Diastereoselective and Enantioselective Conjunctive Cross-Coupling Enabled by Boron Ligand Design

Jesse A. Myhill, Christopher A. Wilhelmsen, Liang Zhang, and James P. Morken*

Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467

Supplementary Material

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General Information

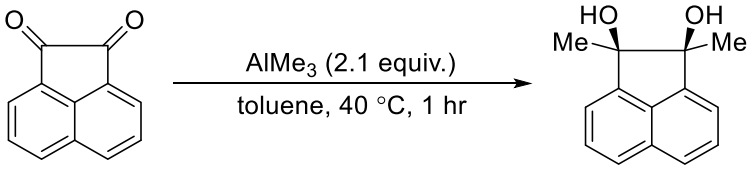
^{1}H NMR spectra were recorded on either a Varian Gemini-500 (500 MHz), Varian Gemini-600 (600 MHz), or Varian Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on either a Varian Gemini-500 (126 MHz), Varian Gemini-600 (151 MHz) or a Varian Inova-500 (126 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.2 ppm). ^{11}B NMR spectra were recorded on a Varian Gemini-500 (128 MHz) or Varian Gemini-600 (160 MHz) spectrometer. ^{19}F NMR spectra were recorded on a Varian Gemini-500 (470 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). Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter. High-resolution mass spectrometry (DART) 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), ceric ammonium molybdate (CAM) in ethanol or phosphomolybdic acid, and cerium(IV) sulfate in ethanol with sulfuric acid (magic stain).

Analytical chiral supercritical fluid chromatography (SFC) was performed on a TharSFC Method Station II equipped with Waters 2998 Photodiode Array Detector with isopropanol or methanol as the modifier.

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. Palladium (II) acetate, (S_p,S_p)-**L**, (R_p,R_p)-**L**, and 1,1'-Bis(diisopropylphosphino)ferrocene were purchased from Strem Chemicals, Inc. and used without further purification. 1,3-Bis(diphenylphosphino)propane was purchased from TCI and used without further purification. Acenaphthylene-1,2-dione, 4-methoxyphenyl trifluoromethanesulfonate, phenyl trifluoromethanesulfonate, and cesium fluoride were purchased from Oakwood Chemicals and used without further purification. Potassium trifluoromethanesulfonate was purchased from Oakwood Chemicals and dried by heating (100 ºC) under vacuum overnight. Alkenyl boronic acids were prepared by hydroboration of alkynes with $HBBr_2$ followed by hydrolysis.[1] All other reagents were purchased from Aldrich, Alfa Aesar, Acros, Combi Blocks, or Oakwood Chemicals and used without further purification.

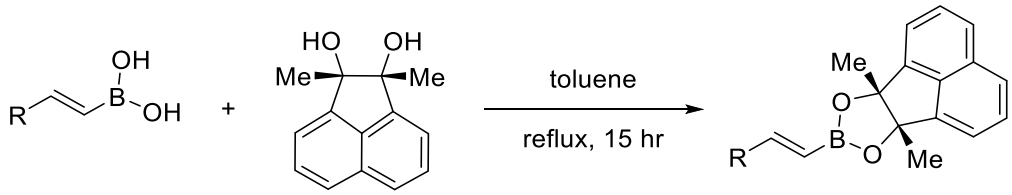
Experimental Procedures

I. Procedure for Preparation of 1,2-dimethyl-1,2-dihydroacenaphthylene-1,2-diol (mac) (4)

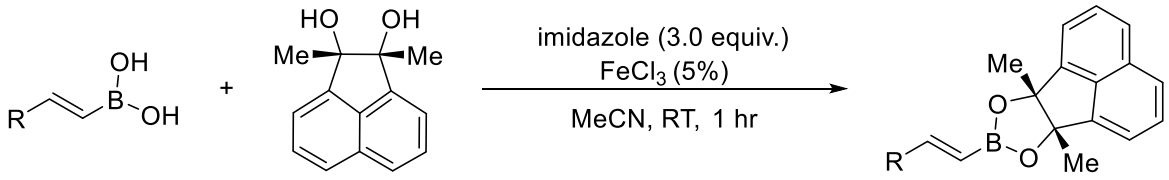


A flame-dried 3-neck 1000 mL RBF was equipped with stir bar, a reflux condenser fitted to the middle neck, and the other two necks were sealed with rubber septa. Acenaphthoquinone (18.22 g, 100 mmol) was added, and the flask was evacuated and backfilled with nitrogen. Dry toluene (100.0 mL, [substrate] = 1.00 M) was added via syringe, and the yellow suspension was stirred at 40 ºC. Trimethyl aluminum (20.1 mL, 210.0 mmol, 2.1 equiv.) was added dropwise via syringe (a 12 mL syringe was used to transfer 5 mL aliquots dropwise). Upon completion of addition, the reaction was allowed to stir for 1 hour at 40 ºC, then cooled to 0 ºC and quenched very slowly with 40 ml H_2O and 20 ml 1M HCl (caution: gas evolution). The reaction was diluted with EtOAc and filtered through a frit funnel, then the filtrate was poured into separatory funnel containing water (200 mL). The organic layer was washed three times with EtOAc (300 mL) then the combined organic layers were washed 3 times with brine, then dried over Na_2SO4, filtered, and concentrated. ^{1}H NMR analysis of the crude material indicates ~4.3:1 syn:anti diol. The crude product was dissolved in hot EtOAc (750 mL) and stored at -20 ºC overnight. The resulting precipitate was collected by filtration and rinsed with pentane to yield *syn*-1,2-dimethyl-1,2-dihydroacenaphthylene-1,2-diol as off-white crystals (11.5 g, 53.7 mmol, 54% yield). Suspected losses in yield of product due to insolubility when transferring between vessels. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.56 (t, J = 7.5 Hz, 2H), 7.48 (d, J = 6.9 Hz, 2H), 2.97 (s, 2H), 1.63 (s, 6H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.36, 134.51, 131.34, 128.68, 125.07, 119.33, 82.38, 23.53.; HRMS (DART) for $C_{14}H_{13}O$ $[M+H-H_2O]^+$: calculated: 197.0961, found: 197.0956.

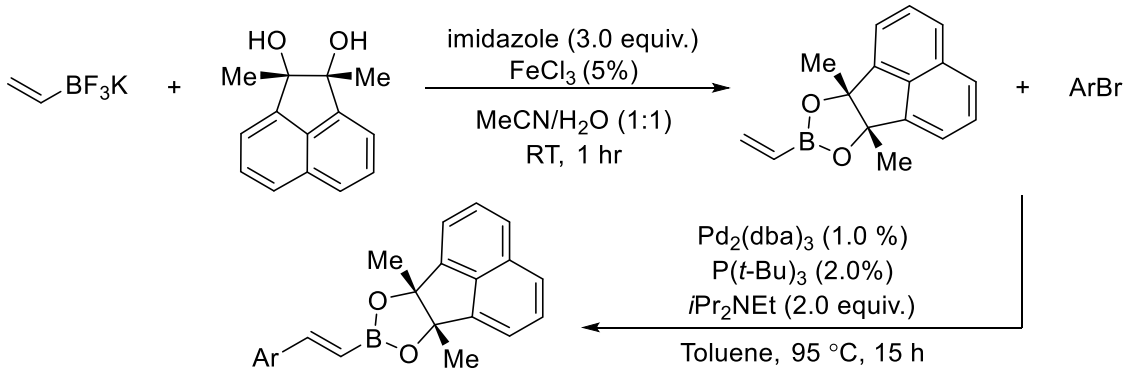
II. Procedures for Preparation of Alkenyl Boronic Esters



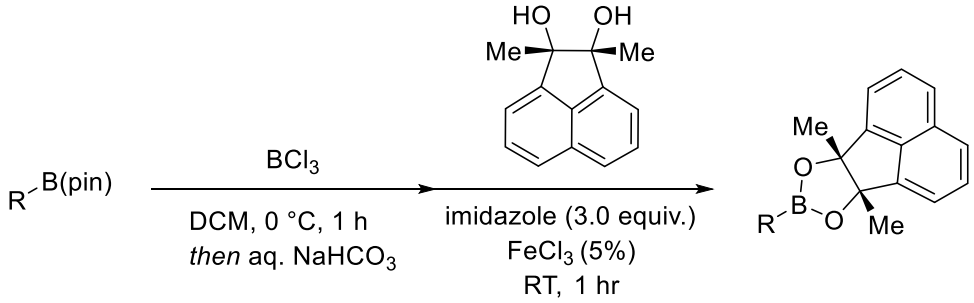
Method A: To a 100-mL RBF equipped with a stir bar was added alkenyl boronic acid (3.0 mmol, 1.0 equiv.) and toluene (12 mL). 1,2-Dimethylacenaphthylene-1,2-diol (3.0 mmol, 1.0 equiv.) was added and a Dean-Stark apparatus equipped with a reflux condenser was attached to the flask. The reaction was heated to reflux for 15 hours then concentrated under vacuum. The crude product was purified by silica gel chromatography to afford the desired product. *This method can be used to synthesis boronic esters containing other diol ligands.*



Method B: According to a modified literature procedure.[2] To a scintillation vial equipped with a stir bar was added alkenyl boronic acid (3.0 mmol, 1.0 equiv.) and MeCN (12.00 mL). To this solution was added sequentially 1,2-dimethylacenaphthylene-1,2-diol (3.00 mmol, 1.0 equiv.), imidazole (9.00 mmol, 3 equiv.), and $FeCl_3$ (60.00 µmol, 0.05 equiv.). The reaction was then stirred at room temperature open to air for 1 hour before being filtered through a pad of silica gel with Et_2O. The crude product was purified by silica gel chromatography to afford the desired product. *This method can be used to synthesis boronic esters containing other diol ligands.*

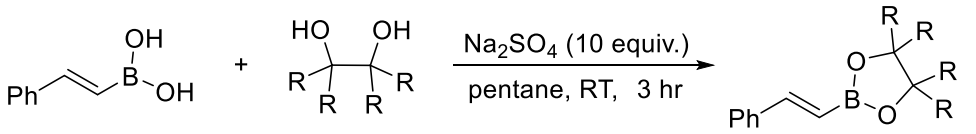


***Method C*:** VinylB(mac) was prepared according to a modified literature procedure, as follows.[2] To a solution of vinyl potassium trifluoroborate (343.9 mg, 2.57 mmol, 1.0 equiv.) in 50% acetonitrile/water (5 mL) was added sequentially open to air at room temperature, 1,2-dimethylacenaphthylene-1,2-diol (550 mg, 2.57 mmol, 1.0 equiv.), imidazole (524.3 mg, 7.70 mmol, 3.0 equiv.), and $FeCl_3$ (20.8 mg, 0.128 mmol, 0.05 equiv.). The reaction was allowed to stir 30 minutes, then filtered through a plug of silica gel with Et_2O and concentrated. The crude material was purified by silica gel column chromatography to affored the desired product (typically 90% yield). The Heck reaction was carried out according to a modified literature procedure.[3] In an argon-filled glovebox, vinylB(mac) (750.30 mg, 3 mmol, 1.0 equiv.), aryl bromide (3.30 mmol, 1.1 equiv.), N,N-diisopropylethylamine (1.05 mL, 6.00 mmol, 2.0 equiv.), tris(dibenzylideneacetone)dipalladium(0) (27.47 mg, 30.00 µmol, 1.0 mol%), tri-*tert*-butylphosphine (10% weight in hexanes, 121.39 mg, 60.00 µmol, 2.0 mol%), and toluene (6.00 mL) were added to an oven-dried scintillation vial equipped with a stir-bar. The vial was sealed and removed from the glovebox. The reaction was then heated to 95 ºC overnight, filtered through a plug of silica gel with Et_2O, and concentrated. The crude product was purified by column chromatography with silica gel. *This method can be used to synthesis boronic esters containing other diol ligands.*



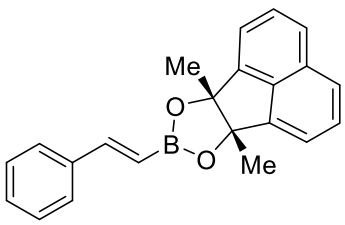
Method D: Boron trichloride (1 M solution in DCM, 17.5 mL, 17.5 mmol, 5.0 equiv.) was added to a solution of boronic acid pinacol ester (3.5 mmol, 1.0 equiv.) in DCM (3.50 mL) at – 78 ºC.

The mixture was stirred at 0 ºC for 1 hour, then quenched with saturated aqueous sodium bicarbonate solution (3.5 mL), and the reaction was warmed to room temperature. To this solution was added 1,2-dimethylacenaphthylene-1,2-diol (3.5 mmol, 1.0 equiv.), imidazole (10.5 mmol, 3.0 equiv.), and FeCl3 (0.18 mmol, 0.05 equiv.). The reaction was stirred for 1 hour at room temperature then filtered through a plug of silica gel with Et_2O and concentrated. The crude product was purified by column chromatography with silica gel. *This method can be used to synthesis boronic esters containing other diol ligands.*



Method E: To a 100-mL RBF equipped with a stir bar was added alkenyl boronic acid (3.0 mmol, 1.0 equiv.) and pentane (12 mL, 0.25 M). The diol (3.0 mmol, 1.0 equiv.) was added followed by anhydrous sodium sulfate (30 mmol, 10.0 equiv.). The reaction was allowed to stir at room temperature for 3 hours, then the reaction mixture was filtered through a cotton plug with Et_2O and concentrated. The crude product was purified by silica gel chromatography to afford the desired product.

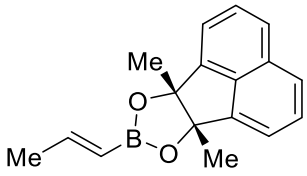
***When to Use Each Method*:**
In instances when boronic acids or potassium trifluoroborates are readily available, Method B is preferred due to operational simplicity, reaction efficiency, and simple product purification. However, if the substrate contains acid-sensitive functionality then Method A or Method E should be used instead. Additionally, if the resulting boronic ester is not stable to silica gel chromatography, then Method E is preferred. In instances when a pinacol boronic ester is more easily obtained than the corresponding boronic acid, Method D is utilized (this method should be avoided if the substrate contains acid-sensitive functionality). Method B is utilized for the synthesis of styrenyl boronic esters as an alternative to the hydroboration of terminal alkynes.



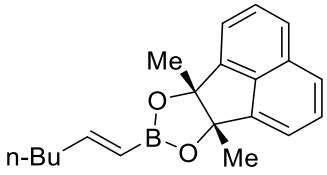
6b,9a-dimethyl-8-((E)-styryl)-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (S-1). The title compound was prepared according to Method A with [(E)-styryl]boronic acid (500 mg, 3.38 mmol, 1.0 equiv.), 1,2-dimethylacenaphthylene-1,2-diol (723 mg, 3.38 mmol, 1.0 equiv.), and toluene (15 mL). The crude product was purified by silica gel chromatography with 5-10% EtOAc / hexane to yield the title compound (1.05 g, 3.21 mmol, 95% yield) as a white solid.

The title compound was be prepared according to Method B with [(E)-styryl]boronic acid (443.90 mg, 3 mmol, 1.0 equiv.), MeCN (12 mL), $FeCl_3$ (24.33 mg, 150 µmol, 0.05 equiv), imidazole (612.72 mg, 9.00 mmol, 3.0 equiv.), and 1,2-dimethylacenaphthylene-1,2-diol (642.78 mg, 3.00 mmol, 1.0 equiv.). The crude product was purified by silica gel chromatography with 5-10% EtOAc / hexane to yield the title compound (881 mg, 2.70 mmol, 90% yield) as a white solid. ^1H

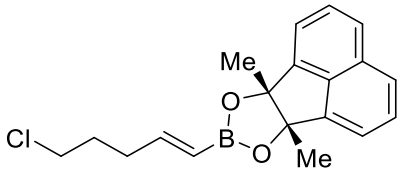
NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, J = 6.9, 2.1 Hz, 2H), 7.67 – 7.57 (m, 4H), 7.42 (d, J = 7.2 Hz, 2H), 7.36 (d, J = 18.4 Hz, 1H), 7.33 – 7.23 (m, 3H), 6.10 (d, J = 18.4 Hz, 1H), 1.85 (s, 6H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.4, 147.4, 140.1, 137.4, 134.1, 131.5, 131.2, 131.2, 129.7, 128.0, 122.2, 94.7, 79.9, 79.7, 79.5, 24.8.; ^{11}B NMR: (160 MHz, $CDCl_3$) δ 30.3.; IR (neat) ν_{max} 3024.6 (w), 2972.4 (w), 2932.9 (w), 1622.7 (s), 1450.0 (m), 1433.7 (m), 1313.1 (s), 1139.6 (s), 788.5 (m), 480.5 (m) cm^{-1}. HRMS (DART) for $C_{22}H_{20}BO_2$ $[M+H]^+$ calculated: 327.1556, found: 327.1543.



6b,9a-dimethyl-8-((E)-prop-1-en-1-yl)-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (S-2). The title compound was prepared according to Method B with [(E)-prop-1-enyl]boronic acid (379 mg, 4.41 mmol, 1.0 equiv.), MeCN (11 mL), 1,2-dimethylacenaphthylene-1,2-diol (1.35 g, 4.41 mmol, 1.0 equiv.), imidazole (901 mg, 13.2 mmol, 3.0 equiv.), and FeCl3 (36 mg, 221 μmol, 0.05 equiv.). The crude product was purified by silica gel chromatography with 5-10% EtOAc / hexane to yield the title compound (1.12 g, 4.24 mmol, 96% yield) as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2H), 7.65 – 7.52 (m, 4H), 6.69 – 6.56 (m, 1H), 5.40 (d, J = 17.8 Hz, 1H), 1.84 – 1.74 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.98, 144.8, 134.7, 131.3, 128.4, 125.2, 119.4, 91.7, 22.1, 21.6. ^{11}B NMR: (160 MHz, $CDCl_3$) δ 29.9; IR (neat) ν_{max} 3044.5 (w), 2973.6 (m), 2933.7 (w), 1639.4 (s), 1347.6 (m), 1214.4 (m), 1077.7 (m), 777.8 (m) cm^{-1}. HRMS (DART) for for C17H18BO_2 $[M+H]^+$: calculated: 265.1400, found: 265.1393.

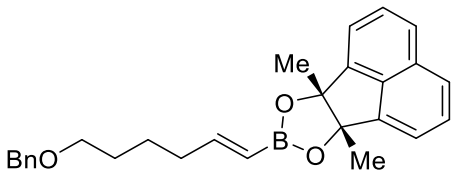


8-((E)-hex-1-en-1-yl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (S-3). The title compound was prepared according to Method B with [(E)-hex-1-enyl]boronic acid (213 mg, 1.67 mmol, 1.0 equiv.), MeCN (6.7 mL), 1,2-dimethylacenaphthylene-1,2-diol (357 g, 1.67 mmol, 1.0 equiv.), imidazole (340 mg, 5.00 mmol, 3.0 equiv.), and $FeCl_3$ (13.5 mg, 83 μmol, 0.05 equiv.). The crude product was purified by silica gel chromatography with 5-10% EtOAc / hexane to yield the title compound (465 mg, 1.52 mmol, 91% yield) as a yellow oil which solidified upon standing. ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, J = 7.9, 1.1 Hz, 2H), 7.65 – 7.51 (m, 4H), 6.61 (dt, J = 18.0, 6.5 Hz, 1H), 5.38 (d, J = 17.9 Hz, 1H), 2.14 – 2.06 (m, 2H), 1.81 (s, 6H), 1.41 – 1.21 (m, 4H), 0.85 (t, J = 7.2 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 144.9, 134.7, 131.3, 128.4, 125.2, 119.4, 91.7, 35.4, 30.3, 22.2, 22.1, 13.9. ^{11}B NMR: (160 MHz, $CDCl_3$) δ 30.0; IR (neat) ν_{max} 3045.2 (w), 2956.9 (m), 2928.2 (m), 2856.8 (w), 1638.0 (m), 1355.2 (m), 1310.6 (m), 1116.4 (m), 1078.4 (m), 805.8 cm^{-1}. HRMS (DART) for $C_{20}H_{24}BO_2$ $[M+H]^+$: calculated: 307.1869, found: 307.1882.

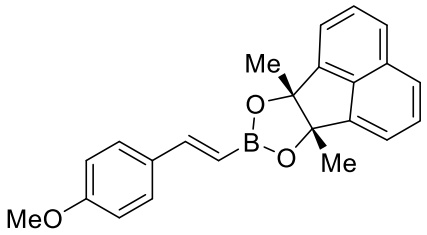


8-((E)-5-chloropent-1-en-1-yl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (S-4). The title compound was prepared according to Method B with (E)-(5-chloropent-1-en-1-yl) boronic acid (367 mg, 2.46 mmol, 1.0 equiv.), MeCN (13 mL), 1,2-dimethylacenaphthylene-1,2-diol (527 mg, 2.46 mmol, 1.0 equiv.), imidazole (503 mg, 7.39 mmol, 3.0 equiv.), and $FeCl_3$ (20 mg, 123 μmol, 0.05 equiv.). The crude product was purified by silica gel chromatography with 5-10% EtOAc / hexane to yield the title compound (530 mg, 1.62 mmol, 66% yield) as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (dt, *J* = 8.0, 1.1 Hz, 2H), 7.63 –

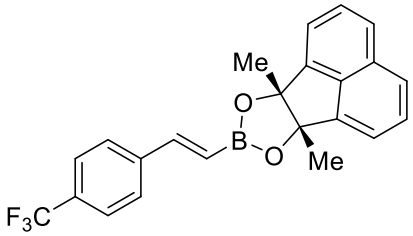
7.53 (m, 4H), 6.59 – 6.50 (m, 1H), 5.42 (dq, *J* = 17.9, 1.5 Hz, 1H), 3.50 – 3.45 (m, 2H), 2.28 – 2.21 (m, 2H), 1.88 – 1.81 (m, 2H), 1.80 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5, 144.9, 134.8, 131.5, 128.6, 125.4, 119.6, 91.9, 44.4, 32.8, 31.0, 22.2. ^{11}B NMR: (160 MHz, $CDCl_3$) δ 29.73; IR (neat) ν_{max} 3042.8 (w), 2975.0 (w), 2933.3 (w), 1637.7 (m), 1347.5 (m), 1311.14 (m), 1114.9 (m), 1076.1 (m), 825.3 (m), 777.6 (s), 640.4 (m) cm^{-1}. HRMS (DART) for $C_{19}H_{20}BClO_2$ $[M+H]^+$ calculated: 327.1323, found: 327.1334.



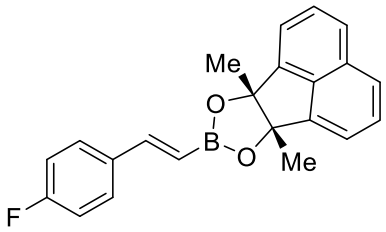
8-((E)-6-(benzyloxy)hex-1-en-1-yl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (S-5). The title compound was prepared according to Method B with (E)-(6-(benzyloxy)hex-1-en-1-yl)boronic acid (497 mg, 2.12 mmol, 1.0 equiv.), MeCN (13 ml), 1,2-dimethylacenaphthylene-1,2-diol (453 mg, 2.12 mmol, 1.0 equiv.), imidazole (433 mg, 6.37 mmol, 3.0 equiv.) and $FeCl_3$ (17.2 mg, 106 μmol, 0.05 equiv.). The crude product was purified by silica gel chromatography with 5-10% EtOAc / hexane to yield the title compound (629 mg, 1.53 mmol, 72% yield) as a thick, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.63 – 7.54 (m, 4H), 7.39 – 7.26 (m, 5H), 6.65 – 6.55 (m, 1H), 5.42 – 5.35 (m, 1H), 4.47 (s, 2H), 3.46 – 3.40 (m, 2H), 2.16 – 2.07 (m, 2H), 1.81 (s, 6H), 1.64 – 1.53 (m, 2H), 1.51 – 1.42 (m, 2H) ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.5, 144.9, 138.7, 134.7, 131.4, 128.5, 128.4, 127.6, 127.5, 125.3, 119.5, 91.7, 72.9, 70.2, 35.5, 29.3, 24.8, 22.2. ^{11}B NMR: (160 MHz, $CDCl_3$) δ 29.94; IR (neat) ν_{max} 3031.0 (w), 2972.4 (w), 2932.6 (w), 2855.4 (w), 1637.1 (m), 1354.9 (m), 1339.4 (m), 1114.4 (m), 1076.0 (m), 805.8 (m), 777.9 (m), 733.4 (m), 696.6 (m), 641.8 (m) cm^{-1}. HRMS (DART) for $C_{27}H_{29}BO_3$ $[M+H]^+$ calculated: 413.2288, found:413.2304.



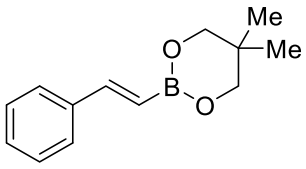
8-((E)-4-methoxystyryl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (S-6). The title compound was prepared according to Method B with [(E)-2-(4-methoxyphenyl)vinyl]boronic acid (186 mg, 1.04 mmol, 1.0 equiv.), MeCN (4.2 mL), 1,2-dimethylacenaphthylene-1,2-diol (223.49 mg, 1.04 mmol, 1.0 equiv.), imidazole (213 mg, 3.13 mmol, 3.0 equiv.), and $FeCl_3$ (8.5 mg, 52.2 μmol, 0.05 equiv.). The crude product was purified by silica gel chromatography with 5-10% EtOAc / hexane to yield the title compound (353 mg, 0.99 mmol, 95% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, J = 6.7, 2.2 Hz, 2H), 7.65 – 7.56 (m, 4H), 7.40 – 7.35 (m, 2H), 7.32 (d, J = 18.4 Hz, 1H), 6.83 (d, J = 8.5 Hz, 2H), 5.95 (d, J = 18.3 Hz, 1H), 3.79 (s, 3H), 1.85 (s, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 149.2, 144.78, 134.7, 131.4, 130.3, 128.5, 128.4, 125.3, 119.4, 113.9, 91.9, 55.2, 22.1. ^{11}B NMR: (160 MHz, $CDCl_3$) δ 31.0.; IR (neat) ν_{max} 3041.3 (w), 2972.0 (w), 2932.7 (w), 2836.1 (w), 1623.7 (m), 1603.1 (m), 1509.4 (m), 1312.9 (m), 1252.7 (m), 1116.0 (m), 1077.2 (m), 815.7 (m) cm^{-1}. HRMS (DART) for $C_{23}H_{22}BO_3$ $[M+H]^+$: calculated: 357.1662, found: 357.1664.



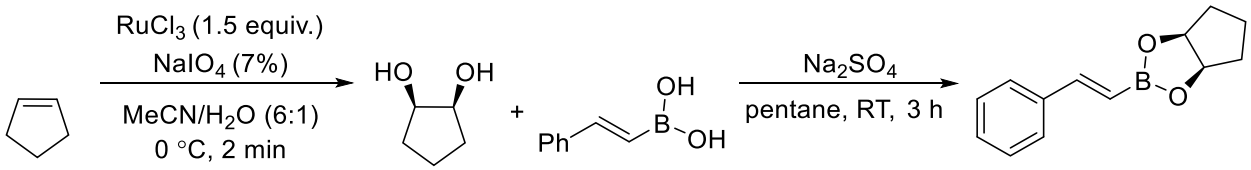
6b,9a-dimethyl-8-((E)-4-(trifluoromethyl)styryl)-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (S-7). The title compound was prepared according to Method B with [(E)-2-[4-(trifluoromethyl)phenyl]vinyl]boronic acid (164 mg, 0.76 mmol, 1.0 equiv.), MeCN (3.0 mL), 1,2-dimethylacenaphthylene-1,2-diol (163 mg, 0.76 mmol, 1.0 equiv.), imidazole (155 mg, 2.28 mmol, 3.0 equiv.), and $FeCl_3$ (6.2 mg, 38 μmol). The crude product was purified by silica gel chromatography with 5-10% EtOAc / hexane to yield the title compound (276 mg, 0.70 mmol, 92% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dt, J = 7.2, 1.6 Hz, 2H), 7.70 – 7.59 (m, 4H), 7.56 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 18.3 Hz, 1H), 6.20 (d, J = 18.4 Hz, 1H), 1.87 (s, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 144.5, 140.7, 134.7, 131.4, 130.4 (q, $^2J_{C\text{-}F}$ = 32.4 Hz), 128.5, 127.1, 125.5 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.4, 124.1 (partially buried, q, $^1J_{C\text{-}F}$ = 271.8 Hz), 119.5, 92.2, 29.7, 22.1. ^{11}B NMR: (160 MHz, $CDCl_3$) δ 30.3.; ^{19}F NMR (470 MHz, $CDCl_3$) δ 62.7.; IR (neat) ν_{max} 3045.7 (w), 2974.7 (w), 2929.0 (w), 1626.9 (m), 1457.6 (m), 1415.8 (m), 1263.2 (m), 1210.6 (m), 825.1 (m), 778.6 (m) cm^{-1}. HRMS (DART) for $C_{23}H_{19}BO_2F_3$ $[M+H]^+$: calculated: 395.1430, found: 395.1441.



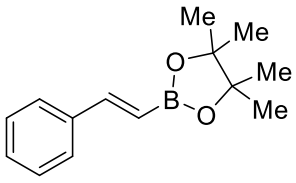
8-((E)-4-fluorostyryl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (S-8). The title compound was prepared according to Method B with [(E)-2-(4-fluorophenyl)vinyl]boronic acid (277 mg, 1.67 mmol, 1.0 equiv.), MeCN (6.67 mL), 1,2-dimethylacenaphthylene-1,2-diol (357 mg, 1.67 mmol, 1.0 equiv.), imidazole (304 mg, 5.00 mmol, 3.0 equiv.), and $FeCl_3$ (14 mg, 83.3 μmol, 0.05 equiv.). The crude product was purified by silica gel chromatography with 5-10% EtOAc / hexane to yield the title compound (535 mg, 1.55 mmol, 93% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, J = 7.1, 1.8 Hz, 2H), 7.66 – 7.56 (m, 4H), 7.46 – 7.36 (m, 2H), 7.32 (d, J = 18.4 Hz, 1H), 7.05 – 6.92 (m, 2H), 6.01 (d, J = 18.4 Hz, 1H), 1.85 (s, 6H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1 (d, $^1J_{C\text{-}F}$ = 248.5 Hz), 148.3, 144.7, 134.7, 133.7, 133.6, 131.4, 128.6 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 128.5, 125.3, 119.5, 115.5 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 92.0, 22.1. ^{11}B NMR: (160 MHz, $CDCl_3$) δ 30.1; ^{19}F NMR: (470 MHz, $CDCl_3$) δ -112.41; IR (neat) ν_{max} 3045.2 (w), 2976.5 (m), 2933.9 (w), 1620.8 (m), 1506.5 (m), 1415.7 (m), 1156.6 (m), 904.0 (m), 778.7 (m) cm^{-1}. HRMS (DART) for $C_{22}H_{19}BO_2F$ $[M+H]^+$: calculated: 345.1462, found: 345.1470.



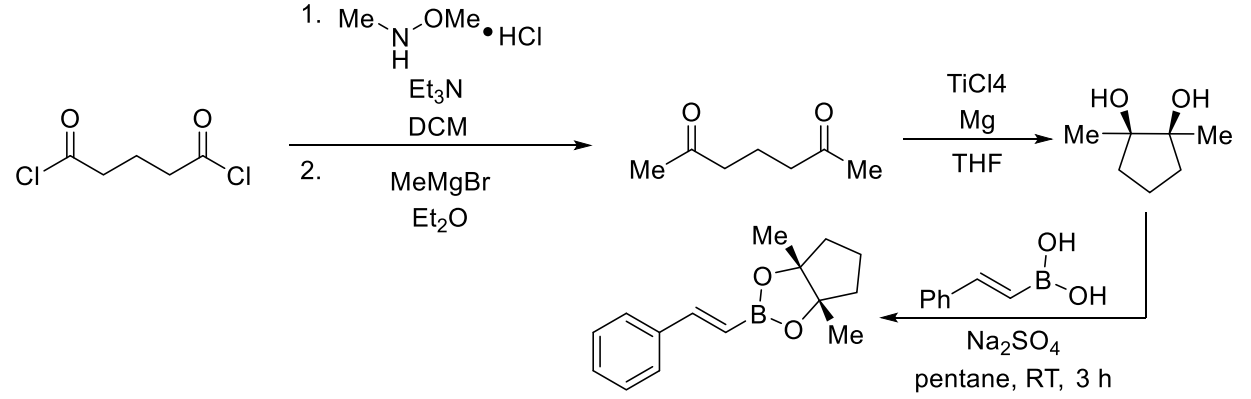
(E)-5,5-dimethyl-2-styryl-1,3,2-dioxaborinane (S-9). The title compound was prepared according to Method E using neopentyl glycol (208 mg, 2.00 mmol, 1 equiv.), (E)-styrylboronic acid (296 mg, 2.00 mmol, 1.0 equiv.), and pentane (20 mL). The crude product was purified by silica gel chromatography with 10% EtOAc / hexanes to yield the title compound (278 mg, 1.29 mmol, 64% yield) as a white solid. Spectral data are in accordance with the literature.[4]



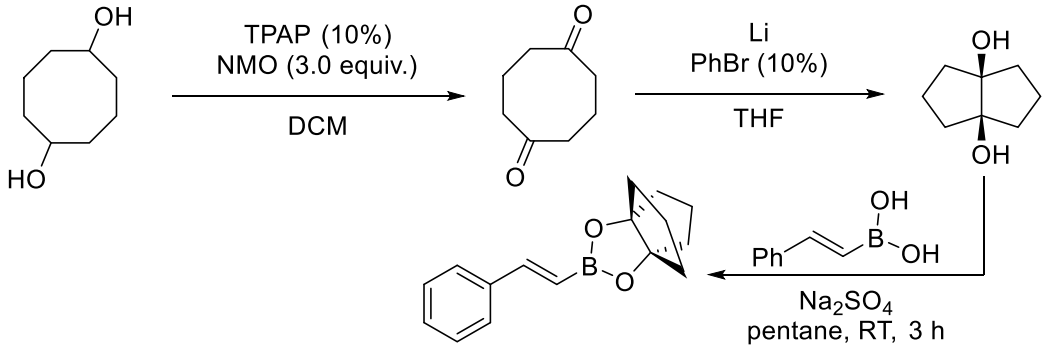
(E)-2-styryltetrahydro-4H-cyclopenta[d][1,3,2]dioxaborole (S-10). The title compound was prepared according to Method E using *syn*-cyclopentane-1,2-diol (prepared using a literature procedure[5]) (109 mg, 1.07 mmol, 1 equiv.) with (E)-styrylboronic acid (158.3 mg, 1.07 mmol, 1 equiv.) and pentane (4 mL). The mixture was allowed to stir overnight in a sealed vial at room temperature. The crude product was purified by silica gel chromatography with 10% EtOAc: hexanes to yield the title compound (174 mg, 0.812 mmol, 76%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.40 (d, J = 18.5 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.32 – 7.28 (m, 1H), 6.17 (d, J = 18.5 Hz, 1H), 4.97 – 4.86 (m, 2H), 2.03 – 1.94 (m, 2H), 1.74 – 1.55 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 137.6, 129.1, 128.7, 127.2, 82.5, 34.9, 21.7. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.2.; IR (neat) ν_{max} 3025.0 (w), 2960.5 (w), 1622.4 (m), 1357.7 (s), 1032.5 (m), 746.8 (s) cm^{-1}. HRMS (DART) for $C_{13}H_{16}BO_2$ $[M+H]^+$ calculated: 215.1243, found: 215.1252.



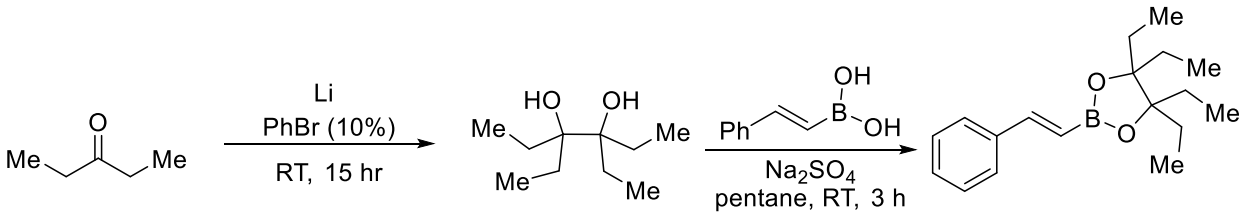
(E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (S-11). The title compound was prepared according to a literature procedure [6] using phenylacetylene (2.14 mg, 21.00 mmol, 1.05 equiv.), pinacolborane (2.56 g, 20.0 mmol, 1.0 equiv.) and Bis(cyclopentadienyl)zirconium(IV) chloride hydride (258 mg, 1 mmol, 0.05 equiv.). The crude product was purified by silica gel chromatography with 5-10% EtOAc / hexanes to yield the title compound (4.25 mg, 18.4 mmol, 92% yield) as a white solid. Spectral data are in accordance with the literature.[7]



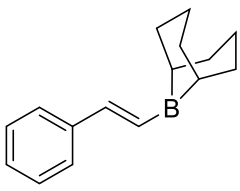
(E)-3a,6a-dimethyl-2-styryltetrahydro-4H-cyclopenta[d][1,3,2]dioxaborole (S-12). The title compound was prepared according to a series of literature reactions[8, 9], then Method E using the cis-1,2-dimethylcyclopentane-1,2-diol (38.6 mg, 296 µmol, 1.0 equiv.) with (E)-styrylboronic acid (43.9 mg, 296 µmol, 1.0 equiv.), and pentane (1 mL). The crude product was purified by silica gel chromatography with 10% EtOAc / hexanes to yield the title compound as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.40 – 7.27 (m, 4H), 6.15 (d, J = 18.4 Hz, 1H), 2.05 (dd, J = 12.9, 5.5 Hz, 2H), 1.69 – 1.50 (m, 4H), 1.37 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4, 137.7, 129.0, 128.7, 127.2, 90.6, 42.0, 23.4, 21.4. ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.7.; IR (neat) ν_{max} 2966.4 (w), 1623.2 (m), 1353.0 (s). HRMS (DART) for $C_{15}H_{19}BO_2$ $[M+H]^+$ calculated: 243.1556, found: 243.1563.



8-((E)-styryl)tetrahydro-1H,4H-3a,6a-(epoxyboranooxy)pentalene (S-13). The title compound was prepared according to Method E with (E)-styrylboronic acid (70.5 mg, 477 µmol, 1.0 equiv.), tetrahydropentalene-3a,6a(1H,4H)-diol (67 mg, 477 µmol, 1.0 equiv.) and 1 mL of pentane. The crude product was purified by silica gel chromatography with 5% EtOAc / hexanes to the yield the title compound (121.1 mg, 338 µmol, 71% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.39 (d, *J* = 18.4 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.15 (d, *J* = 18.4 Hz, 1H), 2.02 – 1.96 (m, 4H), 1.87 – 1.78 (m, 2H), 1.75 – 1.61 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 137.6, 129.0, 128.7, 127.2, 99.8, 39.0, 25.0. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7.; IR (neat) ν_{max} 3025.0 (w), 2960.5 (w), 1622.4 (m), 1357.7 (s), 1032.5 (m), 746.8 (m). HRMS (DART) for $C_{16}H_{19}BO_2$ $[M+H]^+$ calculated: 255.1556 found: 255.1552.



(E)-4,4,5,5-tetraethyl-2-styryl-1,3,2-dioxaborolane (S-14). The title compound was prepared according to Method E using 3,4-diethylhexane-3,4-diol (prepared according to a literature procedure[10]) (79.5 mg, 0.46 mmol, 1.0 equiv.), (E)-styrylboronic acid (67.5 mg, 0.46 mmol, 1.0 equiv.) and pentane (1.5 mL). The crude product was purified by silica gel chromatography with 10% EtOAc / hexanes to yield the title compound (115 mg, 0.40 mmol, 88%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.41 (d, *J* = 18.4 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.31 – 7.27 (m, 1H), 6.20 (d, *J* = 18.3 Hz, 1H), 1.80 – 1.67 (m, 8H), 0.96 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 137.8, 128.9, 128.7, 127.2, 88.5, 26.6, 9.0. ^{11}B NMR (192 MHz, $CDCl_3$) δ 29.1.; IR (neat) ν_{max} 2975.3 (w), 2973.5 (w), 2882.9 (w), 1624.2 (m), 1346.2 (s) cm^{-1}. HRMS (DART) for $C_{18}H_{27}BO_2$ $[M+H]^+$ calculated: 287.2182, found: 287.2189.

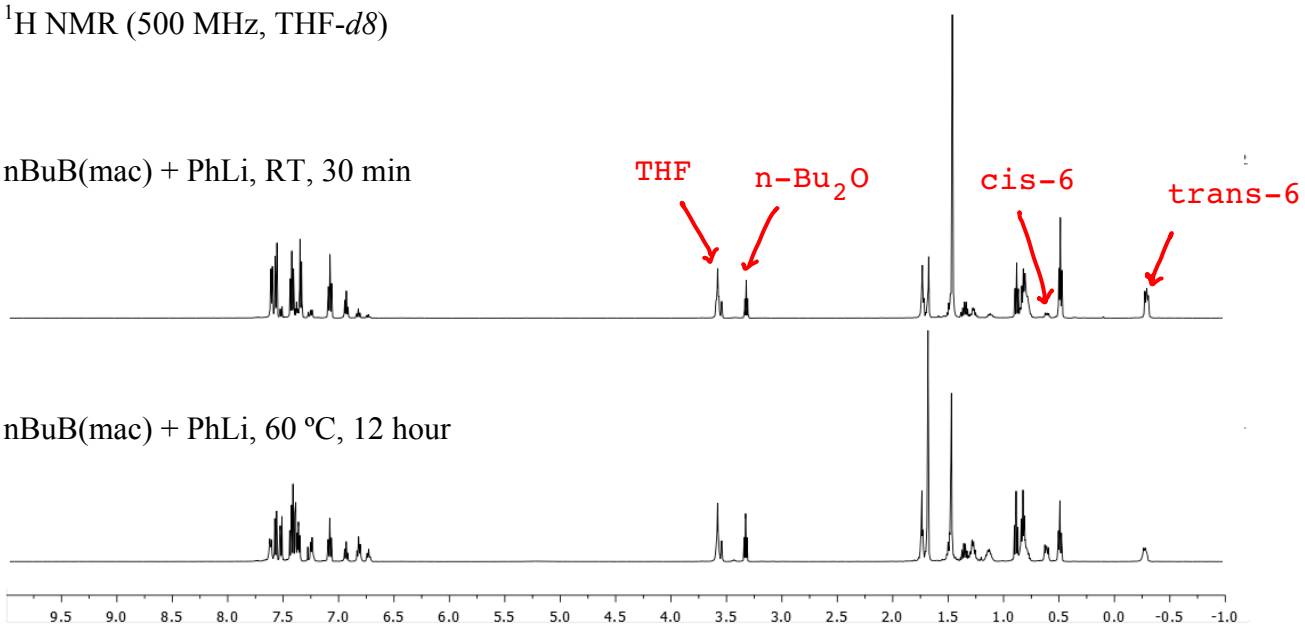


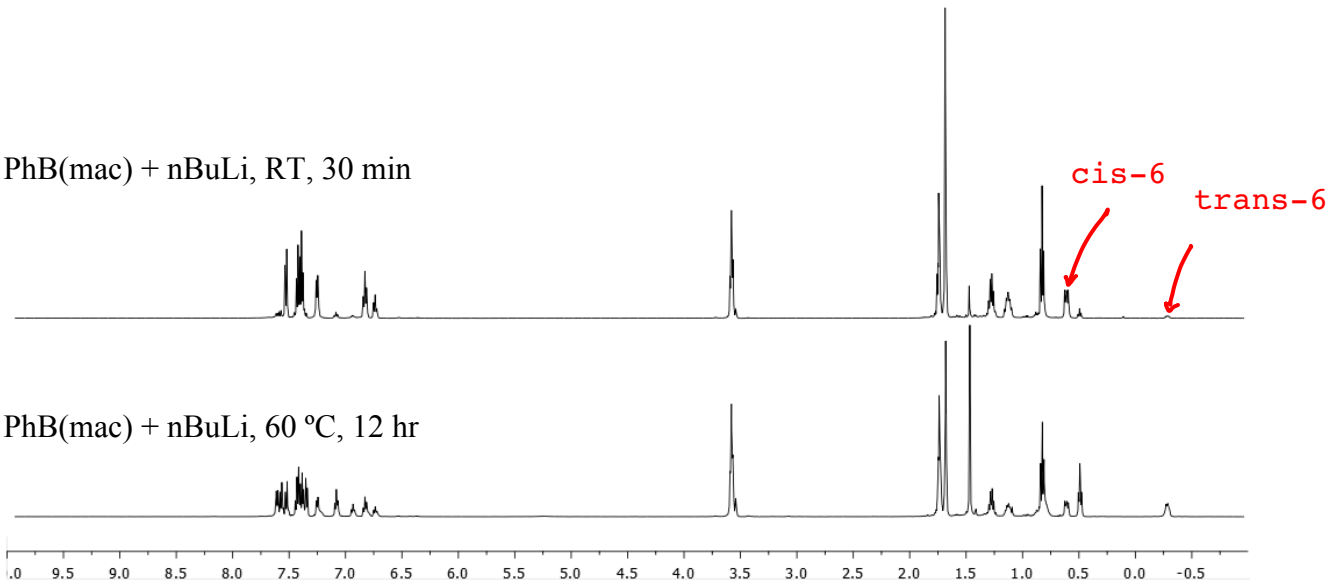
(E)-9-styryl-9-borabicyclo[3.3.1]nonane (S-15). In an argon-filled glovebox, to an oven-dried scintillation vial was added phenylacetylene (102.13 mg, 1 mmol, 1.0 equiv.), followed by 9-borabicyclo[3.3.1]nonane (0.5 M solution in THF, 2.00 mL, 1.0 mmol, 1.0 equiv.). The solution was allowed to stir for 3 hours at room temperature then used without further purification as a ~0.5 M solution in THF.

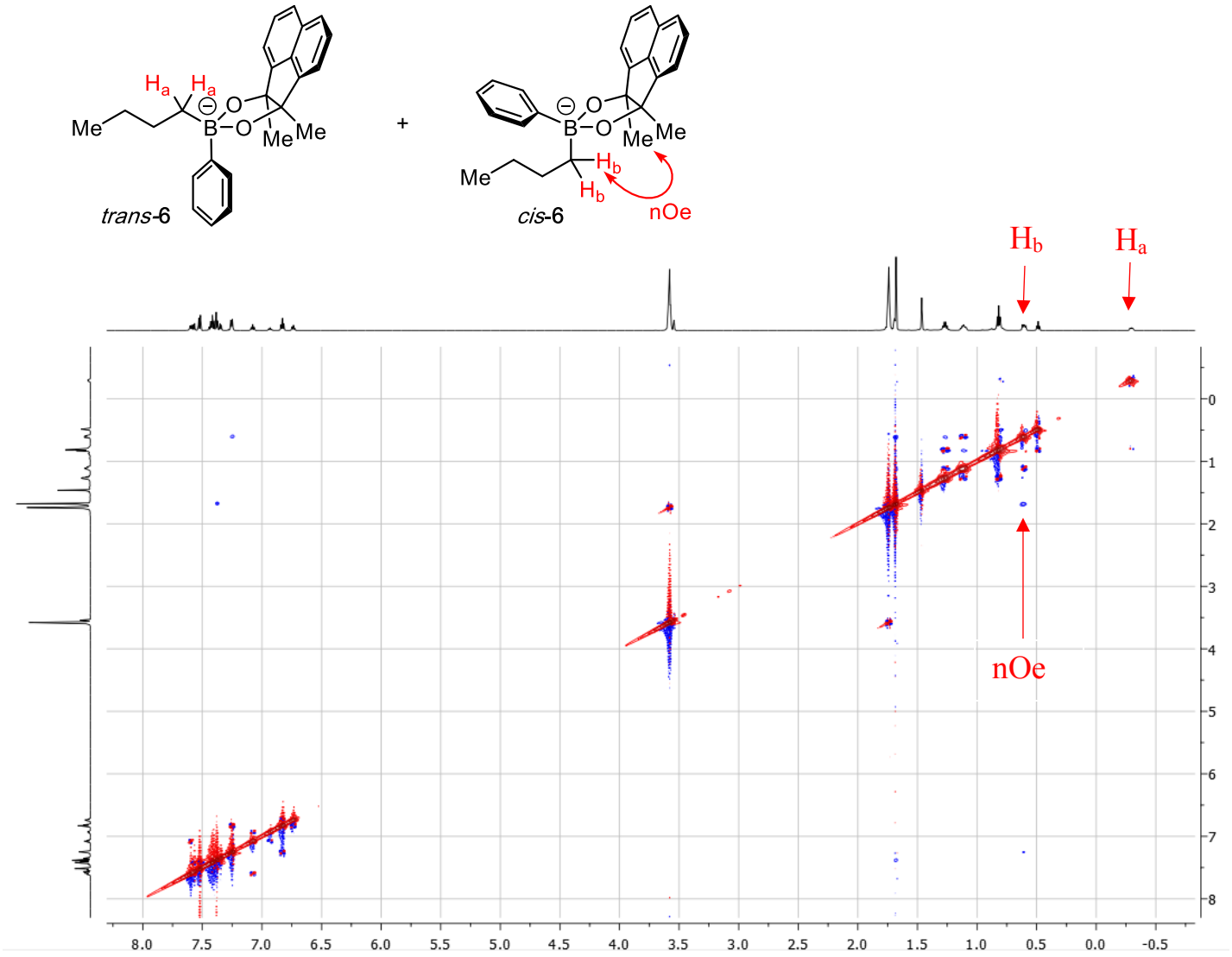
III. Procedure for boron 'ate' complex NMR studies

In an argon-filled glovebox, boronic ester (0.2 mmol, 1.0 equiv.) and THF (0.4 mL) were added to an oven-dried 2-dram vial eqeuipped with a stir bar. The vial was sealed with a septum cap and removed from the glovebox, then cooled to 0 ºC. The organolithium reagent (0.2 mmol, 1.0 equiv; in hexanes for *n*-BuLi or dibutyl ether for PhLi) was added dropwise and reaction was allowed to stir at room temperature for 15 minutes before the solvent was carefully removed under vacuum. The vial was brought back into the glovebox and the 'ate' complex was dissolved in THF-*d8* and transferred to an oven-dried NMR tube. The NMR tube was sealed and a ^{1}H NMR spectrum was obtained. The NMR tube was then heated to 60 ºC for 12 hours before another ^{1}H NMR spectrum was obtained.

