Electronic Supplementary Material (ESI) for ChemComm.

Stereospecific Reaction of Sulfonimidoyl Fluorides with Grignard Reagents for the Synthesis of Enantioenriched Sulfoximines

Stephanie Greed, Oliver Symes and James A. Bull*

Department of Chemistry, Imperial College London, Molecular Sciences Research Hub, White City Campus, Wood Lane W12 0BZ, UK

*E-mail: j.bull@imperial.ac.uk

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General Experimental

All non-aqueous reactions were run under an inert atmosphere (argon) with flame-dried glassware, using standard techniques. Anhydrous solvents were obtained by filtration through drying columns (THF, CH_2Cl_2, DMF, MeCN and toluene) or used as supplied (1,4-dioxane, DMA, DME and 1,2-DCE). Reactions for optimisation were carried out in sealed Biotage microwave vials.

Flash chromatography was performed using 230–400 mesh silica, with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on precoated, glassbacked silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) and stained with aqueous potassium permanganate solution, a ninhydrin solution in ethanol or Dragendorff reagent stain.

Nuclear magnetic resonance spectra were recorded on 400 MHz spectrometers. The frequency used to record the NMR spectra is given in each assignment and spectrum (^{1}H NMR at 400 MHz; ^{13}C NMR at 101 MHz; ^{19}F NMR at 377 MHz). Chemical shifts for ^{1}H NMR spectra are recorded in parts per million with the residual protic solvent resonance as the internal standard ($CDCl_3$: δ = 7.26 ppm, D_2O: δ = 4.79 ppm). Data is reported as follows: chemical shift (multiplicity [s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintet, m = multiplet and br = broad], coupling constant (in Hz), integration and assignment). ^{13}C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million with the residual protic solvent resonance as the internal standard ($^{13}CDCl_3$: δ = 77.2 ppm). Assignments of ^{1}H and ^{13}C spectra were based upon the analysis of ^{1}H and *J* values, as well as DEPT, COSY and HSQC experiments where appropriate. ^{19}F NMR spectra were recorded with or without complete proton decoupling. Decoupling is indicated as (^{19}F{1H}) and where relevant this is stated in each assignment and spectrum. For clarity NMR spectra are displayed as follows unless this would obscure signals: ^{1}H NMR spectra are displayed between 10.0 ppm and 0.0 ppm; ^{13}C NMR spectra are displayed between 210 ppm and 0 ppm; ^{19}F NMR spectra displayed for the full sweep width as acquired.

IR spectra were recorded as solids or neat liquids on an Agilent Cary 630 FTIR spectrometer and are reported in wavenumbers (cm^{-1}) to the nearest integer.

The high resolution mass spectrometry (HRMS) analyses were performed using a Bruker microTOF QII mass spectrometer equipped with an electrospray ion source (ESI) operated in positive ion mode. The sample solutions (CH_3OH or CH_3OH + 0.1%v/v HCOOH) were introduced by continuous infusion at a flow rate of 180 mL min^1 with the aid of a syringe pump.

The instrument was operated with endplate offset and capillary voltages set to –500 V and –4500 V respectively. The nebulizer pressure was 0.4 bar (N_2), and the drying gas (N_2) flow rate was 4.0 L min^{-1}. The capillary exit and skimmer 1 voltages were 90 V and 30 V, respectively. The drying gas temperature was set at 180 °C. The calibration was carried out with sodium formate: a solution made

up of 10 ml of 98% formic acid, 10 ml of sodium hydroxide (1.0 M), 490 mL of *i*-propanol and 490 mL of deionized water. The software used for the simulations was Bruker Daltonics DataAnalysis (version 4.0).

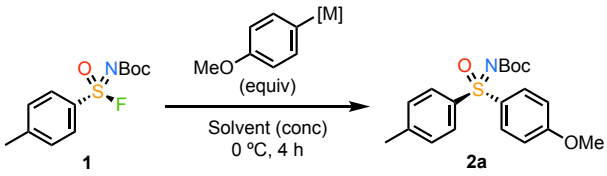
All melting points were determined in open glass capillaries and are uncorrected.

Reagents: Commercial reagents were used as supplied or purified by standard techniques where necessary.

Further experimental data for novel compounds presented in this manuscript can be found at the Imperial College London Research Data Repository. DOI: 10.14469/hpc/10325.
https://doi.org/10.14469/hpc/10325

Complete optimisation table for organometallic reaction with sulfonimidoyl fluoride (*R*)-1

Table S1: Optimisation of SuFEx reaction with organometallic reagents

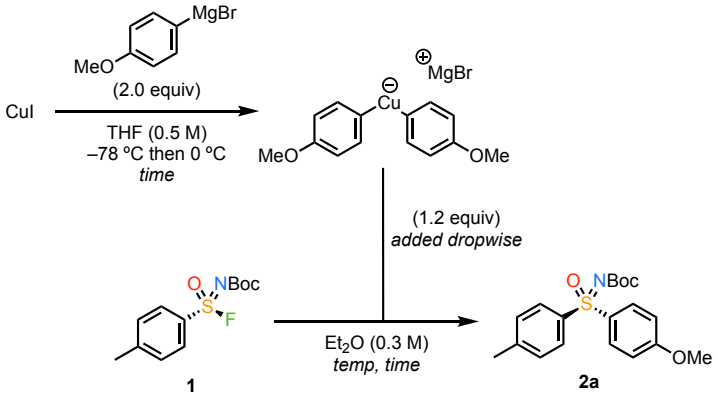


	[M]	RM equiv	Solvent	Solvent concentration (M)	Additive (equiv)	Yield[a] 1	Yield[a] 2a	(*S*)-2a %es [b]
1	MgBr	1.5	THF	0.3	-	31	58	98
2	MgBr	1.5	THF	0.3	LiCl (1.5)	68	9	>99
2	MgBr	1.5	THF	0.3	LiBr (1.5)	62	23	>99
3	MgBr	1.5	1,4-dioxane	0.3	-	50	39	98
4	MgBr	1.5	Et_2O	0.3	-	5	77	99
5	MgBr	1.5	Et_2O	0.1	-	-	70	97
6	MgBr	1.5	Et_2O	0.2	-	-	69	99
7	MgBr	1.5	Et_2O	0.5	-	-	70	98
8	MgBr	1.2	Et_2O	0.3	-	-	81	99
9[c]	MgBr	1.2	Et_2O	0.3	-	-	91	>99
10[d]	MgCl	1.2	Et_2O	0.3	-	-	85	>99
10	MgBr	1.2	CPME	0.3	-	-	(quant)[f]	>99
10[e]	Li	1.2	THF	0.3	-	-	37	>99
11[g]	CuArMgBr	1.2	Et_2O	0.3	-	-	87 (81)[f]	>99
12[h]	ZnCl	1.2	Et_2O	0.3	-	90	0	n/a

Reactions performed on 0.10 mmol scale. [a]Calculated by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b]%*es* determined by HPLC analysis of crude product. [c]Reaction time of 1 h. [d]Grignard reagent generated from 4-iodoanisole and *i*-PrMgCl.LiCl (Turbo Grignard). [e]Addition of organolithium at –78 °C followed by warming to 0 °C. [f]Isolated yield in parentheses. [g]Reaction time of 5 h at rt. [h]Reaction time of 3 h at rt.

Optimisation table for organocuprate reaction with sulfonimidoyl fluoride (*R*)-1

Table S2: Optimisation of SuFEx reaction with organocuprate reagents

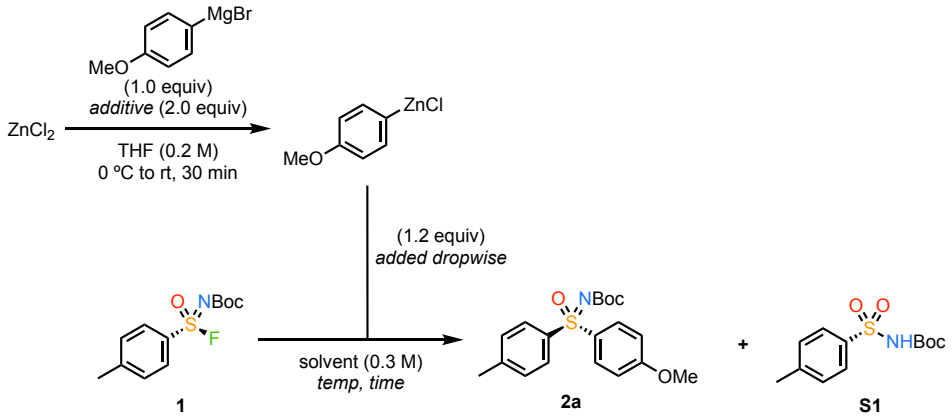


Entry	Cuprate Formation Time (h)	SuFEx Temp (°C)	SuFEx Time (h)	Yield (%)[a]		(*S*)-2a *ee*
				1	2a	
1	0.5	0	1	n.d.	n.d (14)	99
2	1	0 to rt	3	n.d.	n.d. (48)	96
3	1	0	1	53	32	99
4	1	0	3	40	58	98
5	1	rt	1	27	66	97
6	1	rt	3	9	87	99
7	1	rt	5	-	87 (81)	99

Reactions performed at 0.25 mmol scale. [a]%Yield given by analysis of crude 1H NMR in comparison to 1,3,5-trimethoxybenzene as internal standard. Isolated yields in parentheses.

Optimisation table for organozinc reaction with sulfonimidoyl fluoride (*R*)-1

Table S3: Optimisation of SuFEx reaction with organozinc reagents

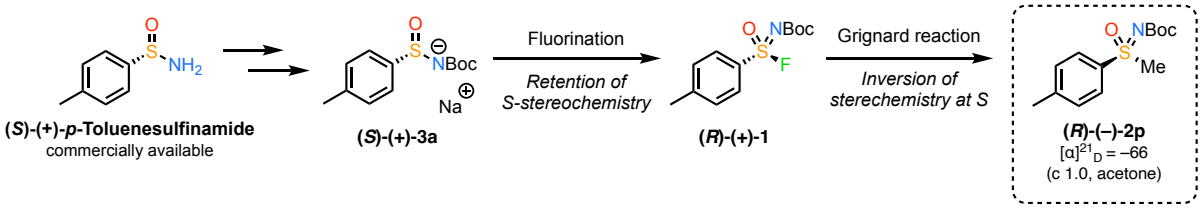


Entry	Solvent	Additive	SuFEx Temp (°C)	SuFEx Time (h)	^{1}H NMR Yield (%)[a]		
					(*R*)-1	(*S*)-2a	S1
1	Et_2O	-	0	1	95	-	3
2	Et_2O	-	rt	1	95	-	3
3	Et_2O	-	rt	3	90	-	3
4	Et_2O	-	rt	5	88	-	5
5	Et_2O	-	reflux	5	73	-	9
6	THF	-	0	1	89	-	3
7	THF	-	rt then 60	5 (rt) then 18 h (60)	17	-	13
8	THF	-	reflux	2	8	-	35
9	Et_2O	LiCl	0	1	73	-	4
10	Et_2O	LiCl	rt	3	74	-	4
11	Et_2O	LiCl	reflux	1	72	-	8
12	THF	LiCl	0	1	84	-	2
13	THF	LiCl	rt	3	92	-	2
14	THF	LiCl	reflux	2	73	-	5

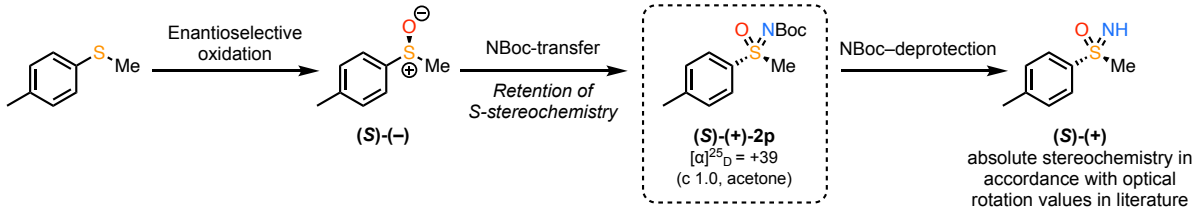
Reactions performed at 0.25 mmol scale. [a]%Yield given by analysis of crude ^{1}H NMR in comparison to 1,3,5-trimethoxybenzene as internal standard. To confirm the organozinc halide was being generated in the first instance, the organozinc halide solution used for entries 12, 13 and 14 was quenched with iodine in THF. The ^{1}H NMR of the resulting indicated formation of the corresponding 4-iodoanisole. No observation of sulfoximine formation under any conditions also indicates that there remains no unreacted Grignard in the organozinc halide solution, as this would provide some corresponding sulfoximine.

Determination of stereochemical outcome of the SuFEx reaction

This Study: Synthesis of enantioenriched sulfoximine from S–C bond formation



Previous Study: Synthesis of enantioenriched sulfoximine from enantioselective oxidation



Scheme S.S1: Product of SuFEx reaction has $[\alpha]_D$ with opposing sign to known compound, **(*S*)-2p**,[1] so can be assigned as **(*R*)-2p** with inversion of stereochemistry as a result of nucleophilic attack of the sulfonimidoyl fluoride.

Experimental details and characterisation

General Procedures

General Procedure A: Synthesis of enantioenriched sulfonimidoyl fluorides

Selectfluor (0.71 g, 2.0 mmol, 2 equiv) was added to a stirred solution of the sulfinamide salt (1.0 mmol, 1 equiv) and potassium acetate (0.20 g, 2.0 mmol, 2.0 equiv) in ethanol (5 mL, 0.2 M) at 0 ºC and slowly warmed to RT over 24 h. The reaction mixture was quenched with water (10 mL) and diluted with CH_2Cl_2 (10 mL). The mixture was extracted with CH_2Cl_2 (3 × 40 mL) and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Typically, no further purification was required giving sulfonimidoyl fluoride.

General Procedure B: Synthesis of racemic sulfonimidoyl fluorides

Selectfluor (1.32 g, 3.75 mmol, 1.5 equiv) was added to a solution of the sulfinamide salt (2.5 mmol, 1 equiv) in DMF (13 mL, 0.2 M) at 0 °C and warmed to 25 °C for 18 h. H_2O (25 mL) was added and the aqueous mixture was extracted with EtOAc (3 × 25 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent removed under reduced pressure to give the racemic sulfonimidoyl fluorides which was typically used with no further purification.

General Procedure C: Synthesis of enantioenriched alkyl sulfonimidoyl fluorides

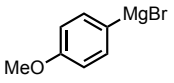
Selectfluor (2.0 mmol, 2.0 equiv) was added to a solution of the sulfinamide salt (1.0 mmol, 1.0 equiv) in ethanol:DMF (2:1, 5.0 mL, 0.3 M) at 0 °C and warmed to 25 °C over 24 h. H_2O (30 mL) was added and the aqueous mixture extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give sulfonimidoyl fluoride.

General Procedure D: Synthesis of sulfoximines

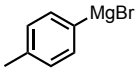
The Grignard reagent (0.3 mmol, 1.2 equiv) was added dropwise to a sulfonimidoyl fluoride (0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. The resulting residue was then purified by silica flash column chromatography as described for each entry to yield the desired sulfonimidamides.

Source of Grignard reagents used in this study

Commercial Reagents



0.5 M in THF



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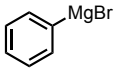
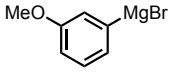
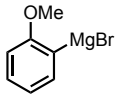


2.7 M in Et_2O



1.0 M in THF



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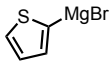

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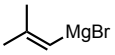
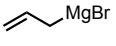
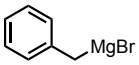


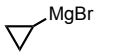
0.5 M in THF



1.0 M in Et_2O

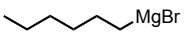


1.0 M in Et_2O

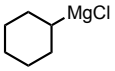


1.0 M in 2-MeTHF

2.8 M in Et_2O

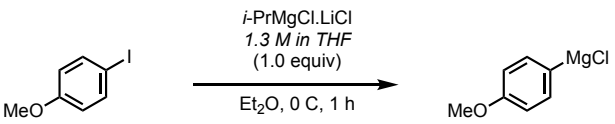


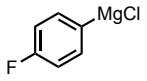
2.0 M in Et_2O

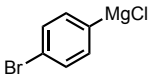


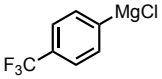
1.0 M in 2-MeTHF

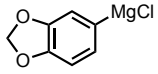
Grignard Reagents generated using Turbo Grignard

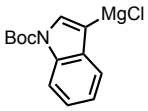


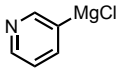




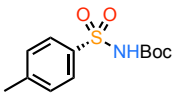




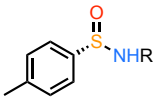




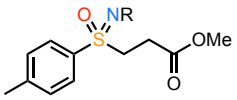
Structures of Additional Compounds in SI



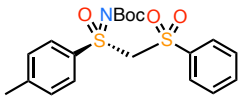
S1



R = Boc **(*S*)-S2**
Cbz **(*S*)-S2-Cbz**
CO_2Me **(*S*)-S2-Cme**
Piv **(*S*)-S2-Piv**



R = Boc **(*rac*)-S3**
Cbz **(*rac*)-S3-Cbz**
CO_2Me **(*rac*)-S3-Cme**



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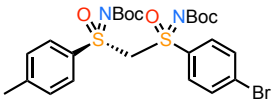

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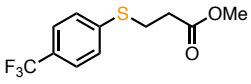

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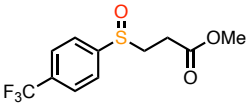

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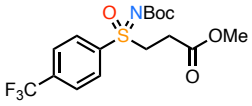

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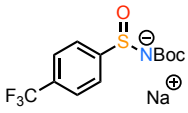

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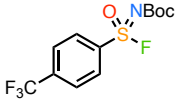
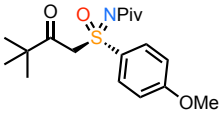


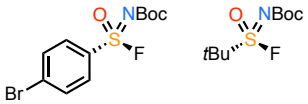
S10



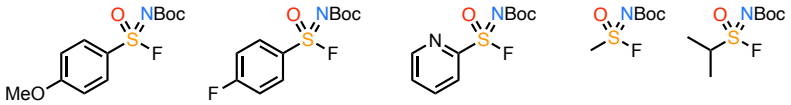
(*S*)-S11

Previously reported sulfonyl fluorides - see Greed *et al.*[3]

enantioenriched

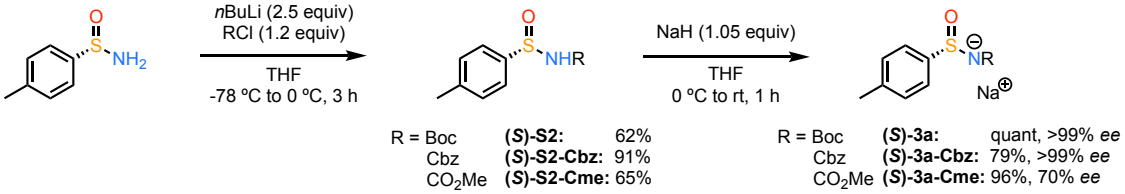


racemic

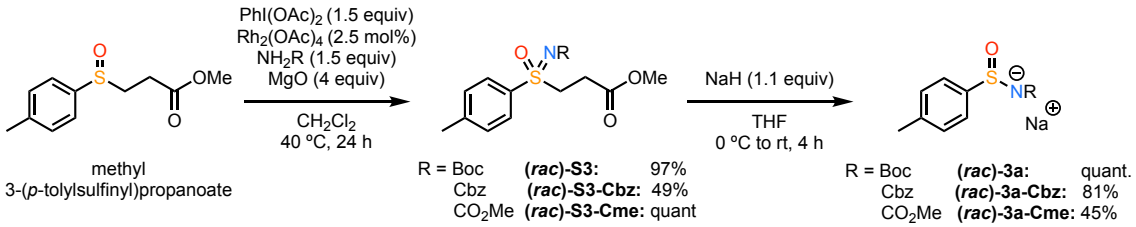


Synthesis of *p*-tolyl sulfinamide salts with different protecting groups

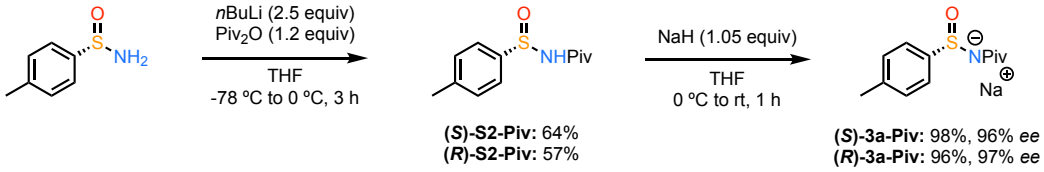
A. Synthesis of enantioenriched sulfinamide salts (*S*)-3a, 3a-Cbz and 3a-Cme from enantioenriched starting material



B. Synthesis of racemic sulfinamide salts (*rac*)-3a, 3a-Cbz and 3a-Cme

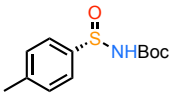


C. Synthesis of enantioenriched NPiv-sulfinamide salts (*S*)-3a-Piv and (*R*)-3a-Piv



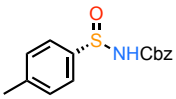
*A. Synthesis of enantioenriched sulfinamide salts **(S)-3a**, **3a-Cbz** and **3a-Moc** from enantioenriched starting material*

***tert*-Butyl (*p*-tolylsulfinyl)carbamate ((*S*)-S2)**



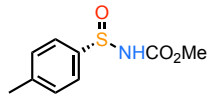
Prepared according to a literature procedure.[2,3] *n*-Butyllithium (1.52 M in hexanes, 10.6 mL, 16.1 mmol, 2.5 equiv) was added dropwise to a stirred solution of (*S*)-*p*-toluenesulfinamide (1.0 g, 6.4 mmol, 1 equiv) in THF (8 mL, 0.8 M) at –78 ºC. The mixture was stirred for 10 min followed by the addition of di-*tert*-butyl carbamate (1.70 g, 7.8 mmol, 1.2 equiv) in THF (5 mL, 1.5 M) and warmed to rt for 3 h. At 0 ºC, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (10 mL) and diluted with CH_2Cl_2 (10 mL). The mixture was extracted with CH_2Cl_2 (5 × 15 mL) and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification by recrystallisation (3:1 hexane/EtOAc) gave sulfinamide **(*S*)-S2** as a white solid (1.03 g, 62%, >99% *ee*). mp = 90–92 °C. IR (film)/cm^{-1} 3116, 3064, 2971, 2922, 2814, 1703, 1595, 1490, 1331, 1156, 1100, 898, 809. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 2H, 2 × Ar–H), 7.32 (d, *J* = 7.9 Hz, 2H, 2 × Ar–H), 2.41 (s, 3H, Ar–CH_3), 1.49 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7 (C=O), 142.5 (Ar–C_q), 140.7 (Ar–C_q), 130.1 (2 × Ar–C), 124.8 (2 × Ar–C), 83.6 ($C(CH_3)_3$), 28.2 ($C(CH_3)_3$), 21.5 (Ar–CH_3). $[\alpha]^{21}_D$ = +80 (c 0.1, $CHCl_3$).

Benzyl (*S*)-(*p*-tolylsulfinyl)carbamate ((*S*)-S2-Cbz)



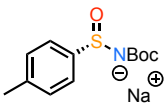
Prepared in a similar manner to a literature procedure.[2,3] *n*-Butyllithium (1.6 M in hexanes, 16.0 mL, 25 mmol, 2.5 equiv) was added dropwise to a stirred solution of (*S*)-*p*-toluenesulfinamide (1.55 g, 10.0 mmol, 1.0 equiv) in THF (13 mL, 0.8 M) at –78 ºC. The mixture was stirred for 10 min followed by the addition of benzyl chloroformate (1.71 mL, 12.0 mmol, 1.2 equiv) and warmed to rt for 3 h. At 0 ºC, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (30 mL) and diluted with EtOAc (30 mL). The mixture was extracted with EtOAc (3 × 30 mL), and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification by column chromatography (25% EtOAc in pentane) gave sulfinamide **(*S*)-S2-Cbz** as a white solid (2.51 g, 9.12 mmol, 91%). mp = 122–123 ºC. R_f 0.27 (25% EtOAc in pentane). IR (film)/cm^{-1} 3064, 2960, 1730, 1431, 1282, 1215, 1103, 1070, 805, 745, 703. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.57 (m, 2H, 2 × Ar–H), 7.39–7.32 (m, 7H, 7 × Ar–H), 6.85 (s, 1H, NH), 5.24 (s, 2H, OCH_2), 2.42 (s, 3H, Ar–CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8 (C=O), 143.0 (Ar–C_q), 140.5 (Ar–C_q), 135.0 (Ar–C_q), 130.2 (2 × Ar–C), 128.8 (4 × Ar–C), 128.6 (Ar–C), 124.8 (2 × Ar–C), 68.8 (OCH_2), 21.6 (Ar–CH_3). HRMS (ES) m/z cald for $C_{15}H_{16}NO_3S$ $[M+H]^+$: 290.0851; Found: 290.0848. $[\alpha]^{22}_D$ = +24 (c 1.0, $CHCl_3$).

Methyl (*S*)-(*p*-tolylsulfinyl)carbamate ((*S*)-S2-Moc)



Prepared in a similar manner to a literature procedure.[2,3] *n*-Butyllithium (1.6 M in hexanes, 16.0 mL, 25 mmol, 2.5 equiv) was added dropwise to a stirred solution of (*S*)-*p*-toluenesulfinamide (1.55 g, 10.0 mmol, 1 equiv) in THF (13 mL, 0.8 M) at –78 ºC. The mixture was stirred for 10 min followed by the addition of methyl chloroformate (0.95 mL, 12.0 mmol, 1.2 equiv) and warmed to rt for 3 h. At 0 ºC, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (30 mL) and diluted with EtOAc (30 mL). The mixture was extracted with EtOAc (3 × 30 mL) and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification by column chromatography (25% EtOAc in pentane) gave sulfinamide **(*S*)-S2-Moc** as a white solid (1.39 g, 6.52 mmol, 65%). mp = 84–86 ºC. R_f 0.17 (25% EtOAc in pentane). IR (film)/cm^{-1} 2922, 2855, 1595, 1410, 1320, 1238, 1178, 1140, 1081, 813, 738. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.58 (m, 2H, 2 × Ar–H), 7.39–7.31 (m, 2H, 2 × Ar–H), 6.83 (s, 1H, NH), 3.84 (s, 3H, OCH_3), 2.43 (s, 3H, Ar–CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6 (C=O), 143.3 (Ar–C_q), 140.8 (Ar–C_q), 130.6 (2 × Ar–C), 125.1 (2 × Ar–C), 54.2 (OCH_3), 21.9 (Ar–CH_3). HRMS (ES) m/z cald for $C_9H_{10}NO_3S$ $[M-H]^-$: 212.0376; Found: 212.0332. $[\alpha]^{22}_D$ = +50 (c 0.4, $CHCl_3$).

Sodium (*tert*-butoxycarbonyl)(*p*-tolylsulfinyl)amide ((*S*)-3a)

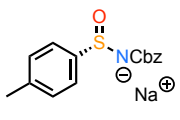


Prepared in a similar manner to a literature procedure.[3] NaH (60% in mineral oil, 52 mg, 1.23 mmol, 1.05 equiv) was added portionwise to sulfinamide **(*S*)-S2** (300 mg, 1.23 mmol, 1 equiv) in THF (13 mL, 0.1 M) and stirred for 1 h at rt. The reaction mixture was quenched with MeOH (0.1 mL, 0.1 mmol, 0.05 equiv) and concentrated under reduced pressure. The precipitate was collected by filtration and washed with hexane to give sulfinamide salt **(*S*)-3a** (340 mg, 1.23 mmol, quant, >99% *ee*) as a white solid. mp = 233–234 °C. IR (film)/cm^{-1} 3086, 3049, 2922, 2960, 1642, 1580, 1480, 1241, 1152, 1021, 798. ^{1}H NMR (400 MHz, D_2O) δ 7.54 (d, *J* = 8.2 Hz,

2H, 2 × Ar–H), 7.35 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 2.37 (s, 3H, Ar–CH_3), 1.41 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, D_2O) δ 165.9 (C=O), 143.2 (Ar–C_q), 141.7 (Ar–C_q), 129.6 (2 × Ar–C), 124.7 (2 × Ar–C), 79.6 ($C(CH_3)_3$), 27.8 ($C(CH_3)_3$), 20.5 (Ar–CH_3). HRMS (ESI) m/z Calcd for $C_{12}H_{16}NO_3S$ $[M]^-$: 254.0844; Found: 254.0851. $[\alpha]^{21}_D$ = +56 (c 1.0, H_2O). Analytical data (^{1}H and ^{13}C NMR) in agreement with those reported in the literature.[3] HPLC Conditions: Chiralpak IB column, 98:2 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm, **((*S*)-S2)** retention time: 22 min. Analytical data (^{1}H and ^{13}C NMR) in agreement with those reported in the literature.[4]

(*rac*)-S2: Determination of *ee* from reprotonation. The minimum MeOH (~0.1 mL) was added to a sample of **(*S*)-3a** (~1 mg) until completely dissolved. An aliquot was removed and diluted with hexane for HPLC analysis of sulfinamide **(*S*)-3a**. HPLC Conditions: Chiralpak IB column, 98:2 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm, retention times: 22 & 24 min.

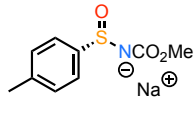
Sodium (*S*)-((Benzyloxy)carbonyl)(*p*-tolylsulfinyl)amide ((*S*)-3a-Cbz)



Prepared in a similar manner to a literature procedure.[3] NaOH (5 M in MeOH, 2.81 mL, 14 mmol, 1.5 equiv) was added to sulfinamide **(*S*)-S2-Cbz** (2.50 g, 9.10 mmol, 1.0 equiv) in CH_2Cl_2 (91 mL, 0.1 M) and stirred for 3 h at rt. The reaction mixture was concentrated, and pentane was added to induce precipitation. The precipitate was collected by filtration and washed with pentane to give sulfinamide salt **(S)-3a-Cbz** (2.02 g, 7.19 mmol, 79%, >99% *ee*) as a white solid. Decomposed at 73–74 ºC. IR (film)/cm^{-1} 2999, 2930, 2251, 1625, 1470, 1439, 1390, 1252, 1081, 1014, 857, 812, 750. ^{1}H NMR (400 MHz, MeOD) δ 7.58–7.50 (m, 2H, 2 × Ar–H), 7.39–7.34 (m, 2H, 2 × Ar–H), 7.33–7.19 (m, 5H, 5 × Ar–H), 5.13–4.99 (m, 2H, OCH_2), 2.35 (s, 3H, Ar–CH_3). ^{13}C NMR (101 MHz, MeOD) δ 180.4 (C=O), 167.0 (Ar–C_q), 141.3 (Ar–C_q), 139.5 (Ar–C_q), 130.2 (2 × Ar–C), 129.2 (2 × Ar–C), 128.6 (2 × Ar–C), 128.4 (Ar–C), 126.3 (2 × Ar–C), 67.5 (OCH_2), 21.3 (Ar–CH_3). HRMS (ES) m/z cald for $C_{15}H_{14}NO_3S$ $[M\text{-}Na]^-$: 288.0689; Found: 288.0689. $[\alpha]^{22}_D$ = +18 (c 1.0, MeOH).

For chiral HPLC analysis: The minimum MeOH (~0.1 mL) was added to completely dissolve a sample of **(*S*)-3a-Cbz** (~1 mg). An aliquot was removed and diluted with hexane for HPLC analysis of sulfinamide **(*S*)-3a-Cbz**. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm. Retention time: 35 min.

Sodium (*S*)-(Methoxycarbonyl)(*p*-tolylsulfinyl)amide ((*S*)-3a-Moc)



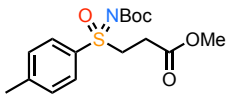
Prepared in a similar manner to a literature procedure.[3] NaOH (5 M in MeOH, 1.97 mL, 10 mmol, 1.5 equiv) was added to sulfinamide **(*S*)-S2-Moc** (1.40 g, 6.5 mmol, 1.0 equiv) in CH_2Cl_2 (65 mL, 0.1 M) and stirred for 18 h at rt. The reaction mixture was concentrated, pentane was added to induce precipitation. The precipitate was collected by filtration and washed with pentane to give sulfinamide salt **(*S*)-3a-Moc** (1.32 g, 6.2 mmol, 96%, 68% *ee*) as a very hygroscopic amorphous solid**.** Melting point analysis was not possible to perform. IR (film)/cm^{-1} 2952, 2855, 2251, 1565,1439, 1275, 1185, 1088, 999, 850, 805, 790. ^{1}H NMR (400 MHz, MeOD) δ 7.55–7.49 (m, 2H, 2 × Ar–H), 7.27–7.16 (m, 2H, 2 × Ar–H), 3.58 (s, 3H, OCH_3), 2.33 (s, 3H,

Ar–CH_3). ^{13}C NMR (101 MHz, MeOD) δ 167.8 (C=O), 146.9 (Ar–C_q), 141.3 (Ar–C_q), 130.2 (2 × Ar–C), 126.3 (2 × Ar–C), 52.5 (OCH_3), 21.3 (Ar–CH_3). HRMS (ES) m/z cald for $C_9H_{10}NO_3S$ $[M-Na]^-$: 212.0376; Found: 212.0373. $[\alpha]^{22}_D$ = +12 (c 1.0, MeOH).

For chiral HPLC analysis: The minimum MeOH (~0.1 mL) was added to a sample of **(*S*)-3a-Moc** (~1 mg) until completely dissolved. An aliquot was removed and diluted with hexane for HPLC analysis of sulfinamide **(S)-3a-Moc**. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention time: 29 min.

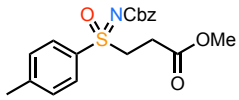
*B. Synthesis of racemic sulfinamide salts **(rac)-S3**, **S3-Cbz** and **(rac)-S3-Moc***

Methyl 3-(*N*-(tert-butoxycarbonyl)-4-methylphenylsulfonimidoyl)propanoate (S3)



Prepared in a similar method to a literature procedure.[1] Magnesium oxide (3.24 g, 80.4 mmol, 4 equiv), *tert*-butyl carbamate (3.53 g, 30.2 mmol, 1.5 equiv), $PhI(OAc)_2$ (9.71 g, 30.2 mmol, 1.5 equiv) and $Rh_2(OAc)_4$ (0.22 g, 0.5 mmol, 2.5 mol%) were added to a stirred solution of methyl 3-(*p*-tolylsulfinyl)propanoate (4.20 g, 20.1 mmol, 1 equiv) in CH_2Cl_2 (200 mL, 0.1 M) at RT and warmed to 40 °C for 18 h. At RT the reaction mixture was filtered through celite and concentrated under reduced pressure. Purification by flash column chromatography (50% EtOAc in pentane) afforded sulfoximine **S3** (4.39 g, 19.4 mmol, 97%) as a white solid. mp = 83–84 °C. R_f 0.34 (50% EtOAc in pentane). IR (film)/cm^{-1} 2978, 1740, 1670, 1439, 1364, 1274, 1252, 1156, 894. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 7.37 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 3.69 (ddd, *J* = 14.3, 9.5, 6.0 Hz, 1H, SC*H*H), 3.61 (s, 3H, OCH_3), 3.55 (ddd, *J* = 14.2, 9.3, 6.0 Hz, 1H, SCH*H*), 2.89–2.67 (m, 2H, SCH_2CH_2), 2.46 (s, 3H, Ar–CH_3), 1.37 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3 (C=O), 157.7 (C=O), 145.2 (Ar–C_q), 133.8 (Ar–C_q), 130.5 (2 × Ar–C), 128.3 (2 × Ar–C), 80.8 ($C(CH_3)_3$), 52.5 (OCH_3), 51.9 (Ar–CH_3), 28.1 ($C(CH_3)_3$), 27.4 (CH_2), 21.8 (CH_2). HRMS (ESI) *m/z* Calcd for $C_{16}H_{25}NO_5S$ $[M+H]^+$: 342.1370; Found: 342.1375. Analytical data (^1H and ^{13}C NMR) in agreement with those reported in the literature.[3]

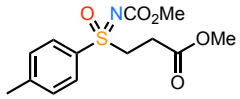
Methyl 3-(*N*-((benzyloxy)carbonyl)-4-methylphenylsulfonimidoyl)propanoate (S3-Cbz)



Prepared according to a literature procedure.[1] Magnesium oxide (1.6 g, 40 mmol, 4 equiv), benzyl carbamate (2.27 g, 15 mmol, 1.5 equiv), $PhI(OAc)_2$ (4.83 g, 15 mmol, 1.5 equiv) and $Rh_2(OAc)_4$ (111 mg, 0.25 mmol, 2.5 mol%) were added to a stirred solution of methyl 3-(*p*-tolylsulfinyl)propanoate (2.26 g, 10 mmol, 1 equiv) in CH_2Cl_2 (70 mL, 0.1 M) at rt and warmed to 40 °C for 18 h. At rt, the reaction mixture was filtered through celite and concentrated under reduced pressure. Purification by flash column chromatography (30% EtOAc in pentane) afforded sulfoximine **S3-Cbz** (1.84 g, 4.9 mmol, 49%) as a pale yellow oil. R_f 0.28 (40% EtOAc in pentane). IR (film)/cm^{-1} 3034, 2952, 1737, 1670, 1491, 1439, 1364, 1238, 1185, 1101, 1059, 984, 902, 813. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83–7.75 (m, 2H, 2 × Ar–H), 7.39–7.34 (m, 2H, 2 × Ar–H), 7.32–7.26 (m, 5H, 5 × Ar–H), 5.15–5.07 (m, 1H, OC*H*H), 5.02 (d, *J* = 12.3 Hz, 1H, OCH*H*), 3.73 (ddd, *J* = 14.3, 9.3, 6.1 Hz, 1H, SC*H*H), 3.62 (ddd, *J* = 14.3, 9.3, 6.1 Hz, 1H, SCH*H*), 3.61 (s, 3H, OCH_3), 2.78 (qdd, *J* = 17.2, 9.2, 6.2 Hz, 2H, $COCH_2$), 2.45 (s, 3H, Ar–CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2

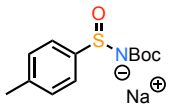
(C=O), 158.6 (C=O), 145.6 (Ar–C_q), 136.3 (Ar–C_q), 133.2 (Ar–C_q), 130.5 (2 × Ar–C), 128.5 (2 × Ar–C), 128.4 (2 × Ar–C), 128.3 (2 × Ar–C), 128.1 (Ar–C), 68.0 (OCH_2), 52.5 ($COOCH_3$), 51.9 (SCH_2), 27.4 ($COCH_2$), 21.8 (Ar–CH_3). HRMS (ES) m/z cald for $C_{19}H_{22}NO_5S$ $[M+H]^+$: 376.1219; Found: 376.1212.

Methyl 3-(*N*-(methoxycarbonyl)-4-methylphenylsulfonimidoyl)propanoate (S3-Moc)



Prepared according to a literature procedure.[1] Magnesium oxide (1.6 g, 40 mmol, 4 equiv), methyl carbamate (1.13 g, 15 mmol, 1.5 equiv), $PhI(OAc)_2$ (4.83 g, 15 mmol, 1.5 equiv) and $Rh_2(OAc)_4$ (111 mg, 0.25 mmol, 2.5 mol%) were added to a stirred solution of methyl 3-(*p*-tolylsulfinyl)propanoate (2.26 g, 10 mmol, 1 equiv) in CH_2Cl_2 (70 mL, 0.1 M) at rt and warmed to 40 °C for 18 h. At rt, the reaction mixture was filtered through celite and concentrated under reduced pressure. Purification by flash column chromatography (30% EtOAc in pentane) afforded sulfoximine **S3-Moc** (2.97 g, 10 mmol, quant.) as a pale yellow oil. R_f 0.24 (30% EtOAc in pentane). IR (film)/cm^{-1} 2997, 2950, 1744, 1677, 1439, 1364, 1252, 1100, 969, 880, 790. ^1H NMR (400 MHz, $CDCl_3$) δ 7.85–7.78 (m, 2H, 2 × Ar–H), 7.43–7.30 (m, 2H, 2 × Ar–H), 3.74 (ddd, *J* = 14.3, 9.2, 6.2 Hz, 1H, SC*H*H), 3.65 (s, 3H, NCO_2CH_3), 3.68–3.59 (m, 1H, SCH*H*), 3.62 (s, 3H, OCH_3), 2.89–2.68 (m, 2H, $COCH_2$), 2.46 (s, 3H, Ar–CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5 (C=O), 159.7 (C=O), 145.9 (Ar–C_q), 133.5 (Ar–C_q), 130.9 (2 × Ar–C), 128.6 (2 × Ar–C), 53.7 (NCO_2CH_3), 52.8 (CO_2CH_3), 52.1 (SCH_2), 27.8 ($COCH_2$), 22.1 (Ar–CH_3). HRMS (ES) m/z cald for $C_{13}H_{18}NO_5S$ $[M+H]^+$: 300.0906; Found: 300.0898.

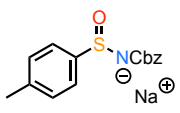
Sodium (*tert*-butoxycarbonyl)(*p*-tolylsulfinyl)amide ((*rac*)-3a)



Prepared in a similar manner to a literature procedure.[3] NaH (60% in mineral oil, 526 mg, 13.1 mmol) was added to sulfoximine **(*rac*)-S3** (4.28 g, 12.5 mmol) in THF (125 mL) at 25 °C and stirred for 3 h. The reaction was quenched with MeOH (25 μL) and concentrated under reduced pressure. The precipitate was collected by filtration and washed with hexane to give sulfinamide salt **(*rac*)-3a** (3.46 g, quant.) as a white solid. The analytical data (^1H and ^{13}C NMR) was identical to that shown for **(*S*)-3a** above.

For chiral HPLC analysis: The minimum MeOH (~0.1 mL) was added to completely dissolve a sample of **(*rac*)-3a** (~1 mg). An aliquot was removed and diluted with hexane for HPLC analysis of sulfinamide **(*rac*)-3a**. HPLC Conditions: Chiralpak IB column, 98:2 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm, retention times: 22 & 24 min.

Sodium ((Benzyloxy)carbonyl)(*p*-tolylsulfinyl)amide ((*rac*)-3a-Cbz)

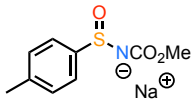


Prepared in a similar manner to a literature procedure.[3] NaH (60% in oil, 216 mg, 5.39 mmol, 1.1 equiv) was added to sulfinamide **(*rac*)-S3-Cbz** (1.84 g, 4.90 mmol, 1.0 equiv) in THF (49 mL, 0.1 M) at 0 °C and stirred, warming to rt, for 3 h. The reaction was quenched with MeOH (25 μL) and concentrated under reduced pressure. Pentane (100 mL) was added to induce precipitation, which was collected by filtration and washed with pentane to give

sulfinamide salt **(*rac*)-3a-Cbz** (1.15 g, 3.99 mmol, 81%) as a white solid. The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*S*)-3a-Cbz** above.

For chiral HPLC analysis: The minimum MeOH (~0.1 mL) was added to completely dissolve a sample of **(*rac*)-3a-Cbz** (~1 mg). An aliquot was removed and diluted with hexane for HPLC analysis of sulfinamide **(*rac*)-3a-Cbz**. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm. Retention times: 35 & 42 min.

Sodium (Methoxycarbonyl)(*p*-tolylsulfinyl)amide ((*rac*)-3a-Moc)

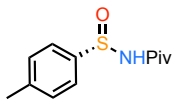


Prepared in a similar manner to a literature procedure.[3] NaH (60% in oil, 437 mg, 10.9 mmol, 1.1 equiv) was added to sulfinamide **(*rac*)-S3-Cbz** (2.97 g, 9.9 mmol, 1.0 equiv) in THF (99 mL, 0.1 M) at 0 °C and stirred, warming to rt, for 18 h. The reaction was quenched with MeOH (25 μL) and concentrated under reduced pressure. Pentane (100 mL) was added to induce precipitation, which was collected by filtration and washed with pentane to give sulfinamide salt **(*rac*)-3a-Moc** (0.94 mg, 4.43 mmol, 45%) as a white solid. The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*S*)-3a-Moc** above.

For chiral HPLC analysis: The minimum MeOH (~0.1 mL) was added to a sample of **(*S*)-3a-Moc** (~1 mg) until completely dissolved. An aliquot was removed and diluted with hexane for HPLC analysis of sulfinamide **(*S*)-3a-Moc**. Racemic material was used for HPLC analysis. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention times: 29 & 43 min.

*C. Synthesis of enantioenriched NPiv-sulfinamide salts **(S)-3a-Piv** and **(R)-3a-Piv***

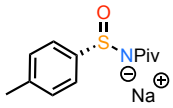
(*S*)-*N*-(*p*-Tolylsulfinyl)pivalamide ((*S*)-S2-Piv)



Prepared in a similar manner to a literature procedure.[2] *n*-BuLi (1.6 M in hexanes, 16.0 mL, 25 mmol, 2.5 equiv) was added dropwise to a stirred solution of (*S*)-*p*-toluenesulfinamide (1.55 g, 10.0 mmol, 1 equiv) in THF (13 mL, 0.8 M) at –78 ºC. The mixture was stirred for 10 min followed by the addition of pivalic anhydride (2.4 mL, 12.0 mmol, 1.2 equiv) and warmed to rt for 3 h. At 0 ºC, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (30 mL) and diluted with EtOAc (30 mL). The mixture was extracted with EtOAc (3 × 30 mL), and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification by column chromatography (25% EtOAc in pentane) gave sulfinamide **(*S*)-S2-Piv** as a white solid (1.52 g, 6.4 mmol, 64%). mp = 128–129 ºC. R_f 0.22 (30% EtOAc in pentane). IR (film)/cm^{-1} 3190, 2968, 2930, 2871, 1691, 1596, 1476, 1396, 1130, 1091, 1065, 1022, 905, 834, 808, 753, 704, 625, 520, 487, 428. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.58 (m, 2H, 2 × Ar–H), 7.41 (s, 1H, NH), 7.36 (d, *J* = 8.0 Hz, 2H, 2 × Ar–H), 2.44 (s, 3H, Ar–CH_3), 1.22 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2 (C=O), 143.3 (Ar–C_q), 141.6 (Ar–C_q), 129.6 (2 × Ar–C), 125.0 (2 × Ar–C), 39.4 (*C*(CH_3)$_3$), 27.6 (C(*C*H_3)$_3$), 20.4 (Ar–CH_3). $[\alpha]^{21}_D$ = +40 (c 0.2,$CHCl_3$). HPLC analysis not run as retention of *ee* is known.[5] Analytical data (^{1}H and ^{13}C NMR) in agreement with those reported in the literature.[5]

(*R*)-S2-Piv: For chiral HPLC analysis, the opposite enantiomer was generated in a similar manner to a literature procedure.[2] The above experimental procedure was carried out on (*R*)-*p*-toluenesulfinamide (1.55 g, 10.0 mmol) to give **(*R*)-S2-Piv** as a white solid (1.37 g, 5.7 mmol, 57%). The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*S*)-S2-Piv** above.

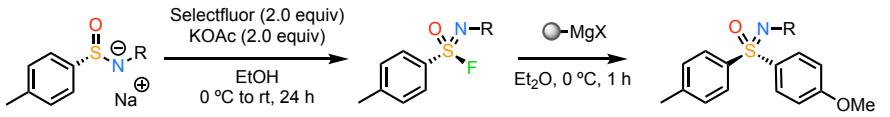
Sodium (*S*)-pivaloyl(*p*-tolylsulfinyl)amide ((*S*)-3-Piv)



Prepared in a similar manner to a literature procedure.[3] NaH (60% in oil, 270 mg, 6.7 mmol, 1.1 equiv) was added to sulfinamide **(*S*)-S2-Piv** (1.52 g, 6.5 mmol, 1.0 equiv) in THF (30 mL, 0.2 M) at 0 °C and stirred, warming to rt, for 3 h. The reaction was quenched with MeOH (~25 μL) and concentrated under reduced pressure. Pentane (100 mL) was added to induce precipitation, and the resulting solid was collected by filtration and washed with pentane and Et_2O to give sulfinamide salt **(*S*)-3-Piv** (1.66 g, 6.4 mmol, 98%, 96% *ee*) as a white solid. mp = 226–228 ºC. IR (film)/cm^{-1} 2952, 2922, 2864, 1512, 1479, 1454, 1391, 1331, 1208, 1177, 1087, 1019, 965, 918, 831, 802, 764, 704, 625, 545, 500, 442. ^{1}H NMR (400 MHz, D_2O) δ 7.54 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 7.39–7.31 (m, 2H, 2 × Ar–H), 2.37 (s, 3H, Ar–CH_3), 1.12 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, D_2O) δ 191.2 (C=O), 143.3 (Ar–C_q), 141.6 (Ar–C_q), 129.6 (2 × Ar–C), 125.0 (2 × Ar–C), 39.4 (*C*(CH_3)$_3$), 27.6 (C(*C*H_3)$_3$), 20.4 (Ar–CH_3). HRMS (ES) m/z cald for $C_{12}H_{18}NO_2S$ $[M+H]^+$: 240.1058; Found: 240.1063. $[\alpha]^{21}_D$ = –40 (c 1.0, H_2O). HPLC Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm. Retention time: 19 min.

(*R*)-3-Piv: For chiral HPLC analysis, the opposite enantiomer was generated in a similar manner to a literature procedure.[3] The above experimental procedure was carried out on **(*R*)-S2-Piv** (1.37 g, 5.4 mmol) to give **(*R*)-3-Piv** as a white solid (1.63 g, 5.3 mmol, 96%, 97% *ee*). The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*S*)-3-Piv** above. HPLC Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm. Retention time: 23 min.

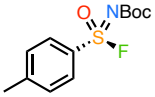
Synthesis of *p*-tolyl sulfoximines with different protecting groups



R = Boc	**3a**	>99% *ee*	R = Boc	**1**	quant, >99% *ee*	R = Boc	**2a**	96%, >99% *ee*
Cbz	**3a-Cbz**	>99% *ee*	Cbz	**1-Cbz**	77%, 96% *ee*	Cbz	**2a-Cbz**	63%, 80% *ee*
CO_2Me	**3a-Cme**	70% *ee*	CO_2Me	**1-Cme**	quant, 0% *ee*	CO_2Me	**2a-Cme**	42%, 0% *ee*
Piv	**3a-Piv**	96% *ee*	Piv	**1-Piv**	98%, 96% *ee*	Piv	**2a-Piv**	quant, 96% *ee*

*Sulfonimidoyl fluorides **1**, **1-Cbz**, **1-Moc**, **1-Piv***

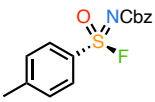
tert-Butyl (*R*)-(fluoro(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (1)



Reaction performed according to General Procedure A. Selectfluor (0.71 g, 2.0 mmol, 2 equiv) was added to a stirred solution of sulfinamide salt **(*S*)-3a** (0.29 g, 1.0 mmol, 1 equiv) and potassium acetate (0.20 g, 2.0 mmol, 2.0 equiv) in ethanol (5 mL, 0.2 M) at 0 ºC and slowly warmed to RT over 24 h. The reaction mixture was quenched with water (10 mL) and diluted with CH_2Cl_2 (10 mL). The mixture was extracted with CH_2Cl_2 (3 × 40 mL) and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. No further purification was required giving sulfonimidoyl fluoride **(*R*)-1** (0.29 g, quant., >99% *ee*) as a colourless viscous oil. IR (film)/cm^{-1} 2982, 2933, 1700, 1595, 1454, 1327, 1141, 1096, 813, 678. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 7.40 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 2.48 (s, 3H, Ar–CH_3), 1.53 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7 (C=O), 147.1 (Ar–C_q), 130.8 (d, *J* = 20.9 Hz, Ar–C_q), 130.2 (2 × Ar–C), 128.3 (2 × Ar–C), 82.7 ($C(CH_3)_3$), 28.0 ($C(CH_3)_3$), 21.9 (Ar–CH_3). ^{19}F NMR (377 MHz, $CDCl_3$) δ 68.8. HRMS (ESI) m/z Calcd for $C_{12}H_{17}NO_3SF$ $[M+H]^+$: 274.0913; Found: 274.0924. $[\alpha]^{21}_D$ = +9 (c 5.0, $CHCl_3$). Analytical data (^{1}H and ^{13}C NMR) in agreement with those reported in the literature.[3] HPLC Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm, retention time: 14 min.

(*rac*)-1: Synthesis of racemic sample for HPLC analysis performed according to General Procedure B. Selectfluor (533 g, 1.51 mmol, 1.5 equiv) was added to a solution of sulfinamide salt **(*rac*)-3a** (250 mg, 1.00 mmol) in DMF (5 mL) at 0 °C and warmed to 25 °C for 16 h. H_2O (10 mL) was added and the aqueous mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent was removed under reduced pressure to give sulfonimidoyl fluoride **(*rac*)-1** (116 mg, 48%) as a colourless oil with characterisation data in accordance with the above. HPLC Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm, retention times: 13 & 14 min.

Benzyl (*R*)-(fluoro(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-1-Cbz)

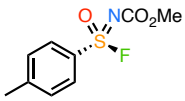


Reaction performed according to General Procedure A. Selectfluor (352 g, 1.0 mmol, 2.0 equiv) was added to a solution of sulfinamide salt **(*R*)-3a-Cbz** (156 mg, 0.50 mmol, >99% *ee*, 1.0 equiv) and potassium acetate (98 mg, 1.0 mmol, 2.0 equiv) in ethanol

(1.5 mL, 0.3 M) at 0 °C and warmed to 25 °C for 24 h. H_2O (30 mL) was added and the aqueous mixture extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give sulfonimidoyl fluoride **(*R*)-1-Cbz** (117 mg, 0.38 mmol, 77%, 96% *ee*) as a colourless oil. IR (film)/cm^{-1} 3034, 2967, 1707, 1595, 1454, 1379, 1252, 1096, 954, 880, 813, 738. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–7.96 (m, 2H, 2 × Ar–H), 7.45–7.28 (m, 7H, 7 × Ar–H), 5.23 (s, 2H, OCH_2), 2.51–2.48 (s, 3H, Ar–CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0 (C=O), 147.5 (Ar–C_q), 135.5 (Ar–C_q), 130.3 (2 × Ar–C), 130.3 (Ar–C_q), 128.7 (2 × Ar–C), 128.5 (Ar–C), 128.4 (2 × Ar–C), 128.3 (2 × Ar–C), 69.0 (OCH_2), 22.0 (Ar–CH_3). ^{19}F NMR (377 MHz, $CDCl_3$) δ 69.12 (S–F). HRMS (ES) m/z cald for $C_{15}H_{15}FNO_3S$ $[M+H]^+$: 308.0751; Found: 308.0762. $[\alpha]^{22}_D$ = –70 (c 0.2, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention time: 45 min.

(*rac*)-1-Cbz: The reaction was completed with racemic sulfinamide salt **(*rac*)-3a-Cbz** to give racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention times: 37 & 45 min.

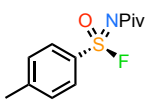
Methyl (*R*)-(fluoro(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (1-Moc)



Reaction performed according to General Procedure A. Selectfluor (352 g, 1.0 mmol, 2.0 equiv) was added to a solution of sulfinamide salt **(*S*)-3a-Moc** (118 mg, 0.50 mmol, 70% *ee*, 1.0 equiv) and potassium acetate (98 mg, 1.0 mmol, 2.0 equiv) in ethanol (1.5 mL, 0.3 M) at 0 °C and warmed to 25 °C for 24 h. H_2O (30 mL) was added and the aqueous mixture extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give sulfonimidoyl fluoride **(*R*)-1-Moc** (105 mg, 0.45 mmol, 91%, 0% *ee*) as a pale-yellow oil. IR (film)/cm^{-1} 2968, 2922, 2848, 1725, 1595, 1439, 1327, 1260, 1096, 984, 887, 813, 738. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–7.95 (m, 2H, 2 × Ar–H), 7.45–7.38 (m, 2H, 2 × Ar–H), 3.82 (s, 3H, OCH_3), 2.48 (s, 3H, Ar–CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6 (C=O), 147.5 (Ar–C_q), 130.3 (2 × Ar–C), 130.2 (Ar–C_q), 128.3 (2 × Ar–C), 54.3 (OCH_2), 22.0 (Ar–CH_3). ^{19}F NMR (377 MHz, $CDCl_3$) δ 69.13 (S–F). HRMS (ES) m/z cald for $C_8H_7FNO_3S$ $[M-Me]^+$: 216.0125; Found: 216.0133. $[\alpha]^{22}_D$ = −15 (c 0.4, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 270 nm. Retention times: 21 & 23 min.

(*rac*)-1-Moc: The reaction was completed with racemic sulfinamide salt **(*rac*)-3a-Moc** to give racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 270 nm. Retention times: 21 & 23 min.

(*R*)-4-Methyl-*N*-pivaloylbenzenesulfonimidoyl fluoride (1-Piv)



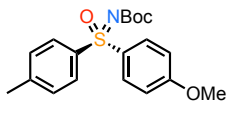
Reaction performed according to General Procedure A. Selectfluor (704 g, 2.0 mmol, 2.0 equiv) was added to a solution of sulfinamide salt **(*S*)-3a-Piv** (261 mg, 1.0 mmol, 96% *ee*, 1.0 equiv) and potassium acetate (196 mg, 2.0 mmol, 2.0 equiv) in ethanol (3.3 mL, 0.3 M) at 0 °C and warmed to 25 °C for 24 h. H_2O (30 mL) was added and the aqueous mixture

extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give sulfonimidoyl fluoride **(*R*)-1-Piv** (252 mg, 0.98 mmol, 98%, 96% *ee*) as an amorphous solid. IR (film)/cm^{-1} 2973, 2933, 2871, 1682, 1595, 1478, 1396, 1299, 1277, 1167, 1107, 1048, 1017, 846, 813, 718, 661, 595, 540, 501. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.93 (m, 2H, 2 × Ar–H), 7.44 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 2.52 (s, 3H, Ar–CH_3), 1.27 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.0 (C=O), 147.0 (Ar–C_q), 130.3 (2 × Ar–C), 128.6 (Ar–C_q), 128.1 (2 × Ar–C), 42.4 (*C*(CH_3)$_3$), 27.3 (C(*C*H_3)$_3$, 22.0 (Ar–CH_3). ^{19}F NMR (377 MHz, $CDCl_3$) δ 65.83 (S–F). HRMS (ES) m/z cald for $C_{12}H_{17}FNO_2S$ $[M+H]^+$: 258.0964; Found: 258.0953. $[\alpha]^{21}_D$ = −33 (c 0.3, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 270 nm. Retention time: **(*R*)-1-Piv** = 8 min.

(*S*)-1-Piv: For chiral HPLC analysis, the opposite enantiomer was generated in a similar manner. The above experimental procedure was carried out on **(*R*)-3a-Piv** (261 mg, 1.0 mmol) to give **(*S*)-1-Piv** as a white solid (250 g, 0.97 mmol, 96%). The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*R*)-1-Piv** above. HPLC Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 270 nm. Retention time: **(*S*)-1-Piv** = 9 min.

*Sulfoximines **(R)-2a**, **2a-Cbz**, **2a-Moc** and **2a-Piv***

***tert*-Butyl (*S*)-((4-methoxyphenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2a)**

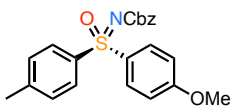


Reaction performed according to General Procedure D. 4-Methoxyphenylmagnesium bromide (0.60 mL, 0.5 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20-30% EtOAc in pentane) gave sulfoximine **(*S*)-2a** as a white solid (86.7 mg, 0.24 mmol, 96%, >99% *ee*). mp = 133–134 ºC. R_f 0.18 (25% EtOAc in pentane). IR (film)/cm^{-1} 3064, 2978, 2930, 2844, 1670, 1595, 1498, 1461, 1252, 1156, 1098, 1025, 895, 835, 805, 864, 764. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.90 (m, 2H, 2 × Ar–H), 7.90–7.83 (m, 2H, 2 × Ar–H), 7.33–7.25 (m, 2H, 2 × Ar–H), 7.01–6.92 (m, 2H, 2 × Ar–H), 3.84 (s, 3H, OCH_3), 2.39 (s, 3H, Ar–CH_3), 1.37 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (Ar–C_q), 157.6 (C=O), 143.9 (Ar–C_q), 137.7 (Ar–C_q), 131.4 (Ar–C_q), 130.1 (2 × Ar–C), 129.9 (2 × Ar–C), 127.6 (2 × Ar–C), 114.7 (2 × Ar–C), 80.5 (*C*(CH_3)$_3$), 55.8 (OCH_3), 28.1 (C(*C*H_3)$_3$), 21.6 (Ar–CH_3). HRMS (+p APCI) m/z Calcd for $C_{19}H_{24}NO_4S^+$ [M+H]: 362.1421; Found: 362.1416. $[\alpha]^{21}_D$ = –4 (c 1.0, acetone). HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm, retention time: 25 min.

(*rac*)-2a: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions:

Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm, retention time: 25 and 28 min.

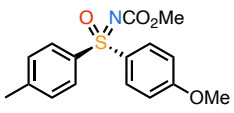
Benzyl (*S*)-((4-methoxyphenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2a-Cbz)



Reaction performed according to General Procedure D. 4-Methoxyphenylmagnesium bromide (0.60 mL, 0.5 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1-Cbz** (77 mg, 0.25 mmol, 1.0 equiv, 96% *ee*) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (25% EtOAc in pentane) gave sulfoximine **(*S*)-2a-Cbz** as a white solid (63.4 mg, 0.16 mmol, 63%, 80% *ee*). mp = 117–118 ºC. R_f 0.20 (30% EtOAc in pentane). IR (film)/cm^{-1} 3039, 3027, 2945, 1670, 1588, 1491, 1449, 1377, 1312, 1230, 1187, 1088, 1021, 910, 731. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.0 Hz, 2H, 2 × Ar–H), 7.84 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 7.27–7.24 (m, 2H, 2 × Ar–H), 6.99–6.89 (m, 2H, 2 × Ar–H), 5.08 (s, 2H, OCH_2), 3.82 (s, 3H, OCH_3), 2.38 (s, 3H, Ar–CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (Ar–C_q), 159.0 (C=O), 144.6 (Ar–C_q), 137.5 (Ar–C_q), 136.8 (Ar–C_q), 131.1 (Ar–C_q), 130.5 (2 × Ar–C), 130.3 (2 × Ar–C), 128.7 (2 × Ar–C), 128.7 (2 × Ar–C), 128.3 (Ar–C), 127.9 (2 × Ar–C), 115.1 (2 × Ar–C), 68.2 (OCH_2), 56.1 (OCH_3), 22.0 (Ar–CH_3). HRMS (ES) m/z cald for $C_{22}H_{22}NO_4S$ $[M+H]^+$: 396.1270; Found: 396.1265. $[\alpha]^{22}_D$ = −6 (c 1.0, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention time: 64 min.

(*rac*)-2a-Cbz: The reaction was completed with racemic sulfonimidoyl fluoride **(*rac*)-1-Cbz** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention times: 64 & 72 min.

Methyl (*S*)-((4-methoxyphenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2a-Moc)

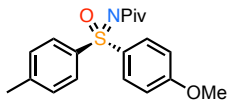


Reaction performed according to General Procedure D. 4-Methoxyphenylmagnesium bromide (0.60 mL, 0.5 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*rac*)-1-Moc** (58 mg, 0.25 mmol, 1.0 equiv, 0% *ee*) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (25% EtOAc in pentane) gave sulfoximine **(*rac*)-2a-Moc** as an amorphous solid (33.8 mg, 0.11 mmol, 42%, 0% *ee*). R_f 0.19 (30% EtOAc in pentane). IR (film)/cm^{-1} 3042, 2959, 2848, 1752, 1595, 1485, 1461, 1349, 1252, 1163, 1088, 1029, 872, 812. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.88 (m, 2H, 2 × Ar–H), 7.87–7.82 (m, 2H, 2 × Ar–H), 7.32–7.27 (m, 2H, 2 × Ar–H), 7.00–6.92 (m, 2H, 2 × Ar–H), 3.83 (s, 3H, Ar–OCH_3), 3.65 (s, 3H, OCH_3), 2.38 (s, 3H, Ar–CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 (Ar–C_q), 159.5 (C=O), 144.3 (Ar–C_q), 137.1 (Ar–

C_q), 130.7 (Ar–C_q), 130.2 (2 × Ar–C), 129.9 (2 × Ar–C), 127.6 (2 × Ar–C), 114.9 (2 × Ar–C), 55.8 (Ar–OCH_3), 53.3 (OCH_3), 21.6 (Ar–CH_3). HRMS (ES) m/z cald for $C_{16}H_{18}NO_4S$ $[M+H]^+$: 320.0957; Found: 320.0950. HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention times: 39 & 44 min.

(*rac*)-2a-Moc: The reaction was completed with racemic sulfonimidoyl fluoride **(*rac*)-1-Moc** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention times: 39 & 44 min.

(*S*)-N-((4-methoxyphenyl)(oxo)(p-tolyl)-λ⁶-sulfaneylidene)pivalamide (2a-Piv)

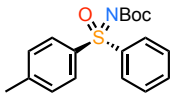


Reaction performed according to General Procedure D. 4-Methoxyphenylmagnesium bromide (0.60 mL, 0.5 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1-Piv** (64 mg, 0.25 mmol, 1.0 equiv, 96% *ee*) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (25% EtOAc in pentane) gave sulfoximine **(*S*)-2a-Piv** as a white solid (87.0 mg, 0.25 mmol, quant, 96% *ee*). mp = 120–121 ºC. R_f 0.20 (25% EtOAc in pentane). IR (film)/cm^{-1} 2969, 2926, 2867, 1643, 1593, 1495, 1285, 1261, 1222, 1166, 1094, 1025, 834, 667, 550, 531. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.84 (m, 2H, 2 × Ar–H), 7.84–7.77 (m, 2H, 2 × Ar–H), 7.28 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 7.00–6.91 (m, 2H, 2 × Ar–H), 3.83 (s, 3H, OCH_3), 2.38 (s, 3H, Ar–CH_3), 1.26 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0 (C=O), 163.4 (Ar–C_q), 143.8 (Ar–C_q), 137.9 (Ar–C_q), 131.6 (Ar–C_q), 130.2 (2 × Ar–C), 129.7 (2 × Ar–C), 127.5 (2 × Ar–C), 114.8 (2 × Ar–C), 55.8 (OCH_3), 41.8 ($C(CH_3)_3$), 27.9 ($C(CH_3)_3$), 21.7 (Ar–CH_3). $[\alpha]^{21}_D$ = −18 (c 1, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 270 nm. Retention time: **(*S*)-2a-Piv** = 32 min. Analytical data (^{1}H and ^{13}C NMR) in agreement with those reported in the literature.[6]

(*R*)-2a-Piv: For chiral HPLC analysis, the opposite enantiomer was generated in a similar manner. The above experimental procedure was carried out on **(*S*)-1-Piv** (64 mg, 0.25 mmol, 96% *ee*) to give **(*R*)-2a-Piv** as a white solid (88.1 g, quant, 96% *ee*). The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*S*)-2a-Piv** above. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 270 nm. Retention time: **(*R*)-2a-Piv** = 36 min.

Scope of sulfoximines from sulfonimidoyl fluoride **(*R*)-1** with Grignard reagents

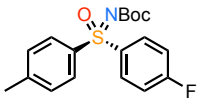
***tert*-Butyl (*R*)-(oxo(phenyl)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2b)**



Reaction performed according to General Procedure D. Phenylmagnesium bromide (0.11 mL, 2.7 M in Et_2O, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20–30% EtOAc in pentane) gave sulfoximine **(*R*)-2b** as a white solid (70.2 mg, 0.21 mmol, 85%, 98% *ee*). mp = 194–197 ºC. R_f 0.17 (25% EtOAc in pentane). IR (film)/cm^{-1} 3064, 2967, 2926, 1666, 1595, 1446, 1394, 1364, 1267, 1230, 1156, 1092, 895, 865, 816, 772, 758, 686. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.94 (m, 2H, 2 × Ar–H), 7.92–7.84 (m, 2H, 2 × Ar–H), 7.56–7.45 (m, 3H, 3 × Ar–H), 7.31–7.27 (m, 2H, 2 × Ar–H), 2.38 (s, 3H, Ar–CH_3), 1.33 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (C=O), 144.3 (Ar–C_q), 140.5 (Ar–C_q), 136.9 (Ar–C_q), 133.1 (Ar–C), 130.2 (2 × Ar–C), 129.4 (2 × Ar–C), 127.9 (2 × Ar–C), 127.7 (2 × Ar–C), 80.7 (*C*(CH_3)$_3$), 28.1 (C(*C*H_3)$_3$), 21.6 (Ar–CH_3). HRMS (ES) m/z cald for $C_{18}H_{22}NO_3S$ $[M+H]^+$: 332.1320; Found: 332.1318. $[\alpha]^{24}_D$ = +52 (c 1.0, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm. Retention time: 31 min.

(*rac*)-2b: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **(*rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm. Retention times: 31 & 36 min.

***tert*-Butyl (*S*)-((4-fluorophenyl)(oxo)(*p*-tolyl)- λ^6-sulfaneylidene)carbamate (2c)**

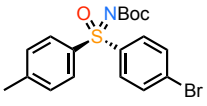


Reaction performed according to General Procedure D. Isopropylmagnesium chloride lithium chloride complex (0.90 mL, 1.13 M, 1 mmol) was added dropwise to 4-fluoroiodobenzene (115 μL, 1 mmol) in THF (0.1 mL) at 0 ºC and stirred for 3 h to make a 4-fluorophenylmagnesium chloride solution (approx. 1 M). The 4-fluorophenylmagnesium chloride solution (0.3 mL, approx. 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20–30% EtOAc in pentane) gave sulfoximine **(*S*)-2c** as a white solid (82.4 mg, 0.24 mmol, 94%, >99% *ee*). mp = 148–149 ºC. R_f 0.17 (25% EtOAc in pentane). IR (film)/cm^{-1} 2972, 2919, 2849, 1697, 1671, 1588, 1489, 1454, 1391, 1365, 1271, 1236, 1150, 1094, 904, 862, 838, 812, 787, 761, 732, 705, 678, 658, 575, 552, 532. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.96 (m, 2H, 2 × Ar–H), 7.87 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 7.36–7.27 (m, 2H,

2 × Ar–H), 7.19–7.12 (m, 2H, 2 × Ar–H), 2.40 (s, 3H, Ar–CH_3), 1.35 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ165.4 (d, *J* = 256.1 Hz, Ar–C_q), 157.4 (C=O), 144.5 (Ar–C_q), 136.7 Ar–C_q), 136.3 (Ar–C_q), 130.5 (d, *J* = 9.5 Hz, 2 × Ar–C), 130.3 (2 × Ar–C), 127.8 (2 × Ar–C), 116.7 (d, *J* = 22.7 Hz, 2 × Ar–C), 80.8 (*C*(CH_3)$_3$), 28.0 (C(*C*H_3)$_3$), 21.6 (Ar–CH_3). ^{19}F NMR (377 MHz, $CDCl_3$) δ –104.71. HRMS (ES) m/z cald for $C_{18}H_{21}NO_3SF$ $[M+H]^+$: 350.1226; Found: 350.1232. $[\alpha]^{21}_D$ = +8 (c 1.0, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 280 nm. Retention time: 15 min.

(***rac*)-2c**: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride (***rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 280 nm. Retention times: 15 & 20 min.

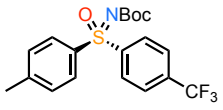
***tert*-Butyl (*S*)-((4-bromophenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2d)**



Reaction performed according to General Procedure D. Isopropylmagnesium chloride lithium chloride complex (0.90 mL, 1.13 M, 1 mmol) was added dropwise to 4-bromoiodobenzene (283 mg, 1 mmol) in THF (0.1 mL) at 0 ºC and stirred for 3 h to make a 4-bromophenylmagnesium chloride solution (approx. 1 M). The 4-bromophenylmagnesium chloride solution (0.3 mL, approx. 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL). The organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20–30% EtOAc in pentane) gave sulfoximine **(*S*)-2d** as a white solid (61.8 mg, 0.15 mmol, 60%, >99% *ee*). mp 164–165 ºC. R_f 0.19 (25% EtOAc in pentane). IR (film)/cm^{-1} 3084, 2972, 2925, 1696, 1668, 1592, 1568, 1471, 1452, 1388, 1365, 1269, 1240, 1150, 1092, 1068, 1008, 898, 861, 816, 789, 762, 645, 620, 579, 541, 509. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.85 (m, 2H, 2 × Ar–H), 7.85–7.80 (m, 2H, 2 × Ar–H), 7.66–7.57 (m, 2H, 2 × Ar–H), 7.30 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 2.39 (s, 3H, Ar–CH_3), 1.35 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4 (C=O), 144.7 (Ar–C_q), 139.7 (Ar–C_q), 136.4 (Ar–C_q), 132.7 (2 × Ar–C), 130.3 (2 × Ar–C), 129.3 (2 × Ar–C), 128.4 (Ar–C_q), 127.9 (2 × Ar–C), 81.0 (*C*(CH_3)$_3$), 28.1 (Ar–CH_3), 21.7 (C(*C*H_3)$_3$). HRMS (ES) m/z cald for $C_{18}H_{21}NO_3SBr$ $[M+H]^+$: 410.0426; Found: 410.0416. $[\alpha]^{21}_D$ = +22 (c 1.0, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention time: 19 min

(***rac*)-2d**: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride (***rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention times: 19 & 21 min.

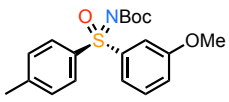
***tert*-Butyl (*S*)-(oxo(*p*-tolyl)(4-(trifluoromethyl)phenyl)-λ^6-sulfaneylidene)carbamate (2e)**



Reaction performed according to General Procedure D. Isopropylmagnesium chloride lithium chloride complex (0.90 mL, 1.13 M, 1 mmol) was added dropwise to 4-trifluoromethyliodobenzene (147 μL, 1 mmol) in THF (0.1 mL) at 0 ºC and stirred for 3 h to make a 4-trifluoromethylphenylmagnesium chloride solution (approx. 1 M). 4-trifluoromethylphenylmagnesium chloride solution (0.3 mL, approx. 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20–30% EtOAc in pentane) gave sulfoximine **(*S*)-2e** as an off-white solid (98.1 mg, 0.25 mmol, 98%, >99% *ee*). mp = 136–137 ºC. R_f 0.18 (20% EtOAc in pentane). IR (film)/cm^{-1} 2974, 2926, 1700, 1668, 1594, 1475, 1451, 1400, 1366, 1319, 1269, 1238, 1129, 1059, 1013, 898, 842, 812, 760, 732, 708, 667, 645, 617, 595, 537, 510, 482, 446. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.07 (m, 2H, 2 × Ar–H), 7.90 (d, *J* = 8.5 Hz, 2H, 2 × Ar–H), 7.74 (d, *J* = 8.3 Hz, 2H, 2 × Ar–H), 7.32 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 2.40 (s, 3H, Ar–CH_3), 1.35 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 (C=O), 144.5 (Ar–C_q), 135.7 (Ar–C_q), 134.7 (d, *J* = 31.6 Hz, Ar–C_q), 130.4 (2 × Ar–C), 128.3 (2 × Ar–C), 128.1 (2 × Ar–C), 126.6 (d, *J* = 3.6 Hz, 2 × Ar–C), 123.2 (d, *J* = 270.4 Hz, Ar–C_q), 81.1 (*C*(CH_3)$_3$), 28.0 (C(*C*H_3)$_3$), 21.7 (Ar–CH_3). ^{19}F NMR (377 MHz, $CDCl_3$) δ −63.15. HRMS (ES) m/z cald for $C_{19}H_{21}NO_3SF_3$ $[M+H]^+$: 400.1194; Found: 400.1187. $[\alpha]^{21}_D$ = +82 (c 1.0, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention time: 22 min

(*rac*)-2e: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **(*rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention times: 22 & 28 min.

***tert*-Butyl (*S*)-((3-methoxyphenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2f)**

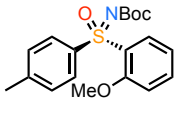


Reaction performed according to General Procedure D. 3-Methoxyphenylmagnesium bromide (0.30 mL, 1.0 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL). The organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20–30% EtOAc in pentane) gave sulfoximine **(*S*)-2f** as a colourless oil (84.5 mg, 0.23 mmol, 94%). R_f 0.24 (25% EtOAc in pentane). IR (film)/cm^{-1} 2974, 2933, 1700, 1679, 1595, 1484, 1271, 1245, 1156, 1092, 1036, 902, 865, 812, 790, 686. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.85 (m, 2H, 2 × Ar–H), 7.54 (ddd, *J* = 7.8, 1.8, 1.0 Hz, 1H, Ar–H), 7.49 (dd, *J* = 2.5, 1.8 Hz, 1H, Ar–H), 7.44–7.39 (m, 1H, Ar–H), 7.32–7.27 (m, 2H, 2 × Ar–H), 7.05 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H, Ar–H), 3.83 (s, 3H, OCH_3), 2.38 (s, 3H, Ar–CH_3), 1.35 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2

(Ar–C_q), 157.5 (C=O), 144.3 (Ar–C_q), 141.7 (Ar–C_q), 136.8 (Ar–C_q), 130.5 (Ar–C), 130.2 (2 × Ar–C), 127.9 (2 × Ar–C), 119.9 (Ar–C), 119.5 (Ar–C), 112.4 (Ar–C), 80.7 ($C(CH_3)_3$), 55.9 (OCH_3), 28.1 ($C(CH_3)_3$), 21.7 (Ar–CH_3). HRMS (ES) m/z cald for $C_{19}H_{24}NO_4S$ $[M+H]^+$: 362.1426; Found: 362.1431. $[\alpha]^{24}_D$ = +250 (c 0.2, $CHCl_3$). HPLC analysis not possible as separation of peaks was not possible.

(*rac*)-2f: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **(*rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. Unfortunately, it was not possible to separate the enantiomers on the HPLC to analyse the *ee* of the enantioenriched material.

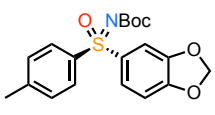
tert-Butyl (*S*)-((2-methoxyphenyl)(oxo)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate (2g)



Reaction performed according to General Procedure D. 2-Methoxyphenylmagnesium bromide (0.30 mL, 1.0 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20-30% EtOAc in pentane) gave sulfoximine **(*S*)-2g** as a colourless oil (67.9 mg, 0.18 mmol, 75%, 97% *ee*). R_f 0.22 (25% EtOAc in pentane). IR (film)/cm^{-1} 3068, 2975, 2933, 1670, 1592, 1532, 1480, 1390, 1275, 1245, 1156, 1062, 1018, 895, 865, 806, 760, 731, 708. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.95 (m, 2H, 2 × Ar–H), 7.92–7.84 (m, 2H, 2 × Ar–H), 7.58–7.45 (m, 3H, 3 × Ar–H), 7.31–7.27 (m, 1H, 1 × Ar–H), 2.38 (s, 3H, Ar–CH_3), 1.33 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2 (C=O), 156.7 (Ar–C_q), 144.0 (Ar–C_q), 136.4 (Ar–C_q), 135.3 (Ar–C), 131.0 (Ar–C), 129.3 (2 × Ar–C), 128.8 (2 × Ar–C), 127.6 (Ar–C_q), 120.9 (Ar–C), 112.6 (Ar–C), 80.1 ($C(CH_3)_3$), 56.0 (OCH_3), 28.1 ($C(CH_3)_3$), 21.7 (Ar–CH_3). HRMS (ES) m/z cald for $C_{19}H_{24}NO_4S$ $[M+H]^+$: 362.1426; Found: 362.1431. $[\alpha]^{24}_D$ = +270 (c 0.2, $CHCl_3$). HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm. Retention time: 36 min.

(*rac*)-2g: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **(*rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm. Retention times: 36 & 46 min.

tert-Butyl (*S*)-(benzo[*d*][1,3]dioxol-5-yl(oxo)(*p*-tolyl)-λ⁶-sulfaneylidene)carbamate (2h)

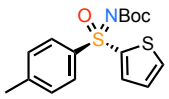


Reaction performed according to General Procedure D. Isopropylmagnesium chloride lithium chloride complex (0.90 mL, 1.13 M, 1 mmol) was added dropwise to 5-iodobenzo[*d*][1,3]dioxole (248 mg, 1 mmol) in THF (0.1 mL) at 0 ºC and stirred for 3 h to make a benzo[*d*][1,3]dioxol-5-ylmagnesium chloride solution (approx. 1 M). benzo[*d*][1,3]dioxol-5-ylmagnesium chloride solution (0.3 mL, approx. 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC

and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20–30% EtOAc in pentane) gave sulfoximine **(*S*)-2h** as a white solid (74.9 mg, 0.20 mmol, 80%, >99% *ee*). mp = 169–170 ºC. R_f 0.21 (25% EtOAc in pentane). IR (film)/cm^{-1} 2973, 2922, 1692, 1670, 1595, 1501, 1477, 1454, 1364, 1270, 1241, 1154, 1110, 1084, 1034, 907, 861, 813, 730, 669, 596, 547. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.81 (m, 2H, 2 × Ar–H), 7.58 (dd, *J* = 8.3, 2.0 Hz, 1H, Ar–H), 7.38 (d, *J* = 2.0 Hz, 1H, Ar–H), 7.33–7.26 (m, 2H, 2 × Ar–H), 6.86 (d, *J* = 8.3 Hz, 1H, Ar–H), 6.04 (q, *J* = 1.3 Hz, 2H, 2 × OCH_2), 2.39 (s, 3H, Ar–CH_3), 1.37 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6 (C=O), 152.0 (Ar–C_q), 148.6 (Ar–C_q), 144.1 (Ar–C_q), 137.4 (Ar–C_q), 133.3 (Ar–C_q), 130.2 (2 × Ar–C), 127.7 (2 × Ar–C), 123.7 (Ar–C), 108.7 (Ar–C), 108.0 (Ar–C), 102.6 (CH_2), 80.7 (*C*(CH_3)$_3$), 28.2 (C(*C*H_3)$_3$), 21.7 (Ar–CH_3). HRMS (ES) m/z cald for $C_{19}H_{22}NO_5S$ $[M+H]^+$: 376.1219; Found: 376.1223. $[\alpha]^{21}_D$ = −14 (c 1.0, $CHCl_3$). HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm. Retention time: 76 min.

(*rac*)-2h: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **(*rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm. Retention times: 71 & 76 min.

***tert*-Butyl (*S*)-(oxo(thiophen-2-yl)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2i)**

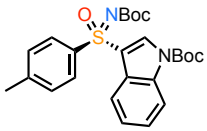


Reaction performed according to General Procedure D. 2-Thienylmagnesium bromide (0.30 mL, 1.0 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. No additional purification steps were required to give sulfoximine **(*S*)-2i** as a white solid (85.3 mg, 0.25 mmol, quant, >99% *ee*). mp = 136–137 ºC. R_f 0.19 (25% EtOAc in pentane). IR (film)/cm^{-1} 3088, 2973, 2925, 1696, 1670, 1593, 1475, 1451, 1397, 1365, 1341, 1270, 1245, 1153, 1094, 1013, 895, 859, 813, 788, 761, 726, 677, 664, 613, 588, 565, 534, 509. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.87 (m, 2H, 2 × Ar–H), 7.67–7.56 (m, 2H, 2 × Ar–H), 7.32–7.27 (m, 2H, 2 × Ar–H), 7.05 (dd, *J* = 4.9, 3.9 Hz, 1H, Ar–H), 2.38 (s, 3H, Ar–CH_3), 1.34 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0 (C=O), 144.4 (Ar–C_q), 141.4 (Ar–C_q), 137.6 (Ar–C_q), 134.4 (Ar–C), 133.6 (Ar–C), 130.2 (2 × Ar–C), 128.2 (Ar–C), 127.6 (2 × Ar–C), 80.8 (*C*(CH_3)$_3$), 28.0 (C(*C*H_3)$_3$), 21.6 (Ar–CH_3). HRMS (ES) m/z cald for $C_{16}H_{20}NO_3S_2$ $[M+H]^+$: 338.0885; Found: 338.0888. $[\alpha]^{24}_D$ = −22 (c 1.0, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm. Retention times: 31 min.

(*rac*)-2i: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **(*rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions:

Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm. Retention times: 31 & 35 min.

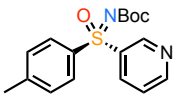
tert-Butyl (_S_)-3-(_N_-(_tert_-butoxycarbonyl)-4-methylphenylsulfonimidoyl)-1_H_-indole-1-carboxylate (2j)



Reaction performed according to General Procedure D. Isopropylmagnesium chloride lithium chloride complex (0.90 mL, 1.13 M, 1 mmol) was added dropwise to *tert*-butyl 3-iodo-1*H*-indole-1-carboxylate (343 mg, 1 mmol) in THF (0.1 mL) at 0 ºC and stirred for 3 h to make a (1-(*tert*-butoxycarbonyl)-1*H*-indol-3-yl)magnesium chloride solution (approx. 1 M). (1-(*tert*-Butoxycarbonyl)-1*H*-indol-3-yl)magnesium chloride solution (0.3 mL, approx. 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20-30% EtOAc in pentane) gave sulfoximine **(*S*)-2j** as a viscous oil (106.9 mg, 0.23 mmol, 91%, >99% *ee*). R_f 0.15 (20% EtOAc in pentane). IR (film)/cm^{-1} 3151, 2974, 2927, 1745, 1672, 1584, 1529, 1473, 1448, 1362, 1332, 1269, 1246, 1226, 1137, 1085, 1063, 979, 906, 857, 730, 646. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H, Ar–H), 8.18 (d, *J* = 8.3 Hz, 1H, Ar–H), 8.04–7.98 (m, 2H, 2 × Ar–H), 7.86–7.81 (m, 1H, Ar–H), 7.39–7.31 (m, 2H, 2 × Ar–H), 7.30–7.27 (m, 2H, 2 × Ar–H), 2.37 (s, 3H, Ar–CH_3), 1.67 (s, 9H, C(CH_3)$_3$), 1.34 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7 (C=O), 148.5 (C=O), 144.3 (Ar–C_q), 137.0 (Ar–C_q), 136.1 (Ar–C_q), 131.7 (Ar–C_q), 130.0 (2 × Ar–C), 127.6 (2 × Ar–C), 126.0 (Ar–C), 124.7 (Ar–C_q), 124.5 (Ar–C), 119.8 (Ar–C), 119.4 (Ar–C_q), 115.9 (Ar–C), 86.0 (*C*(CH_3)$_3$), 80.6 (*C*(CH_3)$_3$), 28.2 (C(*C*H_3)$_3$), 28.1 (C(*C*H_3)$_3$), 21.6 (Ar–CH_3). HRMS (ES) m/z cald for $C_{25}H_{31}N_2O_5S$ $[M+H]^+$: 471.1954; Found: 471.1960. $[\alpha]^{21}_D$ = +30 (c 1.0, $CHCl_3$). HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm. Retention time: 17 min.

(*rac*)-2j: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **(*rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm. Retention times: 17 & 20 min.

tert-Butyl (_S_)-(oxo(pyridin-3-yl)(_p_-tolyl)-λ^6-sulfaneylidene)carbamate (2k)

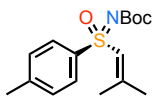


Reaction performed according to General Procedure D. Isopropylmagnesium chloride lithium chloride complex (0.90 mL, 1.13 M, 1 mmol) was added dropwise to 3-iodopyridine (205 mg, 1 mmol) in THF (0.1 mL) at 0 ºC and stirred for 3 h to make a pyridin-3-ylmagnesium chloride solution (approx. 1.0 M). pyridine-3-ylmagnesium chloride solution (0.3 mL, approx. 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl (30 mL) and extracted with EtOAc (3 x 30 mL), the organic layers were combined,

dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography (40% EtOAc in hexane) to afford sulfoximine **(*S*)-2k** (50.4 mg, 61%, >99% *ee*) as a white solid. mp = 130–133 °C. R_f 0.10 (40% EtOAc in hexane). IR (film)/cm^{-1} 2974, 1670 (C=O), 1566, 1238, 1148, 1014, 895, 753. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, *J* = 2.4 Hz, 1H, Ar–H), 8.75 (dd, *J* = 4.9, 1.6 Hz, 1H, Ar–H), 8.27 (ddd, *J* = 8.1, 2.4, 1.6 Hz, 1H, Ar–H), 7.91 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 7.44 (dd, *J* = 8.2, 4.8 Hz, 1H, 1 × Ar–H), 7.33 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 2.41 (s, 3H, Ar–CH_3), 1.35 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0 (C=O), 153.3 (Ar–C), 148.6 (Ar–C), 145.0 (Ar–C_q), 137.5 (Ar–C_q), 135.8 (Ar–C_q), 135.4 (Ar–C), 130.4 (2 × Ar–C), 128.0 (2 × Ar–C), 123.8 (Ar–C), 81.1 ($C(CH_3)_3$), 28.0 ($C(CH_3)_3$), 21.6 (CH_3). HRMS (ESI) m/z: Calcd for $C_{17}H_{21}NO_3S$ $[M+H]^+$: 333.1273; Found: 333.1281. $[\alpha]^{21}_D$ = +17 (c 1.0, $CHCl_3$). HPLC conditions: Chiralpak IA column, 95:10 *n*hexane:iPrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm, **(*S*)-2k** retention time: 26 min.

(*rac*)-2k: Synthesis of racemic sample for HPLC analysis prepared according to General Procedure D to afford sulfoximine **(*rac*)-2k** as a white solid with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm, **(*rac*)-2k** retention times: 27 & 32 min.

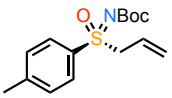
***tert*-Butyl (*R*)-((2-methylprop-1-en-1-yl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2l)**



Reaction performed according to General Procedure D. 2-Methyl-1-propenylmagnesium bromide (0.6 mL, 0.5 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (40% EtOAc in pentane) gave sulfoximine **(*R*)-2l** (41.2 mg, 53%, >99% *ee*) as a white solid. mp = 109–112 °C. R_f 0.30 (40% EtOAc in pentane). IR (film)/cm^{-1} 3049, 2967, 2917, 1658 (C=O), 1630, 1436, 1346, 1269, 1249, 1225, 1148, 1080, 877, 583. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.79 (m, 2H, 2 × Ar–H), 7.33 (d, *J* = 8.0 Hz, 2H, 2 × Ar–H), 6.34 (p, *J* = 1.3 Hz, 1H, SC*H*), 2.43 (s, 3H, Ar–CH_3), 2.00 (d, *J* = 1.2 Hz, 3H, 1 × C(CH_3)), 1.88 (d, *J* = 1.4 Hz, 3H, 1 × C(CH_3)), 1.37 (s, 9H, $C(CH_3)_3$).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9 (C=O), 155.8 ($C(CH_3CH_3)$, 143.8 (Ar–C_q), 137.6 (Ar–C_q), 129.9 (2 × Ar–C), 127.5 (2 × Ar–C), 125.4 (S*C*H), 80.1 ($C(CH_3)_3$), 28.1 ($C(CH_3)_3$), 27.2 (Ar–CH_3), 21.6 (1 × C(CH_3)), 19.2 (1 × C(CH_3)). HRMS (ESI) m/z: Calcd for $C_{16}H_{24}NO_3S$ $[M+H]^+$: 310.1477; Found: 310.1481. $[\alpha]^{21}_D$ = +32 (c 1.0, $CHCl_3$). HPLC conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm, **(*R*)-2l** retention time: 33 min.

(*rac*)-2l: Synthesis of racemic sample for HPLC analysis prepared according to General Procedure D to afford sulfoximine **(*rac*)-2l** as a white solid with characterisation data in accordance with the above. HPLC conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm, **(*rac*)-2l** retention times: 34 & 37 min.

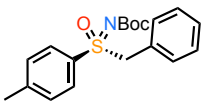
***tert*-Butyl (*R*)-(allyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2m)**



Reaction performed according to General Procedure D. Allylmagnesium bromide (0.3 mL, 1.0 M in Et_2O, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (40% EtOAc in pentane) gave sulfoximine **(*R*)-2m** (69.0 mg, 93%, >99% *ee*) as a pale-yellow gum. R_f 0.59 (40% EtOAc in pentane). IR (film)/cm^{-1} 2972, 1659 (C=O), 1593, 1363, 1268, 1150, 1084, 782, 639. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 7.36 (d, *J* = 8.1 Hz, 2H, 2 × Ar–H), 5.71 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H, SCH_2CH), 5.33 (d, *J* = 10.1 Hz, 1H, CH=C*H*H), 5.12 (dd, *J* = 17.0, 1.2 Hz, 1H, CH=CH*H*), 4.17–4.05 (m, 2H, SCH_2), 2.45 (s, 3H, CH_3), 1.41 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (C=O), 144.8 (Ar–C_q), 133.1 (Ar–C_q), 129.9 (2 × Ar–C), 128.6 (2 × Ar–C), 125.7 (SCH_2CH), 123.9 (HC=CH_2), 80.5 ($C(CH_3)_3$), 60.4 (SCH_2), 28.1 ($C(CH_3)_3$), 21.6 (CH_3). HRMS (ESI) m/z: Calcd for $C_{15}H_{22}NO_3S$ $[M+H]^+$: 296.1320; Found: 296.1314. $[\alpha]^{21}_D$ = –16 (c 0.86, $CHCl_3$). HPLC conditions: Chiralpak IB column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm, **(*R*)-2m** retention time: 17 min.

(*rac*)-2m: Synthesis of racemic sample for HPLC analysis prepared according to General Procedure D to afford sulfoximine **(*rac*)-2m** as a pale-yellow gum with characterisation data in accordance with the above. HPLC conditions: Chiralpak IB column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm, **(*rac*)-2m** retention times: 13 & 17 min.

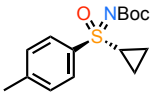
***tert*-Butyl (*R*)-(benzyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2n)**



Reaction performed according to General Procedure D. Benzylmagnesium bromide (0.30 mL, 1.0 M in Et_2O, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20-30% EtOAc in pentane) gave sulfoximine **(*R*)-2n** as a white solid (66.8 mg, 0.19 mmol, 77%, 97% *ee*). mp = 114–115 ºC. R_f 0.18 (25% EtOAc in pentane). IR (film)/cm^{-1} 2973, 2926, 1661, 1593, 1453, 1391, 1365, 1276, 1247, 1154, 1106, 896, 813, 780, 699, 531. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.45 (m, 2H, 2 × Ar–H), 7.32–7.26 (m, 1H, Ar–H), 7.25–7.09 (m, 4H, 4 × Ar–H), 7.01–6.91 (m, 2H, 2 × Ar–H), 4.74–4.60 (m, 2H, SCH_2), 2.40 (s, 3H, Ar–CH_3), 1.43 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3 (C=O), 144.8 (Ar–C_q), 132.4 (Ar–C_q), 131.3 (2 × Ar–C), 129.8 (2 × Ar–C), 129.1 (Ar–C), 128.8 (2 × Ar–C), 128.6 (2 × Ar–C), 127.4 (Ar–C_q), 80.5 ($C(CH_3)_3$), 62.2 (SCH_2), 28.2 ($C(CH_3)_3$), 21.7 (Ar–CH_3). HRMS (ES) m/z cald for $C_{19}H_{24}NO_3S$ $[M+H]^+$: 346.1477; Found: 346.1476. $[\alpha]^{24}_D$ = +44 (c 1.0, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm. Retention time: 46 min.

(***rac*)-2n**: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride (***rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm. Retention times: 40 & 46 min.

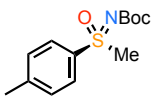
***tert*-Butyl (*R*)-(cyclopropyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2o)**



Reaction performed according to General Procedure D. Cyclopropylmagnesium bromide (0.30 mL, 1.0 M in 2-MeTHF, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20-30% EtOAc in pentane) gave sulfoximine **(*R*)-2o** as an amorphous solid (71.1 mg, 0.24 mmol, 96%, 99% *ee*). R_f 0.15 (25% EtOAc in pentane). IR (film)/cm^{-1} 3044, 3001, 2973, 2926, 1691, 1668, 1593, 1452, 1365, 1273, 1250, 1230, 1156, 1110, 1087, 889, 864, 715, 530, 453. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 7.41–7.34 (m, 2H, 2 × Ar–H), 2.62 (tt, *J* = 7.9, 4.9 Hz, 1H, SCH), 2.45 (s, 3H, Ar–CH_3), 1.35 (s, 9H, $C(CH_3)_3$), 1.18–1.10 (m, 2H, 2 × SCHC*H*H), 0.94–0.83 (m, 2H, 2 × SCHCH*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7 (C=O), 144.4 (Ar–C_q), 136.3 (Ar–C_q), 130.3 (2 × Ar–C), 127.6 (2 × Ar–C), 80.4 (*C*$(CH_3)_3$), 33.7 (SCH), 28.1 (C(*C*$H_3)_3$), 21.7 (Ar–CH_3), 6.4 (1 × SCH*C*H_2), 5.0 (1 × SCH*C*H_2). HRMS (ES) m/z cald for $C_{15}H_{22}NO_3S$ $[M+H]^+$:296.1320; Found: 296.1322. $[\alpha]^{21}_D$ = −97.5 (c 0.8, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm. Retention time: 30 min.

(*rac*)-2o: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **(*rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm. Retention times: 20 & 30 min.

***tert*-Butyl (*R*)-(methyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2p)**

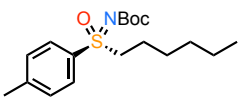


Reaction performed according to General Procedure D. Methylmagnesium bromide (0.09 mL, 2.8 M in Et_2O, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20-30% EtOAc in pentane) gave sulfoximine **(*R*)-2p** as a white solid (51.9 mg, 0.19 mmol, 77%, >99% *ee*). R_f 0.20 (50% EtOAc in pentane). mp = 107–108 ºC. IR (film)/cm^{-1} 3058, 2999, 2972, 2926, 1694, 1667, 1272, 1248, 1232, 1156, 1114, 1092, 963, 894, 864, 814, 787, 757, 687, 664, 642, 564, 538, 511. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.82 (m, 2H, 2 × Ar–H), 7.43–7.35 (m, 2H, 2 × Ar–H), 3.22 (s, 3H, SCH_3), 2.46 (s, 3H,

Ar–CH_3), 1.39 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9 (C=O), 144.9 (Ar–C_q), 135.8 (Ar–C_q), 130.4 (2 × Ar–C), 127.5 (2 × Ar–C), 80.6 (*C*(CH_3)$_3$), 45.0 (SCH_3), 28.2 (C(*C*H_3)$_3$), 21.7 (Ar–CH_3). $[\alpha]^{21}_D$ = –66 (c 1.0, acetone). HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm, retention time: 12 min. Analytical data (^{1}H and ^{13}C NMR) in agreement with those reported in the literature.[1]

(*rac*)-2p: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **(*rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm, retention time: 8 & 12 min.

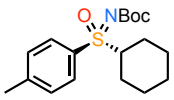
***tert*-Butyl (*R*)-(hexyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2q)**



Reaction performed according to General Procedure D. Hexylmagnesium bromide (0.15 mL, 2.0 M in Et_2O, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20-30% EtOAc in pentane) gave sulfoximine **(*R*)-2q** as a colourless oil (74.6 mg, 0.22 mmol, 88%). R_f 0.26 (25% EtOAc in pentane). IR (film)/cm^{-1} 2960, 2930, 2863, 1666, 1595, 1532, 1454, 1394, 1275, 1152, 1111, 895, 865, 813, 787, 731. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H, 2 × Ar–H), 7.41–7.30 (m, 2H, 2 × Ar–H), 3.34 (ddd, *J* = 14.0, 11.4, 5.0 Hz, 1H, SC*H*H), 3.22 (ddd, *J* = 14.0, 11.4, 4.9 Hz, 1H, SCH*H*), 2.45 (s, 3H, Ar–CH_3), 1.73 (dddd, *J* = 16.1, 8.6, 6.2, 4.7 Hz, 1H, SCH_2C*H*H), 1.56–1.48 (m, 1H, SCH_2CH*H*), 1.37 (s, 9H, C(CH_3)$_3$) 1.34–1.12 (m, 6H, SCH_2CH_2(CH_2)$_3$), 0.83 (t, *J* = 6.7 Hz, 3H, CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (C=O), 144.7 (Ar–C_q), 130.3 (Ar–C_q), 134.3 (2 × Ar–C), 128.2 (2 × Ar–C), 80.4 (*C*(CH_3)$_3$), 56.5 (SCH_2), 31.3 (CH_2), 28.2 (C(*C*H_3)$_3$), 27.8 (CH_2), 22.4 (CH_2), 22.2 (CH_2), 21.8 (Ar–CH_3), 14.0 (CH_3). HRMS (ES) m/z cald for $C_{18}H_{30}NO_3S$ $[M+H]^+$: 340.1946; Found: 340.1949. $[\alpha]^{24}_D$ = −340 (c 0.2, $CHCl_3$). HPLC analysis not possible as separation of enantiomers was not possible.

(*rac*)-2q: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **(*rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. Unfortunately, it was not possible to separate the enantiomers on the HPLC to analyse the *ee* of the enantioenriched material.

