Electronic Supplementary Information

Asymmeric Catalysis with Chiral-at-Osmium Complex

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1. General Information

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. Catalytic reactions were performed in Schlenk tubes (10 mL). Solvents were distilled under nitrogen from calcium hydride or sodium/benzophenone. Reagents from commercial suppliers were used without further purification. Flash column chromatography was performed with silica gel 60 M from Macherey-Nagel (irreg. shaped, 230–400 mesh, pH 6.8, pore volume: 0.81 mL × g^{-1}, mean pore size: 66 Å, specific surface: 492 m^2 × g^{-1}, particle size distribution: 0.5% < 25 μm and 1.7% > 71 μm, water content: 1.6%). ^{1}H NMR, proton decoupled ^{13}C NMR spectra, and proton-coupled ^{19}F NMR spectra were recorded on Bruker Avance 300 or Bruker BioSpin 500 (300 or 500 MHz) spectrometers at ambient temperature. NMR standards were used as follows: ^{1}H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$), 1.94 ppm (CD_3CN). ^{13}C NMR spectroscopy: δ = 77.16 ppm ($CDCl_3$), δ = 1.32 ppm (CD_3CN). All ^{13}C NMR signals are singlets unless noted otherwise. IR spectra were recorded on a Bruker Alpha FT-IR spectrophotometer. CD spectra were recorded on a JASCO J-810 CD spectropolarimeter (250-600, 2 nm bandwidth, 50 nm/min scanning speed, accumulation of 3 scans). High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 TFT-MS instrument. Chiral HPLC chromatography was performed with an Agilent 1260 HPLC system. Optical rotations were measured on a Perkin-Elmer 241 polarimeter with $[\alpha]^{22}_{D}$ values reported in degrees with concentrations reported in 0.5 g/100 mL.

2. Synthesis and Characterization of Osmium Complexes

2.1 Synthesis of 7-Methyl-1,7-Phenanthrolinium Ligands

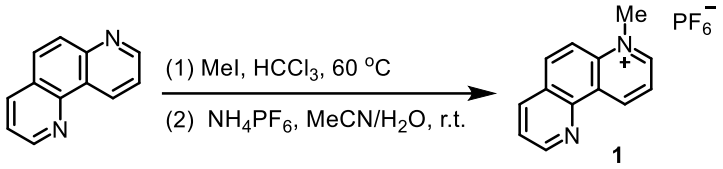


Figure S1. Synthesis of 7-methyl-1,7-phenanthrolinium hexafluorophosphate.

To a solution of commercially available 1,7-phenanthroline (360.4 mg, 2.0 mmol, 1.0 eq.) in 1.8 mL $CHCl_3$ was added MeI (4.26 g, 30.0 mmol, 15.0 eq.) in a 10 mL Schlenk tube. The resulting solution was heated at 60 °C overnight. After cooling to room temperature, the above solution was centrifuged and collected. It was washed with DCM (6 mL for 3 times) and dried under vacuo. The resulting solid was dissolved in 20 mL mixed solvent ($MeCN/H_2O$ = 1:1), then NH_4PF_6 (978.0 mg, 6.0 mmol, 3.0 eq.) was added and the resulting solution was stirred at room temperature for 1 h. After that, the above solution was extracted with DCM (30 mL for 3 times) and washed with 10 mL of deionized water. Solvent was removed under vacuo to give pure **1** (653.0 mg, 96% yield) as pale-yellow solid. The analytical data for **1** matched with previously reported data.[1]

^{1}H NMR (300 MHz, CD_3CN) δ 10.32 (d, J = 8.4 Hz, 1H), 9.25 (dd, J = 4.2, 1.5 Hz, 1H), 9.13 (d, J = 6.0 Hz, 1H), 8.71-8.53 (m, 2H), 8.33 (d, J = 9.6 Hz, 1H), 8.22 (dd, J = 8.4, 6.0 Hz, 1H), 7.92 (dd, J = 8.1, 4.5 Hz, 1H), 4.65 (s, 3H). **^{13}C NMR** (75 MHz, CD_3CN) δ 153.7, 149.7, 144.7, 143.7, 142.1, 138.3, 138.0, 130.6, 127.5, 126.3, 124.1, 117.5, 47.2.

2.2 Synthesis of Auxiliary Ligand (*S*)-4-Phenyl-4,5-dihydrooxazole

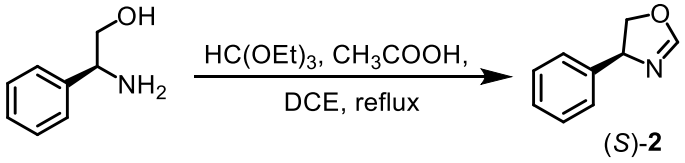


Figure S2. Synthesis (*S*)-4-phenyl-4,5-dihydrooxazole

A solution of (*S*)-2-amino-2-phenylethan-1-ol (1.37 g, 10.0 mmol, 1.0 eq.), triethyl orthoacetate (2.22 g, 15.0 mmol, 1.5 eq.) and acetic acid (60.0 mg, 1.0 mmol, 0.1 eq.) in 10 mL 1,2-dichoroethane was refluxed overnight. After cooling to ambient temperature, the volatiles were removed by rotary evaporation. The residue was purified by reduced distillation (5 mmHg, 140 ℃) to give pure (*S*)-4-phenyl-4,5-dihydrooxazole (*S*)-**2** (1.20 g, 82% yield) as colorless oil.

^{1}H NMR (300 MHz, CD_3CN) δ 7.45-7.20 (m, 5H), 7.04 (d, J = 1.6 Hz, 1H), 5.23-5.10 (m, 1H), 4.57 (dd, J = 10.2, 8.7 Hz, 1H), 3.96 (t, J = 8.4 Hz, 3H). **^{13}C NMR** (75 MHz, CD_3CN) δ 156.2, 143.6, 129.6, 128.4, 127.6, 74.0, 69.5. **HRMS** (ESI, m/z) Calculated for $C_9H_{10}NO$ $[M + H]^+$: 148.0761,

found: 148.0757. **IR** (film): ν (cm^{-1}) 3030, 1624, 1095, 1029, 928, 755, 698, 627, 453.

2.3 Synthesis of Osmium Complex *rac*-Os1

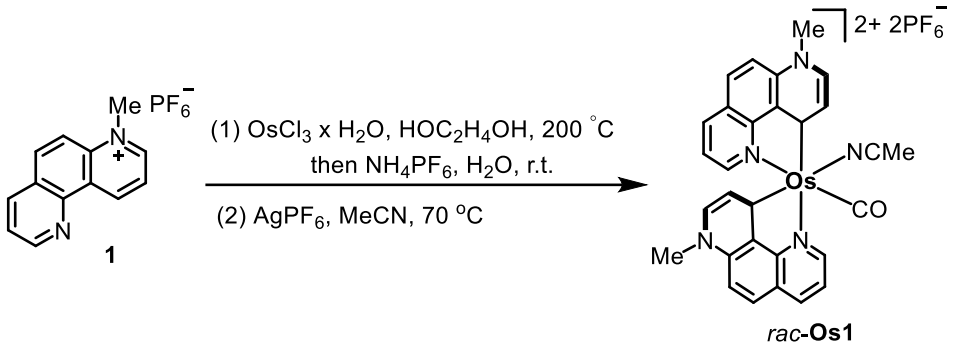


Figure S3. Synthesis of osmium complex *rac*-**Os1**.

To a 10 mL Schlenk tube was added **1** (68.0 mg, 0.2 mmol, 2.0 eq.), $OsCl_3$ x H_2O (31.5 mg, 0.1 mmol, 1.0 eq.) and 1.0 mL HOC_2H_4OH. The resulting solution was heated at 200 °C for 40 h. After cooling to room temperature, NH_4PF_6 (65.2 mg, 0.4 mmol, 4.0 eq.) dissolved in 4.0 mL deionized H_2O was added to the reaction solution. Ultrasonic was used for 10 minutes for counter anion exchange. Liquid phase was removed by filtration and the resulting residue was dissolved in DCM and washed with water. The resulting residue was dried under high vacuo to give crude red solid. To the solution of the obtained solid in 2.0 mL MeCN was added $AgPF_6$ (252.8 mg, 0.1 mmol, 1.0 eq.) in one portion and stirred at 70 °C overnight. After cooling to room temperature, the mixture was collected, evaporated to dryness and purified by column chromatography on silica gel (DCM/MeCN = 5:1, 10.0 eq., NH_4PF_6 as ion exchange reagent added on the top of column) to give yellow solid *rac*-**Os1** with excess NH_4PF_6. The mixture solid was extracted with mixed solvent of DCM/MeCN (20:1, 2.0 mL), filtrated through cotton and washed with mixed solvent of DCM/MeCN (20:1, 2.0 mL). And then the filtrate was evaporated to give pure *rac*-**Os1** (76.0 mg, 40%) as yellow solid.

^{1}H NMR (500 MHz, CD_3CN) δ 9.68 (dd, J = 5.1, 1.4 Hz, 1H), 8.99 (dd, J = 8.3, 1.4 Hz, 1H), 8.66 (d, J = 6.4 Hz, 1H), 8.61 (d, J = 9.4 Hz, 1H), 8.52 (dd, J = 8.1, 1.3 Hz, 1H), 8.40 (d, J = 9.3 Hz, 1H), 8.27 (dd, J = 8.3, 5.1 Hz, 1H), 8.22 (d, J = 9.3 Hz, 1H), 8.19 (d, J = 9.3 Hz, 1H), 8.10 (d, J = 6.4 Hz, 1H), 7.77 (d, J = 6.4 Hz, 1H), 7.54 (dd, J = 5.3, 1.4 Hz, 1H), 7.43 (dd, J = 8.2, 5.3 Hz, 1H), 7.16 (d, J = 6.4 Hz, 1H), 4.31 (s, 3H), 4.14 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (125 MHz, CD_3CN) δ 208.5, 197.5, 181.4, 154.3, 153.7, 153.5, 151.8, 143.2, 142.5, 141.3, 141.2, 140.3, 139.9, 137.9, 137.7, 134.9, 133.7, 133.5, 133.4, 128.6, 127.8, 127.2, 126.9, 125.0, 120.20, 119.98, 44.4, 43.6, 4.5. **^{19}F NMR** (470 MHz, CD_3CN) δ –72.56 (d, J = 851.5 Hz). **^{31}P NMR** (202 MHz, CD_3CN) δ –143.3 (hept, J = 706.4 Hz). **IR** (film): ν (cm^{-1}) 2929, 1930, 1602, 1564, 1093, 820, 813, 773, 750, 695, 555.

2.4 Synthesis of Non-Racemic Osmium Complexes

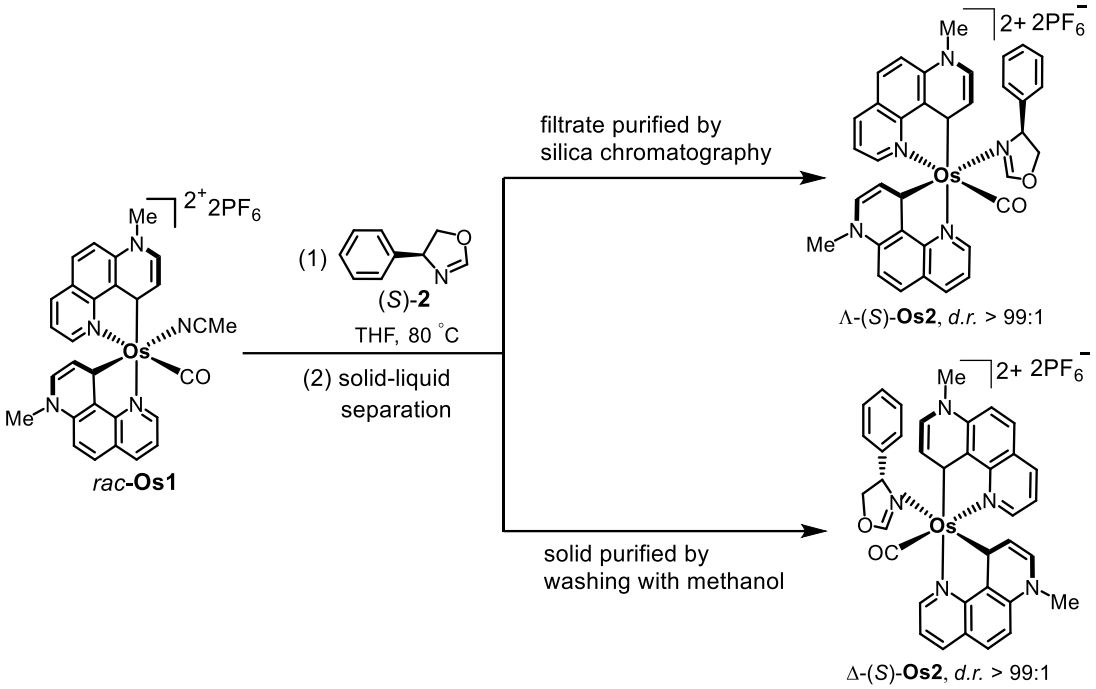


Figure S4. Synthesis of auxiliary complexes.

Λ-(*S*)-Os2 and **Δ-(*S*)-Os2:** A mixture of *rac*-**Os1** (75.0 mg, 0.08 mmol, 1.0 eq.), chiral auxiliary (*S*)-**2** (47.1 mg, 0.32 mmol, 4.0 eq.) in THF (1.6 mL) was stirred at 80 °C for 40 h. After cooling to room temperature, the solid-liquid mixture was separated by filtration and washed with THF (3 x 2 mL). The liquid filtrate was evaporated to dryness and the residue was subjected to silica gel chromatography (CH_2Cl_2/MeOH = 20:1) to remove small amounts of the minor diastereomer to provide Λ-(*S*)-**Os2** (20.8 mg, 25% yield, *d.r.* > 99:1) as red solid. On the other hand, the remaining filtration solid was washed with MeOH (3 x 0.3 mL) to give Δ-(*S*)-**Os2** (29.2 mg, 35% yield, *d.r.* > 99:1) as red solid.

Note: The only moderate yields for the resolved pure diastereomers Λ-(*S*)-**Os2** and Δ-(*S*)-**Os2** are not due to stability problems but rather the result of the required precipitation/chromatography procedure. The yield of Λ-(*S*)-**Os2** is reduced because it needs a careful chromatography to separate it from small amounts of the minor diastereomer. The yield of Δ-(*S*)-**Os2** is reduced due to some remaining solubility in the reaction solvent THF and some solubility in the washing solvent MeOH.

Λ-(*S*)-Os2: **^{1}H NMR** (300 MHz, CD_3CN) δ 9.35 (dd, *J* = 5.2, 1.2 Hz, 1H), 8.98 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.60 (d, *J* = 9.4 Hz, 1H), 8.47 (d, *J* = 6.6 Hz, 1H), 8.38 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.30 (dd, *J* = 8.2, 5.2 Hz, 1H), 8.21-8.08 (m, 3H), 7.89 (d, *J* = 9.3 Hz, 1H), 7.81 (d, *J* = 6.6 Hz, 1H), 7.66 (d, *J* = 6.2 Hz, 1H), 7.59 (dd, *J* = 5.3, 1.2 Hz, 1H), 7.41 (dd, *J* = 8.2, 5.3 Hz, 1H), 6.91 (d, *J* = 6.2 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.53 (t, *J* = 7.8 Hz, 1H), 6.04 (d, *J* = 7.2 Hz, 1H), 4.84 (t, *J* = 10.0 Hz, 1H),

4.71-4.61 (m, 1H), 4.16-4.06 (m, 7H). **^{13}C NMR** (125 MHz, CD_3CN) δ 210.8, 198.1, 182.6, 166.4, 153.7, 153.5, 153.4, 151.5, 142.8, 142.4, 140.4, 140.2, 140.17, 139.9, 138.6, 137.9, 137.2, 135.0, 133.3, 132.9, 132.8, 128.7, 128.6, 128.5, 126.9, 126.8, 126.3, 124.8, 120.2, 120.0, 78.0, 69.6, 44.3, 43.0. **^{19}F NMR** (282 MHz, CD_3CN) δ –72.9 (d, J = 706.8 Hz). **^{31}P NMR** (202 MHz, CD_3CN) δ –143.3 (hept, J = 706.4 Hz). **IR** (film): ν (cm^{-1}) 2922, 1923,1595, 1543, 1174, 1093, 824, 813, 773, 750, 695, 555.

Δ-(*S*)-Os2: **^{1}H NMR** (500 MHz, CD_3CN) δ 9.38 (dd, J = 5.1, 1.4 Hz, 1H), 8.98 (dd, J = 8.2, 1.3 Hz, 1H), 8.61 (d, J = 9.4 Hz, 1H), 8.48 (dd, J = 8.1, 1.3 Hz, 1H), 8.36 (d, J = 9.3 Hz, 1H), 8.28 (dd, J = 8.2, 5.1 Hz, 1H), 8.19 (d, J = 9.4 Hz, 1H), 8.14 (d, J = 9.3 Hz, 1H), 7.68 (d, J = 6.3 Hz, 1H), 7.64 (d, J = 6.6 Hz, 1H), 7.49 (d, J = 6.6 Hz, 1H), 7.43 (dd, J = 5.3, 1.3 Hz, 1H), 7.38-7.30 (m, 2H), 7.10 (t, J = 7.8 Hz, 2H), 7.05 (d, J = 6.3 Hz, 1H), 6.93 (d, J = 1.2 Hz, 1H), 6.72 (d, J = 7.2 Hz, 1H), 5.47-5.38 (m, 1H), 4.92 (t, J = 9.8 Hz, 1H), 4.26 (dd, J = 9.4, 5.5 Hz, 1H), 4.17 (s, 3H), 4.11 (s, 3H). **^{13}C NMR** (125 MHz, CD_3CN) δ 210.3, 198.8, 182.4, 164.7, 153.8, 153.7, 153.2, 151.6, 142.7, 142.1, 140.5, 140.2, 140.1, 139.6, 137.8, 137.3, 135.0, 133.4, 133.0, 132.9, 129.73, 129.68, 128.6, 128.2, 127.3, 126.7, 125.0, 120.2, 120.0, 78.1, 74.6, 44.3, 43.0. **^{19}F NMR** (282 MHz, CD_3CN) δ –72.9 (d, J = 705.6 Hz). **^{31}P NMR** (202 MHz, CD_3CN) δ –143.3 (hept, J = 706.4 Hz). **IR** (film): ν (cm^{-1}) 2925, 1922, 1584, 1543, 1174, 1086, 828, 813, 773, 750, 695, 555.

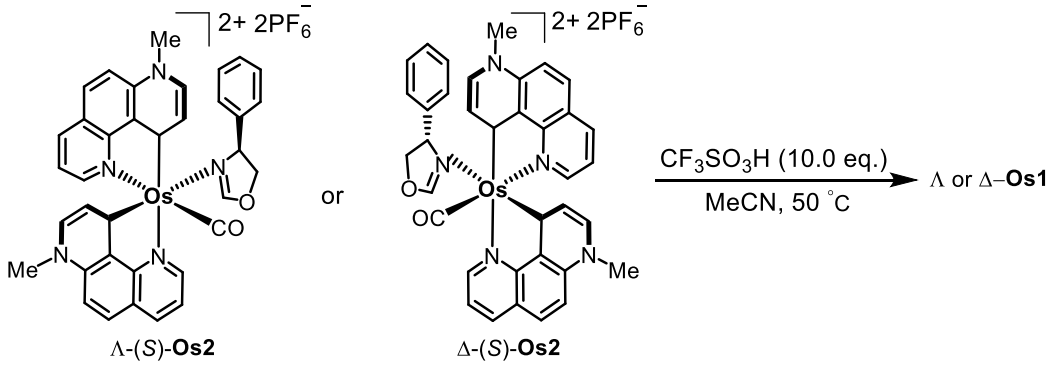


Figure S4. Auxiliary ligand removal of auxiliary osmium diastereomers

To a solution of Λ-(*S*)-**Os2** (20.9 mg, 0.02 mmol, 1.0 eq.) or Δ-(*S*)-**Os2** (20.9 mg, 0.02 mmol, 1.0 eq.) in MeCN (1.0 mL) was added CF_3SO_3H (30.0 mg, 0.2 mmol, 10.0 eq.). The resulting mixture was stirred at 50 ℃ for 10 h. After cooling to room temperature, to the mixture was added $NaHCO_3$ (17.4 mg, 0.2 mmol, 10.0 eq.) and stirred for 10 minutes. The reaction mixture was evaporated to dryness, and then subjected to column chromatography on silica gel (DCM/MeCN = 3:1, 10.0 eq. NH_4PF_6 as ion exchange reagent was added on the top of column) to give yellow solid non-racemic **Os1** combined with excess NH_4PF_6. The solid was extracted with DCM/MeCN (20:1, 1.0 mL), filtrated through cotton and washed with DCM/MeCN (20:1, 1.0 mL). Then the filtrated liquid was evaporated

to give Λ- or Δ-**Os1** (17.9 mg, 95%) as yellow solid. All NMR data of the single enantiomers were in agreement with the racemic catalyst.

2.5 Overview of Investigated Ligands as Chiral Auxiliaries

Figure S5 shows the overview of monodentate and bidentate ligands that were investigated as chiral auxiliaries for obtaining non-racemic **Os1**. For this, *rac*-**Os1** was reacted with the chiral ligands in various solvents and at various temperatures and the reactions were monitored by TLC and ^{1}H NMR. As a result, the bidentate ligands afforded complicated product mixtures which were not further investigated. The monodentate ligands coordinated to osmium and provided mixtures of two diastereomers as confirmed by ^{1}H NMR. However, in our hands, the diastereomers could not be resolved by column chromatography or by crystallization.

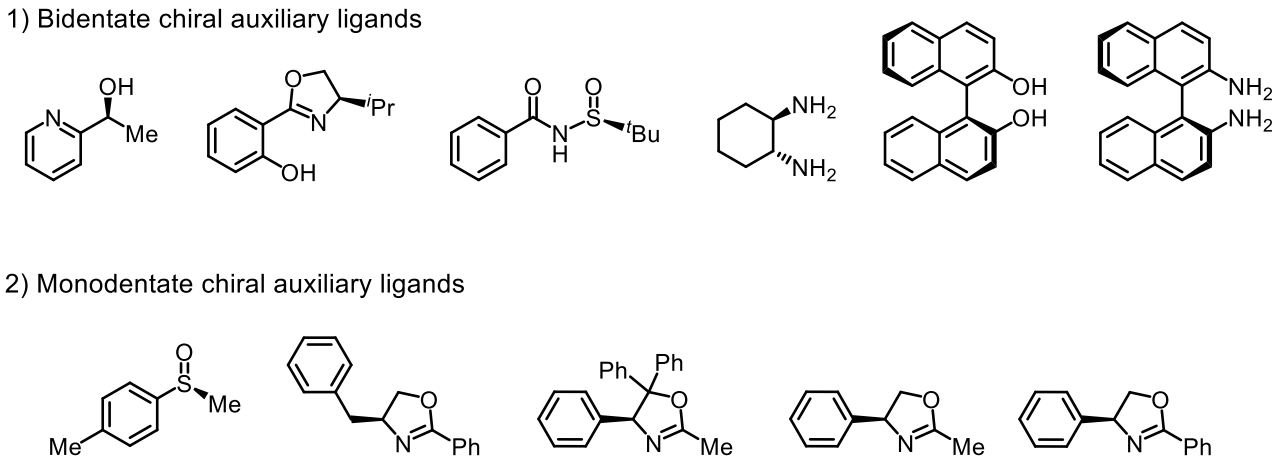


Figure S5. Attempts of other auxiliary ligands.

3. Determination of Enantiomeric Ratios of Non-Racemic Osmium Complexes

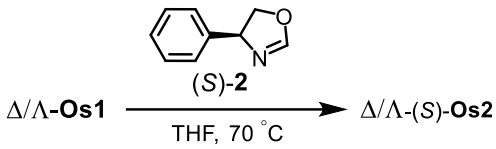


Figure S6. Reaction of Δ/Λ-**Os1** with (*S*)-4-phenyl-4,5-dihydrooxazole.

Method: Coordination to the enantiomerically pure chiral ligand (*S*)-4-phenyl-4,5-dihydrooxazole (*S*)-**2** to Λ/Δ-**Os1** was used to convert it to the corresponding diastereomers Λ/Δ-(*S*)-**Os1**. The diastereomeric ratio was then determined by ^{1}H NMR and used as a measure for the enantiomeric ratio of the purified samples of Λ-**Os1** and Δ-**Os1** (**Figure S6**).

Procedure: Samples of the purified non-racemic complexes Δ- or Λ-**Os1** (3.1 mg, 0.003 mmol) and the ligand (*S*)-4-phenyl-4,5-dihydrooxazole (1.3 mg, 0.009 mmol, 3.0 eq.) in THF (0.2 mL) were stirred at 70 °C for 24 h. The resulting mixture was precipitated with Et_2O and washed with Et_2O (1 mL for 3 times) to remove excess (*S*)-4-phenyl-4,5-dihydrooxazole. The residue was dissolved in CD_3CN and analyzed by ^{1}H NMR.

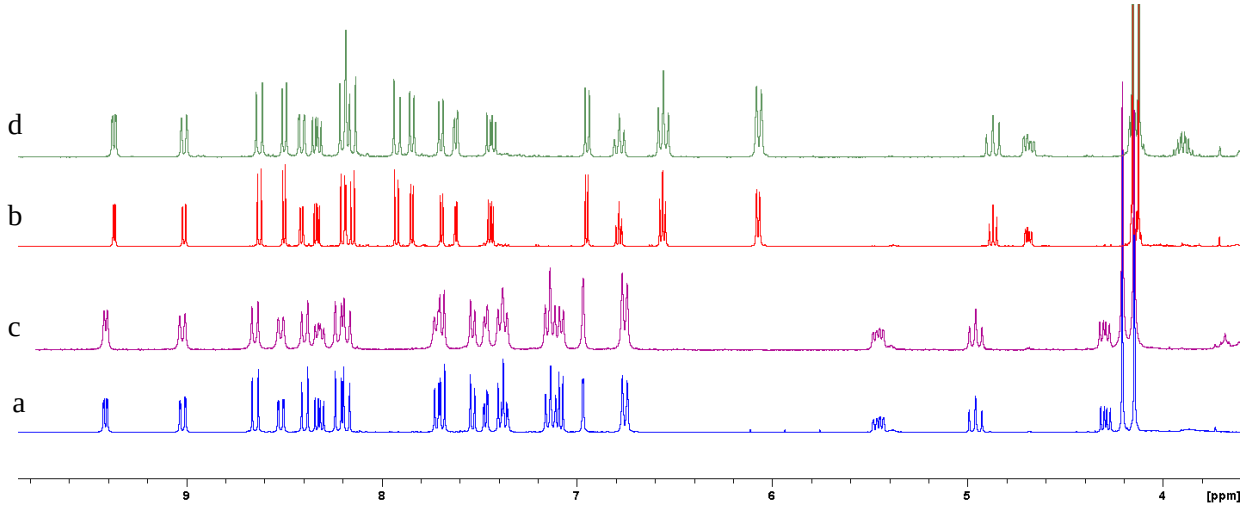


Figure S7. ^{1}H NMR (CD_3CN) spectra. a) Complex Δ-(*S*)-**Os2**. b) Complex Λ-(*S*)-**Os2**. c) Reaction of Δ-**Os1** with chiral ligand (*S*)-4-phenyl-4,5-dihydrooxazole. d) Reaction of Λ-**Os1** with chiral ligand (*S*)-4-phenyl-4,5-dihydrooxazole.

Results: No signals for the minor diastereomers Λ- or Δ-(*S*)-**Os2** could be observed (**Figure S7**). Additional control experiments were performed to determine the detection limit of this NMR experiment. For this, Λ- or Δ-(*S*)-**Os2** were spiked with 1% of the other diastereomer and the ^{1}H-NMR spectra measured. As a result, this 1% of the minor diastereomer could be detected, thus confirming that the detection limit must by below 1% of the minor diastereomer. We thus conclude that Δ-**Os1** and Λ-**Os1** complexes were synthesized with enantiomeric ratios of > 99:1 *e.r.*

4. Synthesis of the Substrates

4.1 Synthesis of the Sufonylazide Substrates

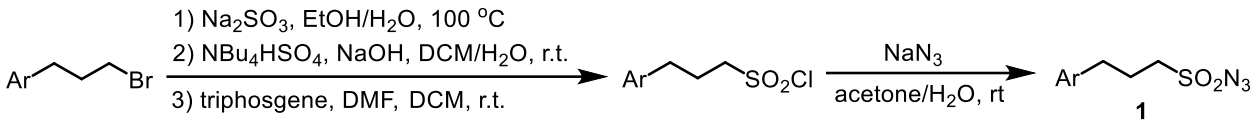
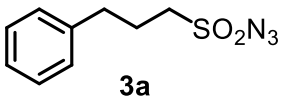


Figure S8. Synthesis of the sufonylazide substrates.

All substrates were synthesized according to procedures.[2]

General procedure: Sodium sulfite (2.2 mmol, 1.1 eq.) was added to a solution of the alkyl bromide (2.0 mmol, 1.0 eq.) in H_2O/EtOH (V/V = 2:1, 12.0 mL) and the reaction mixture was heated up to 100 ºC for 12 hours. Then, the reaction mixture was allowed to cool to room temperature and was diluted with DCM/H_2O (V/V = 1:1, 24 mL). Tetrabutylammonium bisulfate (713.0 mg, 2.1 mmol, 1.05 eq.) and NaOH (80.0 mg, 2.0 mol, 1.0 eq.) were added sequentially and the reaction mixture was stirred for 30 minutes. The organic layer was separated, dried with Na_2SO_4 for 30 minutes and concentrated. The crude product was further dried in high vacuum to remove all the volatiles (~ 6 hours) and then dissolved in DCM (8 mL) and cooled to 0 ºC prior to the addition of triphosgene (296.0 mg, 1.0 mmol, 0.5 eq.). Then, DMF (14.6 mg, 0.2 mmol, 0.1 eq.) was added to initiate the reaction. The reaction mixture was allowed to warm to room temperature while stirring for 1 hour. The reaction mixture was then concentrated and the resulting oil was purified by flash silica gel chromatography. The fractions containing product were collected and the solvent was removed to afford the pure compound alkyl sulfonyl chloride. Then the product was added to a well-stirred suspension of NaN_3 (195.0 mg, 3.0 mmol, 1.5 eq.) in acetone/H_2O (V/V = 1:1, 8 mL) at room temperature and the mixture was allowed to stir overnight. The majority of the acetone was removed under vacuum and the crude mixture was extracted with EtOAc. The organic layers were combined, dried, and concentrated. The crude product was purified by flash silica gel chromatography (conditions were given below). The fractions containing product were collected and the solvent was removed to afford the pure azide compound.

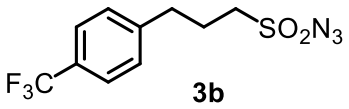
3-Phenylpropane-1-sulfonyl azide (3a) was purified by flash silica gel chromatography (eluent: 20:1 *n*-hexane/EtOAc) to afford a colorless oil (315.0 mg, 70% yield).



3a

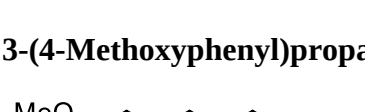
Reported compound.[2] **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38-7.13 (m, 5H), 3.33-3.23 (m, 2H), 2.81 (t, J = 7.3 Hz, 2H), 2.34-2.18 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.3, 129.0, 128.6, 126.9, 55.2, 33.9, 25.0.

3-(4-(Trifluoromethyl)phenyl)propane-1-sulfonyl azide (3b) was purified by flash silica gel chromatography (eluent: 20:1 *n*-hexane/EtOAc) to afford a colorless oil (424.0 mg, 80% yield). **Reported compound**.[2] **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 3.36-3.24 (m, 2H), 2.88 (t, J = 7.5 Hz, 2H), 2.36-2.21 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.5 (d, J = 1.0 Hz), 129.4 (q, J = 32.5 Hz), 128.9, 125.9 (q, J = 3.6 Hz), 124.3 (q, J = 272.0 Hz) , 55.0, 33.6, 24.8.



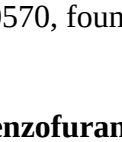
3b

3-(4-Methoxyphenyl)propane-1-sulfonyl azide (3c) was purified by flash silica gel chromatography (eluent: 20:1 *n*-hexane/EtOAc) to afford a colorless oil (388.0 mg, 76% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.24 (t, J = 7.8 Hz, 1H), 6.66-6.86 (m, 3H), 3.81 (s, 3H), 3.36-3.22 (m, 2H), 2.78 (t, J = 7.2 Hz 2H), 2.33-2.16 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.1, 140.9, 130.0, 120.9, 114.5, 112.1, 55.4, 55.2, 33.9, 24.9. **HRMS** (ESI, m/z) Calculated for $C_{10}H_{13}N_3O_3SNa$ $[M + Na]^+$: 278.0570, found: 278.0578. **IR** (film): ν (cm^{-1}) 2924, 2130, 1362, 1263, 1190, 1151, 781, 695, 566.



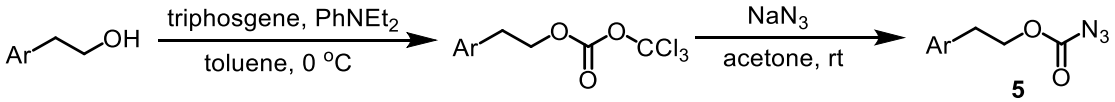
3c

3-(Benzofuran-2-yl)propane-1-sulfonyl azide (3d) was purified by flash silica gel chromatography (eluent: 10:1 *n*-hexane/EtOAc) to afford a colorless oil (503.5 mg, 95% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57-7.47 (m, 1H), 7.47-7.37 (m, 1H), 7.32-7.15 (m, 2H), 6.49 (s, 1H), 3.47-3.33 (m, 2H), 3.30 (t, J = 7.0 Hz, 2H), 2.47-2.31 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.0, 155.0, 128.6, 124.0, 123.0, 120.8, 111.1, 103.8, 55.0, 26.7, 22.0. **HRMS** (ESI, m/z) Calculated for $C_{11}H_{11}N_3O_3SNa$ $[M + Na]^+$: 288.0413, found: 288.0421. **IR** (film): ν (cm^{-1}) 2924, 2131, 1354, 1155, 740, 564, 547.



3d

4.2 Synthesis of the Azidoformate Substrates



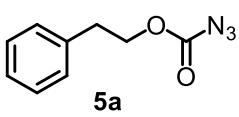
5

Figure S9. Synthesis of the azidoformate substrates.

General procedure: In a 10 ml flask, triphosgene (592.0 mg, 1.0 mmol, 1 eq.) was dissolved in dry toluene (4 mL) followed by cooling in ice bath, after which, diethylaniline (298.0 mg, 2.0 mmol, 1 eq.) was added with stirring over 15 min. Subsequently, aryl ethanol (2.0 mmol, 1 eq.) was slowly added. The resulting mixture was allowed to warm to room temperature and reacted overnight. Then it was washed with ice-cold water for 3 times, brine 1 time and dried with anhydrous $NaSO_4$. The organic phase was concentrated in vacuo and purified by flash silica column to give 2-arylethyl (trichloromethyl) carbonate. Then the product was added to a well-stirred suspension of NaN_3 (195

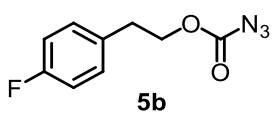
mg, 3.0 mmol, 1.5 eq.) in acetone (4 mL) at room temperature. The mixture was allowed to stir overnight and filtrated through ceilite and washed with DCM. The filtrate was concentrated and further purified by flash silica column (conditions given below) to provide the desired azidoformate substrates.

2-Phenethyl azidoformate (5a) was purified by flash silica gel chromatography (eluent: 20: 1 *n*-hexane/EtOAc) to afford a colorless oil (229.3 mg, 60% yield). **Reported compound**.[3] **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36-7.06 (m, 5H), 4.33 (t, J = 7.2 Hz, 2H), 2.92 (t, J = 7.2 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.5, 136.9, 129.0, 128.8, 127.0, 69.0, 35.0.