^{1}H NMR (500 MHz, THF-*d8*)






Ha
Ha
Me
B
O
O
Me
Me
trans-6
+
Me
B
O
O
Me
Me
Hb
Hb
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cis-6
Hb
Ha
nOe
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
2.5
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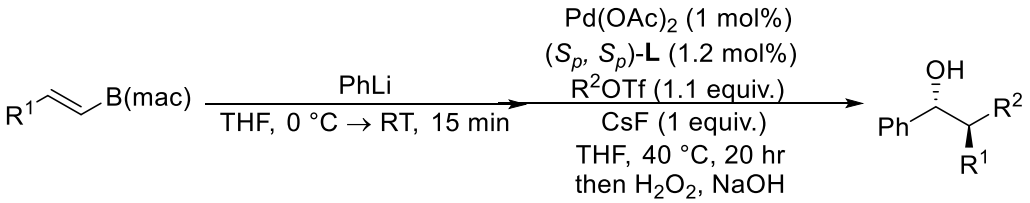
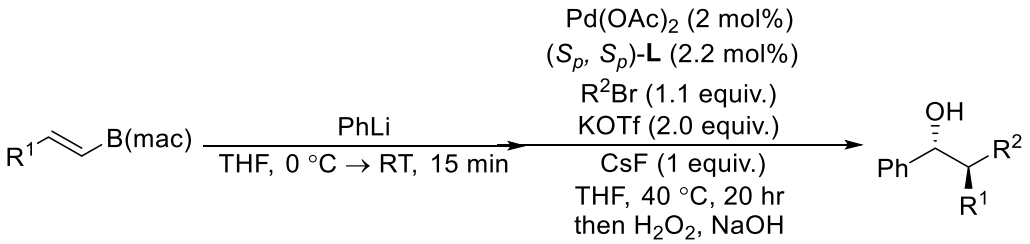
IV. Representative procedure for Conjunctive Cross-Coupling
Method A:



To an oven-dried 2-dram vial equipped with a magnetic stir bar in an Ar-filled glovebox was added alkenyl boronic acid "mac" ester (0.20 mmol, 1.00 equiv.) and THF (0.4 mL). The vial was sealed with a septum cap, and removed from the glovebox. The reaction vial was cooled to 0 °C, and a phenyllithium solution (1.9 M in dibutyl ether, 0.20 mmol, 1.0 equiv.) was added at 0 °C. The reaction vial was allowed to warm to room temperature and stirred for 15 minutes, then the solvent was carefully removed under reduced pressure, and the reaction vial was brought back into the glovebox. Cesium fluoride (0.20 mmol, 1.0 equiv.) was added to the reaction vial, followed by THF (0.6 mL), and the vial was stirred at room temperature for 5 minutes. To a separate oven-dried 2-dram vial equipped with a magnetic stir bar in the glovebox was added $Pd(OAc)_2$ (0.002 mmol, 0.01 equiv.), (S_p, S_p)-**L** (0.0024 mmol, 0.012 equiv.), and THF (0.2 mL). The $Pd(OAc)_2$/(S_p, S_p)-**L** solution was allowed to stir for 15 minutes at room temperature, then it was transferred into the reaction vial, followed by aryl triflate (0.22 mmol, 1.10 equiv.). The reaction vial was sealed with a polypropylene cap, taped, and brought out of the glovebox where it was allowed to stir at 40 °C for 20 hours. The resulting mixture was cooled to room temperature, filtered through a celite plug with diethyl ether, and concentrated under reduced pressure. The crude product was diluted with THF (3 mL) and cooled to 0 °C before 3M NaOH (2 mL) was added, followed by 30% H_2O_2 (1.0 mL) dropwise. The reaction was allowed to warm to room temperature and stirred for 4 hours, then quenched at 0 °C by dropwise addition of saturated aq. $Na_2S_2O_3$ solution (3 mL). This solution was allowed to stir at room temperature for 10 minutes. The mixture was diluted with Et_2O and transferred to a separatory funnel, and the aqueous layer was washed with Et_2O three times. The combined organic layers were washed with brine then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was subsequently purified via silica gel (treated with 2% triethylamine / hexanes prior to use) column chromatography to afford the desired product.

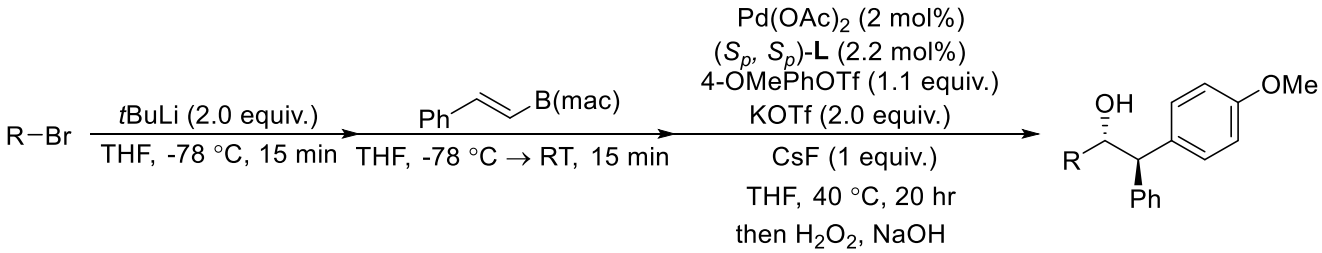
Method B:



To an oven-dried 2-dram vial equipped with a magnetic stir bar in an Ar-filled glovebox was added alkenyl boronic acid "mac" ester (0.20 mmol, 1.00 equiv.) and THF (0.4 mL), sealed with a septum cap, and removed from the glovebox. The reaction vial was cooled to 0 °C, and a phenyllithium solution (1.9M in dibutyl ether, 0.20 mmol, 1.0 equiv.) was added at 0 °C. The reaction vial was allowed to warm to room temperature and stirred for 15 minutes. Then, the solvent was carefully removed under reduced pressure, and the reaction vial was brought back into

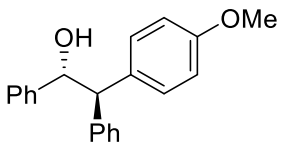
the glovebox. Cesium fluoride (0.20 mmol, 1.0 equiv.) was added to the reaction vial, followed by THF (0.4 mL), and the vial was stirred at room temperature for 5 minutes, then potassium trifluoromethanesulfonate (0.40 mmol, 2.0 equiv) was added. To a separate oven-dried 2-dram vial equipped with a magnetic stirbar in the glovebox was added $Pd(OAc)_2$ (0.004 mmol, 0.020 equiv.), (S_p, S_p)-**L** (0.0044 mmol, 0.022 equiv.), and THF (0.4 mL). The $Pd(OAc)_2$/(S_p, S_p)-**L** solution was allowed to stir for 15 minutes at room temperature, then transferred into the reaction vial, followed by aryl/alkenyl bromide (0.22 mmol, 1.10 equiv.). The reaction vial was sealed with a polypropylene cap, taped, and brought out of the glovebox where it was allowed to stir at 40 °C for 20 hours. The same oxidation and purification procedure was done as in Method A.

Method C:



To an oven-dried 2-dram vial equipped with a magnetic stir bar in an Ar-filled glovebox was added aryl/alkenyl bromide (0.20 mmol, 1.00 equiv.) and THF (0.2 mL), and sealed with a septum cap. To a separate oven-dried 1-dram vial was added styrenyl B(mac) (S-1) (0.2 mmol, 1.0 equiv,) and THF (0.4 mL). Both vials were removed from the glove box. The 2-dram reaction vial was cooled to -78 °C, and a *tert*-butyllithium solution (0.40 mmol, 2.0 equiv.) was added dropwise at -78 °C and the reaction was allowed to stir at that temperature for 15 minutes. The solution of styrenyl B(mac) (S-1) from the 1-dram vial was then added to the reaction vial slowly, and the reaction was warmed to room temperature and stirred for 15 minutes, then the solvent was carefully removed under reduced pressure, and the reaction vial was brought back into the glovebox. Cesium fluoride (0.20 mmol, 1.0 equiv.) was added to the reaction vial, followed by THF (0.4 mL), and the vial was stirred at room temperature for 5 minutes, then potassium trifluoromethanesulfonate (0.40 mmol, 2.0 equiv) was added. To a separate oven-dried 2-dram vial equipped with a magnetic stir bar in the glovebox was added $Pd(OAc)_2$ (0.004 mmol, 0.02 equiv.), (S_p, S_p)-**L** (0.0044 mmol, 0.022 equiv.), and THF (0.4 mL). The $Pd(OAc)_2$/(S_p, S_p)-**L** solution was allowed to stir for 15 minutes at room temperature then transferred into the reaction vial, followed by and 4-methoxyphenyl trifluoromethanesulfonate (0.22 mmol, 1.10 equiv.). The reaction vial was sealed with a polypropylene cap, taped, and brought out of the glovebox where it was allowed to stir at 40 °C for 20 hours. The same oxidation and purification procedure was done as in Method A.

V. Characterization of Conjunctive Cross Coupling Products and Analysis of Stereochemistry



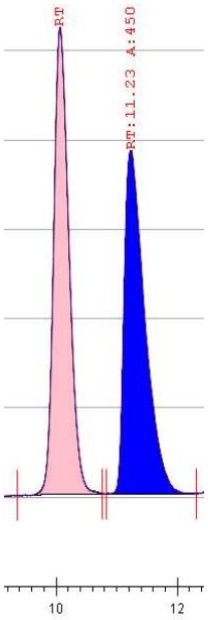
(1R,2R)-2-(4-methoxyphenyl)-1,2-diphenylethan-1-ol (2b). The reaction was performed according to the general procedure ***(Method A)*** with styrenyl B(mac) (S-1) (65.2 mg, 0.20 mmol, 1.0 equiv.), phenyllithium (1.9 M in dibutyl ether, 0.11 mL, .20 mmol, 1.0 equiv.), 4-methoxyphenyl trifluoromethanesulfonate (56.4 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.45 mg, 2.0 µmol, 0.010 equiv.), (S_p, S_p)-**L** (2.5 mg, 2.4 µmol) , 0.012 equiv.), and cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.) in THF (0.80 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (5-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (46 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ (d, J = 8.2 Hz, 2H), 7.29 – 7.05 (m, 10H), 6.89 (d, J = 8.2 Hz, 2H), 5.36 (d, J = 8.5 Hz, 1H), 4.22 (d, J = 8.5 Hz, 1H), 3.80 (s, 3H), 2.16 (br, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.5, 142.3, 141.9, 132.8, 130.0, 128.5, 128.2, 128.0, 127.5, 126.9, 126.3, 114.2, 76.9, 59.4, 55.2.; IR (neat): ν_{max} 3385.3 (br), 3060.4 (w), 3028.0 (m), 2906.4 (m), 2834.7 (w), 1609.2 (m), 1509.4 (s), 1245.9 (s), 1075.1 (s), 785.0 (m), 697.3 (s), 596.5 (m) cm^{-1}. HRMS (DART) for $C_{21}H_{19}O$ $[M+H-H_2O]^+$: calculated: 287.1436, found: 287.1431. $[\alpha]^{20}_D$: -43.242 (c = 1.200, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with $Pd(OAc)_2$ (2 mol%) and 1,3-Bis(diphenylphosphino)propane (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

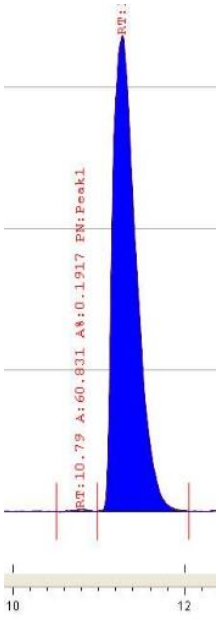
Chiral SFC (OD-H, 12% IPA, 4 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R,2R)-2-(4-methoxyphenyl)-1,2-diphenylethan-1-ol.

Racemic Material

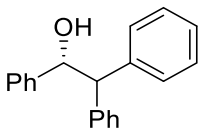


Peak No	% Area	Area	RT (min)
1	50.2496	4554.7092	10.06
2	49.7504	4509.4626	11.23
Total:	100	9064.1718	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.1917	60.831	10.79
2	99.8083	31665.4228	11.27
Total:	100	31726.2538	



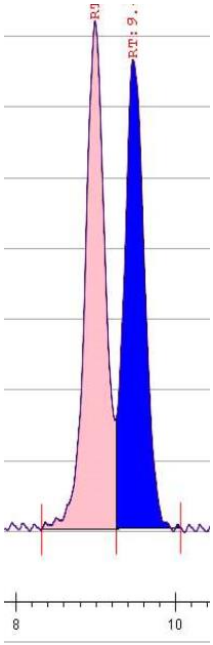
(R)-1,2,2-triphenylethan-1-ol (7). The reaction was performed according to the general procedure ***(Method A)*** with styrenyl B(mac) (S-1) (65.2 mg, 0.20 mmol, 1.0 equiv.), phenyllithium (1.9 M in dibutyl ether, 0.11 mL, .20 mmol, 1.0 equiv.), phenyl trifluoromethanesulfonate (49.8 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.45 mg, 2.0 µmol, 0.010 equiv.), (S_p, S_p)-**L** (2.5 mg, 2.4 µmol) , 0.012 equiv.), cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.) in THF (0.80 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (2-10% EtOAc in hexanes, stain in magic stain) to afford a white solid (47 mg, 86% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, J = 7.3 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.31 – 7.19 (m, 6H), 7.19 – 7.08 (m, 5H), 5.41 (dd, J = 8.8, 2.7 Hz, 1H), 4.27 (d, J = 8.8 Hz, 1H), 2.13 (d, J = 2.9 Hz, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.2, 141.5, 140.9, 128.9, 128.8, 128.6, 128.2, 128.0, 127.6, 127.0, 126.9, 126.4, 76.8, 60.3.; IR (neat): ν_{max} 3341.8 (br), 3060.0 (m), 3027.2 (m), 2908.2 (w), 1598.9 (m), 1493.5 (m), 1451.3 (m), 1301.2 (m), 743.9 (s), 697.0 (s), 598.8 (s) cm^{-1}. HRMS (DART) for $C_{20}H_{17}$ $[M+H-H_2O]^+$: calculated: 257.1325, found: 257.1324. $[\alpha]^{20}_D$: -63.355 (c = 0.960, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the procedure described above with $Pd(OAc)_2$ (2 mol%) and 1,3-Bis(diphenylphosphino)propane (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

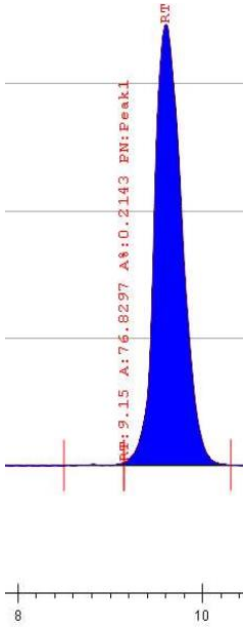
Chiral SFC (Chiralcel OD-H, 10% IPA, 4 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (R)-1,2,2-triphenylethan-1-ol.

Racemic Material

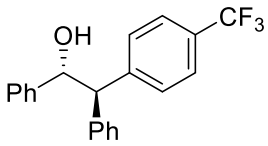


Peak No	% Area	Area	RT (min)
1	51.9085	2512.8466	8.99
2	48.0915	2328.0711	9.47
Total:	100	4840.9177	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.2143	76.8297	9.15
2	99.7857	35770.1731	9.6
Total:	100	35847.0028	



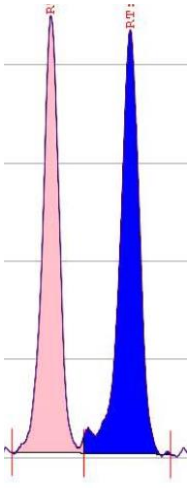
(1R,2R)-1,2-diphenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (8). The reaction was performed according to the general procedure ***(Method B)*** with styrenyl B(mac) (S-1) (65.2 mg, 0.20 mmol, 1.0 equiv.), phenyllithium (1.9 M in dibutyl ether, 0.11 mL, .20 mmol, 1.0 equiv.), 1-bromo-4-(trifluoromethyl)benzene (49.5 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.90 mg, 4.0 µmol, 0.020 equiv.), (S_p, S_p)-**L** (5.0 mg, 4.8 µmol) , 0.024 equiv.), cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.), and potassium trifluoromethanesulfonate (75.3 mg, 0.40 mmol, 2.0 equiv.) in THF (0.80 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (2-10% EtOAc in hexanes, stain in magic stain) to afford a pale yellow oil (30 mg, 44% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.28 – 7.08 (m, 10H), 5.44 (d, J = 8.3 Hz, 1H), 4.33 (d, J = 8.3 Hz, 1H), 2.06 (br, 1H).; ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.9, 144.8, 143.5, 132.1, 131.6 (q, $^2J_{C\text{-}F}$ = 32.4 Hz), 131.2, 131.09, 131.06, 130.9, 130.5, 129.4, 129.3, 128.0 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 126.9 (partially buried, q, $^1J_{C\text{-}F}$ = 271.8 Hz), 79.3, 62.3, 33.0.; ^{19}F NMR (470 MHz, $CDCl_3$): δ -62.4.; IR (neat): ν_{max} 3359.1 (br), 3063.1 (w), 3029.7 (m), 2924.1 (w), 1618.8 (m), 1324.7 (s),1163.9 (m), 1113.7 (m), 1068.7 (m), 746.9 (m) cm^{-1}. HRMS (DART) for $C_{21}H_{16}F_3$ $[M+H-H_2O]^+$: calculated: 325.1204, found: 325.1211. $[\alpha]^{20}_D$: -50.989 (c = 1.055, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with $Pd(OAc)_2$ (2 mol%) and 1,3-Bis(diphenylphosphino)propane (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

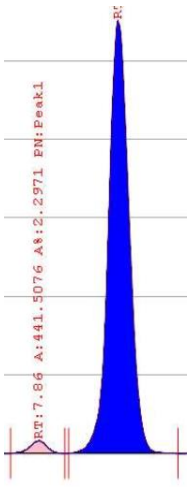
Chiral SFC (Chiralcel OD-H, 10% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R,2R)-1,2-diphenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-ol.

Racemic Material

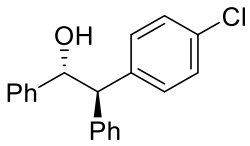


Peak No	% Ar		RT (min)
1	46.6539	1187.7833	7.43
2	53.3461	1358.1622	8.34
Total:	100	2545.9455	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	2.2971	441.5076	7.86
2	97.7029	18778.9673	8.81
Total:	100	19220.4749	



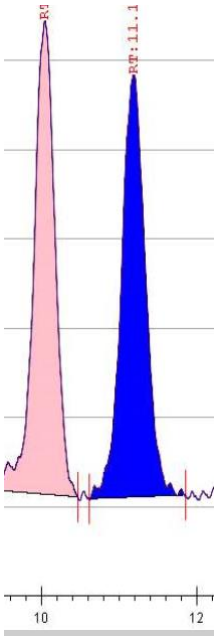
(1R,2R)-2-(4-chlorophenyl)-1,2-diphenylethan-1-ol (9). The reaction was performed according to the general procedure ***(Method B)*** with styrenyl B(mac) (S-1) (65.2 mg, 0.20 mmol, 1.0 equiv.), phenyllithium (1.9 M in dibutyl ether, 0.11 mL, .20 mmol, 1.0 equiv.), 1-bromo-4-chlorobenzene (42.1 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.90 mg, 4.0 µmol, 0.020 equiv.), (S_p, S_p)-**L** (5.0 mg, 4.8 µmol) , 0.024 equiv.), cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.), and potassium trifluoromethanesulfonate (75.3 mg, 0.40 mmol, 2.0 equiv.) in THF (0.80 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (2-10% EtOAc in hexanes, stain in magic stain) to afford a pale yellow oil (29 mg, 47% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.06 (m, 14H), 5.38 (d, J = 8.2 Hz, 1H), 4.24 (d, J = 8.2 Hz, 1H), 2.05 (br, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.4, 141.4, 139.6, 132.8, 130.6, 128.9, 128.7, 128.54, 128.53, 128.3, 127.9, 126.9, 126.8, 76.9, 59.4.; IR (neat): ν_{max} 3350.5, 3061.4, 3028.4, 2920.9, 1491.2, 1453.2, 1014.8, 799.1, 734.8, 698.5 cm^{-1}. HRMS (DART) for $C_{20}H_{16}Cl$ $[M+H-H_2O]^+$: calculated: 291.0941, found: 291.0930. $[\alpha]^{20}_D$: -32.43 (c = 1.00, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with $Pd(OAc)_2$ (2 mol%) and 1,3-Bis(diphenylphosphino)propane (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

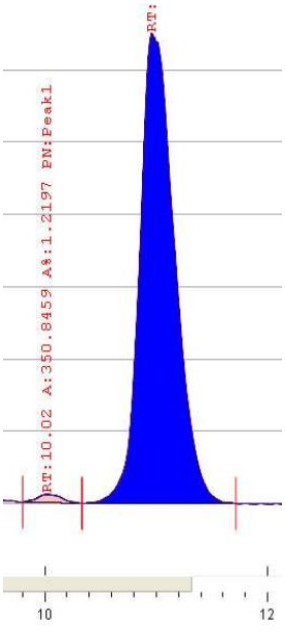
Chiral SFC (Chiralcel OD-H, 10% IPA, 4 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R,2R)-2-(4-chlorophenyl)-1,2-diphenylethan-1-ol.

Racemic Material

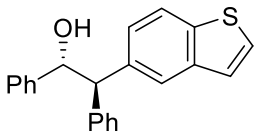


Peak No	% Area	Area	RT (min)
1	50.1967	2046.2136	10.04
2	49.8033	2030.1811	11.19
Total:	100	4076.3947	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	1.2197	350.8459	10.02
2	98.7803	28413.5011	10.96
Total:	100	28764.347	



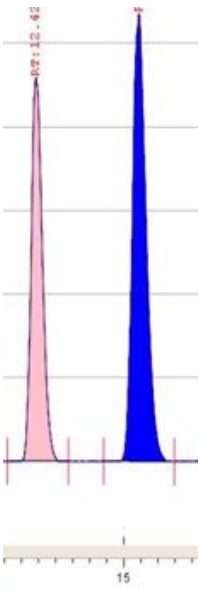
(1R,2R)-2-(benzo[b]thiophen-5-yl)-1,2-diphenylethan-1-ol (10). The reaction was performed according to the general procedure ***(Method B)*** with styrenyl B(mac) (S-1) (65.2 mg, 0.2 mmol, 1 equiv.), phenyllithium in dibutyl ether solution (1.9 M) (0.105 mL, 0.2 mmol, 1 equiv.), 5-bromobenzothiophene (46.9 mg, 0.22 mmol, 1.10 equiv.), palladium (II) acetate (0.45 mg, 0.002 mmol, 0.010 equiv.), (S_p, S_p)-**L** (2.30 mg, 0.0022 mmol, 0.011 equiv.), potassium triflate (75.3 mg, 0.4 mmol, 2 equiv.), and cesium fluoride (30.4 mg, 0.2 mmol, 1 equiv.) in THF (0.8 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (5-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (28.4 mg, 43% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 5.4 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 5.4 Hz, 1H), 7.25 – 7.03 (m, 10H), 5.48 (d, J = 8.7 Hz, 1H), 4.40 (d, J = 8.6 Hz, 1H), 2.16 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.4, 141.8, 140.2, 138.6, 137.2, 128.7, 128.4, 128.2, 127.7, 127.1, 127.0, 126.5, 125.7, 124.0, 123.8, 122.9, 77.0, 60.3. IR (neat): ν_{max} 3356.7 (bm), 3062.1 (m), 3027.3 (m) 2921.4 (m), 2855.0 (w), 1728.2 (w), 1600.1 (m), 1551.5 (m), 1491.9 (m), 1049.7 (m), 753.0 (s), 696.9 (s), 553.5 (m) cm^{-1}. HRMS (DART) for $C_{22}H_{18}OS$ $[M+H-H2O]^+$: calculated: 313.1051, found: 313.1049. $[\alpha]^{20}_D$: -38.828 (c = 0.855, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with styrenyl B(mac), and $Pd(OAc)_2$ (2 mol%) and a mixture of (R_p, R_p)-**L** and (S_p, S_p)-**L** (2.4 mol%) as the catalyst as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

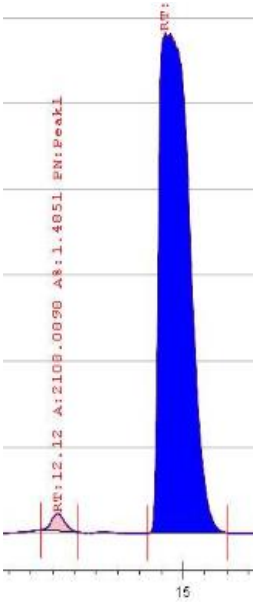
Chiral SFC (Chiralcel ODR-H, 15% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R,2R)-2-(benzo[b]thiophen-5-yl)-1,2-diphenylethan-1-ol

Racemic Material

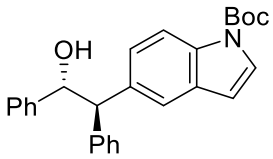


Peak No	% Area	Area	RT (min)
1	41.0665	10437.3868	12.42
2	58.9335	14978.4344	15.44
Total:	100	25415.8212	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	1.4851	2108.0898	12.12
2	98.5149	139837.4666	14.59
Total:	100	141945.5564	



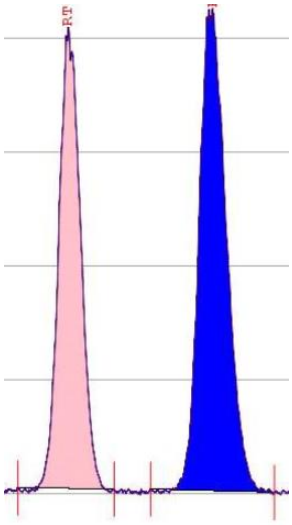
tert-butyl 5-((1R,2R)-2-hydroxy-1,2-diphenylethyl)-1H-indole-1-carboxylate (11). The reaction was performed according to the general procedure ***(Method B)*** with styrenyl B(mac) (S-1) (65.2 mg, 0.20 mmol, 1.0 equiv.), phenyllithium (1.9 M in dibutyl ether, 0.11 mL, .20 mmol, 1.0 equiv.), tert-butyl 5-bromoindole-1-carboxylate (65.2 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.90 mg, 4.0 µmol, 0.020 equiv.), (S_p, S_p)-**L** (5.0 mg, 4.8 µmol) , 0.024 equiv.), cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.), and potassium trifluoromethanesulfonate (75.3 mg, 0.40 mmol, 2.0 equiv.) in THF (0.80 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (2-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (49 mg, 59% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 1H), 7.68 – 7.56 (m, 2H), 7.37 (d, J = 8.4 Hz, 1H), 7.31 – 7.04 (m, 10H), 6.55 (d, J = 3.7 Hz, 1H), 5.46 (d, J = 8.6 Hz, 1H), 4.37 (d, J = 8.6 Hz, 1H), 2.23 (s, 1H), 1.68 (s, 9H).; ^{13}C NMR (151 MHz, $CDCl_3$): δ 149.9, 142.5, 142.1, 135.3, 134.4, 131.2, 128.7, 128.4, 128.2, 127.7, 127.1, 126.5, 126.4, 125.4, 121.3, 115.6, 107.5, 83.9, 77.1, 60.4, 28.4.; IR (neat): ν_{max} 3412. 5 (br), 3061.8 (m), 2978.7 (m), 1730.4 (s), 1492.63 (m), 1371.9 (s), 1163.0 (s), 1083.6 (m), 754.3 (s), 698.7 (s) cm^{-1}. HRMS (DART) for $C_{27}H_{26}NO_2$ $[M+H-H_2O]^+$: calculated: 396.1964, found: 396.1953. $[\alpha]^{20}_D$: -45.59 (c = 1.033, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with $Pd(OAc)_2$ (2 mol%) and a 1:1 mixture of (R_p, R_p)-L and (S_p, S_p)-L (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

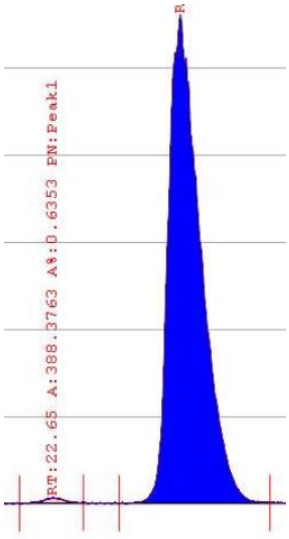
Chiral SFC (Chiralcel OD-H, 10% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of tert-butyl 5-((1R,2R)-2-hydroxy-1,2-diphenylethyl)-1H-indole-1-carboxylate.

Racemic Material

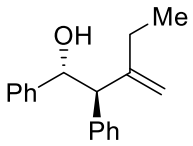


Peak No	% Area	Area	RT (min)
1	43.259	7639.7137	21.79
2	56.741	10020.7002	25.41
Total:	100	17660.4139	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.6353	388.3763	22.65
2	99.3647	60747.6108	25.78
Total:	100	61135.9871	



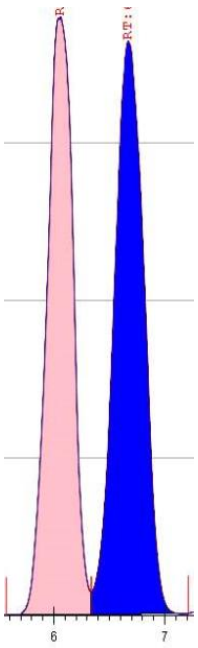
(1R,2S)-3-methylene-1,2-diphenylpentan-1-ol (12). The reaction was performed according to the general procedure ***(Method B)*** with styrenyl B(mac) (S-1) (65.2 mg, 0.20 mmol, 1.0 equiv.), phenyllithium (1.9 M in dibutyl ether, 0.11 mL, .20 mmol, 1.0 equiv.), 2-bromo-1-butene (29.7 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.90 mg, 4.0 µmol, 0.020 equiv.), (S_p, S_p)-**L** (5.0 mg, 4.8 µmol) , 0.024 equiv.), cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.), and potassium trifluoromethanesulfonate (75.3 mg, 0.40 mmol, 2.0 equiv.) in THF (0.80 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (2-10% EtOAc in hexanes, stain in magic stain) to afford a pale yellow oil (32 mg, 63% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 – 7.04 (m, 8H), 6.97 (dt, J = 7.5, 1.4 Hz, 2H), 5.37 (s, 1H), 5.22 (s, 1H), 5.06 (d, J = 9.8 Hz, 1H), 3.54 (d, J = 9.9 Hz, 1H), 2.64 (s, 1H), 2.11 – 1.95 (m, 2H), 1.03 (td, J = 7.4, 1.2 Hz, 3H).; ^{13}C NMR (151 MHz, $CDCl_3$): δ 154.4, 144.4, 142.2, 131.3, 130.6, 130.5, 130.0, 129.6, 129.2, 111.9, 78.6, 64.0, 31.7, 14.8.; IR (neat): ν_{max} 3440.4 (br), 3062.1 (w), 3028.4 (m), 2964.4 (m), 1641.4 (w), 1492.4 (m), 1453.0 (m), 1218.9 (m), 1074.2 (m), 755.3 (s), 696.9 (s) cm^{-1}. HRMS (DART) for $C_{18}H_{19}$ $[M+H-H_2O]^+$: calculated: 235.1487, found: 235.1481. $[\alpha]^{20}_D$: -209.087 (c = 1.020, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with $Pd(OAc)_2$ (2 mol%) and a 1:1 mixture of (R_p, R_p)-L and (S_p, S_p)-L (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

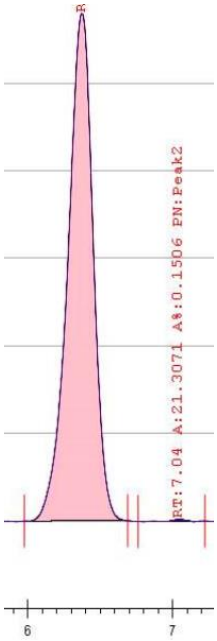
Chiral SFC (Chiralcel OJ-H, 5% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R,2S)-3-methylene-1,2-diphenylpentan-1-ol.

Racemic Material

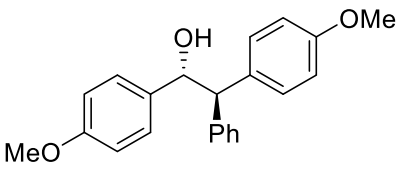


Peak No	% Area	Area	RT (min)
1	47.9207	31092.8311	6.06
2	52.0793	33791.1063	6.67
Total:	100	64883.9374	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	99.8494	14123.3123	6.37
2	0.1506	21.3071	7.04
Total:	100	14144.6194	



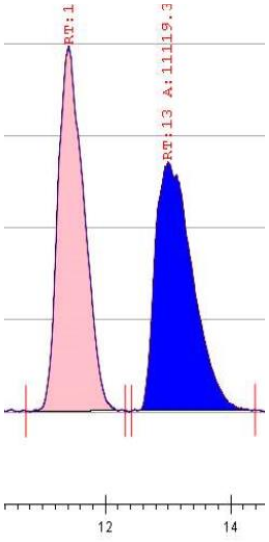
(1R,2R)-1,2-bis(4-methoxyphenyl)-2-phenylethan-1-ol (13). The reaction was performed according to the general procedure ***(Method C)*** with styrenyl B(mac) (S-1) (65.2 mg, 0.20 mmol, 1.0 equiv.), 4-bromoanisole (37.4 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyllithium (1.7 M in pentane, 0.24 mL, 0.40 mmol, 2.0 equiv.), 4-methoxyphenyl trifluoromethanesulfonate (56.4 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.90 mg, 4.0 µmol, 0.020 equiv.), (S_p, S_p)-**L** (5.0 mg, 4.8 µmol) , 0.024 equiv.), cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.), and potassium trifluoromethanesulfonate (75.3 mg, 0.40 mmol, 2.0 equiv.) in THF (0.80 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (5-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (52 mg, 79% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.6 Hz, 2H), 7.19 – 7.03 (m, 6H), 6.89 (d, J = 8.6 Hz, 2H), 6.82 – 6.69 (m, 3H), 5.31 (d, J = 8.7 Hz, 1H), 4.18 (d, J = 8.8 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.08 (br s, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.9, 158.5, 142.0, 134.5, 133.1, 129.9, 128.5, 128.2, 128.0, 126.2, 116.0, 114.8, 114.2, 113.4, 76.5, 59.5, 55.8, 55.24, 55.16.; IR (neat): ν_{max} 3389.0 (b), 3028.0 (w), 3000.8 (m), 2931.9 (m), 2835.0 (m), 1610.7 (m), 1584.3 (s), 1301.9 (w), 1246.2 (s), 1176.8 (m), 1302.9 (m), 828.5 (m), 699.9 (m) cm^{-1}. HRMS (DART) for $C_{22}H_{21}O_2$ $[M+H-H_2O]^+$: calculated: 317.152, found: 317.1547. $[\alpha]^{20}_D$: -37.908 (c = 0.633, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with $Pd(OAc)_2$ (2 mol%) and 1,3-Bis(diphenylphosphino)propane (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

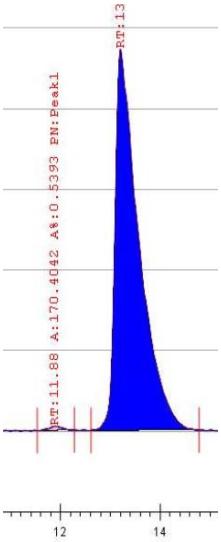
Chiral SFC (Chiralcel OD-H, 15% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R,2R)-1,2-bis(4-methoxyphenyl)-2-phenylethan-1-ol.

Racemic Material

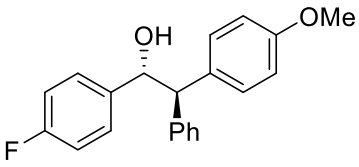


Peak No	% Area	Area	RT (min)
1	50.557	11369.8668	11.42
2	49.443	11119.3306	13
Total:	100	22489.1974	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.5393	170.4042	11.88
2	99.4607	31426.3547	13.2
Total:	100	31596.7589	



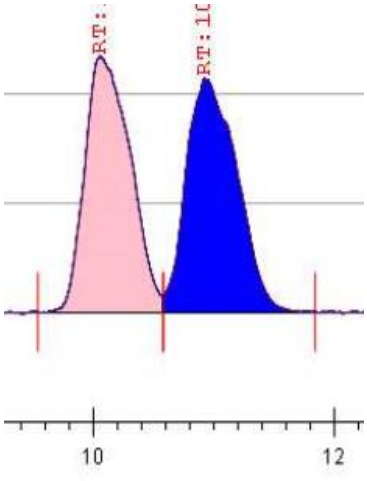
(1R,2R)-1-(4-fluorophenyl)-2-(4-methoxyphenyl)-2-phenylethan-1-ol (14). The reaction was performed according to the general procedure ***(Method C)*** with styrenyl B(mac) (S-1) (65.2 mg, 0.20 mmol, 1.0 equiv.), 1-bromo-4-fluorobenzene (35.0 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyllithium (1.7 M in pentane, 0.24 mL, 0.40 mmol, 2.0 equiv.), 4-methoxyphenyl trifluoromethanesulfonate (56.4 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.90 mg, 4.0 µmol, 0.020 equiv.), (S_p, S_p)-**L** (5.0 mg, 4.8 µmol) , 0.024 equiv.), cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.), and potassium trifluoromethanesulfonate (75.3 mg, 0.40 mmol, 2.0 equiv.) in THF (0.80 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (5-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (45 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 8.6 Hz, 2H), 7.23 – 7.13 (m, 4H), 7.13 – 7.05 (m, 3H), 6.96 – 6.86 (m, 4H), 5.33 (d, J = 8.8 Hz, 1H), 4.14 (d, J = 8.8 Hz, 1H), 3.80 (s, 3H), 2.16 (br, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.1 (d, $^1J_{C\text{-}F}$ = 245.3 Hz), 158.6, 141.6, 138.01, 137.99, 132.5, 129.9, 128.4 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 128.4, 128.3, 126.4, 114.8 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 114.7, 114.3, 76.3, 59.8, 55.2.; ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.0.; IR (neat): ν_{max} 3378.7 (br), 3060.3 (w), 3029.1 (m), 2908.1 (m), 2835.9 (m), 1605.9 (m), 1508.8 (s), 1220.3 (m), 1178.9 (m), 1033.6 (m),699.4 (m), 567.7 (m) cm^{-1}. HRMS (DART) for $C_{21}H_{18}FO$ $[M+H-H_2O]^+$: calculated: 305.1342, found: 305.1342. $[\alpha]^{20}_D$: -58.335 (c = 0.813, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with $Pd(OAc)_2$ (2 mol%) and 1,3-Bis(diphenylphosphino)propane (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

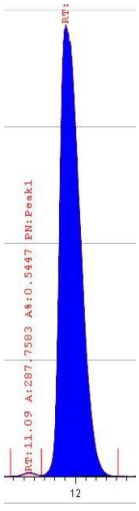
Chiral SFC (Chiralcel OD-H, 12% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R,2R)-1-(4-fluorophenyl)-2-(4-methoxyphenyl)-2-phenylethan-1-ol.

Racemic Material

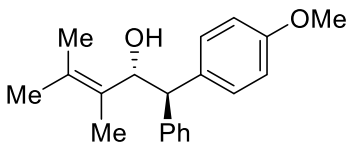


Peak No	% Area	Area	RT (min)
1	49.5931	6149.1124	10.05
2	50.4069	6250.0104	10.92
Total:	100	12399.1228	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.5447	287.7583	11.09
2	99.4553	52539.5337	11.81
Total:	100	52827.292	



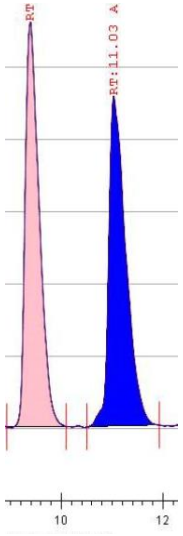
(1R,2R)-1-(4-methoxyphenyl)-3,4-dimethyl-1-phenylpent-3-en-2-ol (15). The reaction was performed according to the general procedure ***(Method C)*** with styrenyl B(mac) (S-1) (65.2 mg, 0.20 mmol, 1.0 equiv.), 2-bromo-3-methyl-but-2-ene (29.8 mg, 0.20 mmol, 1.0 equiv.), *tert*-butyllithium (1.7 M in pentane, 0.24 mL, 0.40 mmol, 2.0 equiv.), 4-methoxyphenyl trifluoromethanesulfonate (56.4 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.90 mg, 4.0 µmol, 0.020 equiv.), (S_p, S_p)-**L** (5.0 mg, 4.8 µmol) , 0.024 equiv.), cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.), and potassium trifluoromethanesulfonate (75.3 mg, 0.40 mmol, 2.0 equiv.) in THF (0.80 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (5-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (33 mg, 56% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 8.6 Hz, 2H), 7.23 – 7.15 (m, 4H), 7.15 – 7.10 (m, 1H), 6.90 (d, J = 8.7 Hz, 2H), 5.28 (d, J = 10.2 Hz, 1H), 4.06 (d, J = 10.1 Hz, 1H), 3.79 (s, 3H), 1.66 (s, 3H), 1.60 (s, 1H), 1.54 (s, 3H), 1.51 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.5, 142.1, 133.7, 129.8, 129.7, 128.1, 127.9, 126.8, 126.2, 114.3, 73.1, 55.7, 55.2, 21.0, 20.1, 12.3.; IR (neat): ν_{max} 3448.0 (br), 3027.5 (w), 2993.8 (m), 2928.2 (m), 2858.4 (m), 1609.7 (m), 1510.4 (s), 1248.5 (s), 1178.1 (m), 1034.7 (m), 699.5 (m) cm^{-1}. HRMS (DART) for $C_{20}H_{23}O$ [M+H-H_2O]$^+$: calculated: 279.1749, found: 279.1751. $[\alpha]^{20}_D$: -8.766 (c = 0.920, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with $Pd(OAc)_2$ (2 mol%) and 1,3-Bis(diphenylphosphino)propane (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

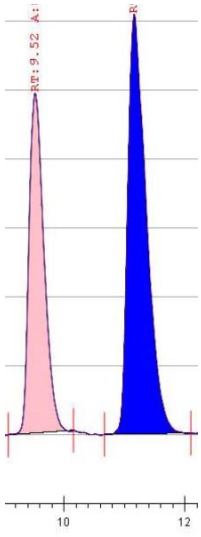
Chiral SFC (Chiralcel ODR-H, 5% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R,2R)-1-(4-methoxyphenyl)-3,4-dimethyl-1-phenylpent-3-en-2-ol.

Racemic Material

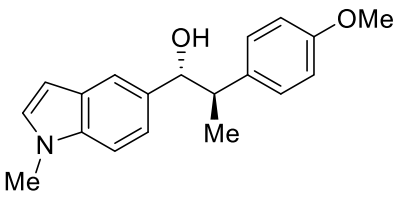


Peak No	% Area	Area	RT (min)
1	50.1135	21398.0761	9.39
2	49.8865	21301.1734	11.03
Total:	100	42699.2495	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	39.509	8442.2713	9.52
2	60.491	12925.7029	11.16
Total:	100	21367.9742	



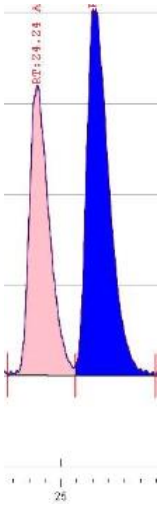
(1R,2R)-2-(4-methoxyphenyl)-1-(1-methyl-1H-indol-5-yl)propan-1-ol (16). The reaction was performed according to the general procedure ***(Method C)*** with (E)-propenyl B(mac) (S-2) (52.8 mg, 0.2 mmol, 1 equiv.), *tert*-butyllithium (1.7 M in pentane, 0.24 mL, 0.40 mmol, 2 equiv.), 5-bromo-1-methyl-indole (42.0 mg, 0.20 mmol, 1.0 equiv.), palladium (II) acetate (0.90 mg, 0.004 mmol, 0.020 equiv.), (S_p, S_p)-**L** (5.0 mg, 0.0048 mmol, 0.024 equiv.), potassium triflate (75.3 mg, 0.4 mmol, 2 equiv.), and cesium fluoride (30.4 mg, 0.2 mmol, 1 equiv.) in THF (0.8 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (5-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (37.8 mg, 64% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 1.5 Hz, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.07 (d, J = 3.1 Hz, 1H), 6.92 (d, J = 8.6 Hz, 2H), 6.49 (d, J = 3.0 Hz, 1H), 4.72 – 4.67 (m, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.07 (dq, J = 8.9, 7.1 Hz, 1H), 1.86 (d, J = 2.1 Hz, 1H), 1.03 (d, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 136.7, 136.2, 133.9, 129.3, 129.1, 128.4, 120.7, 119.7, 114.2, 109.3, 101.2, 80.7, 77.4, 77.2, 76.9, 55.4, 47.7, 33.1, 19.0.; IR (neat): ν_{max} 3435.4 (br), 2956.7 (m), 2923.9 (m) 2852.4 (m), 1610.4 (w), 1582.3 (w), 1511.8 (s), 1245.0 (s), 770.3 (m) cm^{-1}. HRMS (DART) for $C_{19}H_{21}NO_2$ $[M+H]^+$: calculated: 296.1645, found: 296.1639. $[\alpha]^{20}_D$: +95.6726 (c = 1.09, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with (E)-propenyl B(mac) and $Pd(OAc)_2$ (2 mol%) and a mixture of (R_p, R_p)-**L** and (S_p, S_p)-**L** (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

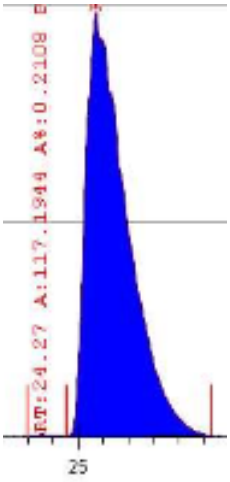
Chiral SFC (Chiralcel ODR-H, 10% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – (1R,2R)-2-(4-methoxyphenyl)-1-(1-methyl-1H-indol-5-yl)propan-1-ol.

Racemic Material

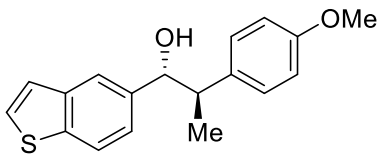


Peak No	% Area	Area	RT (min)
1	41.1283	6949.1704	24.24
2	58.8717	9947.1451	26.01
Total:	100	16896.3155	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.2108	117.1944	24.27
2	99.7892	55478.6465	25.36
Total:	100	55595.8409	



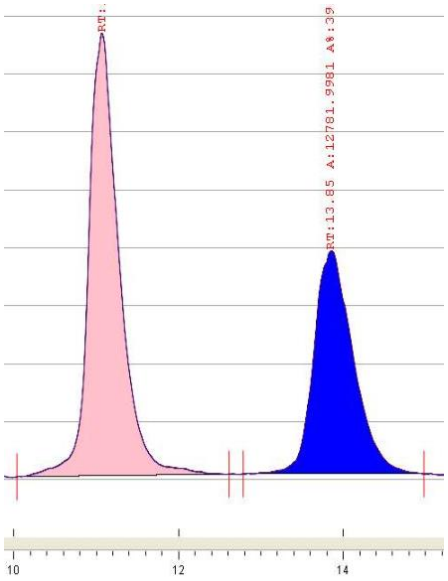
(1R,2R)-1-(benzo[b]thiophen-5-yl)-2-(4-methoxyphenyl)propan-1-ol (17). The reaction was performed according to the general procedure ***(Method C)*** with (E)-propenyl B(mac) (S-2) (52.8 mg, 0.2 mmol, 1 equiv.), *tert*-butyllithium (1.7 M in pentane, 0.24 mL, 0.40 mmol, 2 equiv.), 5-bromobenzothiophene (42.6 mg, 0.20 mmol, 1.0 equiv.), palladium (II) acetate (0.90 mg, 0.004 mmol, 0.020 equiv.), (S_p, S_p)-**L** (5.0 mg, 0.0048 mmol, 0.024 equiv.), potassium triflate (75.3 mg, 0.4 mmol, 2 equiv.), and cesium fluoride (30.4 mg, 0.2 mmol, 1 equiv.) in THF (0.8 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (5-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (35 mg, 59% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 8.5 Hz, 1H), 7.81 (s, 1H), 7.46 (d, J = 5.4 Hz, 1H), 7.41 – 7.31 (m, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 4.72 (d, J = 8.7 Hz, 1H), 3.82 (s, 3H), 3.09 – 2.97 (m, 1H), 1.95 (br, 1H), 1.07 (d, J = 7.1 Hz, 3H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 139.8, 139.3, 139.1, 135.4, 129.2, 126.9, 124.1, 123.5, 122.5, 122.3, 114.3, 80.1, 55.5, 47.7, 18.7.; IR (neat): ν_{max} 3416 (br), 2961 (m), 2928 (m), 1610 (m), 1583 (w), 1511 (s), 1246 (s), 787 (m) cm^{-1}. HRMS (DART) for $C_{18}H_{17}OS$ $[M+H-H_2O]^+$: calculated: 281.0995, found: 281.1002. $[\alpha]^{20}_D$: +52.99 (c = 1.00, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with (E)-propenyl B(mac) and $Pd(OAc)_2$ (2 mol%) and a mixture of (R_p, R_p)-**L** and (S_p, S_p)-**L** (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

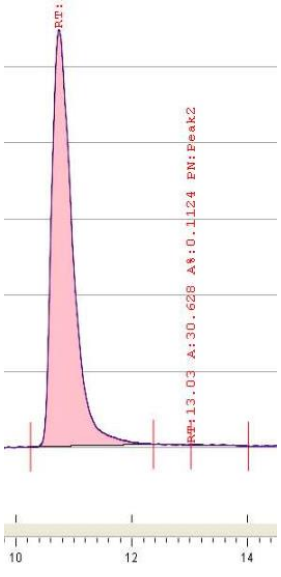
Chiral SFC (Chiralcel AS-H, 10% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – (1R,2R)-1-(benzo[b]thiophen-5-yl)-2-(4-methoxyphenyl)propan-1-ol

Racemic Material

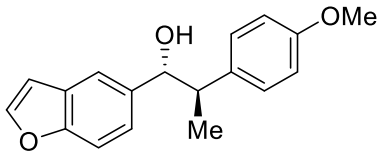


Peak No	% Area	Area	RT (min)
1	60.608	19666.2012	11.07
2	39.392	12781.9981	13.85
Total:	100	32448.1993	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	99.8876	27219.7084	10.74
2	0.1124	30.628	13.03
Total:	100	27250.3364	



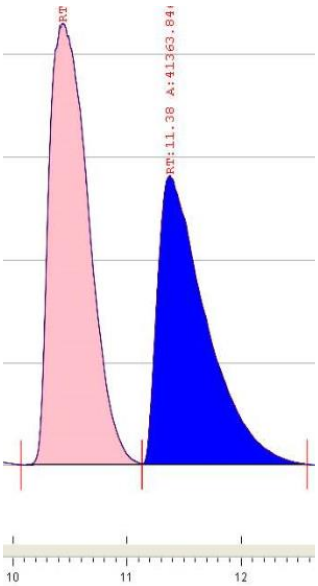
(1R,2R)-1-(benzofuran-5-yl)-2-(4-methoxyphenyl)propan-1-ol (18). The reaction was performed according to the general procedure ***(Method C)*** with (E)-propenyl B(mac) (S-2) (52.8 mg, 0.2 mmol, 1 equiv.), *tert*-butyllithium (1.7 M in pentane, 0.24 mL, 0.40 mmol, 2 equiv.), 5-bromobenzofuran (39.4 mg, 0.20 mmol, 1.0 equiv.), palladium (II) acetate (0.90 mg, 0.004 mmol, 0.020 equiv.), (S_p, S_p)-**L** (5.0 mg, 0.0048 mmol, 0.024 equiv.), potassium triflate (75.3 mg, 0.4 mmol, 2 equiv.), and cesium fluoride (30.4 mg, 0.2 mmol, 1 equiv.) in THF (0.8 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (5-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (28 mg, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 2H), 7.49 (d, J = 8.5 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.28 – 7.21 (m, 2H), 6.94 – 6.89 (m, 2H), 6.80 – 6.75 (m, 1H), 4.70 (d, J = 8.8 Hz, 1H), 3.82 (s, 3H), 3.08 – 2.94 (m, 1H), 1.93 (br, J = 2.1 Hz, 1H), 1.05 (d, J = 7.0 Hz, 3H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 154.8, 145.5, 137.5, 135.5, 129.2, 127.5, 123.5, 119.8, 114.3, 111.3, 106.8, 80.2, 55.5, 47.9, 18.8.; IR (neat): ν_{max} 3441(br), 2960 (m), 2927 (m) 1610 (m), 1583 (s), 1467 (m), 1246 (s), 1179 (m), 1032 (s), 741 (m) cm^{-1}. HRMS (DART) for $C_{18}H_{17}O_2$ $[M+H-H_2O]^+$: calculated: 265.1223, found: 265.1232. $[\alpha]^{20}_D$: +48.50 (c = 0.933, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with (E)-propenyl B(mac) and $Pd(OAc)_2$ (2 mol%) and a mixture of (R_p, R_p)-**L** and (S_p, S_p)-**L** (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

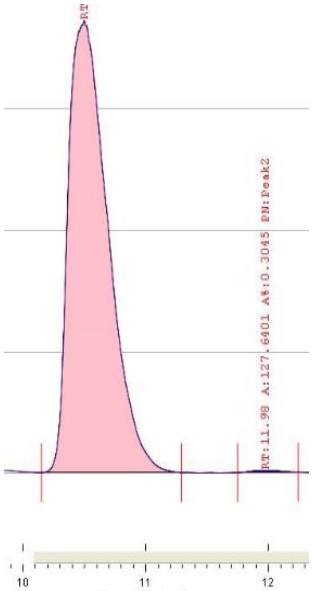
Chiral SFC (Chiralcel ODR-H, 8% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – (1R,2R)-1-(benzofuran-5-yl)-2-(4-methoxyphenyl)propan-1-ol.

