Angewandte Chemie

Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

TABLE OF CONTENTS OF THE SUPPORTING INFORMATION

Characterization data of compound:

Characterization data of compound:

Characterization data of compound:

Synthesis and Characterization data of compound:

SFC and GC chromatograms of compound:

SUPPORTING INFORMATION

Catalytic Enantioselective Reduction of β,β-Disubstituted Vinyl Phenyl Sulfones using Bisphosphine Monoxide Ligands

Jean-Nicolas Desrosiers, André B. Charette*

Département de Chimie, Université de Montréal, P.O. Box 6128, Station Downtown, Québec, Canada H3C 3J7

General experimental procedures. Characterization data for new compounds. ^{1}H and ^{13}C NMR spectra. SFC/GC traces for racemic and enantioenriched compounds.

General: All reactions were run under an inert atmosphere (nitrogen or argon) with rigid exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds.[1] All glassware was stored in the oven and/or was flame-dried prior to use under an inert atmosphere of gas. Anhydrous solvents were obtained either by filtration through drying columns (THF, benzene, methanol, Toluene) on a GlassContour system (Irvine, CA), by distillation over calcium hydride (Et_3N) or by distillation over sodium/benzophenone (DME). Safety warning: benzene is a known carcinogen. Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel (Silicycle F_{254}). Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate or aqueous potassium permanganate. Flash column chromatography was performed using 230-400 mesh silica (EM Science or Silicycle) of the indicated solvent system according to standard technique.[2] Melting points were obtained on a Buchi melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin Elmer Spectrum One FTIR and are reported in reciprocal centimeters (cm^{-1}). Nuclear magnetic resonance spectra (^1H, ^{13}C, DEPT 135, NOESY, HMQC) were recorded either on a Bruker AV 300, AMX 300, AV 400 or ARX 400 spectrometer. Chemical shifts for ^1H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sex = sextet and m = multiplet), coupling constant in Hz and integration. Chemical shifts for ^{13}C NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (77.00 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. Optical rotations were determined with a Perkin-Elmer 341 polarimeter at 589 or 546 nm. Data are reported as follows: $[\alpha]_\lambda^{temp}$, concentration (*c* in g/100 mL), and solvent. High resolution mass spectra were performed by the Centre régional de spectroscopie de masse de l'Université de Montréal. Combustion analyses were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal.

Analytical Supercritical Fluid Chromatography was performed with an instrument equipped with a diode array UV detector. Data are reported as follows: (column type, eluent, flow rate, oven temperature, pressure: retention time (t_r)).

Analytical gas chromatography was carried out on a Hewlett Packard 5880A gas chromatograph equipped with a splitless mode capillary injector and a flame ionization dectector. The injector and detector temperatures were set to 250 ˚C and hydrogen was used as the carrier gas (63 psi). Data are reported as follows: (column type, column length, initial temperature, initial time, rate, final temperature, final time: retention time (t_r)).

Reagents: Unless otherwise stated, commercial reagents were used without purification. Benzaldehyde was freshly distilled before use and acetic anhydride was distilled over P_2O_5. The ligand **3a** and **3b** were synthesized according to previously reported procedure.[3] Vinyl sulfones **1** were prepared according to a modified protocol described in the literature[4] (general procedure #1) or by a condensation between the corresponding ketone and (diethylphosphonyl)(phenylsulfonyl) methane (general procedure #2). The stereochemistry (*E* or *Z*) of vinyl sulfones **1c–g** was confirmed by NOESY experiments. (Diethylphosphonyl)(phenylsulfonyl)methane was synthesized according to previously reported procedure by replacing methyl 4-methylphenyl sulfone by methyl phenyl sulfone and purification by trituration in Et_2O.[5] The absolute configuration of the major isomer of enantioenriched sulfones **2** (except sulfone **2g**) was based on the optical rotation obtained after desulfonylation of sulfone **2e** and compared to data of the literature.[6]

General procedure #1 for the synthesis of vinyl sulfones 1: Compounds **1a**, **1d**, **1e** and **1g** were prepared according to the following general procedure. A flame-dried three-necked round-bottomed flask equipped with a condenser and an egg-shaped magnetic stirring bar was charged with the α-methylstyrene derivative (100 mmoles, 1.0 equiv) and purged under argon. Benzene (150 mL), $PhSO_2Cl$ (12.7 mL, 100 mmoles, 1.0 equiv), $RuCl_2(PPh_3)_3$ (962 mg, 1 mmoles, 1 mol %) followed by Et_3N (14 mL, 100 mmoles, 1 equiv) were added to the reaction flask. The mixture was heated to 65 °C and stirred at that temperature for 3 days. After then, the dark-brown mixture was cooled to room temperature and filtered through a Florisil® pad (60 mL). The mixture was eluted with benzene (1 L). The filtrate was evaporated under reduced pressure and purified by flash chromatography on silica gel (EtOAc/hexane or toluene/hexane/EtOAc). The product was then recrystallized (EtOAc/hexane) or triturated in hexane and in EtOAc. Remaining traces of ruthenium can be removed by dissolving the product in DCM and treating it with activated carbon. Filtration of the mixture on Celite® followed by evaporation under reduced pressure afforded the desired product as a white to off-white powder or crystals.

---

[1] D. F. Shriver, M. A. Drezdzon, *The manipulation of air-sensitive compounds*, 2nd Edition, Wiley,**1986**.

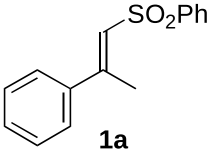
[2] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.

[3] A. Côté, J.-N. Desrosiers, A. A. Boezio, A. B. Charette, *Org. Synth.* **2006**, *83*, 1.

[4] N. Kamigata, H. Sawada, M. Kobayashi, *J. Org. Chem.* **1983**, *48*, 3793.

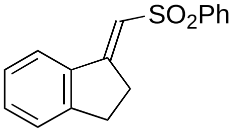
[5] D. Craig, C. J. Etheridge, A. M. Smith, *Tetrahedron Lett.* **1992**, *33*, 7445.

[6] R. D. Broene, S. L. Buchwald, *J. Am. Chem. Soc.* **1993**, *115*, 12569.



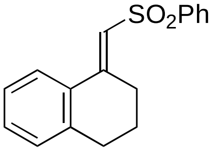
1a

Phenyl (1*E*)-2-phenylprop-1-enyl sulfone (1a): The general procedure #1 was followed. Yield 58%. R_f 0.22 (20% EtOAc/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97−7.94 (m, 2H), 7.59−7.50 (m, 3H), 7.36−7.32 (m, 5H), 6.60−6.59 (m, 1H), 2.50 (dd, J = 1.2, 0.3 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.4, 142.0, 139.9, 133.1, 129.8, 129.1, 128.6, 127.3, 127.1, 126.2, 17.1.The physical and spectroscopic properties were in accordance with those described in the literature.[4]



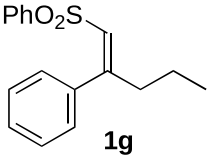
1d

(*E*)-2,3-dihydro-1*H*-inden-1-ylidenemethyl phenyl sulfone (1d): The general procedure #1 was followed. Yield 8%. mp 149.0−150.0 °C; R_f 0.26 (5% EtOAc/35% hexane/60% toluene); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.99 (m, 2H), 7.63−7.48 (m, 4H), 7.40−7.33 (m, 2H), 7.28−7.22 (m, 1H), 6.76 (t, J = 2.5 Hz, 1H), 3.32−3.28 (m, 2H), 3.09−3.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 148.9, 142.1, 138.0, 132.7, 131.5, 128.8, 126.7, 125.4, 121.7, 117.0, 30.2, 29.1; IR (neat) ν 3049, 2923, 1614, 1597, 1445, 1436, 1307, 1285, 1137, 1084, 749, 682 cm^{-1}; Elemental analysis calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22 found: C, 71.20; H, 5.33.



1e

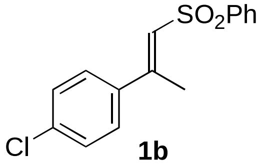
(*E*)-3,4-dihydronaphthalen-1(2*H*)-ylidenemethyl phenyl sulfone (1e): The general procedure #1 was followed. Yield 65%. mp 109.0−110.0 °C; R_f 0.31 (5% EtOAc/35% hexane/60% toluene); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.99 (m, 2H), 7.64−7.52 (m, 4H), 7.32−7.28 (m, 1H), 7.21−7.13 (m, 2H), 6.83 (t, J = 1.6 Hz, 1H), 3.07 (dt, J = 5.7, 1.6 Hz, 2H), 2.79 (t, J = 6.2 Hz, 2H), 1.83 (qn, J = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 142.1, 139.9, 132.7, 131.9, 130.2, 129.1, 128.8, 126.8, 126.2, 124.7, 122.6, 29.3, 26.5, 21.8; IR (neat) ν 3058, 2946, 1583, 1446, 1303, 1287, 1137, 1083, 751, 684, 568 cm^{-1}; Elemental analysis calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67 found: C, 72.06; H, 5.72.



1g

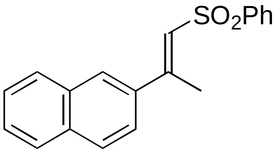
Phenyl (1*Z*)-2-phenylpent-1-enyl sulfone (1g): The general procedure #1 was followed. The geometry of the double bond was confirmed by an NOE NMR experiment. An interation between the vinylic proton and the ones of the methylene at the γ position was observed. The usual coupling between the vinylic proton and the aromatic protons observed for the *E* vinyl sulfones was not present in this case. Yield 19%. mp 104.5−105.0 °C; R_f 0.36 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 6.3, 1.4 Hz, 2H), 7.63 (dt, J = 7.4, 1.2 Hz, 1H), 7.56 (dt, J = 7.0, 1.3 Hz, 2H), 7.40−7.33 (m, 5H), 6.51 (s, 1H), 3.05 (dt, J = 7.8, 1.8 Hz, 2H), 1.36 (sex, J = 7.4 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 142.0, 138.8, 132.9, 129.3, 128.9, 128.4, 127.4, 126.9, 126.3, 31.6, 21.4, 13.5; IR (neat) ν 3060, 2995, 2960, 2931, 2872, 1594, 1568, 1446, 1300, 1284, 1141, 1082, 822, 750, 688, 618 cm^{-1}; HRMS calcd for $C_{17}H_{18}O_2S$ $[M+H]^+$: 287.1100, found 287.1097.

General procedure #2 for the synthesis of vinyl sulfones 1: Compounds **1b**, **1c**, and **1f** were prepared according to the following general procedure. To a magnetically stirred suspension of NaH 60% (228 mg, 5.7 mmoles, 1.0 equiv or less if significant formation of the isomerized vinyl sulfone occurs) in THF (18 mL) under argon in a cold water bath, was slowly added a solution of (diethylphosphonyl)(phenylsulfonyl)methane (2 g, 6.84 mmoles, 1.2 equiv) in THF (18 mL). The resulting yellow solution was stirred at room temperature for 10 min or until no evolution of gas was observed. After, the corresponding ketone (5.7 mmoles, 1.0 equiv) was added to the yellow solution and stirred at room temperature under argon overnight. The reaction mixture was quenched with saturated aqueous NH_4Cl (30 mL). The biphasic mixture was extracted twice with DCM (2 x 40 mL). The combined organic layers were then washed with saturated aqueous NaCl (30 mL). The organic solution was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude vinyl sulfone was purified by flash chromatography on silica gel (EtOAc/hexane) to afford the desired vinyl sulfone **1** as a white to off-white powder or crystals.



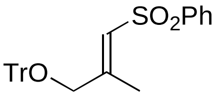
1b

(1*E*)-2-(4-chlorophenyl)prop-1-enyl phenyl sulfone (1b): The general procedure #2 was followed. Yield 41%. R_f 0.36 (30% EtOAc/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95−7.92 (m, 2H), 7.59−7.50 (m, 3H), 7.28 (m, 4H), 6.56 (q, *J* = 1.2 Hz, 1H), 2.47 (d, *J* = 1.26 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 151.9, 141.8, 138.3, 135.9, 133.2, 129.2, 128.8, 127.7, 127.5, 127.1, 16.7. The physical and spectroscopic properties were in accordance with those described in the literature.[4]



1c

(1*E*)-2-(2-naphthyl)prop-1-enyl phenyl sulfone (1c): The general procedure #2 was followed. Yield 22%. mp 114.5−115.0 °C; R_f 0.37 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.04 (m, 2H), 7.89 (d, *J* = 1.5 Hz, 1H), 7.86−7.81 (m, 3H), 7.67−7.57 (m, 3H), 7.55−7.50 (m, 3H), 6.80 (d, *J* = 1.0 Hz, 1H), 2.67 (d, *J* = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 141.8, 136.8, 133.4, 132.9, 132.5, 128.9, 128.2, 128.1, 127.3, 127.2, 126.9, 126.9, 126.4, 125.9, 123.1, 16.8; IR (neat) ν 3063, 1589, 1573, 1446, 1293, 1136, 1085, 816, 799, 743, 706, 683, 587, 559 cm^{-1}; HRMS calcd for $C_{19}H_{16}O_2S$ $[M+H]^+$: 309.0943, found 309.0946.

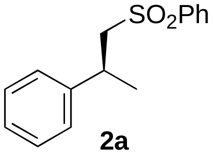


1f

(1*E*)-2-methyl-3-(trityloxy)prop-1-enyl phenyl sulfone (1f): The general procedure #2 was followed. Yield 55%. mp 145.0−146.0 °C; R_f 0.33 (30% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.97 (m, 2H), 7.65−7.56 (m, 3H), 7.42−7.44 (m, 6H), 7.35−7.25 (m, 9H), 6.88 (m, 1H), 3.70 (d, *J* = 1.5 Hz, 2H), 1.99 (d, *J* = 0.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 142.9, 141.9, 132.8, 128.8, 128.1, 127.7, 127.0, 126.8, 124.4, 87.1, 66.9, 14.6; IR (neat) ν 3060, 2902, 2847, 1630, 1597, 1489, 1442, 1304, 1160, 1135, 1080, 762, 747, 708, 691, 590 cm^{-1}; HRMS calcd for $C_{29}H_{26}O_3S$ $[M+Na]^+$: 477.1495, found 477.1499.

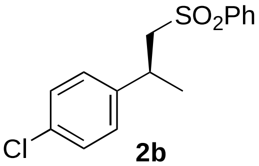
General procedure for the synthesis racemic alkyl sulfones 2: A flame-dried 10 mL round-bottomed flask equipped with an egg-shaped magnetic stirring bar was charged with $CuF_2•H_2O$ (3 mg, 0.025 mmoles, 5 mol %) and purged with argon. Bu_3P (12 μL, 0.05 mmoles, 10 mol %) was then added to the flask via a gas-tight syringe. Benzene (1.5 mL) was added to the mixture and the resulting suspension was stirred at room temperature for 1 h. After then, $PhSiH_3$ (92 μL, 0.75 mmoles, 1.5 equiv) was added and the resulting mixture was stirred exactly 1 min. A 5.5 M aqueous solution of NaOH (18 μL, 0.10 mmoles, 20 mol% of NaOH and equals to 2 equiv of water) was then added and, immediately, a solution of the vinyl sulfone **1** (0.5 mmoles, 1 equiv) dissolved in a minimum amount of benzene (1.5 to 4 mL) under argon was added via a syringe. The heterogeneous mixture was stirred 12 h at room temperature. The mixture was filtered on Celite® and the reaction flask was washed twice with benzene (2 x 2 mL). The filtrate was evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel (10−20% EtOAc/hexane) to afford the desired racemic sulfone **2** as a white powder.