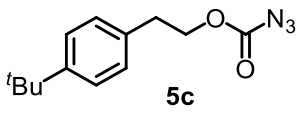
5a

4-Fluorophenethyl azidoformate (5b) was purified by flash silica gel chromatography (eluent: 20: 1 *n*-hexane/EtOAc) to afford a colorless oil (292.6 mg, 70% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.25-7.10 (m, 2H), 7.00 (t, J = 8.5 Hz, 2H), 4.38 (t, J = 6.9 Hz, 2H), 2.97 (t, J = 6.9 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 162.0 (d, J = 245.0 Hz), 157.5, 132.6 (d, J = 3.3 Hz), 130.5 (d, J = 8.0 Hz), 115.6 (d, J = 21.3 Hz), 68.8 (d, J = 0.8 Hz), 32.3. **^{19}F NMR** δ ppm -116.0. **HRMS** (ESI, m/z) Calculated for $C_9H_8FN_3O_2Na$ $[M + Na]^+$: 232.0493, found: 232.0499. **IR** (film): ν (cm^{-1}) 2964, 2135, 1725, 1510, 1216, 1157, 824, 750, 458.



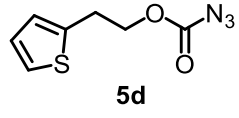
5b

4-(*tert*-Butyl)phenethyl azidoformate (5c) was purified by flash silica gel chromatography (eluent: 20:1 *n*-hexane/EtOAc) to afford a colorless oil (276.8 mg, 56% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 4.42 (t, J = 7.2 Hz, 2H), 2.99 (t, J = 7.2 Hz, 2H), 1.33 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.5, 149.9, 133.8, 128.7, 125.7, 69.1, 34.6, 35.5, 31.5. **HRMS** (ESI, m/z) Calculated for $C_{13}H_{17}N_3O_2Na$ $[M + Na]^+$: 270.1213, found: 270.1220. **IR** (film): ν (cm^{-1}) 2966, 2133, 1731, 1226, 1204, 751, 585.



5c

2-(Thiophen-2-yl)ethyl azidoformate (5d) was purified by flash silica gel chromatography (eluent: 20:1 *n*-hexane/EtOAc) to afford a colorless oil (204.9 mg, 52% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.18 (dd, J = 5.1, 1.2 Hz, 2H), 6.98-6.92 (m, 1H), 6.91-6.85 (m, 1H), 4.42 (t, J = 6.8 Hz, 2H), 3.22 (td, J = 6.8, 0.6 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.4, 138.8, 127.1, 126.0, 124.5, 68.6, 29.2. **HRMS** (ESI, m/z) Calculated for $C_7H_7N_3O_2SNa$ $[M + Na]^+$: 220.0151, found: 220.0157. **IR** (film): ν (cm^{-1}) 2966, 2136, 1724, 1222, 695.



5d

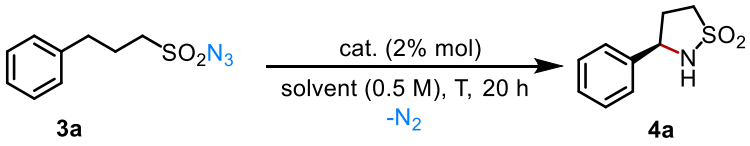
5. Catalytic Asymmetric C(sp^3)-H Amination Reactions

General procedure: A pre-dried 10 mL Schlenk tube was charged with substrates (0.1 mmol, 1.0 eq.) and Δ- or Λ-**Os1** (1.8 mg, 0.002 mmol, 2 mol%) or the catalyst Δ-**Ru** (1.7 mg, 0. 002 mmol, 2 mol%) under an atmosphere of N_2. Dried solvent (0.2 mL, 0.5 M) was added via syringe in sequence. The reaction mixture was stirred at the indicated temperature for the indicated time under an atmosphere of N_2. Afterwards, 1,3,5-trimethyoxybenzene as internal standard was added to detect the crude NMR yield by ^{1}H NMR. Then the mixture was directly transferred to a column and purified by flash chromatography on silica gel to give the analytical pure products. Enantiomeric ratios were determined by HPLC analysis on chiral stationary phase.

5.1 Catalytic Asymmetric C(sp^3)-H Amination of Sulfonylazide Substrates

Solvent and temperature effect on osmium-catalyzed asymmetric amination using **3a** as standard substrate are shown (entry1-7, **Table S1**). We found that the conditions listed in entry 6 were confirmed to be the optimal reaction conditions in quantitative yield and high enantioselectivity (92:8 e.r.). Under the best conditions, ruthenium catalyst (entry 9) showed low reactivity and enantioselectivity (62:38 e.r.).

Table S1. Optimization of Osmium Catalyst and Comparation with Ruthenium Catalyst for Asymmetric Amination of Alkylsulfonyl Azide **3a**[a]

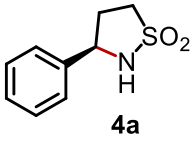


3a **4a**

Entry	Catalyst	solvent	T (°C)	NMR conv. (%)	NMR yield (%)	e.r.
1	Δ-**Os1**	chloroform	70	20	18	n.d.
2	Δ-**Os1**	1,2-dichlorobenzene	70	30	28	n.d.
3	Δ-**Os1**	acetone	70	100	80	75:25
4	Δ-**Os1**	nitrobenzene	70	100	93	87:13
5	Δ-**Os1**	DCE	70	100	95	91:9
6	**Δ-Os1**	**DCE**	**65**	**100**	**99**	**92:8**
7	Δ-**Os1**	DCE	60	40	38	n.d
8	Λ-**Os1**	DCE	65	100	98	8:92
9	**Δ-Ru**	**DCE**	**65**	**30**	**25**	**62:38**

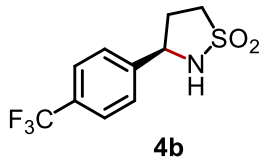
[a] Reactions were carried out on 0.10 mmol scale under N_2; Concentration: 0.5 M; Enantiomeric excess determined by chiral HPLC.

(*R*)-3-Phenylisothiazolidine 1,1-dioxide (4a) was synthesized following General Procedure at 65 ºC in DCE, and purified by flash silica gel chromatography (eluent: 1:1 *n*-hexane/EtOAc), to afford the title compound as white solid (19.0 mg, 96% yield). **Reported compound.**[2] **[α]$^{20}_{D}$** = +16º (c = 0.5, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 7.47-7.28 (m, 5H), 4.81-4.68 (m, 1H), 4.56 (s, H), 3.42-3.30 (m, 1H), 3.28-3.14 (m, 1H), 2.85-2.70 (m, 1H), 2.50-2.32 (m, 1H); **^{13}C NMR** (75 MHz, $CDC1_3$) δ ppm 140.3, 129.1, 128.6, 126.2, 58.3, 48.3, 32.3. **HPLC** (Chiral OD-H, 20% isopropanol/*n*-hexane rate 1 mL/min, column temperature 25 °C, UV detection at 210 nm): Minor t = 20.7 min., Major t = 29.6 min. e.r. = 92:8. Absolute configuration of the product was determined by HPLC and CD spectrum.



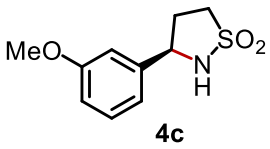
4a

(*R*)-3-(4-Fluorophenyl)isothiazolidine 1,1-dioxide (4b) was synthesized following General Procedure at 65 ºC in DCE, and purified by flash silica gel chromatography (eluent: 1:1 *n*-hexane/EtOAc), to afford the title compound as white solid (25.2 mg, 95% yield). **Reported compound**.[2] **[α]$^{20}_{D}$** = +14º (c = 0.5, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 7.64 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 4.97-4.60 (m, 2H), 3.44-3.30 (m, 1H), 3.29-3.11 (m, 1H), 2.94-2.72 (m, 1H), 2.48-2.27 (m, 1H); **^{13}C NMR** (75 MHz, $CDC1_3$) δ ppm 144.6, 130.8 (q, *J* = 32.6 Hz), 126.5, 126.1 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.0 Hz), 57.6, 48.2, 32.1; **HPLC** (Chiral OD-H, 20% isopropanol/*n*-hexane rate 1 mL/min, column temperature 25 °C, UV detection at 210 nm): Major t = 12.9 min., Minor t = 19.9 min. e.r. = 91:9. Absolute configuration of the product was determined by HPLC and CD spectrum.



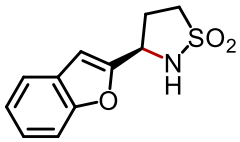
4b

(*R*)-3-(3-Methoxyphenyl)isothiazolidine 1,1-dioxide (4c) was synthesized following General Procedure at 65 ºC in DCE, and purified by flash silica gel chromatography (eluent: 1:1 *n*-hexane/EtOAc), to afford the title compound as white solid (22.0 mg, 97% yield). [**α]$^{20}_{D}$** = +8º (c = 0.5, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 7.34-7.26 (m, 1H), 7.00-6.93 (m, 2H), 6.91-6.82 (m, 1H), 4.80-4.63 (m, 1H), 4.46 (s, 1H), 3.82 (s, 3H), 3.41-3.30 (m, 1H), 3.27-3.13 (m, 1H), 2.85-2.70 (m, 1H), 2.49-2.32 (m, 1H); **^{13}C NMR** (75 MHz, $CDC1_3$) δ ppm 160.2, 142.0, 130.2, 118.3, 114.0, 111.7, 58.1, 55.5, 48.2, 32.2 **HRMS** (ESI, m/z) Calculated for $C_{10}H_{13}NO_3SNa$ $[M + Na]^+$: 250.0508, found: 250.0515. **IR** (film): *v* (cm^{-1}) 3311, 2949, 2841, 1287, 1269, 1258, 1134, 1030, 856, 795, 783, 725, 696, 486, 454. **HPLC** (Chiral IC, 20% isopropanol/*n*-hexane rate 1 mL/min, column temperature 25 °C, UV detection at 210 nm): Major t = 21.4 min., Minor t = 27.4 min. e.r. = 88:12. Absolute configuration of the product was determined by analogy.



4c

(*R*)-3-(Benzofuran-2-yl)isothiazolidine 1,1-dioxide (4d) was synthesized following General Procedure at 65 ºC in DCE, and purified by flash silica gel chromatography (eluent: 1:1 *n*-hexane/EtOAc), to afford the title compound as white solid (23.5 mg, 99% yield). **[α]^{20}D** = -12º (c = 0.5, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 7.34-7.26 (m, 1H), 7.00-6.93 (m, 2H), 6.91-6.82 (m, 1H), 4.80-4.63 (m, 1H), 4.46 (s, 1H), 3.82 (s, 3H), 3.41-3.30 (m, 1H), 3.27-3.13 (m, 1H), 2.85-2.70 (m, 1H), 2.49-2.32 (m, 1H); **^{13}C NMR** (75 MHz, $CDC1_3$) δ ppm 160.2, 142.0, 130.2, 118.3, 114.0, 111.7, 58.1, 55.5, 48.2,32. Calculated for $C_{11}H_{11}NO_3SNa$ $[M + Na]^+$: 260.0352, found: 260.0359. **IR** (film): ν (cm^{-1}) 3247, 1360, 1246, 1179, 1119, 736, 595, 458, 434. **HPLC** (Chiral IA, 10% isopropanol/*n*-hexane rate 1 mL/min, column temperature 25 °C, UV detection at 210 nm): Major t = 23.1 min., Minor t = 28.1 min., e.r. = 90:10. Absolute configuration of the product was determined by analogy.

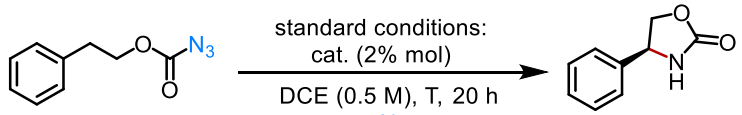


4d

5.2 Catalytic Asymmetric C(sp^3)-H Amination of Azidoformate Substrates

Solvent and temperature effect on osmium-catalyzed asymmetric amination of azidoformate substrates using **5a** as standard substrate are shown (entry1-6, **Table S2**). We found that the conditions listed in entry 5 were confirmed to be the optimal reaction conditions in high yield and enantioselectivity (89:11 e.r.). Under the best conditions, ruthenium catalyst (entry 8) showed low reactivity and enantioselectivity (62:38 e.r.).

Table S2. Optimization of Osmium Catalyst and Comparation with Ruthenium Catalyst for Asymmetric Amination of **5a**[a]

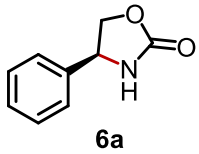


5a **6a**

Entry	Catalyst	solvent	T (°C)	NMR conv. (%)	NMR yield (%)	e.r.
1	Δ-**Os1**	1,2-dichlorobenzene	80	64	52	87:13
2	Δ-**Os1**	chlorobenzene	80	30	20	n.d.
3	Δ-**Os1**	nitrobenzene	80	100	75	85:15
4	Δ-**Os1**	DCE	80	100	85	88:12
5	**Δ-Os1**	**DCE**	**75**	**100**	**89**	**89:11**
6	Δ-**Os1**	DCE	70	89	75	89:11
7	Λ-**Os1**	DCE	75	100	88	11:89
8	**Δ-Ru**	**DCE**	**75**	**50**	**35**	**79:21**

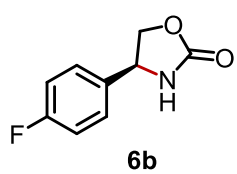
[a] Reactions were carried out on 0.10 mmol scale under N_2; Concentration: 0.5 M; Enantiomeric excess determined by chiral HPLC.

(*S*)-4-Phenyloxazolidin-2-one (6a) was synthesized following General Procedure at 75 ºC in DCE, and purified by flash silica gel chromatography (eluent: 1:1 *n*-hexane/EtOAc), to afford the title compound as white solid (14.0 mg, 86% yield). **Reported compound.**[4] **[α]$^{20}_{D}$**= +24º (c = 0.5, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 7.49-7.29 (m, 5H), 5.38 (s, 1H), 4.96 (t, *J* = 7.8 Hz, 1H), 4.74 (t, *J* = 8.7 Hz, 1H), 4.25-4.16 (m, 1H); **^{13}C NMR** (75 MHz, $CDC1_3$) δ ppm 159.8, 139.6, 129.4, 129.0, 126.2, 72.7, 56.5. **HPLC** (Chiral OD-H, 20% isopropanol-hexanes rate 1 mL/min, column temperature 25 °C, UV detection at 210 nm): Minor t = 13.7 min., Major t = 15.6 min., e.r. = 89:11. Absolute configuration of the product was determined by HPLC and CD spectrum.



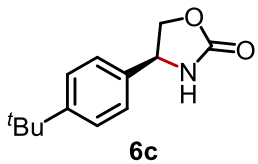
6a

(*S*)-4-(4-Fluorophenyl)oxazolidin-2-one (6b) was synthesized following General Procedure at 75 ºC in DCE, and purified by flash silica gel chromatography (eluent: 1:1 *n*-hexane/EtOAc), to afford the title compound as white solid (14.5 mg, 80% yield). **[α]$^{20}_{D}$** = +31º (c = 0.5, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40-7.28 (m, 2H), 7.16-7.04 (m, 2H), 5.54 (s, 1H), 4.95 (t, *J* = 7.8 Hz, 1H), 4.73 (t, *J* = 8.6 Hz, 1H), 4.21-4.11 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.1 (d, *J* = 247.5 Hz), 159.8, 135.4 (d, *J* = 3.2 Hz), 127.9 (d, *J* = 8.4 Hz), 116.3 (d, *J* = 21.7 Hz), 72.7, 55.9. **^{19}F NMR** (282 MHz, $CDCl_3$) δ ppm -112.6. **HRMS** (ESI, m/z) Calculated for $C_9H_8FNO_2Na$ $[M + Na]^+$: 204.0431, found: 204.0437. **IR** (film): ν (cm^{-1}) 3238, 2925, 1736, 1486, 1219, 1029, 837, 626, 540, 506. **HPLC** (Chiral OD-H, 20% isopropanol/*n*-hexane rate 1 mL/min, column temperature 25 °C, UV detection at 210 nm): Major t = 24.2 min., Minor t = 26.5 min. e.r. = 90:10. Absolute configuration of the product was determined by analogy.



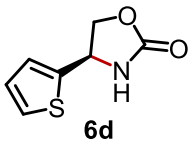
6b

(*S*)-4-(4-(*tert*-Butyl)phenyl)oxazolidin-2-one (6c) was synthesized following General Procedure at 70 ºC in DCE, and purified by flash silica gel chromatography (eluent: 1:1 *n*-hexane/EtOAc), to afford 19.0 mg of the title compound as white solid (18.6 mg, 85% yield). **[α]$^{20}_{D}$** = +20º (c = 0.5, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm 7.46-7.39 (m, 2H), 7.32-7.25 (m, 2H), 5.24 (s, 1H), 4.93 (t, *J* = 7.8 Hz, 1H), 4.72 (t, *J* = 8.6 Hz, 1H), 4.25-4.15 (m, 1H); **^{13}C NMR** (75 MHz, $CDC1_3$) δ ppm 159.8, 152.2, 136.5, 126.2, 126.0, 72.7, 56.3, 34.8, 31.4. **HRMS** (ESI, m/z) Calculated for $C_{13}H_{17}NO_2Na$ $[M + Na]^+$: 242.1152, found: 242.1158. **IR** (film): ν (cm^{-1}) 3279, 2957, 1746, 1717, 1224, 1027, 954, 922, 830, 574, 522. ; **HPLC** (Chiral OD-H, 20% isopropanol/*n*-hexane rate 1 mL/min, column temperature 25 °C, UV detection at 210 nm): Major t = 8.0 min., Minor t = 15.4 min. e.r. = 92:8. Absolute configuration of the product was determined by analogy.



6c

(*R*)-4-(Thiophen-2-yl)oxazolidin-2-one (6d) was synthesized following General Procedure at 70 ºC in DCE, and purified by flash silica gel chromatography (eluent: 1:1 *n*-hexane/EtOAc), to afford the title compound as white solid (15.2 mg, 96% yield).



6d

[α]$^{20}_{D}$ = +13º (c = 0.5, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ ppm) δ 7.33 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.09-7.04 (m, 1H), 7.04-6.96 (m, 1H), 6.91-6.85 (m, 1H), 5.53 (s, 1H), 5.24 (t, *J* = 7.6 Hz, 1H), 4.73 (t, J = 8.6 Hz, 1H), 4.36-4.25 (s, 1H); **^{13}C NMR** (75 MHz, $CDC1_3$) δ ppm 159.2, 143.1, 127.4, 126.1, 125.6, 72.7, 52.5. **HRMS** (ESI, m/z) Calculated for $C_7H_7NO_2SNa$ $[M + Na]^+$: 192.0090, found: 192.0095. **IR** (film): *ν* (cm^{-1}) 3241, 2922, 1703, 1230, 1020, 703, 490. **HPLC** (Chiral IG, 20% isopropanol-hexanes rate 1 mL/min, column temperature 25 °C, UV detection at 210 nm): Minor t = 12.5 min., Major t = 14.0 min. e.r. = 92:8. Absolute configuration of the product was determined by analogy.

6. Mechanistic Study of Catalytic Asymmetric C(sp3)-H Amination Reactions

6.1 Trapping of Os-Nitrenoid Intermediate of Sulfonylazide

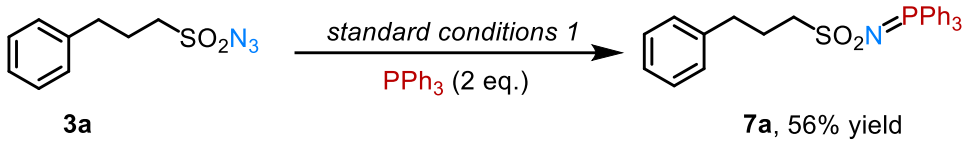


Figure S10. Trapping of Os-nitrenoid intermediate of sufonylazide.

According to the typical procedure, a mixture of **3a** (22.5 mg, 0.1 mmol), triphenylphosphine (52.5 mg, 0.2 mmol) and *rac*-**Os1** (1.8 mg, 2 mol%) in DCE (0.2 mL, 0.5 M) under nitrogen atmosphere was stirred at 65 ºC for 20 hours. After cooling to room temperature, the reaction mixture was purified through silica gel chromatography (eluent: *n*-hexane/EtOAc = 1:1) to give **7a** (25.7 mg, 56% yield) as a colorless liquid. **^{1}H NMR** (300 MHz, CD_3CN) δ 7.94-7.43 (m, 15H), 7.35-7.05 (m, 5H), 2.89-2.52 (m, 4H), 2.10-1.90 (m, 2H). **^{13}C NMR** (75 MHz, CD_3CN) δ 142.5, 134.05, 134.01, 133.9, 133.8, 130.0, 129.8, 129.7, 129.44, 129.38, 128.3, 126.9, 56.13, 34.7, 27.2. **^{31}P NMR** (101 MHz, CD_3CN) δ 15.2. **HRMS** (ESI, m/z) calcd for $C_{27}H_{26}NO_2PSH$ $[M + H]^+$: 460.1495, found: 460.1507. **IR** (film): ν (cm^{-1}) 3062, 3025, 2944, 2922, 1440, 1263, 1112, 721, 695, 526, 500.

6.2 Trapping of Os-Nitrenoid Intermediate of Azidoformate

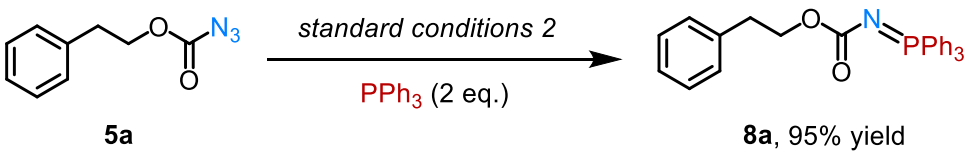
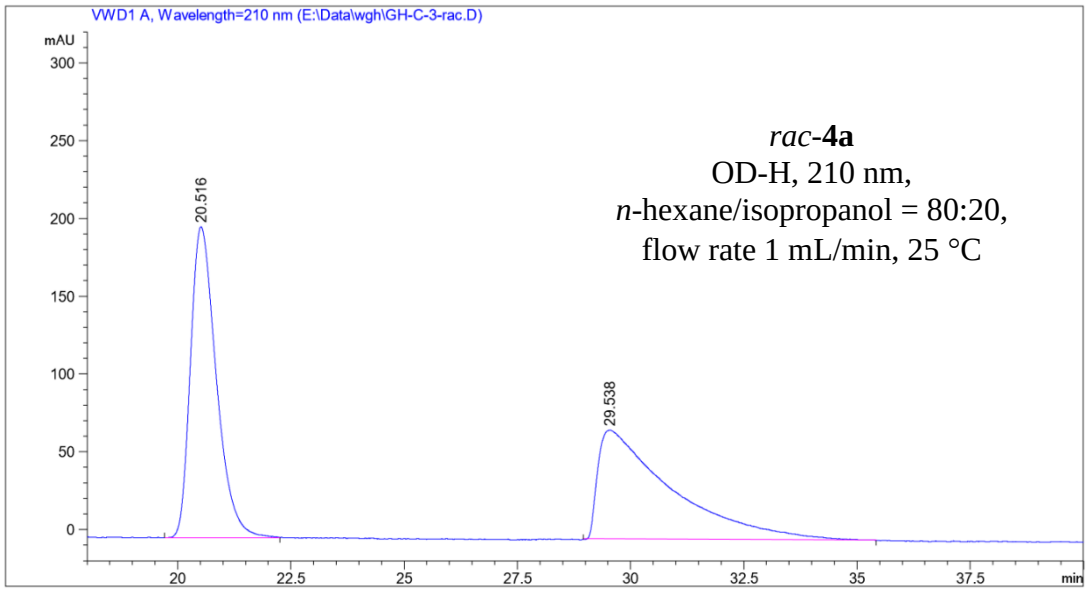


Figure S11. Trapping of Os-nitrenoid intermediate of azidoformate.

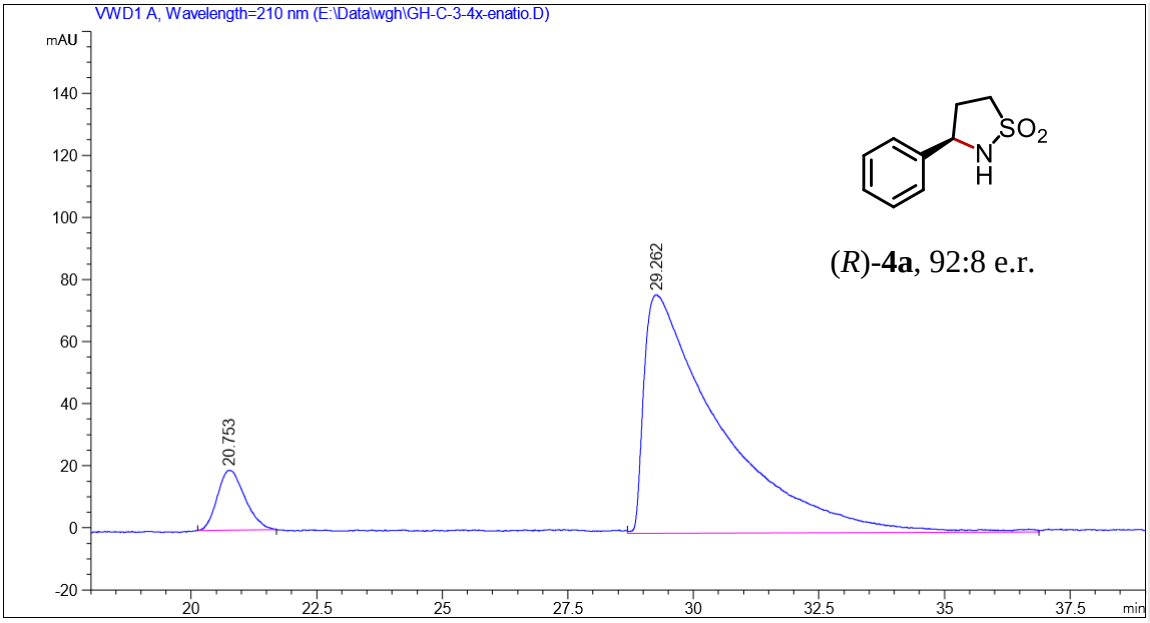
According to the typical procedure, a mixture of **5a** (19.1 mg, 0.1 mmol), triphenylphosphine (52.5 mg, 0.2 mmol) and rac-**Os1** (1.8 mg, 2 mol%) in DCE (0.2 mL, 0.5 M) under nitrogen atmosphere was stirred at 75 ºC for 20 hours. After cooling to room temperature, the reaction mixture was purified through silica gel chromatography (eluent: *n*-hexane/EtOAc = 1:1) to give **8a** (40.2 mg, 95% yield) as a colorless liquid. **^{1}H NMR** (300 MHz, CD_3CN) δ 7.93-7.36 (m, 15H), 7.35-7.05 (m, 5H), 4.30-3.98 (m, 2H), 2.84 (t, J = 6.8 Hz, 2H). **^{13}C NMR** (75 MHz, CD_3CN) δ 162.5, 140.2, 133.8, 133.7, 133.6, 133.5, 130.1, 129.88, 129.86, 129.7, 129.3, 128.8, 127.1, 66.61, 66.56, 36.4. **^{31}P NMR** (101 MHz, CD_3CN) δ 20.2. **HRMS** (ESI, m/z) calcd for $C_{27}H_{24}NO_2PH$ $[M + H]^+$: 426.1617, found: 426.1628. **IR** (film): ν (cm^{-1}) 3058, 3025, 2944, 1632, 1270, 1112, 1097, 721, 692, 533, 518.

7. Determination of Enantiomeric Excess for Catalytic Reactions

Enantiomeric excess of the compounds was determined with Daicel Chiralpak OD-H, IA, IG or IC (250×4.6 mm) HPLC columns on an Agilent 1260 Series HPLC System.

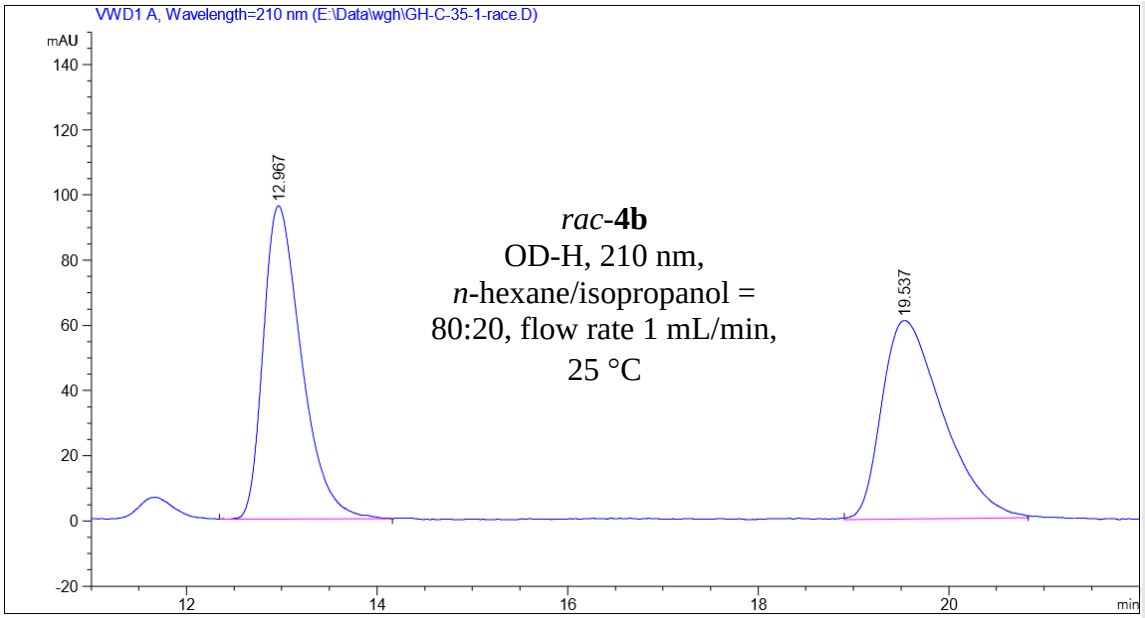


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.516	VV R	0.6070	7926.35107	199.73363	50.3306
2	29.538	MM R	1.8648	7822.22461	69.91074	49.6694



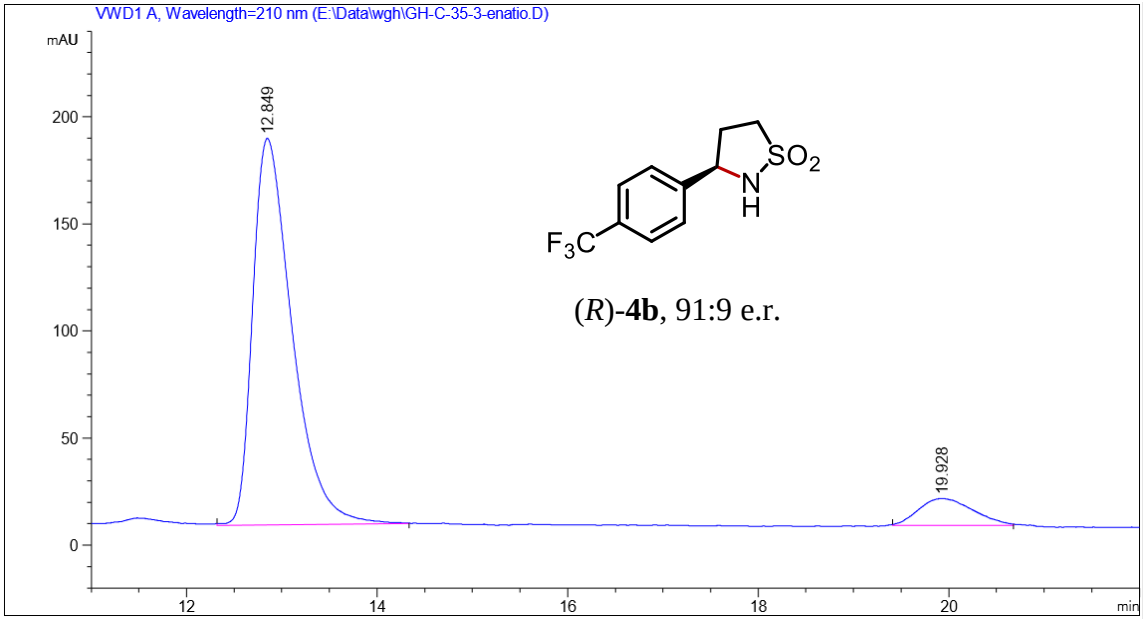
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.753	MM R	0.6373	736.48523	19.25917	8.2900
2	29.262	MM R	1.7687	8147.48096	76.77375	91.7100

Figure S12. HPLC traces of *rac*-**4a** and (*R*)-**4a**.



rac-**4b**
OD-H, 210 nm,
n-hexane/isopropanol =
80:20, flow rate 1 mL/min,
25 °C

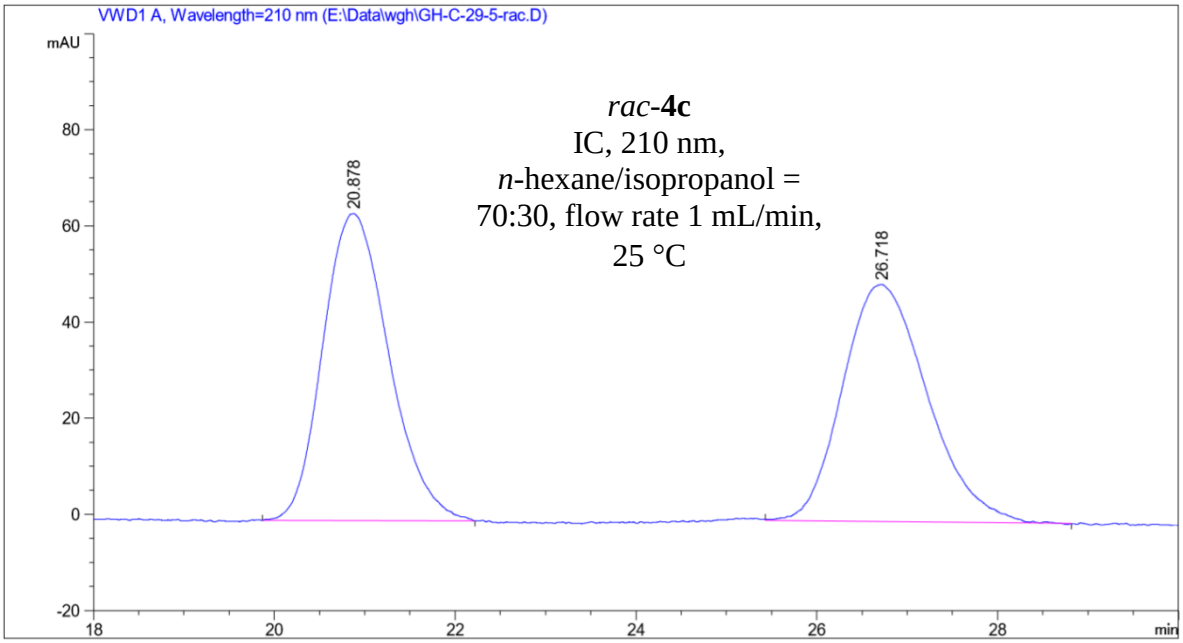
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.967	VV R	0.4226	2673.50757	96.08433	49.6157
2	19.537	MM R	0.7439	2714.92139	60.82475	50.3843



(*R*)-**4b**, 91:9 e.r.

