Supporting Information for

Enantioselective CuH-Catalyzed Hydroallylation of Vinylarenes

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Table of Contents

I. General Information:

General Reagent Information: Unless otherwise noted, reactions were conducted under protection of N_2 using standard Schlenk line techniques. THF was dried and deoxygenated by passage through packed columns of neutral alumina and copper(II) oxide under a positive pressure of argon and stored in a nitrogen-filled glovebox over 4Å molecular sieves. Copper(II) acetate (99.999% Cu) and copper(I) chloride (99.99% Cu) were purchased from Aldrich and Strem, respectively, and were used as received. Both enantiomers of Ph-BPE were purchased from Strem and stored in a nitrogen-filled glovebox. Dimethoxy(methyl)silane was purchased from TCI and stored in a nitrogen-filled glovebox at –20 °C. Lithium *tert*-butoxide was purchased from Strem or Alfa Aesar and stored in a nitrogen-filled glove box. Lithium *tert*-butoxide solution (2.2 M in THF) was purchased from Acros as an AcroSeal^{TM} bottle, which was stored under N_2. Lithium methoxide was purchased from Alfa Aesar and used as received. All other reagents and solvents were obtained from commercial sources 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).

II. Procedures for Copper-Catalyzed Hydroallylation

Preparation of (*S*,*S*)-Ph-BPE/CuCl (1:1) Complex: In a nitrogen-filled glovebox, a 20 mL scintillation vial was charged with (*S*,*S*)-Ph-BPE (253.3 mg, 0.5 mmol), CuCl (49.5 mg, 0.5 mmol) and THF (5 mL). The vial was fitted with a septum cap and transferred out of the glovebox. The grayish suspension was subjected to sonication (Branson 1510 sonicator, 40 kHz) for 30 min, resulting in the formation of a white suspension. Subsequently, the vial was subjected to high vacuum through an 18 G needle for 4 h to yield a white solid. The vial was then transferred into the glovebox where the solid was crushed to a fine powder with a spatula. The powder was dried under high vacuum for an additional 24 h. The white powder thus obtained was used in catalytic reactions without further purification. The complex was stored in the glovebox, although small samples could be stored outside the glovebox in 4 mL scintillation vials for at least a day without any apparent degradation.

General Procedure for Reaction Optimization:
*For entries 1-6 of Table 1, the following procedure was used to prepare a solution of L*CuH:* In a nitrogen-filled glovebox, a 4 mL scintillation vial was charged with a stir bar, the ligand (13.8 μmol, 5.5 mol %) and $Cu(OAc)_2$ (2.3 mg, 12.5 μmol, 5 mol %). THF (0.25 mL) and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 4.0 equiv) were added sequentially, and the vial was capped and stirred for 10 min to afford a pale yellow to orange (color was dependent on the ligand) solution of L*CuH.
Hydroallylation: A screw-cap reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar (10 mm × 5 mm, egg-shaped) was capped with a Teflon/silicone septum screw cap (National, part # C4015-66A) and flame-dried under vacuum. The reaction tube was cooled under argon and charged with the alkene substrate (0.25 mmol, 1.0 equiv) and allylic electrophile (0.50 mmol, 2.0 equiv). The reaction tube was recapped, evacuated and backfilled with argon (this process was repeated a total of three times), and transferred into a nitrogen-filled glovebox. The reaction tube was then uncapped, and LiOMe (38 mg, 1.0 mmol, 4.0 equiv) and the L*CuH solution (prepared above) were added in rapid succession. After resealing with a new screw cap, the reaction tube was transferred out of the glovebox and stirred in an oil bath preheated to the indicated temperature for 16 h. Subsequently, the reaction tube was allowed to cool to room temperature, and the reaction mixture was quenched by addition of CH_2Cl_2 (5 mL). 1,3,5-Trimethoxybenzene (42 mg, 0.25 mmol, 1.0 equiv) was added as an internal standard, and after shaking the reaction tube to ensure homogeneity, an aliquot of the crude reaction mixture was dried under a stream of nitrogen and analyzed by ^1H NMR for determination of the yield. Another portion of the crude reaction mixture was purified by preparative thin layer chromatography for determination of the enantiomeric excess.
*For entries 7-12 of Table 1, general procedure **A** (using the indicated base and allylic electrophile and scaled down to 0.25 mmol) was used for the reaction setup. Reaction workup was performed as described above.*

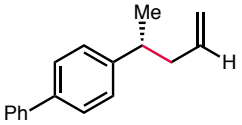
Preparation of Racemic Samples: To obtain racemic samples of the hydroallylation products, (±)-Ph-BPE was used as the ligand. (±)-Ph-BPE was prepared in a nitrogen-

filled glovebox by dissolving a mixture of (*R*,*R*)-Ph-BPE (507 mg, 1.00 mmol) and (*S*,*S*)-Ph-BPE (507 mg, 1.00 mmol) in THF (5 mL) and removing the solvent *in vacuo*. The General Procedure for Reaction Optimization was followed, using a solution of (±)-Ph-BPE•CuH and LiO*t*-Bu (40 mg, 0.50 mmol, 2.0 equiv) as the base in place of LiOMe.

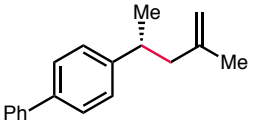
General Procedure A *for the hydroallylation of alkenes:* A screw-cap reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar (10 mm × 5 mm, egg-shaped) was capped with a Teflon/silicone septum screw cap (National, part # C4015-66A) and flame-dried under vacuum. The reaction tube was cooled under argon and charged with the alkene substrate (0.5 mmol, 1.0 equiv) and allylic phosphate reagent (0.75 – 1.25 mmol, 1.5 – 2.5 equiv, as indicated below for each example). The reaction tube was recapped, evacuated and backfilled with argon (this process was repeated a total of three times), and transferred into a nitrogen-filled glovebox. In the glovebox, (*S*,*S*)-Ph-BPE/CuCl (1:1) complex (6.1 mg, 10 μmol, 2 mol %), THF (0.5 mL), and LiO*t*-Bu (60 – 100 mg, 0.75 – 1.25 mmol, 1.5 – 2.5 equiv, 1:1 molar ratio relative to the allylic phosphate) were added in succession. The reaction tube was capped and gently shaken for 1 min to wash the solids into the reaction mixture, and dimethoxy(methyl)silane (0.09 – 0.15 mL, 0.75 – 1.25 mmol, 1.5 – 2.5 equiv, 1:1 molar ratio relative to the allylic phosphate) was subsequently added dropwise. The reaction tube was sealed with a new screw cap, transferred out of the glovebox, and stirred at room temperature for the time period indicated for each example (12 – 24 h). The reaction mixture was then quenched by addition of CH_2Cl_2 (5 mL) and filtered through a plug of silica gel (~3 g, eluting with CH_2Cl_2 (~100 mL)) employing a disposable filter funnel (60 mL, Chemrus, part # CR-1018-40). The eluate was concentrated *in vacuo*, and the resultant crude product was purified by flash column chromatography (~100 g SiO_2 gel) to provide the desired product. Yields reported are the average isolated yields of two runs.

Procedure for the Large Scale Synthesis of 3e: A flame-dried screw-cap reaction tube (16 mm × 125 mm, Fisherbrand, part # 14-959-35A) was charged with a stir bar (1/2" × 5/16"), 4-phenylstyrene (**1a**, 900 mg, 5.0 mmol, 1.0 equiv), allylic phosphate (**2e,** 2.44 g, 7.5 mmol, 1.5 equiv), and (*S*,*S*)-Ph-BPE/CuCl (1:1) complex (30.3 mg, 50 μmol, 1 mol %). The reaction tube was capped and then evacuated and backfilled with argon (this process was repeated a total of three times). Under an argon atmosphere, a solution of LiO*t*-Bu (3.4 mL, 2.2 M in THF, 7.5 mmol, Acros) was added, and the reaction mixture was stirred until it became a homogeneous solution (~2 min). The reaction tube cooled to 0 °C (ice bath), and dimethoxy(methyl)silane (0.92 mL, 7.5 mmol) was added slowly over 1 min. Upon completion of addition, the cap was exchanged with an unpunctured one under a flow of argon, and stirring was continued at 0 °C for 5 min. The ice bath was then removed, and the reaction mixture was stirred at room temperature for 16 h. Subsequently, CH_2Cl_2 (10 mL) was added, and the reaction mixture was filtered through a plug of silica gel (~10 g, eluting with CH_2Cl_2 (~200 mL)). The eluate was concentrated *in vacuo*, and the resultant crude product was purified by flash column chromatography (~100 g SiO_2 gel, 2 – 3% CH_2Cl_2 in hexanes, chromatography was performed twice) to afford **3e** as a colorless oil (1.05 g, 82% yield, 97% ee).

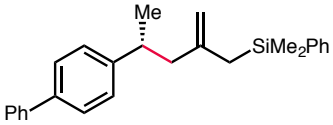
III. Characterization Data for Hydroallylation Products:



(*R*)-4-(Pent-4-en-2-yl)-1,1'-biphenyl (3a): Prepared following General Procedure **A** using 4-phenylstyrene (**1a**, 90 mg, 0.5 mmol, 1.0 equiv), allyl diphenylphosphate (**2a**, 290 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 17 h, and the crude residue was purified by flash column chromatography (0% to 1% Et_2O in pentane) to provide the title compound as a colorless oil. **Yield**: 93 mg, 84%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.59 – 7.53 (m, 2H), 7.49 – 7.41 (m, 2H), 7.39 – 7.32 (m, 1H), 7.32 – 7.27 (m, 2H), 5.85 – 5.71 (m, 1H), 5.10 – 4.97 (m, 2H), 2.94 – 2.81 (m, 1H), 2.52 – 2.40 (m, 1H), 2.40 – 2.29 (m, 1H), 1.32 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.3, 141.3, 139.0, 137.3, 128.8, 127.6, 127.2, 127.1, 116.2, 42.8, 39.6, 21.7 (one signal missing due to overlap). **IR** (thin film) 1485, 912, 834, 764, 732, 696 cm^{-1}. **EA** Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.65; H, 8.20. **Specific rotation** $[\alpha]_D^{24}$ = –25.0 (c = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 99.5:0.5 hexanes/2-propanol, 1.2 mL/min, t_m = 27.2 min, t_M = 33.0 min) indicated *99% ee*.

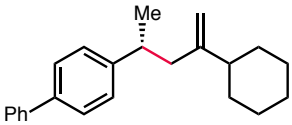


(*R*)-4-(4-Methylpent-4-en-2-yl)-1,1'-biphenyl (3b): Prepared following General Procedure **A** using 4-phenylstyrene (**1a**, 90 mg, 0.5 mmol, 1.0 equiv), 2-methallyl diphenylphosphate (**2b**, 304 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 16 h, and the crude residue was purified by flash column chromatography (0% to 1% CH_2Cl_2 in pentane) to provide the title compound as a colorless oil. **Yield**: 101 mg, 86%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.58 – 7.50 (m, 2H), 7.47 – 7.40 (m, 2H), 7.37 – 7.32 (m, 1H), 7.31 – 7.27 (m, 2H), 4.76 (s, 1H), 4.69 (s, 1H), 3.04 – 2.93 (m, 1H), 2.45 – 2.35 (m, 1H), 2.35 – 2.24 (m, 1H), 1.73 (s, 3H), 1.27 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.8, 144.2, 141.3, 139.0, 128.8, 127.5, 127.2, 127.1, 112.3, 47.0, 37.6, 22.5, 21.8. **IR** (thin film) 2962, 1486, 1451, 1008, 887, 835, 763, 732, 696 cm^{-1}. **EA** Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.22; H, 8.58. **Specific rotation** $[\alpha]_D^{24}$ = +7.02 (c = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 99:1 hexanes/2-propanol, 1.0 mL/min, t_m = 7.7 min, t_M = 8.1 min) indicated *97% ee*.

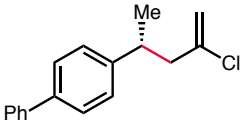


(*R*)-(4-([1,1'-Biphenyl]-4-yl)-2-methylenepentyl)dimethyl(phenyl)silane (3c): Prepared following General Procedure **A** using 4-phenylstyrene (**1a**, 90 mg, 0.5 mmol,

1.0 equiv), 2-((dimethyl(phenyl)silyl)methyl)allyl diphenylphosphate (**2c**, 438 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 16 h, and the crude residue was purified by flash column chromatography (2% to 3% CH_2Cl_2 in hexanes) to provide the title compound as a colorless oil. **Yield**: 153 mg, 83%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.57 – 7.47 (m, 4H), 7.47 – 7.41 (m, 2H), 7.41 – 7.30 (m, 4H), 7.20 – 7.13 (m, 2H), 4.61 (s, 1H), 4.58 (s, 1H), 2.97 – 2.83 (m, 1H), 2.24 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.09 (dd, *J* = 14.1, 8.5 Hz, 1H), 1.86 – 1.72 (m, 2H), 1.24 – 1.15 (m, 3H), 0.40 – 0.27 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.8, 145.2, 141.3, 139.3, 138.9, 133.8, 129.1, 128.8, 127.9, 127.5, 127.1 (two signals), 110.3, 47.3, 37.5, 25.6, 21.5, –2.7, –2.8 (one signal missing due to overlap). **IR** (thin film) 1485, 1247, 1112, 833, 763, 730, 696 cm^{-1}. **EA** Calcd. for $C_{26}H_{30}Si$: C, 84.26; H, 8.16. Found: C, 84.51; H, 8.24. **Specific rotation** $[\alpha]_D^{24}$ = –11.6 (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OD-H column, 95:5 hexanes/2-propanol, 1.0 mL/min, t_m = 8.2 min, t_M = 5.0 min) indicated *98% ee*.

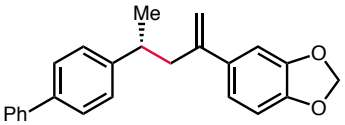


(*R*)-4-(4-Cyclohexylpent-4-en-2-yl)-1,1'-biphenyl (3d): Prepared following General Procedure **A** using 4-phenylstyrene (**1a**, 90 mg, 0.5 mmol, 1.0 equiv), 2-cyclohexylallyl diphenylphosphate (**2d**, 372 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 16 h, and the crude residue was purified by flash column chromatography (hexanes) to provide the title compound as a colorless oil. **Yield**: 135 mg, 89%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.56 – 7.51 (m, 2H), 7.47 – 7.40 (m, 2H), 7.36 – 7.27 (m, 3H), 4.77 (s, 1H), 4.70 (d, *J* = 1.1 Hz, 1H), 3.04 – 2.88 (m, 1H), 2.44 (dd, *J* = 14.2, 6.4 Hz, 1H), 2.25 (dd, *J* = 14.3, 8.4 Hz, 1H), 1.90 – 1.62 (m, 6H), 1.36 – 1.01 (m, 8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.4, 147.0, 141.3, 138.9, 128.8, 127.5, 127.1, 127.1, 127.1, 109.1, 44.3, 43.9, 38.0, 32.8, 32.6, 27.1, 27.0, 26.6, 21.8. **IR** (thin film) 2924, 2850, 1486, 1449, 764, 732, 697 cm^{-1}. **EA** Calcd. for $C_{23}H_{28}$: C, 90.73; H, 9.27. Found: C, 90.56; H, 9.28. **Specific rotation** $[\alpha]_D^{24}$ = –11.6 (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OD-H column, hexanes, 1.0 mL/min, t_m = 17.4 min, t_M = 22.6 min) indicated *98% ee*.

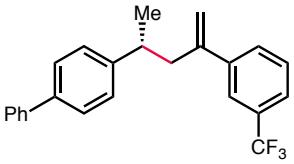


(*R*)-4-(4-Chloropent-4-en-2-yl)-1,1'-biphenyl (3e): Prepared following General Procedure **A** using 4-phenylstyrene (**1a**, 90 mg, 0.5 mmol, 1.0 equiv), 2-chloroallyl diphenylphosphate (**2e**, 325 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (1.5% CH_2Cl_2 in hexanes) to provide the title compound as a colorless oil. **Yield**: 106 mg, 83%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.58 – 7.52 (m, 2H), 7.47 – 7.41 (m, 2H), 7.38 – 7.27 (m, 3H), 5.15 (d, *J* = 1.0 Hz, 1H), 5.06 (d,

J = 0.8 Hz, 1H), 3.30 – 3.15 (m, 1H), 2.67 (dd, J = 14.2, 6.9 Hz, 1H), 2.56 (dd, J = 14.2, 8.0 Hz, 1H), 1.33 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.1, 141.2, 141.1, 139.3, 128.9, 127.5, 127.3, 127.2, 127.1, 114.0, 48.1, 37.0, 21.0. **IR** (thin film) 1634, 1486, 883, 835, 764, 732, 697 cm^{-1}. **EA** Calcd. for $C_{17}H_{17}Cl$: C, 79.52; H, 6.67. Found: C, 79.71; H, 6.74. **Specific rotation** $[\alpha]_D^{24}$ = –19.9 (c = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 98:2 hexanes/2-propanol, 1.0 mL/min, t_m = 9.9 min, t_M = 10.6 min) indicated *98% ee*.

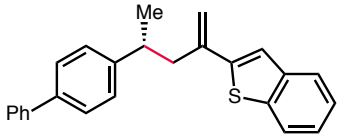


(*R*)-5-(4-([1,1'-Biphenyl]-4-yl)pent-1-en-2-yl)benzo[*d*][1,3]dioxole (3f): Prepared following General Procedure **A** using 4-phenylstyrene (**1a**, 90 mg, 0.5 mmol, 1.0 equiv), 2-(benzo[*d*][1,3]dioxol-5-yl)allyl diphenylphosphate (**2f**, 410 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 17 h, and the crude residue was purified by flash column chromatography (10% to 15% CH_2Cl_2 in hexanes) to provide the title compound as a colorless oil. **Yield**: 156 mg, 91%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 2H), 7.57 – 7.49 (m, 2H), 7.48 – 7.40 (m, 2H), 7.38 – 7.30 (m, 1H), 7.25 – 7.20 (m, 2H), 6.93 – 6.87 (m, 2H), 6.83 – 6.77 (m, 1H), 6.01 – 5.95 (m, 2H), 5.16 (d, J = 1.5 Hz, 1H), 4.93 (s, 1H), 2.94 – 2.81 (m, 2H), 2.71 – 2.60 (m, 1H), 1.26 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 147.1, 146.6, 146.5, 141.2, 139.0, 135.5, 128.8, 127.5, 127.1, 120.0, 113.7, 108.2, 107.1, 101.2, 45.0, 37.7, 21.4 (two signals missing due to overlap). **IR** (thin film): 1503, 1488, 1441, 1234, 1040, 766, 698 cm^{-1}. **EA** Calcd. for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.16; H, 6.55. **Specific rotation** $[\alpha]_D^{24}$ = –123 (c = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 65:35 hexanes/2-propanol, 1.0 mL/min, t_m = 72.3 min, t_M = 23.0 min) indicated *98% ee*.

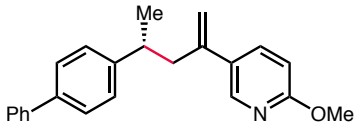


(*R*)-4-(4-(3-(Trifluoromethyl)phenyl)pent-4-en-2-yl)-1,1'-biphenyl (3g): Prepared following General Procedure **A** using 4-phenylstyrene (**1a**, 90 mg, 0.5 mmol, 1.0 equiv), 2-(3-(trifluoromethyl)phenyl)allyl diphenylphosphate (**2g**, 434 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 20 h, and the crude residue was purified by flash column chromatography (1% CH_2Cl_2 in hexanes) to provide the title compound as a colorless oil. **Yield**: 153 mg, 84%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.49 (m, 7H), 7.49 – 7.41 (m, 3H), 7.37 – 7.31 (m, 1H), 7.23 – 7.18 (m, 2H), 5.30 (d, J = 1.2 Hz, 1H), 5.11 (d, J = 1.0 Hz, 1H), 2.96 – 2.89 (m, 1H), 2.89 – 2.79 (m, 1H), 2.79 – 2.71 (m, 1H), 1.28 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.0, 145.9, 142.1, 141.2, 139.2, 130.9 (q, J_{CF} = 32.1 Hz), 129.8 (br), 128.9 (two signals), 127.5, 127.2 (two signals), 127.1, 124.3 (q, J_{CF} = 271 Hz), 124.2 (q, J_{CF} = 3.8 Hz), 123.3 (q, J_{CF} = 3.8 Hz), 116.1, 44.5, 37.9, 21.5. **IR** (thin film) 1486, 1334, 1165, 1125, 1073, 765, 697 cm^{-1}. **EA** Calcd. for $C_{24}H_{21}F_3$: C, 78.67; H, 5.78. Found: C, 78.61; H, 5.88.

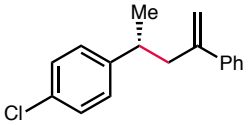
Specific rotation $[\alpha]_D^{24}$ = –82.1 (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 98:2 hexanes/2-propanol, 0.8 mL/min, t_m = 16.1 min, t_M = 15.1 min) indicated *97% ee*.



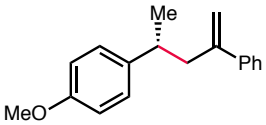
(*R*)-2-(4-([1,1'-Biphenyl]-4-yl)pent-1-en-2-yl)benzo[*b*]thiophene (3h): Prepared following General Procedure **A** using 4-phenylstyrene (**1a**, 90 mg, 0.5 mmol, 1.0 equiv), 2-(benzo[*b*]thiophen-2-yl)allyl diphenylphosphate (**2h**, 422 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 18 h, and the crude residue was purified by flash column chromatography (3% to 5% CH_2Cl_2 in hexanes) to provide the title compound as a colorless solid, **m.p.** 76 – 78 °C. **Yield**: 151 mg, 85%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 2H), 7.63 – 7.58 (m, 2H), 7.58 – 7.52 (m, 2H), 7.48 – 7.40 (m, 2H), 7.38 – 7.26 (m, 6H), 5.51 (s, 1H), 5.04 (s, 1H), 3.24 – 3.06 (m, 1H), 2.92 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.76 (dd, *J* = 14.0, 8.3 Hz, 1H), 1.36 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.2, 145.2, 141.2, 140.5, 140.4, 139.2, 139.2, 128.9, 127.5, 127.3, 127.2, 124.7, 124.5, 123.7, 122.2, 120.5, 115.7, 44.5, 38.3, 21.6 (one signal missing due to overlap). **IR** (thin film) 2925, 1485, 1456, 832, 765, 746, 727, 697 cm^{-1}. **EA** Calcd. for $C_{25}H_{22}S$: C, 84.70; H, 6.26. Found: C, 84.42; H, 6.18. **Specific rotation** $[\alpha]_D^{24}$ = –97.7 (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OD-H column, 95:5 hexanes/2-propanol, 1.0 mL/min, t_m = 17.7 min, t_M = 9.1 min) indicated *98% ee*.



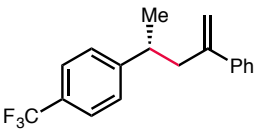
(*R*)-5-(4-([1,1'-Biphenyl]-4-yl)pent-1-en-2-yl)-2-methoxypyridine (3i): Prepared following General Procedure **A** using 4-phenylstyrene (**1a**, 90 mg, 0.5 mmol, 1.0 equiv), 2-(6-methoxypyridin-3-yl)allyl diphenylphosphate (**2i**, 397 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 15 h, and the crude residue was purified by flash column chromatography (70% to 75% CH_2Cl_2 in hexanes) to provide the title compound as a colorless oil. **Yield**: 107 mg, 65%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.24 – 8.18 (m, 1H), 7.62 – 7.56 (m, 3H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 1H), 5.19 (s, 1H), 4.98 (s, 1H), 3.96 (s, 3H), 2.91 – 2.82 (m, 2H), 2.69 (dd, *J* = 16.1, 10.3 Hz, 1H), 1.26 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.7, 146.1, 144.7, 143.8, 141.2, 139.2, 136.9, 130.0, 128.8, 127.5, 127.2, 127.1, 114.3, 110.5, 53.6, 44.6, 37.9, 21.4. **IR** (thin film) 1600, 1490, 1366, 1283, 1024, 832, 765, 697 cm^{-1}. **EA** Calcd. for $C_{23}H_{23}NO$: C, 83.85; H, 7.04. Found: C, 83.56; H, 7.22. **Specific rotation** $[\alpha]_D^{24}$ = –104 (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 80:20 hexanes/2-propanol, 1.0 mL/min, t_m = 21.1 min, t_M = 14.4 min) indicated *98% ee*.



(*R*)-1-Chloro-4-(4-phenylpent-4-en-2-yl)benzene (3j): Prepared following General Procedure **A** using 4-chlorostyrene (**1b**, 69 mg, 0.5 mmol, 1.0 equiv), 2-phenylallyl diphenylphosphate (**2j**, 274 mg, 0.75 mmol, 1.5 equiv), LiO*t*-Bu (60 mg, 0.75 mmol, 1.5 equiv), and dimethoxy(methyl)silane (0.09 mL, 0.75 mmol, 1.5 equiv). The reaction mixture was quenched after 15 h, and the crude residue was purified by flash column chromatography (1% CH_2Cl_2 in hexanes) to provide the title compound as a colorless oil. **Yield**: 111 mg, 86%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 5.21 (d, J = 1.3 Hz, 1H), 4.94 (s, 1H), 2.84 – 2.75 (m, 2H), 2.69 (dd, J = 16.4, 10.4 Hz, 1H), 1.21 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.9, 145.7, 141.1, 131.7, 128.5, 127.6, 126.5, 114.7, 44.7, 37.6, 21.5 (two signals missing due to overlap). **IR** (thin film) 1493, 1092, 1013, 899, 825, 777, 705 cm^{-1}. **EA** Calcd. for $C_{17}H_{17}Cl$: C, 79.52; H, 6.67. Found: C, 79.59; H, 6.73. **Specific rotation** $[\alpha]_D^{24}$ = –81.4 (c = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 99:1 hexanes/2-propanol, 1.0 mL/min, t_m = 14.2 min, t_M = 9.7 min) indicated *91% ee*.

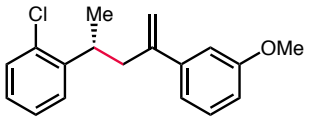


(*R*)-1-Methoxy-4-(4-phenylpent-4-en-2-yl)benzene (3k): Prepared following General Procedure **A** using 4-methoxystyrene (**1c**, 67 mg, 0.5 mmol, 1.0 equiv), 2-phenylallyl diphenylphosphate (**2j**, 457 mg, 1.25 mmol, 2.5 equiv), LiO*t*-Bu (100 mg, 1.25 mmol, 2.5 equiv), and dimethoxy(methyl)silane (0.15 mL, 1.25 mmol, 2.5 equiv). The reaction mixture was quenched after 18 h, and the crude residue was purified by flash column chromatography (6% to 9% CH_2Cl_2 in hexanes) to provide the title compound as a colorless oil. **Yield**: 111 mg, 88%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 5H), 7.11 – 7.05 (m, 2H), 6.86 – 6.80 (m, 2H), 5.22 (d, J = 1.6 Hz, 1H), 4.97 (d, J = 1.0 Hz, 1H), 3.80 (s, 3H), 2.88 – 2.71 (m, 2H), 2.65 (dd, J = 13.1, 7.6 Hz, 1H), 1.20 (d, J = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 147.2, 141.3, 139.5, 128.4, 127.9, 127.5, 126.5, 114.4, 113.8, 55.4, 45.0, 37.2, 21.6. **IR** (thin film) 1512, 1244, 1177, 1038, 828, 778, 704 cm^{-1}. **EA** Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.94; H, 7.93. **Specific rotation** $[\alpha]_D^{24}$ = –66.0 (c = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 95:5 hexanes/2-propanol, 1.0 mL/min, t_m = 15.1 min, t_M = 11.6 min) indicated *99% ee*.

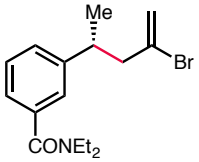


(*R*)-1-(4-Phenylpent-4-en-2-yl)-4-(trifluoromethyl)benzene (3l): Prepared following General Procedure **A** using 4-(trifluoromethyl)styrene (**1d**, 86 mg, 0.5 mmol, 1.0 equiv), 2-phenylallyl diphenylphosphate (**2j**, 274 mg, 0.75 mmol, 1.5 equiv), LiO*t*-Bu (60 mg, 0.75 mmol, 1.5 equiv), and dimethoxy(methyl)silane (0.09 mL, 0.75 mmol, 1.5 equiv). The reaction mixture was quenched after 15 h, and the crude residue was purified by flash column chromatography (1% CH_2Cl_2 in hexanes) to provide the title compound as a

colorless oil. **Yield**: 122 mg, 84%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.27 (m, 5H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.22 (d, *J* = 1.4 Hz, 1H), 4.95 (s, 1H), 2.95 – 2.80 (m, 2H), 2.80 – 2.68 (m, 1H), 1.27 – 1.22 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.3, 146.7, 141.0, 128.5, 127.7, 127.5, 126.5, 125.4 (q, J_{CF} = 3.7 Hz), 124.5 (q, J_{CF} = 273 Hz), 114.8, 44.5, 38.1, 21.4 (a quartet signal at ~128 ppm is obscured). **IR** (thin film) 1325, 1163, 1121, 1069, 1016, 838, 778, 706 cm^{-1}. **EA** Calcd. for $C_{18}H_{17}F_3$: C, 74.47; H, 5.90. Found: C, 74.69; H, 6.09. **Specific rotation** $[\alpha]_D^{24}$ = –61.5 (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 99:1 hexanes/2-propanol, 1.0 mL/min, t_m = 7.8 min, t_M = 5.4 min) indicated *96% ee*.

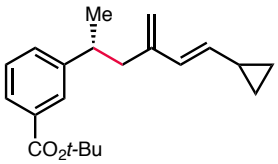


(*R*)-1-Chloro-2-(4-(3-methoxyphenyl)pent-4-en-2-yl)benzene (3m): Prepared following General Procedure **A** using 2-chlorostyrene (**1e**, 69 mg, 0.5 mmol, 1.0 equiv), 2-(3-methoxyphenyl)allyl diphenylphosphate (**2k**, 396 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 12 h, and the crude residue was purified by flash column chromatography (6% to 10% CH_2Cl_2 in hexanes) to provide the title compound as a colorless oil. **Yield**: 134 mg, 93%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.19 (m, 4H), 7.11 (td, *J* = 7.6, 1.8 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.98 – 6.94 (m, 1H), 6.84 (dd, *J* = 8.2, 2.5 Hz, 1H), 5.27 (d, *J* = 0.8 Hz, 1H), 5.04 (s, 1H), 3.83 (s, 3H), 3.49 – 3.35 (m, 1H), 2.97 (dd, *J* = 14.2, 5.9 Hz, 1H), 2.53 (dd, *J* = 14.2, 9.1 Hz, 1H), 1.19 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 146.8, 144.4, 142.6, 133.7, 129.6, 129.3, 127.5, 127.2, 127.1, 119.2, 114.7, 113.1, 112.3, 55.4, 43.2, 33.9, 19.9. **IR** (thin film) 1597, 1576, 1475, 1238, 1036, 753, 731 cm^{-1}. **EA** Calcd. for $C_{18}H_{19}ClO$: C, 75.38; H, 6.68. Found: C, 75.41; H, 6.74. **Specific rotation** $[\alpha]_D^{24}$ = +8.19 (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 99:1 hexanes/ethanol, 1.0 mL/min, t_m = 15.0 min, t_M = 9.7 min) indicated *98% ee*.

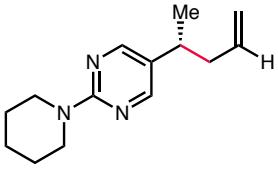


(*R*)-3-(4-Bromopent-4-en-2-yl)-*N*,*N*-diethylbenzamide (3n): Prepared following a modification of General Procedure **A** (see below) using *N*,*N*-diethyl-3-vinylbenzamide (**1f**, 101 mg, 0.5 mmol, 1.0 equiv), 2-bromoallyl diphenylphosphate (**2l**, 369 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction was performed using 4 mol % (*S*,*S*)-Ph-BPE/CuCl (1:1) complex (12.1 mg), and the reaction mixture was stirred at 35 °C for 12 h. The reaction mixture was then allowed to cool to room temperature, quenched with CH_2Cl_2 (5 mL), and filtered through silica gel (~3 g) using 5:1 CH_2Cl_2/EtOAc (~100 mL) as the eluent. After removal of the solvent, the crude residue was purified by flash column chromatography (1.5% acetone in CH_2Cl_2) to provide the title compound as a colorless oil, which became discolored upon exposure to light. **Yield**: 110 mg, 68%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.18 (m, 3H), 5.43 (s, 1H),

5.34 (d, J = 1.5 Hz, 1H), 3.55 (br s, 2H), 3.31 – 3.13 (m, 3H), 2.68 (dd, J = 14.3, 7.2 Hz, 1H), 2.60 (dd, J = 14.3, 7.6 Hz, 1H), 1.32 – 1.19 (m, 6H), 1.10 (br s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.6, 146.1, 137.7, 132.8, 128.6, 128.0, 125.2, 124.5, 118.4, 50.2, 43.4 (br), 39.4 (br), 38.1, 20.8, 14.4 (br), 13.1 (br). **IR** (thin film) 2969, 1630, 1457, 1423, 1380, 1287, 1091, 798 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{16}H_{22}{}^{81}BrNO + H]^+$: 326.0937. Found: 326.0911. **Specific rotation** $[\alpha]_D{}^{24}$ = –20.2 (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 99:1 hexanes/2-propanol, 0.6 mL/min, t_m = 18.9 min, t_M = 20.2 min) indicated *97% ee*.

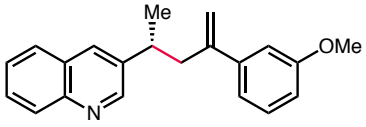


***tert*-Butyl (*R*,*E*)-3-(6-cyclopropyl-4-methylenehex-5-en-2-yl)benzoate (3o):** Prepared following General Procedure **A** using *tert*-butyl 3-vinylbenzoate (**1g**, 102 mg, 0.5 mmol, 1.0 equiv), (*E*)-4-cyclopropyl-2-methylenebut-3-en-1-yl diphenylphosphate (**2m**, 356 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 16 h, and the crude residue was purified by flash column chromatography (10 to 20% CH_2Cl_2 in hexanes) to provide the title compound as a colorless oil. **Yield**: 128 mg, 82%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.37 – 7.28 (m, 2H), 6.12 (d, J = 15.8 Hz, 1H), 5.22 (dd, J = 15.8, 8.8 Hz, 1H), 4.87 (d, J = 1.9 Hz, 1H), 4.69 (s, 1H), 3.05 – 2.91 (m, 1H), 2.49 (ddd, J = 13.9, 6.5, 0.8 Hz, 1H), 2.36 (dd, J = 14.0, 8.2 Hz, 1H), 1.60 (s, 9H), 1.48 – 1.39 (m, 1H), 1.24 (d, J = 6.9 Hz, 3H), 0.77 (ddd, J = 8.1, 6.2, 4.3 Hz, 2H), 0.46 – 0.37 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 147.8, 144.0, 134.5, 132.1, 131.3, 129.6, 128.2, 128.0, 127.2, 114.5, 81.0, 41.4, 38.3, 28.4, 21.8, 14.4, 7.4 (two signals). **IR** (thin film): 2968, 1712, 1368, 1295, 1160, 1113, 954, 909, 756, 726, 698 cm^{-1}. **EA:** Calcd. for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.88; H, 9.18. **Specific rotation** $[\alpha]_D{}^{24}$ = –18.7 (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, hexanes, 0.4 mL/min, t_m = 13.1 min, t_M = 14.4 min) indicated *94% ee*.

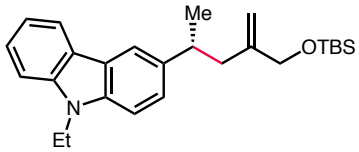


(*R*)-5-(Pent-4-en-2-yl)-2-(piperidin-1-yl)pyrimidine (3p): Prepared following General Procedure **A** using 2-(piperidin-1-yl)-5-vinylpyrimidine (**1h**, 94 mg, 0.5 mmol, 1.0 equiv), allyl diphenylphosphate (**2a**, 290 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 16 h, and the crude residue was purified by flash column chromatography (3% MeCN in hexanes) to provide the title compound as a colorless oil. **Yield**: 75 mg, 65%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.14 (s, 2H), 5.76 – 5.62 (m, 1H), 5.04 – 4.92 (m, 2H), 3.83 – 3.66 (m, 4H), 2.68 – 2.60 (m, 1H), 2.33 – 2.22 (m, 2H), 1.69 – 1.63 (m, 2H), 1.63 – 1.56 (m, 4H), 1.22 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.2, 156.7, 136.5, 126.4, 116.8, 45.1, 42.4, 34.6, 25.9, 25.0, 21.3.

IR (thin film) 2930, 1601, 1538, 1500, 1464, 1448, 1271, 1256 cm^{-1}. **EA** Calcd. for $C_{14}H_{21}N_3$: C, 72.69; H, 9.15. Found: C, 72.93; H, 9.33. **Specific rotation** $[\alpha]_D^{24} = -13.9$ (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 99:1 hexanes/2-propanol, 1.0 mL/min, t_m = 5.9 min, t_M = 5.2 min) indicated *96% ee*.

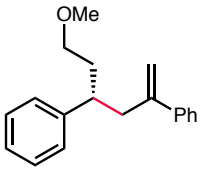


(*R*)-3-(4-(3-Methoxyphenyl)pent-4-en-2-yl)quinoline (3q): Prepared following a modification of General Procedure **A** (see below) using 3-vinylquinoline (**1i**, 77 mg, 0.5 mmol, 1.0 equiv), 2-(3-methoxyphenyl)allyl diphenylphosphate (**2k**, 297 mg, 0.75 mmol, 1.5 equiv), LiO*t*-Bu (60 mg, 0.75 mmol, 1.5 equiv), and dimethoxy(methyl)silane (0.09 mL, 0.75 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature for 16 h, quenched with CH_2Cl_2 (5 mL), and filtered through silica gel (~3 g) using 5:1 CH_2Cl_2/EtOAc (~100 mL) as the eluent. After removal of the solvent, the crude residue was purified by flash column chromatography (6% to 10% EtOAc in CH_2Cl_2) to provide the title compound as a yellow oil. **Yield**: 138 mg, 91%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.77 – 8.66 (m, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.85 – 7.80 (m, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.69 – 7.61 (m 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.20 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.91 – 6.86 (m, 1H), 6.84 (dd, *J* = 8.2, 2.2 Hz, 1H), 5.20 (s, 1H), 4.95 (s, 1H), 3.81 (s, 3H), 3.11 – 2.99 (m, 1H), 2.91 (dd, *J* = 14.0, 7.1 Hz, 1H), 2.84 (dd, *J* = 14.2, 7.6 Hz, 1H), 1.36 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.8, 151.4, 147.2, 146.5, 142.5, 139.5, 132.9, 129.6, 129.3, 128.7, 128.3, 127.6, 126.6, 119.1, 115.2, 112.9, 112.5, 55.4, 44.7, 35.9, 21.4. **IR** (thin film) 1597, 1575, 1488, 1456, 1285, 1231, 1047, 905, 787, 752, 727cm^{-1}. **EA** Calcd. for $C_{21}H_{21}NO$: C, 83.13; H, 6.98. Found: C, 82.83; H, 7.09. **Specific rotation** $[\alpha]_D^{24} = -91.2$ (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 97:3 hexanes/2-propanol, 1.0 mL/min, t_m = 24.3 min, t_M = 21.9 min) indicated *91% ee*.

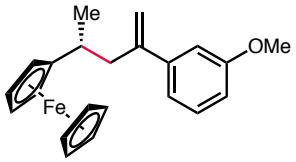


(*R*)-3-(4-(((*tert*-Butyldimethylsilyl)oxy)methyl)pent-4-en-2-yl)-9-ethyl-9*H*-carbazole (3r): Prepared following General Procedure **A** using 9-ethyl-3-vinyl-9*H*-carbazole (**1j**, 110 mg, 0.5 mmol, 1.0 equiv), 2-(((*tert*-butyldimethylsilyl)oxy)methyl)allyl diphenylphosphate (**2n**, 434 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 18 h, and the crude residue was purified by flash column chromatography (5% to 12 % CH_2Cl_2 in hexanes) to provide the title compound as a colorless oil. **Yield**: 105 mg, 51%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.91 (s, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 5.04 (s, 1H), 4.83 (s, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.07 – 3.97 (m, 2H), 3.16 – 3.05 (m, 1H), 2.47 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.37 (dd, *J* = 14.1, 8.2 Hz, 1H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.35 (d, *J* = 6.9 Hz, 3H), 0.90 (s, 9H), 0.03 (d, *J* = 3.8 Hz,

6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.3, 140.5, 138.9, 138.1, 125.6, 125.0, 123.2, 120.5, 118.7, 118.5, 110.6, 108.5, 108.4, 66.2, 42.8, 38.6, 37.7, 26.1, 22.7, 18.6, 14.0, –5.2 (one signal missing due to overlap). **IR** (thin film) 2954, 2928, 1490, 1471, 1462, 1251, 1232, 1113, 1085, 836, 777, 745 cm^{-1}. **EA** Calcd. for $C_{26}H_{37}NOSi$: C, 76.60; H, 9.15. Found: C, 76.87; H, 9.25. **Specific rotation** $[\alpha]_D^{24}$ = –10.2 (*c* = 1.0, $CHCl_3$). **HPLC analysis** (AD-H column, pentane, 1.0 mL/min, t_m = 20.2 min, t_M = 18.6 min) indicated *93% ee*.

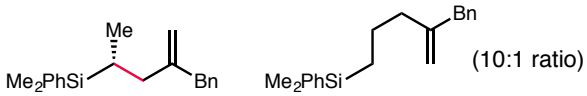


(*S*)-(6-Methoxyhex-1-ene-2,4-diyl)dibenzene (3s): Prepared following General Procedure **A** using cinnamyl methyl ether (**1k**, 74 mg, 0.5 mmol, 1.0 equiv), 2-phenylallyl diphenylphosphate (**2j**, 457 mg, 1.25 mmol, 2.5 equiv), LiO*t*-Bu (100 mg, 1.25 mmol, 2.5 equiv), and dimethoxy(methyl)silane (0.15 mL, 1.25 mmol, 2.5 equiv). The reaction mixture was quenched after 15 h, and the crude residue was purified by flash column chromatography (1,2-dichloroethane) to provide the title compound as a colorless oil. **Yield**: 101 mg, 76%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.30 – 7.26 (m, 3H), 7.21 – 7.17 (m, 1H), 7.11 – 7.07 (m, 2H), 5.18 (d, *J* = 1.5 Hz, 1H), 4.92 (s, 1H), 3.22 – 3.14 (m, 4H), 3.14 – 3.07 (m, 1H), 2.90 – 2.76 (m, 3H), 2.09 – 2.01 (m, 1H), 1.84 – 1.76 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.8, 144.8, 141.3, 128.4, 128.4, 127.8, 127.5, 126.5, 126.3, 114.6, 71.0, 58.5, 43.4, 40.9, 35.7. **IR** (thin film) 1494, 1452, 1119, 897, 778, 761, 699 cm^{-1}. **EA** Calcd. for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.91; H, 8.37. **Specific rotation** $[\alpha]_D^{24}$ = –23.6 (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OJ-H column, 90:10 hexanes/2-propanol, 1.0 mL/min, t_m = 13.9 min, t_M = 6.3 min) indicated *98% ee*.