General procedure for the synthesis enantioenriched alkyl sulfones 2: A flame-dried 10 mL round-bottomed flask equipped with an egg-shaped magnetic stirring bar was charged with $CuF_2•H_2O$ (3 mg, 0.025 mmoles, 5 mol %) and ligand **3a** (8.8 mg, 0.027 mmoles, 5.5 mol %) in a glove-box. Benzene (1.5 mL) was added to the mixture and the resulting suspension was stirred under argon at room temperature for 1 h. After then, $PhSiH_3$ (92 μL, 0.75 mmoles, 1.5 equiv) was added and the resulting mixture was stirred exactly 1 min. A 5.5 M aqueous solution of NaOH (18 μL, 0.10 mmoles, 20 mol% of NaOH and equals to 2 equiv of water) was then added and, immediately, a solution of the vinyl sulfone **1** (0.5 mmoles, 1 equiv) dissolved in a minimum amount of benzene (1.5 to 4 mL) under argon was added via a syringe. The heterogeneous mixture was stirred 12 h at room temperature. The mixture was filtered on Celite® and the reaction flask was washed twice with benzene (2 x 2 mL). The filtrate was evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel (10−20% EtOAc/hexane) to afford the desired enantioenriched sulfone **2** as a white powder.



2a

Phenyl (2*S*)-2-phenylpropyl sulfone (2a): The general procedure was followed. Yield 85%, enantiomeric excess (98%) was determined by SFC analysis (Chiralpak AD, 3% MeOH, 2 mL/min, 40 °C, 150 bar: t_r (minor) 14.4 min, t_r (major) 15.2 min). R_f 0.28 (30% EtOAc/hexane); $[\alpha]_D^{20}$ –4.9° (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83−7.81 (m, 2H), 7.59 (dt, *J* = 7.4, 6.8 Hz, 1H), 7.50−7.46 (m, 2H), 7.28−7.15 (m, 3H), 7.12−7.08 (m, 2H), 3.45−3.34 (m, 3H), 1.46 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 139.5, 133.1, 128.8, 128.3, 127.5, 126.5, 126.3, 62.9, 34.7, 21.8. The physical and spectroscopic properties were in accordance with those described in the literature.[7]

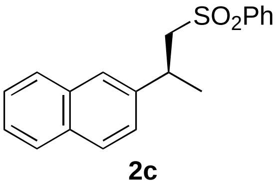


2b

(2*S*)-2-(4-chlorophenyl)propyl phenyl sulfone (2b): The general procedure was followed. Yield 93%, enantiomeric excess (98%) was determined by SFC analysis (Chiralpak AD, 10% MeOH, 2 mL/min, 40 °C, 150 bar: t_r (minor) 8.4 min, t_r (major) 9.8 min). mp 79.0−79.5 °C; R_f 0.30 (30% EtOAc/hexane); $[\alpha]_D^{20}$ –4.7° (*c* 1.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 5.6, 5.1 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 8 Hz, 2H), 7.18 (dt, *J* = 8.4, 2.5 Hz, 2H), 7.03 (dt, *J* = 8.5, 2.4 Hz, 2H), 3.44−3.33 (m, 3H), 1.42 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 139.4, 133.1, 132.2, 128.8, 128.4, 127.7, 127.4, 62.8, 34.2, 21.9; IR (neat) ν 3062, 2967, 2927, 1493, 1323, 1289, 1260, 1135, 1098, 1081, 821, 742, 681, 573 cm^{-1}; HRMS calcd for $C_{15}H_{15}ClO_2S$ $[M+H]^+$: 295.0554, found 295.0557.

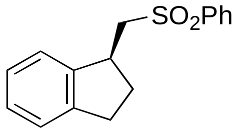
---

[7]. M. Isobe, M. Kitamura, T. Goto, *Chem. Lett.* **1980**, 331.



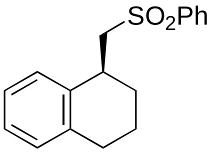
2c

(2*S*)-2-(2-naphthyl)propyl phenyl sulfone (2c): The general procedure was followed. Yield 85%, enantiomeric excess (98%) was determined by SFC analysis (Chiralpak AD, 5% MeOH, 2 mL/min, 40 °C, 150 bar: t_r (minor) 26.0 min, t_r (major) 27.8 min). mp 62.0−63.0 °C; R_f 0.31 (30% EtOAc/hexane); $[\alpha]_D^{20}$ 10.9° (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80−7.70 (m, 5H), 7.53−7.37 (m, 6H), 7.28−7.20 (m, 1H), 3.63−3.44 (m, 3H), 1.55 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 139.4, 133.0, 132.9, 132.0, 128.6, 128.2, 127.4, 127.2, 127.1, 125.8, 125.4, 125.0, 124.4, 62.9, 34.8, 21.8; IR (neat) ν 3054, 2966, 2927, 1732, 1446, 1294, 1138, 1084, 745, 732, 688 cm^{-1}; HRMS calcd for $C_{19}H_{18}O_2S$ $[M+H]^+$: 311.1100, found 311.1097.



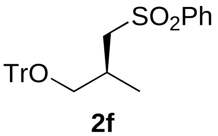
2d

(1*S*)-2,3-dihydro-1*H*-inden-1-ylmethyl phenyl sulfone (2d): The general procedure was followed. Yield 97%, enantiomeric excess (99%) was determined by SFC analysis (Chiralpak AD, 5% MeOH, 2 mL/min, 40 °C, 150 bar: t_r (minor) 17.9 min, t_r (major) 18.6 min). mp 94.5−95.5 °C; R_f 0.33 (30% EtOAc/hexane); $[\alpha]_D^{20}$ 18.9° (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.3, 1.2 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 2H), 7.28−7.13 (m, 4H), 3.73−3.59 (m, 1H), 3.61 (dd, *J* = 14.1, 3.1 Hz ,1H), 3.23 (dd, *J* = 14.1, 10.3 Hz, 1H), 3.00−2.85 (m, 2H), 2.52−2.43 (m, 1H), 1.98 (dq, *J* = 13.0, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 143.2, 139.4, 133.4, 129.0, 127.6, 126.9, 126.2, 124.4, 122.9, 60.9, 39.0, 31.9, 31.0; IR (neat) ν 3069, 2956, 2845, 1474, 1448,1430, 1303, 1292, 1145, 1085, 759, 730, 719, 609, 576 cm^{-1}; HRMS calcd for $C_{16}H_{16}O_2S$ $[M+H]^+$: 273.0943, found 273.0947.



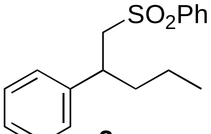
2e

Phenyl (1*S*)-1,2,3,4-tetrahydronaphthalen-1-ylmethyl sulfone (2e): The general procedure was followed. Yield 90%, enantiomeric excess (99%) was determined by SFC analysis (Chiralpak AD, 5% MeOH, 2 mL/min, 40 °C, 150 bar: t_r (major) 19.0 min, t_r (minor) 20.4 min). mp 103.0−103.5 °C; R_f 0.36 (30% EtOAc/hexane); $[\alpha]_D^{20}$ –30.0° (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.70 (dt, *J* = 7.2, 2.3 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 2H), 7.14−7.05 (m, 3H), 6.99−6.97 (m, 1H), 3.57−3.52 (m, 1H), 3.44 (dd, *J* = 14.3, 9.5 Hz, 1H), 3.35 (dd, *J* = 14.3, 2.6 Hz, 1H), 2.82−2.70 (m, 2H), 2.18−2.11 (m, 1H), 2.02−1.93 (m, 1H), 1.85−1.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 137.2, 136.9, 133.4, 129.1, 129.0, 128.3, 127.6, 126.2, 125.9, 62.4, 32.4, 28.7, 27.1, 18.5; IR (neat) ν 3065, 3015, 2935, 2839, 1448, 1302, 1289, 1145, 1116, 1084, 733, 717, 684 cm^{-1}; Elemental analysis calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34 found: C, 71.23; H, 6.26.



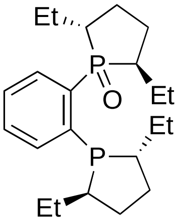
2f

(2*S*)-2-methyl-3-(trityloxy)propyl phenyl sulfone (2f): The general procedure was followed except that ligand **3b** (0.027 mmoles 5.5 mol %) was used. Yield 94%, enantiomeric excess (90%) was determined by SFC analysis (Chiralcel OD, 5% MeOH, 2 mL/min, 40 °C, 150 bar: t_r (minor) 22.9 min, t_r (major) 23.9 min). mp 105.5−106.0 °C; R_f 0.32 (30% EtOAc/hexane); $[\alpha]_D^{20}$ 1.7° (*c* 2.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.68 (dt, *J* = 7.4, 2 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 2H), 7.37−7.24 (m, 15H), 3.44 (dd, *J* = 14.3, 3.4 Hz, 1H), 3.10 (dd, *J* = 9.1, 5.1 Hz, 1H), 2.95−2.88 (m, 2H), 2.36−2.33 (m, 1H), 1.13 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 139.5, 133.2, 128.9, 128.2, 127.5, 127.4, 126.7, 86.2, 66.5, 59.3, 29.6, 16.8; IR (neat) ν 3057, 3023, 2919, 1595, 1489, 1446, 1304, 1144, 1070, 1030, 745, 706, 697, 688 cm^{-1}; HRMS calcd for $C_{29}H_{28}O_3S$ $[M+Na]^+$: 479.1651, found 479.1650.



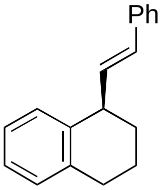
2g

Phenyl 2-phenylpentyl sulfone (2g): The general procedure was followed. The starting material was separated from the desired reduced product by performing a dihydroxylation/oxidative cleavage of the vinyl sulfone with $KMnO_4$ (3.6 equiv) and $BnEt_3NCl$ as a phase transfer agent in DCM/H_2O. Yield 61%, enantiomeric excess (97%) was determined by SFC analysis (Chiralpak AD, 5% MeOH, 2 mL/min, 40 °C, 150 bar: t_r (minor) 10.9 min, t_r (major) 11.8 min). mp 66.5−67.5 °C; R_f 0.40 (30% EtOAc/hexane); $[\alpha]_D^{20}$ 17.1° (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.55 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.42 (dt, *J* = 7.4, 1.6 Hz, 2H), 7.21−7.12 (m, 3H), 7.02 (dd, *J* = 9.8, 1.6 Hz, 2H), 3.47 (ddd, *J* = 18.5, 12.7, 7.2 Hz, 2H), 3.28−3.21 (m, 1H), 1.91−1.82 (m, 1H), 1.68−1.58 (m, 1H), 1.20−1.08 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 139.5, 132.9, 128.6, 128.1, 127.4, 127.1, 126.5, 62.0, 40.0, 38.2, 19.8, 13.4; IR (neat) ν 3060, 3030, 2953, 2930, 2857, 1448, 1305, 1284, 1135, 1082, 781, 742, 696, 682 cm^{-1}; HRMS calcd for $C_{17}H_{20}O_2S$ $[M+H]^+$: 289.1256, found 289.1253.



3b

(2*R*,5*R*)-1-{2-[(2*R*,5*R*)-2,5-diethylphospholan-1-yl]phenyl}-2,5-diethylphospholane 1-oxide (3b): R_f 0.50 (10% MeOH/EtOAc); $[\alpha]_D^{20}$ −148.8° (*c* 7.9, benzene); ^1H NMR (400 MHz, C_6D_6) δ 7.75−7.71 (m, 1H), 7.64−7.61 (m, 1H), 7.29−7.20 (m, 2H), 2.53−2.42 (m, 3H), 2.20−2.03 (m, 7H), 1.97−1.95 (m, 2H), 1.83−1.70 (m, 4H), 1.44−1.38 (m, 4H), 1.06 (dt, *J* = 11.4, 7.3 Hz, 6H), 0.98−0.84 (m, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 144.4 (dd, J_{C-P} = 37.8, 9.7 Hz), 140.2 (dd, J_{C-P} = 79.2, 32.5 Hz), 133.8 (dd, J_{C-P} = 10.5, 2.5 Hz), 131.3 (dd, J_{C-P} = 11.1, 9.5 Hz), 129.5 (d, J_{C-P} = 2.6 Hz), 127.3 (d, J_{C-P} = 10 Hz), 44.3 (dd, J_{C-P} = 65.6, 2.9 Hz), 42.4 (d, J_{C-P} = 13.4 Hz), 40.7 (d, J_{C-P} = 14.1 Hz), 39.4 (dd, J_{C-P} = 67.1, 2.6 Hz), 32.7 (d, J_{C-P} = 6.4 Hz), 32.5 (d, J_{C-P} = 1.7 Hz), 28.9 (d, J_{C-P} = 9.7 Hz), 28.3 (dd, J_{C-P} = 9.0, 3.5 Hz), 27.6 (d, J_{C-P} = 33 Hz), 25.3 (d, J_{C-P} = 3.1 Hz), 23.8 (d, J_{C-P} = 8.0 Hz), 21.5 (d, J_{C-P} = 1.1 Hz), 13.5 (d, J_{C-P} = 6.7 Hz), 13.4 (d, J_{C-P} = 12.6 Hz), 13.1 (d, J_{C-P} = 7.8 Hz), 12.6 (d, J_{C-P} = 13.4 Hz); ^{31}P NMR (162 MHz, C_6D_6) δ 60.6 (d, *J* =3.7 Hz), 2.5; IR (neat) ν 3050, 2957, 2928, 2869, 1446, 1170, 1148, 1128, 1112, 741, 632 cm^{-1}; HRMS calcd for $C_{22}H_{36}OP_2$ $[M+H]^+$: 379.2319, found 379.2314.



