Supporting Information for

Enantioselective Synthesis of Carbo- and Heterocycles Through a CuH-Catalyzed Hydroalkylation Approach

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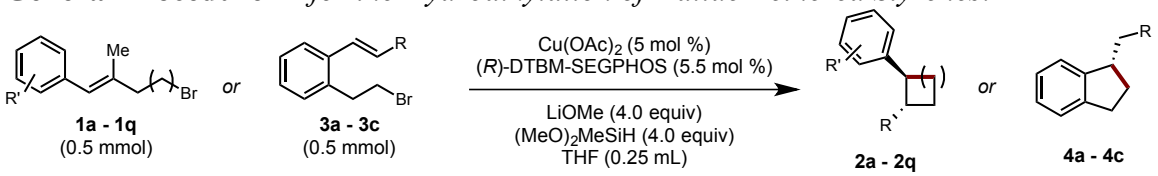
General Information:

General Reagent Information: THF and CH_2Cl_2 were dried and deoxygenated by passage through packed columns of neutral alumina and copper(II) oxide under a positive pressure of argon. Copper(II) acetate (99.999%, trace metal basis) was purchased from Sigma Aldrich and used as received. (*R*)- and (*S*)-DTBM-SEGPHOS was purchased from Takasago International Co. and Strem Chemical Co. and used as received. Tetrabutylammonium fluoride (1.0 M in THF), trimethylaluminum (2.0 M in hexanes), and diisobutylaluminum hydride (1.0 M in hexanes) were purchased from Sigma Aldrich in Sure/Seal® bottles and used as received. Dimethoxy(methyl)silane and diethoxy(methyl)silane was purchased from TCI and stored in a nitrogen-filled glove box at -20 °C. Lithium methoxide was purchased from Strem or Alfa Aesar and stored in a nitrogen-filled glove box. (*Note:* Lithium methoxide from other sources was found to exhibit poorer reactivity.) All other reagents and solvents were purchased from Oakwood, Combi-Blocks, Alfa Aesar, or Sigma Aldrich and used as received. Compounds were purified by flash column chromatography using SiliCycle *SiliaFlash® F60* silica gel, unless otherwise indicated.

General Analytical Information: New compounds were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. Copies of the ^{1}H NMR and ^{13}C NMR spectra can be found at the end of the Supporting Information. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz, Varian 500 MHz, or Bruker 600 MHz instrument. All ^{1}H NMR data are reported in δ units, parts per million (ppm), and were measured relative to the residual proton signal in the deuterated solvent at 7.26 ppm ($CDCl_3$) or 5.32 ppm (CD_2Cl_2). All ^{13}C NMR spectra are ^{1}H decoupled and reported in ppm relative to the solvent signal at 77.16 ppm ($CDCl_3$) or 53.84 ppm (CD_2Cl_2). IR spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer (iD5 ATR, diamond) and are reported in terms of frequency of absorption (cm^{-1}). Melting points were measured on a Mel-Temp capillary melting point apparatus. Achiral gas chromatography (GC) analyses were performed on an Agilent 7890A gas chromatograph with an FID detector using a J & W DB-1 column. Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates. Compounds were visualized by irradiation with UV light, or stained with iodine/silica gel, potassium permanganate, or phosphomolybdic acid (PMA). Yields refer to isolated compounds, unless otherwise indicated. The enantiomeric excesses (ee) of the products were determined by high-performance liquid chromatography (HPLC) analysis performed on Agilent 1200 Series chromatographs using a chiral column (25 cm) as noted for each compound or by GC on an Agilent 6850 gas chromatograph with an FID detector using a CP-Chirasil-Dex CB column. Copies of chiral HPLC and GC traces can be found at the end of the Supporting Information. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. High resolution mass spectra were obtained from on a Bruker Daltonics APEXIV 4.7 Tesla Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS).

General Procedure A *for the Hydroalkylation of Halide-Tethered Styrenes:*

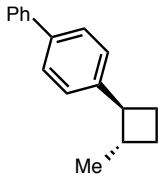


1a - 1q (0.5 mmol) | **3a - 3c** (0.5 mmol) | **2a - 2q** | **4a - 4c**

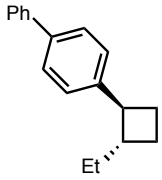
Preparation of the copper hydride solution: In a nitrogen-filled glove box, an oven-dried 4 mL vial equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (4.5 mg, 0.025 mmol, 5 mol%), (*R*)-DTBM-SEGPHOS (33 mg, 0.028 mmol, 5.5 mol %), and THF (0.25 mL). The vial was capped and stirred until a homogeneous, dark green solution was obtained (~10 min). Then, (dimethoxy)methylsilane (250 μL, 2.0 mmol, 4.0 equiv) was added, the vial was recapped, and the reaction mixture was stirred until a vibrant orange solution of L*CuH was obtained (~5 min).

Hydroalkylation: A flame-dried screw-cap reaction tube (16 mm × 125 mm, Fisherbrand 14-959-35A) equipped with a magnetic stir bar (1/2" × 5/16", cylindrical, no pivot ring) was capped with a Teflon/silicone septum (Thermo/National B7995-15) screw cap and flame dried under vacuum. The reaction tube was cooled under argon, charged with hydroalkylation substrate (0.5 mmol, 1.0 equiv), and recapped. The reaction tube was placed under vacuum for 5 min and transferred into the glove box. LiOMe (76 mg, 2.0 mmol, 4.0 equiv) and the prepared L*CuH solution were added in rapid succession, and the reaction tube was capped using a new septum and removed from the glove box. The reaction tube was placed in an oil bath, preheated to 55 °C, where it was stirred for 18 to 36 h at 750 rpm. (*Notes:* For consistent reactivity, powdery LiOMe should be used, with vigorous, but even stirring maintained during the course of the reaction. For certain substrates, reaction temperature was found to strongly affect the outcome and should therefore be carefully monitored). After completion of the reaction, as indicated by the reaction mixture becoming dark brown-black, the reaction mixture was allowed to cool to room temperature, diluted with CH_2Cl_2 (5 mL), and filtered through a plug of silica gel, eluting with CH_2Cl_2. The crude mixture was concentrated in vacuo and purified by flash column chromatography (100 g silica gel for 0.5 mmol of substrate) to provide the desired product. Yields reported are the average isolated yields on two runs.

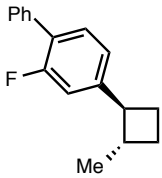
Characterization data for hydroalkylation products (2a – 2r, 4a – 4c):



4-((1*S*,2*S*)-2-Methylcyclobutyl)-1,1'-biphenyl (2a): Prepared following general procedure **A** using (*E*)-4-(4-bromo-2-methylbut-1-en-1-yl)-1,1'-biphenyl (**1a**, 150 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 36 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 0 to 2% Et_2O in pentane to provide the title compound as a colorless solid, **m.p.** 50–52 °C. **Yield**: 92 mg, 83%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 – 7.52 (m, 4H), 7.49 – 7.40 (m, 2H), 7.38 – 7.28 (m, 3H), 3.09 – 3.00 (m, 1H), 2.50 – 2.39 (m, 1H), 2.29 – 2.20 (m, 1H), 2.12 – 1.98 (m, 2H), 1.67 – 1.56 (m, 1H), 1.18 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.5, 141.3, 138.9, 128.9, 127.2, 127.1 (2 resonances), 48.4, 39.6, 26.7, 25.9, 21.2. **IR** (thin film) 2948, 2862, 1486, 1448, 1008, 833, 759, 731, 696 cm^{-1}. **EA** Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.55; H, 8.11. **Specific rotation** $[\alpha]_D^{24}$ = +74.8 (*c* = 1.0, $CHCl_3$). HPLC analysis (OJ column, 99:1 hexanes/ethanol, 0.7 mL/min, t_m = 57.4 min, t_M = 49.6 min) indicated **99% ee**.

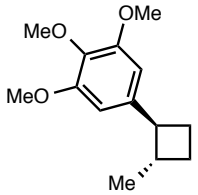


4-((1*S*,2*S*)-2-Ethylcyclobutyl)-1,1'-biphenyl (2b): Prepared following general procedure **A** using (*E*)-4-(4-bromo-2-ethylbut-1-en-1-yl)-1,1'-biphenyl (**1b**, 158 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 36 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 0 – 2% Et_2O in pentane to provide the title compound as a colorless oil. **Yield**: 97 mg, 82%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.56 – 7.50 (m, 2H), 7.45 – 7.39 (m, 2H), 7.35 – 7.28 (m, 3H), 3.13 – 3.04 (m, 1H), 2.37 – 2.27 (m, 1H), 2.27 – 2.20 (m, 1H), 2.09 – 1.94 (m, 2H), 1.69 – 1.54 (m, 2H), 1.51 – 1.40 (m, 1H), 0.83 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.9, 141.3, 138.9, 128.8, 127.3, 127.2, 127.1, 46.7, 46.0, 29.4, 26.1, 24.5, 11.5. **IR** (thin film) 1485, 834, 755, 729, 695 cm^{-1}. **EA** Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.21; H, 8.43. **Specific rotation** $[\alpha]_D^{24}$ = +52.2 (*c* = 1.0, $CHCl_3$). HPLC analysis (AD-H column, 99.5:0.5 pentane/isopropanol, 0.8 mL/min, t_m = 13.0 min, t_M = 10.1 min) indicated **98% ee**.

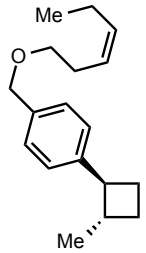


2-Fluoro-4-((1*S*,2*S*)-2-methylcyclobutyl)-1,1'-biphenyl (2c): Prepared following general procedure **A** using (*E*)-4-(4-bromo-2-methylbut-1-en-1-yl)-2-fluoro-1,1'-biphenyl

(**1c**, 160 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 24 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 0 – 2% Et_2O in pentane to provide the title compound as a colorless oil. **Yield**: 105 mg, 87%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 2H), 7.49 – 7.41 (m, 2H), 7.40 – 7.33 (m, 2H), 7.11 – 6.98 (m, 2H), 3.08 – 2.95 (m, 1H), 2.48 – 2.37 (m, 1H), 2.29 – 2.19 (m, 1H), 2.13 – 1.94 (m, 2H), 1.67 – 1.55 (m, 1H), 1.18 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.9 (d, J_{CF} = 247 Hz), 147.2 (d, J_{CF} = 7.3 Hz), 136.1, 130.5 (d, J_{CF} = 3.9 Hz), 129.1 (d, J_{CF} = 2.8 Hz), 128.5, 127.5, 126.5 (d, J_{CF} = 13.7 Hz), 122.6 (d, J_{CF} = 3.0 Hz), 114.2 (d, J_{CF} = 22.5 Hz), 48.2, 39.5, 26.6, 25.8, 21.1. **IR** (thin film) 1483, 1413, 1129, 866, 826, 764, 722, 695 cm^{-1}. **EA** Calcd. for $C_{17}H_{17}F$: C, 84.96; H, 7.13. Found: C, 84.67; H, 7.29. **Specific rotation** $[\alpha]_D^{24}$ = +69.9 (c = 1.0, $CHCl_3$). HPLC analysis (OJ then OJ-H then OJ columns in series, 99.5:0.5 pentane/ethanol, 0.5 mL/min, t_m = 52.8 min, t_M = 54.4 min) indicated **99% ee**.

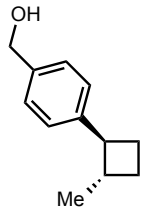


1,2,3-Trimethoxy-5-((1*S*,2*S*)-2-methylcyclobutyl)benzene (2d): Prepared following general procedure **A** using (*E*)-5-(4-bromo-2-methylbut-1-en-1-yl)-1,2,3-trimethoxybenzene (**1d**, 160 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 30 h, and the crude residue was purified by flash column chromatography, eluting with 5% EtOAc in hexanes to provide the title compound as a colorless oil. **Yield**: 55 mg, 47%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.43 (s, 2H), 3.87 (s, 6H), 3.83 (s, 3H), 2.96 – 2.85 (m, 1H), 2.42 – 2.30 (m, 1H), 2.24 – 2.13 (m, 1H), 2.07 – 1.88 (m, 2H), 1.58 – 1.48 (m, 1H), 1.14 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.2, 141.2, 136.2, 103.5, 61.0, 56.2, 49.1, 39.5, 26.4, 26.1, 21.1. **IR** (thin film) 1585, 1506, 1451, 1416, 1237, 1127, 1013 cm^{-1}. **EA** Calcd. for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.29; H, 8.40. **Specific rotation** $[\alpha]_D^{24}$ = +55.1 (c = 1.0, $CHCl_3$). HPLC analysis (OD-H column, 98:2 hexanes/isopropanol, 0.5 mL/min, t_m = 15.0 min, t_M = 15.7 min) indicated **97% ee**.

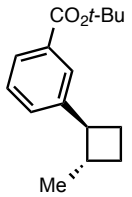


1-((((*Z*)-Hex-3-en-1-yl)oxy)methyl)-4-((1*S*,2*S*)-2-methylcyclobutyl)benzene (2e): Prepared following general procedure **A** using 1-((*E*)-4-bromo-2-methylbut-1-en-1-yl)-4-((((*Z*)-hex-3-en-1-yl)oxy)methyl)benzene (**1e**, 168 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 24 h, and the crude residue was purified by flash column chromatography, eluting with 2.5% MTBE in hexanes to provide the title

compound as a colorless oil. **Yield**: 89 mg, 69%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 5.50 (ddd, J = 12.6, 9.8, 7.1 Hz, 1H), 5.39 (ddd, J = 10.8, 9.8, 7.1 Hz, 1H), 4.52 (s, 2H), 3.50 (t, J = 7.1 Hz, 2H), 3.05 – 2.94 (m, 1H), 2.48 – 2.32 (m, 3H), 2.28 – 2.16 (m, 1H), 2.16 – 1.93 (m, 4H), 1.67 – 1.54 (m, 1H), 1.16 (d, J = 6.6 Hz, 3H), 1.00 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.7, 136.1, 133.7, 127.8, 126.6, 125.0, 72.9, 70.1, 48.5, 39.5, 28.0, 26.7, 25.8, 21.1, 20.8, 14.4. **IR** (thin film) 2959, 2861, 1452, 1358, 1095, 1020, 815, 731 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{18}H_{26}O + NH_4]^+$: 276.2322. Found: 276.2316. **Specific rotation** $[\alpha]_D^{24}$ = +41.9 (c = 1.0, $CHCl_3$). HPLC analysis (IC column, 98:2 hexanes/isopropanol, 0.8 mL/min, t_m = 5.9 min, t_M = 5.5 min) indicated **97% ee**.



(3-((1*S*,2*S*)-2-Methylcyclobutyl)phenyl)methanol (2f): Prepared following general procedure **A** with changes as noted below. (*E*)-(3-(4-bromo-2-methylbut-1-en-1-yl)phenyl)methanol (**1f**, 128 mg, 0.5 mmol, 1.0 equiv), 4.8 equiv. dimethoxy(methyl)silane (300 µL, 2.4 mmol) and 0.20 mL THF were used. The reaction mixture was stirred for 10 min at room temperature before the reaction tube was transferred to an oil bath at 55 °C and stirred for 24 h. After the reaction mixture was diluted with dichloromethane, a saturated solution of ammonium fluoride in methanol (2 mL) was added dropwise, and the reaction mixture was stirred for 5 min. The crude residue was filtered through a plug of SiO_2 (dichloromethane), carefully concentrated (volatile), and purified by flash column chromatography, eluting with a gradient of 25% to 33% Et_2O in pentane to provide the title compound as a colorless oil. **Yield**: 60 mg, 68%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.15 (m, 4H), 4.72 (s, 2H), 3.08 – 2.96 (m, 1H), 2.51 – 2.36 (m, 1H), 2.31 – 2.16 (m, 1H), 2.12 – 1.95 (m, 2H), 1.74 – 1.51 (m, 2H), 1.18 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8, 140.9, 128.6, 126.1, 125.4, 124.7, 65.7, 48.7, 39.4, 26.7, 25.9, 21.1.**IR** (thin film) 3336, 2949, 2862, 1451, 1020, 798, 780, 700 cm^{-1}. **EA** Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.49; H, 9.36. **Specific rotation** $[\alpha]_D^{24}$ = +34.6 (c = 0.4, $CHCl_3$). HPLC analysis (OD-H column, 95:5 hexanes/isopropanol, 0.8 mL/min, t_m = 12.5 min, t_M = 11.0 min) indicated **97% ee**.

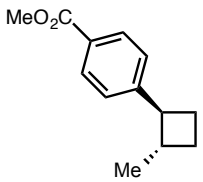


***tert*-Butyl 3-((1*S*,2*S*)-2-methylcyclobutyl)benzoate (2g):** Prepared following general procedure **A** was using *tert*-butyl (*E*)-4-(4-bromo-2-methylbut-1-en-1-yl)benzoate (**1g**, 163 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 24 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of

2.5 to 5% Et_2O in pentane to provide the title compound as a colorless oil. **Yield**: 91 mg, 74%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 2H), 7.39 – 7.29 (m, 2H), 3.06 – 2.95 (m, 1H), 2.49 – 2.33 (m, 1H), 2.29 – 2.14 (m, 1H), 2.11 – 1.91 (m, 2H), 1.70 – 1.52 (m, 10H), 1.15 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.2, 145.5, 132.0, 130.9, 128.2, 127.6, 127.1, 81.0, 48.4, 39.4, 28.3, 26.7, 25.9, 21.1. **IR** (thin film) 2971, 1713, 1368, 1295, 1257, 1162, 1111, 753 cm^{-1}. **EA** Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.78; H, 8.91. **Specific rotation** $[\alpha]_D^{24}$ = +51.3 (c = 1.0, $CHCl_3$).

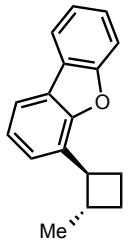
To determine the enantiomeric excess, the corresponding benzyl alcohol was prepared. An aliquot (20 mg, 0.081 mmol, 1.0 equiv) of the desired product in CH_2Cl_2 (5 mL) was treated with DIBAL-H (25 wt. % in toluene) (0.5 mL, large excess) at room temperature. The reaction mixture was stirred for 5 min before a saturated aqueous solution of Na_2SO_4 (1 mL) was carefully added, and the reaction mixture was stirred for an additional 10 min. The solid precipitate was removed by filtration through a medium porosity sintered funnel, and the filtrate was concentrated and purified by preparative thin layer chromatography (5:1 hexanes/EtOAc) to afford benzyl alcohol **2f** (7.0 mg, 49% yield). HPLC analysis (OD-H column, 95:5 hexanes/isopropanol, 0.8 mL/min, t_m = 12.5 min, t_M = 11.0 min) indicated **98% ee**.

4.0 mmol-scale synthesis of **2g**: In a nitrogen-filled glove box, an oven-dried 20 mL vial was charged with $Cu(OAc)_2$ (36.3 mg, 0.20 mmol, 0.05 equiv) and (*R*)-DTBM-SEGPHOS (260 mg, 0.22 mmol, 0.055 equiv) and THF (1.0 mL). The vial was capped, and the suspension was stirred until a homogeneous forest-green solution was obtained (~15 min). Dimethoxy(methyl)silane (2.0 mL, 16.2 mmol, 4.05 equiv) was added, the vial was recapped, and the reaction mixture was stirred until a vibrant orange solution of L*CuH was obtained (~5 min). Meanwhile, an oven-dried thick-walled reaction tube (14 mL, Ace 8648-124) equipped with a Teflon plug and stir bar (3/8'' × 3/16'', cylindrical, no pivot ring) was cooled in a desiccator and charged with **1g** (1.30 g, 4.0 mmol, 1.0 equiv). The reaction tube was transferred into the glove box, and LiOMe (608 mg, 16 mmol, 4.0 equiv) and the prepared L*CuH solution were added in rapid succession. The reaction tube was sealed with the Teflon plug and transferred out of the glove box. The reaction mixture was stirred in an oil bath preheated to 55 °C for 36 h at 1000 rpm. Subsequently, the reaction tube was allowed to cool to room temperature, and the reaction mixture was filtered through a plug of SiO_2 gel (CH_2Cl_2) and concentrated to afford the crude product, which was purified by flash column chromatography (pentane to 5% Et_2O in pentane) to provide the title compound. **Yield:** 764 mg, 78%. HPLC analysis on the corresponding benzyl alcohol indicated **98% ee**.

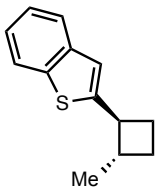


Methyl 4-((1*S*,2*S*)-2-methylcyclobutyl)benzoate (2h): Prepared following general procedure **A** with changes as noted below. Methyl (*E*)-4-(4-bromo-2-methylbut-1-en-1-yl)benzoate (**1h**, 142 mg, 0.5 mmol, 1.0 equiv), 2.4 equiv dimethoxy(methyl)silane (150 μL, 1.2 mmol), and 0.35 mL THF were used. The reaction mixture was quenched after 24 h, and the crude residue was purified by flash column chromatography, eluting with 5% Et_2O in pentane to provide the title compound as a colorless oil. **Yield:** 60 mg, 59%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 3.90 (s, 3H), 3.10 – 2.95 (m, 1H), 2.47 – 2.33 (m, 1H), 2.31 – 2.15 (m, 1H), 2.10 – 1.91 (m, 2H), 1.65 – 1.54 (m, 1H), 1.15 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.3, 150.8, 129.8, 127.8, 126.6, 52.1, 48.6, 39.4, 26.7, 25.6, 21.1. **IR** (thin film) 2949, 1720, 1610, 1435, 1275, 1177, 1110, 1019, 704 cm^{-1}. **EA** Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.69; H, 8.06. **Specific rotation** $[\alpha]_D^{24}$ = +68.7 (*c* = 0.4, $CHCl_3$). HPLC analysis (AD-H column, 95:5 hexanes/isopropanol, 0.8 mL/min, t_m = 7.7 min, t_M = 7.4 min) indicated **98% ee**.

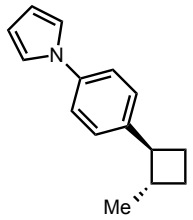


4-((1*S*,2*S*)-2-Methylcyclobutyl)dibenzo[*b*,*d*]furan (2i): Prepared following general procedure **A** using (*E*)-4-(4-bromo-2-methylbut-1-en-1-yl)dibenzo[*b*,*d*]furan (**1i**, 158 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 36 h, and the crude residue was purified by flash column chromatography, eluting with pentane to provide the title compound as a colorless oil. **Yield:** 103 mg, 87%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.40 – 7.29 (m, 3H), 3.62 – 3.50 (m, 1H), 2.78 – 2.64 (m, 1H), 2.45 – 2.33 (m, 1H), 2.29 – 2.11 (m, 2H), 1.77 – 1.66 (m, 1H), 1.26 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.2, 154.5, 129.3, 127.0, 124.9, 124.6, 123.9, 122.8, 122.6, 120.8, 118.2, 111.8, 43.3, 38.4, 27.1, 25.4, 21.3. **IR** (thin film) 2948, 1450, 1420, 1183, 843, 747 cm^{-1}. **EA** Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.17; H, 6.98. **Specific rotation** $[\alpha]_D^{24}$ = +48.0 (*c* = 1.0, $CHCl_3$). HPLC analysis (OJ column, 98:2 hexanes/isopropanol, 0.8 mL/min, t_m = 6.7 min, t_M = 6.0 min) indicated **98% ee**.

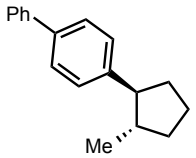


2-((1*S*,2*S*)-2-Methylcyclobutyl)benzo[*b*]thiophene (2j): Prepared following general procedure **A** using (*E*)-2-(4-bromo-2-methylbut-1-en-1-yl)benzo[*b*]thiophene (**1j**, 140 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 24 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 0 to 2% Et_2O in pentane to provide the title compound as a colorless solid, **m.p.** 37–39 °C. **Yield**: 80 mg, 79%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.28 – 7.22 (m, 1H), 7.00 (s, 1H), 3.28 – 3.18 (m, 1H), 2.56 – 2.42 (m, 1H), 2.38 – 2.28 (m, 1H), 2.16 – 2.03 (m, 2H), 1.67 – 1.55 (m, 1H), 1.18 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.5, 140.3, 139.2, 124.2, 123.5, 122.9, 122.4, 118.7, 44.6, 41.0, 27.3, 26.7, 20.7. **IR** (thin film) 2947, 1457, 1436, 819, 742, 577 cm^{-1}. **EA** Calcd. for $C_{13}H_{14}S$: C, 77.18; H, 6.98. Found: C, 77.08; H, 6.85. **Specific**

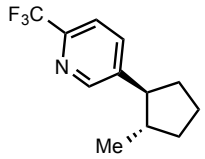
rotation $[\alpha]_D^{24}$ = +95.6 (*c* = 0.8, $CHCl_3$). HPLC analysis (OJ-H column, pentane, 0.8 mL/min, t_m = 25.2 min, t_M = 27.1 min) indicated **99% ee**.



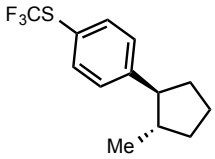
1-(4-((1*S*,2*S*)-2-Methylcyclobutyl)phenyl)-1*H*-pyrrole (2k): Prepared following general procedure **A** using (*E*)-1-(4-(4-bromo-2-methylbut-1-en-1-yl)phenyl)-1*H*-pyrrole (**1k**, 145 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 36 h, and the crude residue was purified by flash column chromatography, eluting with hexanes to provide the title compound as a colorless solid, **m.p.** 54–56 °C. **Yield**: 100 mg, 95%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.07 (s, 2H), 6.34 (s, 2H), 3.04 – 2.96 (m, 1H), 2.45 – 2.35 (m, 1H), 2.27 – 2.19 (m, 1H), 2.10 – 1.93 (m, 2H), 1.65 – 1.54 (m, 1H), 1.16 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.0, 138.9, 127.7, 120.7, 119.6, 110.2, 48.2, 39.6, 26.7, 26.0, 21.1. **IR** (thin film) 2953, 1522, 1325, 1071, 823, 717 cm^{-1}. **EA** Calcd. for $C_{15}H_{17}N$: C, 85.26; H, 8.11. Found: C, 84.96; H, 8.18. **Specific rotation** $[\alpha]_D^{24}$ = +76.7 (*c* = 1.0, $CHCl_3$). HPLC analysis (OJ column, 99:1 hexanes/isopropanol, 0.8 mL/min, t_m = 11.1 min, t_M = 11.7 min) indicated **99% ee**.



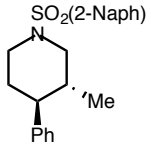
4-((1*S*,2*S*)-2-Methylcyclopentyl)-1,1'-biphenyl (2l): Prepared following general procedure **A** using (*E*)-4-(4-bromo-2-methylpent-1-en-1-yl)-1,1'-biphenyl (**1l**, 158 mg, 0.5 mmol, 1.0 equiv) at a reaction temperature of 45 °C. The reaction mixture was quenched after 36 h, and the crude residue was purified by flash column chromatography, eluting with cyclohexane to provide the title compound as a colorless oil. **Yield**: 87 mg, 74%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 – 7.49 (m, 4H), 7.49 – 7.37 (m, 2H), 7.37 – 7.27 (m, 3H), 2.53 – 2.40 (m, 1H), 2.16 – 2.07 (m, 1H), 2.07 – 1.91 (m, 2H), 1.85 – 1.70 (m, 3H), 1.42 – 1.28 (m, 1H), 0.97 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.8, 141.3, 138.9, 128.8, 128.1, 127.2, 127.1, 127.1, 54.3, 43.2, 35.6, 35.0, 24.1, 18.8. **IR** (thin film) 2953, 1522, 1325, 1071, 823, 717 cm^{-1}. **EA** Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.19; H, 8.53. **Specific rotation** $[\alpha]_D^{24}$ = +50.0 (*c* = 0.5, $CHCl_3$). GC analysis (CP-Chirasil-Dex CB column, 25 m × 0.25 mm × 0.25 μm, H_2 2.7 mL/min, 165 °C (constant), t_m = 176.1 min, t_M = 173.6 min) indicated **98% ee**.



5-((1*S*,2*S*)-2-methylcyclopentyl)-2-(trifluoromethyl)pyridine (2m): Prepared following general procedure **A** using (*E*)-5-(5-bromo-2-methylpent-1-en-1-yl)-2-(trifluoromethyl)pyridine (**1m**, 154 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 36 h, and the crude residue was purified by flash column chromatography, eluting with a gradient of 0 – 2% Et_2O in hexanes to provide the title compound as a colorless oil. The title product was somewhat volatile. **Yield**: 99 mg, 84%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.68 (d, J = 7.9 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 2.57 – 2.47 (m, 1H), 2.20 – 2.10 (m, 1H), 2.10 – 2.00 (m, 1H), 2.00 – 1.89 (m, 1H), 1.89 – 1.67 (m, 3H), 1.42 – 1.32 (m, 1H), 0.94 (d, J = 6.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.9, 146.2 (q, J_{CF} = 34.3 Hz), 144.3, 135.9, 121.9 (d, J_{CF} = 274 Hz), 120.4, 51.8, 43.5, 35.3, 34.8, 24.1, 18.4. **IR** (thin film) 2957, 1339, 1176, 1137, 1087 cm^{-1}. **EA** Calcd. for $C_{12}H_{14}F_3N$: C, 62.87; H, 6.16. Found: C, 62.71; H, 6.32. **Specific rotation** $[\alpha]_D^{24}$ = +16.3 (c = 1.0, $CHCl_3$). GC analysis (CP-Chirasil-Dex CB column, 25 m × 0.25 mm × 0.25 μm, H_2 2.7 mL/min, 50 °C to 150 °C @ 4 °C/min then 150 °C (constant), t_m = 28.9 min, t_M = 28.2 min) indicated **97% ee**.

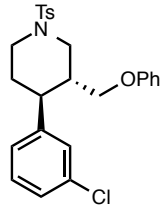


(4-((1*S*,2*S*)-2-methylcyclopentyl)phenyl)(trifluoromethyl)sulfane (2n): Prepared following general procedure **A** using (*E*)-(4-(5-bromo-2-methylpent-1-en-1-yl)phenyl)(trifluoromethyl)sulfane (**1n**, 169 mg, 0.5 mmol, 1.0 equiv) at a reaction temperature of 50 °C. The reaction mixture was quenched after 20 h, and the crude residue was purified by flash column chromatography, eluting with cyclohexane to provide the title compound as a colorless oil. **Yield**: 92 mg, 71%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.53 (m, 2H), 7.37 – 7.19 (m, 2H), 2.52 – 2.41 (m, 1H), 2.19 – 2.08 (m, 1H), 2.08 – 1.98 (m, 1H), 1.98 – 1.87 (m, 1H), 1.86 – 1.67 (m, 3H), 1.41 – 1.27 (m, 1H), 0.95 (d, J = 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.1, 136.6, 129.9 (q, *JCF* = 308 Hz), 128.8, 121.3, 54.4, 43.4, 35.5, 34.9, 24.1, 18.7. **IR** (thin film) 2955, 1110, 1086, 1016, 825, 756 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{13}H_{15}F_3S]^+$: 260.0841. Found: 260.0853. **Specific rotation** $[\alpha]_D^{23}$ = +37.5 (c = 0.8, $CHCl_3$). GC analysis (CP-Chirasil-Dex CB column, 25 m × 0.25 mm × 0.25 μm, H_2 2.7 mL/min, 50 °C to 150 °C @ 4 °C/min then 150 °C (constant), t_m = 30.1 min, t_M = 29.5 min) indicated **98% ee**.

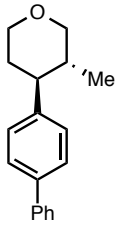


(3*R*,4*S*)-3-Methyl-1-(naphthalen-2-ylsulfonyl)-4-phenylpiperidine (2o): Prepared following general procedure **A** using (*E*)-*N*-(2-bromoethyl)-*N*-(2-methyl-3-phenylallyl)naphthalene-2-sulfonamide (**1o**, 222 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 36 h, and the crude residue was purified by flash column chromatography, eluting with 60% CH_2Cl_2 in hexanes to provide the title compound as a colorless solid, **m.p.** 146 – 148 °C. **Yield**: 131 mg, 72%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ

8.38 (s, 1H), 8.01 (d, J = 8.5 Hz, 2H), 7.95 (d, J = 8.1 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.74 – 7.60 (m, 2H), 7.34 – 7.24 (m, 2H), 7.24 – 7.17 (m, 1H), 7.07 (d, J = 7.2 Hz, 2H), 4.10 – 3.91 (m, 2H), 2.46 – 2.30 (m, 1H), 2.14 – 1.78 (m, 5H), 0.64 (d, J = 5.7 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.8, 135.0, 133.5, 132.4, 129.4, 129.3, 129.1, 128.9, 128.7, 128.1, 127.7, 127.6, 126.8, 123.2, 53.4, 49.9, 47.2, 36.3, 33.8, 17.1. **IR** (thin film) 1347, 1336, 1162, 1132, 751, 702, 656, 647 cm^{-1}. **EA** Calcd. for $C_{22}H_{23}NO_2S$: C, 72.30; H, 6.34. Found: C, 72.17; H, 6.28. **Specific rotation** $[\alpha]_D^{26}$ = +31.1 (c = 1.0, $CHCl_3$). HPLC analysis (IA column, 90:10 hexanes/isopropanol, 0.8 mL/min, t_m = 15.0 min, t_M = 14.2 min) indicated **99% ee**.

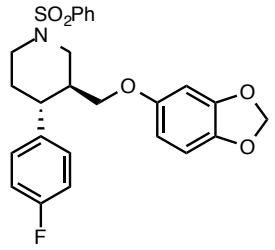


(3*R*,4*S*)-4-(3-Chlorophenyl)-3-(phenoxymethyl)-1-tosylpiperidine (2p): Prepared following general procedure **A** using (*Z*)-*N*-(2-bromoethyl)-*N*-(3-(3-chlorophenyl)-2-(phenoxymethyl)allyl)-4-methylbenzenesulfonamide (**1p**, 268 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 30 h, and the crude residue was purified by flash column chromatography, eluting with 12% EtOAc in hexanes to provide the title compound as a colorless solid, **m.p.** 112 – 116 °C. **Yield**: 150 mg, 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.29 – 7.16 (m, 4H), 7.10 (s, 1H), 7.05 – 6.97 (m, 1H), 6.92 (t, J = 7.3 Hz, 1H), 6.72 (d, J = 7.9 Hz, 2H), 4.23 – 4.12 (m, 1H), 4.01 – 3.90 (m, 1H), 3.68 (dd, J = 9.6, 2.3 Hz, 1H), 3.48 (dd, J = 9.6, 6.2 Hz, 1H), 2.53 – 2.42 (m, 4H), 2.42 – 2.25 (m, 3H), 1.99 – 1.82 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 145.0, 143.8, 134.8, 133.4, 130.2, 129.9, 129.6, 127.9, 127.6, 127.4, 125.8, 121.2, 114.6, 67.6, 49.6, 46.8, 43.9, 41.4, 33.3, 21.7. **IR** (thin film) 1597, 1338, 1241, 1161, 751, 693, 669, 658 cm^{-1}. **EA** Calcd. for $C_{25}H_{26}ClNO_3S$: C, 65.85; H, 5.75. Found: C, 65.60; H, 5.73. **Specific rotation** $[\alpha]_D^{26}$ = +125 (c = 1.0, $CHCl_3$). HPLC analysis (IA column, 90:10 hexanes/isopropanol, 0.8 mL/min, t_m = 16.7 min, t_M = 21.4 min) indicated **95% ee**.

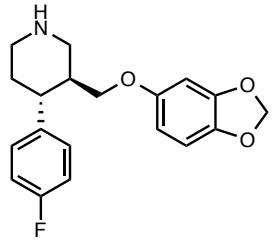


(3*R*,4*S*)-4-([1,1'-Biphenyl]-4-yl)-3-methyltetrahydro-2*H*-pyran (2q): Prepared following general procedure **A** was followed using (*E*)-4-(3-(2-bromoethoxy)-2-methylprop-1-en-1-yl)-1,1'-biphenyl (**1q**, 166 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 36 h, and the crude residue was purified by flash column chromatography, eluting with 2.5% EtOAc in hexanes to provide the title compound as a colorless oil. **Yield**: 74 mg, 59%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.55 (d, J = 8.1 Hz, 2H), 7.44 (t, J = 7.7 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.29 – 7.24 (m, 2H), 4.09 (dd, J = 11.3, 4.1 Hz, 1H), 4.00 (dd, J = 11.4, 4.2 Hz, 1H), 3.56 – 3.48 (m, 1H),

3.14 (t, J = 11.1 Hz, 1H), 2.33 (td, J = 11.7, 3.8 Hz, 1H), 2.01 – 1.84 (m, 2H), 1.79 – 1.69 (m, 1H), 0.66 (d, J = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.7, 141.1, 139.4, 128.9, 128.1, 127.3, 127.2, 127.1, 74.7, 68.8, 49.6, 36.8, 34.9, 15.1. **IR** (thin film) 2949, 1486, 1134, 1087, 1007, 885, 763, 697 cm^{-1}. **EA** Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.74; H, 7.82. **Specific rotation** $[\alpha]_D^{24}$ = +32.8 (c = 0.4, $CHCl_3$). HPLC analysis (IA column, 97:3 hexanes/isopropanol, 0.8 mL/min, t_m = 8.8 min, t_M = 7.8 min) indicated **93% ee**.

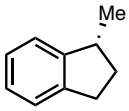


(3*S*,4*R*)-3-((Benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)-1-(phenylsulfonyl)piperidine (2r): Prepared following general procedure **A** using (*Z*)-*N*-(2-((benzo[*d*][1,3]dioxol-5-yloxy)methyl)-3-(4-fluorophenyl)allyl)-*N*-(2-bromoethyl)-benzenesulfonamide (**1r**, 335 mg, 0.5 mmol, 1.0 equiv) and (*S*)-DTBM-SEGPHOS (33 mg, 0.028 mmol, 5.5 mol %). The reaction mixture was quenched after 36 h, and the crude residue was purified by flash column chromatography, eluting with 33% Et_2O in pentane to provide the title compound as an off-white gum. **Yield**: 148 mg, 63%. Spectral data were in agreement with those reported in the literature.[1] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.66 – 7.60 (m, 1H), 7.60 – 7.53 (m, 2H), 7.12 – 7.03 (m, 2H), 7.01 – 6.92 (m, 2H), 6.65 – 6.58 (m, 1H), 6.35 – 6.29 (m, 1H), 6.14 – 6.07 (m, 1H), 5.88 (s, 2H), 4.18 – 4.11 (m, 1H), 4.01 – 3.92 (m, 1H), 3.58 (dd, J = 9.5, 2.2 Hz, 1H), 3.39 (dd, J = 9.4, 6.6 Hz, 1H), 2.50 – 2.43 (m, 1H), 2.41 – 2.30 (m, 2H), 2.29 – 2.18 (m, 1H), 1.98 – 1.83 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.8 (d, J_{CF} = 245 Hz), 154.1, 148.3, 141.9, 138.4 (d, J_{CF} = 3.2 Hz), 136.3, 133.0, 129.3, 128.9 (d, J_{CF} = 7.7 Hz), 127.9, 115.8 (d, J_{CF} = 21.2 Hz), 108.0, 105.6, 101.3, 98.1, 68.6, 49.6, 46.8, 43.2, 41.8, 33.4. **Specific rotation** $[\alpha]_D^{24}$ = –85.2 (c = 0.8, MeOH). HPLC analysis (IA column, 85:15 hexanes/isopropanol, 0.8 mL/min, t_m = 23.8 min, t_M = 15.8 min) indicated **99% ee**.

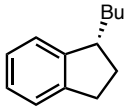


(-)-Paroxetine: To a solution of SmI_2 in THF (0.1 M, 11 mL, 10 equiv) under argon was added a solution of **2r** (50 mg, 0.107 mmol, 1.0 equiv) in anhydrous THF (0.5 mL). Water (0.06 mL, 3.3 mmol, 30 equiv) and pyrrolidine (0.18 mL, 2.2 mmol, 20 equiv) were added sequentially. The reaction mixture was stirred for 5 min at room temperature, upon which the reaction mixture was poured into ether (20 mL) and water (10 mL). The organic and aqueous phases were separated, and the aqueous phase was extracted with additional ether (4 × 10 mL). The combined organic phases were dried (Na_2SO_4) and

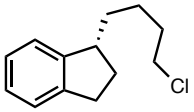
concentrated to afford the crude product, which was purified by preparative thin layer chromatography (10% Et_3N in EtOAc) to afford (-)-paroxetine as a yellow oil. **Yield**: 21.5 mg, 61% yield. Spectral data were in agreement with those reported in the literature.[2] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 2H), 7.04 – 6.92 (m, 2H), 6.62 (d, J = 8.5 Hz, 1H), 6.33 (d, J = 2.5 Hz, 1H), 6.12 (dd, J = 8.5, 2.5 Hz, 1H), 5.87 (s, 2H), 3.57 (dd, J = 9.4, 3.0 Hz, 1H), 3.48 – 3.37 (m, 2H), 3.24 – 3.11 (m, 1H), 2.83 – 2.52 (m, 3H), 2.11 – 2.00 (m, 1H), 1.87 – 1.63 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.6 (d, J_{CF} = 244 Hz), 154.5, 148.3, 141.7, 140.1 (d, J_{CF} = 3.2 Hz), 128.9 (d, J_{CF} = 7.8 Hz), 115.5 (d, J_{CF} = 21.0 Hz), 108.0, 105.6, 101.2, 98.1, 69.7, 50.6, 47.3, 44.8, 43.2, 35.6. **Specific rotation** $[\alpha]_D^{24}$ = –80.1 (c = 1.0, MeOH), lit. (ref. 2): $[\alpha]_D^{24}$ = –90.7 (c = 1.0, MeOH).



(*R*)-1-Methylindane (4a): Prepared following general procedure **A** with changes as noted below. 2-(2-Bromoethyl)styrene (**3a**, 106 mg, 0.5 mmol, 1.0 equiv), 2.4 equiv dimethoxy(methyl)silane (150 μL, 1.2 mmol), and 0.35 mL THF were used at a reaction temperature of 50 °C. The reaction mixture was quenched after 18 h, and the crude residue was purified by preparative thin layer chromatography, using pentane as the eluent. The title compound was obtained after careful concentration from CH_2Cl_2 as a colorless oil. **Yield**: 46 mg, 70%. Spectral data were in agreement with those reported in the literature.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.06 (m, 4H), 3.28 – 3.09 (m, 1H), 2.99 – 2.76 (m, 2H), 2.43 – 2.22 (m, 1H), 1.69 – 1.48 (m, 1H), 1.30 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.9, 144.0, 126.2 (2 resonances), 124.5, 123.3, 39.6, 34.9, 31.6, 20.0. **Specific rotation** $[\alpha]_D^{24}$ = +2.35 (c = 1.0, $CHCl_3$). GC analysis (CP-Chirasil-Dex CB column, 25 m × 0.25 mm × 0.25 μm, H_2 2.7 mL/min, 120 °C to 220 °C @ 0.5 °C/min, t_m = 57.8 min, t_M = 58.3 min) indicated **88% ee**.



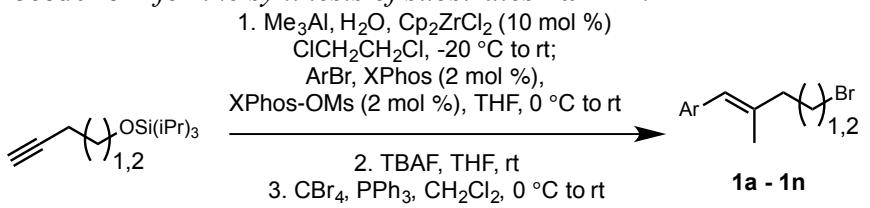
(*R*)-1-Butylindane (4b): Prepared following general procedure **A** using (*E*)-1-(2-bromoethyl)-2-(pent-1-en-1-yl)benzene (**3b**, 126 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was quenched after 36 h, and the crude residue was purified by flash column chromatography, eluting with pentane to provide the title compound as a colorless oil. **Yield**: 80 mg, 92%. Spectral data were in agreement with those reported in the literature.[4] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.20 – 7.13 (m, 2H), 3.17 – 3.06 (m, 1H), 3.00 – 2.89 (m, 1H), 2.89 – 2.80 (m, 1H), 2.36 – 2.24 (m, 1H), 1.95 – 1.80 (m, 1H), 1.77 – 1.63 (m, 1H), 1.51 – 1.33 (m, 5H), 1.00 – 0.91 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.0, 144.2, 126.3, 126.1, 124.5, 123.7, 45.0, 34.9, 32.3, 31.6, 30.1, 23.1, 14.3. **Specific rotation** $[\alpha]_D^{24}$ = –12.8 (c = 1.0, $CHCl_3$). HPLC analysis (OD-H then OD-H then OD columns in series, 98.5:1.5 hexanes/isopropanol, 0.7 mL/min, t_m = 16.8 min, t_M = 16.3 min) indicated **85% ee**.



(*R*)-1-(4-Chlorobutyl)indane (4c): Prepared following general procedure **A** using (*E*)-1-(2-bromoethyl)-2-(5-chloropent-1-en-1-yl)benzene (**3c**, 144 mg, 0.5 mmol, 1.0 equiv) at 50 °C. (The starting material used was contaminated with 4% of the corresponding alkyne. The yield reported is not corrected.) The crude residue was purified by flash column chromatography, eluting with hexanes to provide the title compound as a colorless oil. **Yield**: 73 mg, 70%. Spectral data were in agreement with those reported in the literature.[5] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.14 (m, 4H), 3.63 – 3.56 (m, 2H), 3.18 – 3.08 (m, 1H), 2.99 – 2.92 (m, 1H), 2.90 – 2.81 (m, 1H), 2.38 – 2.26 (m, 1H), 1.94 – 1.82 (m, 3H), 1.75 – 1.67 (m, 1H), 1.64 – 1.54 (m, 2H), 1.50 – 1.41 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.5, 144.1, 126.4, 126.2, 124.6, 123.6, 45.2, 44.8, 34.4, 33.0, 32.2, 31.5, 25.1. **Specific rotation** $[\alpha]_D^{24}$ = +3.01 (*c* = 0.3, $CHCl_3$). HPLC analysis (OD-H column, hexanes, 0.8 mL/min, t_m = 13.0 min, t_M = 14.0 min) indicated **85% ee**.

Experimental procedures and characterization of substrates:

General Procedure B *for the synthesis of substrates* **1a – 1n***:*



Caution: Me_3Al is pyrophoric and should only be used by an experienced individual with appropriate safety precautions.

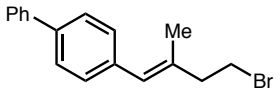
Step 1: A 50 mL round bottom flask (24/40 joint), equipped with a magnetic stir bar and rubber septum, was charged with Cp_2ZrCl_2 (584 mg, 2.0 mmol, 10 mol %) and 1,2-dichloroethane (10 mL) and placed under argon. The flask was cooled to –20 °C (ice/salt bath), and Me_3Al (2.0 M in hexanes, 16 mL, 32 mmol, 1.6 equiv) was slowly added via syringe. Water (36 μL, 1.0 mmol, 0.1 equiv) was carefully added to the yellow solution (*Caution: vigorous reaction!*), and the reaction mixture was stirred for an additional 5 min at –20 °C. (But-3-yn-1-yloxy)triisopropylsilane or (pent-4-yn-1-yloxy)triisopropylsilane (24 mmol, 1.2 equiv) was then added by syringe. The reaction mixture was stirred for 2 h at room temperature. The septum was exchanged for a 24/40 hose adapter, which was connected to an external trap cooled in a dry ice/acetone bath. Solvent and excess Me_3Al were removed by placement of the external trap under vacuum until a yellow paste remained in the round bottom flask. After backfilling with argon, the flask was sealed with a rubber septum and cooled to 0 °C. (*Caution: The quenching of Me_3Al can be extremely exothermic and should be carried out with all necessary safety precautions*. *Quench procedure: While still immersed in the dry ice/acetone bath, the trap was detached from the vacuum line, and CH_2Cl_2 (50 mL) was added into the trap. This was followed by the dropwise addition of MeOH (20 mL). Finally, the trap was allowed to slowly warm to room temperature overnight.*) To the flask containing the vinylaluminum reagent at 0 °C was added a solution of aryl halide (20 mmol, 1.0 equiv), XPhos-OMs (G3) precatalyst (338 mg, 0.4 mmol, 2 mol %), and XPhos (191 mg, 0.4 mmol, 2 mol%) in anhydrous THF (20 mL). The resulting yellow solution was allowed to warm to room temperature and stirred until the reaction was determined to be complete by TLC analysis (4 to 16 h). Subsequently, the reaction mixture was transferred to a 250 mL Erlenmeyer flask, diluted with Et_2O (100 mL), and slowly quenched with a saturated aqueous solution of sodium potassium tartrate with stirring until gas evolution ceased and a heavy solid precipitated. The solution was dried (Na_2SO_4), and solids were removed using a medium porosity sintered funnel. The filtrate was concentrated, and the crude material was used directly in the following step.

Step 2: To the crude material obtained above was added THF (20 mL) and tetrabutylammonium fluoride (1.0 M in THF, 24 mL, 1.2 equiv). The flask was sealed with a rubber septum and the reaction mixture, which became dark over time, was stirred at room temperature until reaction was determined to be complete by TLC analysis (1 to 2 h). The reaction mixture was then concentrated to a paste, adsorbed onto silica gel, and purified directly by flash column chromatography to afford the intermediate alcohol.

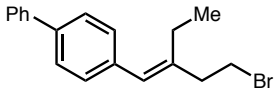
Step 3: A round bottom flask equipped with a magnetic stir bar was charged with the alcohol obtained above (1.0 equiv), CBr_4 (1.2 equiv), and anhydrous CH_2Cl_2 (0.33

M). The solution was stirred at 0 °C and triphenylphosphine (1.1 equiv) was added portionwise over 2 min. The reaction mixture was then allowed to warm to room temperature and stirred for 30 min. The reaction mixture was then concentrated and purified directly by column chromatography, first eluting with hexanes to remove CBr_4 and $CHBr_3$, then eluting with a gradient of Et_2O or EtOAc in pentane or hexanes to provide the desired alkyl bromide. Alkyl bromides were stored under refrigeration at –20 °C and were warmed to room temperature before use.

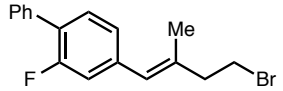
Characterization of substrates 1a – 1n:



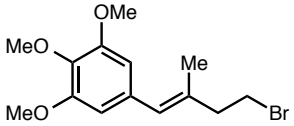
(*E*)-4-(4-Bromo-2-methylbut-1-en-1-yl)-1,1'-biphenyl (1a): Prepared following general procedure **B** using 4-bromobiphenyl (4.66 g, 20 mmol, 1.0 equiv) and (but-3-yn-1-yloxy)triisopropylsilane (5.42 g, 24 mmol, 1.2 equiv) to provide the corresponding homoallylic alcohol (1.86 g, 7.8 mmol), which was converted to the bromide using CBr_4 (3.10 g, 9.4 mmol, 1.2 equiv) and triphenylphosphine (2.25 g, 8.6 mmol, 1.1 equiv). The residue was purified by flash column chromatography, eluting with a gradient of 0 – 2% Et_2O in hexanes to provide the title compound as a colorless solid, **m.p.** 38 – 40 °C. **Yield**: 1.96 g, 33% over 3 steps. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.59 – 7.54 (m, 2H), 7.46 – 7.41 (m, 2H), 7.37 – 7.31 (m, 3H), 6.39 (s, 1H), 3.57 (t, J = 7.4 Hz, 2H), 2.76 (t, J = 7.4 Hz, 2H), 1.94 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141, 139.2, 137.0, 135.7, 129.4, 128.9, 127.6, 127.4, 127.1, 127.0, 44.0, 31.4, 17.7. **IR** (thin film) 1485, 1007, 857, 758, 736, 695, 667, 619 cm^{-1}. **EA** Calcd. for $C_{17}H_{17}Br$: C, 67.79; H, 5.69. Found: C, 68.02; H, 5.80.



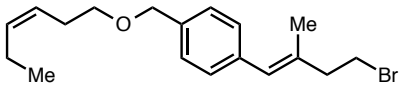
(*E*)-4-(4-Bromo-2-ethylbut-1-en-1-yl)-1,1'-biphenyl (1b): Prepared following general procedure **B** on 10 mmol scale using 4-bromobiphenyl (2.33 g, 10 mmol, 1 equiv), (but-3-yn-1-yloxy)triisopropylsilane (2.71 g, 12 mmol, 1.2 equiv), and triethylaluminum (1.85 M in toluene, 5.5 mL, 1.0 equiv) in place of trimethylaluminum to afford the corresponding homoallylic alcohol (780 mg, 3.1 mmol), which was converted to the bromide using CBr_4 (1.23 g, 3.7 mmol, 1.2 equiv) and triphenylphosphine (893 mg, 3.4 mmol, 1.1 equiv). The residue was purified by flash column chromatography, eluting with a gradient of 0 – 2% Et_2O in hexanes to provide the title compound as a colorless oil. **Yield**: 470 mg, 15% over 3 steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.53 (m, 4H), 7.53 – 7.40 (m, 2H), 7.40 – 7.28 (m, 3H), 6.35 (s, 1H), 3.56 (t, J = 7.7 Hz, 2H), 2.76 (t, J = 7.6 Hz, 2H), 2.33 (q, J = 7.5 Hz, 2H), 1.13 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8, 141.0, 139.3, 136.9, 129.1, 128.9, 127.4, 127.1, 127.1, 127.0, 40.3, 31.5, 23.8, 13.2. **IR** (thin film) 2965, 1486, 763, 737, 697 cm^{-1}. **EA** Calcd. for $C_{18}H_{19}Br$: C, 68.58; H, 6.08. Found: C, 68.85; H, 5.94.