Racemic Material

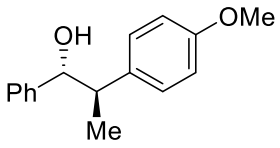


Peak No	% Area	Area	RT (min)
1	55.5182	51626.6428	10.44
2	44.4818	41363.8463	11.38
Total:	100	92990.4891	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	99.6955	41790.8039	10.5
2	0.3045	127.6401	11.98
Total:	100	41918.444	



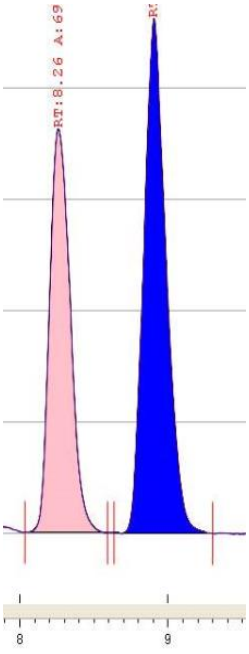
(1R,2R)-2-(4-methoxyphenyl)-1-phenylpropan-1-ol (19). The reaction was performed according to the general procedure (**Method A**) with (E)-propenyl B(mac) (S-2) (52.8 mg, 0.20 mmol, 1.0 equiv.), phenyllithium (1.9 M in dibutyl ether, 0.11 mL, .20 mmol, 1.0 equiv.), 4-methoxyphenyl trifluoromethanesulfonate (56.4 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.45 mg, 2.0 µmol, 0.010 equiv.), (S*p*, S*p*)-L (2.5 mg, 2.4 µmol) , 0.012 equiv.), cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.) in THF (1.60 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (2-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (34 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 7.22 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 4.61 (d, J = 8.6 Hz, 1H), 3.82 (s, 3H), 3.04 – 2.92 (m, 1H), 1.88 (s, 1H), 1.07 (d, J = 7.1 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.5, 142.6, 135.2, 129.0, 128.2, 127.7, 127.0, 114.1, 79.8, 55.3, 47.3, 18.4.; IR (neat): ν_{max} 3444.8 (br), 3030.4 (w), 2961.7 (m), 2931.5 (m), 2834.8 (w), 1610.5 (w), 1583.1 (s), 1245.5 (s), 1178.3 (m), 1036.7 (m), 724.3 (m) cm^{-1}. HRMS (DART) for $C_{16}H_{17}O$ $[M+H-H_2O]^+$:calculated: 225.1274, found: 225.1270. $[\alpha]^{20}_D$: -69.455 (c = 1.000, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with (E)-propenyl B(mac)**,** and $Pd(OAc)_2$ (2 mol%) and a mixture of (R_p, R_p)-L and (S_p, S_p)-L (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

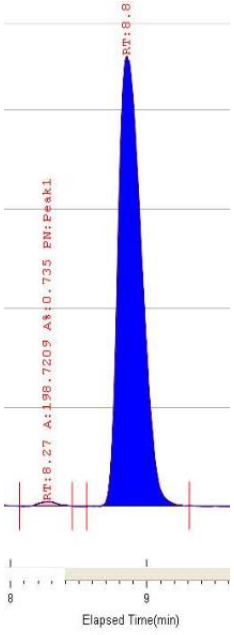
Chiral SFC (Chiralcel OJ-H, 10% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R,2R)-2-(4-methoxyphenyl)-1-phenylpropan-1-ol.

Racemic Material

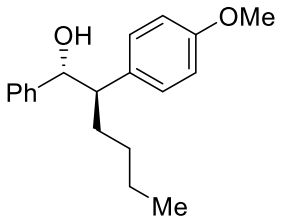


Peak No	% Area	Area	RT (min)
1	42.1696	6987.3301	8.26
2	57.8304	9582.2447	8.9
Total:	100	16569.5748	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.735	198.7209	8.27
2	99.265	26839.1094	8.85
Total:	100	27037.8303	



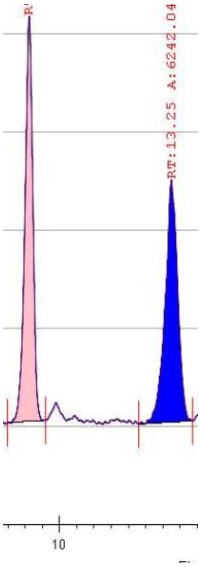
(1R,2R)-2-(4-methoxyphenyl)-1-phenylhexan-1-ol (20). The reaction was performed according to the general procedure (**Method A**) with (E)-hexenyl B(mac) (S-3) (61.2 mg, 0.20 mmol, 1.0 equiv.), phenyllithium (1.9 M in dibutyl ether, 0.11 mL, .20 mmol, 1.0 equiv.), 4-methoxyphenyl trifluoromethanesulfonate (56.4 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.45 mg, 2.0 µmol, 0.010 equiv.), (S*p*, S*p*)-L (2.5 mg, 2.4 µmol) , 0.012 equiv.), cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.) in THF (0.80 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (2-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (36 mg, 63% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 5H), 7.16 (dd, J = 8.6, 1.8 Hz, 2H), 6.90 (dd, J = 8.6, 1.7 Hz, 2H), 4.66 (d, J = 8.4 Hz, 1H), 3.82 (s, 3H), 2.83 – 2.75 (m, 1H), 1.84 (br, 1H), 1.62 – 1.47 (m, 1H), 1.43 – 1.32 (m, 1H), 1.26 – 1.04 (m, 2H), 1.04 – 0.92 (m, 2H), 0.73 (td, J = 7.3, 1.6 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.5, 142.9, 133.1, 129.7, 128.2, 127.6, 127.0, 114.0, 76.8, 55.2, 53.5, 31.7, 29.5, 22.5, 13.9.; IR (neat): ν_{max} 3458.4 (br), 2996.4 (m), 2954.1 (m), 2857.2 (m), 1610.0 (m), 1507.1 (s), 1244.8 (s), 1177.1 (m), 1034.9 (m), 700.2 (s) cm^{-1}. HRMS (DART) for $C_{19}H_{23}O$ $[M+H-H_2O]^+$: calculated: 267.1749, found: 267.1756. $[\alpha]^{20}_D$: +37.172 (c = 1.300, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with (E)-hexenyl B(mac),, and $Pd(OAc)_2$ (2 mol%) and 1,3-Bis(diphenylphosphino)propane (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

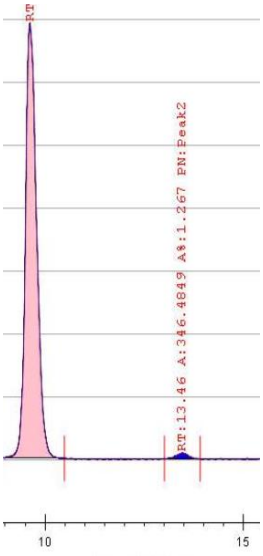
Chiral SFC (Chiralcel OJ-H, 5% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R,2R)-2-(4-methoxyphenyl)-1-phenylhexan-1-ol

Racemic Material

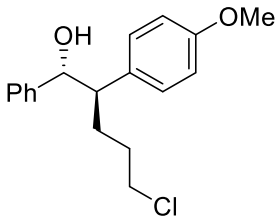


Peak No	% Area	Area	RT (min)
1	51.3895	6598.905	9.12
2	48.6105	6242.0449	13.25
Total:	100	12840.9499	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	98.733	27000.6134	9.62
2	1.267	346.4849	13.46
Total:	100	27347.0983	



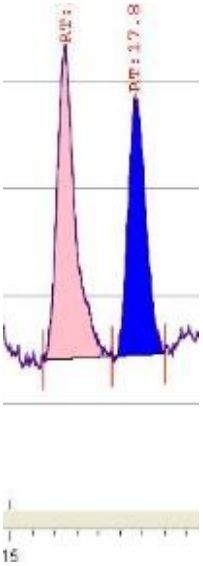
(1R,2R)-5-chloro-2-(4-methoxyphenyl)-1-phenylpentan-1-ol (21). The reaction was performed according to the general procedure ***(Method A)*** with (E)-5-chloro-pentenyl B(mac) (S-4) (65.3 mg, 0.2 mmol, 1.0 equiv.), phenyllithium in dibutyl ether solution (1.9 M) (0.105 mL, 0.2 mmol, 1.0 equiv.), (4-methoxyphenyl) trifluoromethanesulfonate (56.4 mg, 0.22 mmol, 1.10 equiv.), palladium (II) acetate (0.45 mg, 0.002 mmol, 0.010 equiv.), (S_p, S_p)-**L** (2.30 mg, 0.0022 mmol, 0.011 equiv.) and cesium fluoride (30.4 mg, 0.2 mmol, 1 equiv.) in THF (0.8 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (5-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (31.1 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 5H), 7.17 – 7.11 (m, 2H), 6.91 – 6.85 (m, 2H), 4.65 (d, J = 8.2 Hz, 1H), 3.80 (s, 3H), 3.38 – 3.25 (m, 2H), 2.83 – 2.75 (m, 1H), 1.81 (s, 1H), 1.70 – 1.43 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.7, 142.5, 132.2, 129.6, 128.3, 127.8, 126.9, 114.2, 78.8, 55.2, 52.9, 44.8, 30.5, 29.3. IR (neat): ν_{max} 3466.9 (br), 2995.5 (w), 2953.4 (w), 1609.7 (w), 1510.6 (s), 1453.8 (w), 1301.7 (w), 1247.0 (s), 1178.4 (m), 1034.2 (m), 701.56 (m) cm^{-1}. HRMS (DART) for $C_{18}H_{21}ClO_2$ [M+H-H_2O]$^+$: calculated: 287.1203, found:287.1212. [α]$^{20}_D$: +14.145 (c = 0.82, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with (E)-5-chloro-pentenyl B(mac), and $Pd(OAc)_2$ (2 mol%) and a mixture of (R_p, R_p)-L and (S_p, S_p)-L (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

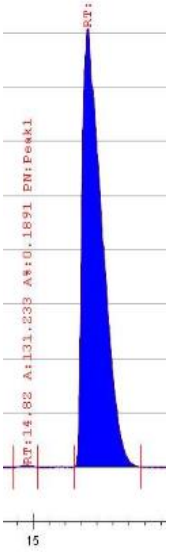
Chiral SFC (Chiralcel ODR-H, 5% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R,2R)-5-chloro-2-(4-methoxyphenyl)-1-phenylpentan-1-ol.

Racemic Material

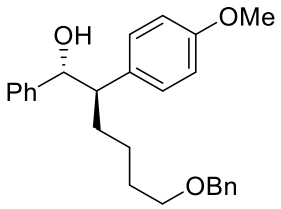


Peak No	% Area	Area	RT (min)
1	55.7361	839.1701	16.25
2	44.2639	666.443	17.83
Total:	100	1505.6131	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.1891	131.233	14.82
2	99.8109	69250.2415	16.72
Total:	100	69381.4745	



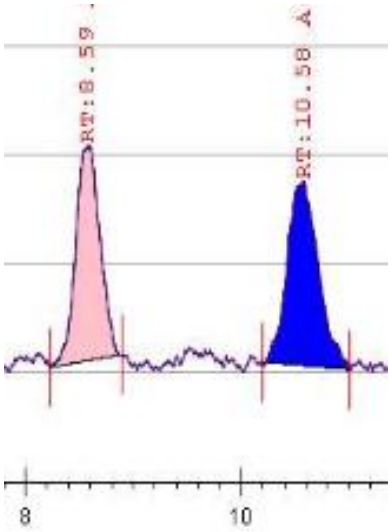
(1R,2R)-6-(benzyloxy)-2-(4-methoxyphenyl)-1-phenylhexan-1-ol (22). The reaction was performed according to the general procedure ***(Method A)*** with (E)-6-(benzyloxy)hexenyl B(mac) (S-5) (82.5 mg, 0.2 mmol, 1.0 equiv.), phenyllithium in dibutylether solution (1.9 M) (0.105 mL, 0.2 mmol, 1.0 equiv.), (4-methoxyphenyl) trifluoromethanesulfonate (56.4 mg, 0.22 mmol, 1.10 equiv.), palladium (II) acetate (0.45 mg, 0.002 mmol, 0.010 equiv.), (S_p, S_p)-**L** (2.30 mg, 0.0022 mmol, 0.011 equiv.), and cesium fluoride (30.4 mg, 0.2 mmol, 1 equiv.) in THF (0.8 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (5-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (39.1 mg, 50.0% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ. 7.42 – 7.21 (m, 10H), 7.19 – 7.12 (m, 2H), 6.95 – 6.86 (m, 2H), 4.65 (d, J = 8.4, 2.4 Hz, 1H), 4.38 (s, 2H), 3.82 (s, 3H), 3.35 – 3.24 (m, 2H), 2.87 – 2.73 (m, 1H), 1.82 (s, 1H), 1.61 – 1.34 (m, 4H), 1.18 – 1.01 (m, 2H).; ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 142.9, 138.7, 133.0, 129.8, 128.40, 128.37, 127.8, 127.7, 127.6, 127.1, 114.2, 78.9, 72.9, 70.2, 55.3, 53.5, 31.9, 29.6, 24.0.; IR (neat): ν_{max} 3438.8 (br), 3060.1 (w), 3029.9 (w), 2932.3 (m), 2857.5 (m), 1609.6 (m), 1510 (s), 1453.3 (m), 1245.8 (s), 1177.5 (m), 1093.9 (m), 1029.1 (s), 698.4 (s) cm^{-1}. HRMS (DART) for $C_{26}H_{30}O_3$ $[M+H-H_2O]^+$: calculated: 373.2168, found: 373.215. $[\alpha]^{20}_D$: +18.497 (c = 0.955, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with (E)-6-(benzyloxy)hexenyl B(mac), and $Pd(OAc)_2$ (2 mol%) and a mixture of (R_p, R_p)-L and (S_p, S_p)-L (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

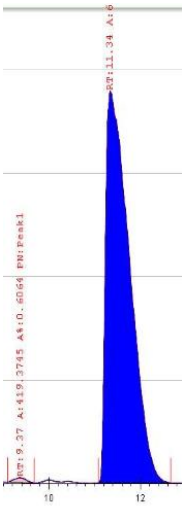
Chiral SFC (Chiralcel ODR-H ,15% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R,2R)-6-(benzyloxy)-2-(4-methoxyphenyl)-1-phenylhexan-1-ol.

Racemic Material

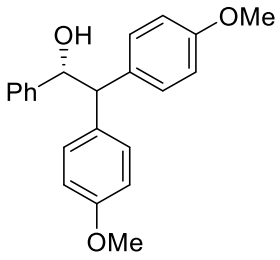


Peak No	% Area	Area	RT (min)
1	47.6343	616.1072	8.59
2	52.3657	677.3049	10.58
Total:	100	1293.4121	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.6064	419.3745	9.37
2	99.3936	68741.3181	11.34
Total:	100	69160.6926	



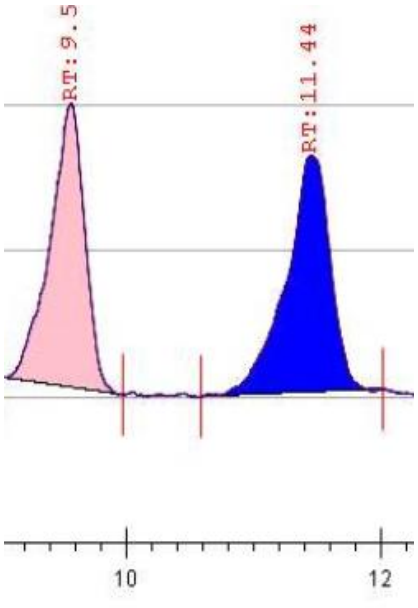
(R)-2,2-bis(4-methoxyphenyl)-1-phenylethan-1-ol (23). The reaction was performed according to the general procedure (**Method A**) with 4-methoxy-styrenyl B(mac) (S-6) (71.2 mg, 0.20 mmol, 1.0 equiv.), phenyllithium (1.9 M in dibutyl ether, 0.11 mL, .20 mmol, 1.0 equiv.), 4-methoxyphenyl trifluoromethanesulfonate (56.4 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.45 mg, 2.0 µmol, 0.010 equiv.), (S*p*, S*p*)-L (2.5 mg, 2.4 µmol) , 0.012 equiv.), cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.) in THF (0.80 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (2-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (32 mg, 48% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, J = 7.6 Hz, 2H), 7.28 – 7.17 (m, 5H), 7.02 (d, J = 8.2 Hz, 2H), 6.89 (d, J = 8.5 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 5.30 (d, J = 8.6 Hz, 1H), 4.17 (d, J = 8.6 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 2.13 (br, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.5, 157.9, 142.4, 134.1, 133.1, 129.9, 129.4, 128.0, 127.4, 126.9, 114.2, 113.6, 77.0, 58.6, 55.2, 55.1.; IR (neat): ν_{max} 3429.1 (br), 3060.9 (w), 3030.9 (w), 2932.3 (m), 2834.9 (m), 1608.3 (m), 1508.8 (s), 1245.1 (s), 1176.8 (m), 1032.8 (m), 814.5 (m), 700.5 (m) cm^{-1}. HRMS (DART) for $C_{22}H_{21}O_2$ $[M+H-H_2O]^+$: calculated: 317.1536, found: 317.1535. $[\alpha]^{20}_D$: -51.455 (c = 1.105, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Racemic compound was prepared according to the procedure described above $Pd(OAc)_2$ (2 mol%) and 1,3-Bis(diphenylphosphino)propane (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

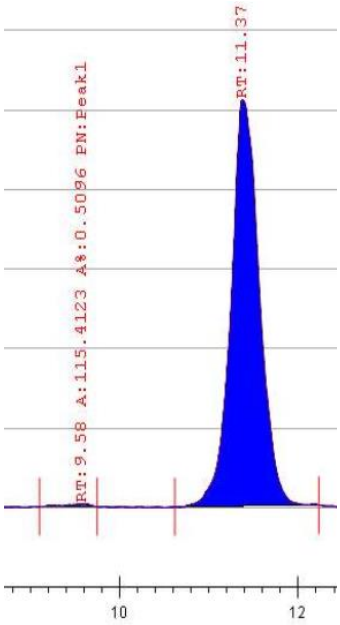
Chiral SFC (Chiralcel OJ-H, 15% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (R)-2,2-bis(4-methoxyphenyl)-1-phenylethan-1-ol

Racemic Material

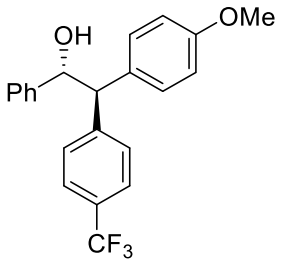


Peak No	% Area	Area	RT (min)
1	48.6093	3676.123	9.57
2	51.3907	3886.4641	11.44
Total:	100	7562.5871	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.5096	115.4123	9.58
2	99.4904	22531.7318	11.37
Total:	100	22647.1441	



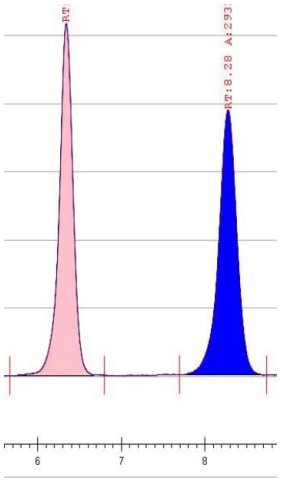
(1R)-2-(4-methoxyphenyl)-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (24). The reaction was performed according to the general procedure (**Method A**) at 60 ºC with 4-trifluoromethyl-styrenyl B(mac) (S-7) (78.8 mg, 0.20 mmol, 1.0 equiv.), phenyllithium (1.9 M in dibutyl ether, 0.11 mL, .20 mmol, 1.0 equiv.), 4-methoxyphenyl trifluoromethanesulfonate (56.4 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (1.35 mg, 6.0 µmol, 0.030 equiv.), (S*p*, S*p*)-L (6.7 mg, 6.4 µmol) , 0.032 equiv.), cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.) in THF (0.80 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (2-20% EtOAc in hexanes, stain in magic stain) to afford a yellow oil (51 mg, 69% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 8.1 Hz, 2H), 7.34 – 7.12 (m, 9H), 6.90 (d, J = 8.8 Hz, 2H), 5.35 (d, J = 8.4 Hz, 1H), 4.27 (d, J = 8.4 Hz, 1H), 3.80 (s, 3H), 2.16 (s, 1H).; ^{13}C NMR (151 MHz, $CDCl_3$): δ 161.4, 148.7, 144.5, 134.5, 132.6, 131.5, 131.2 (q, $^{2}J_{C\text{-}F}$ = 32.4 Hz), 130.9, 130.8, 130.5, 129.5, 127.8 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 126.8 (q, $^{1}J_{C\text{-}F}$ = 271.8 Hz), 117.0, 79.3, 61.8, 57.9.; ^{19}F NMR (564 MHz, $CDCl_3$): δ -62.48.; IR (neat): ν_{max} 3405.1 (br), 3033,4 (w), 2929.2 (m), 2837.9 (w), 1612.4 (m), 1510.8 (s), 1324.0 (s), 1249.5 (s), 1162.8 (s), 1115.1 (s), 1035.4 (s), 814.5 (s), 754.3 (s), 700.4 (s), 605.7 (s) cm^{-1}. HRMS (DART) for $C_{22}H_{18}F_3O$ $[M+H-H_2O]^+$: calculated: 355.1310, found: 355.1311. $[\alpha]^{20}_D$: -27.50 (c = 1.115, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with $Pd(OAc)_2$ (2 mol%) and 1,3-Bis(diphenylphosphino)propane (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

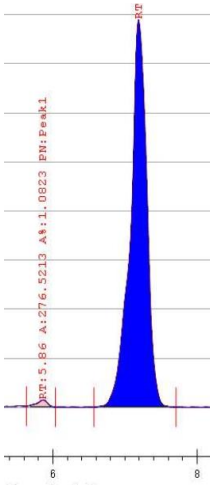
Chiral SFC (Chiralcel OJ-H, 10% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R)-2-(4-methoxyphenyl)-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-ol

Racemic Material

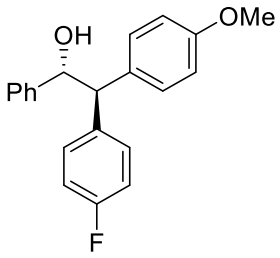


Peak No	% Area	Area	RT (min)
1	50.2702	2965.8056	6.34
2	49.7298	2933.9292	8.28
Total:	100	5899.7348	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	1.0823	276.5213	5.86
2	98.9177	25273.2809	7.19
Total:	100	25549.8022	



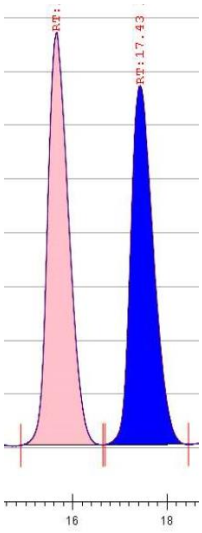
(1R)-2-(4-fluorophenyl)-2-(4-methoxyphenyl)-1-phenylethan-1-ol (25). The reaction was performed according to the general procedure (**Method A**) at 60 ºC with 4-fluoro-styrenyl B(mac) (S-8) (68.8 mg, 0.20 mmol, 1.0 equiv.), phenyllithium (1.9 M in dibutyl ether, 0.11 mL, .20 mmol, 1.0 equiv.), 4-methoxyphenyl trifluoromethanesulfonate (56.4 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.45 mg, 2.0 µmol, 0.010 equiv.), (S*p*, S*p*)-L (2.5 mg, 2.4 µmol) , 0.012 equiv.), cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.) in THF (0.80 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (2-20% EtOAc in hexanes, stain in magic stain) to afford a yellow oil (38 mg, 59% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, J = 8.6 Hz, 2H), 7.26 – 7.17 (m, 5H), 7.08 – 7.03 (m, 2H), 6.90 (d, J = 8.9 Hz, 2H), 6.83 (t, J = 8.6 Hz, 2H), 5.29 (d, J = 8.6 Hz, 1H), 4.19 (d, J = 8.7 Hz, 1H), 3.80 (s, 3H), 2.14 (br, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.3 (d, $^{1}J_{C\text{-}F}$ = 244.7 Hz), 158.6, 142.2, 137.7, 137.7, 132.6, 129.9 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 129.8, 128.1, 127.6, 126.8, 115.0 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 114.2, 77.0, 58.7, 55.3.; ^{19}F NMR (470 MHz, $CDCl_3$): δ -116.7.; IR (neat): ν_{max} 3383.7 (br), 3062.4 (w), 3031.9 (w), 2905.6 (w), 2835.8 (w), 1605.4 (s), 1247.9 (m), 1033.8 (m), 819.4 (m), 752.9 (m), 700.4 (m), 576.7 (m) cm^{-1}. HRMS (DART) for $C_{21}H_{18}OF$ $[M+H\text{-}H_2O]^+$:calculated: 305.1336, found: 305.1369. $[\alpha]^{20}_{D}$: -42.020 (c = 1.315, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with $Pd(OAc)_2$ (2 mol%) and 1,3-Bis(diphenylphosphino)propane (2.4 mol%) as the catalyst. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

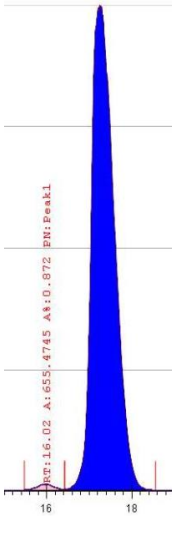
Chiral SFC (Chiralcel OD-H, 9% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (1R)-2-(4-fluorophenyl)-2-(4-methoxyphenyl)-1-phenylethan-1-ol.

Racemic Material



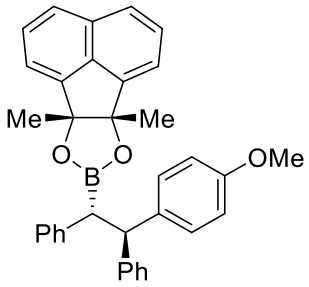
Peak No	% Area	Area	RT (min)
1	51.6168	23769.3094	15.65
2	48.3832	22280.2598	17.43
Total:	100	46049.5692	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	0.872	655.4745	16.02
2	99.128	74514.8681	17.25
Total:	100	75170.3426	

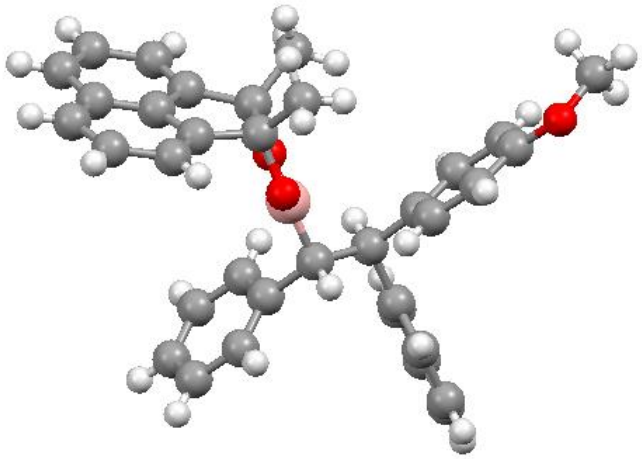
VI. Gram-scale Reaction and Transformations of Products



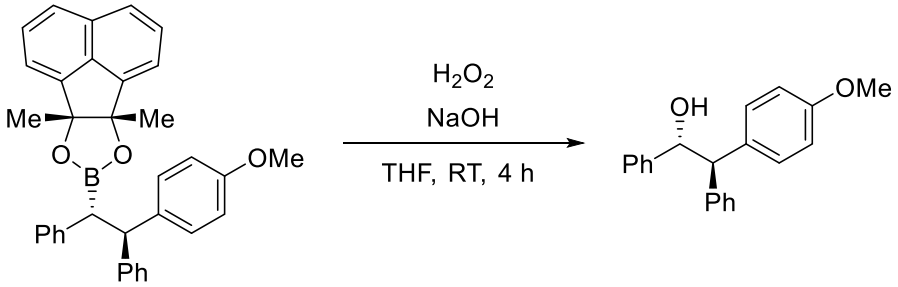
8-((1R,2R)-2-(4-methoxyphenyl)-1,2-diphenylethyl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (26). The reaction was performed according to the general procedure ***(Method A)*** with styrenyl B(mac) (S-1) (1.00 g, 3.07 mmol, 1.0 equiv.), phenyllithium (1.9 M in dibutyl ether, 1.6 mL, 3.07 mmol, 1.0 equiv.), 4-methoxyphenyl trifluoromethanesulfonate (864.0 mg, 3.37 mmol, 1.1 equiv.), palladium (II) acetate (6.9 mg, 30 µmol, 0.010 equiv.), (S_p, S_p)-**L** (38.7 mg, 37 µmol) , 0.012 equiv.), and cesium fluoride (465.7 mg, 3.07 mmol, 1.0 equiv.) in THF (12.3 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (2-10% EtOAc in hexanes, stain in magic stain) to afford a white solid (1.1 g, 70 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.58 – 7.49 (m, 2H), 7.41 (dd, J = 16.5, 6.9 Hz, 2H), 7.15 (d, J = 7.2 Hz, 2H), 7.09 (t, J = 7.6 Hz, 2H), 7.05 – 6.90 (m, 8H), 6.18 (d, J = 8.7 Hz, 2H), 4.25 (d, J = 12.6 Hz, 1H), 3.61 (s, 3H), 3.15 (d, J = 12.6 Hz, 1H), 1.55 (d, J = 14.6 Hz, 6H).; ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.9, 147.1, 146.9, 146.8, 143.4, 139.0, 137.4, 137.3, 133.9, 131.8, 131.1, 131.0, 130.84, 130.77, 130.66, 130.5, 130.4, 130.3, 128.2, 127.92, 127.89, 127.7, 127.6, 122.2, 121.8, 121.7, 115.5, 94.5, 94.4, 57.5, 56.7, 24.9, 24.40, 24.35.; ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.2.; IR (neat): ν_{max} 3058.3 (w), 3026.7 (w), 2972.6 (w), 2932.0 (w), 1607.0 (m), 1494.3 (m), 1316.6 (m), 1176.6 (m), 1034.5 (m), 846.8 (m), 699.6 (m) cm^{-1}. HRMS (DART) $C_{35}H_{35}BO_3N$ $[M+H]^+$: calculated: 528.2716, found: 528.2725. $[\alpha]^{20}_D$: -80.816 (c = 0.667, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Racemic compound was prepared according to the procedure described above with $Pd(OAc)_2$ (2 mol%) and 1,3-Bis(diphenylphosphino)propane (2.4 mol%) as the catalyst. Enantiomeric ratio was determined by chiral SFC analysis of the corresponding alcohol (see Compound 2b). Absolute stereochemistry was determined by single crystal X-ray diffraction.

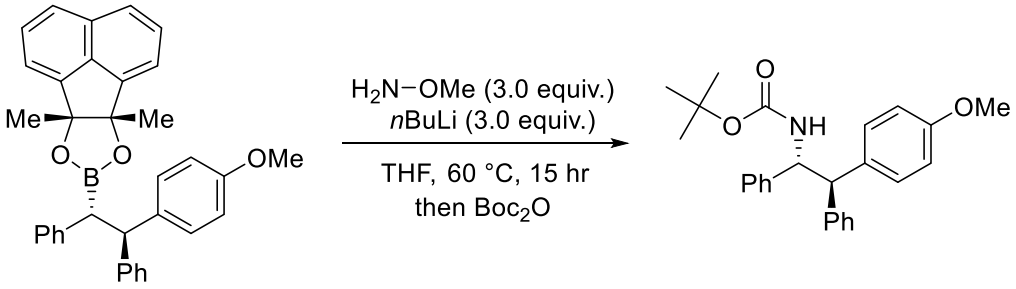


Oxidation



(1R,2R)-2-(4-methoxyphenyl)-1,2-diphenylethan-1-ol (2b). 8-((1R,2R)-2-(4-methoxyphenyl)-1,2-diphenylethyl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (26) (51.0 mg, 0.1 mmol, 1.0 equiv.) was dissolved in THF (2 mL) and cooled to 0 °C. 3M NaOH (1.0 mL) was added, followed by 30% H_2O_2 (0.5 mL), dropwise. The reaction mixture was allowed to stir at room temperature for 4 hours. The reaction mixture was cooled to 0 °C and saturated aq. $Na_2S_2O_3$ solution (3 mL) was added dropwise. After stirring at room temperature for 10 minutes, the reaction mixture was poured into a separatory funnel and the aqueous layer was washed three times with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography with silica gel (silica gel was treated with 2% triethylamine / hexanes prior to use.) (2%-20% EtOAc / hexane, stain in magic stain) to afford the desired product as a white solid (28.0 mg, 92.0% yield).

Amination



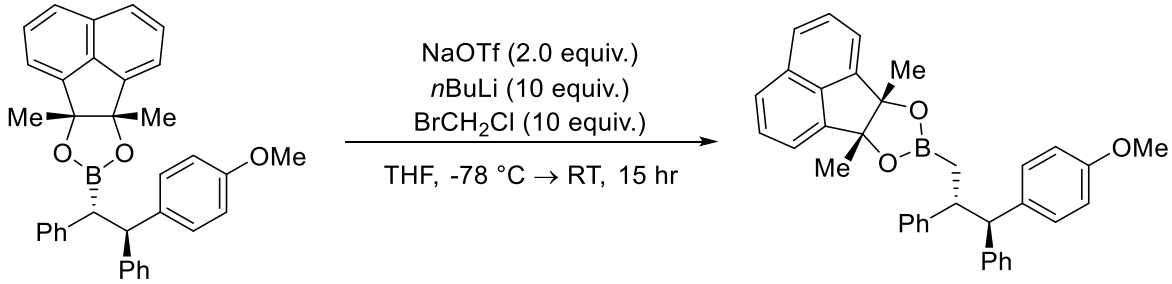
tert-butyl ((1R,2R)-2-(4-methoxyphenyl)-1,2-diphenylethyl)carbamate (27). The title compound was prepared according to a literature procedure[11]. A flame-dried, 2-dram vial equipped with a magnetic stir bar and septum was purged with N_2. After 5 minutes, O-methylhydroxylamine (2 M in THF, 150.00 uL, 0.3 mmol, 3.0 equiv.) was added and diluted with THF (1 mL). The reaction flask was cooled to -78 °C. A solution of n-butyllithium (2.5 M in hexanes, 120.00 uL, 0.3 mmol, 3.0 equiv.) was added dropwise and the reaction was allowed to stir at -78 °C for 30 min. A separate flame-dried 1-dram vial was charged with 8-((1R,2R)-2-(4-methoxyphenyl)-1,2-diphenylethyl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (26) (51.0 mg, .1 mmol, 1.0 equiv.) and diluted with THF (0.5 mL) under N_2. The solution of boronic ester was then added dropwise to the solution of deprotonated O-methylhydroxylamine dropwise via syringe. The reaction vial was warmed to room temperature and then heated to 60 °C. After stirring at 60 °C for 12 h, the reaction flask was cooled to room temperature and tert-butoxycarbonyl tert-butyl carbonate (1 M in THF, 320.00 uL, 0.32 mmol, 3.2 equiv.) was added and reaction was allowed to stir for 2 h at room temperature. The reaction was filtered through a plug of celite with Et_2O and concentrated in vacuo to give the crude reaction mixture and subsequently purified by silica gel column chromatography (silica gel was treated

with 2% triethylamine / hexanes prior to use) (5%-20% EtOAc / hexane, stain in magic stain) to afford the desired product as a white solid (36.0 mg, 89.2% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.01 (m, 12H), 6.87 – 6.80 (m, 2H), 5.35 (br, J = 59.7 Hz, 1H), 4.86 (br, 1H), 4.17 (d, J = 9.3 Hz, 1H), 3.78 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.4, 155.0, 142.0, 129.8, 128.4, 128.2, 128.0, 127.0, 126.9, 126.3, 113.9, 57.3, 55.2, 28.3.; IR (neat): ν_{max} 3402.9 (m), 3029.3 (w), 2975.3 (m), 2934.1 (w), 1682.8 (s), 1511.6 (s), 1248.6 (m), 1169.4 (m), 1015.3 (m), 696.5 (m) cm^{-1}. HRMS (DART) for $C_{26}H_{30}NO_3$ $[M+H]^+$: calculated: 404.2226, found: 404.2226. $[\alpha]^{20}_D$: -66.337 (c = 1.150, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

The enantiospecificity was determined by the diastereomer ratio (>20:1) as detected by ^{1}H NMR.

Homologation

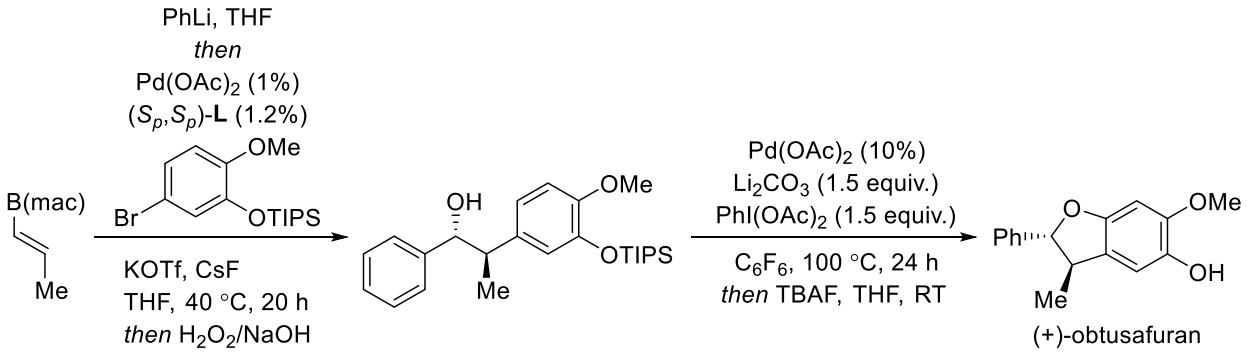


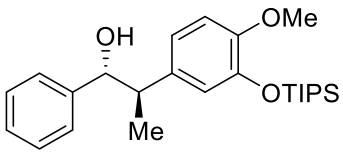
8-((2R,3R)-3-(4-methoxyphenyl)-2,3-diphenylpropyl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (28). The title compound was prepared according to a literature procedure with slight modification.[12] In an argon-filled glovebox, an oven-dried 2-dram equipped with magnetic stir bar was charged with 8-((1R,2R)-2-(4-methoxyphenyl)-1,2-diphenylethyl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (26) (51.0 mg, 0.1 mmol, 1.0 equiv.), sodium triflate (34.4 mg, 0.2 mmol, 2.0 equiv.), bromo(chloro)methane (129.4 mg, 1.0 mmol, 10 equiv.), and THF (0.75 mL). The vial was sealed with a septum cap and removed from glovebox. The reaction was cooled to -78 °C and *n*-butyllithium (2.5 M in hexane, 400.00 uL, 1.0 mmol, 10 equiv.) was added dropwise. The resulting mixture was stirred for 1 hour at –78 °C, then allowed to slowly warm to room temperature and stirred overnight. The reaction was filtered through a plug of celite with Et_2O and concentrated in vacuo. The crude product was purified by silica gel column chromatography (2%-5% EtOAc / hexane, stain in magic stain) to afford the desired product as a white solid (44.0 mg, 83.9% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, J = 5.1, 3.1 Hz, 2H), 7.56 (dt, J = 8.2, 7.1 Hz, 2H), 7.46 (ddd, J = 11.0, 6.9, 0.8 Hz, 2H), 7.32 – 7.23 (m, 2H), 7.17 – 7.08 (m, 2H), 7.08 – 7.00 (m, 4H), 6.98 – 6.90 (m, 1H), 6.90 – 6.78 (m, 3H), 6.75 (dd, J = 204.7, 8.8 Hz, 2H), 4.04 (d, J = 11.4 Hz, 1H), 3.72 (s, 3H), 3.62 (td, J = 11.1, 4.6 Hz, 1H), 1.54 (s, 3H), 1.48 (s, 3H), 1.11 (dd, J = 15.0, 4.6 Hz, 1H), 0.99 (dd, J = 15.1, 11.1 Hz, 1H).; ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.5, 147.40, 147.37, 147.32, 146.8, 139.0, 137.2, 134.0, 132.0, 131.0, 130.9, 130.6, 130.5, 130.1, 128.1, 128.1, 127.7, 121.88, 121.85, 116.5, 94.2, 94.1, 79.9, 79.7, 79.5, 61.8, 57.8, 48.7, 24.5, 24.3.; IR (neat): ν_{max} 3059.9 (m), 3027.5 (m), 2970.5 (m), 2931.8 (m), 1608.9 (s), 1582.9 (s), 1357.0 (s), 1250.1 (s), 1175.5 (m), 1077.3 (m), 806.8 (m), 724.7 (s), 667.3 (s) cm^{-1}. HRMS (DART) for $C_{36}H_{37}BO_3N$ $[M+NH_4]^+$: calculated: 542.2866, found: 542.2894. $[\alpha]^{20}_D$: +20.029 (c = 1.000, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

The enantiospecificity was determined by the diastereomer ratio (>20:1) as detected by ^{1}H NMR.

VII. Synthesis of (+)-Obtusafuran (31)

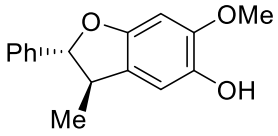




(1R,2R)-2-(4-methoxy-3-((triisopropylsilyl)oxy)phenyl)-1-phenylpropan-1-ol (30). The reaction was performed according to the general procedure ***(Method B)*** with (E)-propenyl B(mac) (S-2) (52.8 mg, 0.2 mmol, 1.0 equiv.), phenyllithium (1.9 M in dibutyl ether, 0.11 mL, 0.20 mmol, 1.0 equiv.), (5-bromo-2-methoxyphenoxy)triisopropylsilane (79.1 mg, 0.22 mmol, 1.1 equiv.), palladium (II) acetate (0.45 mg, 0.002 mmol, 0.010 equiv.), (S_p, S_p)-**L** (2.5 mg, 0.0024 mmol, 0.012 equiv.), potassium triflate (37.6 mg, 0.2 mmol, 1.0equiv.), and cesium fluoride (30.4 mg, 0.2 mmol, 1.0 equiv.) in THF (0.8 mL, 0.25 M). The crude mixture was purified by silica gel chromatography (5-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (56 mg, 68% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 4H), 7.31 – 7.23 (m, 1H), 6.86 – 6.76 (m, 3H), 4.57 (d, J = 8.3 Hz, 1H), 3.80 (s, 3H), 2.91 (q, J = 7.4 Hz, 1H), 1.90 (br, 1H), 1.35 – 1.18 (m, 3H), 1.18 – 0.98 (m, 21H).. ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 145.8, 142.6, 135.5, 128.4, 127.8, 127.13, 121.07, 120.3, 112.4, 79.8, 55.7, 47.7, 18.4, 18.11, 18.08, 18.05, 13.1. IR (neat): ν_{max} 2943, 2866, 1509, 1443, 1278, 1165, 1029, 883, 700 cm^{-1}. HRMS (DART) for $C_{25}H_{39}O_3Si$ $[M+H]^+$: calculated: 415.2663, found: 415.2659. $[\alpha]^{20}_D$: +37.25 (c = 1.02, $CHCl_3$, l = 50 mm).

Analysis of Stereochemistry:

Diastereomer ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Absolute stereochemistry was assigned by analogy (see compounds 26, 31).

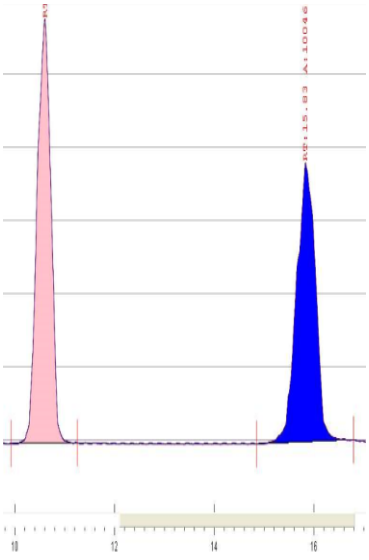


(2R,3R)-6-methoxy-3-methyl-2-phenyl-2,3-dihydrobenzofuran-5-ol ((+)-obtusafuran) (31). The reaction was performed according to a literature procedure.[13] In an argon-filled glovebox, to an oven-dried 1-dram vial was added 2-(4-methoxy-3-triisopropylsilyloxy-phenyl)-1-phenyl-propan-1-ol (56 mg, 135 µmol, 1.0 equiv.), lithium carbonate (14.97 mg, 203 µmol, 1.5 equiv.), diacetoxyiodobenzene (64.84 mg, 203 µmol, 1.5 equiv.), palladium (II) acetate (3mg, 14 µmol, 0.10 equiv.), and hexafluorobenzene (0.14 mL, 1 M). The vial was sealed with a screwcap and placed in a 100 ºC oil bath. After stirring at this temperature for 24 hours, the reaction was cooled down to room temperature and filtered through a plug of silica gel with Et_2O. The crude mixture was concentrated, then dissolved in THF (0.54 mL). Tetrabutylammonium fluoride hydrate (53 mg, 203 µmol, 1.5 equiv.) was added and the reaction was stirred at room temperature for 24 hours then filtered through a plug of silica gel with Et_2O. The solvent was evaporated and the crude product was purified by silica gel chromatography (5-20% EtOAc in hexanes, stain in magic stain) to afford a white solid (14 mg, 54 µmol, 40% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 5H), 6.73 (s, 1H), 6.51 (s, 1H), 5.28 (s, 1H), 5.12 (d, J = 8.5 Hz, 1H), 3.87 (s, 3H), 3.45 – 3.32 (m, 1H), 1.39 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 146.4, 141.2, 140.1, 128.8, 128.7, 128.3, 126.3, 126.2, 123.1, 109.7, 94.4, 93.0, 56.4, 45.9, 18.6. $[\alpha]^{20}_D$: +56.2 (c = 0.90, MeOH, l = 50 mm).

Analysis of Stereochemistry:

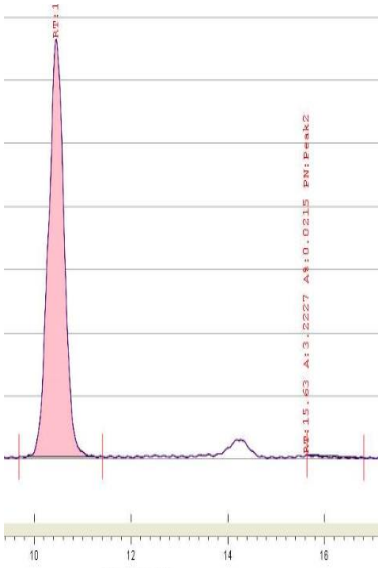
Racemic compound was prepared according to a literature procedure.[14] Absolute stereochemistry was determined by comparison of optical rotation to the literature[15] (Measured: $[\alpha]^{20}_D$: +56.2 (c = 0.90, MeOH, l = 50 mm), literature: $[\alpha]^{20}_D$: +50 (c = 0.33, MeOH), 99:1 *e.r* for (2R,3R)-6-methoxy-3-methyl-2-phenyl-2,3-dihydrobenzofuran-5-ol), and the absolute stereochemistry was assigned to be (2R,3R)-6-methoxy-3-methyl-2-phenyl-2,3-dihydrobenzofuran-5-ol.