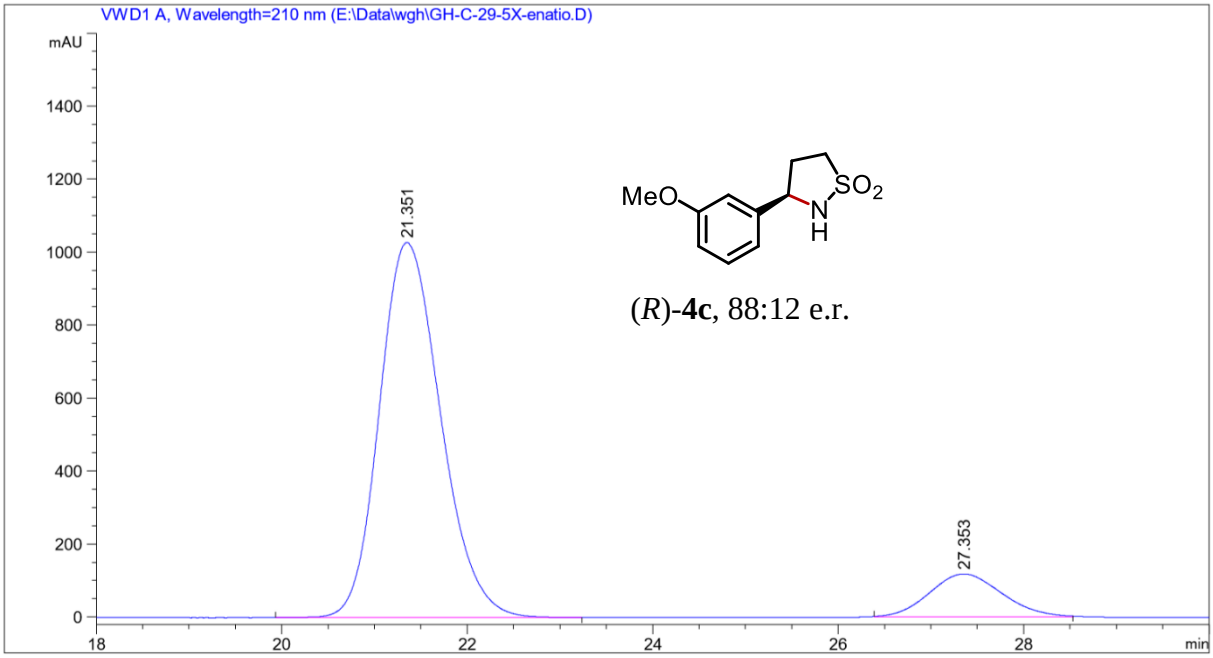
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.849	MM R	0.4788	5183.97217	180.45546	91.2525
2	19.928	MM R	0.6622	496.93863	12.50733	8.7475

Figure S13. HPLC traces of *rac*-**4b** and (*R*)-**4b**.



rac-**4c**
IC, 210 nm,
n-hexane/isopropanol =
70:30, flow rate 1 mL/min,
25 °C

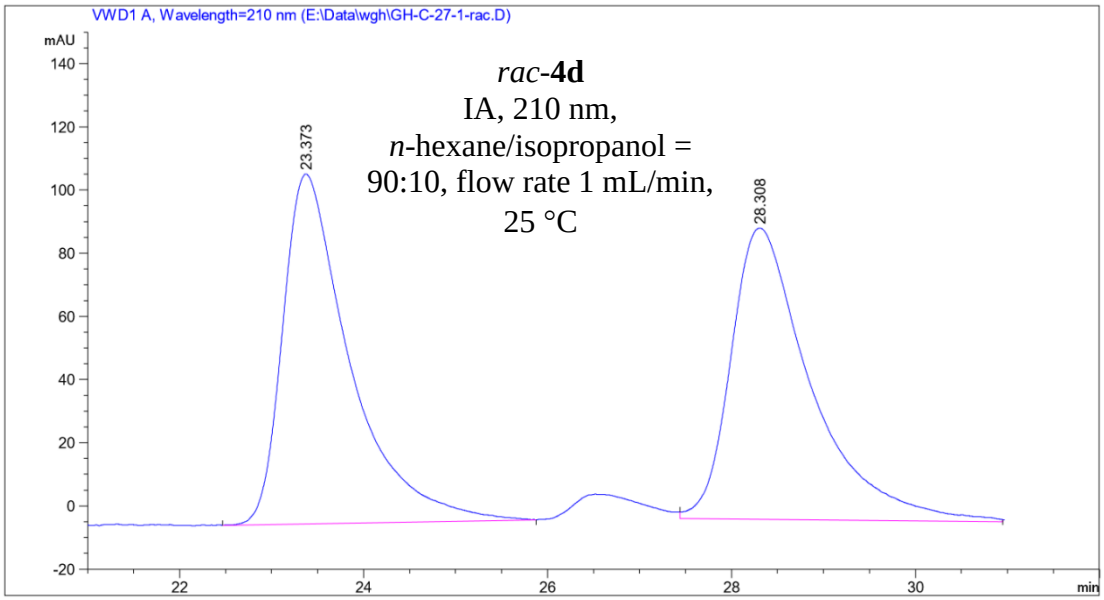
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.225	VV R	0.7028	2521.43872	43.91929	50.1659
2	42.942	MM R	1.2997	2504.76123	32.12011	49.8341



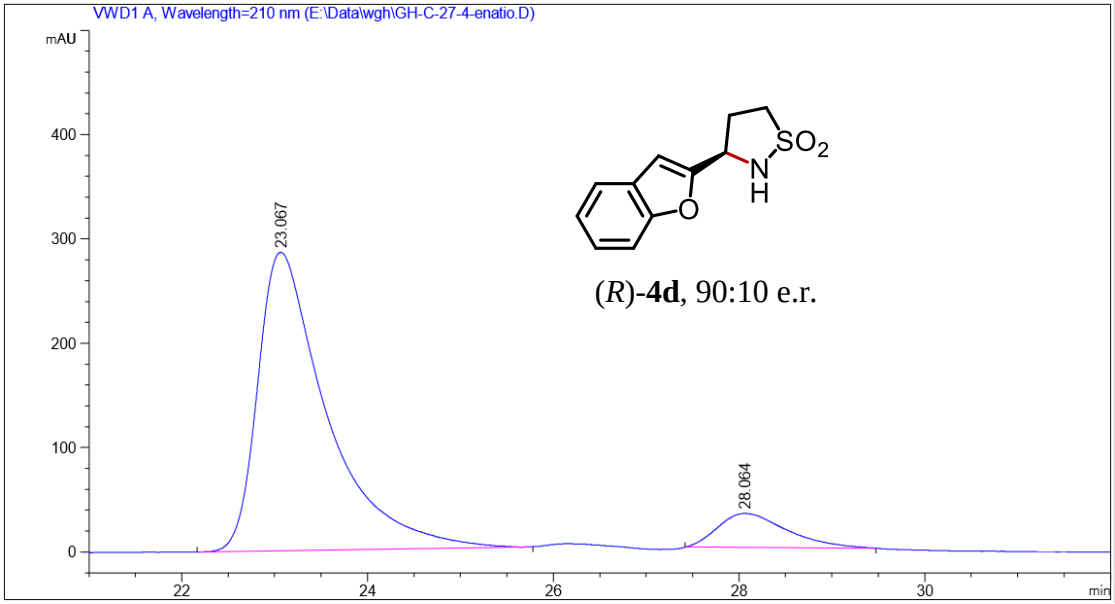
(*R*)-**4c**, 88:12 e.r.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.986	MM R	1.3343	7.72971e4	965.49194	88.0131
2	40.030	MM R	1.6805	1.05274e4	104.40786	11.9869

Figure S14. HPLC traces of *rac*-**4c** and (*R*)-**4c**.

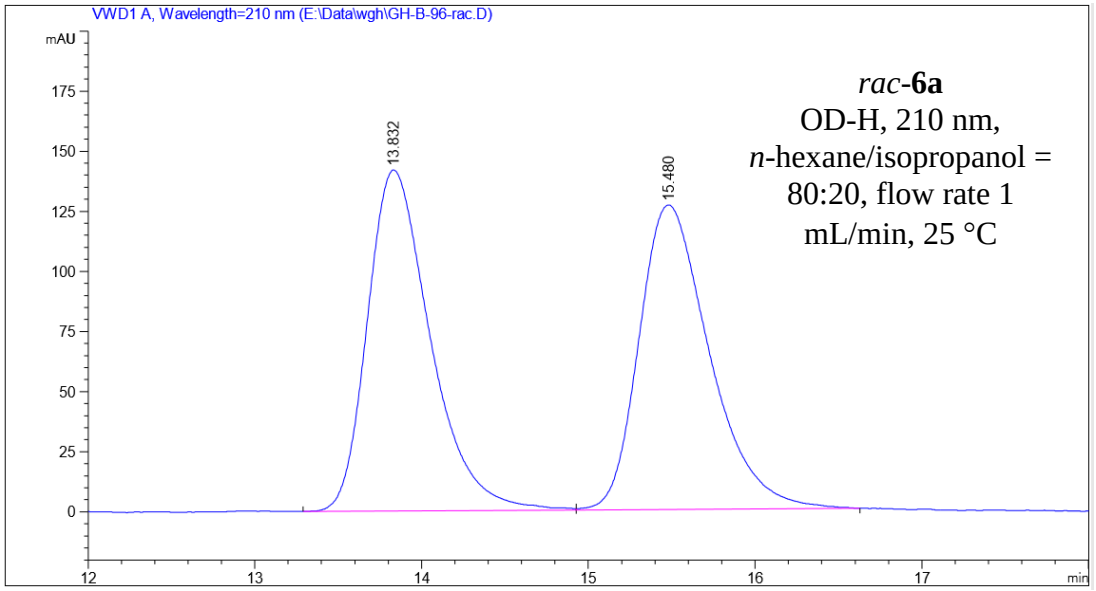


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.373	VB R	0.7155	5615.41455	110.75332	50.1541
2	28.308	MM R	1.0089	5580.89990	92.19626	49.8459

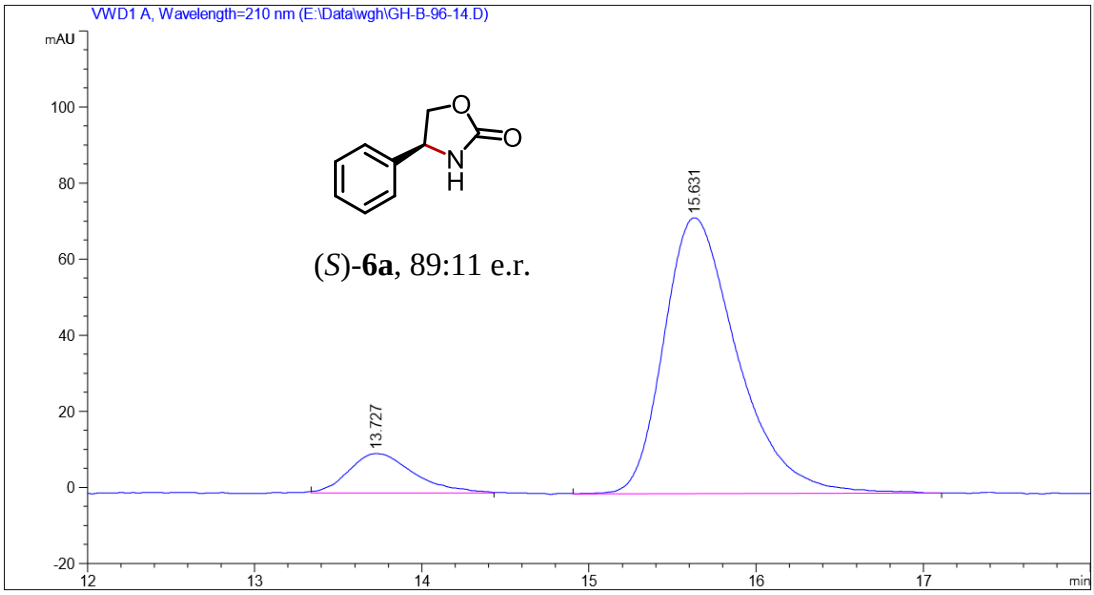


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.067	MM R	0.8625	1.48049e4	286.08401	89.8387
2	28.064	MM R	0.8596	1674.52759	32.46788	10.1613

Figure S15. HPLC traces of *rac*-**4d** and (*R*)-**4d**.

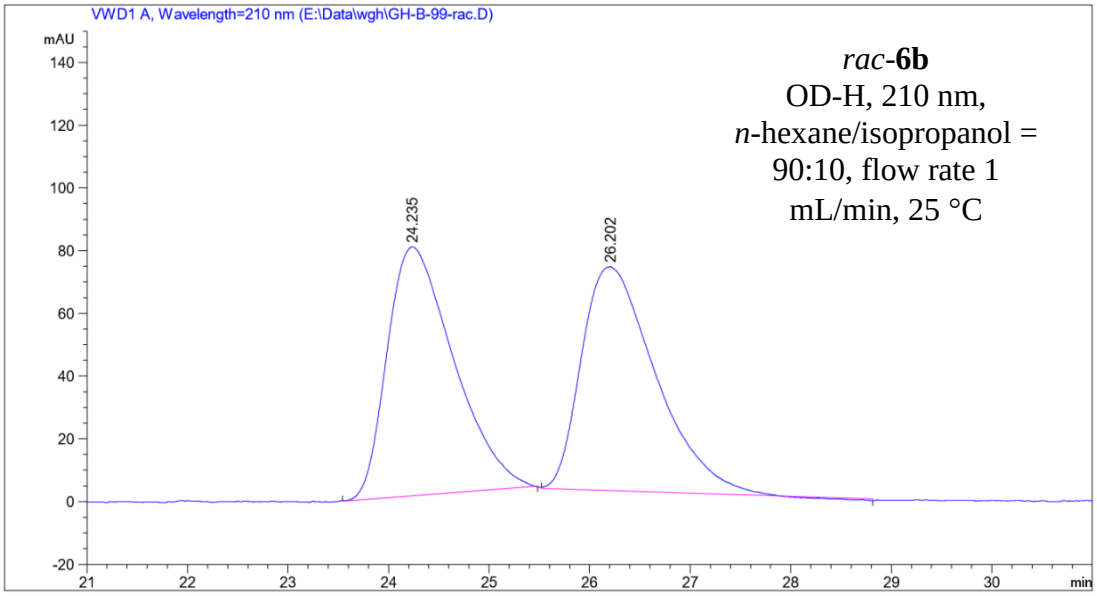


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.832	BV R	0.3940	3721.16577	141.87639	50.0134
2	15.480	VV R	0.4475	3719.17212	126.67075	49.9866

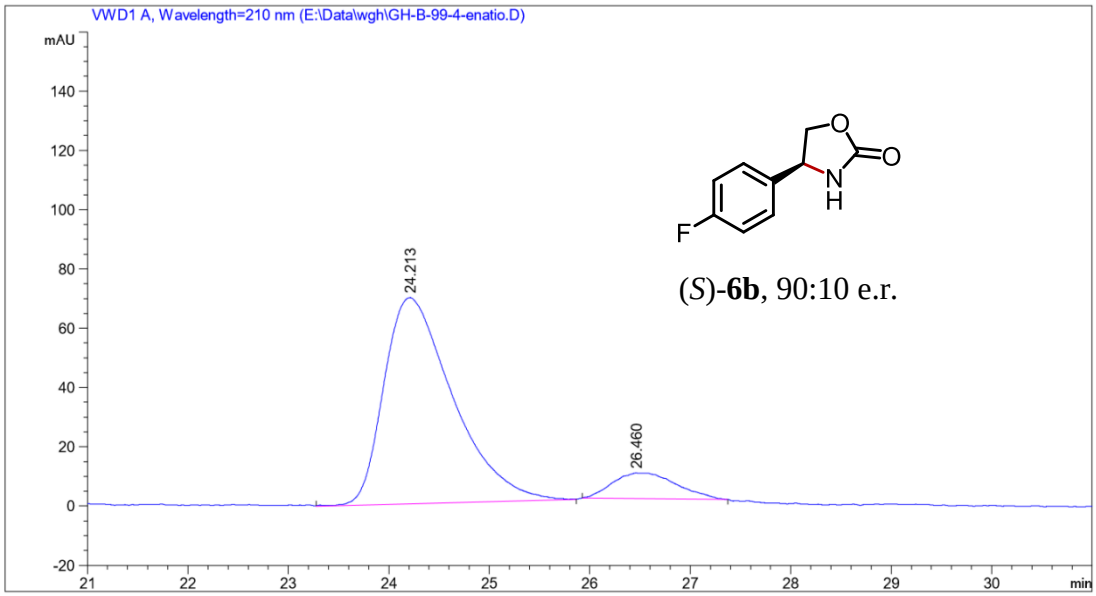


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.727	MM R	0.4491	277.15524	10.28505	11.1148
2	15.631	MM R	0.5094	2216.41797	72.51174	88.8852

Figure S16. HPLC traces of *rac*-**6a** and (*S*)-**6a**.

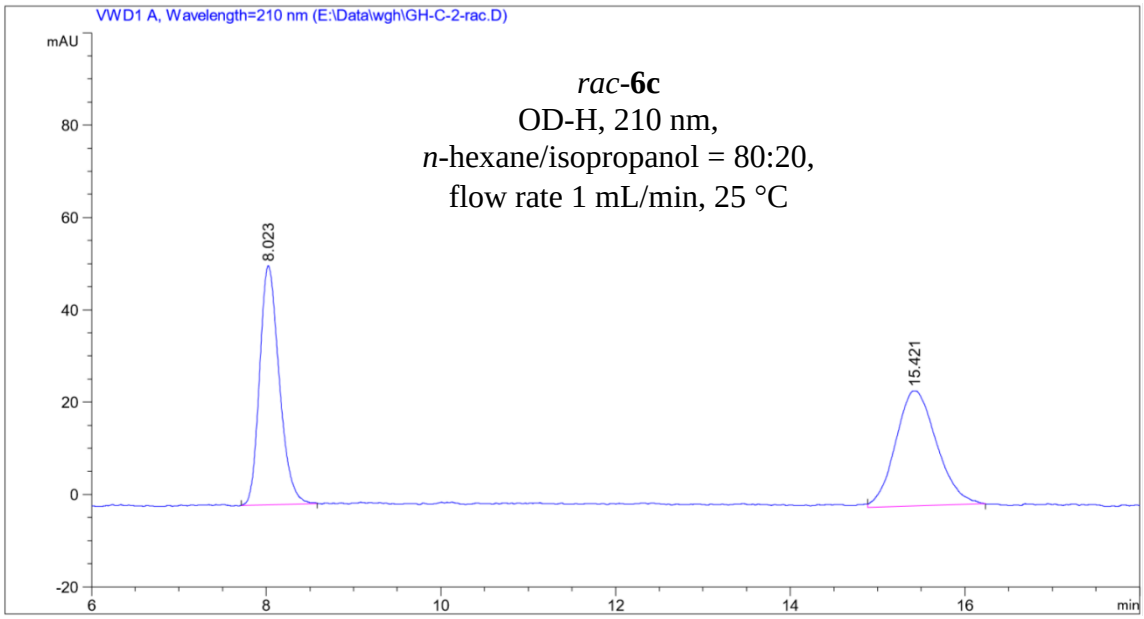


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.235	MM R	0.7654	3644.49243	79.36236	49.7529
2	26.202	MM R	0.8600	3680.68945	71.32825	50.2471

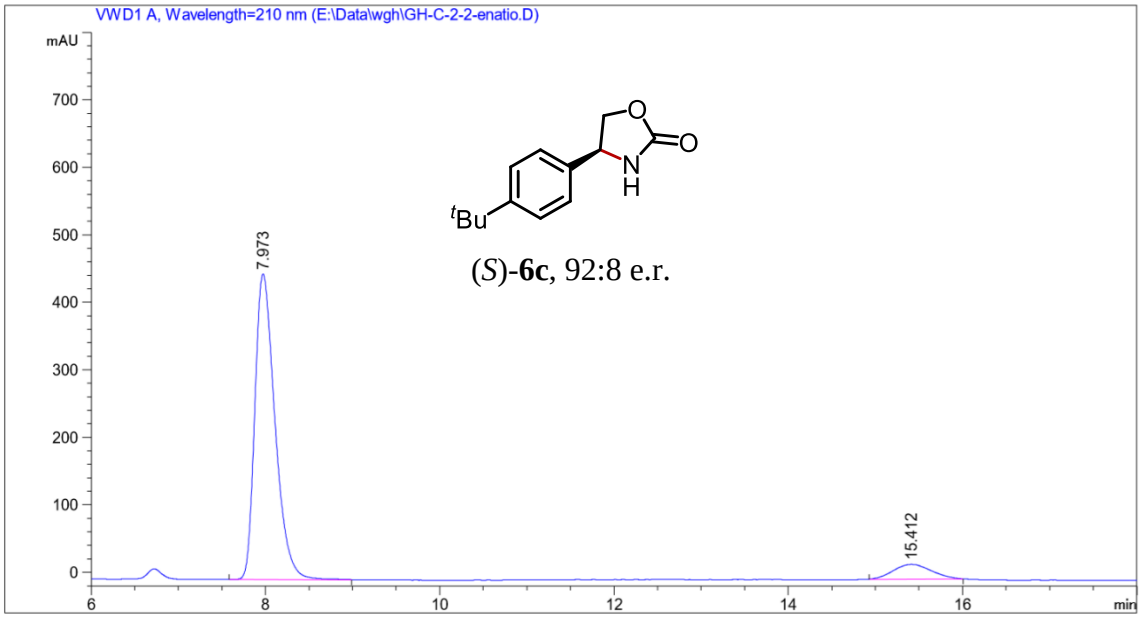


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.213	MM R	0.7934	3309.48608	69.52328	89.6283
2	26.460	MM R	0.7368	382.96890	8.66257	10.3717

Figure S17. HPLC traces of *rac*-**6b** and (*S*)-**6b**.

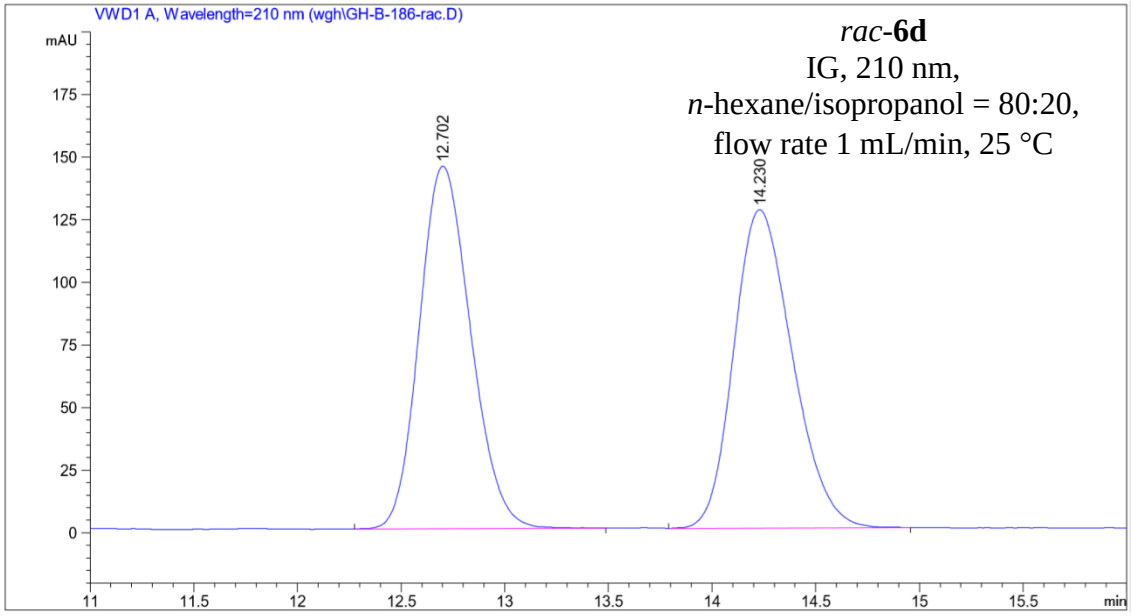


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.023	MM R	0.2599	807.69031	51.78618	49.8099
2	15.421	MM R	0.5447	813.85699	24.90155	50.1901



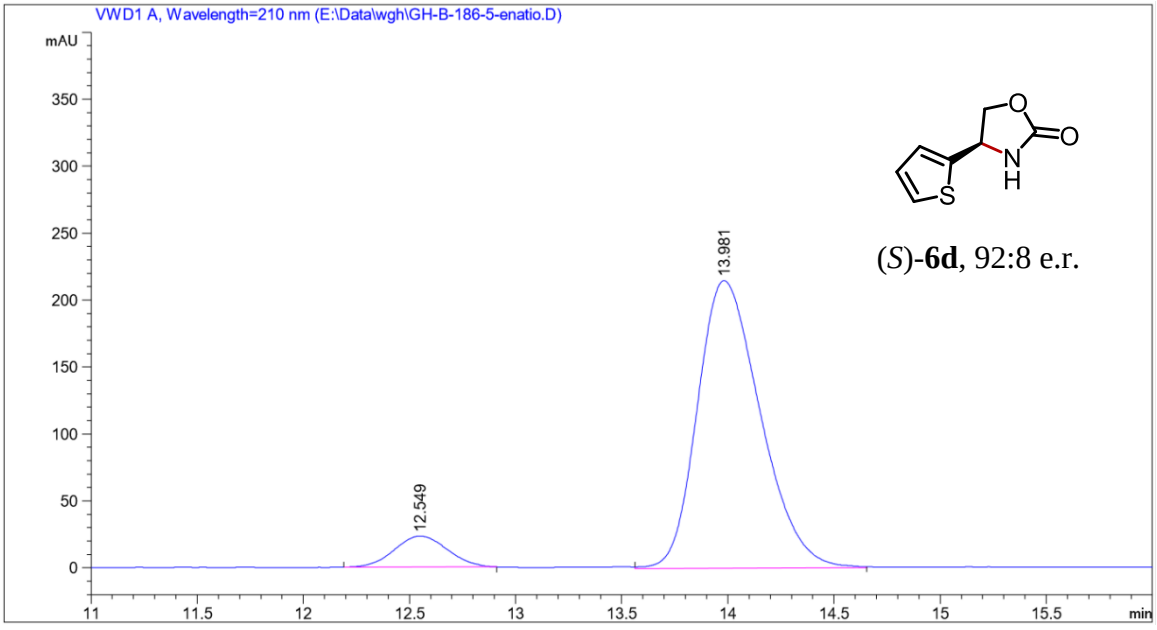
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.973	MM R	0.2674	7262.29980	452.62204	91.6602
2	15.412	MM R	0.5062	660.77136	21.75559	8.3398

Figure S18. HPLC traces of *rac*-**6c** and (*S*)-**6c**.



rac-**6d**
IG, 210 nm,
n-hexane/isopropanol = 80:20,
flow rate 1 mL/min, 25 °C

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.702	BV R	0.2682	2497.11938	144.82988	49.9737
2	14.230	BV R	0.3014	2499.74683	127.11968	50.0263

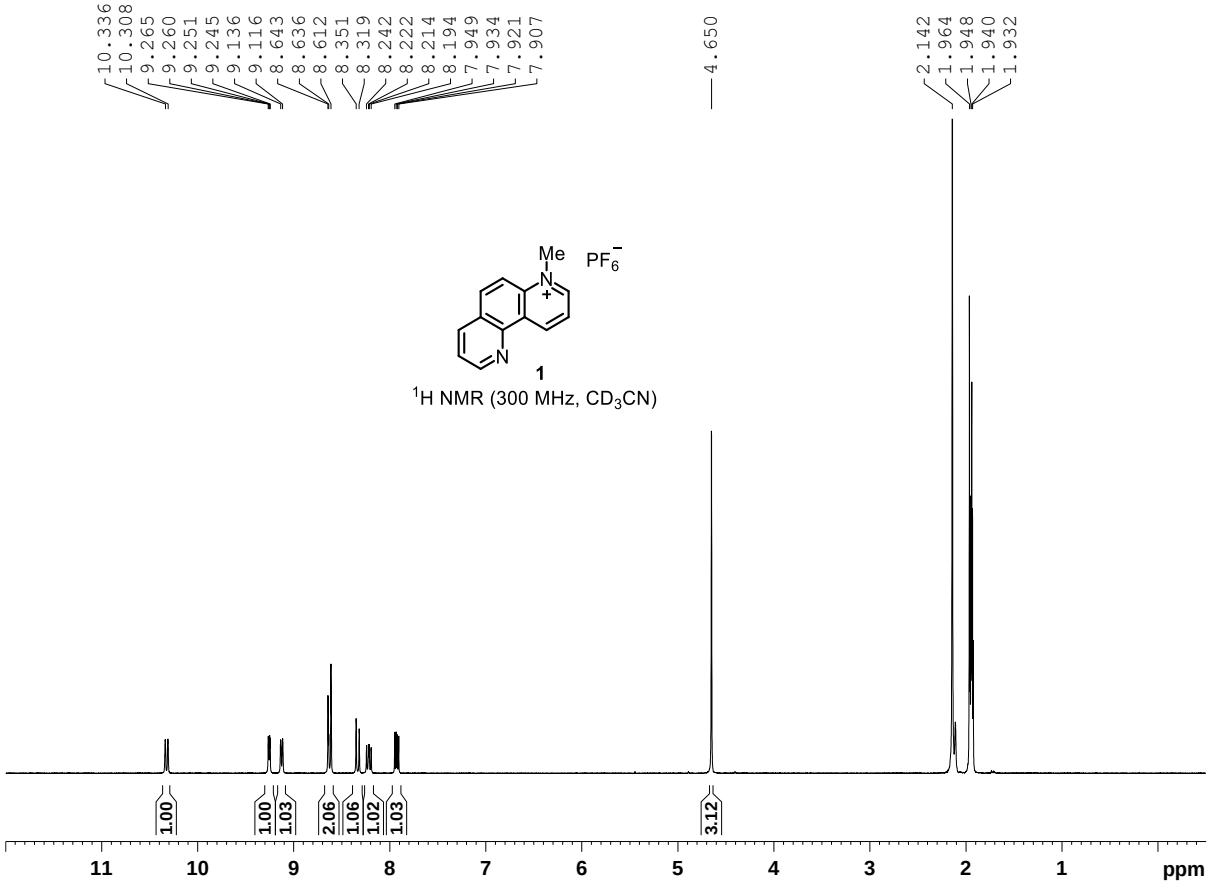


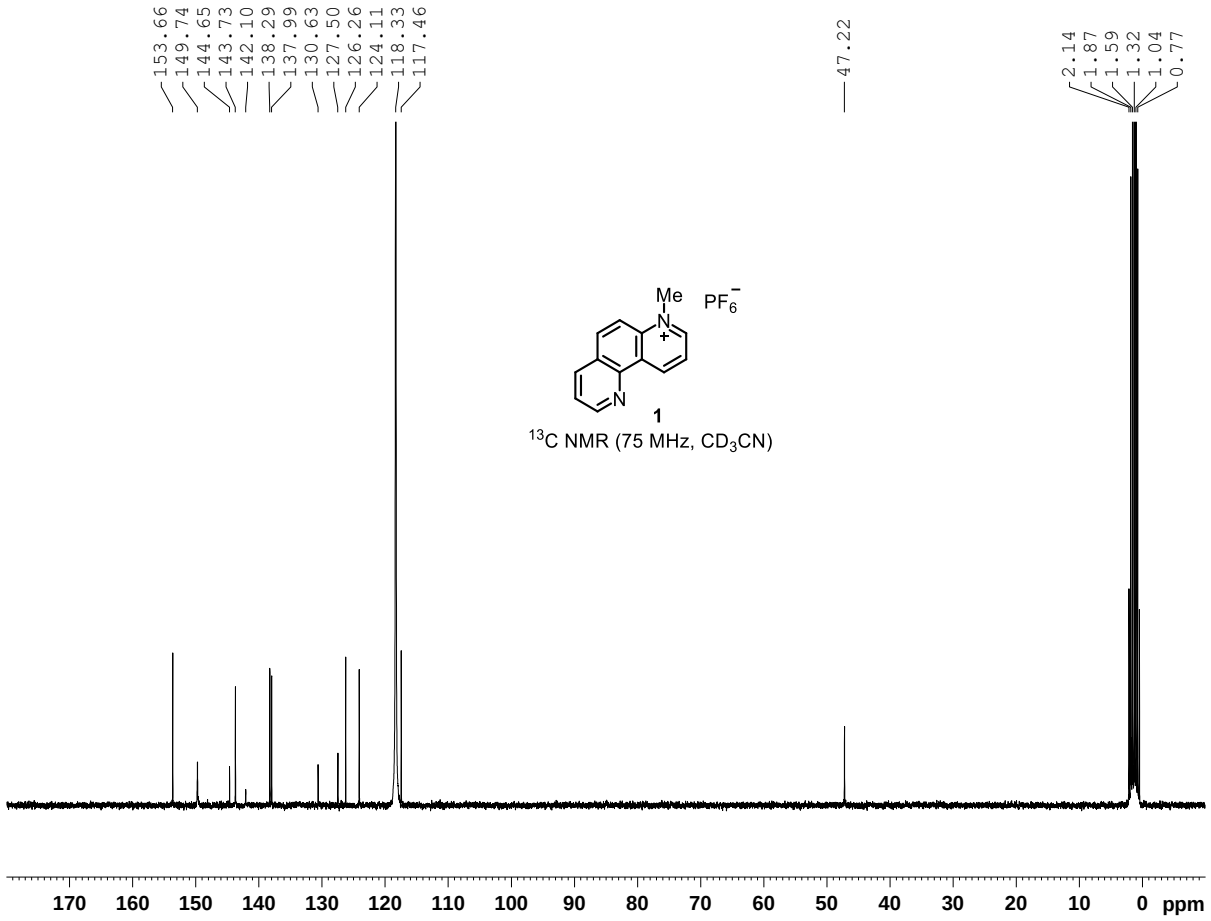
(*S*)-**6d**, 92:8 e.r.

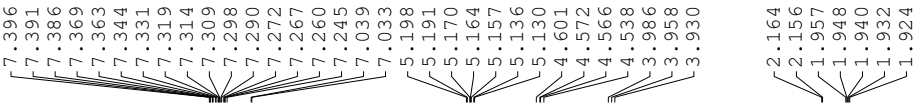
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.549	MM R	0.2885	400.80737	23.15078	8.2802
2	13.981	MM R	0.3443	4439.71631	214.91705	91.7198

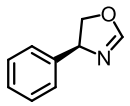
Figure S19. HPLC traces of *rac*-**6d** and (*S*)-**6d**.