(*E*)-4-(4-Bromo-2-methylbut-1-en-1-yl)-2-fluoro-1,1'-biphenyl (1c): Prepared following general procedure **B** on 10 mmol scale using 2-fluoro-4-bromobiphenyl (2.51 g, 10 mmol, 1.0 equiv) and (but-3-yn-1-yloxy)triisopropylsilane (2.71 g, 12 mmol, 1.2 equiv) to provide the corresponding homoallylic alcohol (1.20 g, 4.7 mmol), which was converted to the bromide using CBr_4 (1.86 g, 5.6 mmol, 1.2 equiv) and triphenylphosphine (1.36 g, 5.2 mmol, 1.1 equiv). The residue was purified by flash column chromatography, eluting with a gradient of 0 – 2% Et_2O in hexanes to provide the title compound as a colorless oil. **Yield**: 1.37 g, 43% over 3 steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H), 7.52 – 7.30 (m, 4H), 7.15 – 7.03 (m, 2H), 6.34 (s, 1H), 3.57 (t, J = 7.3 Hz, 2H), 2.76 (t, J = 7.3 Hz, 2H), 1.95 (d, J = 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6 (d, J_{CF} = 248 Hz), 139.1 (d, J_{CF} = 8.2 Hz), 136.9, 135.8, 130.4 (d, J_{CF} = 4.1 Hz), 129.1 (d, J_{CF} = 3.1 Hz), 128.6, 127.7, 127.0 (d, J_{CF} = 13.6 Hz), 126.7 (d, J_{CF} = 1.9 Hz), 125.1 (d, J_{CF} = 3.2 Hz), 116.4 (d, J_{CF} = 23.3 Hz), 43.8, 31.1, 17.7. **IR** (thin film) 1482, 1410, 1267, 1128, 886, 765, 718, 697 cm^{-1}. **EA** Calcd. for $C_{17}H_{16}BrF$: C, 63.96; H, 5.05. Found: C, 63.92; H, 5.17.

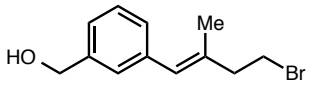


(*E*)-5-(4-Bromo-2-methylbut-1-en-1-yl)-1,2,3-trimethoxybenzene (1d): Prepared following general procedure **B** on 10 mmol scale using 5-bromo-1,2,3-trimethoxybenzene (2.47 g, 10 mmol, 1.0 equiv) and (but-3-yn-1-yloxy)triisopropylsilane (2.71 g, 12 mmol, 1.2 equiv) to provide the corresponding homoallylic alcohol (925 mg, 3.7 mmol), which was converted to the bromide using CBr_4 (1.47 g, 4.4 mmol, 1.2 equiv) and triphenylphosphine (1.06 g, 4.1 mmol, 1.1 equiv). The residue was purified by flash column chromatography, eluting with a gradient of 5 – 20% Et_2O in hexanes to provide the title compound as a colorless oil. **Yield**: 856 mg, 27% over 3 steps. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.46 (s, 2H), 6.30 (s, 1H), 3.86 (s, 6H), 3.85 (s, 3H), 3.55 (t, J = 7.4 Hz, 2H), 2.72 (t, J = 7.3 Hz, 2H), 1.91 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 136.9, 135.2, 133.6, 128.0, 106.2, 61.1, 56.2, 43.8, 31.3, 17.7. **IR** (thin film) 2925, 1579, 1505, 1452, 1414, 1331, 1237, 1124, 1007 cm^{-1}. **EA** Calcd. for $C_{14}H_{19}BrO_3$: C, 53.35; H, 6.08. Found: C, 53.38; H, 6.14.

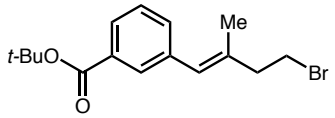


1-((*E*)-4-Bromo-2-methylbut-1-en-1-yl)-4-((((*Z*)-hex-3-en-1-yl)oxy)methyl)benzene (1e): Prepared following general procedure **B** using (*Z*)-1-bromo-4-((hex-3-en-1-yloxy)methyl)benzene (5.38 g, 20 mmol, 1.0 equiv) and (but-3-yn-1-yloxy)triisopropylsilane (5.42 g, 24 mmol, 1.2 equiv) to provide the corresponding homoallylic alcohol (2.30 g, 8.4 mmol), a portion (1.00 g, 3.65 mmol) of which was converted to the bromide using CBr_4 (1.45 g, 4.4 mmol, 1.2 equiv) and triphenylphosphine (1.05 g, 4.1 mmol, 1.1 equiv). The residue was purified by flash column chromatography, eluting with a gradient of 0 – 1% Et_2O in pentane to provide the

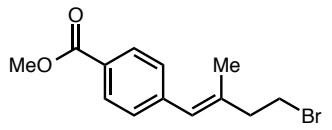
title compound as a colorless oil. **Yield**: 950 mg, 65% over 3 steps. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.34 (s, 1H), 5.48 (ddd, *J* = 12.7, 9.8, 7.2 Hz, 1H), 5.37 (ddd, *J* = 10.7, 9.7, 7.2 Hz, 1H), 4.51 (s, 2H), 3.55 (t, *J* = 7.5 Hz, 2H), 3.48 (t, *J* = 7.0 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.38 (q, *J* = 7.0 Hz, 2H), 2.15 – 2.02 (m, 2H), 1.88 (d, *J* = 0.9 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 137.2, 136.7, 135.5, 133.8, 129.0, 127.7, 127.6, 125.0, 72.8, 70.2, 43.9, 31.4, 28.0, 20.8, 17.5, 14.4. **IR** (thin film) 2961, 2853, 1357, 1264, 1212, 1097, 1017 cm^{-1}. **EA** Calcd. for $C_{18}H_{25}BrO$: C, 64.10; H, 7.47. Found: C, 64.31; H, 7.38.



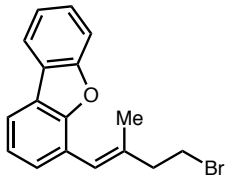
(*E*)-(3-(4-Bromo-2-methylbut-1-en-1-yl)phenyl)methanol (1f): To a solution of *tert*-butyl (*E*)-3-(4-bromo-2-methylbut-1-en-1-yl)benzoate (*vide infra*) (480 mg, 1.47 mmol, 1.0 equiv) in dichloromethane (10 mL) at 0 °C was added a solution of DIBAL-H (1 M in toluene, 3.2 mL, 3.2 mmol, 2.2 equiv). After the reaction mixture was stirred for 30 min at 0 °C, Na_2SO_4 (sat.) was carefully added at room temperature, and stirring was continued until a solid precipitated and the supernatant solution became clear. The solids were removed by filtration, and the filtrate was concentrated to afford the crude product, which was purified by flash column chromatography, eluting with 25% EtOAc in hexanes to provide the title compound as a colorless oil. **Yield**: 250 mg, 67%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 1H), 7.27 – 7.14 (m, 3H), 6.36 (s, 1H), 4.70 (s, 2H), 3.55 (t, *J* = 7.4 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 1.89 (s, 3H), 1.63 (br. s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9, 138.3, 135.8, 128.5, 128.3, 127.8, 127.6, 125.2, 65.6, 43.8, 31.3, 17.6. **IR** (thin film) 3302, 1436, 1264, 1212, 1012, 763, 713, 700 cm^{-1}. **EA** Calcd. for $C_{12}H_{15}BrO$: C, 56.49; H, 5.93. Found: C, 56.73; H, 5.85.



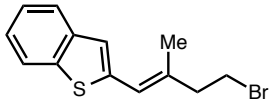
***tert*-Butyl (*E*)-3-(4-bromo-2-methylbut-1-en-1-yl)benzoate (1g):** Prepared following general procedure **B** using *tert*-butyl 3-bromobenzoate (5.14 g, 20 mmol, 1.0 equiv) and (but-3-yn-1-yloxy)triisopropylsilane (5.42 g, 24 mmol, 1.2 equiv) to provide the corresponding homoallylic alcohol (3.12 g, 11.9 mmol), which was converted to the bromide using CBr_4 (4.75 g, 14.3 mmol, 1.2 equiv) and triphenylphosphine (3.43 g, 13.1 mmol, 1.1 equiv). The residue was purified by flash column chromatography, eluting with a gradient of 0 – 2.5% Et_2O in pentane to provide the title compound as a colorless oil. **Yield**: 3.32 g, 51% over 3 steps. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 – 7.80 (m, 2H), 7.43 – 7.33 (m, 2H), 6.37 (s, 1H), 3.55 (t, *J* = 7.4 Hz, 2H), 2.74 (td, *J* = 7.4, 0.7 Hz, 2H), 1.88 (d, *J* = 1.3 Hz, 3H), 1.60 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.9, 137.9, 136.5, 132.9, 132.0, 129.9, 128.1, 127.5, 127.2, 81.1, 43.7, 31.2, 28.3, 17.5. **IR** (thin film) 1710, 1367, 1296, 1257, 1158, 1109, 1081, 849, 745 cm^{-1}. **EA** Calcd. for $C_{16}H_{21}BrO_2$: C, 59.09; H, 6.51. Found: C, 59.35; H, 6.54.



Methyl (*E*)-4-(4-bromo-2-methylbut-1-en-1-yl)benzoate (1h): Prepared following general procedure **B** using methyl 4-bromobenzoate (4.30 g, 20 mmol, 1.0 equiv) and (but-3-yn-1-yloxy)triisopropylsilane (5.42 g, 24 mmol, 1.2 equiv) to provide the corresponding homoallylic alcohol (3.12 g, 6.68 mmol), which was converted to the bromide using CBr_4 (2.66 g, 8.0 mmol, 1.2 equiv) and triphenylphosphine (1.92 g, 7.3 mmol, 1.1 equiv). The residue was purified by flash column chromatography, eluting with 5% Et_2O in pentane to provide the title compound as a colorless oil. **Yield**: 1.21 g, 21% over 3 steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.38 (s, 1H), 3.91 (s, 3H), 3.55 (t, *J* = 7.3 Hz, 2H), 2.75 (t, *J* = 7.3 Hz, 2H), 1.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 142.7, 137.8, 129.6, 128.9, 128.1, 127.3, 52.2, 43.8, 31.0, 17.7. **IR** (thin film) 1716, 1434, 1275, 1178, 1102, 757 cm^{-1}. **EA** Calcd. for $C_{13}H_{15}BrO_2$: C, 55.14; H, 5.34. Found: C, 55.24; H, 5.41.



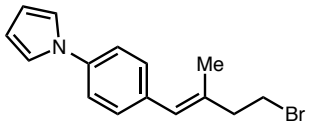
(*E*)-4-(4-Bromo-2-methylbut-1-en-1-yl)dibenzo[*b*,*d*]furan (1i): Prepared following general procedure **B** on 10 mmol scale using 4-bromodibenzo[*b*,*d*]furan (2.47 g, 10 mmol, 1.0 equiv) and (but-3-yn-1-yloxy)triisopropylsilane (2.71 g, 12 mmol, 1.2 equiv) to provide the corresponding homoallylic alcohol (795 mg, 3.15 mmol), which was converted to the bromide using CBr_4 (1.25 g, 3.8 mmol, 1.2 equiv) and triphenylphosphine (907 mg, 3.5 mmol, 1.1 equiv). The residue was purified by flash column chromatography, eluting with 1% Et_2O in hexanes to provide the title compound as a colorless solid, **m.p.** 43 – 43 °C. **Yield**: 705 mg, 22% over 3 steps. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.41 (m, 1H), 7.41 – 7.29 (m, 3H), 6.71 (s, 1H), 3.65 (t, *J* = 7.5 Hz, 2H), 2.88 (t, *J* = 7.5 Hz, 2H), 1.94 (d, *J* = 0.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.1, 154.0, 138.2, 127.5, 127.2, 124.5, 124.2, 122.8, 122.6, 122.6, 121.2, 120.8, 119.1, 111.9, 43.7, 31.3, 18.1. **IR** (thin film) 1449, 1412, 1264, 1186, 845, 747 cm^{-1}. **EA** Calcd. for $C_{17}H_{15}BrO$: C, 64.78; H, 4.80. Found: C, 64.92; H, 4.82.



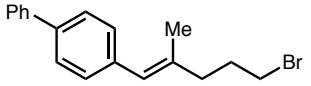
(*E*)-2-(4-Bromo-2-methylbut-1-en-1-yl)benzo[*b*]thiophene (1j): Prepared following general procedure **B** on 10 mmol scale using 2-bromobenzo[*b*]thiophene (2.13 g, 10 mmol, 1.0 equiv) and (but-3-yn-1-yloxy)triisopropylsilane (2.71 g, 12 mmol, 1.2 equiv) to provide the corresponding homoallylic alcohol (205 mg, 0.94 mmol), which was converted to the bromide using CBr_4 (374 mg, 1.1 mmol, 1.2 equiv) and triphenylphosphine (271 mg, 1.0 mmol, 1.1 equiv). The residue was purified by flash column chromatography, eluting with 2% Et_2O in hexanes to provide the title compound as a colorless solid, **m.p.** 86 – 87 °C. **Yield**: 160 mg, 6% over 3 steps. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.27 (m, 2H), 7.16 (s, 1H), 6.53 (s, 1H), 3.55 (t, *J* = 7.4 Hz, 2H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.09 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.8, 139.8, 139.6, 136.9, 124.5, 124.2, 123.4, 123.4,

122.1, 121.7, 44.3, 30.9, 18.3. **IR** (thin film) 1233, 1211, 833, 885, 752, 729, 651 cm^{-1}. **EA** Calcd. for $C_{13}H_{13}BrS$: C, 55.53; H, 4.66. Found: C, 55.56; H, 4.63.

(Alternatively, the homoallylic alcohol prepared above could be accessed in higher yield by Suzuki coupling: A mixture of thiophene-2-boronic acid (765 mg, 4.3 mmol, 1.4 equiv), (*E*)-*tert*-butyl((4-iodo-3-methylbut-3-en-1-yl)oxy)dimethylsilane (978 mmol, 3 mmol, 1.0 equiv), $Pd(OAc)_2$ (34 mg, 0.15 mmol, 5 mol %), XPhos (143 mg, 0.30 mmol, 10 mol %), K_3PO_4•H_2O (2.07 g, 9 mmol, 3.0 equiv) in dioxane/H_2O (6 mL:0.6 mL) was degassed and stirred vigorously under argon at 90 °C for 4 h. Subsequently, the reaction mixture was filtered through a pad of silica gel (CH_2Cl_2) and concentrated. The crude product was dissolved in THF (6 mL) and treated with tetrabutylammonium fluoride (1.0 M in THF, 6 mL, 6 mmol). The reaction mixture was stirred for 2 h at room temperature, concentrated, and purified by column chromatography to afford the homoallylic alcohol. Yield: 359 mg, 55% over 2 steps)

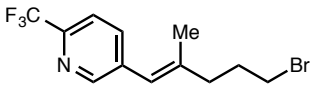


(*E*)-1-(4-(4-Bromo-2-methylbut-1-en-1-yl)phenyl)-1*H*-pyrrole (1k): Prepared following general procedure **B** on 5 mmol scale using 1-(4-iodophenyl)-1*H*-pyrrole (1.35 g, 5 mmol, 1.0 equiv) and (but-3-yn-1-yloxy)triisopropylsilane (396 mg, 6 mmol, 1.2 equiv) to provide the corresponding homoallylic alcohol (396 mg, 1.74 mmol), which was converted to the bromide using CBr_4 (692 mg, 2.1 mmol, 1.2 equiv) and triphenylphosphine (501 mg, 1.9 mmol, 1.1 equiv). The residue was purified by flash column chromatography, eluting with 2.5% EtOAc in hexanes to provide the title compound as a colorless solid, **m.p.** 61 – 62 °C. **Yield**: 473 mg, 33% over 3 steps. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.15 – 7.05 (m, 2H), 6.45 – 6.28 (m, 3H), 3.56 (t, *J* = 7.4 Hz, 2H), 2.75 (t, *J* = 7.4 Hz, 2H), 1.91 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.0, 135.7, 135.4, 130.1, 127.1, 120.2, 119.4, 110.5, 43.8, 31.3, 17.6. **IR** (thin film) 1525, 1329, 1077, 884, 826, 718, 611 cm^{-1}. **EA** Calcd. for $C_{15}H_{16}BrN$: C, 62.08; H, 5.56. Found: C, 61.80; H, 5.38.

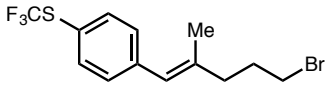


(*E*)-4-(5-Bromo-2-methylpent-1-en-1-yl)-1,1'-biphenyl (1l): Prepared following general procedure **B** using 4-bromobiphenyl (4.66 g, 20 mmol, 1.0 equiv) and (pent-4-yn-1-yloxy)triisopropylsilane (5.76 g, 24 mmol, 1.2 equiv) to provide the corresponding bishomoallylic alcohol (1.42 g, 5.6 mmol), which was converted to the bromide using CBr_4 (2.23 g, 6.7 mmol, 1.2 equiv) and triphenylphosphine (1.61 g, 6.2 mmol, 1.1 equiv). The residue was purified by flash column chromatography, eluting with a gradient of 0 – 2% Et_2O in hexanes to provide the title compound as a colorless solid, **m.p.** 68 – 69 °C. **Yield**: 1.30 g, 21% over 3 steps. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.60 – 7.56 (m, 2H), 7.50 – 7.42 (m, 2H), 7.39 – 7.30 (m, 3H), 6.38 (s, 1H), 3.48 (t, *J* = 6.7 Hz, 2H), 2.37 (t, *J* = 7.3 Hz, 2H), 2.15 – 2.08 (m, 2H), 1.94 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.0, 139.0, 137.4 (2 resonances), 129.4, 128.9, 127.3, 127.1, 126.9, 125.9, 39.2, 33.4, 31.1, 18.0. **IR** (thin film) 1487, 1408, 1246, 877, 763,

756, 734, 688 cm^{-1}. **EA** Calcd. for $C_{18}H_{19}Br$: C, 68.58; H, 6.08. Found: C, 68.81; H, 6.10.

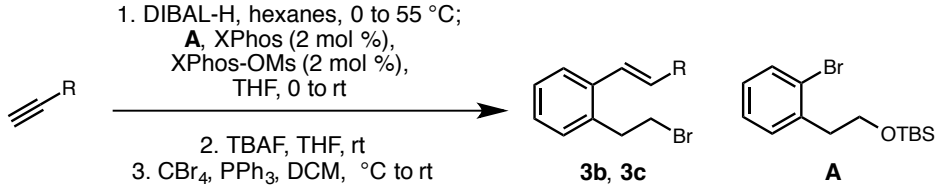


(*E*)-5-(5-Bromo-2-methylpent-1-en-1-yl)-2-(trifluoromethyl)pyridine (1m): Prepared following general procedure **B** on 10 mmol scale using 5-bromo-2-(trifluoromethyl)pyridine (2.26 g, 10 mmol, 1.0 equiv) and (pent-4-yn-1-yloxy)triisopropylsilane (2.88 g, 12 mmol, 1.2 equiv) to provide the corresponding bishomoallylic alcohol (929 mg, 3.8 mmol), which was converted to the bromide using CBr_4 (1.38 g, 4.2 mmol, 1.1 equiv) and triphenylphosphine (1.09 g, 4.2 mmol, 1.1 equiv). The residue was purified by flash column chromatography, eluting with a gradient of 0 – 10% EtOAc in hexanes to provide the title compound as a yellow oil, which was immediately refrigerated at -20 °C upon isolation. **Yield**: 920 mg, 30% over 3 steps. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 1.5 Hz, 1H), 7.69 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 6.31 (s, 1H), 3.45 (t, *J* = 6.6 Hz, 2H), 2.54 – 2.25 (m, 2H), 2.20 – 1.98 (m, 2H), 1.89 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.3, 142.6, 137.0, 121.6, 120.2 – 120.0 (m), 39.1, 33.2, 30.9, 18.1. **IR** (thin film) 1336, 1175, 1132, 1086, 1024 cm^{-1}. **EA** Calcd. for $C_{12}H_{13}BrF_3N$: C 46.77; H, 4.25. Found: C, 46.63; H, 4.11.



(*E*)-(4-(5-Bromo-2-methylpent-1-en-1-yl)phenyl)(trifluoromethyl)sulfane (1n): Prepared following general procedure **B** using 4-bromophenyl trifluoromethyl sulfide (5.14 g, 20 mmol, 1.0 equiv) and (pent-4-yn-1-yloxy)triisopropylsilane (5.76 g, 24 mmol, 1.2 equiv) to provide the corresponding bishomoallylic alcohol (1.56 mg, 5.7 mmol), which was converted to the bromide using CBr_4 (2.25 g, 6.8 mmol, 1.2 equiv) and triphenylphosphine (1.63 g, 6.2 mmol, 1.1 equiv). The residue was purified by flash column chromatography, eluting with 1% EtOAc in pentane to provide the title compound as a colorless oil. **Yield**: 1.57 g, 23% over 3 steps. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.35 (s, 1H), 3.48 (t, *J* = 6.4 Hz, 2H), 2.38 (t, *J* = 7.0 Hz, 2H), 2.21 – 2.04 (m, 2H), 1.91 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.1, 139.6, 136.3, 129.9, 129.8 (q, J_{CF} = 308 Hz), 125.1, 121.6, 39.1, 33.2, 30.9, 18.0. **IR** (thin film) 1492, 1153, 1114, 1085, 1015, 865, 756 cm^{-1}. **EA** Calcd. for $C_{13}H_{14}BrF_3S$: C 46.03; H, 4.16. Found: C, 46.03; H, 4.13.

General procedure C *for the Synthesis of Substrates* **3b** *and* **3c***:*



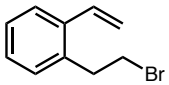
Step 1: A flame-dried screw-top reaction tube equipped with a magnetic stir bar and Teflon screw cap was charged with a solution of DIBAL-H (1.0 M in hexanes, 5 mL, 5

mmol, 1 equiv) via syringe. Under argon, the solution was cooled to 0 °C and terminal alkyne (5 mmol, 1 equiv) was slowly added by syringe. The reaction tube was allowed to warm to room temperature and then immersed in an oil bath preheated to 55 °C and stirred for 2 h to afford a solution of the vinylaluminum reagent. The reaction tube containing the vinylaluminum reagent was cooled to 0 °C, and a solution of aryl bromide (5 mmol, 1.0 equiv), XPhos-OMs (G3) precatalyst (85 mg, 0.1 mmol, 2 mol %), and XPhos (48 mg, 0.1 mmol, 2 mol %) in THF (5 mL) was added slowly by syringe. After the addition was complete, the pale yellow solution was warmed to room temperature and stirred until reaction was determined to be complete by TLC analysis (2 to 16 h). Subsequently, the reaction mixture was transferred to a 250 mL Erlenmeyer flask and diluted with Et_2O. A saturated solution of sodium potassium tartrate was carefully added with stirring until no further precipitation of white solid was observed. $MgSO_4$ was then added, and the reaction mixture was filtered through a sintered funnel. The filtrate was concentrated to afford the crude product, which was used without further purification.

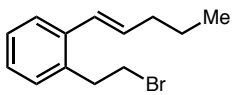
Step 2: The crude product obtained above was dissolved in THF (25 mL), and tetrabutylammonium fluoride (1 M in THF, 6 mL, 6 mmol, 1.2 equiv) was added. The reaction mixture was stirred at room temperature until the process was judged to be complete by TLC (~1 h). The mixture was then diluted with water (50 mL) and extracted with Et_2O (3 × 25 mL). The combined organic layers were dried ($MgSO_4$), filtered through a pad of silica gel, and concentrated. The crude residue was then purified by flash column chromatography, eluting with a gradient of EtOAc in hexanes to provide the desired alcohol.

Step 3: A round bottom flask equipped with a magnetic stir bar was charged with the alcohol obtained above (1.0 equiv), CBr_4 (1.2 equiv), and anhydrous CH_2Cl_2 (0.33 M). The solution was stirred at 0 °C and triphenylphosphine (1.1 equiv) was added portionwise over 2 min. The reaction mixture was then allowed to warm to room temperature and stirred for 30 min. The reaction mixture was then concentrated and purified directly by column chromatography, first eluting with hexanes to remove CBr_4 and $CHBr_3$, then eluting with a gradient of Et_2O or EtOAc in pentane or hexanes to provide the desired alkyl bromide. Alkyl bromides were stored under refrigeration at -20 °C and were warmed to room temperature before use.

Characterization of substrates 3a – 3c:

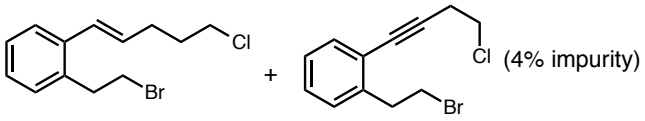


1-(2-Bromoethyl)-2-vinylbenzene (3a): The title compound was prepared according to a literature procedure.[6] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 1H), 7.36 – 7.24 (m, 2H), 7.24 – 7.16 (m, 1H), 6.99 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.71 (dd, *J* = 17.3, 1.0 Hz, 1H), 5.39 (dd, *J* = 10.9, 1.0 Hz, 1H), 3.61 – 3.48 (m, 2H), 3.33 – 3.20 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.9, 136.3, 134.0, 130.1, 128.1, 127.6, 126.3, 116.8, 37.2, 32.1.



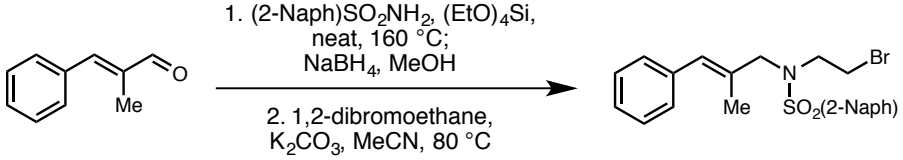
(*E*)-1-(bromomethyl)-2-(pent-1-en-1-yl)benzene (3b): Prepared following general procedure **C** using 1-pentyne (500 µL, 5 mmol, 1 equiv) and ((2-bromobenzyl)oxy)(*tert*-

butyl)dimethylsilane (1.50 g, 5 mmol, 1 equiv) to provide the corresponding phenethyl alcohol (780 mg, 4.1 mmol), which was converted to the bromide using CBr_4 (1.63 g, 4.9 mmol, 1.2 equiv) and triphenylphosphine (1.18 g, 4.5 mmol, 1.1 equiv). The residue was purified by column chromatography, eluting with a gradient of 0 – 3% EtOAc in hexanes to provide the title compound as a colorless oil. **Yield**: 760 mg, 60%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.4 Hz, 1H), 7.29 – 7.11 (m, 3H), 6.60 (d, *J* = 15.5 Hz, 1H), 6.15 (dt, *J* = 15.4, 7.0 Hz, 1H), 3.60 – 3.44 (m, 2H), 3.31 – 3.16 (m, 2H), 2.32 – 2.19 (m, 2H), 1.64 – 1.44 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.1, 135.7, 134.0, 130.0, 127.5, 127.2, 126.8, 126.5, 37.3, 35.5, 32.1, 22.7, 13.9. **IR** (thin film) 2957, 1454, 1210, 963, 748, 647 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{13}H_{17}Br + NH_4]^+$: 270.0853. Found: 270.0854.



(*E*)-1-(2-bromoethyl)-2-(5-chloropent-1-en-1-yl)benzene (3c): Prepared following general procedure **C** using 5-chloro-1-pentyne (501 mg, 5 mmol, 1 equiv) and ((2-bromobenzyl)oxy)(*tert*-butyl)dimethylsilane (1.50 g, 5 mmol, 1 equiv) to provide the phenethyl alcohol (675 mg, 90% purity), which was converted to the bromide using CBr_4 (1.29 g, 3.9 mmol, ~1.3 equiv) and triphenylphosphine (1.02 g, 3.9 mmol, ~1.3 equiv). The residue was purified by column chromatography, eluting with a gradient of 0 – 3% EtOAc in hexanes to provide the title compound as a colorless oil, which contained 4% of the corresponding alkyne as an impurity. **Yield**: 510 mg, 34%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.26 – 7.14 (m, 3H), 6.66 (d, *J* = 15.5 Hz, 1H), 6.08 (dt, *J* = 15.5, 7.1 Hz, 1H), 3.61 (t, *J* = 6.5 Hz, 2H), 3.55 – 3.46 (m, 2H), 3.27 – 3.20 (m, 2H), 2.47 – 2.39 (m, 2H), 2.03 – 1.92 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.8, 136.0, 131.8, 130.2, 128.3, 127.6, 126.6, 44.6, 37.3, 32.3, 32.2, 30.6. **IR** (thin film) 2955, 1483, 1440, 1302, 1261, 1210, 964, 749 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{13}H_{16}BrCl + NH_4]^+$: 306.0446. Found: 306.0446.

Experimental procedures and characterization of 1o – 1r:

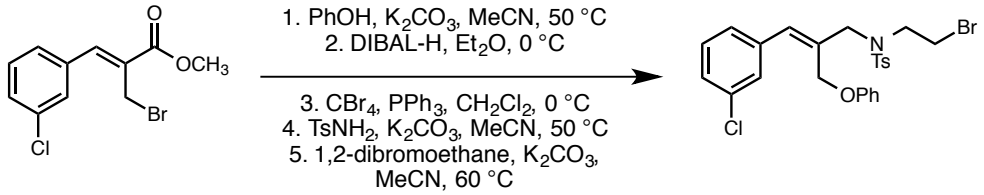


(*E*)-*N*-(2-bromoethyl)-*N*-(2-methyl-3-phenylallyl)naphthalene-2-sulfonamide (1o): *Step 1:* A pressure tube (30 mL) was charged with *trans*-α-methylcinnamaldehyde (3.22 g, 22 mmol, 1.1 equiv) and 2-naphthalenesulfonamide (4.10 g, 20 mmol, 1.0 equiv) and tetraethyl orthosilicate (20 mL), flushed with nitrogen, and sealed. Behind a blast shield, the reaction mixture was stirred at 160 °C for 16 h. The reaction mixture was allowed to cool to room temperature and the crude sulfonimide was taken up in MeOH (50 mL) and cooled to 0 °C with stirring. Sodium borohydride (0.91 g, 24 mmol, 1.2 equiv) was added portionwise over 2 min to the stirred reaction mixture. The reaction mixture was allowed to warm to room temperature and stirred for 30 min before it was partitioned

between CH_2Cl_2 (250 mL) and water (250 mL). The aqueous phase was extracted with CH_2Cl_2 (100 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated to afford the crude product as a brown solid. The crude material was recrystallized (hexanes/acetone) to afford the secondary sulfonamide as a beige solid (3.93 g, 11.6 mmol).

Step 2: A round-bottom flask was charged with the secondary sulfonamide obtained above (1.25 g, 3.71 mmol, 1.0 equiv) and K_2CO_3 (1.54 g, 11.2 mmol, 3.0 equiv). MeCN (50 mL) and 1,2-dibromoethane (3.7 mL) were added, and the reaction mixture was vigorously stirred under reflux for 24 h. After cooling to room temperature, the reaction mixture was filtered (CH_2Cl_2) through a medium-porosity sintered funnel, and the filtrate was concentrated to afford the crude product, which was purified by flash column chromatography (6:1 hexanes/EtOAc) to deliver the title compound as a colorless solid, **m.p.** 110 – 111 °C.

Yield: 1.33 g, 47% over 2 steps. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.04 – 7.97 (m, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.83 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.67 (dt, *J* = 14.8, 7.1 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.17 (m, 3H), 6.41 (s, 1H), 3.94 (s, 2H), 3.62 – 3.41 (m, 4H), 1.90 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 136.9, 136.2, 135.0, 133.2, 132.4, 130.0, 129.8, 129.4, 129.1, 129.0, 128.7, 128.4, 128.1, 127.9, 127.2, 122.5, 58.5, 49.9, 29.2, 15.9. **IR** (thin film) 1347, 1336, 1155, 1074, 747, 699, 650, 615 cm^{-1}. **EA** Calcd. for $C_{22}H_{22}BrNO_2S$: C 59.46; H, 4.99. Found: C, 59.59; H, 4.96.



(*Z*)-*N*-(2-bromoethyl)-*N*-(3-(3-chlorophenyl)-2-(phenoxymethyl)allyl)-4-methylbenzenesulfonamide (1p):

Step 1: A round-bottom flask (250 mL) was charged with methyl (*Z*)-2-(bromomethyl)-3-(3-chlorophenyl)acrylate (5.79 g, 20 mmol, 1.0 equiv), phenol (1.85 g, 20 mmol, 1.0 equiv), and MeCN (50 mL). K_2CO_3 (5.52 g, 40 mmol, 2.0 equiv) was added, and the reaction mixture was stirred vigorously at 50 °C for 14 h. After cooling to room temperature, the reaction mixture was filtered (CH_2Cl_2) through a medium porosity sintered funnel, and the filtrate was concentrated to give the crude phenyl ether as a yellow oil, which was used without further purification.

Step 2: The crude phenyl ether obtained above was dissolved in anhydrous Et_2O (50 mL) and cooled to 0 °C. DIBAL-H (1.0 M in toluene, 50 mL, 50 mmol) was added dropwise, and the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Na_2SO_4 (sat.) was carefully added with continued stirring until a solid precipitated, and the supernatant liquid became clear. The solid material was removed by filtration through a sintered funnel, and the filtrate was concentrated to provide the crude product, which was partially purified (~90% purity) by column chromatography to afford the allylic alcohol (2.40 g) as a colorless oil.

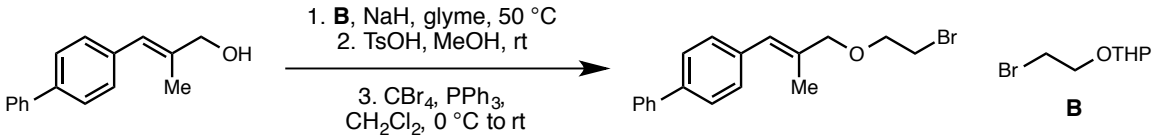
Step 3: The allylic alcohol obtained above was dissolved in anhydrous CH_2Cl_2 (50 mL) and cooled to 0 °C. CBr_4 (3.19 g, 9.6 mmol, ~1.1 equiv) and triphenylphosphine (2.40 g, 9.2 mmol, ~1.05 equiv) were added sequentially. The reaction mixture was stirred for 30

min at 0 °C, whereupon it was concentrated and filtered through a plug of silica gel (10% EtOAc in hexanes) to afford the allylic bromide, which was used without further purification.

Step 4: The crude allylic bromide obtained above was taken up in MeCN (25 mL), and *p*-toluenesulfonamide (2.99 g, 17 mmol) and K_2CO_3 (3.61 g, 26 mmol) were added. The reaction mixture was stirred vigorously at 50 °C for 12 h. Upon cooling to room temperature, the reaction mixture was filtered through a sintered funnel, and the filtrate was concentrated to afford the crude product, which was purified by column chromatography (5:1 to 4:1 hexanes/EtOAc) to afford the desired secondary sulfonamide as a colorless solid (1.63 g, 3.8 mmol).

Step 5: A round-bottom flask was charged with a portion (856 mg, 2.0 mmol, 1.0 equiv) of the secondary sulfonamide obtained above and K_2CO_3 (828 mg, 6.0 mmol, 3.0 equiv). MeCN (10 mL) and 1,2-dibromoethane (2 mL) were added, and the reaction mixture was stirred vigorously under reflux for 24 h. After cooling to room temperature, the reaction mixture was filtered (CH_2Cl_2) through a medium-porosity sintered funnel, and the filtrate was concentrated to afford the crude product, which was purified by column chromatography (9:1 hexanes/EtOAc) to deliver the title compound as an off-white solid, **m.p.** 69 – 71 °C.

Yield: 745 mg, 13% over 5 steps. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.21 (m, 6H), 7.16 (s, 1H), 7.13 – 7.09 (m, 1H), 6.99 (t, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 2H), 6.69 (s, 1H), 4.45 (s, 2H), 4.09 (s, 2H), 3.63 – 3.50 (m, 4H), 2.40 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.1, 144.0, 137.4, 136.3, 134.5, 133.7, 133.0, 130.0, 129.9, 129.7, 129.0, 128.1, 127.4, 127.0, 121.5, 114.9, 64.0, 53.5, 50.2, 29.4, 21.7. **IR** (thin film) 1596, 1494, 1338, 1231, 1155, 1090, 752, 724, 689, 662 cm^{-1}. **EA** Calcd. for $C_{25}H_{25}BrClNO_3S$: C 56.14; H, 4.71. Found: C, 56.14; H, 4.71.



(*E*)-4-(3-(2-bromoethoxy)-2-methylprop-1-en-1-yl)-1,1'-biphenyl (1q):

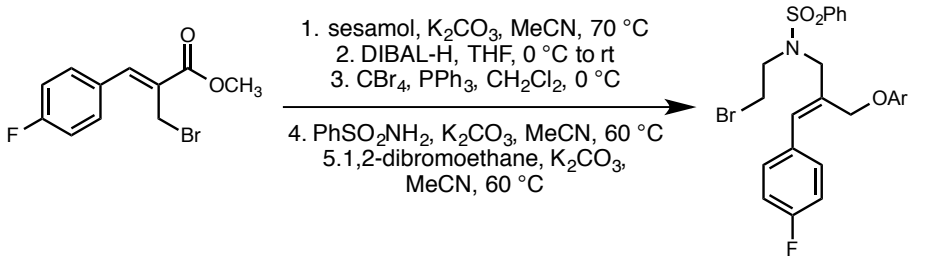
Step 1: A solution of (*E*)-3-([1,1'-biphenyl]-4-yl)-2-methylprop-2-en-1-ol (2.24 g, 10 mmol, 1.0 equiv) in glyme (5 mL) was dropwise to a suspension of NaH (95%, 288 mg, 12 mmol, 1.2 equiv) in glyme (20 mL) at room temperature under argon. The reaction mixture was stirred for 1 h at room temperature before **B** (2.51 g, 12 mmol, 1.2 equiv) was added. The reaction mixture was then stirred at 50 °C for 24 h. Another aliquot of **B** (2.51 g, 12 mmol, 1.2 equiv) was added, and the reaction mixture was stirred for an additional 24 h. Upon cooling to room temperature, the reaction mixture was partitioned between water (50 mL) and EtOAc (50 mL). The aqueous layer was extracted with ethyl acetate (2 × 50 mL), and the combined organic layers were dried (Na_2SO_4), concentrated, and partially purified (~85% purity) by column chromatography to afford the desired tetrahydropyran ether.

Step 2: The tetrahydropyran ether obtained above was taken up in MeOH (100 mL) and *p*-TsOH (100 mg) was added. After stirring for 15 min at room temperature, the reaction mixture was quenched with sat. $NaHCO_3$ (100 mL) and partitioned between water (200 mL) and EtOAc (200 mL). The aqueous layer was extracted with EtOAc (3 × 100 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated. The crude

product was purified by column chromatography to afford the desired alcohol (1.30 g, 4.9 mmol) as a colorless solid.

Step 3: A portion (1.02 g, 3.81 mmol, 1.0 equiv) of the alcohol prepared above was dissolved in anhydrous CH_2Cl_2 (20 mL) and cooled to 0 °C. CBr_4 (1.52 g, 4.6 mmol, 1.2 equiv) and triphenylphosphine (1.10 g, 4.2 mmol, 1.1 equiv) were added sequentially. The reaction mixture was allowed to warm to room temperature and stirred at room temperature for 30 min and concentrated. The resultant oil was purified directly by column chromatography (hexanes to 15:1 hexanes/EtOAc) to afford the title compound as a colorless oil.

Yield: 981 mg, 34% over 3 steps. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 – 7.54 (m, 4H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.32 (m, 3H), 6.56 (s, 1H), 4.13 (s, 2H), 3.81 (t, *J* = 6.1 Hz, 2H), 3.54 (t, *J* = 6.1 Hz, 2H), 1.97 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.9, 139.5, 136.5, 135.1, 129.5, 128.9, 127.4, 127.2, 127.1, 127.0, 77.5, 69.8, 30.8, 15.7. **IR** (thin film) 1485, 1105, 1007, 871, 762, 738, 696 cm^{-1}. **EA** Calcd. for $C_{18}H_{19}BrO$: C 65.27; H, 5.78. Found: C, 64.97; H, 5.70.



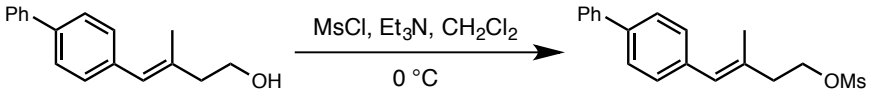
(*Z*)-*N*-(2-((benzo[*d*][1,3]dioxol-5-yloxy)methyl)-3-(4-fluorophenyl)allyl)-*N*-(2-bromoethyl)benzenesulfonamide (1r):

Step 1: To a solution of methyl (*Z*)-4-(bromomethyl)-3-(4-fluorophenyl)-2-propenoate (9.55 g, 35 mmol, 1.0 equiv) and sesamol (4.83 g, 35 mmol, 1.0 equiv) in MeCN (100 mL) was added K_2CO_3 (9.66 g, 70 mmol, 2.0 equiv). The reaction mixture was stirred vigorously at 70 °C for 9 h. Upon cooling to room temperature, the reaction mixture was filtered through a sintered funnel (CH_2Cl_2) and concentrated to provide the desired allylic ether, which was used in the next step without further purification.

Step 2: The crude allylic ether obtained above was dissolved in anhydrous THF (100 mL) and cooled to 0 °C. DIBAL-H (1.0 M in cyclohexane, 70 mL, 70 mmol) was added dropwise, and the reaction mixture was stirred for 10 min at room temperature. Na_2SO_4 (sat.) was carefully added with continued stirring until a solid precipitated, and the supernatant liquid became clear. The solid material was removed by filtration through a sintered funnel, and the filtrate was concentrated to provide the crude product, which was purified by recrystallization (hexanes/toluene) to provide the desired allylic alcohol as a colorless solid (4.03 g, 13.3 mmol).

Step 3: The allylic alcohol obtained above was dissolved in anhydrous CH_2Cl_2 (100 mL) and cooled to 0 °C. CBr_4 (5.30 g, 16.0 mmol, 1.2 equiv) and triphenylphosphine (3.83 g, 14.3 mmol, 1.1 equiv) were added sequentially. The reaction mixture was stirred for 30 min at 0 °C, whereupon it was concentrated and filtered through a plug of silica gel (10% EtOAc in hexanes) to afford the desired allylic bromide, which was used without further purification.

Step 4: The crude allylic bromide obtained above was taken up in MeCN (100 mL), and benzenesulfonamide (3.70 g, 23.6 mmol) and K_2CO_3 (6.5 g, 47 mmol) were added. The reaction mixture was stirred vigorously at 50 °C for 12 h. Additional benzenesulfonamide (1.23 g, 7.8 mmol) was added, and the reaction mixture was stirred at 60 °C for a further 24 h. Upon cooling to room temperature, the reaction mixture was filtered through a sintered funnel, and the filtrate was concentrated to afford the crude product, which was purified by column chromatography (6:1 hexanes/EtOAc) to afford the desired secondary sulfonamide as a yellow solid (2.30 g, 3.8 mmol).
Step 5: A round-bottom flask was charged with a portion (481 mg, 1.10 mmol, 1.0 equiv) of the secondary sulfonamide obtained above and K_2CO_3 (500 mg, 3.6 mmol, 3.2 equiv). MeCN (5 mL) and 1,2-dibromoethane (1.1 mL) were added, and the reaction mixture was stirred vigorously at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered (CH_2Cl_2) through a medium-porosity sintered funnel, and the filtrate was concentrated to afford the crude product, which was purified by column chromatography (9:1 hexanes/EtOAc) to deliver the title compound as a viscous, pale yellow oil.
Yield: 433 mg, 8% over 5 steps. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.19 (dd, J = 7.9, 5.8 Hz, 2H), 7.02 (t, J = 8.6 Hz, 1H), 6.72 (s, 1H), 6.68 (d, J = 8.4 Hz, 1H), 6.46 – 6.39 (d, J = 2.3 Hz, 1H), 6.22 (dd, J = 8.5, 2.3 Hz, 1H), 5.92 (s, 2H), 4.38 (s, 2H), 4.06 (s, 2H), 3.60 – 3.54 (m, 2H), 3.54 – 3.48 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.5 (d, J_{CF} = 248 Hz), 153.6, 148.4, 142.3, 139.2, 133.8, 133.0, 132.1, 131.6 (d, J_{CF} = 3.4 Hz), 130.7 (d, J_{CF} = 8.1 Hz), 129.4, 127.3, 115.7 (d, J_{CF}= 21.6 Hz), 108.1, 106.1, 101.4, 98.5, 65.0, 53.9, 50.1, 29.3. **IR** (thin film) 1507, 1485, 1179, 1158, 1090, 1038, 736 cm^{-1}. **EA** Calcd. for $C_{18}H_{19}BrO$: C 65.27; H, 5.78. Found: C, 64.97; H, 5.70. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{25}H_{23}BrFNO_5S + NH_4]^+$: 565.0803. Found: 565.0818.



(*E*)-4-([1,1'-biphenyl]-4-yl)-3-methylbut-3-en-1-yl methanesulfonate: A solution of (*E*)-4-([1,1'-biphenyl]-4-yl)-3-methylbut-3-en-1-ol (1.19 g, 5 mmol) (prepared by general procedure **B**, steps 1 and 2) and triethylamine (0.83 mL, 6 mmol) in dichloromethane (25 mL) was cooled to 0 °C and methanesulfonyl chloride (0.43 mL, 5.5 mmol) was added dropwise over 1 min. The reaction mixture was stirred for an additional 30 min, and water (50 mL) was added. The organic and aqueous phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried (Na_2SO_4) and concentrated to afford the crude product, which was recrystallized (hexane/CH_2Cl_2) to provide the title compound as a colorless solid, **m.p.** 95 – 97 °C.
Yield: 1.44 g, 91%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.51 (m, 4H), 7.50 – 7.38 (m, 2H), 7.38 – 7.27 (m, 3H), 6.41 (s, 3H), 4.43 (t, J = 6.8 Hz, 2H), 3.03 (s, 3H), 2.65 (t, J = 6.8 Hz, 2H), 1.97 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.9, 139.4, 136.8, 133.4, 129.4, 128.9, 128.2, 127.4, 127.1, 127.0, 68.2, 40.2, 37.8, 18.1. **IR** (thin film) 1350, 1171, 952, 826, 804, 761, 698 cm^{-1}.