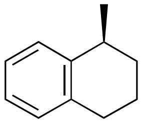
4

(1*R*)-1-[(*E*)-2-phenylvinyl]-1,2,3,4-tetrahydronaphthalene (4): (Modified literature procedure)[8]: A flame-dried round-bottomed flask equipped with an egg-shaped magnetic stirring bar was charged with sulfone **2e** (200 mg, 0.70 mmoles, 1.0 equiv) and purged under argon. THF (3.5 mL) was added and the solution was cooled to -78 °C. BuLi (248 μL, 1.6 M in hexane, 0.76 mmoles, 1.1 equiv) was added and the resulting yellow solution was stirred for 10 min. A solution of benzaldehyde (71 μL, 0.70 mmoles, 1 equiv) in THF (1.5 mL) at -78 °C was added and the mixture was stirred for 30 min. Ac_2O (132 μL, 1.40 mmoles, 2 equiv) was added at -78 °C and the mixture was stirred for 4 h at that temperature. The mixture was then warmed to room temperature and stirred for 1h. The reaction mixture was quenched with saturated aqueous NH_4Cl (8 mL). The biphasic mixture was extracted three

---

[8]. J. M. J. Williams in *Preparation of Alkenes: A Practical Approach*, (Ed.: A. Armstrong), Oxford University, Oxford, **1996**, pp. 71−77.

times with Et_2O (3 x 15 mL). The combined organic layers were then washed with saturated aqueous NaCl (20 mL). The organic solution was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude acetoxy sulfone was transferred into another flame-dried round-bottomed flask equipped with an egg-shaped magnetic stirring bar and it was purged with argon. The product was dissolved in MeOH (3 mL) and a minimum amount of THF (~2 mL). The solution was cooled to -20 °C with a cryostat and Na(Hg) 5% (698 mg) was added as quickly as possible in one portion. The mixture was stirred at -20 °C for 8 h. The reaction mixture was quenched with water (25 mL). The biphasic mixture was extracted three times with Et_2O (3 x 30 mL). The combined organic layers were then washed with saturated aqueous NaCl (30 mL). The organic solution was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude alkene was purified by flash chromatography on silica gel (0−2% EtOAc/hexane) to afford the desired alkene **4** (a 85:15 mixture of *E*/*Z* isomers, determined by ^{1}H NMR) as a volatile colorless oil (92 mg, 56% yield): enantiomeric excess (98%) was determined by SFC analysis (Chiralcel OD, 5% iPrOH, 2 mL/min, 40 °C, 150 bar: t_r (minor) 6.9 min, t_r (major) 7.4 min). R_f 0.37 (5% EtOAc/hexane); *E* (major isomer): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.16 (m, 9H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.36 (dd, *J* = 15.8, 8.3 Hz, 1H), 3.70 (q, *J* = 6.8 Hz, 1H), 2.93−2.86 (m, 2H), 2.14−1.99 (m, 2H), 1.90−1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 137.2, 136.7, 134.7, 130.1, 129.3, 128.9, 128.2, 126.7, 125.8, 125.7, 125.3, 42.6, 30.1, 29.3, 20.6; *Z* (minor isomer): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.16 (m, 9H), 6.69 (d, *J* = 11.5 Hz, 1H), 5.76 (t, *J* = 10.6 Hz, 1H), 4.13 (dq, *J* = 5.5, 5.4 Hz, 1H), 2.93−2.86 (m, 2H), 2.14−1.99 (m, 2H), 1.90−1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 137.1, 136.6, 136.3, 128.8, 128.5, 128.1, 128.0, 126.5, 125.8, 125.7, 125.4, 37.6, 31.3, 30.2, 21.5; IR (neat) ν 3022, 2928, 2856, 1599, 1489, 1448, 1205, 1151, 1068, 965, 747, 693, 631 cm^{-1}; HRMS calcd for $C_{18}H_{18}$ $[M+H]^+$: 235.1479, found 235.1481.



5

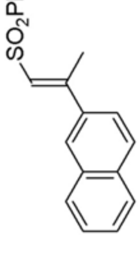
(1*S*)-1-methyl-1,2,3,4-tetrahydronaphthalene (5): (Modified literature procedure)[9]: A flame-dried round-bottomed flask equipped with an egg-shaped magnetic stirring bar was charged with sulfone **2e** (100 mg, 0.349 mmoles, 1.0 equiv) and purged under argon. The sulfone was dissolved in MeOH (3.5 mL) and a minimum amount of THF (~2 mL). Solid Na_2HPO_4 (200 mg, 1.4 mmoles, 4 equiv) was added at room temperature followed by Na(Hg) 5% (600 mg). The mixture was stirred at room temperature for 1 h. The reaction mixture was quenched with water (10 mL) and 1,3,5-trimethoxybenzene (0.05 mmoles, internal standard) was added to the mixture. The biphasic mixture was extracted three times with Et_2O (3 x 15 mL). The combined organic layers were then washed with saturated aqueous NaCl (20 mL). The organic solution was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (100% hexane) to afford the desired product **5** as a volatile colorless oil (96% yield by ^{1}H NMR according to the internal standard): enantiomeric excess (98%) was determined by GC analysis (Cyclodex B, 30 m, 35 °C, 0 min, 5 °C/min, 80 °C, 60 min: t_r (minor) 60.2 min, t_r (major) 61.1 min). R_f 0.59 (100% hexane); $[\alpha]_D^{20}$ 12.8° (*c* 1.2, dioxane)[6]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.24 (m, 1H), 7.19−7.10 (m, 3H), 2.96 (sex, *J* = 6.4 Hz), 2.87−2.78 (m, 2H), 1.99−1.88 (m, 2H), 1.79−1.76 (m, 1H), 1.62−1.57 (m, 1H), 1.33 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 136.5, 128.6, 127.7, 125.2, 125.0, 32.1, 31.3, 29.6, 22.3, 20.1. The physical and spectroscopic properties were in accordance with those described in the literature.[10]

---

[9]. B. M. Trost, H. C. Arndt, P. E. Strege, T. R. Verhoeven, *Tetrahedron Lett.* **1976**, *39*, 3477.

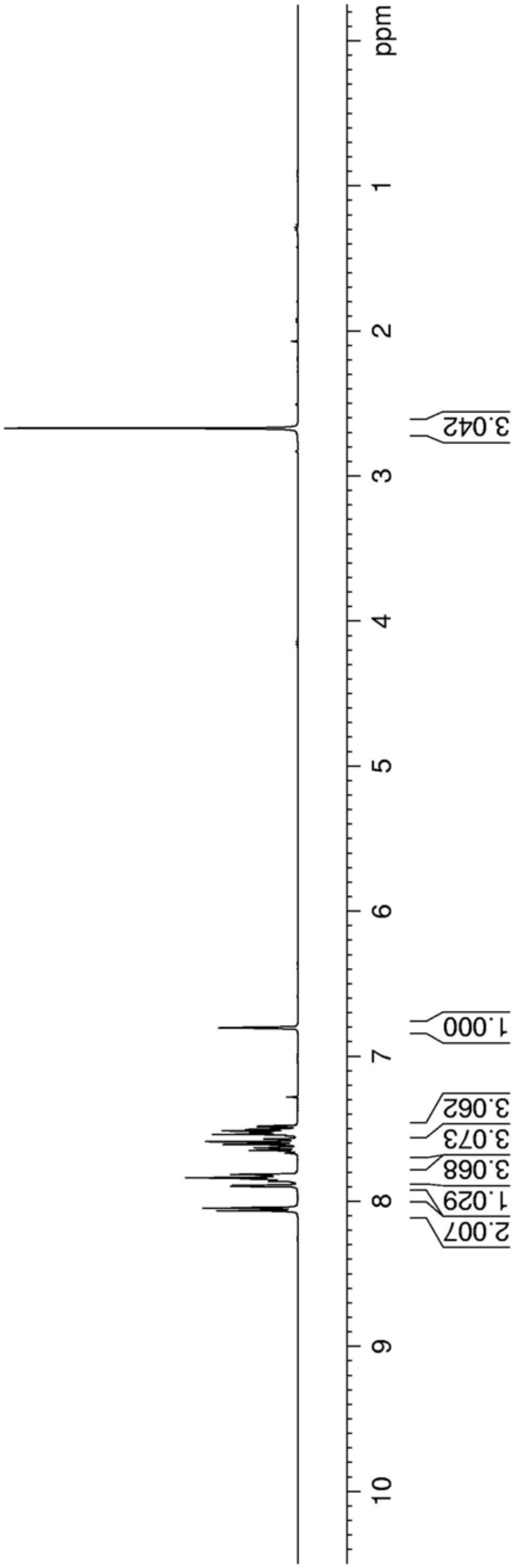
[10]. R. R. Cesati, III, J. Armas, A. H. Hoveyda, *Org. Lett.* **2002**, *4*, 395.

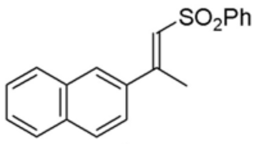
^{1}H and ^{13}C NMR Spectra of selected compounds



1c

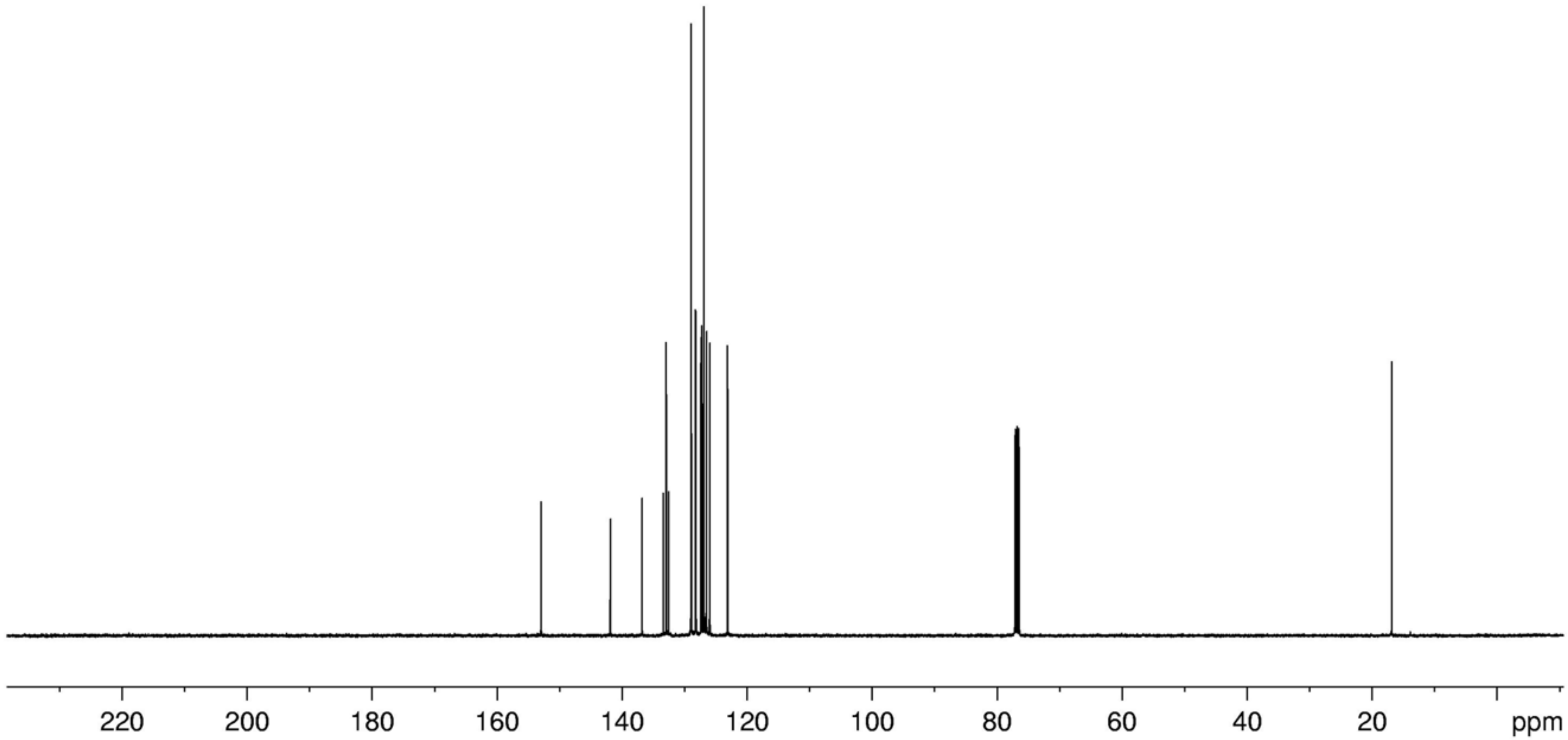
^{1}H NMR (400 MHz, CDCl$_3$)

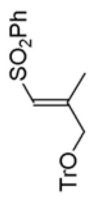




1c

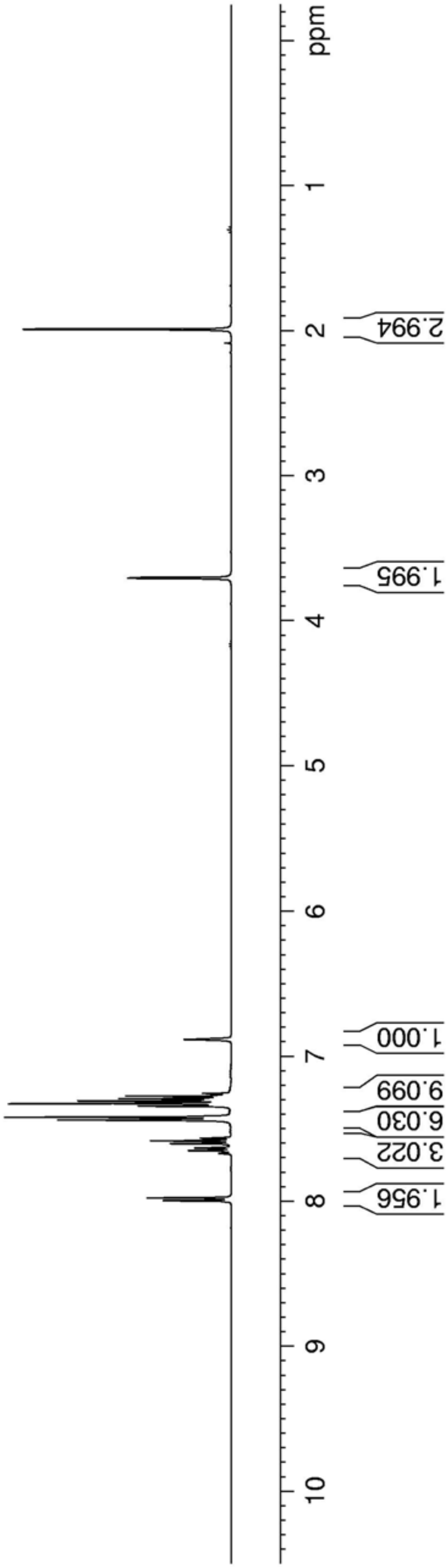
^{13}C NMR (100 MHz, CDCl$_3$)

