Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information for

Catalytic Asymmetric Conjugate Boration of α,β-Unsaturated Sulfones

Abraham L. Moure, Ramón Gómez-Arrayás* and Juan C. Carretero*

Departamento de Química Orgánica, Universidad Autónoma de Madrid (UAM), Cantoblanco, 28049, Madrid, Spain.

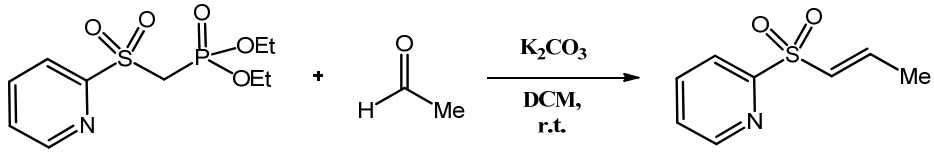
Contents:

Experimental Section

General methods

All the reactions were carried out in anhydrous solvents and under inert atmosphere. Melting points were taken in open-end capillary tubes. NMR spectra were recorded on a Brucker AC-300 instrument [300 MHz (^{1}H), 75 MHz (^{13}C)], at room temperature and calibrated using residual non-deuterated solvent ($CDCl_3$) as internal reference. Mass spectra (MS) were determined at an ionizing voltage of 70 eV. HPLC experiments were conducted on an Agilent 1100 instrument, using Daicel Chiralpak IA, AD, AS-H and Chiralcel OJ-H columns as chiral stationary phase. Optical rotations were measured on a Perkin-Elmer 241C polarimeter. Reactions were monitored by thin-layer chromatography, carried out on 0.25 mm. Merck silica gel plates (Merck-60 230-400 mesh). Flash column chromatography was performed using silica gel Merk-60 (230-400 mesh). CuCl, NaO*t*Bu, and bis(pinacolato)diboron [$B_2(pin)_2$] were purchased from commercial sources and used as received. 1-Alkenyl phenyl sulfones were prepared according to literature procedures[1]. Characterization data for compounds not described in the literature is provided.

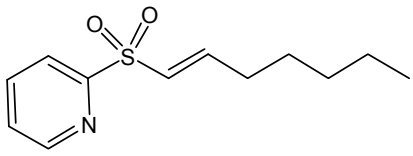
Typical procedure for the synthesis of α,β-unsaturated 2-pyridylsulfones[2]



2-[(1*E*)-Prop-1-en-1-ylsulfonyl]pyridine (2b)[2] To a suspension of K_2CO_3 (707 mg, 5.11mmol) in anhydrous CH_2Cl_2 (10 mL), at room temperature under argon atmosphere, was added via syringe a solution of diethyl (2-pyridylsulfonyl)methylphosphonate (1.0 g, 3.41 mmol) in anhydrous CH_2Cl_2 (5 mL). The suspension was stirred at room temperature for 5 min before acetaldehyde (287µL, 5.11mmol) was added, and the mixture was stirred for further 24 h. at room temperature. The solution was quenched with saturated aqueous NH_4Cl (5 mL) and diluted with CH_2Cl_2 (10 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL), and the combined organic phase was dried (Na_2SO_4) and concentrated in vacuo. The crude mixture was purified by column chromatography (50% EtOAc in hexanes) to give **2b** as a white solid; yield: 463 mg (74%); mp: 50-55 °C.

^{1}H NMR (300MHz): δ 8.73 (d, *J*=4.5 Hz, 1 H), 8.09 (d, *J*=7.9 Hz, 1 H), 7.94 (td, *J*=8.1, 1.5 Hz, 1 H), 7.51 (dd, *J*=7.0, 4.8 Hz, 1 H), 7.12 (dq, *J*=15.0, 7.0 Hz, 1 H), 6.57 (dd, *J*=15.1, 1.4 Hz, 1 H), 1.99 (dd, *J*=6.9, 1.4 Hz, 3 H). **^{13}C NMR** (75 MHz): δ 158.4, 150.2, 145.5, 138.1, 129.0, 127.0, 121.7, 17.5. **HRMS-ESI** (*m/z*): Calcd. for [$C_8H_9NO_2S$+H] 184.0426, found 184.0434.

2-[(1*E*)-Hept-1-en-1-ylsulfonyl]pyridine[2]



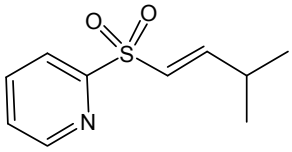
Following the general procedure, the reaction of diethyl (2-pyridylsulfonyl)methylphosphonate (500 mg, 1.71 mmol) with hexanal (314 µL, 2.56 mmol) in CH_2Cl_2 (5 mL)

[1] P.Mauleón, A.A.Nuñez, I. Alonso, J. C. Carretero, *Chem. Eur. J*. 2003, **9**, 1511.
[2] P.Mauleón, J. C. Carretero, *Org. Lett.*, 2004, **6**, 3195.

afforded, after flash chromatography (40% EtOAc in hexanes), the titled compound as a colorless oil; yield: 297 mg (75%).

^{1}H NMR (300MHz): δ8.68 (d, J=4.6 Hz, 1 H), 8.03 (d, J=7.8 Hz, 1 H), 7.91 (td, J=7.7, 1.7 Hz, 1 H), 7.48 (ddd, J=7.6, 4.7, 1.0 Hz, 1 H), 7.07 (dt, J=15.1, 6.8 Hz, 1 H), 6.50 (dt, J=15.2, 1.4 Hz, 1 H), 2.25 (qd, J=7.3, 1.4 Hz, 2 H), 1.37 - 1.52 (m, 2 H), 1.15 - 1.34 (m, 4 H), 0.77 - 0.88 (m, 3 H). **^{13}C NMR** (75 MHz): δ 158.4, 150.2, 150.1,138.1, 127.4, 127.0, 121.7, 31.6, 31.0, 27.0, 22.1, 13.7. **HRMS-ESI** (*m/z*): Calcd. for [$C_{12}H_{17}NO_2S$+H] 240.1052, found 240.1064.

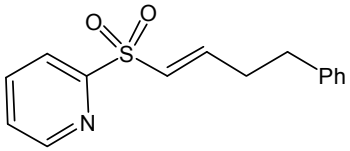
2-{[(1*E*)-3-Methylbut-1-en-1-yl]sulfonyl}pyridine[2]



Following the general procedure, the reaction of diethyl (2-pyridylsulfonyl)methylphosphonate (500 mg, 1.71 mmol) with isobutyraldehyde (233 µL, 2.56 mmol) in CH_2Cl_2(5 mL) afforded, after flash chromatography (40% EtOAc in hexanes,) the titled compound as a colorless oil; yield: 273 mg (74%).

^{1}H NMR (300MHz): δ 8.64 (d, *J*=4.5 Hz, 1 H), 7.99 (d, *J*=7.8 Hz, 1 H), 7.88 (td, *J*=7.6, 1.4 Hz, 1 H), 7.40 - 7.50 (m, 1 H), 6.99 (dd, *J*=15.2, 6.2 Hz, 1 H), 6.42 (dd, *J*=15.3, 1.3 Hz, 1 H), 2.35 - 2.62 (m, 1 H), 0.95 - 1.05 (m, 6 H). **^{13}C NMR** (75MHz): δ 158.2, 155.4, 150.0, 138.0, 126.9, 125.4, 121.5, 30.6, 20.5. **HRMS-ESI** (*m/z*): Calcd. for [$C_{10}H_{13}NO_2S$+H] 212.0739, found 212.0744.

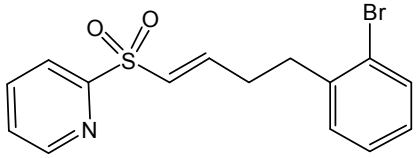
(*E*)-2-((4-Phenylbut-1-en-1-yl)sulfonyl)pyridine[3]



Following the general procedure, the reaction of diethyl (2-pyridylsulfonyl)methylphosphonate (534 mg, 1.82 mmol) with hydrocinnamaldehyde (360µL, 2.73 mmol) in CH_2Cl_2 (10 mL) afforded, after flash chromatography (50% EtOAc in hexanes), the titled compound as a white solid; yield: 386 mg (77%); mp: 103-105 °C.

^{1}H NMR (300MHz): δ 8.68 - 8.79 (m, 1 H), 8.07 (dt, *J*=7.9, 0.9 Hz, 1 H), 7.94 (td, *J*=7.7, 1.7 Hz, 1 H), 7.52 (ddd, *J*=7.6, 4.7, 1.2 Hz, 1 H), 7.08 - 7.34 (m, 6 H), 6.56 (dt, *J*=15.2, 1.5 Hz, 1 H), 2.74 - 2.88 (m, 2 H), 2.55 - 2.69 (m, 2 H).**^{13}C NMR** (75MHz): δ158.5, 150.3, 148.8, 140.0, 138.1, 128.5, 128.4, 128.3, 127.0, 126.4, 121.8, 33.8, 33.4. **HRMS-ESI** (*m/z*): Calcd. for [$C_{15}H_{15}NO_2S$+H] 274.0896, found 274.0904.

(*E*)-2-((4-(2-Bromophenyl)but-1-en-1-yl)sulfonyl)pyridine



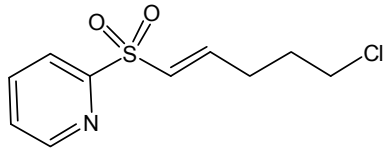
Following the general procedure, the reaction of diethyl (2-pyridylsulfonyl)methylphosphonate (700 mg, 2.38 mmol) with 3-(2-bromophenyl)propanal[4] (761 mg, 3.57 mmol) in CH_2Cl_2 (20 mL) afforded, after flash chromatography (70% EtOAc in hexanes), the titled compound as a colorless oil; yield: 711 mg (85%).

^{1}H NMR (300MHz): δ 8.82 (d, *J*=4.4 Hz, 1 H), 8.16 (d, *J*=7.9 Hz, 1 H), 8.03 (td, *J*=7.7, 1.5 Hz, 1 H), 7.54 - 7.66 (m, 2 H), 7.09 - 7.38 (m, 4 H), 6.66 (d, *J*=15.2 Hz, 1 H), 3.01 (t, *J*=7.3 Hz, 2 H), 2.71 (q, *J*=7.3 Hz, 2 H). **^{13}C NMR** (75MHz): δ 158.4, 150.2, 148.3, 139.2, 138.1, 132.9, 130.4, 128.6,

[3] S. F. Wnuk, P. I. Garcia, Jr., Z. Wang, *Org. Lett.*, 2004, **6**, 2047.
[4] J. S. Nakhla, J. W. Kampf, J. P. Wolfe, *J. Am. Chem. Soc.*, 2006, **128**, 2893.

128.1, 127.6, 127.0, 124.2, 121.8, 34.1, 31.7. **HRMS-ESI** (*m/z*): Calcd. for [$C_{15}H_{14}BrNO_2S$+H] 352.0001, found 352.0000.

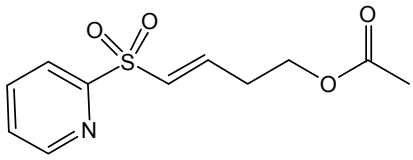
(*E*)-2-((5-Chloropent-1-en-1-yl)sulfonyl)pyridine



Following the general procedure, the reaction of diethyl (2-pyridylsulfonyl)methylphosphonate (680 mg, 2.31 mmol) with 4-chlorobutanal[5] (370 mg, 3.47 mmol) in CH_2Cl_2 (10 mL) afforded, after flash chromatography (50% EtOAc in hexanes) the titled compound as a colorless oil; yield: 411 mg (72%).

^{1}H NMR (300MHz): δ 8.74 (d, *J*=4.1 Hz, 1 H), 8.11 (d, *J*=7.8 Hz, 1 H), 7.96 (td, *J*=7.7, 1.6 Hz, 1 H), 7.49 - 7.59 (m, 1 H), 7.11 (dt, *J*=15.2, 6.8 Hz, 1 H), 6.62 (d, *J*=15.2 Hz, 1 H), 3.57 (t, *J*=6.2 Hz, 2 H), 2.44 - 2.57 (m, 2 H), 1.92 - 2.07 (m, 2 H). **^{13}C NMR** (75MHz): δ 158.4, 150.3, 147.9, 138.2, 128.9, 127.1, 121.8, 43.6, 30.2, 28.8. **HRMS-ESI** (*m/z*): Calcd. for [$C_{10}H_{12}ClNO_2S$+H] 246.0350, found 246.0349.

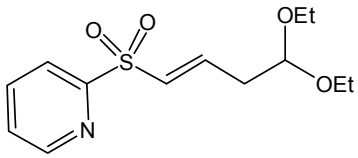
(*E*)-4-(Pyrid-2-ylsulfonyl)but-3-en-1-yl acetate



Following the general procedure, the reaction of diethyl (2-pyridylsulfonyl)methylphosphonate (319 mg, 1.08 mmol) with 3-(acetyloxy)-propanal (189 mg, 1.63 mmol) in CH_2Cl_2 (10 mL) afforded, after flash chromatography (70% EtOAc in hexanes), the titled compound as a white solid; yield: 137 mg (50%); mp: 54-56 °C.

^{1}H NMR (300MHz): δ 8.70 (d, *J*=4.1 Hz, 1 H), 8.06 (d, *J*=7.8 Hz, 1 H), 7.94 (td, *J*=7.7, 1.6 Hz, 1 H), 7.51 (ddd, *J*=7.5, 4.7, 1.0 Hz, 1 H), 7.05 (dt, *J*=15.2, 6.8 Hz, 1 H), 6.64 (dt, *J*=15.2, 1.4 Hz, 1 H), 4.17 (t, *J*=6.3 Hz, 2 H), 2.61 (qd, *J*=6.5, 1.3 Hz, 2 H), 1.92 - 2.04 (s, 3 H). **^{13}C NMR** (75MHz): δ 170.6, 158.1, 150.2, 144.9, 138.1, 129.9, 127.1, 121.8, 61.4, 30.8, 20.6. **HRMS-ESI** (*m/z*): Calcd. for [$C_{11}H_{13}NO_4S$+H] 256.0638, found 256.0638.

(*E*)-2-((4,4-Diethoxybut-1-en-1-yl)sulfonyl)pyridine

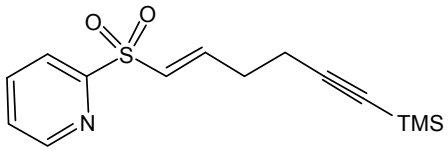


Following the general procedure, the reaction of diethyl (2-pyridylsulfonyl)methylphosphonate (530 mg, 1.80 mmol) with 3,3-diethoxy-propanal[6] (394 mg,2.70 mmol) in CH_2Cl_2 (10 mL) afforded, after flash chromatography (60% EtOAc in hexanes), the titled compound as a colorless oil; yield: 229 mg (44%).

^{1}H NMR (300MHz): δ 8.74 (d, *J*=3.9 Hz, 1 H), 8.09 (d, *J*=7.7 Hz, 1 H), 7.94 (td, *J*=7.7, 1.5 Hz, 1 H), 7.44 - 7.60 (m, 1 H), 7.08 (dt, *J*=14.3, 6.7 Hz, 1 H), 6.68 (d, *J*=15.2 Hz, 1 H), 4.61 (t, *J*=6.0 Hz, 1 H), 3.39 - 3.73 (m, 4 H), 2.62 (t, *J*=6.2 Hz, 2 H), 1.18 (t, *J*=7.3 Hz, 6 H). **^{13}C NMR** (75MHz): δ 158.5, 150.2, 144.6, 138.1, 130.0, 127.0, 121.8, 100.6, 61.8, 36.5, 15.2. **HRMS-ESI** (*m/z*): Calcd. for [$C_{13}H_{19}NO_4S$+Na] 308.0927, found 308.0925.

[5] S. A. Snyder, Z.-Y. Tang, R. Gupta, *J. Am. Chem. Soc.*, 2009, **131**, 5744.
[6] J. Uenishi, M. Motoyama, Y. Nishiyama, S. Wakabayashi, *J. Chem. Soc., Chem. Commun.*, 1991, 1421.

(*E*)-2-((6-(Trimethylsilyl)hex-1-en-5-yn-1-yl)sulfonyl)pyridine



Following the general procedure, the reaction of diethyl (2-pyridylsulfonyl)methylphosphonate (500 mg, 1.70 mmol) with 5-(trimethylsilyl)-4-pentynal[7] (394 mg, 2.56 mmol) in CH_2Cl_2 (10 mL) afforded, after flash chromatography (60% EtOAc in hexanes), the titled compound as a white solid; yield: 244 mg (51%); mp: 52-55 °C.

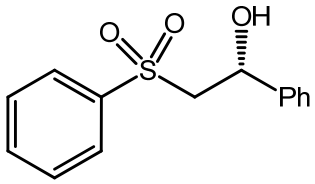
^{1}H NMR (300MHz): δ 8.73 (d, *J*=4.5 Hz, 1 H), 8.10 (d, *J*=7.9 Hz, 1 H), 7.94 (td, *J*=7.8, 1.5 Hz, 1 H), 7.52 (ddd, *J*=7.6, 4.9, 1.0 Hz, 1 H), 7.12 (dt, *J*=15.2, 6.1 Hz, 1 H), 6.66 (d, *J*=15.2 Hz, 1 H), 2.36 - 2.60 (m, 4 H), 0.09 (s, 9 H). **^{13}C NMR** (75MHz): δ 158.5, 150.4, 147.3, 138.2, 128.9, 127.1, 121.9, 104.4, 86.6, 30.8, 18.3, 0.0. **HRMS-ESI** (*m/z*): Calcd. for [$C_{14}H_{19}NO_2SSi$+H] 294.0978, found 294.0973.

General procedure for the enantioselective conjugate boration of α,β-unsaturated sulfones

To a mixture of the corresponding sulfone (0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.020 mmol, 10 mol%), NaO^{t}Bu (2.9 mg, 0.030 mmol, 15 mol%), josiphos or taniaphos ligand (0.024 mmol, 12 mol%, specified for each case) and bis(pinacolato)diboron (55.9 mg, 0.22 mmol, 1.1 equiv) in anhydrous THF (0.4 mL), at room temperature under argon atmosphere, was added MeOH (16μL, 0.40 mmol, 2.0 equiv). The mixture was stirred until no starting material was detected (TLC monitoring, typically 6-8 h) and then it was quenched with MeOH (1 mL). After 5 min of further stirring at room temperature, the mixture was filtered through a pad of Celite and the filtrate was concentrated to dryness. The residue was dissolved in a 1:1 mixture of THF/H_2O (2 mL) and sodium perborate tetrahydrate (92.3 mg, 0.60 mmol, 3.0 equiv) was added. The mixture was stirred at room temperature for 1-2 h before it was extracted with EtOAc (2 x 10 mL). The combined organic phase was dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash chromatography (the eluent is indicated for each case) to afford the desired enantioenriched β-hydroxysulfone.

The racemic products were prepared under identical conditions using (±)-BINAP (12 mol%) as the ligand, instead of josiphos or taniaphos.

***(R)*-1-Phenyl-2-(phenylsulfonyl)ethanol (3a)**[8]



Following the general procedure, the conjugate boration of **1a** (48.9 mg, 0.20 mmol) afforded, after flash chromatography (30% EtOAc in hexanes), the product **3a** as a white solid.

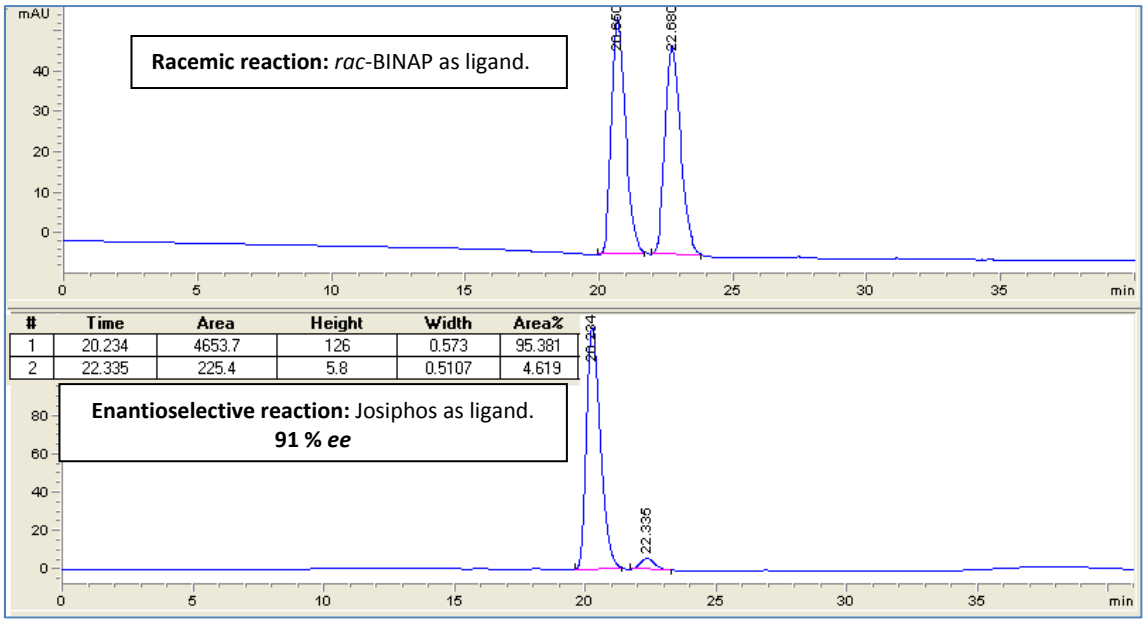
Reaction with Josiphos ligand: yield: 26.2 mg (50%); 91% *ee*.

^{1}H NMR (300MHz): δ 7.84 - 7.98 (m, 2 H), 7.45 - 7.72 (m, 3 H), 7.17 - 7.33 (m, 5 H), 5.24 (dd, *J*=10.0, 1.5 Hz, 1 H), 3.62 (br. s., 1 H), 3.47 (dd, *J*=14.4, 10.2 Hz, 1 H), 3.30 (dd, *J*=14.8, 1.8 Hz, 1 H). **^{13}C NMR** (75MHz): δ 140.6, 139.1, 134.1, 129.4, 128.7, 128.3,

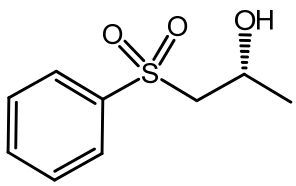
[7] H. Makabe, Y. Kimura, M. Higuchi, H. Konno, M. Murai, H. Miyoshi, *Bioorg. Med. Chem.* 2006, **14**, 3119.
[8] X. Wan; Q. Meng; H. Zhang; Y. Sun; W. Fan, Z. Zhang, *Org. Lett.*, 2007, ***9***, 5613.

128.0, 125.6, 68.4, 63.9. **HRMS-ESI** (*m/z*): Calcd. for $[C_{14}H_{14}O_3S+H-18]^+$ 245.0636, found 245.0636. **$[\alpha]_D$**= –30.6 (*c* 1, $CHCl_3$); lit$[\alpha]_D$= +38.6 (c 2.15, $CHCl_3$, 94% ee sample, *S*-enantiomer).[9]

HPLC: Daicel Chiralpak AD, i-PrOH-hexane 20/80, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 20.2 **(*R*-enantiomer)**; 22.3 (*S*-enantiomer).



