CuH-Catalyzed Asymmetric Reduction of α,β-Unsaturated Carboxylic Acids to β-Chiral Aldehydes

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Contents

I. General Information.

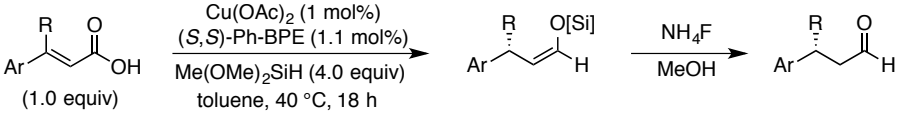
General reagent information. All reactions were performed under a nitrogen atmosphere using the indicated method in the general procedures. Toluene and tetrahydrofuran (THF) were purchased from J.T. Baker in CYCLE-TAINER® solvent delivery kegs and purified by passage under argon pressure through two packed columns of neutral alumina and copper(II) oxide. Copper(II) acetate was purchased from Strem and was used as received. 1,2-Bis((2*S*,5*S*)2,5-diphenylphospholano)ethane, 1,2-Bis((2*R*,5*R*)2,5-diphenylphospholano)ethane (Ph-BPE) ligands were purchased from Namena Corp. and stored in a nitrogen-filled glove box. Josiphos ligand (*R*)-(-)-1-{(S_p)-2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphino]ferrocenyl}ethyldicyclohexylphosphine (Josiphos SL-J007-1) was purchased from Strem Chemicals Inc. or Sigma Aldrich Co. and stored in a nitrogen-filled glove box. Dimethoxy(methyl)silane (DMMS) was purchased from Tokyo Chemical Industry Co. (TCI) and stored in a nitrogen-filled glove box at −20 °C for long term storage. (***Caution****: Dimethoxy(methyl)silane (DMMS, CAS #16881-77-9) is listed by several vendors (TCI, Alfa Aesar) SDS or MSDS as a H318, a category 1 Causes Serious Eye Damage Other vendors (Sigma-Aldrich, Gelest) list DMMS as a H319, a category II Eye Irritant. DMMS should be handled in a well-ventilated fumehood using proper precaution as outlined for the handling of hazardous materials in prudent practices in the laboratory. At the end of the reaction either ammonium fluoride in methanol, aqueous sodium hydroxide (1 M) or aqueous hydrochloric acid (1 M) should be carefully added to the reaction mixture. This should be allowed to stir for at least 30 minutes or the time indicated in the detailed reaction procedure.*) All other solvents and commercial reagents were used as received from Sigma Aldrich, Alfa Aesar, Acros Organics, TCI and Combi-Blocks, unless otherwise noted. Flash column chromatography was performed using 40-63 μm silica gel (SiliaFlash® F60 from Silicycle), or with the aid of a Biotage Isolera Automated Flash Chromatography System using prepacked SNAP silica cartridges (10-100 g). Organic solutions were concentrated in vacuo using a Buchi rotary evaporator.

General analytical information. All new compounds were characterized by NMR spectroscopy, IR spectroscopy, elemental analysis or high resolution mass spectrometry, optical rotation and melting point analysis (if solids). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker AMX-400 spectrometer. Chemical shifts for ^{1}H NMR are reported as follows: chemical shift in reference to residual $CHCl_3$ at 7.26 ppm (δ ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, sex = sextet, sep = septet, ddd = doublet of double of doublets, td = triplet of doublets, m = multiplet), coupling constant (Hz), and integration. Chemical shifts for ^{13}C NMR are reported in terms of chemical shift in reference to the $CDCl_3$ solvent signal (77.16 ppm). Chemical shifts for ^{19}F-NMR are reported in terms of chemical shift in reference to an external standard (α,α,α-trifluorotoluene set to δ −63.7 ppm). 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. Optical rotations were measured using a Jasco P-1010 digital polarimeter. Elemental analyses were performed by Atlantic Microlabs Inc.,

Norcross, GA. ESI- and DART-MS spectrometric data were recorded on a Bruker Daltonics APEXIV 4.7 Tesla Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS). Enantiomeric excesses (ee's) were determined by chiral SFC analysis using a Waters Acquity UPC2 instrument; specific columns and analytical methods are provided in the experimental details for individual compounds; the wavelengths of light used for chiral analyses are provided with the associated chromatograms. Thin-layer chromatography (TLC) was performed on silica gel 60Å F_{254} plates (SiliaPlate from Silicycle) and visualized with UV light or potassium permanganate stain. Preparatory thin-layer chromatography (Prep-TLC) was performed on silica gel GF with UV 254 (20 x 20 cm, 1000 microns, catalog # TLG-R10011B-341 from Silicycle) and visualized with UV light. Isolated yields reported in Tables 1 and 2 of the manuscript reflect the average values from two independent runs.

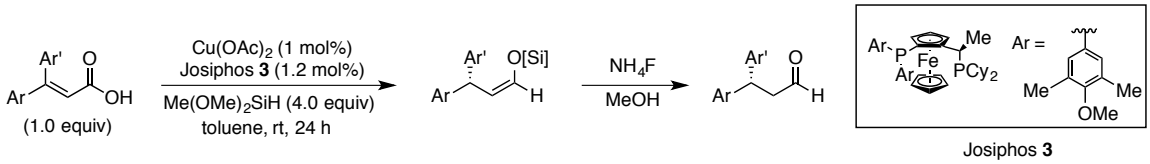
II. Procedures for CuH-Catalyzed Acid Reduction Reactions.

General procedure A for 1 mmol scale reduction of β-alkyl, β-aryl acrylic acids.



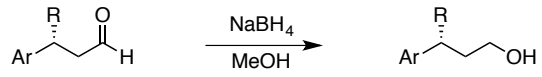
An oven-dried reaction tube (Fisherbrand, 20 x 125 mm, catalog no. 1495937A) containing a magnetic stir bar was charged with unsaturated carboxylic acid (1.0 mmol, 1.0 equiv). The reaction tube was loosely capped (Cap: Kimble Chase Open Top S/T Closure catalog no. 73804-15425; Septum: Thermo Scientific 1.3 mm silicone/PTFE catalog no. B7995-18) and then brought into a nitrogen-filled glove box. $Cu(OAc)_2$ (1.8 mg, 0.010 mmol, 0.010 equiv) and (*S,S*)-Ph-BPE (5.6 mg, 0.011 mmol, 0.011 equiv), was then added to the reaction tube, followed by the addition of toluene (2 mL) *via* syringe. The reaction tube was capped, and then was removed from the glove box. The cap was wrapped in parafilm, and the reaction tube was inserted into an oil bath preheated to 40 °C. Dimethoxymethylsilane (DMMS, 0.49 mL, 4.0 mmol, 4.0 equiv) was then added *via* a 1 mL syringe by piercing the Teflon septum with the needle. The resulting mixture was stirred for 18 h, removed from the oil bath, and allowed to cool to rt, at which time the cap was removed and EtOAc (3 mL) was added to the reaction tube to dilute the reaction mixture. The reaction tube was then inserted to an ice bath, and sat. NH_4F in MeOH (10 mL) was slowly added to quench the reaction as part of the workup (***Caution****: gas evolution observed*). The mixture was stirred uncapped for 15 min, transferred to a 50 mL round bottom flask, and concentrated *in vacuo*. The resulting residue was redissolved in EtOAc, and filtered through a plug of silica gel and washed with additional EtOAc. The collected EtOAc solution was concentrated *in vacuo,* and the crude material was immediately purified by silica gel column chromatography or Biotage Isolera Automated Flash Chromatography System. (***Note****: If not purified immediately, the crude material will form an insoluble gel upon standing making purification more difficult.*)

General procedure B for 1 mmol scale reduction of β, β-diaryl acrylic acids.



An oven-dried reaction tube (Fisherbrand, 20 x 125 mm, catalog no. 1495937A) containing a magnetic stir bar was charged with unsaturated carboxylic acid (1.0 mmol, 1.0 equiv). The reaction tube was loosely capped (Cap: Kimble Chase Open Top S/T Closure catalog no. 73804-15425; Septum: Thermo Scientific 1.3 mm silicone/PTFE catalog no. B7995-18) and then brought into a nitrogen-filled glove box. $Cu(OAc)_2$ (1.8 mg, 0.010 mmol, 0.010 equiv) and Josiphos **3** (*R*)-(-)-1-{(*S*)-2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphino]ferrocenyl}ethyldicyclohexylphosphine (Josiphos SL-J007-1, 8.5 mg, 0.012 mmol, 0.012 equiv), was then added to the reaction tube, followed by the addition of toluene (2 mL) *via* syringe. Dimethoxymethylsilane (DMMS, 0.49 mL, 4.0 mmol, 4.0 equiv) was then added *via* a 1 mL syringe. The reaction tube was capped, and then was removed from the glove box. The cap was wrapped in parafilm, and the resulting mixture was stirred at rt for 24 h. The cap was removed, and EtOAc (3 mL) was added to the reaction tube to dilute the reaction mixture. The reaction tube was then inserted to an ice bath, and sat. NH_4F in MeOH (10 mL) was slowly added to quench the reaction as part of the workup (***Caution****: gas evolution observed*). The mixture was stirred uncapped for 15 min, transferred to a 50 mL round bottom flask, and concentrated *in vacuo*. The resulting residue was redissolved in EtOAc, and filtered through a plug of silica gel and washed with additional EtOAc. The collected EtOAc solution was concentrated *in vacuo,* and the crude material was immediately added to a chromatography column and purified by silica gel column chromatography or Biotage Isolera Automated Flash Chromatography System. (***Note****: If not purified immediately, the crude material will form an insoluble gel upon standing making purification more difficult.*)

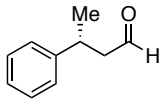
General procedure C for aldehyde reduction reaction.



An oven-dried reaction tube (Fisherbrand, 13 x 100 mm, catalog no. 1495925A) containing a magnetic stir bar was charged with alkyl aldehyde (0.20 mmol, 1.0 equiv), followed by the addition of methanol (2 mL) *via* syringe. The reaction tube was then inserted to an ice bath, and sodium borohydride (61 mg, 1.6 mmol, 8.0 equiv) was added in one portion. The reaction mixture was stirred uncapped for 30 min, and the reaction was quenched by slow addition of aqueous sat. NH_4Cl solution (5 mL) over 5 min (***Caution****: gas evolution observed*). The mixture was then extracted with diethyl ether (3×), washed with brine, dried with Na_2SO_4, filtered, concentrated *in vacuo* and purified by silica gel chromatography to afford the corresponding alcohol product.

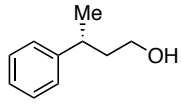
III. Characterization Data for Aldehyde and Alcohol Products

(*R*)-3-phenylbutanal (2a)

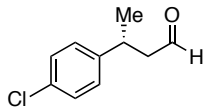


The general procedure **A** was followed using (*E*)-3-phenylbut-2-enoic acid (162 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 0% EtOAc/hexanes for 1 column volume (CV), 0-8% EtOAc/hexanes for 10 CV, then 8% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 103 mg, 70% yield, 94% ee; Run 2: 108 mg, 73% yield, 94% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (t, J = 2.0 Hz, 1H), 7.29-7.34 (m, 2H), 7.19-7.24 (m, 3H), 3.36 (sex, J = 7.2 Hz, 1H), 2.76 (ddd, J = 16.4 Hz, J = 6.8 Hz, J = 2.0 Hz, 1H), 2.66 (ddd, J = 16.4 Hz, J = 7.2 Hz, J = 2.0 Hz, 1H), 1.32 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.0, 145.6, 128.8, 126.9, 126.7, 51.9, 34.4, 22.3. The spectral data match those previously reported in the literature.[1] **Specific rotation** $[\alpha]_D^{23}$: -28.5 (c = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*R*) by comparison to the sign of the specific rotation in the literature.[1]

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2a-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.32 (m, 2H), 7.17-7.22 (m, 3H), 3.51-3.62 (m, 2H), 2.89 (sex, J = 7.2 Hz, 1H), 1.84-1.89 (m, 2H), 1.28 (d, J = 7.2 Hz, 3H & br, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0, 128.6, 127.1, 126.2, 61.3, 41.1, 36.6, 22.5. The spectral data match those previously reported in the literature.[2] **Specific rotation** $[\alpha]_D^{23}$: -22.7 (c = 0.5, $CHCl_3$). **SFC** analysis: CEL2 (5:95 IPA: $scCO_2$ to 10:90 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 1.75 mL/min), 2.07 min (major), 2.40 min (minor), 94% ee. The absolute stereochemistry was assigned as (*R*) by comparison to the sign of the specific rotation in the literature.[2]

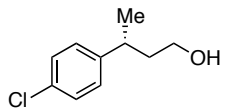


(*R*)-3-(4-chlorophenyl)butanal (2b)



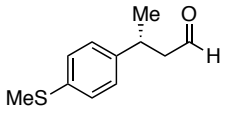
The general procedure **A** was followed using (*E*)-3-(4-chlorophenyl)but-2-enoic acid (197 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 0% EtOAc/hexanes for 1 column volume (CV), 0-8% EtOAc/hexanes for 10 CV, then 8% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 140 mg, 77% yield, 95% ee; Run 2: 134 mg, 73% yield, 96% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.70 (t, J = 2.0 Hz, 1H), 7.25-7.29 (m, 2H), 7.13-7.17 (m, 2H), 3.34 (sex, J = 7.2 Hz, 1H), 2.72 (ddd, J = 16.8 Hz, J = 7.2 Hz, J = 2.0 Hz, 1H), 2.65 (ddd, J = 16.8 Hz, J = 7.6 Hz, J = 2.0 Hz, 1H), 1.29 (d, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.4, 144.1, 132.3, 128.9, 128.3, 51.8, 33.8, 22.3. The spectral data match those previously reported in the literature.[3] **Specific rotation** $[\alpha]_D^{23}$: -26.4 (c = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*R*) by comparison to the sign of the specific rotation in the literature.[3]

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2b-ol** was prepared according to general procedure **C**. **^{1}H**



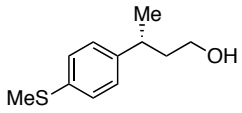
NMR (400 MHz, $CDCl_3$) δ 7.25-7.28 (m, 2H), 7.12-7.15 (m, 2H), 3.48-3.61 (m, 2H), 2.89 (sex, J = 6.8 Hz, 1H), 1.75-1.89 (m, 2H), 1.32 (br, 1H), 1.26 (d, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 131.8, 128.7, 128.5, 61.1, 41.0, 36.0, 22.4. The spectral data match those previously reported in the literature.[4] **Specific rotation** $[\alpha]_D^{23}$: -30.9 (c = 0.5, $CHCl_3$). **SFC** analysis: CEL2 (5:95 IPA: $scCO_2$ to 10:90 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 1.75 mL/min), 2.41 min (minor), 2.57 min (major), 96% ee. The absolute stereochemistry was assigned as (*R*) by comparison to the sign of the specific rotation in the literature.[4]

(*R*)-3-(4-(methylthio)phenyl)butanal (2c)

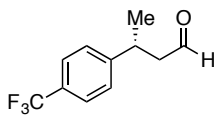


The general procedure **A** was followed using (*E*)-3-(4-(methylthio)phenyl)but-2-enoic acid (208 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 3% EtOAc/hexanes for 1 column volume (CV), 3-10% EtOAc/hexanes for 10 CV, then 10% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 158 mg, 81% yield, 96% ee; Run 2: 170 mg, 87% yield, 96% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.69 (t, J = 2.0 Hz, 1H), 7.20-7.23 (m, 2H), 7.13-7.16 (m, 2H), 3.32 (sex, J = 7.2 Hz, 1H), 2.72 (ddd, J = 16.8 Hz, J = 7.2 Hz, J = 2.0 Hz, 1H), 2.64 (ddd, J = 16.8 Hz, J = 7.2 Hz, J = 2.0 Hz, 1H), 2.46 (s, 3H), 1.29 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.8, 142.6, 136.4, 127.4, 127.3, 51.8, 33.9, 22.3, 16.2. **IR** (neat): 1720, 1495, 1093, 1014, 818, 770 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{11}H_{18}NOS^+$ $[M+NH_4]^+$: 212.1104; 212.1109 found. **Specific rotation** $[\alpha]_D^{23}$: -31.1 (c = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*R*) by analogy.

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2c-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20-7.23 (m, 2H), 7.12-7.15 (m, 2H), 3.50-3.61 (m, 2H), 2.86 (sex, J = 7.2 Hz, 1H), 2.47 (s, 3H), 1.80-1.86 (m, 2H), 1.35 (br, 1H), 1.26 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 135.7, 127.7, 127.4, 61.3, 41.1, 36.1, 22.5, 16.4. **IR** (neat): 3338, 2921, 1495, 1040, 1014, 817 cm^{-1}. **EA** Calcd. for $C_{11}H_{16}OS$: C, 67.30; H, 8.22. Found: C, 67.59; H, 8.18. **Specific rotation** $[\alpha]_D^{23}$: -31.5 (c = 0.5, $CHCl_3$). **SFC** analysis: CEL2 (5:95 IPA: $scCO_2$ to 10:90 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 1.75 mL/min), 3.70 min (minor), 3.97 min (major), 96% ee. The absolute stereochemistry was assigned as (*R*) by analogy.



(*R*)-3-(4-(trifluoromethyl)phenyl)butanal (2d)



The general procedure **A** was followed using (*E*)-3-(4-(trifluoromethyl)phenyl)but-2-enoic acid (230 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 0% EtOAc/hexanes for 1 column volume (CV), 0-8% EtOAc/hexanes for 10 CV, then 8% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 170 mg,

79% yield, 94% ee; Run 2: 160 mg, 74% yield, 94% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (t, J = 2.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 3.44 (sex, J = 6.8 Hz, 1H), 2.79 (ddd, J = 17.2 Hz, J = 6.8 Hz, J = 1.6 Hz, 1H), 2.71 (ddd, J = 17.2 Hz, J = 7.2 Hz, J = 2.0 Hz, 1H), 1.33 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.9, 149.7, 129.0 (q, J = 32.0 Hz), 127.3, 125.8 (q, J = 4.0 Hz), 124.3 (q, J = 270.0 Hz), 51.6, 34.1, 22.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.4. **IR** (neat): 1725, 1323, 1116, 1068, 1016, 838, 606 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{11}H_{15}NOF_3^+$ $[M+NH_4]^+$: 234.1100; 234.1109 found. **Specific rotation** $[\alpha]_D^{23}$: -24.5 (c = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*R*) by analogy.

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2d-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 3.49-3.63 (m, 2H), 2.99 (sex, J = 6.8 Hz, 1H), 1.80-1.92 (m, 2H), 1.36 (br, 1H), 1.29 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.1, 128.6 (q, J = 32.0 Hz), 127.5, 125.6 (q, J = 4.0 Hz), 124.4 (q, J = 270.0 Hz), 61.0, 40.8, 36.4, 22.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.3. **IR** (neat): 3324, 1323, 1117, 1067, 1016, 837 cm^{-1}. **EA** Calcd. for $C_{11}H_{13}F_3O$: C, 60.55; H, 6.00. Found: C, 60.29; H, 6.12. **Specific rotation** $[\alpha]_D^{23}$: -22.7 (c = 0.5, $CHCl_3$). **SFC** analysis: CEL2 (1:99 IPA: $scCO_2$ to 3:97 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 1.75 mL/min), 3.12 min (minor), 3.32 min (major), 94% ee. The absolute stereochemistry was assigned as (*R*) by analogy.

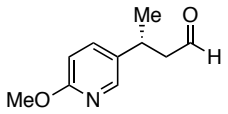
(*R*)-3-(2-fluorophenyl)butanal (2e)

The general procedure **A** was followed using (*E*)-3-(2-fluorophenyl)but-2-enoic acid (180 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 0% EtOAc/hexanes for 1 column volume (CV), 0-8% EtOAc/hexanes for 10 CV, then 8% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 111 mg, 67% yield, 95% ee; Run 2: 123 mg, 74% yield, 95% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (t, J = 2.0 Hz, 1H), 7.17-7.24 (m, 2H), 7.00-7.12 (m, 2H), 3.66 (sex, J = 7.2 Hz, 1H), 2.79 (ddd, J = 16.8 Hz, J = 6.8 Hz, J = 2.0 Hz, 1H), 2.70 (ddd, J = 17.2 Hz, J = 8.0 Hz, J = 2.0 Hz, 1H), 1.34 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.6, 160.7 (d, J = 243.0 Hz), 132.1 (d, J = 14.0 Hz), 128.2, 124.5 (d, J = 4.0 Hz), 115.8 (d, J = 22.0 Hz), 50.5, 28.2, 20.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.2. **IR** (neat): 1723, 1490, 1450, 1226, 1114, 754 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{10}H_{15}NOF^+$ $[M+NH_4]^+$: 184.1132; 184.1140 found. **Specific rotation** $[\alpha]_D^{23}$: -17.4 (c = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*R*) by analogy.

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2e-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14-7.25 (m, 2H), 7.07-7.11 (m, 1H), 6.98-7.03 (m, 1H), 3.53-3.63 (m, 2H), 3.25 (sex, J = 7.2 Hz, 1H), 1.86-1.91 (m, 2H), 1.37 (br, 1H), 1.30 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9 (d, J = 242.0 Hz), 133.3 (d, J = 15.0 Hz), 128.2 (d, J = 6.0 Hz), 127.6 (d, J = 8.0 Hz), 124.4 (d, J = 4.0 Hz), 115.5 (d, J = 23.0 Hz), 61.3, 40.0, 29.4, 21.1; **^{19}F**

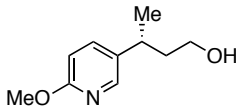
NMR (376 MHz, $CDCl_3$) δ -118.9. The spectral data match those previously reported in the literature.[5] **Specific rotation** $[\alpha]_D^{23}$: -13.6 (*c* = 0.5, $CHCl_3$). **SFC** analysis: OD-H (5:95 IPA: $scCO_2$ to 10:90 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 4.39 min (major), 4.70 min (minor), 95% ee. The absolute stereochemistry was assigned as (*R*) by analogy.

(*R*)-3-(6-methoxypyridin-3-yl)butanal (2f)

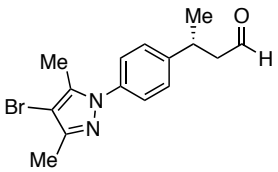


The general procedure **A** was followed using (*E*)-3-(6-methoxypyridin-3-yl)but-2-enoic acid (193 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 5% EtOAc/hexanes for 1 column volume (CV), 5-20% EtOAc/hexanes for 10 CV, then 20% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 107 mg, 60% yield, 97% ee; Run 2: 124 mg, 69% yield, 97% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (t, *J* = 2.0 Hz, 1H), 8.03 (d, *J* = 2.4 Hz, 1H), 7.44 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 1H), 3.91 (s, 3H), 3.30-3.39 (m, 1H), 2.63-2.75 (m, 2H), 1.30 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.3, 163.2, 145.1, 137.3, 133.5, 111.0, 53.5, 51.8, 31.1, 22.2. **IR** (neat): 1721, 1490, 1285, 1255, 1023, 830 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{10}H_{14}NO_2^+$ $[M+H]^+$: 180.1019; 180.1011 found. **Specific rotation** $[\alpha]_D^{23}$: -28.4 (*c* = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*R*) by analogy.

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2f-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.4 Hz, 1H), 7.43 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 3.52-3.60 (m, 2H), 2.83-2.92 (m, 1H), 1.77-1.87 (m, 2H), 1.30 (br, 1H), 1.26 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0, 145.3, 137.3, 134.7, 110.9, 61.0, 53.5, 40.8, 33.1, 22.4. **IR** (neat): 3350, 2929, 1489, 1396, 1281, 1024, 839 cm^{-1}. **EA** Calcd. for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34. Found: C, 65.83; H, 8.34. **Specific rotation** $[\alpha]_D^{23}$: -23.0 (*c* = 0.5, $CHCl_3$). **SFC** analysis: AS-H (5:95 IPA: $scCO_2$ to 10:90 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 3.17 min (major), 3.57 min (minor), 97% ee. The absolute stereochemistry was assigned as (*R*) by analogy.



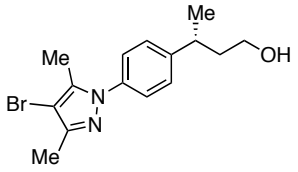
(*R*)-3-(4-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)phenyl)butanal (2g)



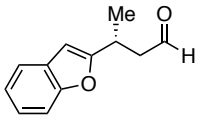
The general procedure **A** was followed using (*E*)-3-(4-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)phenyl)but-2-enoic acid (335 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 5% EtOAc/hexanes for 1 column volume (CV), 5-20% EtOAc/hexanes for 10 CV, then 20% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 250 mg, 78% yield, 98% ee; Run 2: 247 mg, 77% yield, 98% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (t, *J* = 2.0 Hz, 1H), 7.30-7.35 (m, 4H), 3.43 (sex, *J* = 7.2 Hz, 1H), 2.78 (ddd, *J* = 17.2 Hz, *J* = 7.2 Hz, *J* = 2.0 Hz, 1H), 2.69 (ddd, *J* = 16.8 Hz, *J* = 7.2 Hz, *J* = 2.0 Hz, 1H), 2.28-2.29 (2s, 6H), 1.34 (d, *J* =

6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.4, 147.6, 145.5, 138.4, 137.6, 127.7, 125.1, 96.4, 51.8, 34.0, 22.2, 12.5, 11.8. **IR** (neat): 1721, 1516, 1380, 1365, 1078, 1041, 1016, 839 cm^{-1}. **EA** Calcd. for $C_{15}H_{17}BrN_2O$: C, 56.09; H, 5.33. Found: C, 55.64; H, 5.12. **Specific rotation** $[\alpha]_D^{23}$: -17.6 (*c* = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*R*) by analogy.

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2g-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.32 (m, 4H), 3.49-3.62 (m, 2H), 2.96 (sex, *J* = 6.8 Hz, 1H), 2.29 (2s, 6H), 1.82-1.89 (m, 2H), 1.51 (br, 1H), 1.29 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5, 146.9, 138.0, 137.6, 127.8, 124.9, 96.2, 61.0, 41.0, 36.1, 22.4, 12.5, 11.8. **IR** (neat): 3354, 2927, 1516, 1366, 1080, 1044, 732 cm^{-1}. **EA** Calcd. for $C_{15}H_{19}BrN_2O$: C, 55.74; H, 5.93. Found: C, 55.87; H, 5.81. **Specific rotation** $[\alpha]_D^{23}$: -23.5 (*c* = 0.5, $CHCl_3$). **SFC** analysis: CEL2 (5:95 IPA: $scCO_2$ to 10:90 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, and reduces back to 5:95 IPA: $scCO_2$ with 3 min hold time, 1.75 mL/min), 7.61 min (minor), 7.92 min (major), 98% ee. The absolute stereochemistry was assigned as (*R*) by analogy.

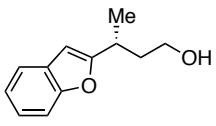


(*R*)-3-(benzofuran-2-yl)butanal (2h)



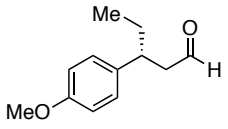
The general procedure **A** was followed using (*E*)-3-(benzofuran-2-yl)but-2-enoic acid (202 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 0% EtOAc/hexanes for 1 column volume (CV), 0-9% EtOAc/hexanes for 10 CV, then 9% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 125 mg, 66% yield, 95% ee; Run 2: 120 mg, 64% yield, 95% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.82 (t, *J* = 1.6 Hz, 1H), 7.48-7.51 (m, 1H), 7.40-7.42 (m, 1H), 7.17-7.25 (m, 2H), 6.43 (t, *J* = 1.0 Hz, 1H), 3.58 (sex, *J* = 7.2 Hz, 1H), 2.94 (ddd, *J* = 17.2 Hz, *J* = 6.4 Hz, *J* = 2.0 Hz, 1H), 2.70 (ddd, *J* = 17.2 Hz, *J* = 7.2 Hz, *J* = 2.0 Hz, 1H), 1.42 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.0, 161.4, 154.8, 128.6, 123.8, 122.8, 120.7, 111.0, 101.5, 49.0, 28.4, 19.0. The spectral data match those previously reported in the literature.[6] **Specific rotation** $[\alpha]_D^{23}$: -33.4 (*c* = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*R*) by comparison to the sign of the specific rotation in the literature.[6]

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2h-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.50 (m, 1H), 7.41-7.43 (m, 1H), 7.16-7.24 (m, 2H), 6.41 (s, 1H), 3.65-3.75 (m, 2H), 3.16 (sex, *J* = 7.2 Hz, 1H), 2.00-2.09 (m, 1H), 1.84-1.93 (m, 1H), 1.38 (d, *J* = 7.2 Hz, 3H & br, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1, 154.7, 128.8, 123.4, 122.6, 120.5, 111.0, 101.1, 60.9, 38.5, 30.4, 19.3. **IR** (neat): 3326, 2933, 1454, 1253, 1040, 751 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{12}H_{15}O_2^+$ $[M+H]^+$: 191.1067; 191.1061 found. **Specific rotation** $[\alpha]_D^{23}$: -34.0 (*c* = 0.5, $CHCl_3$). **SFC** analysis: OJ-H (2:98 MeOH: $scCO_2$ to 5:95 IPA: $scCO_2$ linear gradient over 15 min, 2.50 mL/min), 13.65 min (minor), 13.94 min



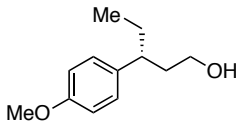
(major), 95% ee. The absolute stereochemistry was assigned as (*R*) by configuration of the corresponding aldehyde.

(*R*)-3-(4-methoxyphenyl)pentanal (2i)

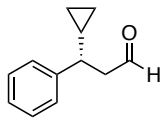


The general procedure **A** was followed using (*E*)-3-(4-methoxyphenyl)pent-2-enoic acid (206 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 0% EtOAc/hexanes for 1 column volume (CV), 0-9% EtOAc/hexanes for 10 CV, then 9% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 135 mg, 70% yield, 96% ee; Run 2: 140 mg, 73% yield, 95% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.66 (t, J = 2.0 Hz, 1H), 7.08-7.12 (m, 2H), 6.83-6.87 (m, 2H), 3.79 (s, 3H), 3.00-3.07 (m, 1H), 2.67-2.70 (m, 2H), 1.57-1.72 (m, 2H), 0.80 (t, J = 7.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.4, 158.3, 135.8, 128.6, 114.1, 55.4, 50.5, 41.2, 29.8, 12.0. The spectral data match those previously reported in the literature.[7] **Specific rotation** $[\alpha]_D^{23}$: -2.58 (c = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*R*) by comparison to the sign of the specific rotation in the literature.[7]

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2i-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06-7.09 (m, 2H), 6.82-6.86 (m, 2H), 3.79 (s, 3H), 3.44-3.57 (m, 2H), 2.50-2.58 (m, 1H), 1.89-1.97 (m, 1H), 1.51-1.80 (m, 3H), 1.30 (br, 1H), 0.78 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 137.0, 128.6, 113.9, 61.5, 55.4, 43.6, 39.6, 30.1, 12.2. The spectral data match those previously reported in the literature.[7] **Specific rotation** $[\alpha]_D^{23}$: -9.50 (c = 0.5, $CHCl_3$). **SFC** analysis: OJ-H (5:95 IPA: $scCO_2$ to 10:90 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 4.86 min (minor), 5.02 min (major), 96% ee. The absolute stereochemistry was assigned as (*R*) by comparison to the sign of the specific rotation in the literature.[7]



(*S*)-3-cyclopropyl-3-phenylpropanal (2j)



The general procedure **A** was followed using (*E*)-3-cyclopropyl-3-phenylacrylic acid (188 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 0% EtOAc/hexanes for 1 column volume (CV), 0-8% EtOAc/hexanes for 10 CV, then 8% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 130 mg, 75% yield, 96% ee; Run 2: 144 mg, 83% yield, 96% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (t, J = 2.4 Hz, 1H), 7.30-7.34 (m, 2H), 7.20-7.25 (m, 3H), 2.86-2.88 (m, 2H), 2.43-2.49 (m, 1H), 1.02-1.08 (m, 1H), 0.58-0.65 (m, 1H), 0.44-0.50 (m, 1H), 0.16-0.28 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.0, 143.9, 128.0, 127.4, 126.8, 50.8, 45.4, 17.5, 5.7, 4.6. **IR** (neat): 1721, 1018, 756, 698 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{12}H_{15}O^+$ $[M+H]^+$: 175.1117; 175.1122 found. **Specific rotation** $[\alpha]_D^{23}$: +52.1 (c = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*S*) by analogy.

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2j-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.33 (m, 2H), 7.19-7.23 (m, 3H), 3.62-3.68 (m, 1H), 3.53-3.59 (m, 1H), 1.94-2.10 (m, 3H), 1.33 (br, 1H), 0.96-1.03 (m, 1H), 0.58-0.64 (m, 1H), 0.35-0.42 (m, 1H), 0.23-0.29 (m, 1H), 0.06-0.12 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 128.5, 127.6, 126.3, 61.3, 47.7, 39.7, 17.6, 5.7, 4.0. The spectral data match those previously reported in the literature.[8] **Specific rotation** $[\alpha]_D^{23}$: +38.0 (*c* = 0.5, $CHCl_3$). **SFC** analysis: CEL2 (5:95 IPA: $scCO_2$ to 10:90 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 1.75 mL/min), 3.12 min (major), 3.42 min (minor), 96% ee. The absolute stereochemistry was assigned as (*S*) by analogy.

(*R*)-2-(chroman-4-yl)acetaldehyde (2k)

The general procedure **A** was followed using (*E*)-2-(chroman-4-ylidene)acetic acid (190 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 5% EtOAc/hexanes for 1 column volume (CV), 5-20% EtOAc/hexanes for 10 CV, then 20% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 129 mg, 73% yield, 91% ee; Run 2: 115 mg, 65% yield, 90% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.87 (t, *J* = 1.6 Hz, 1H), 7.06-7.14 (m, 2H), 6.80-6.89 (m, 2H), 4.14-4.23 (m, 2H), 3.46-3.53 (m, 1H), 2.90-2.96 (m, 1H), 2.75 (ddd, *J* = 17.6 Hz, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 2.16-2.24 (m, 1H), 1.76-1.83 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.1, 154.8, 128.7, 128.0, 124.5, 120.7, 117.4, 63.5, 50.8, 28.2, 27.9. **IR** (neat): 1718, 1488, 1451, 1222, 1041, 752 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{11}H_{12}O_2^+$ $[M+H]^+$: 177.0910; 177.0918 found. **Specific rotation** $[\alpha]_D^{23}$: +9.81 (*c* = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*R*) by analogy.

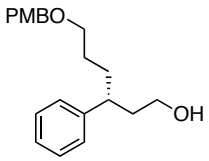
In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2k-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08-7.16 (m, 2H), 6.80-6.88 (m, 2H), 4.18-4.21 (m, 2H), 3.81 (t, *J* = 6.8 Hz, 2H), 2.99-3.05 (m, 1H), 2.03-2.16 (m, 2H), 1.63-1.85 (m, 2H), 1.63 (br, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.6, 129.2, 127.5, 126.0, 120.3, 117.0, 63.4, 60.5, 39.2, 30.3, 27.2. **IR** (neat): 3331, 2935, 1488, 1221, 1043, 701 cm^{-1}. **EA** Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.85; H, 7.93. **Specific rotation** $[\alpha]_D^{23}$: -6.18 (*c* = 0.5, $CHCl_3$). **SFC** analysis: IC (5:95 IPA: $scCO_2$ to 40:60 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 4.23 min (minor), 4.52 min (major), 91% ee. The absolute stereochemistry was assigned as (*S*) by analogy.

(*R*)-6-((4-methoxybenzyl)oxy)-3-phenylhexanal (2l)

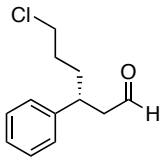
The general procedure **A** was followed using (*E*)-6-((4-methoxybenzyl)oxy)-3-phenylhex-2-enoic acid (326 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 5% EtOAc/hexanes for 1 column volume (CV), 5-15% EtOAc/hexanes for 10 CV, then 15%

EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 234 mg, 75% yield, 92% ee; Run 2: 215 mg, 69% yield, 92% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.65 (t, J = 2.0 Hz, 1H), 7.27-7.32 (m, 2H), 7.16-7.24 (m, 5H), 6.85-6.89 (m, 2H), 4.38 (s, 2H), 3.80 (s, 3H), 3.28 (td, J = 6.4 Hz, J = 1.6 Hz, 2H), 3.15-3.19 (m, 1H), 2.70-2.73 (m, 2H), 1.65-1.78 (m, 2H), 1.42-1.54 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.0, 159.3, 143.6, 130.7, 129.4, 128.8, 127.6, 126.8, 113.9, 72.6, 69.8, 55.4, 50.7, 40.0, 33.3, 27.7. **IR** (neat): 1721, 1512, 1245, 1094, 1032, 701 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{20}H_{28}NO_3^+$ $[M+NH_4]^+$: 330.2064; 330.2060 found. **Specific rotation** $[\alpha]_D^{23}$: -5.14 (c = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*R*) by analogy.

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2l-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14-7.30 (m, 7H), 6.85-6.88 (m, 2H), 4.37 (s, 2H), 3.80 (s, 3H), 3.43-3.53 (m, 2H), 3.35-3.40 (m, 2H), 2.68 (sep, J = 5.2 Hz, 1H), 1.91-1.98 (m, 1H), 1.71-1.85 (m, 2H), 1.59-1.68 (m, 1H), 1.42-1.53 (m, 2H), 1.39 (br, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 144.9, 130.8, 129.4, 128.6, 127.8, 126.4, 113.9, 72.6, 70.1, 61.3, 55.4, 42.4, 39.8, 33.5, 27.8. **IR** (neat): 3391, 2935, 1512, 1246, 1034, 701 cm^{-1}. **EA** Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.11; H, 8.48. **Specific rotation** $[\alpha]_D^{23}$: +27.6 (c = 0.5, $CHCl_3$). **SFC** analysis: OJ-H (5:95 IPA: $scCO_2$ to 40:60 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 5.64 min (major), 6.01 min (minor), 92% ee. The absolute stereochemistry was assigned as (*R*) by analogy.

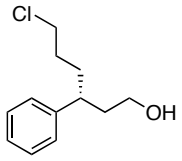


(*R*)-6-chloro-3-phenylhexanal (2m)



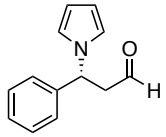
The general procedure **A** was followed using (*E*)-6-chloro-3-phenylhex-2-enoic acid (225 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 5% EtOAc/hexanes for 1 column volume (CV), 5-15% EtOAc/hexanes for 10 CV, then 15% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 140 mg, 67% yield, 92% ee; Run 2: 134 mg, 64% yield, 92% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.68 (t, J = 2.0 Hz, 1H), 7.29-7.34 (m, 2H), 7.18-7.24 (m, 3H), 3.45-3.48 (m, 2H), 3.16-3.23 (m, 1H), 2.69-2.81 (m, 2H), 1.58-1.88 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.5, 143.2, 129.0, 127.6, 127.0, 50.8, 44.9, 39.6, 33.7, 30.5. **IR** (neat): 1722, 1453, 1124, 766, 701 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{12}H_{19}ClO_2^+$ $[M+NH_4]^+$: 228.1150; 228.1141 found. **Specific rotation** $[\alpha]_D^{23}$: -6.48 (c = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*R*) by analogy.

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2m-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.33 (m, 2H), 7.15-7.23 (m, 3H), 3.51-3.57 (m, 1H), 3.43-3.49 (m, 3H), 2.73 (sep, J = 4.8 Hz, 1H), 1.91-1.99 (m, 1H), 1.56-1.87 (m, 5H), 1.21 (br, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 128.8, 127.7, 126.6, 61.1, 45.2, 42.0, 39.8, 34.1, 30.7. **IR** (neat): 3323, 2930, 1452, 1046, 760, 700 cm^{-1}. **EA** Calcd. for $C_{12}H_{17}ClO$: C, 67.76; H, 8.06. Found: C, 67.60; H, 8.04. **Specific rotation** $[\alpha]_D^{23}$: +3.09 (c = 0.5, $CHCl_3$). **SFC** analysis:



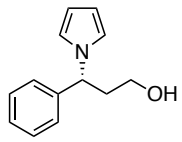
OJ-H (5:95 IPA: $scCO_2$ to 20:80 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 4.13 min (major), 4.32 min (minor), 92% ee. The absolute stereochemistry was assigned as (*R*) by analogy.

(*R*)-3-phenyl-3-(1*H*-pyrrol-1-yl)propanal (2n)

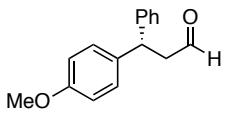


The general procedure **A** was followed using (*Z*)-3-phenyl-3-(1*H*-pyrrol-1-yl)acrylic acid (213 mg, 1.0 mmol, 1.0 equiv), 4 mol% $Cu(OAc)_2$, and 4.4 mol% (*S,S*)-Ph-BPE. Biotage Isolera (25 g SNAP cartridge, 5% EtOAc/hexanes for 1 column volume (CV), 5-20% EtOAc/hexanes for 10 CV, then 20% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 140 mg, 70% yield, 94% ee; Run 2: 143 mg, 72% yield, 94% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.75 (t, J = 1.6 Hz, 1H), 7.26-7.36 (m, 3H), 7.14-7.17 (m, 2H), 6.75 (t, J = 2.0 Hz, 2H), 6.19 (t, J = 2.0 Hz, 2H), 5.76 (dd, J = 8.4 Hz, J = 6.4 Hz, 1H), 3.39 (ddd, J = 17.6 Hz, J = 8.4 Hz, J = 1.6 Hz, 1H), 3.25 (ddd, J = 17.2 Hz, J = 6.4 Hz, J = 1.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.7, 140.6, 129.1, 128.2, 126.3, 119.7, 109.0, 57.4, 49.4. **IR** (neat): 1723, 1488, 1269, 1087, 726, 699 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{13}H_{13}NO^+$ $[M+H]^+$: 200.1070; 200.1063 found. **Specific rotation** $[\alpha]_D^{23}$: -2.57 (c = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*R*) by analogy.

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2n-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.34 (m, 2H), 7.24-7.28 (m, 1H), 7.19-7.22 (m, 2H), 6.78 (t, J = 2.0 Hz, 2H), 6.19 (t, J = 2.0 Hz, 2H), 5.34 (dd, J = 9.2 Hz, J = 6.4 Hz, 1H), 3.64-3.70 (m, 1H), 3.56-3.62 (m, 1H), 2.35-2.49 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8, 128.8, 127.8, 126.5, 119.8, 108.4, 59.8, 59.6, 38.2. **IR** (neat): 3370, 2953, 1489, 1272, 1050, 725, 699 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{13}H_{15}NO^+$ $[M+H]^+$: 202.1226; 202.1223 found. **Specific rotation** $[\alpha]_D^{23}$: +4.56 (c = 0.5, $CHCl_3$). **SFC** analysis: OJ-H (5:95 IPA: $scCO_2$ to 40:60 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 5.57 min (major), 5.71 min (minor), 94% ee. The absolute stereochemistry was assigned as (*R*) by analogy.



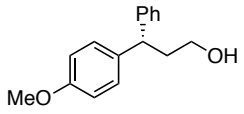
(*S*)-3-(4-methoxyphenyl)-3-phenylpropanal (2o)



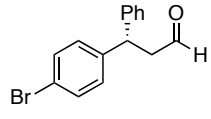
The general procedure **B** was followed using (*E*)-3-(4-methoxyphenyl)-3-phenylacrylic acid (254 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 5% EtOAc/hexanes for 1 column volume (CV), 5-20% EtOAc/hexanes for 10 CV, then 20% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 176 mg, 73% yield, 96% ee; Run 2: 166 mg, 69% yield, 97% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (t, J = 2.0 Hz, 1H), 7.27-7.31 (m, 2H), 7.14-7.23 (m, 5H), 6.82-6.85 (m, 2H), 4.58 (t, J = 8.0 Hz, 1H), 3.77 (s, 3H), 3.13 (dd, J = 8.0 Hz, J = 2.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.3, 158.4, 143.7, 135.4, 128.8, 128.8, 127.7, 126.7, 114.2, 55.4, 49.7, 44.3. The spectral data match those previously reported in the literature.[9] **Specific rotation**

$[\alpha]_D^{23}$: +14.3 (*c* = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*S*) by comparison to the sign of the specific rotation in the literature.[9]

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2o-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23-7.30 (m, 4H), 7.16-7.20 (m, 3H), 6.81-6.85 (m, 2H), 4.09 (t, *J* = 8.0 Hz, 1H), 3.77 (s, 3H), 3.59-3.64 (m, 2H), 2.29 (dt, *J* = 8.0 Hz, *J* = 6.4 Hz, 2H), 1.20 (t, *J* = 5.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 145.0, 136.7, 128.9, 128.6, 127.9, 126.3, 114.0, 61.3, 55.4, 46.6, 38.5. The spectral data match those previously reported in the literature.[10] **Specific rotation** $[\alpha]_D^{23}$: +5.54 (*c* = 0.5, $CHCl_3$). **SFC** analysis: OJ-H (5:95 IPA: $scCO_2$ to 40:60 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 5.85 (major), 6.36 min (minor), 97% ee. The absolute stereochemistry was assigned as (*S*) by comparison to the sign of the specific rotation in the literature.[10]

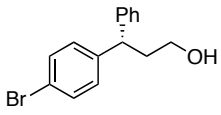


(*S*)-3-(4-bromophenyl)-3-phenylpropanal (2p)

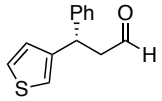


The general procedure **B** was followed using (*E*)-3-(4-bromophenyl)-3-phenylacrylic acid (303 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 5% EtOAc/hexanes for 1 column volume (CV), 5-20% EtOAc/hexanes for 10 CV, then 20% EtOAc/hexanes for 10 CV) yielded the title product as a colorless oil (Run 1: 240 mg, 83% yield, 96% ee; Run 2: 232 mg, 80% yield, 96% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.74 (t, *J* = 2.0 Hz, 1H), 7.40-7.42 (m, 2H), 7.28-7.32 (m, 2H), 7.19-7.24 (m, 3H), 7.10-7.12 (m, 2H), 4.59 (t, *J* = 7.6 Hz, 1H), 3.14-3.17 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 142.8, 142.5, 132.0, 129.6, 129.0, 127.8, 127.1, 120.7, 49.4, 44.4. The spectral data match those previously reported in the literature.[3] **Specific rotation** $[\alpha]_D^{23}$: +6.54 (*c* = 1.0, $CHCl_3$). The absolute stereochemistry was assigned as (*S*) by comparison to the sign of the specific rotation in the literature.[3]

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2p-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.42 (m, 2H), 7.27-7.31 (m, 2H), 7.18-7.23 (m, 3H), 7.11-7.15 (m, 2H), 4.12 (t, *J* = 8.0 Hz, 1H), 3.60 (t, *J* = 6.0 Hz, 2H), 2.24-2.34 (m, 2H), 1.22 (t, *J* = 5.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 143.7, 131.7, 129.7, 128.8, 127.9, 126.6, 120.2, 60.9, 46.8, 38.1. The spectral data match those previously reported in the literature.[11] **Specific rotation** $[\alpha]_D^{23}$: +11.1 (*c* = 0.5, $CHCl_3$). **SFC** analysis: OJ-H (5:95 IPA: $scCO_2$ to 40:60 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 5.11 min (major), 5.52 min (minor), 96% ee. The absolute stereochemistry was assigned as (*S*) by comparison to the sign of the specific rotation in the literature.[11]



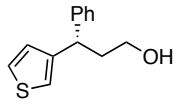
(*S*)-3-phenyl-3-(thiophen-3-yl)propanal (2q)



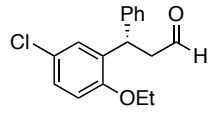
The general procedure **B** was followed using (*E*)-3-phenyl-3-(thiophen-3-yl)acrylic acid (230 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP

cartridge, 5% EtOAc/hexanes for 1 column volume (CV), 5-20% EtOAc/hexanes for 10 CV, then 20% EtOAc/hexanes for 10 CV) yielded the title product as a colorless (Run 1: 170 mg, 79% yield, 95% ee; Run 2: 165 mg, 76% yield, 94% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.74 (t, J = 2.0 Hz, 1H), 7.29-7.33 (m, 2H), 7.21-7.27 (m, 4H), 6.99-7.00 (m, 1H), 6.90 (dd, J = 5.2 Hz, J = 1.6 Hz, 1H), 4.68 (t, J = 7.6 Hz, 1H), 3.17 (ddd, J = 17.2 Hz, J = 7.6 Hz, J = 2.0 Hz, 1H), 3.09 (ddd, J = 16.8 Hz, J = 8.8 Hz, J = 2.0 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.1, 144.2, 143.1, 128.9, 127.8, 127.6, 127.0, 126.3, 120.9, 50.0, 40.9. **IR** (neat): 1721, 1081, 777, 701 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{13}H_{16}NOS^+$ $[M+NH_4]^+$: 234.0947; 234.0946 found. **Specific rotation** $[\alpha]_D^{23}$: +48.2 (c = 1.0, $CHCl_3$). The absolute stereochemistry of the new aldehyde product was assigned as (*S*) by configuration of the corresponding alcohol.

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2q-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.32 (m, 2H), 7.18-7.25 (m, 4H), 7.01-7.03 (m, 1H), 6.92 (dd, J = 5.2 Hz, J = 1.6 Hz, 1H), 4.20 (t, J = 8.0 Hz, 1H), 3.58-3.64 (m, 2H), 2.31-2.40 (m, 1H), 2.19-2.28 (m, 1H), 1.26 (br, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 144.2, 128.7, 128.0, 127.8, 126.6, 125.8, 120.3, 61.1, 43.3, 38.9. The spectral data match those previously reported in the literature.[10] **Specific rotation** $[\alpha]_D^{23}$: +46.2 (c = 0.5, $CHCl_3$). **SFC** analysis: OJ-H (5:95 IPA: $scCO_2$ to 40:60 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 6.30 min (minor), 6.97 min (major), 95% ee. The absolute stereochemistry was assigned as (*S*) by comparison to the sign of the specific rotation in the literature.[10]

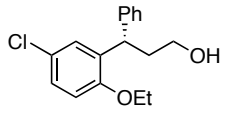


(*S*)-3-(5-chloro-2-ethoxyphenyl)-3-phenylpropanal (2r)



The general procedure **B** was followed using (*E*)-3-(5-chloro-2-ethoxyphenyl)-3-phenylacrylic acid (303 mg, 1.0 mmol, 1.0 equiv). Biotage Isolera (25 g SNAP cartridge, 5% EtOAc/hexanes for 1 column volume (CV), 5-20% EtOAc/hexanes for 10 CV, then 20% EtOAc/hexanes for 10 CV) yielded the title product as a white solid (Run 1: 232 mg, 86% yield, 94% ee; Run 2: 240 mg, 88% yield, 94% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (t, J = 2.0 Hz, 1H), 7.27-7.32 (m, 2H), 7.18-7.26 (m, 3H), 7.12 (dd, J = 8.8 Hz, J = 2.8 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 4.97 (t, J = 7.6 Hz, 1H), 3.92-4.01 (m, 2H), 3.09-3.12 (m, 2H), 1.38 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.2, 154.8, 142.3, 133.7, 128.7, 128.2, 128.1, 127.6, 126.8, 125.5, 112.9, 64.1, 48.4, 38.5, 14.8. **m.p.** 78-80 ^{o}C. **IR** (neat): 1724, 1489, 1473, 1244, 1128, 700 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{17}H_{21}NClO_2^+$ $[M+NH_4]^+$: 306.1255; 306.1265 found. **Specific rotation** $[\alpha]_D^{23}$: +19.3 (c = 1.0, $CHCl_3$). The absolute stereochemistry of the new aldehyde product was assigned as (*S*) by analogy.

In order to determine the enantiomeric ratio of the product, the corresponding primary alcohol **2r-ol** was prepared according to general procedure **C**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.29 (m, 4H), 7.16-7.20 (m, 1H), 7.13 (d, J = 2.4 Hz, 1H), 7.09 (dd, J = 8.4 Hz, J = 2.4 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 6.74 (d, J = 8.8 Hz, 1H), 4.56 (t, J = 8.0 Hz, 1H),

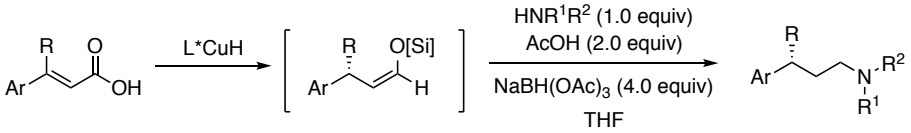


3.90-4.05 (m, 2H), 3.53-3.61 (m, 2H), 2.26-2.33 (m, 1H), 2.15-2.23 (m, 1H), 1.60 (t, J = 5.2 Hz, 1H), 1.39 (t, J = 7.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.0, 143.8, 135.1, 128.5, 128.3, 128.1, 127.1, 126.4, 125.8, 112.9, 64.4, 61.1, 39.4, 37.7, 14.9. **m.p.** 88-90 ^{o}C. **IR** (neat): 3339, 1489, 1244, 1128, 1042, 699 cm^{-1}. **EA** Calcd. for $C_{17}H_{19}ClO_2$: C, 70.22; H, 6.59. Found: C, 70.19; H, 6.57. **Specific rotation** $[\alpha]_D^{23}$: +7.06 (c = 0.5, $CHCl_3$). **SFC** analysis: IC (5:95 IPA: $scCO_2$ to 40:60 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 4.45 min (minor), 4.86 min (major), 94% ee. The absolute stereochemistry of the new alcohol product was assigned as (*S*) by analogy.

IV. Procedure for Mechanistic Studies

General procedure for mechanistic studies. In a nitrogen-filled glove box, a catalyst stock solution was prepared by adding $Cu(OAc)_2$ (19.8 mg, 0.11 mmol), (*S,S*)-Ph-BPE (61.6 mg, 0.12 mmol), and THF (5.5 mL) to an oven-dried 25 mL round bottom flask containing a magnetic stir bar. This mixture was stirred for 10 min as a homogenous blue solution formed. At this time, dimethoxy(methyl)silane (1.35 mL, 11 mmol) was added and the solution was stirred for another 5 min, during which time the solution developed a bright yellow color. An aliquot of this solution (623 μL, corresponds to 4 mol% catalyst loading) was then transferred to a separate reaction vial (Fisherbrand, 13 x 100 mm, catalog no. 1495925A) containing unsaturated acids, aldehydes, or ketene (0.25 mmol, 1.0 equiv). The reaction tube was capped (Thermo Scientific 13 mm screw cap with TEF/SIL septa, catalog no. C4015-66A), removed from the glove box, and stirred for 18 h at rt. Sat. $NaHCO_3$ (3 mL) was added to quench the reaction as part of the workup (***Caution****: gas evolution observed*), and the mixture was extracted with Et_2O (3 x 2 mL). The combined extracted organic solution was dried with anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. A stock solution (1 mL) of 1,1,2,2-tetrachloroethane in $CDCl_3$ (0.25 mmol, 1.0 equiv per mL of solution) was added to dissolve the crude residue. ^{1}H NMR analysis of the solution was used to determine the product yield by comparison to 1,1,2,2-tetrachloroethane standard using the chemical shift of silyl enol ethers. The assignment of peaks of *Z* or *E* silyl enol ethers is based on the chemical shift argument, splitting patterns, and coupling constants.

V. Procedure for One-Pot Chiral Amine Synthesis

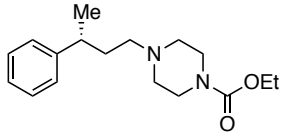


General procedure for one-pot chiral amine synthesis. An oven-dried reaction tube (Fisherbrand, 16 x 125 mm, catalog no. 1495935A) containing a magnetic stir bar was charged with unsaturated carboxylic acid (0.50 mmol, 1.0 equiv). The reaction tube was loosely capped (Cap: Kimble Chase Open Top S/T Closure catalog no. 73804-15425; Septum: Thermo Scientific 1.3 mm silicone/PTFE catalog no. B7995-15) and then brought into a nitrogen-filled glove box. $Cu(OAc)_2$ (1.8 mg, 0.020 mmol, 0.020 equiv)

and (*S,S*)-Ph-BPE (5.6 mg, 0.022 mmol, 0.022 equiv), or Josiphos **3** (8.5 mg, 0.024 mmol, 0.024 equiv) was then added to the reaction tube, followed by the addition of THF (1 mL) or toluene (1 mL) *via* syringe. Dimethoxymethylsilane (DMMS, 0.25 mL, 4.0 mmol, 4.0 equiv) was then added *via* a 1 mL syringe. The reaction tube was capped, and then was removed from the glove box. The cap was wrapped in parafilm, and the resulting mixture was stirred at rt overnight. In a well-ventilated hood, wearing appropriate gloves and eye protection, the cap was removed, and excess silane and solvent were removed using a dual-manifold with a liquid nitrogen-cooled solvent trap by outfitting the reaction tube with a connecting adapter, a 24/40 gas adapter with a greased ground-glass stopcock. The tube was left under vacuum for 1 h. (See Figure SI-1 for a picture of the apparatus. ***Caution****: after removing volatiles from the crude reaction mixture, 10 mL of 1M NaOH was added to the solvent trap, and the resulting mixture was stirred for 30 min and properly disposed*). The reaction tube was removed from the manifold, and THF (1.5 mL) was then added to the reaction tube *via* syringe, followed by the addition of acetic acid (60 mg, 1.0 mmol, 2.0 equiv) and amine (0.50 mmol, 1.0 equiv) using microsyringes. The reaction tube was capped, and the resulting mixture was stirred for 30 min. The cap was removed, and $NaBH(OAc)_3$ (424 mg, 2.0 mmol, 4.0 equiv) was added in one portion (***Caution****: gas evolution observed*). THF (0.5 mL) was added to rinse the reaction tube, and the resulting mixture was stirred uncapped at rt for 1 h. The reaction tube was then capped again, and the mixture was stirred at rt overnight. The reaction mixture was uncapped and quenched by slow addition of sat. $NaHCO_3$ solution (5 mL) over 2 min (***Caution****: gas evolution observed*). The mixture was then extracted with diethyl ether (3×), washed with sat. $NaHCO_3$, water, brine, dried with Na_2SO_4, filtered, concentrated *in vacuo* and purified by preparative thin layer chromatography to afford the corresponding amine product.

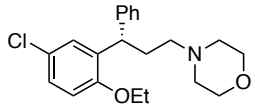
Figure SI-1: apparatus for silane removal from the crude mixture.

Ethyl (*R*)-4-(3-phenylbutyl)piperazine-1-carboxylate (4a)



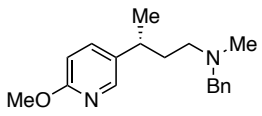
The general procedure was followed using (*E*)-3-phenylbut-2-enoic acid (81 mg, 0.50 mmol, 1.0 equiv), (*S,S*)-Ph-BPE, THF, and ethyl piperazine-1-carboxylate (79 mg, 0.50 mmol, 1.0 equiv). Preparative thin layer chromatography yielded the title product as a pale yellow oil (98 mg, 68% yield, 93% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.30 (m, 2H), 7.16-7.20 (m, 3H), 4.12 (q, J = 7.2 Hz, 2H), 3.45 (t, J = 4.8 Hz, 4H), 2.74 (sex, J = 7.2 Hz, 1H), 1.75-2.35 (m, 6H), 1.77 (t, J = 7.6 Hz, 3H), 1.23-1.27 (2t, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.6, 147.2, 128.5, 127.0, 126.1, 61.4, 57.0, 53.1, 43.8, 38.2, 35.4, 22.6, 14.8. **IR** (neat): 1699, 1429, 1233, 1128, 995, 762, 700 cm^{-1}. **EA** Calcd. for $C_{17}H_{26}N_2O_2$: C, 70.31; H, 9.02. Found: C, 70.04; H, 9.14. **Specific rotation** $[\alpha]_D^{23}$: -20.2 (c = 0.5, $CHCl_3$). **SFC** analysis: AD-H (5:95 MeOH (1% DEA): $scCO_2$ to 40:60 MeOH (1% DEA): $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 3.54 min (major), 4.38 min (minor), 93% ee. The absolute stereochemistry of the new amine product was assigned as (*R*) by configuration of the corresponding aldehyde.

(*S*)-4-(3-(5-chloro-2-ethoxyphenyl)-3-phenylpropyl)morpholine (4b)



The general procedure was followed using (*E*)-3-(5-chloro-2-ethoxyphenyl)-3-phenylacrylic acid (157 mg, 0.50 mmol, 1.0 equiv), Josiphos **3**, tolune, and morpholine (44 mg, 0.50 mmol, 1.0 equiv). Preparative thin layer chromatography yielded the title product as a white solid (140 mg, 78% yield, 94% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.28 (m, 4H), 7.20 (d, J = 2.8 Hz, 1H), 7.15-7.18 (m, 1H), 7.08 (dd, J = 8.8 Hz, J = 2.8 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 4.39 (t, J = 7.6 Hz, 1H), 3.90-3.96 (m, 2H), 3.70 (t, J = 4.4 Hz, 4H), 2.40 (s, 4H), 2.14-2.30 (m, 4H), 1.36 (t, J = 7.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.1, 144.0, 135.4, 128.4, 128.3, 127.7, 126.9, 126.2, 125.5, 112.8, 67.2, 64.1, 57.4, 53.9, 41.6, 31.6, 14.9. **m.p.** 88-90 ^oC. **IR** (neat): 1489, 1473, 1242, 1116, 1044, 699 cm^{-1}. **EA** Calcd. for $C_{21}H_{26}ClNO_2$: C, 70.08; H, 7.28. Found: C, 70.08; H, 7.33. **Specific rotation** $[\alpha]_D^{23}$: +31.9 (c = 0.5, $CHCl_3$). **SFC** analysis: OJ-H (5:95 MeOH (1% DEA): $scCO_2$ to 40:60 MeOH (1% DEA): $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 2.68 min (major), 2.86 min (minor), 95% ee. The absolute stereochemistry of the new amine product was assigned as (*S*) by analogy.

(*R*)-*N*-benzyl-3-(6-methoxypyridin-3-yl)-*N*-methylbutan-1-amine (4c)

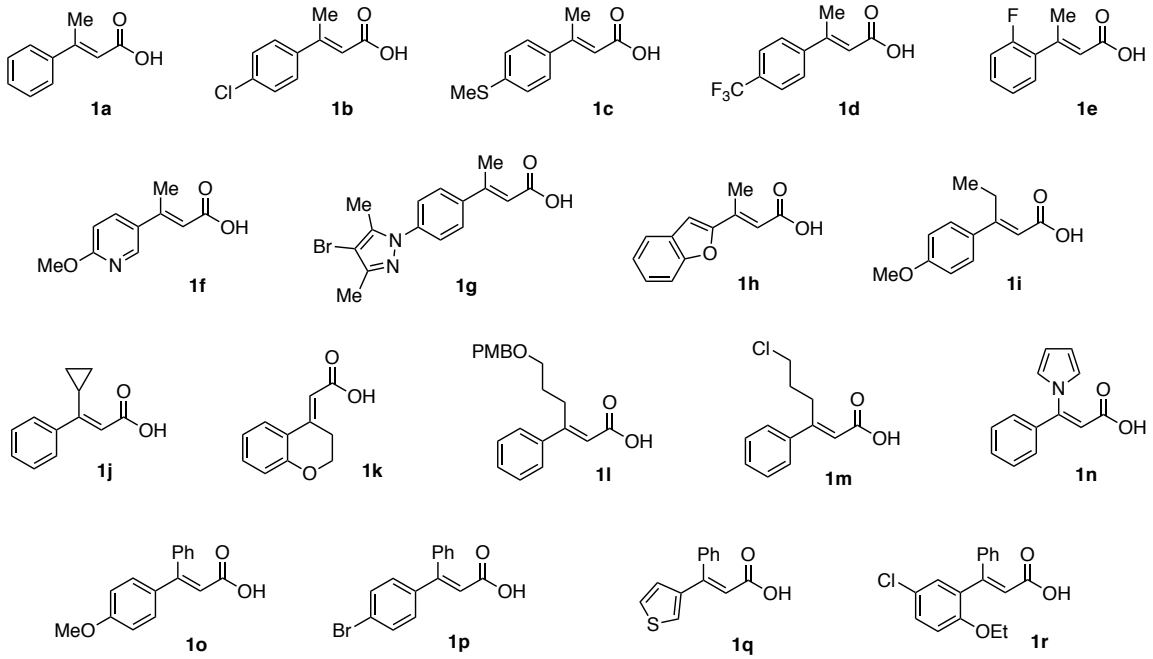


The general procedure was followed using (*E*)-3-(6-methoxypyridin-3-yl)but-2-enoic acid (97 mg, 0.50 mmol, 1.0 equiv), (*S,S*)-Ph-BPE, THF, and *N*-benzylmethylamine (61 mg, 0.50 mmol, 1.0 equiv). Preparative thin layer chromatography yielded the title product as a pale yellow oil (88 mg, 62% yield, 96% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 2.4 Hz, 1H), 7.39 (dd, J = 8.4 Hz, J = 2.8 Hz, 1H), 7.23-7.31 (m, 5H), 6.67 (d, J = 8.4 Hz, 1H), 3.92 (s, 3H), 3.39-3.46 (2d, 2H), 2.78 (sex, J = 7.2 Hz,

1H), 2.23-2.30 (m, 2H), 2.14 (s, 3H), 1.74-1.79 (m, 2H), 1.21 (d, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9, 145.3, 139.2, 137.3, 135.2, 129.1, 128.3, 127.0, 110.7, 62.5, 55.6, 53.4, 42.3, 35.9, 34.5, 22.5. **IR** (neat): 1605, 1489, 1395, 1284, 1255, 1025, 829, 735, 697 cm^{-1}. **EA** Calcd. for $C_{17}H_{26}N_2O_2$: C, 76.02; H, 8.51. Found: C, 75.81; H, 8.56. **Specific rotation** $[\alpha]_D^{23}$: -36.2 (c = 0.5, $CHCl_3$). **SFC** analysis: OJ-H (5:95 MeOH (1% DEA): $scCO_2$ to 30:70 MeOH (1% DEA): $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 2.73 min (minor), 2.82 min (major), 96% ee. The absolute stereochemistry of the new amine product was assigned as (*R*) by analogy.

