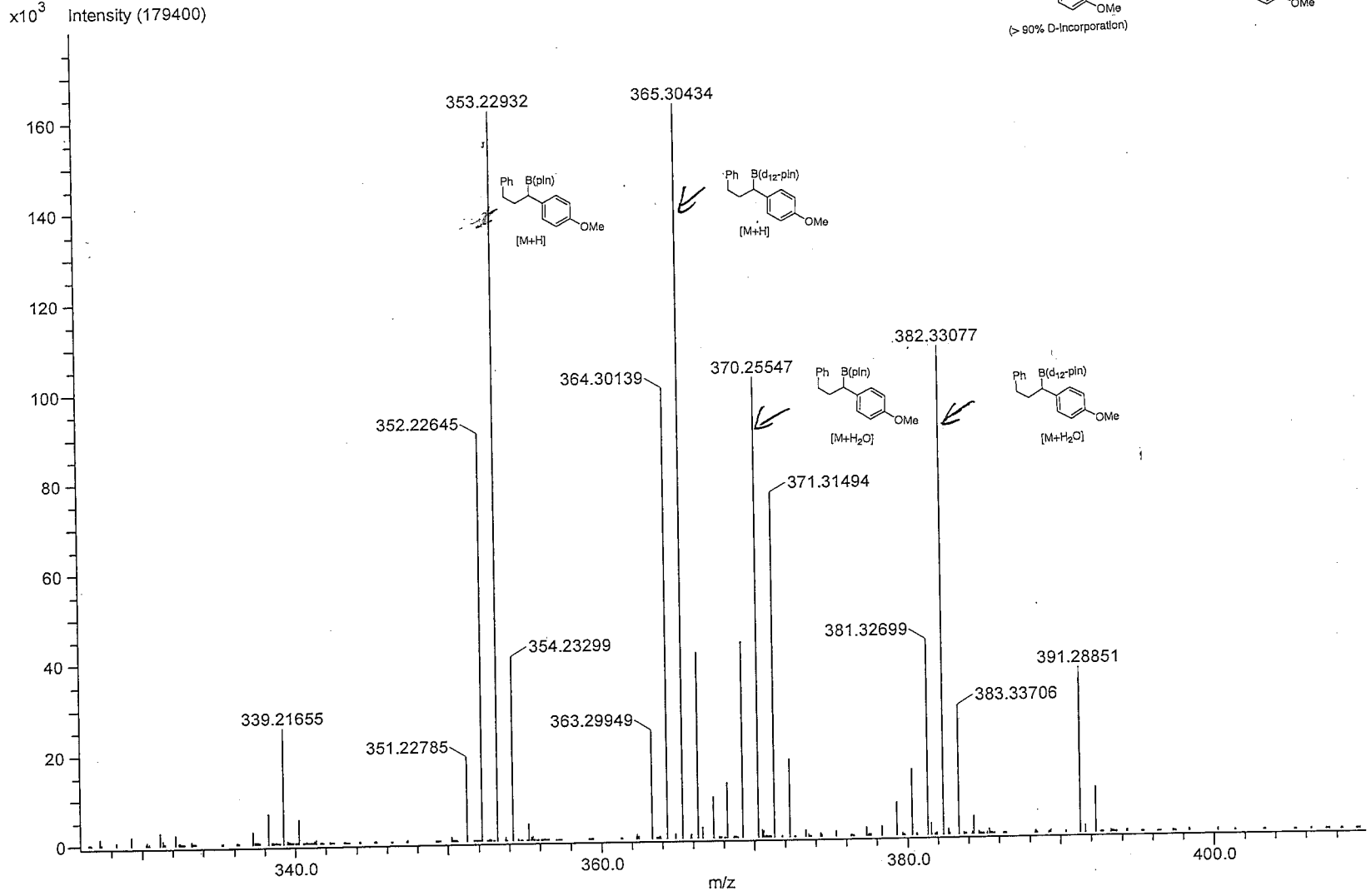


Boronate **5** (9.2 mg, 0.027 mmol) was mixed with **2-d_{12}** (10 mg, 0.027 mmol) in 0.11 mL dioxane and 0.1 mL of KOH (8M) and stirred for 12 hours. Then ether was added and the mixture filtered through silica gel prior to purification by silica gel chromatography to furnish labeled **5** (8 mg) and labeled **2** (8.5 mg).


Acq. Data Name: cs-ll-242-1-1
Creation Parameters: Average([MS[1] Time:0.14..0.15)-1.0*Average([MS[1] Time:0.03..0.11)
Comment: potterbo*CC*cs-ll-242-1-1*2-242*morken
x10^3 Intensity (182110)
m/z
336.23363
337.23381
338.24072
348.30949
349.30930
354.26039
355.26536
365.33556
366.33521
371.31715
[M+H]
[M+H2O]
B(pin)
B(d12-pin)
Me
OMe
KOH
(15 equiv)
H2O/dioxane
12 h
(> 90% D-incorporation)

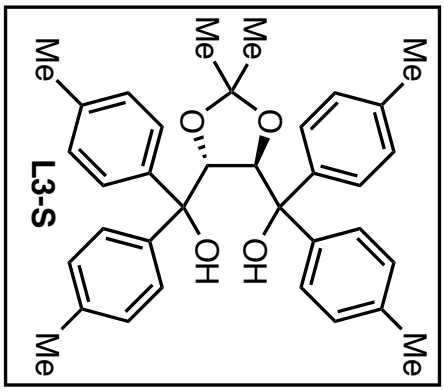


Acq. Data Name: cs-ll-242-2-1
Creation Parameters: Average(MS[1] Time:0.14..0.16)-1.0*Average(MS[1] Time:0.04..0.13)
Comment: potterbo*CC*cs-ll-242-2-1*2-242*morken

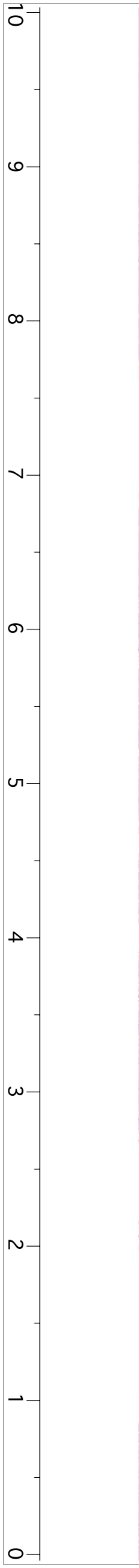


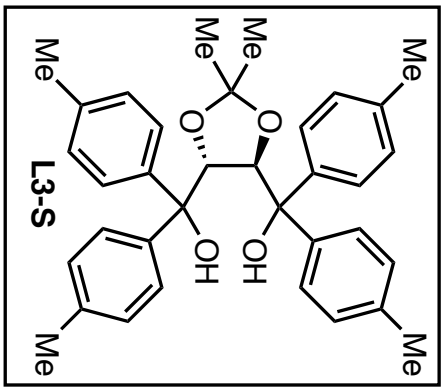
^{1}H and ^{13}C NMR

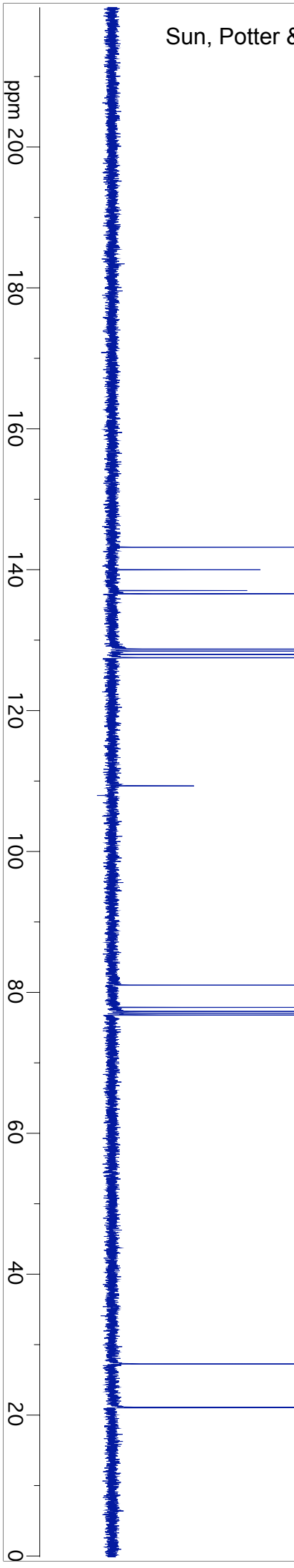
Spectral Data



L3-S




Me
Me
O
O
Me
Me
L3-S
OH
OH
Me
Me


ppm
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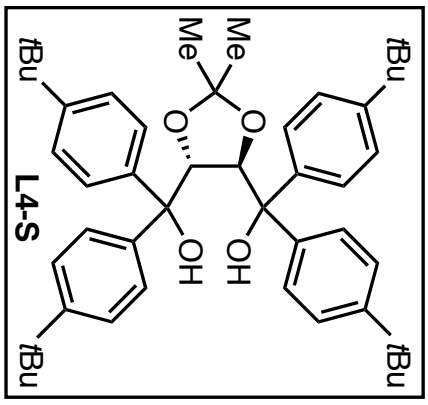
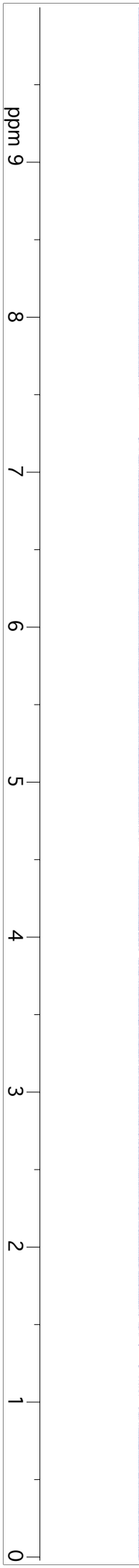
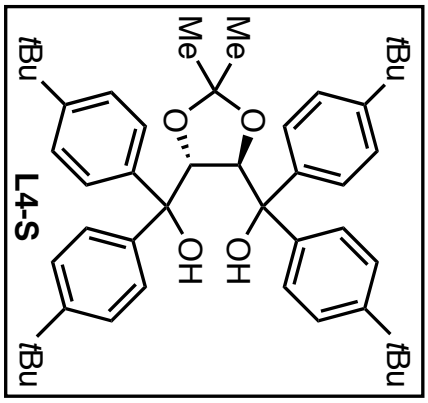
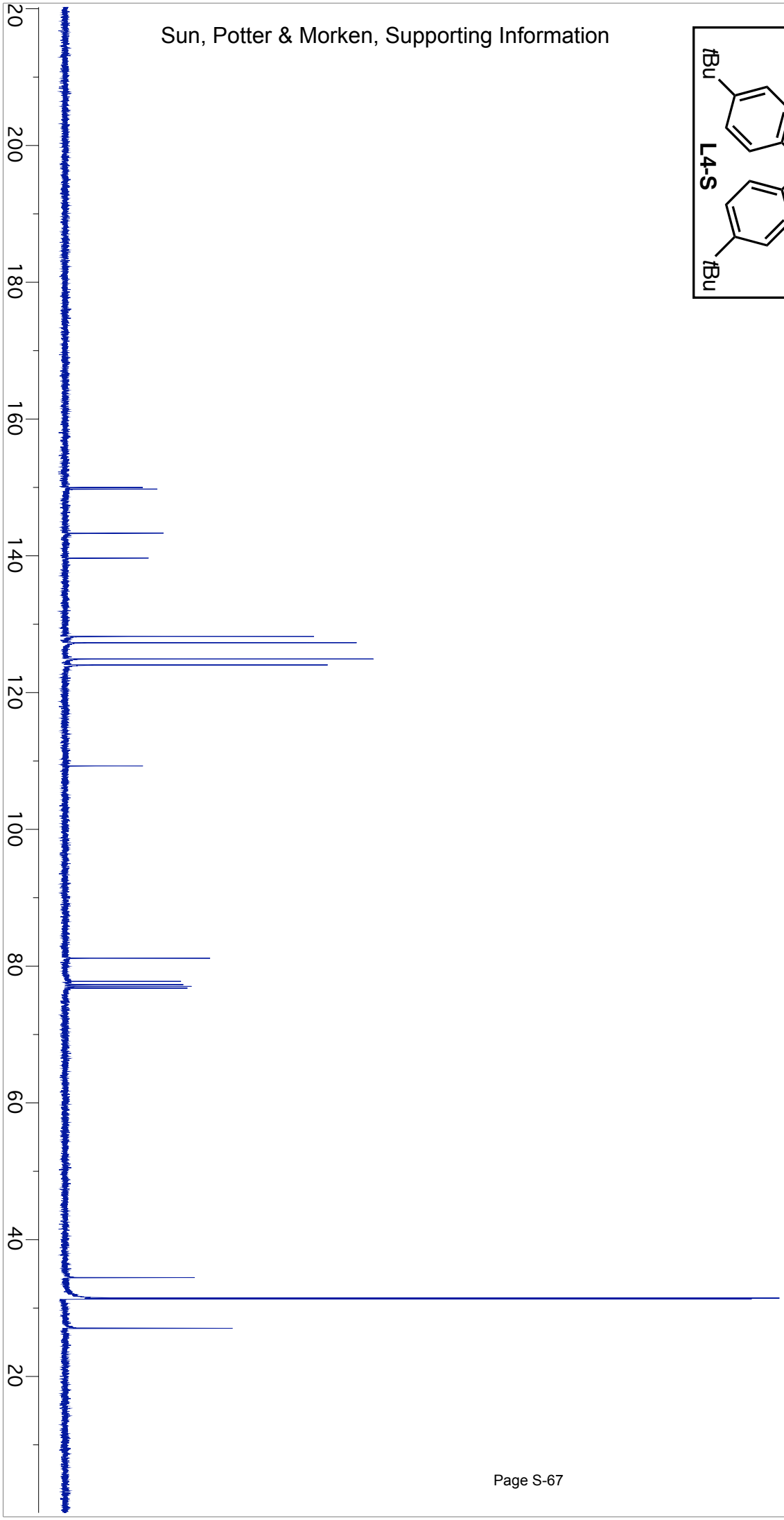
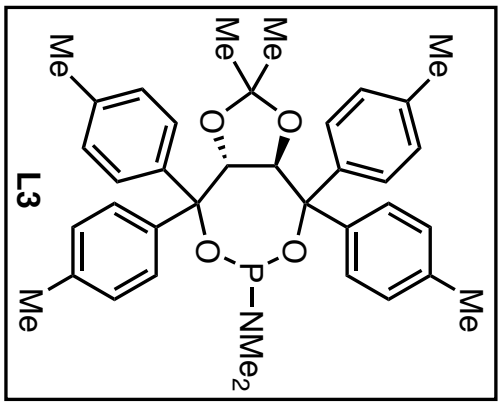
180
160
140
120
100
80
60
40
20
0

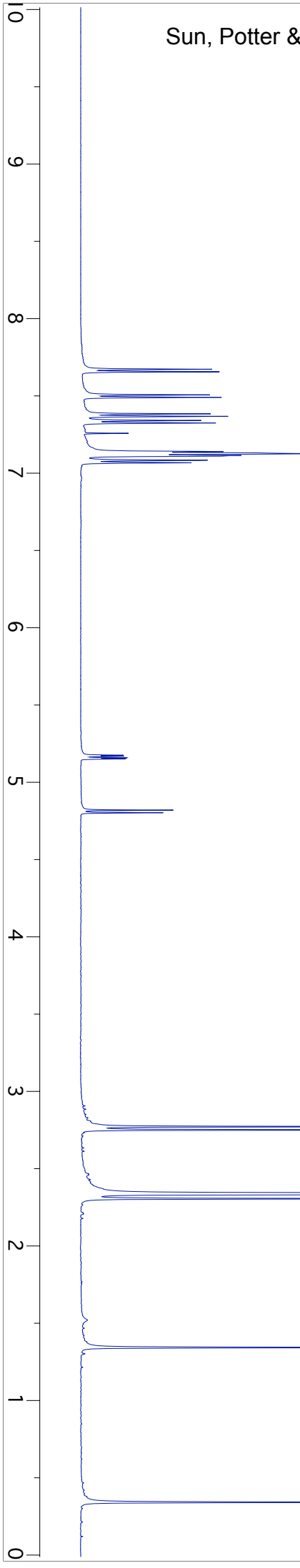

tBu
Me
Me
O
O
tBu
L4-S
OH
OH
tBu
tBu

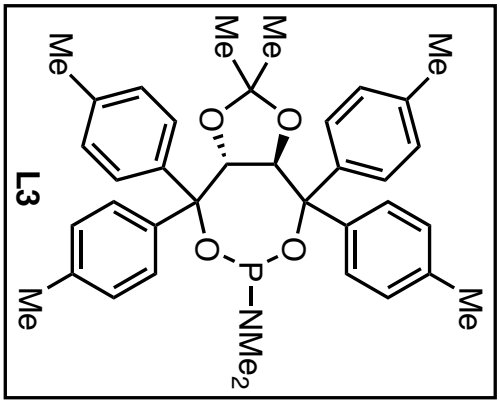

ppm
9
8
7
6
5
4
3
2
1
0

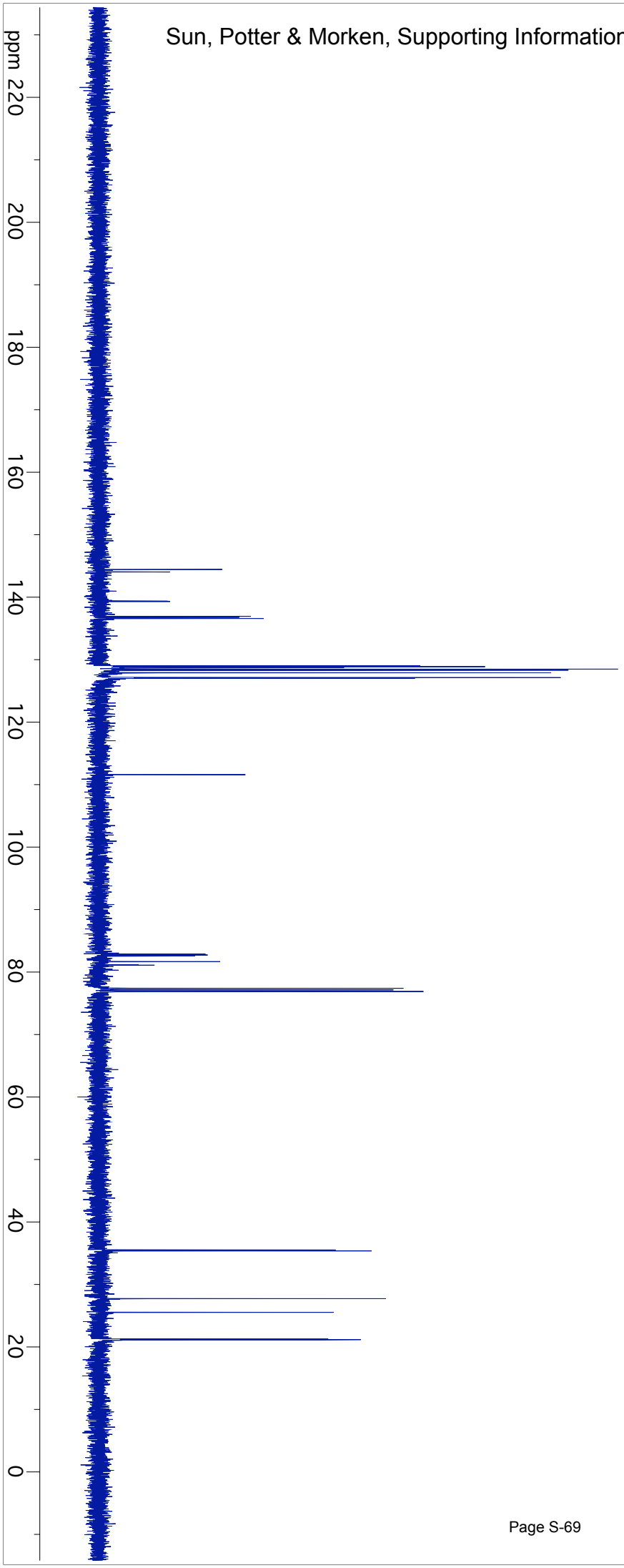

tBu
Me
Me
O
O
tBu
L4-S
OH
OH
tBu
tBu


20
200
180
160
140
120
100
80
60
40
20


Me
Me
Me
Me
O
O
O
O
P–NMe2
Me
Me
Me
L3


10
9
8
7
6
5
4
3
2
1
0


Me
Me
Me
Me
Me
Me
O
O
O
O
O
P–NMe2
L3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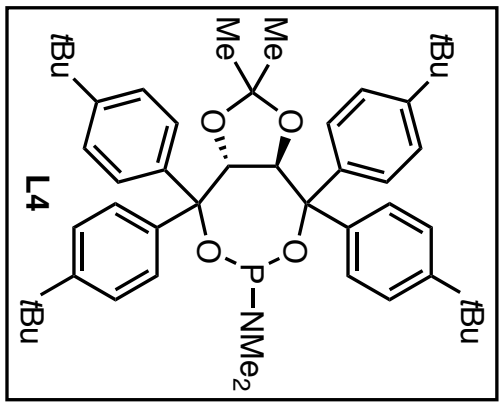
L4
tBu
tBu
tBu
tBu
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Me
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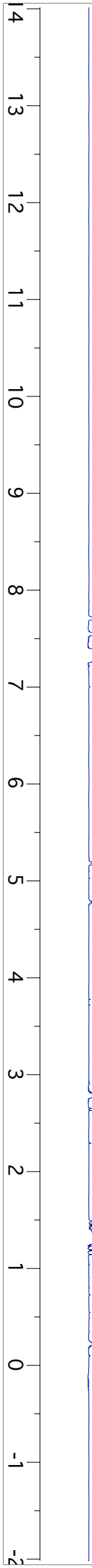
O
O
O
O
P–NMe2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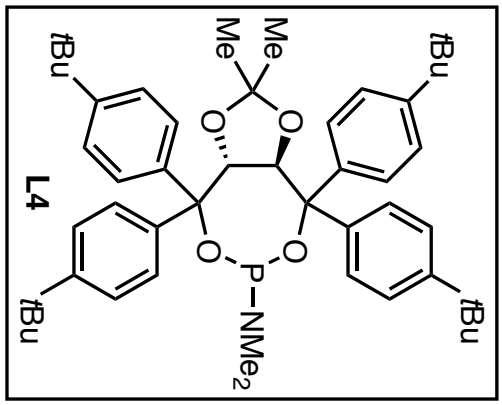
tBu
Me
Me
tBu
O
O
O
O
P–NMe2
tBu
tBu

L4

ppm
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140
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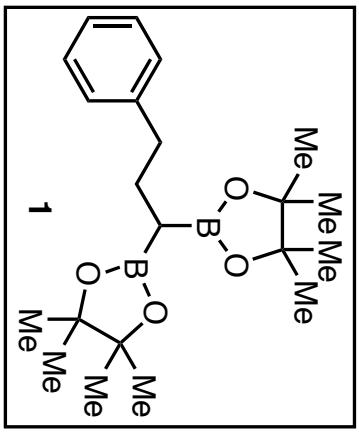
1
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O
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Me
Me
Me
Me
Me
Me
Me

ppm
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7
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3
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1
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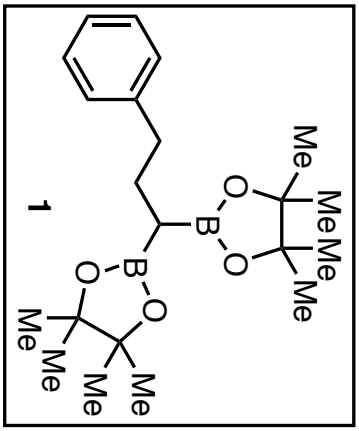
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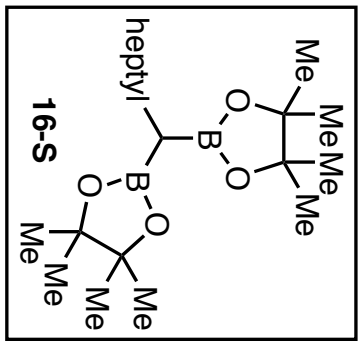
16-S
heptyl
B
O
O
Me
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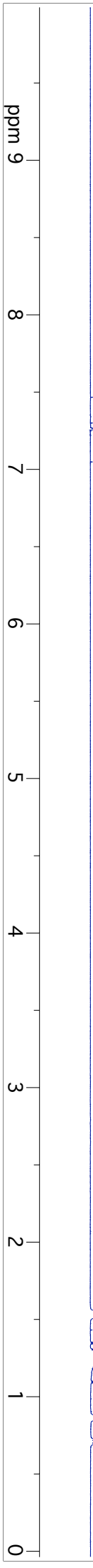
Me
Me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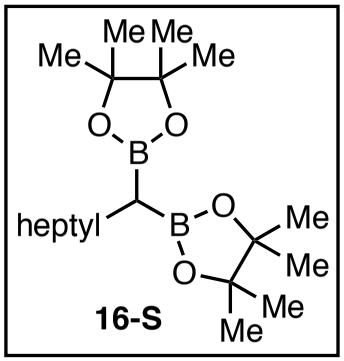
Me Me
Me
Me
O
O
B
heptyl
B
O
Me
Me
O
Me
Me

16-S

ppm 200
180
160
140
120
100
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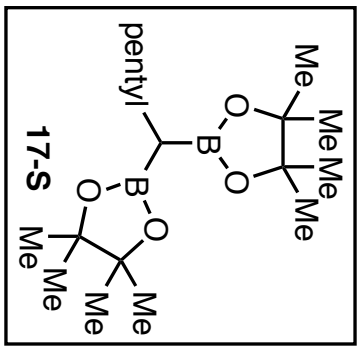
60
40
20
0


pentyl
Me
Me
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Me
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Me
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Me
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17-S

0
9
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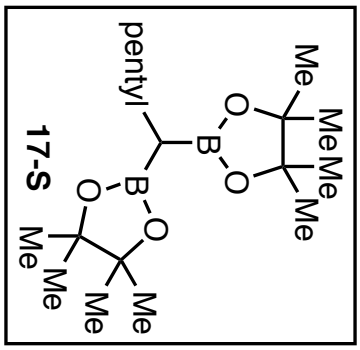
3
2
1
0


pentyl
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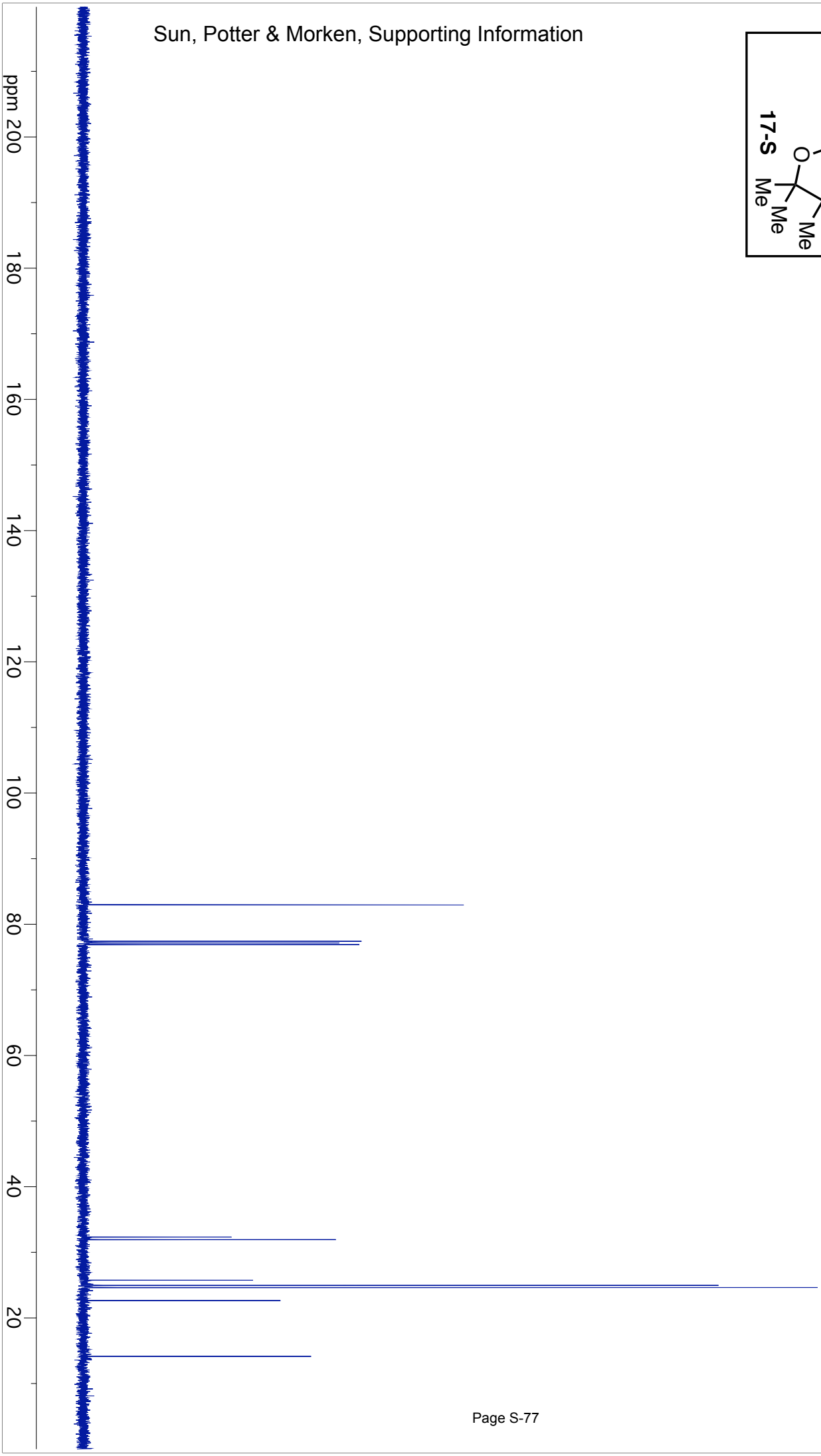
Me
17-S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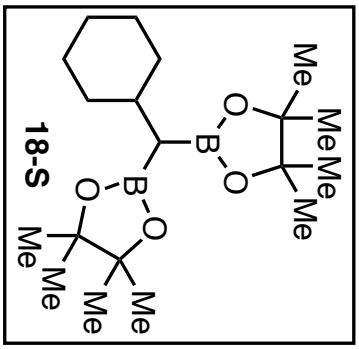
18-S
Me
Me
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Me
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B
B
O
O