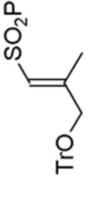




1f

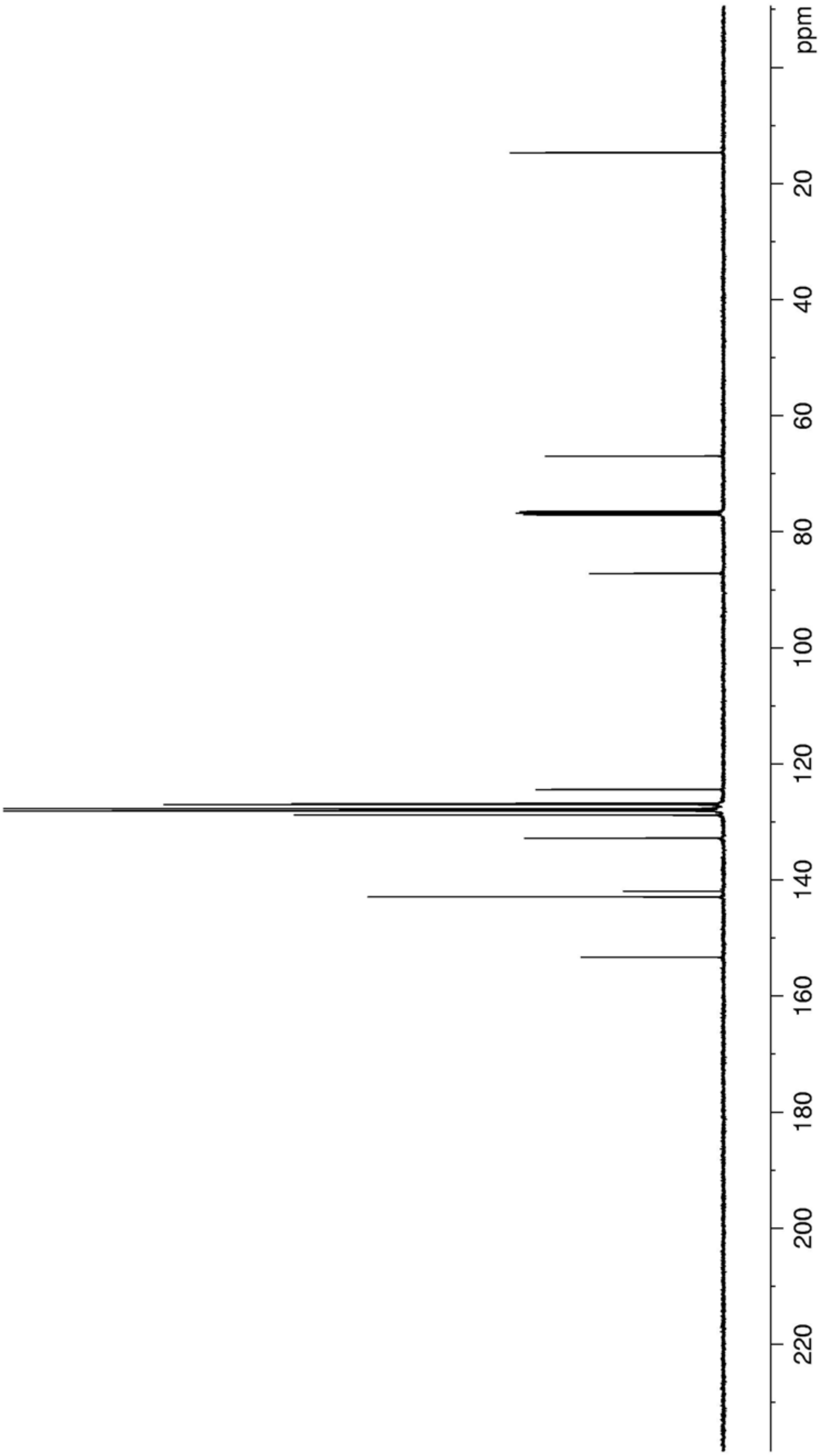
^{1}H NMR (400 MHz, CDCl$_3$)

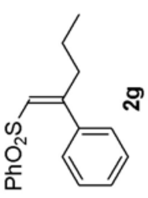




1f

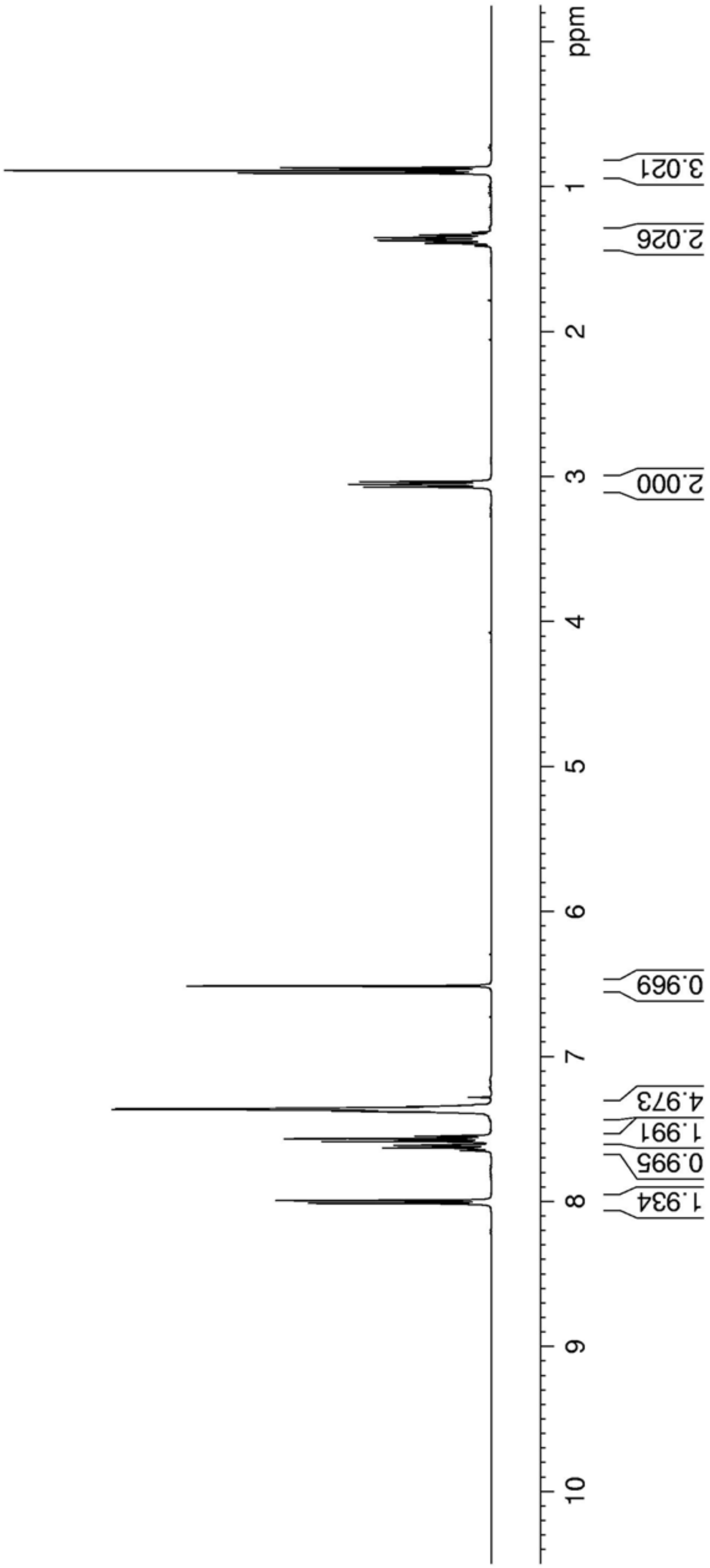
^{13}C NMR (100 MHz, $CDCl_3$)

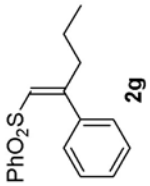




2g

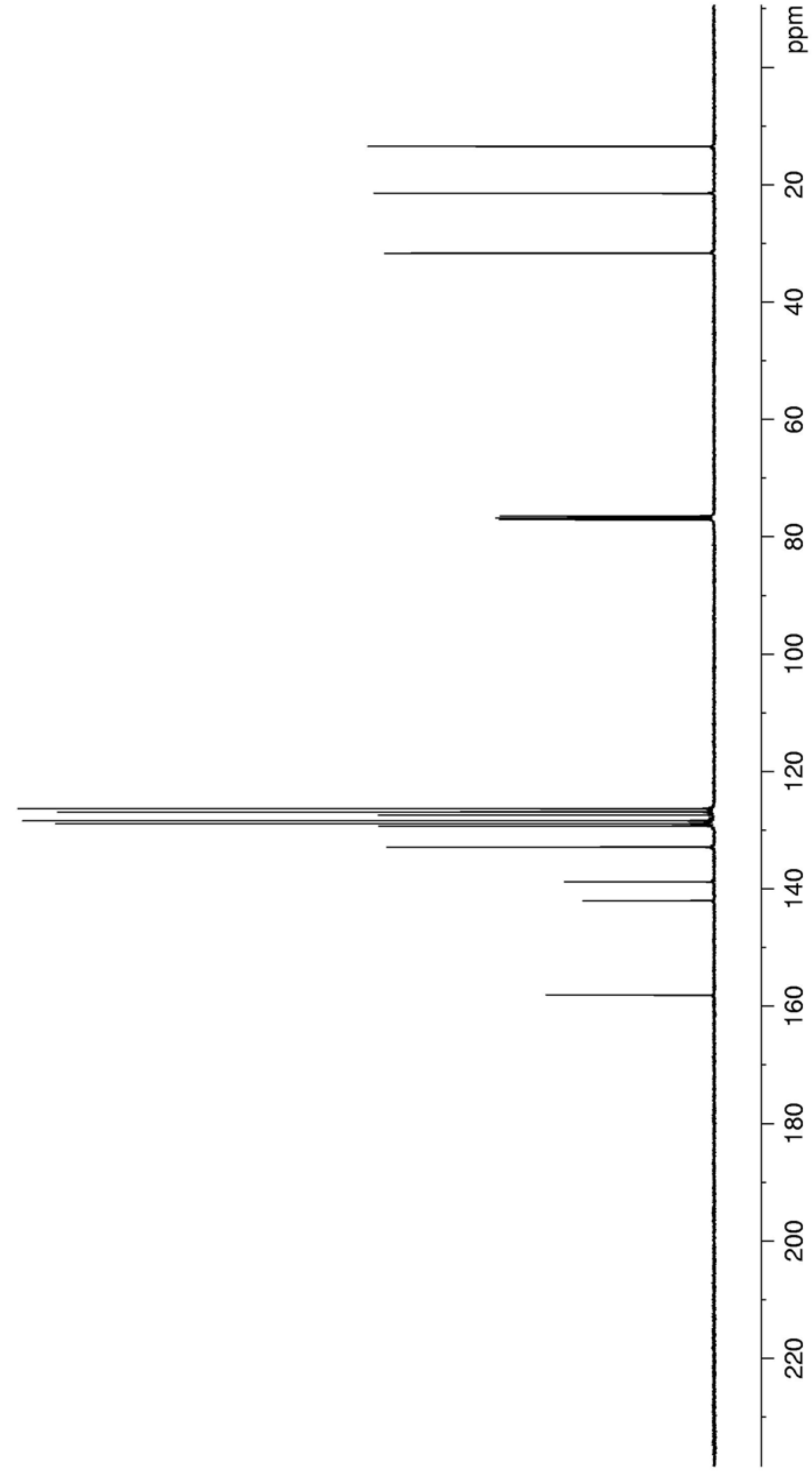
^{1}H NMR (400 MHz, CDCl$_3$)

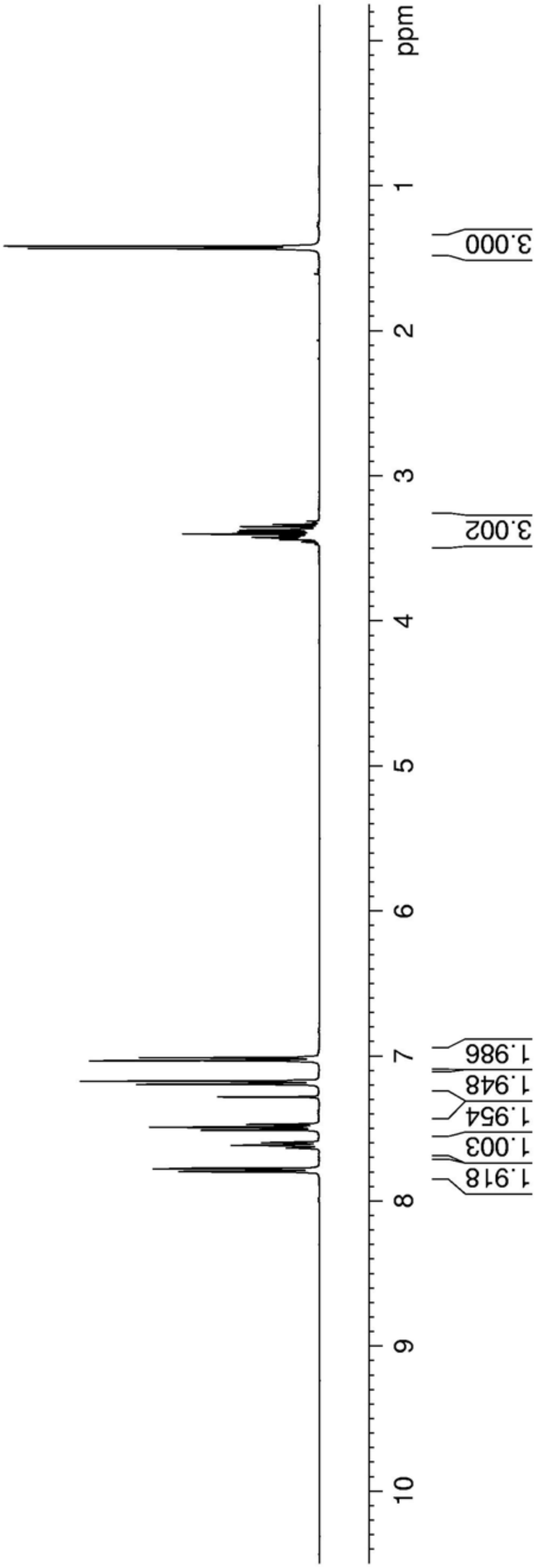


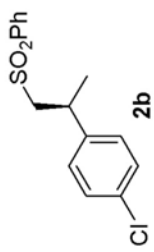


2g

^{13}C NMR (100 MHz, CDCl$_3$)