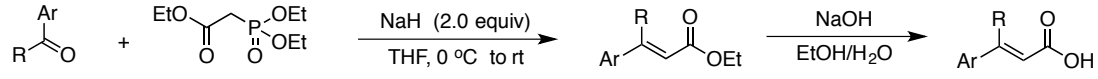
VI. Preparation of Unsaturated Acid Substrates

Acid synthesis: All the α, β-unsaturated acids used in this paper are listed below. Acid **1a**,[12] **1b**,[5] **1d**,[12] **1e**,[5] **1h**,[13] **1i**,[12] **1j**,[12] **1o**,[14] and **1p**[14] are known compounds and were prepared by previously reported procedures.



Scheme SI-1. α,β-Unsaturated acids used in the manuscript.

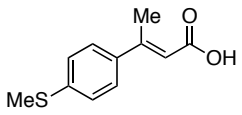
General Procedure D for the synthesis of α,β-unsaturated carboxylic acids.



A 100 mL oven-dried schlenk flask containing a magnetic stir bar was charged with sodium hydride (dry, 95%, 0.96 g, 2.0 equiv) and capped with a septum. The reaction flask was evacuated and backfilled with argon (this process was repeated a total of three

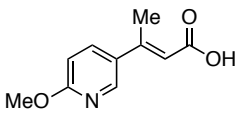
times), and the flask was equipped with a balloon filled with argon. THF (24 mL) was added to the flask, and the mixture was cooled down to 0 °C in an ice bath. Triethylphosphonoacetate (9.0 g, 7.9 mL, 2.0 equiv) was then added dropwise *via* syringe to the suspension of sodium hydride over 15 minutes, and the mixture was stirred for 30 min. The solution of corresponding ketone (20 mmol, 1.0 equiv) in THF (8 mL) was then added to the reaction flask *via* syringe at 0 °C. The reaction mixture was allowed to warm to rt, and was stirred at rt until the ketone was fully consumed (as detected by TLC analysis). The septum and the balloon were removed, and the reaction was carefully quenched by the slow addition of aqueous sat. NH_4Cl solution. The mixture was then extracted with diethyl ether (3×), washed with brine, dried with Na_2SO_4, filtered, concentrated *in vacuo* and purified by silica gel chromatography to afford the corresponding α,β-unsaturated ester. A 25 mL oven-dried round bottom flask containing a magnetic stir bar was charged with sodium hydroxide (0.40 g, 10 mmol, 2.0 equiv). Water (5 mL) was added to the reaction flask, and the mixture was stirred for 5 min until the sodium hydroxide had completely dissolved. Ethanol (6 mL) and α,β-unsaturated ester (5.0 mmol, 1.0 equiv) were then added, and the mixture was stirred at rt until the full conversion of the ester was achieved (as detected by TLC analysis). The reaction mixture was acidified to pH =1 by 1 M HCl. The white precipitate that had formed was filtered, and recrystallization afforded the corresponding unsaturated carboxylic acid as a crystalline solid.

(*E*)-3-(4-(methylthio)phenyl)but-2-enoic acid (1c)



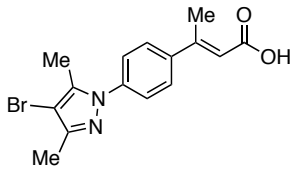
Prepared following general procedure **D** for the synthesis of acid using 1-(4-(methylthio)phenyl)ethan-1-one (3.32 g, 20 mmol). The title compound was obtained as a white solid (1.58 g, 38% yield over two steps) after recrystallization with a mixed solvent of ethyl acetate and hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.02 (br, 1H), 7.42-7.45 (m, 2H), 7.23-7.26 (m, 2H), 6.18 (q, J = 1.2 Hz, 1H), 2.59 (d, J = 1.6 Hz, 3H), 2.51 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.2, 157.8, 140.8, 138.4, 126.9, 126.1, 115.6, 18.1, 15.5. **m.p.** 137-139 ^{o}C. **IR** (neat): 2925, 1674, 1610, 1285, 1209, 1099, 869, 820 cm^{-1}. **EA** Calcd. for $C_{11}H_{12}O_2S$: C, 63.44; H, 5.81. Found: C, 63.41; H, 5.74.

(*E*)-3-(6-methoxypyridin-3-yl)but-2-enoic acid (1f)



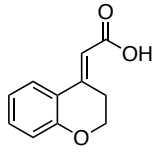
Prepared following general procedure **D** for the synthesis of acid using 1-(6-methoxypyridin-3-yl)ethan-1-one (3.02 g, 20 mmol). The title compound was obtained as a white solid (1.12 g, 29% yield over two steps) after recrystallization with a mixed solvent of ethyl acetate and hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.17 (br, 1H), 8.35 (d, J = 2.8 Hz, 1H), 7.72 (dd, J = 8.8 Hz, J = 2.8 Hz, 1H), 6.77 (d, J = 8.8 Hz, 1H), 6.14 (q, J = 1.2 Hz, 1H), 3.97 (s, 3H), 2.59 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 165.0, 155.0, 145.3, 136.7, 130.6, 115.4, 110.9, 53.9, 17.9. **m.p.** 133-135 ^{o}C. **IR** (neat): 2946, 1684, 1599, 1291, 1215, 859, 830 cm^{-1}. **EA** Calcd. for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74. Found: C, 61.90; H, 5.58.

(*E*)-3-(4-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)phenyl)but-2-enoic acid (1g)



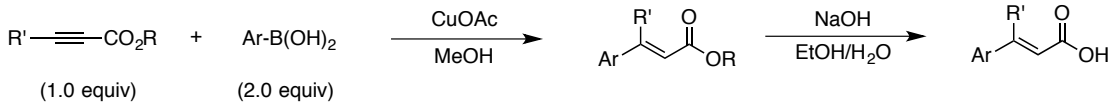
Prepared following general procedure **D** for the synthesis of acid using 1-(4-(4-bromo-3,5-dimethyl-1H-pyrazol-1-yl) phenyl) ethan-1-one (5.86 g, 20 mmol). The title compound was obtained as a white solid (2.34 g, 35% yield over two steps) after recrystallization with a mixed solvent of ethyl acetate and hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.49 (br, 1H), 7.58-7.61 (m, 2H), 7.44-7.47 (m, 2H), 6.21 (q, J = 1.6 Hz, 1H), 2.62 (d, J = 1.2 Hz, 3H), 2.35 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 157.0, 148.2, 141.3, 140.6, 137.7, 127.4, 124.4, 117.1, 97.2, 18.4, 12.5, 12.1. **m.p.** 190-192 ^{o}C. **IR** (neat): 2918, 1624, 1281, 1212, 846, 829 cm^{-1}. **EA** Calcd. for $C_{15}H_{15}BrN_2O_2$: C, 53.75; H, 4.51. Found: C, 53.79; H, 4.42.

(*E*)-2-(chroman-4-ylidene)acetic acid (1k)



Prepared following general procedure **D** for the synthesis of acid using chroman-4-one (2.96 g, 20 mmol). The title compound was obtained as a white solid (0.95 g, 25% yield over two steps) after recrystallization with a mixed solvent of THF and hexane. **^{1}H NMR** (400 MHz, DMSO) δ 12.24 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 6.94 (t, J = 8.0 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 6.38 (s, 1H), 4.18 (t, J = 6.0 Hz, 2H), 3.26 (t, J = 6.0 Hz, 2H); **^{13}C NMR** (101 MHz, DMSO) δ 167.5, 156.1, 146.3, 131.7, 125.0, 121.0, 120.4, 117.7, 110.7, 65.1, 26.2. **m.p.** 214-217 ^{o}C. **IR** (neat): 2988, 1679, 1598, 1221, 1197, 751 cm^{-1}. **EA** Calcd. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.55; H, 5.38.

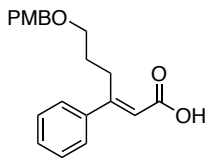
General Procedure E for the synthesis of α,β-unsaturated carboxylic acids.



A 100 mL oven-dried schlenk flask containing a magnetic stir bar was charged with copper acetate (123 mg, 1.0 mmol, 10 mol%), boronic acid (20 mmol, 2.0 equiv), and alkyne (10 mmol, 1.0 equiv) and capped with a septum. The reaction flask was evacuated and backfilled with argon (this process was repeated a total of three times), and the flask was equipped with a balloon filled with argon. Methanol (20 mL) was added to the flask, and the reaction mixture was stirred at rt for 24 h. The septum was removed, and the reaction mixture was then filtered through a silica gel pad, eluted with EtOAc, concentrated *in vacuo*, and purified by silica gel chromatography to afford the corresponding α,β-unsaturated ester. A 25 mL oven-dried round bottom flask containing a magnetic stir bar was charged with sodium hydroxide (0.40 g, 10 mmol, 2.0 equiv). Water (5 mL) was added to the reaction flask, and the mixture was stirred for 5 min until the sodium hydroxide had completely dissolved. Ethanol (6 mL) and α,β-unsaturated ester (5 mmol, 1.0 equiv) were then added, and the mixture was stirred at rt until the full conversion of the ester (as detected by TLC analysis). The reaction mixture was acidified to pH =1 by HCl (1 M). The white precipitate was filtered, redissolved in diethyl ether,

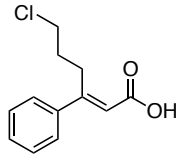
washed with brine, dried with Na_2SO_4, filtered, concentrated *in vacuo*. The resulting unsaturated carboxylic acid was directly used in the reduction reaction, or further purified by silica gel chromatography or recrystallization.

(*E*)-6-((4-methoxybenzyl)oxy)-3-phenylhex-2-enoic acid (1l)



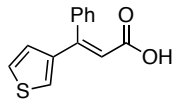
Prepared following general procedure **E** for the synthesis of acid using methyl 6-((4-methoxybenzyl)oxy)hex-2-ynoate[15] (2.62 g, 10 mmol, 1.0 equiv) and phenylboronic acid (2.44 g, 20 mmol, 2.0 equiv). The title compound was obtained as a pale yellow oil (1.83 g, 56% yield over two steps) after purification by silica gel chromatography. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.48 (m, 2H), 7.37-7.39 (m, 3H), 7.23-7.25 (m, 2H), 6.85-6.89 (m, 2H), 6.11 (s, 1H), 4.38 (s, 2H), 3.80 (s, 3H), 3.47 (t, J = 6.4 Hz, 2H), 3.21 (t, J = 7.6 Hz, 2H), 1.74-1.81 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 162.9, 159.2, 141.0, 130.7, 129.4, 129.4, 128.8, 126.9, 117.1, 113.9, 72.6, 69.7, 55.4, 29.0, 28.0. **IR** (neat): 2935, 1683, 1611, 1511, 1245, 1212, 1172, 1033, 729, 696 cm^{-1}. **EA** Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.33; H, 6.79.

(*E*)-6-chloro-3-phenylhex-2-enoic acid (1m)



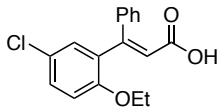
Prepared following general procedure **E** for the synthesis of acid using methyl 6-chlorohex-2-ynoate[16] (1.60 g, 10 mmol) and phenylboronic acid (2.44 g, 20 mmol, 2.0 equiv). The title compound was obtained as a white solid (0.79 g, 35% yield over two steps) after purification by silica gel chromatography. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.44 (br, 1H), 7.47-7.49 (m, 2H), 7.40-7.42 (m, 3H), 6.14 (s, 1H), 3.57 (t, J = 6.8 Hz, 2H), 3.28 (t, J = 7.6 Hz, 2H), 1.91-1.98 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 162.0, 140.5, 129.7, 128.9, 126.9, 117.3, 44.9, 32.0, 28.8. **m.p.** 73-75 ^{o}C. **IR** (neat): 2955, 1679, 1609, 1216, 880, 698 cm^{-1}. **EA** Calcd. for $C_{12}H_{13}ClO_2$: C, 64.15; H, 5.83. Found: C, 64.43; H, 5.82.

(*E*)-3-phenyl-3-(thiophen-3-yl)acrylic acid (1q)



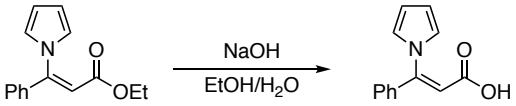
Prepared following general procedure **E** for the synthesis of acid using ethyl 3-phenylpropiolate (1.74 g, 10 mmol, 1.0 equiv) and thiophen-3-ylboronic acid (2.56 g, 20 mmol, 2.0 equiv). The title compound was obtained as a white solid (1.18 g, 51% yield over two steps) after extraction and concentration. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.41 (br, 1H), 7.36-7.40 (m, 3H), 7.32 (dd, J = 5.2 Hz, J = 3.2 Hz, 1H), 7.22-7.26 (m, 3H), 7.02 (dd, J = 3.2 Hz, J = 1.6 Hz, 1H), 6.36 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5, 153.1, 142.8, 138.4, 128.7, 128.4, 128.1, 126.6, 126.0, 114.7 (One peak is missing because of overlap). **m.p.** 154-156 ^{o}C. **IR** (neat): 1660, 1593, 1271, 868, 790, 696 cm^{-1}. **EA** Calcd. for $C_{13}H_{10}O_2S$: C, 67.81; H, 4.38. Found: C, 67.68; H, 4.36.

(*E*)-3-(5-chloro-2-ethoxyphenyl)-3-phenylacrylic acid (1r)



Prepared following general procedure **E** for the synthesis of acid using ethyl 3-phenylpropiolate (1.74 g, 10 mmol, 1.0 equiv) and (5-chloro-2-ethoxyphenyl)boronic acid (4.00 g, 20 mmol, 2.0 equiv). The title compound was obtained as a white solid (1.39 g, 46% yield over two steps) after extraction and concentration. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-7.31 (m, 6H), 7.16-7.17 (m, 1H), 6.76 (d, J = 8.8 Hz, 1H), 6.20 (d, J = 5.6 Hz, 1H), 3.79 (q, J = 6.8 Hz, 2H), 1.06 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 155.6, 155.4, 138.8, 132.6, 130.5, 130.0, 128.9, 128.5, 127.7, 125.4, 119.7, 113.9, 64.5, 14.4. **m.p.** 179-182 ^{o}C. **IR** (neat): 2983, 1695, 1612, 1237, 1201, 837, 803, 699 cm^{-1}. **EA** Calcd. for $C_{17}H_{15}ClO_3$: C, 67.44; H, 4.99. Found: C, 67.24; H, 4.93.

Synthesis of (*Z*)-3-phenyl-3-(1H-pyrrol-1-yl)acrylic acid 1n:



Ethyl (*Z*)-3-phenyl-3-(1*H*-pyrrol-1-yl)acrylate was prepared by previously reported procedures.[17] A 25 mL oven-dried round bottom flask containing a magnetic stir bar was charged with sodium hydroxide (0.40 g, 10 mmol, 2.0 equiv). Water (5 mL) was added to the reaction flask, and the mixture was stirred for 5 min until the sodium hydroxide had completely dissolved. Ethanol (6 mL) and α, β-unsaturated ester (5.0 mmol, 1.0 equiv) were then added, and the mixture was stirred at rt until the full conversion of the ester (detected by TLC). The reaction mixture was acidified to pH =1 by HCl (1 M). The white precipitate was filtered, redissolved in the diethyl ether, washed with brine, dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The title compound was obtained as a pale yellow solid (0.45 g, 42% yield) after purification by silica gel chromatography. The acid was stored in a nitrogen-filled glove box. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.50 (m, 1H), 7.37-7.42 (m, 2H), 7.29-7.32 (m, 2H), 6.74 (t, J = 2.0 Hz, 2H), 6.30 (t, J = 2.0 Hz, 2H), 5.95 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.8, 153.0, 137.2, 131.4, 128.9, 128.8, 123.5, 110.3, 107.6. **m.p.** 139-142 ^{o}C. **IR** (neat): 3057, 1684, 1613, 1478, 1282, 1195, 729, 695 cm^{-1}. **HRMS** (DART) m/z calcd. for $C_{13}H_{12}NO_2^+$ $[M+H]^+$: 214.0863; 214.0859 found.

VII. Computational Details.

All reported calculations were performed using the ORCA software[18] or GAUSSIAN 03[19]. Images of the 3D structures were rendered using CYLView[20]. The geometry of all reactants and transition states were optimized using the B3LYP[21,22] functional in the gas phase. In these geometry optimizations, a mixed basis set of SDD[23] for Cu and 6-31G(d)[24] for all other atoms was used. Ground and transition state geometries were validated by vibrational analysis at the same level, showing zero and one imaginary frequencies respectively. Single point energies were calculated using the M06[25] or PBE0[26] functional on a mixed basis set of SDD[27] for Cu and 6-311+G(2d,p) for all other atoms. In these energy calculations, the SMD solvation model[28] with THF as solvent was

applied. The reported Gibbs free energies and enthalpies include zero-point and thermal corrections calculated at 298 K using B3LYP/SDD-6-31G(d).

Investigation of Ketene Generation from Unsaturated Acids.

As a model system, the reduction of (*E*)-crotonic acid with dimethoxy(methyl)silane was studied computationally, using DCyPE (1,2-bis(dicyclohexylphosphino)ethane) as the supporting ligand on copper. This ligand is known to be competent experimentally, although slightly less efficient than Ph-BPE, but was selected as a simplified, achiral bis(trialkylphosphine) ligand to facilitate computational analysis. (For later studies on related processes wherein stereochemical issues are relevant, the full Ph-BPE ligand could be employed.) The following analysis was performed using free energies at B3LYP/SDD-6-31G(d).

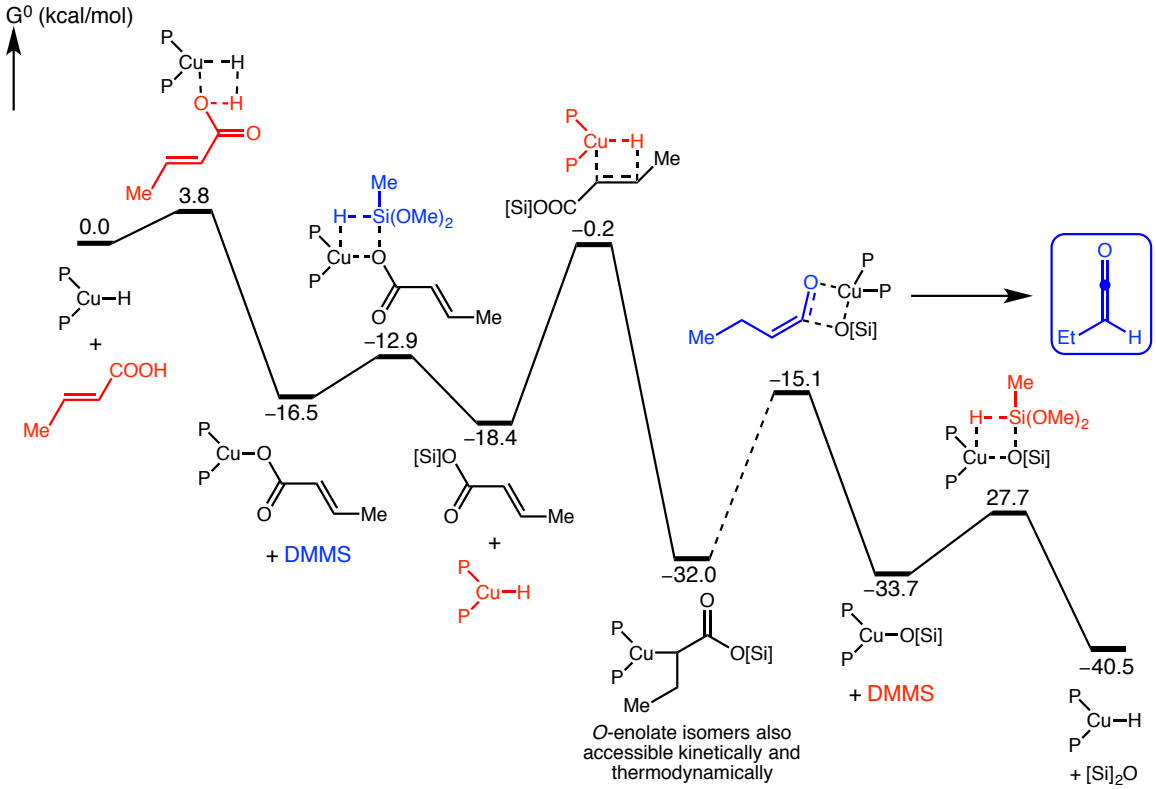


Figure SI-2. DFT Energy Profile of Cu-Catalyzed Ketene Generation.

Rapid deprotonation of the carboxylic acid by copper hydride is expected to generate a copper carboxylate complex, which is quickly silylated by DMMS through a sigma-bond metathesis mechanism. Hydrocupration of the C=C double bond proceeds with a predicted free energy barrier of 18.2 kcal/mol. Alternative hydrocupration processes including 6-membered transition states were found to be higher in transition state energy. The initial product of this hydrocupration is a C-bound enolate, which we predict should quickly isomerize between O- and C-bound forms, with a mixture of olefin geometries for the O-bound form. The lowest-barrier elimination from here proceeds through the O-

enolate, with predicted free energy barrier of 16.9 kcal/mol (dotted line) to generate ethylketene and a copper silanoate complex, which can regenerate the initial copper hydride.

The rate-limiting step appears to be hydrocupration, followed closely by elimination to form ketene. Thus, we believe that DFT cannot conclusively predict which step is rate-limiting, and this may change depending on the substituents on the acid. However, it is clear from this analysis that this proposed pathway is theoretically accessible at ambient temperature, in agreement with the other mechanistic data presented in the main paper.

Stereochemical Outcome of Reduction through a Ketene Intermediate.

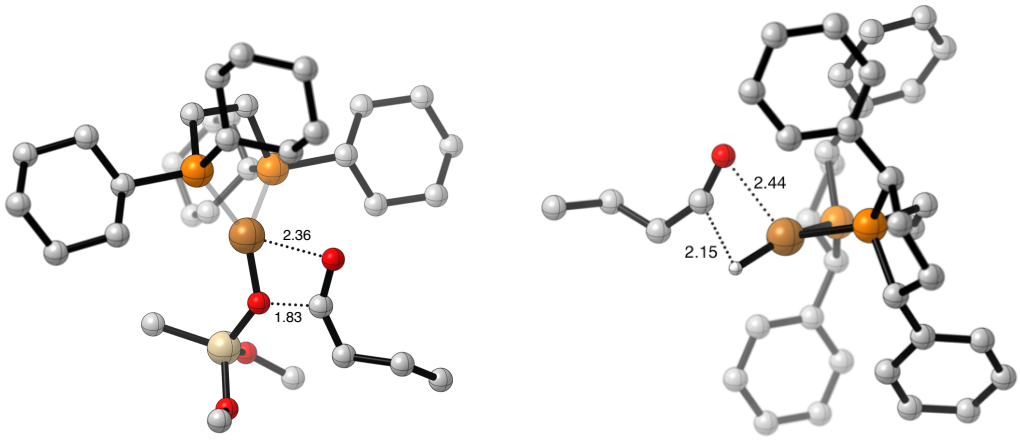
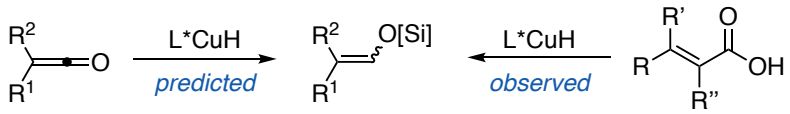
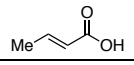
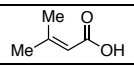
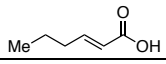
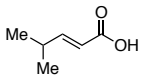
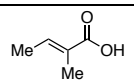


Figure SI-3. Example Transition State Structures for Ketene Generation by Elimination (left) and Hydrocupration of the Resulting Ketene (right).

We proposed that the ketene, generated as described above, is quickly reduced by copper hydride complexes. To provide evidence for our proposed mechanism, the relative rates of formation of the *E*- and *Z*- silyl enol ether products were predicted computationally, assuming that irreversible hydrocupration of a ketene intermediate is selectivity-determining. Using Ph-BPE as the supporting ligand, the relative Gibbs free energy barriers were calculated at M06/SDD-6-311+G(2d,p)/SMD(THF)//B3LYP/SDD-6-31G(d) for the reduction of a number of ketene intermediates through this mechanism. The expected product ratios were predicted using transition state theory at 273 K.

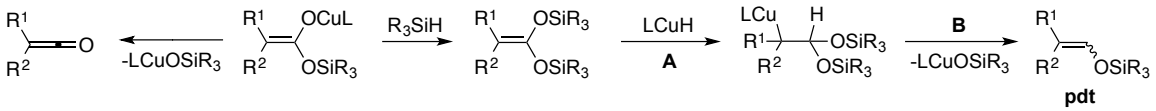
Table SI-1. Theoretical and experimental product ratios for ketene reduction by LCuH (L = (*S*,*S*)-Ph-BPE).



R^1	R^2	Acid Structure	Predicted *E*:*Z*	Observed *E*:*Z*
H	Et		1:6	1:6
H	^{i}Pr		<1:1000	1:14
H	^{n}Bu		1:6	1:7
H	^{i}Bu		1:9	1:10
Me	Ph		<1:1000	*Z* only
Me	Et		1:2.2	1:2.4

Alternative Pathway Involving a Disilyl Ketene Acetal Intermediate.

In addition to the proposed mechanism and the α,β-unsaturated aldehyde reduction mechanism ruled out in the main paper, there is the possibility of forming a disilyl ketene acetal intermediate instead of the proposed elimination to form a ketene (see below). Resulting hydrocupration and elimination from this species would also form the observed silyl enol ether product. Therefore, we decided to model this pathway at B3LYP/SDD-6-31G(d) as well (L = DCyPE, R_3SiH = DMMS, R^1 = Et, R^2 = H).



Several predictions appeared to be inconsistent with experiment:

1. As expected with such an electron-rich olefin, the barrier to hydrocupration **A** is quite high (+41.0 kcal/mol). Given that this reaction proceeds even at cryogenic temperatures, we considered this process to be unlikely.
2. The elimination step **B** can form either the *E*- or *Z*-isomer of product, depending on which –OSiMe(OMe)$_2$ group is eliminated. Calculations predict that the free energy barrier for forming the *E*-isomer (+12.3 kcal/mol from previous intermediate) is lower than the corresponding *Z*-elimination barrier (+15.3 kcal/mol) by 3.0 kcal/mol, suggesting a near-exclusive preference for the *E*-isomer under the reaction conditions. This is inconsistent with experiment (see previous section).