***tert*-Butyl (*R*)-(cyclohexyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (2r)**

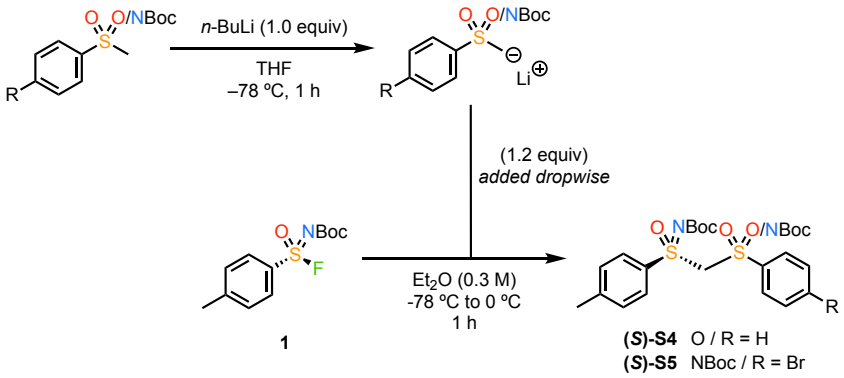


Reaction performed according to General Procedure D. Cyclohexylmagnesium chloride (0.30 mL, 1.0 M in 2-MeTHF, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and

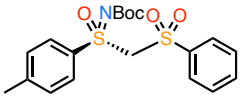
extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20-30% EtOAc in pentane) gave sulfoximine **(*R*)-2r** as a white solid (67.8 mg, 0.20 mmol, 80%, >99% *ee*). mp = 148–149 ºC. R_f 0.28 (25% EtOAc in pentane). IR (film)/cm^{-1} 2969, 2927, 2855, 1665, 1450, 1388, 1363, 1270, 1248, 1126, 1154, 1105, 1084, 892, 866, 815, 730, 666, 645, 620, 866, 530, 499. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 7.38–7.31 (m, 2H, 2 × Ar–H), 3.13 (tt, *J* = 12.1, 3.3 Hz, 1H, SC*H*), 2.43 (s, 3H, Ar–CH_3), 2.36 (dd, *J* = 12.5, 2.2 Hz, 1H, SCHC*H*H), 1.91–1.81 (m, 2H, SCHC*H*H and SCHCH*H*), 1.81–1.73 (m, 1H, SCHCH*H*), 1.67–1.57 (m, 1H, $SCHCH_2CHH$), 1.42–1.34 (m, 1H, $SCHCH_2CHH$), 1.32 (s, 9H, $C(CH_3)_3$), 1.29–0.98 (m, 4H, 2 × $SCHCH_2CH$*H* & $SCHCH_2CH_2CH_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3 (C=O), 144.5 (Ar–C_q), 132.3 (Ar–C_q), 130.1 (2 × Ar–C), 129.0 (2 × Ar–C), 80.1 ($C(CH_3)_3$), 63.8 (SCH), 28.1 ($C(CH_3)_3$), 25.6 (1 × $SCHCH_2$), 25.2 (1 × $SCHCH_2$), 25.2 (1 × $SCHCH_2CH_2$), 25.0 (1 × $SCHCH_2CH_2$), 24.8 ($SCHCH_2CH_2CH_2$), 21.7 (Ar–CH_3). HRMS (ES) m/z cald for $C_{18}H_{28}NO_3S$ $[M+H]^+$: 338.1790; Found: 338.1784. $[\alpha]^{24}_D$ = −56 (c 1.0, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm. Retention time: 24 min.

(*rac*)-2r: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **(*rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm. Retention times: 15 & 24 min.

Scope of sulfoximines from sulfonimidoyl fluoride (*R*)-1 with organolithium reagents



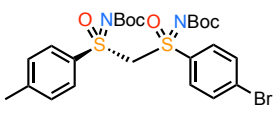
***tert*-Butyl (*S*)-(oxo((phenylsulfonyl)methyl)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-S4)**



n-Butyllithium solution (0.67 mL, 1.6 M, 1 mmol) was added dropwise to (methylsulfonyl)benzene (156 mg, 1 mmol) in THF (0.3 mL) at −78 ºC and stirred for 1 h to make the lithium (phenylsulfonyl)methanide solution (approx. 1 M). Lithium (phenylsulfonyl)methanide solution (0.3 mL, approx. 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (25% EtOAc in pentane) gave sulfoximine **(*S*)-S4** as a colourless gum (74.3 mg, 0.18 mmol, 72%, >99% *ee*). R_f 0.18 (25% EtOAc in pentane). IR (film)/cm^{-1} 3061, 2975, 2921, 1665, 1592, 1475, 1448, 1365, 1330, 1274, 1247, 1150, 1084, 901, 862, 832, 746, 687, 531. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.85 (m, 4H, 4 × Ar–H), 7.73–7.62 (m, 1H, Ar–H), 7.62–7.51 (m, 2H, 2 × Ar–H), 7.43–7.35 (m, 2H, 2 × Ar–H), 5.36 (d, *J* = 14.6 Hz, 1H, SC*H*H), 5.15 (d, *J* = 14.6 Hz, 1H, SCH*H*), 2.47 (s, 3H, Ar–CH_3), 1.42 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4 (C=O), 146.3 (Ar–C_q), 138.8 (Ar–C_q), 134.8 (Ar–C), 132.6 (Ar–C_q), 130.2 (2 × Ar–C), 129.5 (2 × Ar–C), 129.3 (2 × Ar–C), 128.8 (2 × Ar–C), 81.6 (*C*(CH_3)$_3$), 71.8 (SCH_2), 28.2 (C(*C*H_3)$_3$), 21.9 (Ar–CH_3). HRMS (ES) m/z cald for $C_{19}H_{24}NO_5S_2$ $[M+H]^+$: 410.1096; Found: 410.1086. $[\alpha]^{22}_D$ = +44 (c 0.5, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm. Retention time: 79 min.

(*rac*)-S4: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **(*rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm. Retention times: 59 & 79 min.

***tert*-Butyl ((1*S*)-((4-bromo-*N*-(*tert*-butoxycarbonyl)phenylsulfonimidoyl)methyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-S5)**

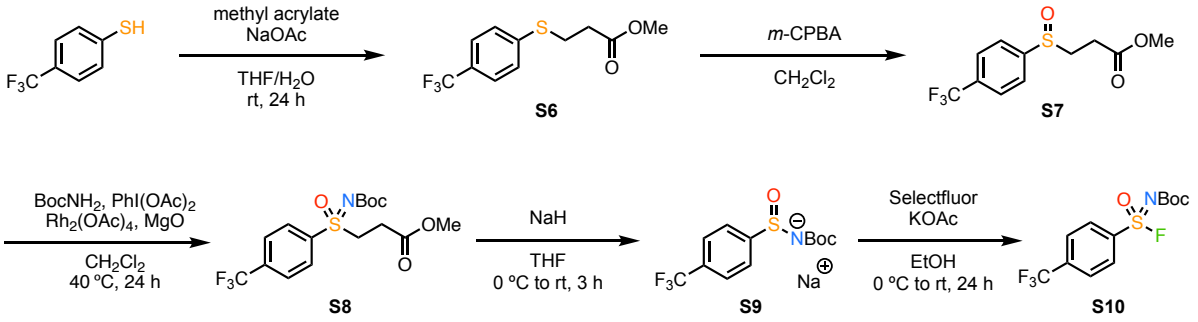


*n*BuLi (2.50 mL, 1.6 M in hexane, 4 mmol) was added dropwise to 2,2,6,6-tetramethylpiperidine (681 μL, 4 mmol) in THF (0.3 mL) at –78 ºC and stirred for 30 min to make LiTMP solution (approx. 1 M). LiTMP (1.0 mL, ~1 M, ~1.0 mmol) was added to *tert*-butyl ((4-bromophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)carbamate (100 mg, 1.0 mmol) in THF (0.8 mL) at –78 ºC and stirred for 30 min to make lithium (*S*)-(4-bromo-*N*-(*tert*-butoxycarbonyl)phenylsulfonimidoyl)methanide solution (~0.5 M). Lithium (*S*)-(4-bromo-*N*-(*tert*-butoxycarbonyl)phenylsulfonimidoyl)methanide solution (1.1 mL, approx. 0.55 mmol, 2.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-1** (69 mg, 0.25 mmol, 1.0 equiv) in THF (0.83 mL, 0.3 M) at –78 ºC and warmed to 0 ºC for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20% EtOAc in pentane) gave sulfoximine **(*S*)-S5** as a white solid (53.9 mg, 0.09 mmol, 37%). mp = 118–120 ºC. IR (film)/cm^{-1} 2982, 2922, 1670, 1476, 1372, 1252, 1148, 1013, 902, 731. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.76 (m, 4H, 4 × Ar–H), 7.71–7.65 (m, 2H, 2 × Ar–H), 7.39–7.31 (m, 2H, 2 × Ar–H), 5.79 (d, *J* = 14.5 Hz, 1H, SC*H*H), 5.59 (d, *J* = 14.5 Hz, 1H, SCH*H*), 2.46 (s, 3H, Ar–CH_3), 1.35 (s, 18H, 2 × C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0 (C=O), 156.7 (C=O), 146.3 (Ar–C_q), 134.7 (Ar–C_q), 132.7 (2 × Ar–C), 132.6 (2 × Ar–C), 130.8 (Ar–C_q), 130.6 (Ar–C_q), 130.2 (2 × Ar–C), 129.1 (2 × Ar–C), 81.8 (*C*(CH_3)$_3$), 81.6 (*C*(CH_3)$_3$), 69.1 (SCH_2), 28.1 (C(*C*H_3)$_3$), 28.1 (C(*C*H_3)$_3$), 21.9 (Ar–CH_3). HRMS (ES) m/z cald for $C_{24}H_{32}BrN_2O_6S_2$ $[M+H]^+$: 587.0885; Found: 587.0878. $[\alpha]^{22}_D$ = 14 (c 1.0, $CHCl_3$). HPLC analysis not possible as separation of enantiomers was not possible.

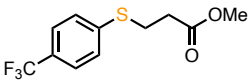
(*rac*)-S5: The reaction was completed on a small scale (~0.1 mmol) with racemic sulfonimidoyl fluoride **(*rac*)-1** to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. Unfortunately, it was not possible to separate the enantiomers on the HPLC to analyse the *ee* of the enantioenriched material.

Synthesis of sulfonimidoyl fluorides

The synthesis of most of the sulfonimidoyl fluorides in this study is reported in Greed *et al*.[3] and is noted in the experimental procedure for the relevant sulfoximines. The synthesis of novel sulfonimidoyl fluorides are reported below.

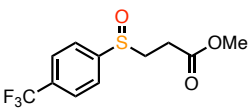


Methyl 3-((4-(trifluoromethyl)phenyl)thio)propanoate (S6)



Methyl acrylate (1.00 mL, 11.0 mmol, 1.1 equiv) and sodium acetate (120 mg, 1.5 mmol, 0.15 equiv) were added to 4-(Trifluoromethyl)thiophenol (1.38 mL, 10.1 mmol, 1.0 equiv) in THF:H_2O (1:1, 67 mL) and stirred at rt for 18 h. Aqueous NaOH (1 M, 50 mL) was added and the aqueous mixture was extracted with EtOAc (3 × 60 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give sulfide **S6** (2.62 g, 99%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 7.39 (d, *J* = 8.1 Hz, 2H, 2 × Ar–H), 3.70 (s, 3H, OCH_3), 3.24 (t, *J* = 7.4 Hz, 2H, SCH_2), 2.68 (t, *J* = 7.4 Hz, 2H, SCH_2CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9 (C=O), 140.9 (Ar–C_q), 128.2 (4 × Ar–C), 125.9 (q, $^2J_{C\text{-}F}$ = 3.2 Hz, Ar–C_q), 125.8 (q, $^1J_{C\text{-}F}$ = 170 Hz, CF_3), 51.9 (OCH_3), 33.8 (SCH_2), 27.8 (SCH_2CH_2). ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –62.49 (s, 3F, CF_3). Analytical data (^{1}H, ^{13}C & ^{19}F{^{1}H} NMR) in agreement with those previously reported.[2]

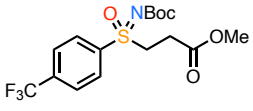
Methyl 3-((4-(trifluoromethyl)phenyl)sulfinyl)propanoate (S7)



m-CPBA (1.46 g, 8.45 mmol, 1.0 equiv) was added portionwise to sulfide **S6** (2.37 g, 8.45 mmol, 1.0 equiv) in CH_2Cl_2 (50 mL, 0.2 M) at 0 ºC and stirred for 2 h. The reaction mixture was quenched with sat. aq. $Na_2S_2O_3$ (50 mL) and the aqueous mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ (50 mL), dried (Na_2SO_4), filtered, and concentrated under reduced pressure to afford sulfoxide **S7** (1.96 g, 83%) as a white solid. mp = 105–110 °C. R_f 0.3 (50% EtOAc in pentane). IR (film)/cm^{-1} 3034, 2959, 2851, 1733 (C=O), 1326, 1162, 1107, 842, 697.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 7.75 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 3.66 (s, 3H, OCH_3), 3.29 (ddd, *J* = 13.3, 7.8, 7.0 Hz, 1H, SC*H*H), 2.97 (ddd, *J* = 13.3, 7.8, 5.7 Hz, 1H, SCH*H*), 2.87 (ddd, *J* = 17.3, 7.8, 7.0 Hz, 1H, SCH_2CHH), 2.57 (ddd, *J* = 17.3, 7.8, 5.7 Hz, 1H, SCH_2CHH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4 (C=O), 147.5 (Ar–C_q), 133.2 (q, $^2J_{C\text{-}F}$ = 32.7 Hz, Ar–C_q), 126.3 (q, $^4J_{C\text{-}F}$ = 3.8 Hz, 2 × Ar–C), 124.6 (2 × Ar–C), 123.5 (q, $^1J_{C\text{-}F}$ = 272.8 Hz, CF_3), 52.2 (CH_2), 51.1 (CH_2), 25.8 (CH_3). ^{19}F{^{1}H} NMR

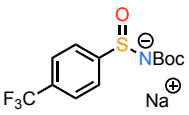
(377 MHz, $CDCl_3$) δ –62.85 (s, 3F, CF_3). HRMS (ESI) *m/z* Calcd for $C_{11}H_{12}F_3O_3S$ $[M+H]^+$: 281.0454; Found: 281.0441.

Methyl 3-(*N*-(*tert*-butoxycarbonyl)-4-(trifluoromethyl)phenylsulfonimidoyl)propanoate (S8)



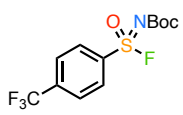
Magnesium oxide (1.11 g, 27.4 mmol, 4.0 equiv), *tert*-butyl carbamate (1.22 g, 10.4 mmol, 1.5 equiv), $PhI(OAc)_2$ (3.34 g, 10.4 mmol, 1.5 equiv) and $Rh_2(OAc)_4$ (76 mg, 0.2 mmol, 2.5 mol%) were added to a stirred solution of sulfoxide **S7** (1.96 g, 6.9 mmol, 1.0 equiv) in CH_2Cl_2 (70 mL, 0.1 M) at rt and warmed to 40 °C for 30 h. At rt the reaction mixture was filtered through celite and concentrated under reduced pressure. Purification by flash column chromatography (20% EtOAc in pentane, then 40% EtOAc in pentane) afforded sulfoximine **S8** (2.34 g, 86%) as a white solid. mp = 103–105 °C. R_f 0.45 (40% EtOAc in pentane). IR (film)/cm^{-1} 2981, 1729 (C=O), 1662 (C=O), 1319, 1278, 1140, 1058, 838. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 7.87 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 3.73 (ddd, *J* = 14.8, 8.9, 6.2 Hz, 1H, SC*H*H), 3.61 (s, 3H, OCH_3), 3.61–3.55 (m, 1H, SCH*H*), 2.83 (qdd, *J* = 17.4, 8.8, 6.3 Hz, 2H, SCH_2CH_2), 1.37 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9 (C=O), 157.2 (C=O), 141.0 (Ar–C_q), 135.7 (q, $^2J_{C\text{-}F}$ = 33.0 Hz, Ar–C_q), 128.8 (2 × Ar–C), 126.8 (q, $^4J_{C\text{-}F}$ = 3.5 Hz, 2 × Ar–C), 124.38 (q, $^1J_{C\text{-}F}$ = 275.9 Hz) 81.3 ($C(CH_3)_3$), 52.5 (OCH_3), 51.5 (SCH_2), 27.9 ($C(CH_3)_3$), 27.0 (SCH_2CH_2). $^{19}F\{^1H\}$ NMR (377 MHz, $CDCl_3$) δ –63.22 (s, 3F, CF_3). HRMS (ESI) *m/z* Calcd for $C_{16}H_{21}NO_5SF_3$ $[M+H]^+$: 396.1093; Found: 396.1106.

Sodium (*tert*-butoxycarbonyl)((4-(trifluoromethyl)phenyl)sulfinyl)amide (S9)



NaH (60% in oil, 250 mg, 6.2 mmol, 1.05 equiv) was added to sulfoximine **S8** (2.34 g, 5.9 mmol, 1.0 equiv) in THF (60 mL, 0.1 M) at 25 °C and stirred for 3 h. The reaction was quenched with MeOH (12 mL, 0.05 equiv) and concentrated under reduced pressure. The precipitate was collected by filtration and washed with hexane to afford sulfinamide salt **S9** (1.89 g, 97%) as a white solid. mp = 206–208 °C. R_f 0.38 (30% EtOAc in pentane). IR (film)/cm^{-1} 2981, 2983, 1640 (C=O), 1326, 1274, 1162, 1125, 1058, 1002, 834. ^1H NMR (400 MHz, D_2O) δ 7.76 (d, *J* = 8.9 Hz, 2H, 2 × Ar–H), 7.71 (d, *J* = 8.4 Hz, 2H,2 × Ar–H), 1.33 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, D_2O) δ 166.0 (C=O), 150.6 (Ar–C_q), 131.8 (q, $^2J_{C\text{-}F}$ = 32.5 Hz, Ar–C_q) 126.1 (q, $^4J_{C\text{-}F}$ = 3.4 Hz, 2 × Ar–C), 125.4 (2 × Ar–C), 79.9 ($C(CH_3)_3$), 27.7 ($C(CH_3)_3$). It was not possible to observe the CF_3 signal due to C-F coupling. $^{19}F\{^1H\}$ NMR (377 MHz, D_2O) δ –62.57 (s, 3F, CF_3). HRMS (ESI) *m/z* Calcd for $C_{12}H_{13}NO_3SF_3$ $[M]^-$: 308.0572; Found: 308.0568.

***tert*-Butyl (fluoro(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (S10)**

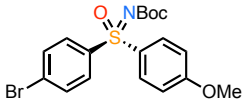


Selectfluor (0.18 g, 0.5 mmol, 2.0 equiv) was added to a stirred solution of sulfinamide salt **S9** (83 mg, 0.25 mmol, 1.0 equiv) and potassium acetate (50 mg, 0.5 mmol, 2.0 equiv) in DMF (1.25 mL, 0.2 M) at 0 °C and slowly warmed to rt over 24 h. The reaction mixture was quenched with water and diluted with CH_2Cl_2. The mixture was extracted with CH_2Cl_2 and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure to afford sulfonimidoyl fluoride **S10** (71.8 mg, 88%) as a white solid. mp = 48–50 °C. R_f 0.50

(10% EtOAc in pentane). IR (film)/cm^{-1} 3101, 3049, 2985, 1714 (C=O), 1320, 1274, 1170, 1129, 1062, 731. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.9 Hz, 2H, 2 × Ar–H), 7.89 (d, *J* = 8.4 Hz, 2H, 2 × Ar–H), 1.53 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7 (C=O), 136.8 (q, $^{2}J_{CF}$ = 33.8 Hz, Ar–C_q), 128.8 (2 × Ar–C), 126.7 (q, $^{4}J_{C\text{-}F}$ = 3.8 Hz, 2 × Ar–C), 122.8 (q, $^{1}J_{C\text{-}F}$ = 273.5 Hz, CF_3), 83.3 ($C(CH_3)$), 27.8 ($C(CH_3)$).$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) δ 69.81 (s, 1F, S–F), –63.43 (s, 3F, CF_3). Mass ion was not found in HRMS.

Scope of sulfoximines with variation of sulfonimidoyl fluorides

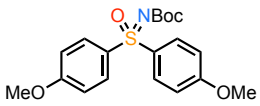
tert-Butyl (_R_)-((4-bromophenyl)(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)carbamate (4)



Reaction performed according to General Procedure D. 4-Methoxyphenylmagnesium bromide (0.60 mL, 0.5 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to *tert*-butyl (*R*)-((4-bromophenyl)fluoro(oxo)-λ^6-sulfaneylidene)carbamate (85 mg, 0.25 mmol, 1.0 equiv, 92% *ee*, synthesis in Greed *et al*.[3]) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (25% EtOAc in pentane) gave sulfoximine **(*R*)-4** as a white solid (69.9 mg, 0.16 mmol, 66%, 91% *ee*). mp = 139–140 ºC. R_f 0.21 (20% EtOAc in pentane). IR (film)/cm^{-1} 3086, 2974, 1670, 1588, 1491, 1238, 1148, 1088, 1052, 1014, 895, 835, 739. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.0 Hz, 2H, 2 × Ar–H), 7.82 (d, *J* = 8.7 Hz, 2H, 2 × Ar–H), 7.61 (d, *J* = 8.7 Hz, 2H, 2 × Ar–H), 6.96 (d, *J* = 9.0 Hz, 2H, 2 × Ar–H), 3.83 (s, 3H, OCH_3), 1.35 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8 (Ar–C_q), 157.4 (C=O), 140.1 (Ar–C_q), 132.7 (2 × Ar–C), 130.3 (Ar–C_q), 130.1 (2 × Ar–C), 129.1 (2 × Ar–C), 128.2 (Ar–C_q), 114.9 (2 × Ar–C), 80.9 ($C(CH_3)_3$), 55.8 (OCH_3), 28.1 ($C(CH_3)_3$). HRMS (ES) m/z cald for $C_{18}H_{21}BrNO_4S$ $[M+H]^+$: 426.0375; Found: 426.0361. $[\alpha]^{22}_D$ = +2 (c 1.0, $CHCl_3$). HPLC Conditions: Chiralpak IF column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm. Retention times: 36 min.

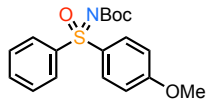
(*rac*)-4: The reaction was completed with the racemic sulfonimidoyl fluoride to give sufficient quantities (~10 mg) of racemic material for HPLC analysis. HPLC Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm. Retention times: 33 & 36 min.

tert-Butyl (bis(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)carbamate (5)



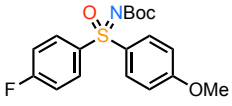
Reaction performed according to General Procedure D. 4-Methoxyphenylmagnesium bromide (0.6 mL, 0.5 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to a stirred solution of *tert*-butyl (fluoro(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)carbamate (72.3 mg, 0.25 mmol, 1.0 equiv, synthesis in Greed *et al*.[3]) in diethyl ether (0.8 mL, 0.3 M) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was quenched with sat. aq. NH_4Cl (30 mL), extracted with EtOAc (3 × 30 mL) and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification by flash column chromatography (30% EtOAc in hexane) to afford sulfoximine **5** (77.7 mg, 82%) as a viscous pale-yellow oil. R_f 0.10 (30% EtOAc in hexane). IR (film)/cm^{-1} 2974, 1670 (C=O), 1588, 1491, 1252, 1148, 1021, 746. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.0 Hz, 4H, 4 × Ar–H), 6.97 (d, *J* = 9.0 Hz, 4H, 4 × Ar–H), 3.85 (s, 6H, 2 × OCH_3), 1.38 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (2 × Ar–C_q–OCH_3), 157.5 (C=O), 131.7 (2 × Ar–C_q), 129.7 (4 × Ar–C), 114.6 (4 × Ar–C), 80.3 ($C(CH_3)_3$), 55.7 (2 × OCH_3), 28.0 ($C(CH_3)_3$). HRMS (ESI) m/z: Calcd for $C_{19}H_{24}NO_5S$ $[M+H]^+$: 378.1375; Found: 378.1380.

***tert*-Butyl ((4-methoxyphenyl)(oxo)(phenyl)-λ^6-sulfaneylidene)carbamate (6)**



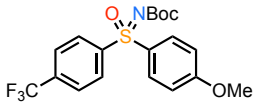
Reaction performed according to General Procedure D. 4-Methoxyphenylmagnesium bromide (0.5 mL, 0.5 M in THF, 0.25 mmol, 1.2 equiv) was added dropwise to a stirred solution of *tert*-butyl (fluoro(oxo)(phenyl)-λ^6-sulfaneylidene)carbamate (53.4 mg, 0.21 mmol, 1.0 equiv, synthesis in Greed *et al*.[3]) in diethyl ether (0.6 mL, 0.3 M) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was quenched with sat. aq. NH_4Cl (30 mL), extracted with EtOAc (3 × 30 mL) and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification by flash column chromatography (20% to 50% EtOAc in hexane) to afford sulfoximine **6** (61.6 mg, 86%) as a pale-yellow gum. R_f 0.10 (30% EtOAc in hexane). IR (film)/cm^{-1} 2974, 1670 (C=O), 1588, 1491, 1245, 1148, 1021, 746. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.91 (m, 4H, 4 × Ar–H), 7.57–7.45 (m, 3H, 3 × Ar–H), 6.99–6.92 (m, 2H, 2 × Ar–H), 3.83 (s, 3H, OCH_3), 1.34 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (Ar–C_q–OCH_3), 157.4 (C=O), 140.8 (Ar–C_q), 132.8 (Ar–C), 130.8 (Ar–C_q), 130.0 (2 × Ar–C), 129.3 (2 × Ar–C), 127.5 (2 × Ar–C), 114.7 (2 × Ar–C), 80.5 ($C(CH_3)_3$), 55.7 (OCH_3), 28.0 ($C(CH_3)_3$). HRMS (ESI) m/z: Calcd for $C_{18}H_{22}NO_4S$ $[M+H]^+$: 348.1270; Found: 348.1271.

***tert*-Butyl ((4-fluorophenyl)(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)carbamate (7)**



Reaction performed according to General Procedure D. 4-Methoxyphenylmagnesium bromide (0.5 mL, 0.5 M in THF, 0.25 mmol, 1.2 equiv) was added dropwise to a stirred solution of *tert*-butyl (fluoro(4-fluorophenyl)(oxo)-λ^6-sulfaneylidene)carbamate (69 mg, 0.25 mmol, 1.0 equiv, synthesis in Greed *et al*.[3]) in diethyl ether (0.6 mL, 0.3 M) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was quenched with sat. aq. NH_4Cl (30 mL), extracted with EtOAc (3 × 30 mL) and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification by flash column chromatography (30% EtOAc in pentane) to afford sulfoximine **7** (79.4 mg, 87%) as a pale-yellow gum. R_f 0.31 (30% EtOAc in pentane). IR (film)/cm^{-1} 2972, 1667 (C=O), 1586, 1489, 1227, 1144, 1091, 1021, 833, 729, 537. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.94 (m, 2H, 2 × Ar_{OMe}–H), 7.92 (d, J = 9.0 Hz, 2H, 2 × Ar_F–H), 7.16 (dd, J = 9.0, 8.2 Hz, 2H, 2 × Ar–H), 6.97 (d, J = 9.1 Hz, 2H, 2 × Ar–H), 3.84 (s, 3H, OCH_3), 1.36 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (d, $^1J_{C\text{-}F}$ = 255.6 Hz, FAr–C_q), 163.6 (Ar–C_q–OCH_3), 157.3 (C=O), 136.6 (Ar–C_q), 130.7 (Ar–C_q), 130.3 (d, $^3J_{C\text{-}F}$ = 9.5 Hz, 2 × Ar–C), 129.9 (2 × Ar–C), 116.6 (d, $^2J_{CF}$ = 22.7 Hz, 2 × Ar–C), 114.8 (2 × Ar–C), 80.7 ($C(CH_3)_3$), 55.7 (OCH_3), 28.0 ($C(CH_3)_3$). ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –104.96. HRMS (ESI) m/z: Calcd for $C_{18}H_{21}NO_4SF$ $[M+H]^+$: 366.1175; Found: 366.1184. $[\alpha]^{21}_D$ = –4 (c 1.0, $CHCl_3$). HPLC conditions: Chiralpak IA column, 90:10 *n*hexane:iPrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm.

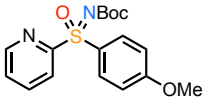
***tert*-Butyl ((4-methoxyphenyl)(oxo)(4-(trifluoromethyl)phenyl)-λ^6-sulfaneylidene)carbamate (8)**



4-Methoxyphenylmagnesium bromide (0.5 mL, 0.5 M in THF, 0.25 mmol, 1.2 equiv) was added dropwise to a stirred solution of *tert*-butyl

(fluoro(oxo)(4-(trifluoromethyl)phenyl)-λ^6-sulfaneylidene)carbamate (82 mg, 0.25 mmol, 1.0 equiv) in diethyl ether (0.6 mL, 0.3 M) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was quenched with sat. aq. NH_4Cl (30 mL), extracted with EtOAc (3 × 30 mL) and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification by flash column chromatography (30% EtOAc in pentane) to afford sulfoximine **8** (103.4 mg, 99%) as a colourless gum. R_f 0.49 (40% EtOAc in pentane). IR (film)/cm^{-1} 3101, 2974, 1669 (C=O), 1591, 1494, 1319, 1238, 1129, 1013, 835. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 7.96 (d, *J* = 9.1 Hz, 2H, 2 × Ar–H), 7.75 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 6.99 (d, *J* = 9.1 Hz, 2H, 2 × Ar–H), 3.85 (s, 3H, OCH_3), 1.36 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (Ar–C_q), 157.2 (C=O), 144.8 (Ar–C_q), 134.5 (q, $^2J_{C\text{-}F}$ = 33.1 Hz, Ar–C_q), 130.2 (2 × Ar–C), 129.5 (Ar–C_q), 128.0 (2 × Ar–C), 126.4 (q, $^4J_{C\text{-}F}$ = 3.7 Hz, 2 × Ar–C), 123.7 (q, $^1J_{C\text{-}F}$ = 272.6 Hz, CF_3), 114.9 (2 × Ar–C), 80.9 ($C(CH_3)_3$), 55.8 (OCH_3), 27.9 ($C(CH_3)_3$). ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –63.13 (s, 3F, CF_3). HRMS (ESI) *m/z* Calcd for $C_{19}H_{21}NO_4SF_3$ $[M+H]^+$: 416.1143; Found: 416.1151.

tert-Butyl ((4-methoxyphenyl)(oxo)(pyridin-2-yl)-λ^6-sulfaneylidene)carbamate (9)



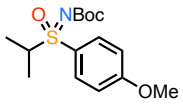
Reaction performed according to General Procedure D. 4-Methoxyphenylmagnesium bromide (0.60 mL, 0.5 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to *tert*-butyl ((4-(difluoromethyl)phenyl)fluoro(oxo)-λ^6-sulfaneylidene)carbamate hydrofluoride (56 mg, 0.25 mmol, 1.0 equiv, synthesis in Greed *et al*.[3]) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (25% EtOAc in pentane) gave sulfoximine **9** as a white solid (63.5 mg, 0.18 mmol, 73%). mp = 110–112 ºC. R_f 0.16 (25% EtOAc in pentane). IR (film)/cm^{-1} 2972, 2926, 2840, 1661, 1589, 1492, 1450, 1421, 1389, 1364, 1232, 1147, 1109, 1085, 1020, 990, 898, 859, 833, 726, 670, 520, 436. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H, Ar–H), 8.29 (dt, *J* = 8.0, 1.0 Hz, 1H, Ar–H), 8.08–8.00 (m, 2H, 2 × Ar–H), 7.90 (td, *J* = 7.8, 1.8 Hz, 1H, Ar–H), 7.41 (ddd, *J* = 7.6, 4.7, 1.1 Hz, 1H, Ar–H), 7.01–6.92 (m, 2H, 2 × Ar–H), 3.82 (s, 3H, OCH_3), 1.33 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (C=O), 158.6 (Ar–C_q), 157.7 (Ar–C_q), 150.3 (Ar–C), 138.2 (Ar–C), 131.4 (2 × Ar–C), 127.5 (Ar–C_q), 126.5 (Ar–C), 123.3 (Ar–C), 114.4 (2 × Ar–C), 80.6 ($C(CH_3)_3$), 55.8 (OCH_3), 28.0 ($C(CH_3)_3$). HRMS (ES) m/z cald for $C_{17}H_{21}N_2O_4S$ $[M+H]^+$: 349.1222; Found: 349.1215.

tert-Butyl ((4-methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)carbamate (10)

Reaction performed according to General Procedure D. 4-Methoxyphenylmagnesium bromide (0.60 mL, 0.5 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to *tert*-butyl (fluoro(methyl)(oxo)-λ^6-sulfaneylidene)carbamate (50 mg, 0.25 mmol, 1.0 equiv, synthesis in Greed *et al*.[3]) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (25% EtOAc in pentane) gave sulfoximine **10**

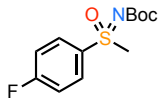
as a white solid (56.7 mg, 0.20 mmol, 80%). mp = 107–108 °C. R_f 0.18 (25% EtOAc in pentane). IR (film)/cm^{-1} 3001, 2971, 2925, 1659, 1591, 1495, 1457, 1364, 1309, 1270, 1249, 1224, 1153, 1109, 1090, 1022, 961, 889, 863, 835, 532, 499, 460. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.0 Hz, 2H, 2 × Ar–H), 7.03 (d, *J* = 9.0 Hz, 2H, 2 × Ar–H), 3.86 (s, 3H, OCH_3), 3.20 (s, 3H, S–CH_3), 1.37 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (C=O), 157.9 (Ar–C_q), 129.8 (Ar–C_q), 129.6 (2 × Ar–C), 115.0 (2 × Ar–C), 80.5 ($C(CH_3)_3$), 55.9 (OCH_3), 45.3 (SCH_3), 28.2 ($C(CH_3)_3$). Analytical data (NMR) in agreement with those reported in the literature.[7]

tert-Butyl (isopropyl(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)carbamate (11)



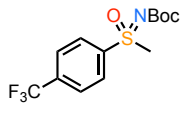
Reaction performed according to General Procedure D. 4-Methoxyphenylmagnesium bromide (0.60 mL, 0.5 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to *tert*-butyl (fluoro(isopropyl)(oxo)-λ^6-sulfaneylidene)carbamate (56 mg, 0.25 mmol, 1.0 equiv, synthesis in Greed *et al*.[3]) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (25% EtOAc in pentane) gave sulfoximine **11** as a white solid (62.4 mg, 0.20 mmol, 80%). mp = 110−111 °C. R_f 0.19 (25% EtOAc in pentane). IR (film)/cm^{-1} 2972, 2929, 1664, 1591, 1494, 1457, 1364, 1249, 1216, 1151, 1105, 1087, 1022, 892, 862, 835, 725, 691, 667, 646, 546, 452. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.73 (m, 2H, 2 × Ar–H), 7.06–6.98 (m, 2H, 2 × Ar–H), 3.87 (s, 3H, Ar–OCH_3), 3.46 (p, *J* = 6.8 Hz, 1H, SCH), 1.37 (d, *J* = 6.8 Hz, 3H, CHC*H*$_3$), 1.33 (s, 9H, $C(CH_3)_3$), 1.18 (d, *J* = 6.8 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8 (C=O), 158.2 (Ar–C_q), 131.1 (2 × Ar–C), 126.0 (Ar–C_q), 114.7 (2 × Ar–C), 80.1 ($C(CH_3)_3$), 56.4 (SCH), 55.8 (OCH_3), 28.1 ($C(CH_3)_3$), 16.0 (CH*C*H$_3$), 15.2 (CH*C*H$_3$). HRMS (ES) m/z cald for $C_{15}H_{24}NO_4S$ $[M+H]^+$: 314.1426; Found: 314.1426.

tert-Butyl (*R*)-((4-fluorophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)carbamate (13)



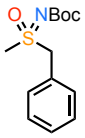
Reaction performed according to General Procedure D. Methylmagnesium bromide (0.09 mL, 2.8 M in Et_2O, 0.3 mmol, 1.2 equiv) was added dropwise to *tert*-butyl (fluoro(4-fluorophenyl)(oxo)-λ^6-sulfaneylidene)carbamate (69 mg, 0.25 mmol, 1.0 equiv, synthesis in Greed *et al*.[3]) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20-30% EtOAc in pentane) gave sulfoximine **13** (74.7 mg, quant) as a yellow gum. IR (film)/cm^{-1} 2973, 2925, 1662 (C=O), 1586, 1490, 1365, 1272, 1224, 1145, 1086, 837. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–7.98 (m, 2H, 2 × Ar–H), 7.31–7.27 (m, 2H, 2 × Ar–H), 3.25 (s, 3H, CH_3), 1.40 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (d, $^1J_{C\text{-}F}$ = 256.7 Hz, Ar–C_q), 157.5 (C=O), 134.7 (Ar–C_q), 130.3 (d, $^3J_{C\text{-}F}$ = 9.5 Hz, 2 × Ar–C), 117.0 (d, $^2J_{C\text{-}F}$ = 23.0 Hz, 2 × Ar–C), 80.8 ($C(CH_3)_3$), 44.9 (CH_3), 28.0 ($C(CH_3)_3$). ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –103.45 (Ar–F). HRMS (ESI) m/z: Calcd for $C_{12}H_{17}NO_3SF$ $[M+H]^+$: 274.0913; Found: 274.0918. $[\alpha]^{21}_D$ = –28 (c 0.8, $CHCl_3$).

***tert*-Butyl (methyl(oxo)(4-(trifluoromethyl)phenyl)-λ^6-sulfaneylidene)carbamate (14)**



Reaction performed according to General Procedure D. Methylmagnesium bromide (0.09 mL, 2.8 M in Et_2O, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **S10** (82 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20-30% EtOAc in pentane) gave sulfoximine **14** (63.5 mg, 79%) as a white solid. mp = 125–130 °C. R_f 0.30 (40% EtOAc in pentane). IR (film)/cm^{-1} 3019, 2983, 1660 (C=O), 1395, 1316, 1267, 1123, 1056, 985, 842, 792. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 7.88 (d, *J* = 8.2 Hz, 2H, 2 × Ar–H), 3.26 (s, 3H, CH_3), 1.39 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4 (C=O), 142.7 (Ar–C_q), 135.5 (q, $^2J_{C–F}$ = 33.4 Hz, Ar–C_q), 128.1 (2 × Ar–C), 126.8 (q, $^4J_{C–F}$ = 3.7 Hz, 2 × Ar–C), 123.1 (d, $^1J_{C–F}$ = 272.8 Hz, CF_3), 81.1 ($C(CH_3)_3$), 44.5 (SCH_3), 27.9 ($C(CH_3)_3$). ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ –63.20 (s, 3F, CF_3). HRMS (ESI) m/z: Calcd for $C_{13}H_{17}NO_3SF_3$ $[M+H]^+$: 324.0881; Found: 324.0885.

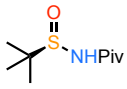
***tert*-Butyl (bis(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)carbamate (15)**



Reaction performed according to General Procedure D. Benzylmagnesium chloride (0.3 mL, 1.0 M in diethyl ether, 0.3 mmol, 1.2 equiv) was added dropwise to *tert*-butyl (fluoro(methyl)(oxo)-λ^6-sulfaneylidene)carbamate (50 mg, 0.25 mmol, 1.0 equiv, synthesis in Greed *et al*.[3]) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (25% EtOAc in pentane) gave sulfoximine **15** (28.0 mg, 42%) as a colourless gum. R_f 0.25 (50% EtOAc in hexane). IR (film)/cm^{-1} 2974, 1655 (C=O), 1245, 1148, 969, 887, 782. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.39 (m, 5H, 5 × Ar–H), 4.82–4.69 (m, 2H, SCH_2), 2.91 (t, *J* = 0.7 Hz, 3H, SCH_3), 1.51 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6 (C=O), 130.9 (2 × Ar–C), 129.6 (Ar–C), 129.3 (2 × Ar–C), 127.7 (Ar–C_q), 80.6 ($C(CH_3)_3$), 59.5 (SCH_2), 38.0 (SCH_3), 28.2 ($C(CH_3)_3$). HRMS (ESI) m/z: Calcd for $C_{13}H_{20}NO_3S$ $[M+H]^+$: 270.1164; Found: 270.1158.

Synthesis of enantioenriched sulfinamide salts **(*S*)-23-25**

(*R*)-*N*-(*tert*-Butylsulfinyl)pivalamide ((*R*)-16)

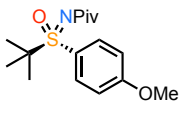


Prepared in a similar manner to a literature procedure.[2] *n*-BuLi (1.6 M in hexanes, 30.0 mL, 48 mmol, 2.5 equiv) was added dropwise to a stirred solution of (*R*)-*t*-butylsulfinamide (2.33 g, 19.2 mmol, 1 equiv) in THF (50 mL, 0.4 M) at –78 ºC. The mixture was stirred for 10 min followed by the addition of pivalic anhydride (4.7 mL, 23.0 mmol, 1.2 equiv) and warmed to rt for 3 h. At 0 ºC, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (30 mL) and diluted with EtOAc (30 mL). The mixture was extracted with EtOAc (3 × 30 mL), and the combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. Following filtration through a pad of silica, washing with EtOAc, no further purification was required, giving sulfinamide **(*R*)-16** as a white solid (4.76 g, 19.2 mmol, quant). mp = 136–137 ºC. IR (film)/cm^{-1} 3176, 2960, 2932, 2871, 1686, 1474, 1396, 1366, 1131, 1067, 1019, 903, 834, 758, 640, 588, 493. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 1H, NH), 1.25 (s, 9H, C(CH_3)$_3$), 1.24 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8 (C=O), 57.4 (S*C*(CH_3)$_3$), 40.1 (CO*C*(CH_3)$_3$), 27.4 (C(*C*H_3)$_3$), 22.1 (C(*C*H_3)$_3$). $[\alpha]^{21}_D$ = +30 (c 1, $CHCl_3$). HPLC analysis not run as retention of *ee* is known,[5] and subsequent products in the reaction sequence have >99% *ee*. Analytical data (^{1}H and ^{13}C NMR) in agreement with those reported in the literature.[5]

(*rac*)-16: For chiral HPLC analysis, the racemic sample was generated in a similar manner. The above experimental procedure was carried out on (*rac*)-*t*-butylsulfinamide (2.33 g, 19.2 mmol) to give **(*rac*)-16** as a white solid (4.68 g, quant). The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*R*)-16** above.

*Sulfoximine intermediates **17-19***

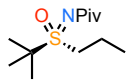
(*S*)-*N*-(*tert*-Butyl(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)pivalamide ((*S*)-17)



Prepared according to a modified literature procedure.[6] DIPEA (0.53 mL, 3.1 mmol, 1.8 equiv) was added to bis(4-methoxyphenyl)iodonium tetrafluoroborate (342 mg, 1.7 mmol, 1.0 equiv, prepared according to a modified literature procedure[8]), sulfinamide **(*R*)-16** (1.07 g, 2.5 mmol, 1.5 equiv), 4Å molecular sieves (1.7 g, 1g/mmol), and copper (II) triflate (62 mg, 0.17 mmol, 0.1 equiv) in DMSO (17 mL, 0.1 M), heated to 60 ºC and stirred for 24 h. At rt, the reaction mixture was filtered through a pad of silica, eluting with EtOAc, then the filtrate was washed with brine (3 × 100 mL), and the organic phase dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification *via* column chromatography (20–30% EtOAc in pentane) afforded the sulfoximine **(*S*)-17** (464 mg, 1.5 mmol, 88%) as a pale-yellow oil. R_f 0.19 (25% EtOAc in pentane). IR (film)/cm^{-1} 2972, 2928, 2866, 1640, 1593, 1496, 1477, 1458, 1390, 1363, 1287, 1261, 1207, 1191, 1162, 1113, 1091, 1023, 971, 846, 665, 626, 547, 527, 466. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 9.0 Hz, 2H, 2 × Ar–H), 7.01 (d, *J* = 9.0 Hz, 2H, 2 × Ar–H), 3.86 (s, 3H, OCH_3), 1.37 (s, 9H, C(CH_3)$_3$), 1.23 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0 (C=O), 163.7 (Ar–C_q), 131.8 (2 × Ar–C), 124.5 (Ar–C_q), 114.6 (2 × Ar–C), 61.4 (S*C*(CH_3)$_3$), 55.8 (OCH_3), 41.8 (NCO*C*(CH_3)$_3$), 28.0 (C(*C*H_3)$_3$), 23.3 (C(*C*H_3)$_3$). $[\alpha]^{21}_D$ = +120 (c 1.0, $CHCl_3$). HPLC analysis not run as retention of *ee* is known and

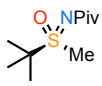
racemic form of **17** not synthesised.[6] Analytical data (NMR) in agreement with those reported in the literature.[6]

(*R*)-*N*-(*tert*-Butyl(oxo)(propyl)-λ⁶-sulfaneylidene)pivalamide ((*R*)-18)



Prepared according to a modified literature procedure.[5] NaH (60% dispersion in mineral oil, 720 mg, 18.0 mmol, 1.2 equiv) and 15-crown-5 (4.0 mL, 18.0 mmol, 1.2 equiv) were added to sulfinamide **(*R*)-16** (3.0 g, 15.0 mmol, 1.0 equiv) in 1,4-dioxane (70 mL, 0.2 M) and stirred for 10 min at rt. Bromopropane (2.8 mL, 30.0 mmol, 2.0 equiv) was added and reaction mixture was heated to 60 ºC for 24 h. At rt, the reaction was quenched with saturated aqueous NH_4Cl (100 mL), extracted with EtOAc (3 × 100 mL), washed with brine (100 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification *via* column chromatography (20–30% EtOAc in pentane) gives sulfoximine **(*R*)-18** (2.55 g, 0.10 mmol, 69%) as a white solid. mp = 67–69 ºC. R_f 0.21 (25% EtOAc in pentane). IR (film)/cm^{-1} 2966, 2932, 2871, 1687, 1629, 1475, 1393, 1365, 1293, 1193, 1167, 1133, 1084, 1064, 1022, 967, 904, 839, 753, 589, 494, 459. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (ddd, *J* = 13.5, 10.9, 5.3 Hz, 1H, SC*H*H), 3.24 (ddd, *J* = 13.6, 10.9, 5.3 Hz, 1H, SCH*H*), 2.03–1.79 (m, 2H, SCH_2CH_2), 1.46 (s, 9H, $C(CH_3)_3$), 1.19 (s, 9H, $C(CH_3)_3$), 1.07 (t, *J* = 7.4 Hz, 3H, CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 48.3 (SCH_2), 28.0 ($C(CH_3)_3$), 23.6 ($C(CH_3)_3$), 17.3 (SCH_2CH_2), 13.5 (CH_2CH_3), 3 × quaternary C peaks not visible. HRMS (ES) m/z cald for $C_{12}H_{26}NO_2S$ $[M+H]^+$: 248.1684; Found: 248.1681. $[\alpha]^{21}_D$ = +27 (c 0.6, $CHCl_3$). HPLC analysis not possible as no detectable UV trace.

(*R*)-*N*-(*tert*-Butyl(methyl)(oxo)-λ⁶-sulfaneylidene)pivalamide ((*R*)-19)

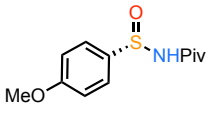


Prepared according to a modified literature procedure.[5] NaH (60% dispersion in mineral oil, 910 mg, 23.0 mmol, 1.2 equiv) and 15-crown-5 (4.5 mL, 23.0 mmol, 1.2 equiv) were added to sulfinamide **(*R*)-16** (3.90 g, 19.0 mmol, 1.0 equiv) in 1,4-dioxane (90 mL, 0.2 M) and stirred for 10 min at rt. Methyl iodide (2.4 mL, 38.0 mmol, 2.0 equiv) was added and reaction mixture was heated to 70 ºC for 24 h. At rt, the reaction was quenched with saturated aqueous NH_4Cl (100 mL), extracted with EtOAc (3 × 100 mL), washed with brine (100 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification *via* column chromatography (20–30% EtOAc in pentane) gives sulfoximine **(*R*)-19** (4.01 g, 18.3 mmol, 96%) as a white solid. mp = 82–83 ºC. R_f 0.14 (30% EtOAc in pentane). IR (film)/cm^{-1} 3023, 2973, 2954, 2868, 1617, 1539, 1476, 1389, 1364, 1289, 1164, 1027, 997, 944, 847, 726, 613, 572, 507, 478, 456. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.25 (s, 3H, SCH_3), 1.48 (s, 9H, $SC(CH_3)_3$), 1.18 (s, 9H, $NC(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 60.3 ($C(CH_3)_3$), 32.2 (SCH_3), 27.9 ($C(CH_3)_3$), 23.1 ($C(CH_3)_3$) (C=O and quaternary carbon signals not observed). $[\alpha]^{21}_D$ = +69 (c 0.7, $CHCl_3$). HPLC analysis not possible as no detectable UV trace. Analytical data (^{1}H and ^{13}C NMR) in agreement with those reported in the literature.[5]

(*rac*)-19: For chiral HPLC analysis, the racemic sample was generated in a similar manner. The above experimental procedure was carried out on **(*rac*)-16** (3.90 g, 19.0 mmol) to give **(*rac*)-19** as a white solid (4.03 g, 97%). The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*R*)-19** above.

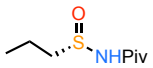
*Sulfinamide intermediates **20**-**22***

(*S*)-*N*-((4-Methoxyphenyl)sulfinyl)pivalamide ((*S*)-20)



The sulfoximine starting material **(*S*)-17** was azeotroped with PhMe three times prior to reaction. Trifluoroacetic acid (138 μL, 2.7 mmol, 1.5 equiv) was added dropwise to **(*S*)-17** (570 mg, 1.8 mmol, 1.0 equiv) in CH_2Cl_2 (4.5 mL, 0.4 M) at rt and stirred for 40 min. CH_2Cl_2 (40 mL) was added, and the organic layer was washed with brine (40 mL) and saturated aqueous $NaHCO_3$ (40 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification *via* column chromatography (20-30% EtOAc in pentane) afforded the sulfinamide **(*S*)-20** (359 mg, 1.4 mmol, 78%) as a white solid. mp = 108–109 ºC. R_f 0.20 (30% EtOAc in pentane). IR (film)/cm^{-1} 3081, 2969, 2912, 2838, 1593, 1495, 1302, 1252, 1176, 1087, 1046, 901, 831, 797, 526, 459. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.60 (m, 2H, 2 × Ar–H), 7.48 (s, 1H, NH), 7.09–7.00 (m, 2H, 2 × Ar–H), 3.87 (s, 3H, OCH_3), 1.22 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7 (C=O), 162.7 (Ar–C_q), 135.3 (Ar–C_q), 126.6 (2 × Ar–C), 115.1 (2 × Ar–C), 55.8 (OCH_3), 39.8 ($C(CH_3)_3$), 27.3 ($C(CH_3)_3$). HRMS (ES) m/z cald for $C_{12}H_{18}NO_3S$ $[M+H]^+$: 255.0929; Found: 255.0932. $[\alpha]^{21}_D$ = +50 (c 0.6, $CHCl_3$). HPLC analysis not run as retention of *ee* in *t*butyl removal is known and racemic form of **20** not synthesised.[6] Analytical data (NMR) in agreement with those reported in the literature.[6]

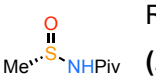
(*S*)-*N*-(Propylsulfinyl)pivalamide ((*S*)-21)



Reaction performed according to a literature procedure.[5] The sulfoximine starting material **(*R*)-18** was dissolved in toluene and concentrated *in vacuo* three times prior to reaction. Trifluoroacetic acid (1.1 mL, 14.6 mmol, 1.5 equiv) was added dropwise to **(*R*)-18** (2.5 g, 9.7 mmol, 1.0 equiv) in CH_2Cl_2 (25 mL, 0.4 M) at rt and stirred for 40 min. CH_2Cl_2 (40 mL) was added, and the organic layer was washed with brine (40 mL) and saturated aqueous $NaHCO_3$ (40 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification *via* column chromatography (20–30% EtOAc in pentane) afforded the sulfinamide **(*S*)-21** (685 mg, 3.6 mmol, 37%) as a white solid. mp = 76–77 ºC. R_f 0.22 (30% EtOAc in pentane). IR (film)/cm^{-1} 3150, 2968, 2932, 2870, 1687, 1473, 1415, 1397, 1365, 1135, 1058, 1019, 937, 905, 840, 764, 637, 591, 493. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H, NH), 3.08–2.89 (m, 2H, SCH_2), 1.82–1.70 (m, 2H, SCH_2CH_2), 1.23 (s, 9H, $C(CH_3)_3$), 1.09 (t, *J* = 7.4 Hz, 3H, CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.2 (C=O), 57.3 (SCH_2), 39.9 ($C(CH_3)_3$), 27.2 ($C(CH_3)_3$), 16.4 (SCH_2CH_2), 13.3 (CH_2CH_3). HRMS (ES) m/z cald for $C_8H_{18}NO_2S$ $[M+H]^+$: 192.1058; Found: 192.1047. $[\alpha]^{21}_D$ = +33 (c 0.6, $CHCl_3$). HPLC analysis not possible as no detectable UV trace.

(*rac*)-21: For chiral HPLC analysis, the racemic sample was generated in a similar manner. The above experimental procedure was carried out on **(*rac*)-18** (1.2 g, 5.1 mmol) to give **(*rac*)-21** as a white solid (950 mg, 97%). The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*S*)-21** above.

(*S*)-*N*-(Methylsulfinyl)pivalamide ((*S*)-22)



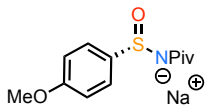
Reaction performed according to a literature procedure.[5] The sulfoximine starting material **(*R*)-19** was dissolved in toluene and concentrated *in vacuo* three times prior to reaction.

Trifluoroacetic acid (2.1 mL, 27.0 mmol, 1.5 equiv) was added dropwise to **(*R*)-19** (4.0 g, 18.0 mmol, 1.0 equiv) in CH_2Cl_2 (45 mL, 0.2 M) at rt and stirred for 40 min. EtOAc (40 mL) was added, and the organic layer was washed with brine (40 mL) and saturated aqueous $NaHCO_3$ (40 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. Following filtration through a pad of silica, eluting with EtOAc, no further purification was required to give sulfinamide **(*S*)-22** as a white solid (1.53 mg, 9.4 mmol, 52%). mp = 132–133 ºC. IR (film)/cm^{-1} 3201, 2969, 2930, 2873, 1689, 1477, 1401, 1371, 1307, 1139, 1073, 1026, 980, 828, 695, 488. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H, NH), 2.85 (s, 3H, SCH_3), 1.24 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8 (C=O), 42.5 (SCH_3), 39.8 ($C(CH_3)_3$), 27.3 ($C(CH_3)_3$). HRMS (ES) m/z cald for $C_6H_{14}NO_2S$ $[M+H]^+$: 164.0745; Found: 164.0738. $[\alpha]^{21}_D$ = 0 (c 0.2, $CHCl_3$). HPLC analysis not run as no detectable UV trace and subsequent products in the reaction sequence have >99% *ee*.

(*rac*)-22: For chiral HPLC analysis, the racemic sample was generated in a similar manner. The above experimental procedure was carried out on **(*rac*)-19** (4.03 g, 18.5 mmol) to give **(*rac*)-22** as a white solid (1.63 g, 55%). The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*S*)-22** above.

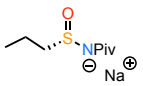
*Enantioenriched sulfinamide salts **23**-**25***

Sodium (*S*)-((4-methoxyphenyl)sulfinyl)(pivaloyl)amide ((*S*)-23)



Prepared in a similar manner to a literature procedure.[3] NaH (60% in oil, 60 mg, 1.5 mmol, 1.1 equiv) was added to sulfinamide **(*S*)-20** (360 g, 1.4 mmol, 1.0 equiv) in THF (10 mL, 0.15 M) at 0 °C and stirred, warming to rt, for 3 h. The reaction was quenched with MeOH (~25 μL) and concentrated under reduced pressure. Pentane (100 mL) was added to induce precipitation, and the resulting solid was collected by filtration and washed with pentane and Et_2O to give sulfinamide salt **(*S*)-23** (270 mg, 1.0 mmol, 69%) as a white solid. Decomposition observed above 225 ºC. IR (film)/cm^{-1} 2950, 2920, 2861, 2835, 1595, 1489, 1390, 1336, 1247, 1207, 1175, 1131, 1088, 1003, 977, 918, 799, 766, 671, 628. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.57 (m, 2H, 2 × Ar–H), 7.11–7.00 (m, 2H, 2 × Ar–H), 3.84 (s, 3H, OCH_3), 1.12 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0 (C=O), 160.9 (Ar–C_q), 138.4 (Ar–C_q), 126.8 (2 × Ar–C), 114.5 (2 × Ar–C), 55.5 (OCH_3), 39.4 ($C(CH_3)_3$), 27.6 ($C(CH_3)_3$). HRMS (ES) m/z cald for $C_{12}H_{16}NO_3S$ $[M]^-$: 254.0851; Found: 254.0860. $[\alpha]^{21}_D$ = –76 (c 1.0, H_2O).

Sodium (*S*)-pivaloyl(propylsulfinyl)amide ((*S*)-24)

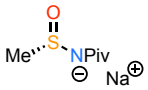


Prepared in a similar manner to a literature procedure.[3] NaH (60% in oil, 130 mg, 3.4 mmol, 1.1 equiv) was added to sulfinamide **(*S*)-21** (0.6 g, 3.1 mmol, 1.0 equiv) in THF (20 mL, 0.15 M) at 0 °C and stirred, warming to rt, for 3 h. The reaction was quenched with MeOH (~25 μL) and concentrated under reduced pressure. Pentane (100 mL) was added to induce precipitation, and the resulting solid was collected by filtration and washed with pentane and Et_2O to give sulfinamide salt **(*S*)-24** (545 mg, 1.1 mmol, 35%) as a white solid. mp = 201–202 ºC. IR (film)/cm^{-1} 2955, 2922, 2966, 1511, 1481, 1455, 1391, 1338, 1212, 998, 968, 917, 822, 798, 770, 671, 601, 542, 520, 411. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71–2.55 (m, 2H, SCH_2), 1.66–1.49 (m, 2H, SCH_2CH_2), 1.08

(s, 9H, $C(CH_3)_3$), 0.96 (t, *J* = 7.5 Hz, 3H, CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7 (C=O), 58.2 (SCH_2), 41.8 ($C(CH_3)_3$), 30.2 ($C(CH_3)_3$), 18.7 (SCH_2CH_2), 15.1 (CH_2CH_3). HRMS (ES) m/z cald for $C_8H_{17}NO_2S$ $[M\text{-}Na+H]^+$: 191.0980; Found: 191.0986. $[\alpha]^{21}_D$ = +2 (c 1.0, $CHCl_3$). HPLC analysis not possible as no detectable UV trace.

(*rac*)-24: For chiral HPLC analysis, the racemic sample was generated in a similar manner. The above experimental procedure was carried out on **(*rac*)-21** (0.9 g, 4.7 mmol) to give **(*rac*)-24** as a white solid (943 mg, 97%). The analytical data (^1H and ^{13}C NMR) was identical to that shown for **(*S*)-24** above.

Sodium (*S*)-(methylsulfinyl)(pivaloyl)amide ((*S*)-25)



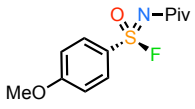
Prepared in a similar manner to a literature procedure.[3] NaH (60% in oil, 400 mg, 10.0 mmol, 1.05 equiv) was added to sulfinamide **(*S*)-22** (1.53 g, 9.4 mmol, 1.0 equiv) in THF (90 mL, 0.1 M) at 0 °C and stirred, warming to rt, for 3 h. The reaction was quenched with MeOH (~25 μL) and concentrated under reduced pressure. Pentane (100 mL) was added to induce precipitation, and the resulting solid was collected by filtration and washed with pentane and Et_2O to give sulfinamide salt **(*S*)-25** (1.31 g, 7.1 mmol, 75%) as a white solid. mp = 147–148 ºC. IR (film)/cm^{-1} 2953, 2866, 1509, 1477, 1392, 1326, 1209, 991, 964, 937, 826, 769, 706, 513. ^1H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H, SCH_3), 1.10 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1 (C=O), 39.8 (SCH_3), 39.1 ($C(CH_3)_3$), 27.6 ($C(CH_3)_3$). HRMS (ES) m/z cald for $C_6H_{12}NO_2S$ $[M\text{-}Na]^-$:162.0589; Found: 162.0593. $[\alpha]^{21}_D$ = +180 (c 1, H_2O). HPLC analysis not possible as no detectable UV trace.

(*rac*)-25: For chiral HPLC analysis, the racemic sample was generated in a similar manner. The above experimental procedure was carried out on **(*rac*)-22** (1.63 g, 10.0 mmol) to give **(*rac*)-25** as a white solid (1.95 g, quant). The analytical data (^1H and ^{13}C NMR) was identical to that shown for **(*S*)-25** above.

Synthesis of enantioenriched sulfoximines *ent*-2a-(*S*)-30

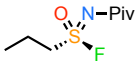
Synthesis of sulfonimidoyl fluoride intermediates ***(R)-26-28***

(*R*)-4-Methoxy-*N*-pivaloylbenzenesulfonimidoyl fluoride ((*R*)-26)



Reaction performed according to General Procedure A. Selectfluor (422 g, 1.2 mmol, 2.0 equiv) was added to a solution of sulfinamide salt **(*S*)-23** (167 mg, 0.60 mmol, 1.0 equiv) and potassium acetate (118 mg, 1.2 mmol, 2.0 equiv) in ethanol (3.0 mL, 0.3 M) at 0 °C and warmed to 25 °C for 24 h. H_2O (30 mL) was added and the aqueous mixture extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give sulfonimidoyl fluoride **(*R*)-26** (138 mg, 0.50 mmol, 84%) as a colourless oil. IR (film)/cm^{-1} 2974, 2871, 1678, 1594, 1498, 1301, 1272, 1197, 1165, 1110, 1020, 910, 838, 808, 730, 545, 471. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–7.95 (m, 2H, 2 × Ar–H), 7.10–7.02 (m, 2H, 2 × Ar–H), 3.91 (s, 3H, OCH_3), 1.24 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.1 (C=O), 165.3 (Ar–C_q), 130.5 (2 × Ar–C), 125.6 (Ar–C_q), 114.9 (2 × Ar–C), 56.1 (OCH_3), 42.4 ($C(CH_3)_3$), 27.3 ($C(CH_3)_3$). ^{19}F NMR (377 MHz, $CDCl_3$) δ 67.22 (S–F). HRMS (ES) m/z cald for $C_{12}H_{17}FNO_3S$ $[M+H]^+$: 274.0913; Found: 274.0900. $[\alpha]^{21}_D$ = −73 (c 0.6, $CHCl_3$). HPLC analysis not carried out as racemic sample of **26** not synthesised.

(*R*)-*N*-Pivaloylpropane-1-sulfonimidoyl fluoride ((*R*)-27)



Reaction performed according to General Procedure C. Selectfluor (422 g, 1.2 mmol, 2.0 equiv) was added to a solution of sulfinamide salt **(*S*)-24** (128 mg, 0.6 mmol, 1.0 equiv) in ethanol/DMF (2:1, 3.0 mL, 0.3 M) at 0 °C and warmed to 25 °C for 24 h. H_2O (30 mL) was added, and the aqueous mixture extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give sulfonimidoyl fluoride **(*R*)-27** (73 mg, 0.35 mmol, 58%) as a colourless oil. IR (film)/cm^{-1} 2973, 2935, 2874, 1676, 1478, 1458, 1395, 1279, 1156, 1094, 1054, 912, 844, 727, 650, 575, 524, 482. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64–3.54 (m, 2H, SCH_2), 2.07–1.94 (m, 2H, SCH_2CH_2), 1.19 (s, 9H, $C(CH_3)_3$), 1.13 (td, *J* = 7.5, 1.1 Hz, 3H, CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 54.3 (SCH_2), 27.2 ($C(CH_3)_3$), 17.1 (SCH_2CH_2), 12.7 (CH_2CH_3) (quaternary carbon signals not observed). ^{19}F NMR (377 MHz, $CDCl_3$) δ 53.34 (S–F). HRMS (ES) m/z cald for $C_8H_{17}FNO_2S$ $[M+H]^+$: 209.0886; Found: 209.0892. $[\alpha]^{22}_D$ = −8 (c 1.0, CHC_3). HPLC analysis not possible as no detectable UV trace.

(*rac*)-27: For chiral HPLC analysis, the racemic sample was generated in a similar manner. The above experimental procedure was carried out on **(*rac*)-24** (128 mg, 0.6 mmol) to give **(*rac*)-27** as a white solid (70 mg, 56%). The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*R*)-27** above.

(*R*)-*N*-Pivaloylmethanesulfonimidoyl fluoride ((*R*)-28)

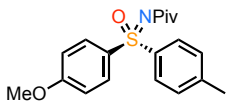
Reaction performed according to General Procedure C. Selectfluor (704 g, 2.0 mmol, 2.0 equiv) was added to a solution of sulfinamide salt **(*S*)-25** (185 mg, 1.0 mmol, 1.0 equiv) in ethanol/DMF (2:1, 5.0 mL, 0.3 M) at 0 °C and warmed to 25 °C for 24 h. H_2O (30 mL) was added, and the aqueous mixture extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried

($MgSO_4$), filtered and the solvent removed under reduced pressure to give sulfonimidoyl fluoride **(*R*)-28** (108 mg, 0.6 mmol, 60%) as an amorphous solid. IR (film)/cm^{-1} 2957, 2927, 2869, 1659, 1501, 1481, 1457, 1439, 1408, 1386, 1313, 1280, 1256, 1183, 1091, 977, 860, 768, 659, 520. NMR spectra are not completely clean but sulfonimidoyl fluoride used immediately after isolation to prevent any potential racemisation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48 (d, *J* = 5.3 Hz, 3H, SCH_3), 1.19 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (C=O), 39.5 (SCH_3), 27.1 ($C(CH_3)_3$), $C(CH_3)_3$ quaternary C signal not visible. ^{19}F NMR (377 MHz, $CDCl_3$) δ −60.43 (S–F). Desired m/z not found in HRMS analysis. $[\alpha]^{21}_D$ = +20 (c 0.6, $CHCl_3$). HPLC analysis not possible as no detectable UV trace.

(*rac*)-28: For chiral HPLC analysis, the racemic sample was generated in a similar manner. The above experimental procedure was carried out on **(*rac*)-25** (185 mg, 1.0 mmol) to give **(*rac*)-28** as a white solid (105 g, 58%). The analytical data (^{1}H and ^{13}C NMR) was identical to that described or **(*S*)-28** above.

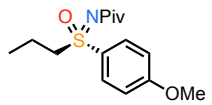
Synthesis of enantioenriched sulfoximines ***ent-2a-(S)-30***

(*R*)-*N*-((4-Methoxyphenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)pivalamide (*ent*-2a)



Reaction performed according to General Procedure D. 4-Tolylmagnesium bromide (0.36 mL, 0.5 M in THF, 0.18 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-26** (43 mg, 0.15 mmol, 1.0 equiv) in Et_2O (0.50 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (25% EtOAc in pentane) gave sulfoximine ***ent*-2a** as a white solid (36.1 mg, 0.10 mmol, 33%, 87% *ee*). The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*S*)-2a**. $[\alpha]^{21}_D$ = +15 (c 0.4, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 270 nm. Retention time: **(*R*)-2a** = 36 min.

(*S*)-*N*-((4-Methoxyphenyl)(oxo)(propyl)-λ^6-sulfaneylidene)pivalamide ((*S*)-29)

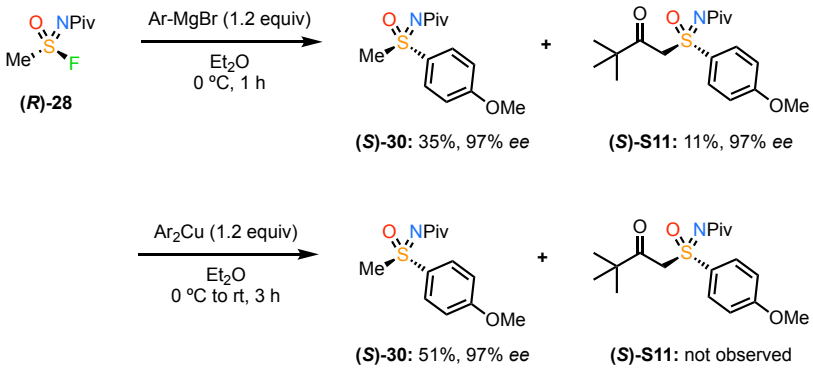


Reaction performed according to General Procedure D. 4-Methoxyphenylmagnesium bromide (0.60 mL, 0.5 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-27** (52 mg, 0.25 mmol, 1.0 equiv) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (25% EtOAc in pentane) gave sulfoximine **(*S*)-29** as an amorphous solid (25.4 mg, 0.13 mmol, 52%, >99% *ee*). R_f 0.18 (25% EtOAc in pentane). IR (film)/cm^{-1} 2969, 2873, 1634, 1594, 1486, 1391, 1288, 1261, 1204, 1170, 1098, 1026, 969, 838, 810, 548, 526, 458. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.80 (m, 2H, 2 × Ar–H), 7.03 (d, *J* = 9.0 Hz, 2H, 2 × Ar–H), 3.88 (s, 3H, OCH_3), 3.51–3.31 (m, 2H, SCH_2), 1.74–1.53 (m, 2H, SCH_2CH_2), 1.22 (s, 9H, $C(CH_3)_3$), 0.95 (t, *J* = 7.4 Hz, 3H, CH_2CH_3).^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5 (C=O), 163.8 (Ar–C_q), 130.0 (2 × Ar–C), 128.6

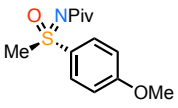
(Ar–C_q), 114.9 (2 × Ar–C), 57.6 (OCH_3), 55.8 (SCH_2), 41.6 ($C(CH_3)_3$), 27.9 ($C(CH_3)_3$), 16.6 (SCH_2CH_2), 12.9 (CH_2CH_3). HRMS (ES) m/z cald for $C_{15}H_{24}NO_3S$ $[M+H]^+$: 298.1477; Found: 298.1481. $[\alpha]^{22}_D$ = +16 (c 0.5, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm. Retention time: 17 min.

(*rac*)-29: For chiral HPLC analysis, the racemic sample was generated in a similar manner. The above experimental procedure was carried out on **(*rac*)-27** (52 mg, 0.25 mmol) to give **(*rac*)-29** as a white solid (18.0 mg, 24%). The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*R*)-29** above. HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm. Retention times: 17 & 27 min.

(*S*)-*N*-((4-Methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)pivalamide ((*S*)-30)

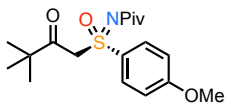


With Ar-MgBr: Reaction performed according to General Procedure D. 4-Methoxyphenylmagnesium bromide (0.60 mL, 0.5 M in THF, 0.3 mmol, 1.2 equiv) was added dropwise to sulfonimidoyl fluoride **(*R*)-28** (45 mg, 0.25 mmol, 1.0 equiv, 96% *ee*) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20–30% EtOAc in pentane) gave the desired sulfoximine **(*S*)-30** as an amorphous solid (23.0 mg, 0.09 mmol, 35%, 97% *ee*) and sulfoximine **(*S*)-S11** as a white solid (9.3 mg, 0.026 mmol, 11%, 97% *ee*).



(*S*)-30: R_f 0.18 (25% EtOAc in pentane). IR (film)/cm^{-1} 2969, 2930, 2868, 1632, 1593, 1498, 1477, 1391, 1287, 1260, 1215, 1170, 1100, 1026, 992, 837, 527, 449. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.0 Hz, 2H, 2 × Ar–H), 7.04 (d, *J* = 9.0 Hz, 2H, 2 × Ar–H), 3.87 (s, 3H, OCH_3), 3.30 (s, 3H, SCH_3), 1.21 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7 (C=O), 163.9 (Ar–C_q), 130.4 (Ar–C_q), 129.3 (2 × Ar–C), 115.0 (2 × Ar–C), 55.9 (OCH_3), 44.6 (SCH_3), 41.6 ($C(CH_3)_3$), 27.8 ($C(CH_3)_3$). HRMS (ESI) m/z cald for $C_{13}H_{20}NO_3S$ $[M+H]^+$: 270.1164; Found: 270.1166. $[\alpha]^{21}_D$ = 0 (c 0.7, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention time: 21 min.

(*S*)-*N*-((3,3-Dimethyl-2-oxobutyl)(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)pivalamide, (*S*)-S11:



mp = 117–119 ºC. R_f 0.23 (25% EtOAc in pentane). IR (film)/cm^{-1} 2969, 2930, 2870, 1713, 1632, 1593, 1498, 1477, 1289, 1262, 1209, 1170, 1099, 1027, 835, 540. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 9.0 Hz, 2H, 2 × Ar–H), 7.03 (d, *J* = 9.0 Hz, 2H, 2 × Ar–H), 4.92 (d, *J* = 15.6 Hz, 1H, SC*H*H), 4.81 (d, *J* = 15.6 Hz, 1H, SCH*H*), 3.88 (s, 3H, OCH_3), 1.24 (s, 9H, $C(CH_3)_3$), 1.07 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2 (C=O), 189.3 (C=O), 164.5 (Ar–C_q), 131.5 (2 × Ar–C), 129.2 (Ar–C_q), 114.8 (2 × Ar–C), 59.4 (SCH_2), 56.2 (OCH_3), 45.7 ($C(CH_3)_3$), 42.2 ($C(CH_3)_3$), 28.1 ($C(CH_3)_3$), 26.2 ($C(CH_3)_3$). HRMS (ESI) m/z cald for $C_{18}H_{28}NO_4S$ $[M+H]^+$: 354.1746; Found: 354.1750. $[\alpha]^{21}_D$ = −12 (c 0.5, $CHCl_3$). HPLC Conditions: Chiralpak IA column, 98:2 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 270 nm. Retention time: 40 min.

(*rac*)-30 and (*rac*)-S11: For chiral HPLC analysis, the racemic samples were generated in a similar manner. The above experimental procedure was carried out on **(*rac*)-28** (45 mg, 0.25 mmol) to give **(*rac*)-30** (23.3 g, 35%) and **(*rac*)-S11** (12.9 mg, 15%). The analytical data (^{1}H and ^{13}C NMR) was identical to that shown for **(*S*)-30** and **(*S*)-S11** above.

(*rac*)-30 HPLC conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm. Retention times: 21 & 30 min.
(*rac*)-S11 HPLC conditions: Chiralpak IA column, 98:2 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 270 nm. Retention times: 40 & 44 min.

With R_2CuMgBr: (4-Methoxyphenyl)magnesium bromide (4 mL, 0.5 M in THF) was added dropwise to a stirred solution of CuI (191 mg, 1.0 mmol) in THF (1 mL, 0.2 M) at –78 °C. The resulting mixture was stirred at –78 °C for 1 h. An aliquot (1.5 mL, 0.3 mmol, 1.2 equiv) of the cuprate reaction mixture was then added dropwise to a stirred solution of sulfonimidoyl fluoride **(*R*)-28** (45 mg, 0.25 mmol, 1.0 equiv, 96% *ee*) in Et_2O (0.83 mL, 0.3 M) at 0 ºC and stirred, warming to rt, for 3 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give the crude product. Purification *via* column chromatography (20-30% EtOAc in pentane) gave the desired sulfoximine **(*S*)-30** as an amorphous solid (34.1 mg, 0.13 mmol, 51%, 97% *ee*).

References

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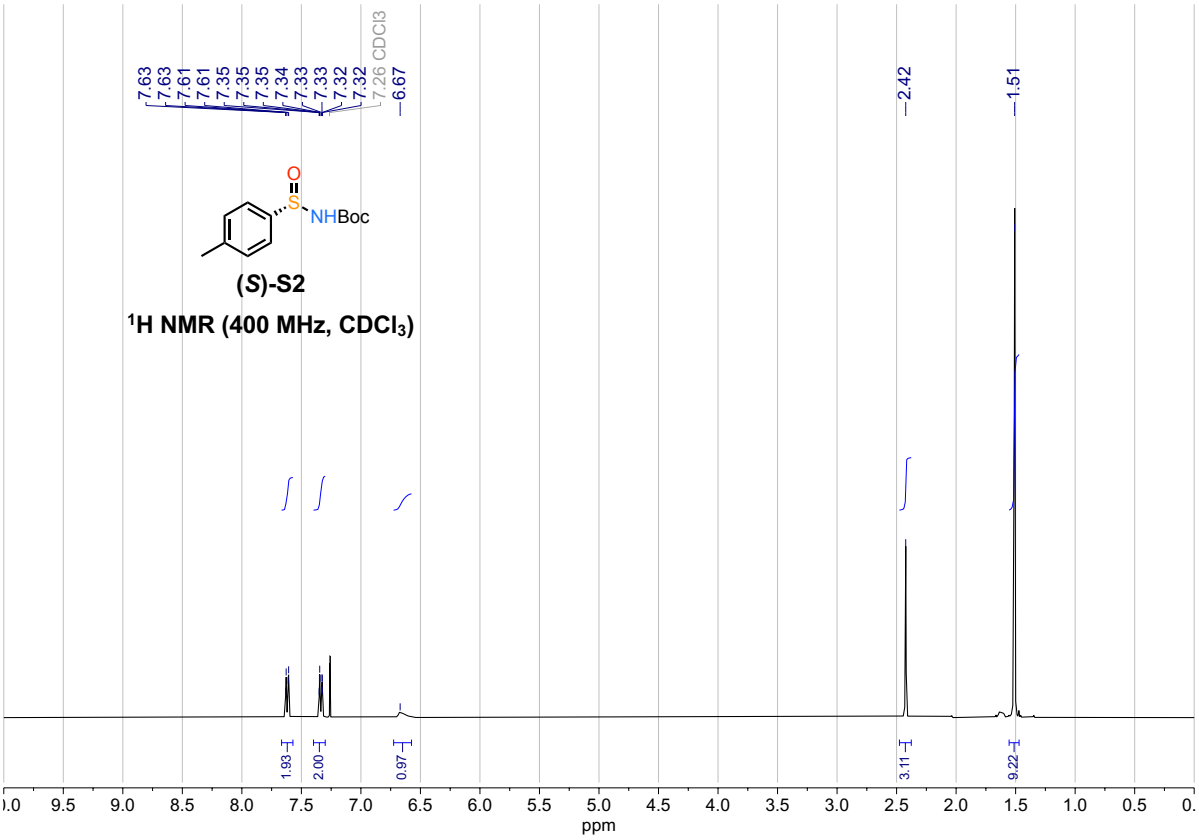
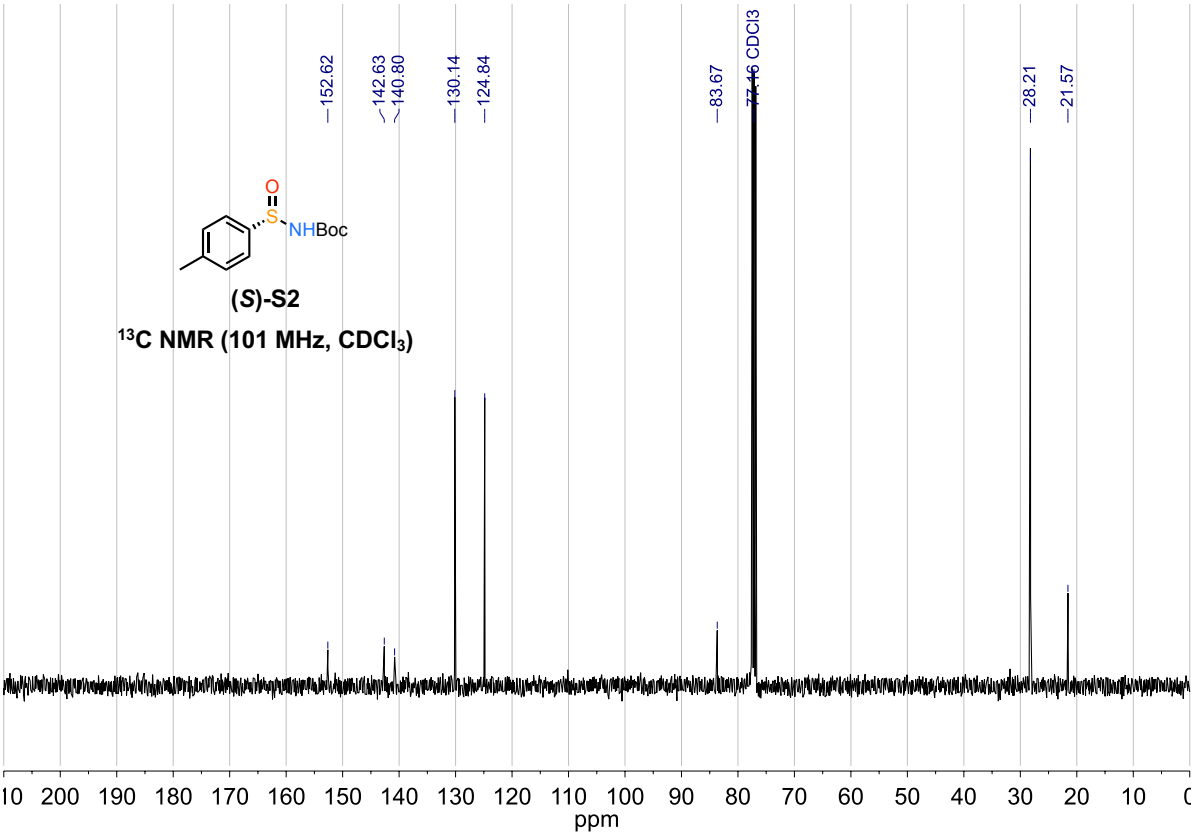
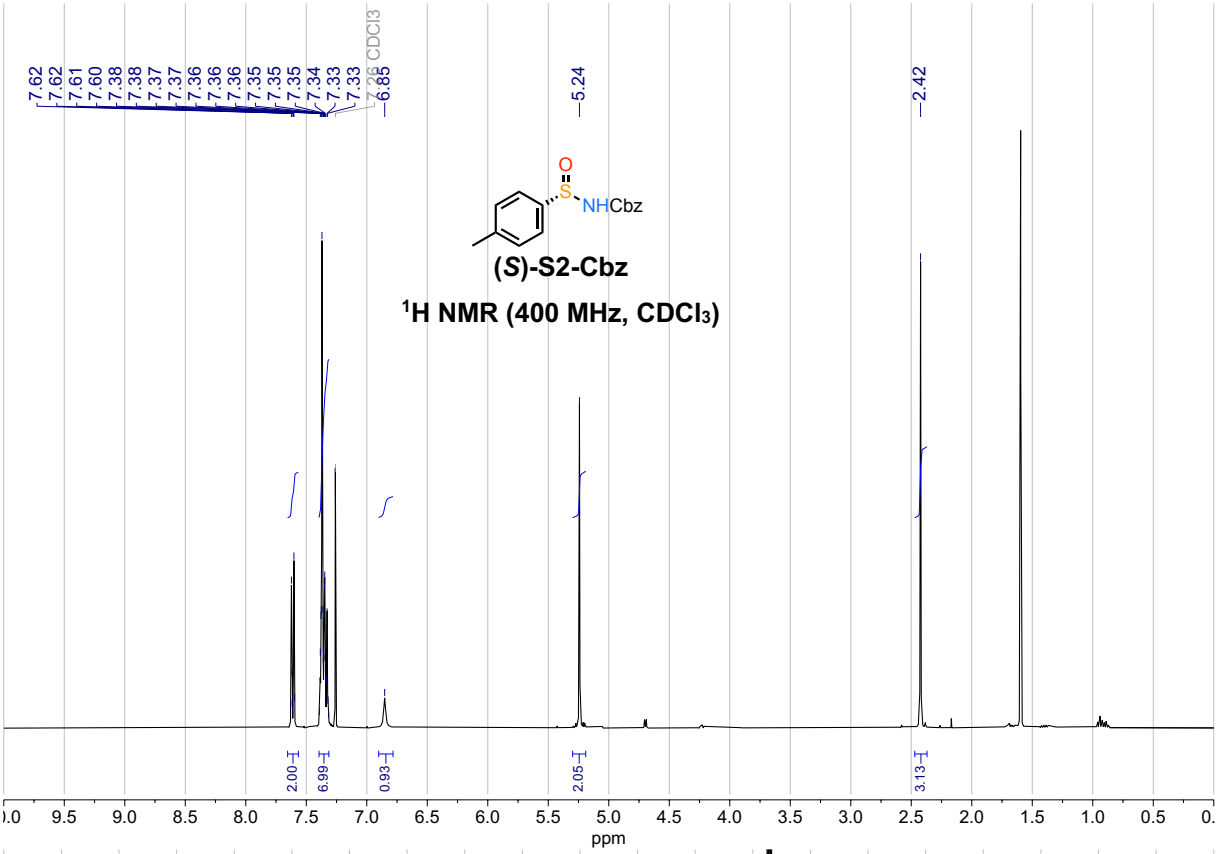
^{1}H and ^{13}C NMR Spectra

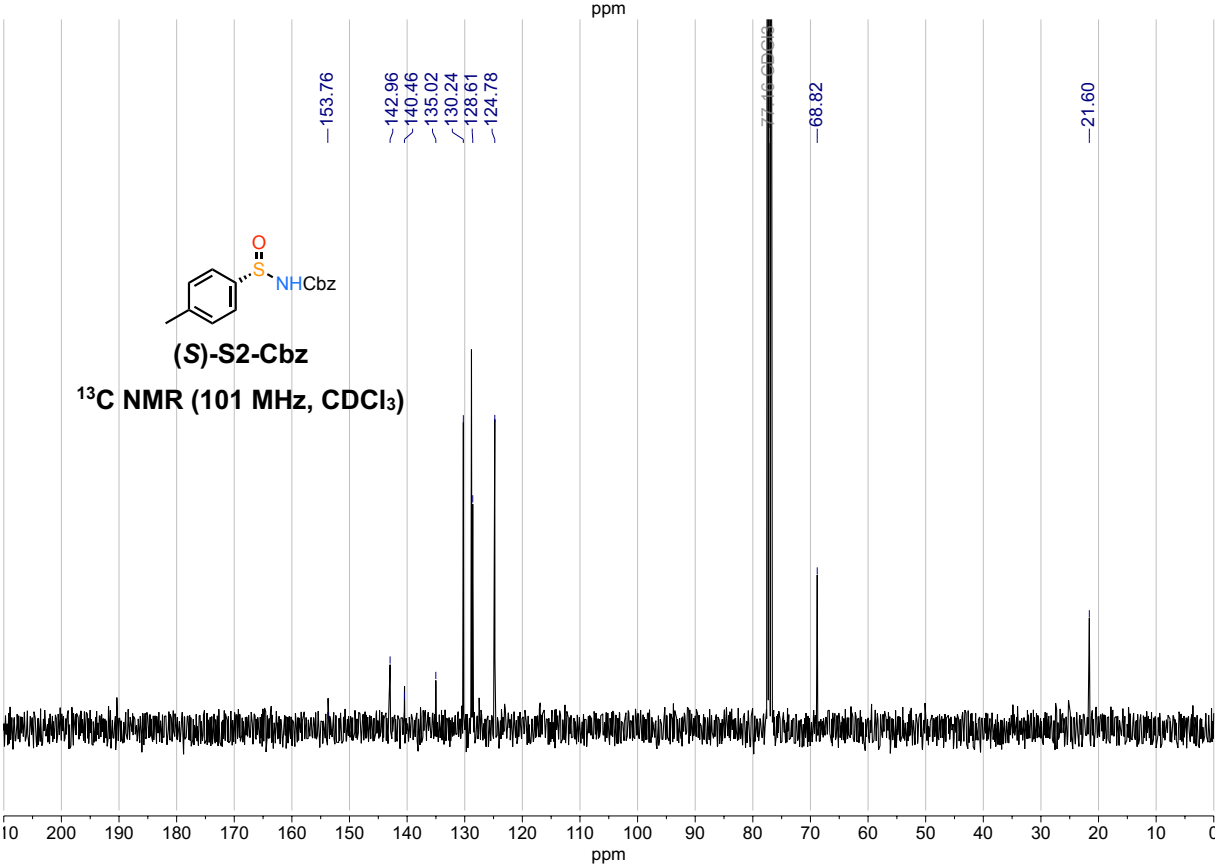
***tert*-Butyl (*p*-tolylsulfinyl)carbamate ((*S*)-S2)**



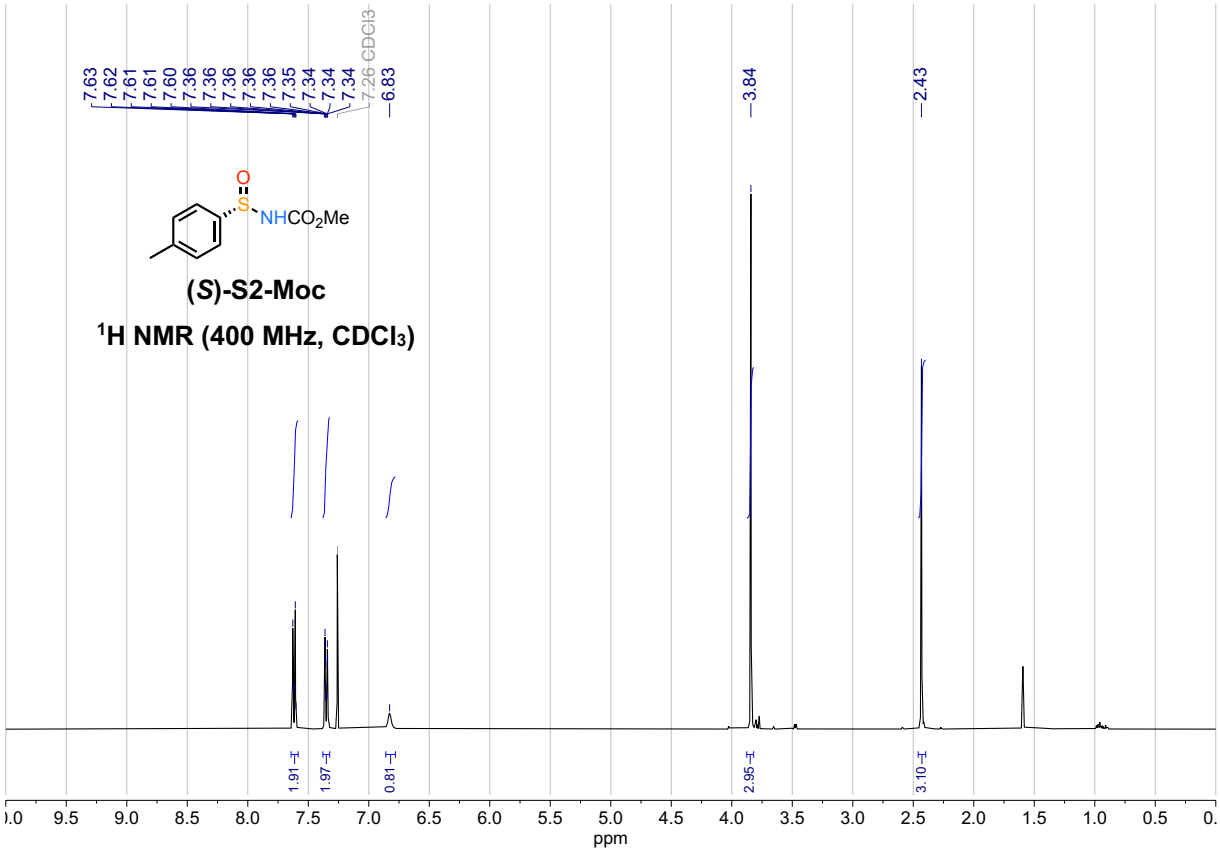


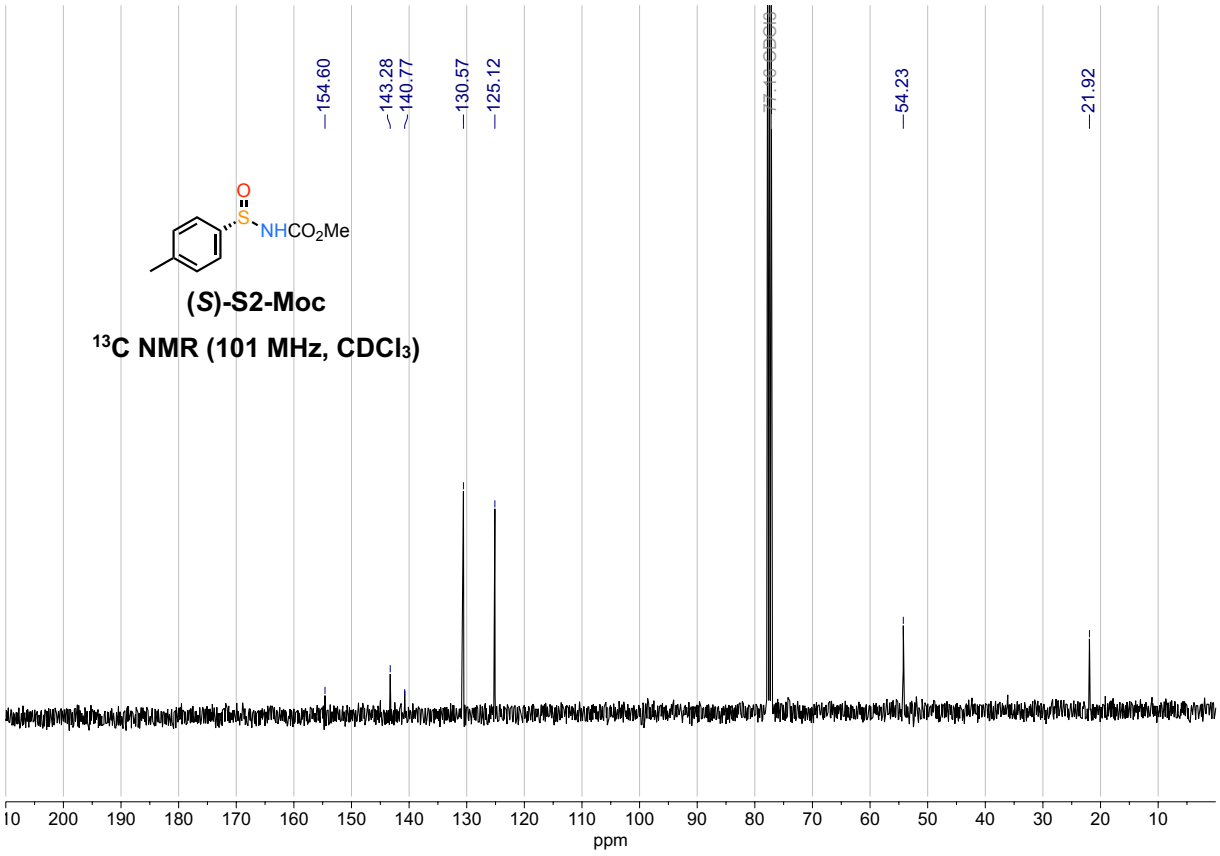
Benzyl (*S*)-(*p*-tolylsulfinyl)carbamate ((*S*)-S2-Cbz)



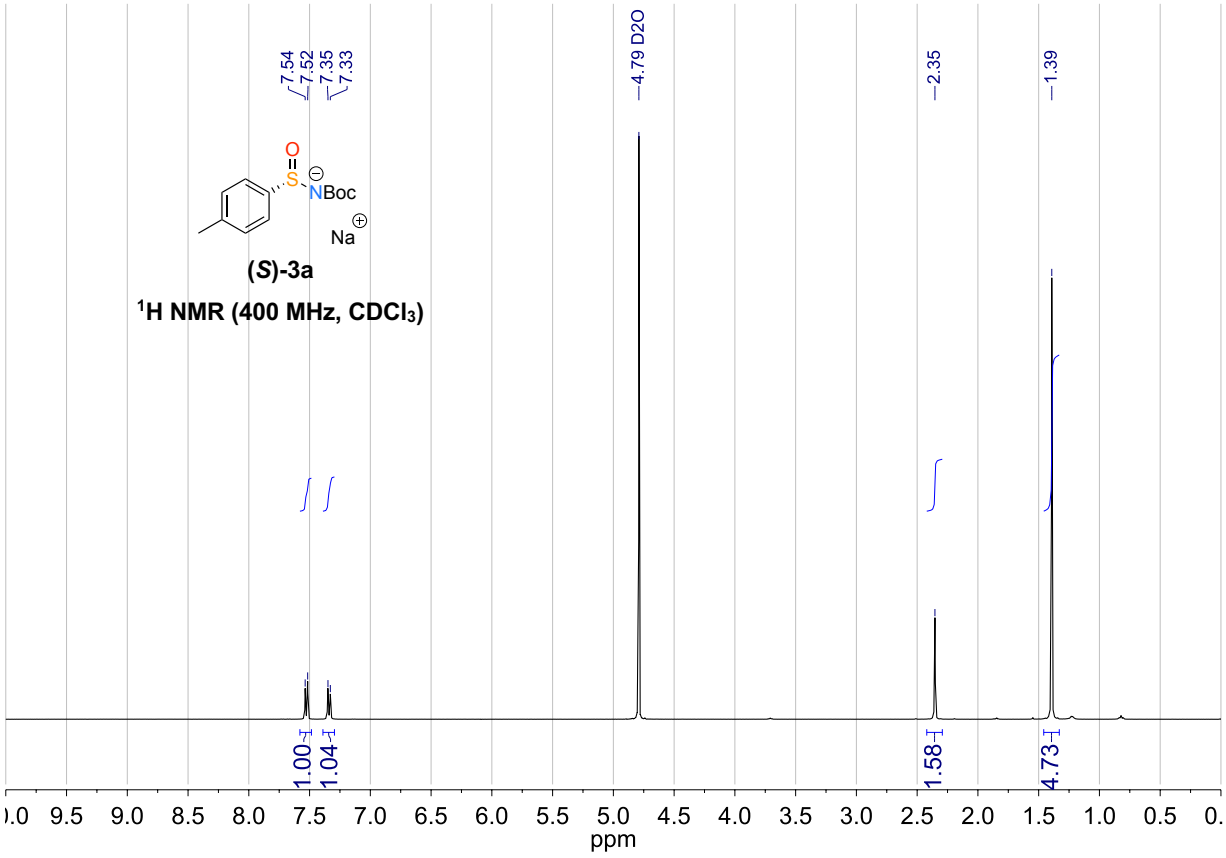


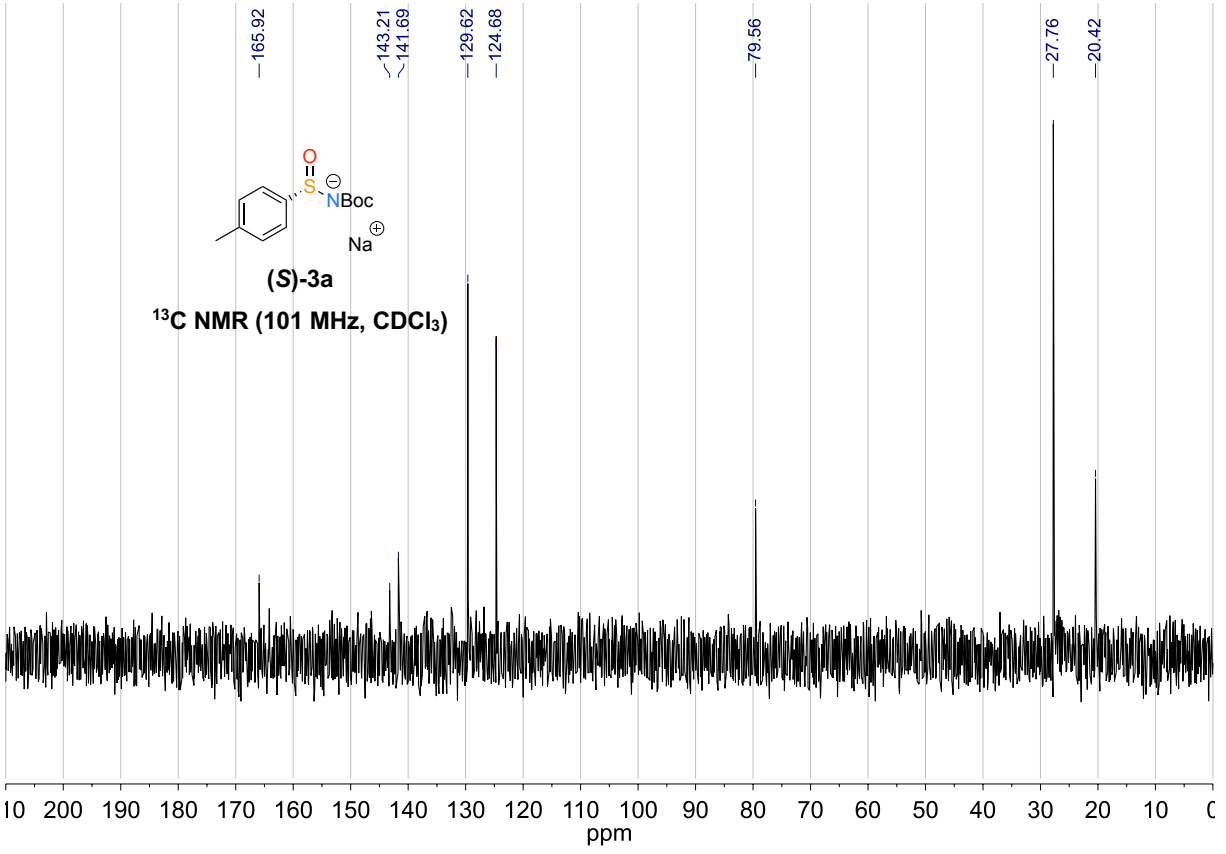
Methyl (*S*)-(*p*-tolylsulfinyl)carbamate ((*S*)-S2-Moc)