(*R*)-1-(Phenylsulfonyl)propan-2-ol (4a)[8]



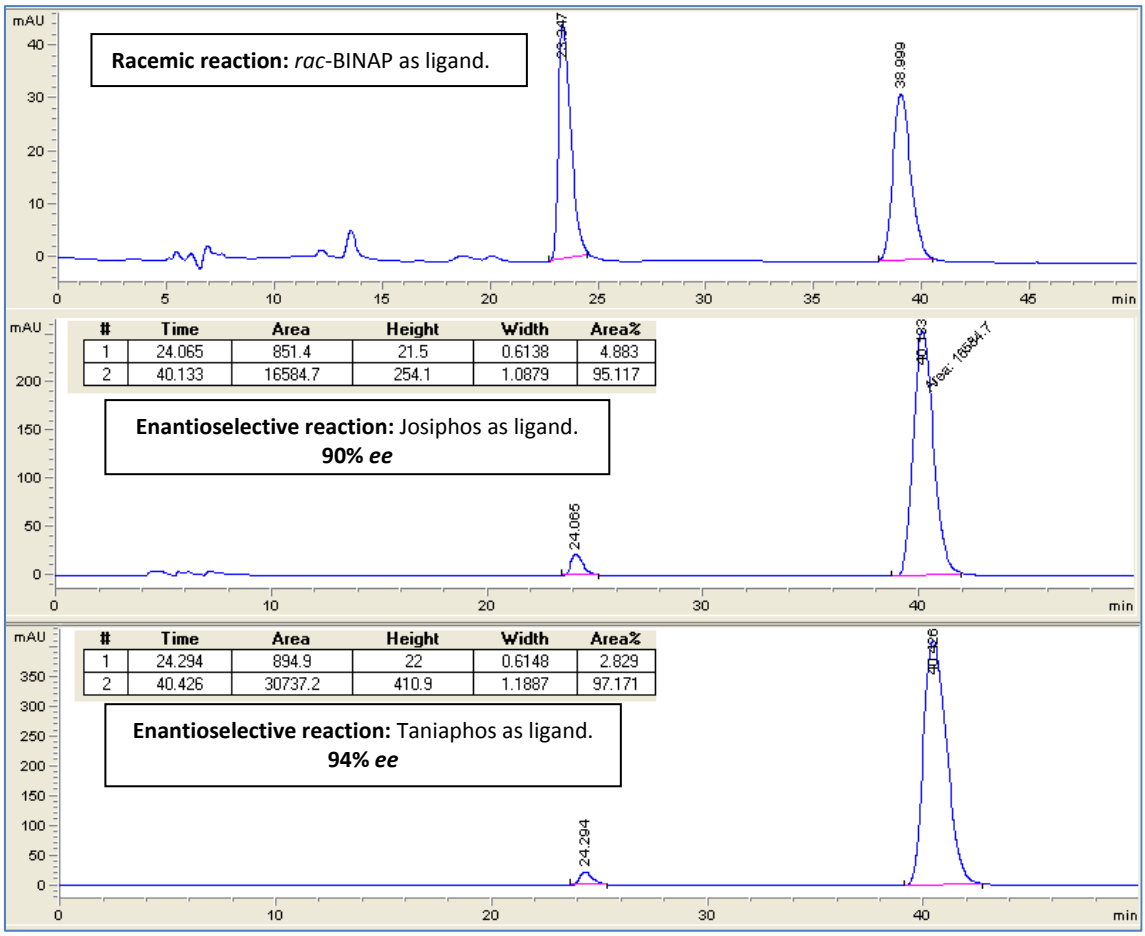
Following the general procedure, the conjugate boration of **2a** (36.5 mg, 0.20 mmol) afforded, after flash chromatography (20% EtOAc in hexanes), product **4a** as a colorless oil.

Reaction with Josiphos ligand: yield: 36.1 mg (90%); 90% *ee*
Reaction with Taniaphos ligand: yield: 28.8 mg (72%); 94% *ee*

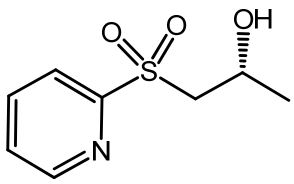
^{1}H NMR (300MHz): δ 7.85 - 7.99 (m, 2 H), 7.53 - 7.72 (m, 3 H), 4.22 - 4.40 (m, 1 H), 3.46 (brs, 1H), 3.23 (dd, *J*=14.3, 9.1 Hz, 1 H), 3.15 (dd, *J*=14.3, 2.5 Hz, 1 H), 1.29 (d, *J* = 6.4 Hz, 2H). **^{13}C NMR** (75MHz): δ = 139.2, 134.0, 129.4, 127.9, 63.3, 62.3, 22.5. **HRMS-ESI**(*m/z*): Calcd. for $[C_9H_{12}O_3S+H]^+$ 201.0585, found 201.0577. **$[\alpha]_D$**= –17.9 (*c 1,* CH_2Cl_2); lit$[\alpha]_D$= –12.0 (*c* 1.1*,* $CHCl_3$, 99% ee sample)[10]

HPLC: Daicel Chiralpak IA, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 24.1 (*S*-enantiomer); 40.1 (***R*-enantiomer**).

[9] G. Zhao, J. Hu, Z. Qian, W. Yin, *Tetrahedron: Asymm*., 2002, **13,** 2095.
[10] P. Kiełbasińskia, M. Rachwalskia, M. Mikołajczyka, M. Moelandsb, B. Zwanenburgb, F. Rutjes, *Tetrahedron: Asymm*, 2005, **16,** 2157.



***(R)*-1-(Pyrid-2-ylsulfonyl)propan-2-ol (4b)**



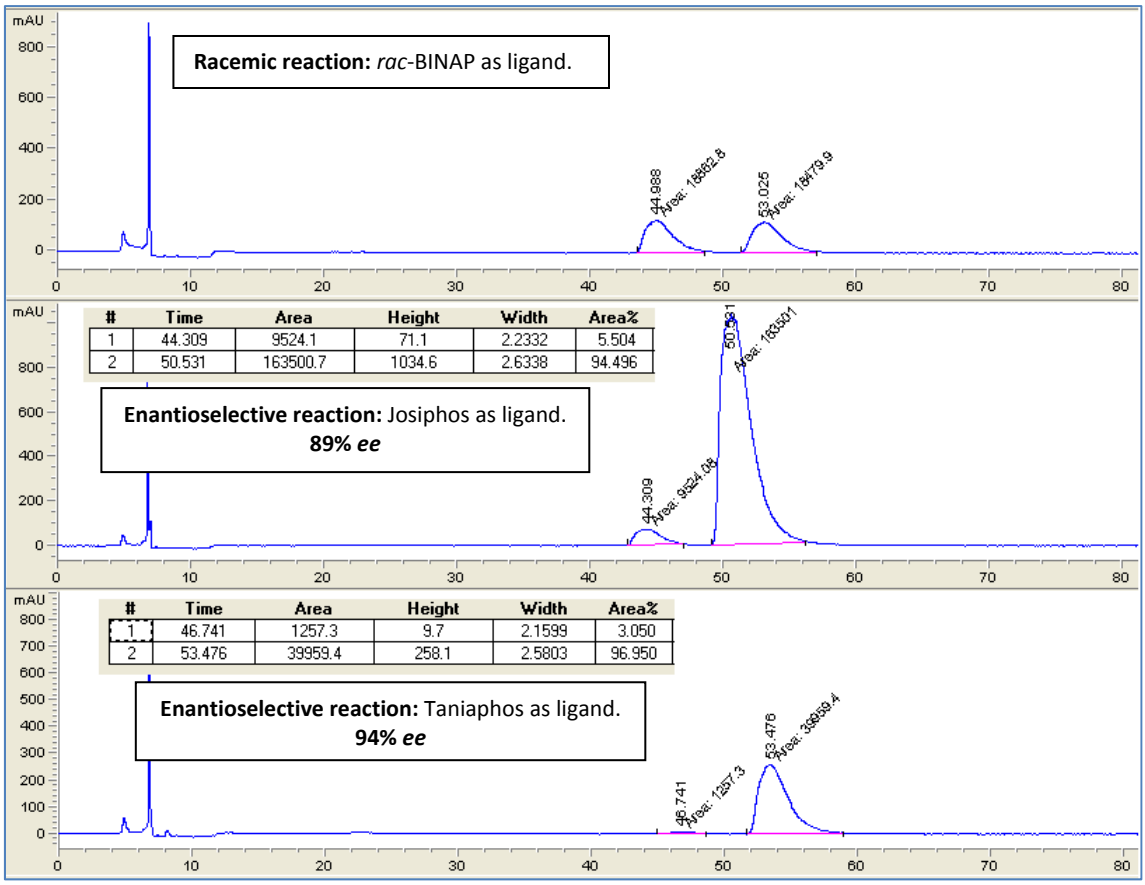
Following the general procedure, the conjugate boration of **2b** (36.6 mg, 0.20 mmol) afforded, after flash chromatography (40% EtOAc in hexanes), the product **4b** as a pale orange oil.

Reaction with Josiphos ligand: yield: 38.3 mg (95%); 89% *ee.*

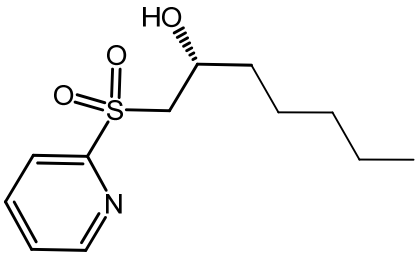
Reaction with Taniaphos ligand: yield: 36.2 mg (90%); 94% *ee*

^{1}H NMR (300MHz): δ 8.72 (d, *J*=4.4 Hz, 1 H), 8.11 (d, *J*=8.0 Hz, 1 H), 7.99 (td, *J*=7.7, 1.5 Hz, 1 H), 7.58 (ddd, *J*=7.5, 4.7, 1.0 Hz, 1 H), 4.31 - 4.52 (m, 1 H), 3.80 (br. s., 1 H), 3.36 - 3.60 (m, 2 H), 1.27 (d, *J*=7.0 Hz, 3 H). **^{13}C NMR** (75MHz): δ 157.4, 150.0, 138.6, 127.6, 121.9, 62.4, 60.4, 22.5. **HRMS-ESI** (*m/z*): Calcd. for [$C_8H_{11}NO_3S$+H] 202.0538, found 202.0527. **$[\alpha]_D$**= –16.5 *(c 1,* CH_2Cl_2).

HPLC: Daicel Chiralpak IA, i-PrOH-hexane 15/85, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 44.3 (*S*-enantiomer); 50.5 (***R*-enantiomer**).



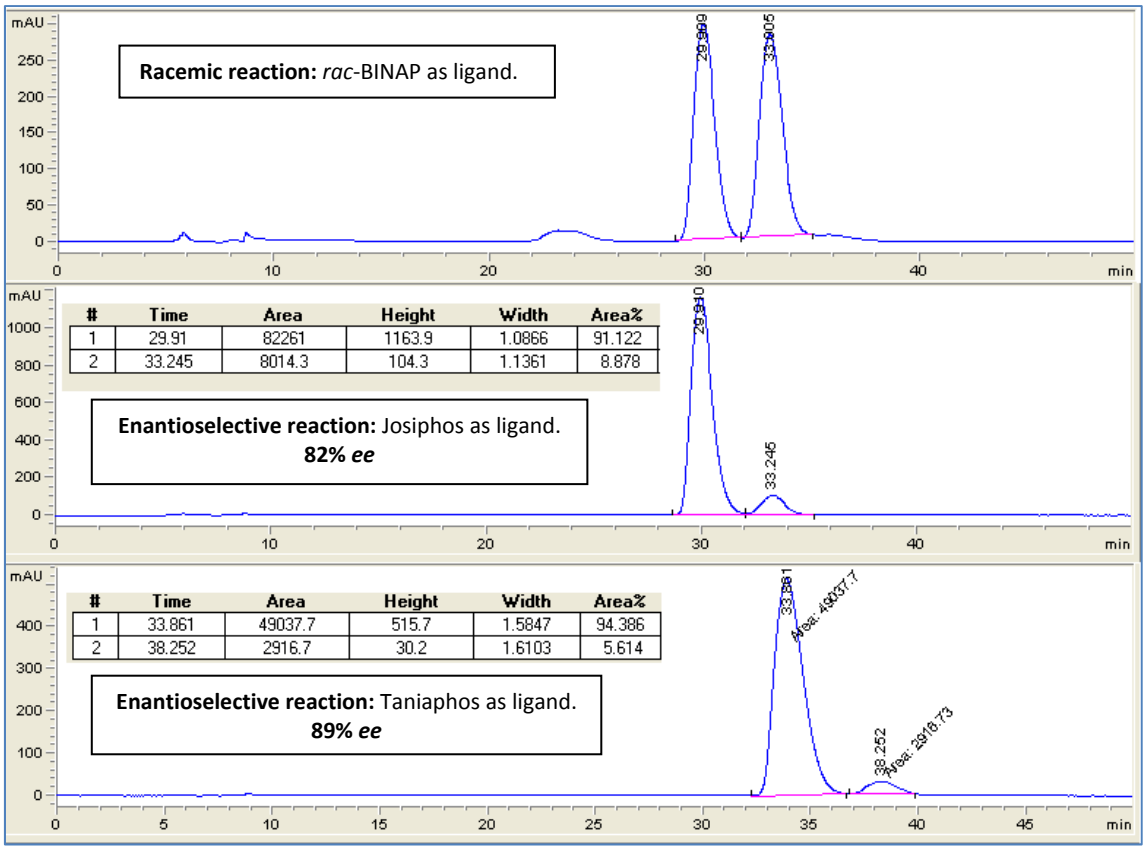
***(R)*-1-(Pyrid-2-ylsulfonyl)heptan-2-ol (5b)**



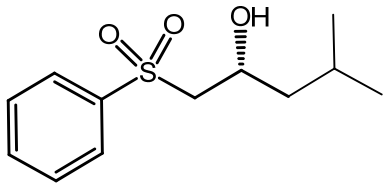
Following the general procedure, the conjugate boration of 2-[(1*E*)-hept-1-en-1-ylsulfonyl]pyridine (47.8 mg, 0.20 mmol) afforded, after flash chromatography (40% EtOAc in hexanes), the product **5b** as a pale orange oil.
Reaction with Josiphos ligand: yield: 42.7 mg (83%); 82% *ee*.
Reaction with Taniaphos ligand: yield: 42.2 mg (82%); 89% *ee.*

^{1}H NMR (300MHz): δ8.74 (d, *J*=4.4 Hz, 1 H), 8.13 (d, *J*=7.8 Hz, 1 H), 8.01 (td, *J*=7.8, 1.6 Hz, 1 H), 7.59 (ddd, *J*=7.6, 4.6, 1.0 Hz, 1 H), 4.15 - 4.38 (m, 1 H), 3.70 - 3.88 (br. S., 1 H), 3.36 - 3.67 (m, 2 H), 1.16 - 1.76 (m, 8 H), 0.88 (t, *J*=6.7 Hz, 3 H). **^{13}C NMR** (75MHz): δ 157.6, 150.0, 138.6, 127.6, 122.0, 66.0, 59.4, 36.4, 31.5, 24.8, 22.5, 14.0. **HRMS-ESI** (*m/z*): Calcd. for [$C_{12}H_{19}NO_3S$+H] 258.1158, found 258.1155**. [α]$_D$ =**–0.12 *(c 1,* CH_2Cl_2).

HPLC: Daicel Chiralpak AD, i-PrOH-hexane 10/90, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 29.9 (***R*-enantiomer**); 33.2min (*S*-enantiomer).



***(R)*-4-methyl-1-(phenylsulfonyl)pentan-2-ol (6a)**[11]



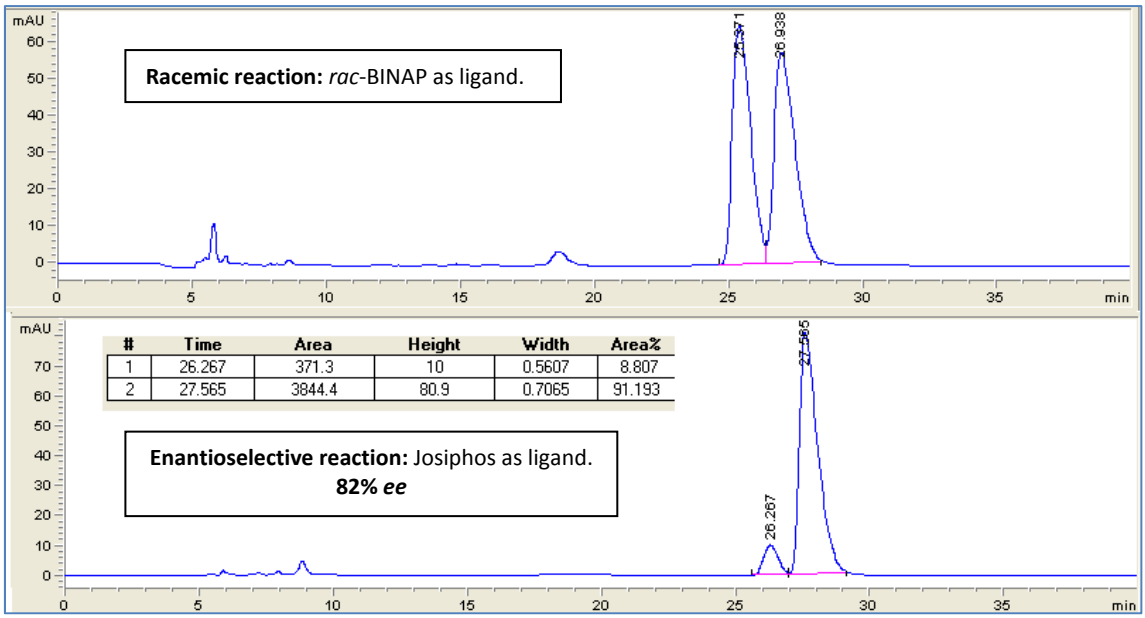
Following the general procedure, the conjugate boration of (1*E*)-4-methylpent-1-en-1-yl phenyl sulfone (44.8 mg, 0.20 mmol) afforded, after flash chromatography (20% EtOAc in hexanes), the product **6a** as a colorless oil.

Reaction with Josiphos ligand: yield: 43.1 mg (89%); 82% ee.

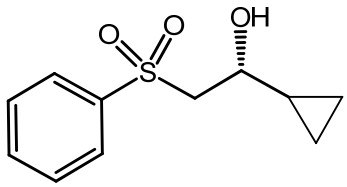
^{1}H NMR (300MHz): δ 7.87 - 8.02 (m, 2 H), 7.51 - 7.74 (m, 3 H), 4.13 - 4.36 (m, 1 H), 3.08 - 3.33 (m, 3 H), 1.65 - 1.84 (m, 1 H), 1.42 - 1.60 (m, 1 H), 1.09 - 1.23 (m, 1 H), 0.81 - 0.92 (m, 6 H). **^{13}C NMR** (75MHz): δ139.4, 134.0, 129.4, 127.8, 64.2, 62.6, 45.3, 24.2, 22.9, 21.8. **HRMS-ESI** (*m/z*): Calcd. for $[C_{12}H_{18}O_3S+H]^+$ 243.1055, found 243.1061. **$[\alpha]_D$**= –11.3 (*c 1,* CH_2Cl_2)

HPLC: Daicel Chiralpak IA, i-PrOH-hexane 10/90, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 26.3 (*S*-enantiomer); 27.6 **(*R*-enantiomer)**.

[11] R. Tanikaga; K. Hosoya; K. Hamamura; A. Kaji, *Tetrahedron. Lett.*, 1987, **28**, 3705.



***(R)*-1-Cyclopropyl-2-(phenylsulfonyl)ethanol (7a)**

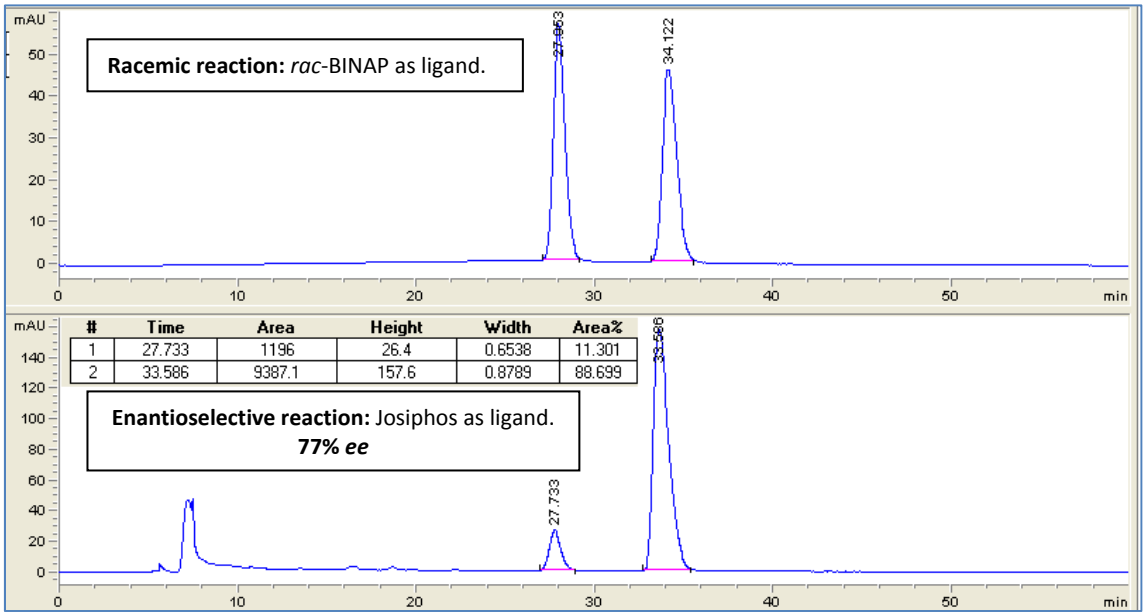


Following the general procedure, the conjugate boration of (*E*)-2-cyclopropylethenyl phenyl sulfone (41.6 mg, 0.20 mmol) afforded, after flash chromatography (50% Et_2O in hexanes), the product **7a** as a colorless oil.

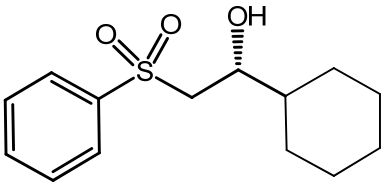
Reaction with Josiphos ligand: yield: 35.7 mg (79%); 77% ee.

^{1}H NMR (300MHz): δ 7.85 - 8.02 (m, 2 H), 7.51 - 7.75 (m, 3 H), 3.46 - 3.59 (m, 1 H), 3.33 - 3.44 (m, 2 H), 3.17 (br. s, 1 H), 0.88 - 1.04 (m, 1 H), 0.37 - 0.70 (m, 3 H), 0.08 - 0.29 (m, 1 H). **^{13}C NMR** (75MHz): δ 139.4, 134.0, 129.4, 127.9, 70.4, 62.4, 16.9, 3.6, 1.9. **HRMS-ESI** (*m/z*): Calcd. for $[C_{11}H_{14}O_3S+Na]^+$ 249.0561, found 249.0556. **$[\alpha]_D$**= –12.0 (*c 1,* CH_2Cl_2).

HPLC: Daicel Chiralpak AD, i-PrOH-hexane 15/85, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 27.7 (*S*-enantiomer); 33.5 **(*R*-enantiomer)**.



***(R)-1*-Cyclohexyl-2-(phenylsulfonyl)ethanol (8a)**[8]

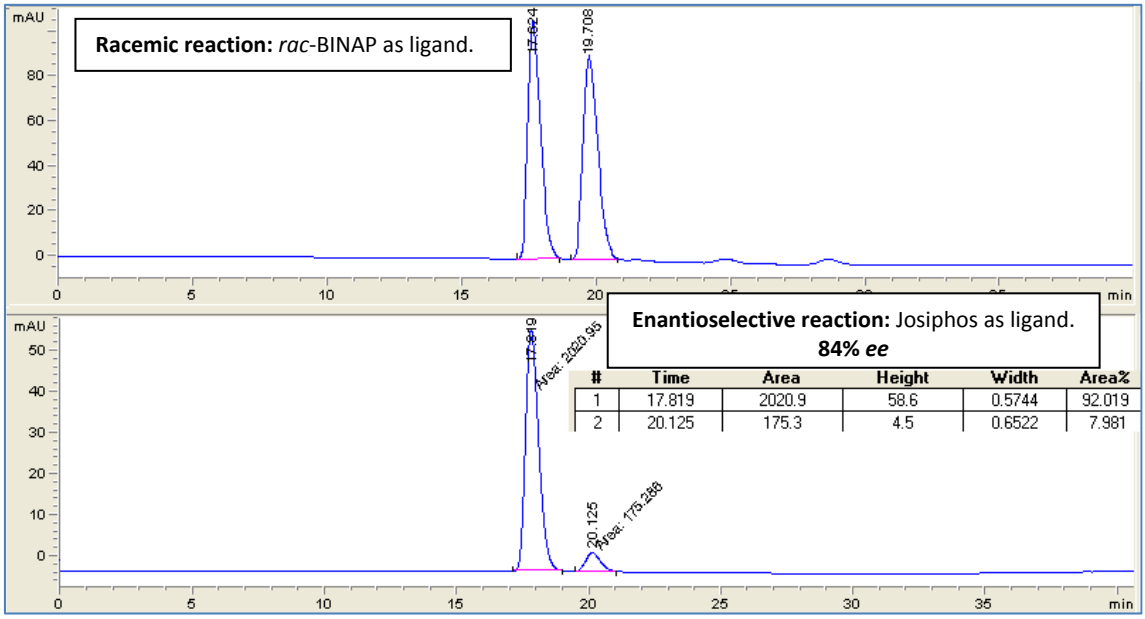


Following the general procedure, the conjugate boration of (*E*)-2-cyclohexylethenyl phenyl sulfone (50.1 mg, 0.20 mmol) afforded, after flash chromatography (20% EtOAc in hexanes), the product 8a as a colorless oil.

