Chiral Sulfinamide/Achiral Sulfonic Acid Co-Catalyzed Enantioselective Protonation of Enol Silanes

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Supporting Information

1. General Information

Materials Protonation reactions were performed in oven-dried 2-dram vials; all other reactions were performed in oven-dried round bottom flasks unless otherwise noted. The vials and flasks were fitted with rubber septa and reactions were conducted under air. Stainless steel syringes were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed using silica gel ZEOprep60 ECO 40–63 micron from American International Chemical, Inc. Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar, Strem, Lancaster or TCI, and used as received with the following exceptions: toluene, dichloromethane, tetrahydrofuran, diethyl ether, *t*-butyl methyl ether and methanol were dried by passing through columns of activated alumina; acetonitrile was dried by passing through a column of activated molecular sieves. Triethylamine and chlorotrimethylsilane were distilled from CaH_2 at 760 torr.

Instrumentation Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Varian Mercury-400 (400 MHz), Inova-500 (500 MHz) and Inova-600 (600 MHz) spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.27). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.0). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p=pentet, m = multiplet), coupling constants in Hertz (Hz), integration. Infrared (IR) spectra were obtained using a Bruker Optics Tensor 27 FTIR spectrophotometer. Data are represented as follows: frequency of absorption (cm^{-1}), intensity of absorption (s = strong). Optical rotations were measured using a 1 mL cell with a 0.5 dm path length on a Jasco DIP 370 digital polarimeter. High Resolution Mass Spectrometry (HRMS) data were obtained at the Harvard University mass spectrometry facility or on an Agilent Technologies 6120 quadrupole LC/MS instrument. Chiral HPLC analysis was performed using an Agilent Technologies 1200 series instrument with commercial Chiralpak and Chiralcel columns.

Abbreviations 2,4-diNBSA – 2,4-dinitrobenzenesulfonic acid, 2,6-(*t*-Bu)$_2$PhOH - 2,6-di-*t*-butyl phenol, ee = enantiomeric excess, HPLC = high performance liquid chromatography, DIPEA = diisopropylethylamine, Et_3N = triethylamine, AcOH = acetic acid, DCM = dichloromethane, TBME = *t*-butyl methyl ether, MeCN = acetonitrile, THF = tetrahydrofuran. LBA = Lewis acid-assisted Brønsted acid ($SnCl_4$ / 2,6-dimethylphenol)

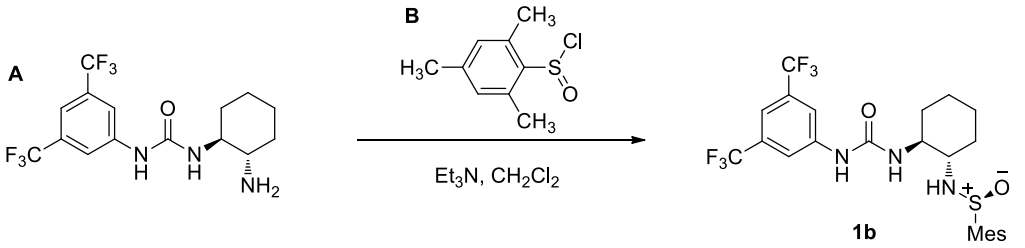
Computational Methods All theoretical work was performed using the Odyssey cluster supported by the FAS Sciences Division Research Computing Group at Harvard University. Calculations were carried out using density functional theory as implemented by the Gaussian 09[1] suite of programs. Structures were fully optimized in gas phase using the meta-GGA functional M05-2X[2] with the 6-31+g(d,p) basis set. Transition states were located using the quasi-Newton searching. Frequency analysis was performed

on all stationary points to verify that transition states had one imaginary frequency corresponding to the motion along the reaction coordinate.

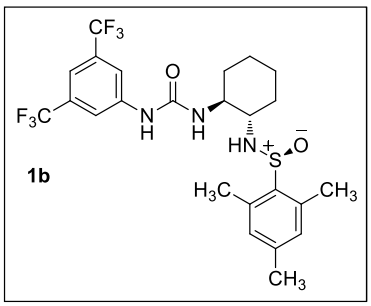
Cartesian coordinates of the optimized transition states were used as input for the NCIPLOT program.[3] Promolecular densities were generated for intermolecular interactions with an r value of 0.95. The default cutoff values for ρ (density) and RDG (reduced density gradient) of 0.2 and 1.0, respectively were used for construction of the isosurface. VMD viewer version 1.9 was used for visualization of the isosurfaces and image rendering. NCI surfaces correspond to s = 0.3 au with the color scale set to $-3.0 < \rho < 3.0$ au.

2. Catalyst preparation and characterization data

Catalysts **1a** and **1c** were prepared using previously reported methods.[4]



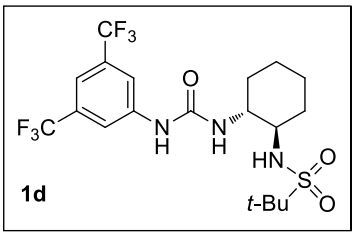
Mesitylenesulfinyl chloride (B)[5] Mesitylene (277 μL, 2.0 mmol, 1.0 equiv) was added dropwise to a suspension of bismuth (III) chloride (31 mg, 0.1 mmol, 5 mol%) in thionyl chloride (1.46 mL, 20 mmol, 10.0 equiv). The flask was equipped with a condenser and the reaction mixture was stirred in an oil bath at 75 ˚C for 1 h. The flask was cooled in an ice bath and the remaining thionyl chloride was removed under vacuum yielding a yellow liquid. In order to remove the bismuth catalyst, 50 mL hexanes was added, and the organic phase was filtered through a plug of cotton wool. The organic phase was concentrated to give mesitylenesulfinyl chloride **B** as a yellow liquid that was used without further purification.



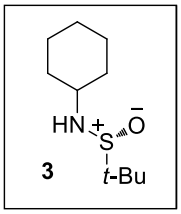
Catalyst *(S,S,S)*-**1b.** A solution of the crude mesitylenesulfinyl chloride **B** (2.0 mmol, 1.0 equiv) in dichloromethane was added dropwise to a solution of *(S,S)*-aminourea **A** (738 mg, 2.0 mmol, 1.0 equiv) and triethylamine (279 μL, 2.0 mmol, 1.0 equiv) in dichloromethane. The reaction mixture was stirred at room temperature for 2 h and then concentrated under vacuum. The crude product was purified by flash column chromatography, eluting with a gradient of 20–45% ethyl acetate in hexanes to give *(S,S,S)*-**1b** as a white solid (578 mg, 1.1 mmol, 54% yield) as well as the diastereomer *(S,S,R)*-**1b'** as a white solid (374 mg, 0.7 mmol, 35% yield). IR (thin film) 3225 (br), 2934, 1699 (s), 1574, 1560, 1476, 1391 (s), 1325 (s), 1277 (s), 1171, 1119 (s) 1067, 1024 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.38 (br s, 1H), 7.71 (br s, 2H), 6.93 (br, s, 2H), 6.84 (d, *J* = 7.7 Hz, 1H), 5.86 (d, *J* = 4.4 Hz, 1H), 3.73 (m, 1H), 3.04 (heptet, *J* = 4.8 Hz, 1H), 2.60 (s, 6H), 2.33 (s, 3H), 2.20–2.38 (m, 2H), 1.86–1.98 (m, 2H), 1.32–1.59 (m, 4H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ = 156.7, 141.5, 141.2, 136.6, 136.1, 131.8 (q, *J* = 33 Hz), 131.1, 123.2 (q, *J* = 173 Hz), 116.9, 114.8, 63.7, 52.4, 35.1, 33.5, 25.0, 25.0, 21.1, 19.3; HRMS (ESI^+) exact mass calculated for [M+H] ($C_{24}H_{28}F_6N_3O_2S$) requires m/z 536.173, found m/z 536.180; $[\alpha]_D^{23.3}$ = +180.4 (*c* = 1.0, $CHCl_3$).

(R,R)-**1d:** *tert*-butyl sulfonyl chloride (86 mg, 0.55 mmol, 1.1 equiv) was added to a solution of *(R,R)*-aminourea **A** (185 mg, 0.5 mmol, 1.0 equiv) and triethylamine (77 μL, 0.55 mmol, 1.1 equiv) in dichloromethane. The reaction mixture was stirred at room temperature for 2 h and then concentrated under vacuum. The crude product was purified by flash column chromatography, eluting with a gradient of 50–85% ethyl acetate in hexanes to give **1d** as a white solid (208 mg, 0.43 mmol, 85% yield). IR (thin film) 3360 (br), 2970 (s), 1709 (s), 1568, 1475, 1447, 1379 (s), 1366 (s), 1279 (s), 1223, 1161, 1128 (s), 951 (s) cm^{-1}; ^1H NMR (500 MHz, d_4-methanol) δ = 8.01 (s, 2H), 7.46 (s, 1H), 3.54 (dt, *J* = 11.0, 4.1 Hz, 1H), 3.11 (dt, *J* = 11.5, 4.1 Hz, 1H), 2.02–2.18 (m, 2H), 1.75–1.82 (m, 2H), 1.29–1.53 (m, 4H), 1.35 (s, 9H); ^{13}C NMR (125 MHz, d_4-methanol) δ = 157.2, 143.6, 133.2 (q, *J* = 33 Hz), 125.0 (q, *J* = 272 Hz), 119.3, 155.5, 60.5, 59.7, 55.6, 35.4, 34.5, 26.4, 26.1, 24.7 HRMS (ESI^+) exact mass calculated for [M+H] ($C_{19}H_{26}F_6N_3O_3S$) requires m/z 490.152, found m/z 490.162; $[\alpha]_D^{23.7}$ = +24.8 (*c* = 1.0, $CHCl_3$).

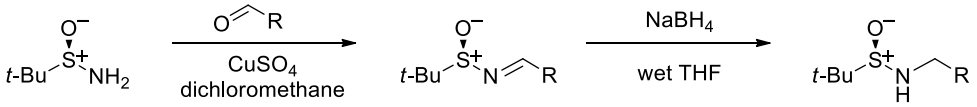


Catalyst **1e** was prepared using a previously reported method.[6]
Catalyst **2** was prepared using a previously reported method.[7]

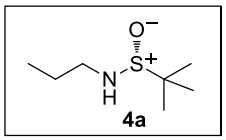


***(R)-N*-(cyclohexyl)-*tert*-butanesulfinamide (3):**[8] $Ti(OEt)_4$ (415 μL, 2.0 mmol, 2.0 equiv) was added to a solution of cyclohexanone (114 μL, 1.1 mmol, 1.1 equiv) and (*R*)-*tert*-butanesulfinamide (121 mg, 1.0 mmol, 1.0 equiv) in THF (4 mL). The reaction mixture was heated at 60 ˚C for 4 h. Upon completion the reaction mixture was cooled to –20 ˚C and $NaBH_4$ (115 mg, 3.0 mmol, 3.0 equiv) was added. After 5 h the reaction was quenched by slow addition of methanol (2 mL). The mixture was poured into brine with rapid stirring. The resulting suspension was filtered through a plug of celite and washed with ethyl acetate. The filtrate was washed with brine and extracted twice with ethyl acetate. The combined organic portions were dried over sodium sulfate, filtered and concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography, eluting with a gradient of 50–85% ethyl acetate in hexanes to give the desired product as a white solid (177 mg, 87% yield). IR (thin film) 3100 (br), 2930 (s), 2855, 1450, 1364, 1184, 1053 (s), 978 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.20 (m, 1H), 2.98 (br d, *J* = 4.4 Hz, 1H), 1.90–2.00 (m, 2H), 1.66–1.76 (m, 2H), 1.54–1.66 (m, 1H), 1.10–1.37 (m, 5H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 55.4, 54.4, 35.5, 34.3, 25.7, 25.0, 24.7, 22.8; HRMS (ESI^+) exact mass calculated for [M+H] ($C_{10}H_{22}NOS$) requires m/z 204.134, found m/z 204.146; $[\alpha]_D^{23.7}$ = –93.2 (*c* = 1.0, $CHCl_3$).

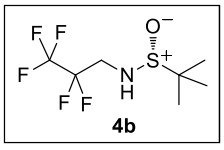
General procedure A for the synthesis of sulfinamide catalysts (4a–4e): Sulfinamide catalysts were prepared following a procedure developed by Ellman et al.[9]



Anhydrous copper (II) sulfate (480 mg, 3.0 mmol, 3.0 equiv) was added to a solution of aldehyde (1.1 mmol, 1.1 equiv) and *(R)-tert*-butanesulfinamide (121 mg, 1.0 mmol, 1.0 equiv) in dichoromethane (0.5 mL, 2.0 M). The reaction mixture was stirred at room temperature for 20 h, diluted with dichloromethane and filtered through a plug of Celite. The solution was concentrated *in vacuo* and dissolved in wet tetrahydrofuran (2 mL). Sodium borohydride (114 mg, 3.0 mmol, 3.0 equiv) was added and the mixture was stirred for 2 h. The reaction was quenched by dropwise addition of saturated aqueous Rochelle's salt (5 mL) and extracted with diethyl ether (2 x 10 mL). The organic phase was washed with brine (5 mL), dried with sodium sulfate, filtered and concentrated. The crude product was purified by flash column chromatography, eluting with a gradient of 55–100% diethyl ether in hexanes.

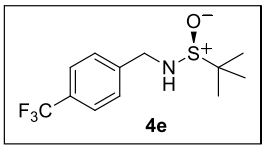


***(R)-N*-(*n*-propyl)-*tert*-butanesulfinamide (4a)** was obtained as a colorless oil (142 mg, 87% yield). IR (thin film) 3200 (br), 2960 (s), 2934, 2874, 1475, 1458, 1364, 1204, 1045 (s), 899 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.13–3.20 (m, 2H), 3.03 (dhex, J = 6.9, 1.6 Hz, 1H), 1.58 (hex, J = 7.2 Hz, 2H), 1.21 (s, 9H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 55.5, 47.5, 24.3, 22.6, 11.3; MS (ESI-APCI) exact mass calculated for [M+H] ($C_7H_{18}NSO$) requires m/z 164.1, found m/z 164.1; $[\alpha]_D^{22.8}$ = –80.4 (c = 1.0, $CHCl_3$).[10]



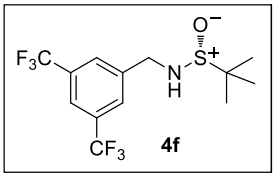
***(R)-N*-(2,2,3,3,3-pentafluoropropyl)-*tert*-butanesulfinamide (4b)** was obtained as a white solid (185 mg, 73% yield). IR (thin film) 3196 (br), 2950, 1352, 1294, 1281, 1223 (s), 1204, 173, 1119 (s), 1061 (s), 959, 912 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 3.84–3.66 (m, 2H), 3.55 (t, J = 7.0 Hz, 1H), 1.25 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 118.8 (qt, J = 286, 35 Hz), 113.2 (tq, J = 254, 37 Hz), 57.1, 45.6 (t, J = 24 Hz), 22.5; HRMS (ESI^+) exact mass calculated for [M+H] ($C_7H_{13}F_5NSO$) requires m/z 254.056, found m/z 254.071; $[\alpha]_D^{23.2}$ = –56.4 (c = 1.0, $CHCl_3$).

***(R)-N*-benzyl-*tert*-butanesulfinamide (4d)** was obtained as a white solid (177 mg, 84% yield) and ^1H NMR was in agreement with the literature.[11]



***(S)-N*-(4-trifluoromethylbenzyl)-*tert*-butanesulfinamide (4e)** was obtained as a white solid (220 mg, 79% yield). IR (thin film) 3187 (br), 2974, 2928, 2866, 1458, 1420, 1367, 1323 (s), 1161 (s), 1123 (s), 1111 (s), 1067 (s), 1040 (s), 1015 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.62 (d, J = 8.2 Hz, 2H), 7.48 (d, J =

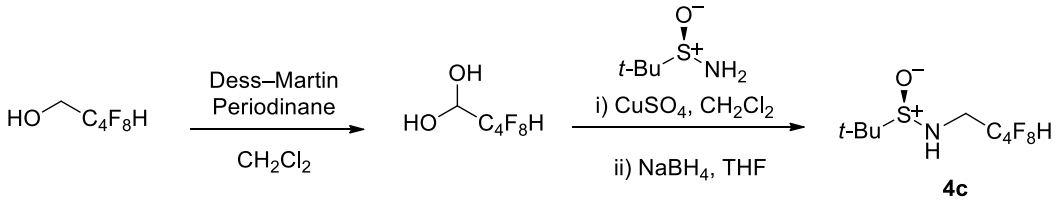
8.2 Hz, 2H), 4.42 (dd, *J* = 14.7, 5.0 Hz, 1H), 4.36 (dd, *J* = 14.2, 6.7 Hz, 1H), 3.59 (br s, 1H), 1.26 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 142.6, 130.0 (q, *J* = 32 Hz), 128.4, 125.6 (q, *J* = 4 Hz), 124.1 (q, *J* = 272 Hz), 56.1, 48.9, 22.7; HRMS (ESI^+) exact mass calculated for [M+H] ($C_{12}H_{17}F_6NOS$) requires m/z 280.090, found m/z 280.100; $[\alpha]_D^{23.2}$ = +62.0 (*c* = 0.1, $CHCl_3$).



4f

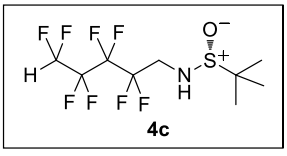
***(R)-N*-(3,5-bis(trifluoromethyl)benzyl)-*tert*-butanesulfinamide (4f)** was obtained as a white solid (271 mg, 78% yield). IR (thin film) 3300 (br), 2978, 2870, 1460, 1381, 1350, 1279 (s), 1228, 1171 (s), 1132 (s), 1055 (s), 887 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.81 (s, 3H), 4.47 (dd, *J* = 14.7, 5.4 Hz, 2H), 4.40 (dd, *J* = 14.7, 5.4 Hz, 1H), 3.66 (br s, 1H), 1.27 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 141.3, 132.1 (q, *J* = 33 Hz), 128.2 (q, *J* = 3 Hz), 123.2 (q, *J* = 273 Hz), 121.7 (q, *J* = 4 Hz), 56.5, 48.5, 22.8; HRMS (ESI^+) exact mass calculated for [M+H] ($C_{13}H_{16}F_6NOS$) requires m/z 348.078, found m/z 348.089; $[\alpha]_D^{23.7}$ = –41.2 (*c* = 1.0, $CHCl_3$).

***(R)-N*-(5,5,4,4,3,3,2,2-octafluoropentyl)-*tert*-butanesulfinamide (4c)**:



4c

Dess–Martin periodinane (3.3 g, 7.8 mmol, 1.3 equiv) was added to 2,2,3,3,4,4,5,5-octafluoropentanol (836 mL, 6.0 mmol, 1.0 equiv) in dichloromethane (20 mL). The reaction was stirred for 2 h at room temperature and quenched with an aqueous solution of 1:1 sodium bicarbonate/sodium thiosulfate. The water layer was extracted with diethyl ether (2 x 50 mL) and the combined organic phases were washed with brine, dried with sodium sulfate, filtered and concentrated to provide the crude hydrate that was used without further purification. Anhydrous copper (II) sulfate (2.8 g, 18.0 mmol, 3.0 equiv) was added to a solution of the crude hydrate (6.0 mmol, 1.0 equiv) and *(R)-tert*-butanesulfinamide (726 mg, 6.0 mmol, 1.0 equiv) in dichoromethane (2.0 mL). The reaction mixture was stirred at room temperature for 20 h, diluted with dichloromethane and filtered through a plug of celite. The solution was concentrated and dissolved in wet tetrahydrofuran (10 mL). Sodium borohydride (684 mg, 18.0 mmol, 3.0 equiv) was added and the mixture was stirred for 2 h. The reaction was quenched by dropwise addition of saturated aqueous Rochelle's salt (20 mL) and extracted with diethyl ether (2 x 100 mL). The organic phase was washed with brine (20 mL), dried with sodium sulfate, filtered and concentrated. The crude product was purified by flash column chromatography, eluting with a gradient of 55–100% diethyl ether in hexanes to give *(R)-N*-(5,5,4,4,3,3,2,2-octafluoropentyl)-*tert*-butanesulfinamide (**4c**) as a white solid (1.37 g, 4.1 mmol, 68% yield). IR (thin film) 3204 (br), 2970, 1460, 1395, 1368, 1289, 1228, 1165 (s), 1126 (s), 1061 (s), 955, 901, 806, 762 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.06 (tt, *J* =52.0, 5.3 Hz, 1H), 3.66–3.89 (m, 2H), 3.64 (br s, 1H), 1.26 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 115.7 (tt, *J* = 255, 31 Hz),

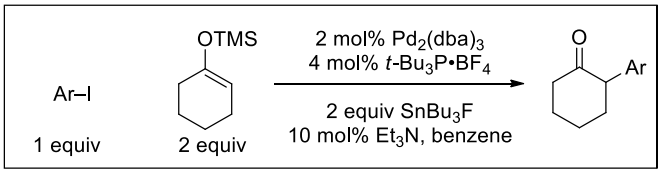


4c

111.0 (m), 110.1 (m), 107.6 (tt, J = 254, 31 Hz), 57.0, 45.8 (t, J = 23 Hz), 22.4; HRMS (ESI^+) exact mass calculated for [M+H] ($C_9H_{14}F_8NOS$) requires m/z 336.059, found m/z 336.070; $[\alpha]_D^{23.0}$ = –39.0 (c = 1.0, $CHCl_3$).

3. Substrate Preparation and Characterization Data

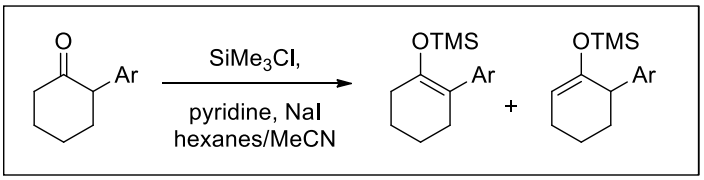
Synthesis of 2-aryl cyclic ketones: All α-aryl cyclic ketones were prepared by α-arylation of trimethylsilyl (TMS) enol ethers with aryl halides as developed by Rawal et al.[12]



General procedure B: To a solution of trimethylsiloxycyclohexene (3.9 mL, 20 mmol, 2.0 equiv), Bu_3SnF (6.18 g, 20 mmol, 2.0 equiv) and aryl iodide (10 mmol, 1.0 equiv) in benzene (40 mL) under nitrogen was added a solution of $Pd_2(dba)_3$ (0.23 g, 0.25 mmol, 2 mol%), t-$Bu_3P•BF_4$ (145 mg, 0.5 mmol, 4 mol%) and triethylamine (174 μL, 1.25 mmol, 10 mol%) in benzene (5 mL) at room temperature. The resultant mixture was heated to 80 ˚C for 24 h. After cooling to room temperature, the reaction mixture was diluted with diethyl ether (200 mL) and filtered through a plug of Celite. The solution was washed with 1 M aqueous NaOH (2 x 30 mL), followed by brine (50 mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography, eluting with a gradient of 8–20% diethyl ether in hexanes.

α-Aryl ketones **6a–j** are all known compounds and ^1H NMR were found to be in agreement with the literature: **6a, 6b, 6f, 6h,**[12] **6c, 6d, 6j**,[13] **6g**,[14] **6e**[15].

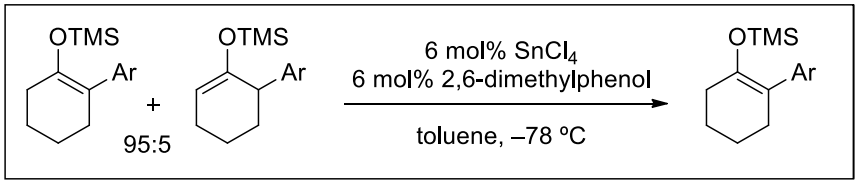
Preparation of silyl enol ether substrates: All silyl enol ether substrates were prepared by a procedure reported by Dunogues et al. [16]



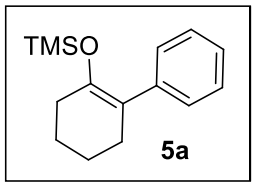
General procedure C: Pyridine (453 μL, 5.6 mmol, 1.25 equiv) and trimethylsilyl chloride (713 μL, 5.6 mmol, 1.25 equiv) were added sequentially to a solution of the ketone (4.5 mmol, 1.0 equiv) in 1:1 hexanes/acetonitrile (50 mL). A solution of sodium iodide (840 mg, 5.6 mmol, 1.25 equiv) in acetonitrile

(10 mL) was added to the reaction mixture dropwise over 30 min. The solution was stirred for 20 h at room temperature and then extracted with hexanes (2 x 30 mL). The hexanes layer was washed with acetonitrile (10 mL) and ice-cold water (10 mL), dried with sodium sulfate, filtered and concentrated. The product was purified using flash column chromatography, eluting with hexanes.

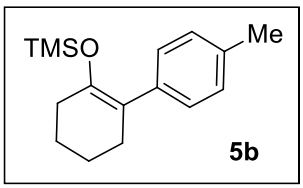
Preparation of silyl enol ethers in >99% regioisomeric purity: All silyl enol ether substrates were purified to >99% purity by a procedure developed by Yamamoto et al.[17]



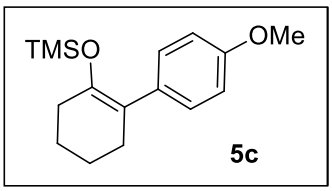
General procedure D: To a solution of 2,6-dimethylphenol (24 mg, 0.2 mmol, 5 mol%) in toluene (5 mL) was added a 1 M solution of tin tetrachloride in dichloromethane (0.2 mL, 0.2 mmol) at room temperature. The solution was cooled to –78 ˚C and a solution of the silyl enol ether (4.0 mmol, 97% purity) in toluene (0.5 ml) was added dropwise. After being stirred for 1 h at –78˚C, the reaction was quenched with $NaHCO_3$, extracted with diethyl ether (2 x 25 mL), dried over sodium sulfate, filtered and concentrated *in vacuo*. The crude oil was purified by column chromatography on silica gel, eluting with hexanes to afford the silyl enol ether (>99% regioisomeric purity).



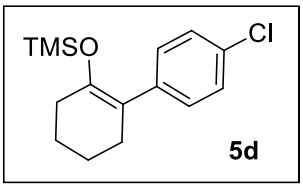
2-Phenyl-1-(trimethylsiloxy)cyclohex-1-ene (**5a**) was prepared using general procedure C. The crude reaction mixture was a 96:4 mixture of thermodynamic/kinetic regioisomers. The crude product could be purified to >99% purity via column chromatography eluting with hexanes or using general procedure D with 6 mol% LBA solution. The silyl enol ether was isolated as a colorless oil (740 mg, 3.0 mmol, 74% yield) with the ^{1}H NMR spectrum in agreement with the literature.[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.12–7.15 (m, 1H), 7.25–7.28 (m, 2H), 2.34–2.38 (m, 2H), 2.15–2.19 (m, 2H), 1.64–1.77 (m, 4H), –0.05 (s, 9H).



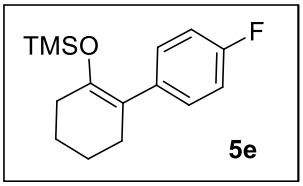
2-(4-Methylphenyl)-1-(trimethylsiloxy)cyclohex-1-ene (**5b**) was prepared using general procedure C. The crude reaction mixture was a 97:3 mixture of thermodynamic/kinetic regioisomers. The crude product could be purified to >99% purity using general procedure D with 5 mol% LBA solution. The silyl enol ether was isolated as a colourless oil (708 mg, 2.7 mmol, 67% yield) with the ^{1}H NMR spectrum in agreement with the literature.[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.26 (d, *J* = 7.9 Hz, 2H). 7.08 (d, *J* = 7.9 Hz, 2H), 2.32–2.36 (m, 2H), 2.31 (s, 3H), 2.15–2.18 (m, 2H), 1.65–1.76 (m, 4H), –0.04 (s, 9H).



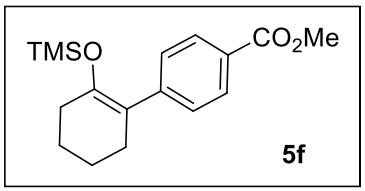
2-(4-Methoxyphenyl)-1-(trimethylsiloxy)cyclohex-1-ene (**5c**) was prepared using general procedure C. The crude reaction mixture was a 96:4 mixture of thermodynamic/kinetic regioisomers. The crude product could be purified to >99% purity using general procedure D using 6 mol% LBA solution. The silyl enol ether was isolated as a colorless oil (980 mg, 3.5 mmol, 88% yield) with the ^{1}H NMR spectrum in agreement with the literature.[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.31–2.35 (m, 2H), 2.14–2.17 (m, 2H), 1.65–1.77 (m, 4H), –0.04 (s, 9H).



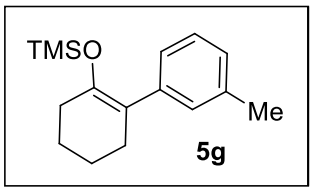
2-(4-Chlorophenyl)-1-(trimethylsiloxy)cyclohex-1-ene (**5d**) was prepared using general procedure C. The crude reaction mixture was a 98:2 mixture of thermodynamic/kinetic regioisomers. The crude product could be purified to >99% purity via column chromatography eluting with hexanes or using general procedure D using 3 mol% LBA solution. The silyl enol ether was isolated as a colorless oil (933 mg, 3.3 mmol, 82% yield) with the ^{1}H NMR spectrum in agreement with the literature.[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 2.31–2.34 (m, 2H), 2.15–2.18 (m, 2H), 1.67–1.75 (m, 4H), –0.02 (s, 9H).



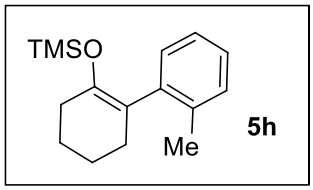
2-(4-fluorophenyl)-1-(trimethylsiloxy)cyclohex-1-ene (**5e**) was prepared using general procedure C. The crude reaction mixture was a 97:3 mixture of thermodynamic/kinetic regioisomers. The crude product could be purified to >99% purity using general procedure D using 5 mol% LBA solution. The silyl enol ether was isolated as a colorless oil (782 mg, 2.9 mmol, 73% yield). IR (thin film) 2932, 1655, 1508 (s), 1356, 1252 (s), 1219, 1192 (s), 1175, 1157, 1132, 1092, 995, 910 (s), 862 (s), 833 (s), 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (ddt, *J* = 8.8, 5.6, 2.6 Hz, 2H), 6.97 (tt, *J* = 8.8, 2.6 Hz, 2H), 2.31–2.35 (m, 2H), 2.13–2.17 (m, 2H), 1.62–1.80 (m, 4H), –0.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.3 (d, *J* = 244 Hz), 145.3, 136.7, 129.5 (d, *J* = 7 Hz), 114.8, 113.8 (d, *J* = 21 Hz), 30.5, 29.0, 22.9, 22.7, 0.0.



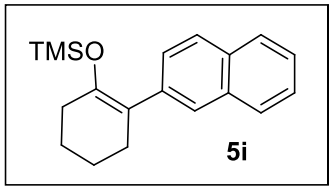
2-(4-Methylbenzoate)-1-(trimethylsiloxy)cyclohex-1-ene (**5f**) was prepared using general procedure C. The crude reaction mixture was a 95:5 mixture of thermodynamic/kinetic regioisomers. The crude product could be purified to >99% using general procedure D using 7 mol% LBA solution. The silyl enol ether was isolated as a colorless oil (850 mg, 2.8 mmol, 69% yield). IR (thin film) 2934, 1721 (s), 1645, 1604, 1435, 1357, 1275 (s), 1250 (s), 1194 (s), 1180 (s), 1136, 1111 (s), 1099 (s), 995, 910 (s), 862 (s), 841 (s), 773, 754, 706 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 2.35–2.39 (m, 2H), 2.14–2.18 (m, 2H), 1.60–1.78 (m, 4H), –0.03 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.8, 147.7, 146.7, 129.2, 128.5, 127.1, 115.5, 52.1, 31.4, 29.1, 23.5, 23.3, 0.87; HRMS (ESI-APCI) exact mass calculated for [M+H] ($C_{17}H_{25}O_2Si$) requires m/z 305.14947, found m/z 305.14952.



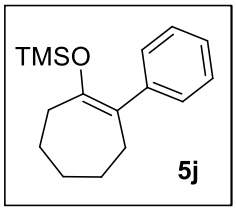
2-(3-Methylphenyl)-1-(trimethylsiloxy)cyclohex-1-ene (**5g**) was prepared using general procedure C. The crude reaction mixture was a 98:2 mixture of thermodynamic/kinetic regioisomers. The crude product could be purified to >99% purity via column chromatography eluting with hexanes or using general procedure D using 3 mol% LBA solution. The silyl enol ether was isolated as a colorless oil (708 mg, 2.7 mmol, 67% yield). IR (thin film) 2930, 1655, 1447, 1356, 1250 (s), 1203 (s), 1178, 1130, 923 (s), 839 (s), 781, 752, 733, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (s, 1H), 7.17–7.21 (m, 2H), 6.98 (d, *J* = 7.0 Hz, 1H), 2.34–2.38 (m, 2H), 2.34 (s, 3H), 2.14–2.18 (m, 2H), 1.62–1.80 (m, 4H), –0.01 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 145.0, 140.7, 136.4, 129.0, 127.0, 125.7, 124.8, 115.8, 30.6, 28.9, 23.0, 22.8, 20.9, 0.0; HRMS (ESI-APCI) exact mass calculated for [M+H] ($C_{16}H_{25}OSi$) requires m/z 261.15964, found m/z 261.16123.



2-(2-Methylphenyl)-1-(trimethylsiloxy)cyclohex-1-ene (**5h**) was prepared using general procedure C. The crude reaction mixture was a 99:1 mixture of thermodynamic/kinetic regioisomers. The crude product could be purified to >99% purity via column chromatography eluting with hexanes. The silyl enol ether was isolated as a colorless oil (612 mg, 2.3 mmol, 58% yield). IR (thin film) 2930, 1668, 1356, 1250 (s), 1207 (s), 1190 (s), 1138, 995, 912 (s), 858 (s), 839 (s), 752 (s), 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.03–7.17 (m, 4H), 2.22 (s, 3H), 2.10–2.24 (m, 4H), 1.81–1.70 (m, 2H), 1.63–1.70 (m, 2H), –0.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.1, 141.5, 136.8, 129.8, 129.5, 126.3, 125.3, 116.9, 30.9, 30.7, 23.9, 23.6, 19.8, 0.5; HRMS (ESI-APCI) exact mass calculated for [M+H] ($C_{16}H_{25}OSi$) requires m/z 260.1596. This compound is not stable under these conditions but the corresponding ketone was observed. HRMS (ESI-APCI) exact mass calculated for [M+H] ($C_{13}H_{17}O$) requires m/z 189.12012, found m/z 189.11666.



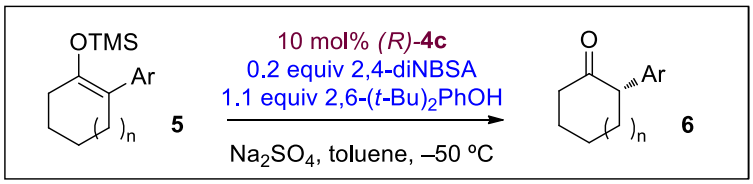
2-Naphthyl-1-(trimethylsiloxy)cyclohex-1-ene (**5i**) was prepared using general procedure C. The crude reaction mixture was a 96:4 mixture of thermodynamic/kinetic regioisomers. The crude product could be purified to >99% purity using general procedure D using 6 mol% LBA solution. The silyl enol ether was isolated as a colorless oil (780 mg, 2.6 mmol, 65% yield) with the ^{1}H NMR spectrum in agreement with the literature.[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73–7.80 (m, 4H), 7.58 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.38–7.43 (m, 2H), 2.47–2.49 (m, 2H), 2.21–2.24 (m, 2H), 1.72–1.82 (m, 4H), –0.06 (s, 9H).