Cartesian Coordinates and Calculated Thermodynamic Properties

```
PhBPECuH
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2197.962326
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.54641147
Single-Point Energy (M06/SDD-6-311G+(2d,p)/SMD(THF)): -2197.344367
Total Free Energy: -2196.797955

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 C                  2.67830300    2.01458400    0.17444800
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 H                  1.38184600    3.91269400    1.70165600
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 H                 -1.38144600   -3.91240300    1.70219400
 H                 -3.41399400   -4.07342300    0.28066500
 H                 -2.46063700   -3.72215700   -1.16130700
 H                 -0.11654700    3.33246700   -0.90334000
 H                  2.92082200    1.88232700    1.23758300
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H	-1.51915000	0.21313000	1.68554100
C	0.63931200	0.43148000	1.56913400
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C	1.19309600	-3.06585900	0.90359700
C	3.66557900	-2.96178100	2.26433300
C	2.38164900	-2.74114000	0.22618900
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H	4.61632000	-2.92414500	2.78932500
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C	-5.82730600	-0.13658600	-2.13361700
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DCyPECuH
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -1900.375094
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.645239
Single-Point Energy (M06/SDD-6-311G+(2d,p)/SMD(THF)): -1899.898139
Total Free Energy: -1899.252900

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Crotonic acid DMMS ester
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/6-31G(d)): -865.697506
Vibrational Energy (B3LYP/6-31G(d)): 0.163356
Total Free Energy: -865.534150

C         3.57141600      -0.23666700      -0.06995200
H         3.42412900      -1.31600900      -0.04415100
C         2.47642900       0.53462700      -0.06826900
H         2.53500700       1.61913100      -0.09436600
C         4.98027100       0.26313700      -0.10630800
H         5.02865000       1.35618300      -0.12804200
H         5.54062500      -0.09225500       0.76882200
H         5.50635700      -0.12530800      -0.98863100
C         1.12391600      -0.06299600      -0.03399700
O         0.89026200      -1.26068100       0.00090200
O         0.15389400       0.87739400      -0.03813000
Si       -1.52524100       0.54480600      -0.10957100
C        -2.31147000       2.20184400      -0.38591600
H        -2.06368700       2.58985600      -1.37928000
H        -3.40120600       2.12389200      -0.31423300
H        -1.97070500       2.92583000       0.36130300
O        -2.03850500      -0.07555500       1.32385700
O        -1.88959400      -0.40759500      -1.39521400
C        -1.34684400      -0.86521200       2.28303000
H        -2.05519400      -1.11602100       3.07822300
H        -0.95387600      -1.78646300       1.84191700
H        -0.51099800      -0.30642400       2.72194200
C        -1.94933600      -1.83012500      -1.45050800
H        -2.33723300      -2.10581900      -2.43563300
H        -0.95635900      -2.26617700      -1.31096800
H        -2.62688800      -2.22384500      -0.68270600
Hydrocupration TS for crotonic acid DMMS ester
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2766.05548411
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.837961
Total Free Energy: -2765.217523

C        -0.63586600      -1.33962600      -4.04739100
H        -0.10454900      -2.08064100      -4.66313200
H        -1.57160500      -1.79868700      -3.71240300
H        -0.88205900      -0.47763700      -4.67360700
C         1.66575200      -2.14615500      -1.12467700
O         1.83541300      -3.07104800      -0.32371300
O         2.72392200      -1.33079000      -1.45175700
Si        4.27847200      -1.84406300      -1.03266100
C         4.69043000      -3.49590700      -1.80767400
H         4.49662400      -3.46718200      -2.88599800
H         5.74772100      -3.74956000      -1.66411400
H         4.08183900      -4.29529700      -1.37552000
O         4.61051900      -1.80275100       0.58724200
O         5.16044800      -0.61087300      -1.69468300
C         4.36911900      -2.83345800       1.53930600
H         4.65414100      -2.44904300       2.52404900
H         3.31503300      -3.12262500       1.54166500
H         4.98075600      -3.72029300       1.32501200
C         6.56503200      -0.49725400      -1.54325700
H         6.88107800       0.44336200      -2.00553100
H         6.85746400      -0.48572900      -0.48587100
H         7.09403700      -1.32014200      -2.04565700
C         0.24251000      -0.95298900      -2.87430300
H         1.11311500      -0.35631100      -3.13471600
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H	-0.80221100	0.57238000	-2.54430900
C	0.42731100	-1.87663200	-1.80968300
H	-0.31900000	-2.65289700	-1.66560800
Cu	-0.54910800	-0.04421900	-1.11041700
C	-2.37037600	0.97705300	1.42159700
H	-3.01690000	0.82319600	2.29252200
H	-2.78359700	1.83115400	0.86996100
C	-0.93372300	1.29772900	1.88023400
H	-0.94878100	2.14330800	2.57543800
H	-0.51723100	0.44395900	2.43011600
P	-2.42447500	-0.47546900	0.24098800
P	0.22634600	1.59257100	0.43486700
C	-4.10702000	-0.26390000	-0.57965700
C	-4.32685200	-1.31897800	-1.68457100
C	-5.35004300	-0.17298400	0.32846200
H	-3.98444500	0.70819000	-1.08313700
C	-5.59881400	-1.02487300	-2.49925100
H	-4.41670100	-2.31655400	-1.22862000
H	-3.45579300	-1.34900100	-2.34887600
C	-6.61391400	0.14409300	-0.49150900
H	-5.49917000	-1.13196700	0.84268100
H	-5.21102300	0.58630500	1.10778700
C	-6.83740300	-0.89431900	-1.60032000
H	-5.75144000	-1.81359600	-3.24703900
H	-5.45482800	-0.08858400	-3.05821200
H	-7.48697400	0.18823200	0.17240200
H	-6.51157300	1.14260200	-0.94167600
H	-7.71666200	-0.62782100	-2.20050600
H	-7.05656300	-1.86993900	-1.14108900
C	-2.56223300	-2.01638200	1.33957600
C	-1.18425400	-2.68288200	1.55329900
C	-3.26315300	-1.83752100	2.70439400
H	-3.17077300	-2.70694700	0.73444600
C	-1.31959500	-4.02737400	2.28610400
H	-0.54803200	-2.01370400	2.15214700
H	-0.65899500	-2.82647800	0.60701200
C	-3.41062000	-3.18367500	3.43830600
H	-2.66272600	-1.16298600	3.33166400
H	-4.24533300	-1.36757200	2.59174800
C	-2.05413700	-3.87816600	3.62539500
H	-0.32434700	-4.46249000	2.43724300
H	-1.87270500	-4.73043100	1.64501300
H	-3.89708500	-3.02297400	4.40935100
H	-4.07856200	-3.83819300	2.85875200
H	-2.19130900	-4.85769500	4.10115900
H	-1.43615800	-3.28044100	4.31220400
C	1.92165900	1.57619800	1.26268200
C	3.03954100	1.86750900	0.23580400
C	2.08089400	2.47116600	2.51013200
H	2.03577300	0.52696400	1.57656200
C	4.43700900	1.74598200	0.86868700
H	2.91947700	2.88733300	-0.15923900
H	2.95855600	1.18289800	-0.61462700
C	3.47854900	2.32315700	3.13693600
H	1.93590300	3.52291100	2.22629300
H	1.31470400	2.23700200	3.25901800
C	4.58302400	2.62843800	2.11615100
H	5.19538400	2.01001200	0.12127700
H	4.61590500	0.69710500	1.13623400
H	3.56421000	2.98501300	4.00897900
H	3.60053600	1.29535700	3.50925200
H	5.57132800	2.48464200	2.57189700
H	4.52301100	3.68927200	1.82809800
C	-0.03276000	3.42009700	-0.03858400
C	-0.77012200	3.57187700	-1.38615600
C	-0.69500800	4.31634600	1.03006100
H	0.99072500	3.79263900	-0.19102600
C	-0.81962300	5.04039000	-1.83915100
H	-1.79567500	3.18649200	-1.28957700
H	-0.29469400	2.94751700	-2.14857800
C	-0.74109800	5.78760500	0.57804000

H	-1.72361100	3.97258600	1.21103400
H	-0.16793800	4.24451400	1.98755900
C	-1.45267700	5.94551500	-0.77286500
H	-1.37314300	5.11795500	-2.78375700
H	0.20325800	5.38838800	-2.04831500
H	-1.23732200	6.39481600	1.34649000
H	0.28708600	6.16987400	0.49414200
H	-1.42845400	6.99448800	-1.09493800
H	-2.51387700	5.67886200	-0.65541900

Pre-ketene intermediate (Cu O-enolate of crotonic acid DMMS ester)
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2766.09896774
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.836772
Total Free Energy: -2765.262195

C	-4.31956800	-0.84158200	-4.25211900
H	-5.10912300	-1.57533200	-4.04341400
H	-4.42073000	-0.03127500	-3.51947700
H	-4.50984200	-0.42408000	-5.25069600
C	-1.68536400	-1.63670300	-1.97734100
O	-0.90432500	-0.62271200	-2.16332400
O	-1.44719500	-2.28946300	-0.73249300
Si	-2.50669300	-3.04680400	0.29591100
C	-1.51401200	-3.46430300	1.82483700
H	-1.11931300	-2.55929700	2.29943900
H	-2.13653500	-3.98925400	2.55723700
H	-0.66433700	-4.11040300	1.57549100
O	-3.17752300	-4.40671900	-0.38144400
O	-3.76530900	-2.09596700	0.78262100
C	-2.44519300	-5.35433500	-1.14497900
H	-3.14343500	-6.12502000	-1.48714900
H	-1.97935300	-4.88478900	-2.01977400
H	-1.66511100	-5.84190200	-0.54272700
C	-4.96117000	-1.85197000	0.04630700
H	-5.60409600	-1.21078900	0.65861200
H	-4.74235700	-1.35015200	-0.90210200
H	-5.48933600	-2.78953600	-0.16284300
C	-2.92370400	-1.48671000	-4.16003000
H	-2.84045500	-2.23428300	-4.96653300
H	-2.16149100	-0.72656200	-4.36498900
C	-2.62829500	-2.12188300	-2.82732300
H	-3.19350800	-3.00372700	-2.54392800
Cu	0.10627500	0.07459500	-0.66875900
C	2.24275300	1.04304700	1.58830300
H	3.26090300	1.27723100	1.91725800
H	1.73948100	0.56466100	2.43939200
C	1.49874200	2.34456800	1.20914800
H	1.49833900	3.03533900	2.05876300
H	2.03420900	2.85051600	0.39494900
P	2.21006700	-0.22904800	0.20525400
P	-0.23456900	2.02096200	0.55363000
C	2.62674800	-1.83649600	1.08411500
C	2.43982500	-3.02889500	0.11847500
C	3.99200700	-1.90875000	1.79758600
H	1.83817300	-1.90982100	1.84998700
C	2.64670400	-4.37332500	0.83667600
H	3.16591700	-2.95024600	-0.70470800
H	1.44289700	-2.98699700	-0.33472300
C	4.17633800	-3.25629900	2.51914700
H	4.79688200	-1.79290300	1.05816900
H	4.09915100	-1.08477100	2.51430500
C	4.00260400	-4.43835400	1.55447700
H	2.55609300	-5.19466300	0.11484200
H	1.84144700	-4.51401600	1.57274000
H	5.16528900	-3.29022400	2.99409100
H	3.43645400	-3.33640800	3.32918400
H	4.10248800	-5.38763500	2.09572600
H	4.81071800	-4.41713300	0.80801200

C	3.67977800	0.14948600	-0.92139900
C	3.19866400	0.82338100	-2.22719800
C	4.84070200	0.95138000	-0.29822500
H	4.06343000	-0.84631400	-1.19125000
C	4.35373200	1.01259800	-3.22420900
H	2.76353100	1.80596800	-1.98827200
H	2.39503000	0.23292400	-2.68171500
C	5.99741400	1.12972900	-1.29890400
H	4.47861700	1.94559500	0.00048100
H	5.20725400	0.46445500	0.61226300
C	5.52234600	1.78971900	-2.60169100
H	3.98740000	1.52505100	-4.12242700
H	4.70860600	0.02439500	-3.55237600
H	6.79718400	1.72351100	-0.83784600
H	6.43093700	0.14481600	-1.52712400
H	6.35374500	1.86495300	-3.31376800
H	5.19998800	2.81983800	-2.38760400
C	-0.61159400	3.58307900	-0.41993200
C	-1.92242500	3.41034700	-1.21989600
C	-0.61238200	4.91043600	0.36459200
H	0.21237400	3.62029200	-1.15091100
C	-2.18292500	4.61787900	-2.13633300
H	-2.76644000	3.30362400	-0.52176700
H	-1.88313300	2.48605300	-1.80778700
C	-0.87154600	6.11126800	-0.56345200
H	-1.39987200	4.87964800	1.13051300
H	0.33854900	5.04877900	0.89465000
C	-2.17602400	5.94033400	-1.35561800
H	-3.13908500	4.48598800	-2.65761500
H	-1.40602000	4.65148400	-2.91439200
H	-0.89914700	7.03632800	0.02683100
H	-0.03045100	6.21314500	-1.26519600
H	-2.31920900	6.78744800	-2.03822700
H	-3.02627100	5.95386300	-0.65739900
C	-1.39611800	2.04450200	2.04529800
C	-1.84675500	0.61053400	2.40265500
C	-0.88590800	2.77630000	3.30381000
H	-2.28285400	2.58209700	1.67590900
C	-2.89966200	0.61117200	3.52233300
H	-0.97005600	0.03018200	2.73065600
H	-2.24560300	0.10075600	1.51978200
C	-1.94970500	2.78332900	4.41697800
H	0.01298700	2.26624100	3.68017900
H	-0.58763400	3.80446700	3.06810000
C	-2.41019800	1.36145100	4.76922900
H	-3.17137500	-0.42166600	3.77011100
H	-3.81647800	1.08978800	3.14717500
H	-1.55071600	3.28953500	5.30559200
H	-2.81535300	3.37417900	4.08279500
H	-3.20062200	1.39691000	5.52959100
H	-1.56952100	0.81172700	5.21912500

Elimination TS to ketene
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2766.077501
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.836202
Total Free Energy: -2765.241300

C	-3.90264100	4.01786900	-1.71036600
H	-4.22625100	4.17093300	-2.74797500
H	-4.31063600	3.05606600	-1.37675200
H	-4.35430800	4.81182400	-1.10234500
C	-0.76494600	2.09366000	-2.17714700
O	-0.07105500	1.16265600	-2.50638400
O	-0.26032100	2.33858700	-0.26996400
Si	0.74737900	3.46852700	0.32708100
C	0.15144000	4.13049100	1.98055400
H	-0.00105000	3.30995800	2.69205800
H	0.85789500	4.84072100	2.42547800

H	-0.80623700	4.64908400	1.85903000
O	0.92267800	4.82256400	-0.62776500
O	2.27040300	2.76548900	0.50401500
C	1.44919000	4.82730000	-1.94582600
H	1.72107100	5.85792800	-2.20093700
H	2.34817300	4.20047200	-2.02878200
H	0.70424500	4.46679200	-2.66445500
C	3.38757200	3.51205100	0.95182800
H	4.27510500	2.87062700	0.90275500
H	3.56569500	4.39820300	0.32769100
H	3.26490700	3.84701500	1.99256900
C	-2.36992800	4.03472000	-1.59344100
H	-2.00941800	5.03896400	-1.86590000
H	-2.07821600	3.87125400	-0.55448600
C	-1.71997900	2.98529900	-2.45359000
H	-2.05890400	2.90002000	-3.48793700
Cu	-0.01429300	0.36939600	-0.10345100
C	0.60960100	-2.77232900	0.35517200
H	1.18172800	-3.58002100	0.82315300
H	0.37372200	-3.10697500	-0.66329700
C	-0.70167900	-2.52849700	1.13797500
H	-1.26907600	-3.46193300	1.21863800
H	-0.46807400	-2.21242600	2.16348800
P	1.62674500	-1.20101600	0.15655800
P	-1.71885500	-1.13994700	0.38846900
C	2.64254800	-1.55024000	-1.38284700
C	3.44635300	-0.29807300	-1.79813800
C	3.54195400	-2.80183800	-1.35708700
H	1.86455800	-1.70263100	-2.14770700
C	4.15817100	-0.51459600	-3.14434900
H	4.19956200	-0.07340100	-1.02799600
H	2.78117800	0.56979800	-1.85300200
C	4.24507500	-3.01088700	-2.71084400
H	4.30685000	-2.68587200	-0.57641800
H	2.95928800	-3.69519400	-1.09828300
C	5.04539300	-1.76798800	-3.12727500
H	4.75490500	0.37202700	-3.39321200
H	3.40186200	-0.61350000	-3.93646100
H	4.90098100	-3.88955100	-2.65682400
H	3.48922100	-3.23067000	-3.47922300
H	5.50436200	-1.92519600	-4.11168400
H	5.87236500	-1.61771300	-2.41694100
C	2.84943300	-1.16727400	1.59964100
C	2.40571800	-0.14520200	2.67169400
C	3.17764200	-2.52432900	2.25595700
H	3.77239300	-0.77833500	1.14367500
C	3.46214300	-0.00038600	3.78013800
H	1.45621000	-0.47871100	3.11946900