8. NMR Spectra



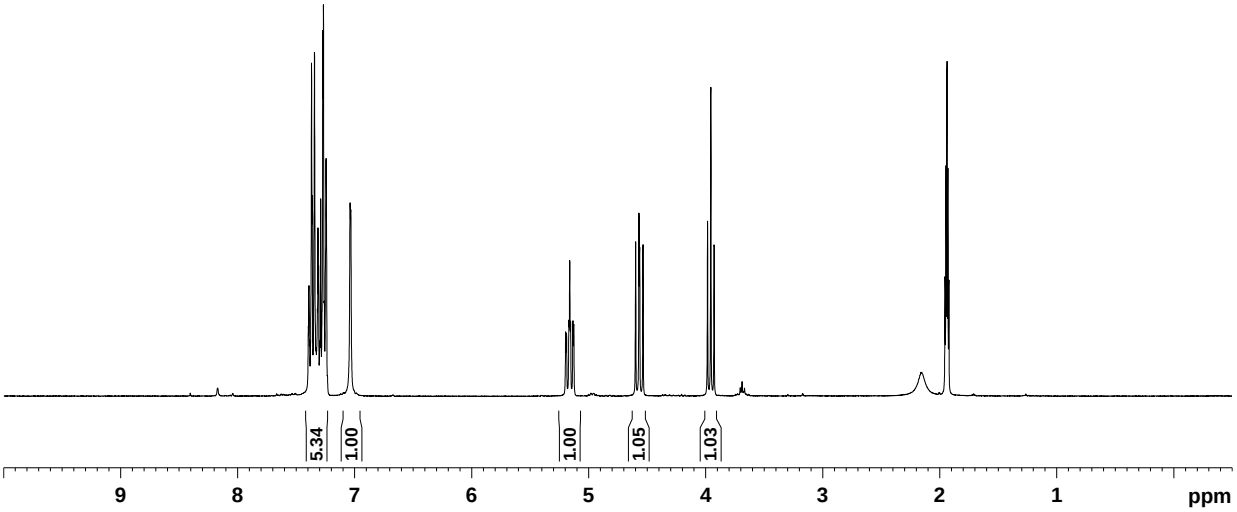


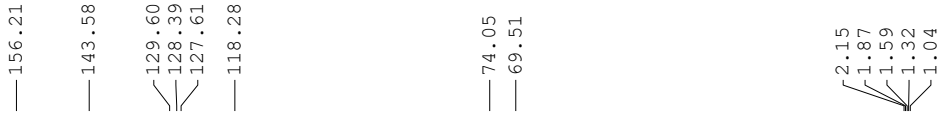


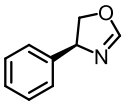


(*S*)-**2**

^{1}H NMR (300 MHz, CD_3CN)

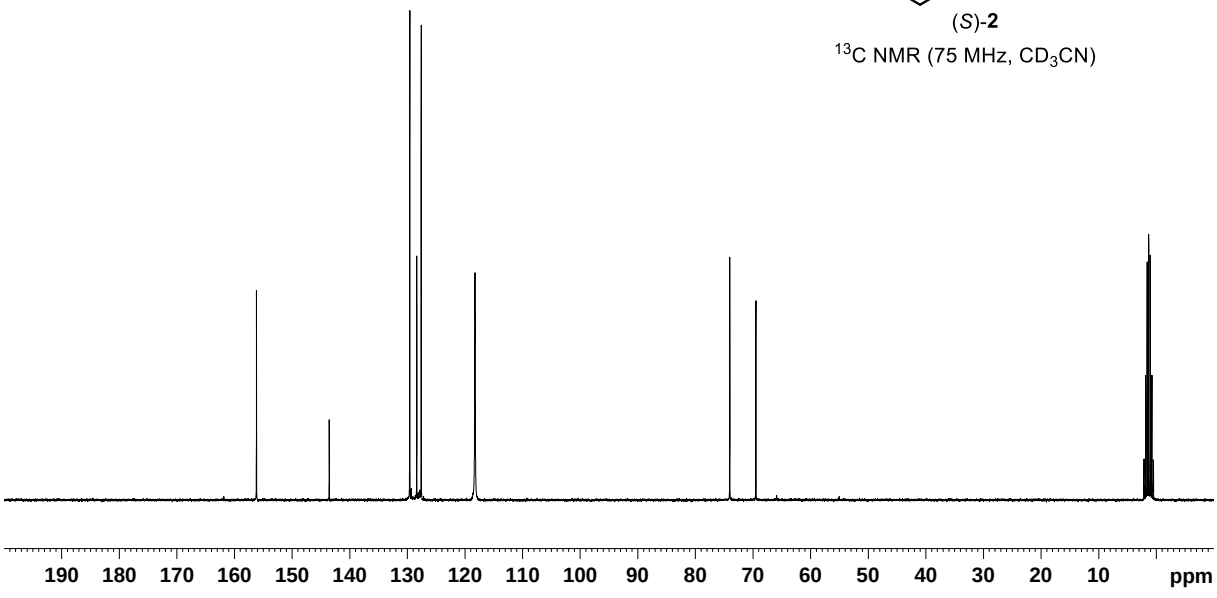


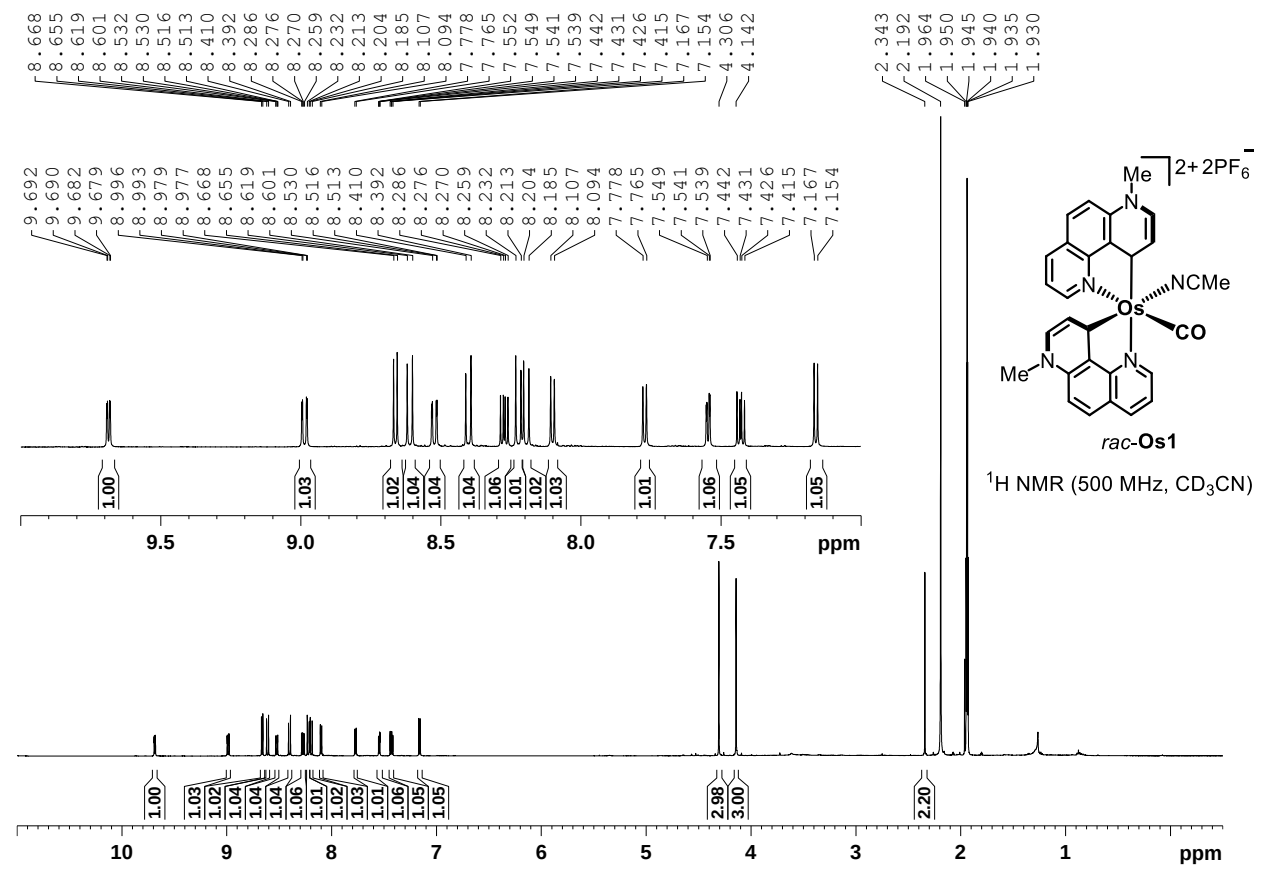


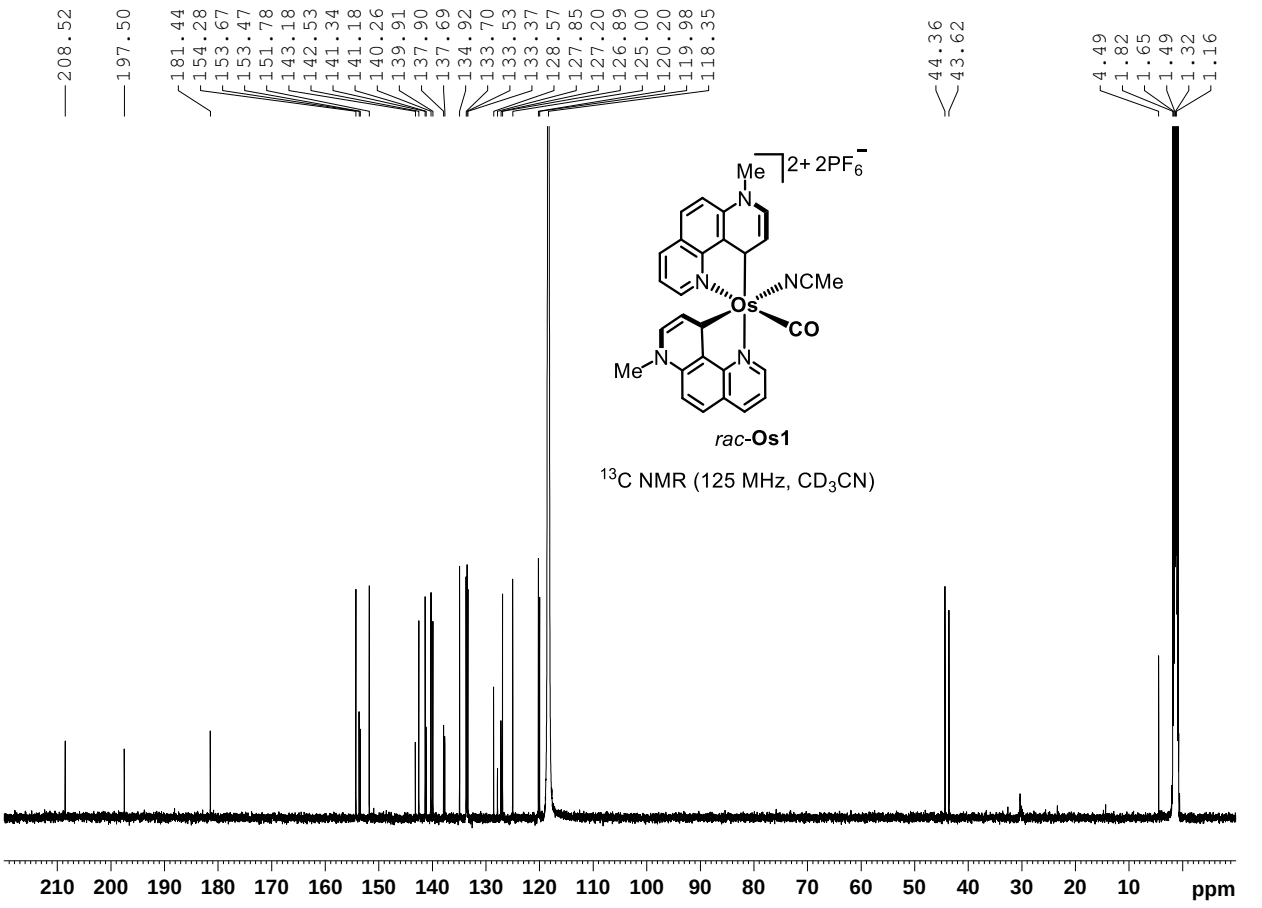


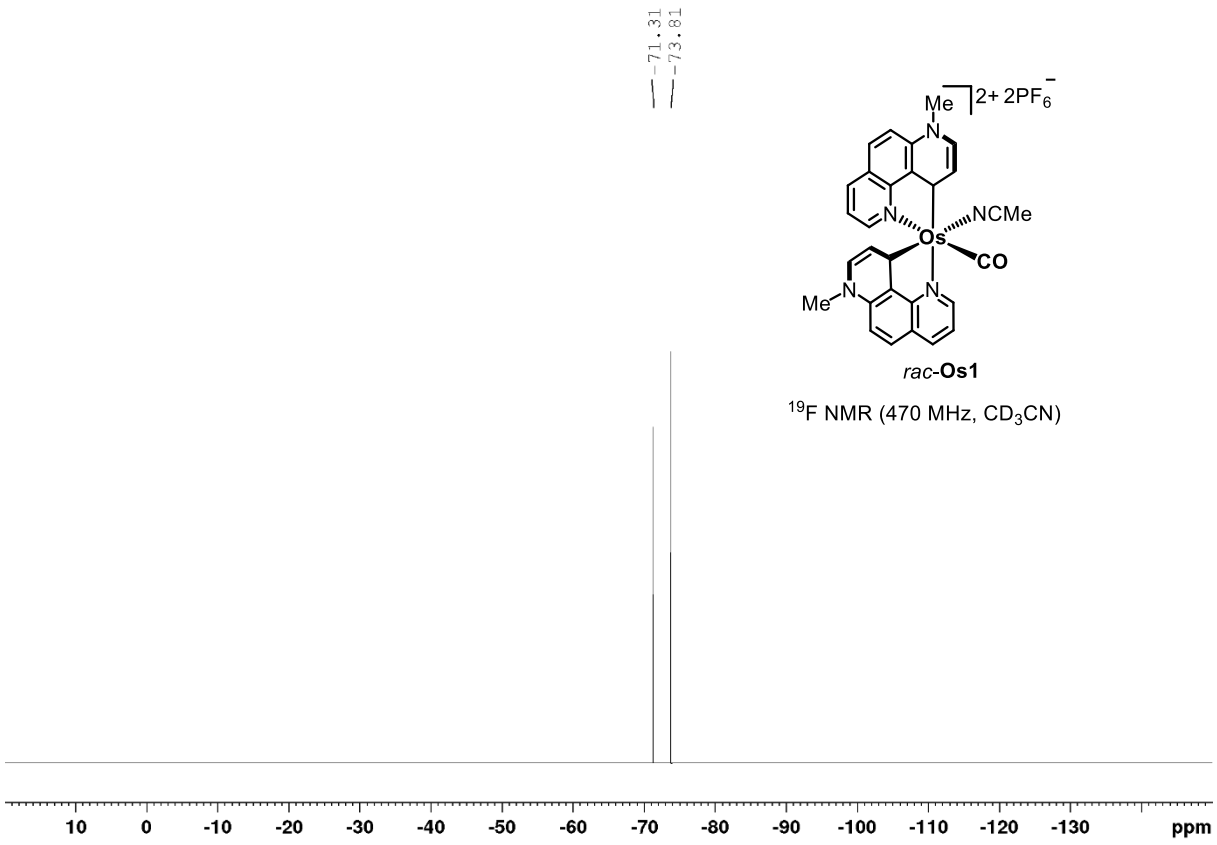
(*S*)-**2**

^{13}C NMR (75 MHz, CD_3CN)



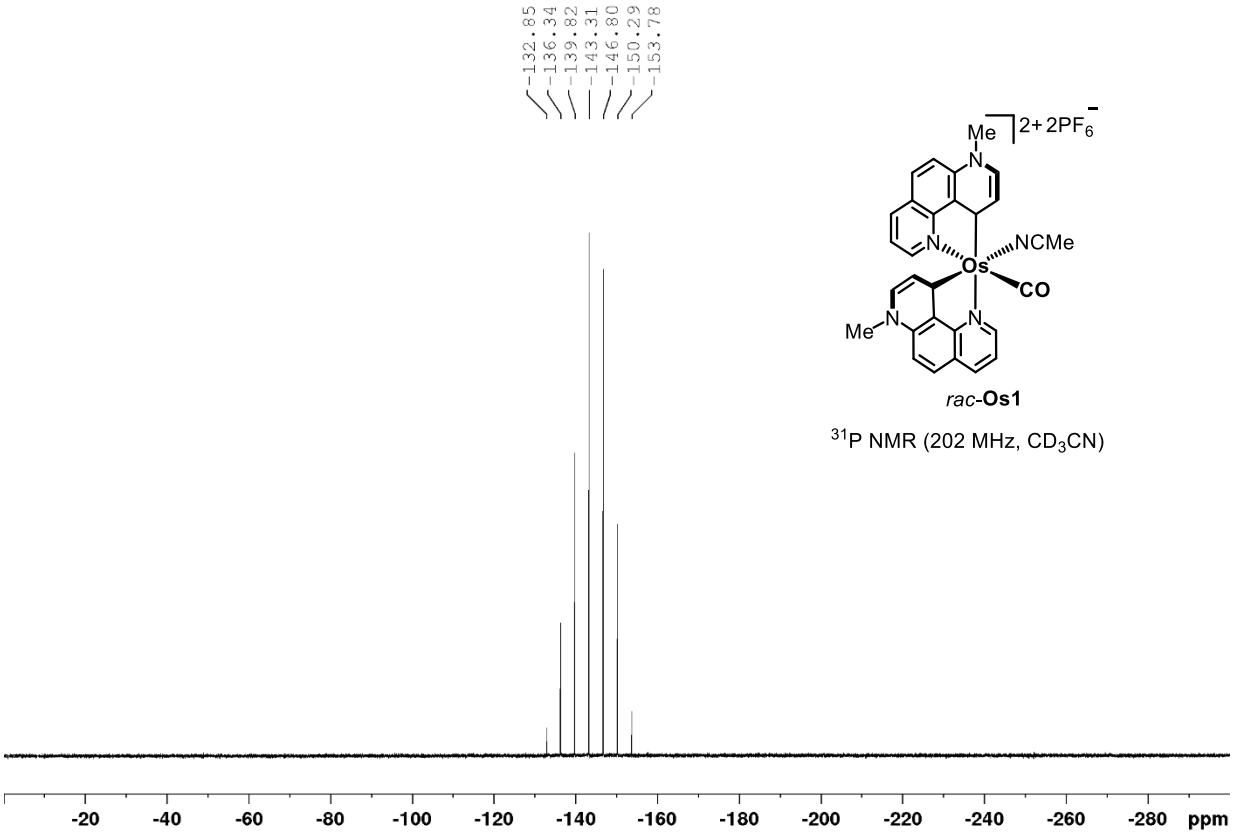

8.668 8.655 8.619 8.601 8.532 8.530 8.516 8.513 8.410 8.392 8.286 8.276 8.270 8.259 8.232 8.213 8.204 8.185 8.107 8.094 7.778 7.765 7.552 7.549 7.541 7.539 7.442 7.431 7.426 7.415 7.167 7.154 4.306 4.142
2.343 2.192 1.964 1.950 1.945 1.940 1.935 1.930
9.692 9.690 9.682 9.679 8.996 8.993 8.979 8.977 8.668 8.655 8.619 8.601 8.530 8.516 8.513 8.410 8.392 8.286 8.276 8.270 8.259 8.232 8.213 8.204 8.185 8.107 8.094 7.778 7.765 7.549 7.541 7.539 7.442 7.431 7.426 7.415 7.167 7.154
1.00 1.03 1.02 1.04 1.04 1.04 1.06 1.01 1.02 1.03 1.01 1.06 1.05 1.05
9.5 9.0 8.5 8.0 7.5 ppm
1.00 1.03 1.02 1.04 1.04 1.04 1.06 1.01 1.02 1.03 1.01 1.06 1.05 1.05 2.98 3.00 2.20
10 9 8 7 6 5 4 3 2 1 ppm
Me 2+ 2PF6
N
NCMe
Os
CO
Me
N
rac-Os1
1H NMR (500 MHz, CD3CN)


208.52 197.50 181.44 154.28 153.67 153.47 151.78 143.18 142.53 141.34 141.18 140.26 139.91 137.90 137.69 134.92 133.70 133.53 133.37 128.57 127.85 127.20 126.89 125.00 120.20 119.98 118.35
44.36 43.62
4.49 1.82 1.65 1.49 1.32 1.16
Me 2+ 2PF6
N
NCMe
Os
CO
Me
N
rac-Os1
13C NMR (125 MHz, CD3CN)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



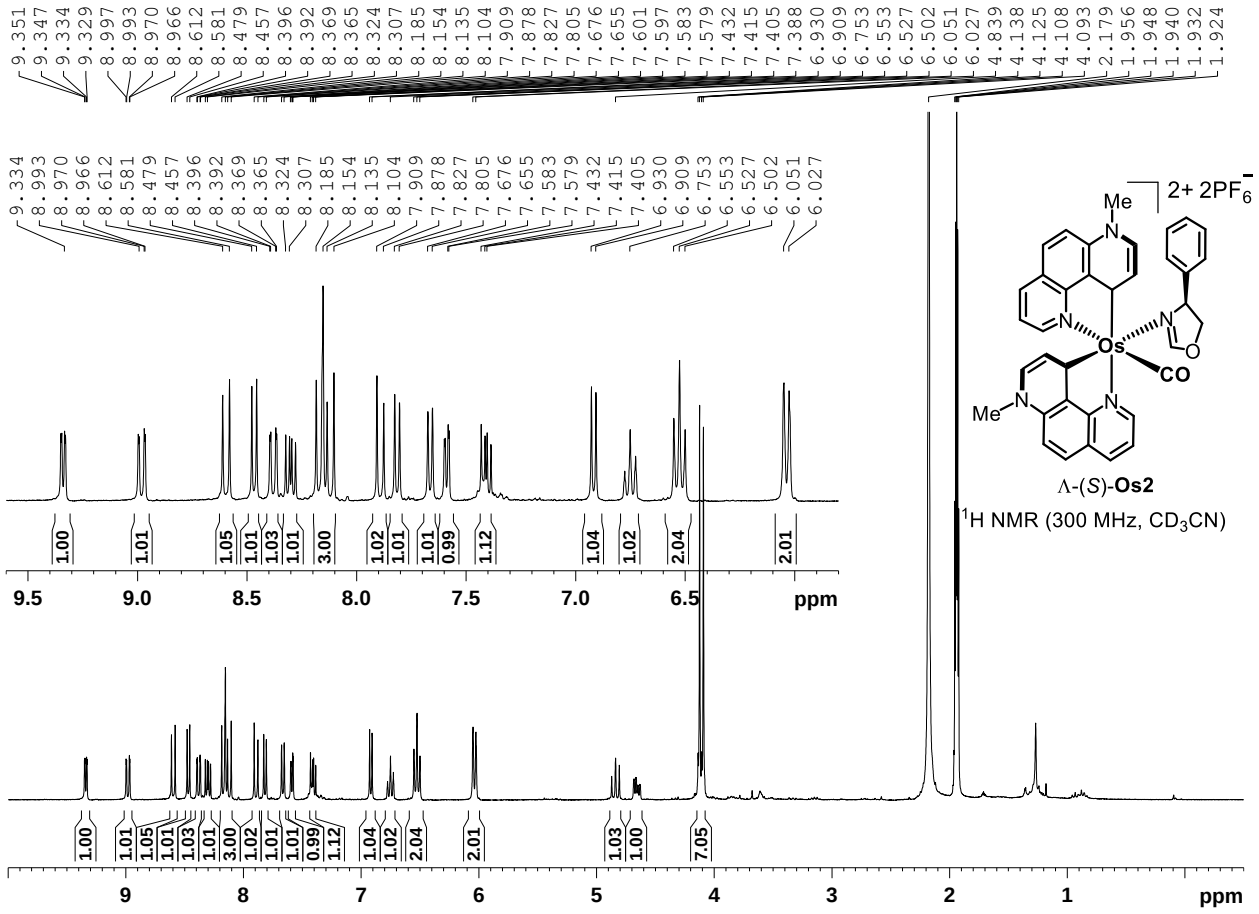
rac-**Os1**

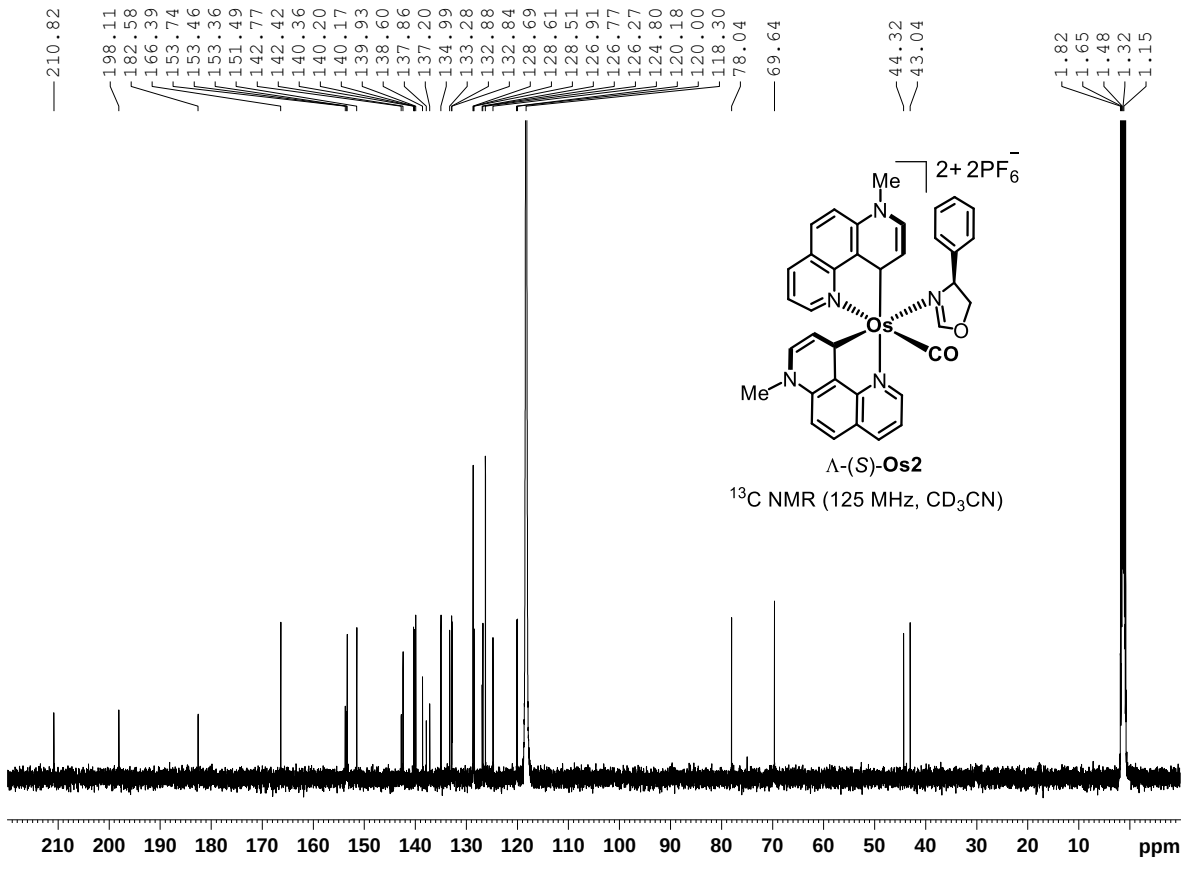
^{19}F NMR (470 MHz, CD_3CN)

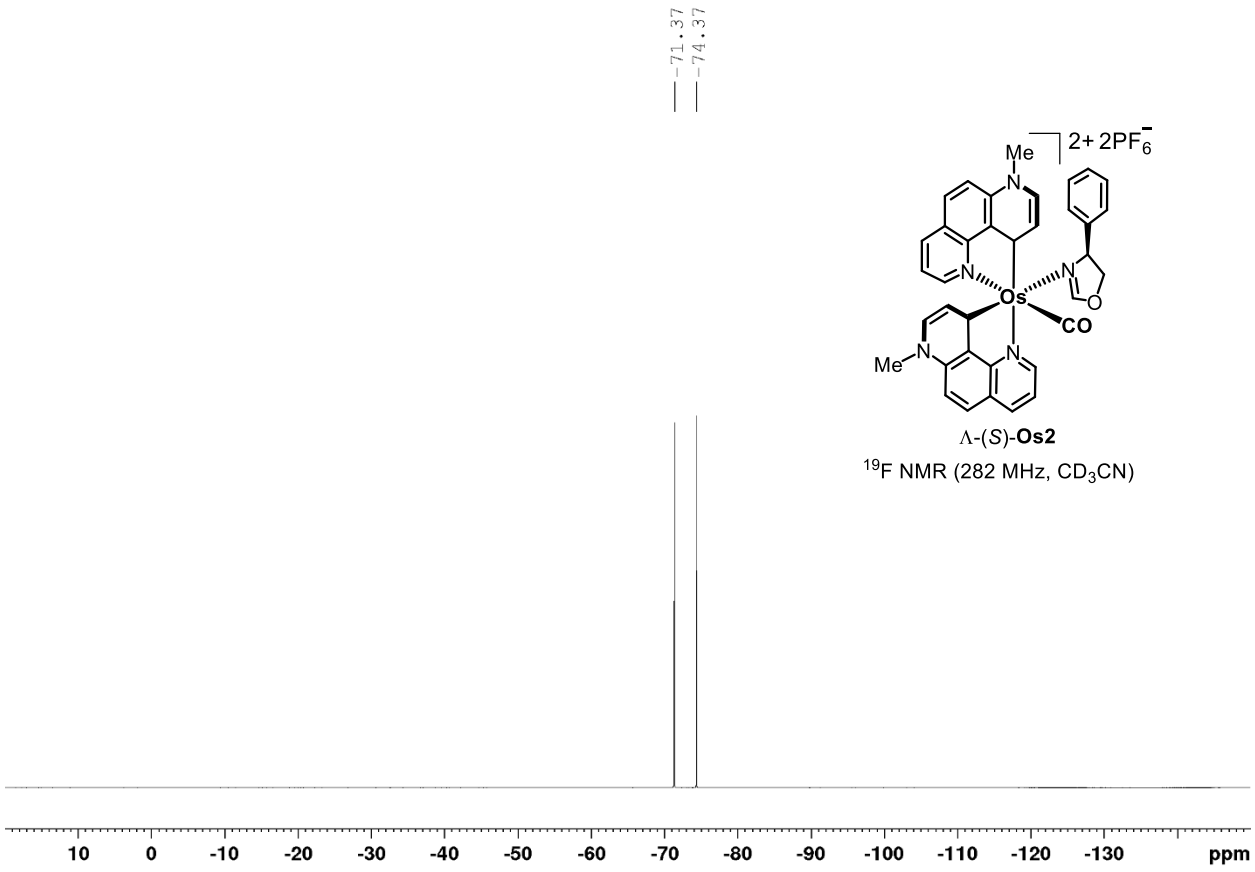


rac-**Os1**

^{31}P NMR (202 MHz, CD_3CN)

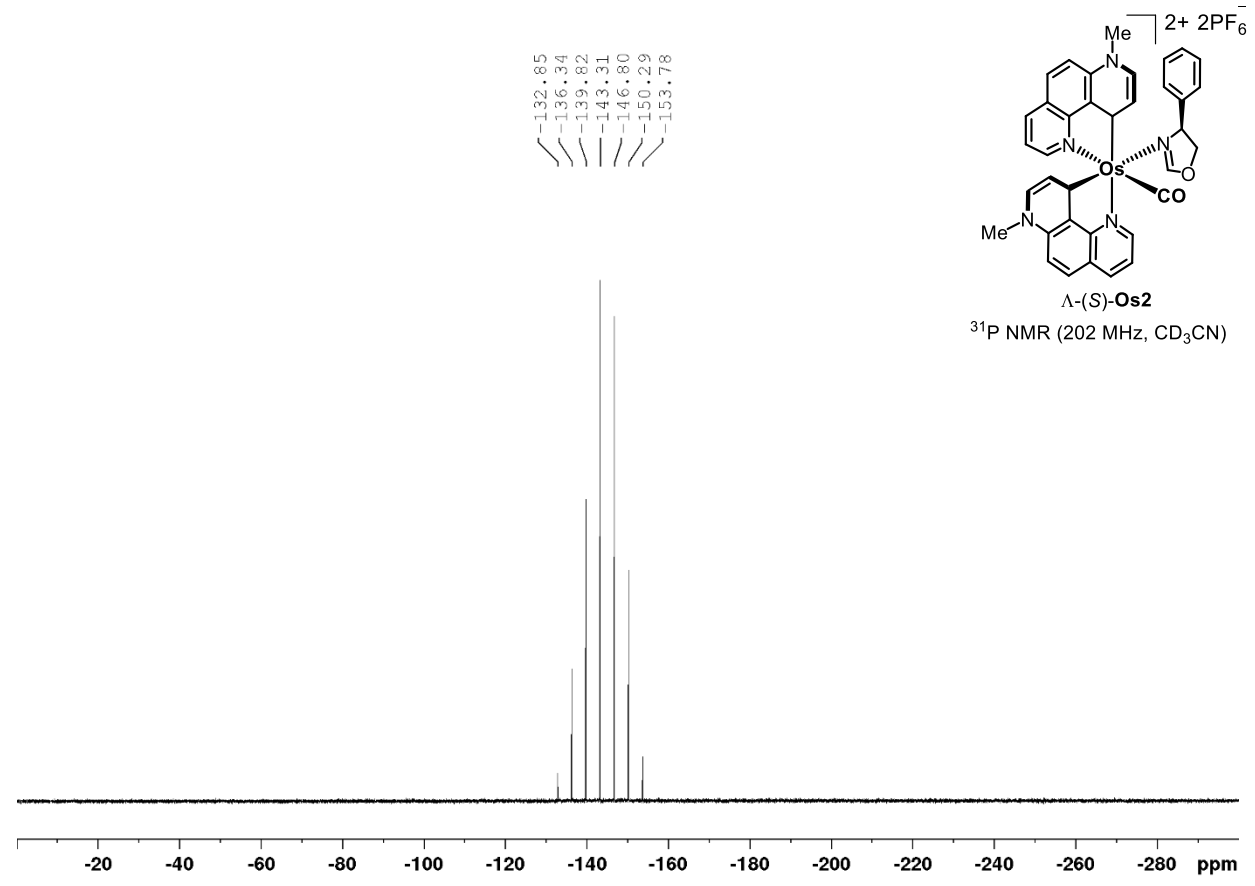

2+ 2PF6
Me
Os
CO
Λ-(S)-Os2
1H NMR (300 MHz, CD3CN)
ppm


2+ 2PF6
Me
Os
CO
Λ-(S)-Os2
13C NMR (125 MHz, CD3CN)
ppm



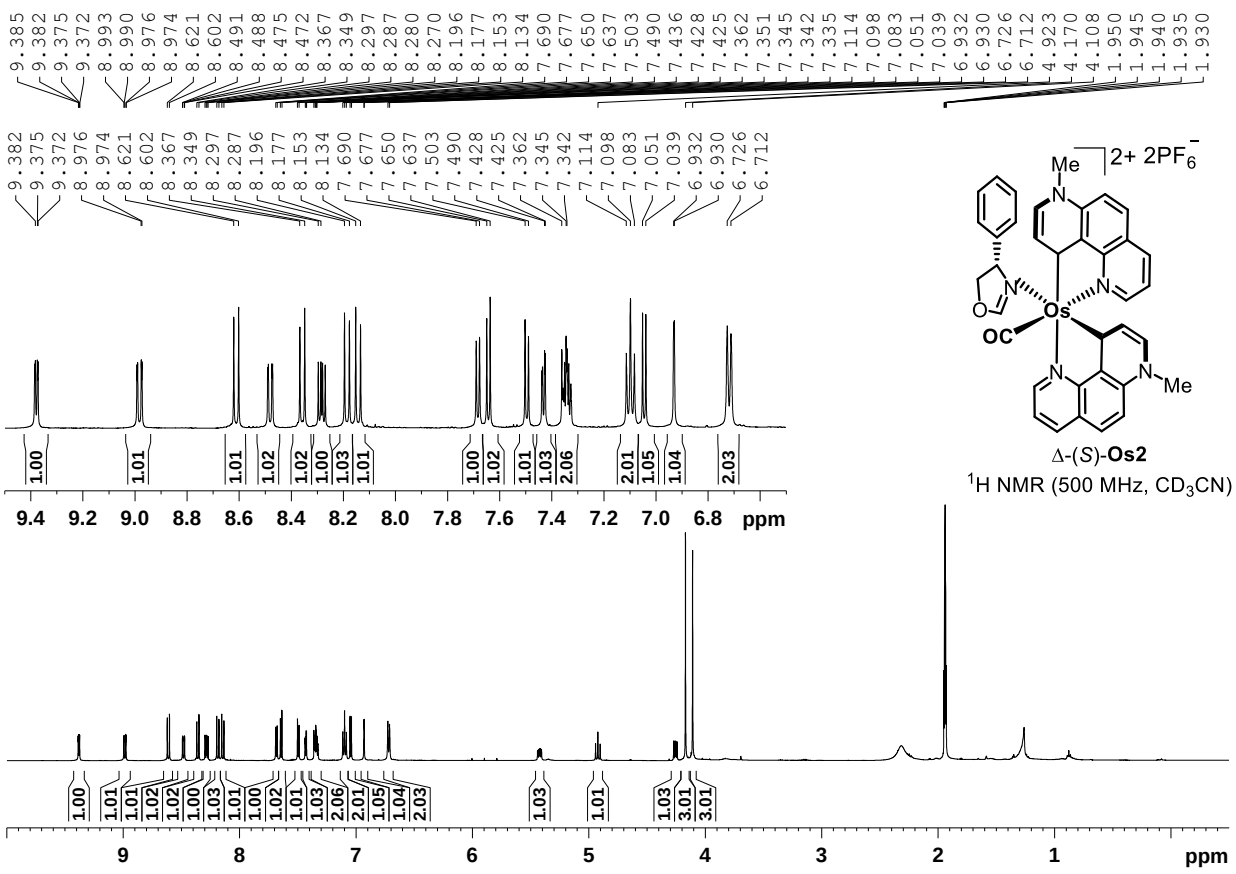
Λ-(*S*)-**Os2**

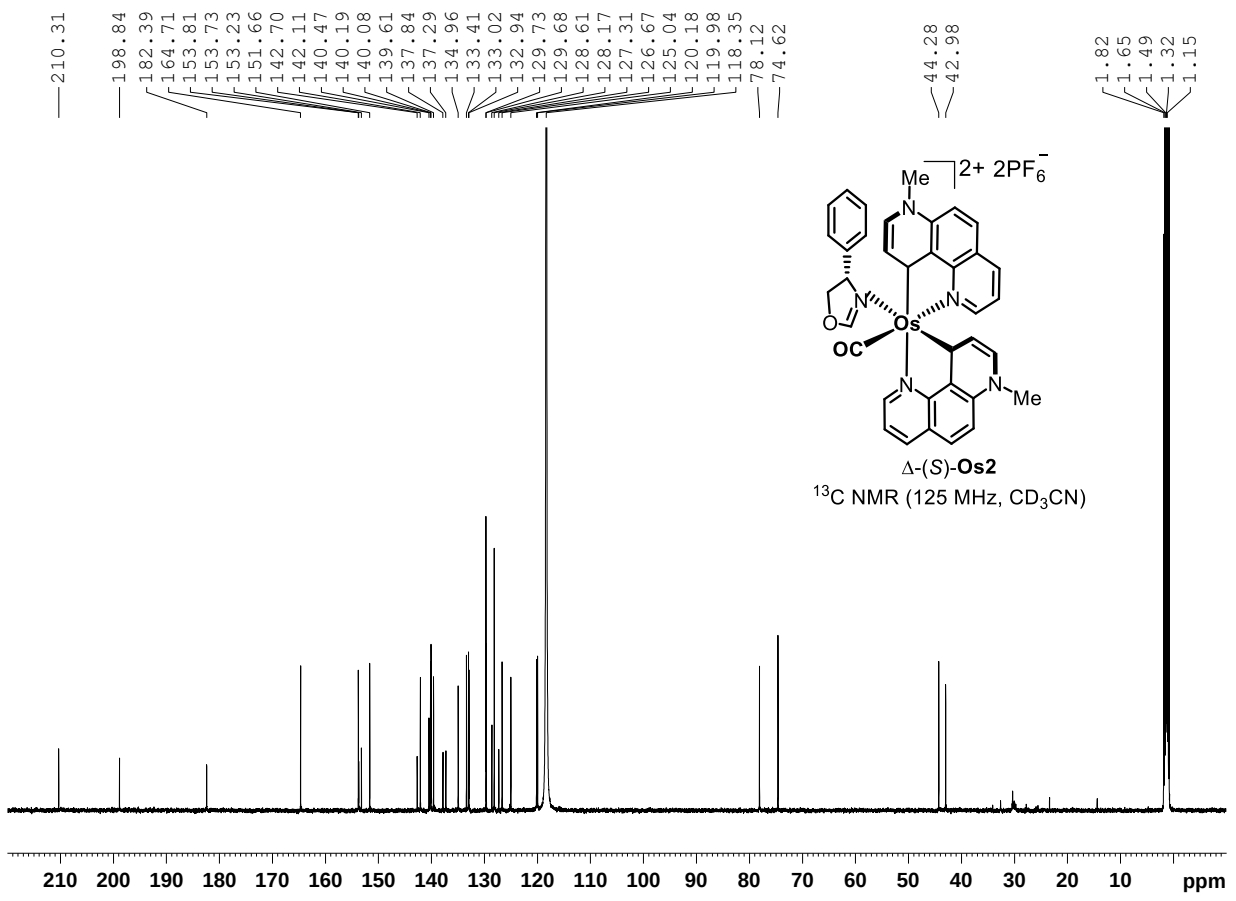
^{19}F NMR (282 MHz, CD_3CN)