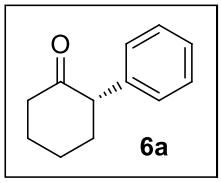
2-Phenyl-1-(trimethylsiloxy)cyclohept-1-ene (**5j**) was prepared using general procedure C. The crude reaction mixture was a 96:4 mixture of thermodynamic/kinetic regioisomers. The crude product could be purified to >99% purity using general procedure D with 6 mol% LBA solution. The silyl enol ether was isolated as a colorless oil (570 mg, 2.2 mmol, 54% yield) with the ^{1}H

NMR spectrum in agreement with the literature.[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25–7.32 (m, 4H), 7.13 (t, *J* = 7.2 Hz, 1H), 2.42–2.47 (m, 4H), 1.78–1.82 (m, 2H), 1.63–1.70 (m, 4H), –0.07 (s, 9H).

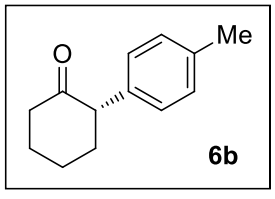
4. General Procedure for Asymmetric Protonation and Product Characterization



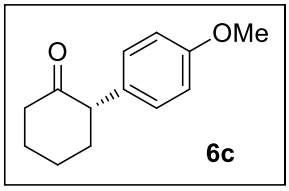
General procedure E: Sodium sulfate (45 mg, 3.0 mmol, 2.0 equiv), 2,4-dinitrobenzene sulfonic acid (7.5 mg, 0.17 mmol, 0.12 equiv) and 2,6-di-*tert*-butyl phenol (34 mg, 1.6 mmol, 1.1 equiv) were weighed into a flame-dried vial. The vial was cooled to –78 ˚C and toluene (1.3 mL) added. After 5 minutes at –78 ˚C a solution of catalyst *(R)*-**4c** (5 mg, 0.015 mmol, 10 mol%) and silyl enol ether (0.15 mmol, 1.0 equiv) in toluene (0.2 mL) was added dropwise to the stirred reaction mixture. The vial was transferred to a –50 ˚C cryo-cool and stirred for 4 d. The reaction was quenched by the addition of saturated aqueous sodium bicarbonate (3 mL) and then extracted with diethyl ether (25 mL). The organic layer was washed with brine (5 mL), dried over sodium sulfate, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography, eluting with a gradient of 10–35% diethyl ether in hexanes.



2-Phenyl-cyclohexanone (**6a**) was obtained as a white solid in 91% yield (24 mg, 0.14 mmol) and 86% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31–7.35 (t, *J* = 7.5 Hz, 2H), 7.23–7.27 (t, *J* = 7.5 Hz, 1H), 7.11–7.16 (d, *J* = 7.5 Hz, 2H), 3.59–3.64 (dd, *J* = 12.5, 5.0 Hz, 1H), 2.45–2.55 (m, 2H), 2.26–2.30 (m, 1H), 2.14–2.15 (m, 1H), 1.99–2.05 (m, 2H), 1.80–1.84 (m, 2H); Enantiomeric excess (ee) was determined by HPLC with a Chiralpak AS-H column (hexanes/2-propanol = 98:2, flow rate = 1.0 mL/min, μ = 210 nm), t_r(minor, *R*) = 11.8 min., t_r(major, *S*) = 13.6 min; $[\alpha]_D^{23.4}$ = –92.6 (*c* = 1.0, $CHCl_3$).

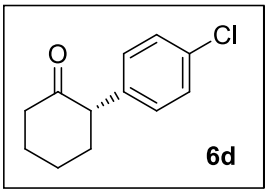


2-(4-Methylphenyl)cyclohexanone (**6b**) was obtained as a white solid in 92 % yield (26 mg, 0.14 mmol) and 88% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.14 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.56 (dd, *J* = 12.0, 5.4 Hz, 1H), 2.39–2.56 (m, 2H), 2.22 (s, 3H), 2.22–2.27 (m, 1H), 2.12–2.17 (m, 1H), 1.95–2.05 (m, 2H), 1.78–1.84 (m, 2H); Enantiomeric excess (ee) was determined by HPLC with a Chiralpak AS-H column (hexanes/2-propanol = 98:2, flow rate = 1.0 mL/min, μ = 210 nm), t_r(minor, *R*) = 9.8 min., t_r(major, *S*) = 11.7 min; $[\alpha]_D^{24.3}$ = –88.9 (*c* = 1.0, $CHCl_3$).

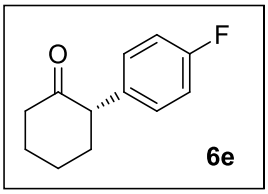


2-(4-Methoxyphenyl)cyclohexanone (**6c**) was obtained as a white solid in 90% yield (27.5 mg, 0.135 mmol) and 86% ee. ^{1}H NMR (400 MHz, $CDCl_3$)

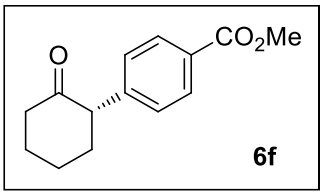
δ = 7.05 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H), 3.56 (dd, *J* = 12.5, 5.5 Hz, 1H), 2.49–2.53 (m, 2H), 2.22–2.26 (m, 1H), 2.10–2.15 (m, 1H), 1.94–2.02 (m, 2H), 1.75–1.85 (m, 2H); Enantiomeric excess (ee) was determined by HPLC with a Chiralcel OD-H column (hexanes/2-propanol = 95:5, flow rate = 1.0 mL/min, μ = 210 nm),), t_r(major, *S*) = 21.9 min., t_r(minor, *R*) = 27.5 min. $[\alpha]_D^{22.8}$ = –85.2 (*c* = 1.0, $CHCl_3$).



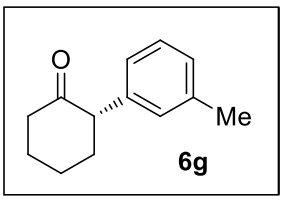
2-(4-Chlorophenyl)cyclohexanone (**6d**) was obtained as a white solid in 89 % yield (28 mg, 0.13 mmol) and 89% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 9.0 Hz, 2H), 7.07 (d, *J* = 9.0 Hz, 2H), 3.59 (dd, *J* = 12.4, 5.4 Hz, 1H), 2.41–2.54 (m, 2H), 2.15–2.28 (m, 2H), 1.95–2.02 (m, 2H), 1.79–1.91 (m, 2H); Enantiomeric excess (ee) was determined by HPLC with a Chiralpak AS-H column (hexanes/2-propanol = 98:2, flow rate = 1.0 mL/min, μ = 210 nm), t_r(minor, *R*) = 12.4 min., t_r(major, *S*) = 14.5 min; $[\alpha]_D^{24.3}$ = –64.5 (*c* = 1.1, $CHCl_3$).



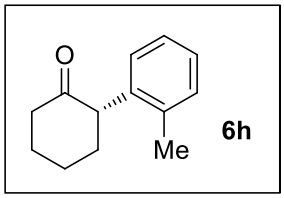
2-(4-Fluorophenyl)cyclohexanone (**6e**) was obtained as a white solid in 88% yield (25 mg, 0.13 mmol) and 82% ee. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.10 (ddt, *J* = 8.8, 5.6, 2.9 Hz, 2H), 7.02 (tt, *J* = 8.8, 2.9 Hz, 2H), 3.60 (dd, *J* = 12.3, 5.0 Hz, 1H), 2.52–2.55 (m, 1H), 2.43–2.48 (m, 1H), 2.24–2.29 (m, 1H), 2.14–2.20 (m, 1H), 1.94–2.04 (m, 2H), 1.77–1.86 (m, 2H); Enantiomeric excess (ee) was determined by HPLC with a Chiralpak AS-H column (hexanes/2-propanol = 98:2, flow rate = 1.0 mL/min, μ = 210 nm), t_r(minor) = 12.2 min., t_r(major) = 13.9 min; $[\alpha]_D^{24.3}$ = –77.2 (*c* = 1.1, $CHCl_3$).



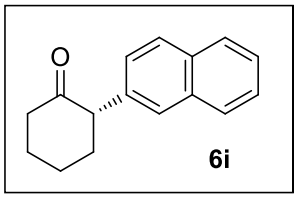
2-(4-Methylbenzoate)cyclohexanone (**6f**) was obtained as a white solid in 84% yield (30.7 mg, 0.126 mmol) and 78% ee. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H), 3.67 (dd, *J* = 12.3, 5.3 Hz, 1H), 2.52–2.56 (m, 1H), 2.44–2.50 (m, 1H), 2.26–2.30 (m, 1H), 2.16–2.20 (m, 1H), 1.99–2.07 (m, 2H), 1.79–1.88 (m, 2H); Enantiomeric excess (ee) was determined by HPLC with a Chiralpak AS-H column (hexanes/2-propanol = 85:15, flow rate = 1.0 mL/min, μ = 210 nm), t_r(minor) = 40.4 min., t_r(major) = 50.7 min; $[\alpha]_D^{24.3}$ = –59.6 (*c* = 1.05, $CHCl_3$).



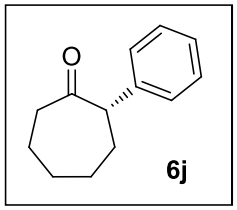
2-(3-Methylphenyl)cyclohexanone (**6g**) was obtained as a white solid in 92 % yield (26 mg, 0.14 mmol) and 84% ee. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.17–7.30 (m, 4H), 3.85 (dd, *J* = 13.2, 5.5 Hz, 1H), 2.52–2.65 (m, 2H), 2.22–2.43 (m, 2H), 2.27 (s, 3H), 2.06–2.17 (m, 2H), 1.85–1.97 (m, 2H); Enantiomeric ratio (er) was determined by HPLC with a Chiralpak AS-H column (hexanes/2-propanol = 98:2, flow rate = 1.0 mL/min, μ = 210 nm), t(minor) = 10.4 min., t(major) = 11.3 min. $[\alpha]_D^{24.0}$ = –81.1 (*c* = 1.1, $CHCl_3$).



2-(2-Methylphenyl)cyclohexanone (**6h**) was obtained as a white solid in 91 % yield (25.5 mg, 0.137 mmol) and 85% ee. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.12–7.22 (m, 4H), 3.78 (dd, *J* = 12.9, 5.6 Hz, 1H), 2.54–2.58 (m, 1H), 2.47–2.52 (m, 1H), 2.25–2.30 (m, 1H), 2.18–2.20 (m, 1H), 2.02–2.09 (m, 2H), 1.78–1.89 (m, 2H); Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column (hexanes/2-propanol = 95:5, flow rate = 1.0 mL/min, μ = 210 nm), t(major) = 16.8 min., t(minor) = 18.5 min; $[\alpha]_D^{23.4}$ = –33.0 (*c* = 1.0, $CHCl_3$).



2-Naphthyl-cyclohexanone (**6i**) was obtained as a white solid in 93% yield (31 mg, 0.14 mmol) and 82% ee. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.77–7.83 (m, 3H), 7.60 (s, 1H), 7.41–7.46 (m, 2H), 7.27 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.77 (dd, *J* = 12.2, 5.6 Hz, 1H), 2.46–2.58 (m, 2H), 2.31–2.36 (m, 1H), 2.12–2.21 (m, 2H), 2.00–2.07 (m,1H), 1.81–1.91 (m, 2H); Enantiomeric excess (ee) was determined by HPLC with a Chiralpak AS-H column (hexanes/2-propanol = 98:2, flow rate = 1.0 mL/min, μ = 210 nm), t_r(minor, *R*) = 15.6 min., t_r(major, *S*) = 20.7 min; $[\alpha]_D^{24.3}$ = –84.2 (*c* = 1.0, $CHCl_3$).



2-Phenyl-cycloheptanone (**6j**) was obtained as an oil in 88 % yield (25 mg, 0.13 mmol) and 73% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30–7.33 (t, *J* = 7 Hz, 2H), 7.20–7.26 (m, 3H), 3.70–3.73 (dd, *J* = 11, 4 Hz, 1H), 2.67–2.72 (m, 1H), 2.47–2.54 (m, 1H), 1.95–2.18 (m, 4H), 1.60–1.69 (m, 1H), 1.43–1.48 (m, 2H); Enantiomeric excess (ee) was determined by HPLC with a Chiralpak AS-H column (hexanes/2-propanol = 97:3, flow rate = 1.0 mL/min, μ = 210 nm), t_r(minor, *S*) = 10.1 min., t_r(major, *R*) = 13.6 min; $[\alpha]_D^{24.3}$ = –129.4 (*c* = 1.0, $CHCl_3$).

5. Reaction Optimization

a) Effect of variation to the urea portion of the sulfinamide–urea catalyst 1a:

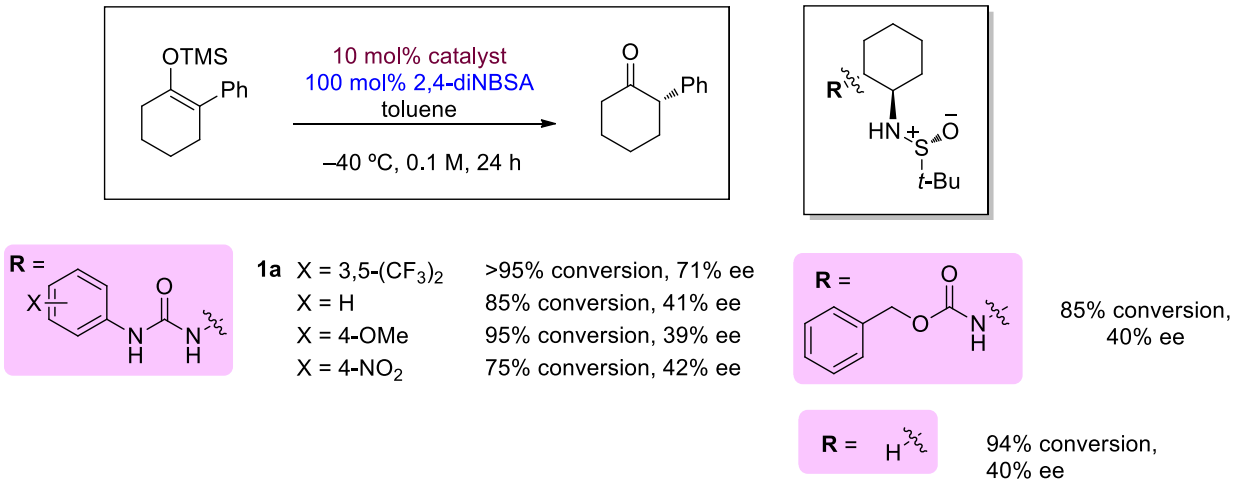
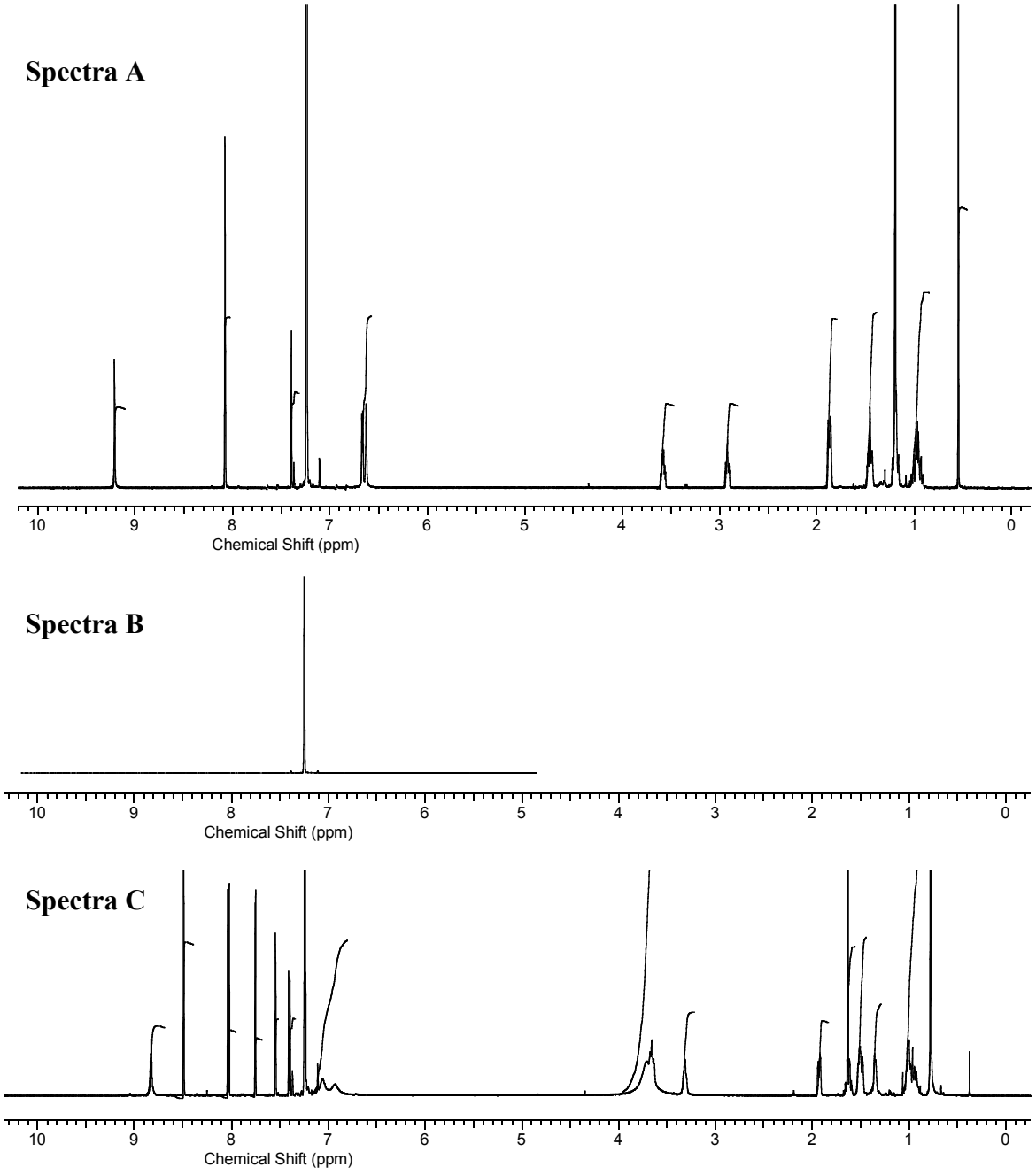


Figure S3: Effect of varying urea portion of catalyst **1a**

3,5-(bistrifluoromethyl)phenylurea catalyst **1a** provides significantly increased reactivity and enantioselectivity relative to all other analogues tested. This points towards a key dual hydrogen bonding interaction, which potentially increases the acidity of the conjugate acid complex and provides greater transition state organization. The results indicate that the urea portion is only advantageous with the very electron deficient 3,5-(bistrifluoromethyl)phenyl substituent and that the sulfinamide group alone is responsible for a significant level of selectivity.

b) NMR solvation studies:

To gain further insight into the phase-transfer proposal we studied the reaction components by NMR.

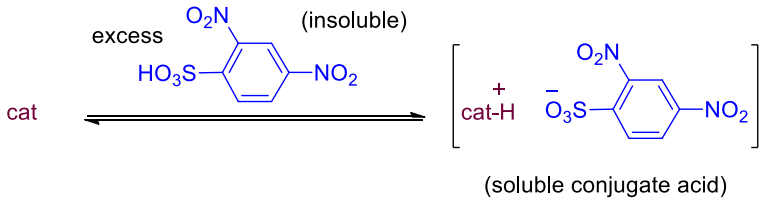


Spectrum A: sulfinamide–urea catalyst **1a** in d_6-benzene.

Spectrum B: NMR analysis of the solution phase when 2,4-diNBSA is stirred in d_6-benzene for 10 min. Only residual solvent is visible by NMR confirming the acid is insoluble.

Spectrum C: NMR analysis of the solution phase when 15 mol% **1a** and 1.0 equiv 2,4-diNBSA were stirred in d_6-benzene for 10 min. Peaks corresponding to protons on the sulfonate counterion are visible and integrate to approximately 0.9 relative to the peaks from the protons on **1a** indicating around 13

mol% 2,4-diNBSA is solubilized in the presence of 15 mol% **1a**. Downfield shifts of the aromatic protons as well as significant broadening of the urea N-H protons are suggestive of the urea being involved in hydrogen bonding interactions.

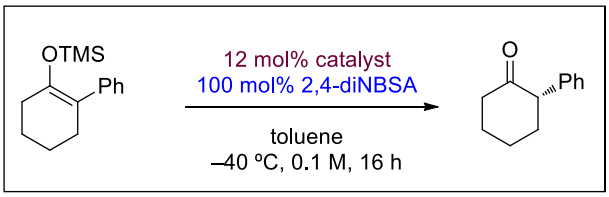


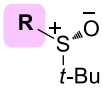
cat	% 2,4-diNBSA solubilized (rel to amount of catalyst)
1a	90
1e	100
2	0
3	75
4c	10
4f	20

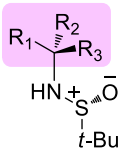
Table S2: Ability of sulfinamide catalysts to solubilize 2,4-diNBSA

When 15 mol% of a urea **2** with no sulfinamide was added, no solubilization was observed. However, addition of 15 mol% sulfinamide **3** or tertiary amine catalyst **1e** brought 0.75 equiv and 1.0 equiv of the acid into solution, respectively. These results indicate the Lewis basic sulfinamide portion is responsible for reactivity, presumably by formation of a soluble conjugate acid species. Notably, for the more electron deficient fluorinated sulfinamide catalysts **4c** and **4f**, less sulfonate is brought into solution. See NMR spectra section for solvation studies with catalysts **3**, **4c** and **4f**.

c) Examination of simple sulfinamide catalyst scaffolds:







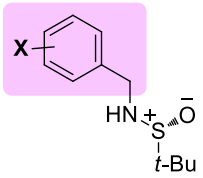
entry	**R**	conversion	ee
1	-NH*n*-Pr	>95%	53%
2	-NH_2	>95%	31%
3	-NHAc	36%	22%
4	-NMeBn	>95%	25%

Table S3: Effect of substitution on nitrogen

entry	R_1	R_2	R_3	conversion	ee
1	Me	Ph	*n*-Bu	31%	9%
2	Me	Ph	H	88%	43%
3	Et	H	H	>95%	53%
4	Ph	H	H	91%	54%
5	*t*-Bu	H	H	85%	64%
6	Mes	H	H	35%	26%
7	1-naph	H	H	56%	61%

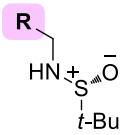
Table S4: Effect of substitution adjacent to nitrogen

A screen of simple sulfinamide structures showed promising levels of enantioinduction for those not fully substituted at nitrogen (RNHSO*t*-Bu) (Table S3). Substitution adjacent to the nitrogen was found to be deleterious both to reactivity and selectivity over a number of different scaffolds (Table S4, compare entries 1–3). Additionally, bulky benzyl derivatives such as mesityl gave poor results (entry 6), indicating that too much steric hindrance close to the sulfinamide functional group hinders reactivity and has a negative effect on enantioselectivity. As such, our attention would focus on *N*-monoalkyl sulfinamides.



entry	X	conversion	ee
1	4-OMe	>95%	51%
2	4-H	>95%	53%
3	4-F	>95%	57%
4	4-NO_2	78%	60%
5	4-CF_3	94%	60%
6	3-CF_3	94%	66%
7	2,4-CF_3	85%	60%
8	3,5-CF_3	>95%	75%

Table S5: Effect of electronic variation on *N*-benzyl-derived catalysts

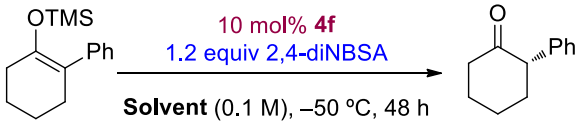


entry	R	conversion	ee
1	C_2F_5	>95%	72%
2	C_3F_7	>95%	83%
3	C_4F_8H	>95%	86%
4	C_4F_9	78%	69%
5	C_5F_{11}	94%	55%
6	C_6F_{13}	60%	32%
7	C_7F_{15}	40%	34%

Table S6: *N*-fluoroalkane-derived catalysts

Table S5 shows a clear correlation between enantioselectivity and electronic properties of the benzyl-derived catalysts, with more electron deficient catalysts providing the highest levels of selectivity. Similarly, for the fluoroalkyl-substituted catalysts (Table S6) an increase in selectivity was observed with additional CF_2 units. It is assumed that the enantioselectivity and reactivity then start to drop as the solubility of the catalysts in toluene decreases.

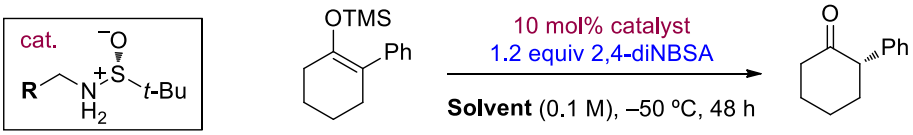
d) Effect of changing solvent:



entry	**Solvent**	conversion	ee
1	hexanes	no reaction	-
2	toluene	>95%	82%
3	pentafluorobenzene	>95%	78%
4	dichloromethane	>95%	71%
5	diethylether	>95%	41%
6	TBME	>95%	26%

Table S7: Effect of changing solvent

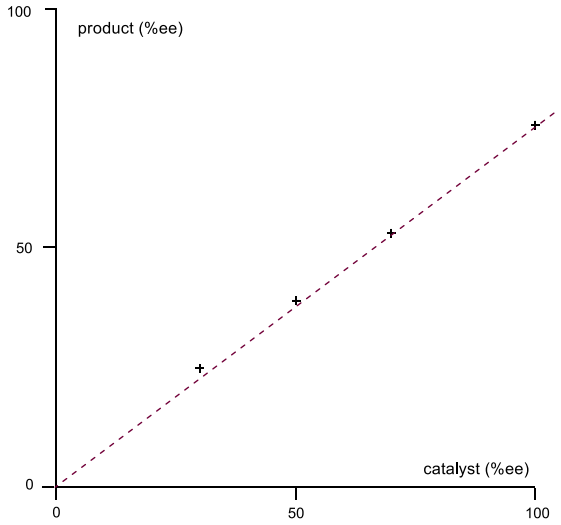
At one extreme, in hexanes where both 2,4-dinitrobenzene sulfonic acid and catalyst **4f** are insoluble, we observe no reactivity. At the other extreme, in ethereal solvents where the catalyst is fully soluble and the sulfonic acid partially soluble, we see good reactivity but low enantioselectivity due to competing background protonation by the achiral sulfonic acid. Optimal reactivity and selectivity are seen in toluene, where the catalyst is fully soluble but the sulfonic acid is completely insoluble enabling a phase transfer type mechanism to operate whereby the achiral acid is brought into solution by protonation of the sulfinamide catalyst. While fluorinated solvents gave no increase in selectivity for optimal catalyst **4f,** solvent effects were observed with longer chain alkyl fluoride chains where switching from toluene to pentafluorobenzene increased both reactivity and selectivity.

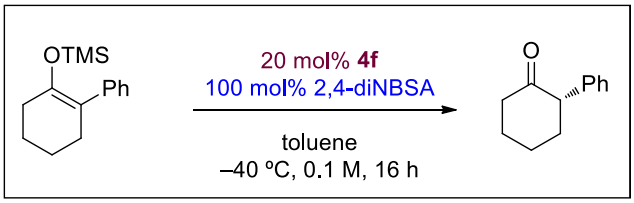


entry	catalyst	**Solvent**	conversion	ee
1	**R** = C_4F_8H	toluene	>95%	85%
2		**pentafluorobenzene**	**>95%**	**80%**
3	**R** = C_4F_9	toluene	65%	70%
4		**pentafluorobenzene**	**85%**	**79%**
5	**R** = C_6F_{13}	toluene	39%	33%
6		**pentafluorobenzene**	**45%**	**75%**

Table S8: Effect of using fluorinated solvents with highly fluorinated catalysts

e) Non-linear effects analysis:



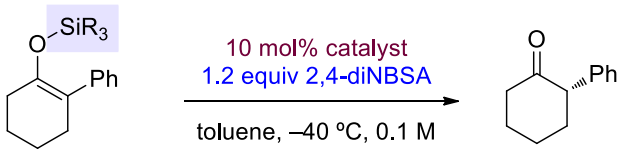


entry	Catalyst (% ee)	product (% ee)
1	100	76
2	70	53
3	50	39
4	30	26
5	0	0

Figure S4: Non-linear effects analysis: effect of catalyst ee on product ee

Data obtained with catalyst **4f** indicates a linear correlation between catalyst and product enantioselectivity, suggesting that only a single molecule of catalyst is involved in the enantiodetermining step.

f) Effect of varying the silyl group:[a]



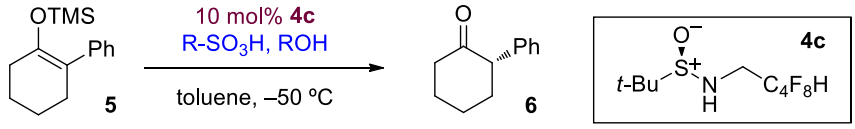
		catalyst **1a**		catalyst **4c**	
entry	**R_3Si-**	conversion[b]	ee[c]	conversion[b]	ee[c]
1	Me_3Si-	>95%	66%	>95%	60%
2	Et_3Si-	42%	67%	31%	28%
3	Me_2BnSi-	47%	66%	34%	58%
4	Me_2*t*-BuSi-	< 2%	n.d.	< 2%	n.d.

[a] Silyl enol ether and catalyst were added as a solution in toluene to 2,4-diNBSA in toluene at –78 °C. Reactions were carried out on 0.05 mmol scale at 0.1 M with stirring for 16 h at –40 °C. [b] ^{1}H NMR conversion based on silyl enol ether. [c] The ee values were determined by chiral HPLC.

Table S9: Effect of varying the silyl enol ether SiR_3 group

The nature of the silyl group greatly affects reactivity under standard enantioselective protonation conditions employing both sulfinamide–urea catalyst **1a** and simple sulfinamide catalyst **4c**, with additional steric bulk causing a significant drop in reactivity. Interestingly, with bulkier silyl groups the enantioselectivity of the product ketone remained the same for catalyst **1a** and either the same or lower for catalyst **4c**. These results suggest that the silyl group is not closely involved in the enantiodetermining step with catalyst **1a** but more information is needed to assert this for **4c**.

g) Effect of varying achiral proton source:



entry	**R**-SO_3H R =	Na_2SO_4	**R**-OH	conversion[b] (%)	ee[c] (%)
1	2,4-dinitrobenzene (1.0 equiv)	-	-	>95	76
2	2,4-dinitrobenzene (1.2 equiv)	Na_2SO_4	-	>95	85
3	2-nitrobenzene (1.2 equiv)	Na_2SO_4	-	>95	69
4	3-nitrobenzene (1.2 equiv)	Na_2SO_4	-	>95	55
5	4-nitrobenzene (1.2 equiv)	Na_2SO_4	-	>95	54
6	2,4,5-trichlorobenzene (1.2 equiv)	Na_2SO_4	-	>95	58
7	2,4-dinitrobenzene (0.2 equiv)	-	H_2O (1.0 equiv)	43	69
8	2,4-dinitrobenzene (0.2 equiv)	-	AcOH (1.0 equiv)	<10	n.d.
9	2,4-dinitrobenzene (0.2 equiv)	-	2,4-dinitrobenzoic aicd (1.0 equiv)	<10	n.d.
10	2,4-dinitrobenzene (0.2 equiv)	-	PhOH (1.0 equiv)	>95	76
11	2,4-dinitrobenzene (0.2 equiv)	-	2,6-$(Me)_2$PhOH (1.0 equiv)	20	80
12	2,4-dinitrobenzene (0.2 equiv)	-	2,6-$(Ph)_2$PhOH (1.0 equiv)	65	80
13	2,4-dinitrobenzene (0.2 equiv)	-	2,6-(t-Bu)$_2$PhOH (1.0 equiv)	70	83
14	2,4-dinitrobenzene (0.2 equiv)	Na_2SO_4	2,6-(t-Bu)$_2$PhOH (1.1 equiv)	78	86

[a] Silyl enol ether and **4c** were added as a solution in toluene to 2,4-diNBSA, R-OH and Na_2SO_4 in toluene at –78 °C. Reactions were carried out on 0.05 mmol scale at 0.1 M stirring for 36 h at –50 °C. [b] ^{1}H NMR conversion based on silyl enol ether. [c] The ee values were determined by chiral HPLC.

Table S10: Effect of varying the achiral proton source

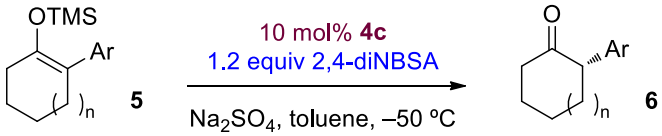
In table S10, entries 2–6, we vary the sulfonate counterion of the sulfonic acid. No protonation is observed in the absence of a sulfinamide catalyst at –50 ˚C for entries 2–6 implying that the difference in enantioselectivity observed in the protonation reaction is not due to differences in a competing

background pathway. This suggests that the sulfonate counterion is closely associated in the key enantiodetermining step. A phase transfer mechanism is proposed whereby the sulfinamide catalyst brings into solution a catalytic quantity of the acid via S=O protonation to form a soluble conjugate acid. (Note: Some background reactivity is observed at higher temperatures and with soluble sulfonic acids such as triflic acid and methane sulfonic acid).

Table S10, entries 7–13 employ a catalytic quantity of the strong sulfonic acid with an additional stoichiometric proton source. For all entries the rate of the reaction is diminished relative to using stoichiometric 2,4-dinitrobenzenesulfonic acid. Interestingly, while water and various alcohols are effective, very poor reactivity is observed with carboxylic acids suggesting that protonation of the stoichiometric proton source maybe necessary to turn over the reaction. Phenols substituted at the 2 and 6 position provide for optimal enantioselectivity.

Comparing entry 7 and entry 1 indicates that addition of water is detrimental to enantioselectivity. The commercial aromatic sulfonic acids are hydroscopic and accordingly, we found that improved selectivity could be achieved by storing them in vacuum desiccators and adding sodium sulfate as a desiccant to the reaction mixture.

h) Scope using stoichiometric 2,4-diNBSA:[a]



entry	enol silane	n	R	ketone	yield[b] (%)	ee[c] (%)
1	**5a**	1	C_6H_5	**6a**	97	85
2	**5b**	1	4-$OMeC_6H_4$	**6b**	96	84
3	**5c**	1	4-MeC_6H_4	**6c**	96	84
4	**5d**	1	4-ClC_6H_4	**6d**	93	81
5	**5e**	1	4-FC_6H_4	**6e**	94	81
6	**5f**	1	4-$CO_2MeC_6H_4$	**6f**	88	76
7	**5g**	1	3-MeC_6H_4	**6g**	95	85
8	**5h**	1	2-MeC_6H_4	**6h**	92	82
9	**5i**	1	2-naphthyl	**6i**	96	78
10	**5j**	2	C_6H_5	**6j**	94	64

[a] Silyl enol ether and **4c** were added as a solution in toluene to 2,4-diNBSA and Na_2SO_4 in toluene at –78 °C. Reactions were carried out on 0.1 mmol scale at 0.1 M with stirring for 36 h at –50 °C. [b] Isolated yield based on silyl enol ether. [c] The ee values were determined by chiral HPLC.

Table S11: Scope for enantioselective protonation reaction using stoichiometric 2,4-diNBSA

Using stoichiometric 2,4-dinitrobenzenesulfonic acid as the sole proton source provides a more rapid reaction with the expense of a slight drop in enantioselectivity.