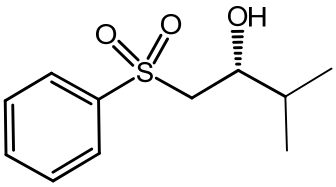
Reaction with Josiphos ligand: yield: 19.9 mg (37%); 84% ee.

^{1}H NMR (300MHz): δ7.86 - 8.02 (m, 2 H), 7.46 - 7.76 (m, 3 H), 3.81 - 4.05 (m, 1 H), 3.11 - 3.33 (m, 3 H), 1.54 - 1.82 (m, 5 H), 1.31 - 1.50 (m, 1 H), 0.89 - 1.27 (m, 5 H). **^{13}CNMR** (75MHz): δ 139.4, 133.9, 129.4, 127.9, 69.8, 60.3, 43.2, 28.5, 27.5, 26.2, 26.0, 25.9. **HRMS-ESI** (*m/z*): Calcd. for $[C_{14}H_{20}O_3S+H]^+$ 269.1211, found 269.1227**. [α]$_D$**= –14.0 (*c 0.5,* CH_2Cl_2); lit[α]$_D$= +23.7 (c 1.19, $CHCl_3$, 87% ee sample, S-enantiomer)[9]

HPLC: Daicel Chiralpak AD, i-PrOH-hexane 20/80, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 17.8 **(*R*-enantiomer)**; 20.1 (*S*-enantiomer).



***(R)*-3-Methyl-1-(phenylsulfonyl)butan-2-ol (9a)**[8]



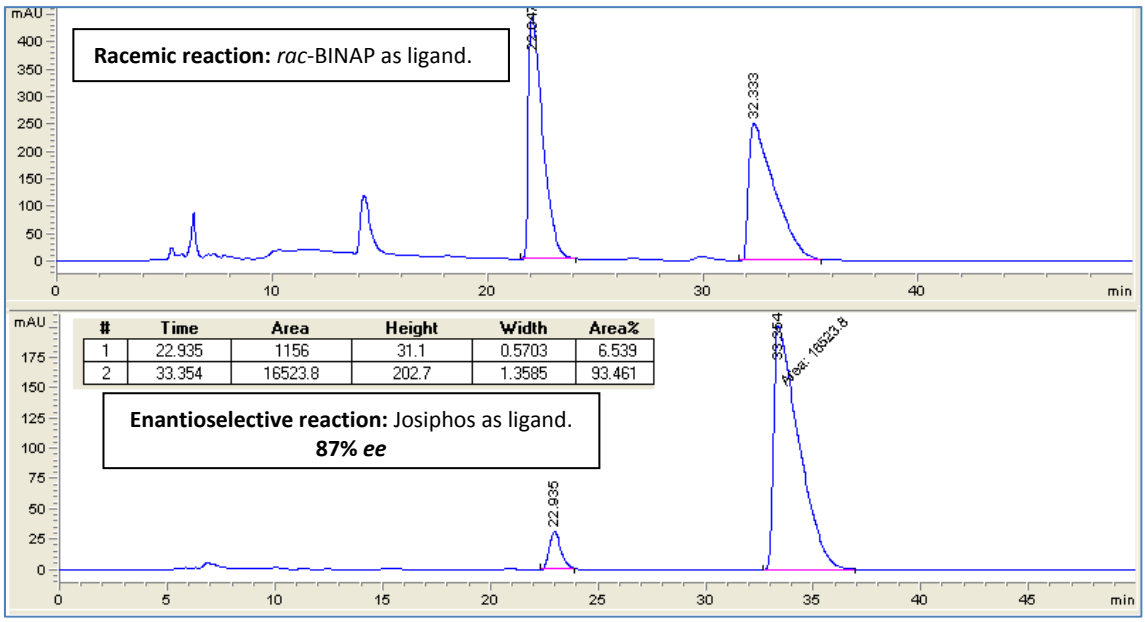
Following the general procedure, the conjugate boration of (1*E*)-3-methylbut-1-en-1-yl phenyl sulfone (42.0 mg, 0.20 mmol) afforded, after flash chromatography (20% EtOAc in hexanes), the product **9a** as a colorless oil.

Reaction with Josiphos ligand: yield: 18.2 mg (40%); 87% ee.

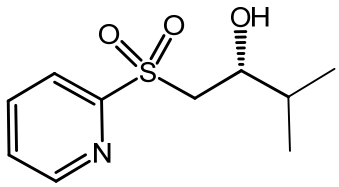
^{1}H NMR (300MHz): δ 7.86 - 8.01 (m, 2 H), 7.51 - 7.76 (m, 3 H), 3.87 - 4.04 (m, 1 H), 3.11 - 3.29 (m, 3 H), 1.66 - 1.82 (m, 1 H), 0.81 - 0.94 (m, 6 H). **^{13}C NMR** (75MHz): δ139.3, 134.0, 129.4, 127.9, 70.2, 60.1, 33.3, 17.9, 17.0. **HRMS-ESI** (*m/z*): Calcd. for $[C_{11}H_{16}O_3S+H]^+$ 229.0898, found 229.0887. **[α]$_D$**= –19.8 (*c 0.5,* CH_2Cl_2); lit[α]$_D$= –16.7 (*c* 0.98*,* EtOH, 94% ee sample)[12]

[12] C. Hiraoka, M. Matsuda, Y. Suzuki, S. Fujieda, M. Tomita, K. Fuhshuku, R. Obata, S. Nishiyama, T.Sugai, *Tetrahedron: Asymm*., 2006, **17**, 3358.

HPLC: Daicel Chiralpak IA, i-PrOH-hexane 20/80, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 22.9 (*S*-enantiomer); 33.3 **(*R*-enantiomer)**.



***(R)*-3-Methyl-1-(pyrid-2-ylsulfonyl)butan-2-ol (9b)**

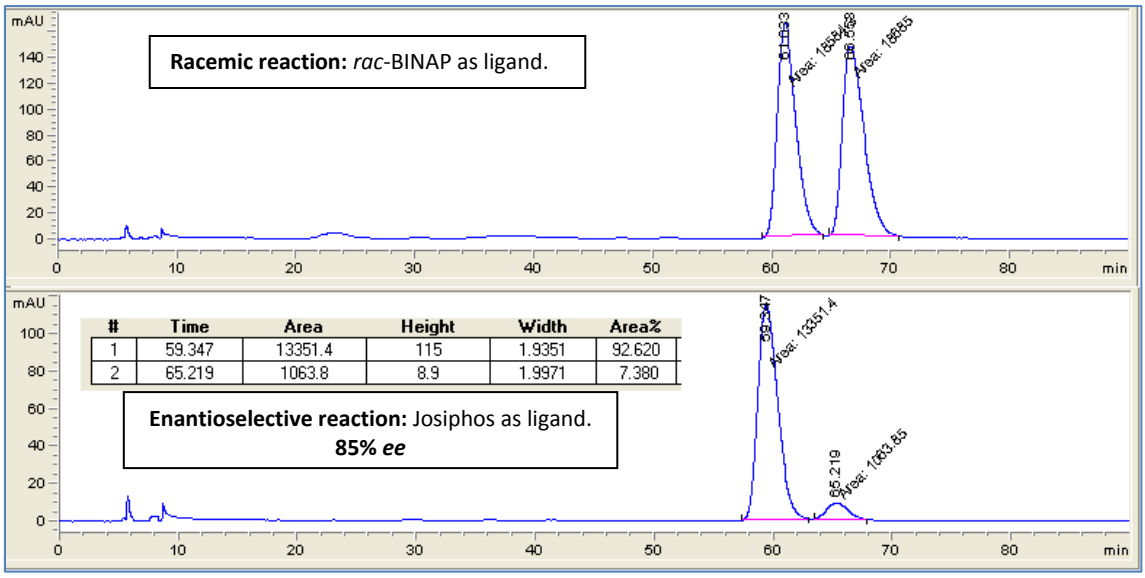


Following the general procedure, the conjugate boration of 2-{[(1*E*)-3-Methylbut-1-en-1-yl]sulfonyl}pyridine (42.2 mg, 0.20 mmol) afforded, after flash chromatography (40% EtOAc in hexanes), the product **9b** as a pale yellow oil.

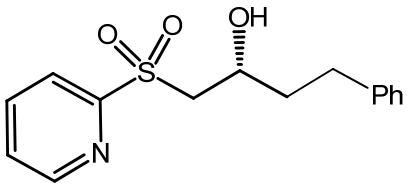
Reaction with Josiphos ligand: yield: 15.6 mg (34%); 85% ee

^{1}H NMR (300MHz): δ 8.73 (d, *J*=4.3 Hz, 1 H), 8.13 (d, *J*=8.1 Hz, 1 H), 8.00 (td, *J*=7.8, 1.5 Hz, 1 H), 7.58 (ddd, *J*=7.5, 4.7, 0.9 Hz, 1 H), 3.97 - 4.12 (m, 1 H), 3.65 - 3.73 (m, 1 H), 3.59 (dd, *J*=14.8, 1.1 Hz, 1 H), 3.42 (dd, *J*=14.7, 9.8 Hz, 1 H), 1.72 - 1.89 (m, 1 H), 0.88 - 0.98 (m, 6 H). **^{13}C NMR** (75MHz): δ 157.6, 149.9, 138.6, 127.6, 121.9, 70.3, 57.1, 33.4, 18.0, 17.2. **HRMS-ESI** (*m/z*): Calcd .for [$C_{10}H_{15}NO_3S$+H] 230.0845, found 230.0849. **$[\alpha]_D$**= –0.24 (*c* 0.5, CH_2Cl_2).

HPLC: Daicel Chiralpak AD, i-PrOH-hexane 10/90, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 59.3 **(*R*-enantiomer)**; 65.2 (*S*-enantiomer).



***(R)*-4-Phenyl-1-(pyrid-2-ylsulfonyl)butan-2-ol (10b)**



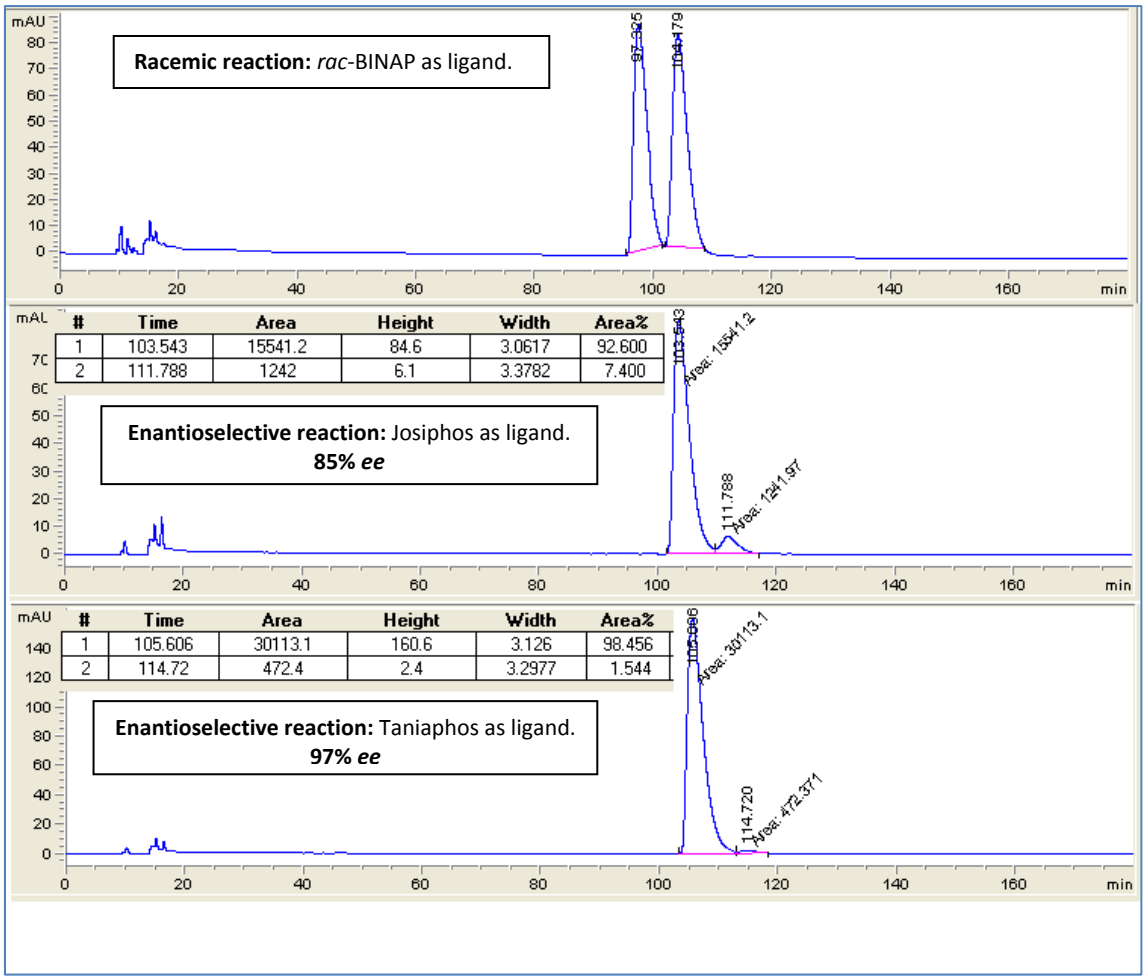
Following the general procedure, the conjugate boration of (*E*)-2-((4-phenylbut-1-en-1-yl)sulfonyl)pyridine (54.6 mg, 0.20 mmol) afforded, after flash chromatography (50% EtOAc in hexanes), the product **10b** as a white solid; mp : 64–66 °C.

Reaction with Josiphos ligand: yield: 50.1 mg (86%); 85% *ee*.

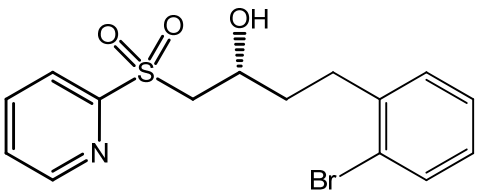
Reaction with Taniaphos ligand: yield: 43.1 mg (74%); 97% *ee.*

^{1}H NMR (300MHz): δ 8.73 (d, *J*=4.4 Hz, 1 H), 8.12 (d, *J*=7.8 Hz, 1 H), 8.00 (td, *J*=7.8, 1.7 Hz, 1 H), 7.59 (ddd, *J*=7.6, 4.8, 1.1 Hz, 1 H), 7.22 - 7.31 (m, 2 H), 7.12 - 7.21 (m, 3 H), 4.22 - 4.38 (m, 1 H), 3.81 - 3.92 (m, 1 H), 3.58 (dd, *J*=14.7, 2.0 Hz, 1 H), 3.48 (dd, *J*=14.7, 9.0 Hz, 1 H), 2.62 - 2.91 (m, 2 H), 1.73 - 2.03 (m, 2 H). **^{13}C NMR** (75MHz): δ 157.5, 149.9, 141.1, 138.6, 128.4, 128.3, 127.6, 126.0, 121.9, 65.3, 59.4, 38.0, 31.4. **HRMS-ESI** (*m/z*): Calcd. for [$C_{15}H_{17}NO_3S$+H] 292.1007, found 292.1000. **[α]$_D$**= + 1.2 (*c 1,* $CHCl_3$).

HPLC: Daicel Chiralpak AD, i-PrOH-hexane 10/90, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 103.5 **(*R*-enantiomer)**; 111.8 (*S*-enantiomer).



***(R)*-4-(2-bromophenyl)-1-(pyrid-2-ylsulfonyl)butan-2-ol (11b)**



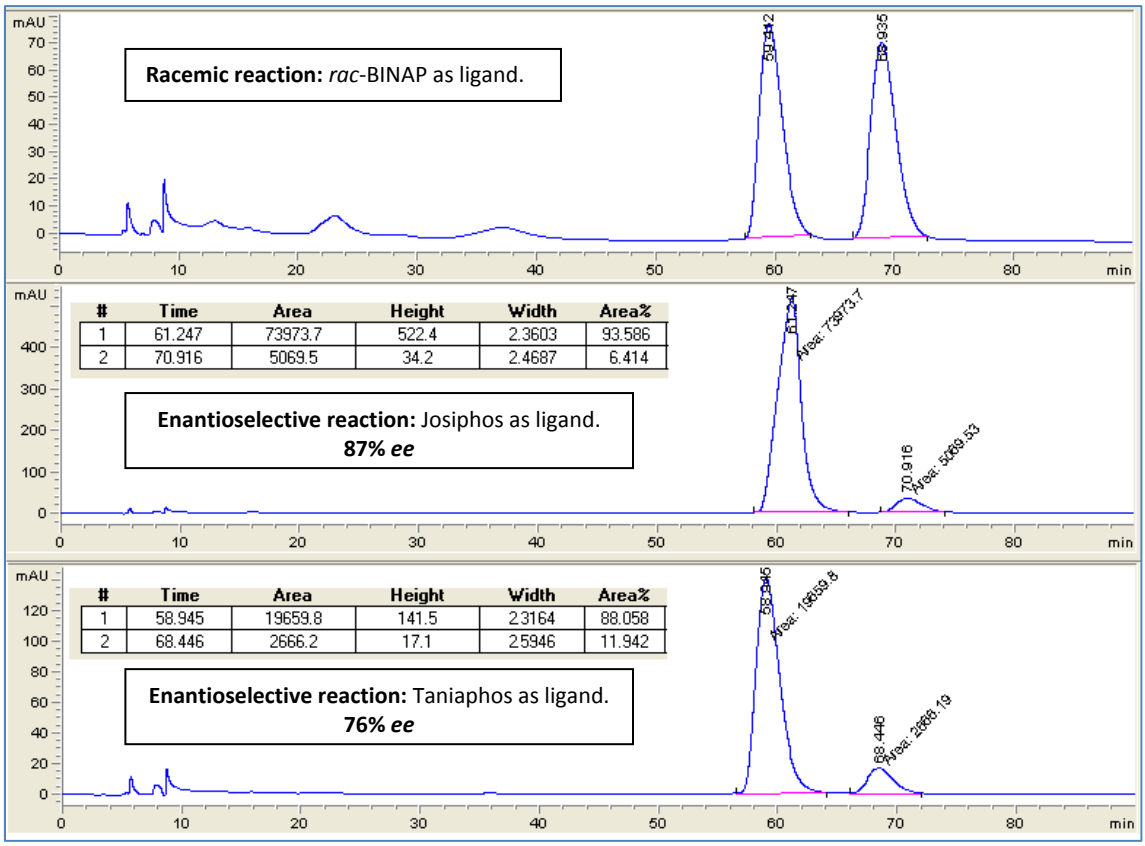
Following the general procedure, the conjugate boration of (*E*)-2-((4-(2-bromophenyl)but-1-en-1-yl)sulfonyl)pyridine (70.5 mg, 0.20 mmol) afforded, after flash chromatography (50% EtOAc in hexanes), the product **11b** as a colorless oil.

Reaction with Josiphos ligand: yield: 49.6 mg (67%); 87% *ee*.

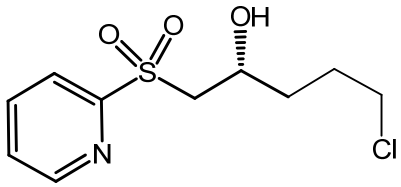
Reaction with Taniaphos ligand: yield: 40.7 mg (55%); 76% *ee.*

^{1}H NMR (300MHz): δ 8.73 (d, *J*=4.2 Hz, 1 H), 8.06 - 8.19 (m, *J*=7.8 Hz, 1 H), 8.01 (td, *J*=7.7, 1.5 Hz, 1 H), 7.55 - 7.63 (m, 1 H), 7.51 (d, *J*=8.1 Hz, 1 H), 7.16 - 7.25 (m, 2 H), 6.99 - 7.11 (m, 1 H), 4.23 - 4.43 (m, 1 H), 3.94 (br. s., 1 H), 3.41 - 3.68 (m, 2 H), 2.71 - 3.04 (m, 2 H), 1.72 - 2.07 (m, 2 H). **^{13}C NMR** (75MHz): δ 157.6, 150.0, 140.4, 138.6, 132.9, 130.5, 127.9, 127.7, 127.6, 124.3, 122.0, 65.4, 59.5, 36.3, 31.9. **HRMS-ESI** (*m/z*): Calcd. for [$C_{15}H_{16}BrNO_3S$+H] 370.0107, found 370.0109. **[α]$_D$**= + 0.10 (*c* 0.5, CH_2Cl_2).

HPLC: Daicel Chiralpak AD, i-PrOH-hexane 10/90, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 61.2 **(*R*-enantiomer)**; 70.9 (*S*-enantiomer).



***(R)*-5-Chloro-1-(pyrid-2-ylsulfonyl)pentan-2-ol (12b)**



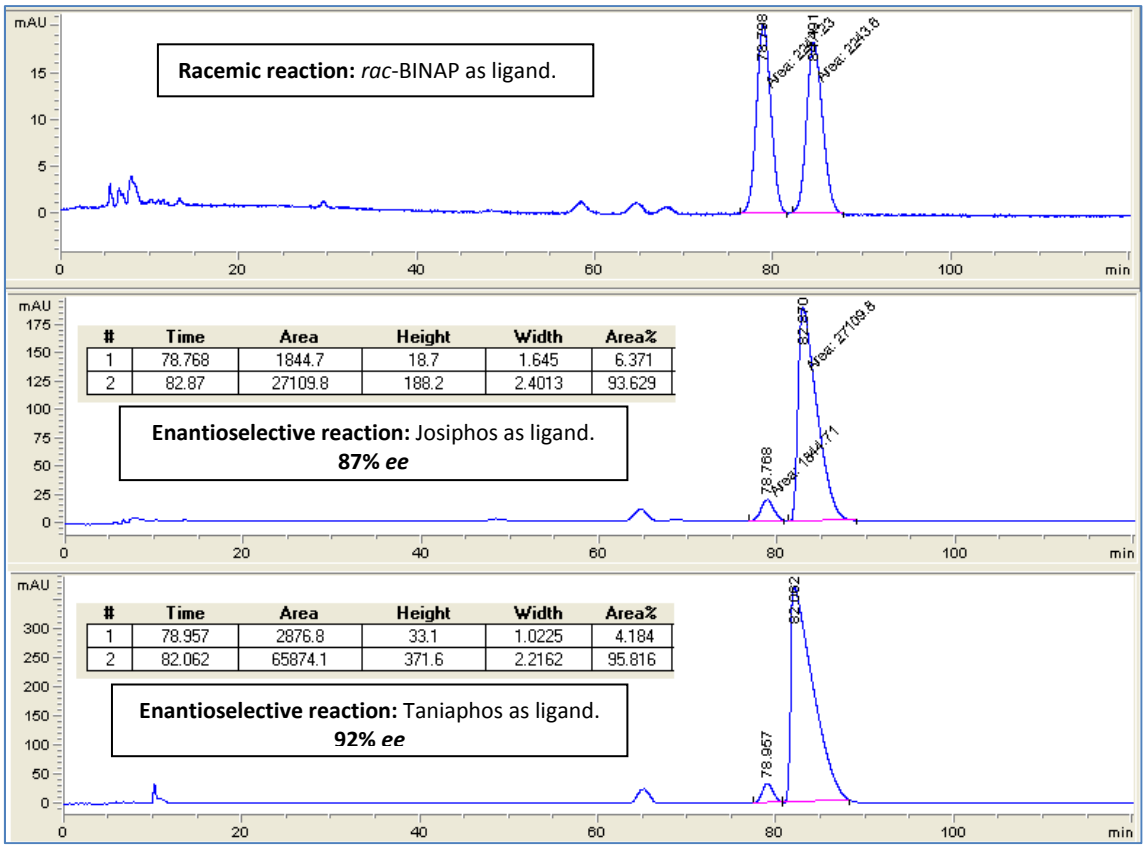
Following the general procedure, the conjugate boration of (*E*)-2-((5-chloropent-1-en-1-yl)sulfonyl)pyridine (49.1 mg, 0.20 mmol) afforded, after flash chromatography (50% EtOAc in hexanes), the product **12b** as a colorless oil.