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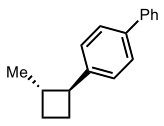
Copies of ^{1}H and ^{13}C NMR spectra for products (**2a – 2r**, **4a – 4c)**, (-)-paroxetine and starting materials (**1a – 1r**, **3a – 3r**):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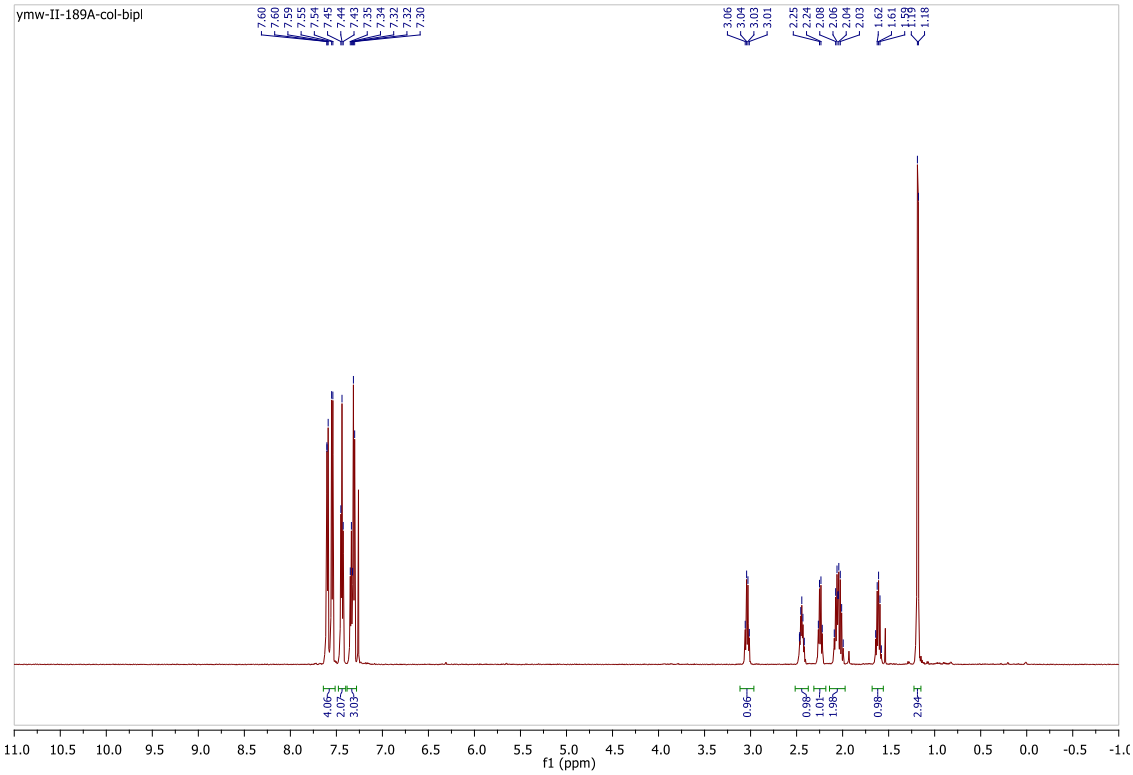
Me

2a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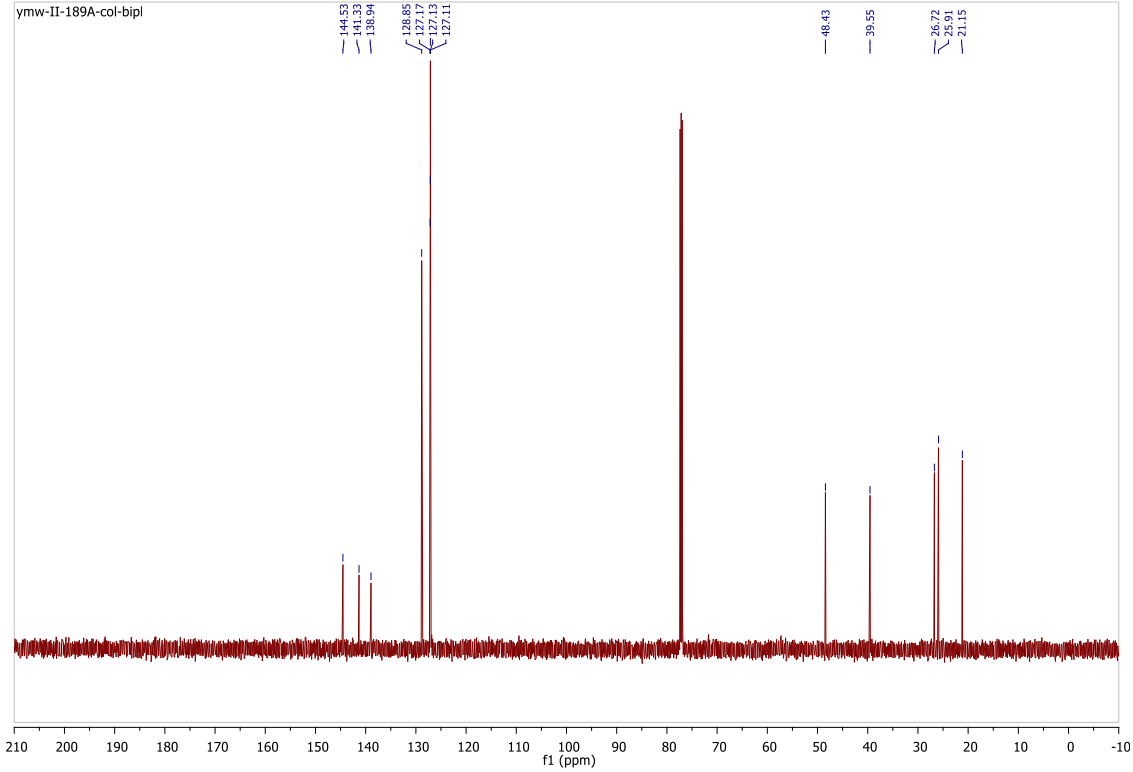
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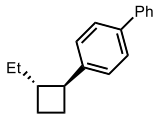
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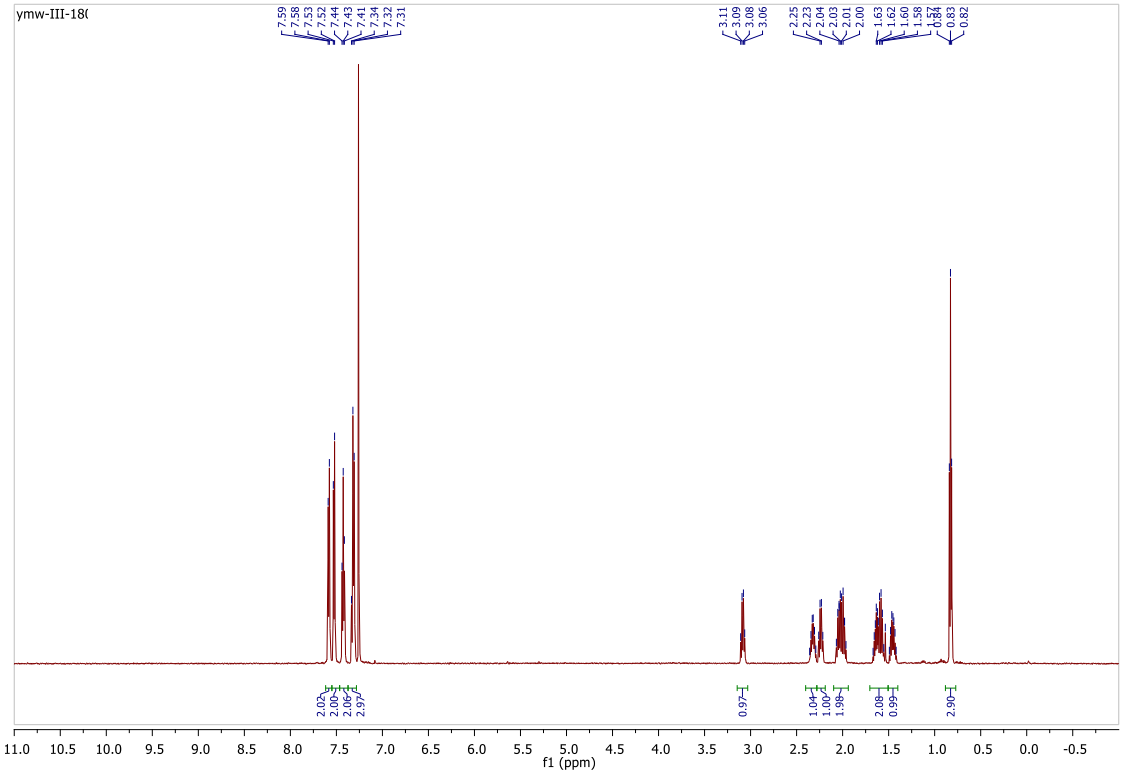
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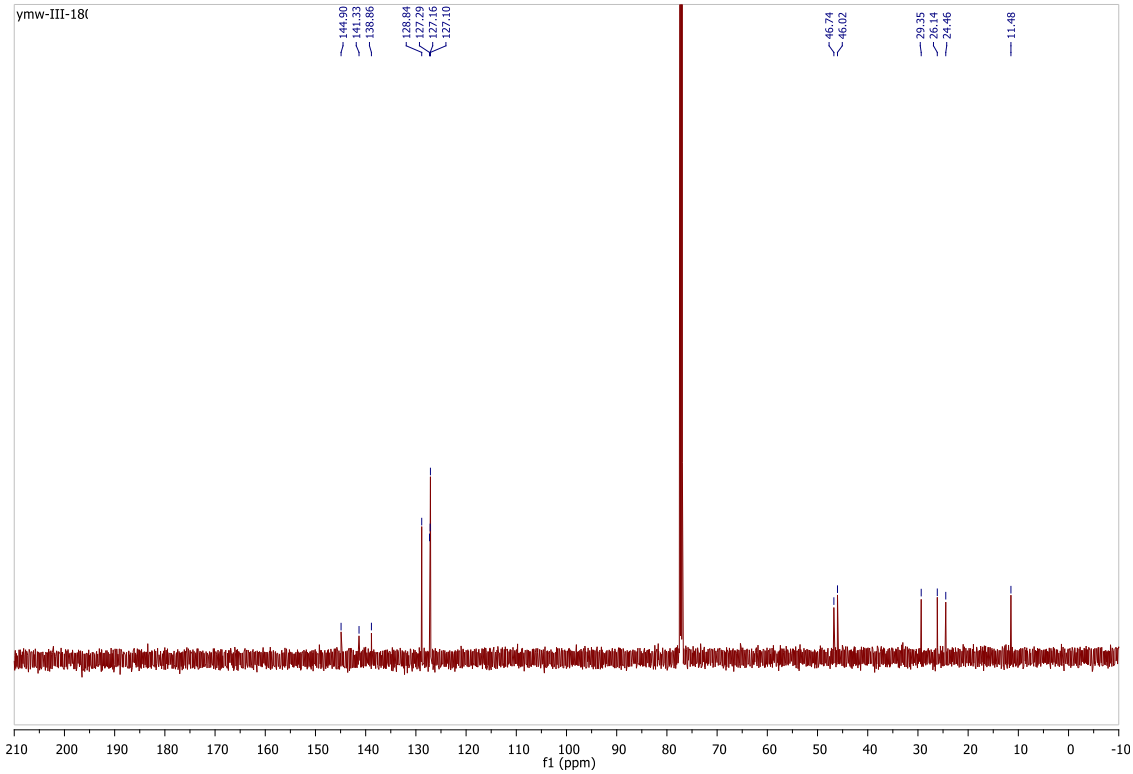
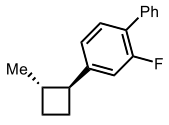
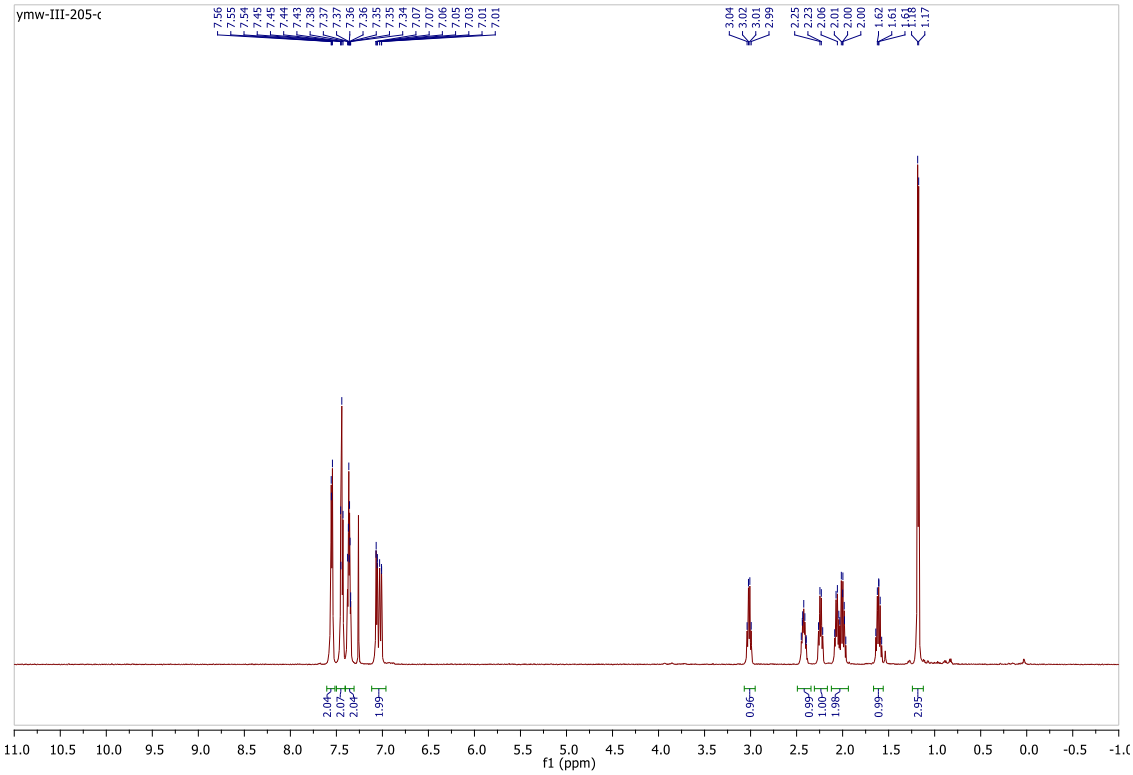
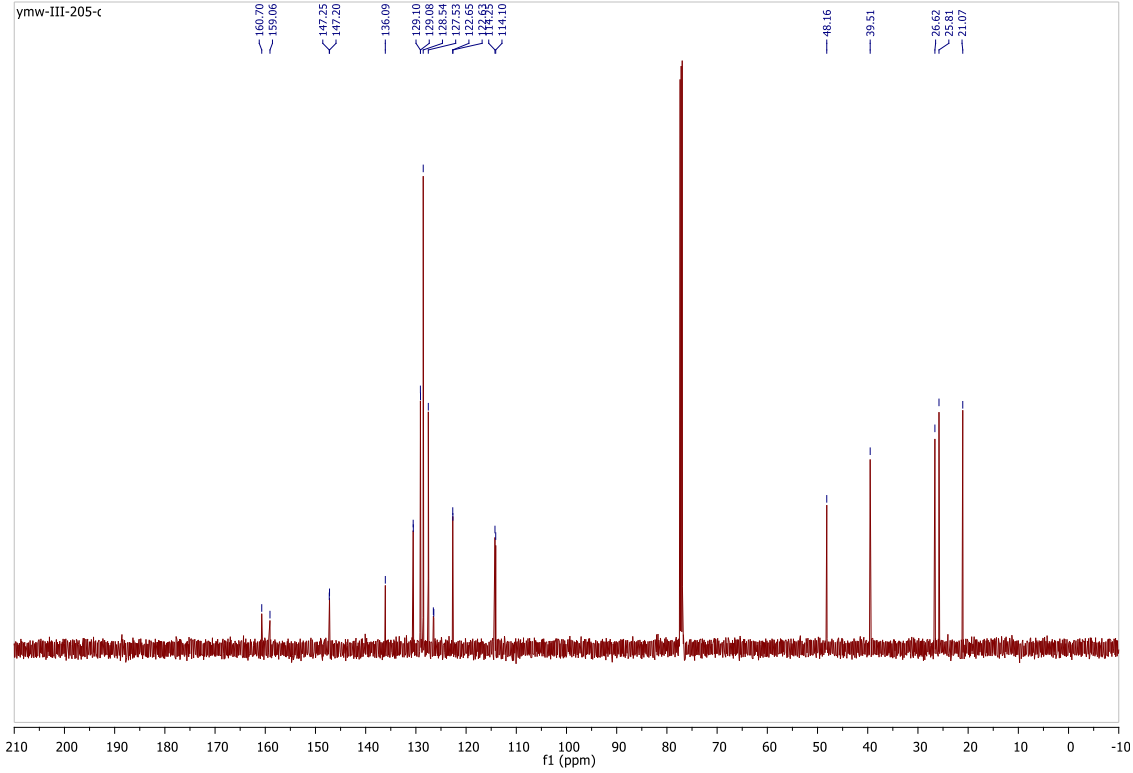
0.97
1.04
1.00
1.98
2.08
0.99
2.90
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

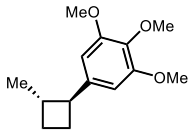

ymw-III-18(
144.90
141.33
138.86
128.84
127.29
127.16
127.10
46.74
46.02
29.35
26.14
24.46
11.48
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
F
Me

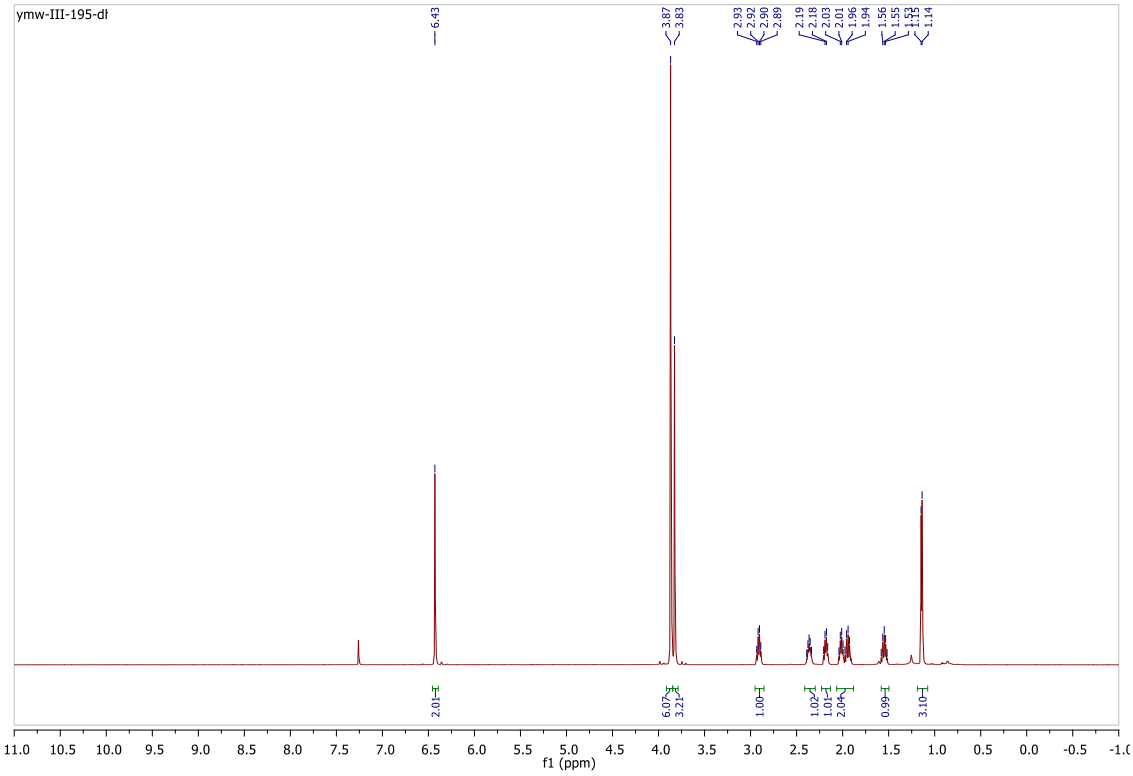
2c

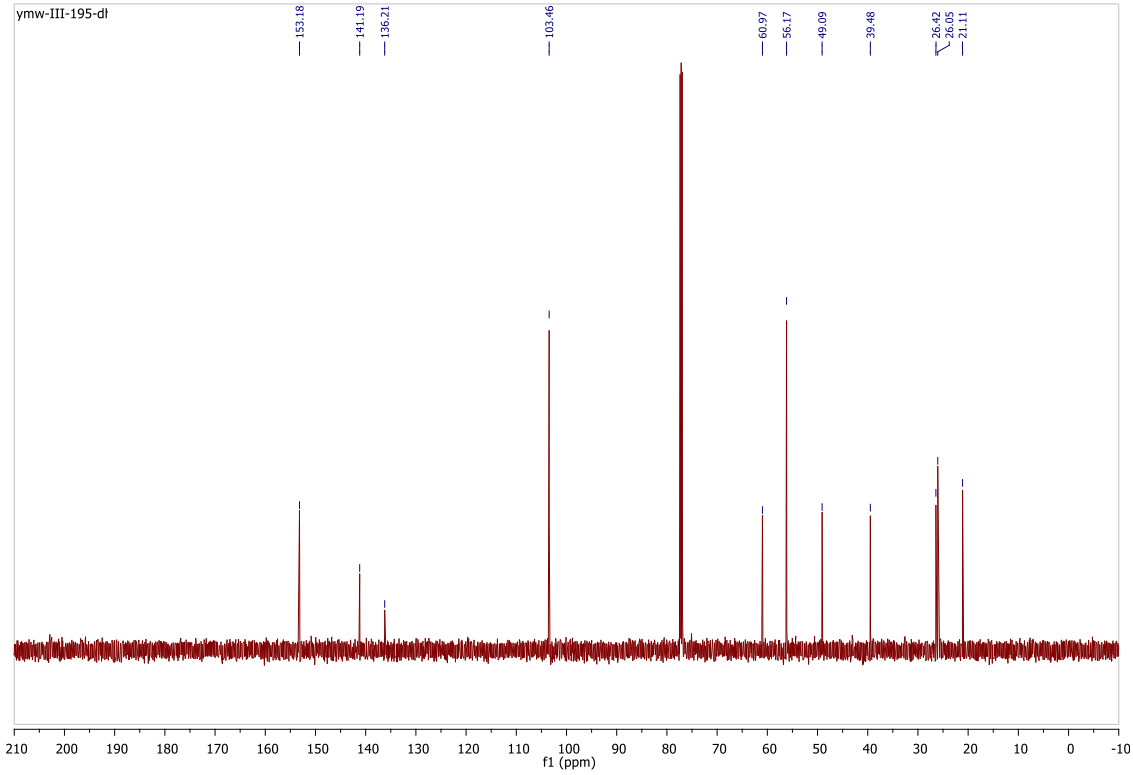

ymw-III-205-c
7.56 7.55 7.54 7.45 7.45 7.44 7.43 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.07 7.07 7.06 7.05 7.03 7.01 7.01
3.04 3.02 3.01 2.99
2.25 2.23 2.06 2.01 2.00 2.00
1.62 1.61 1.18 1.17
2.04 2.07 2.04 1.99 0.96 0.99 1.00 1.98 0.99 2.95
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

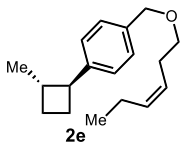

ymw-III-205-c
160.70 159.06 147.25 147.20 136.09 129.10 129.08 128.54 127.53 122.65 114.52 114.25 114.10
48.16 39.51 26.62 25.81 21.07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
OMe
OMe
Me

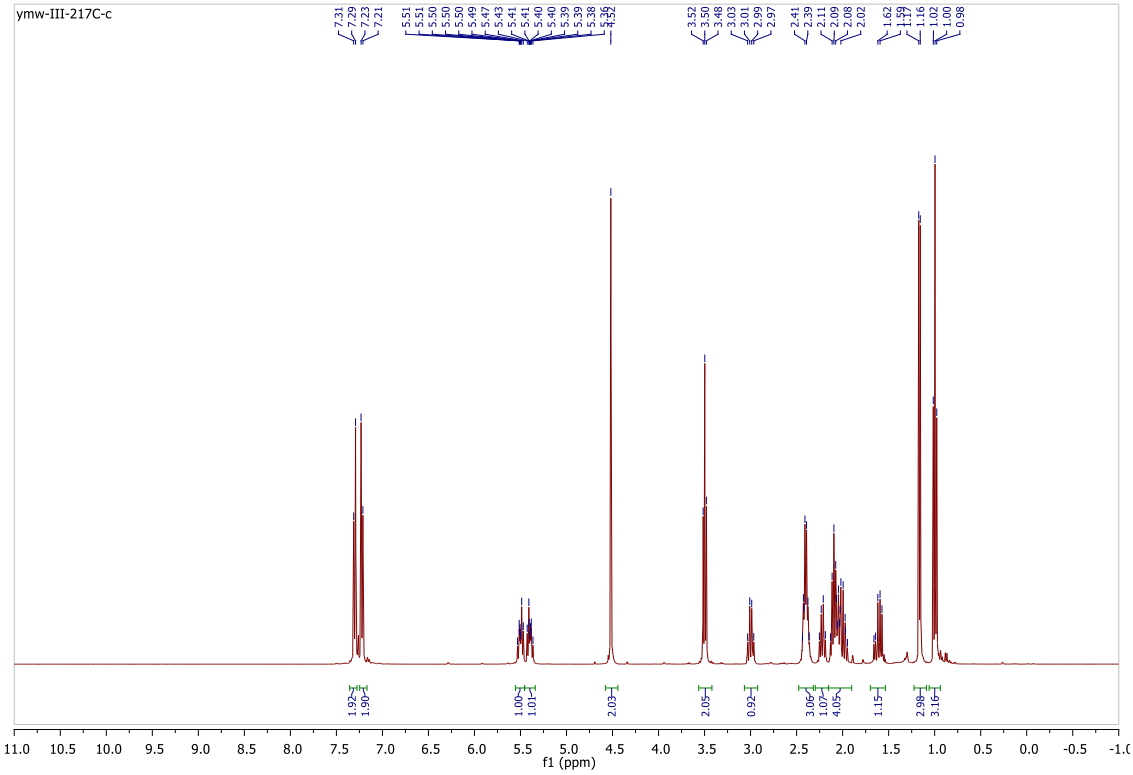
2d

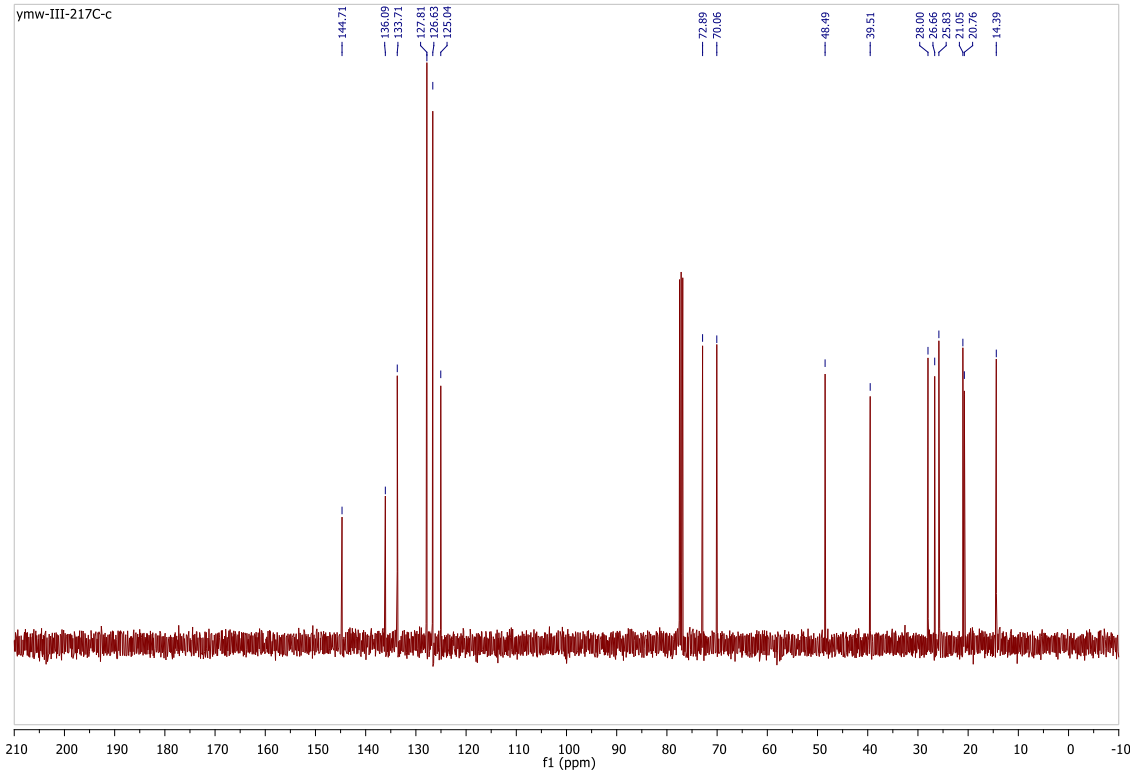

ymw-III-195-dł
6.43
3.87
3.83
2.93
2.92
2.90
2.89
2.19
2.18
2.03
2.01
1.96
1.94
1.56
1.55
1.53
1.15
1.14
2.01
6.07
3.21
1.00
1.02
1.01
1.04
0.99
3.10
f1 (ppm)

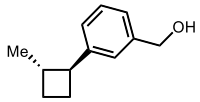

ymw-III-195-dł
153.18
141.19
136.21
103.46
60.97
56.17
49.09
39.48
26.42
26.05
21.11
f1 (ppm)



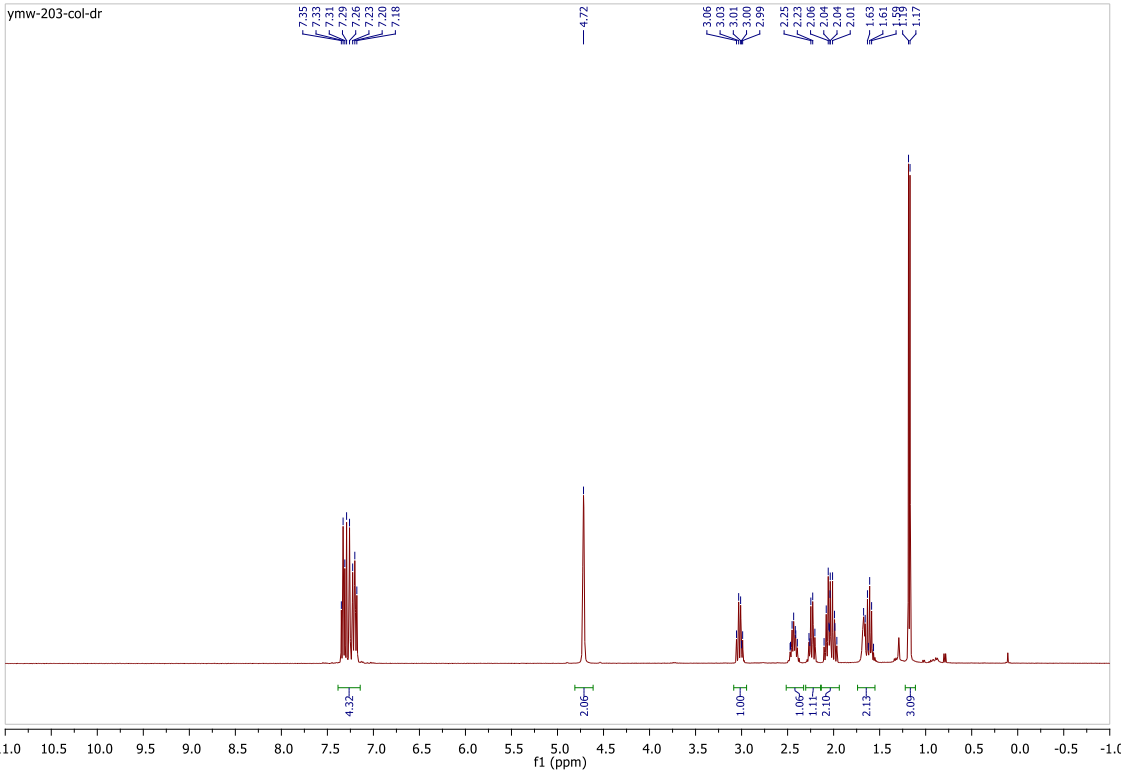
2e

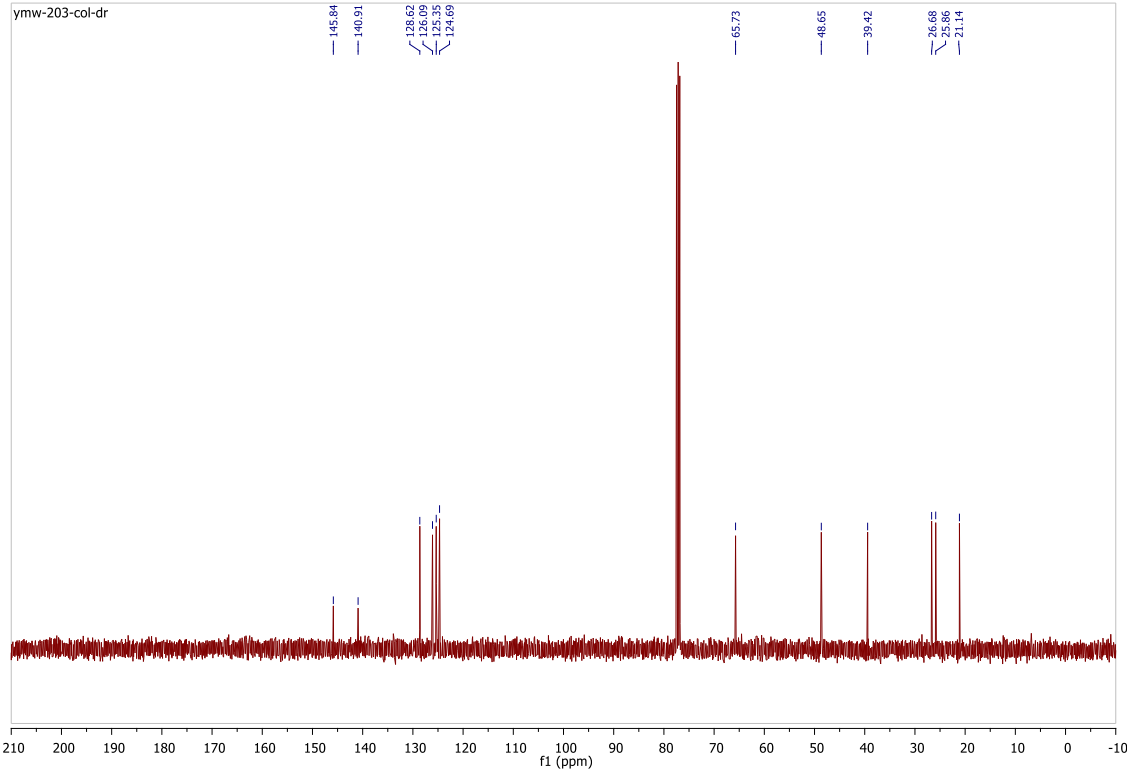


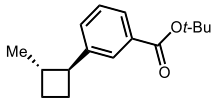



Me
OH

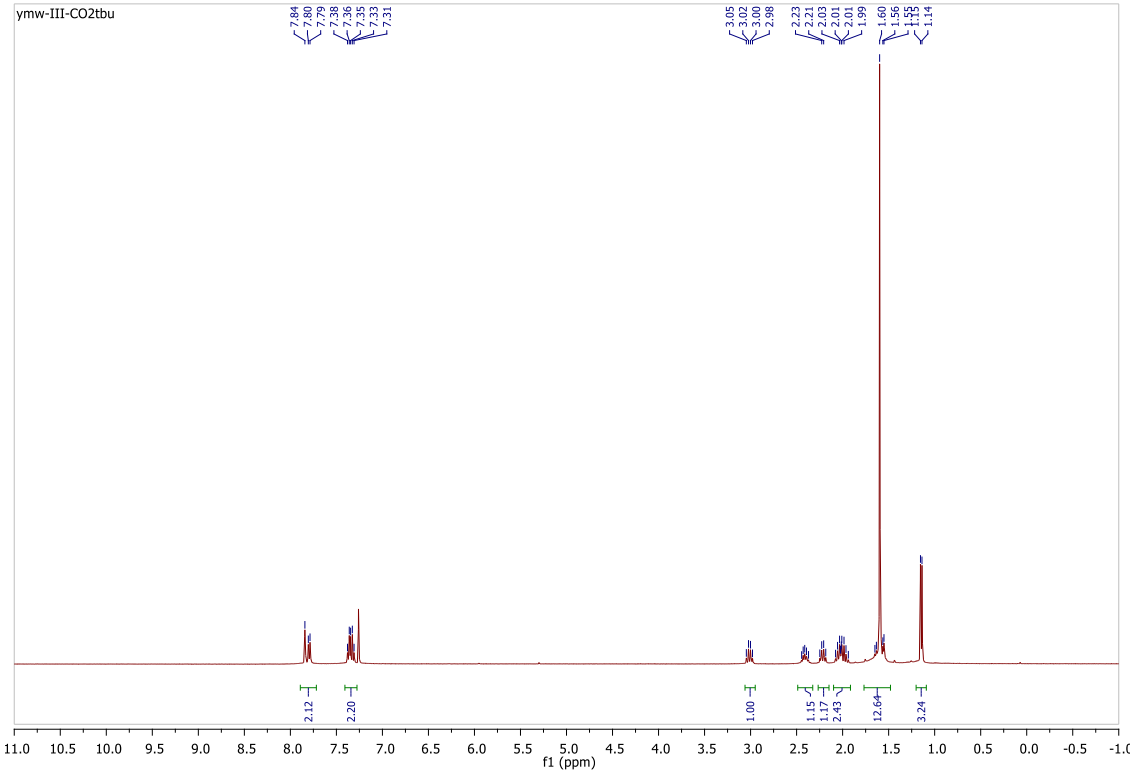
2f

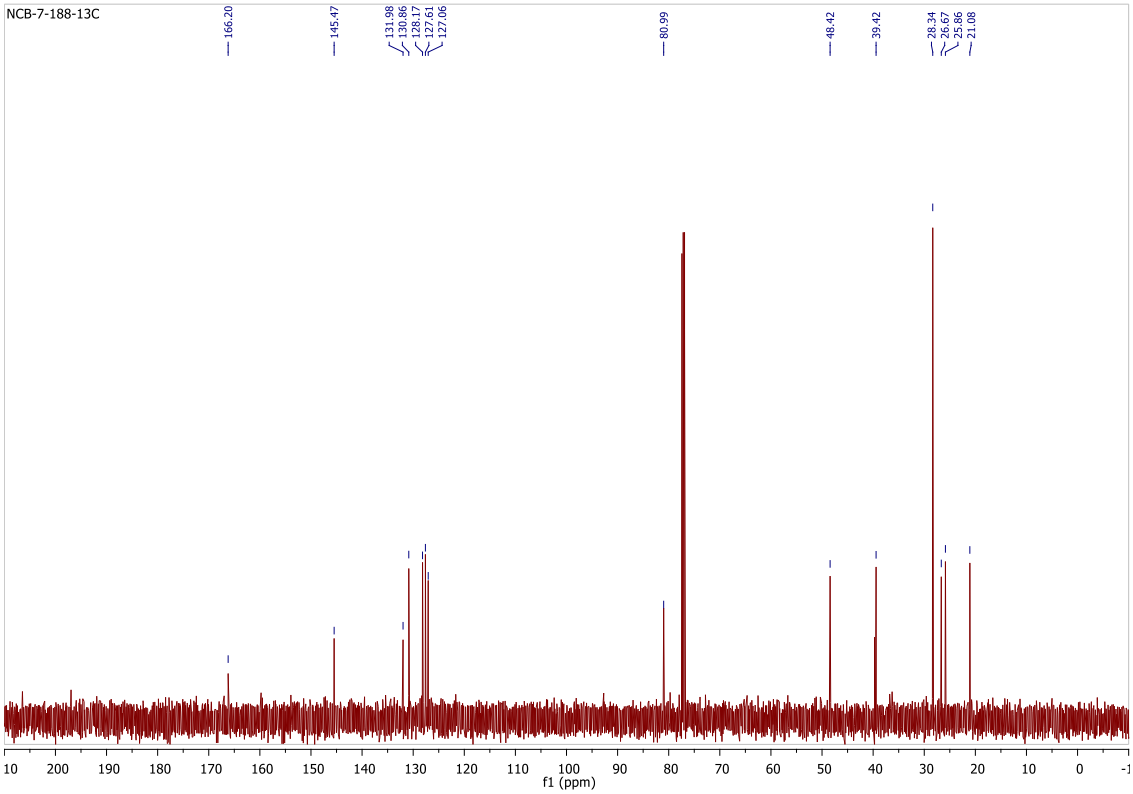

ymw-203-col-dr
7.35
7.33
7.31
7.29
7.26
7.23
7.20
7.18
4.72
3.06
3.03
3.01
3.00
2.99
2.25
2.23
2.06
2.04
2.04
2.01
1.63
1.61
1.59
1.19
1.17
4.32
2.06
1.00
1.06
1.11
2.10
2.13
3.09
f1 (ppm)

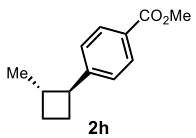

ymw-203-col-dr
145.84
140.91
128.62
126.09
125.35
124.69
65.73
48.65
39.42
26.68
25.86
21.14
f1 (ppm)


Me
Ot-Bu
O

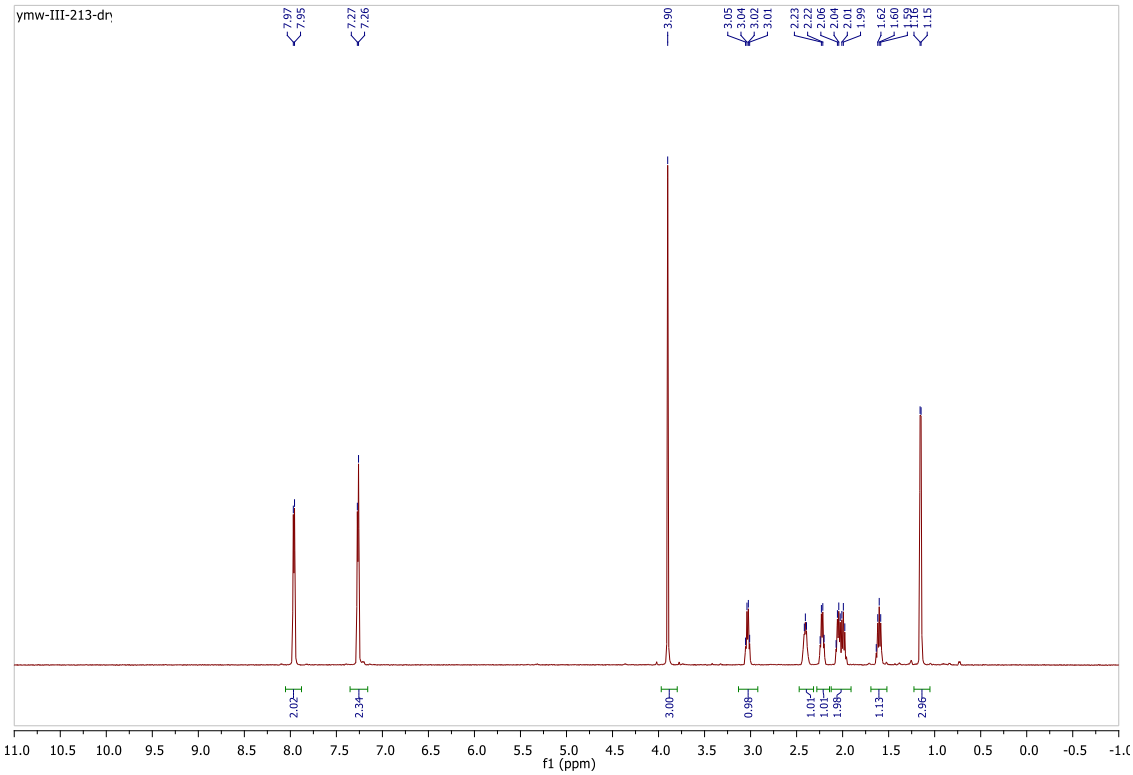
2g

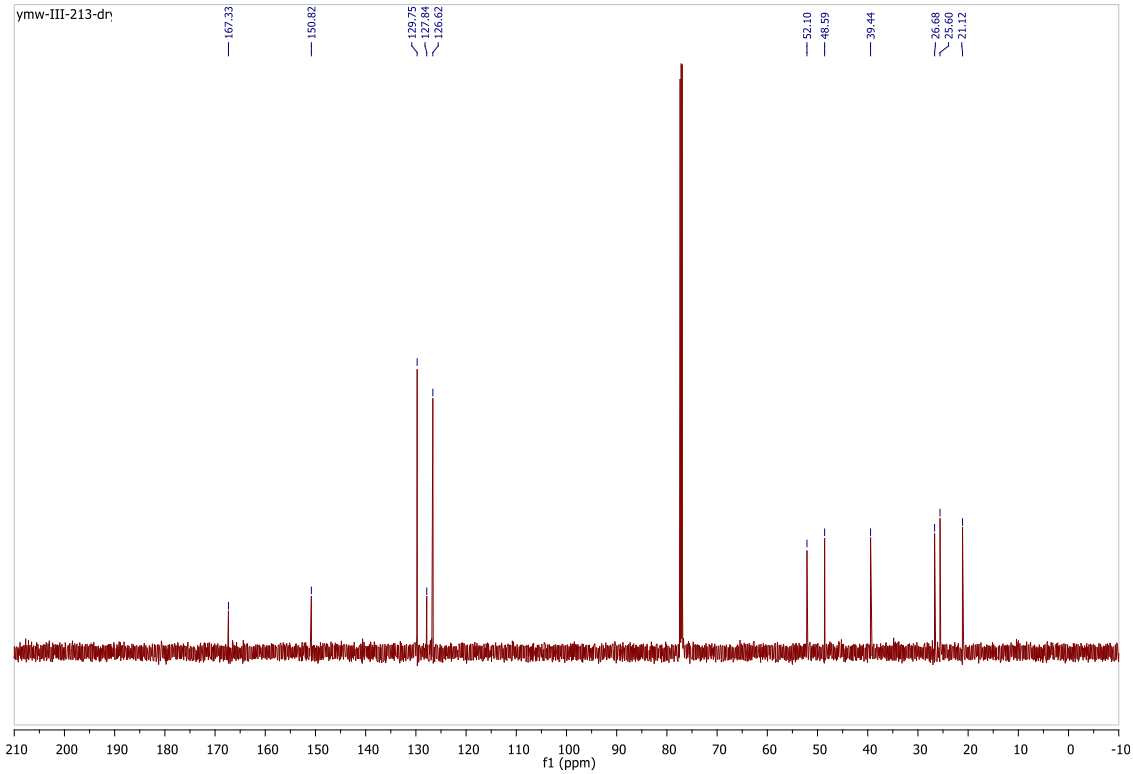

ymw-III-CO2tbu
7.84
7.80
7.79
7.38
7.36
7.35
7.33
7.31
3.05
3.02
3.00
2.98
2.23
2.21
2.03
2.01
2.01
1.99
1.60
1.56
1.55
1.15
1.14
2.12
2.20
1.00
1.15
1.17
2.43
12.64
3.24
f1 (ppm)

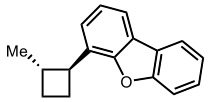

NCB-7-188-13C
166.20
145.47
131.98
130.86
128.17
127.61
127.06
80.99
48.42
39.42
28.34
26.67
25.86
21.08
f1 (ppm)


CO2Me
Me

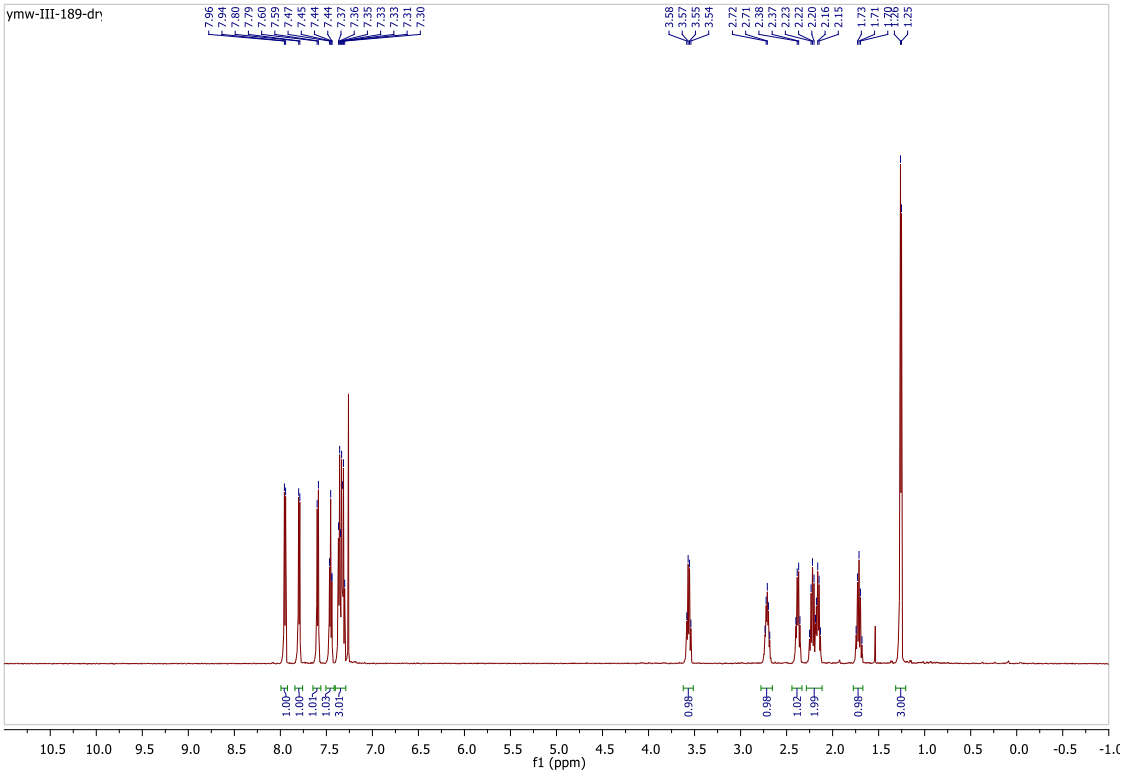
2h

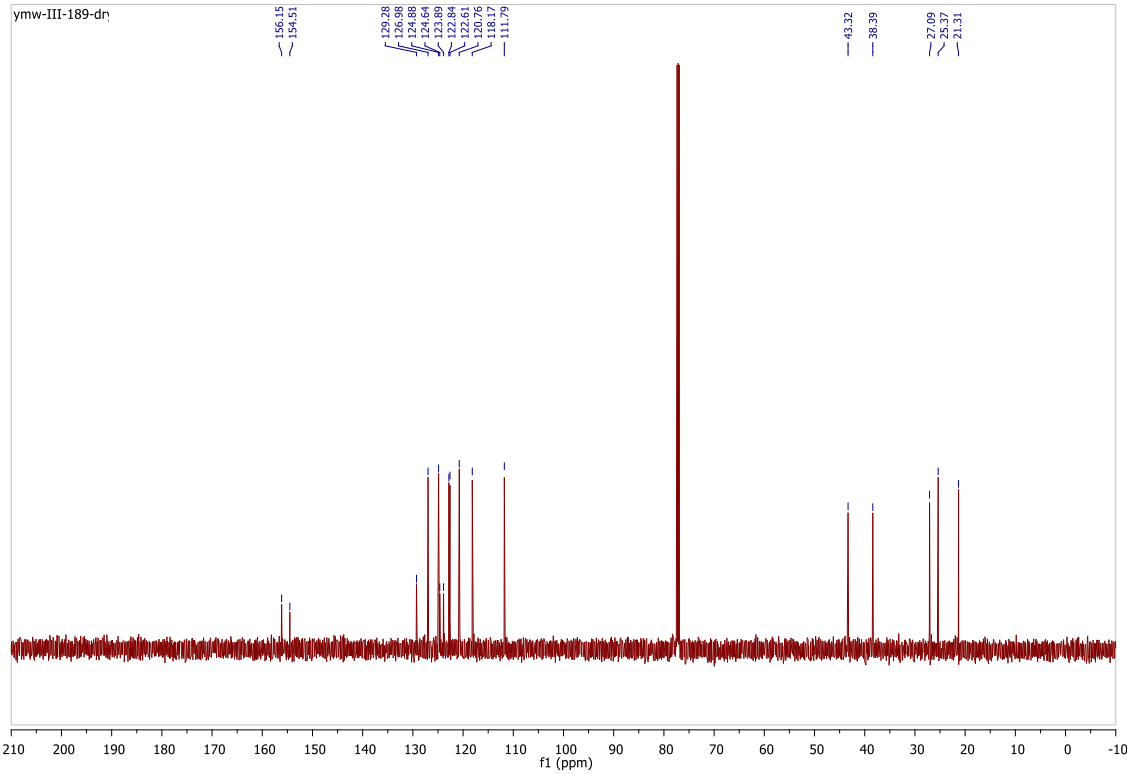

ymw-III-213-dn
7.97
7.95
7.27
7.26
3.90
3.05
3.04
3.02
3.01
2.23
2.22
2.06
2.04
2.01
1.99
1.62
1.60
1.59
1.16
1.15
2.02
2.34
3.00
0.98
1.01
1.01
1.98
1.13
2.96
f1 (ppm)

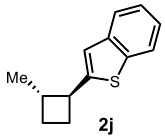

ymw-III-213-dn
167.33
150.82
129.75
127.84
126.62
52.10
48.59
39.44
26.68
25.60
21.12
f1 (ppm)


Me
O

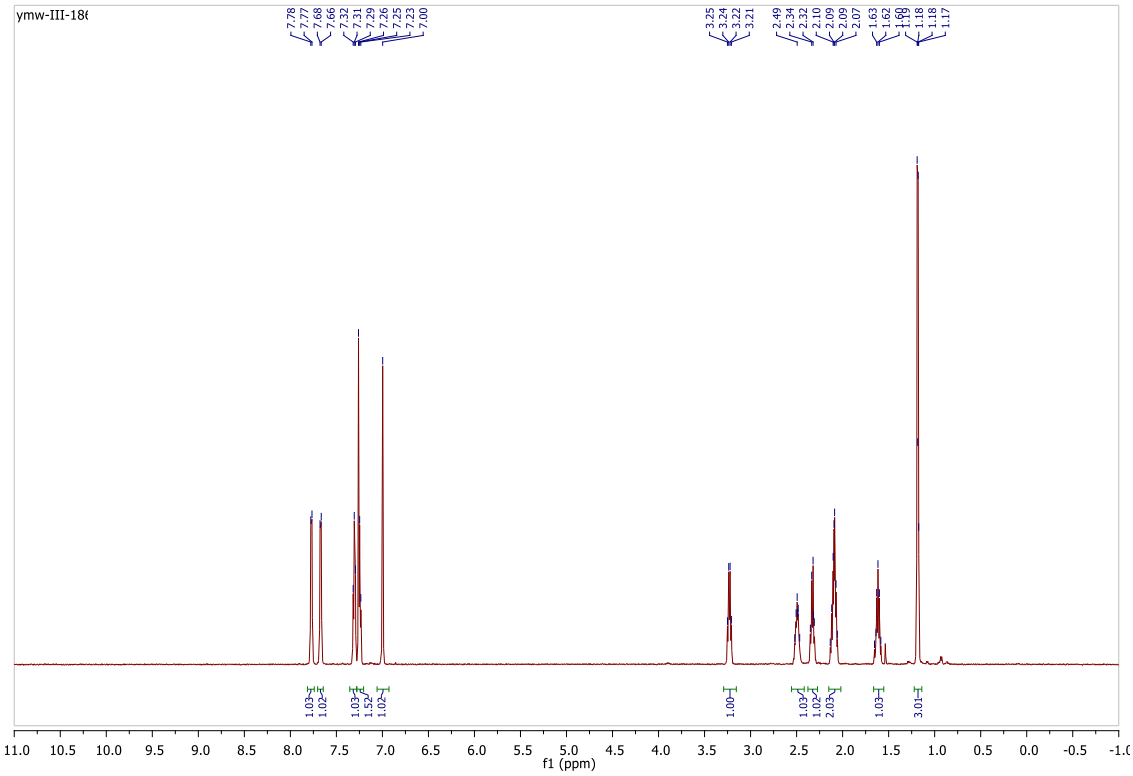
2i

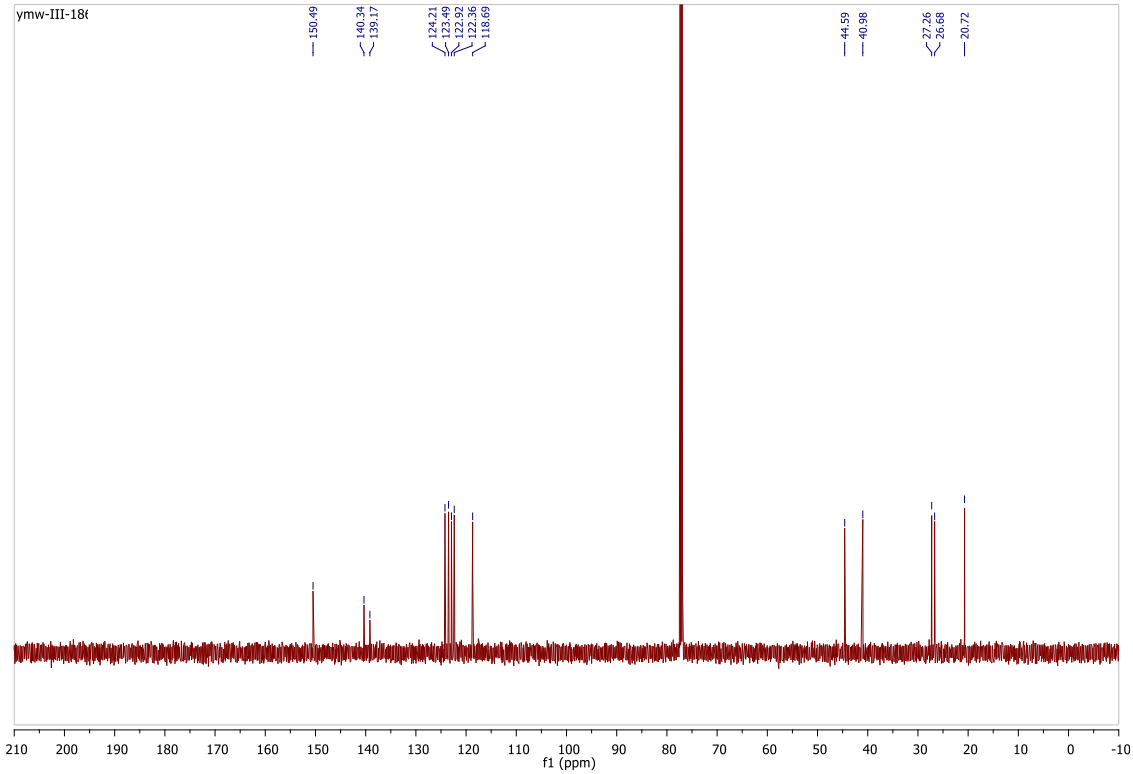

ymw-III-189-dn
7.96 7.94 7.80 7.79 7.60 7.59 7.47 7.45 7.44 7.37 7.36 7.35 7.33 7.33 7.31 7.30
3.58 3.57 3.55 3.54
2.72 2.71 2.38 2.37 2.23 2.22 2.20 2.16 2.15
1.73 1.71 1.70 1.28 1.25
1.00 1.00 1.01 1.03 3.01
0.98 0.98 1.02 1.99 0.98 3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