9. Cartesian Coordinates for Calculated Structures:

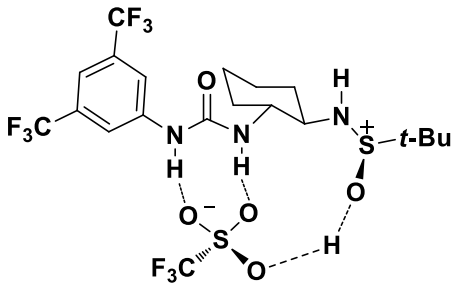


Figure 1B

N	0.00000000	0.00000000	0.00000000
S	1.64208010	0.00000000	0.00000000
O	2.22842808	1.51231272	0.00000000
H	-0.44077203	0.65096357	-0.67177028
C	-1.76275210	1.09335939	1.36028299
C	-2.54682703	1.03789264	2.68246023
C	-3.19481397	-0.33705803	2.90192070
C	-2.15706165	-1.46664072	2.83595958
C	-1.37137277	-1.41982778	1.51668706
H	-0.59862898	-2.19824189	1.49424468
H	-2.04430238	-1.61735861	0.67030348
H	-2.64461515	-2.44285448	2.94237998
H	-1.45824544	-1.37033598	3.67878351
H	-3.70981637	-0.35052990	3.86958294
H	-3.96473680	-0.50531459	2.13509631
H	-1.86131907	1.26587410	3.50923741
H	-3.30675858	1.82729660	2.66949487
H	-2.45639945	0.95378532	0.52304083
N	-1.15392789	2.40609002	1.19083861
C	-0.88278483	2.91308656	-0.05049757
N	-0.21216379	4.11702981	-0.03578519
H	0.22650712	4.37022298	0.85140183
O	-1.22037893	2.31937185	-1.09186910
H	-0.70740265	2.79545364	2.01796906
O	1.51112681	4.30826847	2.32006970
S	1.78041175	3.07433961	3.09736512
O	2.74316328	2.13015038	2.42641571
O	0.57094536	2.40786803	3.63094714
H	2.46866248	1.79224467	0.96807680
C	-0.71553273	-0.04747706	1.31444176
C	2.73938226	3.63775592	4.58783613

C	2.05011047	-0.42919437	-1.78603964
C	0.28500507	4.80380902	-1.15348177
C	1.33848869	5.70861075	-0.93743676
C	-0.24016656	4.65975365	-2.44498503
C	1.85085368	6.45172050	-1.99625520
H	1.75532630	5.81835503	0.05900110
C	0.29712942	5.40868293	-3.49420798
H	-1.04815045	3.96400367	-2.62132358
C	1.33797479	6.31024330	-3.28756363
H	1.73916977	6.89163605	-4.10782596
C	3.58582104	-0.46575141	-1.83552981
H	3.99886196	-1.20366470	-1.13857268
H	3.89055968	-0.75444500	-2.84726830
H	4.01911944	0.51215668	-1.61332696
C	1.44961747	-1.81703561	-2.04141602
H	1.74565300	-2.13777150	-3.04632898
H	1.82394457	-2.56234391	-1.33055817
H	0.35843927	-1.80365062	-1.99179162
C	1.48351583	0.63755048	-2.72893716
H	0.39143679	0.68442928	-2.71046515
H	1.87640769	1.62962402	-2.49657821
H	1.78650277	0.37826545	-3.75005288
H	0.00699451	0.13720802	2.11910068
C	-0.31461619	5.25177304	-4.86167737
C	3.02328111	7.36759651	-1.75915725
F	-0.45987656	3.94694105	-5.19324582
F	0.43175450	5.83106851	-5.82660619
F	-1.54700136	5.80548918	-4.92379674
F	4.20059677	6.71633653	-1.91161695
F	3.03366972	8.40254346	-2.62855291
F	3.01748534	7.88273158	-0.51183814
F	1.98849831	4.47724057	5.30650663
F	3.85458250	4.26526457	4.20738121
F	3.06471612	2.58620501	5.34544476

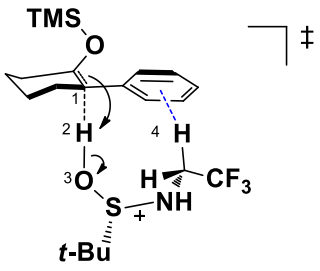


Figure 2A

C	0.72421	-0.11311	2.67782
C	1.17902	-0.41918	1.24622
C	2.44675	0.05551	0.84854
C	3.09902	1.22429	1.53032

H	-0.36580	-0.18787	2.71599
H	2.79963	2.11332	0.96022
O	3.00497	-0.43206	-0.21158
Si	4.40564	-0.06552	-1.20663
S	-1.68471	1.46567	0.21823
O	-0.15968	1.42660	-0.10983
H	0.60736	0.53973	0.58195
C	1.18465	1.26373	3.14928
H	0.69408	2.04431	2.55745
H	4.18027	1.12541	1.41889
H	1.11482	-0.87510	3.35907
H	0.89444	1.41144	4.19042
C	0.61980	-1.65204	0.59112
C	0.16891	-2.72727	1.36358
C	0.48945	-1.72853	-0.80276
C	-0.37851	-3.85897	0.75938
H	0.24858	-2.69580	2.44270
C	-0.05316	-2.85924	-1.40664
H	0.80853	-0.89435	-1.41489
C	-0.48933	-3.93099	-0.62644
H	-0.71507	-4.68364	1.37476
H	-0.13794	-2.90437	-2.48577
H	-0.91211	-4.81061	-1.09467
C	-1.50001	4.10980	-0.16434
H	-1.85872	5.01933	-0.64947
H	-1.68146	4.21030	0.90875
H	-0.42878	4.01847	-0.34215
C	2.69821	1.37978	2.99856
H	3.18444	0.60147	3.59363
H	3.05985	2.34037	3.36647
C	-2.79685	-0.97831	0.15768
H	-2.22070	-1.84332	-0.17339
H	-2.63144	-0.83230	1.22535
C	-2.26296	2.92264	-0.75509
C	-3.76463	3.04226	-0.50499
H	-4.12025	3.93904	-1.01660
H	-4.30876	2.18282	-0.89563
H	-3.98899	3.15108	0.55840
C	-1.93116	2.72735	-2.23021
H	-2.55420	1.95660	-2.68737
H	-2.14216	3.66384	-2.75064
H	-0.87498	2.49132	-2.36944
N	-2.44547	0.22741	-0.57920
H	-2.15069	0.08328	-1.53761
C	4.05983	-1.11130	-2.70398
H	3.91226	-2.15433	-2.41800
H	3.16287	-0.76614	-3.22222
H	4.89509	-1.06381	-3.40592
C	5.90880	-0.62332	-0.25454
H	6.78454	-0.57317	-0.90667
H	6.11545	-0.00183	0.61830

H	5.79754	-1.65857	0.07313
C	4.38699	1.76424	-1.58769
H	4.75498	2.37438	-0.76182
H	5.03492	1.95004	-2.44828
H	3.38261	2.10132	-1.85525
C	-4.26836	-1.26758	-0.04281
F	-4.60928	-2.40023	0.58890
F	-4.55699	-1.41179	-1.34962
F	-5.03730	-0.27386	0.43396

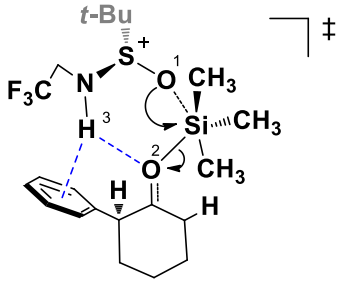


Figure 2B

O	1.25964	-0.47236	-0.36223
Si	0.60851	-2.21559	-1.30238
S	-1.69674	-1.38969	0.83558
C	-1.42076	-1.25014	2.65374
O	-0.36668	-2.08570	0.41717
N	-1.60773	0.15433	0.24761
H	-0.73020	0.65703	0.33650
C	2.34533	-0.10833	0.10326
C	3.52959	-1.01578	0.23585
C	4.77880	-0.38726	-0.41823
C	5.02350	1.02376	0.11023
C	3.79506	1.90157	-0.11389
C	2.53804	1.31030	0.58267
H	5.63318	-1.03582	-0.22262
H	3.71839	-1.13246	1.31023
H	3.30240	-1.99560	-0.17782
H	5.25924	0.98513	1.17925
H	5.88684	1.46367	-0.39147
H	3.94620	2.90748	0.27992
H	3.59404	2.00246	-1.18494
H	2.78985	1.21595	1.64792
H	4.64033	-0.35405	-1.50259
C	1.73005	-1.59232	-2.71046
H	2.77998	-1.48219	-2.43298
H	1.67941	-2.32759	-3.51919
H	1.37640	-0.64029	-3.11519
C	1.40133	-3.76738	-0.60369

H	2.23227	-4.10527	-1.22504
H	1.75043	-3.62688	0.42061
H	0.64435	-4.55416	-0.57350
C	-1.00124	-2.40680	-2.24922
H	-1.79791	-2.89529	-1.68786
H	-1.36302	-1.44245	-2.60905
H	-0.78276	-3.00804	-3.13623
C	1.33257	2.20823	0.44240
C	0.80684	2.84519	1.56970
C	0.77630	2.48592	-0.81206
C	-0.25031	3.74769	1.45158
H	1.24141	2.65439	2.54547
C	-0.27504	3.39127	-0.93340
H	1.16399	1.99897	-1.69969
C	-0.78785	4.02755	0.19745
H	-0.63436	4.24549	2.33313
H	-0.68898	3.60282	-1.91108
H	-1.59292	4.74527	0.09793
C	-2.55483	-0.37389	3.18328
H	-2.50557	-0.36833	4.27387
H	-2.45984	0.65767	2.83796
H	-3.53658	-0.76385	2.90132
C	-0.05300	-0.64412	2.93278
H	0.07532	-0.57376	4.01544
H	0.73916	-1.27462	2.52787
H	0.02848	0.36401	2.52078
C	-1.52561	-2.68301	3.18056
H	-0.74280	-3.31480	2.76011
H	-1.40818	-2.66126	4.26584
H	-2.49995	-3.12339	2.95699
C	-2.80756	0.89887	-0.08553
H	-2.64913	1.94799	0.15975
H	-3.67668	0.54315	0.46965
C	-3.14791	0.80256	-1.55895
F	-4.16175	1.63085	-1.85027
F	-2.10227	1.13126	-2.33856
F	-3.52193	-0.44623	-1.88990

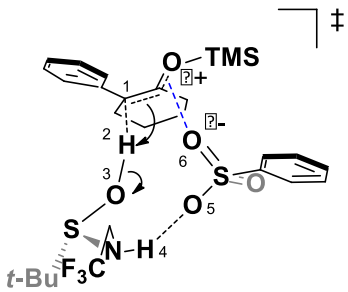


Figure 2C

C	-1.71256	3.31863	-1.53441
C	-0.92883	2.62666	-0.41178
C	0.48325	2.64896	-0.51462
C	1.17106	2.72996	-1.84044
H	-2.73388	2.93014	-1.51866
H	1.31065	1.68688	-2.16329
O	1.19739	2.52457	0.55097
Si	2.84255	2.19843	1.02208
S	-2.61997	-0.62923	-0.70709
O	-1.57552	0.29555	-1.39481
H	-1.08880	1.40265	-0.80510
C	-1.07831	3.07937	-2.90279
H	-1.13606	2.01522	-3.14810
H	2.16511	3.15410	-1.68724
H	-1.77023	4.39631	-1.34341
H	-1.63262	3.63164	-3.66517
C	0.38152	3.52159	-2.88647
H	0.43598	4.59129	-2.65806
H	0.84583	3.37383	-3.86264
C	-3.34311	-1.48871	-2.16698
N	-1.84892	-1.90510	0.01700
H	-1.01415	-2.20990	-0.51554
O	1.73200	-0.46280	-2.25807
S	1.48540	-1.21949	-1.01094
O	1.07686	-0.35420	0.13633
O	0.58550	-2.39491	-1.17760
C	-1.56156	-1.77151	1.43538
H	-0.49305	-1.61782	1.60258
H	-2.11314	-0.93991	1.87667
C	3.45097	3.89657	1.53152
H	2.80985	4.32420	2.30463
H	4.46718	3.82681	1.92809
H	3.46960	4.58090	0.67972
C	2.65656	1.07519	2.49391
H	2.21302	0.13442	2.16888
H	3.63287	0.87673	2.94307
H	2.01457	1.53878	3.24624
C	3.89578	1.51119	-0.36060
H	3.32228	0.92844	-1.08161
H	4.41689	2.31382	-0.88796
H	4.64676	0.84606	0.07562
C	-1.54402	2.61270	0.95717
C	-1.14392	1.64927	1.89424
C	-2.56047	3.50466	1.30879
C	-1.73056	1.60011	3.15457
H	-0.37005	0.94088	1.61944
C	-3.14966	3.45263	2.57176
H	-2.89784	4.25049	0.60025
C	-2.73609	2.50272	3.50035
H	-1.40536	0.85063	3.86775

H	-3.93334	4.15593	2.82599
H	-3.19387	2.46081	4.48088
C	3.07075	-1.90910	-0.54290
C	4.09724	-1.96875	-1.47789
C	3.24233	-2.39526	0.75011
C	5.32348	-2.51683	-1.10559
H	3.92731	-1.57713	-2.47255
C	4.46952	-2.94000	1.11529
H	2.42359	-2.34201	1.45732
C	5.51043	-2.99874	0.18814
H	6.13146	-2.56592	-1.82510
H	4.61363	-3.31969	2.11923
H	6.46484	-3.42322	0.47472
C	-3.99884	-0.37719	-2.98872
H	-4.50590	-0.83303	-3.84183
H	-4.74381	0.16900	-2.40336
H	-3.25060	0.32387	-3.35910
C	-2.23849	-2.18109	-2.95903
H	-1.42500	-1.49108	-3.18709
H	-1.82762	-3.03533	-2.42128
H	-2.67208	-2.54194	-3.89545
C	-4.38324	-2.47140	-1.63430
H	-5.15126	-1.96287	-1.04579
H	-4.86969	-2.95114	-2.48689
H	-3.91797	-3.23989	-1.01748
C	-1.99975	-3.02359	2.15494
F	-1.70360	-2.93294	3.47027
F	-3.32930	-3.22158	2.05674
F	-1.39553	-4.12435	1.67849

Notes and References

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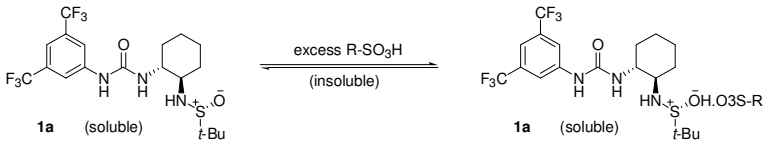
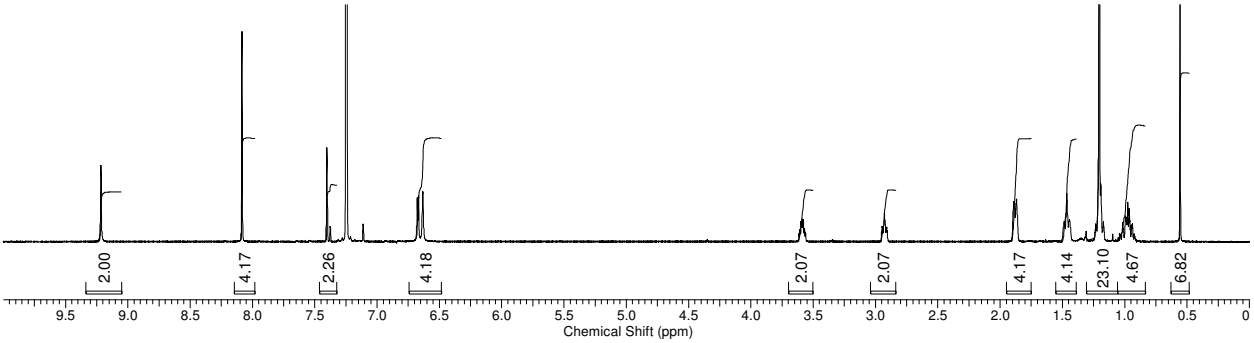
NMR solvation studies:

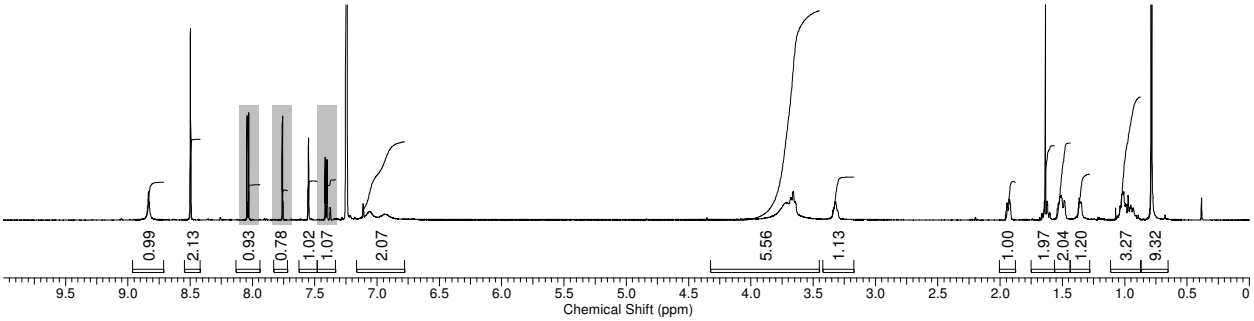
To gain further insight into the phase-transfer proposal we studied the reaction components by NMR:



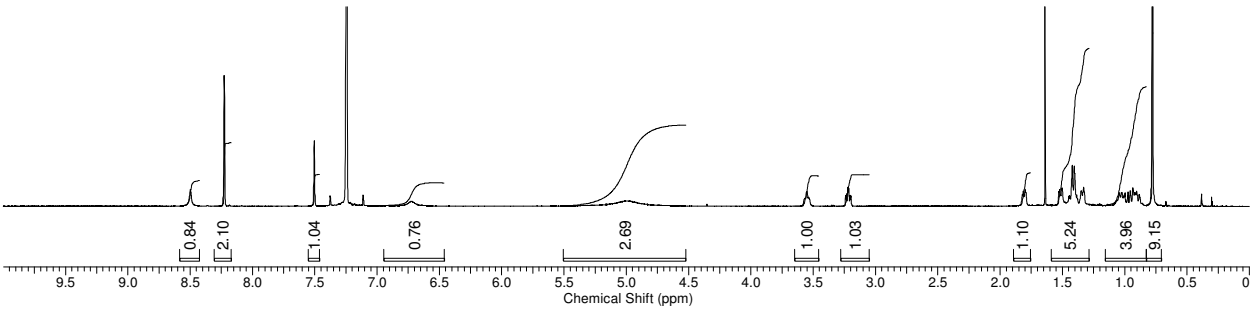
A: Catalyst **1a**, ^{1}H NMR, d_6-benzene



B: Catalyst **1a** after stirring with 2,4-diNBSA



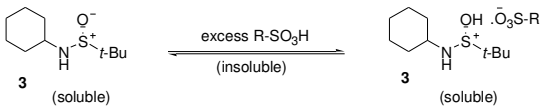
C: Catalyst **1a** after stirring with TfOH



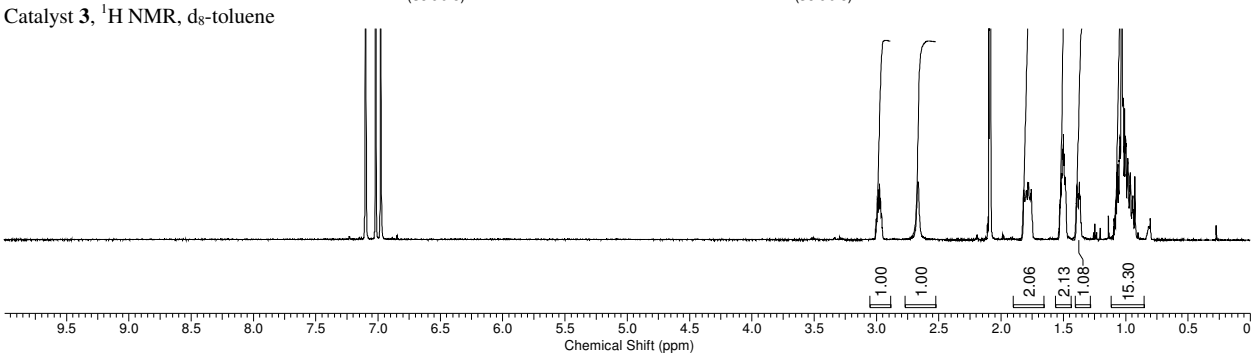
highlighted peaks corresponding to 2,4-dinitrobenzenesulfonic acid protons

Spectra B: NMR analysis of the solution phase when **1a** is stirred with excess 2,4-diNBSA in d_6-benzene at rt for 30mins. Peaks corresponding to 2,4-diNBSA integrate to approx 0.9 relative to **1a** indicating solubilization of just under 1 equiv of the acid. Notably, in the absence of catalyst, no 2,4-diNBSA is brought into the solution phase and only the residual benzene peak is observed.

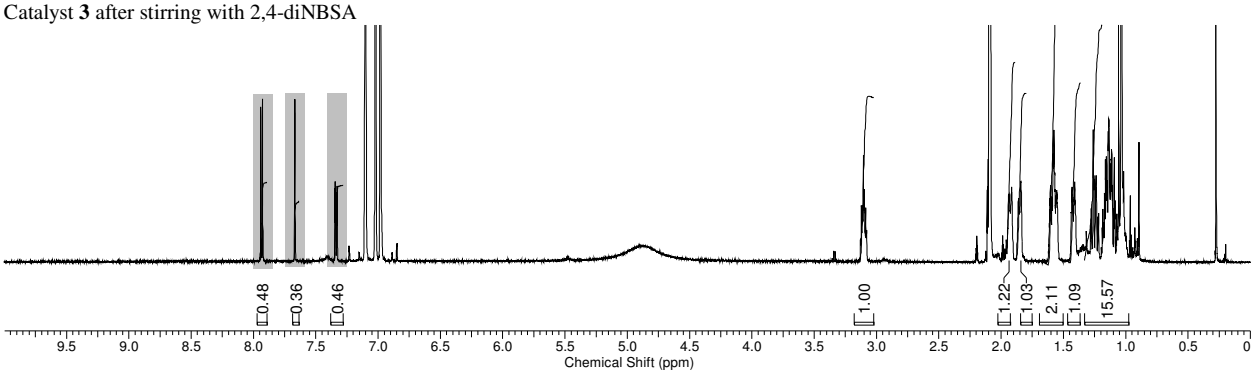
Spectra C: Same procedure with TfOH. For both B and C we observe downfield shifts for the aromatic protons on **1a** as well as broadening of the urea N-H protons which is suggestive of hydrogen bonding interactions.

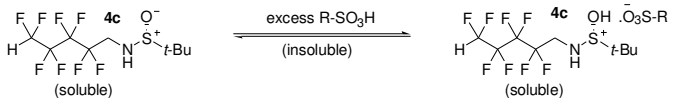


Catalyst **3**, ^{1}H NMR, d_8-toluene

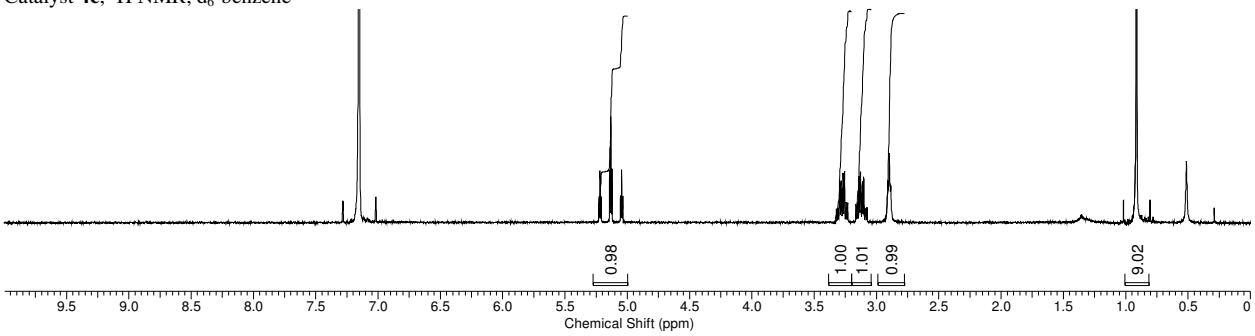


Catalyst **3** after stirring with 2,4-diNBSA

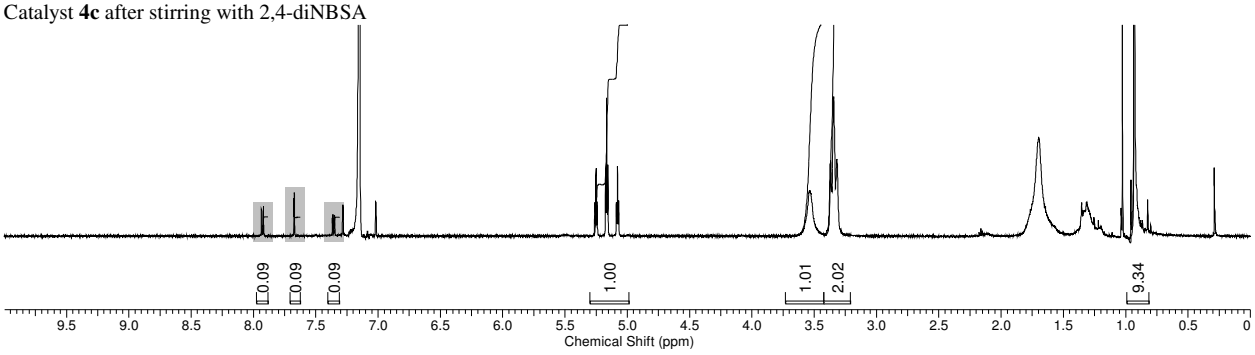


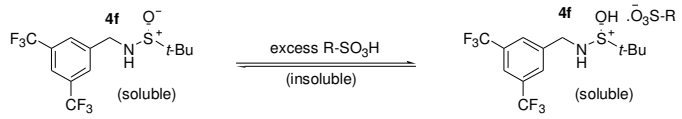


Catalyst **4c**, ^{1}H NMR, d_6-benzene

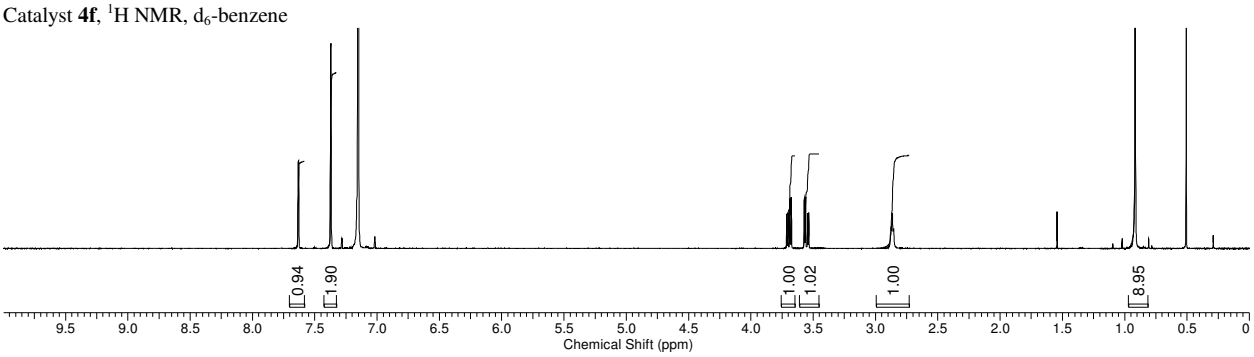


Catalyst **4c** after stirring with 2,4-diNBSA

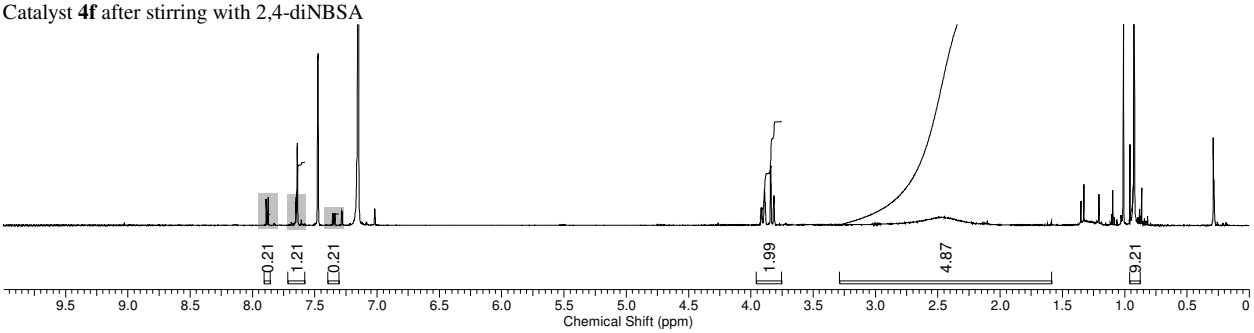




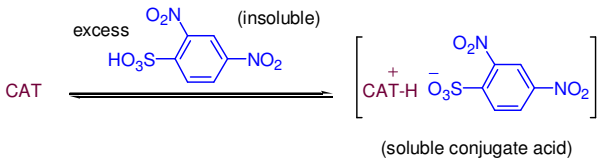
Catalyst **4f**, ^{1}H NMR, d_6-benzene



Catalyst **4f** after stirring with 2,4-diNBSA



NMR solvation studies with other potential catalysts indicate that it is the basic nature of the sulfinamide group that enables solvation of the 2,4-dinitrobenzenesulfonic acid. When achiral urea catalysts **2** is used, no solubilization is observed. In contrast tertiary amine catalyst **1e** brings 1.0 eq. of the acid into solution and simple sulfinamide **3** around 0.75 eq. Notably for the more electron deficient sulfonamide catalysts **4c** and **4f** less acid is brought into solution.

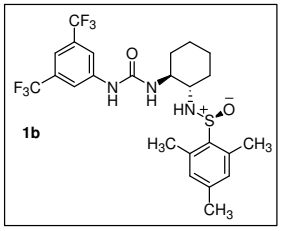


CAT	% 2,4-diNBSA solubilized (rel to amount of catalyst)
1a	90
1e	100
2	0
3	75
4c	10
4f	20

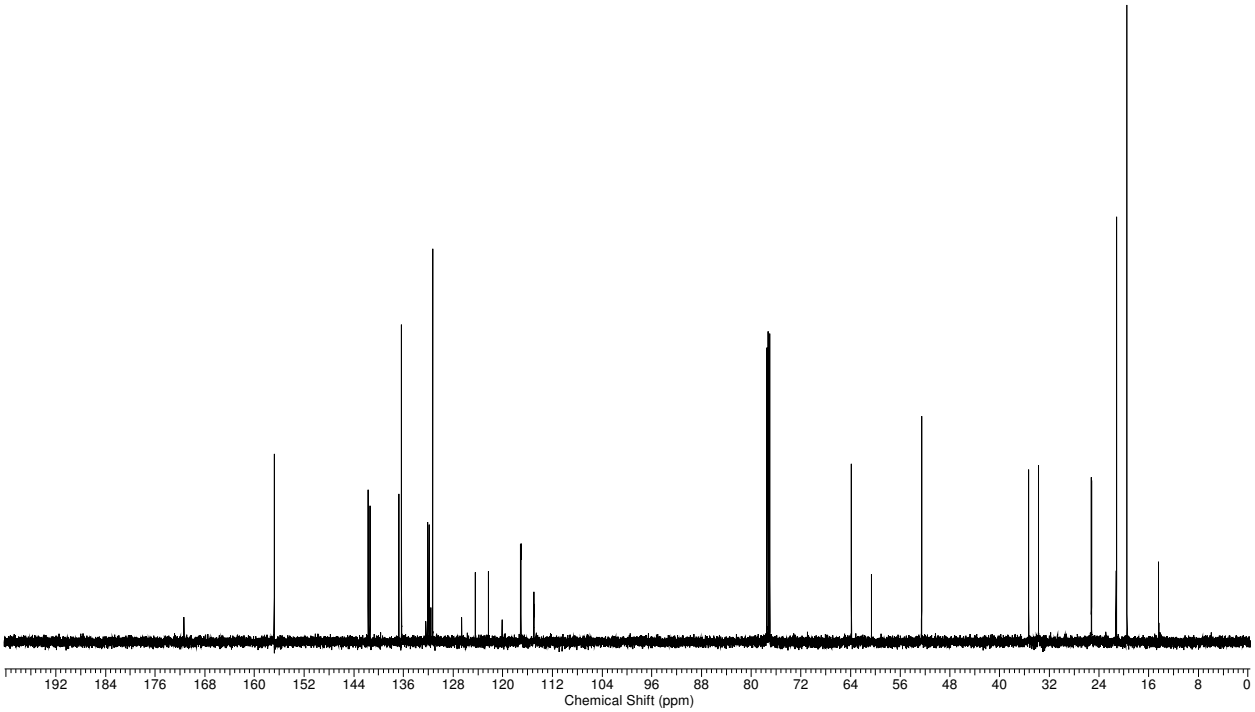
Table S12: Ability of sulfinamide catalysts to solubilize 2,4-diNBSA