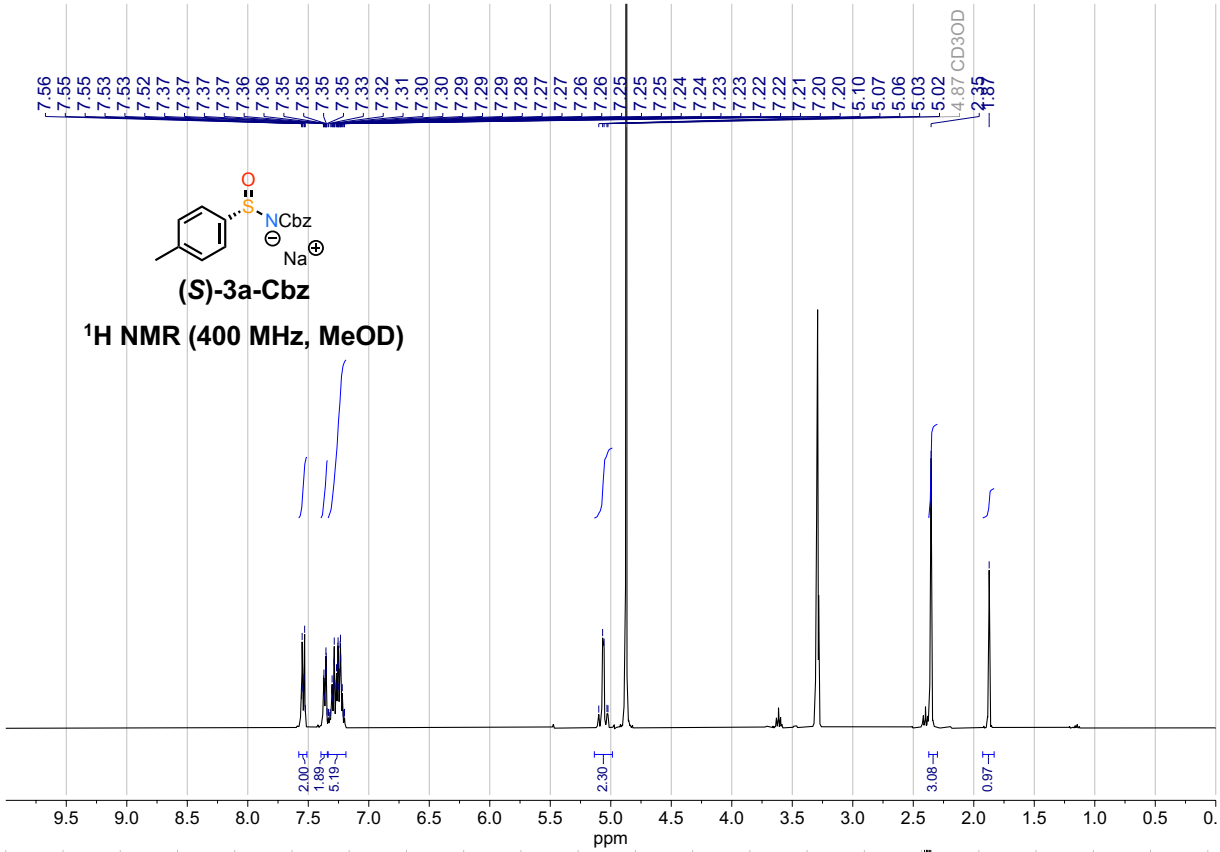


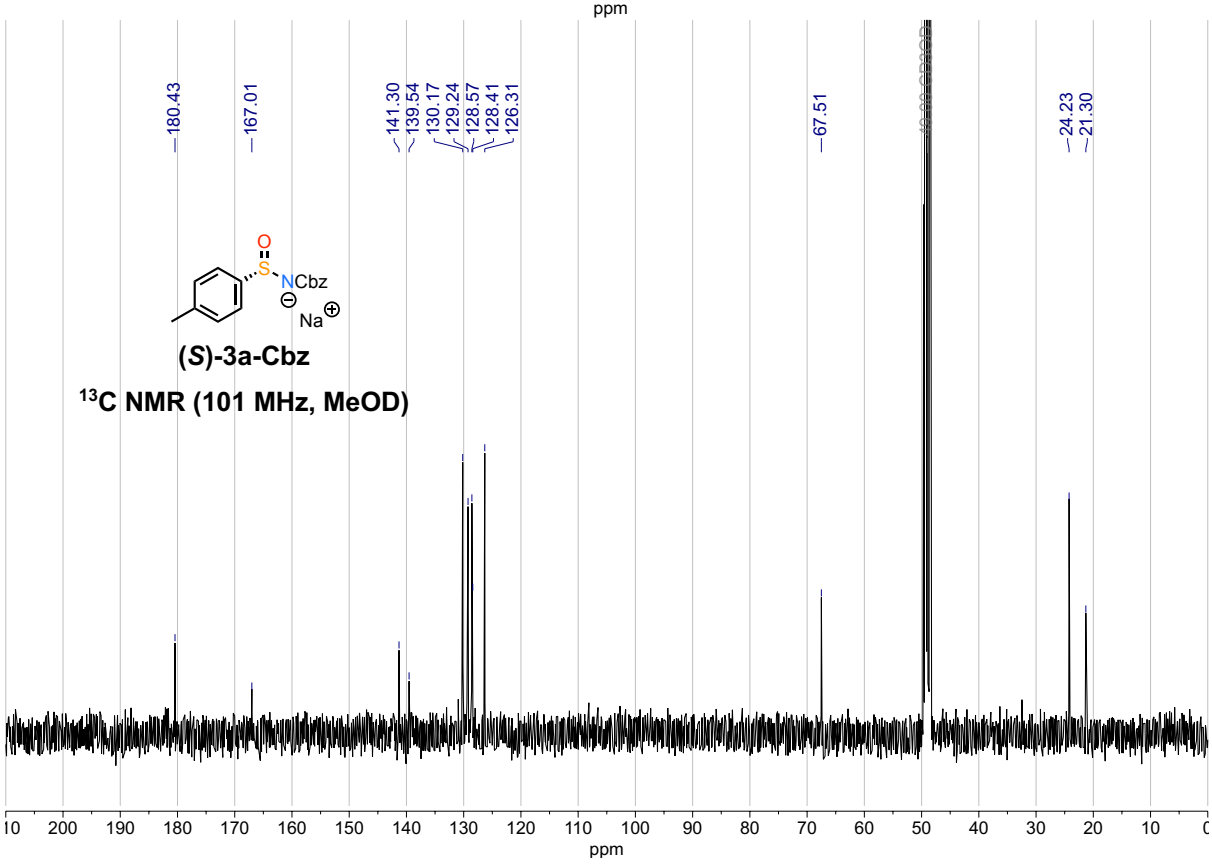
Sodium (*tert*-butoxycarbonyl)(*p*-tolylsulfinyl)amide ((*S*)-3a)



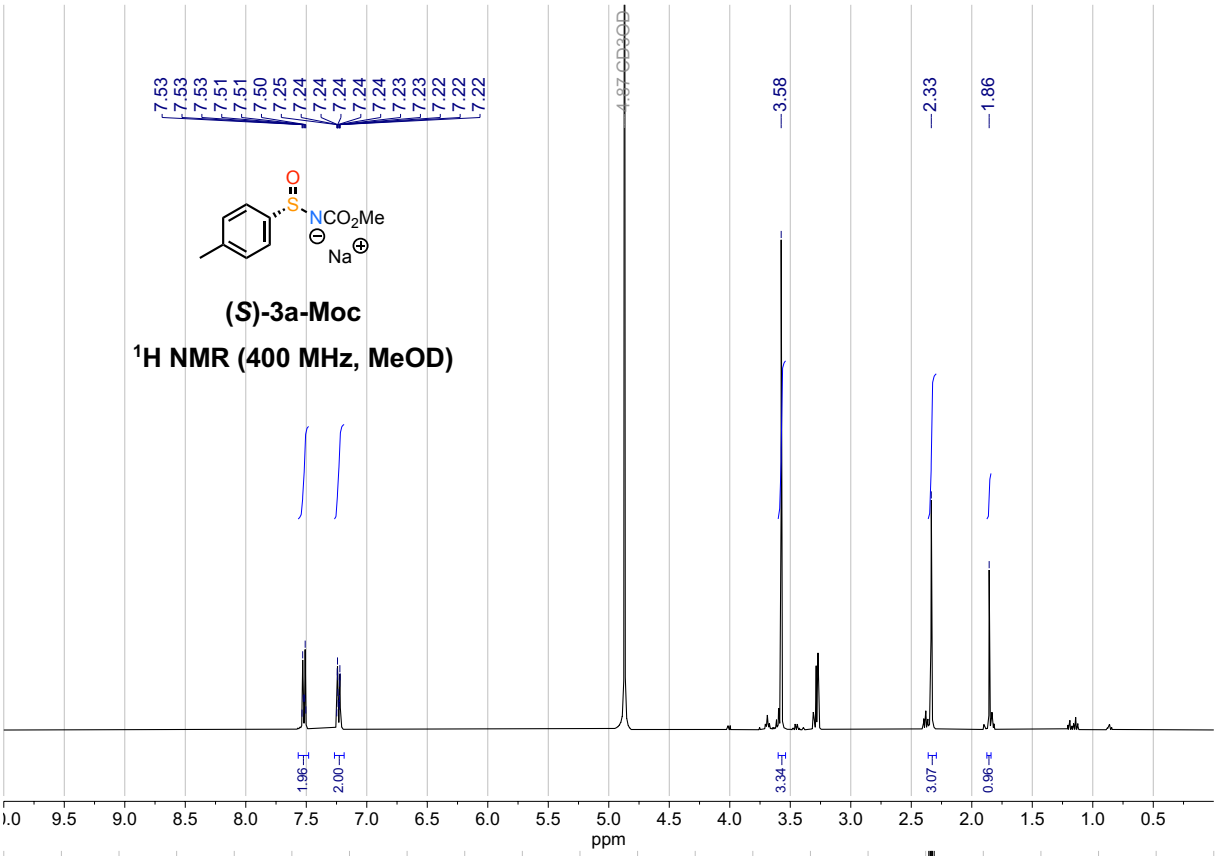


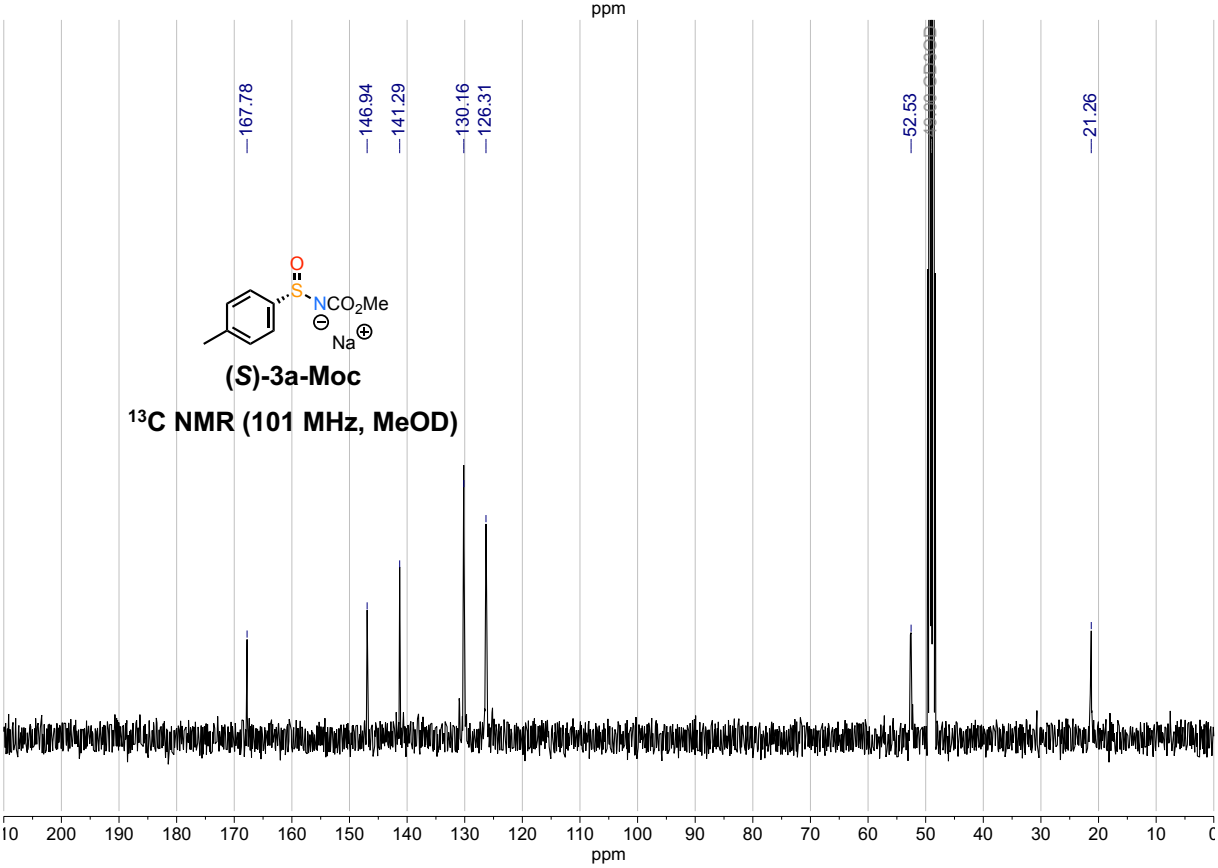
(*S*)-((Benzyloxy)carbonyl)(*p*-tolylsulfinyl)amide ((*S*)-3a-Cbz)



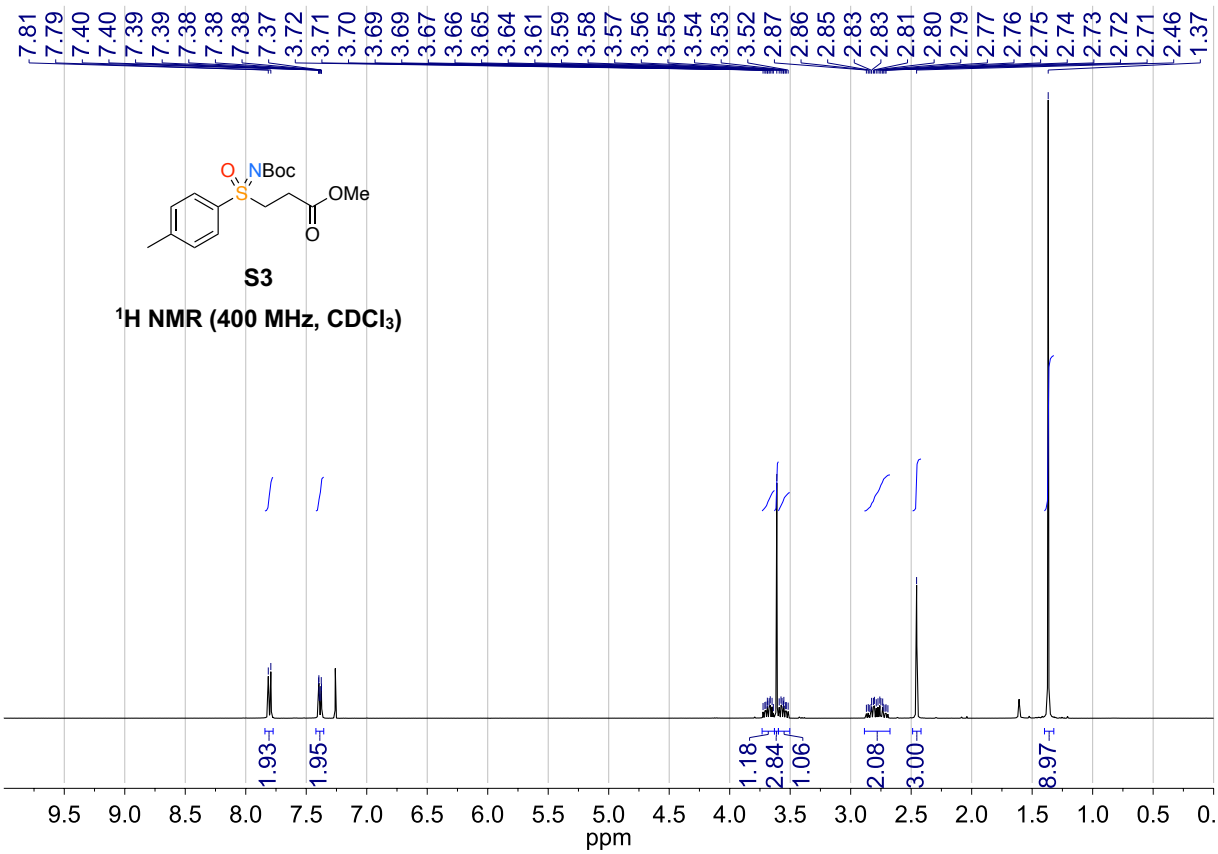


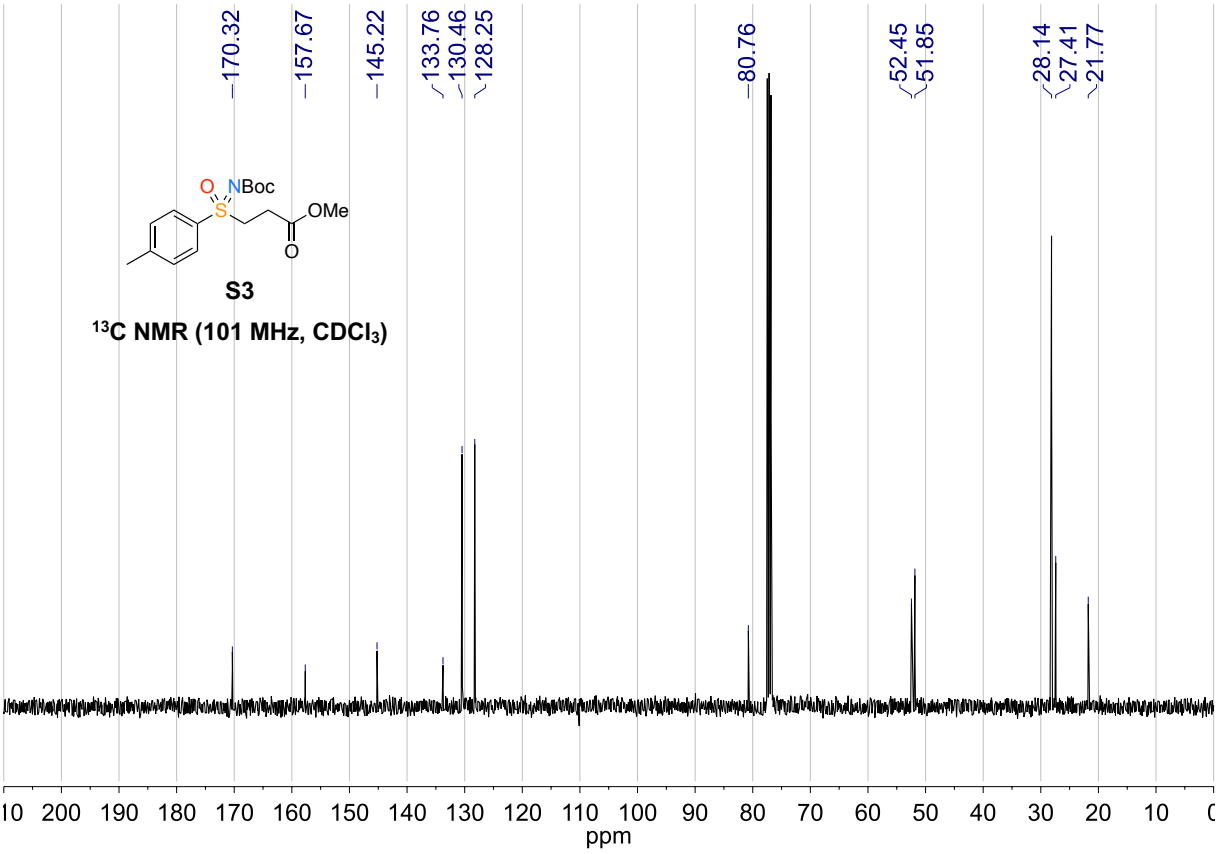
(*S*)-(Methoxycarbonyl)(*p*-tolylsulfinyl)amide ((*S*)-3a-Moc)



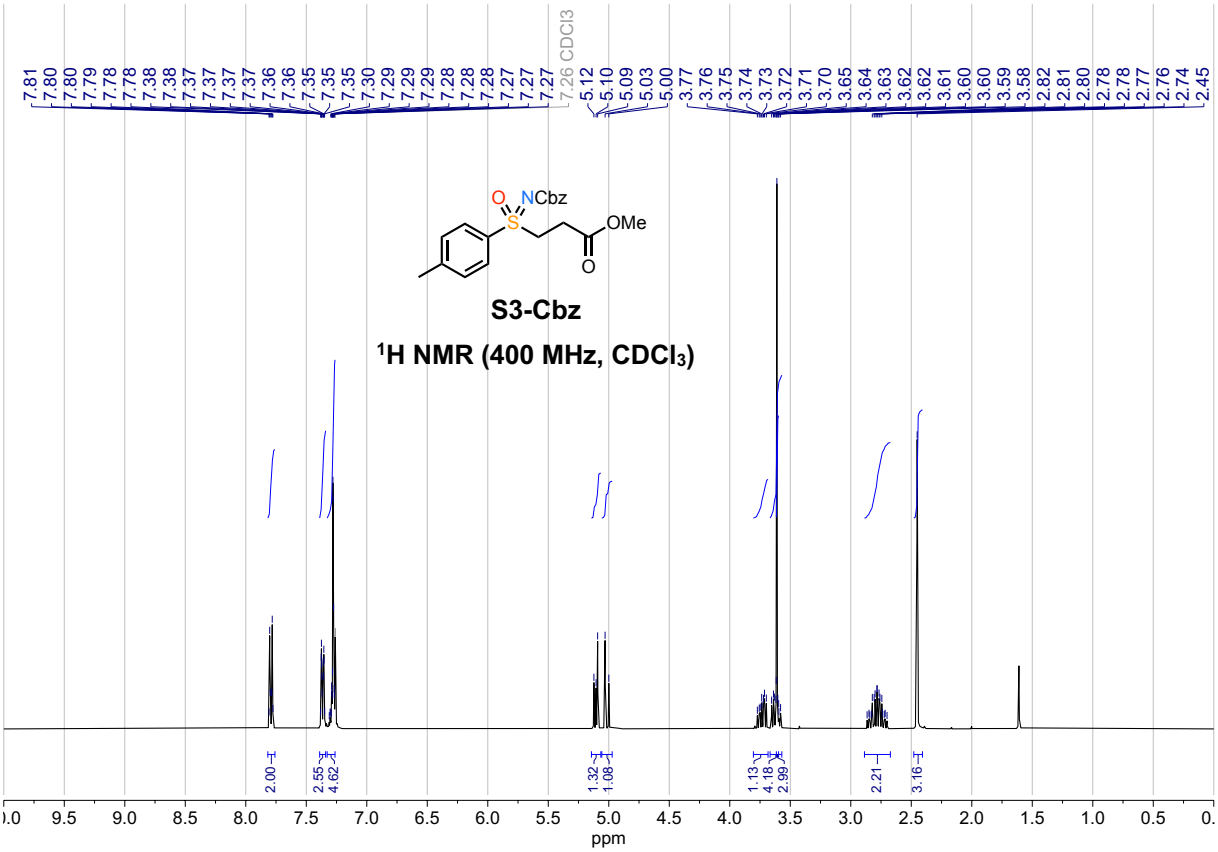


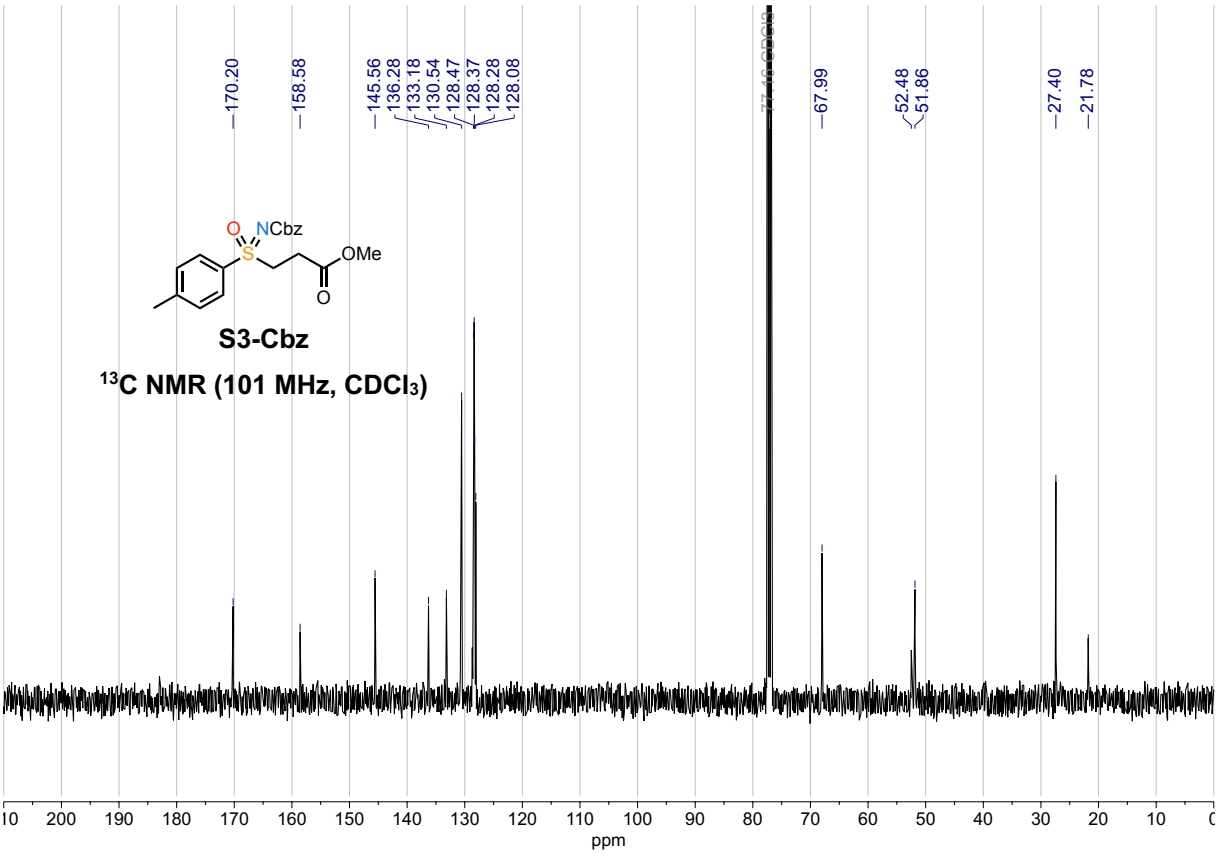
Methyl 3-(N-(*tert*-butoxycarbonyl)-4-methylphenylsulfonimidoyl)propanoate (S3)



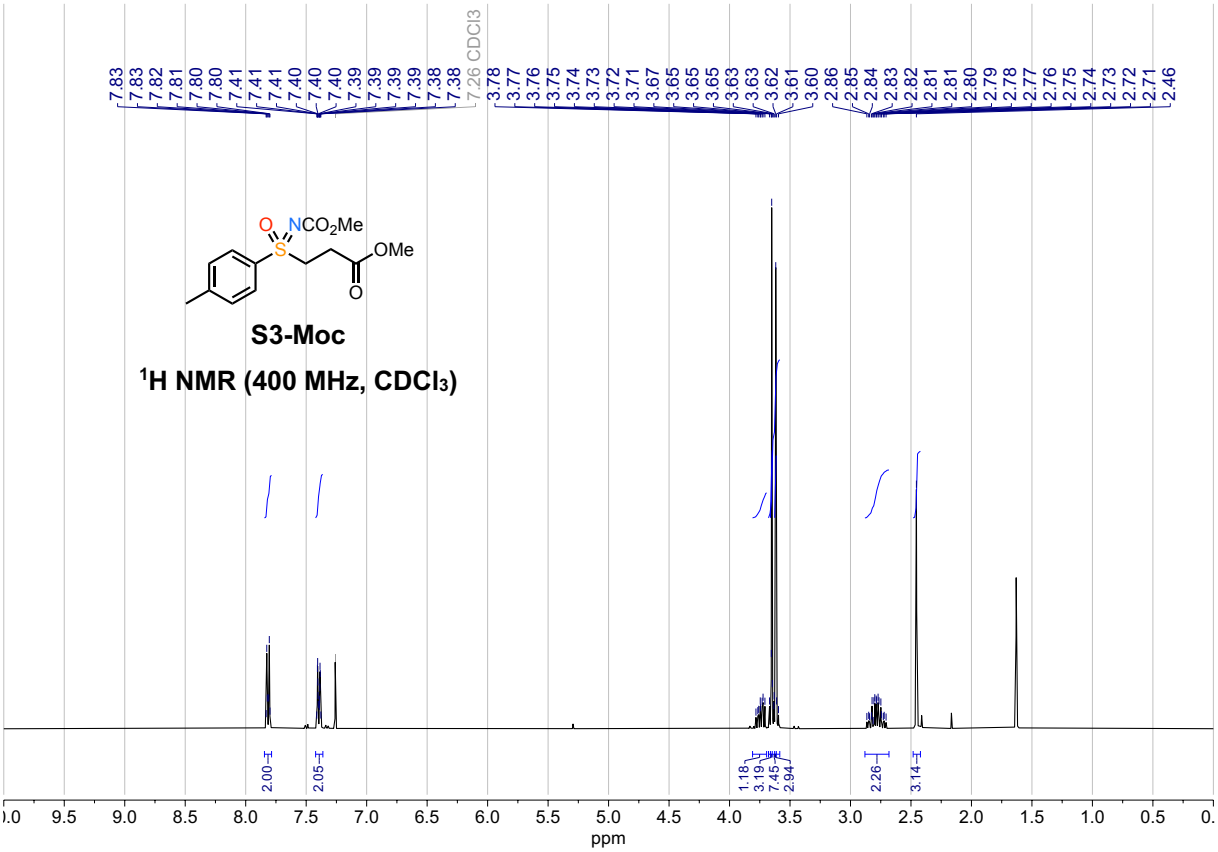


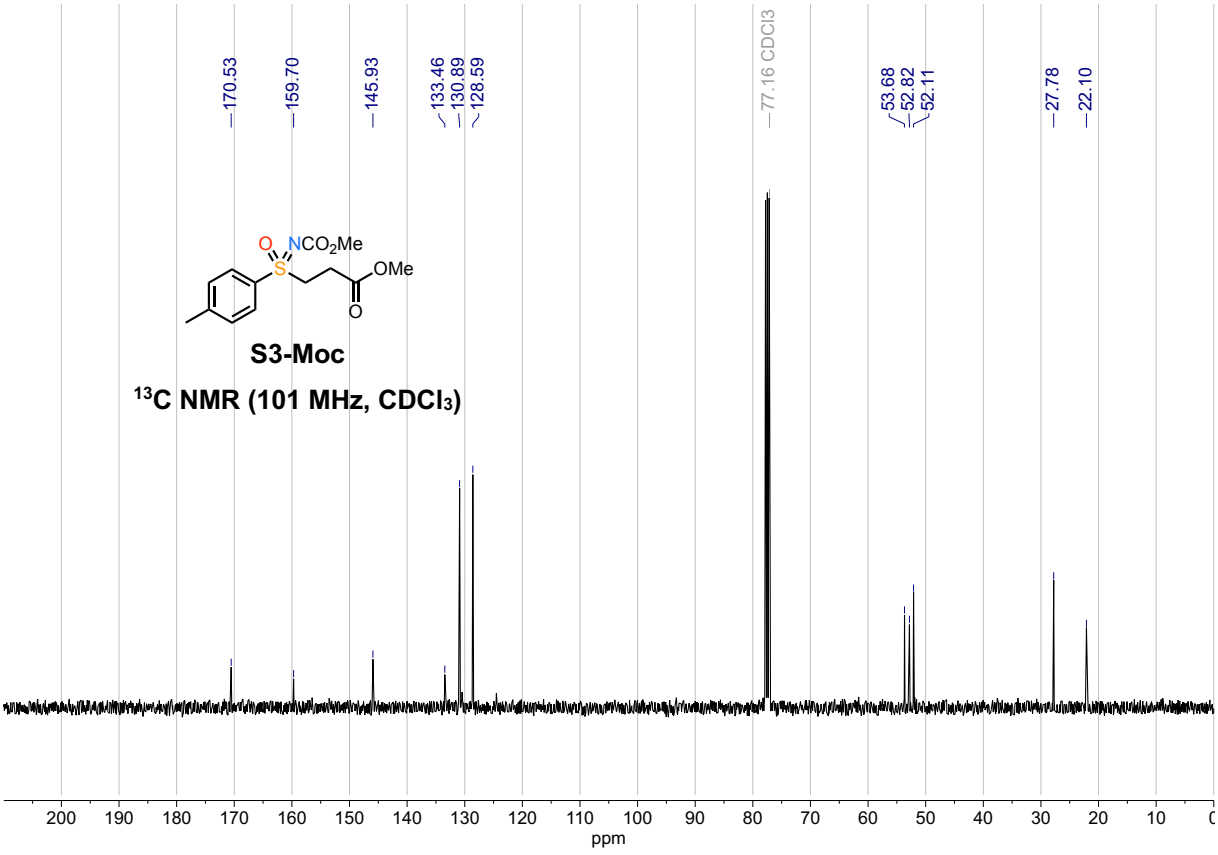
Methyl 3-(*N*-((benzyloxy)carbonyl)-4-methylphenylsulfonimidoyl)propanoate (S3-Cbz)



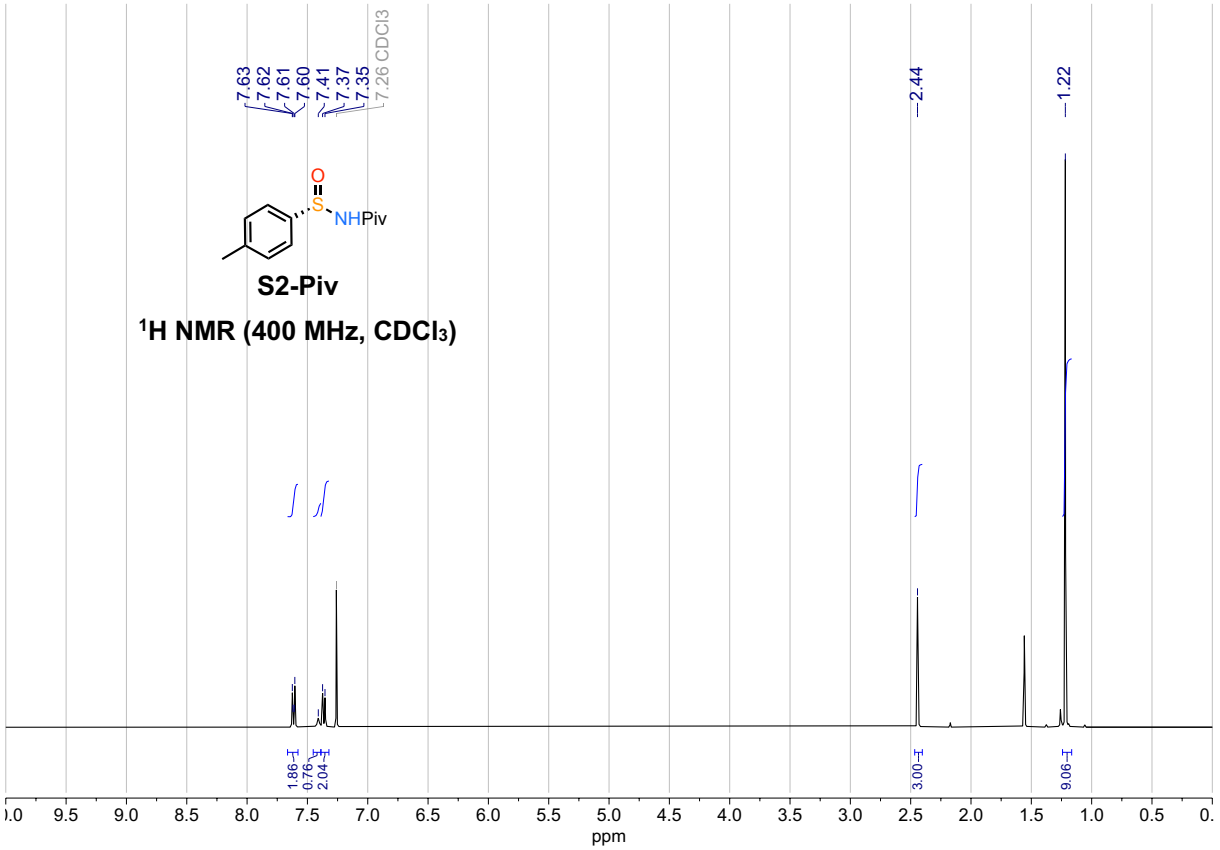


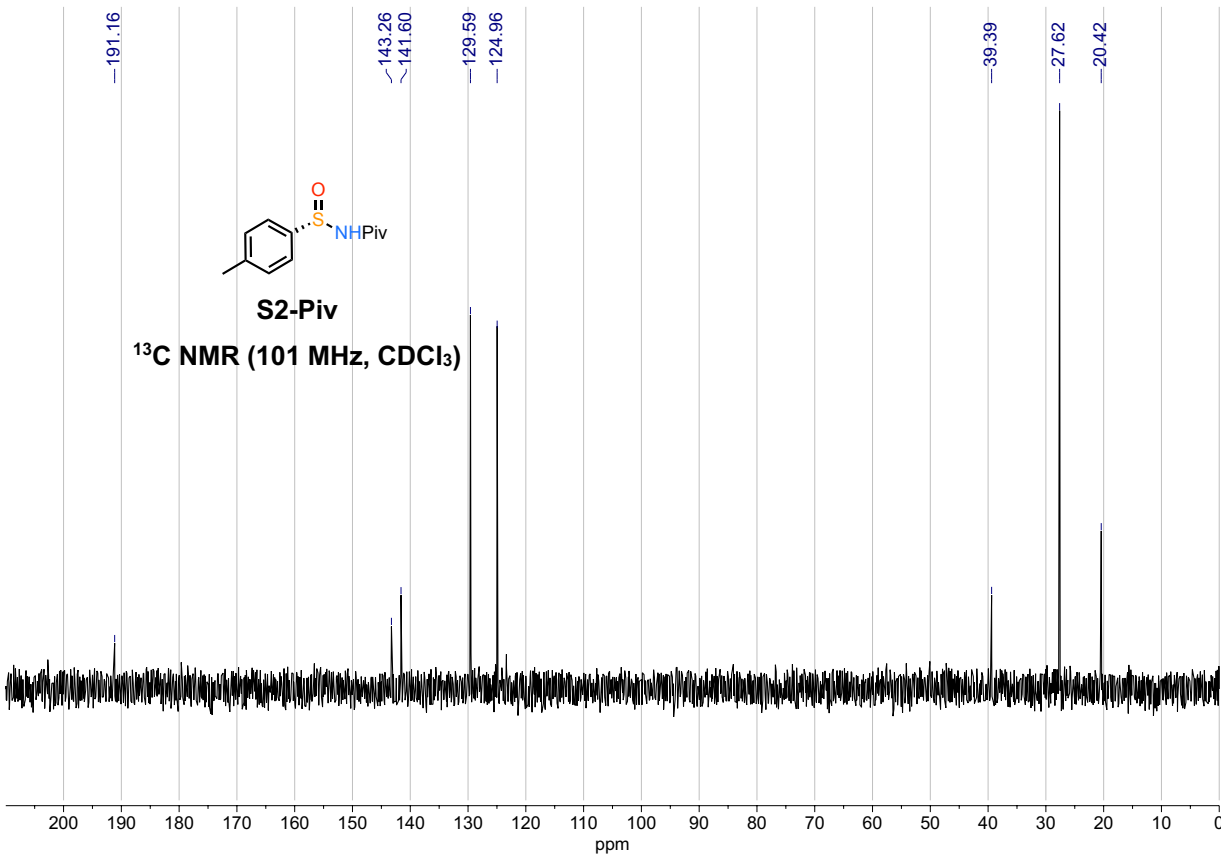
Methyl 3-(*N*-(methoxycarbonyl)-4-methylphenylsulfonimidoyl)propanoate (S3-Moc)



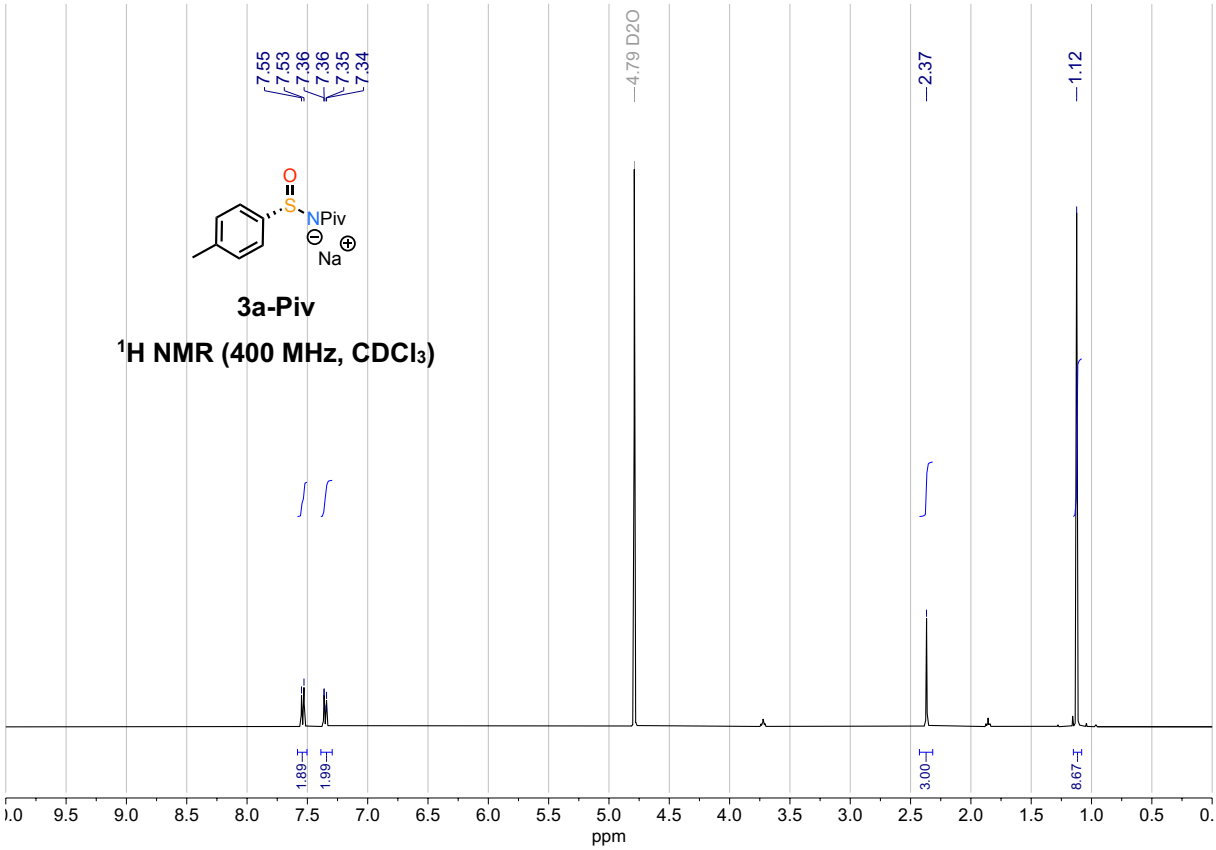


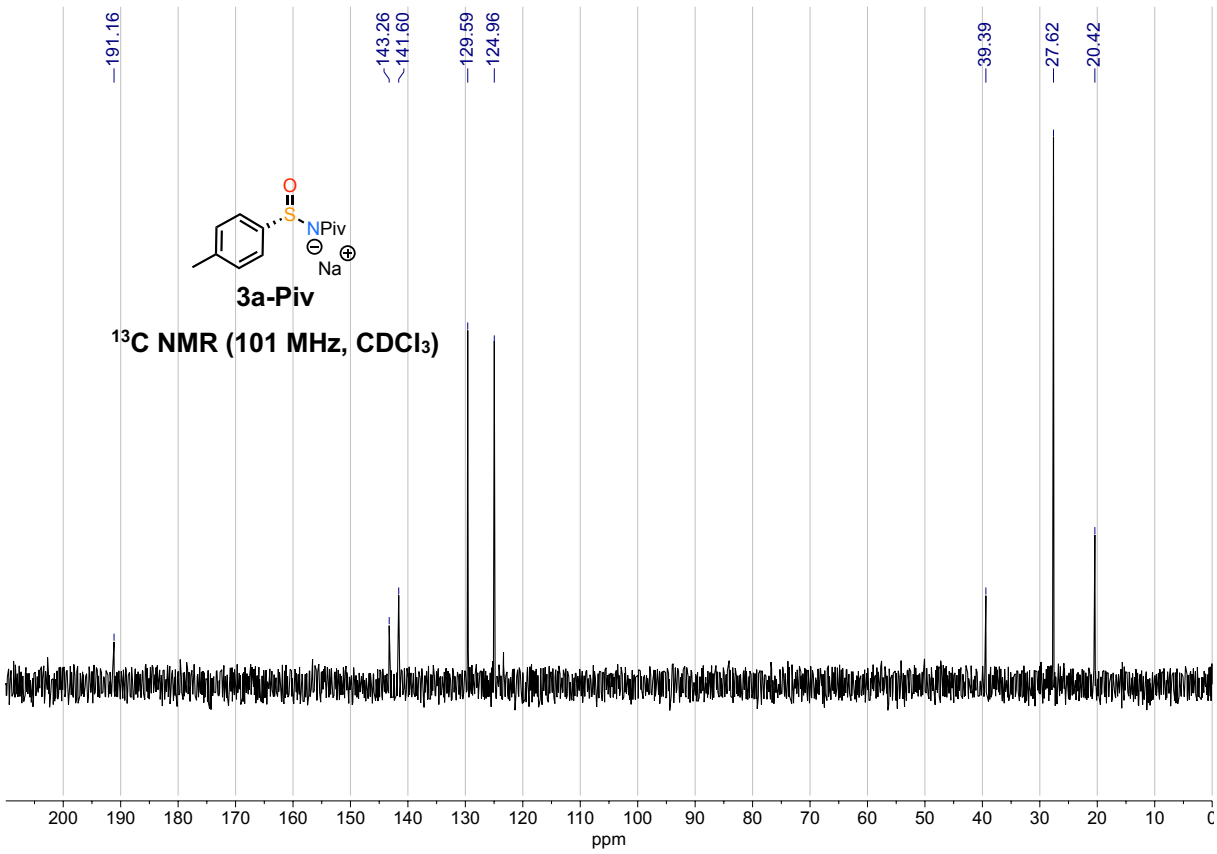
***(S)*-*N*-(*p*-Tolylsulfinyl)pivalamide (S2-Piv)**



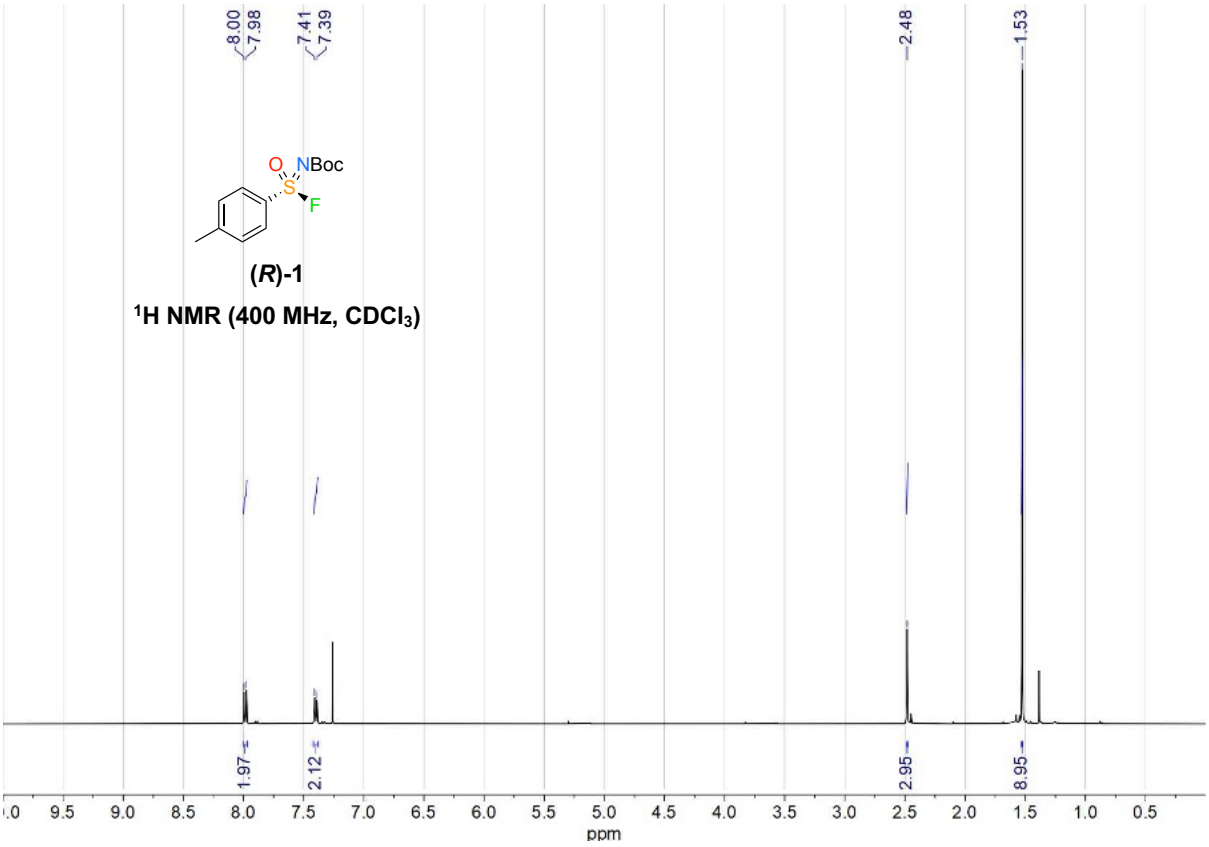


Sodium (*S*)-pivaloyl(*p*-tolylsulfinyl)amide (3a-Piv)



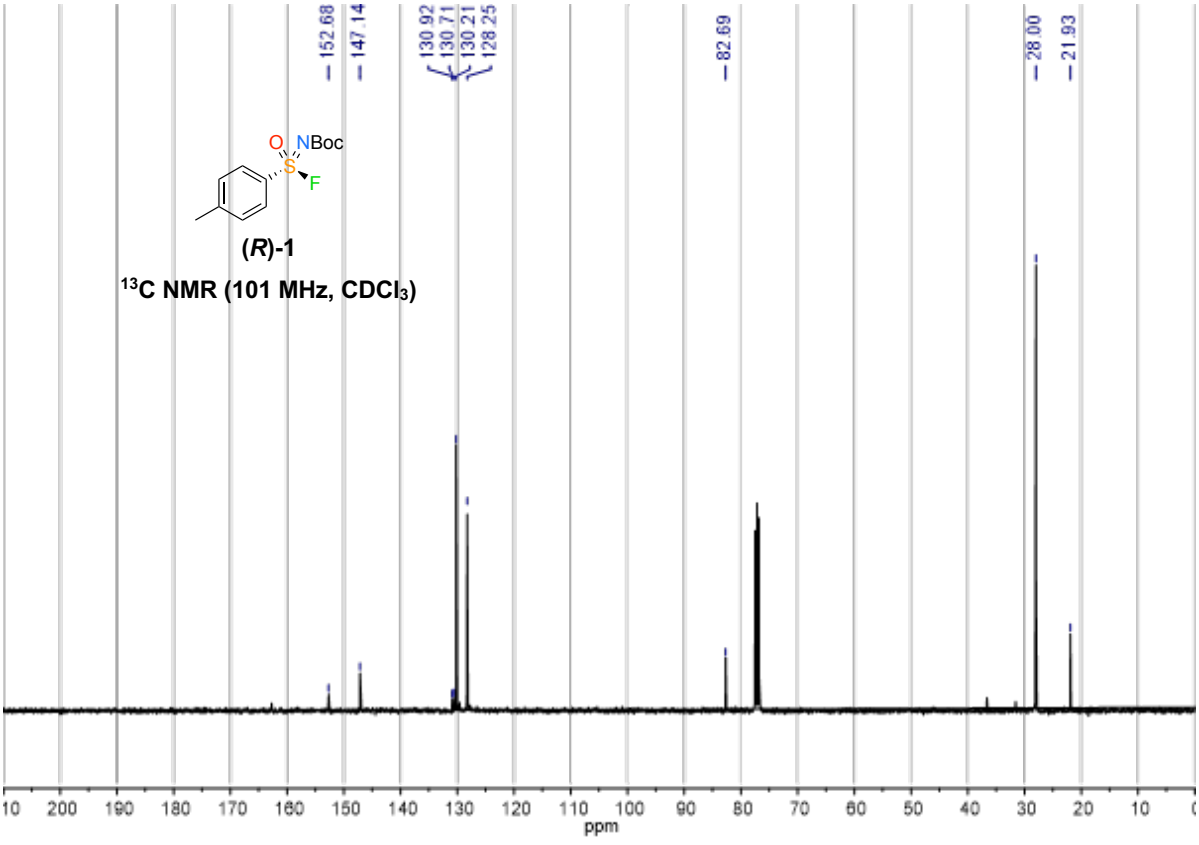


***tert*-Butyl (fluoro(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-1)**



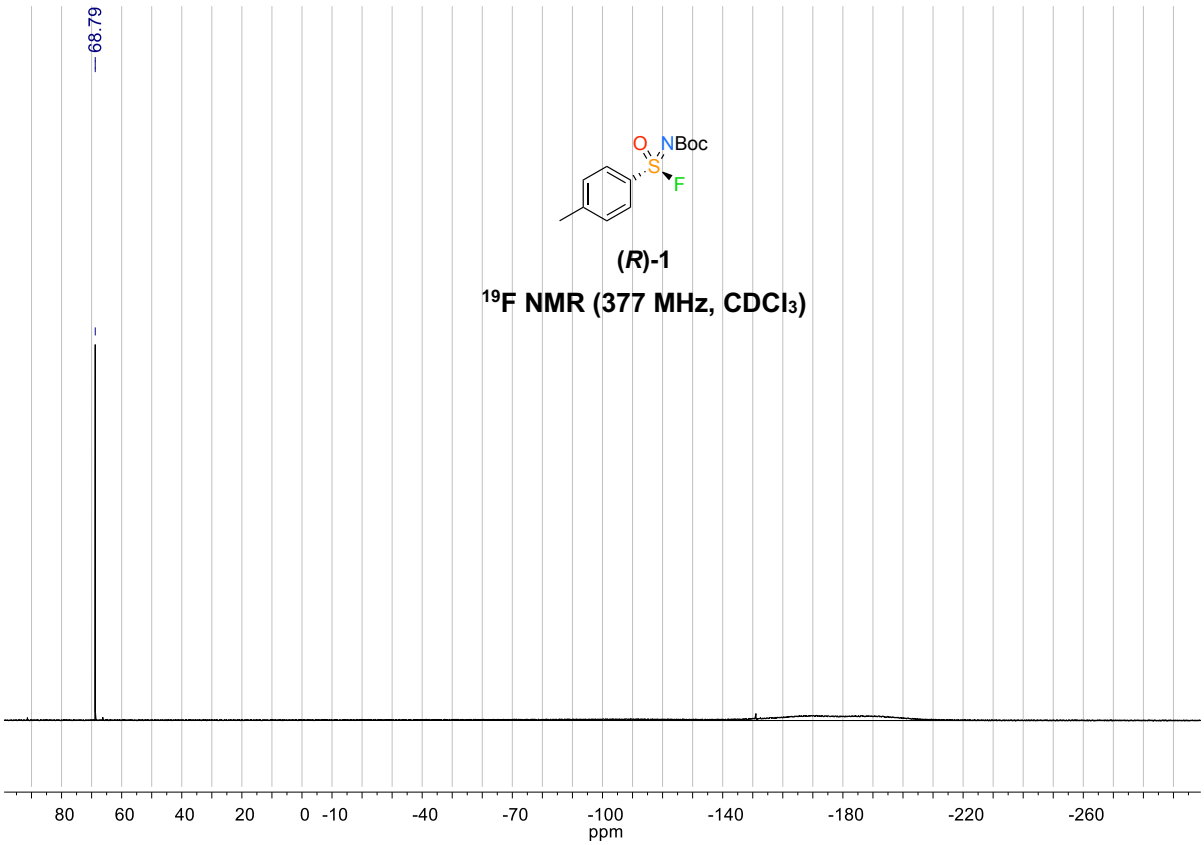
(*R*)-1

^{1}H NMR (400 MHz, $CDCl_3$)



(*R*)-1

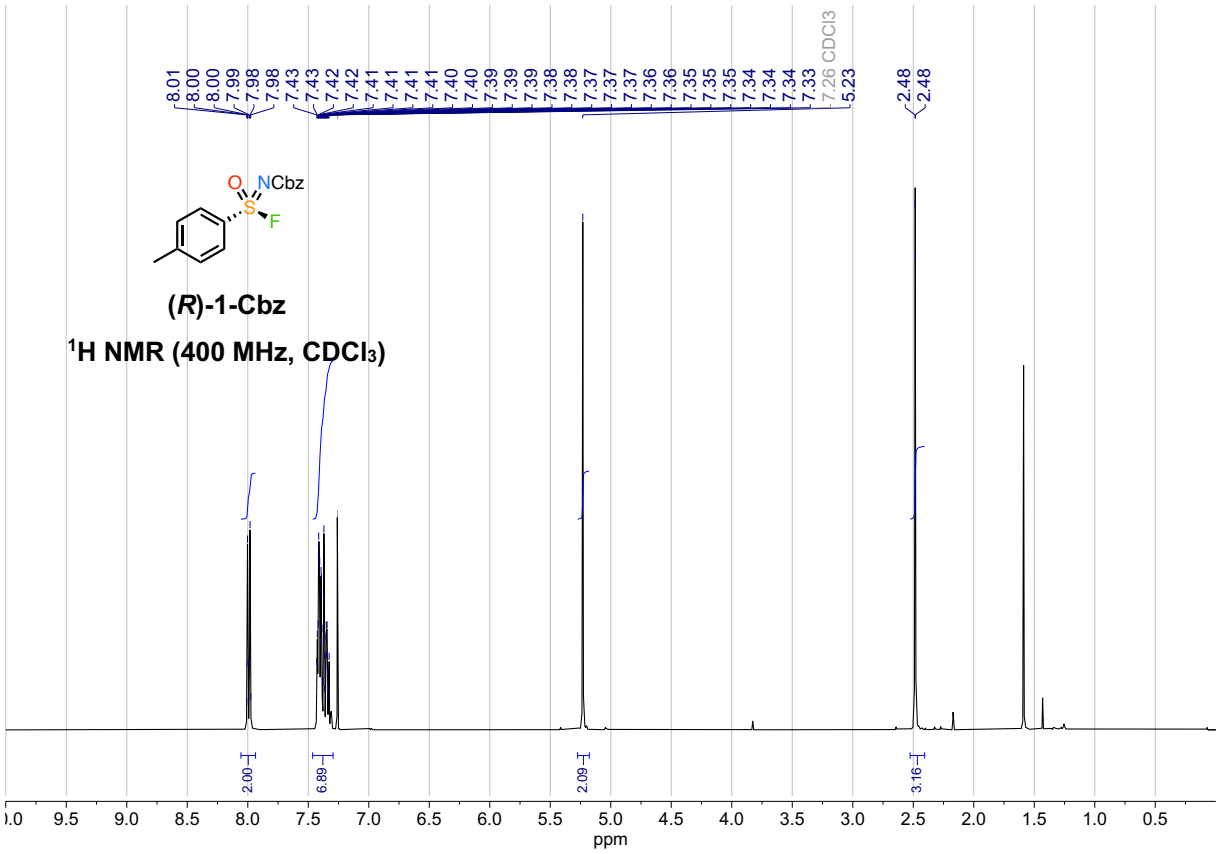
^{13}C NMR (101 MHz, $CDCl_3$)

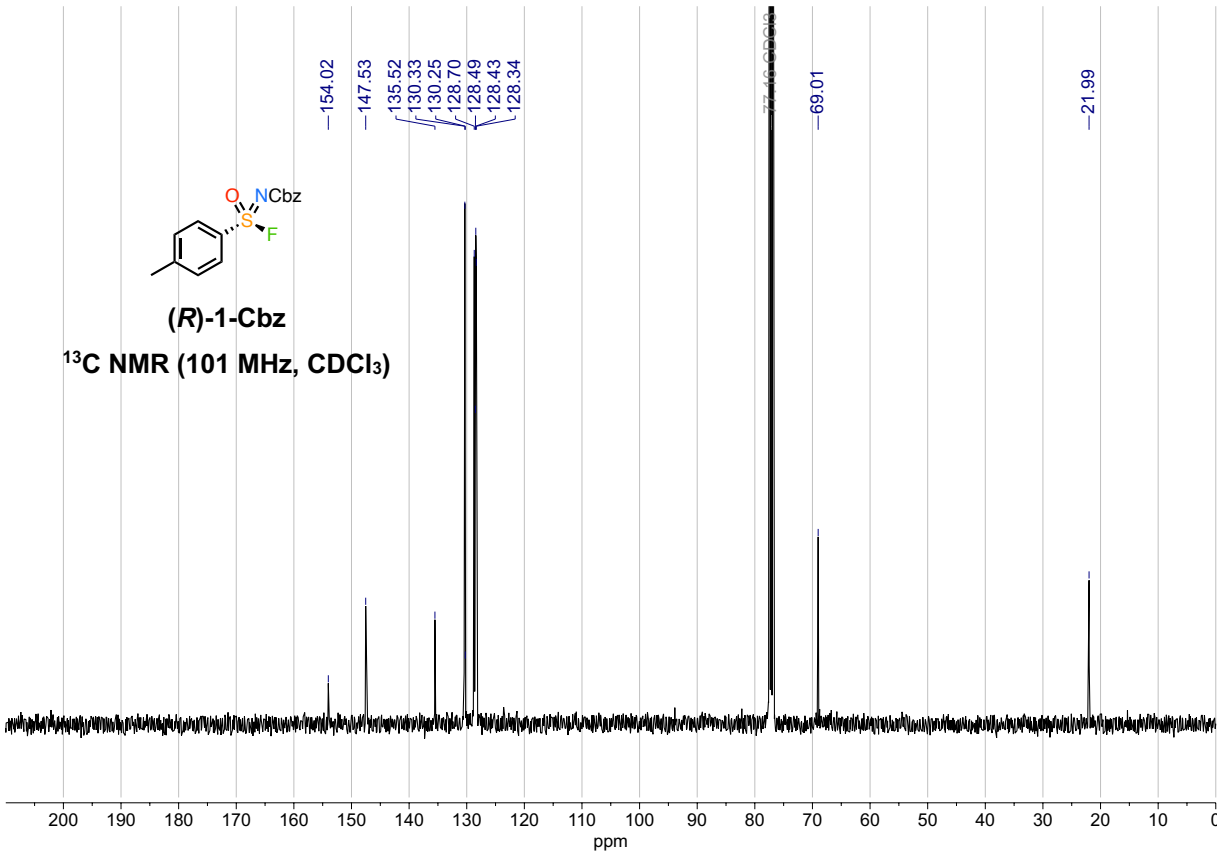


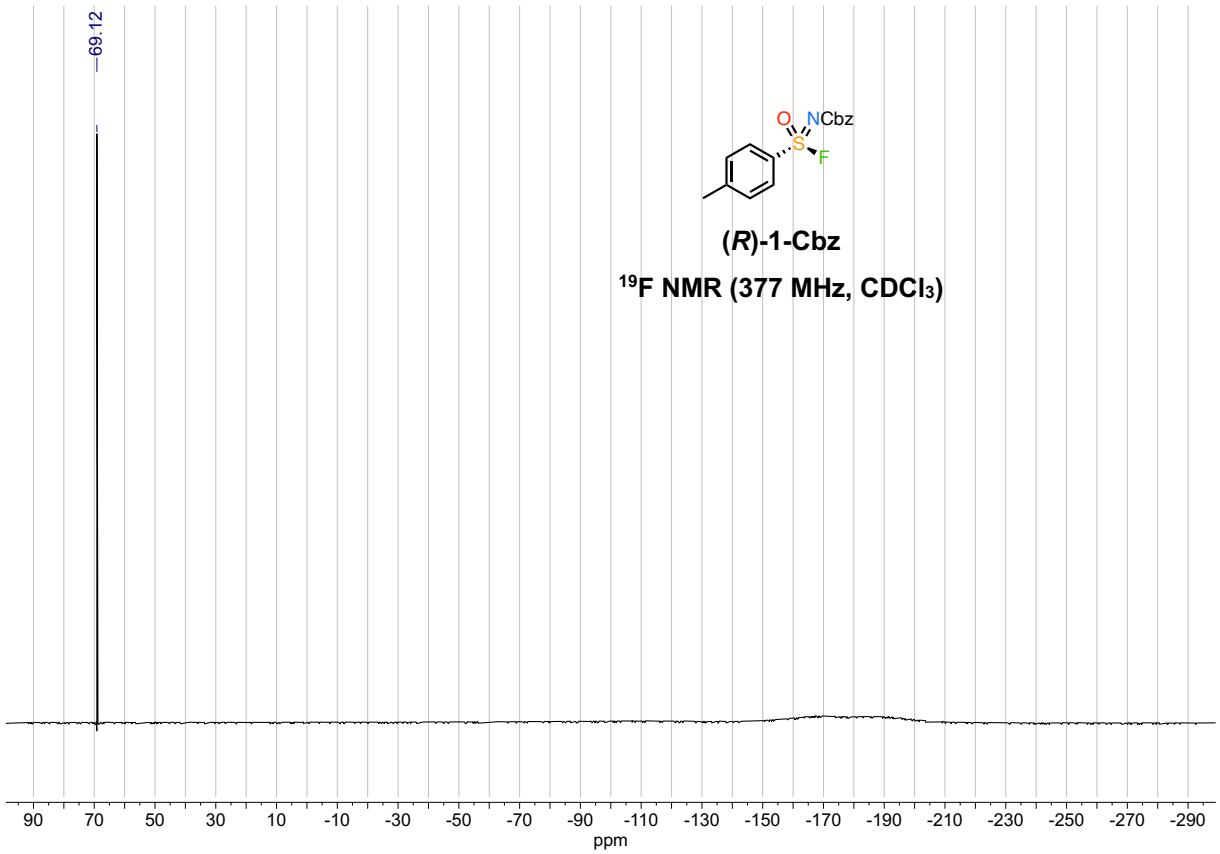
(*R*)-1

^{19}F NMR (377 MHz, $CDCl_3$)

Benzyl (*R*)-(fluoro(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-1-Cbz)



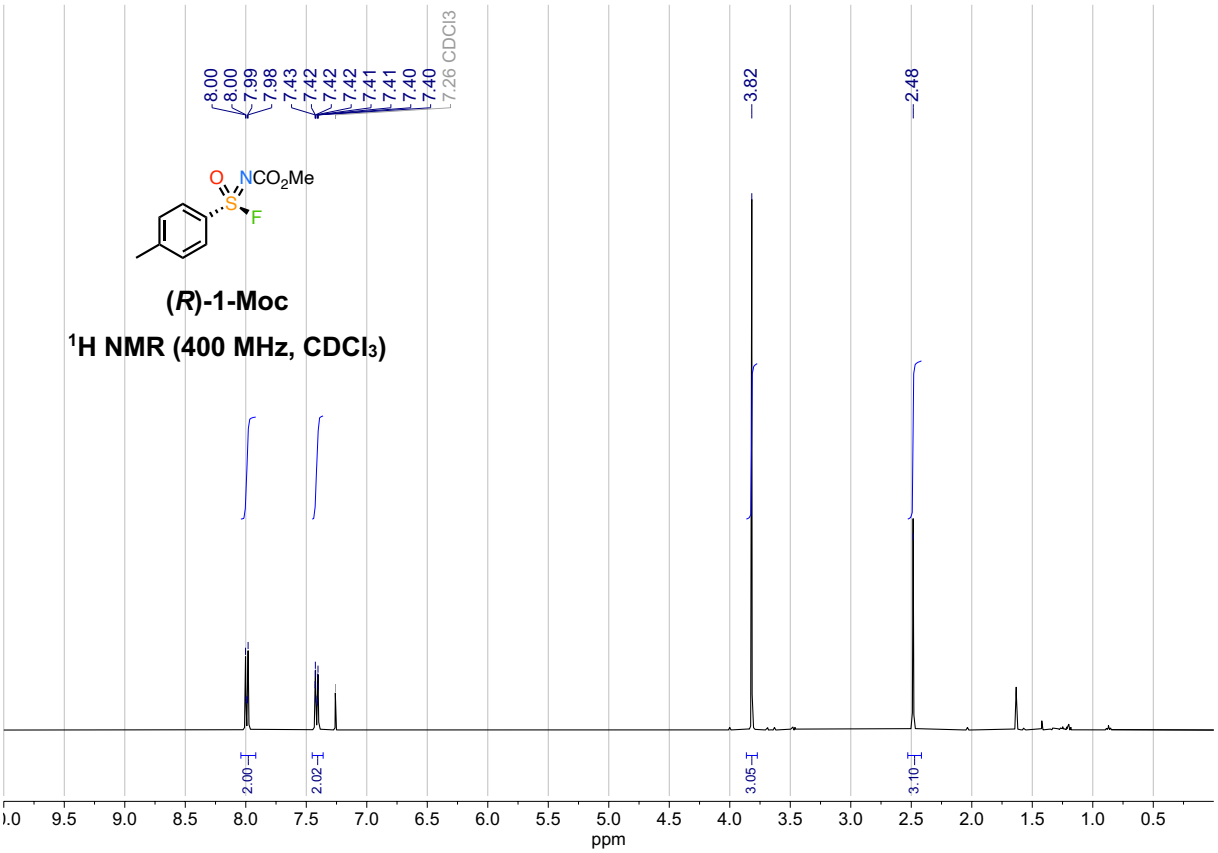


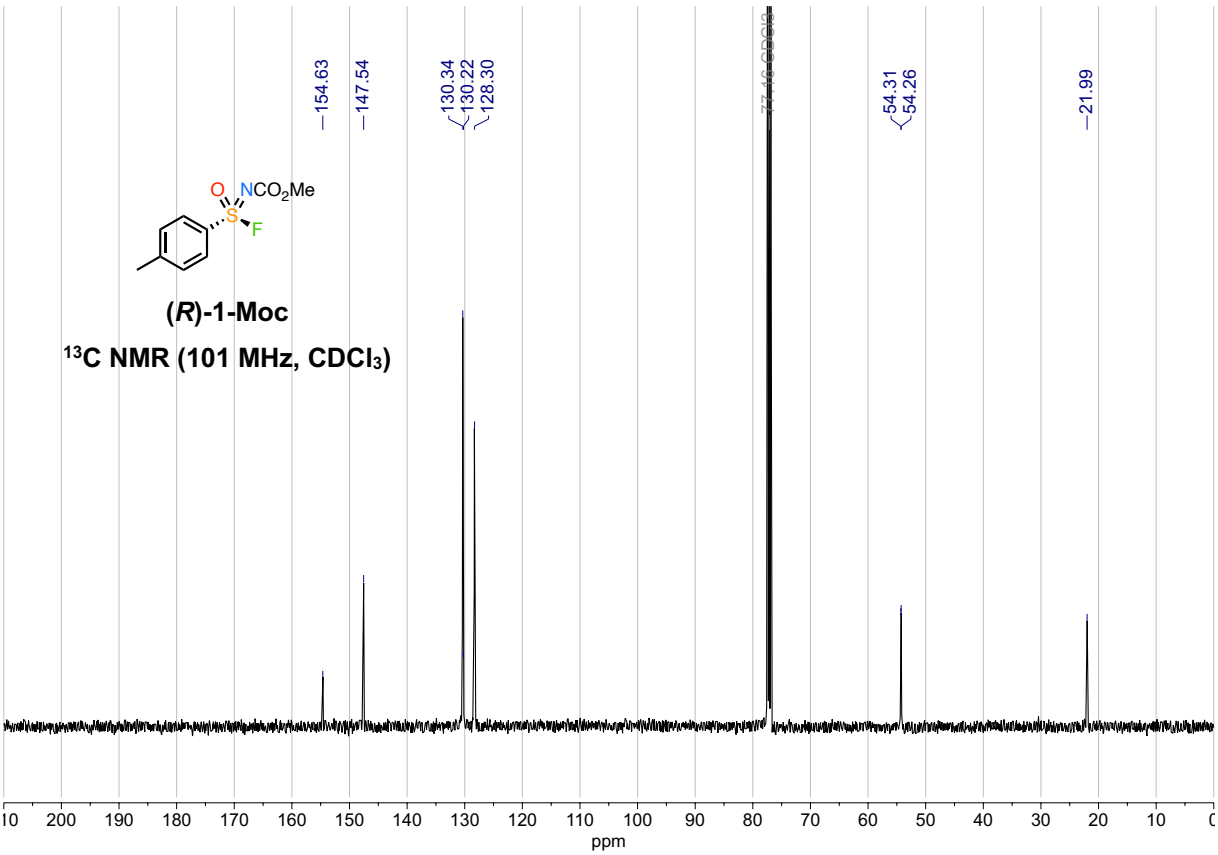


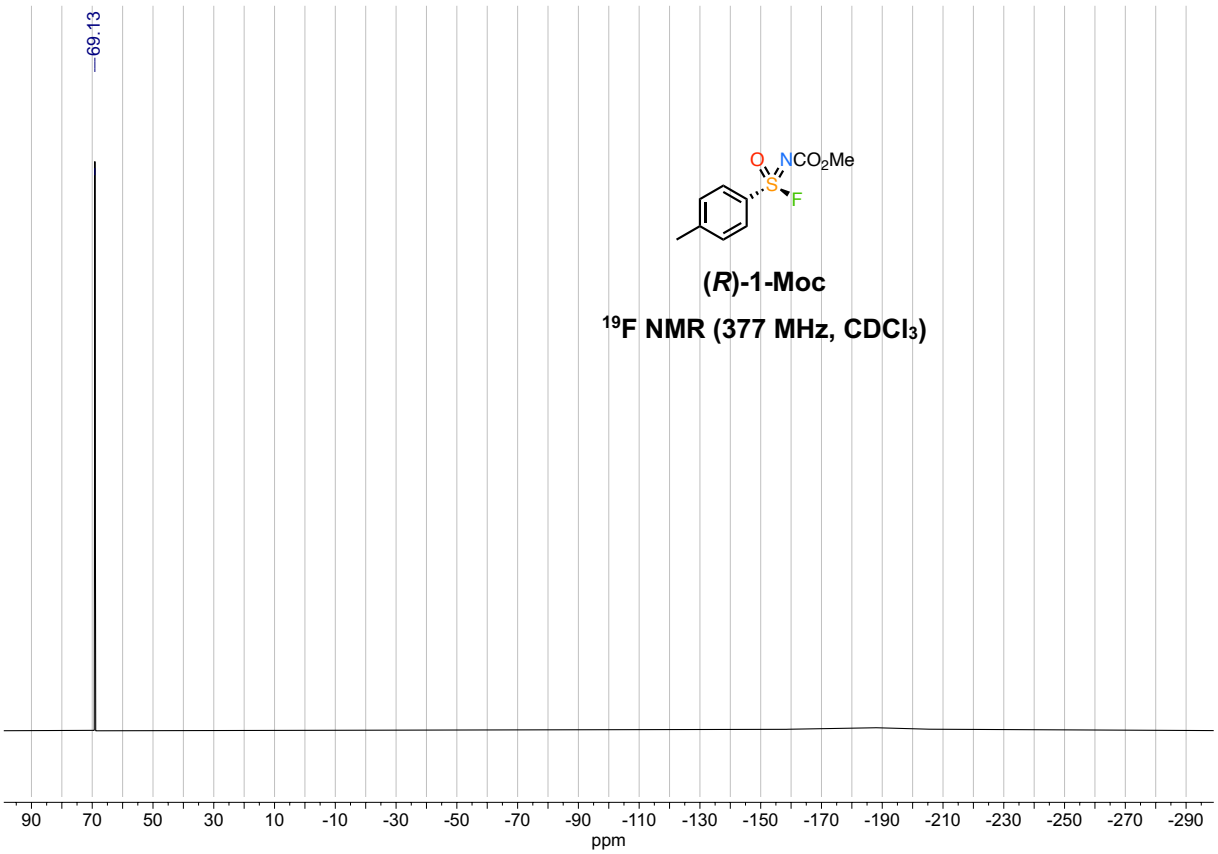
(*R*)-1-Cbz

^{19}F NMR (377 MHz, $CDCl_3$)

Methyl (*R*)-(fluoro(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-1-Moc)



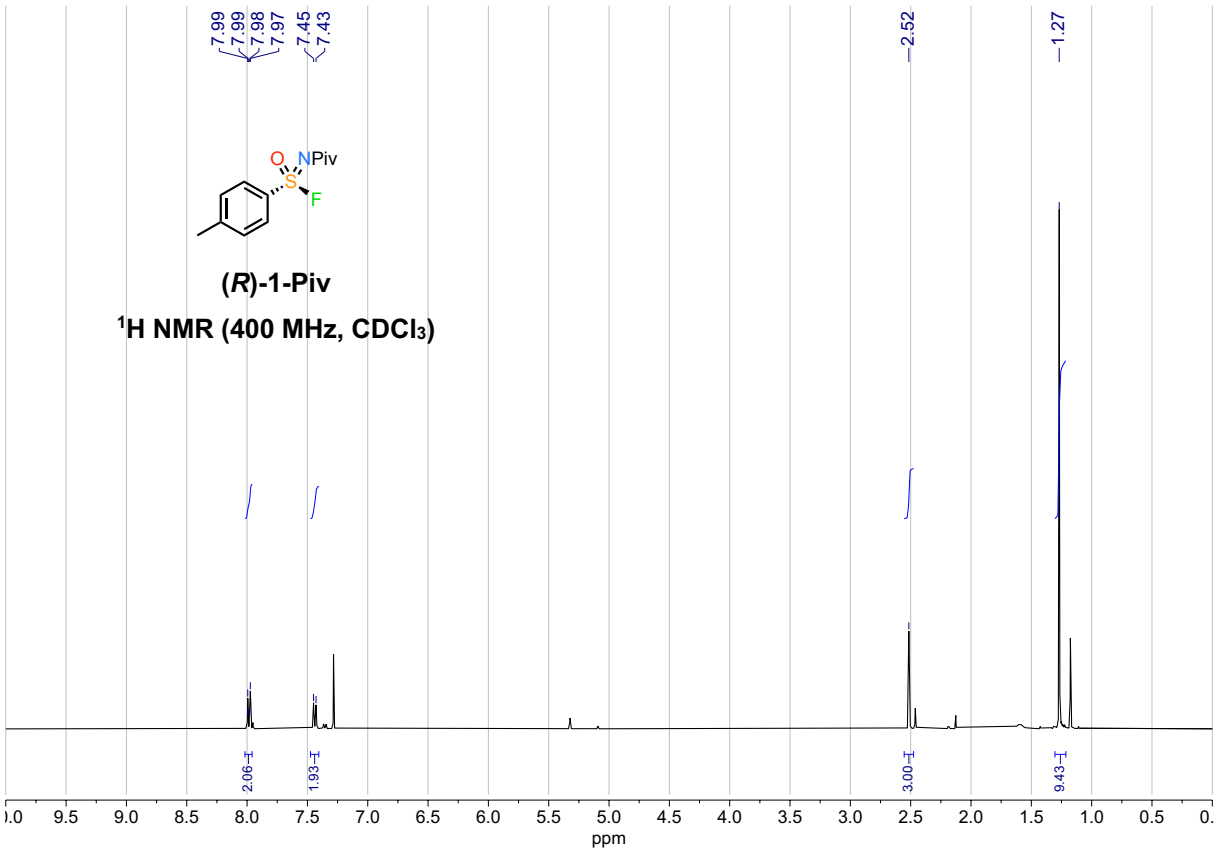


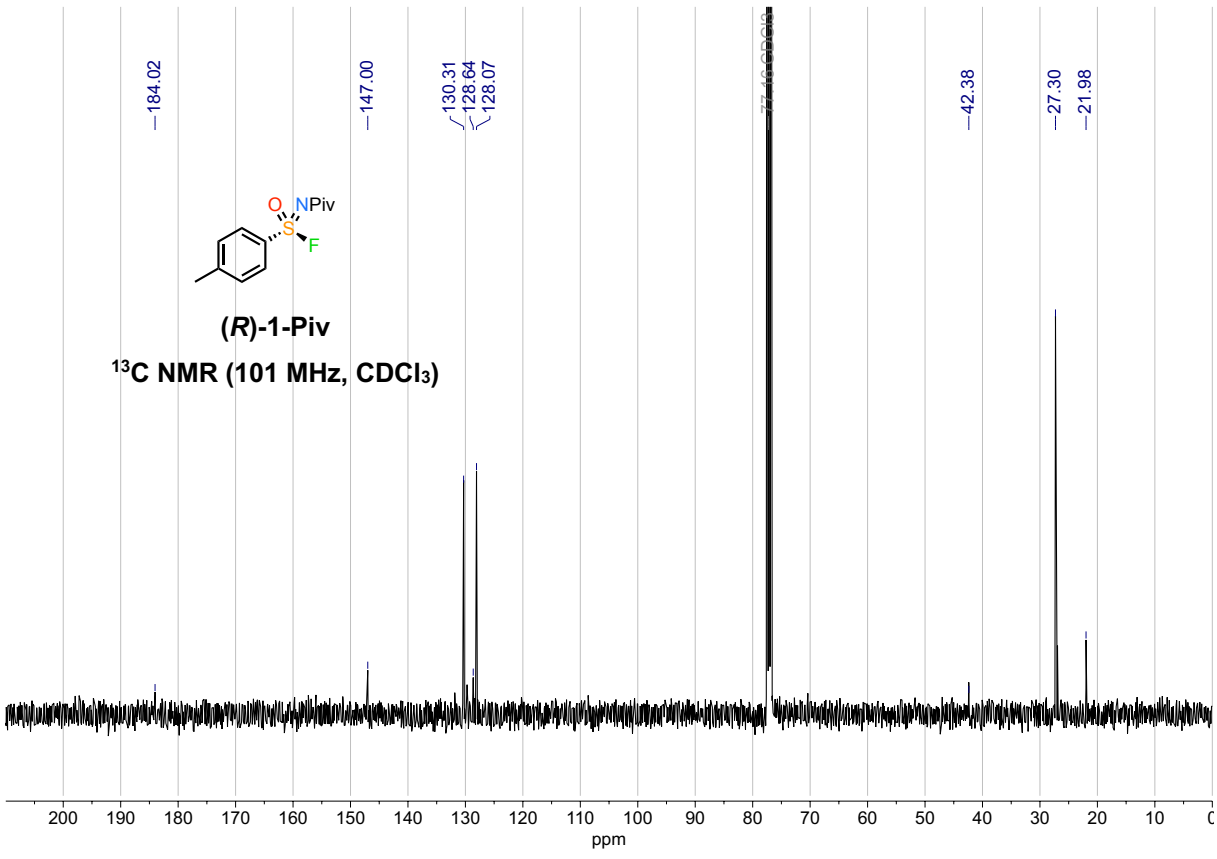


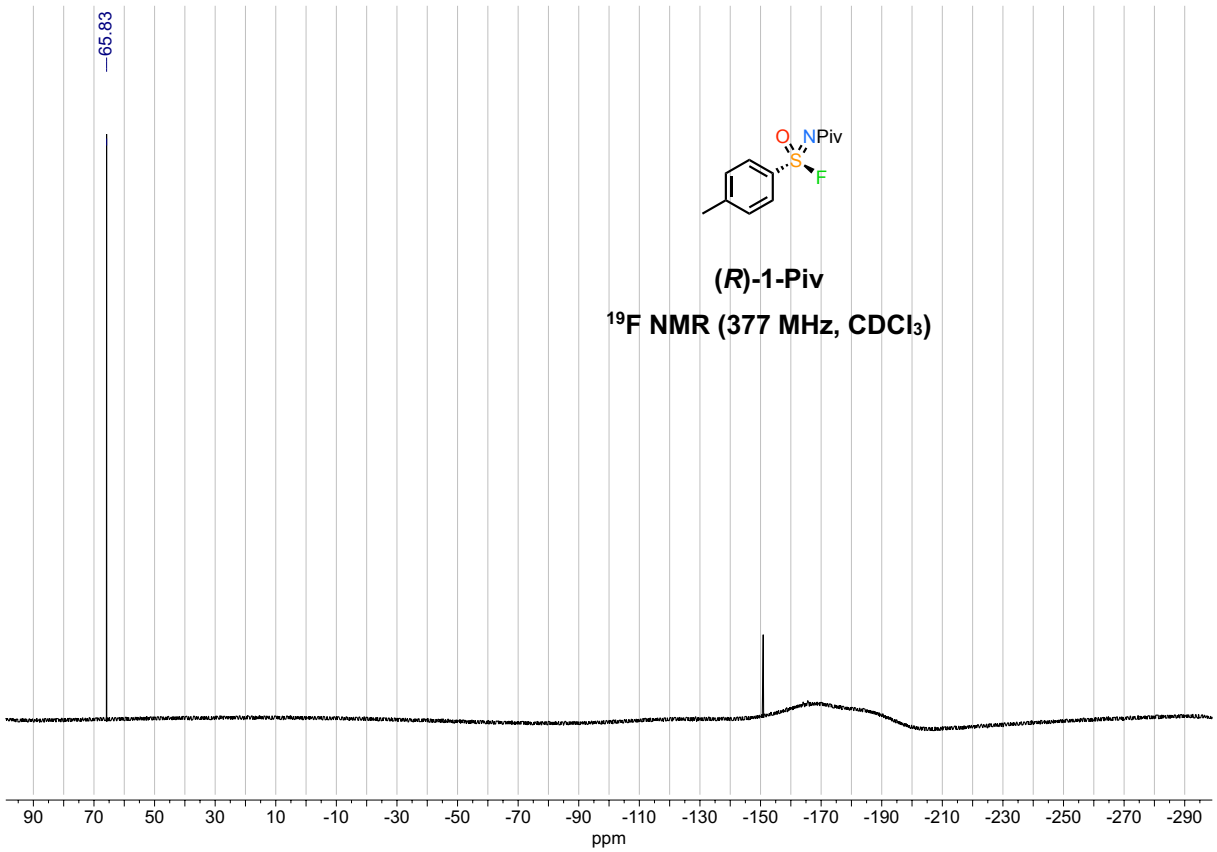
(*R*)-1-Moc

^{19}F NMR (377 MHz, $CDCl_3$)

(*R*)-4-Methyl-*N*-pivaloylbenzenesulfonimidoyl fluoride ((*R*)-1-Piv)



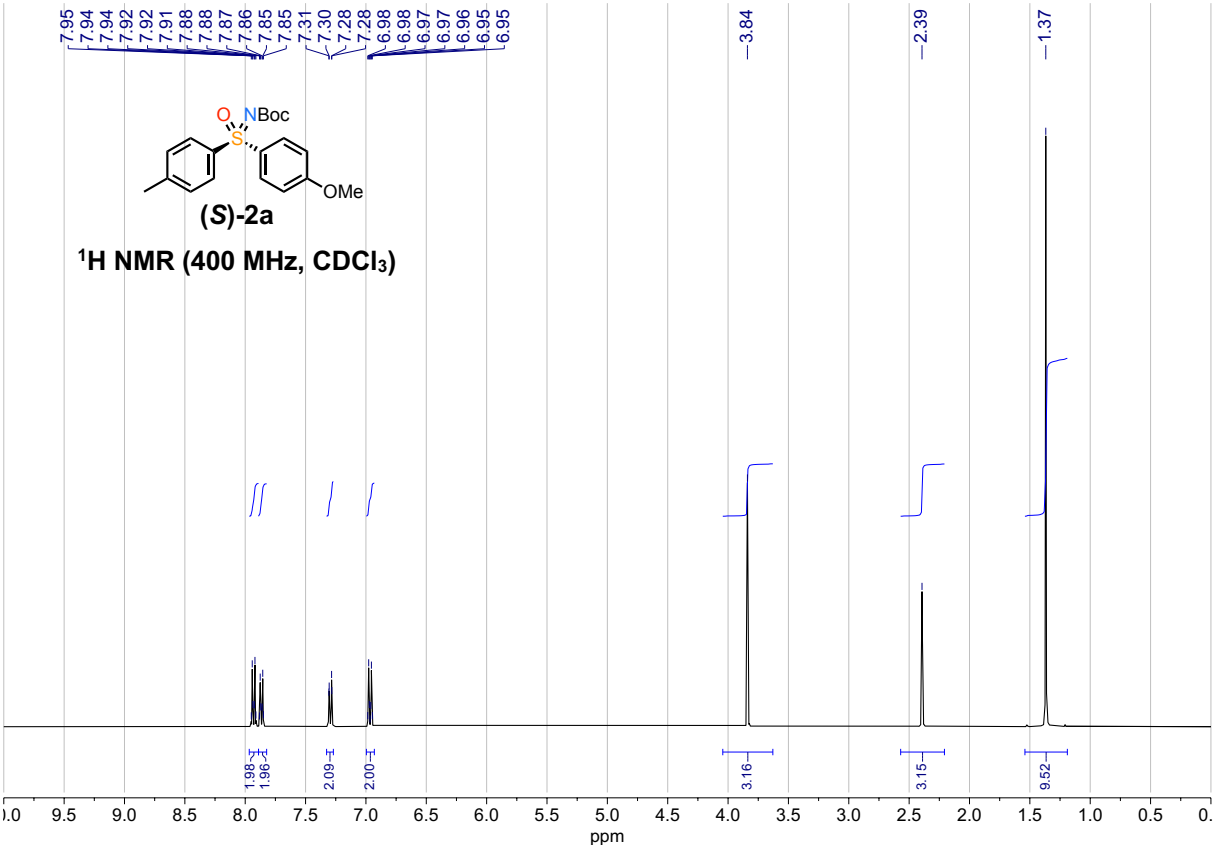


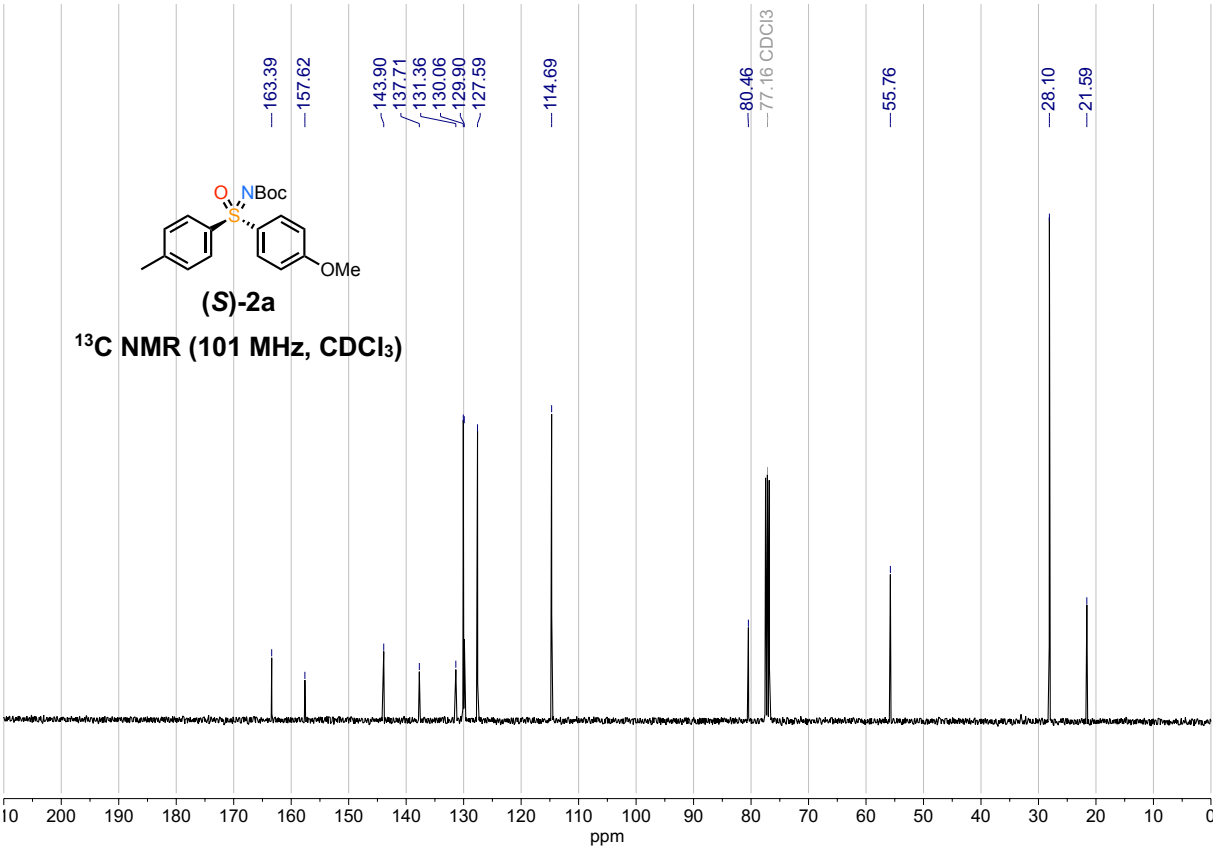


(*R*)-1-Piv

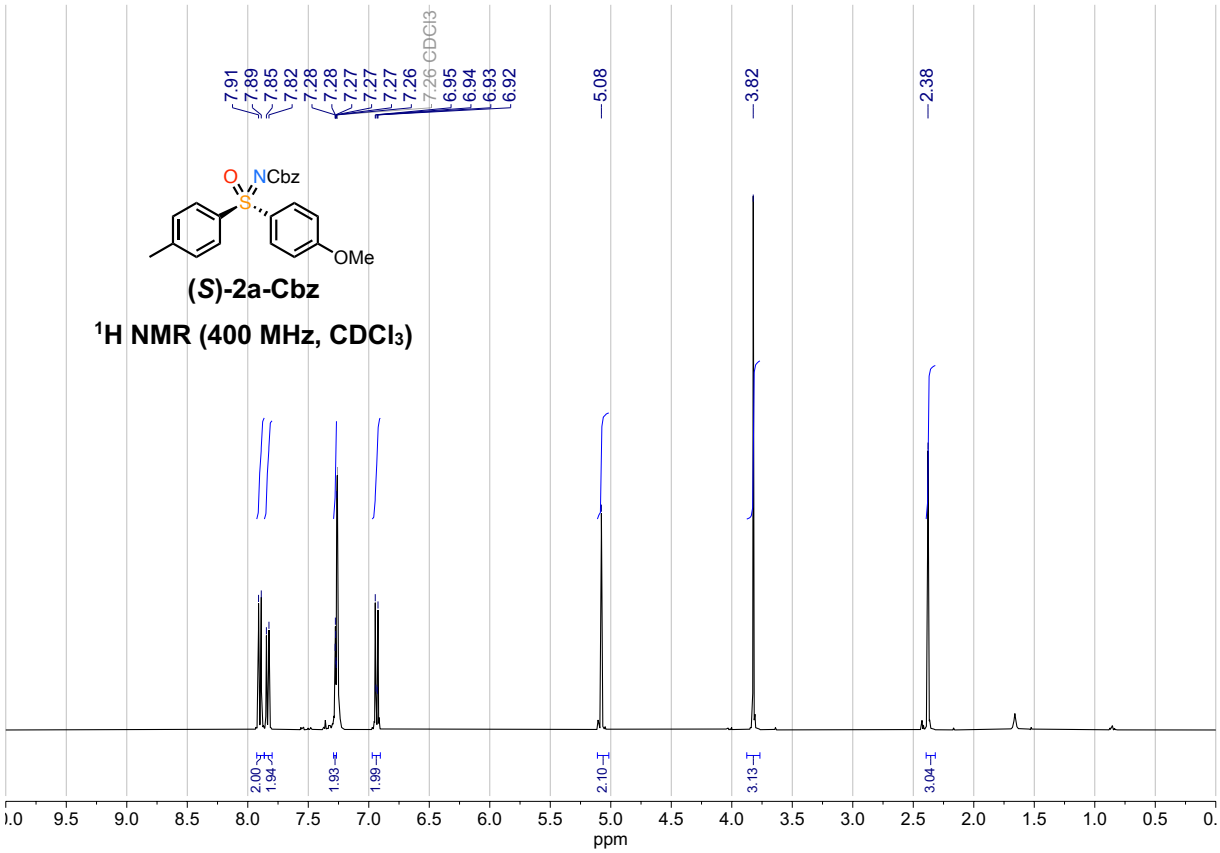
^{19}F NMR (377 MHz, $CDCl_3$)

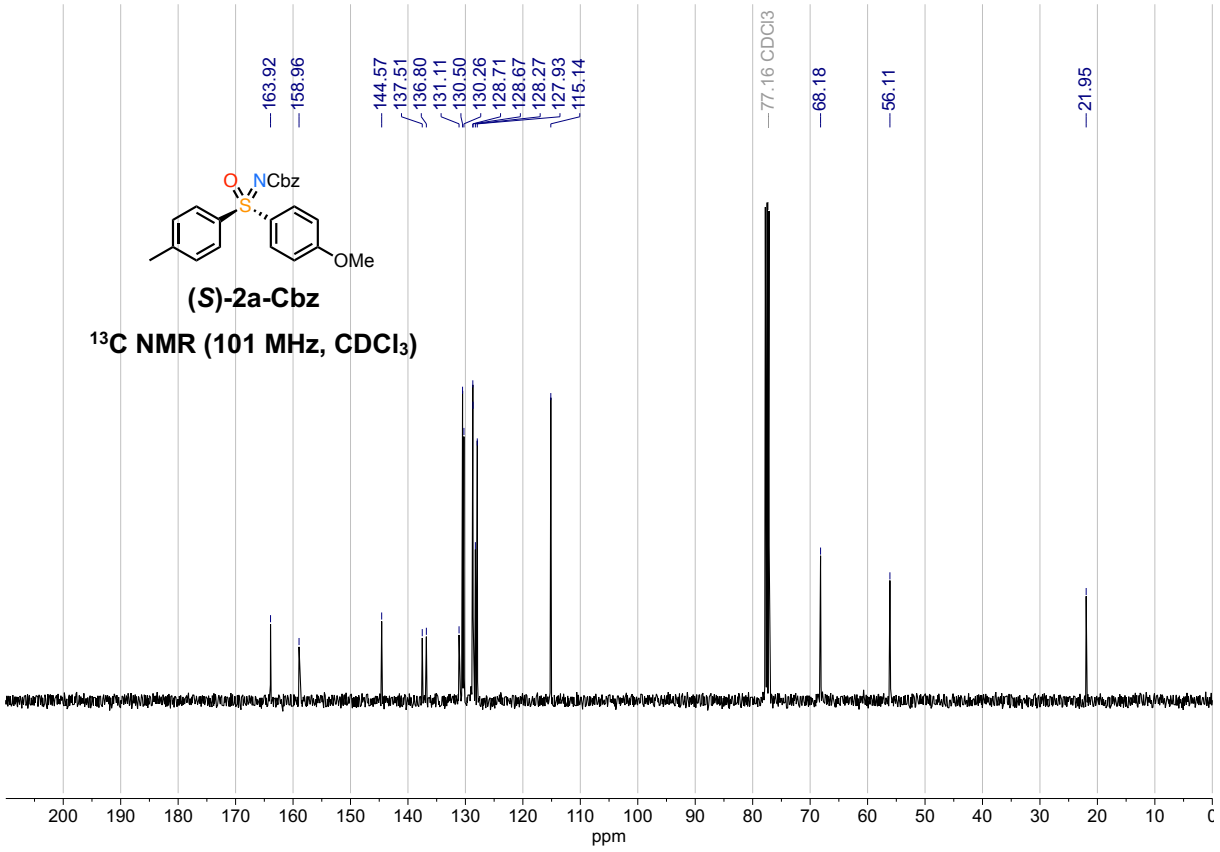
***tert*-Butyl (*S*)-((4-methoxyphenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2a)**