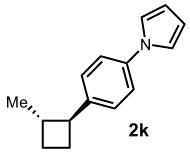

ymw-III-189-dn
156.15 154.51
129.28 126.98 124.88 124.64 123.89 122.84 122.61 120.76 118.17 111.79
43.32 38.39
27.09 25.37 21.31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
S

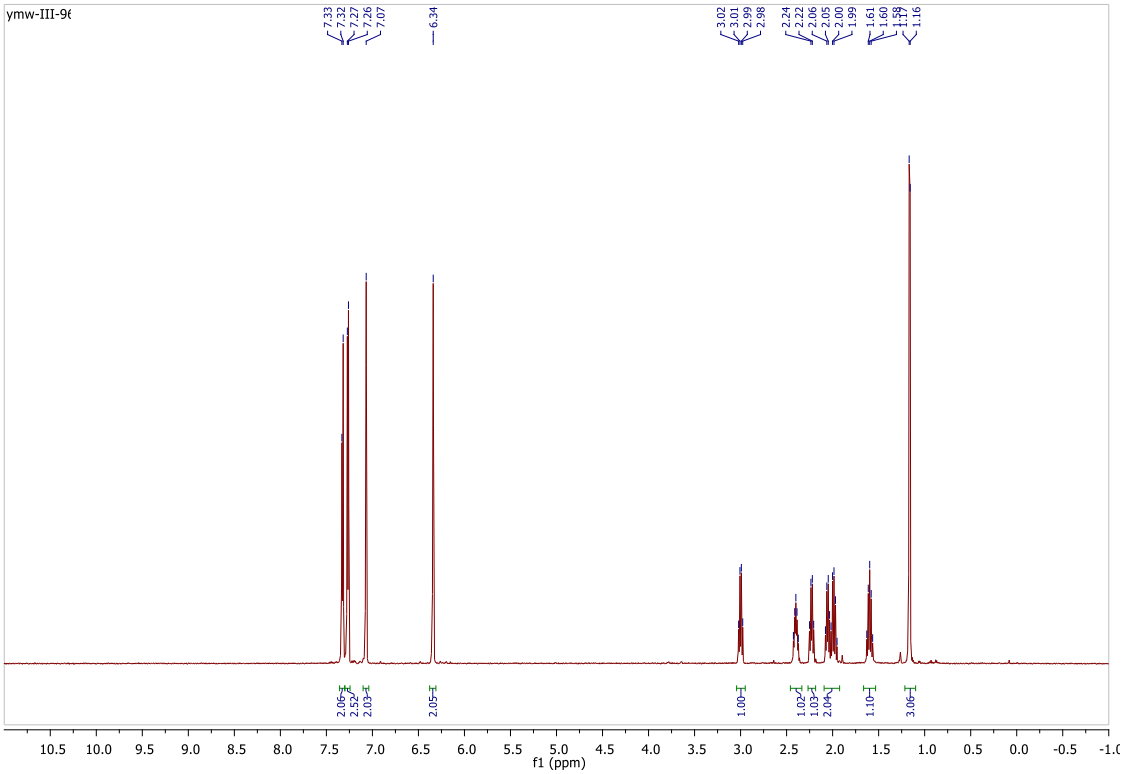
2j


ymw-III-18
7.78
7.77
7.68
7.66
7.32
7.31
7.29
7.26
7.25
7.23
7.00
3.25
3.24
3.22
3.21
2.49
2.34
2.32
2.10
2.09
2.09
2.09
2.07
1.63
1.62
1.60
1.59
1.18
1.18
1.17
1.03
1.02
1.03
1.52
1.02
1.00
1.03
1.02
2.03
1.03
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


ymw-III-18
150.49
140.34
139.17
124.21
123.49
122.92
122.36
118.69
44.59
40.98
27.26
26.68
20.72
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
N

2k


ymw-III-9(
7.33
7.32
7.27
7.26
7.07
6.34
3.02
3.01
2.99
2.98
2.24
2.22
2.06
2.05
2.00
1.99
1.61
1.60
1.58
1.17
1.16
2.06
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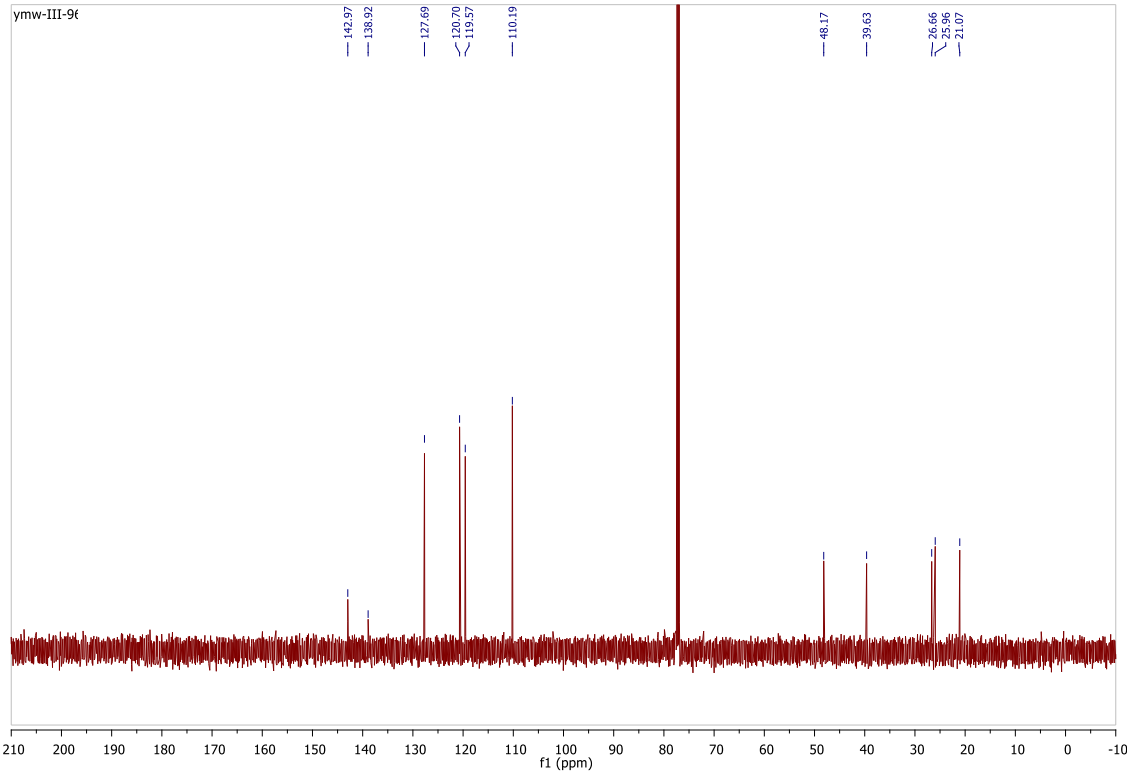
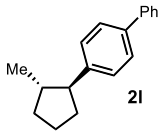
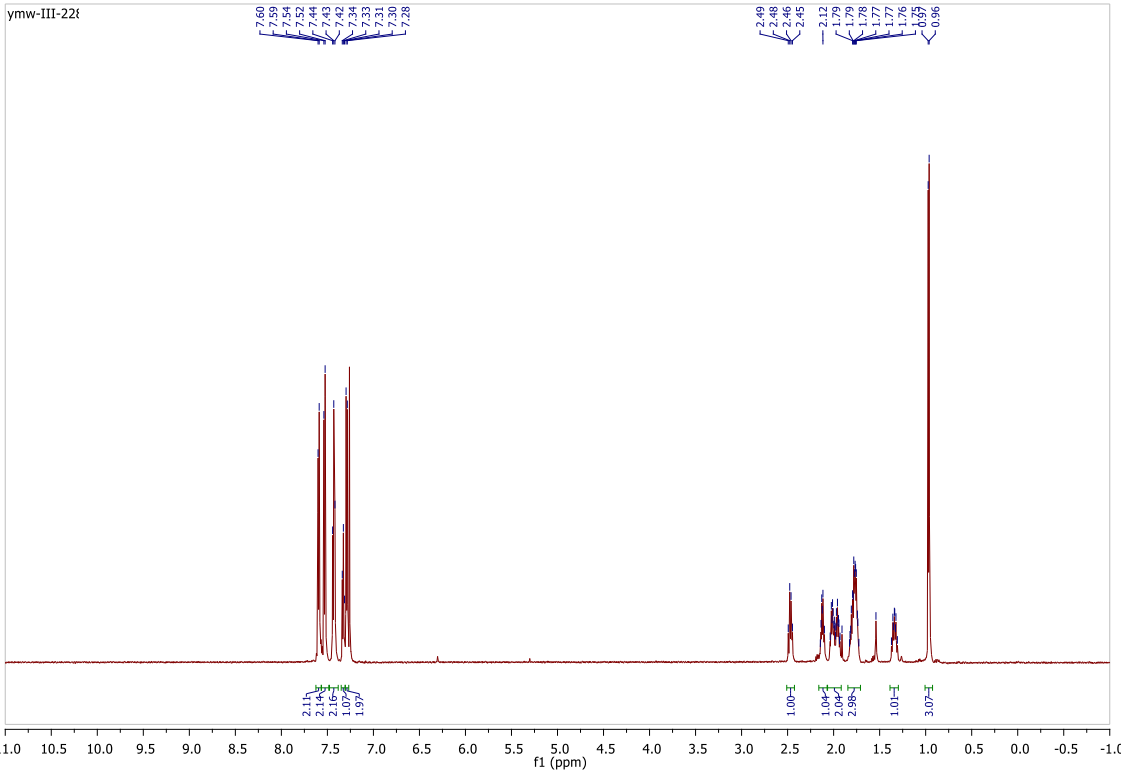
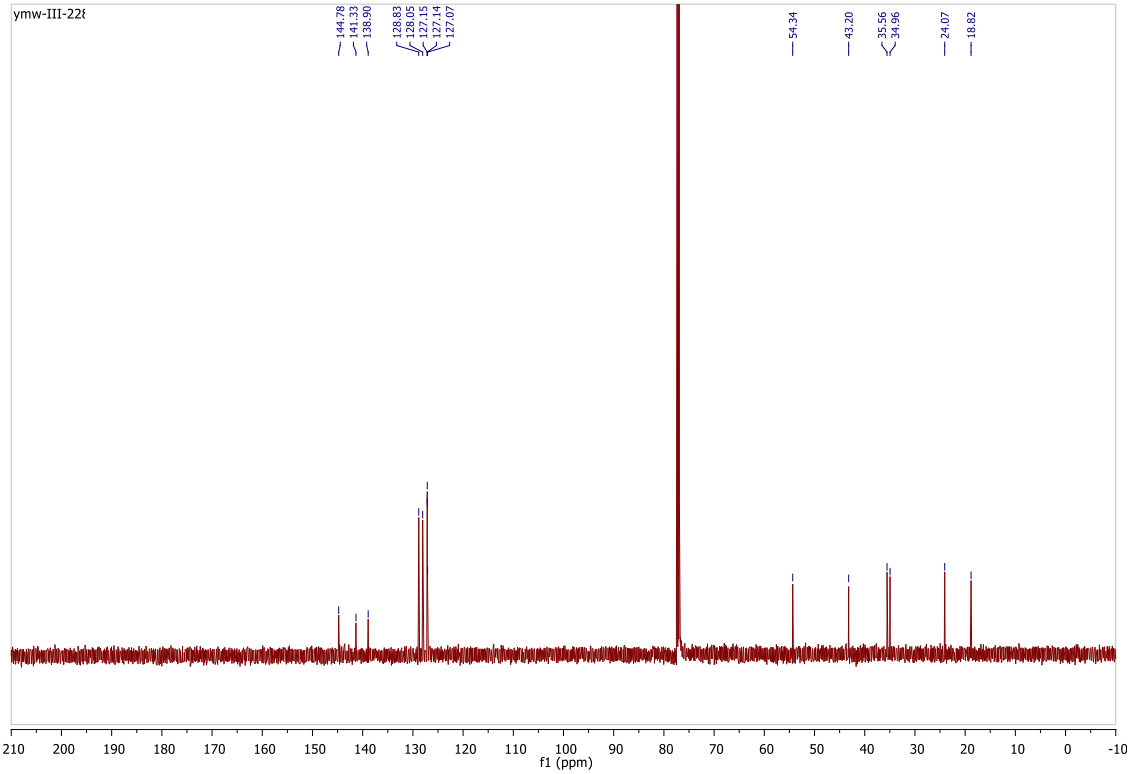
2.03
2.05
1.00
1.02
1.03
2.04
1.10
3.06
f1 (ppm)

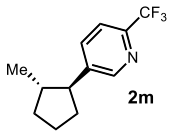

ymw-III-9(
142.97
138.92
127.69
120.70
119.57
110.19
48.17
39.63
26.66
25.96
21.07
f1 (ppm)


Ph
Me

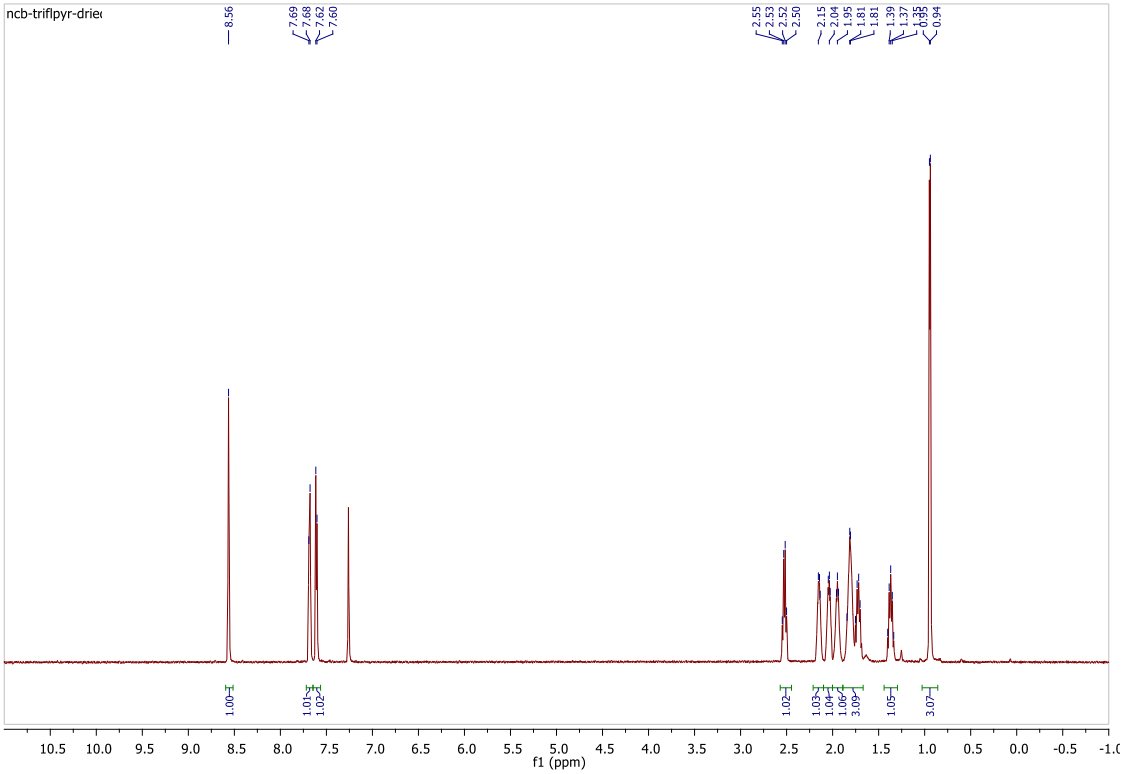
2l

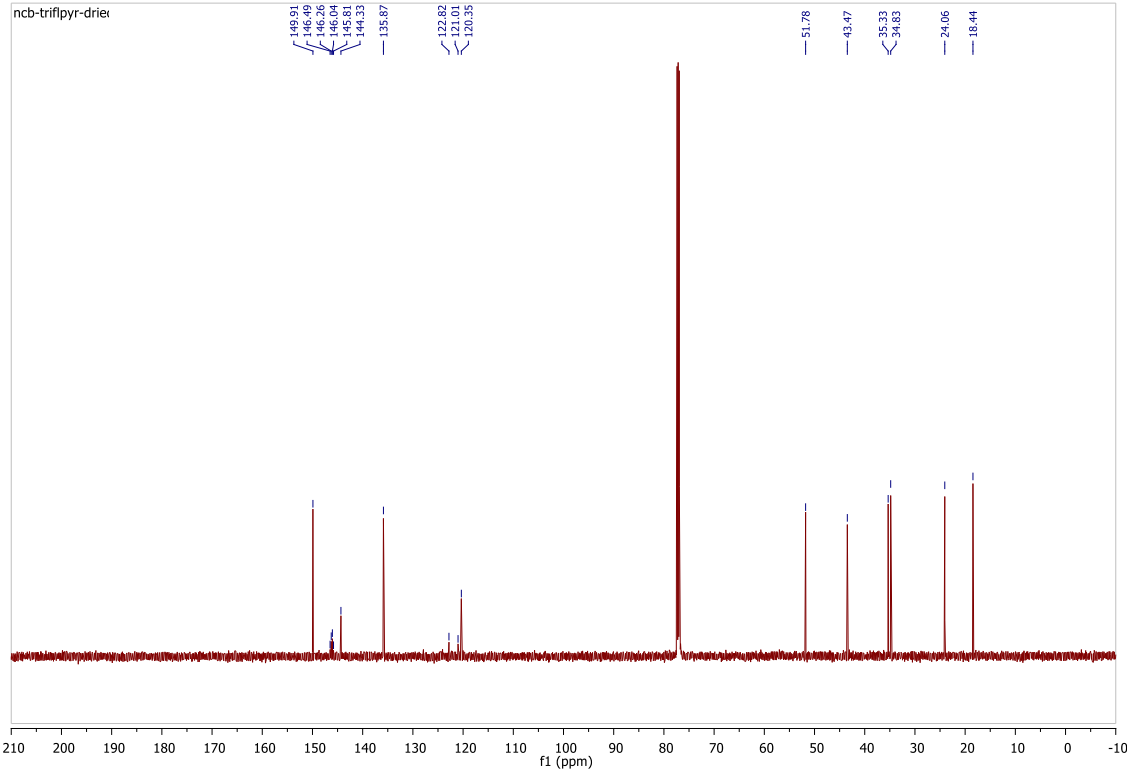

ymw-III-22
7.60
7.59
7.54
7.52
7.44
7.43
7.42
7.34
7.33
7.31
7.30
7.28
2.49
2.48
2.46
2.45
2.12
1.79
1.79
1.78
1.77
1.77
1.76
0.99
0.96
2.11
2.14
2.16
1.07
1.97
1.00
1.04
2.04
2.98
1.01
3.07
f1 (ppm)

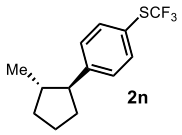

ymw-III-22
144.78
141.33
138.90
128.83
128.05
127.15
127.14
127.07
54.34
43.20
35.56
34.96
24.07
18.82
f1 (ppm)


CF3
N
Me

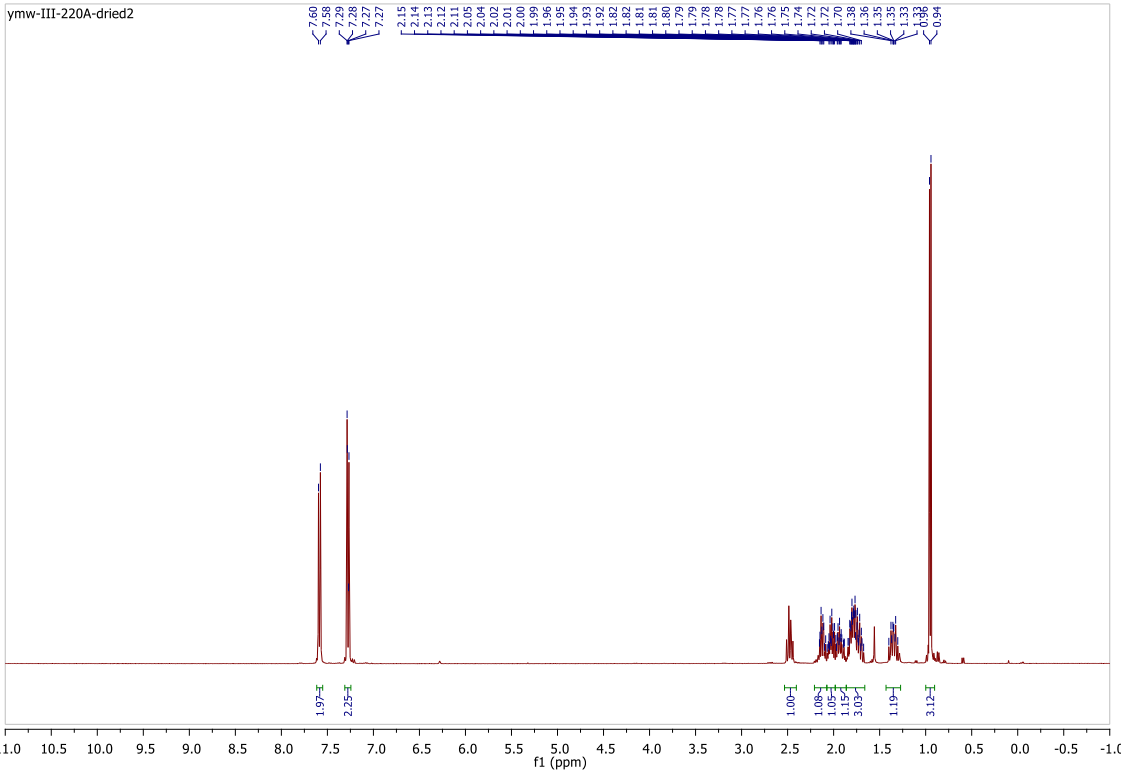
2m

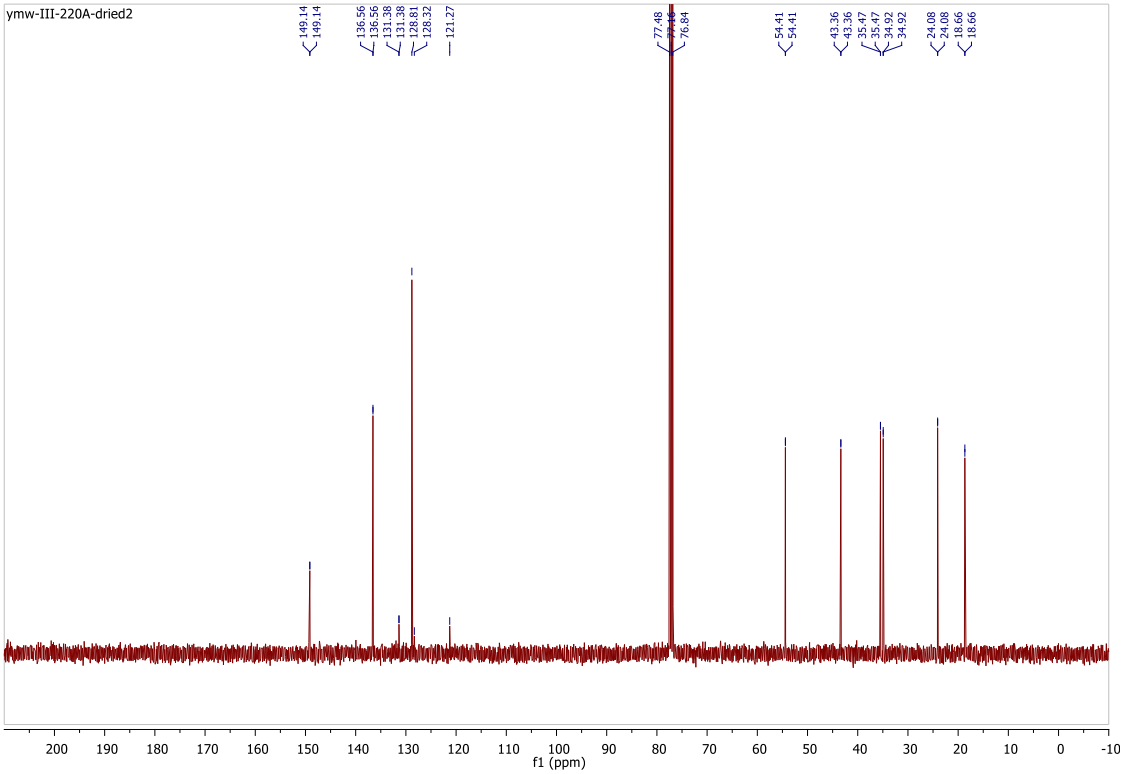

ncb-triflpyr-drie
8.56
7.69
7.68
7.62
7.60
2.55
2.53
2.52
2.50
2.15
2.04
1.95
1.81
1.81
1.39
1.37
0.95
0.94
1.00
1.01
1.02
1.02
1.03
1.04
1.06
3.09
1.05
3.07
f1 (ppm)

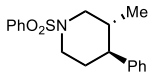

ncb-triflpyr-drie
149.91
146.49
146.26
146.04
145.81
144.33
135.87
122.82
121.01
120.35
51.78
43.47
35.33
34.83
24.06
18.44
f1 (ppm)



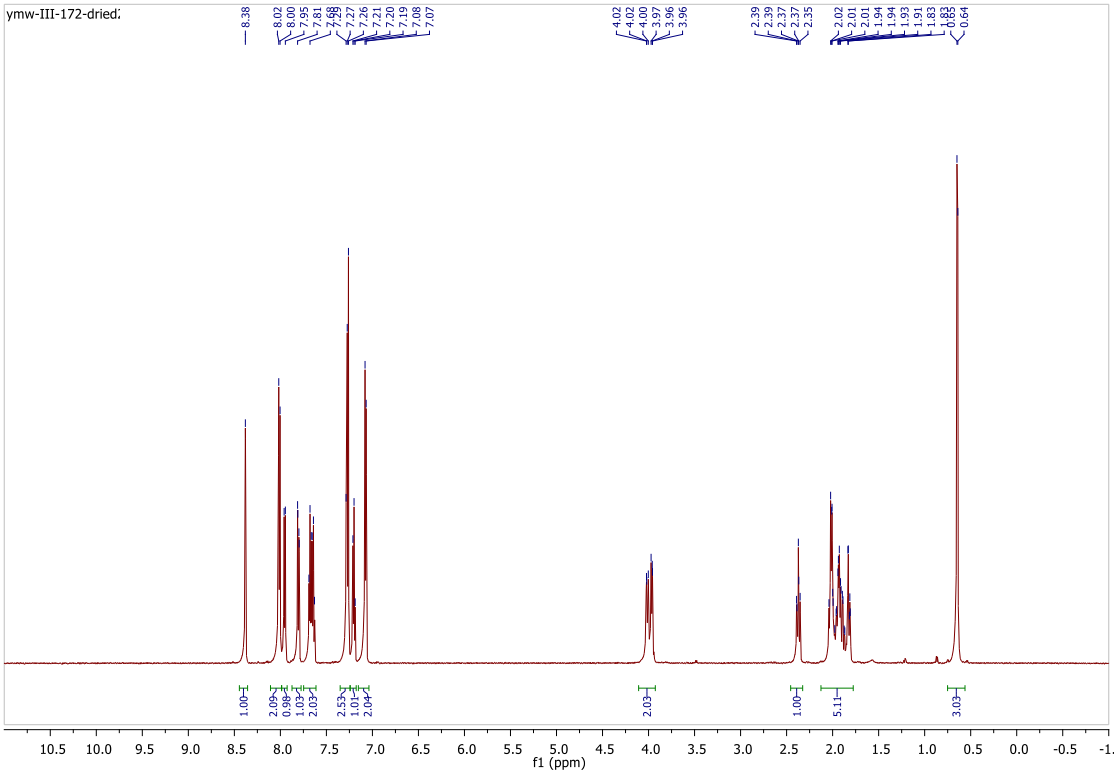
2n

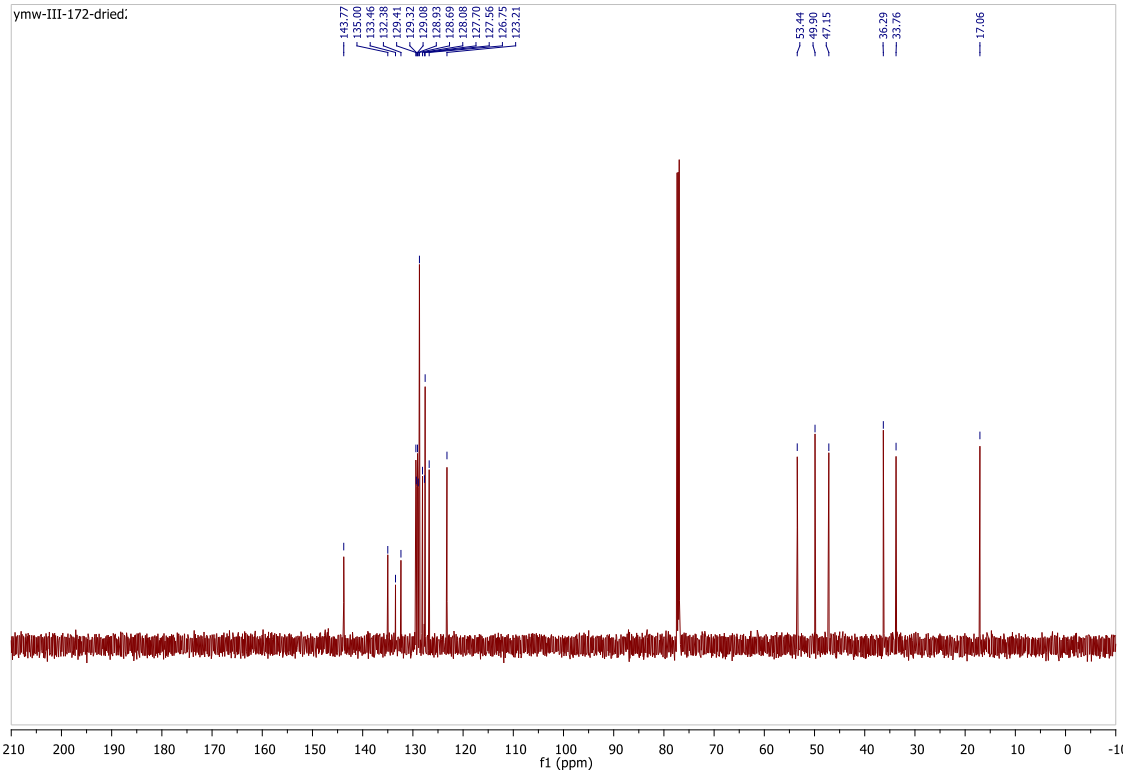


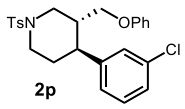



PhO2SN
Me
Ph

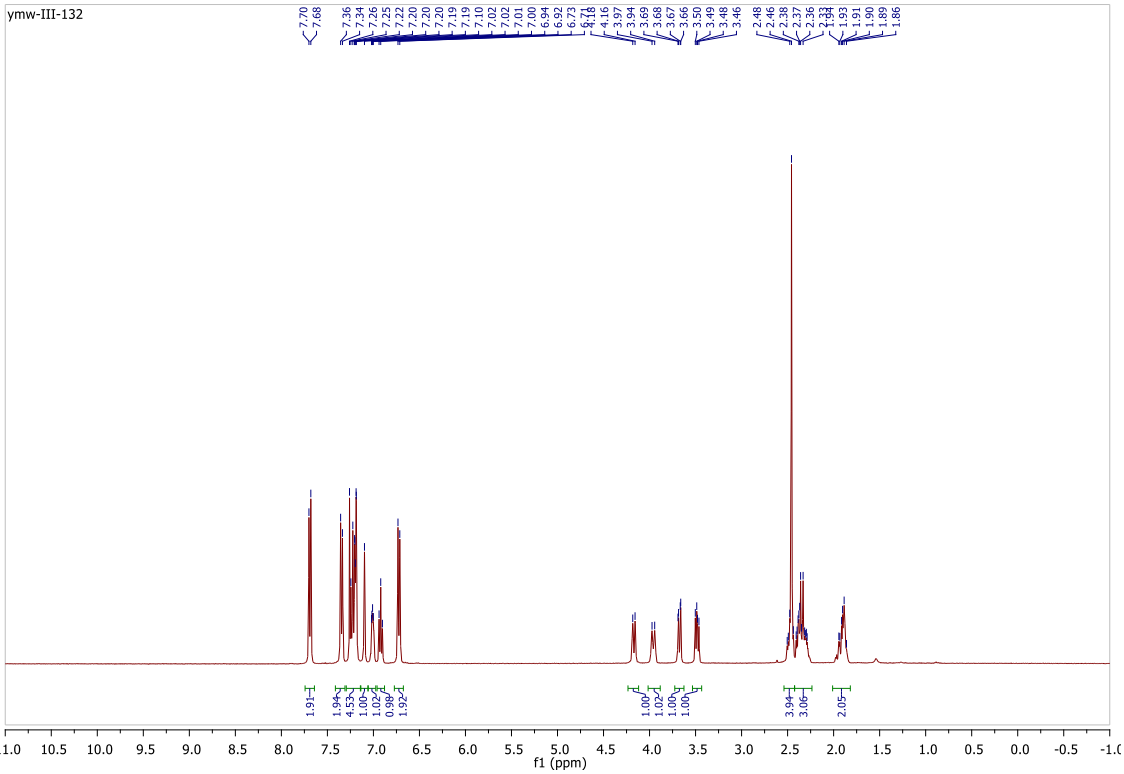
2o

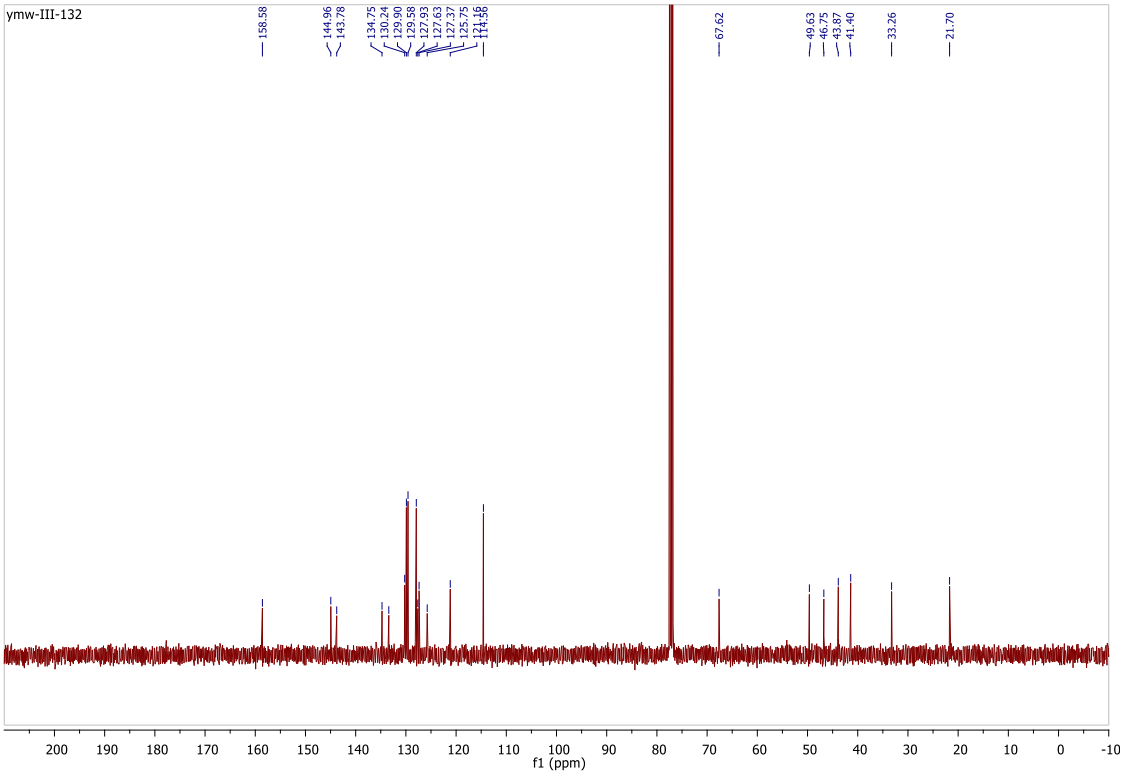

ymw-III-172-dried
8.38
8.02
8.00
7.95
7.81
7.68
7.27
7.26
7.21
7.20
7.19
7.08
7.07
4.02
4.02
4.00
3.97
3.96
3.96
2.39
2.39
2.37
2.37
2.35
2.02
2.01
2.01
1.94
1.94
1.93
1.91
1.83
1.83
0.83
0.64
1.00
2.09
0.98
1.03
2.03
2.53
1.01
2.04
2.03
1.00
5.11
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

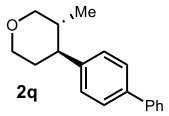

ymw-III-172-dried
143.77
135.00
133.46
132.38
129.41
129.32
129.08
128.93
128.69
128.08
127.70
127.56
126.75
123.21
53.44
49.90
47.15
36.29
33.76
17.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



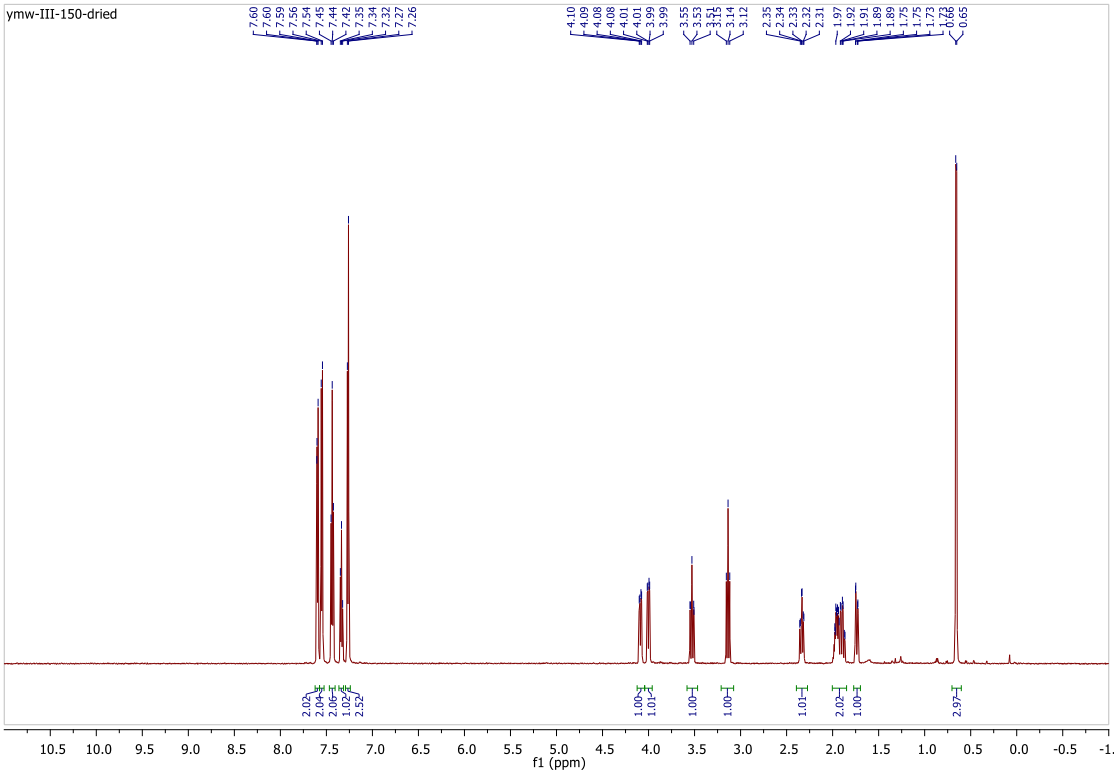
2p

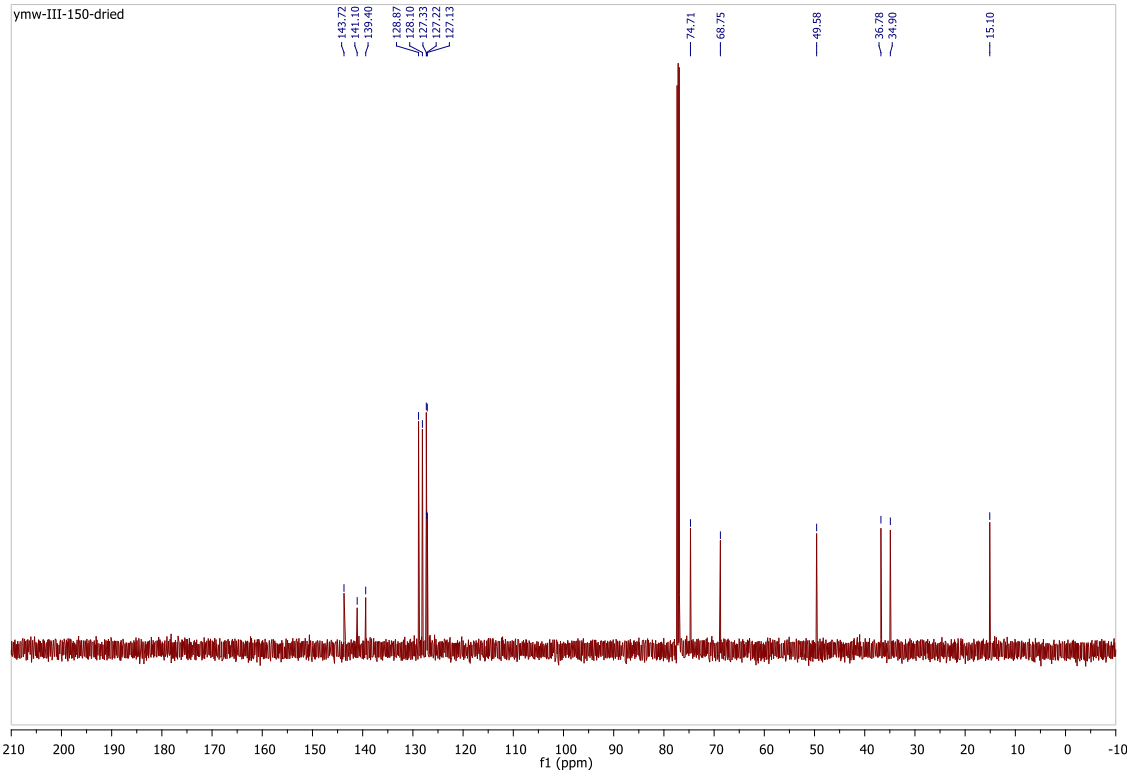


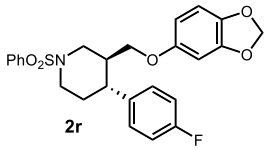



Me
O
Ph

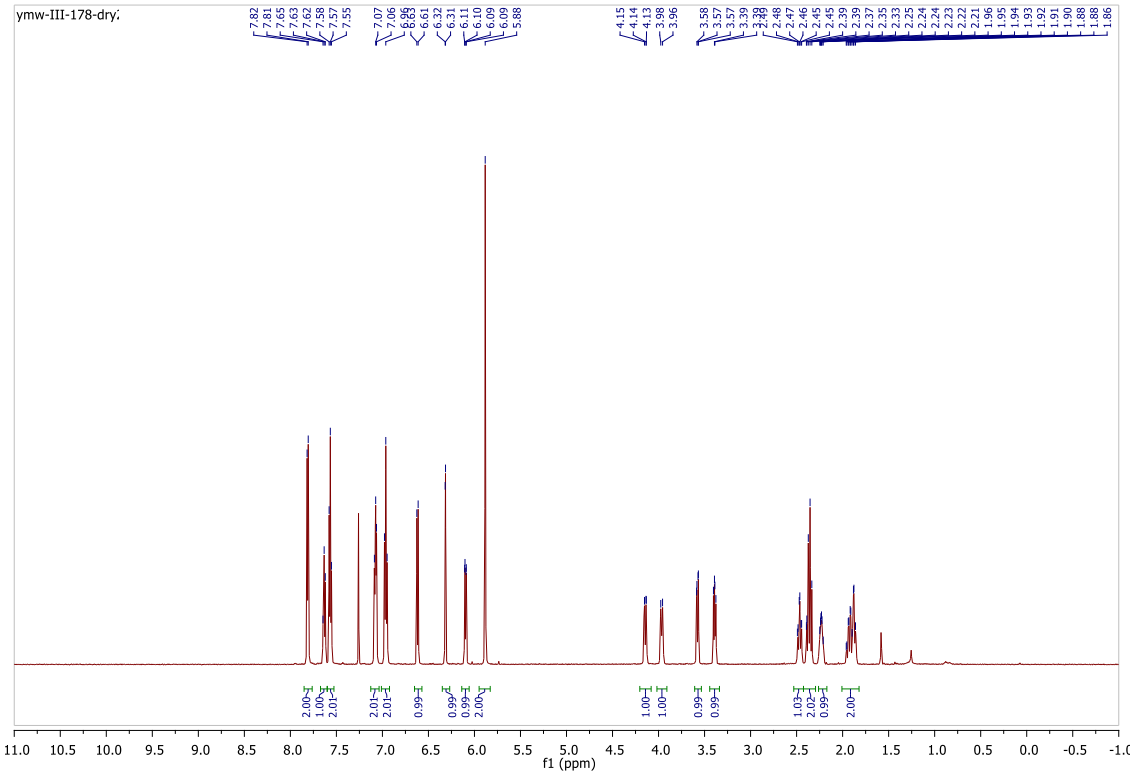
2q

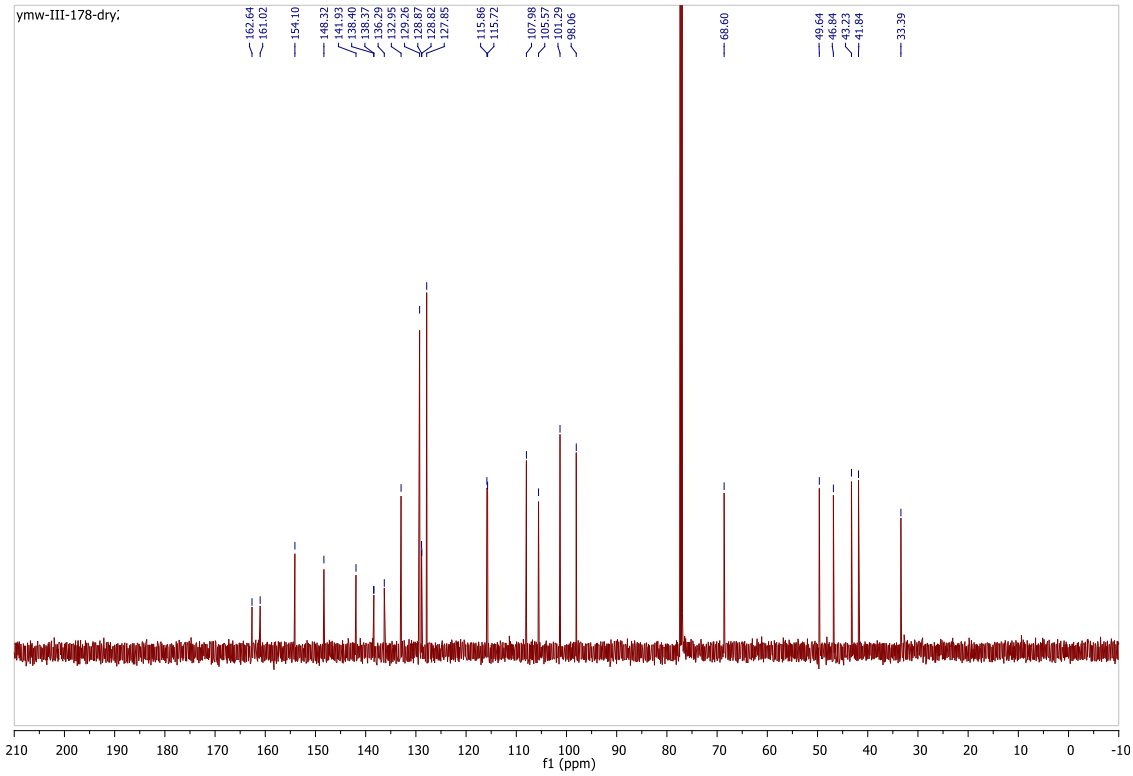

ymw-III-150-dried
7.60
7.60
7.59
7.56
7.54
7.45
7.44
7.42
7.35
7.34
7.32
7.27
7.26
4.10
4.09
4.08
4.08
4.01
4.01
3.99
3.99
3.99
3.55
3.53
3.51
3.50
3.14
3.12
2.35
2.34
2.33
2.32
2.31
1.97
1.92
1.91
1.89
1.89
1.75
1.75
1.73
0.68
0.65
2.02
2.04
2.06
1.02
2.52
1.00
1.01
1.00
1.00
1.01
2.02
1.00
2.97
f1 (ppm)

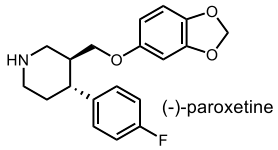

ymw-III-150-dried
143.72
141.10
139.40
128.87
128.10
127.33
127.22
127.13
74.71
68.75
49.58
36.78
34.90
15.10
f1 (ppm)