Catalyst **1b**

^{1}H NMR, d_1-chloroform

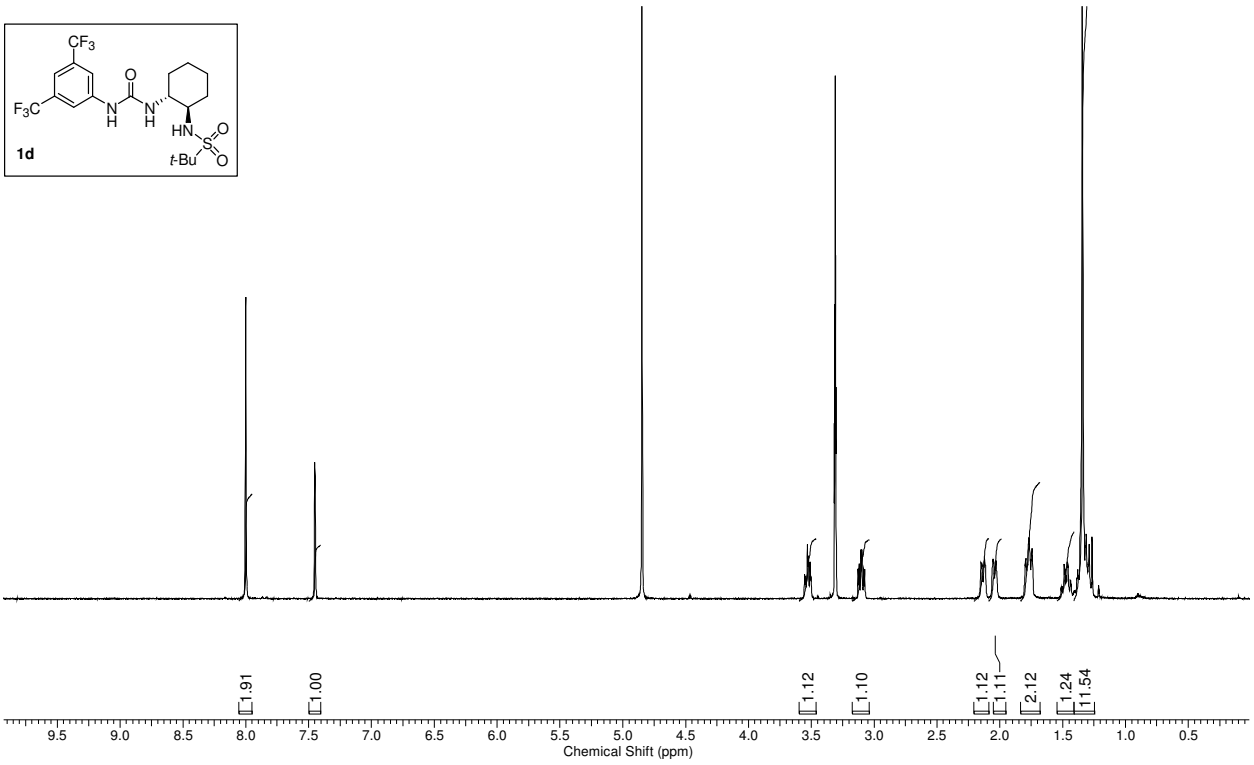


^{13}C NMR, d_1-chloroform

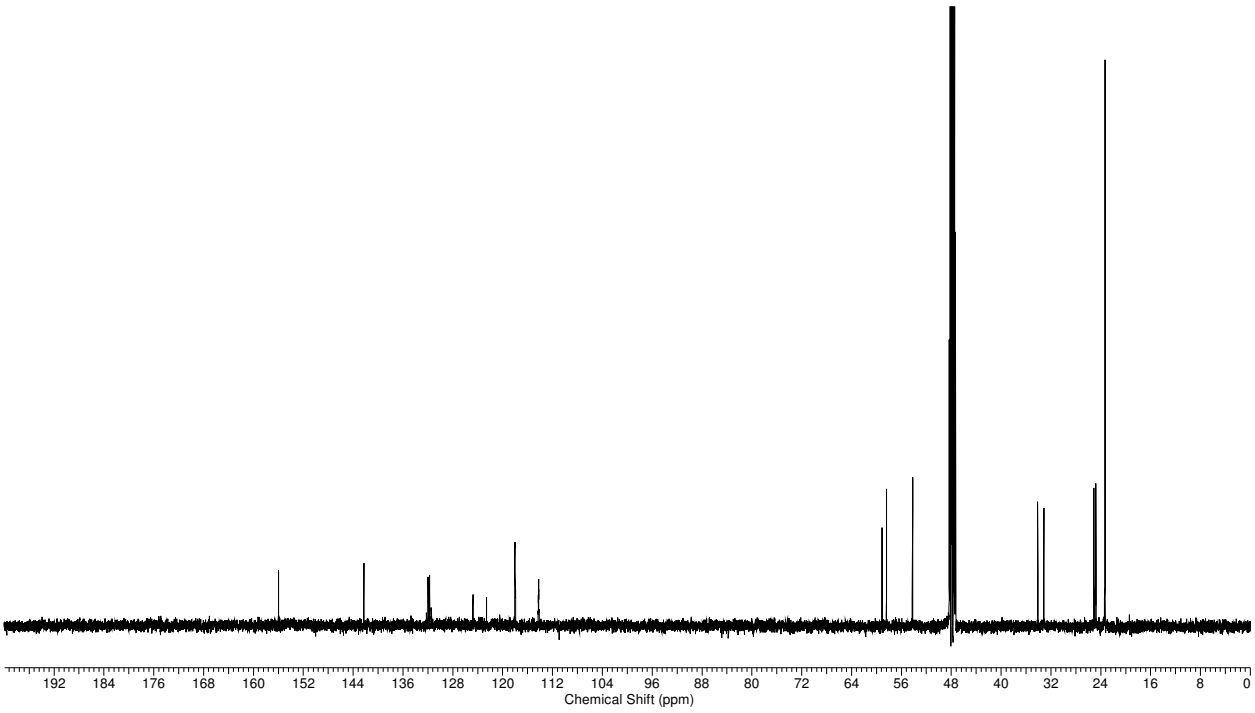


Catalyst **1d**

^{1}H NMR, d_4-methanol

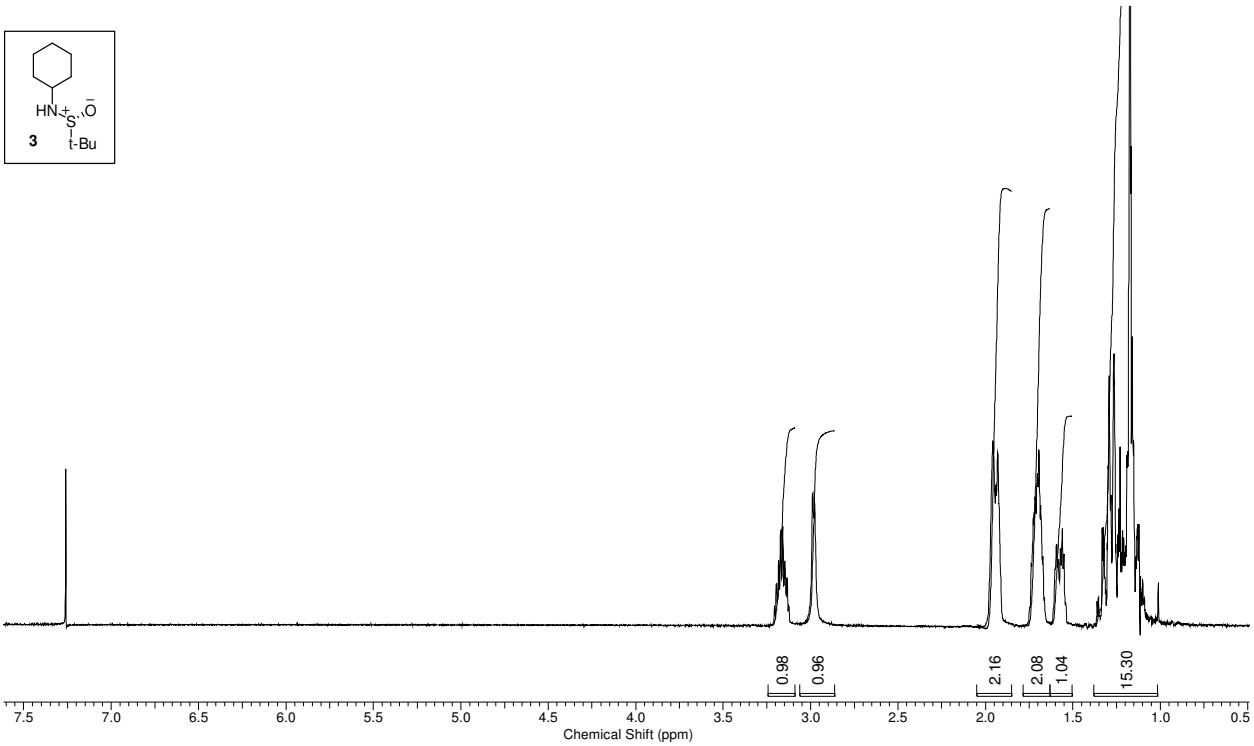


^{13}C NMR, d_4-methanol

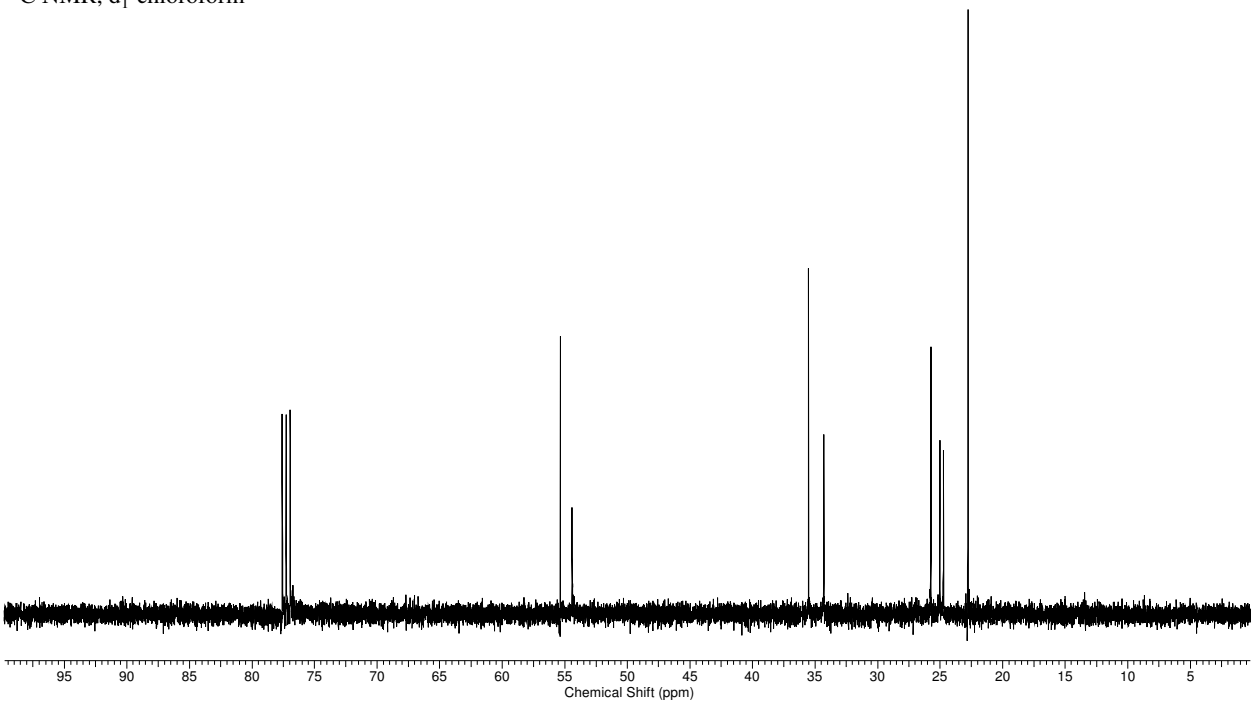


Catalyst **3**

^{1}H NMR, d_1-chloroform

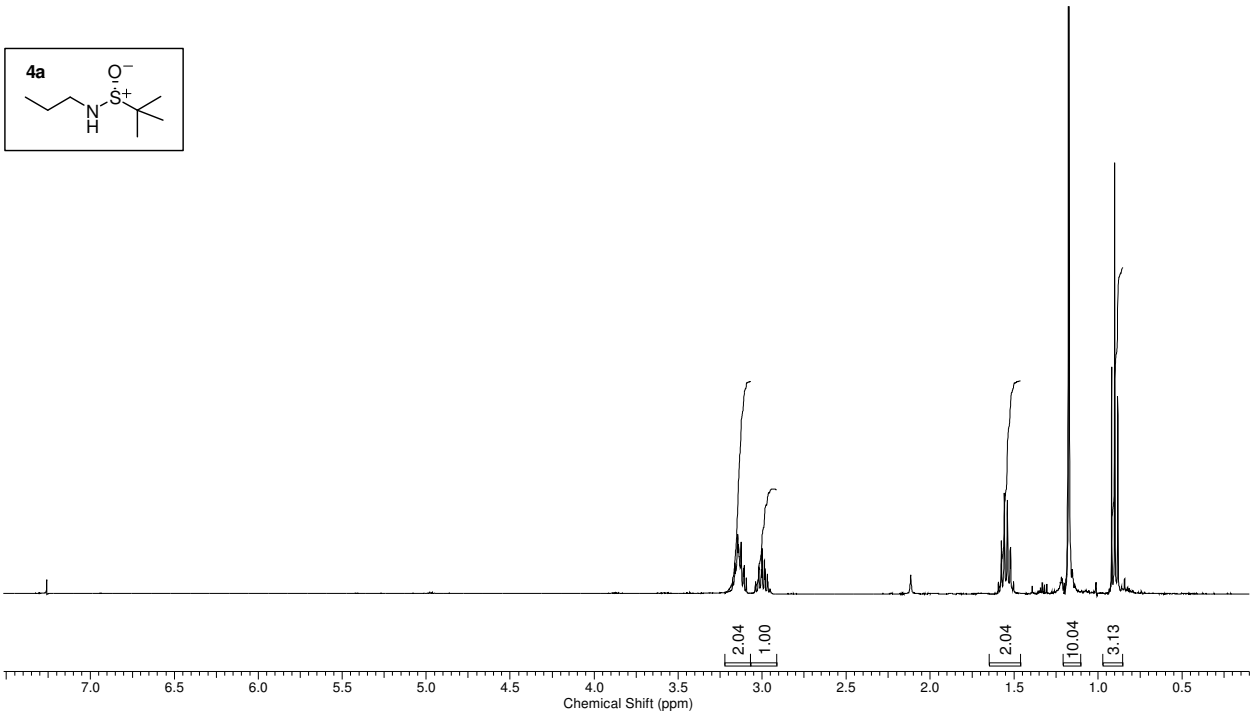


^{13}C NMR, d_1-chloroform

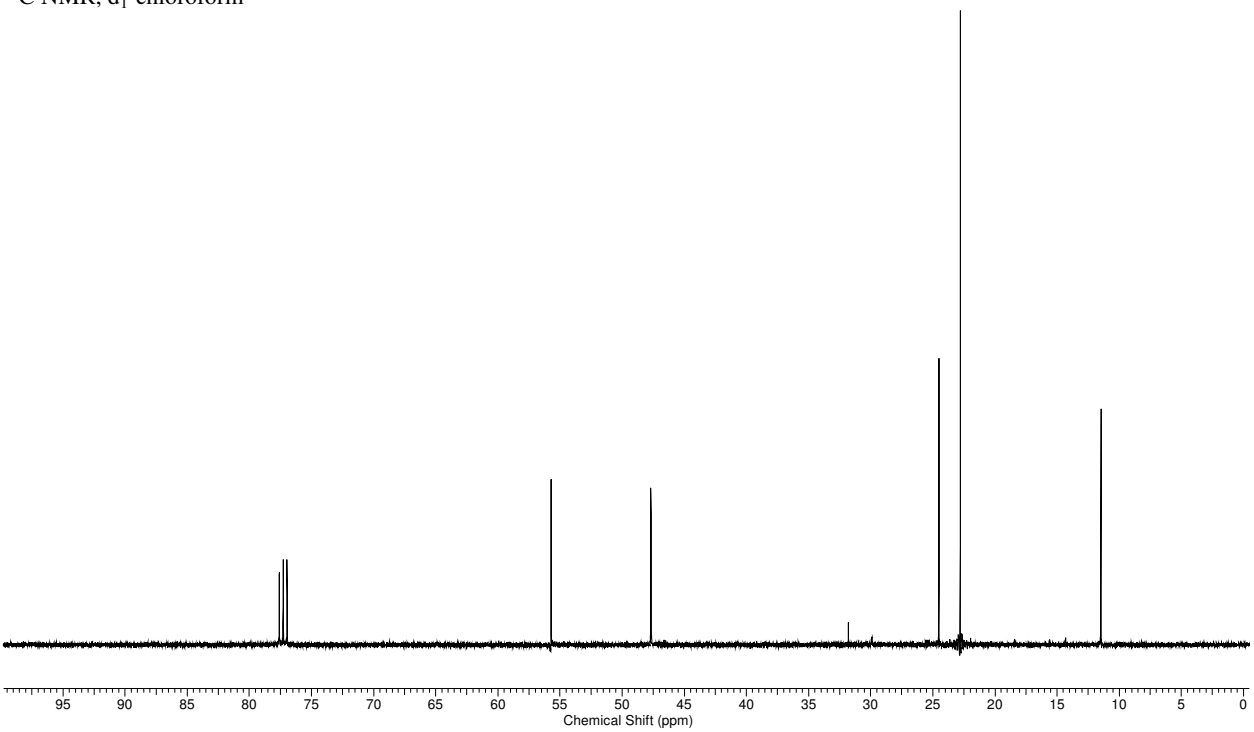


Catalyst **4a**

^{1}H NMR, d_1-chloroform

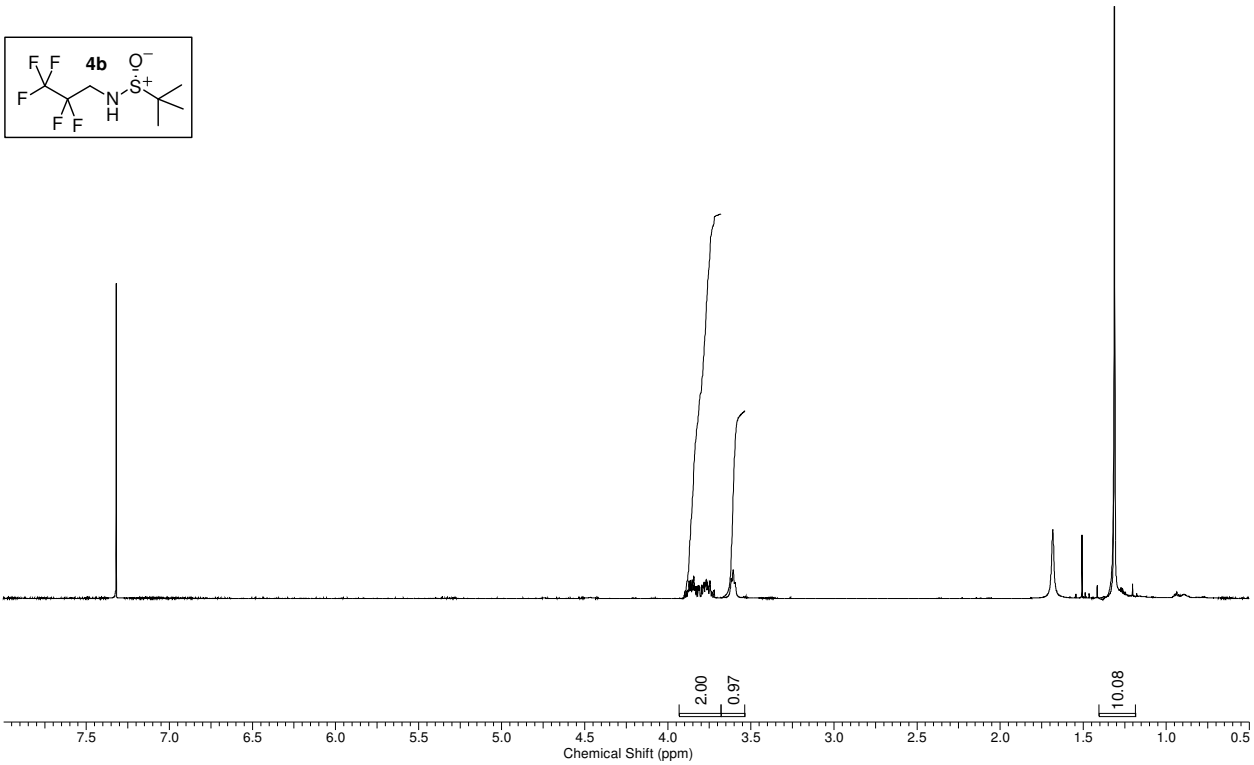


^{13}C NMR, d_1-chloroform

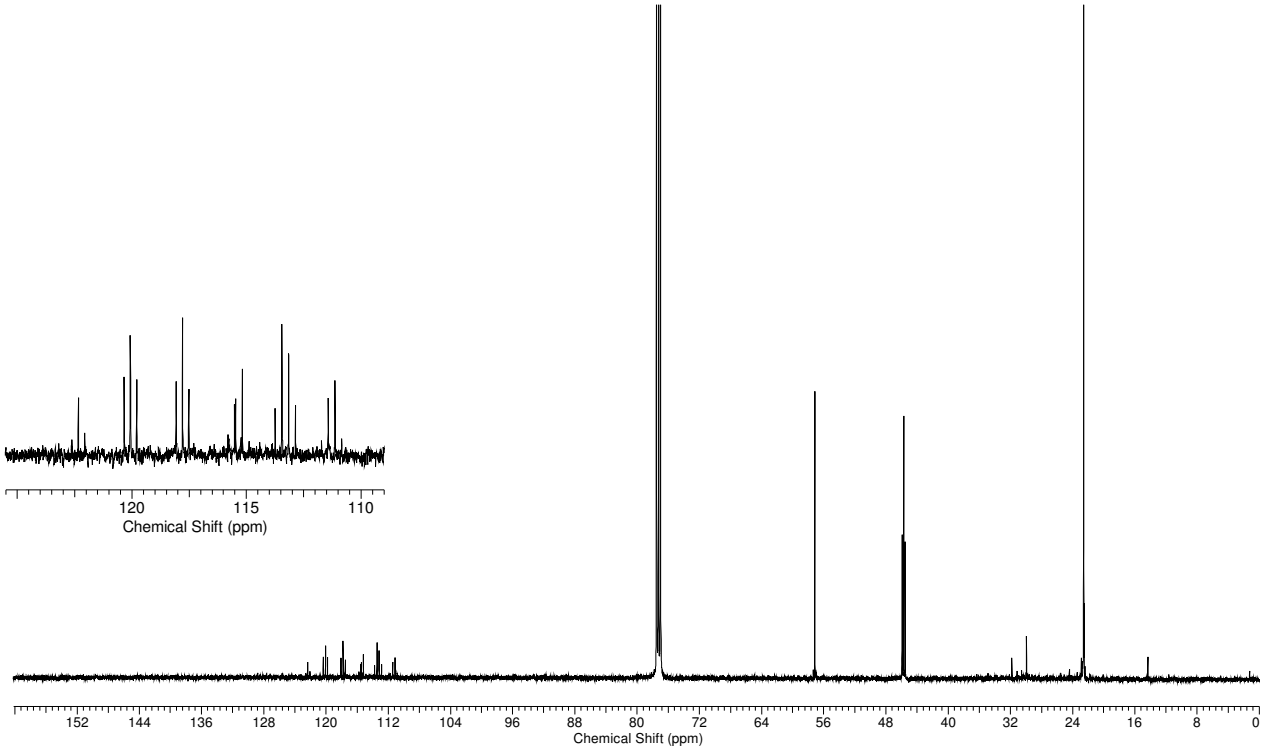


Catalyst **4b**

^{1}H NMR, d_1-chloroform

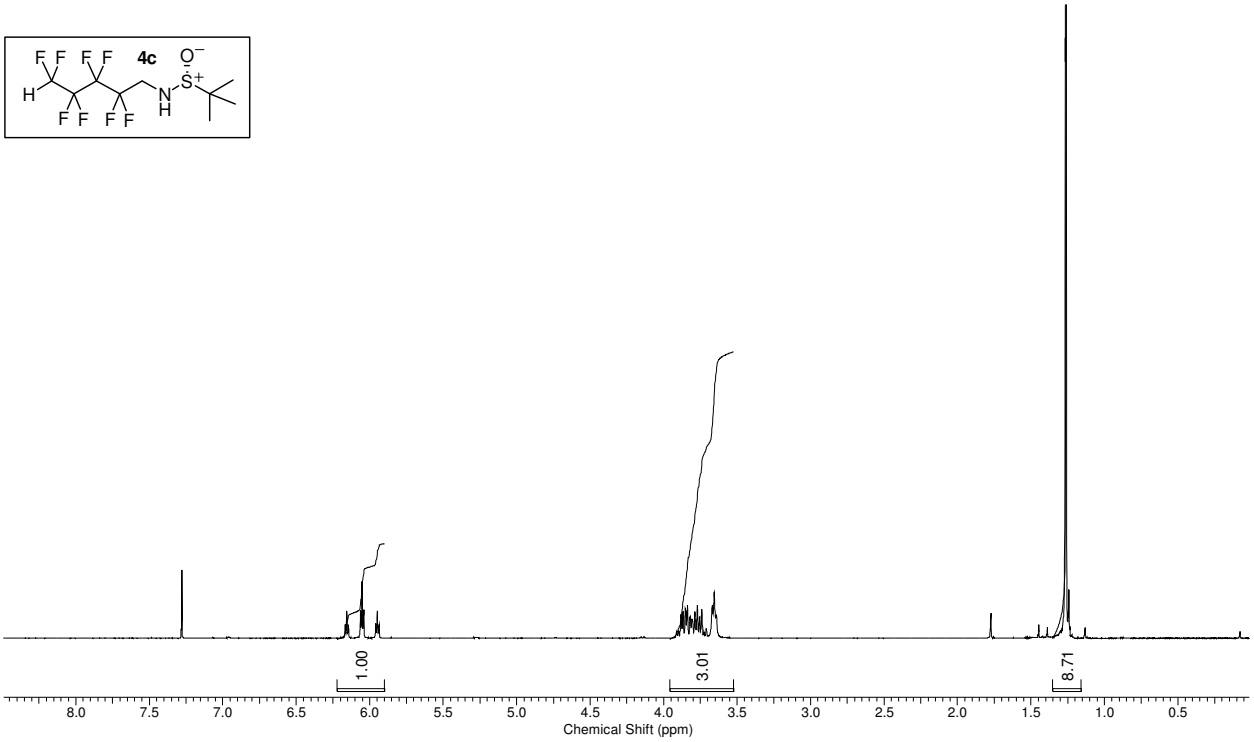


^{13}C NMR, d_1-chloroform

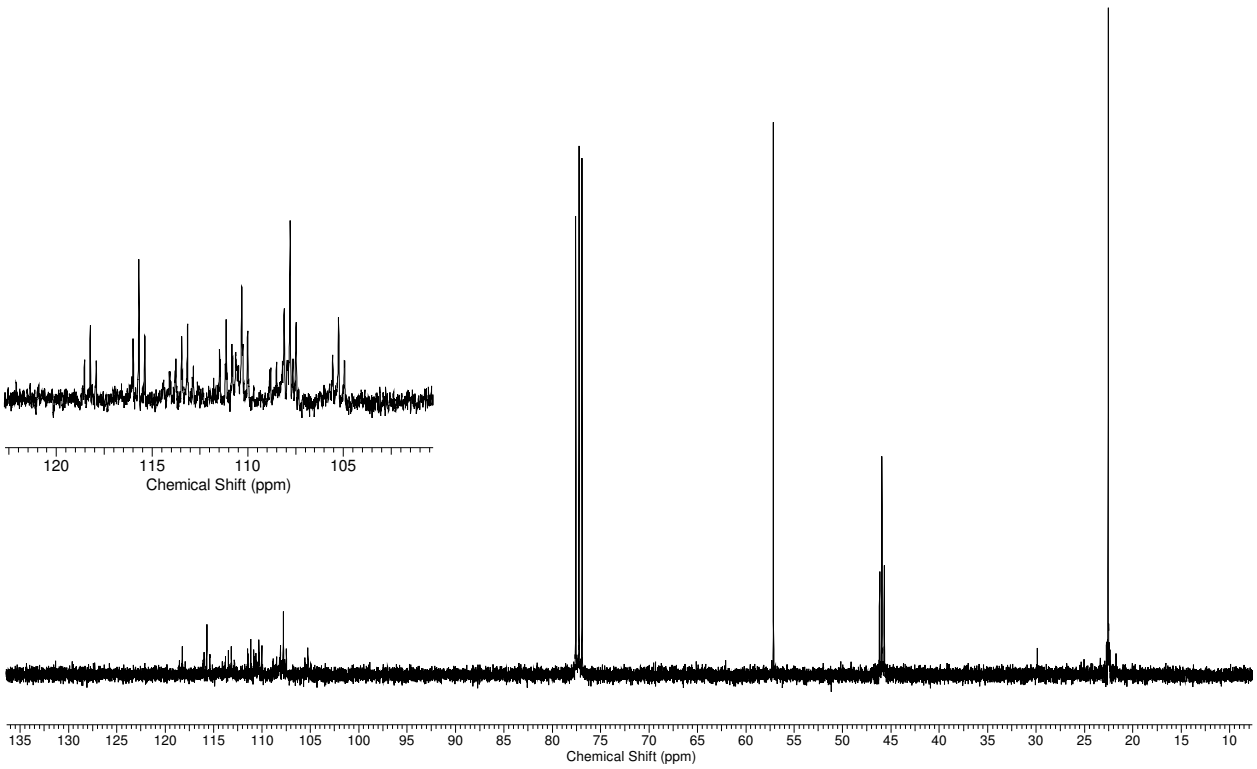


Catalyst **4c**

^{1}H NMR, d_1-chloroform

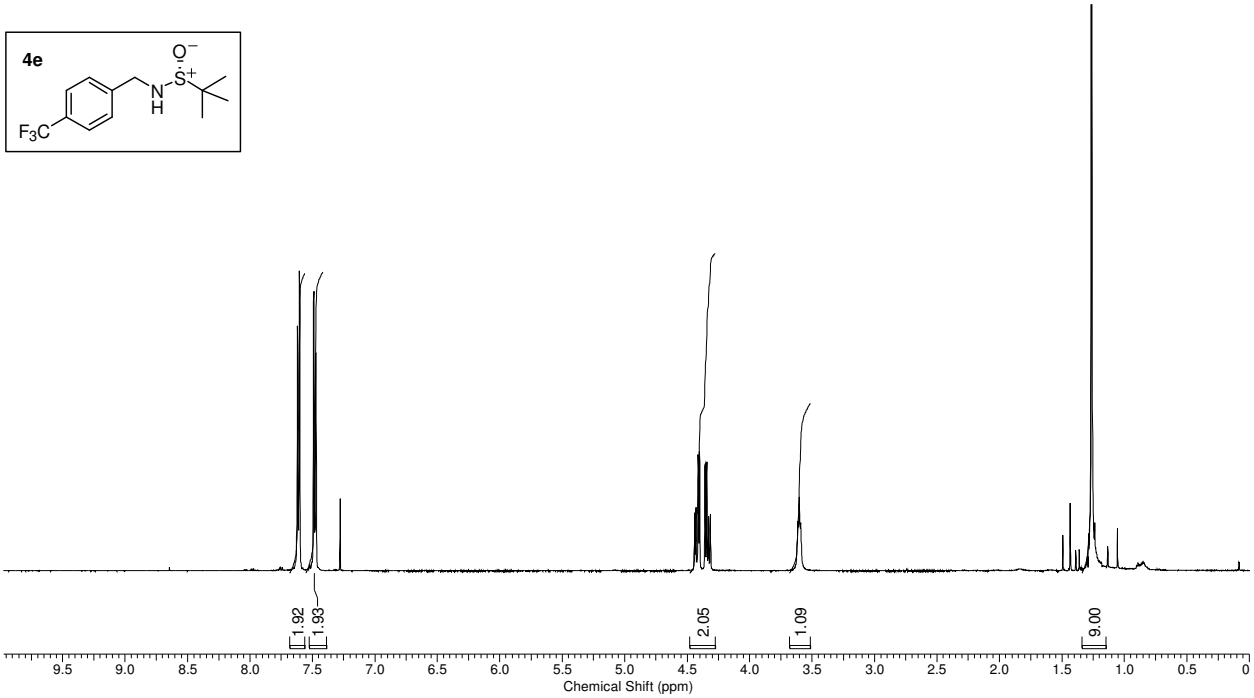


^{13}C NMR, d_1-chloroform

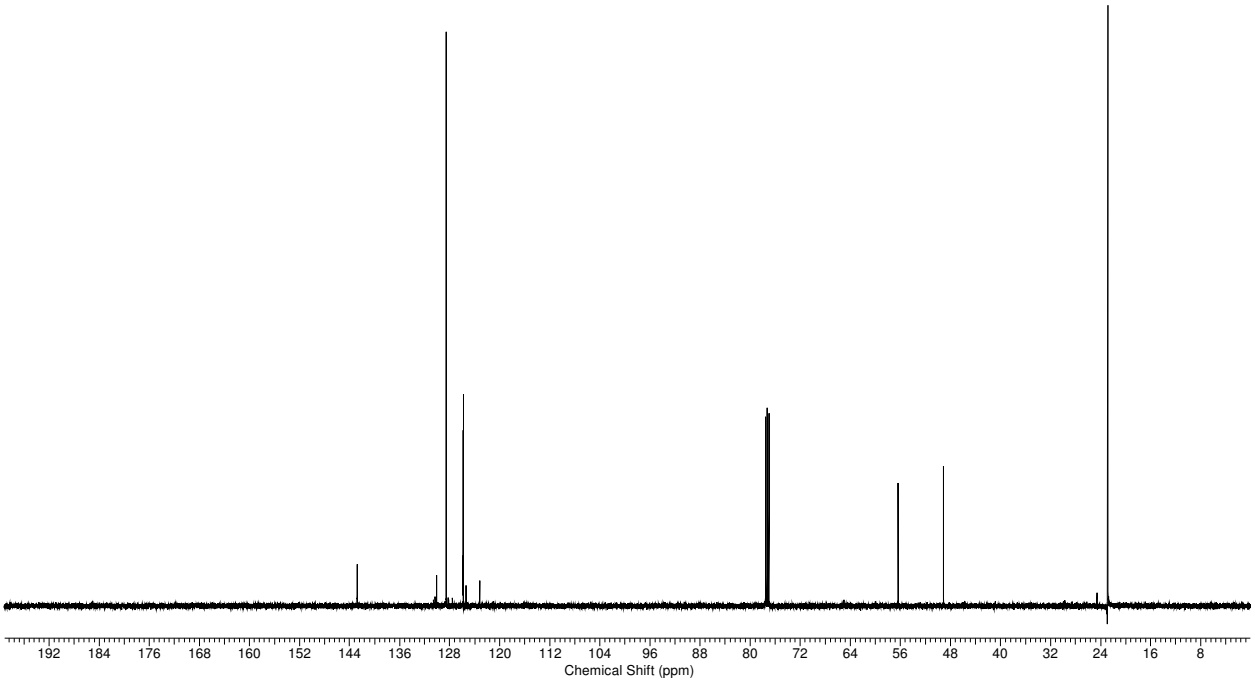


Catalyst **4e**

^{1}H NMR, d_1-chloroform

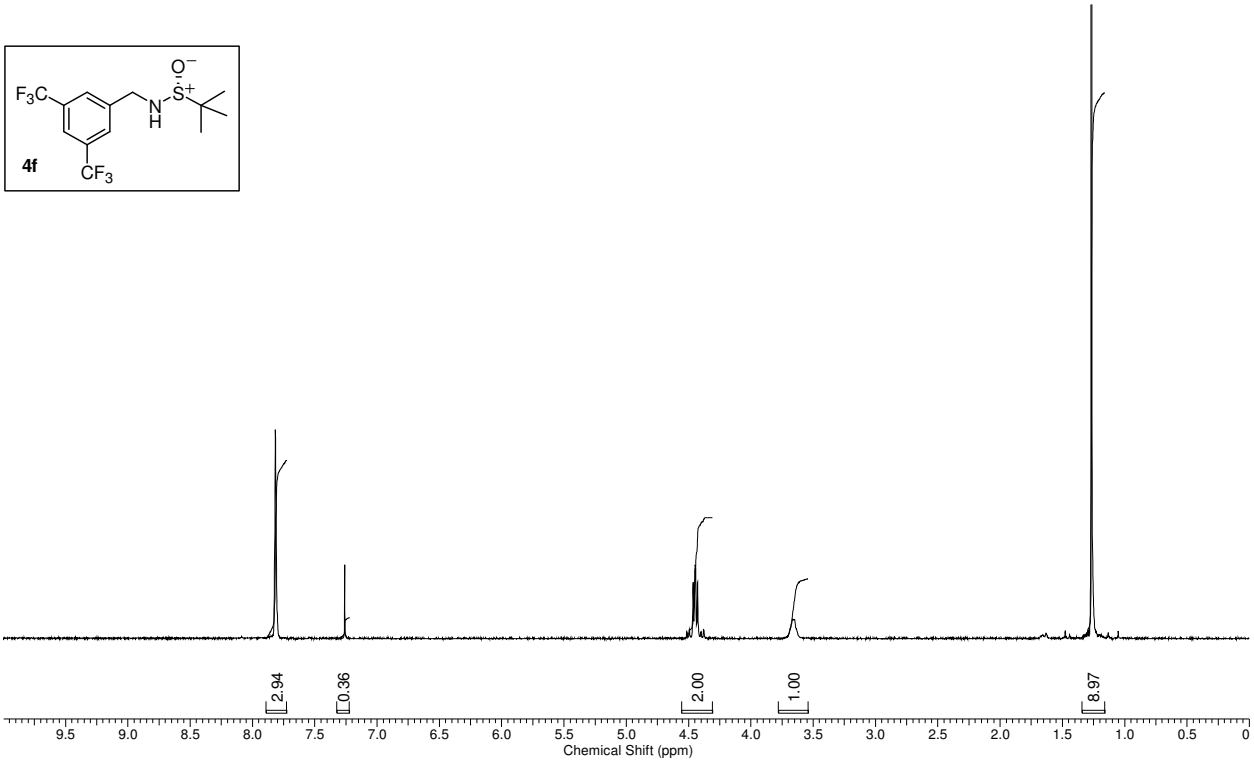


^{13}C NMR, d_1-chloroform

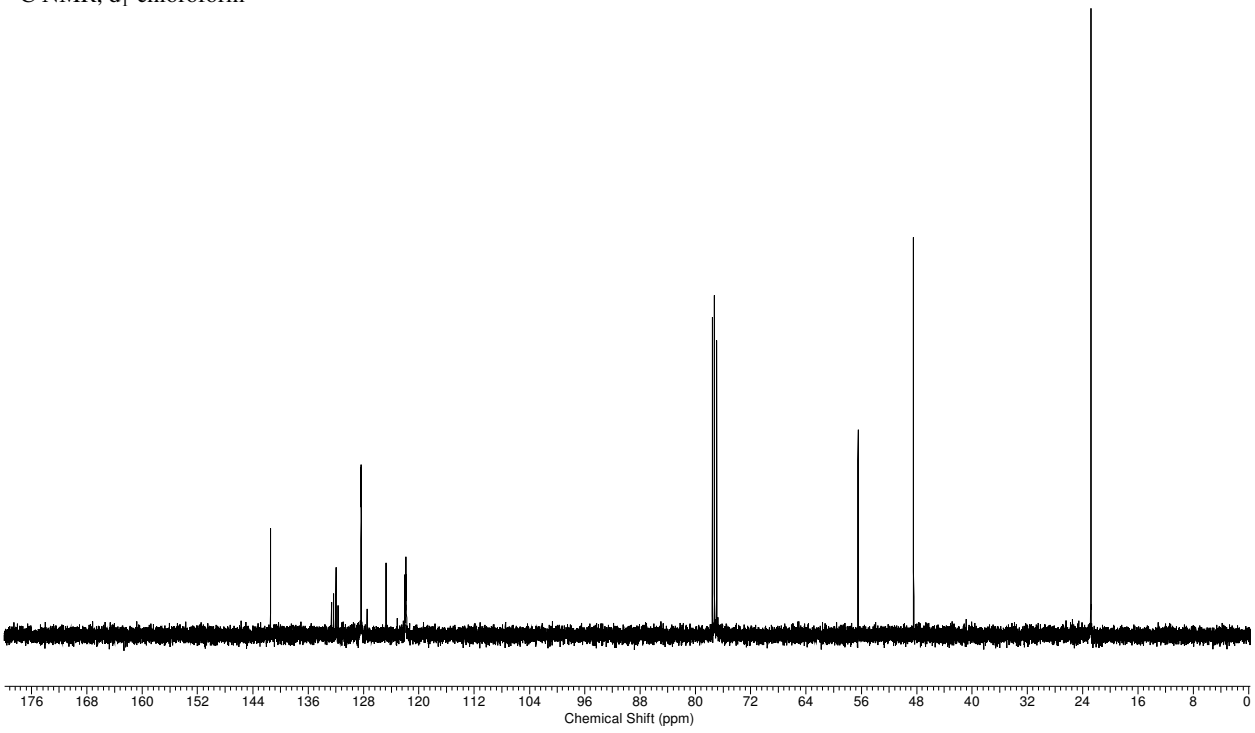


Catalyst **4f**

^{1}H NMR, d_1-chloroform