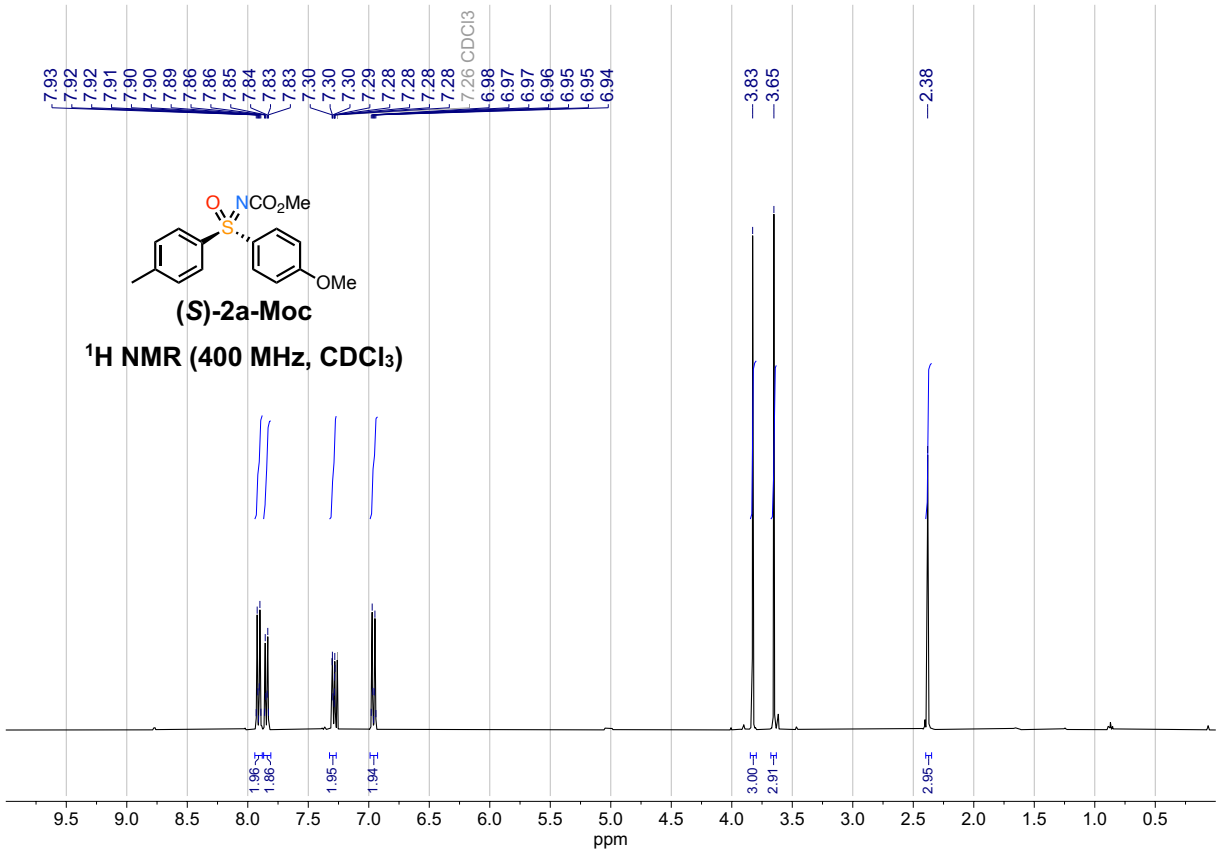


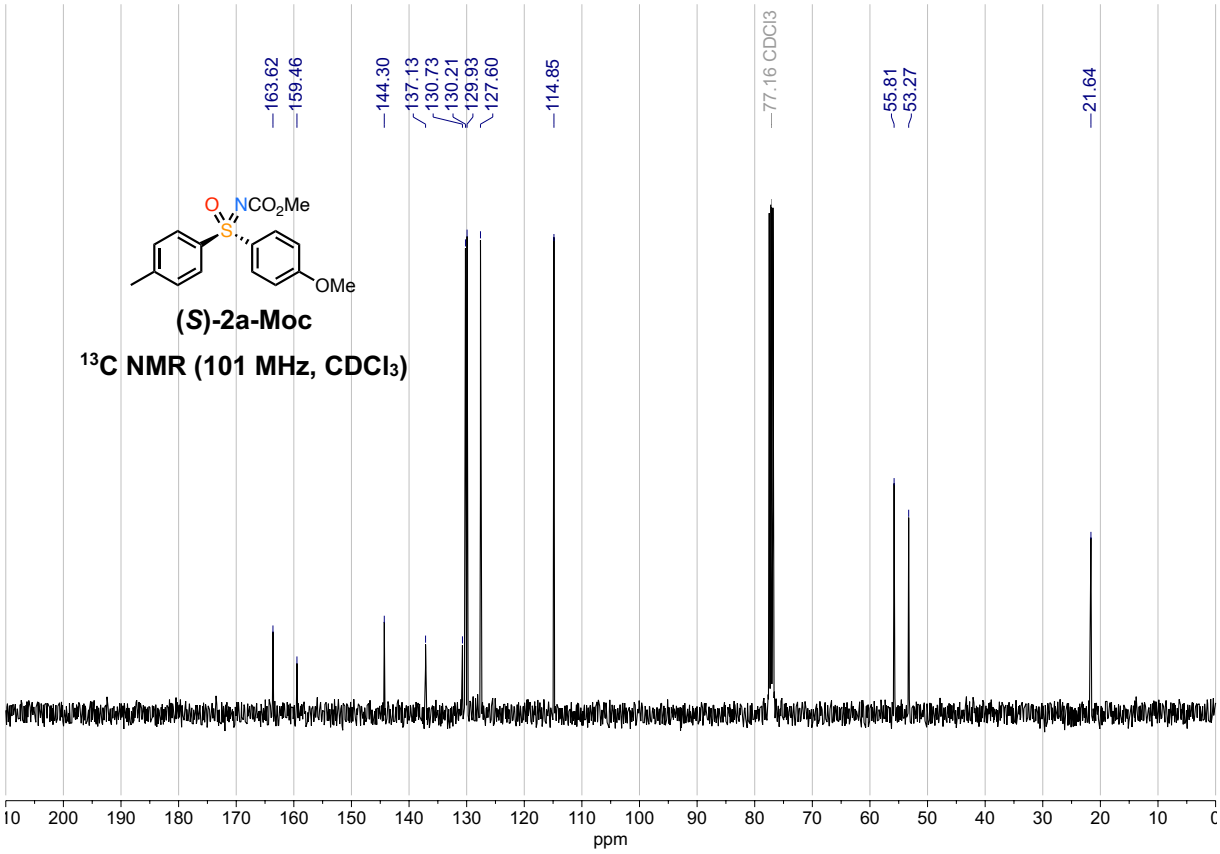
Benzyl (*S*)-((4-methoxyphenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2a-Cbz)



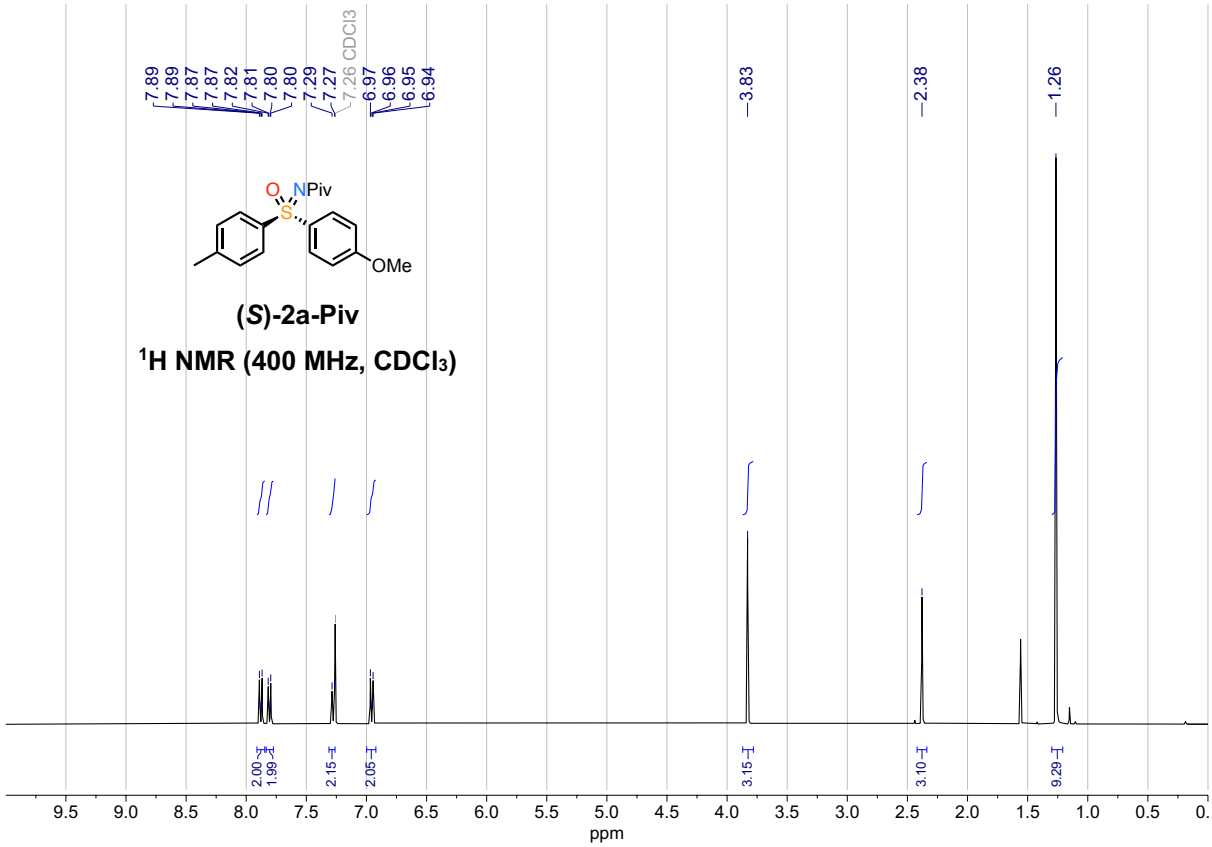


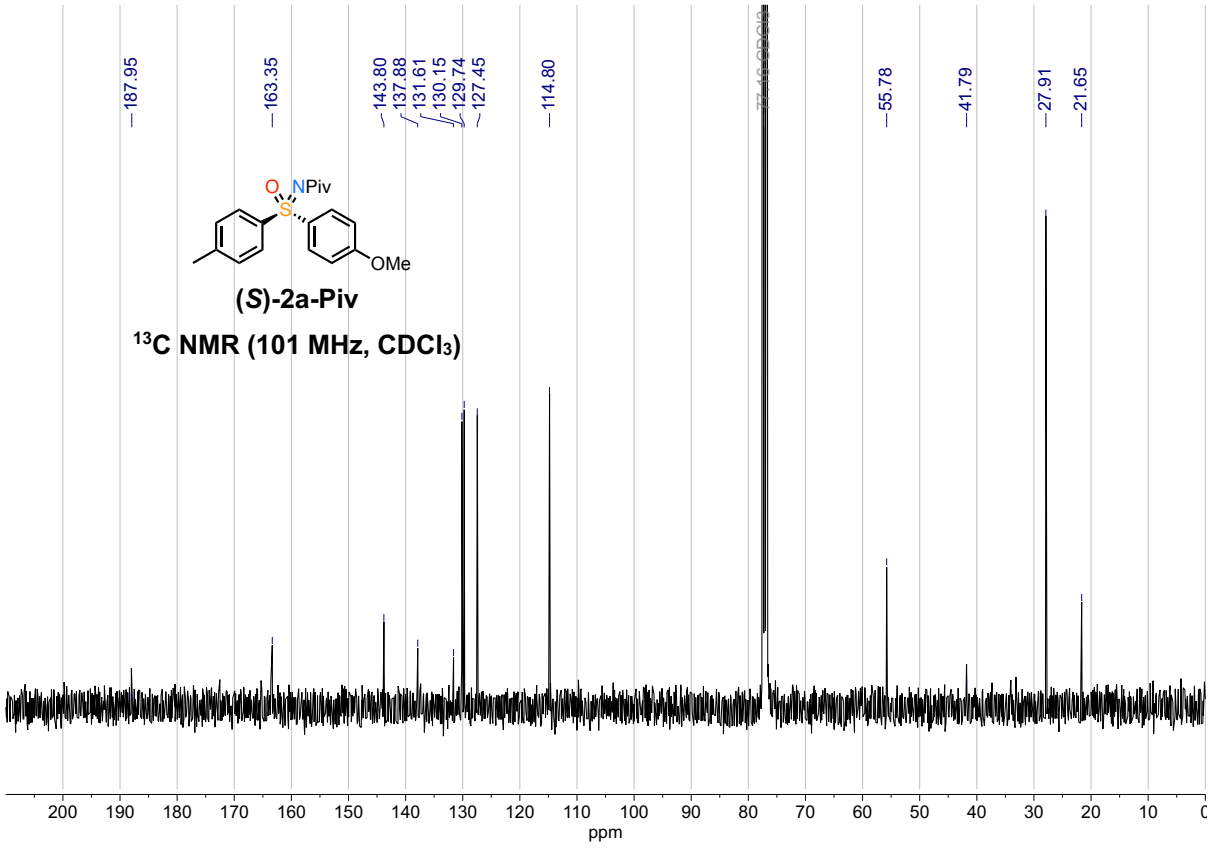
Methyl (*S*)-((4-methoxyphenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2a-Moc)



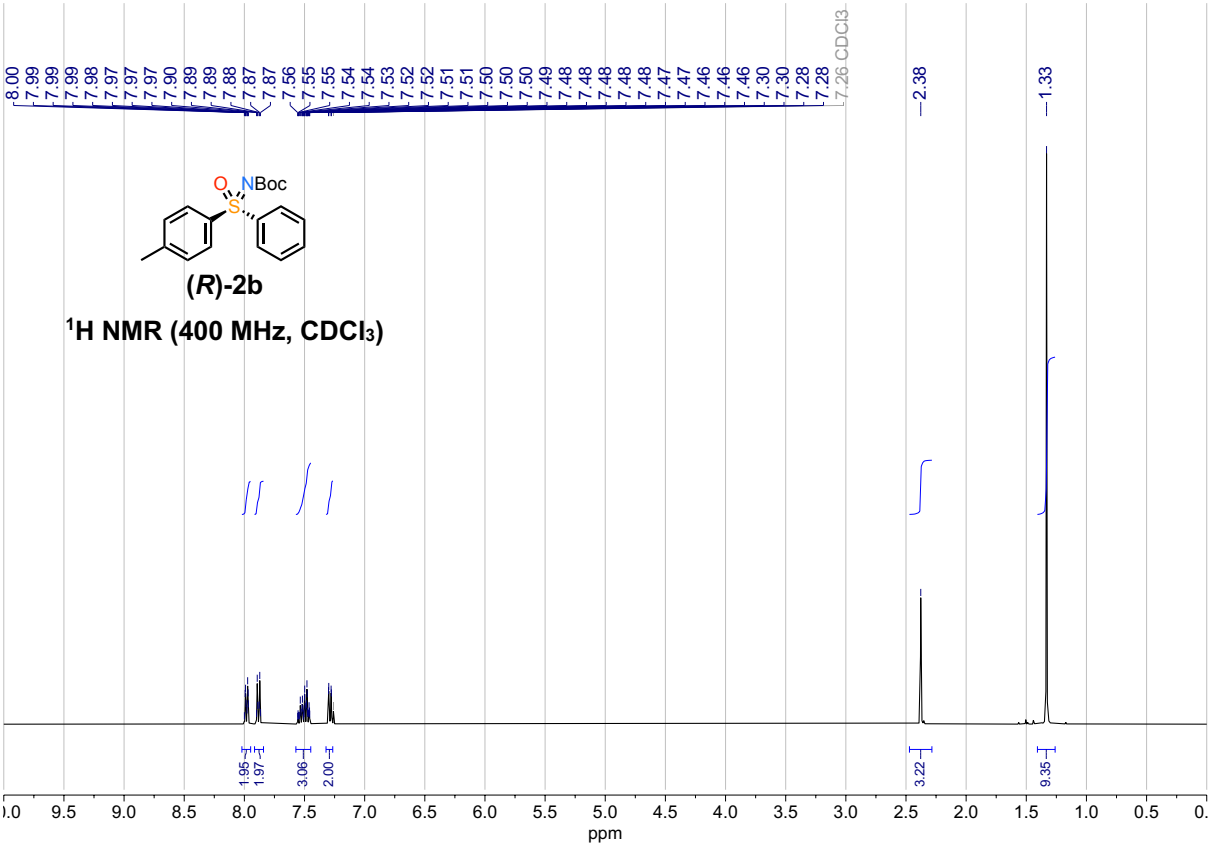


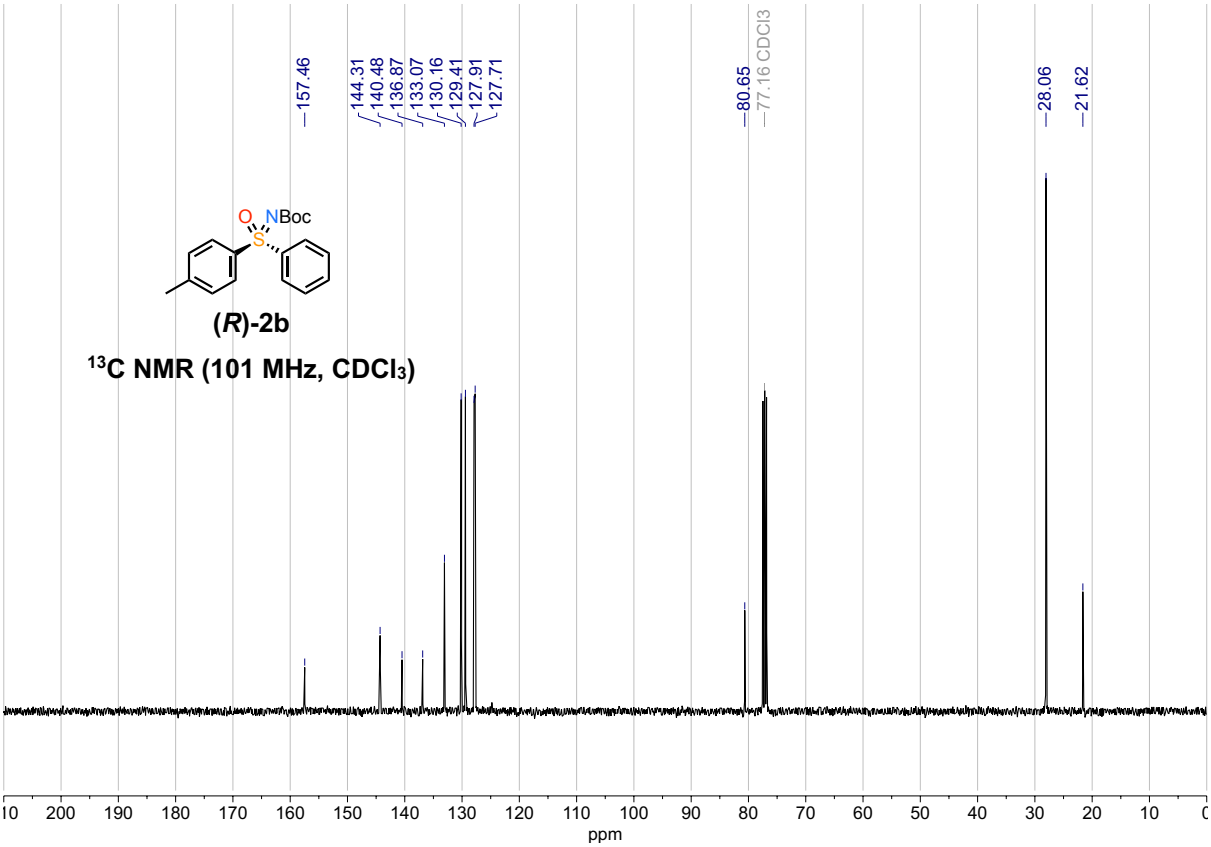
(*S*)-N-((4-methoxyphenyl)(oxo)(p-tolyl)-λ⁶-sulfaneylidene)pivalamide ((*S*)-2a-Piv)



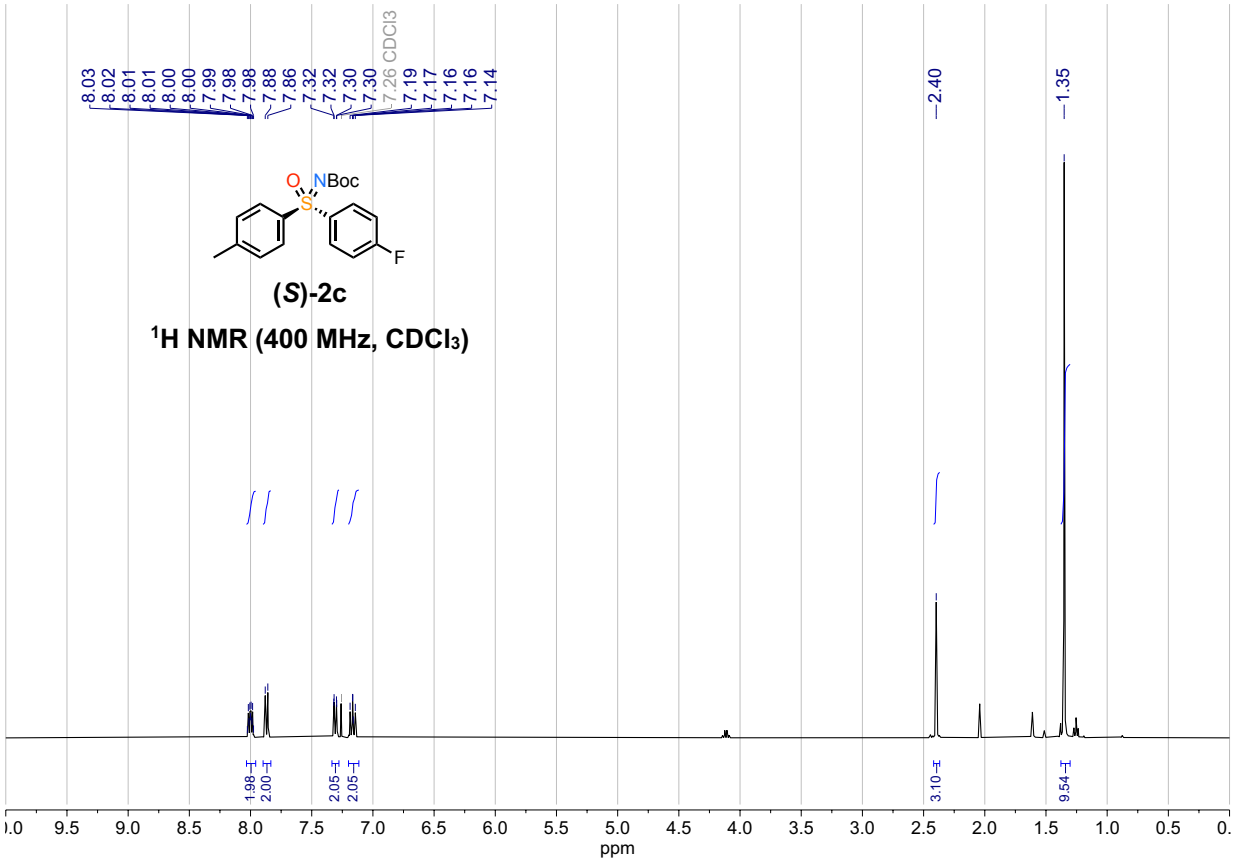


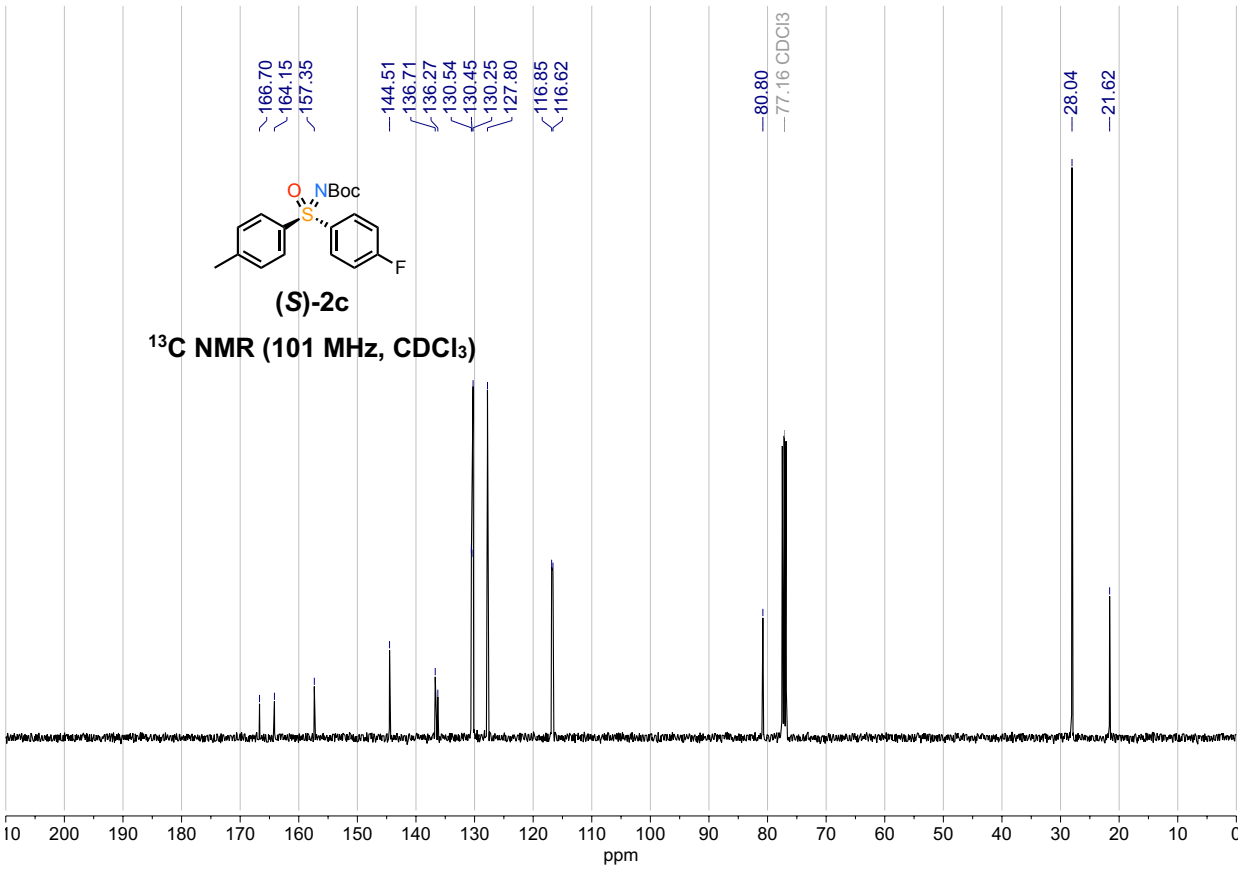
***tert*-Butyl (*R*)-(oxo(phenyl)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-2b)**

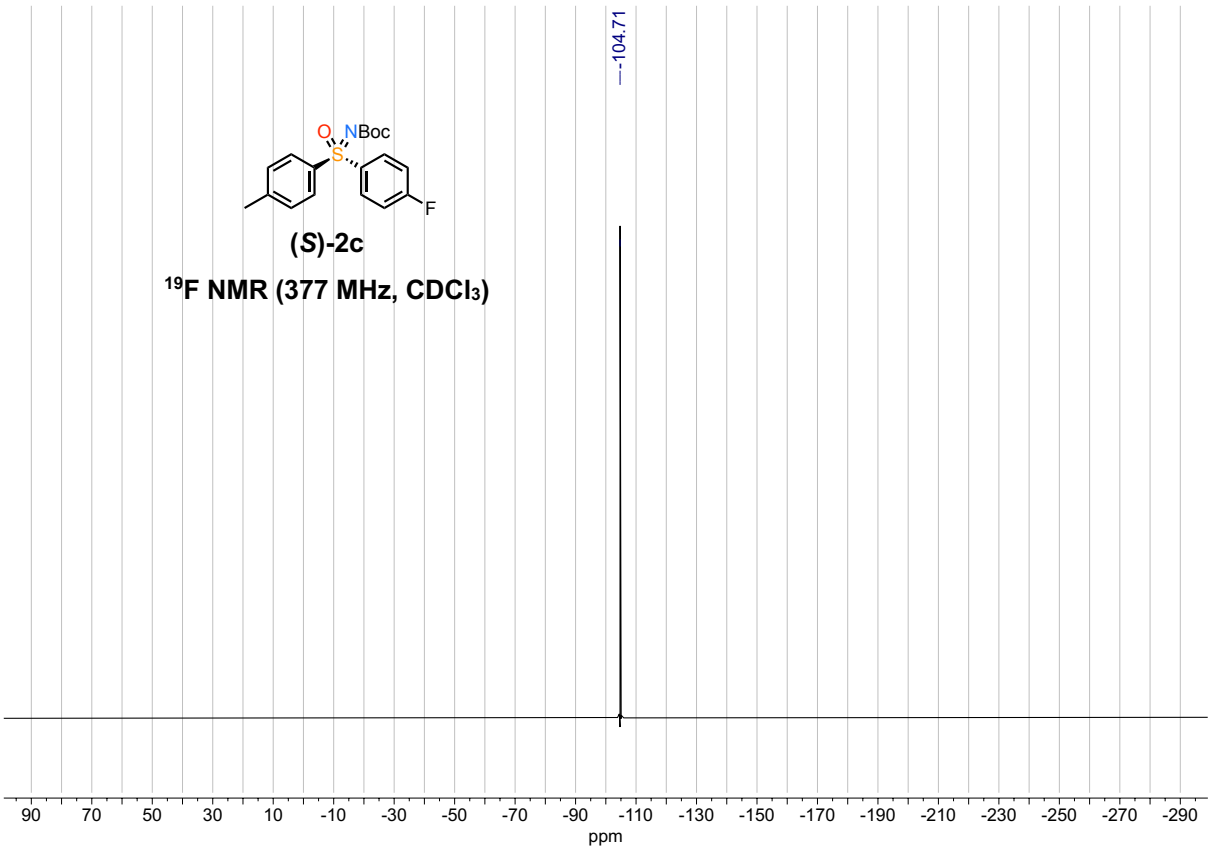




***tert*-Butyl (*S*)-((4-fluorophenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2c)**



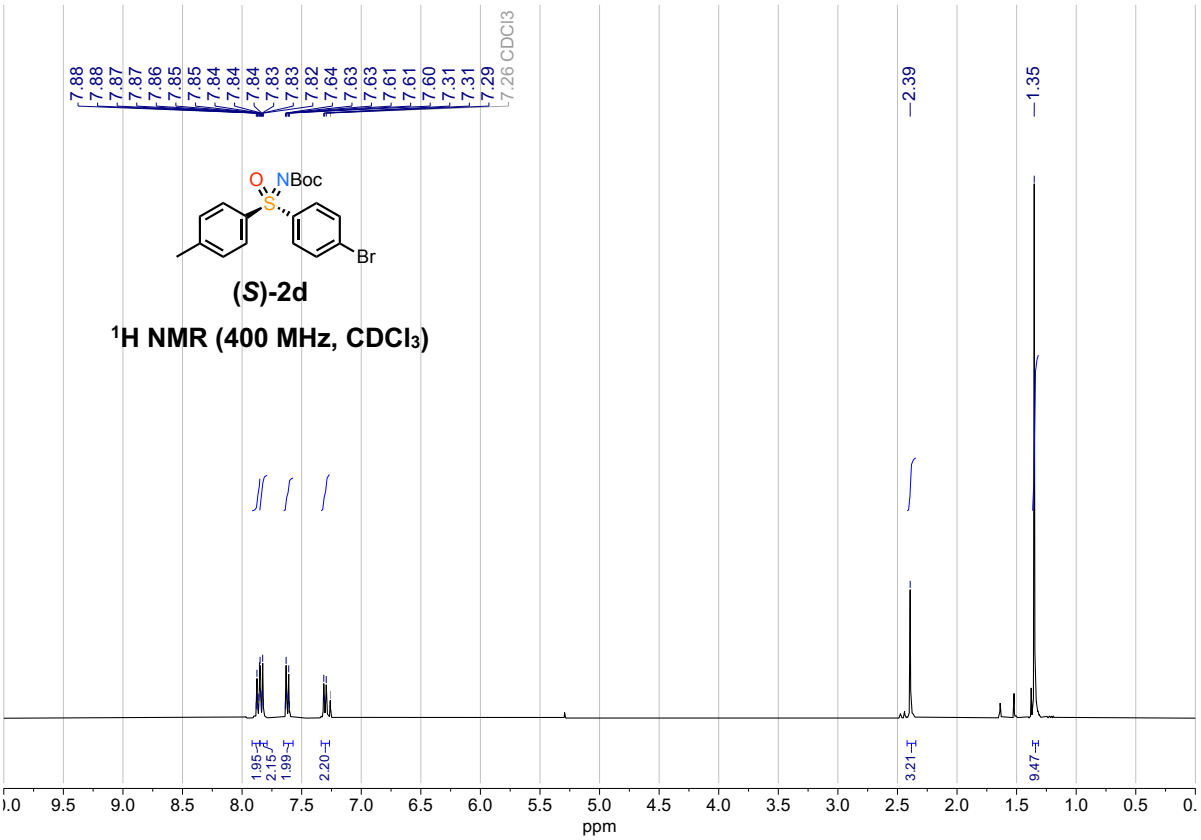


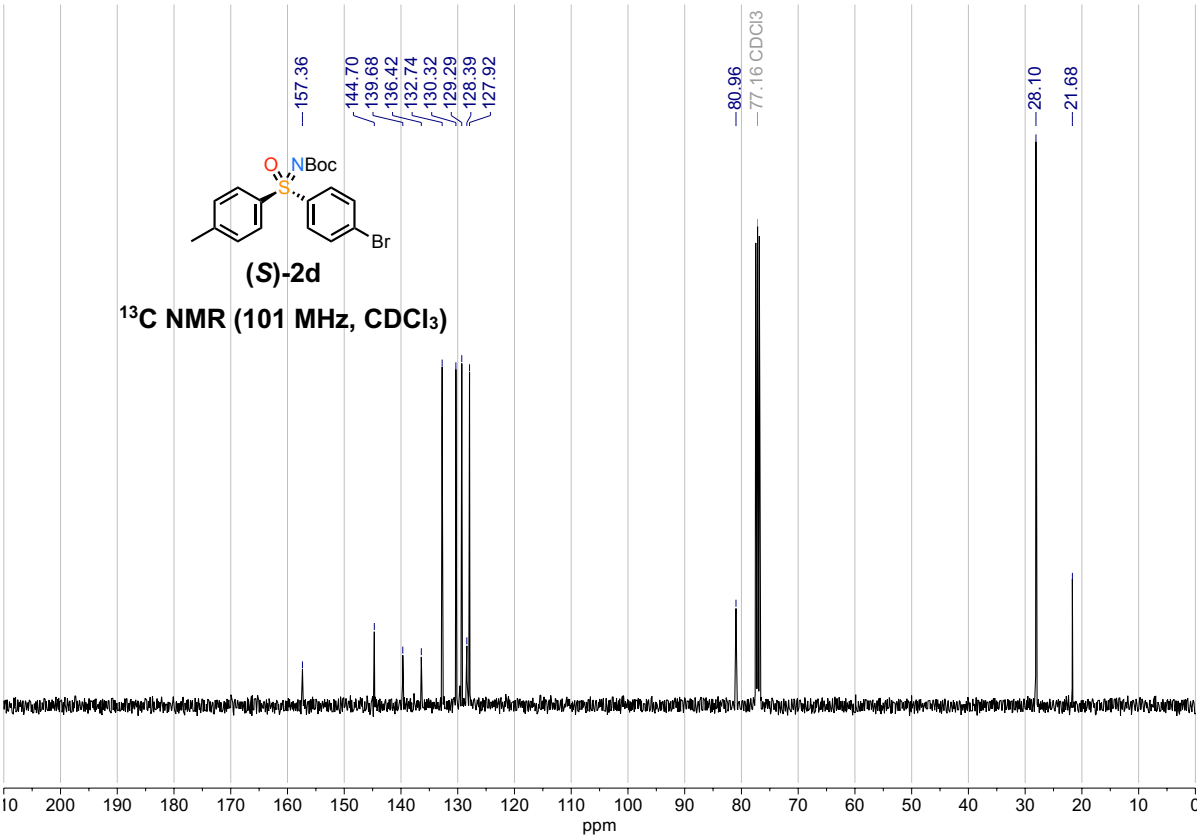


(*S*)-2c

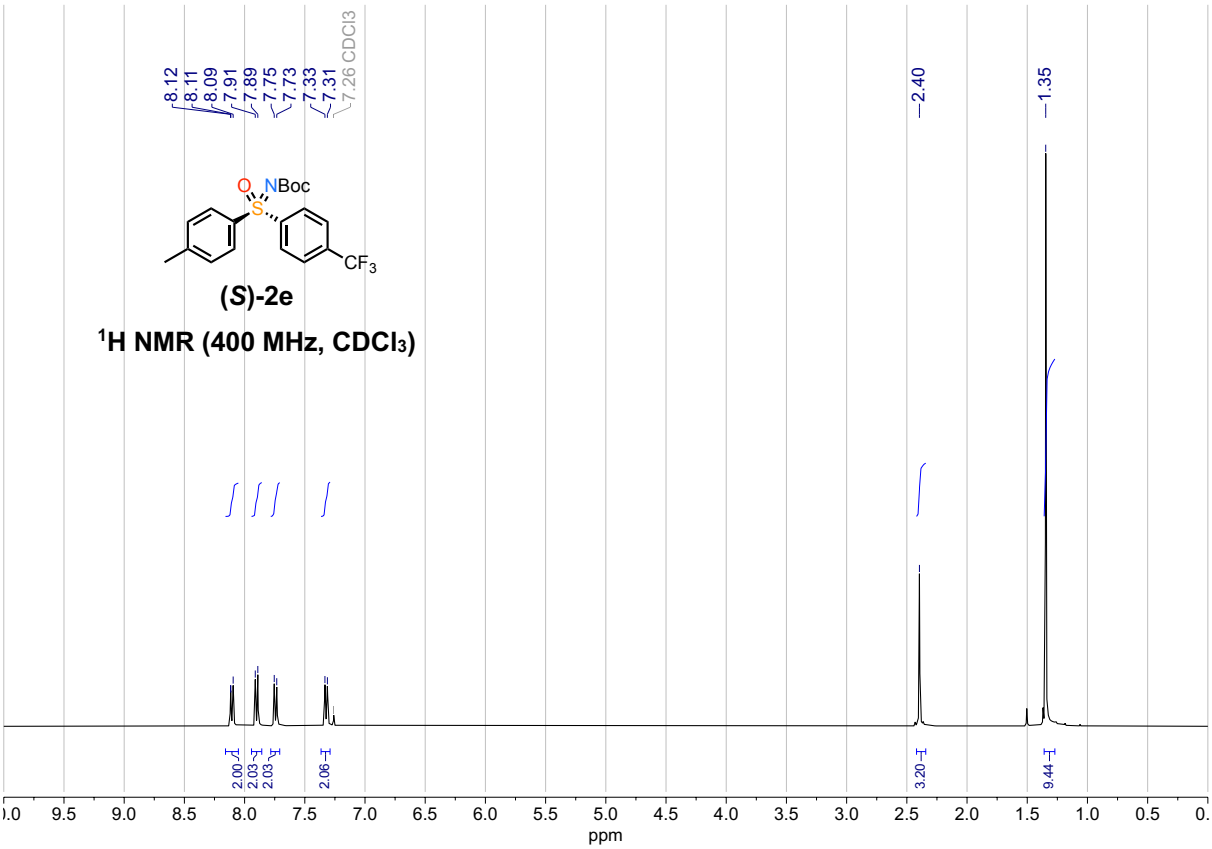
^{19}F NMR (377 MHz, $CDCl_3$)

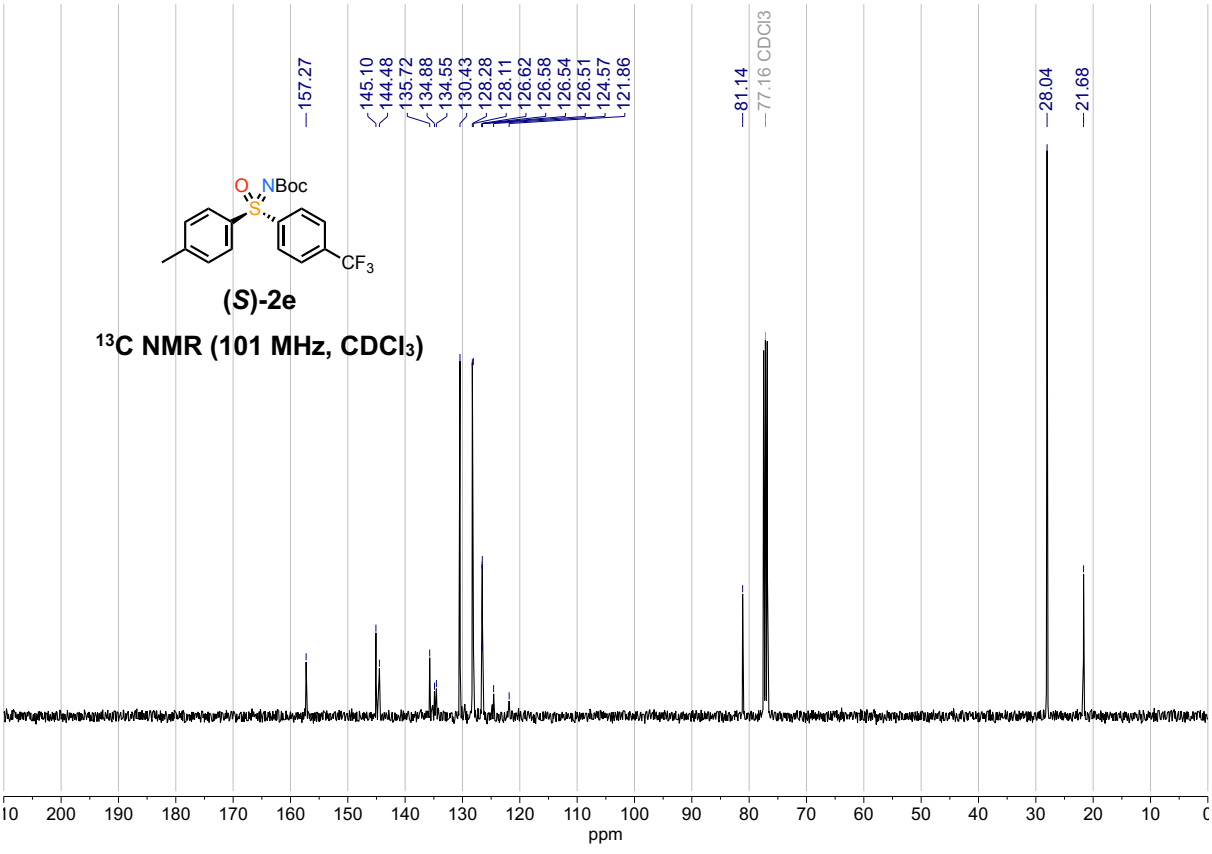
tert-Butyl (_S_)-((4-bromophenyl)(oxo)(_p_-tolyl)-λ^6-sulfaneylidene)carbamate ((_S_)-2d)

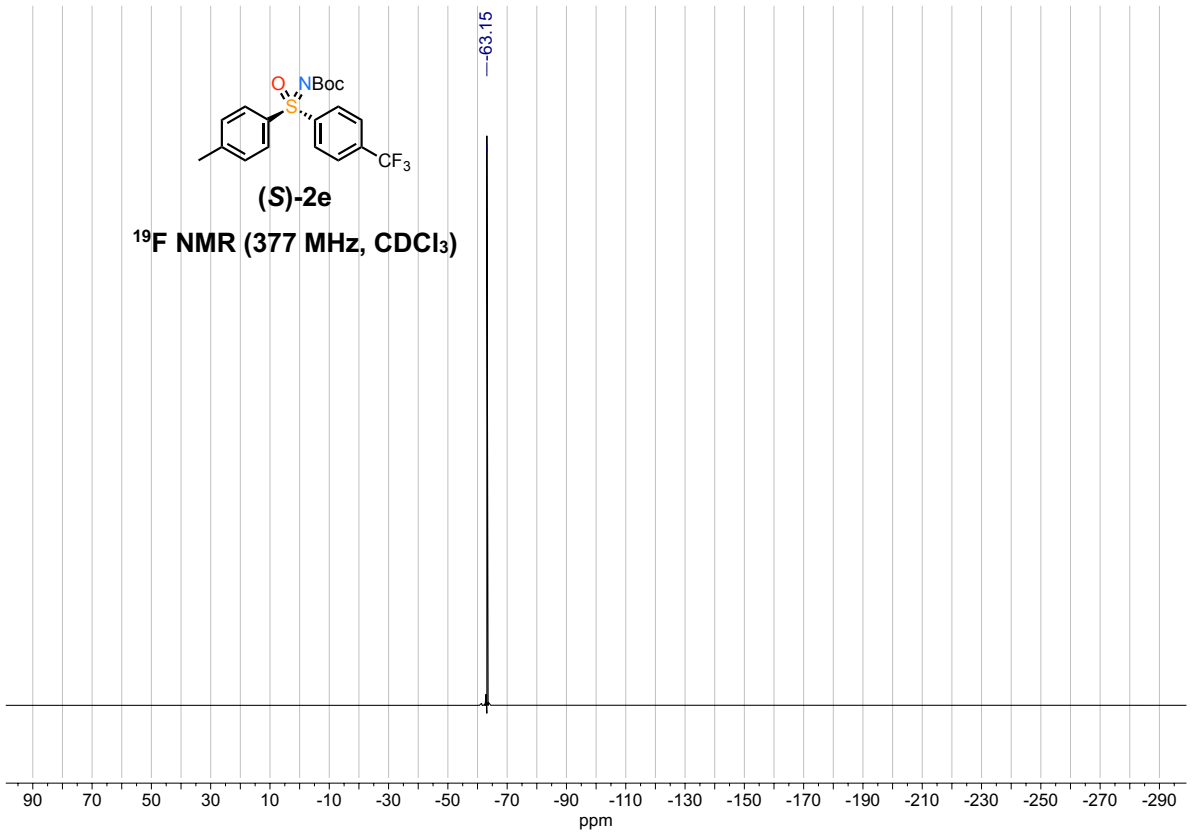




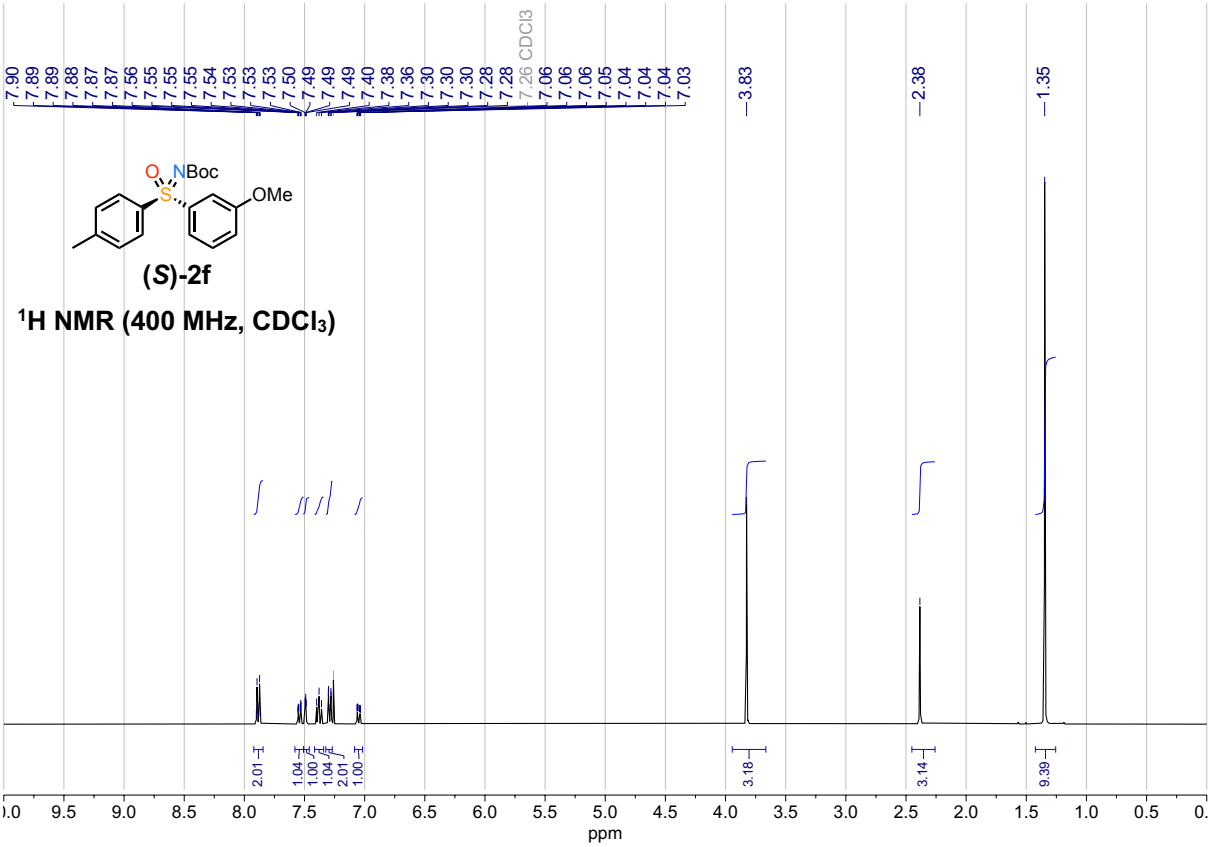
***tert*-Butyl (*S*)-(oxo(*p*-tolyl)(4-(trifluoromethyl)phenyl)- λ^6-sulfaneylidene)carbamate ((*S*)-2e)**

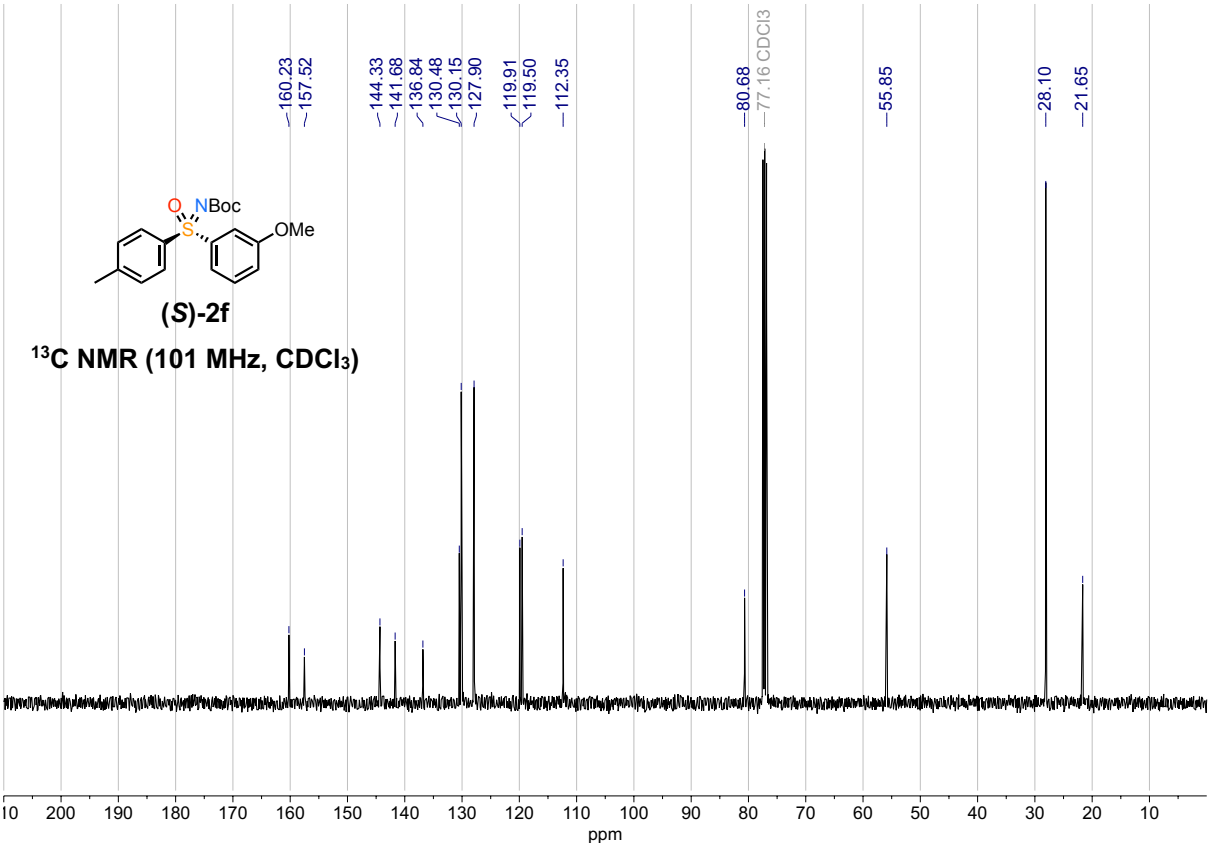




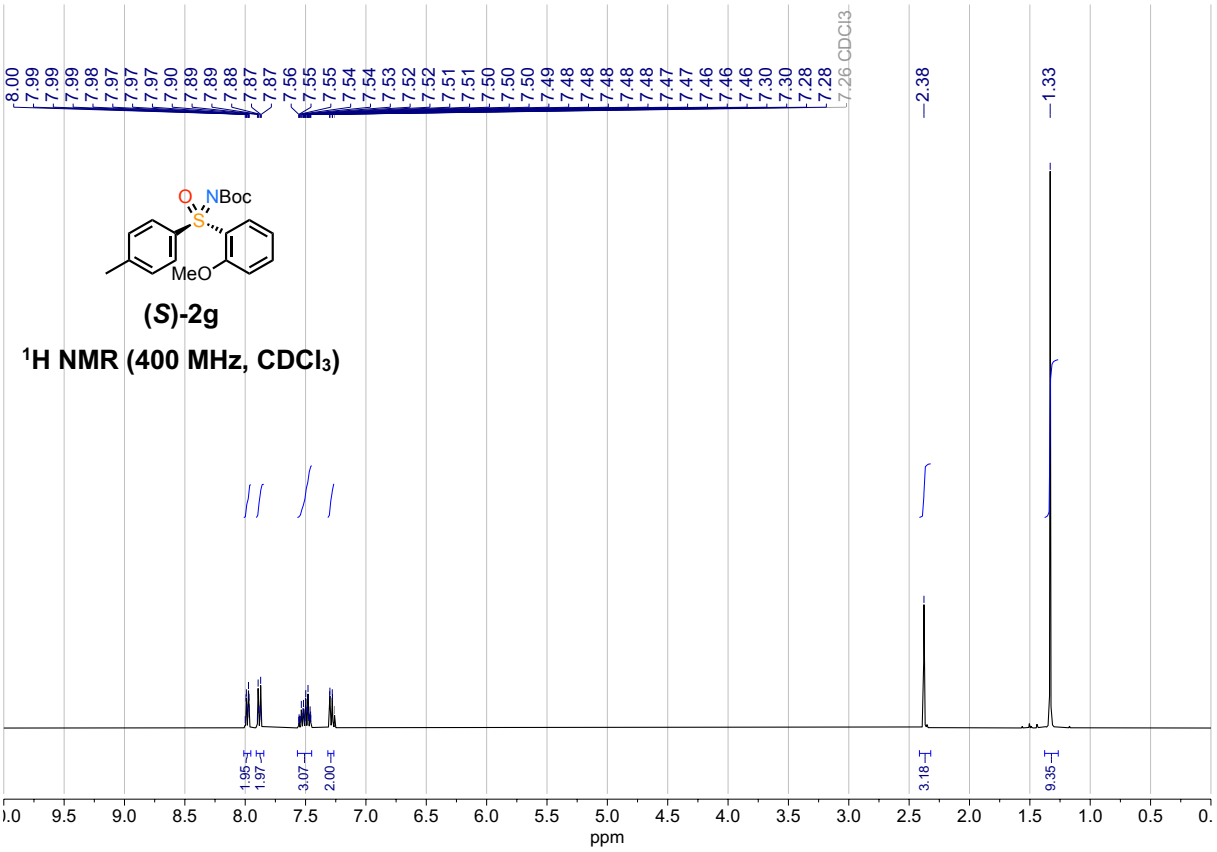

-63.15
O
NBoc
S
CF3
(S)-2e
19F NMR (377 MHz, CDCl3)
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
ppm

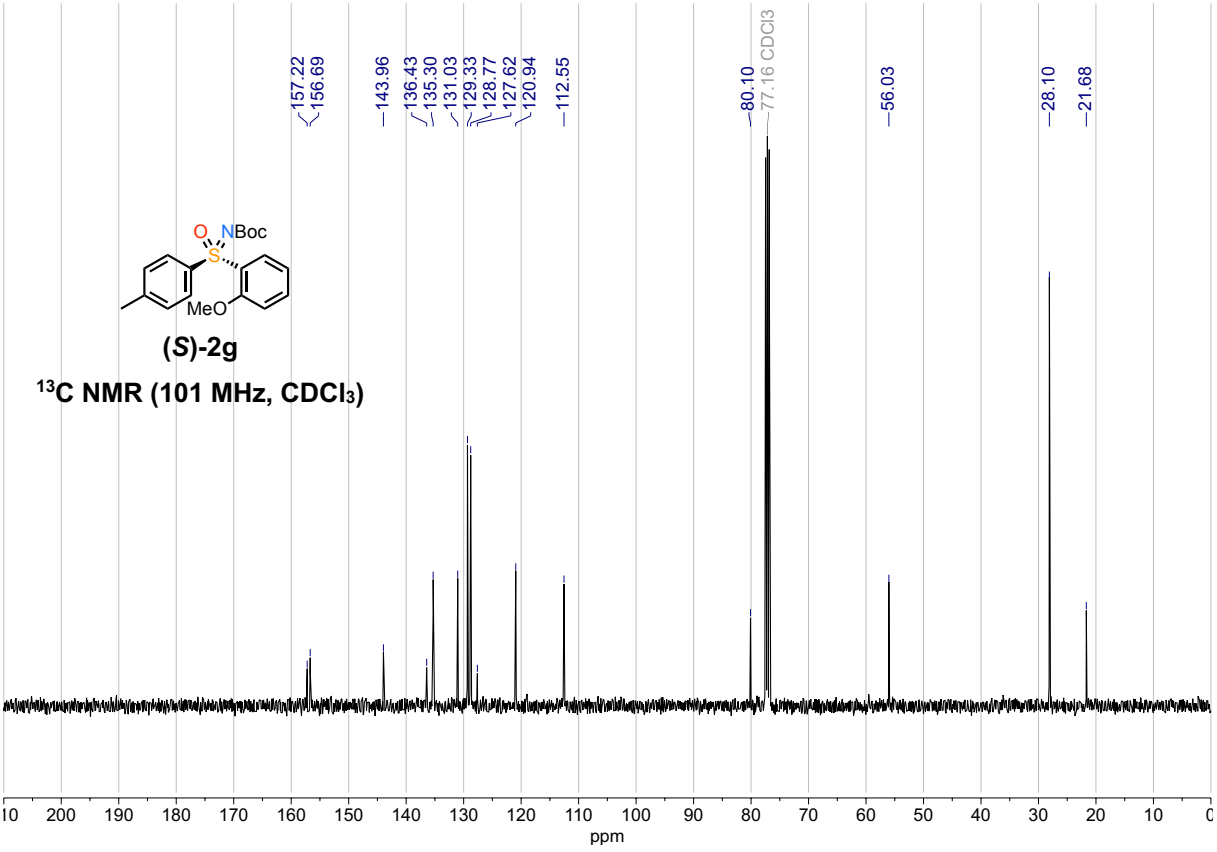
***tert*-Butyl (*S*)-((3-methoxyphenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2f)**



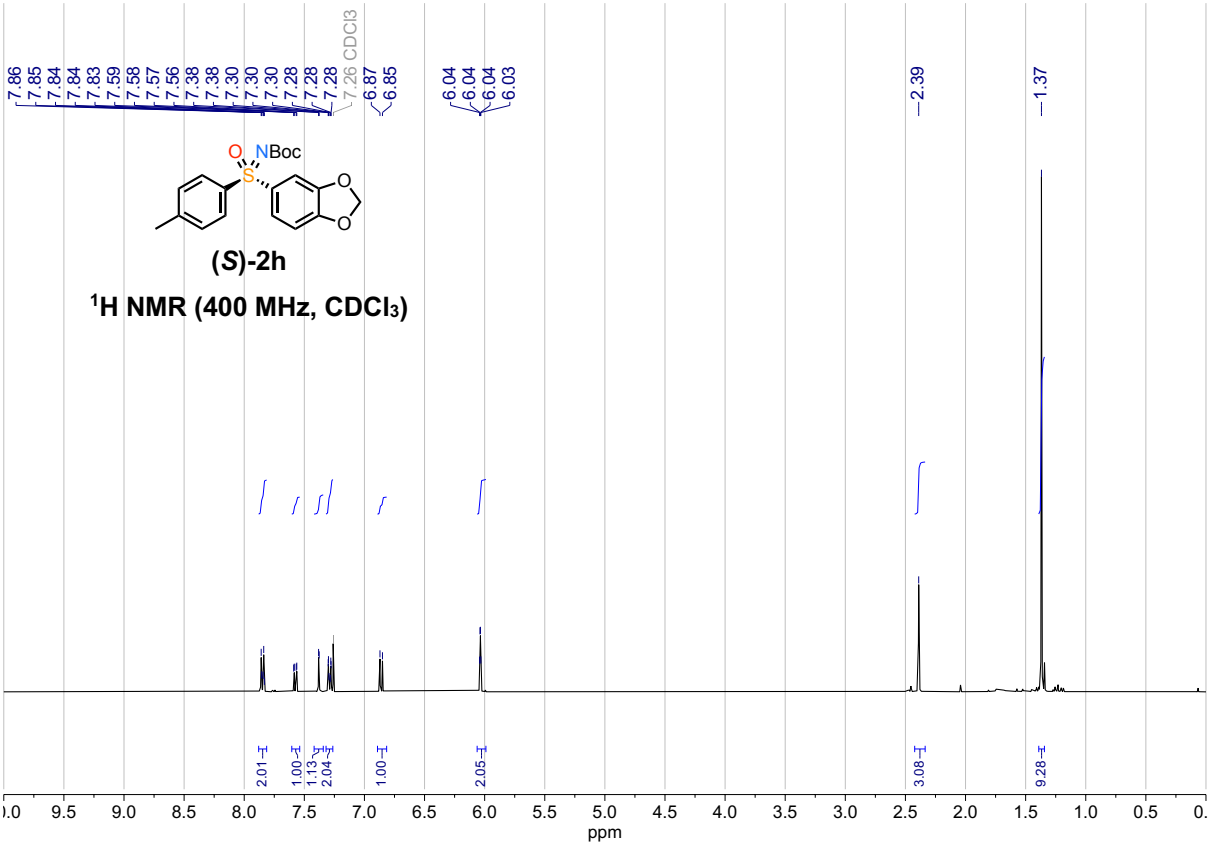


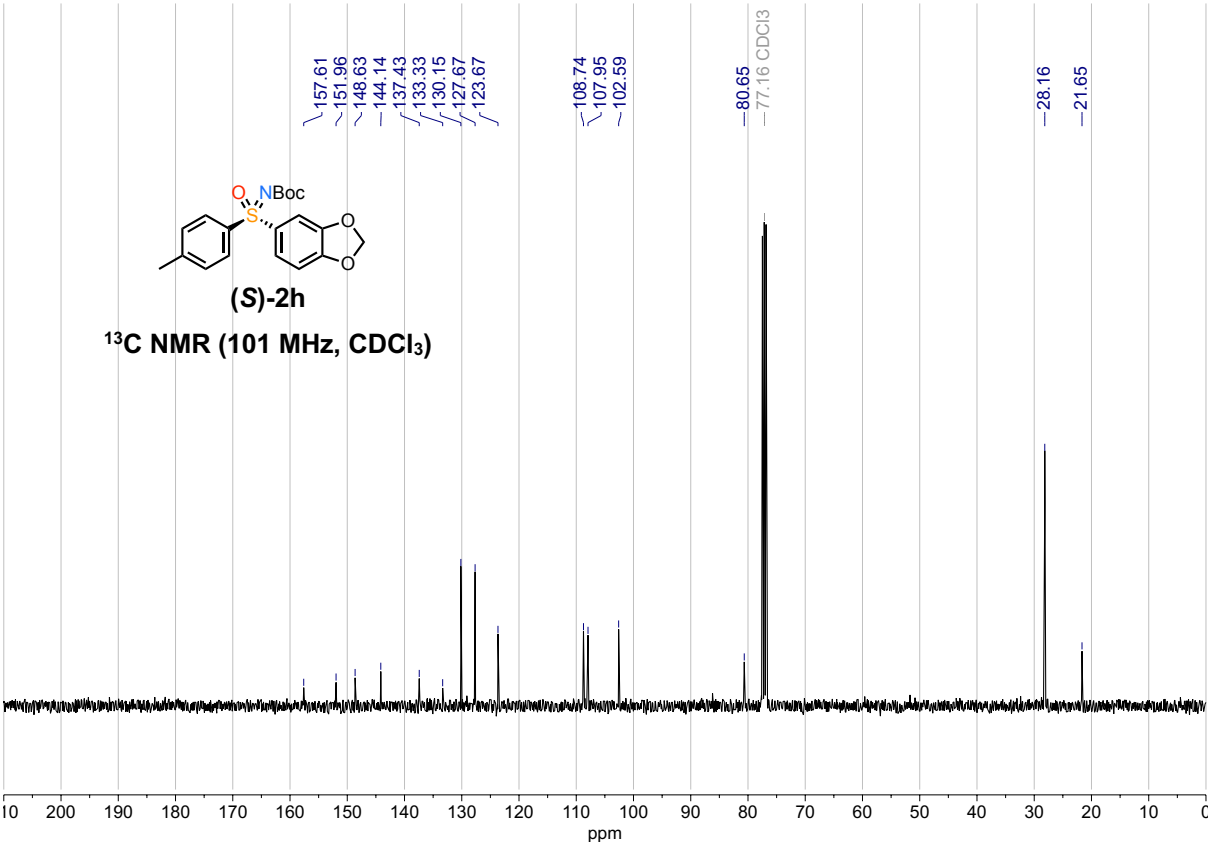
tert-Butyl (_S_)-((2-methoxyphenyl)(oxo)(_p_-tolyl)-λ^6-sulfaneylidene)carbamate ((_S_)-2g)



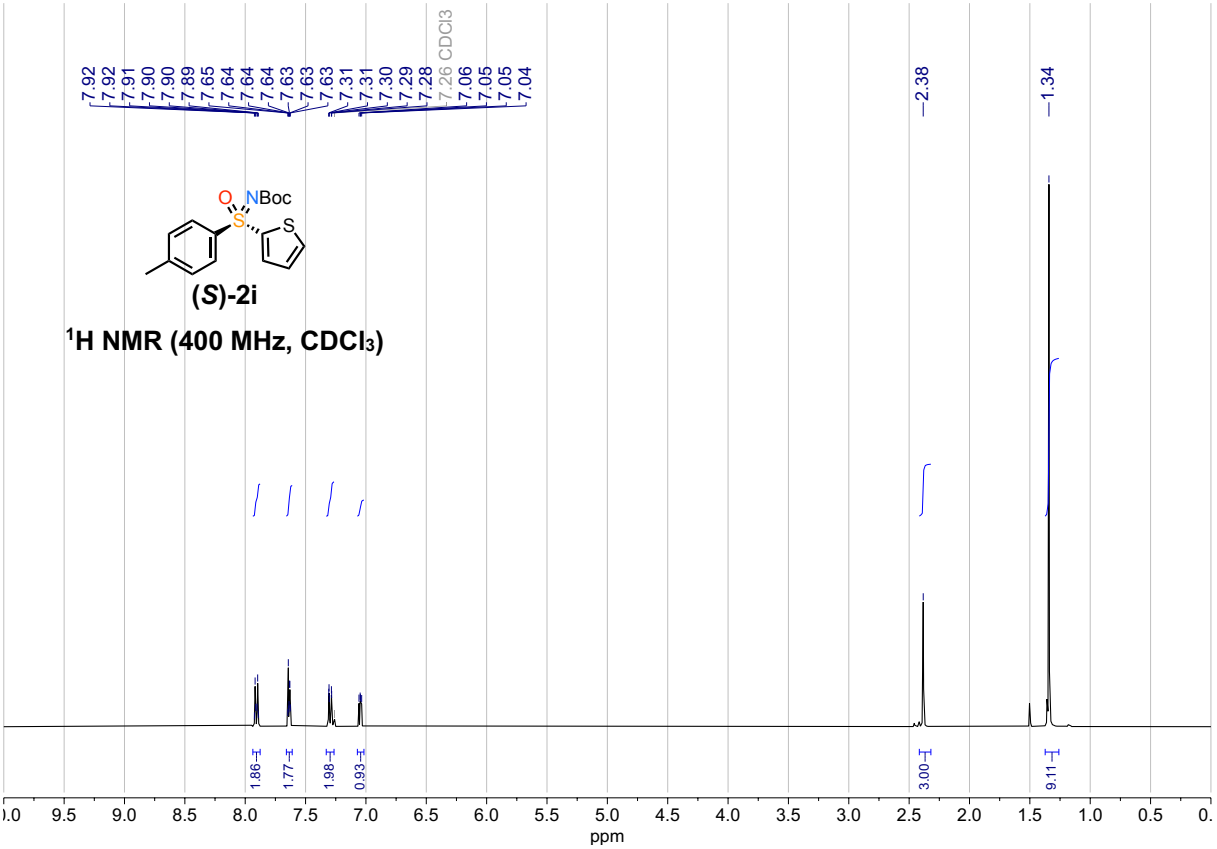


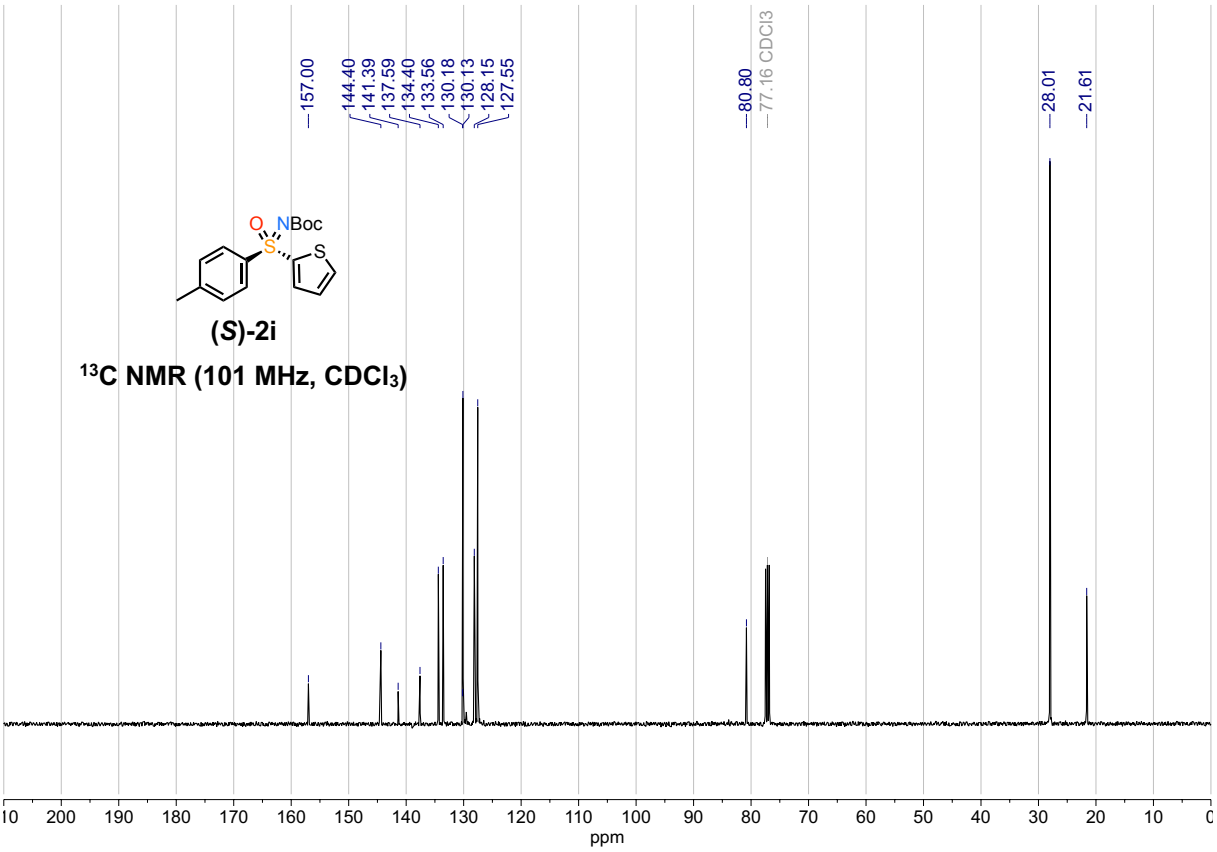
***tert*-Butyl (*S*)-(benzo[*d*][1,3]dioxol-5-yl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2h)**



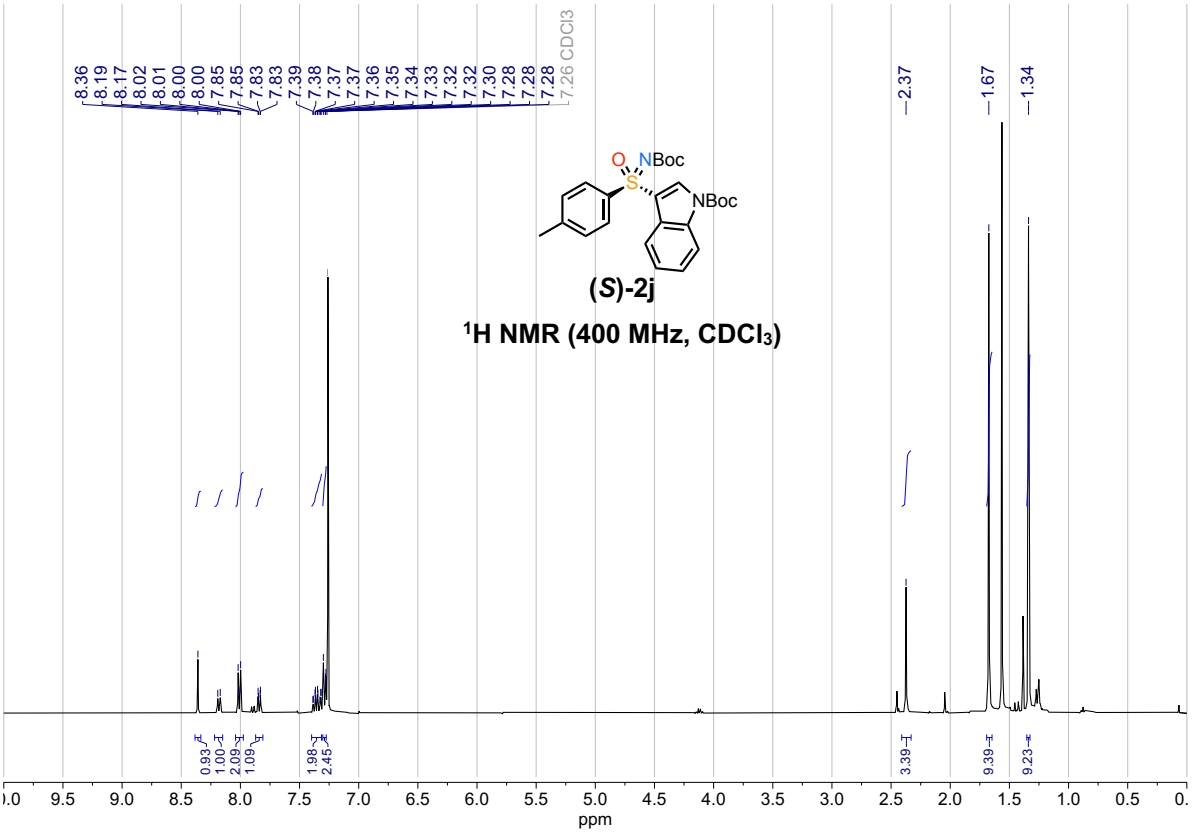


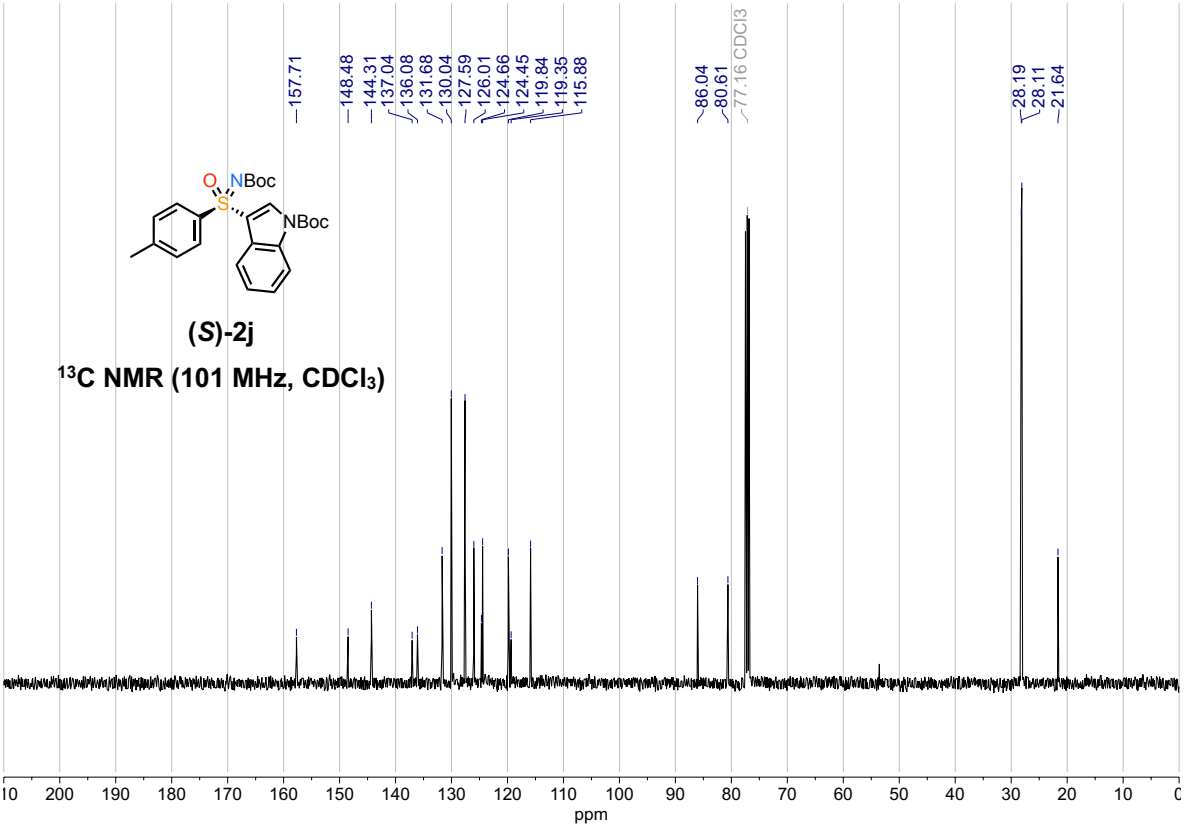
***tert*-Butyl (*S*)-(oxo(thiophen-2-yl)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2i)**



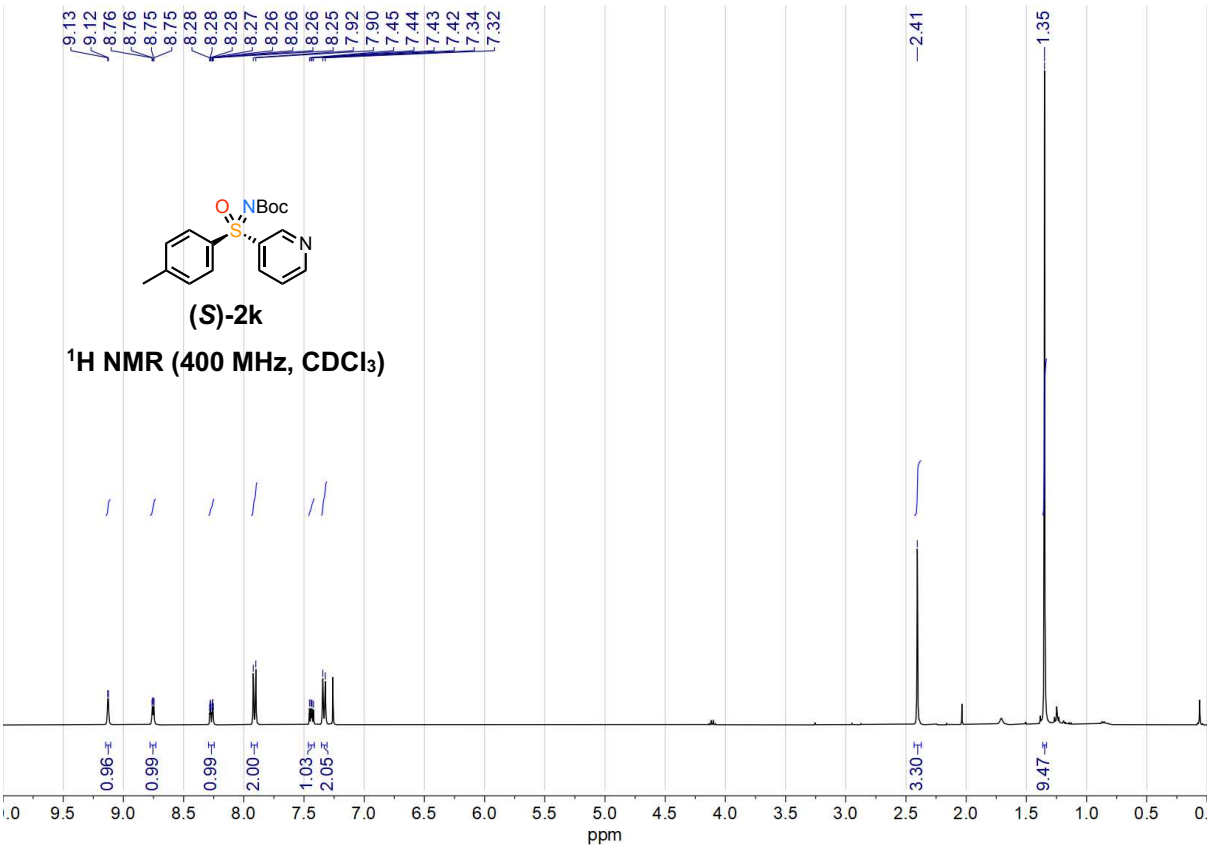


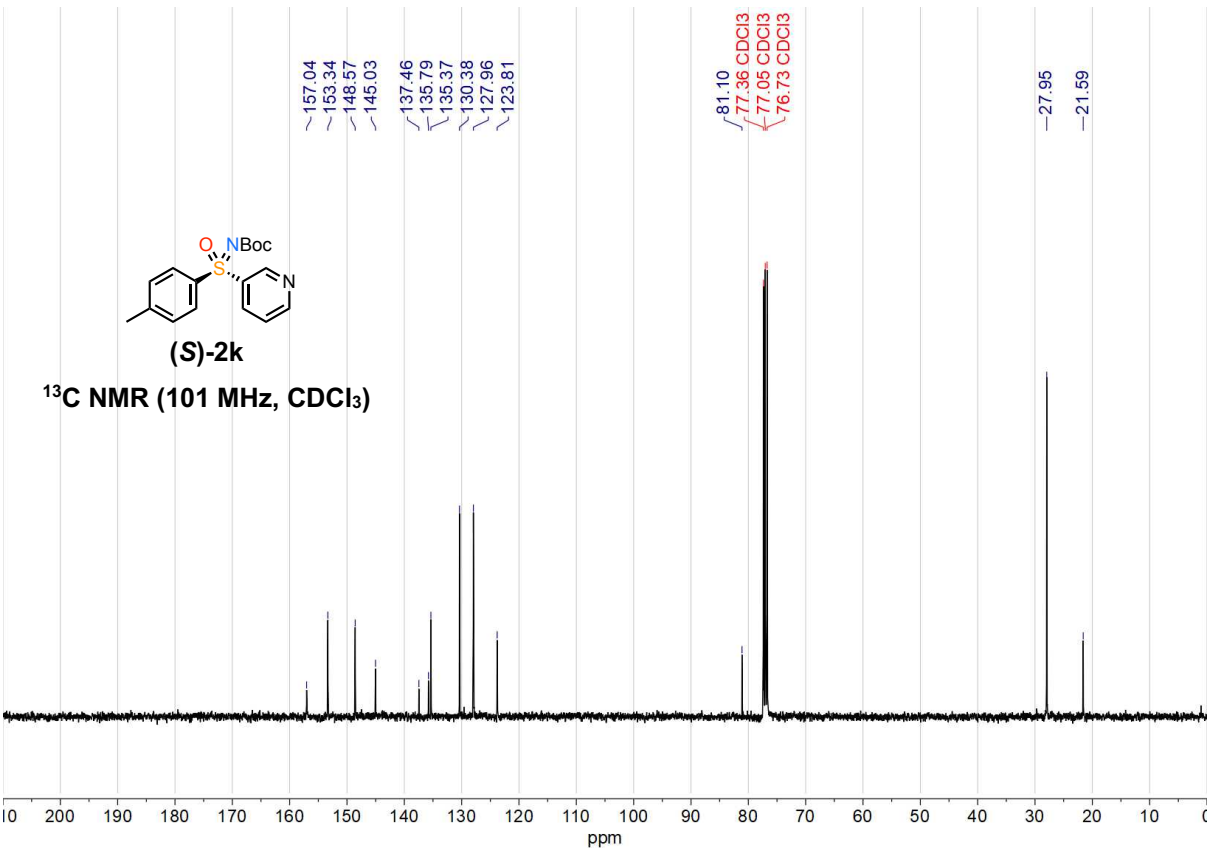
***tert*-Butyl (*S*)-3-(*N*-(*tert*-butoxycarbonyl)-4-methylphenylsulfonimidoyl)-1*H*-indole-1-carboxylate ((*S*)-2j)**



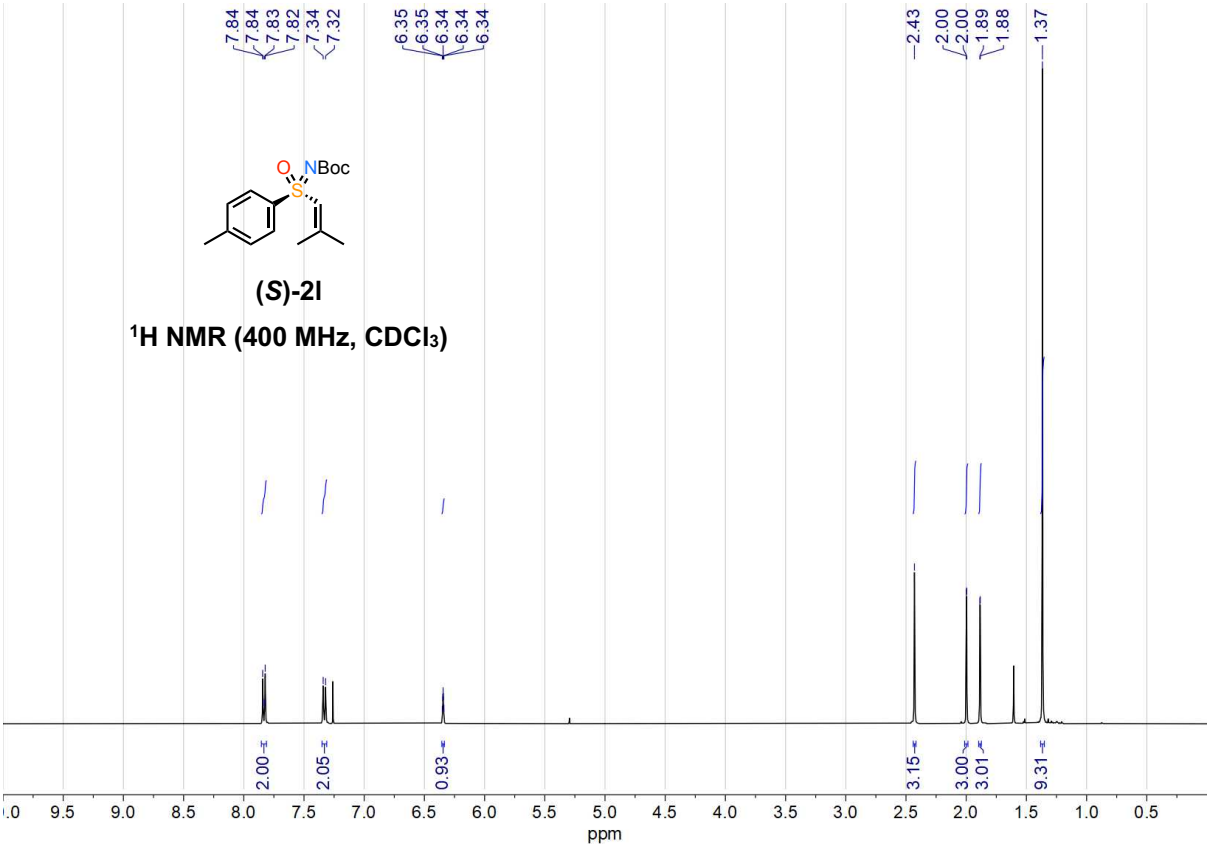


***tert*-Butyl (*S*)-(oxo(pyridin-3-yl)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2k)**



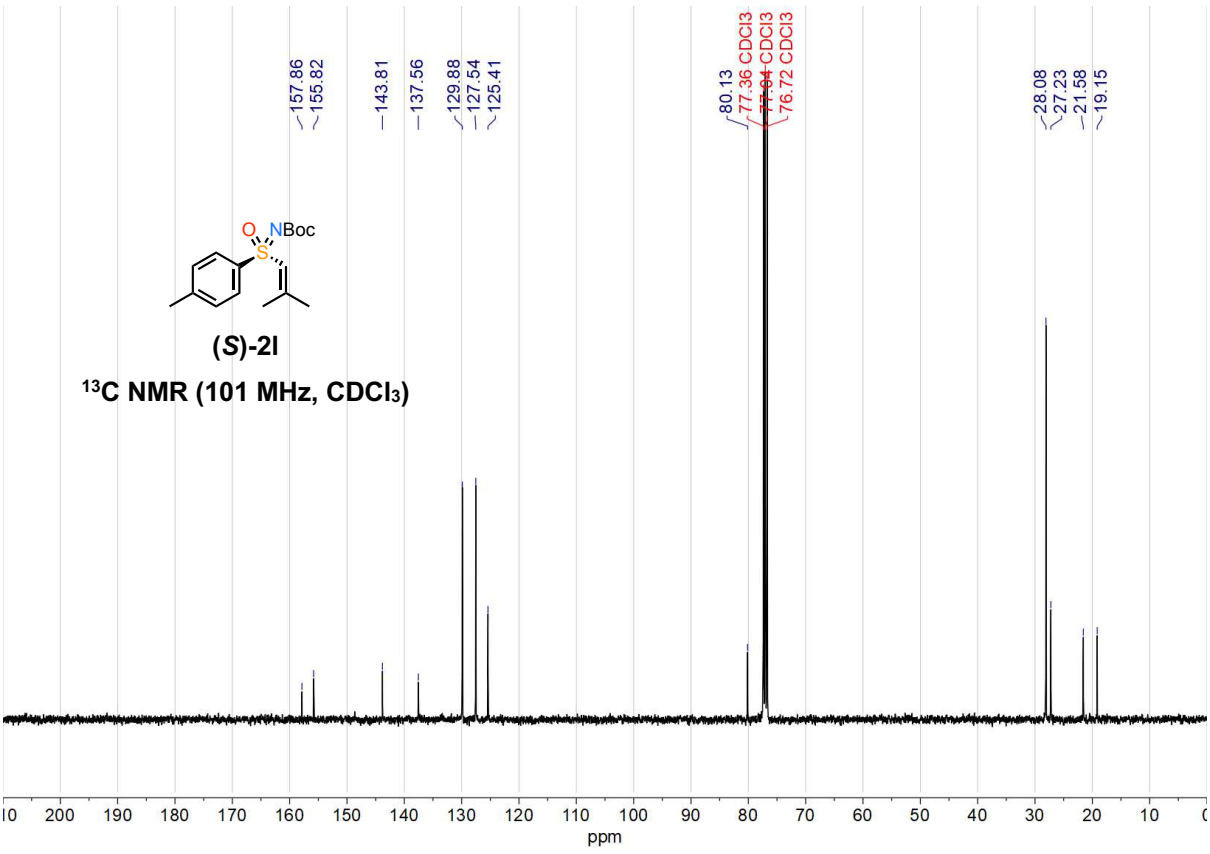


***tert*-Butyl (*R*)-((2-methylprop-1-en-1-yl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2l)**



(*S*)-2l

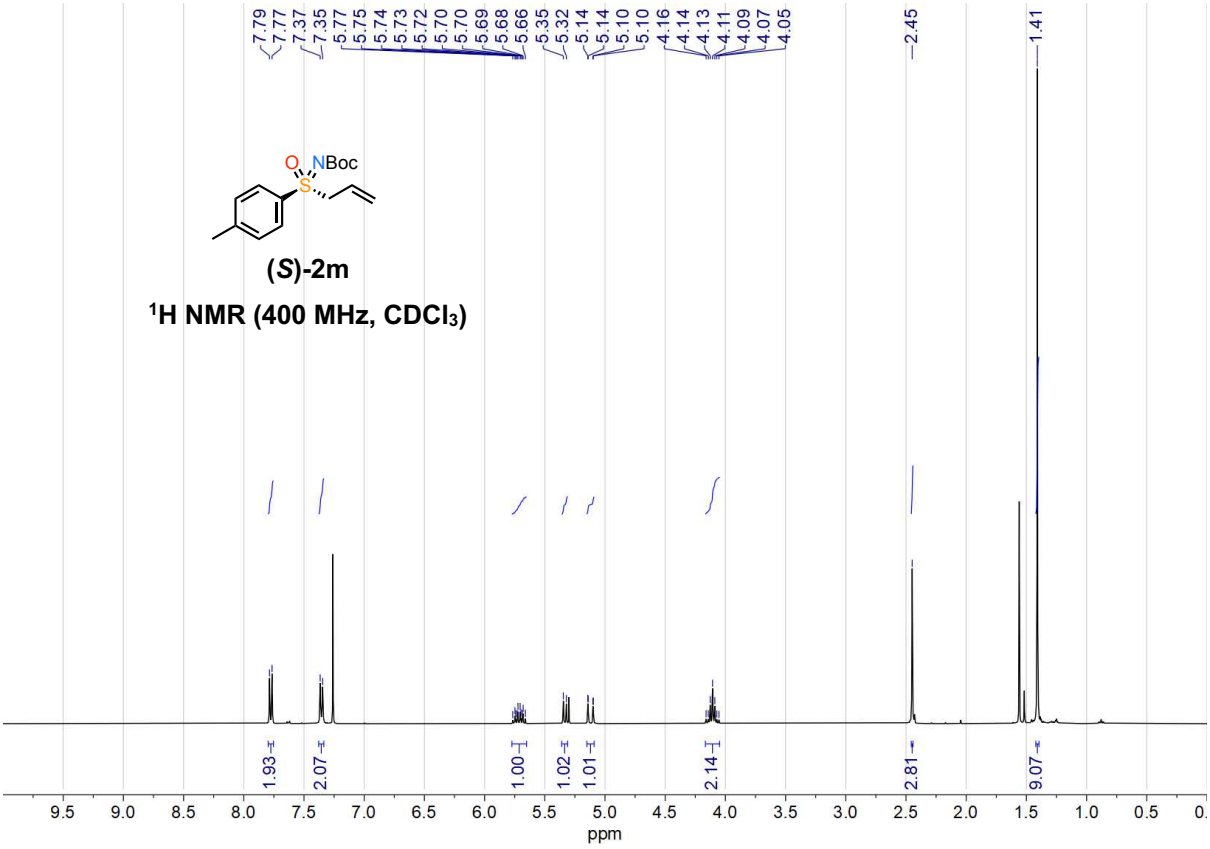
^{1}H NMR (400 MHz, $CDCl_3$)



(*S*)-2l

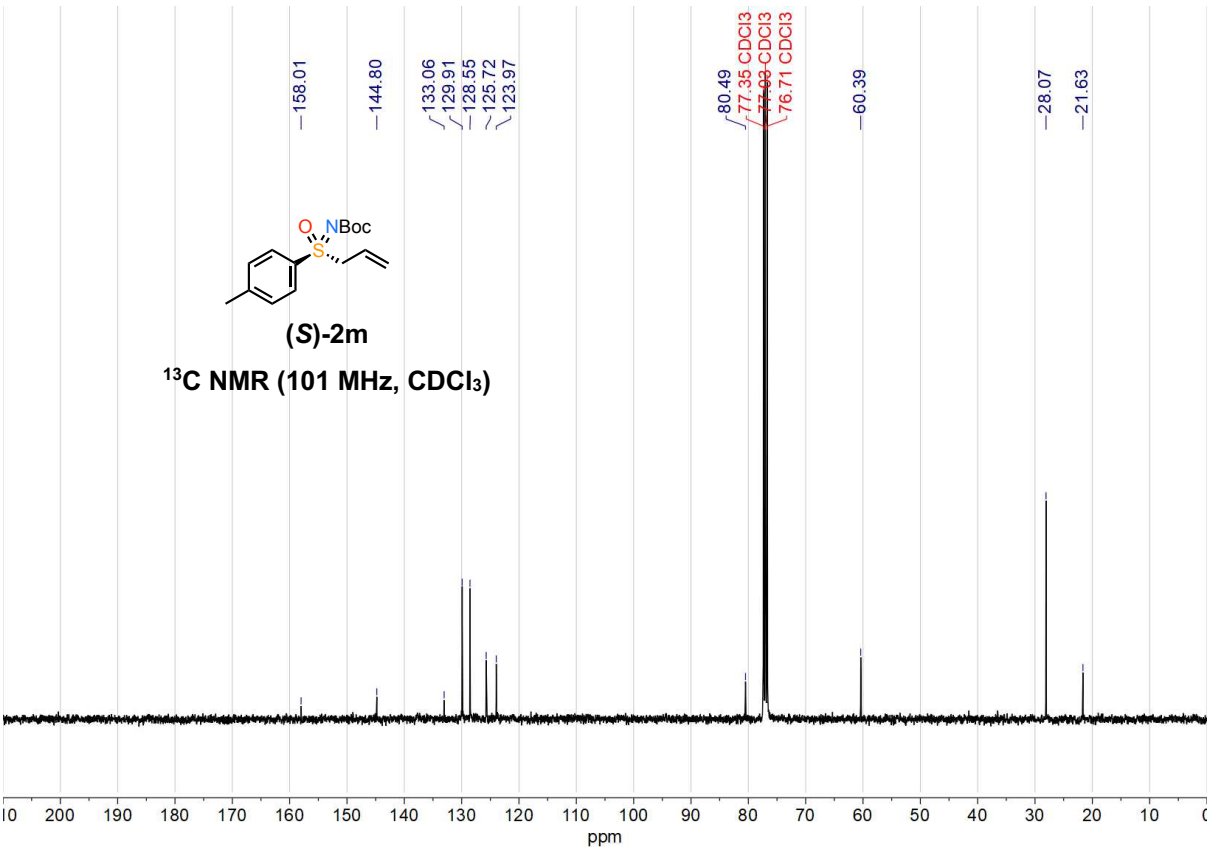
^{13}C NMR (101 MHz, $CDCl_3$)

***tert*-Butyl (*R*)-(allyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2m)**



(*S*)-2m

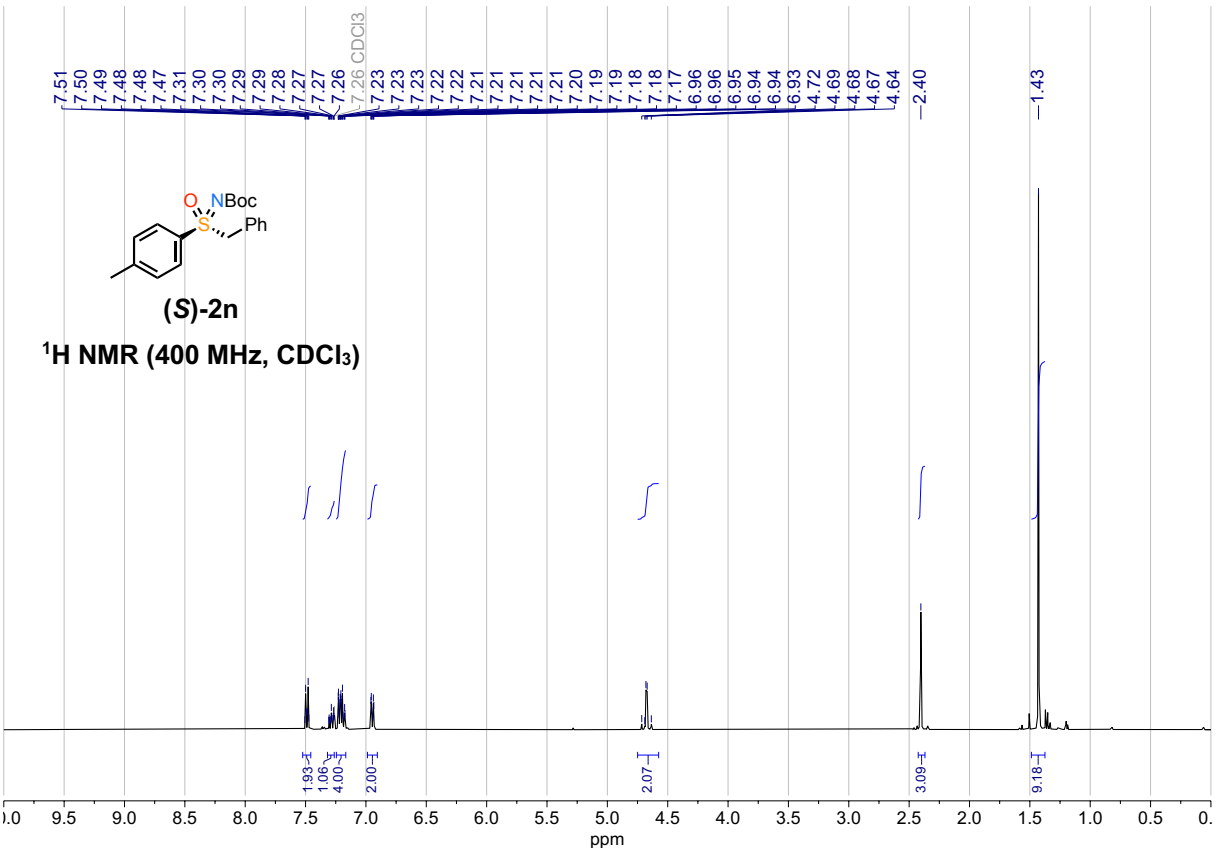
^{1}H NMR (400 MHz, $CDCl_3$)