Racemic material



Peak No	% Area	Area	RT (min)
1	52.64	11166.1069	10.61
2	47.36	10046.088	15.83
Total:	100	21212.1949	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	99.9785	14956.6731	10.45
2	0.0215	3.2227	15.63
Total:	100	14959.8958	

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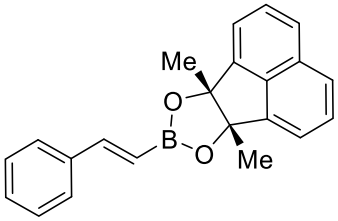
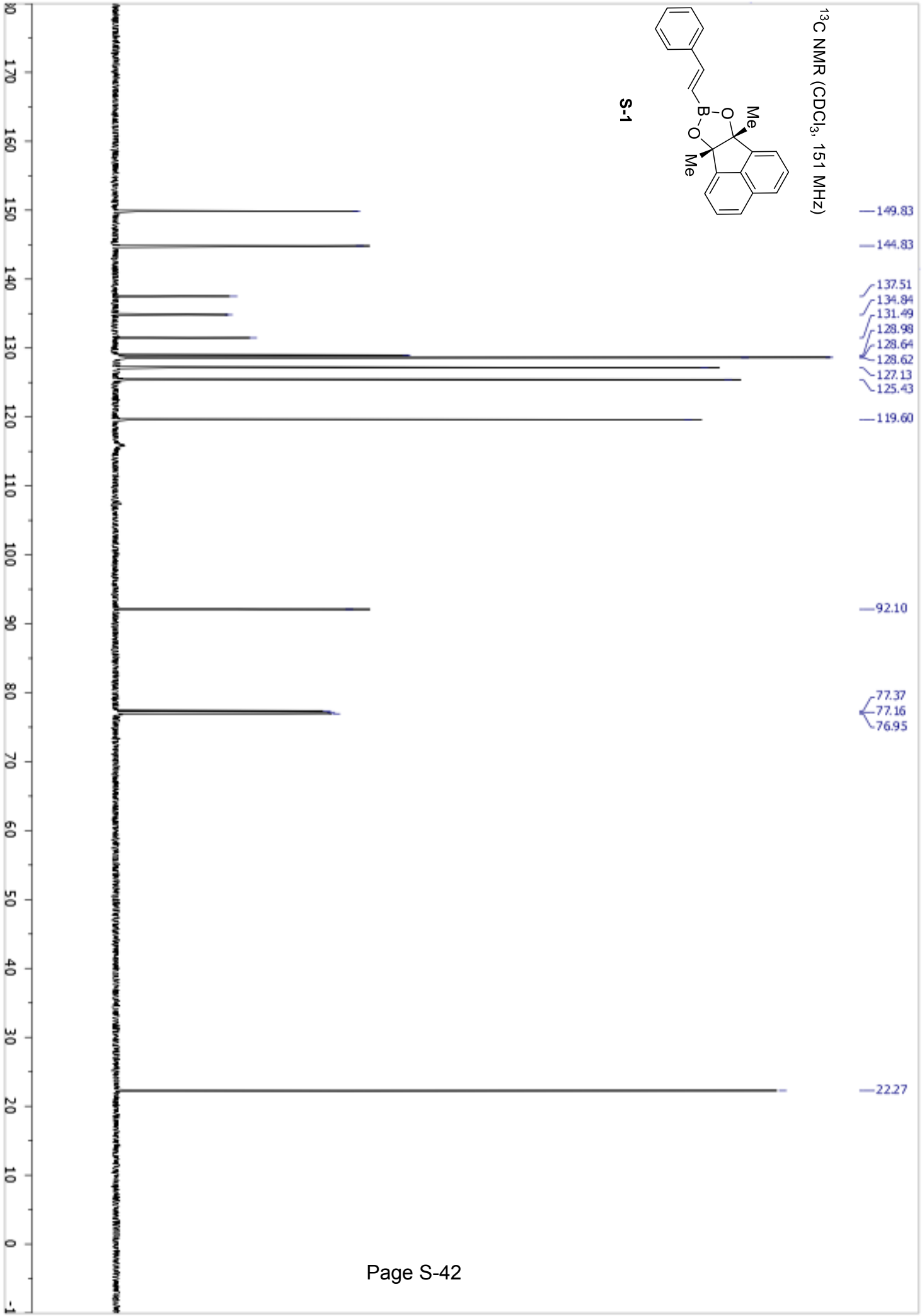
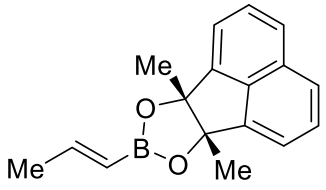
^{1}H NMR ($CDCl_3$, 600 MHz)



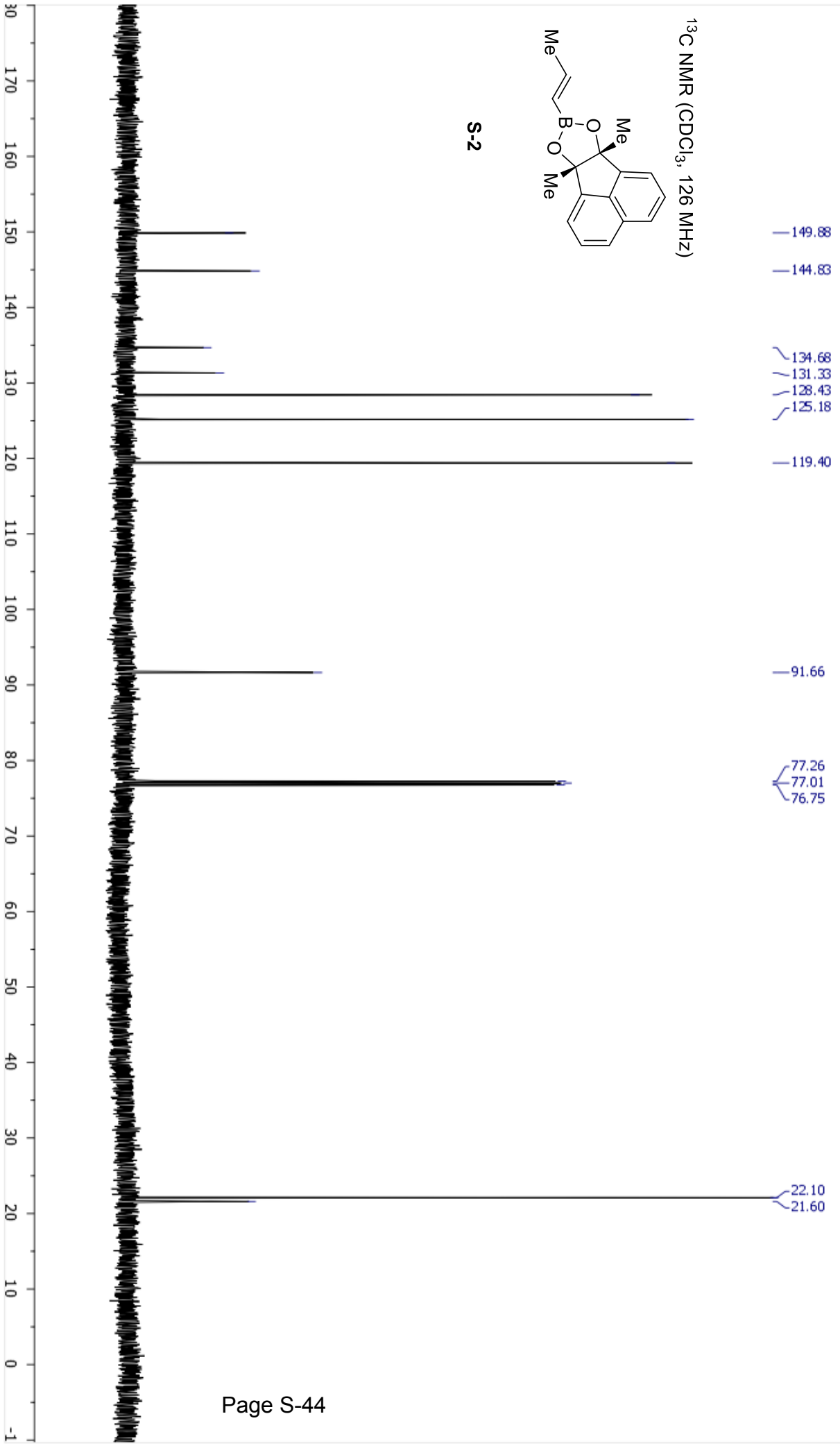
S-1


S-1
Me
Me
O
O
B
^{13}C NMR (CDCl$_3$, 151 MHz)
149.83
144.83
137.51
134.84
131.49
128.98
128.64
128.62
127.13
125.43
119.60
92.10
77.37
77.16
76.95
22.27

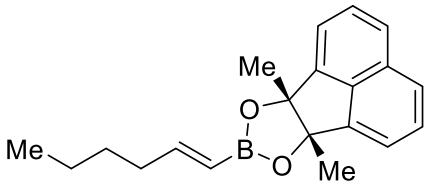
^{1}H NMR ($CDCl_3$, 500 MHz)



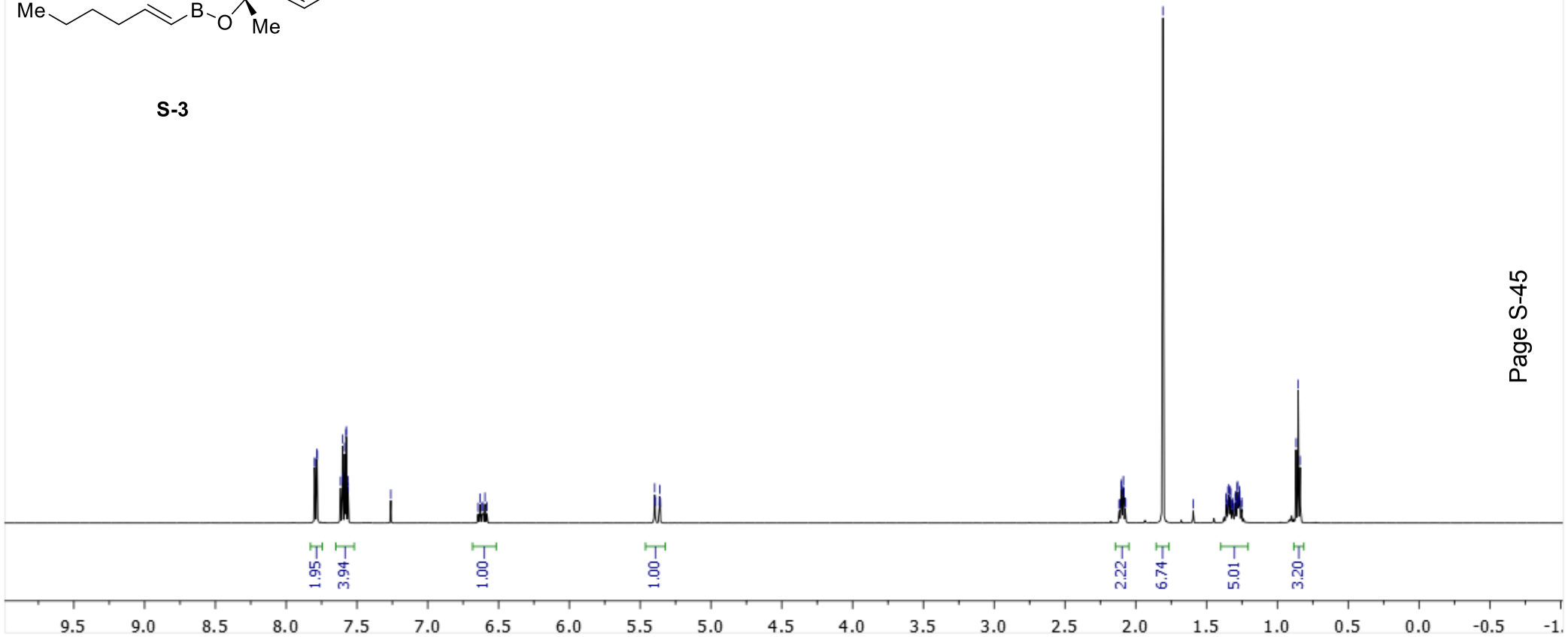
S-2

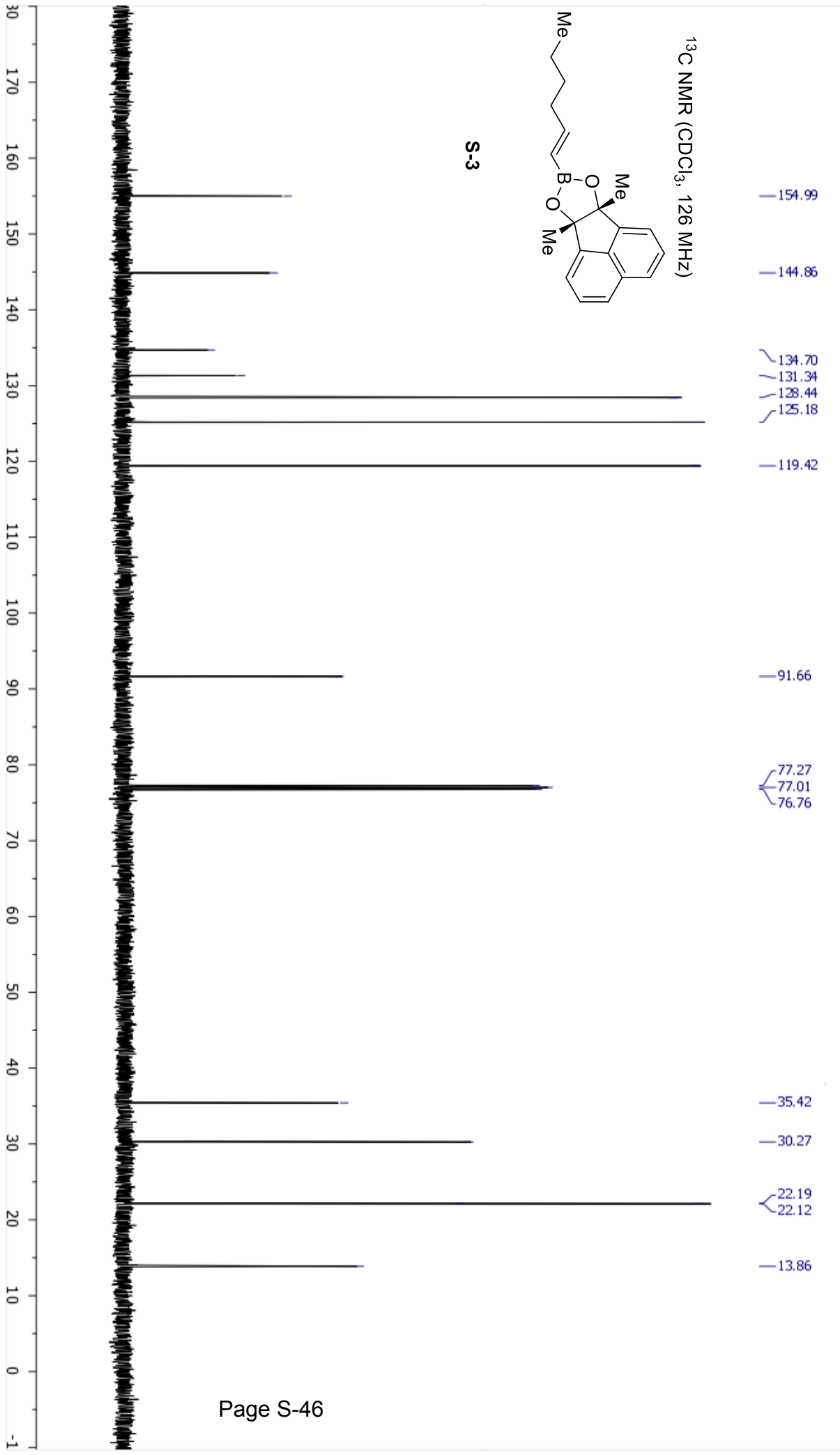

^{13}C NMR (CDCl$_3$, 126 MHz)
S-2
Me
Me
Me
B
O
O
149.88
144.83
134.68
131.33
128.43
125.18
119.40
91.66
77.26
77.01
76.75
22.10
21.60
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

^{1}H NMR ($CDCl_3$, 500 MHz)



S-3




^{13}C NMR (CDCl$_3$, 126 MHz)
S-3
Me
B
O
O
Me
Me
154.99
144.86
134.70
131.34
128.44
125.18
119.42
91.66
77.27
77.01
76.76
35.42
30.27
22.19
22.12
13.86
30
170
160
150
140
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120
110
100
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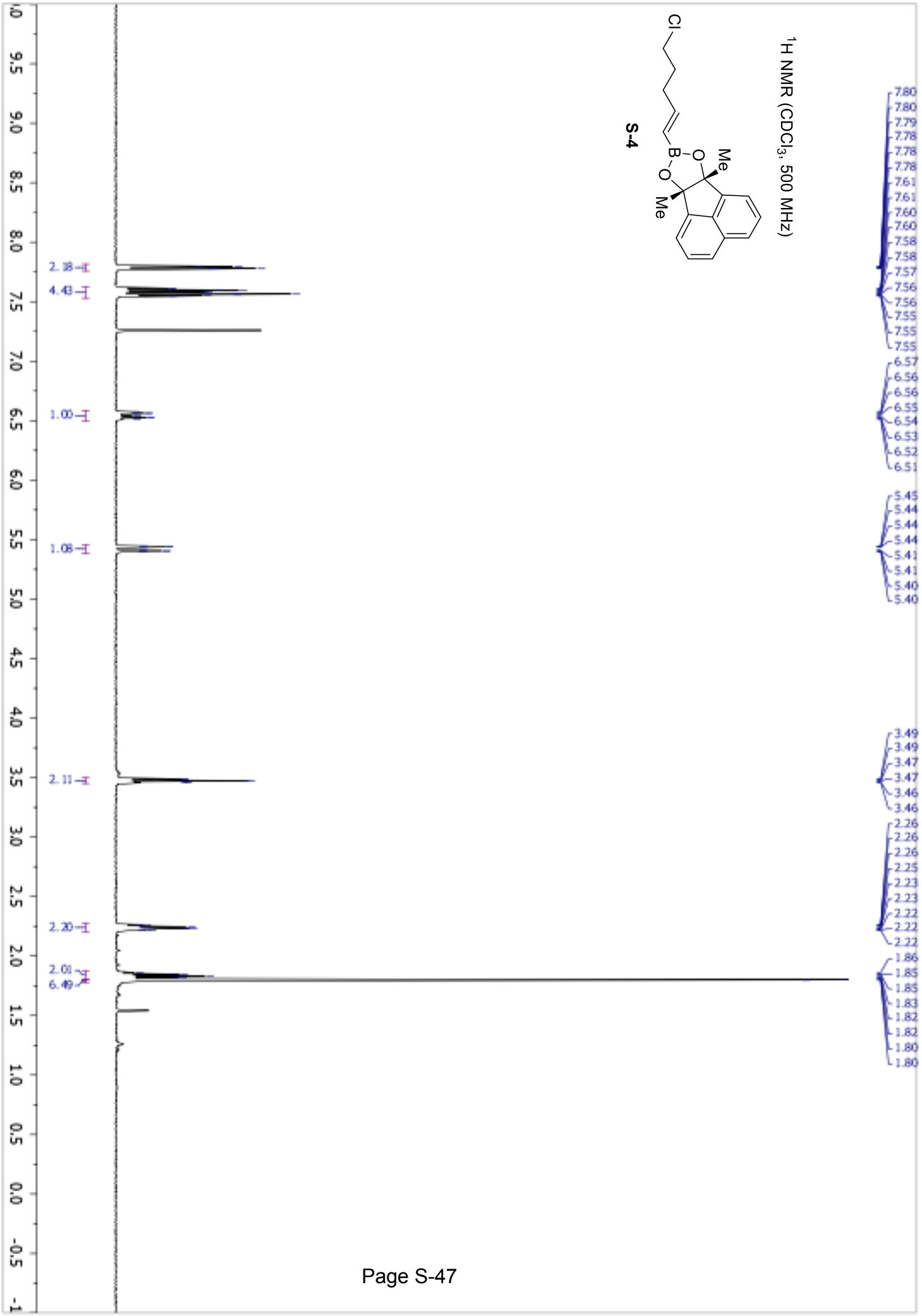
80
70
60
50
40
30
20
10
0
-1


S-4
Cl
B
O
O
Me
Me
^{1}H NMR (CDCl$_3$, 500 MHz)
2.38
4.43
1.00
1.08
2.11
2.20
2.01
6.49
7.80
7.79
7.78
7.61
7.60
7.58
7.57
7.56
7.55
6.57
6.56
6.55
6.54
6.53
6.52
6.51
5.45
5.44
5.41
5.40
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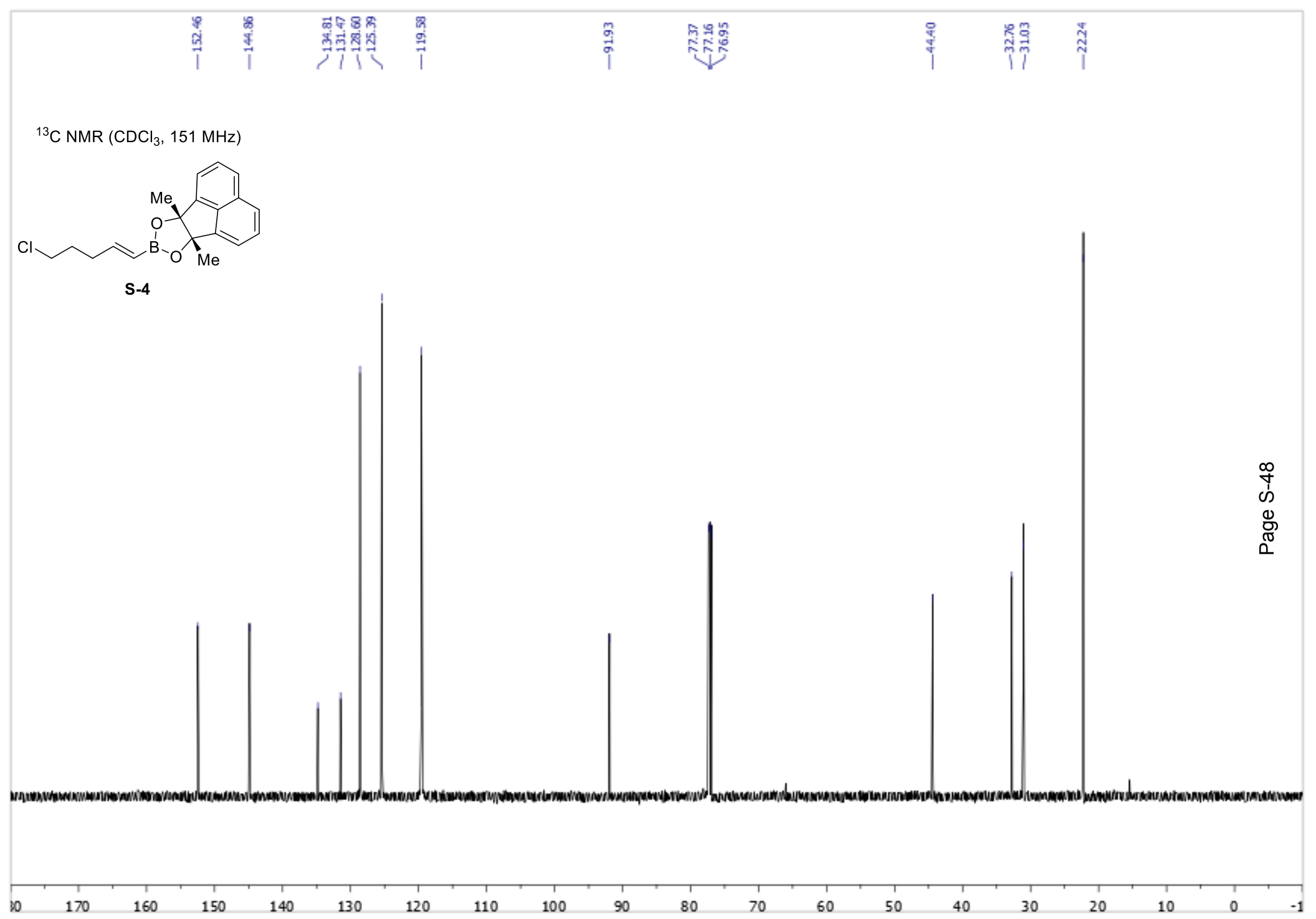
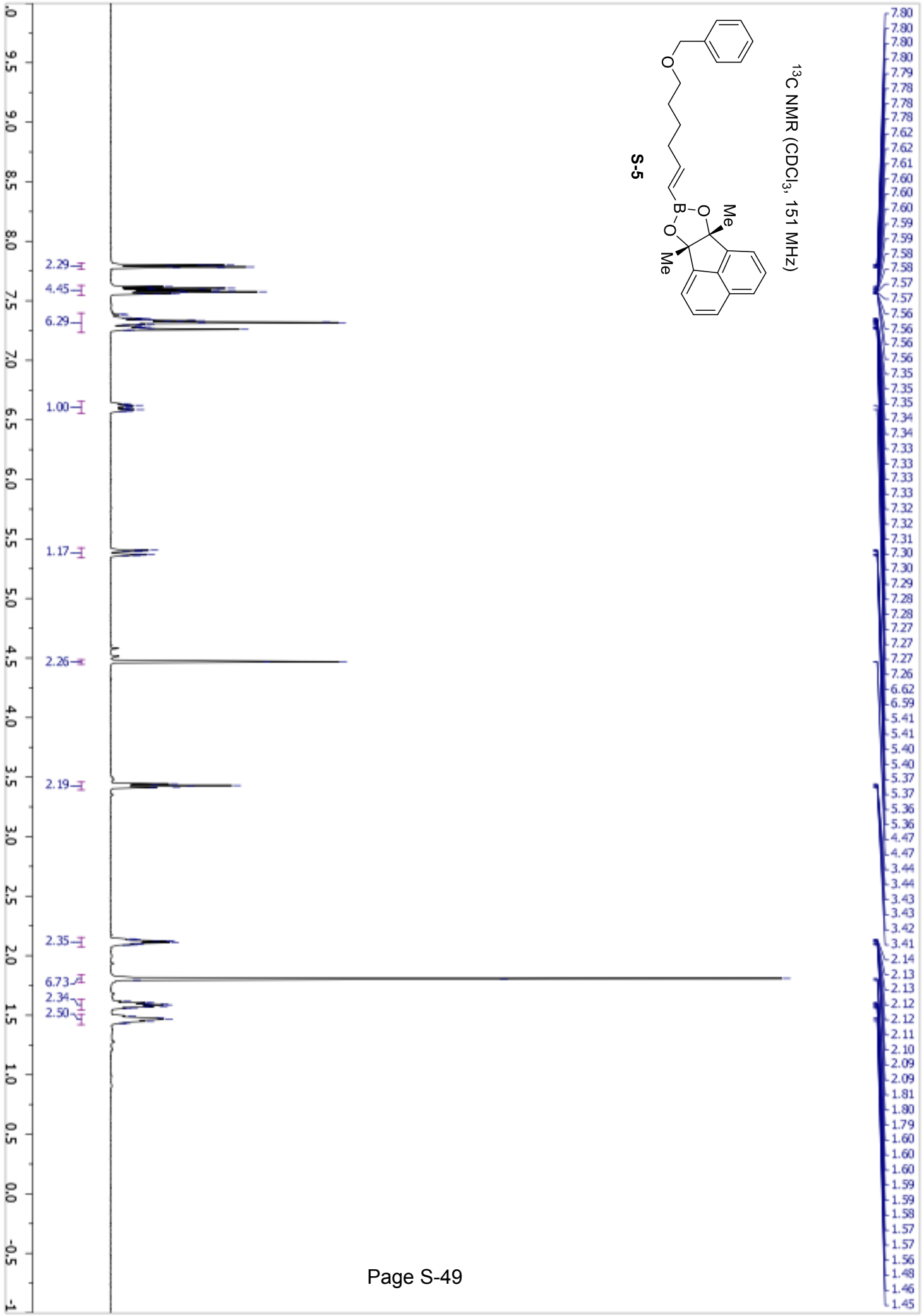
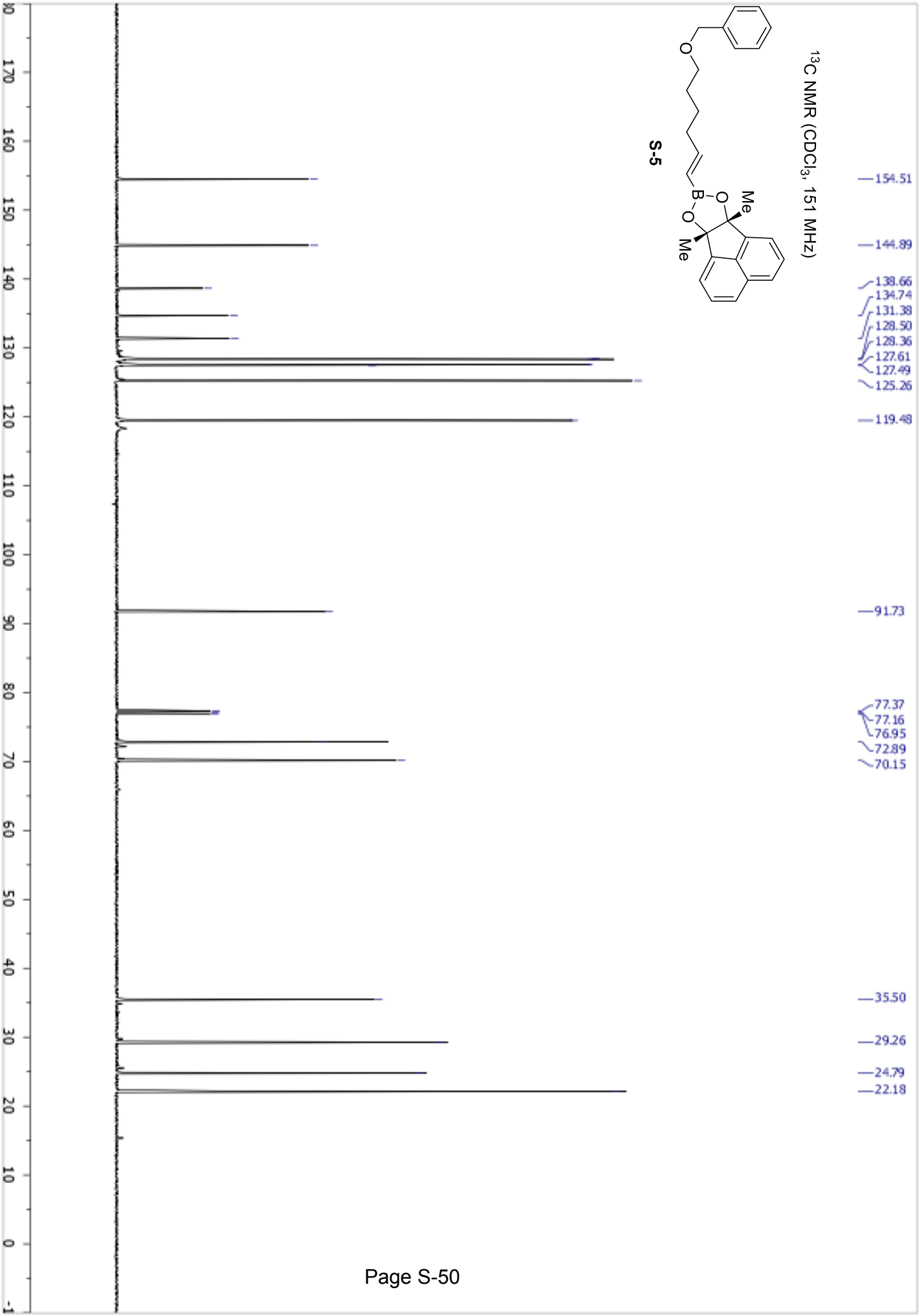
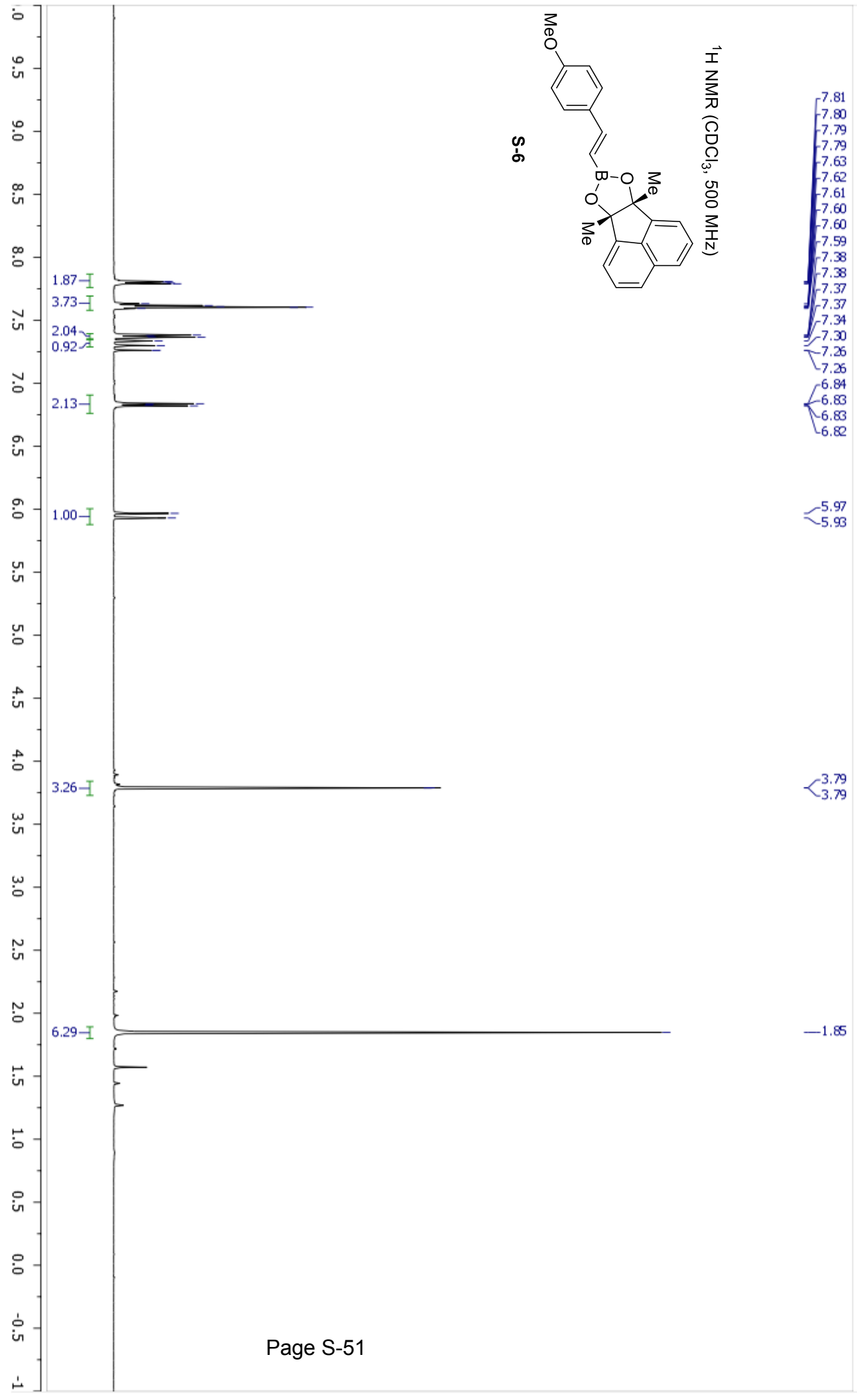
2.22
1.86
1.85
1.83
1.82
1.80


152.46
144.86
134.81
131.47
128.60
125.39
119.58
91.93
77.37
77.16
76.95
44.40
32.76
31.03
22.24
13C NMR (CDCl3, 151 MHz)
Me
O
Cl
B
O
Me
S-4
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1


S-5
^{13}C NMR (CDCl$_3$, 151 MHz)
2.29
4.45
6.29
1.00
1.17
2.26
2.19
2.35
6.73
2.34
2.50


S-5
^{13}C NMR (CDCl$_3$, 151 MHz)
154.51
144.89
138.66
134.74
131.38
128.50
128.36
127.61
127.49
125.26
119.48
91.73
77.37
77.16
76.95
72.89
70.15
35.50
29.26
24.79
22.18


S-6
^{1}H NMR (CDCl$_3$, 500 MHz)
MeO
B
O
O
Me
Me
1.87
3.73
2.04
0.92
2.13
1.00
3.26
6.29
7.81
7.80
7.79
7.79
7.63
7.62
7.61
7.60
7.60
7.59
7.38
7.38
7.37
7.37
7.34
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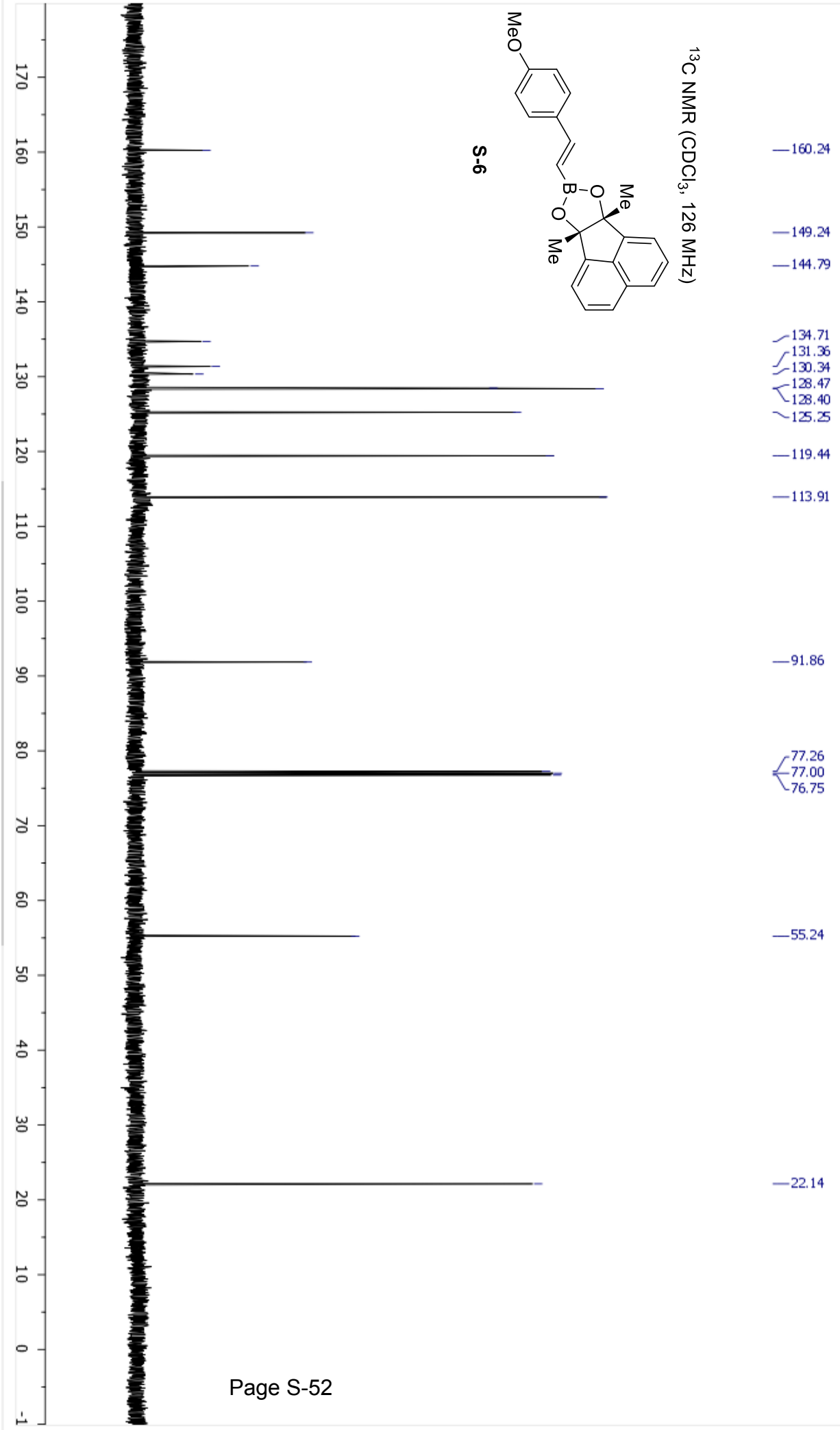
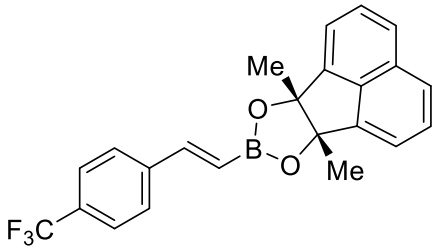
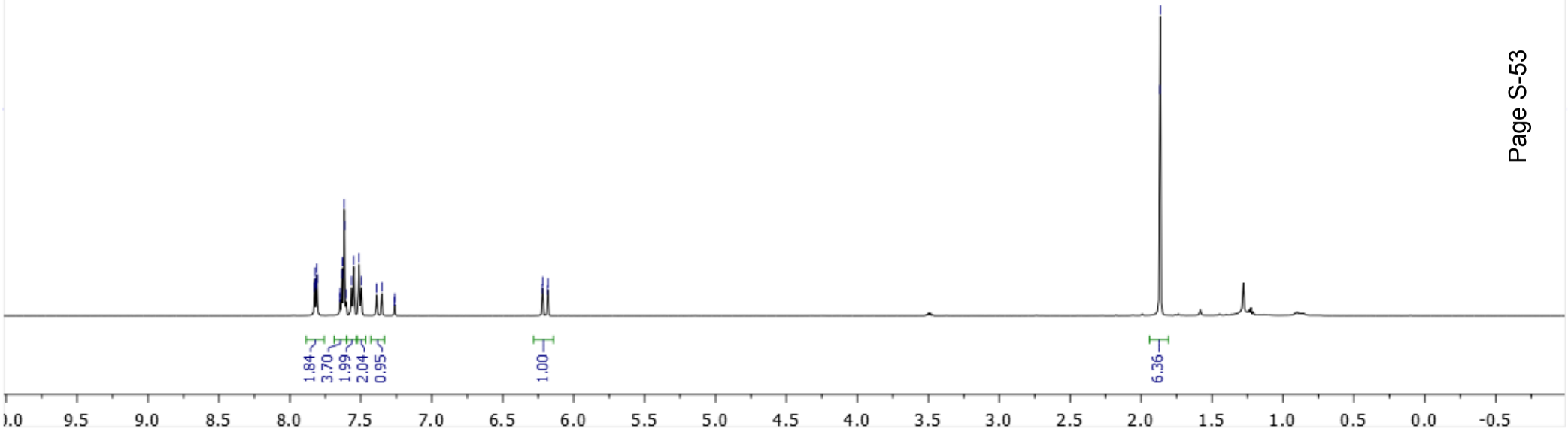
6.82
5.97
5.93
3.79
3.79
1.85

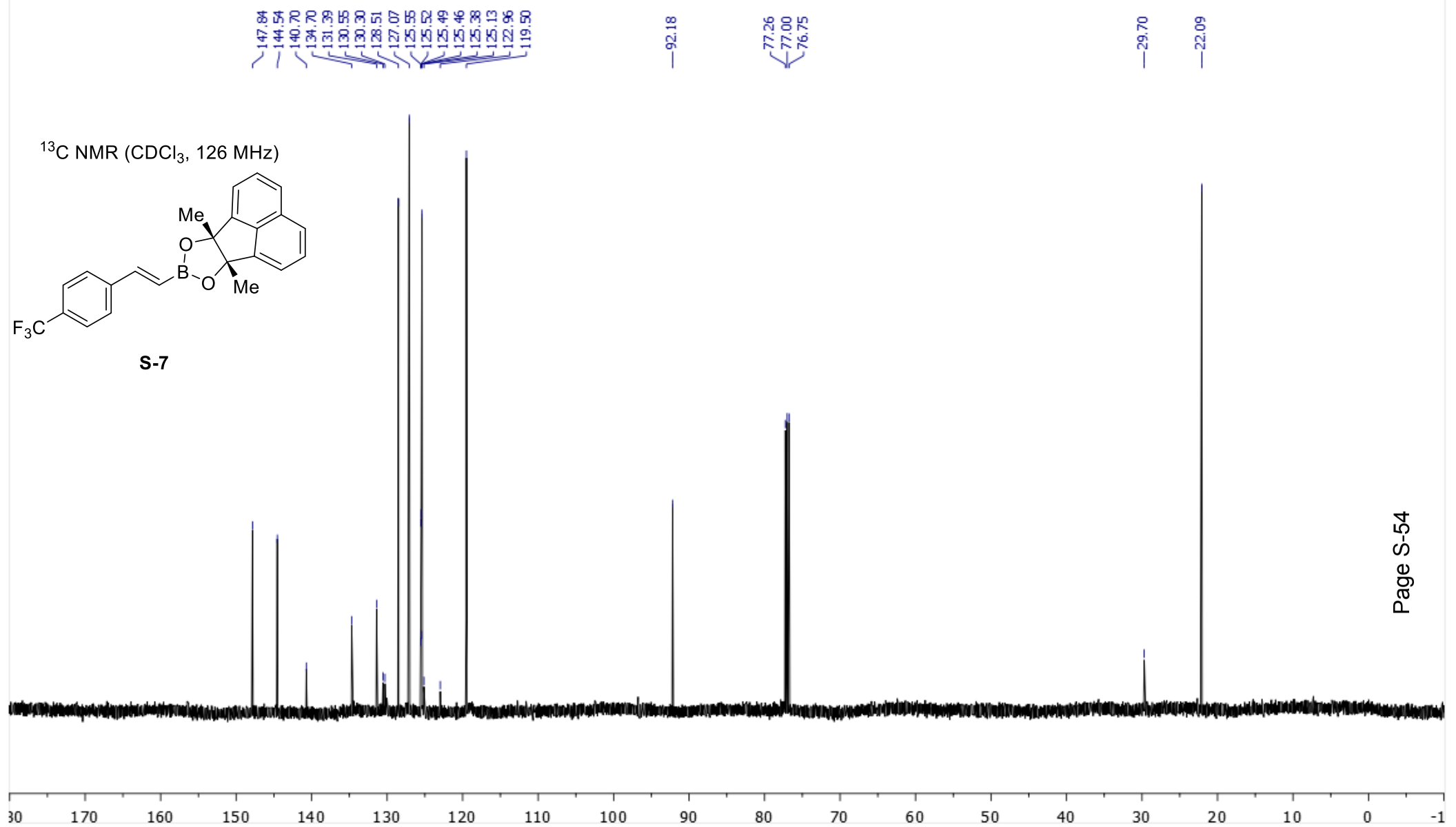

^{13}C NMR (CDCl$_3$, 126 MHz)
S-6
MeO
B
O
O
Me
Me
160.24
149.24
144.79
134.71
131.36
130.34
128.47
128.40
125.25
119.44
113.91
91.86
77.26
77.00
76.75
55.24
22.14
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

^{1}H NMR ($CDCl_3$, 500 MHz)

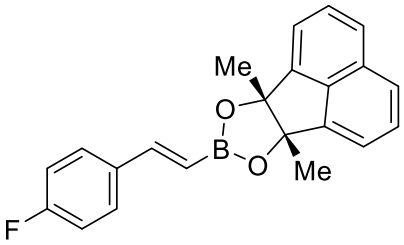


S-7

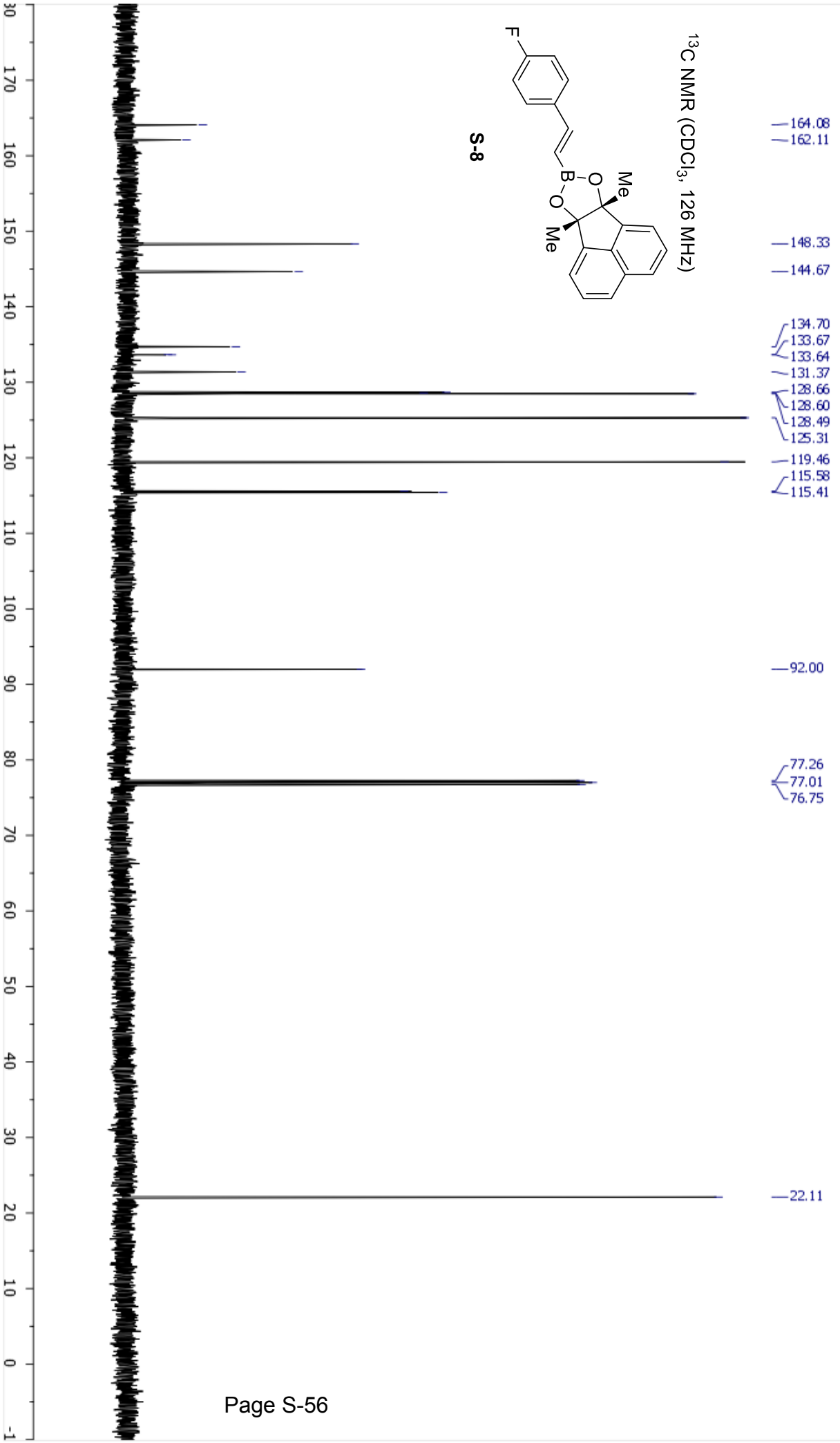


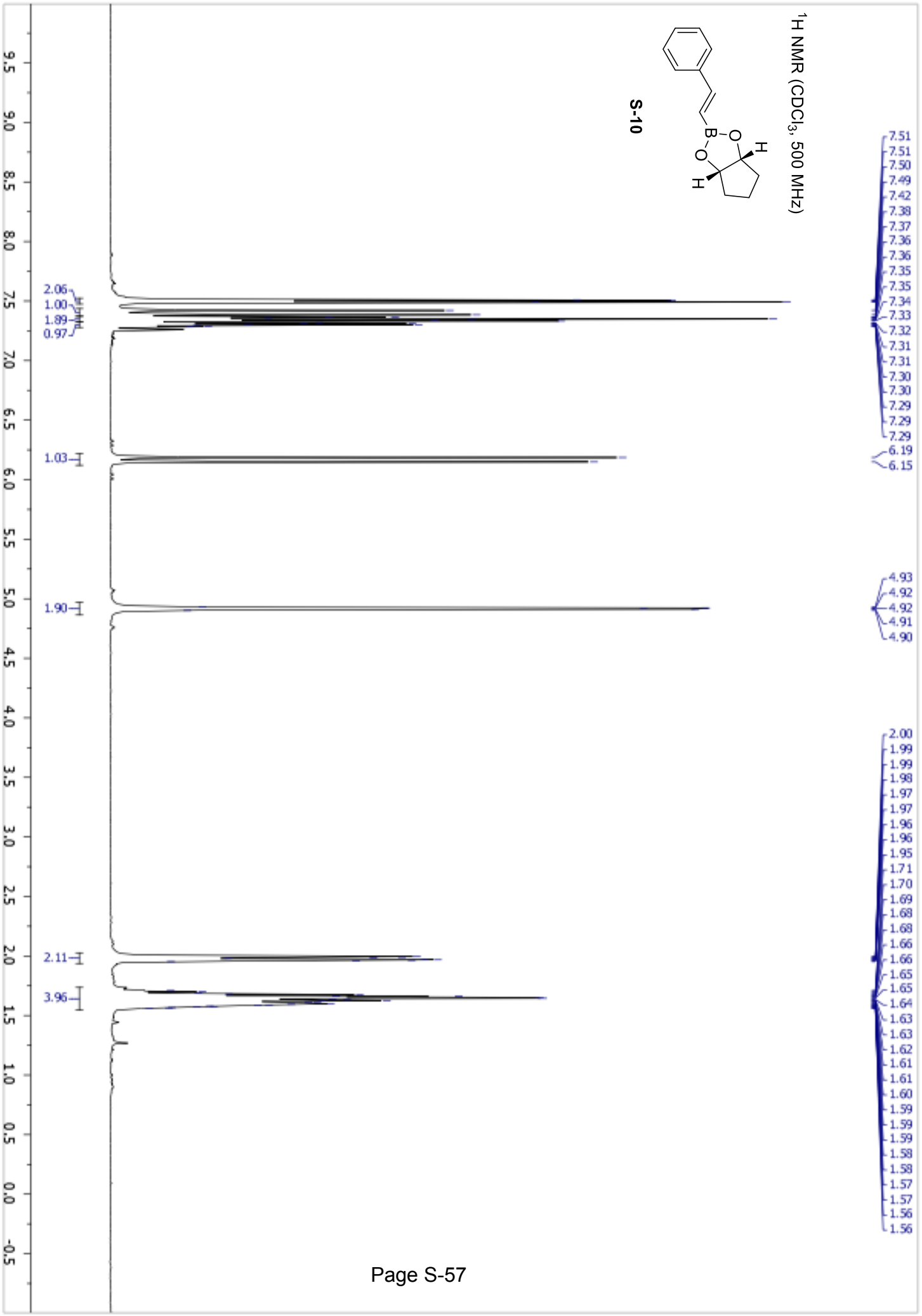

147.84
144.54
140.70
134.70
131.39
130.55
130.30
128.51
127.07
125.55
125.52
125.49
125.46
125.38
125.13
122.96
119.50
92.18
77.26
77.00
76.75
29.70
22.09
13C NMR (CDCl3, 126 MHz)
Me
O
B
O
Me
F3C
S-7
Page S-54
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