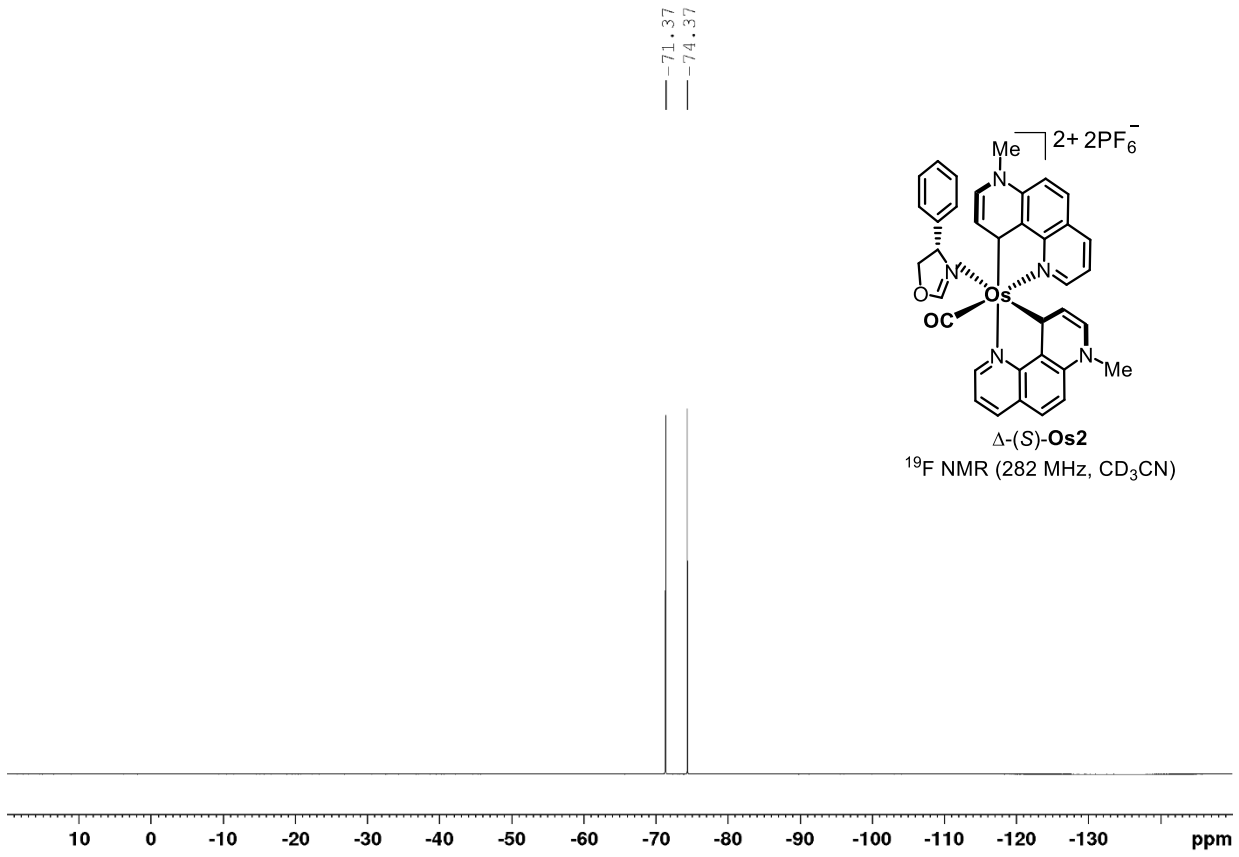


Λ-(*S*)-**Os2**

^{31}P NMR (202 MHz, CD_3CN)

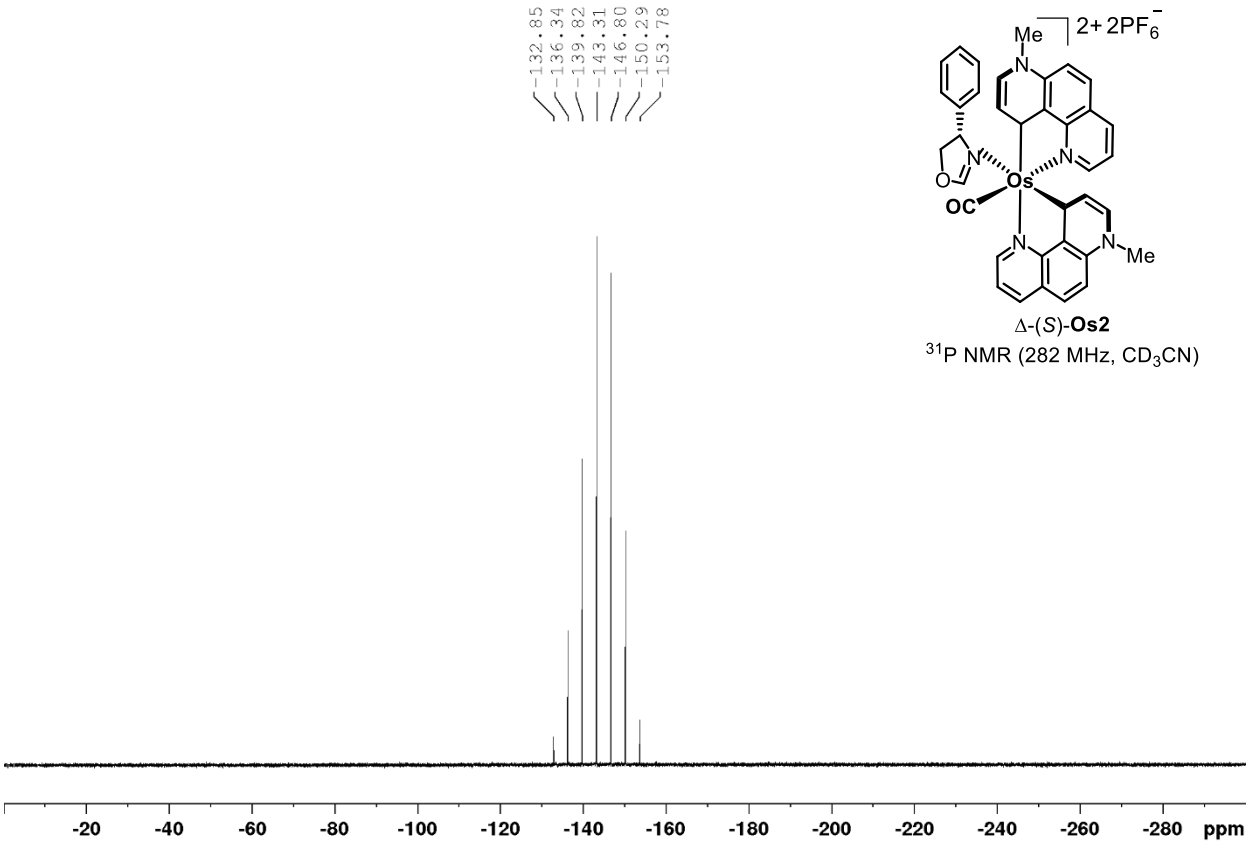

9.385 9.382 9.375 9.372 8.993 8.990 8.976 8.974 8.621 8.602 8.491 8.488 8.475 8.472 8.367 8.349 8.297 8.287 8.280 8.270 8.196 8.177 8.153 8.134 7.690 7.677 7.650 7.637 7.503 7.490 7.436 7.428 7.425 7.362 7.351 7.345 7.342 7.335 7.114 7.098 7.083 7.051 7.039 6.932 6.930 6.726 6.712 4.923 4.170 4.108 1.950 1.945 1.940 1.935 1.930
1.00 1.01 1.01 1.02 1.02 1.00 1.03 1.01 1.00 1.02 1.01 1.03 2.06 2.01 1.05 1.04 2.03
9 8 7 6 5 4 3 2 1 ppm
Me
2+ 2PF6−
N
O
Os
OC
N
N
N
Me
Δ-(S)-Os2
1H NMR (500 MHz, CD3CN)


210.31 198.84 182.39 164.71 153.81 153.73 153.23 151.66 142.70 142.11 140.47 140.19 140.08 139.61 137.84 137.29 134.96 133.41 133.02 132.94 129.73 129.68 128.61 128.17 127.31 126.67 125.04 120.18 119.98 118.35 78.12 74.62
44.28 42.98
1.82 1.65 1.49 1.32 1.15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
Me
2+ 2PF6−
N
O
Os
OC
N
N
N
Me
Δ-(S)-Os2
13C NMR (125 MHz, CD3CN)



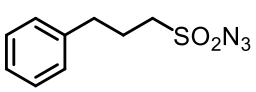
Δ-(*S*)-**Os2**

^{19}F NMR (282 MHz, CD_3CN)



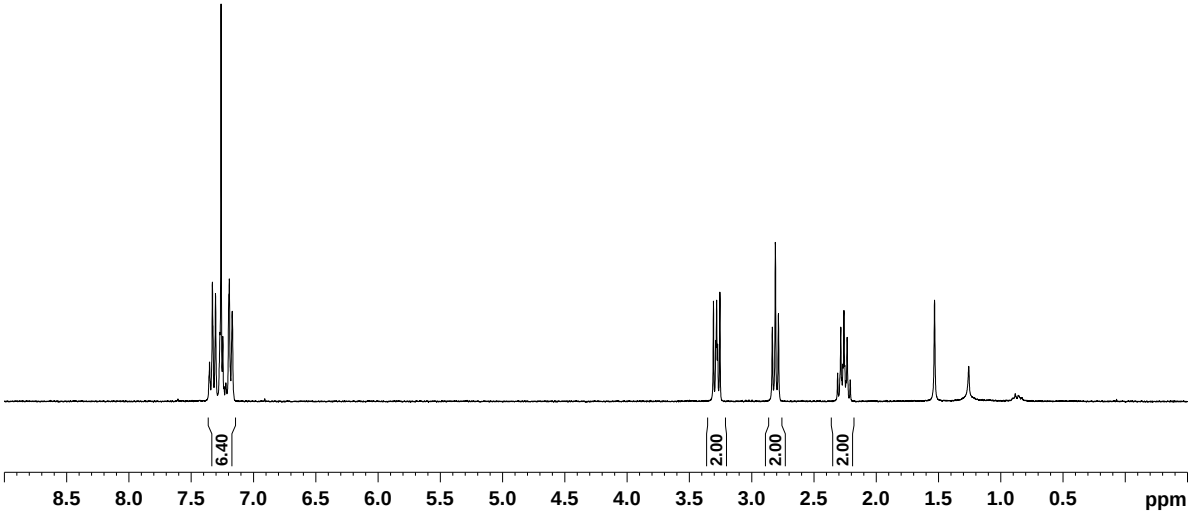
Δ-(*S*)-**Os2**

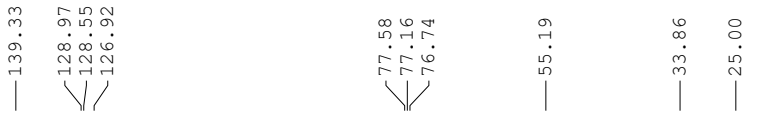
^{31}P NMR (282 MHz, CD_3CN)

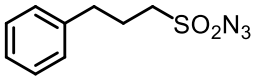


3a

^{1}H NMR (300 MHz, $CDCl_3$)

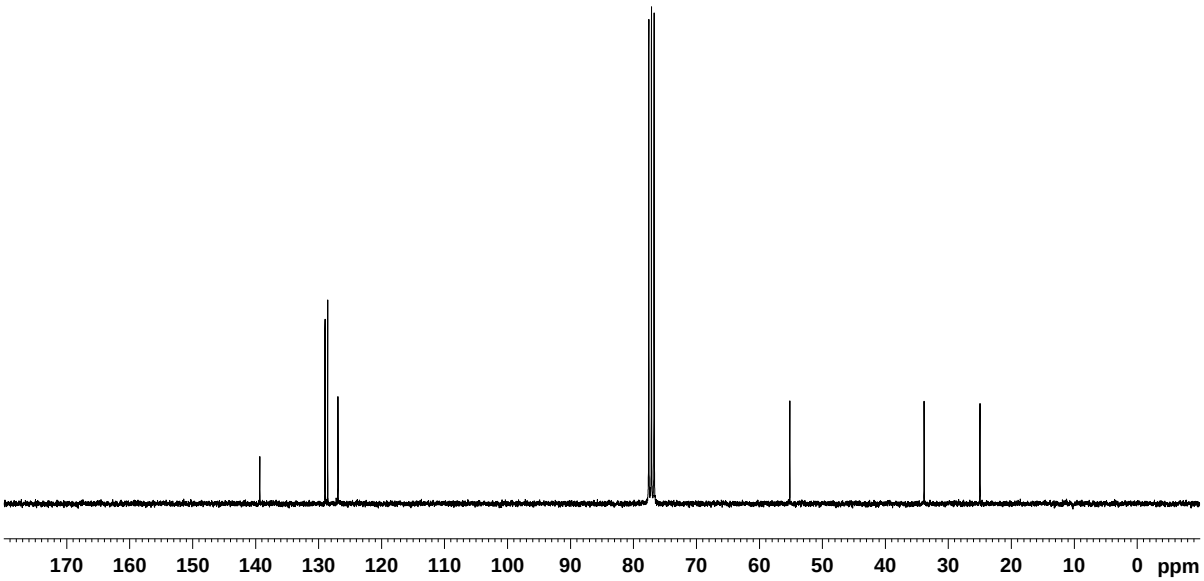


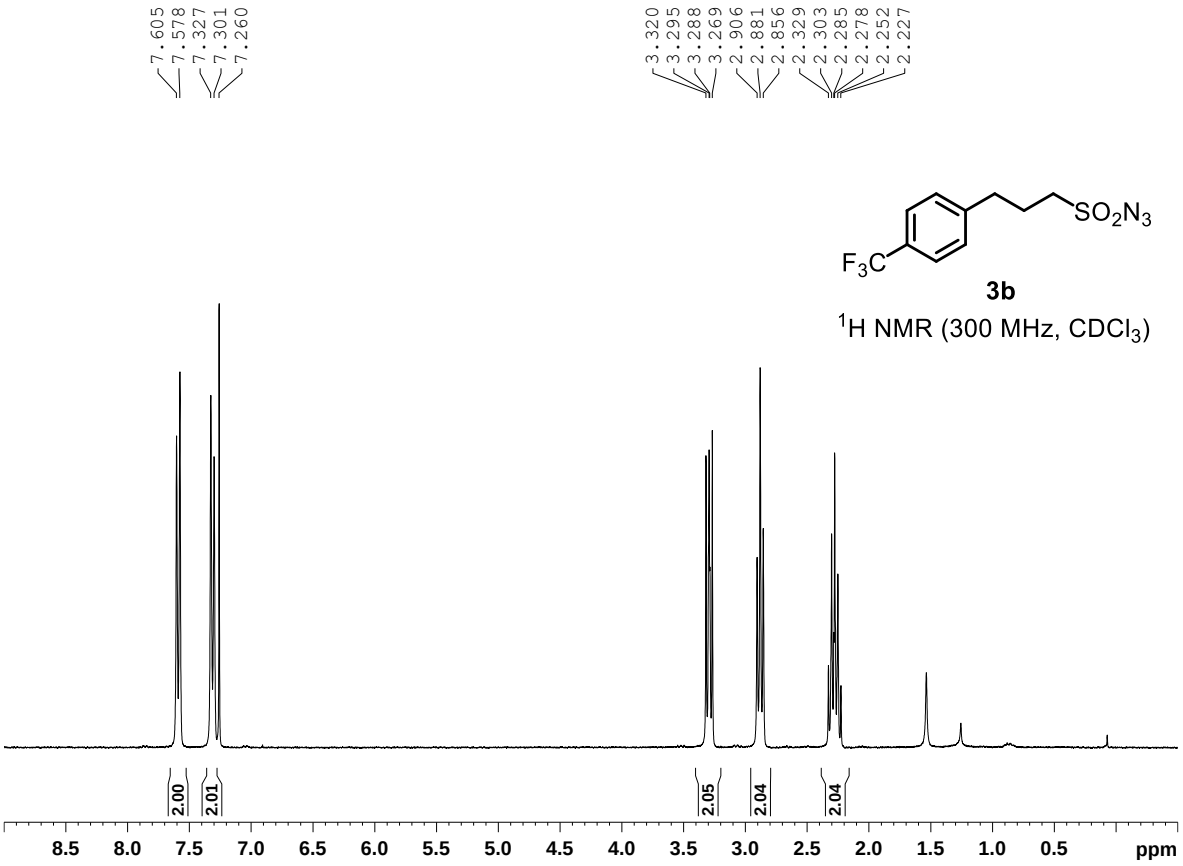


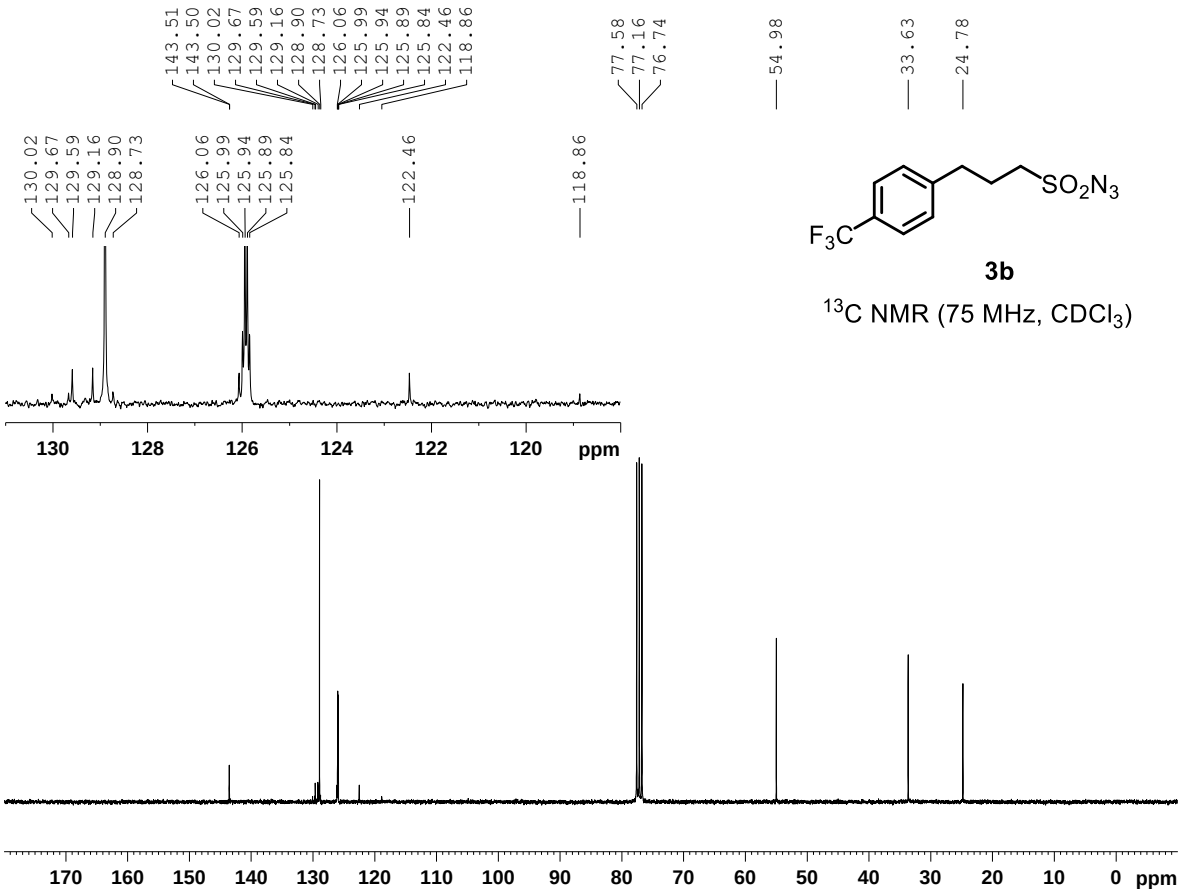


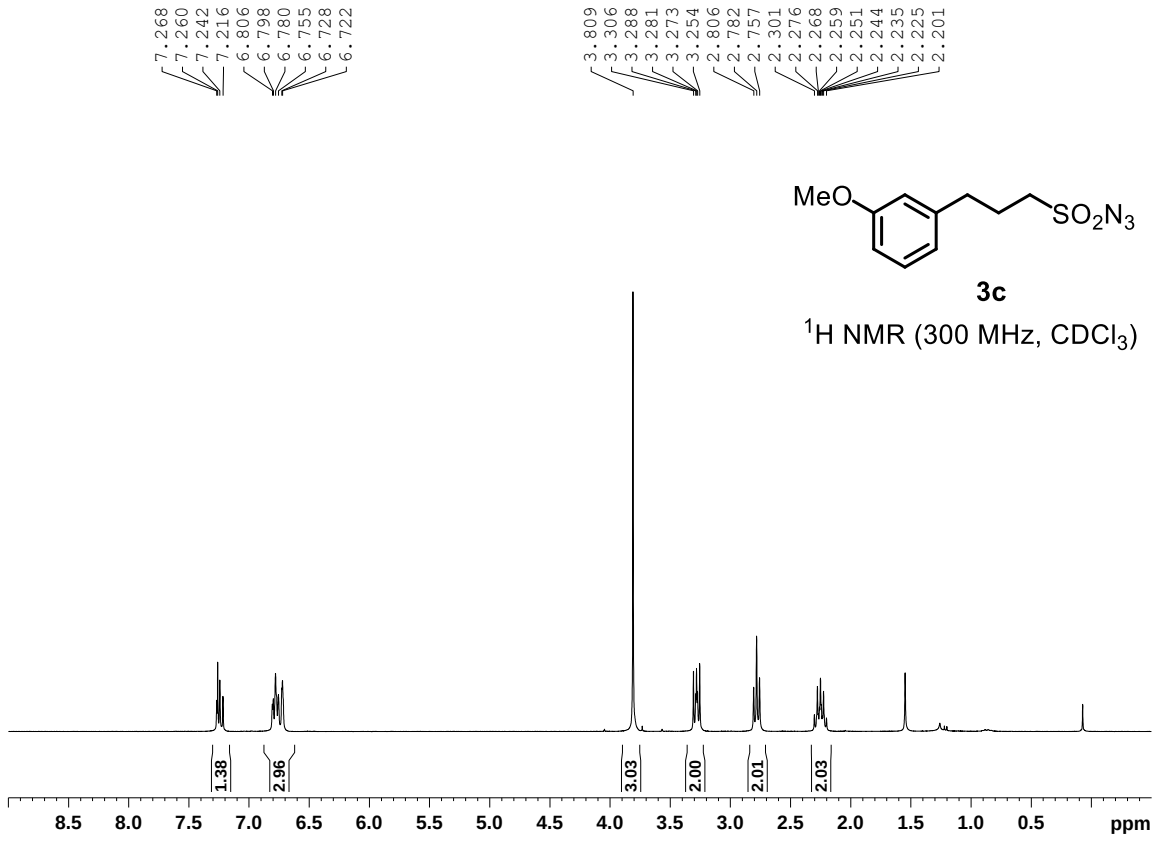
3a

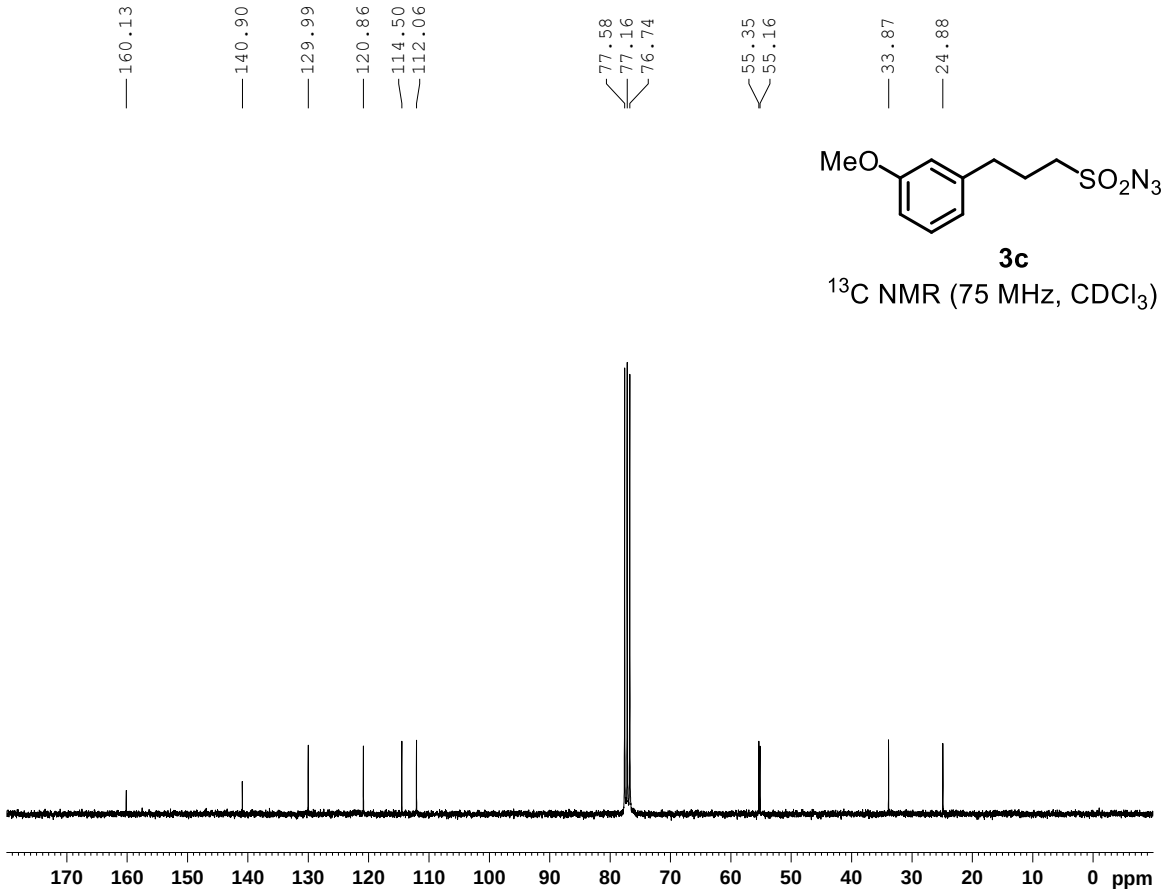
^{13}C NMR (75 MHz, $CDCl_3$)

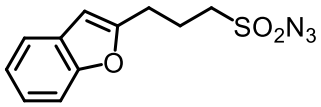



7.605
7.578
7.327
7.301
7.260
3.320
3.295
3.288
3.269
2.906
2.881
2.856
2.329
2.303
2.285
2.278
2.252
2.227
SO2N3
F3C
3b
1H NMR (300 MHz, CDCl3)
2.00
2.01
2.05
2.04
2.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


143.51
143.50
130.02
129.67
129.59
129.16
128.90
128.73
126.06
125.99
125.94
125.89
125.84
122.46
118.86
77.58
77.16
76.74
54.98
33.63
24.78
SO2N3
F3C
3b
13C NMR (75 MHz, CDCl3)
130 128 126 124 122 120 ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

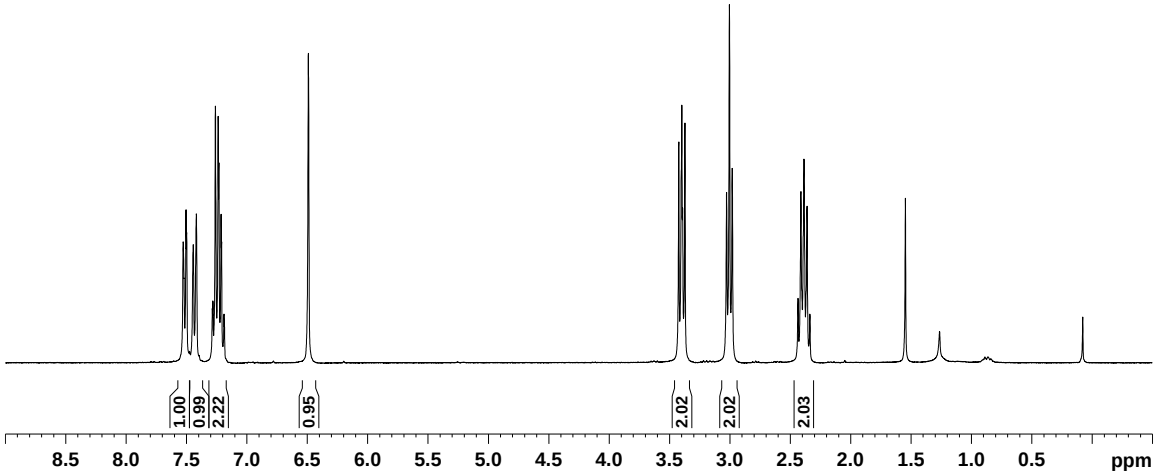

7.268
7.260
7.242
7.216
6.806
6.798
6.780
6.755
6.728
6.722
3.809
3.306
3.288
3.281
3.273
3.254
2.806
2.782
2.757
2.301
2.276
2.268
2.259
2.251
2.244
2.235
2.225
2.201
MeO
SO2N3
3c
1H NMR (300 MHz, CDCl3)
1.38
2.96
3.03
2.00
2.01
2.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

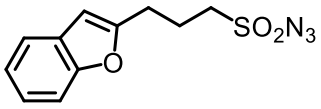

160.13
140.90
129.99
120.86
114.50
112.06
77.58
77.16
76.74
55.35
55.16
33.87
24.88
MeO
SO2N3
3c
13C NMR (75 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



3d

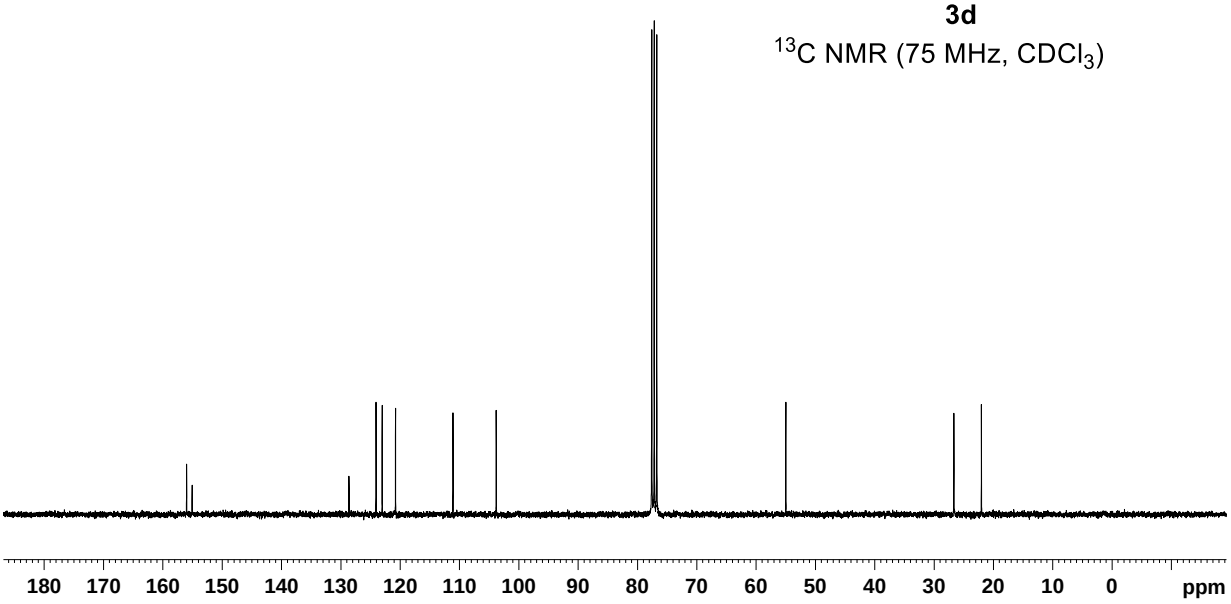
^{1}H NMR (300 MHz, $CDCl_3$)