Reaction with Josiphos ligand: yield: 46.9 mg (89%); 87% *ee*.

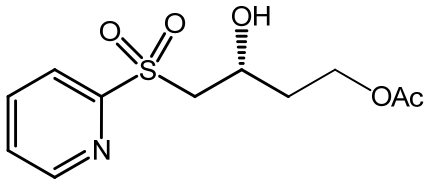
Reaction with Taniaphos ligand: yield: 38.0 mg (72%); 92% *ee.*

^{1}H NMR (300MHz): δ 8.74 (d, *J*=4.1 Hz, 1 H), 8.14 (d, *J*=7.8 Hz, 1 H), 8.02 (td, *J*=7.7, 1.4 Hz, 1 H), 7.56 - 7.65 (m, 1 H), 4.26 - 4.39 (m, 1 H), 3.90 - 4.00 (m, 1 H), 3.53 - 3.64 (m, 3 H), 3.47 (dd, *J*=14.6, 9.0 Hz, 1 H), 1.80 - 2.09 (m, 2 H), 1.65 - 1.78 (m, 2 H). **^{13}C NMR** (75MHz): δ 157.5, 150.0, 138.7, 127.8, 122.0, 65.4, 59.5, 44.6, 33.6, 28.3. **HRMS-ESI** (*m/z*): Calcd. for [$C_{10}H_{14}ClNO_3S$+H] 264.0455, found 264.0467. **[α]$_D$**= –0.26 (*c* 0.5, CH_2Cl_2).

HPLC: Daicel Chiralcel OJ-H, EtOH-hexane 10/90, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 59.3 (*S*-enantiomer); 65.2 **(*R*-enantiomer)**



***(R)*-3-Hydroxy-4-(pyrid-2-ylsulfonyl)butyl acetate (13b)**



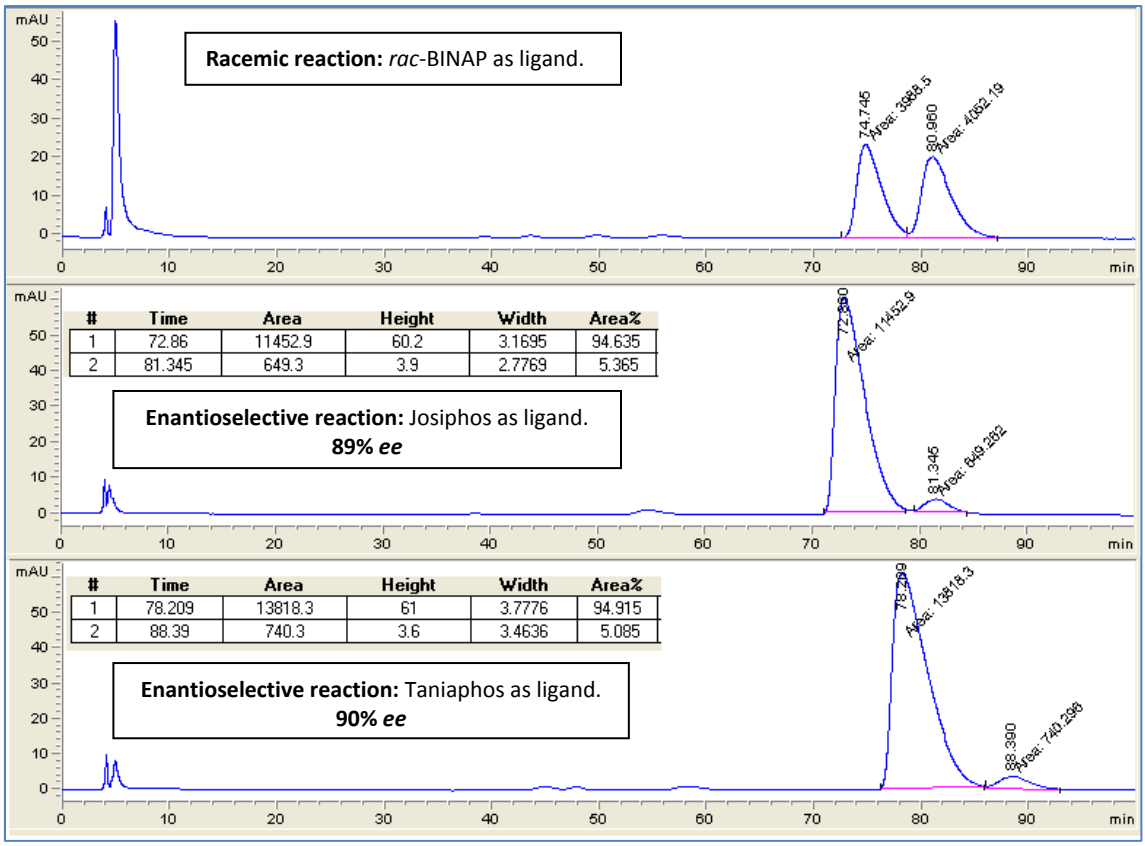
Following the general procedure, the conjugate boration of (*E*)-4-(pyrid-2-ylsulfonyl)but-3-en-1-yl acetate (51.0 mg, 0.20 mmol) afforded, after flash chromatography (40% EtOAc in hexanes), the product **13b** as a colorless oil.

Reaction with Josiphos ligand: yield: 40.4 mg (74%); 89% *ee*.

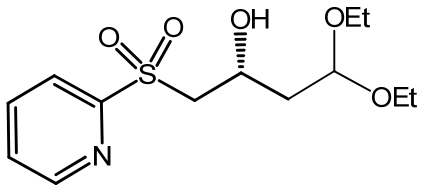
Reaction with Taniaphos ligand: yield: 34.4 mg (63%); 90% *ee.*

^{1}H NMR (300MHz): δ 8.73 (d, *J*=3.6 Hz, 1 H), 8.13 (d, *J*=7.9 Hz, 1 H), 8.01 (td, *J*=7.8, 1.5 Hz, 1 H), 7.54 - 7.66 (m, 1 H), 4.35 - 4.50 (m, 1 H), 4.13 - 4.33 (m, 2 H), 4.02 (br. s, 1 H), 3.48 - 3.62 (m, 2 H), 2.03 (s, 3 H), 1.79 - 1.93 (m, 2 H). **^{13}C NMR** (75MHz): δ 171.1, 157.4, 149.9, 138.7, 127.7, 122.0, 63.2, 60.4, 59.3, 35.2, 20.9. **HRMS-ESI** (*m/z*): Calcd. for $[C_{11}H_{15}NO_5S+H]$ 274.0743, found 274.0756. **$[\alpha]_D$**= –0.11 (*c* 0.5, CH_2Cl_2).

HPLC: Daicel Chiralpak AS-H, *i*-PrOH-hexane 20/80, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 72.9 **(*R*-enantiomer)**; 81.3 (*S*-enantiomer)



***(R)*-4,4-Diethoxy-1-(pyrid-2-ylsulfonyl)butan-2-ol (14b)**



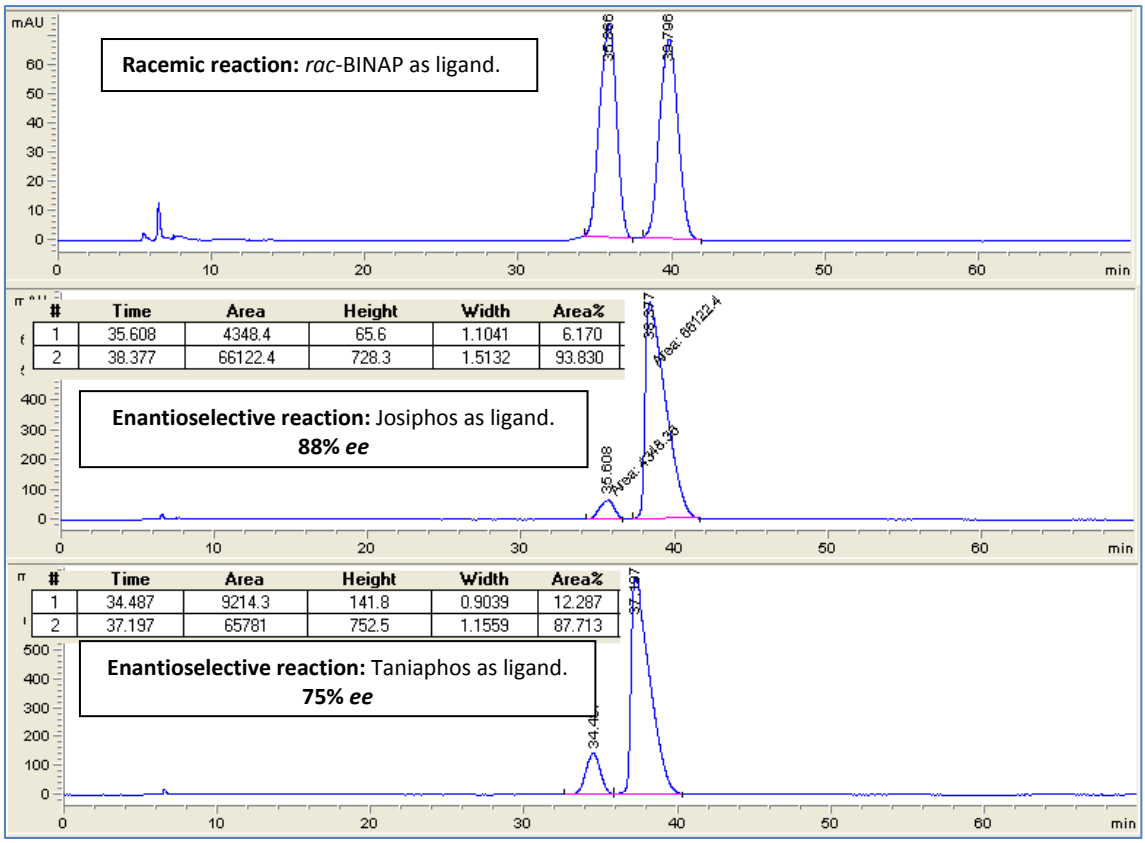
Following the general procedure, the conjugate boration of (*E*)-2-((4,4-diethoxybut-1-en-1-yl)sulfonyl)pyridine (57.1 mg, 0.20 mmol) afforded, after flash chromatography (50% EtOAc in hexanes), the product **14b** as a colorless oil.

Reaction with Josiphos ligand: yield: 49.1 mg (81%); 88% *ee*.

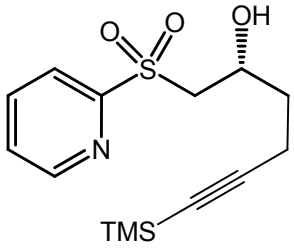
Reaction with Taniaphos ligand: yield: 43.7 mg (72%); 75% *ee.*

^{1}H NMR (300MHz): δ 8.74 (d, *J*=4.2 Hz, 1 H), 8.12 (d, *J*=7.9 Hz, 1 H), 7.98 (td, *J*=7.8, 1.5 Hz, 1 H), 7.51 - 7.61 (m, 1 H), 4.71 (t, *J*=5.4 Hz, 1 H), 4.35 - 4.52 (m, 1 H), 3.84 - 3.93 (m, 1 H), 3.41 - 3.74 (m, 6 H), 1.82 - 1.94 (m, 2 H), 1.18 (t, *J*=7.1 Hz, 6 H). **^{13}C NMR** (C75MHz): d = 157.7, 150.0, 138.4, 127.5, 122.0, 100.9, 63.5, 62.3, 62.2, 58.9, 40.0, 15.3. **HRMS-ESI** (*m/z*): Calcd. for [$C_{13}H_{21}NO_5S$+Na] 326.1032, found 326.1035. **[α]$_D$**= –0.12(*c* 0.5, CH_2Cl_2).

HPLC: Daicel Chiralcel OJ-H, EtOH-hexane 10/90, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 35.6 (*S*-enantiomer); 38.3 **(*R*-enantiomer)**



***(R)*-1-(Pyrid-2-ylsulfonyl)-6-(trimethylsilyl)hex-5-yn-2-ol (15b)**



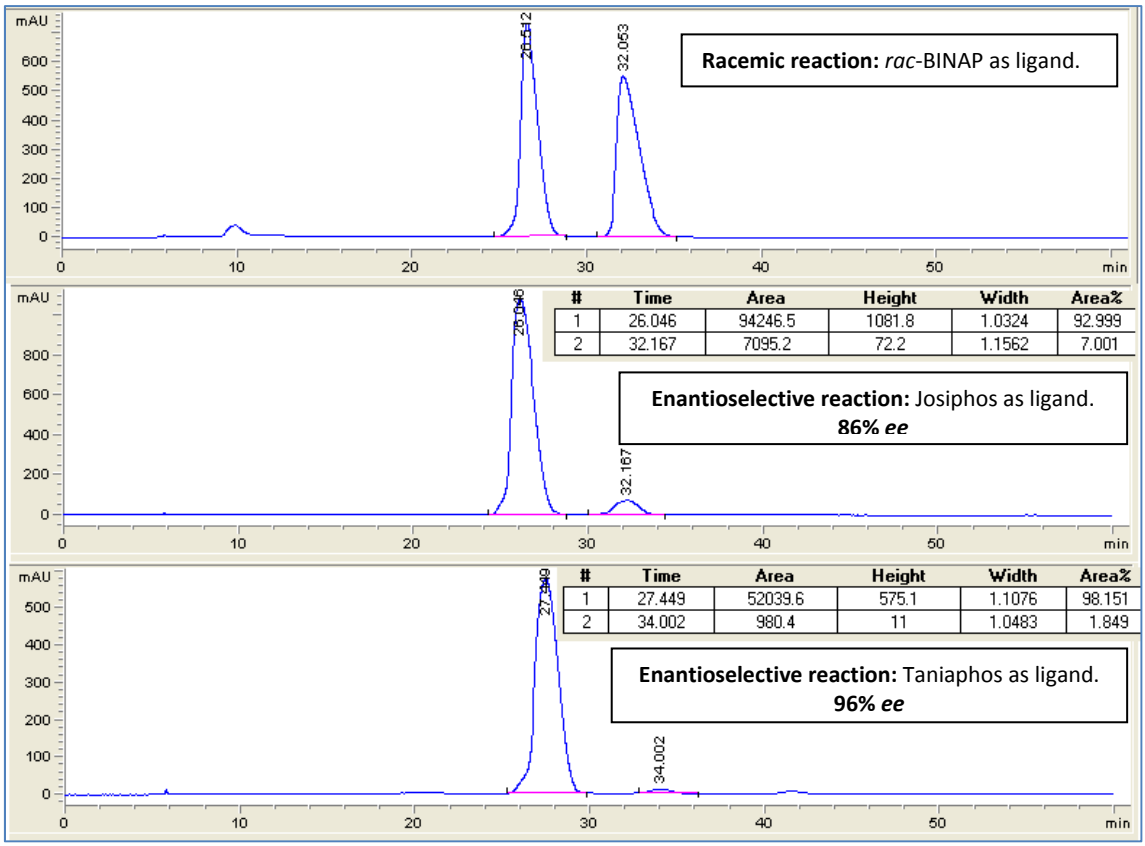
Following the general procedure, the conjugate boration of (*E*)-2-((6-(Trimethylsilyl)hex-1-en-5-yn-1-yl)sulfonyl)pyridine (58.7 mg, 0.20 mmol) afforded, after flash chromatography (50% EtOAc in hexanes), the product **15b** as a colorless oil.

Reaction with Josiphos ligand: yield: 59.2 mg (95%); 86% *ee*.

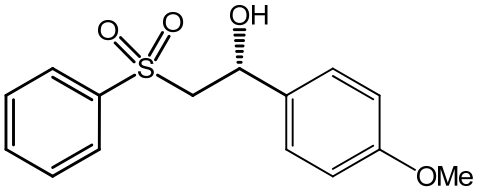
Reaction with Taniaphos ligand: yield: 43.6 mg (70%); 96% *ee*.

^{1}H NMR (300MHz): δ 8.73 (d, *J*=4.2 Hz, 1 H), 8.13 (d, *J*=7.6 Hz, 1 H), 8.01 (td, *J*=7.8, 1.4 Hz, 1 H), 7.54 - 7.64 (m, 1 H), 4.31 - 4.46 (m, 1 H), 3.89 (br. s., 1 H), 3.63 (dd, *J*=14.8, 1.9 Hz, 1 H), 3.51 (dd, *J*=14.9, 9.2 Hz, 1 H), 2.39 (t, *J*=7.0 Hz, 2 H), 1.66 - 1.86 (m, 2 H), 0.10 (s, 9 H). **^{13}C NMR** (75MHz): δ 157.5, 150.0, 138.6, 127.6, 121.9, 105.9, 85.6, 65.0, 59.1, 35.0, 15.8, 0.0. **HRMS-ESI** (*m/z*): Calcd. for [$C_{14}H_{21}NO_3SSi$+H] 312.1084, found 312.1084. **$[\alpha]_D$**= +0.28(*c 1,* CH_2Cl_2).

HPLC: Daicel Chiralpak AS-H, EtOH-hexane 10/90, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 26.0 **(*R*-enantiomer)**; 32.1min (*S*-enantiomer).



***(R)*-1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethanol (18a)**[8]

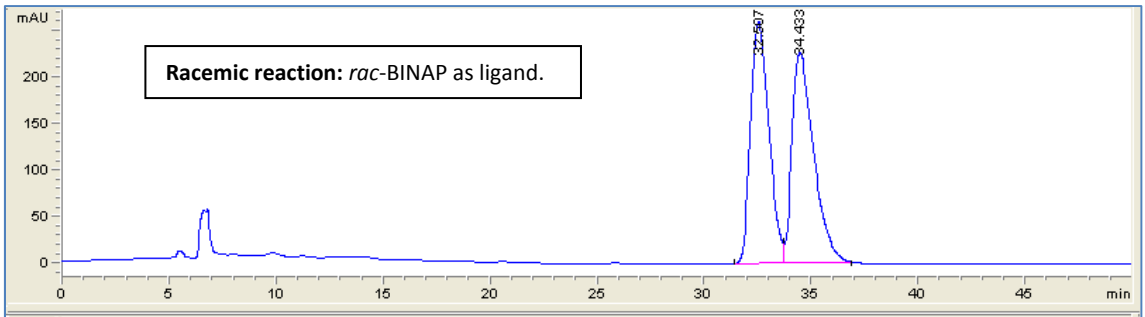


Following the general procedure, the conjugate boration of (*E*)-2-(4-methoxyphenyl)ethenyl phenyl sulfone (54.9 mg, 0.20 mmol) afforded, after flash chromatography (30% EtOAc in hexanes), the product **18a** as a white solid.

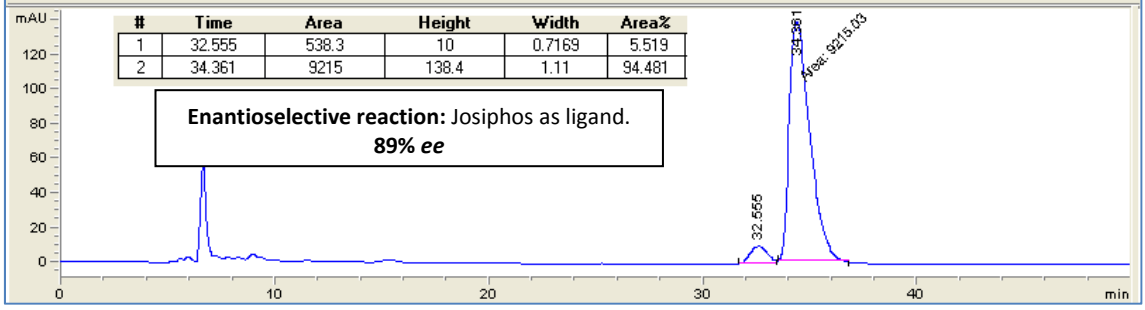
Reaction with Josiphos ligand: yield:42.1 mg (72%); 89% *ee*.

^{1}H NMR (300MHz): δ 7.96 (d, *J*=7.7 Hz, 2 H), 7.52 - 7.77 (m, 3 H), 7.21 (d, *J*=8.6 Hz, 2 H), 6.84 (d, *J*=8.6 Hz, 2 H), 5.23 (d, *J*=9.9 Hz, 1 H), 3.78 (s, 3 H), 3.57 (s, 1 H), 3.50 (dd, *J*=14.3, 10.0 Hz, 1 H), 3.33 (d, *J*=14.1 Hz, 1 H). **^{13}C NMR** (75MHz): δ 159.6, 139.3, 134.0, 132.8, 129.4, 127.9, 126.9, 114.1, 68.1, 63.9, 55.3. **HRMS-ESI** (*m/z*): Calcd. for $[C_{15}H_{16}O_3S+Na]^+$ 315.0667, found 315.0669. **$[\alpha]_D$** = −13.9 (*c 1,* CH_2Cl_2); lit$[\alpha]_D$= +31.8 (c 2.15, CH_2Cl_2, 94% ee sample, S-enantiomer)[9]

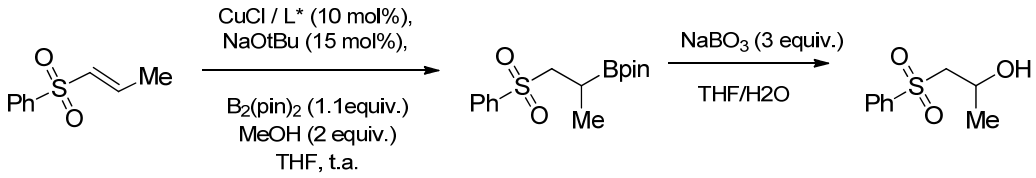
HPLC: Daicel Chiralpak AD, i-PrOH-hexane 20/80, flow rate 0.7 mL/min (λ= 254 nm), t_R (min): 32.5 (*S*-enantiomer); 34.3 **(*R*-enantiomer)**.



#	Time	Area	Height	Width	Area%
1	32.555	538.3	10	0.7169	5.519
2	34.361	9215	138.4	1.11	94.481

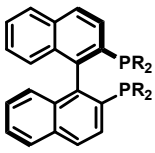


Chiral ligand screening

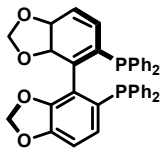


Entry	Ligand (12 mol%)	Conv. (%)[a]	Yield(%)	*ee* (%)
1	*(R)*-Binap	100	85	60
2	*(R)*-Tol-Binap	90	--	53
3	*(R)*-Segphos	100	80	60
4	*(R)*-DTBM-Segphos	100	82	86
5	*(R,R)*-Quinoxp	100	--	33
6	*(S)*-Quinap	89	--	40
7	*(R)*-Fesulphos	92	--	5
8	*(R, S)*-Josiphos **I**	100	90	91
9	*(R, S)*-Josiphos **I**[b]	100	81	91
10	*(R, S)*-Josiphos **II**	33	--	15
11	*(R, S)*-Josiphos **III**	81	--	47
12	*(R, R)*-Taniaphos **I**	100	72	94
13	*(R, R)*-Taniaphos **I** [b]	100	62	94
14	*(R, R)*-Taniaphos **II**	67	--	9
15	*(R, R)*-Walphos	76	--	40
16	*(S, R)*-Mandyphos	100	--	1

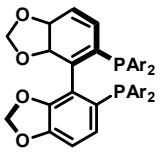
a) Determined by NMR from the crude reaction mixture. b) CuCl 5 mol%, NaOtBu 7,5 mol%, ligand 5 mol%.