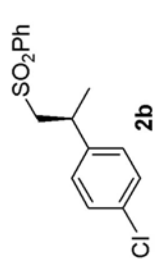






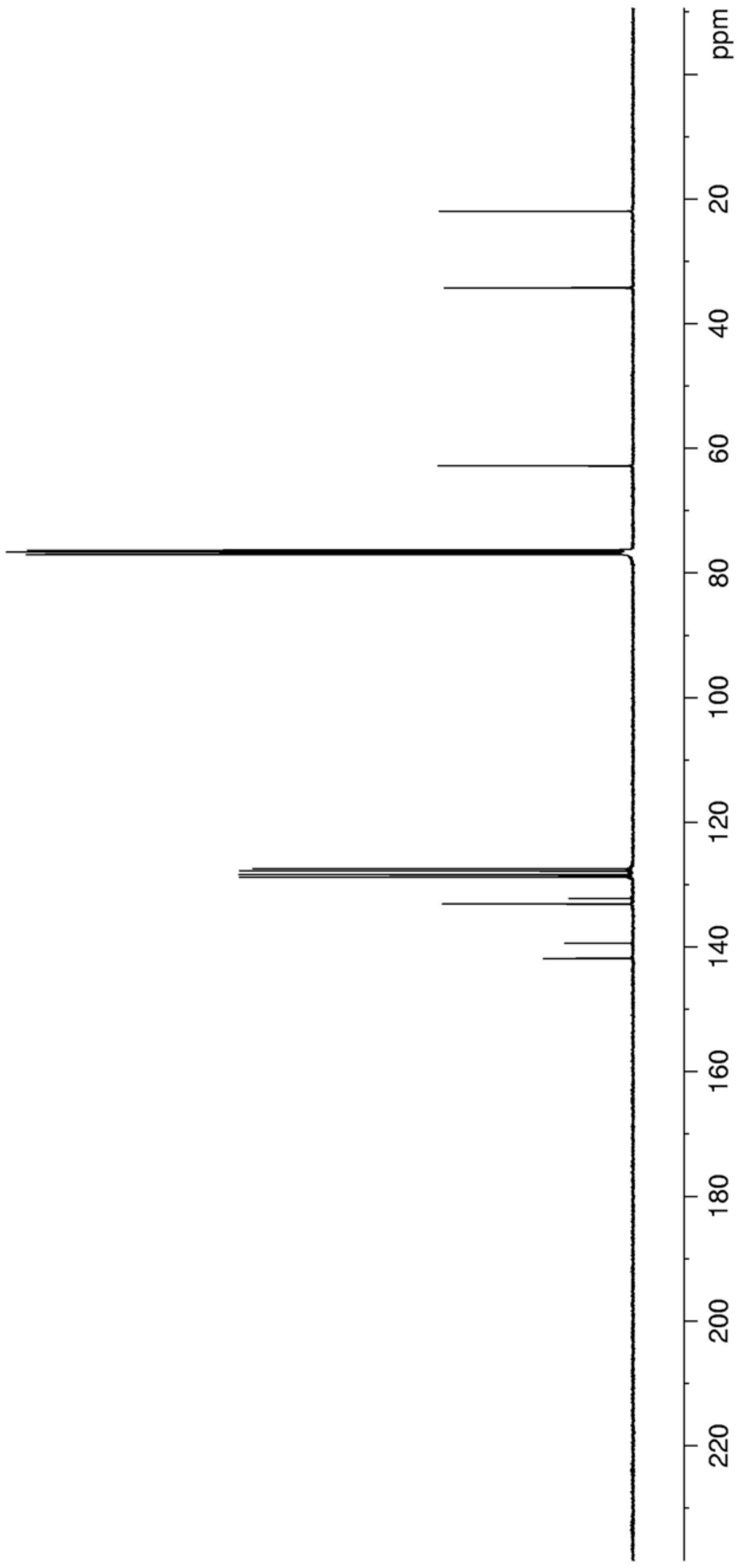
2b

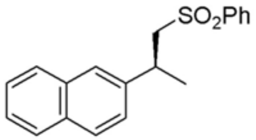
^{1}H NMR (400 MHz, CDCl$_3$)



2b

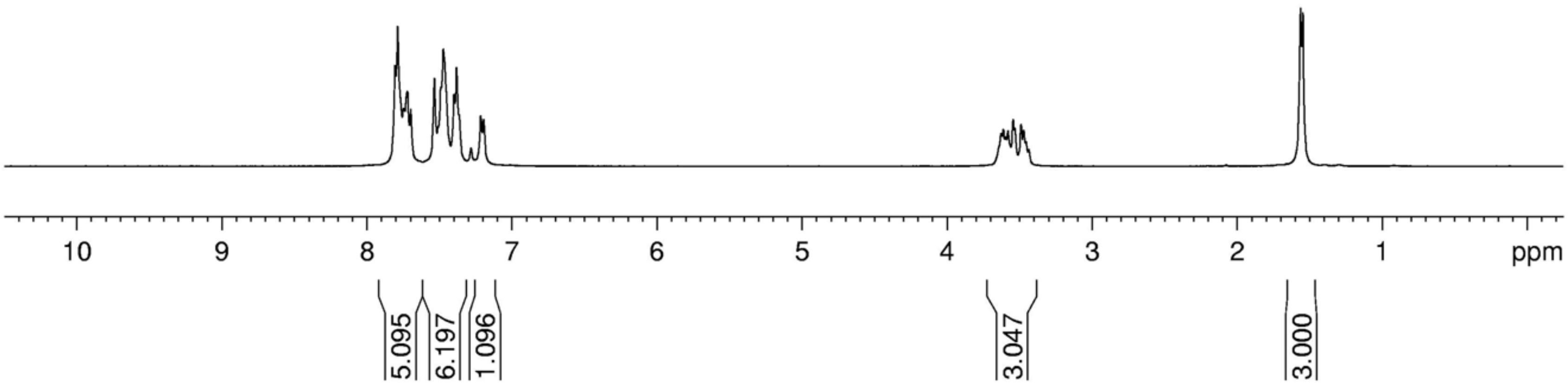
^{13}C NMR (100 MHz, CDCl$_3$)

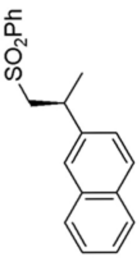




2c

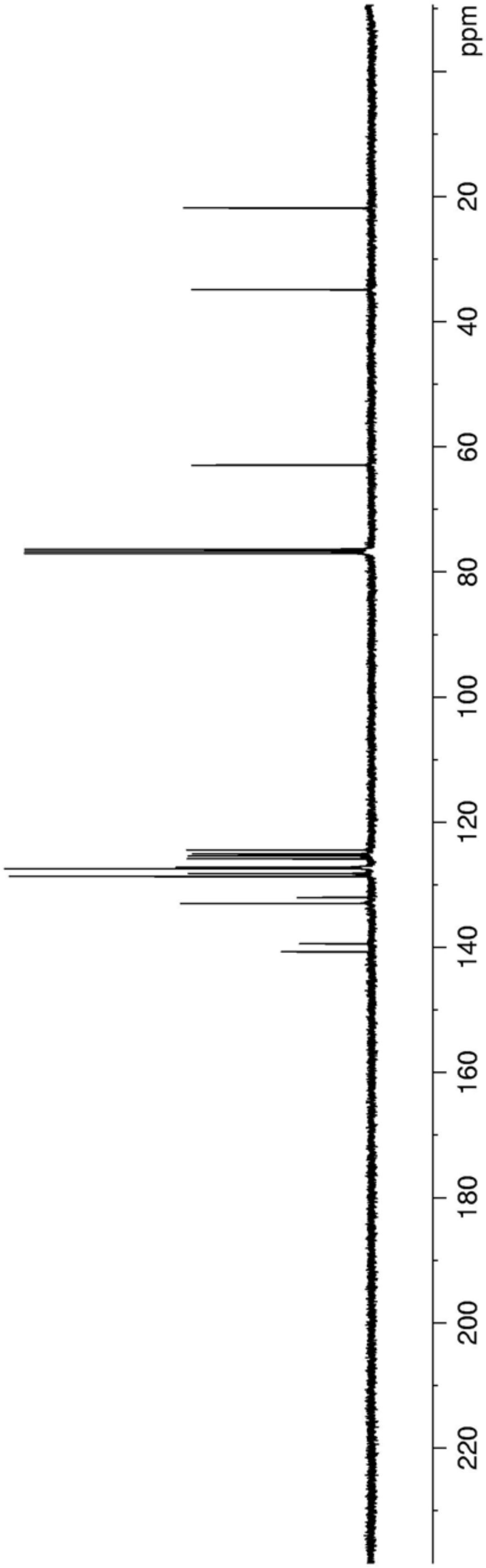
^{1}H NMR (400 MHz, CDCl$_3$)

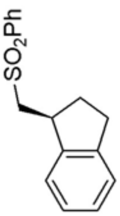




2c

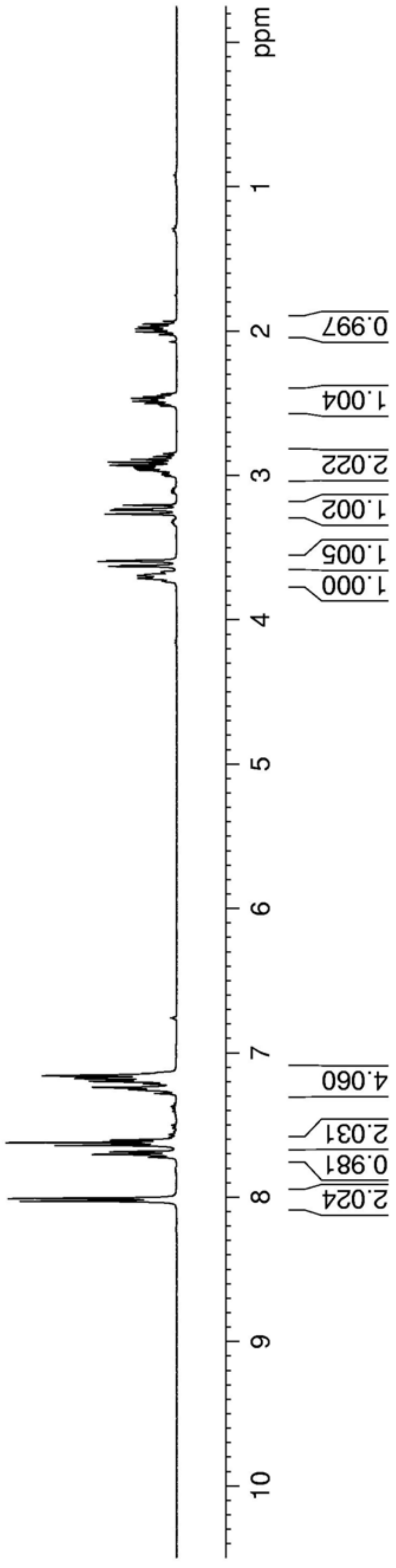
^{13}C NMR (100 MHz, CDCl$_3$)

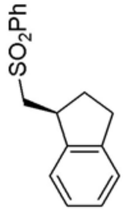




2d

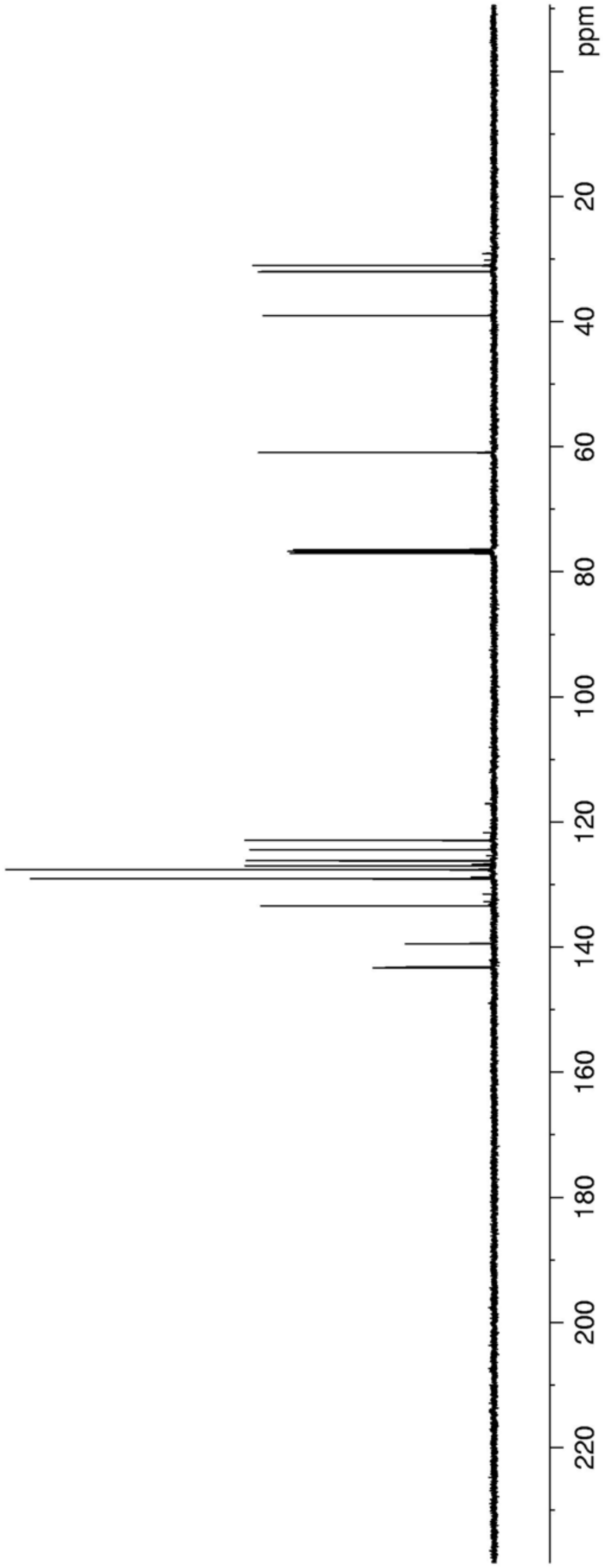
^{1}H NMR (400 MHz, CDCl$_3$)

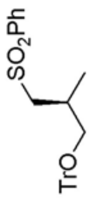




2d

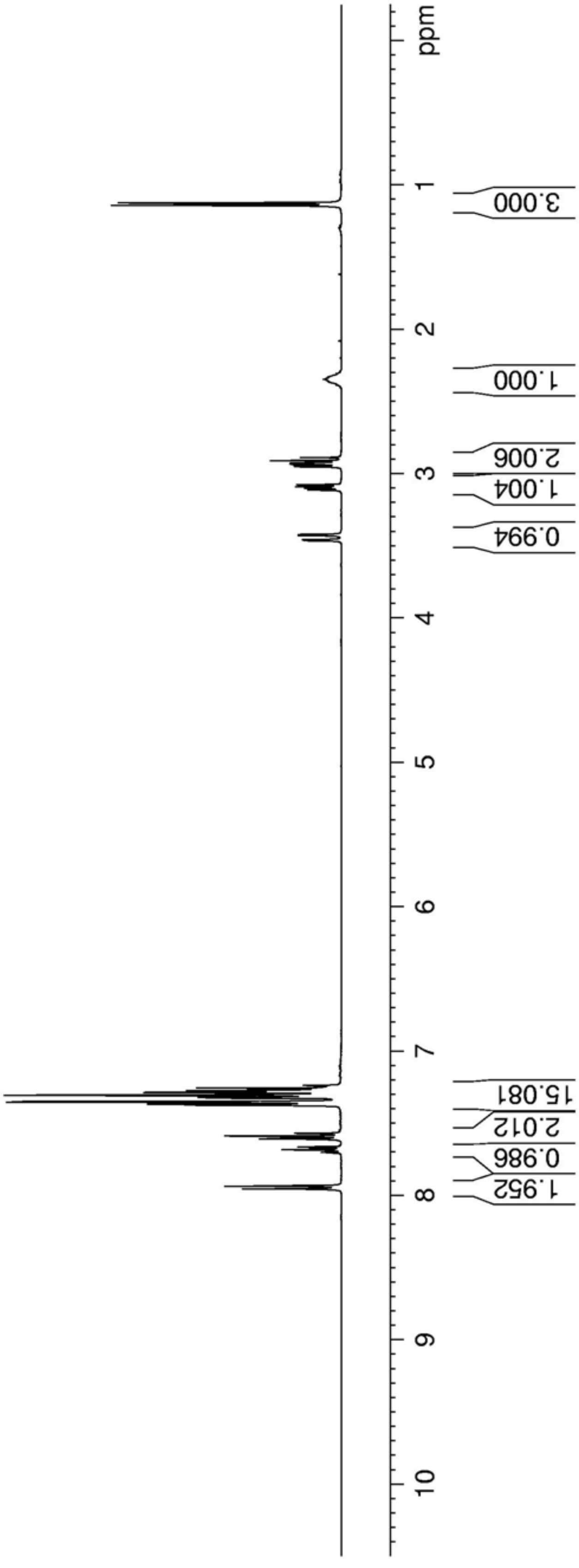
^{13}C NMR (100 MHz, CDCl$_3$)