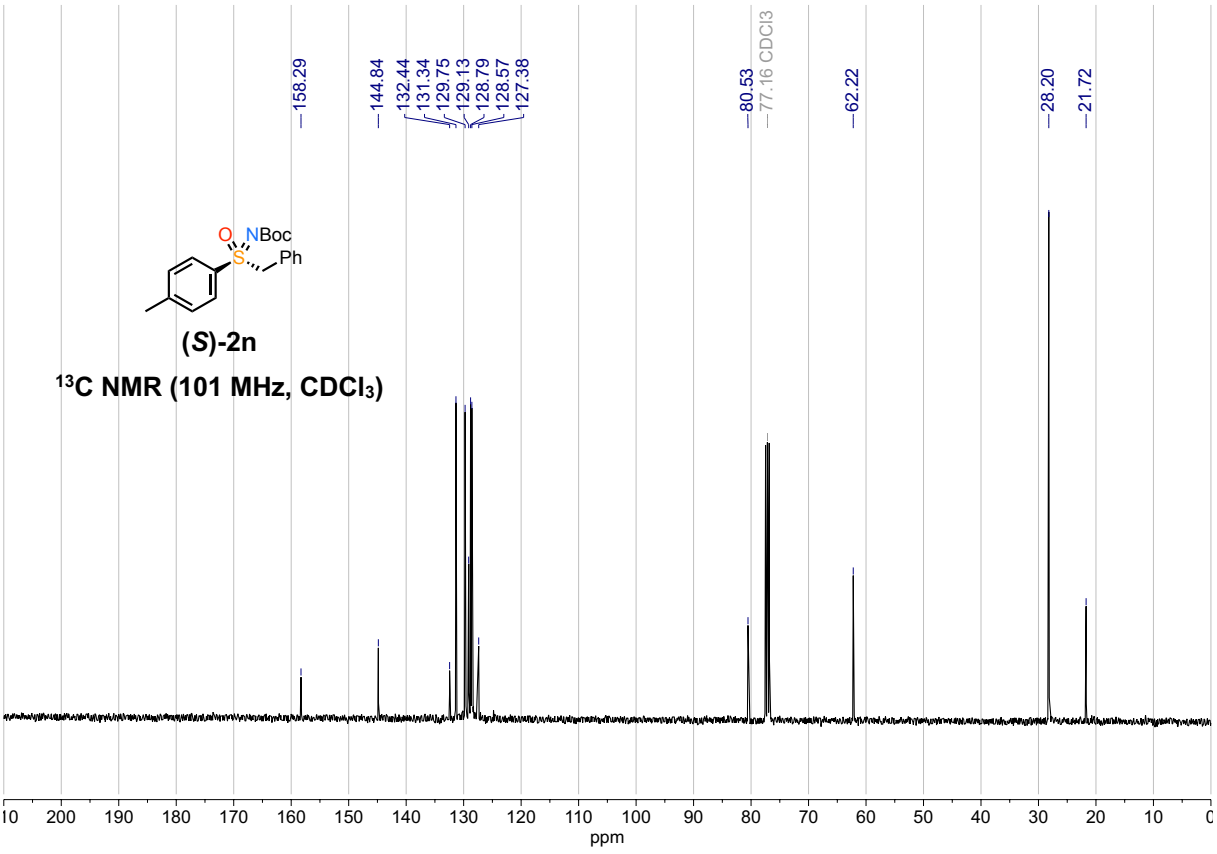


(*S*)-2m

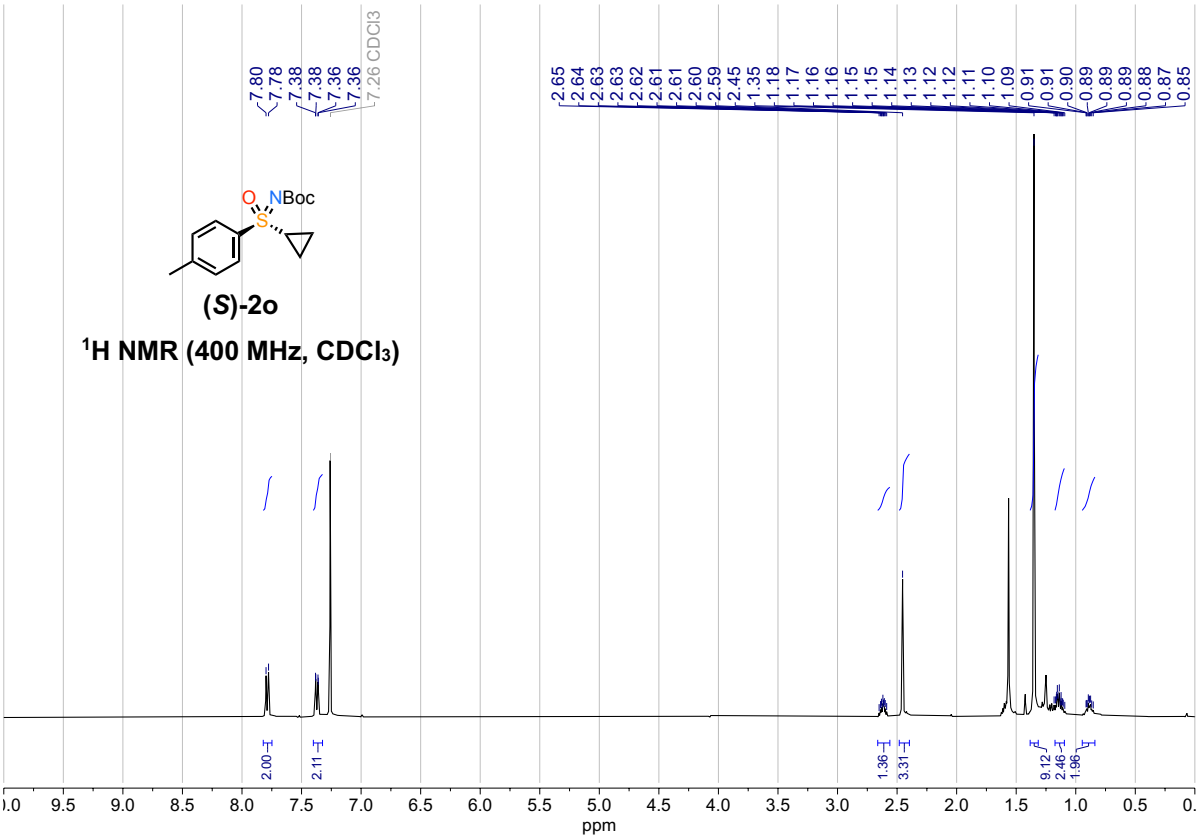
^{13}C NMR (101 MHz, $CDCl_3$)

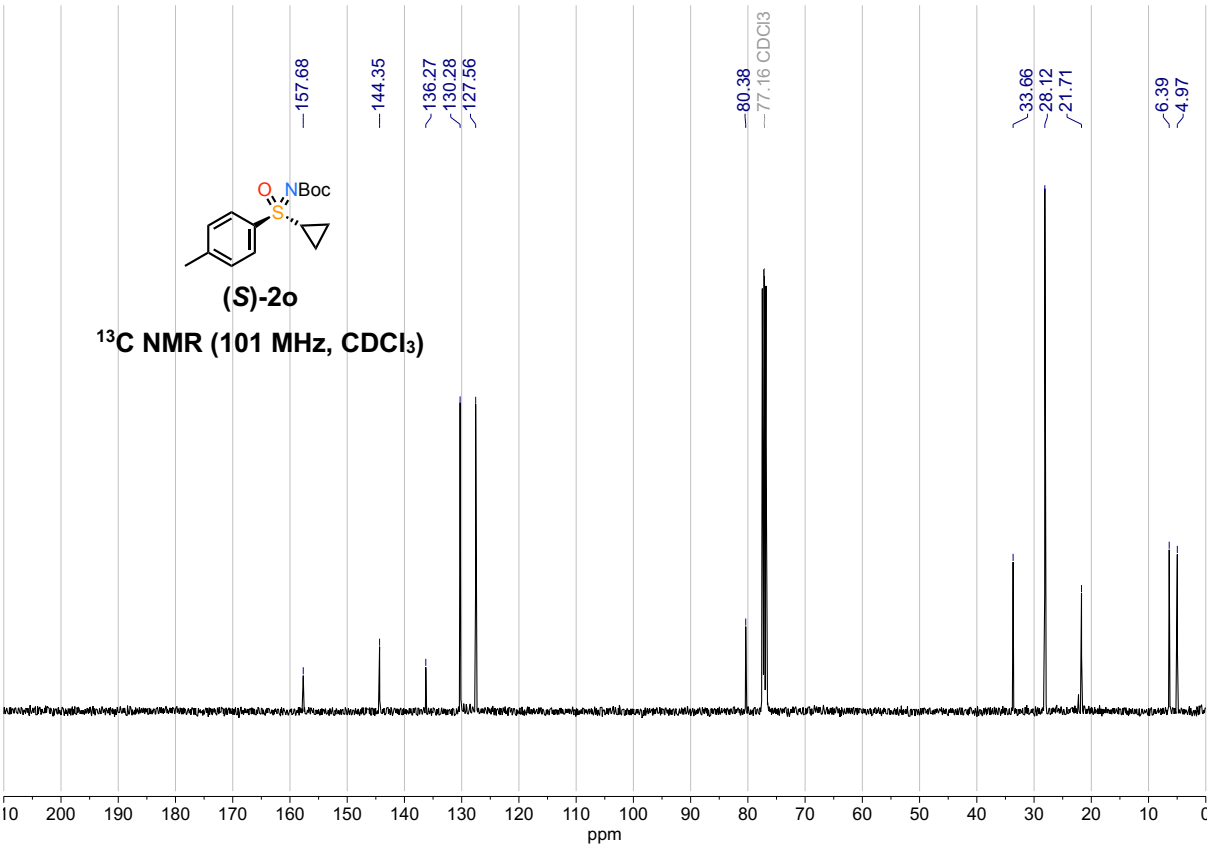
***tert*-Butyl (*R*)-(benzyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2n)**



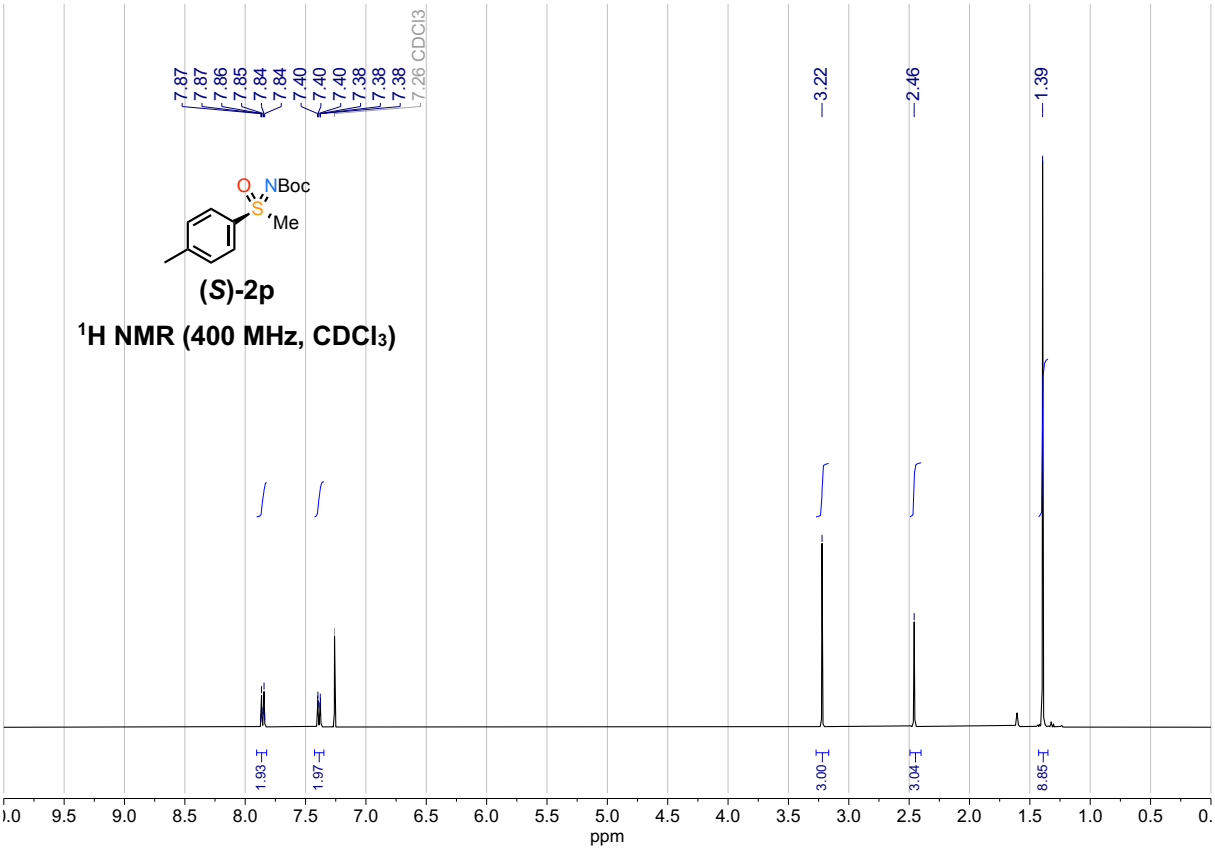


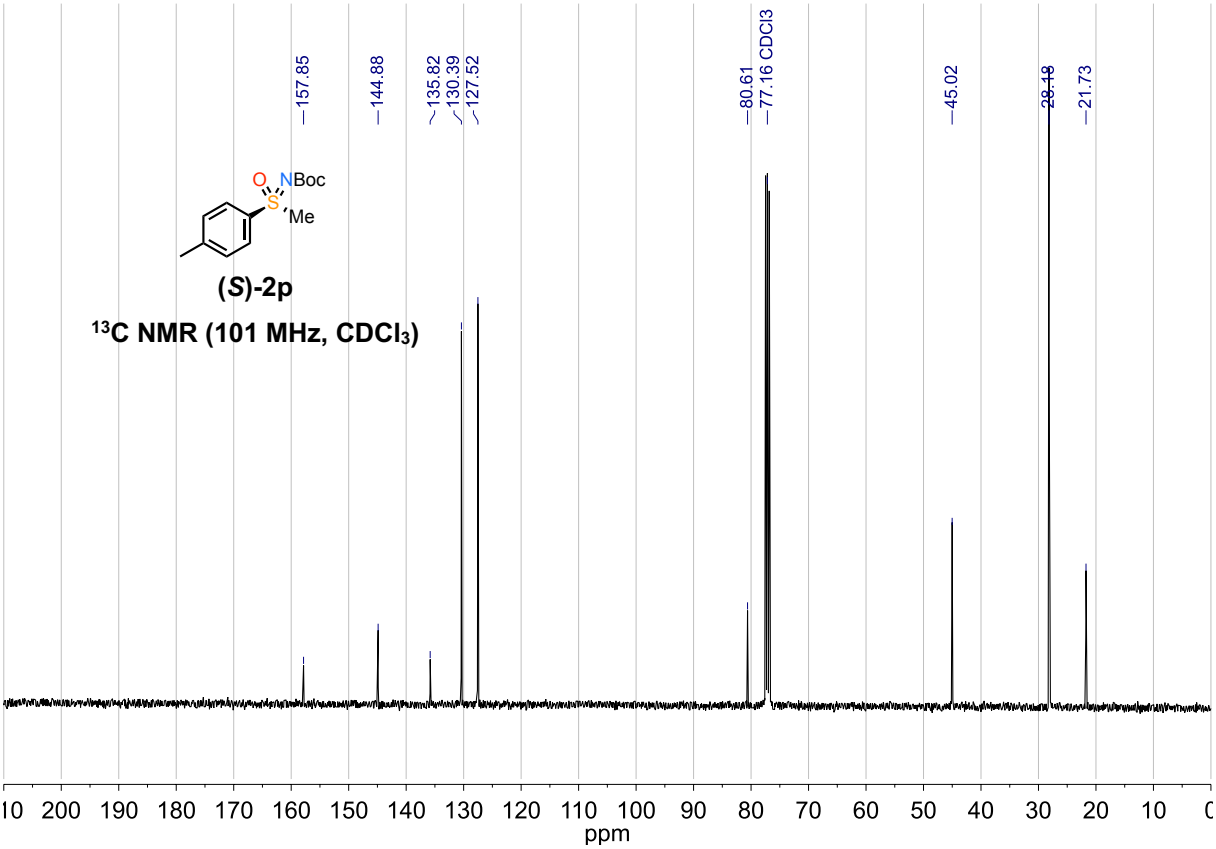
***tert*-Butyl (*R*)-(cyclopropyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2o)**



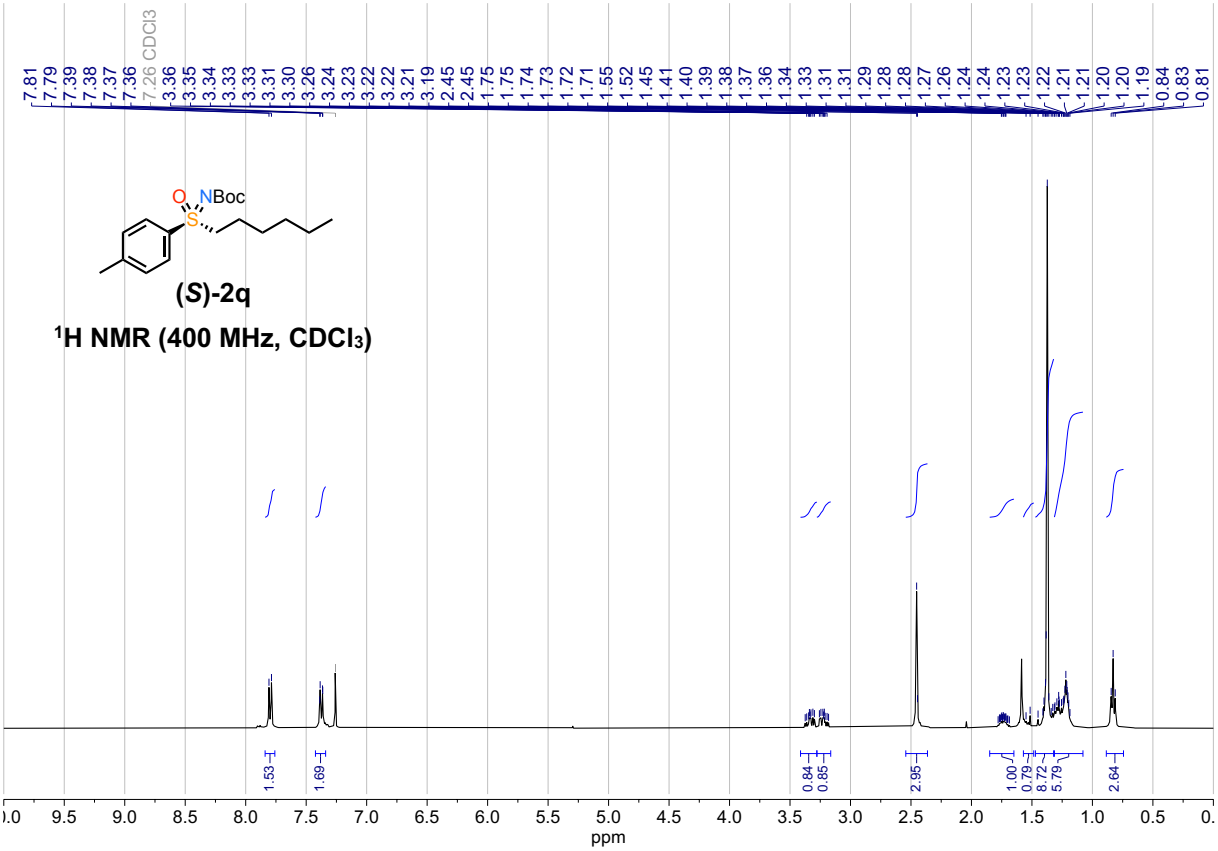


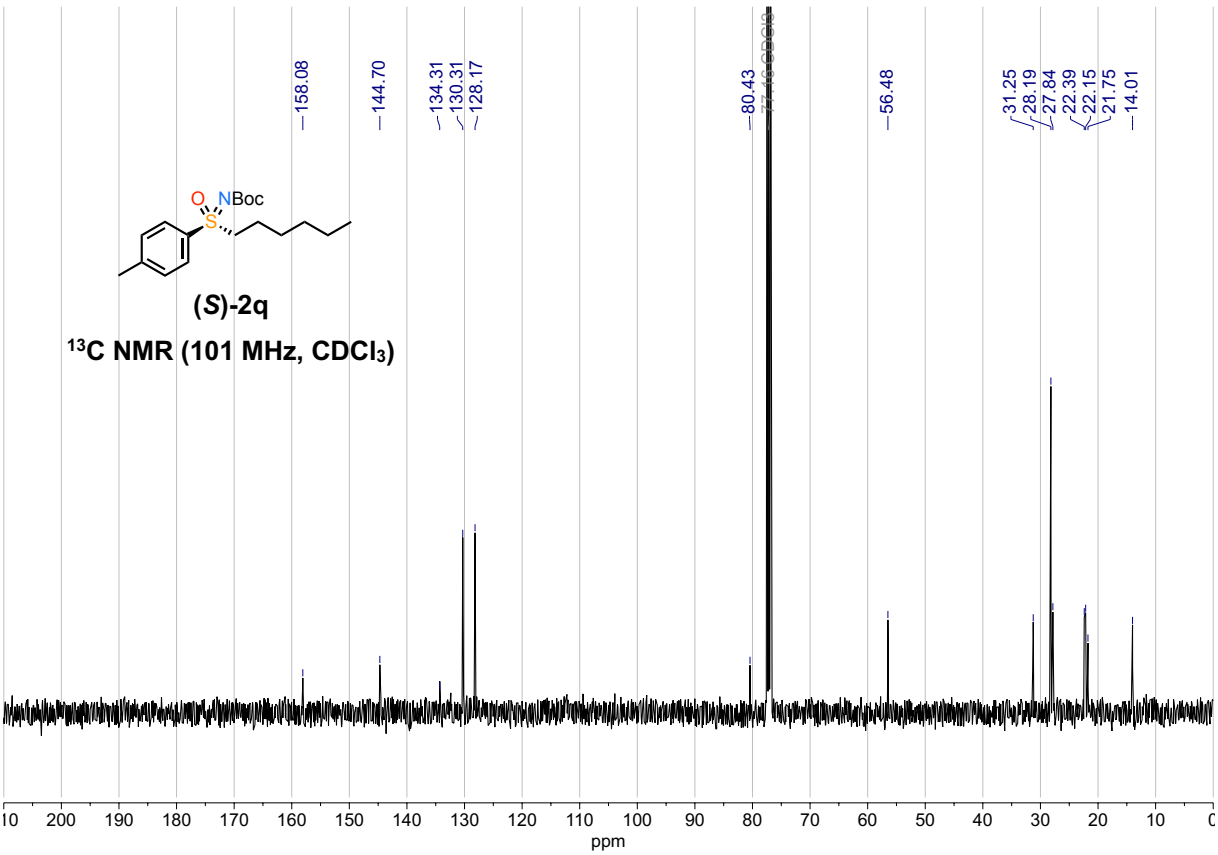
***tert*-Butyl (methyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2p)**



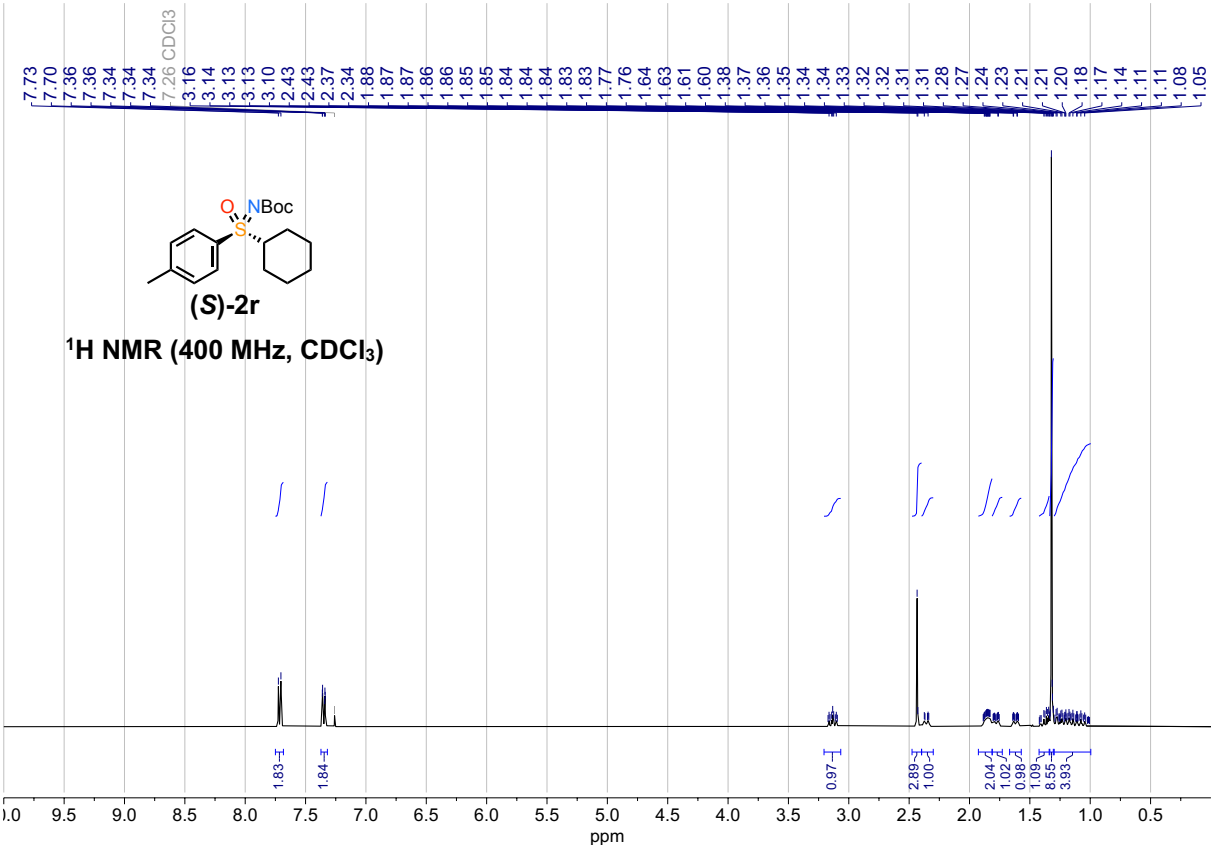


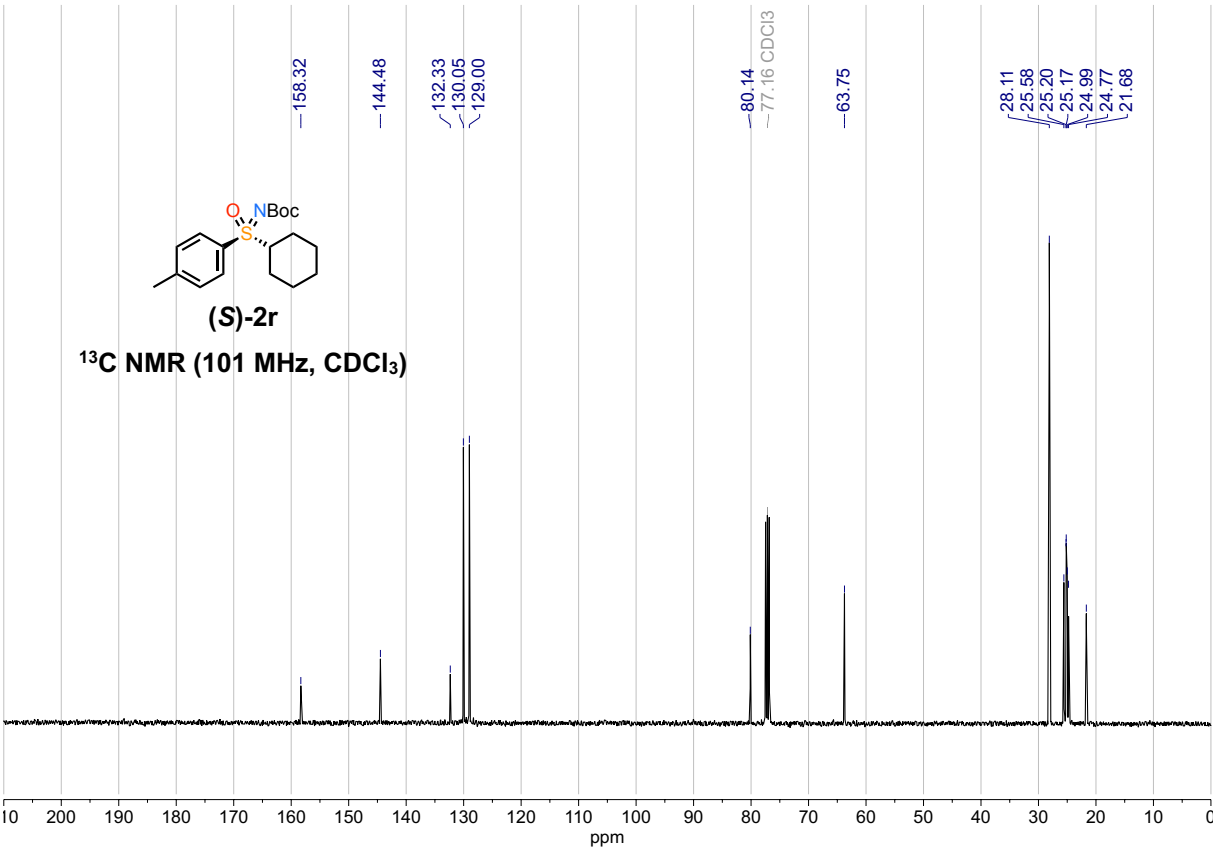
***tert*-Butyl (*R*)-(hexyl(oxo)(*p*-tolyl)- λ^6-sulfaneylidene)carbamate ((*S*)-2q)**



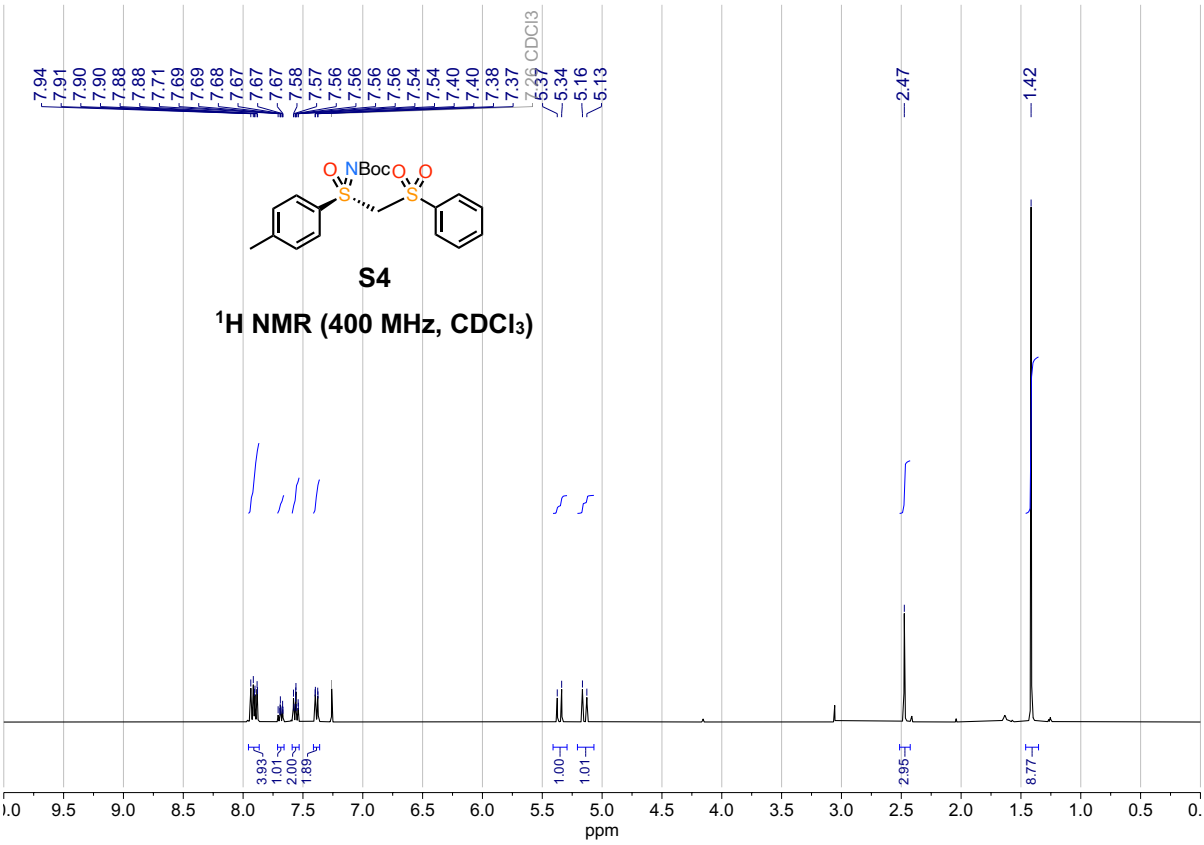


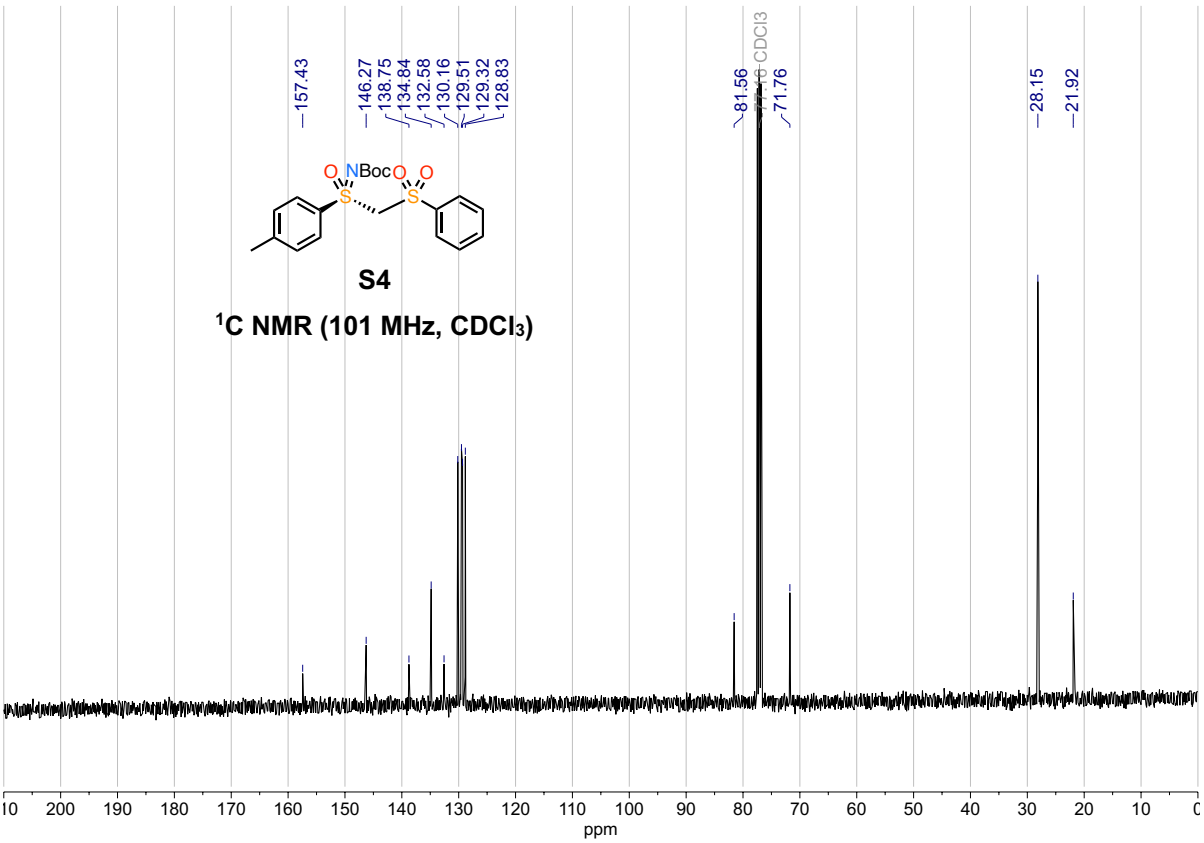
tert-Butyl (_R_)-(cyclohexyl(oxo)(_p_-tolyl)-λ^6-sulfaneylidene)carbamate ((_S_)-2r)



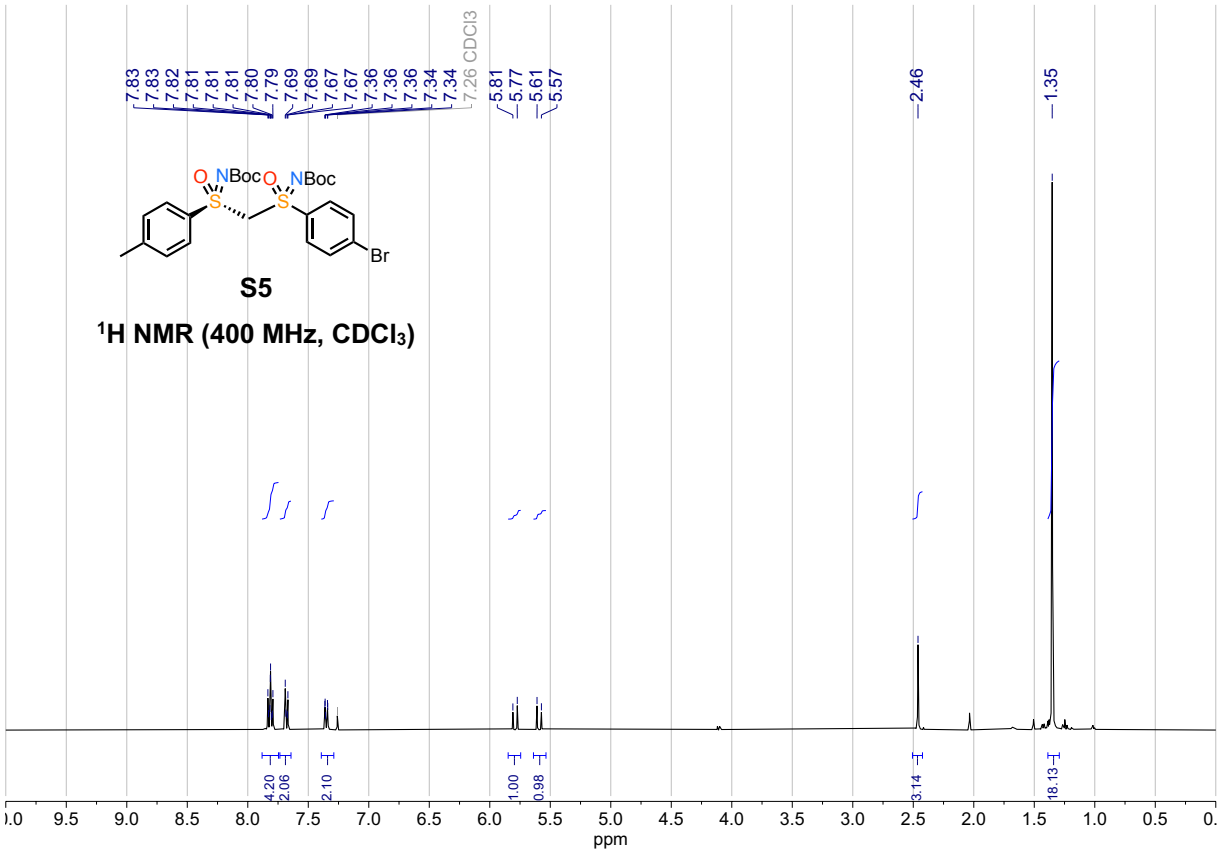


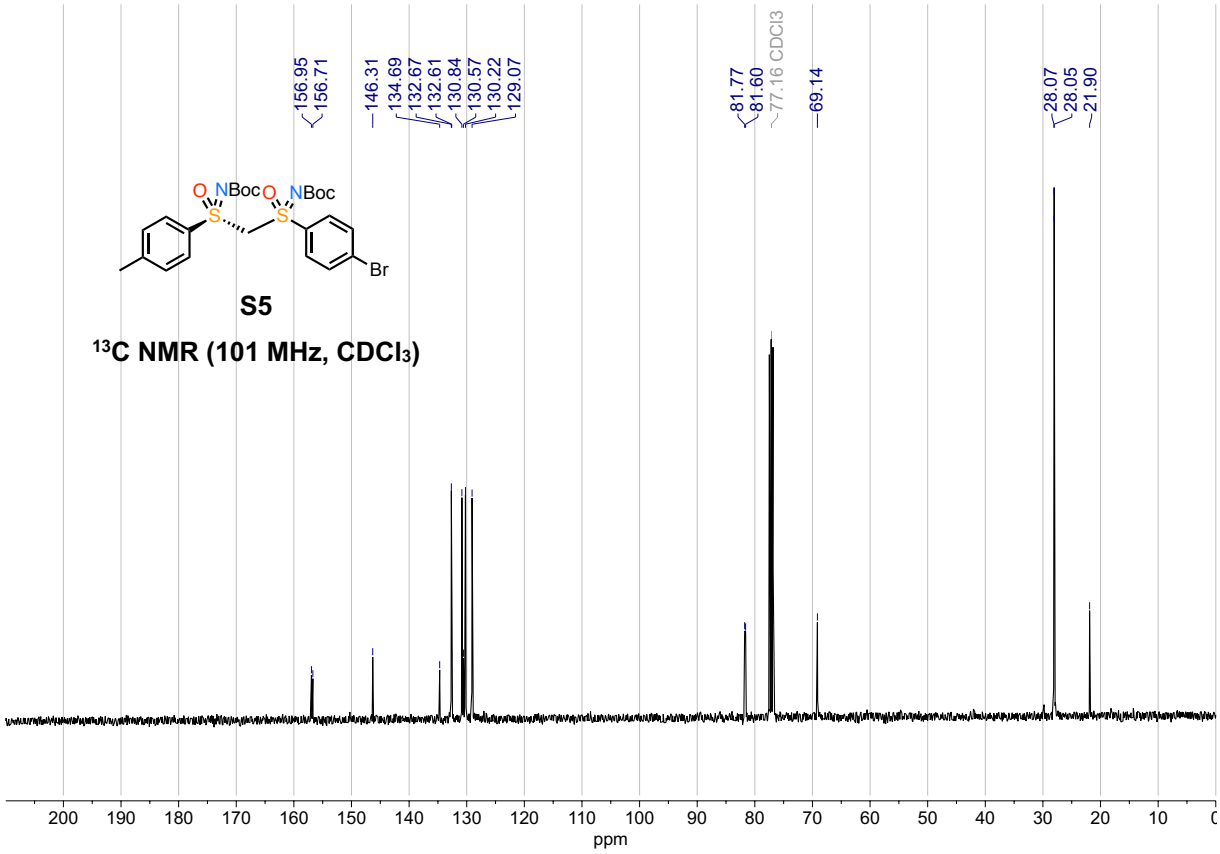
***tert*-Butyl (*S*)-(oxo((phenylsulfonyl)methyl)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (S4)**



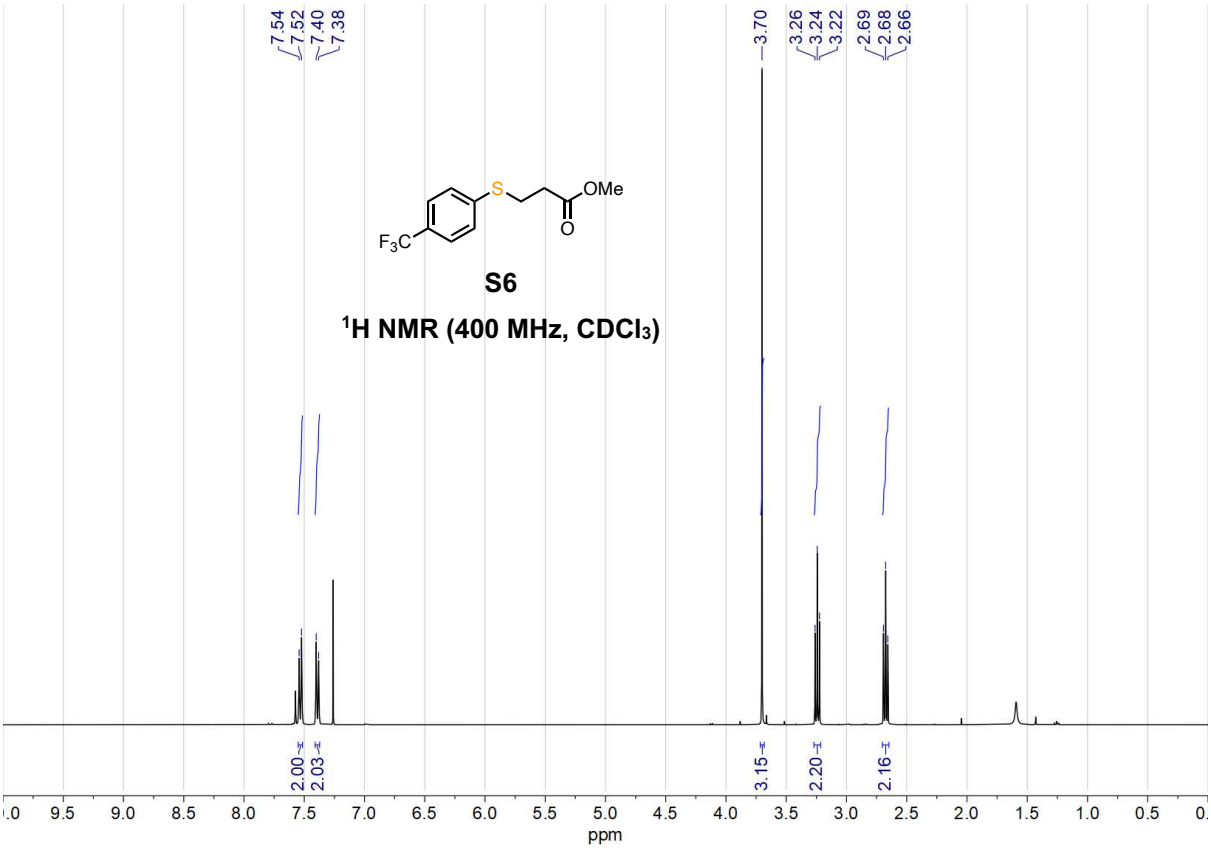


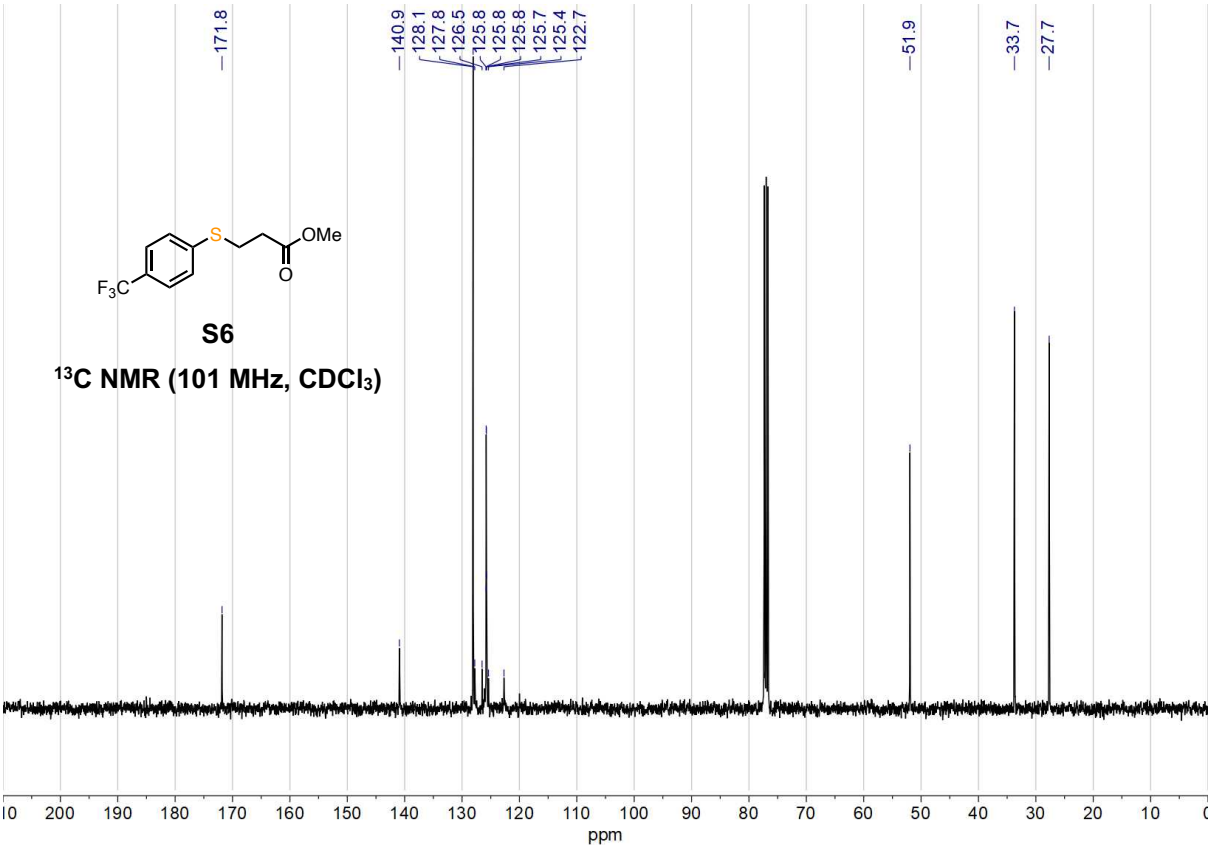
***tert*-Butyl ((1*S*)-((4-bromo-*N*-(*tert*-butoxycarbonyl)phenylsulfonimidoyl)methyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (S5)**

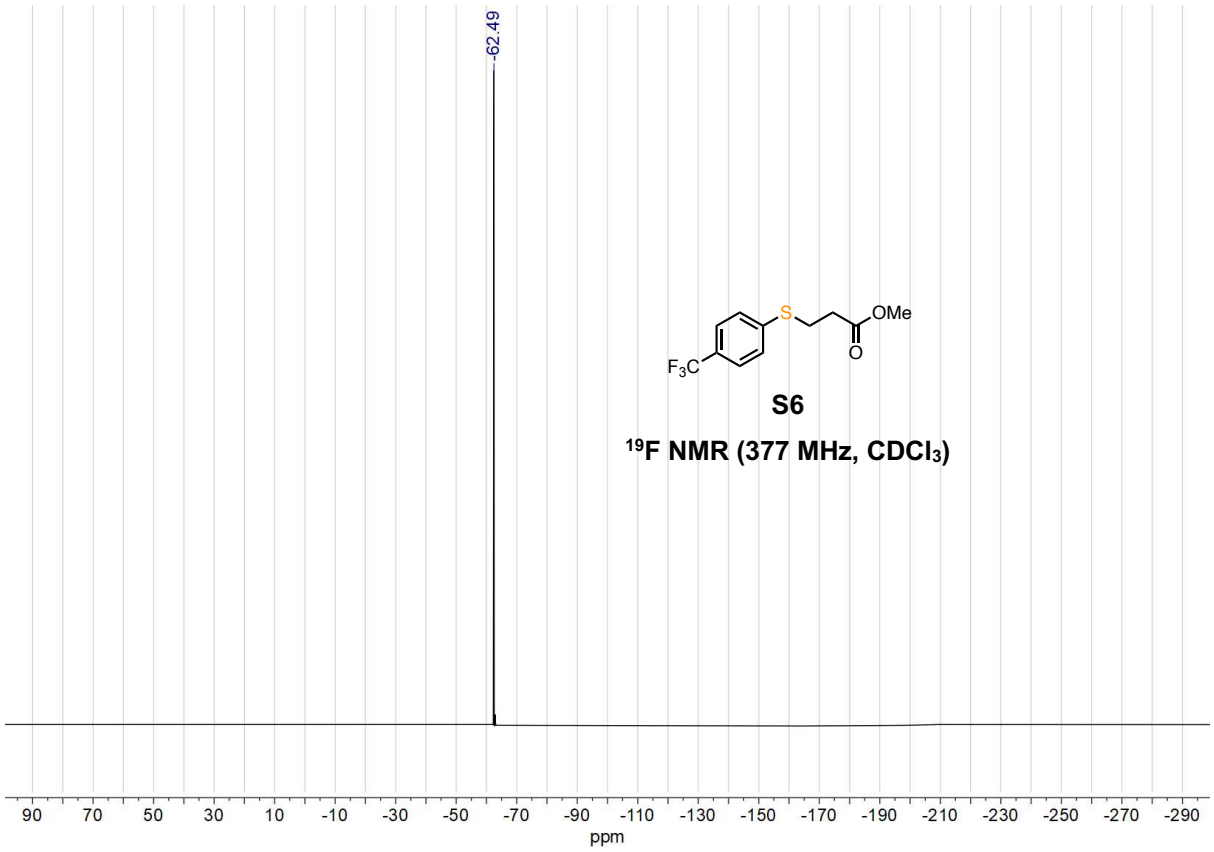




Methyl 3-((4-(trifluoromethyl)phenyl)thio)propanoate (S6)



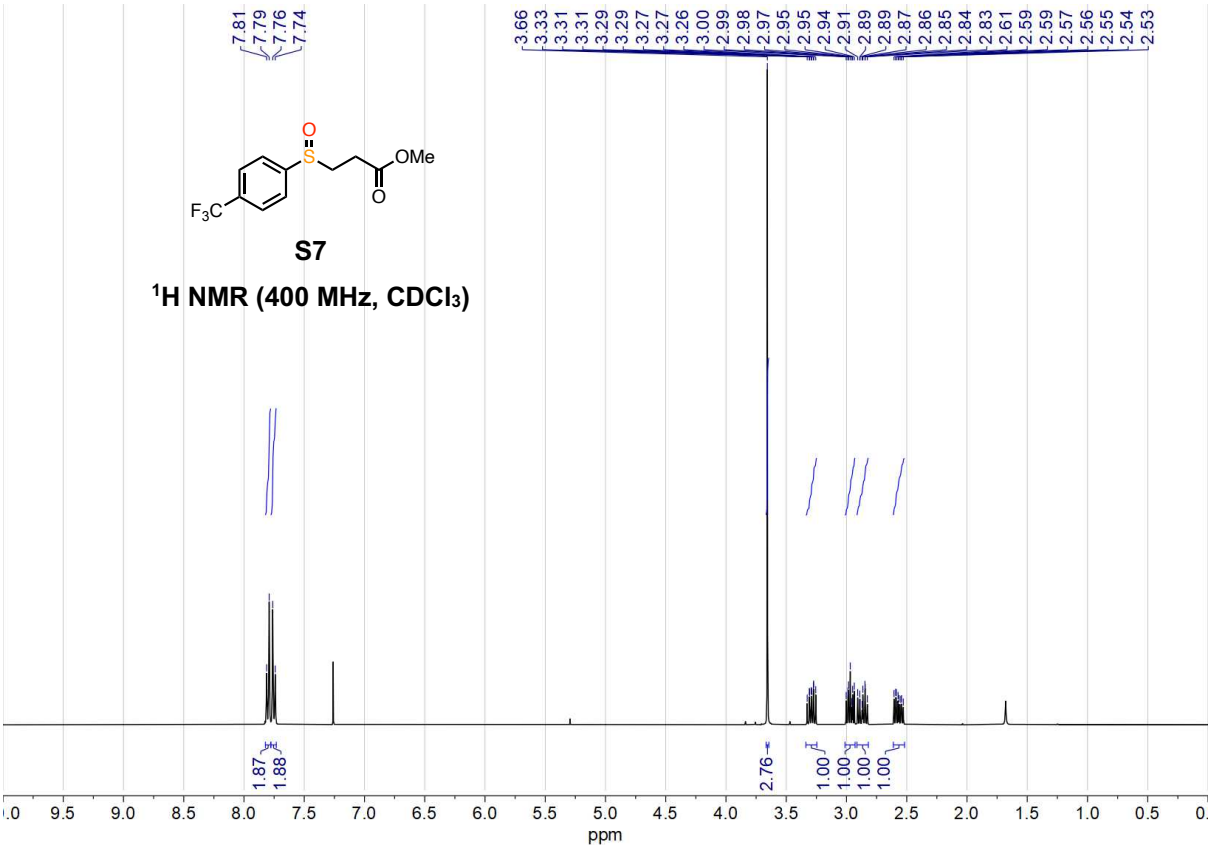


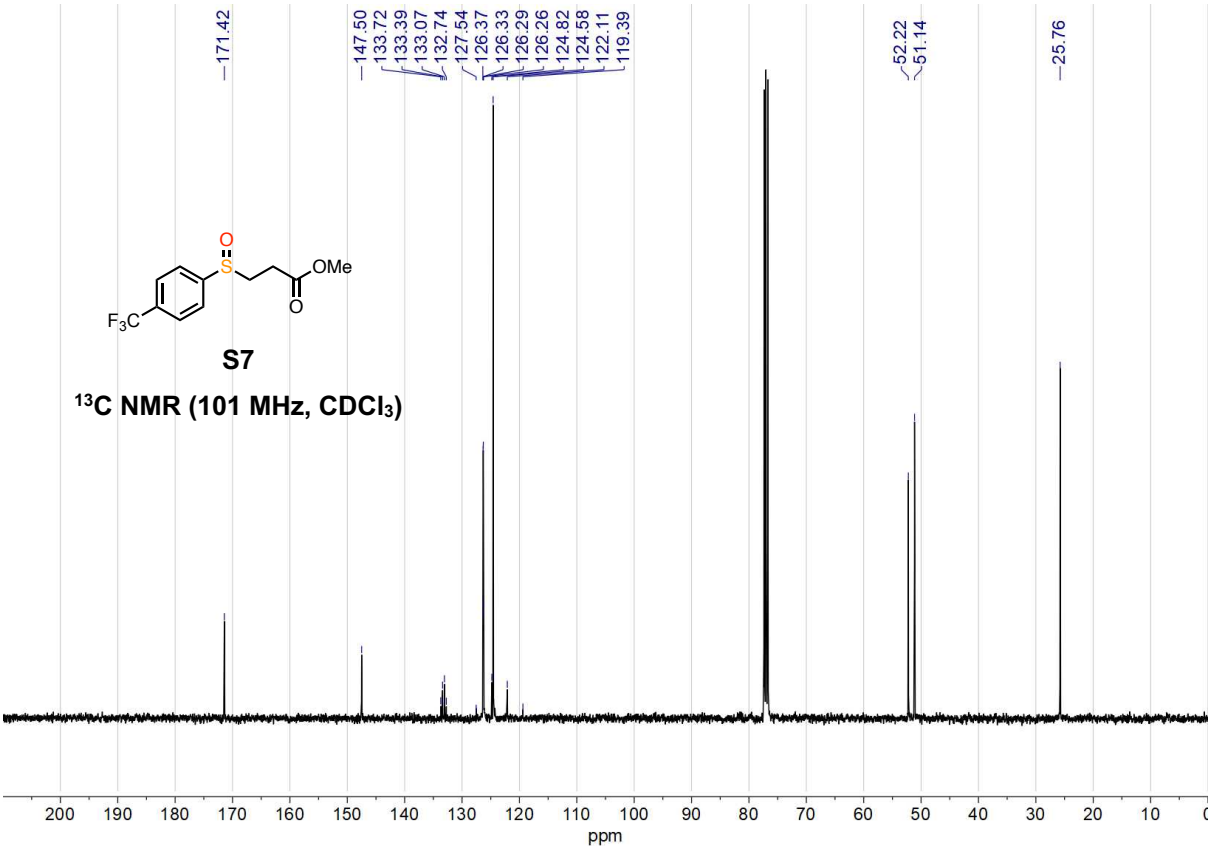


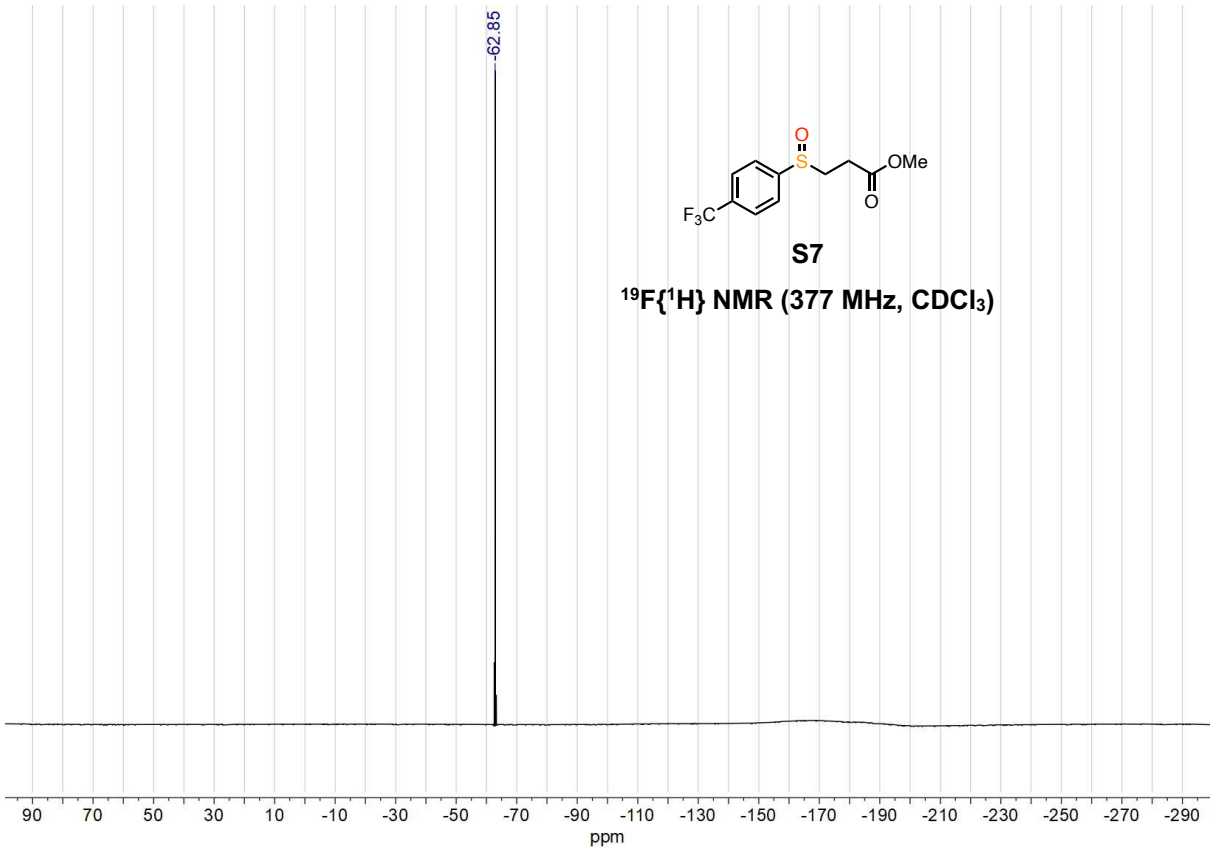
S6

^{19}F NMR (377 MHz, $CDCl_3$)

Methyl 3-((4-(trifluoromethyl)phenyl)sulfinyl)propanoate (S7)



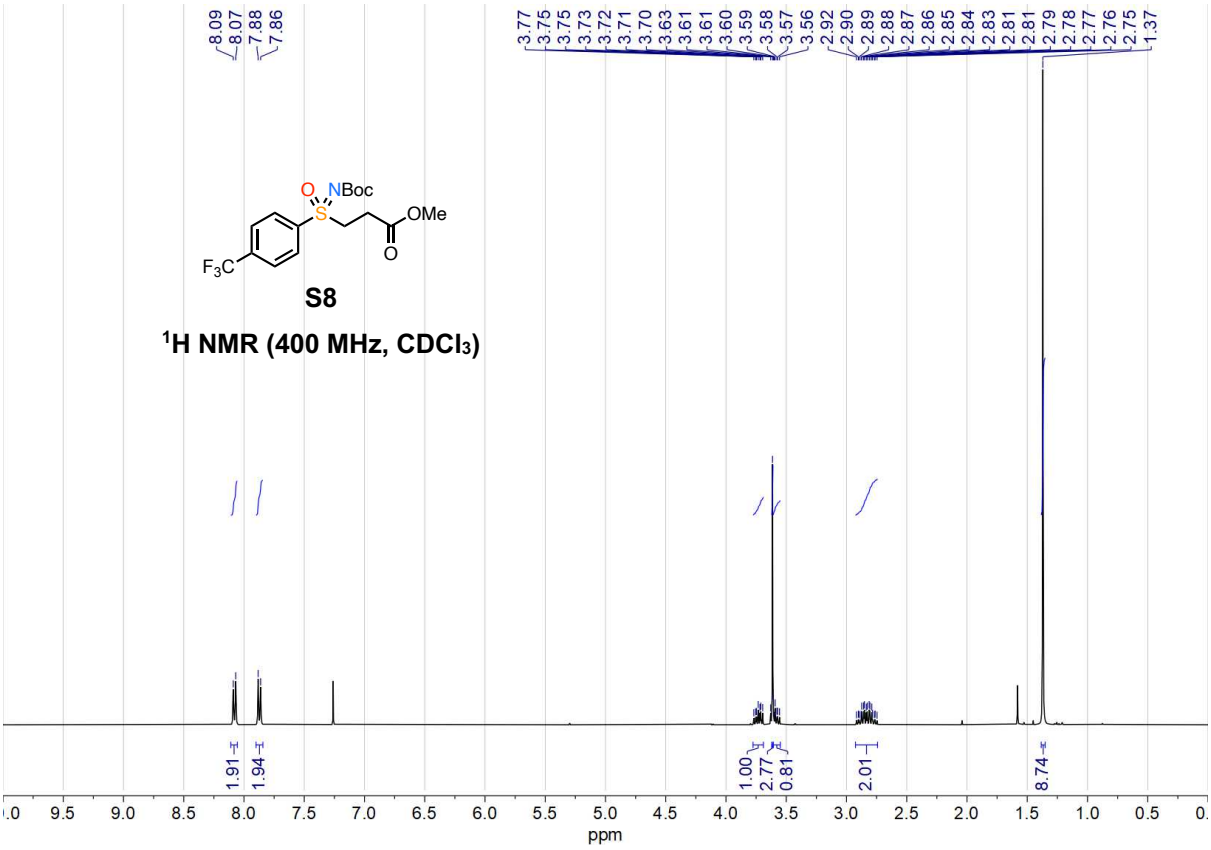




S7

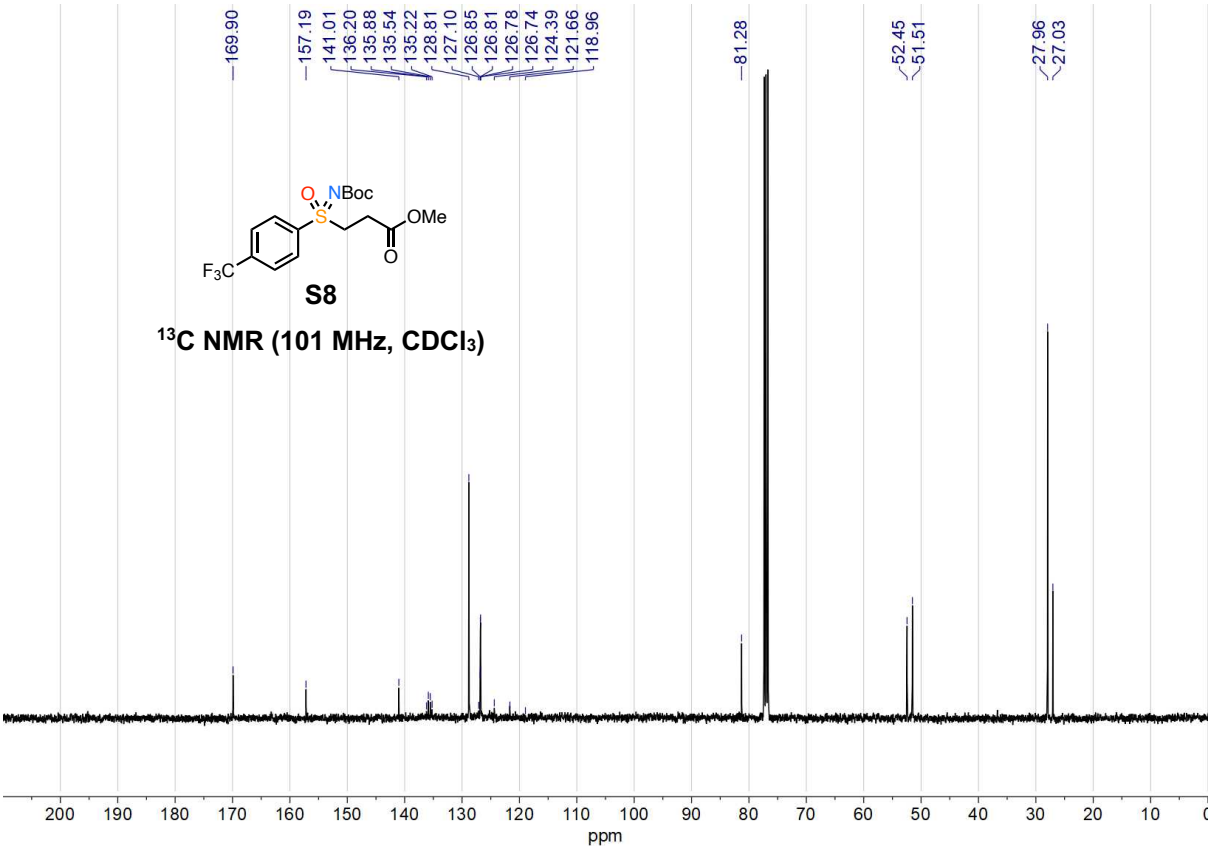
$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$)

Methyl 3-(*N*-(*tert*-butoxycarbonyl)-4-(trifluoromethyl)phenylsulfonimidoyl)propanoate (S8)



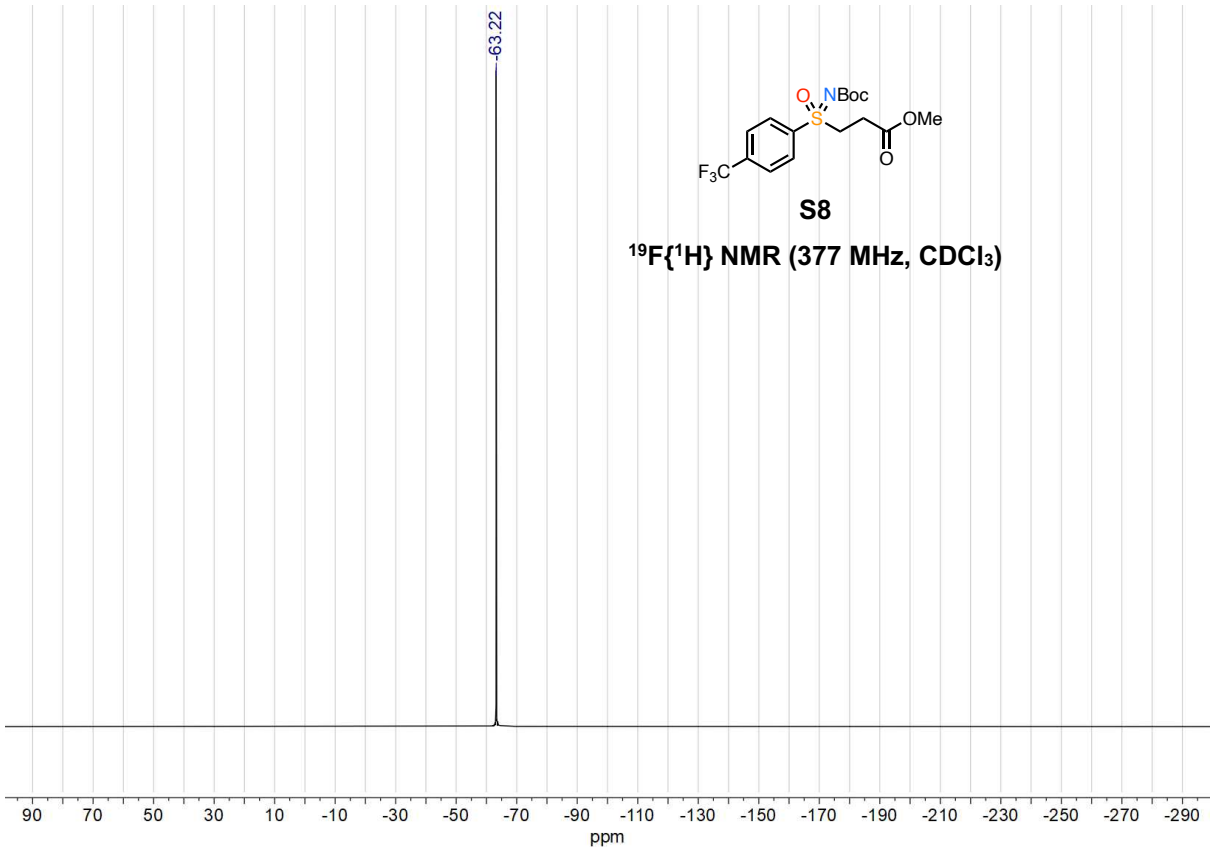
S8

^{1}H NMR (400 MHz, $CDCl_3$)



S8

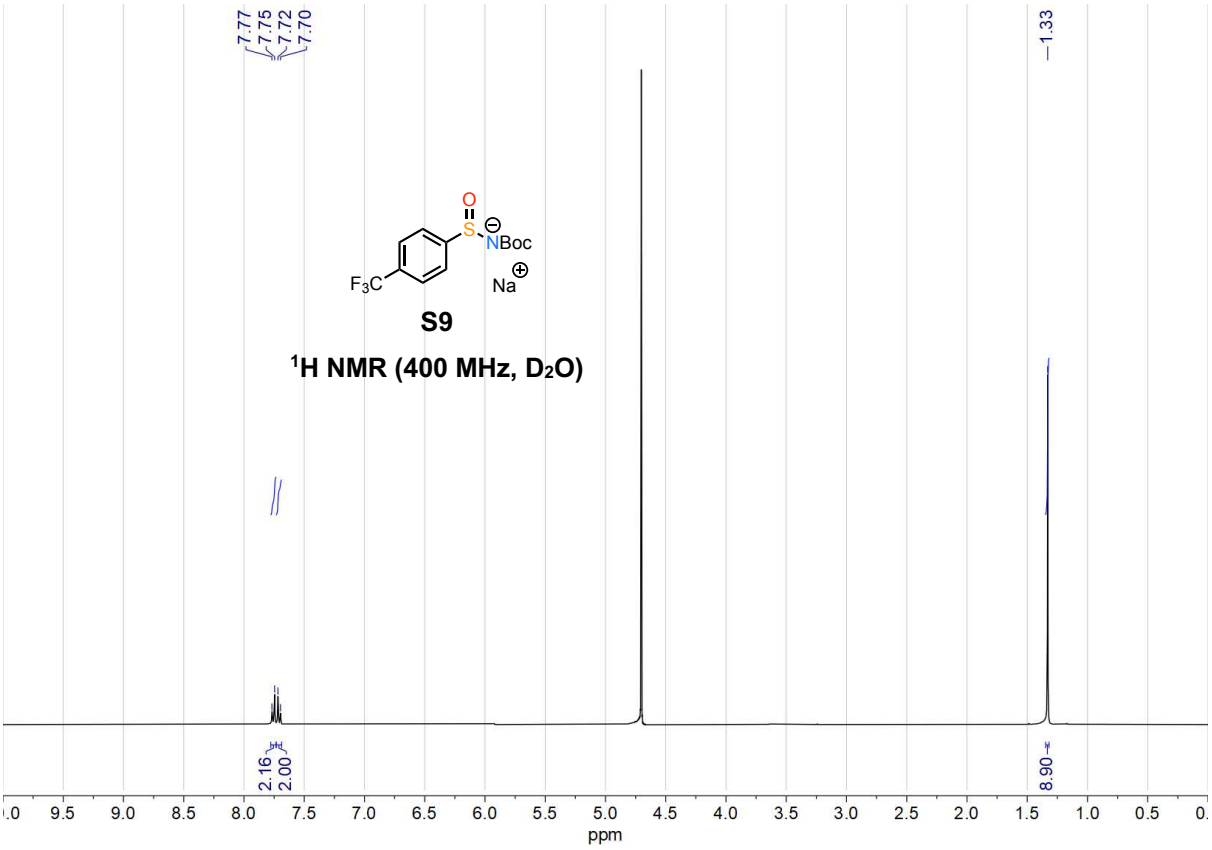
^{13}C NMR (101 MHz, $CDCl_3$)



S8

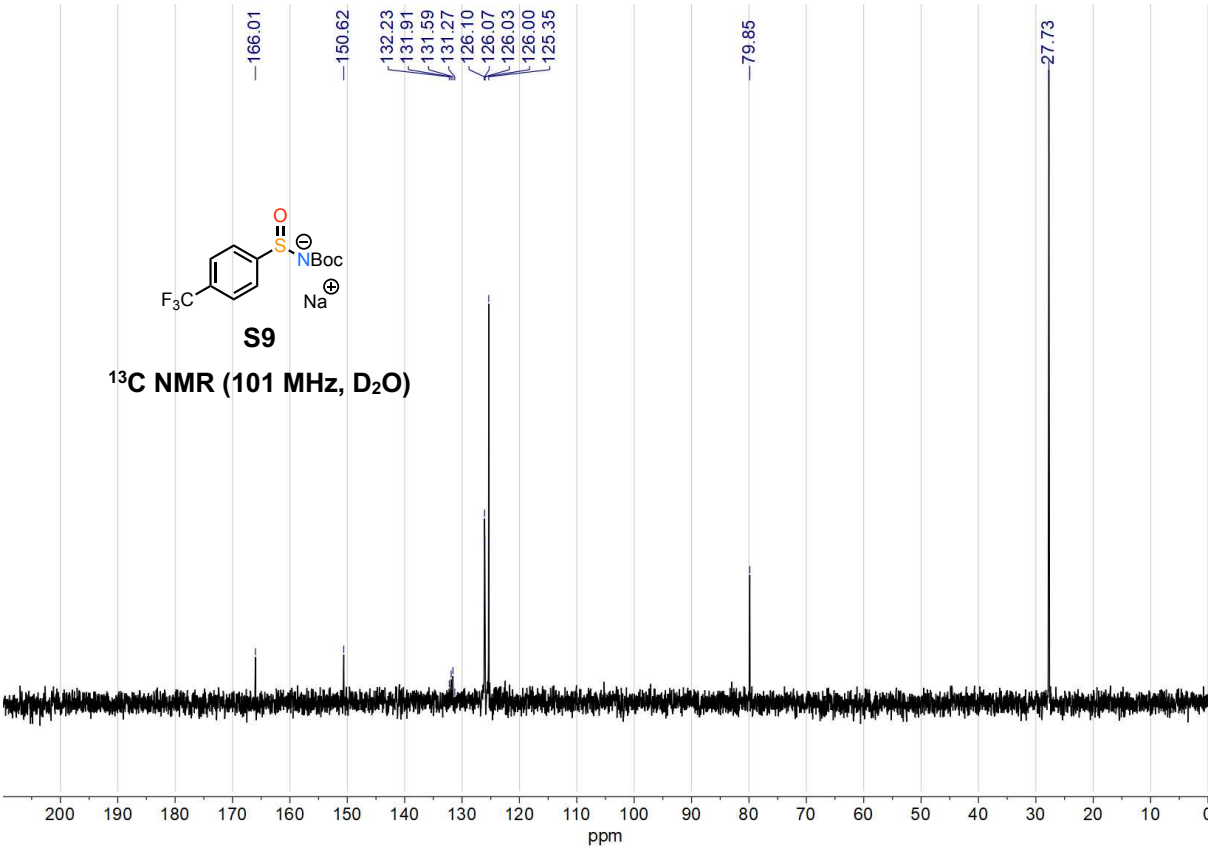
$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$)

Sodium (*tert*-butoxycarbonyl)((4-(trifluoromethyl)phenyl)sulfinyl)amide (S9)



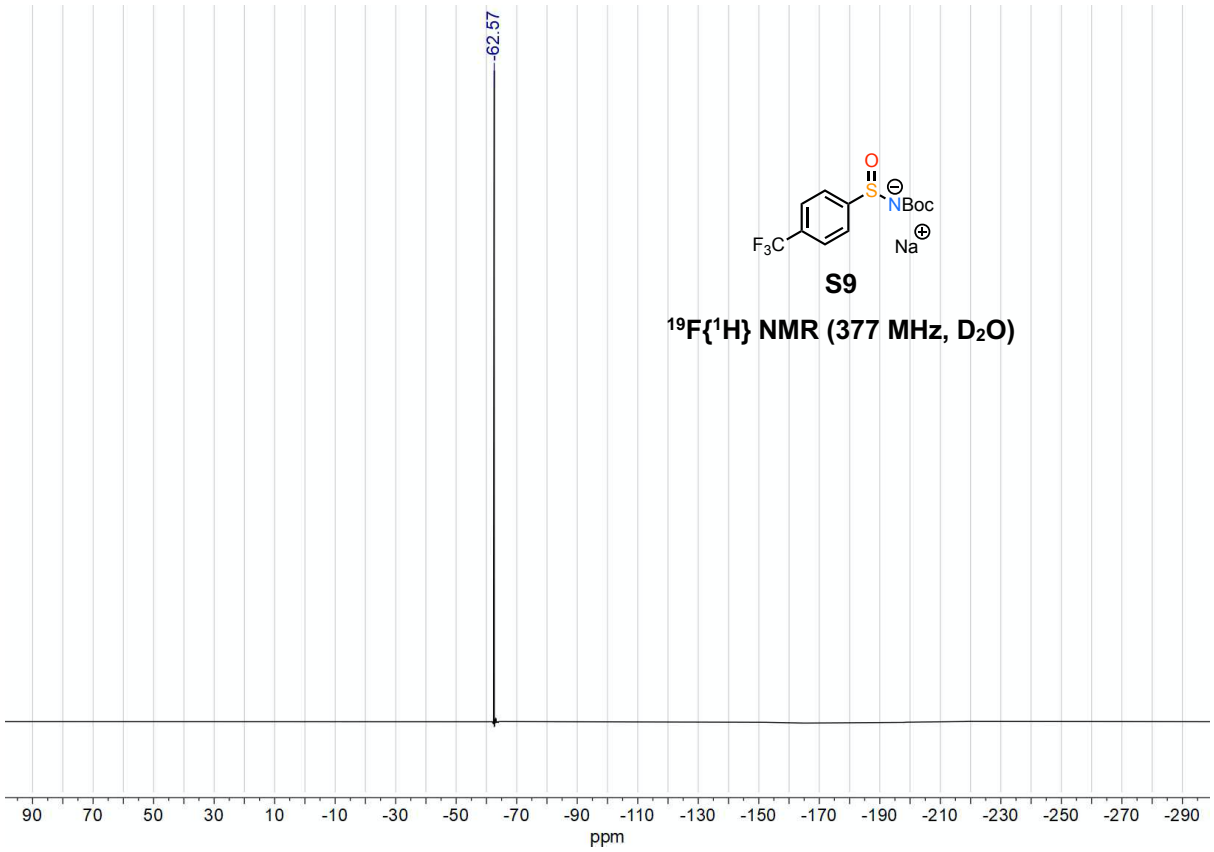
S9

^{1}H NMR (400 MHz, D_2O)



S9

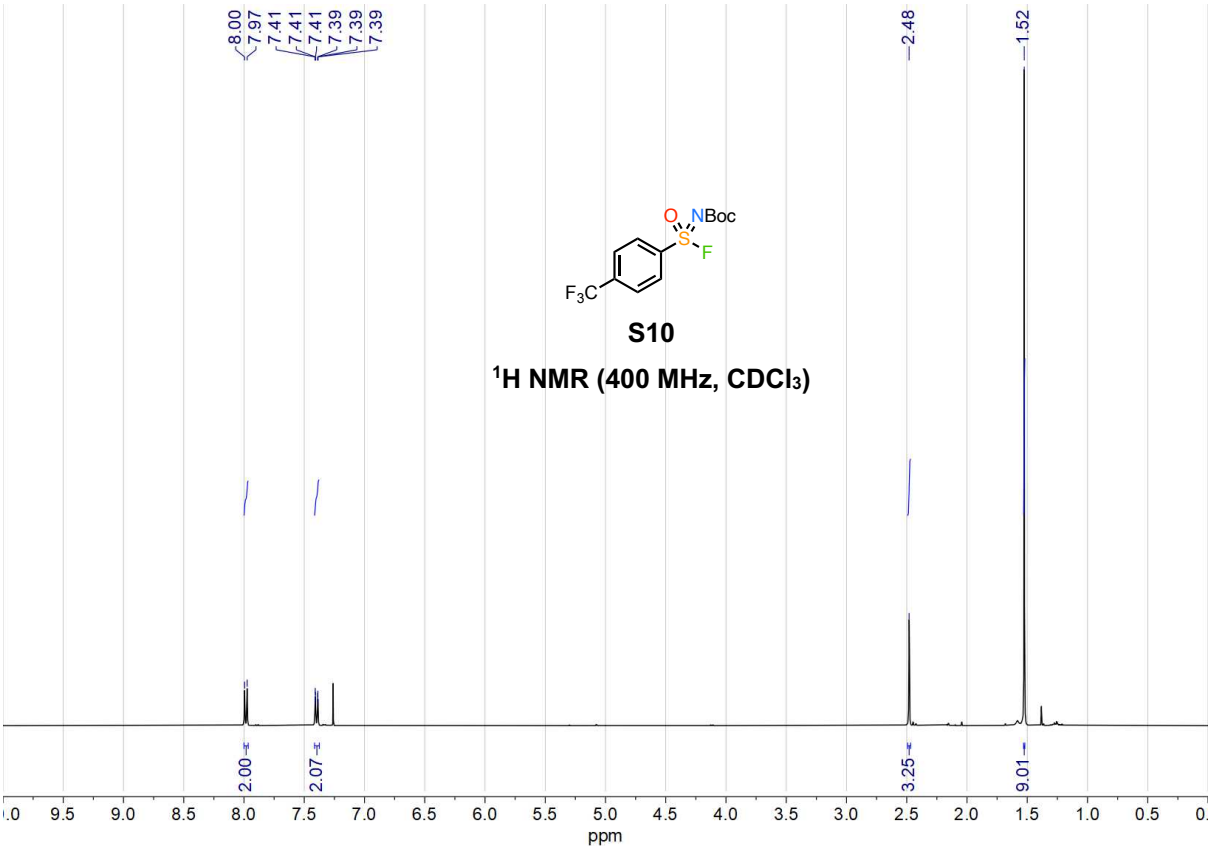
^{13}C NMR (101 MHz, D_2O)



S9

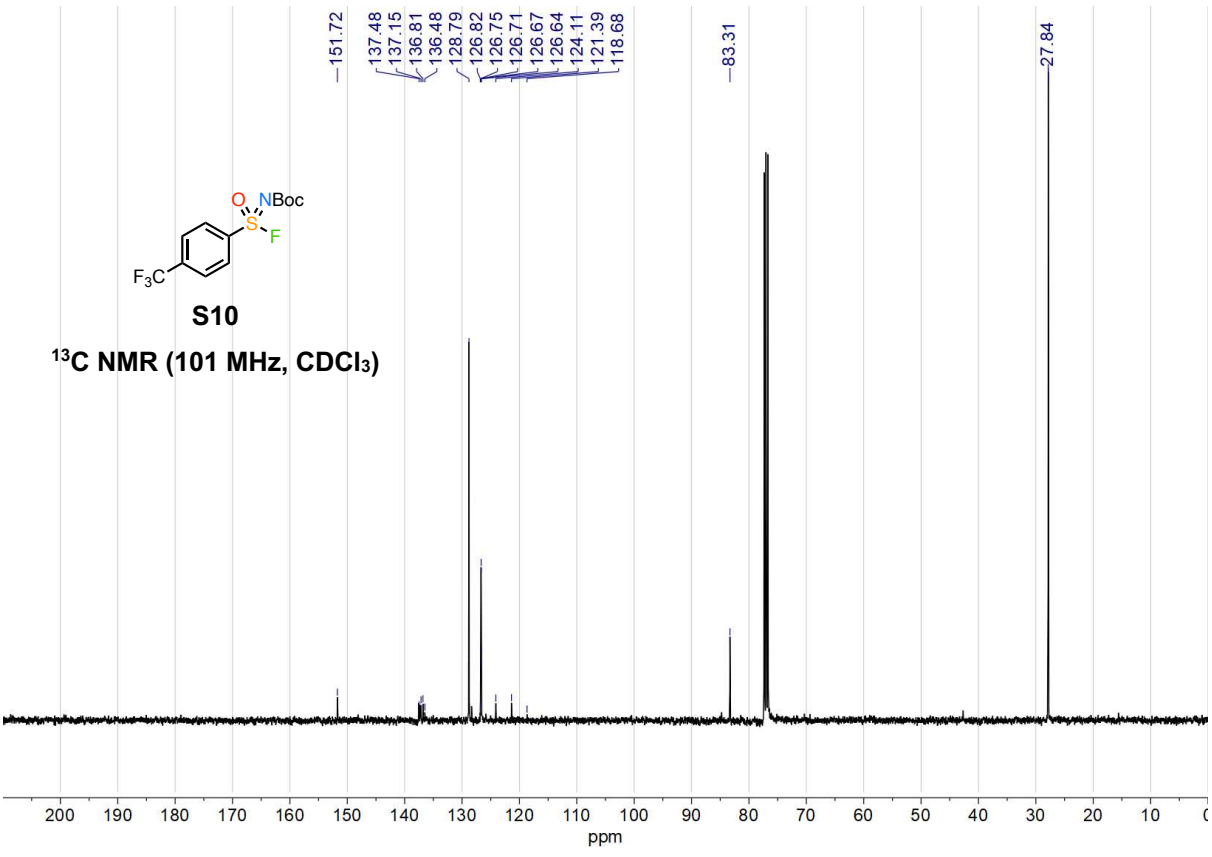
$^{19}F\{^{1}H\}$ NMR (377 MHz, D_2O)

***tert*-Butyl (fluoro(oxo)(4-(trifluoromethyl)phenyl)-λ^6-sulfaneylidene)carbamate (S10)**



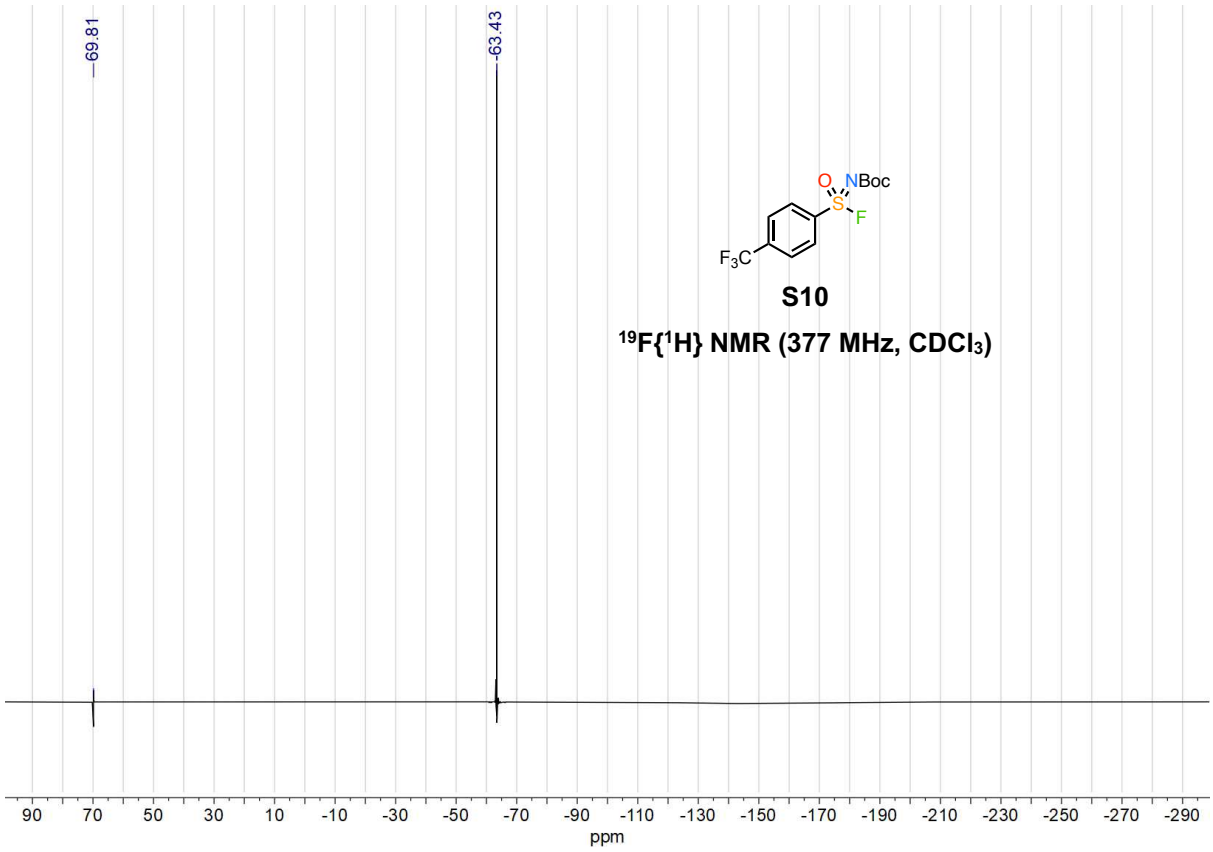
S10

^{1}H NMR (400 MHz, $CDCl_3$)



S10

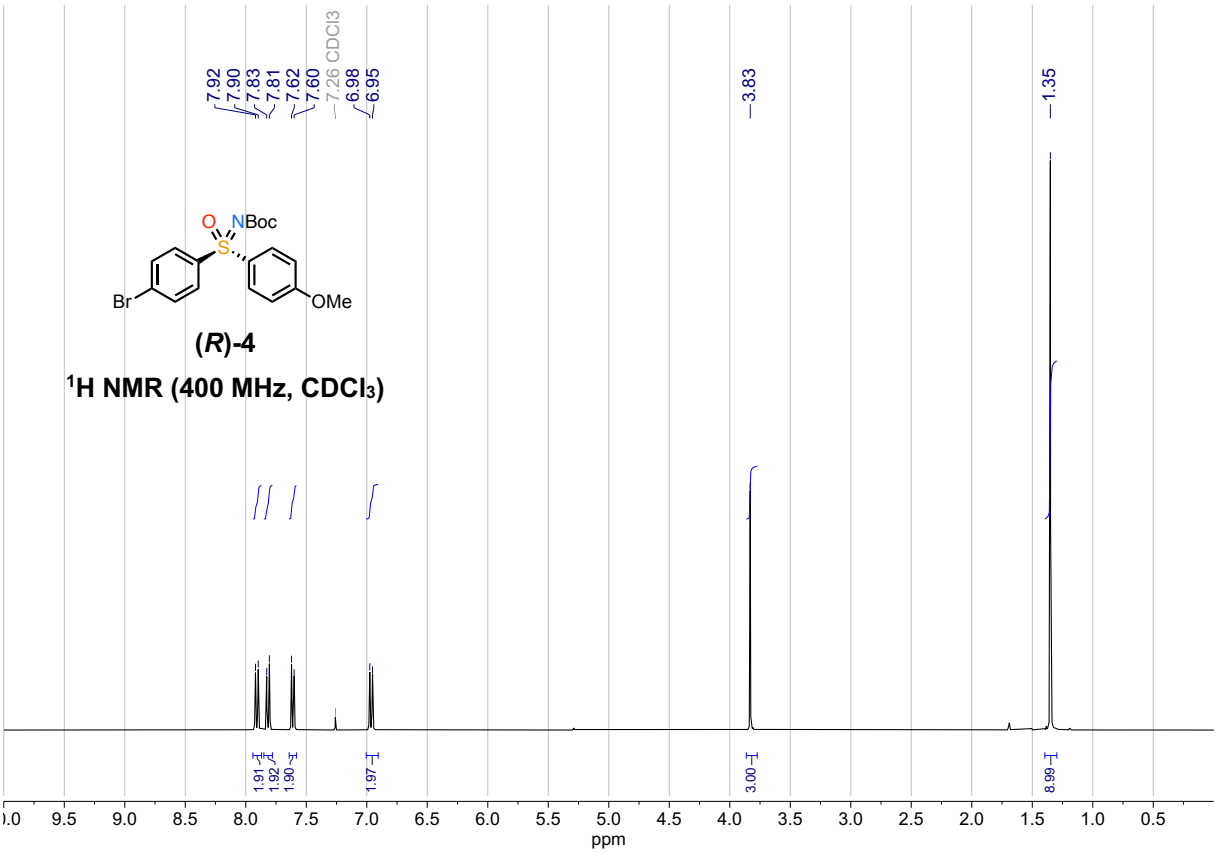
^{13}C NMR (101 MHz, $CDCl_3$)

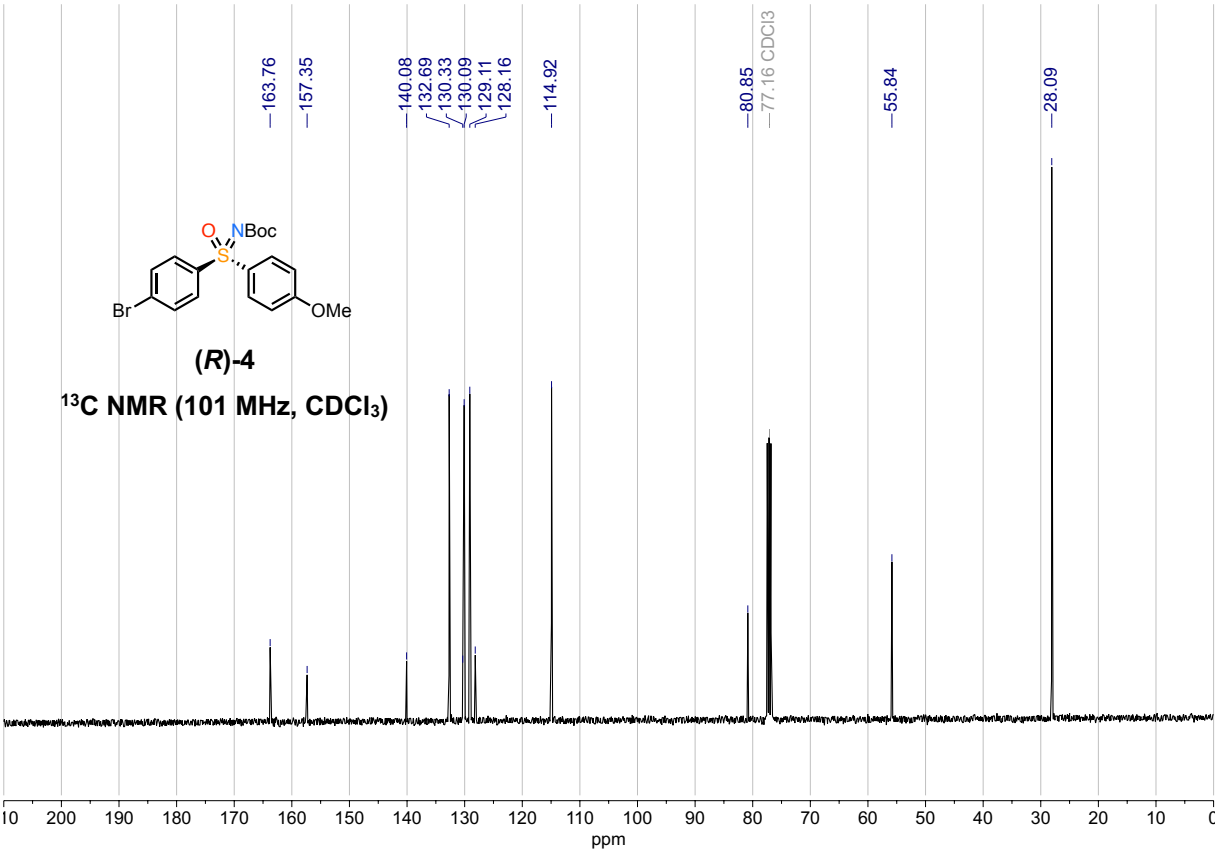


S10

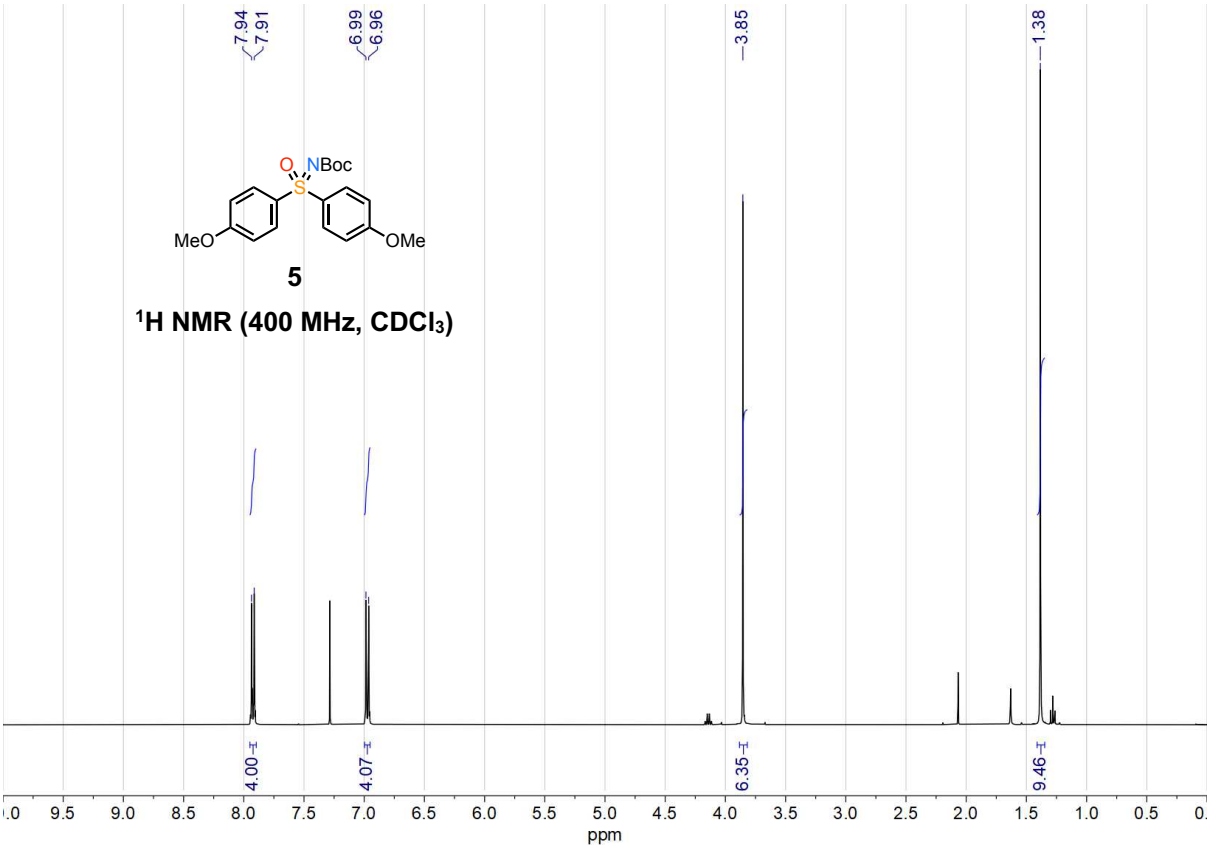
$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$)

***tert*-Butyl (*R*)-((4-bromophenyl)(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)carbamate ((*R*)-4)**



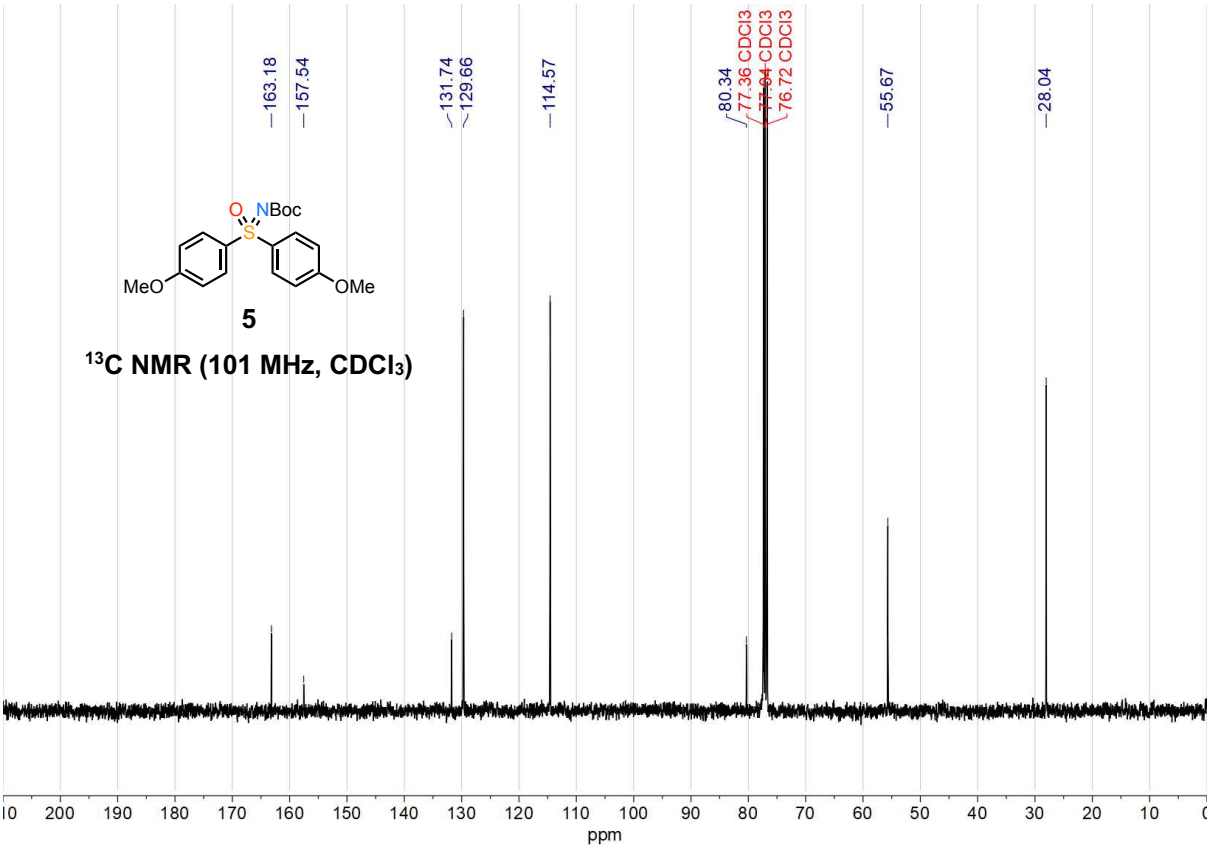


***tert*-Butyl (bis(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)carbamate (5)**



5

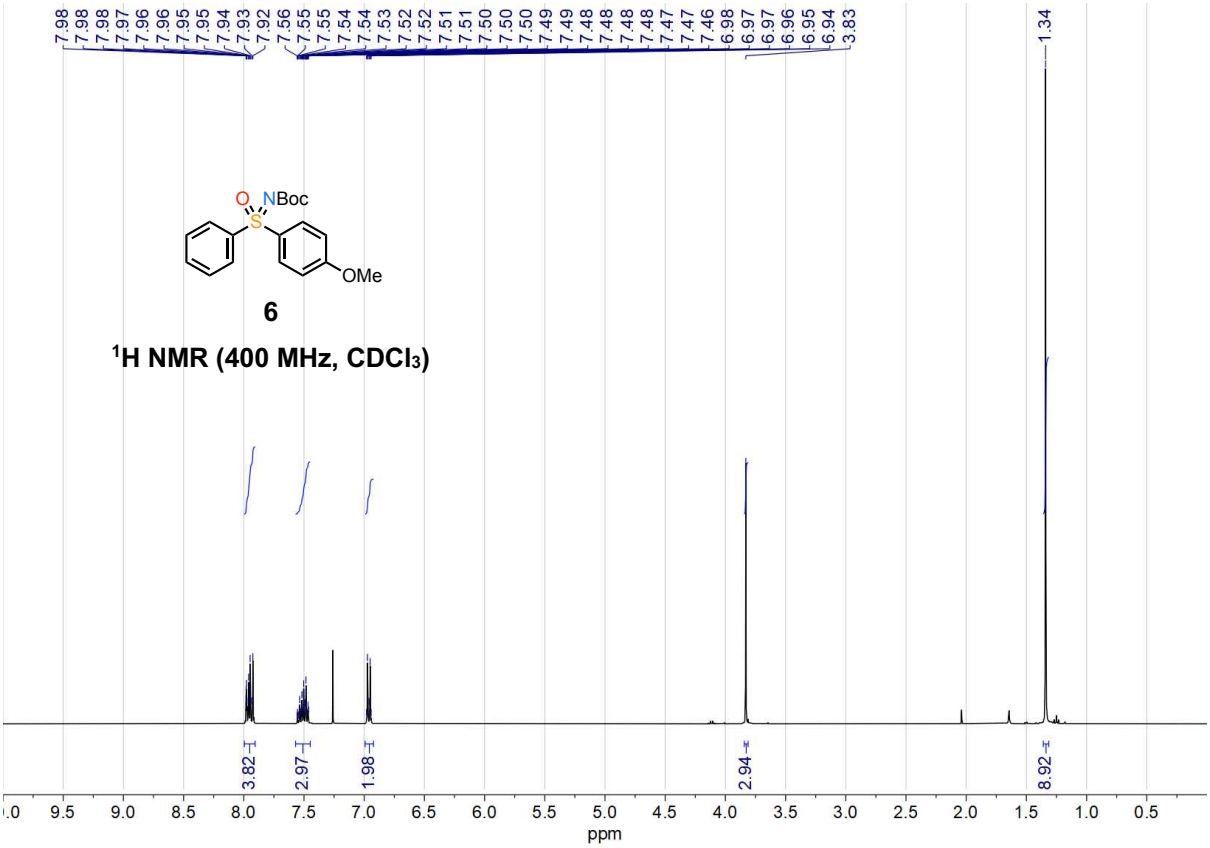
^{1}H NMR (400 MHz, $CDCl_3$)

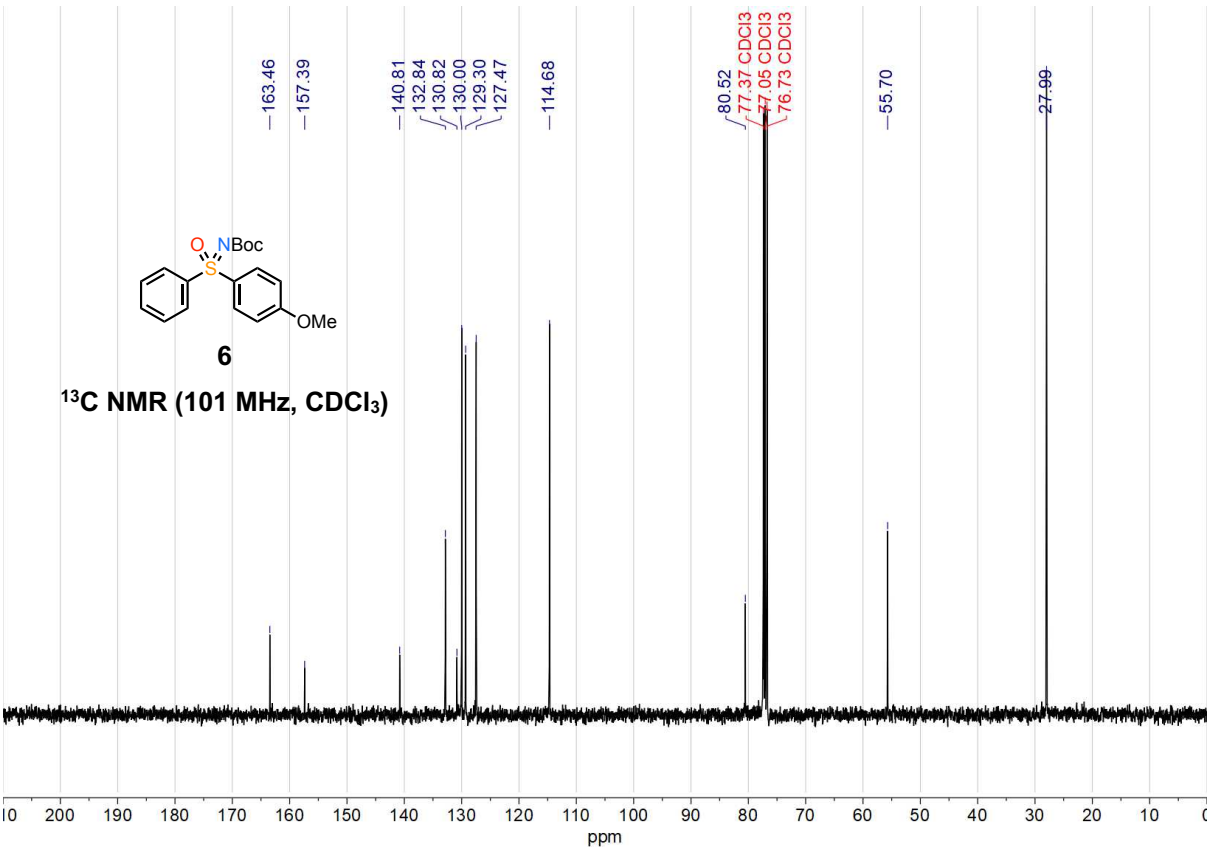


5

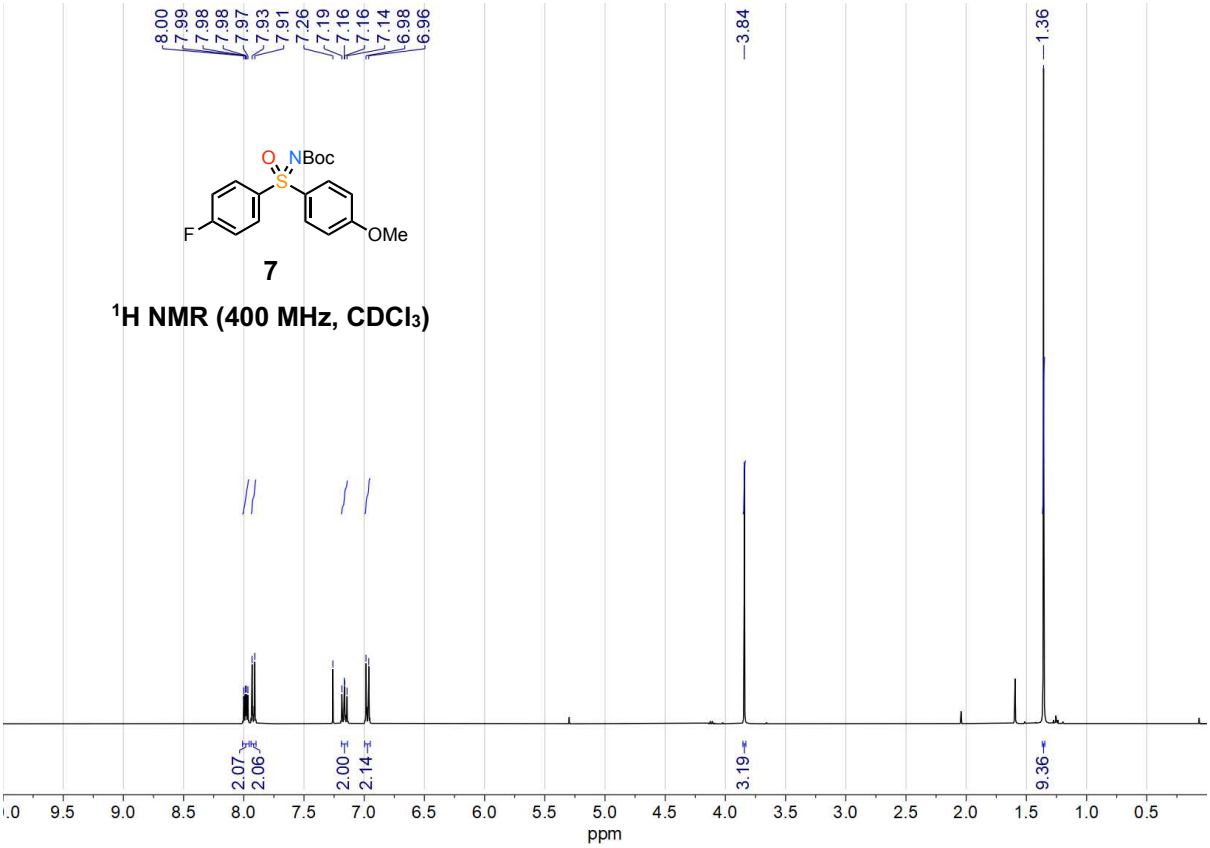
^{13}C NMR (101 MHz, $CDCl_3$)

***tert*-Butyl ((4-methoxyphenyl)(oxo)(phenyl)-λ^6-sulfaneylidene)carbamate (6)**



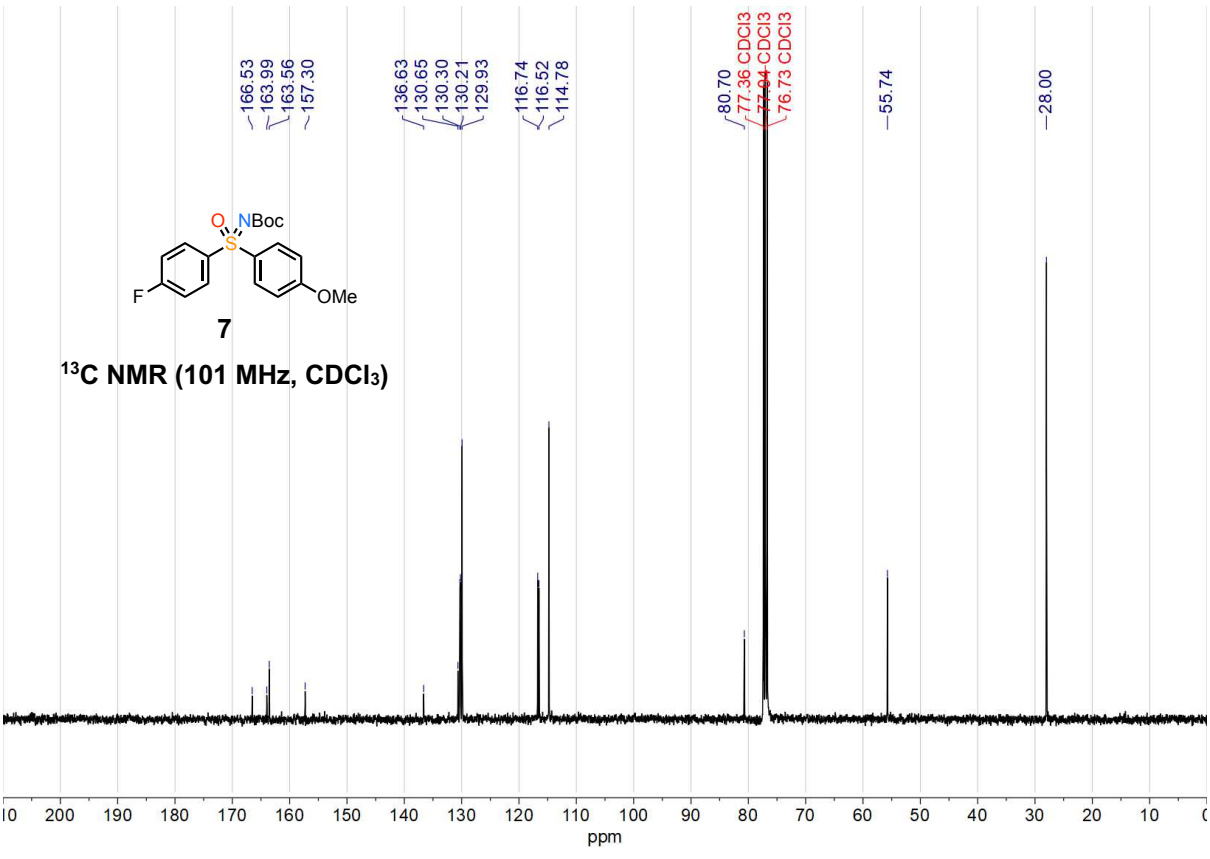


***tert*-Butyl ((4-fluorophenyl)(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)carbamate (7)**



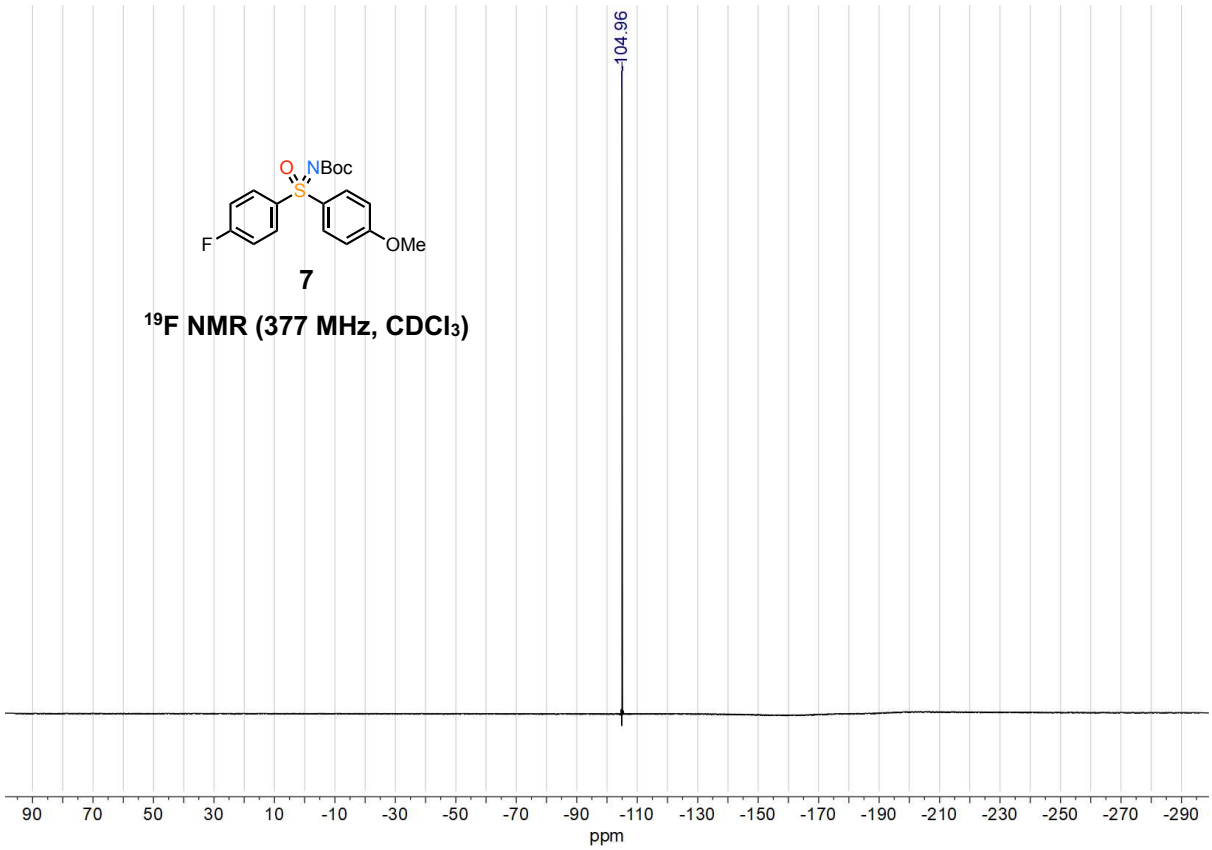
7

^{1}H NMR (400 MHz, $CDCl_3$)



7

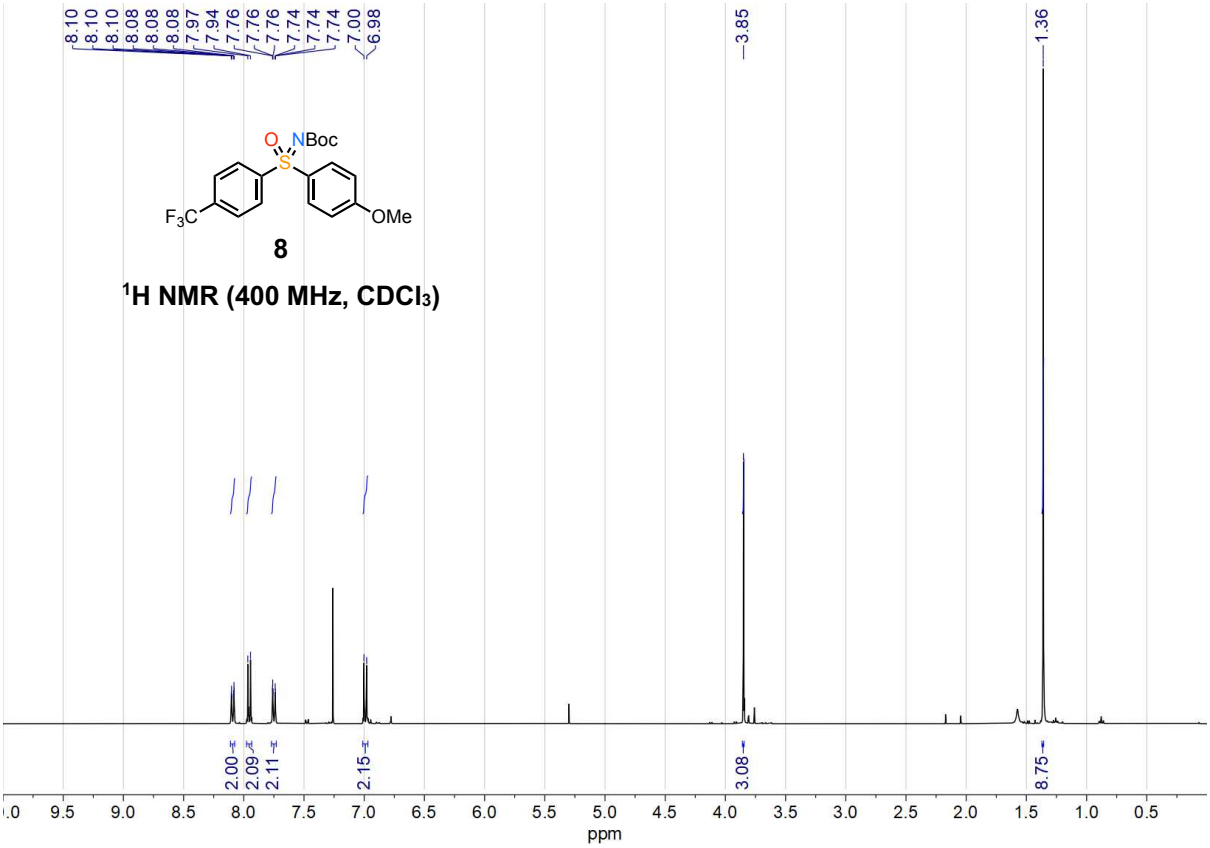
^{13}C NMR (101 MHz, $CDCl_3$)



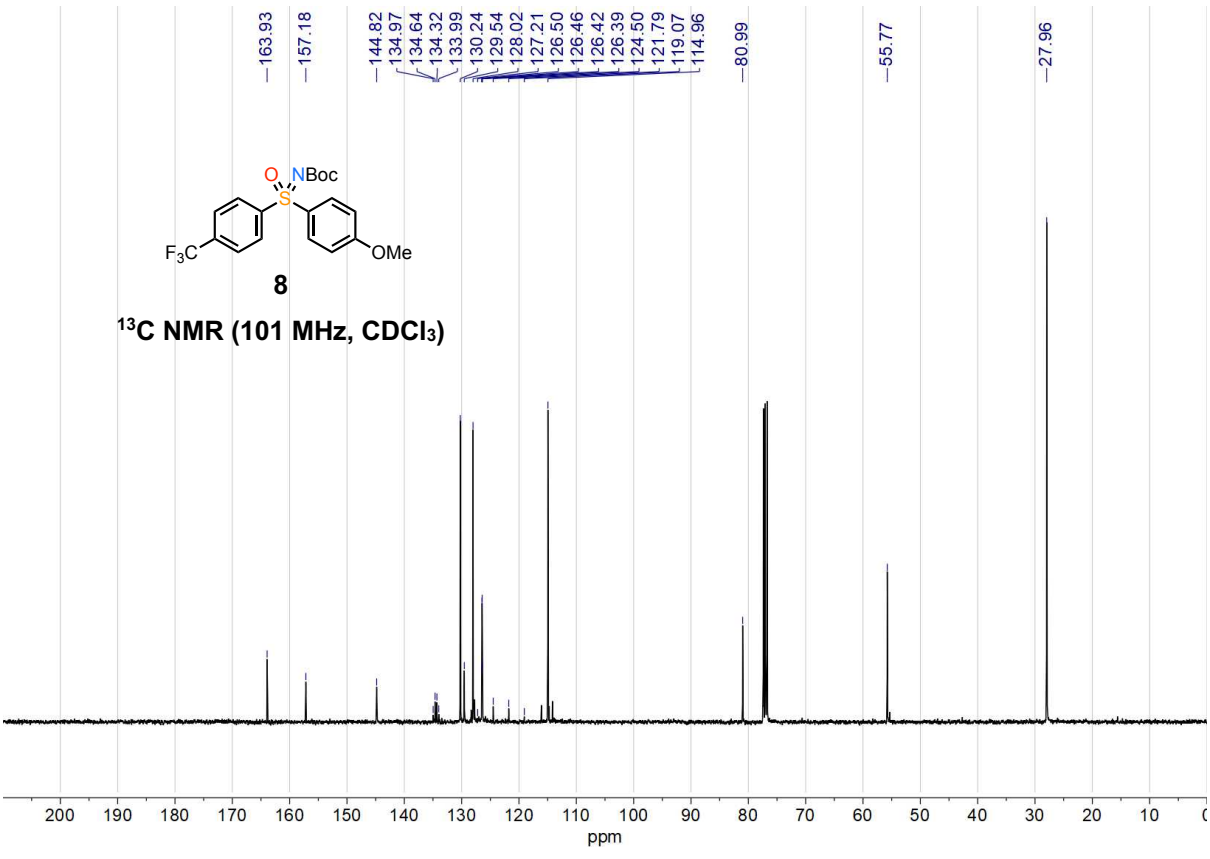
7

^{19}F NMR (377 MHz, $CDCl_3$)

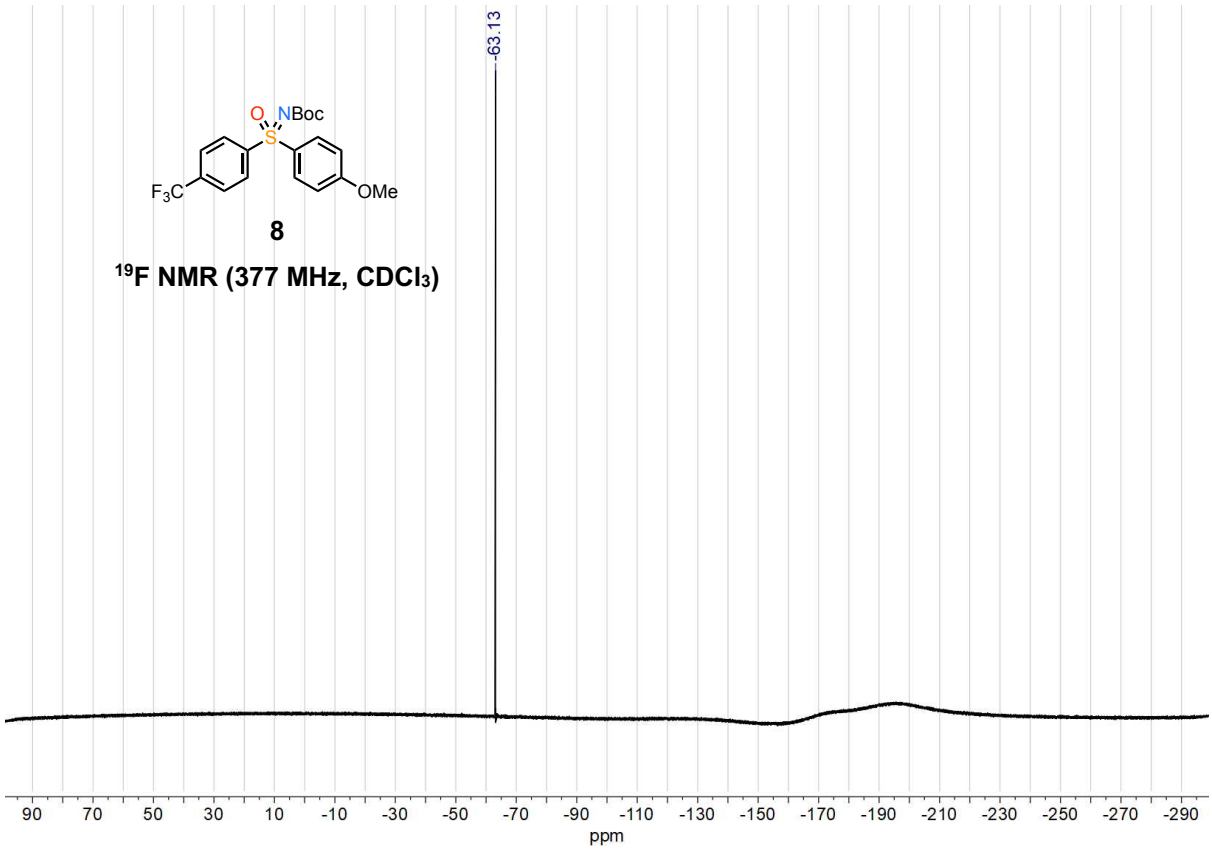
***tert*-Butyl ((4-methoxyphenyl)(oxo)(4-(trifluoromethyl)phenyl)-λ^6-sulfaneylidene)carbamate (8)**



^{1}H NMR (400 MHz, $CDCl_3$)



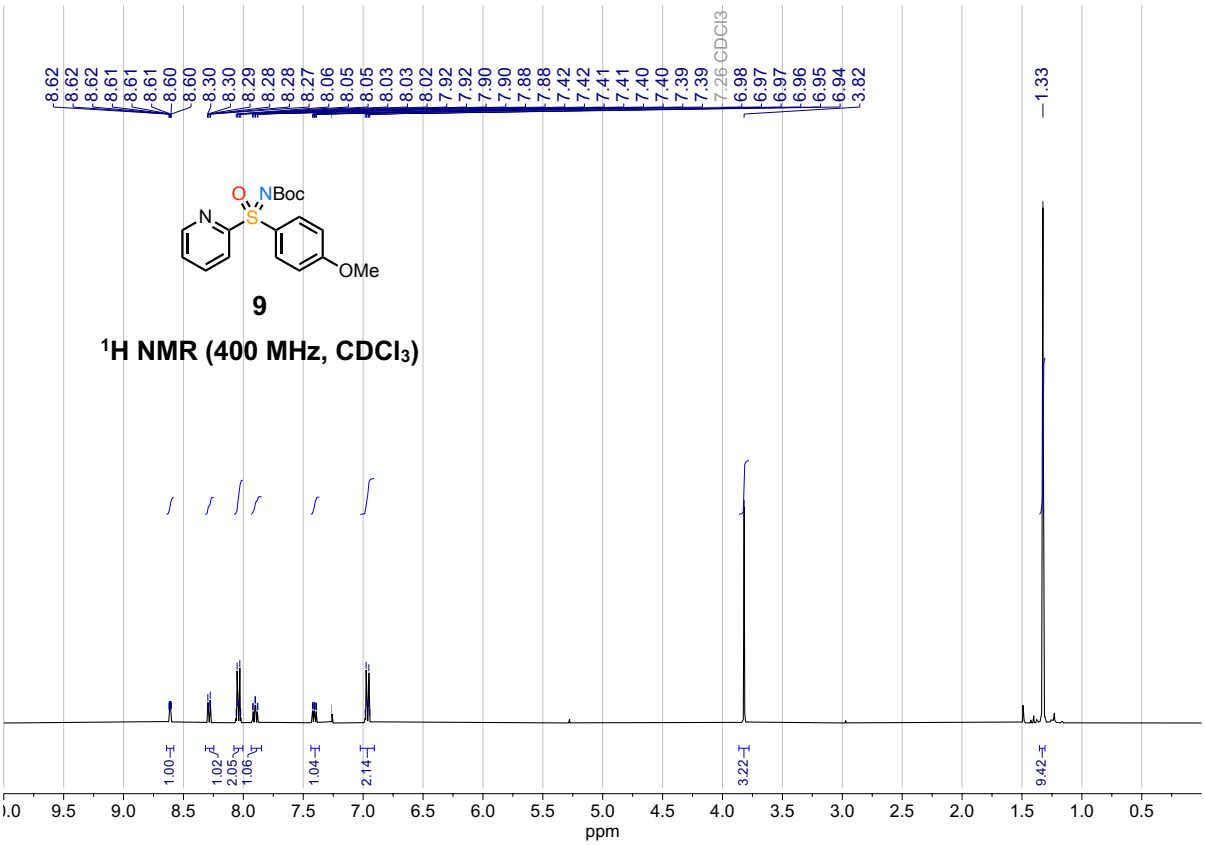
^{13}C NMR (101 MHz, $CDCl_3$)

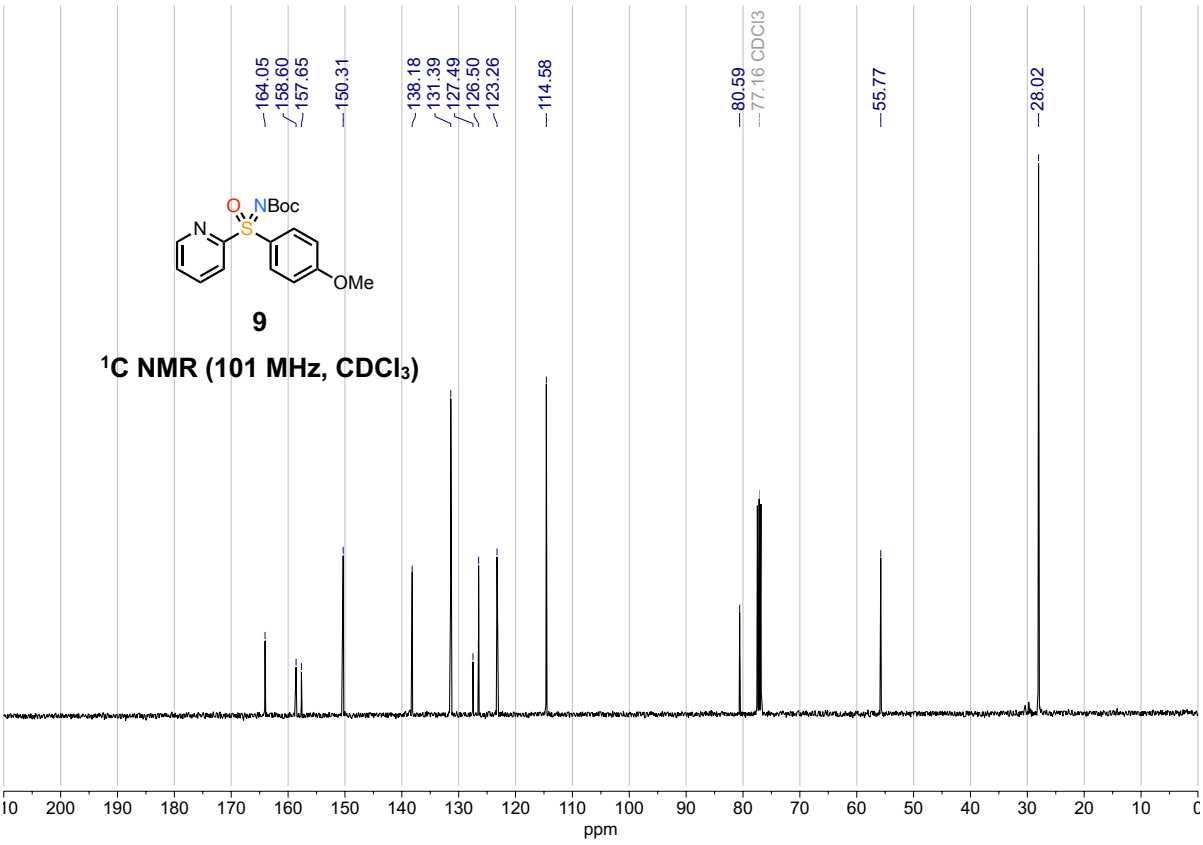


8

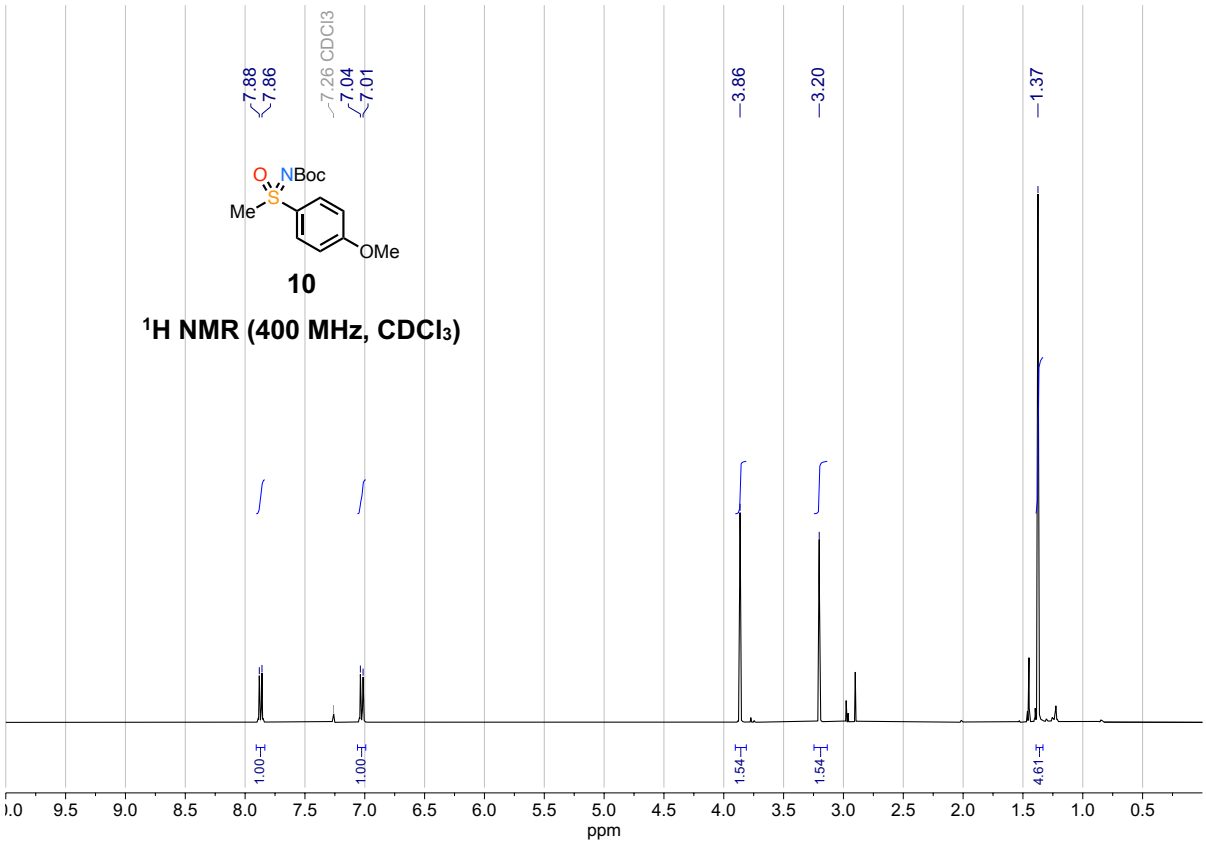
^{19}F NMR (377 MHz, $CDCl_3$)

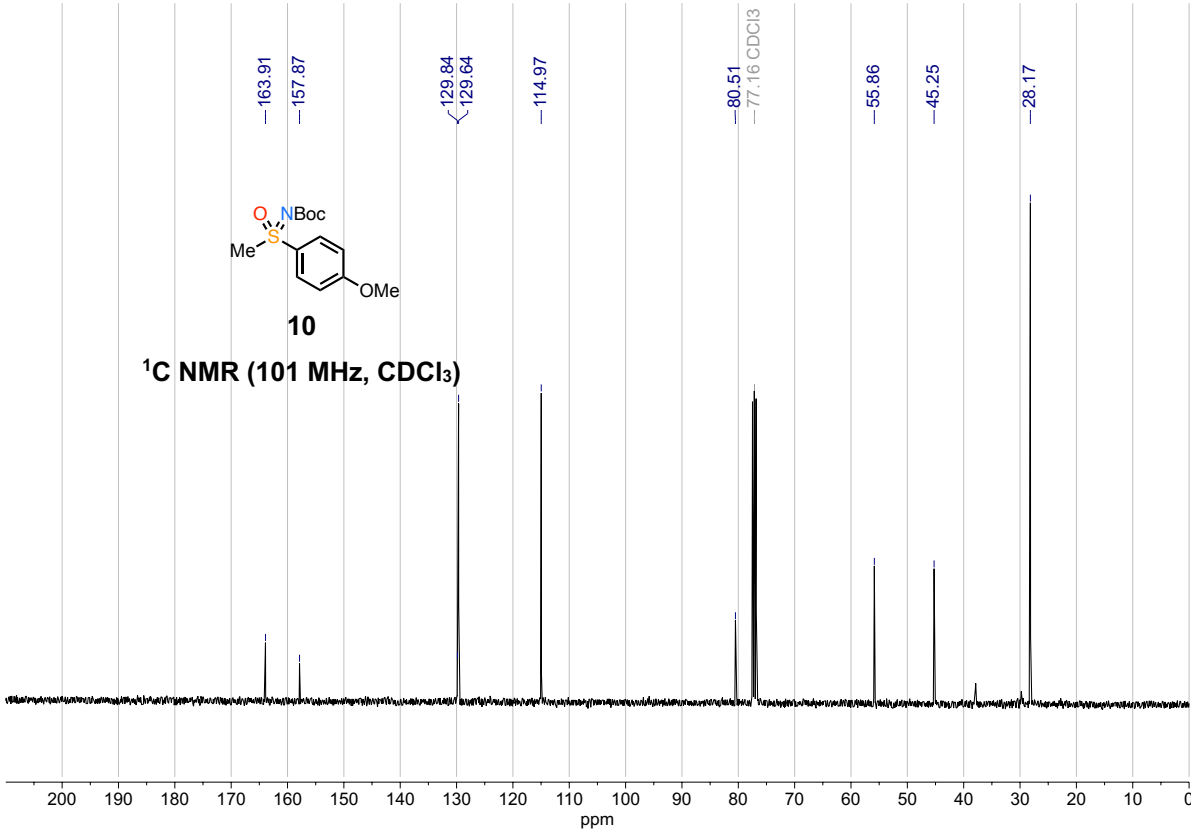
***tert*-Butyl ((4-methoxyphenyl)(oxo)(pyridin-2-yl)-λ^6-sulfaneylidene)carbamate (9)**



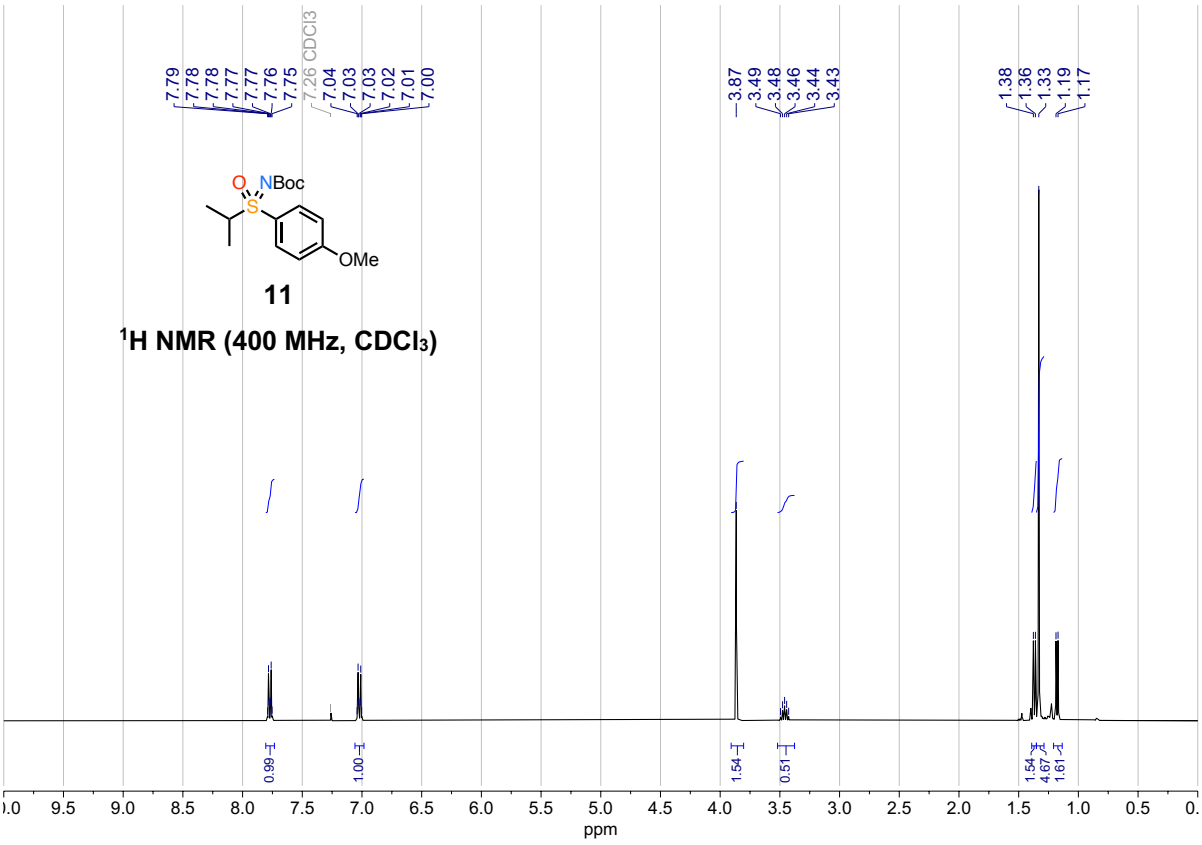


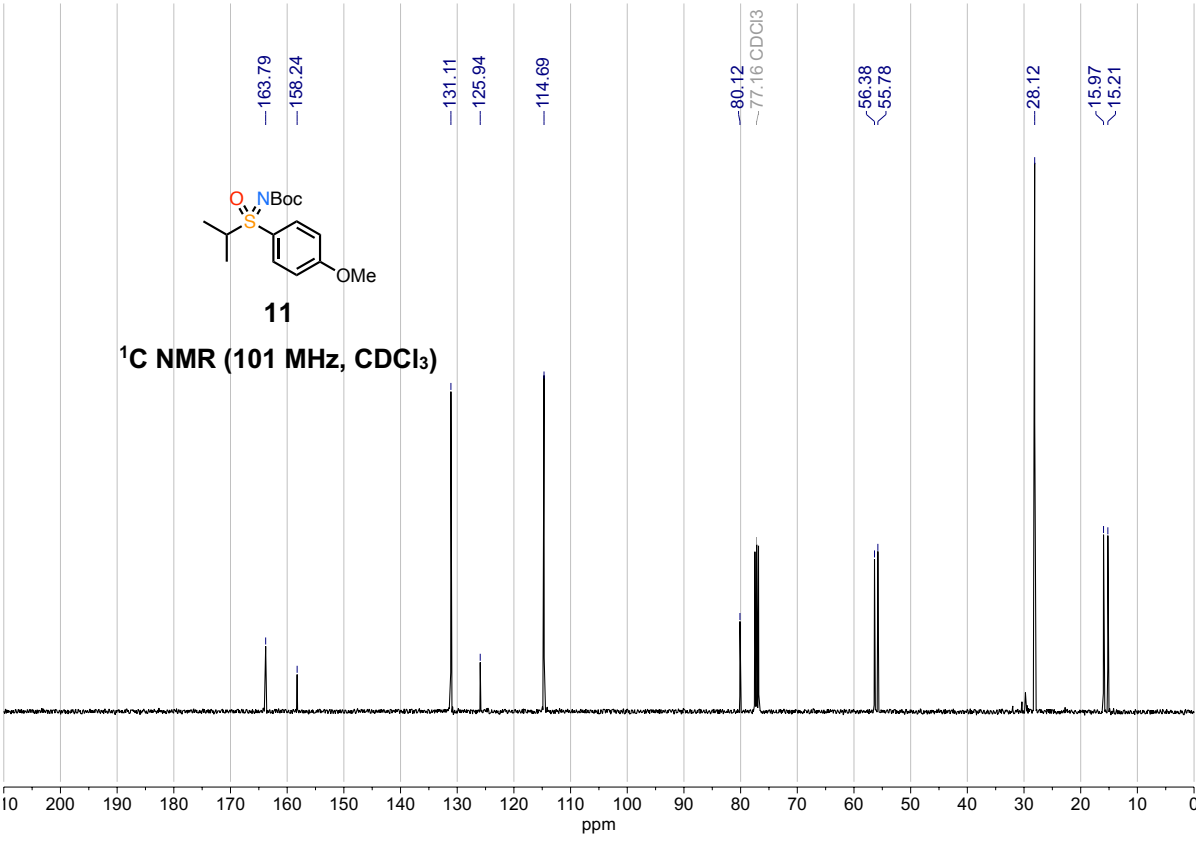
***tert*-Butyl ((4-methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)carbamate (10)**



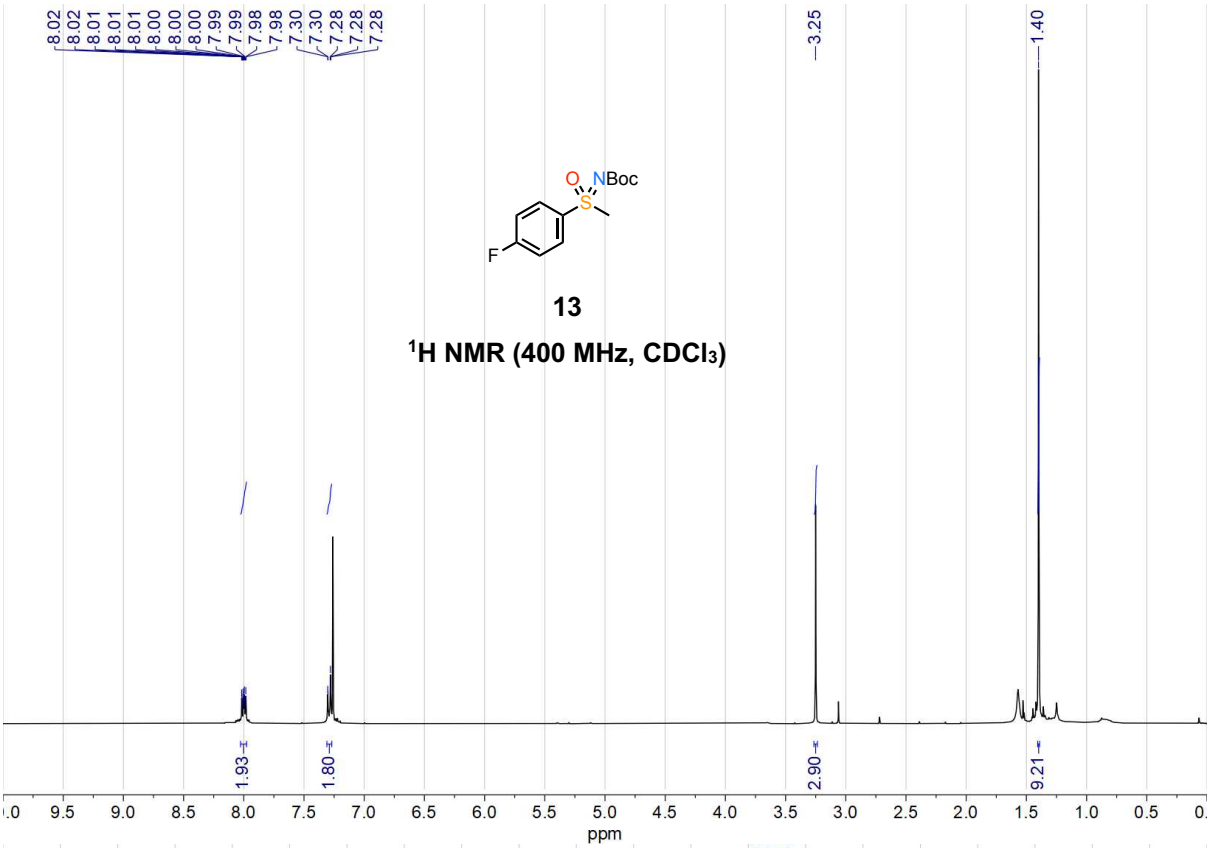


tert-Butyl (isopropyl(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)carbamate (11)



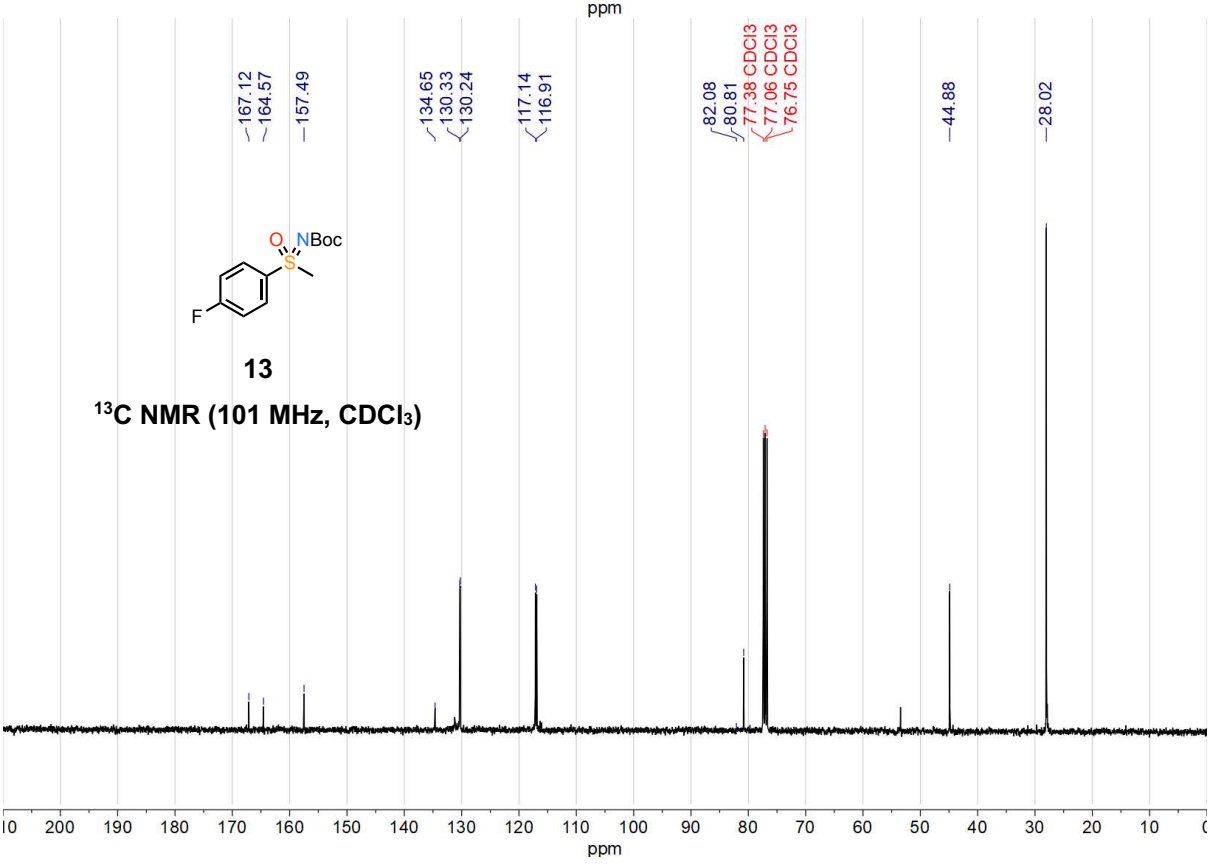


***tert*-Butyl (*R*)-((4-fluorophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)carbamate (13)**



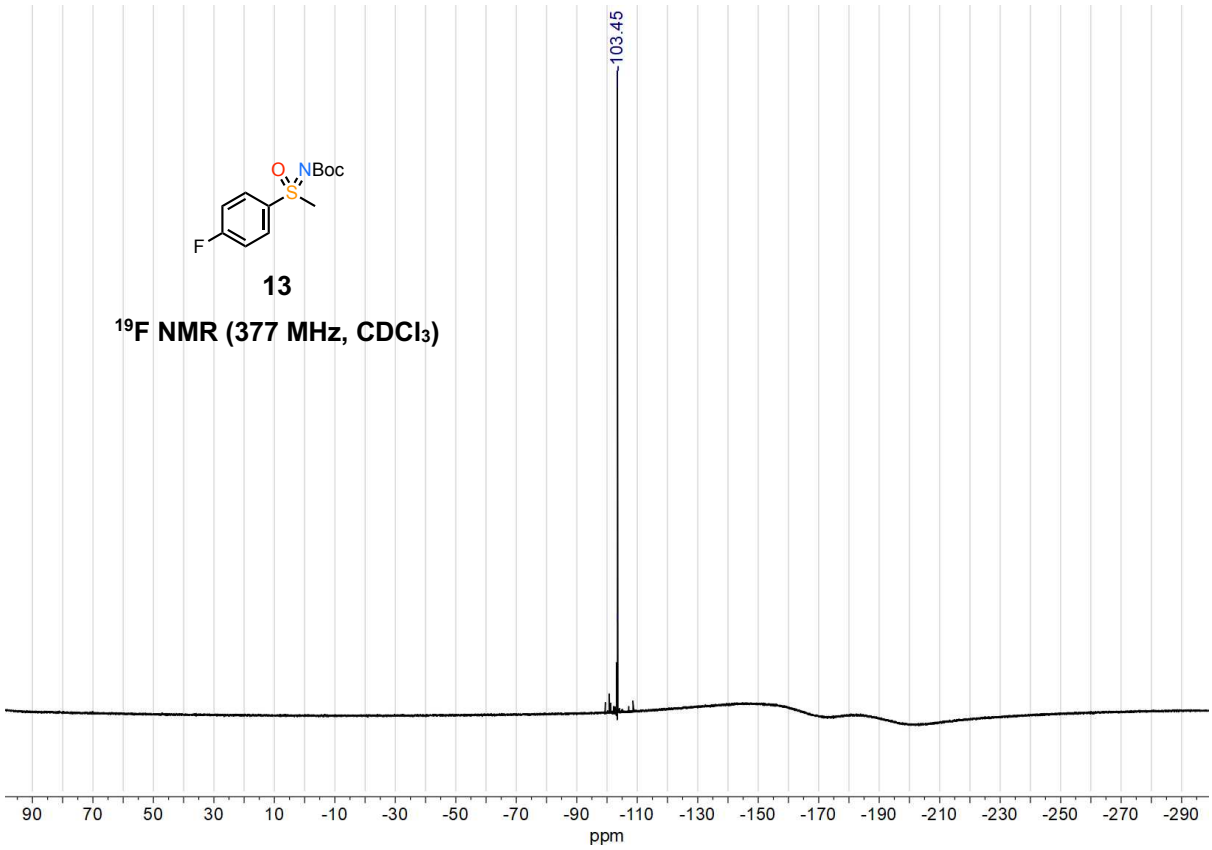
13

^{1}H NMR (400 MHz, $CDCl_3$)



13

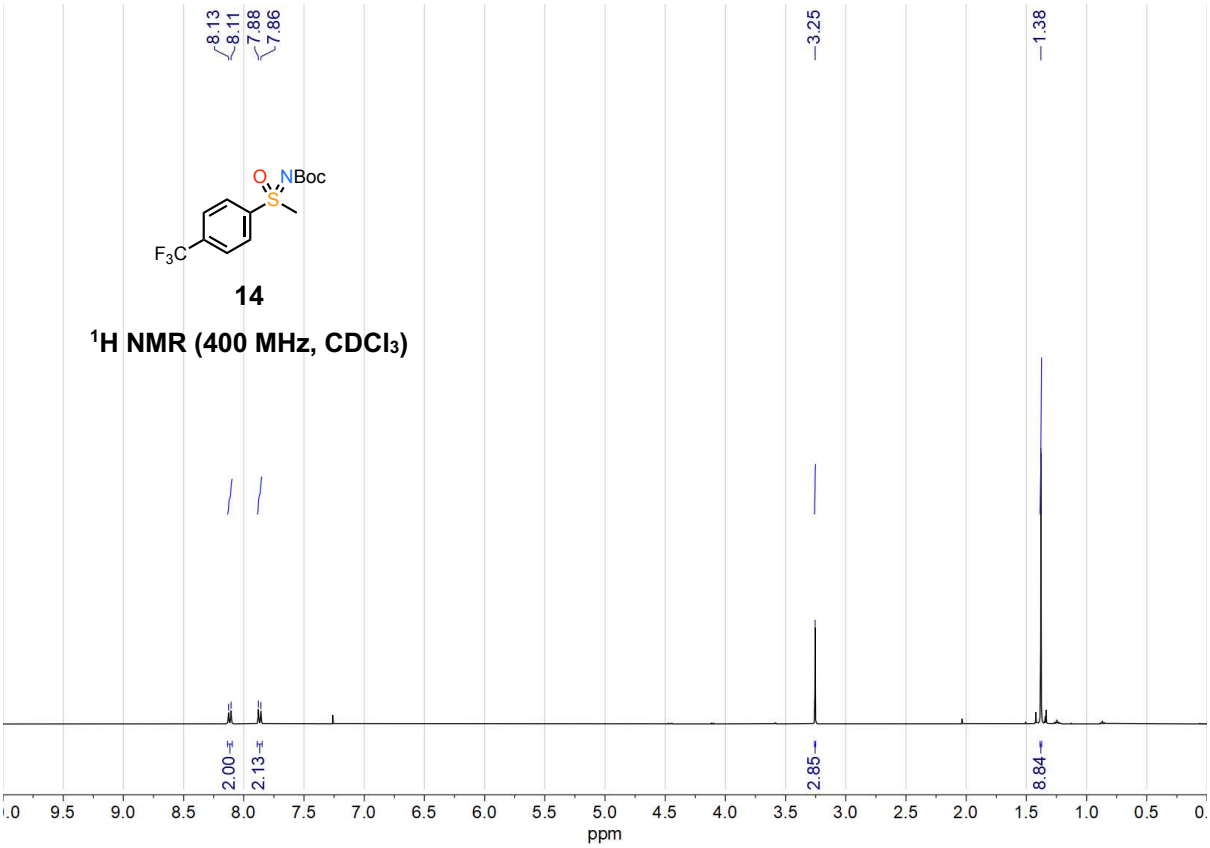
^{13}C NMR (101 MHz, $CDCl_3$)

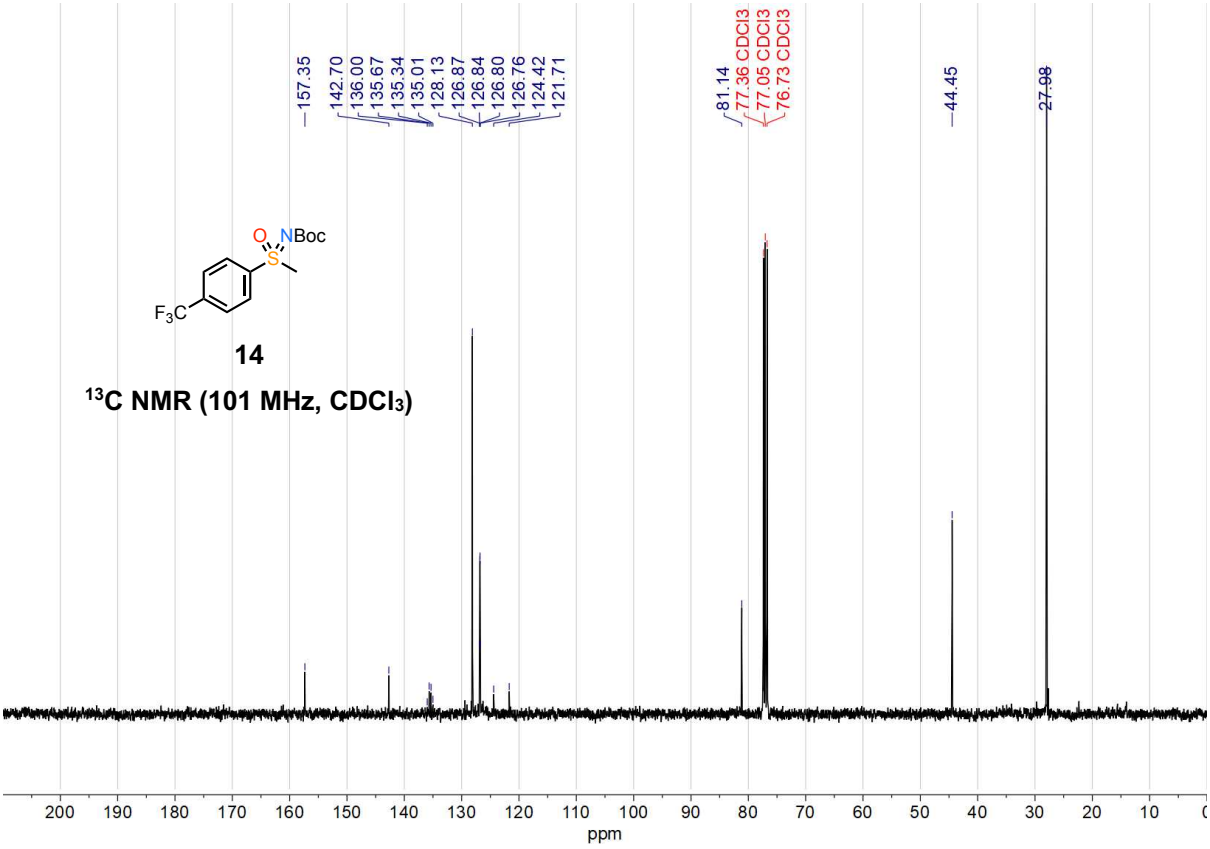


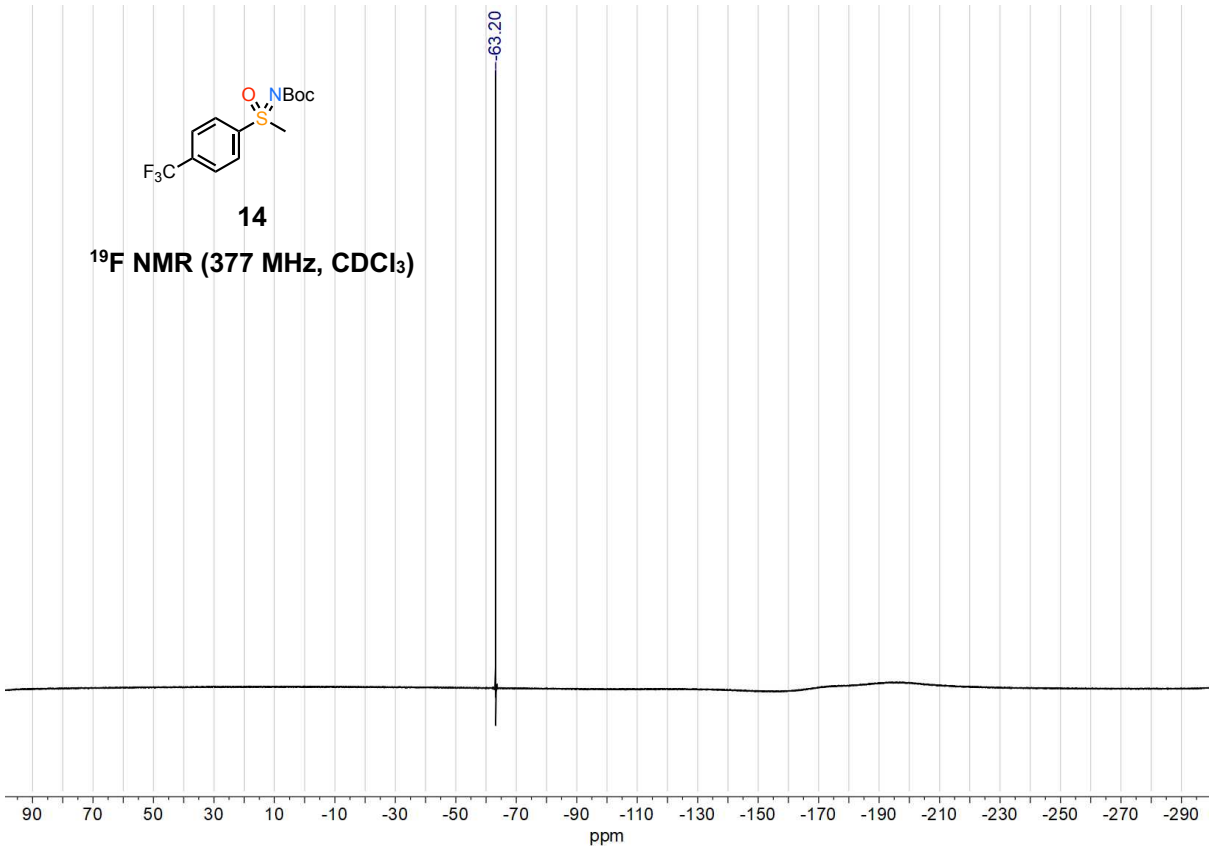
13

^{19}F NMR (377 MHz, $CDCl_3$)

***tert*-Butyl (methyl(oxo)(4-(trifluoromethyl)phenyl)-λ^6-sulfaneylidene)carbamate (14)**



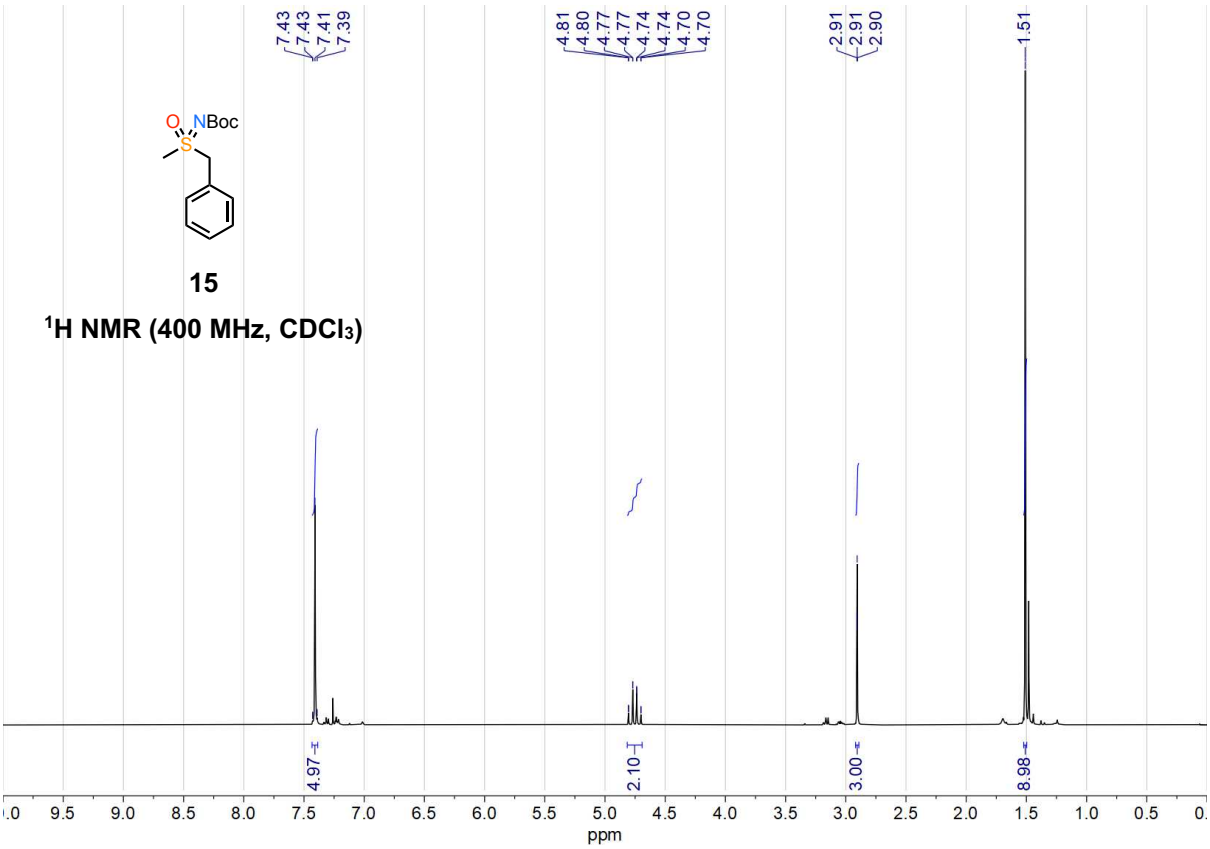


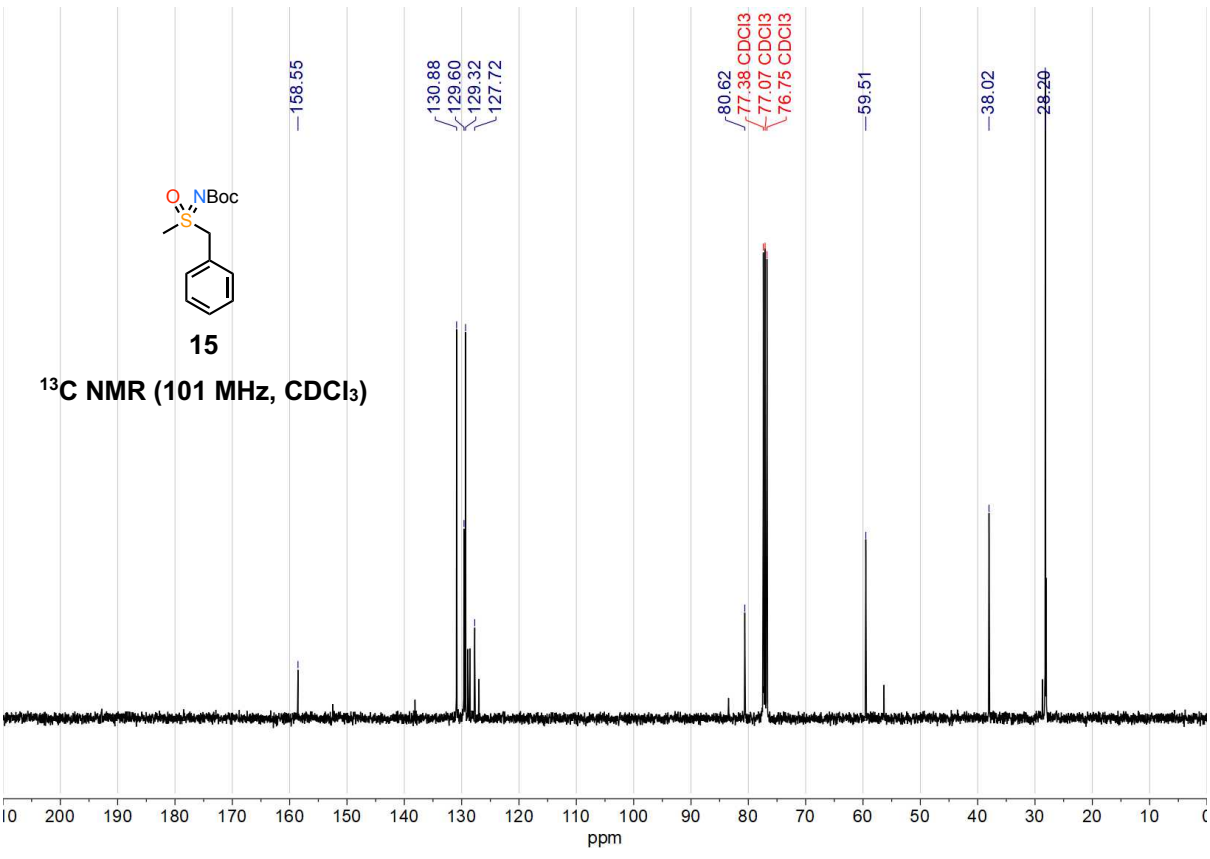


14

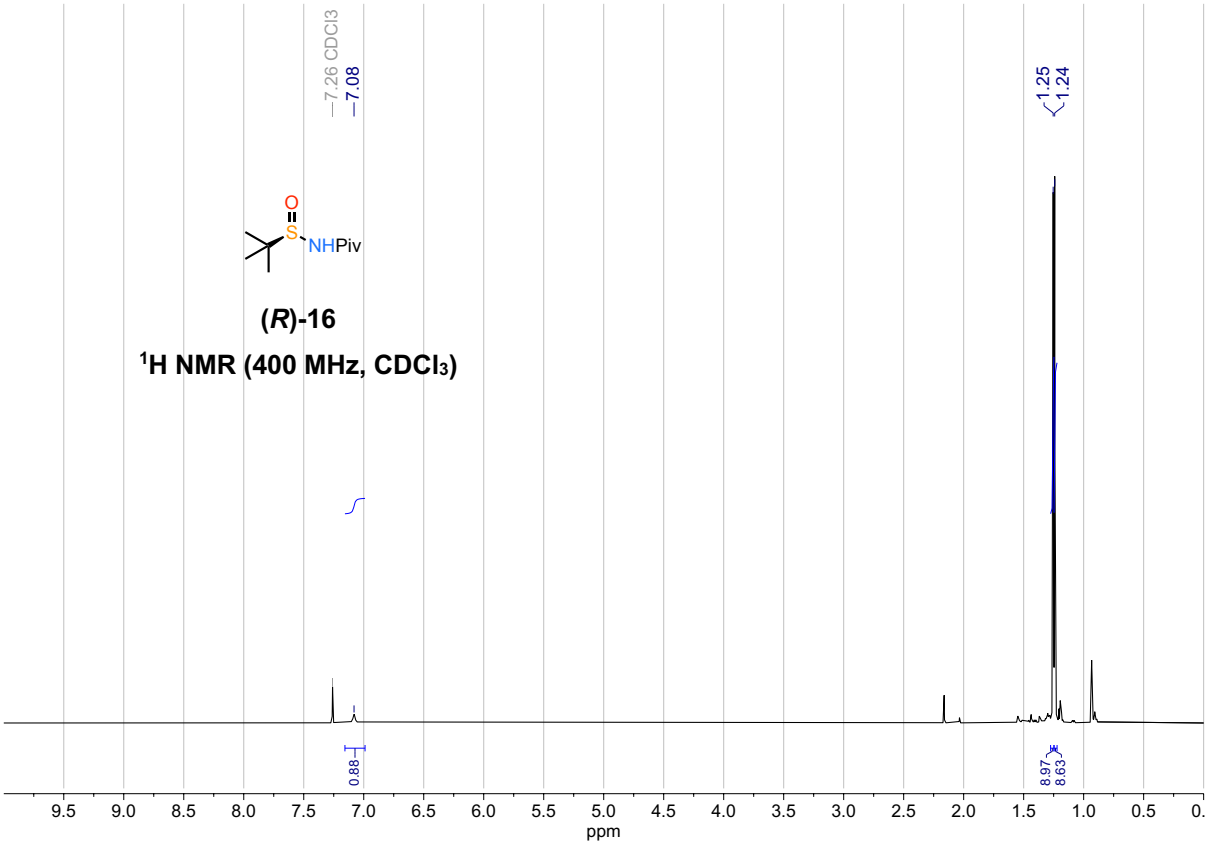
^{19}F NMR (377 MHz, $CDCl_3$)

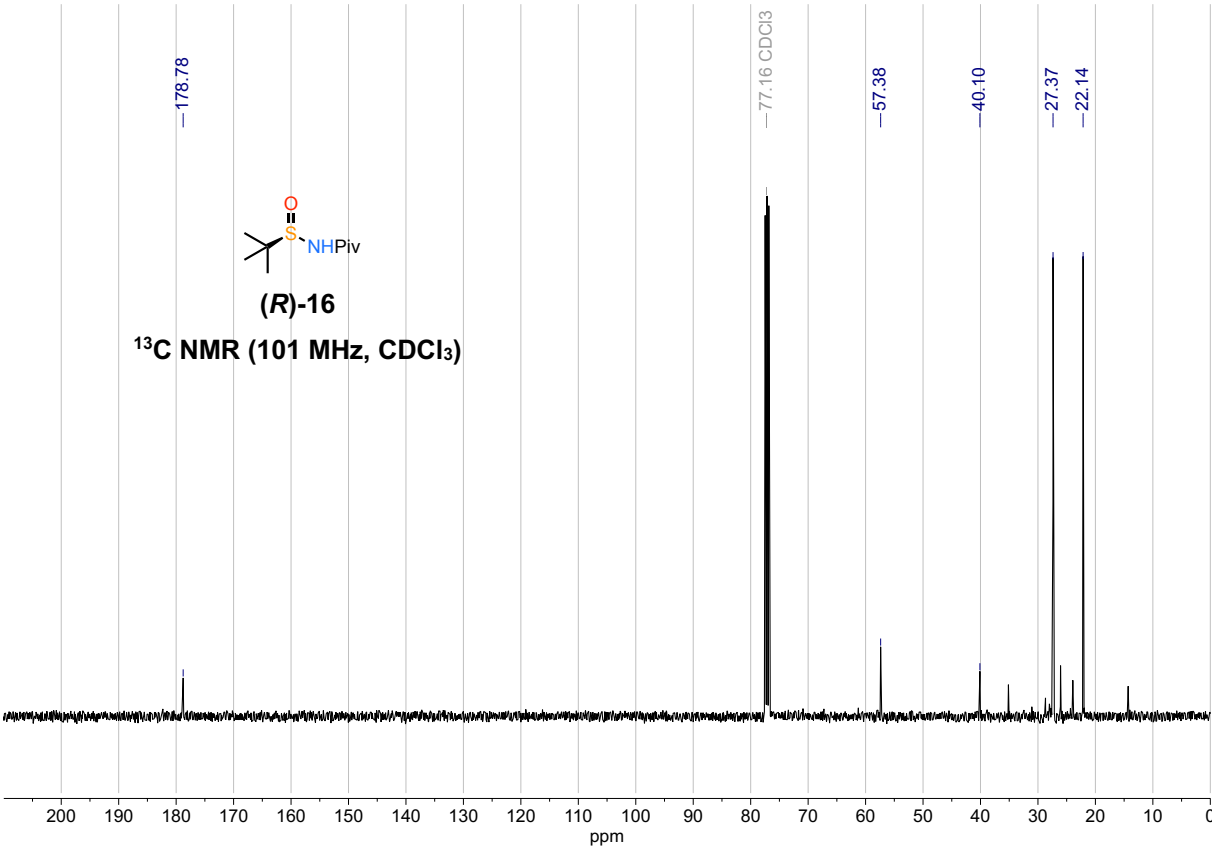
***tert*-Butyl (bis(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)carbamate (15)**



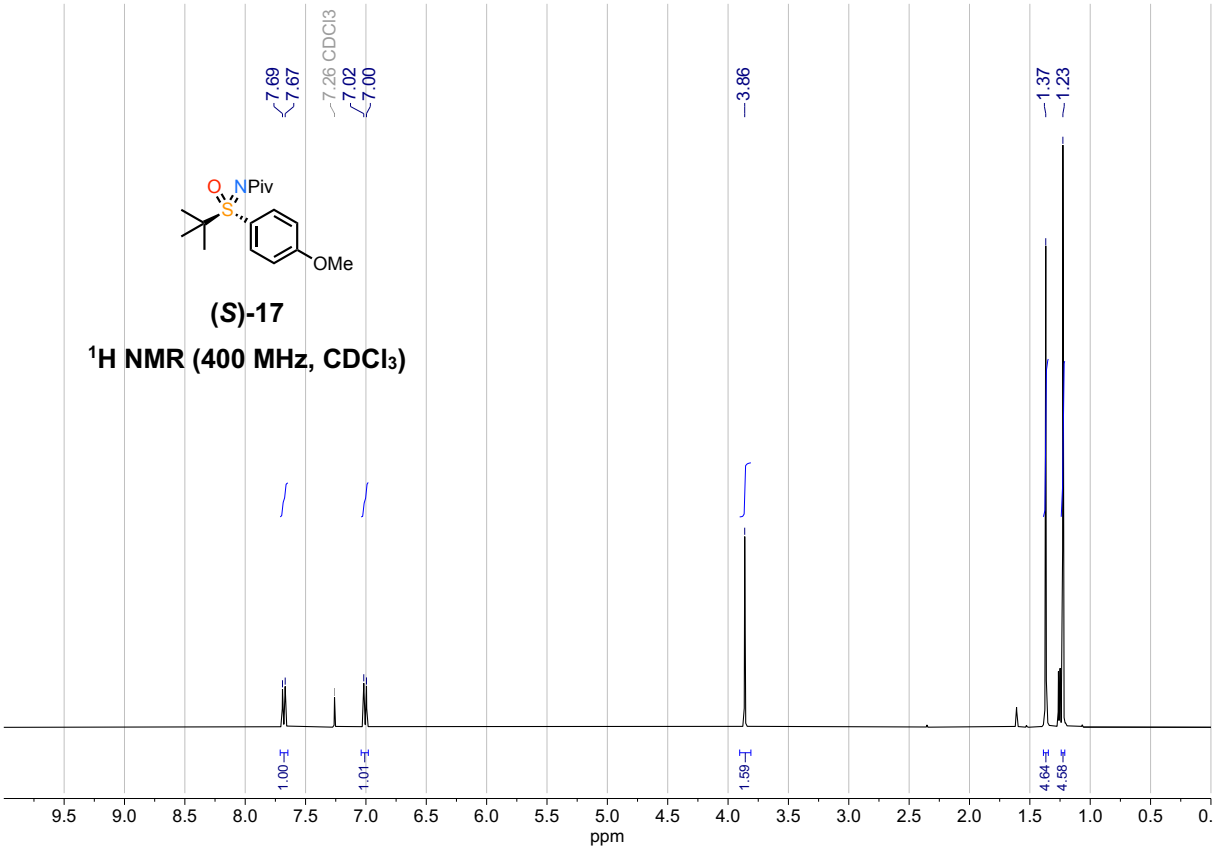


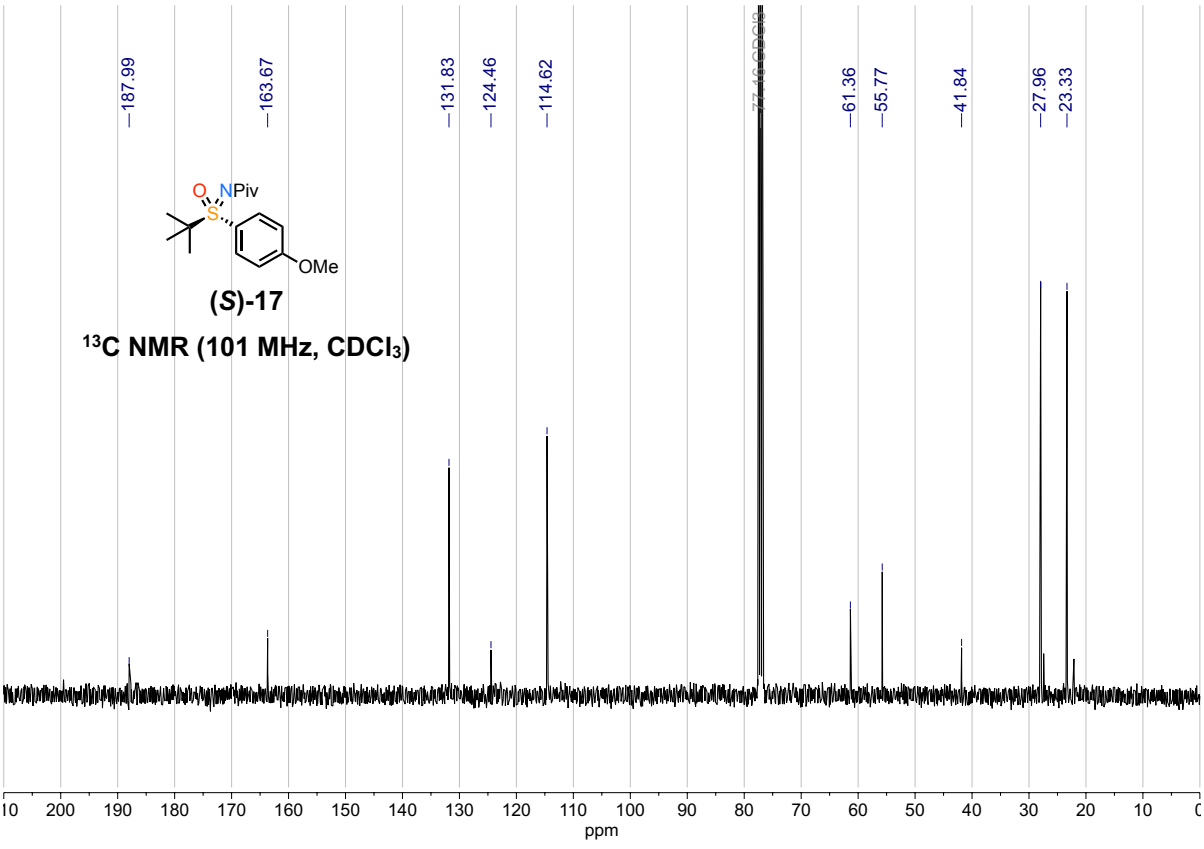
(*R*)-*N*-(*tert*-Butylsulfinyl)pivalamide ((*R*)-16)



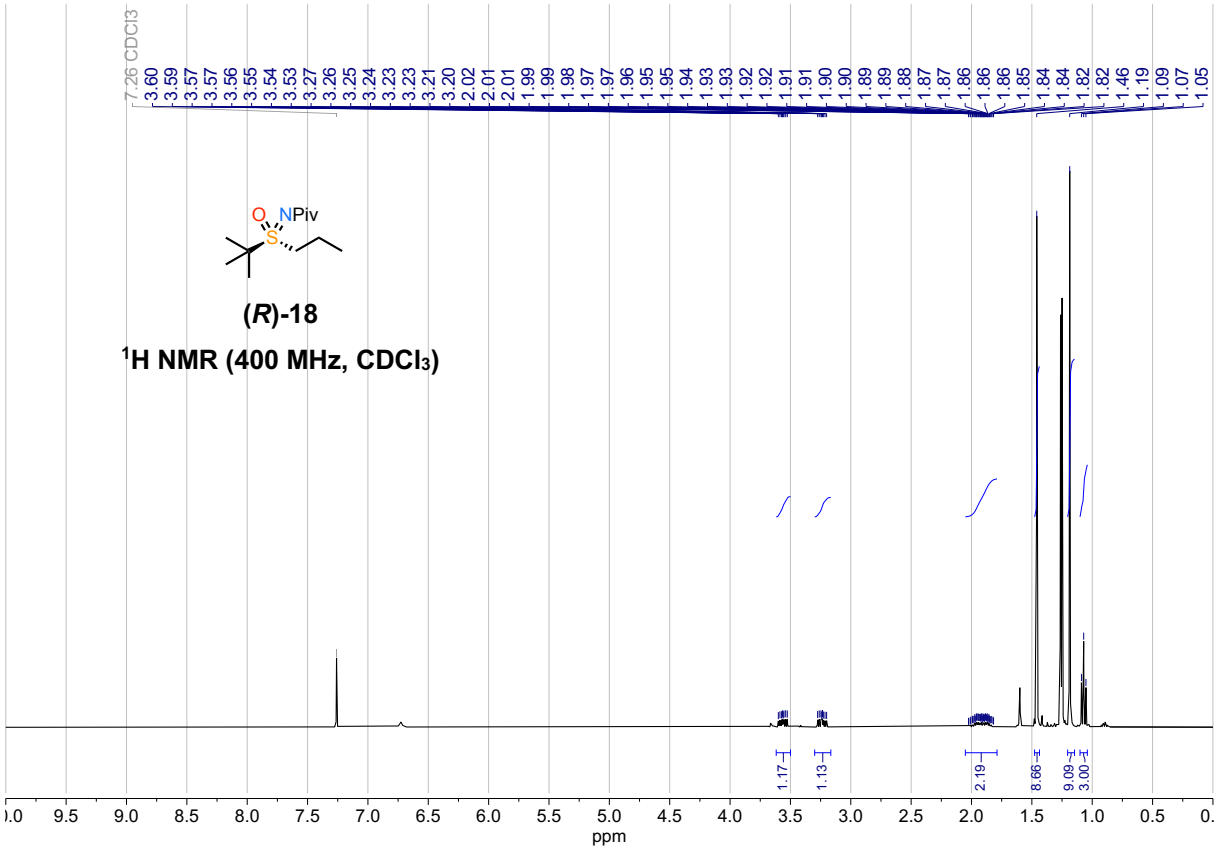


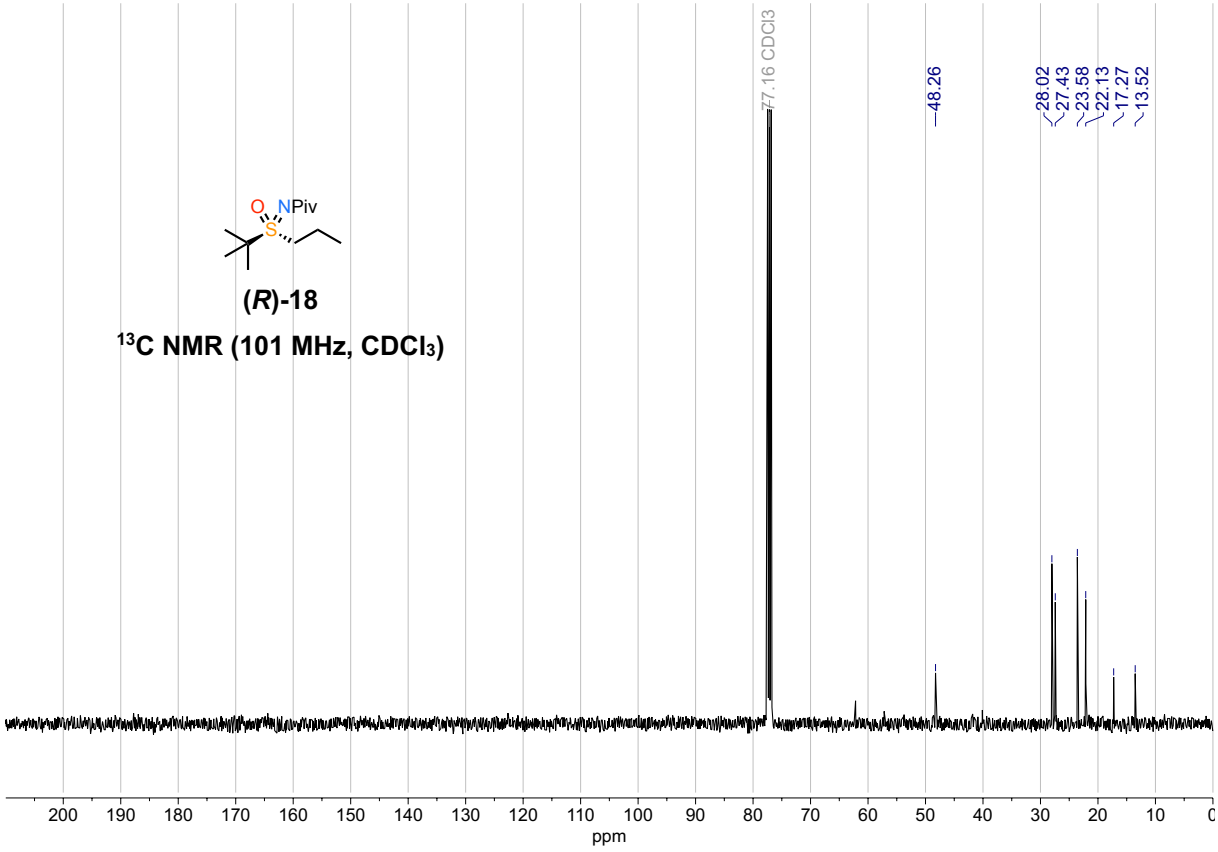
(*S*)-*N*-(*tert*-Butyl(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)pivalamide ((*S*)-17)



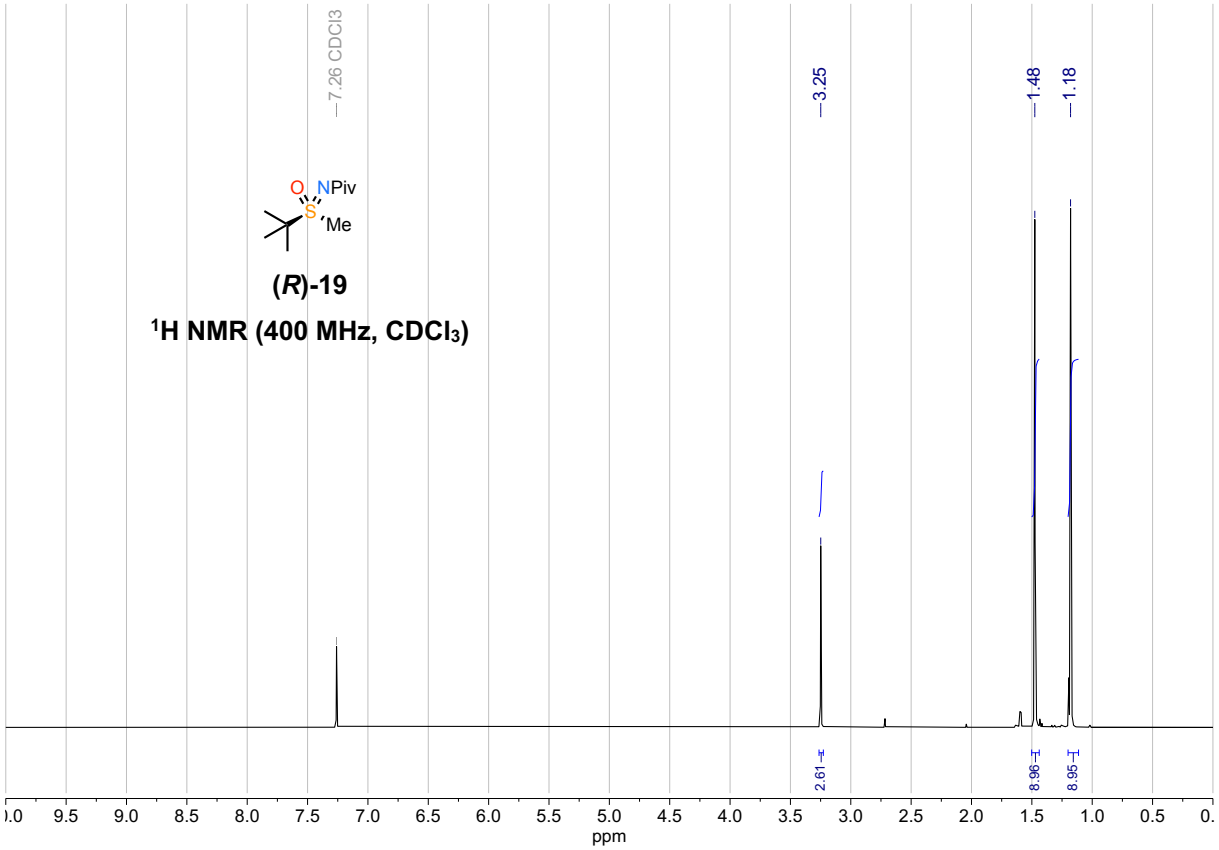


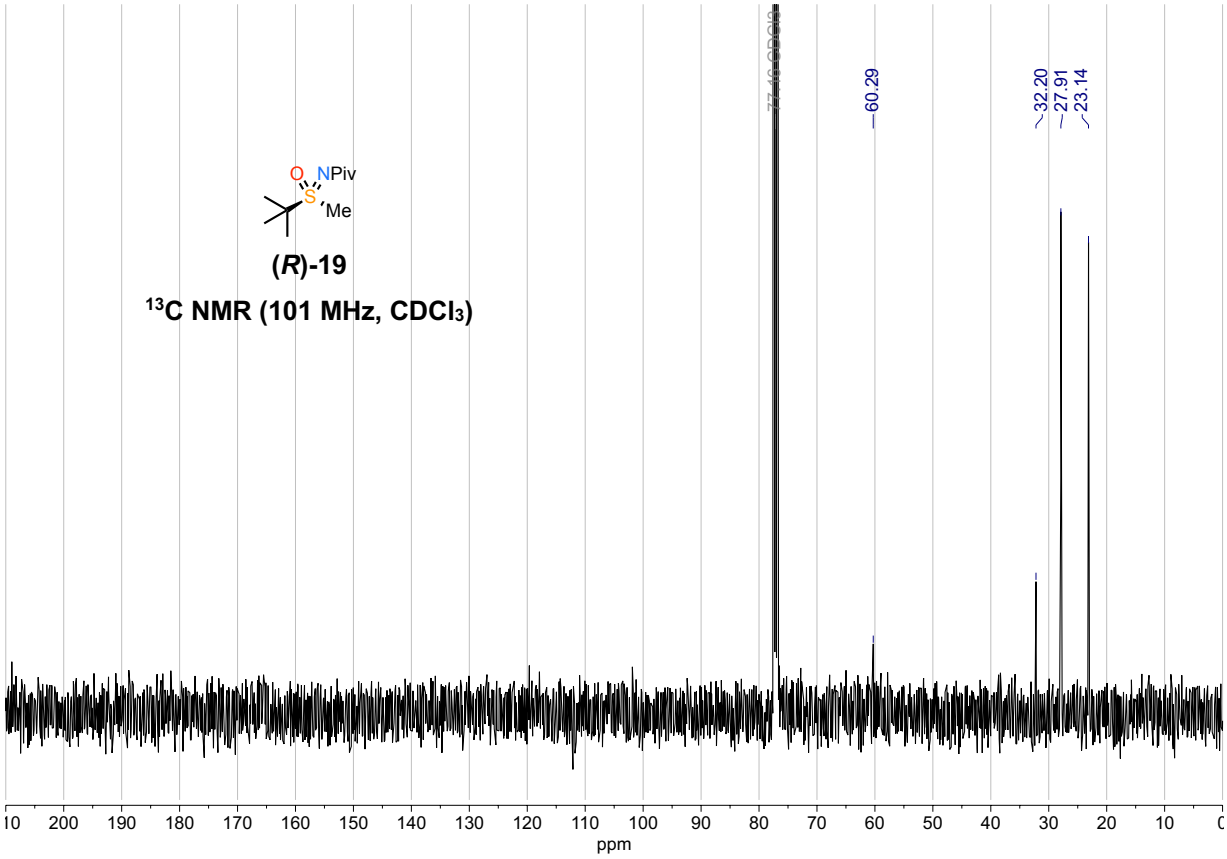
(*R*)-*N*-(*tert*-Butyl(oxo)(propyl)-λ⁶-sulfaneylidene)pivalamide ((*R*)-18)



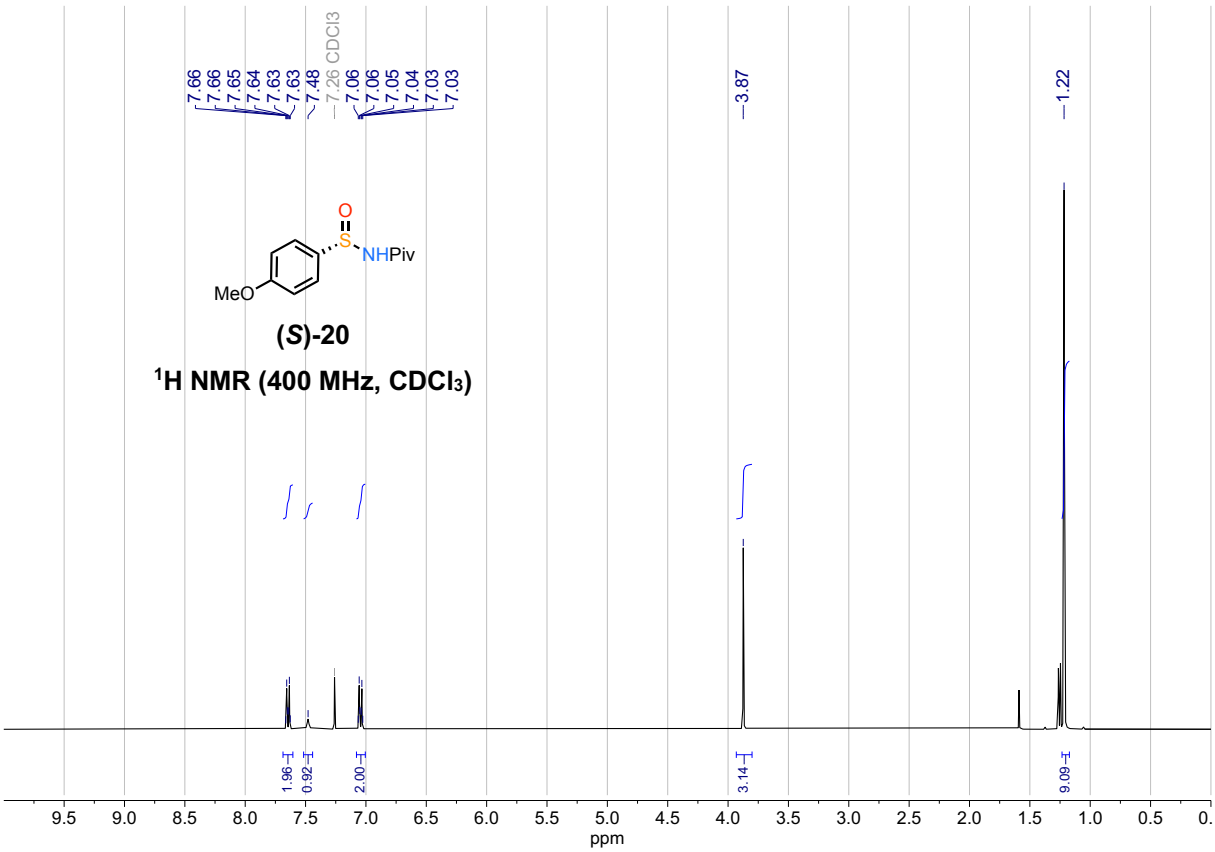


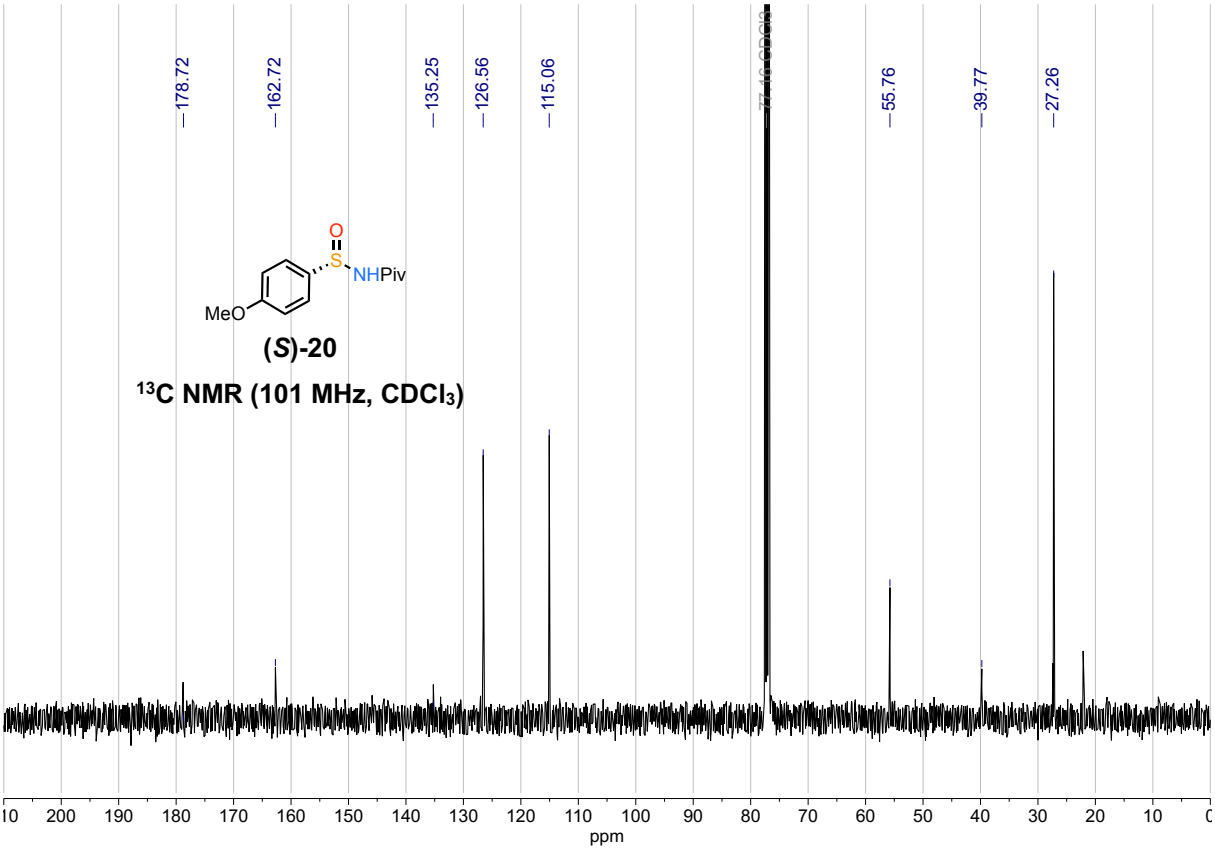
(*R*)-*N*-(*tert*-Butyl(methyl)(oxo)-λ^6-sulfaneylidene)pivalamide ((*R*)-19)



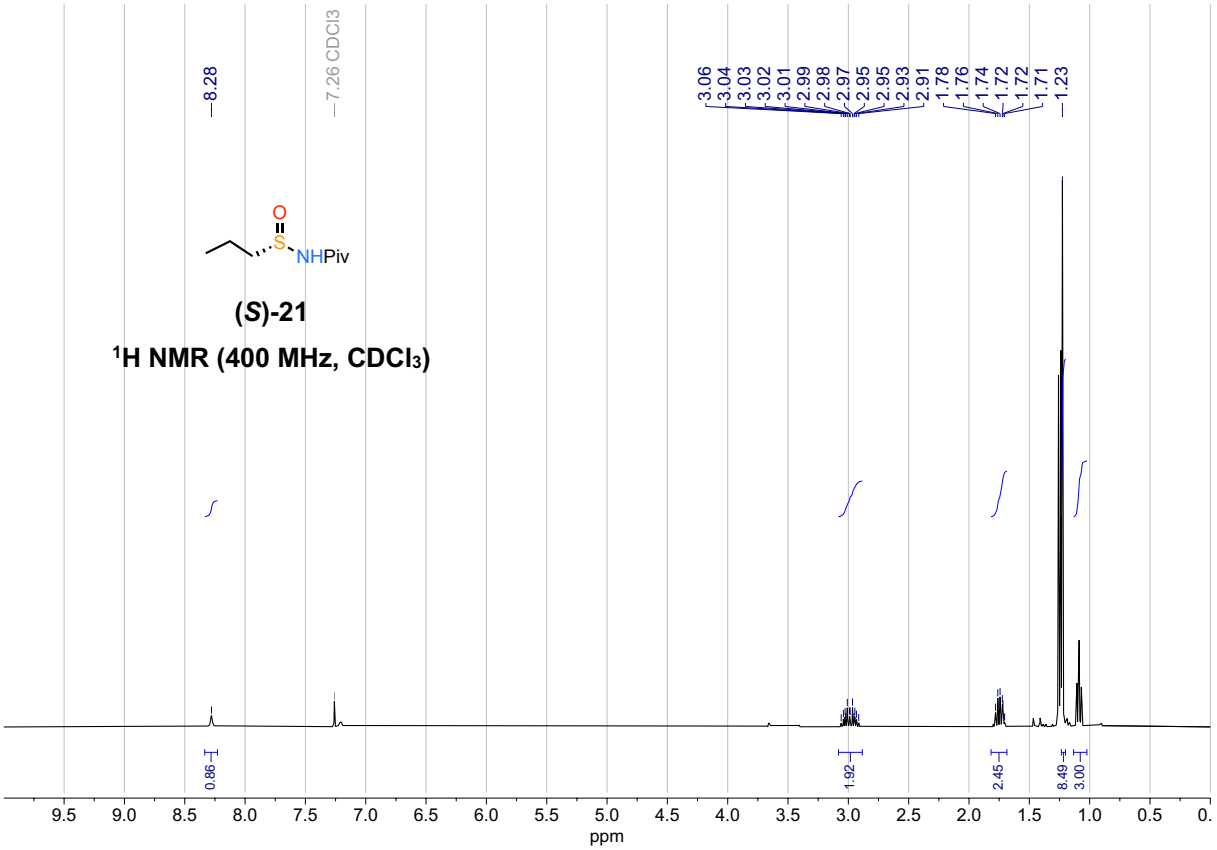


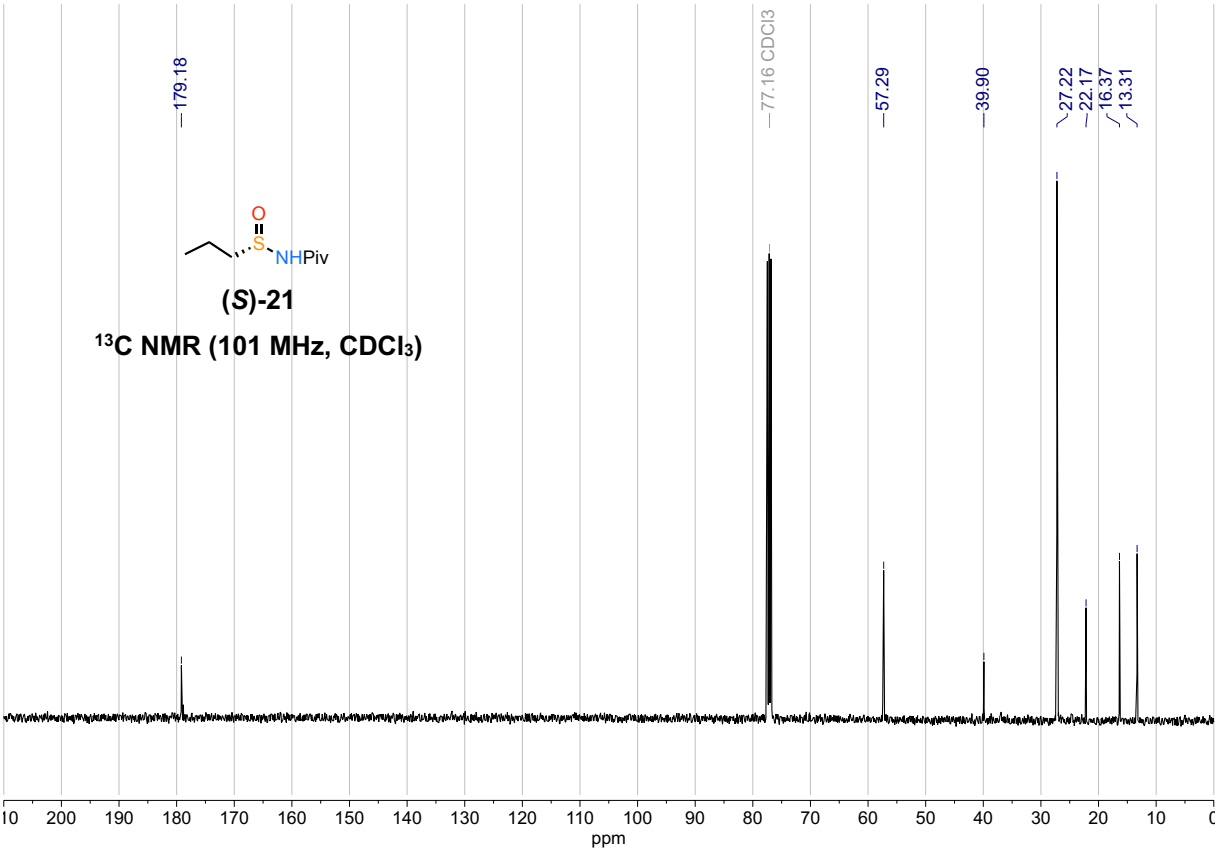
(*S*)-*N*-((4-Methoxyphenyl)sulfinyl)pivalamide ((*S*)-20)



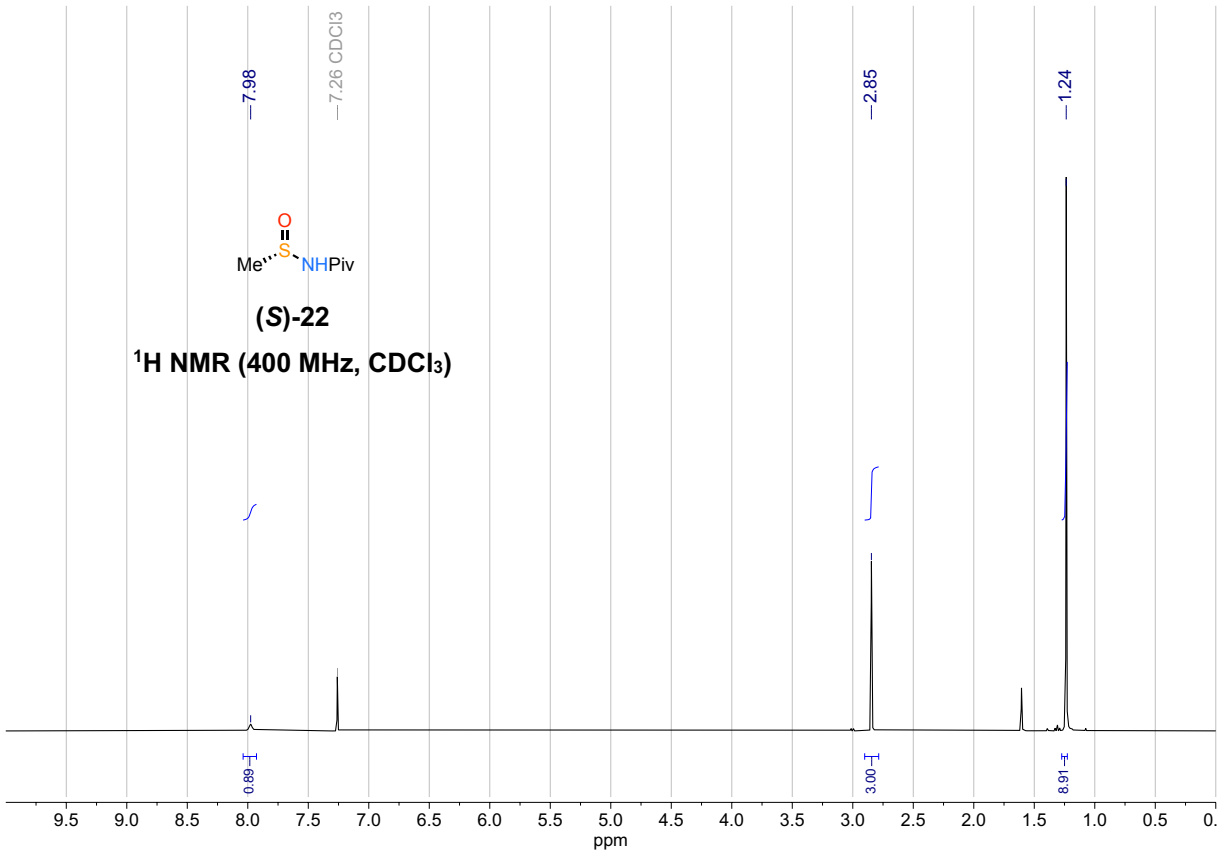


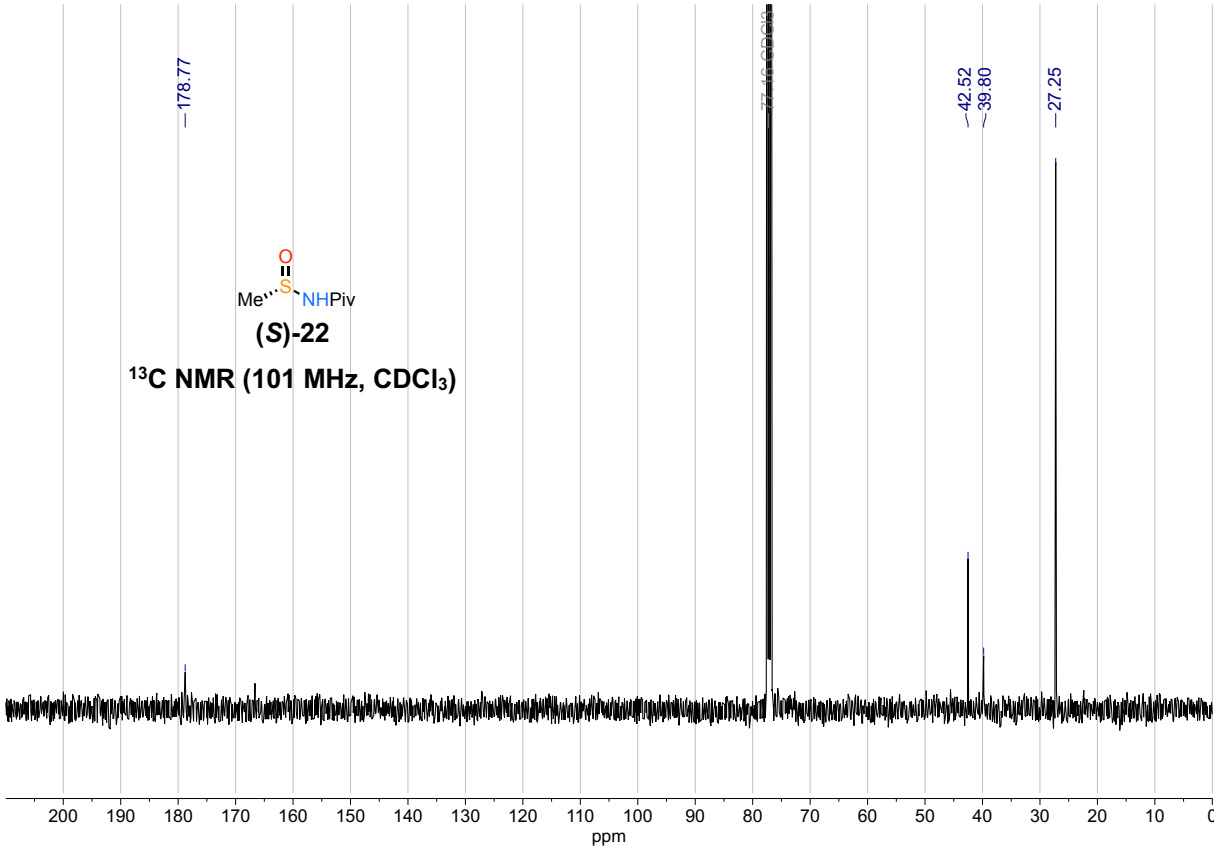
(*S*)-*N*-(Propylsulfinyl)pivalamide ((*S*)-21)



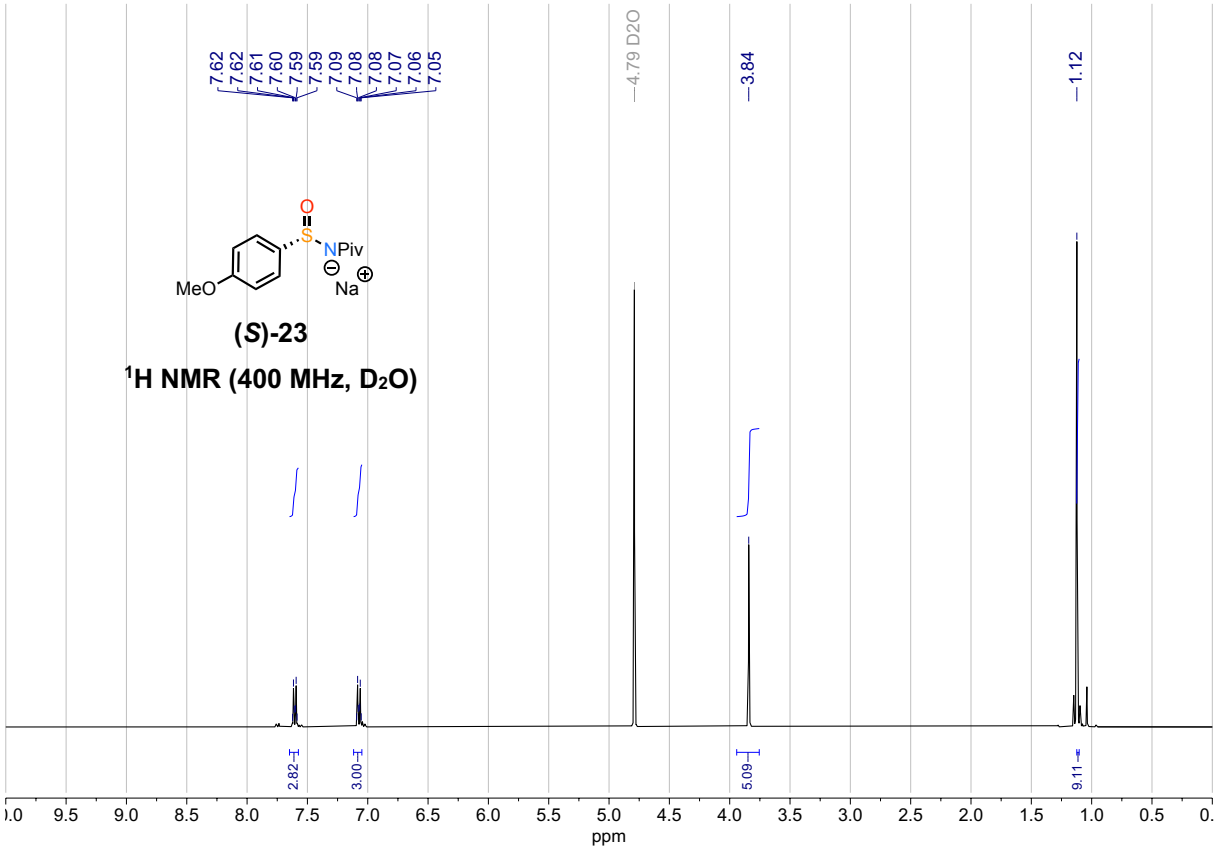


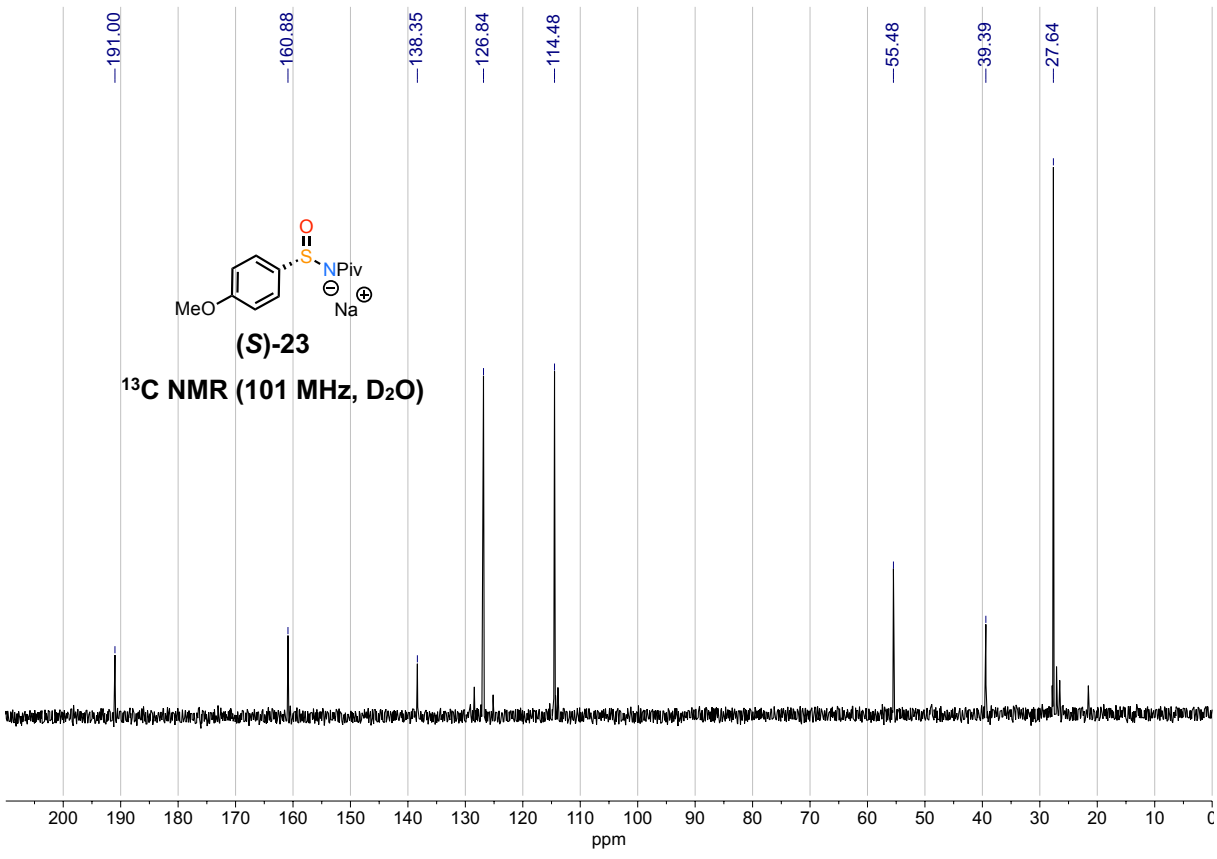
(*S*)-*N*-(Methylsulfinyl)pivalamide ((*S*)-22)



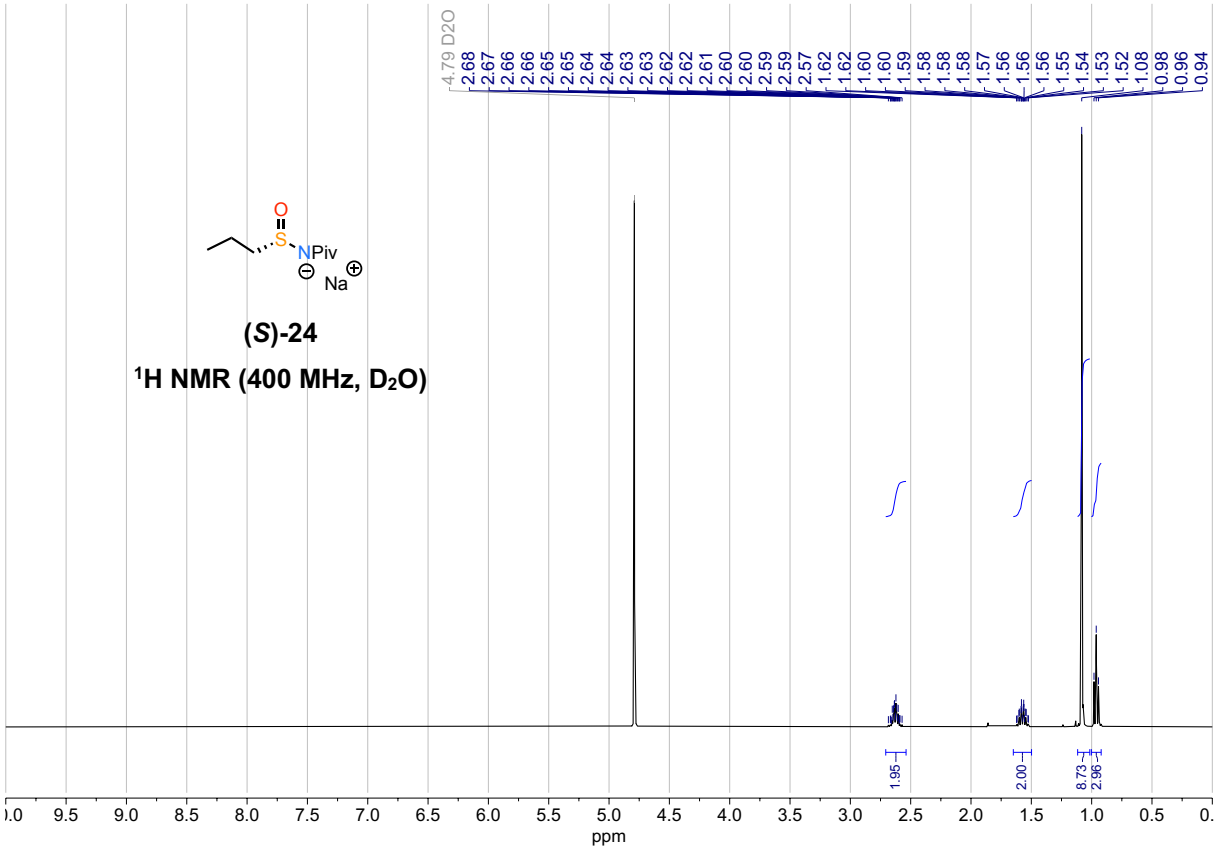


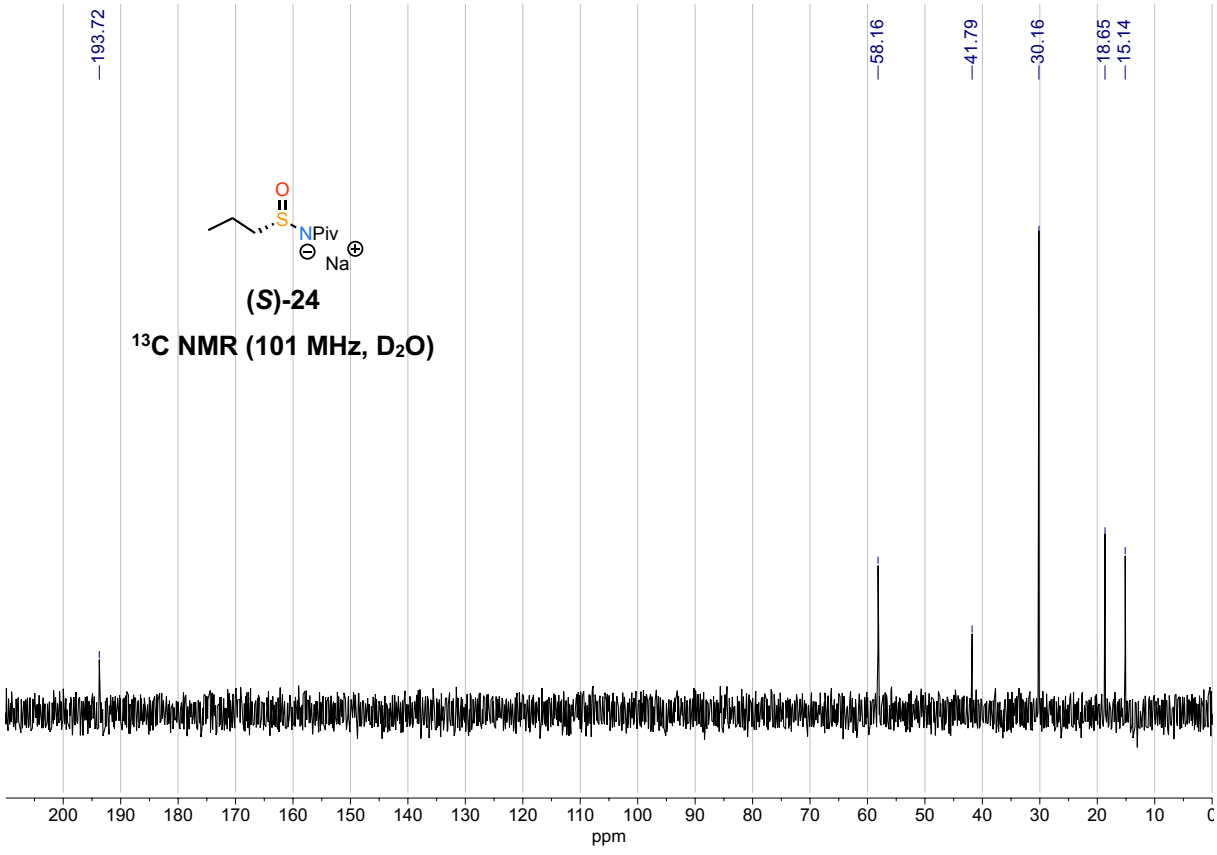
Sodium (*S*)-((4-methoxyphenyl)sulfinyl)(pivaloyl)amide ((*S*)-23)



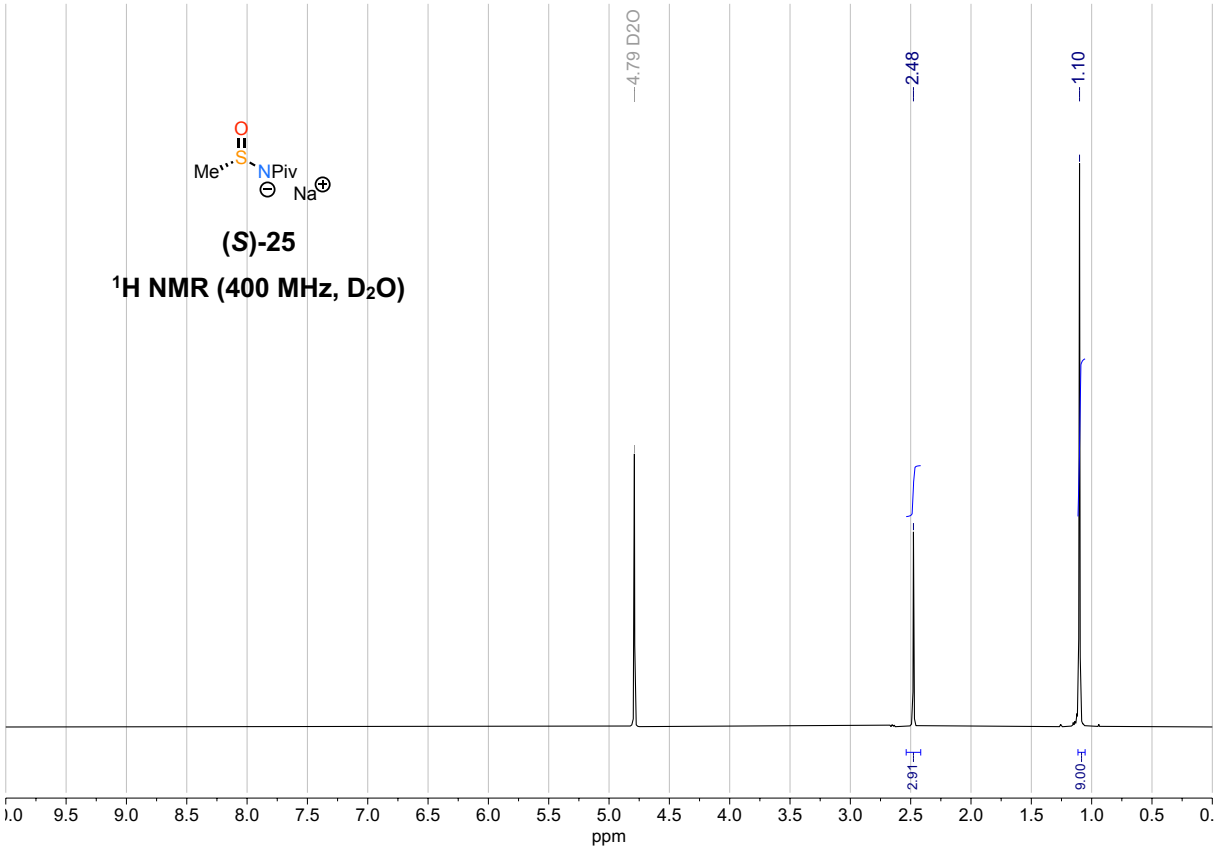


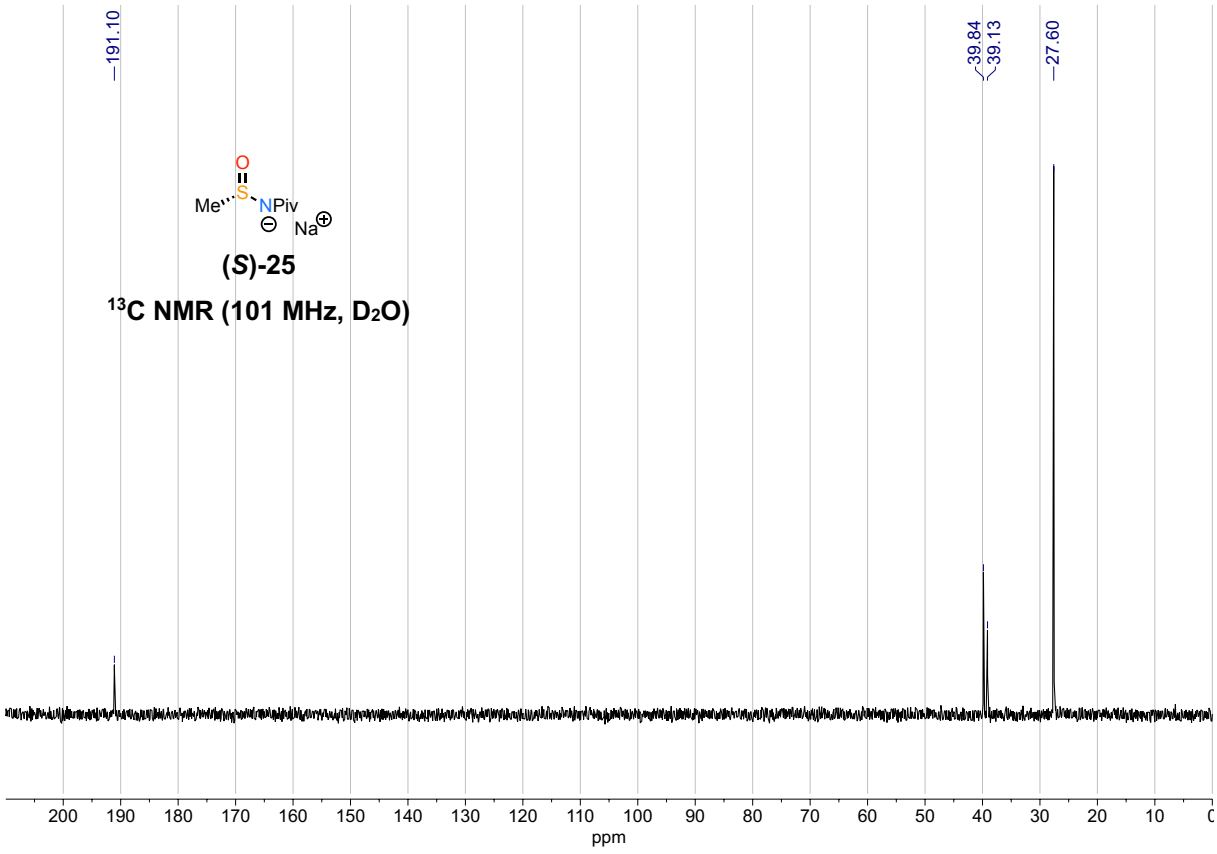
Sodium (*S*)-pivaloyl(propylsulfinyl)amide ((*S*)-24)



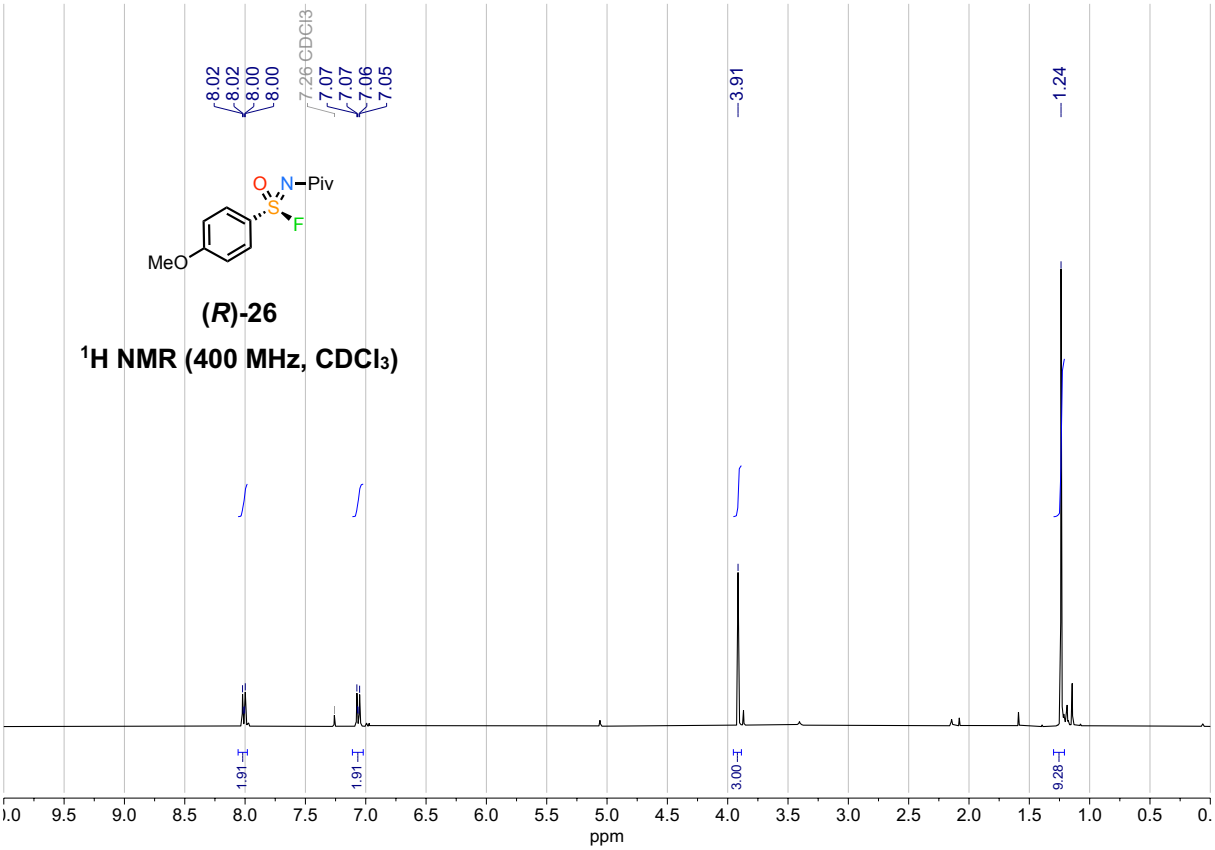


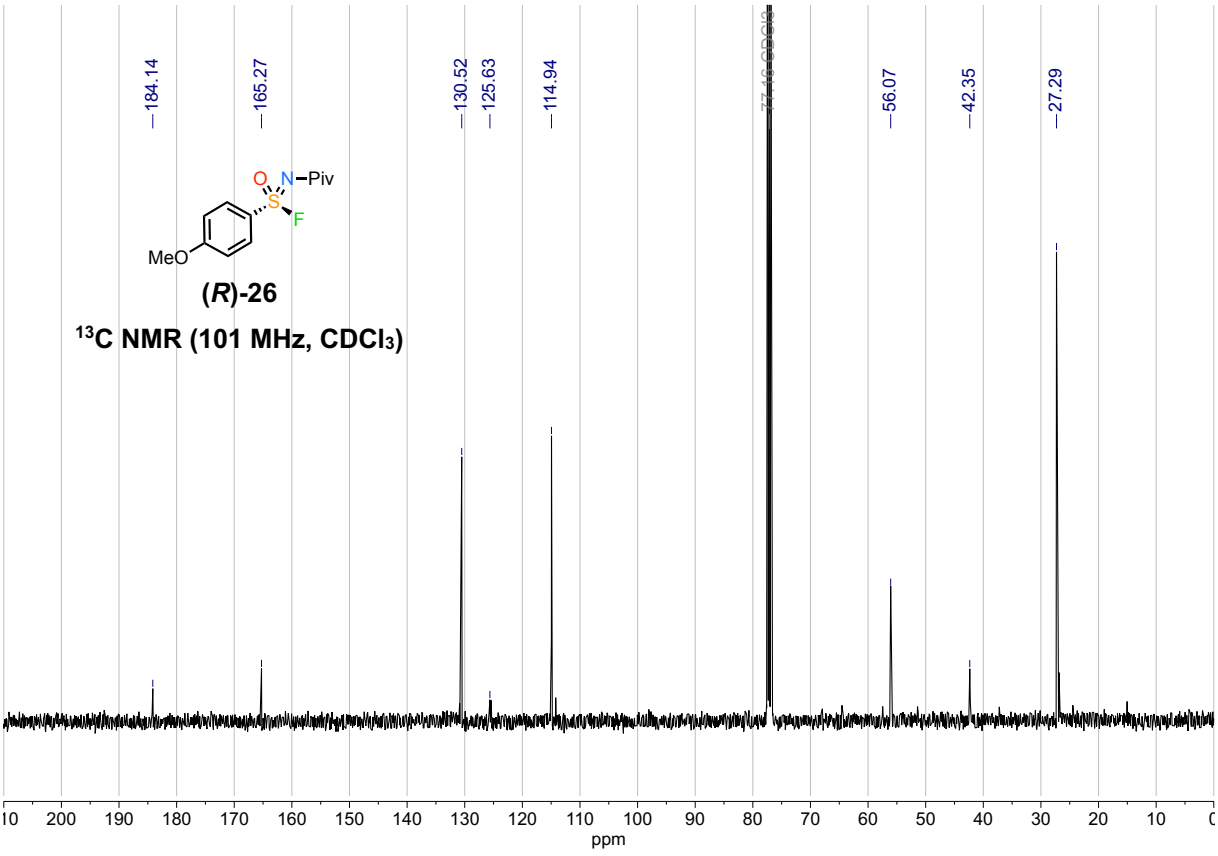
Sodium (*S*)-(methylsulfinyl)(pivaloyl)amide ((*S*)-25)

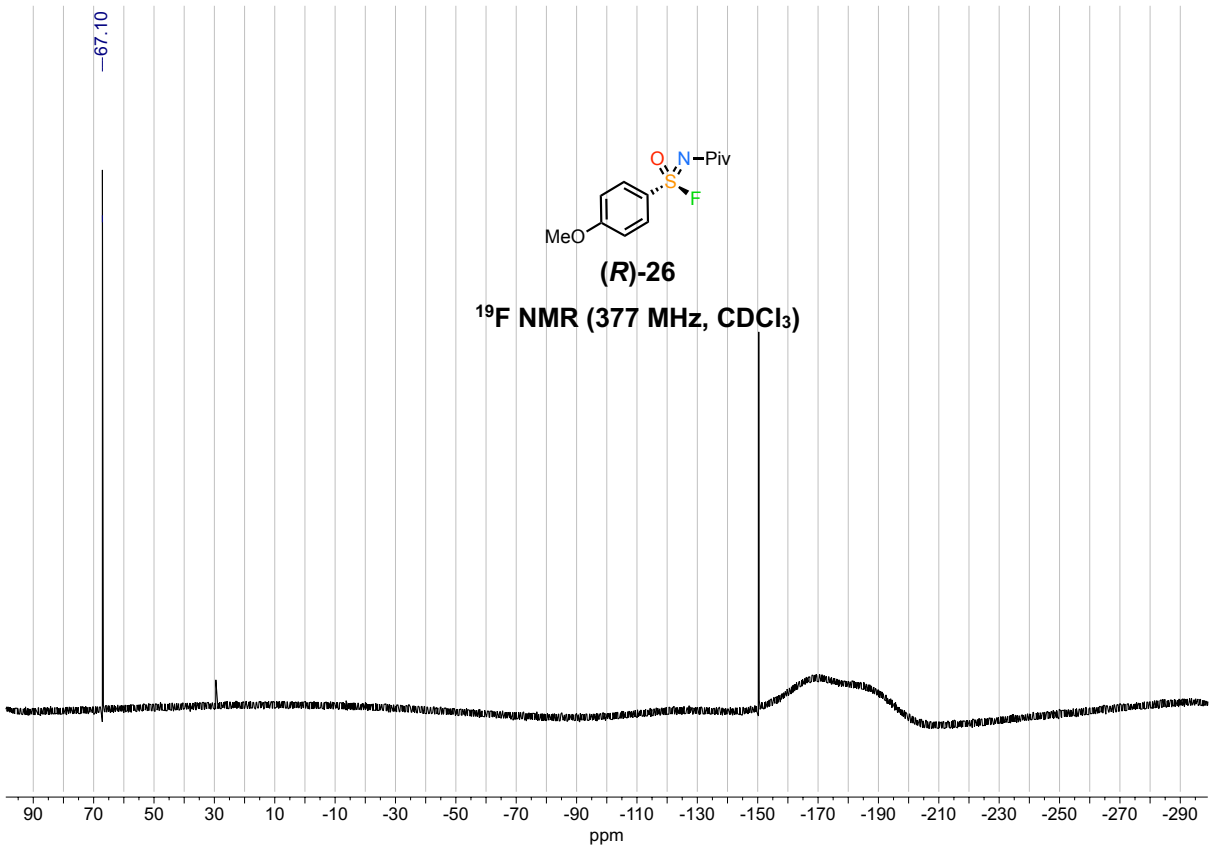




(*R*)-4-Methoxy-*N*-pivaloylbenzenesulfonimidoyl fluoride ((*R*)-26)



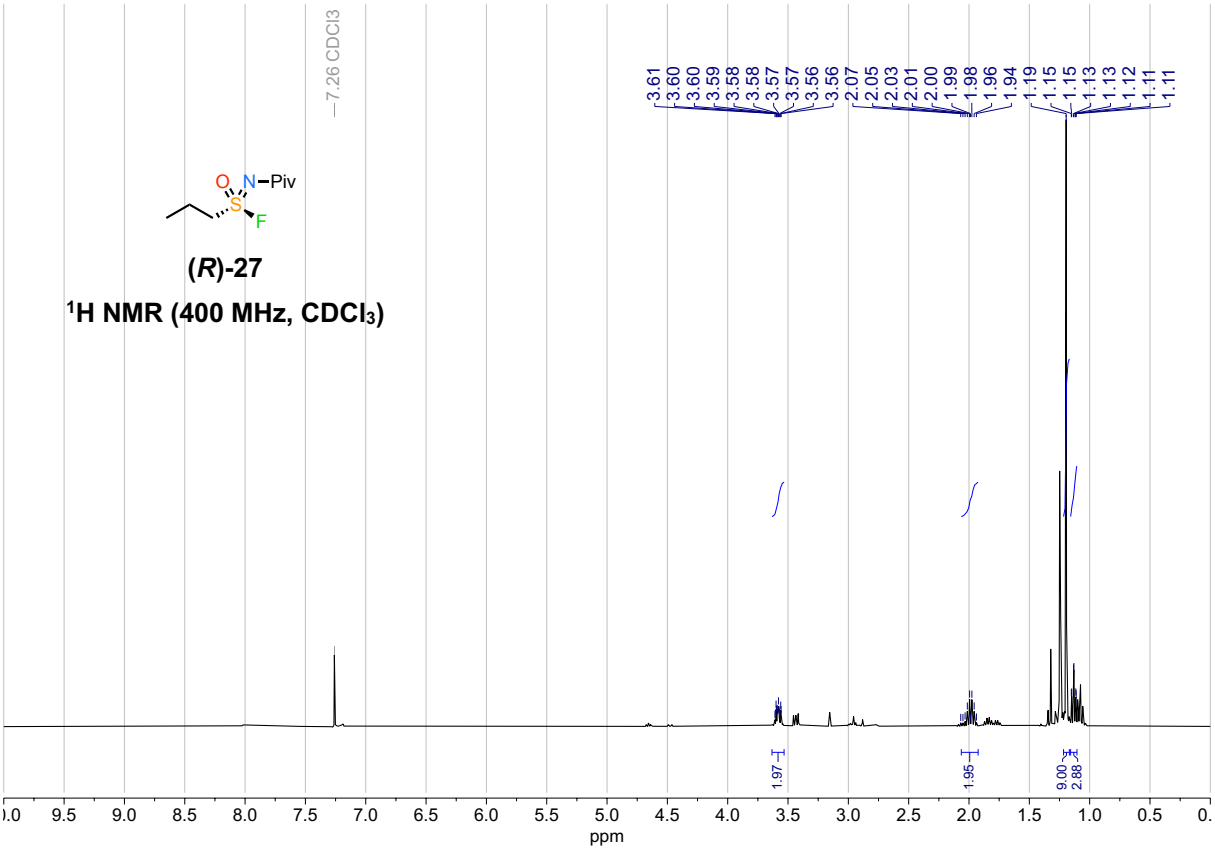


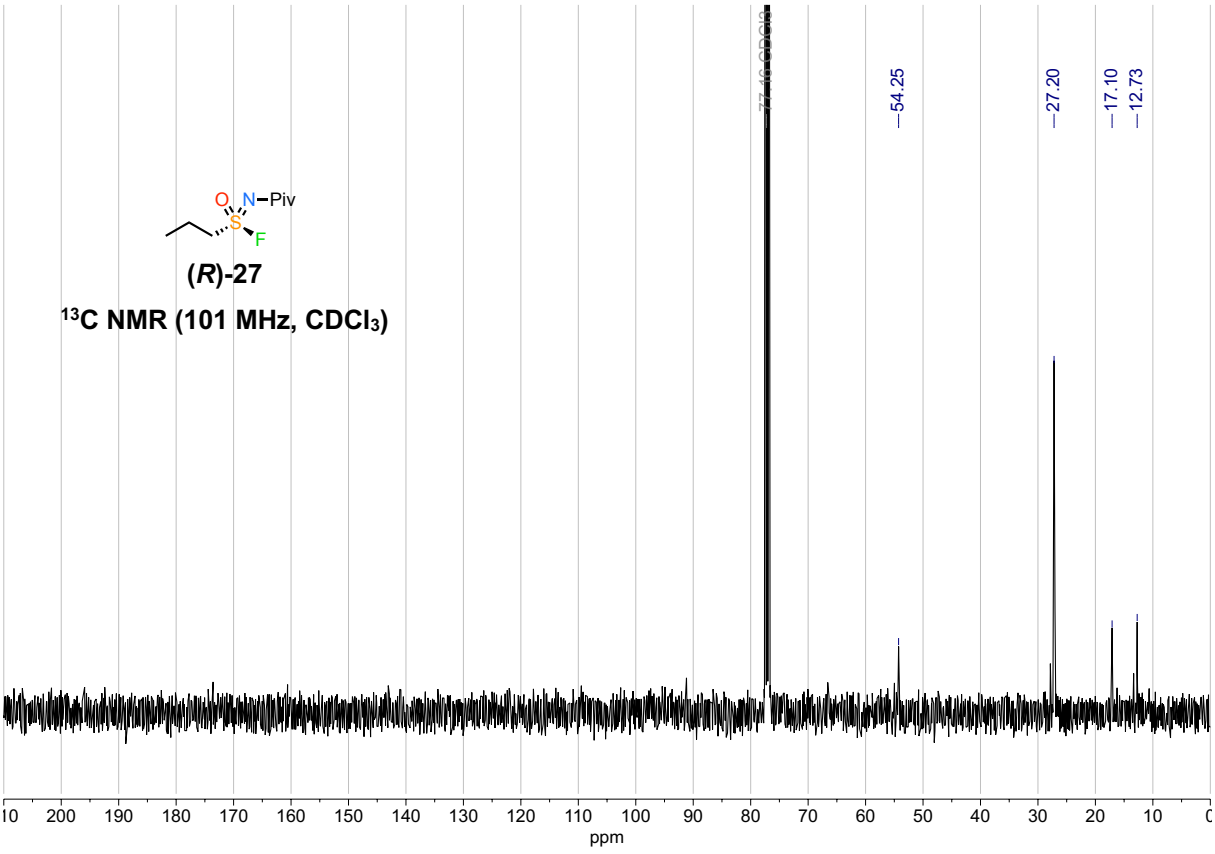


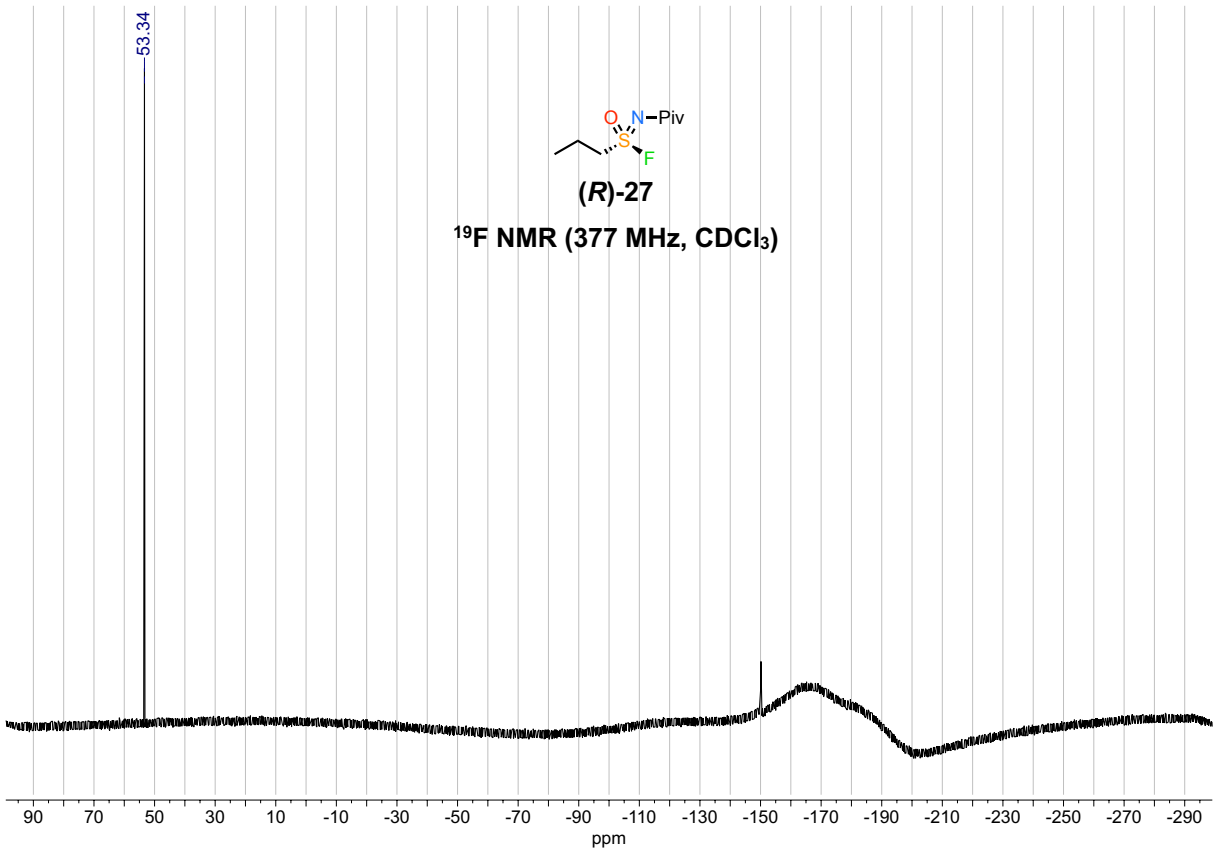
(*R*)-26

^{19}F NMR (377 MHz, $CDCl_3$)

(*R*)-*N*-Pivaloylpropane-1-sulfonimidoyl fluoride ((*R*)-27)



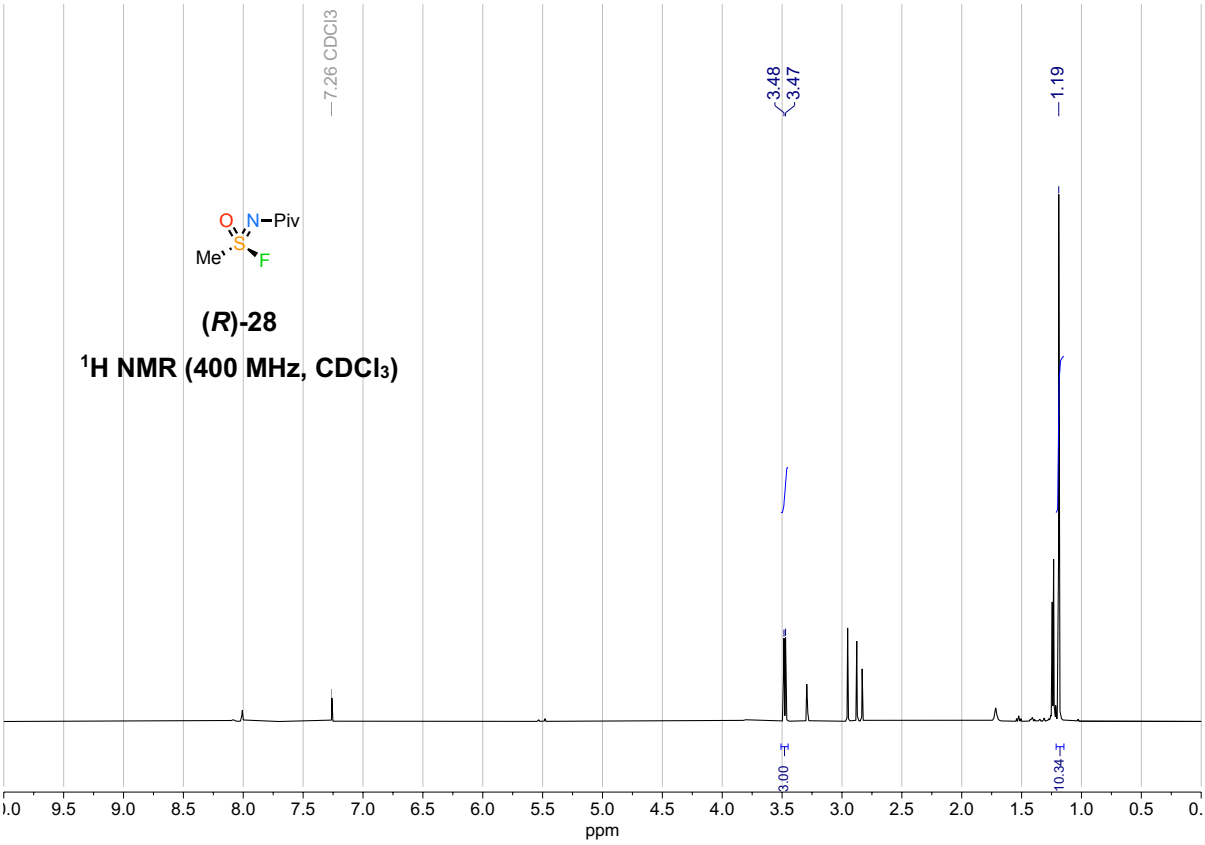


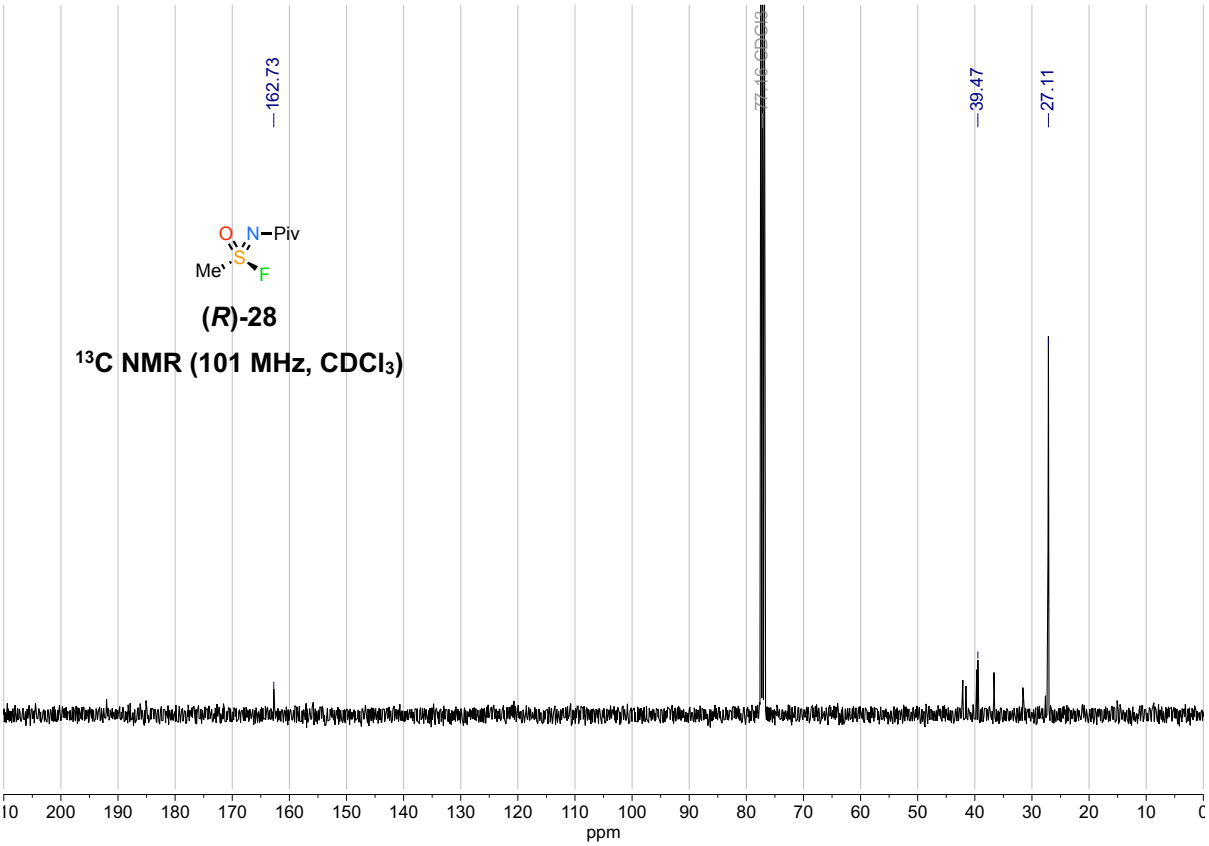


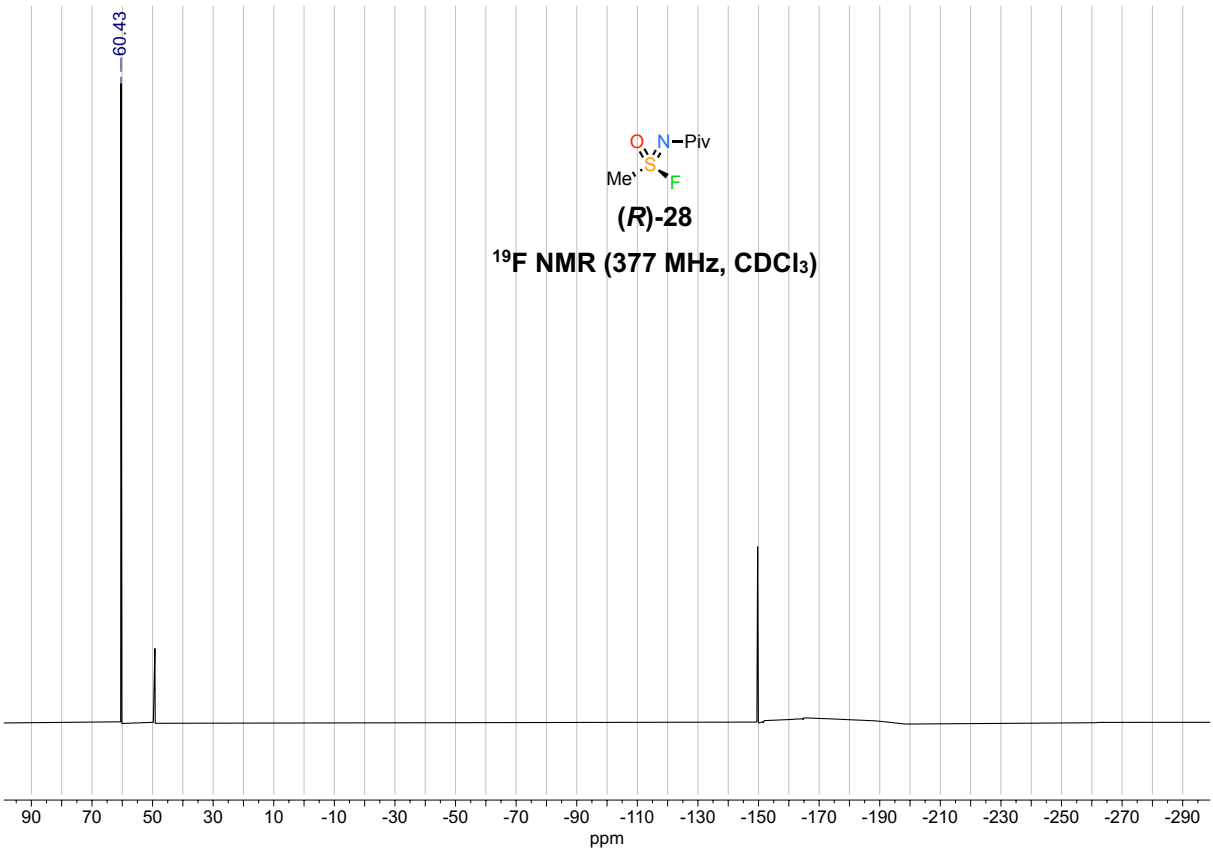
(*R*)-27

^{19}F NMR (377 MHz, $CDCl_3$)

(*R*)-*N*-Pivaloylmethanesulfonimidoyl fluoride ((*R*)-28)



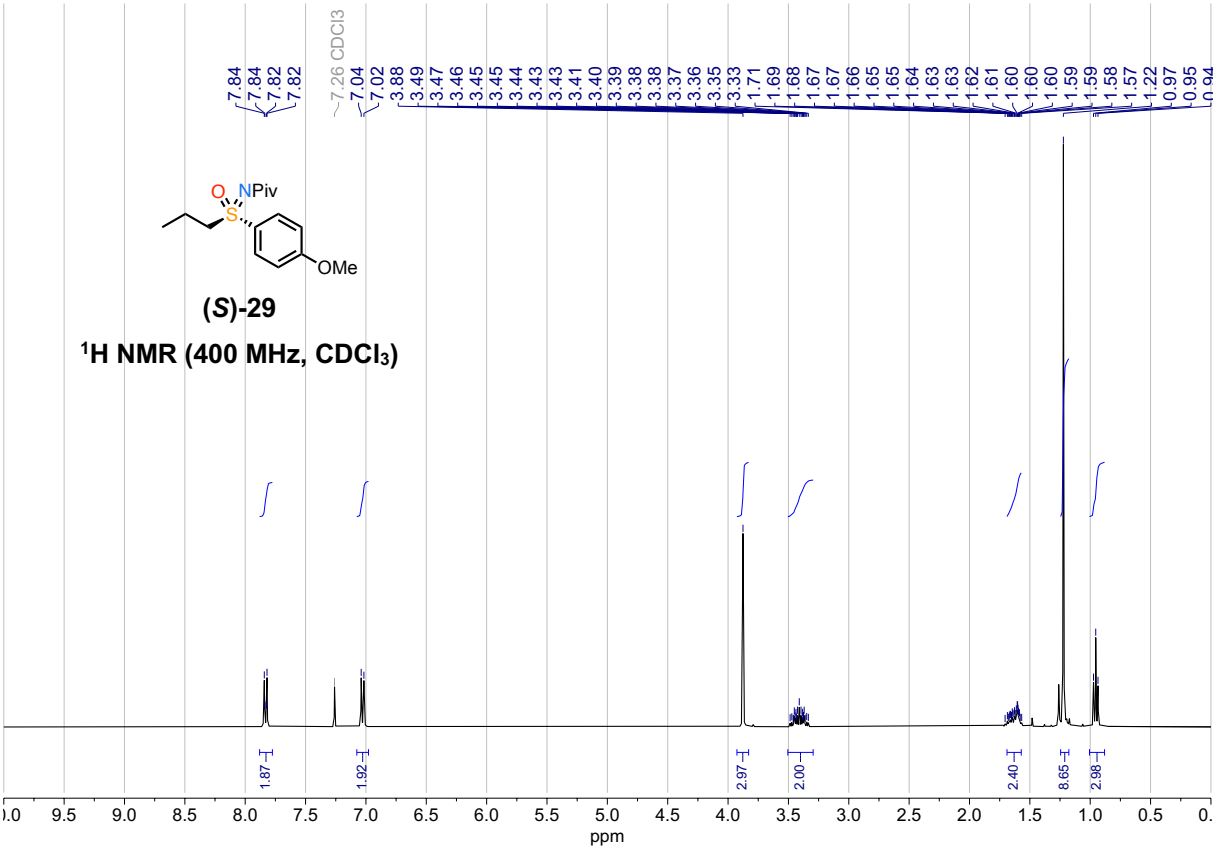


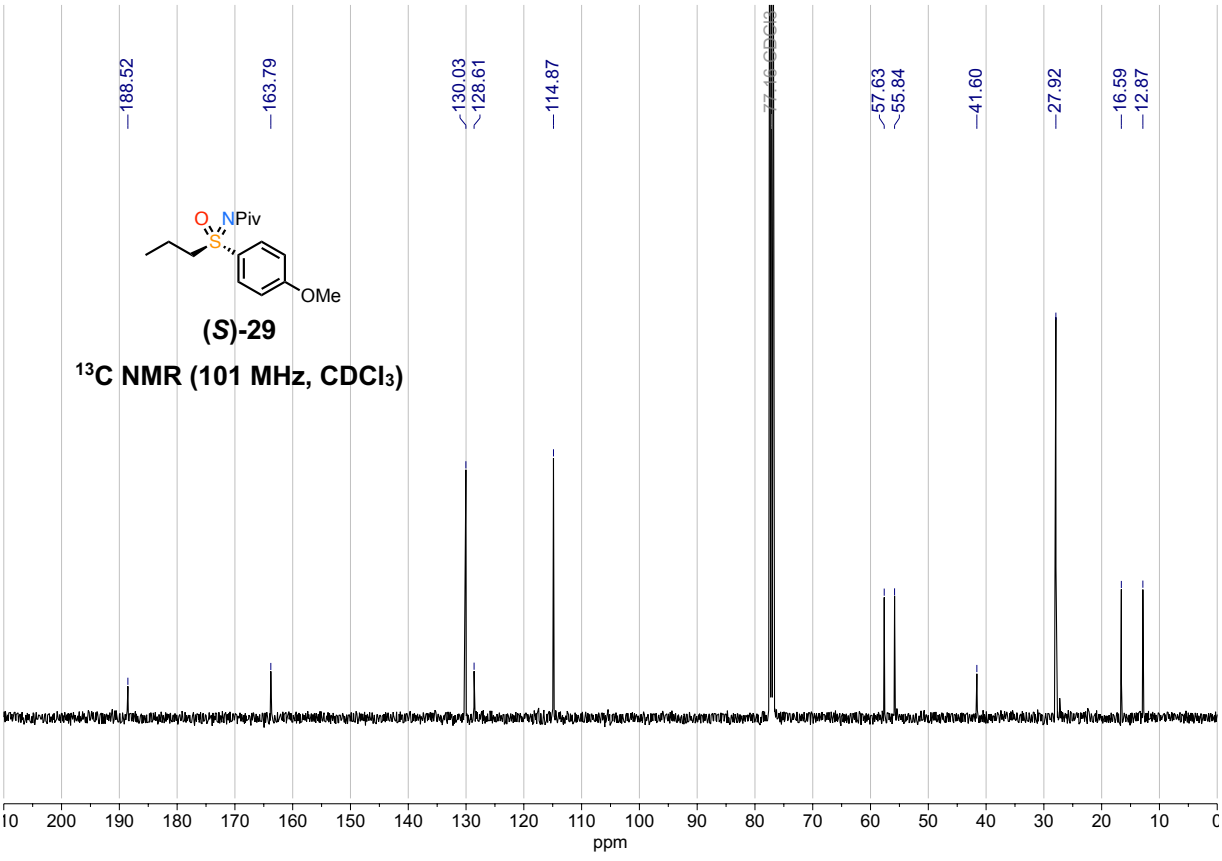


(*R*)-28

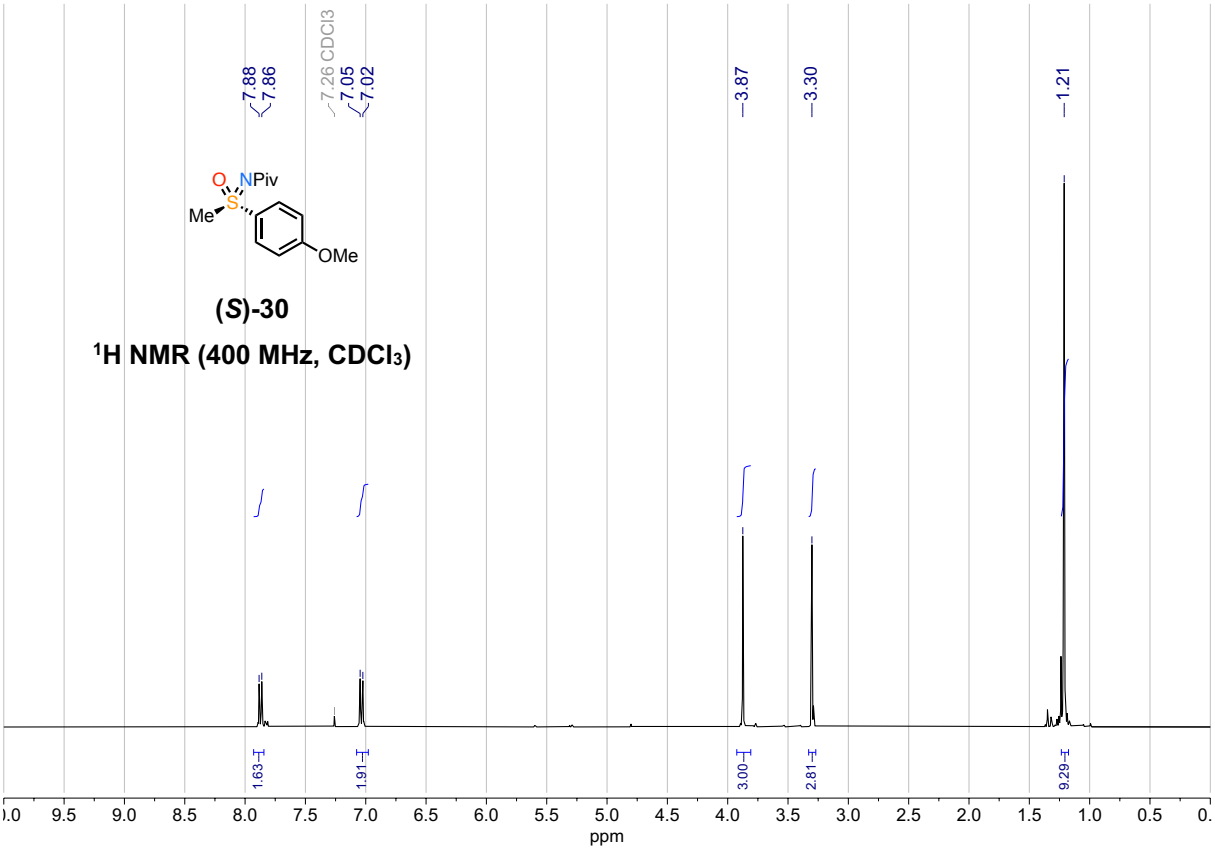
^{19}F NMR (377 MHz, $CDCl_3$)

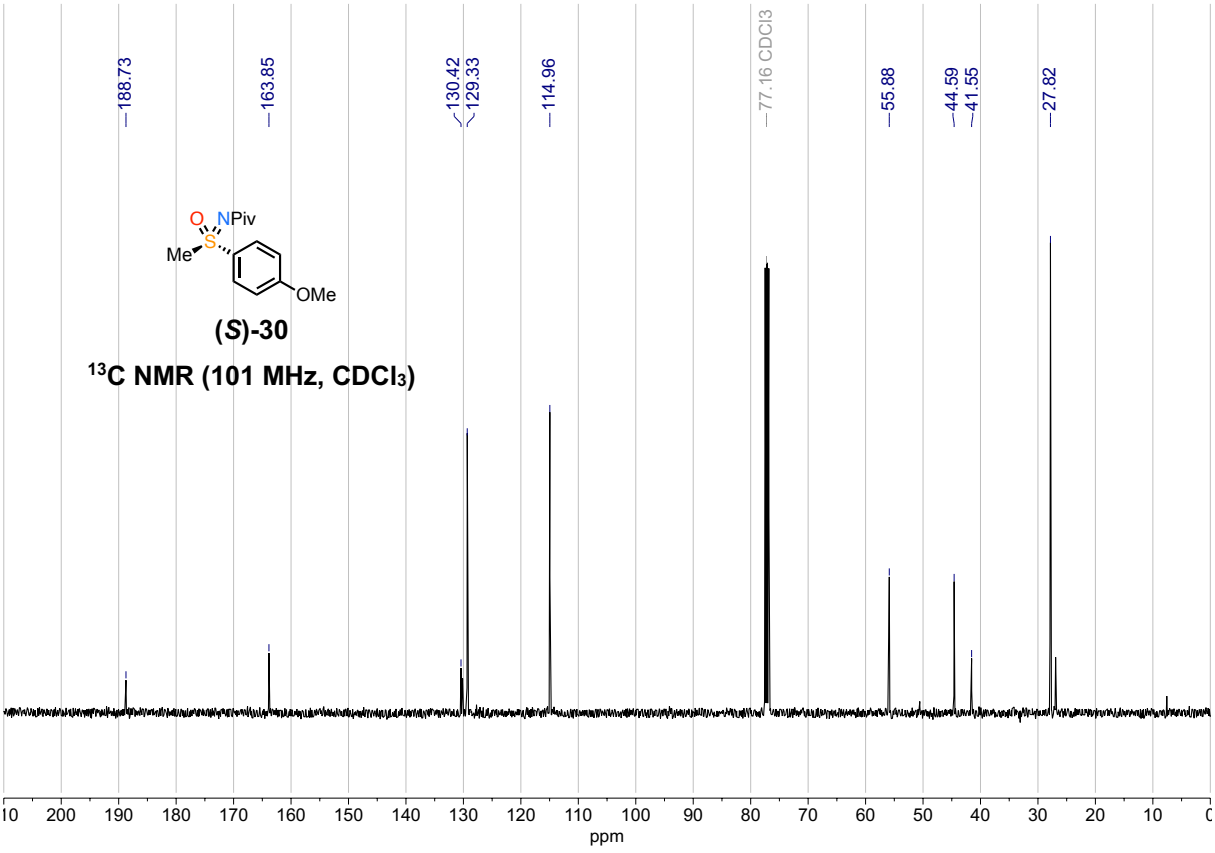
(*S*)-*N*-((4-methoxyphenyl)(oxo)(propyl)-λ^6-sulfaneylidene)pivalamide ((*S*)-29)



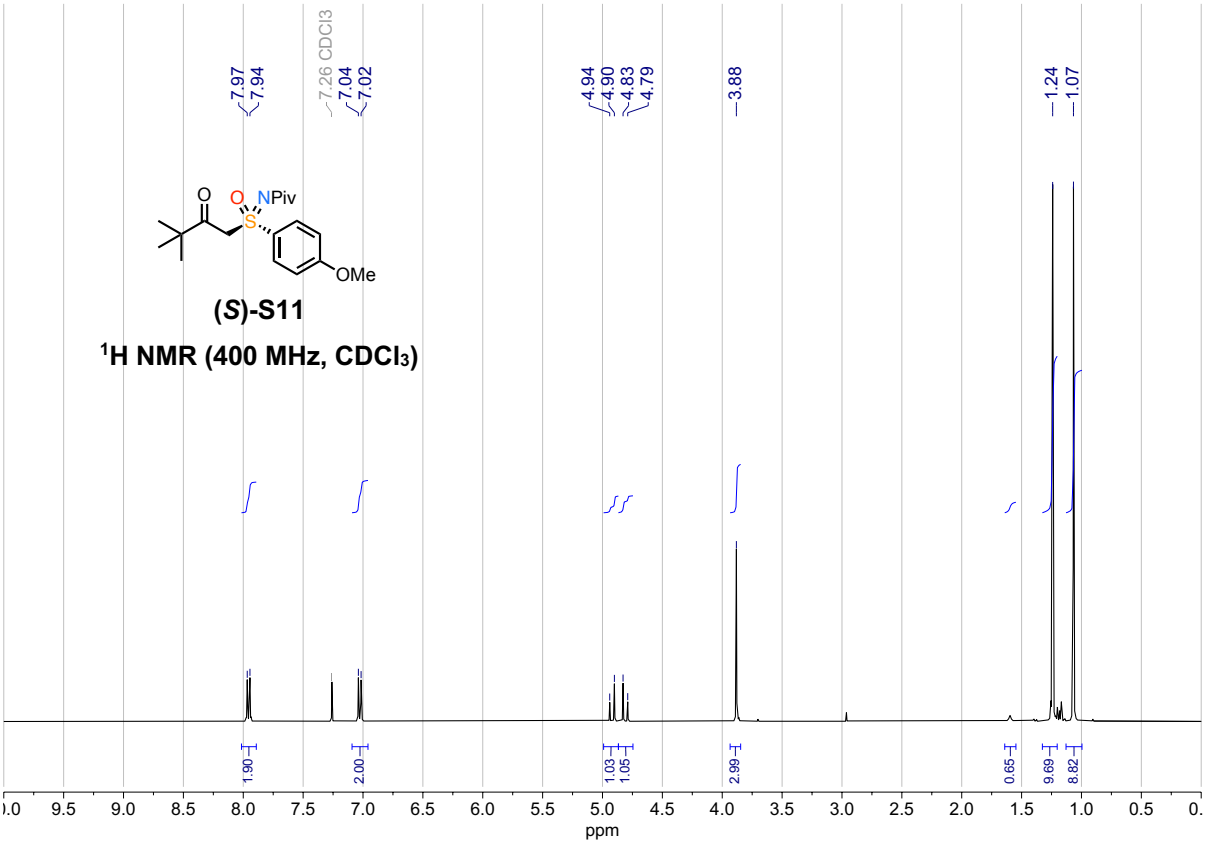


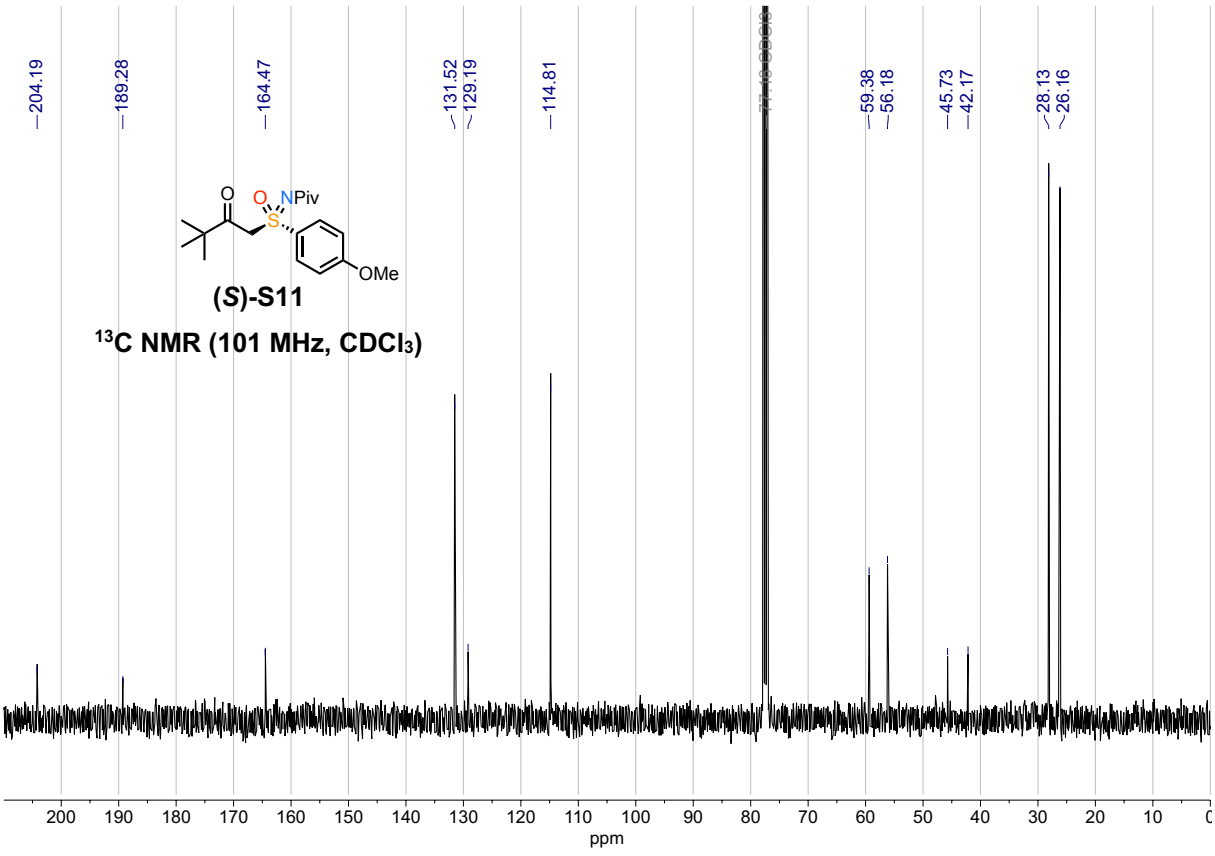
(*S*)-*N*-((4-Methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)pivalamide ((*S*)-30)





(*S*)-*N*-((3,3-Dimethyl-2-oxobutyl)(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)pivalamide ((*S*)-S11)





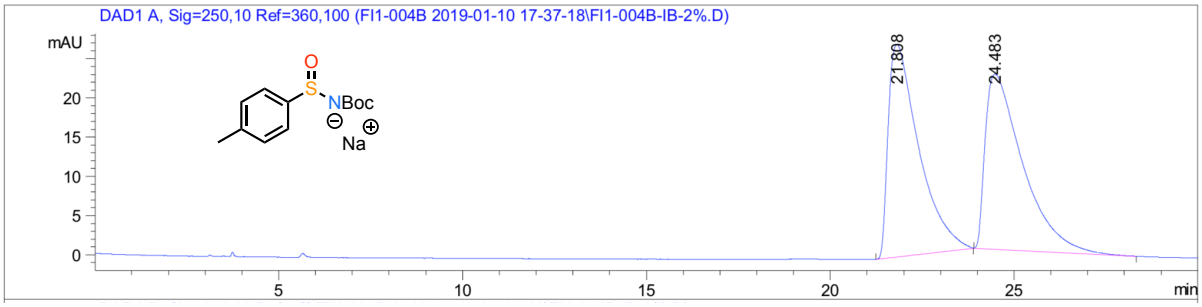
Chiral HPLC Data

Sodium (*tert*-butoxycarbonyl)(*p*-tolylsulfinyl)amide ((*S*)-3a)

Determination of *ee* from reprotonation. The minimum MeOH (~0.1 mL) was added to a sample of **(*S*)-3a** (~1 mg) until completely dissolved. An aliquot was removed and diluted with hexane for HPLC analysis of sulfinamide **(*S*)-3a**.

Conditions: Chiralpak IB column, 98:2 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm.

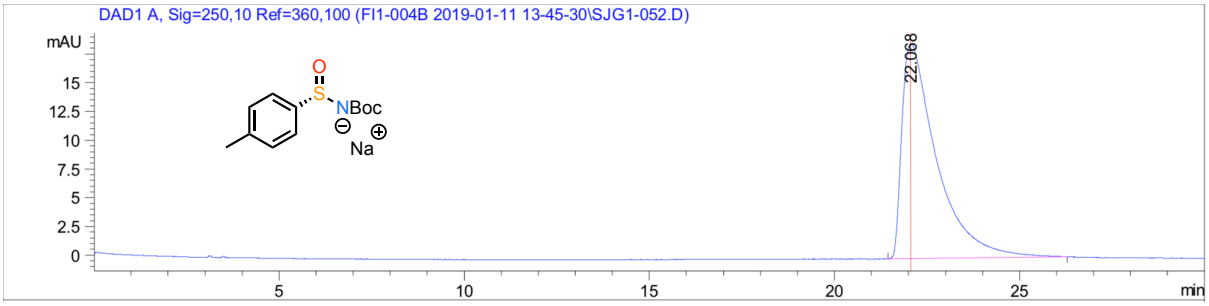
(*rac*)-3a



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.808	BB	0.8231	1568.53638	27.10690	49.7337
2	24.483	BB	0.9969	1585.33215	22.31392	50.2663
Totals :				3153.86853	49.42082	

(*S*)-3a



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.068	BB	0.9253	1221.97766	18.72633	100.0000
Totals :				1221.97766	18.72633	

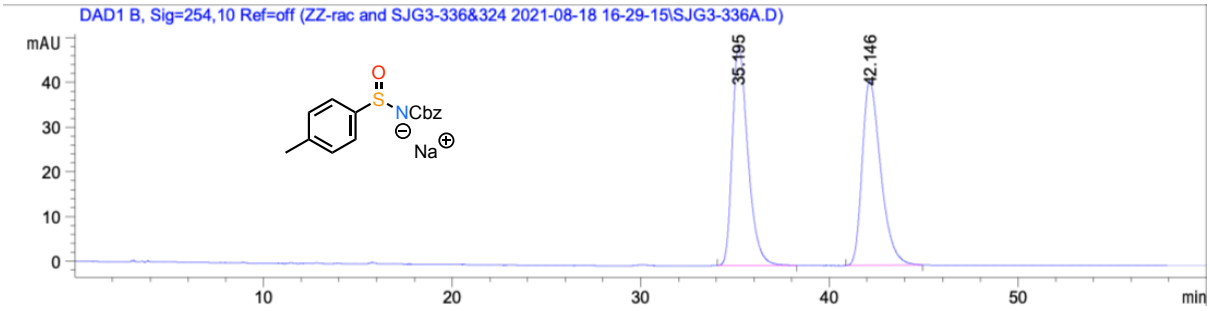
***ee* > 99%**

Sodium (*S*)-((Benzyloxy)carbonyl)(*p*-tolylsulfinyl)amide ((*S*)-3a-Cbz)

Determination of *ee* from reprotonation. The minimum MeOH (~0.1 mL) was added to a sample of **(*S*)-3a-Cbz** (~1 mg) until completely dissolved. An aliquot was removed and diluted with hexane for HPLC analysis of sulfinamide **(*S*)-3a-Cbz**.

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm.

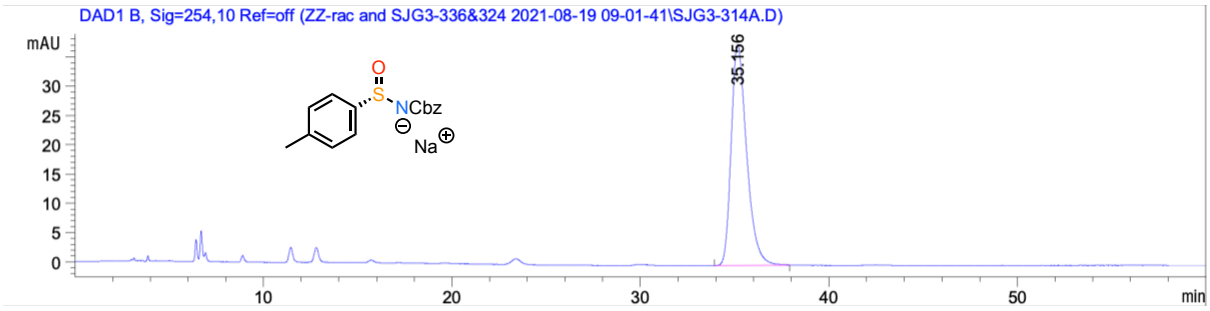
(*rac*)-3a-Cbz



Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.195	BB	0.8693	2812.89819	49.32381	49.9030
2	42.146	BB	0.9955	2823.83813	41.31040	50.0970
Totals :				5636.73633	90.63421	

(*S*)-3a-Cbz



Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.156	BB	0.8482	2145.46191	37.68457	100.0000
Totals :				2145.46191	37.68457	

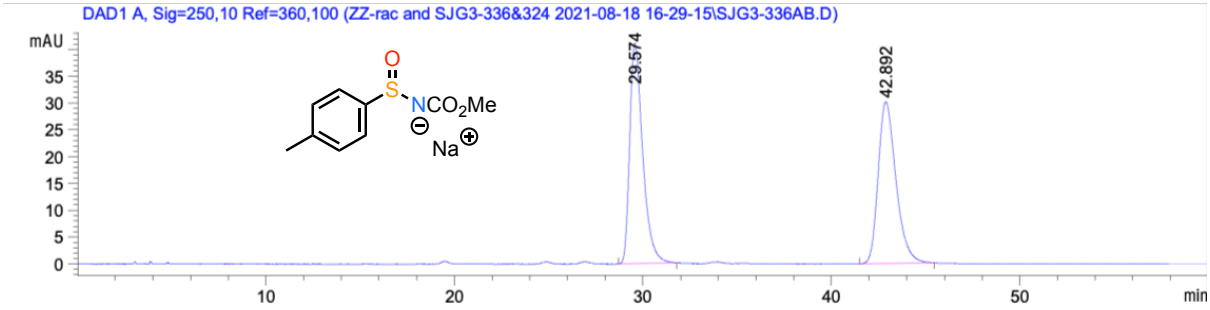
***ee* > 99%**

Sodium (*S*)-(Methoxycarbonyl)(*p*-tolylsulfinyl)amide ((*S*)-3a-Moc)

Determination of *ee* from reprotonation. The minimum MeOH (~0.1 mL) was added to a sample of **(*S*)-3a-Moc** (~1 mg) until completely dissolved. An aliquot was removed and diluted with hexane for HPLC analysis of sulfinamide **(*S*)-3a-Moc**.

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm.

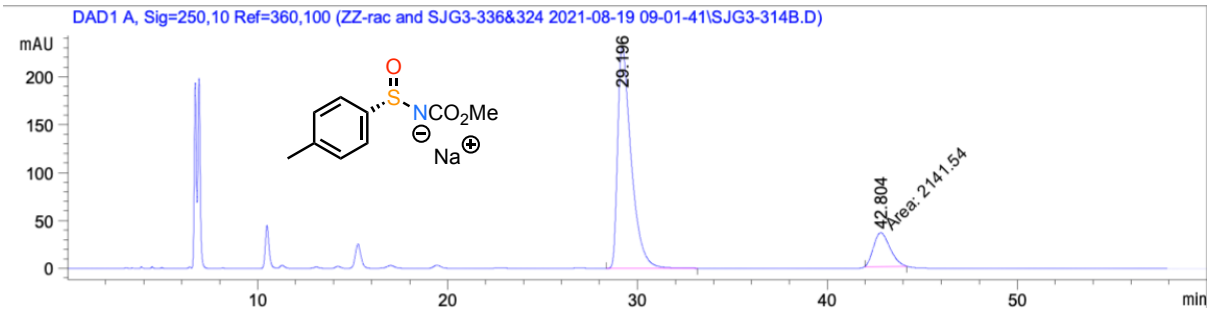
(*rac*)-3a-Moc



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.574	BB	0.7200	1968.56055	41.15968	49.8791
2	42.892	BB	0.9586	1978.10730	30.18266	50.1209
Totals :				3946.66785	71.34234	

(*S*)-3a-Moc



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.196	BB	0.7308	1.14467e4	231.53922	84.2398
2	42.804	MM	1.0050	2141.54419	35.51439	15.7602
Totals :				1.35883e4	267.05360	

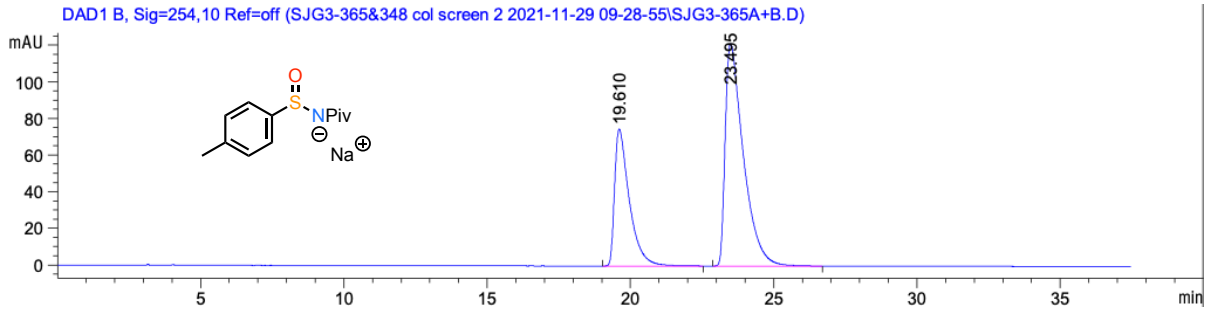
***ee* = 68%**

Sodium (*S*)-pivaloyl(*p*-tolylsulfinyl)amide ((*S*)-3a-Piv)

Determination of *ee* from reprotonation. The minimum MeOH (~0.1 mL) was added to a sample of **(*S*)-3a-Piv** (~1 mg) until completely dissolved. An aliquot was removed and diluted with hexane for HPLC analysis of sulfinamide **(*S*)-3a-Piv**.

Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm.

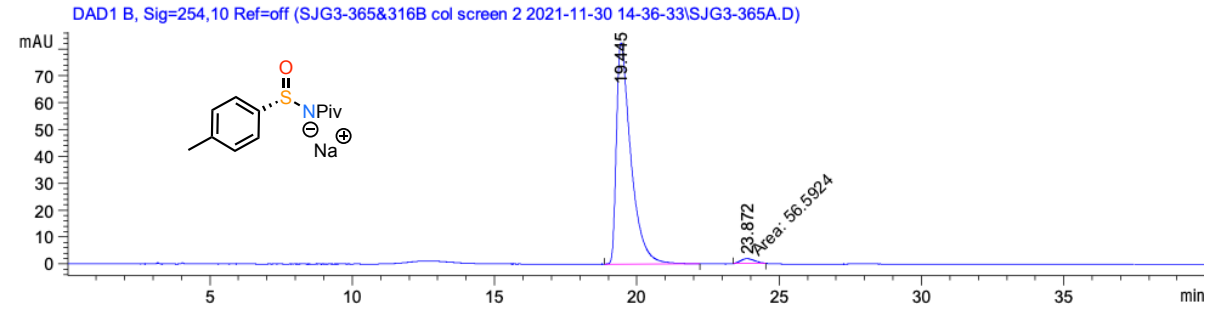
(*R*) + (*S*)-3a-Piv (Ratio: 3/2)



Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.610	BB	0.5283	2669.85840	74.81790	33.2930
2	23.495	BB	0.6484	5349.41455	121.33717	66.7070
Totals :				8019.27295	196.15507	

(*S*)-3a-Piv

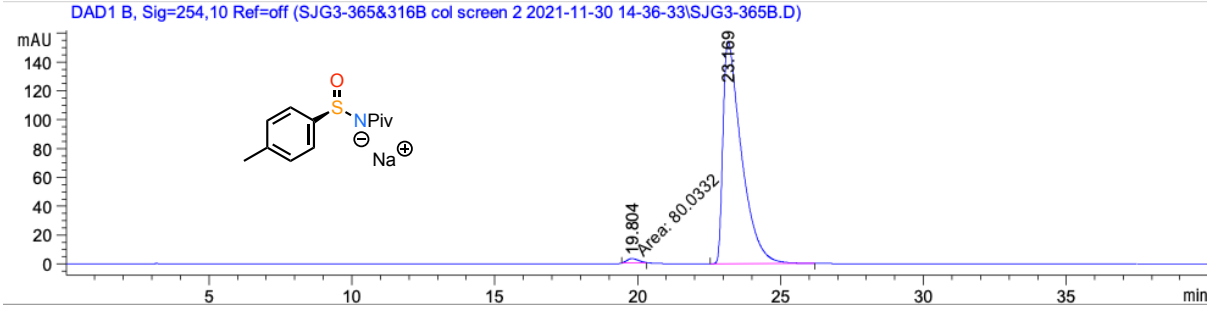


Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.445	BB	0.5181	2907.48193	82.30284	98.0907
2	23.872	MM	0.5461	56.59236	1.72704	1.9093
Totals :				2964.07429	84.02988	

***ee* = 96%**

(*R*)-3a-Piv



Signal 2: DAD1 B, Sig=254,10 Ref=off

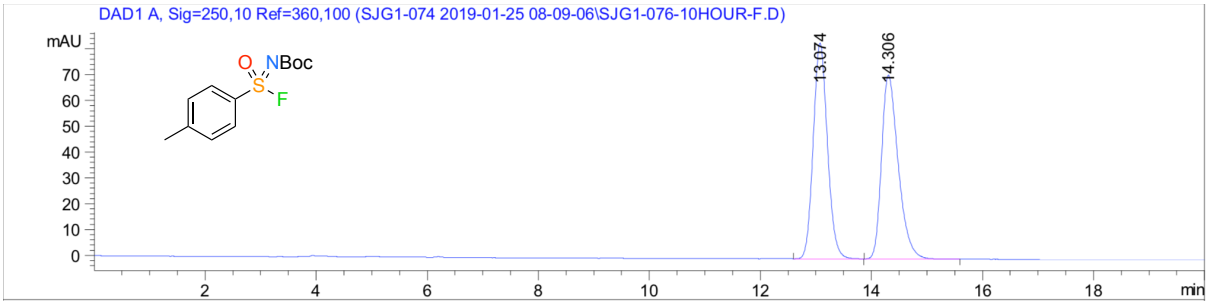
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.804	MM	0.4583	80.03324	2.91074	1.1400
2	23.169	BB	0.6587	6940.12744	154.31912	98.8600
Totals :				7020.16068	157.22986	

***ee* = 97%**

***tert*-Butyl (fluoro(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-1)**

Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm.

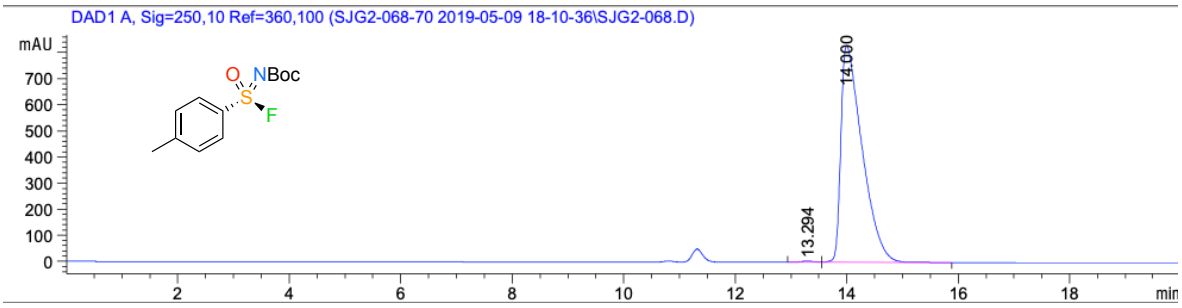
(*rac*)-1



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.074	BB	0.2726	1481.25183	83.62629	49.9140
2	14.306	BB	0.3176	1486.35461	71.18559	50.0860
Totals :				2967.60645	154.81188	

(*R*)-1



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

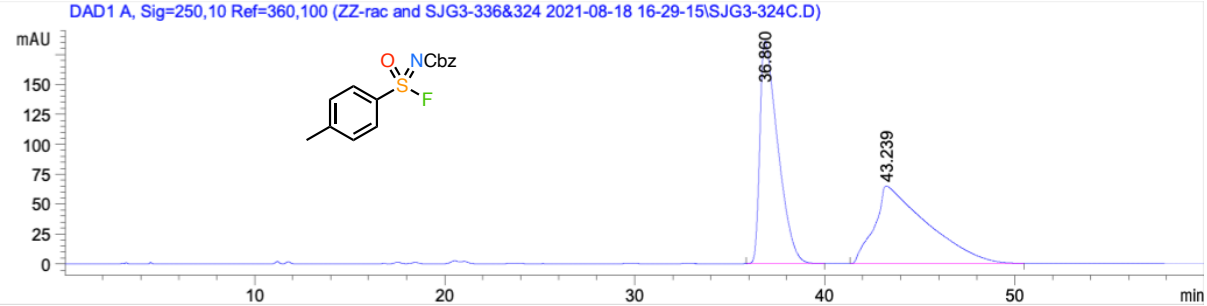
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.294	BV	0.2625	78.58254	4.71449	0.3559
2	14.000	VB	0.3970	2.20035e4	830.72552	99.6441
Totals :				2.20821e4	835.44002	

***ee* > 99%**

Benzyl (*R*)-(fluoro(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-1-Cbz)

Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm.

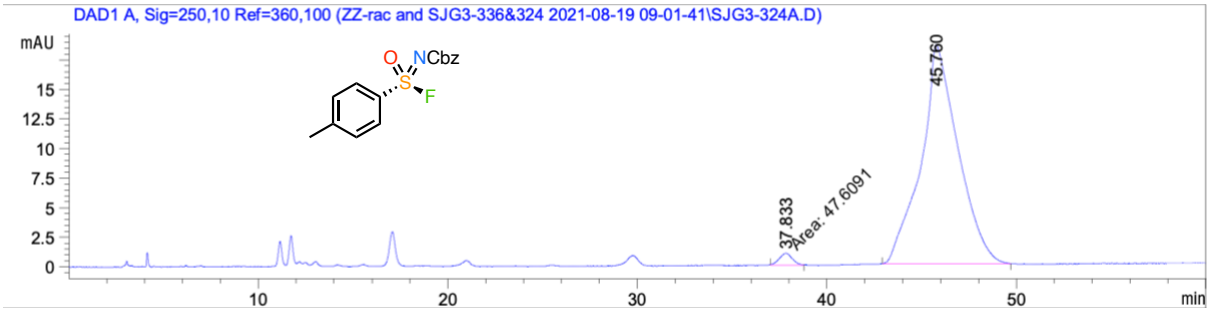
(*rac*)-1-Cbz



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.860	BB	0.9466	1.22198e4	185.97162	49.5715
2	43.239	BB	2.3595	1.24310e4	64.70207	50.4285
Totals :				2.46509e4	250.67369	

(*S*)-1-Cbz



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

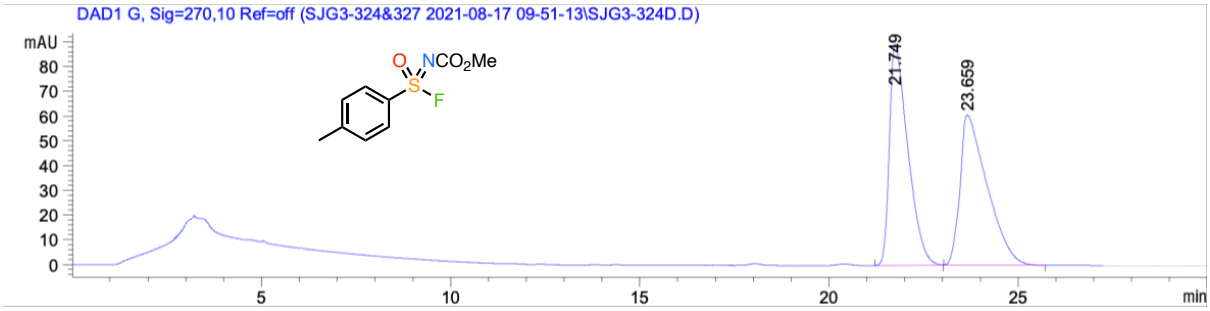
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.833	MM	0.7938	47.60907	9.99618e-1	1.8520
2	45.760	BB	1.6712	2523.09619	18.52287	98.1480
Totals :				2570.70526	19.52249	

***ee* = 96%**

Methyl (*R*)-(fluoro(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-1-Moc)

Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 270 nm.

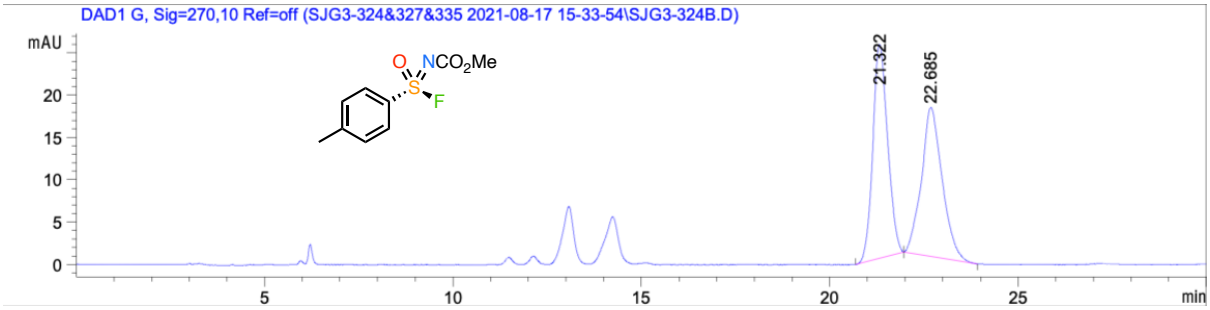
(*rac*)-1-Moc



Signal 7: DAD1 G, Sig=270,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.749	BB	0.5083	3024.89063	89.50022	49.9889
2	23.659	BB	0.6824	3026.22827	60.62586	50.0111
Totals :				6051.11890	150.12608	

(*S*)-1-Moc



Signal 7: DAD1 G, Sig=270,10 Ref=off

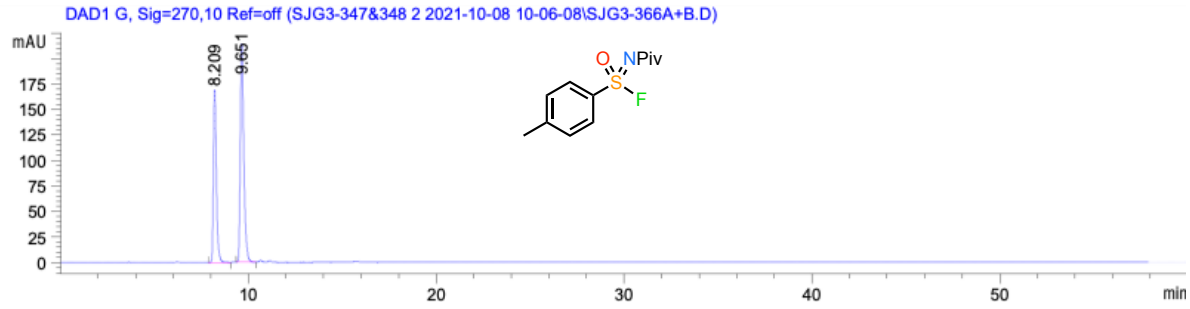
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.322	BB	0.4118	688.59875	25.28201	50.5258
2	22.685	BB	0.5387	674.26794	17.60870	49.4742
Totals :				1362.86670	42.89070	

***ee* = 0%**

(*R*)-4-Methyl-*N*-pivaloylbenzenesulfonimidoyl fluoride ((*R*)-1-Piv)

Conditions: Chiralpak IA column, 99:1 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 270 nm.

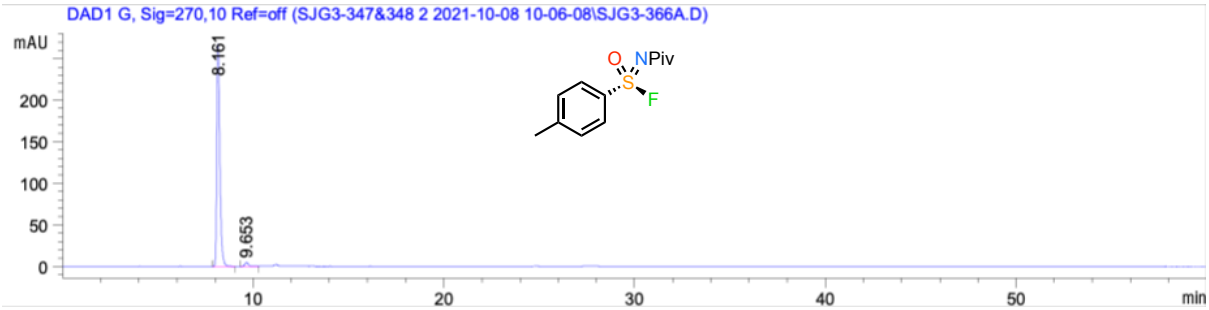
(*R*) + (*S*)-1-Piv (Ratio: 2/3)



Signal 7: DAD1 G, Sig=270,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.209	BB	0.1642	1830.34326	169.24657	39.7202
2	9.651	BB	0.1948	2777.74927	214.88147	60.2798
Totals :				4608.09253	384.12804	

(*R*)-1-Piv

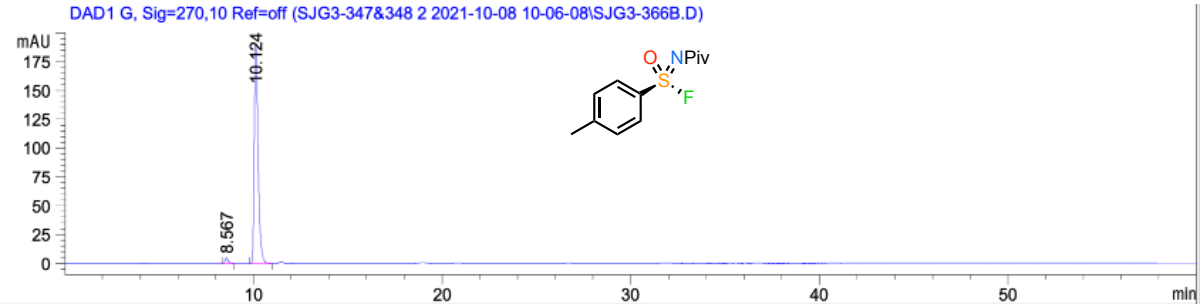


Signal 7: DAD1 G, Sig=270,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.161	BB	0.1662	2939.24243	267.51196	98.0173
2	9.653	BB	0.1933	59.45520	4.71057	1.9827
Totals :				2998.69764	272.22254	

ee = 96%

(*S*)-1-Piv



Signal 7: DAD1 G, Sig=270,10 Ref=off

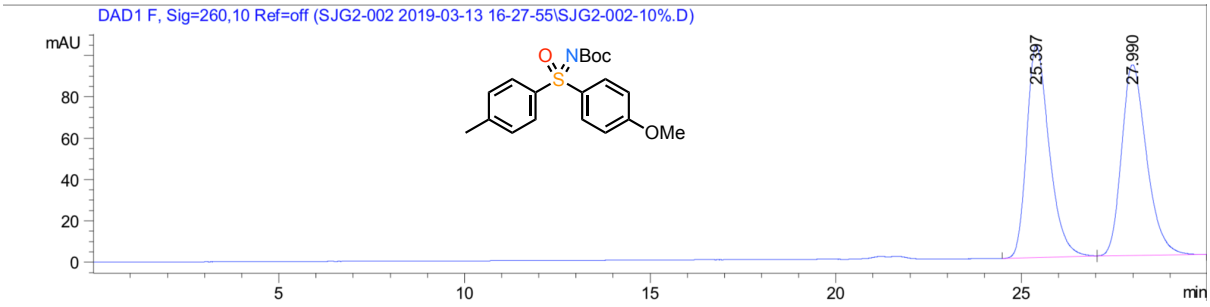
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.567	BB	0.1707	53.41816	4.76929	1.9521
2	10.124	BB	0.2138	2683.00122	191.10678	98.0479
Totals :				2736.41938	195.87608	

ee = 96%

***tert*-Butyl (*S*)-((4-methoxyphenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2a)**

Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm.

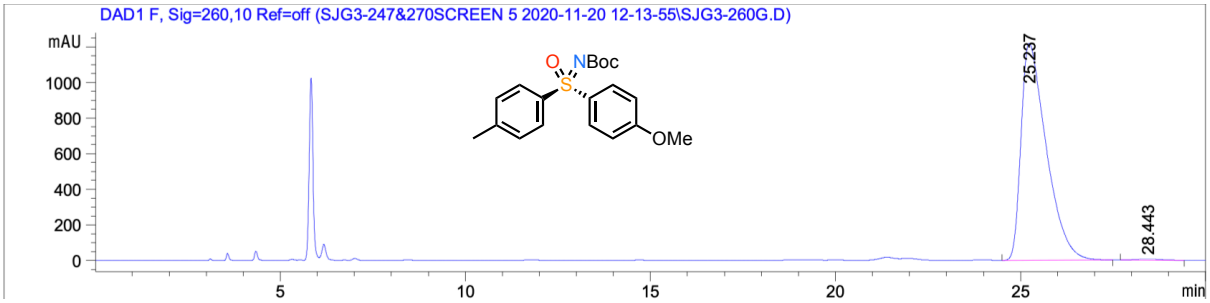
(*rac*)-2a



Signal 6: DAD1 F, Sig=260,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.397	BB	0.6437	4322.15771	102.97759	50.0178
2	27.990	BBA	0.7055	4319.08691	92.37070	49.9822
Totals :				8641.24463	195.34830	

(*S*)-2a



Signal 6: DAD1 F, Sig=260,10 Ref=off

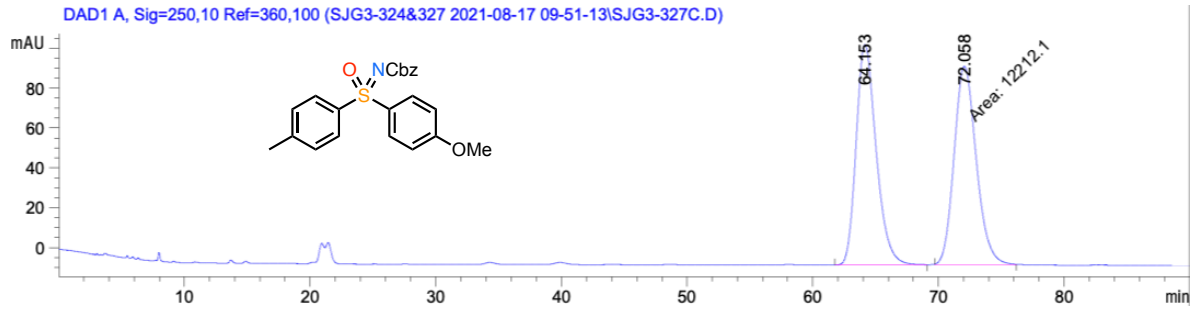
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.237	BB	0.6804	5.76861e4	1218.43481	99.4338
2	28.443	BB	0.5404	328.46756	7.47838	0.5662
Totals :				5.80146e4	1225.91320	

ee = 99%

Benzyl (*S*)-((4-methoxyphenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2a-Cbz)

Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm.

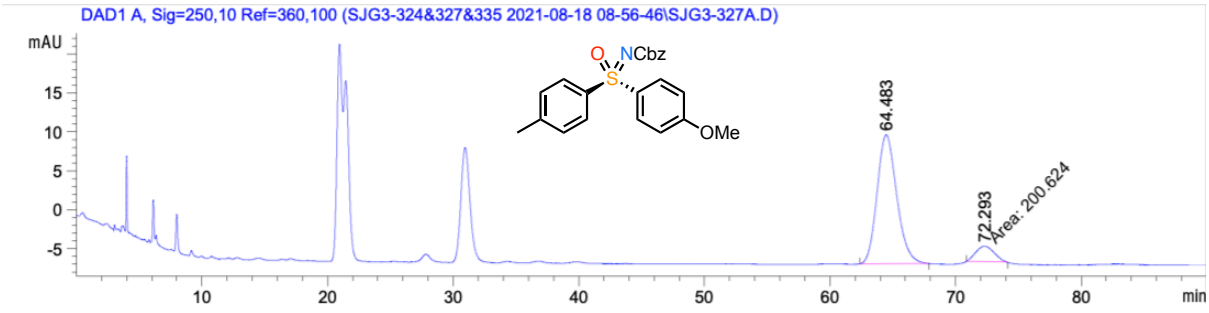
(*rac*)-2a-Cbz



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	64.153	BB	1.6244	1.22513e4	110.59022	50.0800
2	72.058	MM	2.0447	1.22121e4	99.54491	49.9200
Totals :				2.44634e4	210.13512	

(*S*)-2a-Cbz



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

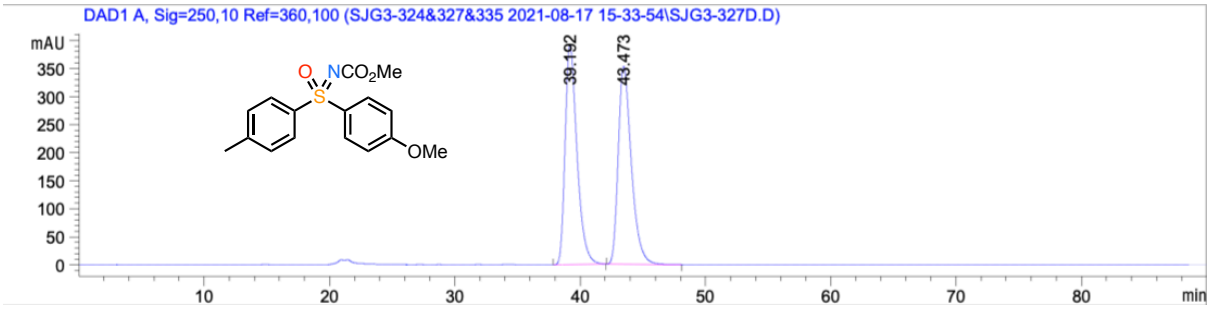
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	64.483	BB	1.2938	1804.81104	16.55584	89.9960
2	72.293	MM	1.6855	200.62444	1.98377	10.0040
Totals :				2005.43547	18.53961	

***ee* = 80%**

Methyl (*S*)-((4-methoxyphenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2a-Moc)

Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm.

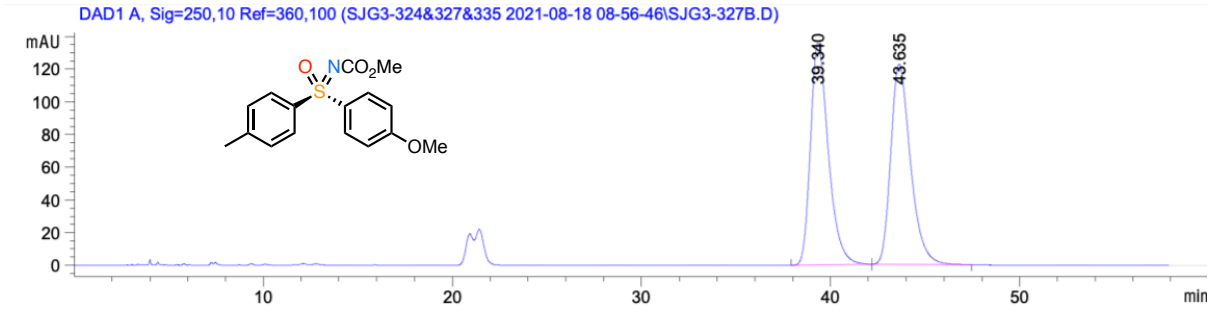
(*rac*)-2a-Moc



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.192	BB	0.9976	2.57183e4	391.93210	50.0279
2	43.473	BB	1.1092	2.56896e4	352.92987	49.9721
Totals :				5.14079e4	744.86197	

(*S*)-2a-Moc



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

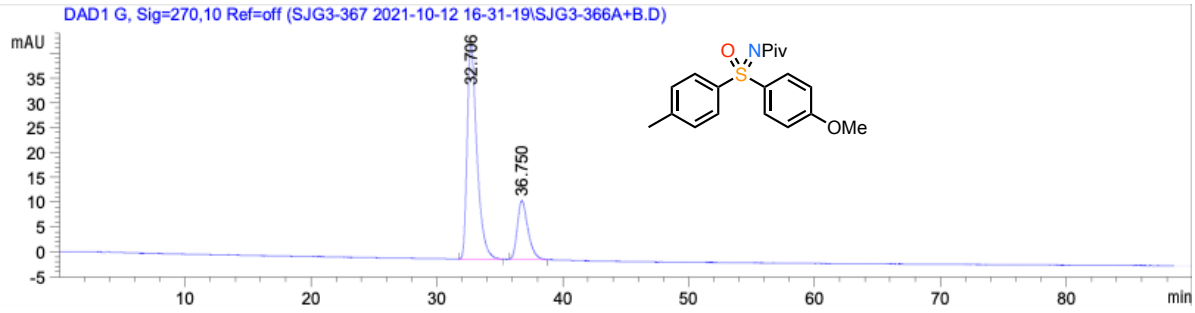
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.340	BB	0.9899	8899.65430	135.56238	50.0097
2	43.635	BB	1.0967	8896.20605	122.58479	49.9903
Totals :				1.77959e4	258.14717	

***ee* = 0%**

(*S*)-N-((4-Methoxyphenyl)(oxo)(p-tolyl)-λ6-sulfaneylidene)pivalamide ((*S*)-2a-Piv)

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 270 nm.

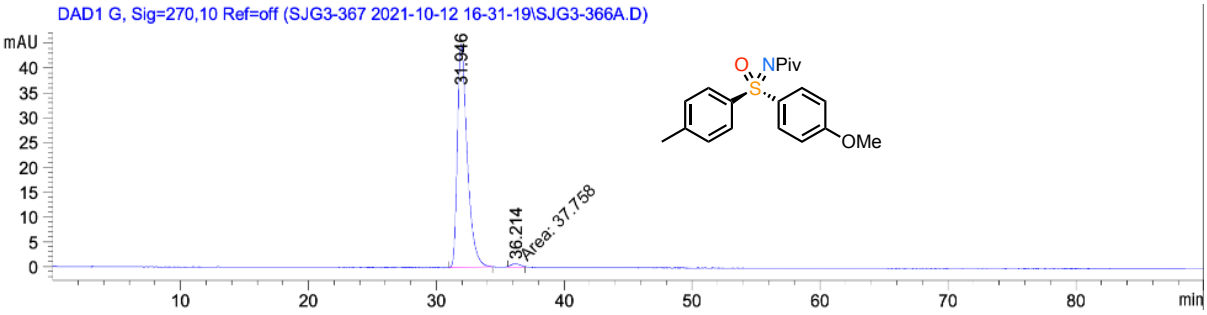
(*S*) + (*R*)-2a-Piv (Ratio: approx. 3/1)



Signal 7: DAD1 G, Sig=270,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.706	BB	0.8007	2323.46875	43.25305	77.0035
2	36.750	BB	0.7996	693.88416	11.84195	22.9965
Totals :				3017.35291	55.09500	

(*S*)-2a-Piv

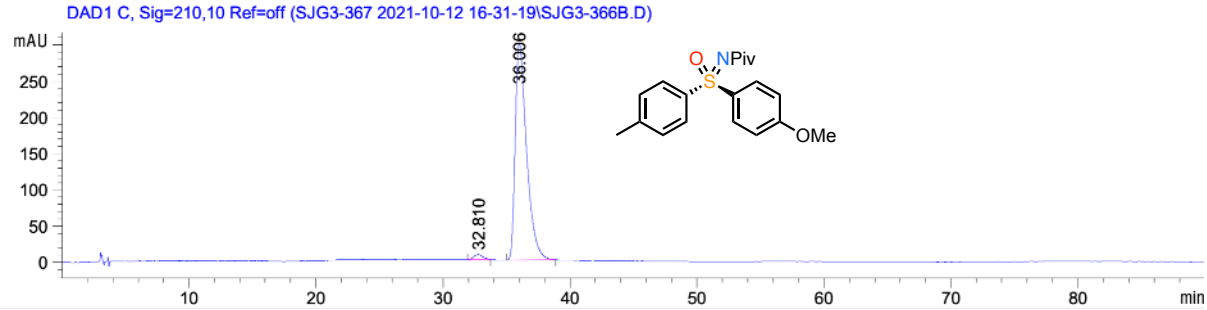


Signal 7: DAD1 G, Sig=270,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.946	BB	0.7808	2409.17529	44.98889	98.4569
2	36.214	MM	0.8813	37.75797	7.14086e-1	1.5431
Totals :				2446.93326	45.70297	

ee = 97%

(*R*)-2a-Piv

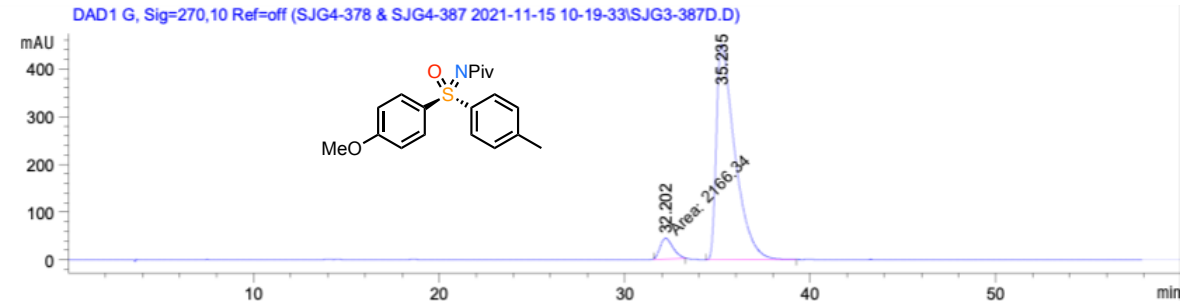


Signal 3: DAD1 C, Sig=210,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.810	BB	0.5958	351.17502	6.97027	1.8483
2	36.006	BB	0.9085	1.86483e4	299.44830	98.1517
Totals :				1.89995e4	306.41857	

ee = 96%

***ent*-2a (from (*R*)-26))**



Signal 7: DAD1 G, Sig=270,10 Ref=off

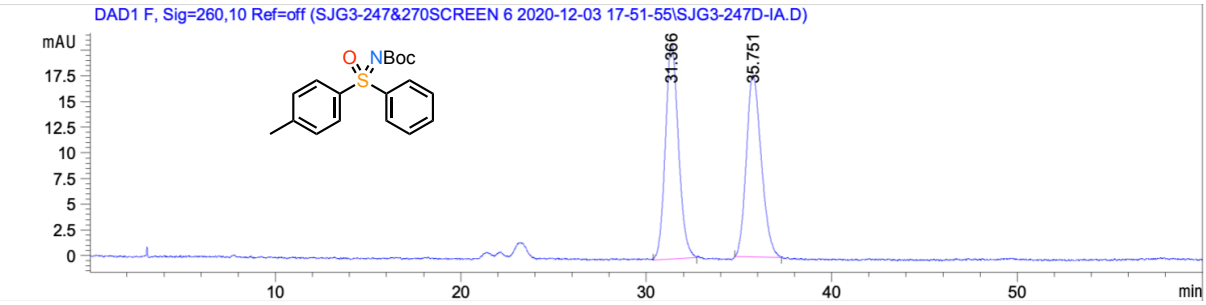
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.202	MM	0.8105	2166.33838	44.55000	6.5023
2	35.235	BB	1.0263	3.11502e4	450.75229	93.4977
Totals :				3.33166e4	495.30229	

ee = 87%

***tert*-Butyl (*R*)-(oxo(phenyl)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-2b)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm.

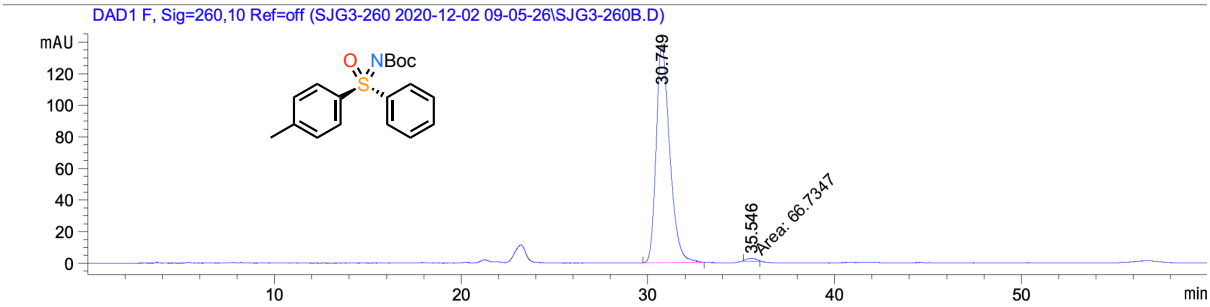
(*rac*)-2b



Signal 6: DAD1 F, Sig=260,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.366	BB	0.6267	1025.38440	20.96338	50.7318
2	35.751	BB	0.6685	995.80316	17.69739	49.2682
Totals :				2021.18756	38.66077	

(*R*)-2b



Signal 6: DAD1 F, Sig=260,10 Ref=off

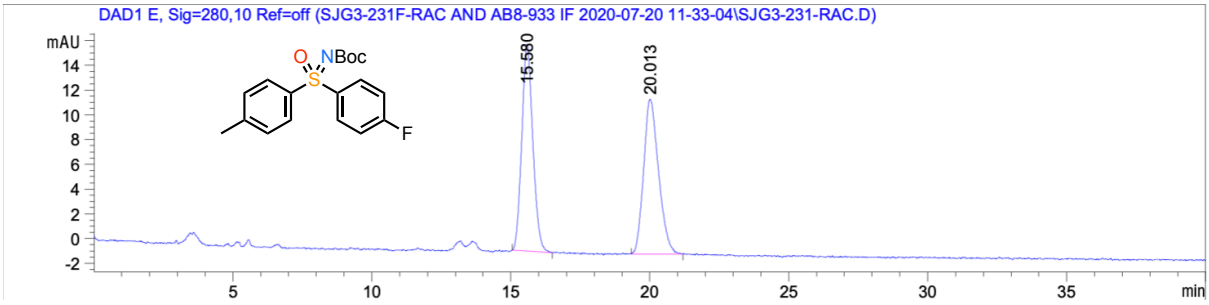
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.749	BB	0.7319	6927.30811	137.94543	99.0458
2	35.546	MM	0.6040	66.73475	1.84146	0.9542
Totals :				6994.04285	139.78689	

ee = 98%

***tert*-Butyl (*S*)-((4-fluorophenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2c)**

Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 280 nm.

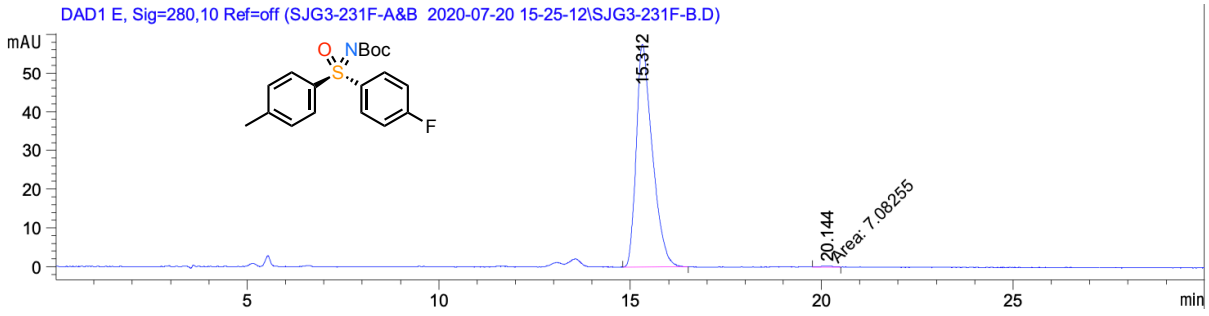
(*rac*)-2c



Signal 5: DAD1 E, Sig=280,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.580	BB	0.3979	461.78876	16.73513	49.6950
2	20.013	BB	0.4879	467.45700	12.51059	50.3050
Totals :				929.24576	29.24572	

(*S*)-2c



Signal 5: DAD1 E, Sig=280,10 Ref=off

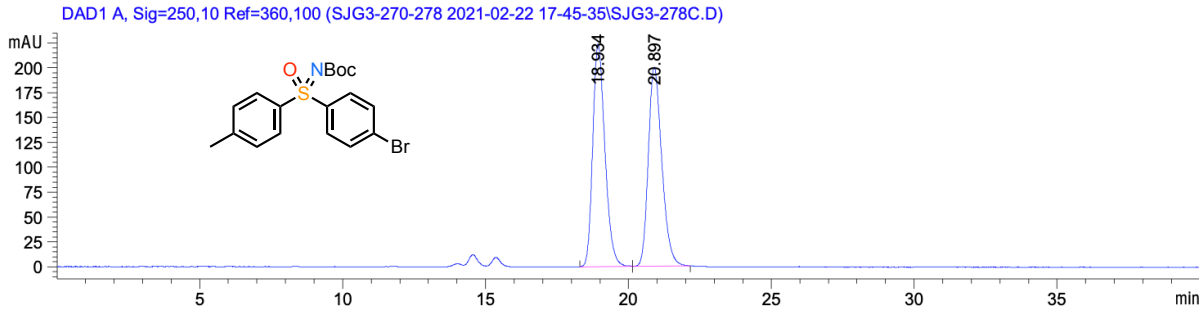
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.312	BB	0.4180	1676.23730	57.52406	99.5793
2	20.144	MM	0.5268	7.08255	2.24084e-1	0.4207

***ee* >99%**

***tert*-Butyl (*S*)-((4-bromophenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2d)**

Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm.

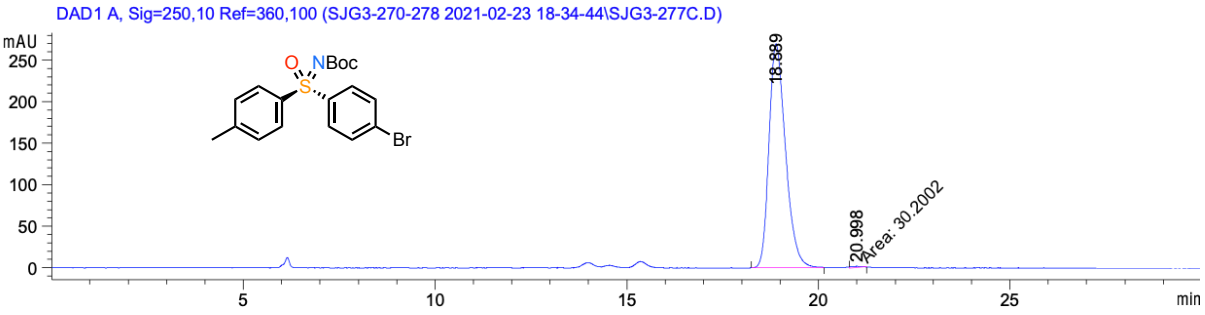
(*rac*)-2d



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.934	BB	0.4540	6638.42822	223.84180	50.2006
2	20.897	BB	0.5002	6585.38330	199.98198	49.7994
Totals :				1.32238e4	423.82378	

(*S*)-2d



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

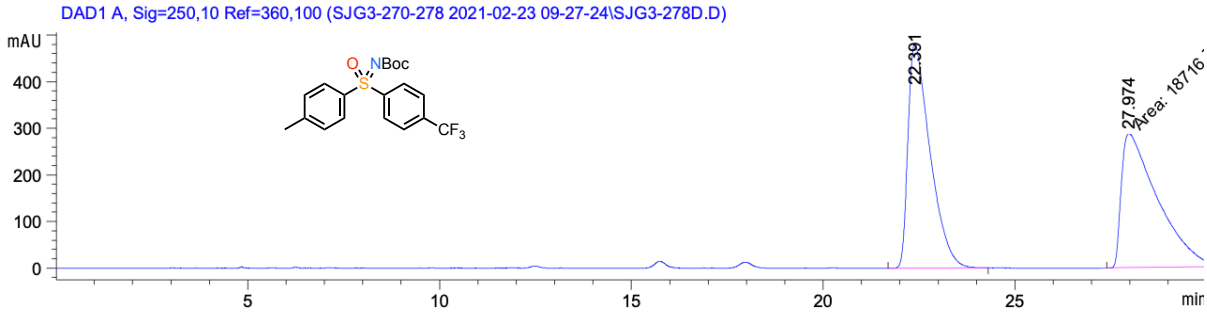
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.889	BB	0.4554	8077.20508	269.70667	99.6275
2	20.998	MM	0.3169	30.20021	1.58819	0.3725
Totals :				8107.40528	271.29485	

***ee* >99%**

***tert*-Butyl (*S*)-(oxo(*p*-tolyl)(4-(trifluoromethyl)phenyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2e)**

Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm.

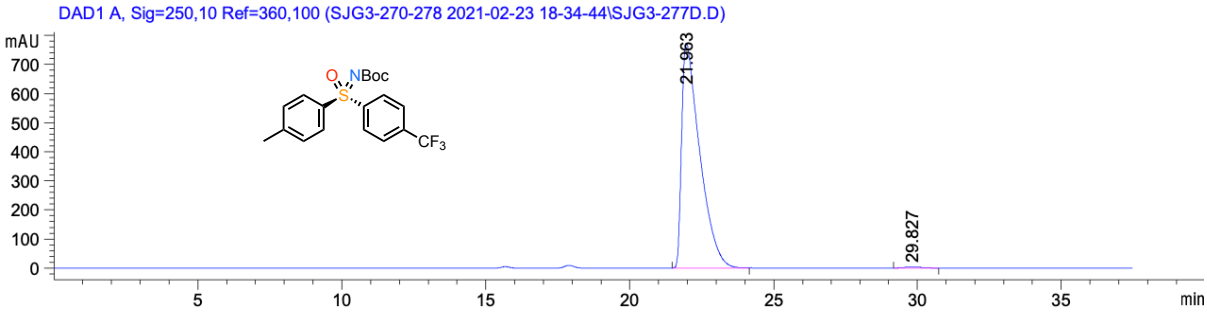
(*rac*)-2e



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.391	BB	0.5775	1.92433e4	482.31946	50.6936
2	27.974	MM	1.0856	1.87167e4	287.35263	49.3064
Totals :				3.79600e4	769.67209	

(*S*)-2e



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

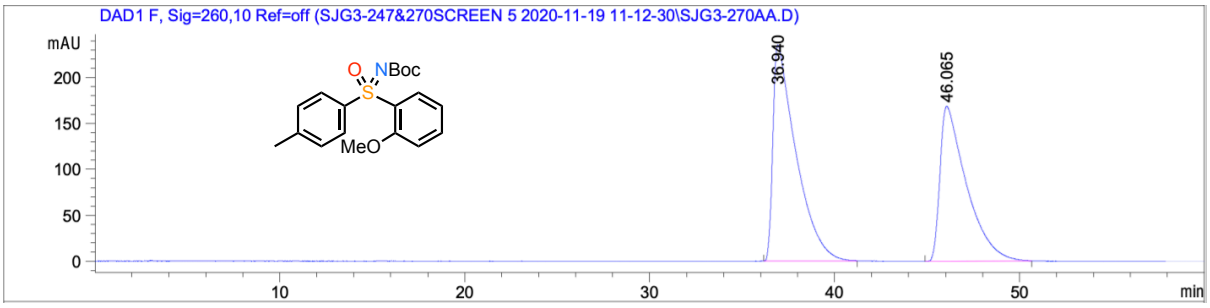
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.963	BB	0.6132	3.37574e4	773.42578	99.5028
2	29.827	BB	0.5401	168.66426	3.72609	0.4972
Totals :				3.39260e4	777.15187	

***ee* >99%**

***tert*-Butyl (*S*)-((2-methoxyphenyl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2g)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm.

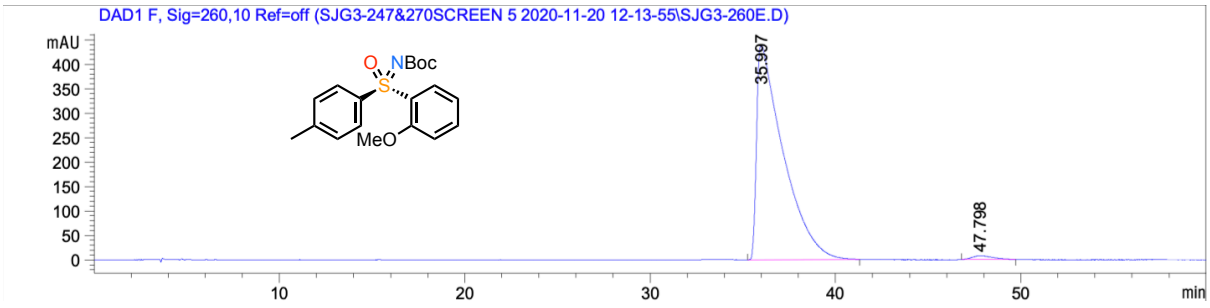
(*rac*)-2g



Signal 6: DAD1 F, Sig=260,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.940	BB	1.1583	2.03867e4	235.42796	54.8694
2	46.065	BB	1.3178	1.67683e4	168.67809	45.1306
Totals :				3.71551e4	404.10605	

(*S*)-2g



Signal 6: DAD1 F, Sig=260,10 Ref=off

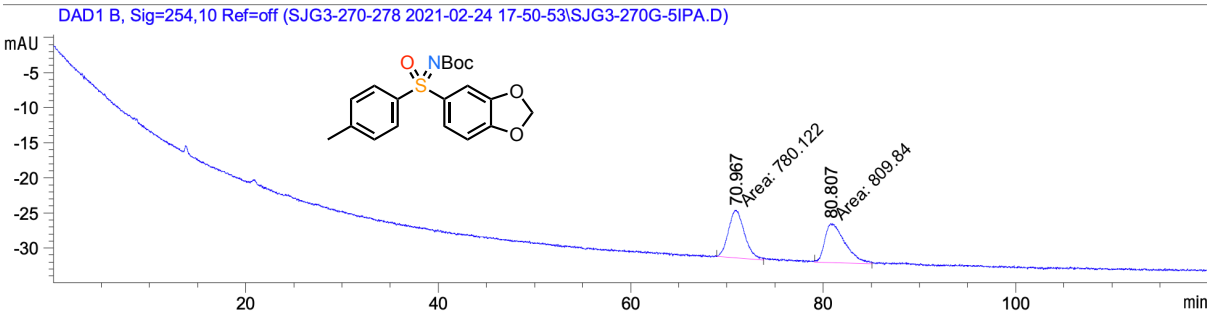
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.997	BB	1.2739	4.37335e4	439.87189	98.6425
2	47.798	BB	0.9369	601.86139	7.57540	1.3575
Totals :				4.43354e4	447.44729	

***ee* = 97%**

***tert*-Butyl (*S*)-(benzo[*d*][1,3]dioxol-5-yl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate (*S*)-2h**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm.

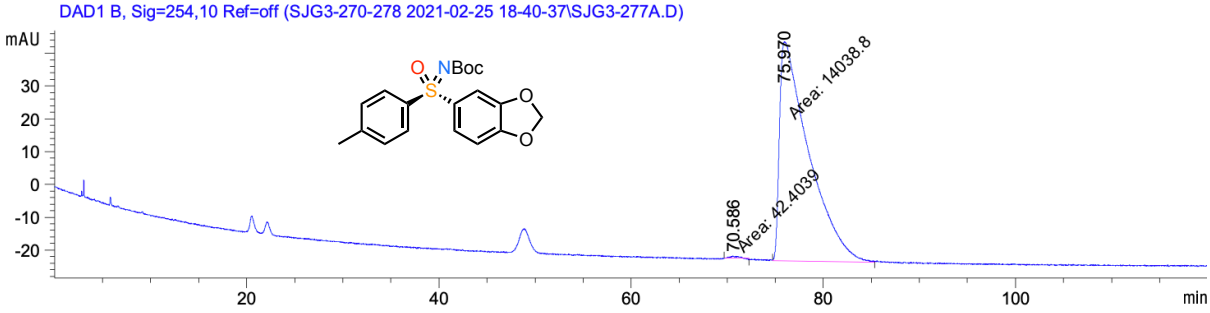
(*rac*)-2h



Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	70.967	MM	1.9020	780.12238	6.83581	49.0655
2	80.807	MM	2.4128	809.83990	5.59415	50.9345
Totals :				1589.96228	12.42996	

(*S*)-2h



Signal 2: DAD1 B, Sig=254,10 Ref=off

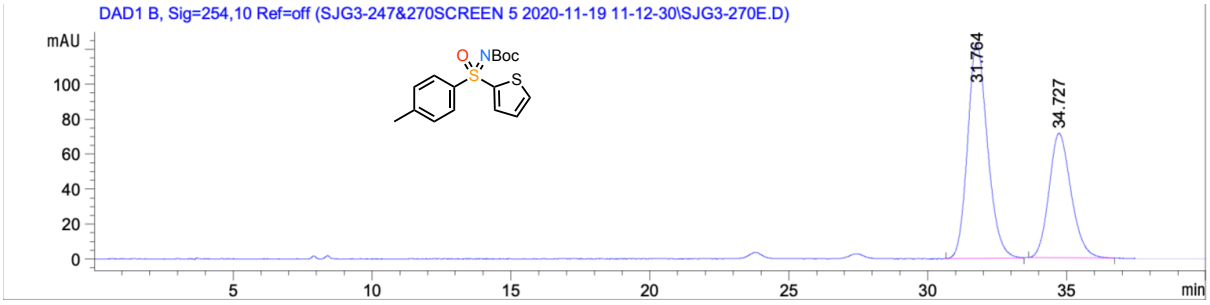
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	70.586	MM	1.0305	42.40389	6.85823e-1	0.3011
2	75.970	MM	3.5017	1.40388e4	66.81847	99.6989
Totals :				1.40812e4	67.50430	

***ee* >99%**

***tert*-Butyl (*S*)-(oxo(thiophen-2-yl)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2i)**

Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm.

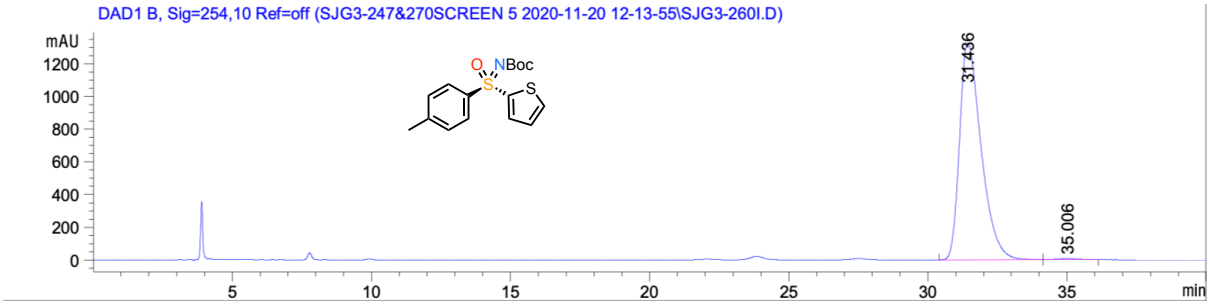
(*rac*)-2i



Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.764	BB	0.7173	6125.07227	123.34473	60.8660
2	34.727	BB	0.7471	3938.13794	71.21909	39.1340
Totals :				1.00632e4	194.56383	

(*S*)-2i



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

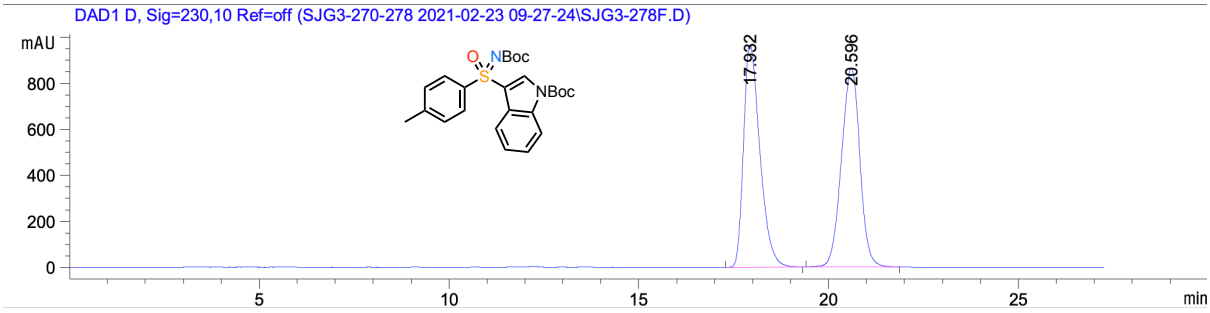
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.438	BB	0.7723	7.36825e4	1359.45337	99.5323
2	35.043	BB	0.6274	346.21600	6.54256	0.4677
Totals :				7.40287e4	1365.99593	

***ee* >99%**

***tert*-Butyl (*S*)-3-(*N*-(*tert*-butoxycarbonyl)-4-methylphenylsulfonimidoyl)-1*H*-indole-1-carboxylate ((*S*)-2j)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm.

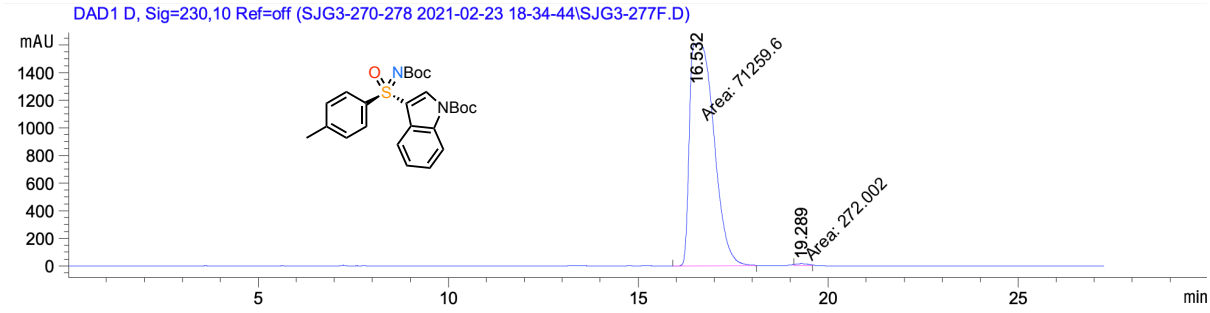
(*rac*)-2j



Signal 4: DAD1 D, Sig=230,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.932	BB	0.4496	2.89442e4	965.84668	49.7501
2	20.596	BV	0.5212	2.92350e4	863.11011	50.2499
Totals :				5.81792e4	1828.95679	

(*S*)-2j



Signal 4: DAD1 D, Sig=230,10 Ref=off

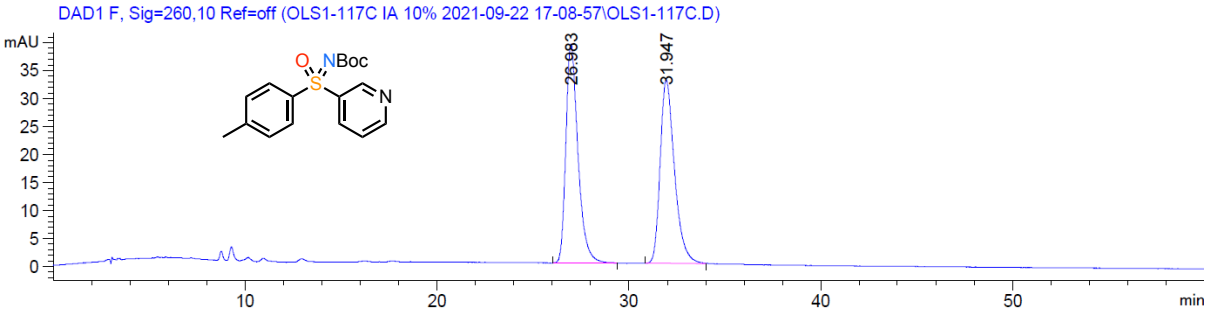
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.532	MM	0.7375	7.12596e4	1610.30066	99.6197
2	19.289	MM	0.3695	272.00177	12.26786	0.3803
Totals :				7.15316e4	1622.56852	

***ee* >99%**

***tert*-Butyl (*S*)-(oxo(pyridin-3-yl)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-2k)**

Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm.

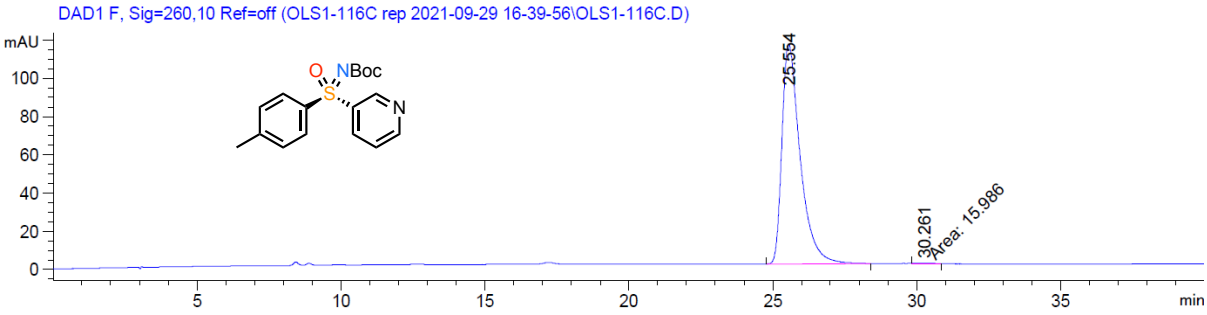
(*rac*)-2k



Signal 6: DAD1 F, Sig=260,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.983	BB	0.6531	1713.20850	39.10720	50.2519
2	31.947	BB	0.7688	1696.03418	32.71922	49.7481
Totals :				3409.24268	71.82642	

(*S*)-2k



Signal 6: DAD1 F, Sig=260,10 Ref=off

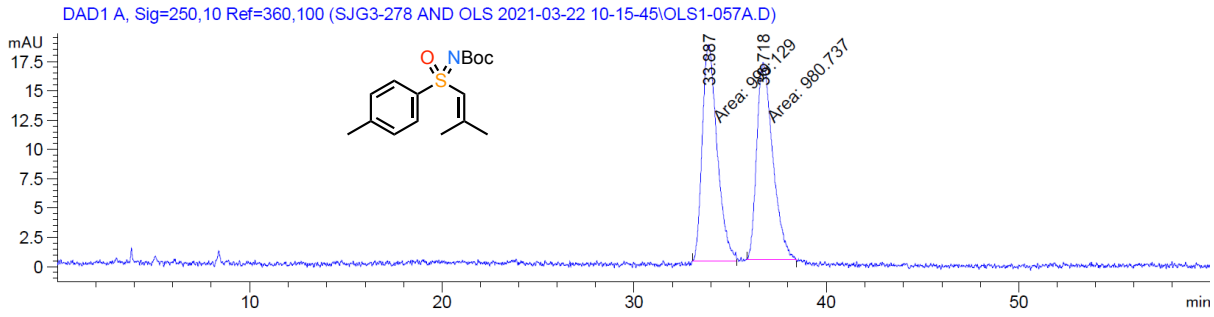
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.554	BB	0.6536	5043.70850	115.01371	99.6841
2	30.261	MM	0.6933	15.98597	3.84279e-1	0.3159
Totals :				5059.69447	115.39799	

***ee* >99%**

***tert*-Butyl (*R*)-((2-methylprop-1-en-1-yl)(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-2l)**

Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm.

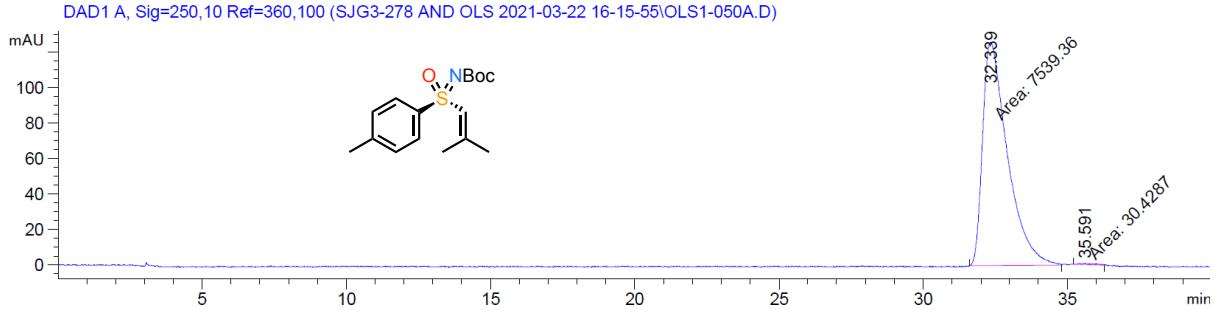
(*rac*)-2l



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.887	MM	0.9011	999.12939	18.47940	50.4645
2	36.718	MM	0.9696	980.73749	16.85896	49.5355
Totals :				1979.86688	35.33836	

(*R*)-2l



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

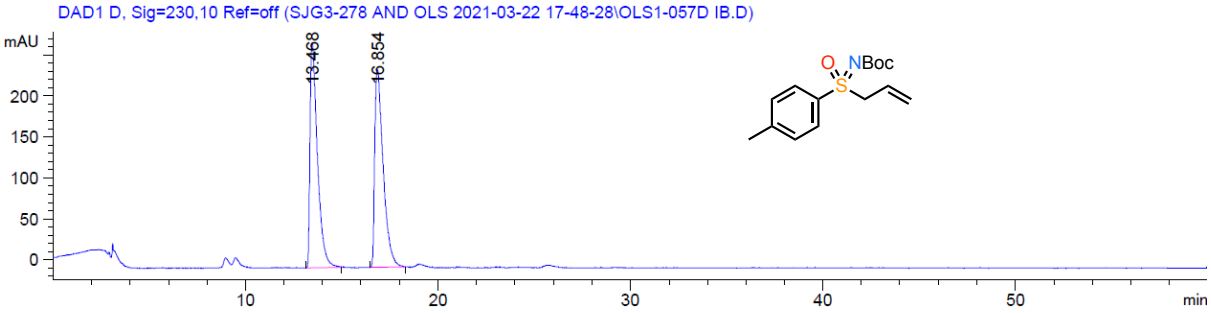
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.339	MM	0.9981	7539.35742	125.89311	99.5980
2	35.591	MM	0.5084	30.42869	9.97521e-1	0.4020
Totals :				7569.78612	126.89063	

***ee* >99%**

***tert*-Butyl (*R*)-(allyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-2m)**

Conditions: Chiralpak IB column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm.

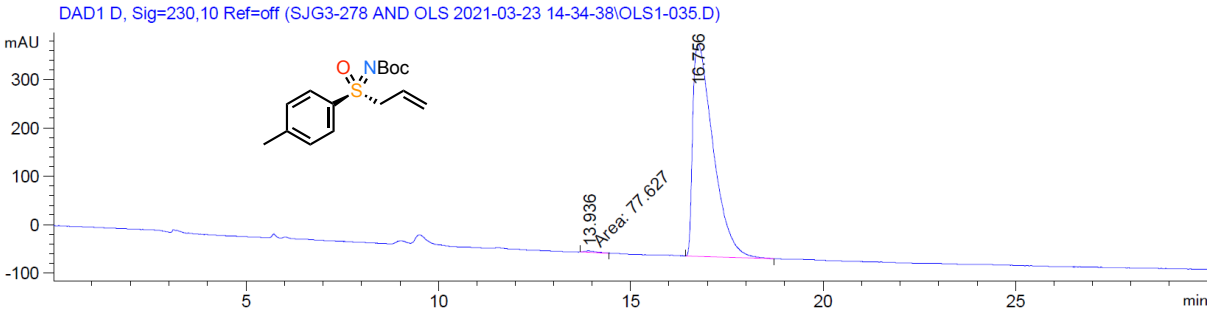
(*rac*)-2m



Signal 4: DAD1 D, Sig=230,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.468	VV	0.3919	7392.82813	274.74112	50.0220
2	16.854	BB	0.4339	7386.31104	242.15961	49.9780
Totals :				1.47791e4	516.90073	

(*R*)-2m



Signal 4: DAD1 D, Sig=230,10 Ref=off

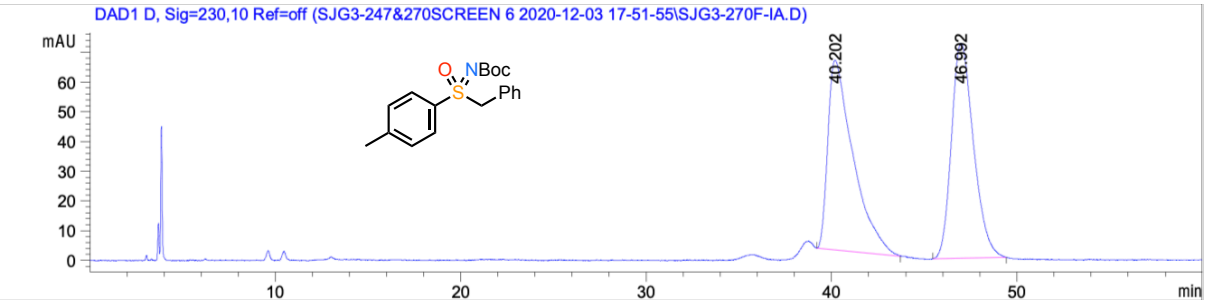
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.936	MM	0.4155	77.62698	3.11383	0.4778
2	16.756	BV	0.5261	1.61706e4	438.58426	99.5222
Totals :				1.62482e4	441.69809	

***ee* >99%**

***tert*-Butyl (*R*)-(benzyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-2n)**

Conditions: Chiralpak IA column, 97:3 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm.

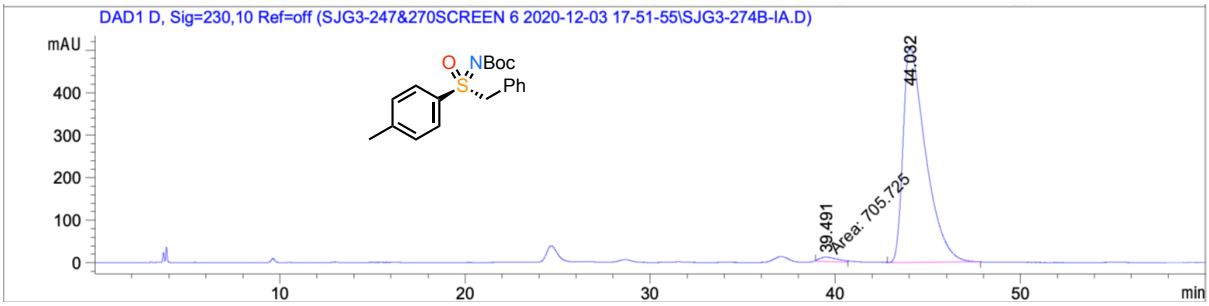
(*rac*)-2n



Signal 4: DAD1 D, Sig=230,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.202	BB	1.1596	6066.03613	63.89467	50.2534
2	46.992	BB	0.9842	6004.86670	72.35873	49.7466
Totals :				1.20709e4	136.25340	

(*R*)-2n



Signal 4: DAD1 D, Sig=230,10 Ref=off

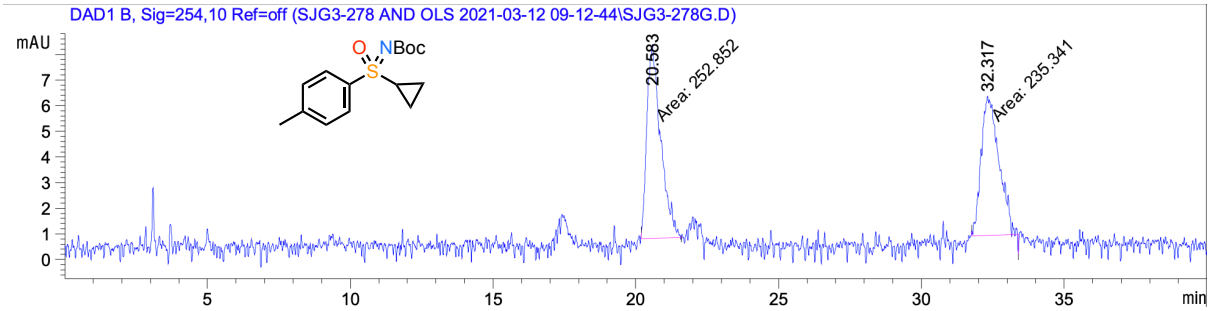
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.491	MM	1.1236	705.72504	10.46806	1.6200
2	44.032	BB	1.1197	4.28574e4	508.27042	98.3800
Totals :				4.35632e4	518.73847	

***ee* = 97%**

***tert*-Butyl (*R*)-(cyclopropyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-2o)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 254 nm.

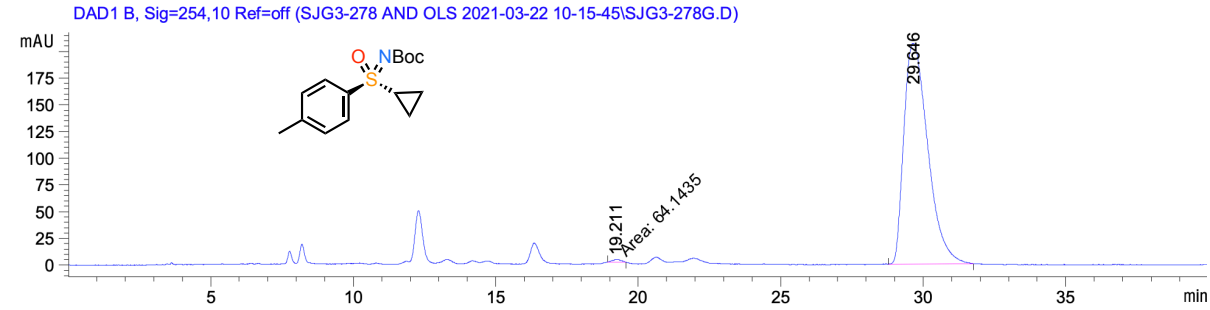
(*rac*)-2o



Signal 2: DAD1 B, Sig=254,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.583	MM	0.5578	252.85196	7.55437	51.7934
2	32.317	MM	0.7208	235.34149	5.44174	48.2066
Totals :				488.19345	12.99611	

(*R*)-2o



Signal 2: DAD1 B, Sig=254,10 Ref=off

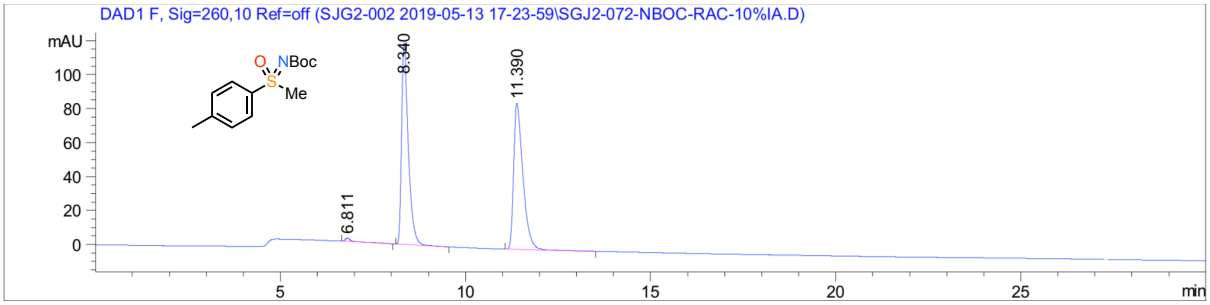
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.211	MM	0.3855	64.14353	2.77305	0.5291
2	29.646	BV	0.8027	1.20586e4	206.69022	99.4709
Totals :				1.21228e4	209.46327	

***ee* = 99%**

***tert*-Butyl (*R*)-(methyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-2p)**

Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm.

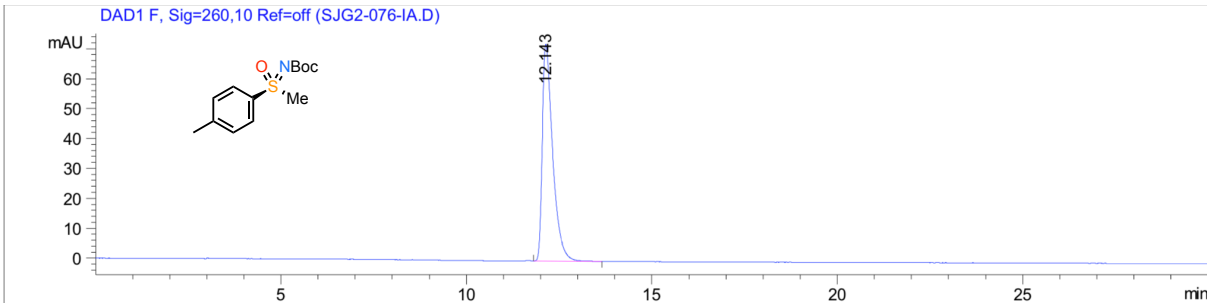
(*rac*)-2p



Signal 6: DAD1 F, Sig=260,10 Ref=off

Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.811	BB	0.1638	22.04514	1.95167	0.7279
2	8.340	BB	0.1895	1498.33643	118.49247	49.4741
3	11.390	BB	0.2623	1508.14673	86.13755	49.7980
Totals :				3028.52829	206.58169	

(*R*)-2p



Signal 5: DAD1 F, Sig=260,10 Ref=off

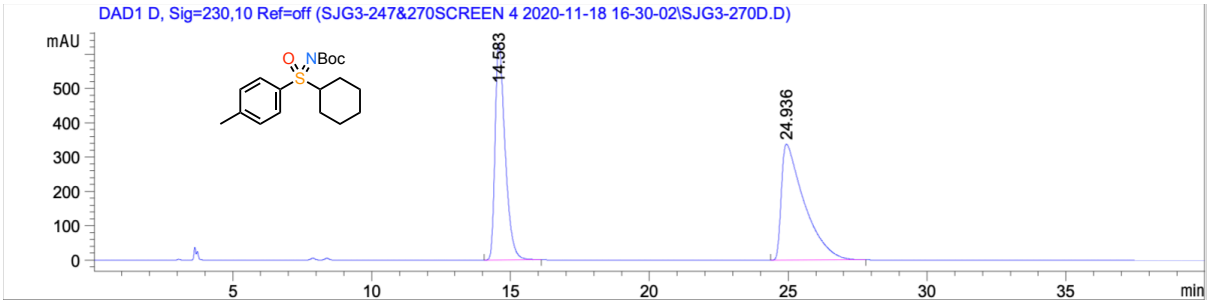
Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.143	BB	0.2892	1411.03613	72.44751	100.0000
Totals :				1411.03613	72.44751	

***ee* >99%**

***tert*-Butyl (*R*)-(cyclohexyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*R*)-2r)**

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm.

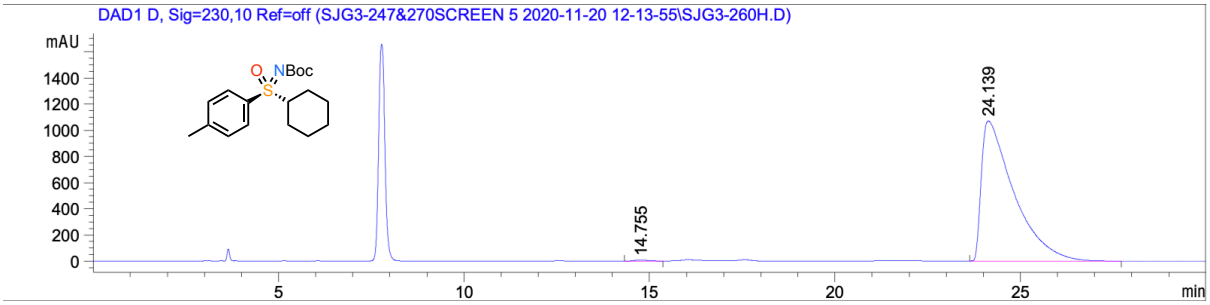
(*rac*)-2r



Signal 4: DAD1 D, Sig=230,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.583	BB	0.3767	1.58590e4	632.15033	45.0425
2	24.936	BB	0.7885	1.93499e4	337.69049	54.9575
Totals :				3.52089e4	969.84082	

(*R*)-2r



Signal 4: DAD1 D, Sig=230,10 Ref=off

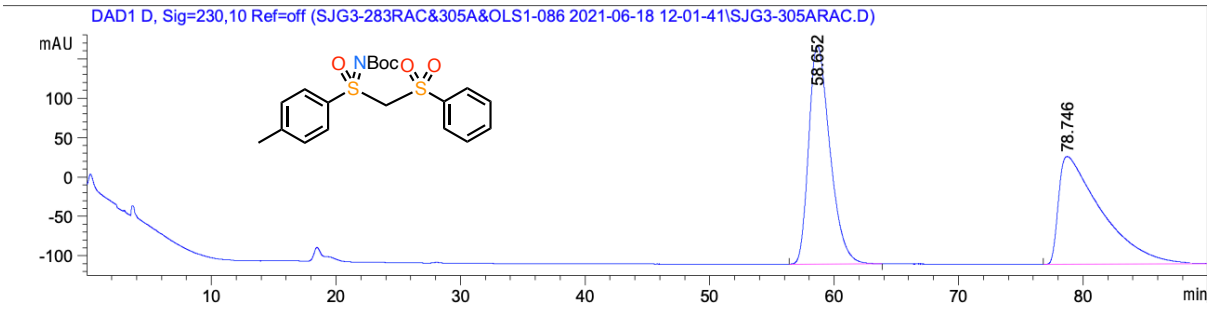
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.755	BB	0.3274	199.32239	8.26496	0.3053
2	24.139	BB	0.8161	6.50917e4	1069.49402	99.6947
Totals :				6.52910e4	1077.75898	

***ee* >99%**

***tert*-Butyl (*S*)-(oxo((phenylsulfonyl)methyl)(*p*-tolyl)-λ^6-sulfaneylidene)carbamate ((*S*)-S4)**

Conditions: Chiralpak IA column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 230 nm.

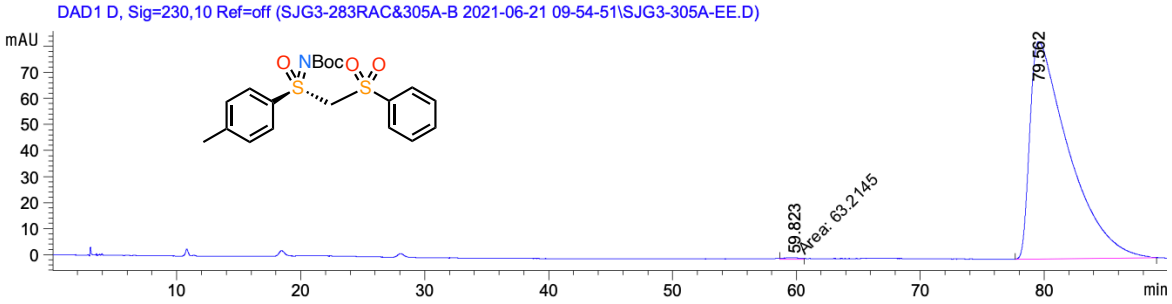
(*rac*)-S4



Signal 4: DAD1 D, Sig=230,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	58.652	BB	1.7339	3.28363e4	277.21286	50.2215
2	78.746	BBA	3.0880	3.25466e4	136.68341	49.7785
Totals :				6.53829e4	413.89627	

(*S*)-S4



Signal 4: DAD1 D, Sig=230,10 Ref=off

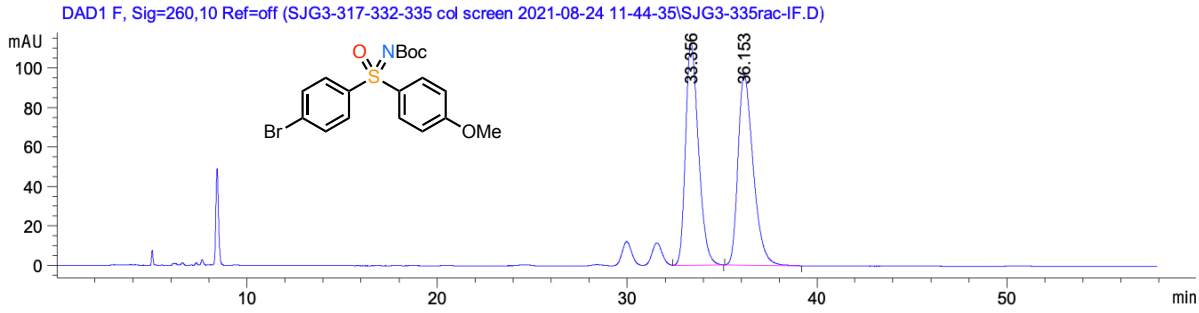
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	59.823	MM	1.6902	63.21451	6.23345e-1	0.3470
2	79.562	BB	2.7688	1.81551e4	83.42975	99.6530
Totals :				1.82184e4	84.05309	

ee > 99%

***tert*-Butyl (*R*)-((4-bromophenyl)(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)carbamate ((*R*)-S5)**

Conditions: Chiralpak IF column, 90:10 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm.

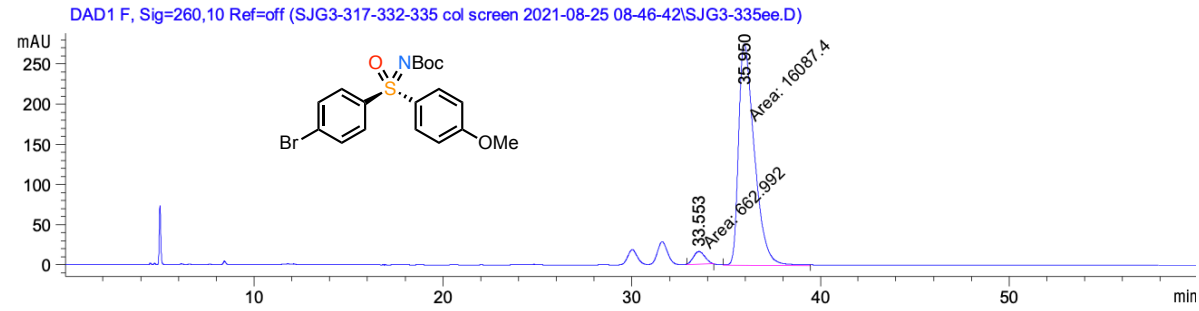
(*rac*)-S5



Signal 6: DAD1 F, Sig=260,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.356	BB	0.7275	5293.63281	112.39899	49.7625
2	36.153	BB	0.8499	5344.16846	96.22720	50.2375
Totals :				1.06378e4	208.62619	

(*R*)-S5



Signal 6: DAD1 F, Sig=260,10 Ref=off

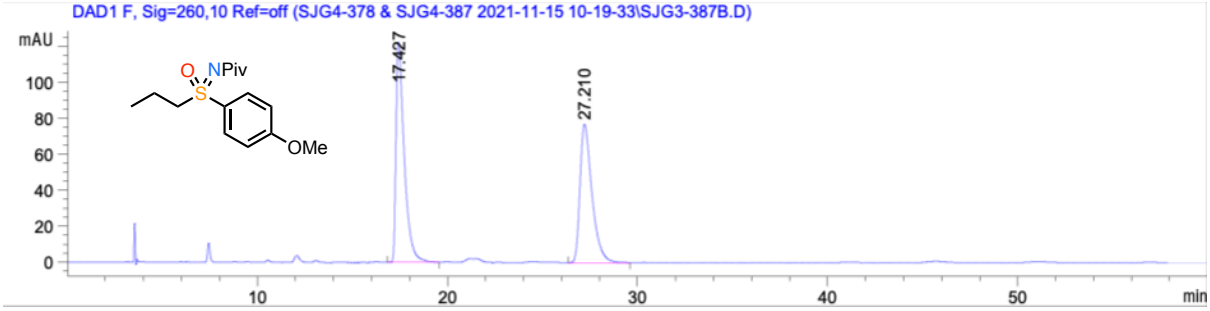
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.553	MM	0.6983	662.99194	15.82368	3.9581
2	35.950	MM	0.9727	1.60874e4	275.65680	96.0419
Totals :				1.67504e4	291.48048	

***ee* = 92%**

(*S*)-*N*-((4-Methoxyphenyl)(oxo)(propyl)-λ^6-sulfaneylidene)pivalamide ((*S*)-29)

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 260 nm.

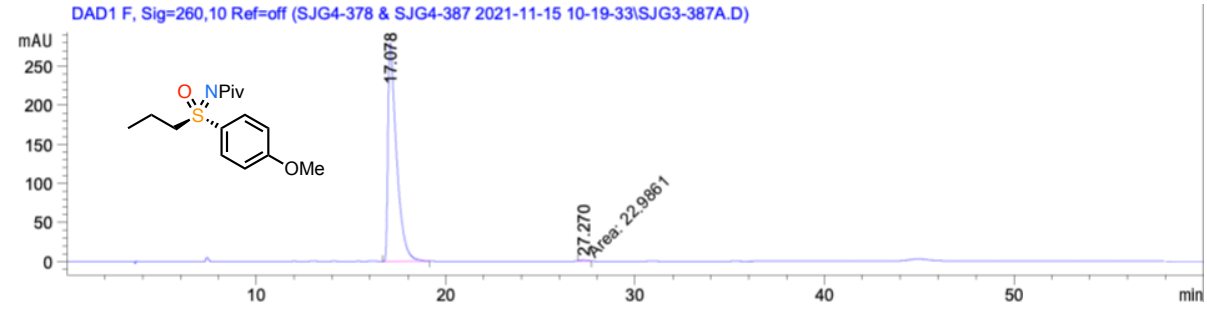
(*rac*)-29



Signal 6: DAD1 F, Sig=260,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.427	BB	0.4364	3653.83691	122.35462	52.1777
2	27.210	BB	0.6573	3348.83569	76.71486	47.8223
Totals :				7002.67261	199.06948	

(*S*)-29



Signal 6: DAD1 F, Sig=260,10 Ref=off

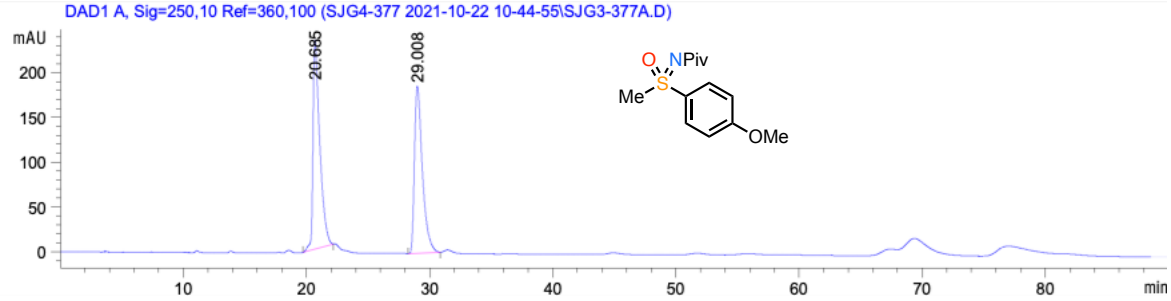
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.078	BB	0.4532	8794.44434	279.45135	99.7393
2	27.270	MM	0.4331	22.98613	8.84639e-1	0.2607
Totals :				8817.43047	280.33599	

***ee* >99%**

(*S*)-*N*-((4-Methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)pivalamide ((*S*)-30)

Conditions: Chiralpak IA column, 95:5 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 250 nm.

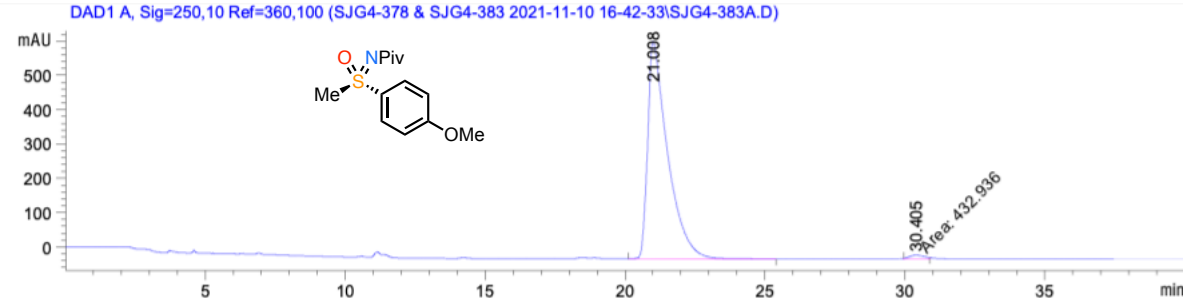
(*rac*)-30



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.685	BB	0.5481	8889.26172	233.51221	51.5756
2	29.008	BB	0.6707	8346.12793	186.28915	48.4244
Totals :				1.72354e4	419.80136	

(*S*)-30



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

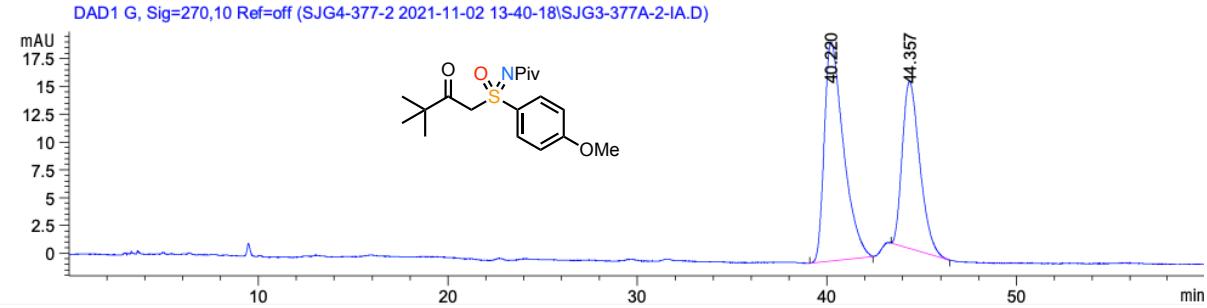
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.008	BB	0.6904	3.13342e4	634.27618	98.6372
2	30.405	MM	0.6411	432.93610	11.25581	1.3628
Totals :				3.17672e4	645.53199	

ee = 97%

(*S*)-*N*-((3,3-Dimethyl-2-oxobutyl)(4-methoxyphenyl)(oxo)-λ^6-sulfaneylidene)pivalamide ((*S*)-S11)

Conditions: Chiralpak IA column, 98:2 *n*hexane:*i*PrOH, flow rate: 1 mL min^{-1}, 35 °C, UV detection wavelength: 270 nm.

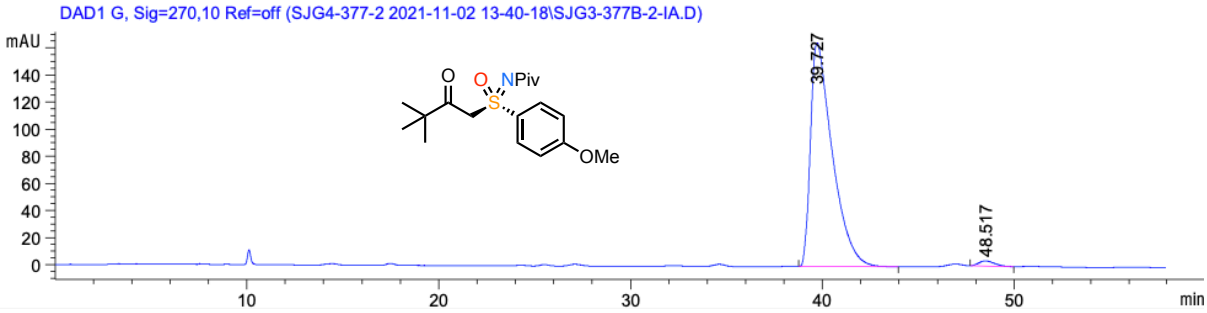
(*rac*)-S11



Signal 7: DAD1 G, Sig=270,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.220	BB	0.9536	1383.89111	19.65179	58.9398
2	44.357	BB	0.8636	964.08368	15.00557	41.0602
Totals :				2347.97479	34.65736	

(*S*)-S11



Signal 7: DAD1 G, Sig=270,10 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.727	BB	1.1132	1.30624e4	165.07417	98.4007
2	48.517	BB	0.6702	212.29916	3.78600	1.5993
Totals :				1.32747e4	168.86017	

ee = 97%