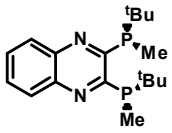
(*R*)-Binap, R=Ph
(*R*)-Tol-Binap, R=p-Tolyl



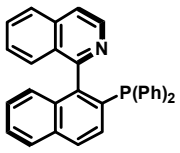
(*R*)-Segphos



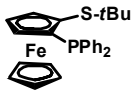
(*R*)-DBTM-Segphos
Ar = 3,5-di-tert-butyl-4-methoxyphenyl



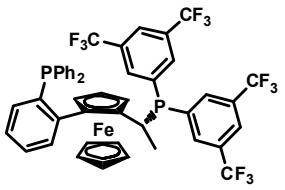
(R,R)-QuinoxP*



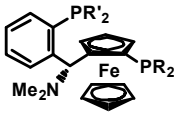
(R)-Quinap



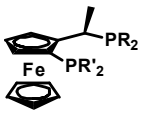
(*R*)-Fesulphos



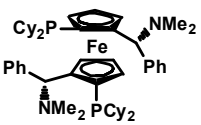
(*R,R*)-Walphos



(*R,R*)-Taniaphos
I, R=R'=Ph
II, R=R'=Cy



(*R,S*)-Josiphos
I, R=Cy, R'=Ph
II, R=R'=Cy
III, R=3,5-dimethylphenyl, R'=Ph



(*S,R*)-Mandyphos

X-Ray data

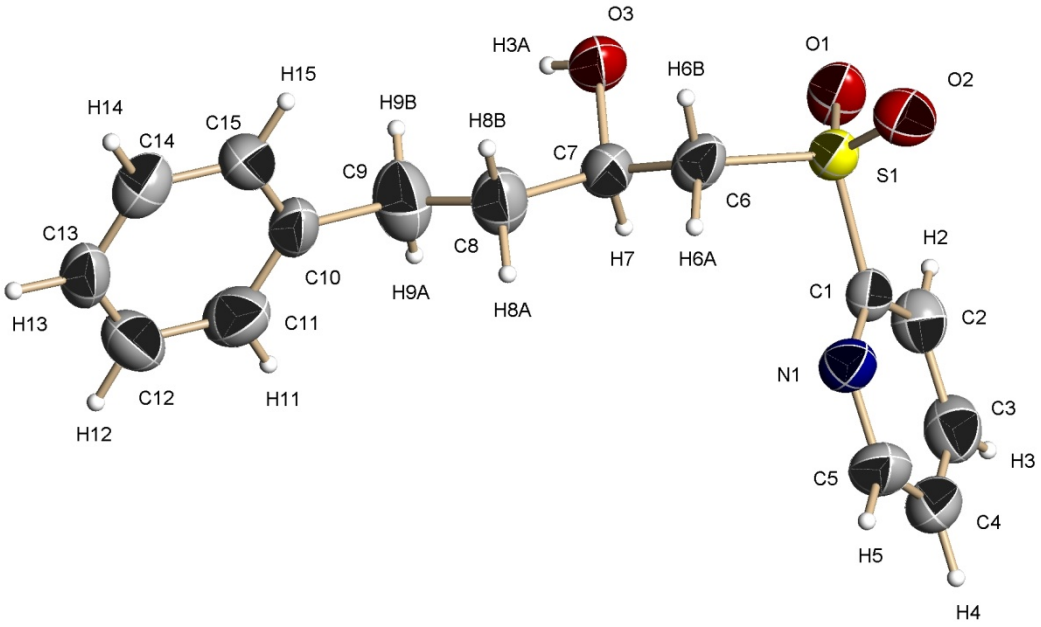


Table 1. Crystal data and structure refinement for **10b**

Empirical formula	C15 H17 N O3 S	
Formula weight	291.36	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.1538(11) Å	α= 90°.
	b = 21.310(4) Å	β= 95.366(8)°.
	c = 11.187(2) Å	γ = 90°.

Volume	1460.6(5) $Å^3$
Z	4
Density (calculated)	1.325 Mg/m^3
Absorption coefficient	0.228 mm^{-1}
F(000)	616
Crystal size	0.24 x 0.18 x 0.16 mm^3
Theta range for data collection	1.83 to 27.88°.
Index ranges	-8<=h<=8, -28<=k<=28, -14<=l<=14
Reflections collected	51919
Independent reflections	6941 [R(int) = 0.0284]
Completeness to theta = 27.88°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9644 and 0.9473
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6941 / 1 / 361
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0524, wR2 = 0.1481
R indices (all data)	R1 = 0.0591, wR2 = 0.1592
Absolute structure parameter	0.01(8)
Largest diff. peak and hole	0.724 and -0.267 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **10b** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2279(1)	1592(1)	2499(1)	43(1)
S(2)	2541(1)	3966(1)	-2453(1)	44(1)
C(1)	3994(4)	2101(1)	3443(2)	39(1)
C(2)	6062(5)	2235(2)	3171(3)	52(1)
C(3)	7237(6)	2673(2)	3877(4)	64(1)
C(4)	6299(6)	2944(2)	4813(4)	63(1)
C(5)	4175(6)	2765(2)	5024(3)	60(1)
C(6)	1085(6)	1090(2)	3508(3)	51(1)
C(7)	2473(6)	548(2)	3979(3)	56(1)

C(8)	1355(7)	252(2)	5031(3)	66(1)
C(9)	2545(8)	-326(2)	5478(4)	77(1)
C(10)	1457(7)	-645(2)	6494(3)	61(1)
C(11)	2620(7)	-709(2)	7563(4)	69(1)
C(12)	1907(7)	-1047(2)	8483(3)	70(1)
C(13)	-75(7)	-1322(2)	8362(3)	62(1)
C(14)	-1423(6)	-1244(2)	7308(4)	62(1)
C(15)	-638(7)	-904(2)	6372(3)	66(1)
C(16)	4227(4)	3409(1)	-1599(3)	42(1)
C(17)	6354(5)	3305(2)	-1830(3)	54(1)
C(18)	7465(6)	2837(2)	-1180(4)	70(1)
C(19)	6458(7)	2504(2)	-366(4)	75(1)
C(20)	4316(7)	2648(2)	-194(4)	72(1)
C(21)	1637(5)	4509(2)	-1385(3)	51(1)
C(22)	3044(6)	5083(2)	-1178(3)	55(1)
C(23)	2155(6)	5561(2)	-339(3)	60(1)
C(24)	1682(9)	5316(2)	871(3)	77(1)
C(25)	1156(7)	5828(2)	1726(3)	60(1)
C(26)	2731(7)	6026(2)	2641(4)	72(1)
C(27)	2266(8)	6491(2)	3438(4)	75(1)
C(28)	275(8)	6770(2)	3342(4)	69(1)
C(29)	-1277(7)	6605(2)	2433(4)	75(1)
C(30)	-815(7)	6132(2)	1643(4)	75(1)
N(1)	3022(4)	2347(1)	4349(2)	49(1)
N(2)	3176(4)	3097(2)	-795(3)	56(1)
O(1)	3663(4)	1255(1)	1753(2)	59(1)
O(2)	543(4)	1961(1)	1905(2)	60(1)
O(3)	2549(4)	114(1)	3010(2)	57(1)
O(4)	677(4)	3631(1)	-2993(2)	58(1)
O(5)	3856(4)	4287(1)	-3263(2)	59(1)
O(6)	5168(4)	4881(1)	-735(2)	68(1)

Table 3. Bond lengths [Å] and angles [°] for **10b**

S(1)-O(1)	1.439(2)

S(1)-O(2)	1.439(3)
S(1)-C(6)	1.764(3)
S(1)-C(1)	1.789(3)
S(2)-O(4)	1.435(2)
S(2)-O(5)	1.443(2)
S(2)-C(21)	1.789(3)
S(2)-C(16)	1.792(3)
C(1)-N(1)	1.331(4)
C(1)-C(2)	1.366(4)
C(2)-C(3)	1.382(5)
C(2)-H(2)	0.9300
C(3)-C(4)	1.370(6)
C(3)-H(3)	0.9300
C(4)-C(5)	1.403(5)
C(4)-H(4)	0.9300
C(5)-N(1)	1.329(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.502(5)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-O(3)	1.429(4)
C(7)-C(8)	1.551(5)
C(7)-H(7)	0.9800
C(8)-C(9)	1.496(5)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.531(5)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.342(6)
C(10)-C(15)	1.398(6)
C(11)-C(12)	1.363(6)
C(11)-H(11)	0.9300
C(12)-C(13)	1.348(6)
C(12)-H(12)	0.9300
C(13)-C(14)	1.387(6)
C(13)-H(13)	0.9300
C(14)-C(15)	1.395(5)

C(14)-H(14)	0.9300
C(15)-H(15)	0.9300
C(16)-N(2)	1.333(4)
C(16)-C(17)	1.376(4)
C(17)-C(18)	1.378(6)
C(17)-H(17)	0.9300
C(18)-C(19)	1.350(7)
C(18)-H(18)	0.9300
C(19)-C(20)	1.384(6)
C(19)-H(19)	0.9300
C(20)-N(2)	1.332(5)
C(20)-H(20)	0.9300
C(21)-C(22)	1.504(5)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-O(6)	1.420(4)
C(22)-C(23)	1.522(4)
C(22)-H(22)	0.9800
C(23)-C(24)	1.504(5)
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(24)-C(25)	1.506(5)
C(24)-H(24A)	0.9700
C(24)-H(24B)	0.9700
C(25)-C(30)	1.370(6)
C(25)-C(26)	1.407(6)
C(26)-C(27)	1.381(6)
C(26)-H(26)	0.9300
C(27)-C(28)	1.357(6)
C(27)-H(27)	0.9300
C(28)-C(29)	1.373(7)
C(28)-H(28)	0.9300
C(29)-C(30)	1.388(6)
C(29)-H(29)	0.9300
C(30)-H(30)	0.9300
O(3)-H(3A)	0.8200
O(6)-H(6)	0.8200

O(1)-S(1)-O(2)	117.34(15)
O(1)-S(1)-C(6)	111.93(16)
O(2)-S(1)-C(6)	106.95(16)
O(1)-S(1)-C(1)	107.25(14)
O(2)-S(1)-C(1)	108.18(15)
C(6)-S(1)-C(1)	104.37(14)
O(4)-S(2)-O(5)	116.41(14)
O(4)-S(2)-C(21)	108.42(15)
O(5)-S(2)-C(21)	109.86(16)
O(4)-S(2)-C(16)	107.22(15)
O(5)-S(2)-C(16)	108.57(15)
C(21)-S(2)-C(16)	105.84(14)
N(1)-C(1)-C(2)	125.6(3)
N(1)-C(1)-S(1)	113.9(2)
C(2)-C(1)-S(1)	120.4(2)
C(1)-C(2)-C(3)	117.5(3)
C(1)-C(2)-H(2)	121.2
C(3)-C(2)-H(2)	121.2
C(4)-C(3)-C(2)	119.1(3)
C(4)-C(3)-H(3)	120.4
C(2)-C(3)-H(3)	120.4
C(3)-C(4)-C(5)	118.6(3)
C(3)-C(4)-H(4)	120.7
C(5)-C(4)-H(4)	120.7
N(1)-C(5)-C(4)	122.9(3)
N(1)-C(5)-H(5)	118.5
C(4)-C(5)-H(5)	118.5
C(7)-C(6)-S(1)	115.7(2)
C(7)-C(6)-H(6A)	108.4
S(1)-C(6)-H(6A)	108.4
C(7)-C(6)-H(6B)	108.4
S(1)-C(6)-H(6B)	108.4
H(6A)-C(6)-H(6B)	107.4
O(3)-C(7)-C(6)	106.8(3)
O(3)-C(7)-C(8)	111.1(3)
C(6)-C(7)-C(8)	107.5(3)
O(3)-C(7)-H(7)	110.4
C(6)-C(7)-H(7)	110.4

C(8)-C(7)-H(7)	110.4
C(9)-C(8)-C(7)	110.5(3)
C(9)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8A)	109.5
C(9)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	108.1
C(8)-C(9)-C(10)	112.3(3)
C(8)-C(9)-H(9A)	109.1
C(10)-C(9)-H(9A)	109.1
C(8)-C(9)-H(9B)	109.1
C(10)-C(9)-H(9B)	109.1
H(9A)-C(9)-H(9B)	107.9
C(11)-C(10)-C(15)	117.2(3)
C(11)-C(10)-C(9)	118.2(4)
C(15)-C(10)-C(9)	124.5(3)
C(10)-C(11)-C(12)	123.0(4)
C(10)-C(11)-H(11)	118.5
C(12)-C(11)-H(11)	118.5
C(13)-C(12)-C(11)	120.4(4)
C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8
C(12)-C(13)-C(14)	119.8(3)
C(12)-C(13)-H(13)	120.1
C(14)-C(13)-H(13)	120.1
C(13)-C(14)-C(15)	118.6(3)
C(13)-C(14)-H(14)	120.7
C(15)-C(14)-H(14)	120.7
C(14)-C(15)-C(10)	120.9(3)
C(14)-C(15)-H(15)	119.6
C(10)-C(15)-H(15)	119.6
N(2)-C(16)-C(17)	125.2(3)
N(2)-C(16)-S(2)	113.4(2)
C(17)-C(16)-S(2)	121.3(3)
C(16)-C(17)-C(18)	116.8(3)
C(16)-C(17)-H(17)	121.6
C(18)-C(17)-H(17)	121.6
C(19)-C(18)-C(17)	120.0(3)

C(19)-C(18)-H(18)	120.0
C(17)-C(18)-H(18)	120.0
C(18)-C(19)-C(20)	118.7(4)
C(18)-C(19)-H(19)	120.7
C(20)-C(19)-H(19)	120.7
N(2)-C(20)-C(19)	123.5(4)
N(2)-C(20)-H(20)	118.2
C(19)-C(20)-H(20)	118.2
C(22)-C(21)-S(2)	114.8(2)
C(22)-C(21)-H(21A)	108.6
S(2)-C(21)-H(21A)	108.6
C(22)-C(21)-H(21B)	108.6
S(2)-C(21)-H(21B)	108.6
H(21A)-C(21)-H(21B)	107.6
O(6)-C(22)-C(21)	107.8(3)
O(6)-C(22)-C(23)	111.1(3)
C(21)-C(22)-C(23)	113.9(3)
O(6)-C(22)-H(22)	108.0
C(21)-C(22)-H(22)	108.0
C(23)-C(22)-H(22)	108.0
C(24)-C(23)-C(22)	115.7(3)
C(24)-C(23)-H(23A)	108.4
C(22)-C(23)-H(23A)	108.4
C(24)-C(23)-H(23B)	108.4
C(22)-C(23)-H(23B)	108.4
H(23A)-C(23)-H(23B)	107.4
C(23)-C(24)-C(25)	113.0(3)
C(23)-C(24)-H(24A)	109.0
C(25)-C(24)-H(24A)	109.0
C(23)-C(24)-H(24B)	109.0
C(25)-C(24)-H(24B)	109.0
H(24A)-C(24)-H(24B)	107.8
C(30)-C(25)-C(26)	117.0(3)
C(30)-C(25)-C(24)	122.7(4)
C(26)-C(25)-C(24)	120.3(4)
C(27)-C(26)-C(25)	121.0(4)
C(27)-C(26)-H(26)	119.5
C(25)-C(26)-H(26)	119.5

C(28)-C(27)-C(26)	120.2(4)
C(28)-C(27)-H(27)	119.9
C(26)-C(27)-H(27)	119.9
C(27)-C(28)-C(29)	120.5(4)
C(27)-C(28)-H(28)	119.8
C(29)-C(28)-H(28)	119.8
C(28)-C(29)-C(30)	119.2(4)
C(28)-C(29)-H(29)	120.4
C(30)-C(29)-H(29)	120.4
C(25)-C(30)-C(29)	122.2(4)
C(25)-C(30)-H(30)	118.9
C(29)-C(30)-H(30)	118.9
C(5)-N(1)-C(1)	116.2(3)
C(20)-N(2)-C(16)	115.7(3)
C(7)-O(3)-H(3A)	109.5
C(22)-O(6)-H(6)	109.5

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **10b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	51(1)	40(1)	40(1)	-3(1)	13(1)	-4(1)
S(2)	48(1)	49(1)	36(1)	-1(1)	11(1)	-1(1)
C(1)	43(1)	35(1)	41(1)	3(1)	8(1)	1(1)
C(2)	44(1)	57(2)	56(2)	7(2)	13(1)	1(1)
C(3)	49(2)	74(2)	69(2)	18(2)	-2(2)	-15(2)
C(4)	72(2)	55(2)	60(2)	5(2)	-8(2)	-19(2)
C(5)	78(2)	54(2)	50(2)	-12(1)	10(2)	-7(2)
C(6)	61(2)	43(2)	54(2)	-6(1)	22(1)	-10(1)
C(7)	81(2)	44(2)	45(2)	-2(1)	11(1)	-11(2)
C(8)	94(3)	50(2)	57(2)	3(2)	24(2)	6(2)
C(9)	90(3)	72(3)	73(2)	18(2)	30(2)	11(2)
C(10)	94(2)	44(2)	46(2)	1(1)	21(2)	-12(2)
C(11)	69(2)	70(3)	69(2)	-9(2)	11(2)	-19(2)
C(12)	87(3)	71(2)	49(2)	3(2)	-3(2)	6(2)

C(13)	93(3)	45(2)	51(2)	4(1)	26(2)	-3(2)
C(14)	64(2)	49(2)	75(2)	-2(2)	16(2)	-6(1)
C(15)	92(3)	54(2)	51(2)	4(2)	-7(2)	-7(2)
C(16)	41(1)	45(1)	40(1)	-11(1)	9(1)	-4(1)
C(17)	38(1)	79(2)	47(2)	-13(2)	12(1)	-2(1)
C(18)	49(2)	86(3)	75(2)	-25(2)	5(2)	16(2)
C(19)	77(2)	70(2)	73(2)	-6(2)	-18(2)	20(2)
C(20)	71(2)	75(3)	70(2)	20(2)	5(2)	3(2)
C(21)	50(2)	56(2)	49(2)	-5(1)	12(1)	10(1)
C(22)	73(2)	49(2)	45(2)	-4(1)	14(1)	9(2)
C(23)	78(2)	45(2)	58(2)	-3(1)	17(2)	6(2)
C(24)	130(4)	48(2)	56(2)	-1(2)	26(2)	1(2)
C(25)	83(2)	52(2)	49(2)	-4(1)	21(2)	-5(2)
C(26)	71(2)	74(3)	72(2)	-11(2)	12(2)	8(2)
C(27)	88(3)	75(3)	62(2)	-14(2)	1(2)	-8(2)
C(28)	101(3)	56(2)	54(2)	-9(2)	30(2)	-4(2)
C(29)	71(2)	73(2)	85(3)	-2(2)	25(2)	11(2)
C(30)	80(3)	78(3)	65(2)	-15(2)	3(2)	-2(2)
N(1)	54(1)	47(1)	47(1)	-8(1)	14(1)	-3(1)
N(2)	46(1)	64(2)	60(2)	14(1)	16(1)	3(1)
O(1)	77(2)	50(1)	55(1)	-8(1)	33(1)	0(1)
O(2)	57(1)	63(2)	57(1)	0(1)	-5(1)	-1(1)
O(3)	78(2)	45(1)	50(1)	-7(1)	13(1)	0(1)
O(4)	48(1)	74(2)	53(1)	-3(1)	1(1)	-6(1)
O(5)	73(1)	64(2)	41(1)	1(1)	15(1)	-13(1)
O(6)	59(1)	80(2)	64(1)	-8(1)	2(1)	7(1)

Table 5.Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **10b**

	x	y	z	U(eq)
H(2)	6658	2039	2535	62
H(3)	8645	2781	3719	77
H(4)	7055	3241	5298	76

H(5)	3546	2946	5665	72
H(6A)	706	1338	4186	62
H(6B)	-261	925	3109	62
H(7)	3946	692	4258	68
H(8A)	1339	554	5680	79
H(8B)	-144	147	4761	79
H(9A)	4033	-216	5764	92
H(9B)	2601	-619	4819	92
H(11)	3975	-514	7680	83
H(12)	2793	-1089	9199	84
H(13)	-537	-1563	8983	74
H(14)	-2821	-1414	7227	74
H(15)	-1521	-849	5659	80
H(17)	7011	3540	-2398	65
H(18)	8909	2750	-1302	84
H(19)	7190	2184	70	90
H(20)	3637	2419	373	87
H(21A)	166	4642	-1657	61
H(21B)	1577	4294	-625	61
H(22)	3150	5287	-1956	66
H(23A)	3199	5901	-217	72
H(23B)	818	5736	-732	72
H(24A)	2941	5084	1220	92
H(24B)	460	5028	767	92
H(26)	4105	5840	2711	87
H(27)	3321	6613	4042	90
H(28)	-41	7075	3894	83
H(29)	-2620	6808	2349	90
H(30)	-1878	6017	1037	89
H(3A)	3296	-190	3237	86
H(6)	5995	4917	-1265	102

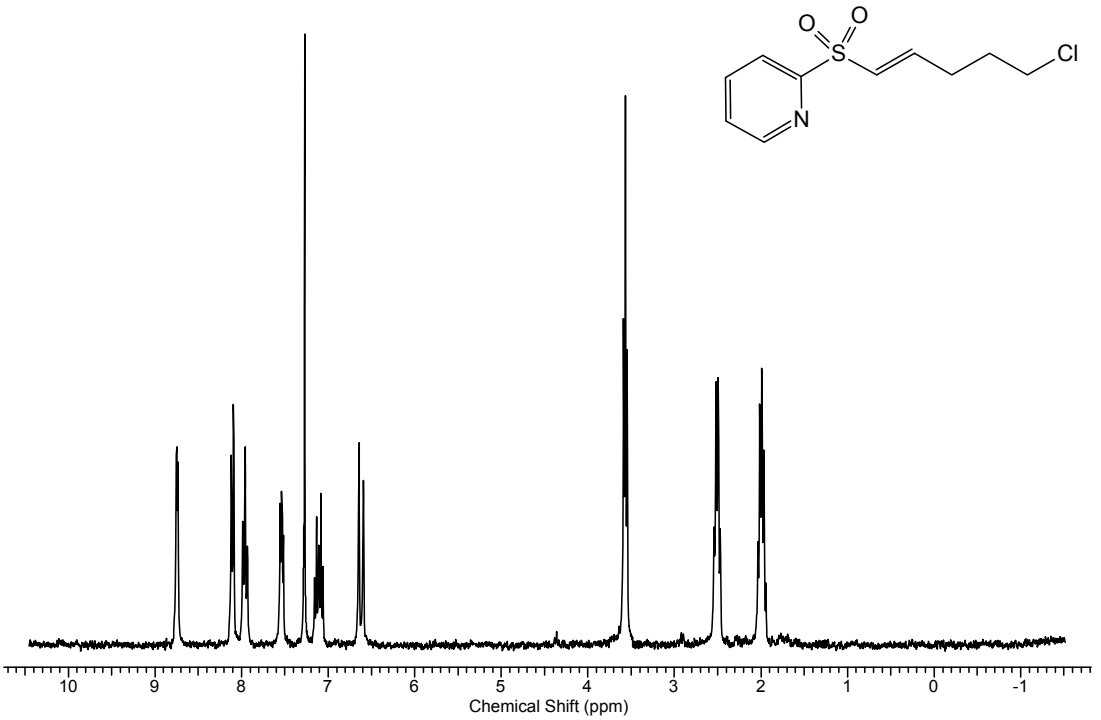
Table 6. Torsion angles [°] for **10b**

O(1)-S(1)-C(1)-N(1)	-166.8(2)
O(2)-S(1)-C(1)-N(1)	65.7(2)