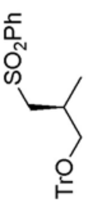




2f

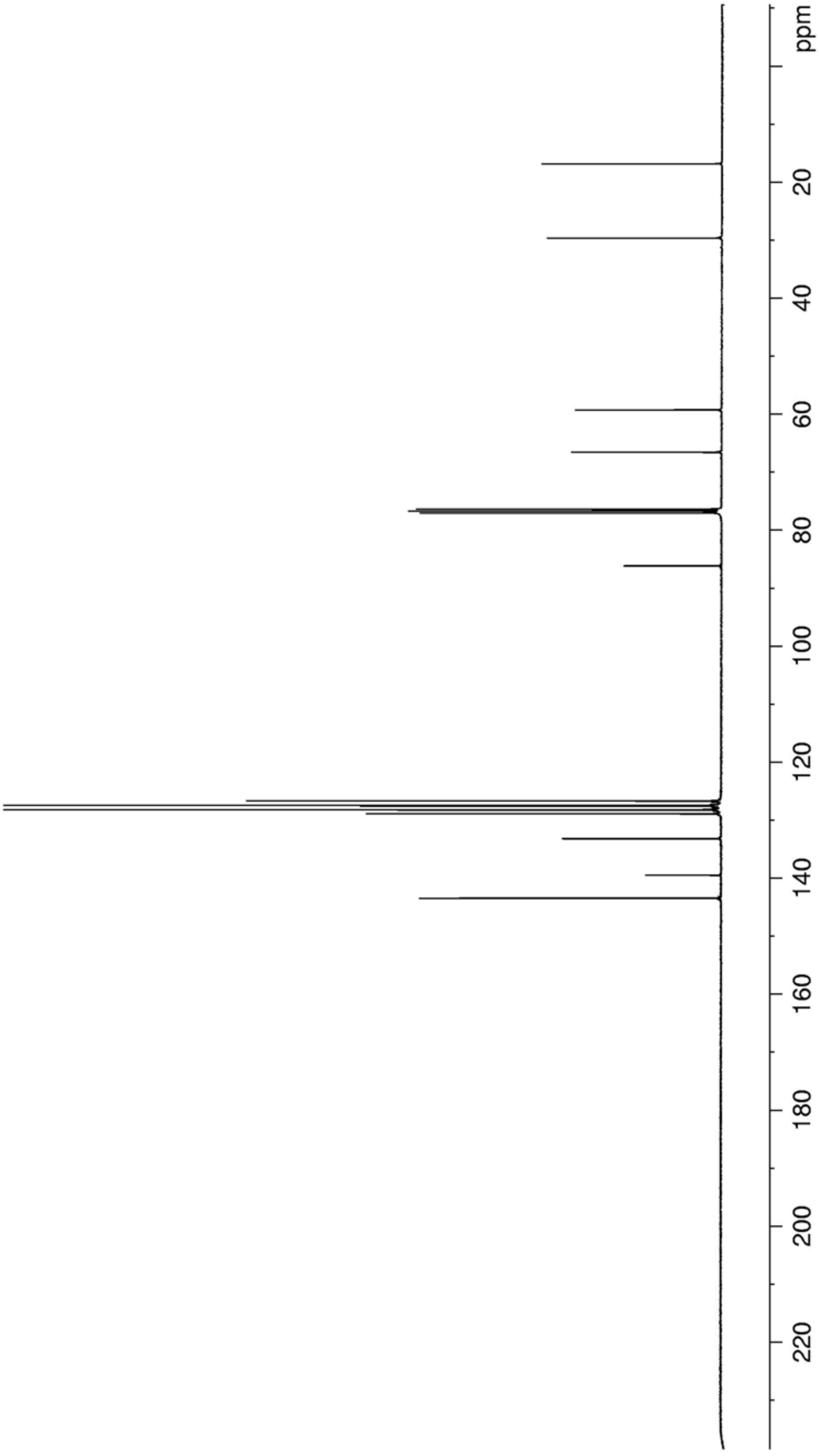
^{1}H NMR (400 MHz, CDCl$_3$)

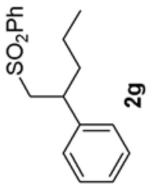




2f

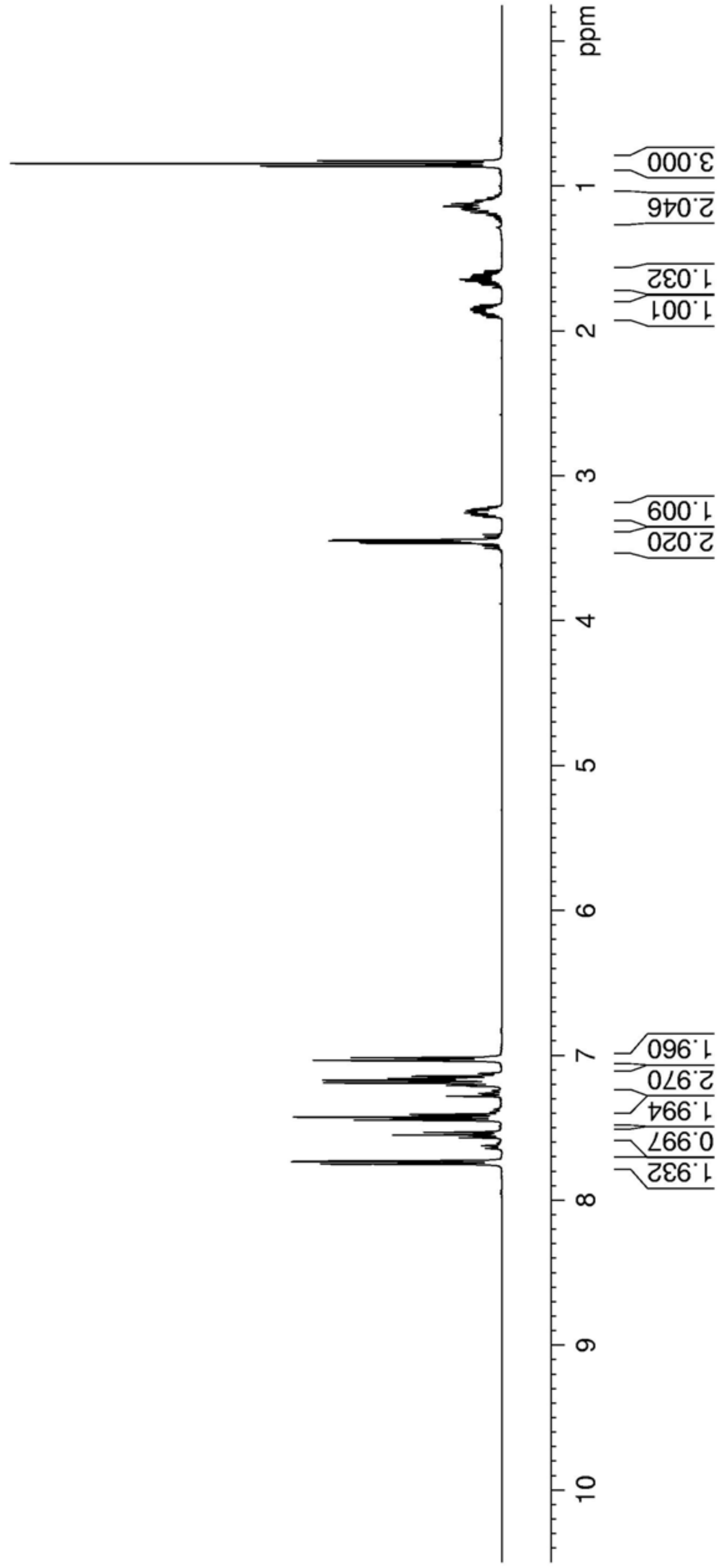
^{13}C NMR (100 MHz, CDCl$_3$)

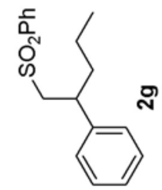




2g

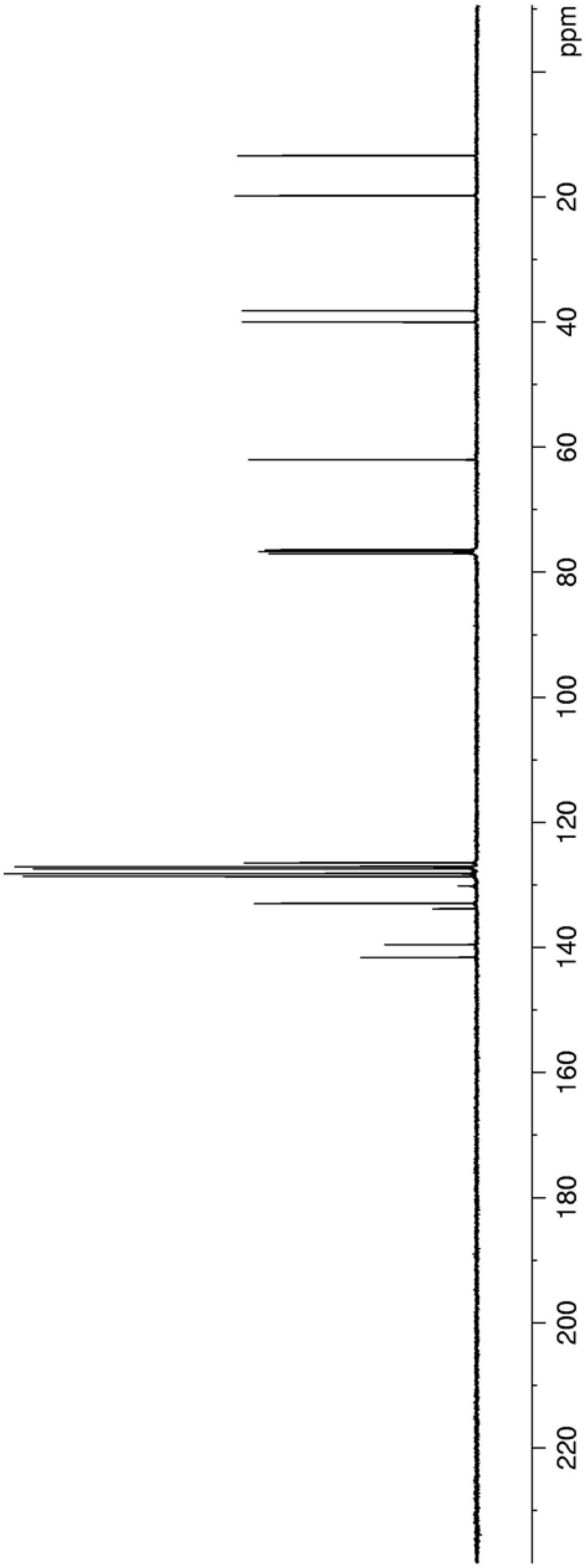
^{1}H NMR (400 MHz, CDCl$_3$)

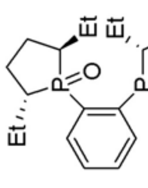




2g

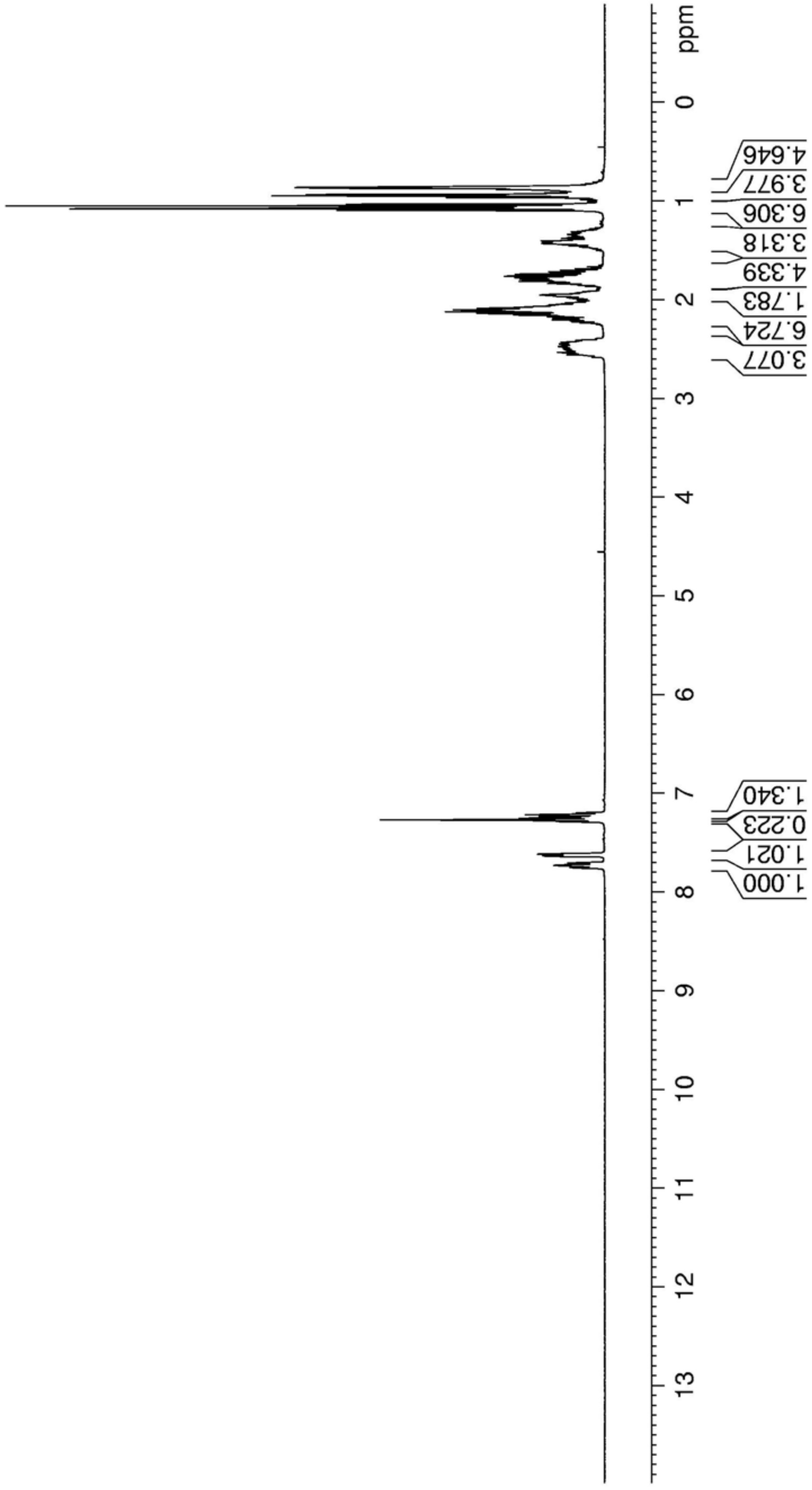
^{13}C NMR (100 MHz, CDCl$_3$)