H	2.21335400	0.82441600	2.20127400
C	4.24767700	-2.37108700	3.35142700
H	2.26686800	-2.93681300	2.71356300
H	3.51182500	-3.25349600	1.50921200
C	3.81961100	-1.35125800	4.41670100
H	3.10292700	0.69927200	4.54559200
H	4.36990300	0.44899800	3.35051900
H	4.44782400	-3.34668100	3.81320100
H	5.19147500	-2.04343600	2.89090300
H	4.61404700	-1.22440400	5.16318900
H	2.94327400	-1.74130700	4.95598900
C	-2.89742300	-0.66906400	1.77646400
C	-3.67008800	0.61620300	1.40341100
C	-3.85829000	-1.75242300	2.30521800
H	-2.20457900	-0.40528300	2.59237700
C	-4.51152100	1.12787800	2.58520400
H	-4.33692300	0.40794200	0.55308400
H	-2.96986600	1.39091200	1.07092400
C	-4.68597400	-1.23195500	3.49499400
H	-4.54734000	-2.04992000	1.50308400
H	-3.30605000	-2.65374000	2.60063500
C	-5.45588800	0.04499100	3.12755400
H	-5.08193200	2.01295500	2.27703100

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H        -3.83656500       1.45616500       3.38941300
H        -5.37842900      -2.01303000       3.83471300
H        -4.01293800      -1.02166900       4.33940400
H        -6.00642100       0.42060800       3.99934300
H        -6.20856600      -0.19596400       2.36207900
C        -2.76747900      -1.93372100      -0.96905000
C        -2.11458900      -1.73207100      -2.35656900
C        -3.14893700      -3.41758200      -0.78157400
H        -3.69316600      -1.33765700      -0.95453400
C        -3.04150600      -2.21248900      -3.48539400
H        -1.17601700      -2.30569300      -2.39887700
H        -1.83563500      -0.68498300      -2.50594100
C        -4.08616500      -3.89732000      -1.90562600
H        -2.23603800      -4.03029000      -0.80076100
H        -3.62006300      -3.58899100       0.19199100
C        -3.46657400      -3.67551800      -3.29292100
H        -2.54160200      -2.08398400      -4.45365700
H        -3.93645500      -1.57307500      -3.51022000
H        -4.32734700      -4.95820800      -1.75872400
H        -5.03711700      -3.34841900      -1.83927900
H        -4.17347200      -3.97578300      -4.07682500
H        -2.58538900      -4.32576700      -3.40109200

Et,H-ketene
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/6-31G(d)): -231.227460
Vibrational Energy (B3LYP/6-31G(d)): 0.061077
Total Free Energy: -231.166384

C        -1.36688200       0.09369800      -0.08760300
O        -2.43354300      -0.39503700      -0.02747500
C        -0.16992600       0.63672800      -0.14521300
H        -0.06221500       1.51025000      -0.78270900
C         1.03424300       0.09078300       0.60227600
H         1.40323900       0.85867200       1.29639800
H         0.72703500      -0.75846300       1.22353700
C         2.17151300      -0.33934300      -0.33512800
H         2.50529500       0.49789500      -0.95932300
H         3.03536400      -0.69519900       0.23881700
H         1.84593400      -1.14404800      -1.00290600

Z-reduction TS for Et,H-ketene
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2429.187057
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.62453021
Single-Point Energy (M06/SDD-6-311+G(2d,p)/SMD(THF)): -2428.454019
Total Free Energy: -2427.829489

P        -1.12558000      -1.43405200      -0.69815700
C        -0.48689000      -2.94864600      -1.67154100
C        -1.72762300      -3.83563400      -1.90018400
C        -2.91180600      -2.89504200      -2.15102800
C        -2.95026800      -1.87687200      -0.98363800
H        -1.56357400      -4.52905000      -2.73421700
H        -1.93963900      -4.44516500      -1.01281400
H        -3.86394600      -3.43439600      -2.21892100
H        -2.77686700      -2.36202900      -3.10119600
P         0.93375200       0.36422600       1.09969200
C         0.22206700       1.62257700       2.34493000
C         1.35375200       1.86609200       3.36441800
C         2.67601000       1.83698300       2.58919000
C         2.70444000       0.52225400       1.77015400
H         1.20367600       2.81723000       3.88972800
H         1.37022800       1.07772000       4.12751700
H         3.54798800       1.89257800       3.25165900
H         2.73270800       2.69691800       1.90977700
H        -0.21126600      -2.51254200      -2.63997100
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H	-3.27135700	-2.41970400	-0.08447900
Cu	0.07419700	0.54519200	-1.06573900
C	0.43966300	-1.34518300	1.69928100
H	0.41036900	-1.38618700	2.79470800
H	1.24678600	-2.00974300	1.36819400
C	-0.90599000	-1.83184100	1.12313000
H	0.11740300	2.52486300	1.73149200
H	2.83090800	-0.30654600	2.47964000
C	-1.15209100	1.27241000	2.87425000
C	-3.75325100	0.59537300	3.73413100
C	-2.28242600	1.66316100	2.13440100
C	-1.35267800	0.54549800	4.05774900
C	-2.64095400	0.21235900	4.48480900
C	-3.56826700	1.32426500	2.55611800
H	-2.14394200	2.23717000	1.22172000
H	-0.50411100	0.24133900	4.66388300
H	-2.77206000	-0.34518100	5.40893900
H	-4.42367600	1.62913400	1.95990600
H	-4.75452700	0.33540200	4.06747000
C	3.81071800	0.43749500	0.74041300
C	5.92996000	0.29172400	-1.11176700
C	3.84639500	1.28915200	-0.37604800
C	4.85172300	-0.48634900	0.90835300
C	5.90458900	-0.56034600	-0.00682100
C	4.89654800	1.21497200	-1.29149200
H	3.04313700	2.00249000	-0.54518400
H	4.84003300	-1.15307100	1.76820500
H	6.70449100	-1.28028400	0.14778300
H	4.90350800	1.87996600	-2.15114500
H	6.74676400	0.23786300	-1.82667000
C	-3.89478800	-0.71149300	-1.19471500
C	-5.73111700	1.38414300	-1.61322500
C	-5.10658000	-0.66512400	-0.49100700
C	-3.61577500	0.31385200	-2.11222800
C	-4.52507200	1.35185500	-2.31750100
C	-6.01998100	0.37088500	-0.69780700
H	-5.33822500	-1.45050300	0.22565900
H	-2.67107300	0.31995100	-2.64956900
H	-4.28323200	2.14186400	-3.02314700
H	-6.95515200	0.38434000	-0.14357000
H	-6.43688500	2.19474400	-1.77381000
C	0.75499900	-3.58893500	-1.09058500
C	3.12416000	-4.66389600	0.00709300
C	0.71226000	-4.69366700	-0.22679700
C	2.01193300	-3.03972000	-1.39858000
C	3.18341700	-3.56482600	-0.85408400
C	1.88521200	-5.22713000	0.31425900
H	-0.23812500	-5.15555900	0.02350900
H	2.06854200	-2.18496800	-2.06932100
H	4.13885900	-3.11066500	-1.10034200
H	1.82649300	-6.08799100	0.97547300
H	4.03499700	-5.08009500	0.42901800
H	0.14135400	1.49808900	-2.30850100
H	-1.02649500	-2.90558700	1.31165100
H	-1.73088700	-1.31605300	1.62897900
C	0.18584500	3.34351800	-1.32384500
O	-0.73504400	3.39294500	-0.56577000
C	1.24791700	3.78866300	-1.99543300
H	1.74735200	3.13043400	-2.69037700
C	1.67795900	5.24080600	-1.86479900
H	2.73819500	5.28241100	-1.57217500
C	1.48667800	6.04405500	-3.16170900
H	1.84363800	7.07564600	-3.04631600
H	2.04081700	5.58765200	-3.99082100
H	0.42944500	6.07479700	-3.44736200
H	1.11931000	5.72167400	-1.05248400

E-reduction TS for Et,H-ketene
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1

Single-Point Energy (B3LYP/SDD-6-31G(d)): -2429.18858
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.62664113
Single-Point Energy (M06/SDD-6-311+G(2d,p)/SMD(THF)): -2427.828021
Total Free Energy: -2427.828021

P	0.68424100	1.34843400	-0.75428100
C	-0.20108600	2.48753000	-2.01004600
C	0.84796500	3.54597500	-2.41285200
C	2.21720200	2.85500500	-2.41405000
C	2.37471400	2.15771000	-1.04077500
H	0.60209300	3.98417500	-3.38777400
H	0.86865600	4.36892700	-1.68782100
H	3.03815100	3.56219600	-2.58132700
H	2.26728600	2.10843400	-3.21751600
P	-1.05327900	-0.57840300	1.23916200
C	-0.17236600	-1.45155400	2.69256100
C	-1.30174600	-1.86349100	3.66143200
C	-2.52678500	-2.22869200	2.81439900
C	-2.78759300	-1.04470900	1.85036100
H	-0.97886800	-2.69521000	4.29941600
H	-1.56711200	-1.03368300	4.32810000
H	-3.41325800	-2.42361400	3.42963100
H	-2.32940000	-3.14079800	2.23660700
H	-0.34684600	1.82414100	-2.87120700
H	2.45893400	2.94851800	-0.28278300
Cu	-0.02801800	-0.85992200	-0.84964100
C	-0.99480900	1.26774400	1.57136200
H	-1.04700000	1.47765900	2.64613600
H	-1.90571100	1.67137700	1.11285700
C	0.24568700	1.95720800	0.96596800
H	0.21610900	-2.35943100	2.21818600
H	-3.13647100	-0.19747100	2.45634500
C	1.00879300	-0.69421100	3.26109400
C	3.25752100	0.72807100	4.20359200
C	2.27439700	-0.87108000	2.67377500
C	0.89594700	0.20345100	4.33417300
C	2.00963800	0.90573300	4.80230000
C	3.38518800	-0.16482300	3.13622200
H	2.38101500	-1.56713400	1.84530000
H	-0.06227100	0.35559500	4.82292100
H	1.89855000	1.59010900	5.63976200
H	4.34920600	-0.31308500	2.65763700
H	4.12293300	1.27468300	4.56900500
C	-3.81682100	-1.31032800	0.77214500
C	-5.79113200	-1.82034000	-1.17444100
C	-3.58155100	-2.22655500	-0.26622700
C	-5.05578900	-0.65519400	0.81342000
C	-6.03703700	-0.90665500	-0.14845700
C	-4.55916300	-2.47746700	-1.22923000
H	-2.62025800	-2.72775700	-0.33981600
H	-5.25605500	0.05769900	1.61072800
H	-6.99239100	-0.39075300	-0.09233800
H	-4.35301000	-3.18500500	-2.02792500
H	-6.55106700	-2.01844200	-1.92571100
C	3.58199500	1.25206700	-0.91293400
C	5.88164500	-0.36127700	-0.68924100
C	4.69358900	1.68176000	-0.17371200
C	3.64187400	-0.00278400	-1.53812100
C	4.77890800	-0.80292800	-1.42418600
C	5.83605700	0.88631500	-0.06410600
H	4.66366500	2.65034500	0.32149200
H	2.78666300	-0.37638000	-2.09441800
H	4.78671900	-1.77979800	-1.89939400
H	6.68727000	1.24150100	0.51143500
H	6.76638700	-0.98613500	-0.59997600
C	-1.56766300	2.96610800	-1.56985000
C	-4.14648500	3.73270800	-0.71271000
C	-1.77341300	4.18429900	-0.90457300
C	-2.68393000	2.14390300	-1.80218100
C	-3.95812000	2.51693200	-1.37527000
C	-3.05020700	4.56484300	-0.48327400

H	-0.93823600	4.85276100	-0.71781600
H	-2.54718300	1.19589200	-2.31805900
H	-4.79920700	1.85415500	-1.55752100
H	-3.18519500	5.51695100	0.02366800
H	-5.13844400	4.03037100	-0.38366300
H	-0.01501000	-2.09637300	-1.81725700
H	0.11184000	3.04568300	0.97727700
H	1.12743100	1.72900900	1.57693300
C	1.60906800	-3.22931300	-1.10294700
O	1.56248100	-3.15554600	0.08771300
C	2.05795500	-3.62135100	-2.29282500
H	2.87090400	-4.34327600	-2.18550800
C	1.56351100	-3.32502500	-3.68297300
H	2.41997400	-3.05584000	-4.31935600
H	0.90506400	-2.45314700	-3.64085900
C	0.81591100	-4.50436900	-4.32780900
H	0.51526000	-4.26565900	-5.35624800
H	1.44115300	-5.40529600	-4.36166600
H	-0.08525300	-4.74556100	-3.75291400

Z-reduction TS for iBu,H-ketene
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2507.815158
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.68066431
Single-Point Energy (M06/SDD-6-311+G(2d,p)/SMD(THF)): -2507.040589
Total Free Energy: -2506.359924

P	1.89963200	0.47269300	-0.94976300
C	2.18641700	1.86548000	-2.22223800
C	3.65821000	1.72003000	-2.65721900
C	3.95567600	0.21786100	-2.72810800
C	3.53037000	-0.40539800	-1.37392500
H	3.83490000	2.22405300	-3.61547100
H	4.32925400	2.18247500	-1.92240100
H	5.01399300	0.01210600	-2.92730200
H	3.38087300	-0.24280800	-3.54204400
P	-0.49075400	0.69467200	1.26787300
C	-0.49412200	-0.53945000	2.72417900
C	-1.37737400	0.11439400	3.80719300
C	-2.50763700	0.85774700	3.08586000
C	-1.85139500	1.78040900	2.02905100
H	-1.75862800	-0.64254600	4.50339400
H	-0.80037100	0.83432000	4.40144200
H	-3.12498800	1.44565800	3.77544000
H	-3.17322500	0.14065200	2.58882100
H	1.56142300	1.54974200	-3.06716700
H	4.25430200	-0.07405900	-0.61777400
Cu	-0.31044400	-0.30173400	-0.83673600
C	1.03308100	1.77453300	1.45135300
H	1.26236900	1.95846500	2.50773200
H	0.75867700	2.73691600	1.00298900
C	2.27609800	1.20221800	0.73891400
H	-1.04370100	-1.39006000	2.30567600
H	-1.32939600	2.58151200	2.56937200
C	0.87406500	-1.04152700	3.13307300
C	3.44827100	-2.00532800	3.77270900
C	1.40322200	-2.17280000	2.48704400
C	1.65695600	-0.41004300	4.11210300
C	2.93062900	-0.88845400	4.43026500
C	2.67774000	-2.64678600	2.79922200
H	0.80502600	-2.67943100	1.73400200
H	1.27423500	0.45669600	4.64346400
H	3.51598000	-0.38675900	5.19688100
H	3.06669200	-3.51645000	2.27716300
H	4.43901200	-2.37655800	4.02144700
C	-2.81243400	2.41613000	1.04777300
C	-4.63978800	3.63889800	-0.71554600
C	-3.54877500	1.64656800	0.13166000
C	-3.00743200	3.80431700	1.06117500

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C        -3.91341300       4.41363100       0.18984700
C        -4.45245400       2.25428000      -0.74025600
H        -3.40615800       0.56952600       0.08469200
H        -2.44635600       4.41550500       1.76510500
H        -4.05271200       5.49136600       0.22329000
H        -5.00970500       1.64181100      -1.44427000
H        -5.34598500       4.10822300      -1.39538700
C         3.49571000      -1.91998900      -1.36308200
C         3.53302000      -4.73707200      -1.38765000
C         4.51347400      -2.63193500      -0.71245000
C         2.49252000      -2.64459100      -2.02597500
C         2.51101800      -4.03957500      -2.03600300
C         4.53615500      -4.02824300      -0.72478000
H         5.29812100      -2.08636800      -0.19207100
H         1.67501400      -2.11957400      -2.51323600
H         1.71741800      -4.58054800      -2.54402400
H         5.33711700      -4.55945000      -0.21663200
H         3.54403300      -5.82372300      -1.39536200
C         1.69802800       3.22732400      -1.77866400
C         0.67461400       5.71117900      -0.90988700
C         2.53739800       4.18717800      -1.19377400
C         0.33571600       3.54215100      -1.92540300
C        -0.17390000       4.76575100      -1.49256200
C         2.03098300       5.41781900      -0.76645300
H         3.59834100       3.98716500      -1.07675900
H        -0.33280300       2.81330300      -2.37894200
H        -1.23351700       4.97524000      -1.60686300
H         2.70295800       6.14828800      -0.32303300
H         0.28282600       6.66844300      -0.57669600
H        -1.15094200      -1.13521000      -1.86321000
H         3.05719600       1.96972400       0.67480300
H         2.68242300       0.36911500       1.32405700
C        -2.09486000      -2.40469600      -0.47060900
O        -1.25848000      -2.90600200       0.21800800
C        -3.31897300      -2.18716200      -0.95316800
H        -3.45043600      -1.45595600      -1.73504500
C        -4.48163600      -3.03647300      -0.46493700
H        -5.33951700      -2.37950600      -0.24887400
C        -4.94580800      -4.13790500      -1.44877900
H        -4.07747400      -4.78445800      -1.64237700
C        -5.40930700      -3.55358600      -2.78977700
H        -4.61065900      -2.98103700      -3.27338600