(*R*)-1-(4-Ferrocenylpent-1-en-2-yl)-3-methoxybenzene (3t): Prepared following a modification of General Procedure **A** (see below) using vinylferrocene (**1l**, 106 mg, 0.5 mmol, 1.0 equiv), 2-(3-methoxyphenyl)allyl diphenylphosphate (**2k**, 495 mg, 1.25 mmol, 1.5 equiv), LiO*t*-Bu (100 mg, 1.25 mmol, 1.5 equiv), and dimethoxy(methyl)silane (0.15 mL, 1.25 mmol, 2.5 equiv). The reaction was performed using 4 mol % (*S*,*S*)-Ph-BPE/CuCl (1:1) complex (12.1 mg), and the reaction mixture was stirred at 35 °C for 12 h. The reaction mixture was then allowed to cool to room temperature, quenched with CH_2Cl_2 (5 mL), and filtered through silica gel (~3 g) using CH_2Cl_2 (~100 mL) as the eluent. After removal of the solvent, the crude residue was purified by flash column chromatography under argon pressure (5% to 25 % CH_2Cl_2 in hexanes) to provide the title compound as a red oil. **Yield**: 90 mg, 50%. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.98 – 6.95 (m, 1H), 6.85 (dd, *J* = 8.2, 2.3 Hz, 1H), 5.27 (s, 1H), 5.01 (s, 1H), 4.10 (s, 5H), 4.09 – 4.04 (m, 3H), 4.04 – 4.00 (m, 1H),

3.84 (s, 3H), 2.89 (dd, J = 13.7, 4.6 Hz, 1H), 2.57 – 2.47 (m, 1H), 2.40 (dd, J = 13.7, 9.7 Hz, 1H), 1.16 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.9, 147.5, 143.1, 129.4, 119.1, 114.5, 112.8, 112.6, 95.9, 68.5, 67.1, 67.1, 67.0, 65.9, 55.4, 45.2, 31.4, 20.4. **IR** (thin film) 1596, 1494, 1324, 1232, 1156, 1092, 813, 754 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{22}H_{24}FeO]^+$: 360.1181. Found: 360.1168. **Specific rotation** $[\alpha]_D^{24}$ = –1.27 (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OD-H column, 99:1 hexanes/2-propanol, 0.5 mL/min, t_m = 18.0 min, t_M = 17.3 min) indicated *98% ee*.

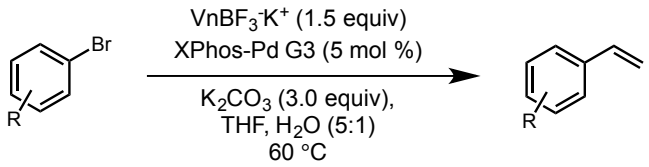


(*R*)-(4-benzylpent-4-en-2-yl)dimethyl(phenyl)silane (3u) + isomer 3u': Prepared following general procedure **A** using dimethylphenylvinylsilane (**1m**, 81 mg, 0.5 mmol, 1.0 equiv), 2-benzylallyl diphenylphosphate (**2o**, 380 mg, 1.0 mmol, 2.0 equiv), LiO*t*-Bu (80 mg, 1.0 mmol, 2.0 equiv), and dimethoxy(methyl)silane (0.12 mL, 1.0 mmol, 2.0 equiv). The reaction mixture was quenched after 24 h, and the crude residue was purified by flash column chromatography (1% CH_2Cl_2 in hexanes) to provide the title compound as a colorless oil. **Yield**: 132 mg, 90%, as a 10:1 mixture of branched/linear isomers. An asterisk in the characterization data indicates a signal attributed to the minor isomer. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.38 – 7.30 (m, 3H), 7.29 – 7.22 (m, 2H), 7.21 – 7.16 (m, 1H), 7.10 (d, J = 7.1 Hz, 2H), 4.79 – 4.72 (m, 2H), 3.30 (d, J = 14.9 Hz, 1H), 3.28* (s, 2H, benzylic), 3.21 (d, J = 14.9 Hz, 1H), 2.16 (dd, J = 14.1, 2.1 Hz, 1H), 1.98* (t, J = 7.4 Hz, 2H, allylic), 1.68 (dd, J = 13.8, 12.1 Hz, 1H), 1.15 – 1.05 (m, 1H), 0.88 (d, J = 7.3 Hz, 3H), 0.23 (m, 6H). **^{13}C NMR** (151 MHz, CDCl3) δ 148.1, 140.0, 138.5, 134.1, 133.7*, 129.2, 129.0, 128.4, 127.8, 126.1, 112.5, 43.1*, 42.1, 37.8, 16.8, 13.7, -4.8, -5.0. **IR** (thin film) 2953, 1427, 1248, 1112, 892, 832, 812, 770, 735, 699 cm^{-1}. **EA** Calcd. for $C_{20}H_{26}Si$: C, 81.57; H, 8.90. Found: C, 81.67; H, 8.95. **Specific rotation** $[\alpha]_D^{24}$ = –35.4 (*c* = 1.0, $CHCl_3$). **HPLC analysis** (OD-H column, hexanes, 1.0 mL/min, t_m = 6.9 min, t_M = 6.3 min) indicated *90% ee*.

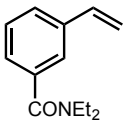
IV. Synthetic Procedures and Characterization Data for Hydroallylation Substrates:

Preparation of Vinylarenes:
Vinylarenes **1b-e**, **1l**, and vinylsilane **1m** were commercially available and were used as received. Vinylarenes **1a**,[S1] **1i**,[S2] **1j**,[S3] and **1k**,[S4] were prepared by previously reported procedures.

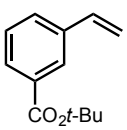
General Procedure B *for the synthesis of* **1f-1h:**



A 100 mL round-bottom flask equipped with a large stir bar was charged with aryl bromide (1.0 equiv), potassium vinyltrifluoroborate (1.5 equiv), XPhos-Pd G3 precatalyst (5 mol %) and potassium carbonate (3.0 equiv). The flask was evacuated and placed under nitrogen. Degassed THF (1 mL/mmol ArBr) and water (0.2 mL/mmol ArBr) were added sequentially by syringe, and the reaction mixture was stirred vigorously under nitrogen at 60 °C for 12 h. The reaction mixture was allowed to cool to room temperature and anhydrous sodium sulfate (~2 g/mL water) was added to the reaction mixture, then stirred for 5 min and filtered through a plug of silica gel (EtOAc). The eluate was concentrated *in vacuo* to afford the crude material, which was purified by flash column chromatography to provide the desired product.

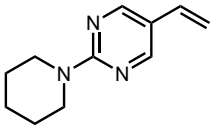


***N*,*N*-Diethyl-3-vinylbenzamide (1f):** Prepared following General Procedure **B** on 10 mmol scale using *N*,*N*-diethyl-3-bromobenzamide (2.56 g, 10 mmol, 1.0 equiv), potassium vinyltrifluoroborate (2.01 g, 15 mmol, 1.5 equiv), and XPhos G3 precatalyst (423 mg, 0.5 mmol, 5 mol %). The crude residue was purified by flash column chromatography (3:1 hexanes/EtOAc) to provide the title compound as an orange oil. **Yield**: 1.29 g, 63% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.36 – 7.31 (m, 1H), 7.25 – 7.21 (m, 1H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.77 (d, *J* = 17.6 Hz, 1H), 5.28 (d, *J* = 10.9 Hz, 1H), 3.54 (br s, 2H), 3.25 (br s, 2H), 1.32 – 0.99 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.2, 138.0, 137.7, 136.4, 128.7, 127.0, 125.6, 124.3, 114.9, 43.4, 39.4, 14.3, 13.0. **IR** (thin film) 1628, 1471, 1458, 1424, 1290, 803 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{13}H_{17}NO + H]^+$: 204.1383. Found: 204.1373.



***tert*-Butyl 3-vinylbenzoate (1g):** Prepared following General Procedure **B** on 25 mmol scale using *tert*-butyl 3-bromobenzoate (6.42 g, 25 mmol, 1.0 equiv), potassium vinyltrifluoroborate (5.02 g, 38 mmol, 1.5 equiv), and XPhos G3 precatalyst (1.05 g, 1.25

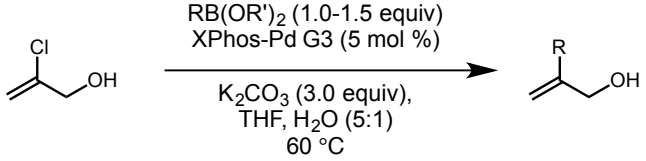
mmol, 5 mol %). The crude residue was purified by flash column chromatography (30:1 hexanes/EtOAc) to provide the title compound as a red oil. **Yield**: 3.90 g, 76% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.82 (d, *J* = 17.6 Hz, 1H), 5.31 (d, *J* = 10.9 Hz, 1H), 1.61 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.8, 137.8, 136.3, 132.5, 130.1, 128.8, 128.5, 127.4, 115.0, 81.2, 28.3. **IR** (thin film) 1712, 1368, 1295, 1271, 1160, 1115, 909, 763 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{13}H_{16}O_2 + H]^+$: 205.1223. Found: 205.1226.



2-(Piperidin-1-yl)-5-vinylpyrimidine (1h): Prepared following General Procedure **B** on 10 mmol scale using *tert*-butyl 3-bromobenzoate (2.42 g, 10 mmol, 1.0 equiv), potassium vinyltrifluoroborate (2.01 g, 15 mmol, 1.5 equiv), and XPhos G3 precatalyst (423 mg, 0.5 mmol, 5 mol %). The crude residue was purified by flash column chromatography (20:1 hexanes/EtOAc) to provide the title compound as a yellow oil. **Yield**: 1.36 g, 72% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.34 (s, 2H), 6.48 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.56 (d, *J* = 17.7 Hz, 1H), 5.09 (d, *J* = 11.1 Hz, 1H), 3.89 – 3.71 (m, 4H), 1.85 – 1.45 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.2, 155.7, 131.1, 119.3, 111.3, 45.1, 25.9, 25.0. **IR** (thin film) 1595, 1503, 1462, 1444, 1362, 1272, 1226, 946 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{11}H_{15}N_3 + H]^+$: 190.1339. Found: 190.1328.

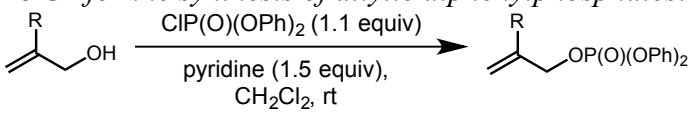
Preparation of Allylic Diphenylphosphates:

General Procedure C1 *for the synthesis of 2-substituted allylic alcohols:*



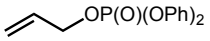
A 100 mL round-bottom flask equipped with a large stir bar was charged with 2-chloroallyl alcohol (1.0 equiv), boronic acid or boronic ester (1.0 to 1.5 equiv), XPhos-Pd G3 precatalyst (5 mol %) and potassium carbonate (3.0 equiv). The flask was evacuated and placed under nitrogen. Degassed THF (1 mL/mmol chloride) and water (0.2 mL/mmol chloride) were added sequentially by syringe, and the reaction mixture was stirred vigorously under nitrogen at 60 °C for 12 h. The reaction mixture was allowed to cool to room temperature and anhydrous sodium sulfate (~2 g/mL water) was added to the reaction mixture, which was stirred for an additional 5 min and filtered through a plug of silica gel (EtOAc). The eluate was concentrated *in vacuo* to afford the crude material, which was purified by flash column chromatography to provide the desired product.

General Procedure C2 *for the synthesis of allylic diphenylphosphates:*

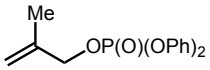


A 50 mL round-bottom flask equipped with a stir bar was charged with allylic alcohol (1.0 equiv), CH_2Cl_2 (3 mL/mmol allylic alcohol), and pyridine (1.5 equiv). Diphenyl

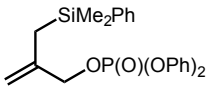
chlorophosphate (1.1 equiv) was added, the flask was stoppered with a vented septum, and the reaction mixture was stirred under air at room temperature for 12 h. The reaction mixture was then diluted with CH_2Cl_2 (3 mL/mmol allylic alcohol) and water (3 mL/mmol allylic alcohol) and transferred to a separatory funnel. The phases were partitioned, and the aqueous layer was extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo* to afford the crude material, which was purified by flash column chromatography to provide the desired product.



Allyl diphenylphosphate (2a): Prepared following General Procedure **C2** on 20 mmol scale using allyl alcohol (1.16 g, 20 mmol, 1.0 equiv), diphenyl chlorophosphate (5.92 g, 22 mmol, 1.1 equiv), and pyridine (2.4 mL, 30 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (5:1 hexanes/EtOAc) to provide the title compound as a colorless oil. **Yield**: 4.35 g, 75% yield. The NMR data are consistent with those previous reported.[S5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 4H), 7.25 – 7.14 (m, 6H), 6.01 – 5.88 (m, 1H), 5.38 (ddd, J = 17.1, 2.8, 1.5 Hz, 1H), 5.31 – 5.23 (m, 1H), 4.74 (ddt, J = 8.6, 5.6, 1.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.7 (d, J_{CP} = 7.2 Hz), 131.9 (d, J_{CP} = 6.8 Hz), 129.9, 125.5, 120.2 (d, J_{CP} = 4.9 Hz), 119.1, 69.6 (d, J_{CP} = 6.0 Hz).

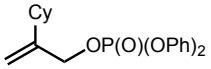


2-Methallyl diphenylphosphate (2b): Prepared following General Procedure **C2** on 30 mmol scale using 2-methallyl alcohol (2.16 g, 30 mmol, 1.0 equiv), diphenyl chlorophosphate (8.87 g, 33 mmol, 1.1 equiv), and pyridine (3.6 mL, 45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (10:1 hexanes/EtOAc) to provide the title compound as a colorless oil. **Yield**: 4.52 g, 50% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.26 – 7.16 (m, 6H), 5.06 (s, 1H), 4.96 (s, 1H), 4.64 (d, J = 7.6 Hz, 2H), 1.75 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.7 (d, J_{CP} = 8.6 Hz), 139.5 (d, J_{CP} = 6.5 Hz), 129.9, 125.5, 120.2 (d, J_{CP} = 4.9 Hz), 114.3, 72.37 (d, J_{CP} = 6.1 Hz), 19.0. **IR** (thin film) 1487, 1187, 1162, 1008, 941, 754, 688 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{16}H_{17}O_4P + H]^+$: 305.0937. Found: 305.0936.

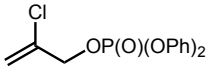


2-((Dimethyl(phenyl)silyl)methyl)allyl diphenylphosphate (2c): 2-((Dimethyl(phenyl)silyl)methyl)allyl alcohol was first prepared as follows: To a solution of (dimethylphenylsilyl)methylmagnesium chloride (2.0 M in Et_2O, 25 mL, 50 mmol, 2.0 equiv) at 0 °C in a two-neck round-bottom flask equipped with a reflux condenser was added cuprous iodide (475 mg, 2.5 mmol, 10 mol %) in one portion. The suspension was stirred at 0 °C for 10 min, after which propargyl alcohol (1.40 g, 25 mmol, 1.0 equiv) was added dropwise over 5 min. The reaction mixture was stirred at room temperature for 30 min and then at reflux for an additional 30 min. The reaction mixture was allowed to cool to room temperature, after which it was carefully quenched with saturated aqueous

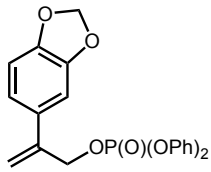
NH_4Cl (25 mL) and diluted with water (75 mL). Et_2O (100 mL) was added, and the reaction mixture was transferred to a separatory funnel. The phases were separated, and the aqueous phase was extracted with EtOAc (3 × 100 mL). The combined organic layers were dried (Na_2SO_4), filtered, concentrated *in vacuo*, and purified by flash column chromatography (10:1 hexanes/EtOAc) to afford the previously reported allylic alcohol as a colorless oil (1.33 g, 26% yield).[S6] The title allylic phosphate was prepared following General Procedure **C2** on a 6 mmol scale using 2-((dimethyl(phenyl)silyl)methyl)allyl alcohol (1.23 g, 6 mmol, 1.0 equiv), diphenyl chlorophosphate (1.78 g, 6.6 mmol, 1.1 equiv), and pyridine (0.73 mL, 9 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (10:1 hexanes/EtOAc) to provide the title compound as a colorless oil. **Yield**: 1.73 g, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.41 – 7.28 (m, 7H), 7.22 – 7.12 (m, 6H), 4.98 (s, 1H), 4.74 (s, 1H), 4.42 (d, J = 7.3 Hz, 2H), 1.76 (s, 2H), 0.30 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.7 (d, J_{CP} = 7.1 Hz), 140.7 (d, J_{CP} = 7.5 Hz), 138.2, 133.7, 129.9, 129.4, 128.0, 125.4, 120.2 (d, J_{CP} = 4.9 Hz), 111.8, 72.2 (d, J_{CP} = 6.1 Hz), 22.0, -3.0. **IR** (thin film) 1487, 1187, 1024, 940, 831, 753, 730, 667 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{24}H_{27}O_4PSi + H]^+$: 439.1489. Found: 439.1496.



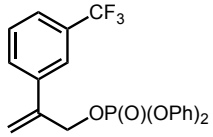
2-Cyclohexylallyl diphenylphosphate (2d): Prepared following General Procedure **C2** on 20 mmol scale using 2-cyclohexylallyl alcohol[S7] (2.80 g, 20 mmol, 1.0 equiv), diphenyl chlorophosphate (5.92 g, 22 mmol, 1.1 equiv), and pyridine (2.4 mL, 45 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (10:1 hexanes/EtOAc) to provide the title compound as a yellow oil. **Yield**: 5.62 g, 76% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.25 – 7.21 (m, 4H), 7.21 – 7.16 (m, 2H), 5.08 (s, 1H), 4.96 (s, 1H), 4.71 (d, J = 7.1 Hz, 2H), 1.94 (t, J = 11.6 Hz, 1H), 1.81 – 1.61 (m, 5H), 1.30 – 1.07 (m, 5H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.8 (d, J_{CP} = 6.2 Hz), 148.8 (d, J_{CP} = 7.9 Hz), 129.9, 125.4, 120.2 (d, J_{CP} = 4.8 Hz), 112.1, 70.9 (d, J_{CP} = 6.1 Hz), 40.7, 32.2, 26.7, 26.3. **IR** (thin film) 1488, 1292, 1190, 1163, 1024, 1008, 945, 771, 688 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{21}H_{25}O_4P + H]^+$: 373.1563. Found: 373.1572.



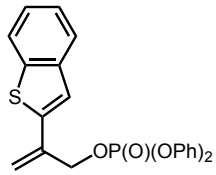
2-Chloroallyl diphenylphosphate (2e): Prepared following general procedure **C2** on 40 mmol scale using 2-chloroallyl alcohol (3.70 g, 40 mmol, 1.0 equiv), diphenyl chlorophosphate (11.8 g, 44 mmol, 1.1 equiv), and pyridine (4.9 mL, 60 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (10:1 hexanes/EtOAc) to provide the title compound as a colorless oil. **Yield**: 10.2 g, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 4H), 7.27 – 7.17 (m, 6H), 5.56 – 5.50 (m, 1H), 5.47 – 5.38 (m, 1H), 4.74 (d, J = 8.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5 (d, J_{CP} = 7.2 Hz), 135.2 (d, J_{CP} = 8.7 Hz), 130.0, 125.7 (d, J_{CP} = 1.2 Hz), 120.2 (d, J_{CP} = 4.9 Hz), 115.5, 69.9 (d, J_{CP} = 5.3 Hz). **IR** (thin film): 1487, 1293, 1186, 1162, 1050, 1025, 1009, 949, 769, 754, 688 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve): Calcd. for $[C_{15}H_{14}{}^{35}ClO_4P + H]^+$: 325.0391. Found: 325.0397.



2-(Benzo[*d*][1,3]dioxol-5-yl)allyl diphenylphosphate (2f): Prepared following General Procedure **C2** on 10 mmol scale using 2-(benzo[*d*][1,3]dioxol-5-yl)prop-2-en-1-ol[S8] (1.78 g, 10 mmol, 1.0 equiv), diphenyl chlorophosphate (2.96 g, 11 mmol, 1.1 equiv), and pyridine (1.2 mL, 15 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (10:1 hexanes/EtOAc) to provide the title compound as a colorless oil. **Yield**: 3.30 g, 80% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 7.24 – 7.15 (m, 6H), 6.90 (d, J = 1.7 Hz, 1H), 6.87 (dd, J = 8.1, 1.8 Hz, 1H), 6.74 (d, J = 8.1 Hz, 1H), 5.96 (s, 2H), 5.45 (s, 1H), 5.34 (s, 1H), 5.05 (d, J = 7.7 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.6 (d, J_{CP} = 7.2 Hz), 148.0, 147.7, 141.8 (d, J_{CP} = 7.5 Hz), 131.6, 129.9, 125.4, 120.2, 120.0, 115.5, 108.3, 106.8 (d, J_{CP} = 9.2 Hz), 101.3, 70.43 (d, J_{CP} = 5.8 Hz). **IR** (thin film) 1488, 1230, 1187, 1036, 1024, 1009, 946, 688 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{22}H_{19}O_6P + H]^+$: 411.0992. Found: 411.0975.

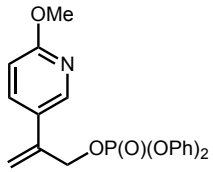


2-(3-(Trifluoromethyl)phenyl)allyl diphenylphosphate (2g): Prepared following General Procedure **C2** on 10 mmol scale using 2-(3-(trifluoromethyl)phenyl)prop-2-en-1-ol[S9] (2.02 g, 10 mmol, 1.0 equiv), diphenyl chlorophosphate (2.96 g, 11 mmol, 1.1 equiv), and pyridine (1.2 mL, 15 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (10:1 hexanes/EtOAc) to provide the title compound as a colorless oil. **Yield**: 1.83 g, 42% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 1H), 7.59 – 7.52 (m, 2H), 7.43 (t, J = 7.8 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.22 – 7.10 (m, 6H), 5.62 (s, 1H), 5.52 (s, 1H), 5.12 (dd, J = 8.0, 0.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.5 (d, J_{CP} = 7.3 Hz), 141.33 (d, J_{CP} = 7.1 Hz), 138.2, 131.1 (q, J_{CF} = 32.3 Hz), 129.9, 129.5, 129.2, 125.5 (d, J_{CP} = 1.1 Hz), 125.0 (q, J_{CF} = 3.8 Hz), 124.1 (q, J_{CF} = 273 Hz) 123.1 (q, J_{CF} = 3.8 Hz), 120.1 (d, J_{CP} = 4.9 Hz), 118.3, 70.0 (d, J_{CP} = 5.7 Hz). **IR** (thin film) 1488, 1187, 1162, 1121, 1024, 1001, 946, 688 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{22}H_{18}F_3O_4P + H]^+$: 435.0968. Found: 435.0954.

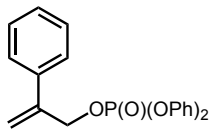


2-(Benzo[*b*]thiophen-2-yl)allyl diphenylphosphate (2h): 2-(Benzo[*b*]thiophen-2-yl)prop-2-en-1-ol was prepared on 25 mmol scale following General Procedure **C1** using 2-chloroallyl alcohol (2.31 g, 25 mmol, 1.0 equiv), benzo[*b*]thiophene-2-boronic acid (6.67 g, 37.5 mmol, 1.5 equiv) and XPhos G3 precatalyst (1.05 g, 1.25 mmol, 5 mol %). The crude product was purified by flash column chromatography (9:1 to 7:1 hexanes/EtOAc) to afford the allylic alcohol (1.75 g, 37% yield). The title allylic

phosphate was prepared following General Procedure **C2** on 9 mmol scale using 2-(benzo[*b*]thiophen-2-yl)prop-2-en-1-ol (1.71 g, 9 mmol, 1.0 equiv), diphenyl chlorophosphate (2.66 g, 9.9 mmol, 1.1 equiv), and pyridine (1.1 mL, 13.5 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (9:1 hexanes/EtOAc) to provide the title compound as a colorless solid, **m.p.** 49 – 50 °C. **Yield**: 2.46 g, 65% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 1H), 7.69 – 7.62 (m, 1H), 7.38 – 7.27 (m, 6H), 7.25 – 7.20 (m, 5H), 7.20 – 7.14 (m, 2H), 5.69 (s, 1H), 5.47 (s, 1H), 5.14 (d, J = 7.5 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.6 (d, J_{CP} = 7.9 Hz), 141.0, 140.3, 139.0, 136.6 (d, J_{CP} = 8.7 Hz), 129.9, 125.6, 125.2, 124.6, 124.1, 122.2, 121.6, 120.2 (d, J_{CP} = 4.9 Hz), 117.6, 69.7 (d, J_{CP} = 5.7 Hz). **IR** (thin film) 1488, 1291, 1188, 1162, 1023, 1001, 949, 752, 688 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{23}H_{19}O_4PS + H]^+$: 423.0814. Found: 423.0820.

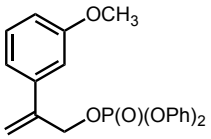


2-(6-Methoxypyridin-3-yl)allyl diphenylphosphate (2i): 2-(6-Methoxypyridin-3-yl)prop-2-en-1-ol was prepared on 10 mmol scale following General Procedure **C1** using 2-chloroallyl alcohol (925 mg, 10 mmol, 1.0 equiv), (6-methoxypyridin-3-yl)boronic acid (1.53 g, 10 mmol, 1.0 equiv) and XPhos G3 precatalyst (423 mg, 0.5 mmol, 5 mol %). The crude product was purified by flash column chromatography (2:1 hexanes/EtOAc) to afford the allylic alcohol (841 mg, 51% yield). The title allylic phosphate was prepared following General Procedure **C2** on 5 mmol scale using 2-(6-methoxypyridin-3-yl)prop-2-en-1-ol (825 mg, 5 mmol, 1.0 equiv), diphenyl chlorophosphate (1.48 g, 5.5 mmol, 1.1 equiv), and pyridine (0.61 mL, 7.5 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (3:1 hexanes/EtOAc) to provide the title compound as a colorless oil. **Yield**: 1.45 g, 73% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.24 – 8.18 (m, 1H), 7.57 (dd, J = 8.6, 2.4 Hz, 1H), 7.33 – 7.27 (m, 4H), 7.22 – 7.13 (m, 6H), 6.67 (d, J = 8.6 Hz, 1H), 5.48 (s, 1H), 5.38 (s, 1H), 5.06 (d, J = 8.0 Hz, 2H), 3.94 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.1, 150.6 (d, J_{CP} = 5.8 Hz), 144.7, 139.4, 136.5, 129.9, 126.4, 125.5, 120.2 (d, J_{CP} = 4.9 Hz), 116.1, 110.7, 70.1 (d, J_{CP} = 5.8 Hz), 53.7. **IR** (thin film) 1602, 1489, 1286, 1188, 1023, 1009, 950, 767, 689 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{21}H_{20}NO_5P + H]^+$: 398.1152. Found: 398.1136.

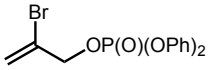


2-Phenylallyl diphenylphosphate (2j): Prepared following General Procedure **C2** on 37 mmol scale using 2-phenylallyl alcohol[S7] (4.95 g, 37 mmol, 1.0 equiv), diphenyl chlorophosphate (11.0 g, 41 mmol, 1.1 equiv), and pyridine (4.5 mL, 55 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (10:1 hexanes/EtOAc) to provide the title compound as a colorless oil. **Yield**: 9.81 g, 72% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.37 – 7.27 (m, 7H), 7.22 – 7.14 (m, 6H), 5.57 (s, 1H), 5.43 (s, 1H), 5.13 (d, J = 7.5 Hz, 2H). **^{13}C NMR** (151 MHz,

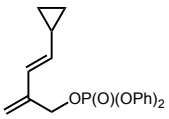
$CDCl_3$) δ 150.6 (d, J_{CP} = 6.5 Hz), 142.3 (d, J_{CP} = 6.1 Hz), 137.4, 129.9, 128.7, 128.3, 126.2, 125.4, 120.2 (d, J_{CP} = 4.8 Hz), 116.3, 70.3 (d, J_{CP} = 5.8 Hz). **IR** (thin film) 1487, 1285, 1186, 1162, 1023, 1008, 941, 774, 754, 707, 687 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{21}H_{19}O_4P + H]^+$: 367.1096. Found: 367.1096.



2-(3-Methoxyphenyl)allyl diphenyl phosphate (2k): Prepared following General Procedure **C2** on 18 mmol scale using 2-(3-methoxyphenyl)allyl alcohol[S9] (3.00 g, 18 mmol, 1.0 equiv), diphenyl chlorophosphate (5.38 g, 20 mmol, 1.1 equiv), and pyridine (2.2 mL, 27 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (5:1 hexanes/EtOAc) to provide the title compound as a yellow oil. **Yield**: 5.61 g, 78% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 7.25 – 7.17 (m, 6H), 7.02 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.00 – 6.95 (m, 1H), 6.92 – 6.85 (m, 1H), 5.59 (s, 1H), 5.45 (s, 1H), 5.13 (d, *J* = 7.6 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.8, 150.6 (d, J_{CP} = 7.3 Hz), 142.2 (d, J_{CP} = 7.4 Hz), 138.9, 129.9, 126.1, 125.5, 120.2 (d, J_{CP} = 4.6 Hz), 118.7, 116.5, 113.95 (d, J_{CP} = 6.7 Hz), 112.0 (d, J_{CP} = 8.0 Hz), 70.3 (d, J_{CP} = 5.7 Hz), 55.4. **IR** (thin film) 1487, 1185, 1023, 1009, 943, 754, 687 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{22}H_{21}O_5P + H]^+$: 397.1199. Found: 397.1204.

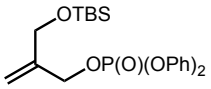


2-Bromoallyl diphenylphosphate (2l): Prepared following General Procedure **C2** on 8 mmol scale using 2-bromoallyl alcohol (1.1 g, 8 mmol, 1.0 equiv), diphenyl chlorophosphate (2.42 g, 9 mmol, 1.1 equiv), and pyridine (0.97 mL, 12 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (7:1 hexanes/EtOAc) to provide the title compound as a colorless oil. **Yield**: 2.71 g, 92% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.26 – 7.18 (m, 6H), 5.97 (s, 1H), 5.65 (d, *J* = 0.9 Hz, 1H), 4.79 (d, *J* = 8.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.5 (d, J_{CP} = 6.7 Hz), 130.0, 125.7, 125.4 (d, J_{CP} = 8.0 Hz), 120.2 (d, J_{CP} = 4.8 Hz), 119.5, 71.4 (d, J_{CP} = 5.3 Hz). **IR** (thin film) 1487, 1291, 1186, 1162, 1045, 1024, 1009, 947, 769, 688 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{15}H_{14}{}^{79}BrO_4P + H]^+$: 368.9886. Found: 368.9881.

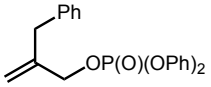


(*E*)-4-Cyclopropyl-2-methylenebut-3-en-1-yl diphenylphosphate (2m): (*E*)-4-Cyclopropyl-2-methylenebut-3-en-1-ol was prepared on 10 mmol scale following General Procedure **C1** using 2-chloroallyl alcohol (925 mg, 10 mmol, 1.0 equiv), (*E*)-(2-cyclopropylvinyl)boronic acid pinacol ester (2.52 g, 13 mmol, 1.3 equiv) and XPhos G3 precatalyst (423 mg, 0.5 mmol, 5 mol %). The crude product was purified by flash column chromatography (2:1 hexanes/EtOAc) to afford the allylic alcohol (722 mg, 58% yield). The title allylic phosphate was prepared following General Procedure **C2** on 4

mmol scale using (*E*)-cyclopropyl-2-methylenebut-3-en-1-ol (496 mg, 4 mmol, 1.0 equiv), diphenyl chlorophosphate (1.18 g, 4.4 mmol, 1.1 equiv), and pyridine (0.49 mL, 6 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (10:1 to 5:1 hexanes/EtOAc) to provide the title compound as a colorless oil. **Yield**: 985 mg, 69% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 4H), 7.26 – 7.16 (m, 6H), 6.13 (d, J = 16.1 Hz, 1H), 5.24 (dd, J = 16.0, 8.9 Hz, 1H), 5.13 (s, 1H), 5.09 (s, 1H), 4.84 (d, J = 7.3 Hz, 2H), 1.49 – 1.34 (m, 1H), 0.82 – 0.72 (m, 2H), 0.43 – 0.34 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.8 (d, J_{CP} = 7.5 Hz), 140.0 (d, J_{CP} = 6.9 Hz), 136.2, 129.9, 126.2, 125.5, 120.3 (d, J_{CP} = 4.9 Hz), 115.6, 68.9 (d, J_{CP} = 5.8 Hz), 14.5, 7.4. **IR** (thin film) 1487, 1187, 1162, 1023, 1008, 940, 903, 753, 687 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{24}H_{21}O_4P + H]^+$: 357.1250. Found: 357.1257.



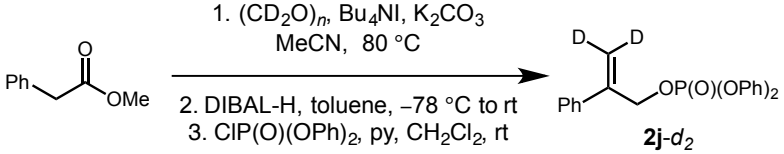
2-(((*tert*-Butyldimethylsilyl)oxy)methyl)allyl diphenylphosphate (2n): Prepared following General Procedure **C2** on 36 mmol scale using 2-(((*tert*-butyldimethylsilyl)oxy)methyl)prop-2-en-1-ol[S10] (7.26 g, 36 mmol, 1.0 equiv), diphenyl chlorophosphate (10.8 g, 40 mmol, 1.1 equiv), and pyridine (4.4 mL, 54 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (20:1 to 10:1 hexanes/EtOAc) to provide the title compound as a colorless oil. **Yield**: 5.01 g, 32% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.25 – 7.14 (m, 6H), 5.26 (s, 1H), 5.20 (s, 1H), 4.75 (d, J = 7.6 Hz, 2H), 4.15 (s, 2H), 0.89 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.8 (d, J_{CP} = 7.1 Hz), 143.0 (d, J_{CP} = 7.2 Hz), 129.9, 125.5, 120.2 (d, J_{CP} = 4.9 Hz), 114.1, 69.4 (d, J_{CP} = 5.9 Hz), 63.5, 26.0, 18.5, –5.3. **IR** (thin film) 1489, 1189, 1024, 1009, 947, 836, 775, 688 cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{22}H_{31}O_5PSi + H]^+$: 435.1751. Found: 435.1739.



2-Benzylallyl diphenylphosphate (2o): Prepared following General Procedure **C2** on 14 mmol scale using 2-benzylprop-2-en-1-ol[S11] (2.07 g, 14 mmol, 1.0 equiv), diphenyl chlorophosphate (4.06 g, 15.5 mmol, 1.1 equiv), and pyridine (1.7 mL, 21 mmol, 1.5 equiv). The crude residue was purified by flash column chromatography (8:1 hexanes/EtOAc) to provide the title compound as a colorless solid, **m.p.** 59 – 60 °C. **Yield**: 1.65 g, 31% yield. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.30 – 7.26 (m, 2H), 7.25 – 7.17 (m, 7H), 7.16 – 7.11 (m, 2H), 5.20 (s, 1H), 4.99 (s, 1H), 4.62 (d, J = 7.5 Hz, 2H), 3.40 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.7 (d, J_{CP} = 7.0 Hz), 142.9 (d, J_{CP} = 7.0 Hz), 138.2, 129.9 (d, J_{CP} = 8.8 Hz), 129.1, 128.7 (d, J_{CP} = 7.0 Hz), 126.6, 125.5, 120.2, 115.7, 70.8 (d, J_{CP} = 5.9 Hz), 39.5. **IR** (thin film) 1487, 1187, 1023, 1008, 940, 753, 699, 687. cm^{-1}. **HRMS** (*m/z*, DART-TOF, +'ve) Calcd. for $[C_{22}H_{21}O_4P + H]^+$: 381.1250. Found: 381.1271.

V. Deuterium Labeling Study:

Synthesis of 2j-d_2:



Step 1 (Aldol condensation). A 50 mL round-bottom flask equipped with a large stir bar was charged with methyl phenylacetate (500 mg, 3.4 mmol, 1.0 equiv), paraformaldehyde-d_2 (>98 atom% D, 192 mg, 6.0 mmol, 1.8 equiv), tetrabutylammonium iodide (124 mg, 0.34 mmol, 10 mol %), and dry acetonitrile (2 mL). The reaction mixture was stirred vigorously under nitrogen at 80 °C for 21 h, then allowed to cool to room temperature and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a plug of silica gel, rinsing with CH_2Cl_2. The eluate was concentrated *in vacuo*, and the crude material was purified by flash column chromatography (20:1 hexanes/EtOAc) to afford the desired deuterated acrylate as a colorless oil (120 mg, 21% yield).
Step 2 (*Ester reduction)*. The deuterated acrylate prepared above (120 mL, 0.73 mmol, 1.0 equiv) was diluted with dry toluene (2 mL) and cooled to –78 °C (dry ice/acetone bath). A solution of DIBAL-H (1.4 M in toluene, 1.30 mL, 1.82 mmol, 2.5 equiv) was added dropwise over 2 min, and stirring at –78 °C was continued for 90 min. Subsequently, EtOAc (1 mL) was slowly added to quench the reaction mixture, and then allowed to warm to room temperature. Et_2O (10 mL) was added, followed by $Na_2SO_4 \bullet 10H_2O$ (2.0 g), and stirred at room temperature for an additional 30 min before the reaction mixture was filtered through a pad of silica gel, eluting with CH_2Cl_2. The eluate was carefully concentrated *in vacuo*, and the crude deuterated allylic alcohol was used directly in the next step.
Step 3 (Phosphorylation). The deuterated allylic alcohol prepared above was dissolved in in dry CH_2Cl (1 mL). Pyridine (0.13 mL, 1.6 mmol, 2.2 equiv) and diphenyl chlorophosphate (0.25 mL, 1.2 mmol, 1.6 equiv) were added sequentially via syringe. The reaction mixture was stirred under nitrogen for 18 h, concentrated *in vacuo* and purified by column chromatography (10:1 hexanes/EtOAc). The product obtained was further purified by preparative thin layer chromatography (15:1 hexanes/EtOAc) to provide the desired product as a colorless oil (182 mg, 68% yield over 2 steps). ^{1}H NMR and GC-MS analysis confirmed full (≥98% at each of the vinylic positions) deuterium incorporation at the terminal position. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.36 – 7.28 (m, 7H), 7.21 – 7.13 (m, 6H), 5.12 (d, J = 7.5 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.8 (d, J_{CP} = 7.6 Hz), 137.6, 129.9, 128.7, 128.4, 126.3, 125.5, 120.3 (d, J_{CP} = 4.9 Hz), 70.3 (d, J_{CP} = 5.5 Hz) (signals expected at 142.3 and 116.3 ppm not observed due to deuterium coupling).

Hydroallylation Reaction of 4-(Trifluoromethyl)styrene (1d) and 2j-d_2: General procedure **A** was scaled down to 0.08 mmol scale using **1d** (13.8 mg, 0.08 mmol, 1.0 equiv), **2j-d_2** (44.2 mg, 0.12 mmol, 1.5 equiv), LiO*t*-Bu (9.6 mg, 0.12 mmol, 1.5 equiv), and dimethoxy(methyl)silane (15 μL, 0.12 mmol, 1.5 equiv) in THF (0.1 mL). The reaction mixture was quenched after 18 h, after which CH_2Cl_2 (2 mL) and 1,3,5-trimethoxybenzene (13.4 mg, 0.08 mmol, 1.0 equiv) was added. The crude reaction

mixture was then subjected to ^{1}H NMR and GC-MS analysis for yield and isotopic distribution. The NMR yield was determined to be >95%, with full (≥98% at each of the diastereotopic allylic positions) deuterium incorporation at the allylic position of the hydroallylation product. An aliquot of the crude product was purified by preparative thin layer chromatography. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 5.21 (d, *J* = 1.4 Hz, 1H), 4.94 (d, *J* = 1.4 Hz, 1H), 2.86 (q, *J* = 6.6 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 3H).

Figure S1. Stacked NMR plots of 2j (top) and 2j-*d*$_2$ (bottom).

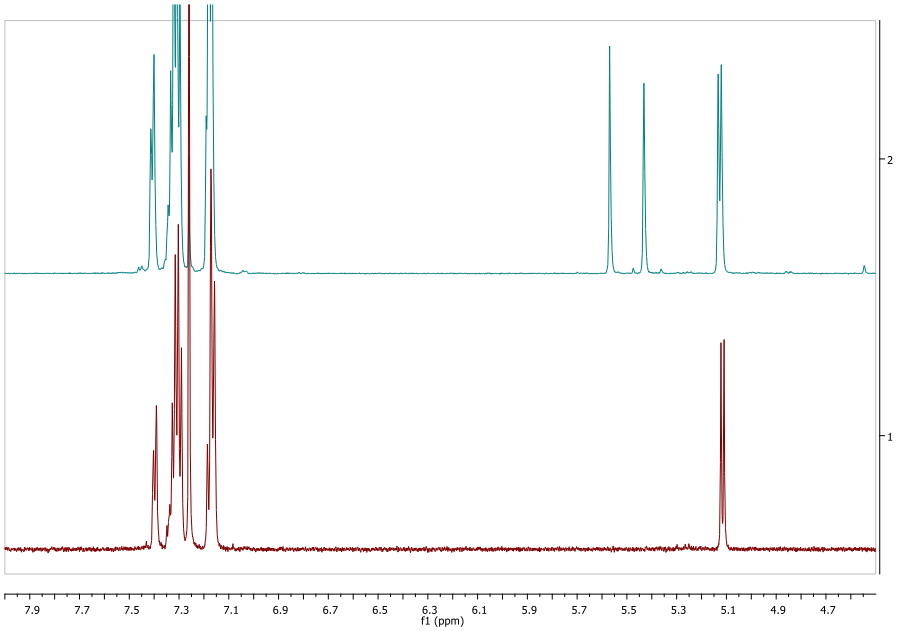
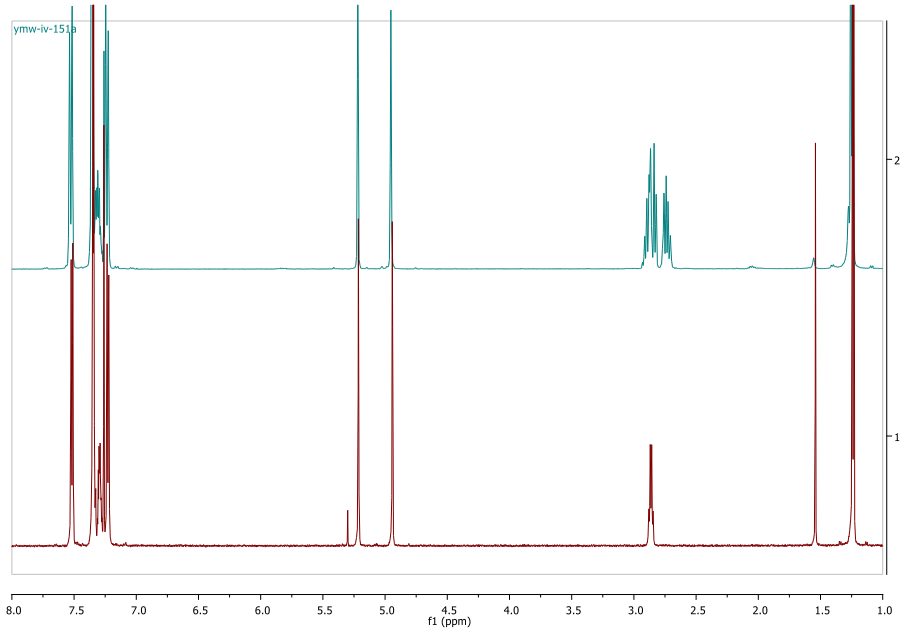


Figure S2. Stacked NMR plots of 3l (top) and 3l-*d*$_2$ (bottom). H_2O and CH_2Cl_2 are observed as impurities in the bottom plot.