10
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6
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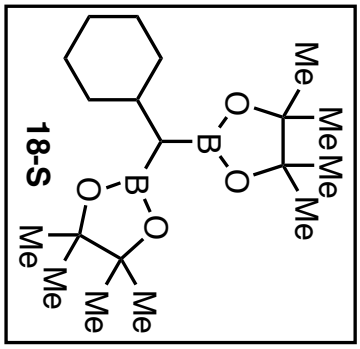
2
1
H2O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Me
Me
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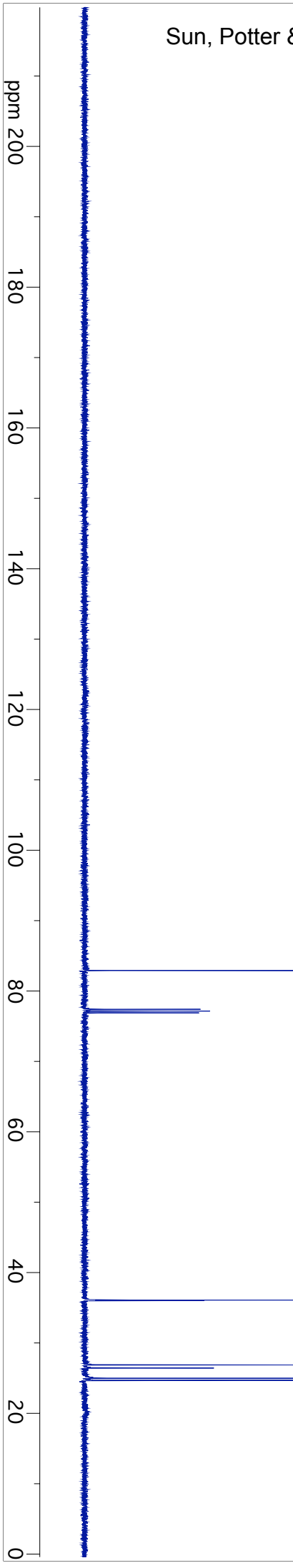
O
B
O
O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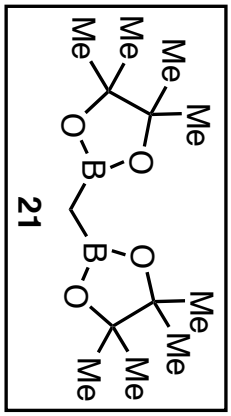

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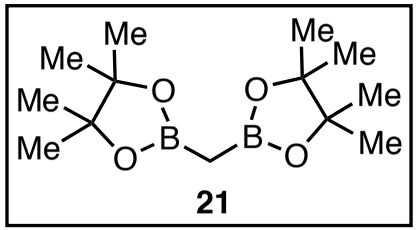

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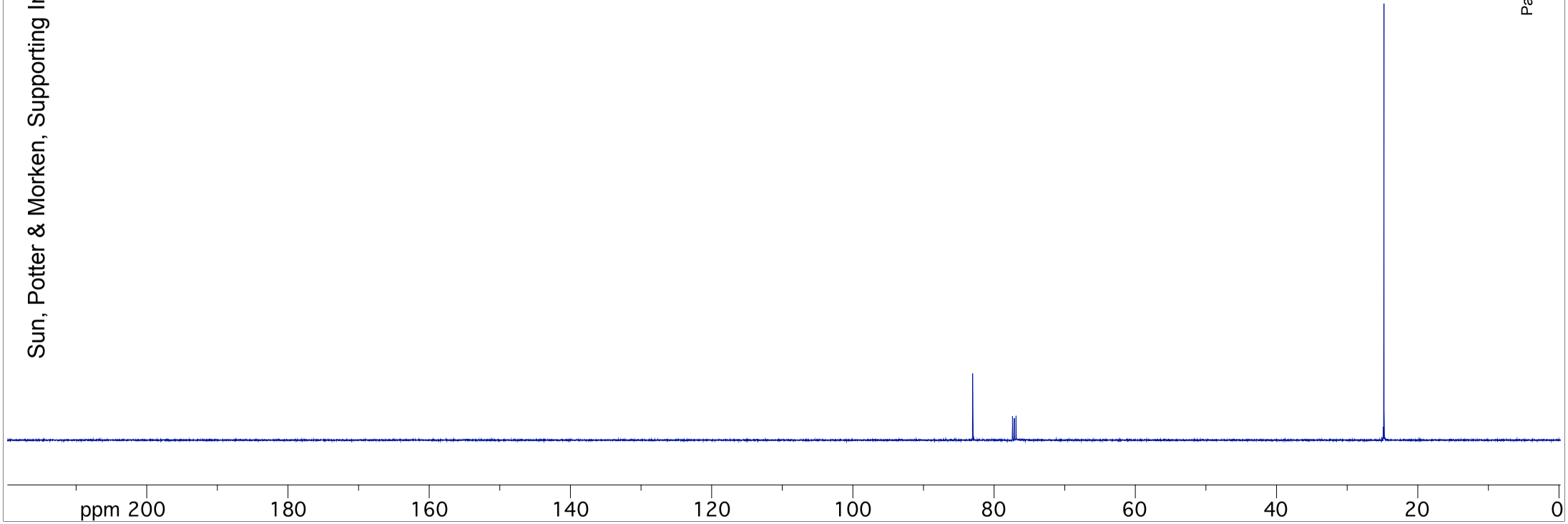
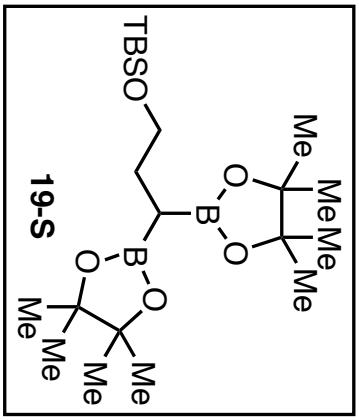
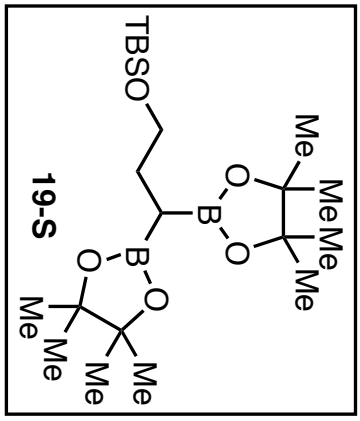




19-S


TBSO
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
O
O
B
B
O
O
O
O

19-S

ppm
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140
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100
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60
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20
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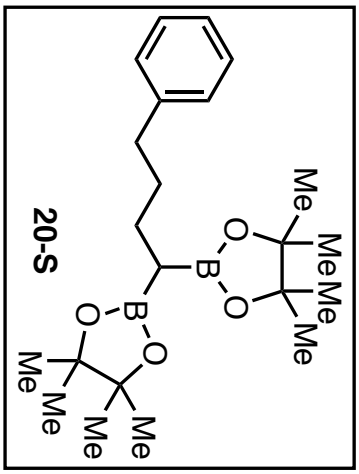
20-S
Me
Me
Me
Me
Me
Me
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B
B
O
O

ppm
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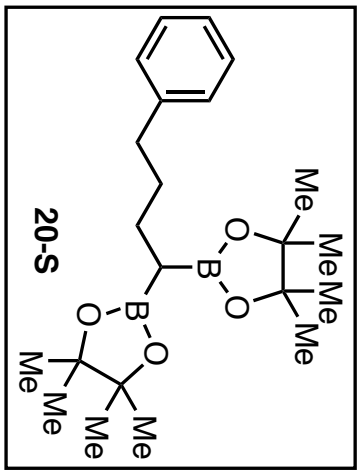
H2O


20-S
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Me
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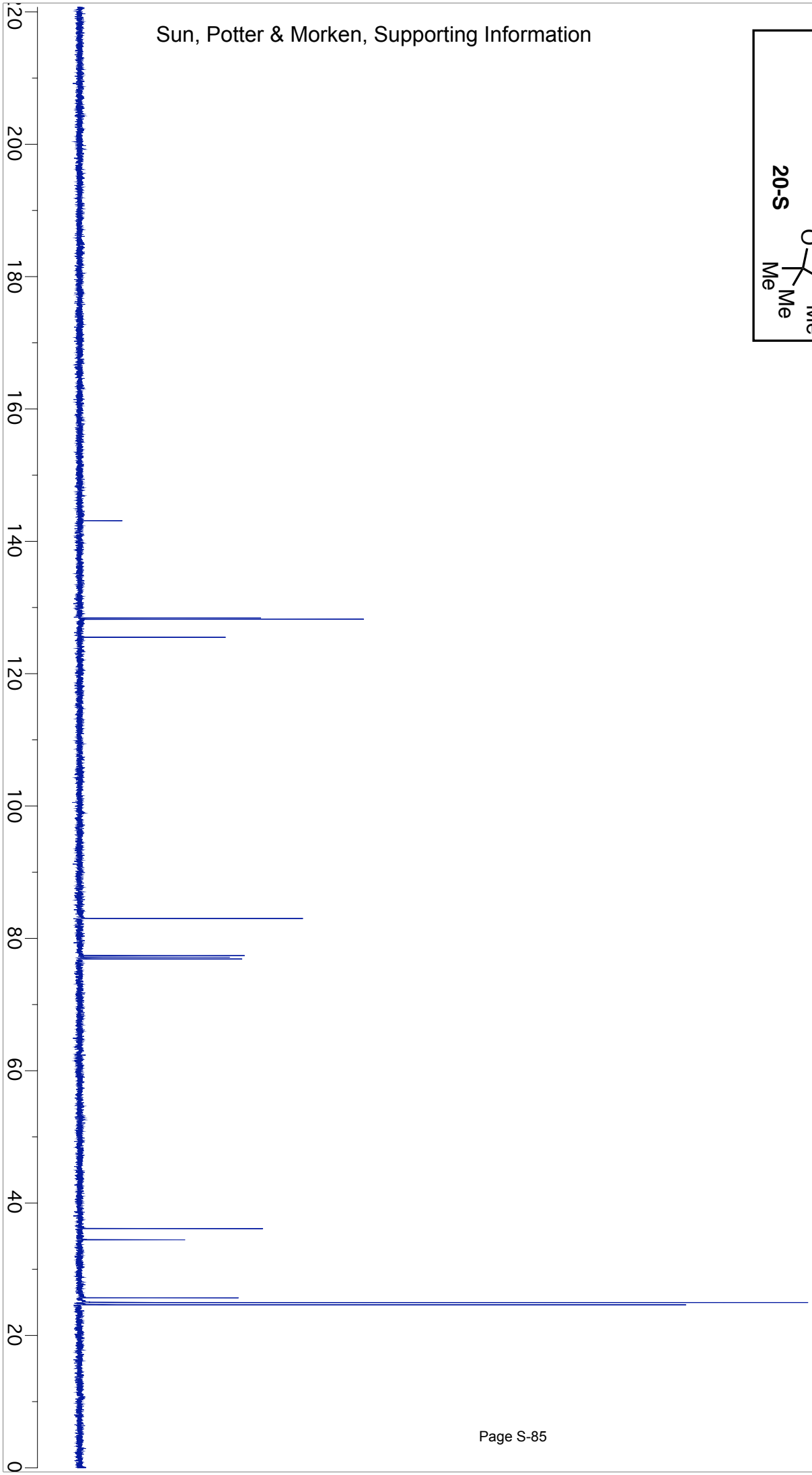
Me
Me
Me
Me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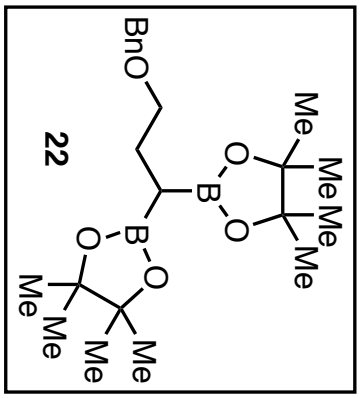

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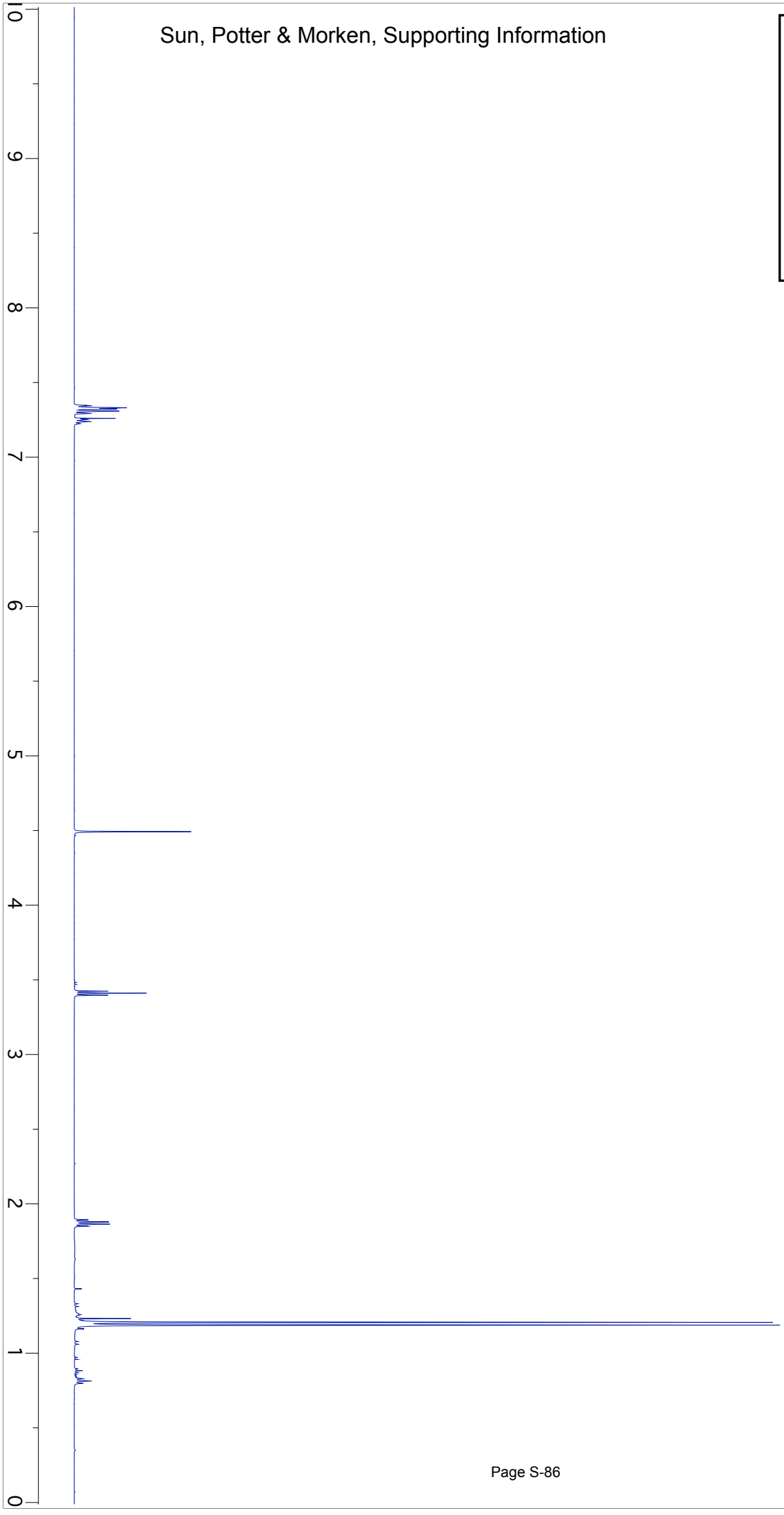

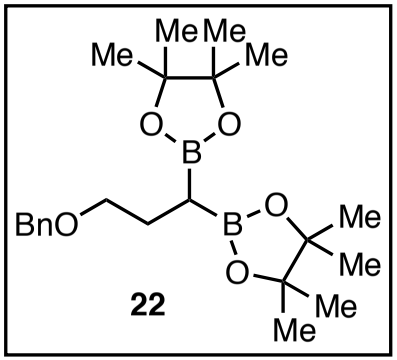
Me
Me
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O
O
B
BnO
B
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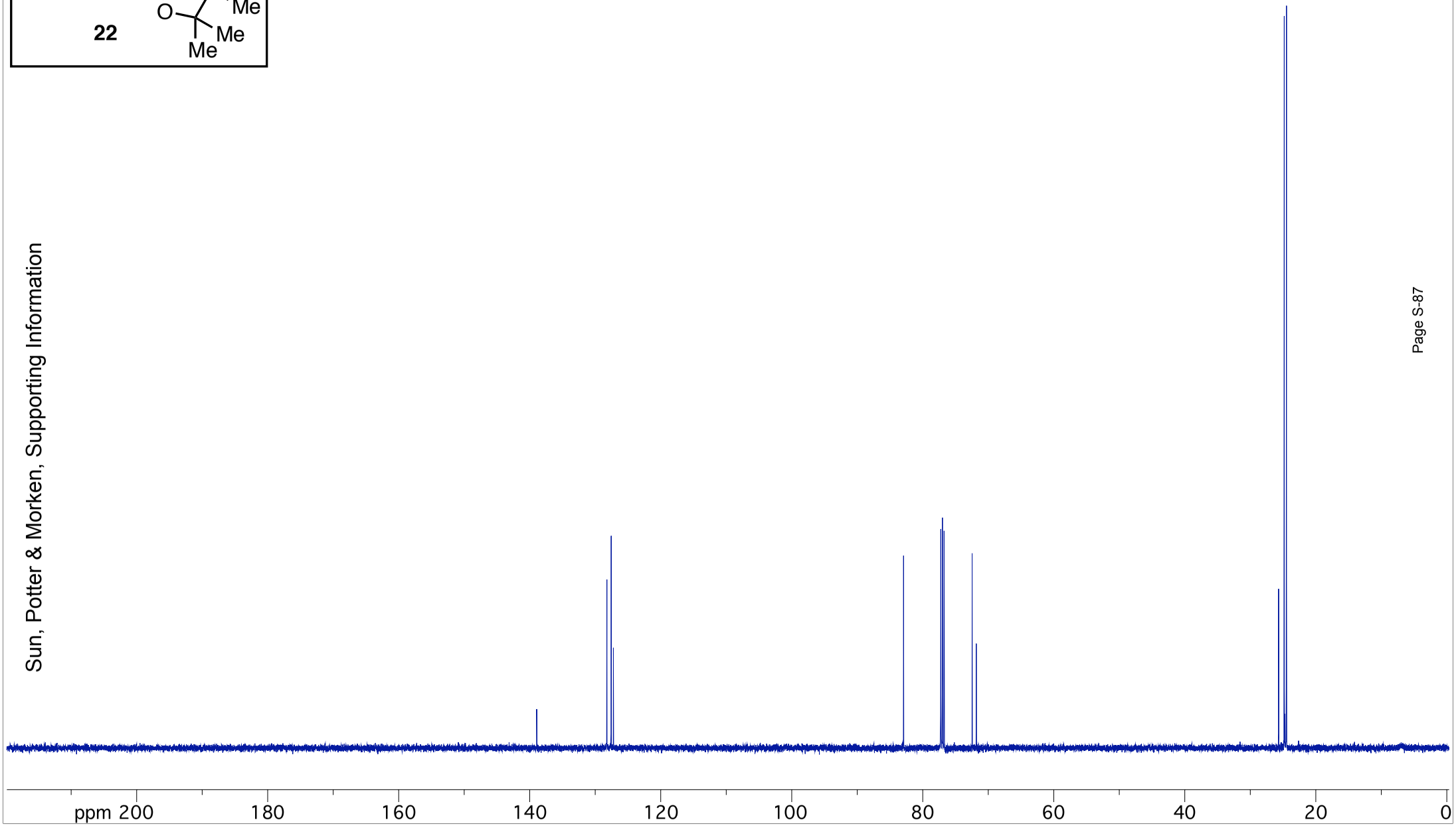
Me
Me
O
Me
Me
22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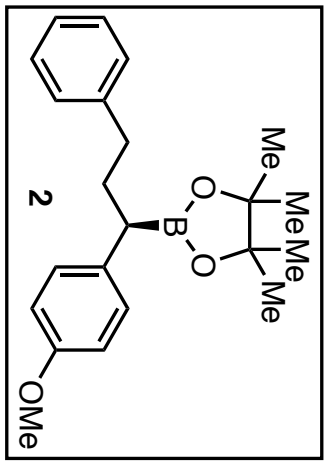
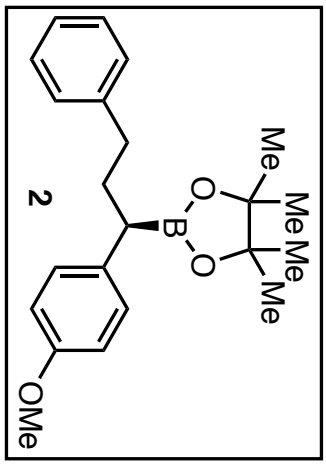

2
Me
Me
Me
Me
O
B
O
OMe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Me
Me
Me
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O
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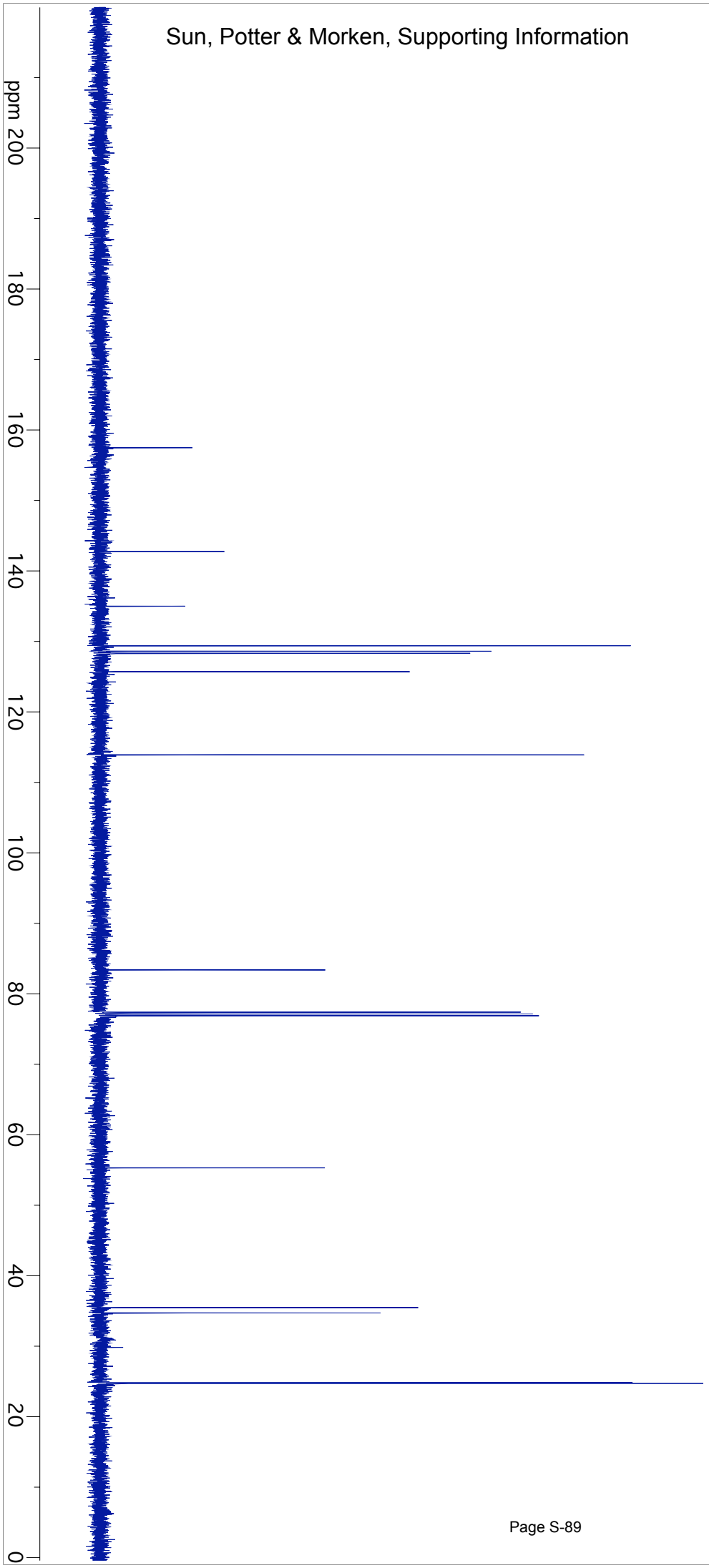
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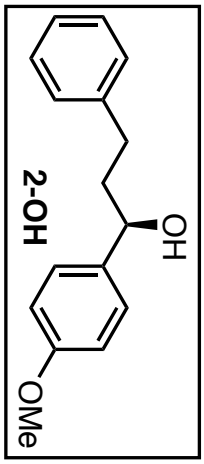
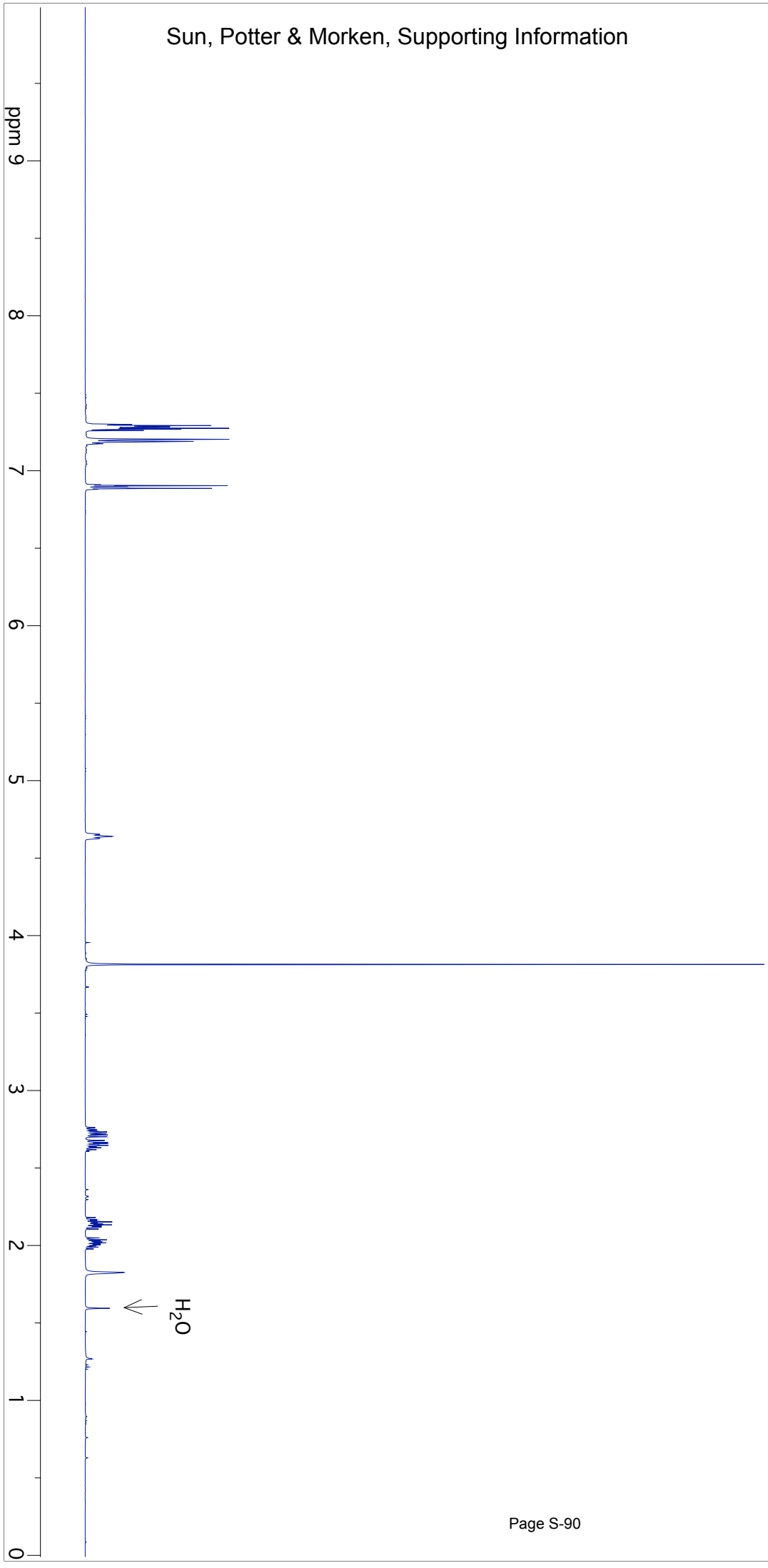