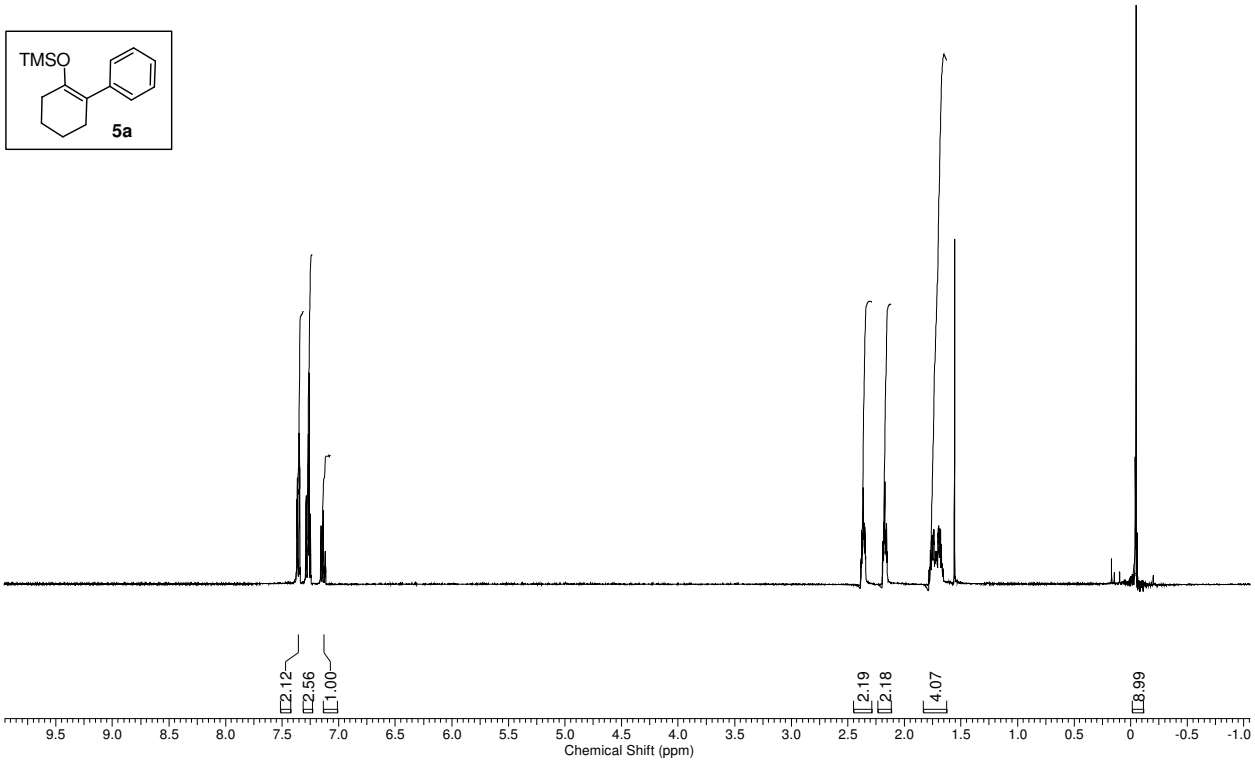


^{13}C NMR, d_1-chloroform

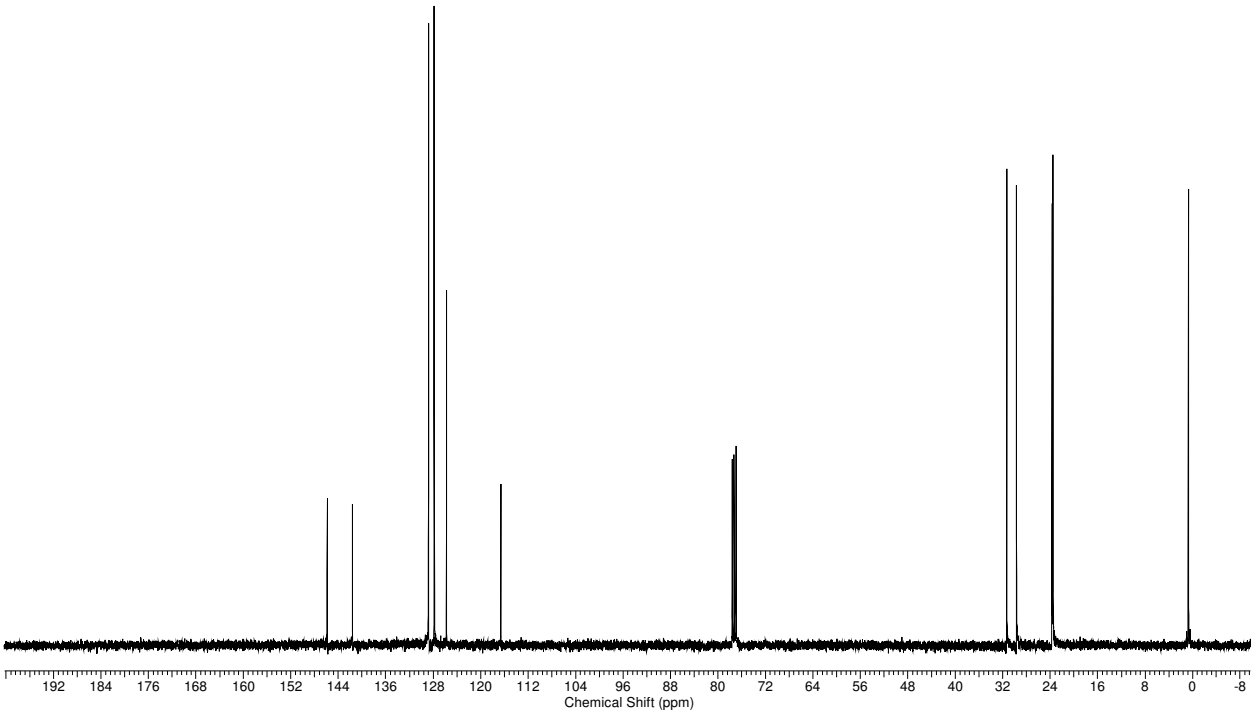


2-Phenyl-1-(trimethylsiloxy)cyclohex-1-ene (5a)

^{1}H NMR, d_1-chloroform

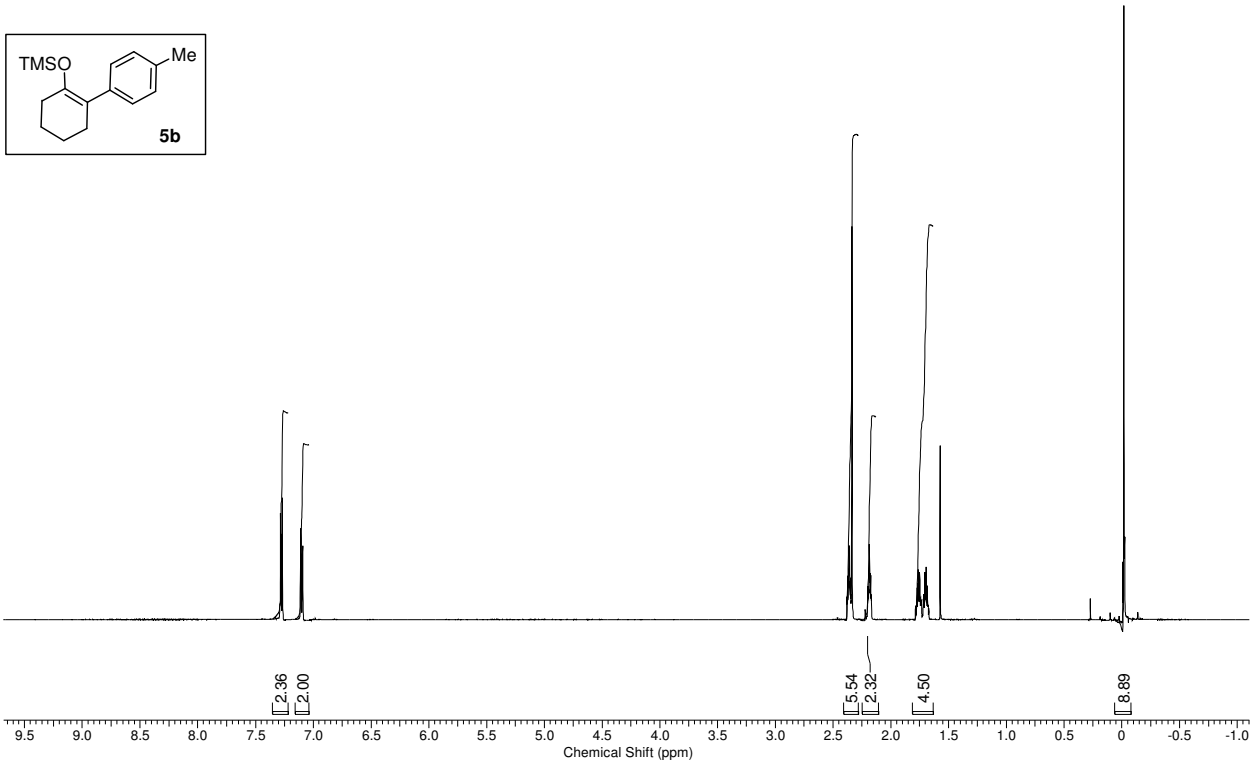


^{13}C NMR, d_1-chloroform

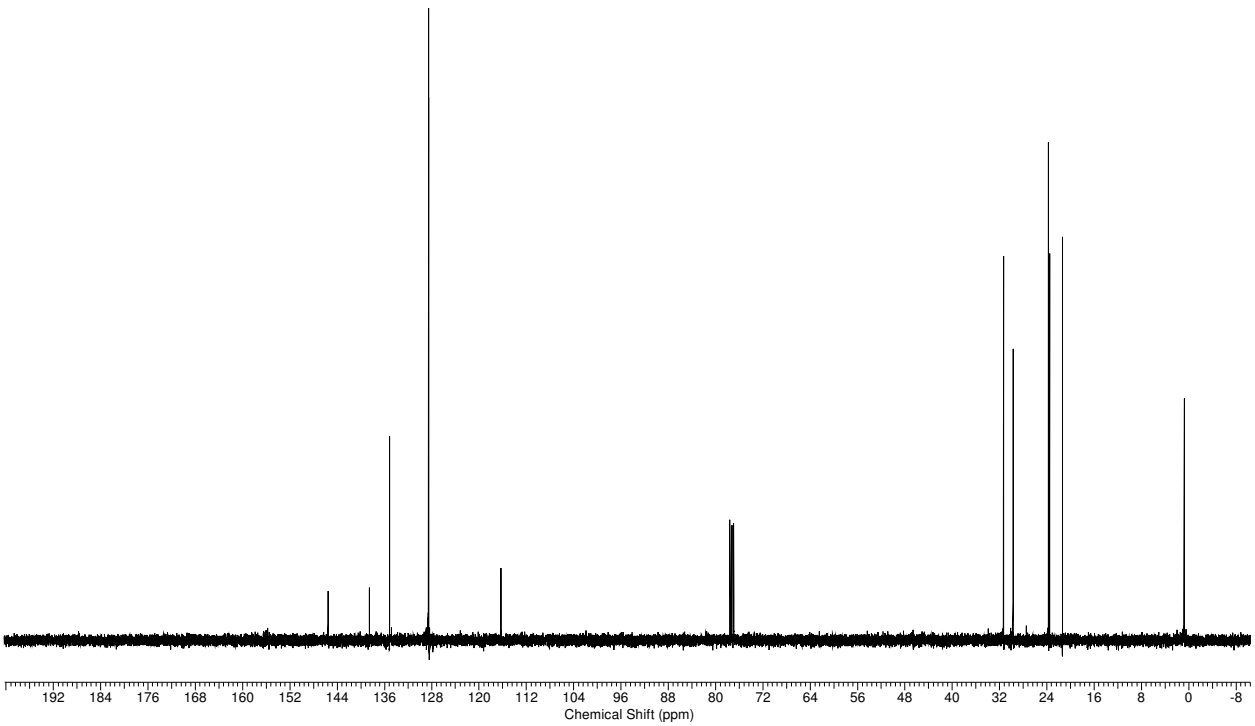


2-(4-methylphenyl)-1-(trimethylsiloxy)cyclohex-1-ene (5b)

^{1}H NMR, d_1-chloroform

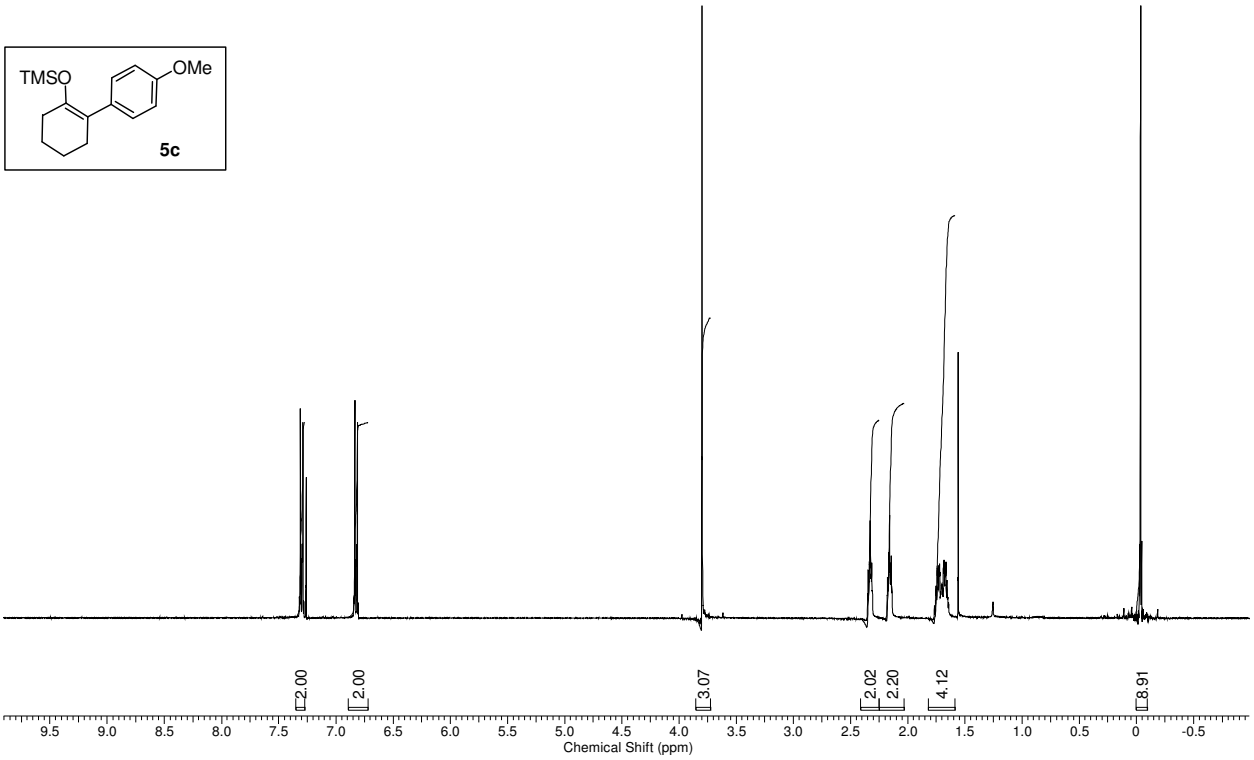


^{13}C NMR, d_1-chloroform

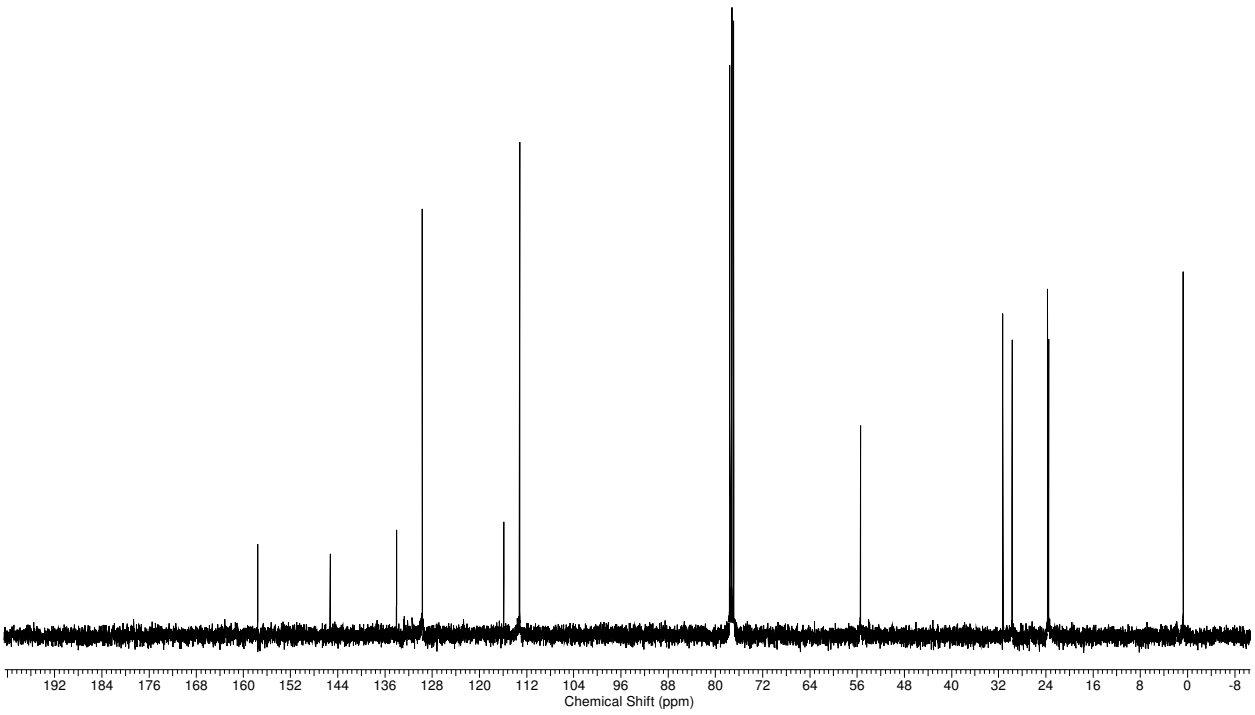


2-(4-methoxyphenyl)-1-(trimethylsiloxy)cyclohex-1-ene (5c)

^{1}H NMR, d_1-chloroform

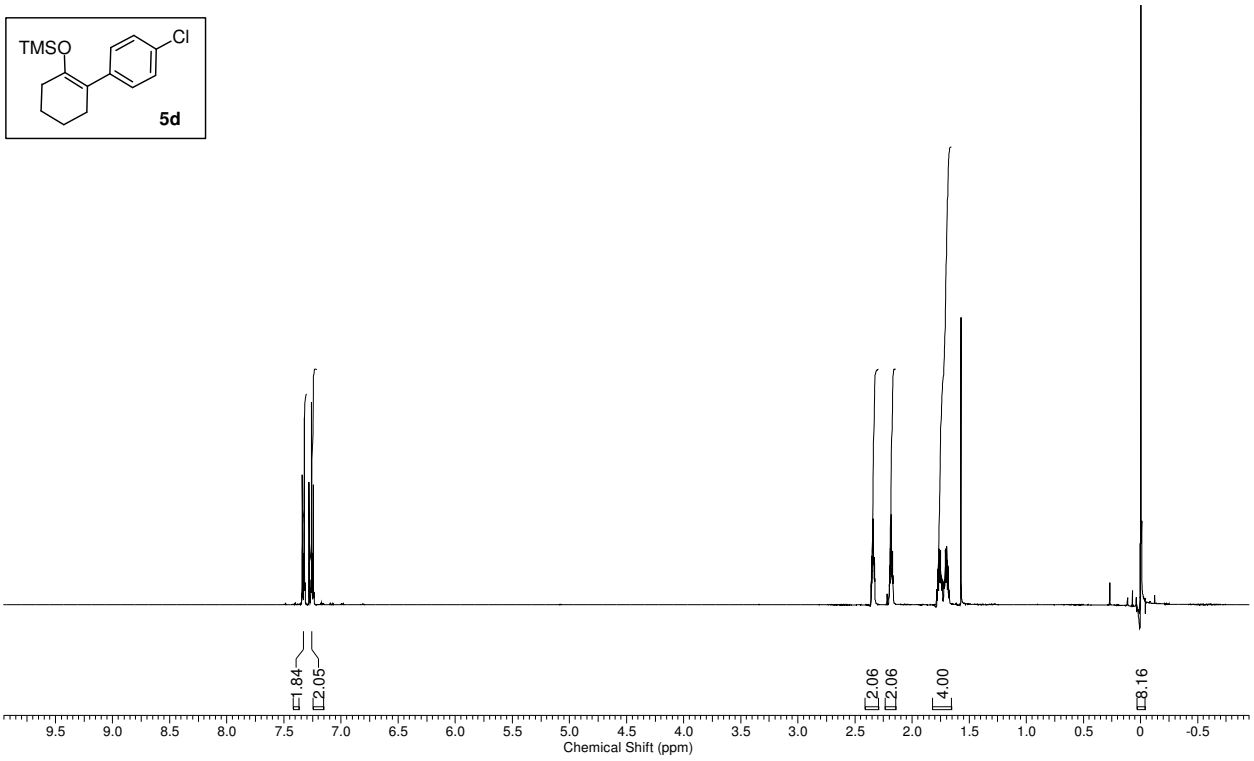


^{13}C NMR, d_1-chloroform

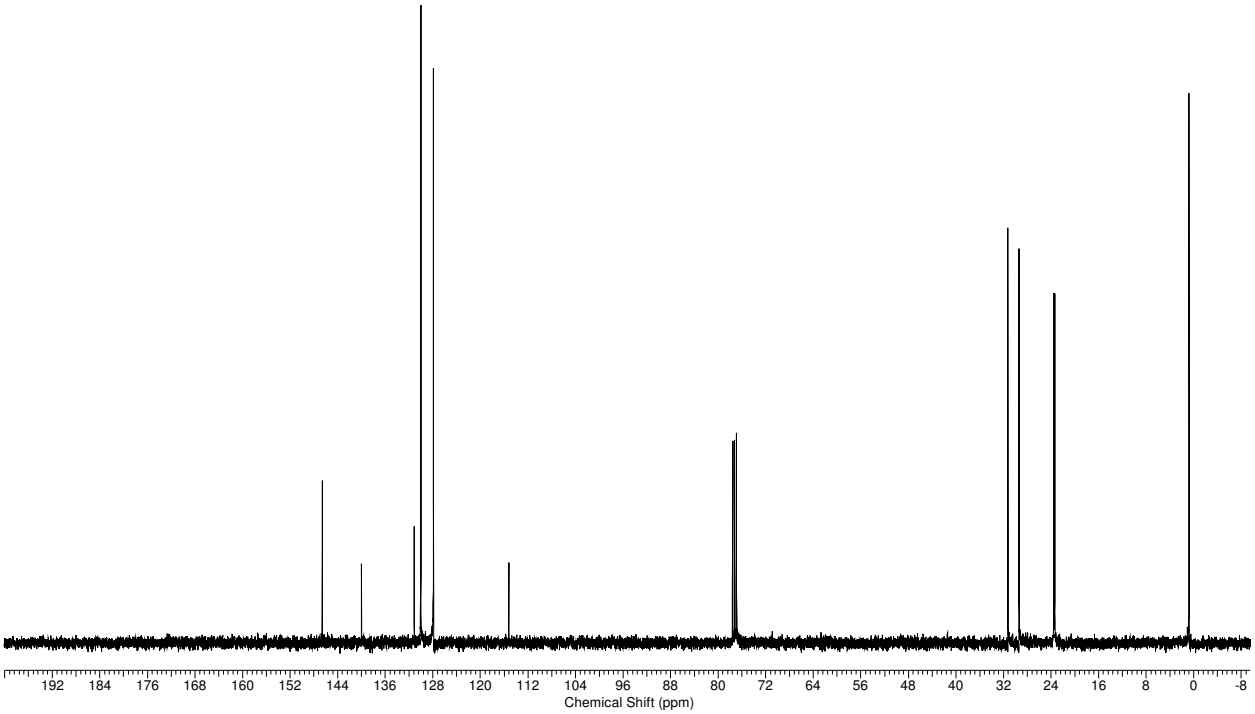


2-(4-chlorophenyl)-1-(trimethylsiloxy)cyclohex-1-ene (5d)

^{1}H NMR, d_1-chloroform

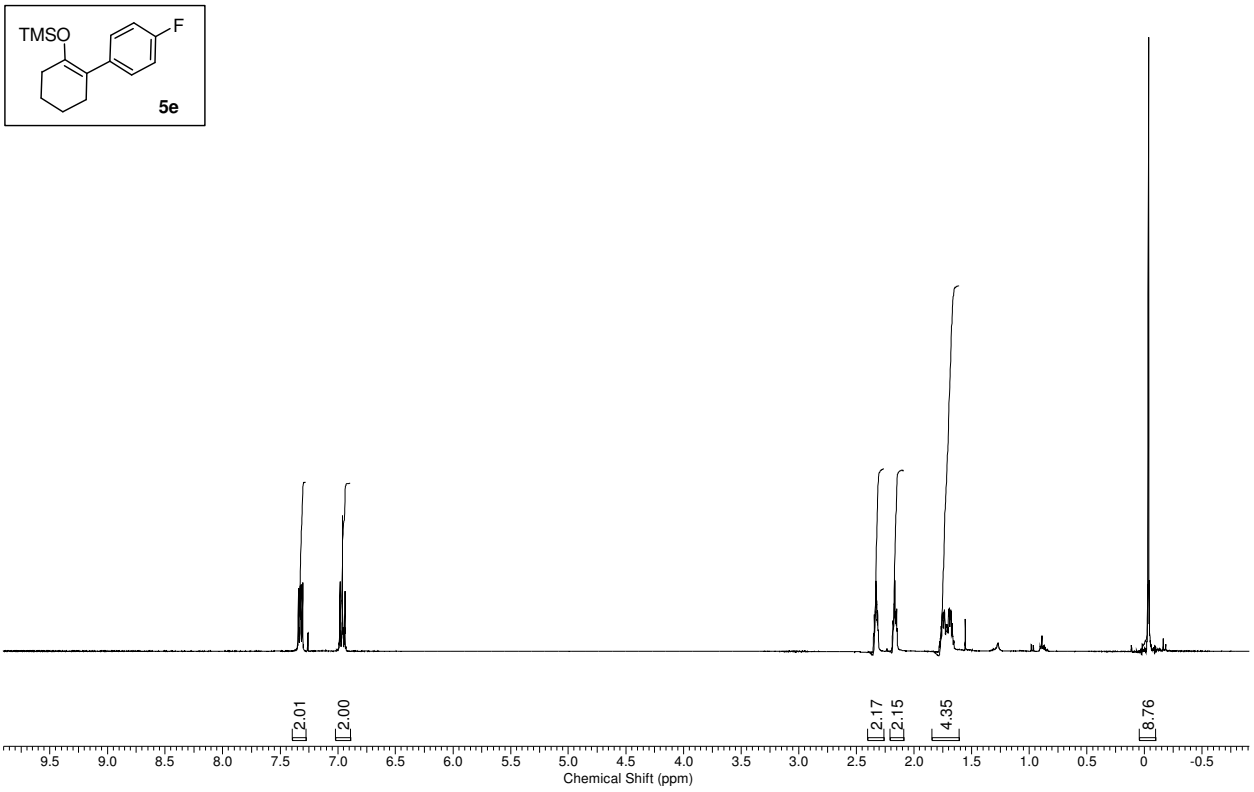


^{13}C NMR, d_1-chloroform

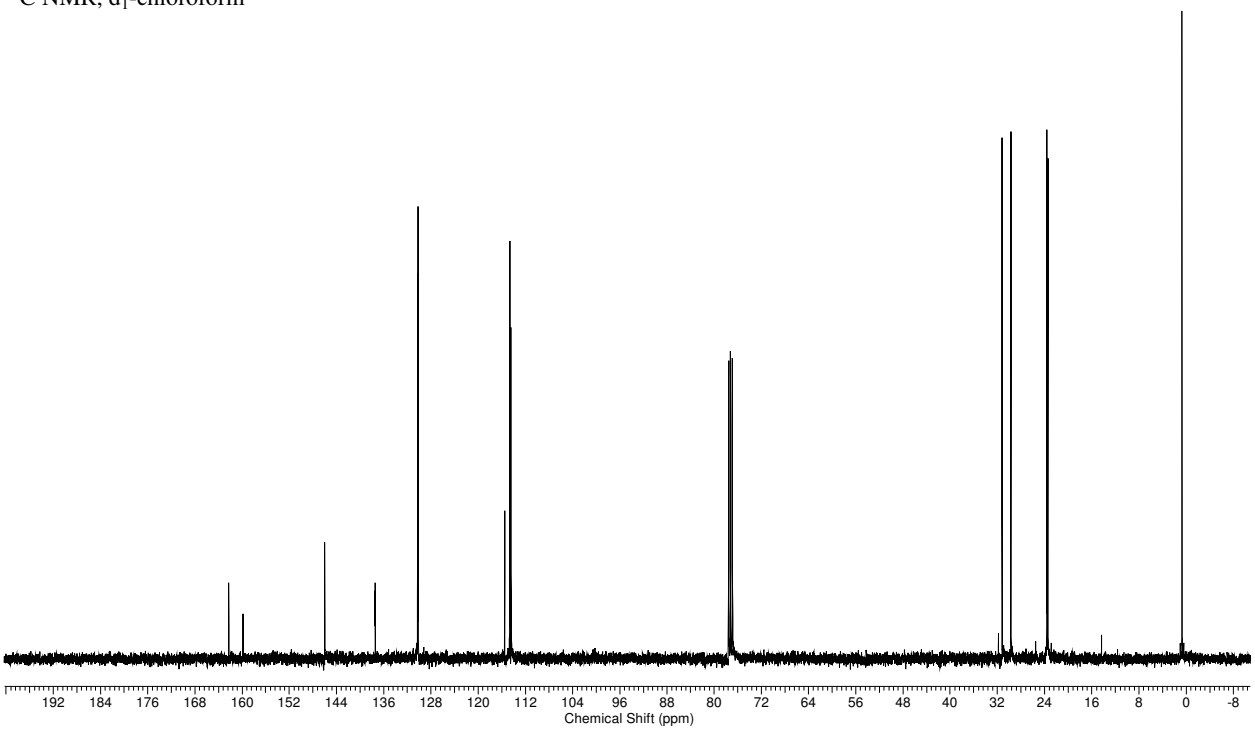


2-(4-fluorophenyl)-1-(trimethylsiloxy)cyclohex-1-ene (5e)

^{1}H NMR, d_1-chloroform

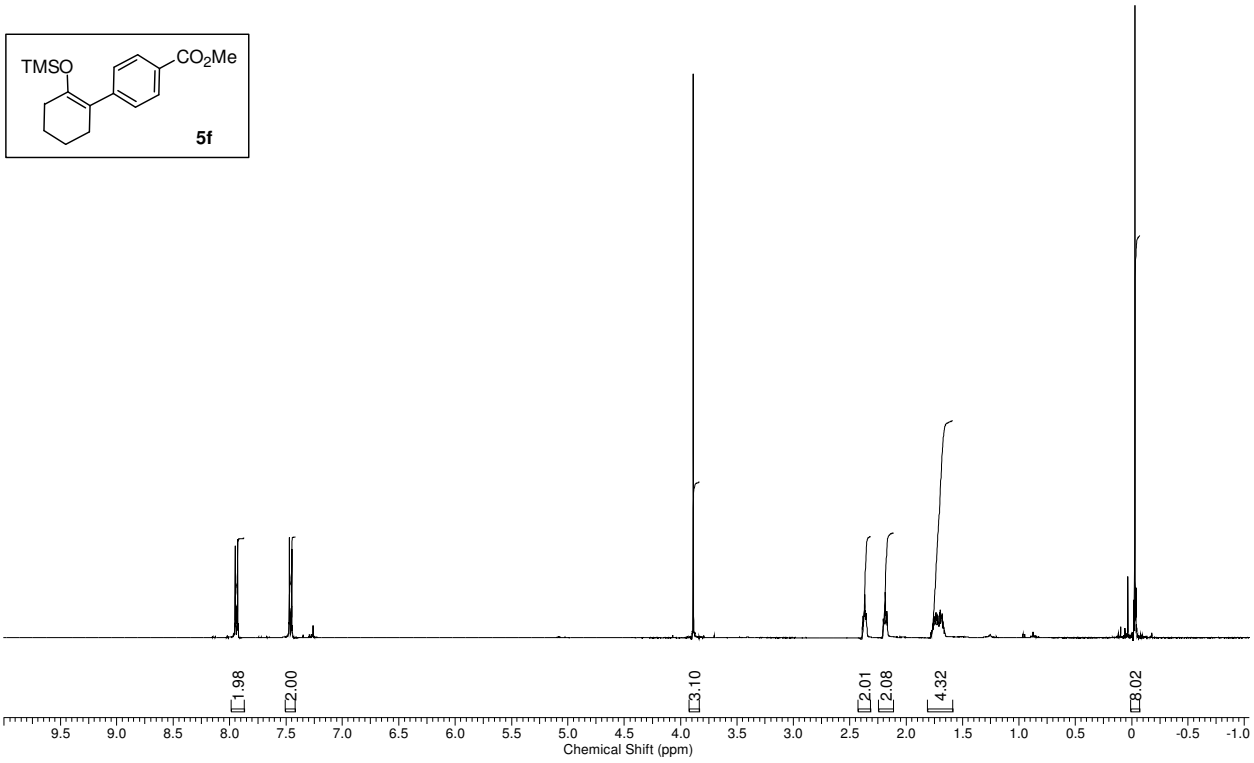


^{13}C NMR, d_1-chloroform

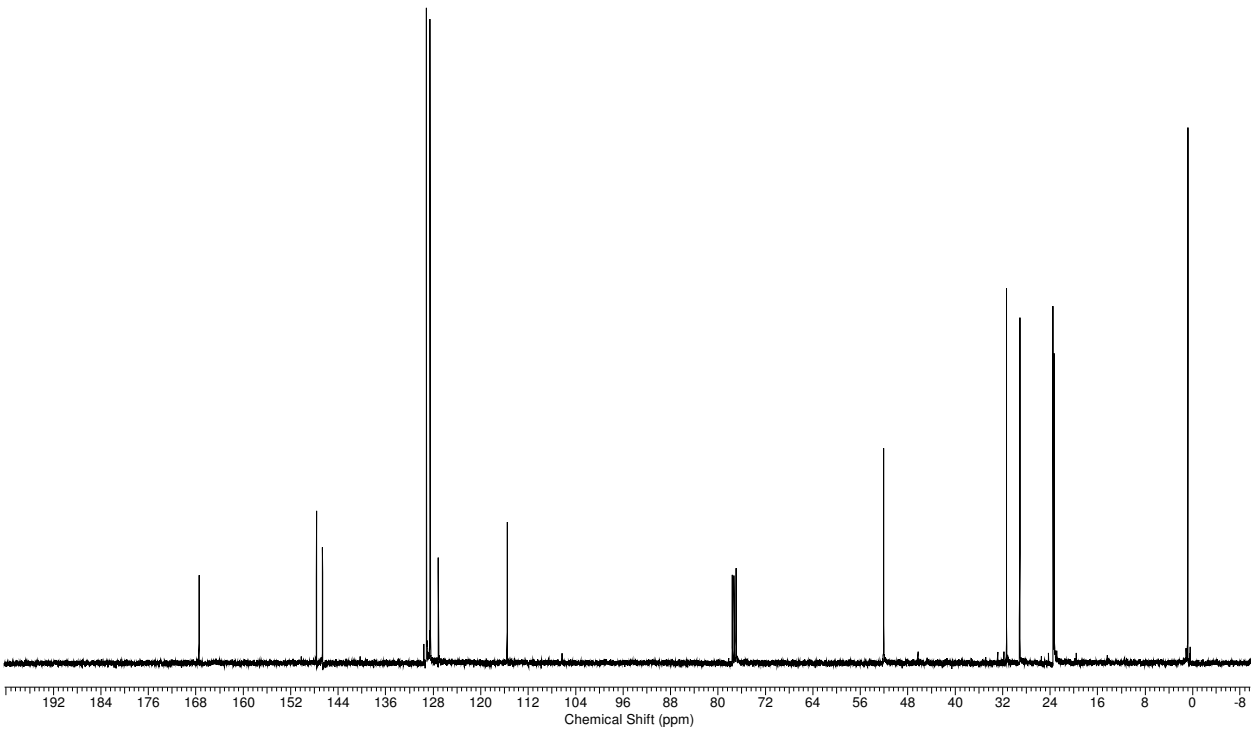


2-(4-methylbenzoate)-1-(trimethylsiloxy)cyclohex-1-ene (5f)