VI. References for the Supporting Information:

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S7. Smith, S. M.; Hoang, G. L.; Pal, R.; Khaled, M. O. B.; Pelter, L. S. W.; Zeng. X. C.; Takacs, J. M. *Chem. Commun.* **2012**, *48*, 12180.
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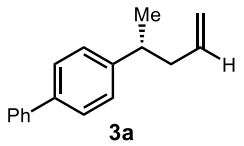
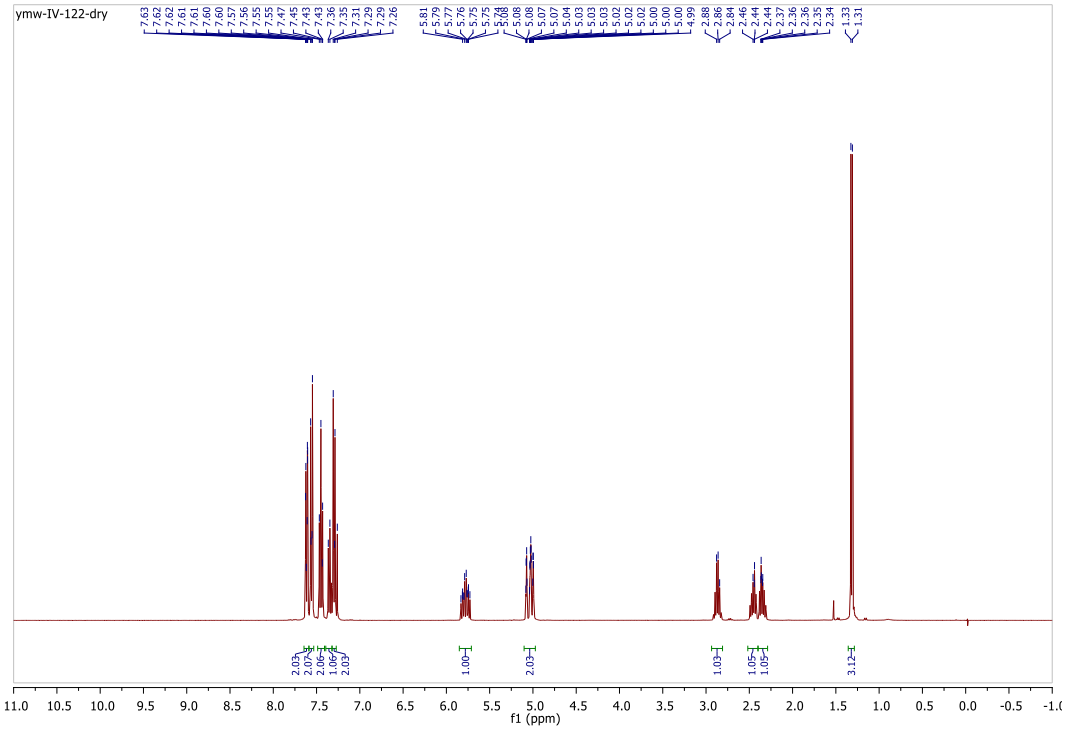
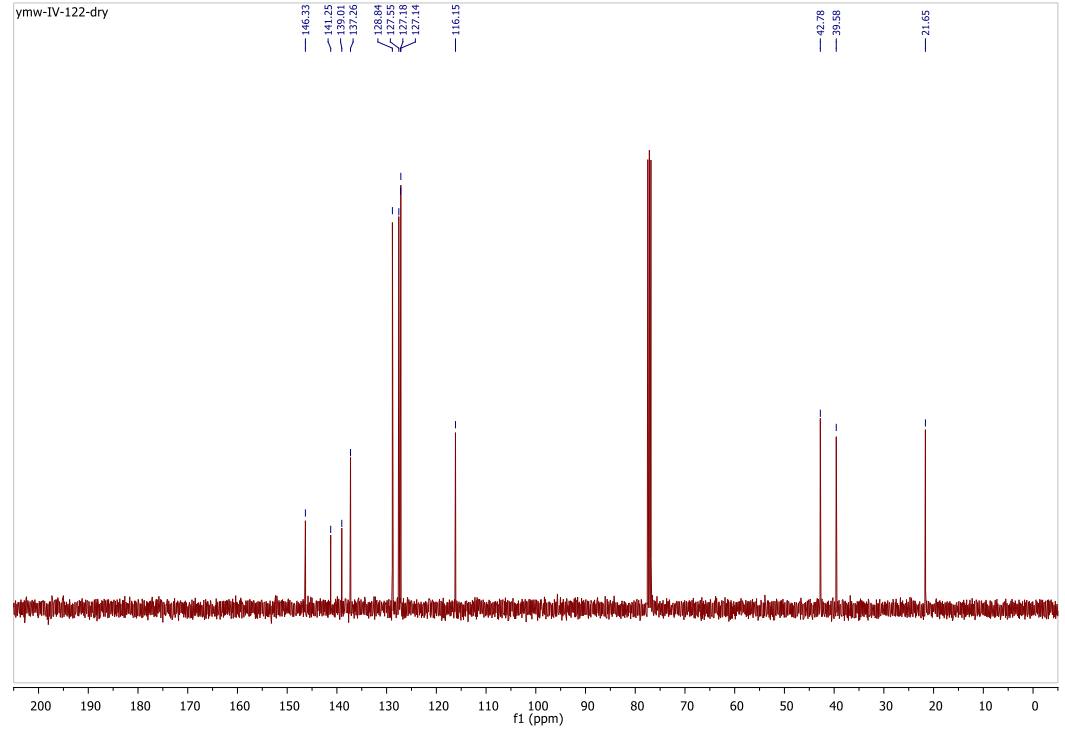
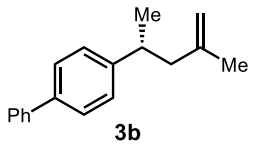
VII. Copies of NMR Spectra for Hydroallylation Products and Previously Unreported Substrates.



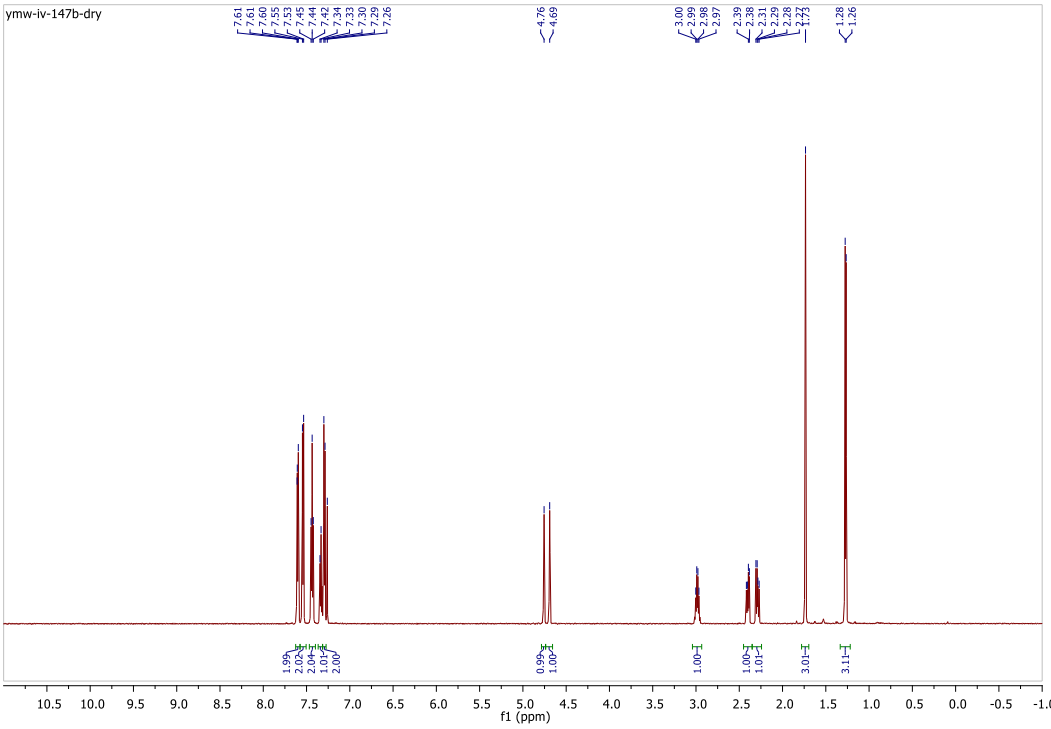
3a






Me
Me
Ph

3b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7.61
7.60
7.55
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7.44
7.42
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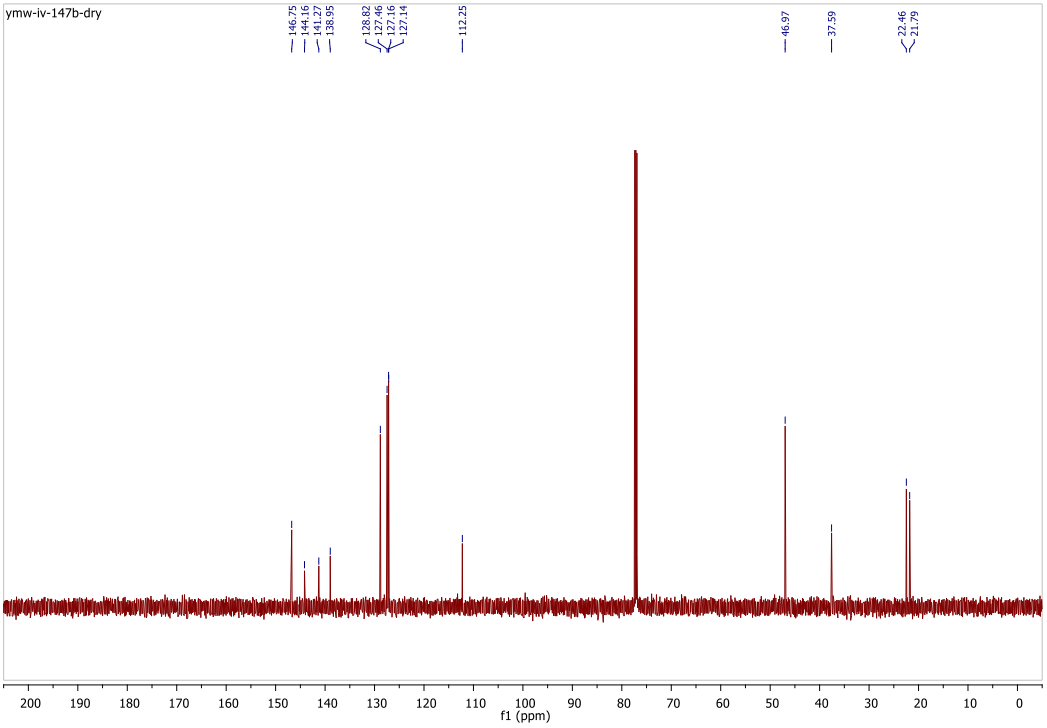
7.33
7.30
7.29
7.26
4.76
4.69
3.00
2.99
2.98
2.97
2.39
2.38
2.31
2.29
2.28
2.27
1.73
1.28
1.26
1.99
2.07
2.04
1.01
2.00
0.99
1.00
1.00
1.00
1.01
3.01
3.11
f1 (ppm)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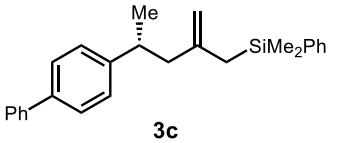
f1 (ppm)



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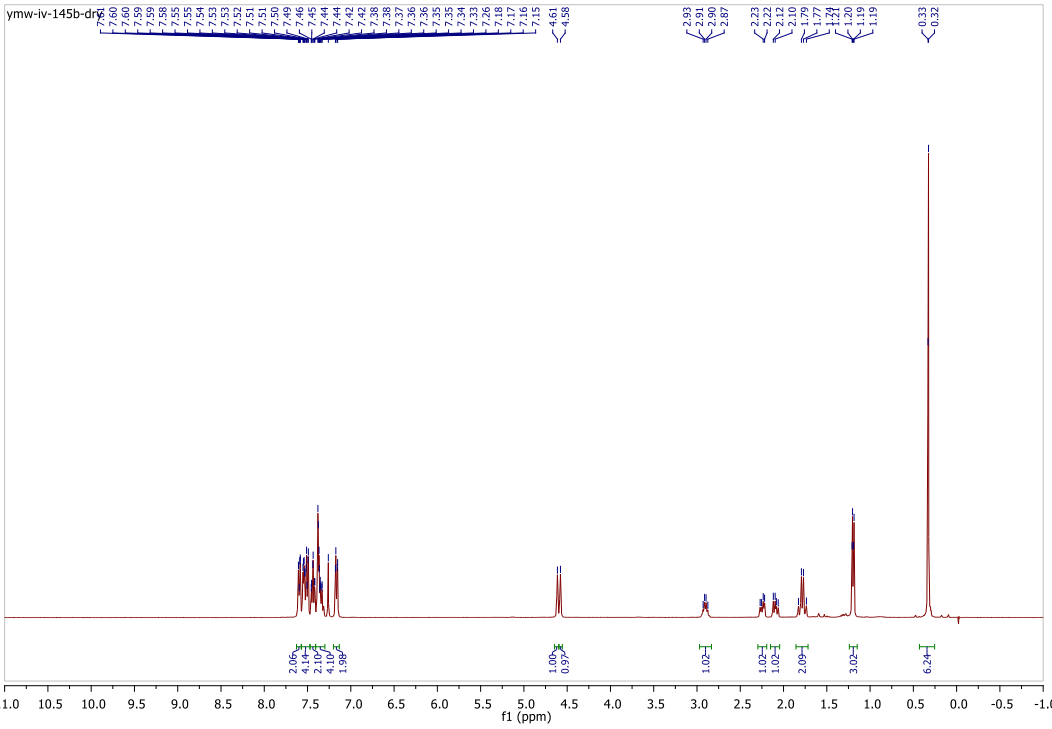
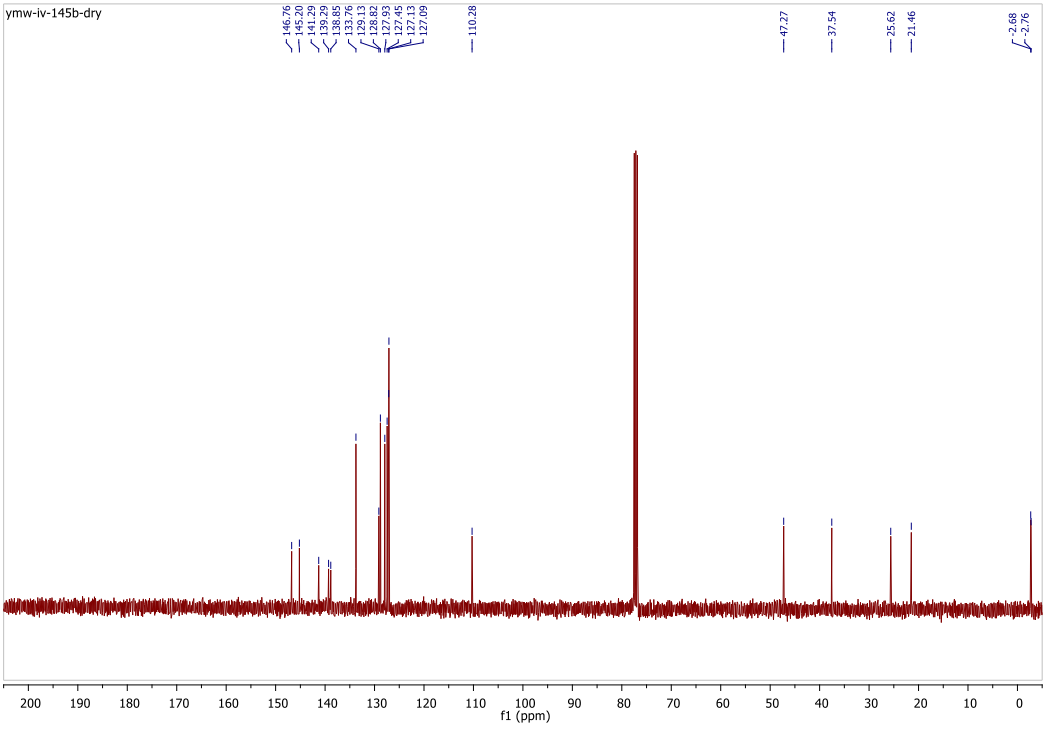
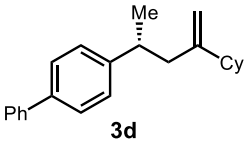
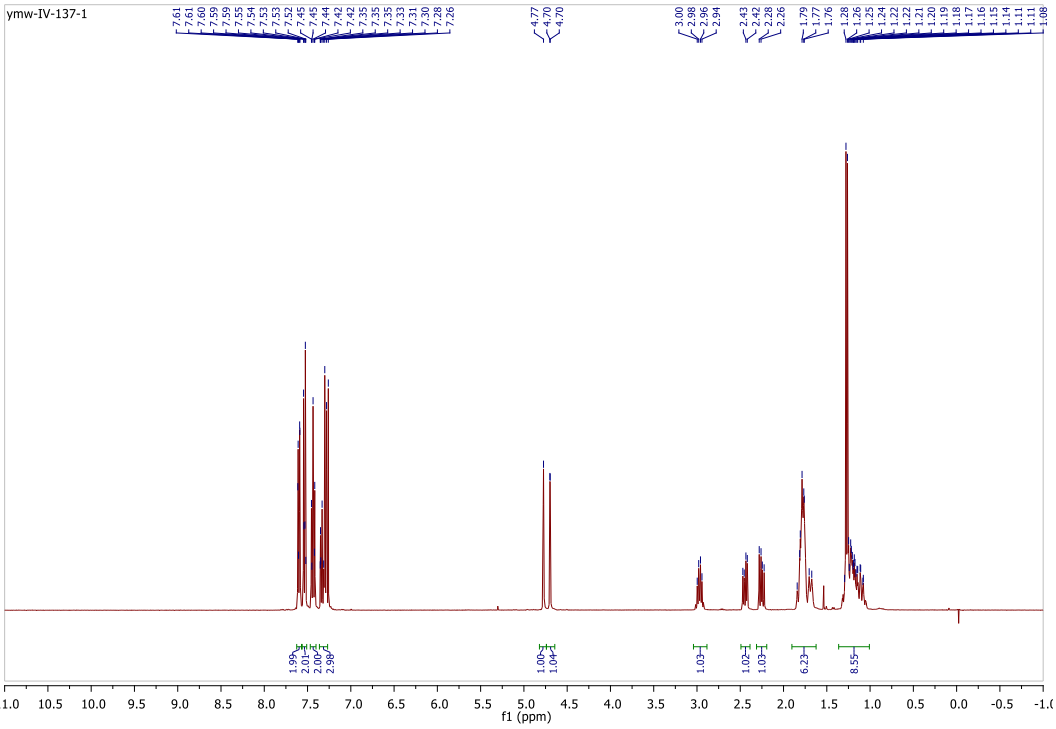
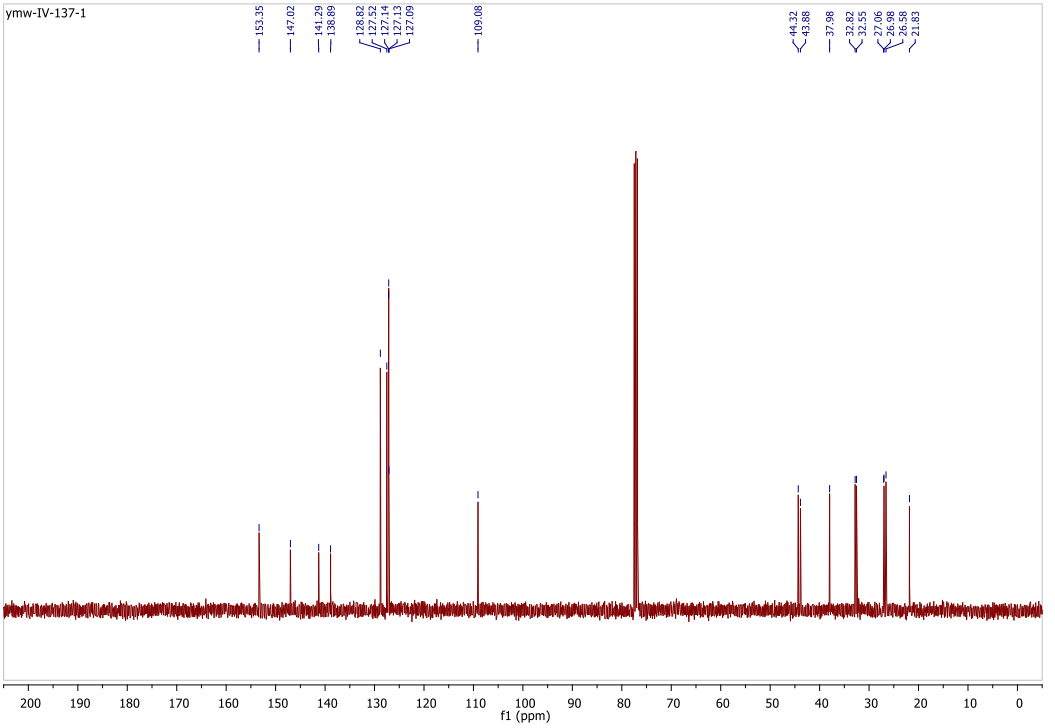


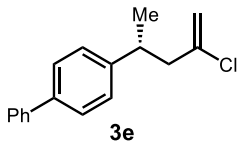




3d







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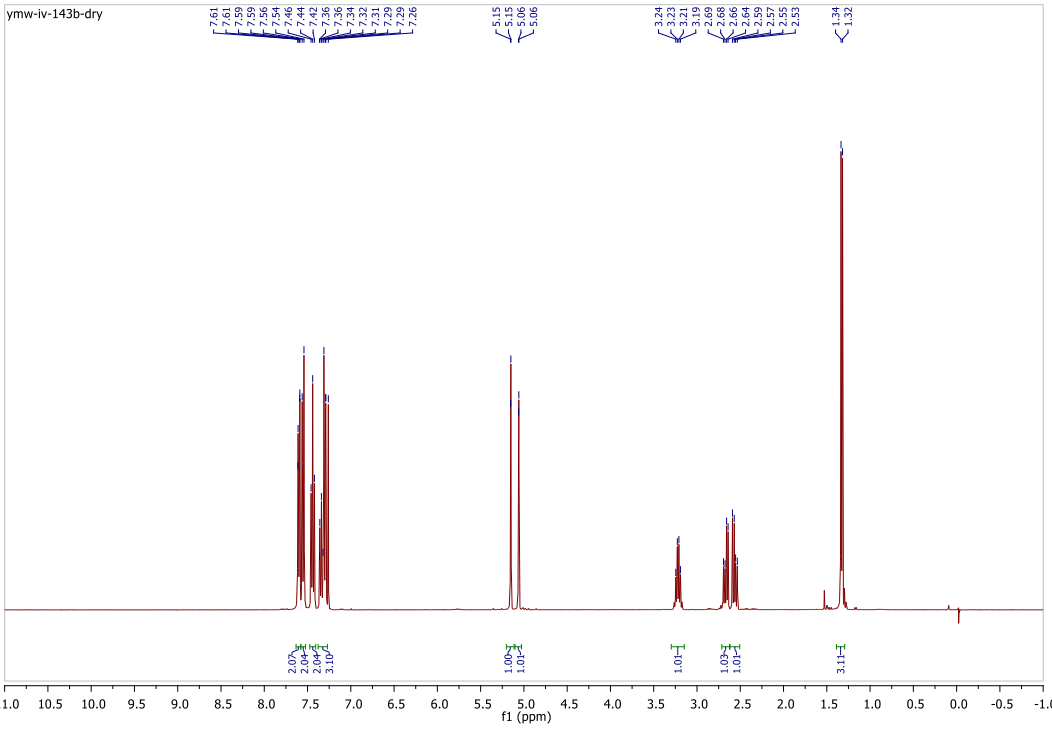

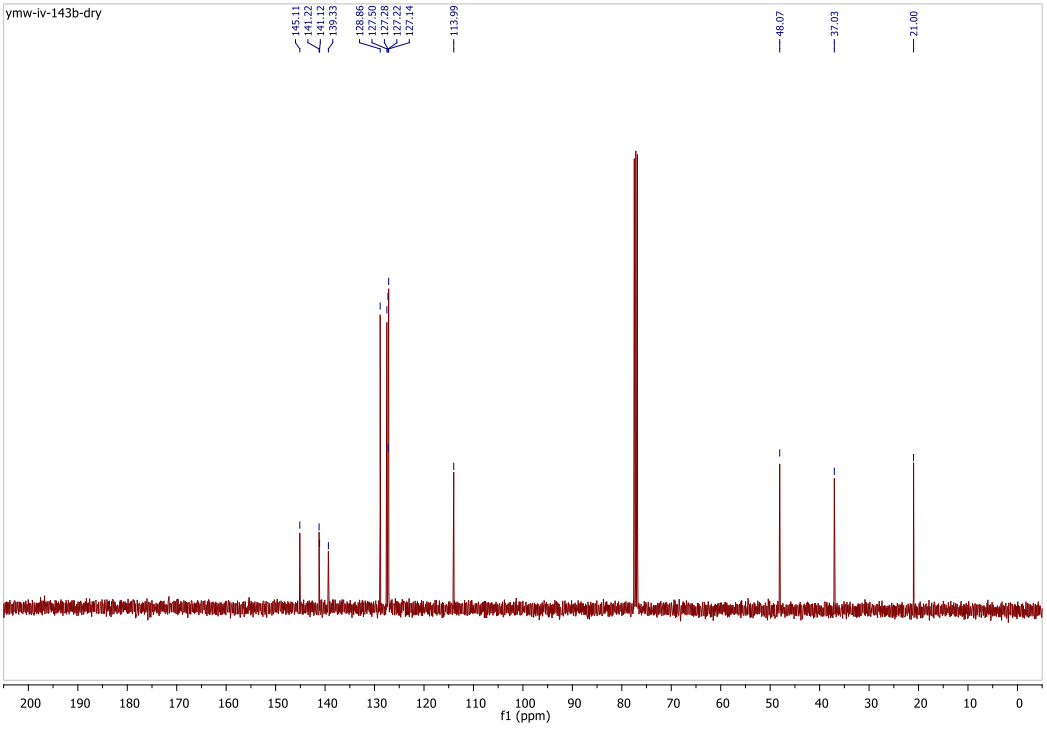

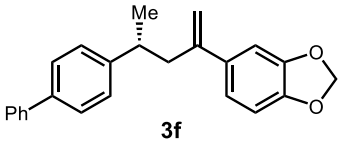

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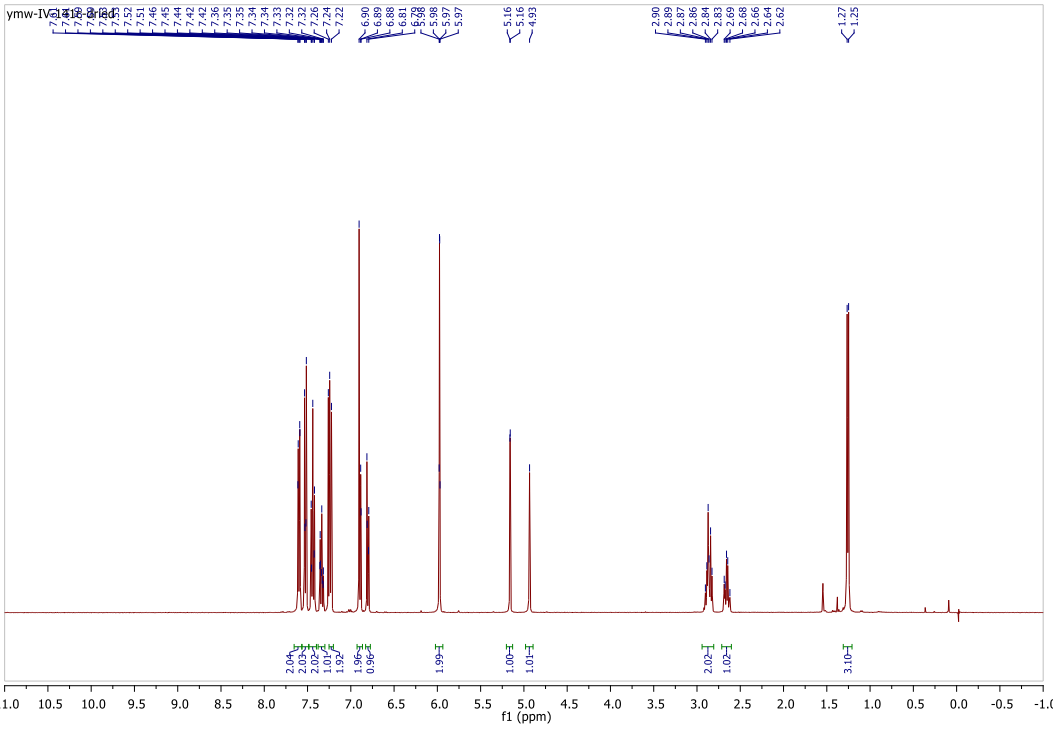

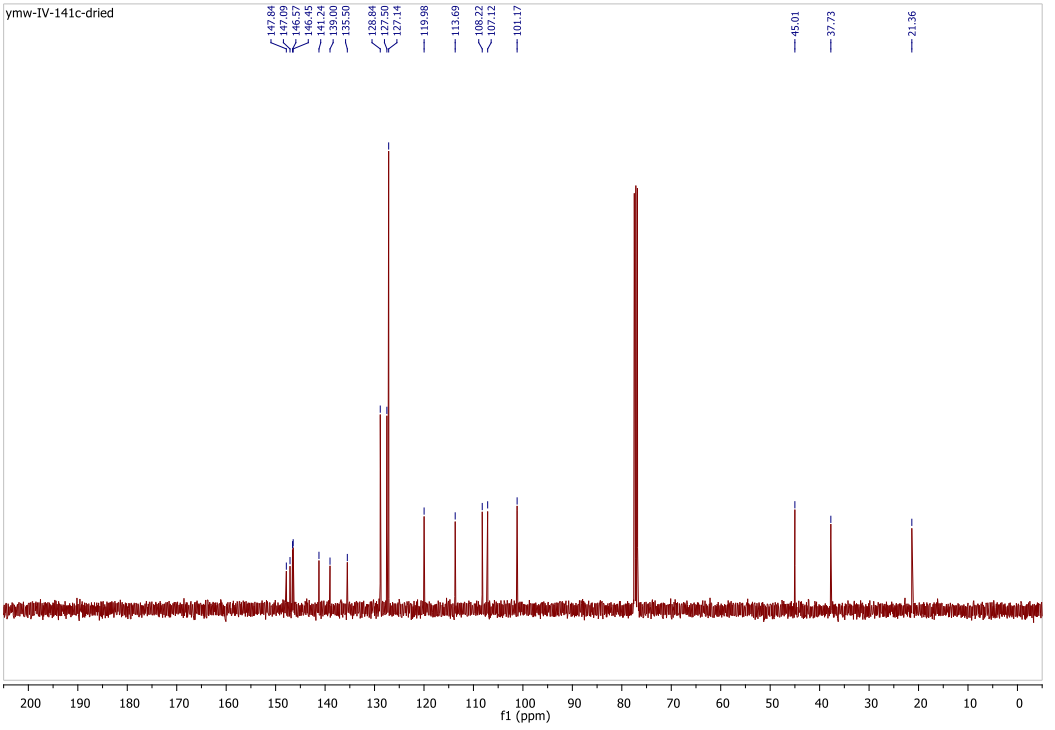

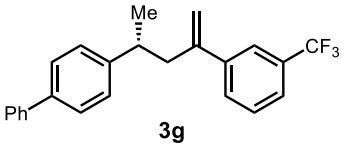

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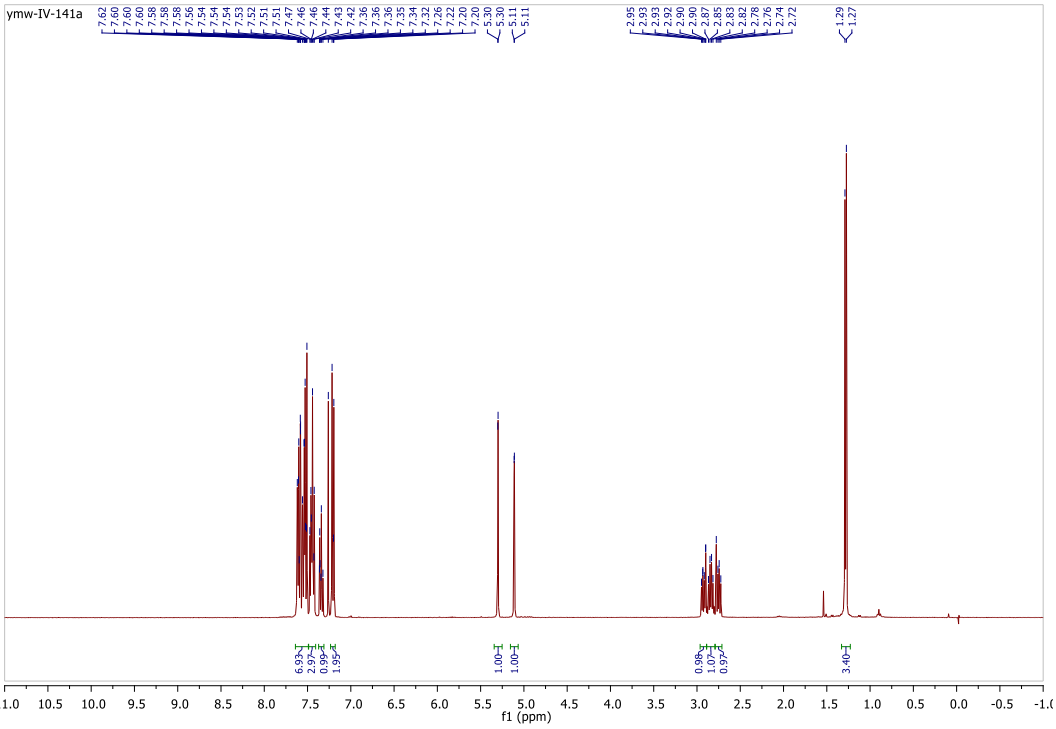

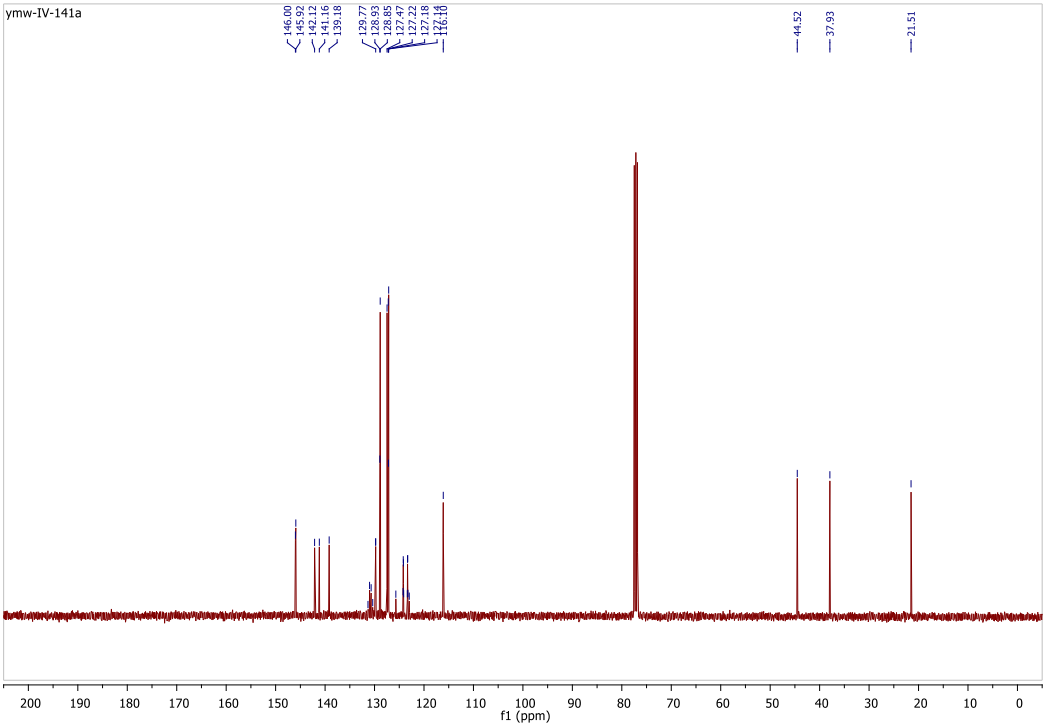

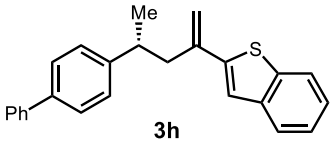

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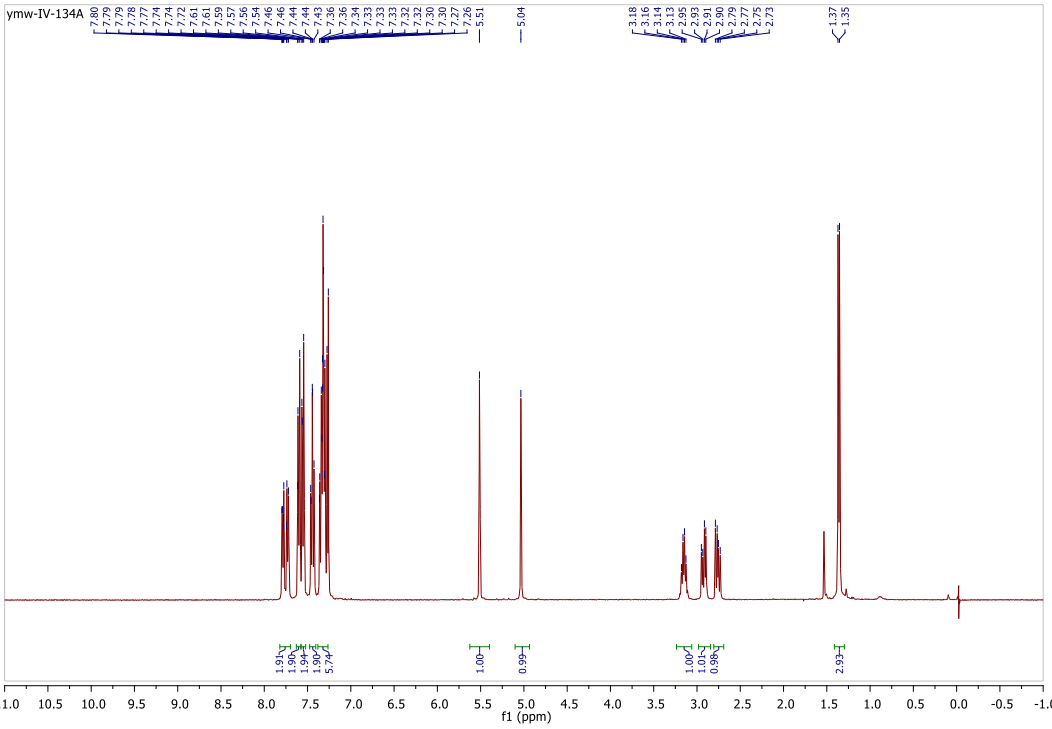
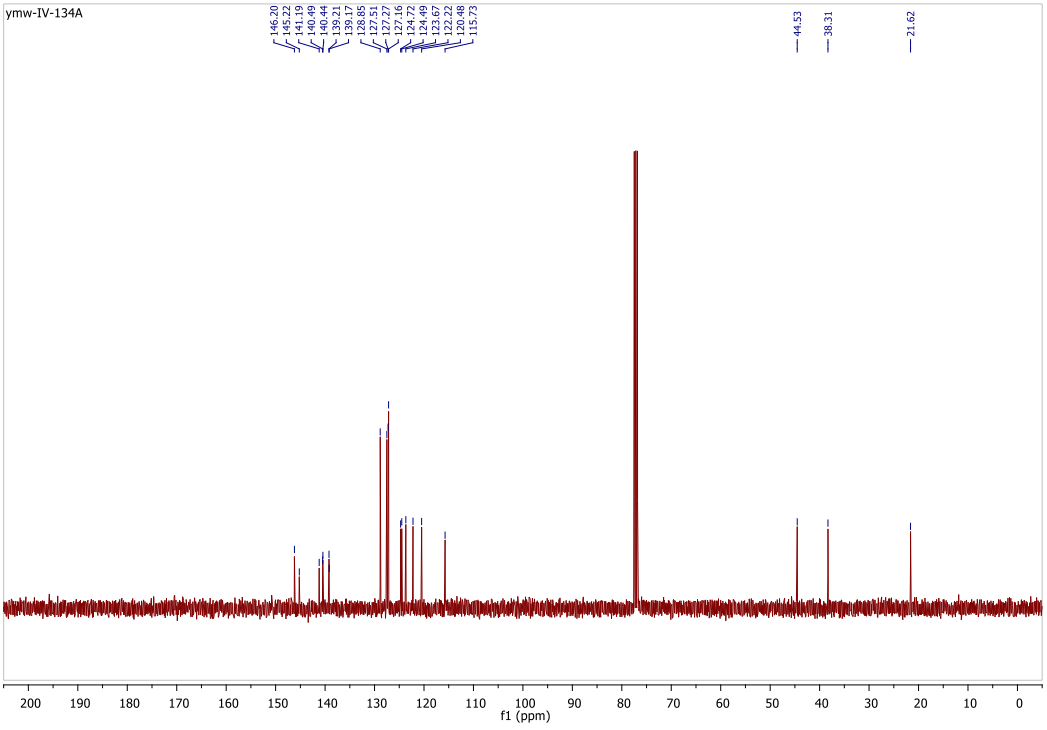
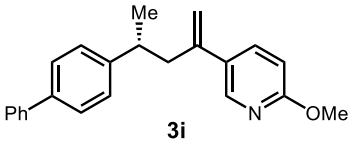
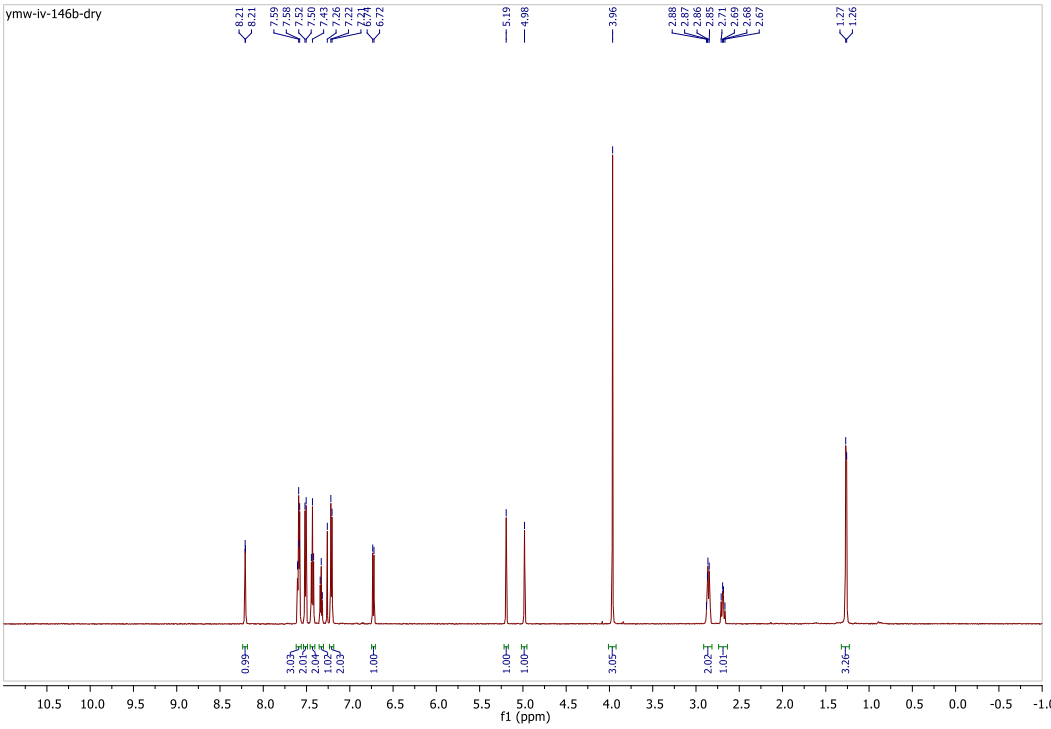