C(6)-S(1)-C(1)-N(1)	-47.9(3)
O(1)-S(1)-C(1)-C(2)	16.6(3)
O(2)-S(1)-C(1)-C(2)	-110.9(3)
C(6)-S(1)-C(1)-C(2)	135.5(3)
N(1)-C(1)-C(2)-C(3)	-1.6(5)
S(1)-C(1)-C(2)-C(3)	174.6(2)
C(1)-C(2)-C(3)-C(4)	0.7(5)
C(2)-C(3)-C(4)-C(5)	0.3(5)
C(3)-C(4)-C(5)-N(1)	-0.6(6)
O(1)-S(1)-C(6)-C(7)	34.4(3)
O(2)-S(1)-C(6)-C(7)	164.2(2)
C(1)-S(1)-C(6)-C(7)	-81.3(3)
S(1)-C(6)-C(7)-O(3)	-72.2(3)
S(1)-C(6)-C(7)-C(8)	168.4(2)
O(3)-C(7)-C(8)-C(9)	58.6(4)
C(6)-C(7)-C(8)-C(9)	175.1(3)
C(7)-C(8)-C(9)-C(10)	-178.3(3)
C(8)-C(9)-C(10)-C(11)	-119.9(5)
C(8)-C(9)-C(10)-C(15)	63.5(5)
C(15)-C(10)-C(11)-C(12)	4.6(7)
C(9)-C(10)-C(11)-C(12)	-172.3(4)
C(10)-C(11)-C(12)-C(13)	-2.0(7)
C(11)-C(12)-C(13)-C(14)	-2.0(6)
C(12)-C(13)-C(14)-C(15)	3.1(6)
C(13)-C(14)-C(15)-C(10)	-0.3(6)
C(11)-C(10)-C(15)-C(14)	-3.4(6)
C(9)-C(10)-C(15)-C(14)	173.3(4)
O(4)-S(2)-C(16)-N(2)	-55.2(3)
O(5)-S(2)-C(16)-N(2)	178.3(2)
C(21)-S(2)-C(16)-N(2)	60.4(3)
O(4)-S(2)-C(16)-C(17)	121.4(3)
O(5)-S(2)-C(16)-C(17)	-5.2(3)
C(21)-S(2)-C(16)-C(17)	-123.0(3)
N(2)-C(16)-C(17)-C(18)	0.5(5)
S(2)-C(16)-C(17)-C(18)	-175.6(3)
C(16)-C(17)-C(18)-C(19)	0.2(5)
C(17)-C(18)-C(19)-C(20)	-0.7(6)
C(18)-C(19)-C(20)-N(2)	0.5(7)

O(4)-S(2)-C(21)-C(22)	-152.2(2)
O(5)-S(2)-C(21)-C(22)	-24.0(3)
C(16)-S(2)-C(21)-C(22)	93.0(3)
S(2)-C(21)-C(22)-O(6)	-60.6(3)
S(2)-C(21)-C(22)-C(23)	175.7(2)
O(6)-C(22)-C(23)-C(24)	-67.2(4)
C(21)-C(22)-C(23)-C(24)	54.7(5)
C(22)-C(23)-C(24)-C(25)	170.7(4)
C(23)-C(24)-C(25)-C(30)	75.6(5)
C(23)-C(24)-C(25)-C(26)	-102.7(5)
C(30)-C(25)-C(26)-C(27)	2.1(6)
C(24)-C(25)-C(26)-C(27)	-179.5(4)
C(25)-C(26)-C(27)-C(28)	-0.6(7)
C(26)-C(27)-C(28)-C(29)	-1.8(7)
C(27)-C(28)-C(29)-C(30)	2.5(7)
C(26)-C(25)-C(30)-C(29)	-1.3(6)
C(24)-C(25)-C(30)-C(29)	-179.7(4)
C(28)-C(29)-C(30)-C(25)	-1.0(7)
C(4)-C(5)-N(1)-C(1)	-0.1(5)
C(2)-C(1)-N(1)-C(5)	1.3(5)
S(1)-C(1)-N(1)-C(5)	-175.1(3)
C(19)-C(20)-N(2)-C(16)	0.2(6)
C(17)-C(16)-N(2)-C(20)	-0.8(5)
S(2)-C(16)-N(2)-C(20)	175.7(3)

NMR Spectra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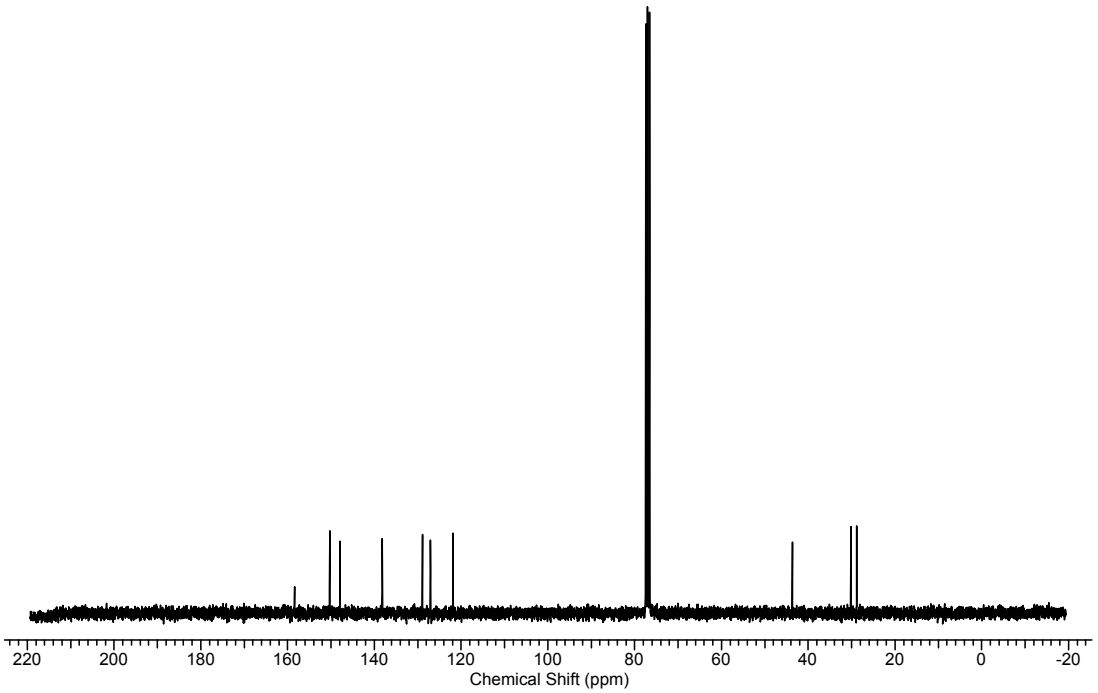
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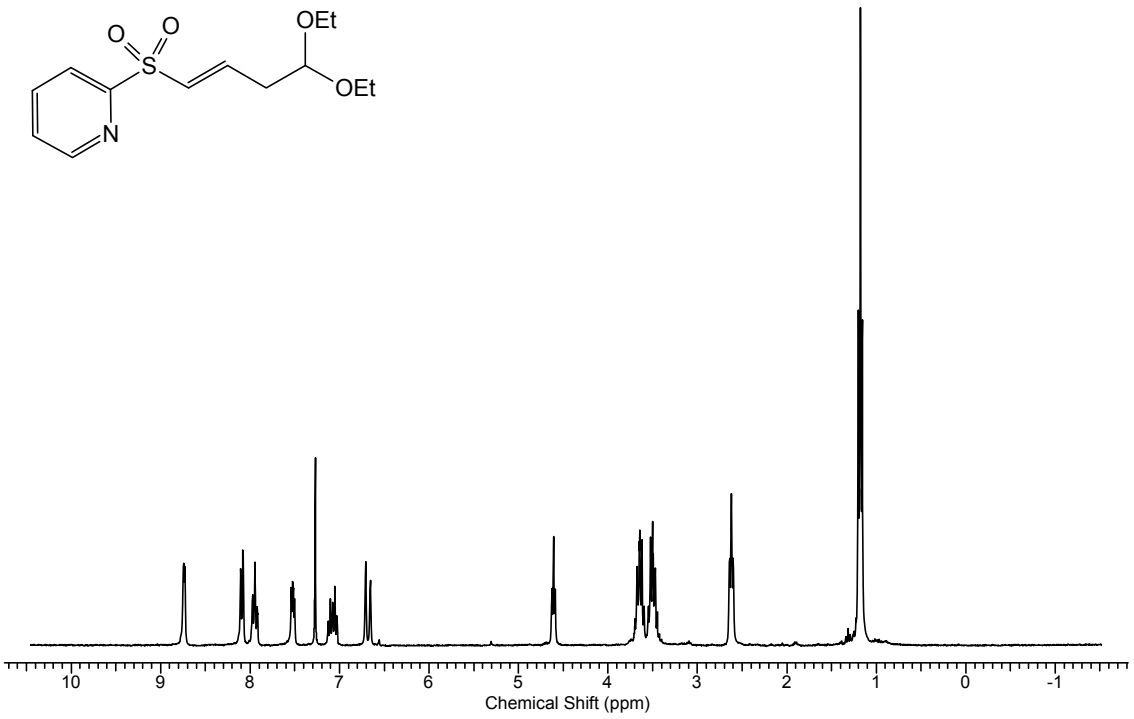

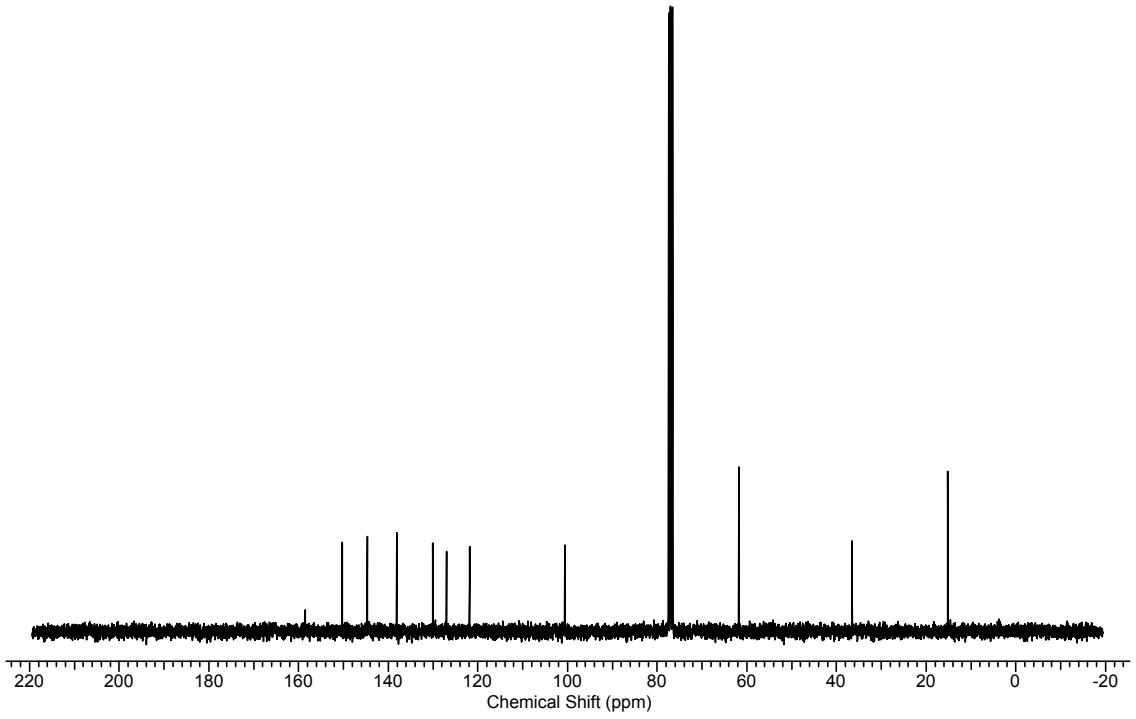

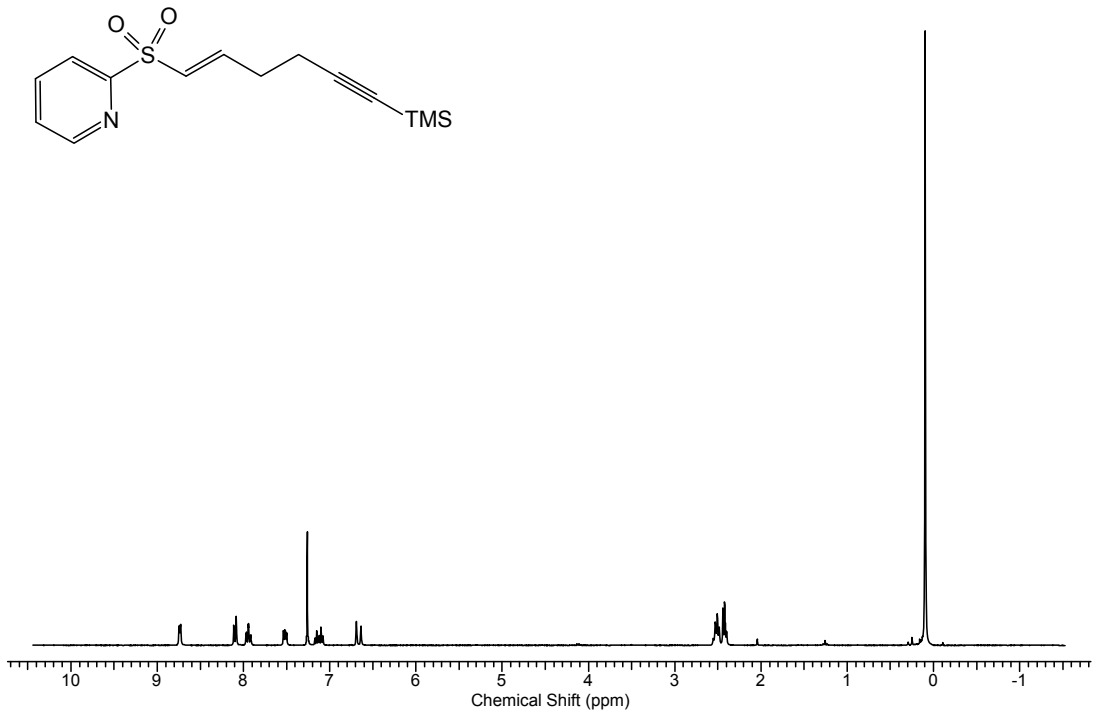
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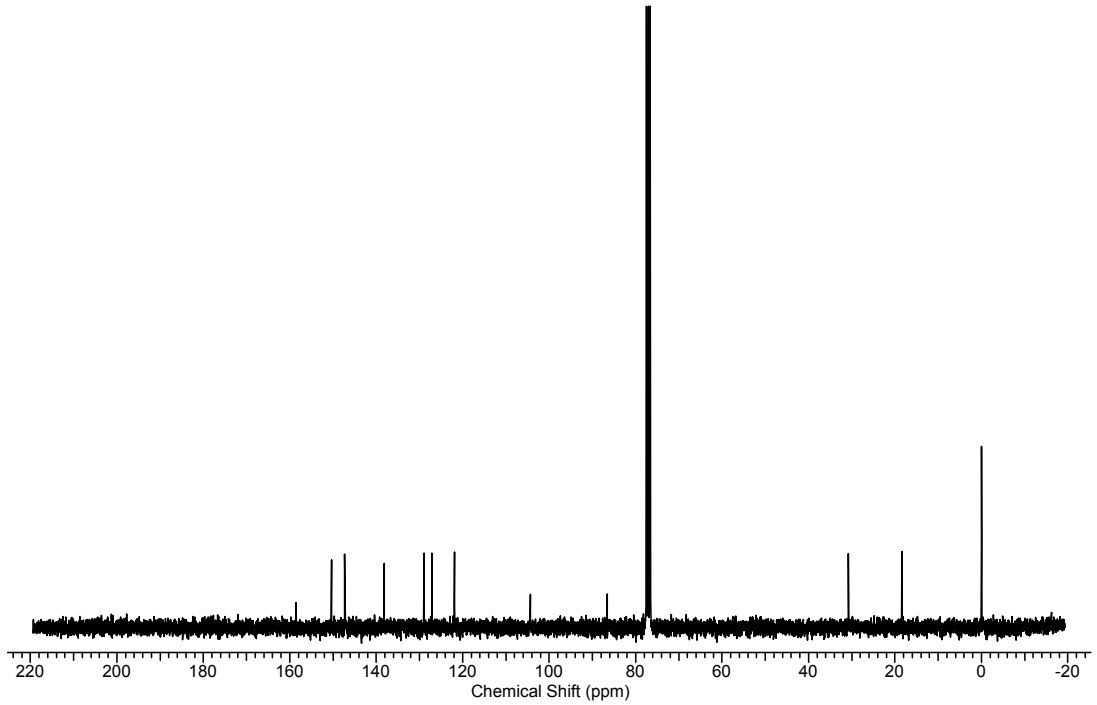
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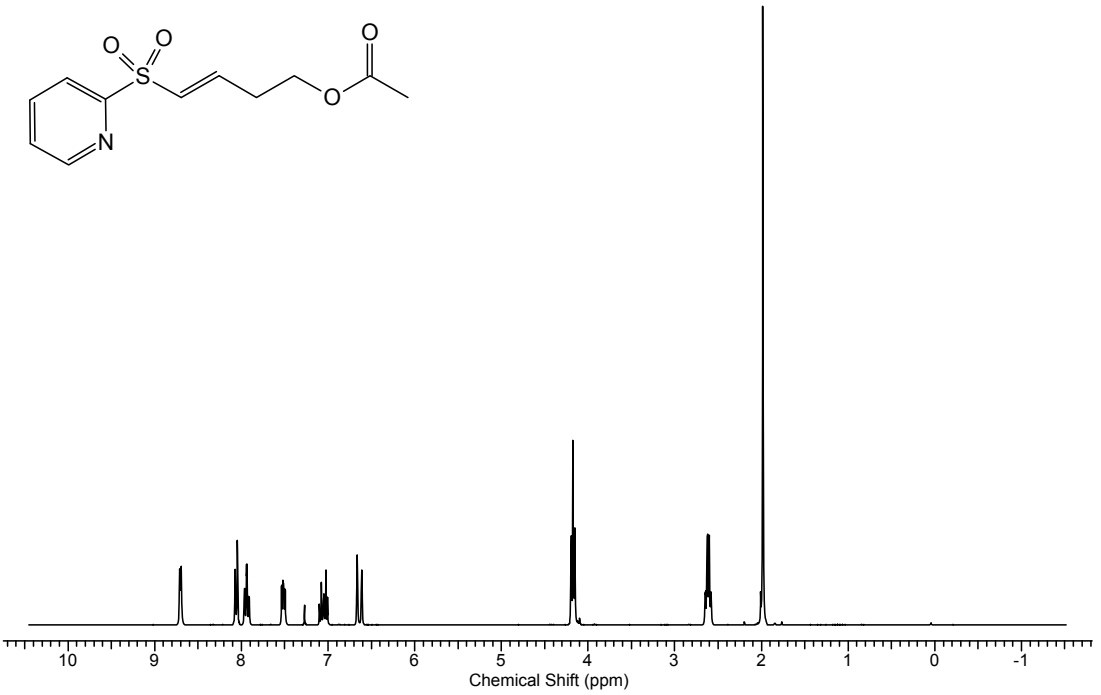
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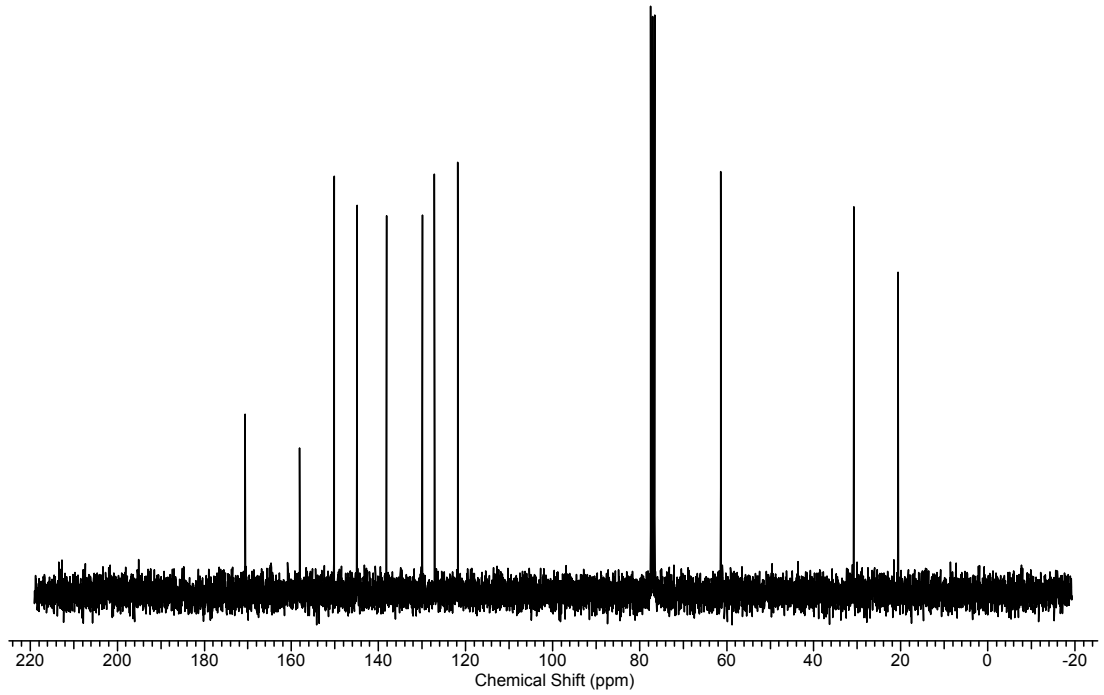
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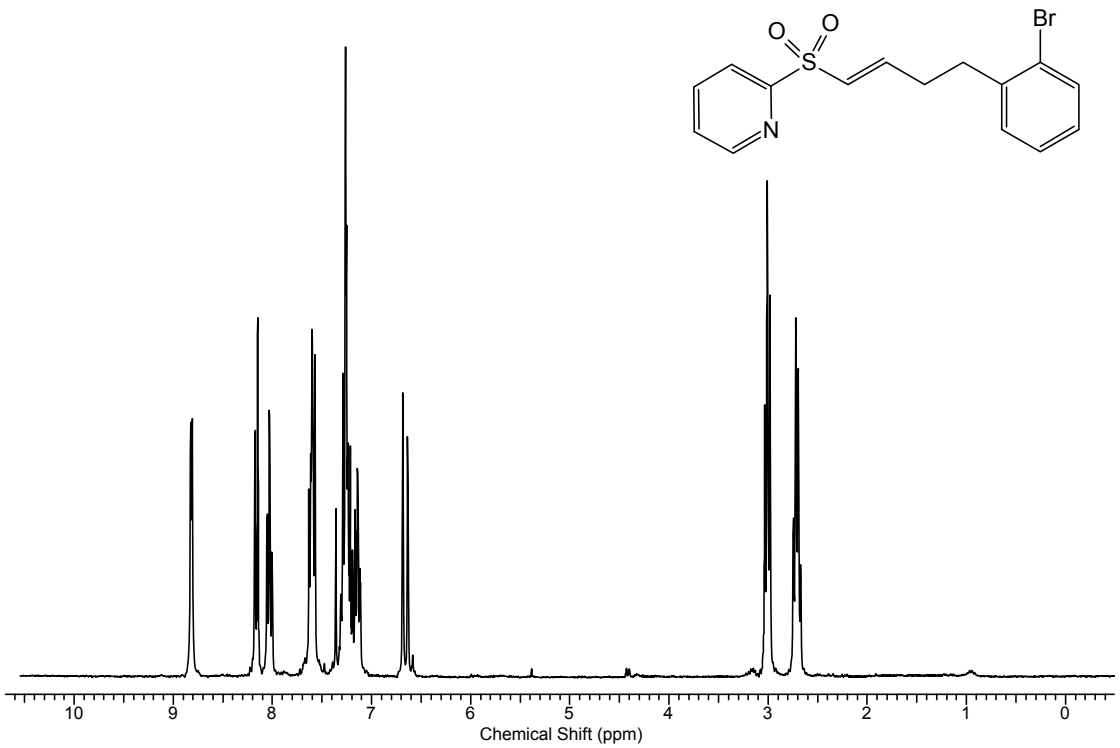
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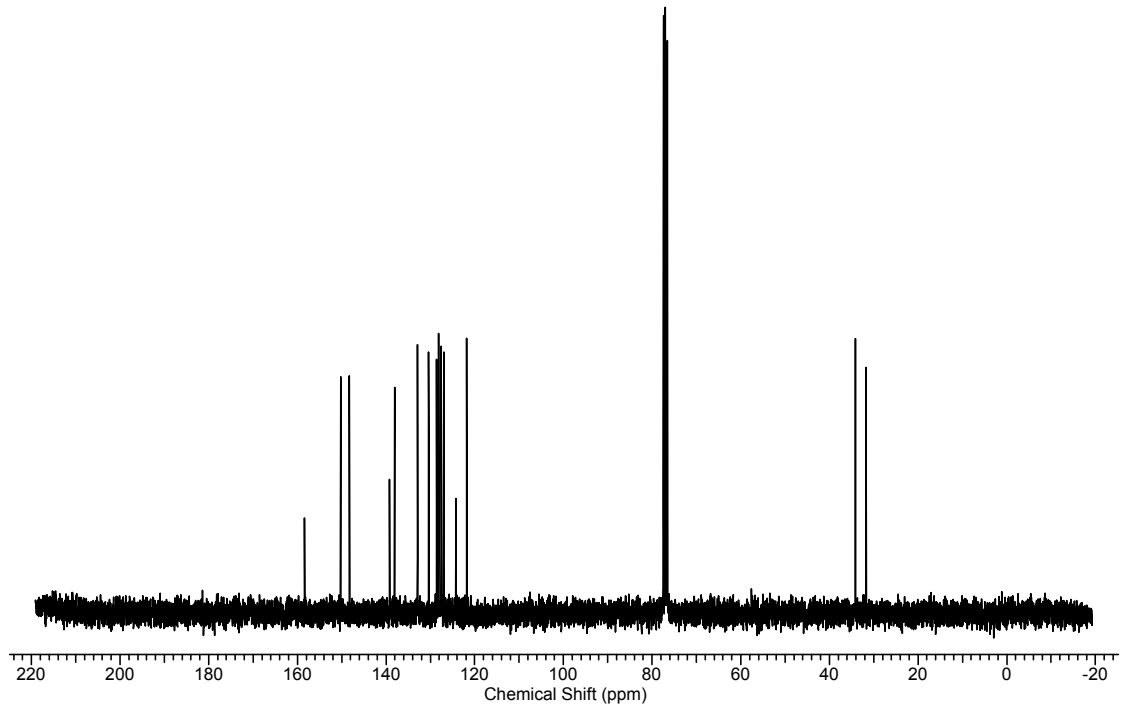
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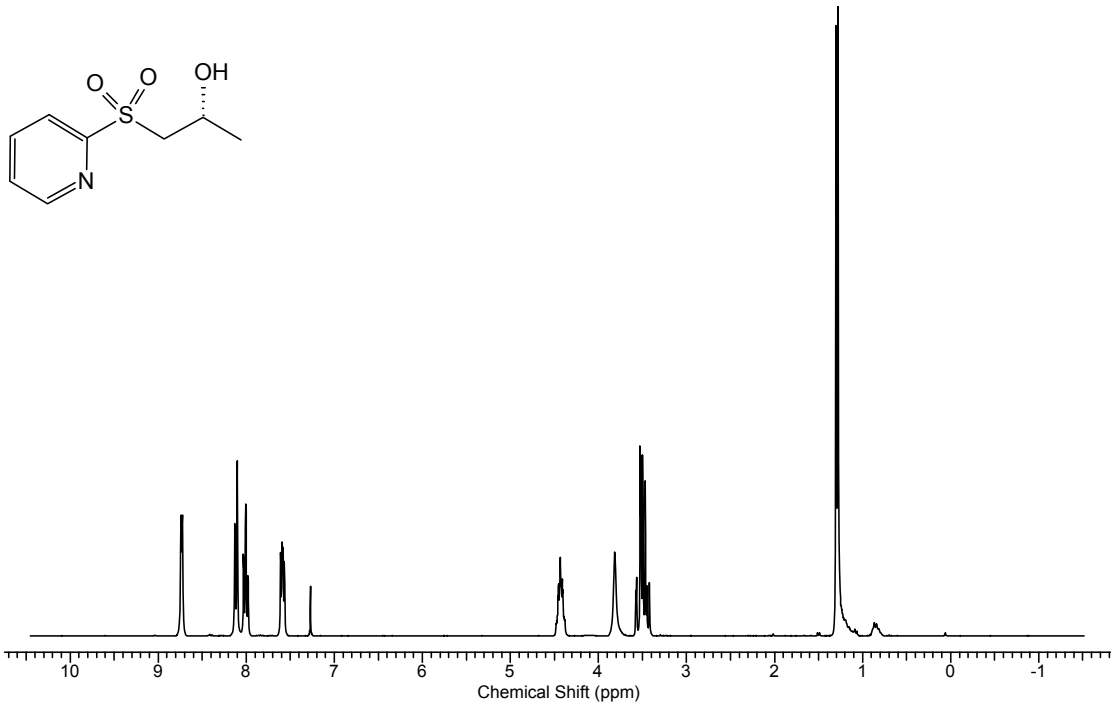
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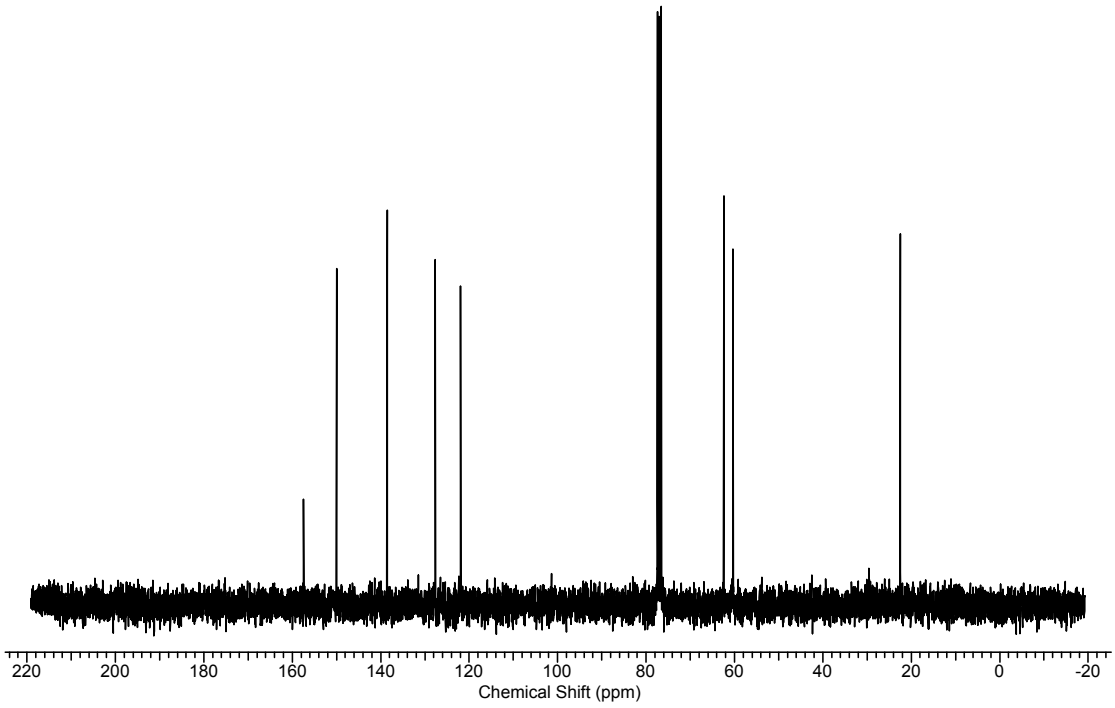
Chemical Shift (ppm)