H        -5.71806000      -4.34756000      -3.48067800
H        -6.26964000      -2.88443000      -2.64888600
C        -6.05118000      -4.99320700      -0.81153900
H        -5.71525700      -5.44631700       0.12936900
H        -6.93951800      -4.38625900      -0.59011400
H        -6.36375700      -5.80367200      -1.48120300
H        -4.21515300      -3.51180200       0.48788700

E-reduction TS for iBu,H-ketene
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2507.814144
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.68074234
Single-Point Energy (M06/SDD-6-311+G(2d,p)/SMD(THF)): -2506.358172
Total Free Energy: -2506.358172

P        -1.28399200      -0.80822300      -1.26358600
C        -0.62292700      -1.63482900      -2.85427300
C        -1.87837300      -2.01790100      -3.66371700
C        -2.90474700      -0.89921600      -3.45478900
C        -3.06020200      -0.69132900      -1.92718900
H        -1.63106100      -2.16262600      -4.72260500
H        -2.30292300      -2.96243600      -3.30108200
H        -3.87463300      -1.13471700      -3.90861300
H        -2.55091900       0.03060800      -3.91882100
P         0.60034100      -0.67783500       1.40941100
C        -0.19905900      -0.16649300       3.06475700
C         0.73674300      -0.72555800       4.15625000
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C	2.17188100	-0.59170800	3.63487800
C	2.21707000	-1.24623200	2.23193200
H	0.58928800	-0.19155900	5.10294400
H	0.52461400	-1.78472600	4.34922500
H	2.90250100	-1.06635400	4.30061100
H	2.44711000	0.46789400	3.55873800
H	-0.13877700	-0.79861400	-3.37409000
H	-3.58959900	-1.56712900	-1.52833700
Cu	0.17995600	0.78190600	-0.36524500
C	-0.17010900	-2.31489800	0.90452300
H	-0.40223100	-2.92912200	1.78298000
H	0.61160300	-2.83696200	0.33923600
C	-1.43076700	-2.16217500	0.02870400
H	-0.08773000	0.92358900	3.04831100
H	2.11475500	-2.33088200	2.37024300
C	-1.67788700	-0.47039700	3.17345200
C	-4.45170300	-0.98158700	3.26049000
C	-2.60171000	0.47080700	2.68567400
C	-2.17286800	-1.66688700	3.71485100
C	-3.54659400	-1.91897100	3.76019700
C	-3.97285100	0.21642200	2.72341900
H	-2.23440600	1.40785300	2.27514200
H	-1.48947200	-2.40989000	4.11588300
H	-3.90710300	-2.84993600	4.19078000
H	-4.66477600	0.95578100	2.32999000
H	-5.51985900	-1.17910100	3.29601700
C	3.48425300	-0.98635000	1.44641800
C	5.88741900	-0.53986700	0.04276800
C	3.83971000	0.30581200	1.02570600
C	4.35243400	-2.04622600	1.14907800
C	5.54508400	-1.82838700	0.45506800
C	5.02939200	0.52480200	0.33090000
H	3.17893200	1.14545900	1.22586100
H	4.09352300	-3.05372700	1.46820200
H	6.20591700	-2.66506900	0.24217700
H	5.28127000	1.53157300	0.00901900
H	6.81397200	-0.36534000	-0.49775900
C	-3.83835700	0.54920400	-1.53931500
C	-5.36644100	2.82656100	-0.89387200
C	-5.15562900	0.42424000	-1.07566700
C	-3.29632500	1.83745400	-1.67196700
C	-4.05336100	2.96437500	-1.35060100
C	-5.91658000	1.55109700	-0.75734100
H	-5.59096200	-0.56691100	-0.96512500
H	-2.26817700	1.96238300	-2.00184300
H	-3.61029000	3.95158300	-1.44936700
H	-6.93725000	1.43042500	-0.40303200
H	-5.95352500	3.70596600	-0.64290400
C	0.42975000	-2.69624100	-2.62219900
C	2.45431000	-4.59666300	-2.10826400
C	0.12730500	-4.06284400	-2.52346400
C	1.77054600	-2.30400200	-2.46577600
C	2.77190900	-3.23935900	-2.20681100
C	1.12971000	-5.00334400	-2.27143800
H	-0.89440700	-4.40752700	-2.65257800
H	2.02841200	-1.24972800	-2.54189200
H	3.79689700	-2.90415500	-2.07768000
H	0.87092100	-6.05719000	-2.20653600
H	3.23241600	-5.32949300	-1.91238100
H	0.60232600	2.19890700	-0.88325000
H	-1.68205600	-3.12484400	-0.43281800
H	-2.28153400	-1.86789200	0.65467400
C	0.65222900	3.27958500	0.99054500
O	-0.35734000	3.00361100	1.56202400
C	1.81255500	3.89195800	0.76474600
H	2.04118500	4.59674200	1.56611300
C	2.72816800	3.84382300	-0.43016000
H	3.76693800	3.95358900	-0.08016200
C	2.45948600	4.92462400	-1.50518100
H	1.42352000	4.77968700	-1.84323900
H	2.64381400	2.85984200	-0.90063400

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C         3.39077400       4.72041300      -2.70895100
H         3.18542300       5.45068500      -3.50136900
H         4.44357600       4.83776600      -2.41689300
H         3.27314900       3.71729700      -3.13696900
C         2.58679500       6.34820000      -0.94725000
H         1.89625700       6.51139300      -0.11253400
H         3.60665200       6.53882600      -0.58435400
H         2.36527700       7.09732500      -1.71752300

Z-reduction TS for iPr,H-ketene
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2468.501173
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.65288721
Single-Point Energy (M06/SDD-6-311+G(2d,p)/SMD(THF)): -2467.094315
Total Free Energy: -2467.094315

P        -1.20544300      -1.48614800      -0.72601500
C        -0.63043000      -2.99550400      -1.74746700
C        -1.90828100      -3.81784000      -2.00816100
C        -3.04906400      -2.81822400      -2.22885900
C        -3.04658100      -1.83991300      -1.02691900
H        -1.77274900      -4.48928700      -2.86500300
H        -2.15017100      -4.44696600      -1.14245900
H        -4.02376900      -3.31253400      -2.31685700
H        -2.88802300      -2.25916500      -3.15976300
P         0.93313500       0.16047200       1.12258900
C         0.26585200       1.40948300       2.40185400
C         1.40898600       1.59266800       3.42249400
C         2.72838500       1.52844900       2.64428200
C         2.70554200       0.22944100       1.80037400
H         1.29496200       2.53888800       3.96535400
H         1.39735000       0.79069300       4.17117000
H         3.60247600       1.53803300       3.30620500
H         2.81722300       2.39856200       1.98135100
H        -0.33102300      -2.53904400      -2.69919700
H        -3.39243700      -2.39900700      -0.14702900
Cu        0.10373700       0.43381400      -1.03928100
C         0.36320200      -1.54372500       1.66844400
H         0.33399500      -1.61719300       2.76218200
H         1.13787200      -2.23435900       1.31396100
C        -1.00443600      -1.94871900       1.08143600
H         0.18628200       2.33053900       1.81309600
H         2.79521000      -0.61710200       2.49435400
C        -1.11570300       1.09016300       2.93225200
C        -3.73192500       0.47799700       3.79539000
C        -2.23772600       1.54702900       2.21823000
C        -1.33194800       0.32878300       4.09106800
C        -2.62741100       0.02740300       4.51965000
C        -3.53124600       1.24098600       2.64188900
H        -2.08653800       2.14406000       1.32255000
H        -0.48963200      -0.02909700       4.67630700
H        -2.77015100      -0.55848600       5.42430400
H        -4.38041500       1.59804700       2.06598900
H        -4.73889100       0.24313400       4.13020000
C         3.80892300       0.11846100       0.77020300
C         5.91931900      -0.08359700      -1.08627300
C         3.88466100       0.99326900      -0.32627800
C         4.80547600      -0.85653600       0.91635700
C         5.85385500      -0.95879600      -0.00123000
C         4.93050100       0.89108100      -1.24394600
H         3.11479000       1.74630800      -0.47868300
H         4.76201800      -1.54164500       1.76055600
H         6.61912600      -1.71880400       0.13592900
H         4.96887900       1.57423500      -2.08839500
H         6.73281900      -0.15924200      -1.80298700
C        -3.93992700      -0.62835700      -1.19804800
C        -5.68247000       1.55890100      -1.54233200
C        -5.15646000      -0.56100400      -0.50423400
C        -3.60808100       0.42278300      -2.06749800
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C	-4.47106800	1.50600300	-2.23595200
C	-6.02356800	0.52037700	-0.67440200
H	-5.42891700	-1.36586100	0.17549900
H	-2.65820600	0.41163100	-2.59577800
H	-4.18833700	2.31490700	-2.90397000
H	-6.96333600	0.54951400	-0.12859100
H	-6.35181900	2.40483600	-1.67411100
C	0.57949600	-3.70955400	-1.18559000
C	2.89441500	-4.93027300	-0.12590700
C	0.48417600	-4.83999000	-0.36026400
C	1.86081000	-3.20831300	-1.47417400
C	3.00585900	-3.80588200	-0.94838400
C	1.63027300	-5.44571500	0.16188800
H	-0.48702000	-5.26574100	-0.12626200
H	1.95740300	-2.33400100	-2.11448400
H	3.98177800	-3.38865000	-1.17919700
H	1.53076700	-6.32524800	0.79297300
H	3.78438300	-5.40291200	0.28086100
H	0.24201900	1.35596100	-2.29976200
H	-1.17536300	-3.02054400	1.24014500
H	-1.80332600	-1.40905600	1.60364100
C	0.25429400	3.16032600	-1.26093500
O	-0.69810300	3.18908500	-0.53805000
C	1.34371400	3.62622800	-1.87379300
H	1.85545800	2.97995300	-2.57142200
C	1.80554600	5.07528300	-1.72945000
H	2.89225200	5.04322700	-1.55016800
C	1.58285300	5.85028400	-3.04287100
H	2.00968000	6.86060200	-2.98380700
H	2.04917500	5.33476700	-3.89037200
H	0.51151000	5.94175300	-3.25815500
C	1.16999100	5.81418900	-0.54340900
H	1.37587400	5.30210000	0.40340000
H	1.56724400	6.83351900	-0.47138300
H	0.08183900	5.88465600	-0.65384800

E-reduction TS for iPr,H-ketene
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2468.494600
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.6538361
Single-Point Energy (M06/SDD-6-311+G(2d,p)/SMD(THF)): -2467.741859
Total Free Energy: -2467.088022

P	-0.69561100	-0.88985500	-1.30372300
C	0.15492000	-1.23539400	-2.97937800
C	-0.89820700	-1.98539100	-3.82136900
C	-2.26562300	-1.38622800	-3.47148700
C	-2.40493000	-1.43110600	-1.92950600
H	-0.67000000	-1.90537800	-4.89125900
H	-0.90562200	-3.05430000	-3.57383200
H	-3.09110100	-1.92955800	-3.94619000
H	-2.32415100	-0.34613400	-3.81780700
P	1.06962500	-0.26564600	1.38388800
C	0.23434200	-0.29869800	3.09971200
C	1.39061800	-0.45825200	4.10968000
C	2.59404500	0.31514200	3.55776100
C	2.82283800	-0.16623000	2.10282200
H	1.08942600	-0.10021300	5.10173500
H	1.66903800	-1.51352800	4.22146000
H	3.49815400	0.16033200	4.15849900
H	2.38558800	1.39278600	3.56239600
H	0.25980500	-0.22994000	-3.40541400
H	-2.51086700	-2.48594700	-1.64188600
Cu	0.00455800	1.04651100	-0.23255400
C	1.01801200	-2.01335200	0.70118200
H	1.09555600	-2.75484300	1.50534900
H	1.91699100	-2.10707300	0.08017300
C	-0.23618700	-2.29819800	-0.15056000
H	-0.15690500	0.72103500	3.18855200

H	3.19173700	-1.19972800	2.15095400
C	-0.93962000	-1.24956900	3.20853400
C	-3.17351900	-2.97262700	3.29991400
C	-2.21343300	-0.80308300	2.81296800
C	-0.81077500	-2.57337200	3.65632500
C	-1.91720500	-3.42559700	3.70438000
C	-3.31687500	-1.65598900	2.85383400
H	-2.33132900	0.22040000	2.46613200
H	0.15445300	-2.94980100	3.98267300
H	-1.79369700	-4.44486100	4.06201300
H	-4.28756400	-1.28829300	2.53283000
H	-4.03319200	-3.63658900	3.33793300
C	3.81474900	0.65600200	1.30763500
C	5.72255700	2.17479000	-0.10578000
C	3.54180800	1.98169100	0.93209700
C	5.05631400	0.10696600	0.95757700
C	6.00480400	0.85743300	0.25856700
C	4.48693000	2.73257800	0.23296200
H	2.57594100	2.42204300	1.16444000
H	5.28474900	-0.91876900	1.23991300
H	6.96355800	0.41269900	0.00361000
H	4.25288800	3.75477000	-0.05227600
H	6.45746100	2.76219700	-0.64983600
C	-3.59018600	-0.67051300	-1.37123200
C	-5.84707200	0.69314100	-0.37709300
C	-4.70407700	-1.37538700	-0.89294700
C	-3.62680400	0.73209800	-1.34300500
C	-4.74218300	1.40709900	-0.84688700
C	-5.82562600	-0.70236700	-0.40339500
H	-4.69321000	-2.46345200	-0.90481900
H	-2.76964200	1.30580000	-1.68370000
H	-4.73293700	2.49297600	-0.81311400
H	-6.67952800	-1.26964600	-0.04147100
H	-6.71476600	1.22002100	0.01093900
C	1.54193900	-1.83024400	-2.86985500
C	4.15826900	-2.84964200	-2.56968200
C	1.78587600	-3.21154900	-2.90614000
C	2.63934500	-0.97073400	-2.68749300
C	3.93183000	-1.47119200	-2.53325300
C	3.08098000	-3.71562800	-2.76045600
H	0.96619700	-3.90767100	-3.05760600
H	2.47431100	0.10431000	-2.65956900
H	4.75784100	-0.78243700	-2.38077700
H	3.24495100	-4.78955500	-2.79909100
H	5.16461300	-3.24359100	-2.45609000
H	-0.07714200	2.60769900	-0.40088900
H	-0.10775100	-3.23626700	-0.70387300
H	-1.10636700	-2.42080400	0.50513600
C	-1.52971700	3.26314500	0.90061800
O	-1.56857300	2.44115400	1.76776500
C	-1.86990700	4.38690300	0.27543200
H	-2.63902700	4.90465300	0.85279000
C	-1.37118800	5.08490100	-0.98207200
H	-1.95274100	6.01606000	-1.02440500
C	0.11215800	5.49670200	-0.90708400
H	0.39525600	6.08597500	-1.78966700
H	0.30139600	6.10436600	-0.01467600
H	0.75427000	4.61261200	-0.86012200
C	-1.67716600	4.31916900	-2.28415500
H	-2.74925600	4.10400800	-2.36709000
H	-1.38116900	4.91234100	-3.15987100
H	-1.13221800	3.37123800	-2.30776200

Z-reduction TS for Me,Et-ketene
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2468.500423
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.65582743
Single-Point Energy (M06/SDD-6-311+G(2d,p)/SMD(THF)): -2467.741479
Total Free Energy: -2467.085651

P	-0.71338100	-1.20209700	-1.01133800
C	0.10560400	-1.91227900	-2.58282400
C	-0.87751000	-2.97598000	-3.10745800
C	-2.28980000	-2.42484600	-2.88525300
C	-2.39705200	-2.00417800	-1.39735800
H	-0.68250800	-3.20692600	-4.16214300
H	-0.77103500	-3.91411500	-2.54807500
H	-3.06727700	-3.15757100	-3.13217200
H	-2.45812700	-1.55088100	-3.52786600
P	1.15770500	0.12109300	1.35285200
C	0.31361100	0.48805600	3.02588800
C	1.46490000	0.65393100	4.04111300
C	2.64779600	1.28752400	3.29919300
C	2.90210400	0.43746900	2.03068300
H	1.14155600	1.25832900	4.89726800
H	1.77859400	-0.31937100	4.43801100
H	3.55134200	1.32974400	3.91887200
H	2.40722200	2.31960300	3.01247000
H	0.07400200	-1.05979700	-3.27313900
H	-2.43884600	-2.92281300	-0.79699500
Cu	0.04086200	1.04123000	-0.48873000
C	1.15751700	-1.73496900	1.10386100
H	1.30438800	-2.25567700	2.05796600
H	2.03781800	-1.93733100	0.48208400
C	-0.10919900	-2.27297000	0.40736500
H	-0.12763400	1.47625200	2.85057000
H	3.27654500	-0.54099100	2.36128100
C	-0.81582400	-0.45441200	3.38622300
C	-2.96920500	-2.18905600	3.95431700
C	-2.10759700	-0.18697500	2.89882400
C	-0.62717100	-1.60669700	4.16483700
C	-1.69354900	-2.46386600	4.44868500
C	-3.17131300	-1.04612400	3.17616500
H	-2.27182600	0.69512100	2.28530600
H	0.35420900	-1.84166700	4.56662400
H	-1.52374800	-3.34627300	5.06065400
H	-4.15661300	-0.82060600	2.77797100
H	-3.79805700	-2.85597500	4.17680200
C	3.90711300	1.02498900	1.06418100
C	5.84749400	2.12541800	-0.65912300
C	3.65992200	2.22402200	0.37695000