OH
2-OH
OMe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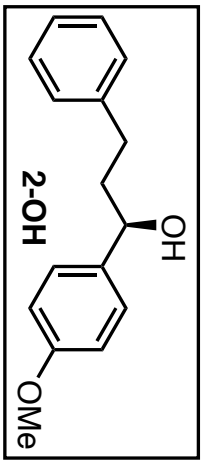
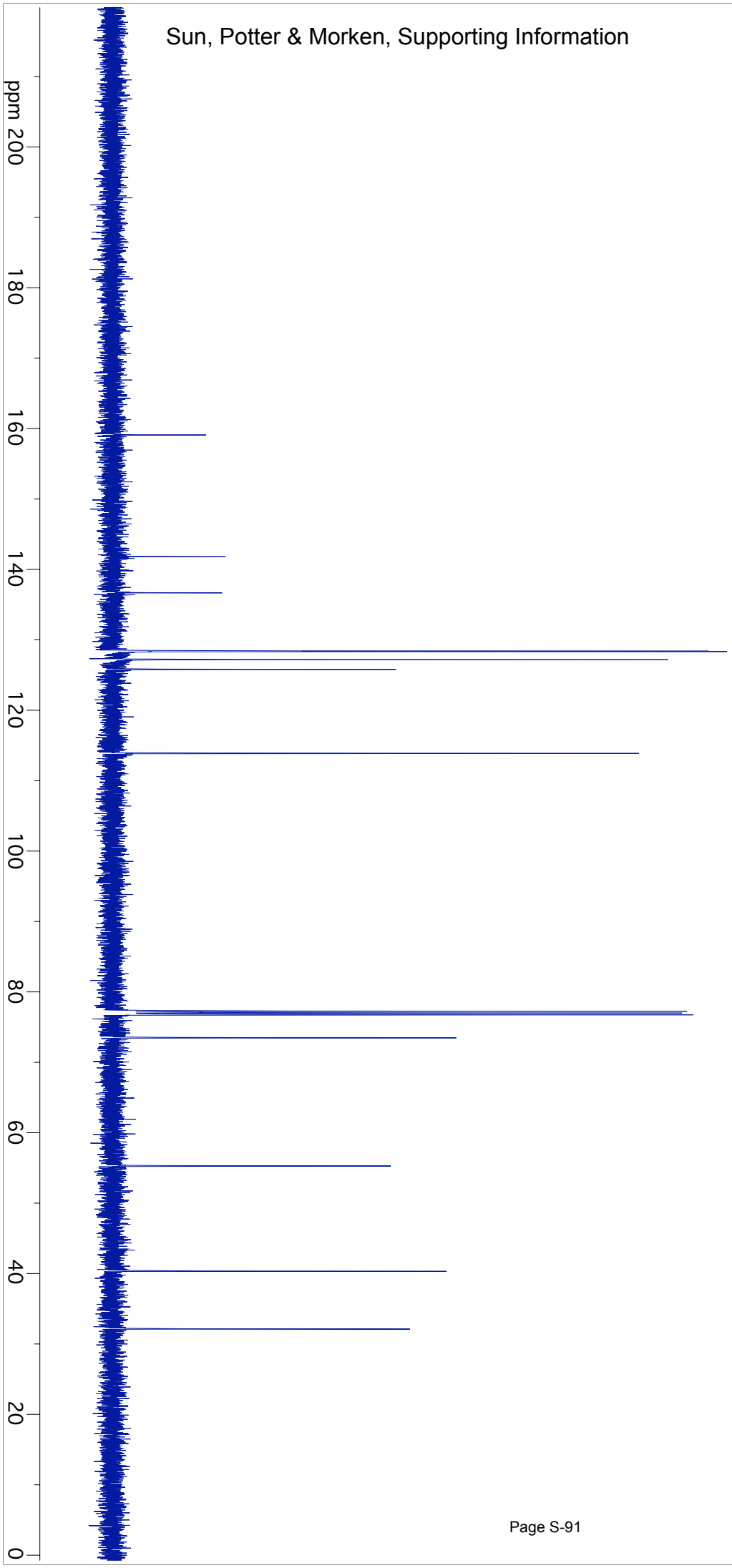

2-OH
OH
OMe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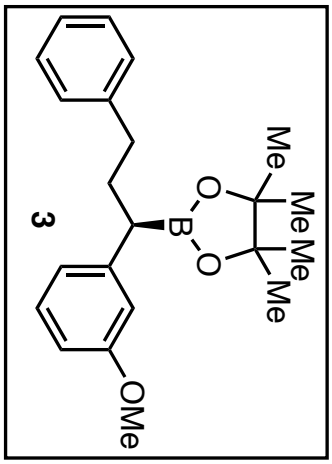
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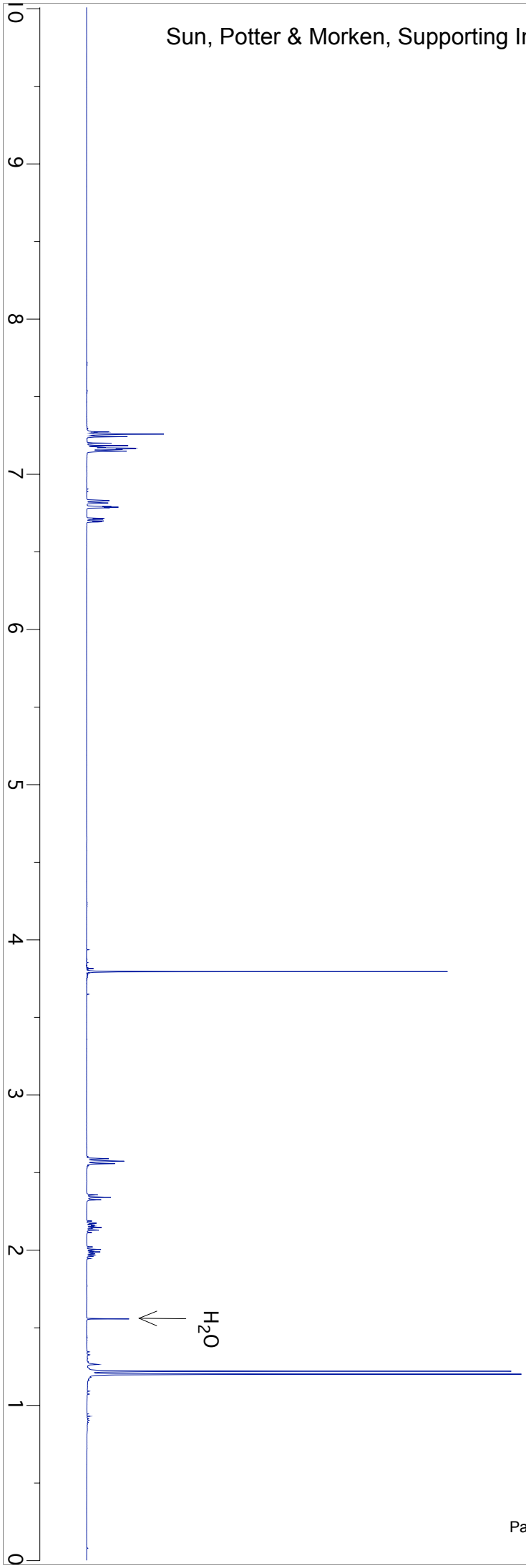
Me
Me
Me
Me
O
B
O
OMe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9
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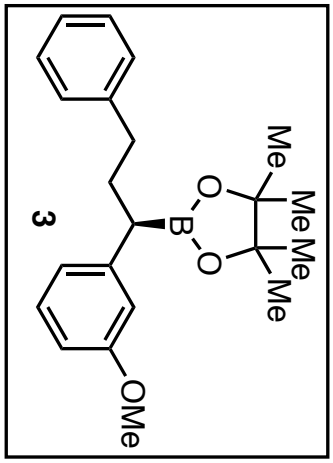
6
5
4
3
2
1
0
H2O


3
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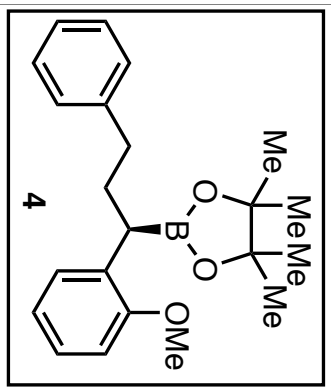
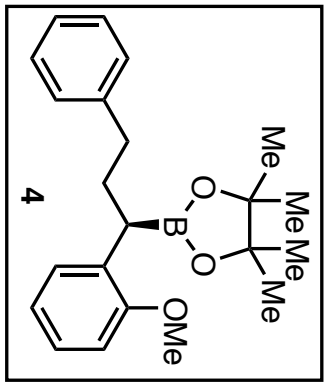
Me
Me
Me
O
B
O
OMe


4
Me
Me
Me
Me
O
B
O
OMe

10
9
8
7
6
5
4
3
2
1
H2O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Me
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Me
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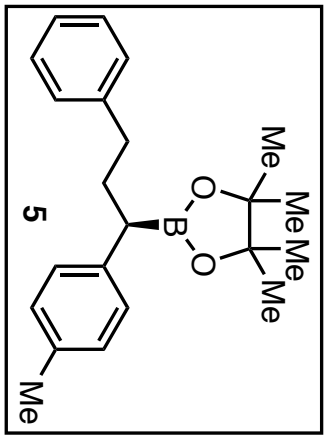
B
O
OMe


Me
Me Me
Me
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B
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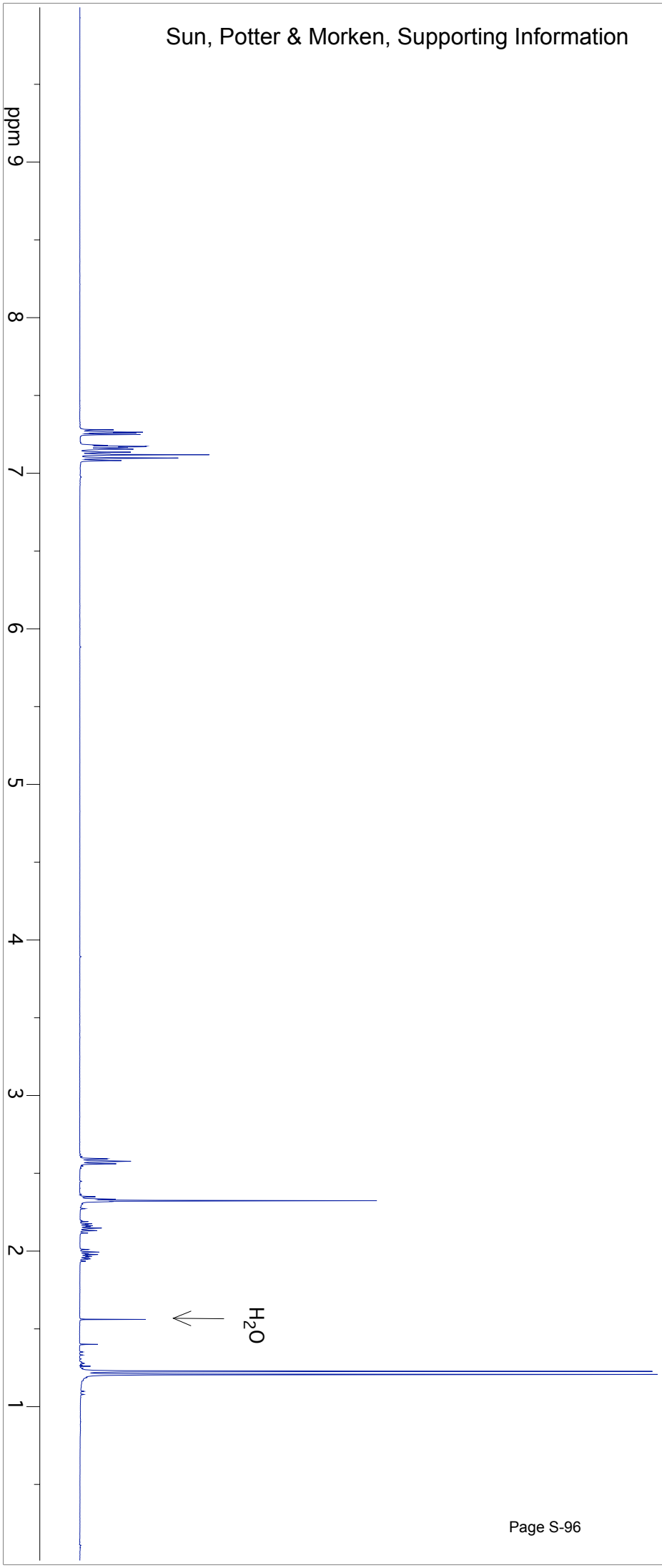
Me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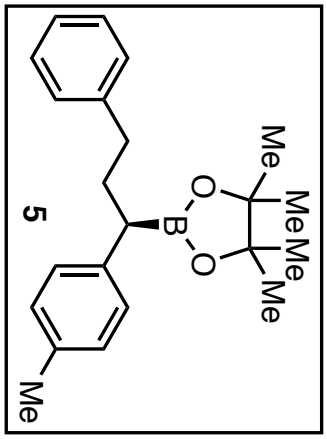
H2O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Me
Me
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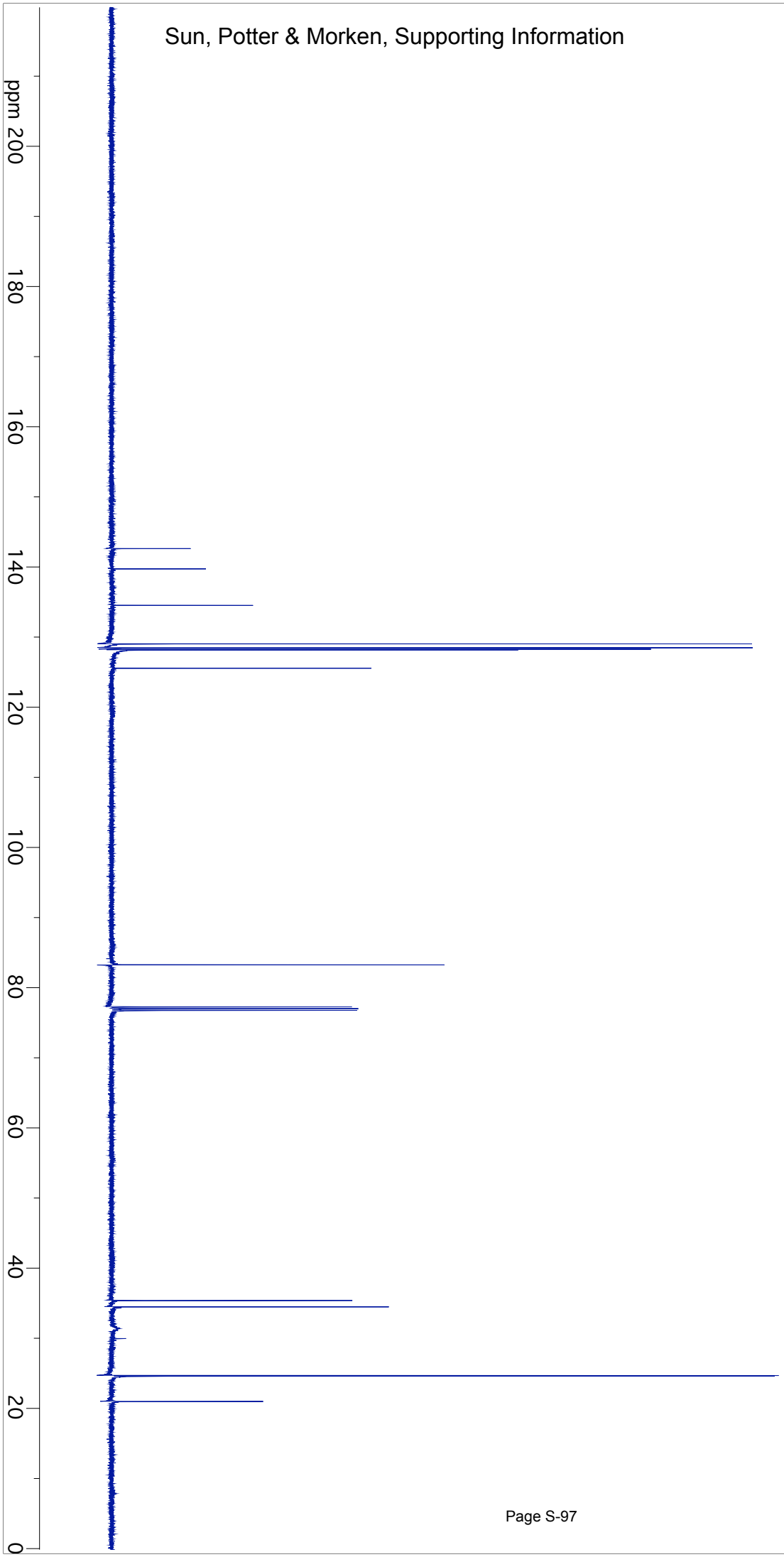
O
B
O
Me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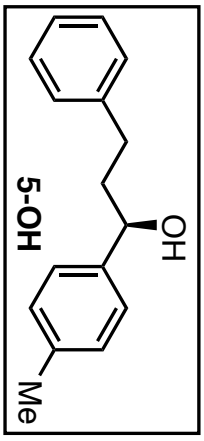
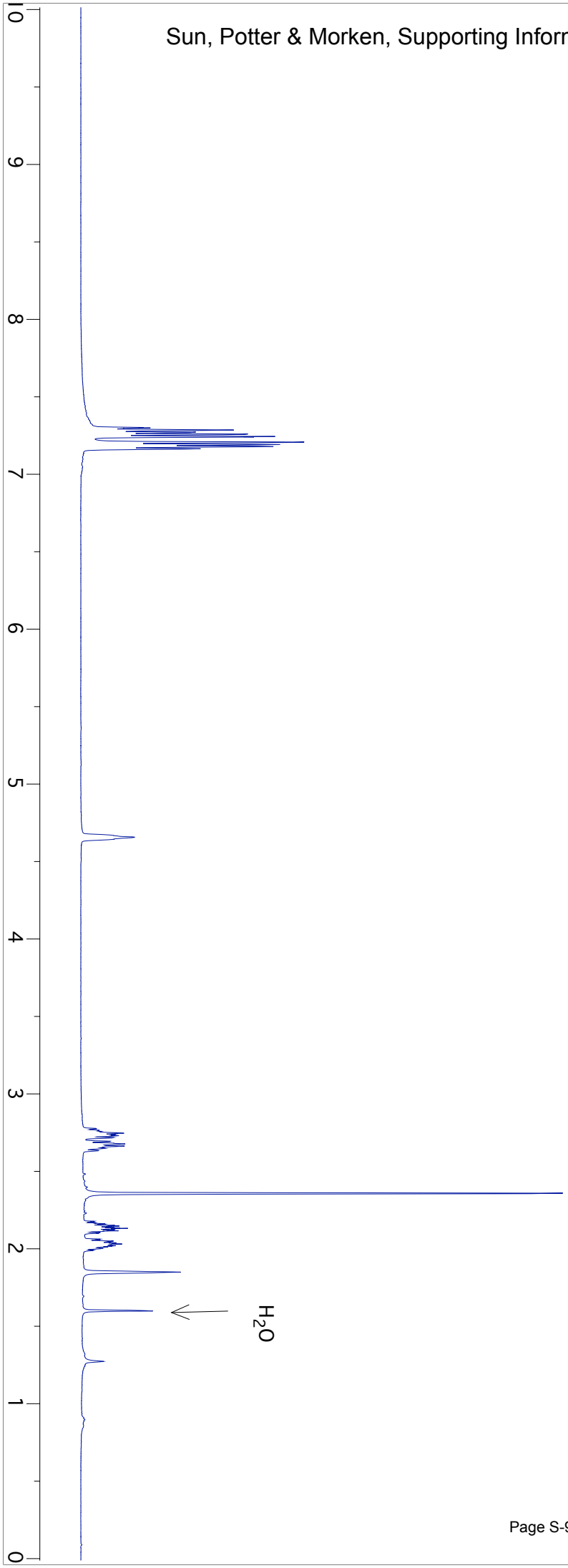

5-OH
OH
Me


10
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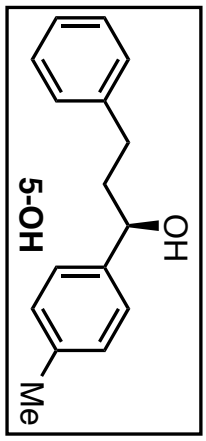
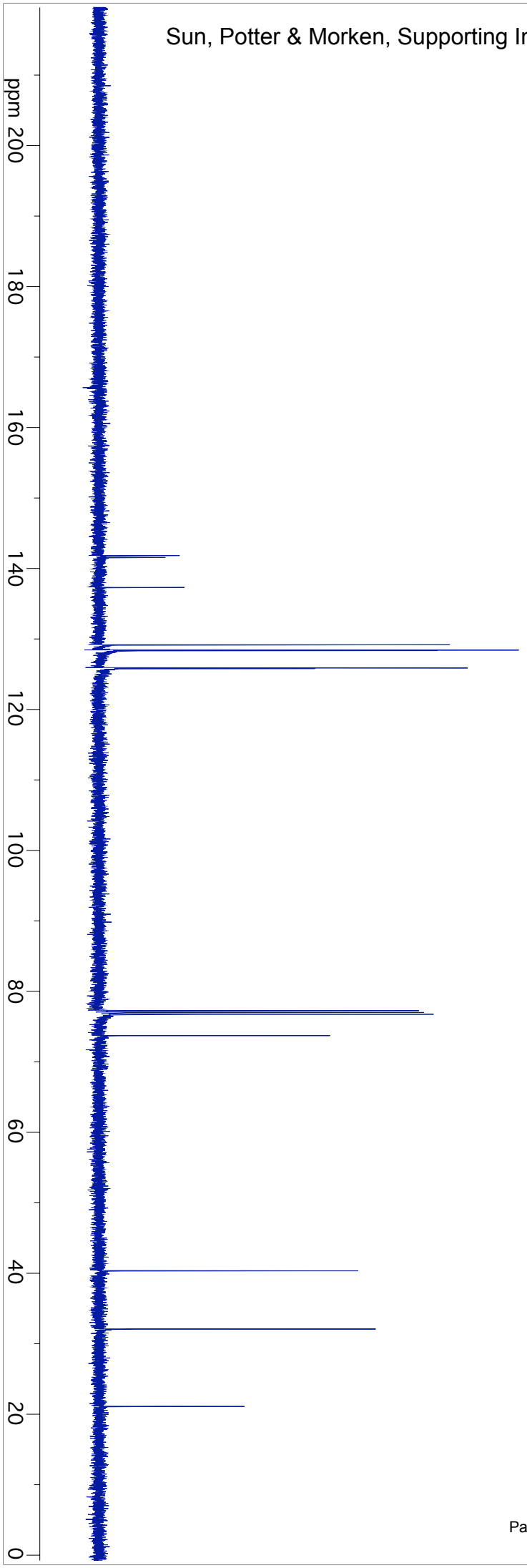
6
5
4
3
2
1
0
H2O


OH
5-OH
Me


ppm
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120
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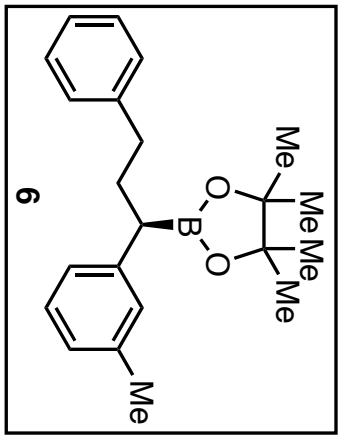
6
Me
Me
Me
Me
O
B
O
Me