^{1}H NMR, d_1-chloroform

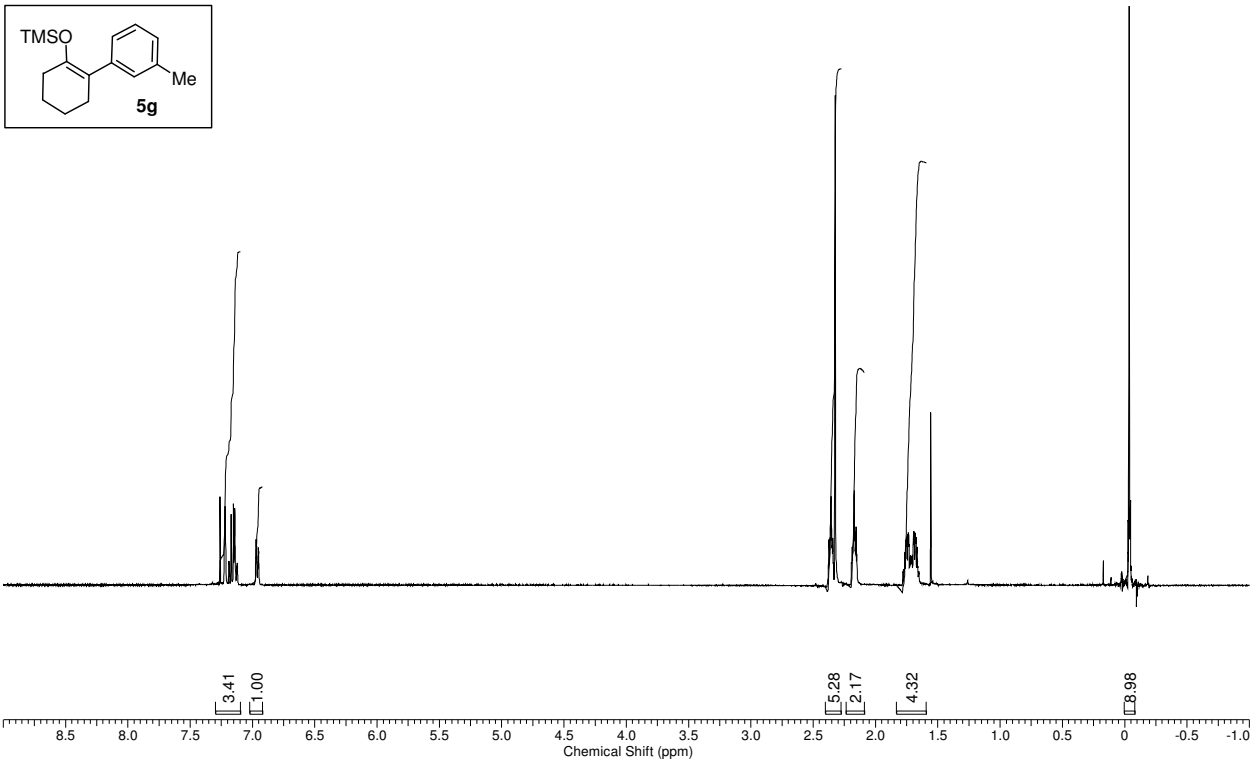


^{13}C NMR, d_1-chloroform

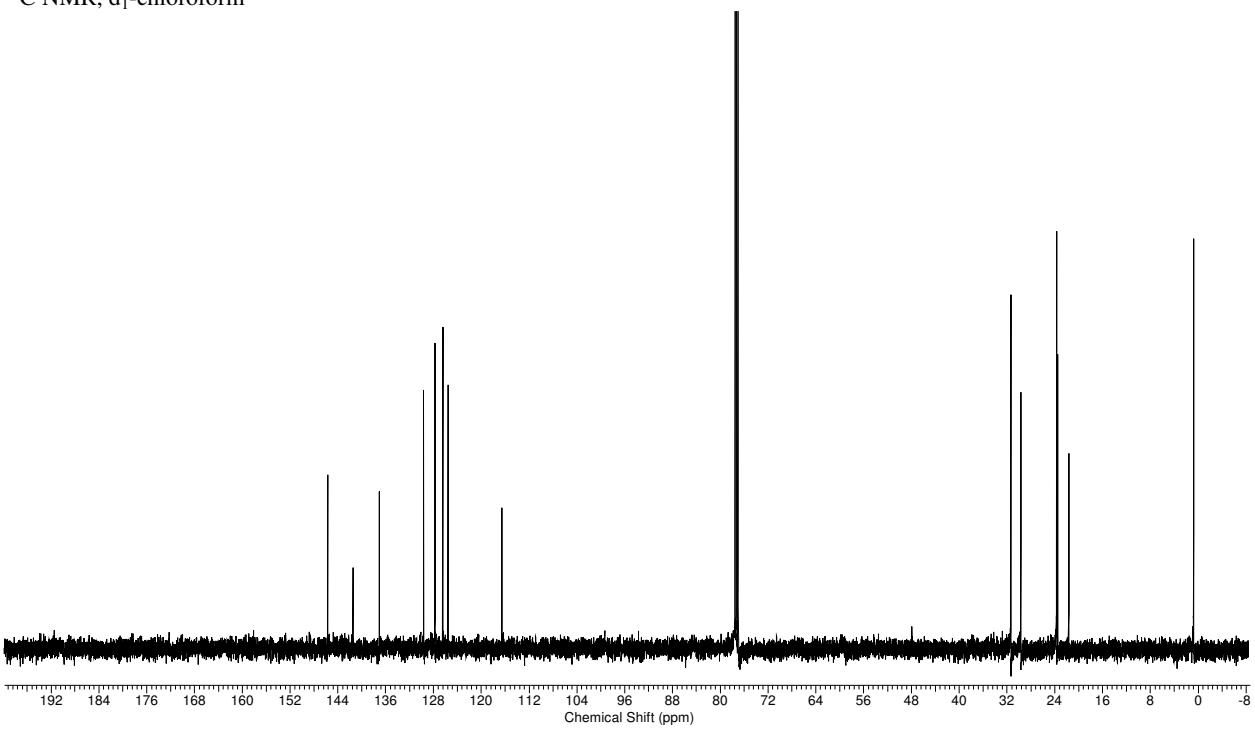


2-(3-methylphenyl)-1-(trimethylsiloxy)cyclohex-1-ene (5g)

^{1}H NMR, d_1-chloroform

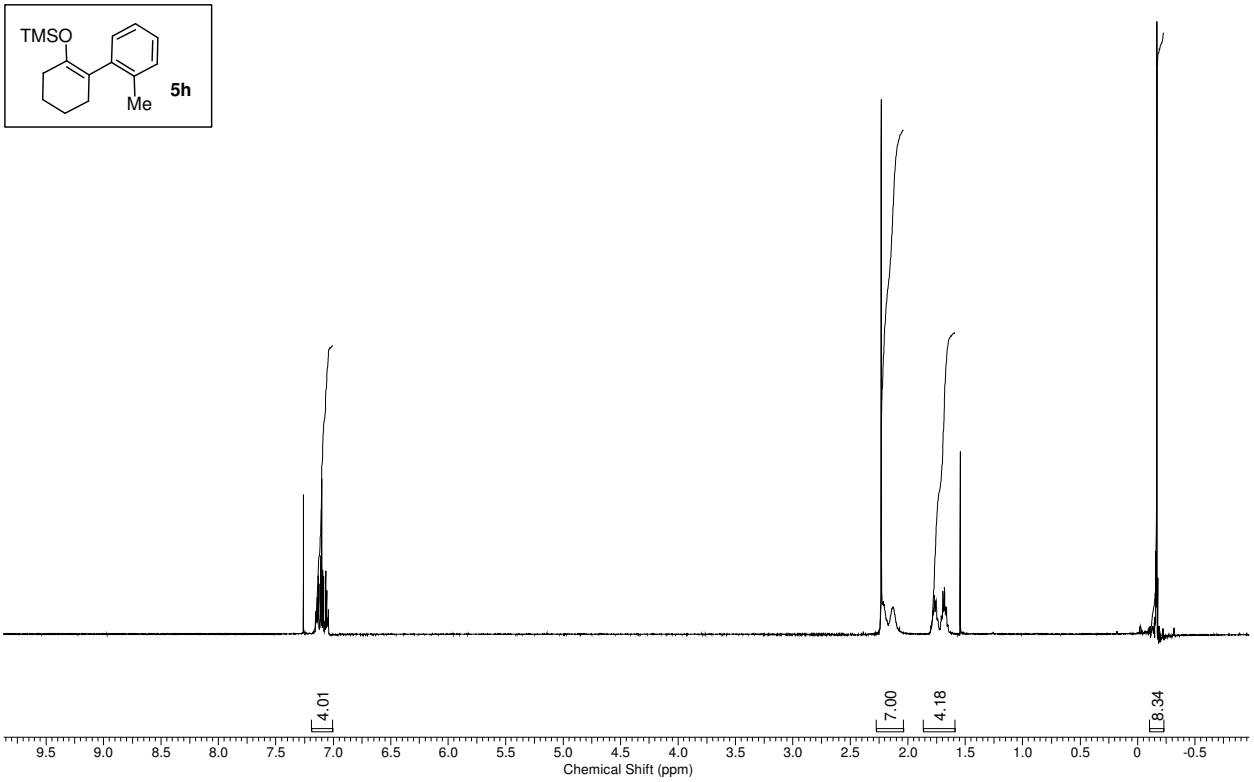


^{13}C NMR, d_1-chloroform

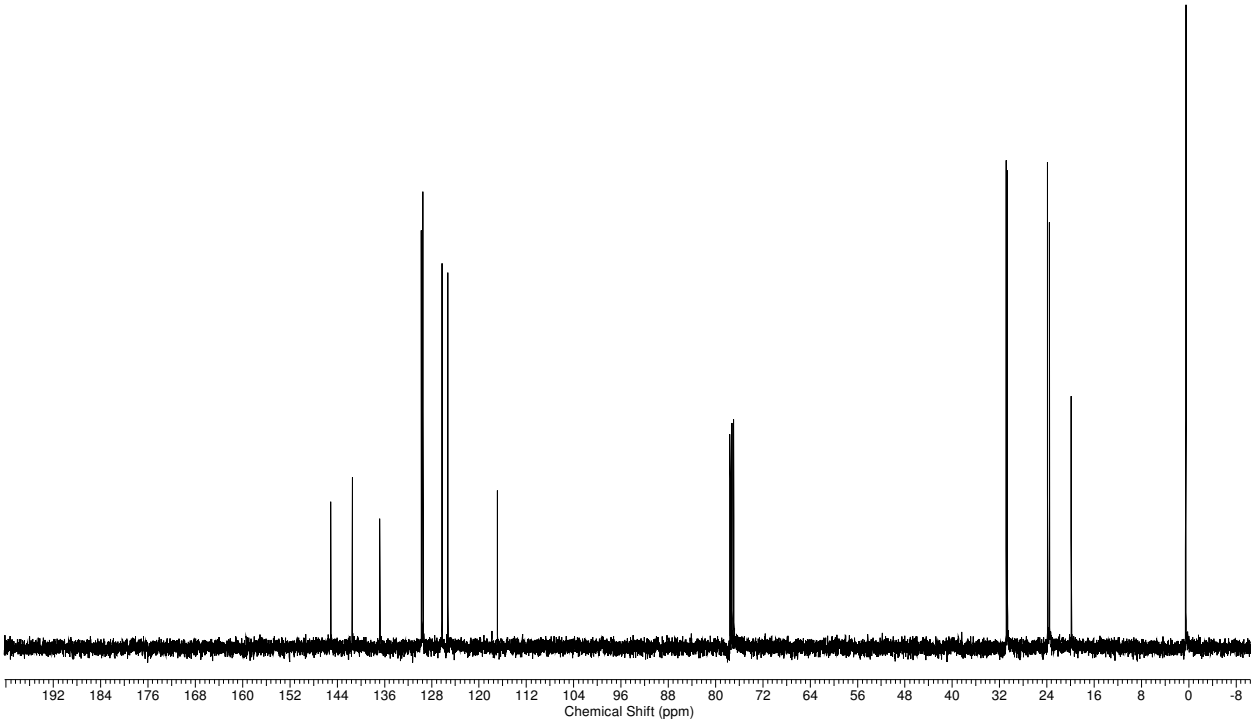


2-(2-methylphenyl)-1-(trimethylsiloxy)cyclohex-1-ene (5h)

^{1}H NMR, d_1-chloroform

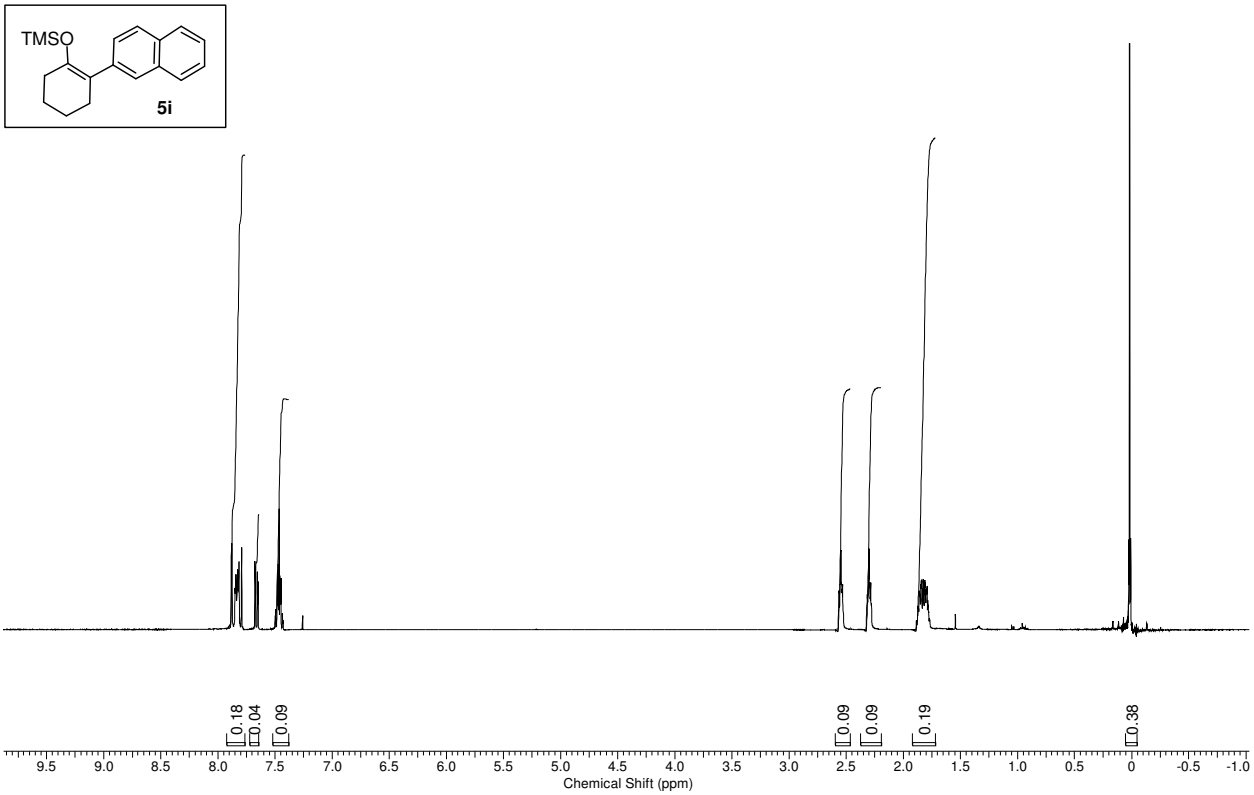


^{13}C NMR, d_1-chloroform

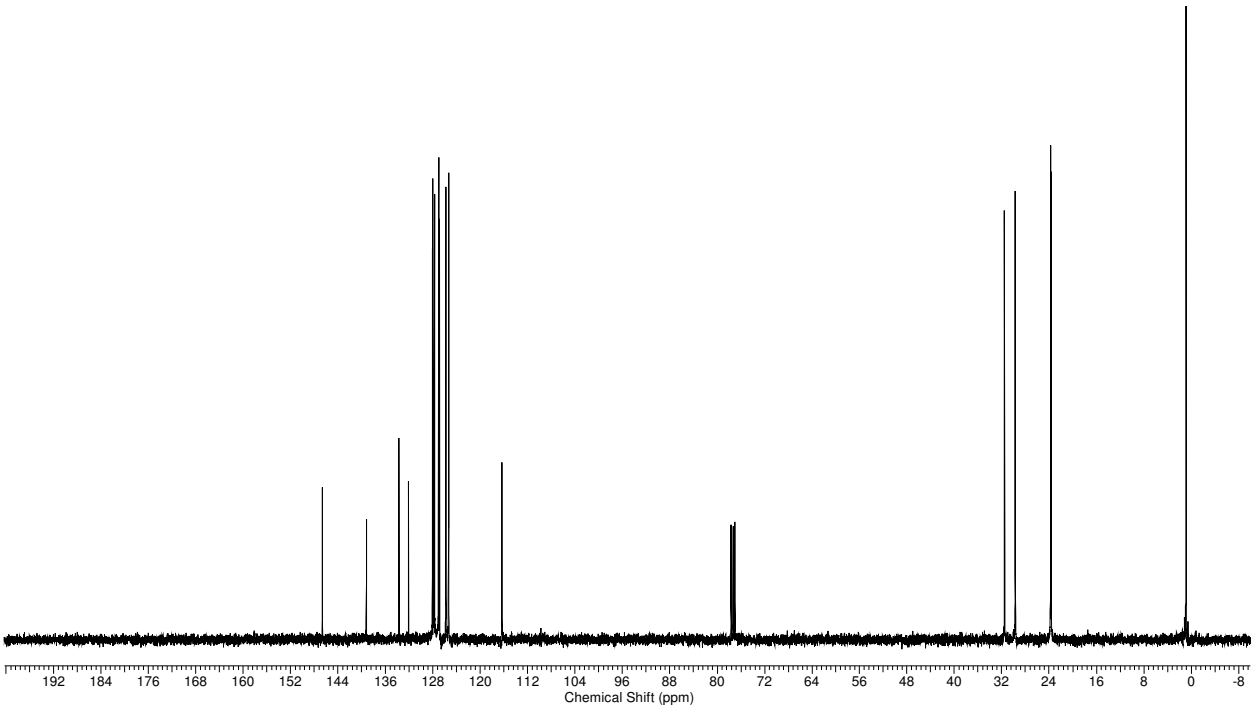


2-(2-Napthyl)-1-(trimethylsiloxy)cyclohex-1-ene (5i)

^{1}H NMR, d_1-chloroform

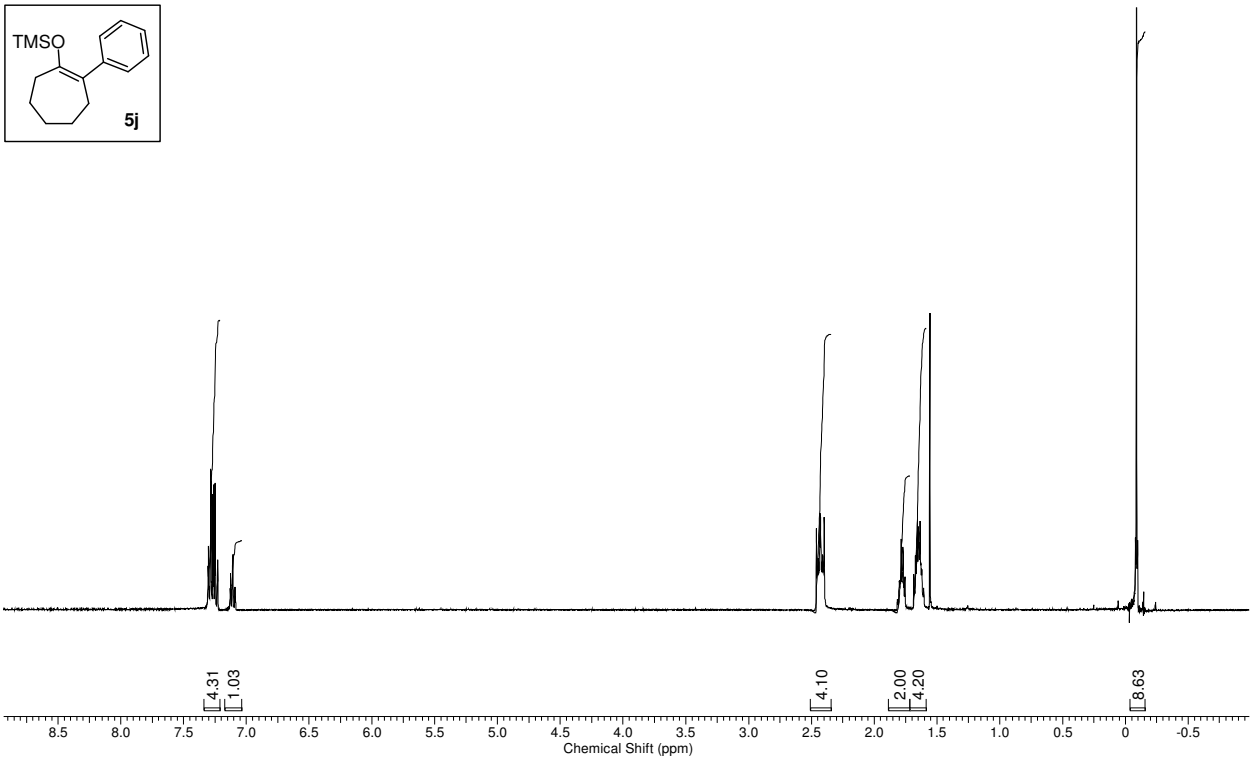


^{13}C NMR, d_1-chloroform

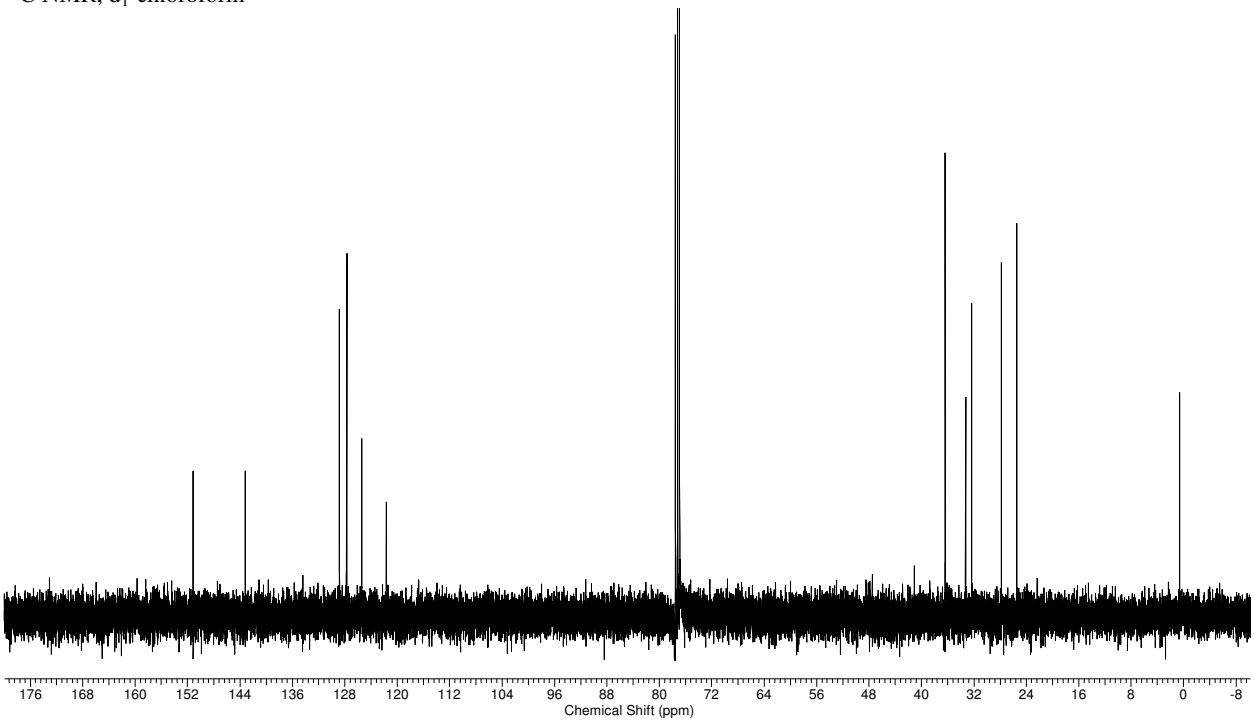


2-phenyl-1-(trimethylsiloxy)cyclohept-1-ene (5i)

^{1}H NMR, d_1-chloroform

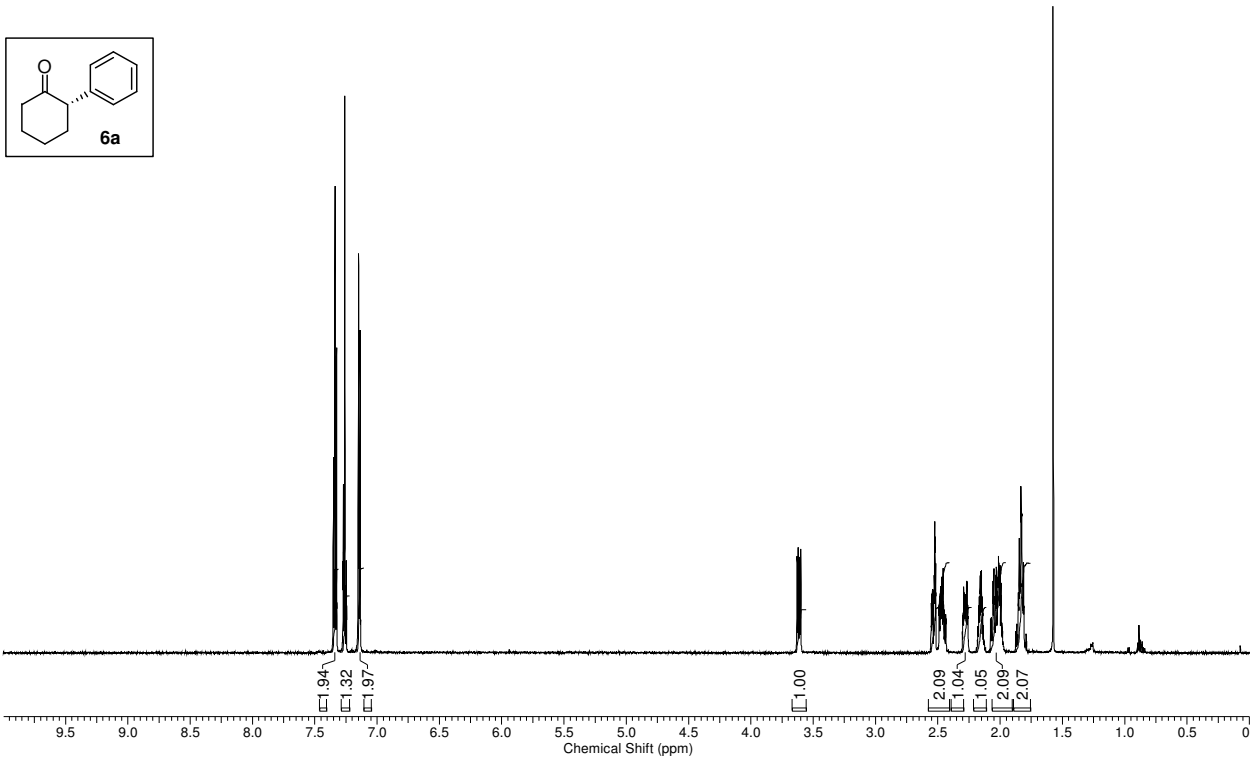


^{13}C NMR, d_1-chloroform



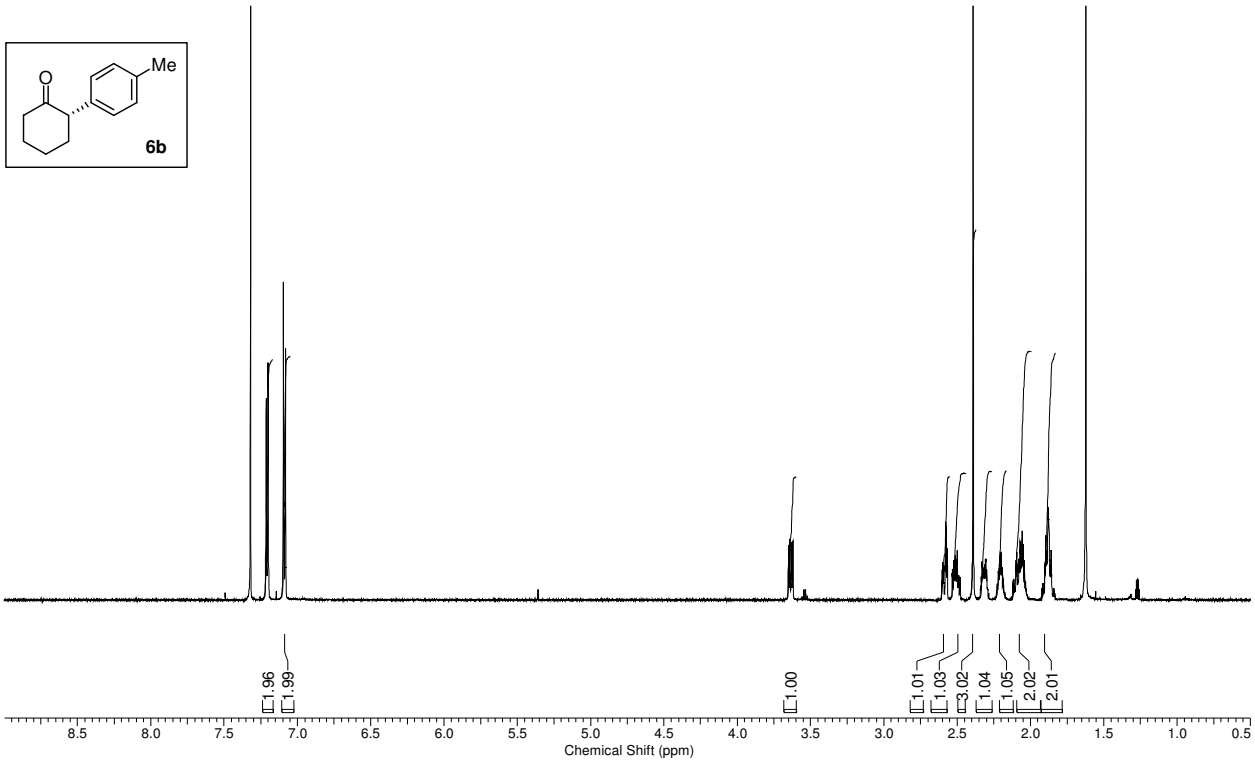
2-phenyl-cyclohexanone (6a)

^{1}H NMR, d_1-chloroform



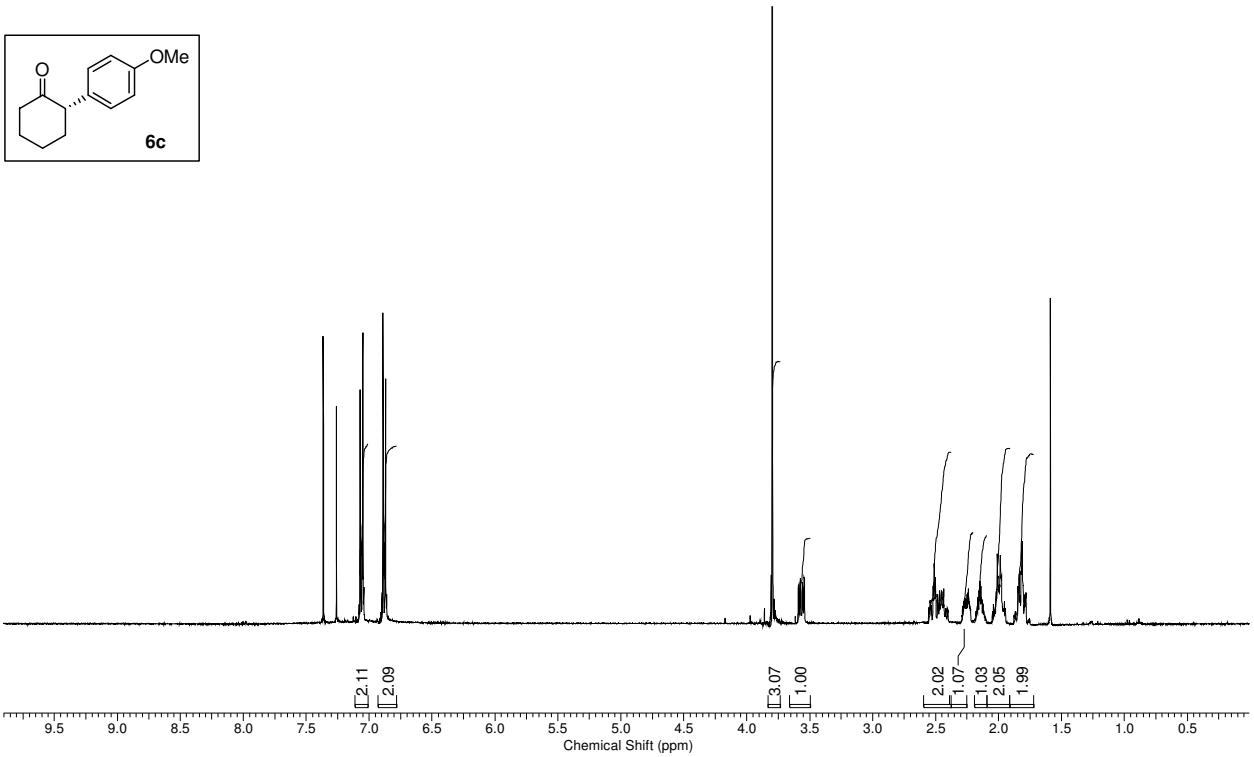
2-(4-methylphenyl)-cyclohexanone (6b)