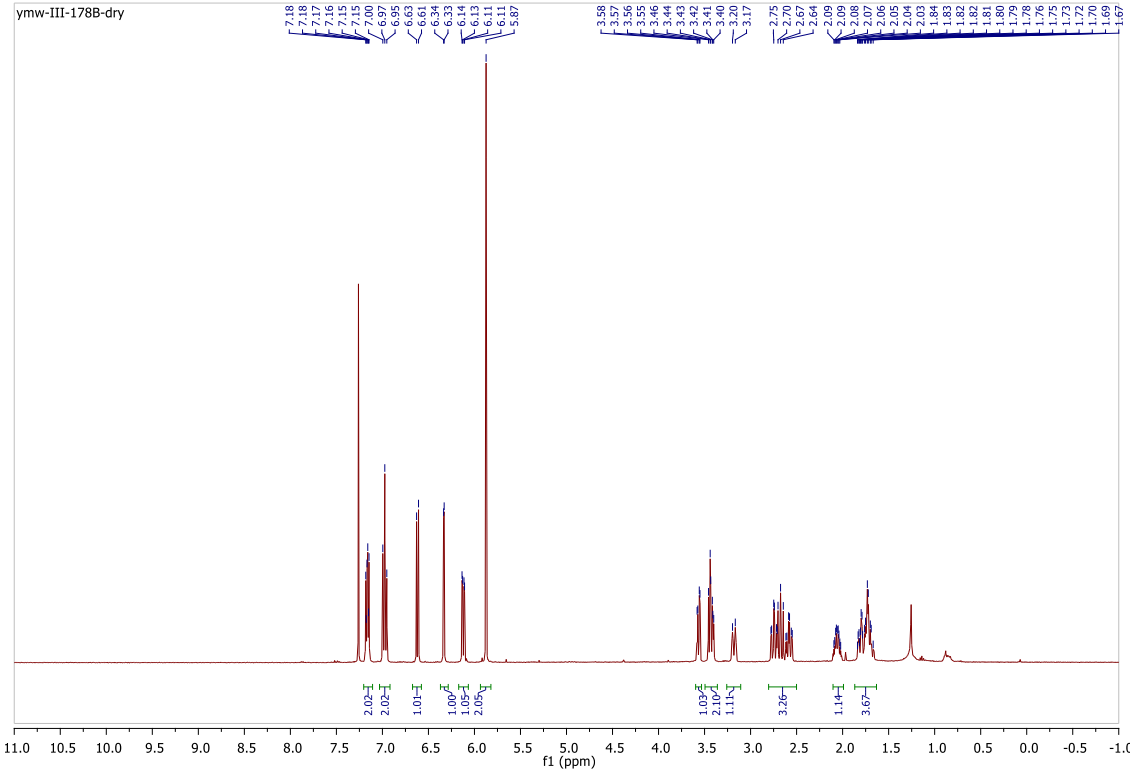
2r

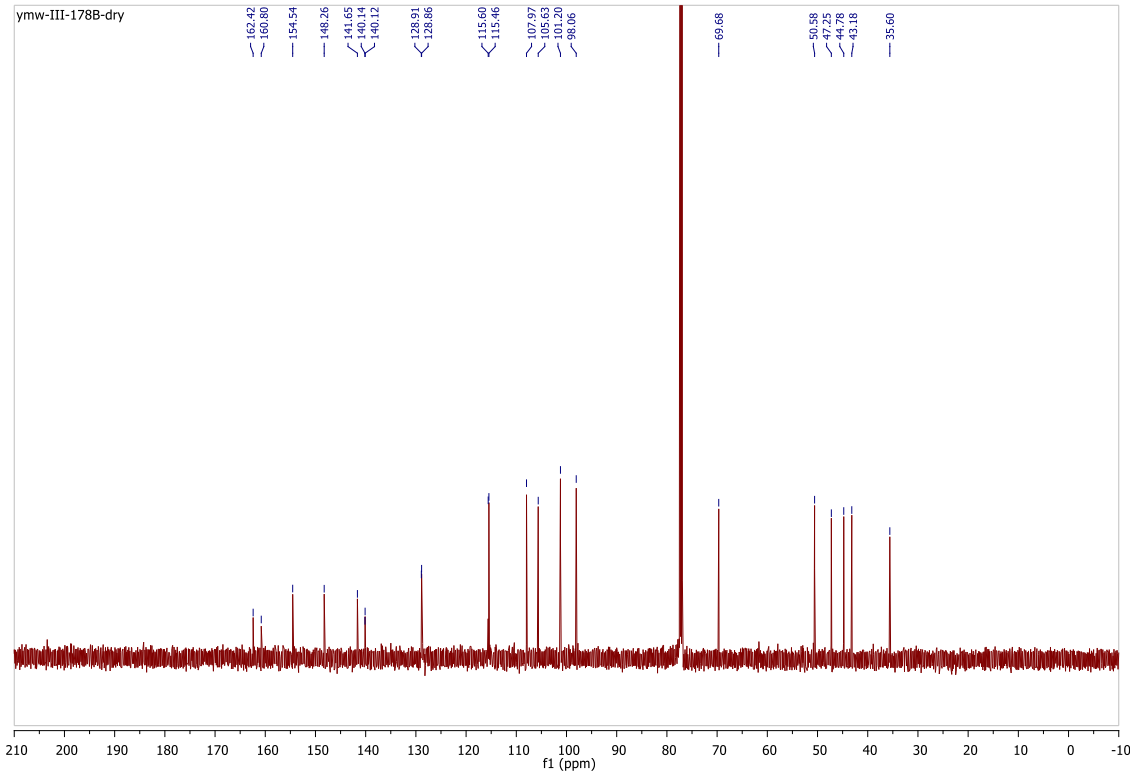


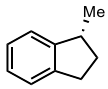



HN
O
O
O
F

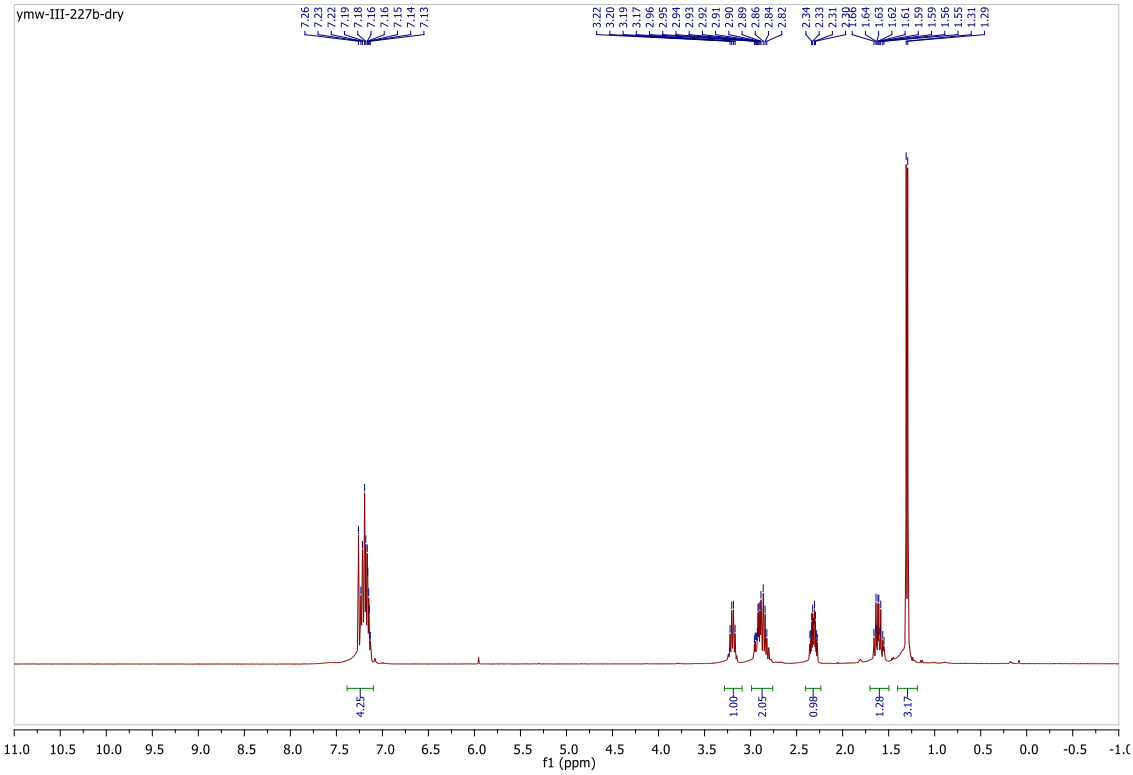
(-)-paroxetine

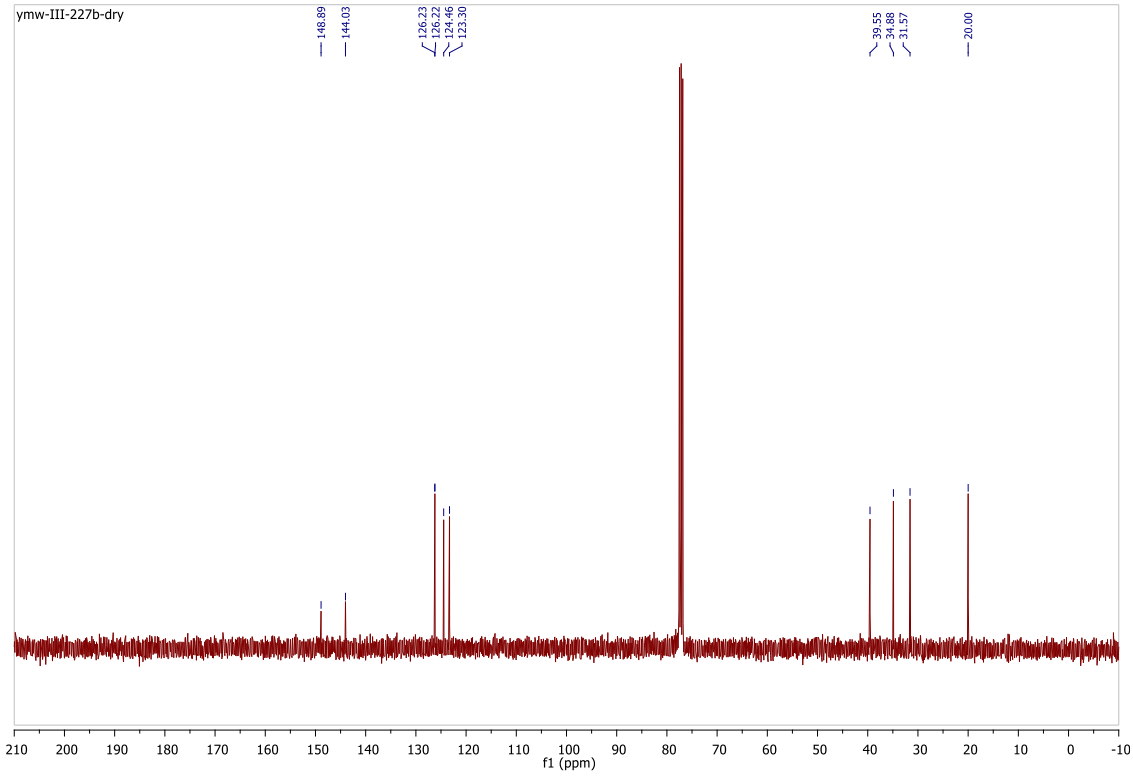

ymw-III-178B-dry
7.18 7.18 7.17 7.16 7.15 7.15 7.00 6.97 6.95 6.63 6.61 6.34 6.33 6.14 6.13 6.11 6.11 5.87
3.58 3.57 3.56 3.55 3.46 3.44 3.43 3.42 3.41 3.40 3.20 3.17 2.75 2.70 2.67 2.64 2.09 2.09 2.08 2.07 2.06 2.05 2.04 2.03 1.84 1.83 1.82 1.82 1.81 1.80 1.79 1.78 1.76 1.75 1.73 1.72 1.70 1.69 1.67
2.02 2.02 1.01 1.00 1.05 2.05 1.03 2.10 1.11 3.26 1.14 3.67
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

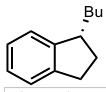

ymw-III-178B-dry
162.42 160.80 154.54 148.26 141.65 140.14 140.12 128.91 128.86 115.60 115.46 107.97 105.63 101.20 98.06 69.68 50.58 47.25 44.78 43.18 35.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me

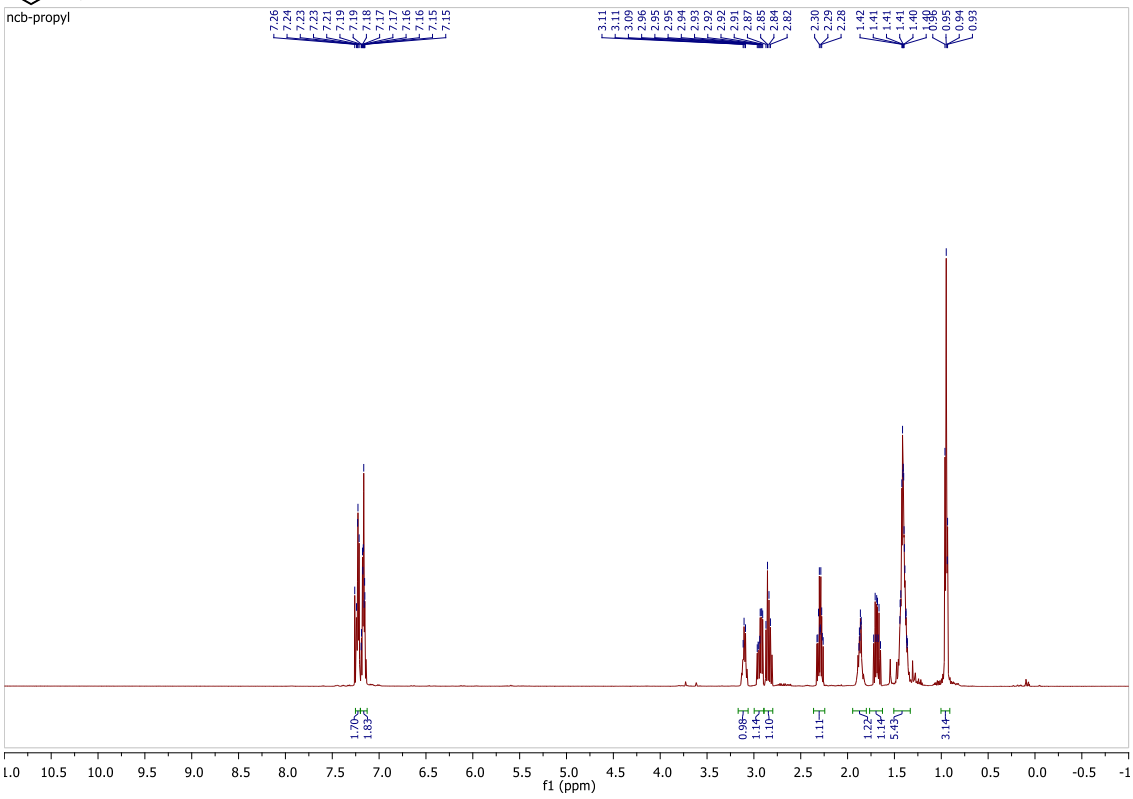
4a

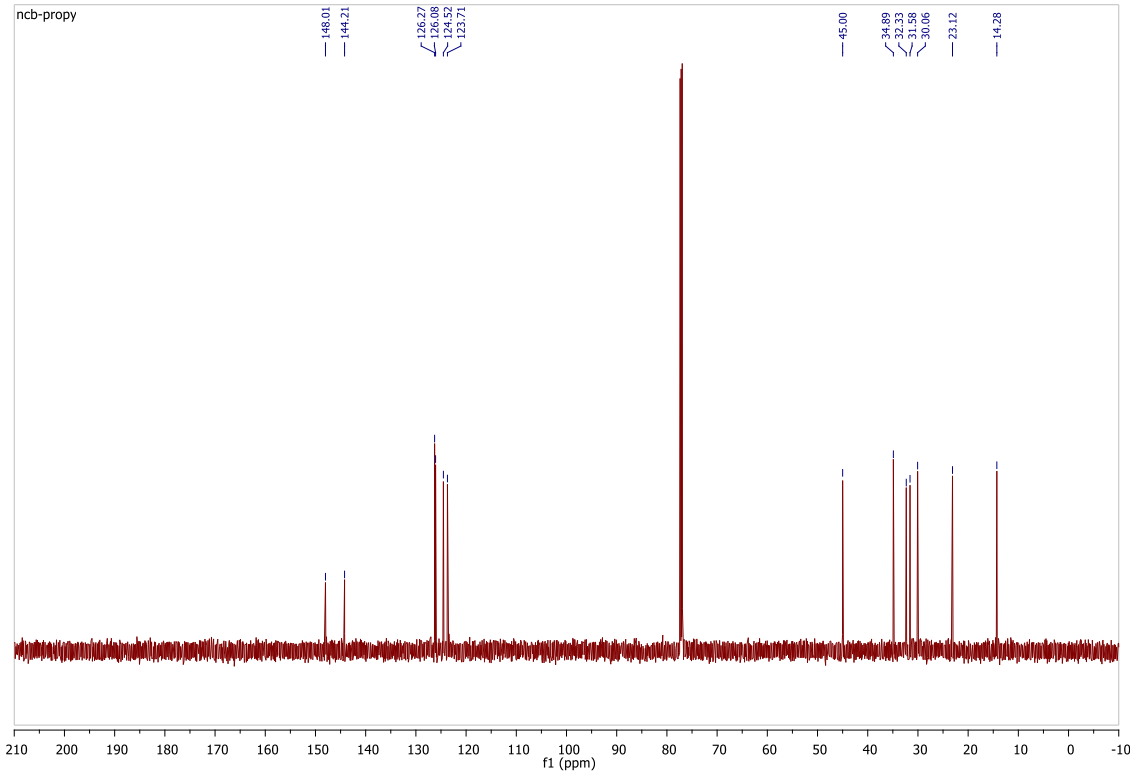

ymw-III-227b-dry
7.26
7.23
7.22
7.19
7.18
7.16
7.16
7.15
7.14
7.13
3.22
3.20
3.19
3.17
2.96
2.95
2.94
2.93
2.92
2.91
2.90
2.89
2.86
2.84
2.82
2.34
2.33
2.31
2.30
2.30
1.64
1.63
1.62
1.61
1.59
1.59
1.59
1.56
1.55
1.31
1.29
4.25
1.00
2.05
0.98
1.28
3.17
f1 (ppm)

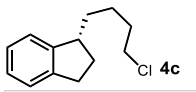

ymw-III-227b-dry
148.89
144.03
126.23
126.22
124.46
123.30
39.55
34.88
31.57
20.00
f1 (ppm)


Bu

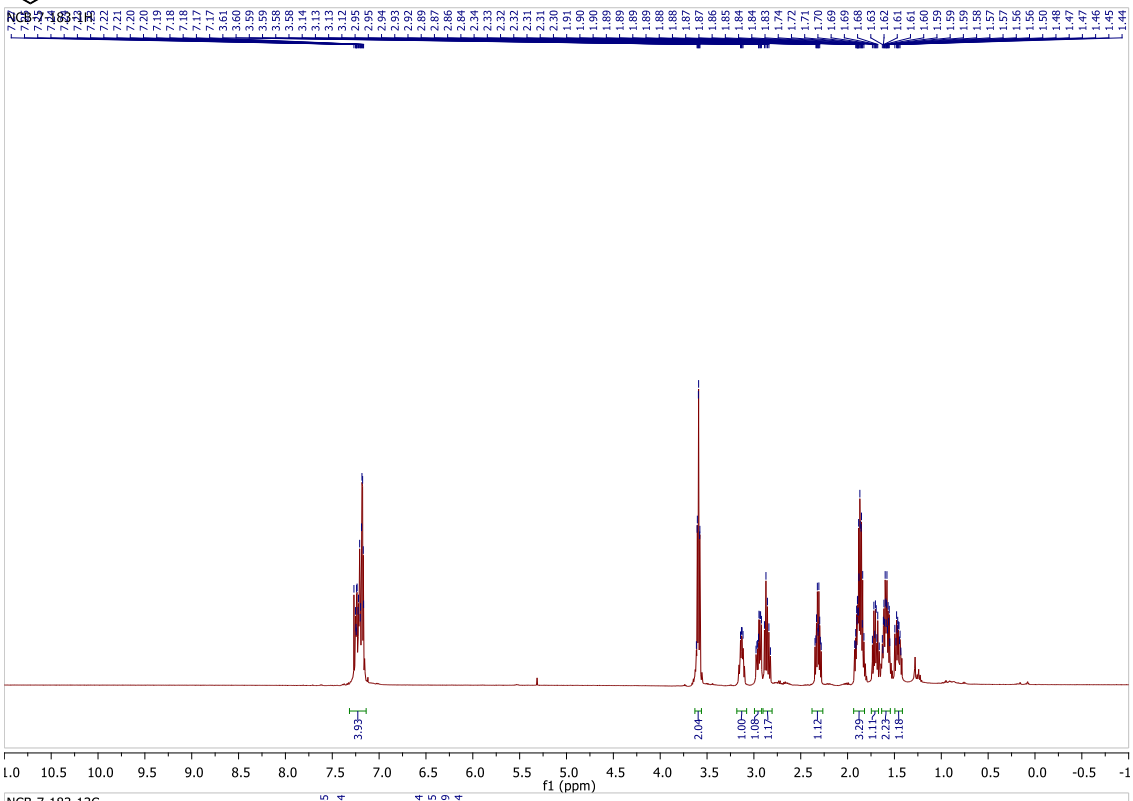
4b

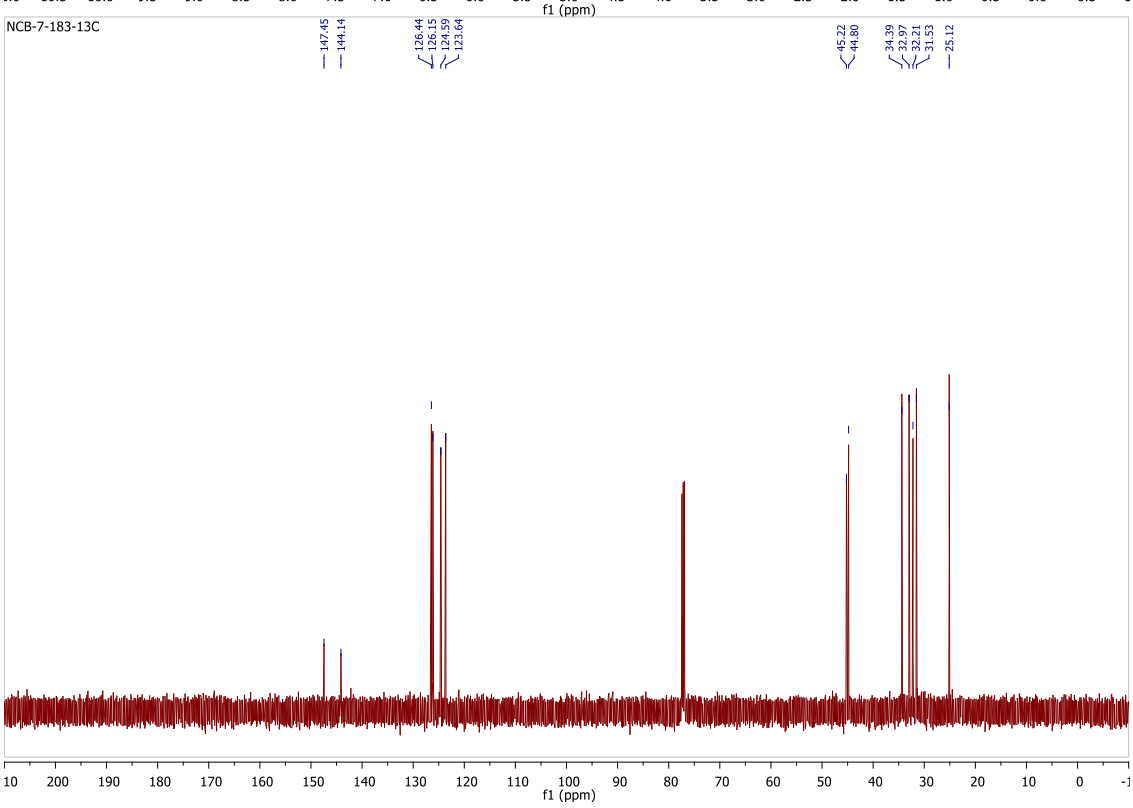

ncb-propyl
7.26 7.24 7.23 7.23 7.21 7.19 7.19 7.18 7.17 7.17 7.16 7.15 7.15
3.11 3.11 3.09 2.96 2.95 2.95 2.94 2.93 2.92 2.92 2.91 2.87 2.85 2.84 2.82
2.30 2.29 2.28
1.42 1.41 1.41 1.41 1.40 0.98 0.98 0.95 0.94 0.93
1.70
1.83
0.98
1.14
1.10
1.11
1.22
1.14
5.43
3.14
f1 (ppm)

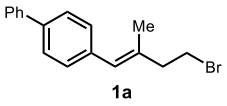

ncb-propy
148.01 144.21
126.27 126.08 124.52 123.71
45.00
34.89 32.33 31.58 30.06
23.12
14.28
f1 (ppm)


Cl

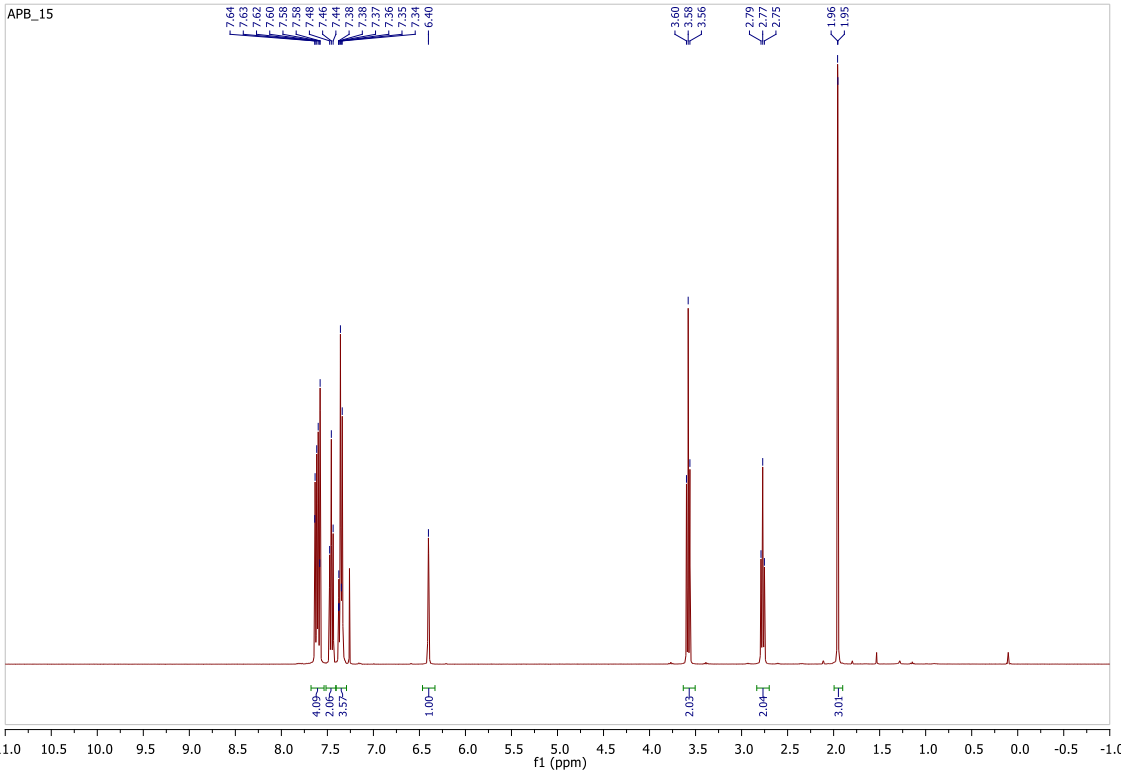
4c

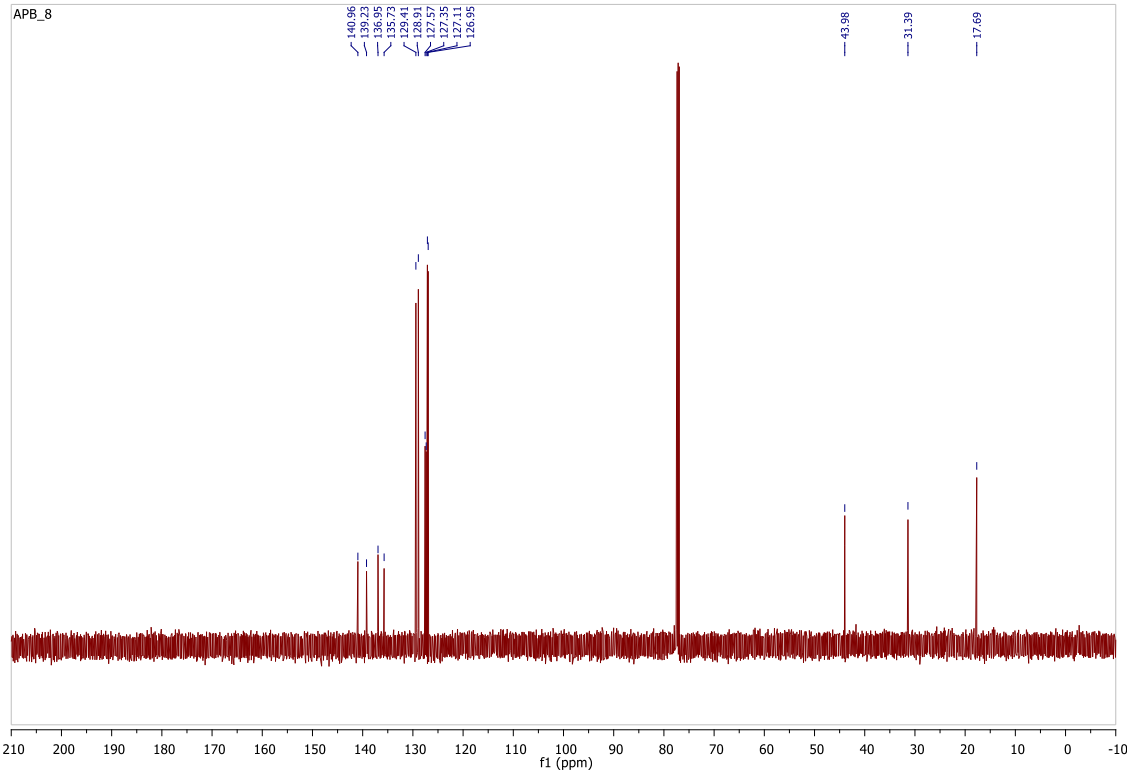

NCB-7-183-1H
3.93
2.04
1.00
1.08
1.17
1.12
3.29
1.11
2.23
1.18
f1 (ppm)

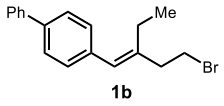

NCB-7-183-13C
147.45
144.14
126.44
126.15
124.59
123.64
45.22
44.80
34.39
32.97
32.21
31.53
25.12
f1 (ppm)


Ph
Me
Br

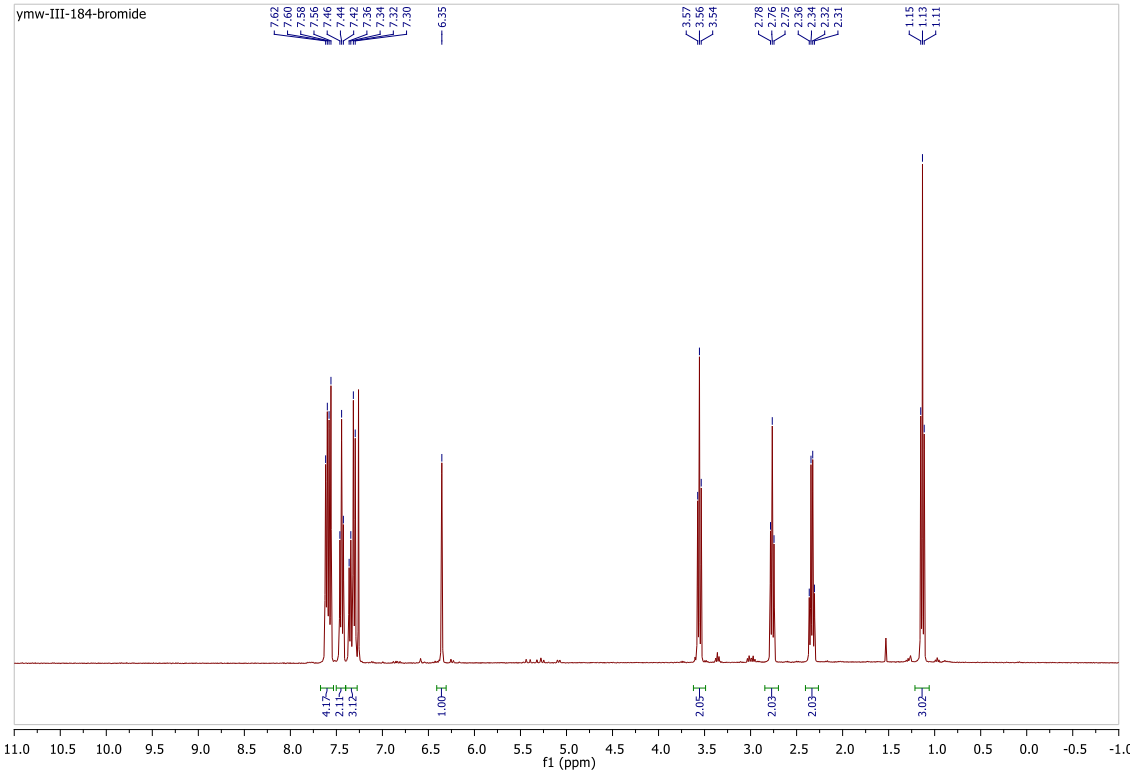
1a

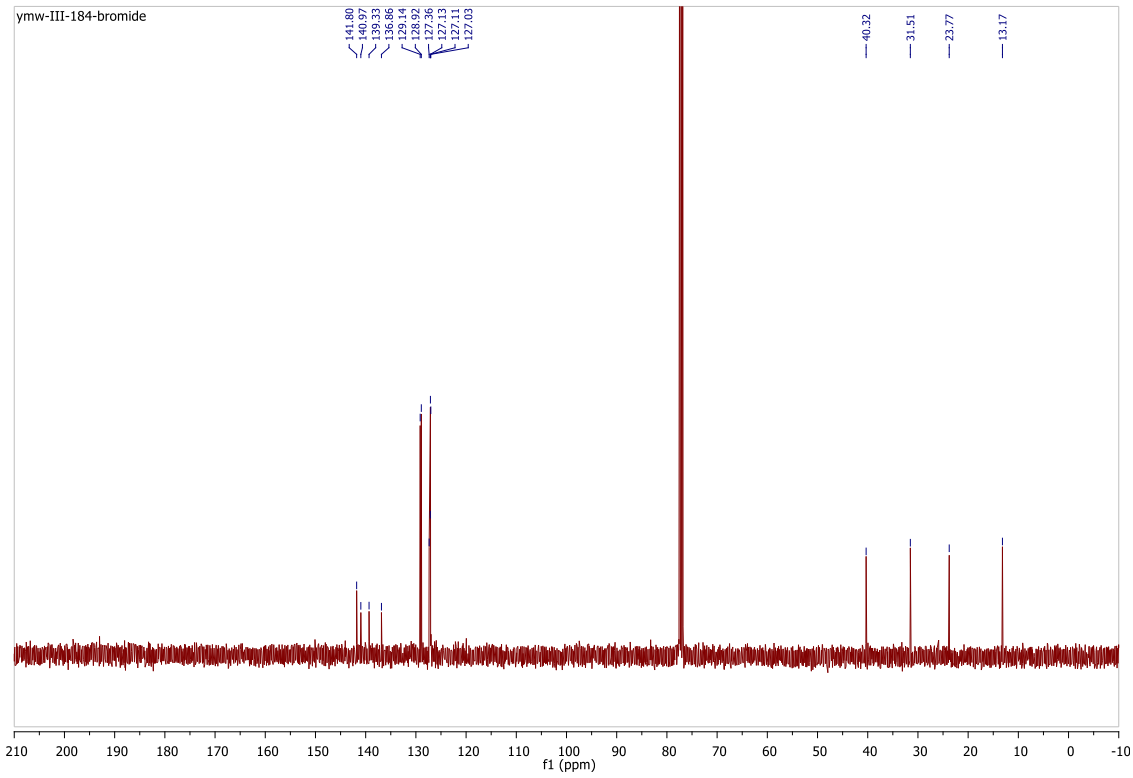

APB_15
7.64
7.63
7.62
7.60
7.58
7.58
7.48
7.46
7.44
7.38
7.38
7.37
7.36
7.35
7.34
6.40
3.60
3.58
3.56
2.79
2.77
2.75
1.96
1.95
4.09
2.06
3.57
1.00
2.03
2.04
3.01
f1 (ppm)

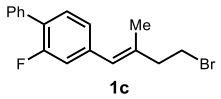

APB_8
140.96
139.23
136.95
135.73
129.41
128.91
127.57
127.35
127.11
126.95
43.98
31.39
17.69
f1 (ppm)


Ph
Me
Br

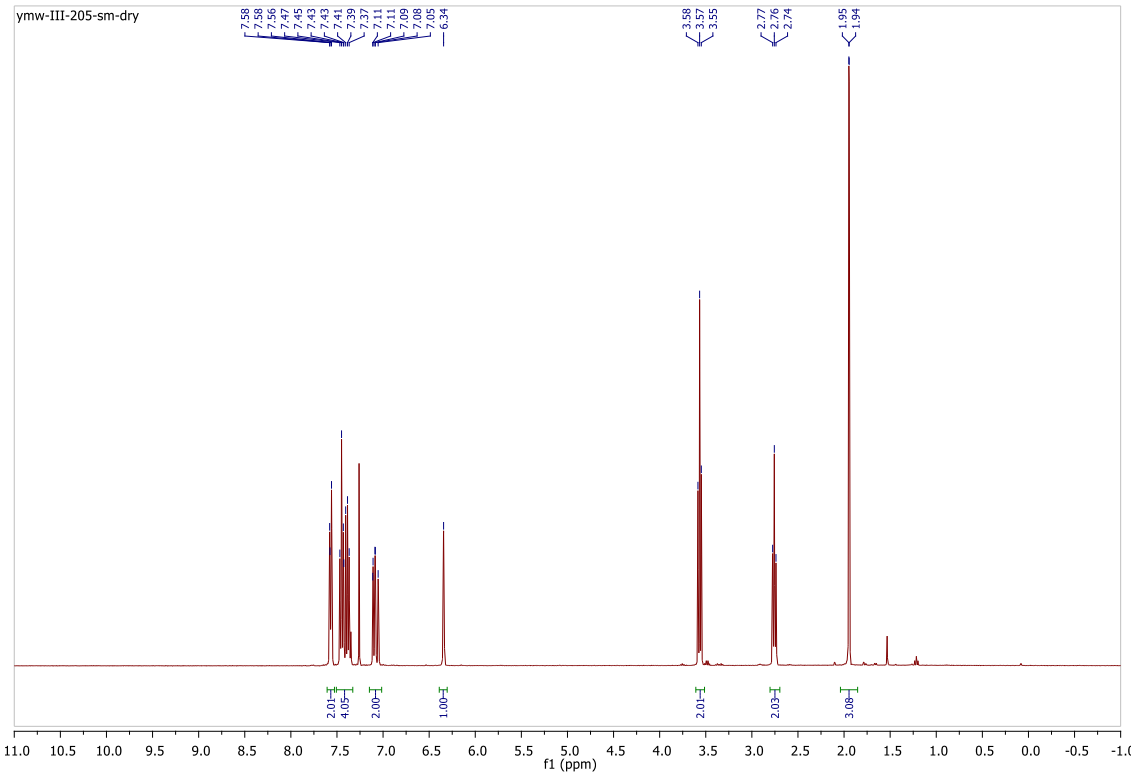
1b

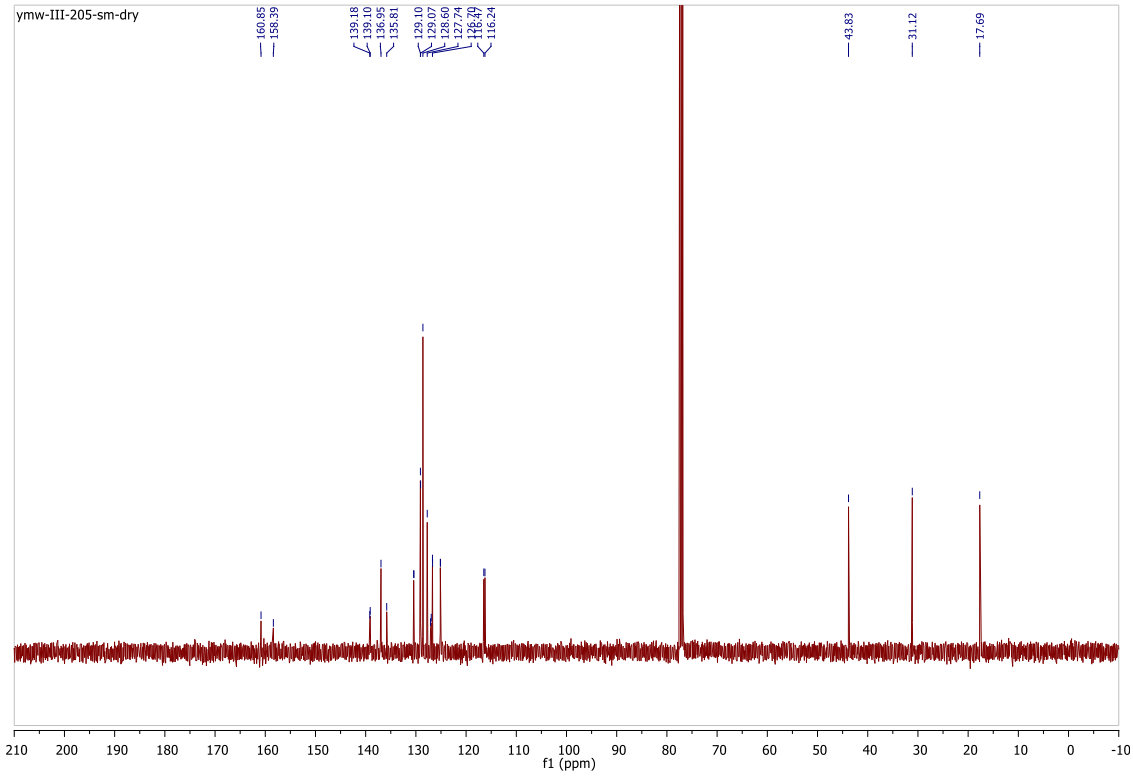

ymw-III-184-bromide
7.62
7.60
7.58
7.56
7.46
7.44
7.42
7.36
7.34
7.32
7.30
6.35
3.57
3.56
3.54
2.78
2.76
2.75
2.36
2.34
2.32
2.31
1.15
1.13
1.11
4.17
2.11
3.12
1.00
2.05
2.03
2.03
3.02
f1 (ppm)

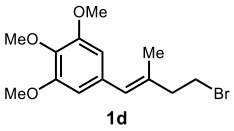

ymw-III-184-bromide
141.80
140.97
139.33
136.86
129.14
128.92
127.36
127.13
127.11
127.03
40.32
31.51
23.77
13.17
f1 (ppm)


Ph
Me
F
Br

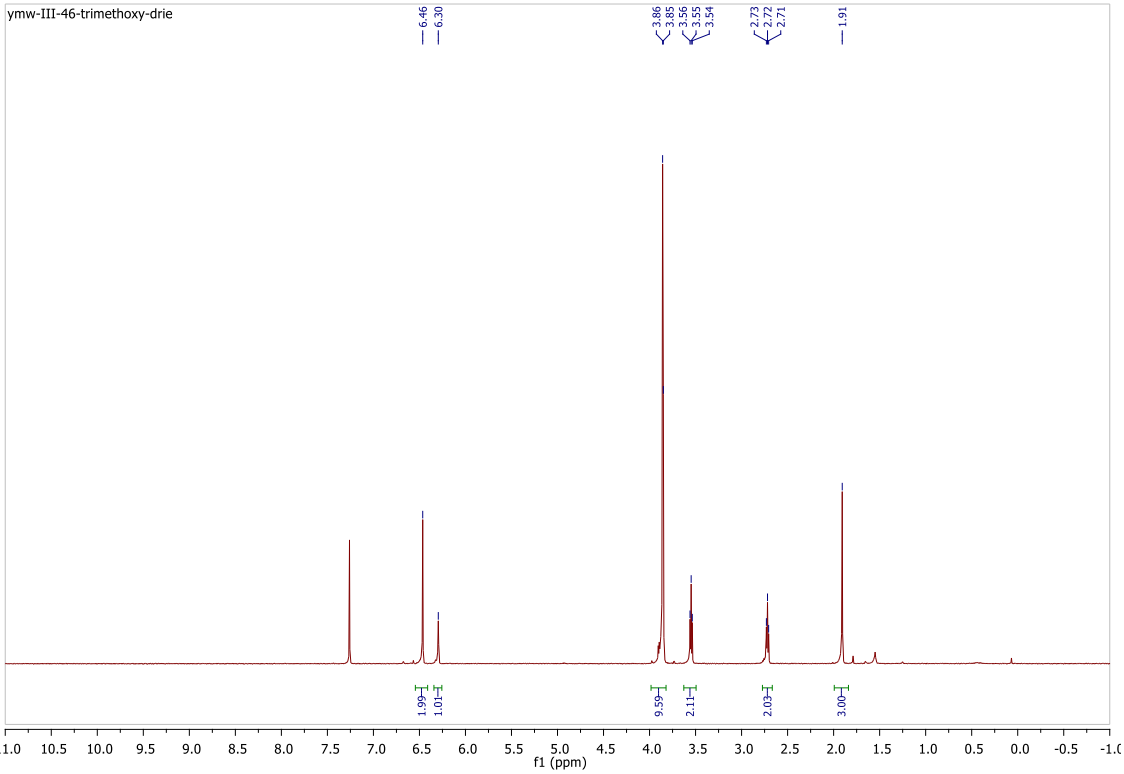
1c

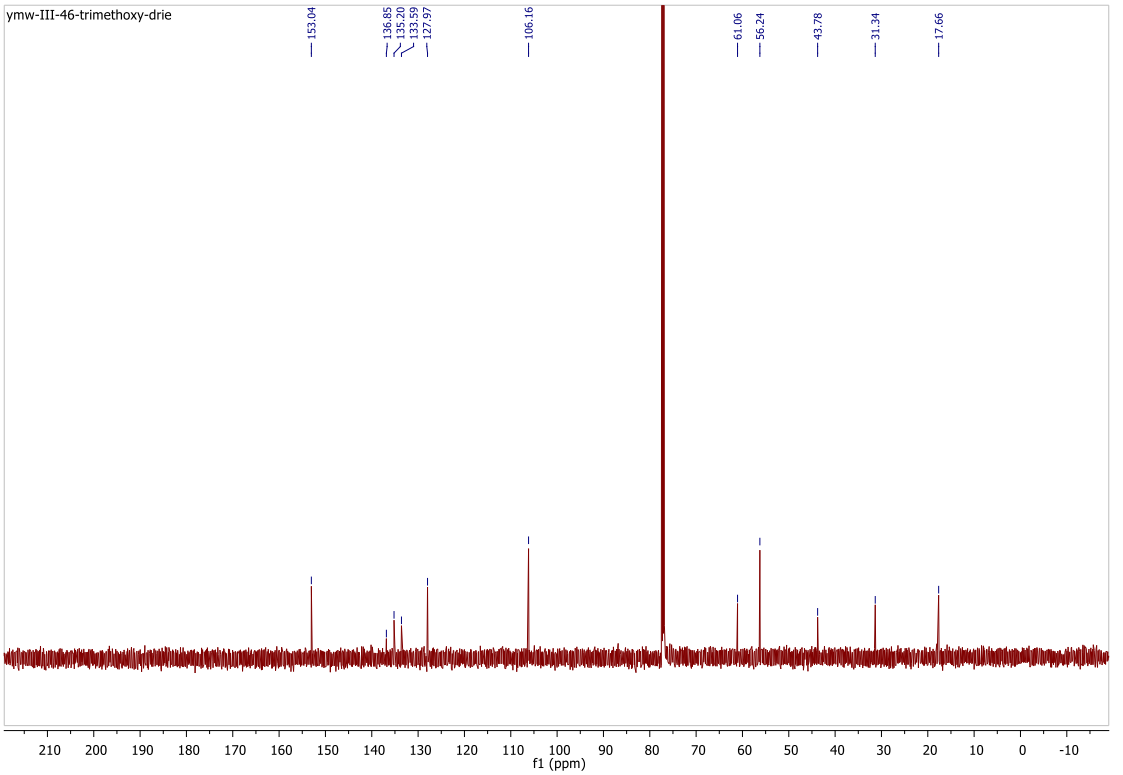

ymw-III-205-sm-dry
7.58
7.58
7.56
7.47
7.45
7.43
7.43
7.41
7.39
7.37
7.11
7.11
7.09
7.08
7.05
6.34
3.58
3.57
3.55
2.77
2.76
2.74
1.95
1.94
2.01
4.05
2.00
1.00
2.01
2.03
3.08
f1 (ppm)

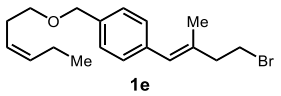

ymw-III-205-sm-dry
160.85
158.39
139.18
139.10
136.95
135.81
129.10
129.07
128.60
127.74
116.24
43.83
31.12
17.69
f1 (ppm)


OMe
MeO
Me
MeO
Br

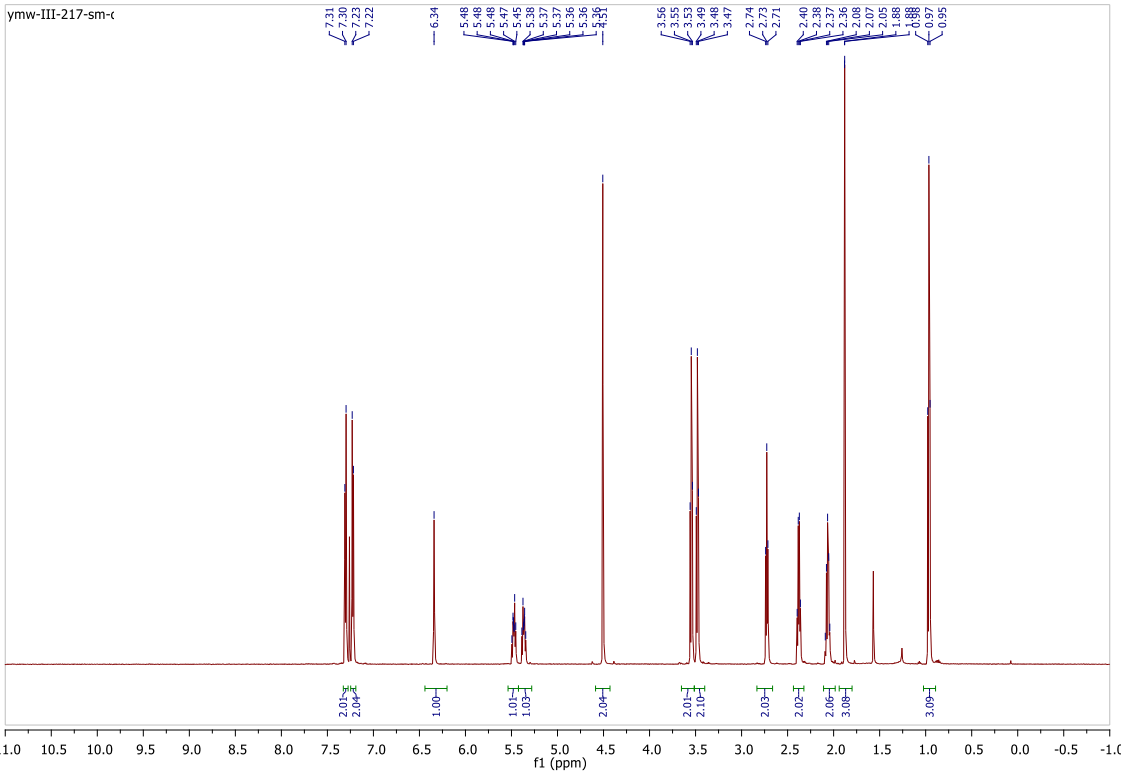
1d

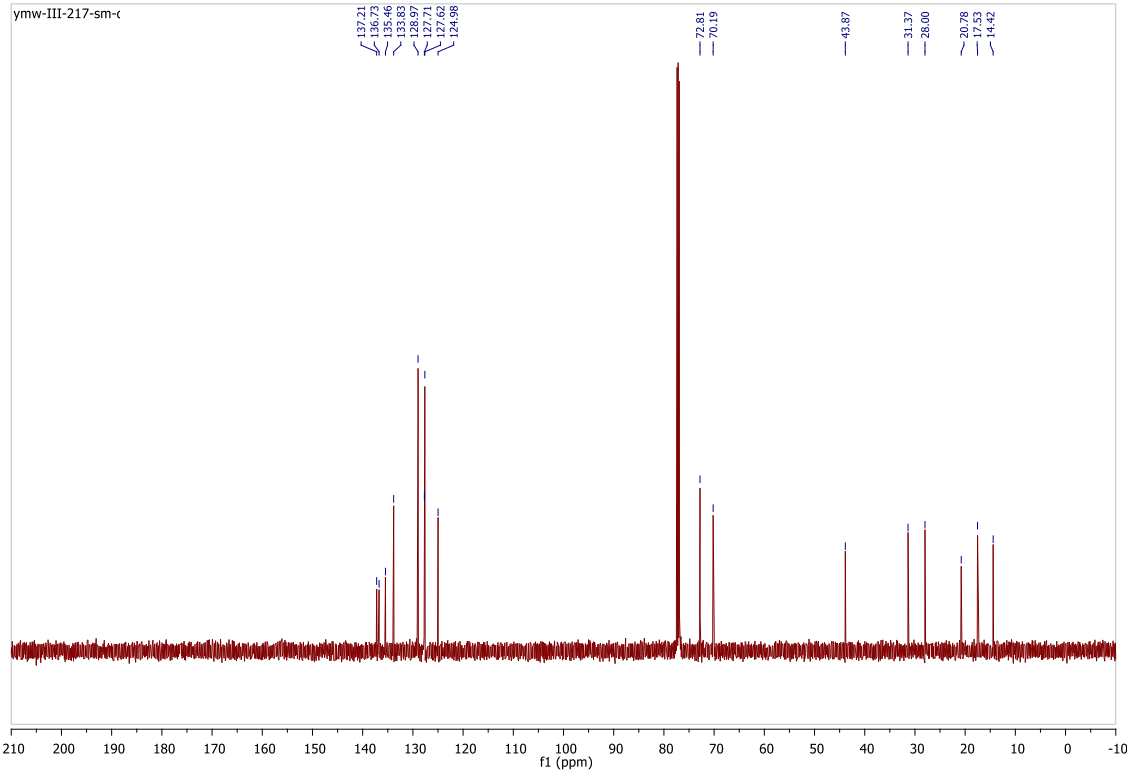

ymw-III-46-trimethoxy-drie
6.46
6.30
3.86
3.85
3.56
3.55
3.54
2.73
2.72
2.71
1.91
1.99
1.01
9.59
2.11
2.03
3.00
f1 (ppm)