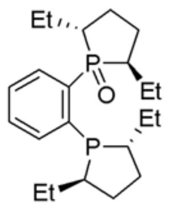




3b

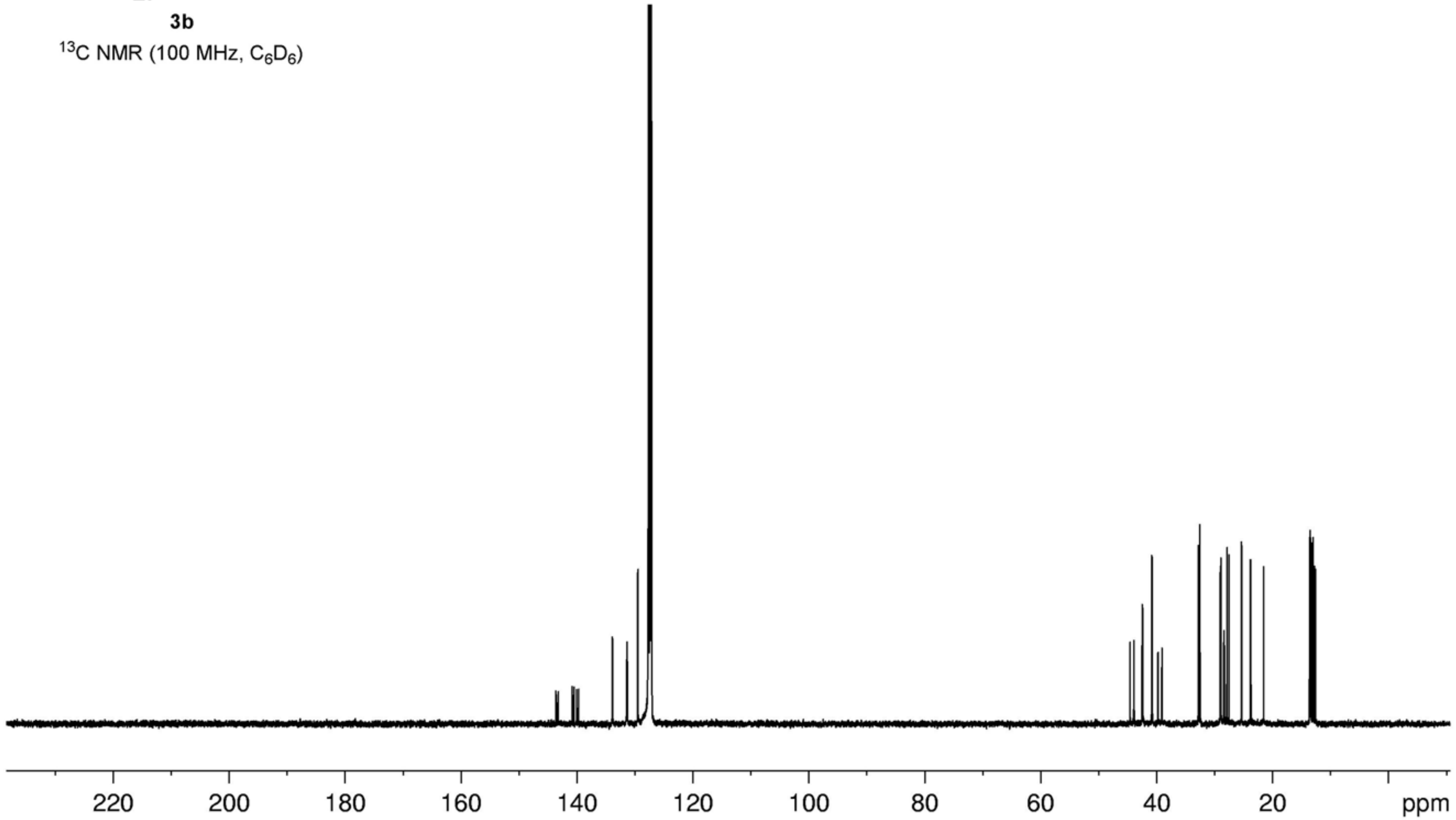
^{1}H NMR (400 MHz, C_6D_6)





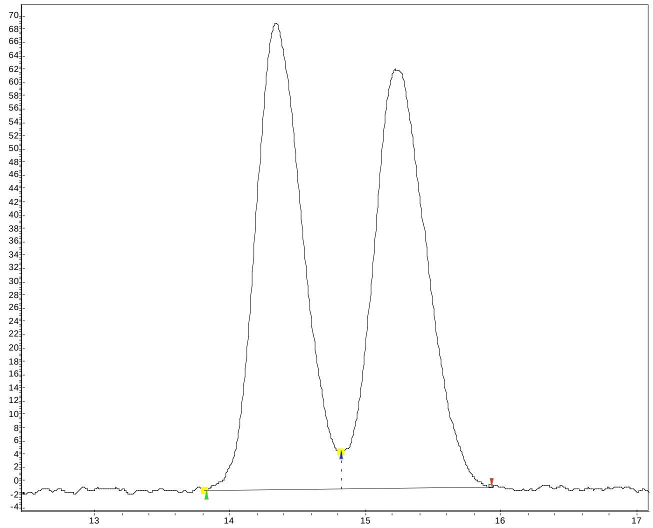
3b

^{13}C NMR (100 MHz, C_6D_6)

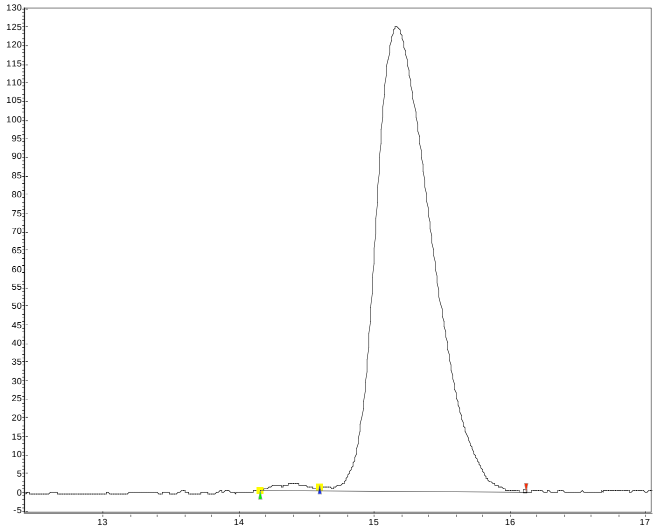


SFC/GC Traces of racemic and enantioenriched compounds

Compound **2a** (racemic and enantioenriched):

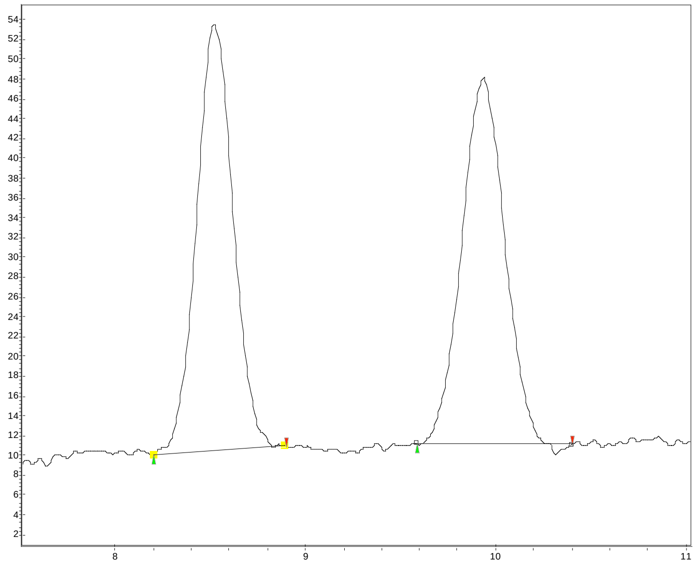


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	13.81	14.34	14.82	49.55	70.2	28.4	49.545
2	14.82	15.22	15.92	50.45	63	28.9	50.455
Total				100	133.2	57.3	100

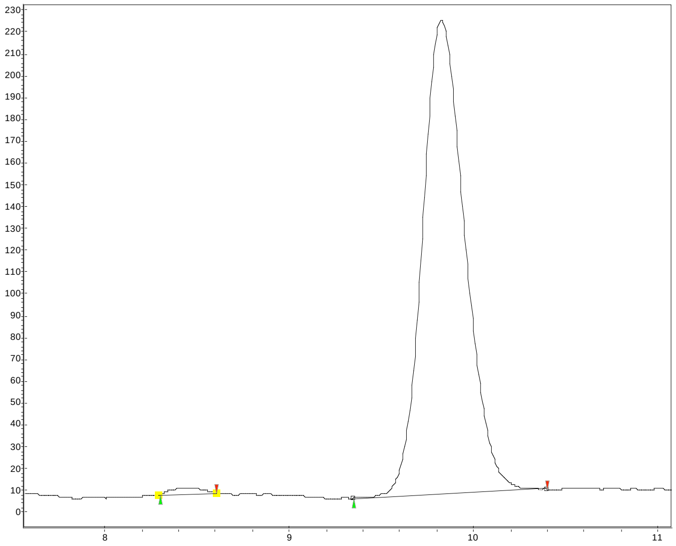


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	14.16	14.41	14.6	0.7	1.9	0.4	0.704
2	14.6	15.16	16.12	99.3	124.6	59.6	99.296
Total				100	126.5	60	100

Compound **2b** (racemic and enantioenriched):

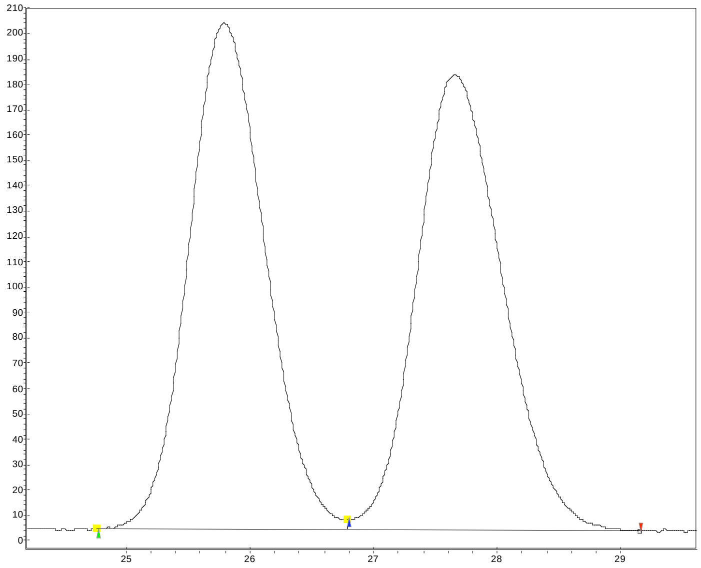


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	8.2	8.52	8.9	50.14	43	9.7	50.14
2	9.58	9.94	10.4	49.86	36.9	9.6	49.86
Total				100	80	19.3	100

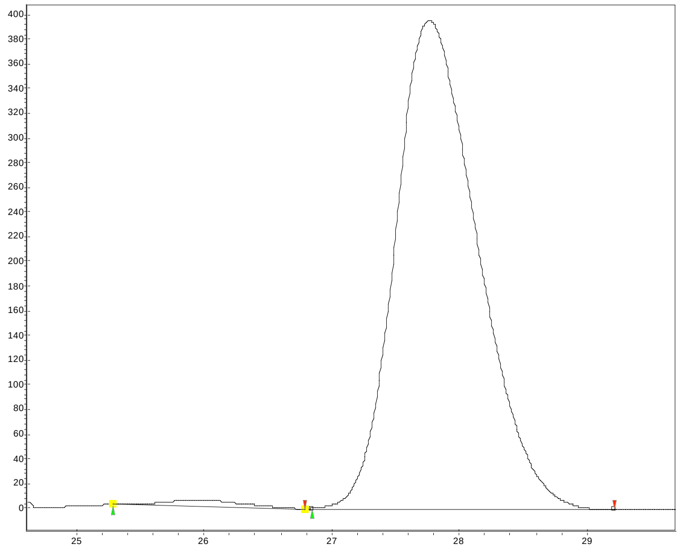


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	8.3	8.43	8.61	0.96	2.9	0.6	0.961
2	9.34	9.83	10.39	99.04	216.8	58.1	99.039
Total				100	219.7	58.7	100

Compound **2c** (racemic and enantioenriched):

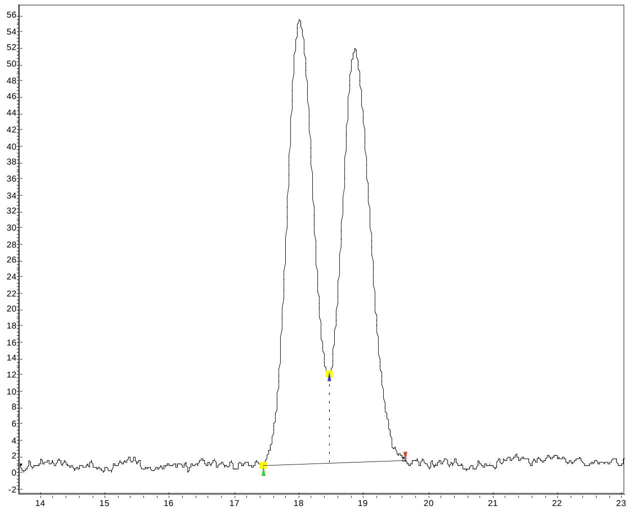


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	24.76	25.79	26.79	49.81	199.4	143.4	49.808
2	26.79	27.66	29.15	50.19	179.4	144.5	50.192
Total				100	378.8	287.9	100

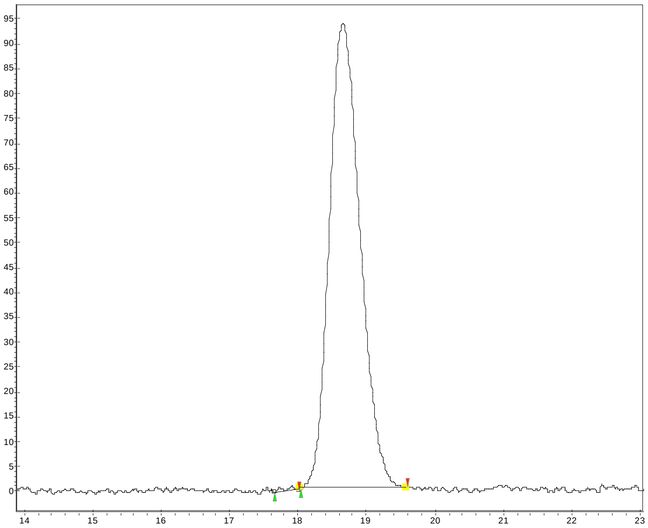


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	25.28	26.04	26.78	1.19	5.4	3.6	1.187
2	26.84	27.77	29.22	98.81	395.3	295.7	98.813
Total				100	400.7	299.2	100

Compound **2d** (racemic and enantioenriched):