C	5.14095500	0.38875800	0.86870000
C	6.10526600	0.93171900	0.01660400
C	4.62026400	2.76794800	-0.47571300
H	2.70240800	2.72440300	0.48927100
H	5.35078200	-0.54115900	1.39320700
H	7.05686300	0.42276400	-0.11495200
H	4.40477300	3.69335700	-1.00310600
H	6.59464800	2.55171300	-1.32329500
C	-3.62168700	-1.17344900	-1.07508000
C	-5.96782600	0.29392100	-0.54030400
C	-4.68408400	-1.74776500	-0.36265900
C	-3.75341100	0.15376400	-1.51177800
C	-4.91457600	0.87957100	-1.24682900
C	-5.84882000	-1.02410300	-0.09731700
H	-4.59916600	-2.77518900	-0.01457300
H	-2.93687800	0.63676100	-2.04233300
H	-4.98987100	1.90917400	-1.58571800
H	-6.66130700	-1.49194000	0.45311800
H	-6.87103000	0.86189700	-0.33366200
C	1.55787300	-2.30458300	-2.41172300
C	4.28599200	-2.93199800	-2.04442900
C	1.97029000	-3.62836200	-2.19839900
C	2.54290900	-1.30108400	-2.44365100
C	3.89018200	-1.60835200	-2.25728900
C	3.32138500	-3.93928400	-2.01917600
H	1.24134600	-4.43297900	-2.18254300
H	2.24224100	-0.26729000	-2.59784800
H	4.62812400	-0.81142500	-2.27277400
H	3.61650800	-4.97400100	-1.86345300

H	5.33603900	-3.17497400	-1.90490900
H	0.68165400	1.83439200	-1.63112700
H	0.06315400	-3.30462600	0.07690300
H	-0.94058000	-2.29304300	1.12130400
C	-1.20262600	2.69839800	-0.67063700
O	-1.51320500	2.20961400	0.42510400
C	-1.48871600	3.63475200	-1.58284100
C	-2.22827800	5.99653600	-0.88541500
H	-1.67888100	6.46554700	-1.70958600
H	-3.10300400	6.62342000	-0.67004400
H	-1.57813100	6.00396500	-0.00311300
C	-0.78116300	3.85754800	-2.88759200
H	0.01934300	3.12548800	-3.02150800
H	-1.47721100	3.77394600	-3.73686100
H	-0.33499000	4.86098400	-2.94540000
C	-2.65454200	4.56004300	-1.23477100
H	-3.22024700	4.13986700	-0.39528400
H	-3.34419200	4.59416900	-2.09337600

E-reduction TS for Me,Et-ketene
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2468.500242
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.6556841
Single-Point Energy (M06/SDD-6-311+G(2d,p)/SMD(THF)): -2467.740693
Total Free Energy: -2467.085009

P	-0.83450800	-0.36148400	1.35554700
C	-0.08214400	-1.49057600	2.70080500
C	-1.15615100	-1.59456300	3.80220600
C	-2.51855400	-1.61714400	3.10174100
C	-2.56679300	-0.40031100	2.14409400
H	-0.99367600	-2.48341100	4.42428900
H	-1.11689500	-0.72479500	4.47004600
H	-3.35265700	-1.57788000	3.81252000
H	-2.63277500	-2.54475300	2.52572500
P	1.20282700	1.23677800	-0.68798800
C	0.46361100	2.62496000	-1.76814300
C	1.65885000	3.52151000	-2.15101500
C	2.86643800	2.60140500	-2.36121700
C	2.99697700	1.71139100	-1.09982200
H	1.42958000	4.11559400	-3.04406500
H	1.88963000	4.22981900	-1.34563600
H	3.79302400	3.16306900	-2.52860900
H	2.71031400	1.97030600	-3.24570300
H	-0.03235900	-2.46108500	2.19173800
H	-2.63705800	0.50403400	2.76338800
Cu	0.11955800	-0.82903600	-0.84259000
C	1.05123800	1.78767600	1.09593200
H	1.19169700	2.87231800	1.17889000
H	1.88975300	1.30870700	1.61490600
C	-0.27693100	1.38210900	1.76586400
H	0.14979100	2.08289800	-2.66852500
H	3.32808600	2.35689200	-0.27533200
C	-0.76587400	3.29016400	-1.18522000
C	-3.10197900	4.42347700	-0.07907200
C	-2.02171000	2.68605400	-1.37473500
C	-0.70635400	4.47465200	-0.43539100
C	-1.86339500	5.03735600	0.11021100
C	-3.17597600	3.24363700	-0.82442100
H	-2.08801300	1.76282800	-1.94463300
H	0.24387400	4.97656600	-0.27835100
H	-1.79267300	5.95981800	0.68123900
H	-4.13155100	2.74939100	-0.97484400
H	-4.00121800	4.86198100	0.34557100
C	3.98307700	0.57126100	-1.23190100
C	5.89393600	-1.48145600	-1.51120100
C	3.78024100	-0.48002100	-2.13975000
C	5.15696100	0.57102500	-0.46564100
C	6.10671500	-0.44405600	-0.60232600

C	4.72605200	-1.49546300	-2.27800900
H	2.86764000	-0.51897800	-2.72778000
H	5.33089400	1.37770200	0.24349200
H	7.01263100	-0.41980900	-0.00180500
H	4.54534400	-2.30323300	-2.98208400
H	6.62996100	-2.27346200	-1.62090900
C	-3.73801600	-0.40906900	1.18465100
C	-5.98794800	-0.44998600	-0.51224100
C	-4.80640900	0.47691100	1.38327200
C	-3.81450900	-1.31584600	0.11603200
C	-4.92823900	-1.33557400	-0.72328700
C	-5.92360900	0.45847700	0.54538500
H	-4.76373600	1.18834000	2.20546600
H	-2.99187500	-1.99899600	-0.07950800
H	-4.96140200	-2.03958500	-1.55025700
H	-6.74174600	1.15249500	0.72136800
H	-6.85398900	-0.46642800	-1.16860600
C	1.32690800	-1.12580300	3.11772200
C	3.98551700	-0.44105100	3.77981300
C	1.60910200	-0.33206900	4.23999600
C	2.40695200	-1.57432900	2.33684000
C	3.72031600	-1.23361000	2.65961200
C	2.92498200	0.00484500	4.56900800
H	0.80362200	0.02342400	4.87573700
H	2.20819000	-2.18108700	1.45664500
H	4.53370500	-1.58406400	2.03063900
H	3.11771800	0.61494400	5.44799200
H	5.00834100	-0.17920000	4.03756000
H	0.82161400	-2.18283100	-0.97262400
H	-0.20049000	1.52844900	2.85020200
H	-1.08457700	2.02883400	1.40390000
C	-0.99334400	-1.77210000	-2.30601800
O	-1.32193900	-0.57977700	-2.40574600
C	-1.21999800	-3.01993000	-2.73499000
C	-1.40881500	-5.18351800	-1.38731800
H	-2.31726900	-5.49651500	-1.91583300
H	-0.86598900	-6.09197900	-1.09740200
H	-1.71746900	-4.66454200	-0.47185000
C	-2.27367300	-3.17140400	-3.82349800
H	-2.71565000	-2.20793000	-4.09431300
H	-1.83775900	-3.61145900	-4.73289600
H	-3.08905700	-3.83788600	-3.50739900
C	-0.52573600	-4.26699200	-2.25390800
H	0.36226000	-3.97869200	-1.68269800
H	-0.17454700	-4.84121200	-3.12633500

Z-reduction TS for nBu,H-ketene
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2507.814846
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.67906628
Single-Point Energy (M06/SDD-6-311+G(2d,p)/SMD(THF)): -2507.036146
Total Free Energy: -2506.35708

P	1.97351900	-0.22196400	-0.98636000
C	2.68922100	0.95412600	-2.30875000
C	4.00354200	0.29334600	-2.77004400
C	3.75591900	-1.21924000	-2.79704100
C	3.18460000	-1.62211300	-1.41372500
H	4.31418800	0.68096400	-3.74817600
H	4.81718800	0.50881800	-2.06600100
H	4.66901100	-1.78645500	-3.01316600
H	3.03020200	-1.46904000	-3.58193900
P	-0.12895200	0.88709400	1.25608300
C	-0.53184300	-0.22906100	2.75144500
C	-1.08165600	0.72628500	3.83113400
C	-1.89718200	1.80536700	3.11007500
C	-0.99493800	2.40365300	2.00190900
H	-1.68240100	0.17566200	4.56529700
H	-0.26357600	1.20699000	4.38236800

H	-2.23877700	2.59371100	3.79130900
H	-2.79252700	1.36078700	2.65707500
H	1.96753800	0.85816900	-3.12990100
H	4.00223700	-1.54624300	-0.68461100
Cu	-0.36640000	-0.15141500	-0.81847300
C	1.68352100	1.36040500	1.38543600
H	1.98891500	1.47185300	2.43273200
H	1.75602000	2.34922400	0.91693500
C	2.62887300	0.37332000	0.66950900
H	-1.36598200	-0.83137700	2.37399500
H	-0.20670900	2.98704000	2.49658000
C	0.57590400	-1.18307400	3.14372400
C	2.64779400	-2.99936800	3.75546900
C	0.65160900	-2.43439800	2.50657400
C	1.55343300	-0.86558900	4.09932800
C	2.57814300	-1.76553200	4.40386100
C	1.67811000	-3.33069100	2.80523200
H	-0.10333900	-2.69996700	1.77104600
H	1.51704800	0.08502100	4.62357300
H	3.32000000	-1.49986800	5.15293300
H	1.71870900	-4.28661800	2.29073900
H	3.44491900	-3.69876200	3.99351600
C	-1.70719500	3.30627600	1.01728500
C	-3.05363900	5.03675900	-0.75384400
C	-2.68841700	2.81349000	0.14103100
C	-1.41381300	4.67677400	0.98711700
C	-2.08023900	5.53762700	0.11178100
C	-3.35336900	3.67201400	-0.73477500
H	-2.92378800	1.75189600	0.12563900
H	-0.65714600	5.07588800	1.65945600
H	-1.84030300	6.59804600	0.11087500
H	-4.10589000	3.26985500	-1.40800600
H	-3.57450200	5.70249500	-1.43697700
C	2.62551000	-3.02896100	-1.35040400
C	1.67670200	-5.68087900	-1.27514800
C	3.35433600	-4.03598300	-0.70183900
C	1.40890300	-3.37278600	-1.96089100
C	0.93919000	-4.68587300	-1.92124000
C	2.88810400	-5.35192600	-0.66479800
H	4.29837400	-3.78679100	-0.22140500
H	0.80816400	-2.60713100	-2.44492700
H	-0.01143000	-4.92728500	-2.38877500
H	3.47169500	-6.11711500	-0.15899700
H	1.30754900	-6.70253300	-1.24429200
C	2.71984500	2.41011800	-1.89810000
C	2.65362300	5.11343000	-1.08620000
C	3.85882500	3.02900900	-1.36175400
C	1.54872700	3.17748000	-2.02543300
C	1.51099800	4.51106000	-1.61994500
C	3.82659600	4.36821600	-0.96288800
H	4.78640500	2.47342600	-1.26080700
H	0.65418000	2.71769900	-2.44054400
H	0.58764000	5.07469000	-1.71763600
H	4.72447500	4.82778200	-0.55742200
H	2.63059200	6.15430700	-0.77484700
H	-1.45622300	-0.64317500	-1.82999400
H	3.62428400	0.82148900	0.56308000
H	2.74108300	-0.53293300	1.27634600
C	-2.76903900	-1.46508300	-0.38925300
O	-2.14967200	-2.20299600	0.31651000
C	-3.84556500	-0.85417100	-0.88345500
H	-3.72830800	-0.15597500	-1.69841100
C	-5.22997900	-1.22854500	-0.38049400
H	-5.76880000	-0.31506600	-0.08361500
H	-5.14511000	-1.83975100	0.52743800
C	-6.07442200	-1.98587500	-1.42235500
H	-6.13158200	-1.38775300	-2.34364600
H	-5.55325500	-2.91410600	-1.69411000
C	-7.49324300	-2.30938500	-0.93564800
H	-8.00646600	-1.37508800	-0.66518700
H	-7.43326700	-2.90113200	-0.01069600

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C        -8.32868600      -3.06823700      -1.97259600
H        -9.33682900      -3.28202200      -1.59833500
H        -8.43248100      -2.48844700      -2.89825300
H        -7.86009700      -4.02502700      -2.23419900

E-reduction TS for nBu,H-ketene
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2507.813449
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.67928251
Single-Point Energy (M06/SDD-6-311+G(2d,p)/SMD(THF)): -2507.035833
Total Free Energy: -2506.356551

P         0.79158300      -0.61764900       1.47390700
C        -0.07449800      -0.49395600       3.17333400
C         1.01278400      -0.84178800       4.21131300
C         2.33722100      -0.27425000       3.68689400
C         2.51890600      -0.79668100       2.23977200
H         0.75072100      -0.44111900       5.19816700
H         1.11225800      -1.92862700       4.32287000
H         3.19041100      -0.56840600       4.30949400
H         2.30584800       0.82316700       3.68301600
P        -0.98228700      -1.00587000      -1.24784500
C        -0.09070700      -1.47106900      -2.87276800
C        -1.19504600      -2.03216200      -3.79409300
C        -2.48154500      -1.25185700      -3.49923800
C        -2.71092500      -1.30680000      -1.96827500
H        -0.89636400      -1.95441000      -4.84657700
H        -1.37209400      -3.09520600      -3.58918600
H        -3.34762200      -1.66357700      -4.03098100
H        -2.37421400      -0.20754800      -3.81995400
H        -0.27895600       0.58037400       3.25862200
H         2.70633900      -1.87720800       2.30531600
Cu       -0.08954800       0.83621000      -0.11273700
C        -0.78389900      -2.45207900      -0.06841300
H        -0.77700500      -3.40550900      -0.60988800
H        -1.68295800      -2.43790000       0.55974000
C         0.47415400      -2.34819200       0.81877600
H         0.21197100      -0.49334800      -3.26389500
H        -2.97024200      -2.34251800      -1.71058100
C         1.16564000      -2.29636800      -2.68778500
C         3.54562300      -3.75163600      -2.25644800
C         2.38442500      -1.63527300      -2.45156900
C         1.16680900      -3.69962900      -2.71132200
C         2.34539700      -4.42019600      -2.50054000
C         3.55990900      -2.35441100      -2.23326900
H         2.40291300      -0.54832400      -2.43388900
H         0.24763600      -4.24468500      -2.90590500
H         2.32214800      -5.50674400      -2.53070400
H         4.48576800      -1.81882700      -2.04266600
H         4.46169400      -4.31308400      -2.09258800
C        -3.81062600      -0.40034100      -1.45641500
C        -5.91919400       1.24623400      -0.56882600
C        -3.67894200       0.99795100      -1.45872200
C        -5.01423800      -0.95517000      -0.99885700
C        -6.06178200      -0.14220600      -0.55973700
C        -4.72328800       1.81167500      -1.01888600
H        -2.74633500       1.45395200      -1.77991500
H        -5.13396400      -2.03667900      -0.99048500
H        -6.98787500      -0.59499200      -0.21431300
H        -4.59755400       2.89113300      -1.02318500
H        -6.73133200       1.88266800      -0.22743300
C         3.66325900      -0.16695800       1.47239900
C         5.85338400       0.97633500       0.11649100
C         4.84681600      -0.89315200       1.27547100
C         3.59525200       1.14353300       0.97544200
C         4.67813000       1.70802800       0.30117200
C         5.93506700      -0.32816800       0.60722200
H         4.91715400      -1.91224500       1.65056700
H         2.68266700       1.72253500       1.08603200
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H	4.58729600	2.71617900	-0.09306400
H	6.84383900	-0.90878900	0.46951400
H	6.69587100	1.41666800	-0.41027300
C	-1.40134300	-1.21638600	3.25474200
C	-3.91090200	-2.51028400	3.28599600
C	-1.52799100	-2.53183400	3.72630400
C	-2.56150000	-0.56087100	2.80692500
C	-3.80149500	-1.19891600	2.81565500
C	-2.77057400	-3.17089900	3.74439400
H	-0.65733300	-3.06721800	4.09341200
H	-2.48634300	0.46034300	2.43951100
H	-4.67820700	-0.67123600	2.45113800
H	-2.84411400	-4.18799900	4.12100100
H	-4.87610500	-3.00929800	3.30014900
H	-0.23493100	2.37511900	-0.38326600
H	0.41556200	-3.07536400	1.63744100
H	1.36386100	-2.59270900	0.22600000
C	1.38283500	2.70296100	-1.70803300
O	1.42881800	1.74357800	-2.41740000
C	1.71717700	3.90285200	-1.24010400
H	2.49295700	4.36117200	-1.85758500
C	1.13636500	4.72195900	-0.11978700
H	1.95752000	5.14016800	0.48310400
H	0.55759800	4.06303900	0.53451200
C	0.23888400	5.87836500	-0.60013100
H	0.79676800	6.50944000	-1.30809900
H	-0.60351800	5.45484300	-1.16417800
C	-0.28985900	6.74641400	0.54896600
H	0.55953900	7.15805700	1.11380000
H	-0.84453600	6.11124800	1.25468500
C	-1.19079700	7.89317300	0.07740500
H	-1.55099300	8.49560300	0.91992200
H	-0.65367500	8.56305400	-0.60575200
H	-2.06847200	7.51118800	-0.45871100

Disilyl ketene acetal
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/6-31G(d)): -1426.071438
Vibrational Energy (B3LYP/6-31G(d)): 0.285109
Total Free Energy: -1425.786330

C	0.88471300	4.16875900	1.15094500
H	0.82218900	3.52352100	2.03428400
H	1.94756000	4.32407300	0.92881900
H	0.45009300	5.14312100	1.40589400
O	-1.20063500	0.91838900	-0.07784000
Si	-2.20041600	-0.40435700	-0.30087400
C	-2.30690500	-0.89163200	-2.10032500
H	-1.31291500	-1.12480000	-2.49339200
H	-2.94552200	-1.77335700	-2.22987600
H	-2.72890700	-0.08213400	-2.70760500