220
200
180
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140
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100
80
60
40
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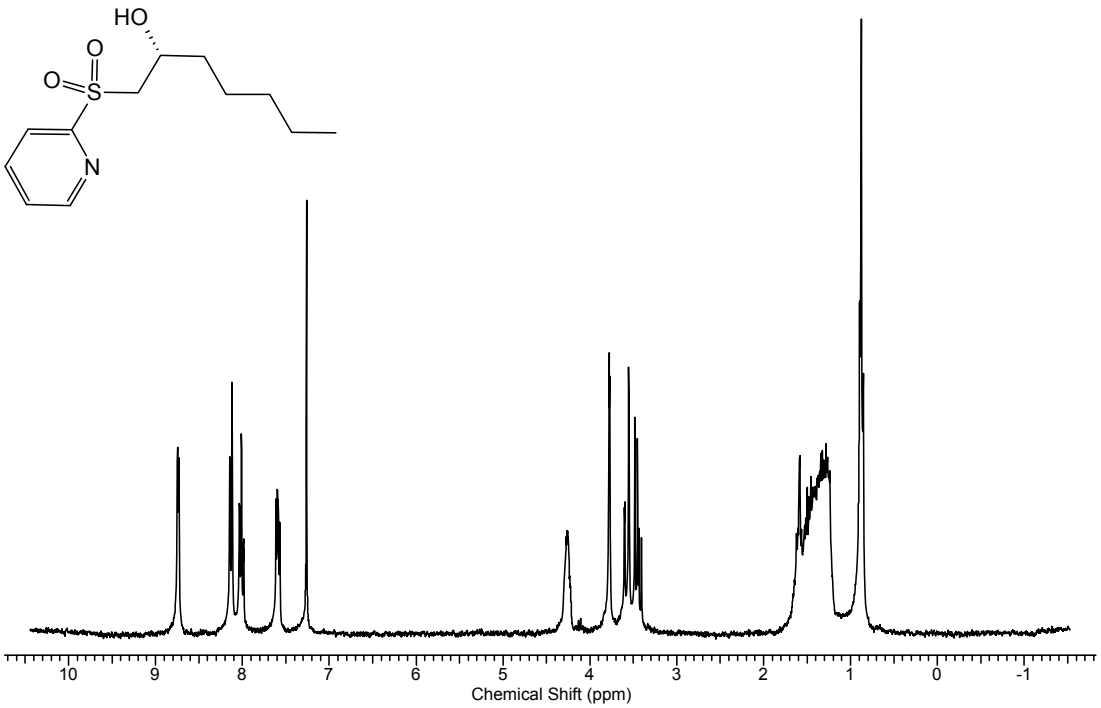
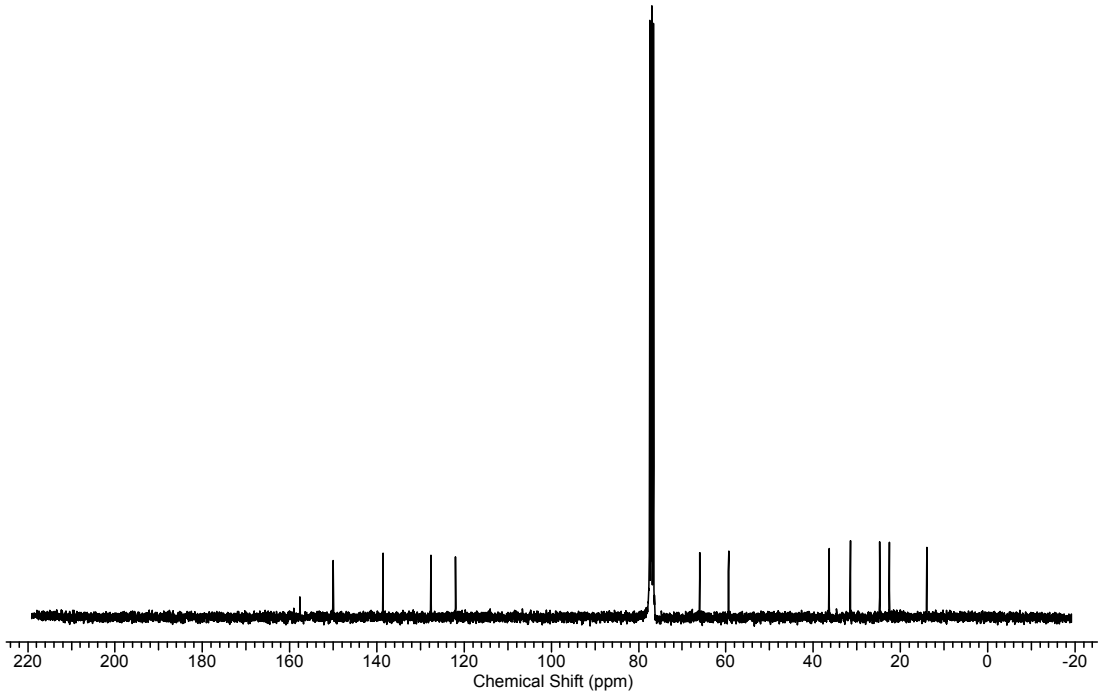
0
-20
Chemical Shift (ppm)


HO
O
O
S
N
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)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200
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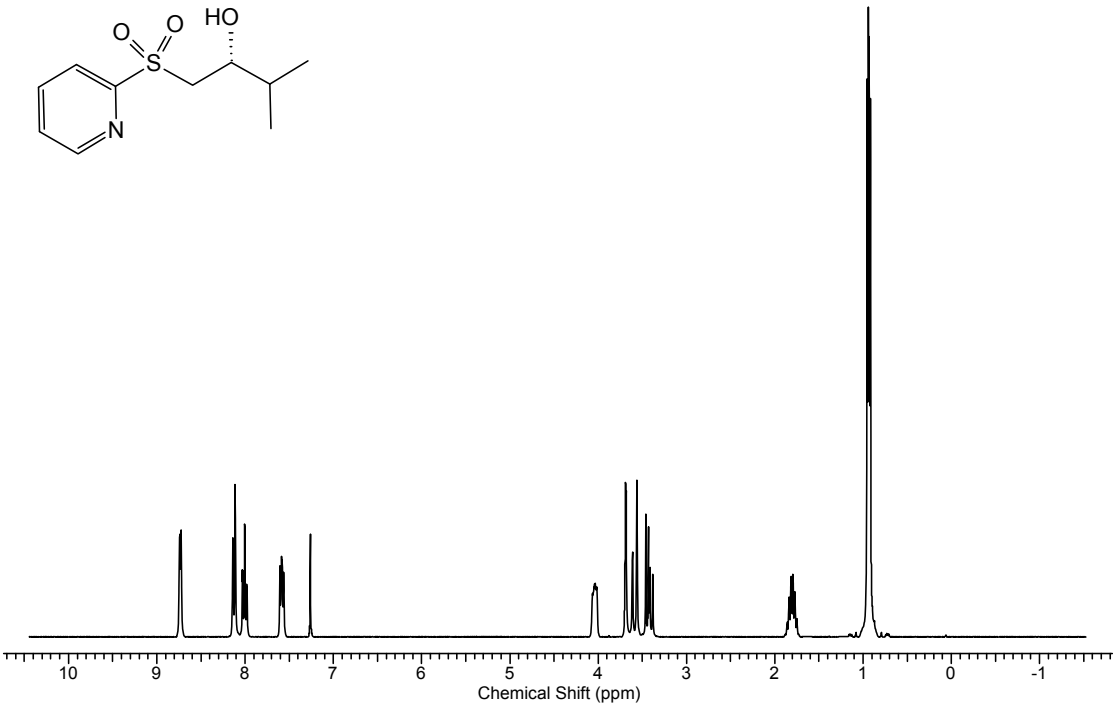
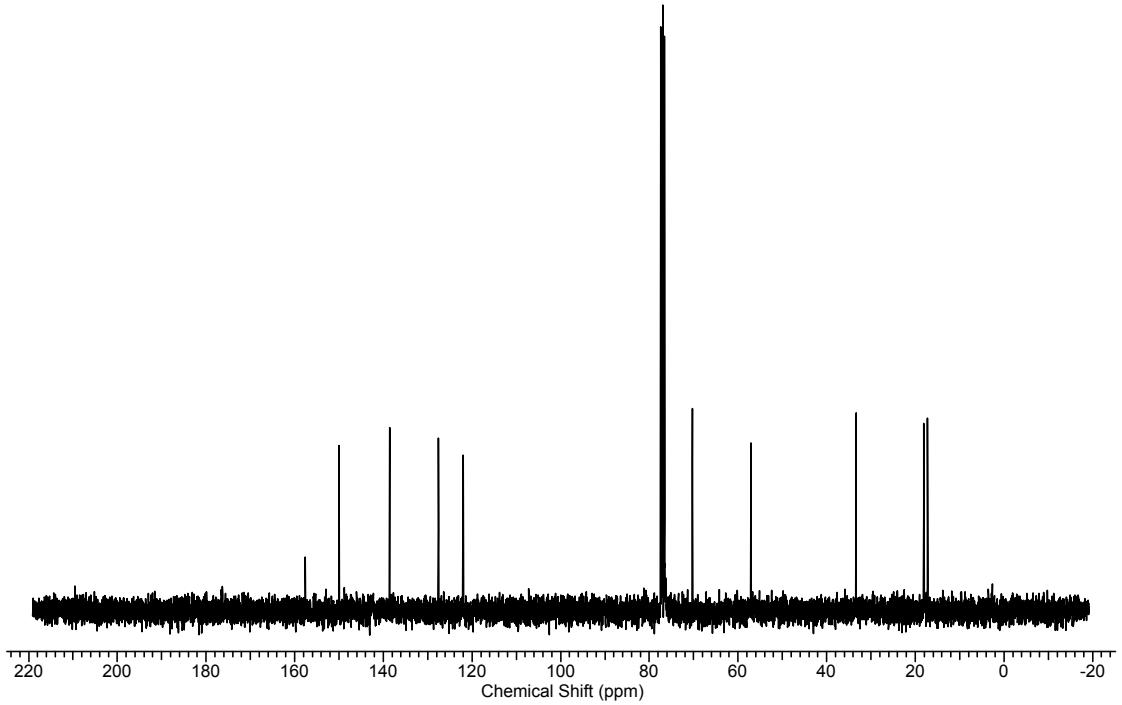
100
80
60
40
20
0
-20
Chemical Shift (ppm)


HO
O
O
S
N
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)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200
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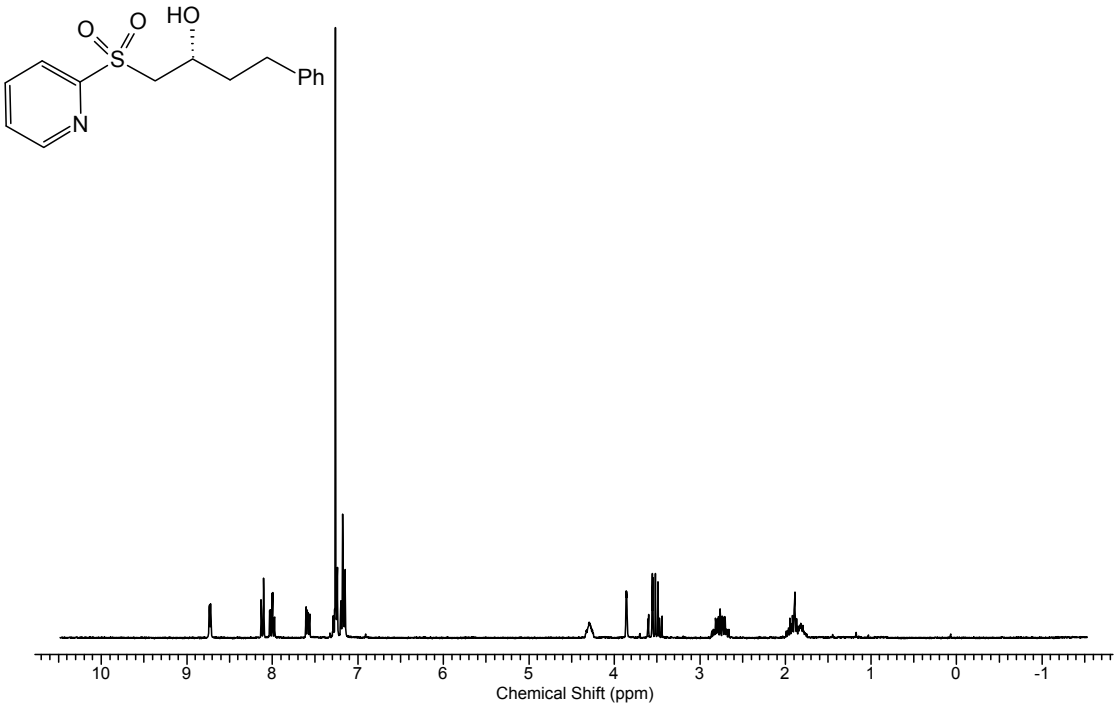
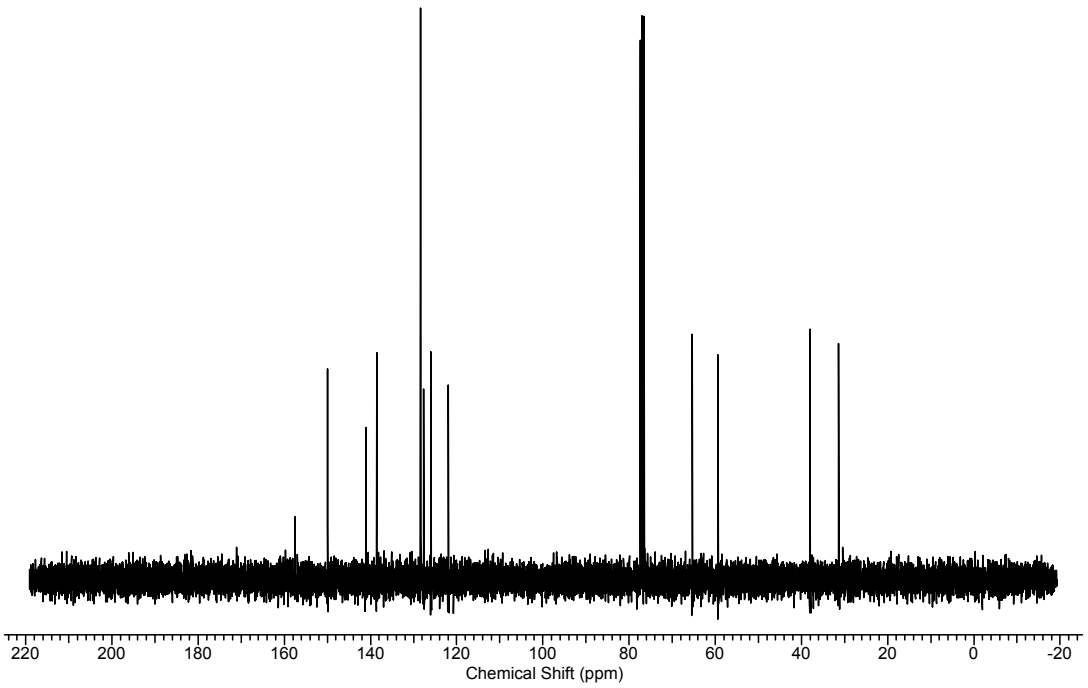
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