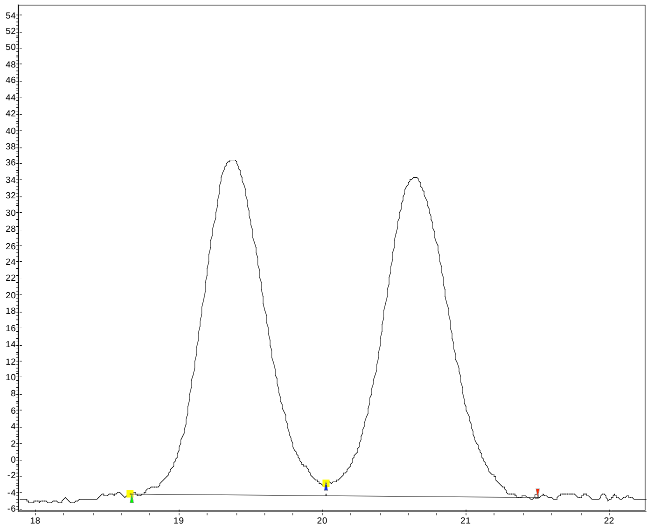


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	17.45	18.01	18.47	50	54.5	26.4	50.004
2	18.47	18.87	19.64	50	50.6	26.4	49.996
Total				100	105.1	52.8	100

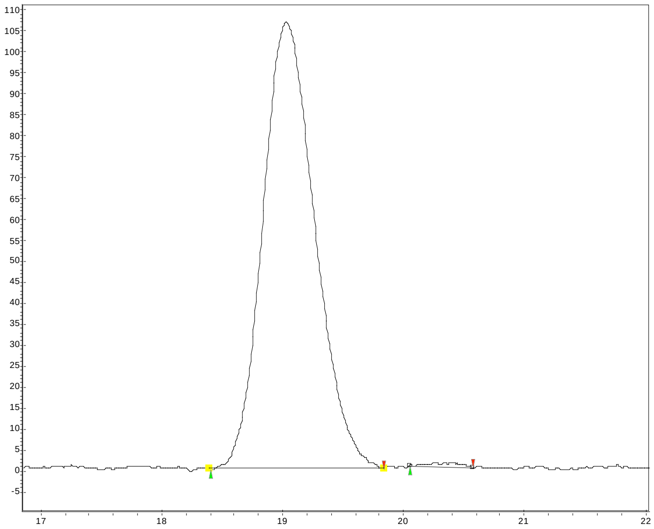


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
2	17.65	17.91	18.01	0.19	0.8	0.1	0.19
1	18.03	18.66	19.58	99.81	93.3	48.7	99.81
Total				100	94.2	48.8	100

Compound **2e** (racemic and enantioenriched):

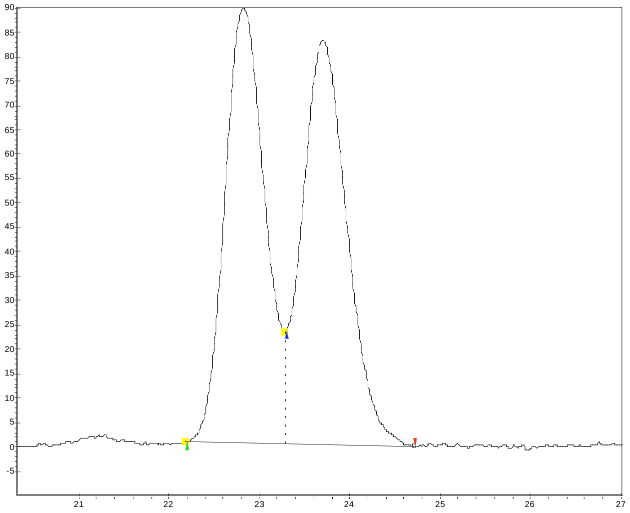


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	18.66	19.38	20.03	49.73	40.6	20.7	49.728
2	20.03	20.65	21.5	50.27	38.8	20.9	50.272
Total				100	79.4	41.5	100

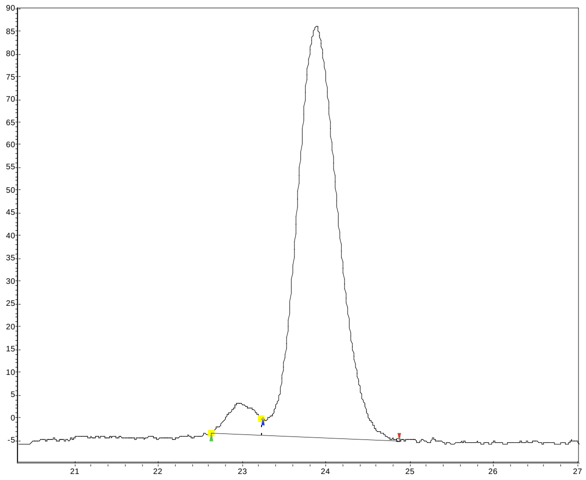


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	18.4	19.03	19.83	99.47	106.3	53.2	99.466
2	20.05	20.4	20.57	0.53	1.1	0.3	0.534
Total				100	107.4	53.5	100

Compound **2f** (racemic and enantioenriched):

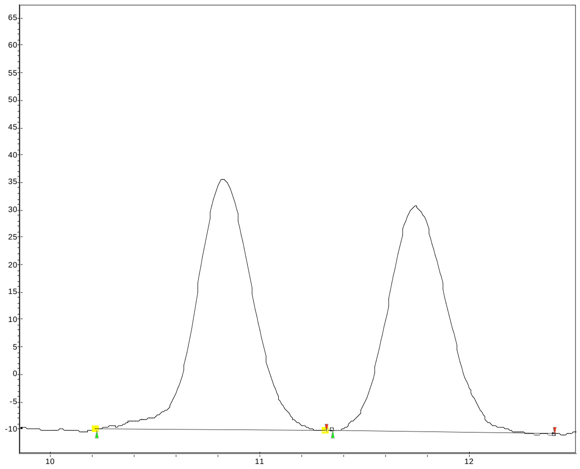


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	22.19	22.82	23.29	48.97	89	45.9	48.968
2	23.29	23.7	24.71	51.03	82.7	47.9	51.032
Total				100	171.7	93.8	100

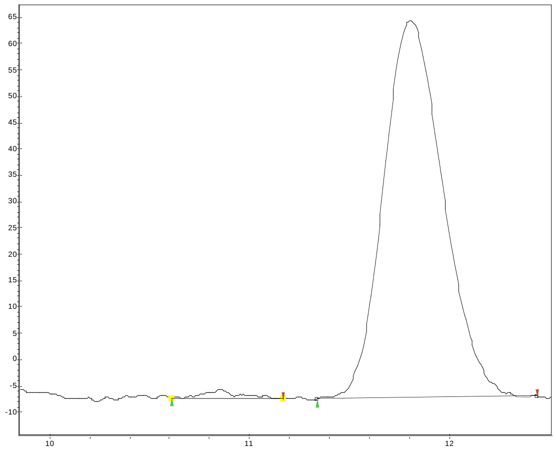


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	22.63	22.96	23.23	4.86	6.9	2.6	4.86
2	23.23	23.89	24.86	95.14	90.3	51.5	95.14
Total				100	97.2	54.1	100

Compound **2g** (racemic and enantioenriched):

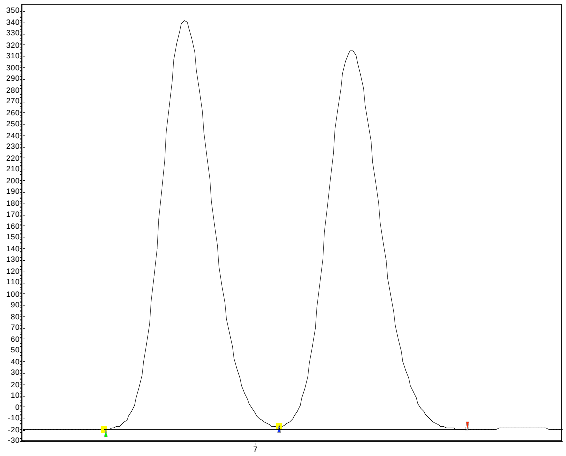


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	10.21	10.83	11.31	51.61	45.8	14.3	51.613
2	11.34	11.74	12.41	48.39	41	13.4	48.387
Total				100	86.9	27.8	100

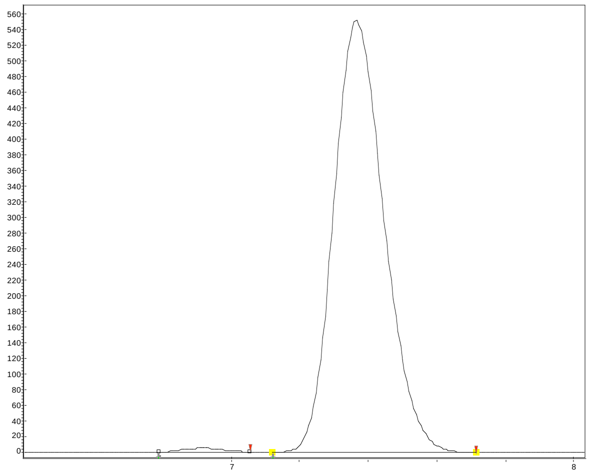


#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	10.61	10.85	11.16	1.3	1.8	0.3	1.297
2	11.34	11.81	12.44	98.7	71.6	24.7	98.703
Total				100	73.3	25.1	100

Compound **4** (racemic and enantioenriched):



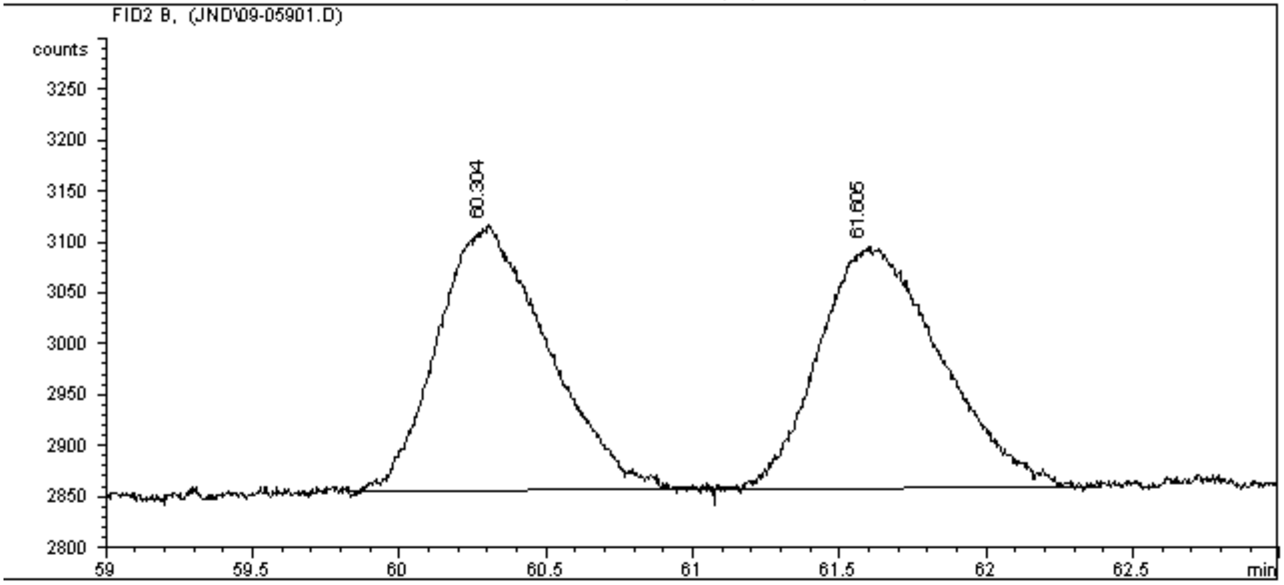
#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
1	6.6	6.81	7.06	50.86	361.7	57.5	50.861
2	7.06	7.25	7.56	49.14	335.2	55.5	49.139
Total				100	696.9	113	100



#	Start [Min]	Time [Min]	End [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area [%]
2	6.78	6.92	7.05	0.77	5.3	0.7	0.768
1	7.12	7.37	7.71	99.23	551.3	94.4	99.232
Total				100	556.5	95.1	100

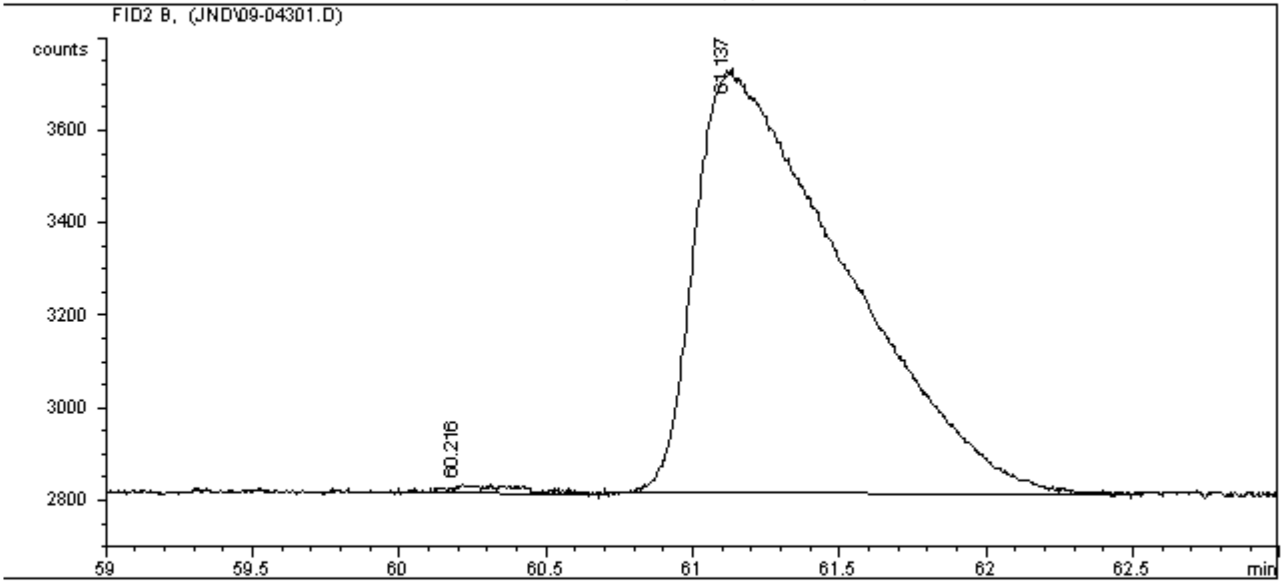
Compound **5** (racemic and enantioenriched):

```
Data File name:                          C:\HPCHEM\1\DATA\JND\09-05901.D
  Method name:                           C:\HPCHEM\1\METHODS\AC.M
```



```
Meas.RT        Area          Height           Area        Width        Symm.
  min        mAU*sec          mAU              %           min
---------------------------------------------------------------------------
  60.30      6783.0          260.0            49.5        0.435        0.821
  61.60      6922.1          238.9            50.5        0.483        0.707
---------------------------------------------------------------------------
```

```
Data File name:                          C:\HPCHEM\1\DATA\JND\09-04301.D
  Method name:                           C:\HPCHEM\1\METHODS\AC.M
```



```
Meas.RT        Area          Height           Area        Width        Symm.
  min        mAU*sec          mAU              %           min
---------------------------------------------------------------------------
  60.22       289.2           18.9             0.9        0.255        0.300
  61.14      3251->          919.7            99.1        0.589        0.331
---------------------------------------------------------------------------
```