10
9
8
7
6
5
4
3
2
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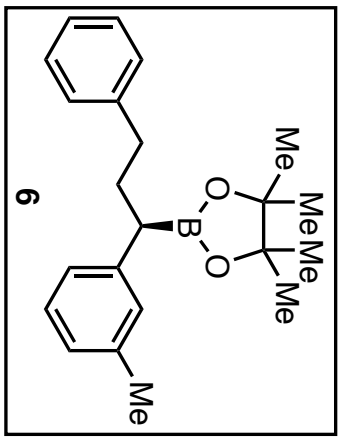
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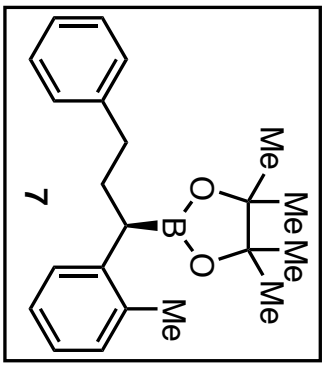
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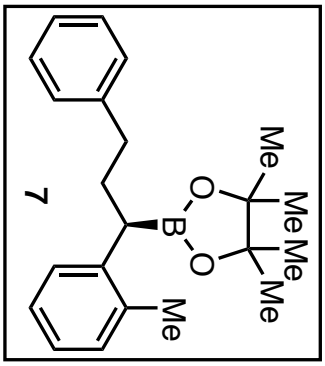
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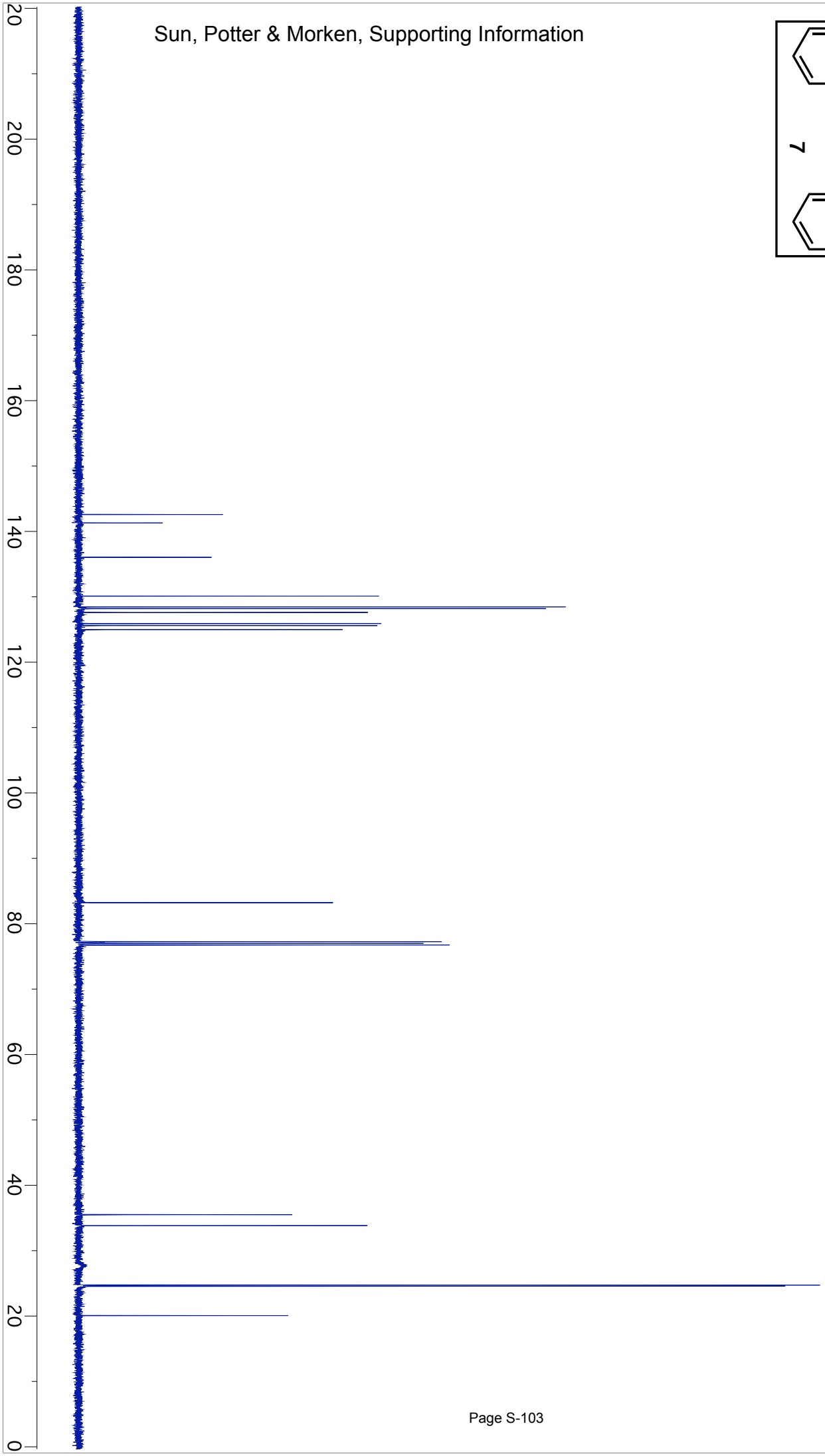
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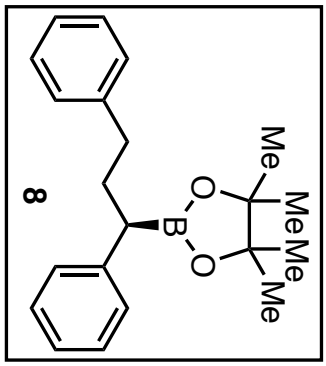
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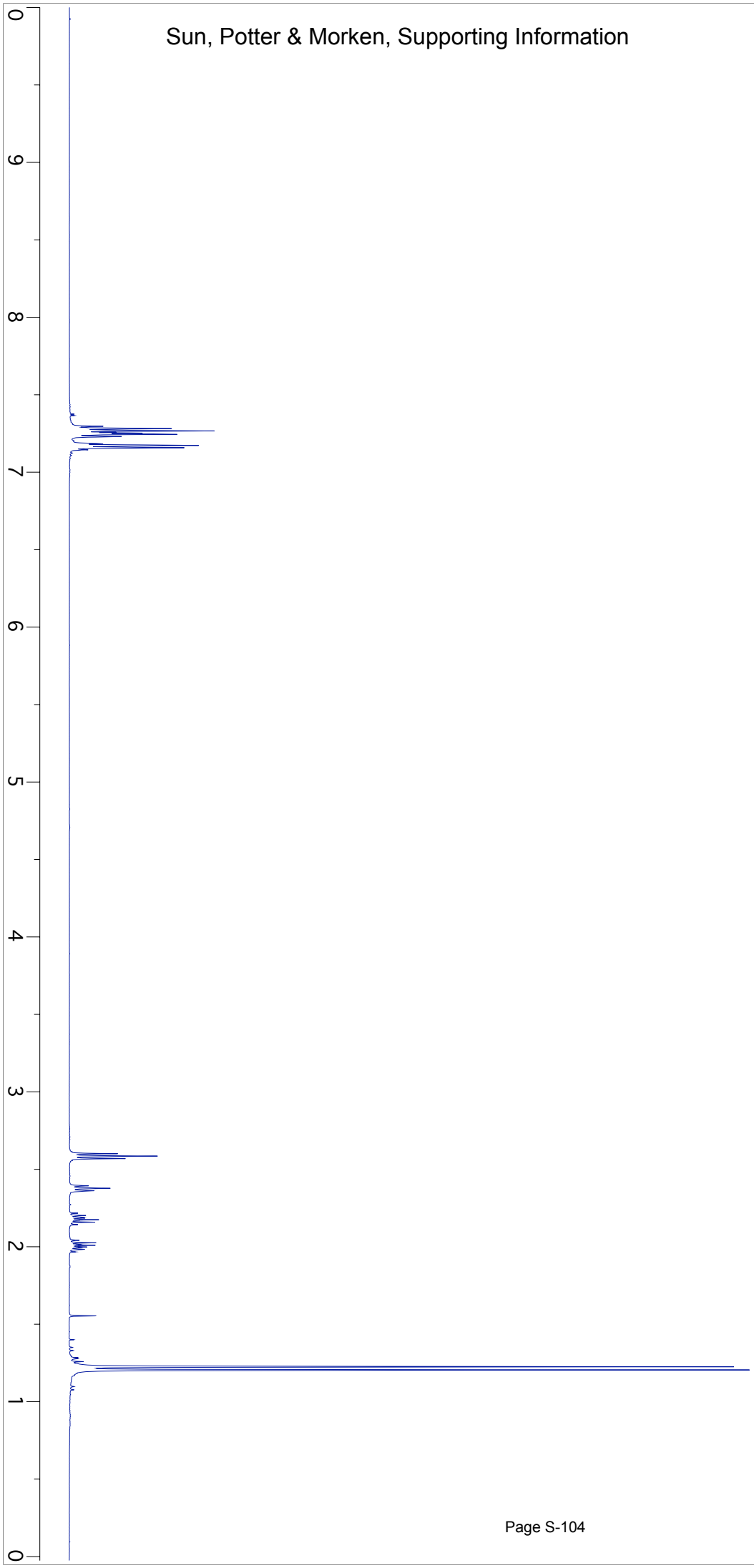
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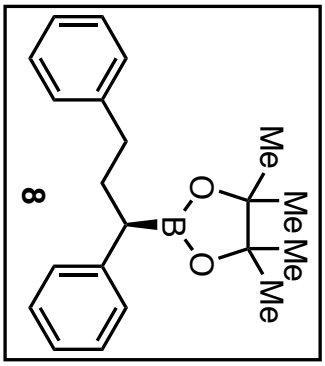
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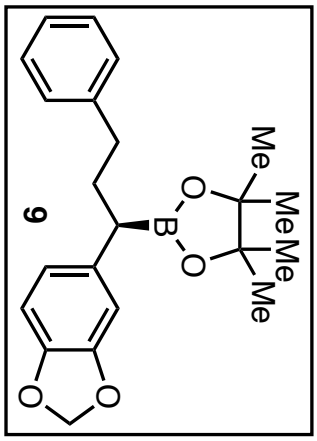
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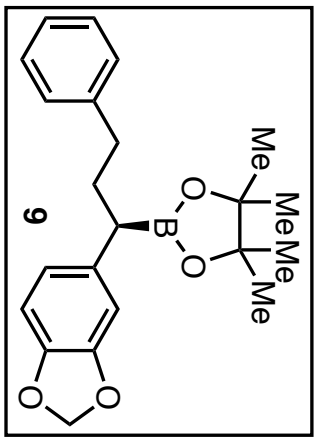
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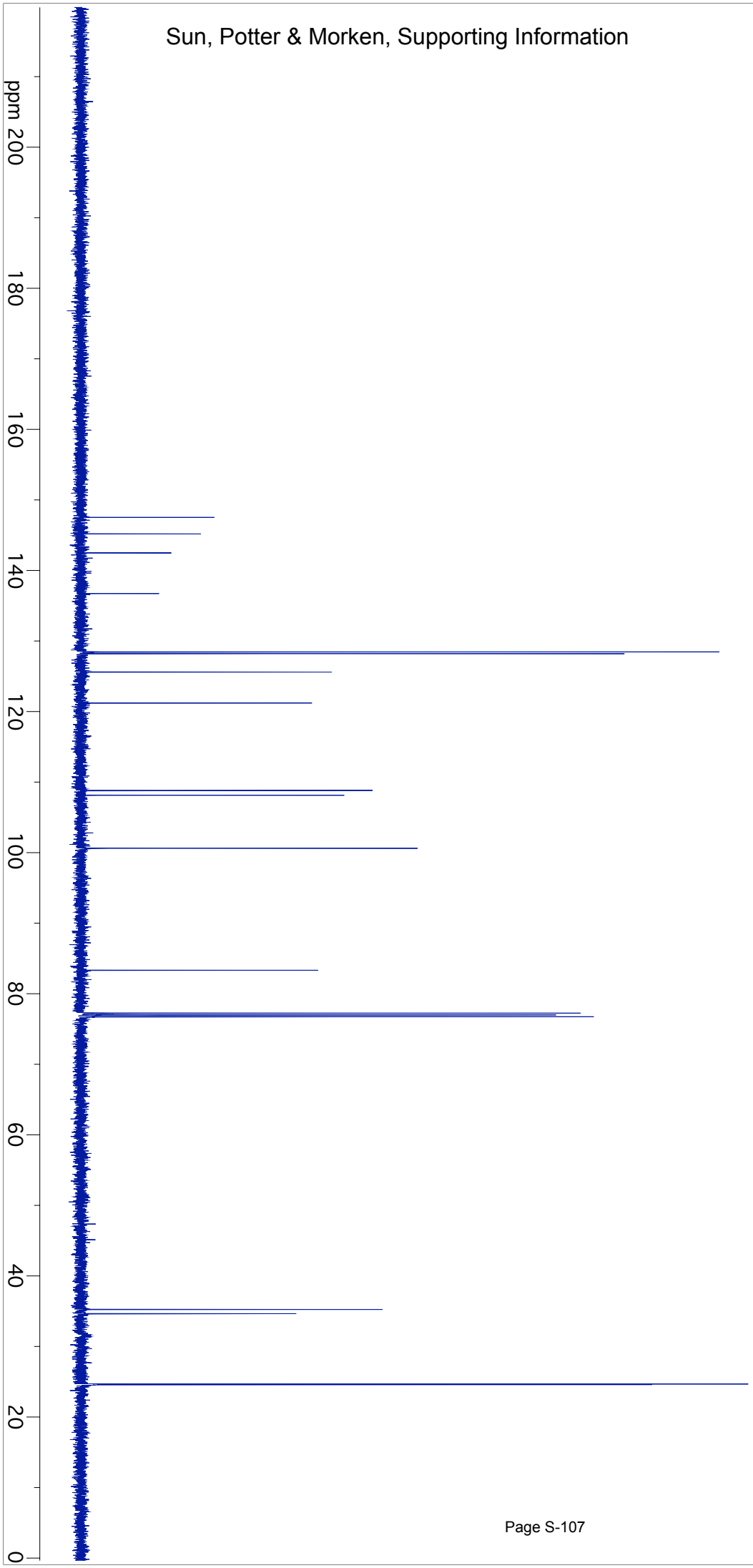
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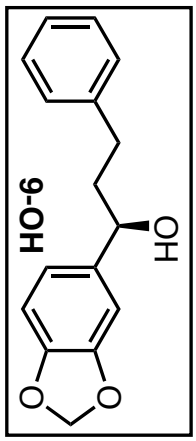
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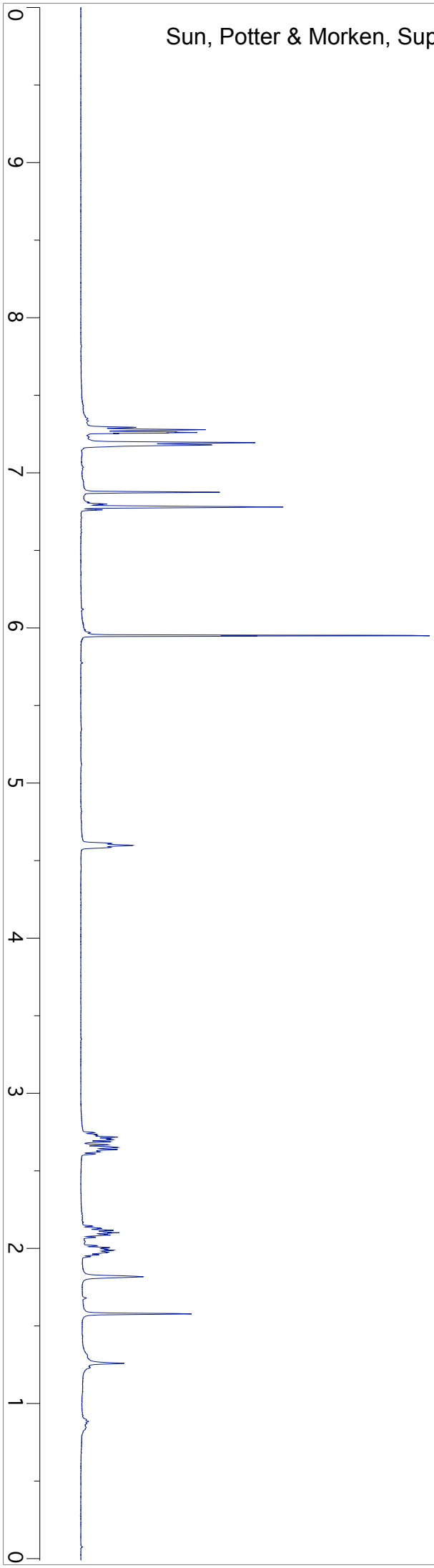
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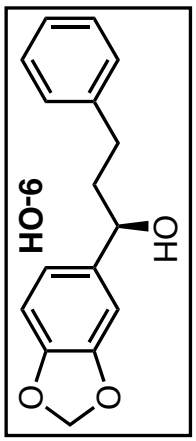
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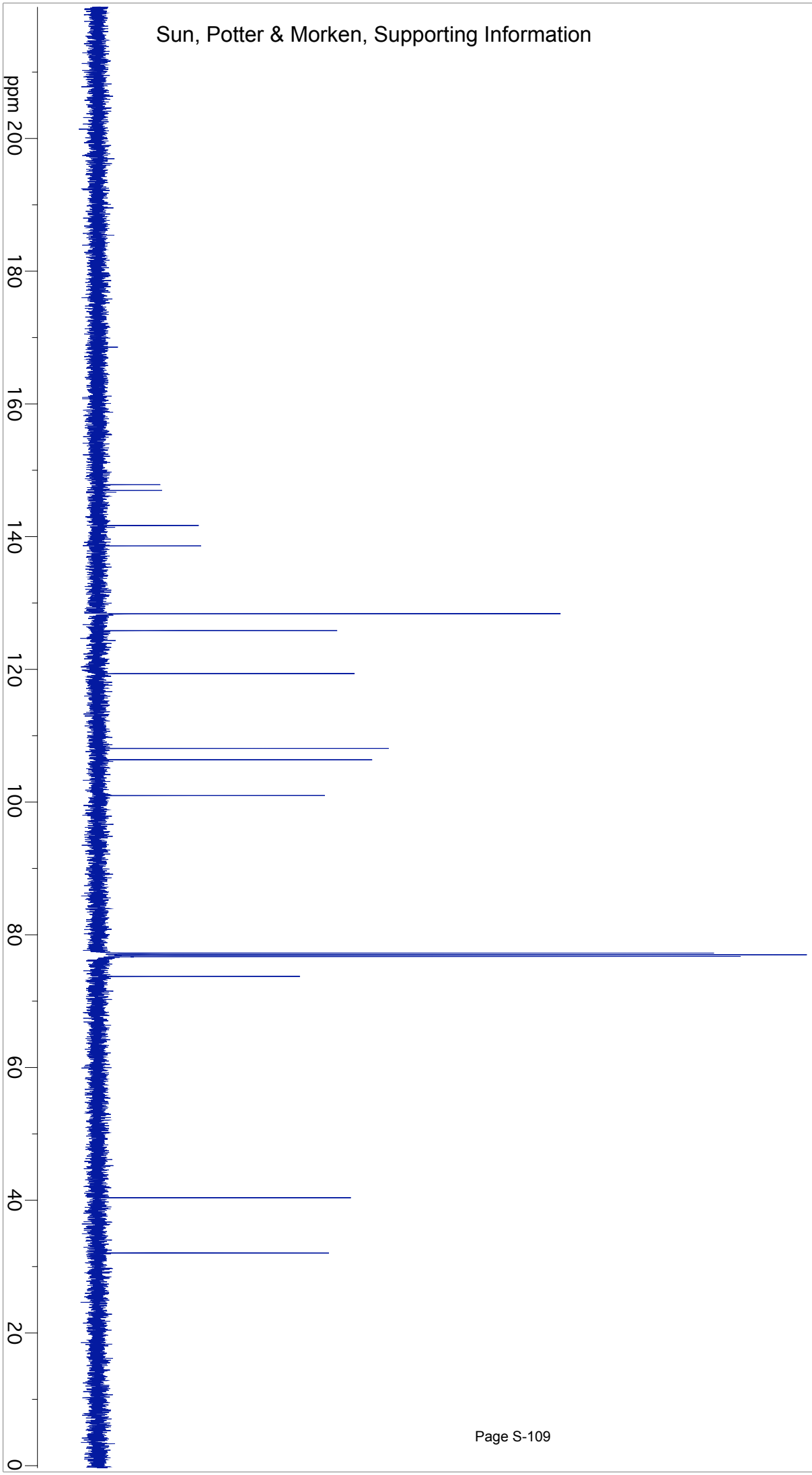
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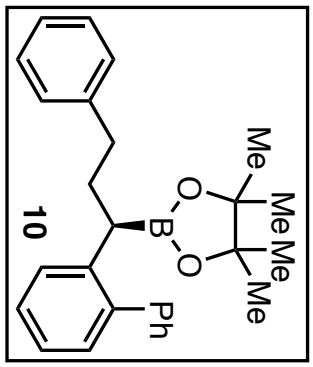
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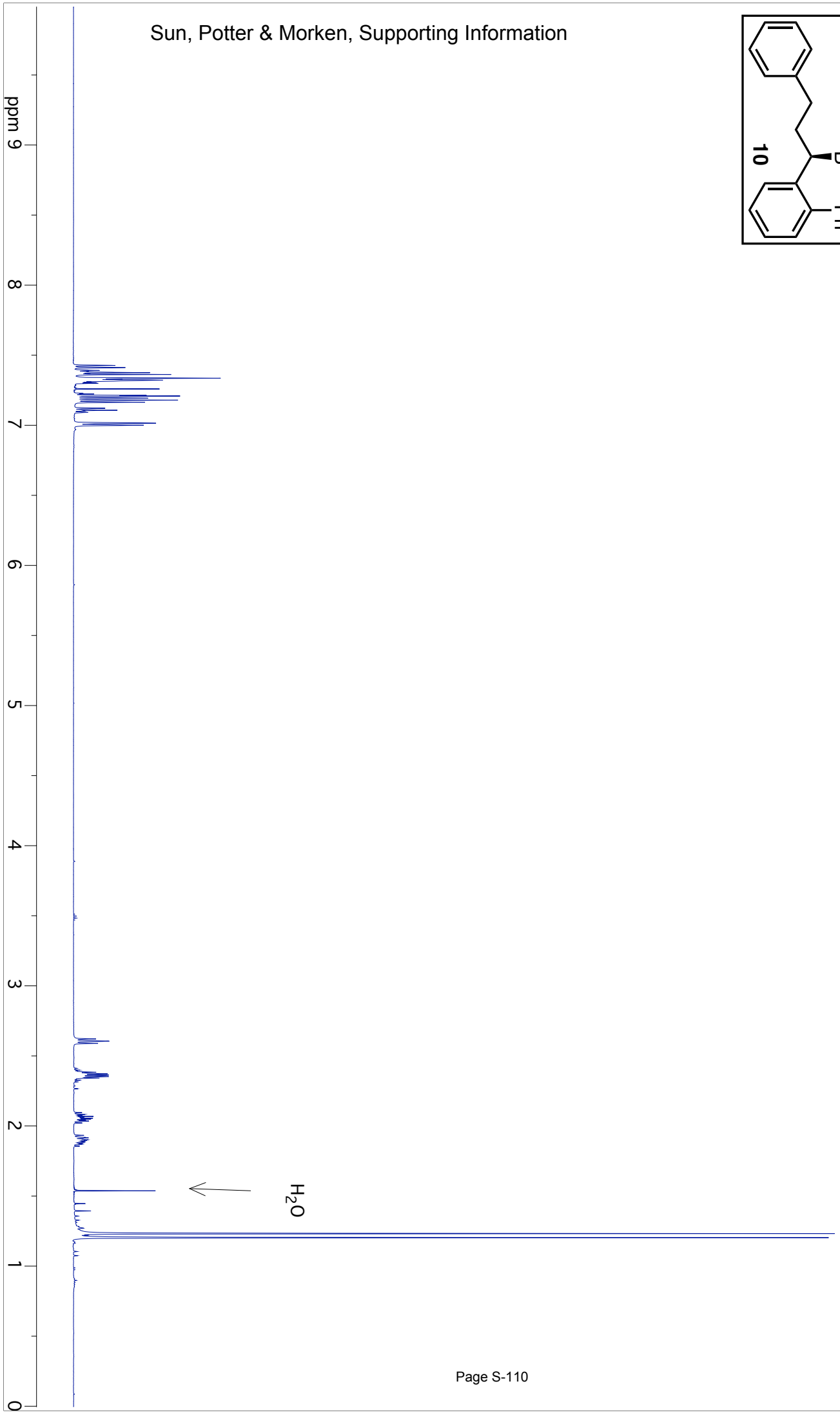
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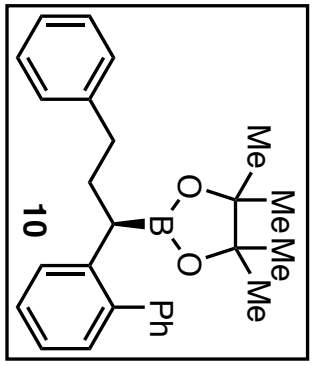
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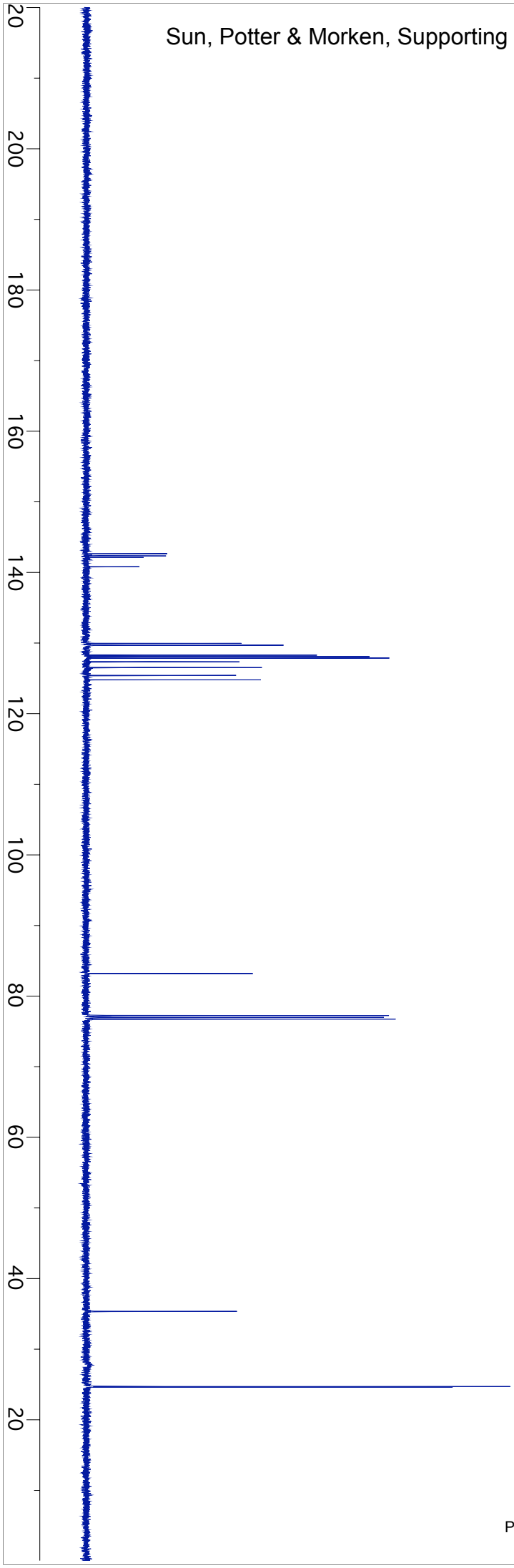
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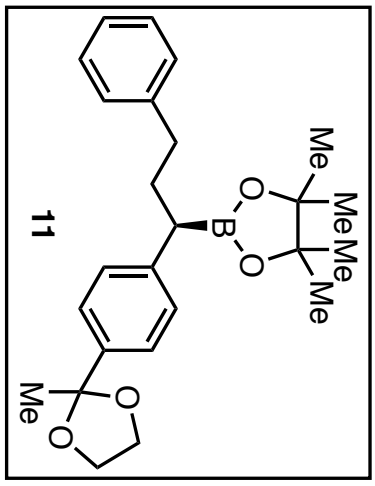
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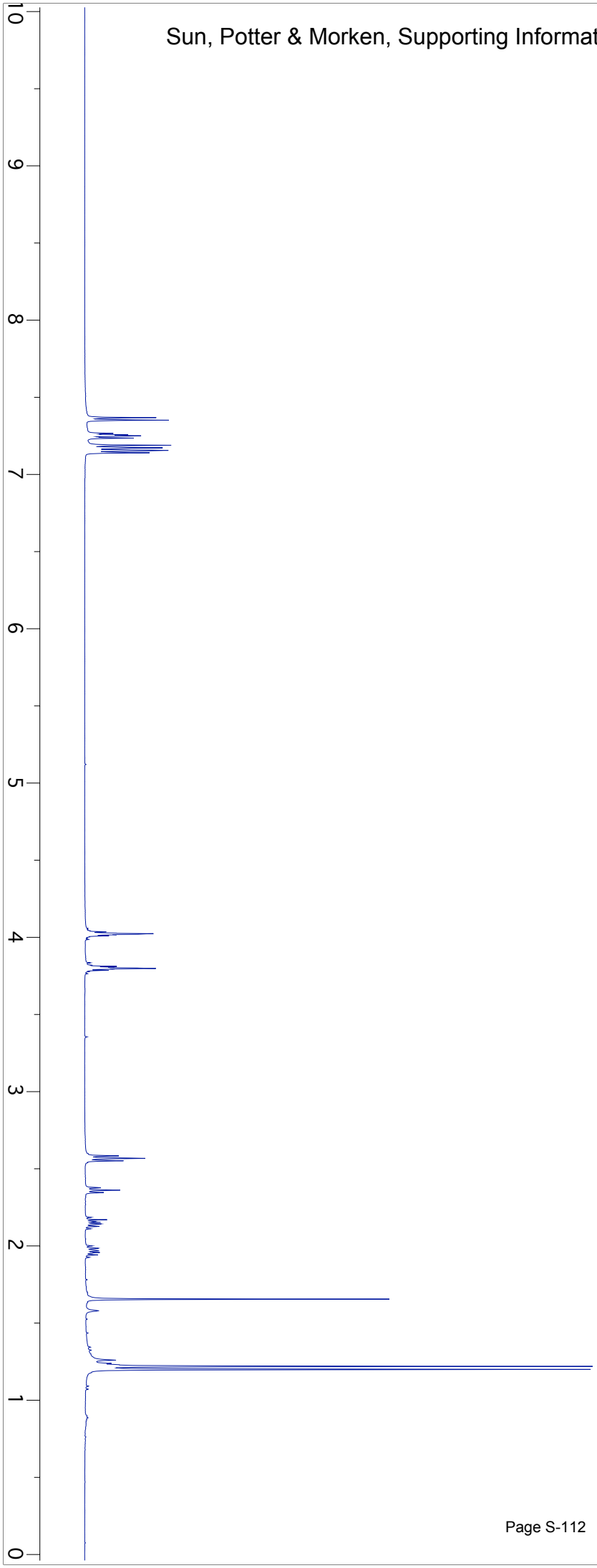
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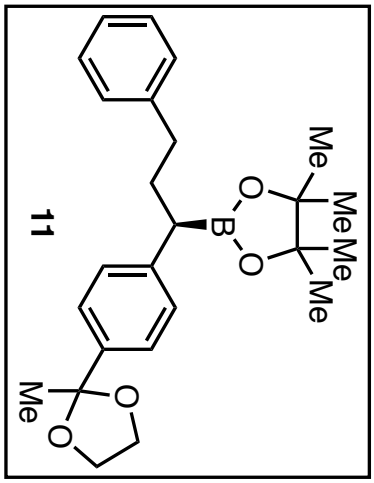
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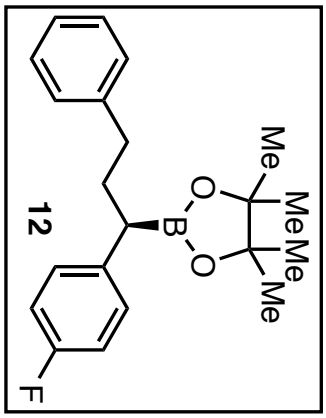
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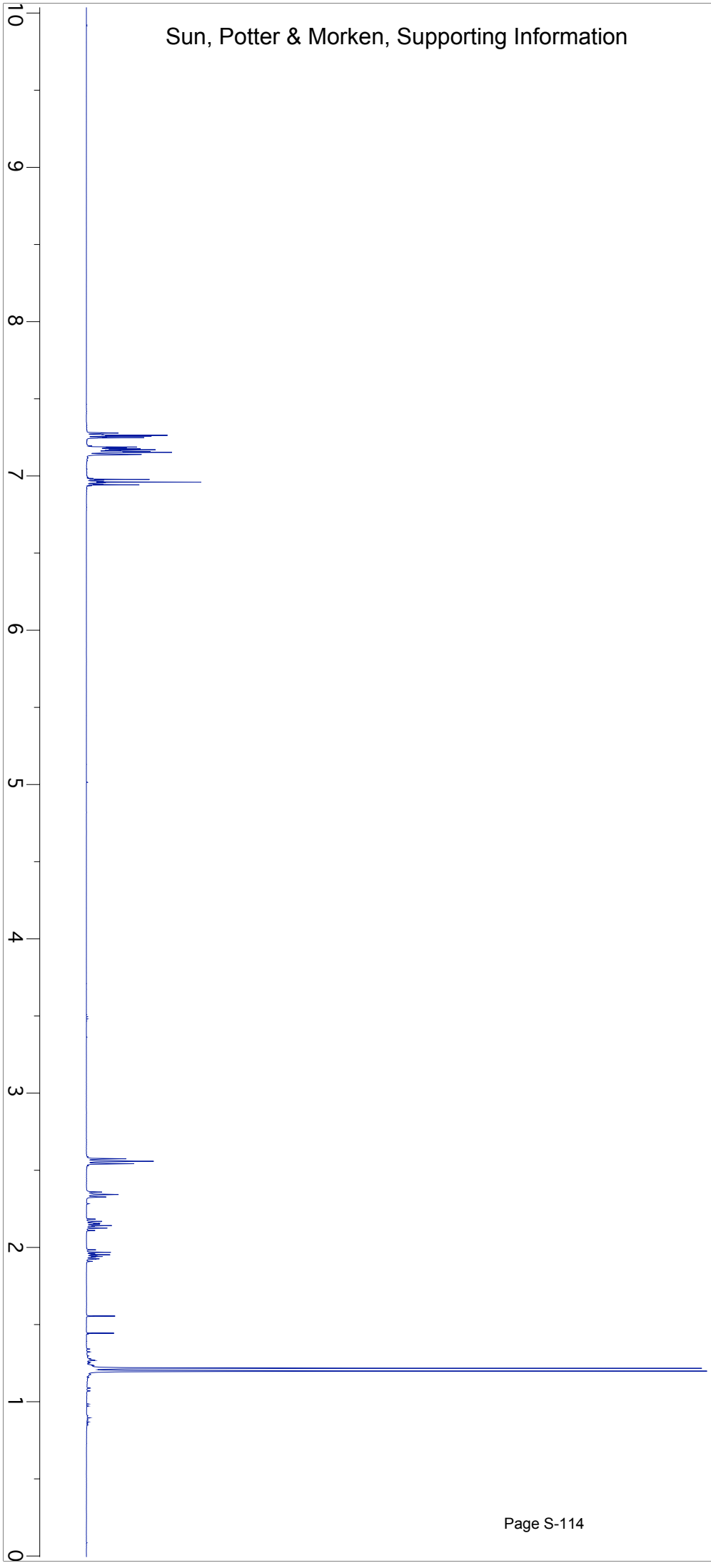
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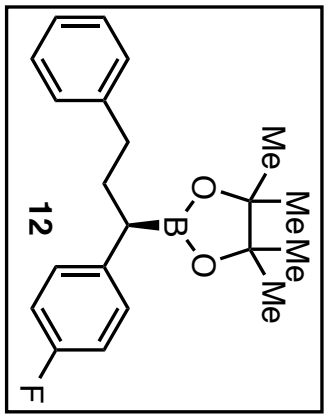
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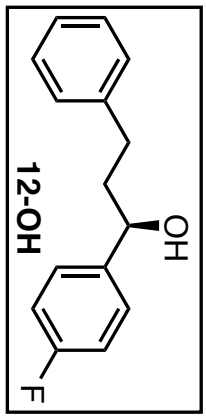
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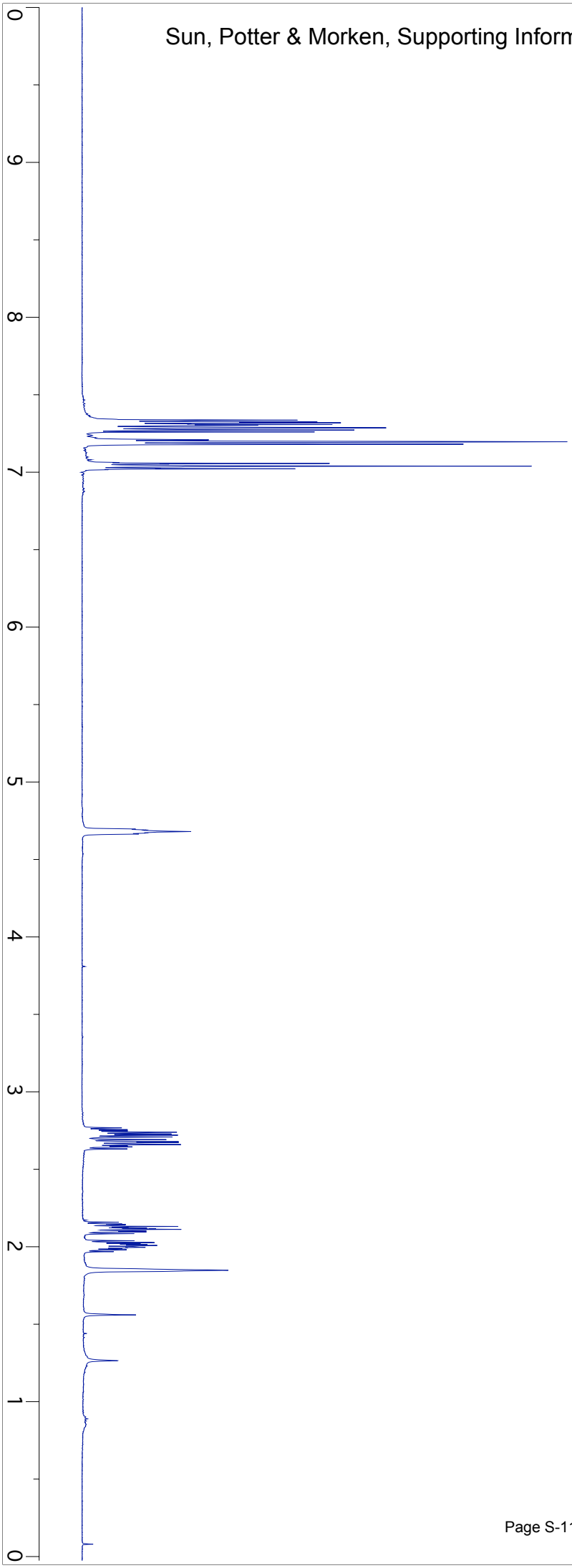
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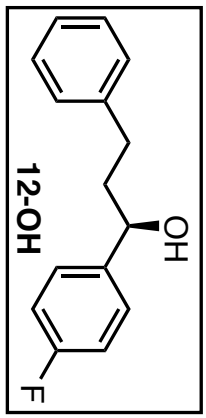
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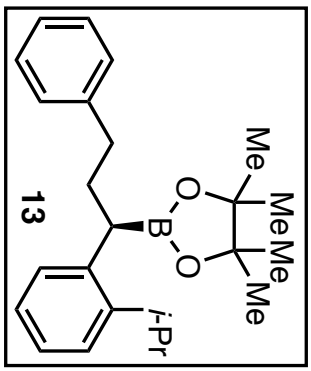
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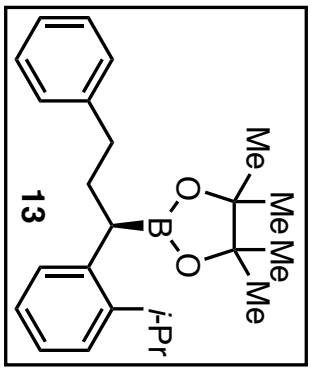
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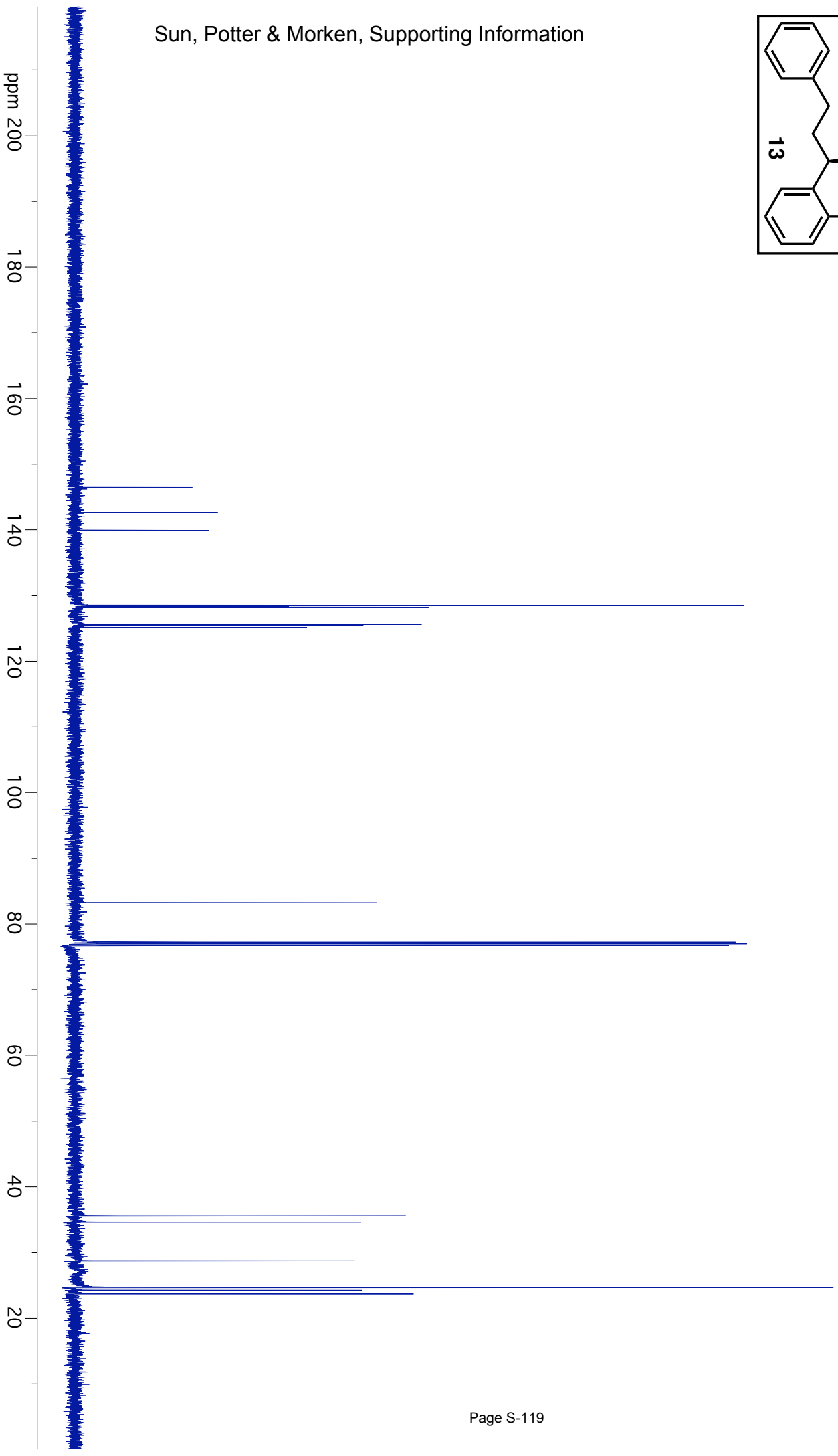
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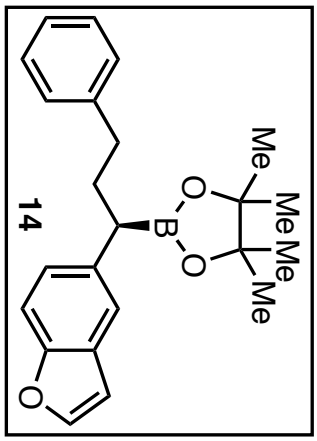
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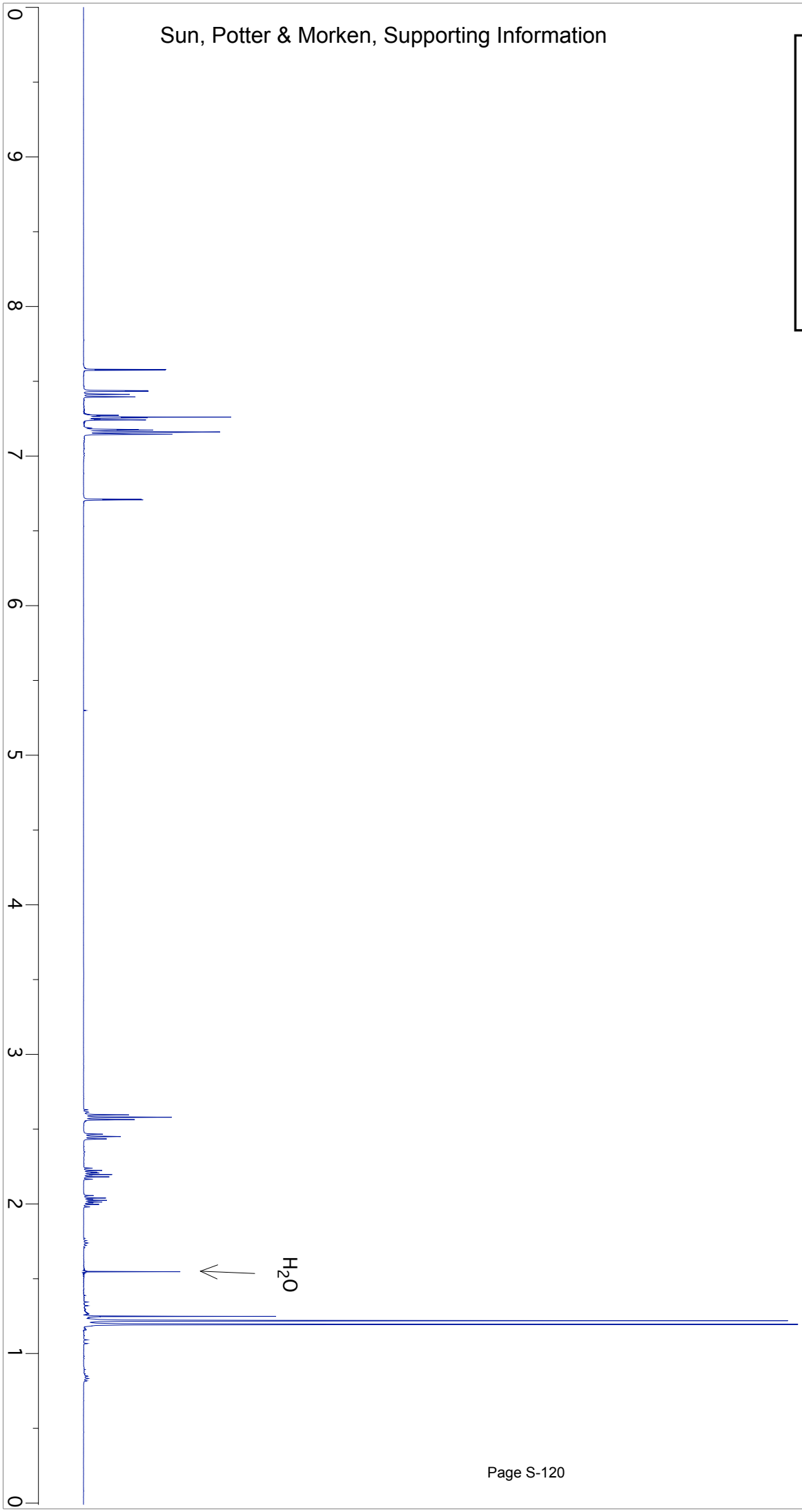
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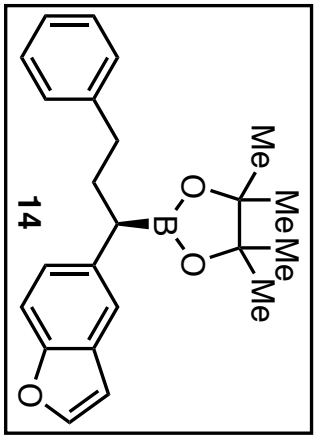
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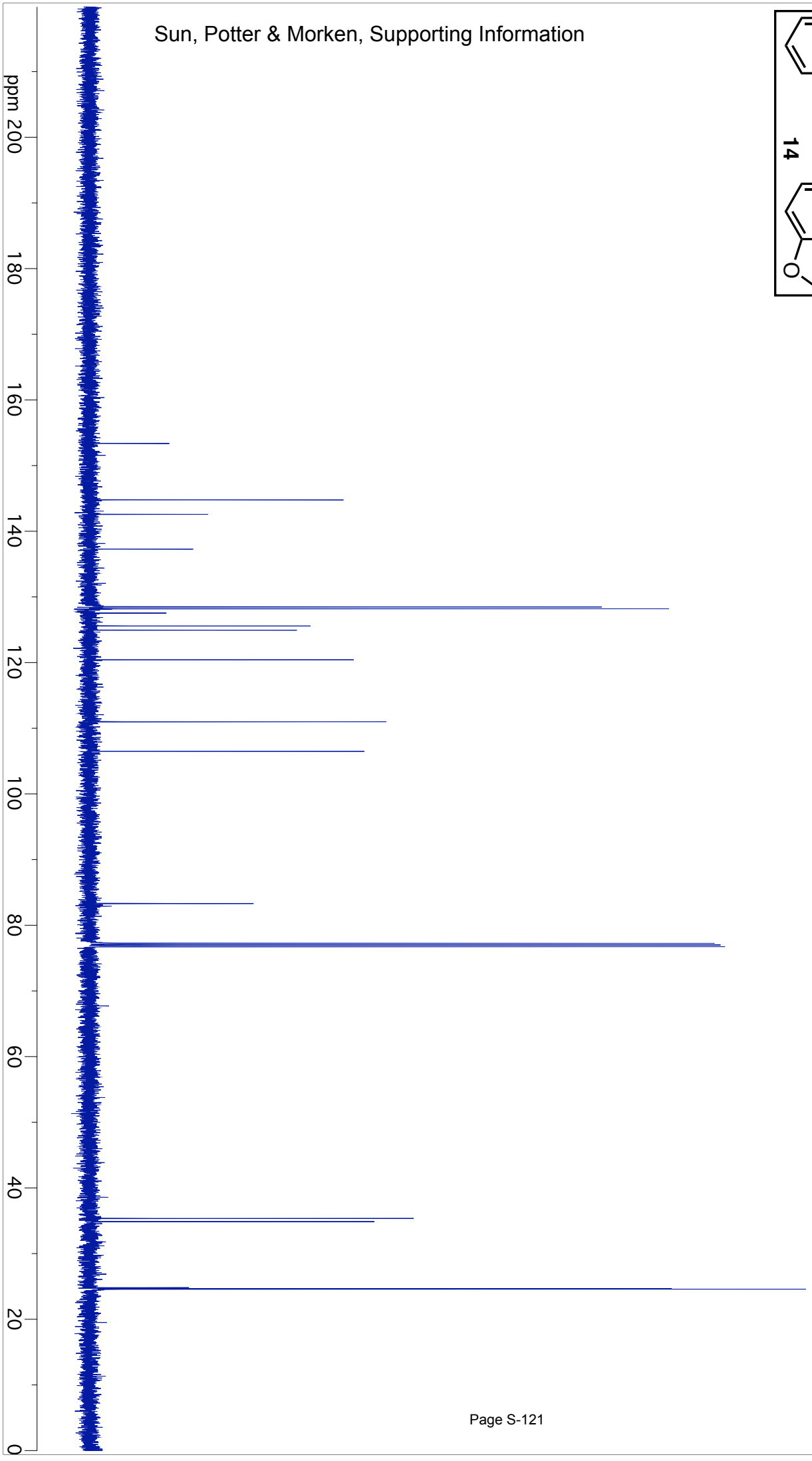
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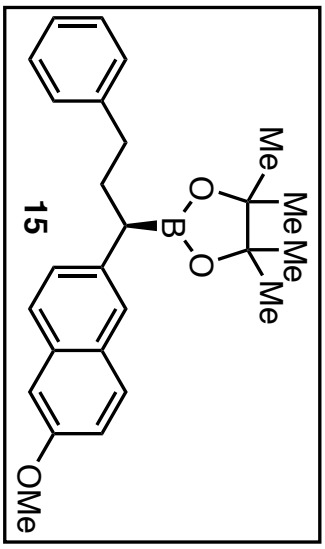
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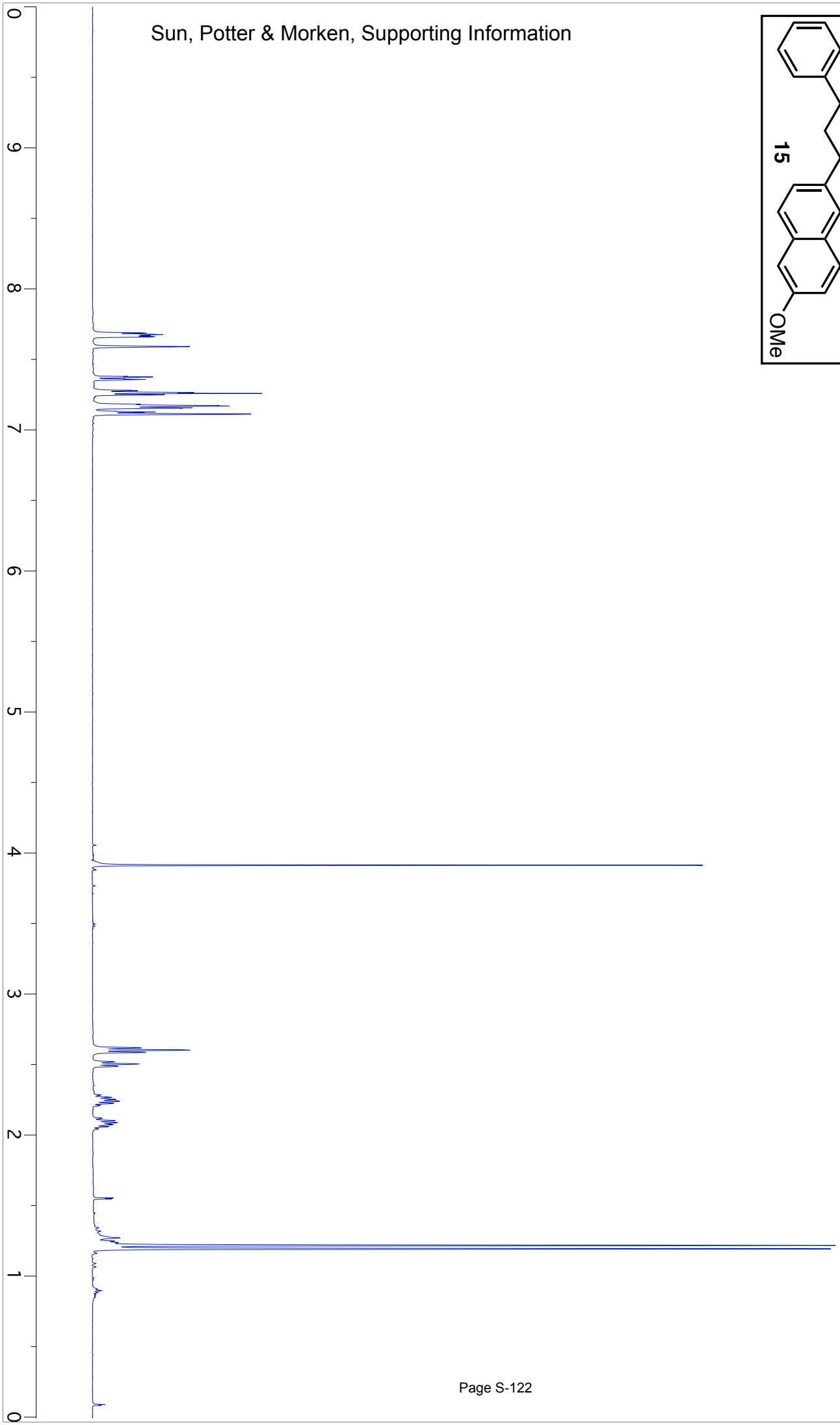
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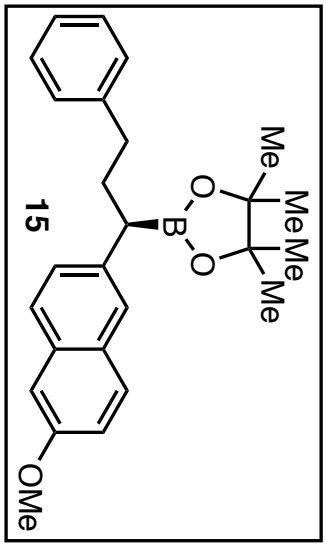
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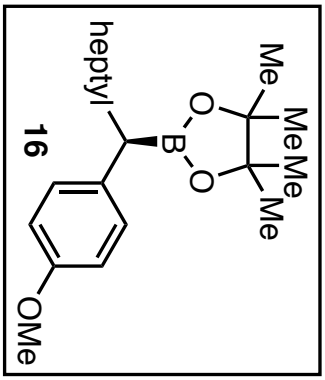
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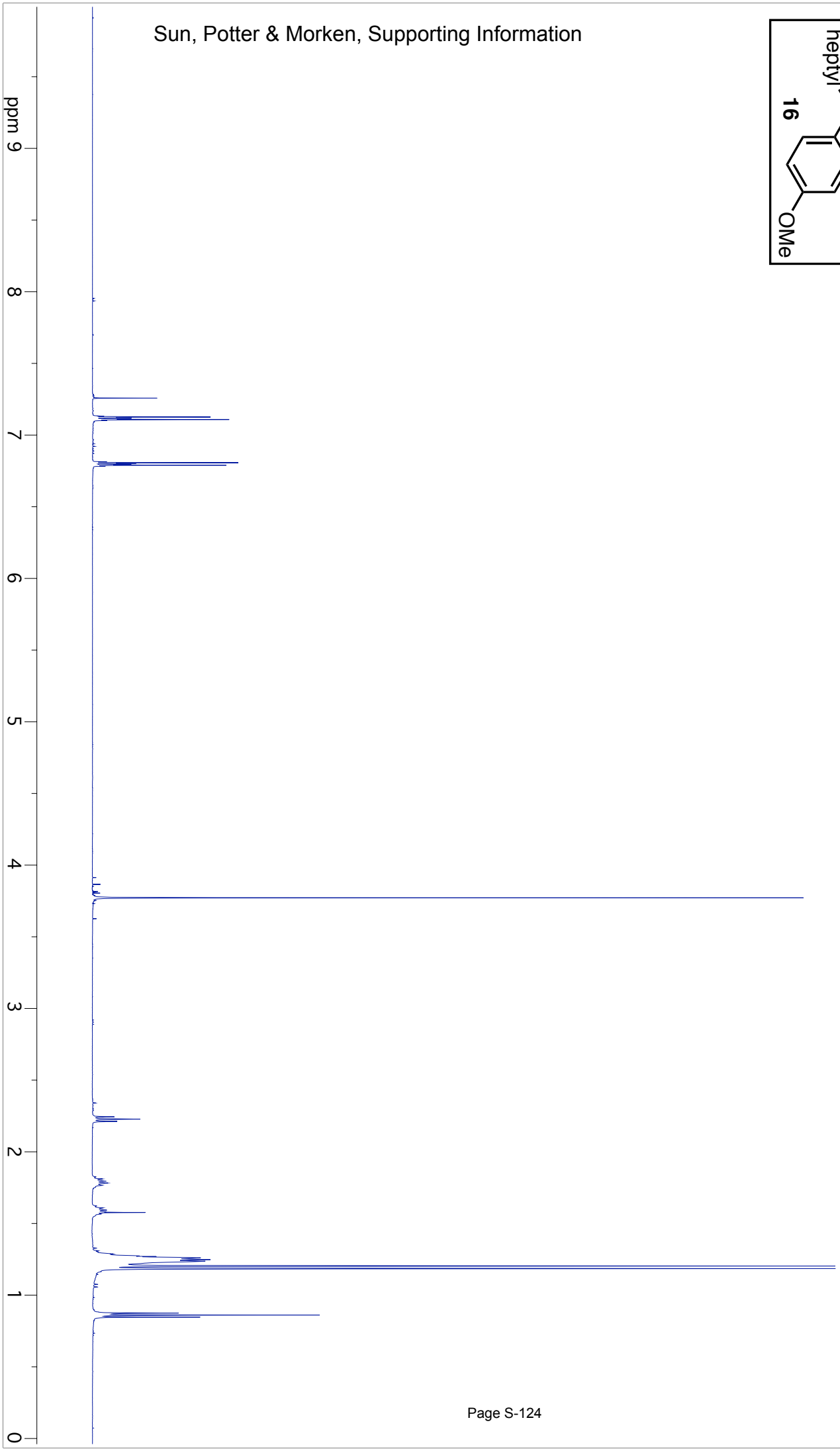
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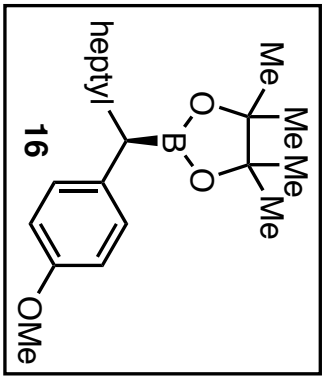
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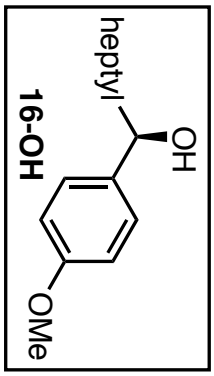
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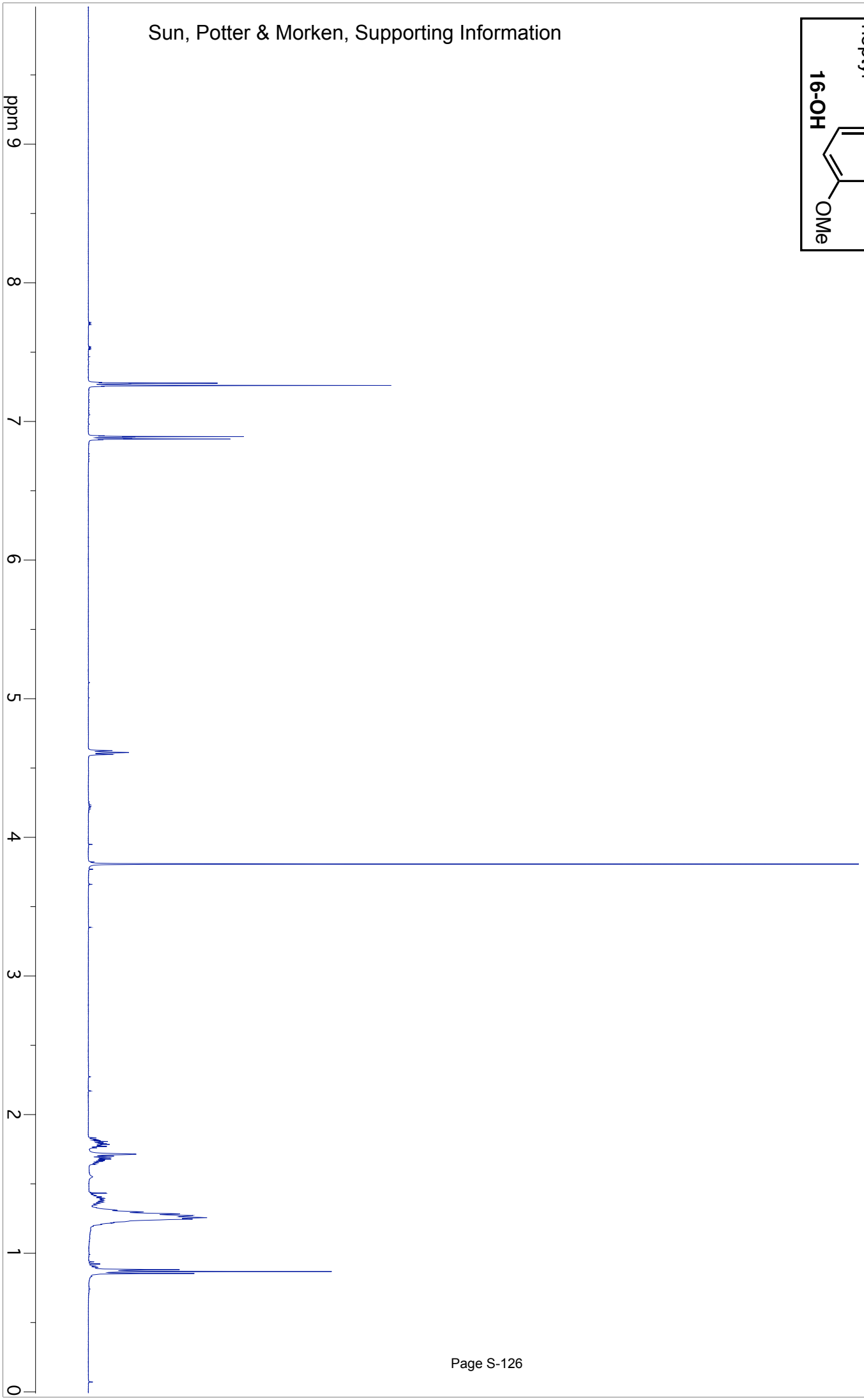
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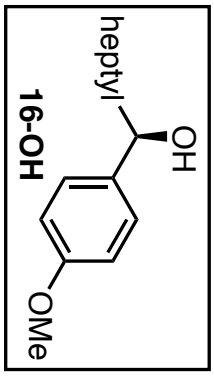
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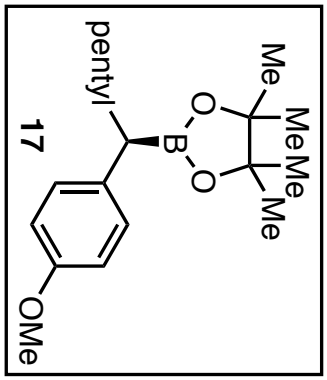
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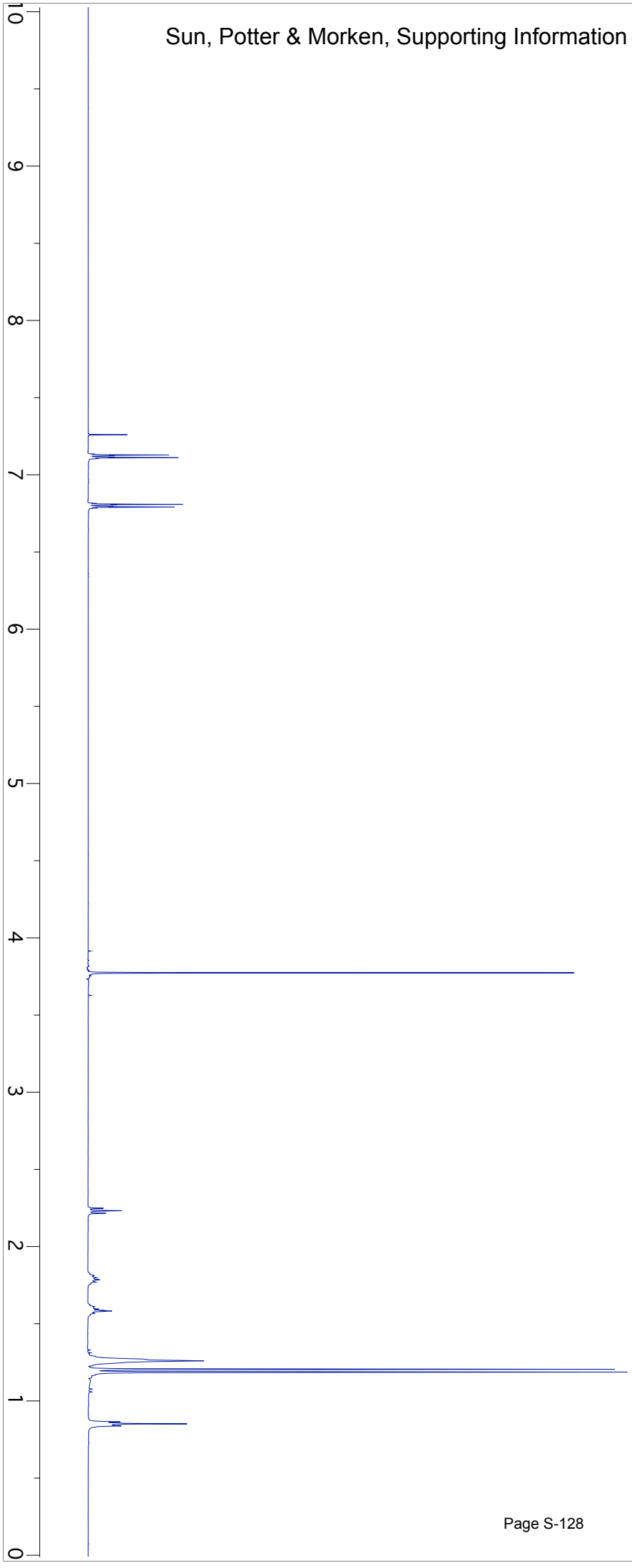
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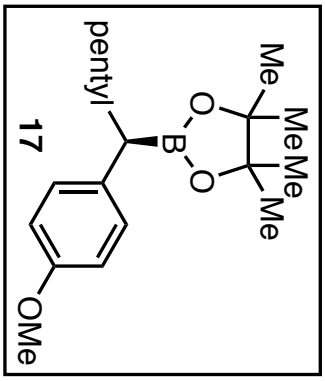
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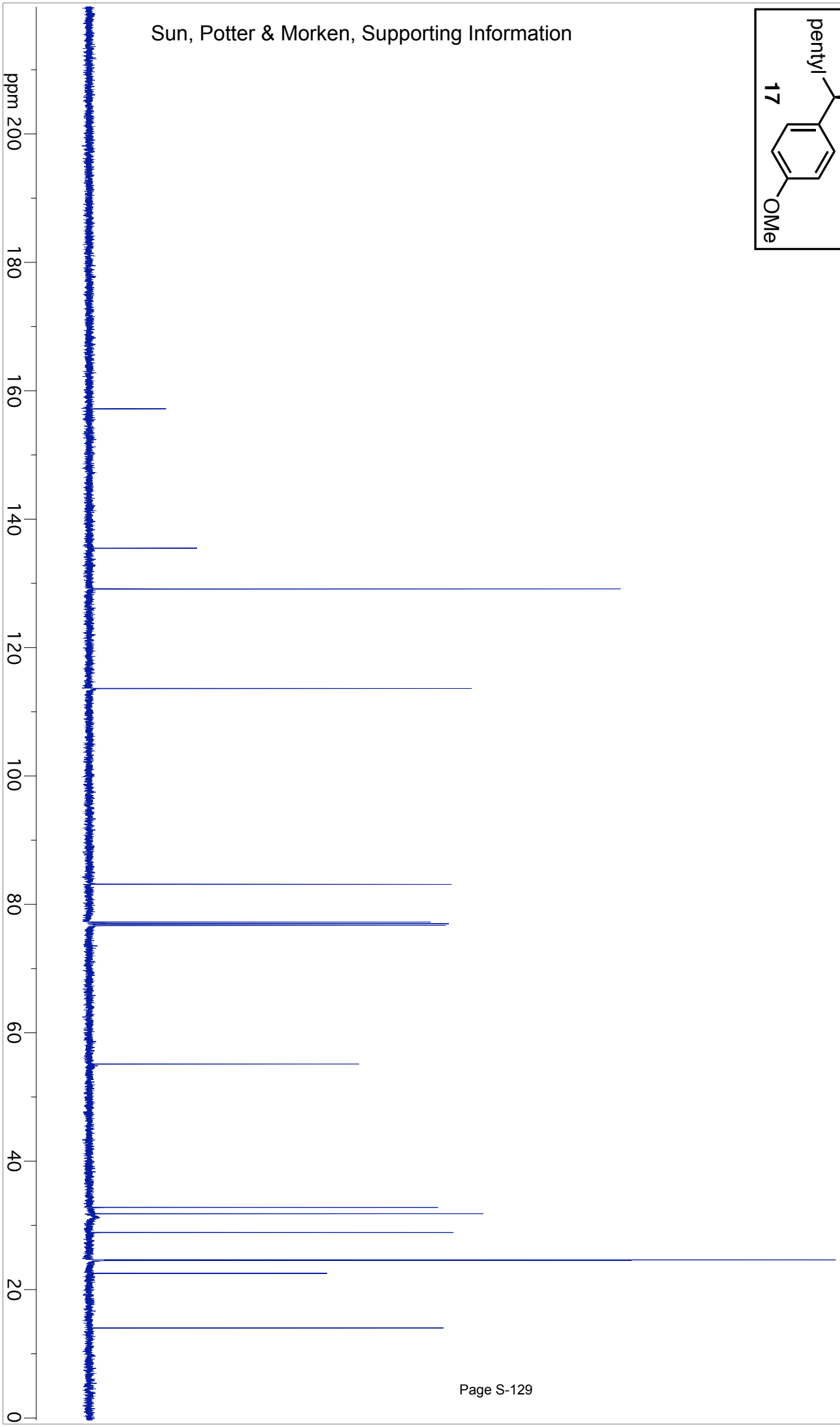
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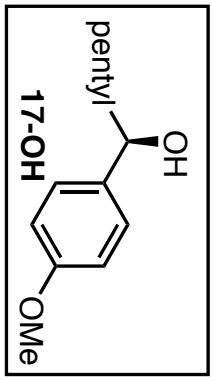
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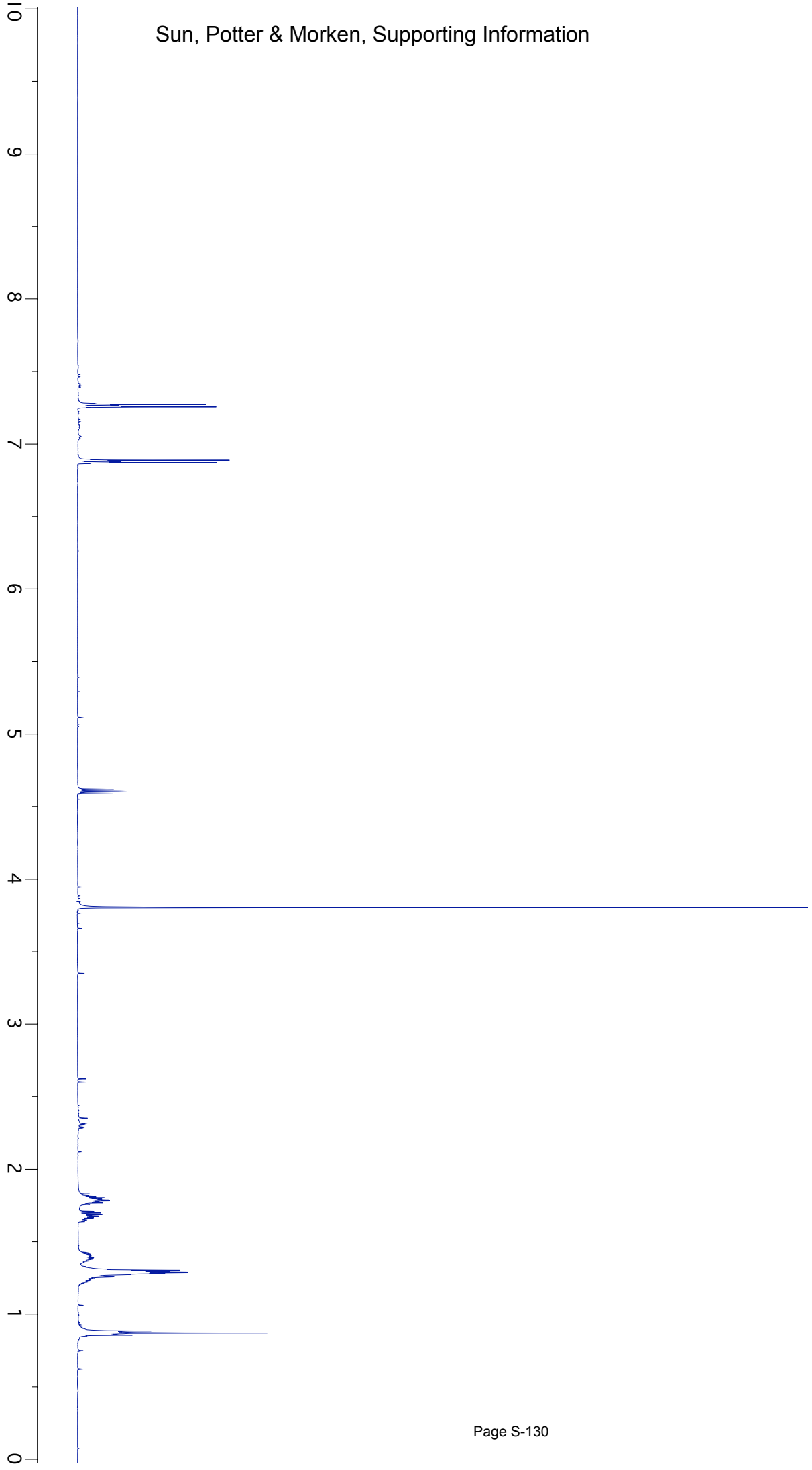
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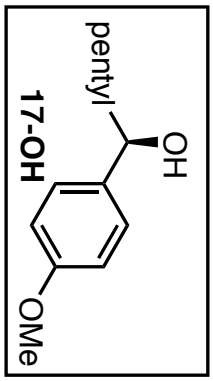
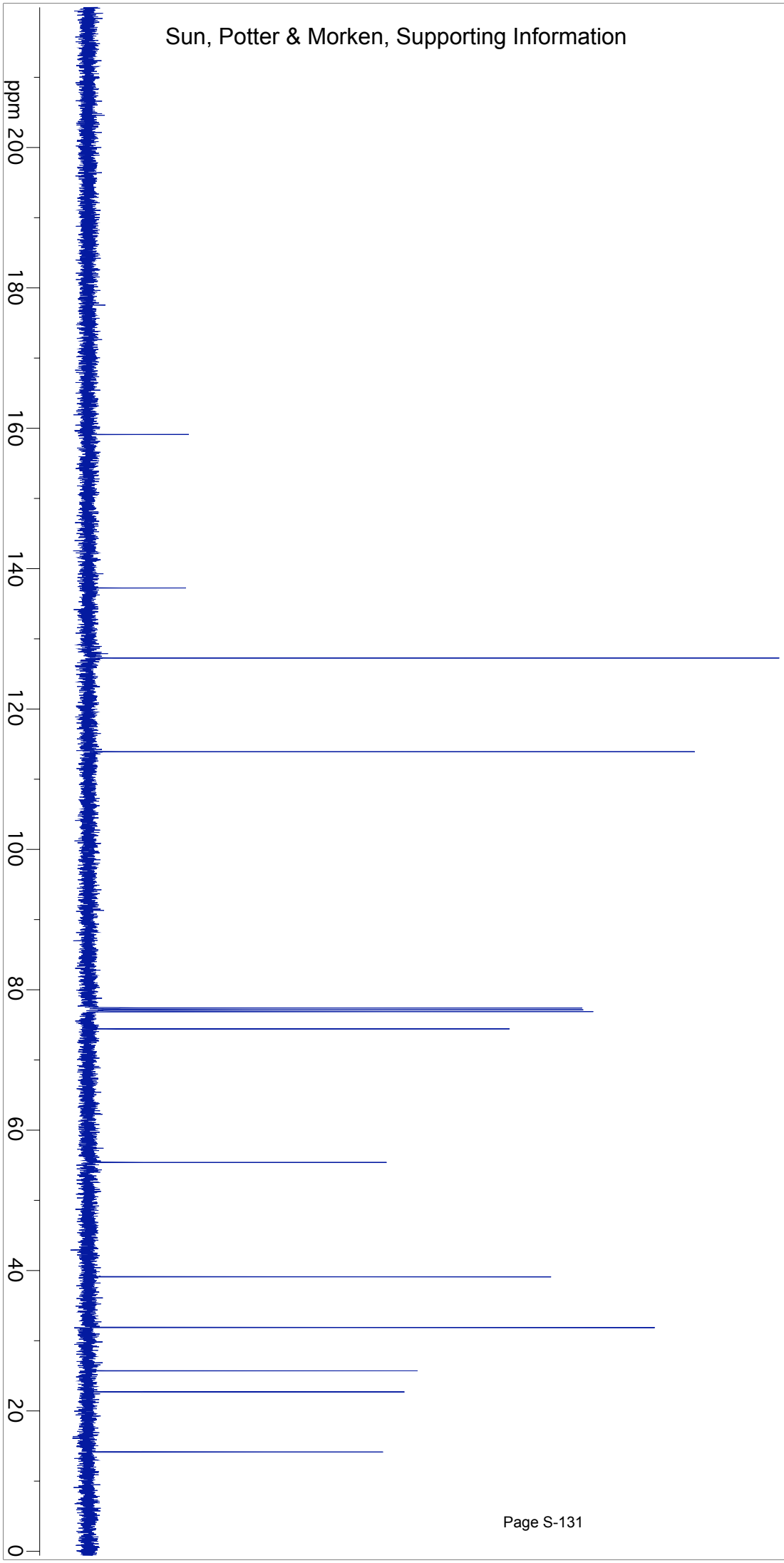

pentyl
OH
17-OH
OMe


ppm
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180
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140
120
100
80
60
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20
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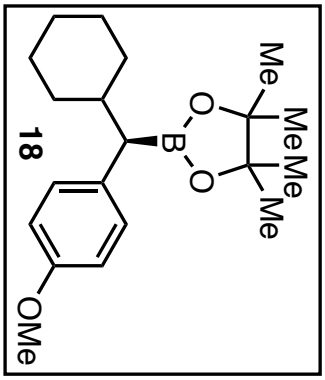
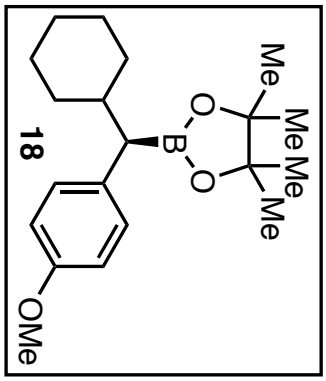
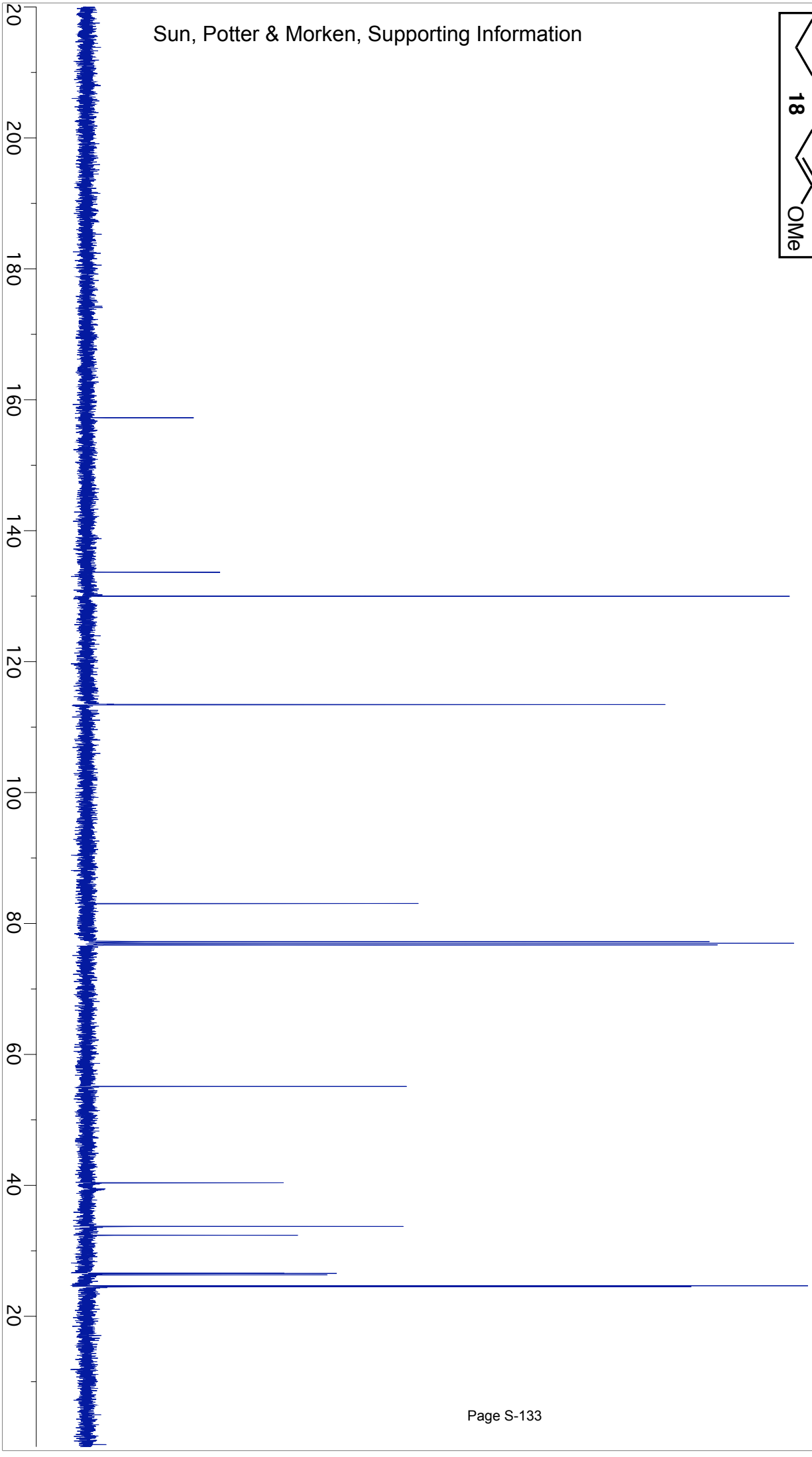

18
OMe
O
B
O
Me
Me
Me
Me

10
9
8
7
6
5
4
3
2
1
0
H2O


18
Me
Me
Me
Me
O
B
O
OMe


20
200
180
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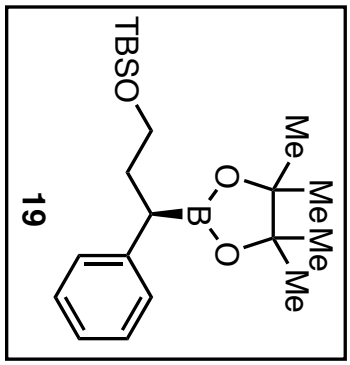
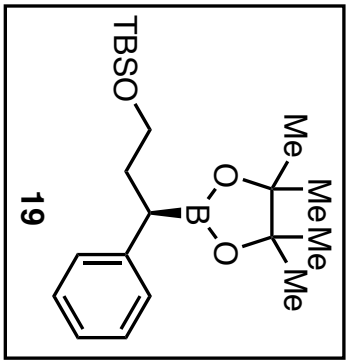
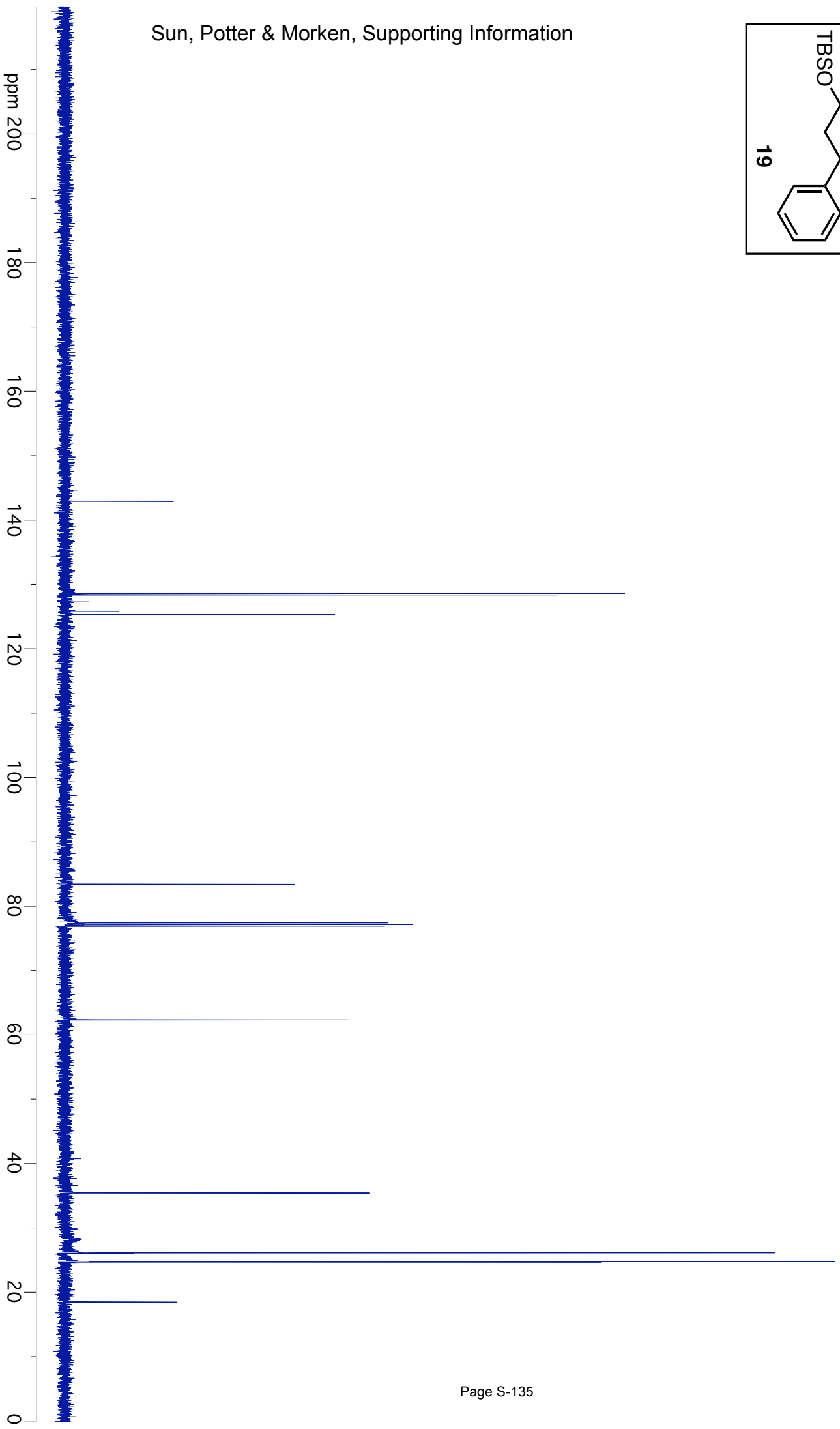
60
40
20


TBSO
Me
Me
Me
Me
O
B
O
O
19

ppm
9
8
7
6
5
4
3
2
1
0


TBSO
Me
Me
Me
Me
O
B
O
O
19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140
120
100
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60
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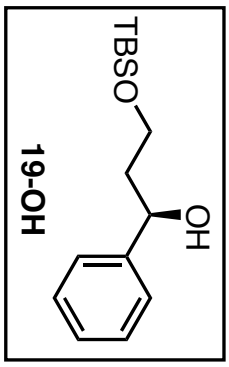
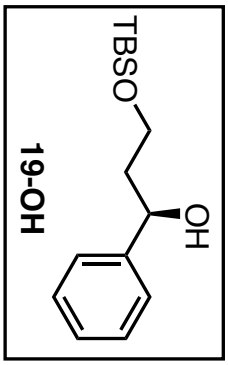
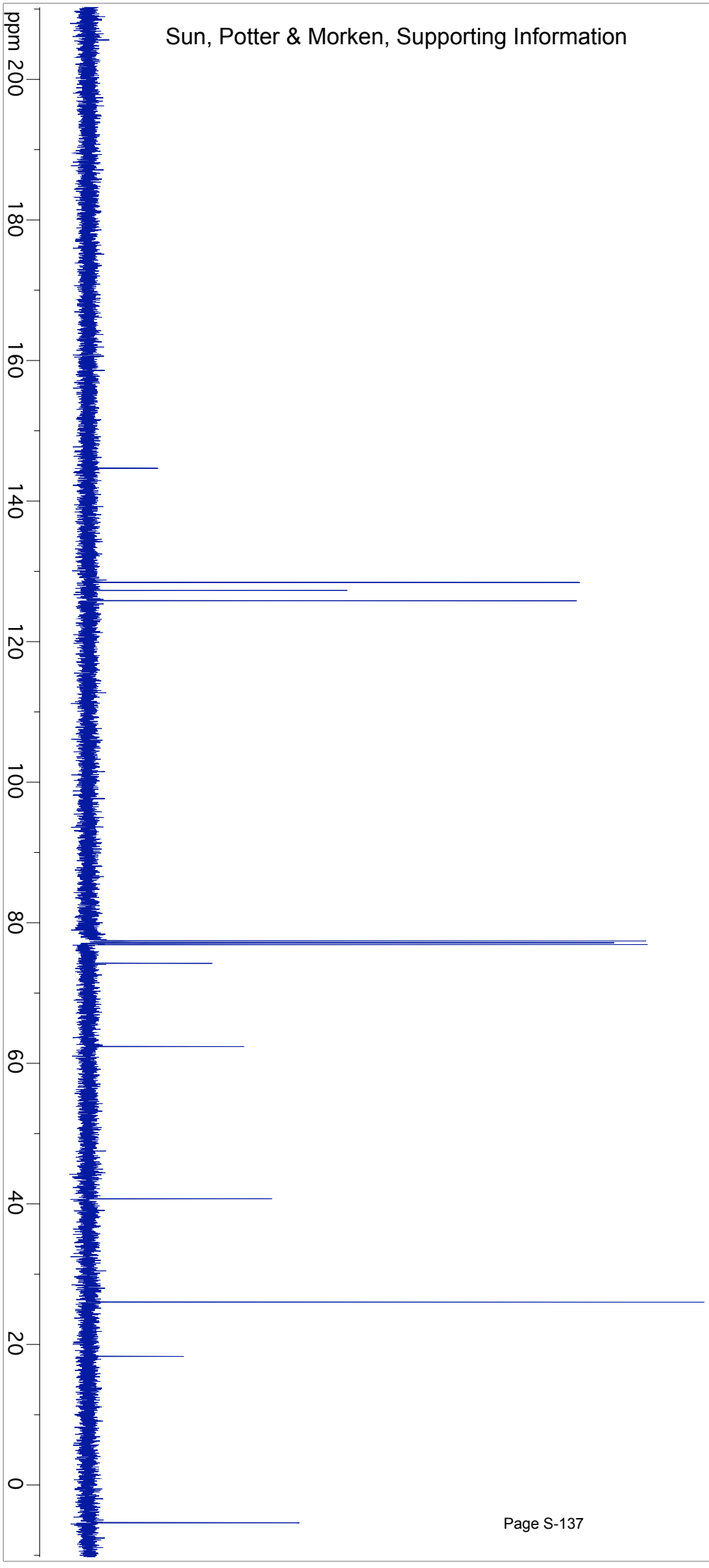
20
0


TBSO
OH
19-OH

ppm
9
8
7
6
5
4
3
2
1
0


TBSO
OH
19-OH


ppm
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100
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60
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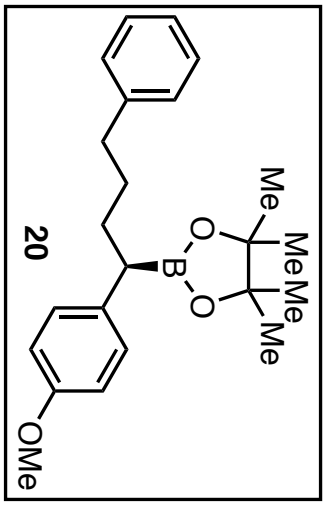
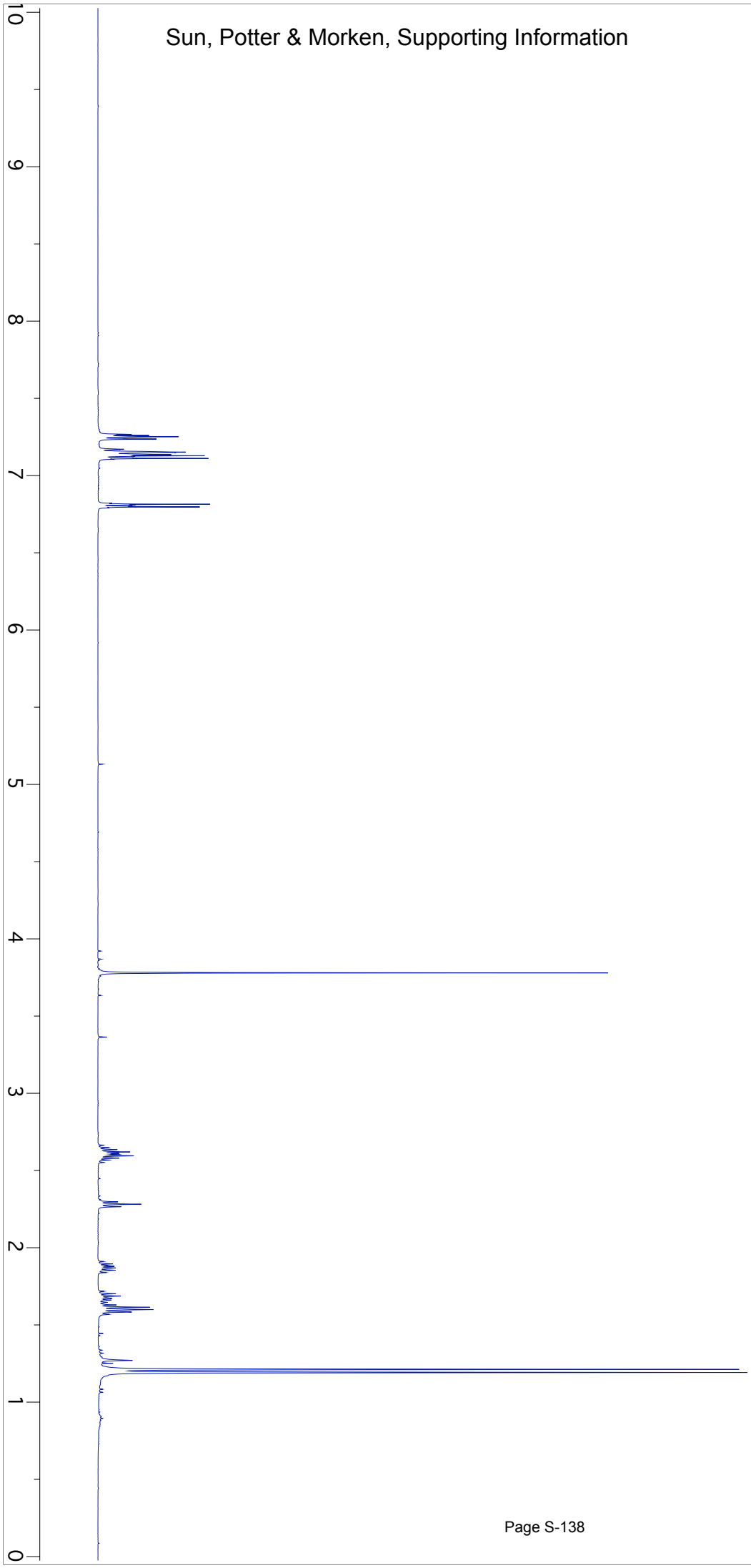

20
Me
Me
Me
Me
O
B
O
OMe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5
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3
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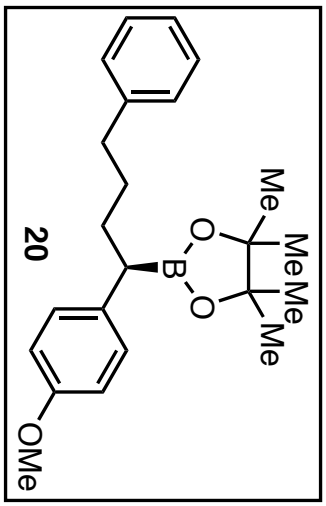
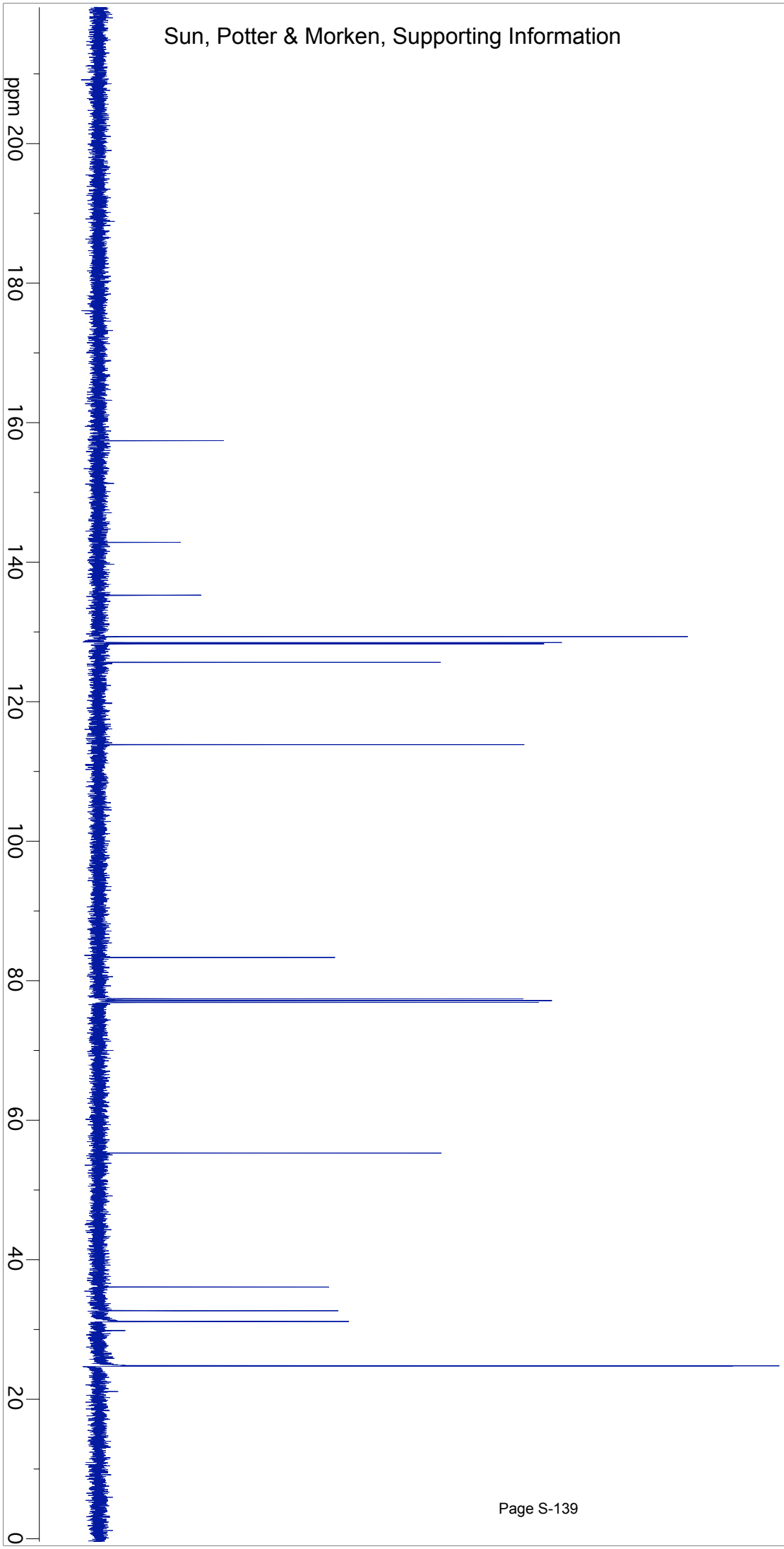
0


20
Me
Me
Me
Me
O
B
O
OMe


ppm
200
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140
120
100
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60
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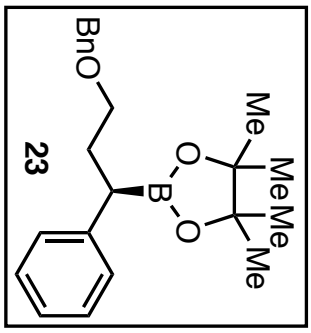
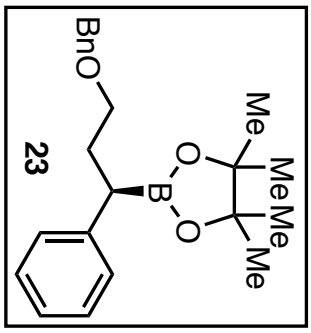
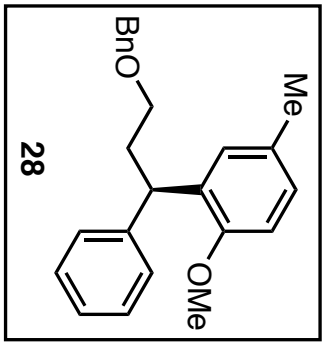
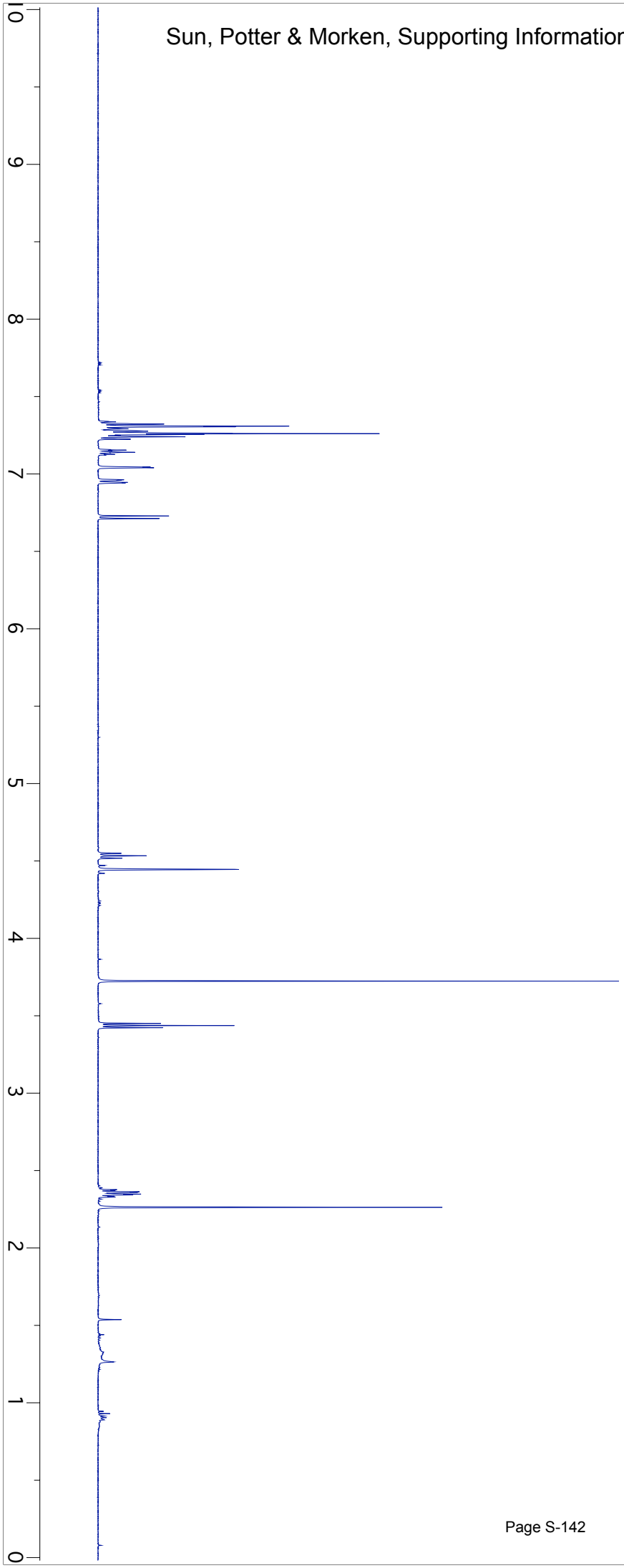

BnO
23
Me
Me
Me
Me
O
B
O

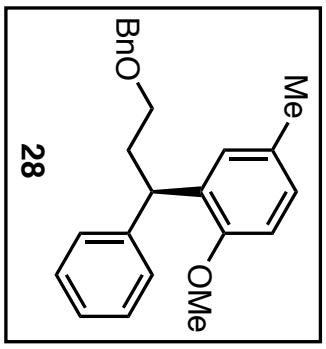
ppm
9
8
7
6
5
4
3
2
1
0
H2O


BnO
23
Me
Me
Me
Me
O
B
O

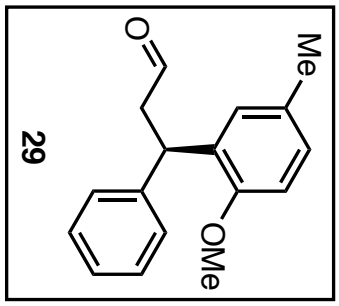
220
200
180
160
140
120
100
80
60
40
20
0


BnO
Me
OMe
28

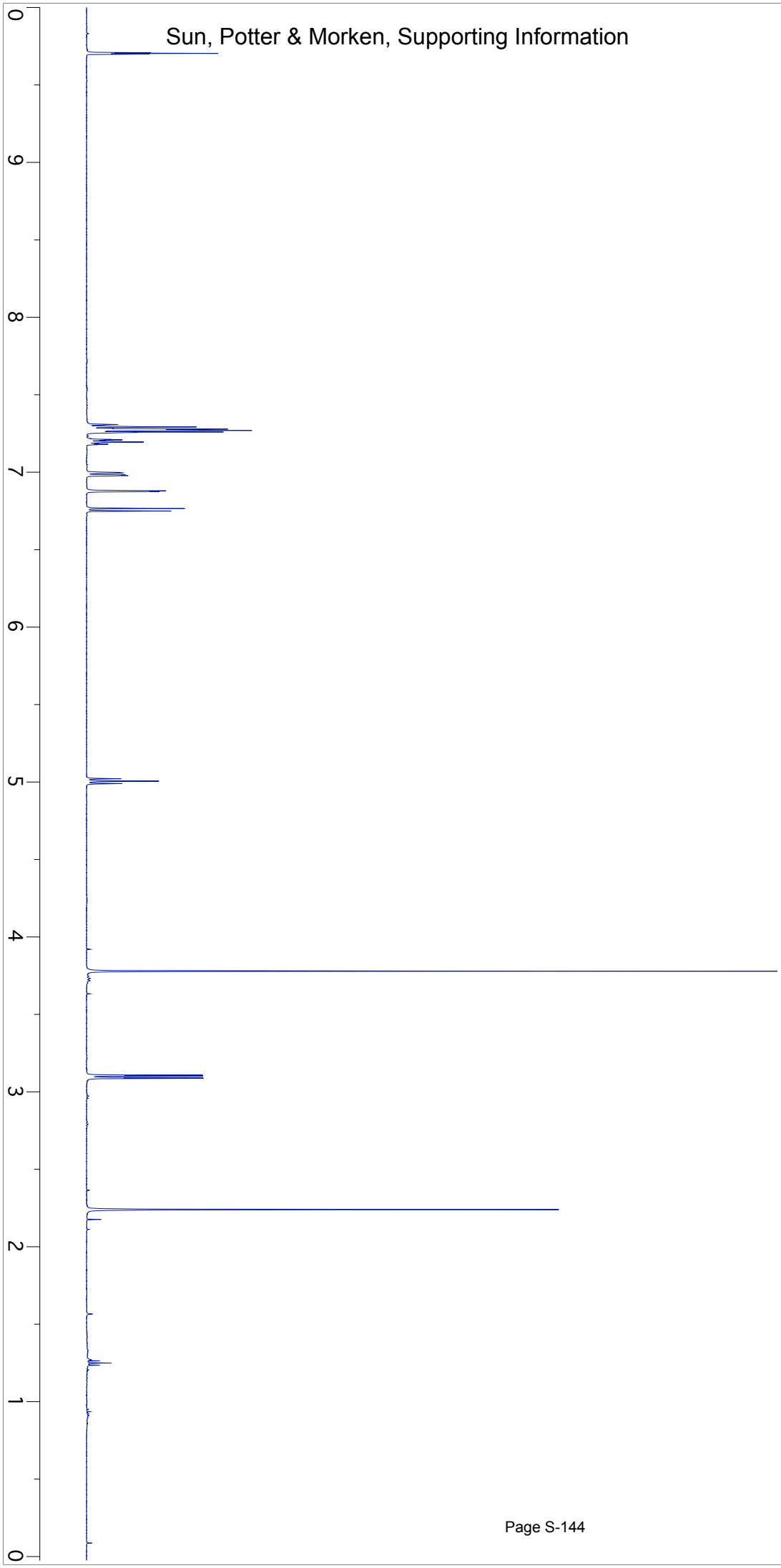

10
9
8
7
6
5
4
3
2
1
0

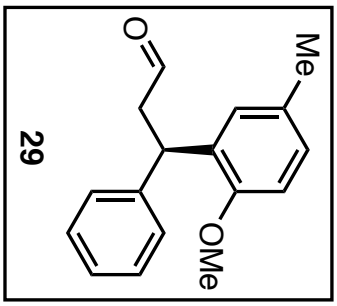


28

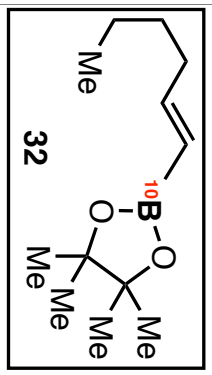


29

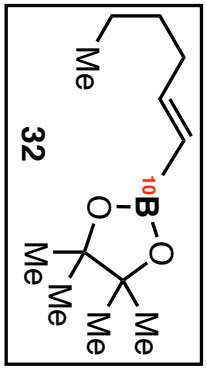


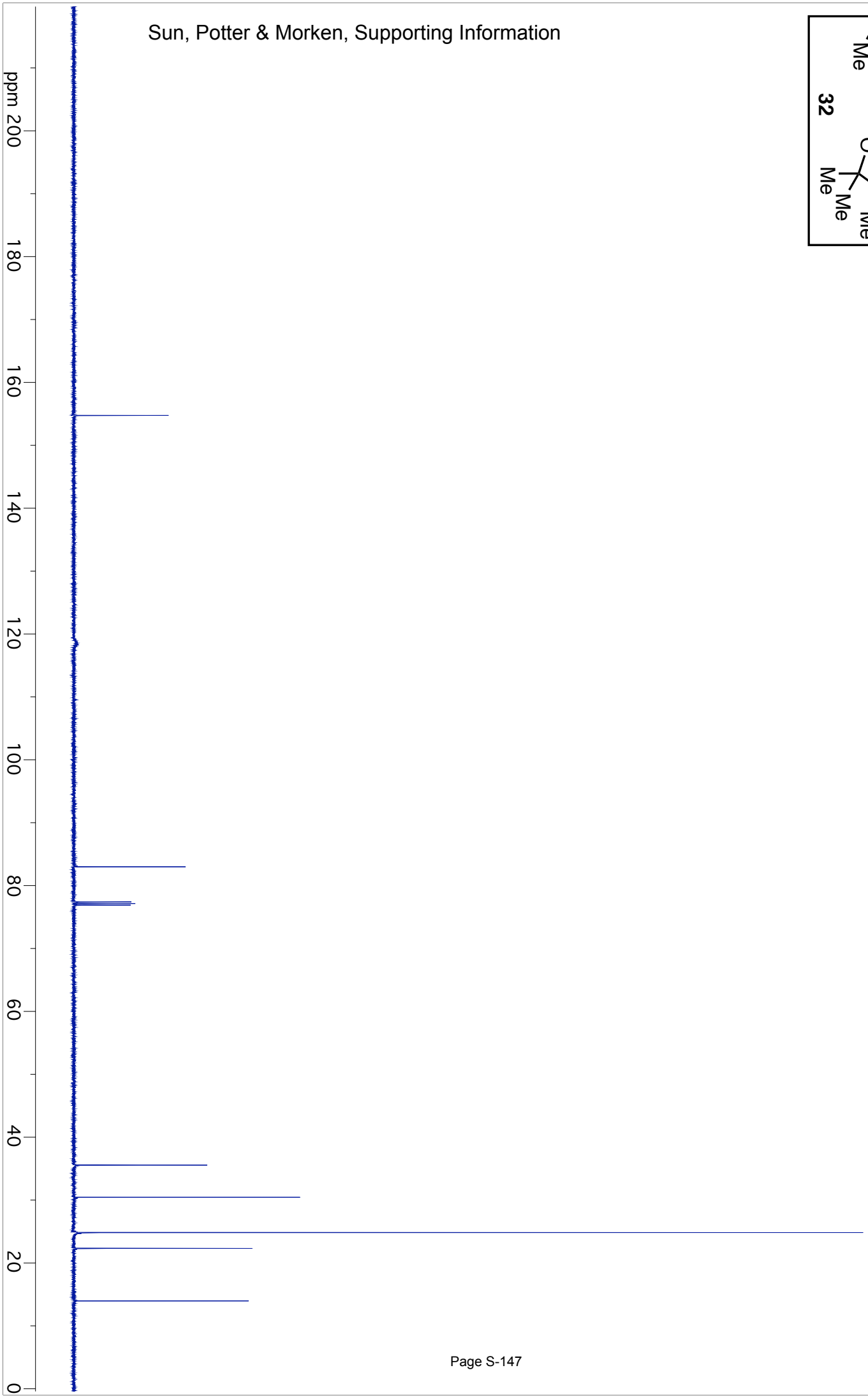


29


Me
32
10B
O
O
Me
Me
Me
Me
Me

10
9
8
7
6
5
4
3
2
1
0


Me
32
10B
O
O
Me
Me
Me
Me


ppm
200
180
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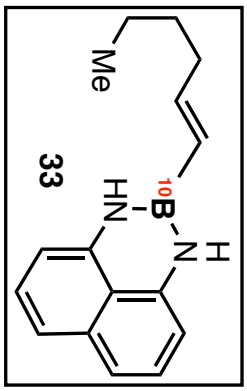
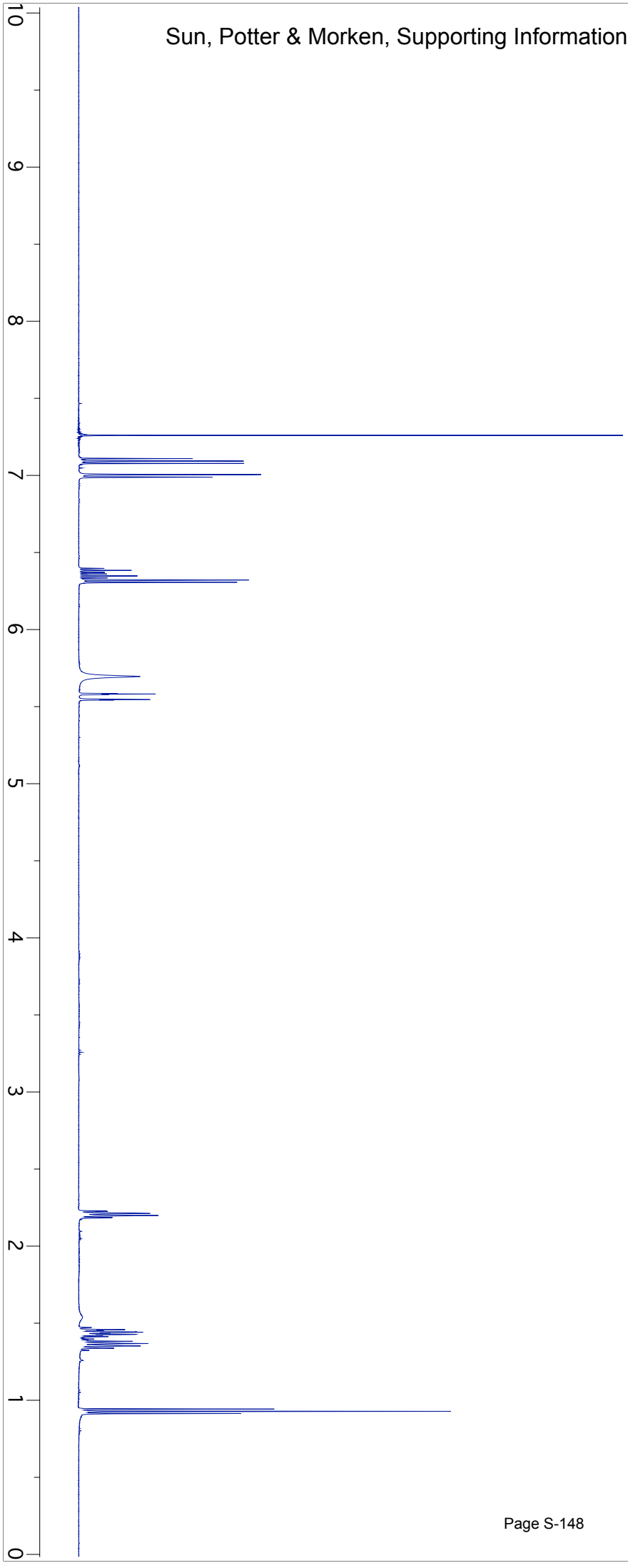
140
120
100
80
60
40
20
0


Me
33
HN
10B
N
H


10
9
8
7
6
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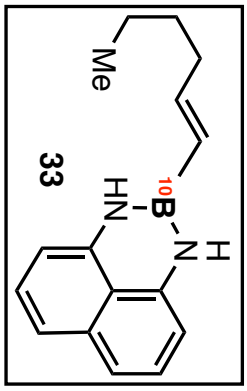
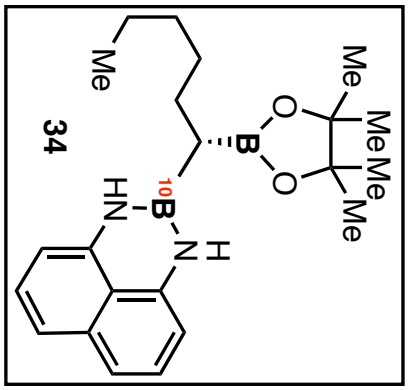
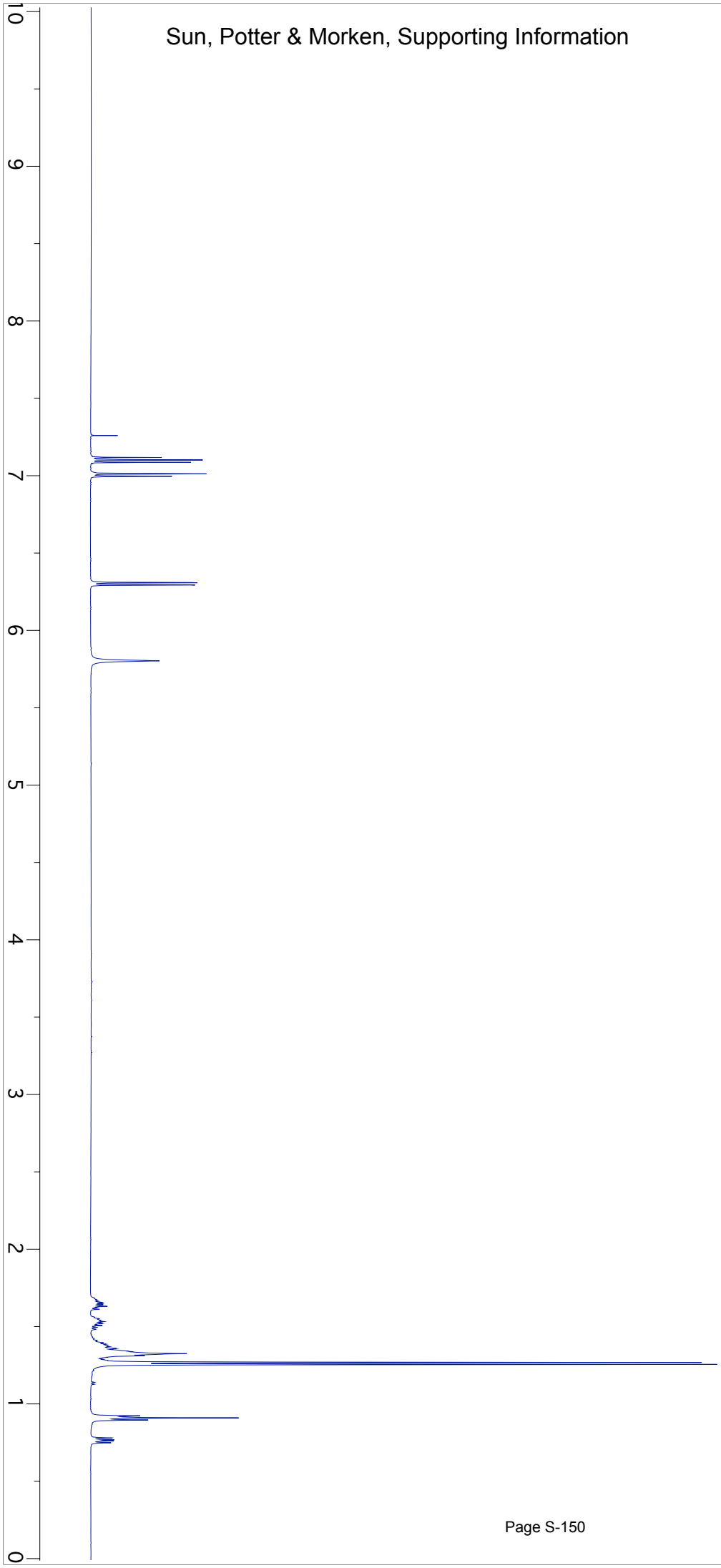
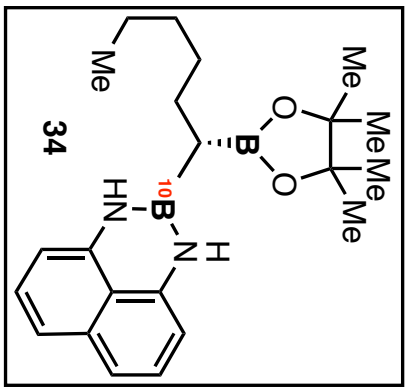
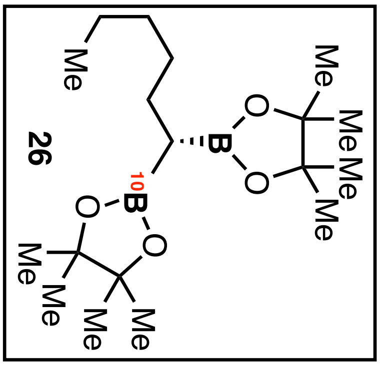
4
3
2
1
0