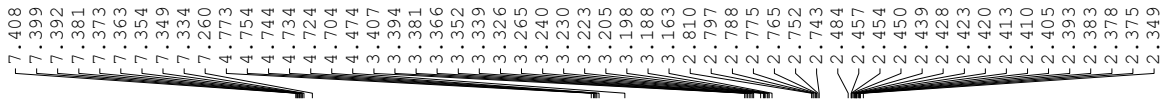


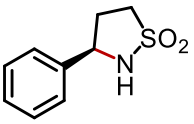


3d

^{13}C NMR (75 MHz, $CDCl_3$)

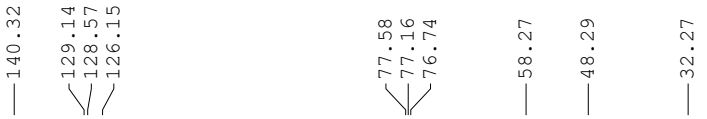


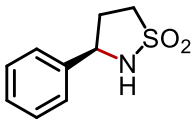




4a

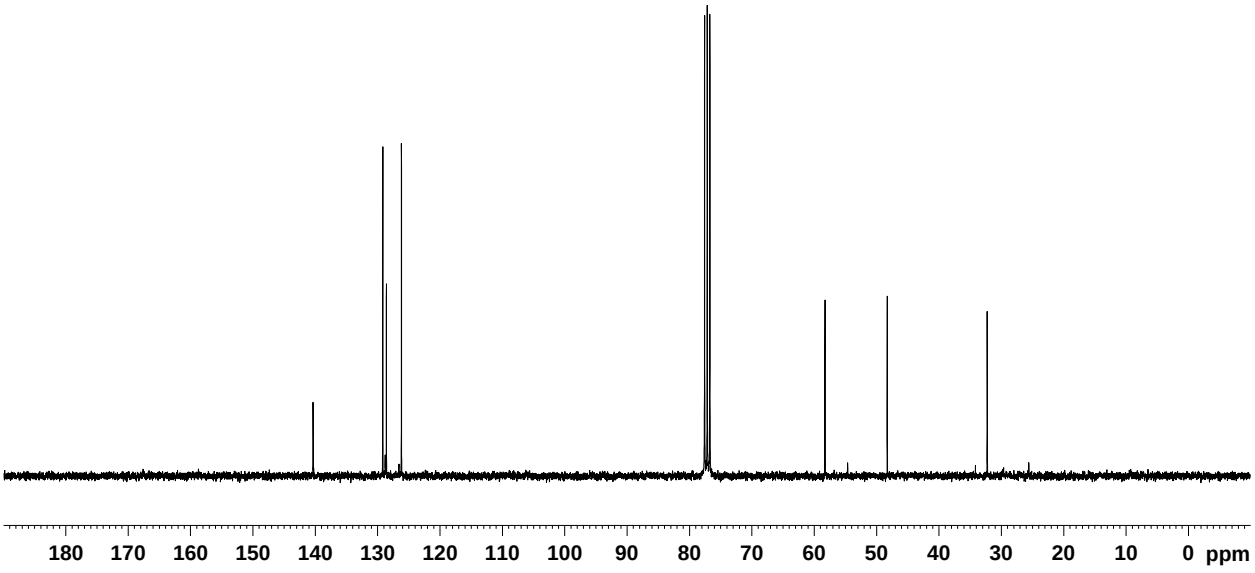
^{1}H NMR (300 MHz, $CDCl_3$)

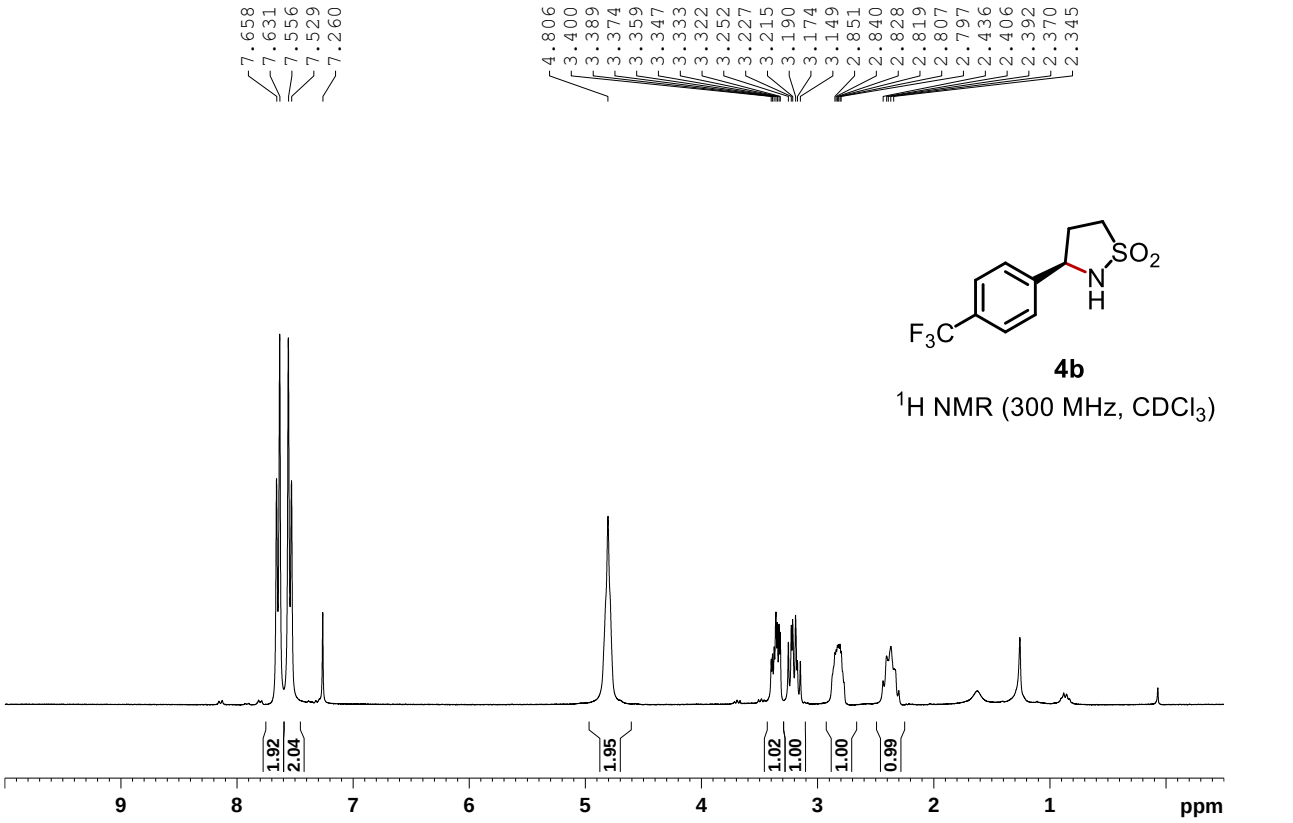




4a

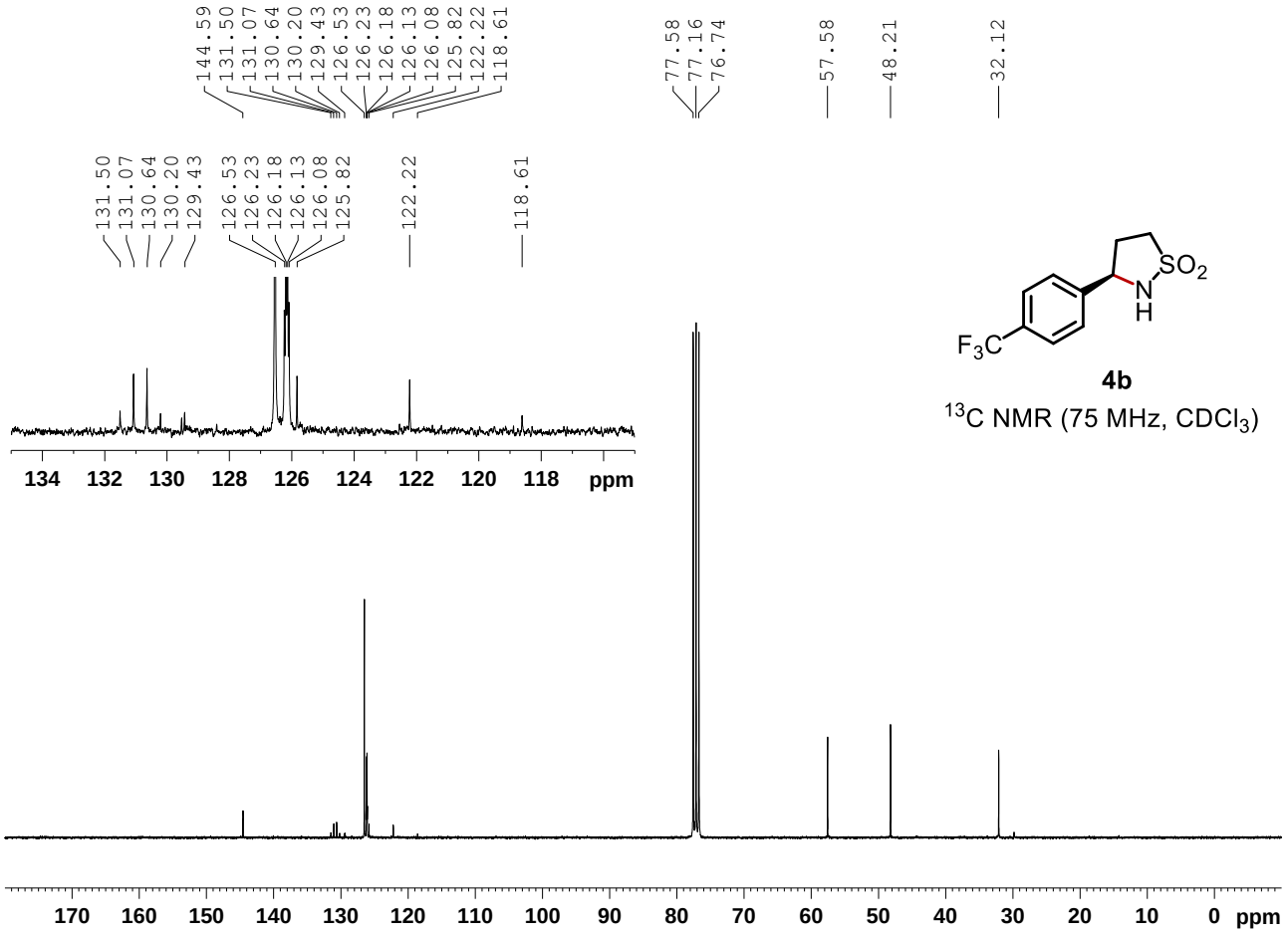
^{13}C NMR (75 MHz, $CDCl_3$)





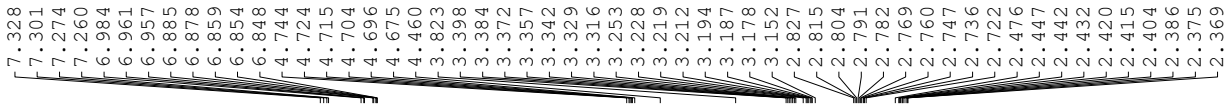
4b

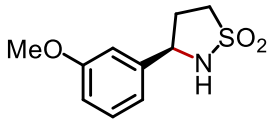
^{1}H NMR (300 MHz, $CDCl_3$)



4b

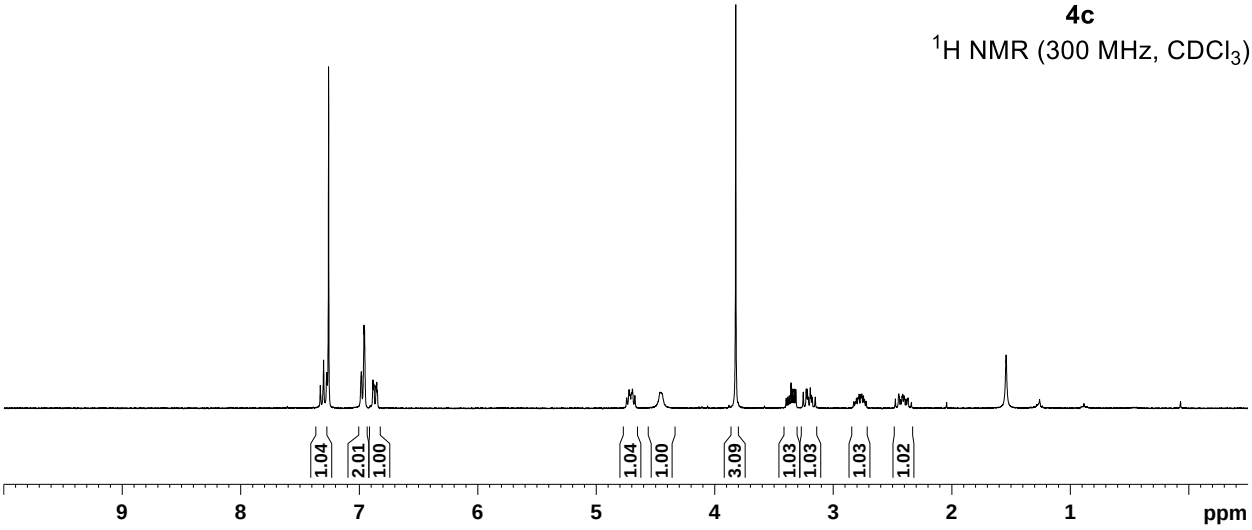
^{13}C NMR (75 MHz, $CDCl_3$)

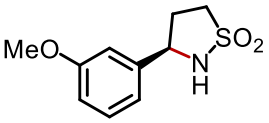




4c

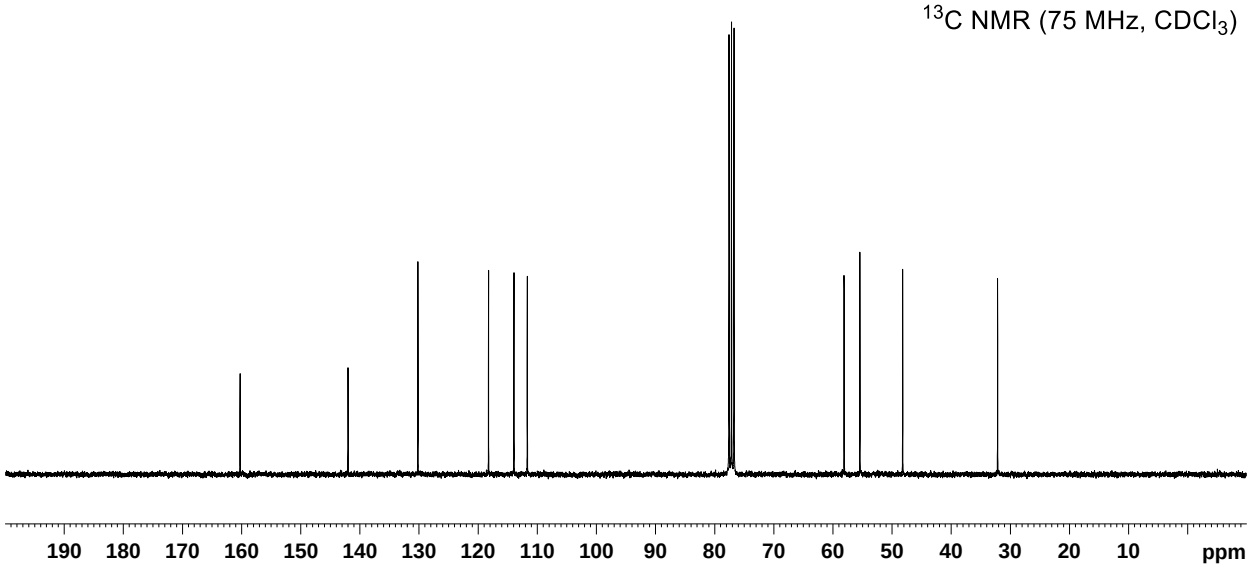
^{1}H NMR (300 MHz, $CDCl_3$)

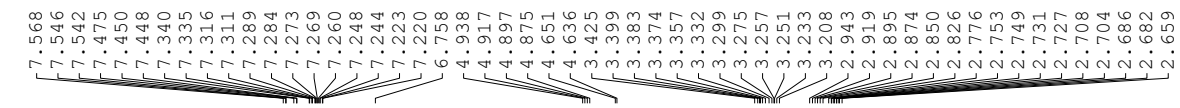


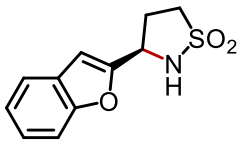


4c

^{13}C NMR (75 MHz, $CDCl_3$)

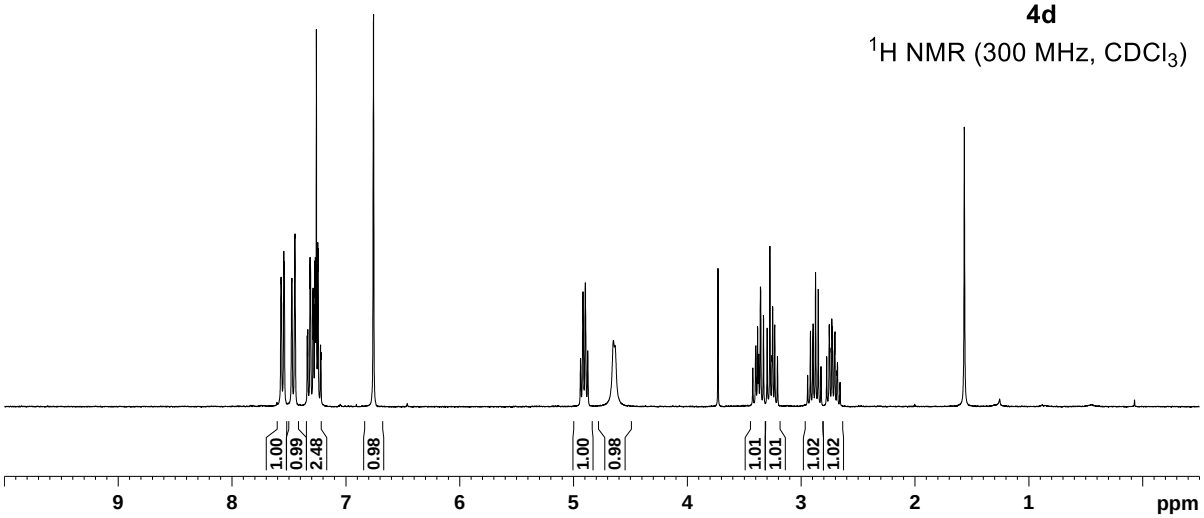


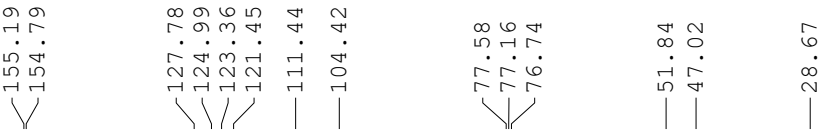


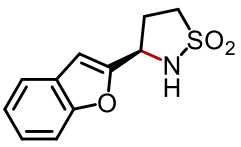


4d

^{1}H NMR (300 MHz, $CDCl_3$)

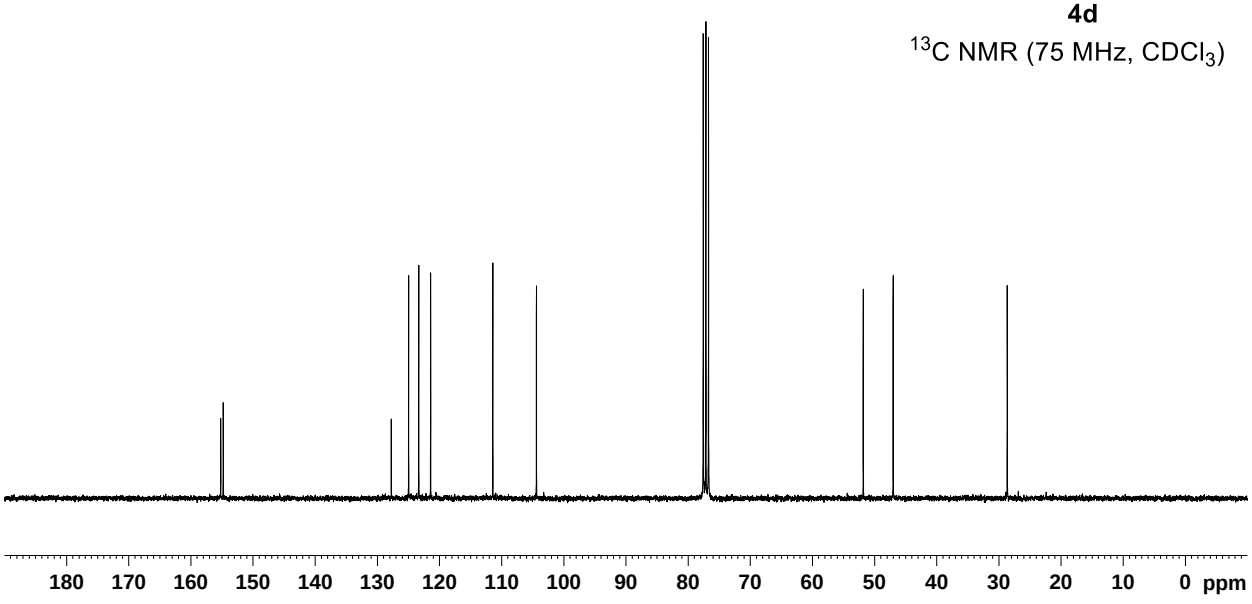


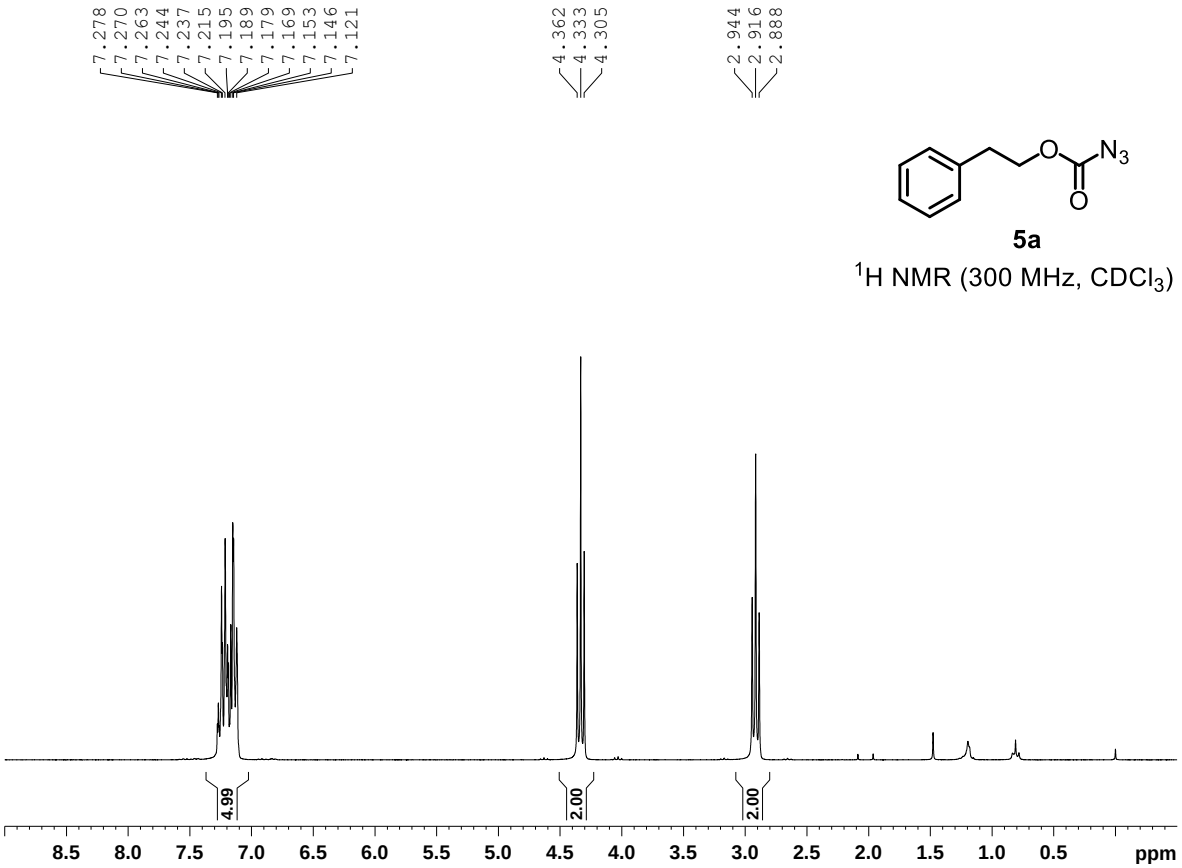


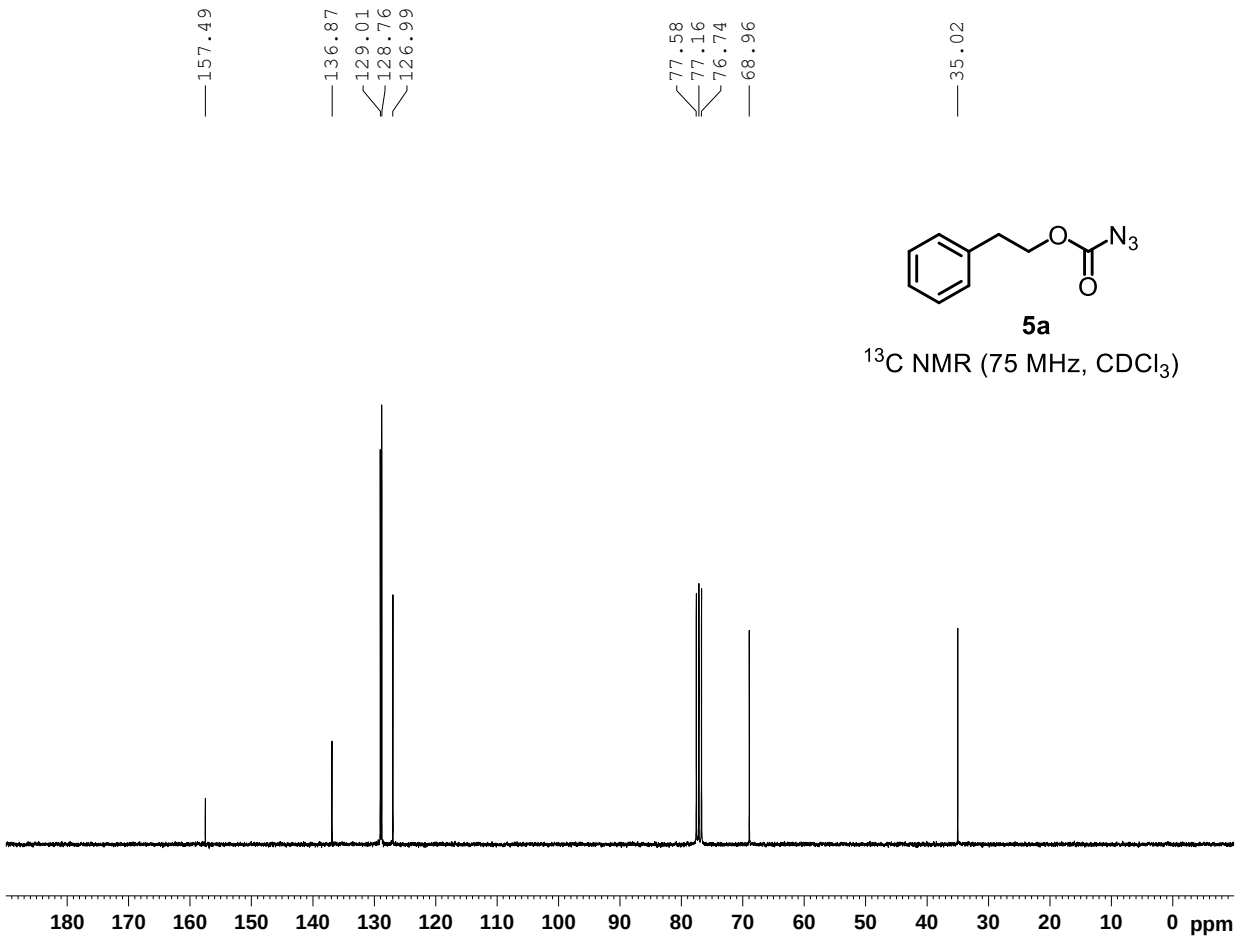


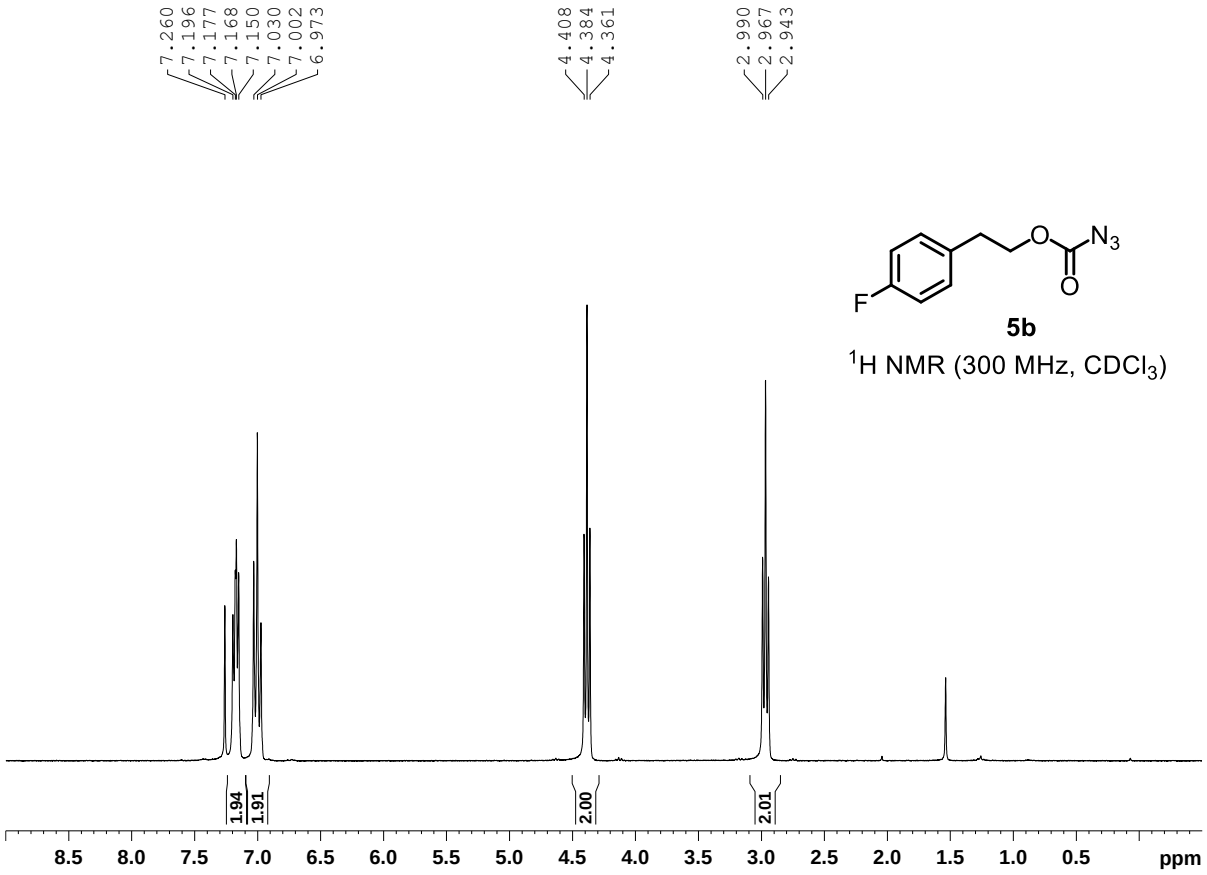
4d

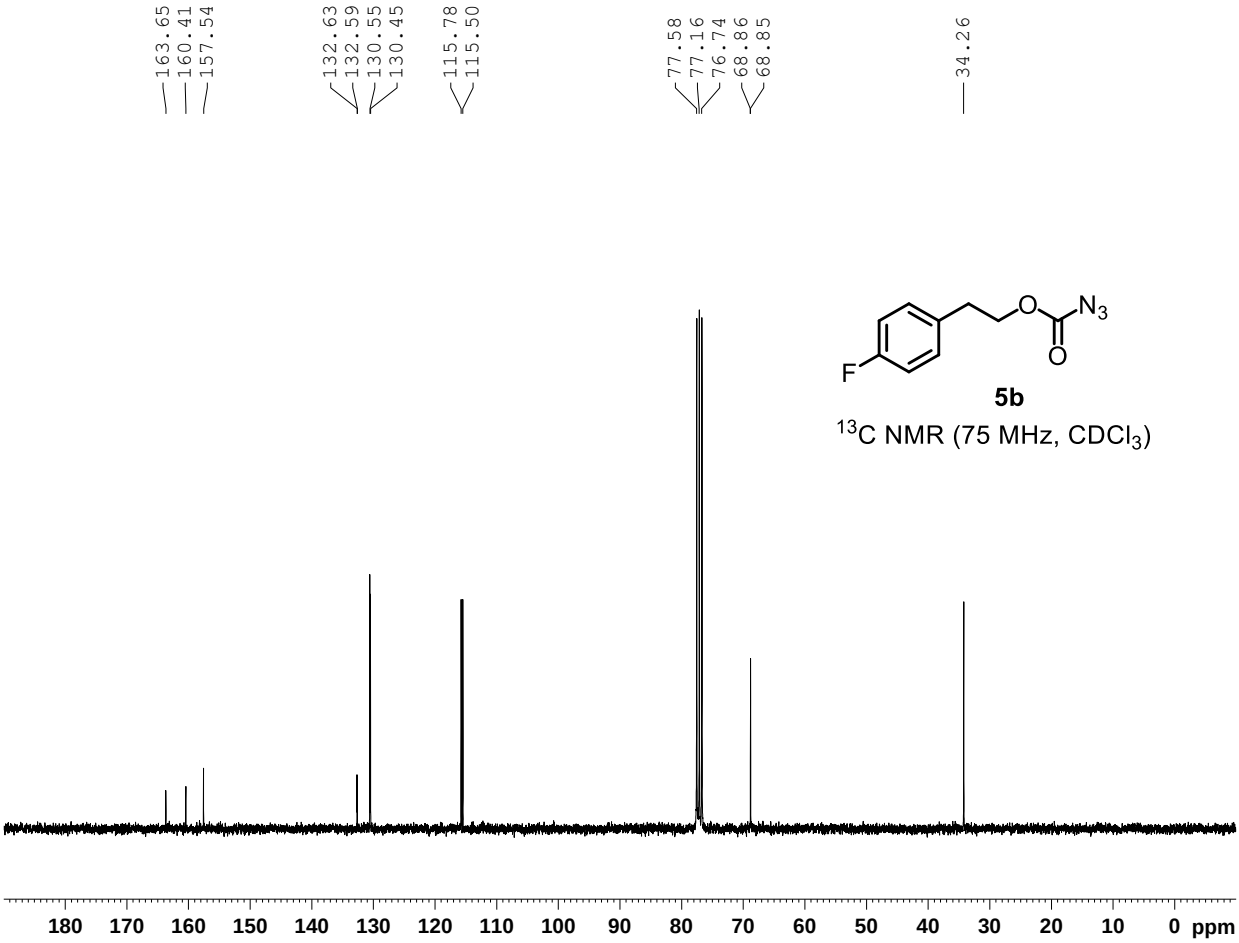
^{13}C NMR (75 MHz, $CDCl_3$)