Me
Ph
N
OMe

3i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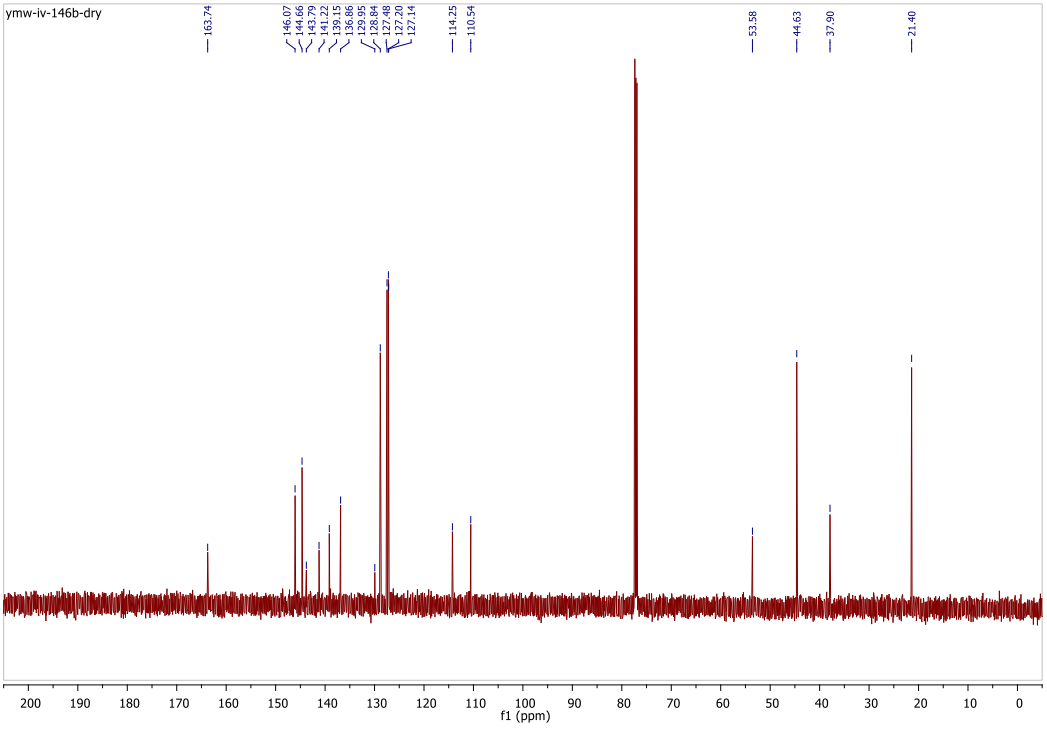
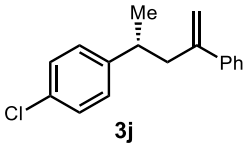
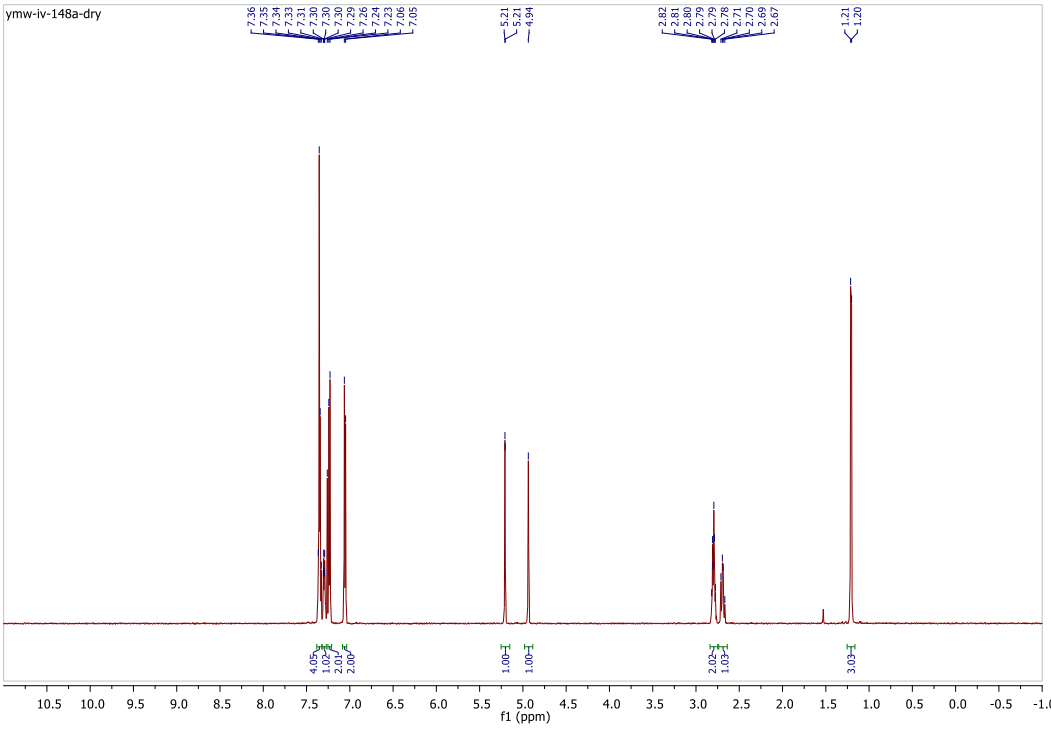
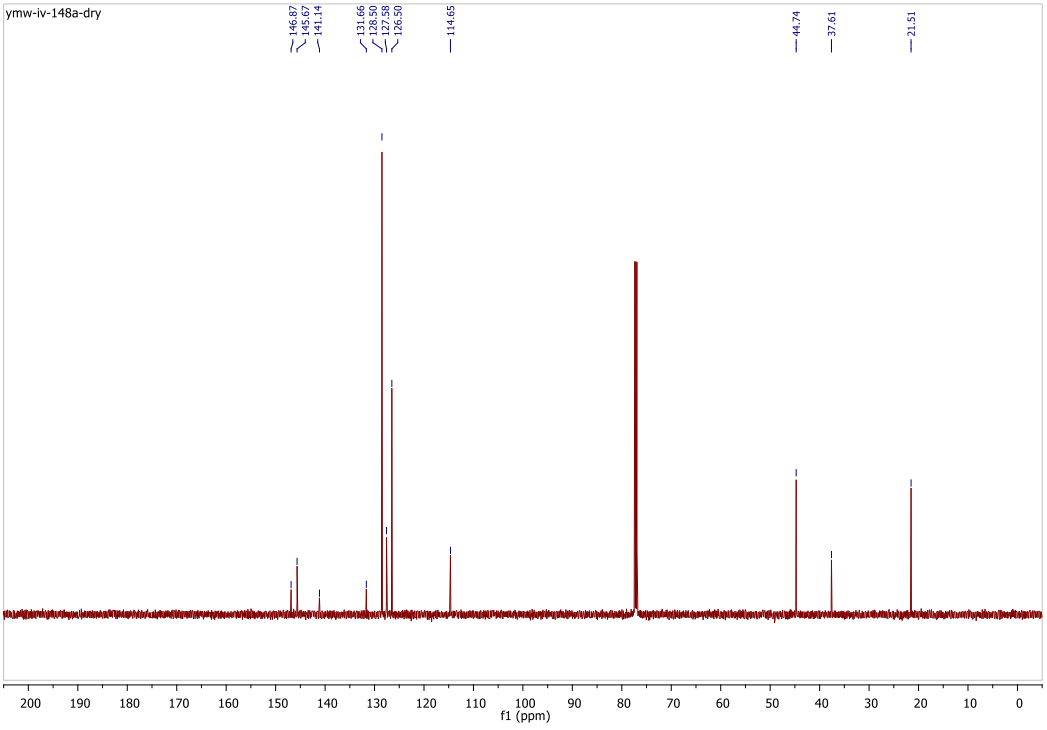
6.72
5.19
4.98
3.96
2.88
2.87
2.86
2.85
2.71
2.69
2.68
2.67
1.27
1.26
0.99
3.03
2.01
2.04
1.02
2.05
1.00
1.00
1.00
3.05
2.02
1.01
3.26
f1 (ppm)

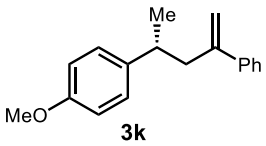

ymw-iv-146b-dry
163.74
146.07
144.66
143.76
141.22
139.15
136.86
129.95
128.84
127.48
127.20
127.14
114.25
110.54
53.58
44.63
37.90
21.40
f1 (ppm)


Me
Ph
Cl

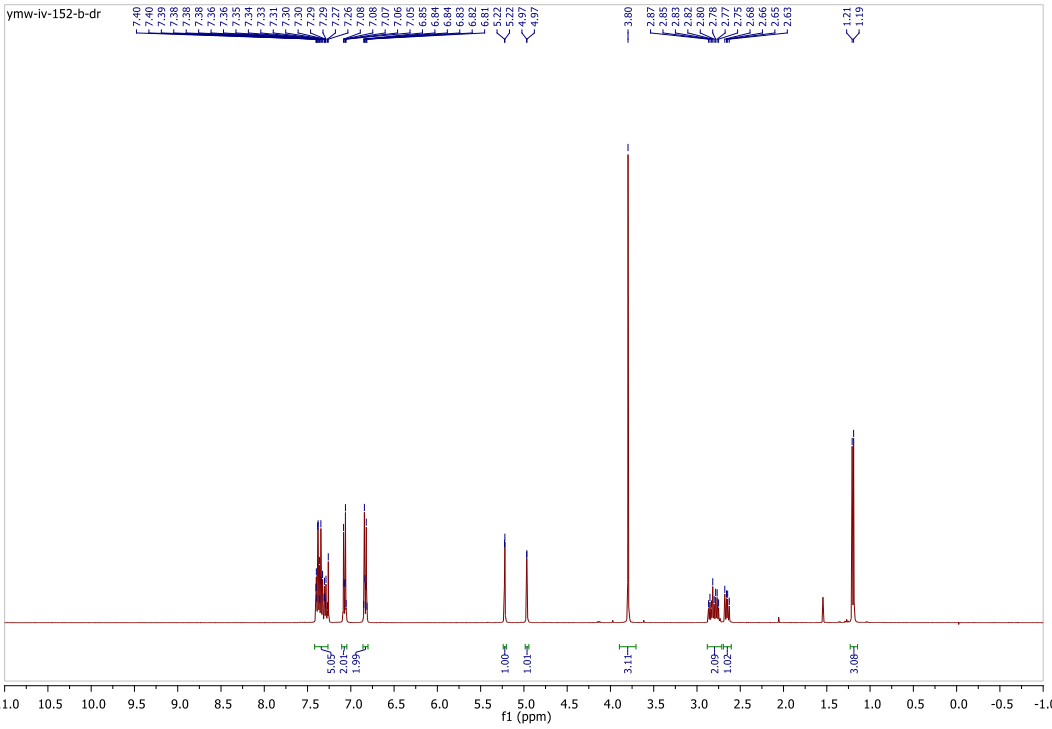
3j

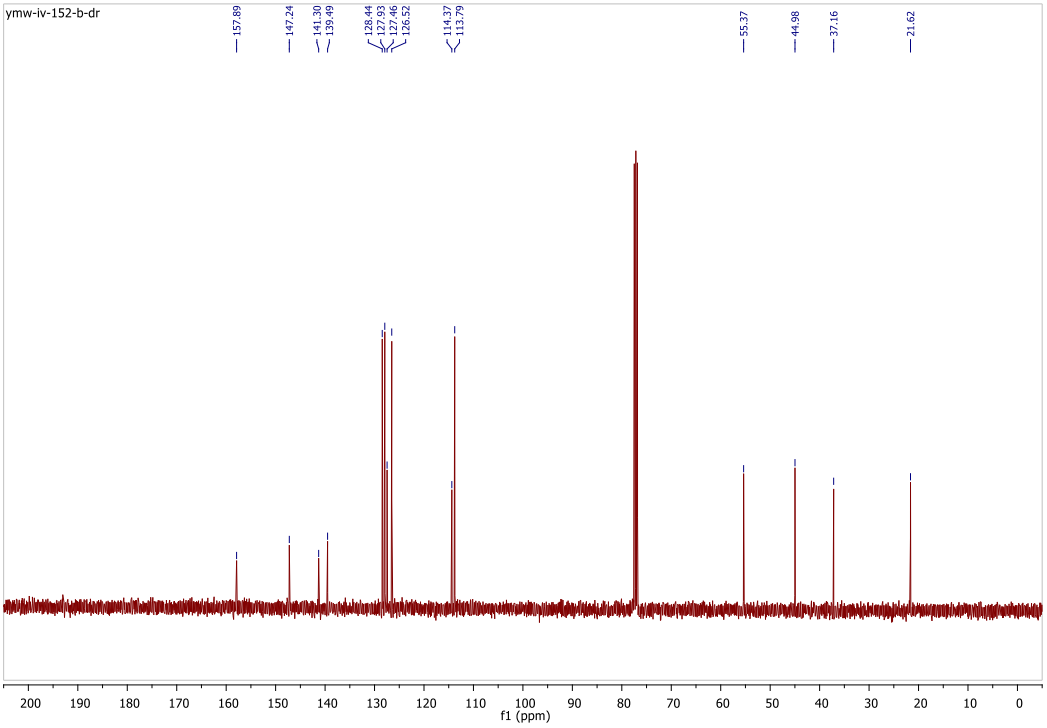

ymw-iv-148a-dry
7.36
7.35
7.34
7.33
7.31
7.30
7.30
7.30
7.29
7.26
7.24
7.23
7.06
7.05
5.21
5.21
4.94
2.82
2.81
2.80
2.79
2.79
2.78
2.71
2.70
2.69
2.67
1.21
1.20
4.05
1.02
2.01
2.00
1.00
1.00
2.02
1.03
3.03
f1 (ppm)

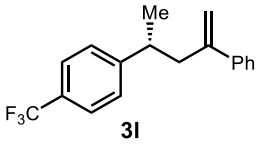

ymw-iv-148a-dry
146.87
145.67
141.14
131.66
128.50
127.58
126.50
114.65
44.74
37.61
21.51
f1 (ppm)



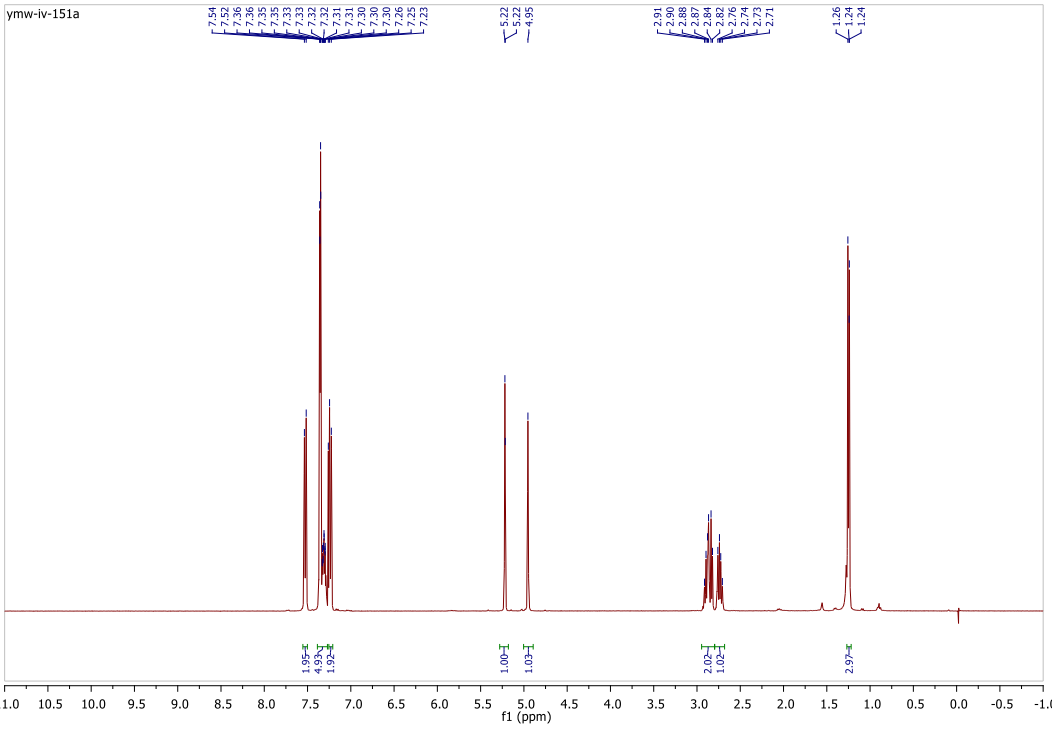
3k

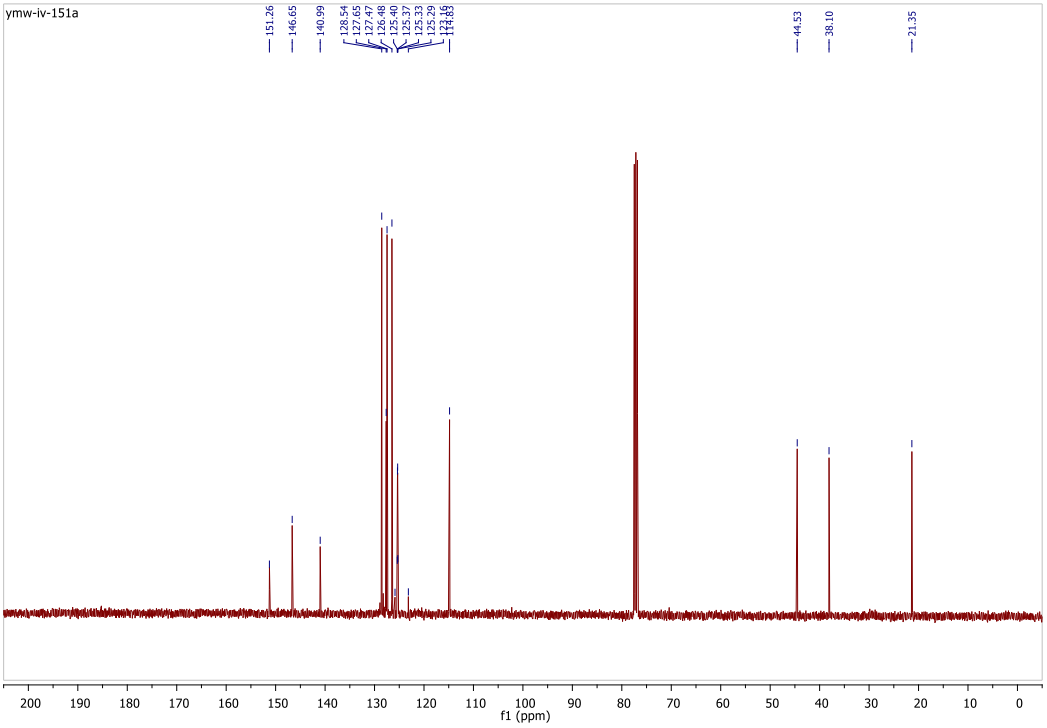


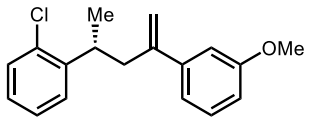




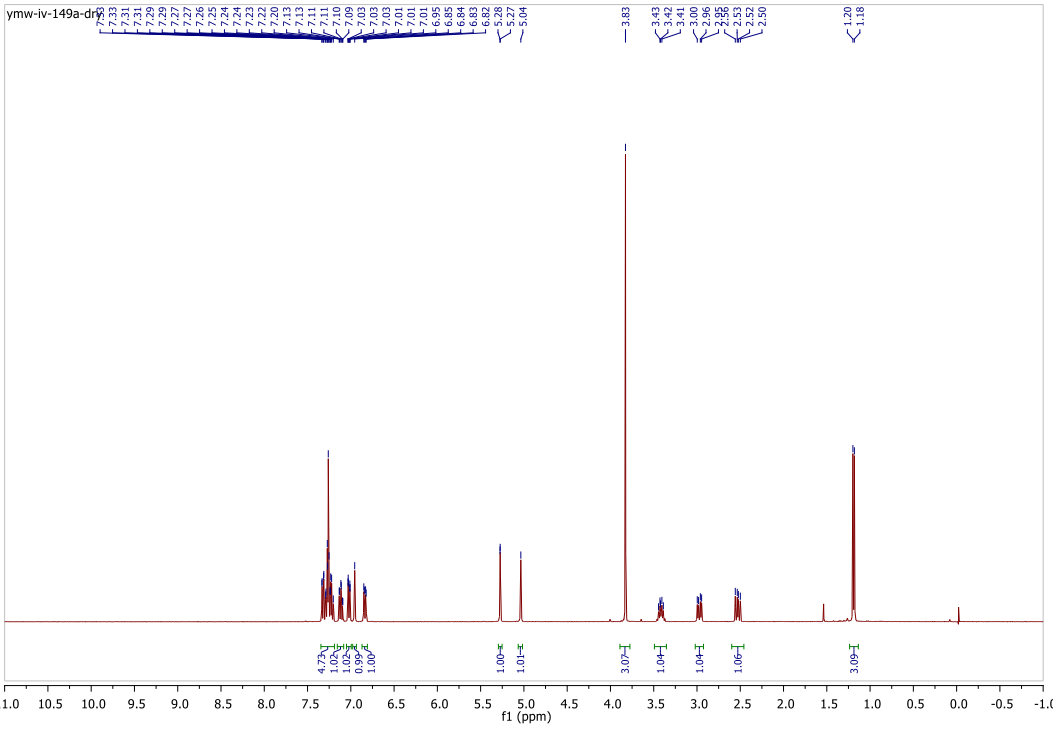
3l

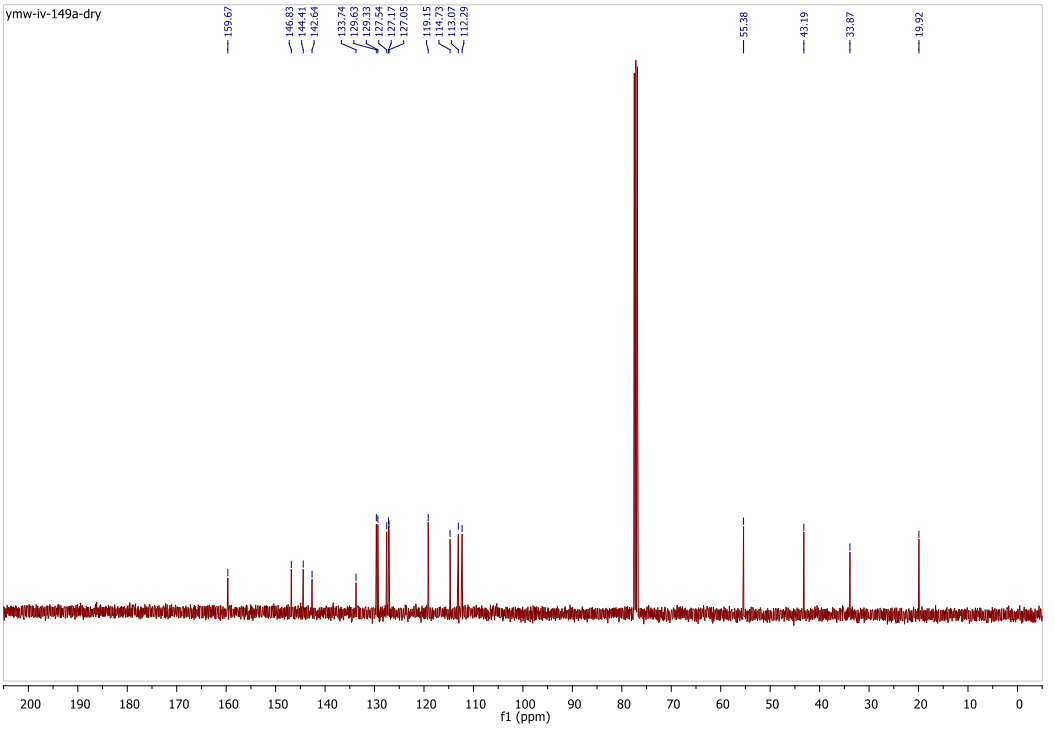


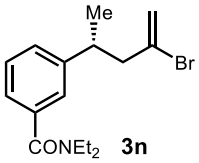




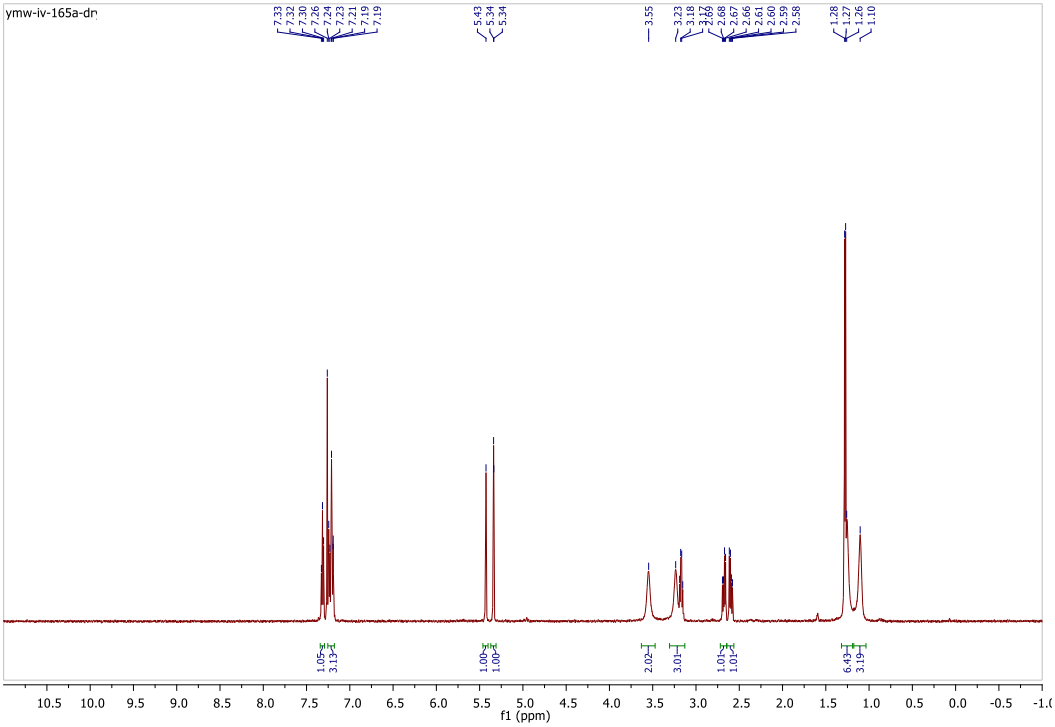
3m

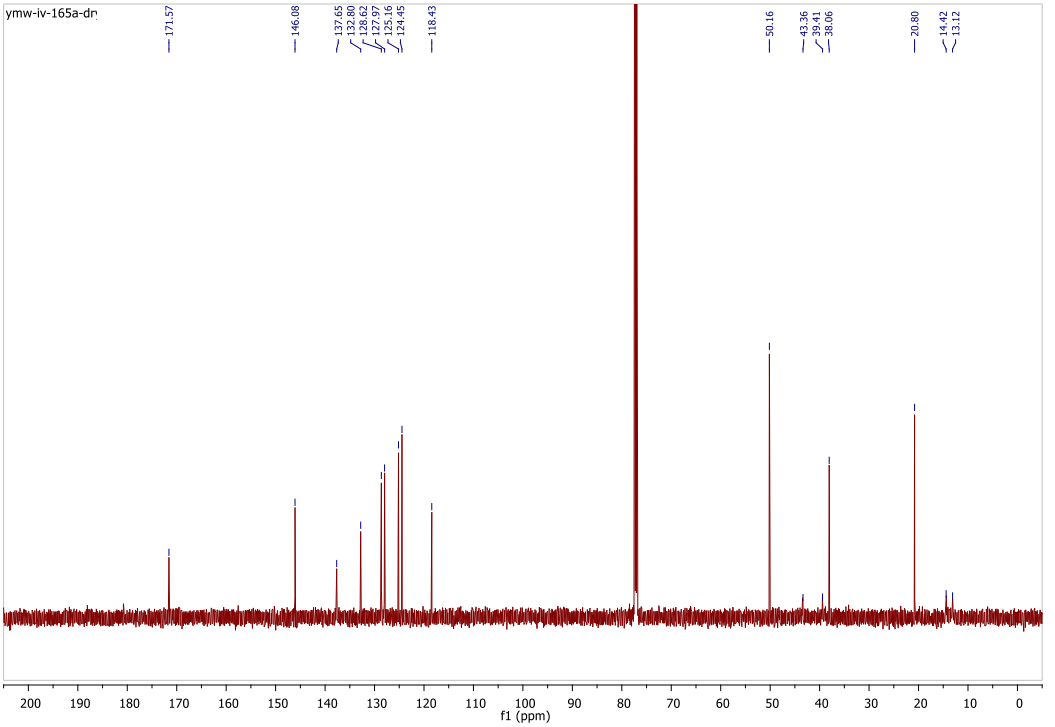


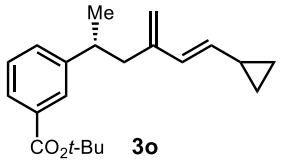



Me
Br
CONEt2

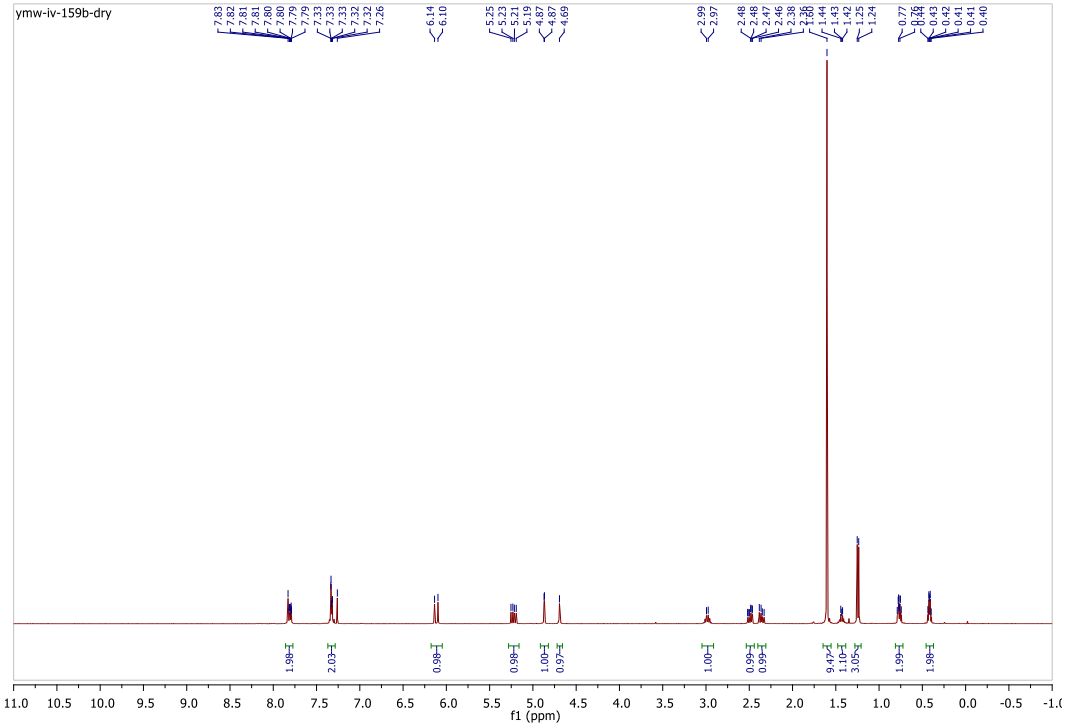
3n

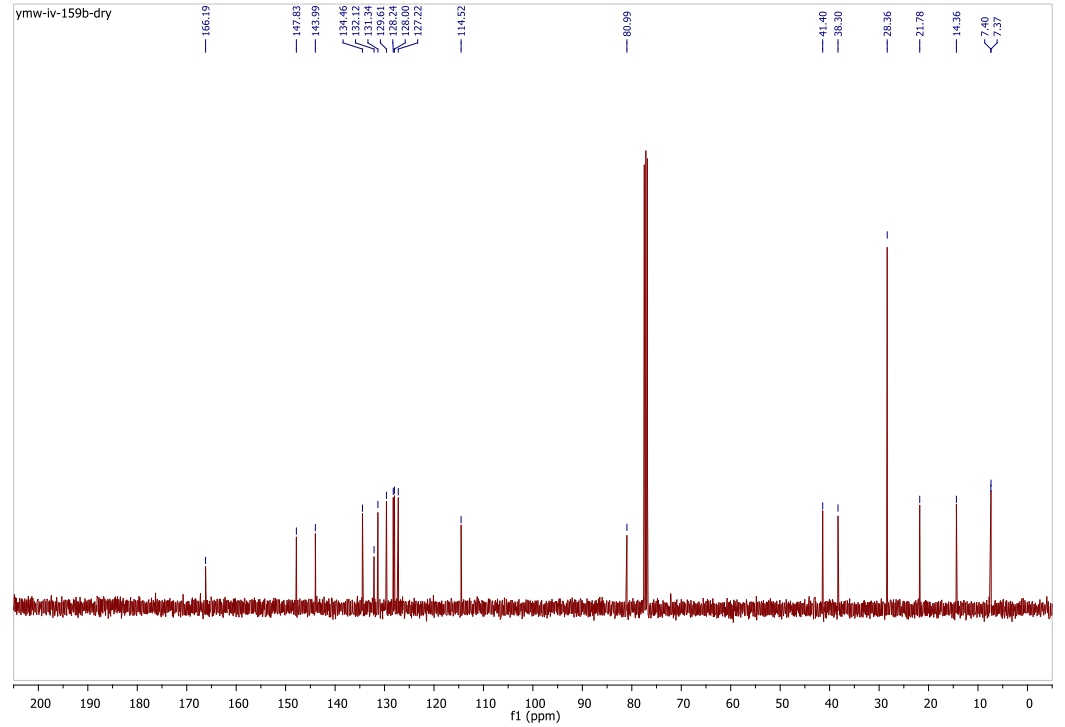

ymw-iv-165a-dr
7.33
7.32
7.30
7.26
7.24
7.23
7.21
7.19
7.19
5.43
5.34
5.34
3.55
3.23
3.18
3.17
2.69
2.68
2.67
2.66
2.61
2.60
2.59
2.58
1.28
1.27
1.26
1.10
1.05
3.13
1.00
1.00
2.02
3.01
1.01
1.01
6.43
3.19
f1 (ppm)

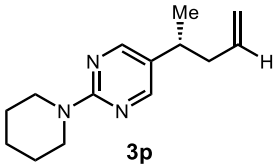

ymw-iv-165a-dr
171.57
146.08
137.65
132.80
128.62
127.97
125.16
124.45
118.43
50.16
43.36
39.41
38.06
20.80
14.42
13.12
f1 (ppm)



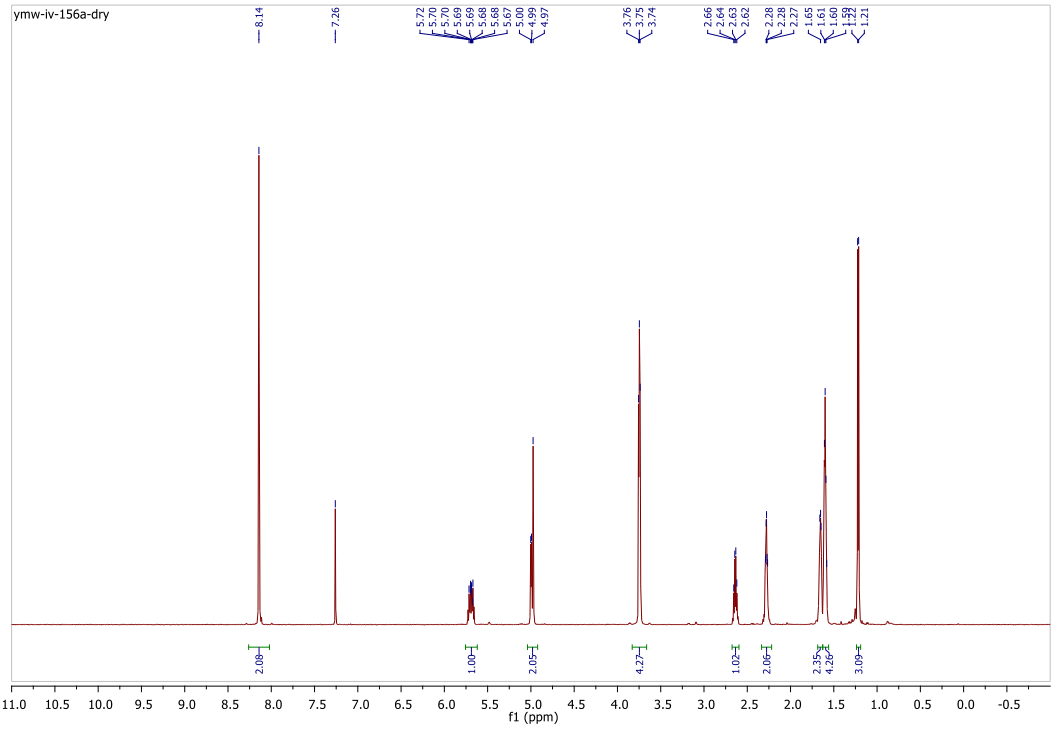
3o

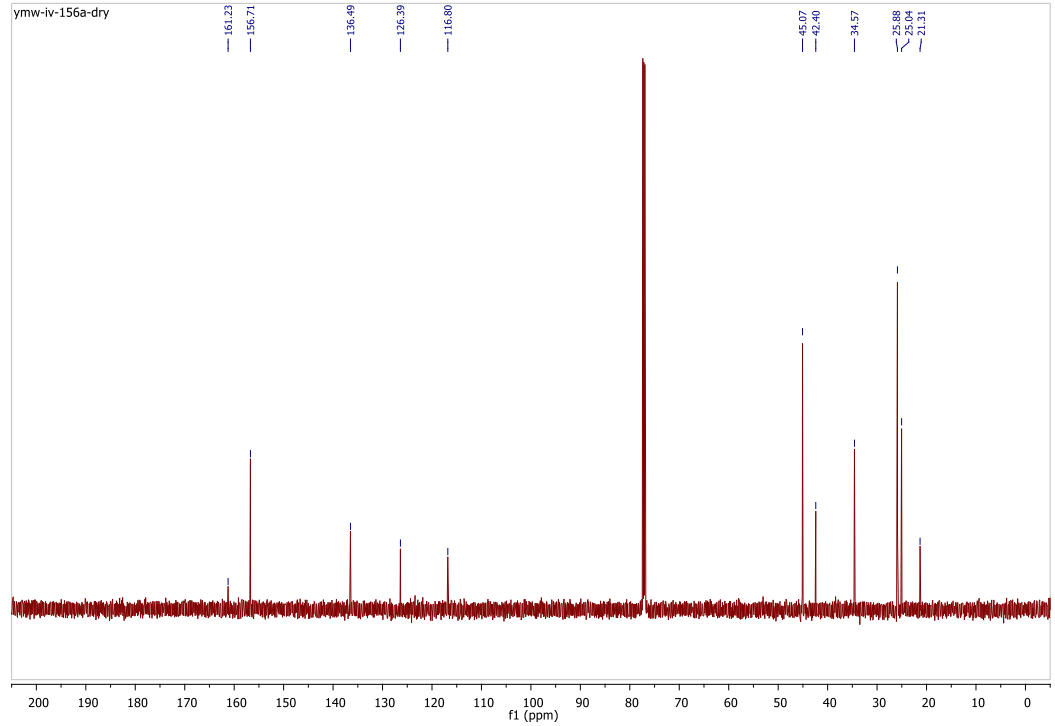


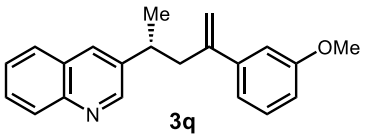



Me
N
N
N
H

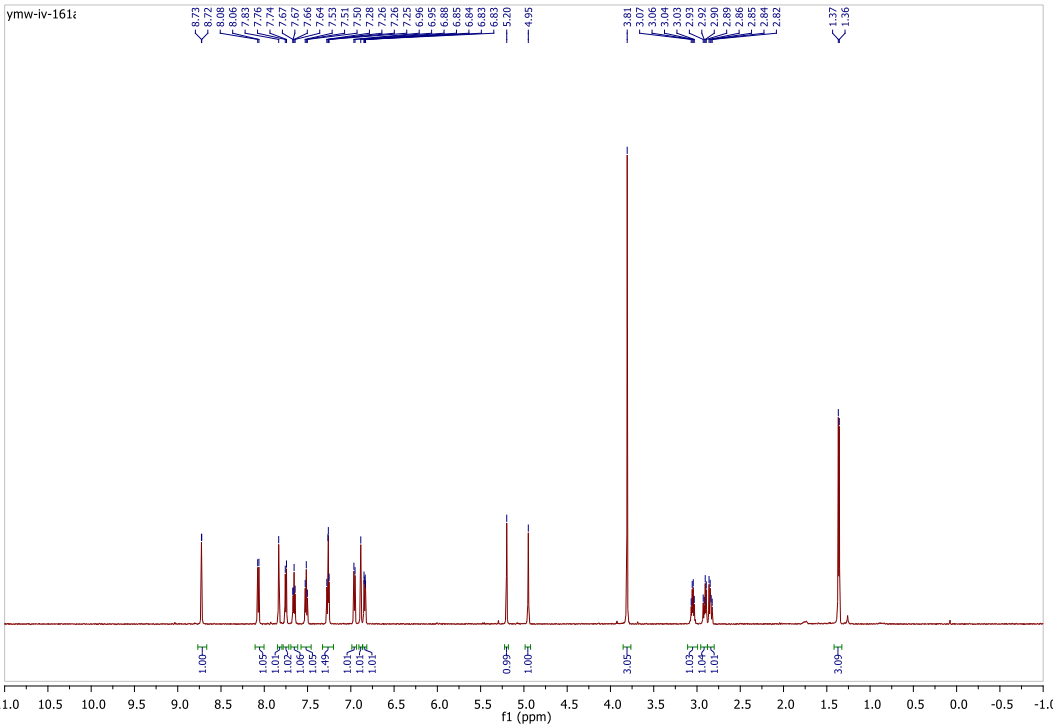
3p

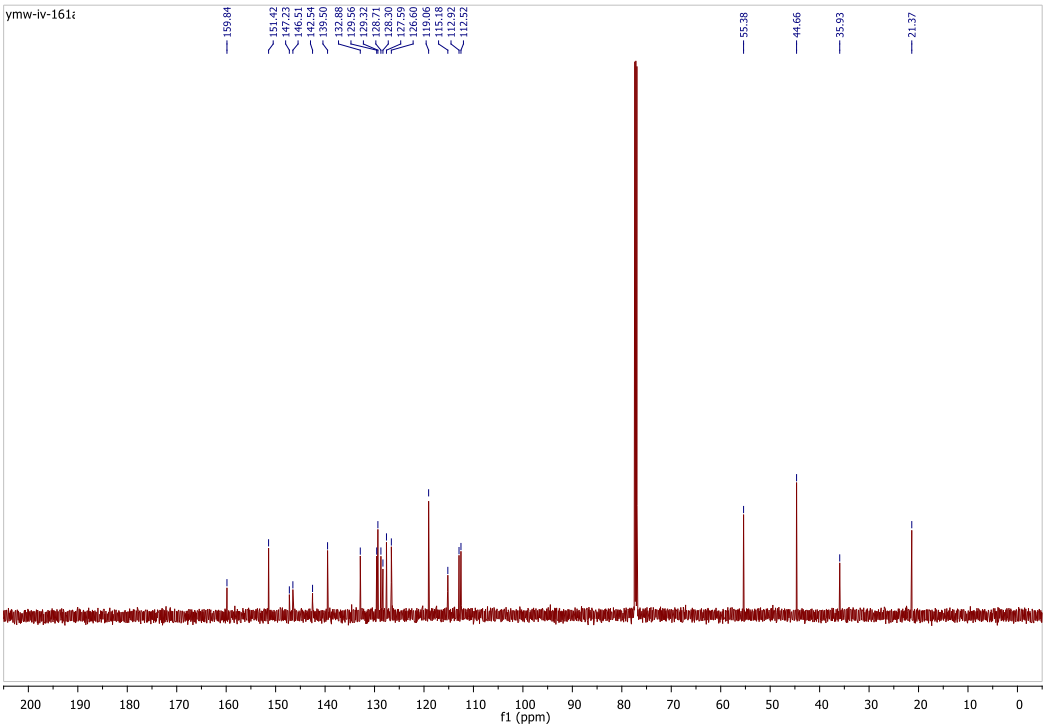

ymw-iv-156a-dry
8.14
7.26
5.72
5.70
5.70
5.69
5.69
5.68
5.68
5.67
5.00
4.99
4.97
3.76
3.75
3.74
2.66
2.64
2.63
2.62
2.28
2.28
2.27
1.65
1.61
1.60
1.39
1.37
1.21
2.08
1.00
2.05
4.27
1.02
2.06
2.35
4.26
3.09
f1 (ppm)

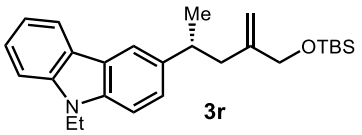

ymw-iv-156a-dry
161.23
156.71
136.49
126.39
116.80
45.07
42.40
34.57
25.88
25.04
21.31
f1 (ppm)



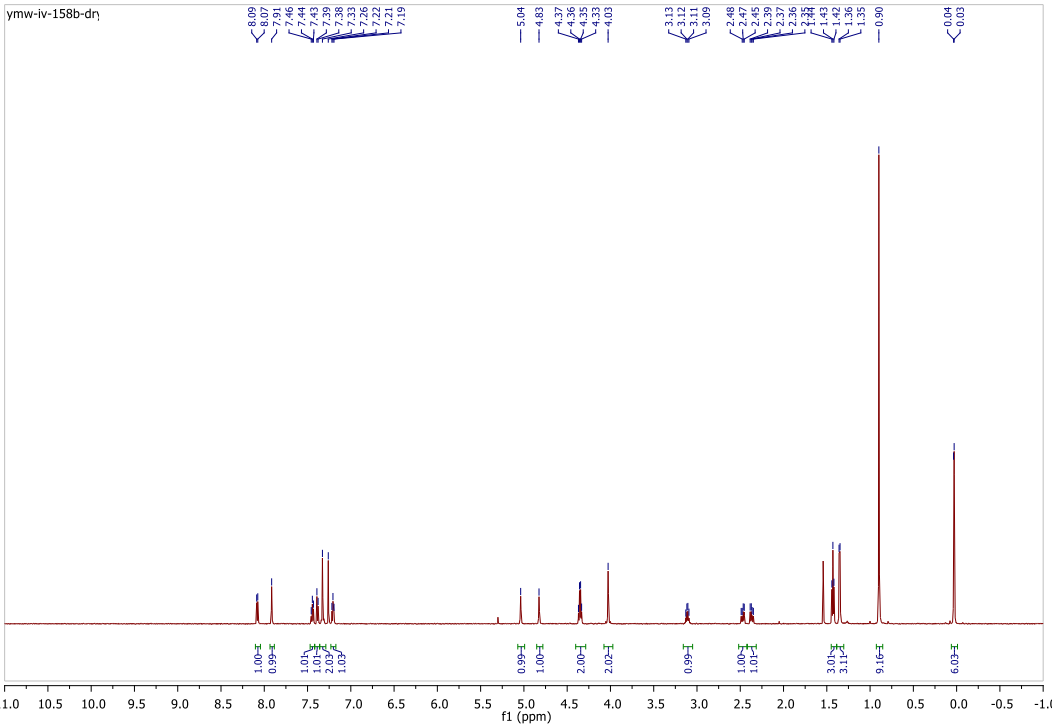
3q

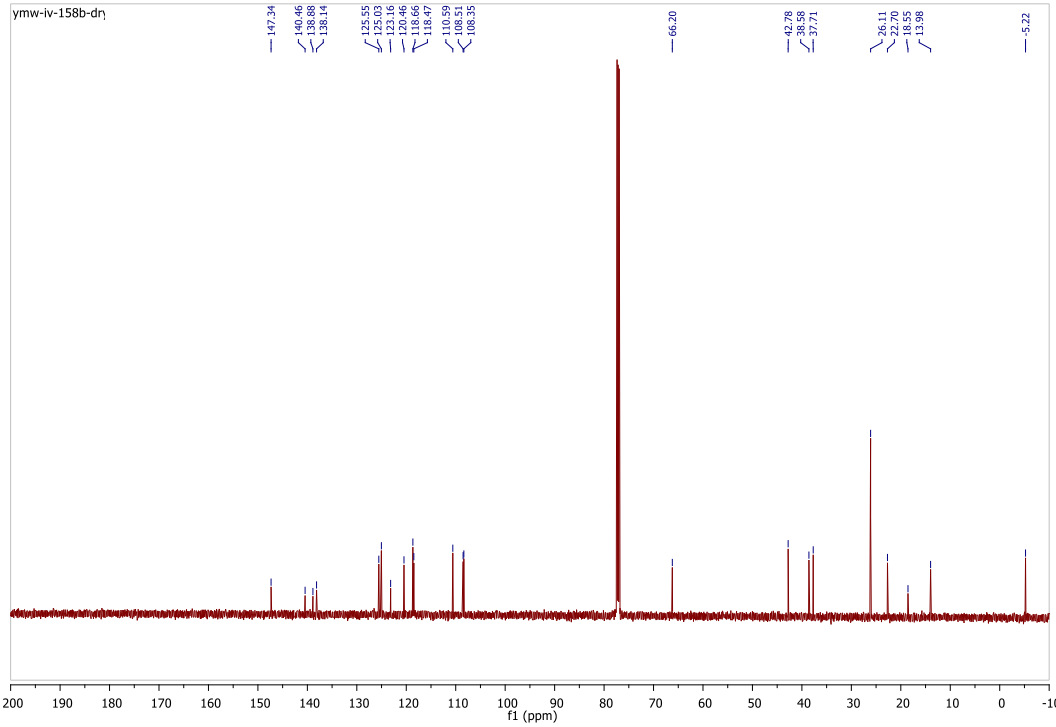


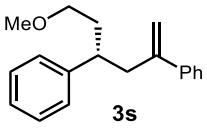




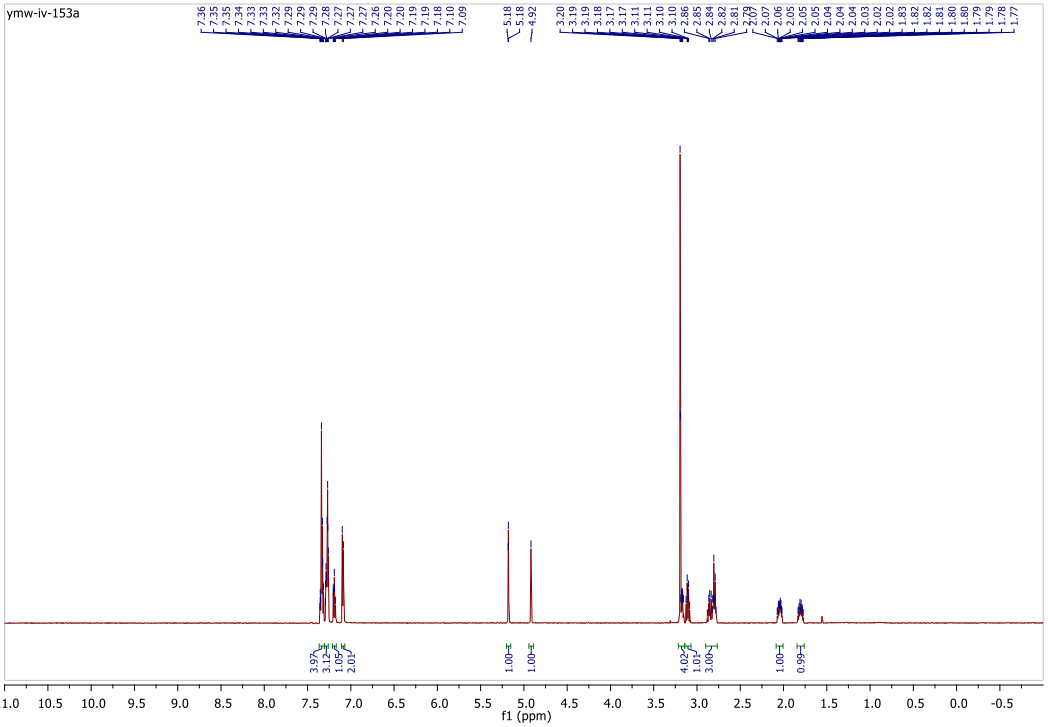
3r

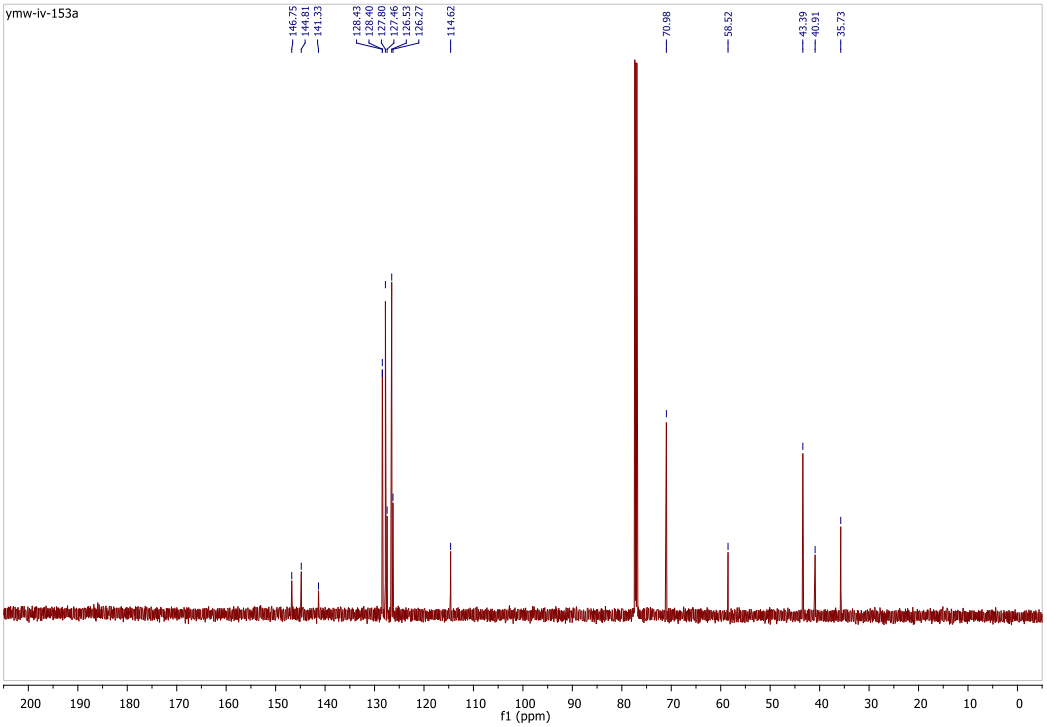


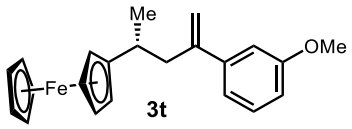




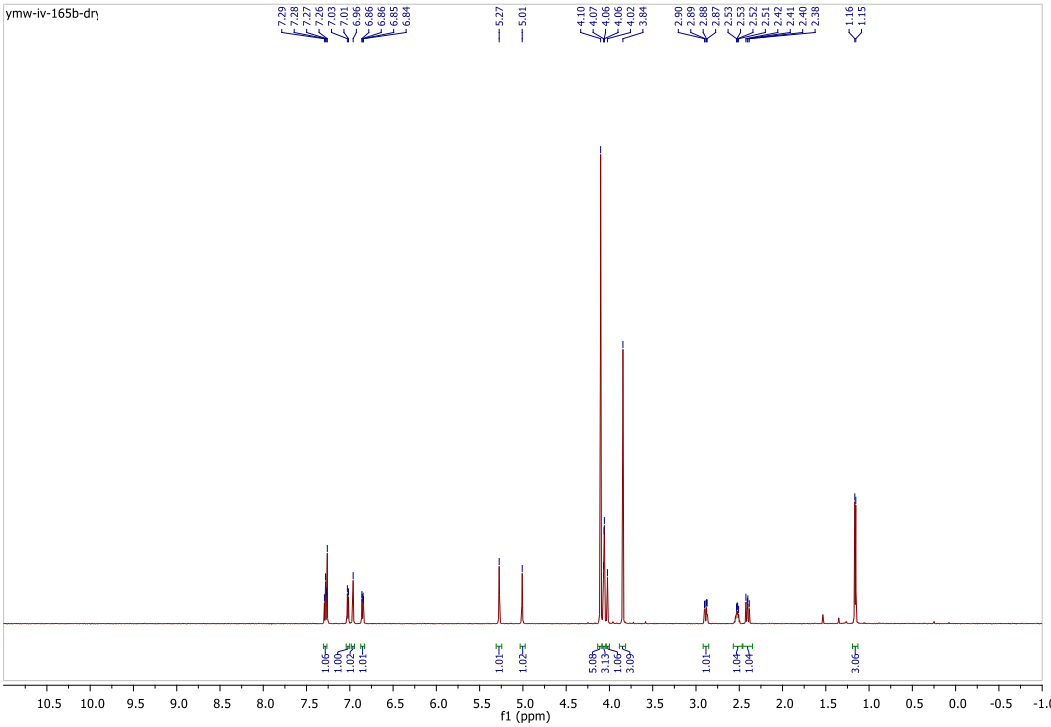
3s

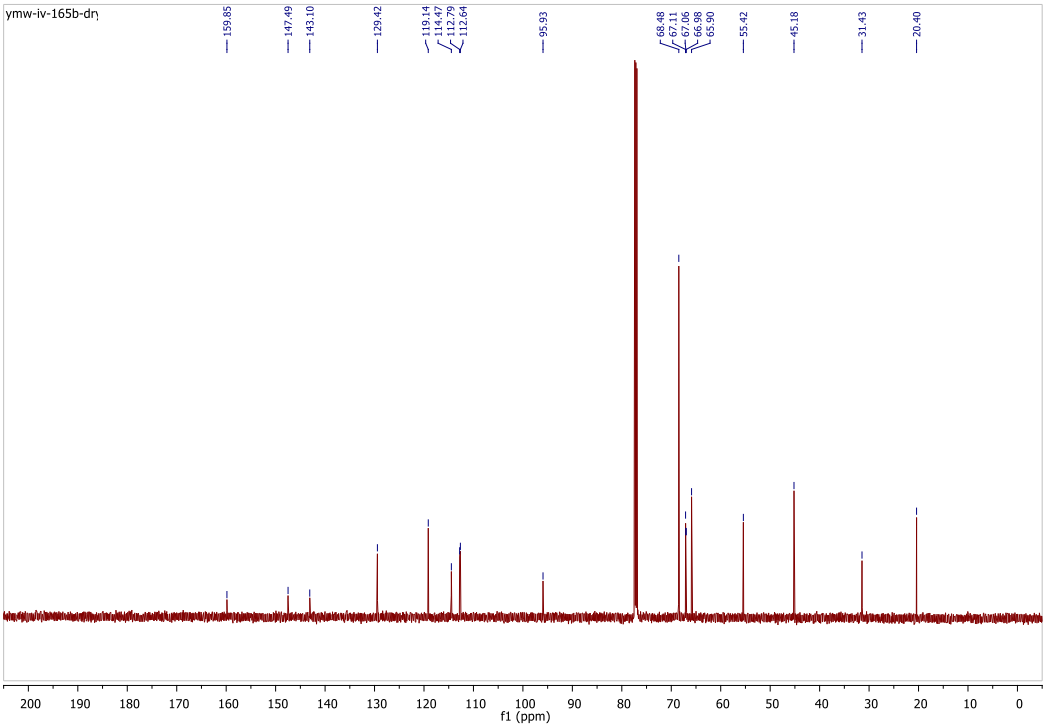


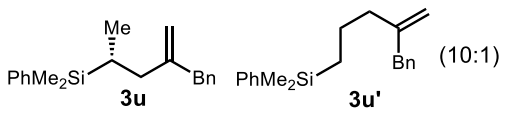


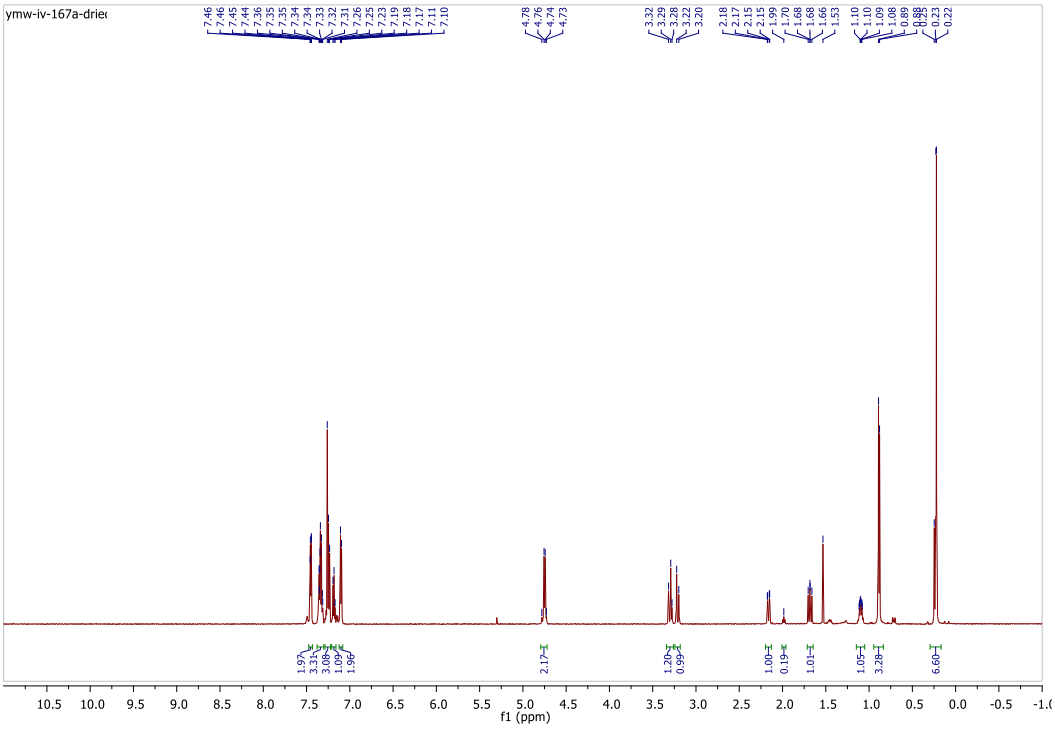

Me
OMe
Fe

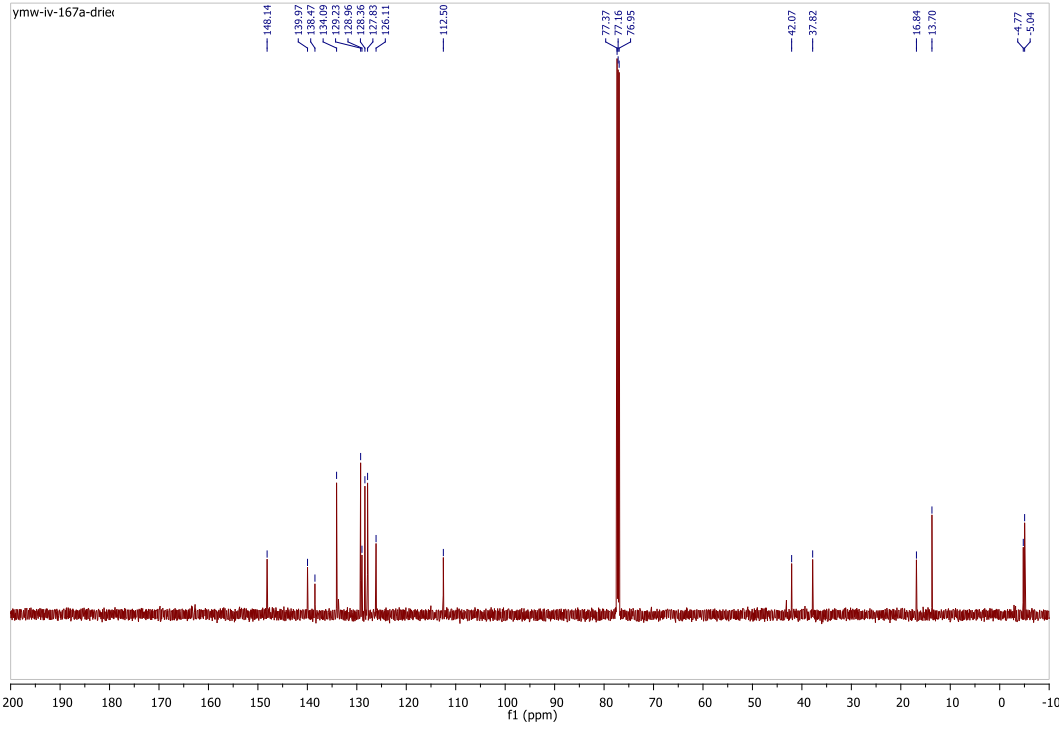
3t

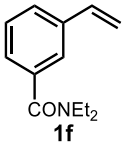

ymw-iv-165b-dr
7.29
7.28
7.27
7.26
7.03
7.01
6.86
6.86
6.86
6.85
6.84
5.27
5.01
4.10
4.07
4.06
4.06
4.02
3.84
3.00
2.88
2.88
2.87
2.53
2.53
2.52
2.51
2.42
2.41
2.40
2.38
1.16
1.15
1.06
1.00
1.02
1.01
1.01
1.02
5.08
3.13
1.06
3.09
1.01
1.04
1.04
3.06
f1 (ppm)


ymw-iv-165b-dr
159.85
147.49
143.10
129.42
119.14
114.47
112.79
112.64
95.93
68.48
67.11
67.06
66.98
65.90
55.42
45.18
31.43
20.40
f1 (ppm)

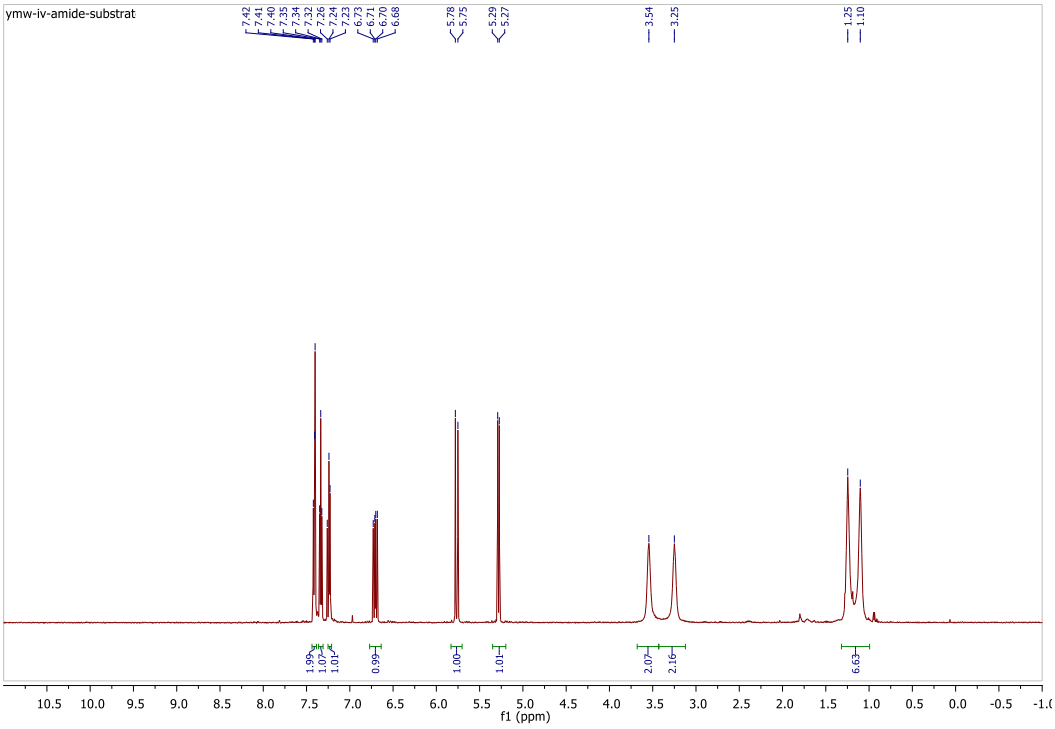

Me
PhMe2Si
Bn
3u
PhMe2Si
Bn
3u'
(10:1)

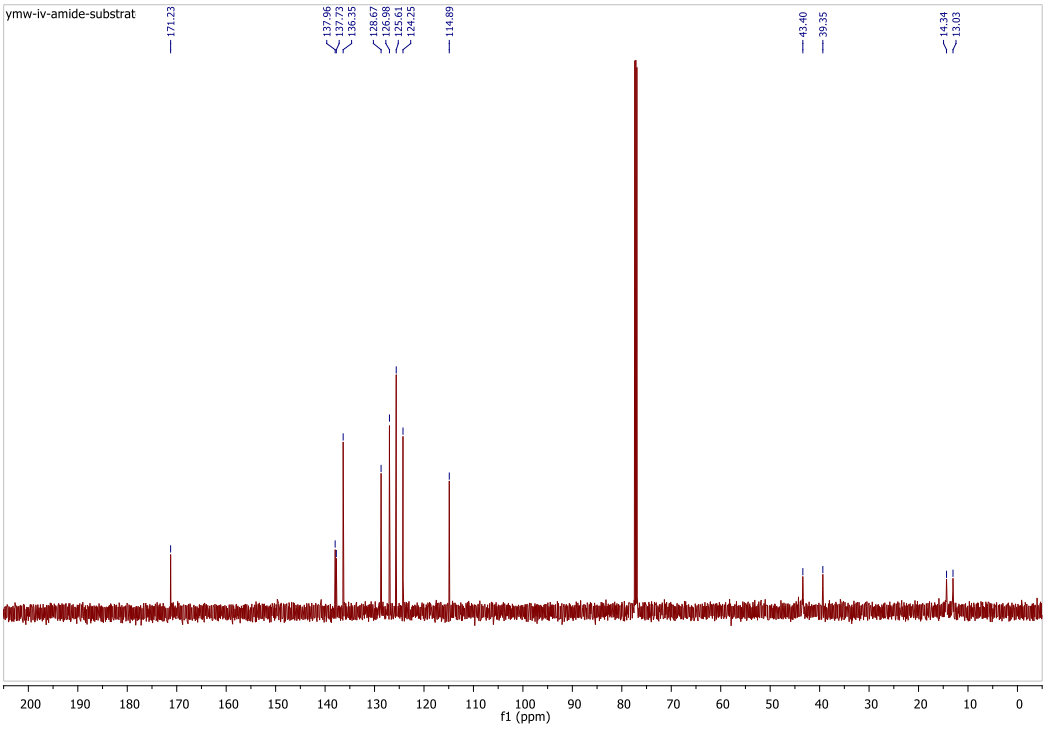

ymw-iv-167a-drie
f1 (ppm)

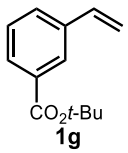

ymw-iv-167a-drie
f1 (ppm)


CONEt2

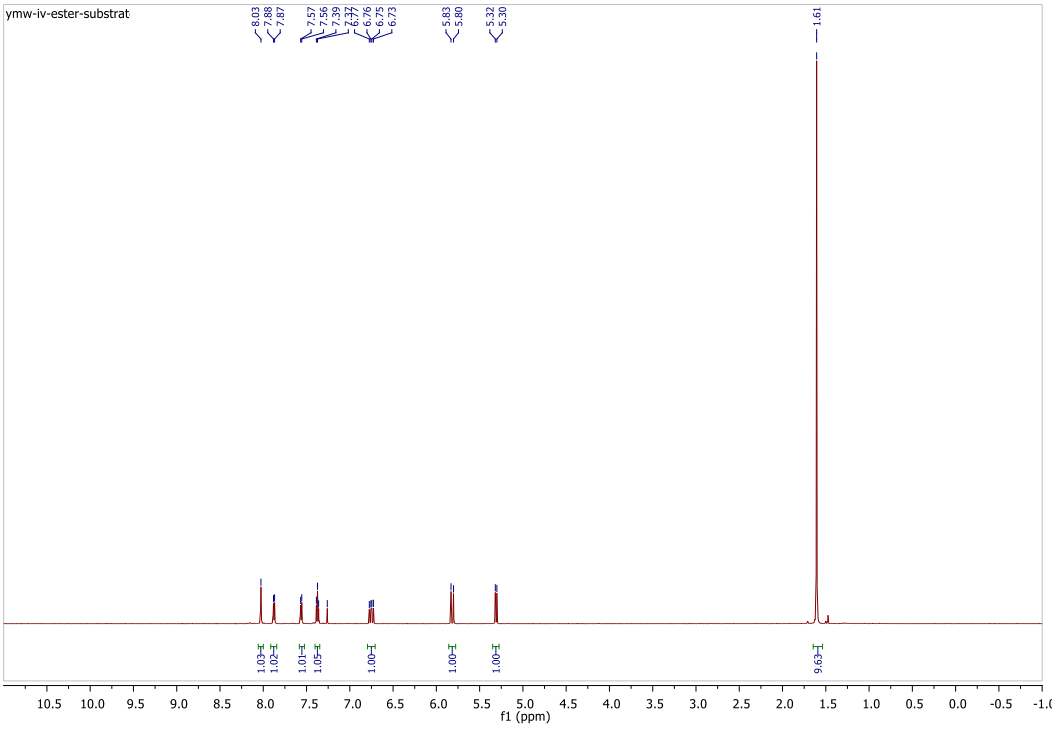
1f

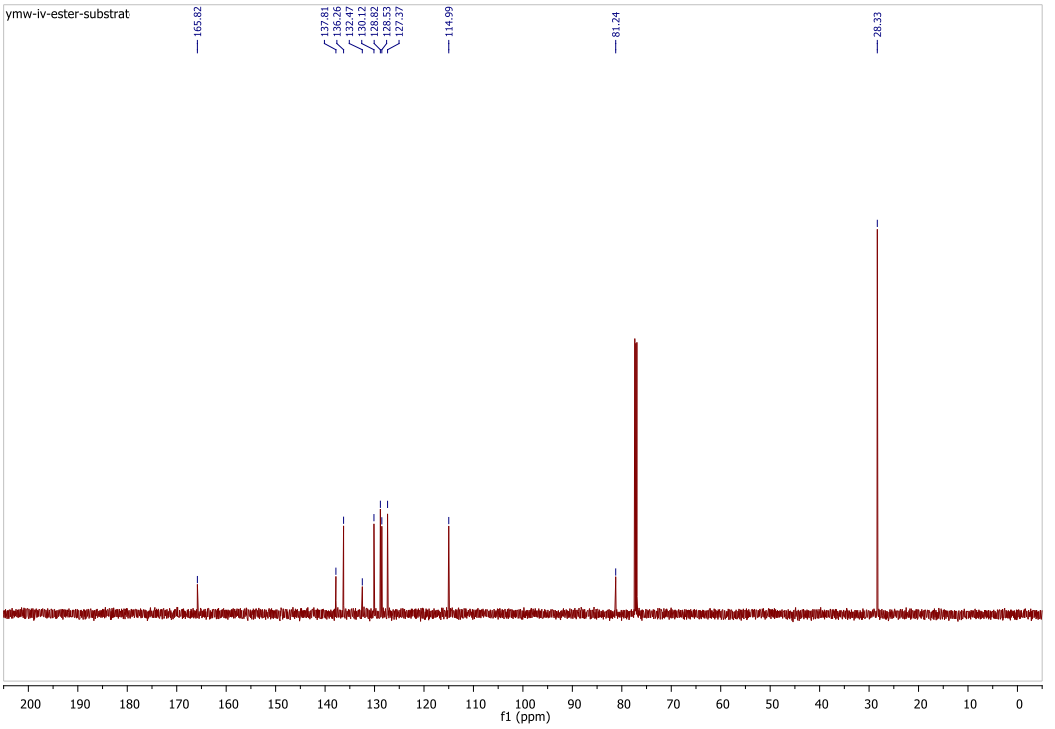

ymw-iv-amide-substrat
7.42
7.41
7.40
7.35
7.34
7.32
7.26
7.24
7.23
6.73
6.71
6.70
6.68
5.78
5.75
5.29
5.27
3.54
3.25
1.25
1.10
1.99
1.07
1.01
0.99
1.00
1.01
2.07
2.16
6.63
f1 (ppm)

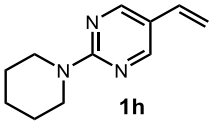

ymw-iv-amide-substrat
171.23
137.96
137.73
136.35
128.67
126.98
125.61
124.25
114.89
43.40
39.35
14.34
13.03
f1 (ppm)


CO2t-Bu

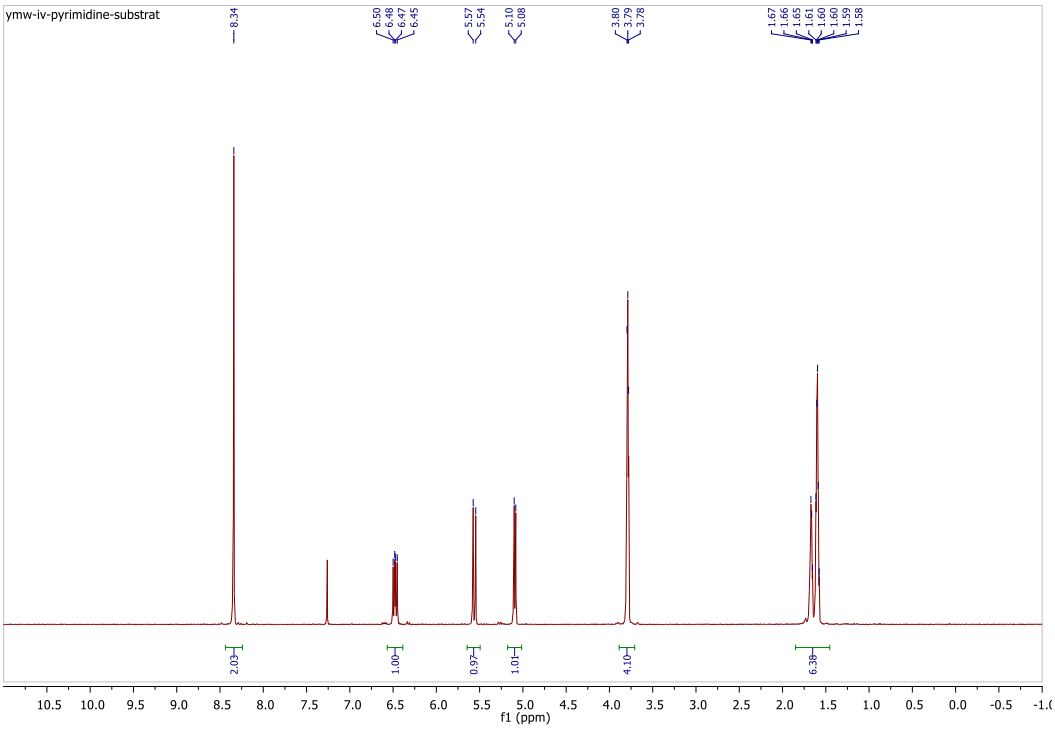
1g

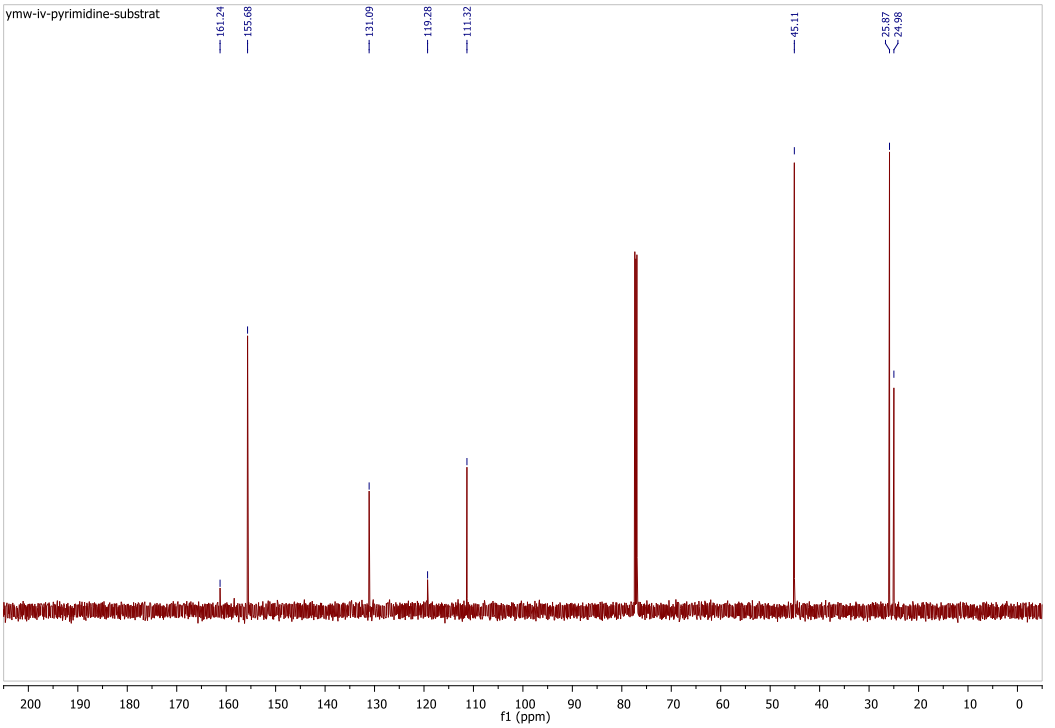

ymw-iv-ester-substrat
8.03
7.88
7.87
7.57
7.56
7.39
6.76
6.75
6.73
5.83
5.80
5.32
5.30
1.61
1.03
1.02
1.01
1.05
1.00
1.00
1.00
9.63
f1 (ppm)

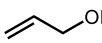

ymw-iv-ester-substrat
165.82
137.81
136.26
132.47
130.12
128.82
128.53
127.37
114.99
81.24
28.33
f1 (ppm)



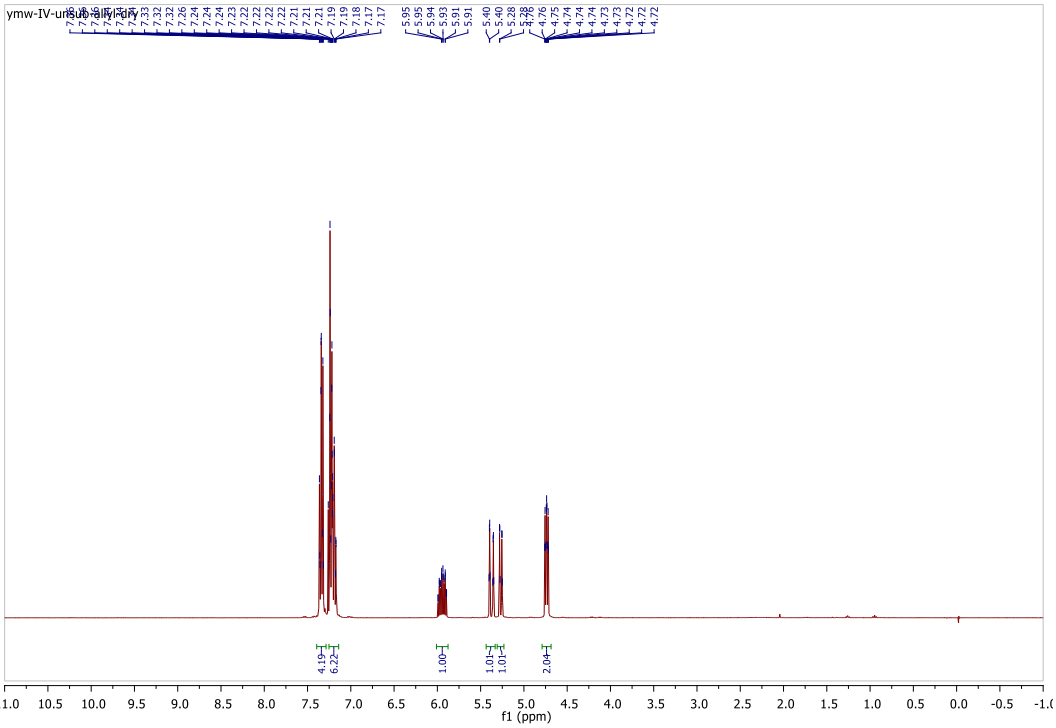
1h

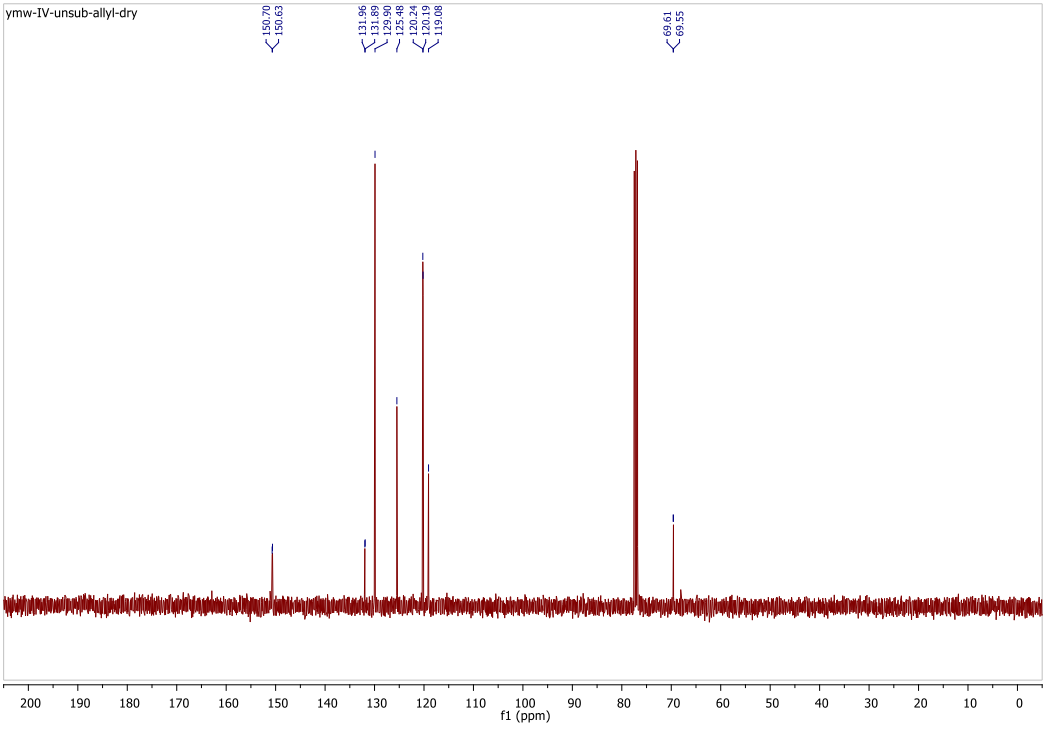

ymw-iv-pyrimidine-substrat
8.34
6.50
6.48
6.47
6.45
5.57
5.54
5.10
5.08
3.80
3.79
3.78
1.67
1.66
1.65
1.61
1.60
1.60
1.59
1.58
2.03
1.00
0.97
1.01
4.10
6.38
f1 (ppm)

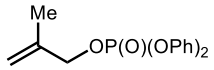

ymw-iv-pyrimidine-substrat
161.24
155.68
131.09
119.28
111.32
45.11
25.87
24.98
f1 (ppm)


OP(O)(OPh)2

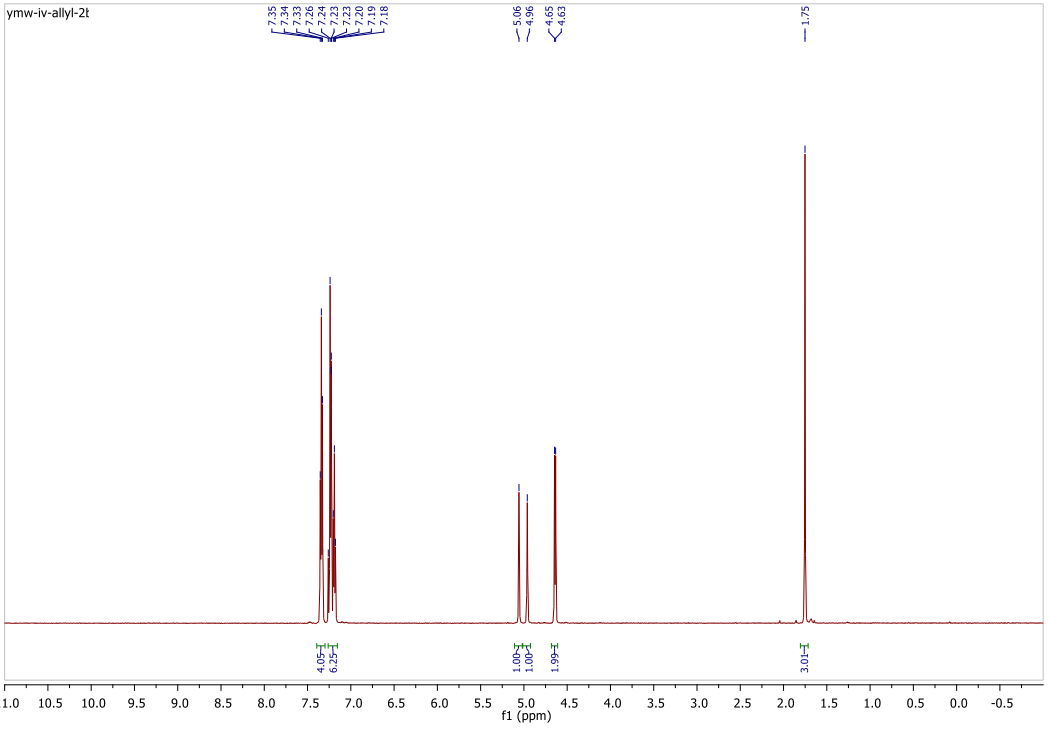
2a

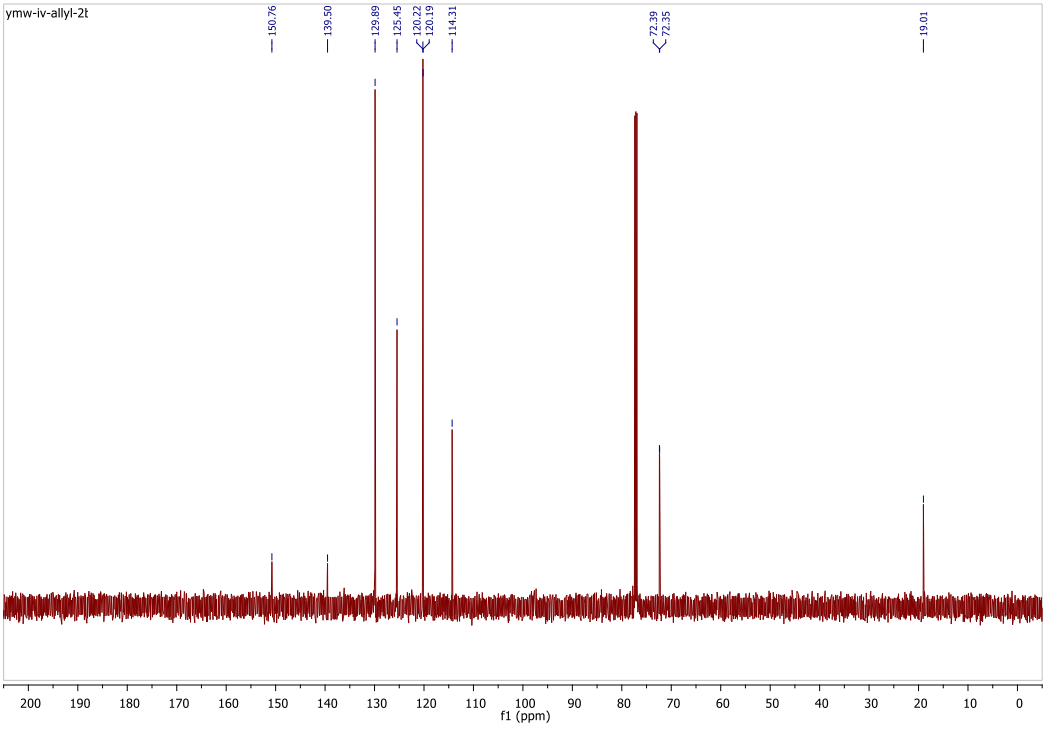

ymw-IV-unsub-allyl-dry
f1 (ppm)

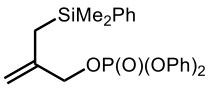

ymw-IV-unsub-allyl-dry
150.70
150.63
131.96
131.89
129.90
125.48
120.24
120.19
119.08
69.61
69.55
f1 (ppm)


Me
OP(O)(OPh)2

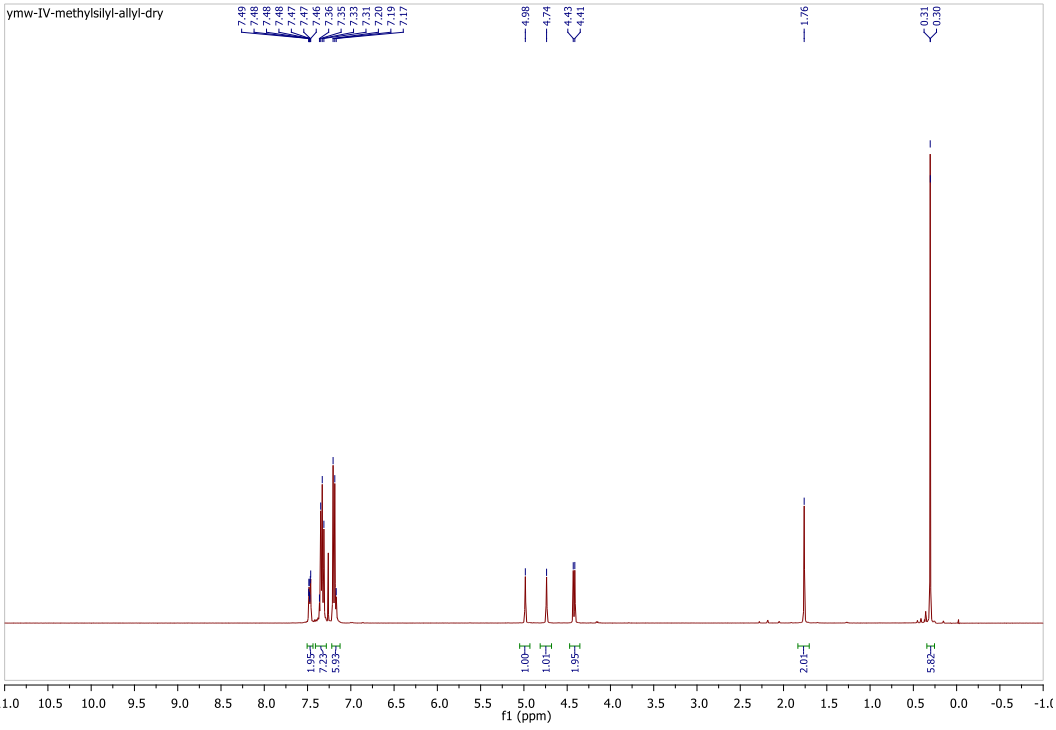
2b

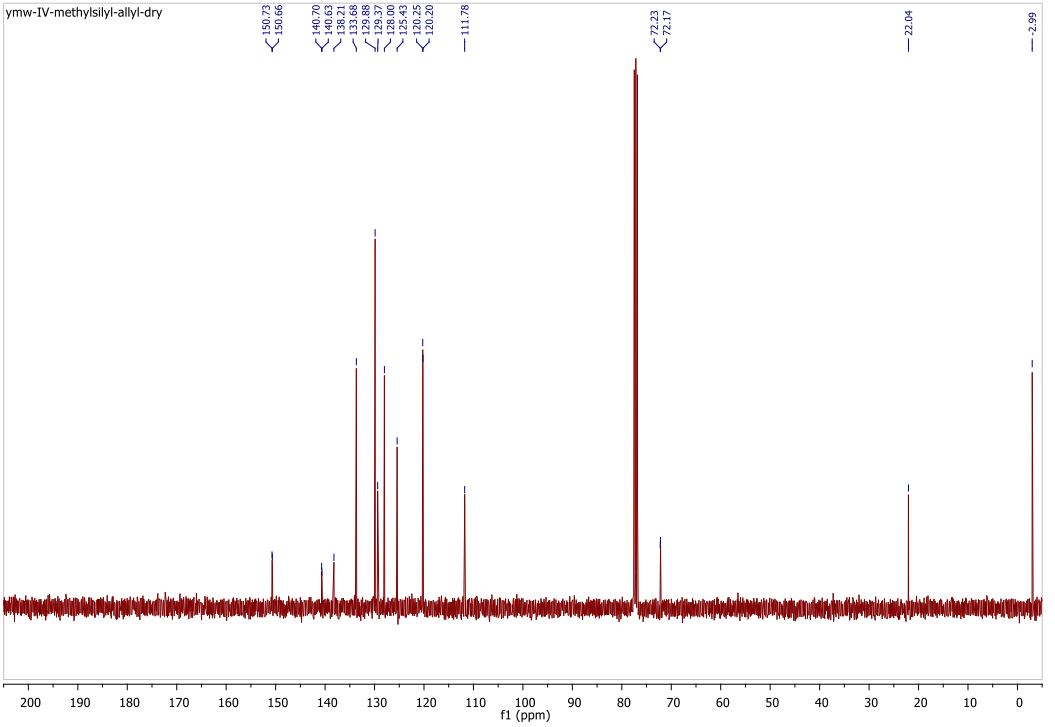

ymw-iv-allyl-2t
7.35
7.34
7.33
7.26
7.24
7.23
7.23
7.20
7.19
7.18
5.06
4.96
4.65
4.63
1.75
4.05
6.25
1.00
1.00
1.99
3.01
f1 (ppm)

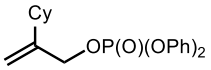

ymw-iv-allyl-2t
150.76
139.50
129.89
125.45
120.22
120.19
114.31
72.39
72.35
19.01
f1 (ppm)


SiMe2Ph
OP(O)(OPh)2

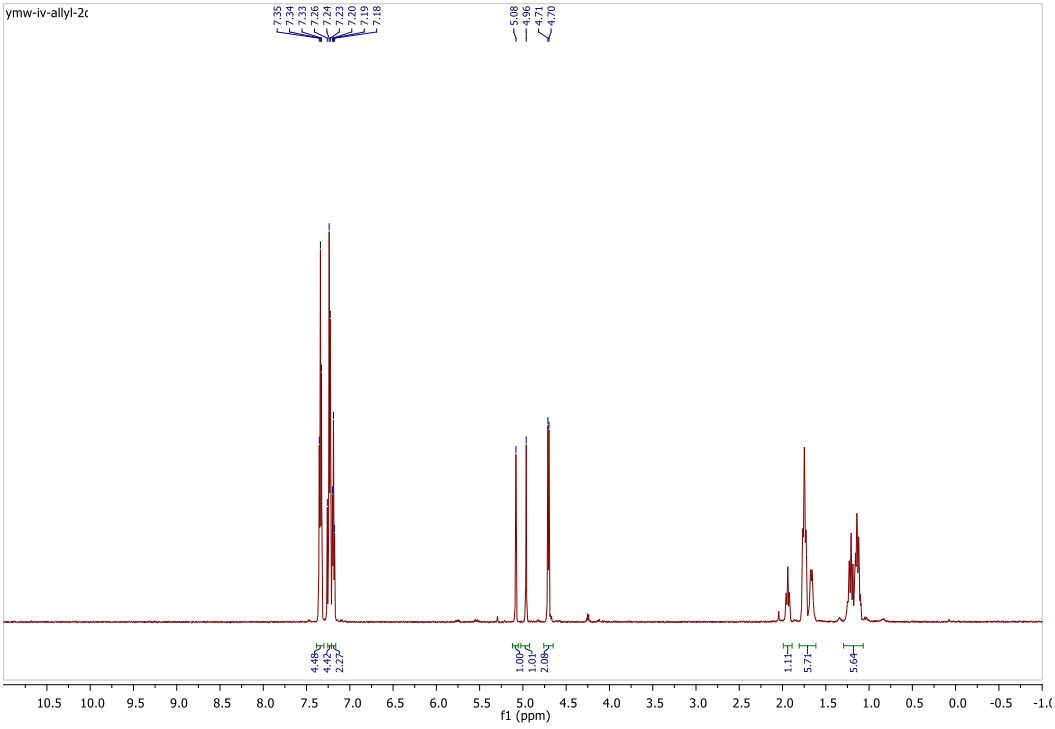
2c

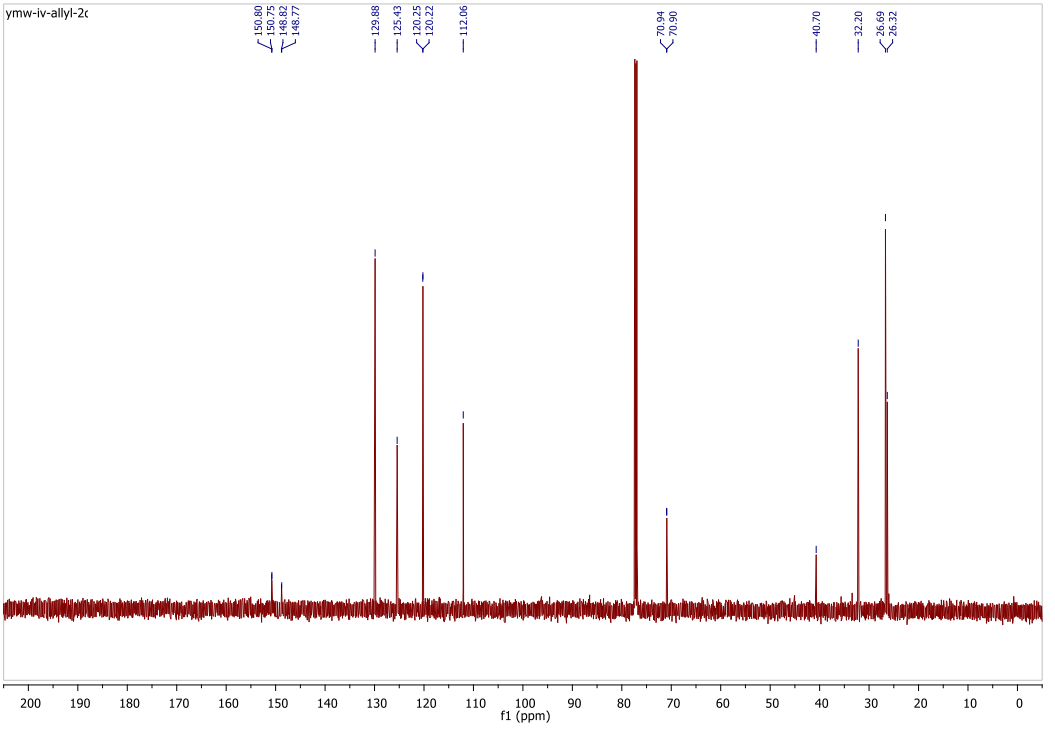

ymw-IV-methylsilyl-allyl-dry
f1 (ppm)

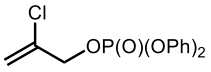

ymw-IV-methylsilyl-allyl-dry
f1 (ppm)


Cy
OP(O)(OPh)2

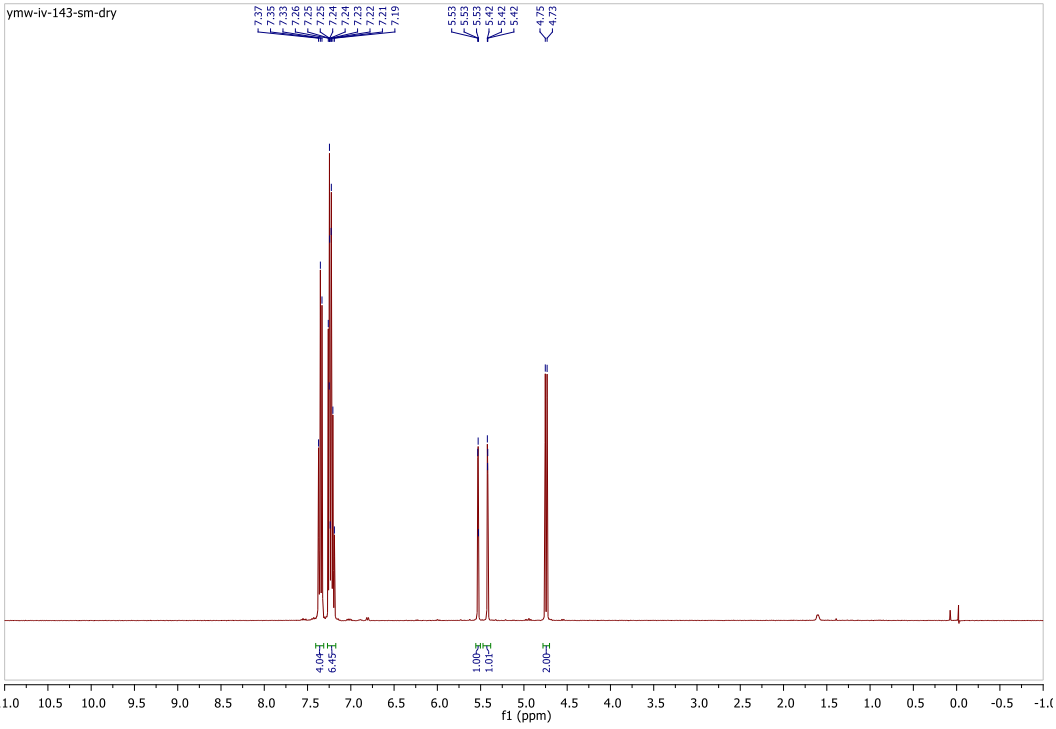
2d

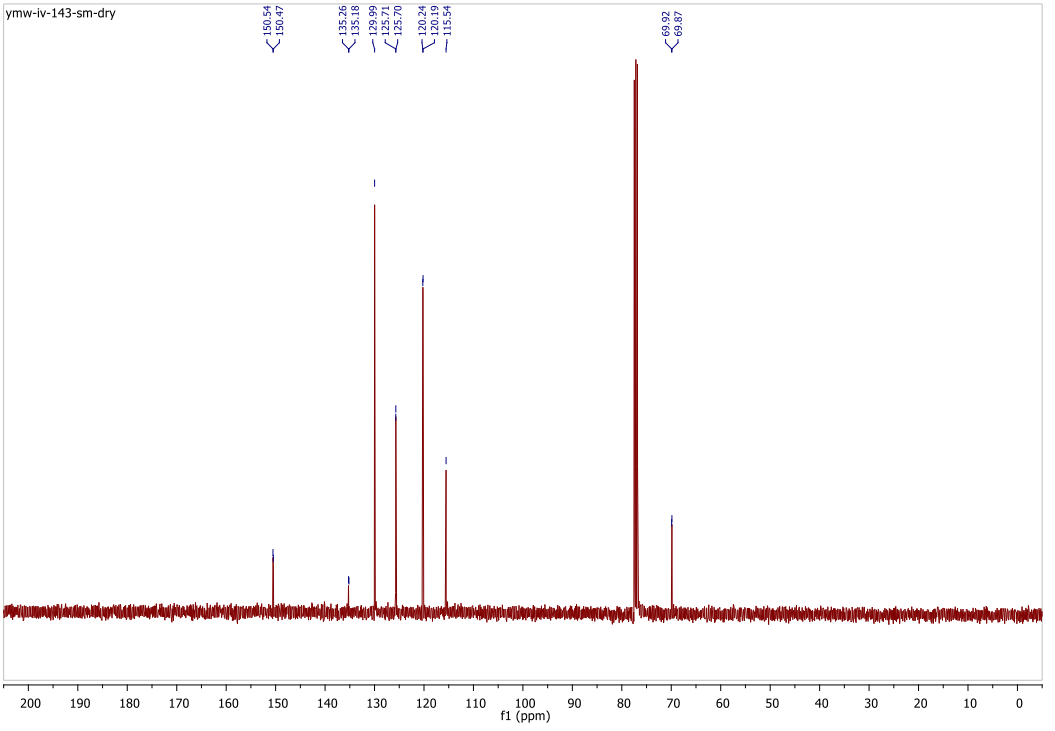

ymw-iv-allyl-2c
7.35
7.34
7.33
7.26
7.24
7.23
7.20
7.19
7.18
5.08
4.96
4.71
4.70
4.48
4.43
2.25
1.00
1.01
2.08
1.11
5.71
5.64
f1 (ppm)

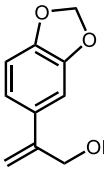

ymw-iv-allyl-2c
150.80
150.75
148.82
148.77
129.88
125.43
120.25
120.22
112.06
70.94
70.90
40.70
32.20
26.69
26.32
f1 (ppm)


Cl
OP(O)(OPh)2

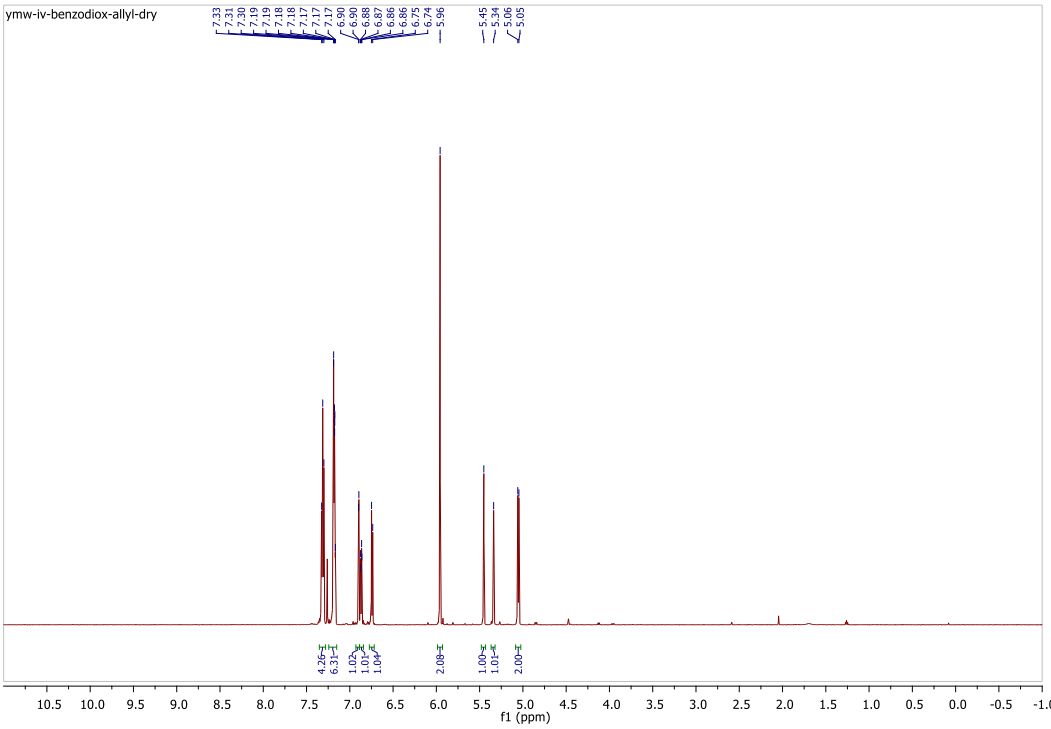
2e

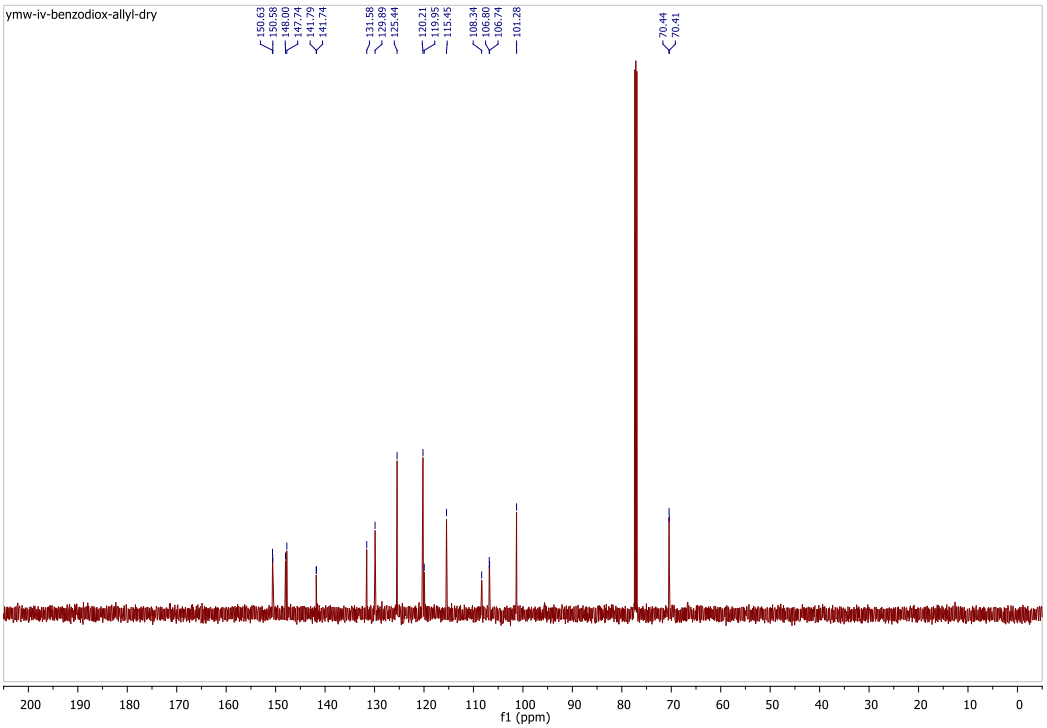

ymw-iv-143-sm-dry
7.37
7.35
7.33
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.21
7.19
5.53
5.53
5.53
5.42
5.42
5.42
4.75
4.73
4.04
6.45
1.00
1.01
2.00
f1 (ppm)

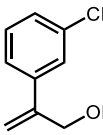

ymw-iv-143-sm-dry
150.54
150.47
135.26
135.18
129.99
125.71
125.70
120.24
120.19
115.54
69.92
69.87
f1 (ppm)


O
O
OP(O)(OPh)2

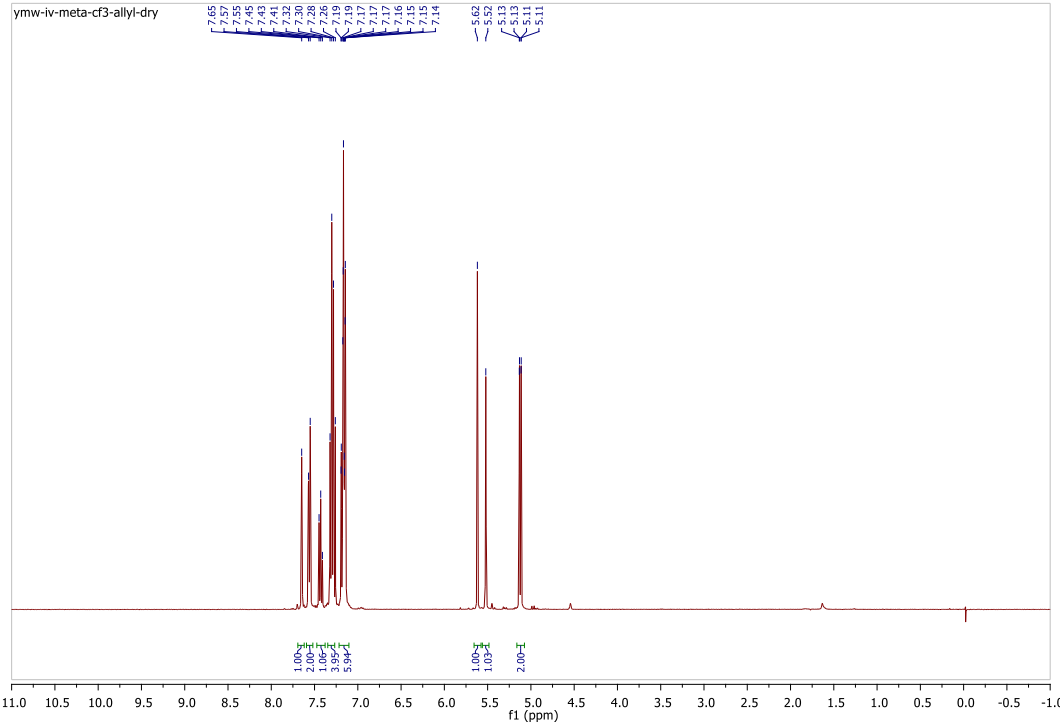
2f

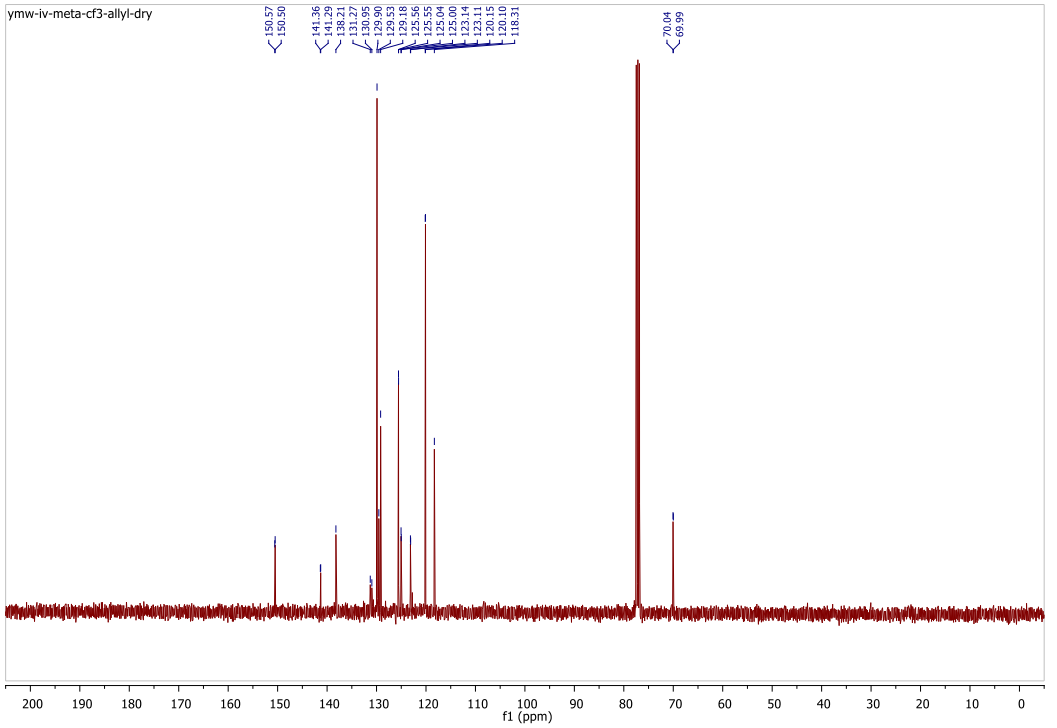

ymw-iv-benzodiox-allyl-dry
7.33
7.31
7.30
7.19
7.19
7.18
7.18
7.17
7.17
7.17
7.17
6.90
6.90
6.88
6.87
6.86
6.86
6.75
6.74
5.96
5.45
5.44
5.06
5.05
4.26
6.31
1.02
1.01
1.04
2.08
1.00
1.01
2.00
f1 (ppm)

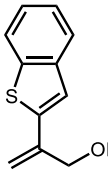

ymw-iv-benzodiox-allyl-dry
150.63
150.58
148.00
147.74
141.79
141.74
131.58
129.89
125.44
120.21
119.95
115.45
108.34
106.80
106.74
101.28
70.44
70.41
f1 (ppm)


CF3
OP(O)(OPh)2

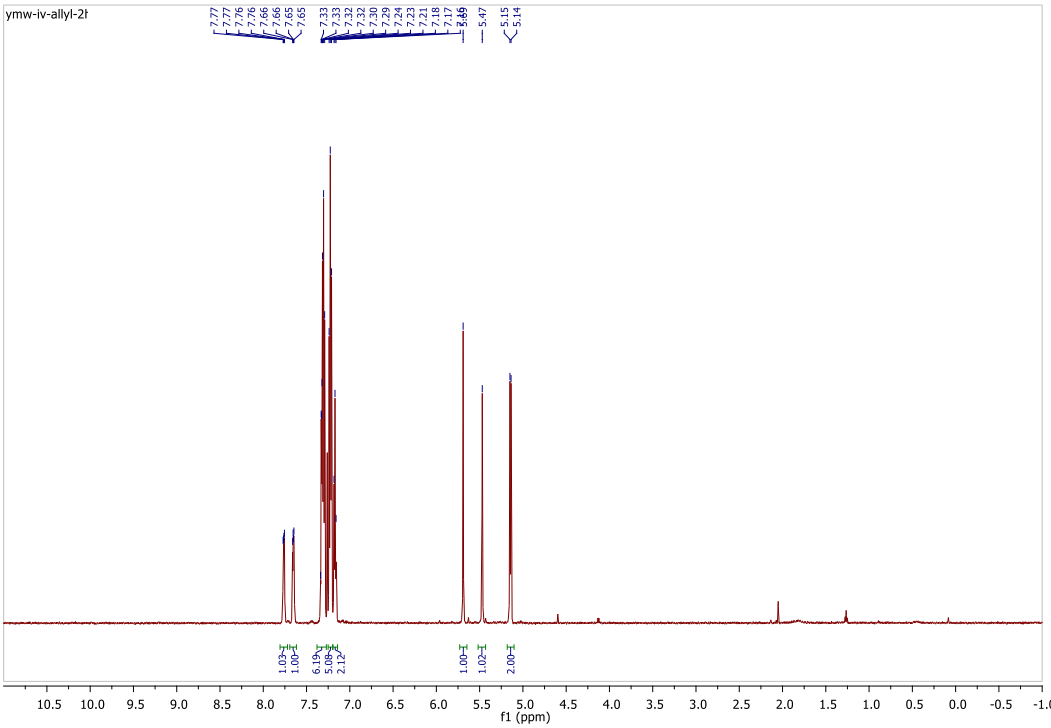
2g

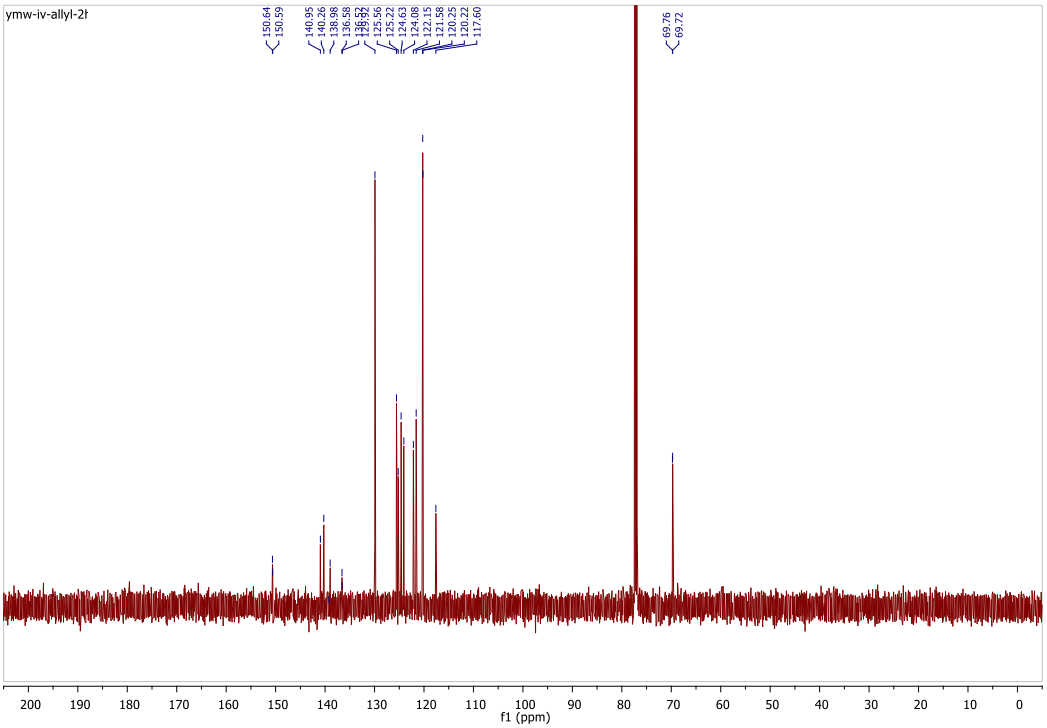

ymw-iv-meta-cf3-allyl-dry
7.65
7.57
7.55
7.45
7.43
7.41
7.32
7.30
7.28
7.26
7.19
7.19
7.17
7.17
7.16
7.15
7.15
7.14
5.62
5.52
5.13
5.13
5.11
5.11
1.00
2.00
1.06
1.94
5.94
1.00
1.03
2.00
f1 (ppm)

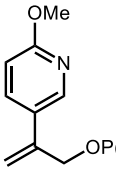

ymw-iv-meta-cf3-allyl-dry
150.57
150.50
141.36
141.29
138.21
131.27
130.95
129.90
129.53
129.18
125.56
125.55
125.04
125.00
123.14
123.11
120.15
120.10
118.31
70.04
69.99
f1 (ppm)


S
OP(O)(OPh)2

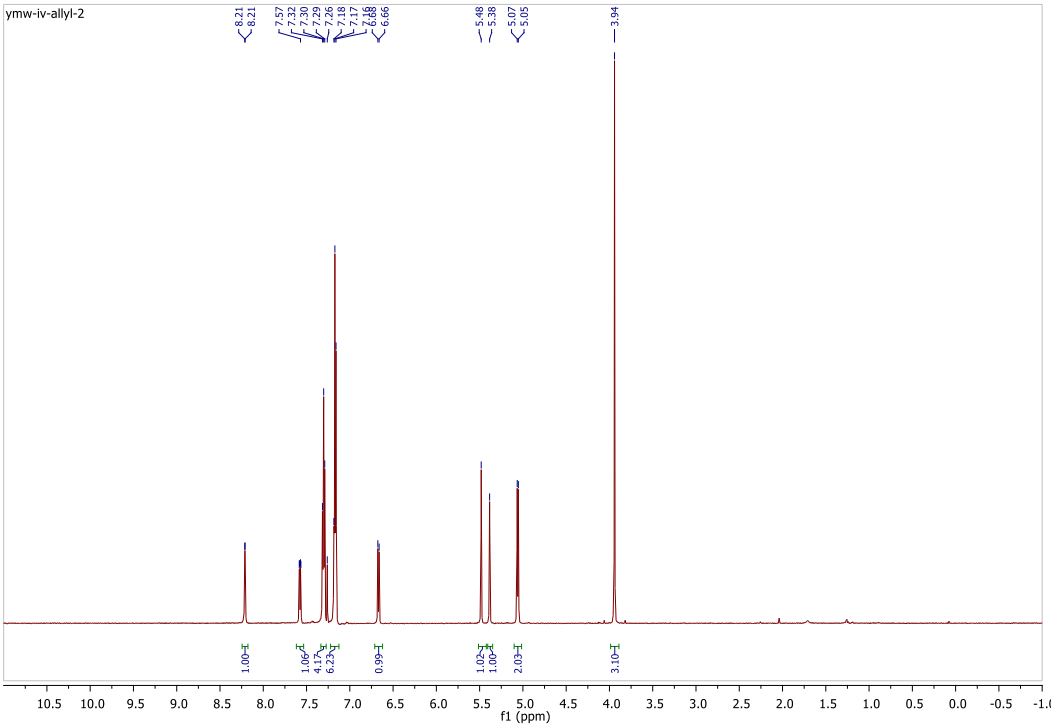
2h

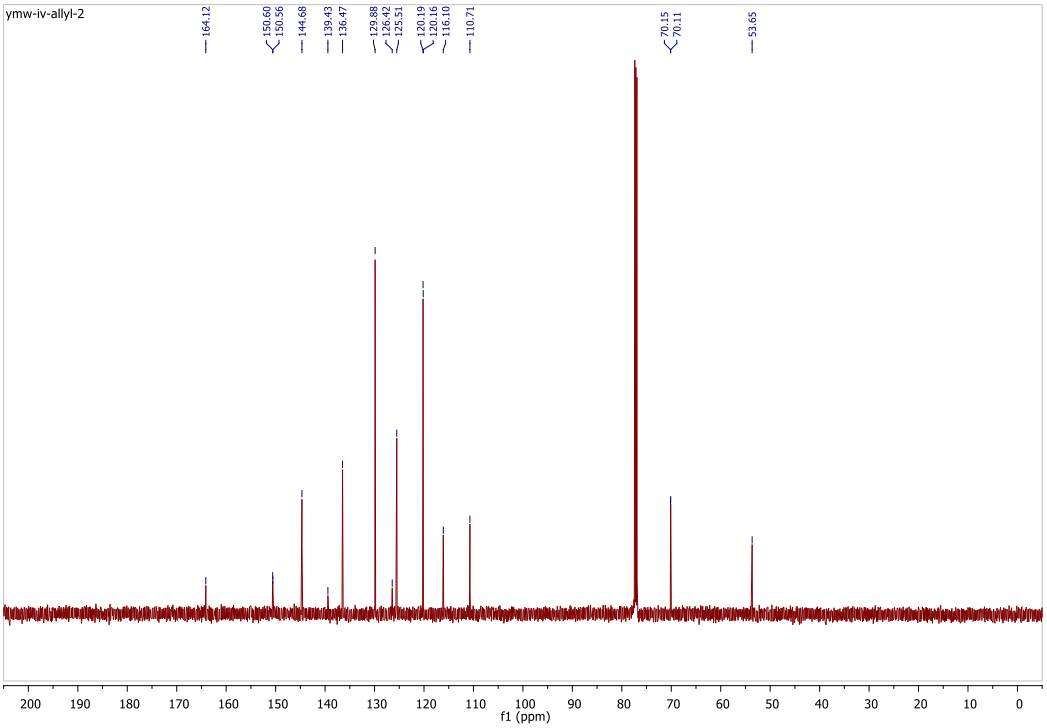

ymw-iv-allyl-2f
7.77
7.77
7.76
7.76
7.66
7.66
7.65
7.65
7.33
7.33
7.32
7.32
7.30
7.29
7.24
7.23
7.21
7.18
7.17
5.47
5.15
5.14
1.03
1.00
6.19
5.09
2.12
1.00
1.02
2.00
f1 (ppm)

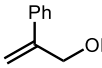

ymw-iv-allyl-2f
150.64
150.59
140.95
140.26
138.98
136.58
125.56
125.22
124.63
124.08
122.15
121.58
120.25
120.22
117.60
69.76
69.72
f1 (ppm)


OMe
N
OP(O)(OPh)2

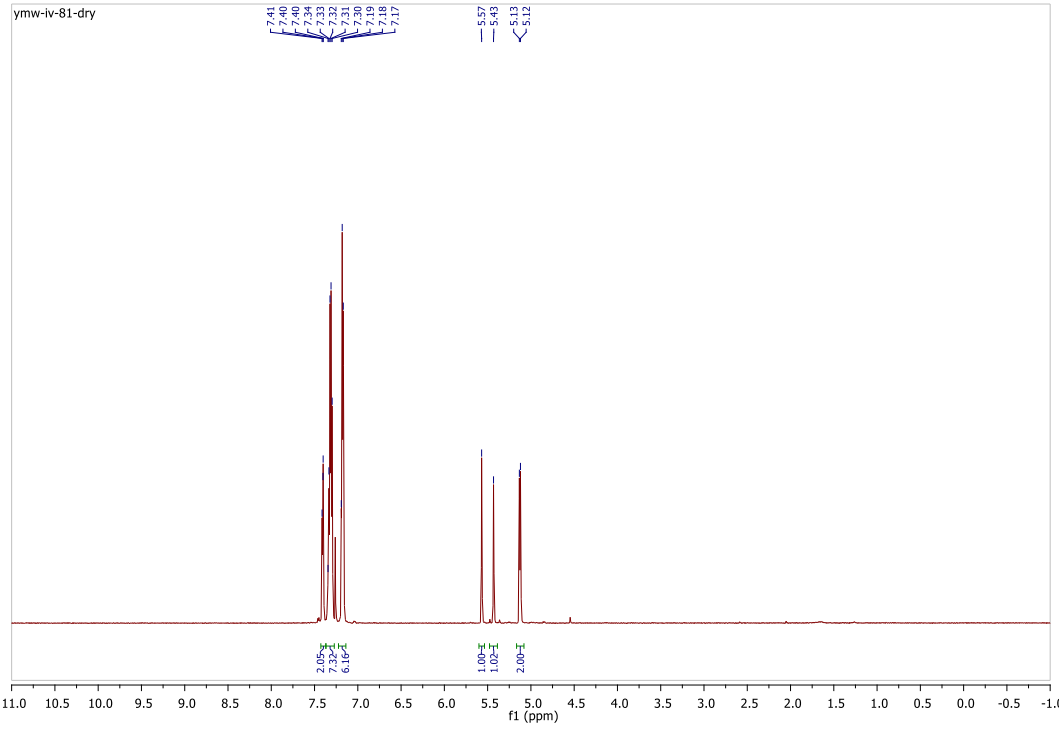
2i

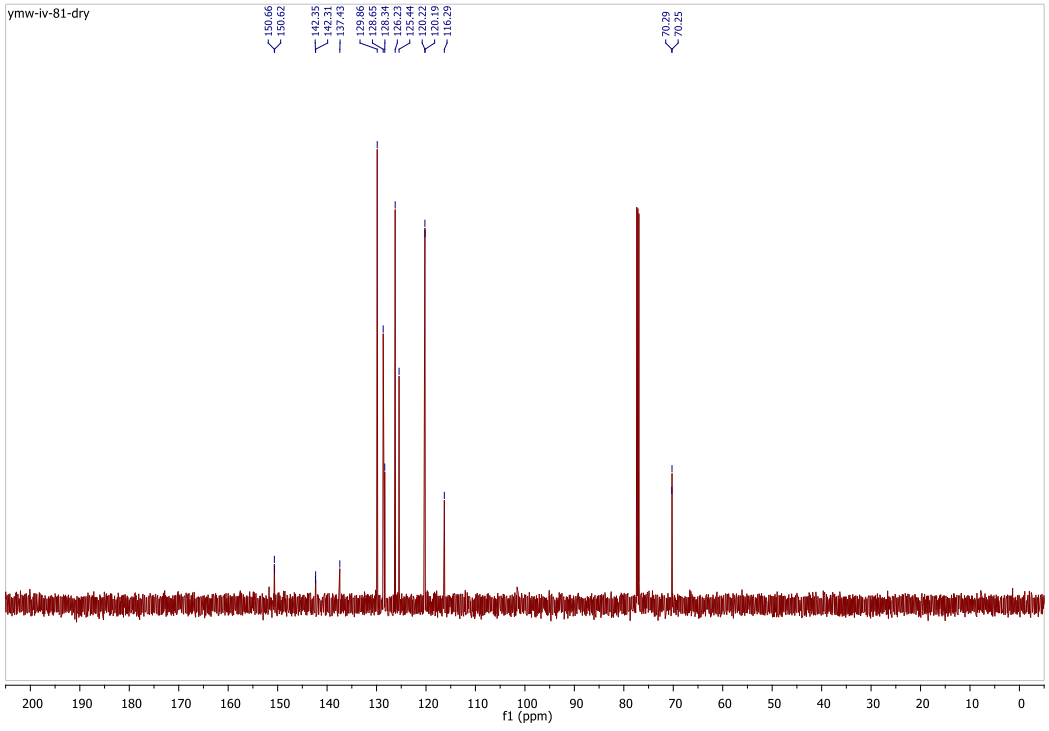

ymw-iv-allyl-2
8.21
8.21
7.57
7.32
7.30
7.29
7.26
7.18
7.17
7.16
6.88
6.66
5.48
5.38
5.07
5.05
3.94
1.00
1.06
4.17
6.23
0.99
1.02
1.00
2.03
3.10
f1 (ppm)

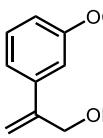

ymw-iv-allyl-2
164.12
150.60
150.56
144.68
139.43
136.47
129.88
126.42
125.51
120.19
120.16
116.10
110.71
70.15
70.11
53.65
f1 (ppm)


Ph
OP(O)(OPh)2

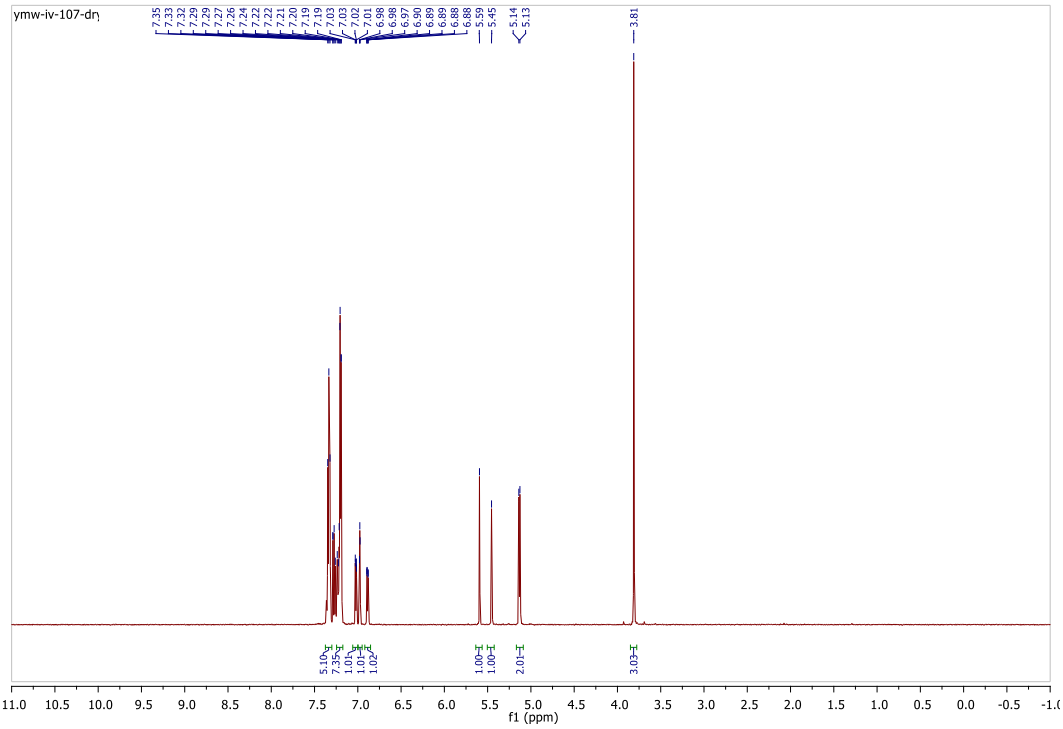
2j

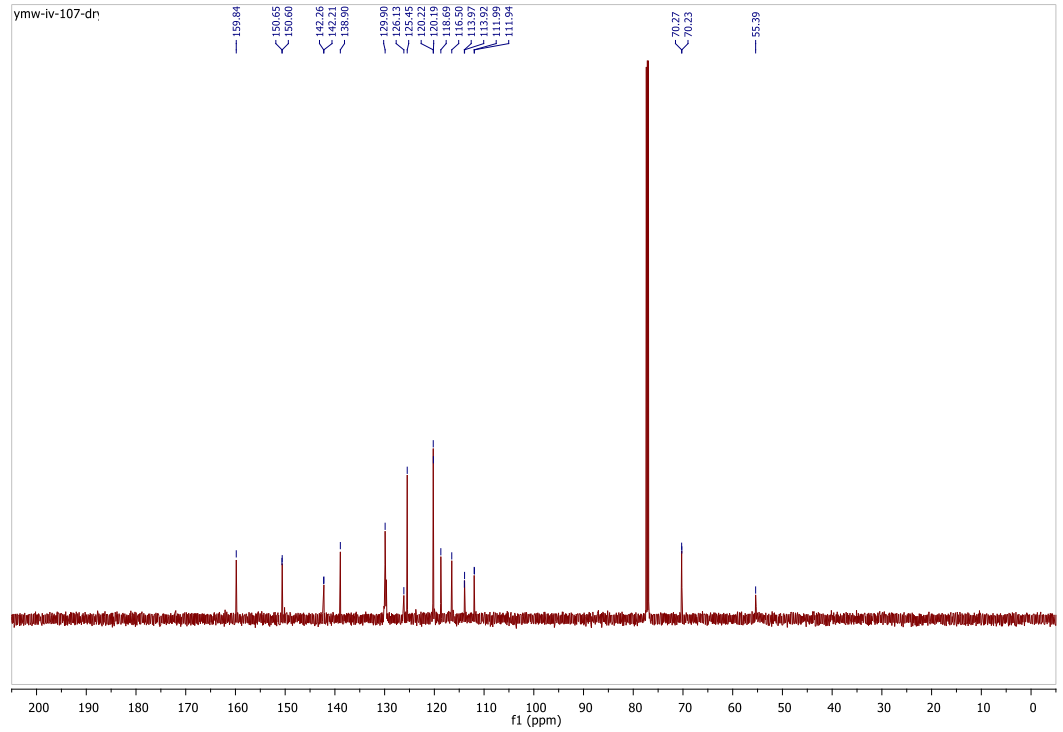

ymw-iv-81-dry
7.41
7.40
7.40
7.34
7.33
7.32
7.31
7.30
7.19
7.18
7.17
5.57
5.43
5.13
5.12
2.05
7.32
6.16
1.00
1.02
2.00
f1 (ppm)

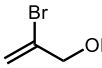

ymw-iv-81-dry
150.66
150.62
142.35
142.31
137.43
129.86
128.65
128.34
126.23
125.44
120.22
120.19
116.29
70.39
70.25
f1 (ppm)



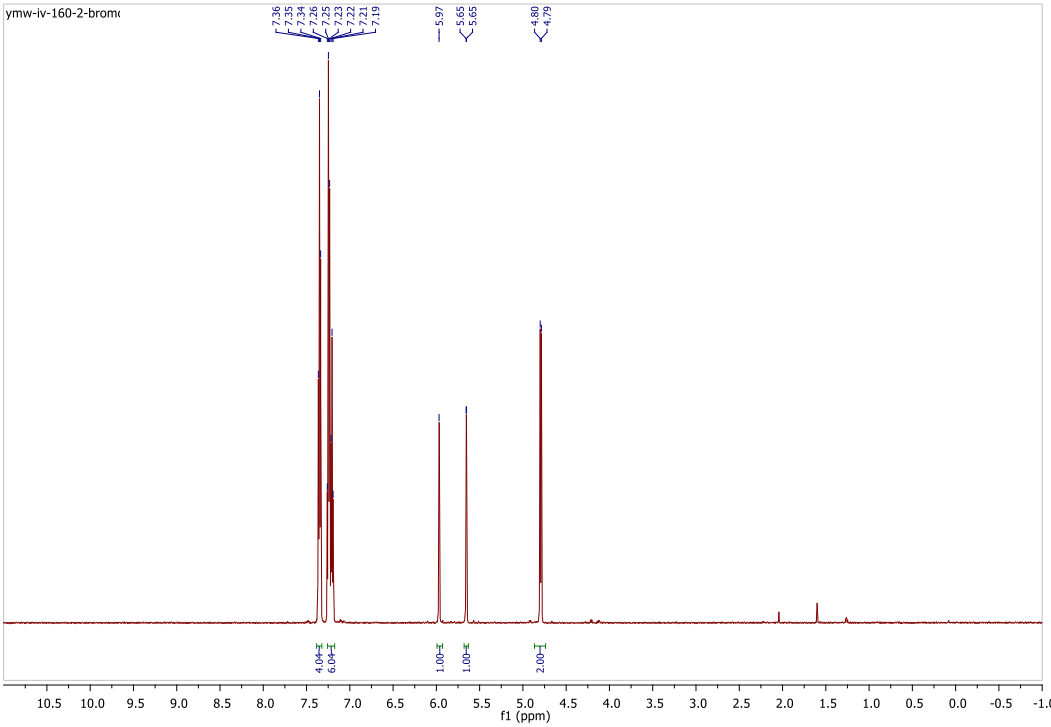
2k

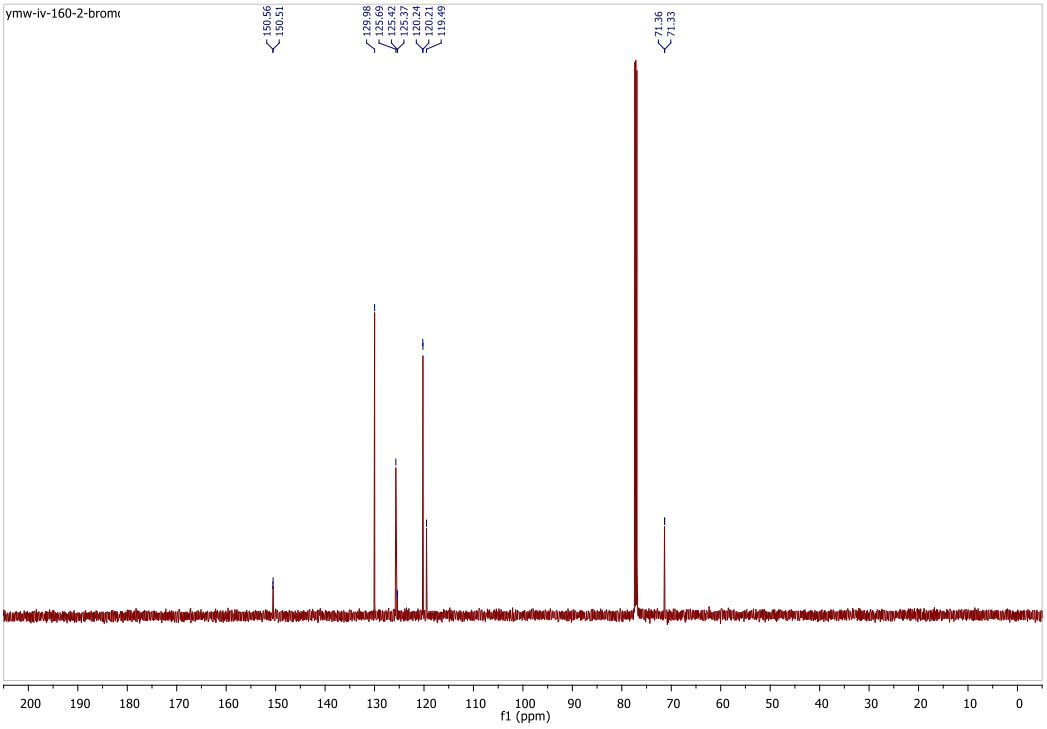


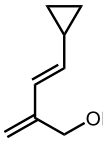



Br
OP(O)(OPh)2

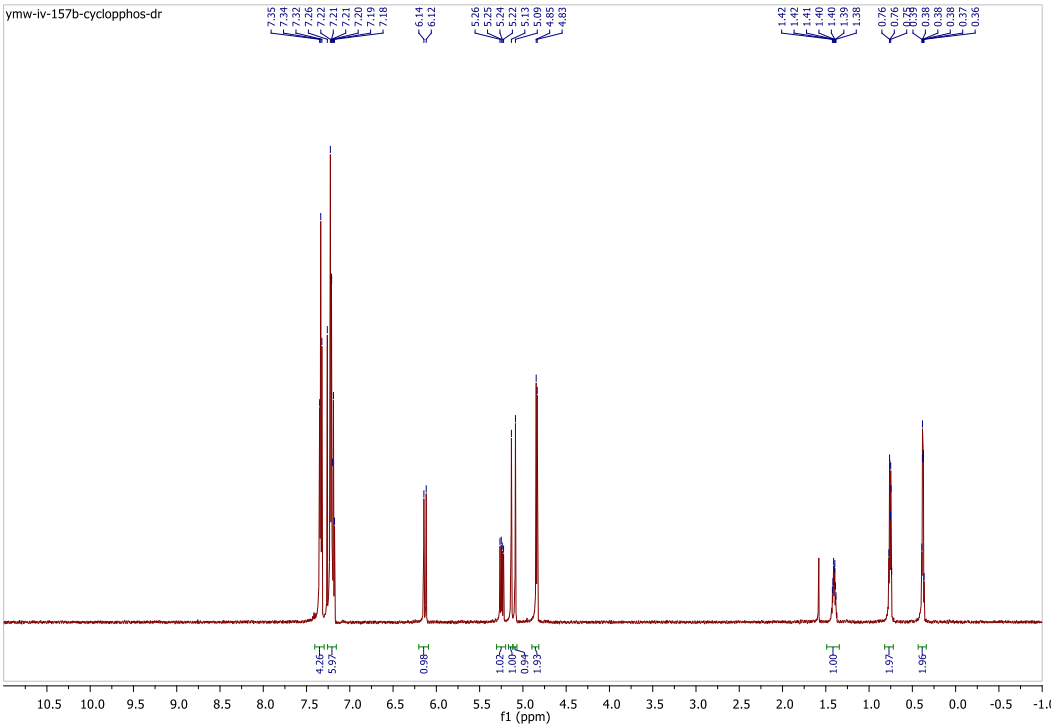
2l

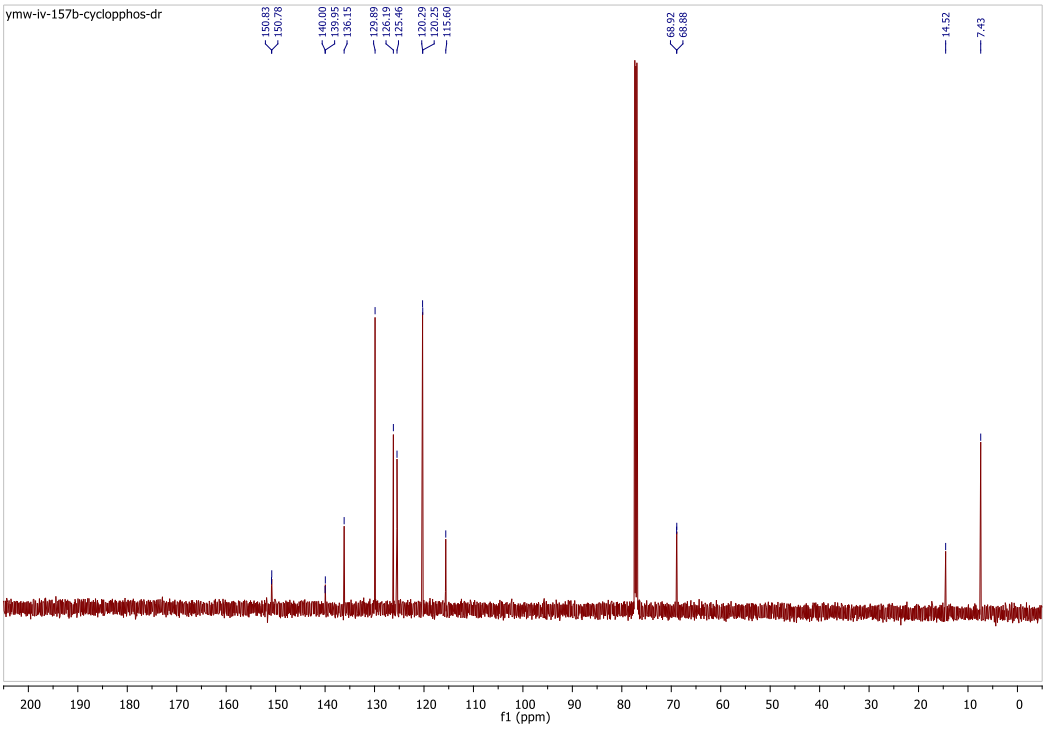

ymw-iv-160-2-brom
7.36
7.35
7.34
7.26
7.25
7.23
7.22
7.21
7.19
5.97
5.65
5.65
4.80
4.79
4.04
6.04
1.00
1.00
2.00
f1 (ppm)


ymw-iv-160-2-brom
150.56
150.51
129.98
125.69
125.42
125.37
120.24
120.21
119.49
71.36
71.33
f1 (ppm)


OP(O)(OPh)2

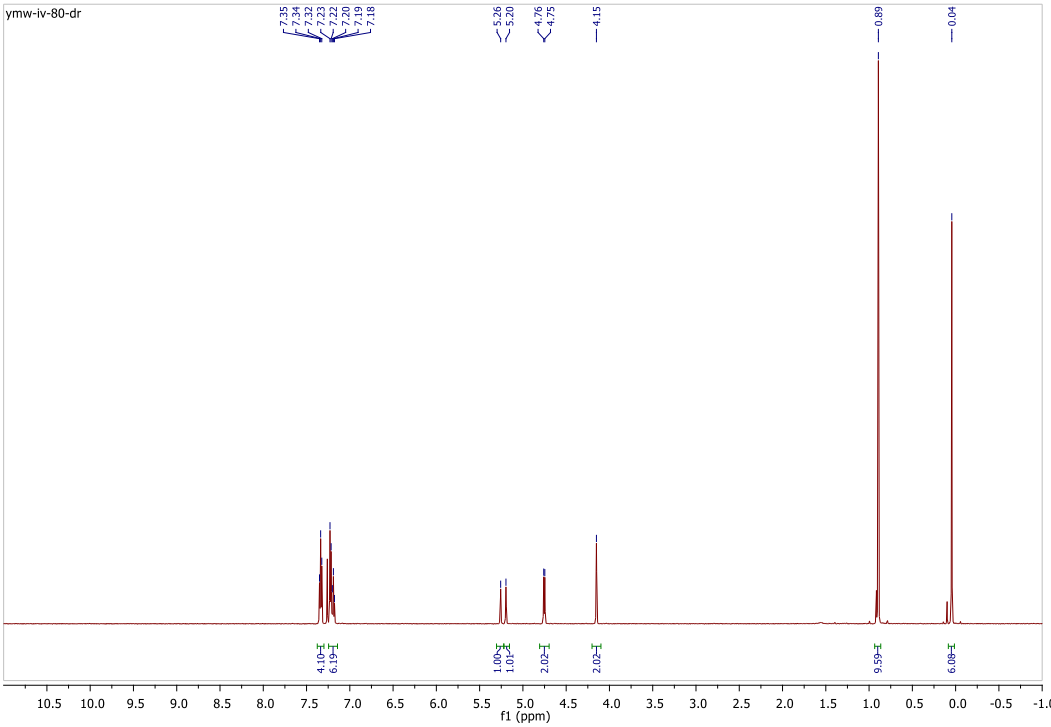
2m

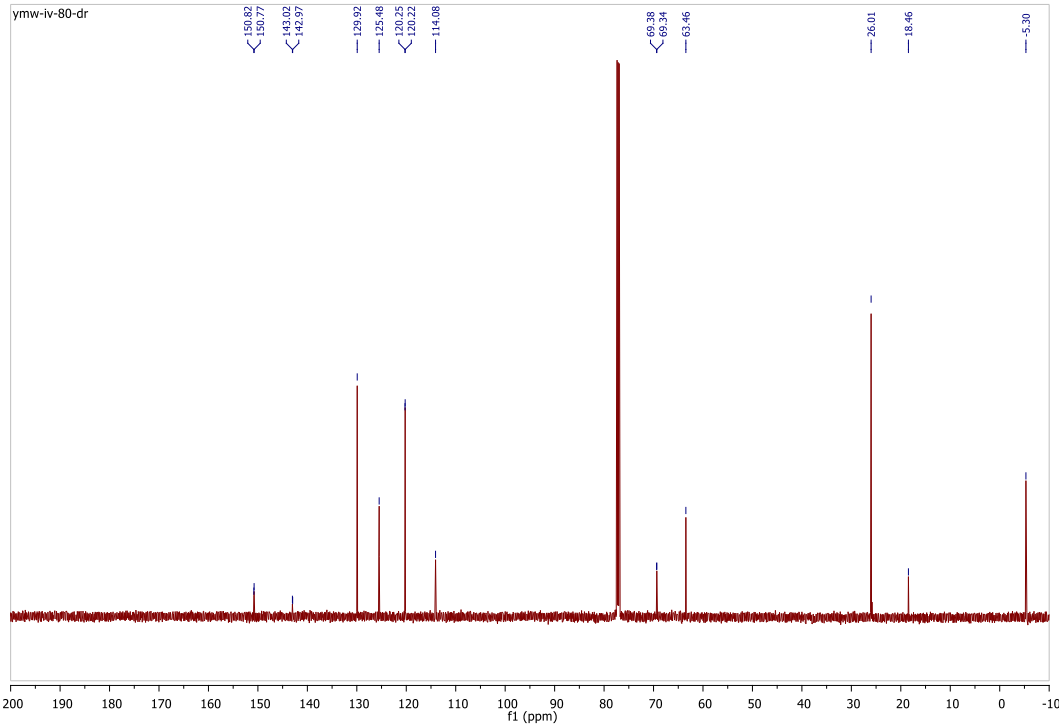

ymw-iv-157b-cyclopphos-dr
7.35
7.34
7.32
7.26
7.22
7.21
7.21
7.20
7.19
7.18
6.14
6.12
5.26
5.25
5.24
5.22
5.13
5.09
4.85
4.83
1.42
1.42
1.41
1.40
1.40
1.39
1.38
0.76
0.76
0.38
0.38
0.38
0.37
0.36
4.26
5.97
0.98
1.02
1.00
0.94
1.93
1.00
1.97
1.96
f1 (ppm)


ymw-iv-157b-cyclopphos-dr
150.83
150.78
140.00
139.95
136.15
129.89
126.19
125.46
120.29
120.25
115.60
68.92
68.88
14.52
7.43
f1 (ppm)


OTBS
OP(O)(OPh)2

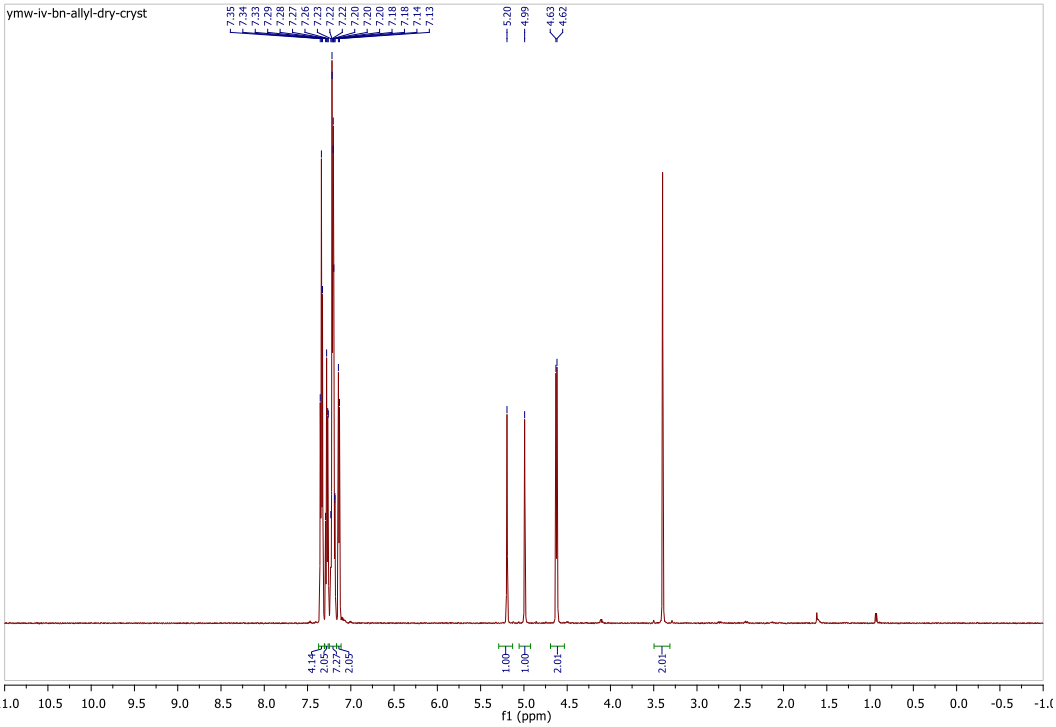
2n

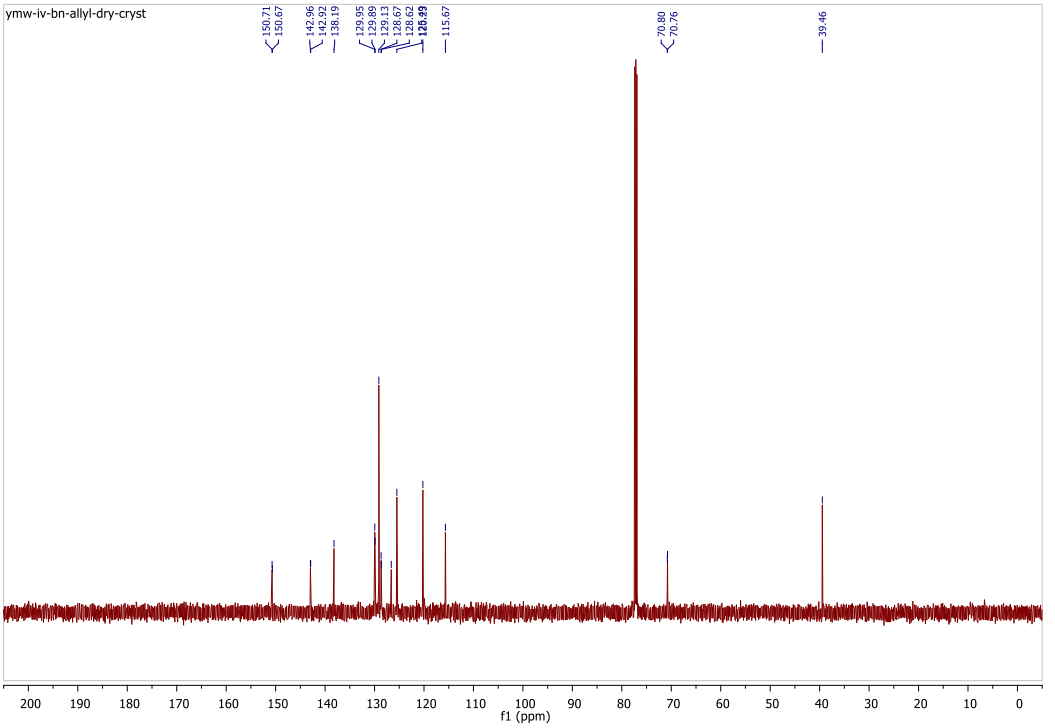

ymw-iv-80-dr
7.35
7.34
7.32
7.23
7.22
7.20
7.19
7.18
5.26
5.20
4.76
4.75
4.15
0.89
0.04
4.10
6.19
1.00
1.01
2.02
2.02
9.59
6.08
f1 (ppm)


ymw-iv-80-dr
150.82
150.77
143.02
142.97
129.92
125.48
120.25
120.22
114.08
69.38
69.34
63.46
26.01
18.46
-5.30
f1 (ppm)

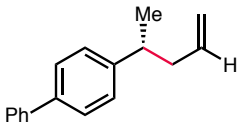

Ph
OP(O)(OPh)2

2o


ymw-iv-bn-allyl-dry-cryst
7.35
7.34
7.33
7.29
7.28
7.27
7.26
7.23
7.22
7.21
7.20
7.20
7.20
7.18
7.18
7.14
7.13
5.20
4.99
4.63
4.62
4.14
2.05
7.27
2.05
1.00
1.00
2.01
2.01
f1 (ppm)

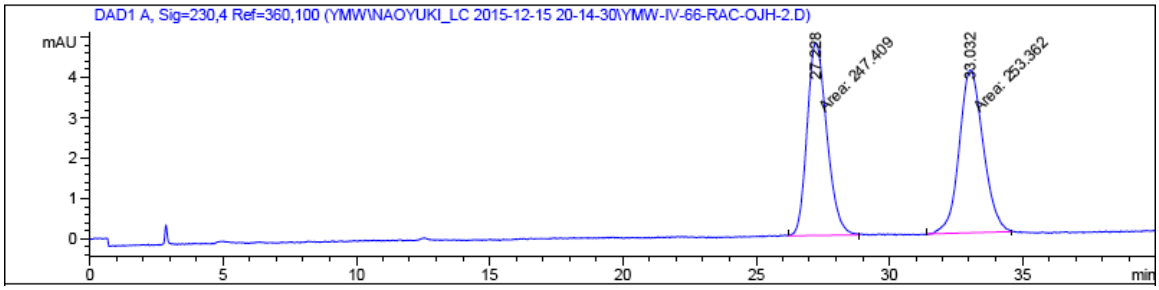

ymw-iv-bn-allyl-dry-cryst
150.71
150.67
142.96
142.92
138.19
129.95
129.89
129.13
128.67
128.62
125.49
125.43
115.67
70.80
70.76
39.46
f1 (ppm)

VIII. Copies of HPLC Traces for Hydroallylation Products



3a

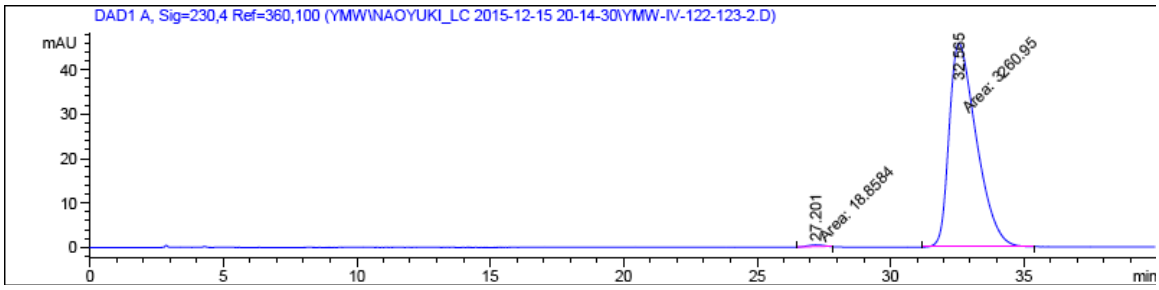
Racemic trace:



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

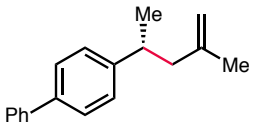
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.228	MM	0.8618	247.40915	4.78464	49.4056
2	33.032	MM	1.0458	253.36198	4.03784	50.5944

Enantioenriched trace:



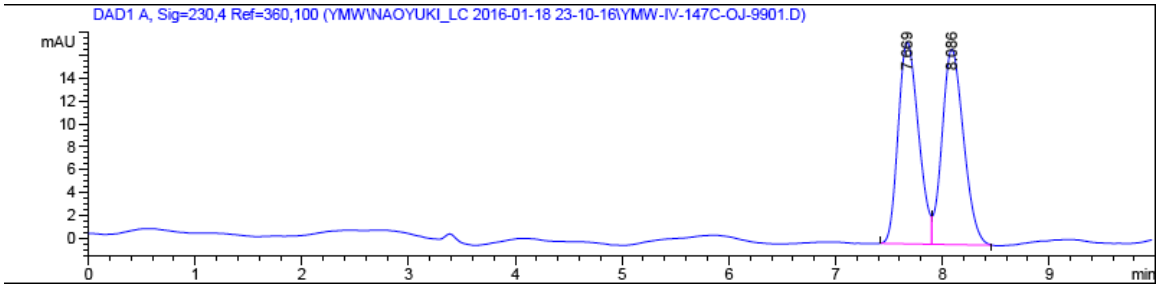
Signal 1: DAD1 A, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.201	MM	0.6986	18.85841	4.49920e-1	0.5750
2	32.565	MM	1.1863	3260.94824	45.81387	99.4250



3b

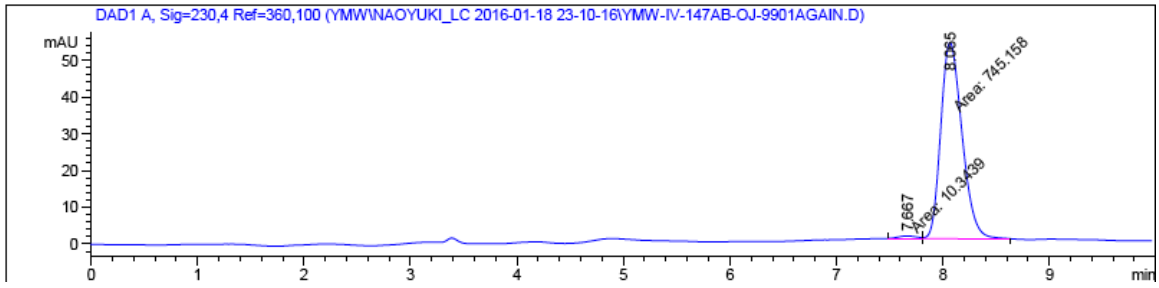
Racemic trace:



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

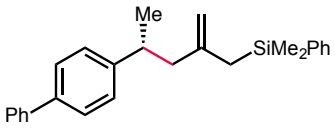
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.669	BV	0.2067	234.26471	17.66362	49.3615
2	8.086	VB	0.2160	240.32545	17.09696	50.6385

Enantioenriched trace:



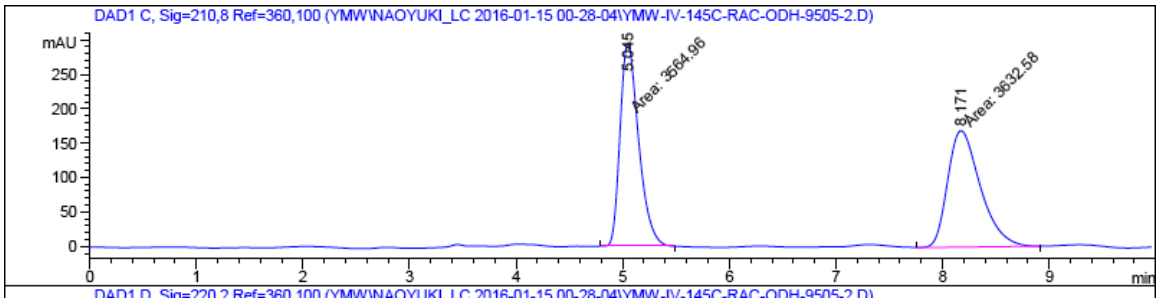
Signal 1: DAD1 A, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.667	MF	0.2131	10.34394	8.08946e-1	1.3691
2	8.065	FM	0.2322	745.15753	53.47482	98.6309



3c

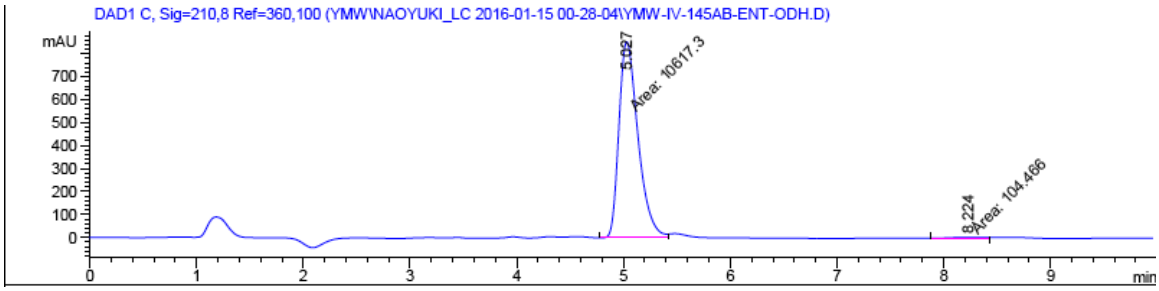
Racemic trace:



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

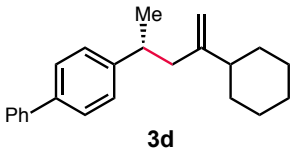
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.045	MM	0.2014	3564.96094	294.96338	49.5303
2	8.171	MM	0.3569	3632.57617	169.62183	50.4697

Enantioenriched trace:



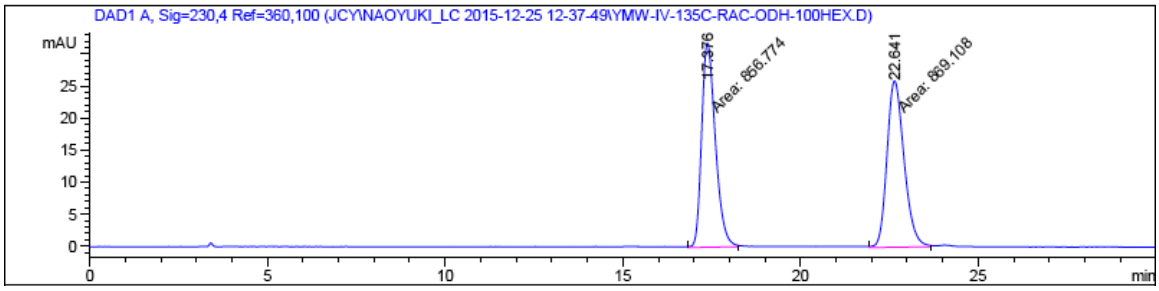
Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.027	MF	0.2072	1.06173e4	853.88837	99.0257
2	8.224	MF	0.3587	104.46644	4.85378	0.9743



3d

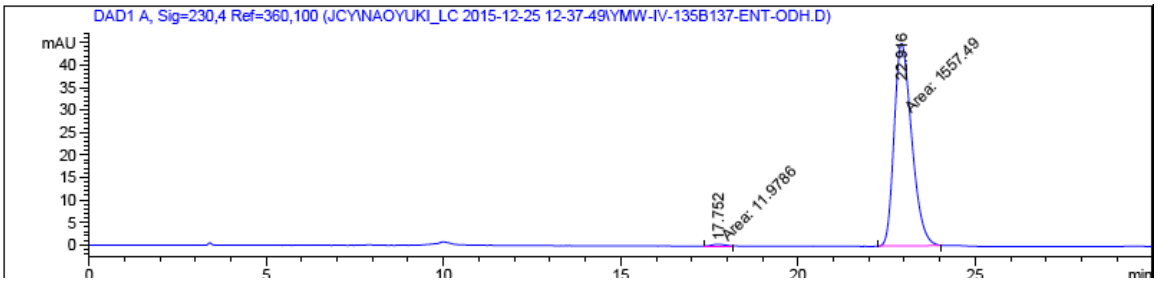
Racemic trace:



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

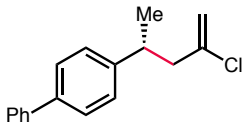
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.376	MM	0.4481	856.77429	31.86580	49.6427
2	22.641	MM	0.5578	869.10834	25.96797	50.3573

Enantioenriched trace:



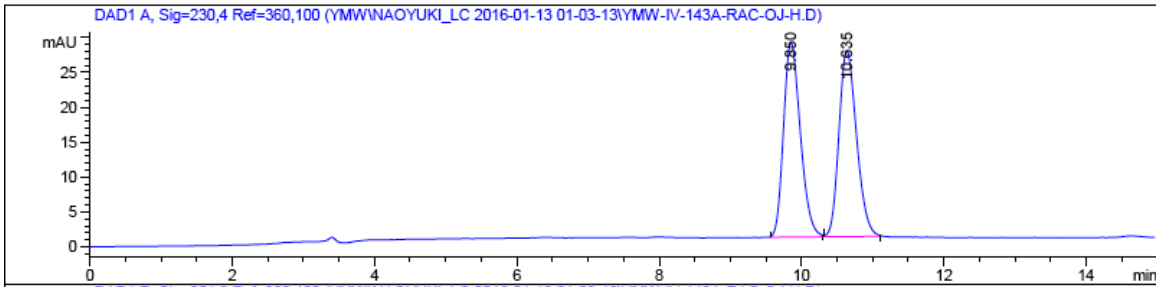
Signal 1: DAD1 A, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.752	MM	0.4542	11.97862	4.39590e-1	0.7632
2	22.916	MM	0.5768	1557.48755	45.00037	99.2368



3e

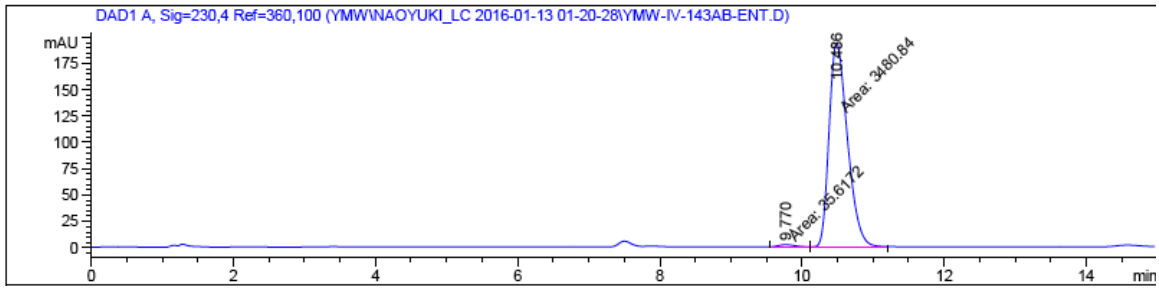
Racemic trace:



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

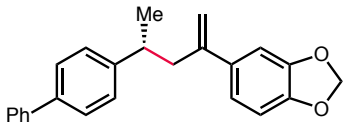
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.850	BB	0.2538	458.29398	27.88170	49.8728
2	10.635	BB	0.2673	460.63129	26.69983	50.1272

Enantioenriched trace:



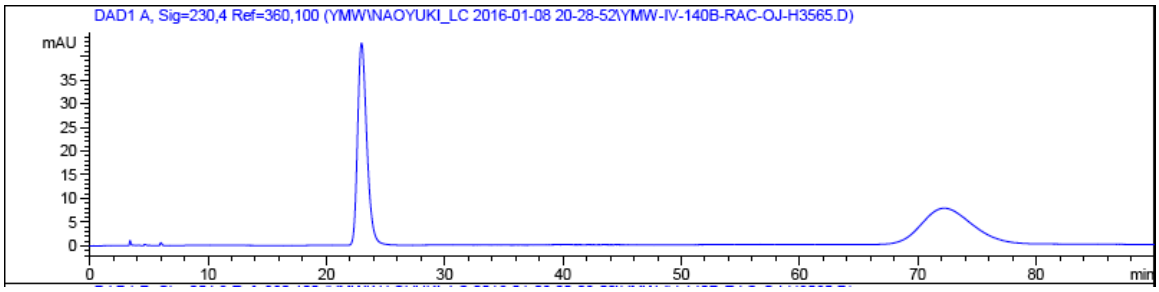
Signal 1: DAD1 A, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.770	MF	0.2745	35.61716	2.16233	1.0129
2	10.486	FM	0.2997	3480.84326	193.56577	98.9871



3f

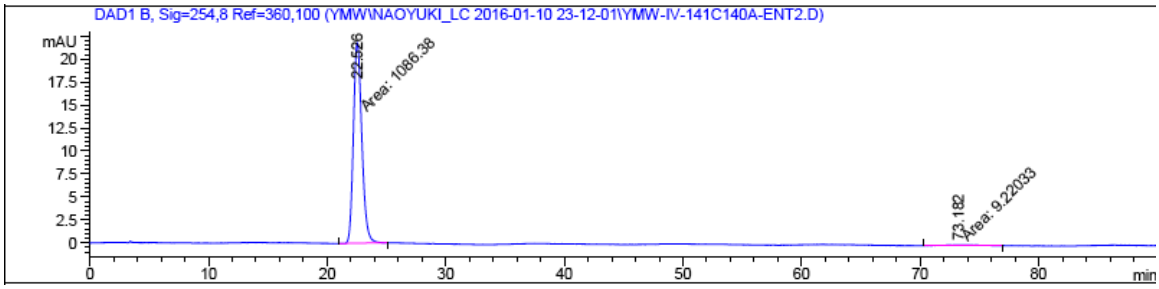
Racemic trace:



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

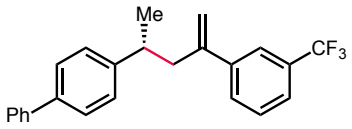
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.968	MM	0.9077	5058.63770	92.88747	50.1160
2	72.268	MM	5.0452	5035.22217	16.63361	49.8840

Enantioenriched trace:



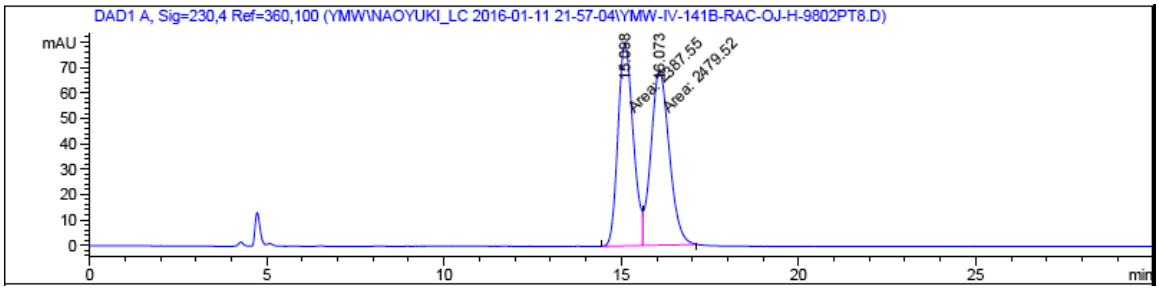
Signal 2: DAD1 B, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.526	MM	0.8275	1086.38403	21.88153	99.1584
2	73.182	MM	2.4431	9.22033	6.29003e-2	0.8416



3g

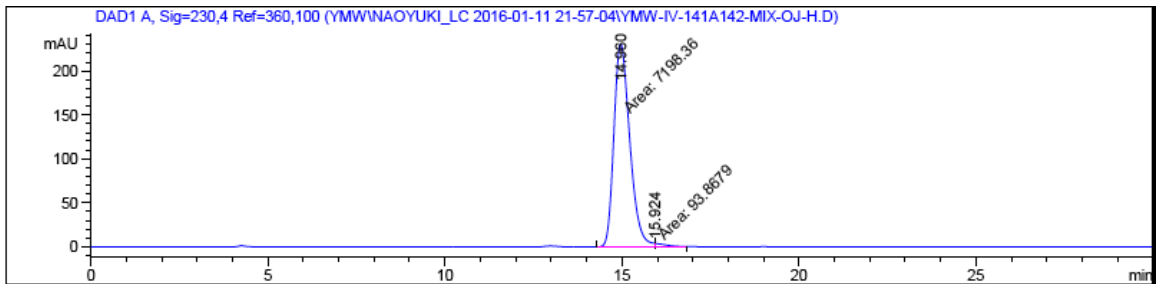
Racemic trace:



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

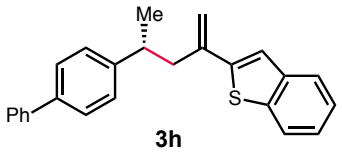
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.098	MF	0.4995	2387.54883	79.65701	49.0552
2	16.073	FM	0.6022	2479.52100	68.62137	50.9448

Enantioenriched trace:



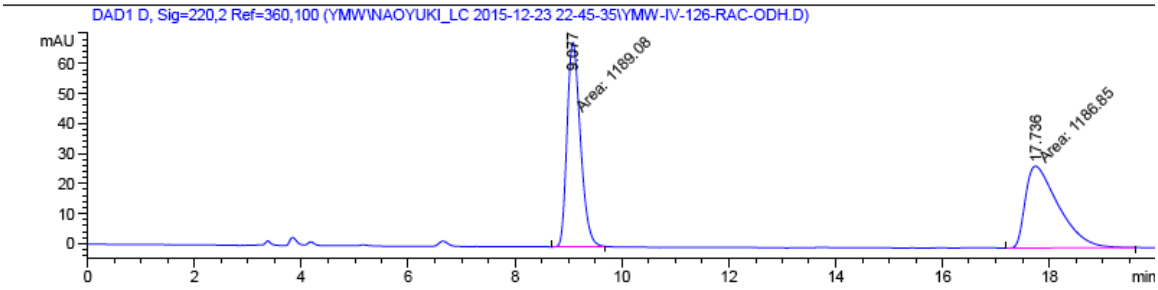
Signal 1: DAD1 A, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.960	MF	0.5200	7198.36084	230.73122	98.7128
2	15.924	FM	0.3860	93.86793	4.05327	1.2872



3h

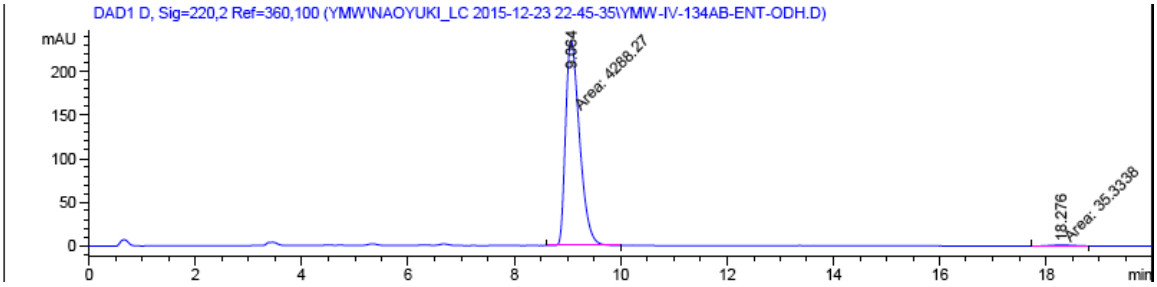
Racemic trace:



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

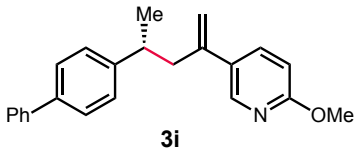
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.077	MM	0.2906	1189.08069	68.20097	50.0469
2	17.736	MM	0.7235	1186.85144	27.34204	49.9531

Enantioenriched trace:



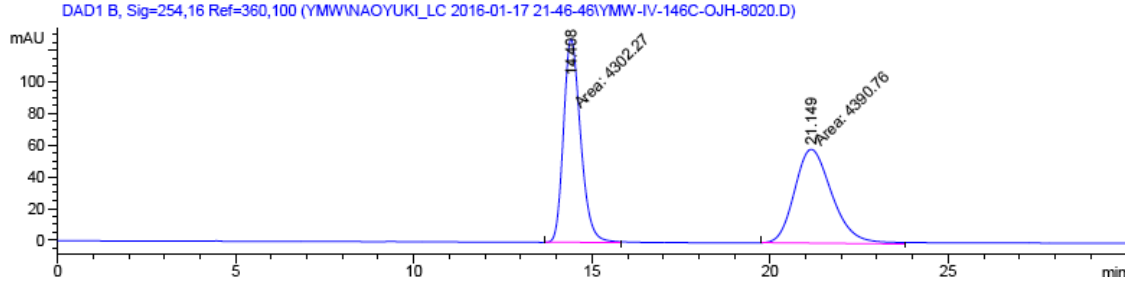
Signal 2: DAD1 D, Sig=220,2 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.064	MM	0.3038	4288.26611	235.23453	99.1828
2	18.276	MM	0.5107	35.33376	1.15322	0.8172



3i

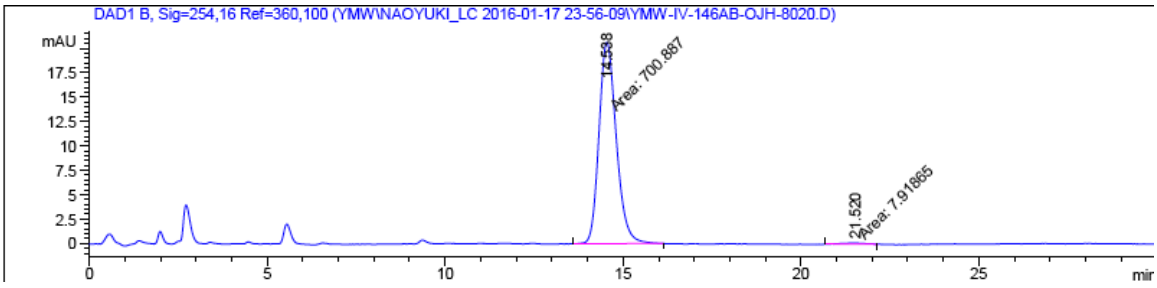
Racemic trace:



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

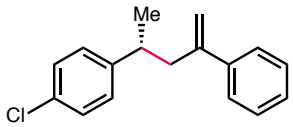
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.408	MM	0.5575	4302.26660	128.62900	49.4910
2	21.149	MM	1.2305	4390.76074	59.47044	50.5090

Enantioenriched trace:



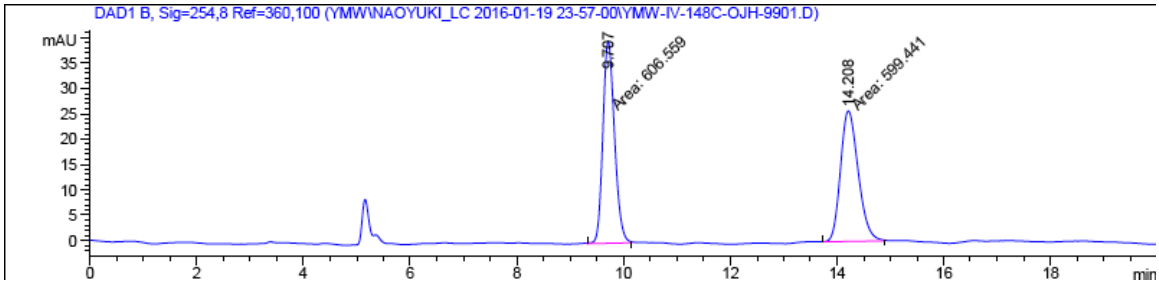
Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.538	MM	0.5657	700.88690	20.65008	98.8828
2	21.520	MM	0.9168	7.91865	1.43951e-1	1.1172



3j

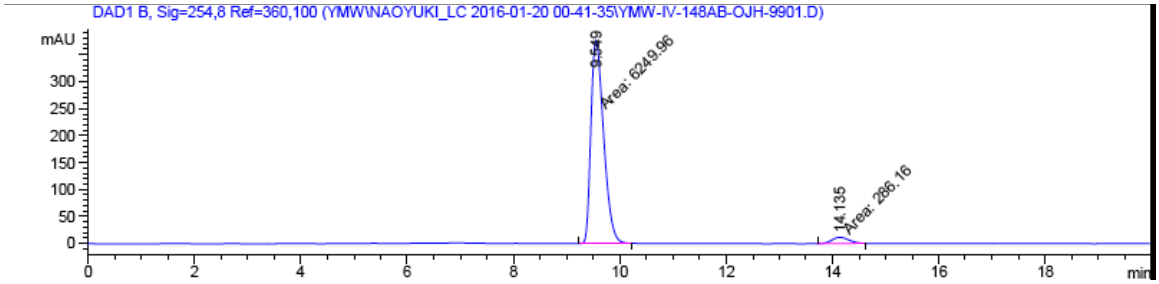
Racemic trace:



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

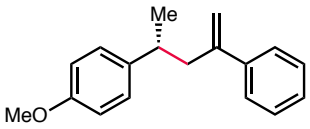
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.707	MM	0.2534	606.55896	39.89882	50.2951
2	14.208	MM	0.3868	599.44080	25.82815	49.7049

Enantioenriched trace:



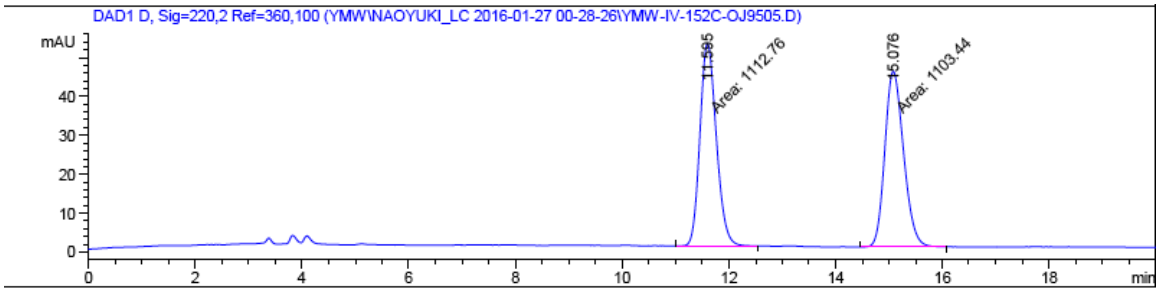
Signal 2: DAD1 B, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.549	MM	0.2762	6249.96240	377.11398	95.6219
2	14.135	MM	0.3937	286.16043	12.11511	4.3781



3k

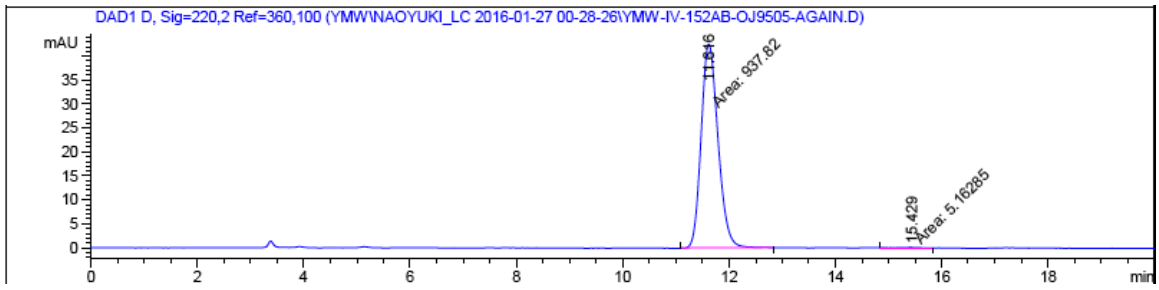
Racemic trace:



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

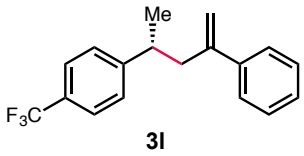
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.595	MM	0.3559	1112.76111	52.10436	50.2102
2	15.076	MM	0.4073	1103.44360	45.14952	49.7898

Enantioenriched trace:



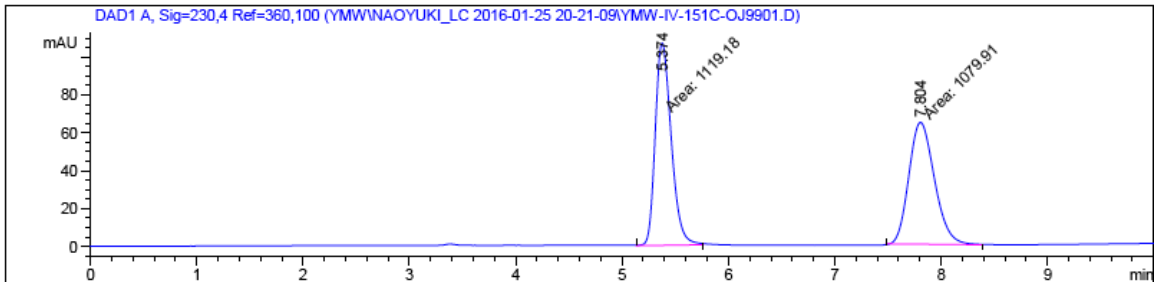
Signal 2: DAD1 D, Sig=220,2 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.616	MM	0.3671	937.82019	42.57429	99.4525
2	15.429	MM	0.5458	5.16285	1.57647e-1	0.5475



3l

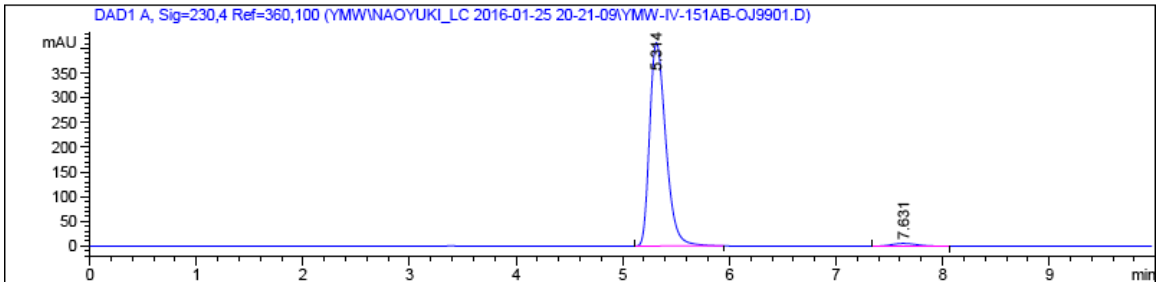
Racemic trace:



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

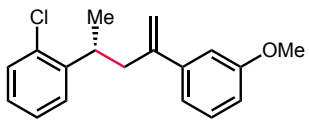
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.374	MM	0.1746	1119.17920	106.86213	50.8929
2	7.804	MM	0.2798	1079.90625	64.32069	49.1071

Enantioenriched trace:



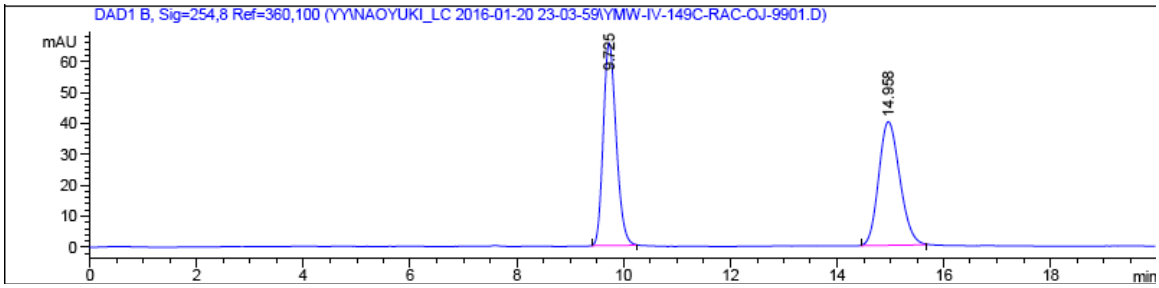
Signal 1: DAD1 A, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.314	BB	0.1632	4345.88379	411.56857	97.8929
2	7.631	BB	0.2558	93.54115	5.63242	2.1071



3m

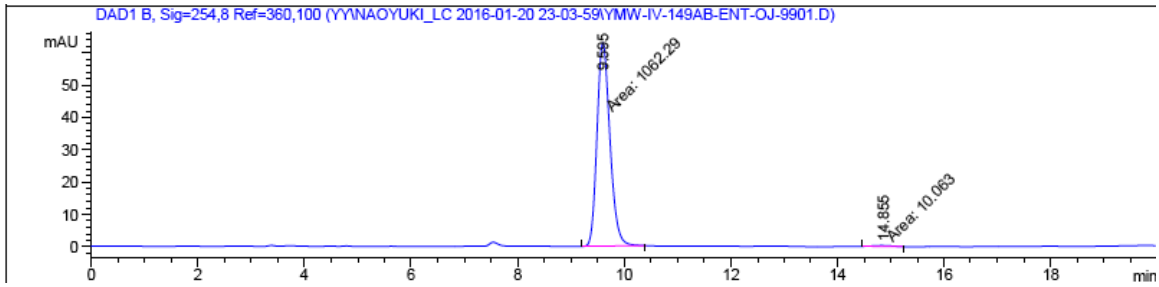
Racemic trace:



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

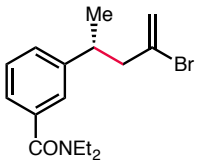
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.725	BB	0.2608	1106.60242	65.60091	50.1231
2	14.958	BB	0.4292	1101.16492	39.99708	49.8769

Enantioenriched trace:



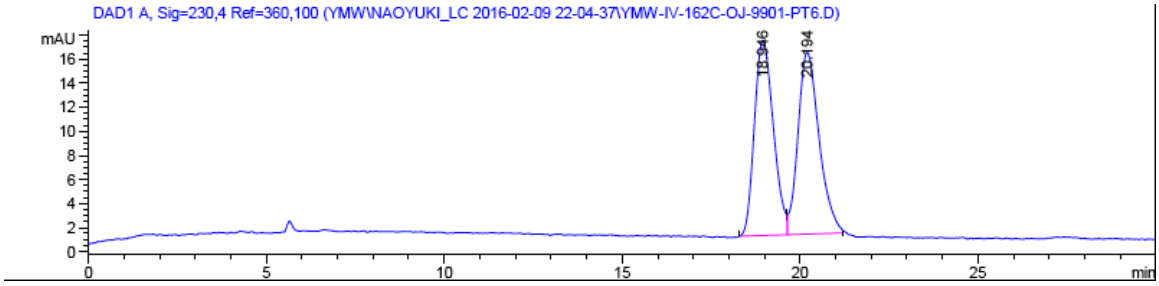
Signal 2: DAD1 B, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.595	MM	0.2815	1062.28784	62.89900	99.0616
2	14.855	MM	0.4955	10.06295	3.38504e-1	0.9384



3n

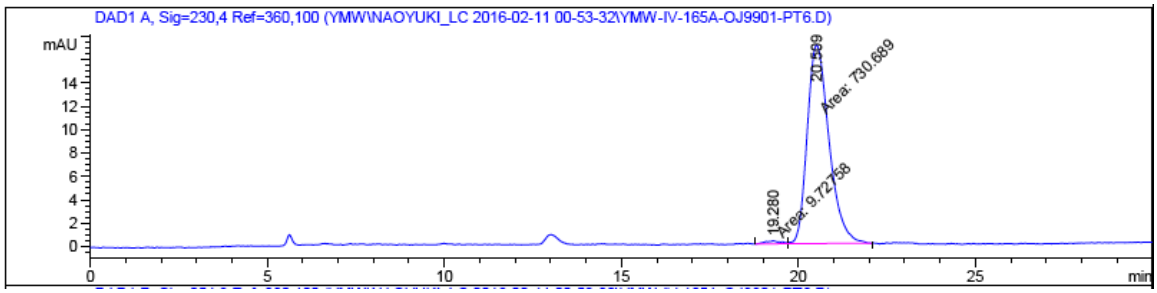
Racemic trace:



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

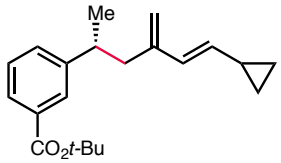
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.946	BV	0.5691	602.90991	16.23997	49.0119
2	20.194	VB	0.6018	627.22021	15.12500	50.9881

Enantioenriched trace:



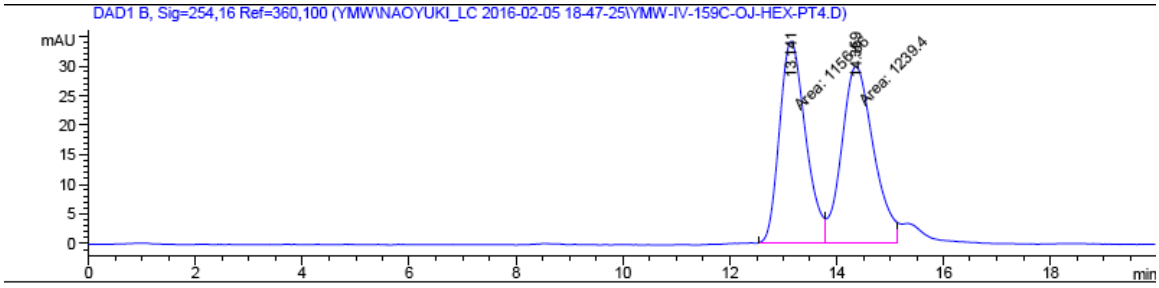
Signal 1: DAD1 A, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.280	MF	0.5548	9.72758	2.92225e-1	1.3138
2	20.509	FM	0.7165	730.68909	16.99646	98.6862



3o

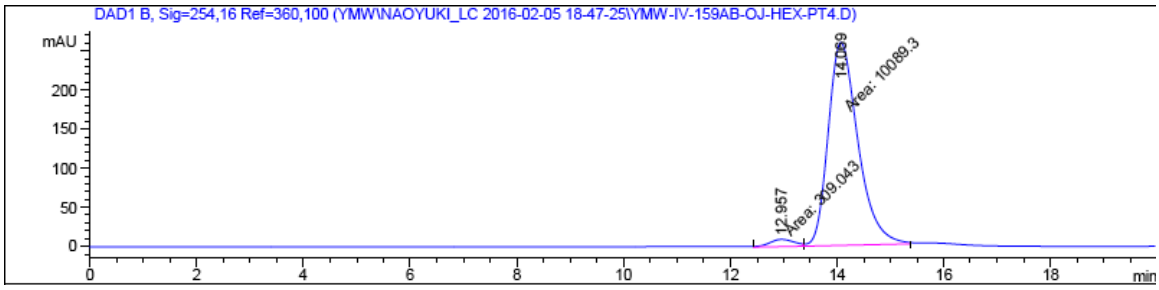
Racemic trace:



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

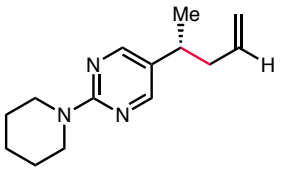
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.141	MF	0.5663	1156.85876	34.04664	48.2776
2	14.359	MF	0.6918	1239.40393	29.85740	51.7224

Enantioenriched trace:



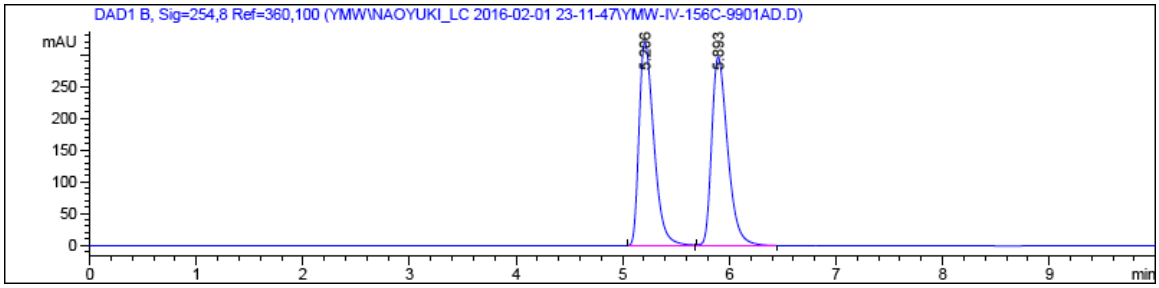
Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.957	MF	0.5451	309.04327	9.44902	2.9720
2	14.069	FM	0.6478	1.00893e4	259.59286	97.0280



3p

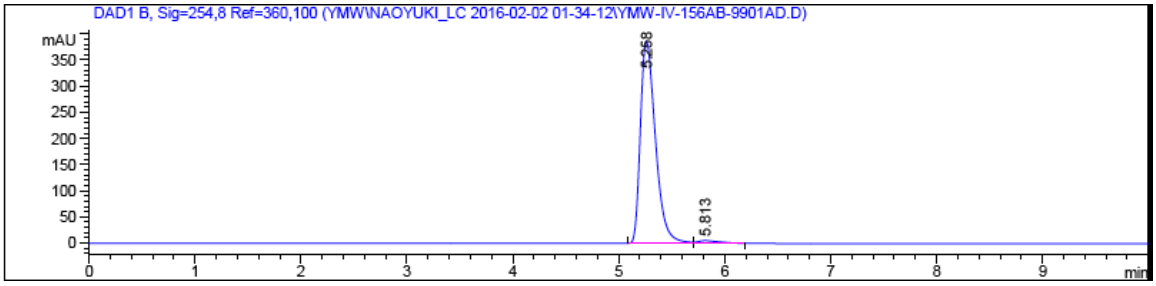
Racemic trace:



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

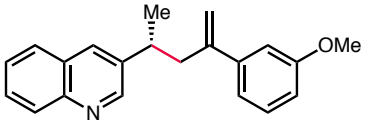
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.206	BB	0.1490	3098.81006	319.86285	50.0067
2	5.893	BB	0.1618	3097.98462	296.74374	49.9933

Enantioenriched trace:



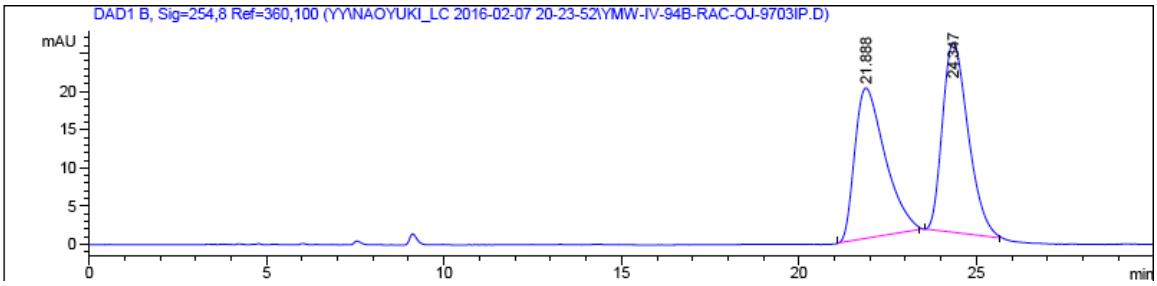
Signal 2: DAD1 B, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.258	BV	0.1533	3817.98267	386.37653	97.9832
2	5.813	VB	0.1982	78.58738	5.45168	2.0168



3q

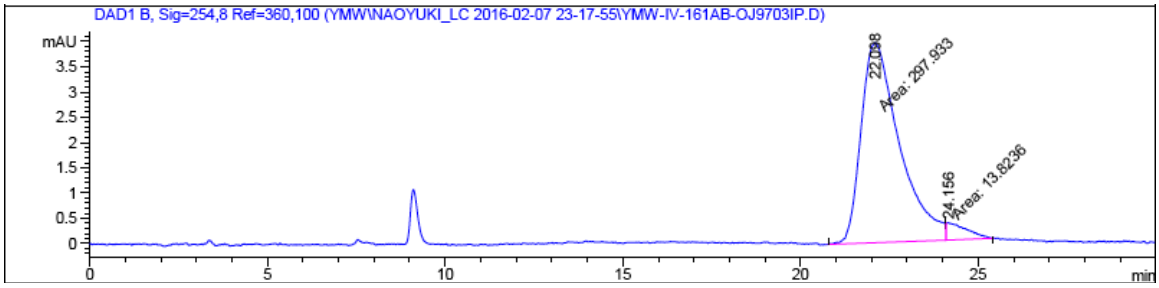
Racemic trace:



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

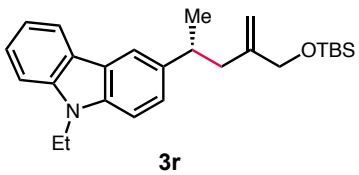
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.888	BB	0.8665	1171.52783	19.68013	48.2752
2	24.347	BB	0.7649	1255.23999	24.86617	51.7248

Enantioenriched trace:



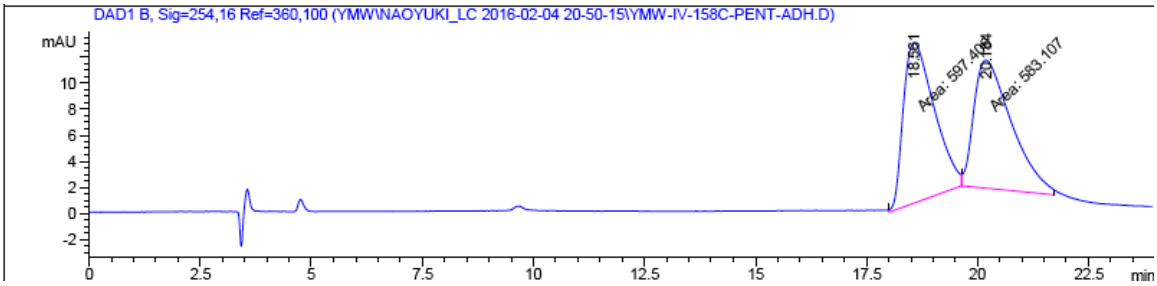
Signal 2: DAD1 B, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.098	MF	1.2542	297.93286	3.95907	95.5659
2	24.156	FM	0.6662	13.82365	3.45835e-1	4.4341



3r

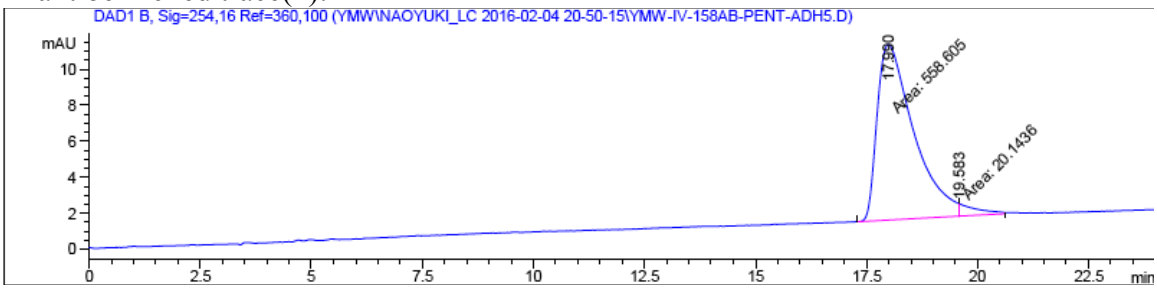
Racemic trace:



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.561	MM	0.8078	597.40613	12.32610	50.6056
2	20.184	MM	0.9890	583.10699	9.82623	49.3944

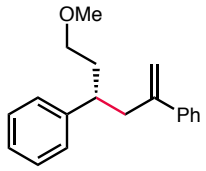
Enantioenriched trace(*):



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

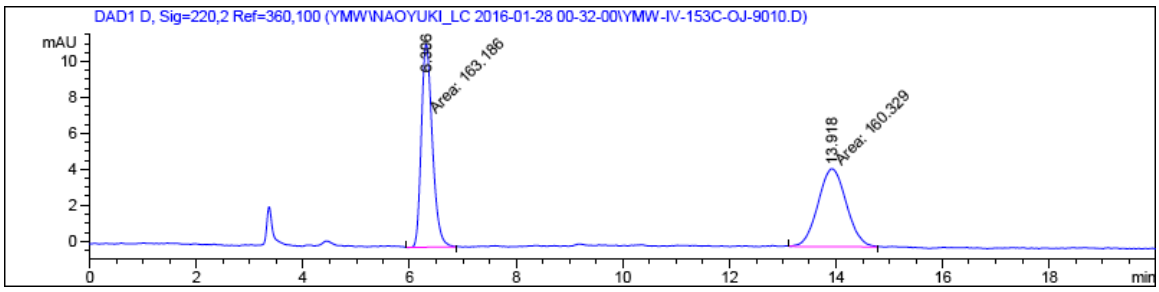
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.990	MF	0.9542	558.60522	9.75746	96.5195
2	19.583	FM	0.4728	20.14359	7.10018e-1	3.4805

(*)Due to the poor resolution of the peaks, we can only infer from the HPLC trace that **3r** was obtained in *at least* 93% ee.



3s

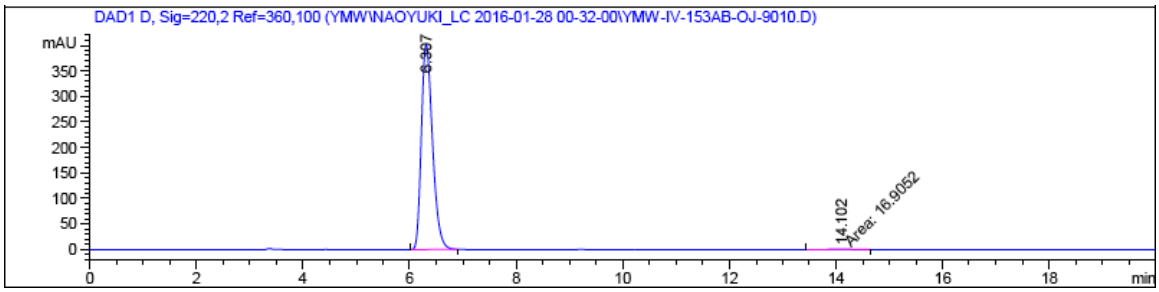
Racemic trace:



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

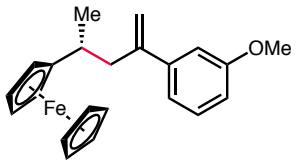
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.306	MM	0.2403	163.18571	11.31674	50.4415
2	13.918	MM	0.6163	160.32899	4.33612	49.5585

Enantioenriched trace:



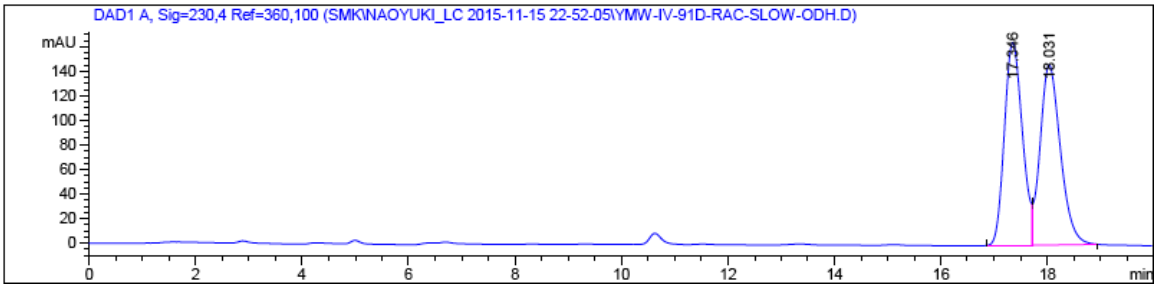
Signal 2: DAD1 D, Sig=220,2 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.307	BB	0.2238	5851.59570	402.02600	99.7119
2	14.102	MM	0.5611	16.90520	5.02139e-1	0.2881



3t

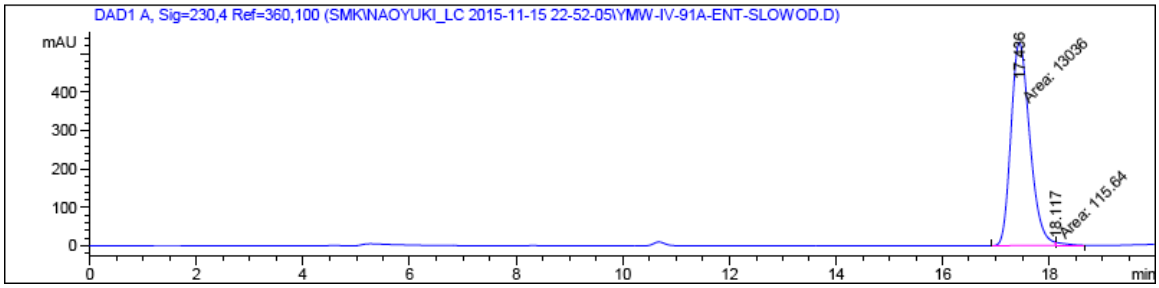
Racemic trace:



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

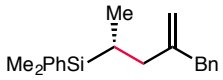
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.346	BV	0.3655	3872.08008	165.19290	49.7108
2	18.031	VB	0.4075	3917.13184	146.70502	50.2892

Enantioenriched trace:



Signal 1: DAD1 A, Sig=230,4 Ref=360,100

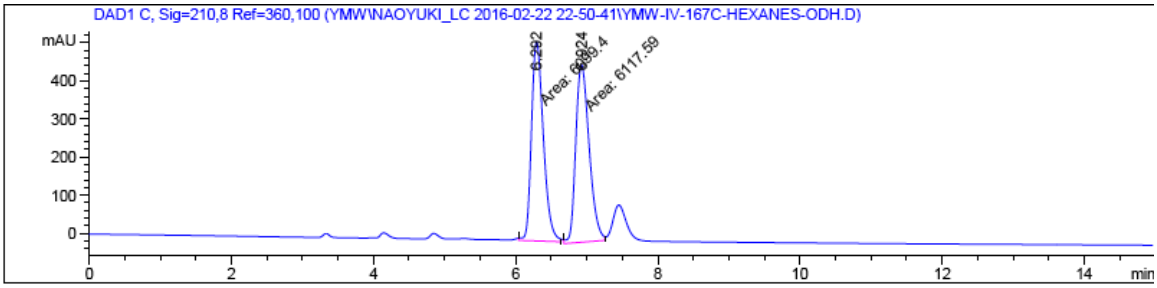
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.436	MF	0.4103	1.30360e4	529.55310	99.1207
2	18.117	FM	0.2174	115.63977	8.86700	0.8793



3u

(10:1 branched/linear)

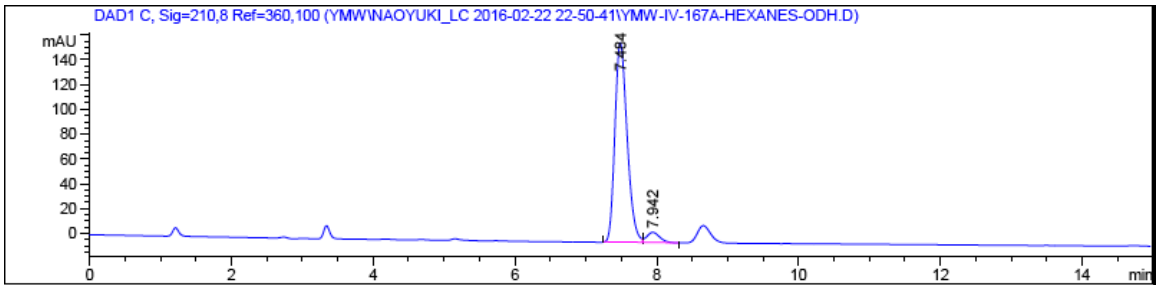
Racemic trace:



Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.292	MM	0.1941	6099.40283	523.63208	49.9256
2	6.924	MM	0.2188	6117.58984	466.06213	50.0744

Enantioenriched trace:



Signal 3: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.484	BV	0.1860	1928.48096	160.70779	94.8055
2	7.942	VB	0.1949	105.66372	8.28096	5.1945