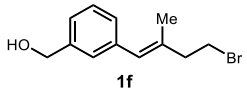

ymw-III-46-trimethoxy-drie
153.04
136.85
135.20
133.59
127.97
106.16
61.06
56.24
43.78
31.34
17.66
f1 (ppm)


O
Me
Me
Br

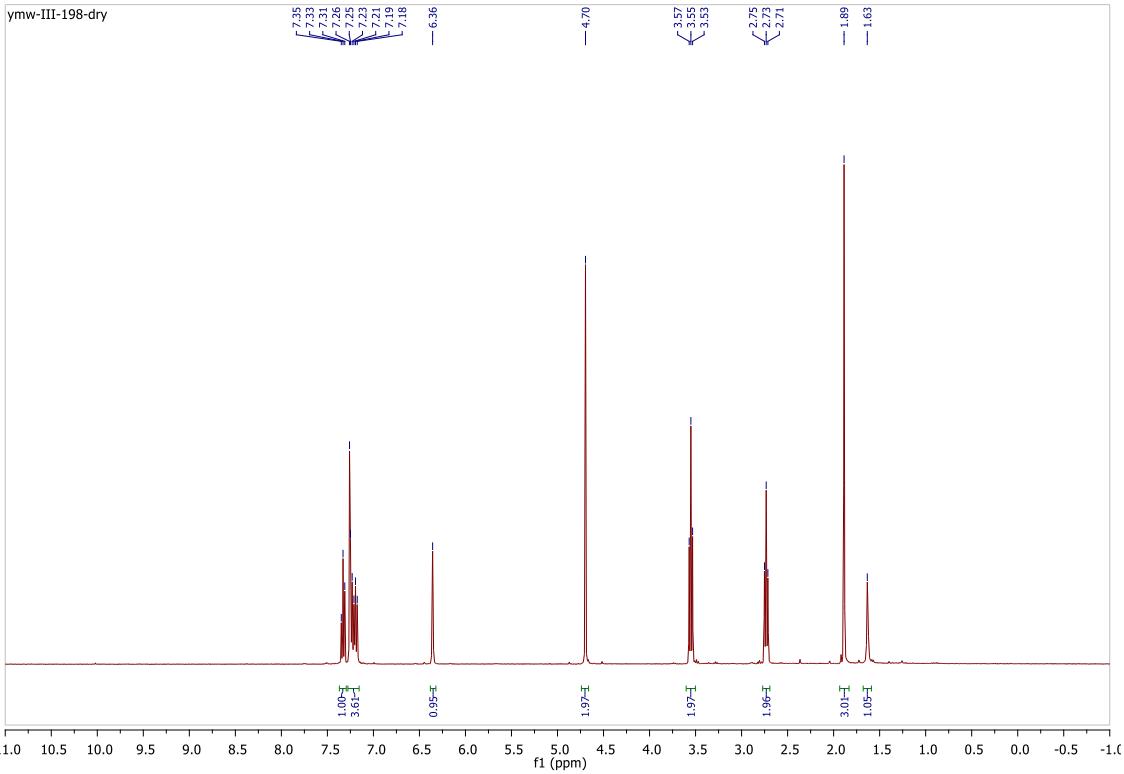
1e

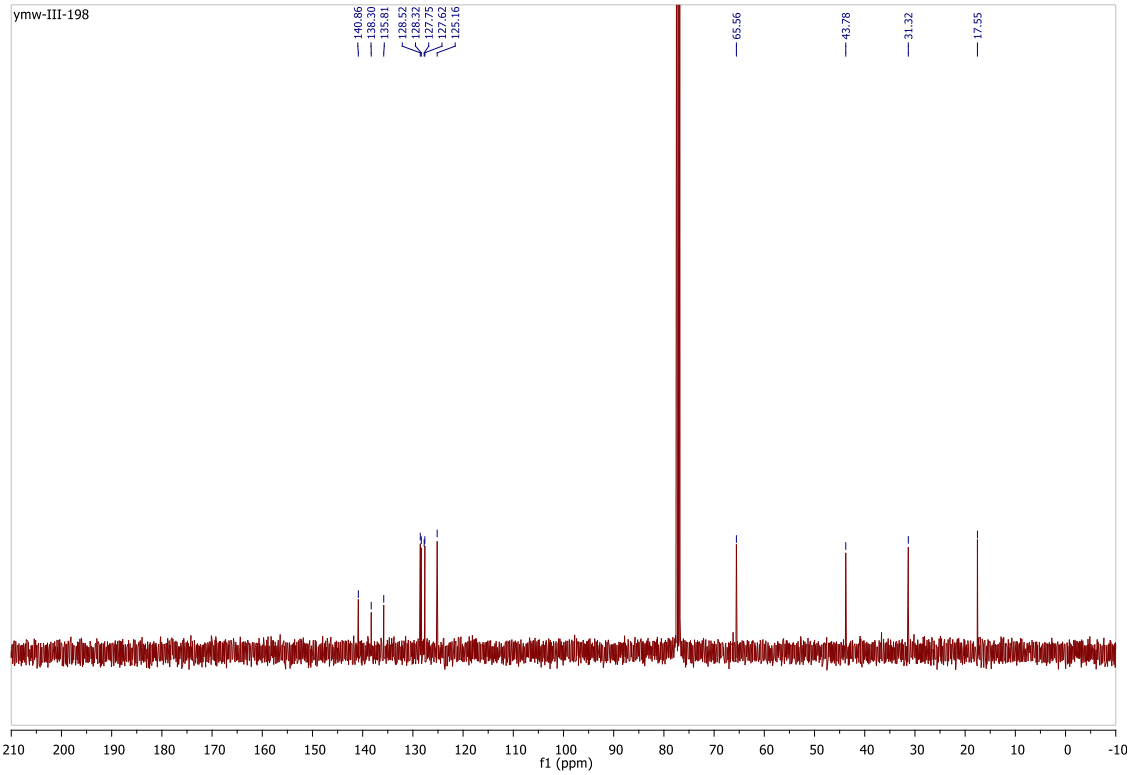

ymw-III-217-sm-(
7.31
7.30
7.23
7.22
6.34
5.48
5.48
5.48
5.47
5.45
5.38
5.37
5.37
5.36
5.36
3.56
3.55
3.53
3.49
3.48
3.47
2.74
2.73
2.71
2.40
2.38
2.37
2.36
2.08
2.07
2.05
1.88
0.97
0.95
2.01
2.04
1.00
1.01
1.03
2.04
2.01
2.10
2.03
2.02
2.06
3.08
3.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

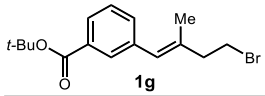

ymw-III-217-sm-(
137.21
136.73
135.46
133.83
128.97
127.71
127.62
124.98
72.81
70.19
43.87
31.37
28.00
20.78
17.53
14.42
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
HO
Br

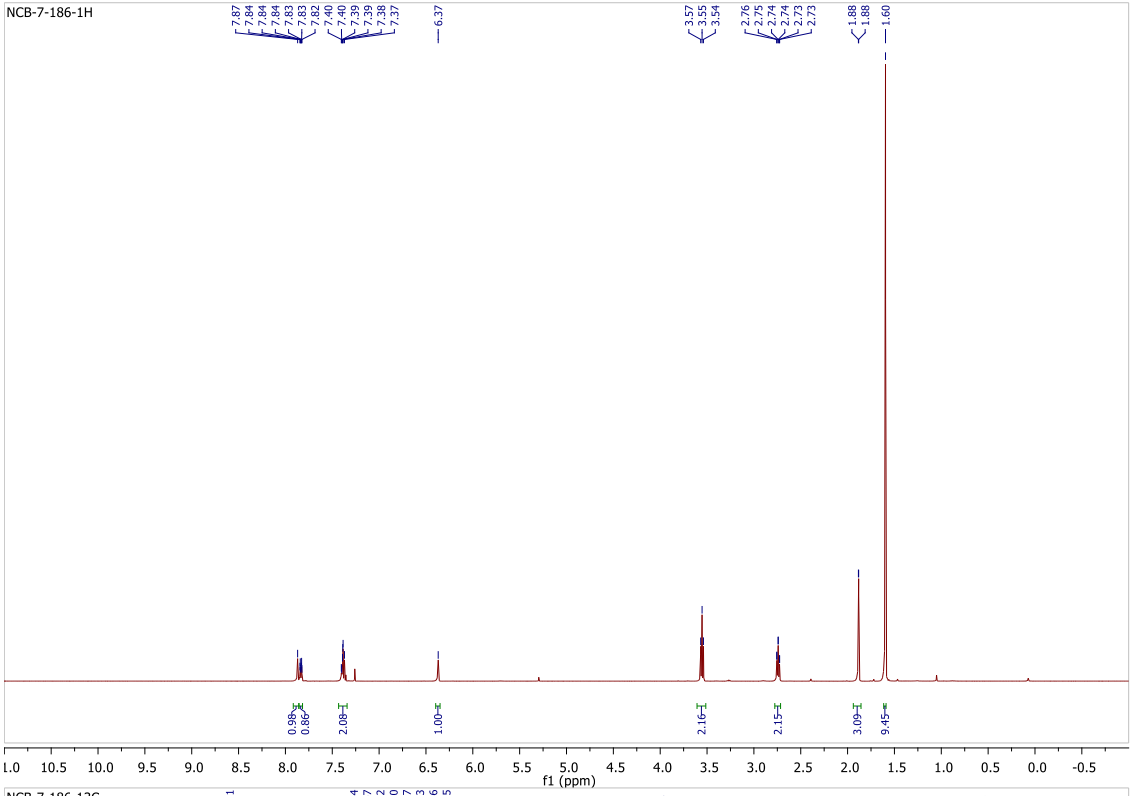
1f

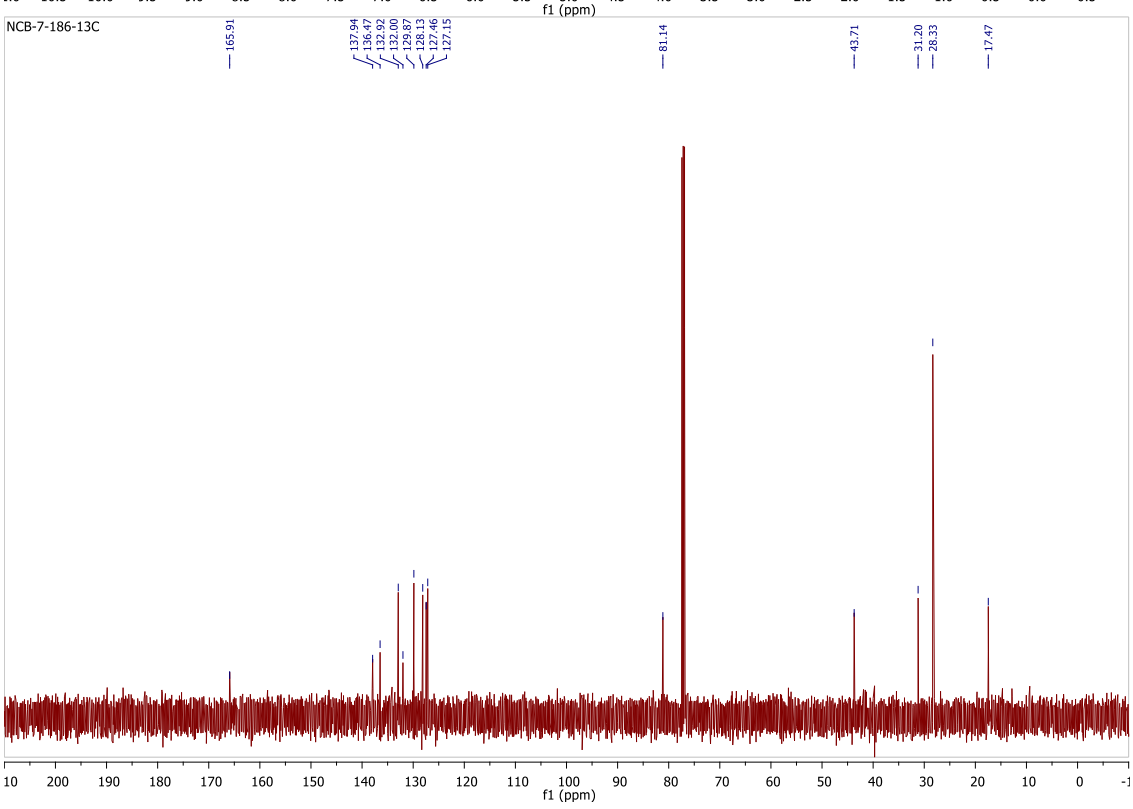

ymw-III-198-dry
7.35
7.33
7.31
7.26
7.25
7.23
7.21
7.19
7.18
6.36
4.70
3.57
3.55
3.53
2.75
2.73
2.71
1.89
1.63
1.00
3.61
0.95
1.97
1.97
1.96
3.01
1.05
f1 (ppm)

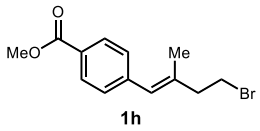

ymw-III-198
140.86
138.30
135.81
128.52
128.32
127.75
127.62
125.16
65.56
43.78
31.32
17.55
f1 (ppm)


t-BuO
O
Me
Br

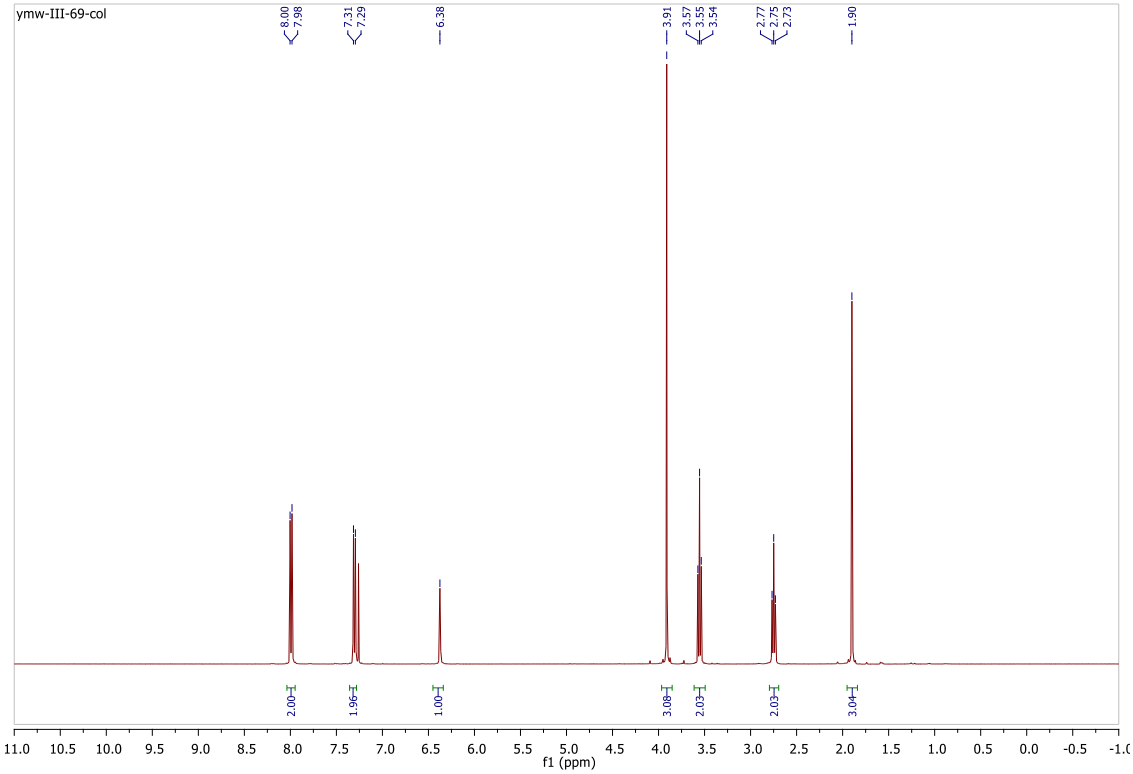
1g

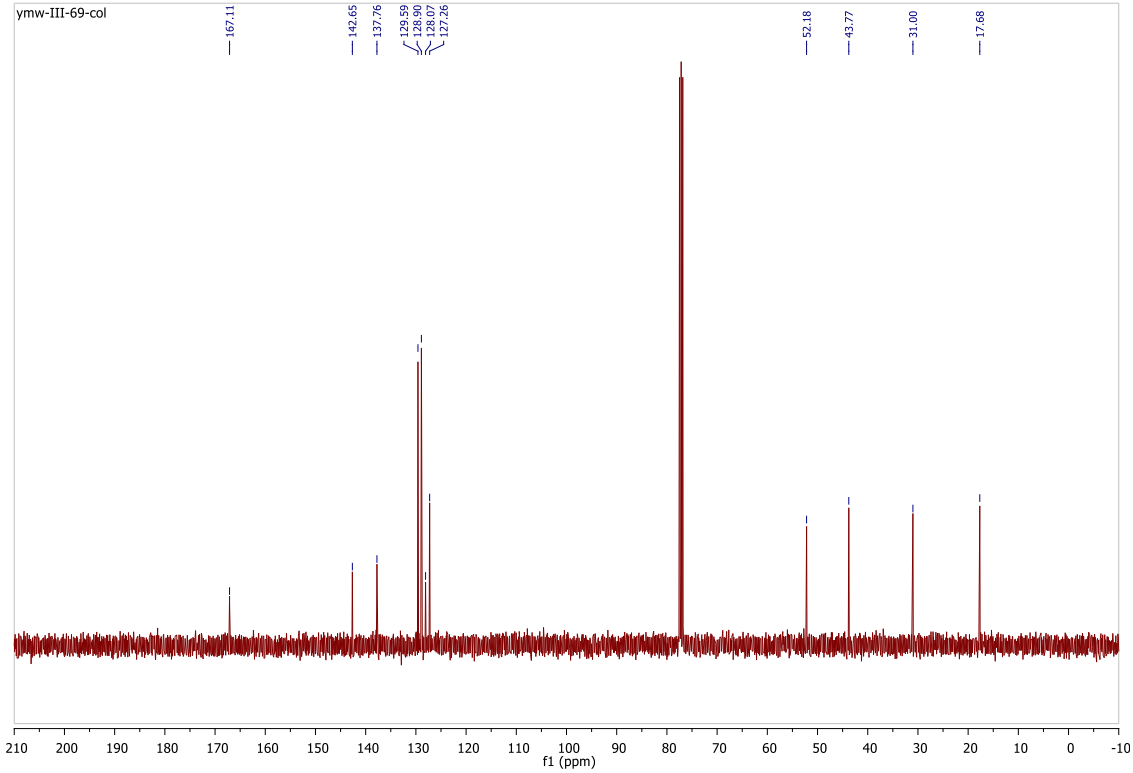

NCB-7-186-1H
7.87
7.84
7.84
7.84
7.83
7.83
7.82
7.40
7.40
7.39
7.39
7.38
7.37
6.37
3.57
3.55
3.54
2.76
2.75
2.74
2.74
2.73
2.73
1.88
1.88
1.60
0.98
0.86
2.08
1.00
2.16
2.15
3.09
9.45
f1 (ppm)

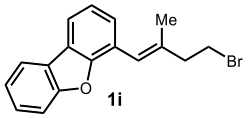

NCB-7-186-13C
165.91
137.94
136.47
132.92
131.00
129.81
128.13
127.46
127.15
81.14
43.71
31.20
28.33
17.47
f1 (ppm)


O
MeO
Me
Br

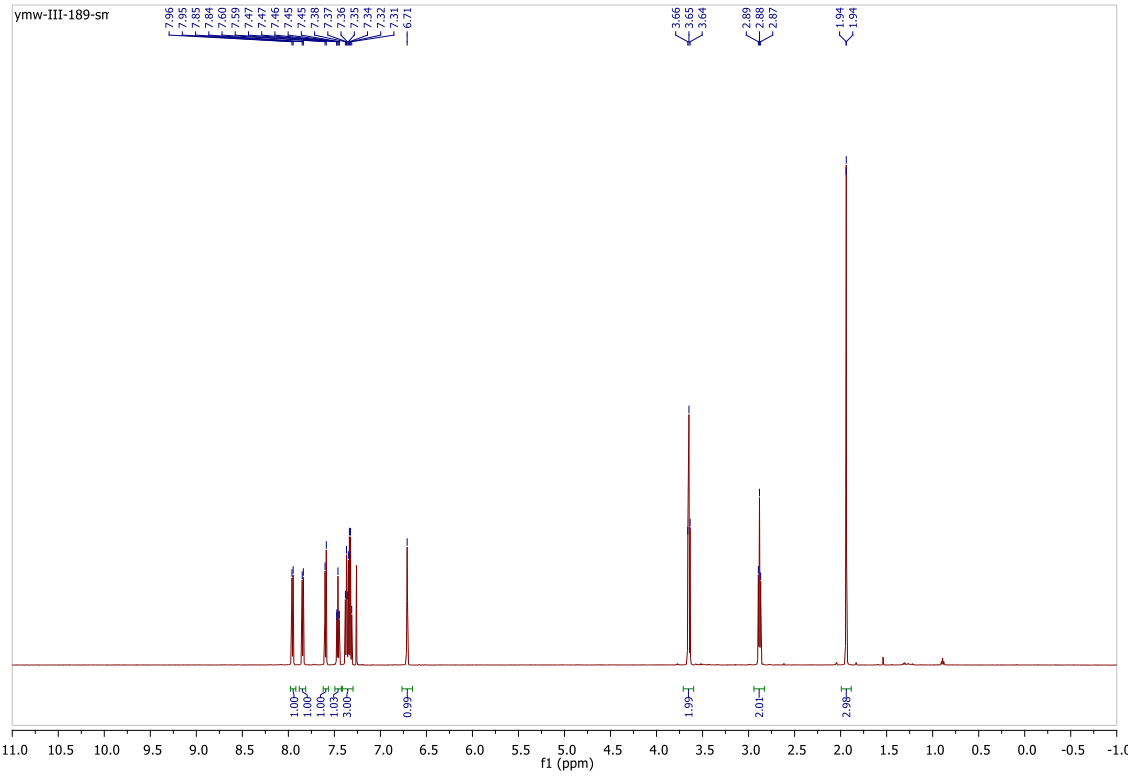
1h

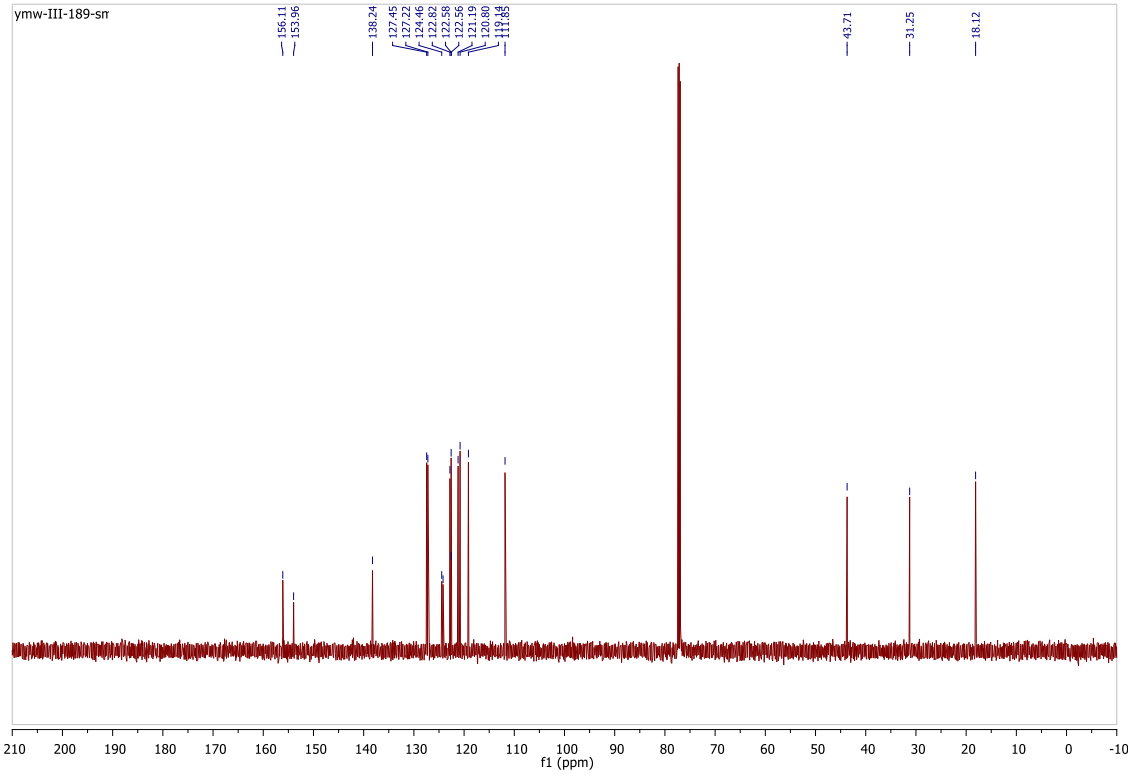

ymw-III-69-col
8.00
7.98
7.31
7.29
6.38
3.91
3.57
3.55
3.54
2.77
2.75
2.73
1.90
2.00
1.96
1.00
3.08
2.03
2.03
3.04
f1 (ppm)

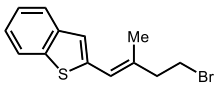

ymw-III-69-col
167.11
142.65
137.76
129.59
128.90
128.07
127.26
52.18
43.77
31.00
17.68
f1 (ppm)


Me
Br
O

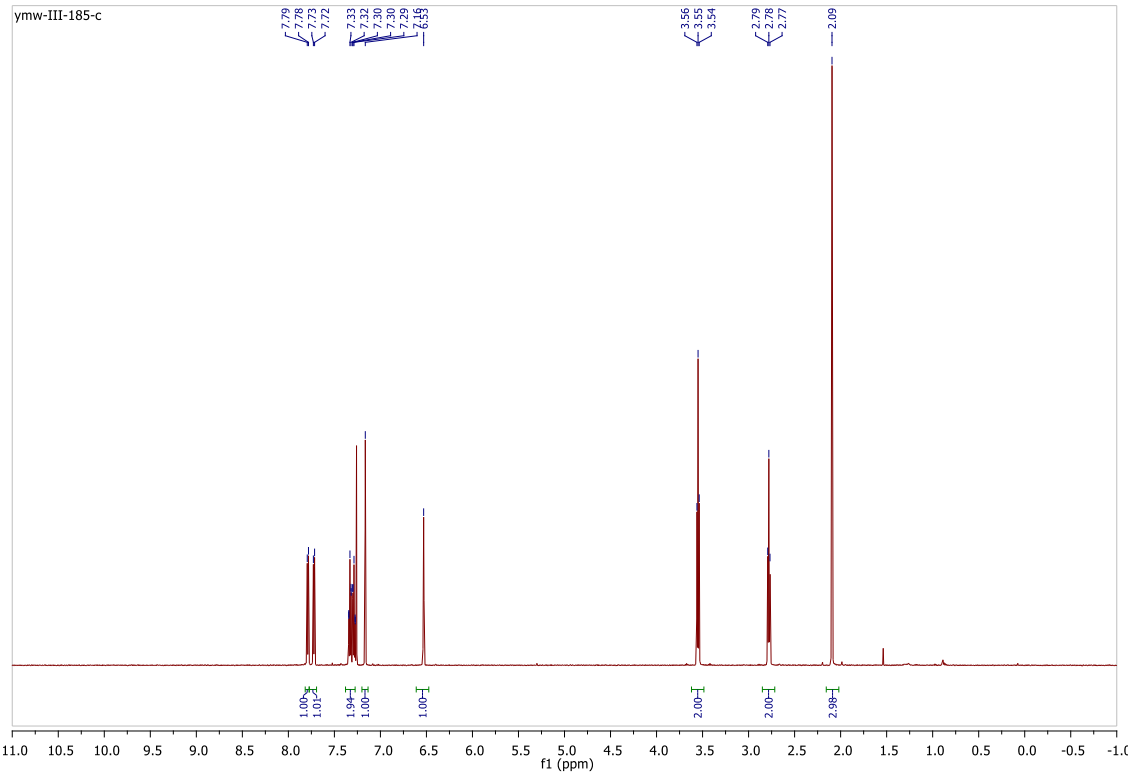
1i

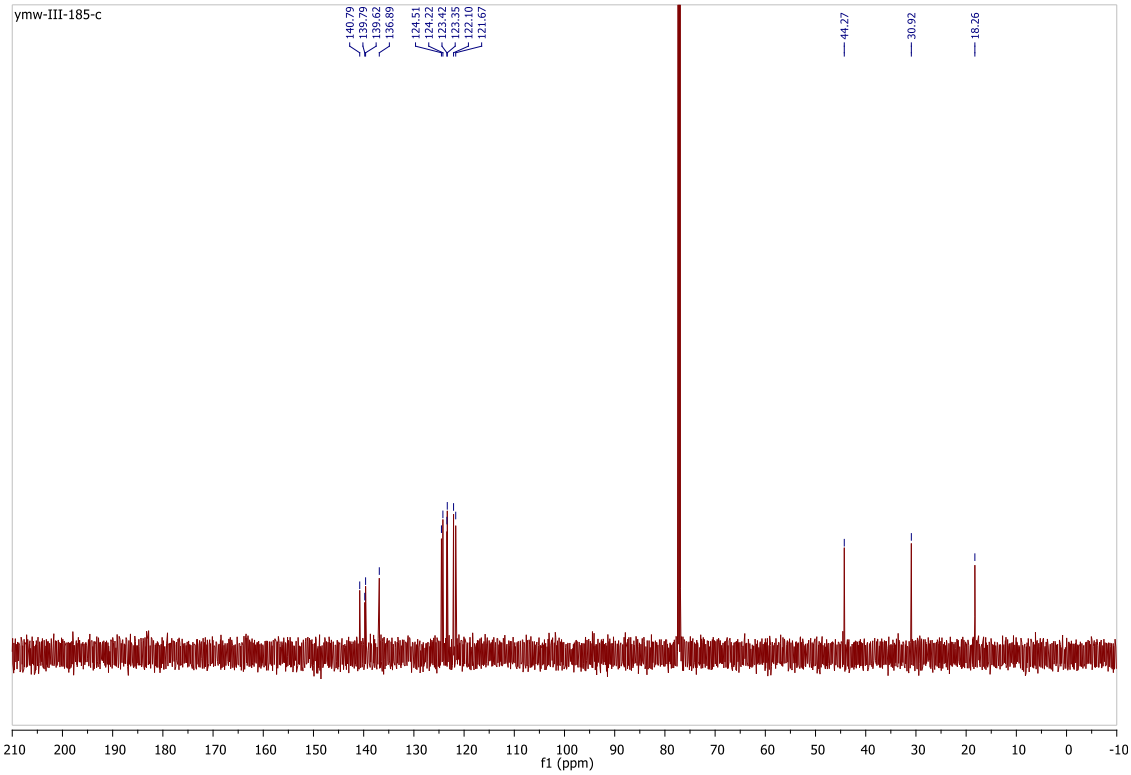

ymw-III-189-sm
7.96
7.95
7.85
7.84
7.60
7.59
7.47
7.47
7.46
7.45
7.45
7.38
7.37
7.36
7.35
7.34
7.32
7.31
6.71
3.66
3.65
3.64
2.89
2.88
2.87
1.94
1.94
1.00
1.00
1.00
1.03
3.00
0.99
1.99
2.01
2.98
f1 (ppm)

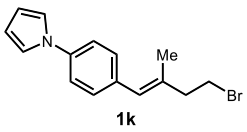

ymw-III-189-sm
156.11
153.96
138.24
127.45
127.22
124.46
122.82
122.58
122.56
121.19
120.80
111.85
43.71
31.25
18.12
f1 (ppm)


Me
S
Br

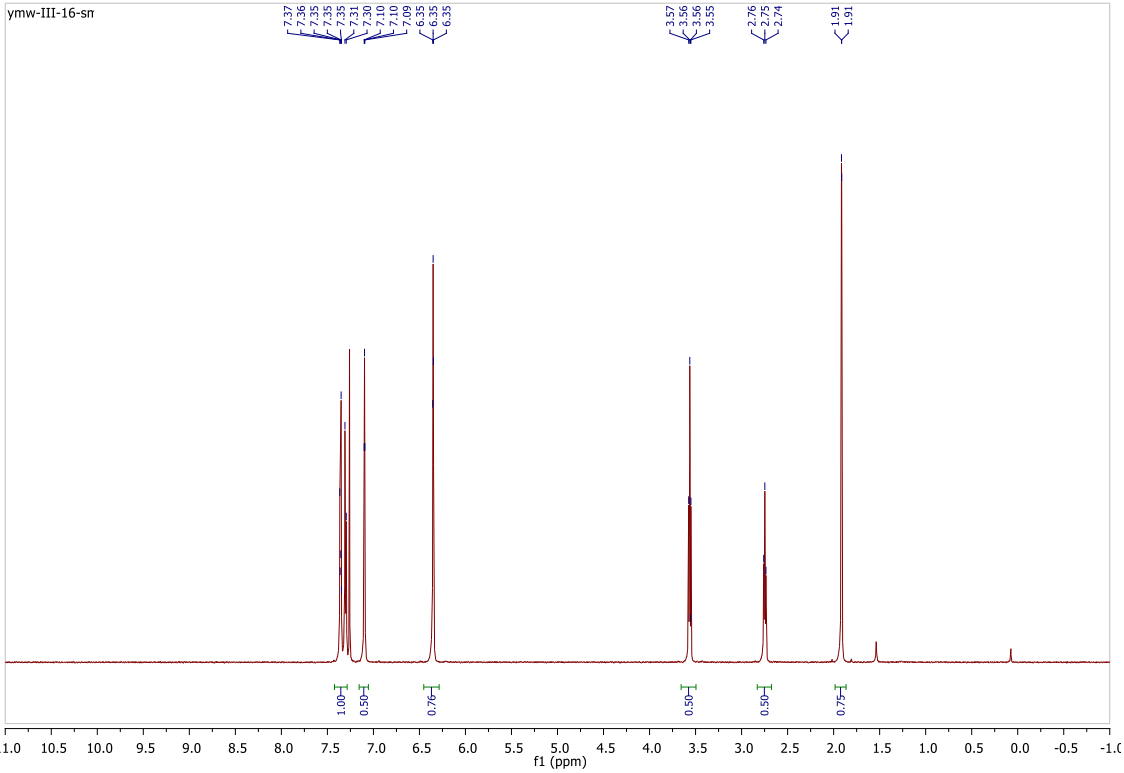
1j

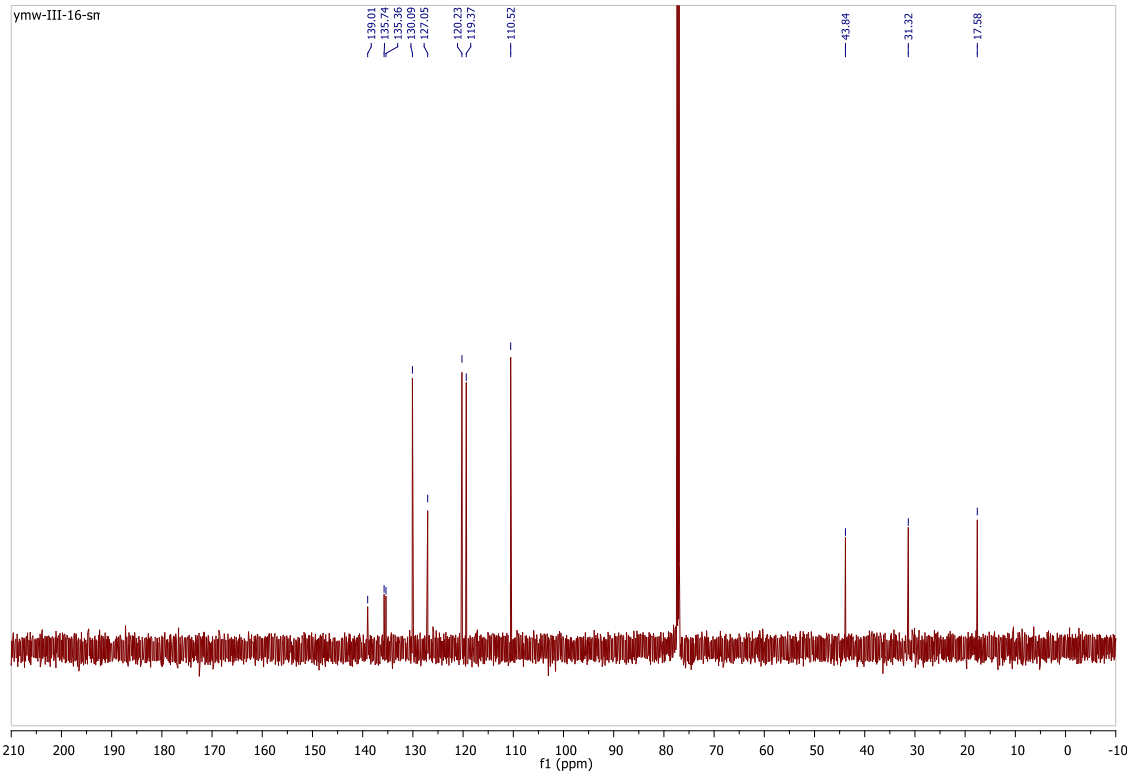

ymw-III-185-c
7.79
7.78
7.73
7.72
7.33
7.32
7.30
7.29
7.16
6.53
3.56
3.55
3.54
2.79
2.78
2.77
2.09
1.00
1.01
1.94
1.00
1.00
2.00
2.00
2.98
f1 (ppm)

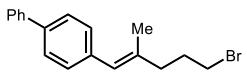

ymw-III-185-c
140.79
139.79
139.62
136.89
124.51
124.22
123.42
123.35
122.10
121.67
44.27
30.92
18.26
f1 (ppm)


N
Me
Br

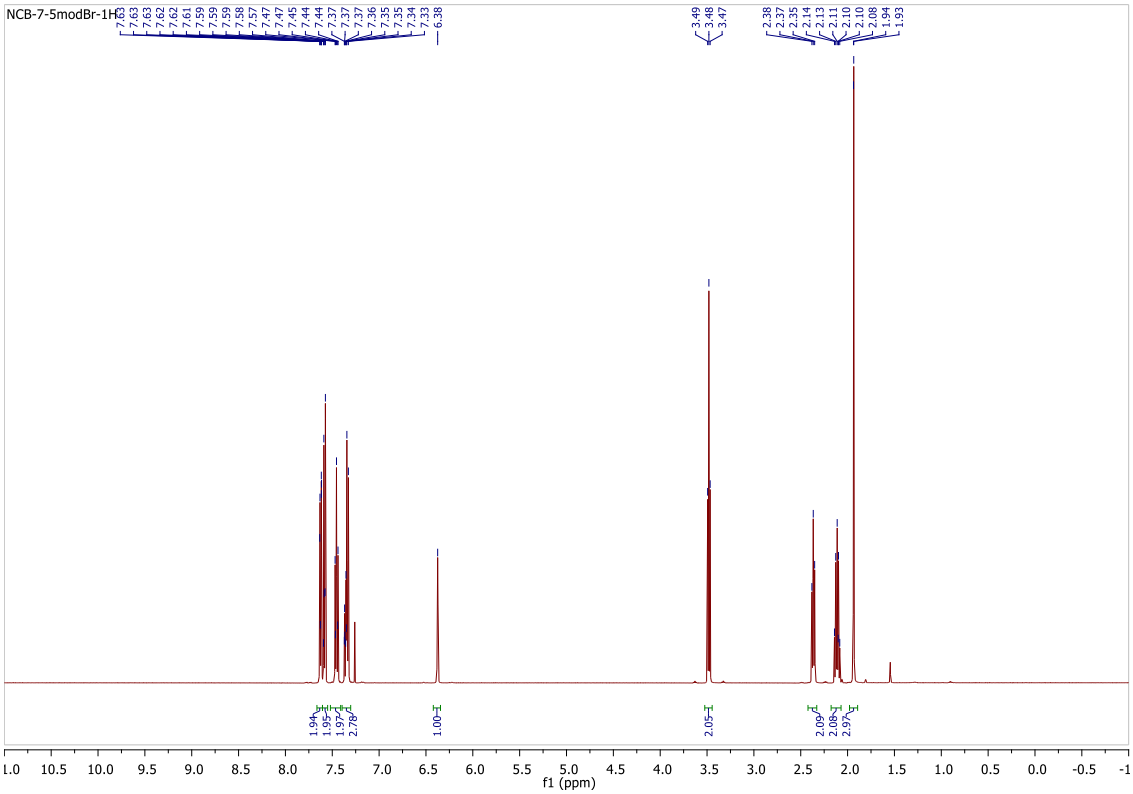
1k

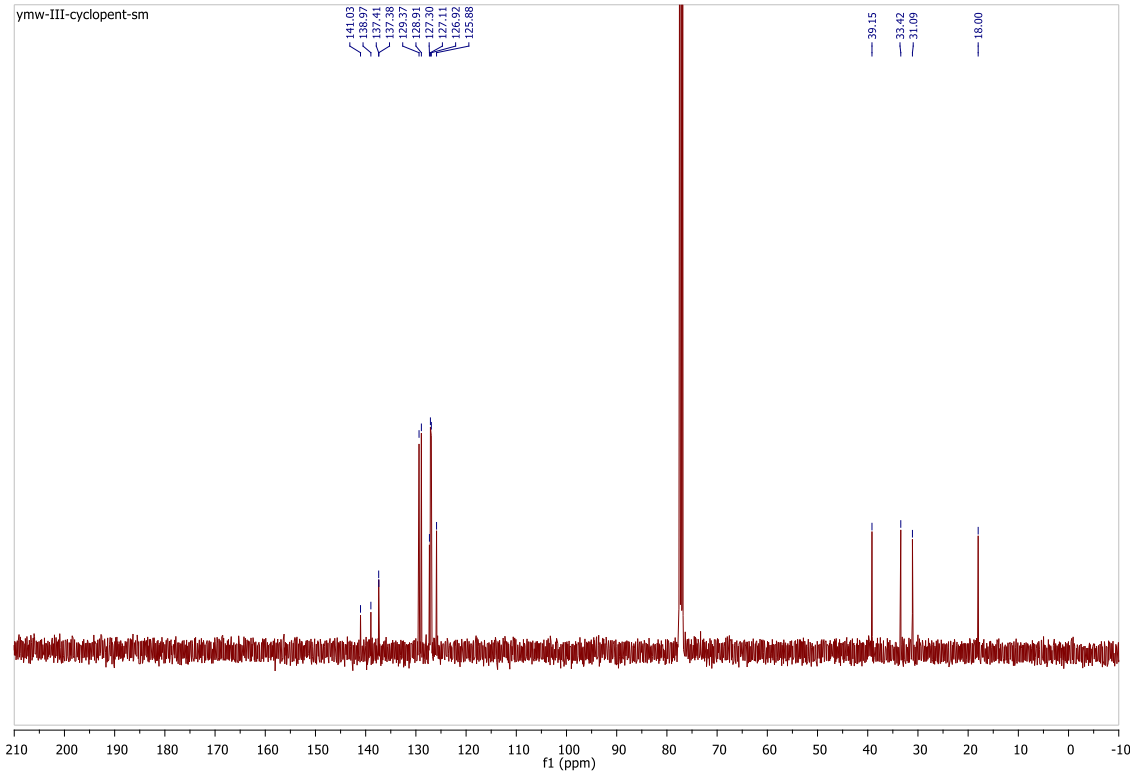

ymw-III-16-sn
7.37
7.36
7.35
7.35
7.31
7.30
7.10
7.09
6.35
6.35
3.57
3.56
3.56
3.55
2.76
2.75
2.74
1.91
1.91
1.00
0.50
0.76
0.50
0.50
0.75
f1 (ppm)

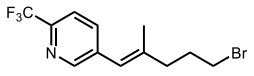

ymw-III-16-sn
139.01
135.74
135.36
130.09
127.05
120.23
119.37
110.52
43.84
31.32
17.58
f1 (ppm)



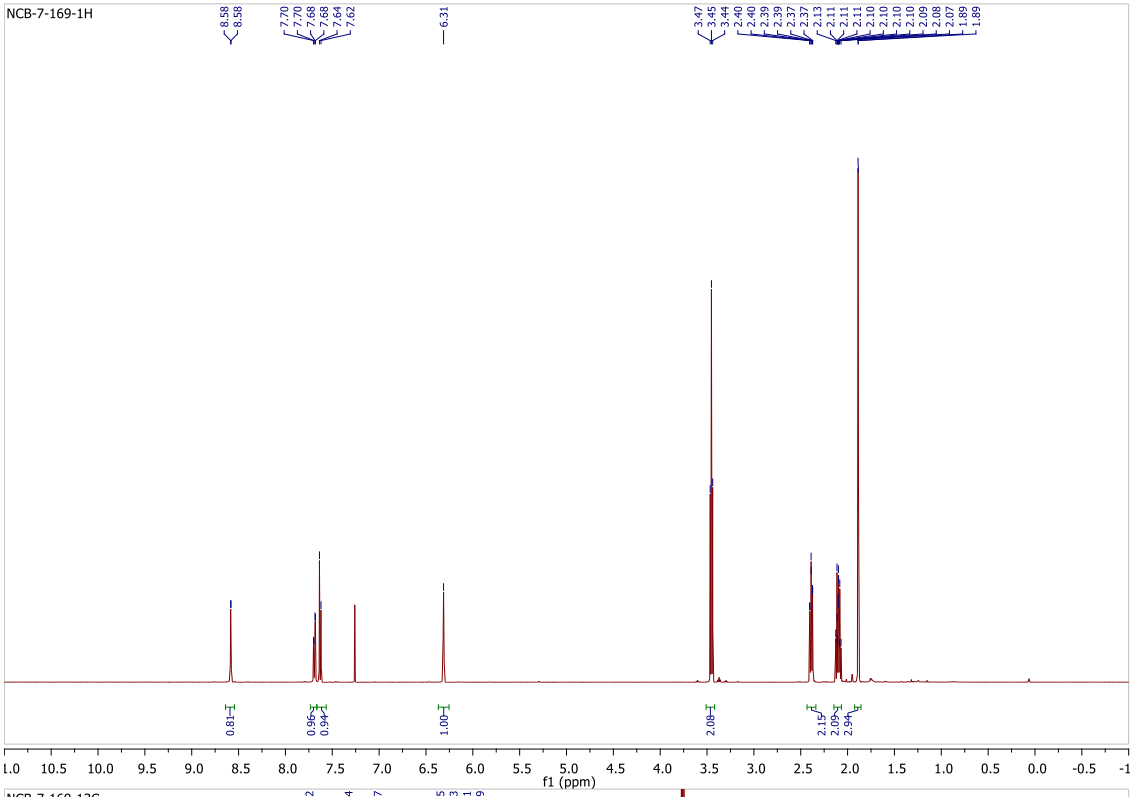
1l

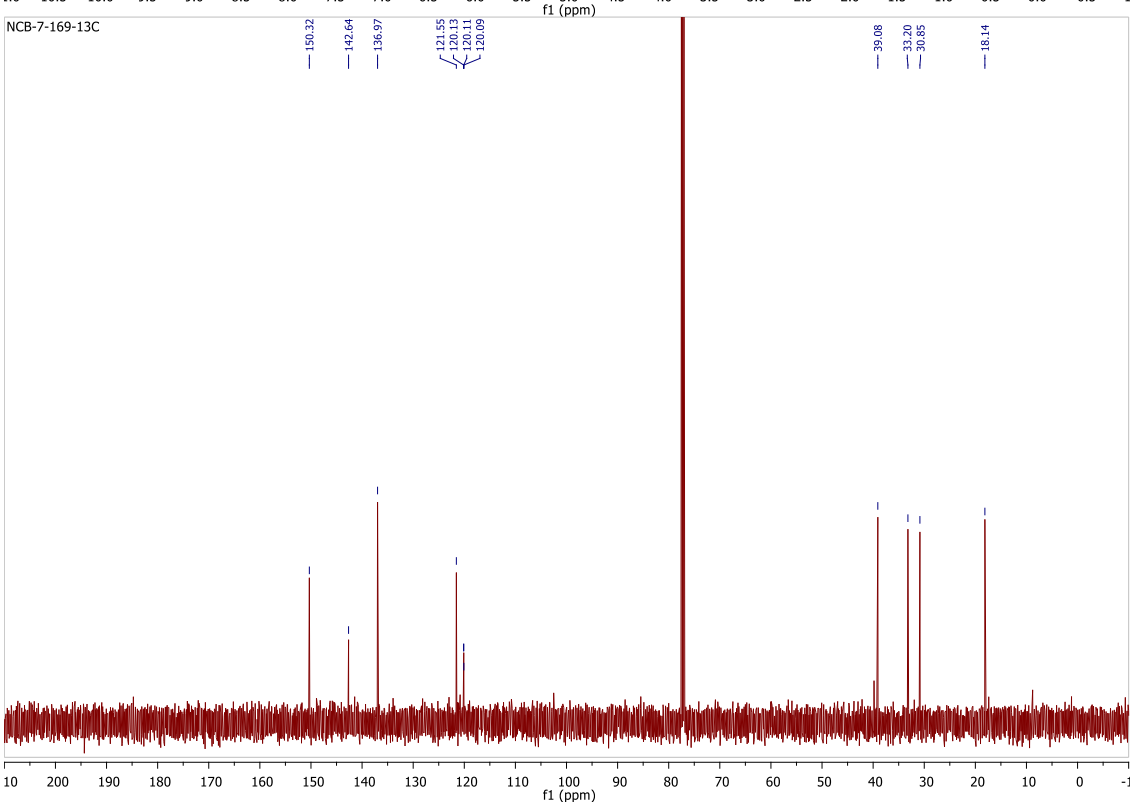


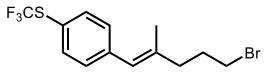



F3C
N
Br

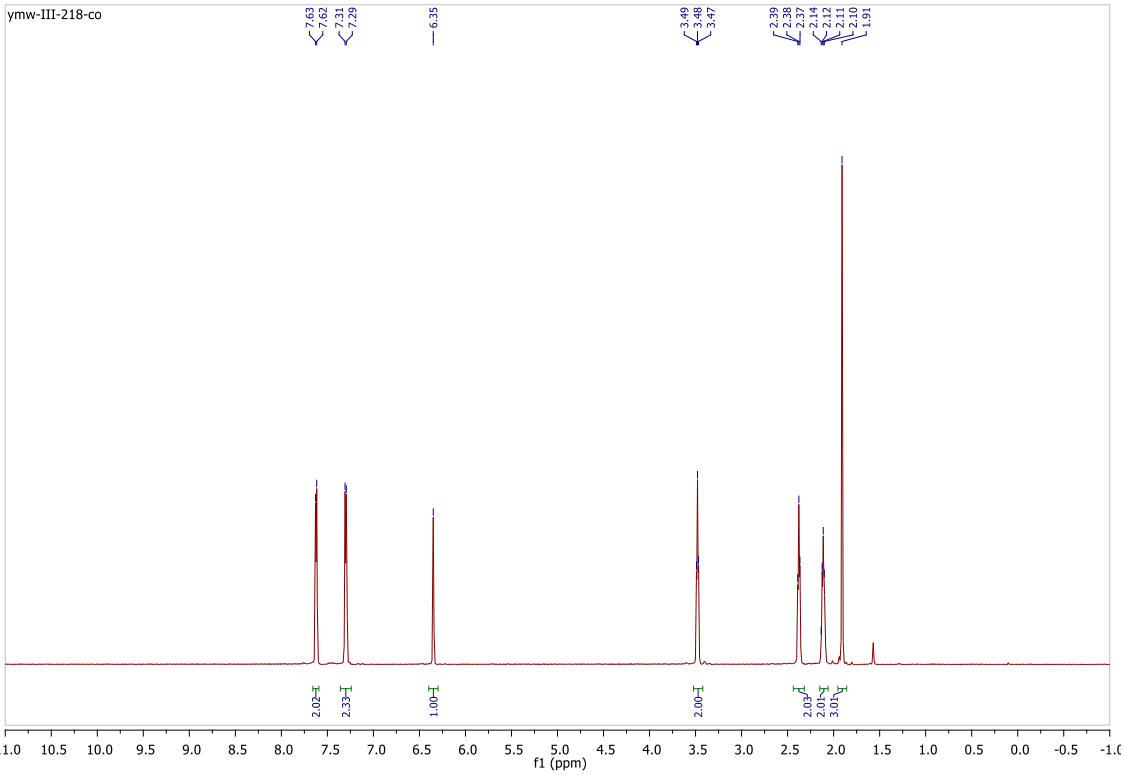
1m

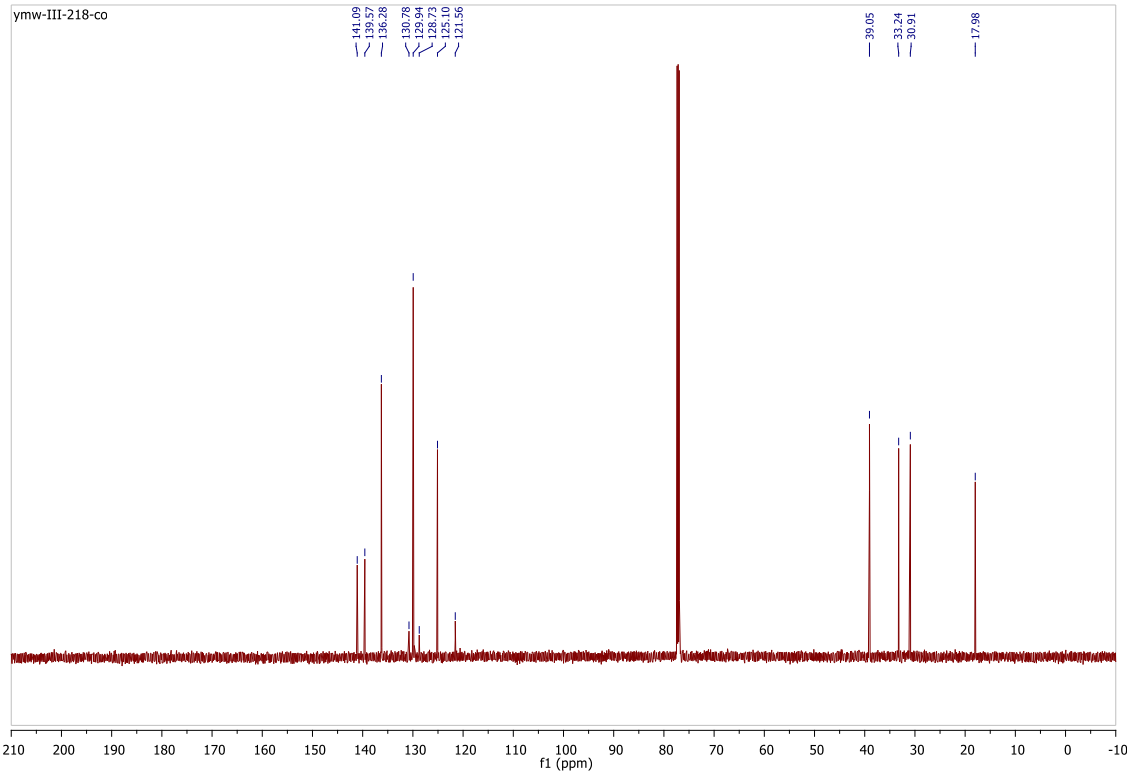

NCB-7-169-1H
8.58
8.58
7.70
7.70
7.68
7.68
7.64
7.62
6.31
3.47
3.45
3.44
2.40
2.40
2.39
2.39
2.37
2.37
2.13
2.11
2.11
2.11
2.10
2.10
2.10
2.09
2.08
2.07
1.89
1.89
0.81
0.96
0.94
1.00
2.08
2.15
2.09
2.94
f1 (ppm)