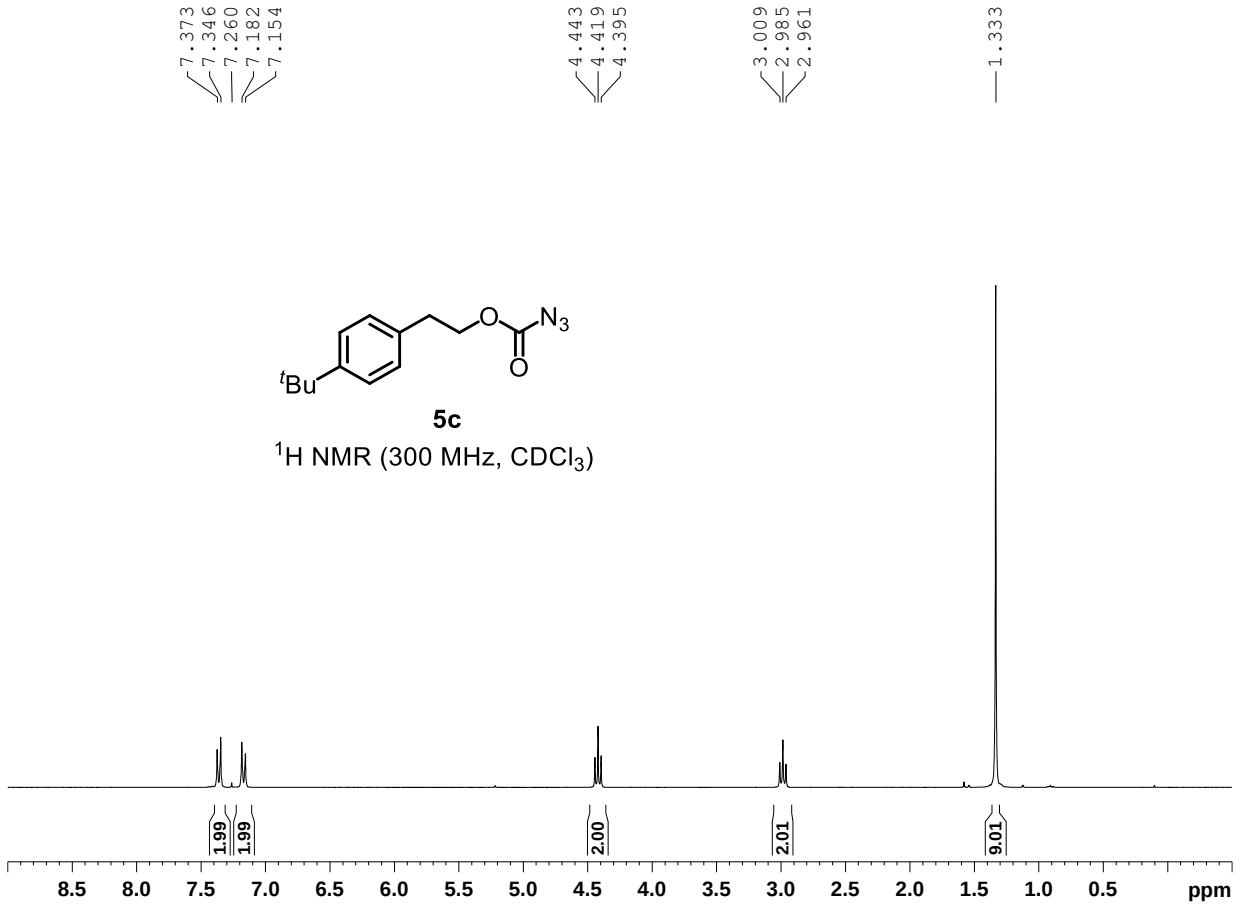



7.278
7.270
7.263
7.244
7.237
7.215
7.195
7.189
7.179
7.169
7.153
7.146
7.121
4.362
4.333
4.305
2.944
2.916
2.888
O
N3
O
5a
1H NMR (300 MHz, CDCl3)
4.99
2.00
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


157.49
136.87
129.01
128.76
126.99
77.58
77.16
76.74
68.96
35.02
O
N3
O
5a
13C NMR (75 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

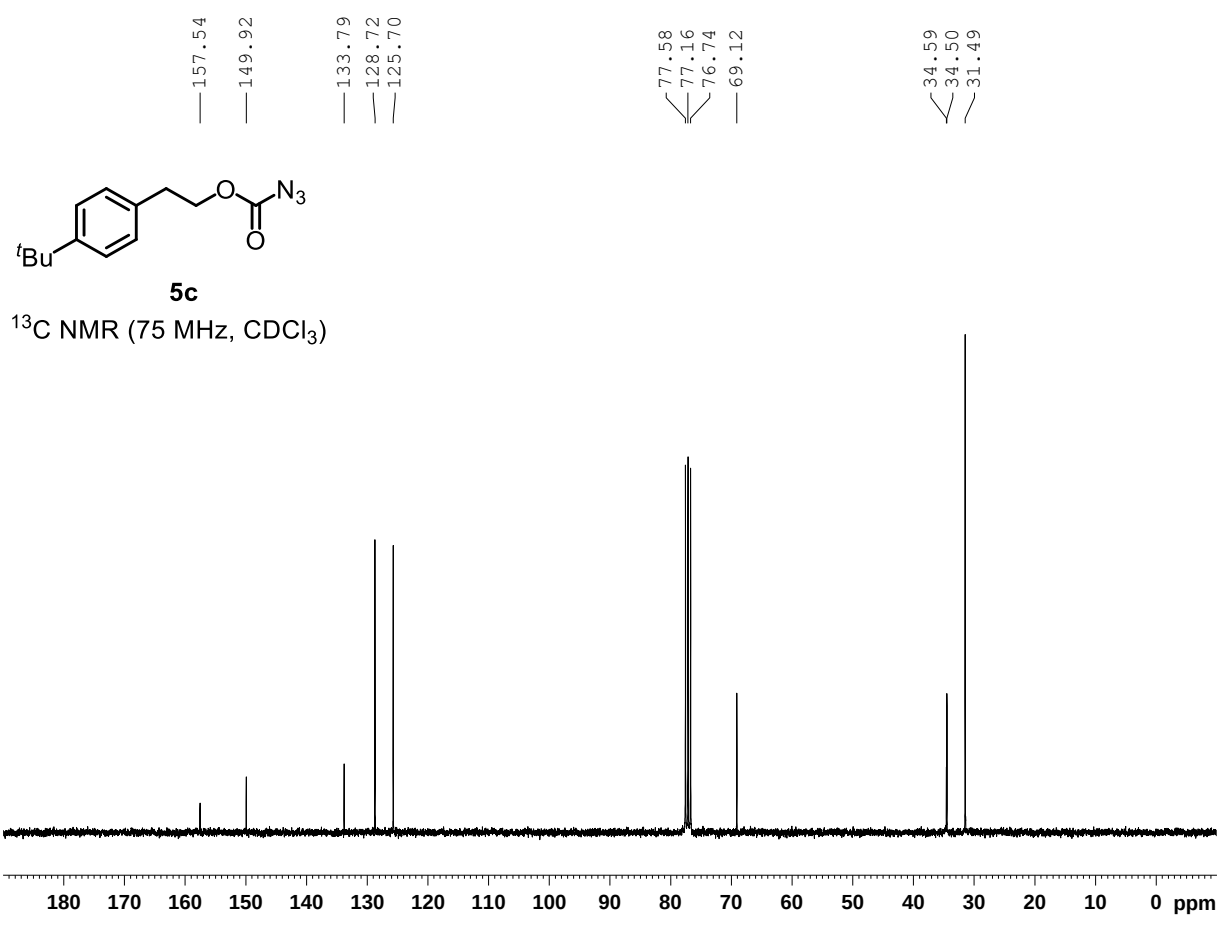

7.260
7.196
7.177
7.168
7.150
7.030
7.002
6.973
4.408
4.384
4.361
2.990
2.967
2.943
O
N3
O
F
5b
1H NMR (300 MHz, CDCl3)
1.94
1.91
2.00
2.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm


163.65
160.41
157.54
132.63
132.59
130.55
130.45
115.78
115.50
77.58
77.16
76.74
68.86
68.85
34.26
O
N3
O
F
5b
13C NMR (75 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



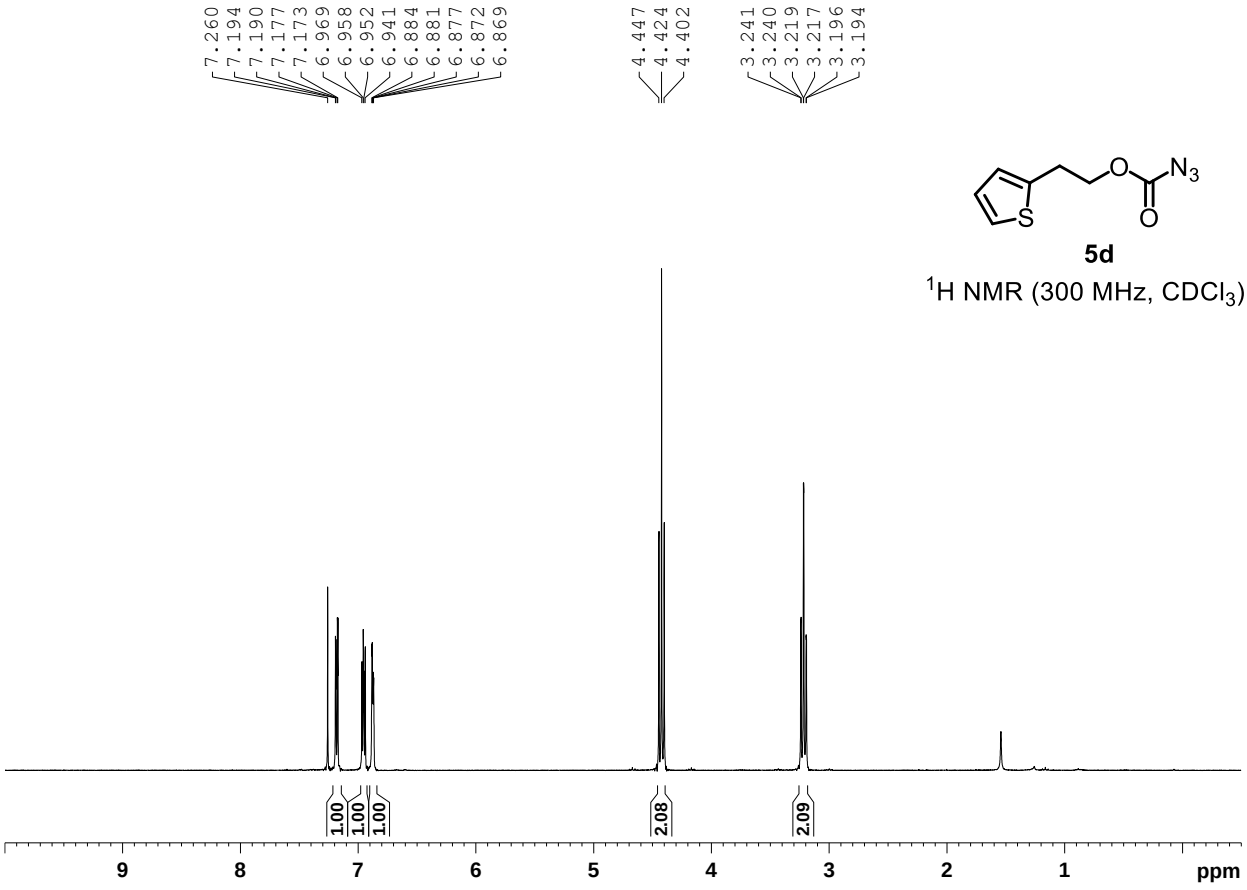
5c

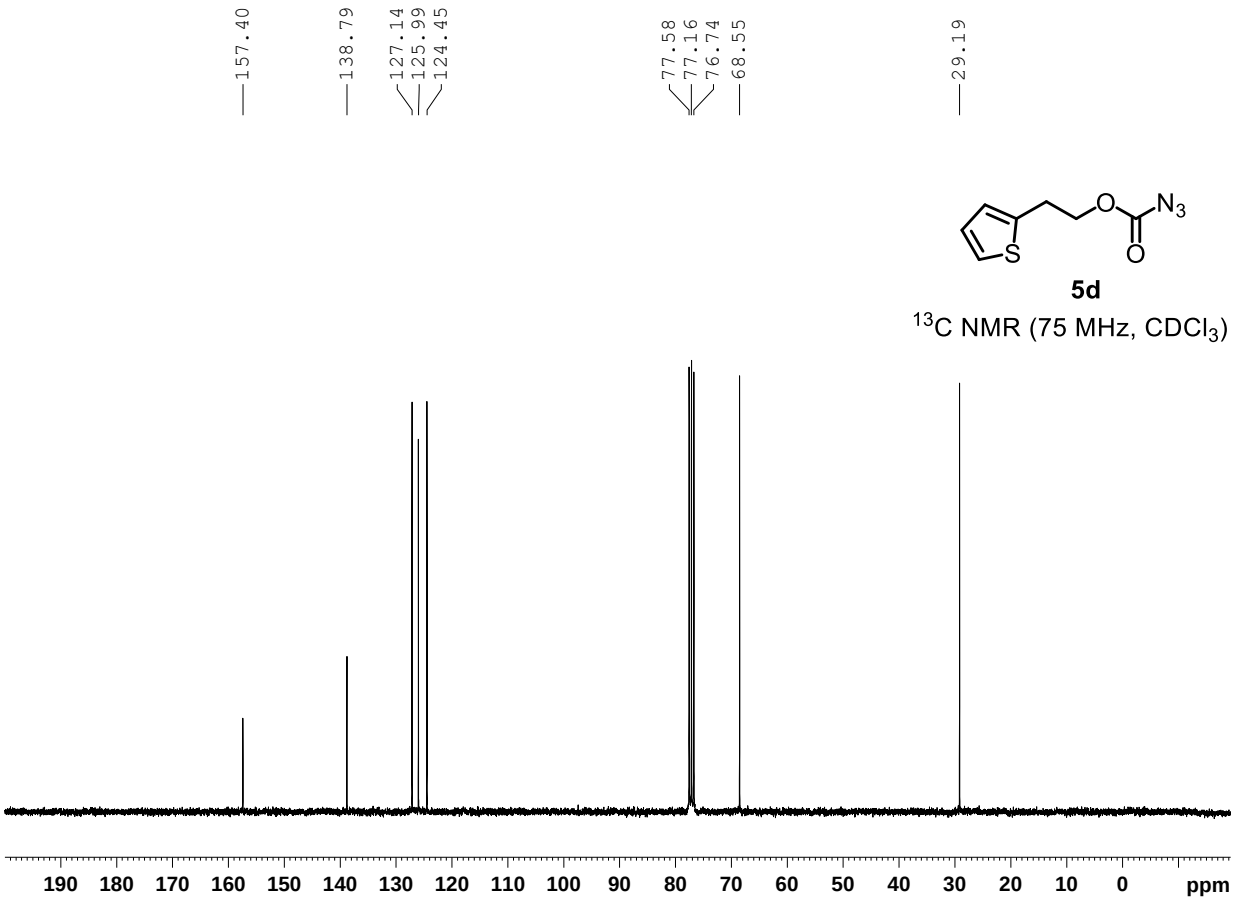
^{1}H NMR (300 MHz, $CDCl_3$)

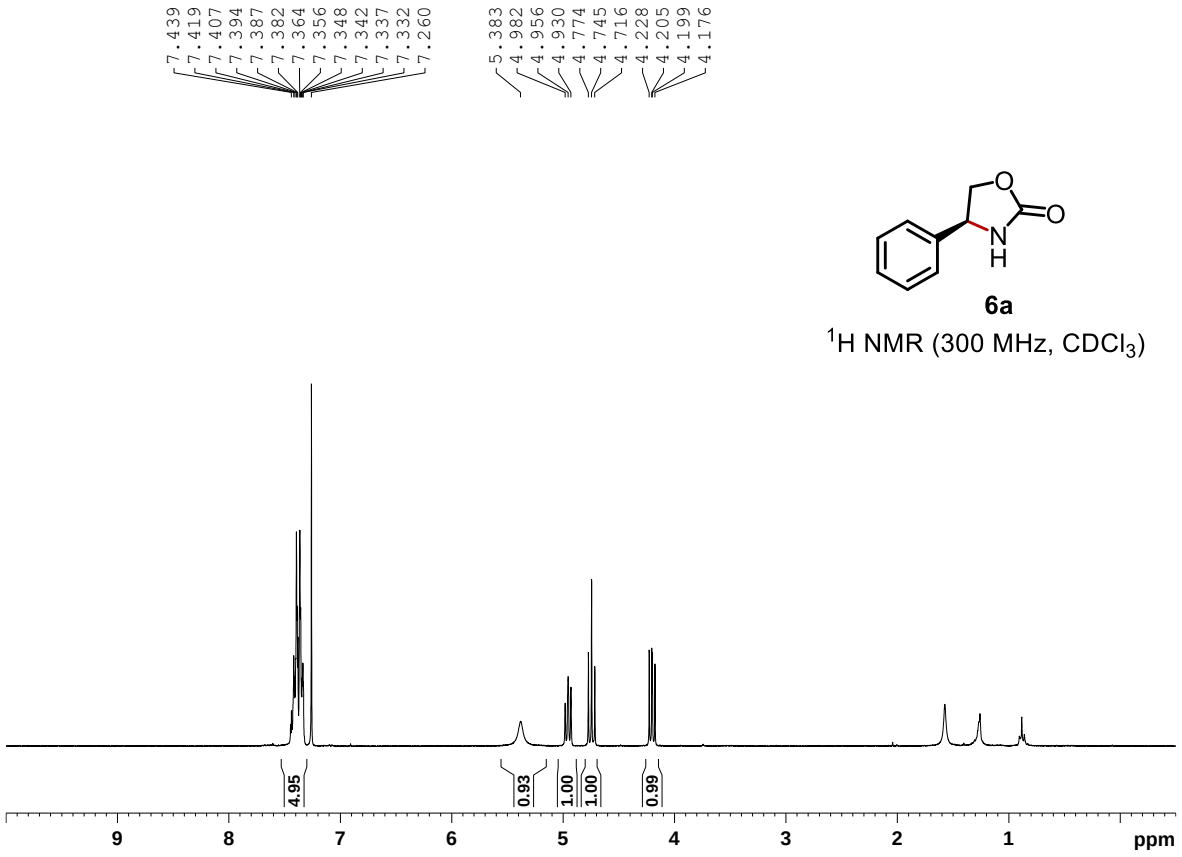


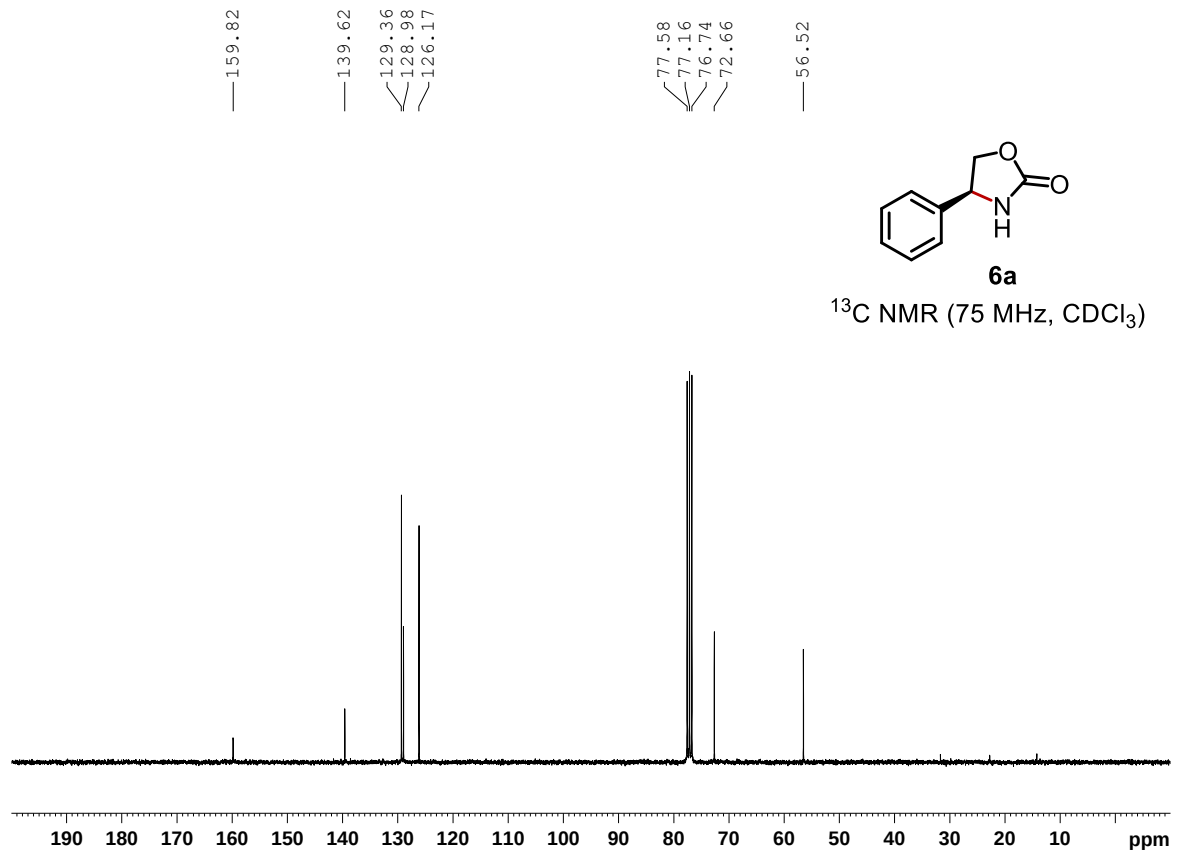
5c

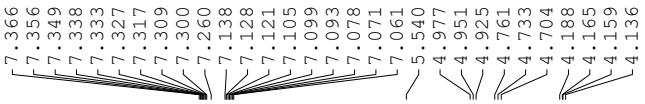
^{13}C NMR (75 MHz, $CDCl_3$)

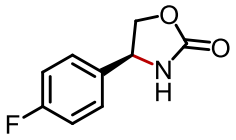

7.260
7.194
7.190
7.177
7.173
6.969
6.958
6.952
6.941
6.884
6.881
6.877
6.872
6.869
4.447
4.424
4.402
3.241
3.240
3.219
3.217
3.196
3.194
O
N3
S
O
5d
1H NMR (300 MHz, CDCl3)
1.00
1.00
1.00
2.08
2.09
9
8
7
6
5
4
3
2
1
ppm


157.40
138.79
127.14
125.99
124.45
77.58
77.16
76.74
68.55
29.19
O
N3
S
O
5d
13C NMR (75 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.439
7.419
7.407
7.394
7.387
7.382
7.364
7.356
7.348
7.342
7.337
7.332
7.260
5.383
4.982
4.956
4.930
4.774
4.745
4.716
4.228
4.205
4.199
4.176
O
O
N
H
6a
1H NMR (300 MHz, CDCl3)
4.95
0.93
1.00
1.00
0.99
9
8
7
6
5
4
3
2
1
ppm

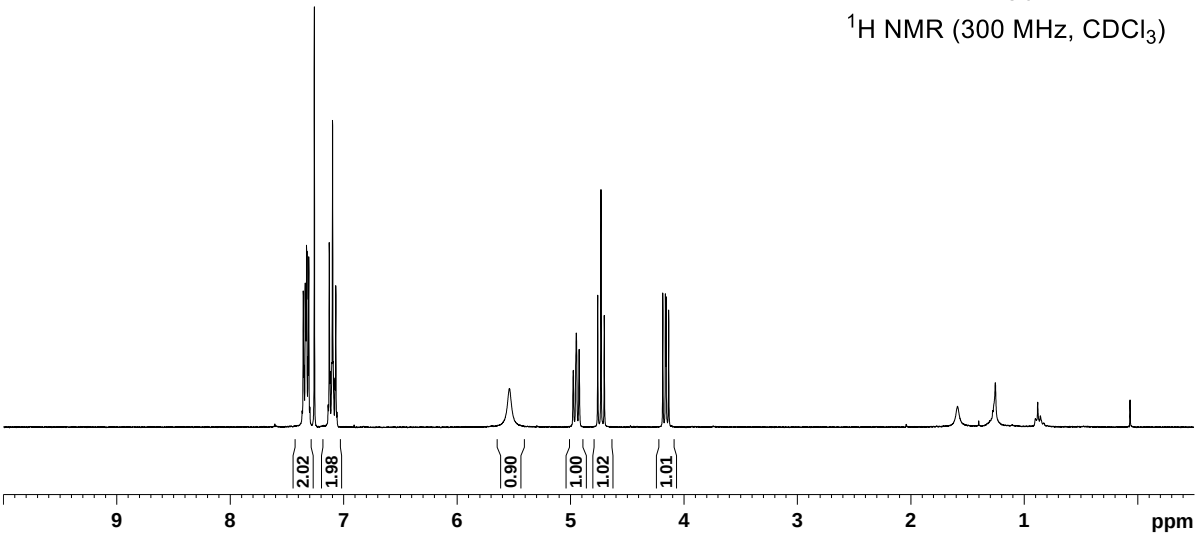

159.82
139.62
129.36
128.98
126.17
77.58
77.16
76.74
72.66
56.52
O
O
N
H
6a
13C NMR (75 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

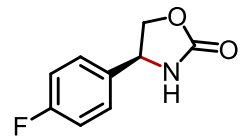




6b

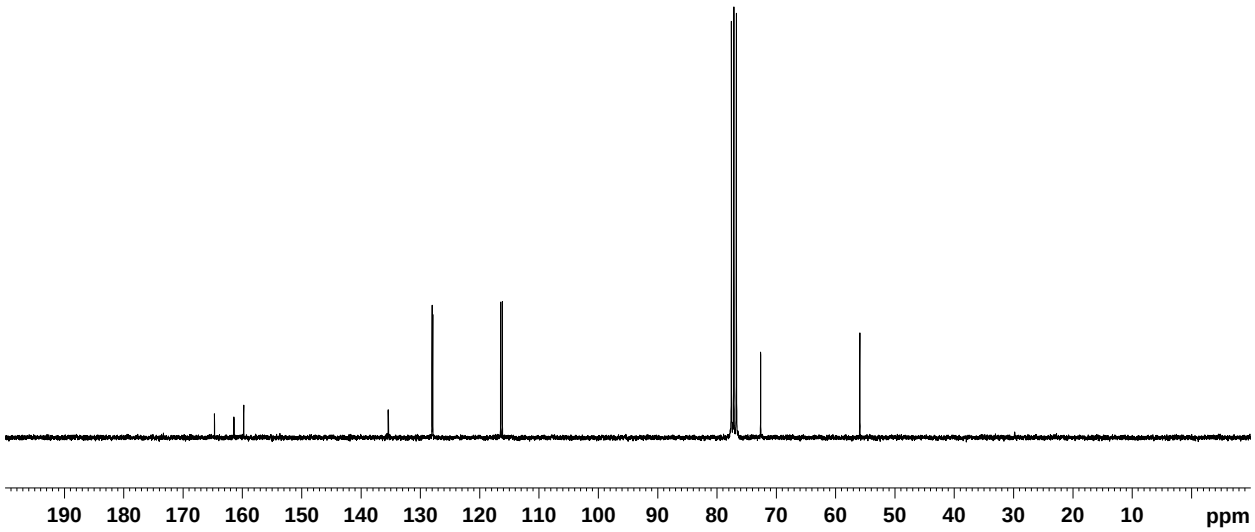
^{1}H NMR (300 MHz, $CDCl_3$)

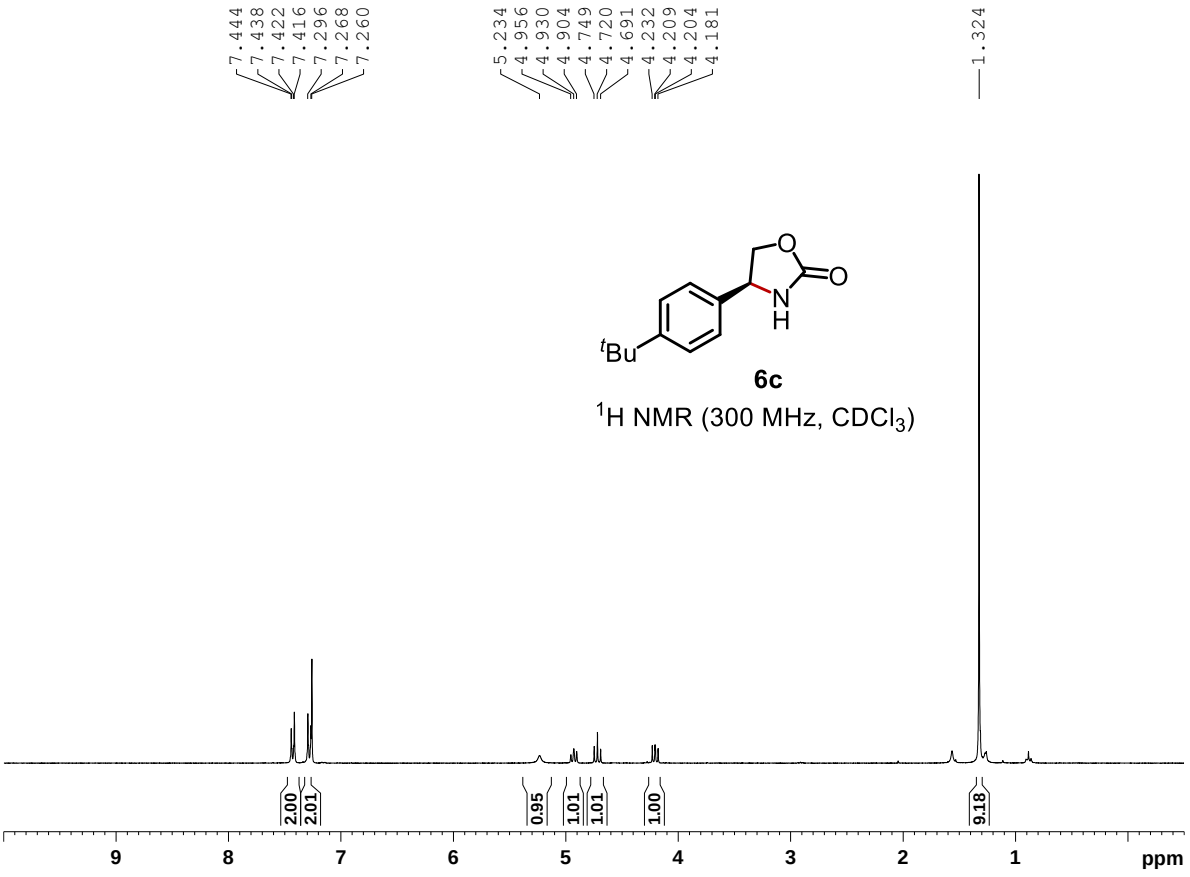




6b

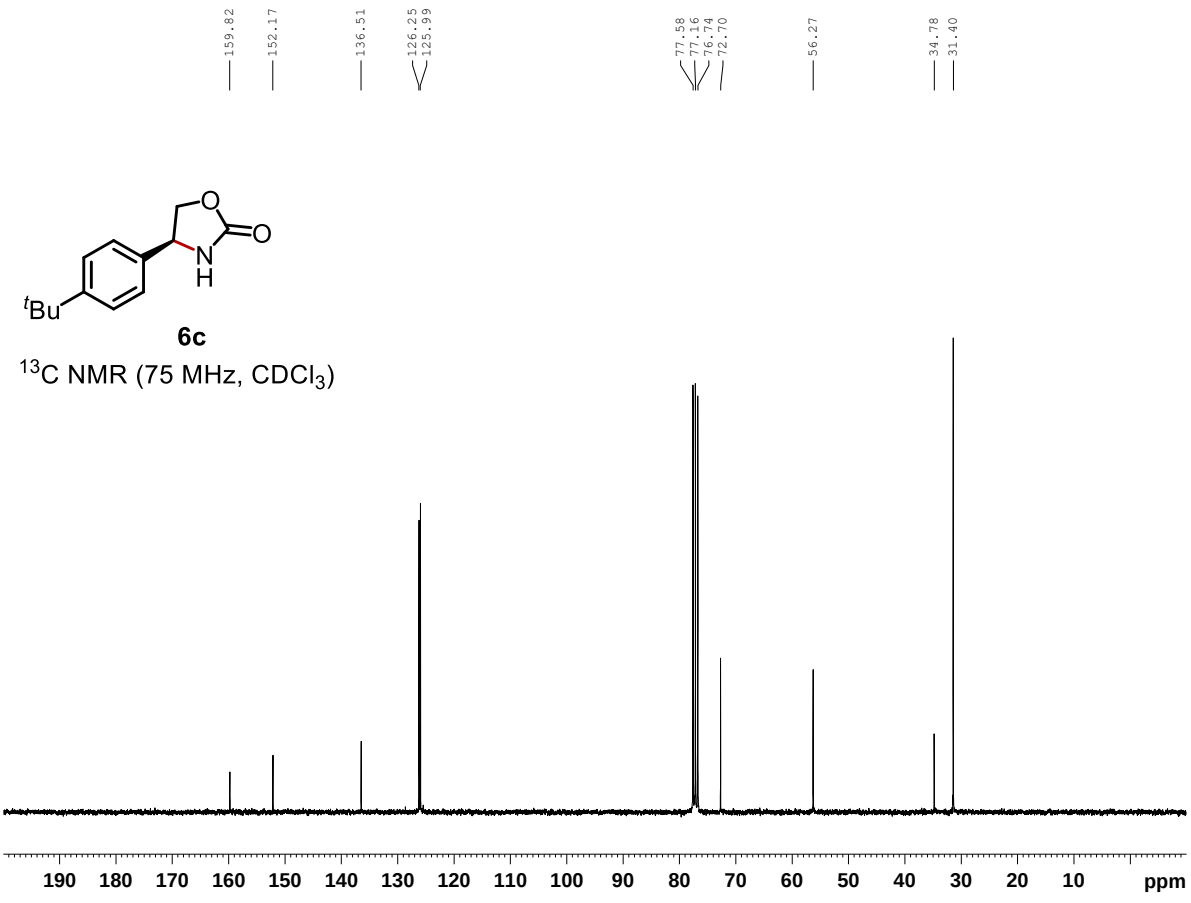
^{13}C NMR (75 MHz, $CDCl_3$)





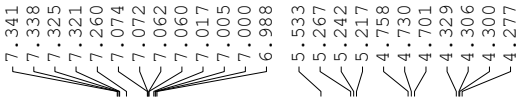
6c

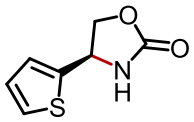
^{1}H NMR (300 MHz, $CDCl_3$)



6c

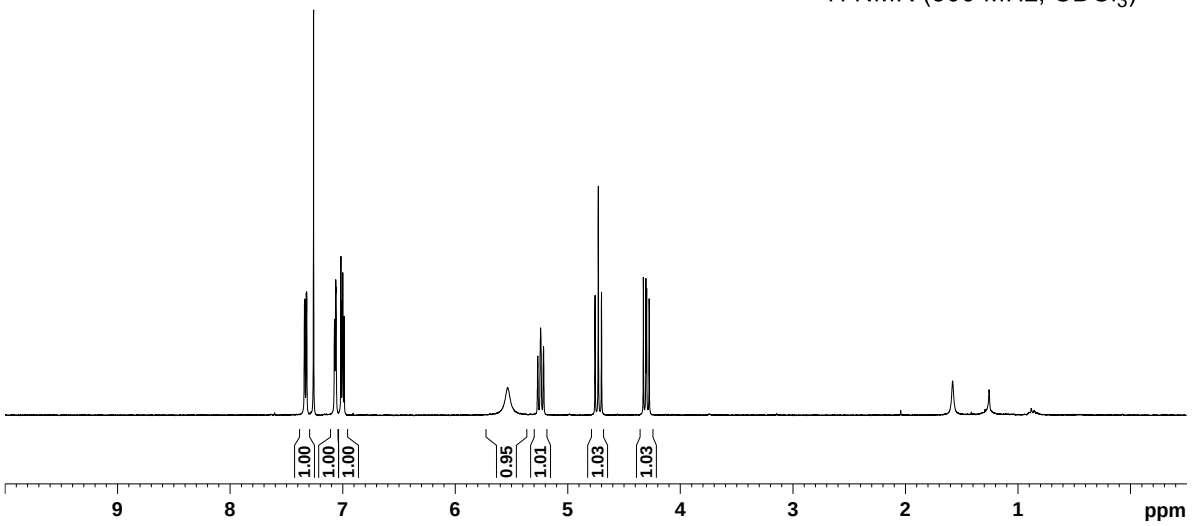
^{13}C NMR (75 MHz, $CDCl_3$)