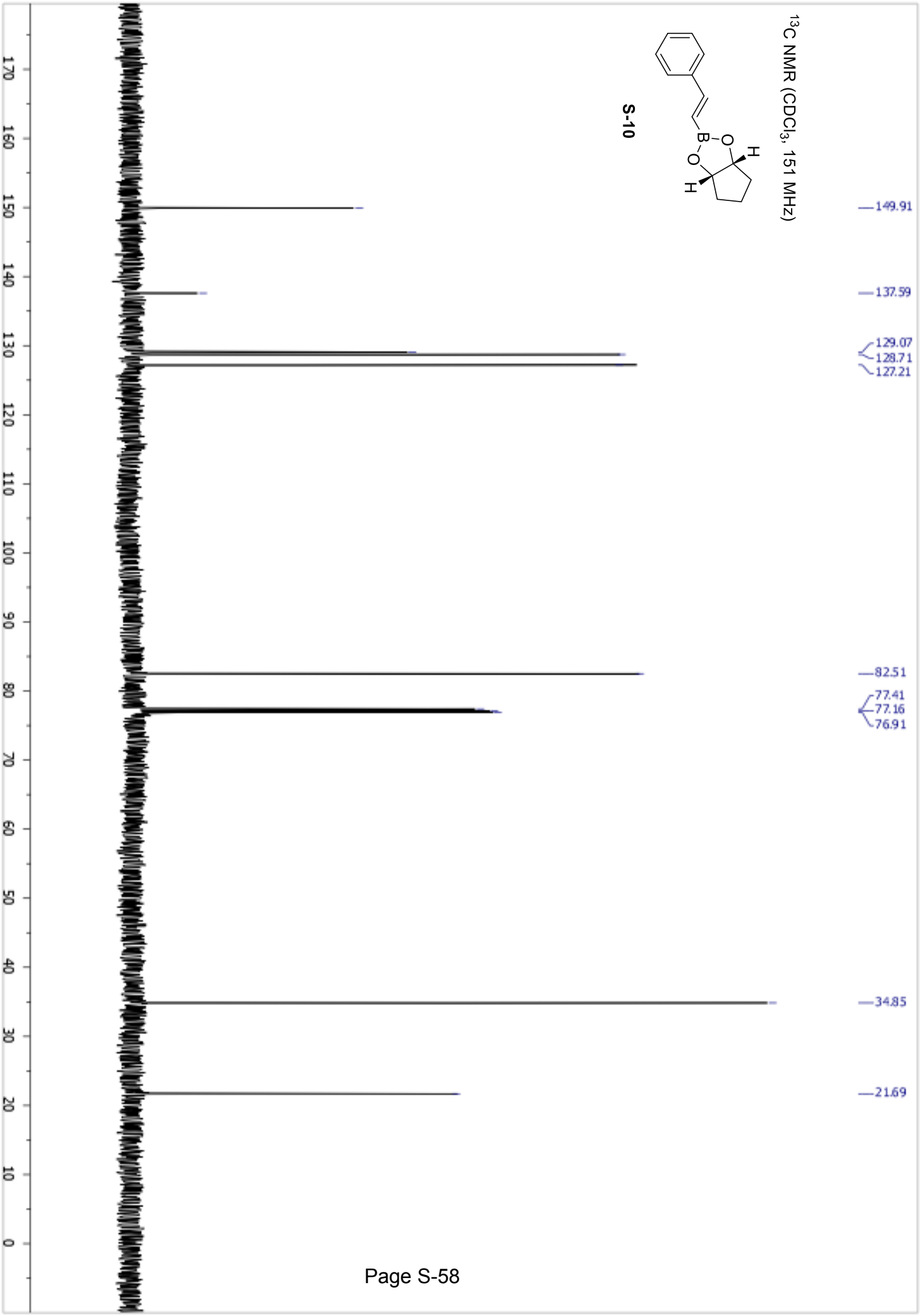
^{1}H NMR ($CDCl_3$, 500 MHz)



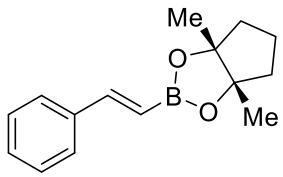
S-8


S-8
^{13}C NMR (CDCl$_3$, 126 MHz)
F
B
O
O
Me
Me
164.08
162.11
148.33
144.67
134.70
133.67
133.64
131.37
128.66
128.60
128.49
125.31
119.46
115.58
115.41
92.00
77.26
77.01
76.75
22.11
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

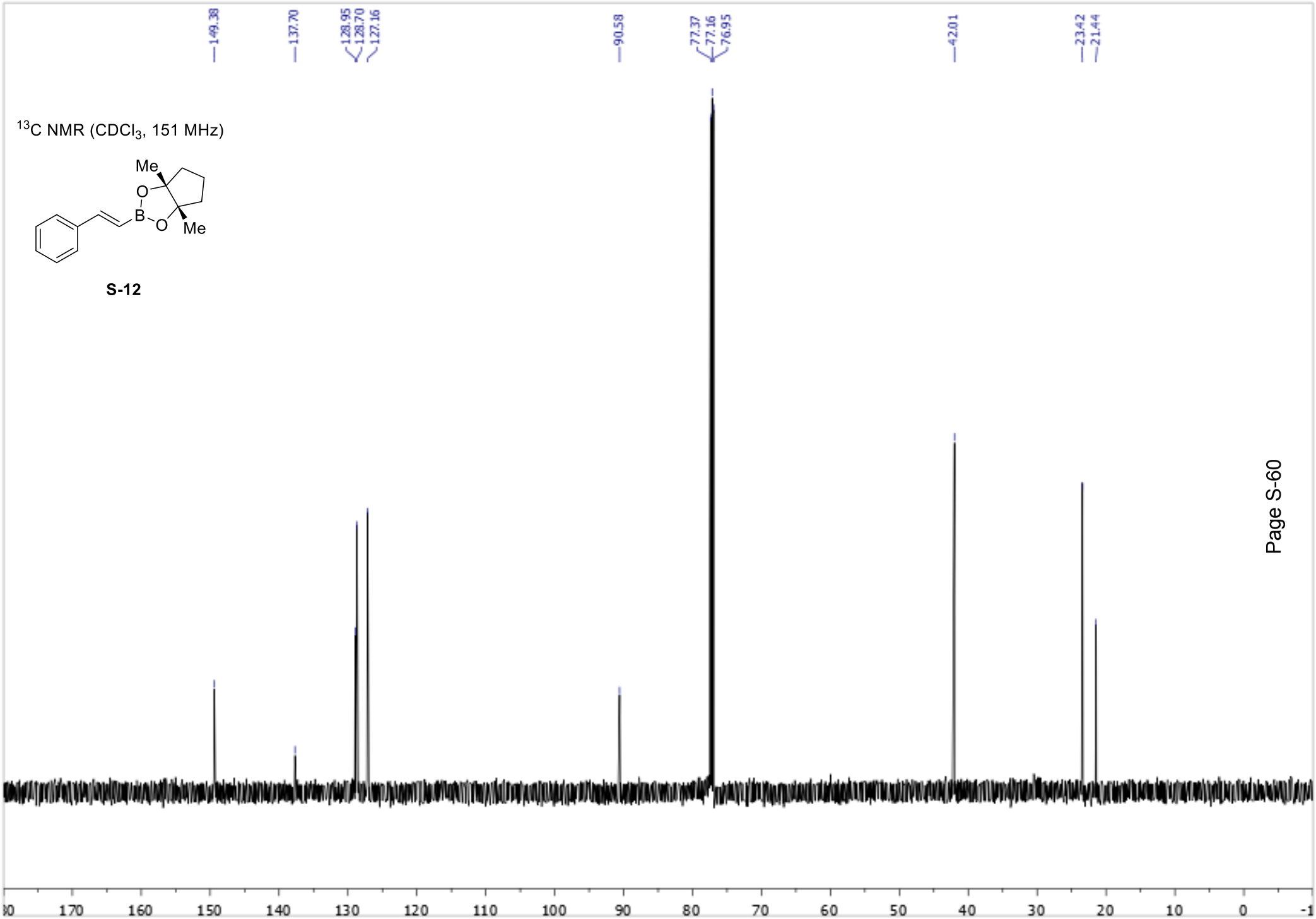

S-10
^{1}H NMR (CDCl$_3$, 500 MHz)
2.06
1.00
1.89
0.97
1.03
1.90
2.11
3.96
7.51
7.51
7.50
7.49
7.42
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.29
6.19
6.15
4.93
4.92
4.92
4.91
4.90
2.00
1.99
1.99
1.98
1.97
1.97
1.96
1.96
1.95
1.71
1.70
1.69
1.68
1.68
1.66
1.66
1.65
1.65
1.64
1.63
1.63
1.62
1.61
1.61
1.60
1.59
1.59
1.59
1.58
1.58
1.57
1.57
1.56
1.56


^{13}C NMR (CDCl$_3$, 151 MHz)
S-10
B
O
O
H
H
149.91
137.59
129.07
128.71
127.21
82.51
77.41
77.16
76.91
34.85
21.69
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

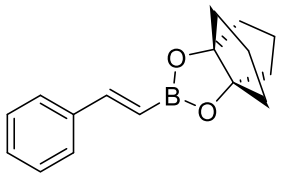
^{1}H NMR ($CDCl_3$, 600 MHz)



S-12

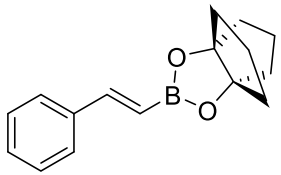

149.38
137.70
128.95
128.70
127.16
90.58
77.37
77.16
76.95
42.01
23.42
21.44
13C NMR (CDCl3, 151 MHz)
Me
O
B
O
Me
S-12
Page S-60
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{1}H NMR ($CDCl_3$, 500 MHz)



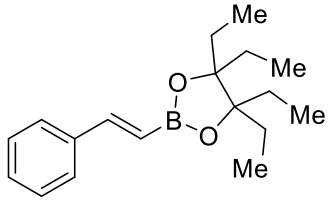
S-13

^{13}C NMR ($CDCl_3$, 126 MHz)

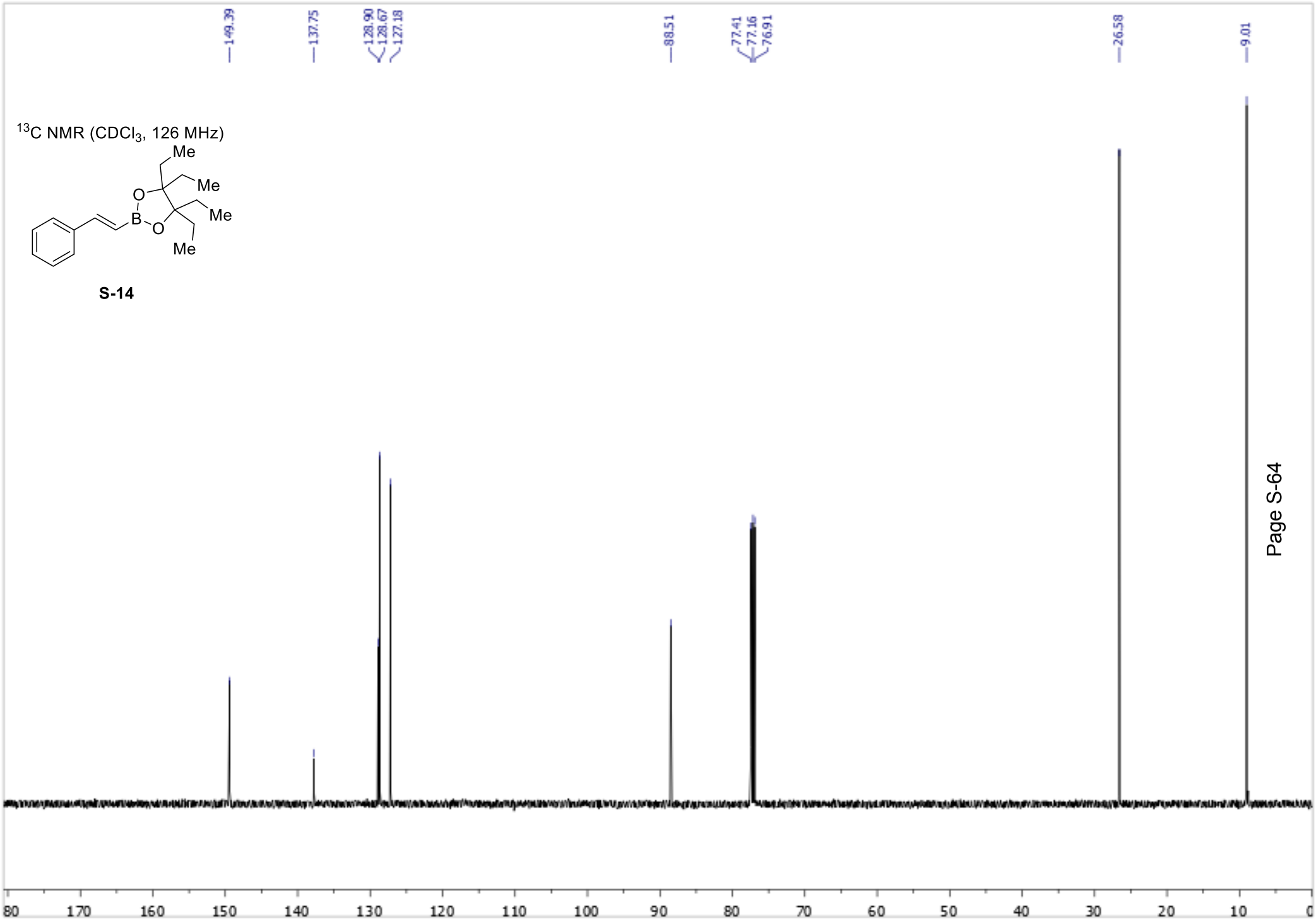


S-13

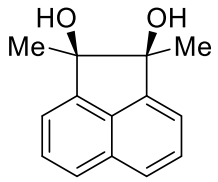
^{1}H NMR ($CDCl_3$, 600 MHz)



S-14

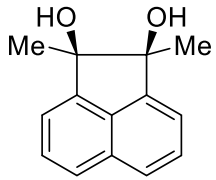

149.39
137.75
128.90
128.67
127.18
88.51
77.41
77.16
76.91
26.58
9.01
^{13}C NMR ($CDCl_3$, 126 MHz)
Me
Me
Me
Me
O
B
O
S-14
Page S-64
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{1}H NMR ($CDCl_3$, 600 MHz)

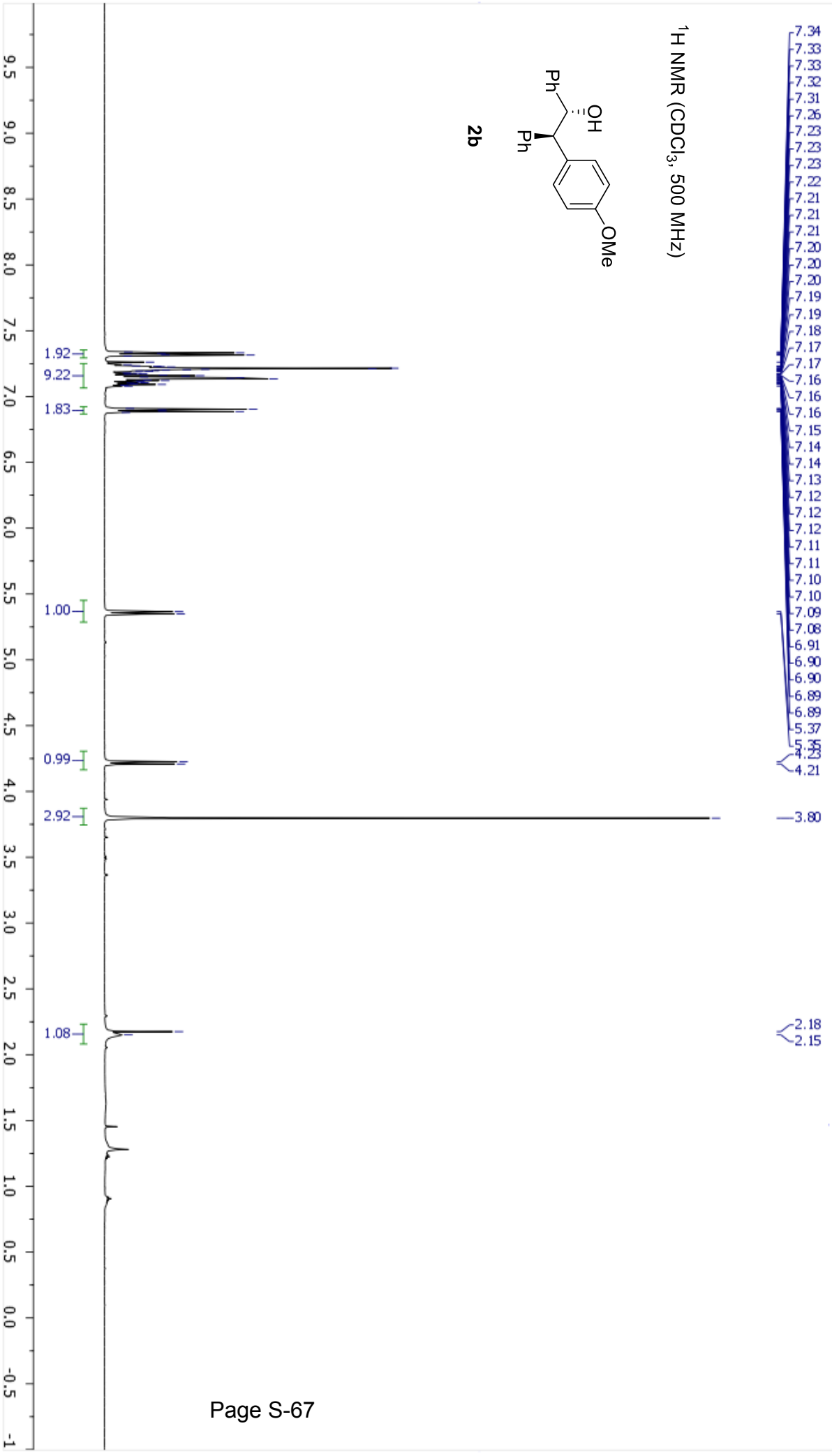


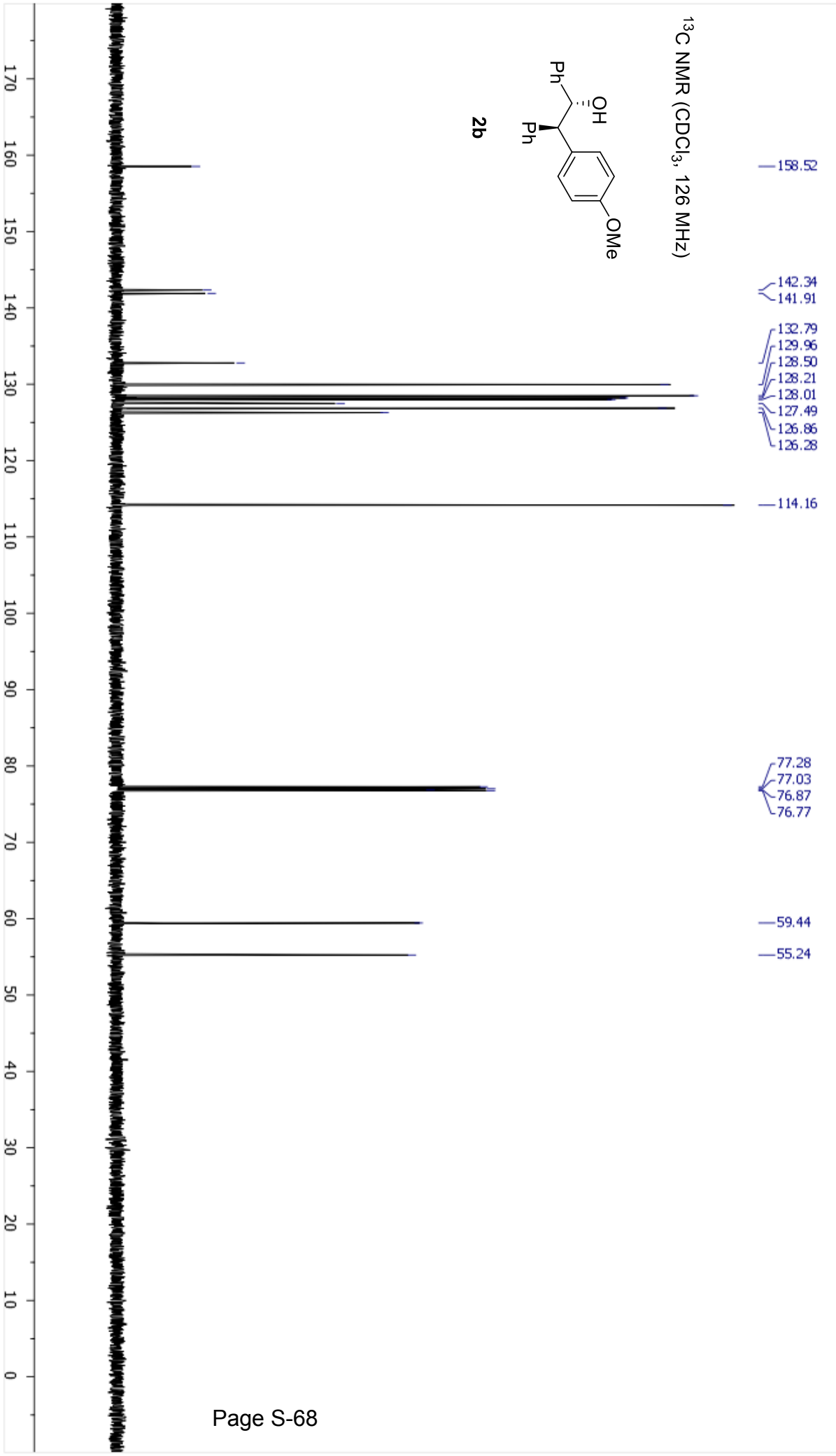
4

^{13}C NMR ($CDCl_3$, 151 MHz)

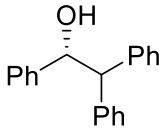


4

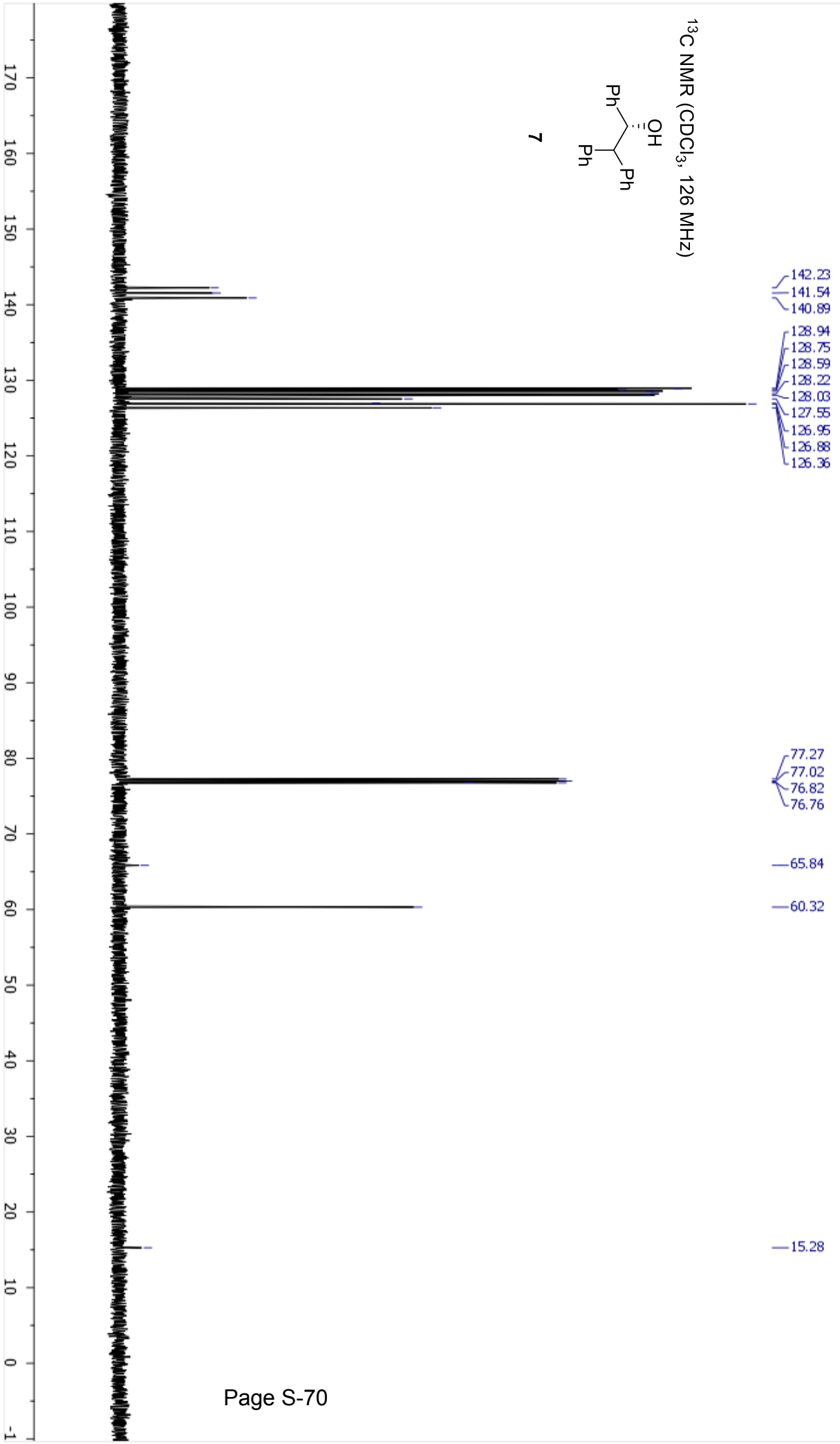

^{1}H NMR (CDCl$_3$, 500 MHz)
2b
Ph
OH
Ph
OMe
1.92
9.22
1.83
1.00
0.99
2.92
1.08
7.34
7.33
7.33
7.32
7.31
7.26
7.23
7.23
7.23
7.22
7.21
7.21
7.21
7.20
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.16
7.15
7.14
7.14
7.13
7.12
7.12
7.12
7.11
7.11
7.10
7.10
7.09
7.08
6.91
6.90
6.90
6.89
6.89
5.37
4.23
4.21
3.80
2.18
2.15

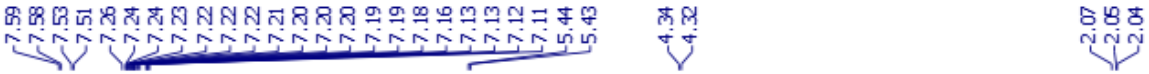

^{13}C NMR (CDCl$_3$, 126 MHz)
2b
Ph
OH
Ph
OMe
158.52
142.34
141.91
132.79
129.96
128.50
128.21
128.01
127.49
126.86
126.28
114.16
77.28
77.03
76.87
76.77
59.44
55.24
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{1}H NMR ($CDCl_3$, 600 MHz)

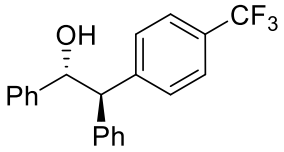


7

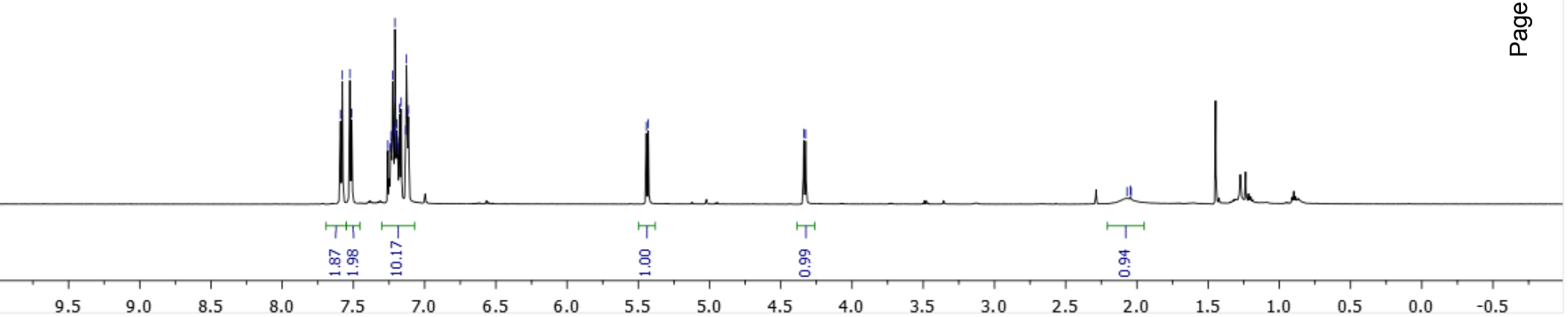

^{13}C NMR (CDCl$_3$, 126 MHz)
7
OH
Ph
Ph
Ph
142.23
141.54
140.89
128.94
128.75
128.59
128.22
128.03
127.55
126.95
126.88
126.36
77.27
77.02
76.82
76.76
65.84
60.32
15.28
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

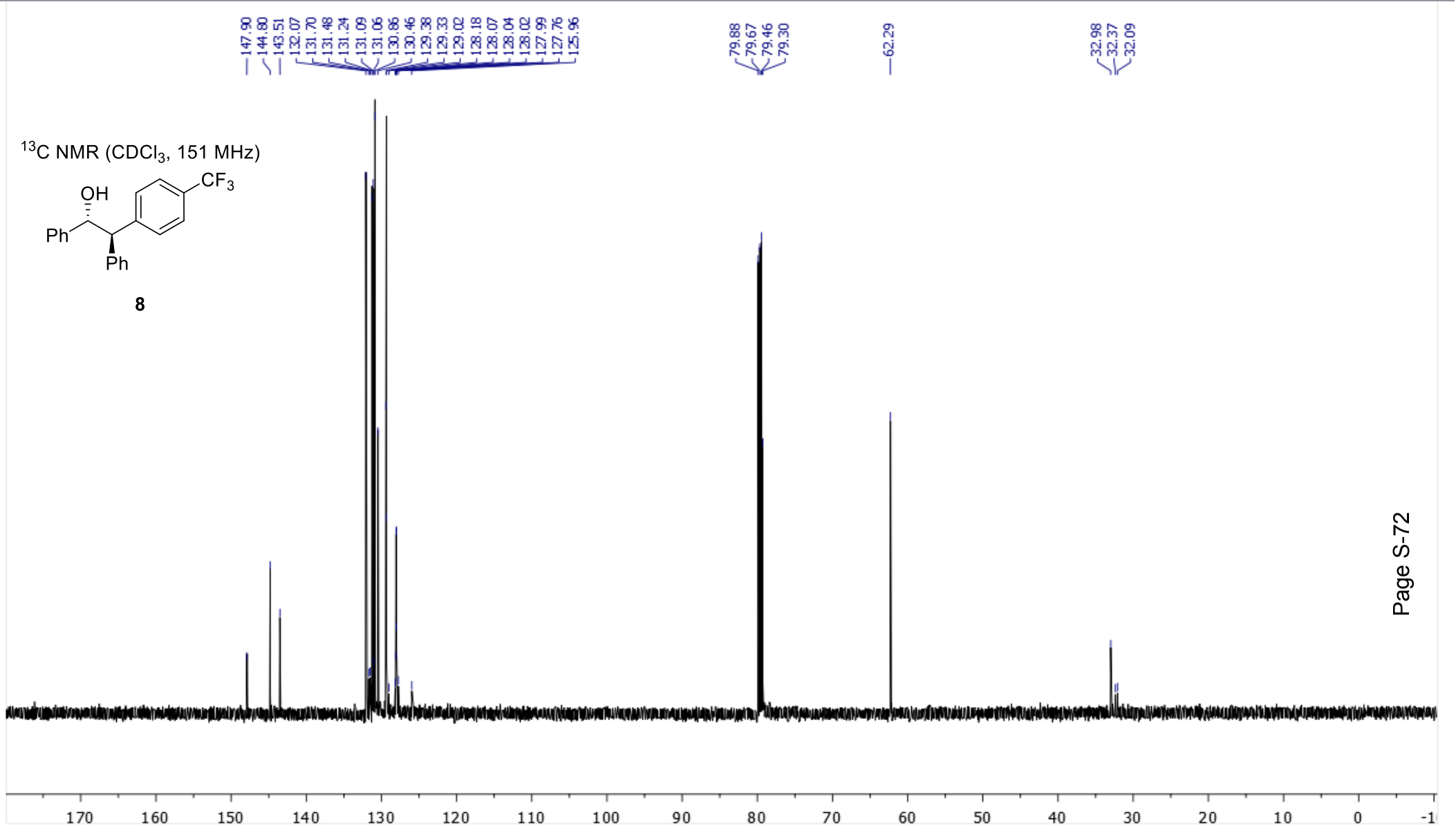


^{1}H NMR ($CDCl_3$, 600 MHz)

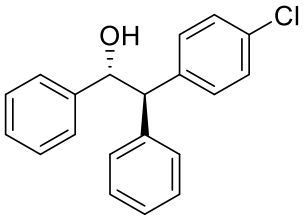


8

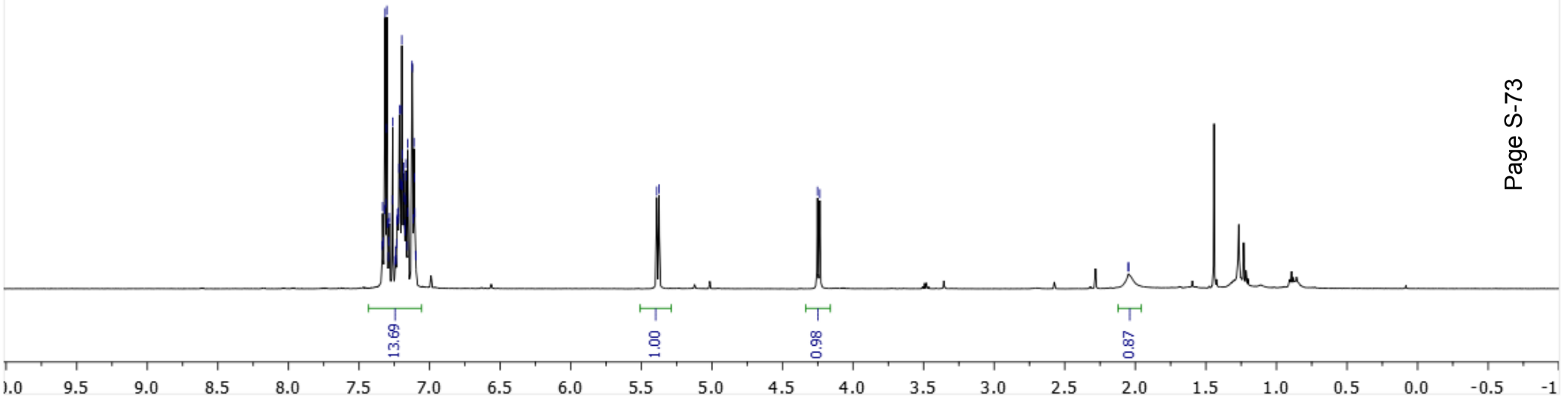



147.90
144.80
143.51
132.07
131.70
131.48
131.24
131.09
131.06
130.86
130.46
129.38
129.33
129.02
128.18
128.07
128.04
128.02
127.99
127.76
125.96
79.88
79.67
79.46
79.30
62.29
32.98
32.37
32.09
13C NMR (CDCl3, 151 MHz)
OH
CF3
Ph
Ph
8
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

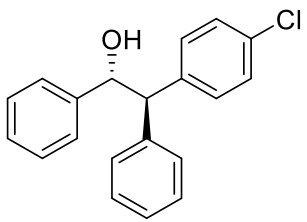
^{1}H NMR ($CDCl_3$, 500 MHz)



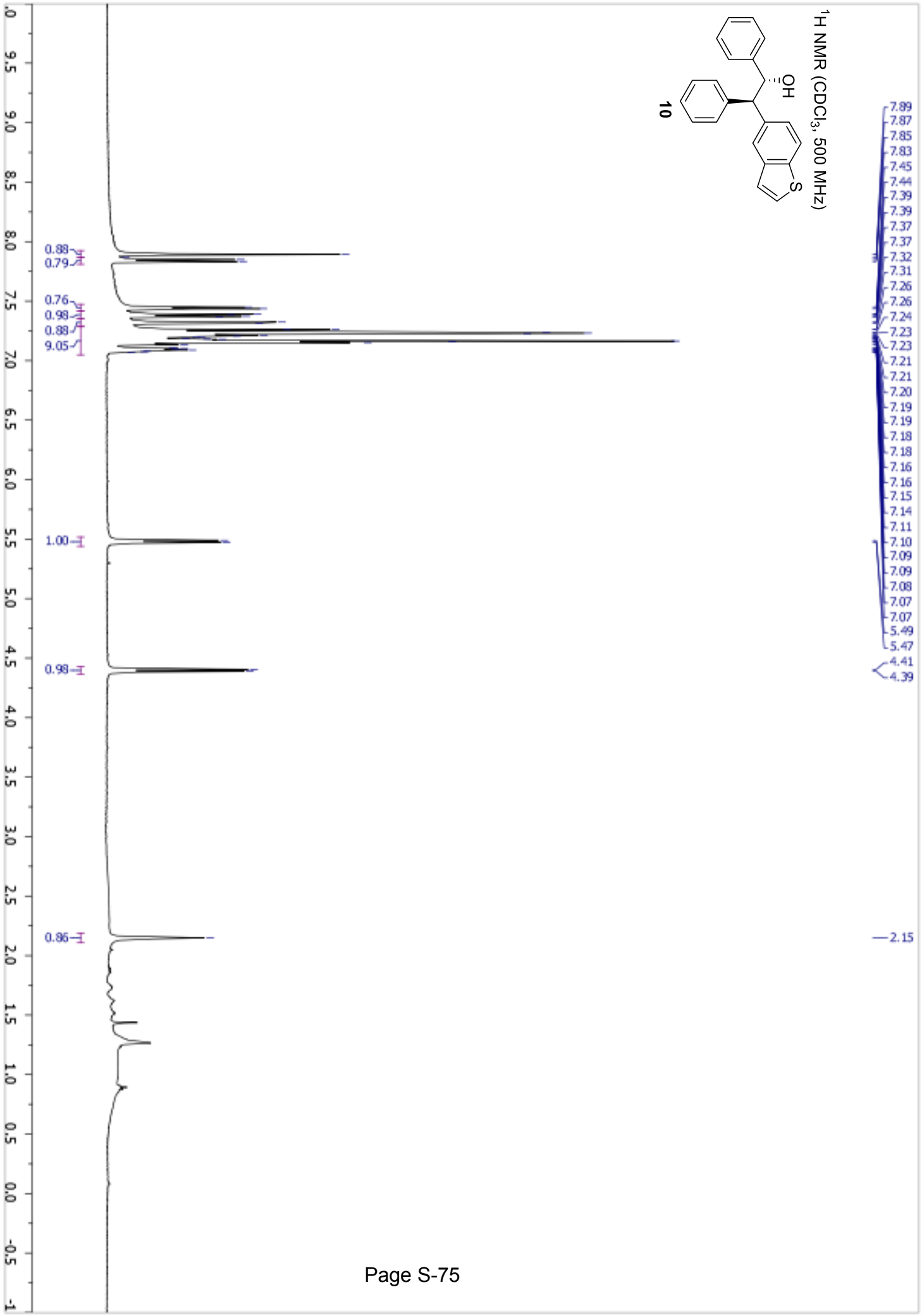
9

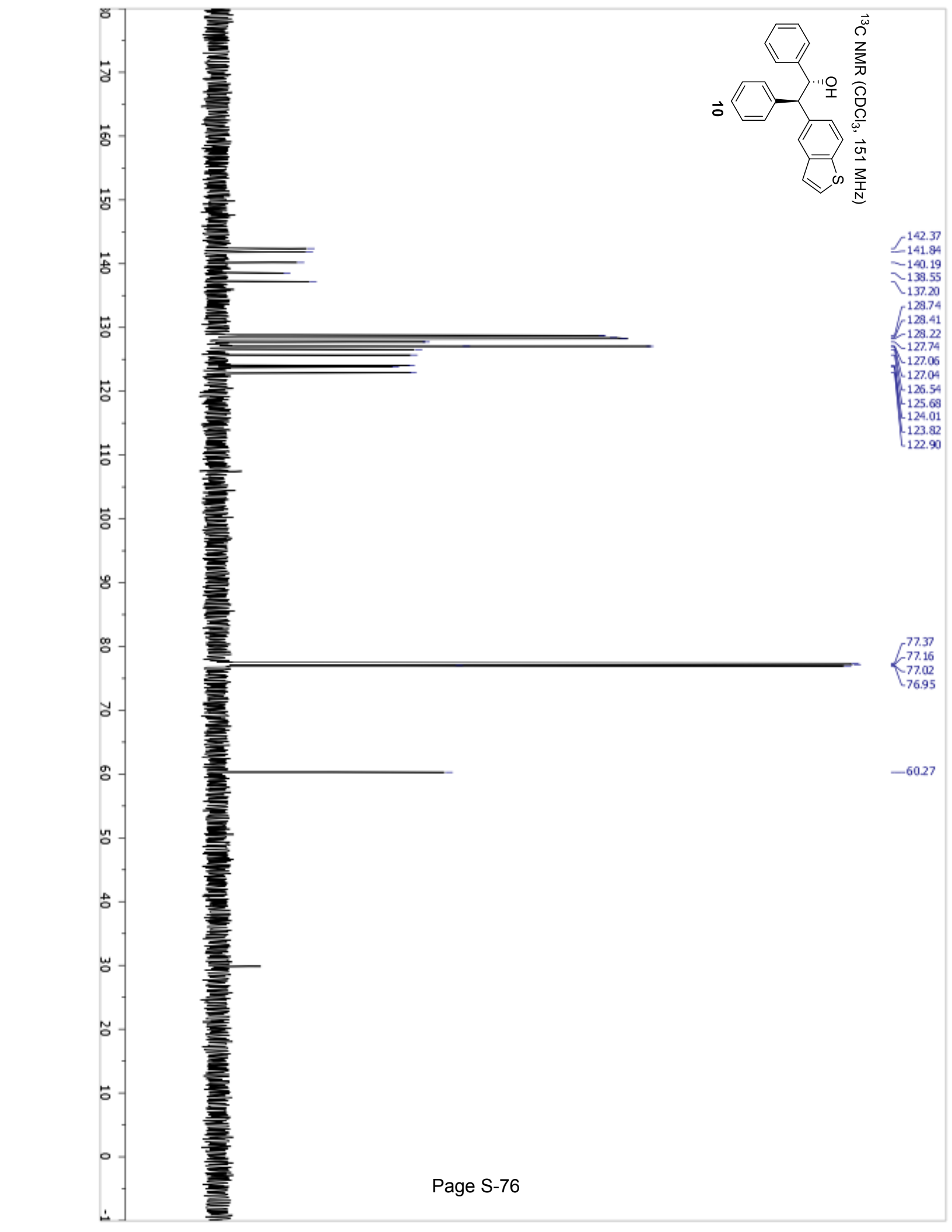


^{13}C NMR ($CDCl_3$, 151 MHz)

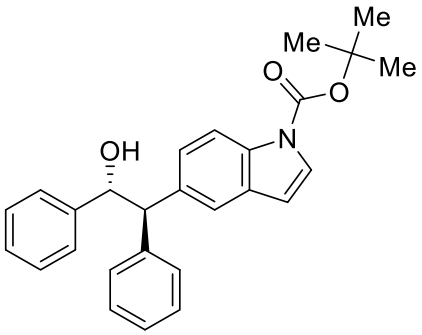


9

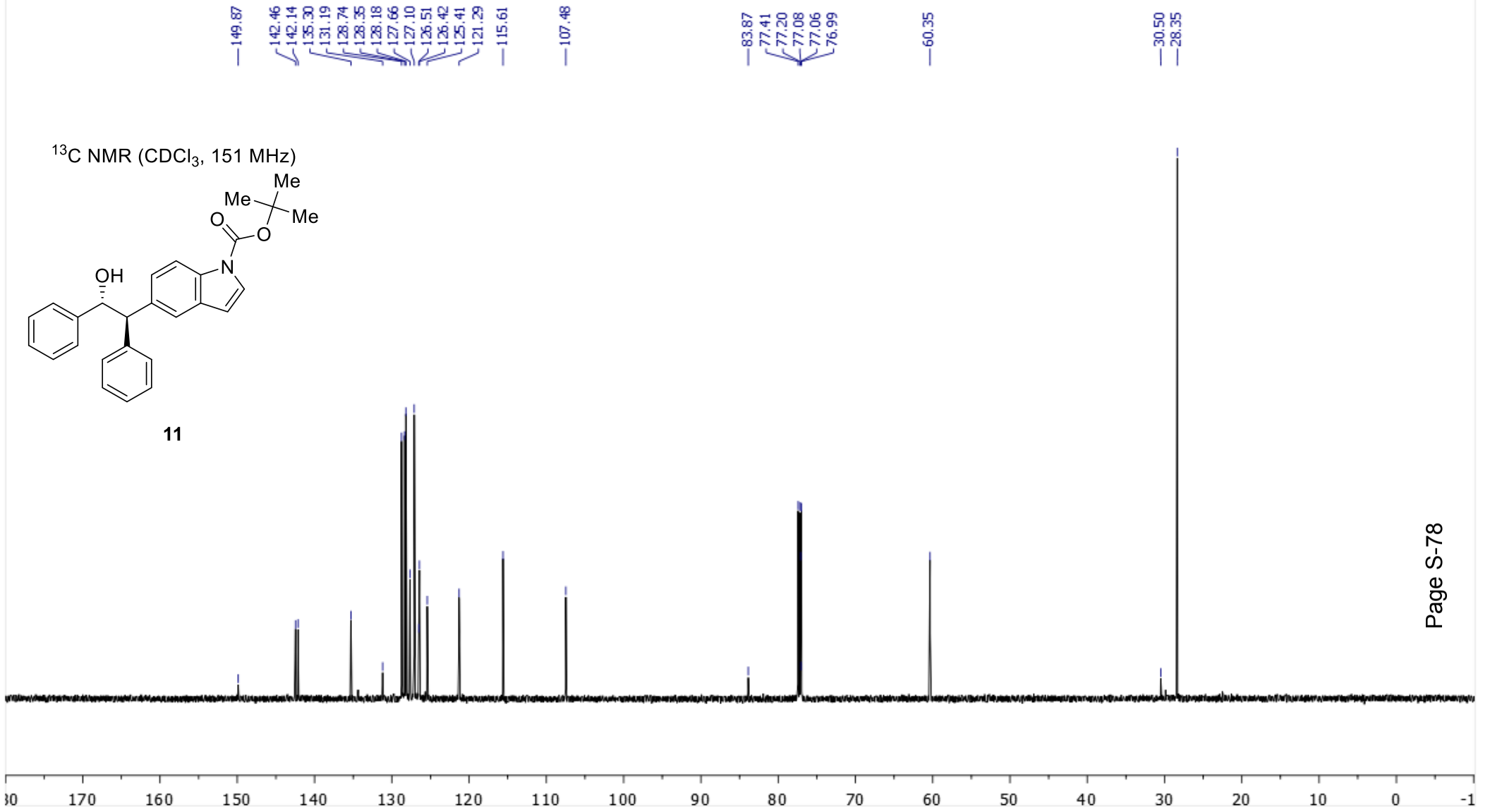

^{1}H NMR (CDCl$_3$, 500 MHz)
10
OH
S
0.88
0.79
0.76
0.98
0.88
9.05
1.00
0.98
0.86
7.89
7.87
7.85
7.83
7.45
7.44
7.39
7.39
7.37
7.37
7.32
7.31
7.26
7.26
7.24
7.23
7.23
7.21
7.21
7.20
7.19
7.19
7.18
7.18
7.16
7.16
7.15
7.14
7.11
7.10
7.09
7.09
7.08
7.07
7.07
5.49
5.47
4.41
4.39
2.15


^{13}C NMR (CDCl$_3$, 151 MHz)
10
OH
S
142.37
141.84
140.19
138.55
137.20
128.74
128.41
128.22
127.74
127.06
127.04
126.54
125.68
124.01
123.82
122.90
77.37
77.16
77.02
76.95
60.27

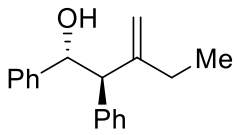
^{1}H NMR ($CDCl_3$, 600 MHz)