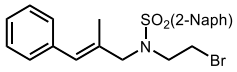

NCB-7-169-13C
150.32
142.64
136.97
121.55
120.13
120.11
120.09
39.08
33.20
30.85
18.14
f1 (ppm)


F3CS
Br

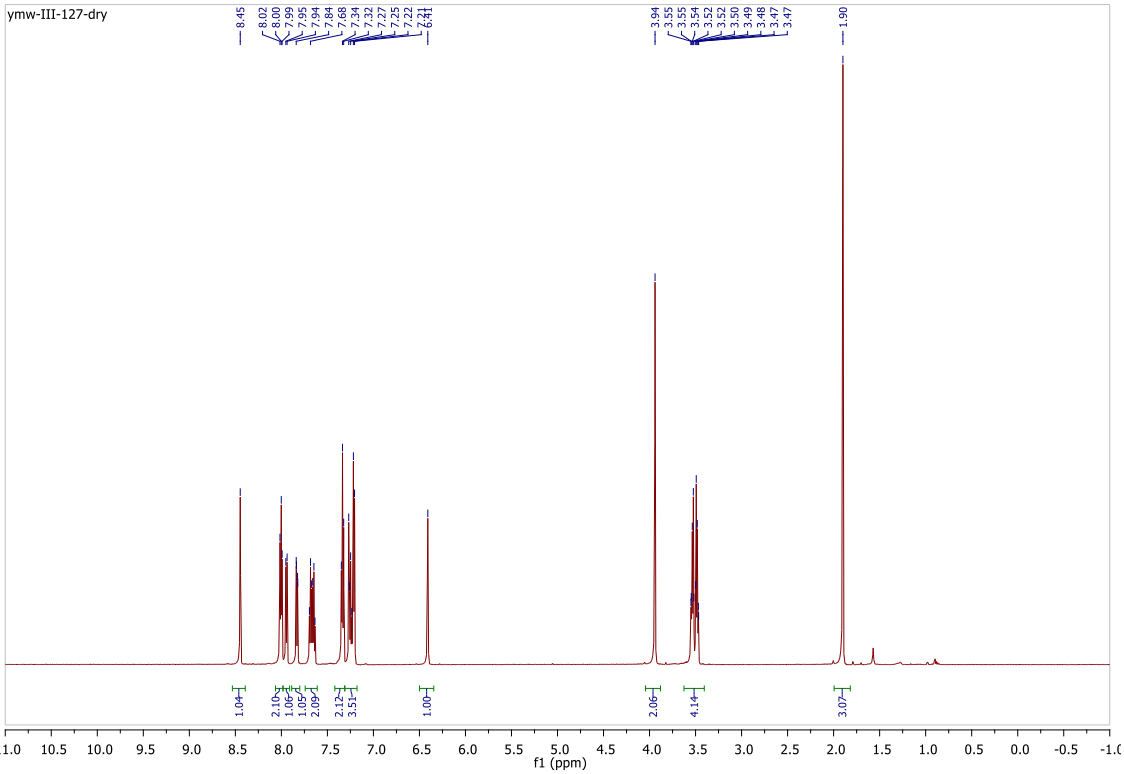
1n

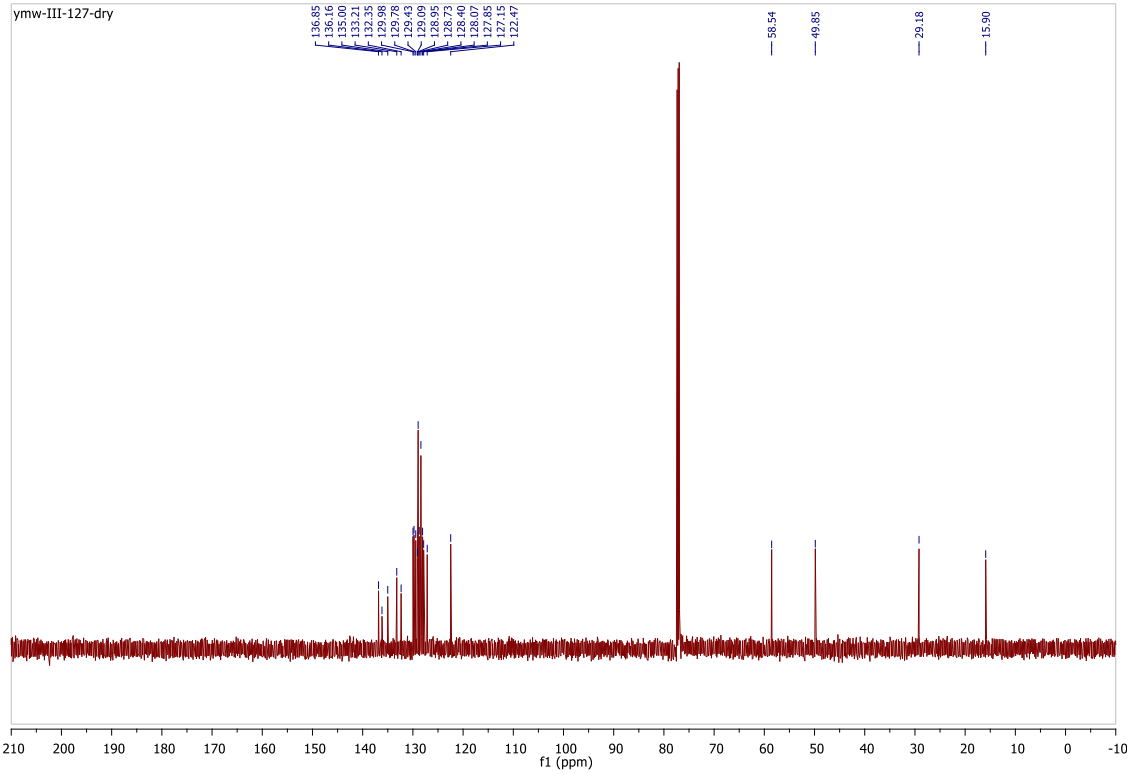

ymw-III-218-co
7.63
7.62
7.31
7.29
6.35
3.49
3.48
3.47
2.39
2.38
2.37
2.14
2.12
2.11
2.10
1.91
2.02
2.33
1.00
2.00
2.03
2.01
3.01
f1 (ppm)

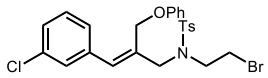

ymw-III-218-co
141.09
139.57
136.28
130.78
129.94
128.73
125.10
121.56
39.05
33.24
30.91
17.98
f1 (ppm)


SO2(2-Naph)
N
Br

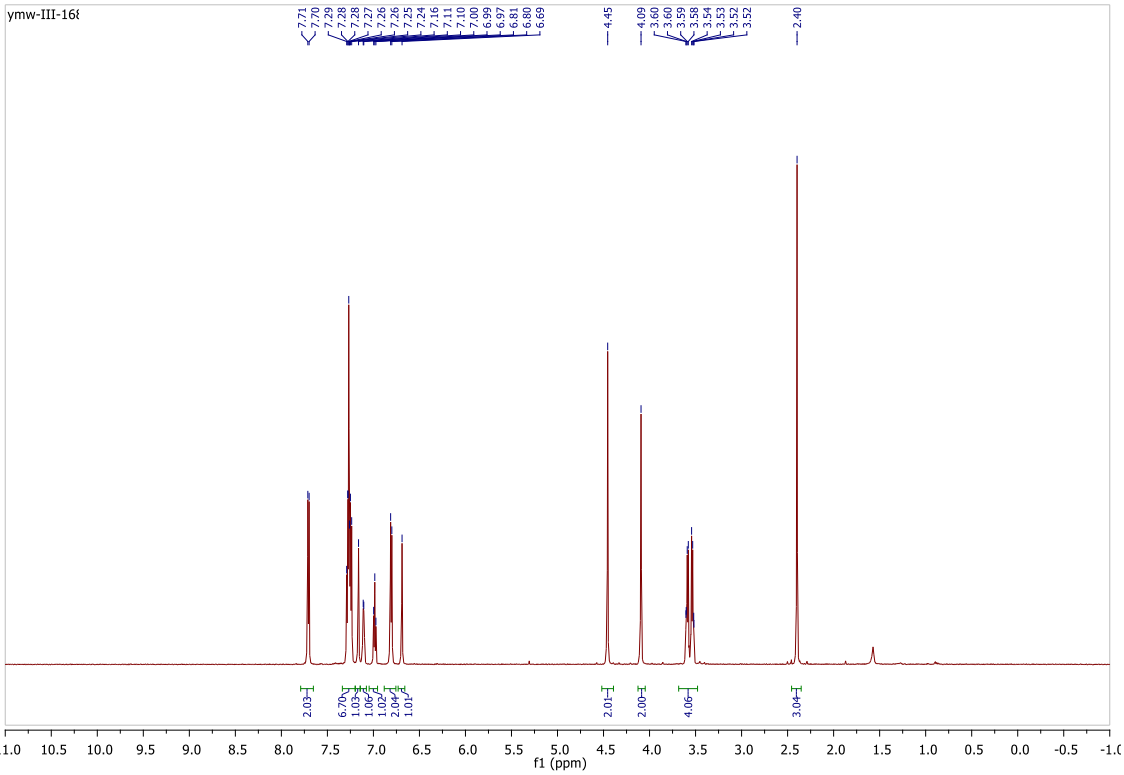
1o

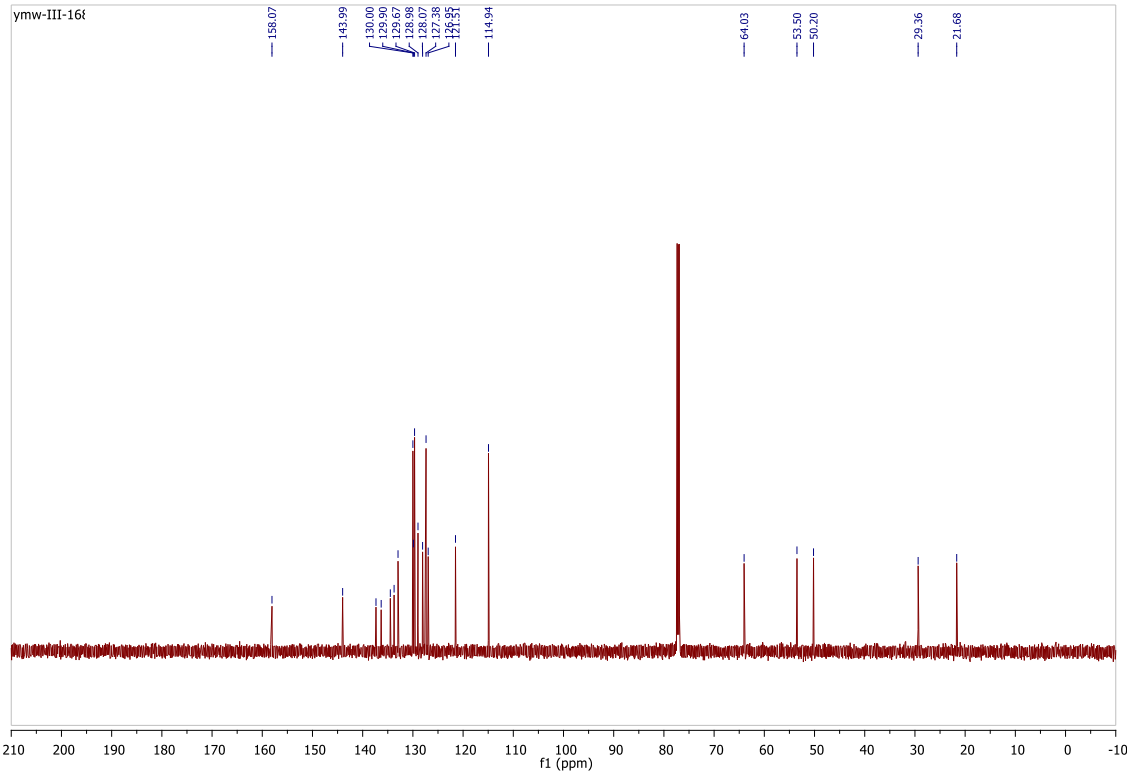

ymw-III-127-dry
8.45
8.02
8.00
7.99
7.95
7.94
7.84
7.68
7.34
7.32
7.27
7.25
7.22
7.21
6.41
3.94
3.55
3.55
3.54
3.52
3.52
3.50
3.49
3.48
3.47
3.47
1.90
1.04
2.10
1.06
1.05
2.09
2.12
3.51
1.00
2.06
4.14
3.07
f1 (ppm)

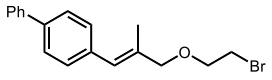

ymw-III-127-dry
136.85
136.16
135.00
133.21
132.35
129.98
129.78
129.43
129.09
128.95
128.73
128.60
128.07
127.85
127.15
122.47
58.54
49.85
29.18
15.90
f1 (ppm)


OPh
Ts
N
Cl
Br

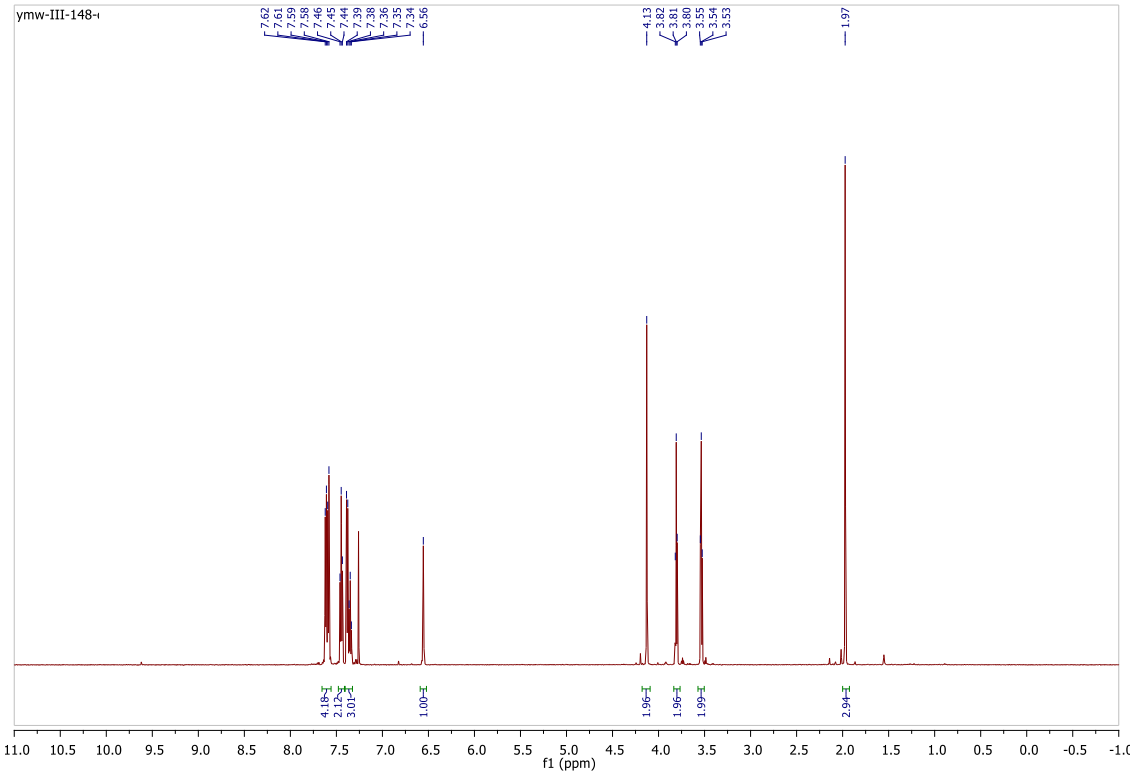
1p

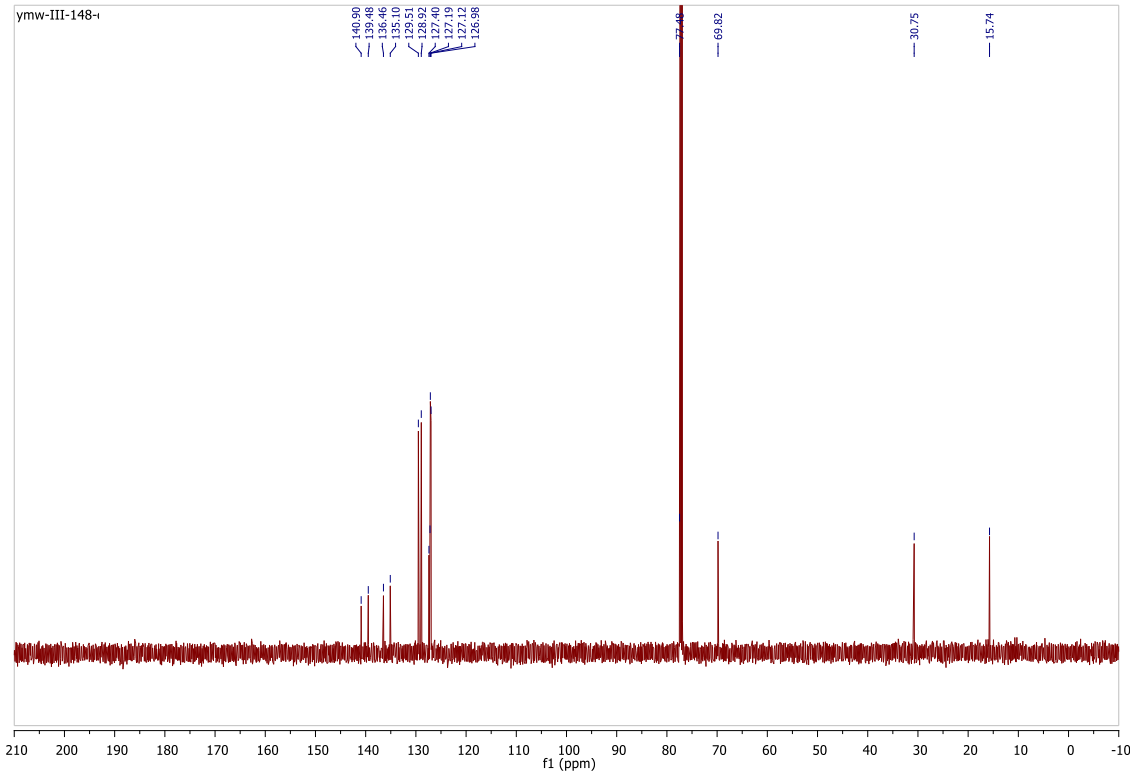

ymw-III-16
7.71
7.70
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.16
7.11
7.10
7.00
6.99
6.97
6.81
6.80
6.69
4.45
4.09
3.60
3.60
3.59
3.58
3.54
3.53
3.52
3.52
2.40
2.03
6.70
1.03
1.06
1.02
2.04
1.01
2.01
2.00
4.06
3.04
f1 (ppm)

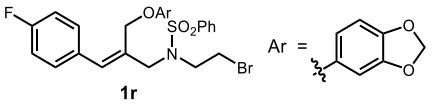

ymw-III-16
158.07
143.99
130.00
129.90
129.67
128.98
128.07
127.38
114.94
64.03
53.50
50.20
29.36
21.68
f1 (ppm)


Ph
O
Br

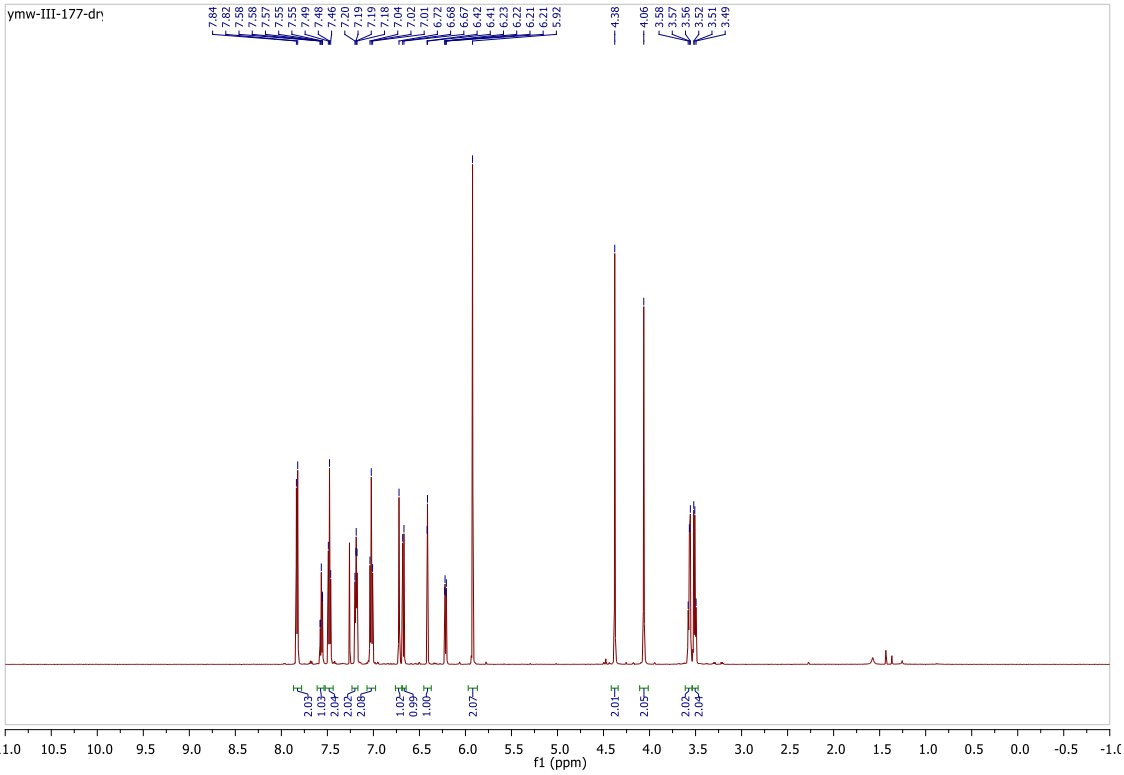
1q

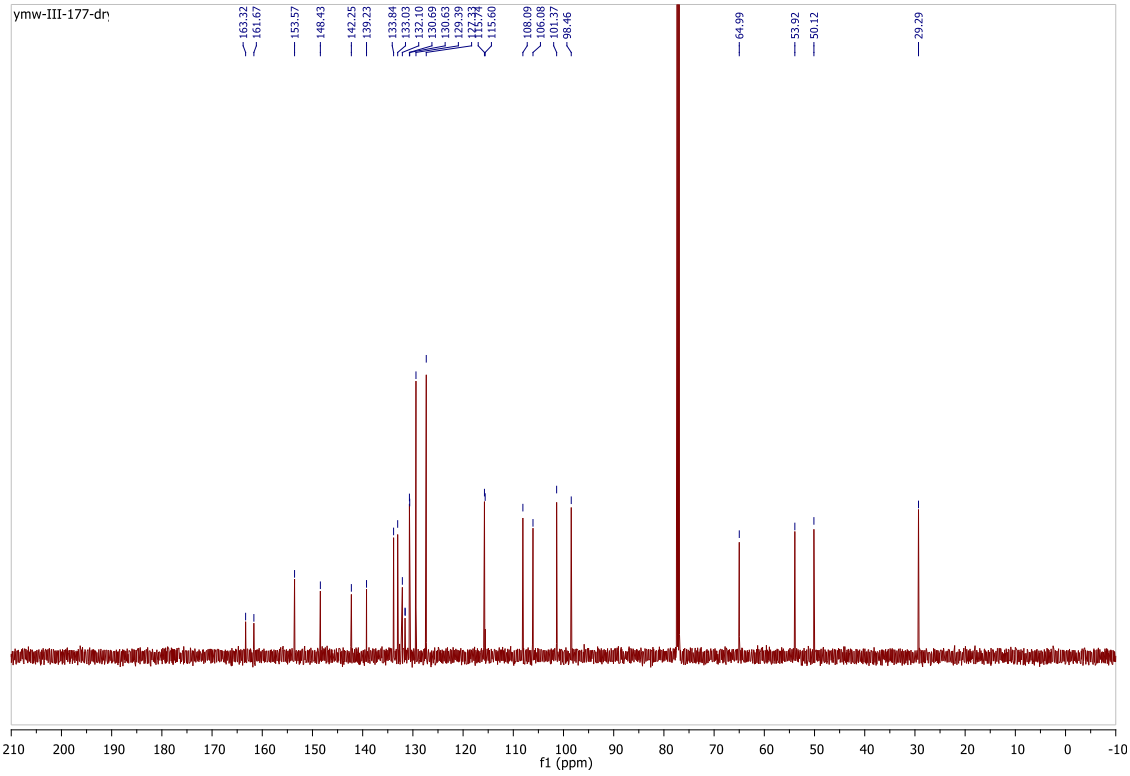

ymw-III-148-1
7.62
7.61
7.59
7.58
7.46
7.45
7.44
7.39
7.38
7.36
7.35
7.34
6.56
4.13
3.82
3.81
3.80
3.55
3.54
3.53
1.97
4.18
3.12
3.01
1.00
1.96
1.96
1.99
2.94
f1 (ppm)

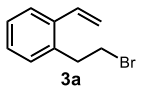

ymw-III-148-1
140.90
139.48
136.46
135.10
129.51
128.92
127.40
127.19
127.12
126.98
77.48
69.82
30.75
15.74
f1 (ppm)


F
OAr
SO2Ph
N
Br
Ar =
O
O

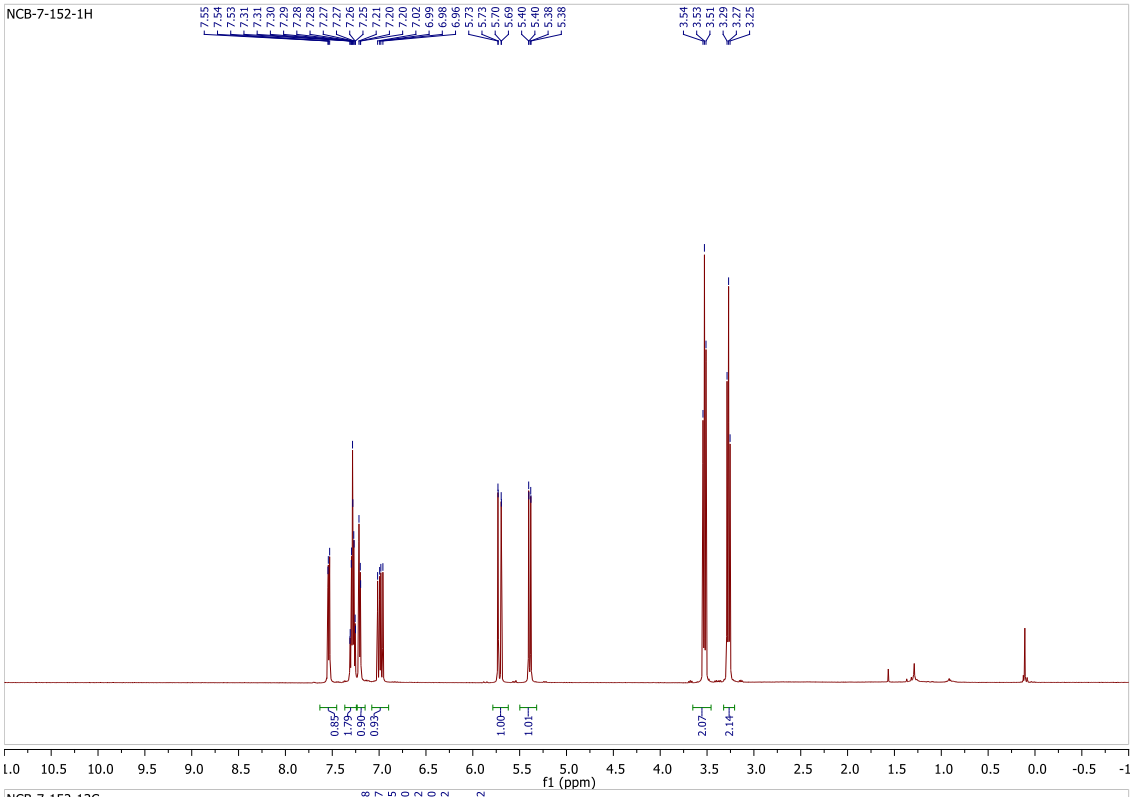
1r

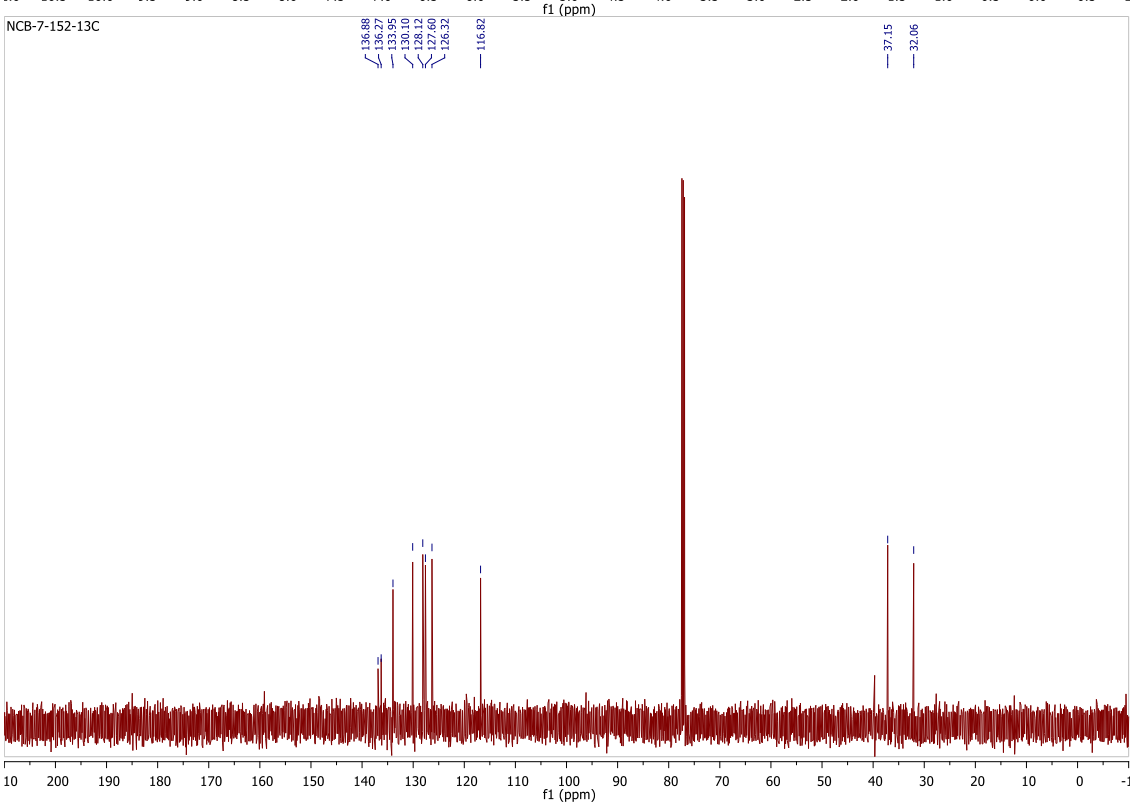

ymw-III-177-dn
7.84
7.82
7.58
7.58
7.57
7.55
7.55
7.49
7.48
7.46
7.20
7.19
7.19
7.18
7.04
7.02
7.01
6.72
6.68
6.67
6.42
6.41
6.23
6.22
6.21
6.21
5.92
4.38
4.06
3.58
3.57
3.56
3.52
3.51
3.49
2.03
1.03
2.04
2.02
2.06
1.02
0.99
1.06
2.07
2.01
2.05
2.02
2.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

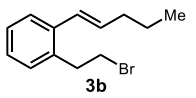

ymw-III-177-dn
163.32
161.67
153.57
148.43
142.25
139.23
133.84
133.03
132.10
130.69
130.63
129.39
127.33
115.74
115.60
108.09
106.08
101.37
98.46
64.99
53.92
50.12
29.29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Br

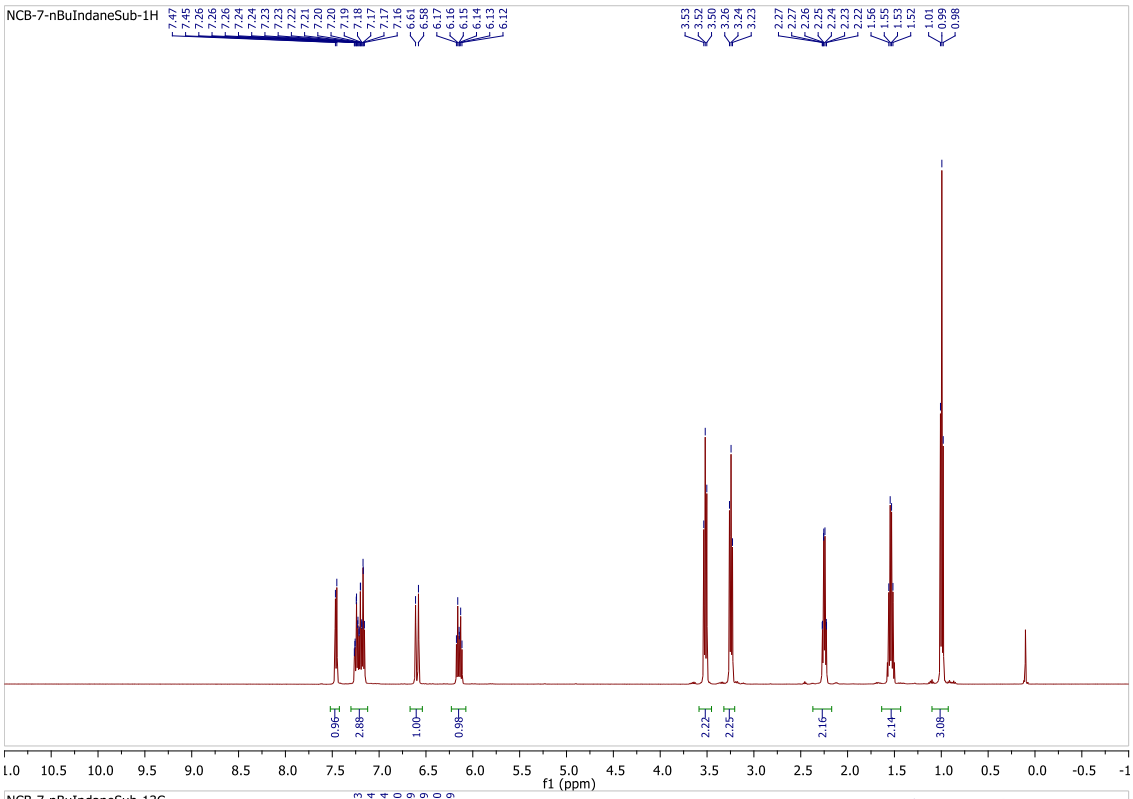
3a

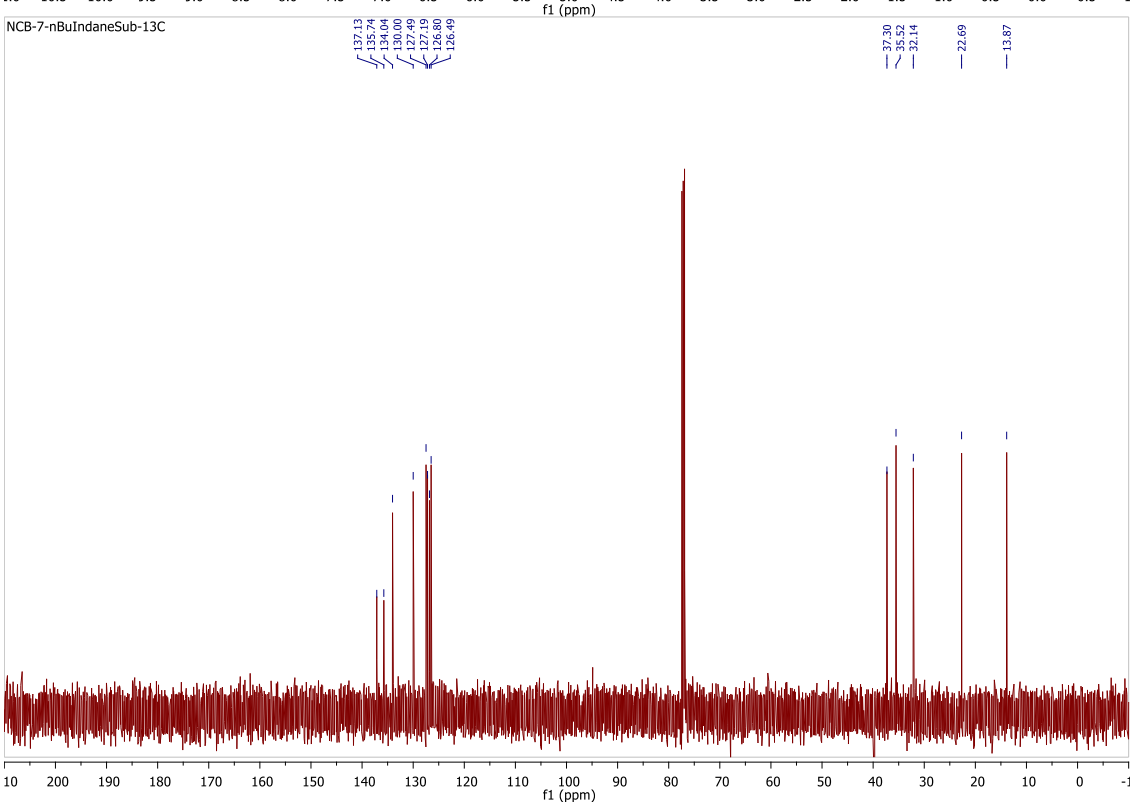

NCB-7-152-1H
7.55
7.54
7.53
7.31
7.31
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.21
7.20
7.20
7.02
6.99
6.98
6.96
5.73
5.73
5.70
5.69
5.40
5.40
5.38
5.38
3.54
3.53
3.51
3.29
3.27
3.25
0.85
1.79
0.96
0.93
1.00
1.01
2.07
2.14
f1 (ppm)

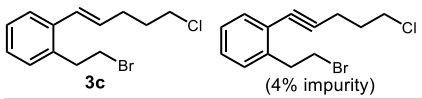

NCB-7-152-13C
136.88
136.27
133.95
130.10
128.12
127.60
126.32
116.82
37.15
32.06
f1 (ppm)


Me
Br

3b

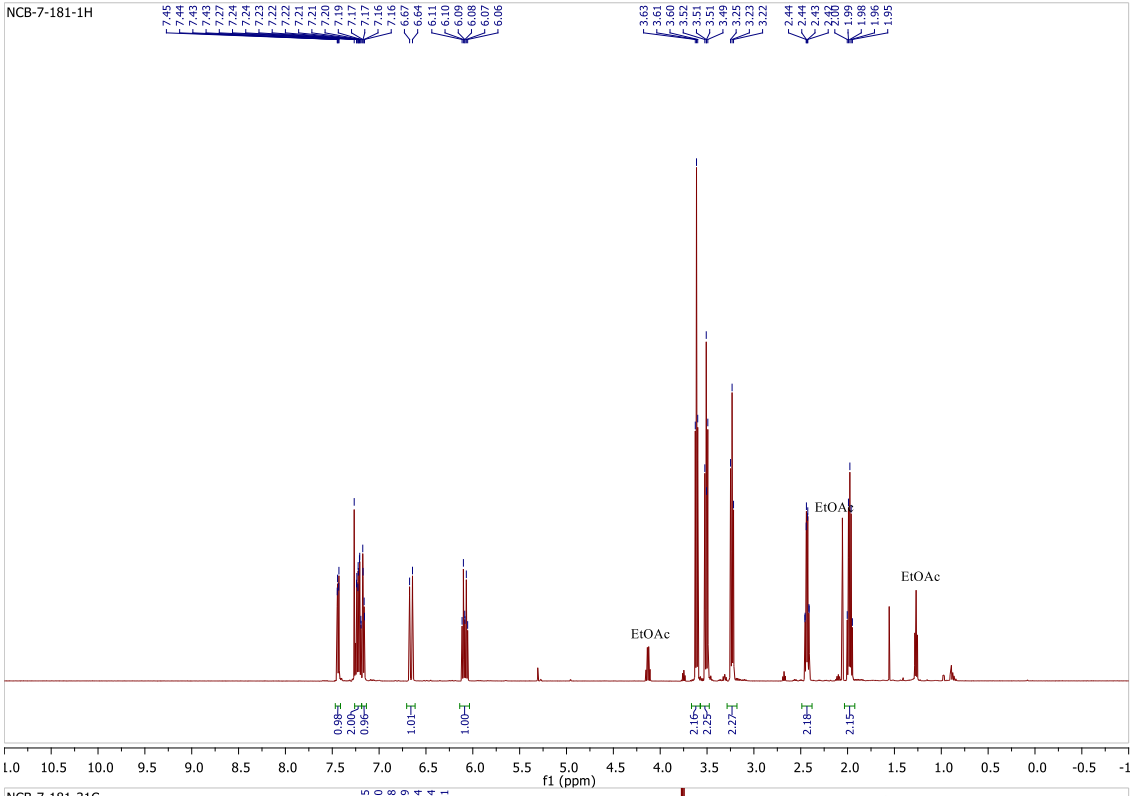

NCB-7-nBuIndaneSub-1H
7.47
7.45
7.26
7.26
7.26
7.24
7.24
7.23
7.23
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.17
7.16
6.61
6.58
6.17
6.16
6.15
6.14
6.13
6.12
3.53
3.52
3.50
3.26
3.24
3.23
2.27
2.27
2.26
2.25
2.24
2.23
2.22
1.56
1.55
1.53
1.52
1.01
0.99
0.98
0.96
2.88
1.00
0.98
2.22
2.25
2.16
2.14
3.08
f1 (ppm)

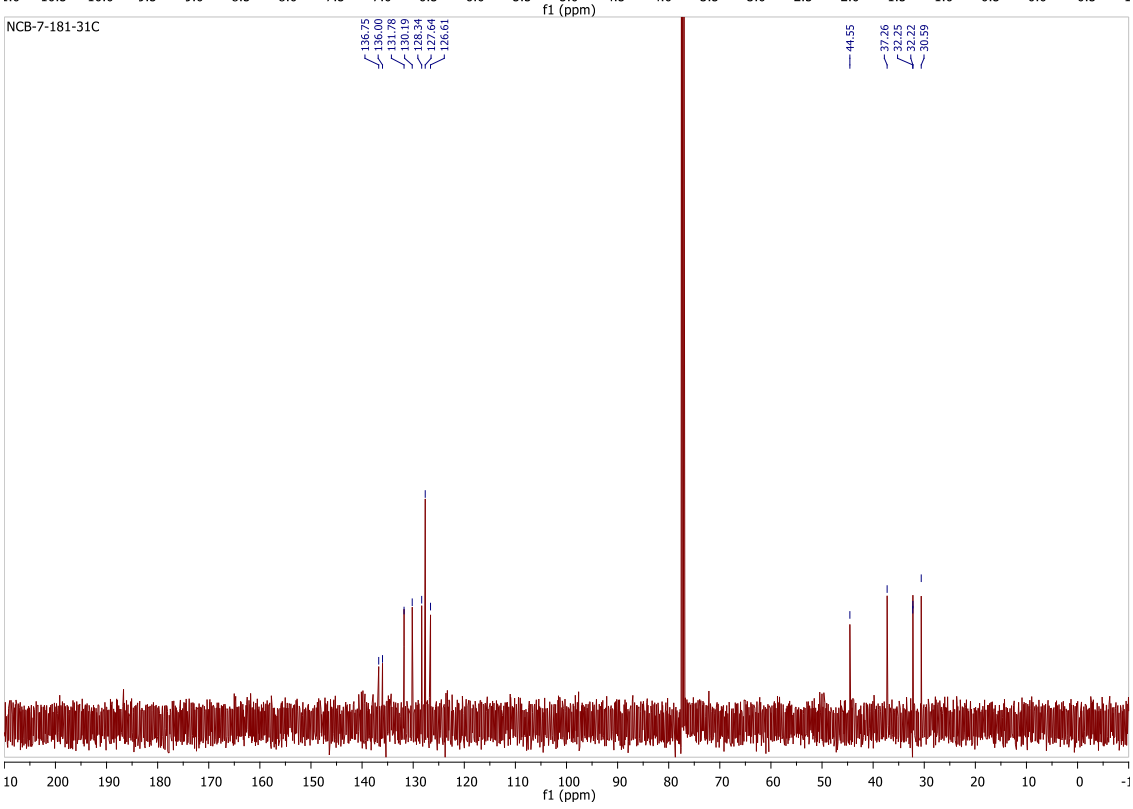

NCB-7-nBuIndaneSub-13C
137.13
135.74
134.04
130.00
127.49
127.19
126.80
126.49
37.30
35.52
32.14
22.69
13.87
f1 (ppm)



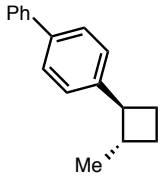
3c

(4% impurity)

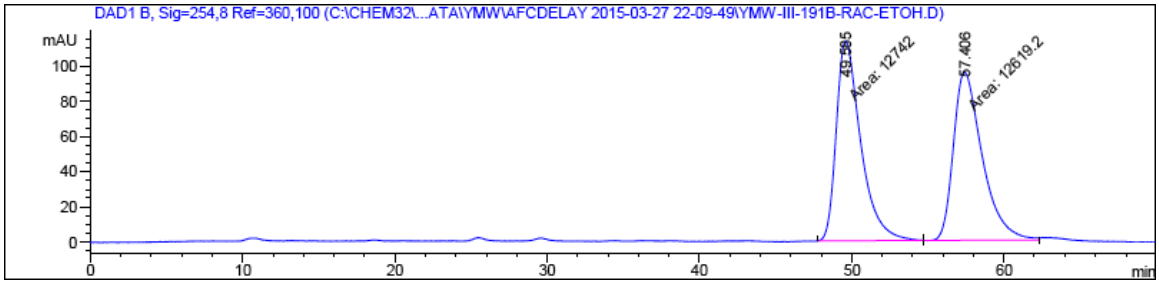




Copies of HPLC and GC traces for **2a – 2r** and **4a – 4c**:



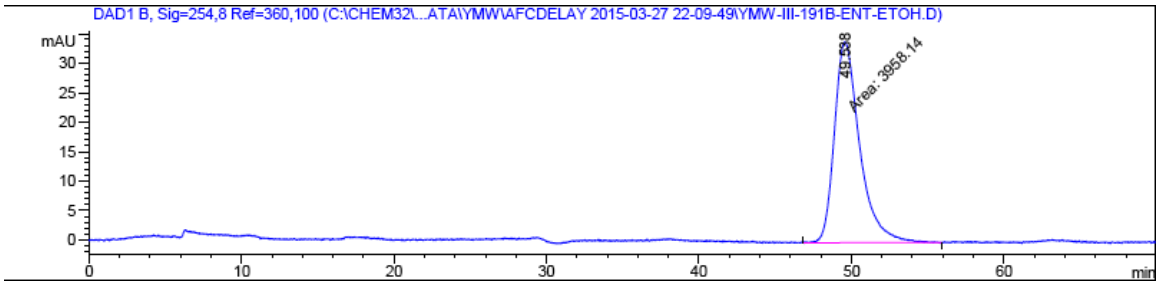
Racemic **2a**:



Signal 2: DAD1 B, Sig=254,8 Ref=360,100

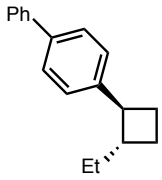
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.585	MM	1.8706	1.27420e4	113.52948	50.2421
2	57.406	MM	2.1991	1.26192e4	95.63958	49.7579

Enantioenriched **2a**:

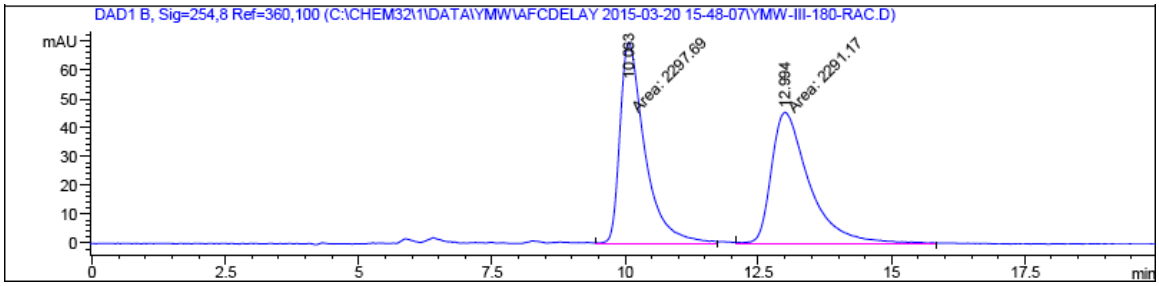


Signal 2: DAD1 B, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.538	MM	1.9332	3958.13550	34.12496	100.0000



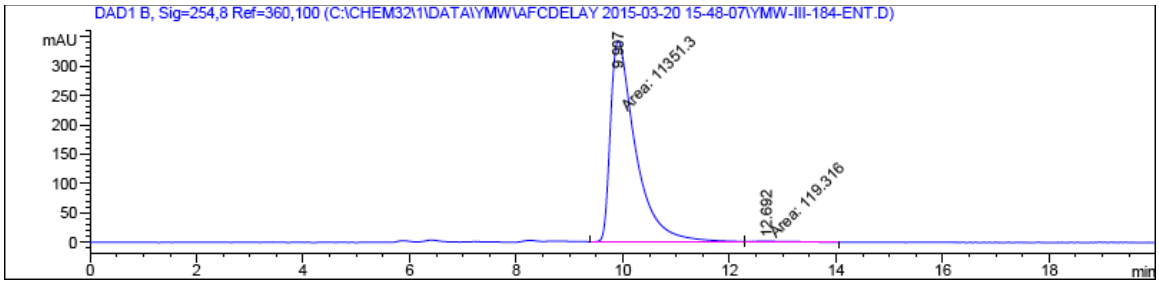
Racemic **2b**:



Signal 2: DAD1 B, Sig=254,8 Ref=360,100

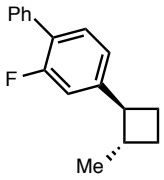
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.063	MM	0.5477	2297.68652	69.92495	50.0710
2	12.994	MM	0.8357	2291.17480	45.69621	49.9290

Enantioenriched **2b**:

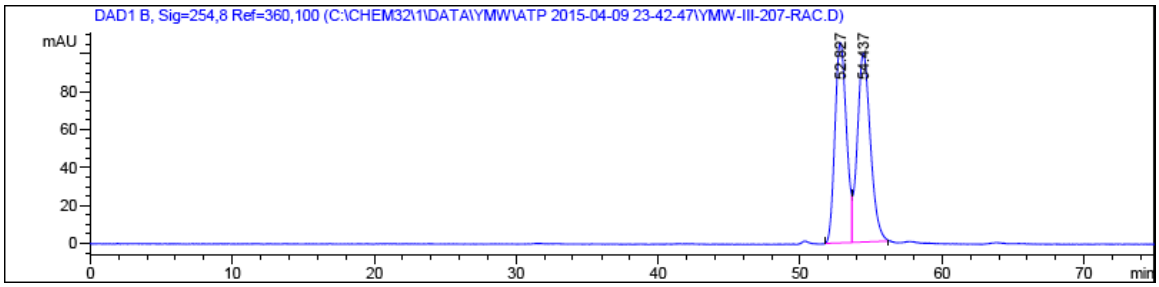


Signal 2: DAD1 B, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.907	MF	0.5516	1.13513e4	342.95947	98.9598
2	12.692	FM	1.0049	119.31648	1.97901	1.0402



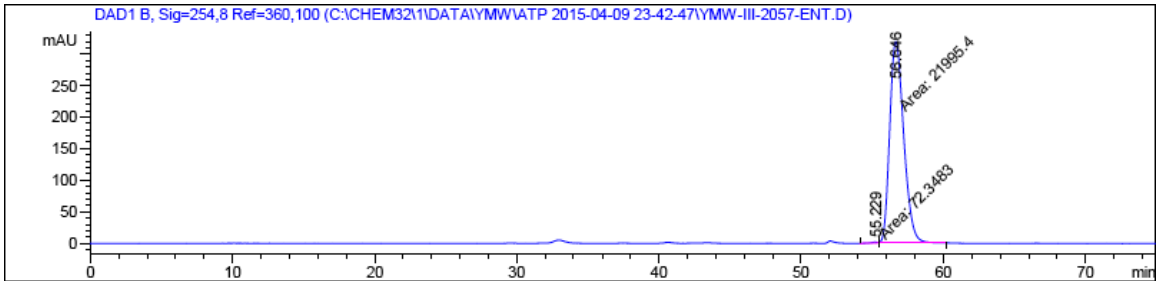
Racemic **2c**:



Signal 2: DAD1 B, Sig=254,8 Ref=360,100

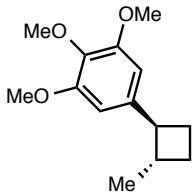
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.827	BV	0.8311	5952.37939	105.67712	48.2572
2	54.437	VB	0.8125	6382.31982	99.74817	51.7428

Enantioenriched **2c**:

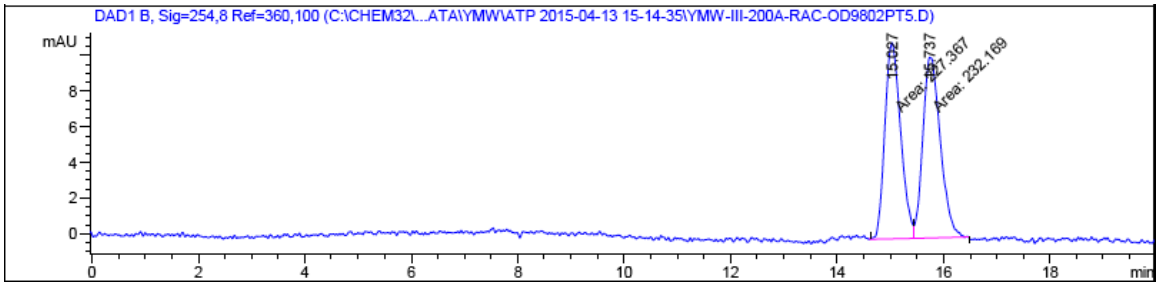


Signal 2: DAD1 B, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	55.229	MF	0.6439	72.34834	1.87269	0.3278
2	56.646	FM	1.1454	2.19954e4	320.05380	99.6722



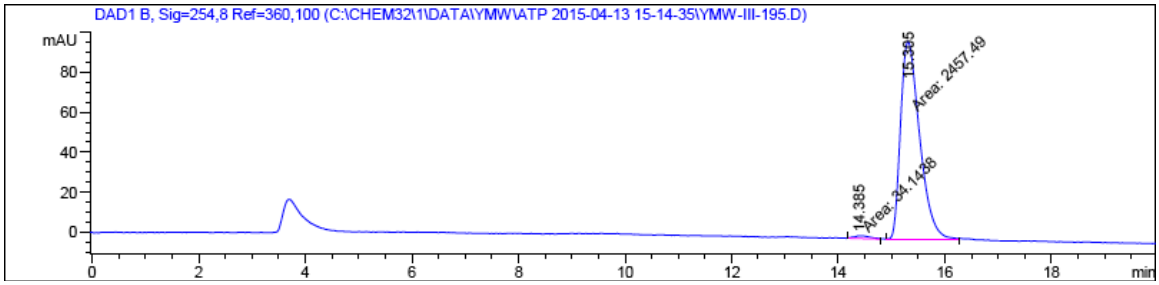
Racemic **2d**:



Signal 2: DAD1 B, Sig=254,8 Ref=360,100

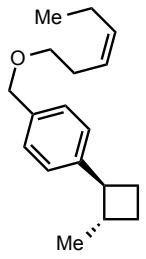
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.027	MF	0.3443	227.36719	11.00466	49.4775
2	15.737	FM	0.3814	232.16902	10.14473	50.5225

Enantioenriched **2d**:

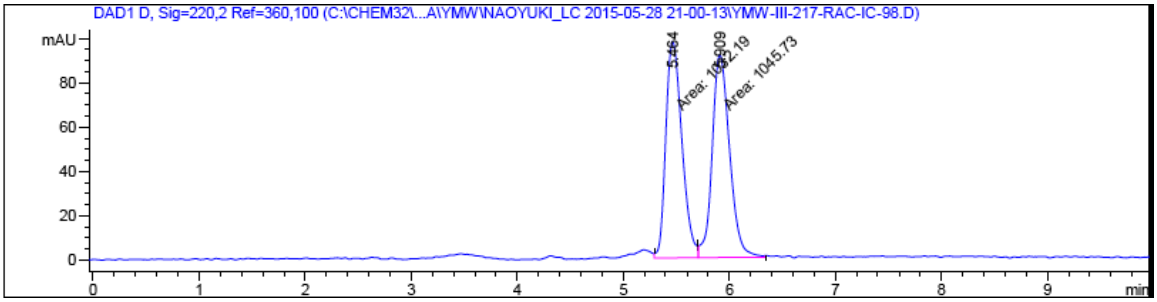


Signal 2: DAD1 B, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.385	MM	0.3673	34.14381	1.54928	1.3703
2	15.305	MM	0.4138	2457.49316	98.97387	98.6297



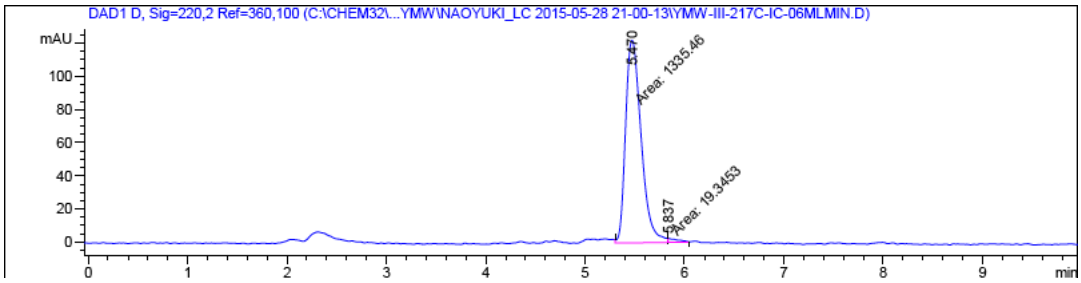
Racemic **2e**:



Signal 4: DAD1 D, Sig=220,2 Ref=360,100

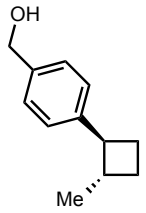
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.464	MF	0.1763	1032.18616	97.59855	49.6740
2	5.909	FM	0.1905	1045.73462	91.49982	50.3260

Enantioenriched **2e**:

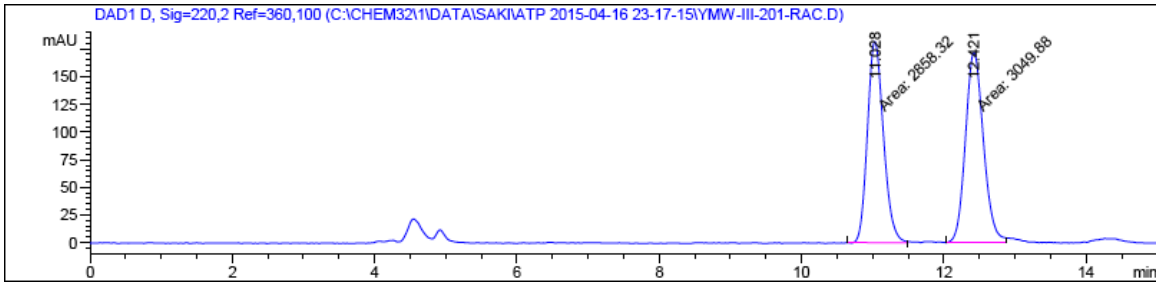


Signal 4: DAD1 D, Sig=220,2 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.470	MF	0.1820	1335.45801	122.30920	98.5721
2	5.837	FM	0.1198	19.34533	2.69174	1.4279



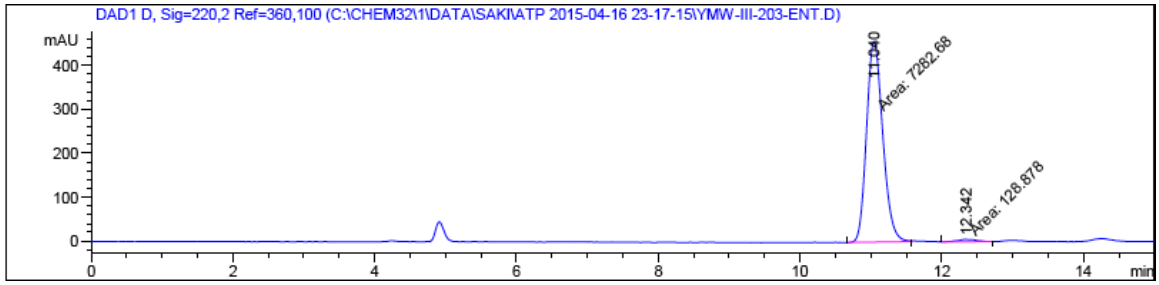
Racemic **2f**:



Signal 4: DAD1 D, Sig=220,2 Ref=360,100

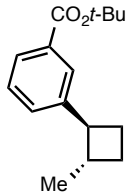
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.028	MM	0.2620	2858.32471	181.85948	48.3789
2	12.421	MF	0.2953	3049.88428	172.13083	51.6211

Enantioenriched **2f**:

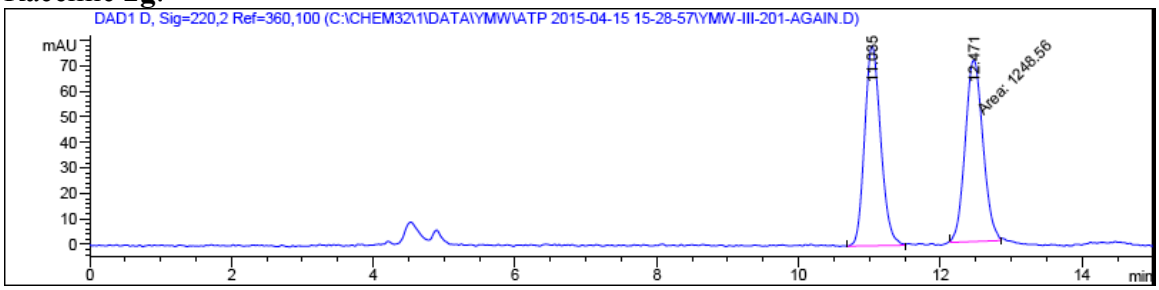


Signal 4: DAD1 D, Sig=220,2 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.040	MM	0.2657	7282.67578	456.87079	98.2611
2	12.342	MM	0.3692	128.87827	5.81869	1.7389



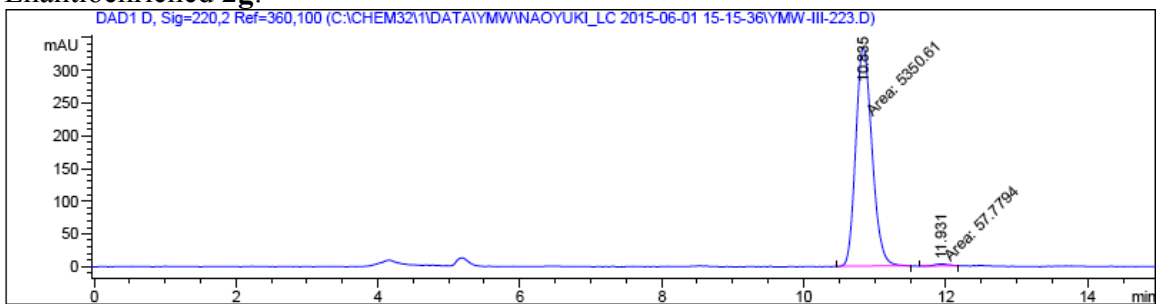
Racemic **2g**:



Signal 4: DAD1 D, Sig=220,2 Ref=360,100

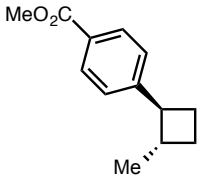
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.035	VV	0.2465	1240.81665	78.44220	49.8445
2	12.471	MM	0.2922	1248.55884	71.21598	50.1555

Enantioenriched **2g**:

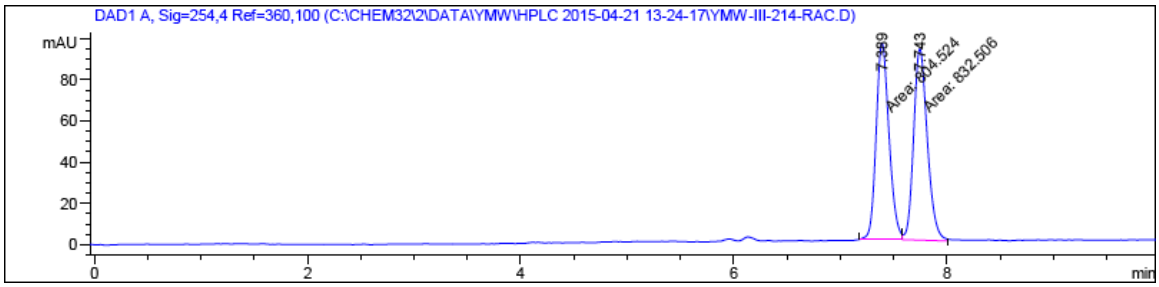


Signal 4: DAD1 D, Sig=220,2 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.835	MM	0.2659	5350.61230	335.34192	98.9317
2	11.931	MM	0.2770	57.77937	3.47645	1.0683



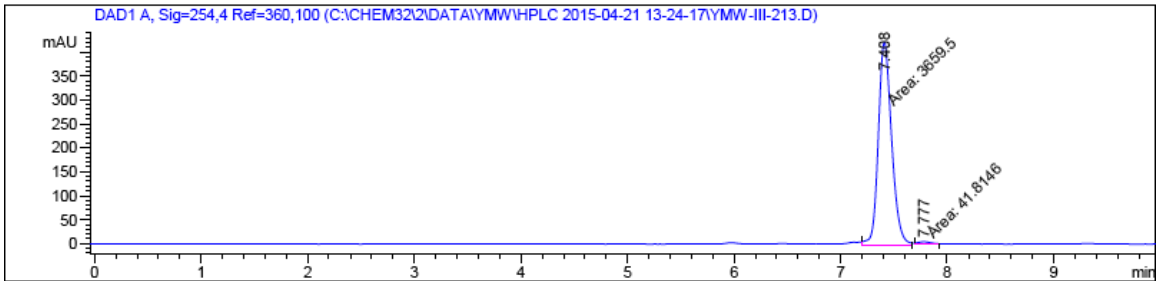
Racemic **2h**:



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

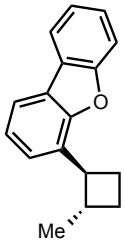
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.389	MM	0.1400	804.52411	95.79789	49.1453
2	7.743	MM	0.1489	832.50635	93.17208	50.8547

Enantioenriched **2h**:

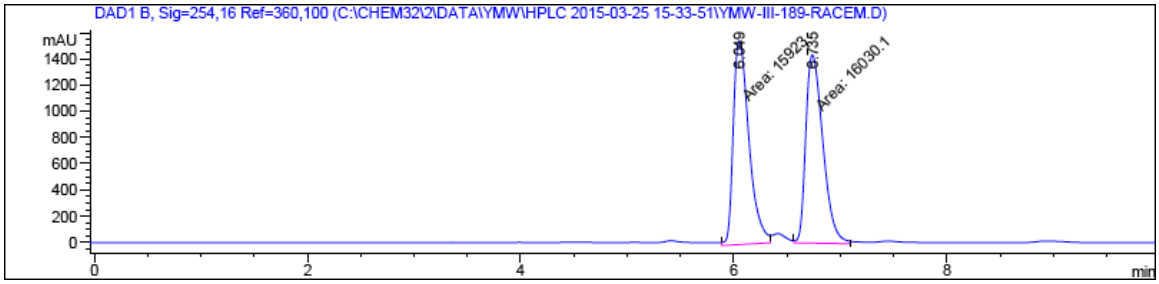


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.408	MM	0.1440	3659.49951	423.68835	98.8703
2	7.777	MM	0.1429	41.81459	4.87660	1.1297



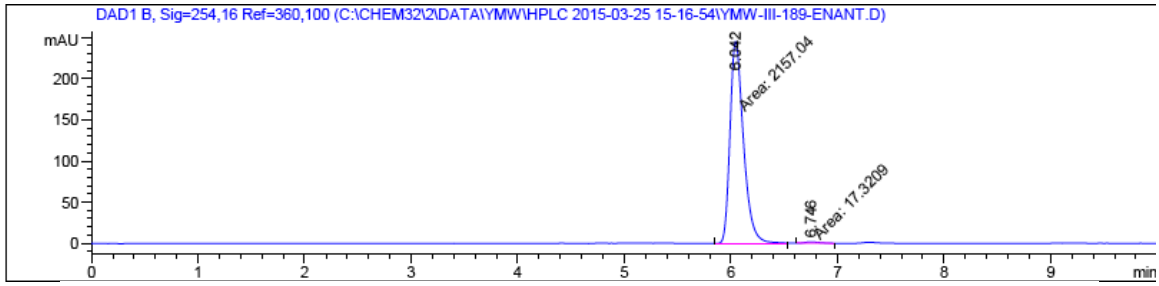
Racemic **2i**:



Signal 2: DAD1 B, Sig=254,16 Ref=360,100

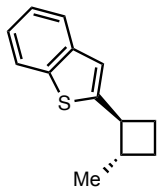
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.049	MM	0.1706	1.59230e4	1555.91479	49.8324
2	6.735	MM	0.1861	1.60301e4	1435.57251	50.1676

Enantioenriched **2i**:

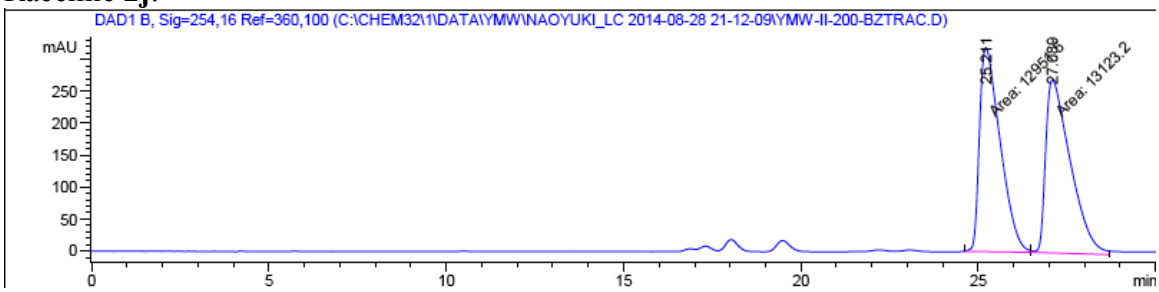


Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.042	MM	0.1465	2157.04419	245.44554	99.2034
2	6.746	MM	0.1739	17.32091	1.65958	0.7966



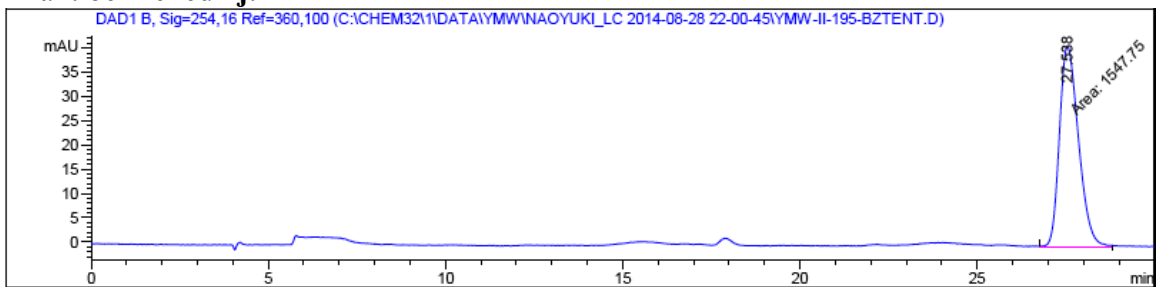
Racemic **2j**:



Signal 2: DAD1 B, Sig=254,16 Ref=360,100

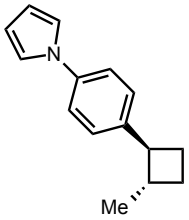
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.211	MM	0.6756	1.29515e4	319.49527	49.6707
2	27.089	MM	0.8061	1.31232e4	271.31689	50.3293

Enantioenriched **2j**:

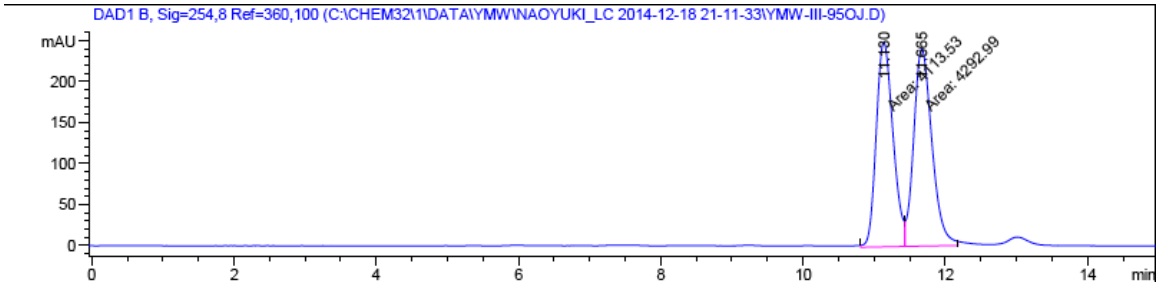


Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.538	MM	0.6241	1547.74841	41.32977	100.0000



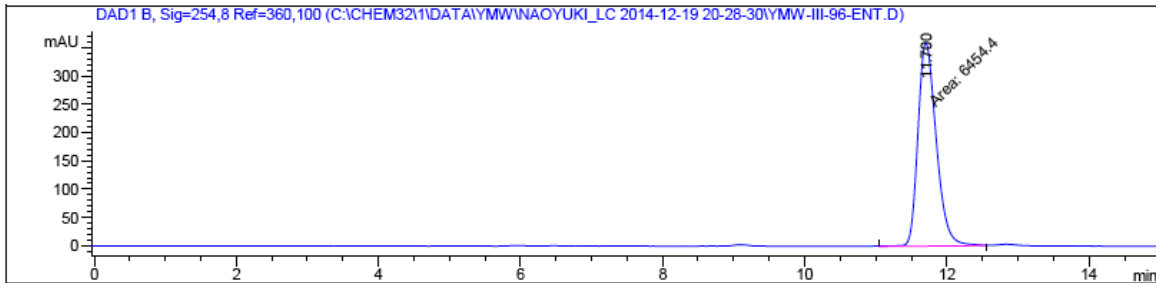
Racemic **2k**:



Signal 2: DAD1 B, Sig=254,8 Ref=360,100

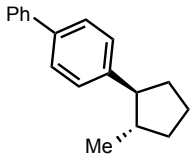
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.130	MF	0.2744	4113.52686	249.86801	48.9326
2	11.665	FM	0.2971	4292.98926	240.83388	51.0674

Enantioenriched **2k**:

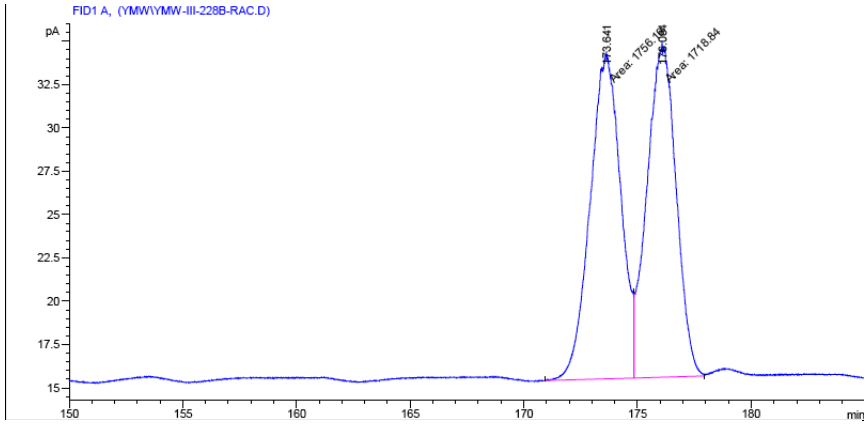


Signal 2: DAD1 B, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.700	MM	0.2987	6454.40234	360.11734	100.0000



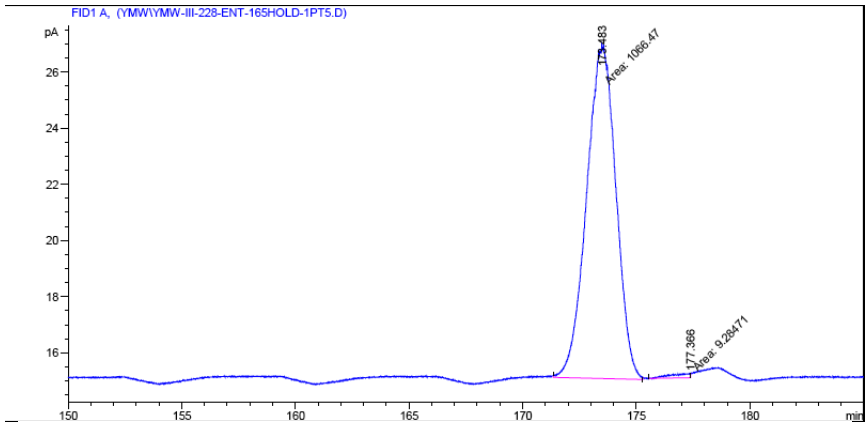
Racemic **2l**:



Signal 1: FID1 A,

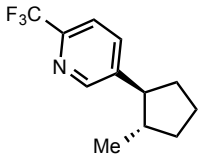
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	173.641	MF	1.5522	1756.19092	18.85754	50.53742
2	176.084	FM	1.4769	1718.84021	19.39677	49.46258

Enantioenriched **2l**:

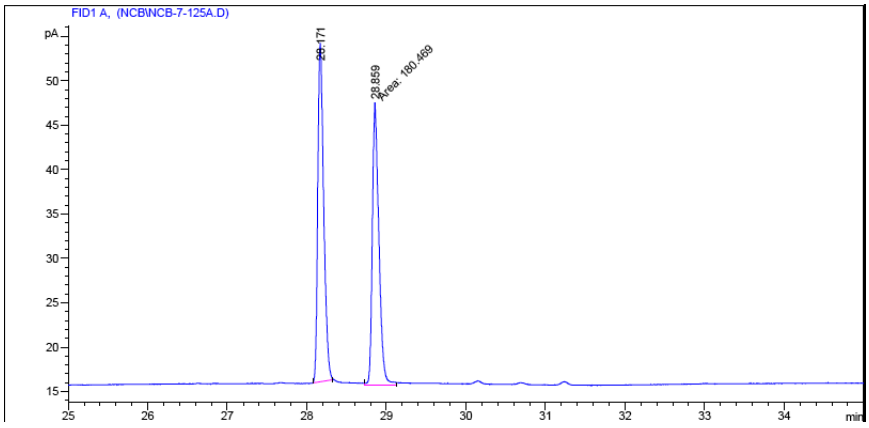


Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	173.483	MM	1.4843	1066.46802	11.97507	99.13691
2	177.366	MM	1.0072	9.28471	1.53638e-1	0.86309



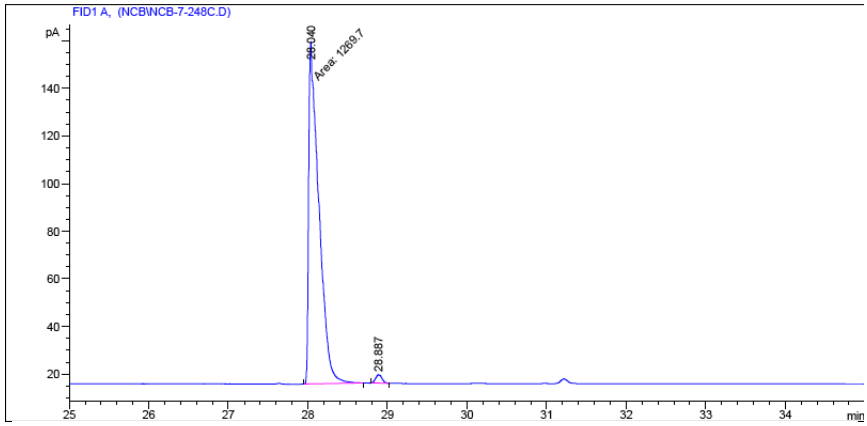
Racemic **2m**:



Signal 1: FID1 A,

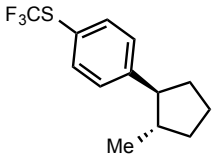
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	28.171	BB	0.0752	196.78378	38.10927	52.16228
2	28.859	MM	0.0946	180.46925	31.79614	47.83772

Enantioenriched **2m**:

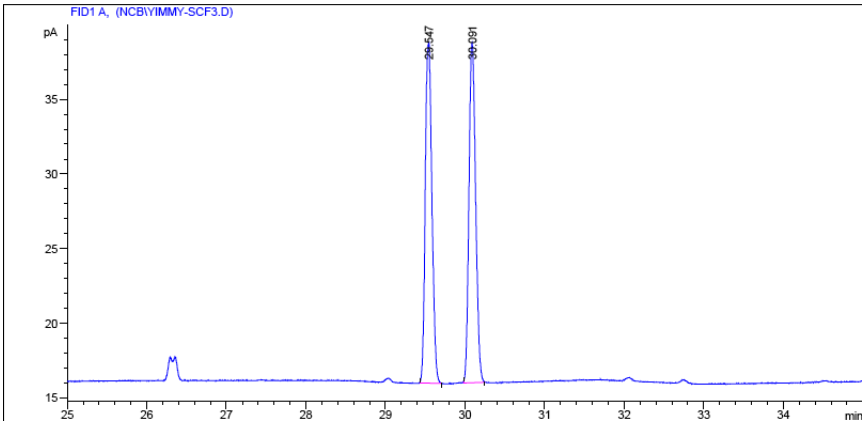


Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	28.040	MM	0.1473	1269.70105	143.65744	98.49776
2	28.887	BB	0.0709	19.36490	3.53327	1.50224



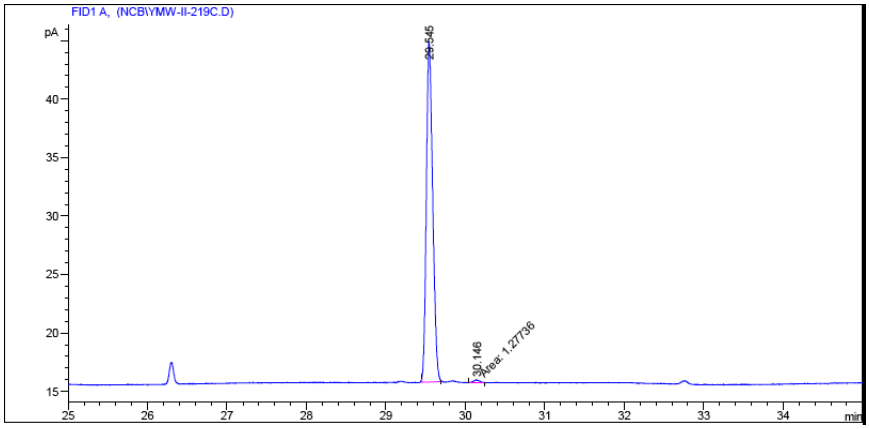
Racemic **2n**:



Signal 1: FID1 A,

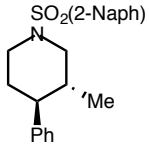
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	29.547	BB	0.0766	132.48047	22.85815	49.98904
2	30.091	BB	0.0848	132.53857	22.81592	50.01096

Enantioenriched **2n**:

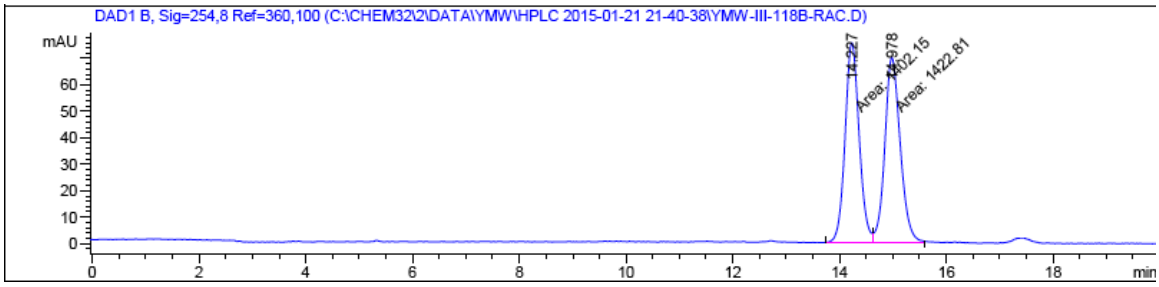


Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	29.545	BB	0.0786	160.68417	29.02345	99.21132
2	30.146	MM	0.0897	1.27736	2.37379e-1	0.78868



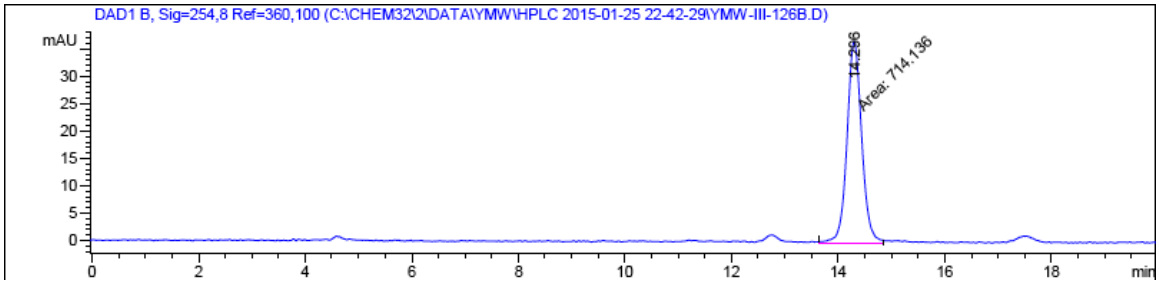
Racemic **2o**:



Signal 2: DAD1 B, Sig=254,8 Ref=360,100

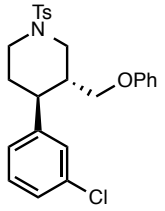
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.227	MF	0.3081	1402.14856	75.86118	49.6342
2	14.978	FM	0.3378	1422.81482	70.19015	50.3658

Enantioenriched **2o**:

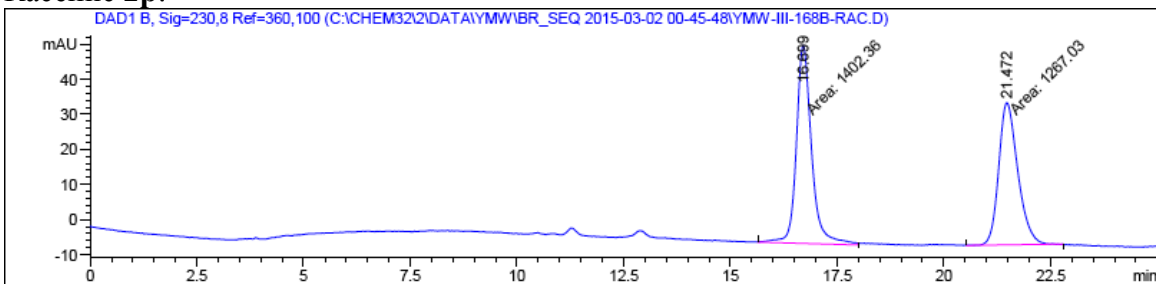


Signal 2: DAD1 B, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.296	MM	0.3225	714.13617	36.90207	100.0000



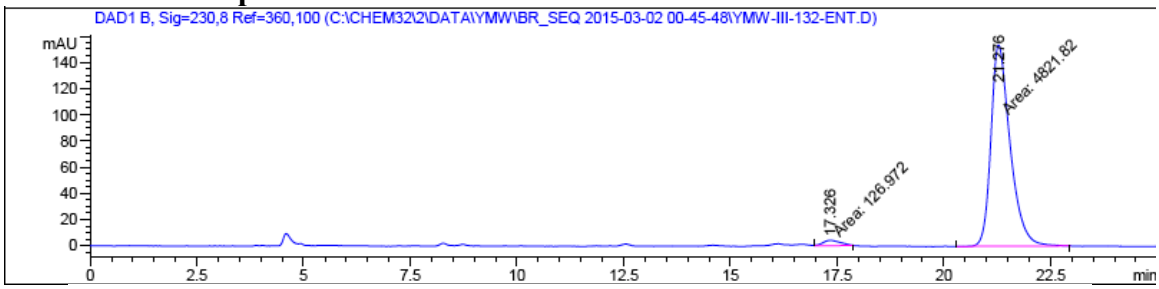
Racemic **2p**:



Signal 2: DAD1 B, Sig=230,8 Ref=360,100

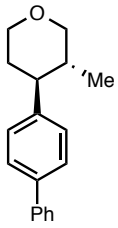
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.699	MM	0.4142	1402.36401	56.43433	52.5349
2	21.472	MM	0.5203	1267.02930	40.58829	47.4651

Enantioenriched **2p**:

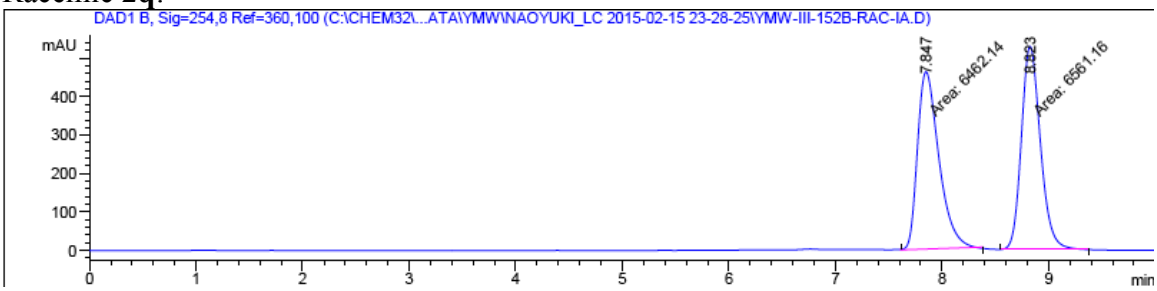


Signal 2: DAD1 B, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.326	FM	0.4993	126.97158	4.23867	2.5657
2	21.276	MM	0.5226	4821.81738	153.78175	97.4343



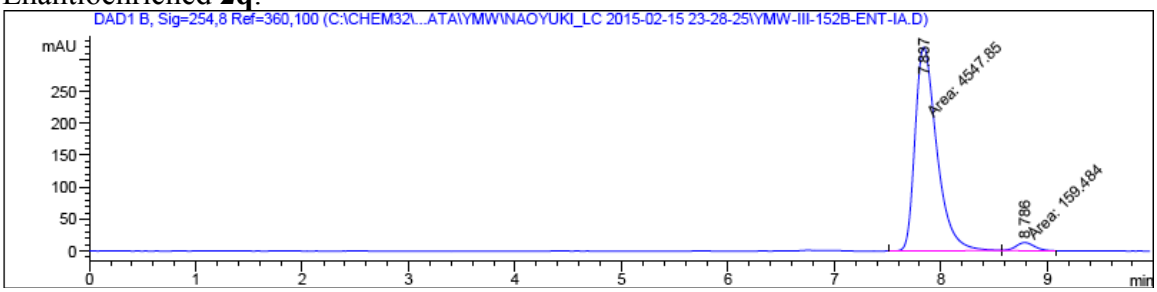
Racemic **2q**:



Signal 2: DAD1 B, Sig=254,8 Ref=360,100

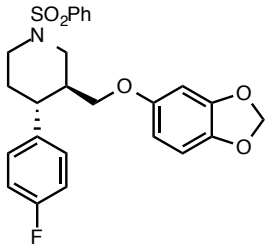
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.847	MM	0.2328	6462.14160	462.65054	49.6198
2	8.823	MM	0.2066	6561.16162	529.38330	50.3802

Enantioenriched **2q**:

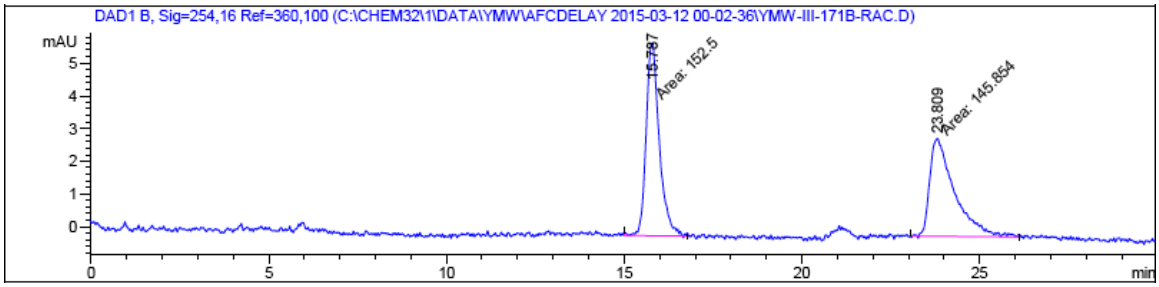


Signal 2: DAD1 B, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.837	MM	0.2369	4547.85254	319.94186	96.6120
2	8.786	MM	0.2073	159.48389	12.82190	3.3880



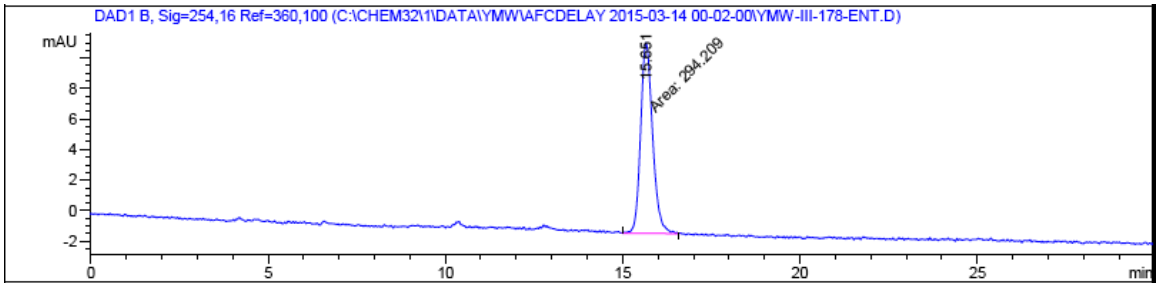
Racemic **2r**:



Signal 2: DAD1 B, Sig=254,16 Ref=360,100

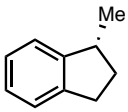
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.787	MM	0.4307	152.50032	5.90180	51.1139
2	23.809	MM	0.8104	145.85382	2.99974	48.8861

Enantioenriched **2r**:

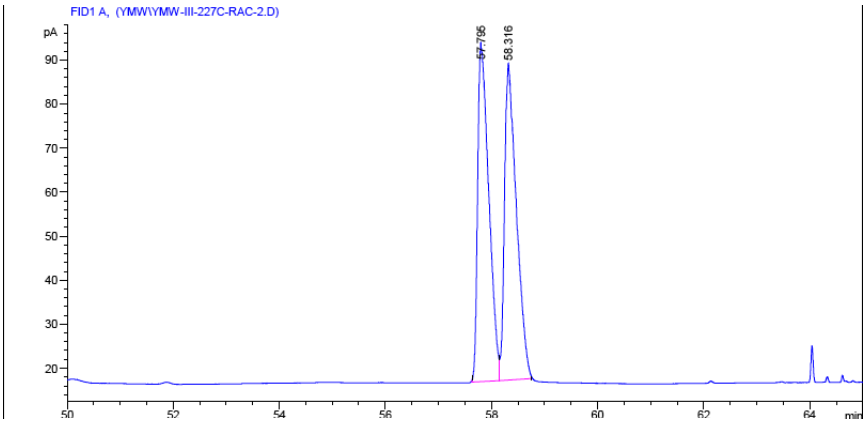


Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.651	MM	0.3927	294.20929	12.48640	100.0000



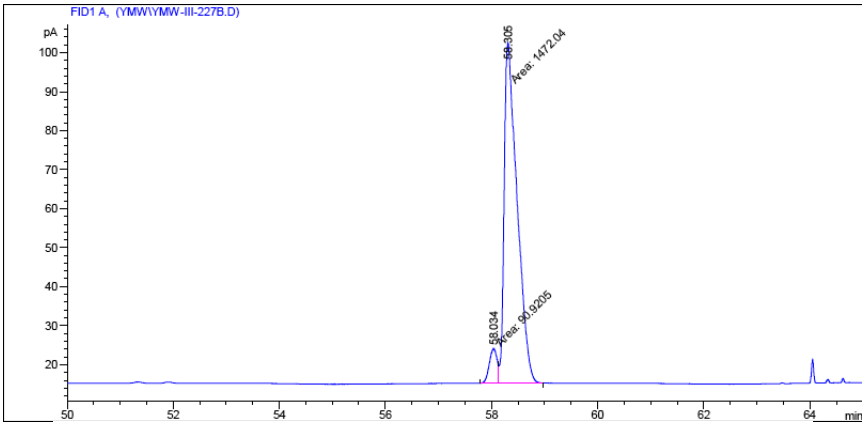
Racemic **4a**:



Signal 1: FID1 A,

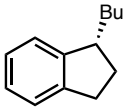
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	57.795	BV	0.1784	1120.37927	77.15198	50.10628
2	58.316	VB	0.1900	1115.62622	71.90934	49.89372

Enantioenriched **4a**:

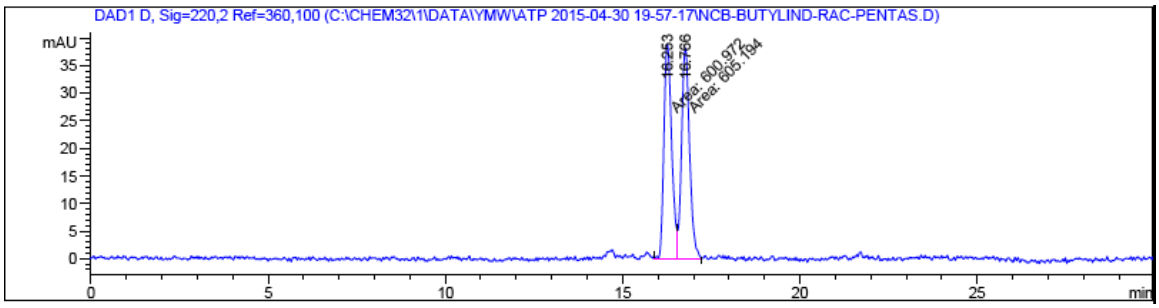


Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	58.034	MF	0.1710	90.92048	8.86404	5.81721
2	58.305	FM	0.2805	1472.03760	87.46353	94.18279



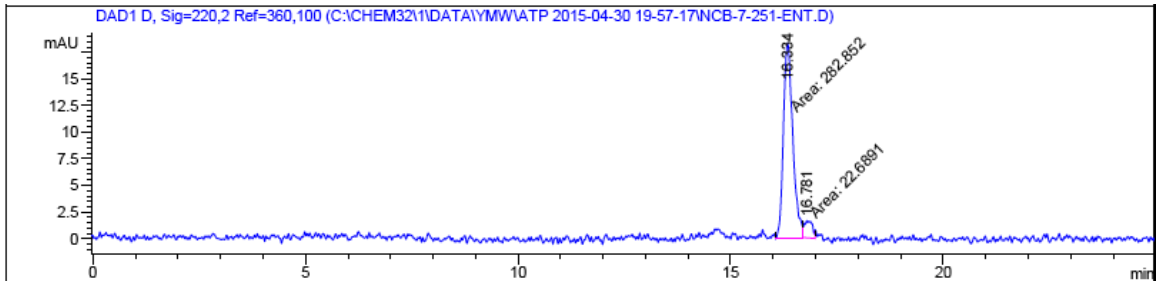
Racemic **4b**:



Signal 4: DAD1 D, Sig=220,2 Ref=360,100

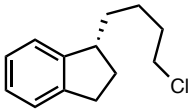
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.253	MF	0.2568	600.97211	39.00263	49.8250
2	16.766	FM	0.2635	605.19354	38.28640	50.1750

Enantioenriched **4b**:

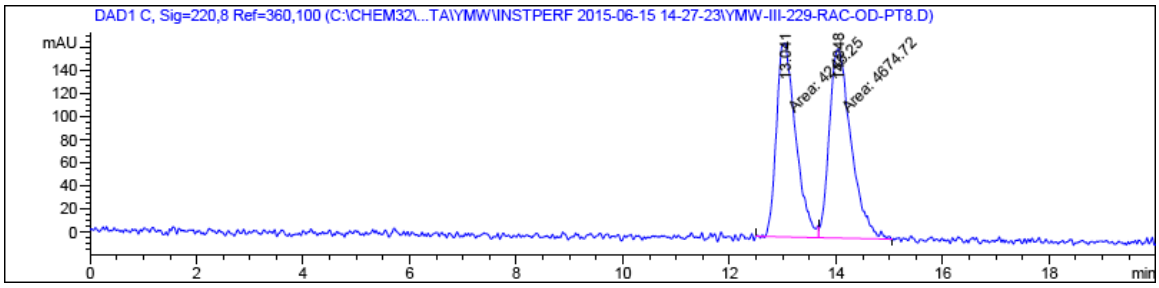


Signal 4: DAD1 D, Sig=220,2 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.334	MF	0.2569	282.85226	18.34714	92.5741
2	16.781	MM	0.2351	22.68913	1.60876	7.4259



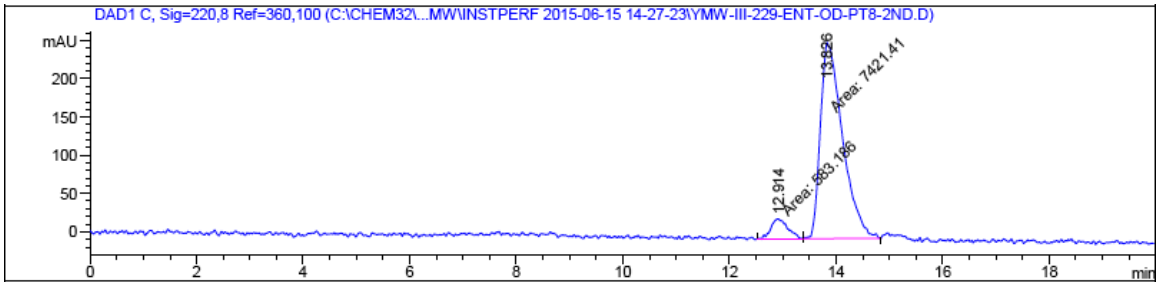
Racemic **4c**:



Signal 3: DAD1 C, Sig=220,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.041	MF	0.4208	4246.25488	168.17352	47.5986
2	14.048	FM	0.4758	4674.71582	163.73685	52.4014

Enantioenriched **4c**:



Signal 3: DAD1 C, Sig=220,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.914	MF	0.3710	583.18622	26.19545	7.2856
2	13.826	FM	0.4822	7421.40820	256.50671	92.7144