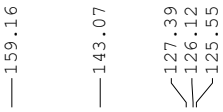


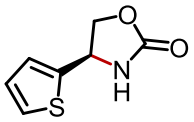


6d

^{1}H NMR (300 MHz, $CDCl_3$)

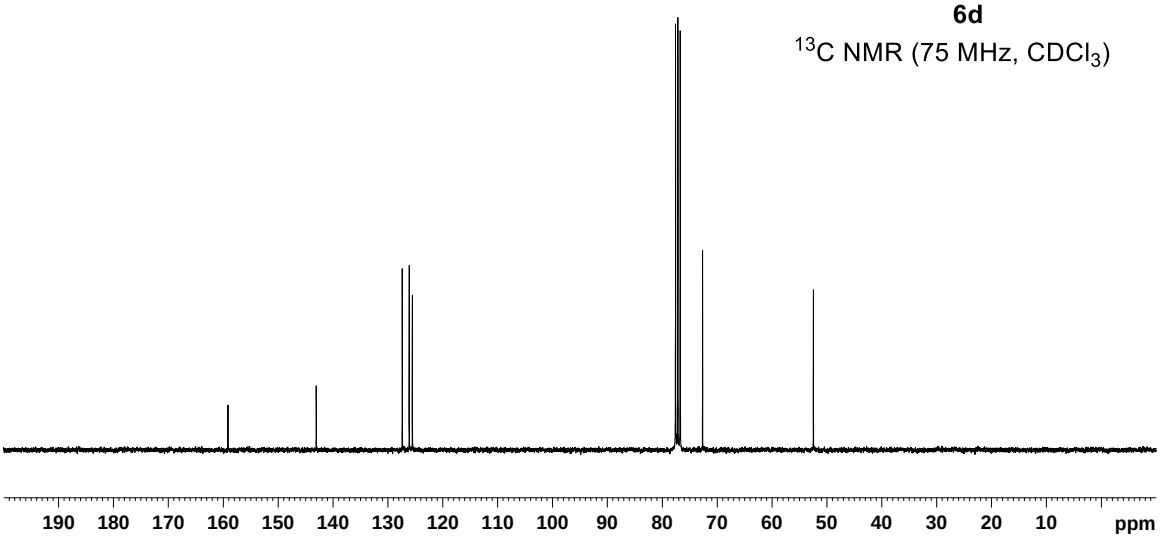


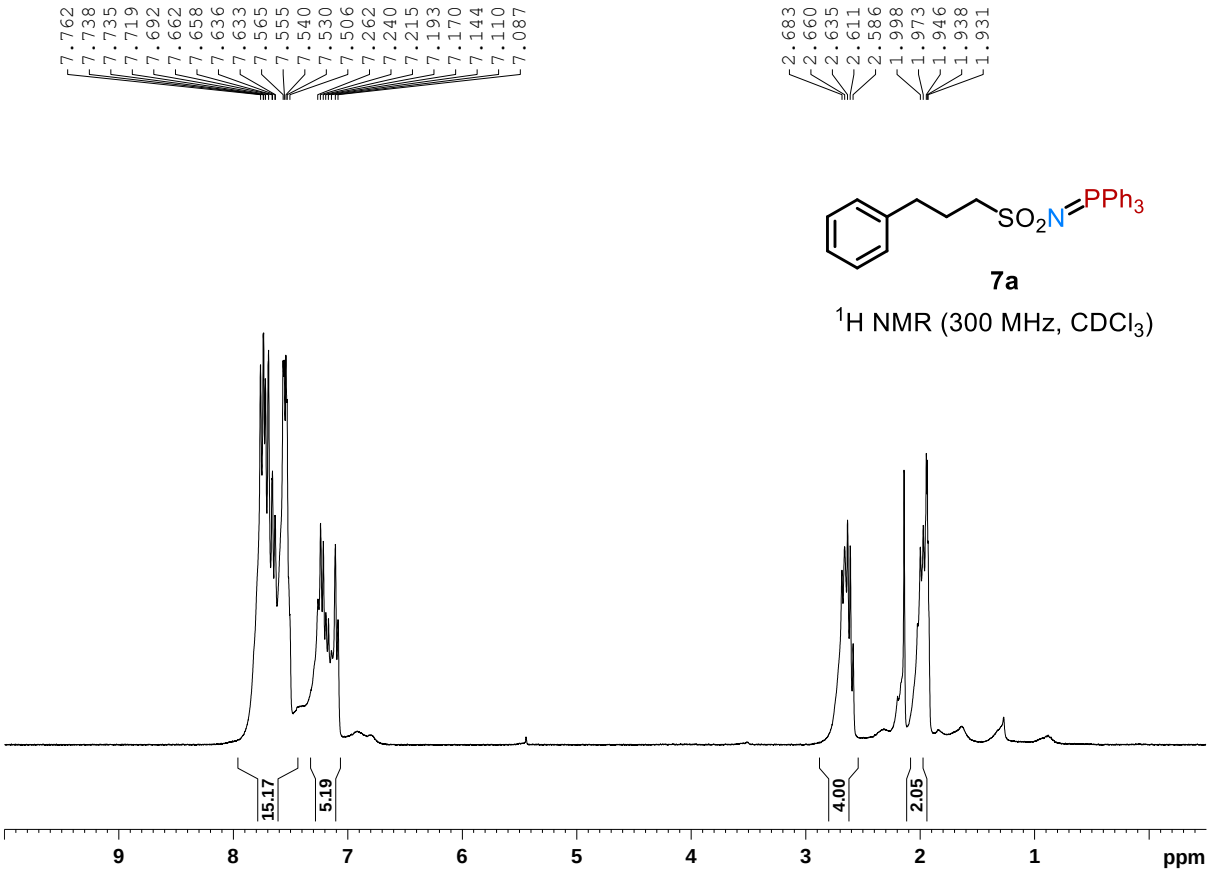


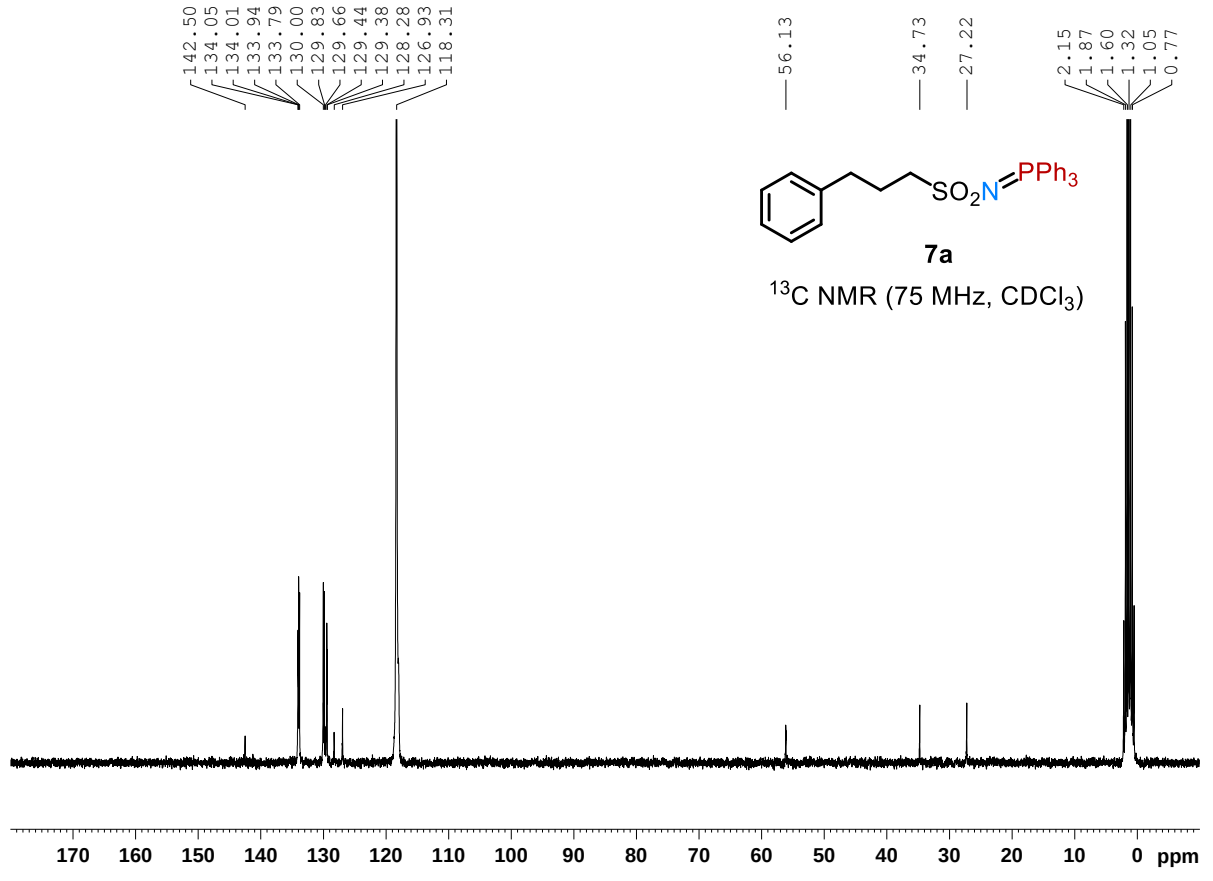


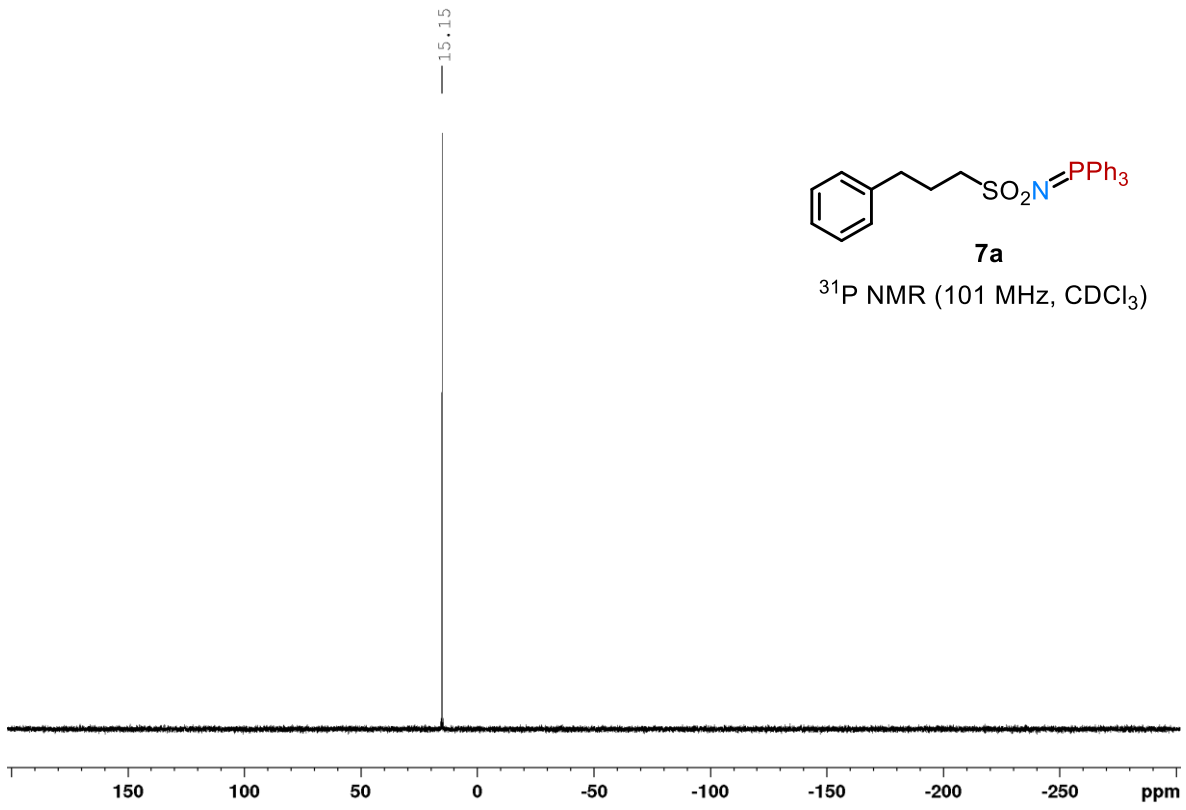
6d

^{13}C NMR (75 MHz, $CDCl_3$)



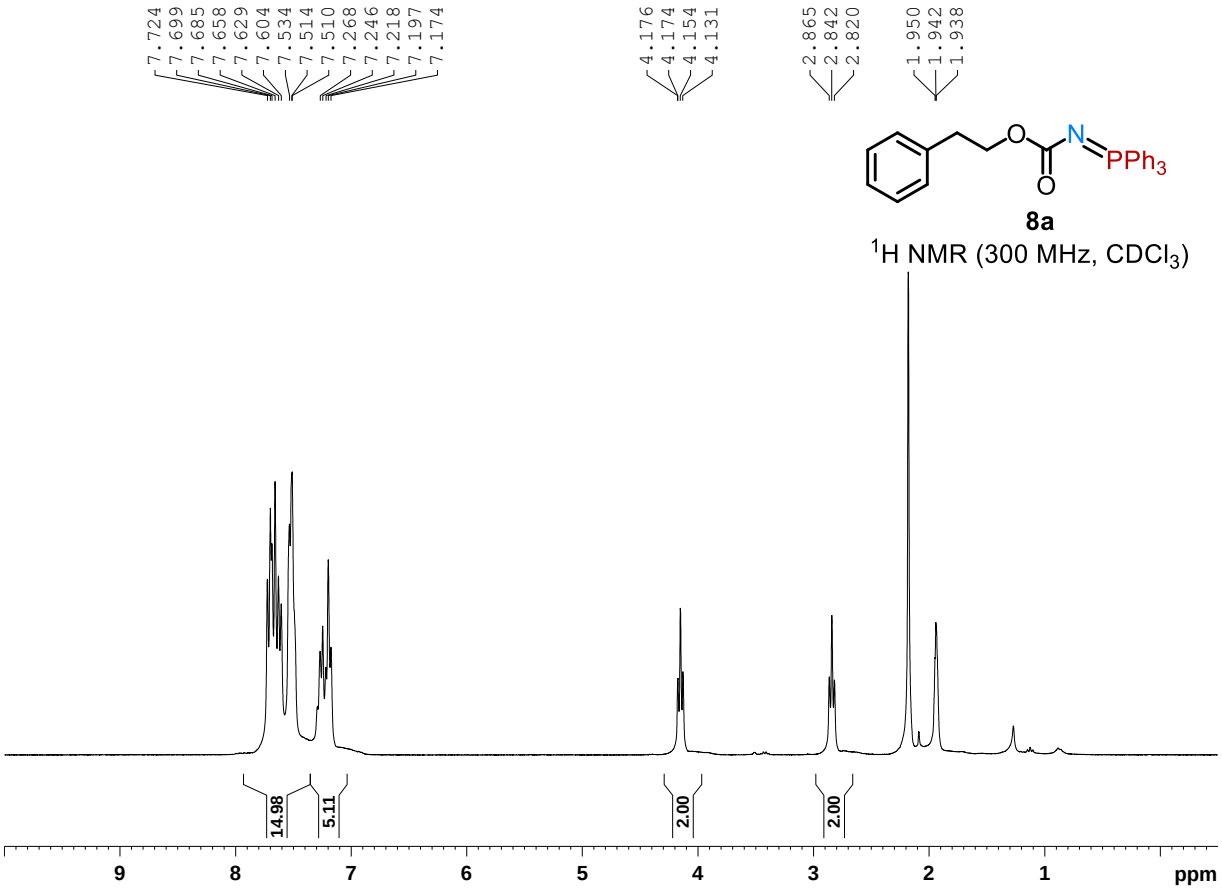

7.762
7.738
7.735
7.719
7.692
7.662
7.658
7.636
7.633
7.565
7.555
7.540
7.530
7.506
7.262
7.240
7.215
7.193
7.170
7.144
7.110
7.087
2.683
2.660
2.635
2.611
2.586
1.998
1.973
1.946
1.938
1.931
SO2N=PPh3
7a
1H NMR (300 MHz, CDCl3)
15.17
5.19
4.00
2.05
9
8
7
6
5
4
3
2
1
ppm


142.50
134.05
134.01
133.94
133.79
130.00
129.83
129.66
129.44
129.38
128.28
126.93
118.31
56.13
34.73
27.22
2.15
1.87
1.60
1.32
1.05
0.77
SO2N=PPh3
7a
13C NMR (75 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



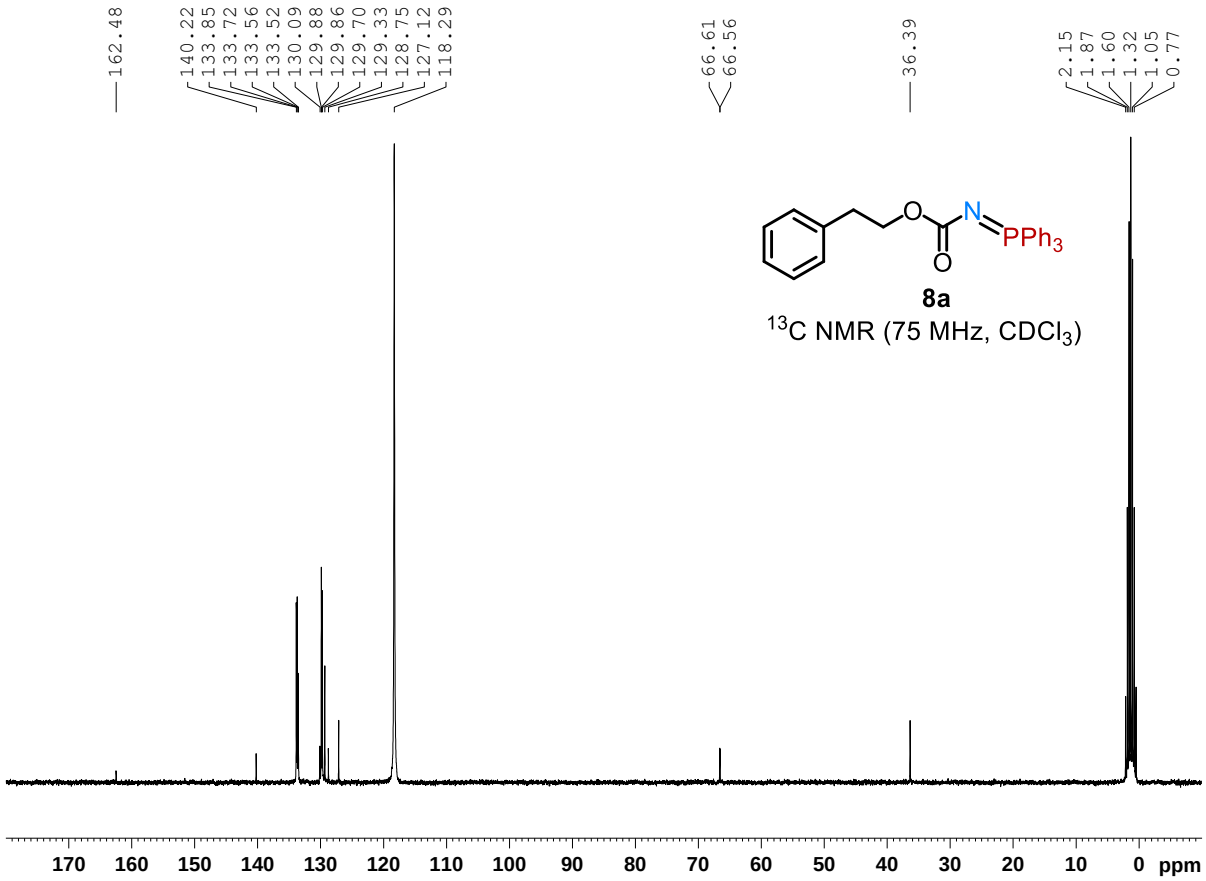
7a

^{31}P NMR (101 MHz, $CDCl_3$)



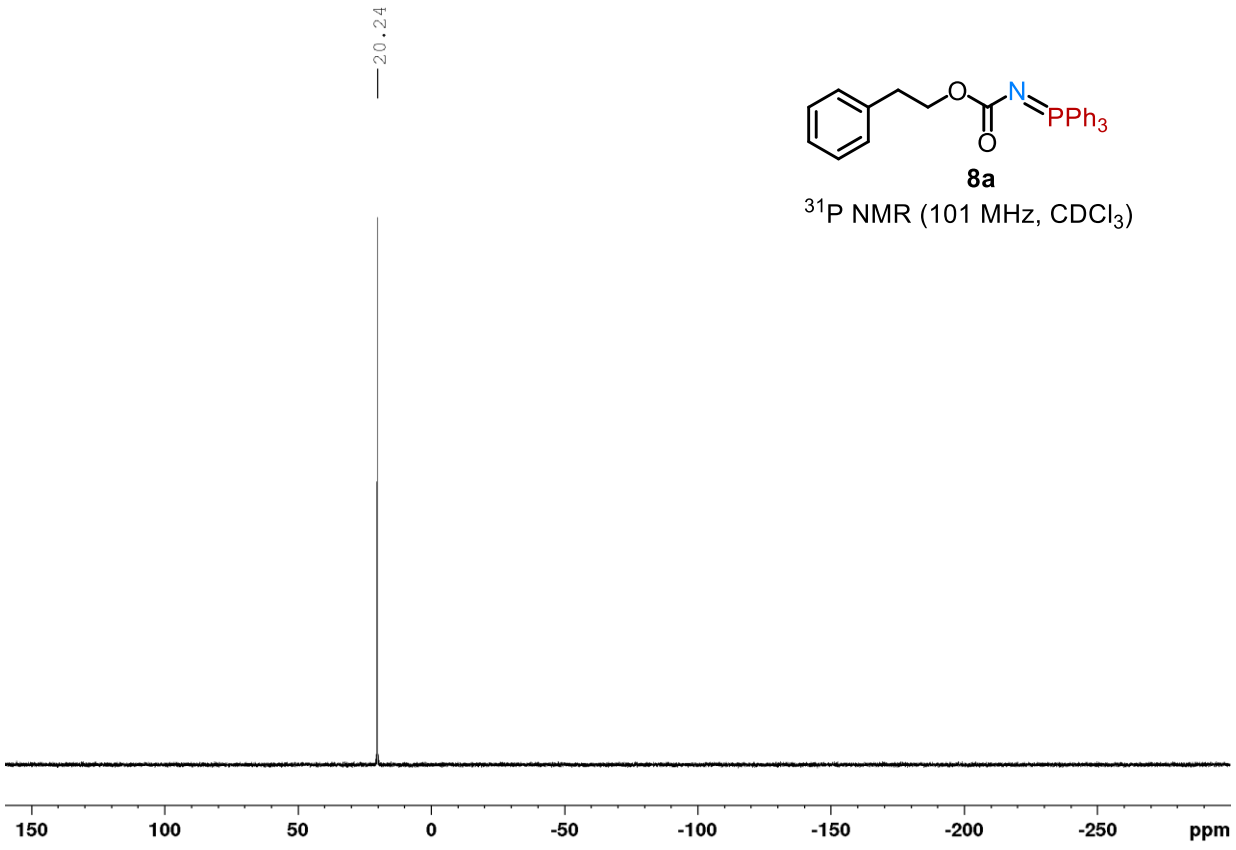
8a

^{1}H NMR (300 MHz, $CDCl_3$)



8a

^{13}C NMR (75 MHz, $CDCl_3$)



8a

^{31}P NMR (101 MHz, $CDCl_3$)

9. CD Spectra of Chiral Osmium Complexes

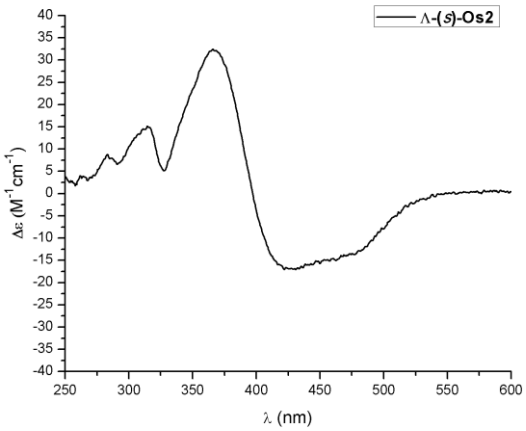


Figure S20. CD spectrum of complex Λ-(*S*)-**Os2** in CH_3CN (1.0 mM).

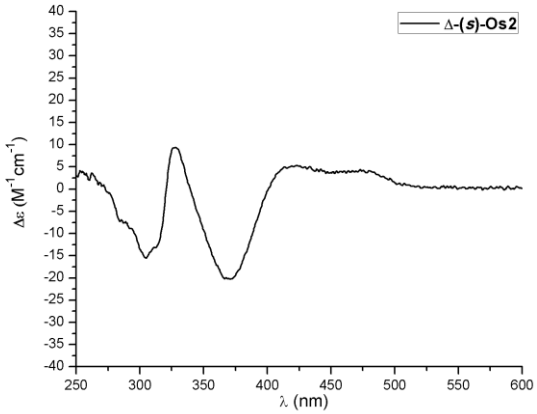


Figure S21. CD spectrum of complex Δ-(*S*)-**Os2** in CH_3CN (1.0 mM).

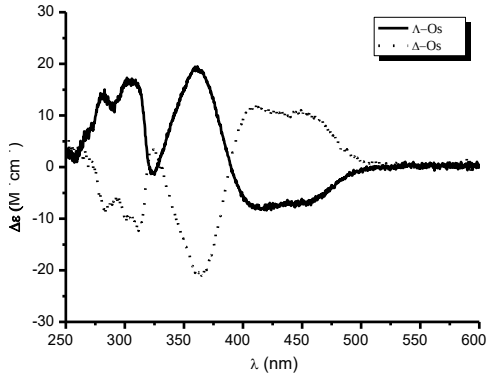


Figure S22. CD spectra of complexes Λ-**Os1** and Δ-**Os1** recorded in CH_3CN (1.0 mM).

10. Single Crystal X-Ray Diffraction Studies

10.1 Single Crystal X-Ray Diffraction of Λ-Os1

Single crystals of Λ-**Os1** suitable for X-ray diffraction were obtained from slowly diffusion of Et_2O to a solution of Λ-**Os1** in CH_3CN at room temperature in NMR tube. A suitable crystal was selected under inert oil and mounted using a MiTeGen loop. Intensity data of the crystal were recorded with a D8 Quest diffractometer (Bruker AXS). The instrument was operated with Mo-Kα radiation (0.71073 Å, microfocus source) and equipped with a PHOTON 100 detector. Evaluation, integration and reduction of the diffraction data was carried out using the Bruker APEX 3 software suite.[5] Multi-scan absorption correction was applied using the TWINABS program.[6] The structure was solved using dual-space methods (SHELXT-2014/5) and refined against F^2 (SHELXL-2018/3 using ShelXle interface) as a non-merohedral twin (twin operation is 180° rotation around the reciprocal [110] axis).[7-9] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined using the "riding model" approach with isotropic displacement parameters 1.2 times (for CH_3 groups 1.5 times) of that of the preceding carbon atom. Some of the $[PF_6]^-$ anions showed signs of disorder. An attempt to introduce split fluorine atoms for them was unsuccessful and, therefore SIMU restraints were applied. One cation of interest (that with the Os4 atom) was either slightly disordered or was affected by the twinning and problematic absorption correction. Additional SIMU and RIGU restraints were applied to handle this problem. CCDC 1995741 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Crystal structure, data and details of the structure determination for Λ-**Os1** are showed in the **Figure S23** and **Table S3**.

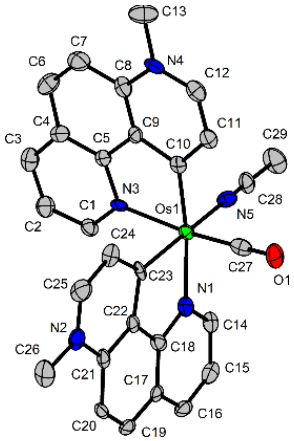


Figure S23. Crystal structure of Λ-**Os1**. ORTEP drawing with 50% probability thermal ellipsoids. The hexafluorophosphate counteranion, solvent and all hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1-C27 1.826(14) Os1-C10 1.996(12), Os1-C23 2.015(10), Os1-N5 2.091(11), Os1-N3 2.148(9), Os1-N1 2.183(10), C27-Os1-C10 91.1(5), C27-Os1-C23 90.7(5), C10-Os1-C23 96.1(5), C27-Os1-N5 97.2(5), C10-Os1-N5 91.4(4), C23-Os1-N5 169.0(4), C27-Os1-N3 170.6(5), C10-Os1-N3 79.9(4), C23-Os1-N3 87.3(4), N5-Os1-N3 86.1(4), C27-Os1-N1 94.2(5), C10-Os1-N1 173.1(4), C23-Os1-N1 79.5(4), N5-Os1-N1 92.3(4), N3-Os1-N1 94.5(4).

Table S3. Crystal data and structure refinement for Λ-**Os1**.

Identification code	**Λ-Os1**
Empirical formula	$C_{29}H_{23}F_{12}N_5OOsP_2$
Molar mass / g·mol^{-1}	937.66
Space group (No.)	*P*1 (1)
a / Å	14.2056(8)
b / Å	15.5349(9)
c / Å	16.0807(9)
α / °	70.816(2)
β / °	78.674(2)
γ / °	76.497(2)
V / Å^3	3231.2(3)
Z	4
$\rho_{calc.}$ / g·cm^{-3}	1.927
μ / mm^{-1}	4.149
Color	green
Crystal habitus	block
Crystal size / mm^3	0.106 x 0.073 x 0.064
T / K	100
λ / Å	0.71073 (Mo-K$_\alpha$)
θ range / °	2.137 to 28.363
Range of Miller indices	$-18 \le h \le 18$
	$-20 \le k \le 20$
	$-21 \le l \le 21$
Absorption correction	multi-scan
T_{min}, T_{max}	0.686536, 0.745687
R_{int}, R_σ	0.0743, 0.0692
Completeness of the data set	0.999
No. of measured reflections	243051
No. of independent reflections	30785
No. of parameters	1814
No. of restrains	471
S (all data)	1.038
$R(F)$ ($I \ge 2\sigma(I)$, all data)	0.0476, 0.0677
$wR(F^2)$ ($I \ge 2\sigma(I)$, all data)	0.0831, 0.0886
Flack parameter *x* (Parsons)	-0.014(2)
Volume fraction of the 2nd twin component	0.1693(8)
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e·Å^{-3}	2.307, –1.936

10.2 Single Crystal X-Ray Diffraction of Δ-(*S*)-Os2

Single crystals of Δ-(S)-**Os2** suitable for X-ray diffraction were obtained from slowly diffusion of Et_2O to a solution of Δ-(S)-**Os2** in CH_3CN at room temperature in NMR tube. A suitable crystal was selected under inert oil and mounted using a MiTeGen loop. Intensity data of the crystal were recorded with a D8 Quest diffractometer (Bruker AXS). The instrument was operated with Mo-Kα radiation (0.71073 Å, microfocus source) and equipped with a PHOTON 100 detector. Evaluation, integration and reduction of the diffraction data was carried out using the Bruker APEX 3 software suite.[5] Multi-scan and numerical absorption corrections were applied using the SADABS program.[10,11] The structure was solved using dual-space methods (SHELXT-2014/5) and refined against F^2 (SHELXL-2018/3).[7,8] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined using the "riding model" approach with isotropic displacement parameters 1.2 times (for CH_3 groups 1.5 times) of that of the preceding carbon atom. The $[PF_6]^-$ anions showed signs of orientation disorder and therefore their fluorine atoms were split in two positions with complementarily refined occupancies, restrained bond lengths and constrained anisotropic displacement parameters. Although the difference Fourier map contains high positive and negative peaks, their magnitudes are comparable and can be attributed to the problematic absorption correction of the needle-shape crystal. CCDC 1981335 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Crystal structure, data and details of the structure determination for Δ-(S)-**Os2** are showed in the **Figure S24** and **Table S4**.

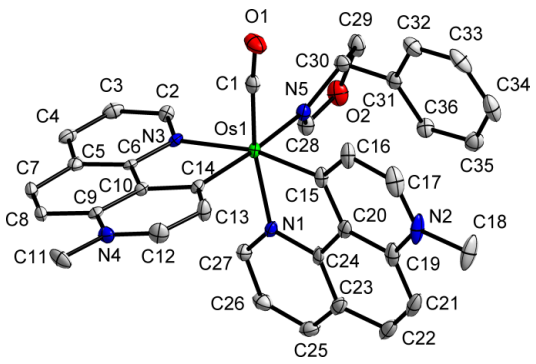


Figure S24. Crystal structure of Δ-(S)-**Os2**. ORTEP drawing with 50% probability thermal ellipsoids. The hexafluorophosphate counter anion, solvent and all hydrogens are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1-C1 1.846(6), Os1-C15 2.005(6), Os1-C14 2.037(6), Os1-N1 2.160(4), Os1-N5 2.174(5), Os1-N3 2.193(5), C1-Os1-C15 91.1(3), C1-Os1-C14 91.2(2), C15-Os1-C14 93.5(2), C1-Os1-N1 170.1(2), C15-Os1-N179.5(2), C14-Os1-N1 92.33(19), C1-Os1-N5 92.6(2), C15-Os1-N5 95.5(2), C14-Os1-N5170.2(2), N1-Os1-N5 85.49(19), C1-Os1-N3 99.1(2), C15-Os1-N3 167.3(2), C14-Os1-N3 78.7(2), N1-Os1-N3 90.60(17), N5-Os1-N3 91.69(19).

Table S4. Crystal data and structure refinement for Δ-(S)-**Os2**.

Identification code	**Δ-(S)-Os2**
Empirical formula	$C_{36}H_{29}F_{12}N_5O_2OsP_2$
Molar mass / g·mol^{-1}	1043.78
Space group (No.)	$P2_12_12_1$ (19)
a / Å	9.2495(3)
b / Å	10.7934(4)
c / Å	35.8310(11)
V / Å^3	3577.1(2)
Z	4
$\rho_{calc.}$ / g·cm^{-3}	1.938
μ / mm^{-1}	3.761
Color	yellow
Crystal habitus	needle
Crystal size / mm^3	0.287 x 0.082 x 0.062
T / K	100
λ / Å	0.71073 (Mo-K$_\alpha$)
θ range / °	2.203 to 32.073
Range of Miller indices	$-13 \leq h \leq 13$
	$-16 \leq k \leq 13$
	$-53 \leq l \leq 53$
Absorption correction	multi-scan and numerical
T_{min}, T_{max}	0.6497, 0.7463
R_{int}, R_σ	0.0571, 0.0499
Completeness of the data set	0.999
No. of measured reflections	60283
No. of independent reflections	12430
No. of parameters	551
No. of restrains	324
No. of constrains	8
S (all data)	1.147
$R(F)$ ($I \geq 2\sigma(I)$, all data)	0.0411, 0.0491
$wR(F^2)$ ($I \geq 2\sigma(I)$, all data)	0.0674, 0.0692
Extinction coefficient	not refined
Flack parameter x	–0.011(3)
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e·Å^{-3}	2.471, –4.409

11. References

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