O
O
HO
S
Ph
N
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)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200
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120
100
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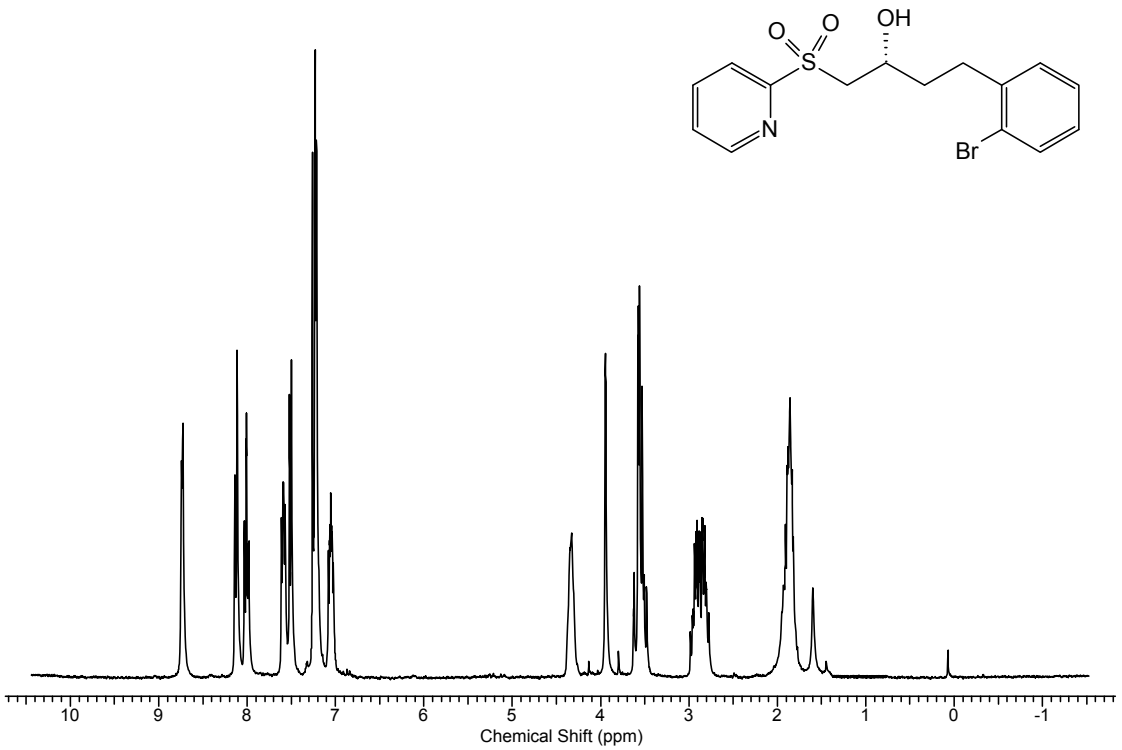
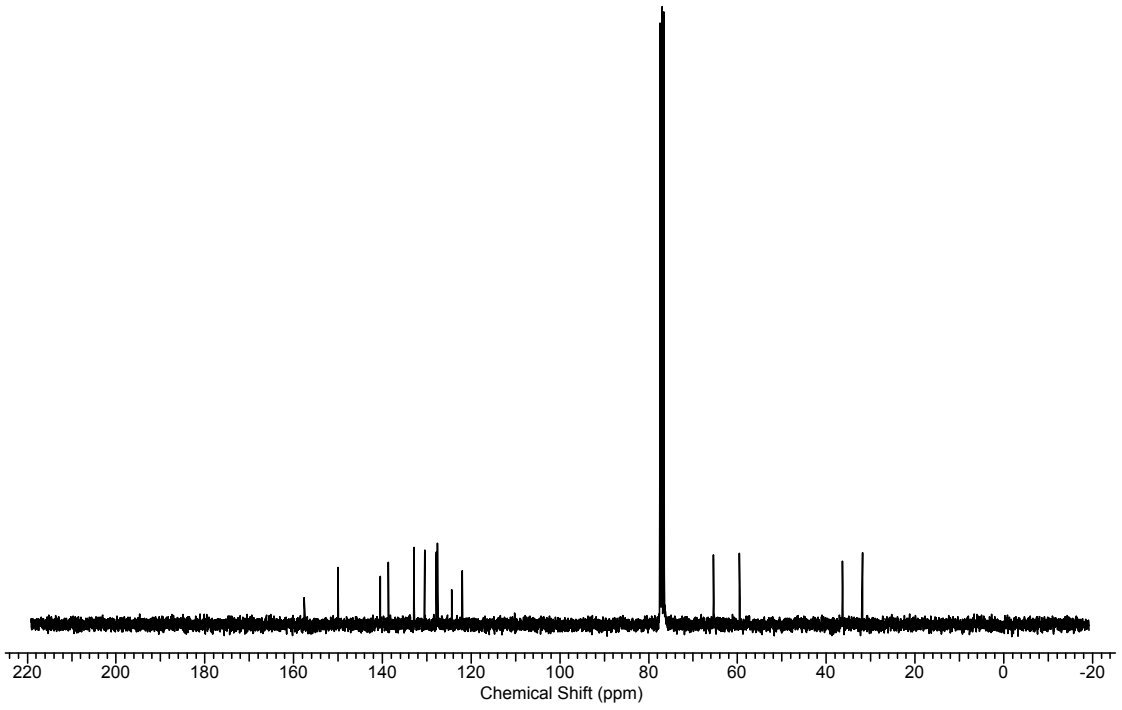
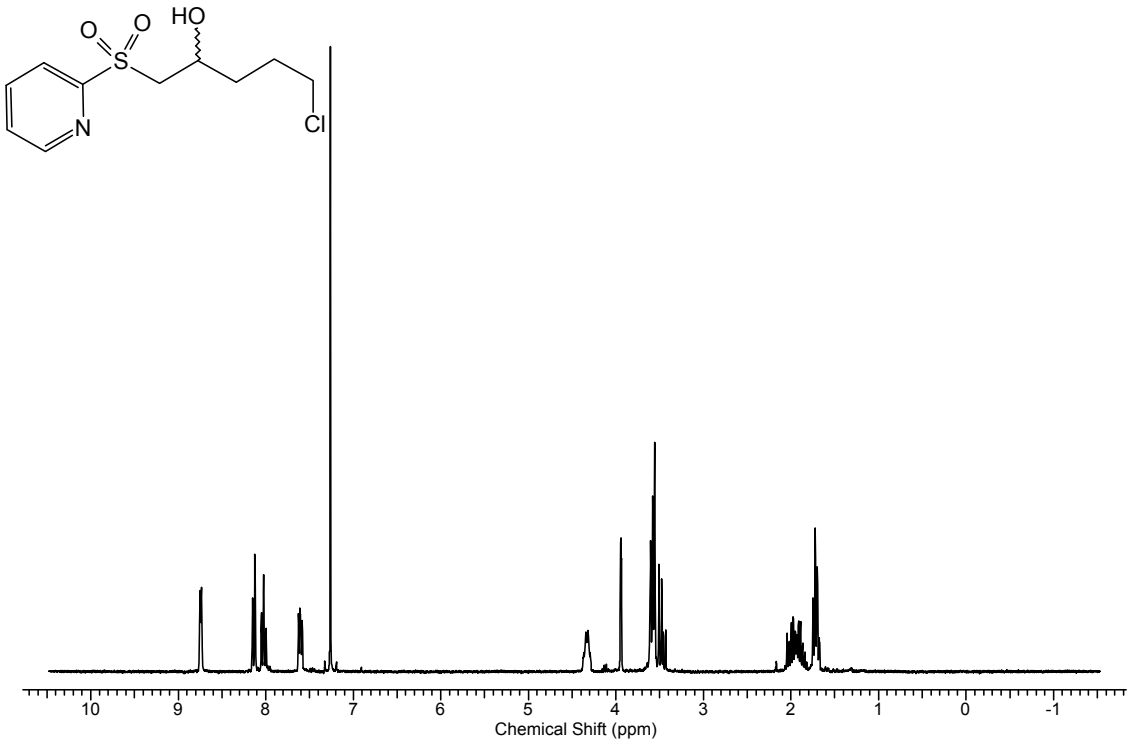
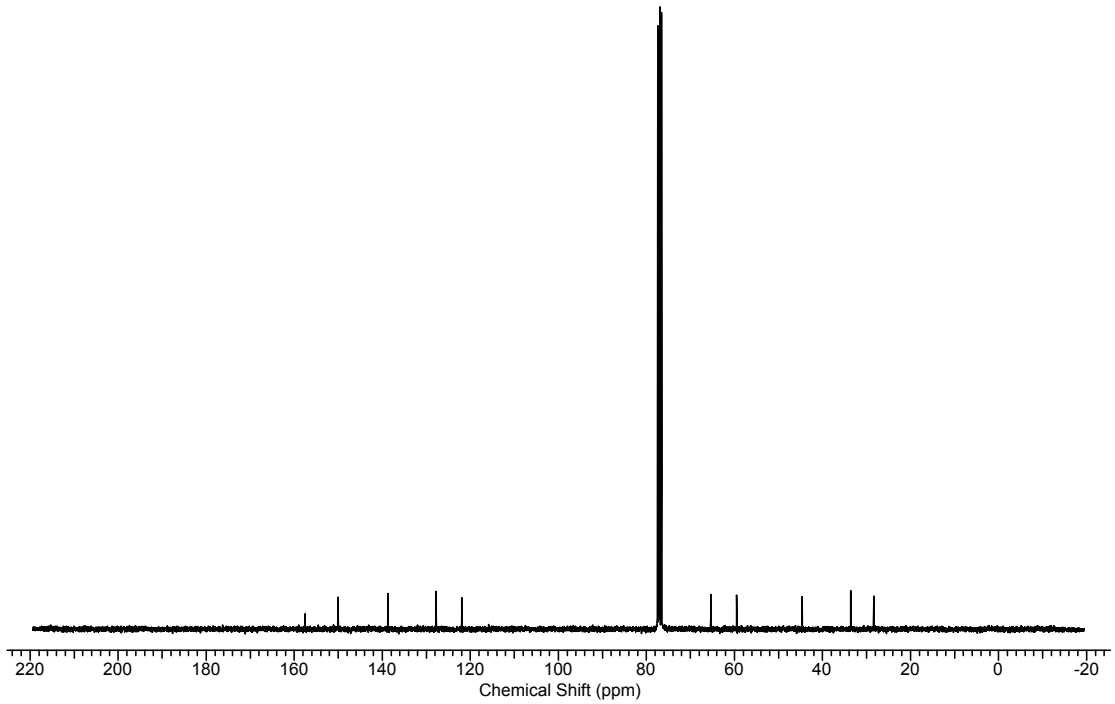
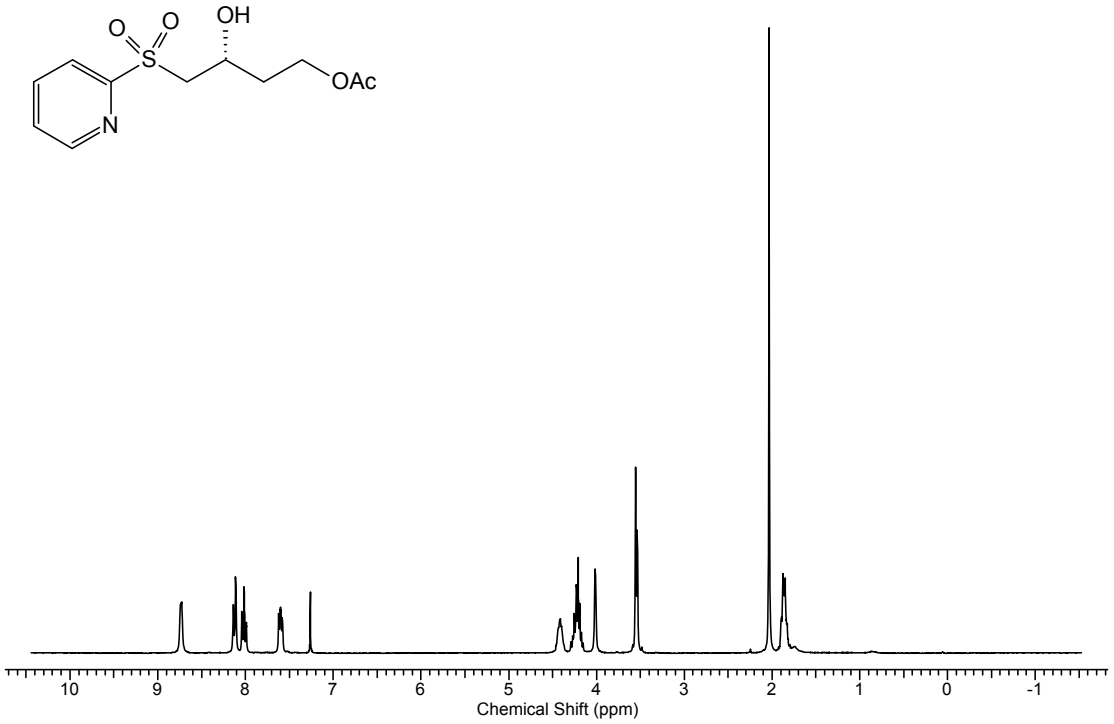
60
40
20
0
-20
Chemical Shift (ppm)

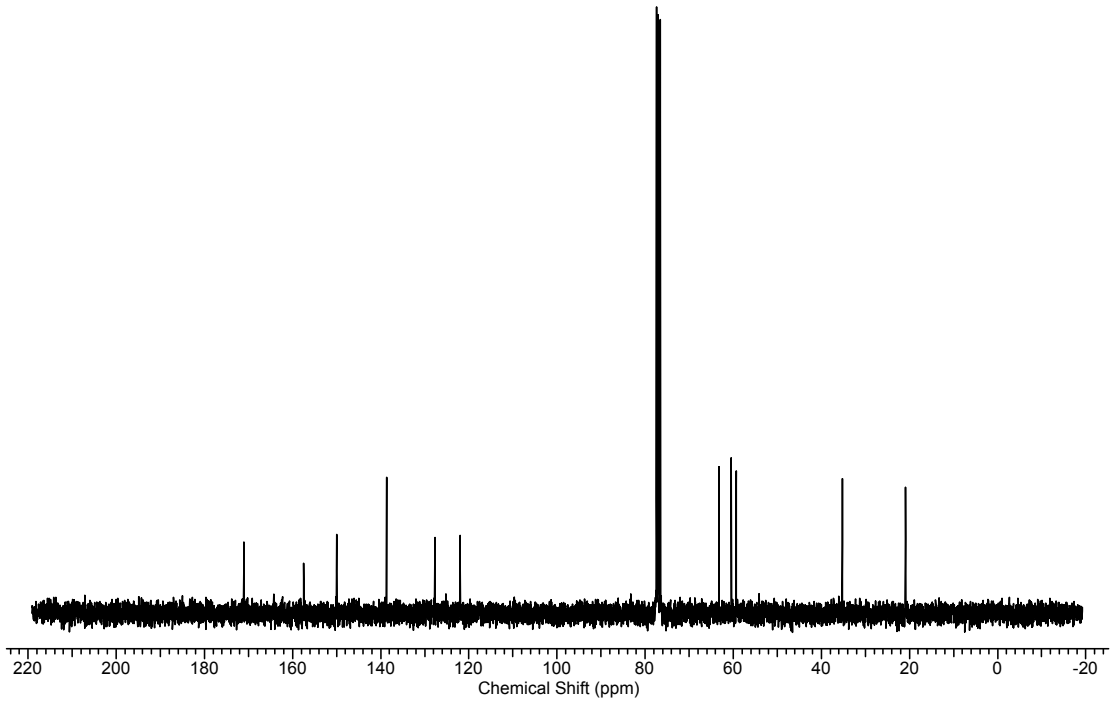









O
O
S
OH
OAc
N
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)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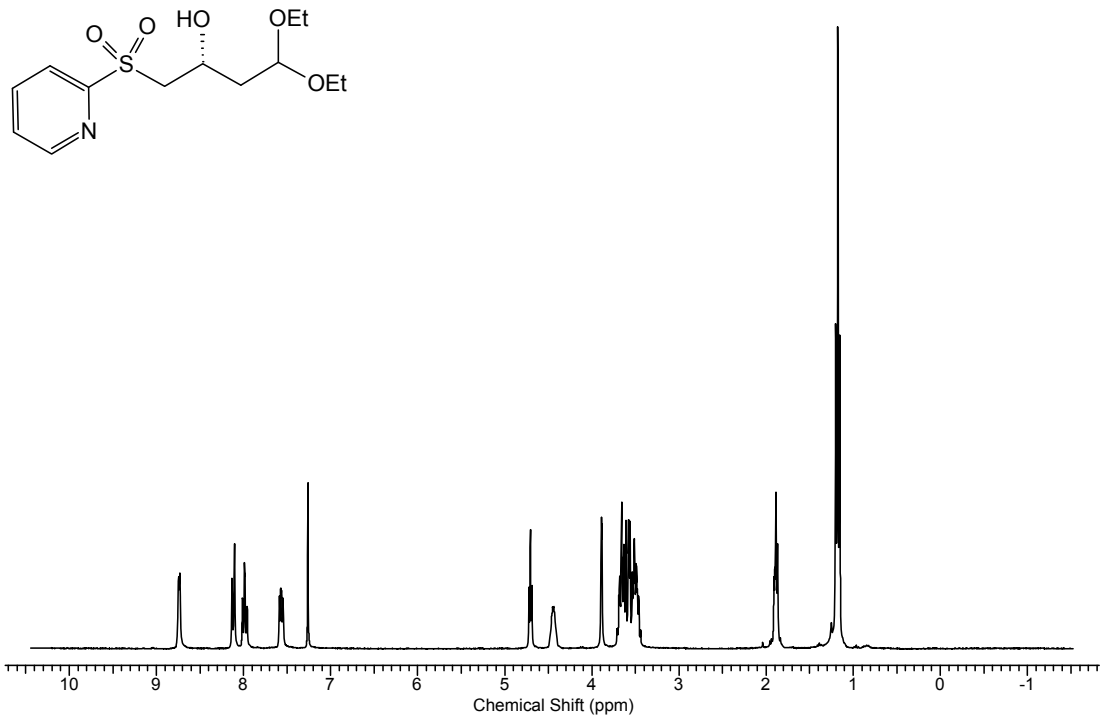
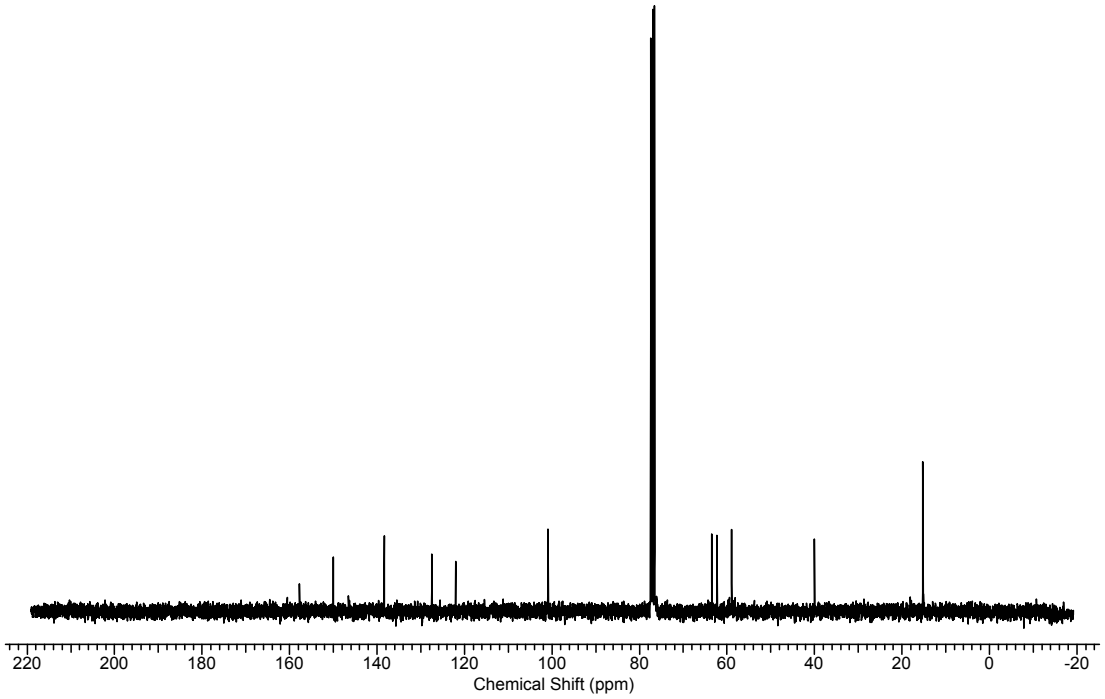
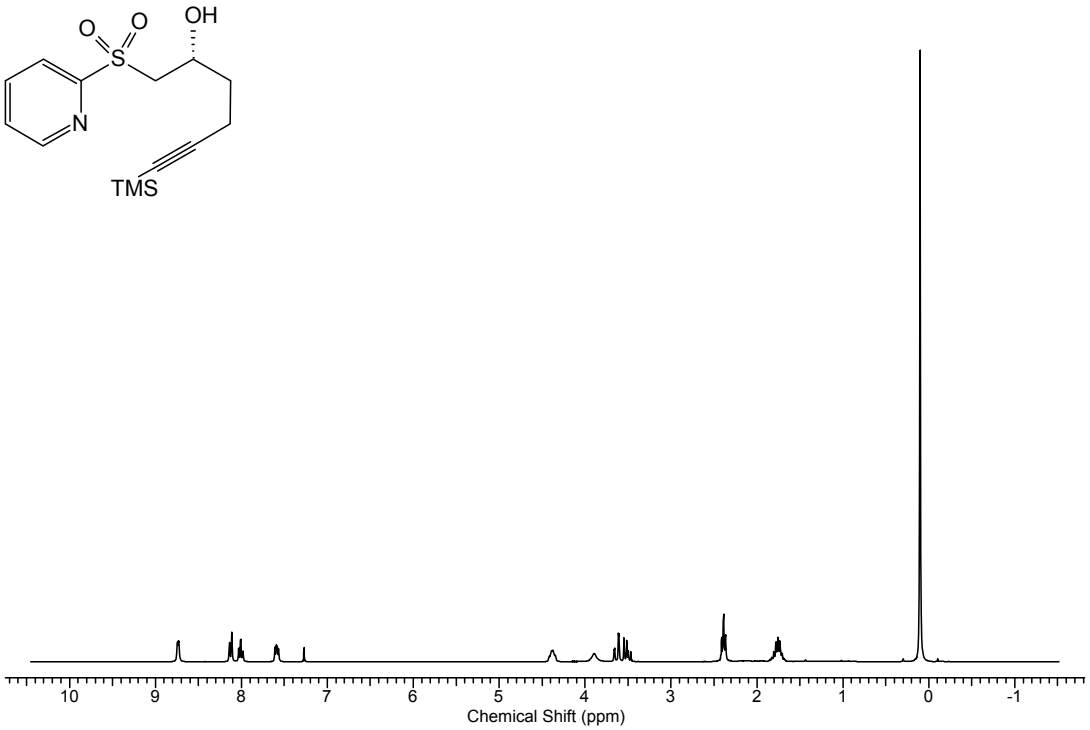
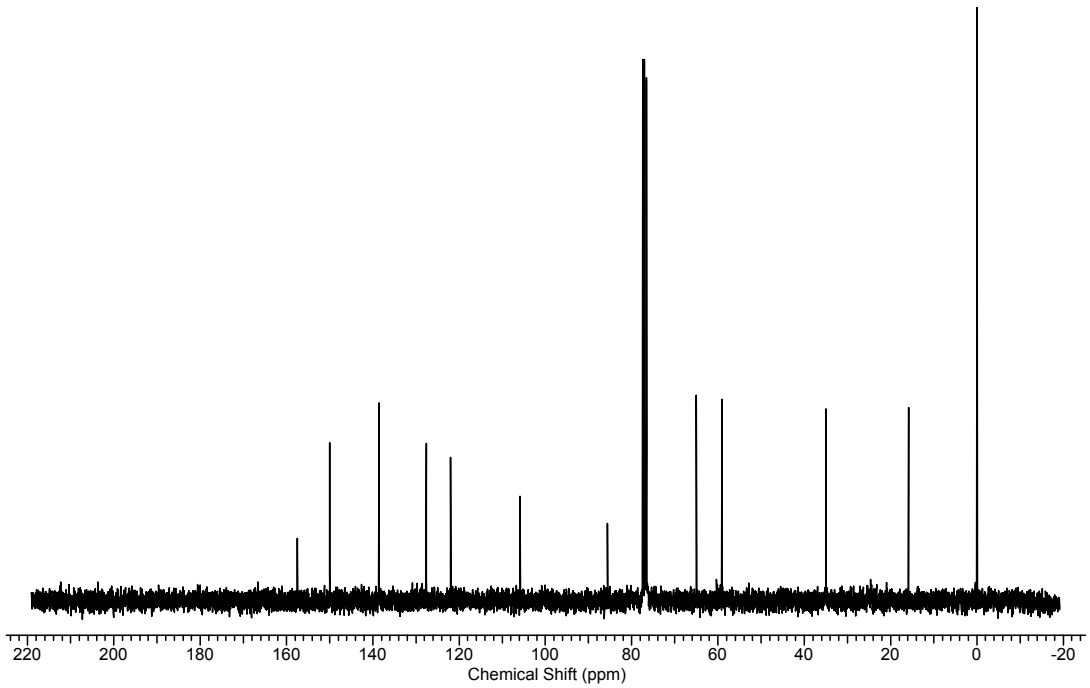
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


O
O
S
HO
OEt
OEt
N
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


O
O
S
OH
N
TMS
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)