^{1}H NMR, d_1-chloroform



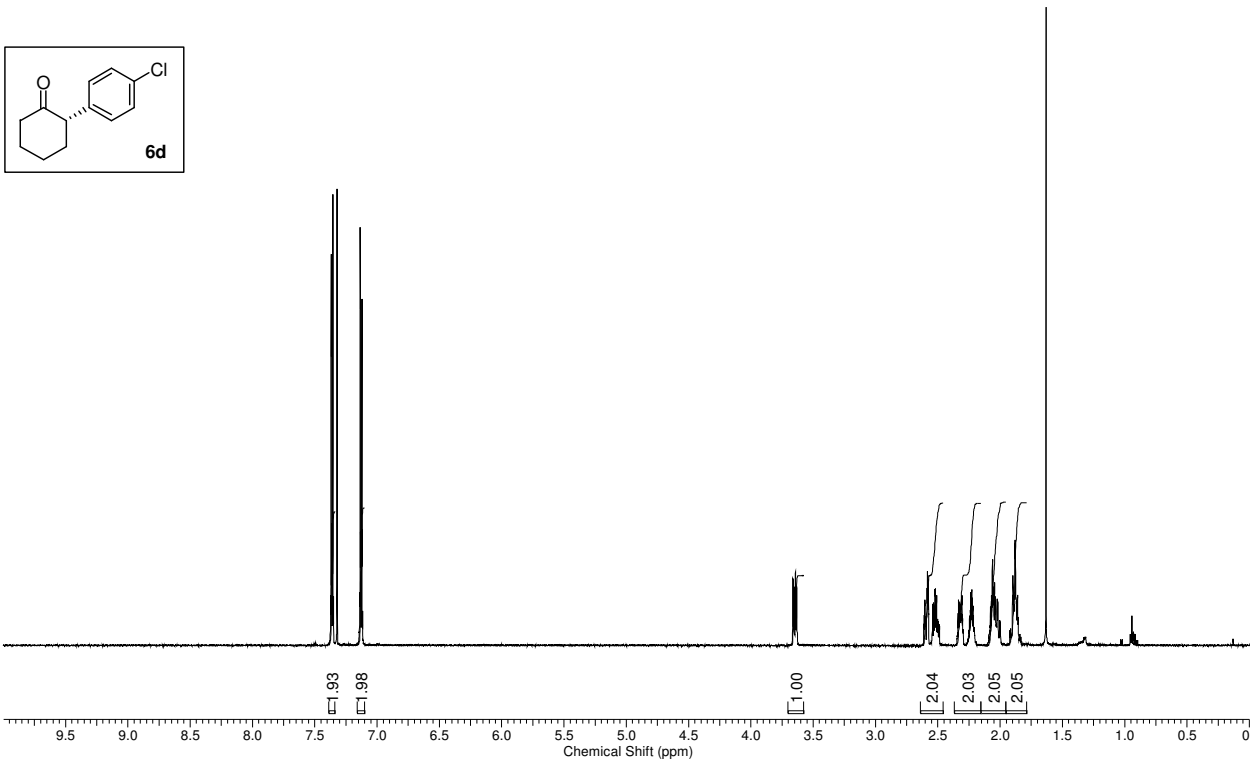
2-(4-methoxyphenyl)-cyclohexanone (6c)

^{1}H NMR, d_1-chloroform



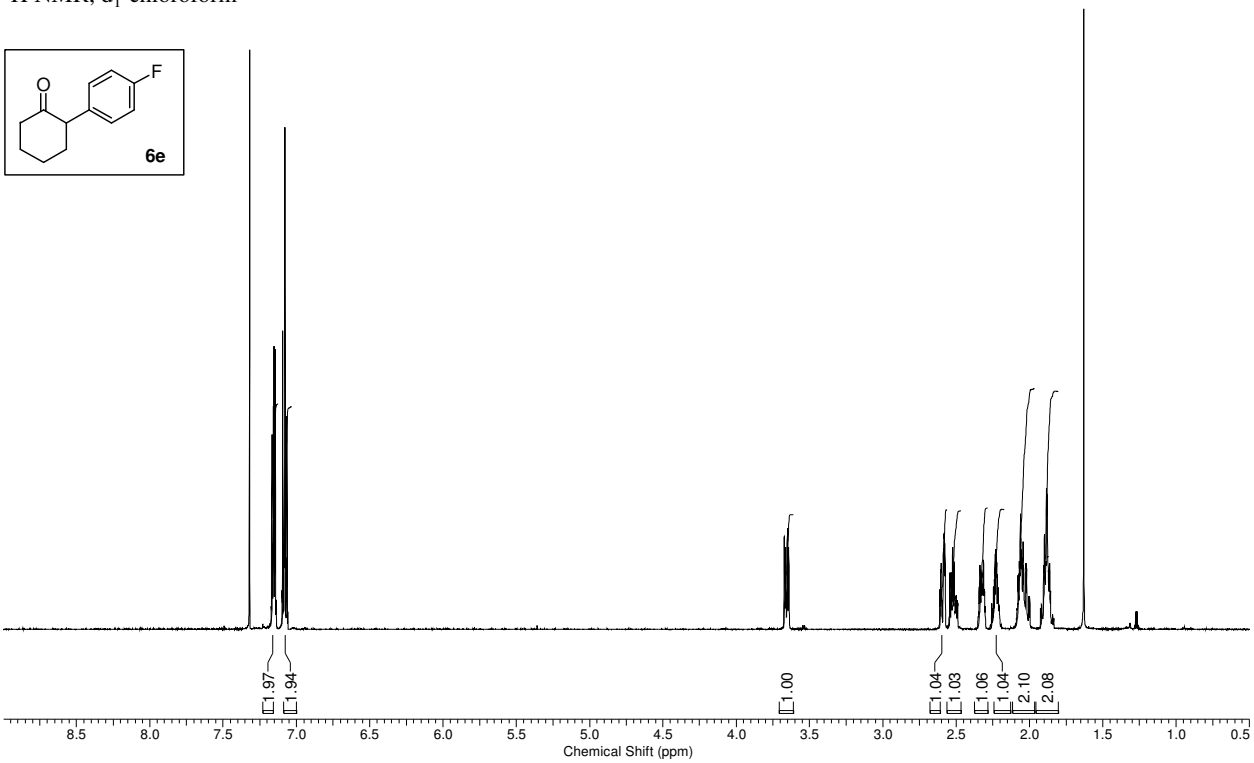
2-(4-chlorophenyl)-cyclohexanone (6d)

^{1}H NMR, d_1-chloroform



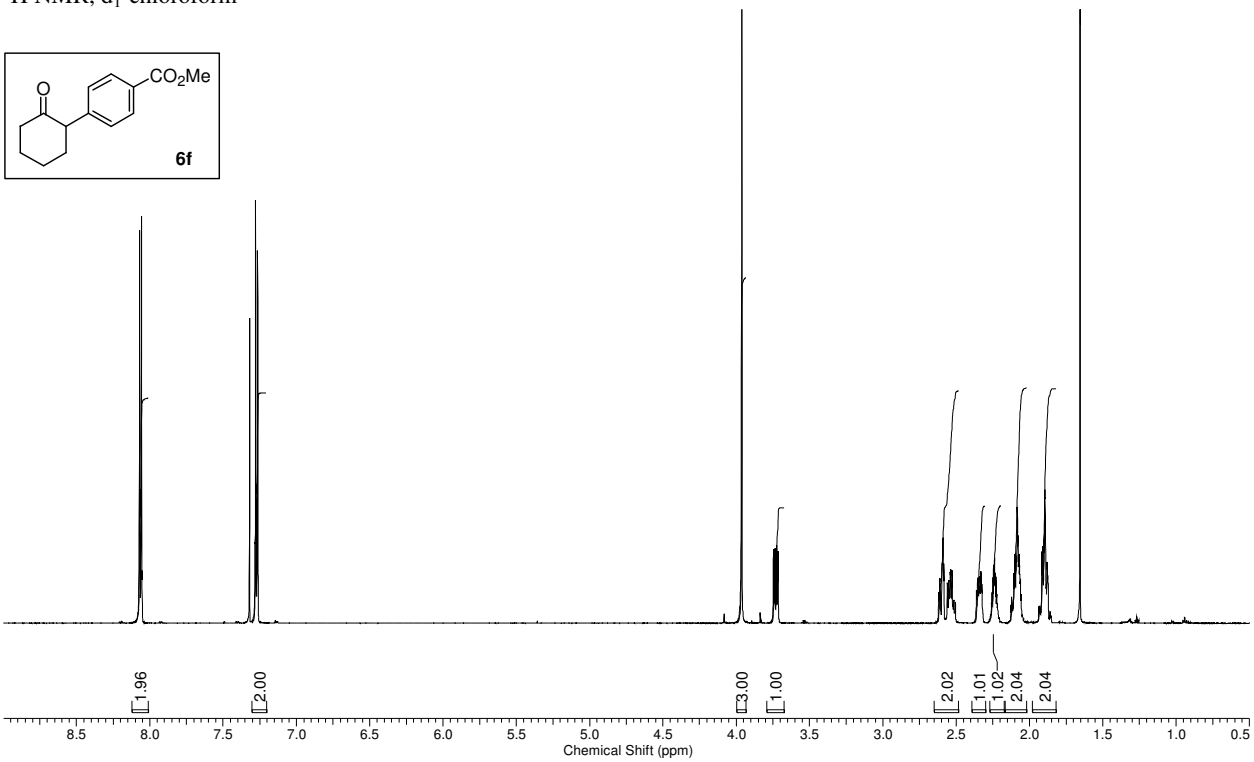
2-(4-fluorophenyl)-cyclohexanone (6e)

^{1}H NMR, d_1-chloroform



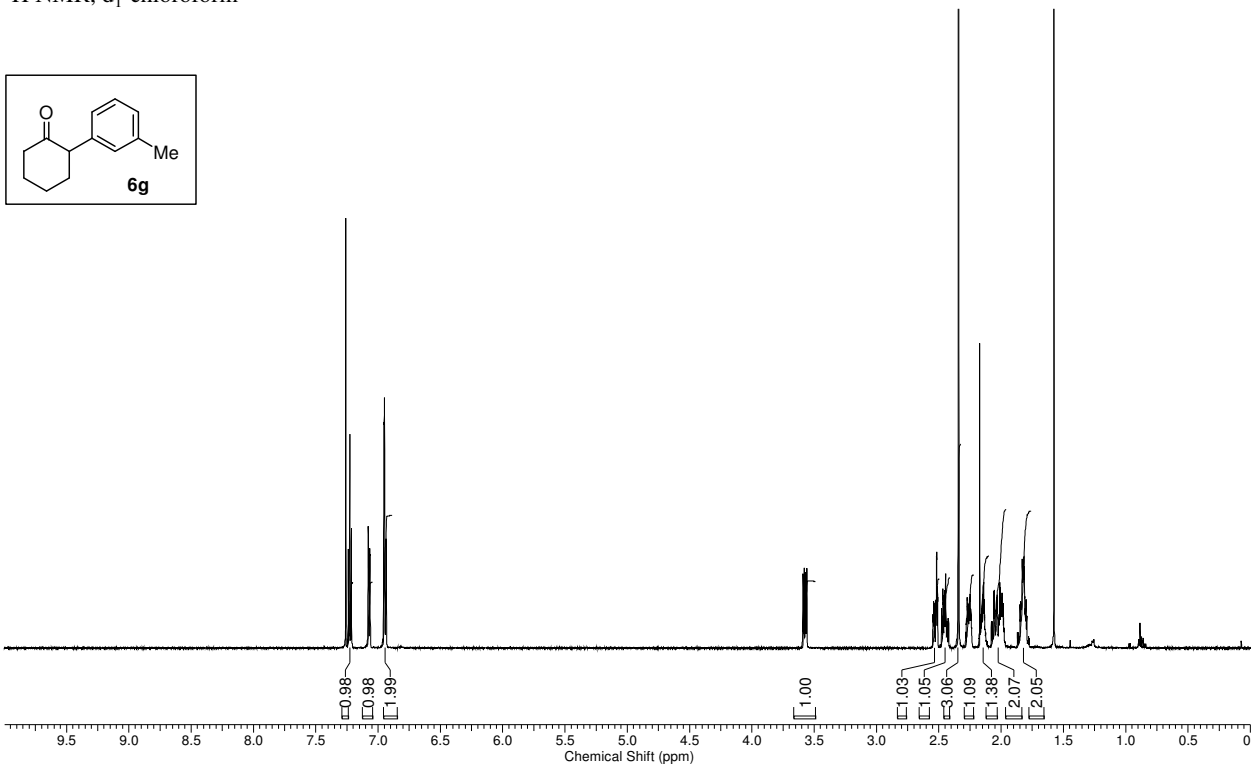
2-(4-methyl benzoate)-cyclohexanone (6f)

^{1}H NMR, d_1-chloroform



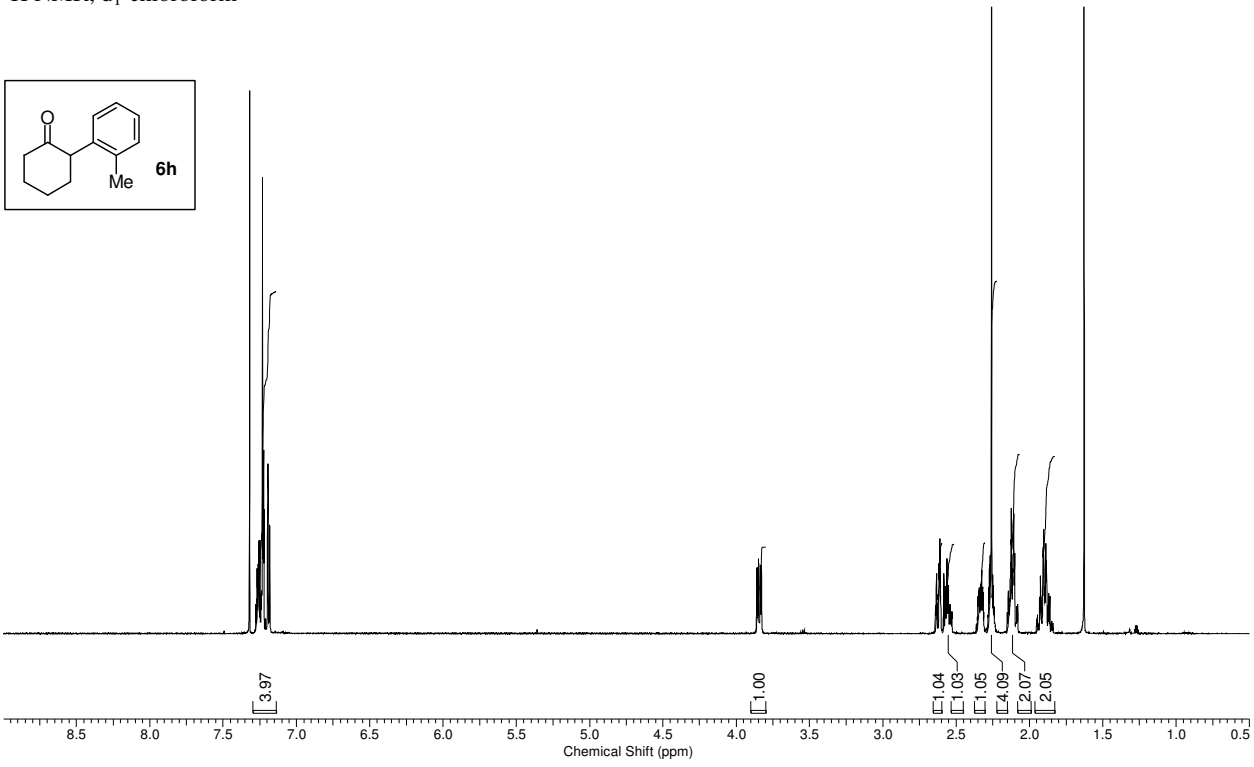
2-(3-methylphenyl)-cyclohexanone (6g)

^{1}H NMR, d_1-chloroform



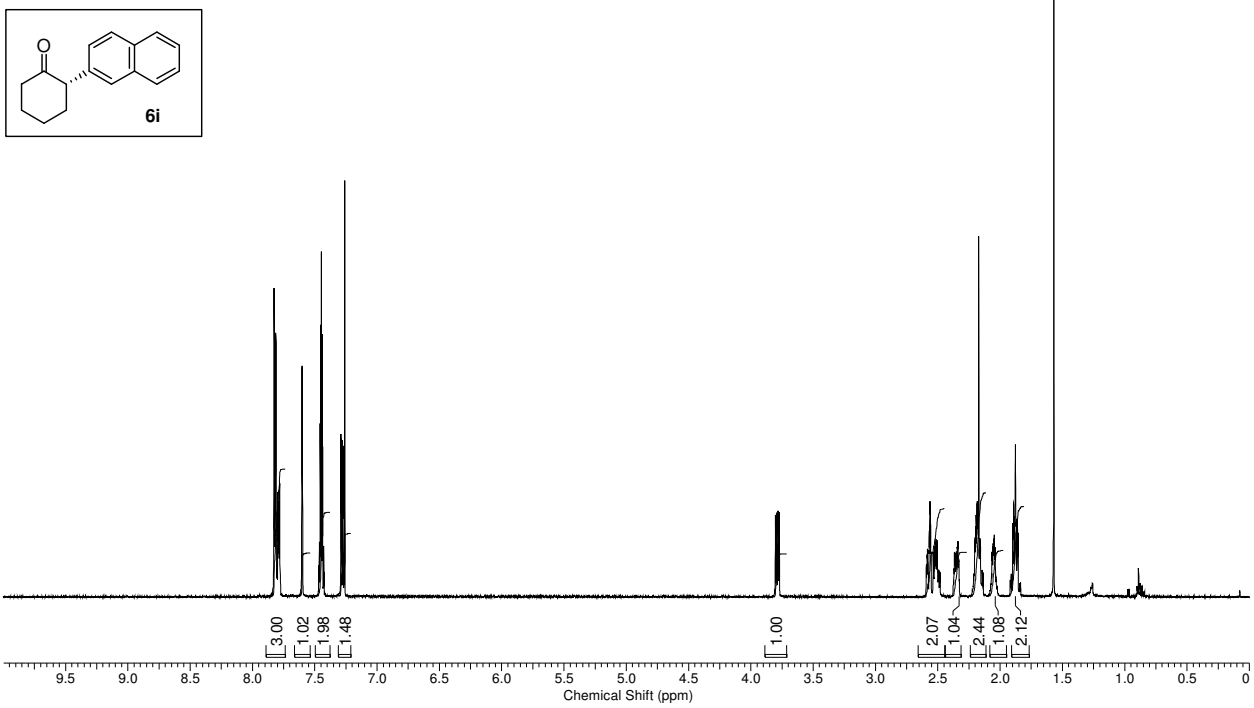
2-(2-methyl)-cyclohexanone (6h)

^{1}H NMR, d_1-chloroform



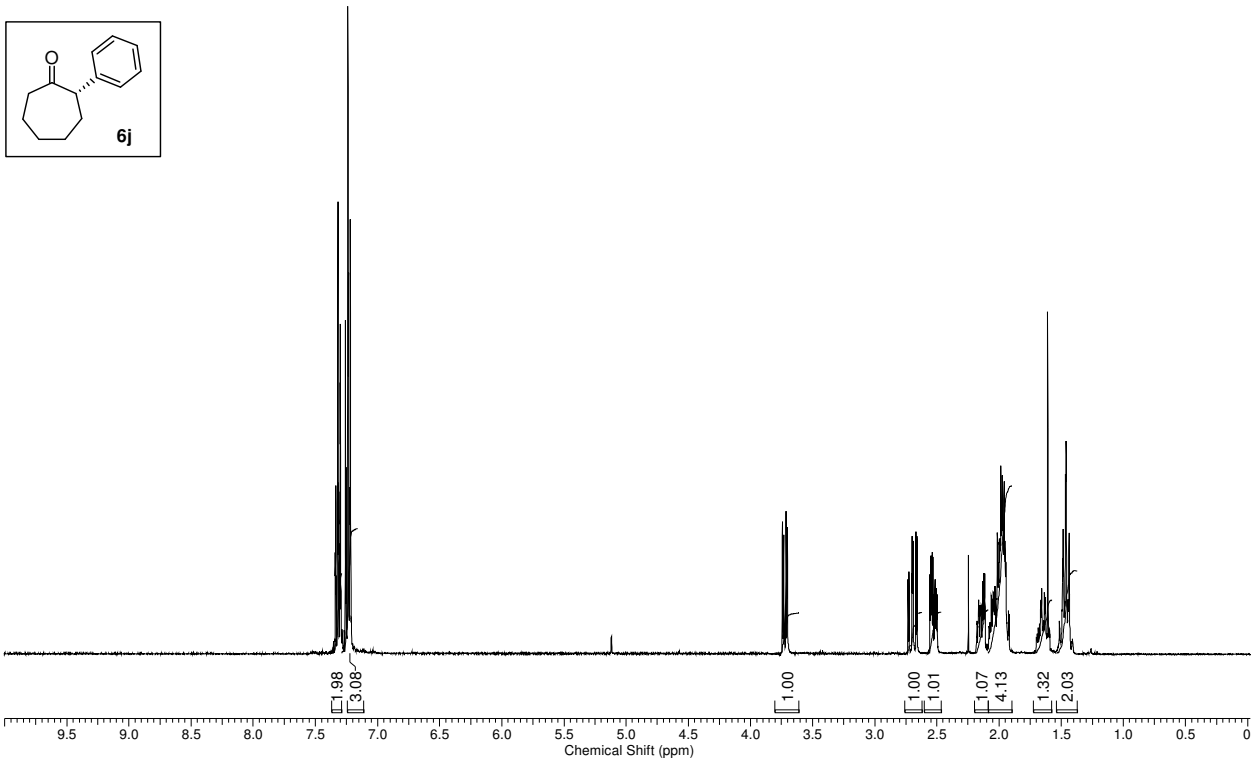
2-(2-Napthyl)-cycloheptanone (6i)

^{1}H NMR, d_1-chloroform

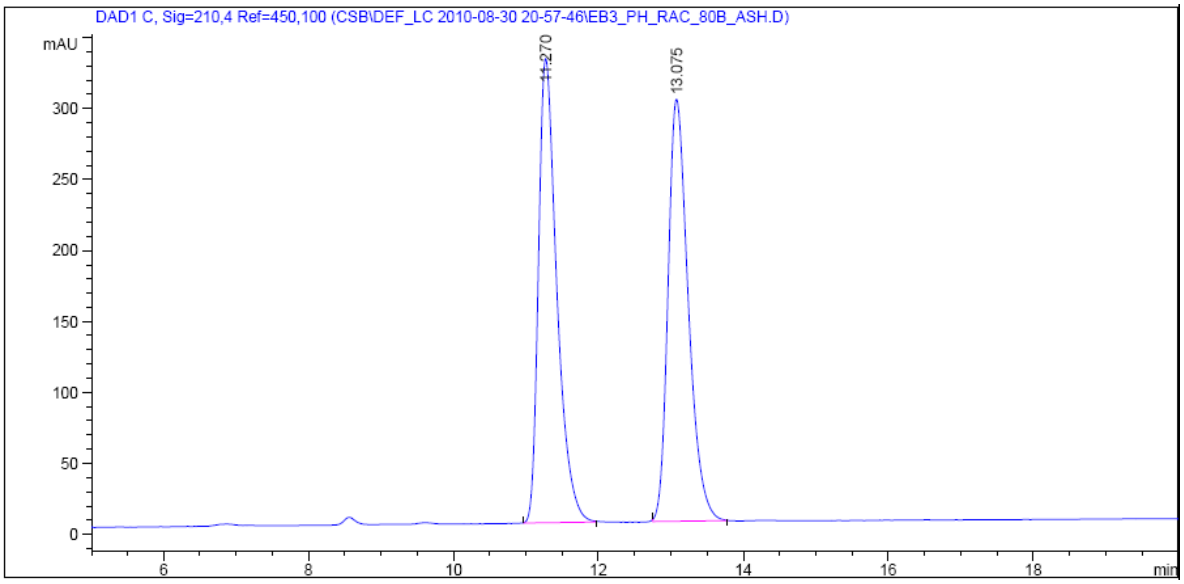


2-(phenyl)-cycloheptanone (6j)

^{1}H NMR, d_1-chloroform

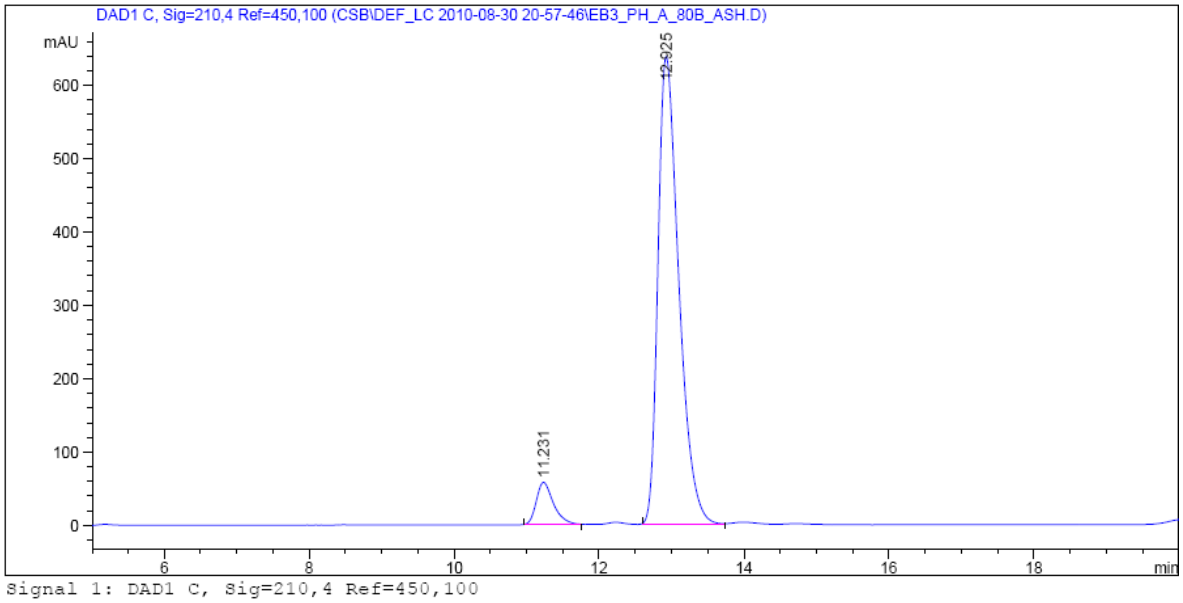


2-Phenyl-cyclohexanone (6a)



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

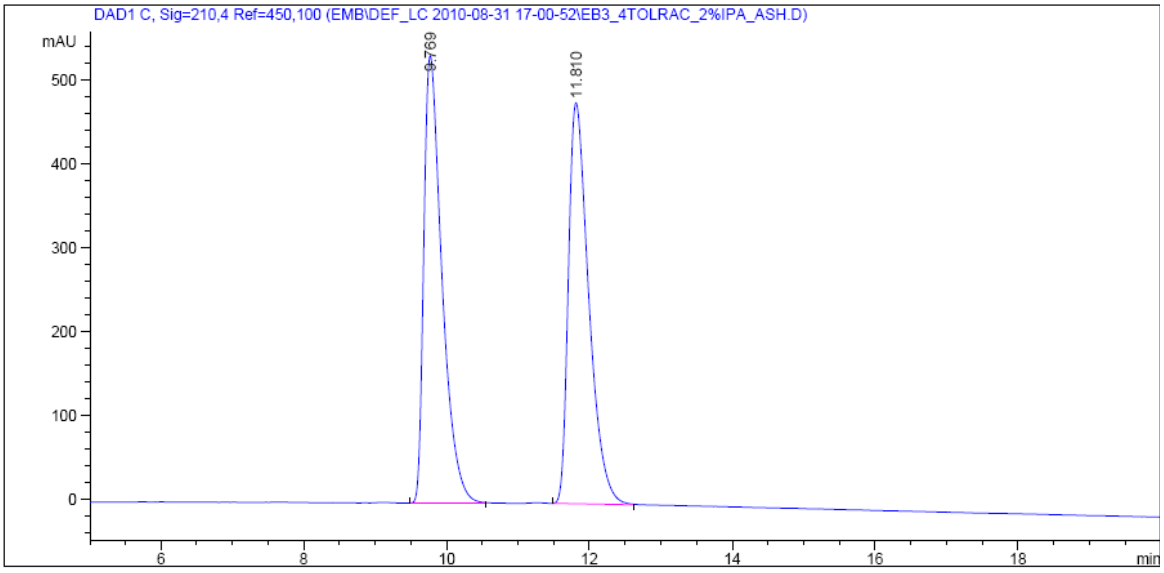
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.270	BB	0.2701	5776.71484	326.92444	49.9701
2	13.075	BB	0.2988	5783.63477	297.53464	50.0299
Totals :				1.15603e4	624.45908	



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

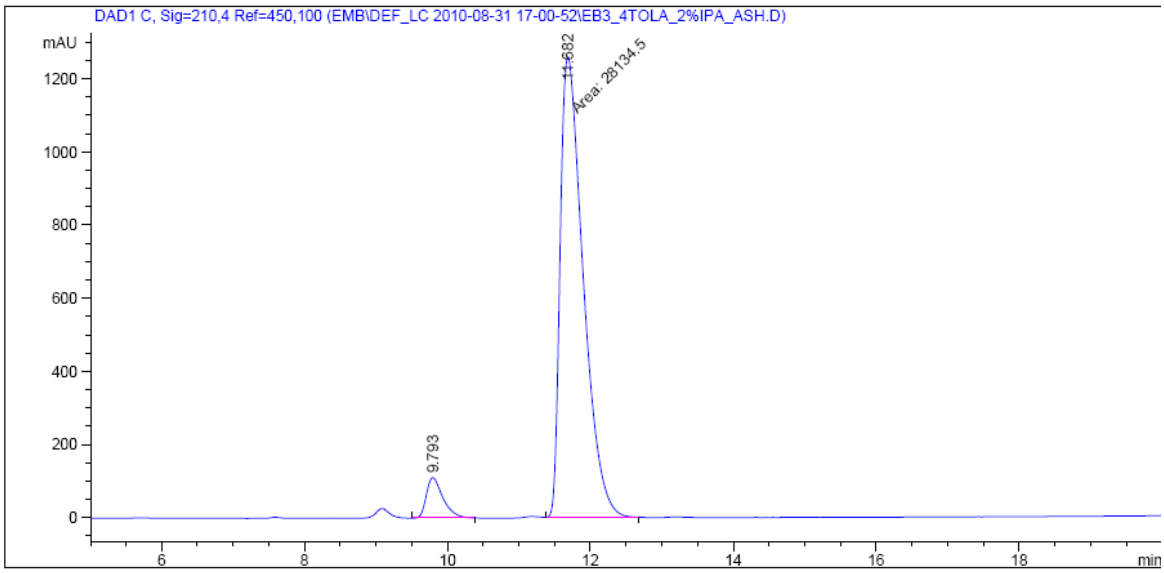
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.231	BB	0.2530	953.36414	57.63974	6.9795
2	12.925	BB	0.3047	1.27061e4	636.92834	93.0205
Totals :				1.36595e4	694.56809	

2-(4-methylphenyl)-cyclohexanone (6b)



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

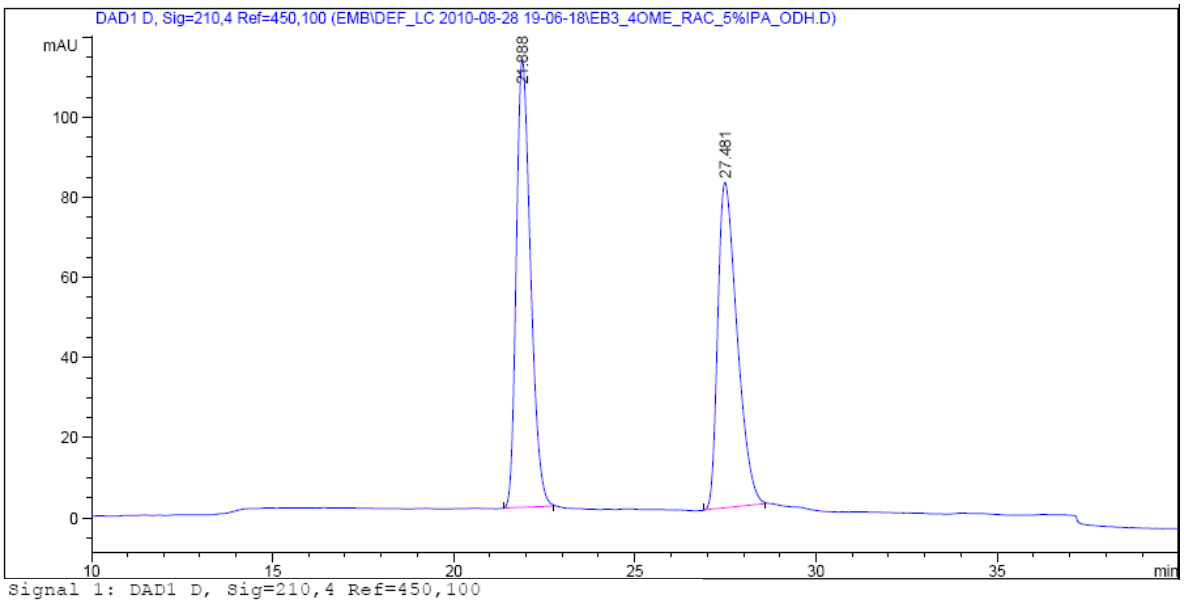
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.769	BB	0.2702	9408.94141	532.22510	49.8833
2	11.810	BB	0.3030	9452.95898	477.37283	50.1167
Totals :				1.88619e4	1009.59793	



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

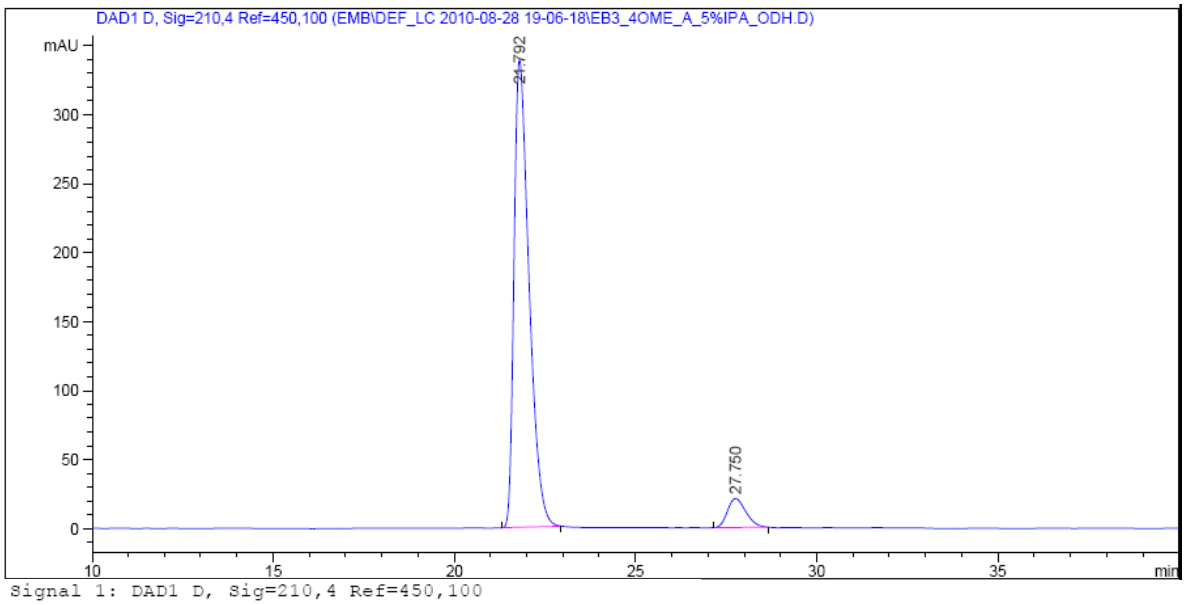
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.793	BB	0.2490	1790.88232	110.54996	5.9845
2	11.682	MM	0.3722	2.81345e4	1259.78979	94.0155
Totals :				2.99253e4	1370.33975	