O	-3.66689000	0.05605700	0.30459000
O	-1.67882300	-1.64287000	0.66272500
C	-4.35048300	1.25238400	-0.03721500
H	-5.28044900	1.28762100	0.53830300
H	-3.74850500	2.13554200	0.20747300
H	-4.60420000	1.28244100	-1.10601500
C	-2.52514000	-2.64013700	1.22210800
H	-1.94280900	-3.19942300	1.96093800
H	-3.39500600	-2.19431600	1.71632900
H	-2.87390000	-3.34254600	0.45291000
C	0.15556700	3.53159800	-0.04516600
H	-0.90313700	3.39640800	0.20026500
H	0.19188700	4.23396100	-0.89222000
C	0.75124600	2.21415600	-0.45854400
H	1.78875400	2.19219700	-0.77743300
C	0.10499000	1.04344000	-0.44377300
O	0.64790500	-0.15752700	-0.82497100
Si	2.07087200	-0.85699800	-0.28899100

C	2.01383400	-2.59439400	-0.96608700
O	2.23178400	-0.79425100	1.35077700
O	3.31532200	0.03525200	-0.90031500
H	1.91487200	-2.57488800	-2.05687600
H	2.92553100	-3.15013700	-0.71915900
H	1.15774300	-3.14554500	-0.56130400
C	1.39356300	-1.43782400	2.30534600
C	4.64556600	0.03526100	-0.39954700
H	1.68597000	-1.08288400	3.29813300
H	0.33734900	-1.20505500	2.13474500
H	1.52601000	-2.52779700	2.27250200
H	5.18697800	0.85360900	-0.88364800
H	4.66426400	0.18615200	0.68543100
H	5.15875000	-0.90686800	-0.63655100

Disilyl ketene acetal hydrocupration TS
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -3326.409506
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.958651
Total Free Energy: -3325.450855

C	-0.61353100	-0.32799200	-4.23537400
H	-1.35711800	0.43194400	-4.50825100
H	0.32552700	0.19291700	-4.01640000
H	-0.45751000	-0.96792300	-5.11251500
O	-2.09963100	-2.15726100	-0.55762600
Si	-1.47667000	-3.57840600	0.02390200
C	0.08432400	-4.10851400	-0.84896200
H	0.82217000	-3.30143600	-0.86070500
H	0.53647300	-4.98248400	-0.36563000
H	-0.14667800	-4.38103700	-1.88428700
O	-2.58629600	-4.75072800	-0.32651700
O	-1.29101300	-3.42306400	1.66845000
C	-3.91738100	-4.80974600	0.17690400
H	-3.93891900	-5.32951300	1.14414100
H	-4.35701500	-3.81471600	0.30126700
H	-4.52239100	-5.38189100	-0.53426400
C	-0.92430200	-4.50499100	2.51033000
H	-0.90169100	-4.13952900	3.54160600
H	-1.64376600	-5.33248000	2.44738900
H	0.07297900	-4.89318300	2.26114900
C	-1.08489100	-1.13953400	-3.02366600
H	-2.01067300	-1.67082400	-3.30653200
H	-0.35213400	-1.92856400	-2.81359500
Cu	0.21240600	0.06480200	-0.32042800
C	2.19606600	2.63935200	-0.46268200
H	2.57714400	3.63441900	-0.20817900
H	2.20106200	2.56365500	-1.55758500
C	3.10967200	1.55894100	0.14405100
H	4.13774100	1.69401900	-0.20511500
H	3.13650600	1.67533700	1.23448600
P	0.41146800	2.39738000	0.05574300
P	2.49605700	-0.19542100	-0.17853400
C	-0.50423500	3.55139600	-1.11820400
C	-2.02255700	3.54323800	-0.83557700
C	0.00619400	5.00125400	-1.24560500
H	-0.35200500	3.05283200	-2.08844400
C	-2.79797200	4.30899900	-1.92140900
H	-2.21538000	4.02111700	0.13658100
H	-2.38869300	2.51488900	-0.75440500
C	-0.76581100	5.76861600	-2.33528900
H	-0.12460400	5.52190400	-0.28656100
H	1.07904900	5.02053400	-1.47240400
C	-2.28015900	5.74616600	-2.08019600
H	-3.86893100	4.31445500	-1.68080800
H	-2.69680600	3.77644000	-2.87840500
H	-0.40273600	6.80331900	-2.39017900
H	-0.55534800	5.31091100	-3.31324600
H	-2.81016000	6.25579600	-2.89502000

H	-2.49925400	6.31258300	-1.16246600
C	0.26139100	3.21703000	1.76334000
C	0.19807200	2.14817400	2.87696500
C	1.30626800	4.29547200	2.11921200
H	-0.72427700	3.70549600	1.73169400
C	-0.08939500	2.77806600	4.24968200
H	1.15823000	1.61185500	2.92088100
H	-0.55479300	1.39234800	2.62925200
C	1.01403400	4.92964200	3.49179300
H	2.30675700	3.83992400	2.14904600
H	1.34284900	5.07725400	1.35232400
C	0.93150500	3.87059400	4.60035000
H	-0.09610500	1.99930500	5.02329300
H	-1.09891200	3.21604900	4.23987800
H	1.78630500	5.67309600	3.72947100
H	0.06052300	5.47598700	3.43960500
H	0.67571700	4.34190300	5.55804200
H	1.92229800	3.41033400	4.73337700
C	3.08509100	-1.04231500	1.40519500
C	2.55329600	-2.48382800	1.52265700
C	4.60194600	-0.99470000	1.68179100
H	2.57642000	-0.45064700	2.18220000
C	2.91351900	-3.10998400	2.88167700
H	2.98195500	-3.10401600	0.72034500
H	1.46653200	-2.48313000	1.38878500
C	4.94671300	-1.61246400	3.04918500
H	5.13419000	-1.55549400	0.90082700
H	4.97494700	0.03618500	1.63895400
C	4.42137900	-3.05016400	3.16387100
H	2.56083800	-4.14908400	2.91666600
H	2.37454600	-2.57153800	3.67514600
H	6.03316100	-1.58728100	3.20495500
H	4.50174000	-0.99803900	3.84589200
H	4.64103800	-3.45805500	4.15886900
H	4.95226500	-3.68707600	2.44032800
C	3.62780800	-0.92243600	-1.52710000
C	2.86098700	-1.08647800	-2.85526300
C	4.96566500	-0.19782600	-1.78307900
H	3.85954800	-1.93249400	-1.15466800
C	3.70180000	-1.82035900	-3.91299800
H	2.58331700	-0.09272900	-3.23508500
H	1.91895400	-1.61715100	-2.68378800
C	5.81560400	-0.94000300	-2.83096100
H	4.76203200	0.81723000	-2.15396900
H	5.53846700	-0.08494900	-0.85614000
C	5.05141900	-1.12741700	-4.14910800
H	3.13833000	-1.88953300	-4.85211800
H	3.87875100	-2.85376800	-3.57843100
H	6.75037900	-0.39114300	-3.00493200
H	6.10136300	-1.92457100	-2.43170800
H	5.65722000	-1.70079100	-4.86233000
H	4.87700700	-0.14247000	-4.60747400
C	-1.31899200	-0.26387000	-1.80598000
H	-1.72600800	0.72117000	-2.02120400
C	-1.77957700	-0.80649800	-0.57196600
H	-0.64683700	-0.84528900	0.71048100
O	-2.68869600	-0.04763700	0.15726600
Si	-4.34806400	-0.22084200	0.24542200
C	-4.96344200	1.39703800	0.94265700
O	-4.77662100	-1.50754100	1.20409100
O	-5.07917000	-0.44707500	-1.21109800
H	-4.77582100	2.21803000	0.24276500
H	-6.04190500	1.34811700	1.12729800
H	-4.46412100	1.64288800	1.88650400
C	-4.26682600	-1.70453200	2.51943800
C	-5.23150500	-1.66538600	-1.92693900
H	-4.83902500	-2.51571500	2.98185800
H	-3.20819200	-1.98323800	2.49350700
H	-4.39012500	-0.80504500	3.13883400
H	-4.26369700	-2.13878700	-2.12387100
H	-5.86447300	-2.36824700	-1.37172300

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H        -5.71622400      -1.43274800      -2.88048400

Disilyl ketene acetal hydrocuprated intermediate
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -3326.46965217
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.962958
Total Free Energy: -3325.506695

C         0.21503000      -1.05067600      -3.66276000
H         0.07921300      -2.12994000      -3.51409800
H        -0.72994000      -0.56092000      -3.39338300
H         0.39264800      -0.88444500      -4.73379100
O         3.61513100      -0.94931400      -0.89751600
Si        5.04780000      -0.33904200      -1.41979200
C         4.84874700       0.87421400      -2.83700800
H         4.15899900       1.68351700      -2.57093200
H         5.81051200       1.32847000      -3.10371200
H         4.45168500       0.38303100      -3.73187000
O         6.00313600      -1.61896500      -1.85864800
O         5.82338700       0.42151200      -0.16105500
C         5.53715100      -2.80058100      -2.49130700
H         6.36914400      -3.51105600      -2.53662800
H         4.71094600      -3.25214700      -1.93072100
H         5.19757000      -2.60070500      -3.51758700
C         7.17041600       0.86100800      -0.21825800
H         7.41826100       1.32821300       0.74056000
H         7.85683700       0.02250600      -0.39001200
H         7.32271900       1.60679200      -1.01178700
C         1.37233600      -0.52370200      -2.80743700
H         2.30097300      -0.98866200      -3.18230000
H         1.48488200       0.55575500      -3.00270000
Cu       -0.49072900      -0.01386300      -0.50471300
C        -3.74774400       0.65581900      -0.08406500
H        -4.76119400       0.46292700       0.28364900
H        -3.84745200       0.99058500      -1.12569300
C        -3.07786000       1.76075000       0.75961400
H        -3.69310600       2.66653800       0.75758000
H        -3.00789700       1.43195200       1.80473300
P        -2.69323300      -0.90061700      -0.13530400
P        -1.30830400       2.08757100       0.21050500
C        -3.45850500      -1.87811100      -1.54923400
C        -2.66481900      -3.18135500      -1.78838200
C        -4.97153000      -2.16736000      -1.48622300
H        -3.27465700      -1.22486800      -2.41761500
C        -3.15082800      -3.91150200      -3.05196600
H        -2.78799100      -3.84973000      -0.92309500
H        -1.59528000      -2.95691500      -1.86315400
C        -5.45436700      -2.89340600      -2.75621000
H        -5.18586600      -2.80133100      -0.61450000
H        -5.54064100      -1.23932300      -1.35023000
C        -4.66144100      -4.18465100      -3.00530800
H        -2.59687000      -4.85088400      -3.17435300
H        -2.91904500      -3.29498700      -3.93270200
H        -6.52689400      -3.11267300      -2.67387200
H        -5.33777800      -2.22252400      -3.62026900
H        -4.99269600      -4.65905000      -3.93780800
H        -4.87538300      -4.90052400      -2.19743900
C        -3.13821600      -1.86339400       1.43732900
C        -2.00244100      -1.75164300       2.47950200
C        -4.49971400      -1.53442400       2.08482800
H        -3.16866500      -2.91221000       1.10529900
C        -2.27740600      -2.62712800       3.71333100
H        -1.90659900      -0.70209600       2.79965500
H        -1.04500600      -2.03108800       2.02734800
C        -4.76889700      -2.42066900       3.31464500
H        -4.50819700      -0.48160100       2.40221300
H        -5.31514600      -1.64782800       1.36157900
C        -3.63929400      -2.31295000       4.34852300
H        -1.47200900      -2.49559100       4.44681300
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H	-2.25344000	-3.68532100	3.41268400
H	-5.73058600	-2.14372300	3.76616000
H	-4.86644500	-3.46738600	2.99023700
H	-3.83255800	-2.98515300	5.19425300
H	-3.62190900	-1.29167500	4.75826500
C	-0.55874500	2.89023200	1.74051200
C	0.96355200	3.08577600	1.56668200
C	-1.22966200	4.18579300	2.23921200
H	-0.69942500	2.11555500	2.51164600
C	1.61379300	3.61650800	2.85598200
H	1.15063300	3.80210100	0.75201400
H	1.43064300	2.13887700	1.27610600
C	-0.57428100	4.69756300	3.53490200
H	-1.13694100	4.96278400	1.46752900
H	-2.30344000	4.02921600	2.40210300
C	0.93733300	4.90019300	3.35824200
H	2.68364200	3.78916100	2.68443900
H	1.54493800	2.84190100	3.63400400
H	-1.05370800	5.63424000	3.84797200
H	-0.75237800	3.97033500	4.34098700
H	1.38975900	5.22594500	4.30360200
H	1.11029900	5.71026000	2.63367800
C	-1.41299100	3.47561900	-1.07845100
C	-1.16471900	2.92034800	-2.49909800
C	-2.68954400	4.34097400	-1.06335700
H	-0.56105300	4.12736800	-0.83044600
C	-1.09450500	4.04754900	-3.54335700
H	-1.97966800	2.23024800	-2.76659300
H	-0.24444100	2.32609300	-2.51416000
C	-2.61295100	5.47451600	-2.10295400
H	-3.55939600	3.70972900	-1.29624700
H	-2.86646800	4.76352600	-0.06785500
C	-2.34969400	4.93111000	-3.51453200
H	-0.95080900	3.61899100	-4.54330900
H	-0.20928300	4.66861400	-3.34002600
H	-3.54283300	6.05775300	-2.08403400
H	-1.80460400	6.16593200	-1.82248800
H	-2.25096000	5.75877900	-4.22832200
H	-3.21763500	4.33883600	-3.84118700
C	1.19818300	-0.76670900	-1.29714600
H	1.17967600	-1.85493600	-1.12741500
C	2.40107300	-0.23938300	-0.54683500
H	2.55782100	0.82550300	-0.76649900
O	2.27195100	-0.30593800	0.87158100
Si	2.34811000	-1.58557100	1.91386900
C	1.75458300	-0.86723000	3.54107300
O	3.83890100	-2.28305700	2.09640500
O	1.36149400	-2.82487400	1.42723500
H	0.74246600	-0.46064600	3.43924300
H	1.73637100	-1.63321300	4.32507500
H	2.40611700	-0.05290000	3.87933100
C	5.00679300	-1.59824700	2.52952900
C	1.70188400	-4.20166600	1.38655000
H	5.81375500	-2.33358800	2.61646300
H	5.30445200	-0.82938400	1.80972900
H	4.85788600	-1.13656800	3.51675800
H	1.00741100	-4.70233900	0.70342000
H	2.72606700	-4.35477300	1.03187600
H	1.60510300	-4.66106300	2.38000700

Z-Elimination TS(B-E) from disilyl ketene acetal pathway
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -3326.442245
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.960025
Total Free Energy: -3325.482220

O	-3.62460300	-1.45918100	-0.58597800
Si	-4.57884000	-2.82416800	-0.46621200
C	-4.20304000	-4.04260000	-1.82832400

H	-3.13860900	-4.30314700	-1.83798900
H	-4.78022300	-4.96757400	-1.71798900
H	-4.45261300	-3.60867400	-2.80217800
O	-6.15044600	-2.39332600	-0.65077700
O	-4.22793200	-3.44161800	1.03589200
C	-6.91622700	-1.51145100	0.17208300
H	-7.41981900	-2.08242100	0.96232400
H	-6.29688000	-0.73283500	0.62691700
H	-7.68024200	-1.04649800	-0.45910700
C	-4.76152000	-4.65665300	1.53936100
H	-4.31933800	-4.84042900	2.52321900
H	-5.85233900	-4.60118200	1.65213600
H	-4.52066100	-5.50761800	0.88761200
Cu	-0.38081300	0.37986600	-0.34134300
C	2.88042400	1.49950200	-0.69795200
H	3.50631200	2.39916000	-0.72434000
H	2.79780400	1.14810800	-1.73422500
C	3.58367800	0.43648000	0.17386600
H	4.64816800	0.43393300	-0.08516000
H	3.53090500	0.72668900	1.22959400
P	1.14463800	1.98927500	-0.19482600
P	2.86721300	-1.30393600	0.09311900
C	0.70205700	3.28963700	-1.48538700
C	-0.74147300	3.80009200	-1.27406100
C	1.66148600	4.47966100	-1.69283100
H	0.70338100	2.69445600	-2.41280200
C	-1.19926200	4.68427400	-2.44595400
H	-0.78791200	4.39005000	-0.34658600
H	-1.43741200	2.96373500	-1.14301400
C	1.20771000	5.35243800	-2.87772300
H	1.67813000	5.09973300	-0.78620600
H	2.68896900	4.13585100	-1.86192900
C	-0.23266700	5.85183700	-2.69343200
H	-2.21100600	5.05913100	-2.24850000
H	-1.26560800	4.06805400	-3.35478900
H	1.89482300	6.20021500	-2.99690500
H	1.27422700	4.76293600	-3.80420200
H	-0.54846500	6.43119300	-3.57040200
H	-0.26814100	6.53975300	-1.83530400
C	1.33348400	2.89681600	1.45125400
C	1.05117900	1.94213100	2.63566900
C	2.65071100	3.66812300	1.68696300
H	0.51431100	3.63190900	1.43057300
C	1.02475300	2.70085700	3.97281100
H	1.83090900	1.16759200	2.67771500
H	0.10370100	1.41706300	2.47571700
C	2.61541600	4.43094400	3.02447900
H	3.49213900	2.96188100	1.70750000
H	2.85222800	4.36868100	0.86978500
C	2.31844700	3.49530100	4.20476000
H	0.85711600	1.99480200	4.79621500
H	0.16800700	3.39022000	3.97430000
H	3.57022700	4.95031900	3.17856000
H	1.84072600	5.21030500	2.97384900
H	2.25182800	4.07007100	5.13726200
H	3.15749200	2.79413200	4.32941800
C	3.77541700	-2.08004700	1.56374300
C	3.25198400	-3.51142000	1.81425500
C	5.31738400	-2.06216300	1.56319000
H	3.43398700	-1.46167100	2.41048000
C	3.83406900	-4.11624800	3.10330600
H	3.52477400	-4.15580900	0.96454800