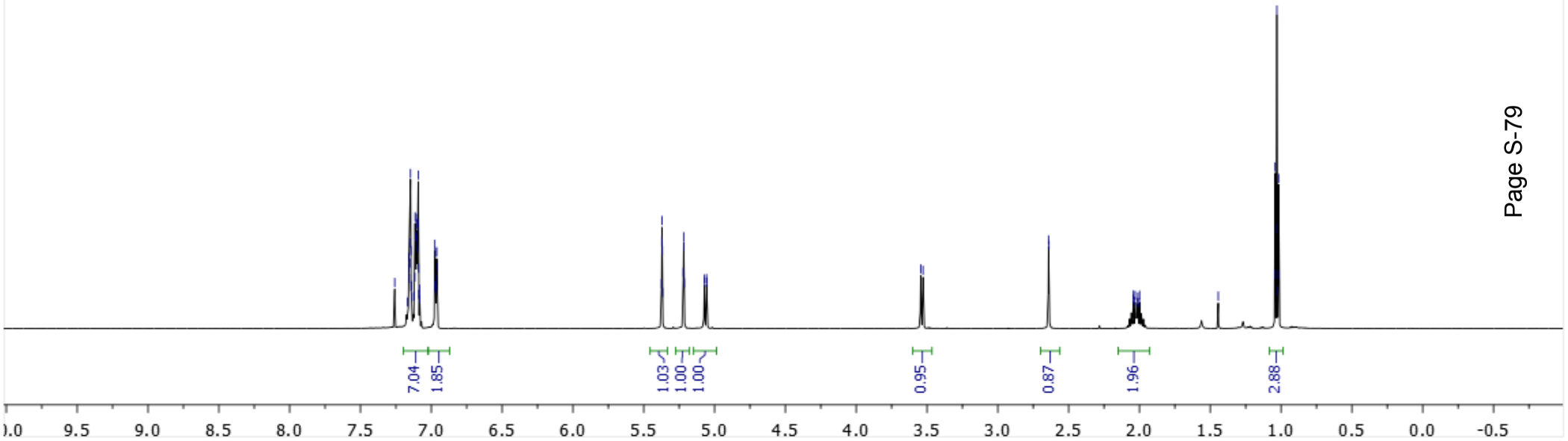
11

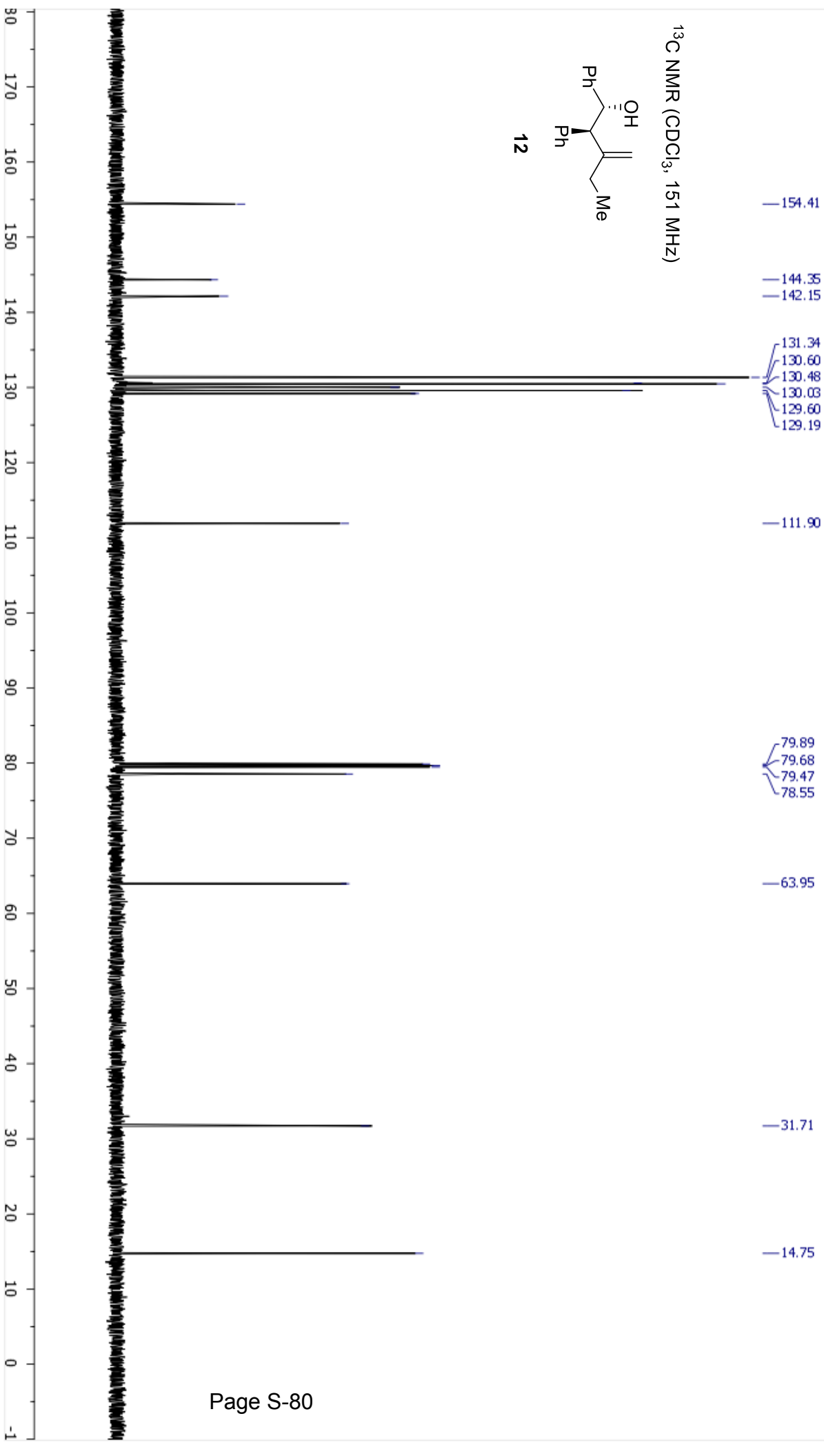

149.87
142.46
142.14
135.30
131.19
128.74
128.35
128.18
127.66
127.10
126.51
126.42
125.41
121.29
115.61
107.48
83.87
77.41
77.20
77.08
77.06
76.99
60.35
30.50
28.35
13C NMR (CDCl3, 151 MHz)
Me
Me
Me
O
O
N
OH
11
Page S-78
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{1}H NMR ($CDCl_3$, 600 MHz)

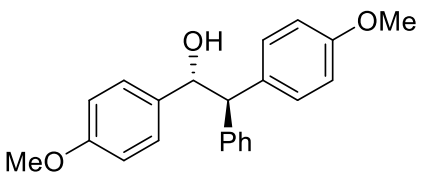


12

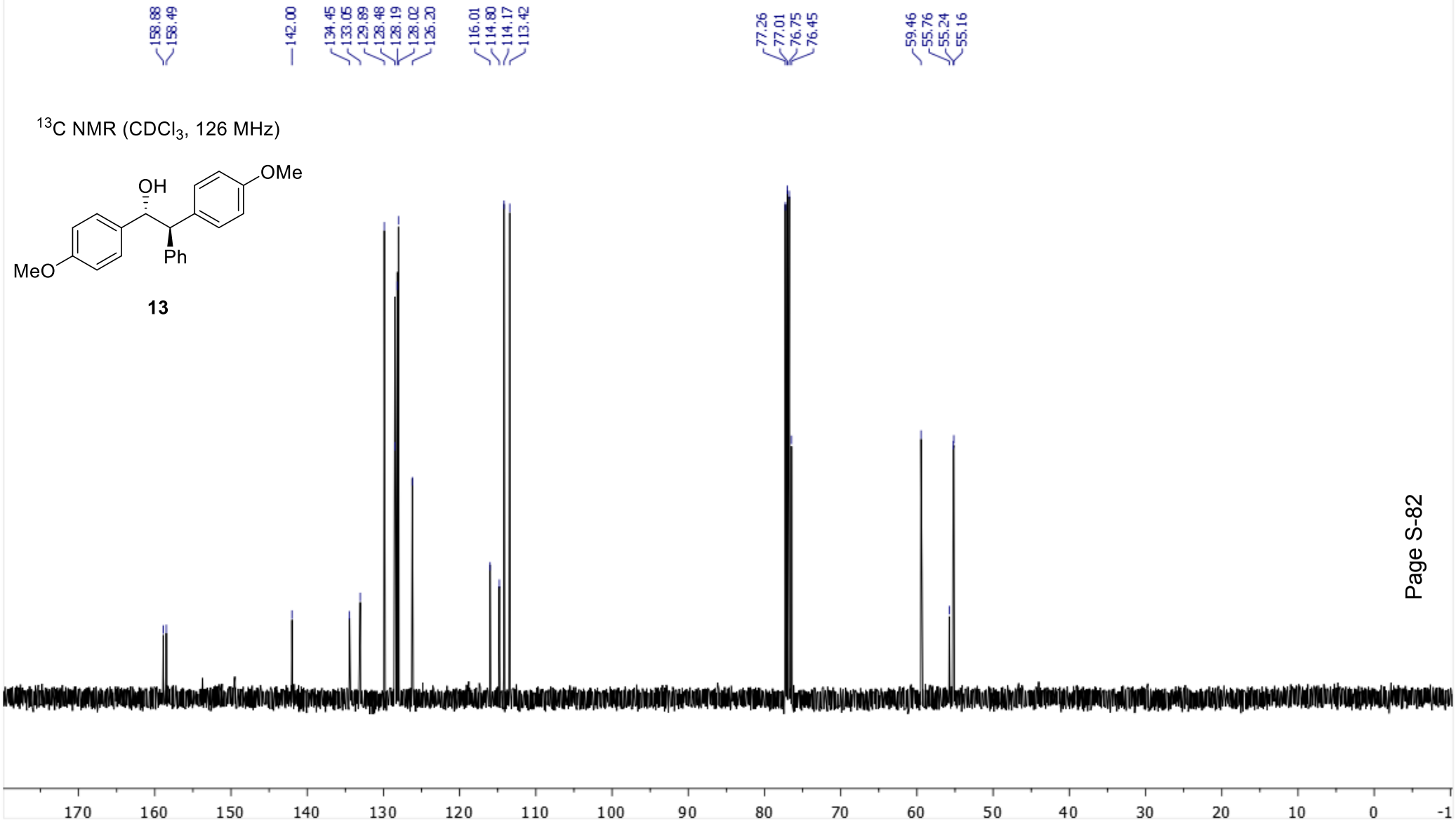



^{13}C NMR (CDCl$_3$, 151 MHz)
OH
Ph
Ph
Me
12
154.41
144.35
142.15
131.34
130.60
130.48
130.03
129.60
129.19
111.90
79.89
79.68
79.47
78.55
63.95
31.71
14.75

^{1}H NMR ($CDCl_3$, 500 MHz)

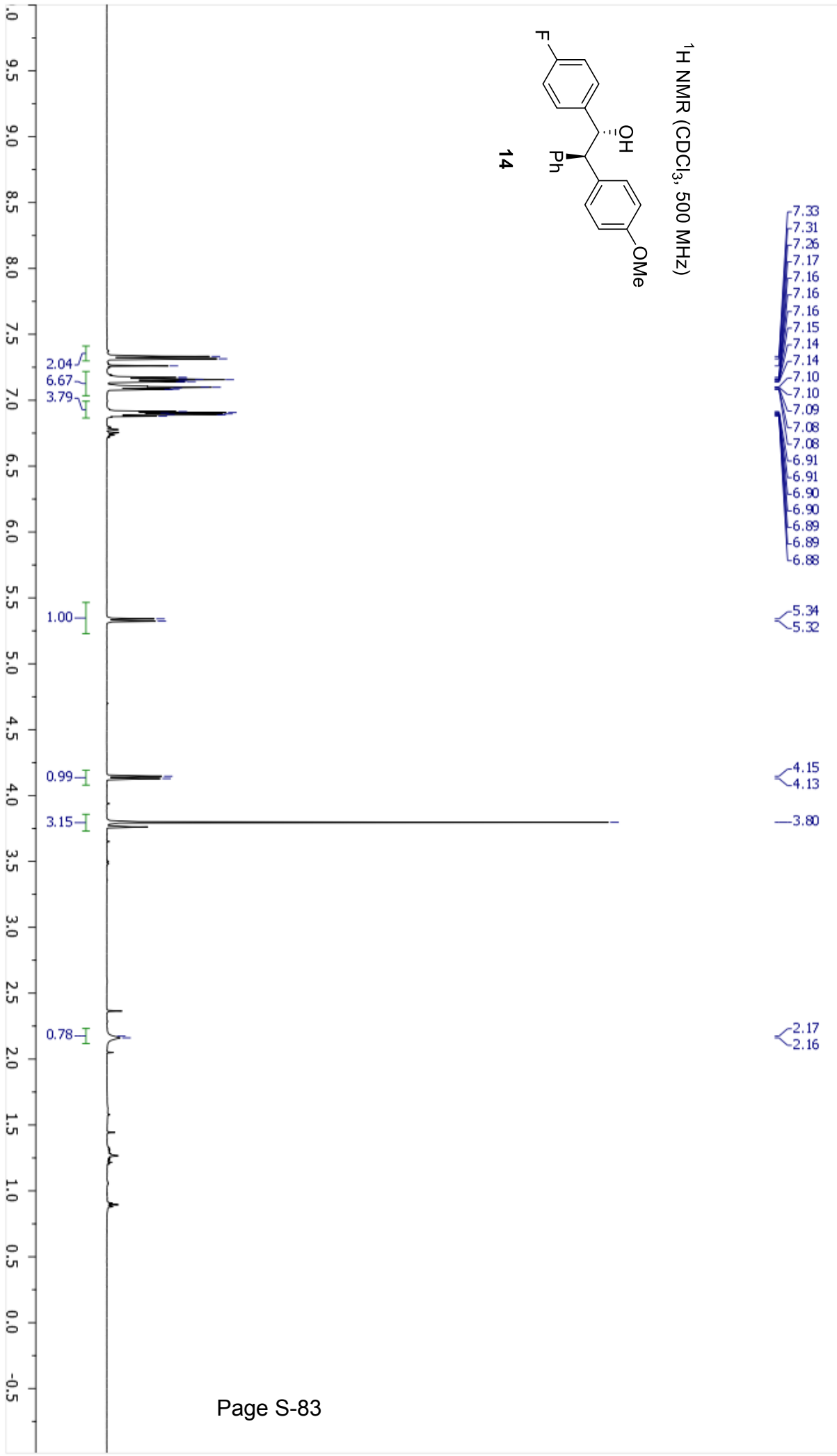


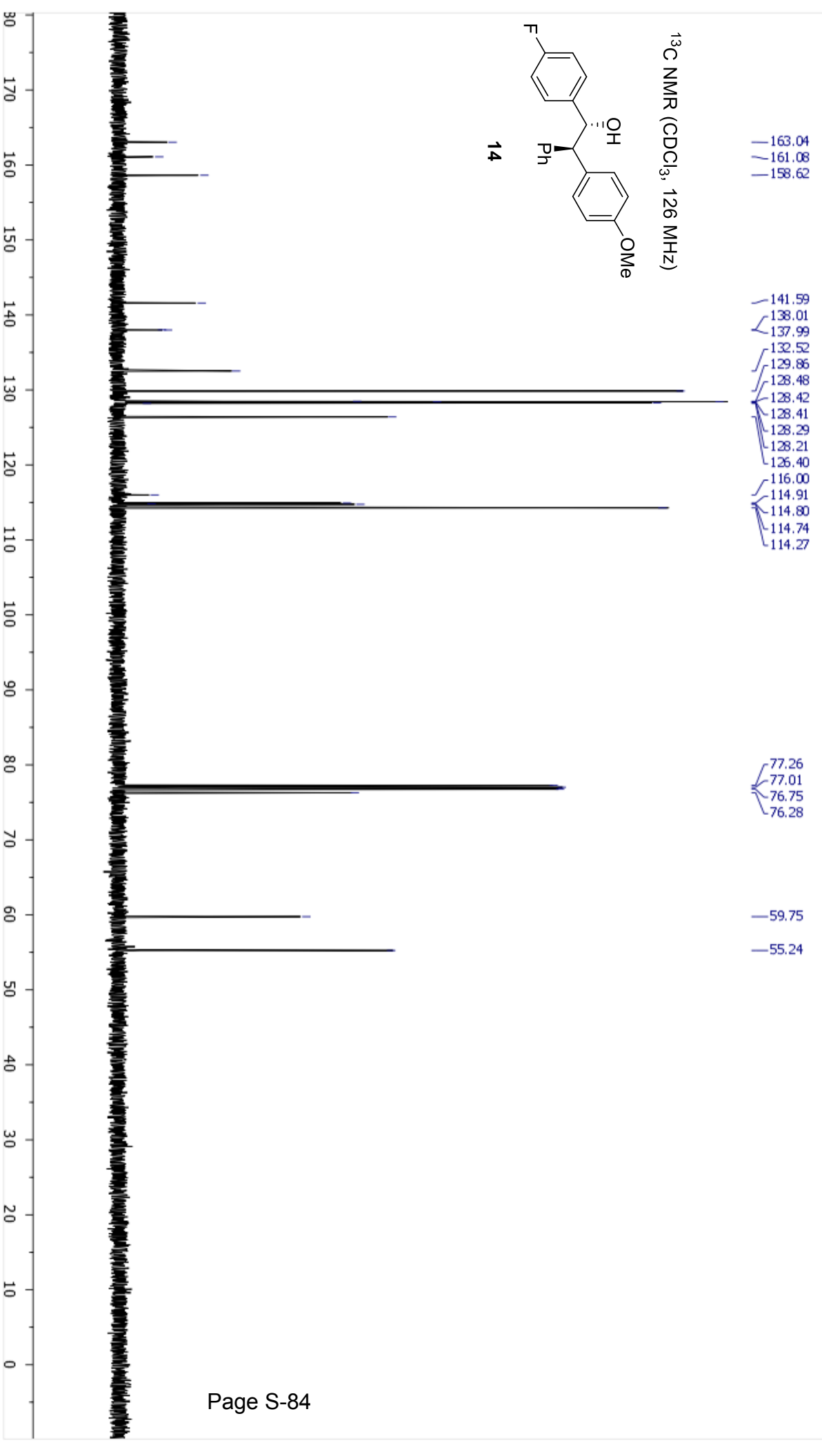
13



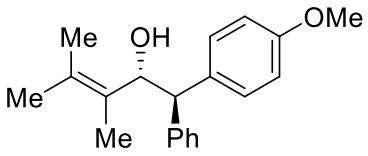
^{13}C NMR ($CDCl_3$, 126 MHz)

13

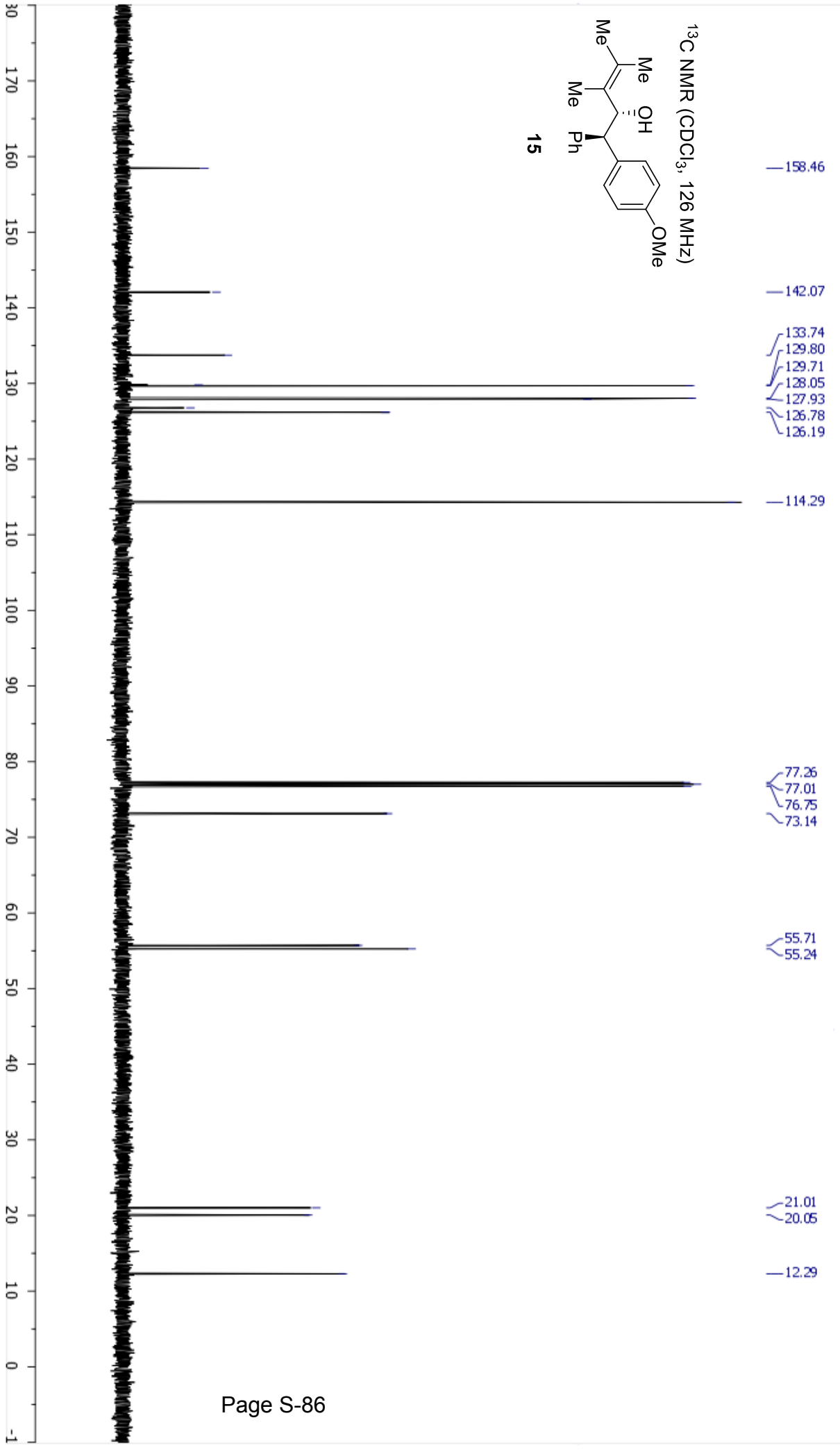

^{1}H NMR ($CDCl_3$, 500 MHz)
14
F
OH
Ph
OMe
7.33
7.31
7.26
7.17
7.16
7.16
7.16
7.16
7.15
7.14
7.14
7.10
7.10
7.09
7.08
7.08
6.91
6.91
6.90
6.90
6.89
6.89
6.88
5.34
5.32
4.15
4.13
3.80
2.17
2.16
2.04
6.67
3.79
1.00
0.99
3.15
0.78

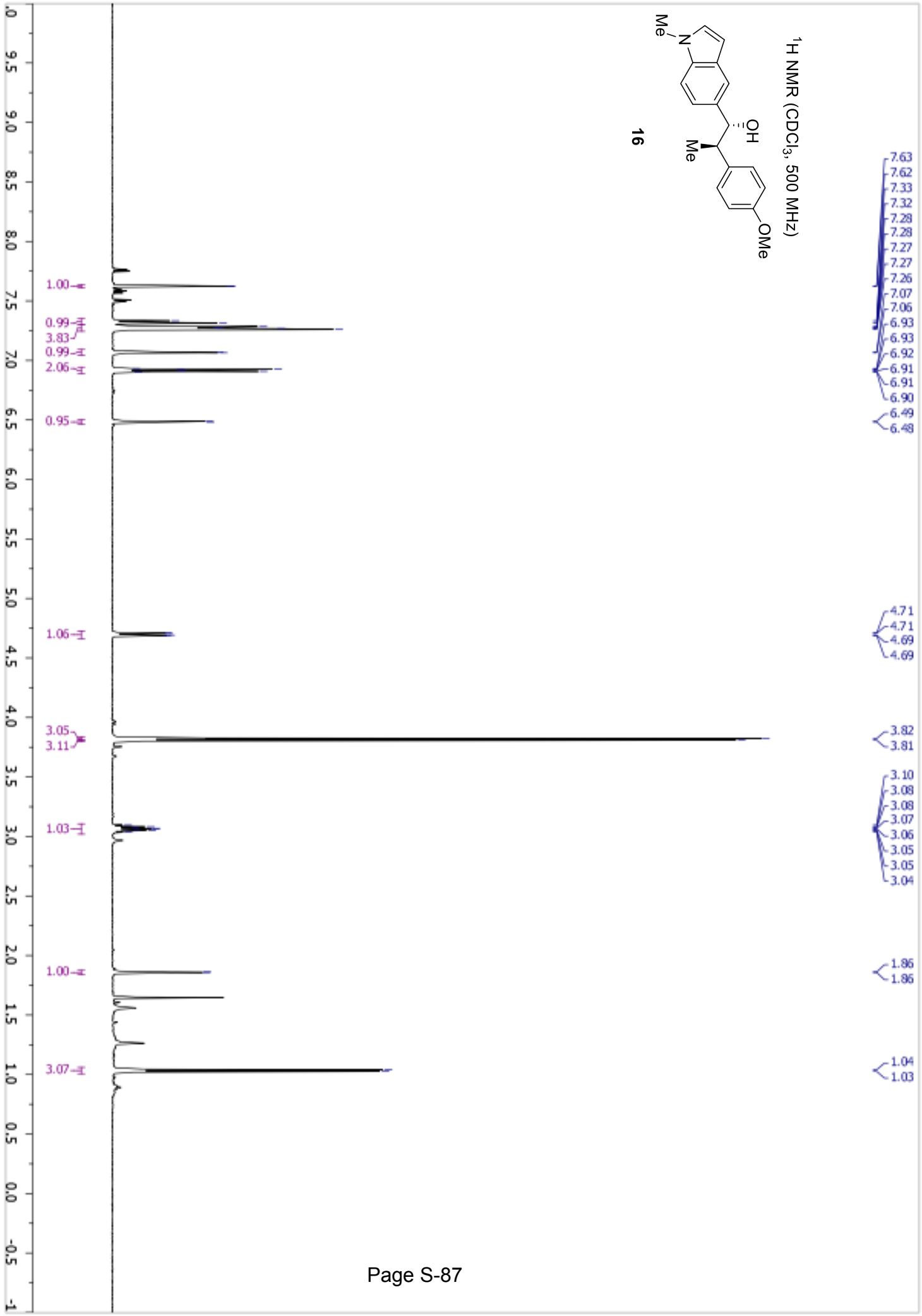

^{13}C NMR (CDCl$_3$, 126 MHz)
F
OH
Ph
OMe
14
163.04
161.08
158.62
141.59
138.01
137.99
132.52
129.86
128.48
128.42
128.41
128.29
128.21
126.40
116.00
114.91
114.80
114.74
114.27
77.26
77.01
76.75
76.28
59.75
55.24

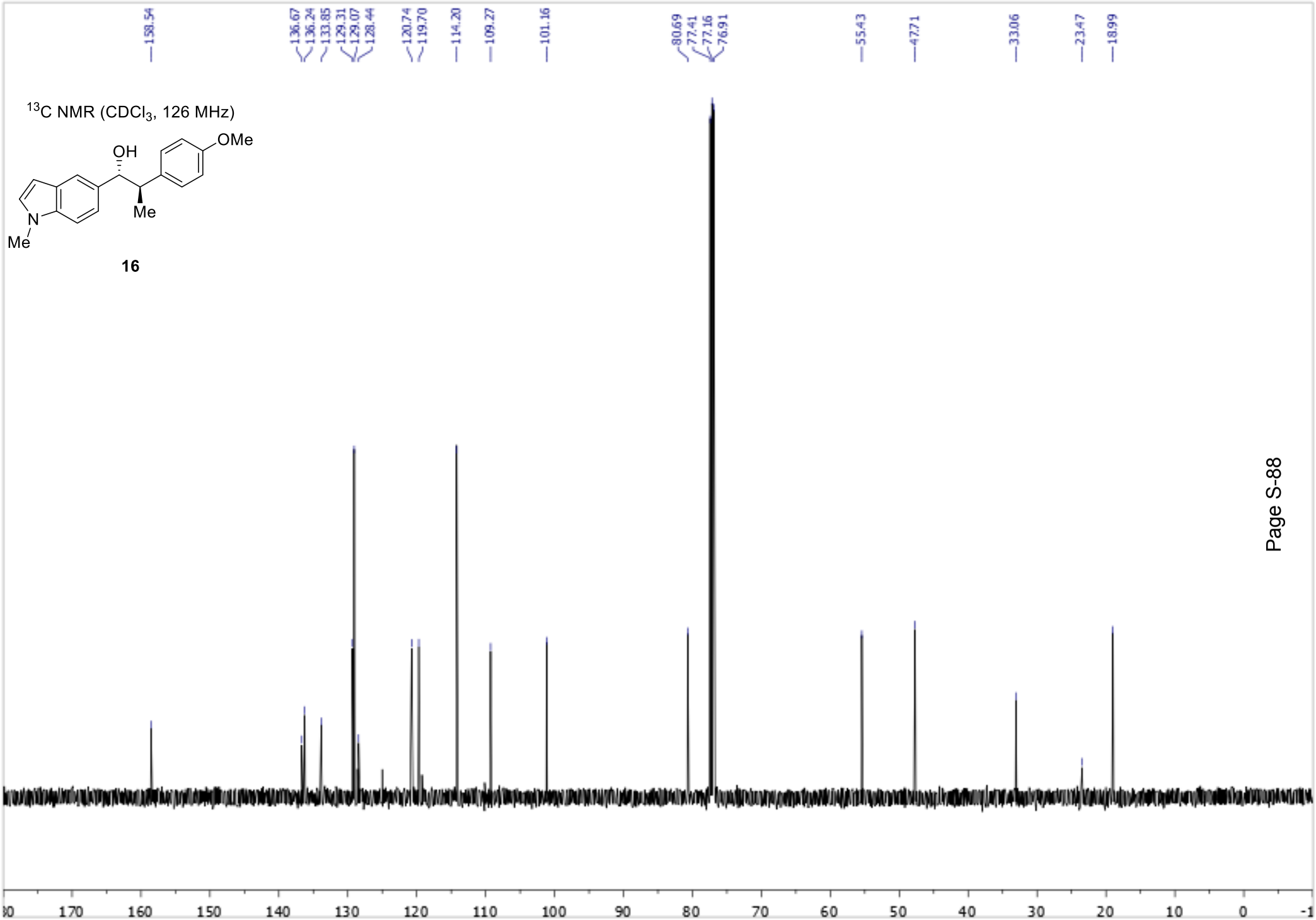
^{1}H NMR ($CDCl_3$, 500 MHz)



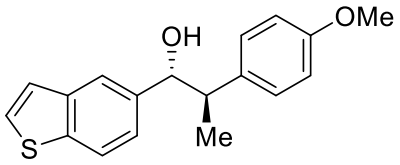
15


^{13}C NMR (CDCl$_3$, 126 MHz)
Me
Me
OH
Me
Ph
OMe
15
158.46
142.07
133.74
129.80
129.71
128.05
127.93
126.78
126.19
114.29
77.26
77.01
76.75
73.14
55.71
55.24
21.01
20.05
12.29
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

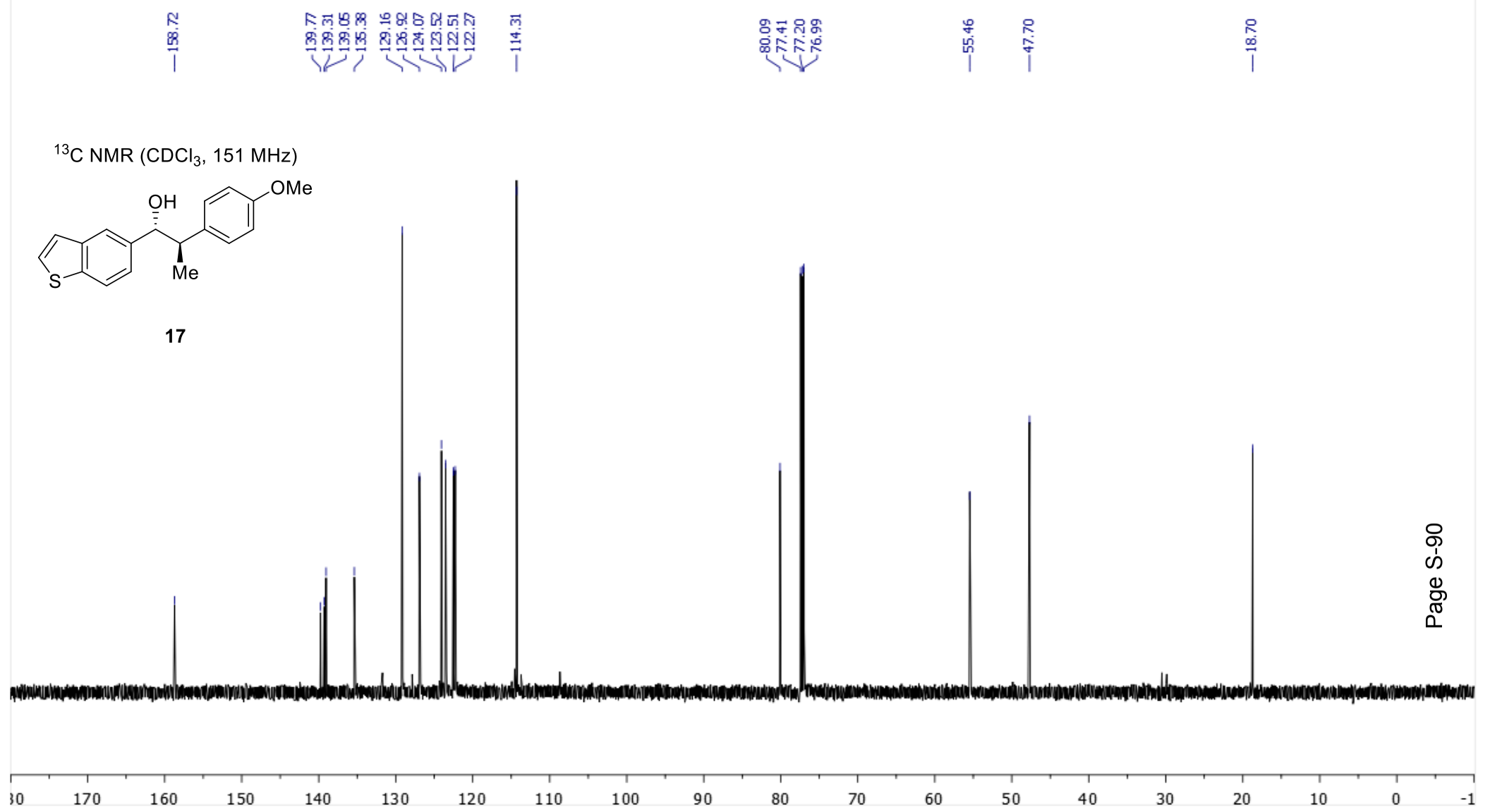

^{1}H NMR (CDCl$_3$, 500 MHz)
16
Me
N
OH
Me
OMe
1.00
0.99
3.83
0.99
2.06
0.95
1.06
3.05
3.11
1.03
1.00
3.07
7.63
7.62
7.33
7.32
7.28
7.28
7.27
7.27
7.26
7.07
7.06
6.93
6.93
6.92
6.91
6.91
6.90
6.49
6.48
4.71
4.71
4.69
4.69
3.82
3.81
3.10
3.08
3.08
3.07
3.06
3.05
3.05
3.04
1.86
1.86
1.04
1.03


158.54
136.67
136.24
133.85
129.31
129.07
128.44
120.74
119.70
114.20
109.27
101.16
80.69
77.41
77.16
76.91
55.43
47.71
33.06
23.47
18.99
^{13}C NMR ($CDCl_3$, 126 MHz)
OH
OMe
Me
N
Me
16
Page S-88
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

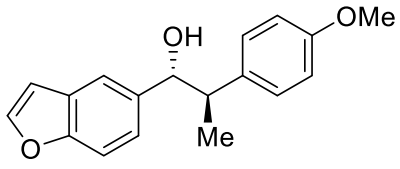
^{1}H NMR ($CDCl_3$, 500 MHz)



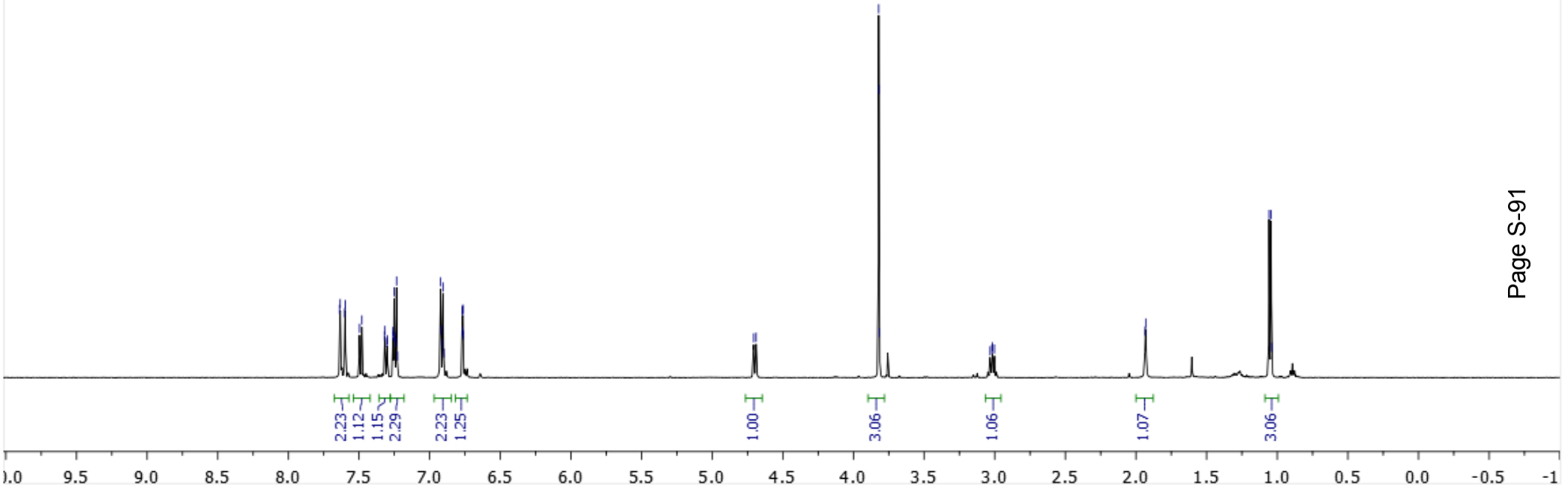
17

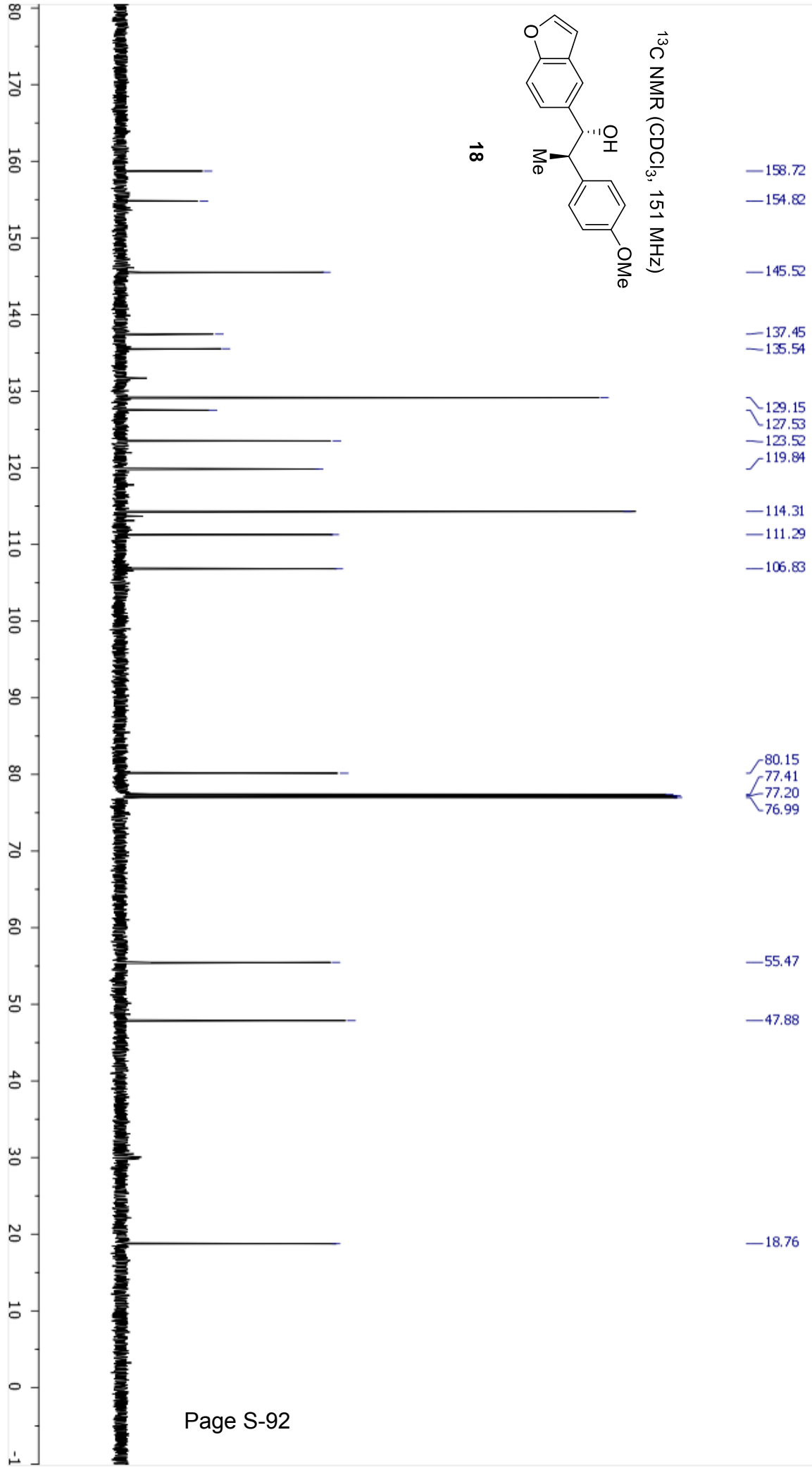

158.72
139.77
139.31
139.05
135.38
129.16
126.92
124.07
123.52
122.51
122.27
114.31
80.09
77.41
77.20
76.99
55.46
47.70
18.70
13C NMR (CDCl3, 151 MHz)
OH
OMe
Me
S
17
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

^{1}H NMR ($CDCl_3$, 500 MHz)

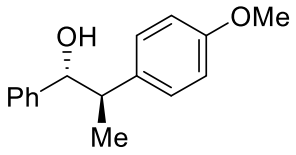


18

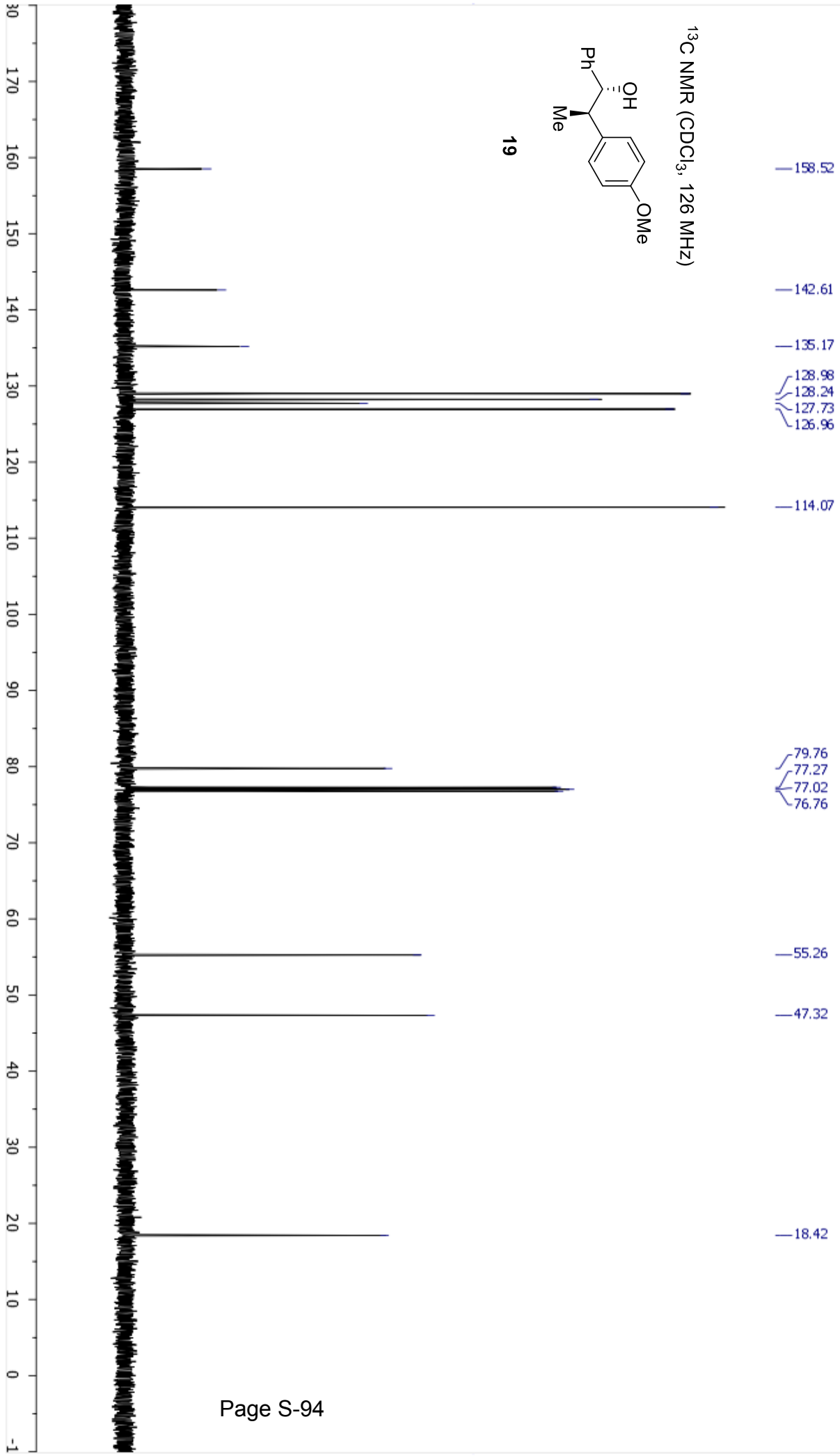



^{13}C NMR (CDCl$_3$, 151 MHz)
18
OH
Me
OMe
158.72
154.82
145.52
137.45
135.54
129.15
127.53
123.52
119.84
114.31
111.29
106.83
80.15
77.41
77.20
76.99
55.47
47.88
18.76

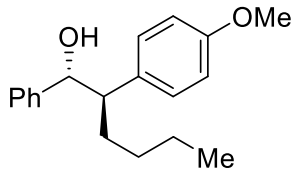
^{1}H NMR ($CDCl_3$, 500 MHz)



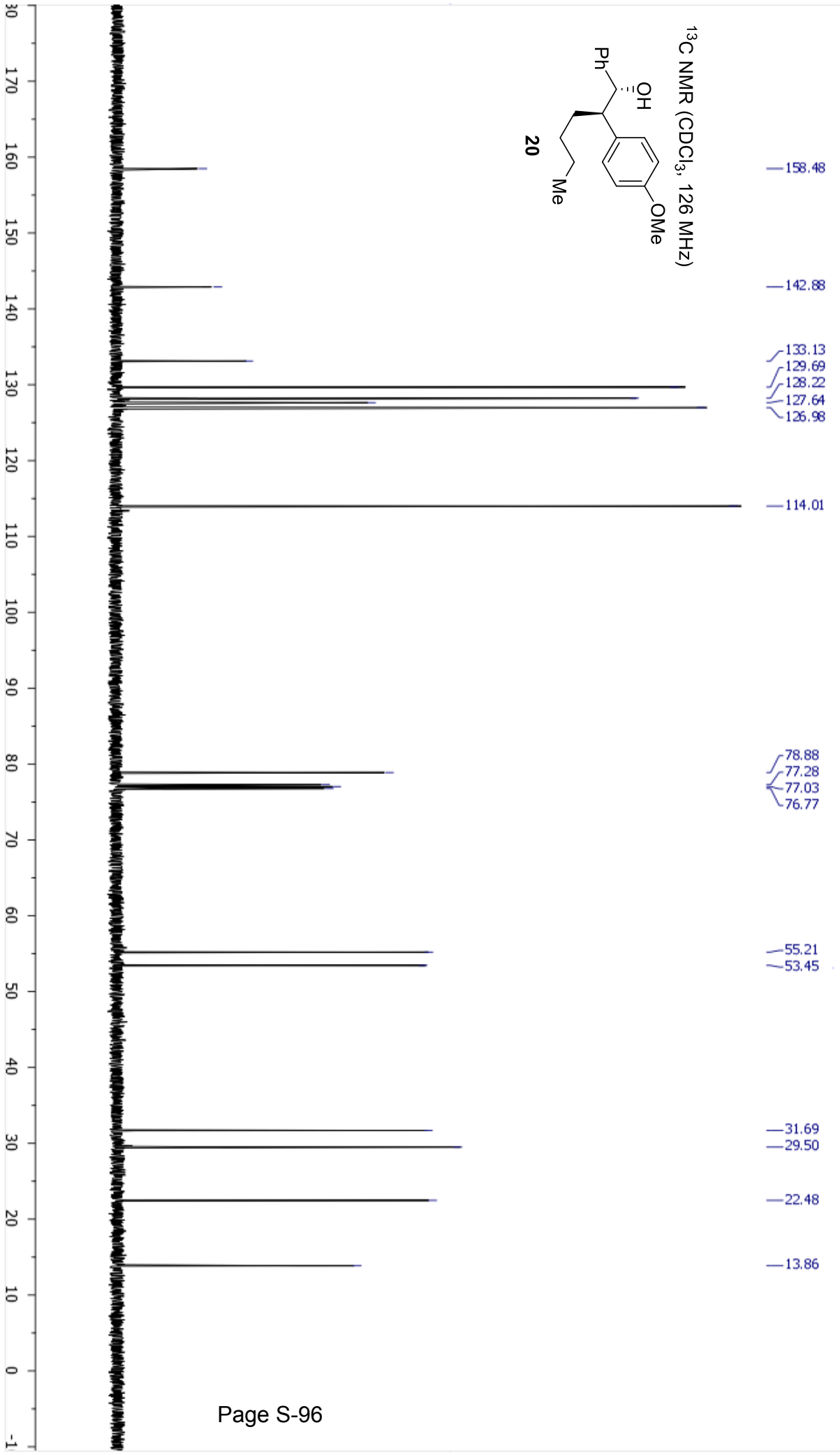
19


^{13}C NMR (CDCl$_3$, 126 MHz)
19
Ph
OH
Me
OMe
158.52
142.61
135.17
128.98
128.24
127.73
126.96
114.07
79.76
77.27
77.02
76.76
55.26
47.32
18.42
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

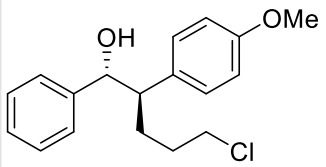
^{1}H NMR ($CDCl_3$, 500 MHz)