2-(4-methoxyphenyl)-cyclohexanone (6c)



Signal 1: DAD1 D, Sig=210,4 Ref=450,100

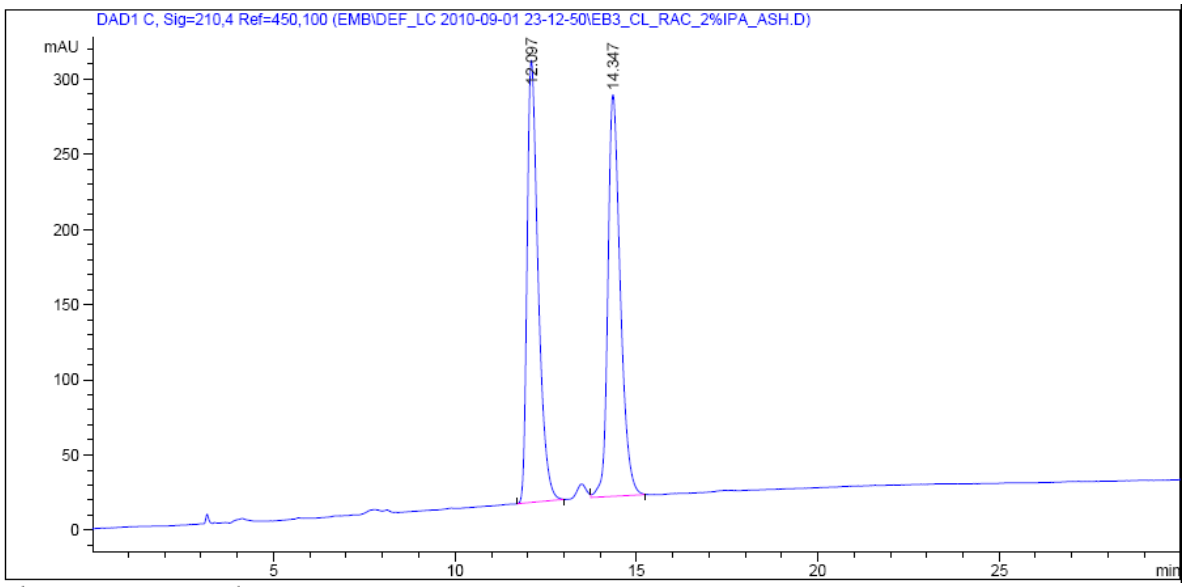
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.888	BB	0.4228	3071.41309	111.70066	50.5464
2	27.481	BB	0.5676	3005.01050	81.22805	49.4536
Totals :				6076.42358	192.92871	



Signal 1: DAD1 D, Sig=210,4 Ref=450,100

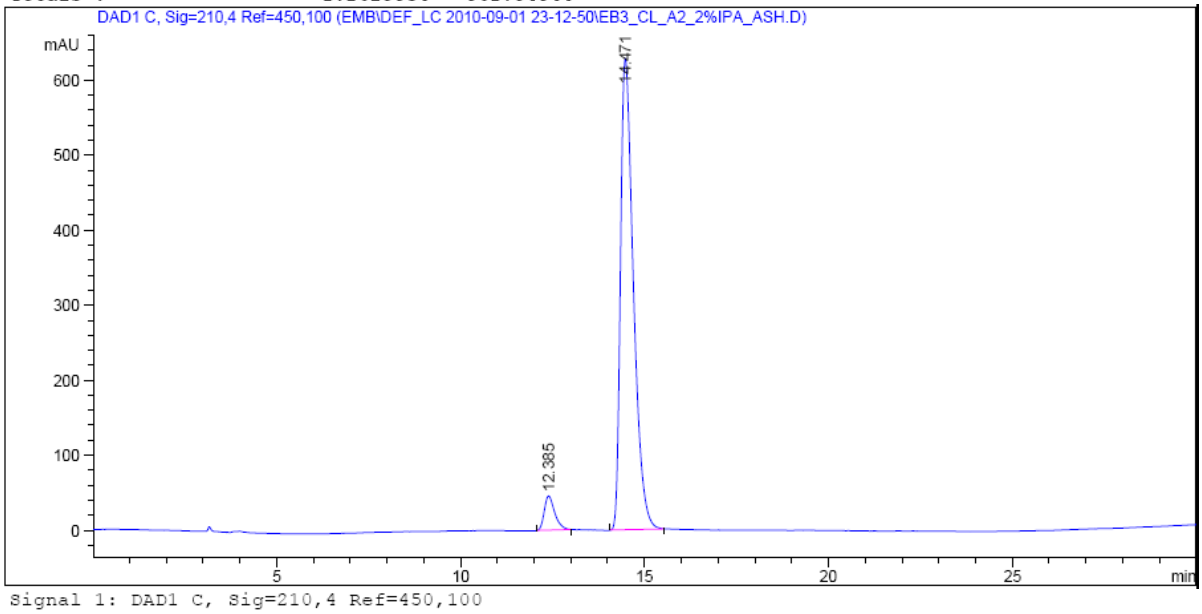
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.792	BB	0.4402	9764.79687	338.84769	92.8480
2	27.750	BB	0.5439	752.17145	21.09768	7.1520
Totals :				1.05170e4	359.94537	

2-(4-chlorophenyl)-cyclohexanone (6d)



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

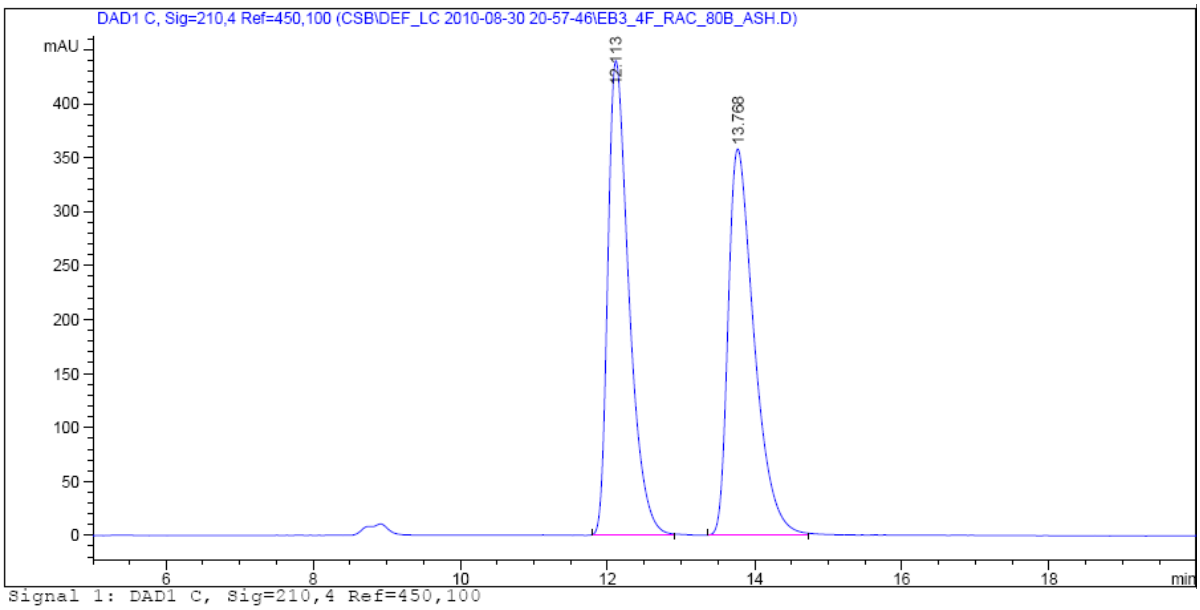
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.097	BB	0.3198	6246.21826	294.08542	49.4817
2	14.347	VB	0.3602	6377.06836	267.46002	50.5183
Totals :				1.26233e4	561.54544	



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

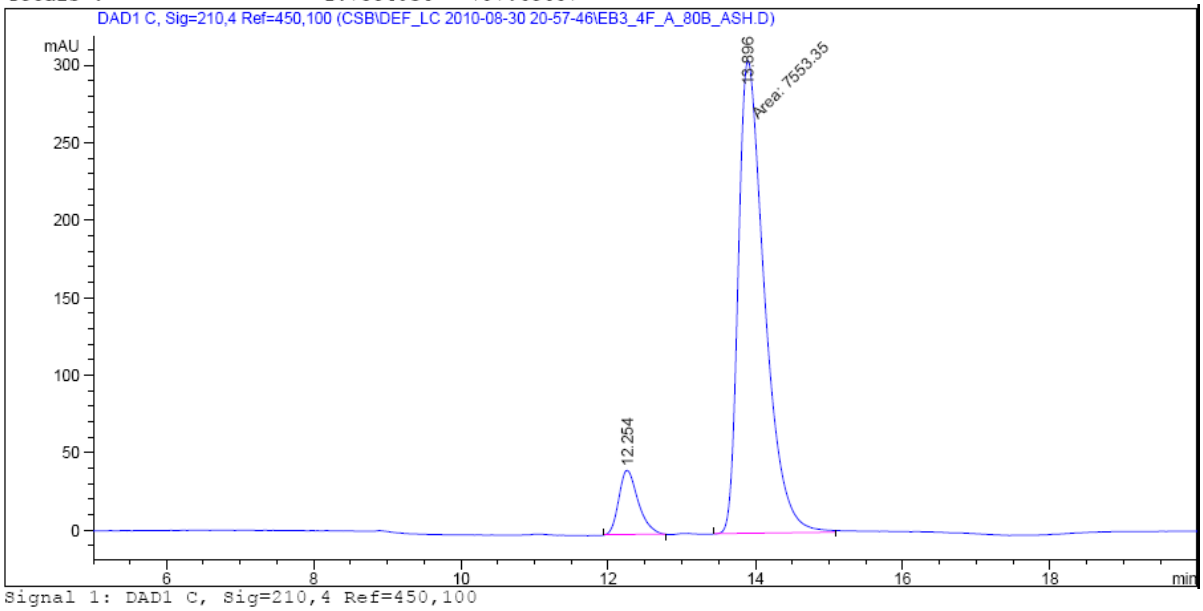
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.385	BB	0.2950	918.12317	45.97141	5.6607
2	14.471	BB	0.3721	1.53010e4	628.23822	94.3393
Totals :				1.62191e4	674.20963	

2-(4-fluorophenyl)-cyclohexanone (6e)



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

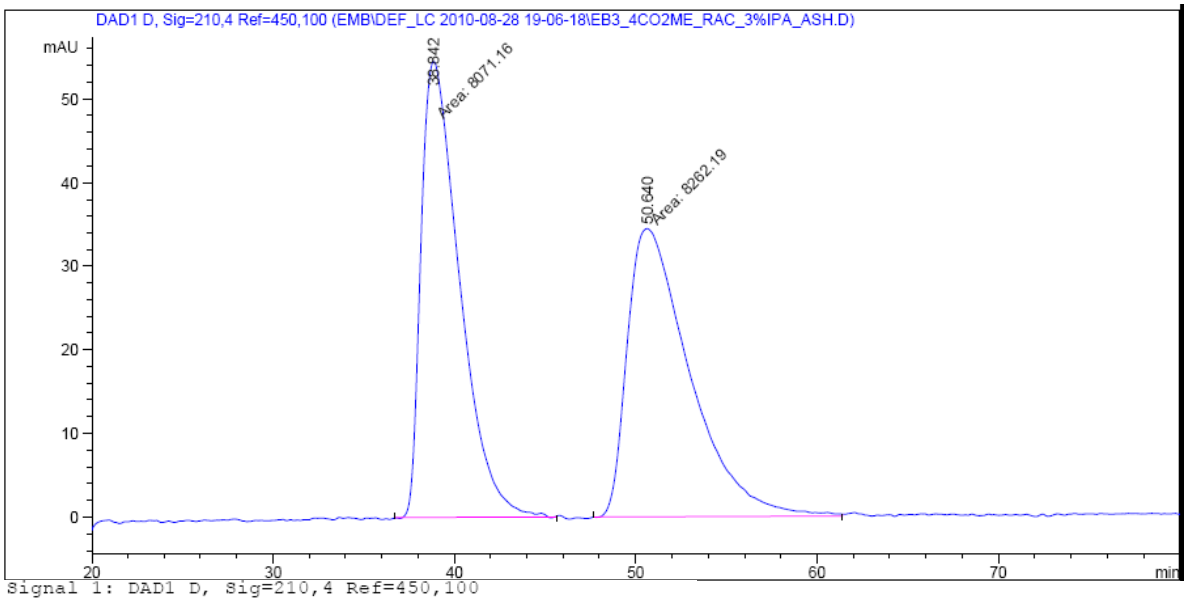
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.113	BB	0.3048	8774.26660	439.71652	49.9845
2	13.768	BB	0.3742	8779.72461	357.92035	50.0155
Totals :				1.75540e4	797.63687	



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

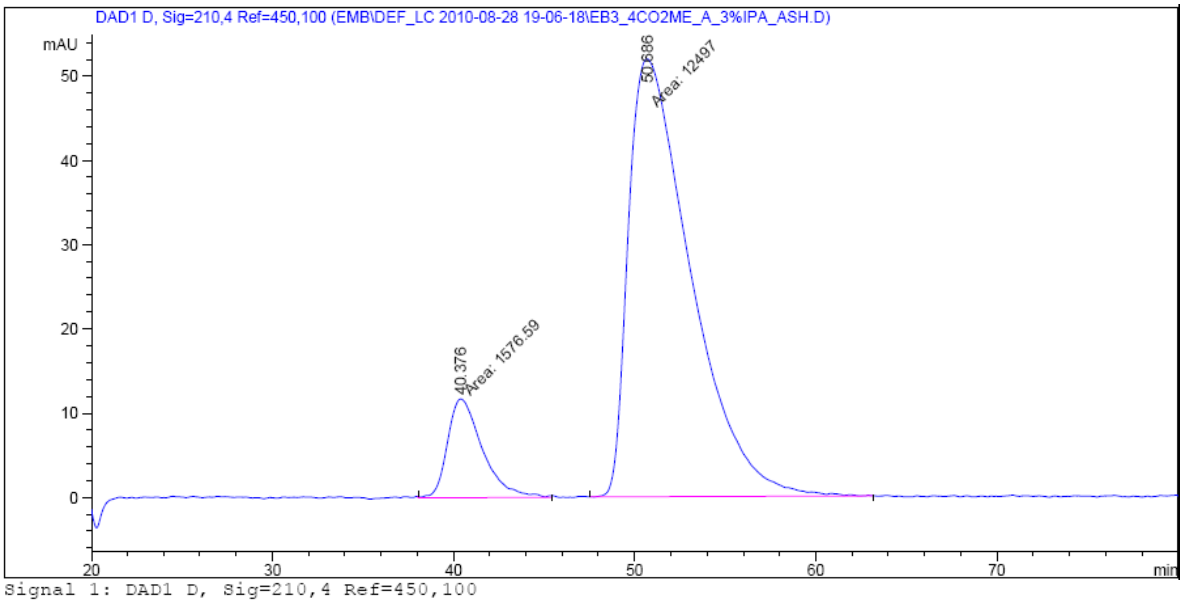
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.254	BB	0.2782	762.37726	41.53272	9.1679
2	13.896	MM	0.4126	7553.34863	305.07642	90.8321
Totals :				8315.72589	346.60913	

2-(4-methylbenzoate)-cyclohexanone (6f)



Signal 1: DAD1 D, Sig=210,4 Ref=450,100

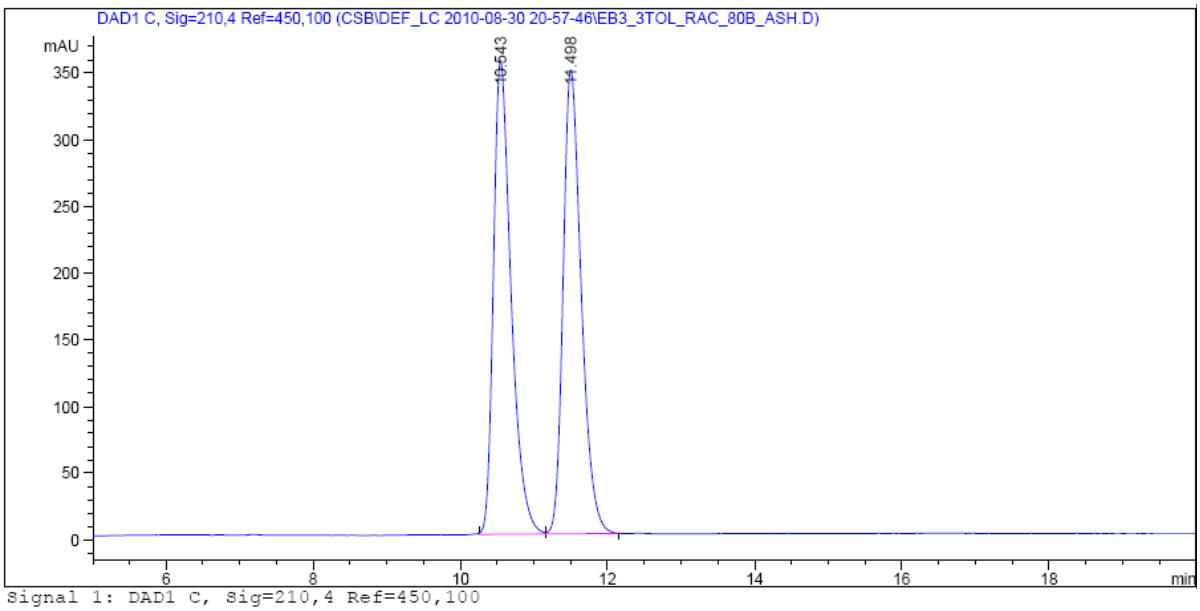
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.842	MF	2.4650	8071.16309	54.57156	49.4152
2	50.640	FM	3.9939	8262.19434	34.47828	50.5848
Totals :				1.63334e4	89.04985	



Signal 1: DAD1 D, Sig=210,4 Ref=450,100

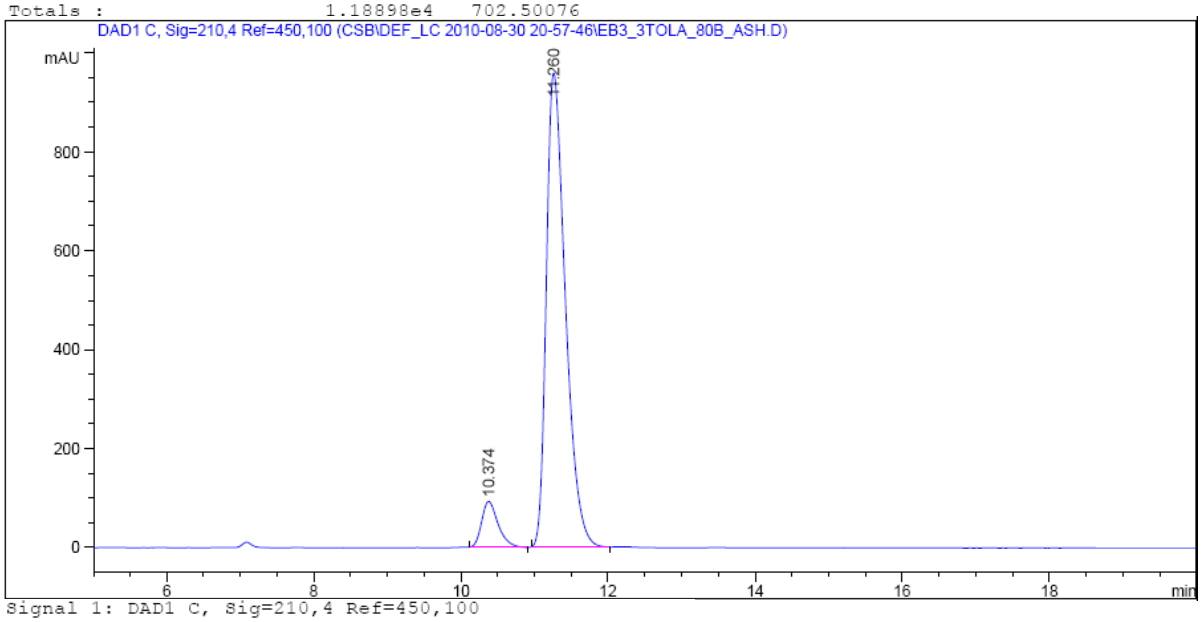
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.376	MF	2.2375	1576.59448	11.74350	11.2025
2	50.686	FM	4.0008	1.24970e4	52.06075	88.7975
Totals :				1.40736e4	63.80424	

2-(3-methylphenyl)-cyclohexanone (6g)



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

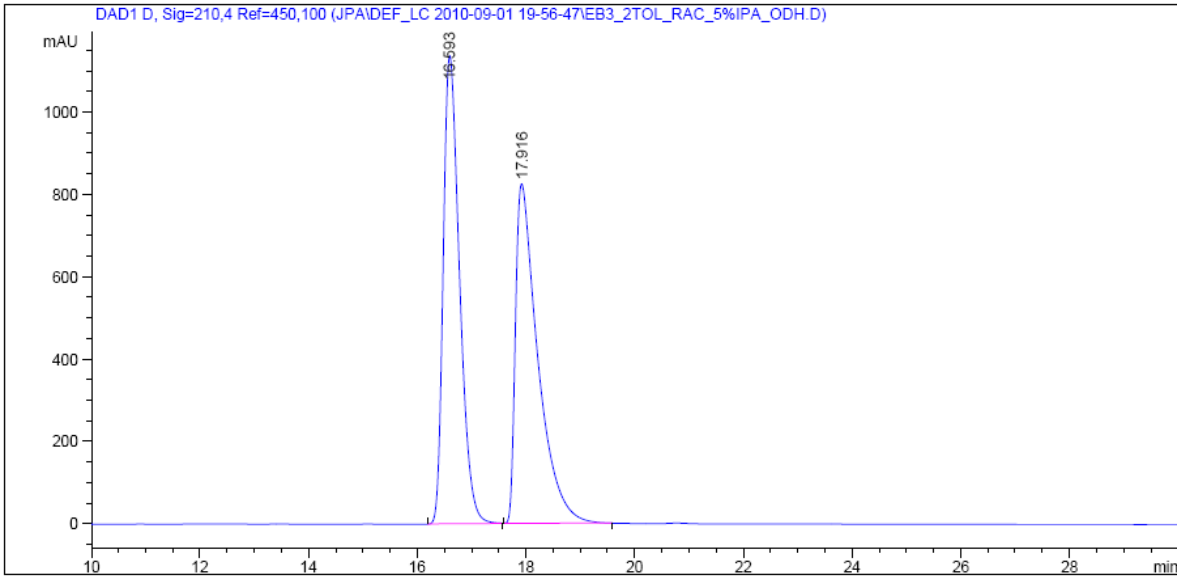
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.543	BV	0.2545	5918.18115	354.95862	49.7753
2	11.498	VB	0.2645	5971.61328	347.54214	50.2247
Totals :				1.18898e4	702.50076	



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

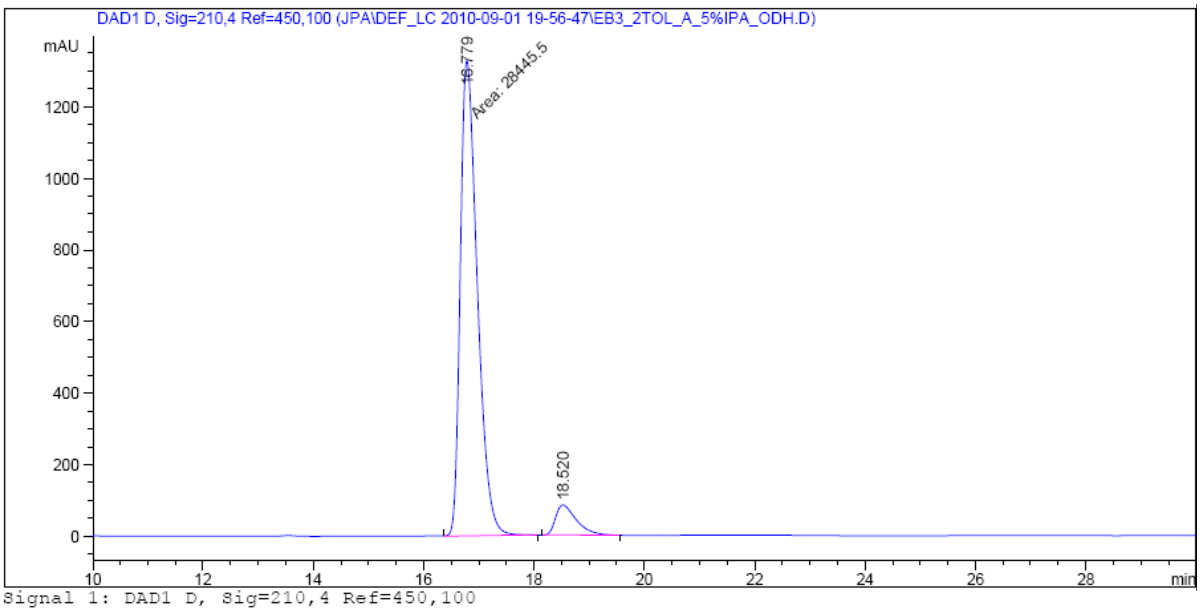
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.374	BB	0.2395	1468.32959	93.32932	7.8251
2	11.260	BB	0.2744	1.72961e4	958.96777	92.1749
Totals :				1.87645e4	1052.29709	

2-(2-methylphenyl)-cyclohexanone (6h)



Signal 1: DAD1 D, Sig=210,4 Ref=450,100

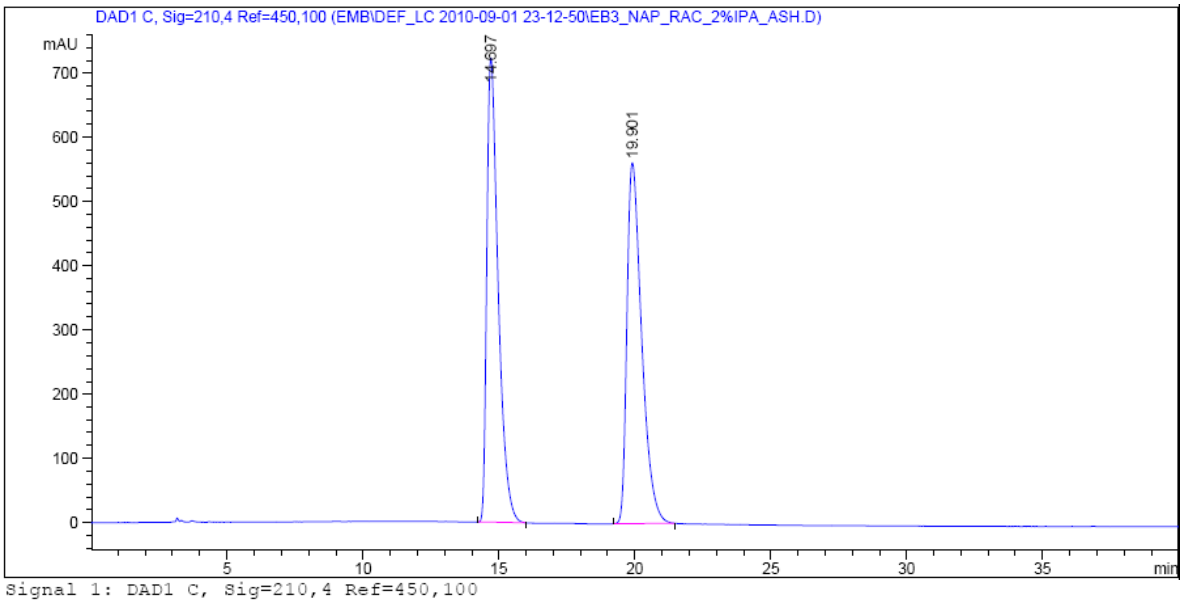
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.593	BB	0.3215	2.37381e4	1137.15259	50.1358
2	17.916	BB	0.4156	2.36095e4	825.71130	49.8642
Totals :				4.73475e4	1962.86389	



Signal 1: DAD1 D, Sig=210,4 Ref=450,100

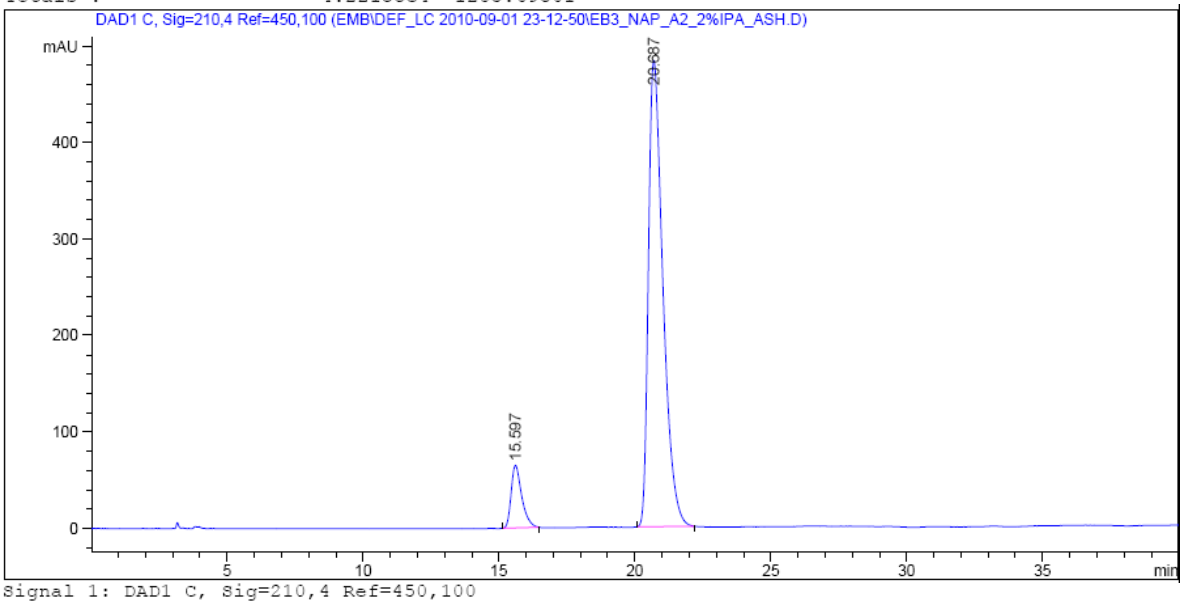
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.779	MM	0.3571	2.84455e4	1327.54675	92.6942
2	18.520	BB	0.3998	2241.96045	84.42985	7.3058
Totals :				3.06875e4	1411.97660	

2-(2-Napthyl)-cyclohexanone (6i)



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

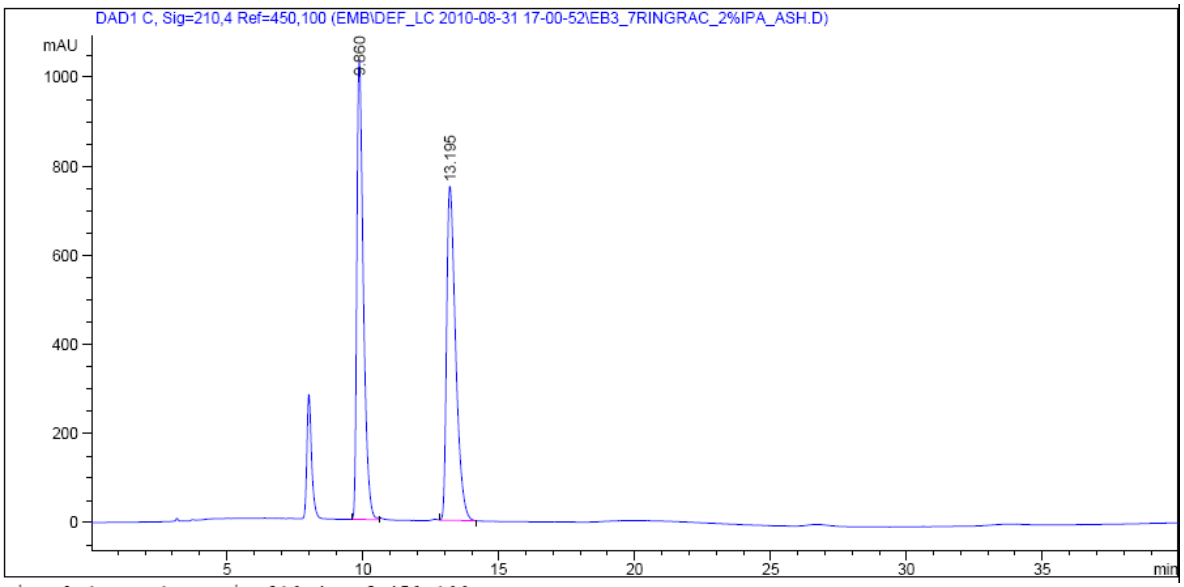
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.697	BB	0.4390	2.10221e4	723.45898	49.7974
2	19.901	BB	0.5778	2.11932e4	562.23602	50.2026
Totals :				4.22153e4	1285.69501	



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

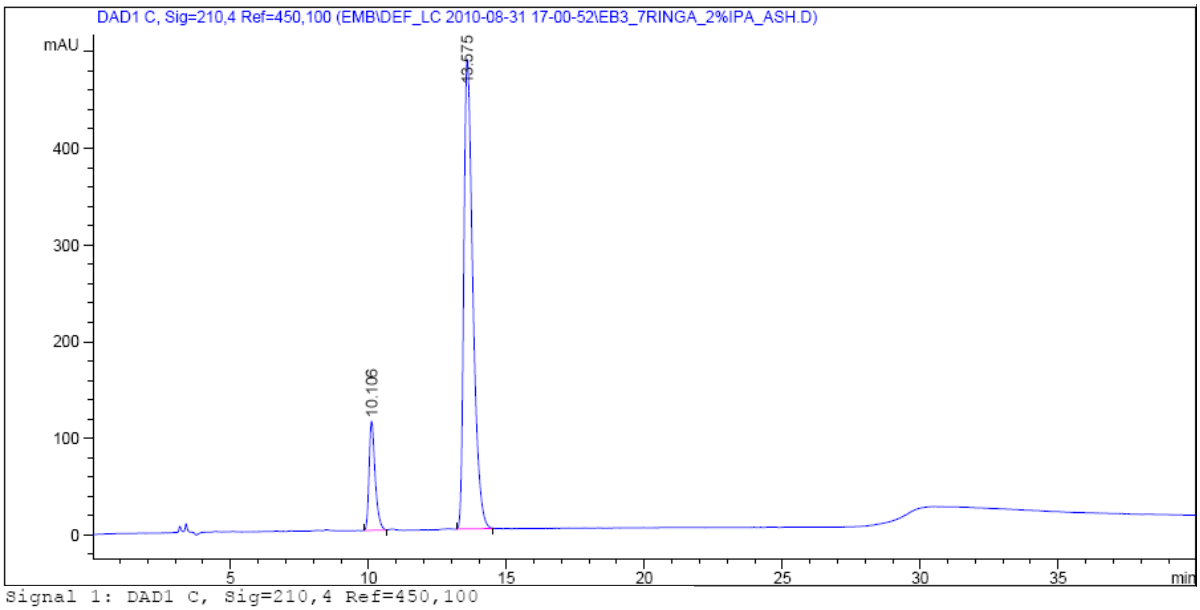
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.597	BB	0.4122	1789.92188	65.22630	9.0773
2	20.687	BB	0.5705	1.79287e4	483.64871	90.9227
Totals :				1.97186e4	548.87502	

2-phenyl-cycloheptanone (6j)



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.860	BB	0.2551	1.72441e4	1030.98535	49.8078
2	13.195	BB	0.3542	1.73772e4	750.21948	50.1922
Totals :				3.46213e4	1781.20483	



Signal 1: DAD1 C, Sig=210,4 Ref=450,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.106	BB	0.2356	1733.78613	112.64581	13.5166
2	13.575	BB	0.3506	1.10933e4	485.38708	86.4834
Totals :				1.28271e4	598.03289	