H	2.15616700	-3.50484800	1.86067500
C	5.89398600	-2.66121800	2.85915500
H	5.68934000	-2.64639600	0.70965200
H	5.69377600	-1.04002500	1.43222700
C	5.36929700	-4.08319600	3.10469500
H	3.47459500	-5.14589300	3.22818500
H	3.45853100	-3.54799800	3.96729900
H	6.99104400	-2.66081700	2.81482500
H	5.61540600	-2.01968100	3.70844800

H	5.75835700	-4.47502000	4.05327600
H	5.74658600	-4.74838600	2.31346800
C	3.72156600	-2.09452700	-1.41752000
C	2.69160100	-2.30500600	-2.54989500
C	4.98356400	-1.40166700	-1.97092500
H	4.01890300	-3.09359200	-1.06160000
C	3.29167200	-3.07357500	-3.73882900
H	2.32492600	-1.32778100	-2.89639300
H	1.81372600	-2.83445000	-2.16121200
C	5.58765900	-2.18111900	-3.15335800
H	4.72352300	-0.39025800	-2.31589600
H	5.73944100	-1.27856700	-1.18711300
C	4.56001500	-2.39310800	-4.27378500
H	2.54428300	-3.17026200	-4.53692900
H	3.53953400	-4.09658300	-3.41752900
H	6.46870500	-1.65007700	-3.53726600
H	5.94338600	-3.15919200	-2.79641300
H	4.99866500	-2.98586900	-5.08669900
H	4.29236900	-1.41763600	-4.70700800
C	-2.28091400	-1.42104800	-0.30528900
H	-1.97502400	-2.08025700	0.50233900
O	-2.18105200	0.05380200	0.86794600
Si	-3.34261600	1.13579300	1.25055200
C	-2.70465700	2.40930700	2.48087500
O	-4.71134100	0.40343700	1.89586700
O	-3.90746300	2.05044700	-0.02224600
H	-1.90647800	3.01901800	2.04367300
H	-3.51597900	3.08456400	2.77578300
H	-2.30597200	1.93749300	3.38624600
C	-4.62631300	-0.46987400	3.01066900
C	-4.91038900	1.67944700	-0.95109300
H	-5.64533100	-0.70714200	3.33834800
H	-4.11689700	-1.40548700	2.75116100
H	-4.10152700	-0.00112600	3.85628000
H	-4.68075700	0.72648900	-1.44178300
H	-5.88976600	1.59412100	-0.46219800
H	-4.97320800	2.46325300	-1.71499400
C	-1.89664100	-0.80505800	-2.73800900
H	-2.54018600	-1.61362900	-3.12580600
H	-2.54726200	0.07680500	-2.67610700
C	-0.79488500	-0.53820400	-3.76861500
H	-0.17254300	0.31380800	-3.46672800
H	-0.13201300	-1.40679300	-3.87221000
H	-1.21613300	-0.32184300	-4.75835400
C	-1.35386100	-1.15366200	-1.35349500
H	-0.53844900	-1.88551100	-1.35553400

VIII. References

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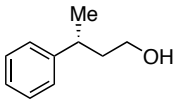
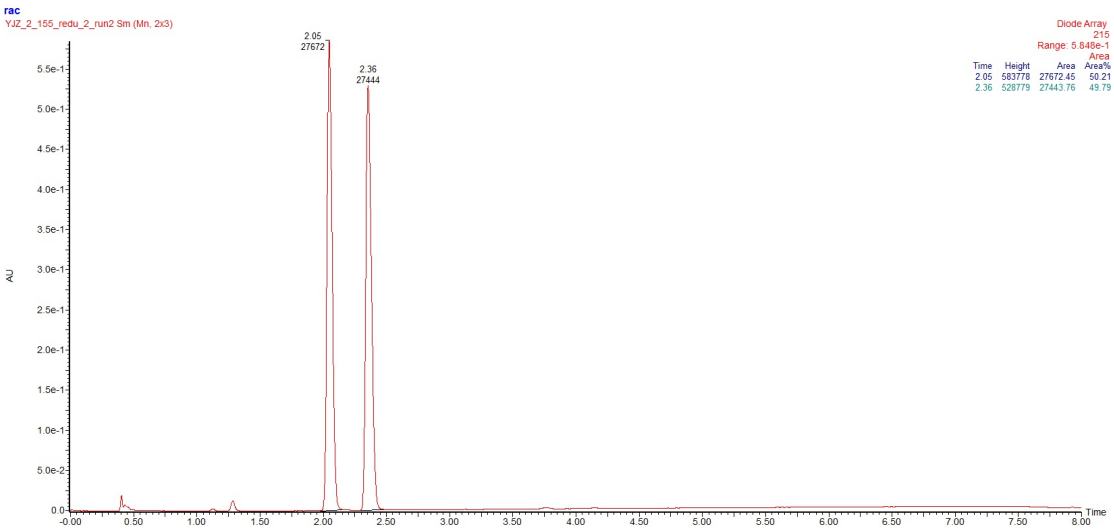
IX. Copies of Chiral SFC Traces

(*R*)-3-phenylbutan-1-ol (2a-ol)

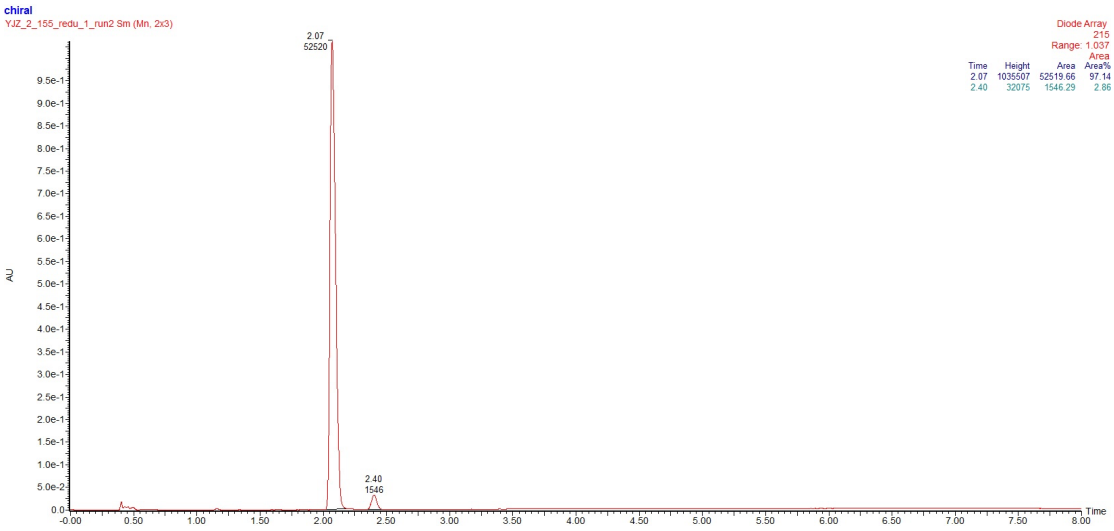


2a-ol

Racemic trace:



Enantioenriched trace:



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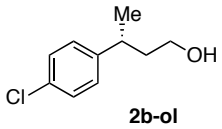
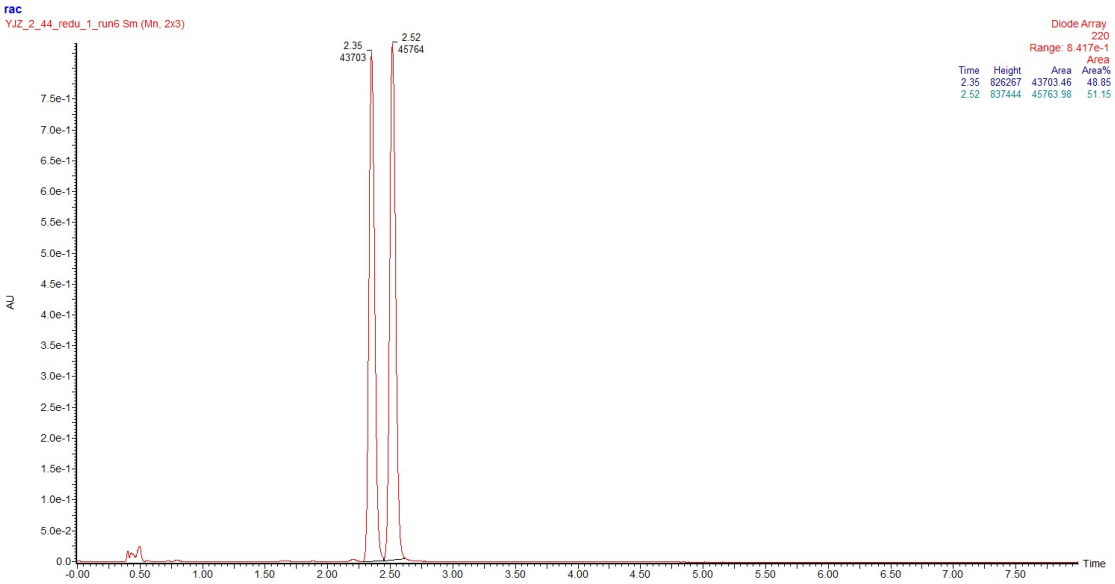


2b-ol

Racemic trace:



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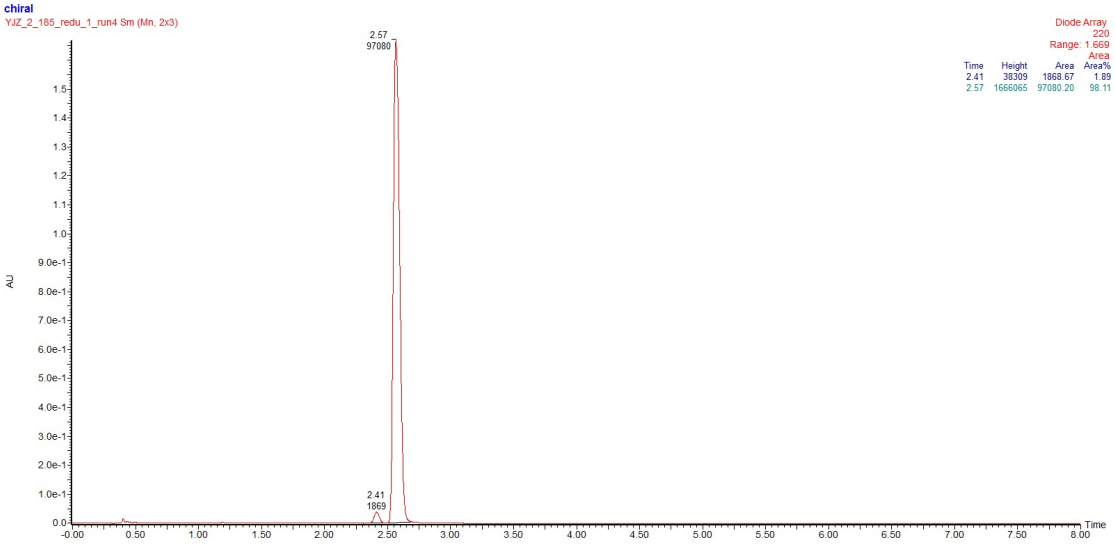

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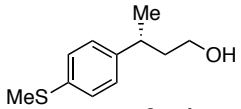

2c-ol

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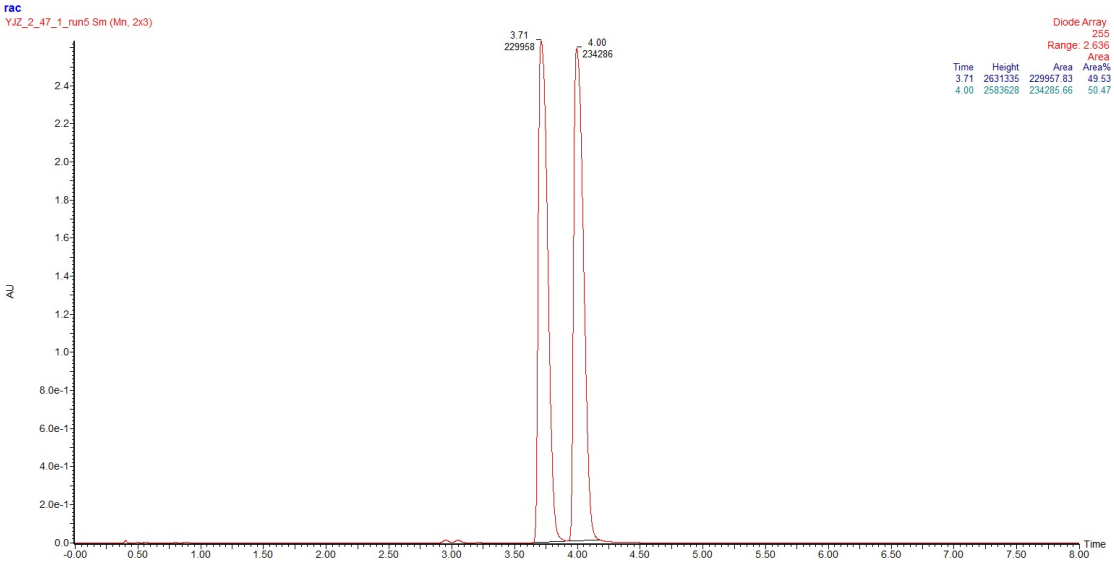

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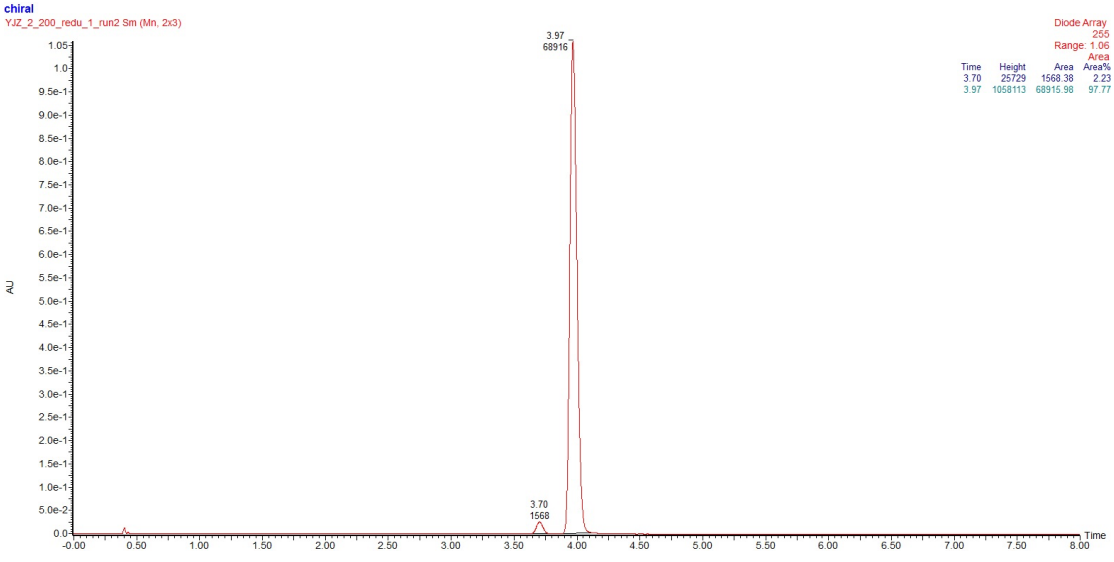

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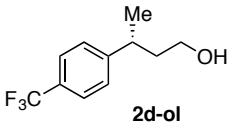
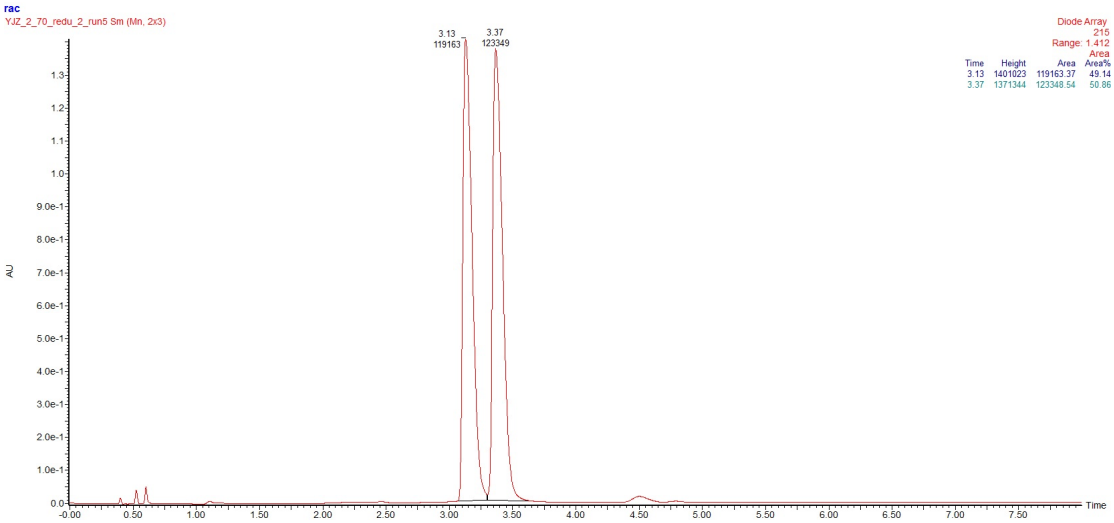


2d-ol

Racemic trace:



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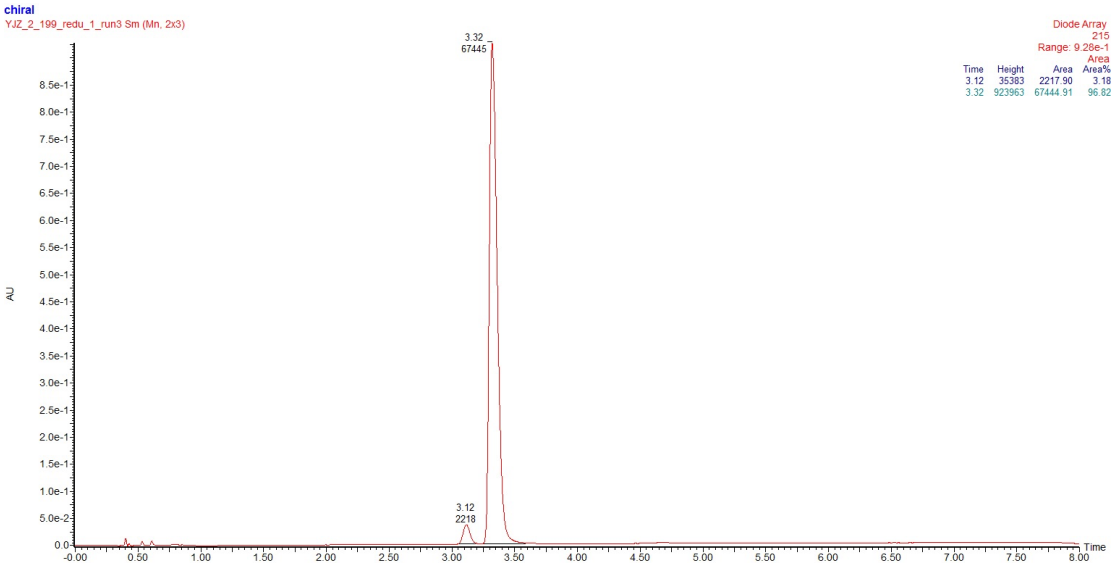
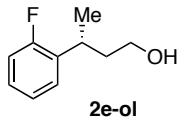


(*R*)-3-(2-fluorophenyl)butan-1-ol (2e-ol)



2e-ol

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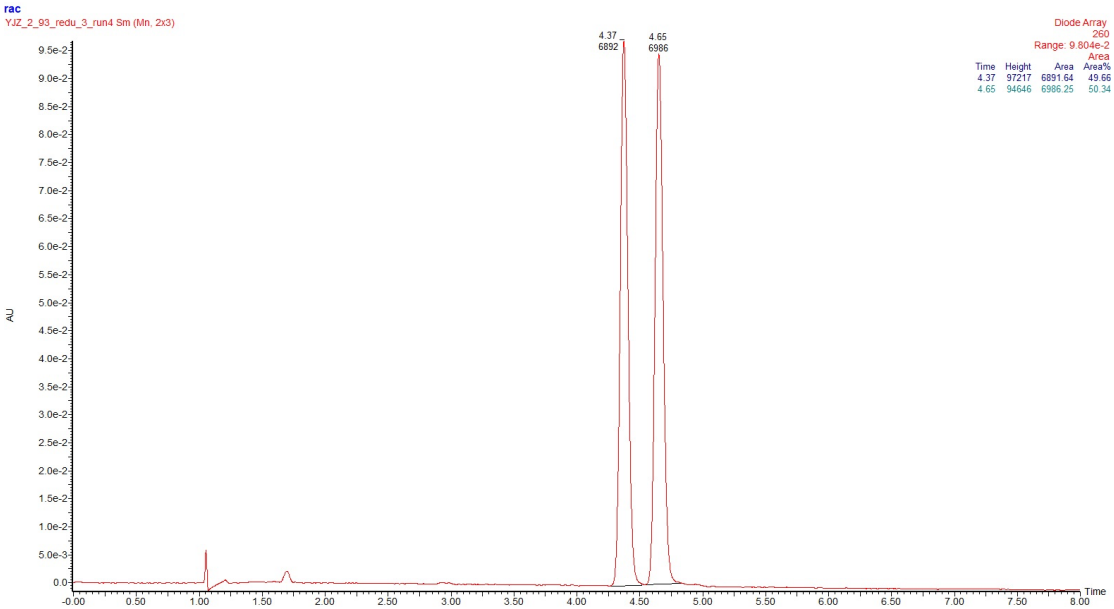

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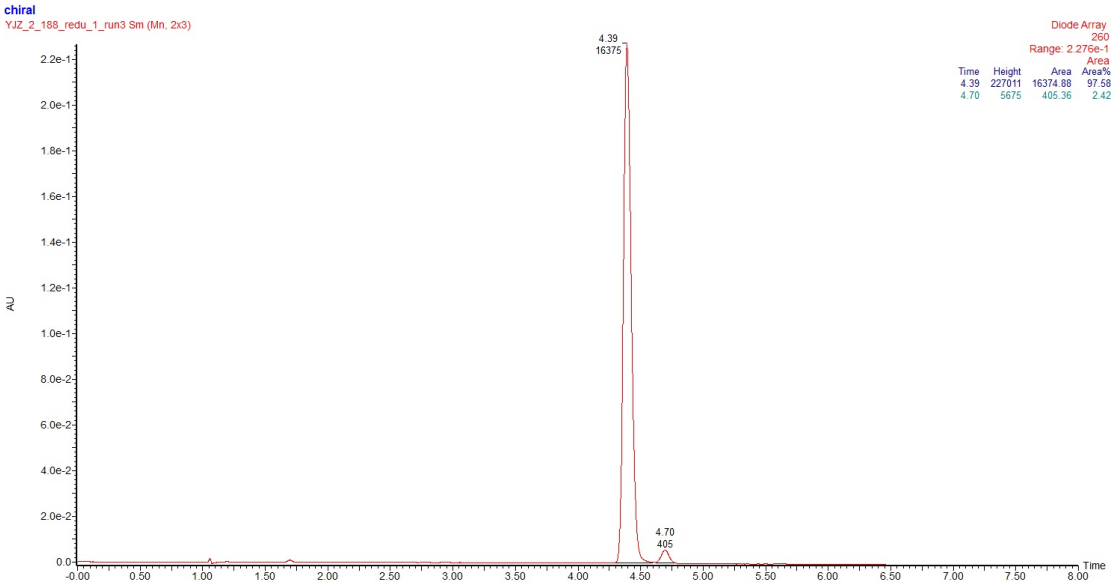
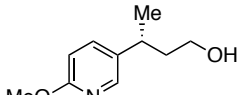


(*R*)-3-(6-methoxypyridin-3-yl)butan-1-ol (2f-ol)



2f-ol

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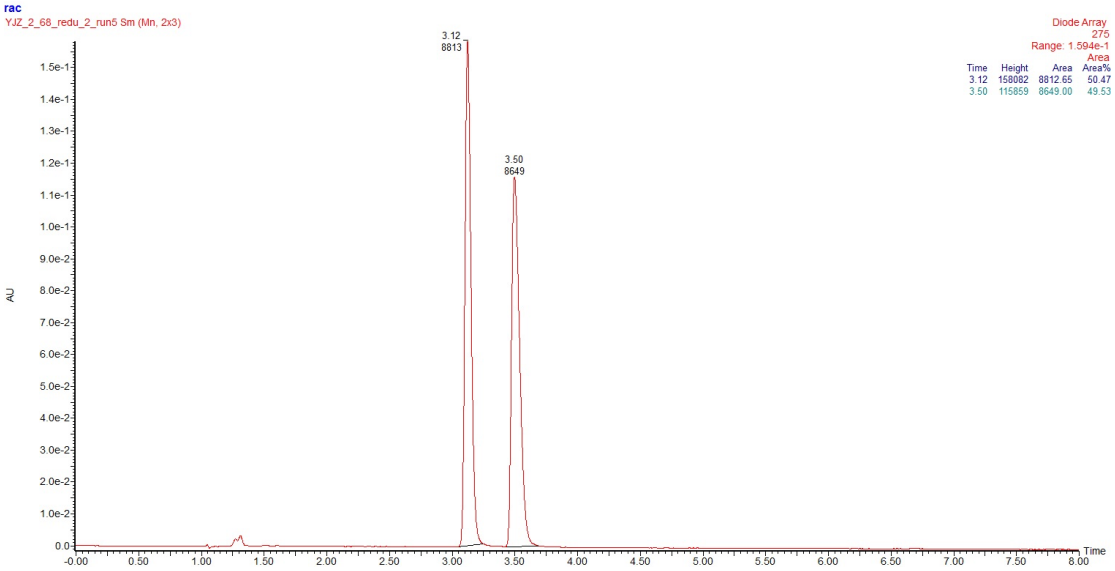

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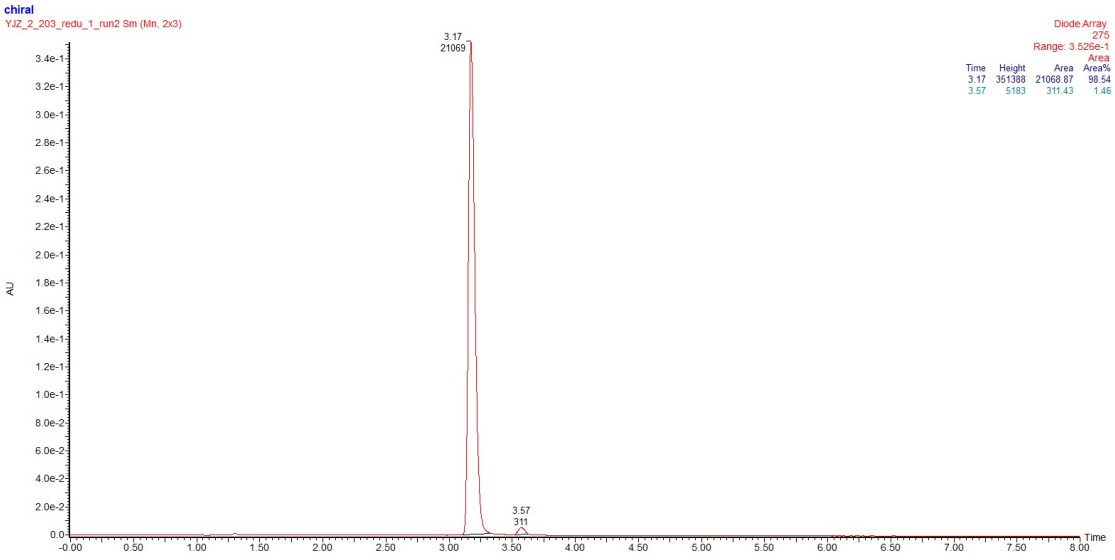
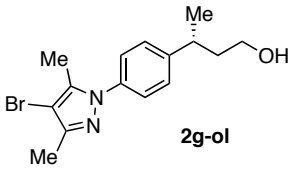


(*R*)-3-(4-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)phenyl)butan-1-ol (2g-ol)



2g-ol

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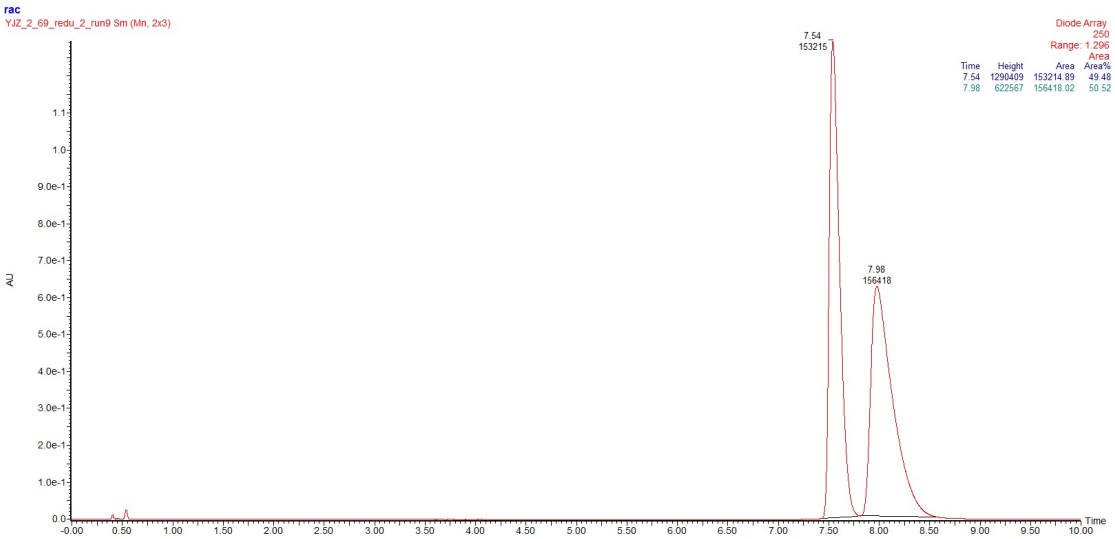

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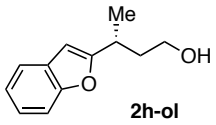
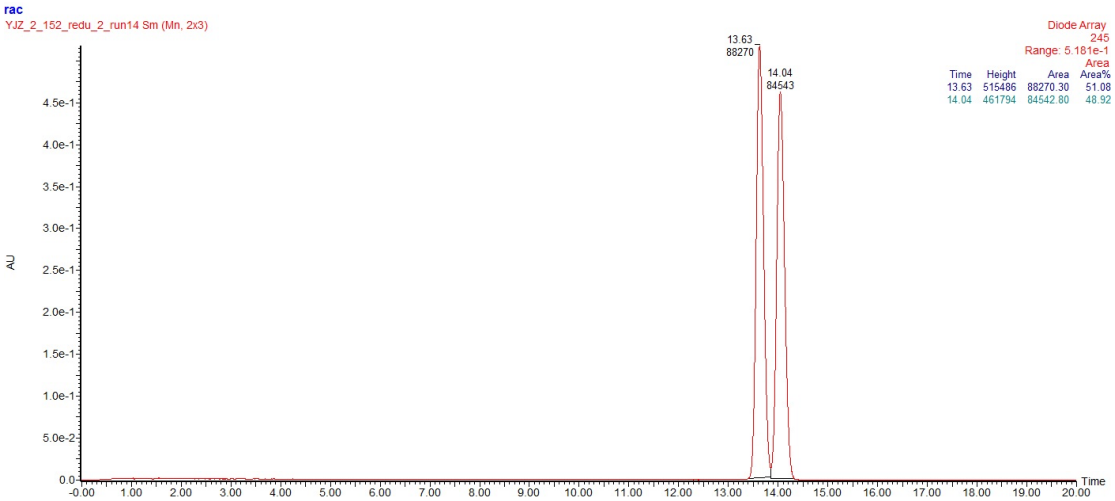


2h-ol

Racemic trace:



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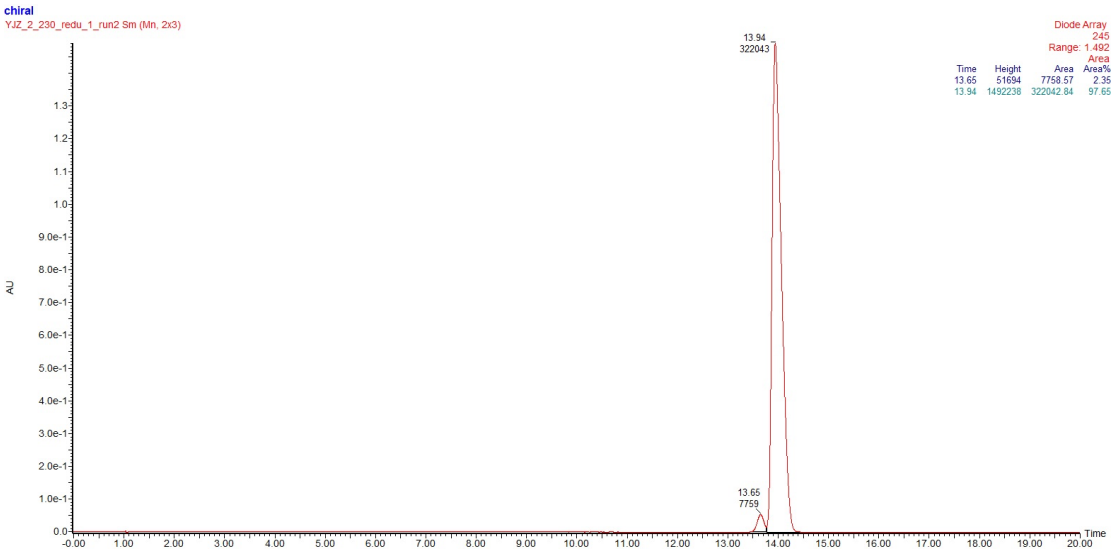
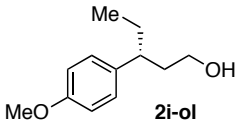


(*R*)-3-(4-methoxyphenyl)pentan-1-ol (2i-ol)



2i-ol

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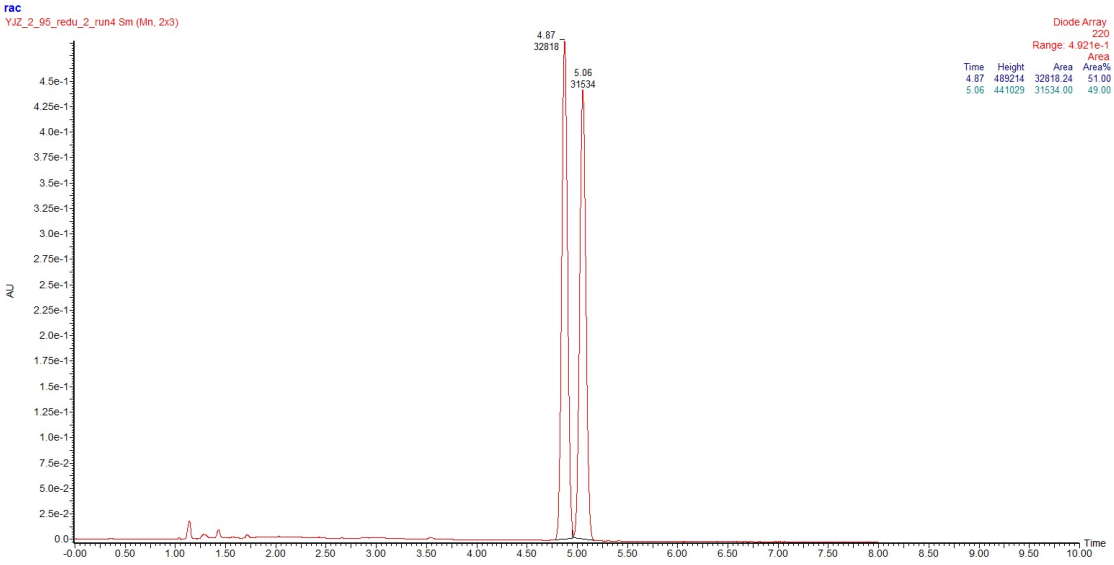

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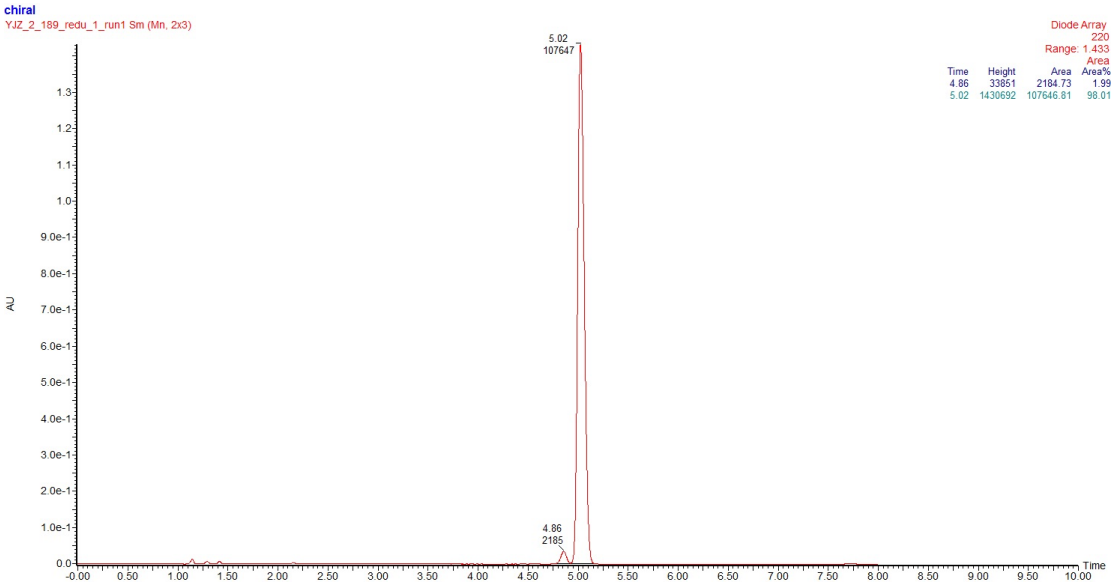
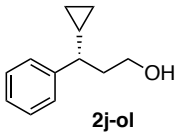


(*R*)-3-cyclopropyl-3-phenylpropan-1-ol (2j-ol)



2j-ol

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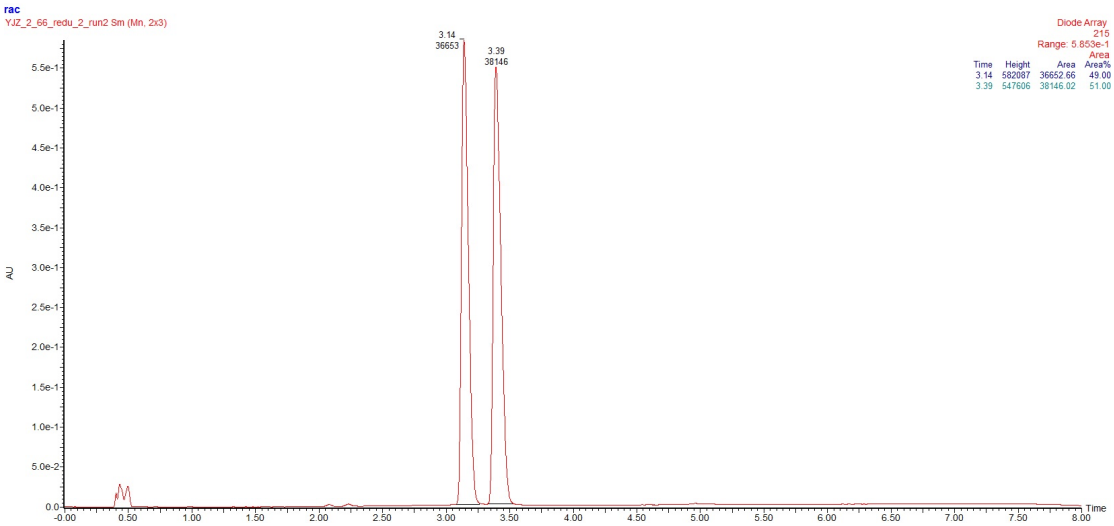

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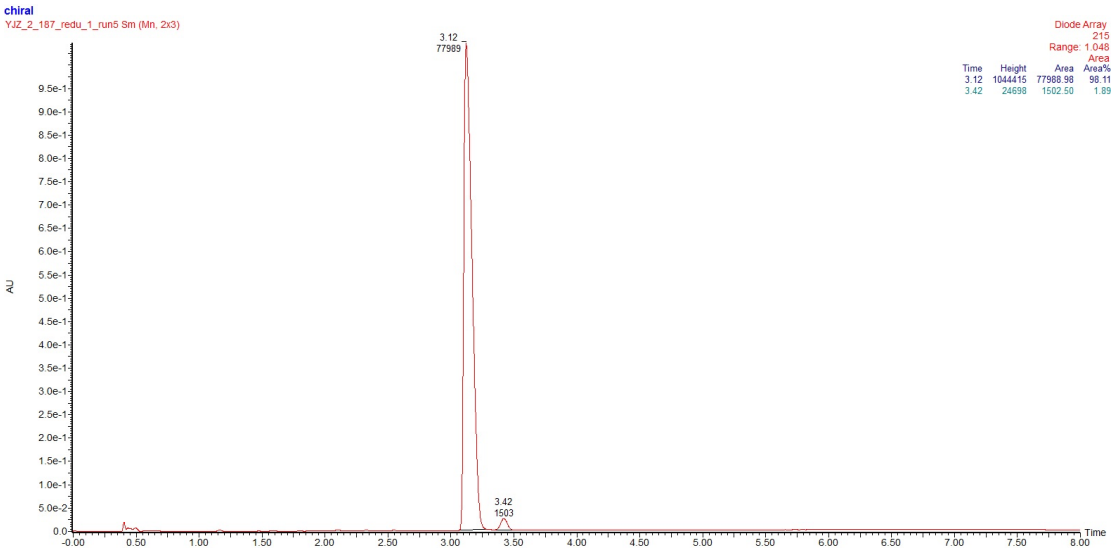

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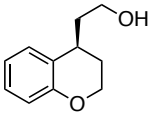

2k-ol

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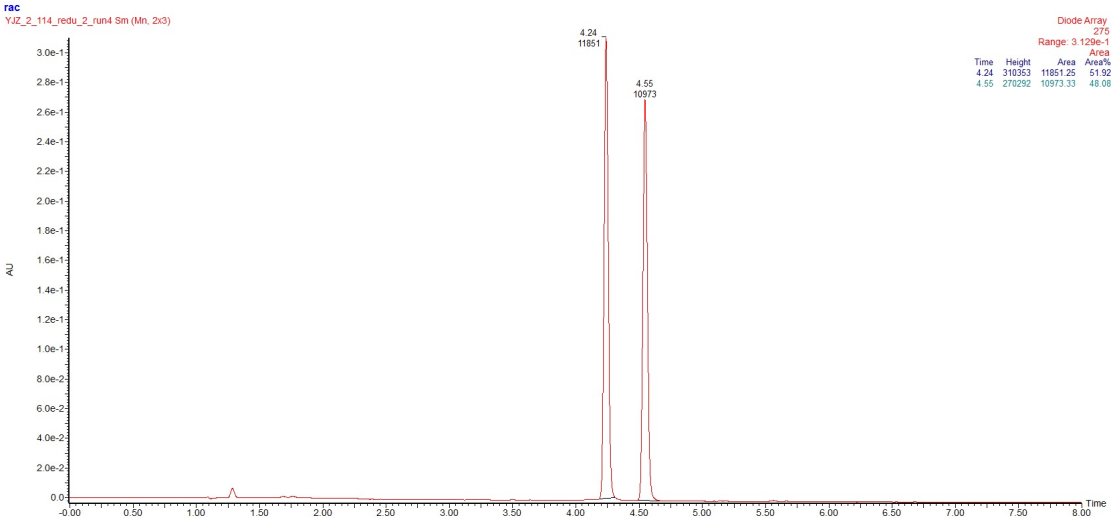

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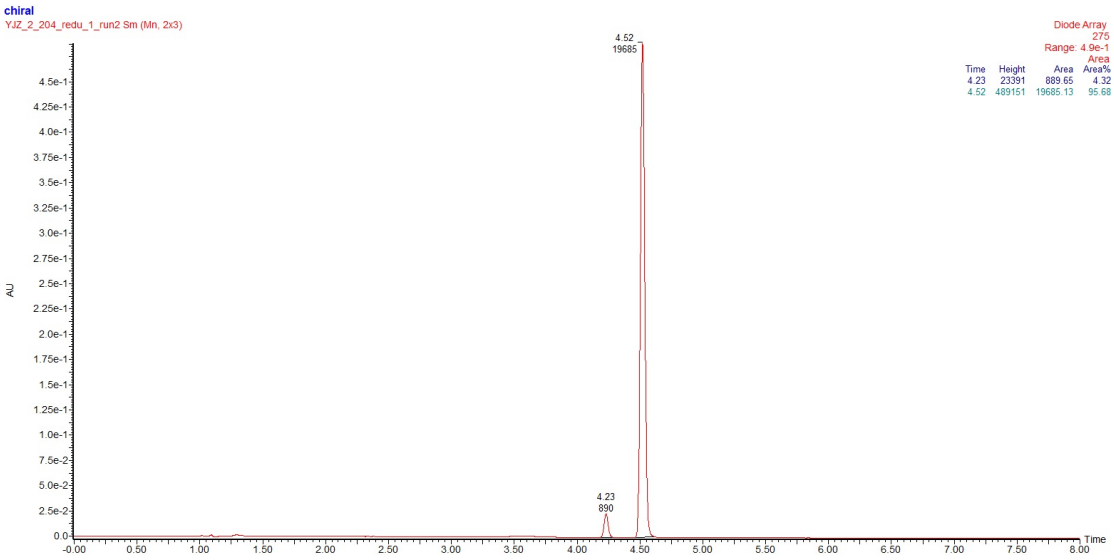
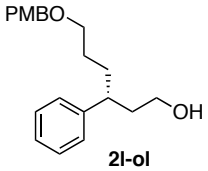


(*R*)-6-((4-methoxybenzyl)oxy)-3-phenylhexan-1-ol (2l-ol)



2l-ol

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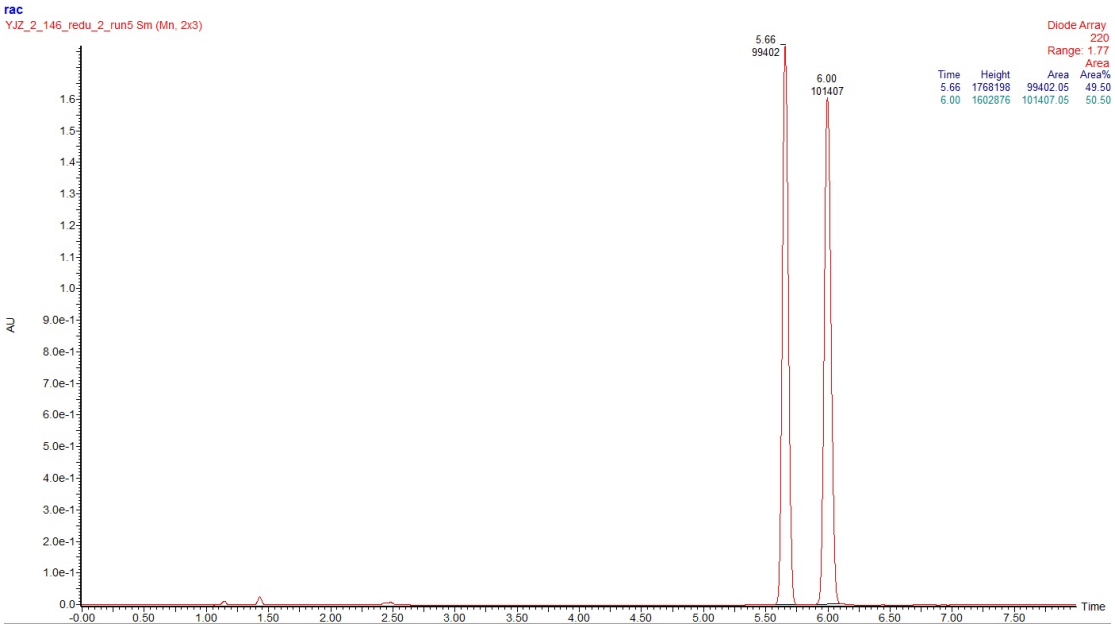

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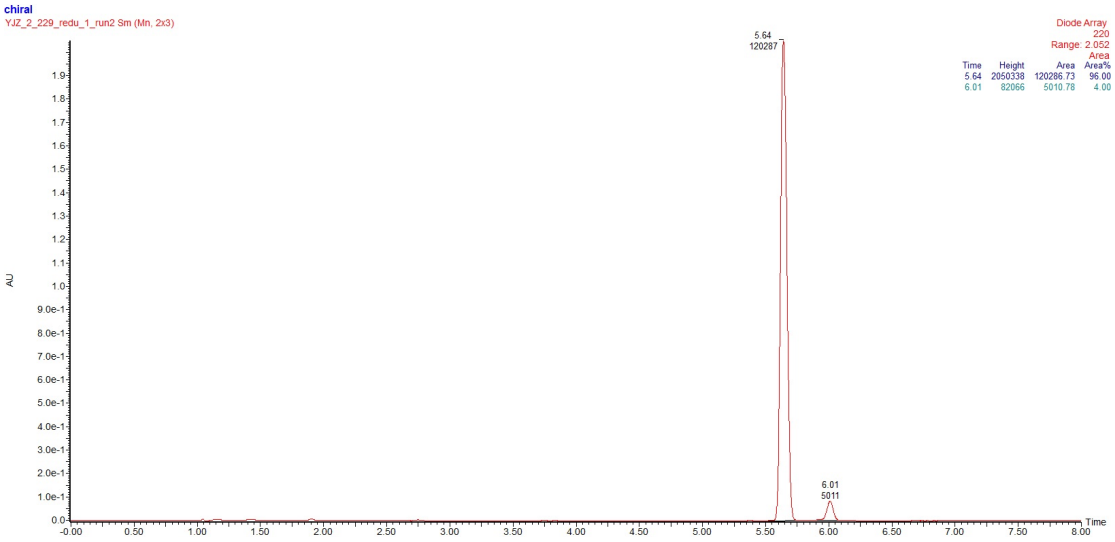

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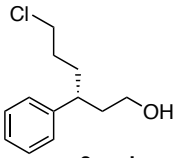

2m-ol

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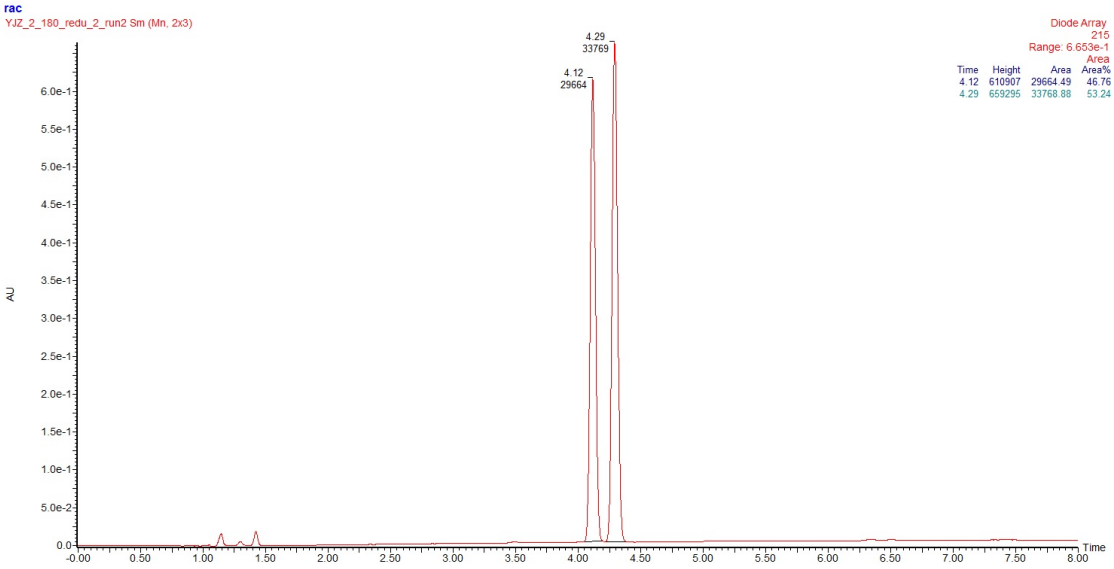

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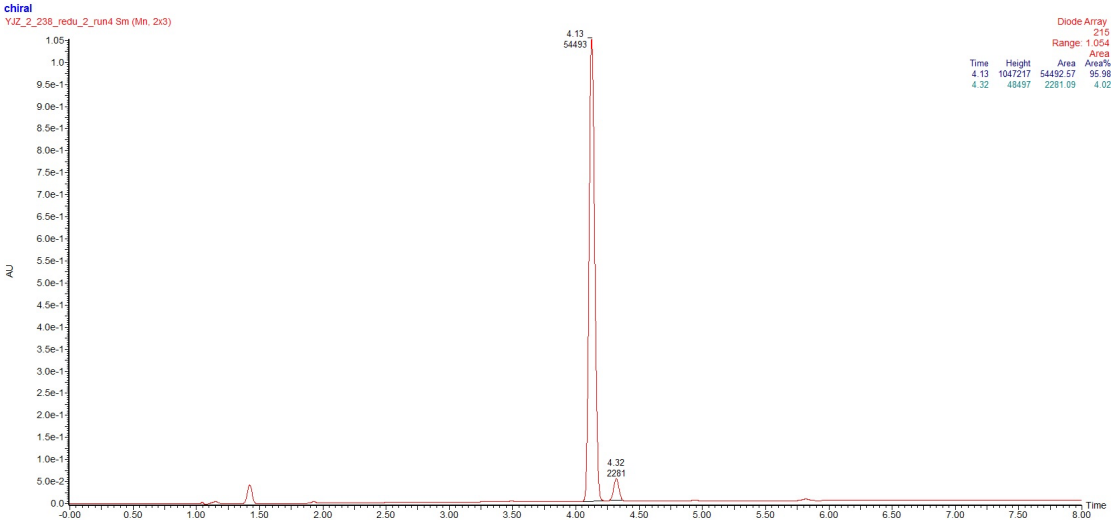
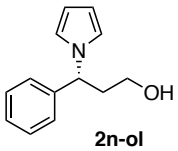
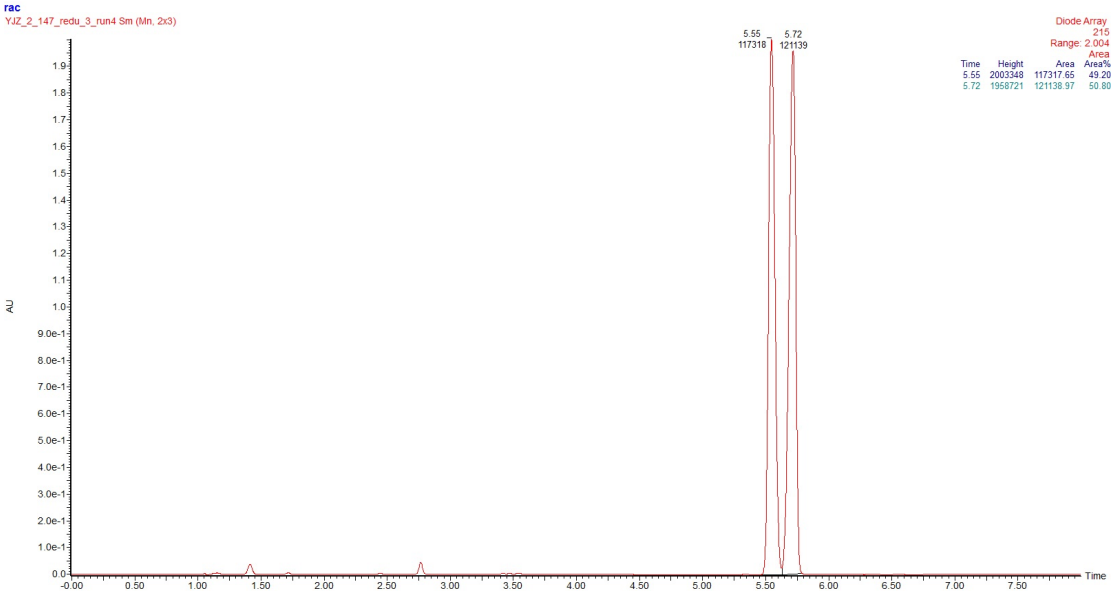


(*R*)-3-phenyl-3-(1*H*-pyrrol-1-yl)propan-1-ol (2n-ol)

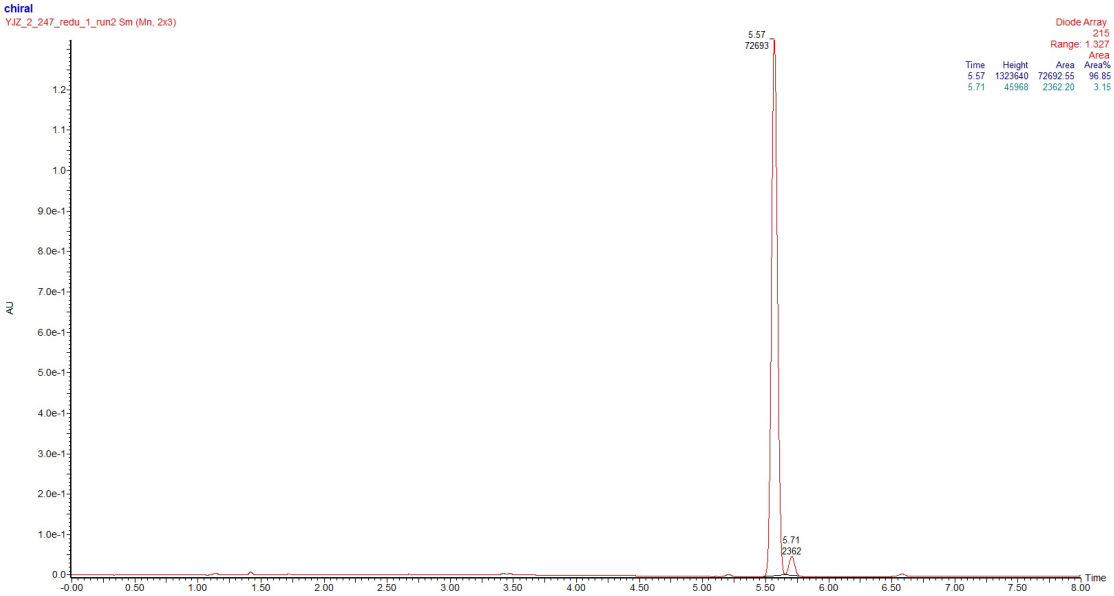


2n-ol

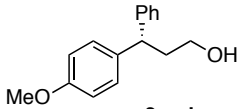
Racemic trace:



Enantioenriched trace:

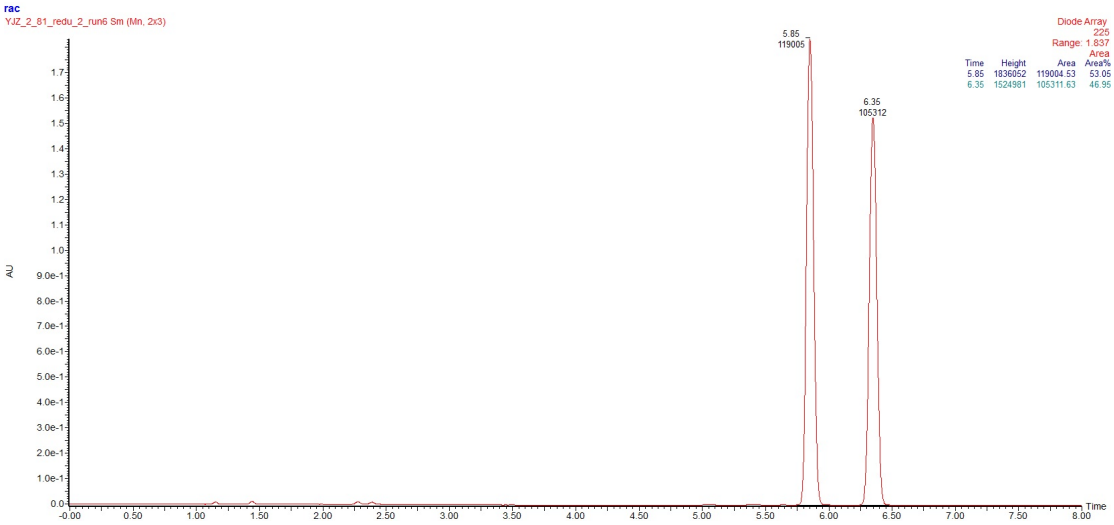


(*S*)-3-(4-methoxyphenyl)-3-phenylpropan-1-ol (2o-ol)



2o-ol

Racemic trace:



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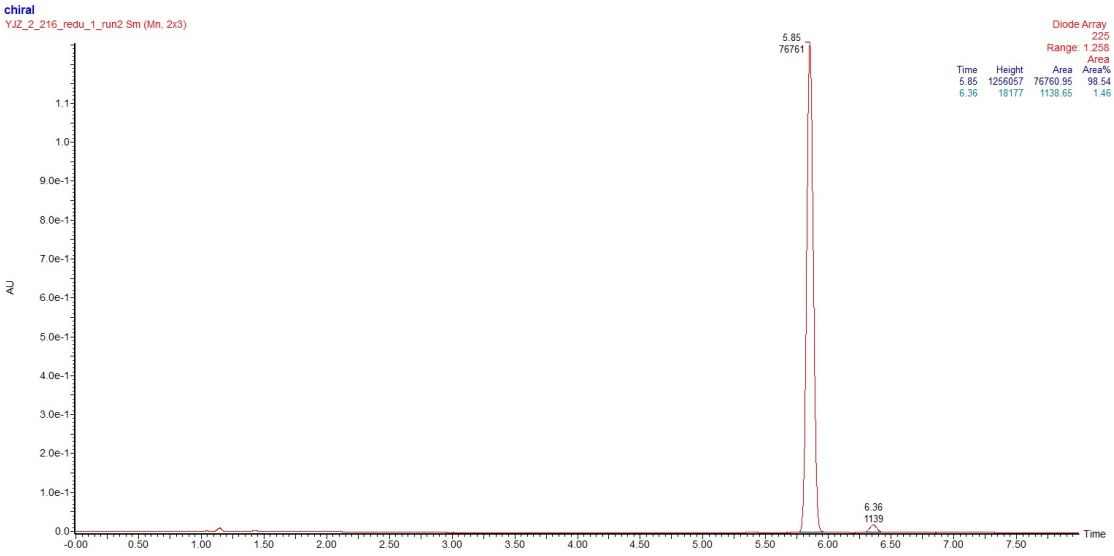
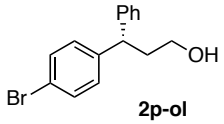
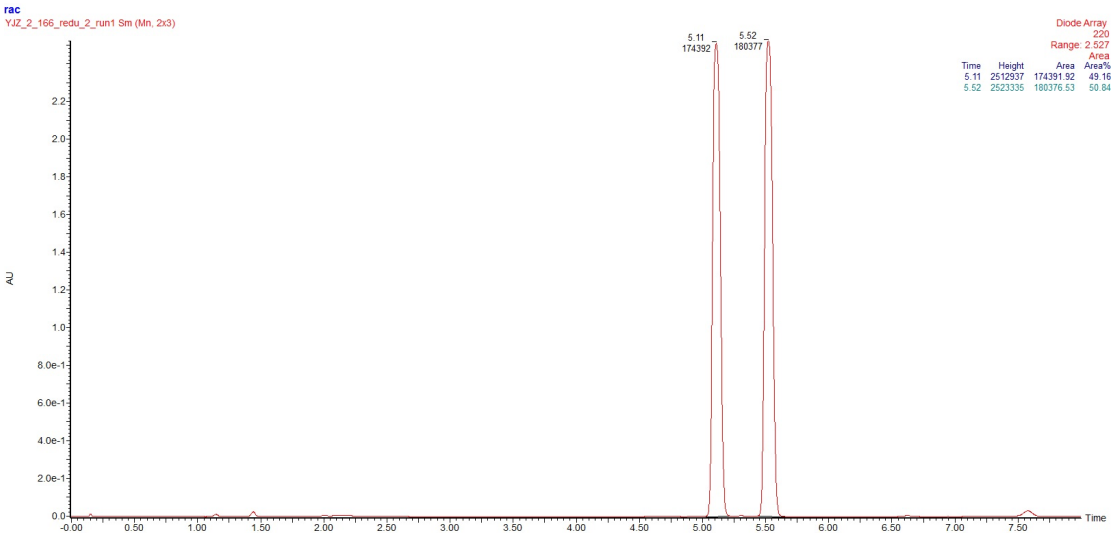


(*S*)-3-(4-bromophenyl)-3-phenylpropan-1-ol (2p-ol)



2p-ol

Racemic trace:



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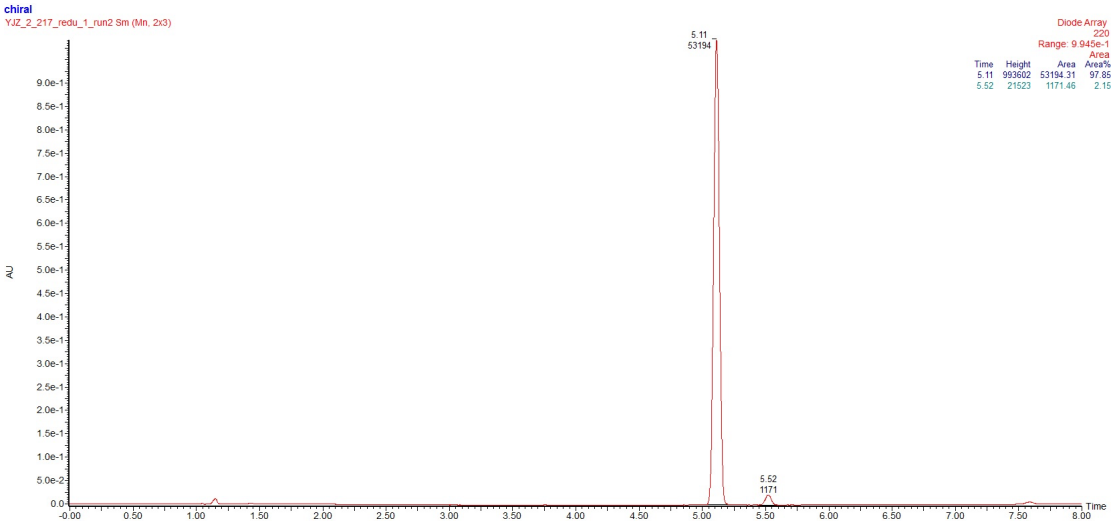
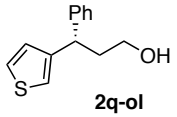
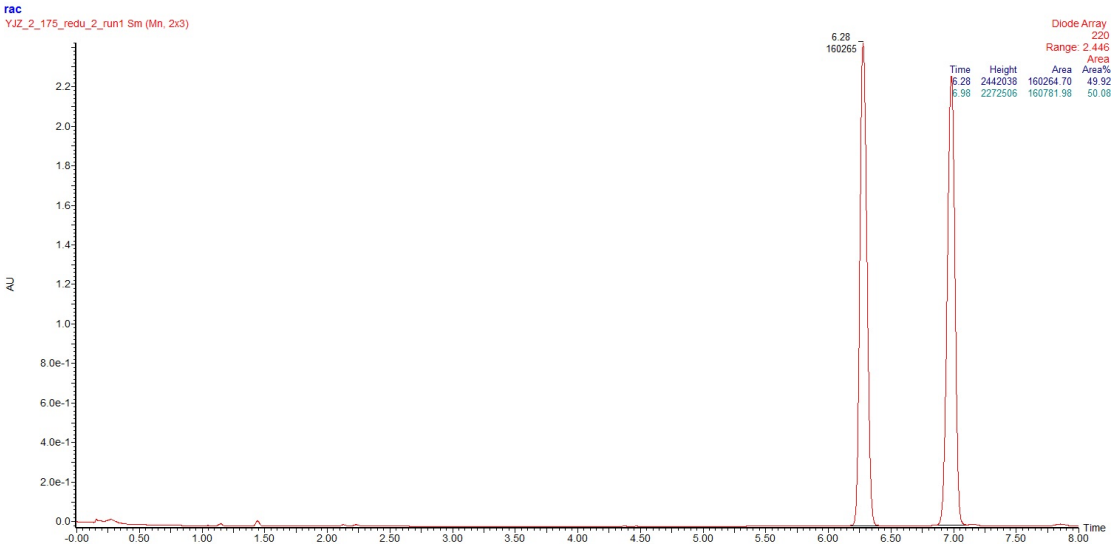


(*S*)-3-phenyl-3-(thiophen-3-yl)propan-1-ol (2q-ol)



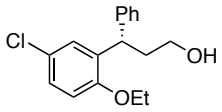
2q-ol

Racemic trace:



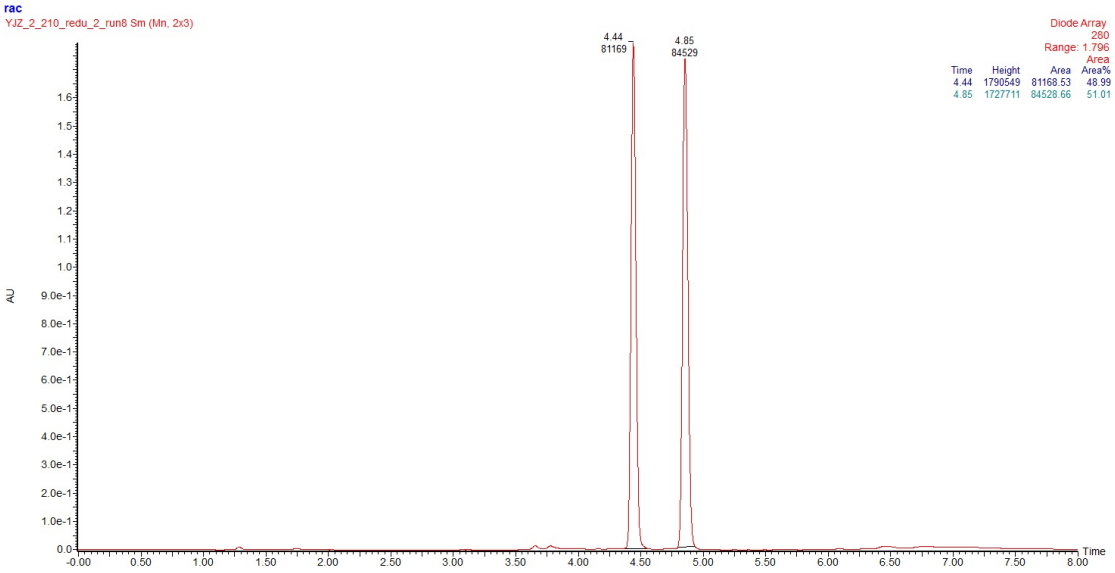
Enantioenriched trace:

(*S*)-3-(5-chloro-2-ethoxyphenyl)-3-phenylpropan-1-ol (2r-ol)



2r-ol

Racemic trace:



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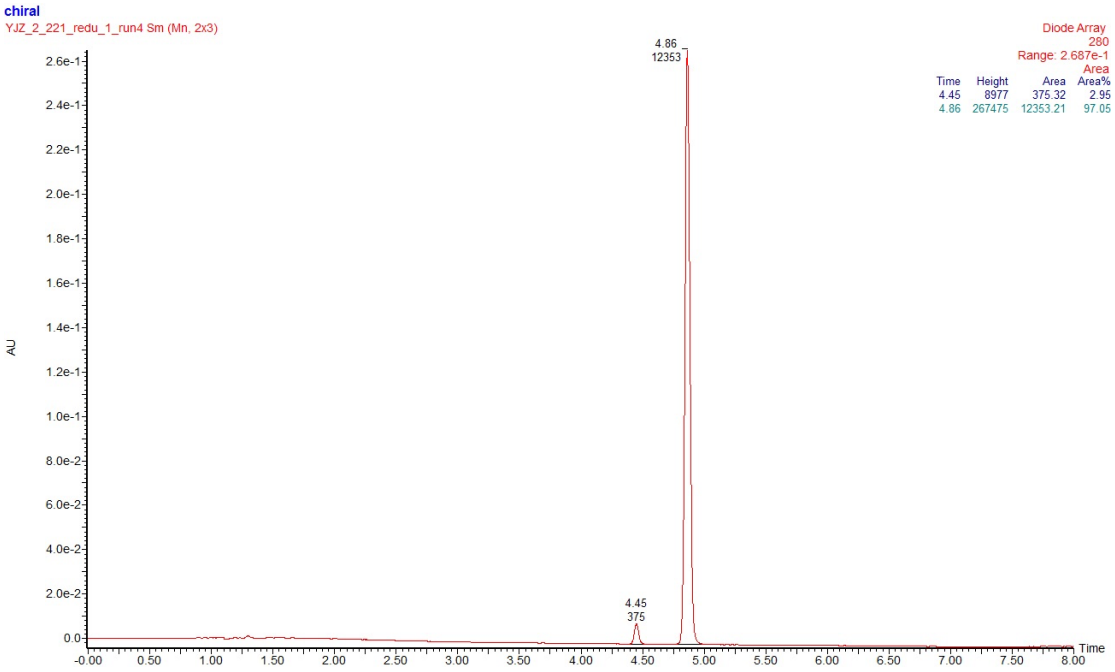
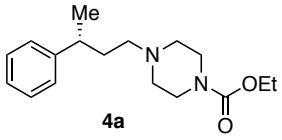
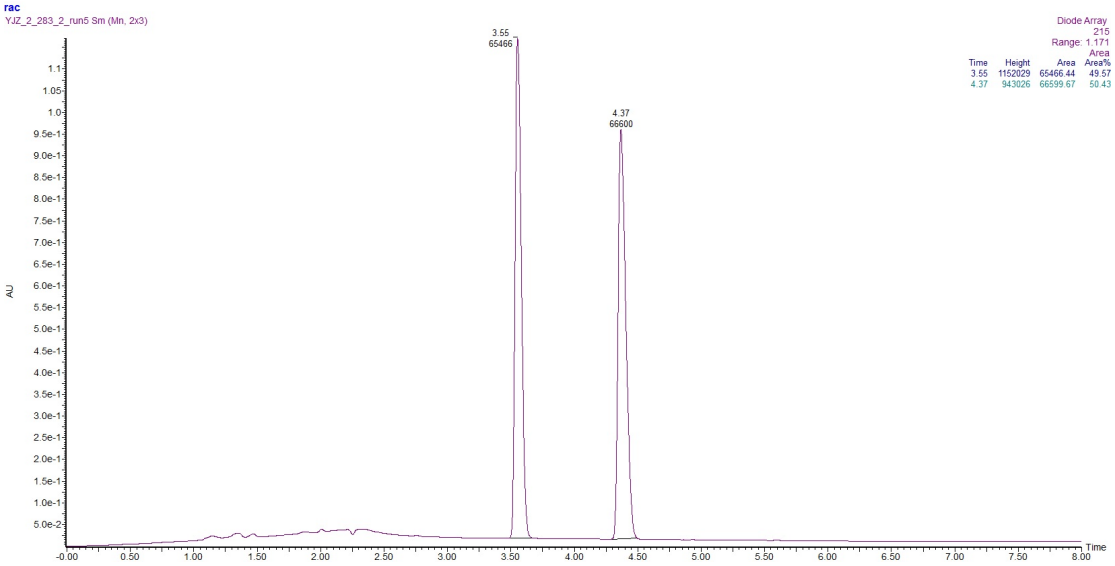


Ethyl (*R*)-4-(3-phenylbutyl)piperazine-1-carboxylate (4a)

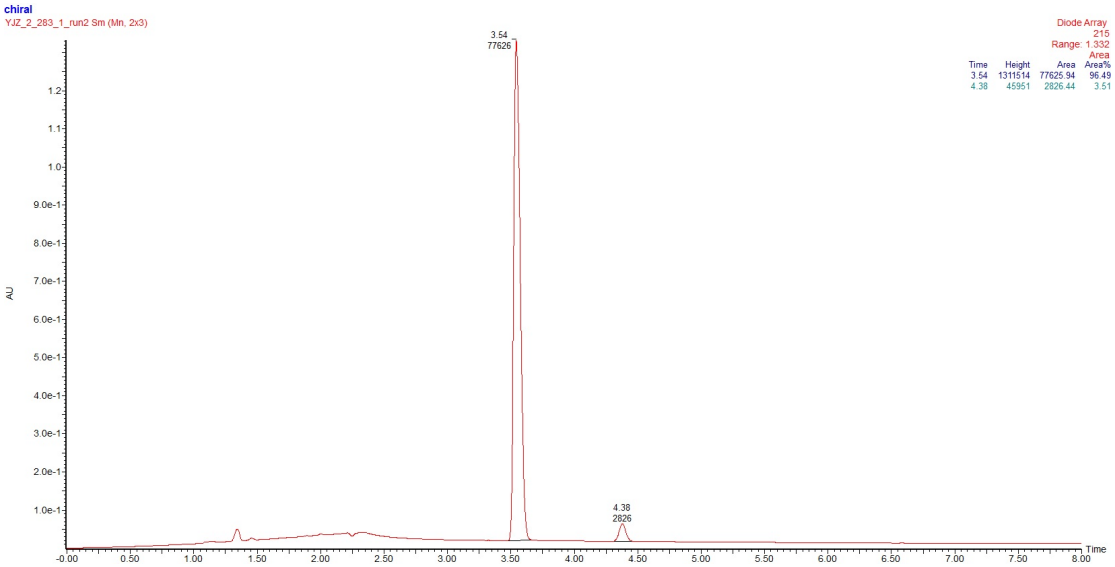


4a

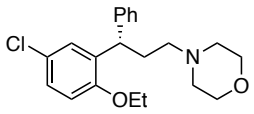
Racemic trace:



Enantioenriched trace:

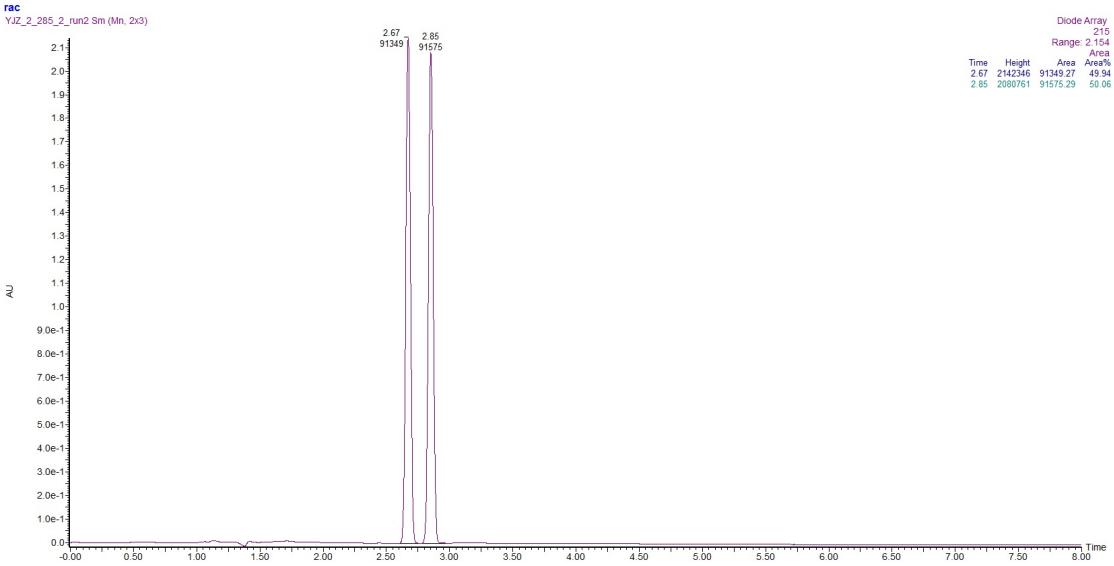


(*S*)-4-(3-(5-chloro-2-ethoxyphenyl)-3-phenylpropyl)morpholine (4b)

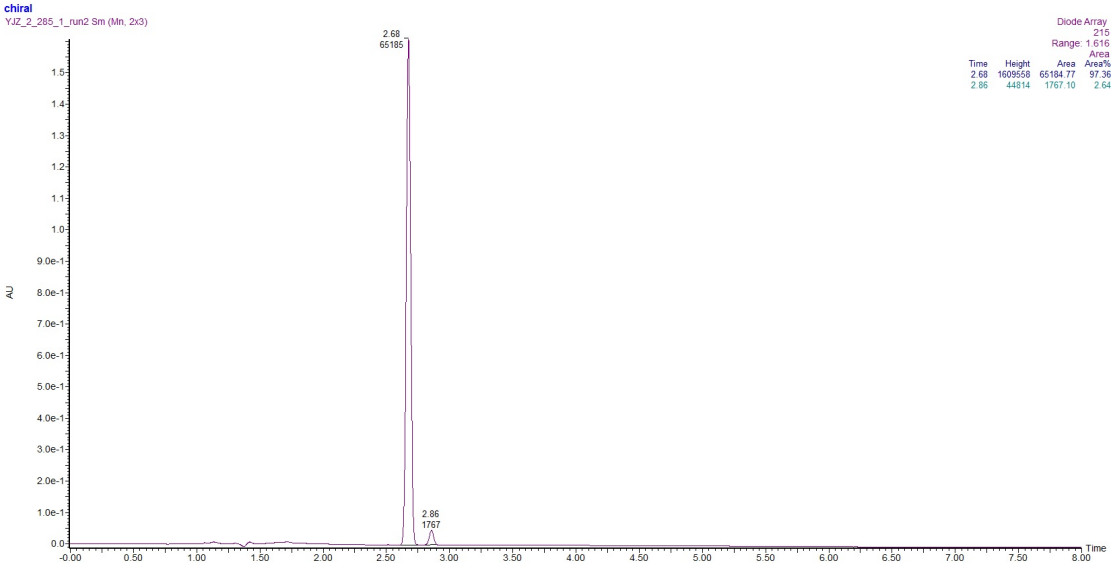


4b

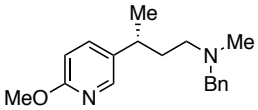
Racemic trace:



Enantioenriched trace:

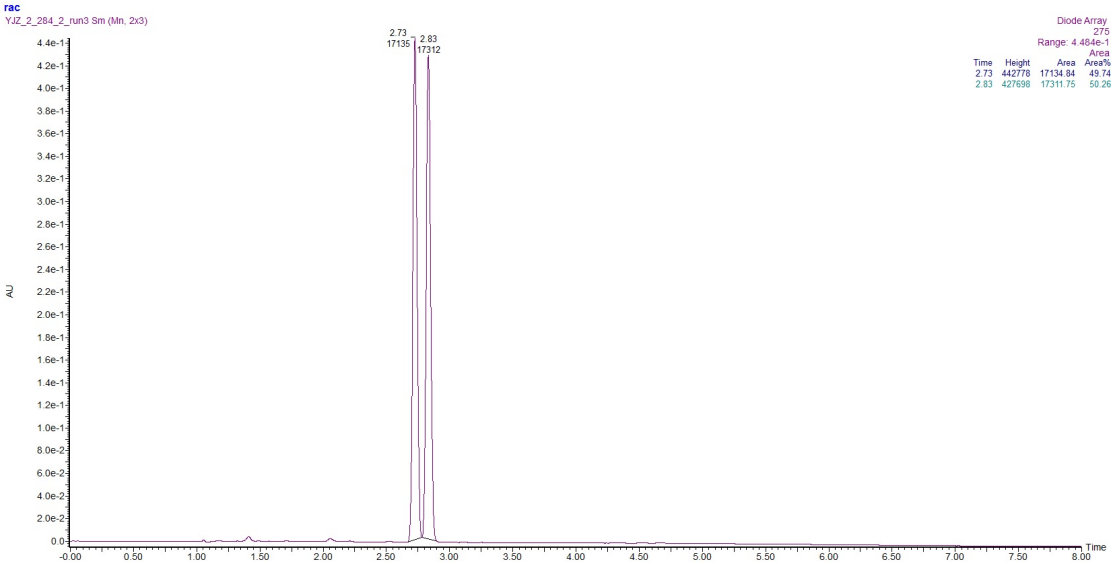


(*R*)-*N*-benzyl-3-(6-methoxypyridin-3-yl)-*N*-methylbutan-1-amine (4c)



4c

Racemic trace:



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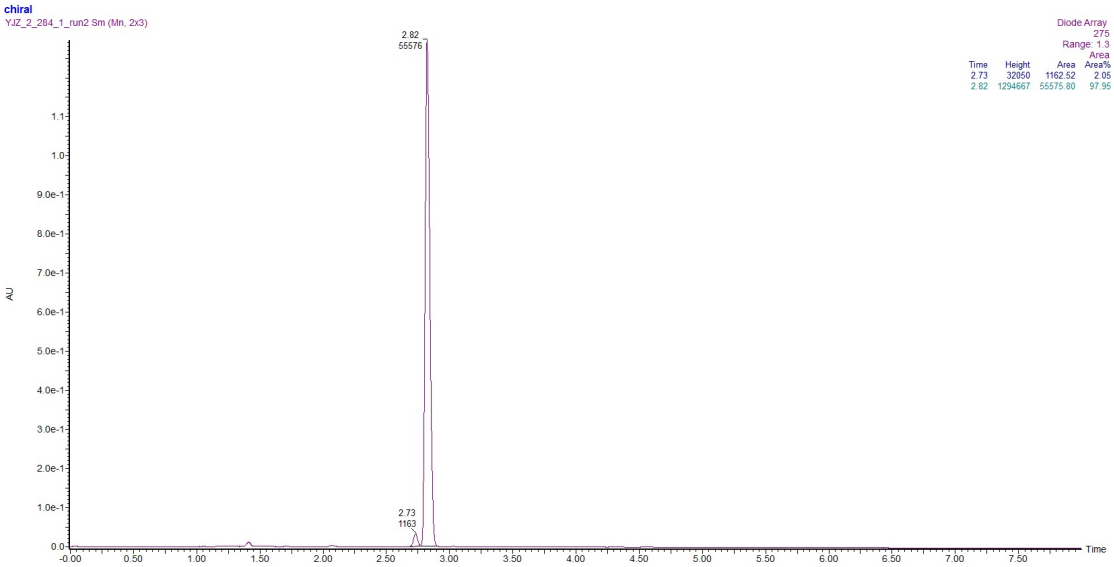
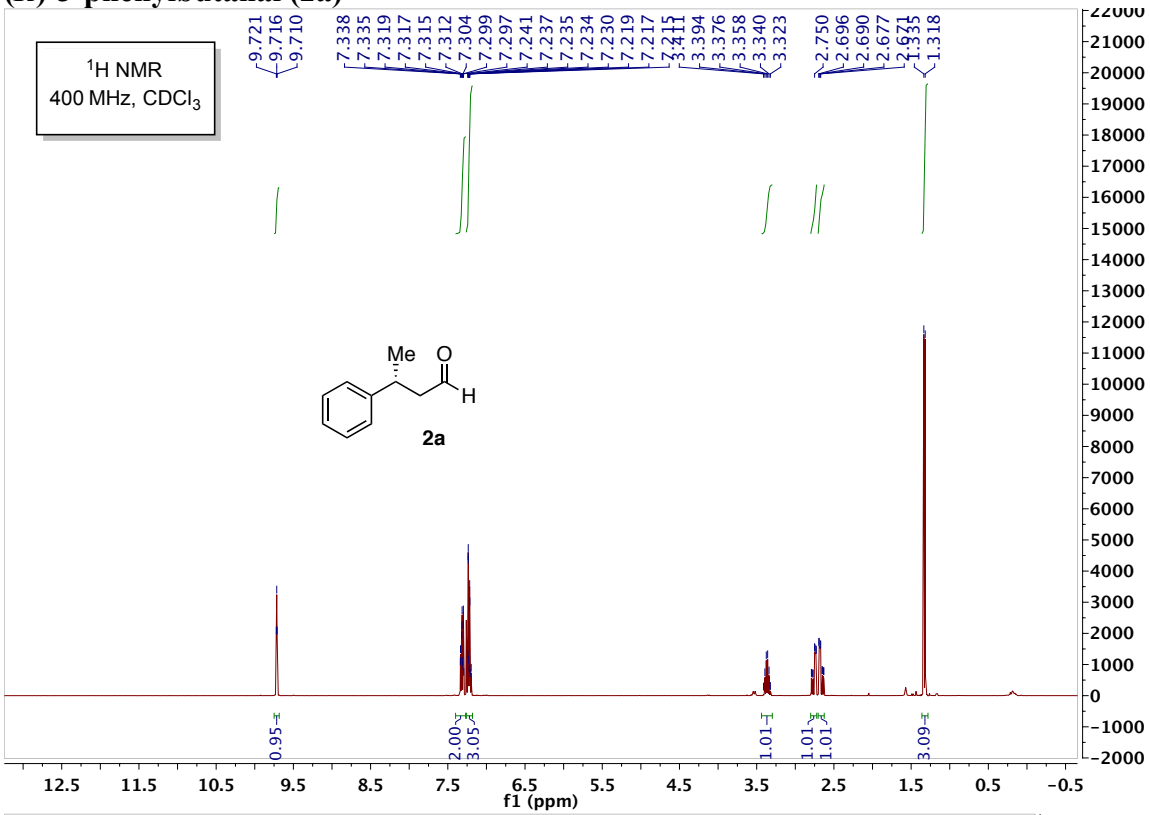
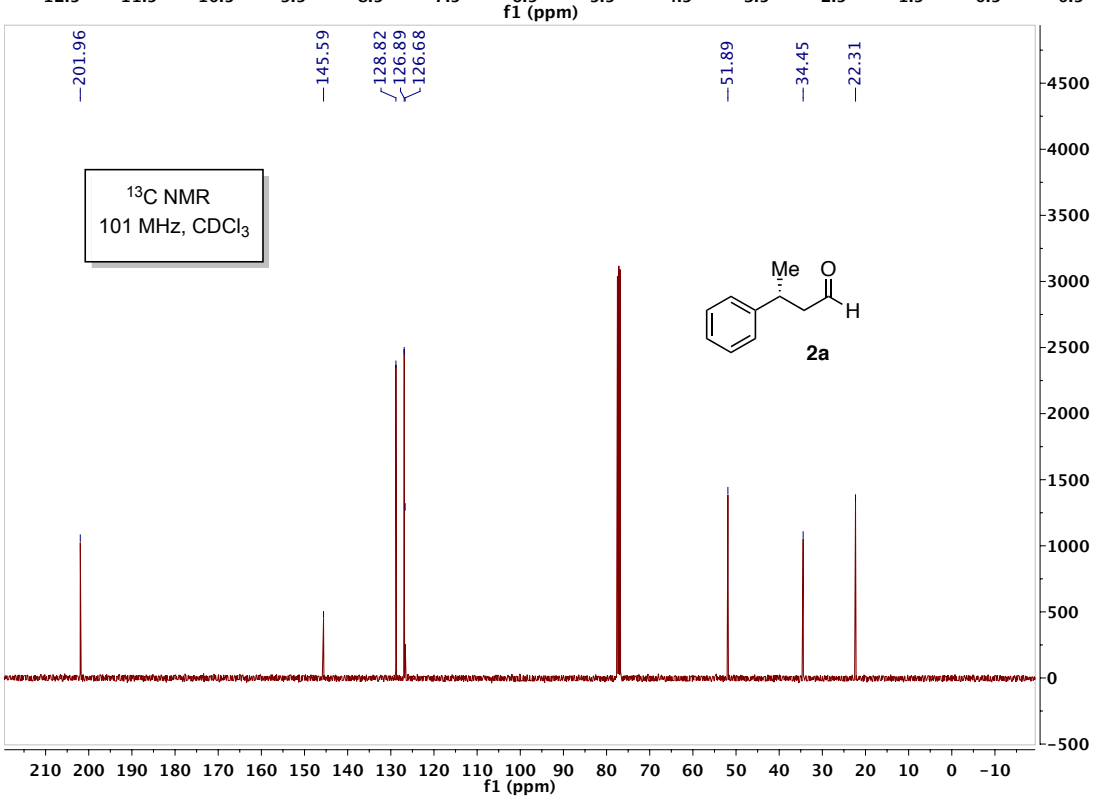


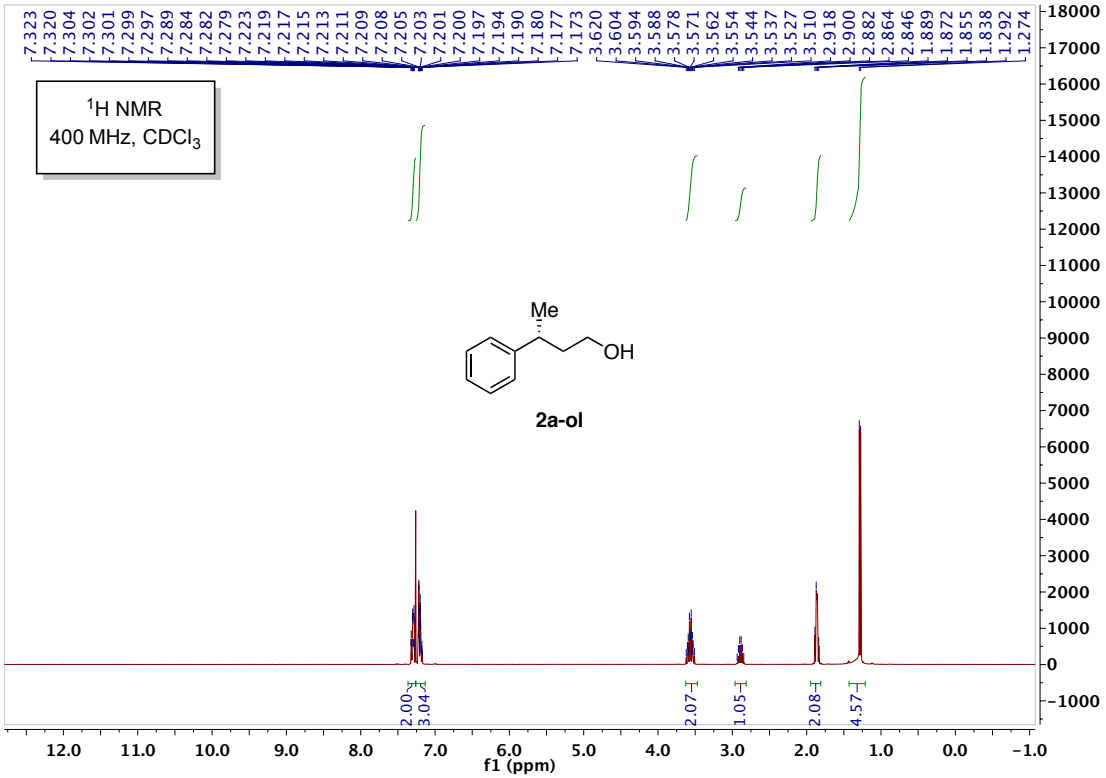
X. Copies of NMR Spectra

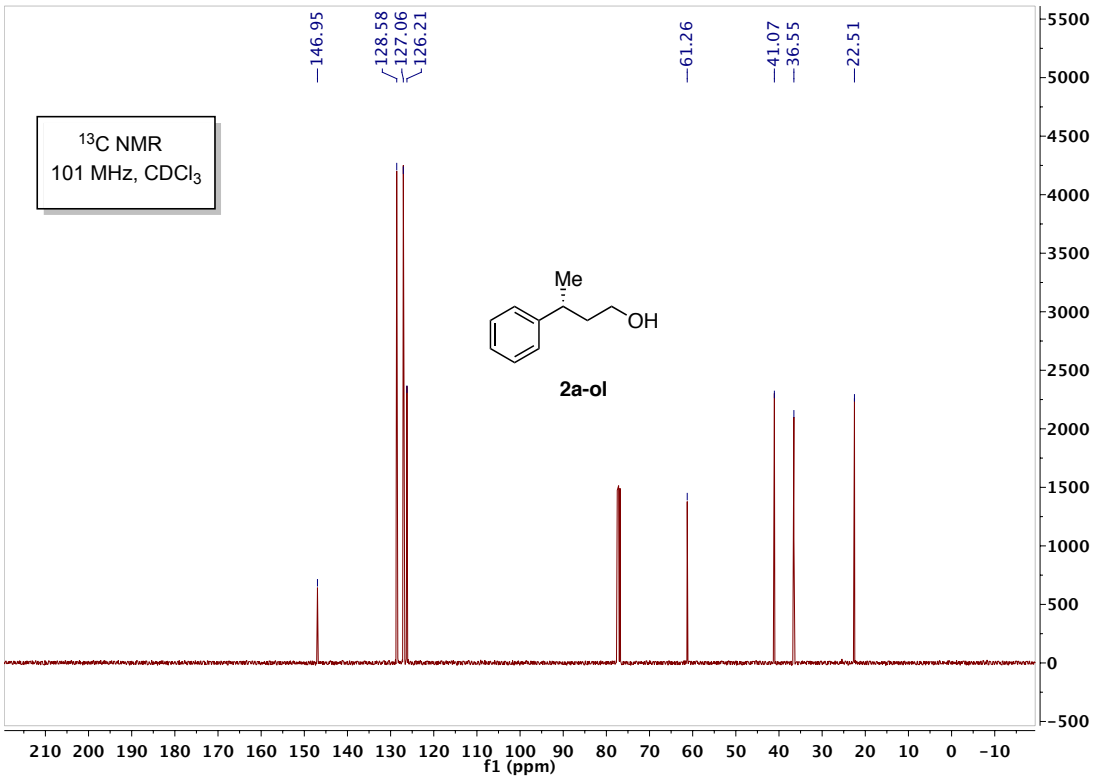
(*R*)-3-phenylbutanal (2a)



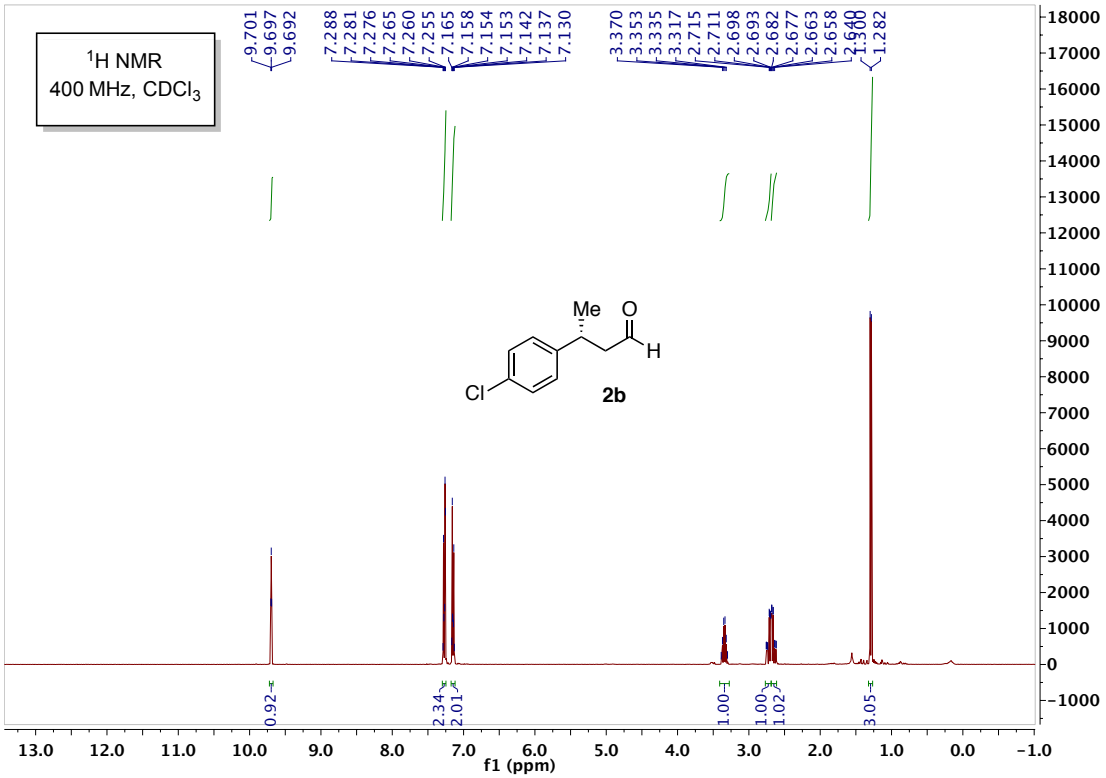


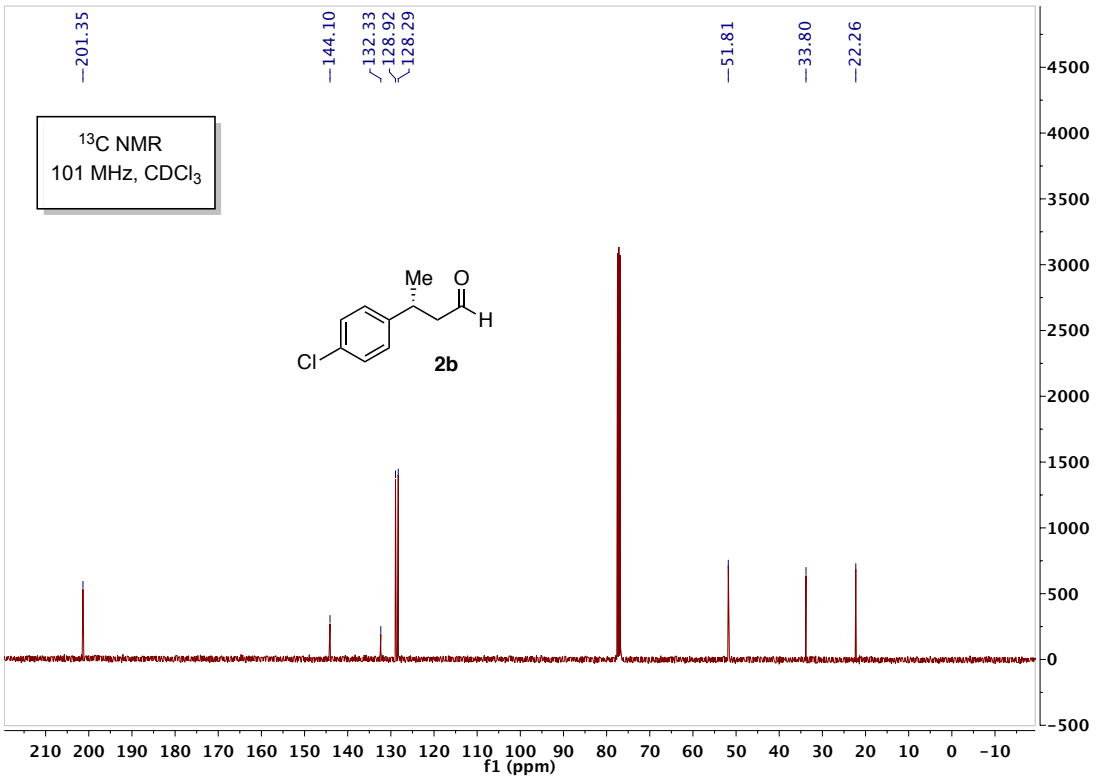
(*R*)-3-phenylbutan-1-ol (2a-ol)



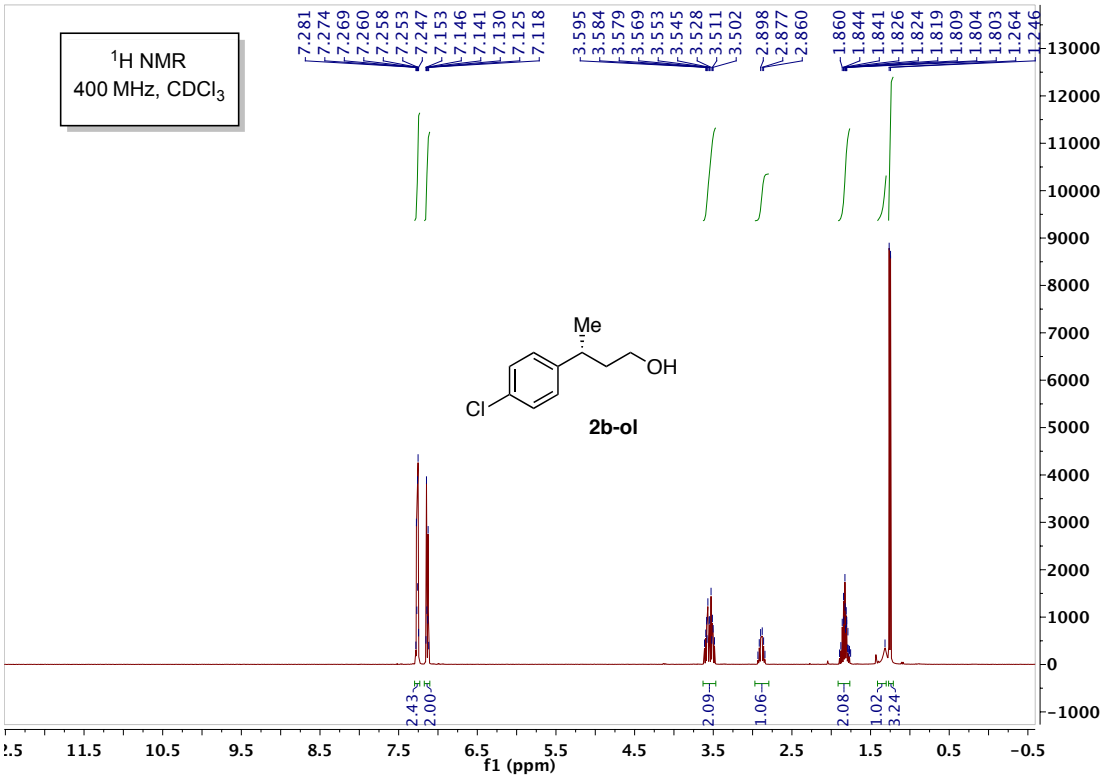


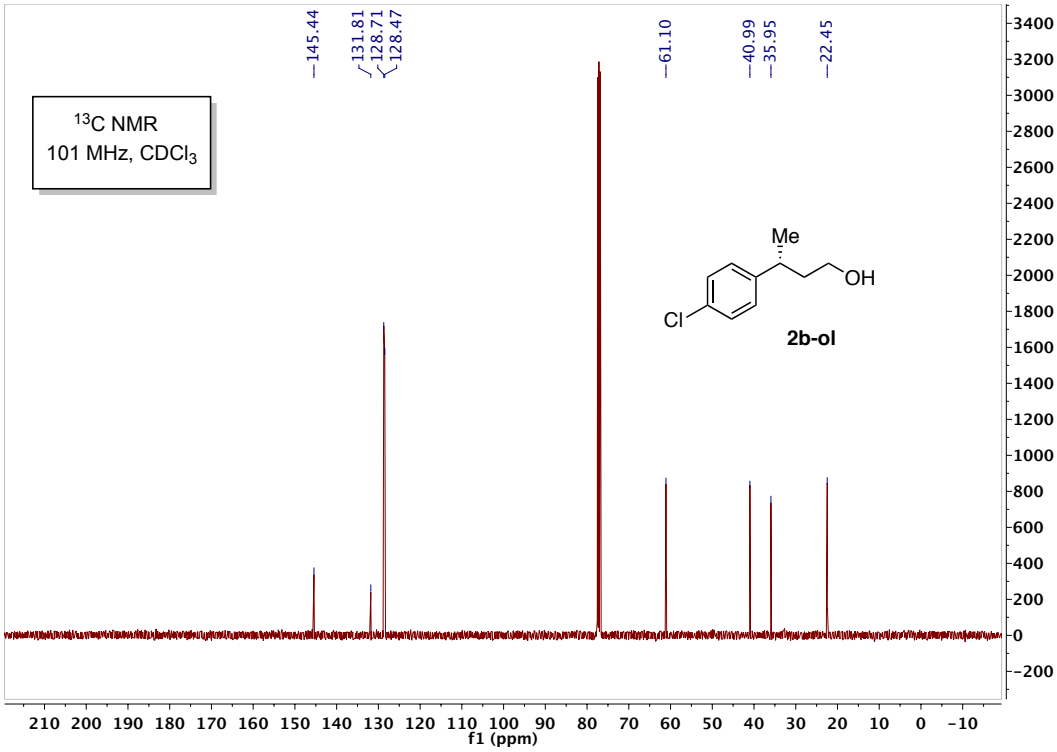
(*R*)-3-(4-chlorophenyl)butanal (2b)



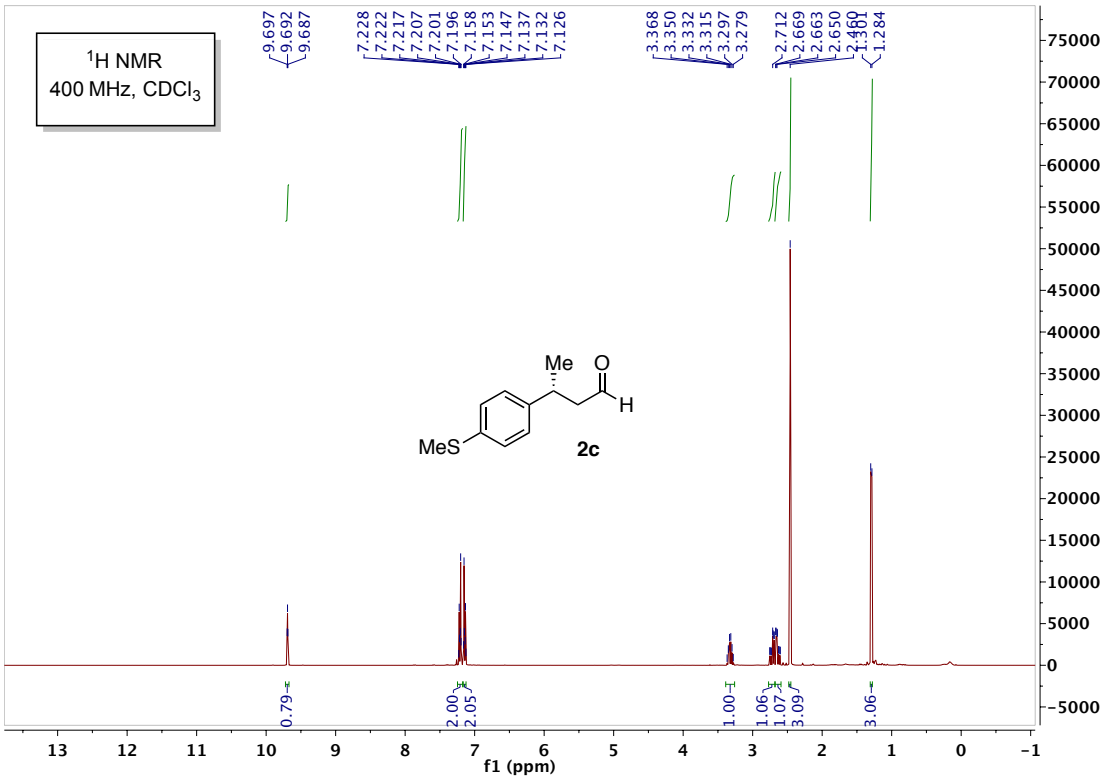


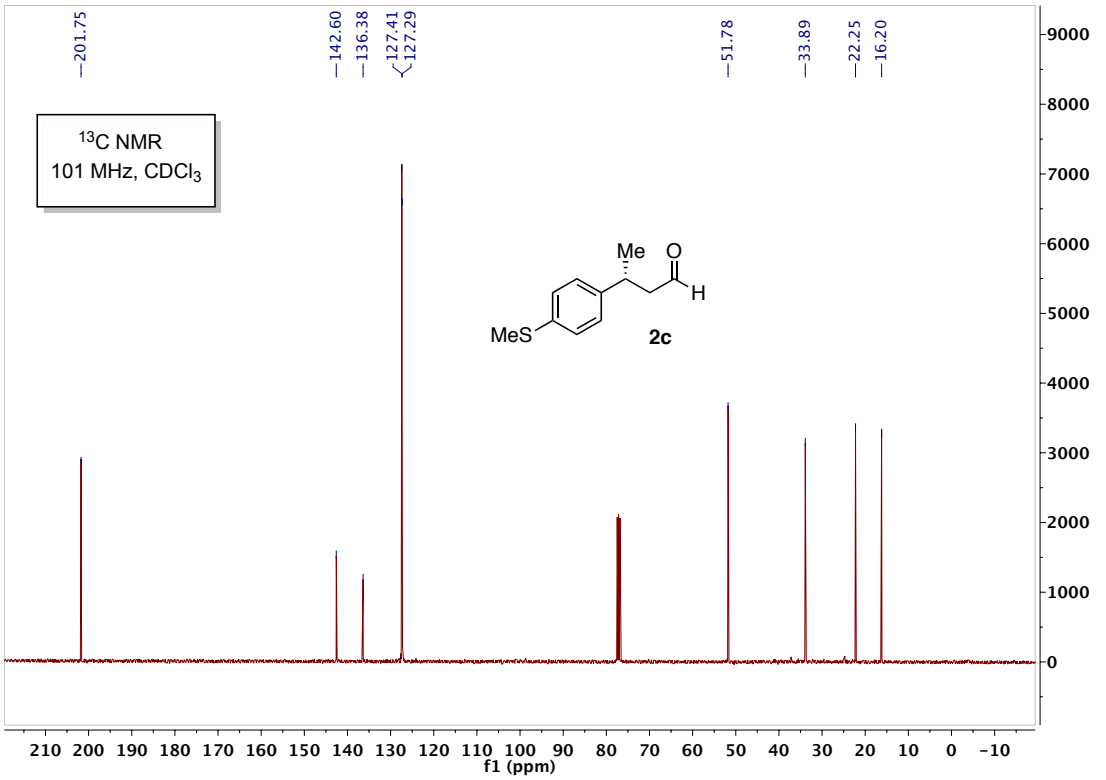
(*R*)-3-(4-chlorophenyl)butan-1-ol (2b-ol)



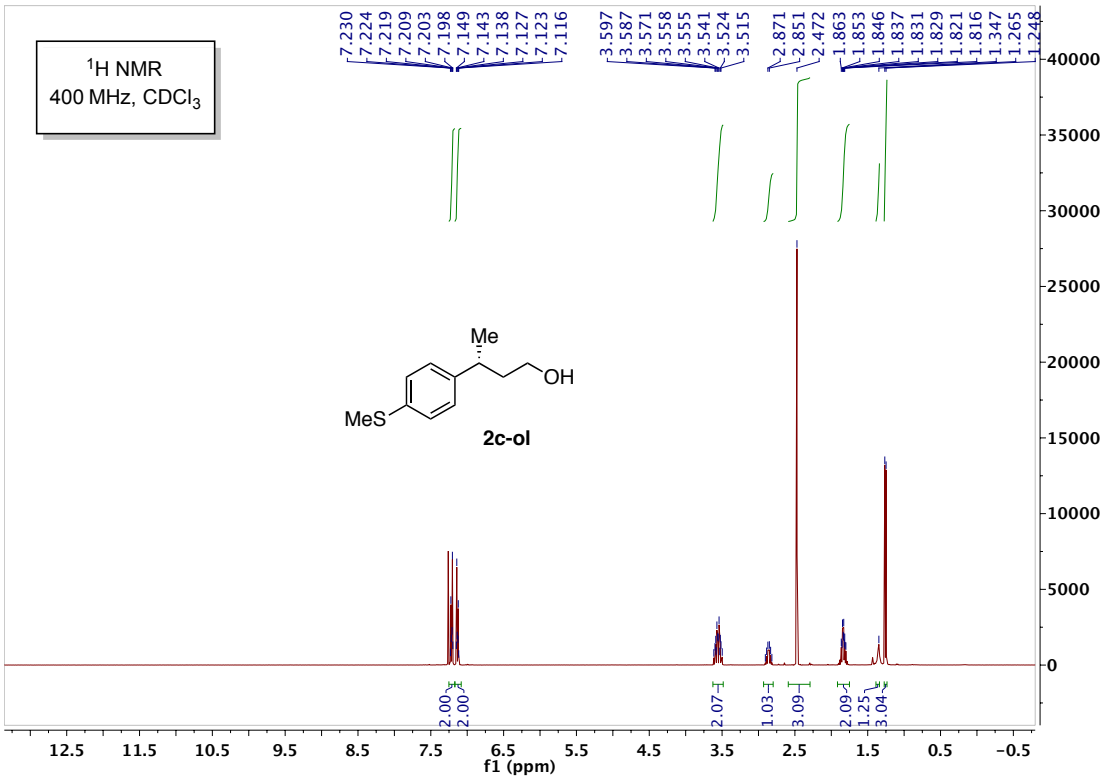


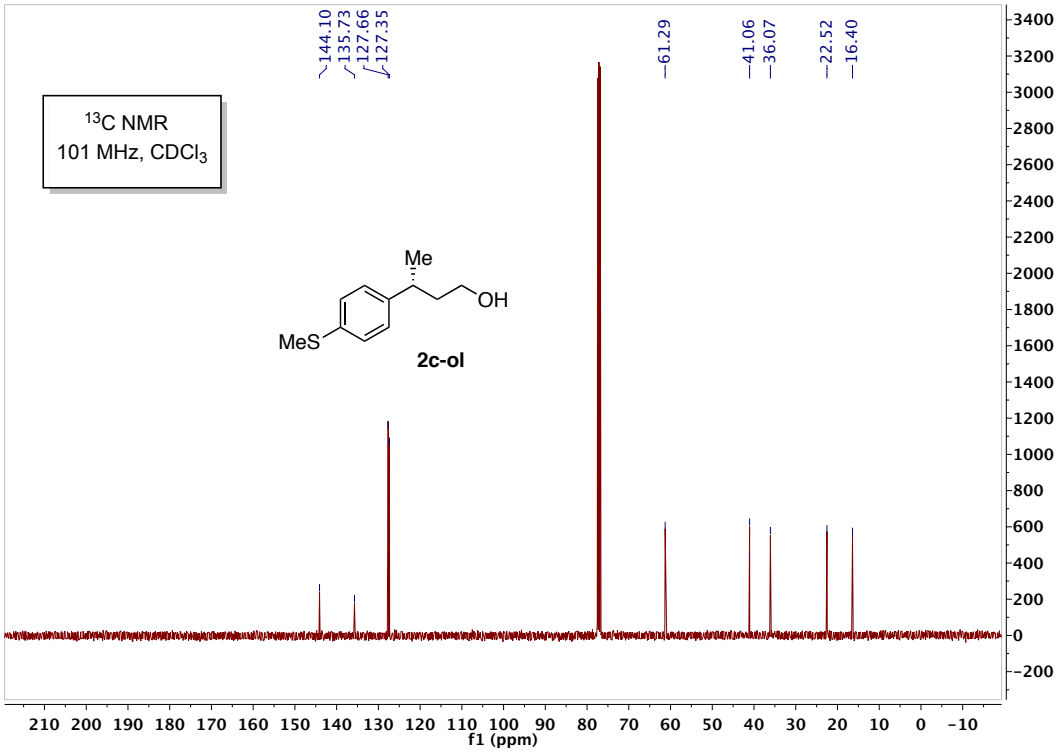
(*R*)-3-(4-(methylthio)phenyl)butanal (2c)



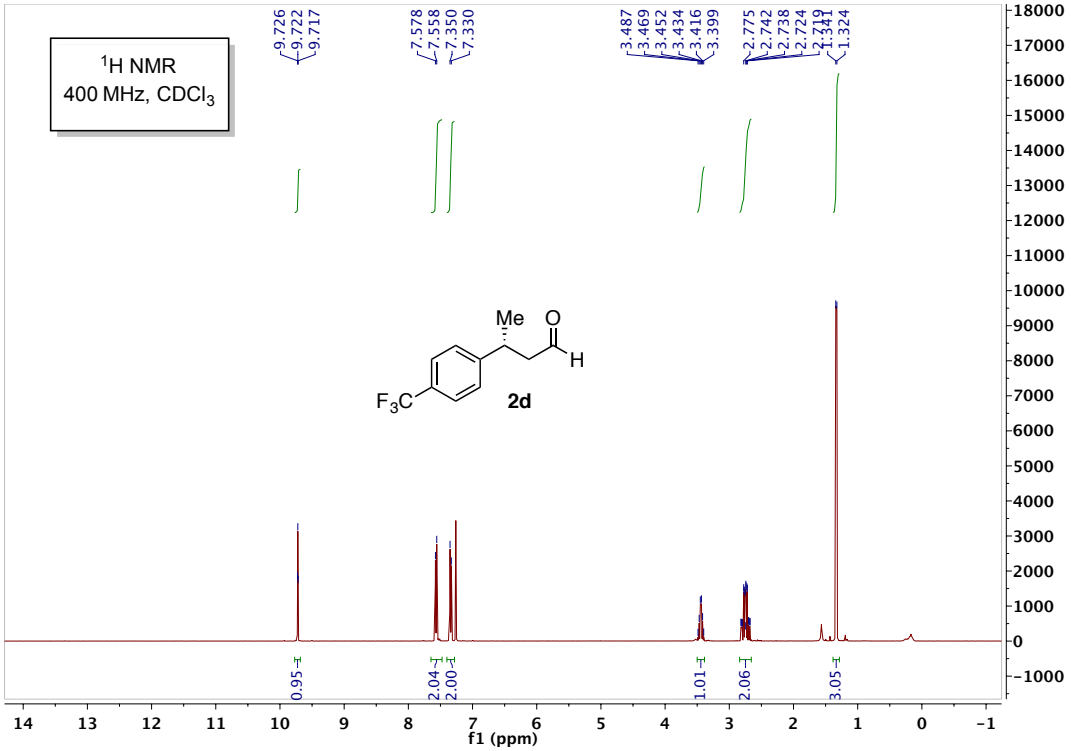


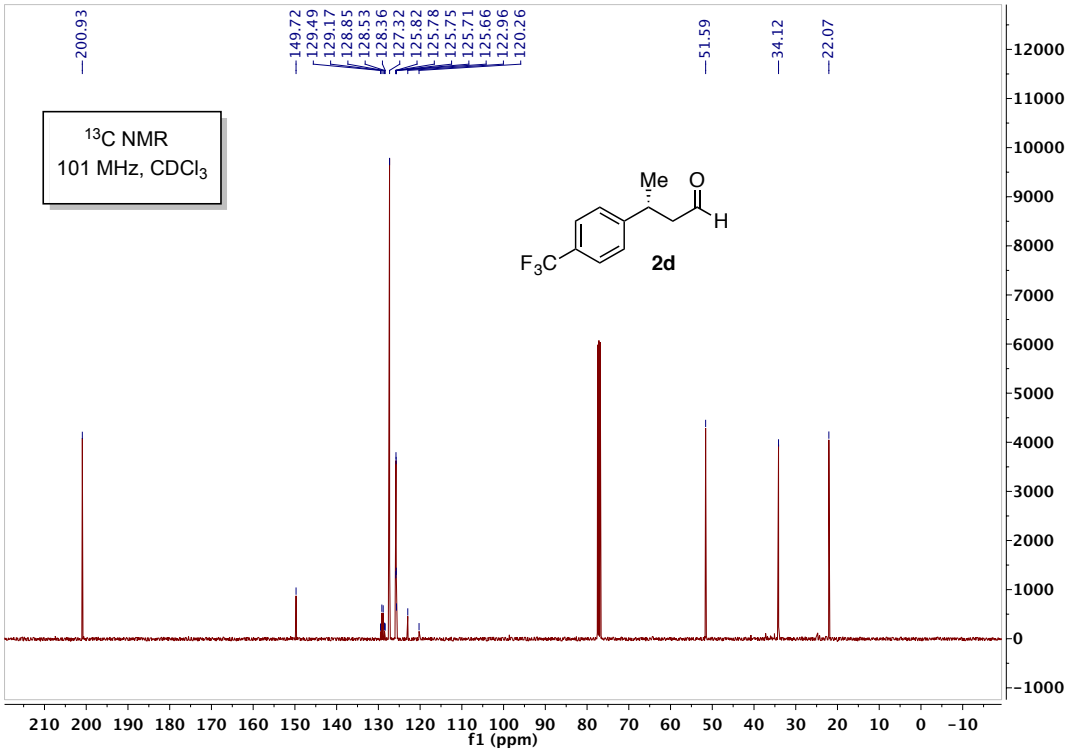
(*R*)-3-(4-(methylthio)phenyl)butan-1-ol (2c-ol)



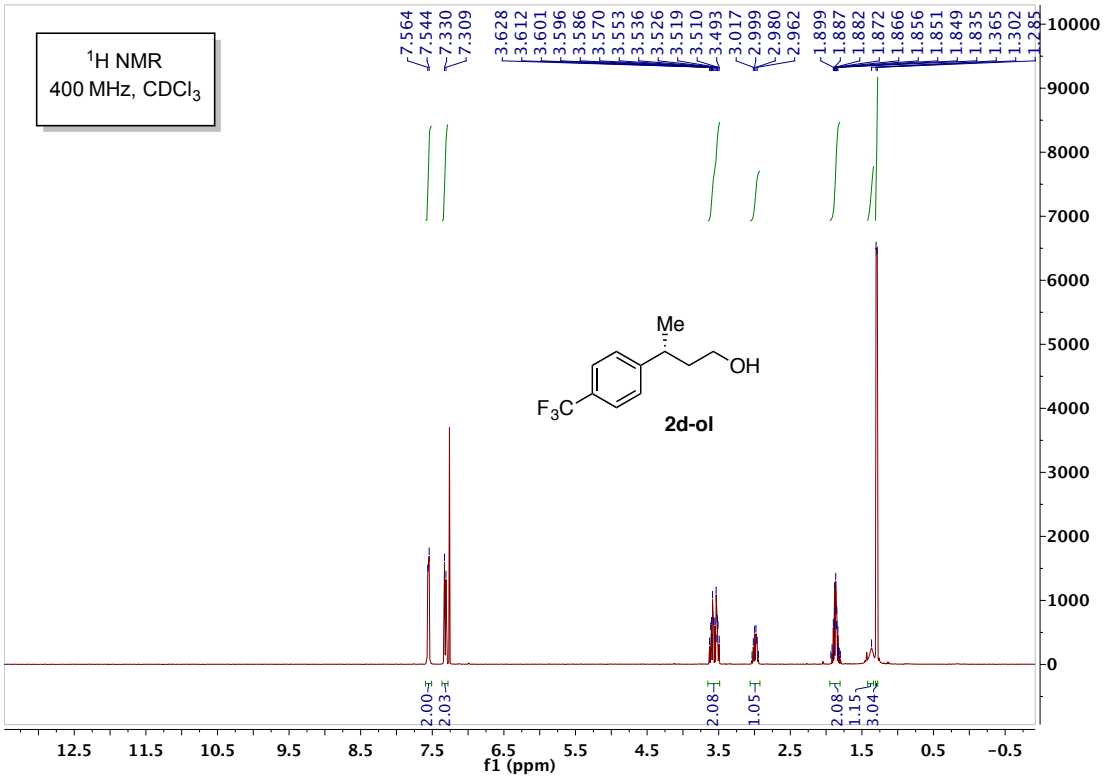


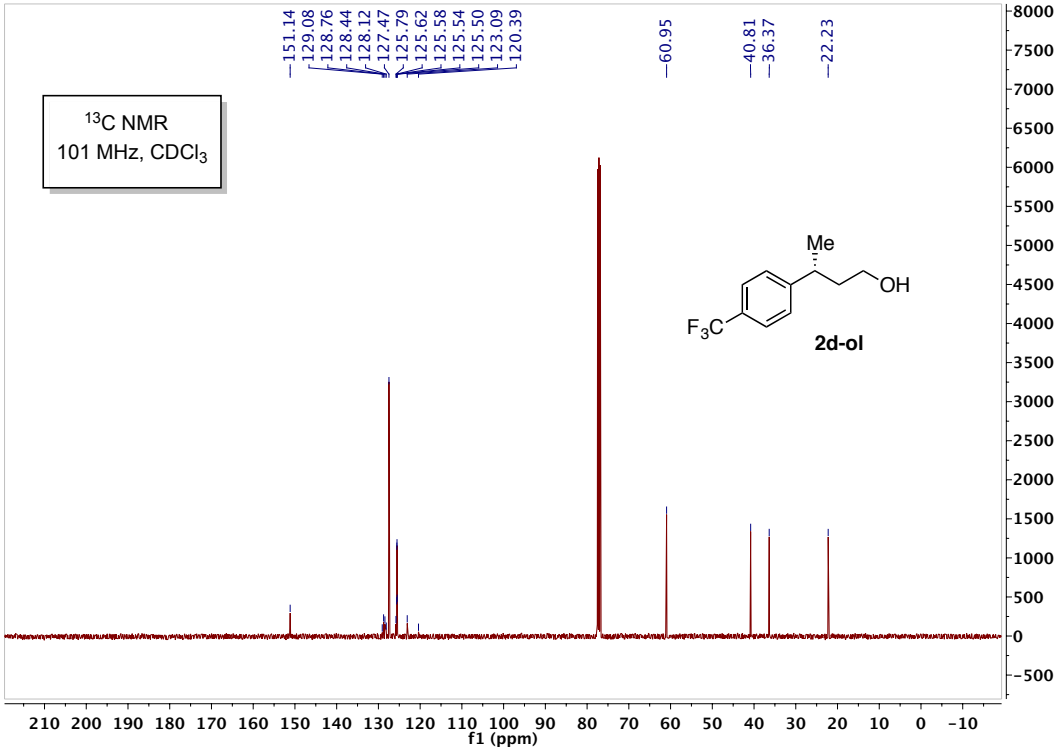
(*R*)-3-(4-(trifluoromethyl)phenyl)butanal (2d)



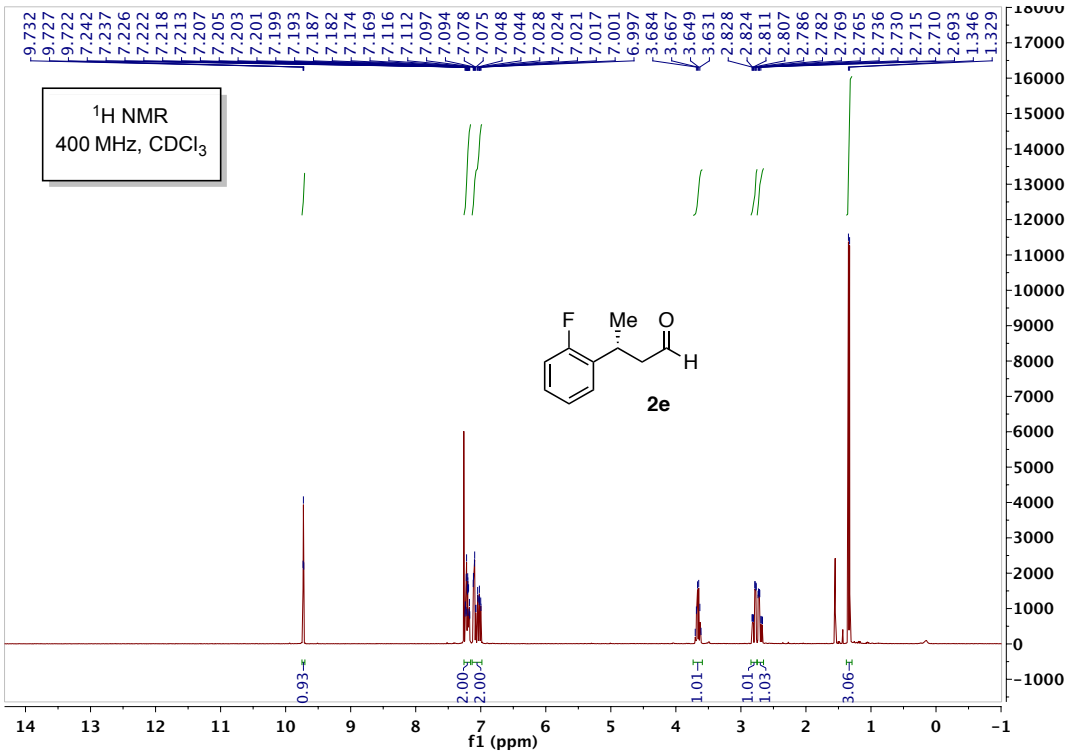


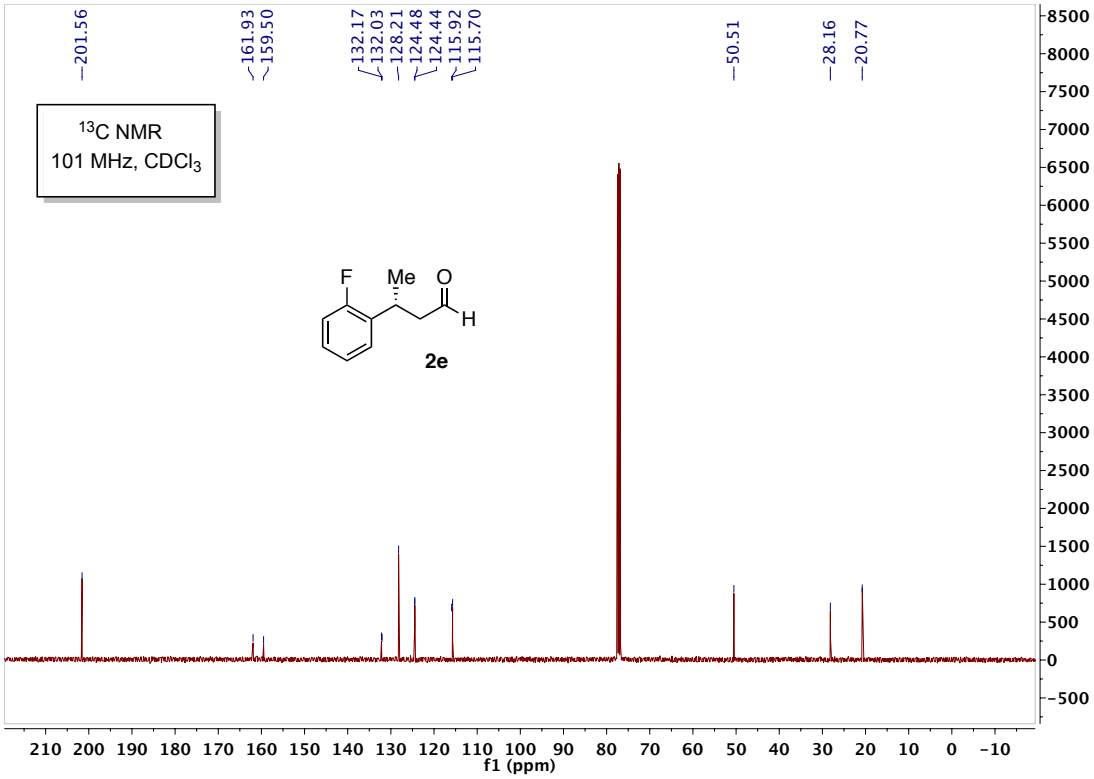
(*R*)-3-(4-(trifluoromethyl)phenyl)butan-1-ol (2d-ol)



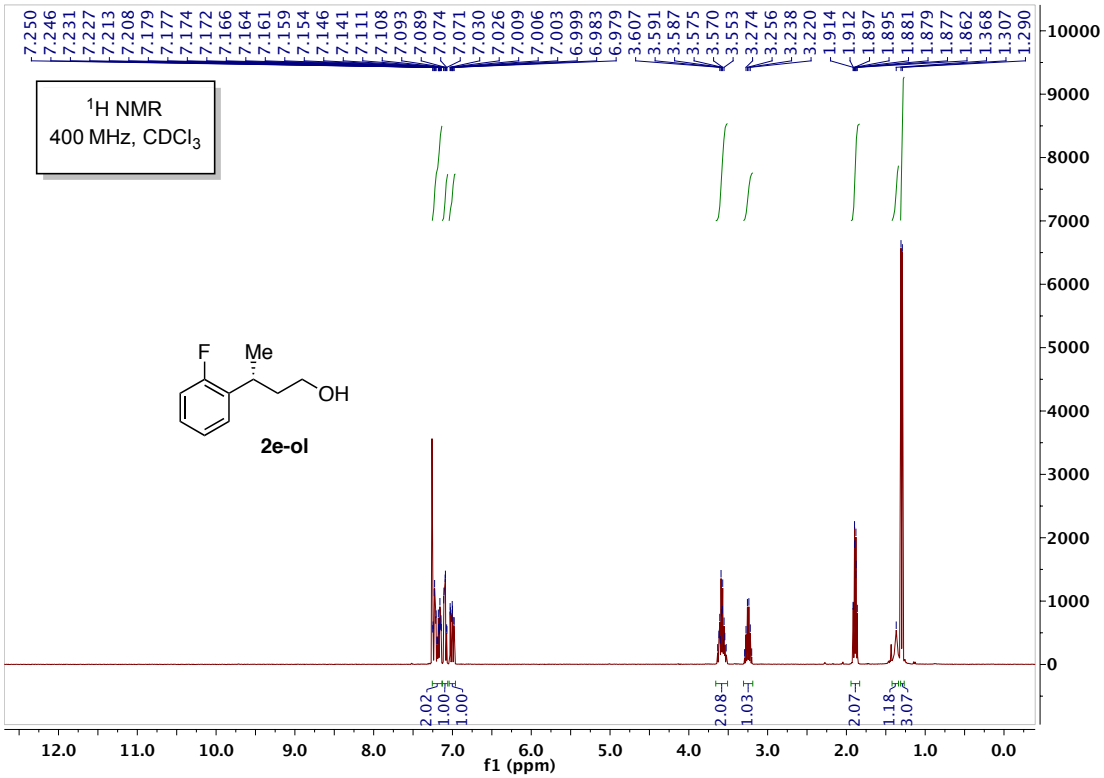


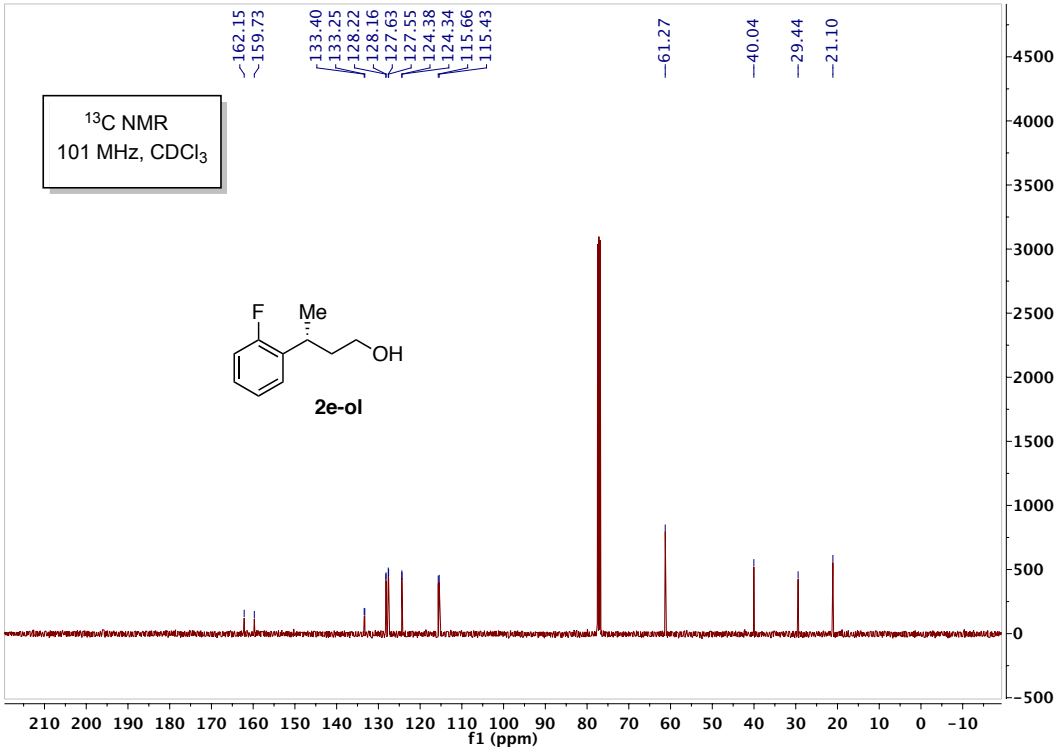
(*R*)-3-(2-fluorophenyl)butanal (2e)



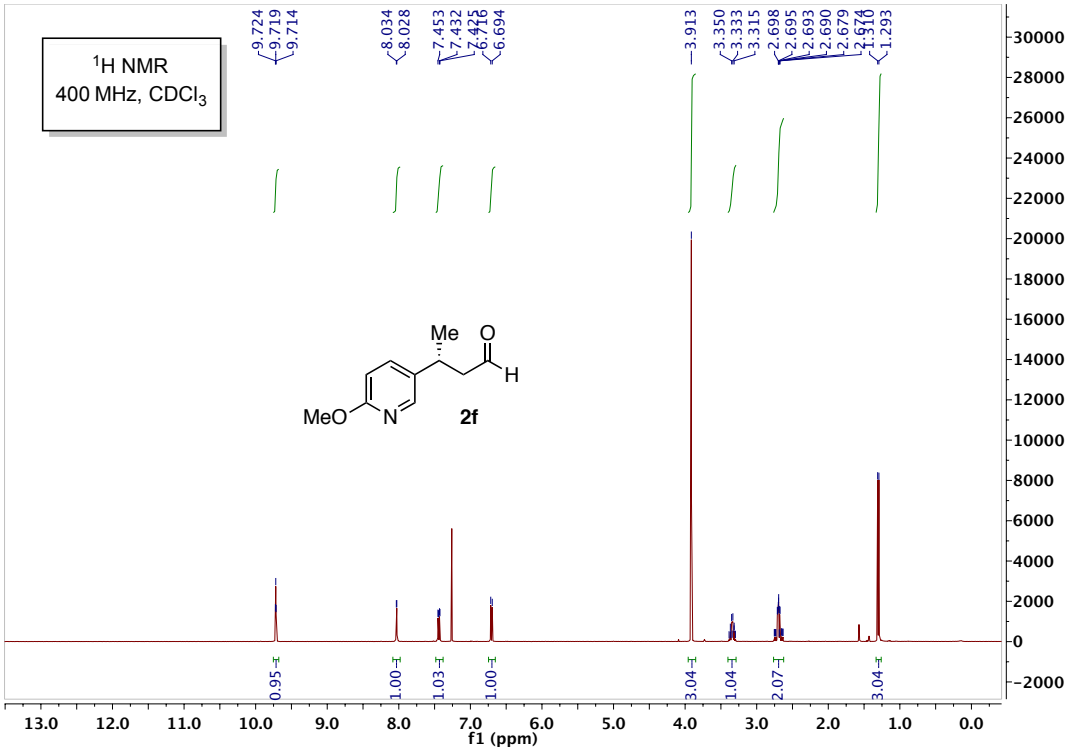


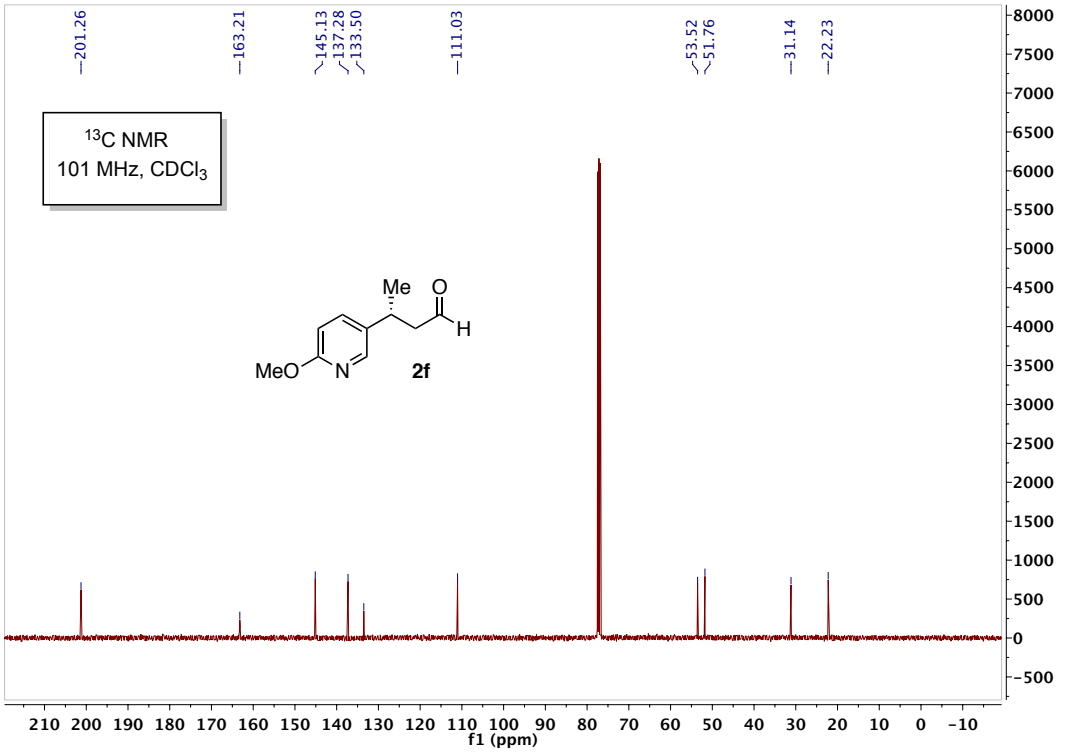
(*R*)-3-(2-fluorophenyl)butan-1-ol (2e-ol)



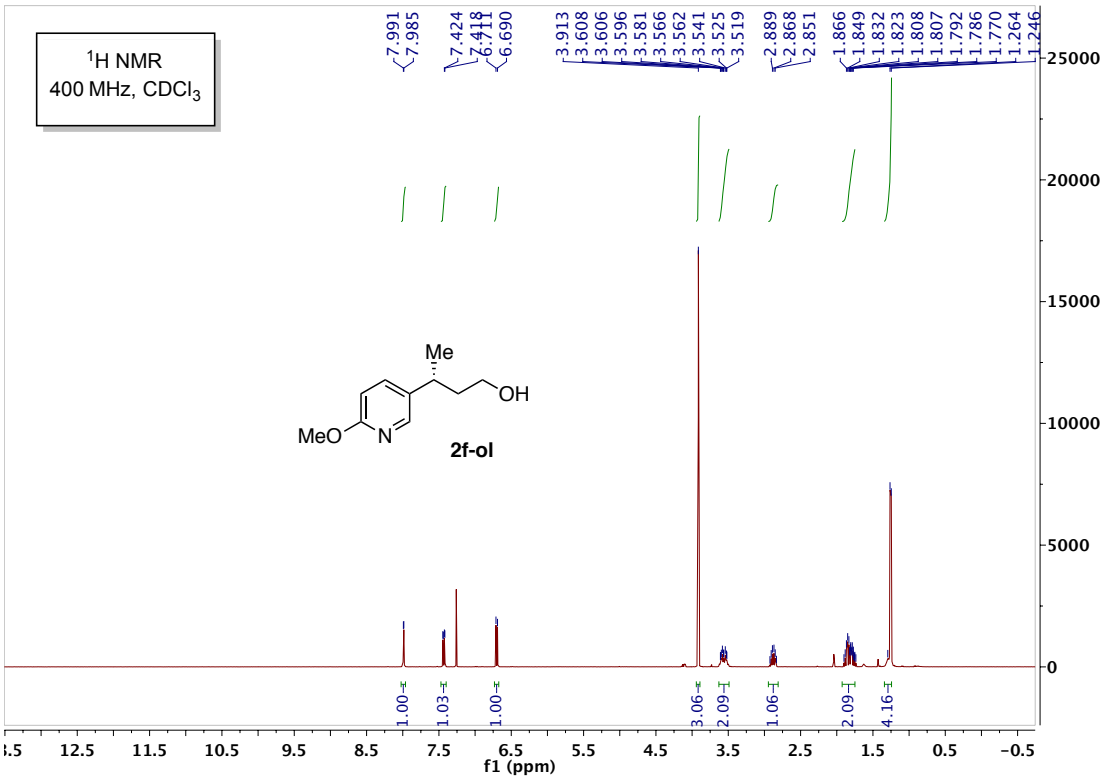


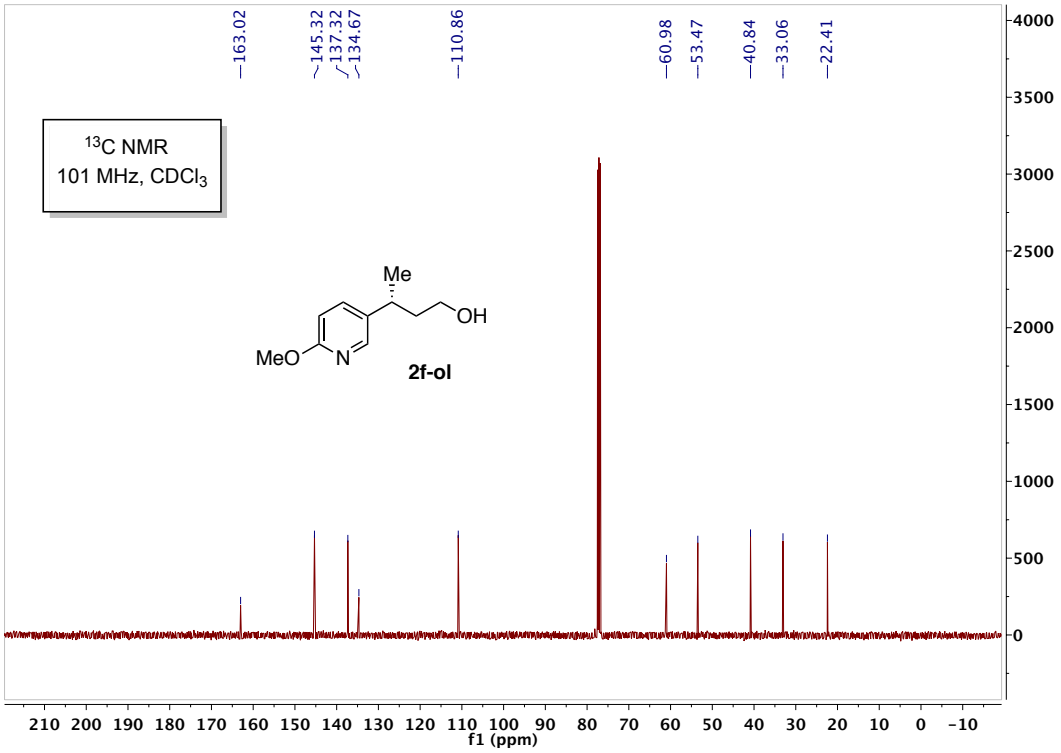
(*R*)-3-(6-methoxypyridin-3-yl)butanal (2f)



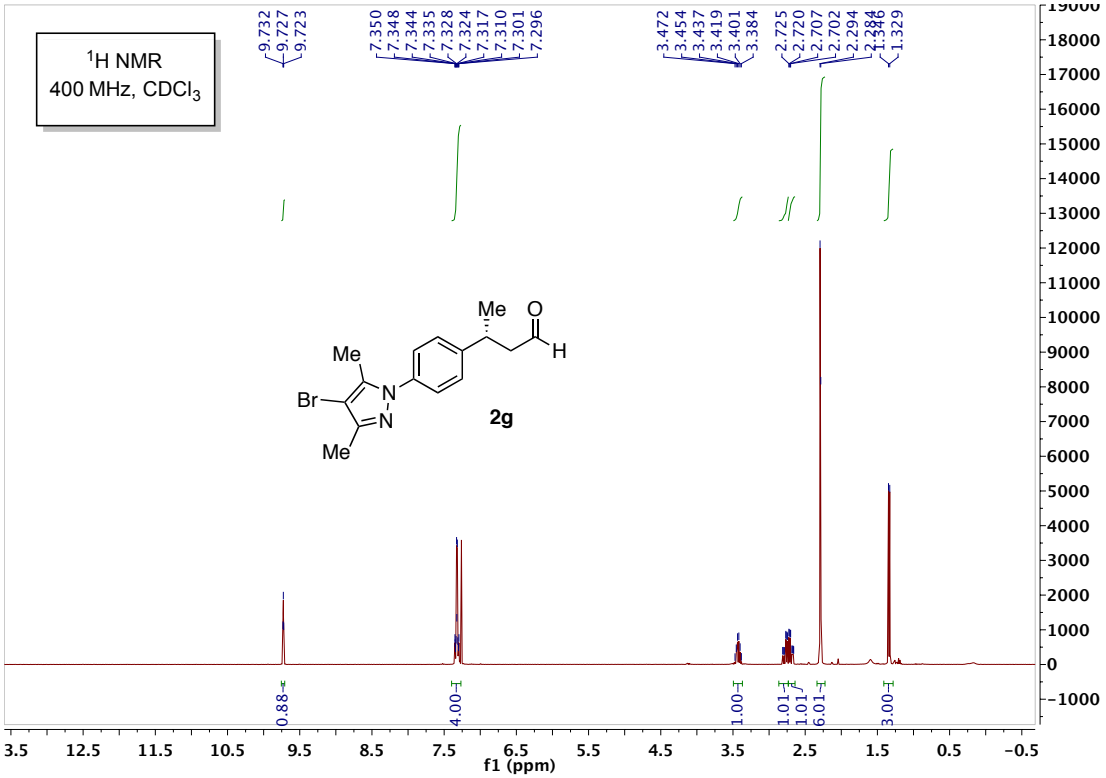


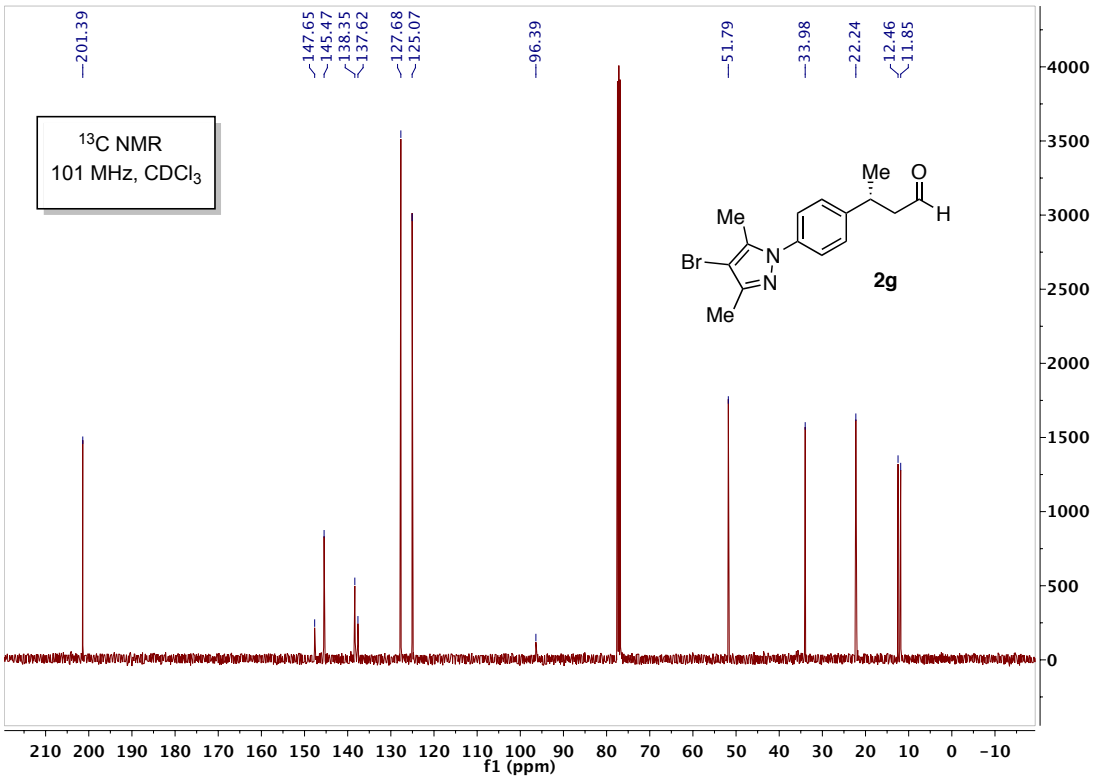
(*R*)-3-(6-methoxypyridin-3-yl)butan-1-ol (2f-ol)



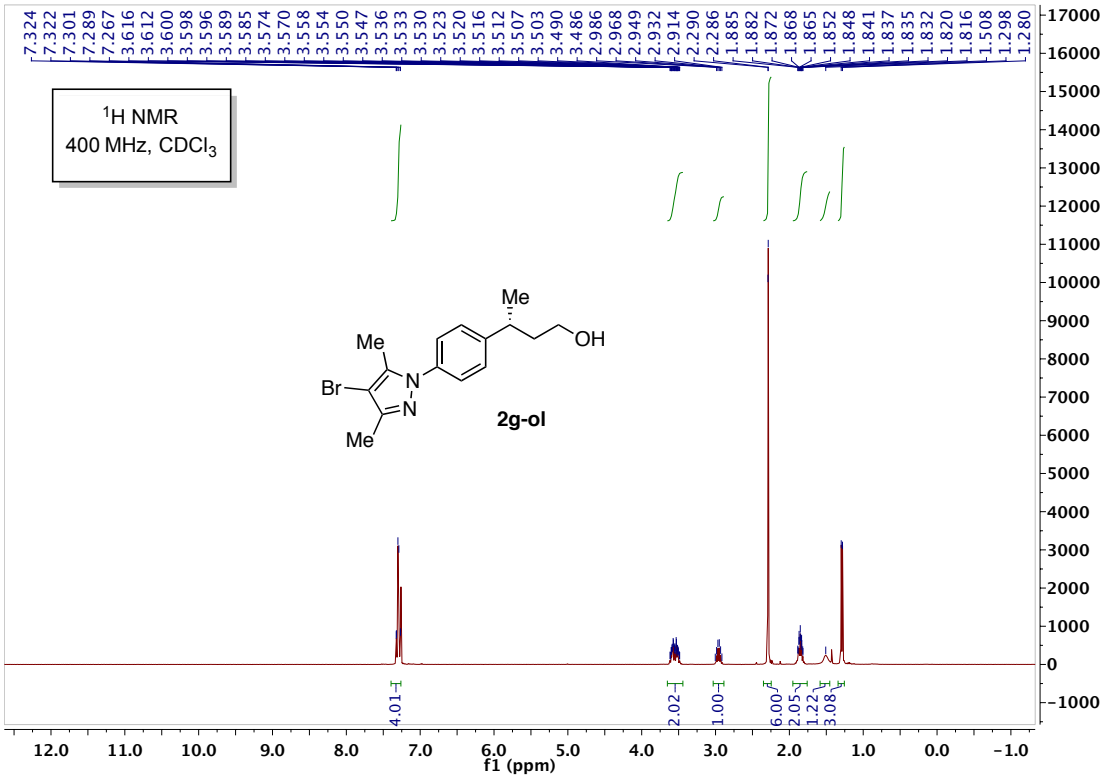


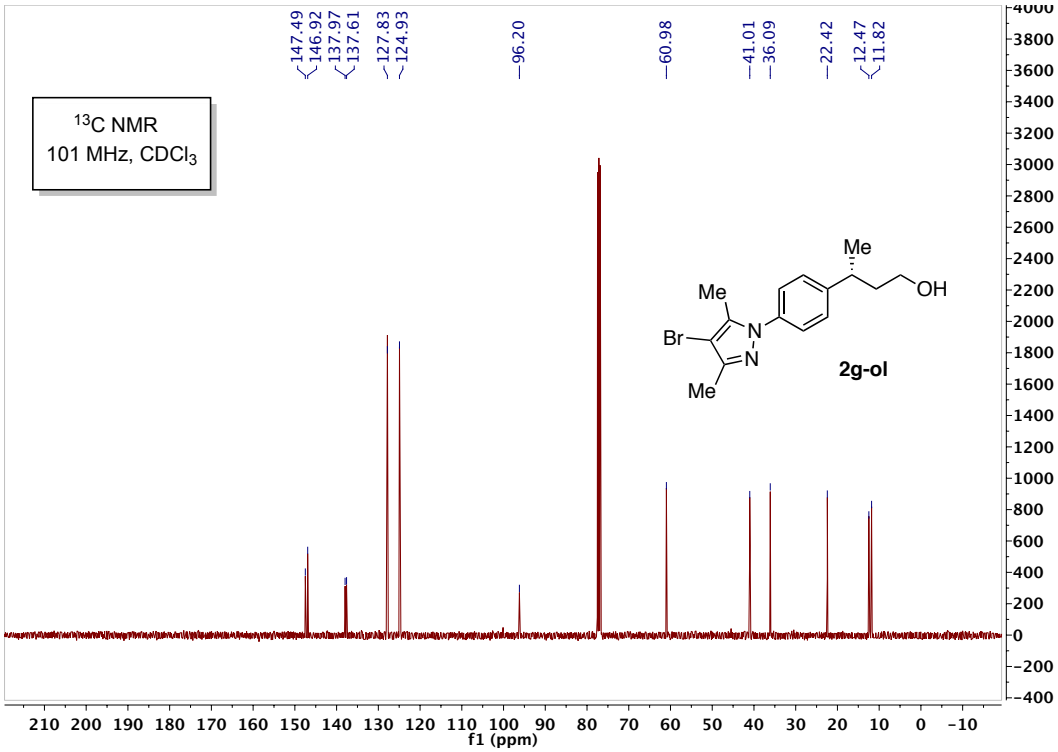
(*R*)-3-(4-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)phenyl)butanal (2g)



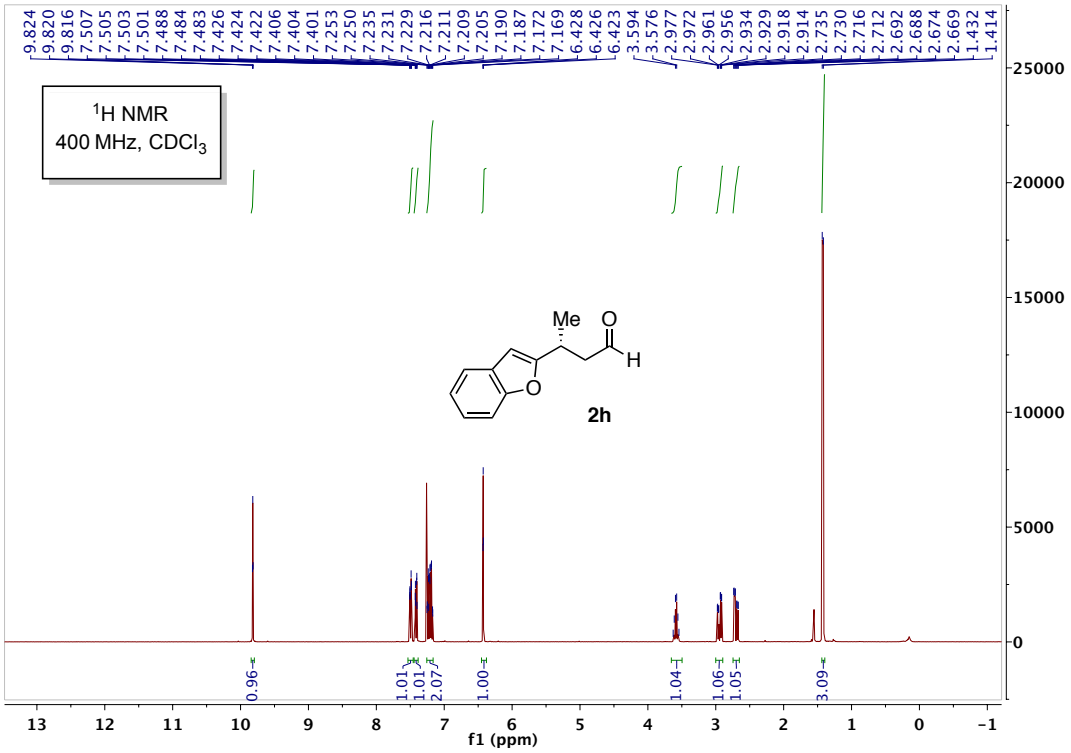


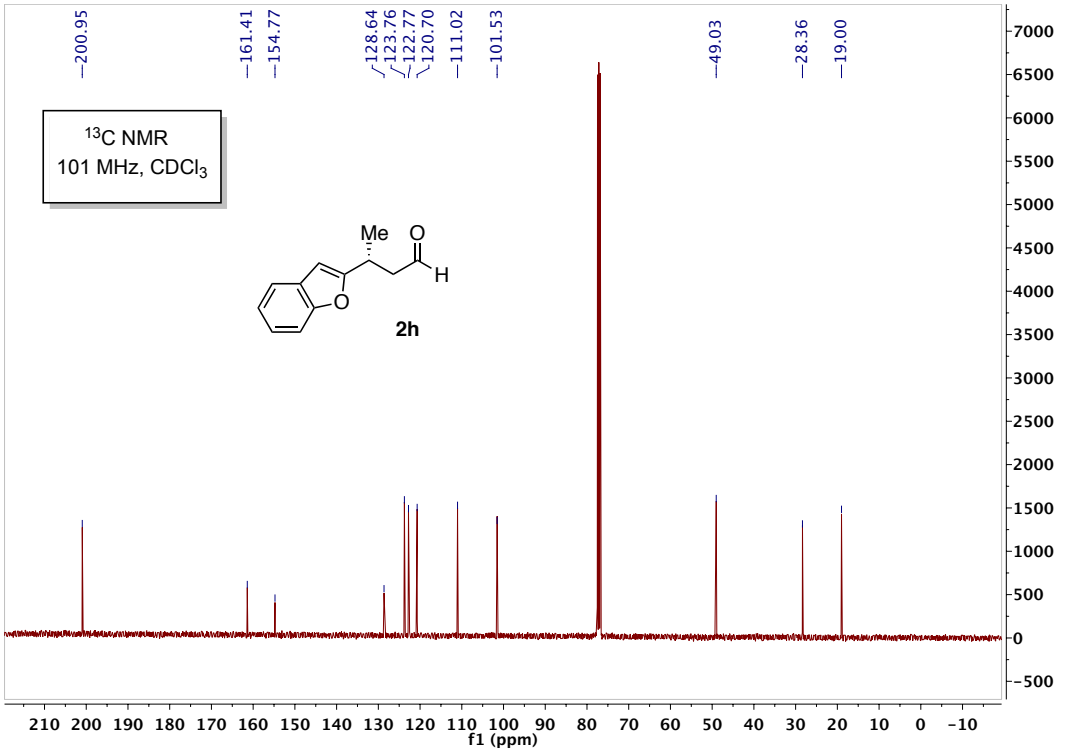
(*R*)-3-(4-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)phenyl)butan-1-ol (2g-ol)



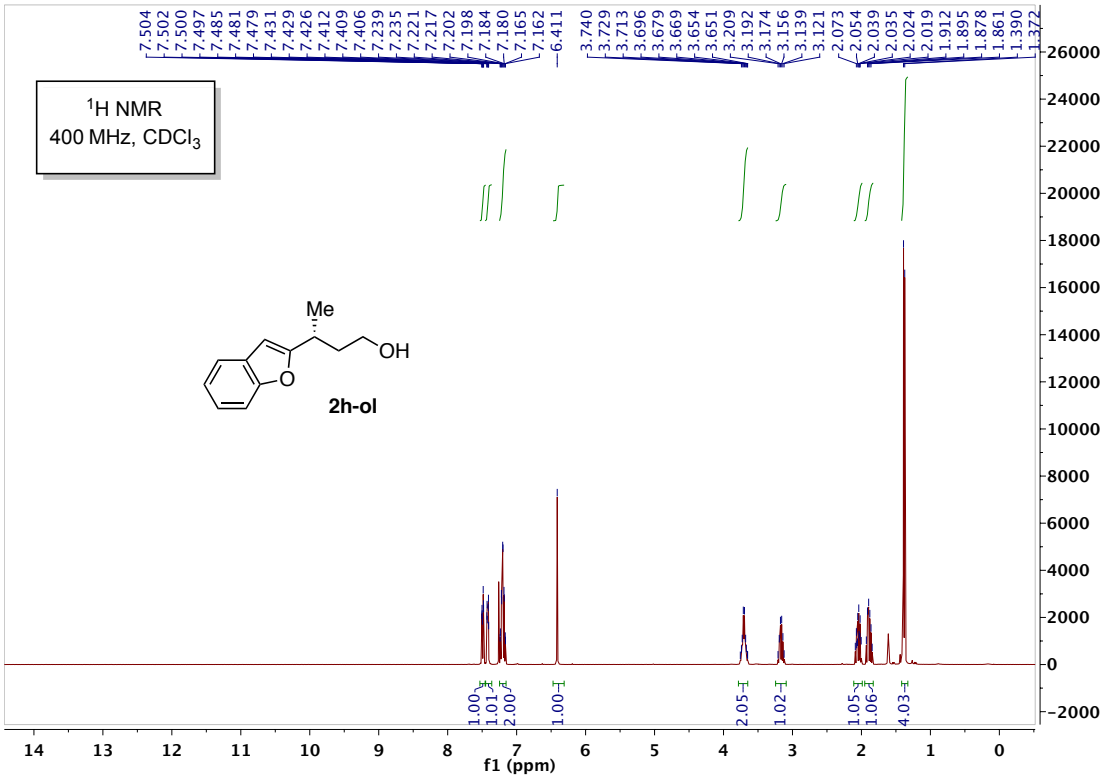


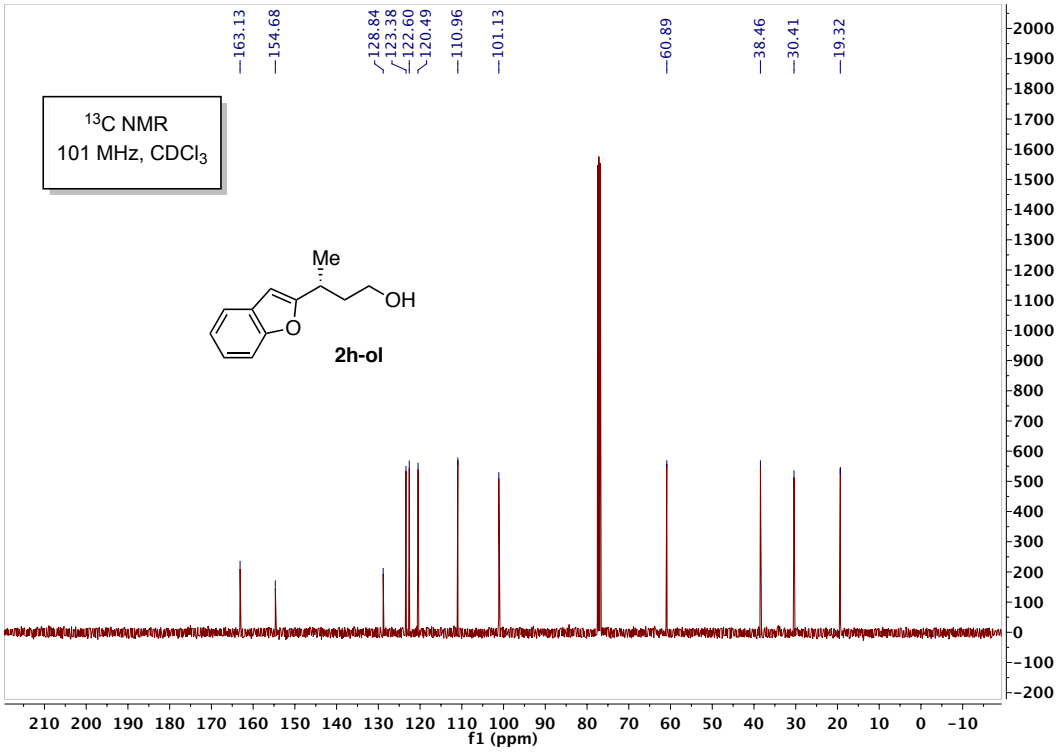
(*R*)-3-(benzofuran-2-yl)butanal (2h)



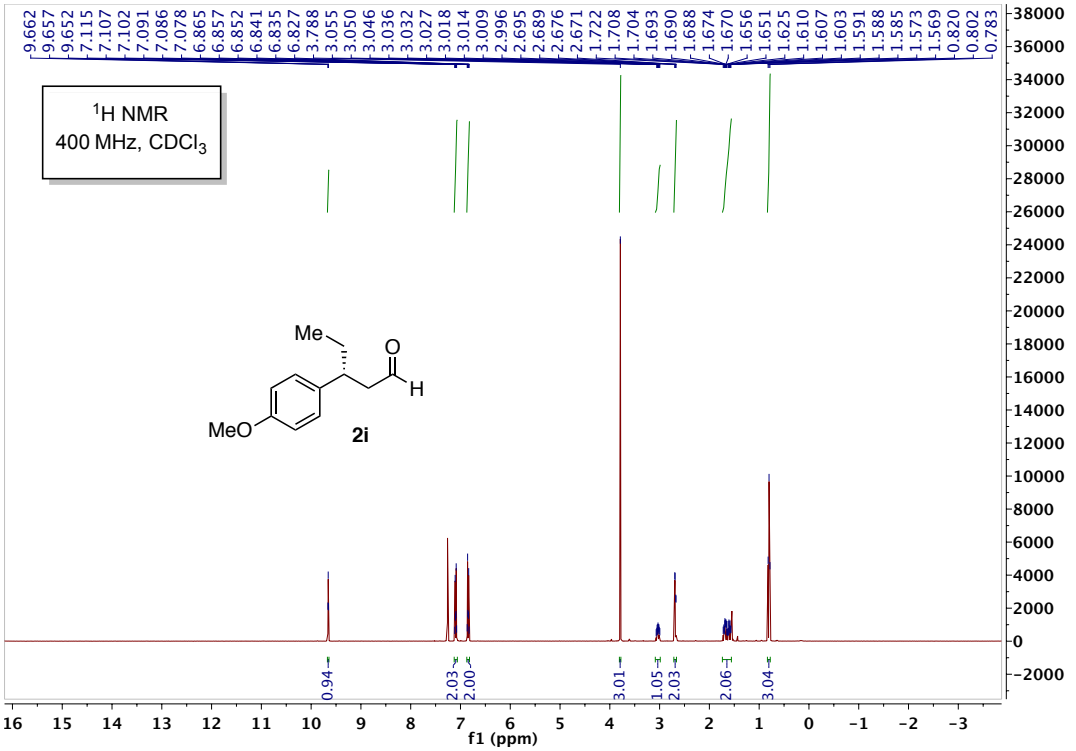


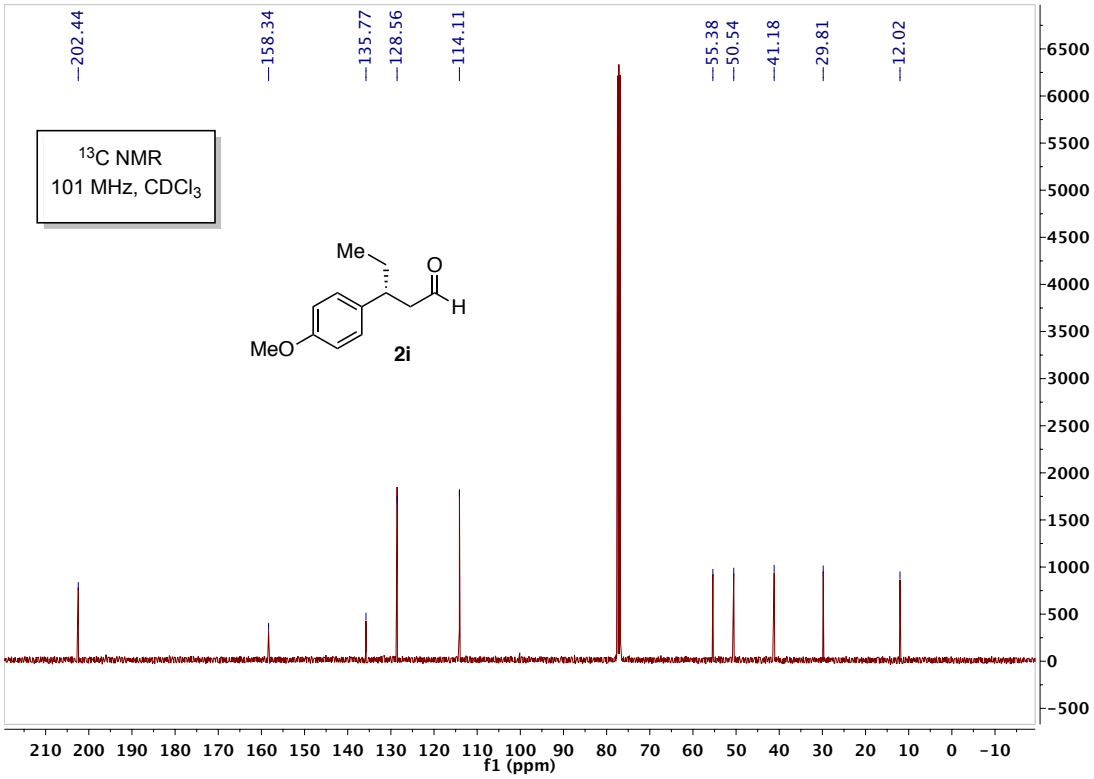
(*R*)-3-(benzofuran-2-yl)butan-1-ol (2h-ol)



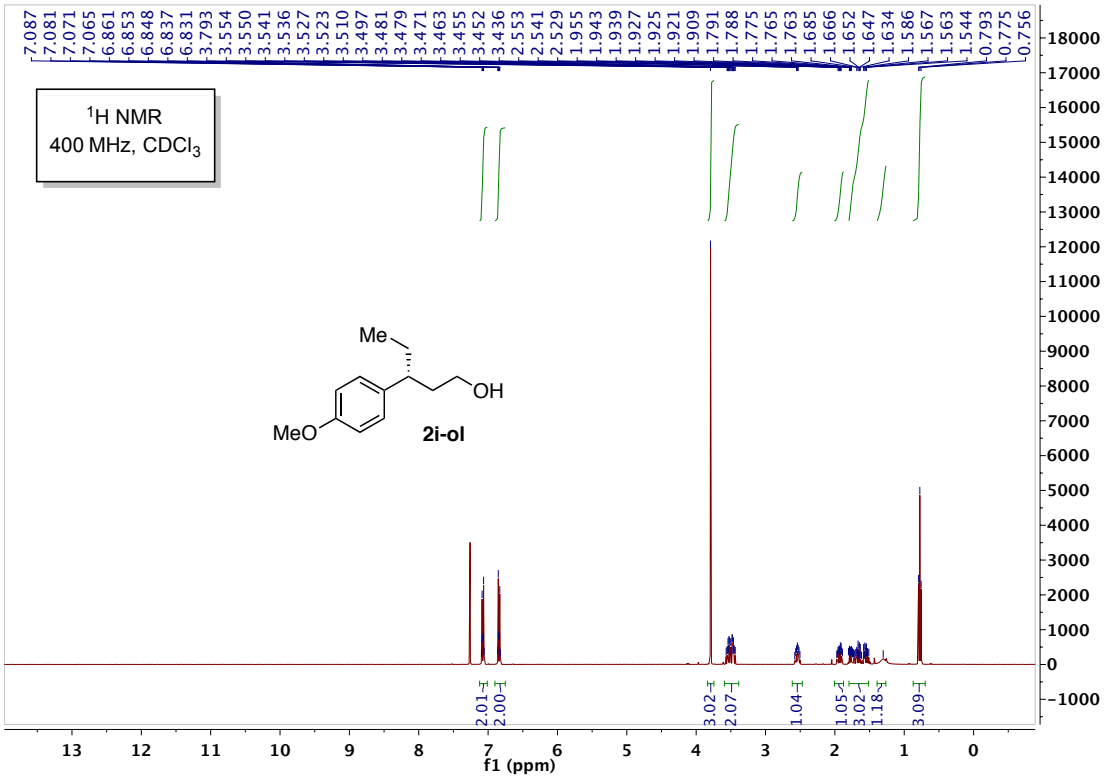


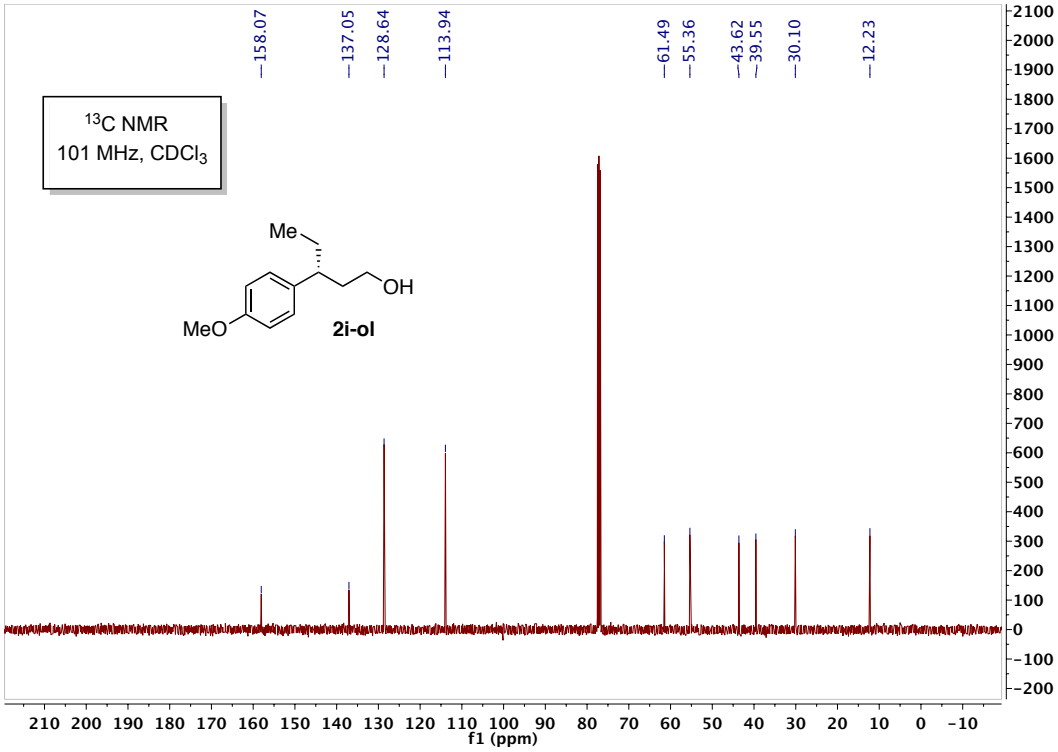
(*R*)-3-(4-methoxyphenyl)pentanal (2i)



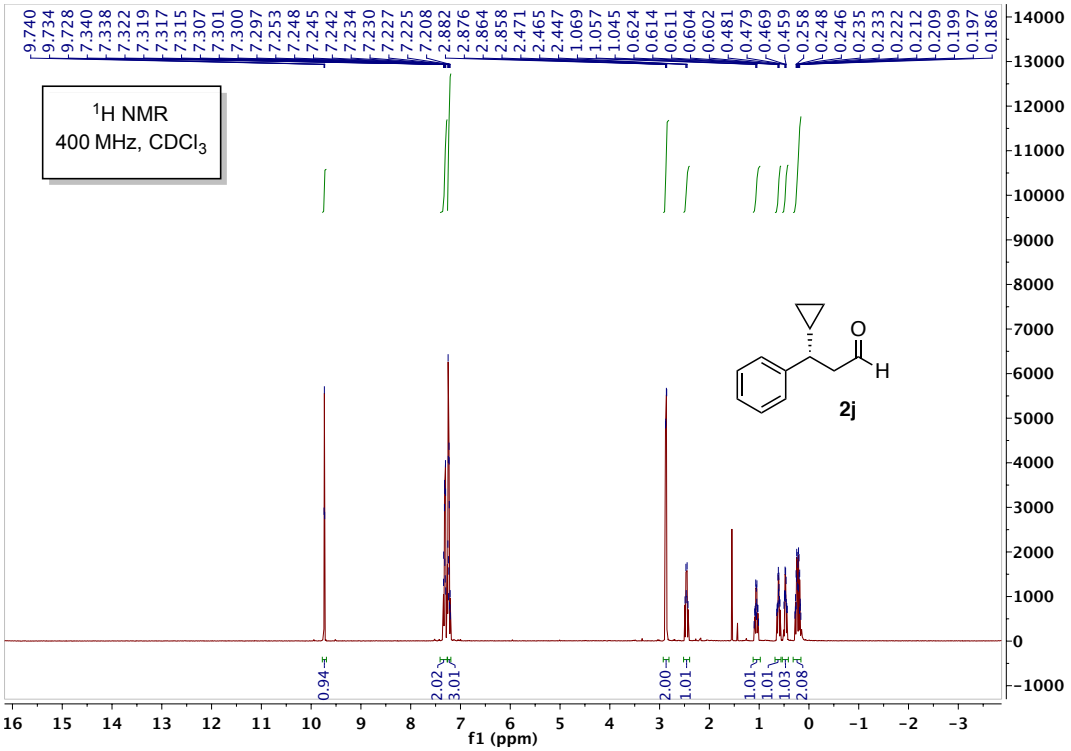


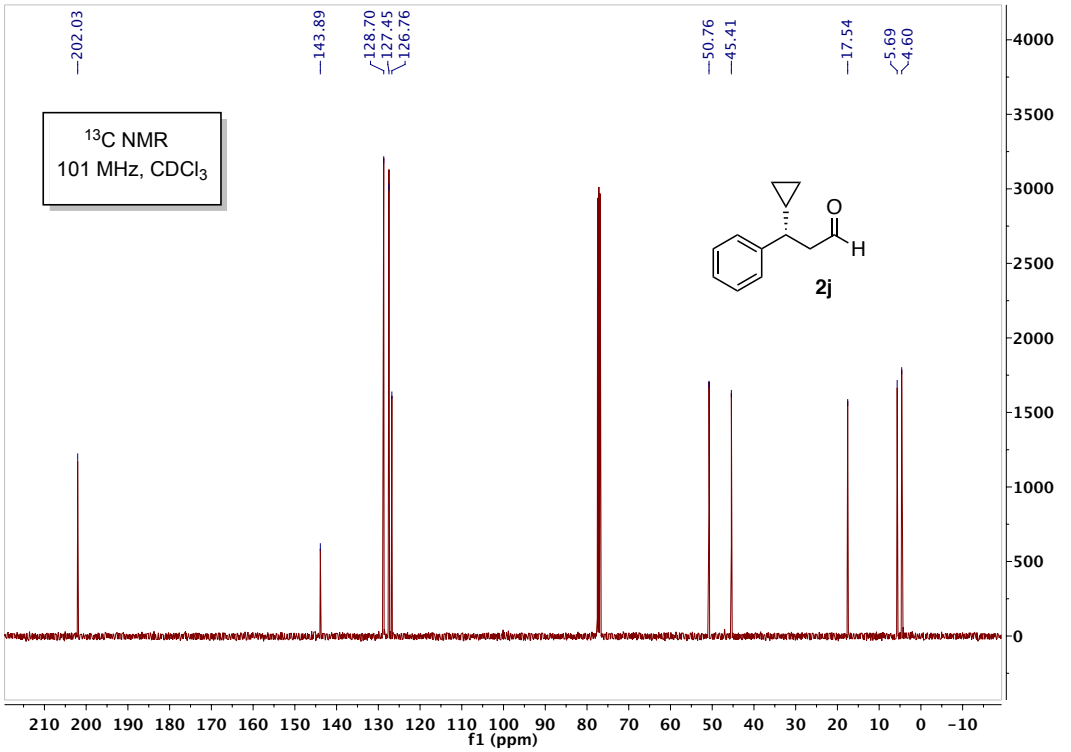
(*R*)-3-(4-methoxyphenyl)pentan-1-ol (2i-ol)



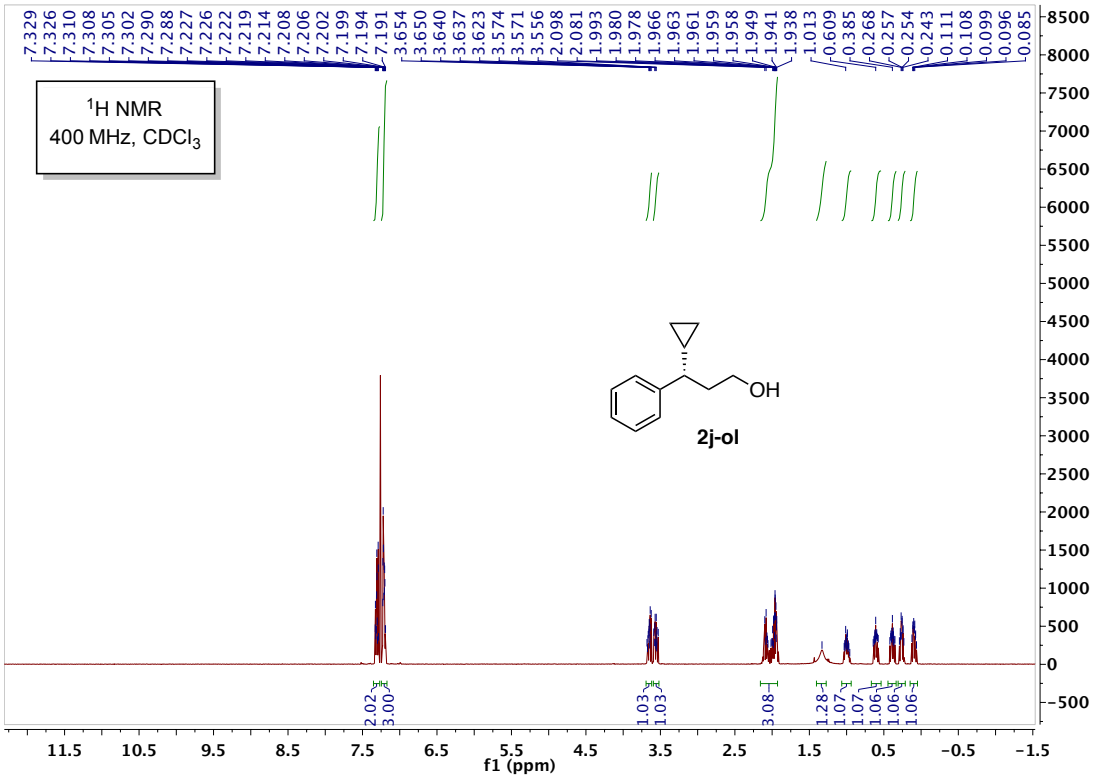


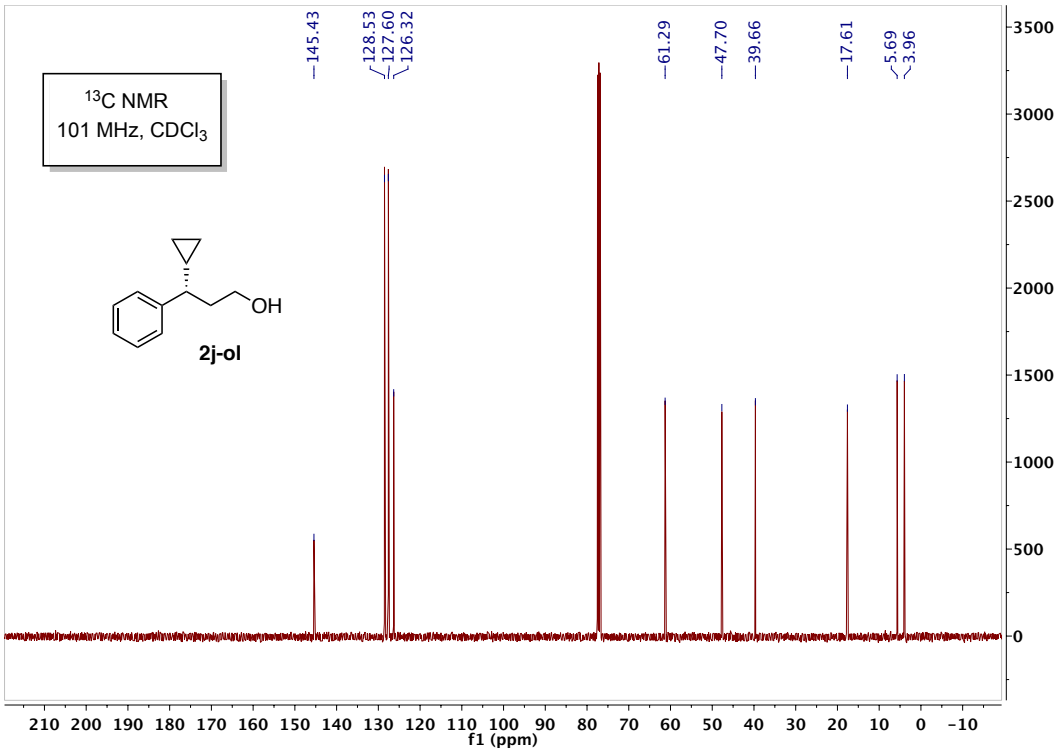
(*S*)-3-cyclopropyl-3-phenylpropanal (2j)



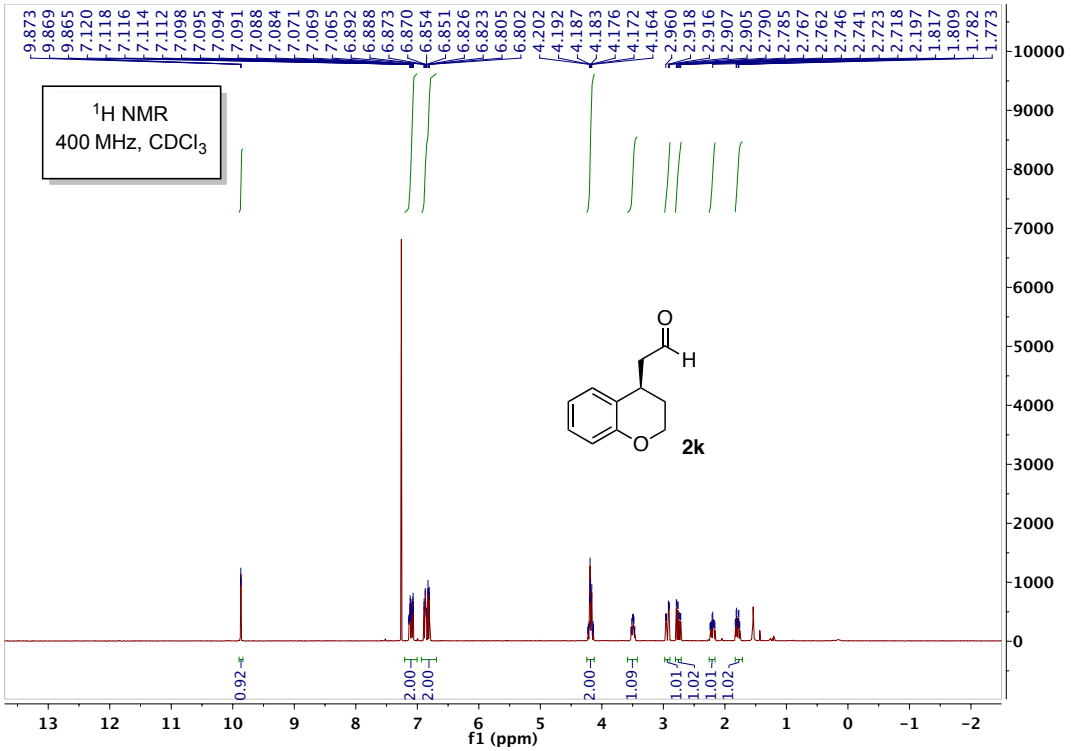


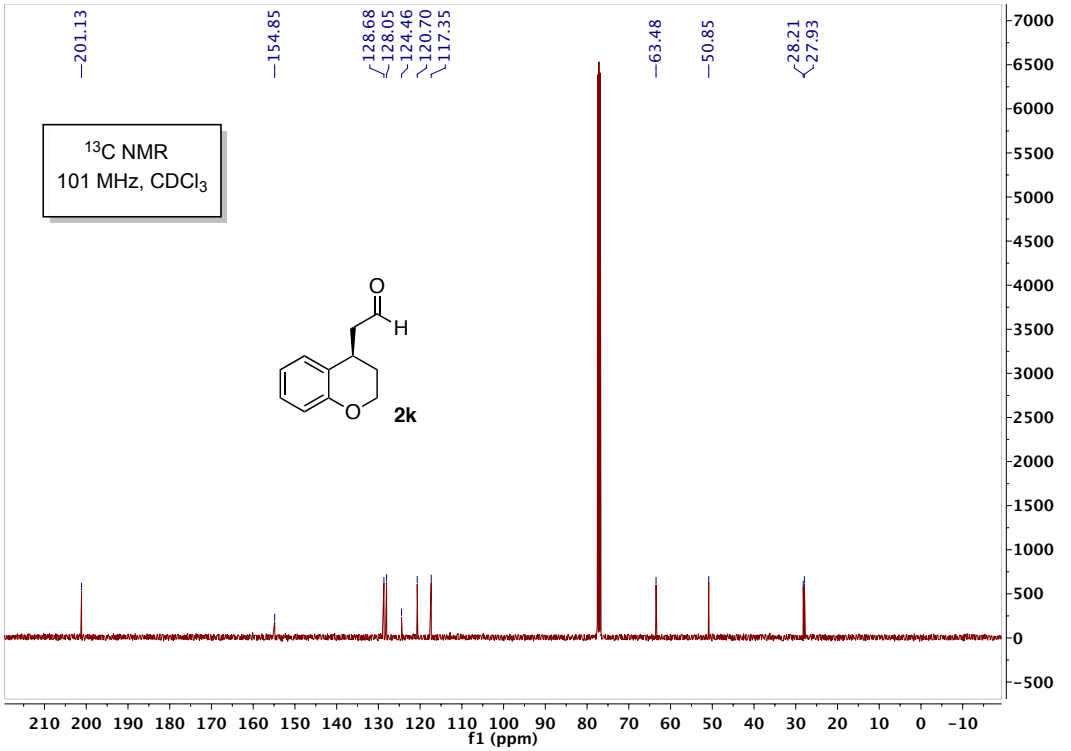
(*S*)-3-cyclopropyl-3-phenylpropan-1-ol (2j-ol)



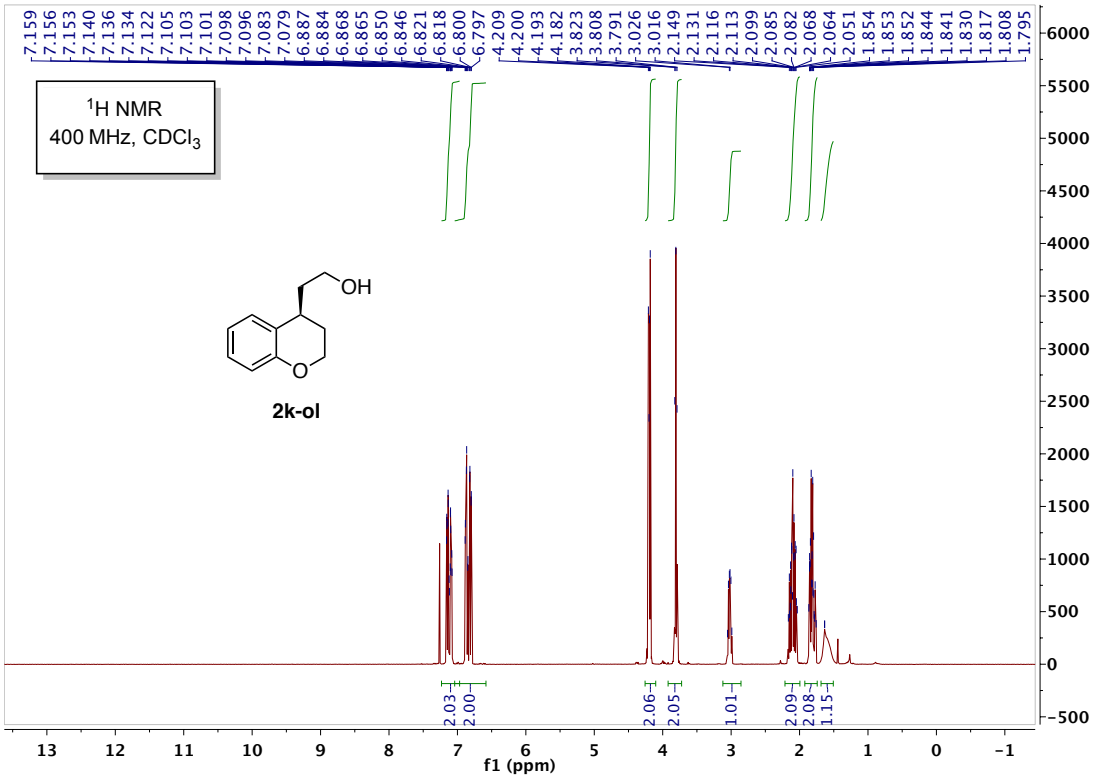


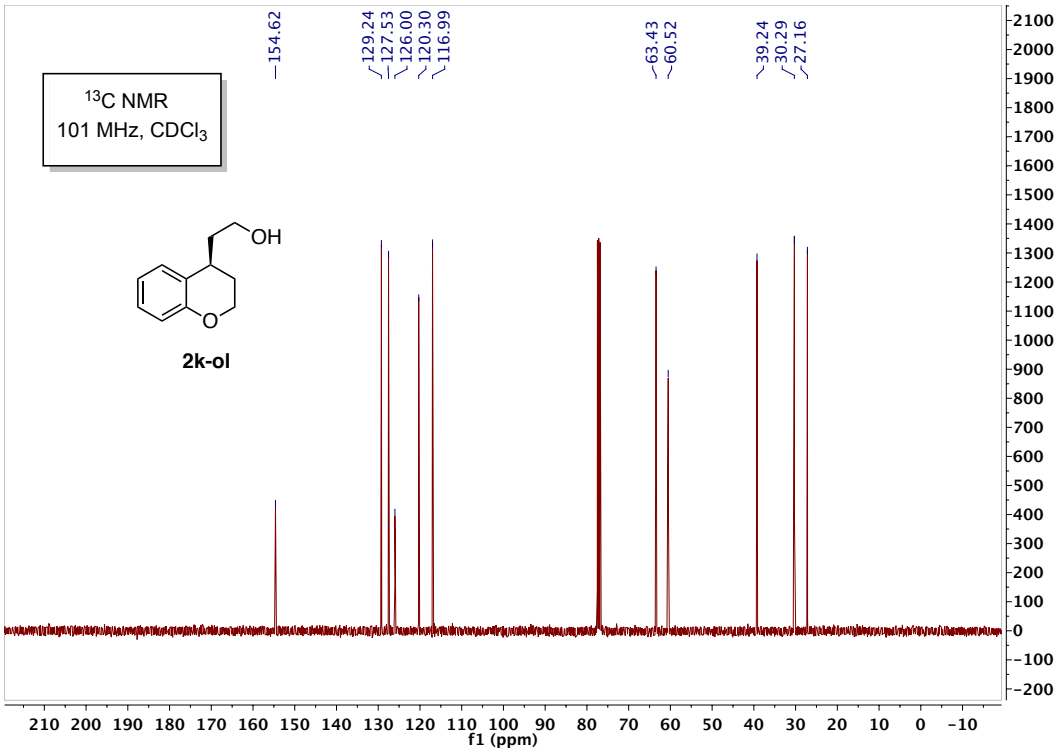
(*R*)-2-(chroman-4-yl)acetaldehyde (2k)



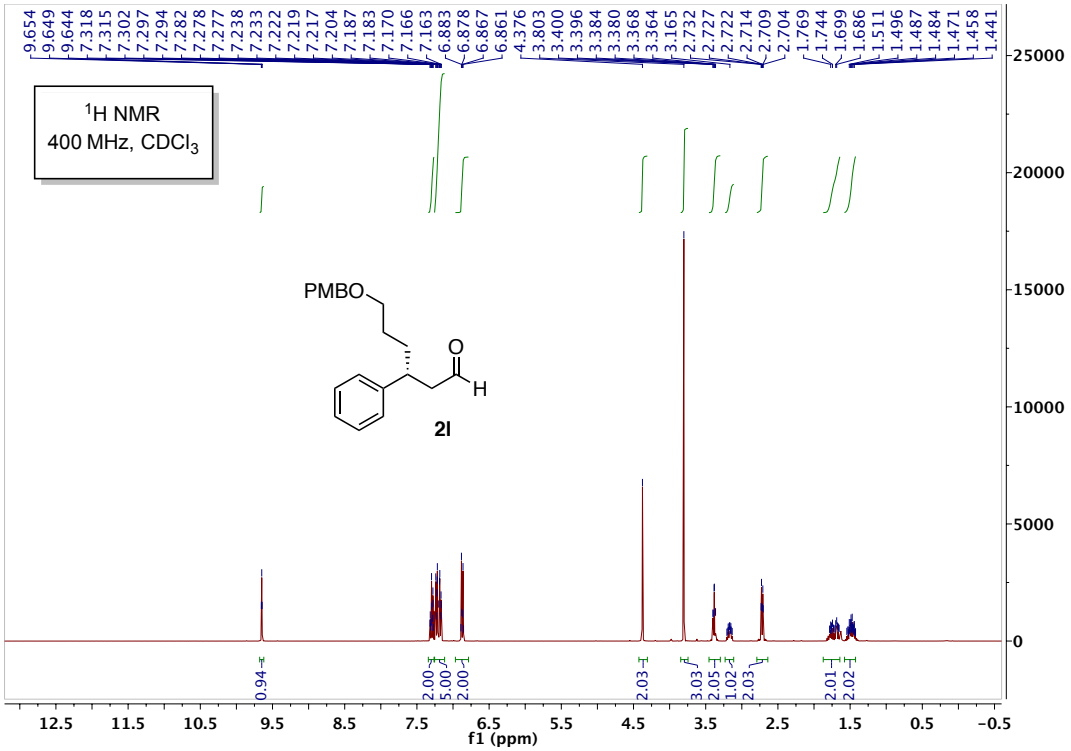


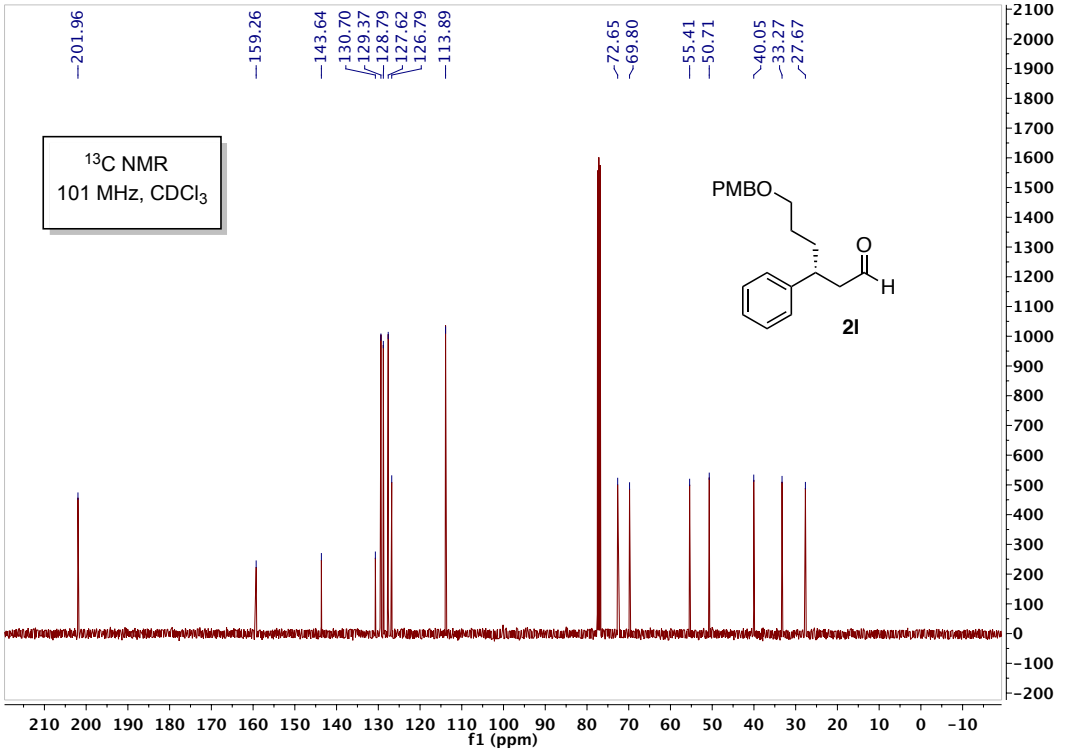
(*S*)-2-(chroman-4-yl)ethan-1-ol (2k-ol)



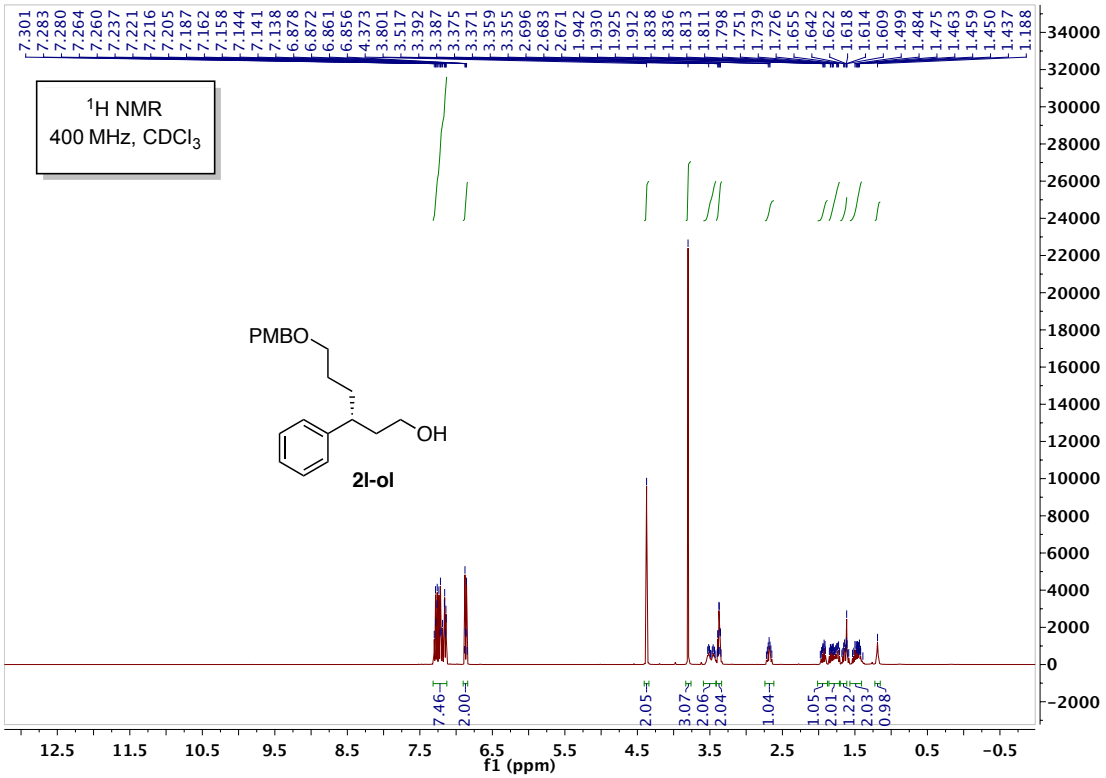


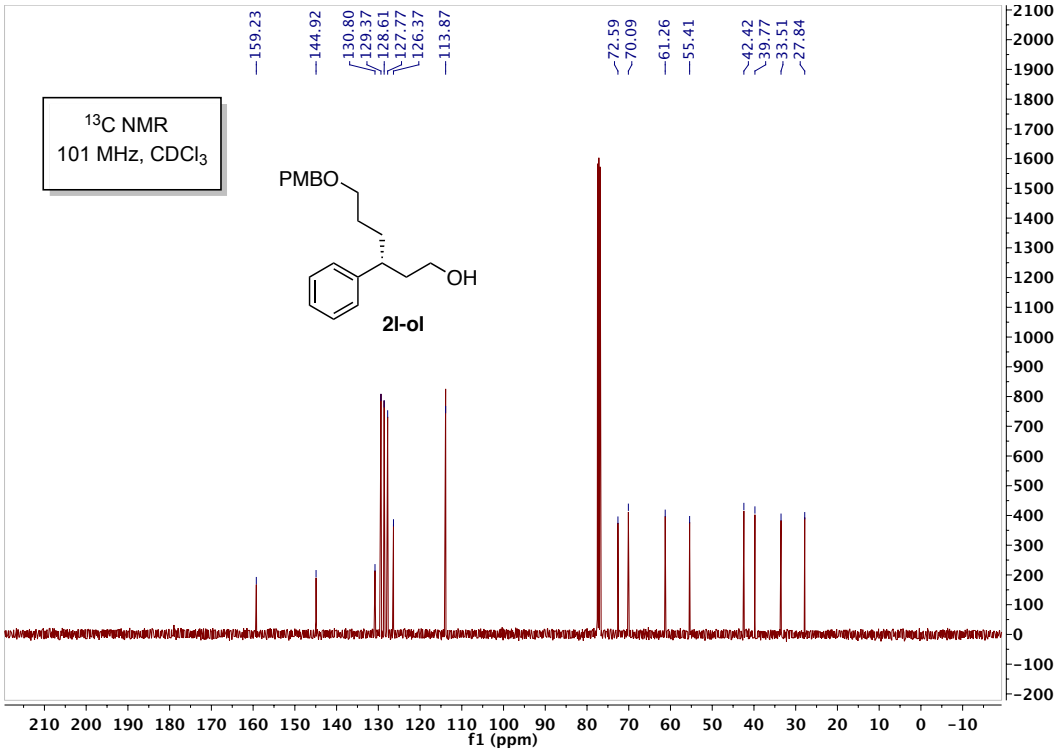
(*R*)-6-((4-methoxybenzyl)oxy)-3-phenylhexanal (2l)



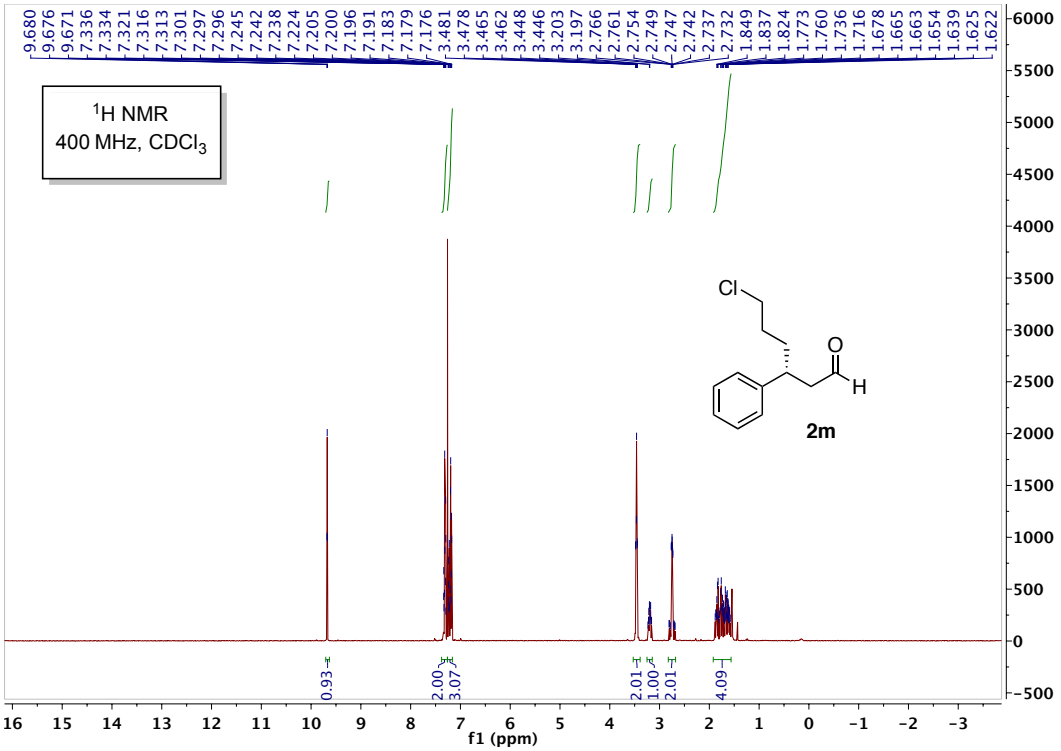


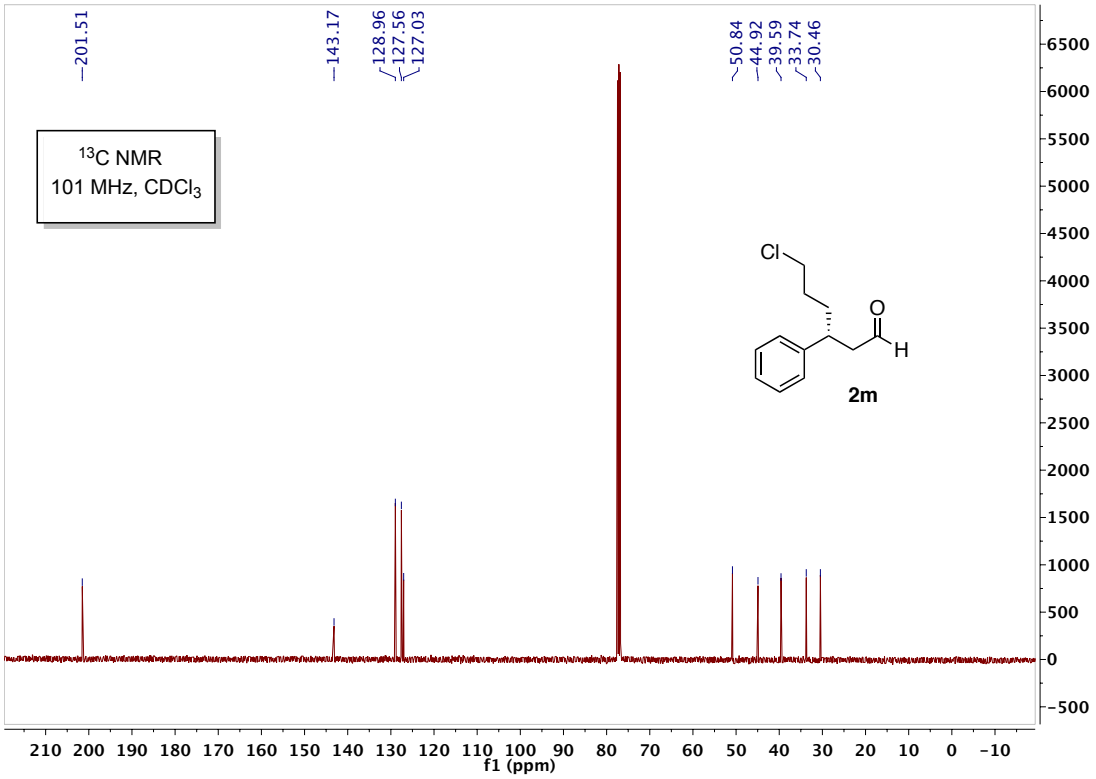
(*R*)-6-((4-methoxybenzyl)oxy)-3-phenylhexan-1-ol (2l-ol)



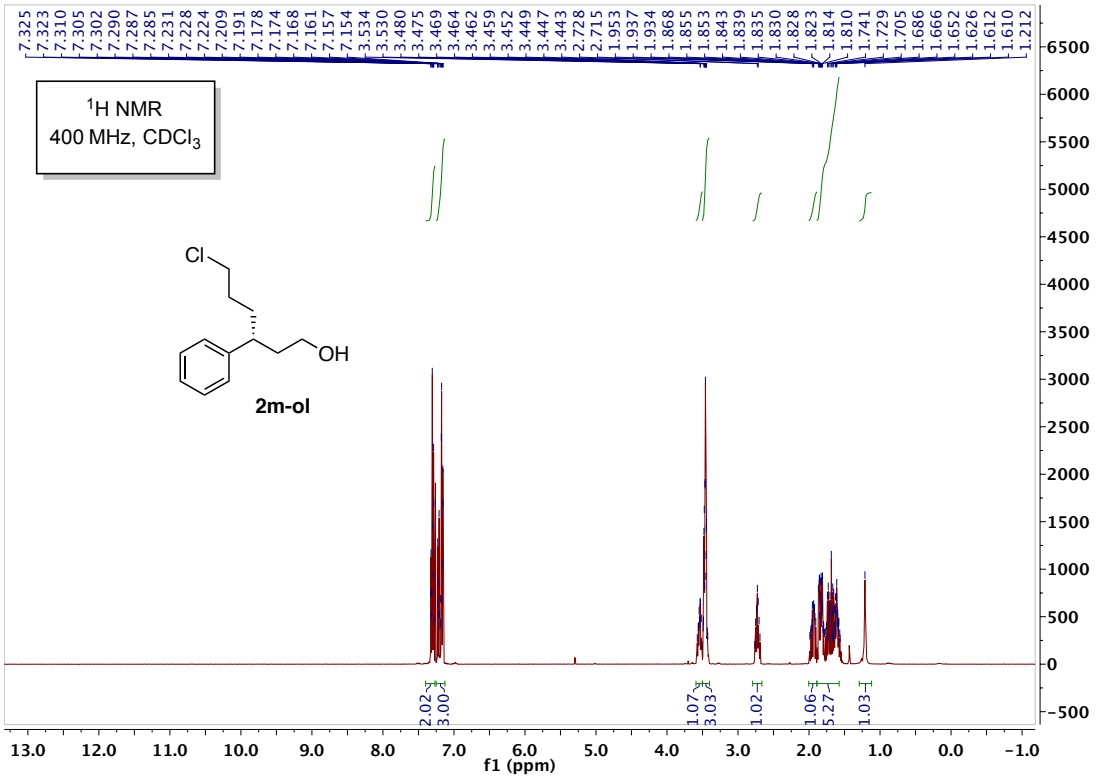


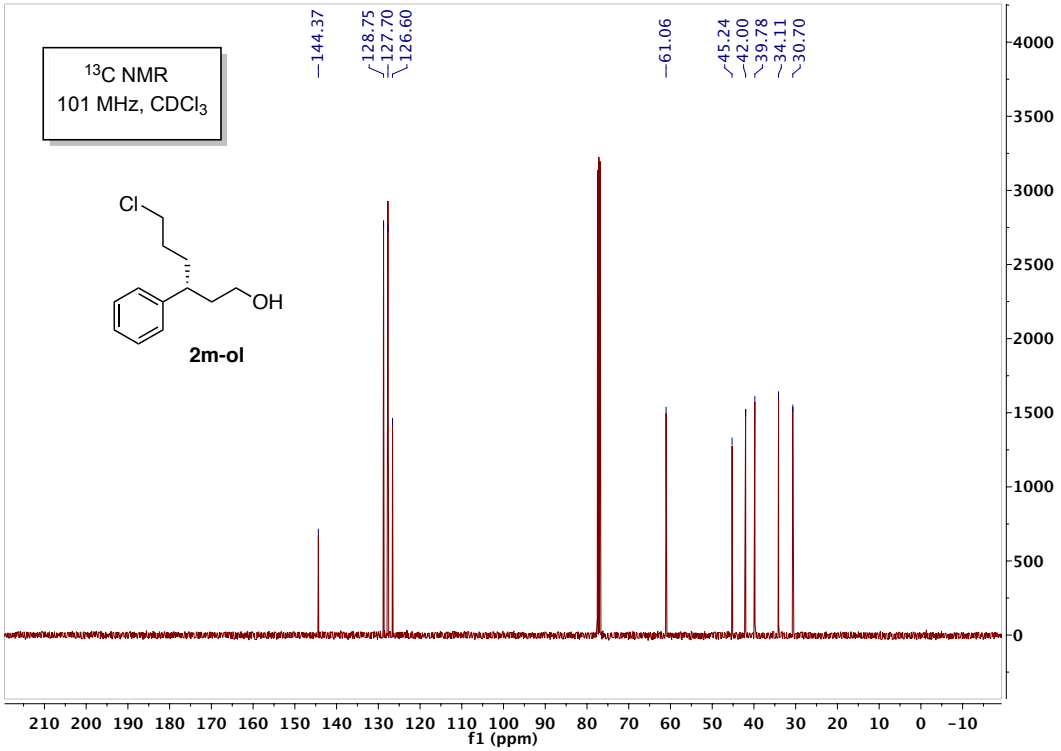
(*R*)-6-chloro-3-phenylhexanal (2m)



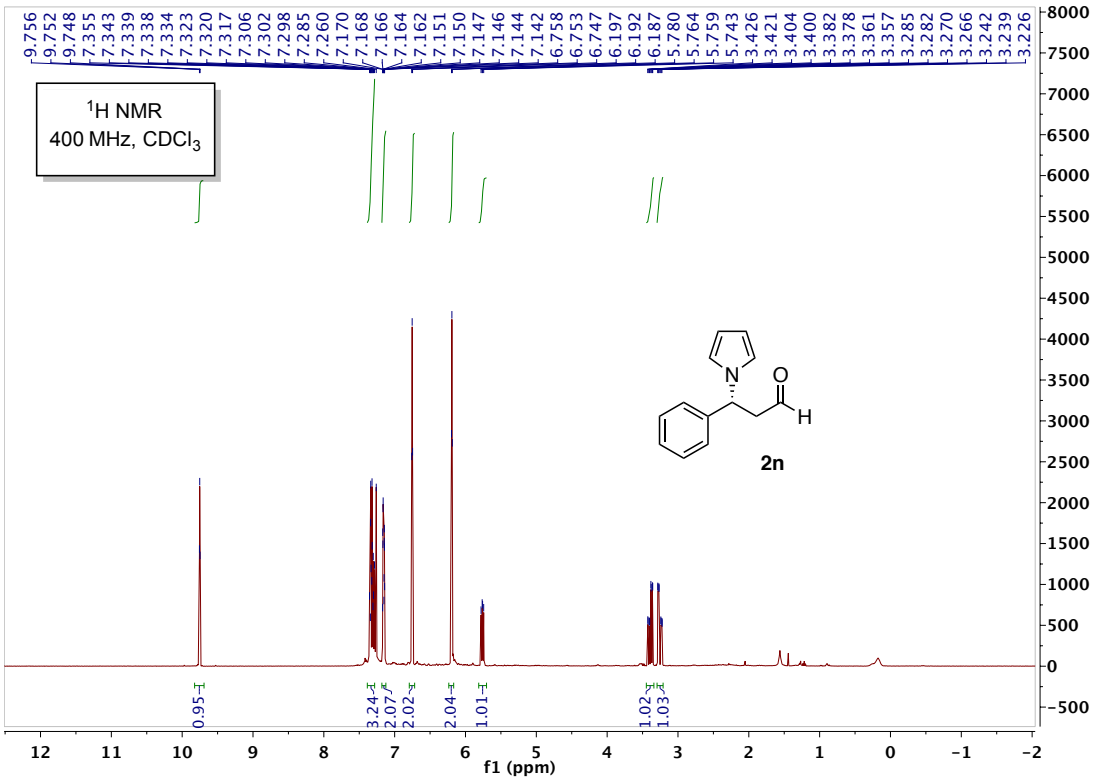


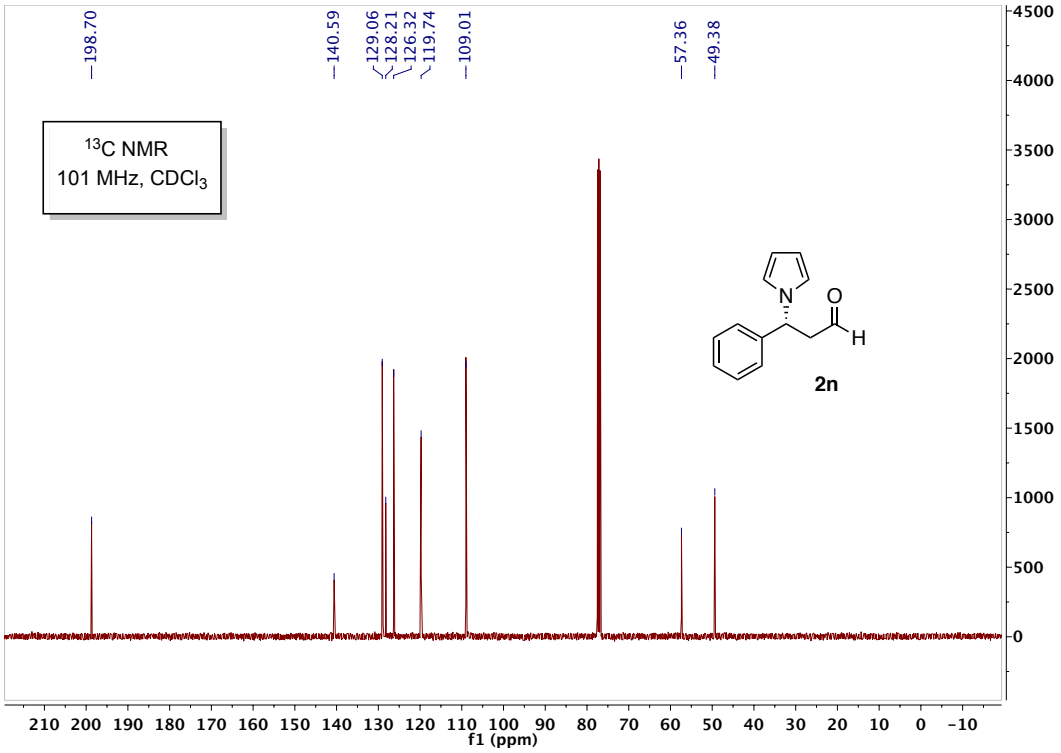
(*R*)-6-chloro-3-phenylhexan-1-ol (2m-ol)



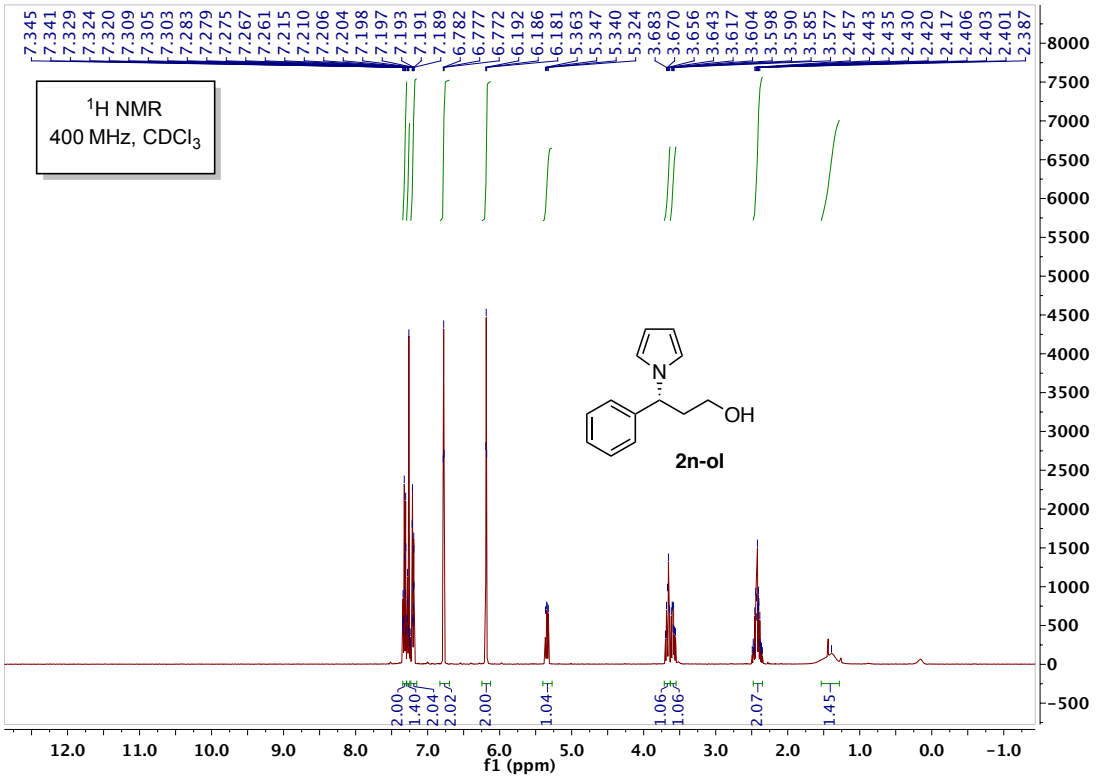


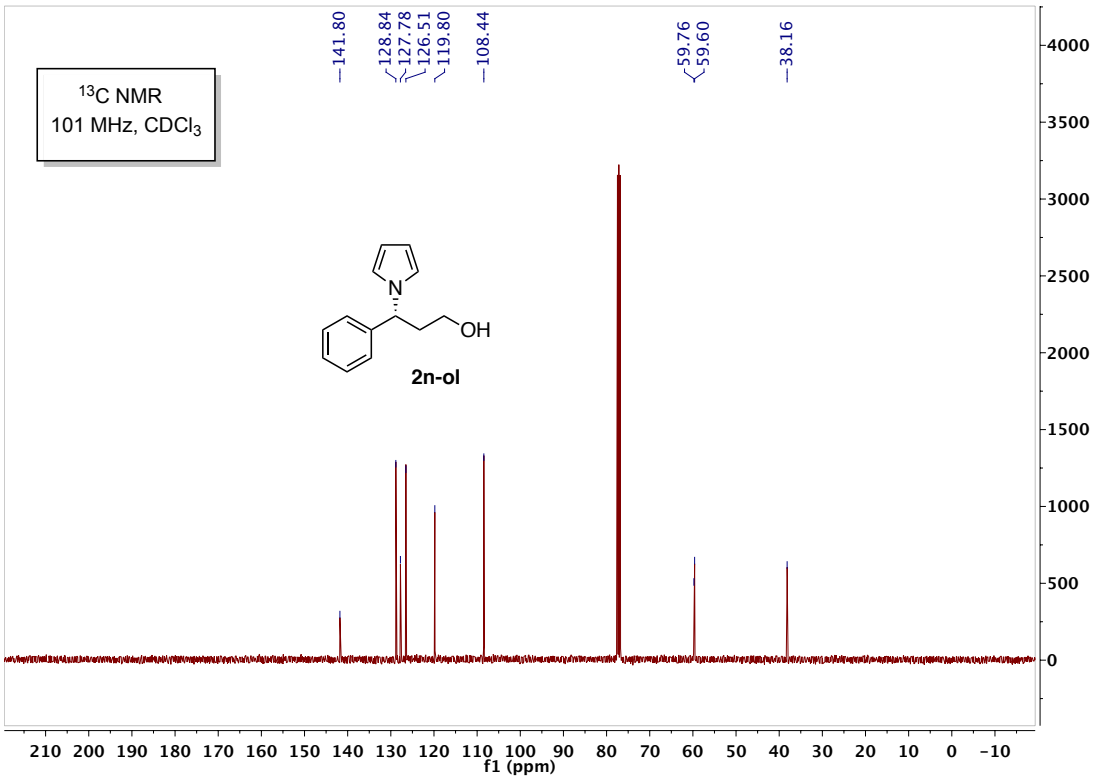
(*R*)-3-phenyl-3-(1*H*-pyrrol-1-yl)propanal (2n)



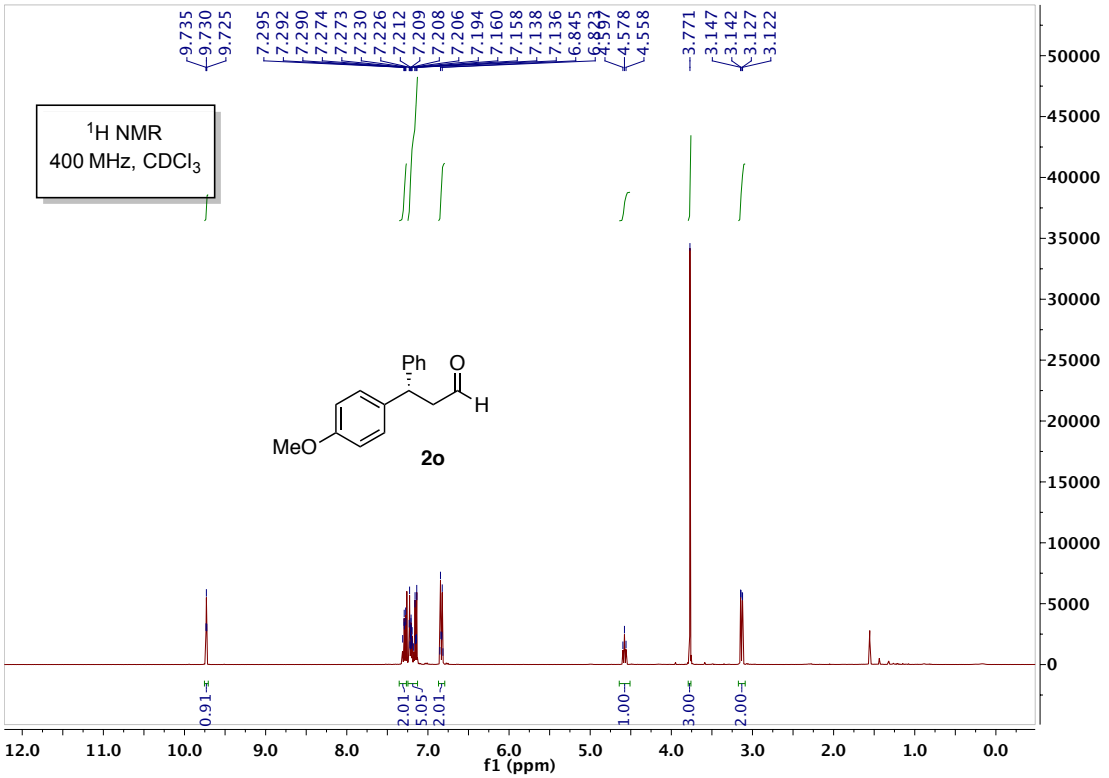


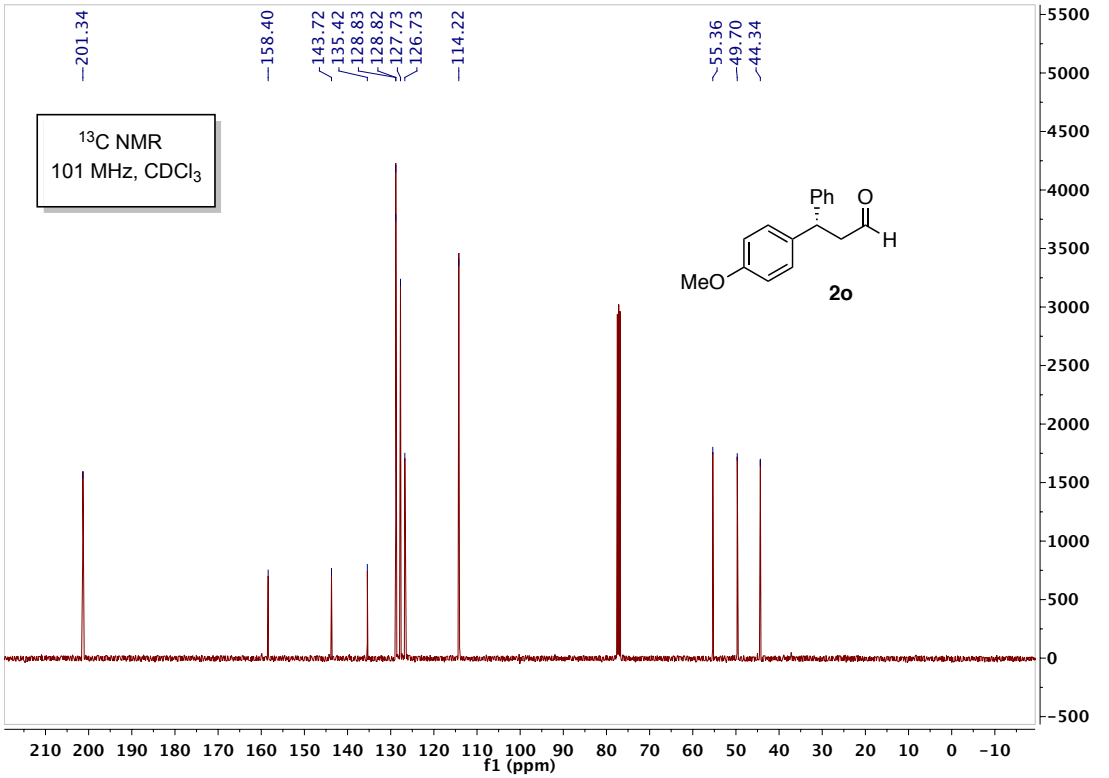
(*R*)-3-phenyl-3-(1*H*-pyrrol-1-yl)propan-1-ol (2n-ol)



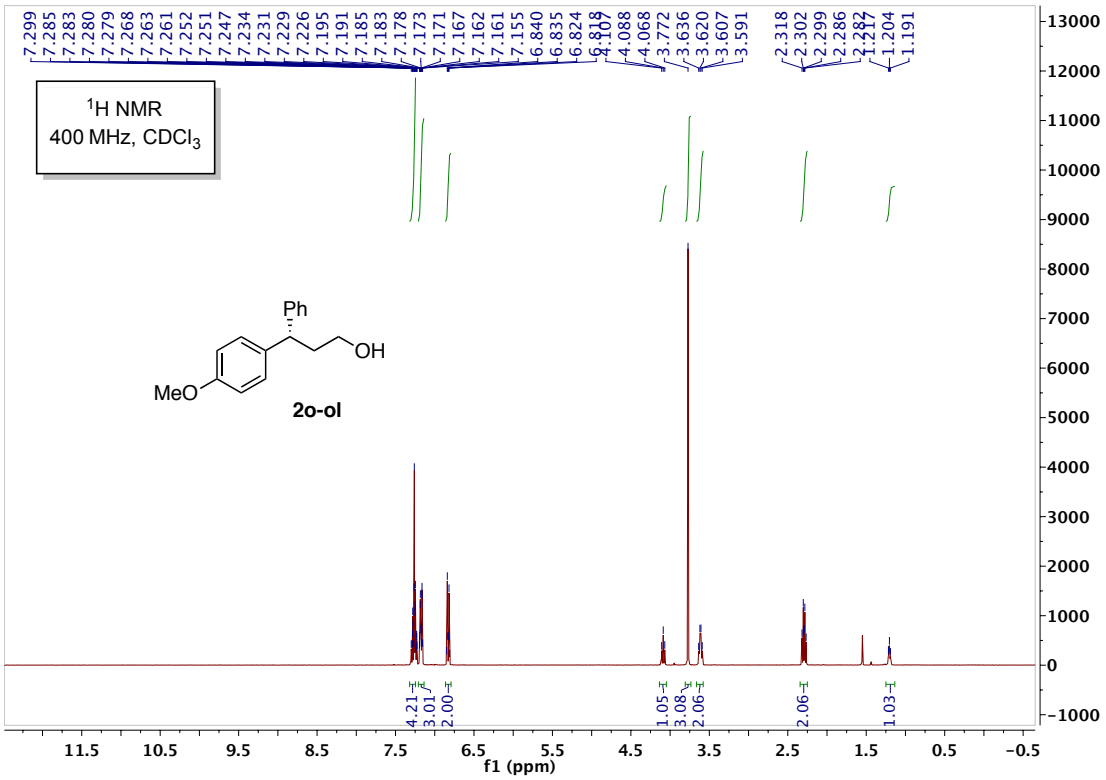


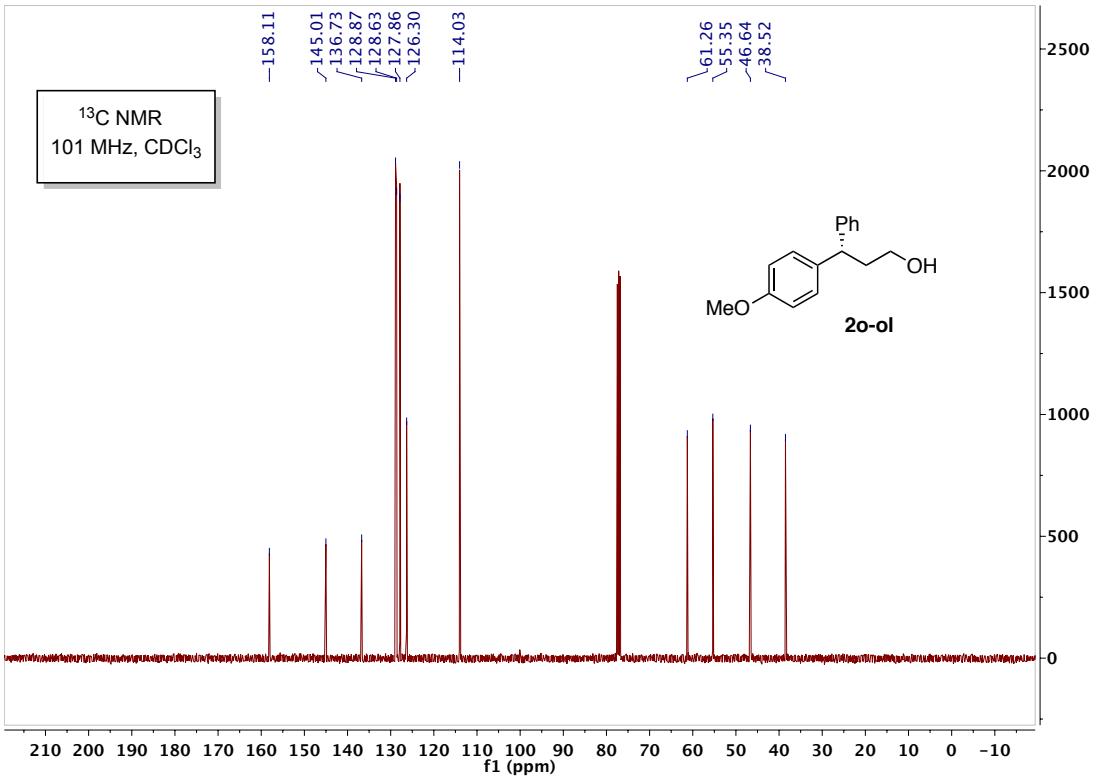
(*S*)-3-(4-methoxyphenyl)-3-phenylpropanal (2o)



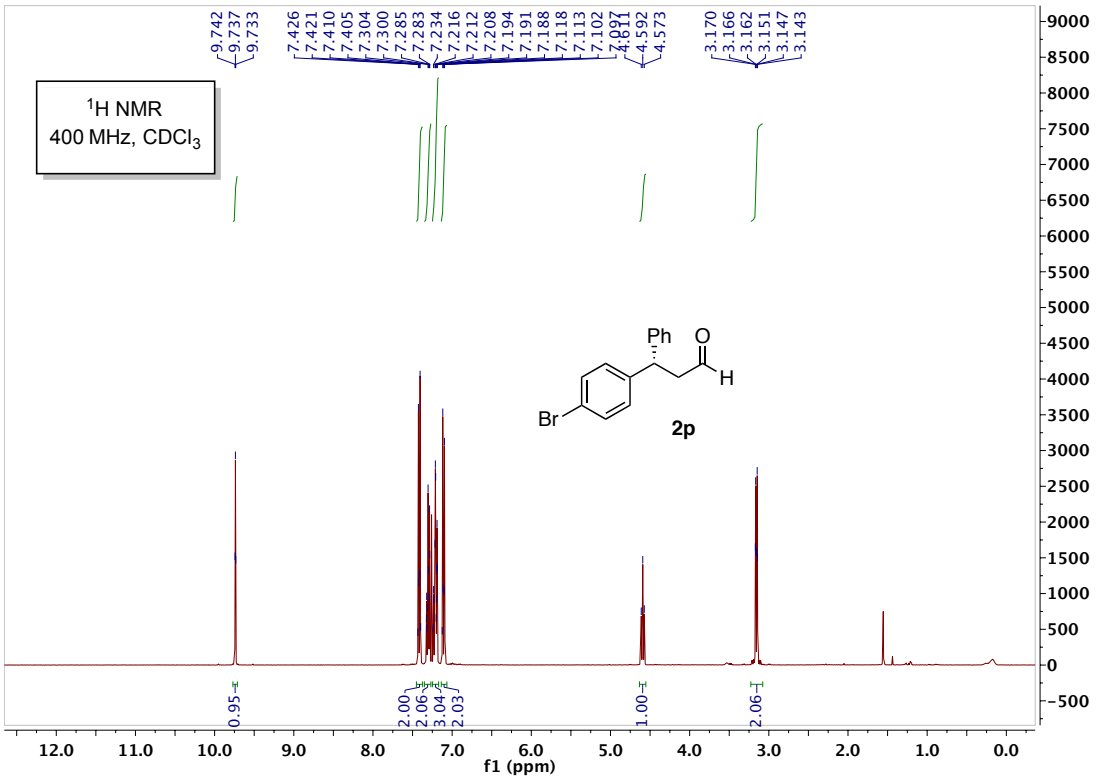


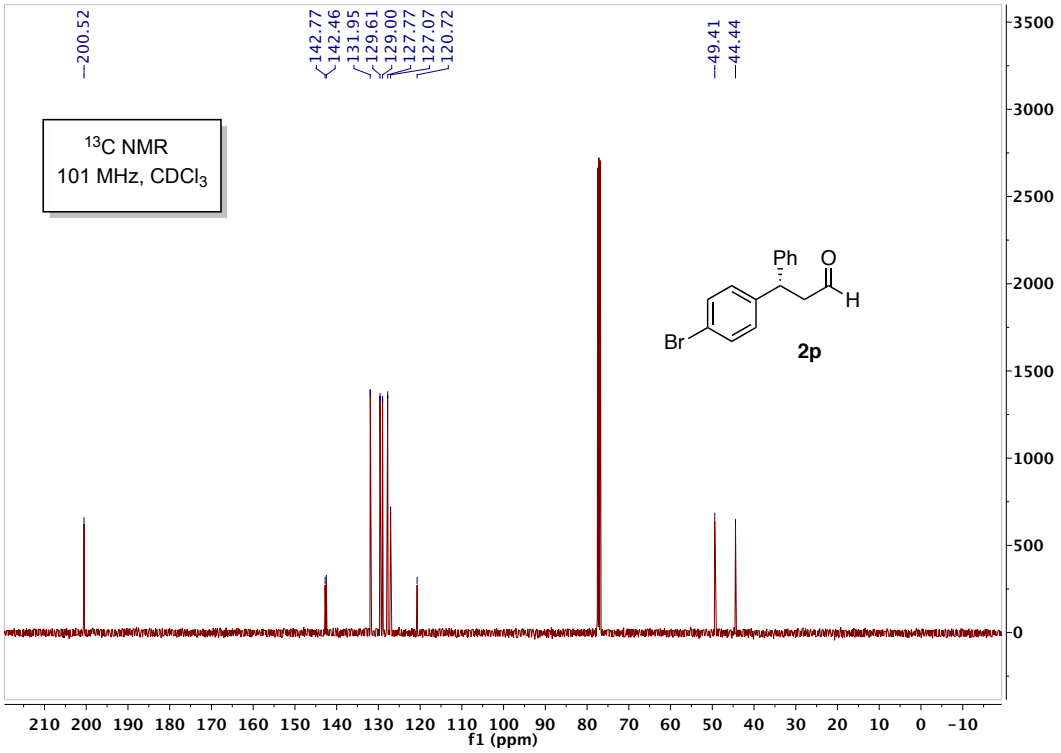
(*S*)-3-(4-methoxyphenyl)-3-phenylpropan-1-ol (2o-ol)



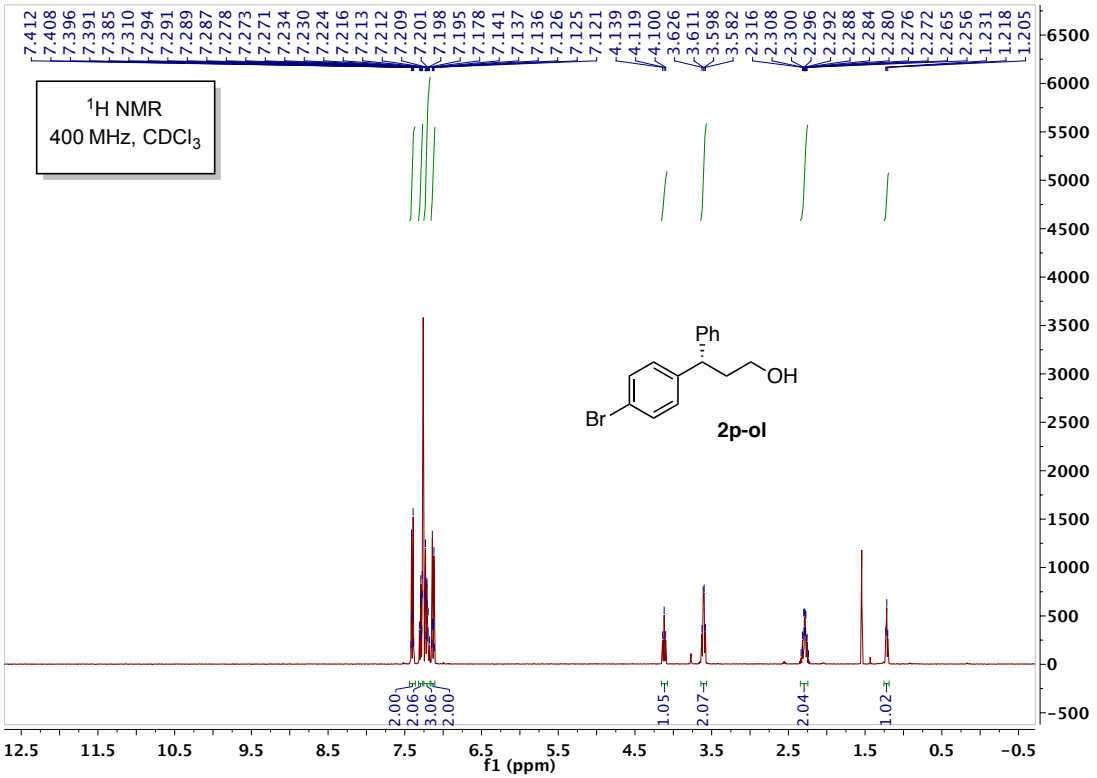


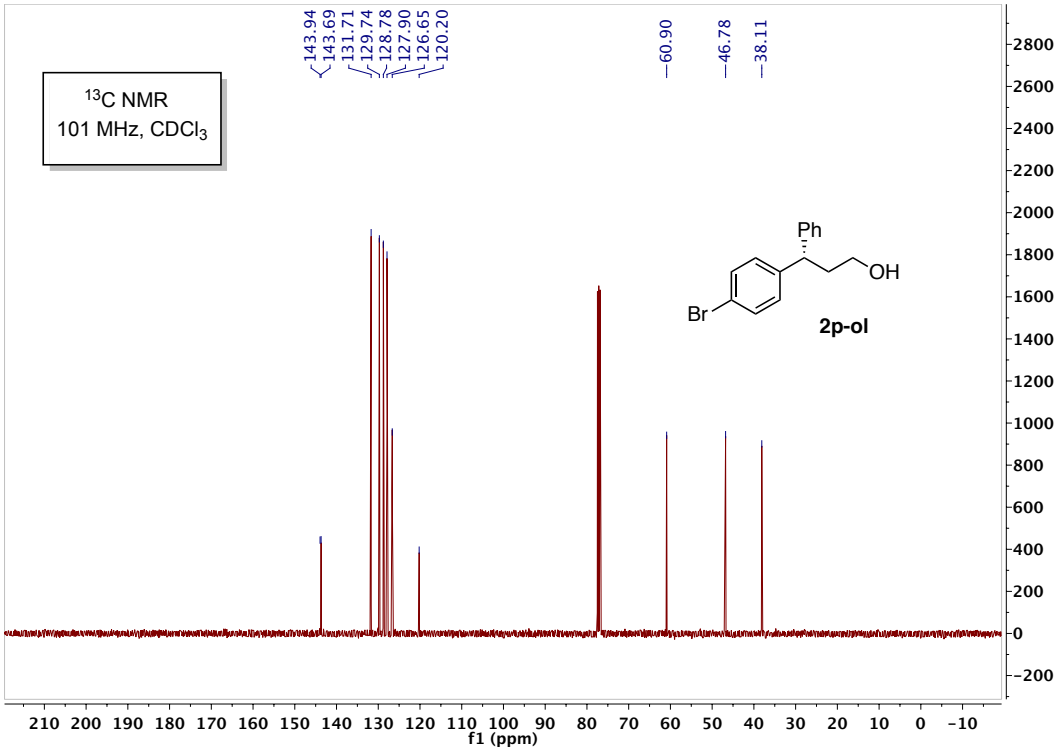
(*S*)-3-(4-bromophenyl)-3-phenylpropanal (2p)



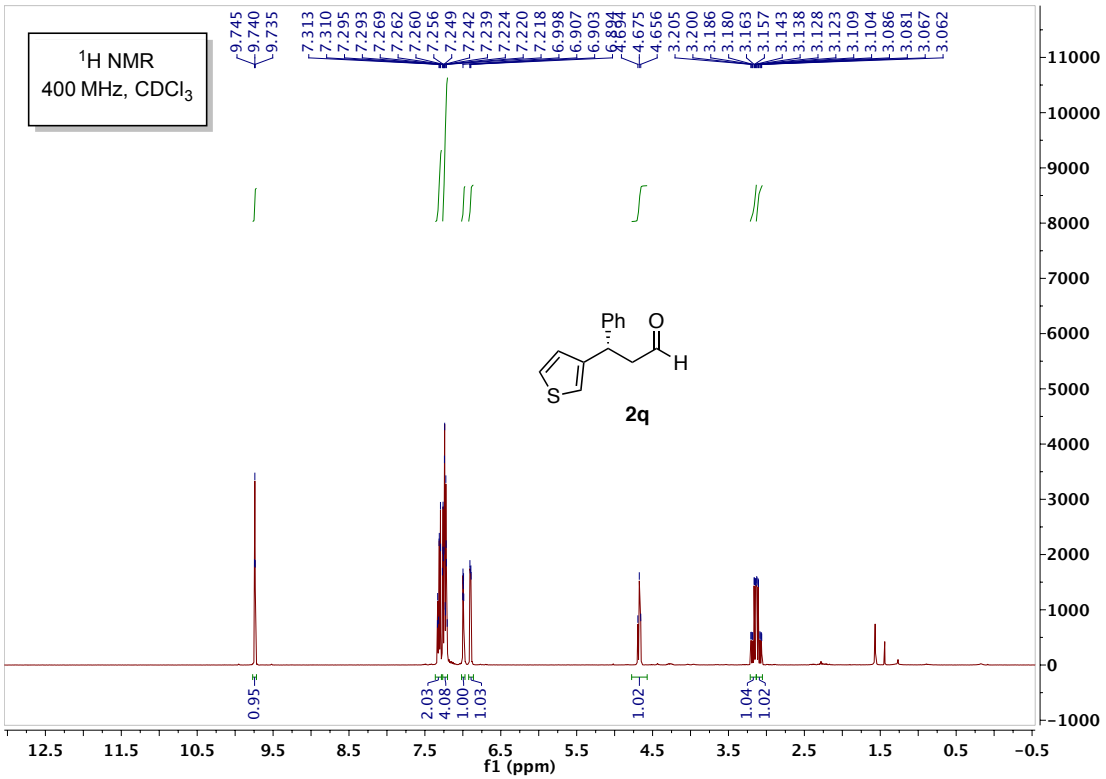


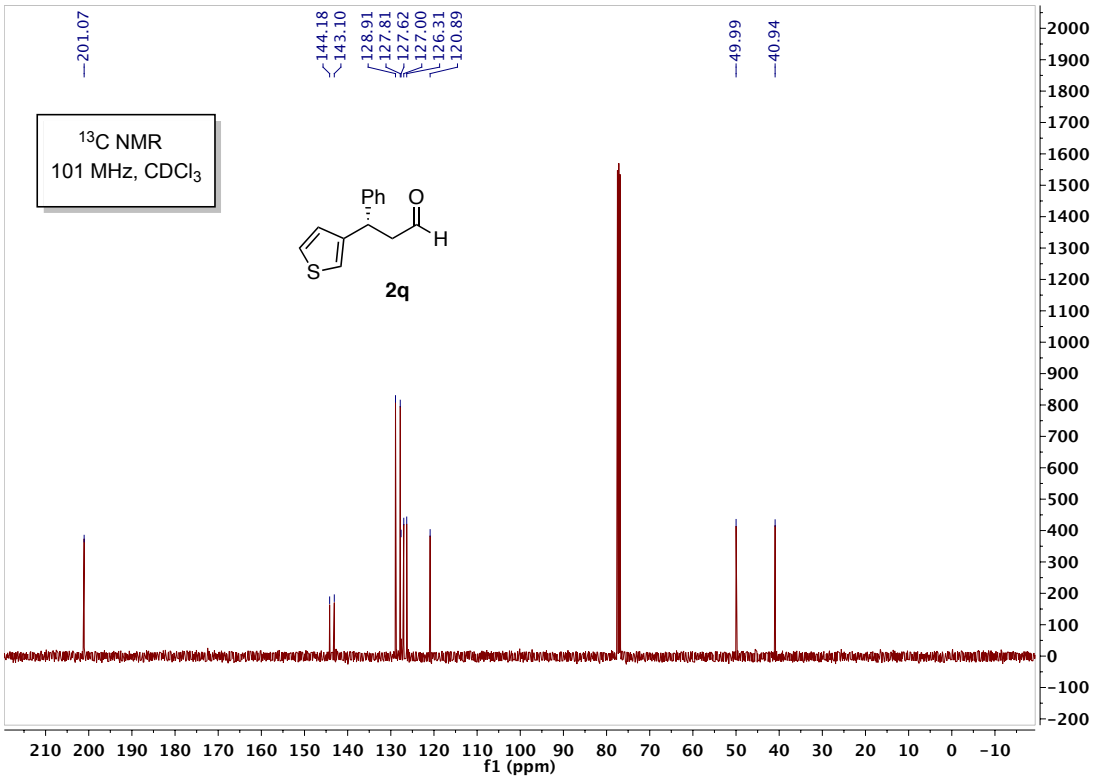
(*S*)-3-(4-bromophenyl)-3-phenylpropan-1-ol (2p-ol)



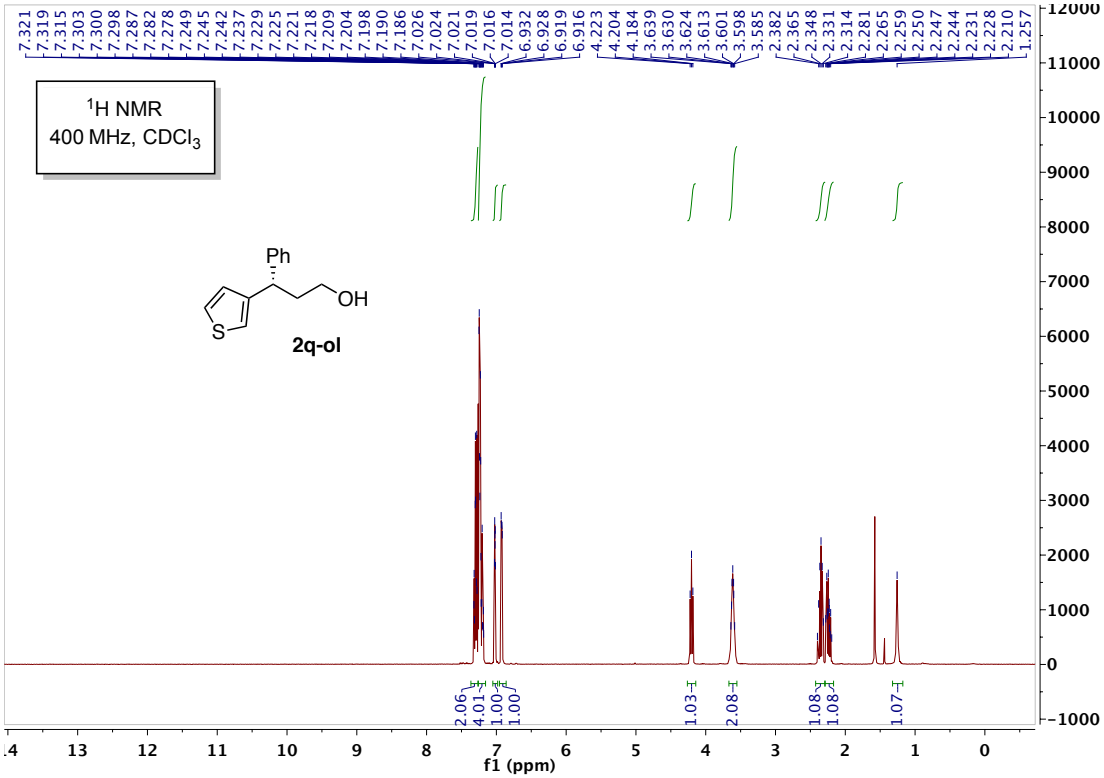


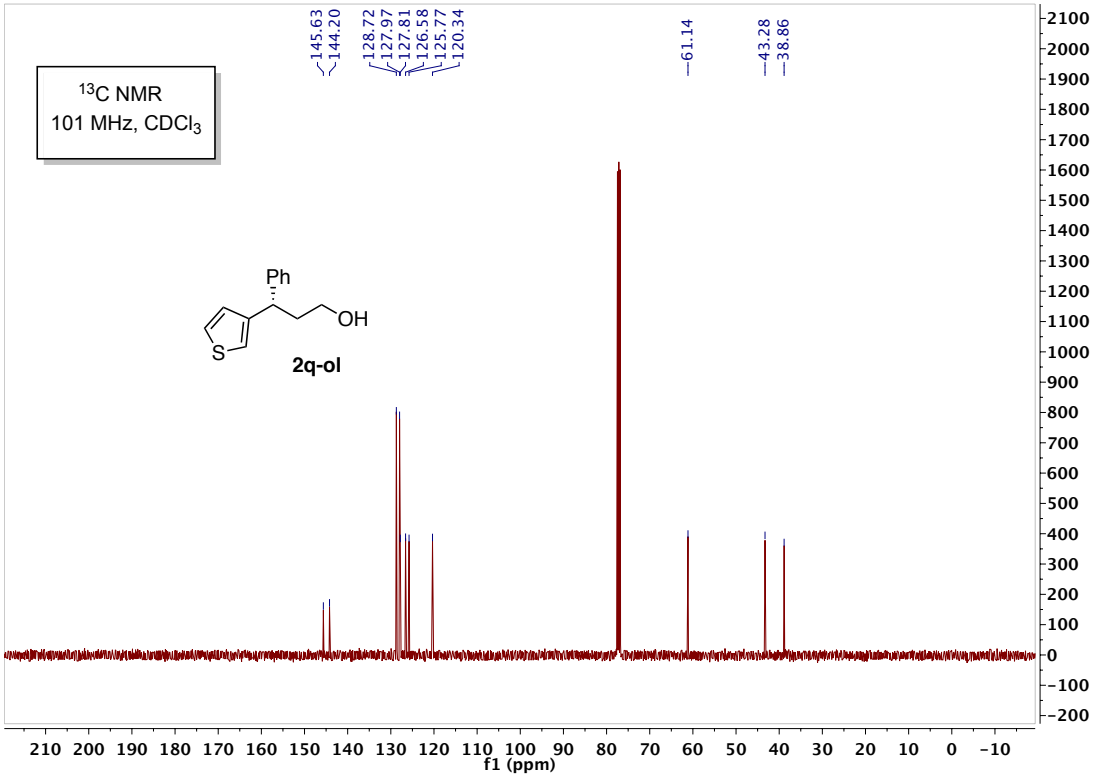
(*S*)-3-phenyl-3-(thiophen-3-yl)propanal (2q)



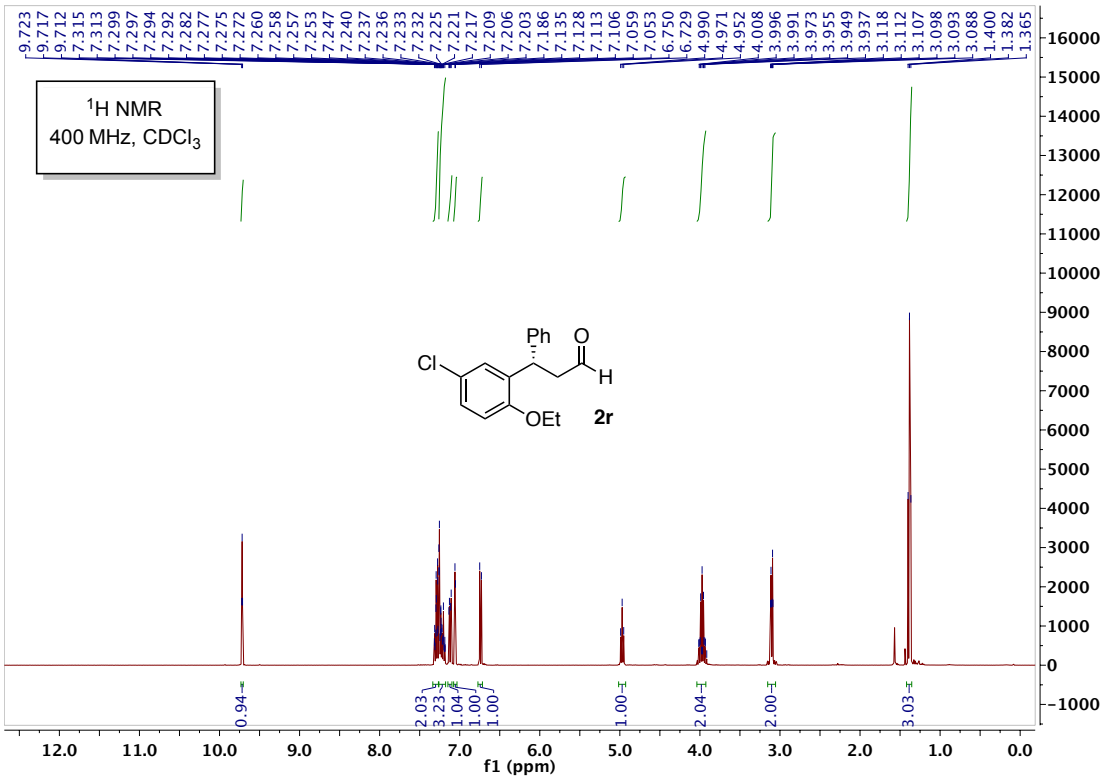


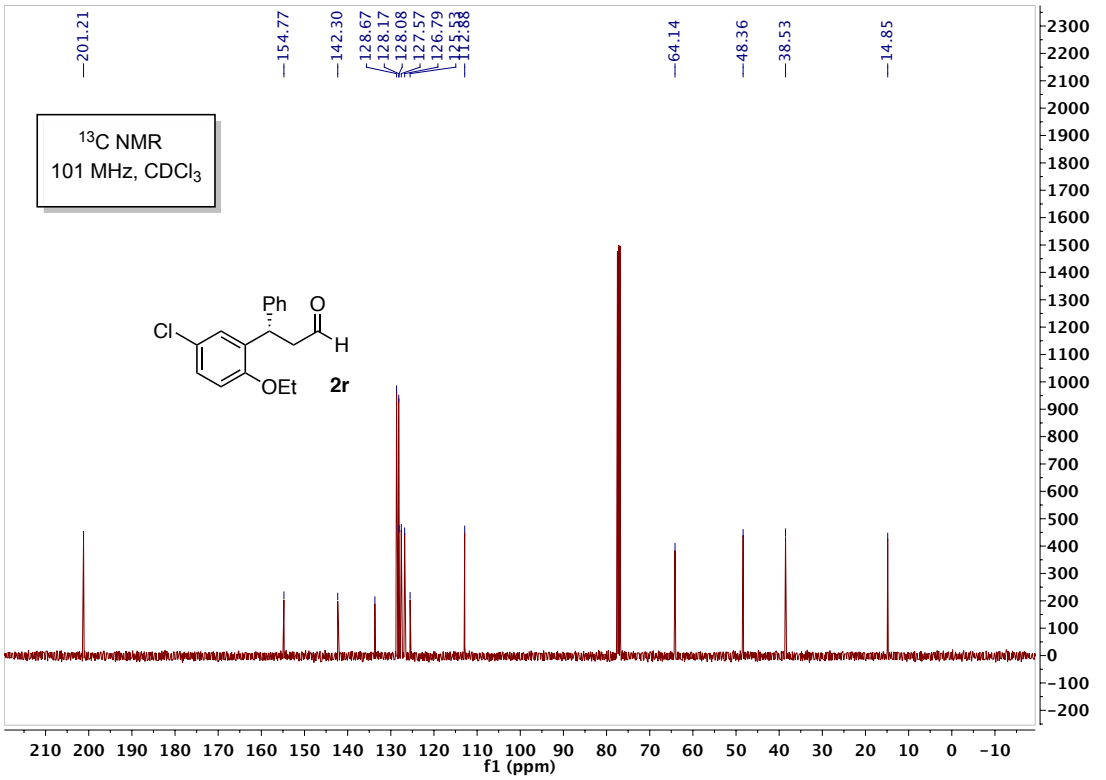
(*S*)-3-phenyl-3-(thiophen-3-yl)propan-1-ol (2q-ol)



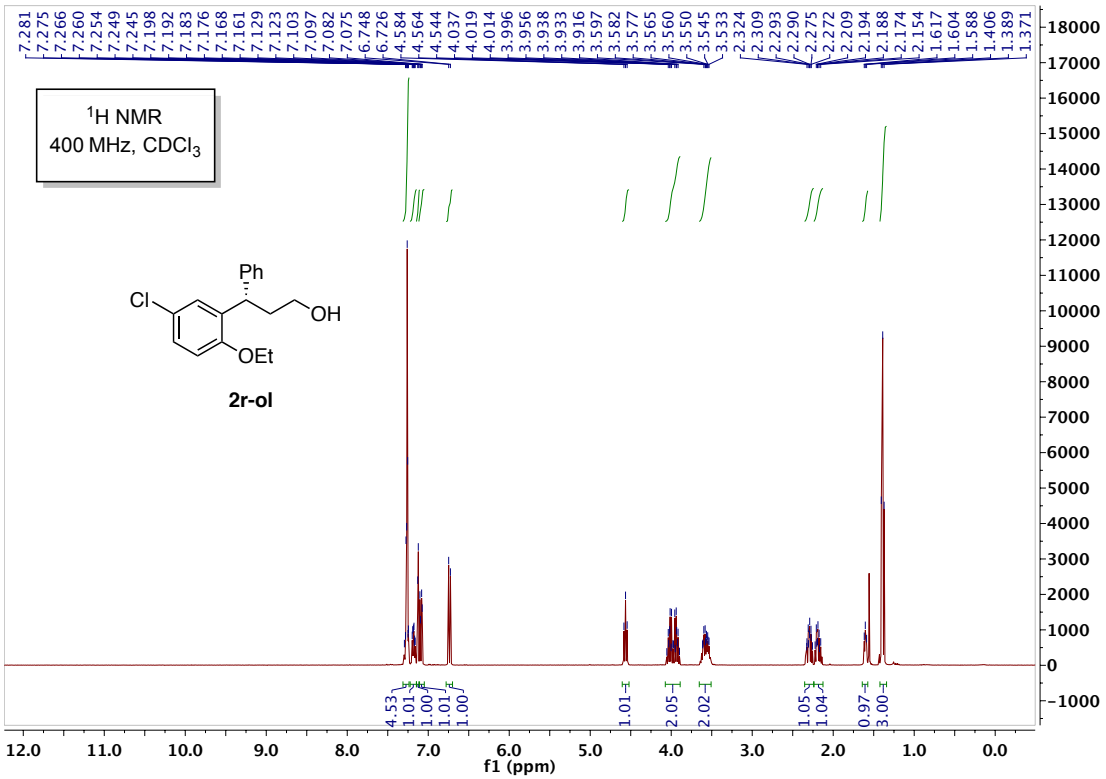


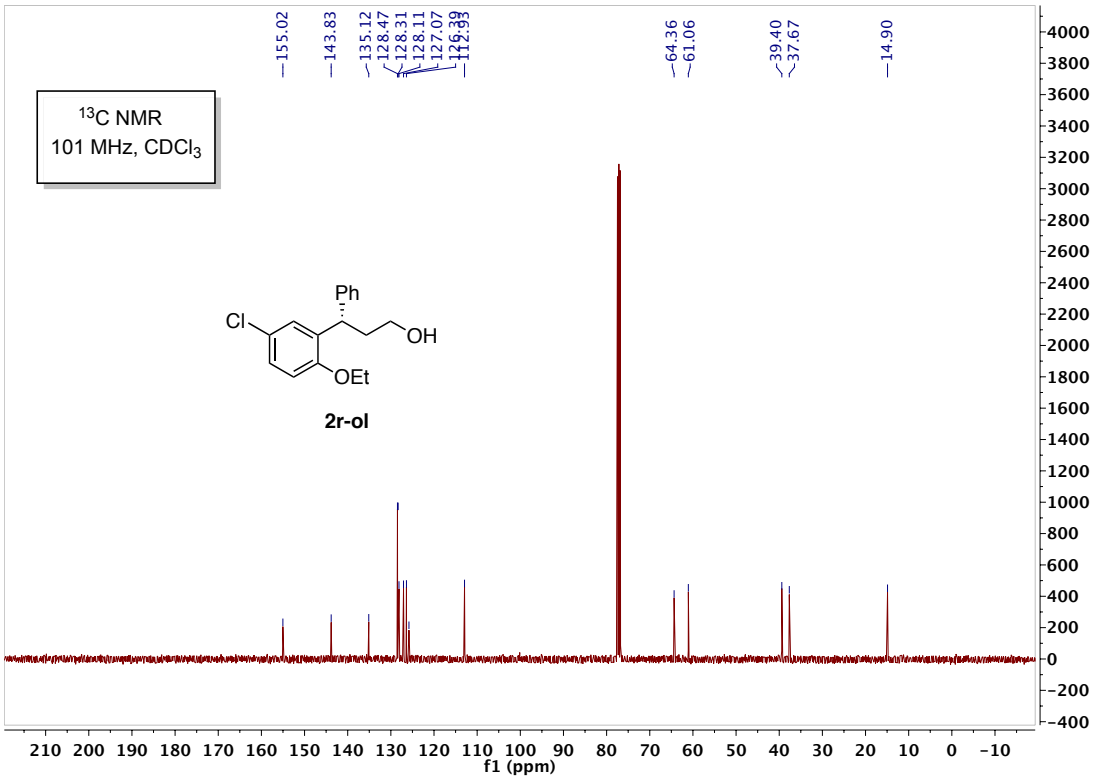
(*S*)-3-(5-chloro-2-ethoxyphenyl)-3-phenylpropanal (2r)



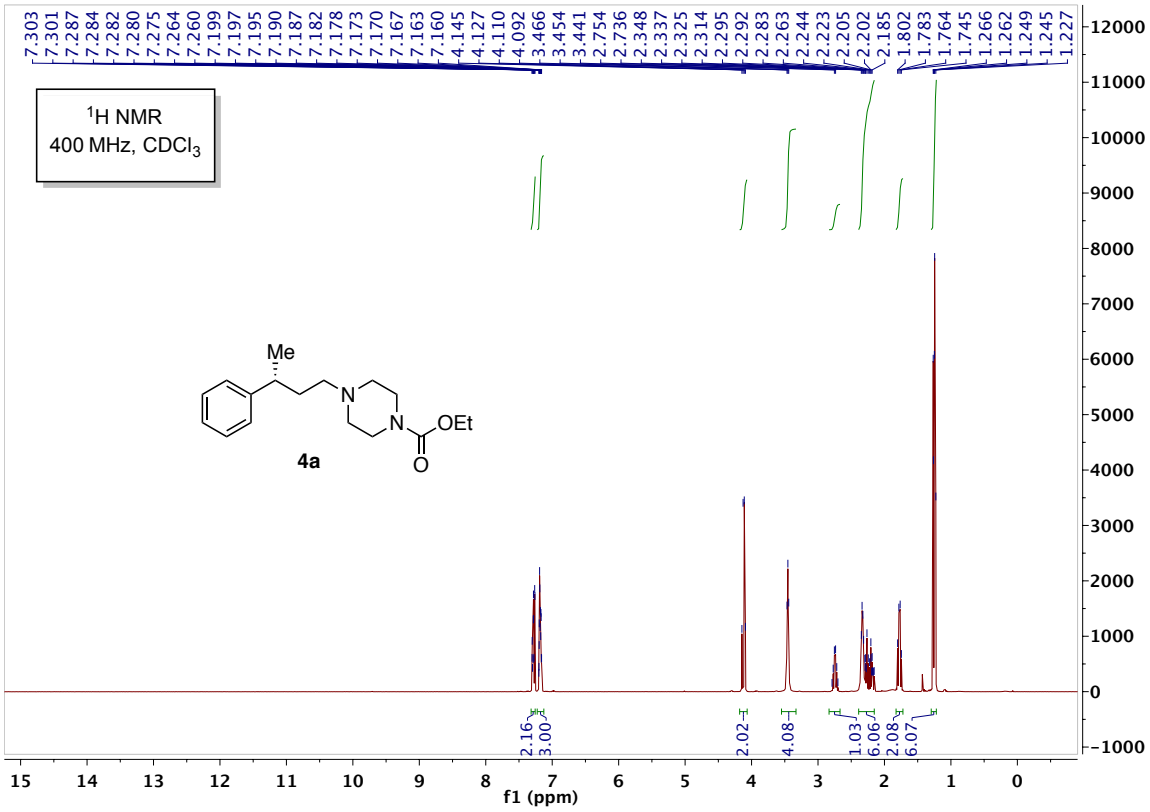


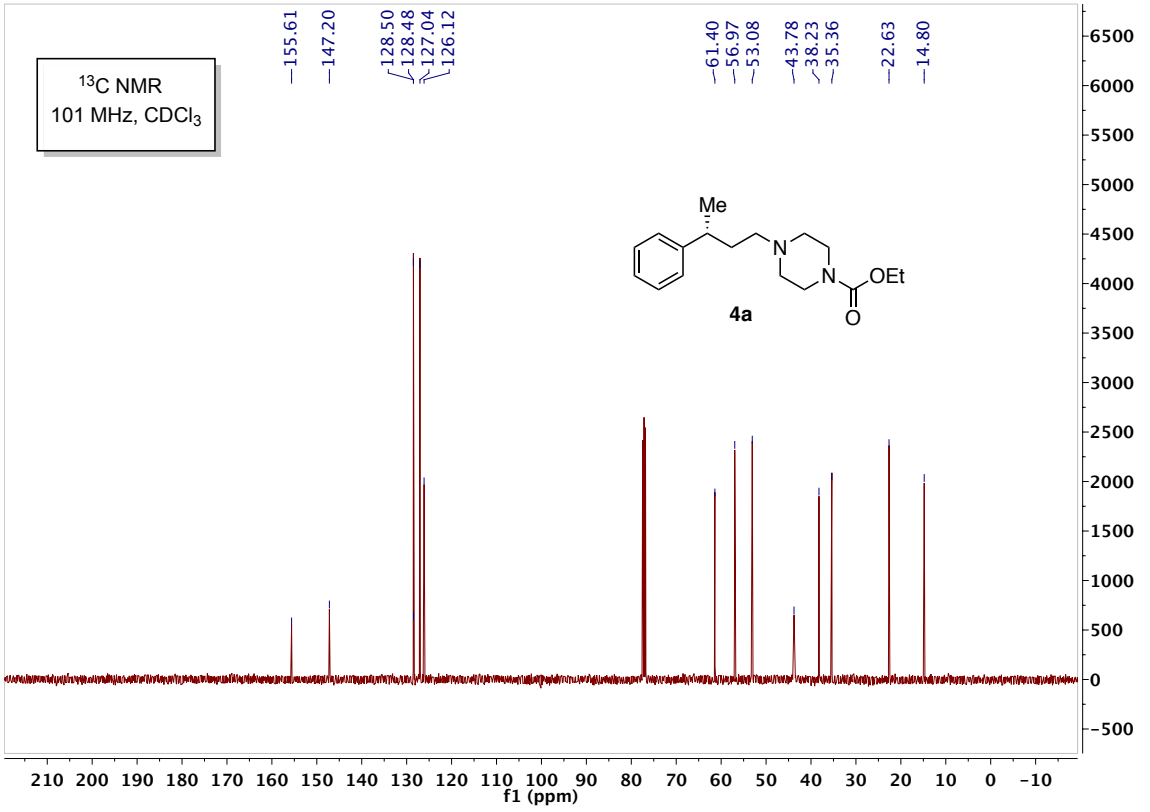
(*S*)-3-(5-chloro-2-ethoxyphenyl)-3-phenylpropan-1-ol (2r-ol)



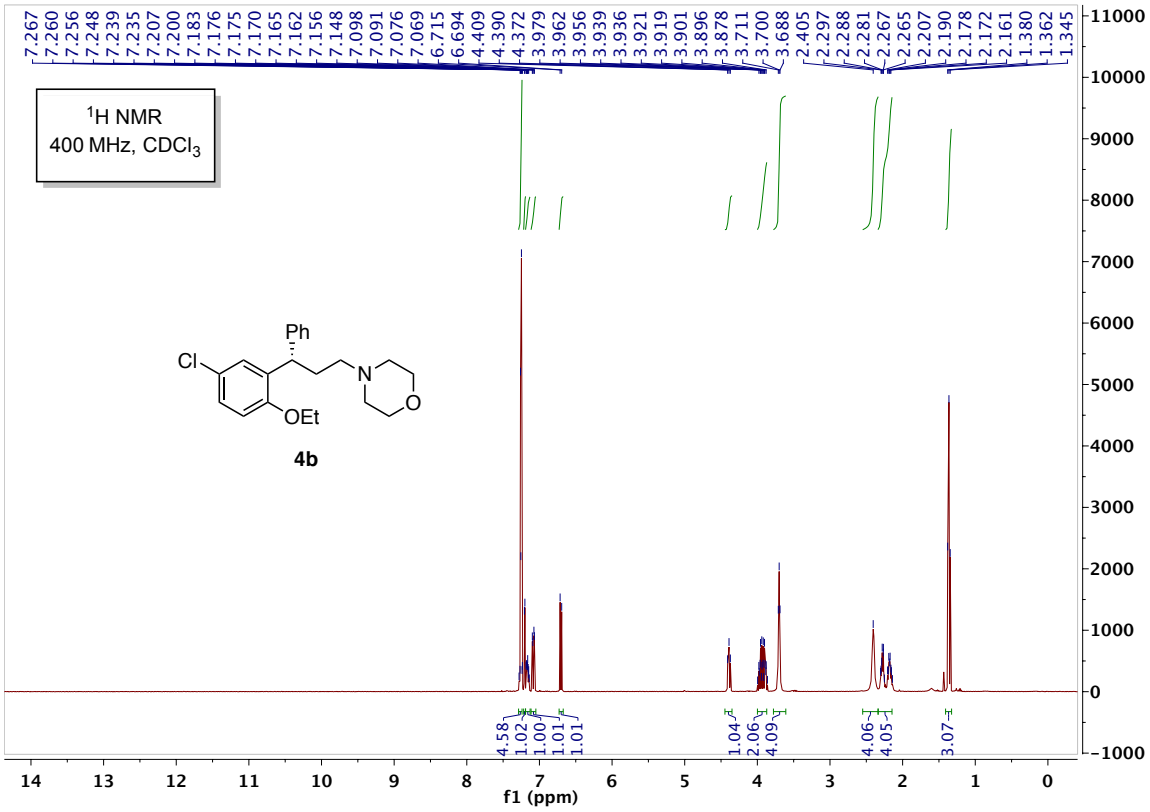


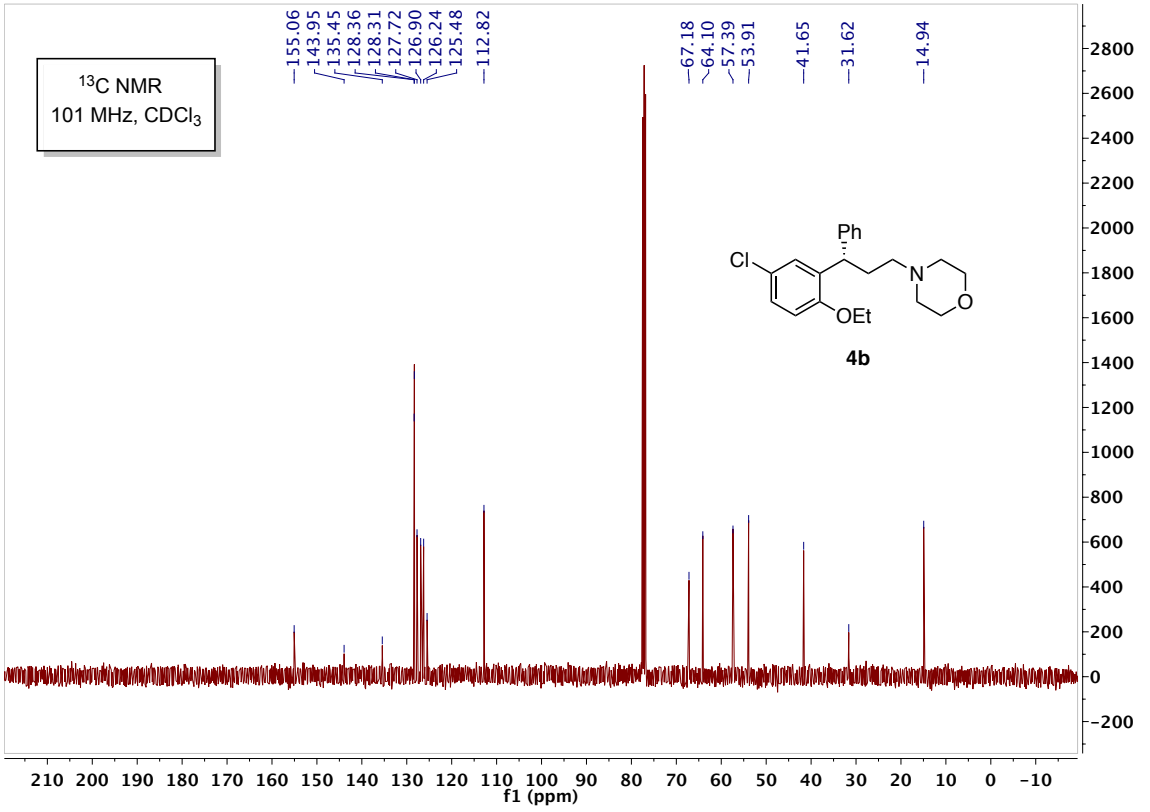
Ethyl (*R*)-4-(3-phenylbutyl)piperazine-1-carboxylate (4a)



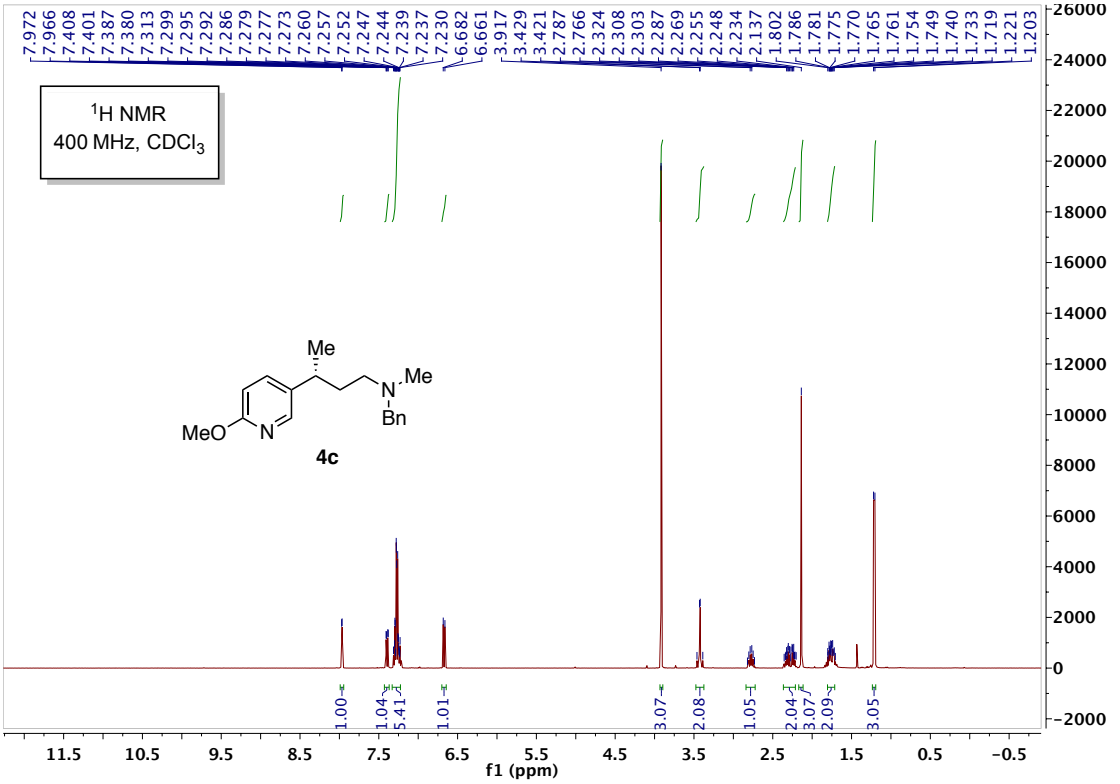


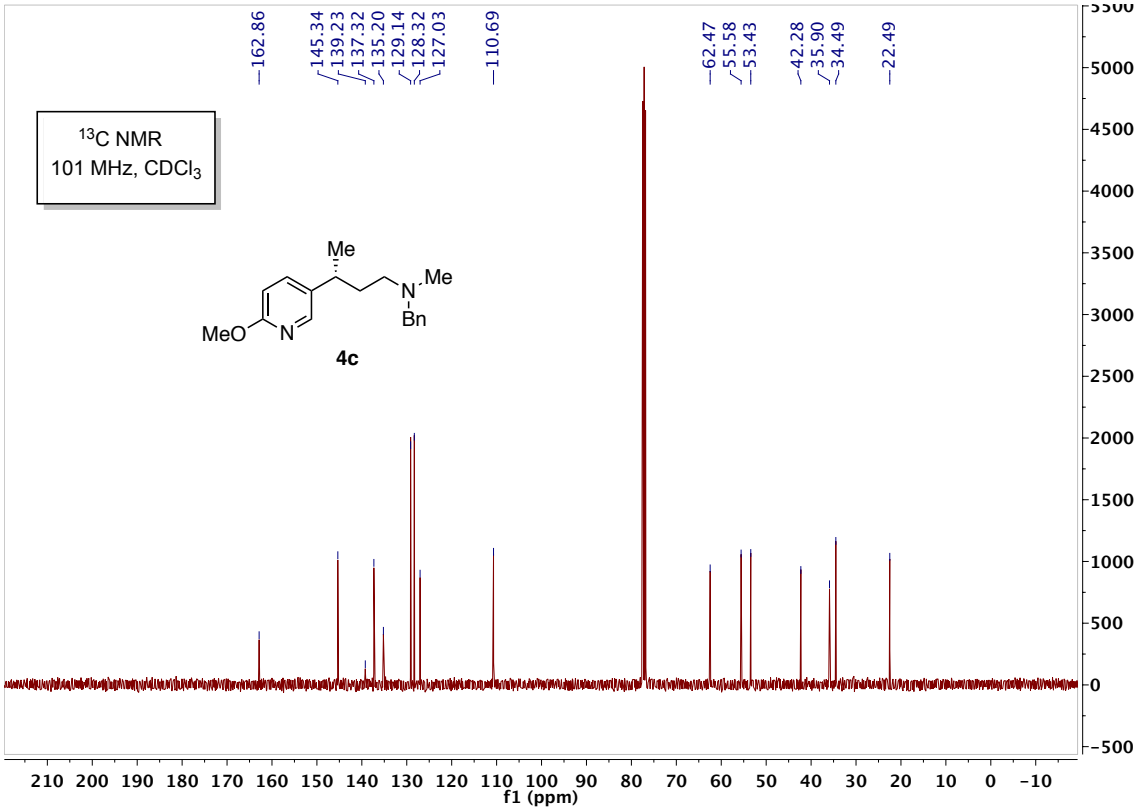
(*S*)-4-(3-(5-chloro-2-ethoxyphenyl)-3-phenylpropyl)morpholine (4b)



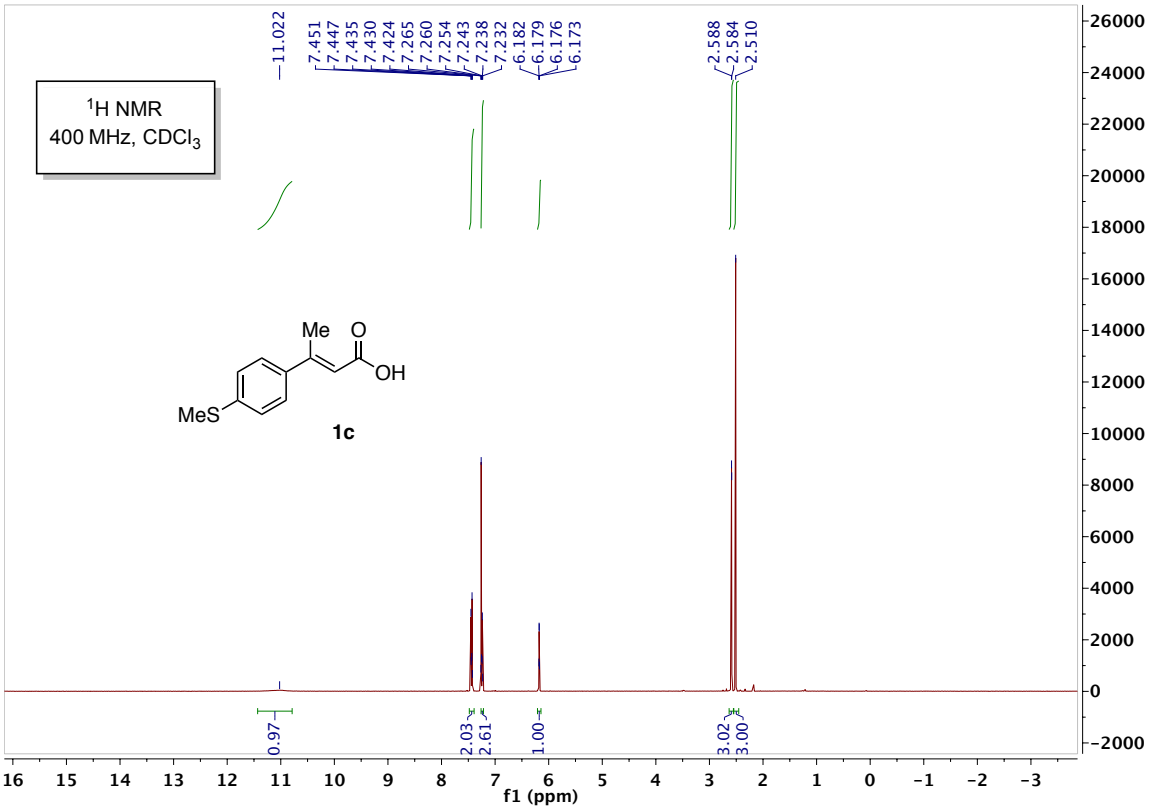


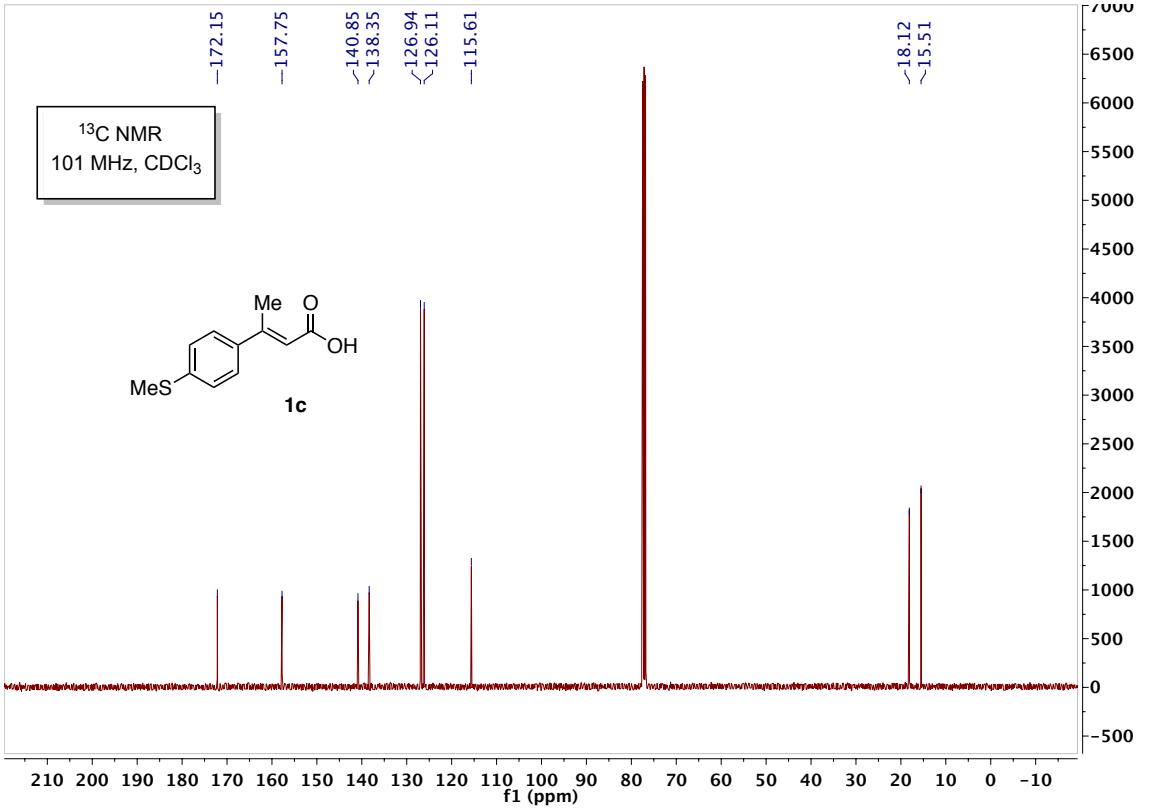
(*R*)-*N*-benzyl-3-(6-methoxypyridin-3-yl)-*N*-methylbutan-1-amine (4c)



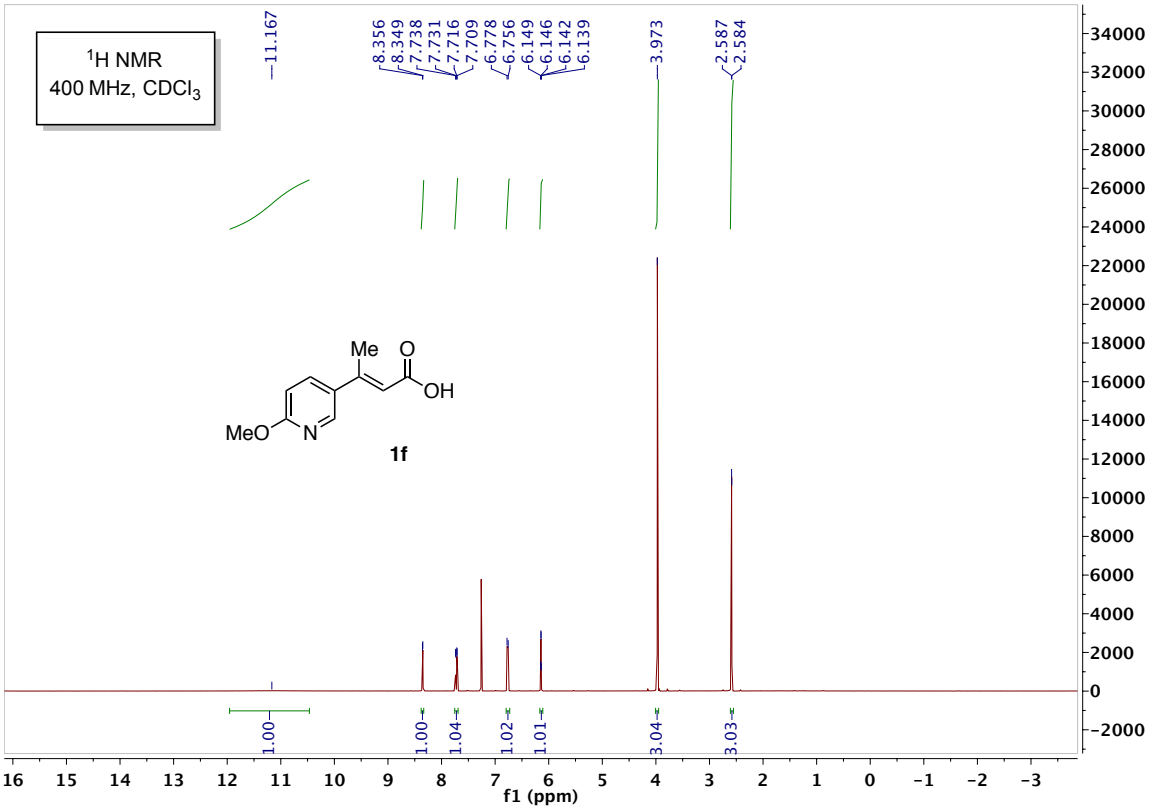


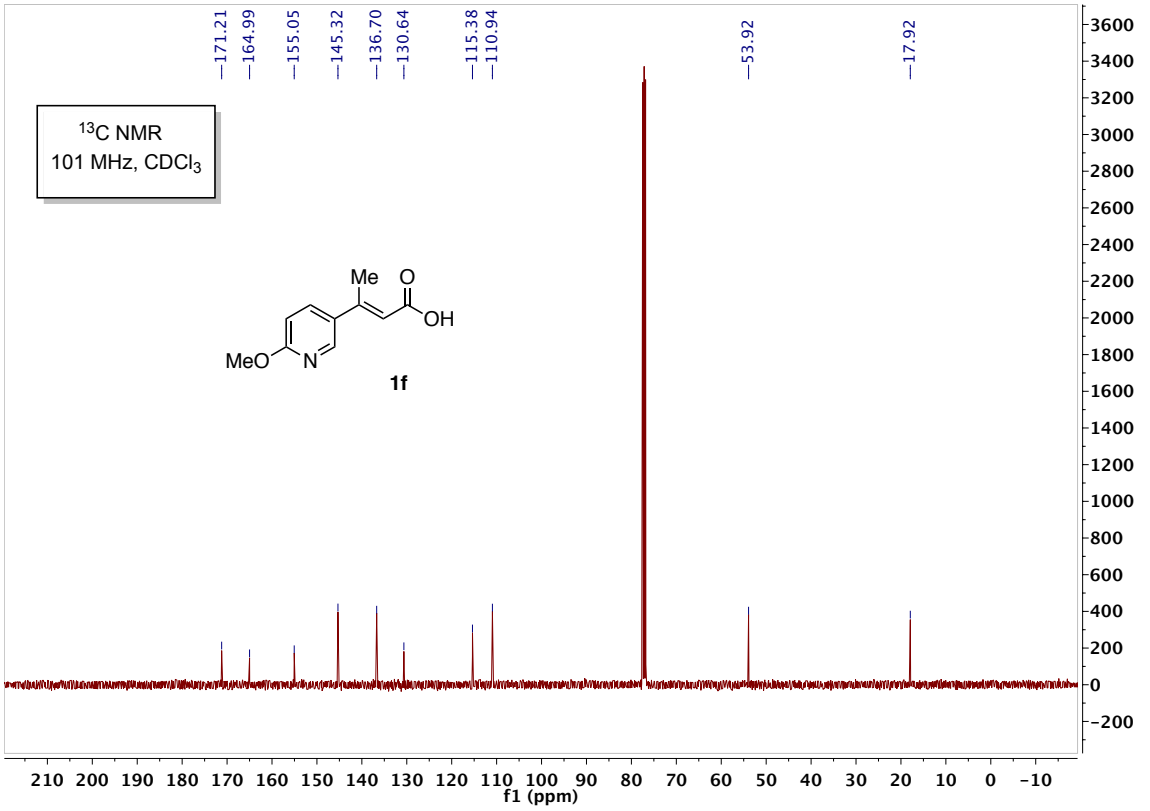
(*E*)-3-(4-(methylthio)phenyl)but-2-enoic acid (1c)



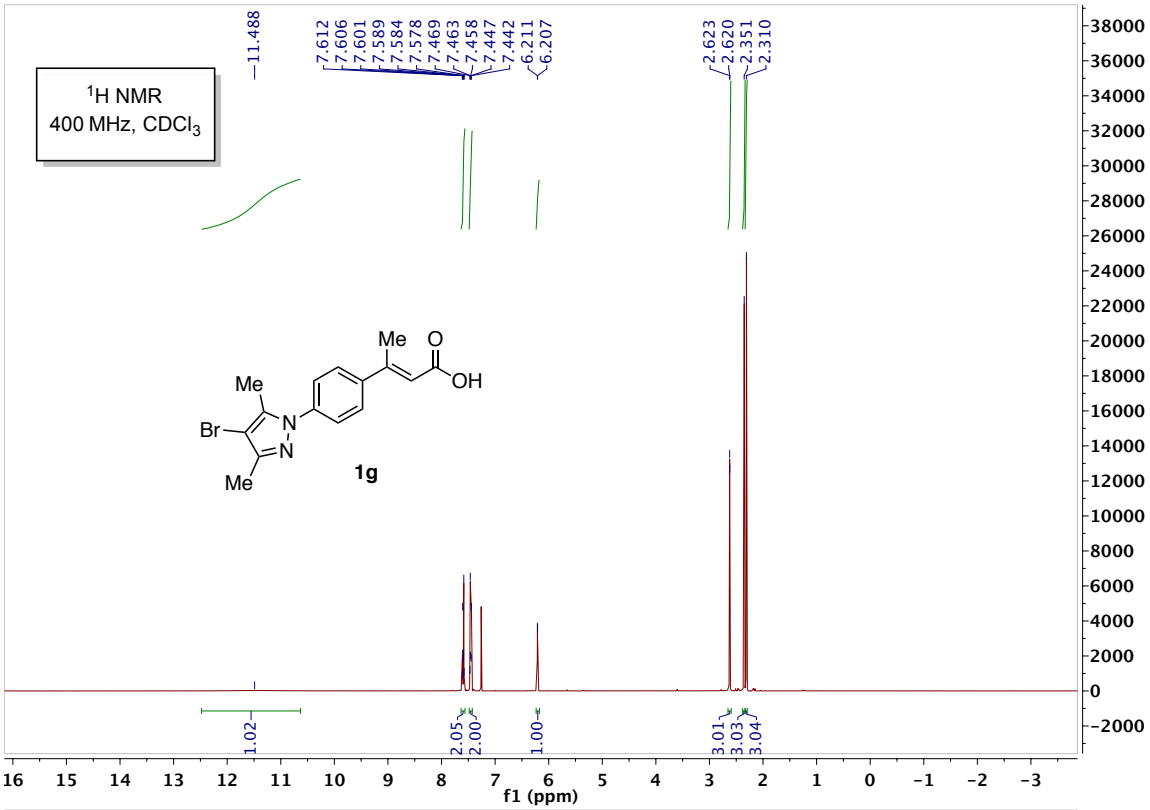


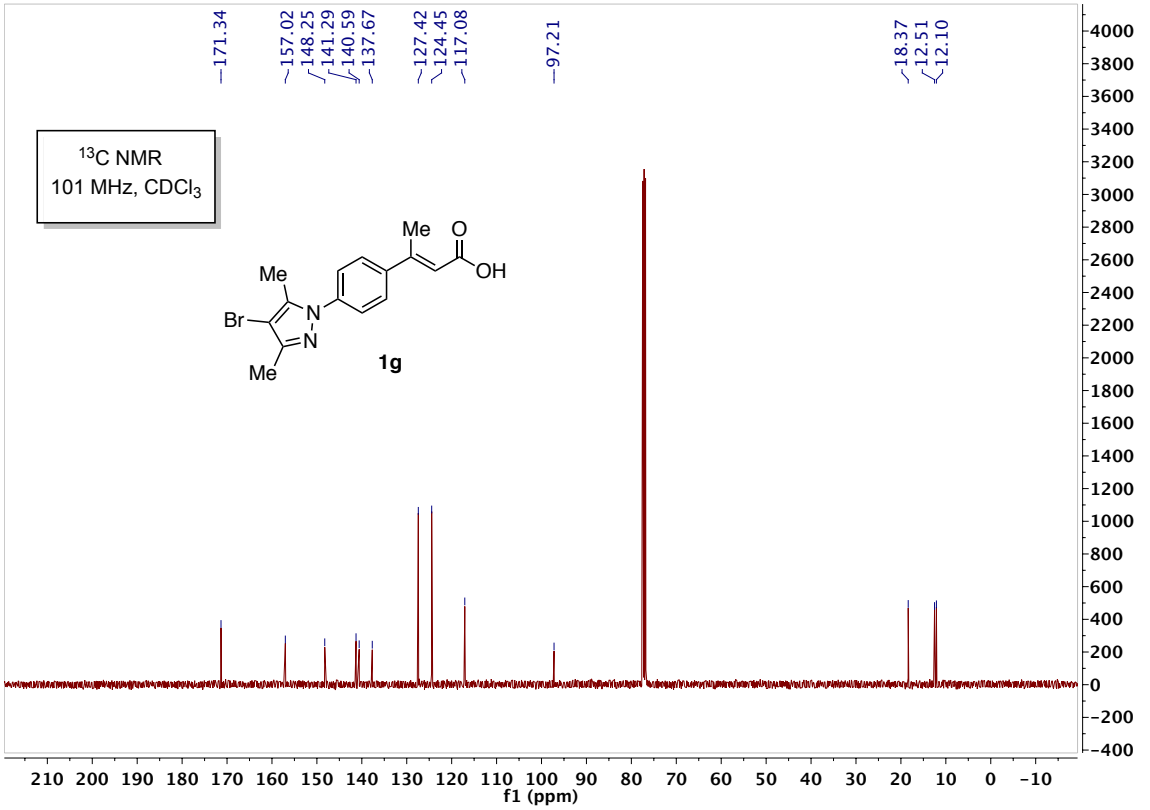
(*E*)-3-(6-methoxypyridin-3-yl)but-2-enoic acid (1f)



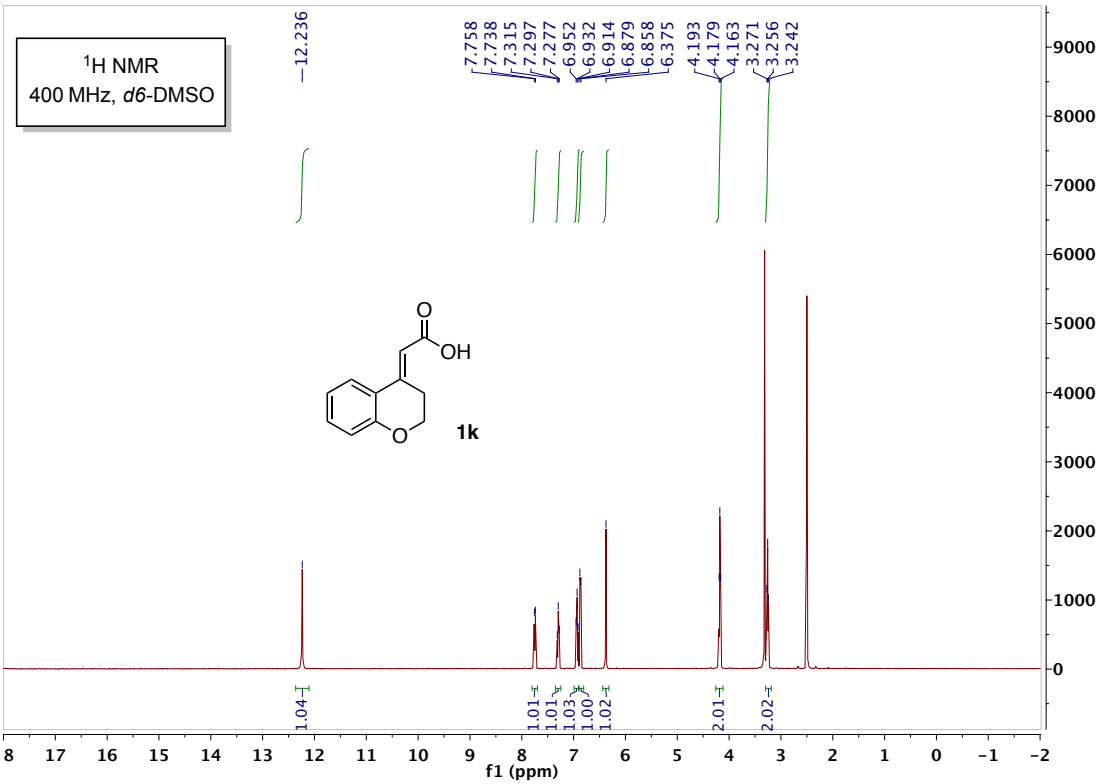


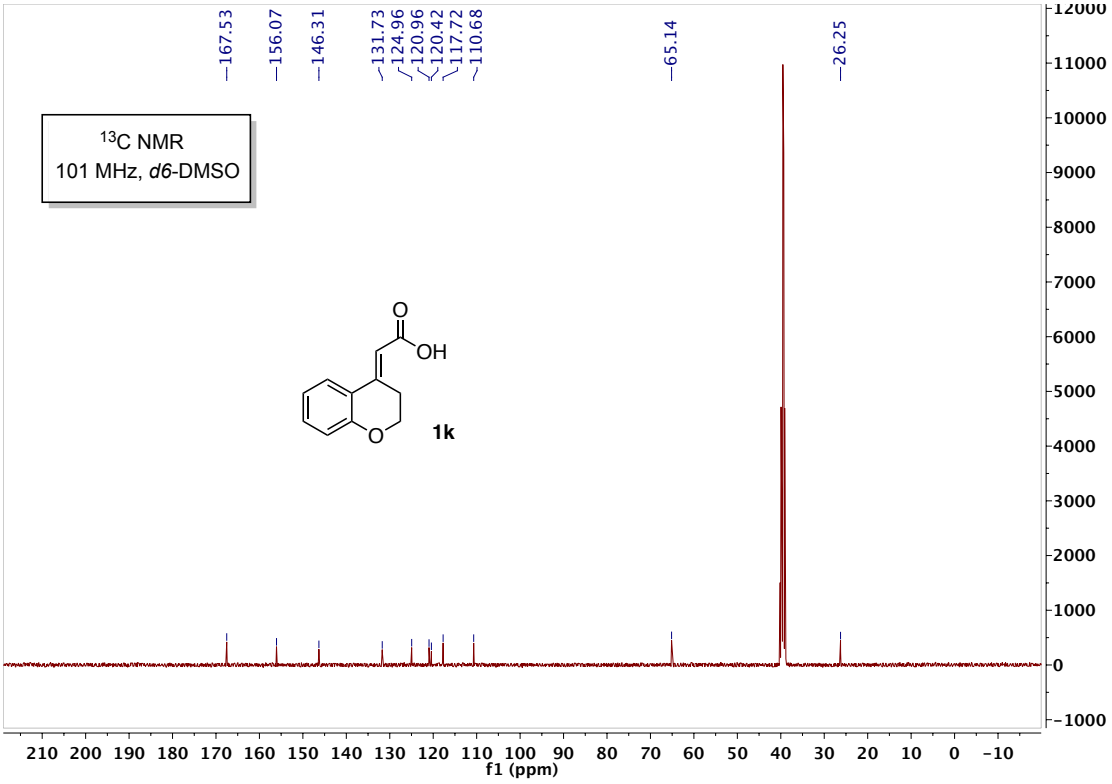
(*E*)-3-(4-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)phenyl)but-2-enoic acid (1g)



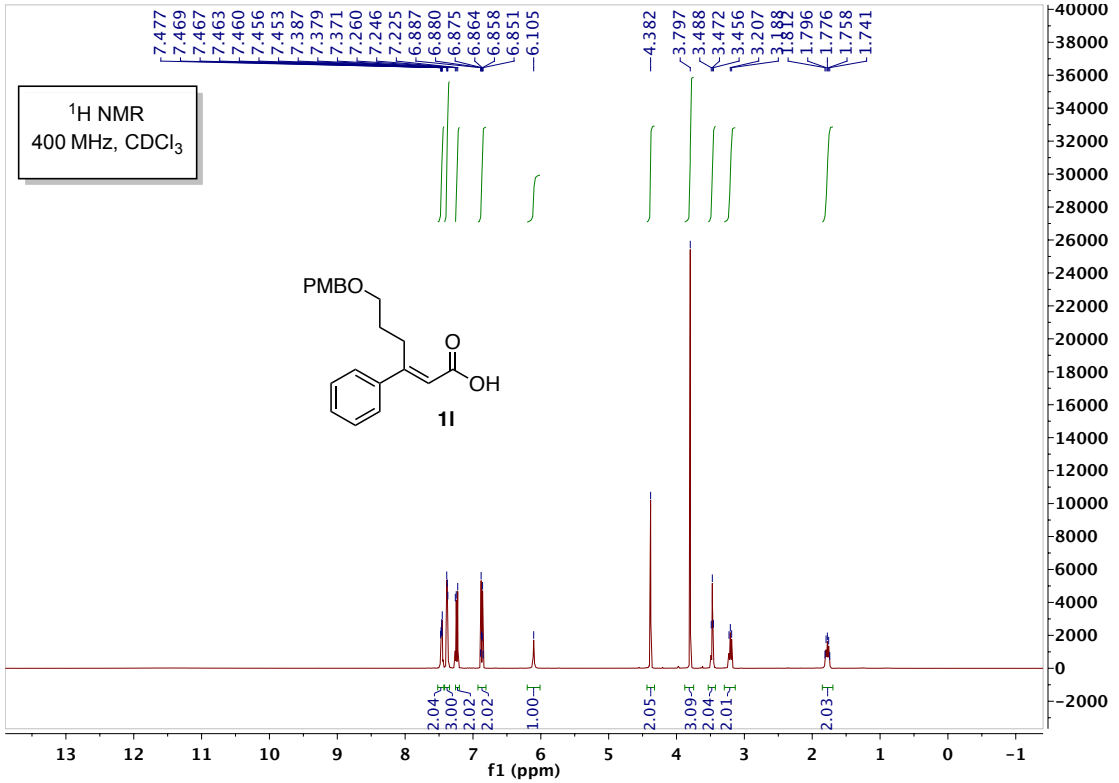


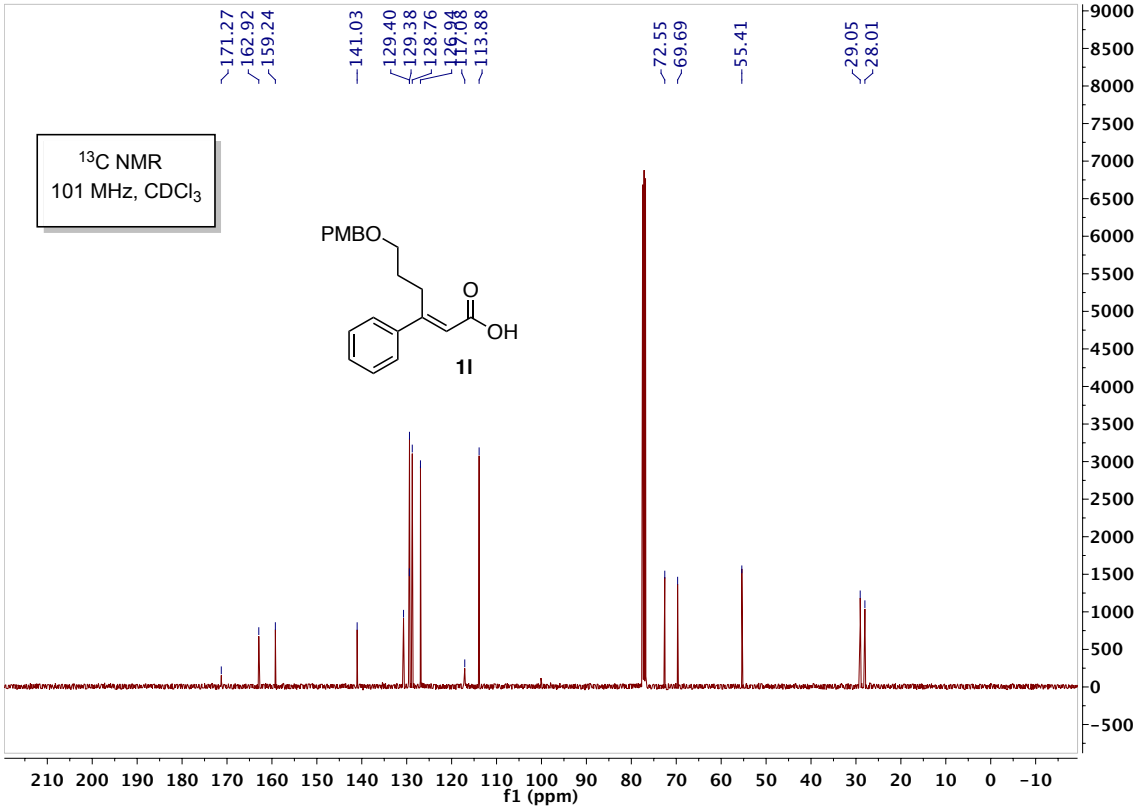
(*E*)-2-(chroman-4-ylidene)acetic acid (1k)



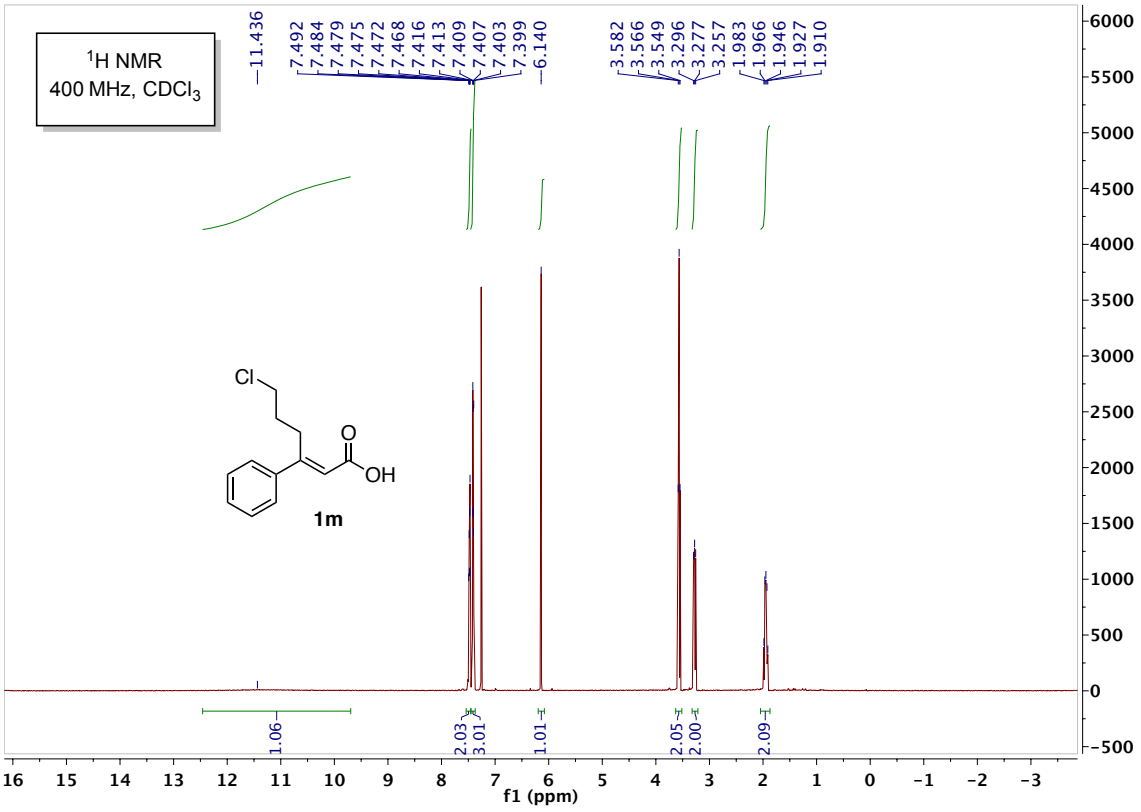


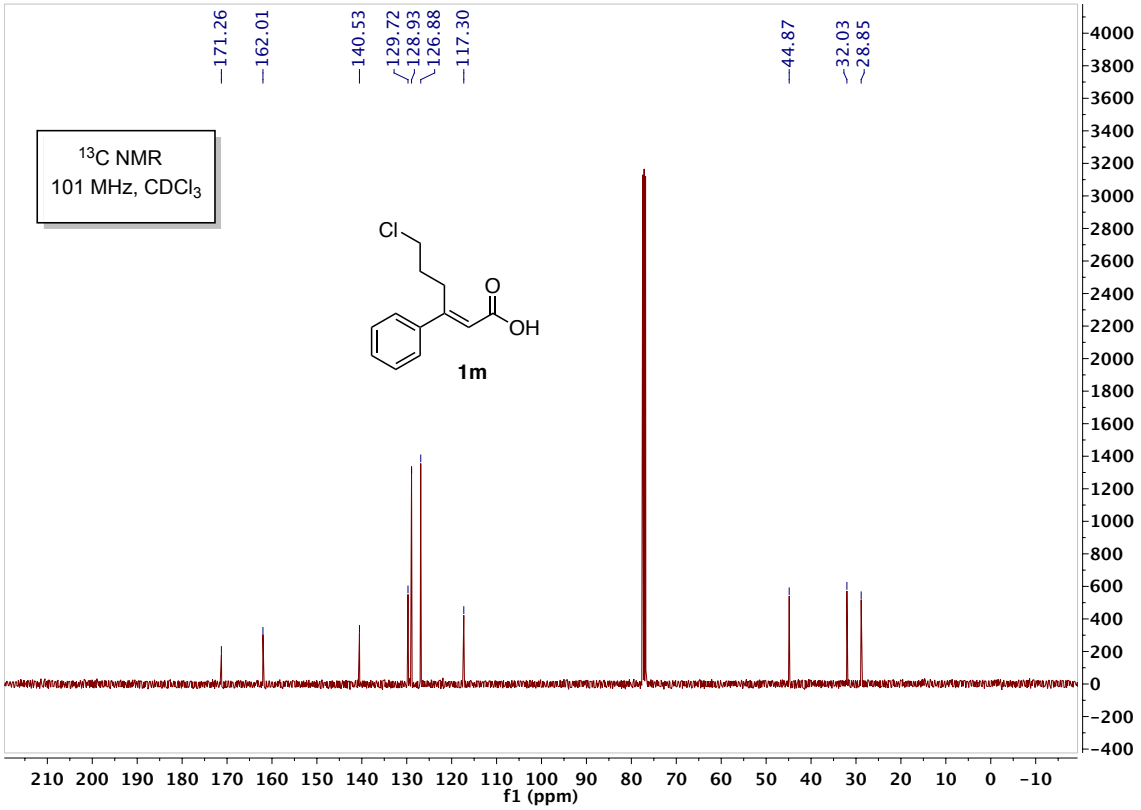
(*E*)-6-((4-methoxybenzyl)oxy)-3-phenylhex-2-enoic acid (1l)



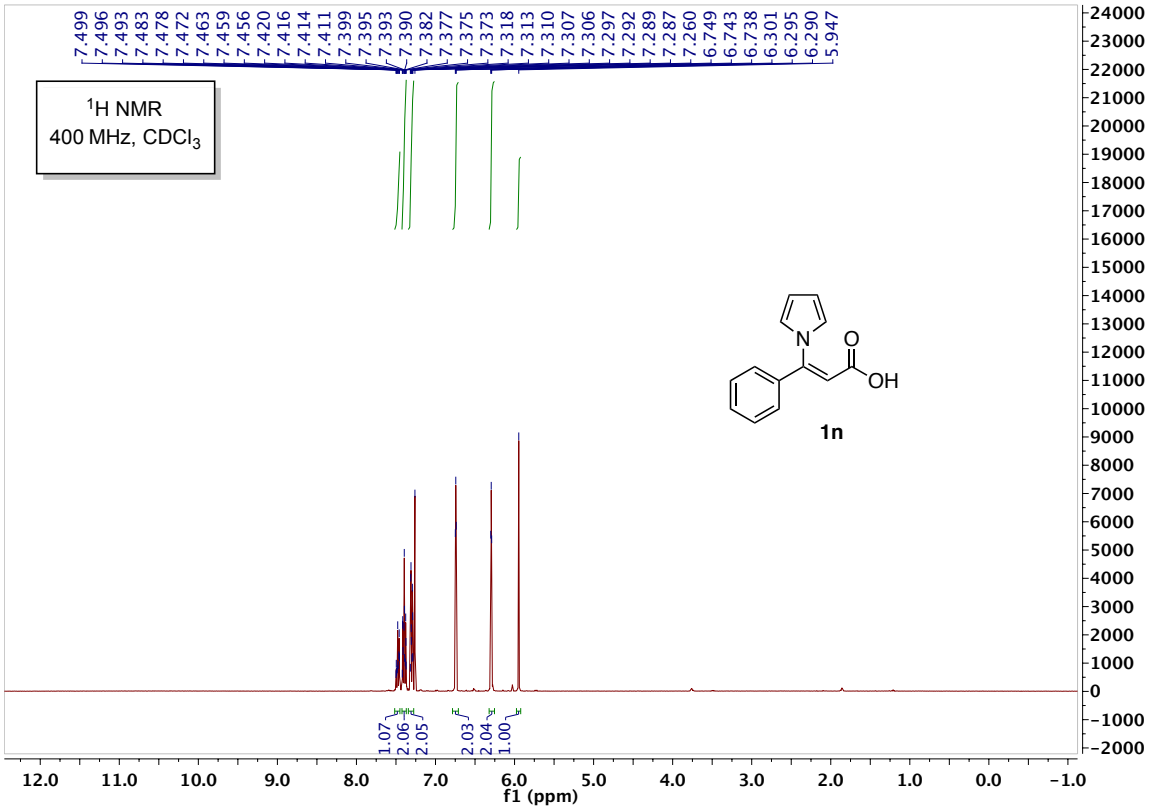


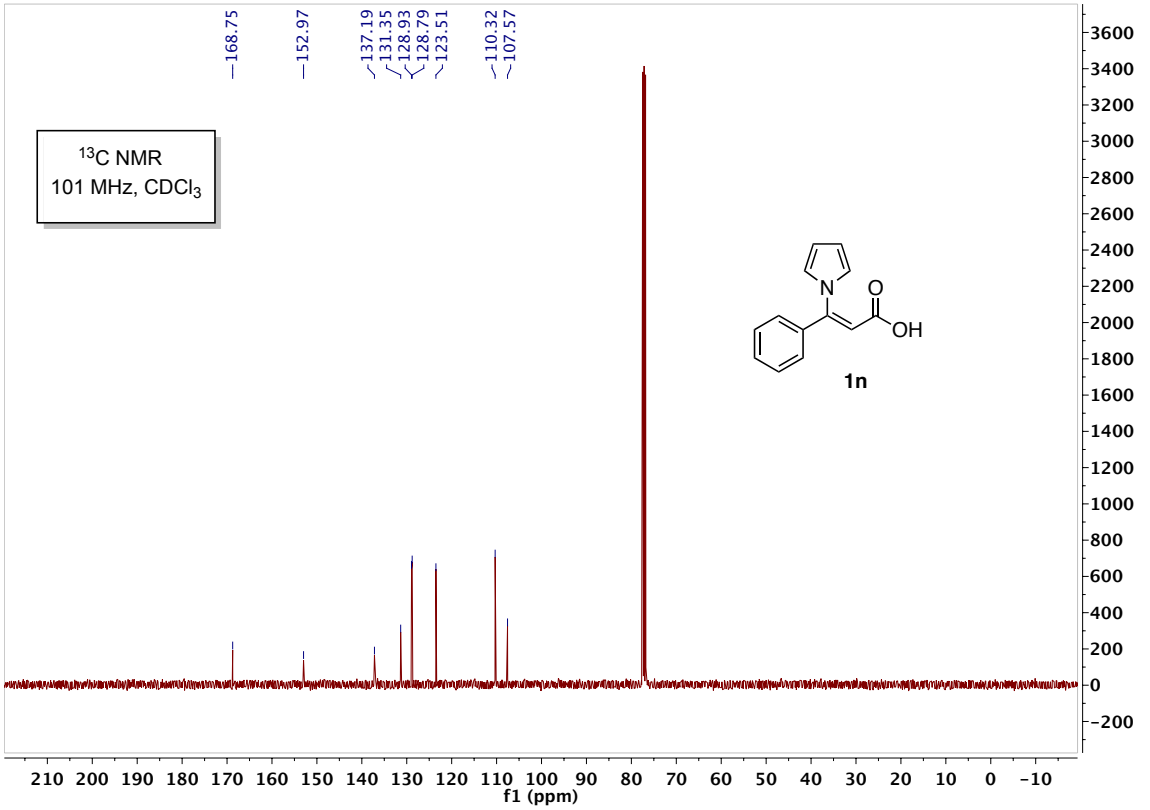
(*E*)-6-chloro-3-phenylhex-2-enoic acid (1m)



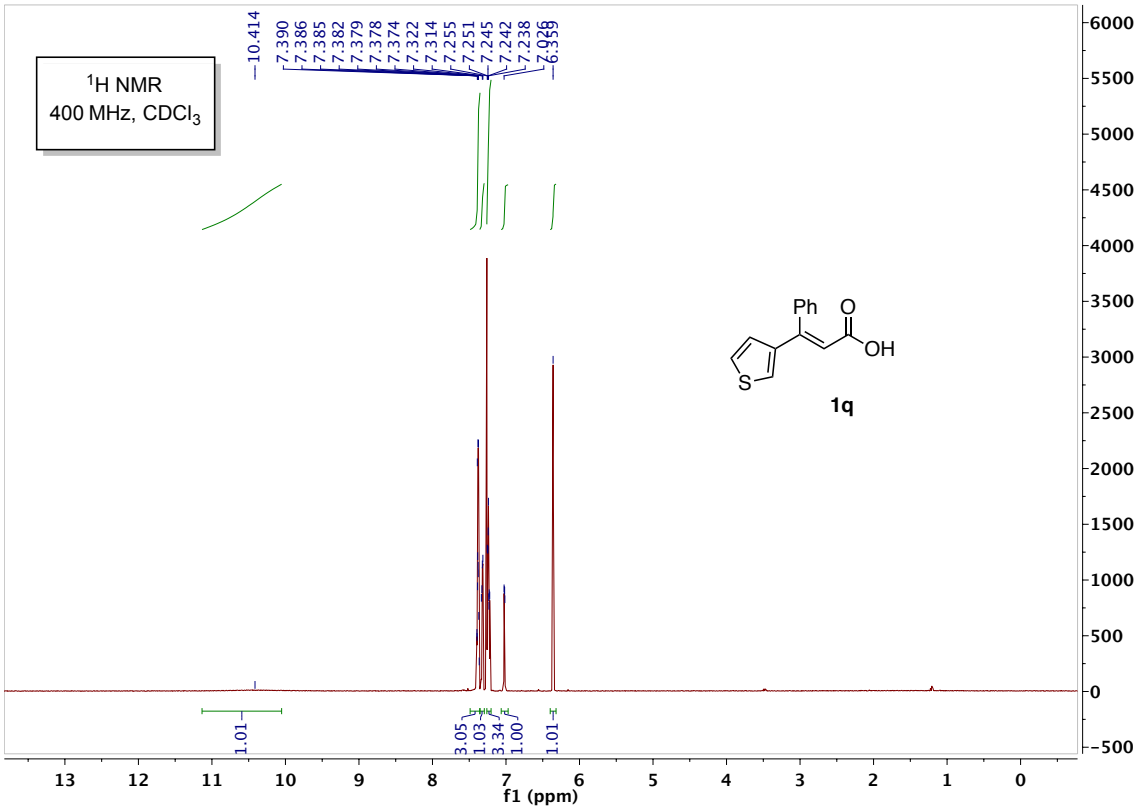


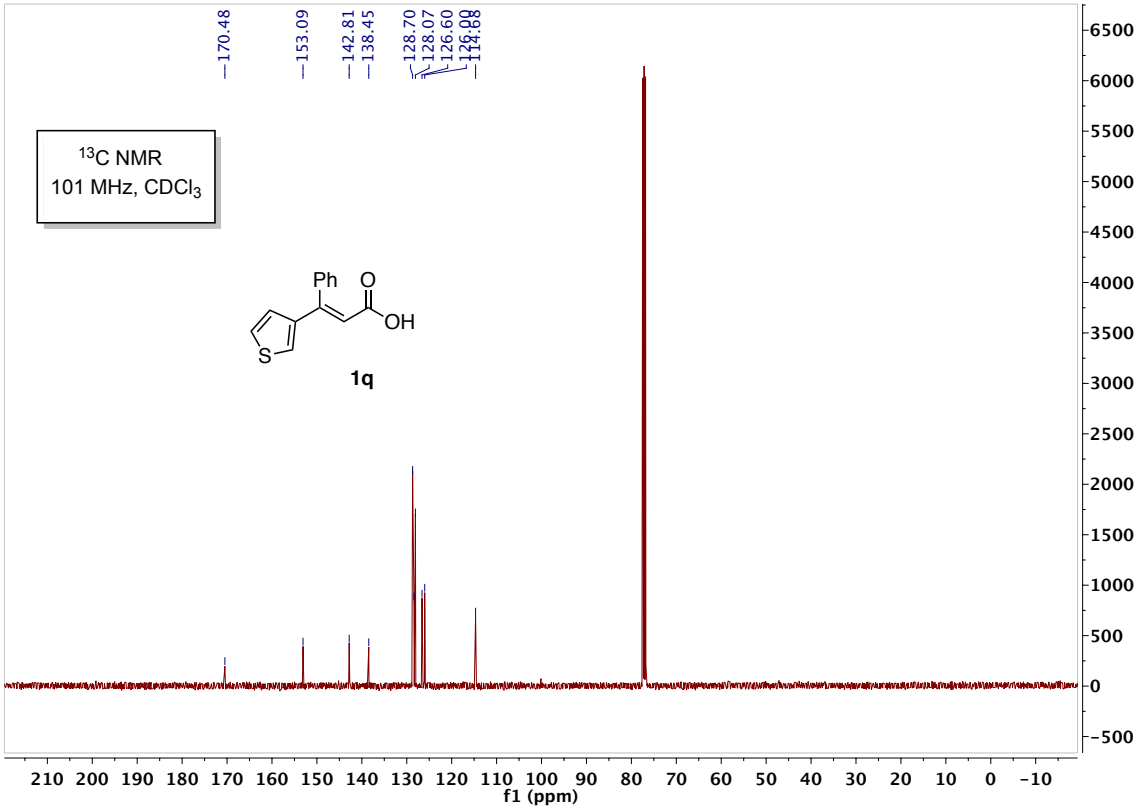
(*Z*)-3-phenyl-3-(1H-pyrrol-1-yl)acrylic acid (1n)





(*E*)-3-phenyl-3-(thiophen-3-yl)acrylic acid (1q)





(*E*)-3-(5-chloro-2-ethoxyphenyl)-3-phenylacrylic acid (1r)