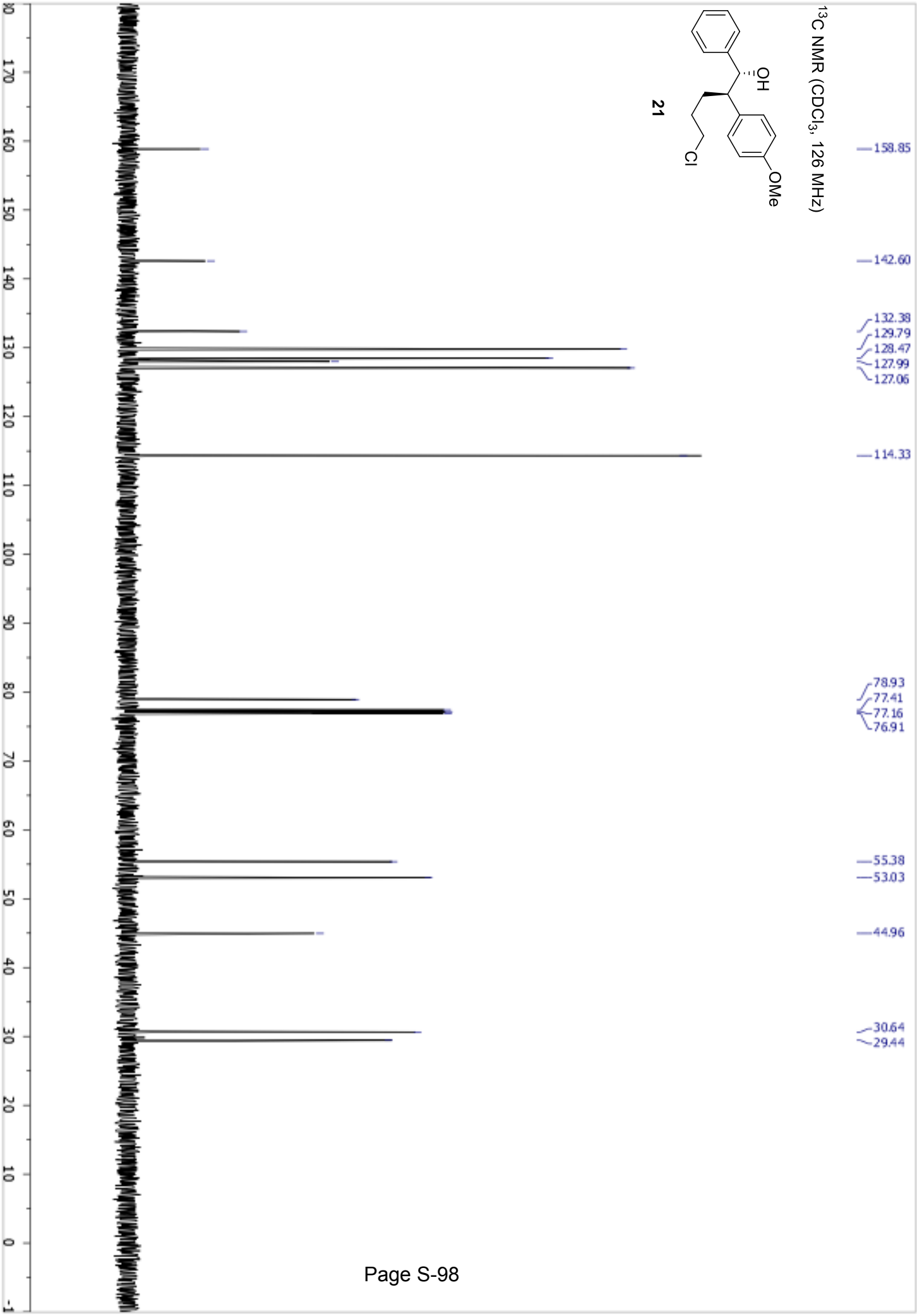
20


^{13}C NMR (CDCl$_3$, 126 MHz)
Ph
OH
Me
OMe
20
158.48
142.88
133.13
129.69
128.22
127.64
126.98
114.01
78.88
77.28
77.03
76.77
55.21
53.45
31.69
29.50
22.48
13.86

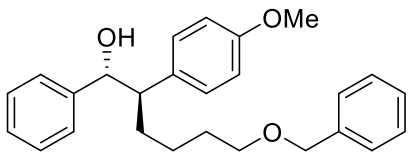
^{1}H NMR ($CDCl_3$, 500 MHz)



21

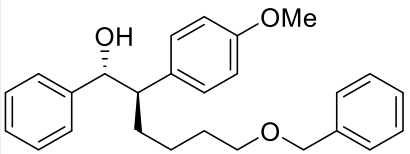

^{13}C NMR (CDCl$_3$, 126 MHz)
OH
Cl
OMe
21
158.85
142.60
132.38
129.79
128.47
127.99
127.06
114.33
78.93
77.41
77.16
76.91
55.38
53.03
44.96
30.64
29.44

^{1}H NMR ($CDCl_3$, 600 MHz)



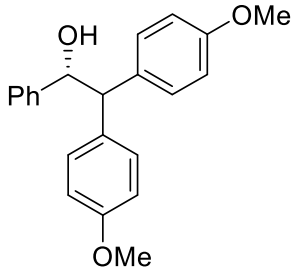
22

^{13}C NMR ($CDCl_3$, 151 MHz)

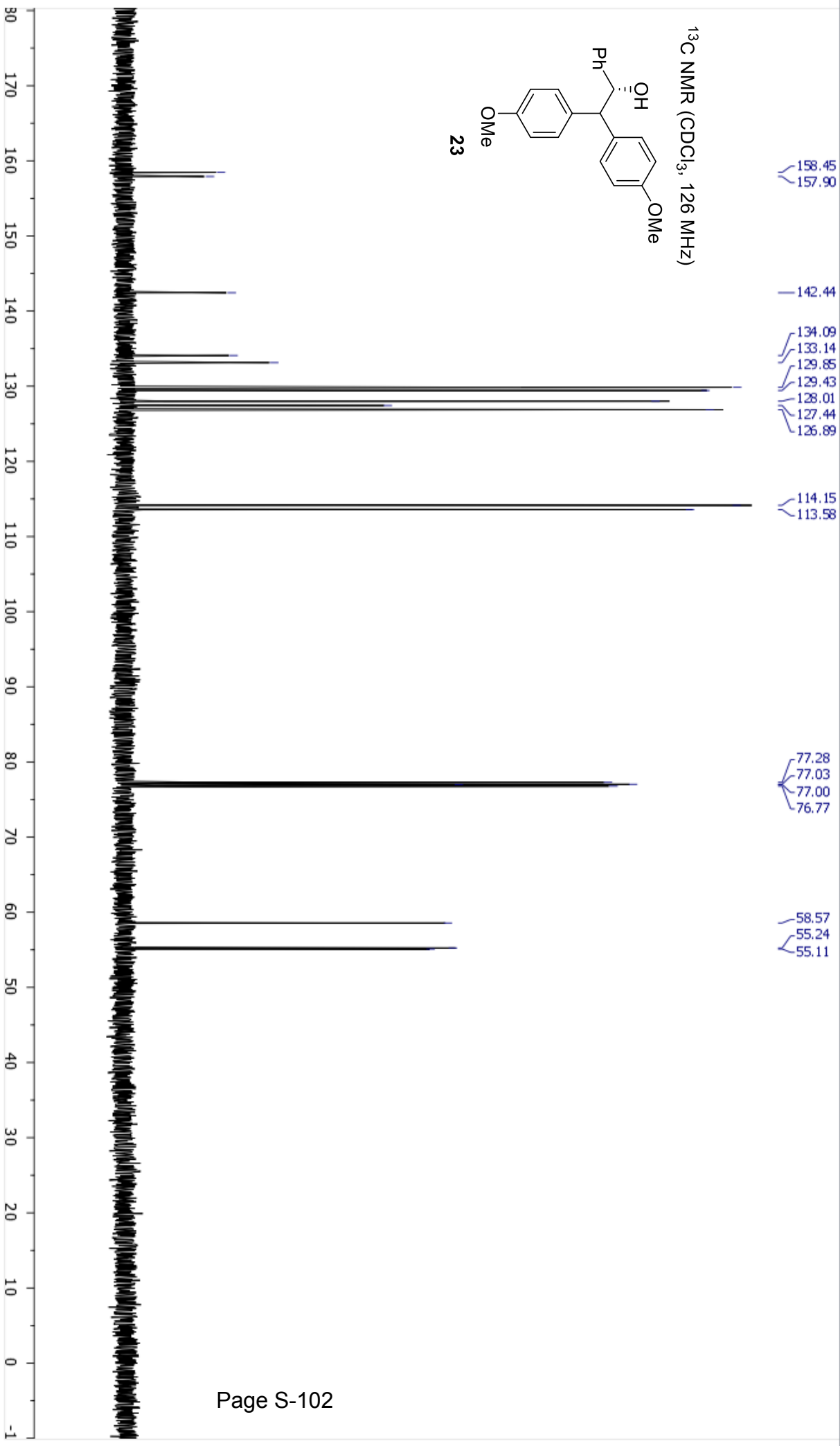


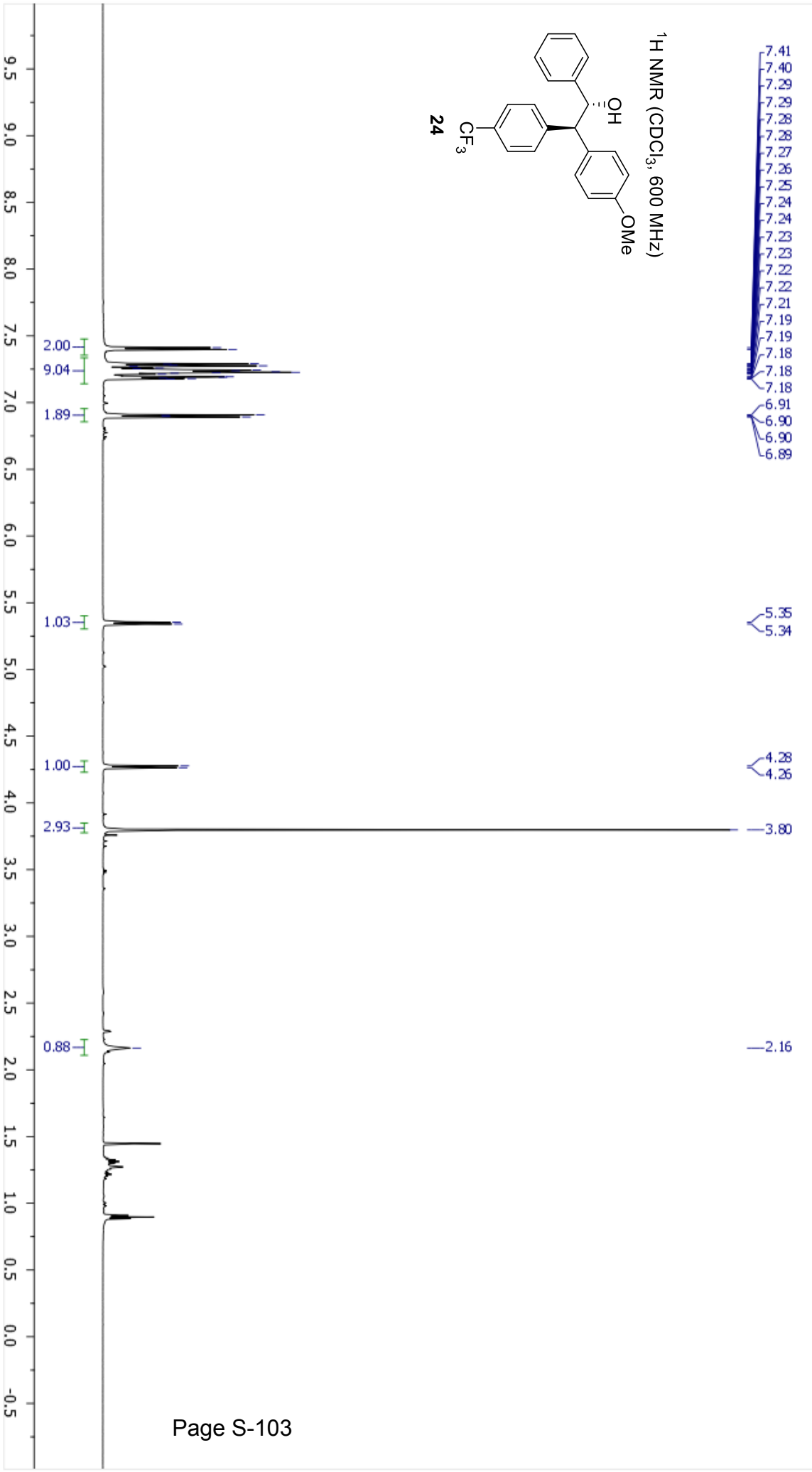
22

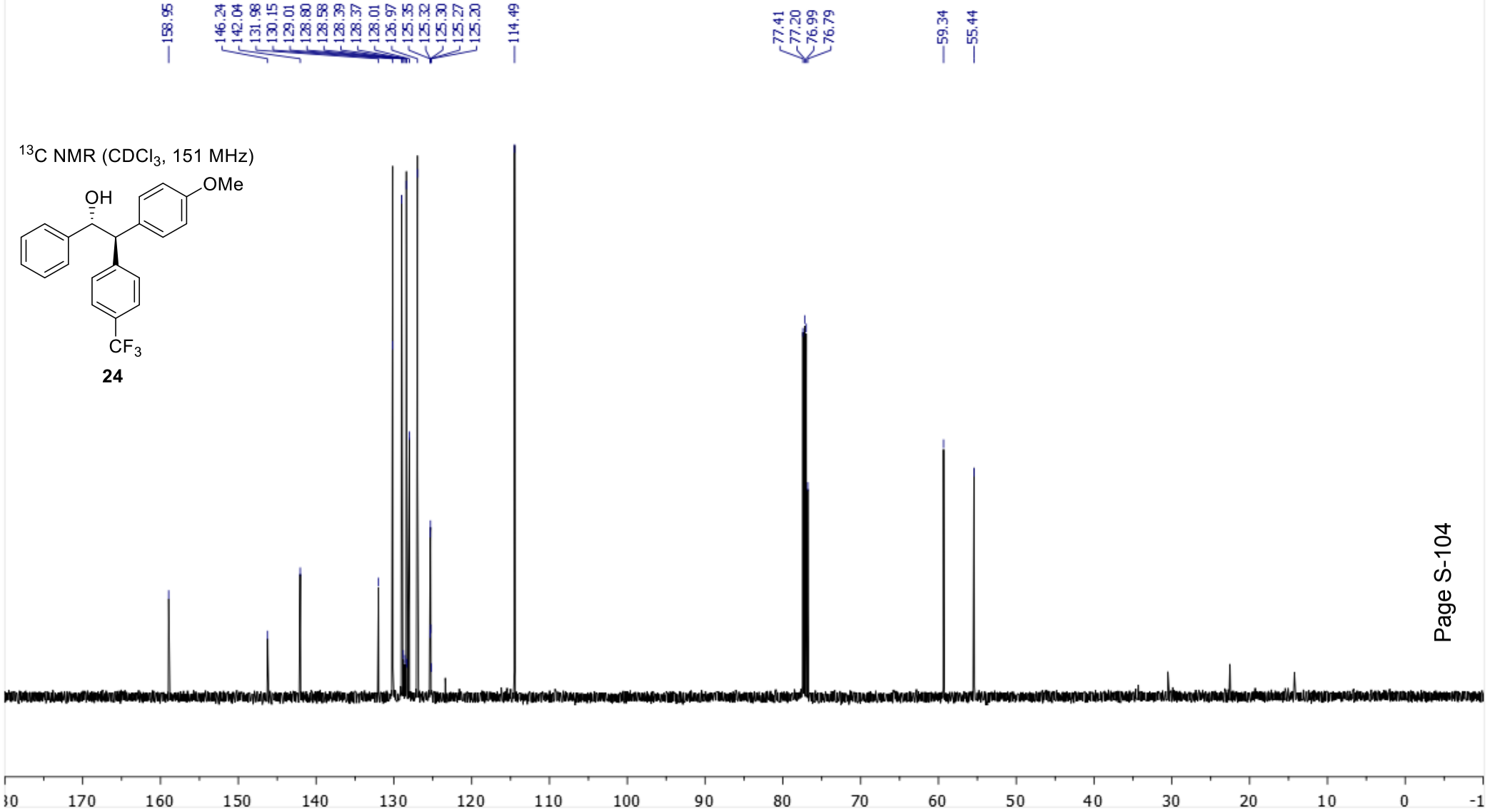
^{1}H NMR ($CDCl_3$, 500 MHz)

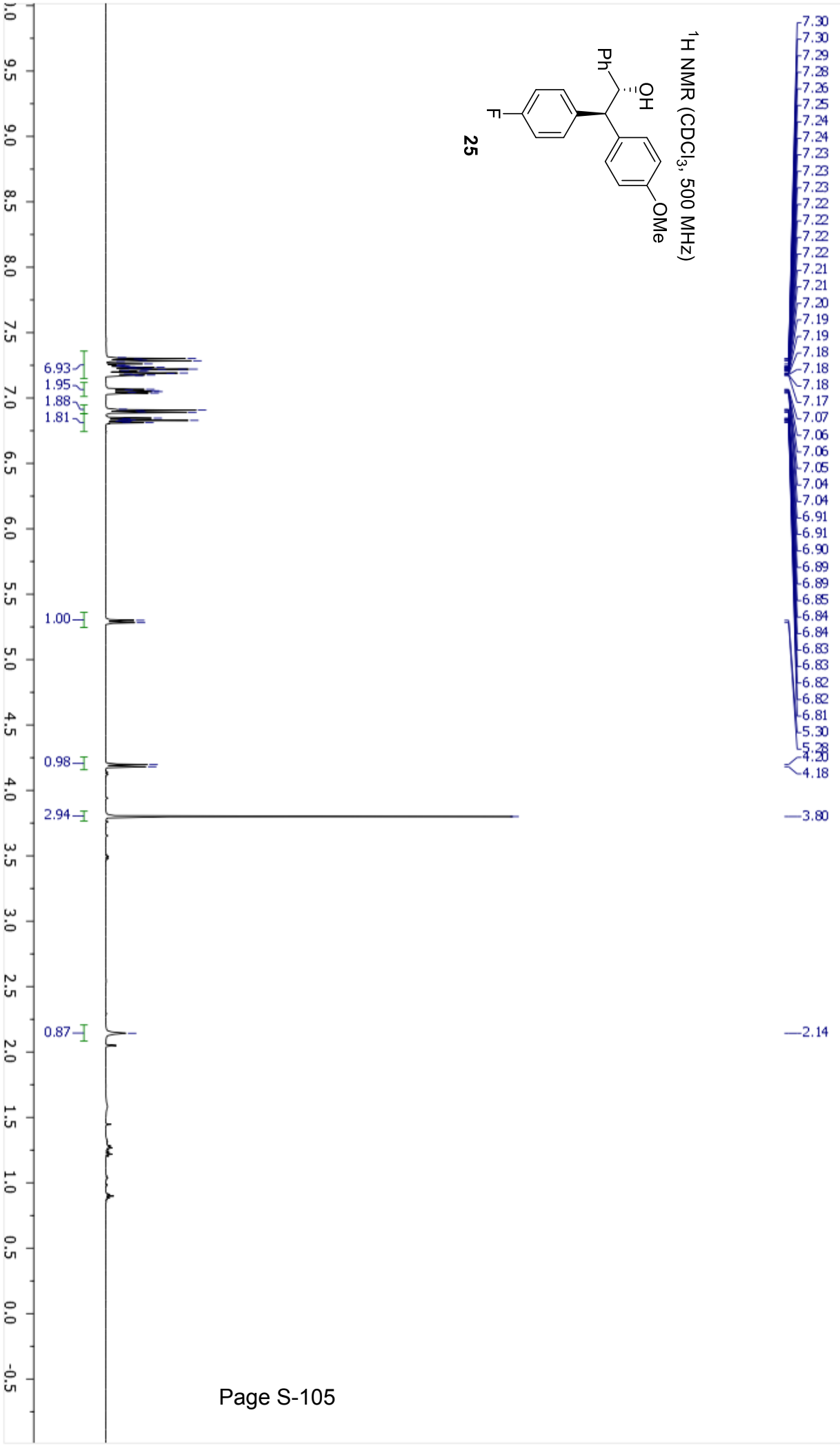


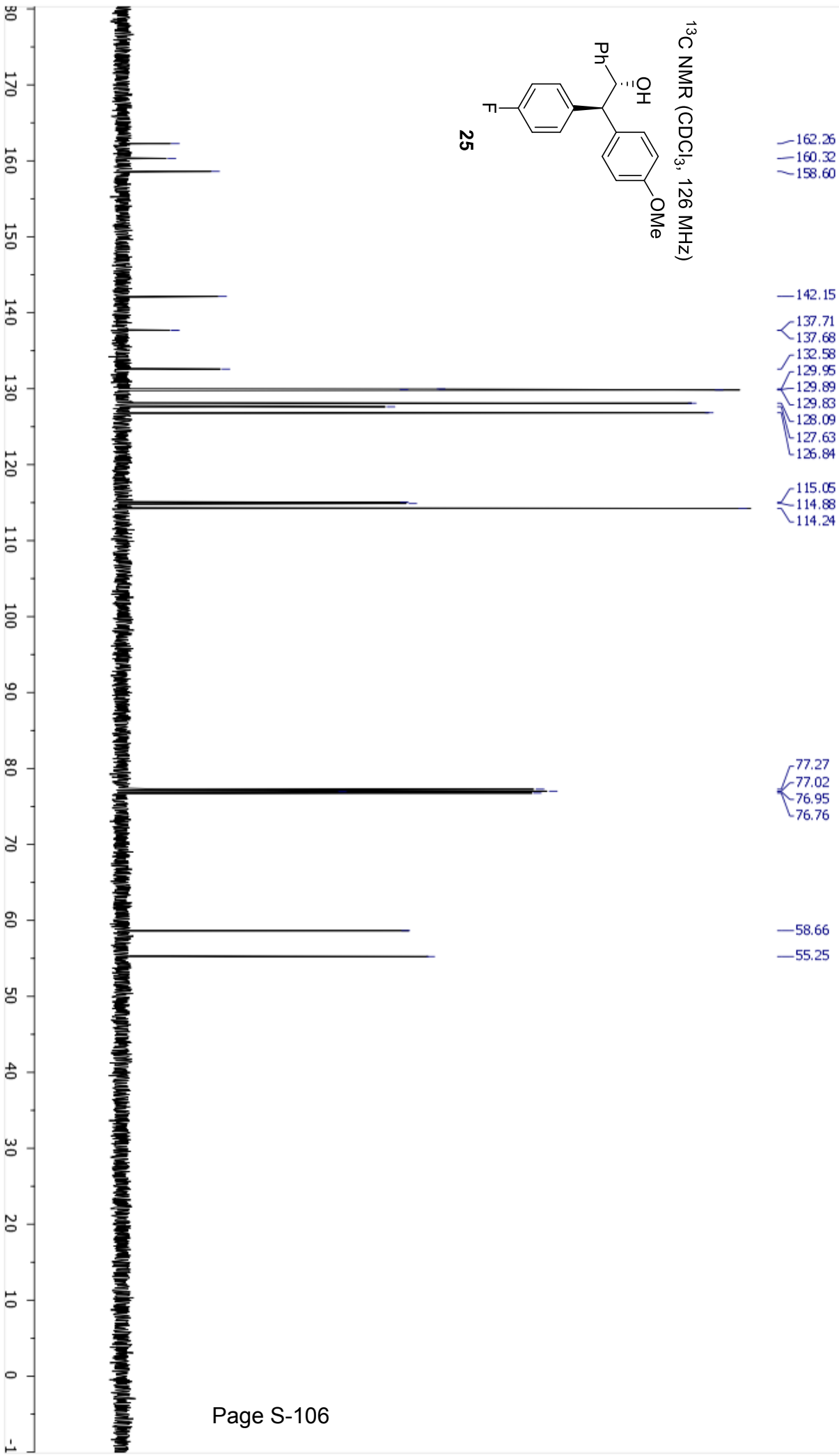
23


^{13}C NMR (CDCl$_3$, 126 MHz)
Ph
OH
OMe
OMe
23
158.45
157.90
142.44
134.09
133.14
129.85
129.43
128.01
127.44
126.89
114.15
113.58
77.28
77.03
77.00
76.77
58.57
55.24
55.11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

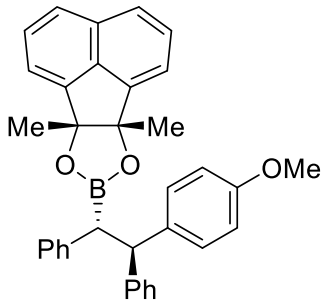

24
OH
CF3
OMe
1H NMR (CDCl3, 600 MHz)
7.41
7.40
7.29
7.29
7.28
7.28
7.27
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.19
7.19
7.18
7.18
7.18
6.91
6.90
6.90
6.89
5.35
5.34
4.28
4.26
3.80
2.16
2.00
9.04
1.89
1.03
1.00
2.93
0.88


158.95
146.24
142.04
131.98
130.15
129.01
128.80
128.58
128.39
128.37
128.01
126.97
125.35
125.32
125.30
125.27
125.20
114.49
77.41
77.20
76.99
76.79
59.34
55.44
13C NMR (CDCl3, 151 MHz)
OH
OMe
CF3
24
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

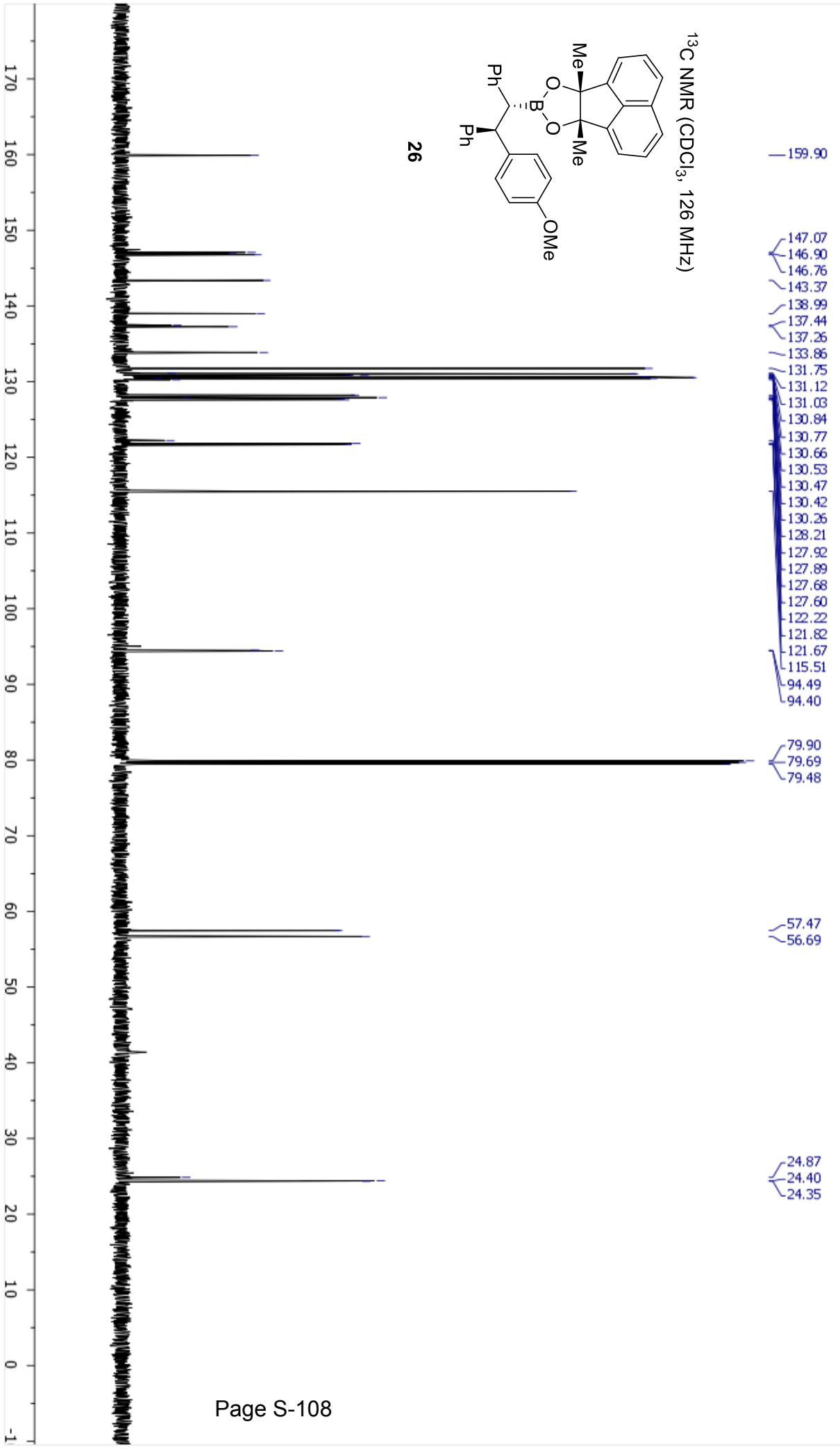

25
Ph
OH
F
OMe
^{1}H NMR (CDCl$_3$, 500 MHz)
6.93
1.95
1.88
1.81
1.00
0.98
2.94
0.87
7.30
7.30
7.29
7.28
7.26
7.25
7.24
7.24
7.23
7.23
7.23
7.23
7.22
7.22
7.22
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.18
7.18
7.17
7.07
7.06
7.06
7.05
7.04
7.04
6.91
6.91
6.90
6.89
6.89
6.85
6.84
6.84
6.83
6.83
6.82
6.82
6.81
5.30
5.28
4.20
4.18
3.80
2.14


^{13}C NMR (CDCl$_3$, 126 MHz)
25
Ph
OH
F
OMe
162.26
160.32
158.60
142.15
137.71
137.68
132.58
129.95
129.89
129.83
128.09
127.63
126.84
115.05
114.88
114.24
77.27
77.02
76.95
76.76
58.66
55.25

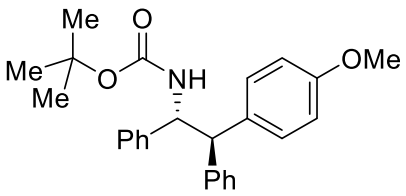
^{1}H NMR ($CDCl_3$, 500 MHz)



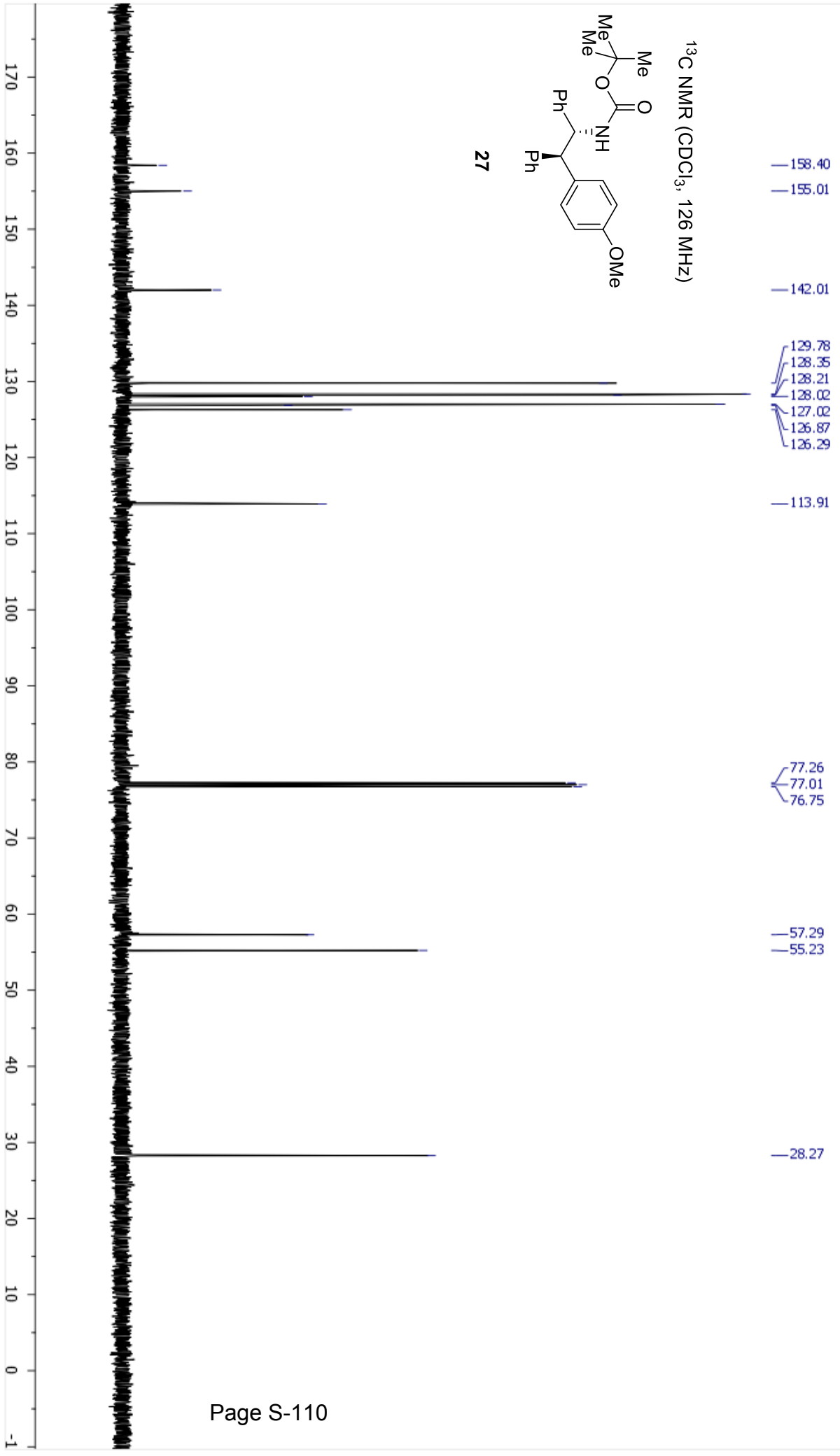
26


^{13}C NMR (CDCl$_3$, 126 MHz)
26
Me
Me
O
B
O
Ph
Ph
OMe
159.90
147.07
146.90
146.76
143.37
138.99
137.44
137.26
133.86
131.75
131.12
131.03
130.84
130.77
130.66
130.53
130.47
130.42
130.26
128.21
127.92
127.89
127.68
127.60
122.22
121.82
121.67
115.51
94.49
94.40
79.90
79.69
79.48
57.47
56.69
24.87
24.40
24.35
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

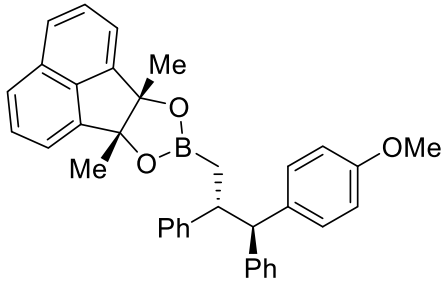
^{1}H NMR ($CDCl_3$, 500 MHz)



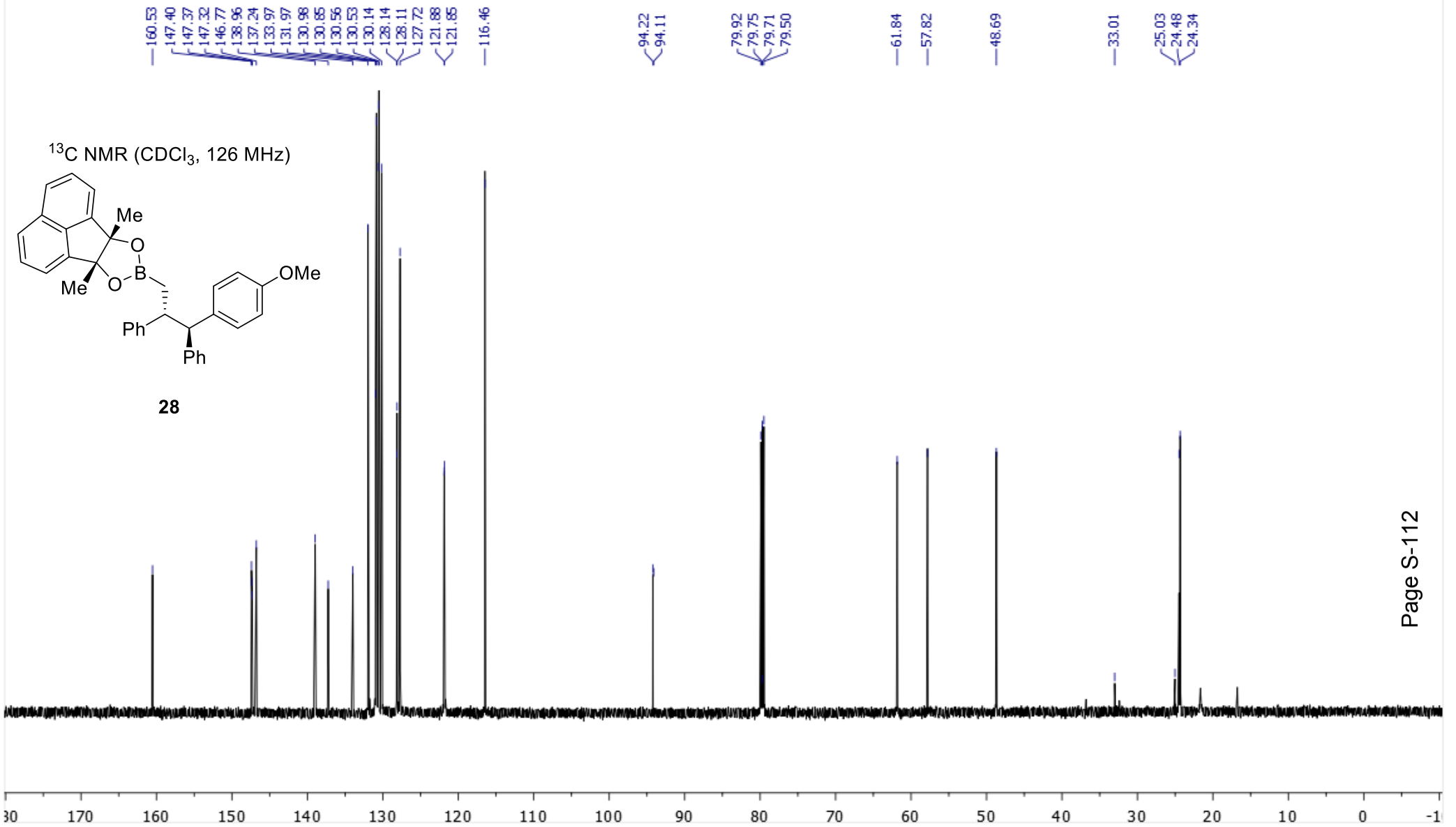
27

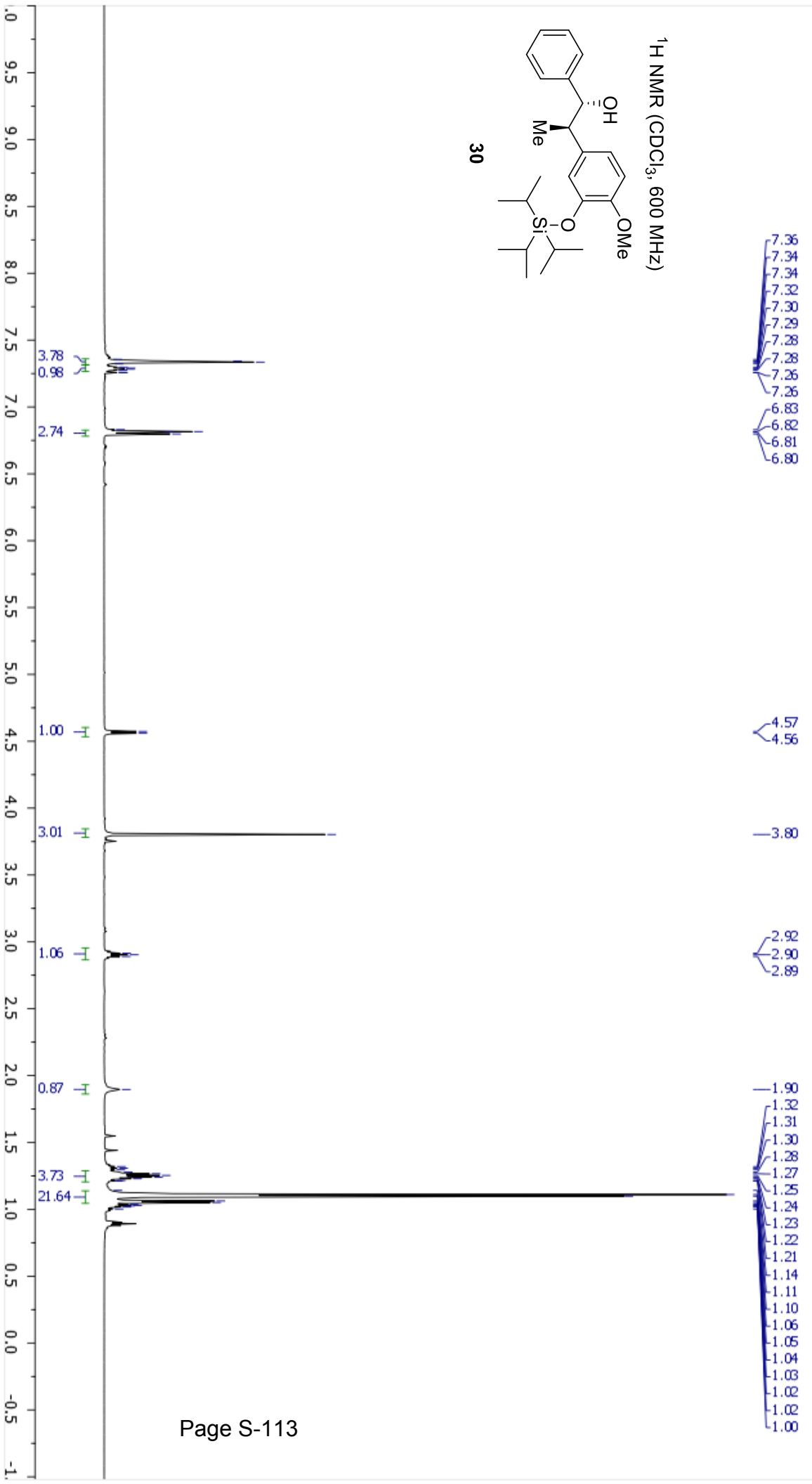

27
^{13}C NMR (CDCl$_3$, 126 MHz)
158.40
155.01
142.01
129.78
128.35
128.21
128.02
127.02
126.87
126.29
113.91
77.26
77.01
76.75
57.29
55.23
28.27

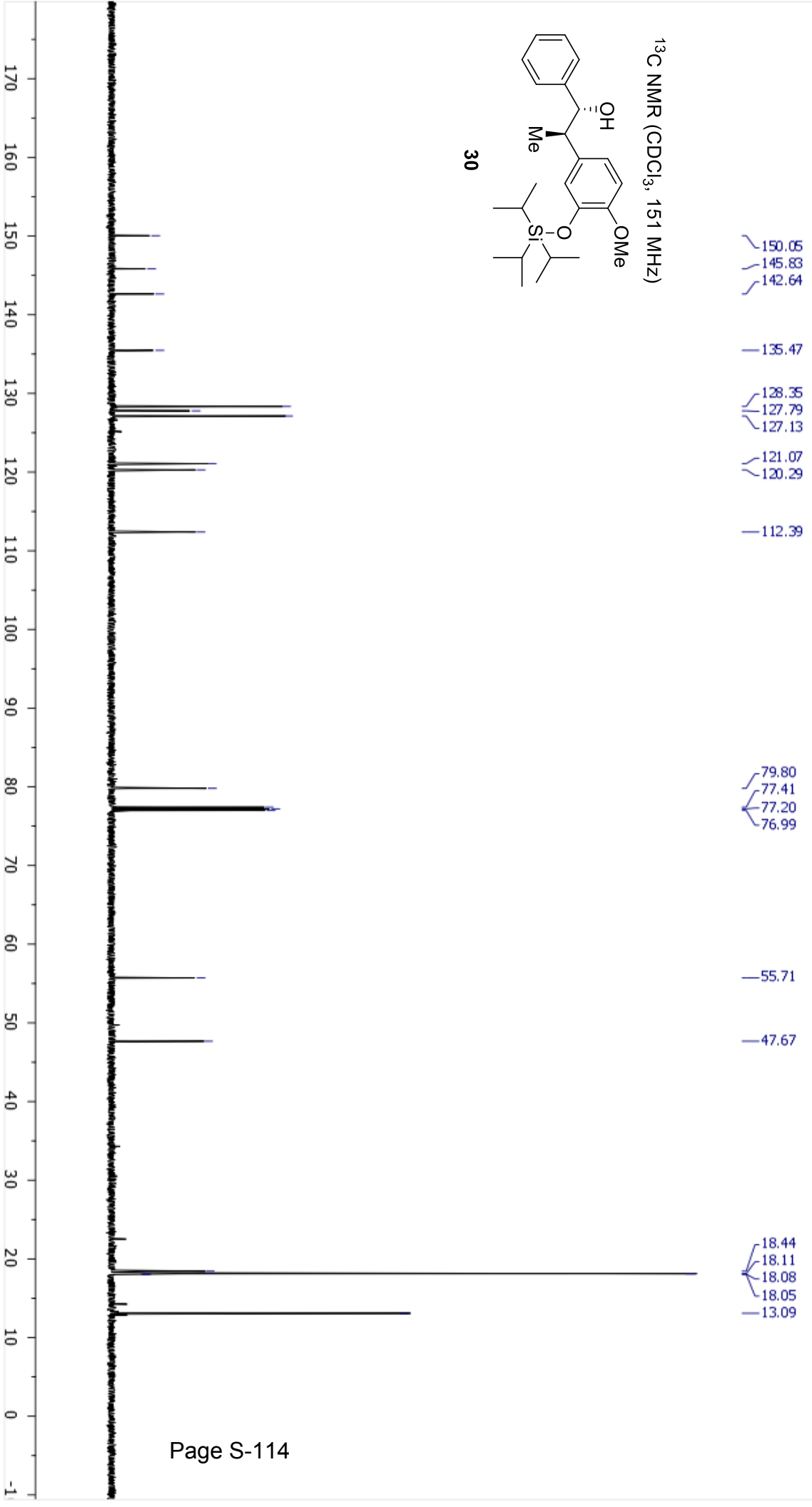
^{1}H NMR ($CDCl_3$, 500 MHz)

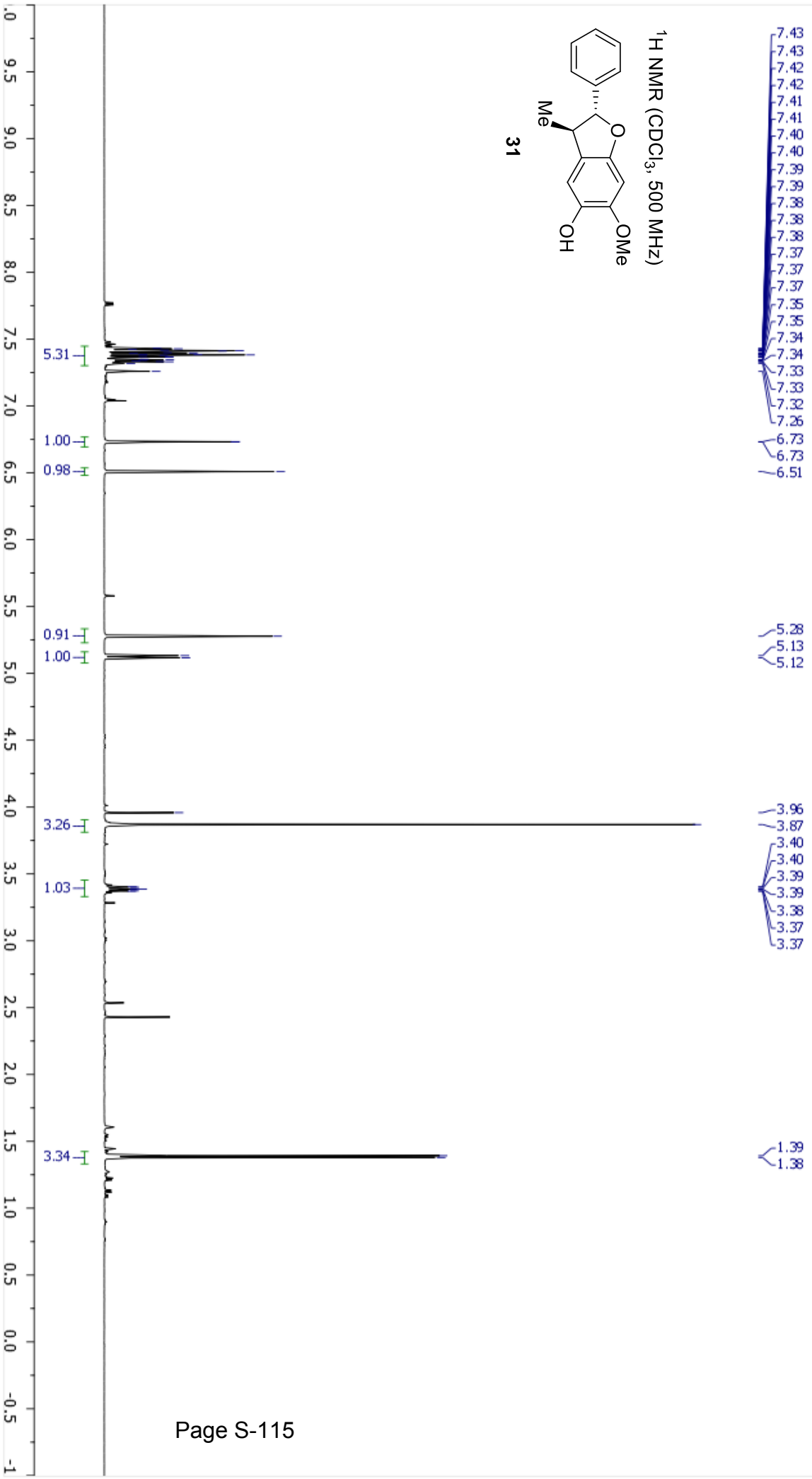


28


160.53
147.40
147.37
147.32
146.77
138.96
137.24
133.97
131.97
130.98
130.85
130.56
130.53
130.14
128.14
128.11
127.72
121.88
121.85
116.46
94.22
94.11
79.92
79.75
79.71
79.50
61.84
57.82
48.69
33.01
25.03
24.48
24.34
^{13}C NMR ($CDCl_3$, 126 MHz)
Me
O
B
O
Me
OMe
Ph
Ph
28
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


30
^{1}H NMR (CDCl$_3$, 600 MHz)
OH
Me
Si
O
OMe
3.78
0.98
2.74
1.00
3.01
1.06
0.87
3.73
21.64
7.36
7.34
7.34
7.32
7.30
7.29
7.28
7.28
7.26
7.26
6.83
6.82
6.81
6.80
4.57
4.56
3.80
2.92
2.90
2.89
1.90
1.32
1.31
1.30
1.28
1.27
1.25
1.24
1.23
1.22
1.21
1.14
1.11
1.10
1.06
1.05
1.04
1.03
1.02
1.02
1.00


^{13}C NMR (CDCl$_3$, 151 MHz)
30
OH
Me
Si
O
OMe
150.05
145.83
142.64
135.47
128.35
127.79
127.13
121.07
120.29
112.39
79.80
77.41
77.20
76.99
55.71
47.67
18.44
18.11
18.08
18.05
13.09


^{1}H NMR (CDCl$_3$, 500 MHz)
31
Me
O
OH
OMe
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.26
6.73
6.73
6.51
5.28
5.13
5.12
3.96
3.87
3.40
3.40
3.39
3.39
3.38
3.37
3.37
1.39
1.38
5.31
1.00
0.98
0.91
1.00
3.26
1.03
3.34

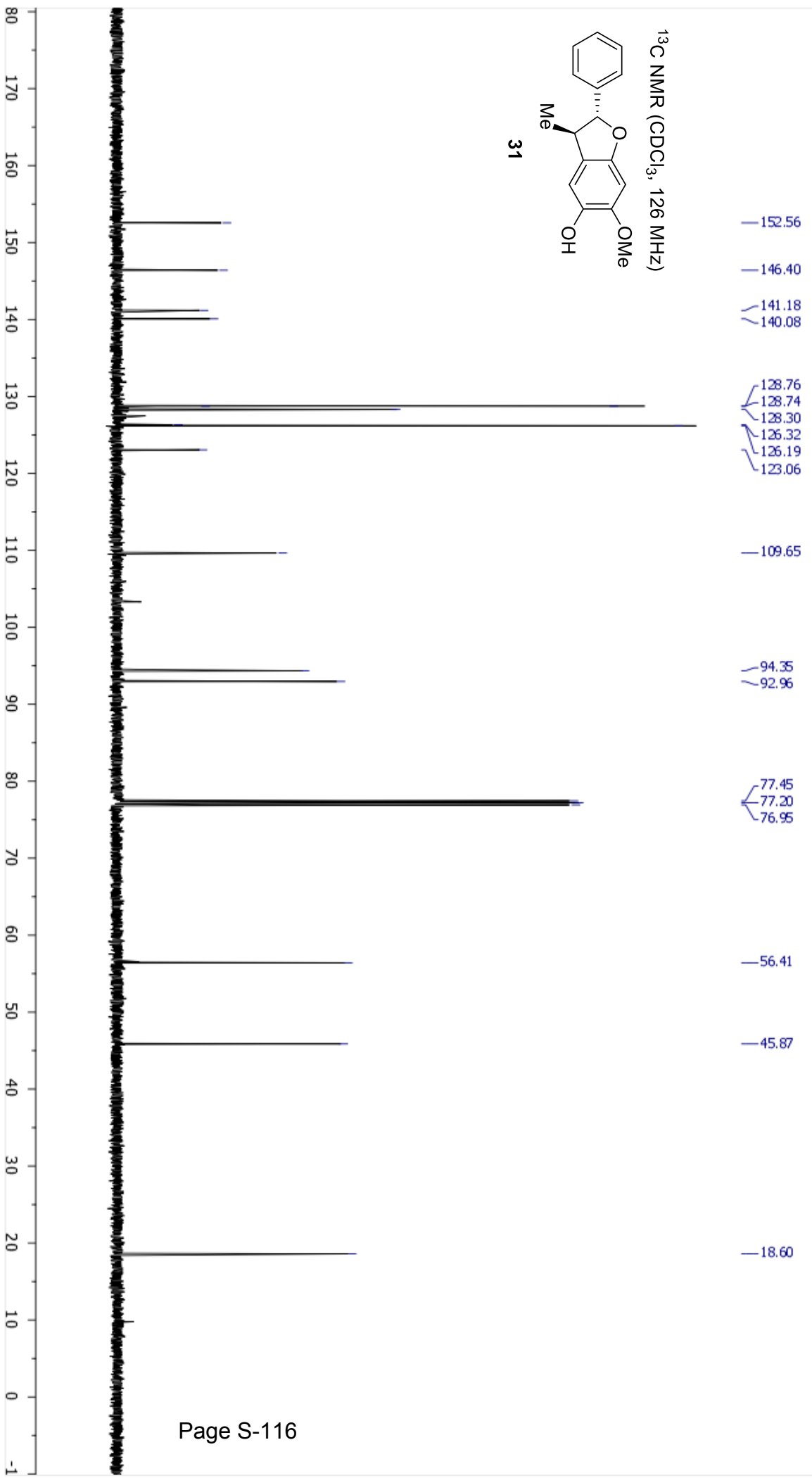

^{13}C NMR (CDCl$_3$, 126 MHz)
31
Me
O
OMe
OH
152.56
146.40
141.18
140.08
128.76
128.74
128.30
126.32
126.19
123.06
109.65
94.35
92.96
77.45
77.20
76.95
56.41
45.87
18.60
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

Table 1. Crystal data and structure refinement for C35H31BO3.