Me
33
HN
10B
N
H

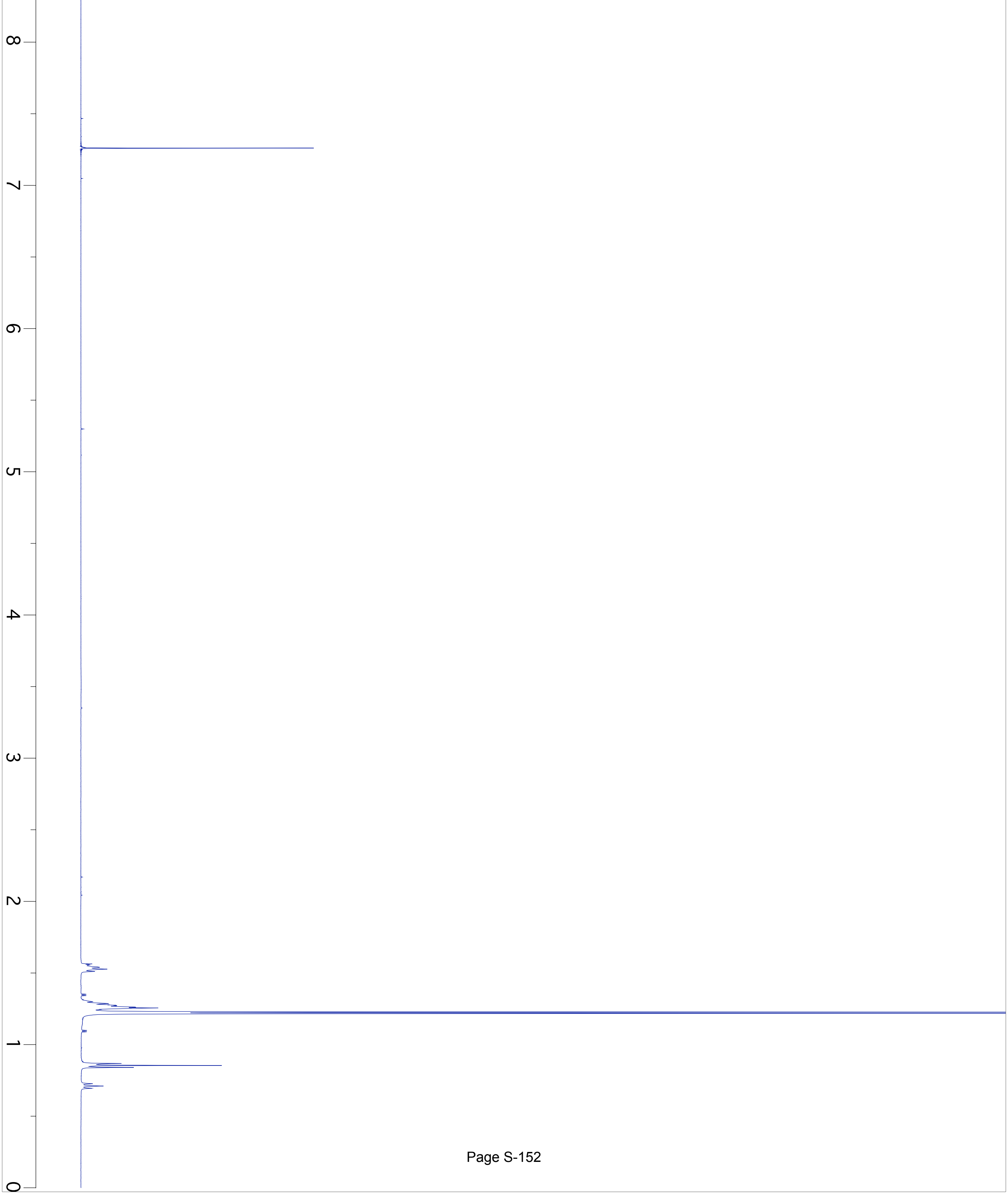

Me
34
HN
10B
N
H
B
O
O
Me
Me
Me
Me

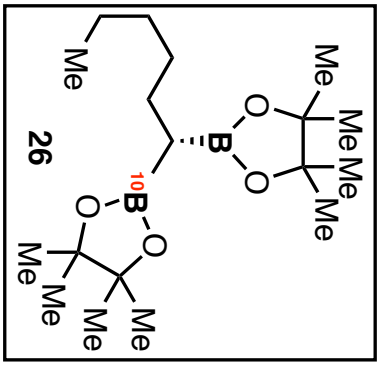

10
9
8
7
6
5
4
3
2
1
0


Me
34
HN
10B
N
H
O
B
O
Me
Me
Me
Me

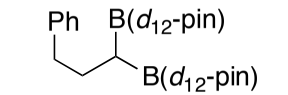


26

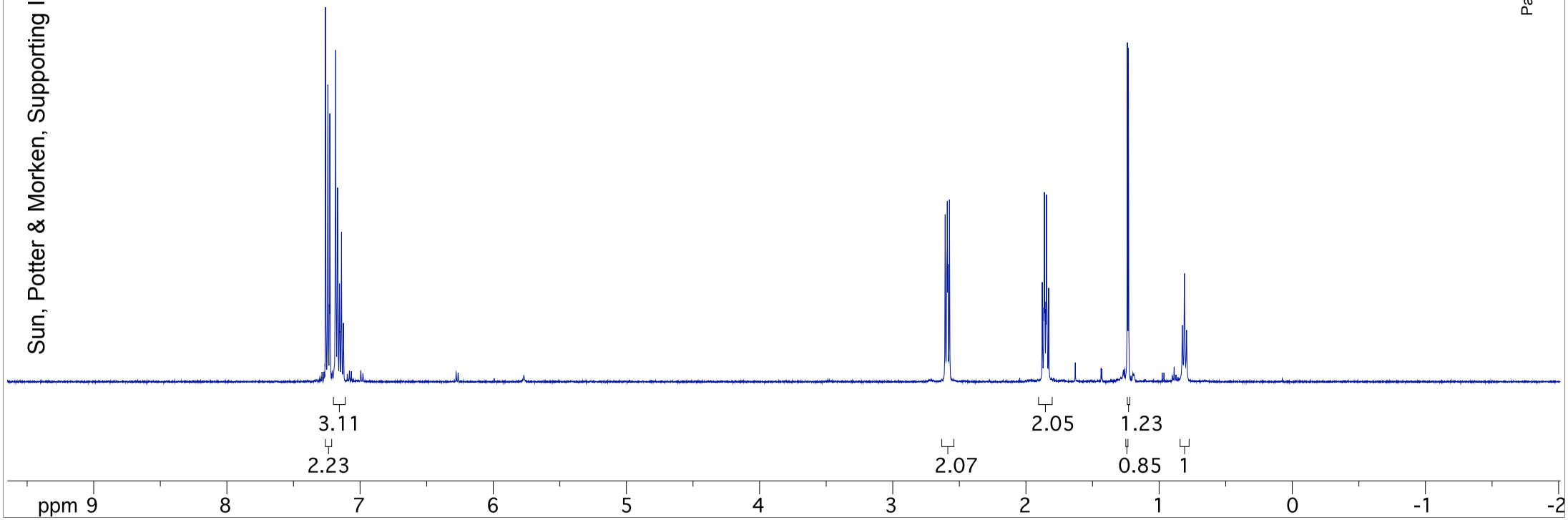


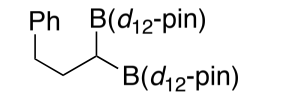

Me
26
10B
O
O
B
O
O
Me
Me
Me
Me
Me
Me
Me
Me
Me

ppm
200
180
160
140
120
100
80
60
40
20
0



(>90% D-incorporation)

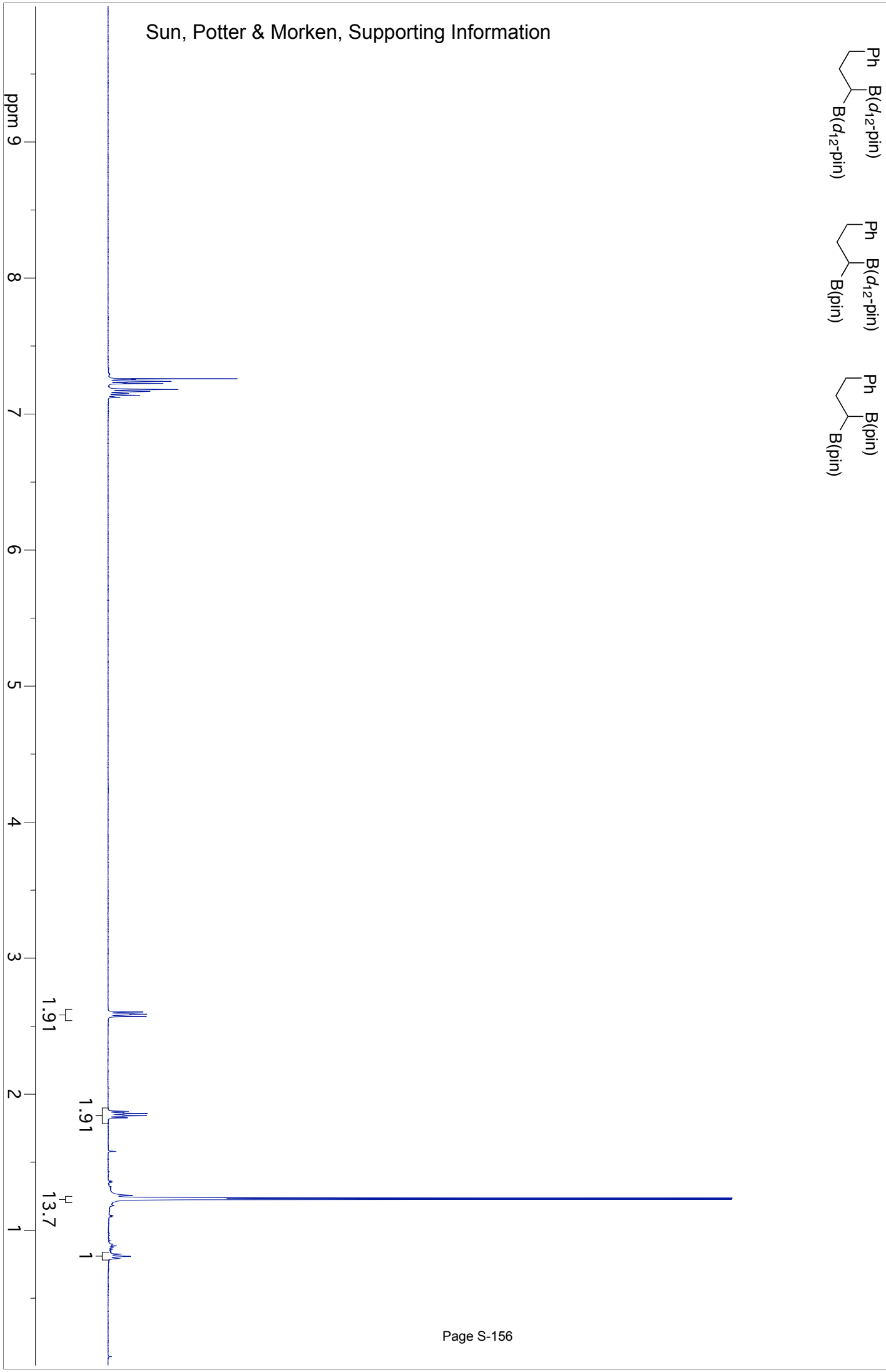


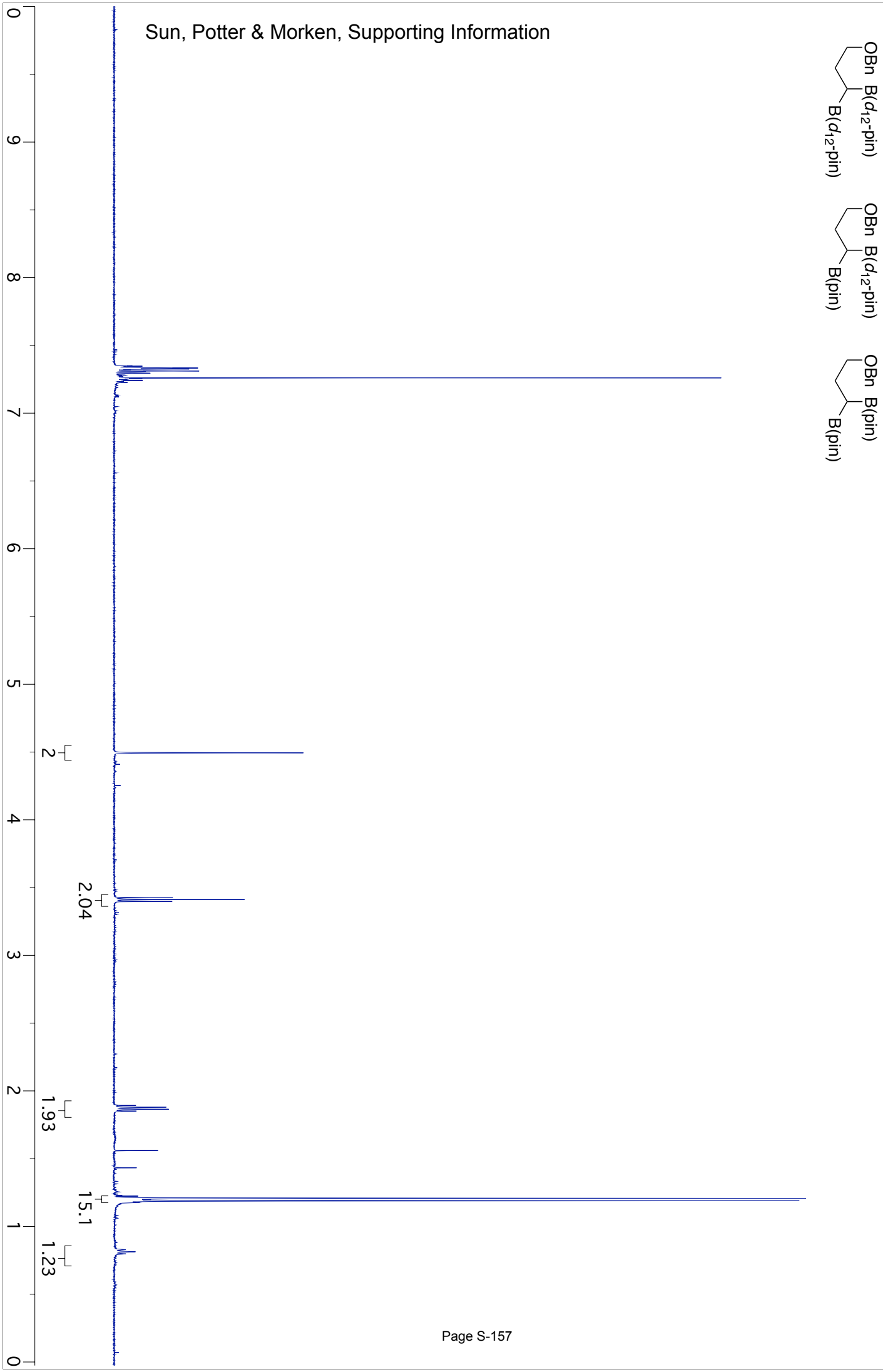


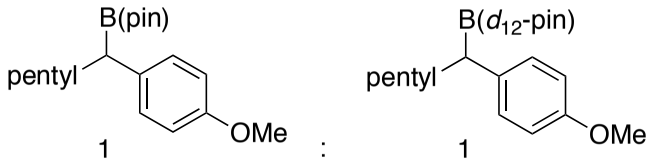
1-d_{24}

(>90% D-incorporation)

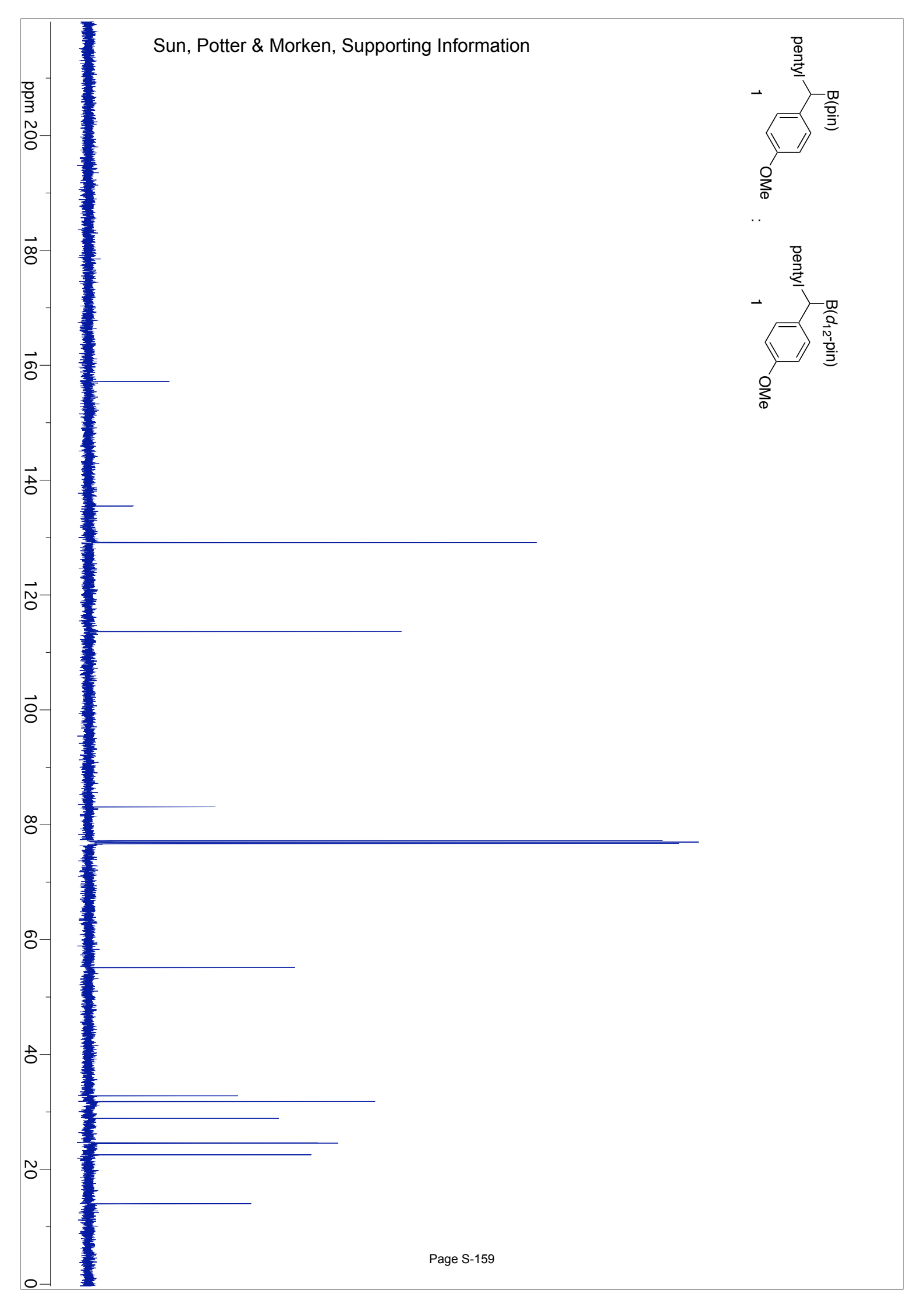
ppm 220 200 180 160 140 120 100 80 60 40 20 0

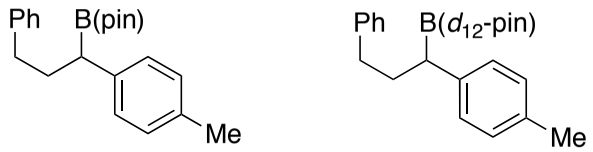

Ph
B(d12-pin)
B(d12-pin)
Ph
B(d12-pin)
B(pin)
Ph
B(pin)
B(pin)
ppm
9
8
7
6
5
4
3
2
1
1.91
1.91
13.7
1


OBn
B(d12-pin)
B(d12-pin)
OBn
B(d12-pin)
B(pin)
OBn
B(pin)
B(pin)
2
2.04
1.93
15.1
1.23

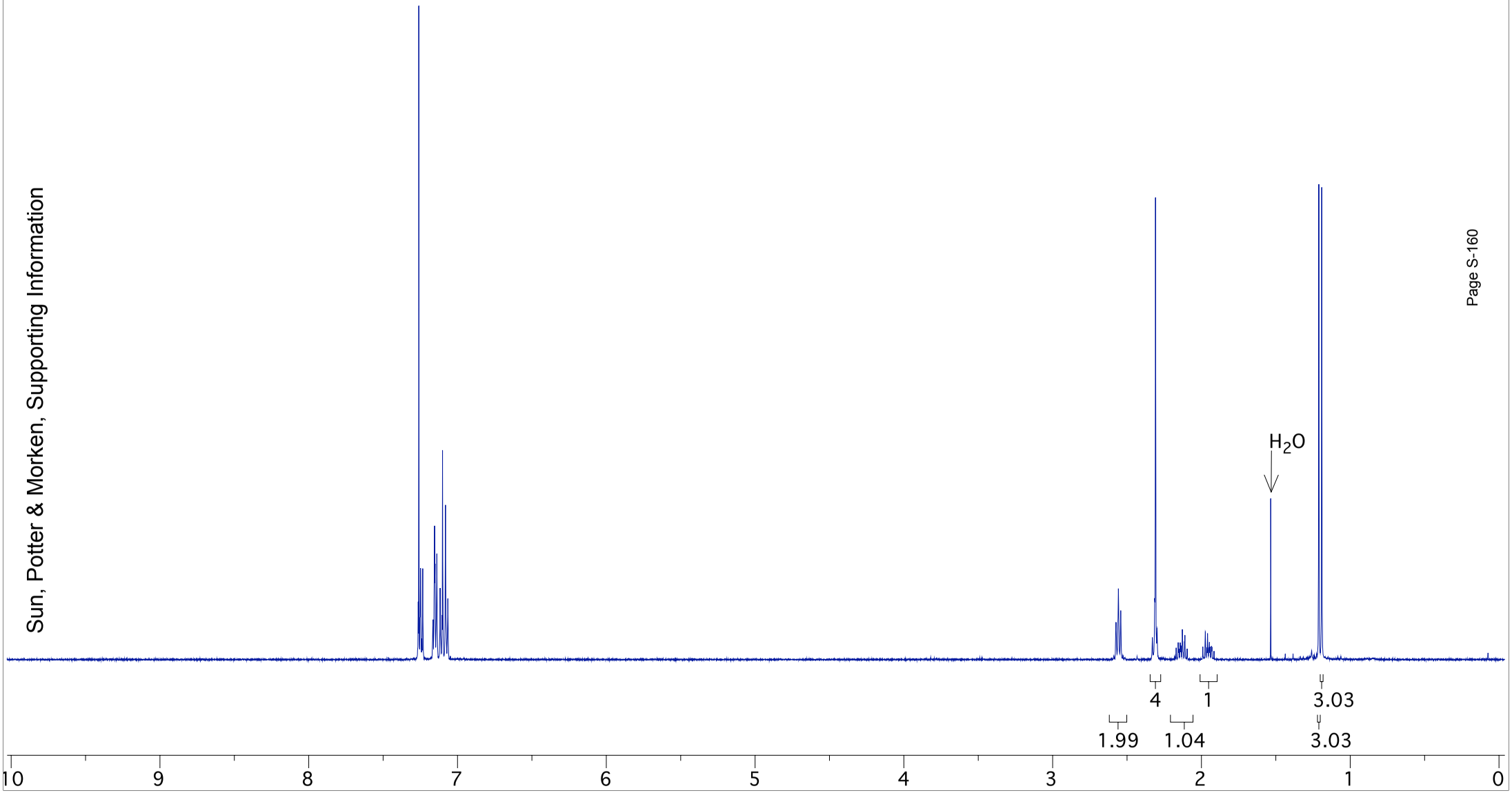

B(pin)
pentyl
OMe
1
:
B(d_{12}-pin)
pentyl
OMe
1

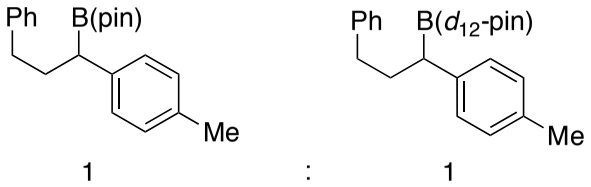
1.93
1.95
2.98
1
0.987
3.23
3.09
1.02
6.28
3.33
0
9
8
7
6
5
4
3
2
1
0


pentyl
B(pin)
1
OMe
:
pentyl
B(d12-pin)
1
OMe
ppm
200
180
160
140
120
100
80
60
40
20
0

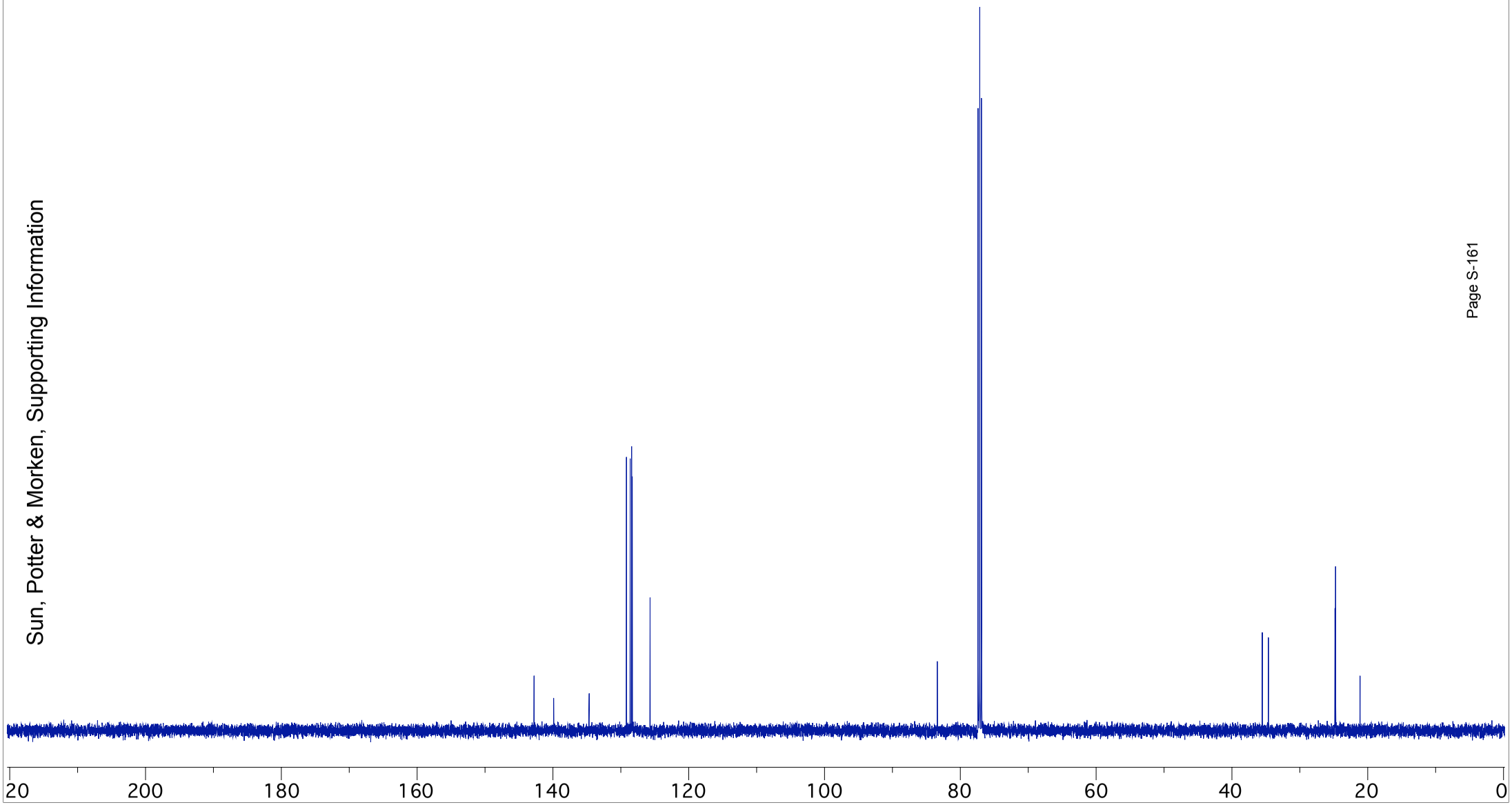


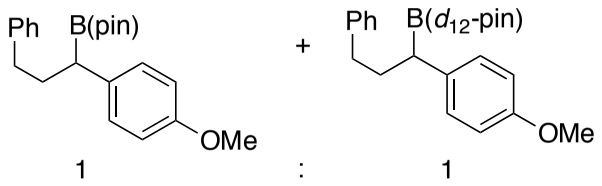
1 : 1





1 : 1

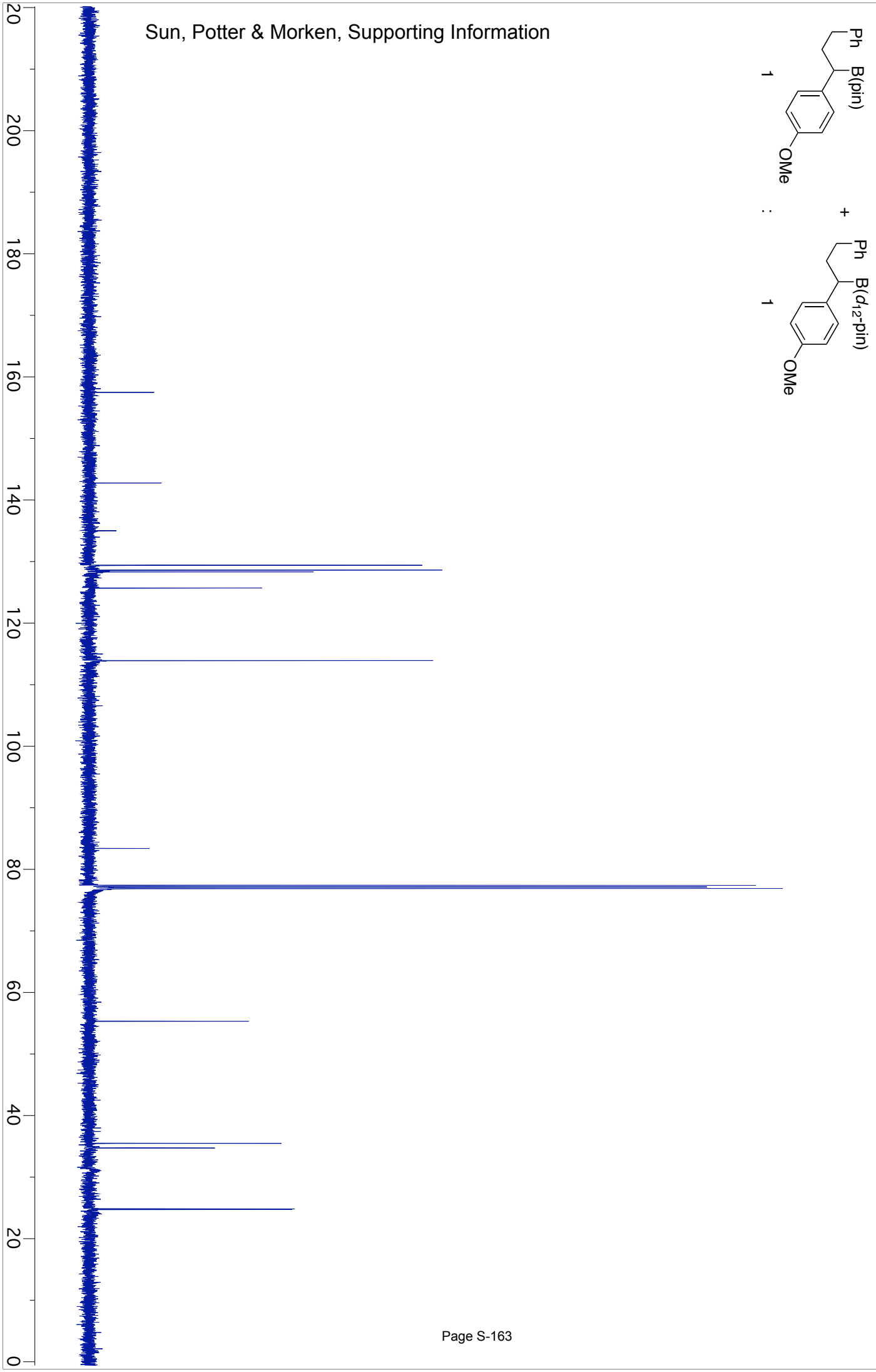



Ph
B(pin)
OMe
1

:

Ph
B(d12-pin)
OMe
1

1.92
1.01
2.64
2.88
0.927
1
3.04
10
9
8
7
6
5
4
3
2
1
0


Ph
B(pin)
OMe
1
:
+
Ph
B(d_{12}-pin)
OMe
1
220
200
180
160
140
120
100
80
60
40
20
0