Identification code	C35H31BO3	
Empirical formula	C35 H31 B O3	
Formula weight	510.41	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 10.1118(3) Å	α= 83.3770(10)°.
	b = 11.8308(4) Å	β= 70.4740(10)°.
	c = 12.5795(4) Å	γ = 72.0230(10)°.
Volume	1348.98(8) $Å^3$	
Z	2	
Density (calculated)	1.257 Mg/m^3	
Absorption coefficient	0.611 mm^{-1}	
F(000)	540	
Crystal size	0.600 x 0.560 x 0.480 mm^3	
Theta range for data collection	3.728 to 66.684°.	
Index ranges	-12<=h<=12, -14<=k<=14, -14<=l<=14	
Reflections collected	25450	
Independent reflections	9064 [R(int) = 0.0484]	
Completeness to theta = 66.684°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6878	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9064 / 3 / 709	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1164	
R indices (all data)	R1 = 0.0450, wR2 = 0.1165	
Absolute structure parameter	-0.16(14)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.242 and -0.207 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for C35H31BO3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4672(2)	8507(2)	6018(2)	28(1)
O(2)	4074(2)	3215(2)	8406(2)	16(1)
O(3)	5215(2)	2995(2)	6498(2)	16(1)
B(1)	3926(3)	3316(2)	7359(2)	15(1)
C(1)	4580(4)	9395(3)	6731(3)	29(1)
C(2)	3893(3)	7698(3)	6483(2)	22(1)
C(3)	4155(3)	6776(3)	5788(2)	24(1)
C(4)	3429(3)	5910(2)	6171(2)	20(1)
C(5)	2434(3)	5938(2)	7248(2)	17(1)
C(6)	2195(3)	6869(3)	7936(2)	24(1)
C(7)	2915(3)	7755(3)	7556(3)	25(1)
C(8)	1550(3)	5039(2)	7672(2)	15(1)
C(9)	2394(3)	3790(2)	7145(2)	15(1)
C(10)	1524(3)	2892(2)	7575(2)	16(1)
C(11)	1382(4)	2187(3)	6836(3)	27(1)
C(12)	639(4)	1334(3)	7230(3)	35(1)
C(13)	16(3)	1175(3)	8371(3)	30(1)
C(14)	133(3)	1874(3)	9120(3)	27(1)
C(15)	886(3)	2723(3)	8725(2)	23(1)
C(16)	56(3)	5519(2)	7494(2)	14(1)
C(17)	-68(3)	5735(2)	6408(2)	17(1)
C(18)	-1439(3)	6192(2)	6266(2)	22(1)
C(19)	-2694(3)	6438(2)	7193(3)	24(1)
C(20)	-2586(3)	6229(2)	8266(3)	23(1)
C(21)	-1214(3)	5775(2)	8411(2)	20(1)
C(22)	5634(3)	2852(2)	8288(2)	15(1)
C(23)	6414(3)	2646(2)	6972(2)	15(1)
C(24)	6085(3)	1633(2)	8817(2)	14(1)
C(25)	5863(3)	1260(2)	9918(2)	17(1)
C(26)	6493(3)	46(3)	10149(2)	23(1)
C(27)	7314(3)	-762(2)	9304(2)	21(1)

C(28)	7579(3)	-398(2)	8157(2)	17(1)
C(29)	8460(3)	-1100(2)	7193(2)	20(1)
C(30)	8637(3)	-601(2)	6125(2)	21(1)
C(31)	7984(3)	620(2)	5944(2)	18(1)
C(32)	7149(3)	1316(2)	6867(2)	15(1)
C(33)	6940(3)	809(2)	7950(2)	15(1)
C(34)	5932(3)	3813(2)	8795(2)	21(1)
C(35)	7470(3)	3368(2)	6381(2)	22(1)
O(4)	5748(2)	1425(2)	2607(2)	25(1)
O(5)	4948(2)	6967(2)	3036(2)	19(1)
O(6)	5674(2)	6822(2)	1110(2)	17(1)
B(2)	6079(3)	6697(3)	2057(2)	17(1)
C(36)	4884(3)	968(3)	3601(3)	30(1)
C(37)	6230(3)	2349(2)	2721(2)	19(1)
C(38)	7034(3)	2789(3)	1721(2)	24(1)
C(39)	7596(3)	3714(3)	1735(2)	23(1)
C(40)	7367(3)	4231(2)	2749(2)	17(1)
C(41)	6527(3)	3804(3)	3732(2)	21(1)
C(42)	5957(3)	2872(3)	3730(2)	21(1)
C(43)	8049(3)	5195(2)	2813(2)	17(1)
C(44)	7745(3)	6263(2)	1996(2)	17(1)
C(45)	8232(3)	7286(2)	2220(2)	19(1)
C(46)	9251(3)	7727(3)	1373(3)	27(1)
C(47)	9685(4)	8673(3)	1573(3)	38(1)
C(48)	9124(4)	9174(3)	2632(3)	36(1)
C(49)	8112(4)	8743(3)	3478(3)	32(1)
C(50)	7662(3)	7816(3)	3271(3)	25(1)
C(51)	9681(3)	4669(2)	2649(2)	16(1)
C(52)	10185(3)	4415(2)	3574(2)	19(1)
C(53)	11670(3)	3911(2)	3431(3)	23(1)
C(54)	12669(3)	3652(2)	2366(3)	24(1)
C(55)	12182(3)	3892(2)	1432(2)	21(1)
C(56)	10707(3)	4401(2)	1575(2)	18(1)
C(57)	3578(3)	7328(2)	2778(2)	16(1)
C(58)	4083(3)	7232(2)	1441(2)	15(1)
C(59)	2813(3)	8640(2)	3005(2)	16(1)

C(60)	2130(3)	9262(3)	3986(2)	20(1)
C(61)	1443(3)	10503(3)	3918(2)	23(1)
C(62)	1459(3)	11091(2)	2912(3)	22(1)
C(63)	2201(3)	10468(2)	1879(2)	19(1)
C(64)	2337(3)	10928(2)	769(3)	23(1)
C(65)	3079(3)	10200(3)	-144(2)	24(1)
C(66)	3703(3)	8962(2)	-29(2)	20(1)
C(67)	3573(3)	8492(2)	1035(2)	15(1)
C(68)	2848(3)	9244(2)	1970(2)	15(1)
C(69)	2639(3)	6545(3)	3455(2)	25(1)
C(70)	3580(3)	6360(2)	979(2)	21(1)

Table 3. Bond lengths [Å] and angles [°] for C35H31BO3.

O(1)-C(2)	1.380(3)
O(1)-C(1)	1.421(4)
O(2)-B(1)	1.364(3)
O(2)-C(22)	1.461(3)
O(3)-B(1)	1.365(3)
O(3)-C(23)	1.454(3)
B(1)-C(9)	1.579(4)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(7)	1.376(4)
C(2)-C(3)	1.383(4)
C(3)-C(4)	1.391(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.388(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.393(4)
C(5)-C(8)	1.533(4)
C(6)-C(7)	1.407(4)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-C(16)	1.525(3)
C(8)-C(9)	1.556(3)
C(8)-H(8)	1.0000
C(9)-C(10)	1.524(4)
C(9)-H(9)	1.0000
C(10)-C(11)	1.387(4)
C(10)-C(15)	1.391(4)
C(11)-C(12)	1.390(5)
C(11)-H(11)	0.9500
C(12)-C(13)	1.377(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.379(5)
C(13)-H(13)	0.9500

C(14)-C(15)	1.392(4)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(16)-C(21)	1.386(4)
C(16)-C(17)	1.400(4)
C(17)-C(18)	1.387(4)
C(17)-H(17)	0.9500
C(18)-C(19)	1.384(4)
C(18)-H(18)	0.9500
C(19)-C(20)	1.378(5)
C(19)-H(19)	0.9500
C(20)-C(21)	1.391(4)
C(20)-H(20)	0.9500
C(21)-H(21)	0.9500
C(22)-C(34)	1.516(3)
C(22)-C(24)	1.518(3)
C(22)-C(23)	1.588(3)
C(23)-C(32)	1.518(3)
C(23)-C(35)	1.519(3)
C(24)-C(25)	1.370(4)
C(24)-C(33)	1.407(4)
C(25)-C(26)	1.419(4)
C(25)-H(25)	0.9500
C(26)-C(27)	1.374(4)
C(26)-H(26)	0.9500
C(27)-C(28)	1.418(4)
C(27)-H(27)	0.9500
C(28)-C(33)	1.407(4)
C(28)-C(29)	1.417(4)
C(29)-C(30)	1.381(4)
C(29)-H(29)	0.9500
C(30)-C(31)	1.418(4)
C(30)-H(30)	0.9500
C(31)-C(32)	1.370(4)
C(31)-H(31)	0.9500
C(32)-C(33)	1.399(4)

C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
O(4)-C(37)	1.366(3)
O(4)-C(36)	1.422(4)
O(5)-B(2)	1.360(3)
O(5)-C(57)	1.452(3)
O(6)-B(2)	1.362(4)
O(6)-C(58)	1.455(3)
B(2)-C(44)	1.581(4)
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-C(42)	1.383(4)
C(37)-C(38)	1.392(4)
C(38)-C(39)	1.384(4)
C(38)-H(38)	0.9500
C(39)-C(40)	1.397(4)
C(39)-H(39)	0.9500
C(40)-C(41)	1.387(4)
C(40)-C(43)	1.526(4)
C(41)-C(42)	1.393(4)
C(41)-H(41)	0.9500
C(42)-H(42)	0.9500
C(43)-C(51)	1.523(4)
C(43)-C(44)	1.555(3)
C(43)-H(43)	1.0000
C(44)-C(45)	1.524(4)
C(44)-H(44)	1.0000
C(45)-C(50)	1.390(4)
C(45)-C(46)	1.392(4)
C(46)-C(47)	1.396(5)
C(46)-H(46)	0.9500

C(47)-C(48)	1.385(6)
C(47)-H(47)	0.9500
C(48)-C(49)	1.381(5)
C(48)-H(48)	0.9500
C(49)-C(50)	1.390(4)
C(49)-H(49)	0.9500
C(50)-H(50)	0.9500
C(51)-C(52)	1.388(4)
C(51)-C(56)	1.401(4)
C(52)-C(53)	1.391(4)
C(52)-H(52)	0.9500
C(53)-C(54)	1.382(4)
C(53)-H(53)	0.9500
C(54)-C(55)	1.389(4)
C(54)-H(54)	0.9500
C(55)-C(56)	1.382(4)
C(55)-H(55)	0.9500
C(56)-H(56)	0.9500
C(57)-C(59)	1.517(4)
C(57)-C(69)	1.519(3)
C(57)-C(58)	1.593(3)
C(58)-C(67)	1.508(4)
C(58)-C(70)	1.523(3)
C(59)-C(60)	1.367(4)
C(59)-C(68)	1.406(4)
C(60)-C(61)	1.424(4)
C(60)-H(60)	0.9500
C(61)-C(62)	1.370(4)
C(61)-H(61)	0.9500
C(62)-C(63)	1.423(4)
C(62)-H(62)	0.9500
C(63)-C(68)	1.401(4)
C(63)-C(64)	1.416(4)
C(64)-C(65)	1.370(4)
C(64)-H(64)	0.9500
C(65)-C(66)	1.416(4)

C(65)-H(65)	0.9500
C(66)-C(67)	1.369(4)
C(66)-H(66)	0.9500
C(67)-C(68)	1.406(4)
C(69)-H(69A)	0.9800
C(69)-H(69B)	0.9800
C(69)-H(69C)	0.9800
C(70)-H(70A)	0.9800
C(70)-H(70B)	0.9800
C(70)-H(70C)	0.9800

C(2)-O(1)-C(1)	117.9(2)
B(1)-O(2)-C(22)	108.67(19)
B(1)-O(3)-C(23)	108.5(2)
O(2)-B(1)-O(3)	114.6(2)
O(2)-B(1)-C(9)	123.2(2)
O(3)-B(1)-C(9)	122.2(2)
O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(7)-C(2)-O(1)	125.0(3)
C(7)-C(2)-C(3)	119.7(3)
O(1)-C(2)-C(3)	115.3(3)
C(2)-C(3)-C(4)	120.2(3)
C(2)-C(3)-H(3)	119.9
C(4)-C(3)-H(3)	119.9
C(5)-C(4)-C(3)	121.7(3)
C(5)-C(4)-H(4)	119.1
C(3)-C(4)-H(4)	119.1
C(4)-C(5)-C(6)	117.2(3)
C(4)-C(5)-C(8)	123.1(2)
C(6)-C(5)-C(8)	119.7(2)
C(5)-C(6)-C(7)	121.6(3)

C(5)-C(6)-H(6)	119.2
C(7)-C(6)-H(6)	119.2
C(2)-C(7)-C(6)	119.6(3)
C(2)-C(7)-H(7)	120.2
C(6)-C(7)-H(7)	120.2
C(16)-C(8)-C(5)	110.7(2)
C(16)-C(8)-C(9)	111.64(19)
C(5)-C(8)-C(9)	112.7(2)
C(16)-C(8)-H(8)	107.1
C(5)-C(8)-H(8)	107.1
C(9)-C(8)-H(8)	107.1
C(10)-C(9)-C(8)	112.8(2)
C(10)-C(9)-B(1)	110.5(2)
C(8)-C(9)-B(1)	110.2(2)
C(10)-C(9)-H(9)	107.7
C(8)-C(9)-H(9)	107.7
B(1)-C(9)-H(9)	107.7
C(11)-C(10)-C(15)	117.7(3)
C(11)-C(10)-C(9)	121.1(2)
C(15)-C(10)-C(9)	121.2(2)
C(10)-C(11)-C(12)	121.1(3)
C(10)-C(11)-H(11)	119.5
C(12)-C(11)-H(11)	119.5
C(13)-C(12)-C(11)	120.6(3)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
C(12)-C(13)-C(14)	119.3(3)
C(12)-C(13)-H(13)	120.4
C(14)-C(13)-H(13)	120.4
C(13)-C(14)-C(15)	120.2(3)
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-H(14)	119.9
C(10)-C(15)-C(14)	121.2(3)
C(10)-C(15)-H(15)	119.4
C(14)-C(15)-H(15)	119.4
C(21)-C(16)-C(17)	118.5(2)

C(21)-C(16)-C(8)	120.4(2)
C(17)-C(16)-C(8)	121.1(2)
C(18)-C(17)-C(16)	120.1(2)
C(18)-C(17)-H(17)	119.9
C(16)-C(17)-H(17)	119.9
C(19)-C(18)-C(17)	120.5(3)
C(19)-C(18)-H(18)	119.7
C(17)-C(18)-H(18)	119.7
C(20)-C(19)-C(18)	119.9(3)
C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
C(19)-C(20)-C(21)	119.7(3)
C(19)-C(20)-H(20)	120.1
C(21)-C(20)-H(20)	120.1
C(16)-C(21)-C(20)	121.2(3)
C(16)-C(21)-H(21)	119.4
C(20)-C(21)-H(21)	119.4
O(2)-C(22)-C(34)	107.8(2)
O(2)-C(22)-C(24)	111.05(19)
C(34)-C(22)-C(24)	113.2(2)
O(2)-C(22)-C(23)	103.62(19)
C(34)-C(22)-C(23)	116.5(2)
C(24)-C(22)-C(23)	104.3(2)
O(3)-C(23)-C(32)	110.7(2)
O(3)-C(23)-C(35)	108.1(2)
C(32)-C(23)-C(35)	112.6(2)
O(3)-C(23)-C(22)	104.40(18)
C(32)-C(23)-C(22)	104.6(2)
C(35)-C(23)-C(22)	116.2(2)
C(25)-C(24)-C(33)	119.3(2)
C(25)-C(24)-C(22)	131.9(2)
C(33)-C(24)-C(22)	108.7(2)
C(24)-C(25)-C(26)	118.7(2)
C(24)-C(25)-H(25)	120.6
C(26)-C(25)-H(25)	120.6
C(27)-C(26)-C(25)	122.1(2)

C(27)-C(26)-H(26)	119.0
C(25)-C(26)-H(26)	119.0
C(26)-C(27)-C(28)	120.4(2)
C(26)-C(27)-H(27)	119.8
C(28)-C(27)-H(27)	119.8
C(33)-C(28)-C(29)	116.2(2)
C(33)-C(28)-C(27)	116.4(2)
C(29)-C(28)-C(27)	127.4(2)
C(30)-C(29)-C(28)	120.3(2)
C(30)-C(29)-H(29)	119.8
C(28)-C(29)-H(29)	119.8
C(29)-C(30)-C(31)	122.2(2)
C(29)-C(30)-H(30)	118.9
C(31)-C(30)-H(30)	118.9
C(32)-C(31)-C(30)	118.2(2)
C(32)-C(31)-H(31)	120.9
C(30)-C(31)-H(31)	120.9
C(31)-C(32)-C(33)	119.8(2)
C(31)-C(32)-C(23)	131.4(2)
C(33)-C(32)-C(23)	108.7(2)
C(32)-C(33)-C(28)	123.3(2)
C(32)-C(33)-C(24)	113.5(2)
C(28)-C(33)-C(24)	123.1(2)
C(22)-C(34)-H(34A)	109.5
C(22)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(22)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(23)-C(35)-H(35A)	109.5
C(23)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(23)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(37)-O(4)-C(36)	117.7(2)

B(2)-O(5)-C(57)	108.8(2)
B(2)-O(6)-C(58)	108.3(2)
O(5)-B(2)-O(6)	115.0(2)
O(5)-B(2)-C(44)	123.6(2)
O(6)-B(2)-C(44)	121.4(2)
O(4)-C(36)-H(36A)	109.5
O(4)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
O(4)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
O(4)-C(37)-C(42)	125.2(3)
O(4)-C(37)-C(38)	115.6(2)
C(42)-C(37)-C(38)	119.2(3)
C(39)-C(38)-C(37)	120.7(3)
C(39)-C(38)-H(38)	119.6
C(37)-C(38)-H(38)	119.6
C(38)-C(39)-C(40)	120.9(3)
C(38)-C(39)-H(39)	119.6
C(40)-C(39)-H(39)	119.6
C(41)-C(40)-C(39)	117.5(3)
C(41)-C(40)-C(43)	119.7(2)
C(39)-C(40)-C(43)	122.7(2)
C(40)-C(41)-C(42)	122.2(3)
C(40)-C(41)-H(41)	118.9
C(42)-C(41)-H(41)	118.9
C(37)-C(42)-C(41)	119.5(2)
C(37)-C(42)-H(42)	120.3
C(41)-C(42)-H(42)	120.3
C(51)-C(43)-C(40)	110.7(2)
C(51)-C(43)-C(44)	111.8(2)
C(40)-C(43)-C(44)	113.3(2)
C(51)-C(43)-H(43)	106.9
C(40)-C(43)-H(43)	106.9
C(44)-C(43)-H(43)	106.9
C(45)-C(44)-C(43)	111.4(2)

C(45)-C(44)-B(2)	110.8(2)
C(43)-C(44)-B(2)	111.6(2)
C(45)-C(44)-H(44)	107.6
C(43)-C(44)-H(44)	107.6
B(2)-C(44)-H(44)	107.6
C(50)-C(45)-C(46)	117.9(3)
C(50)-C(45)-C(44)	121.1(2)
C(46)-C(45)-C(44)	121.0(3)
C(45)-C(46)-C(47)	121.1(3)
C(45)-C(46)-H(46)	119.5
C(47)-C(46)-H(46)	119.5
C(48)-C(47)-C(46)	120.1(3)
C(48)-C(47)-H(47)	120.0
C(46)-C(47)-H(47)	120.0
C(49)-C(48)-C(47)	119.3(3)
C(49)-C(48)-H(48)	120.3
C(47)-C(48)-H(48)	120.3
C(48)-C(49)-C(50)	120.4(3)
C(48)-C(49)-H(49)	119.8
C(50)-C(49)-H(49)	119.8
C(49)-C(50)-C(45)	121.2(3)
C(49)-C(50)-H(50)	119.4
C(45)-C(50)-H(50)	119.4
C(52)-C(51)-C(56)	118.1(2)
C(52)-C(51)-C(43)	120.3(2)
C(56)-C(51)-C(43)	121.6(2)
C(51)-C(52)-C(53)	120.6(3)
C(51)-C(52)-H(52)	119.7
C(53)-C(52)-H(52)	119.7
C(54)-C(53)-C(52)	120.5(3)
C(54)-C(53)-H(53)	119.7
C(52)-C(53)-H(53)	119.7
C(53)-C(54)-C(55)	119.6(3)
C(53)-C(54)-H(54)	120.2
C(55)-C(54)-H(54)	120.2
C(56)-C(55)-C(54)	119.8(3)

C(56)-C(55)-H(55)	120.1
C(54)-C(55)-H(55)	120.1
C(55)-C(56)-C(51)	121.4(3)
C(55)-C(56)-H(56)	119.3
C(51)-C(56)-H(56)	119.3
O(5)-C(57)-C(59)	110.9(2)
O(5)-C(57)-C(69)	108.5(2)
C(59)-C(57)-C(69)	112.6(2)
O(5)-C(57)-C(58)	103.77(19)
C(59)-C(57)-C(58)	104.4(2)
C(69)-C(57)-C(58)	116.4(2)
O(6)-C(58)-C(67)	110.5(2)
O(6)-C(58)-C(70)	107.7(2)
C(67)-C(58)-C(70)	113.1(2)
O(6)-C(58)-C(57)	104.19(19)
C(67)-C(58)-C(57)	104.5(2)
C(70)-C(58)-C(57)	116.6(2)
C(60)-C(59)-C(68)	119.4(2)
C(60)-C(59)-C(57)	131.8(2)
C(68)-C(59)-C(57)	108.8(2)
C(59)-C(60)-C(61)	118.2(2)
C(59)-C(60)-H(60)	120.9
C(61)-C(60)-H(60)	120.9
C(62)-C(61)-C(60)	122.5(2)
C(62)-C(61)-H(61)	118.7
C(60)-C(61)-H(61)	118.7
C(61)-C(62)-C(63)	120.2(3)
C(61)-C(62)-H(62)	119.9
C(63)-C(62)-H(62)	119.9
C(68)-C(63)-C(64)	116.0(2)
C(68)-C(63)-C(62)	116.1(3)
C(64)-C(63)-C(62)	127.9(3)
C(65)-C(64)-C(63)	120.7(3)
C(65)-C(64)-H(64)	119.6
C(63)-C(64)-H(64)	119.6
C(64)-C(65)-C(66)	122.3(3)

C(64)-C(65)-H(65)	118.9
C(66)-C(65)-H(65)	118.9
C(67)-C(66)-C(65)	118.2(2)
C(67)-C(66)-H(66)	120.9
C(65)-C(66)-H(66)	120.9
C(66)-C(67)-C(68)	119.5(2)
C(66)-C(67)-C(58)	131.3(2)
C(68)-C(67)-C(58)	109.2(2)
C(63)-C(68)-C(59)	123.6(2)
C(63)-C(68)-C(67)	123.2(2)
C(59)-C(68)-C(67)	113.2(2)
C(57)-C(69)-H(69A)	109.5
C(57)-C(69)-H(69B)	109.5
H(69A)-C(69)-H(69B)	109.5
C(57)-C(69)-H(69C)	109.5
H(69A)-C(69)-H(69C)	109.5
H(69B)-C(69)-H(69C)	109.5
C(58)-C(70)-H(70A)	109.5
C(58)-C(70)-H(70B)	109.5
H(70A)-C(70)-H(70B)	109.5
C(58)-C(70)-H(70C)	109.5
H(70A)-C(70)-H(70C)	109.5
H(70B)-C(70)-H(70C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C35H31BO3. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	33(1)	34(1)	22(1)	4(1)	-9(1)	-20(1)
O(2)	12(1)	18(1)	16(1)	-1(1)	-4(1)	0(1)
O(3)	13(1)	19(1)	15(1)	0(1)	-5(1)	-2(1)
B(1)	15(1)	12(1)	17(1)	1(1)	-3(1)	-4(1)
C(1)	31(2)	29(2)	33(2)	2(1)	-12(1)	-16(1)
C(2)	21(1)	26(1)	26(1)	6(1)	-14(1)	-10(1)
C(3)	25(1)	30(2)	19(1)	2(1)	-6(1)	-10(1)
C(4)	22(1)	21(1)	18(1)	1(1)	-8(1)	-6(1)
C(5)	16(1)	17(1)	20(1)	1(1)	-10(1)	-2(1)
C(6)	20(1)	29(2)	23(1)	-6(1)	-2(1)	-9(1)
C(7)	25(1)	24(1)	29(1)	-6(1)	-9(1)	-8(1)
C(8)	14(1)	17(1)	13(1)	-1(1)	-4(1)	-2(1)
C(9)	14(1)	16(1)	13(1)	0(1)	-5(1)	-2(1)
C(10)	11(1)	13(1)	24(1)	2(1)	-9(1)	2(1)
C(11)	31(2)	29(2)	25(1)	1(1)	-14(1)	-9(1)
C(12)	42(2)	34(2)	44(2)	4(1)	-28(2)	-19(2)
C(13)	23(2)	29(2)	47(2)	11(1)	-20(1)	-12(1)
C(14)	18(1)	26(1)	33(2)	5(1)	-4(1)	-6(1)
C(15)	22(1)	19(1)	24(1)	-2(1)	-5(1)	-4(1)
C(16)	15(1)	9(1)	18(1)	-1(1)	-6(1)	-2(1)
C(17)	18(1)	13(1)	18(1)	-4(1)	-5(1)	-1(1)
C(18)	27(2)	15(1)	28(1)	-4(1)	-17(1)	-2(1)
C(19)	16(1)	14(1)	46(2)	-4(1)	-16(1)	-1(1)
C(20)	14(1)	17(1)	36(2)	-3(1)	-3(1)	-5(1)
C(21)	20(1)	16(1)	21(1)	0(1)	-4(1)	-5(1)
C(22)	11(1)	14(1)	18(1)	0(1)	-5(1)	-2(1)
C(23)	11(1)	16(1)	17(1)	-1(1)	-4(1)	-3(1)
C(24)	11(1)	13(1)	19(1)	0(1)	-6(1)	-3(1)
C(25)	15(1)	18(1)	18(1)	-2(1)	-6(1)	-5(1)
C(26)	24(1)	23(1)	23(1)	7(1)	-12(1)	-9(1)
C(27)	22(1)	17(1)	27(1)	5(1)	-12(1)	-6(1)

C(28)	15(1)	13(1)	27(1)	1(1)	-10(1)	-5(1)
C(29)	17(1)	13(1)	31(1)	-5(1)	-10(1)	-2(1)
C(30)	16(1)	18(1)	27(1)	-10(1)	-5(1)	-2(1)
C(31)	14(1)	22(1)	18(1)	-5(1)	-3(1)	-5(1)
C(32)	11(1)	15(1)	19(1)	-1(1)	-6(1)	-5(1)
C(33)	13(1)	14(1)	20(1)	-2(1)	-8(1)	-6(1)
C(34)	24(1)	17(1)	23(1)	-4(1)	-7(1)	-7(1)
C(35)	18(1)	20(1)	27(1)	2(1)	-3(1)	-7(1)
O(4)	21(1)	26(1)	30(1)	-2(1)	-7(1)	-11(1)
O(5)	16(1)	23(1)	16(1)	0(1)	-7(1)	-2(1)
O(6)	13(1)	19(1)	17(1)	-3(1)	-5(1)	-1(1)
B(2)	18(1)	16(1)	16(1)	-1(1)	-5(1)	-5(1)
C(36)	24(2)	27(2)	38(2)	4(1)	-7(1)	-11(1)
C(37)	11(1)	22(1)	23(1)	0(1)	-7(1)	-3(1)
C(38)	20(1)	35(2)	18(1)	-7(1)	-4(1)	-12(1)
C(39)	20(1)	33(2)	16(1)	-3(1)	-1(1)	-12(1)
C(40)	10(1)	20(1)	17(1)	-2(1)	-6(1)	1(1)
C(41)	20(1)	24(1)	15(1)	-3(1)	-6(1)	-2(1)
C(42)	19(1)	23(1)	18(1)	4(1)	-6(1)	-6(1)
C(43)	17(1)	18(1)	14(1)	-3(1)	-5(1)	-2(1)
C(44)	14(1)	20(1)	13(1)	0(1)	-5(1)	0(1)
C(45)	12(1)	20(1)	24(1)	2(1)	-9(1)	1(1)
C(46)	17(1)	28(2)	32(2)	6(1)	-9(1)	-3(1)
C(47)	21(2)	34(2)	59(2)	15(2)	-15(2)	-11(1)
C(48)	26(2)	25(2)	66(2)	-4(2)	-22(2)	-8(1)
C(49)	27(2)	28(2)	46(2)	-10(1)	-18(1)	-3(1)
C(50)	21(1)	26(1)	28(2)	-3(1)	-9(1)	-5(1)
C(51)	16(1)	12(1)	21(1)	-3(1)	-6(1)	-4(1)
C(52)	24(1)	13(1)	21(1)	-3(1)	-10(1)	-4(1)
C(53)	25(1)	16(1)	35(2)	1(1)	-19(1)	-6(1)
C(54)	15(1)	14(1)	44(2)	-3(1)	-12(1)	-3(1)
C(55)	17(1)	14(1)	30(2)	-3(1)	-3(1)	-5(1)
C(56)	19(1)	15(1)	20(1)	-2(1)	-6(1)	-4(1)
C(57)	13(1)	16(1)	17(1)	0(1)	-4(1)	-5(1)
C(58)	12(1)	16(1)	17(1)	-2(1)	-6(1)	-3(1)
C(59)	10(1)	18(1)	21(1)	0(1)	-5(1)	-7(1)

C(60)	16(1)	26(1)	19(1)	-2(1)	-3(1)	-9(1)
C(61)	20(1)	23(1)	25(1)	-11(1)	-2(1)	-6(1)
C(62)	16(1)	17(1)	33(2)	-6(1)	-5(1)	-6(1)
C(63)	15(1)	16(1)	28(1)	-2(1)	-7(1)	-7(1)
C(64)	25(1)	15(1)	31(2)	2(1)	-11(1)	-7(1)
C(65)	27(2)	23(1)	25(1)	6(1)	-11(1)	-8(1)
C(66)	20(1)	20(1)	19(1)	-2(1)	-6(1)	-5(1)
C(67)	10(1)	17(1)	21(1)	-1(1)	-6(1)	-6(1)
C(68)	12(1)	17(1)	19(1)	0(1)	-5(1)	-8(1)
C(69)	26(1)	24(1)	23(1)	4(1)	-4(1)	-12(1)
C(70)	23(1)	16(1)	27(1)	-4(1)	-11(1)	-6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for C35H31BO3.

	x	y	z	U(eq)
H(1A)	3564	9896	7007	43
H(1B)	5211	9886	6305	43
H(1C)	4901	9015	7373	43
H(3)	4832	6733	5048	29
H(4)	3620	5283	5683	24
H(6)	1530	6907	8682	29
H(7)	2727	8387	8036	30
H(8)	1372	4943	8504	18
H(9)	2585	3880	6311	18
H(11)	1799	2289	6046	32
H(12)	561	857	6709	42
H(13)	-489	590	8638	37
H(14)	-301	1777	9908	33
H(15)	966	3195	9249	28
H(17)	787	5567	5767	21
H(18)	-1516	6338	5528	26
H(19)	-3629	6750	7089	29
H(20)	-3446	6394	8904	28
H(21)	-1146	5638	9153	23
H(25)	5298	1803	10516	20
H(26)	6341	-215	10912	27
H(27)	7706	-1570	9490	25
H(29)	8931	-1918	7282	24
H(30)	9215	-1092	5490	25
H(31)	8122	946	5202	22
H(34A)	5607	4578	8429	31
H(34B)	6985	3619	8678	31
H(34C)	5397	3863	9605	31
H(35A)	7899	3164	5580	33
H(35B)	8251	3187	6725	33

H(35C)	6941	4217	6456	33
H(36A)	5436	707	4138	45
H(36B)	4646	292	3407	45
H(36C)	3977	1591	3941	45
H(38)	7199	2450	1023	28
H(39)	8145	4001	1045	28
H(41)	6334	4158	4429	25
H(42)	5386	2598	4417	25
H(43)	7580	5513	3596	20
H(44)	8338	5985	1211	20
H(46)	9658	7379	648	32
H(47)	10367	8973	981	45
H(48)	9431	9807	2775	44
H(49)	7721	9083	4206	38
H(50)	6952	7540	3858	30
H(52)	9510	4588	4311	22
H(53)	12001	3743	4072	27
H(54)	13683	3311	2273	29
H(55)	12859	3706	697	25
H(56)	10383	4572	931	22
H(60)	2113	8876	4694	24
H(61)	956	10941	4597	28
H(62)	972	11918	2904	26
H(64)	1910	11750	656	28
H(65)	3179	10537	-879	29
H(66)	4197	8471	-674	24
H(69A)	3182	5709	3285	37
H(69B)	1735	6745	3256	37
H(69C)	2394	6675	4262	37
H(70A)	3967	6364	154	31
H(70B)	2507	6596	1218	31
H(70C)	3942	5560	1270	31

Table 6. Torsion angles [°] for C35H31BO3.

C(22)-O(2)-B(1)-O(3)	3.8(3)
C(22)-O(2)-B(1)-C(9)	-175.0(2)
C(23)-O(3)-B(1)-O(2)	-1.0(3)
C(23)-O(3)-B(1)-C(9)	177.7(2)
C(1)-O(1)-C(2)-C(7)	7.0(4)
C(1)-O(1)-C(2)-C(3)	-172.9(3)
C(7)-C(2)-C(3)-C(4)	0.2(4)
O(1)-C(2)-C(3)-C(4)	180.0(3)
C(2)-C(3)-C(4)-C(5)	-0.1(4)
C(3)-C(4)-C(5)-C(6)	-0.4(4)
C(3)-C(4)-C(5)-C(8)	176.3(3)
C(4)-C(5)-C(6)-C(7)	0.8(4)
C(8)-C(5)-C(6)-C(7)	-176.0(3)
O(1)-C(2)-C(7)-C(6)	-179.5(3)
C(3)-C(2)-C(7)-C(6)	0.3(4)
C(5)-C(6)-C(7)-C(2)	-0.8(4)
C(4)-C(5)-C(8)-C(16)	-94.0(3)
C(6)-C(5)-C(8)-C(16)	82.7(3)
C(4)-C(5)-C(8)-C(9)	31.9(3)
C(6)-C(5)-C(8)-C(9)	-151.5(2)
C(16)-C(8)-C(9)-C(10)	-55.2(3)
C(5)-C(8)-C(9)-C(10)	179.4(2)
C(16)-C(8)-C(9)-B(1)	-179.3(2)
C(5)-C(8)-C(9)-B(1)	55.3(3)
O(2)-B(1)-C(9)-C(10)	-69.9(3)
O(3)-B(1)-C(9)-C(10)	111.5(3)
O(2)-B(1)-C(9)-C(8)	55.5(3)
O(3)-B(1)-C(9)-C(8)	-123.1(2)
C(8)-C(9)-C(10)-C(11)	131.5(3)
B(1)-C(9)-C(10)-C(11)	-104.6(3)
C(8)-C(9)-C(10)-C(15)	-50.6(3)
B(1)-C(9)-C(10)-C(15)	73.3(3)
C(15)-C(10)-C(11)-C(12)	-0.6(4)
C(9)-C(10)-C(11)-C(12)	177.3(3)

C(10)-C(11)-C(12)-C(13)	0.4(5)
C(11)-C(12)-C(13)-C(14)	0.2(5)
C(12)-C(13)-C(14)-C(15)	-0.6(5)
C(11)-C(10)-C(15)-C(14)	0.1(4)
C(9)-C(10)-C(15)-C(14)	-177.8(2)
C(13)-C(14)-C(15)-C(10)	0.5(4)
C(5)-C(8)-C(16)-C(21)	-114.2(3)
C(9)-C(8)-C(16)-C(21)	119.3(2)
C(5)-C(8)-C(16)-C(17)	64.5(3)
C(9)-C(8)-C(16)-C(17)	-62.0(3)
C(21)-C(16)-C(17)-C(18)	-0.1(4)
C(8)-C(16)-C(17)-C(18)	-178.8(2)
C(16)-C(17)-C(18)-C(19)	-0.1(4)
C(17)-C(18)-C(19)-C(20)	0.1(4)
C(18)-C(19)-C(20)-C(21)	0.2(4)
C(17)-C(16)-C(21)-C(20)	0.4(4)
C(8)-C(16)-C(21)-C(20)	179.1(2)
C(19)-C(20)-C(21)-C(16)	-0.4(4)
B(1)-O(2)-C(22)-C(34)	119.5(2)
B(1)-O(2)-C(22)-C(24)	-116.0(2)
B(1)-O(2)-C(22)-C(23)	-4.5(2)
B(1)-O(3)-C(23)-C(32)	110.1(2)
B(1)-O(3)-C(23)-C(35)	-126.2(2)
B(1)-O(3)-C(23)-C(22)	-1.9(2)
O(2)-C(22)-C(23)-O(3)	3.9(2)
C(34)-C(22)-C(23)-O(3)	-114.3(2)
C(24)-C(22)-C(23)-O(3)	120.2(2)
O(2)-C(22)-C(23)-C(32)	-112.5(2)
C(34)-C(22)-C(23)-C(32)	129.4(2)
C(24)-C(22)-C(23)-C(32)	3.8(2)
O(2)-C(22)-C(23)-C(35)	122.8(2)
C(34)-C(22)-C(23)-C(35)	4.7(3)
C(24)-C(22)-C(23)-C(35)	-120.9(2)
O(2)-C(22)-C(24)-C(25)	-75.1(3)
C(34)-C(22)-C(24)-C(25)	46.3(4)
C(23)-C(22)-C(24)-C(25)	173.9(3)

O(2)-C(22)-C(24)-C(33)	108.3(2)
C(34)-C(22)-C(24)-C(33)	-130.3(2)
C(23)-C(22)-C(24)-C(33)	-2.7(3)
C(33)-C(24)-C(25)-C(26)	-0.6(4)
C(22)-C(24)-C(25)-C(26)	-176.9(2)
C(24)-C(25)-C(26)-C(27)	-0.1(4)
C(25)-C(26)-C(27)-C(28)	1.0(4)
C(26)-C(27)-C(28)-C(33)	-1.1(4)
C(26)-C(27)-C(28)-C(29)	176.4(3)
C(33)-C(28)-C(29)-C(30)	-0.9(4)
C(27)-C(28)-C(29)-C(30)	-178.4(3)
C(28)-C(29)-C(30)-C(31)	1.3(4)
C(29)-C(30)-C(31)-C(32)	-0.2(4)
C(30)-C(31)-C(32)-C(33)	-1.2(4)
C(30)-C(31)-C(32)-C(23)	174.4(2)
O(3)-C(23)-C(32)-C(31)	68.4(3)
C(35)-C(23)-C(32)-C(31)	-52.7(4)
C(22)-C(23)-C(32)-C(31)	-179.7(3)
O(3)-C(23)-C(32)-C(33)	-115.6(2)
C(35)-C(23)-C(32)-C(33)	123.2(2)
C(22)-C(23)-C(32)-C(33)	-3.7(3)
C(31)-C(32)-C(33)-C(28)	1.6(4)
C(23)-C(32)-C(33)-C(28)	-174.9(2)
C(31)-C(32)-C(33)-C(24)	178.7(2)
C(23)-C(32)-C(33)-C(24)	2.2(3)
C(29)-C(28)-C(33)-C(32)	-0.6(4)
C(27)-C(28)-C(33)-C(32)	177.2(2)
C(29)-C(28)-C(33)-C(24)	-177.4(2)
C(27)-C(28)-C(33)-C(24)	0.4(4)
C(25)-C(24)-C(33)-C(32)	-176.6(2)
C(22)-C(24)-C(33)-C(32)	0.4(3)
C(25)-C(24)-C(33)-C(28)	0.5(4)
C(22)-C(24)-C(33)-C(28)	177.5(2)
C(57)-O(5)-B(2)-O(6)	-0.1(3)
C(57)-O(5)-B(2)-C(44)	-179.8(2)
C(58)-O(6)-B(2)-O(5)	0.3(3)

C(58)-O(6)-B(2)-C(44)	-180.0(2)
C(36)-O(4)-C(37)-C(42)	0.6(4)
C(36)-O(4)-C(37)-C(38)	-178.2(3)
O(4)-C(37)-C(38)-C(39)	-179.1(3)
C(42)-C(37)-C(38)-C(39)	2.0(4)
C(37)-C(38)-C(39)-C(40)	-0.2(4)
C(38)-C(39)-C(40)-C(41)	-1.7(4)
C(38)-C(39)-C(40)-C(43)	175.8(3)
C(39)-C(40)-C(41)-C(42)	1.8(4)
C(43)-C(40)-C(41)-C(42)	-175.8(2)
O(4)-C(37)-C(42)-C(41)	179.4(3)
C(38)-C(37)-C(42)-C(41)	-1.9(4)
C(40)-C(41)-C(42)-C(37)	0.0(4)
C(41)-C(40)-C(43)-C(51)	103.6(3)
C(39)-C(40)-C(43)-C(51)	-73.9(3)
C(41)-C(40)-C(43)-C(44)	-129.9(3)
C(39)-C(40)-C(43)-C(44)	52.7(3)
C(51)-C(43)-C(44)-C(45)	-63.1(3)
C(40)-C(43)-C(44)-C(45)	170.9(2)
C(51)-C(43)-C(44)-B(2)	172.5(2)
C(40)-C(43)-C(44)-B(2)	46.5(3)
O(5)-B(2)-C(44)-C(45)	-72.9(3)
O(6)-B(2)-C(44)-C(45)	107.5(3)
O(5)-B(2)-C(44)-C(43)	51.9(3)
O(6)-B(2)-C(44)-C(43)	-127.7(3)
C(43)-C(44)-C(45)-C(50)	-58.4(3)
B(2)-C(44)-C(45)-C(50)	66.4(3)
C(43)-C(44)-C(45)-C(46)	122.2(3)
B(2)-C(44)-C(45)-C(46)	-113.0(3)
C(50)-C(45)-C(46)-C(47)	-0.1(4)
C(44)-C(45)-C(46)-C(47)	179.3(3)
C(45)-C(46)-C(47)-C(48)	1.3(5)
C(46)-C(47)-C(48)-C(49)	-1.2(5)
C(47)-C(48)-C(49)-C(50)	0.1(5)
C(48)-C(49)-C(50)-C(45)	1.1(5)
C(46)-C(45)-C(50)-C(49)	-1.1(4)

C(44)-C(45)-C(50)-C(49)	179.5(3)
C(40)-C(43)-C(51)-C(52)	-99.2(3)
C(44)-C(43)-C(51)-C(52)	133.4(2)
C(40)-C(43)-C(51)-C(56)	79.3(3)
C(44)-C(43)-C(51)-C(56)	-48.1(3)
C(56)-C(51)-C(52)-C(53)	0.1(4)
C(43)-C(51)-C(52)-C(53)	178.6(2)
C(51)-C(52)-C(53)-C(54)	-0.1(4)
C(52)-C(53)-C(54)-C(55)	-0.4(4)
C(53)-C(54)-C(55)-C(56)	0.8(4)
C(54)-C(55)-C(56)-C(51)	-0.9(4)
C(52)-C(51)-C(56)-C(55)	0.4(4)
C(43)-C(51)-C(56)-C(55)	-178.1(2)
B(2)-O(5)-C(57)-C(59)	-111.6(2)
B(2)-O(5)-C(57)-C(69)	124.3(2)
B(2)-O(5)-C(57)-C(58)	-0.1(3)
B(2)-O(6)-C(58)-C(67)	111.3(2)
B(2)-O(6)-C(58)-C(70)	-124.7(2)
B(2)-O(6)-C(58)-C(57)	-0.4(3)
O(5)-C(57)-C(58)-O(6)	0.3(2)
C(59)-C(57)-C(58)-O(6)	116.5(2)
C(69)-C(57)-C(58)-O(6)	-118.8(2)
O(5)-C(57)-C(58)-C(67)	-115.7(2)
C(59)-C(57)-C(58)-C(67)	0.5(2)
C(69)-C(57)-C(58)-C(67)	125.2(2)
O(5)-C(57)-C(58)-C(70)	118.7(2)
C(59)-C(57)-C(58)-C(70)	-125.1(2)
C(69)-C(57)-C(58)-C(70)	-0.3(3)
O(5)-C(57)-C(59)-C(60)	-70.2(3)
C(69)-C(57)-C(59)-C(60)	51.5(4)
C(58)-C(57)-C(59)-C(60)	178.6(3)
O(5)-C(57)-C(59)-C(68)	111.2(2)
C(69)-C(57)-C(59)-C(68)	-127.1(2)
C(58)-C(57)-C(59)-C(68)	0.0(3)
C(68)-C(59)-C(60)-C(61)	1.5(4)
C(57)-C(59)-C(60)-C(61)	-177.0(2)

C(59)-C(60)-C(61)-C(62)	-0.7(4)
C(60)-C(61)-C(62)-C(63)	-1.1(4)
C(61)-C(62)-C(63)-C(68)	2.0(4)
C(61)-C(62)-C(63)-C(64)	-179.6(3)
C(68)-C(63)-C(64)-C(65)	-0.7(4)
C(62)-C(63)-C(64)-C(65)	-179.2(3)
C(63)-C(64)-C(65)-C(66)	1.9(4)
C(64)-C(65)-C(66)-C(67)	-1.1(4)
C(65)-C(66)-C(67)-C(68)	-0.7(4)
C(65)-C(66)-C(67)-C(58)	178.9(2)
O(6)-C(58)-C(67)-C(66)	68.0(3)
C(70)-C(58)-C(67)-C(66)	-52.8(4)
C(57)-C(58)-C(67)-C(66)	179.5(3)
O(6)-C(58)-C(67)-C(68)	-112.4(2)
C(70)-C(58)-C(67)-C(68)	126.8(2)
C(57)-C(58)-C(67)-C(68)	-0.9(3)
C(64)-C(63)-C(68)-C(59)	-179.8(2)
C(62)-C(63)-C(68)-C(59)	-1.2(4)
C(64)-C(63)-C(68)-C(67)	-1.1(4)
C(62)-C(63)-C(68)-C(67)	177.5(2)
C(60)-C(59)-C(68)-C(63)	-0.6(4)
C(57)-C(59)-C(68)-C(63)	178.2(2)
C(60)-C(59)-C(68)-C(67)	-179.4(2)
C(57)-C(59)-C(68)-C(67)	-0.6(3)
C(66)-C(67)-C(68)-C(63)	1.8(4)
C(58)-C(67)-C(68)-C(63)	-177.9(2)
C(66)-C(67)-C(68)-C(59)	-179.4(2)
C(58)-C(67)-C(68)-C(59)	1.0(3)

Symmetry transformations used to generate equivalent atoms: