SUPPORTING INFORMATION

Electronic Supporting Information for

Chiral *N*,*N*′-Dioxide–Iron(III)-Catalyzed Asymmetric Sulfoxidation with Hydrogen Peroxide

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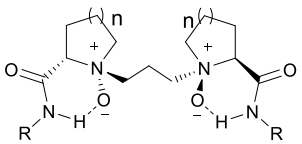
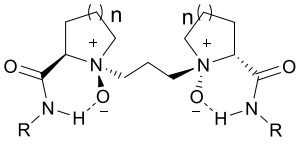
1. General remarks

^{1}H NMR spectra were recorded on bruker ASCEND™ 400M (400MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26, DMSO-d_6, δ = 2.54) Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets), coupling constants (Hz), integration and assignment. $^{13}C\{^1H\}$ NMR spectra were collected on bruker ASCEND™ 400M (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0, DMSO-d_6, δ = 39.5). $^{19}F\{^1H\}$ NMR spectra were collected on bruker ASCEND™ 400M (376 MHz) with complete proton decoupling. HRMS was recorded on a Thermo Q-Exactive Focus (FTMS+c ESI). Enantiomeric excesses (*ee*) were determined by HPLC and UPC^2 analysis using the corresponding commercial chiral column as stated in the experimental procedures at 23 °C with UV detector at 254 nm. Optical rotations were reported as follows: $[\alpha]^{22}_D$ (*c* g/100 mL, in solvent). Unless otherwise indicated, the reaction was performed under nitrogen atmosphere and reagents obtained from commercial sources were used without further purification. Solvents were dried and distilled prior to use according to the standard methods. Chloroform and acetone were dried over powdered CaH_2 and distilled under nitrogen just before use. $Fe(OTf)_3$ was purchased from Alfa. The chiral *N*,*N*′-dioxide ligands were synthesized by the same procedure in the literature.[1]

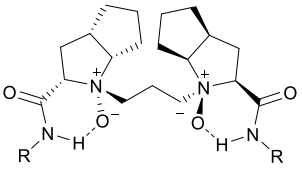
2. The scope of the ligands



L-PrPr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$, n = 1
L-PiEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$, n = 2
L-PiEt$_2$-Me: R = 2,6-Et$_2$-4-MeC$_6$H$_2$, n = 2
L-PiPr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$, n = 2
L-PiPr$_3$: R = 2,4,6-*i*Pr$_3$C$_6$H$_2$, n = 2
L-PiPr$_2$-Ad: R = 2,6-*i*Pr$_2$-4-(1-adamantyl)C$_6$H$_2$, n = 2



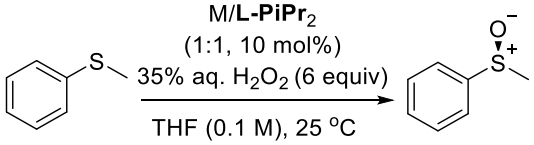
ent-**L-PiEt$_2$-Me**: R = 2,6-Et$_2$-4-MeC$_6$H$_2$, n = 2



L-RaPr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$

3. Extra information for the catalytic asymmetric sulfoxide reaction

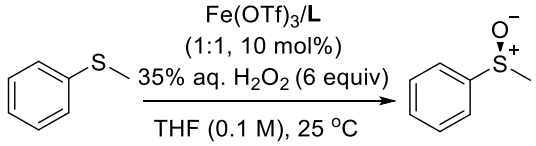
(a) The screen of metal salts[a]



entry	metal salt	yield (%)[b]	*ee* (%)[c]
1	$VO(acac)_2$	42	0
2	$V(acac)_3$	30	6
3	$Mn(C_2H_3O_3)_3 \cdot 2H_2O$	12	<5
4	$Ti(OiPr)_4$	13	0
5	$TiO(acac)_2$	11	7
6	$Fe(OTf)_2$	50	0
7	$Fe(OTf)_3$	52	63
8	$Fe(ClO_4)_3 \cdot H_2O$	42	10
9	$Fe(acac)_3$	32	0

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), metal salt (10 mol%), **L-PiPr$_2$** (10 mol%) and 35% aq. H_2O_2 (0.60 mmol) in THF (1.0 mL) at 25 °C for 4 h. [b] Yield of isolated product. [c] Determined by chiral HPLC.

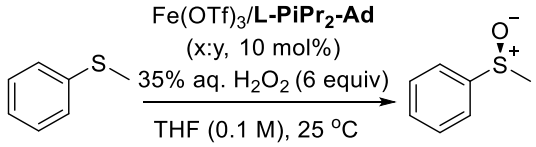
(b) The screen of ligand[a]



entry	ligand	yield (%)[b]	*ee* (%)[c]
1	**L-PrPr$_2$**	30	7
2	**L-RaPr$_2$**	27	53
3	**L-PiEt$_2$**	55	56
4	**L-PiEt$_2$-Me**	62	54
5	**L-PiPr$_2$**	52	63
6	**L-PiPr$_3$**	61	87
7	**L-PiPr$_2$-Ad**	70	93

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), Fe(OTf)$_3$ (10 mol%), **L** (10 mol%) and 35% aq. H_2O_2 (0.60 mmol) in THF (1.0 mL) at 25 °C for 4 h. [b] Yield of isolated product. [c] Determined by chiral HPLC.

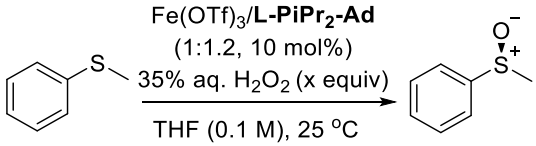
(c) The screen of ligand/metal salt ratio[a]



entry	x:y	yield (%)[b]	*ee* (%)[c]
1	1.2:1	50	46
2	1.5:1	31	16
3	2:1	16	8
4	1:1	69	91
5	1:1.1	71	96
6	1:1.2	70	98
7	1:1.5	64	99
8	1:2	66	99

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), Fe(OTf)$_3$ (10x mol%), **L-PiPr$_2$-Ad** (10y mol%) and 35% aq. H_2O_2 (0.60 mmol) in THF (1.0 mL) at 25 °C for 4 h. [b] Yield of isolated product. [c] Determined by chiral HPLC.

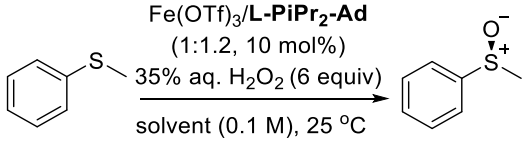
(d) The screen of 1a/oxidant ratio[a]



entry	x	yield (%)[b]	*ee* (%)[c]
1	1	50	95
2	2	54	97
3	3	60	91
4	4	65	92
5	5	65	99
6	6	70	98
7	7	71	96
8	8	70	98

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), Fe(OTf)$_3$ (10 mol%), **L-PiPr$_2$-Ad** (12 mol%) and 35% aq. H_2O_2 (x mmol) in THF (1.0 mL) at 25 °C for 4 h. [b] Yield of isolated product. [c] Determined by chiral HPLC.

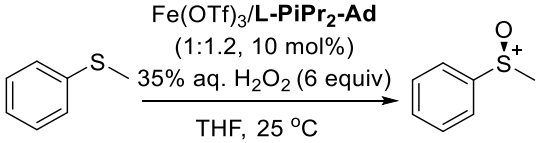
(e) The screen of solvent[a]



entry	solvent	yield (%)[b]	*ee* (%)[c]
1	Toluene	39	30
2	Et_2O	44	98
3	THF	70	98
4	MeOH	33	13
5	*i*PrOH	44	13
6	EA	53	54
7	CH_3CN	48	22
8	DCM	12	68

a) Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), $Fe(OTf)_3$ (10 mol%), **L-PiPr$_2$-Ad** (12 mol%) and 35% aq. H_2O_2 (0.60 mmol) in solvent (1.0 mL) at 25 °C for 4 h. b) Yield of isolated product. c) Determined by chiral HPLC.

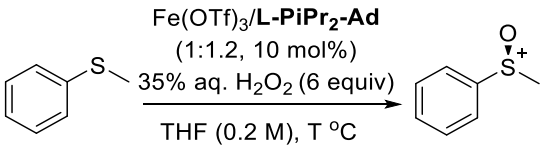
(f) The screen of solvent dosage[a]



entry	THF (mL)	yield (%)[b]	*ee* (%)[c]
1	0.5	80	98
2	1	71	97
3	1.5	66	92
4	2	67	95
5	3	63	94
6	4	66	97

a) Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), $Fe(OTf)_3$ (10 mol%), **L-PiPr$_2$-Ad** (12 mol%) and 35% aq. H_2O_2 (0.60 mmol) in THF at 25 °C for 4 h. b) Yield of isolated product. c) Determined by chiral HPLC.

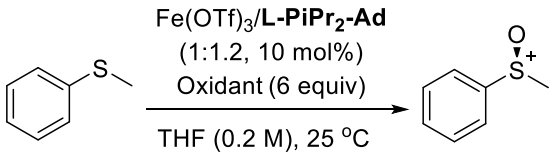
(g) The screen of temperature[a]



entry	T (°C)	yield (%)[b]	*ee* (%)[c]
1	−10	59	93
2	15	71	93
3	20	73	96
4	25	81	98
5	30	77	95
6	35	76	98
7	40	75	97
8	55	70	73

a) Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), $Fe(OTf)_3$ (10 mol%), **L-PiPr$_2$-Ad** (12 mol%) and 35% aq. H_2O_2 (0.60 mmol) in THF (0.5 mL) at T °C for 4 h. b) Yield of isolated product. c) Determined by chiral HPLC.

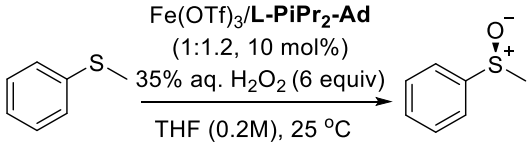
(h) The screen of oxidant[a]



entry	Oxidant	yield (%)[b]	*ee* (%)[c]
1	*m*-CPBA	0	0
2	CHP	31	82
3	TBHP	10	86
4	PhIO	52	30

a) Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), $Fe(OTf)_3$ (10 mol%), **L-PiPr$_2$-Ad** (12 mol%) and Oxidant (0.60 mmol) in THF (0.5 mL) at 25 °C for 4 h. b) Yield of isolated product. c) Determined by chiral HPLC.

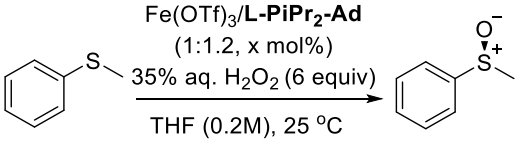
(i) The screen of time[a]



entry	t (h)	yield (%)[b]	*ee* (%)[c]
1	0.5	65	91
2	1	62	90
3	2	70	92
4	3	83	95
5	4	80	98
6	9	41	99

a) Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), $Fe(OTf)_3$ (10 mol%), **L-PiPr$_2$-Ad** (12 mol%) and 35% aq. H_2O_2 (0.60 mmol) in THF (0.5 mL) at 25 °C for t h. b) Yield of isolated product. c) Determined by chiral HPLC.

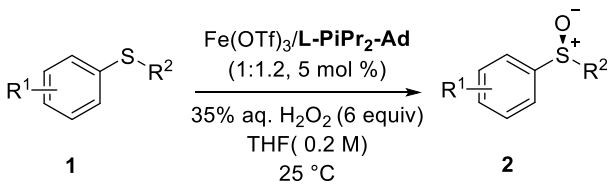
(j) The screen of catalyst loading[a]



entry	x	yield (%)[b]	*ee* (%)[c]
1	2.5	75	85
2	5.0	80	98
3	7.5	81	98
4	10	82	99

a) Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), $Fe(OTf)_3$ (x mol%), **L-PiPr$_2$-Ad** (1.2x mol%) and 35% aq. H_2O_2 (0.60 mmol) in THF (0.5 mL) at 25 °C for 4 h. b) Yield of isolated product. c) Determined by chiral HPLC.

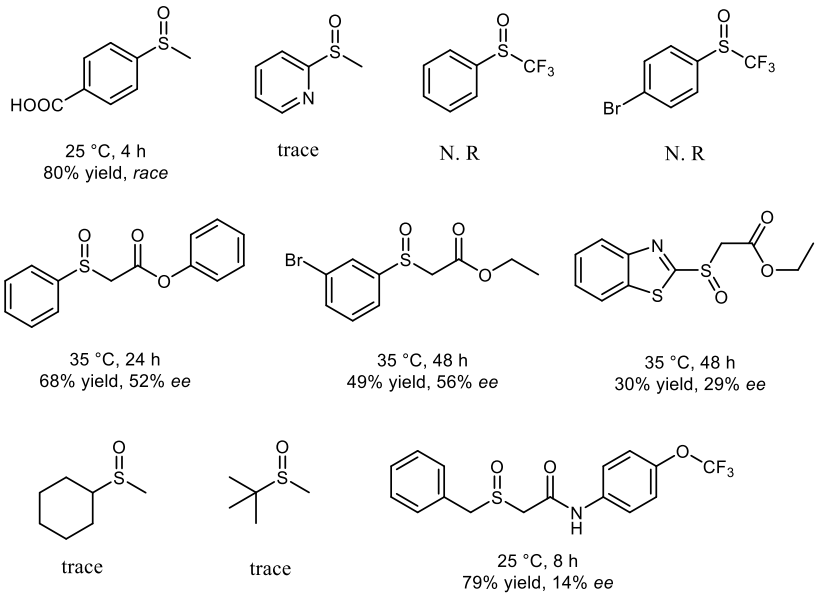
4. General procedure for the catalytic asymmetric sulfoxide reaction



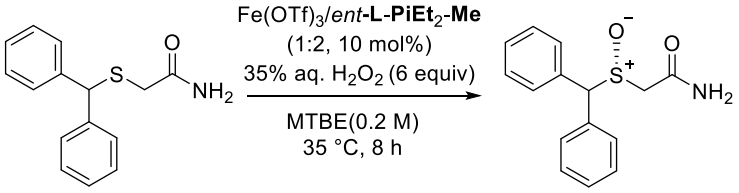
1 **2**

The reaction was conducted with $Fe(OTf)_3$ (10 mol%), **L-PiPr$_2$-Ad** (12 mol%) and sulfide **1** (0.10 mmol) in 0.5 mL of THF. The mixture was stirred at 35 °C for 30 min and then cooled to 25 °C. 35 % aqueous hydrogen peroxide solution (0.60 mmol) was added and the resulting mixture was stirred at 25 °C for 4 h. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether–ethyl acetate v/v, 1:1) to afford the corresponding product **2**.

5. Scope limitation

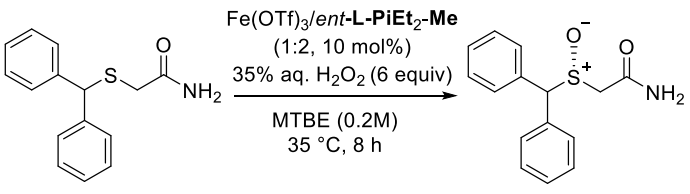


6. General procedure for the catalytic asymmetric synthesis of (*R*)-modafinil



The reaction was conducted with $Fe(OTf)_3$ (10 mol%), ***ent*-L-PiEt$_2$-Me** (20 mol%) and sulfide **1ae** (0.10 mmol) in 0.5 mL of MTBE. The mixture was stirred at 35 °C for 30 min and then 35 % aqueous hydrogen peroxide solution (0.60 mmol) was added and the resulting mixture was stirred at 35 °C for 8 h. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether–ethyl acetate v/v, 1:4) to afford the corresponding product.

7. Experimental procedure for the scale-up reaction



A dry reaction 100 mL round-bottom flask was charged with $Fe(OTf)_3$ (10 mol%, 200.0 mg), ***ent*-L-PiEt$_2$-Me** (20 mol%, 497.6 mg) and the substrate **1ae** (4.0 mmol, 1.028 g). Then, MTBE (20.0 mL) was added and the mixture was stirred at 35 °C for 1 h. Then 35 % aqueous hydrogen peroxide solution (6 equiv, 2.331 g) was added under stirring at 35 °C. The reaction mixture was stirred at 35 °C for 8 h. The solvent was removed in vacuo and the residue was subjected to column chromatography on silica gel and eluted with petroleum ether–ethyl acetate (v/v, 1:4) to afford the correspond product.

8. Mechanism study

8.1 Spectroscopic characterization of Fe^{III} and catalytic reaction mixtures

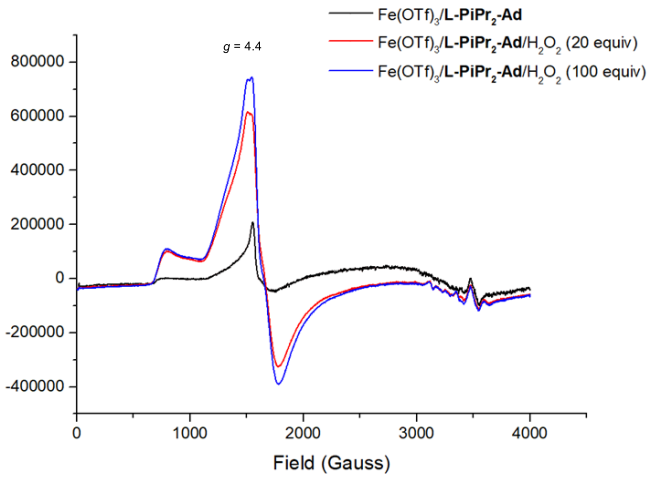


Figure S1. EPR spectrum of **L-PiPr₂-Ad**-Fe(OTf)$_3$ (1:1.2) with 20–100 equivalents of 35% aq. H_2O_2 in THF. Conditions: [**L-PiPr₂-Ad**-Fe(OTf)$_3$] = 3.3 x 10^{-2} M; temperature, 120 K with liquid nitrogen cooling. EPR spectra were recorded on a Bruker ESP-300E: Receiver Gain = 1.78 e+003; Phase = 0 deg; Harmoni = 1; Mod. Frequency = 100.000 KHz; Mod. Amplitude = 0.50G; Center Field = 3364.010 G; Sweep width 40.000 G; Resolution = 2048 points; Conversion Time =40.00ms; Time const. = 20.48 m; Sweep time = 81.92s; Power = 29.55 mw.
It was indicated that only a high spin Fe^{III} specie (g = 4.4) was detected after addition of H_2O_2.

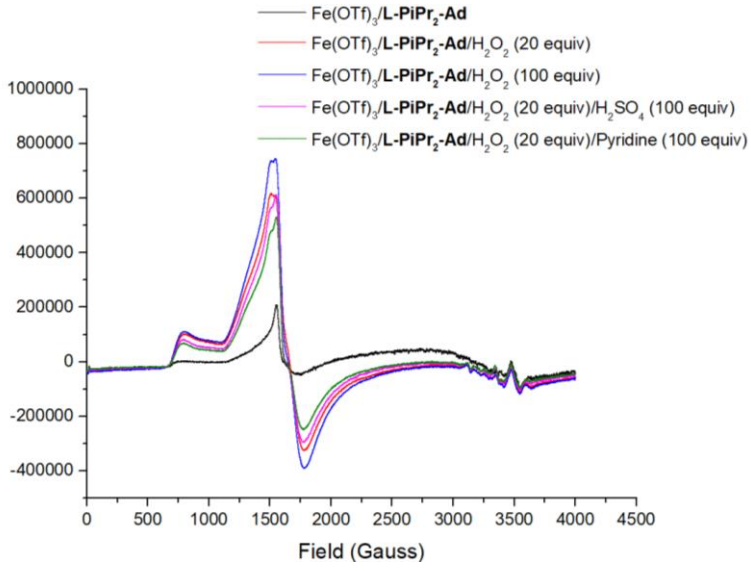


Figure S2: EPR spectrum of **L-PiPr₂-Ad**-Fe^{III} in THF. Conditions: [**L-PiPr₂-Ad**-Fe^{III}] = 3.3 x 10^{-2} M; temperature, 120 K with liquid nitrogen cooling.

It was indicated that only a high spin Fe^{III} specie (g = 4.4) was detected after addition of acid or base.

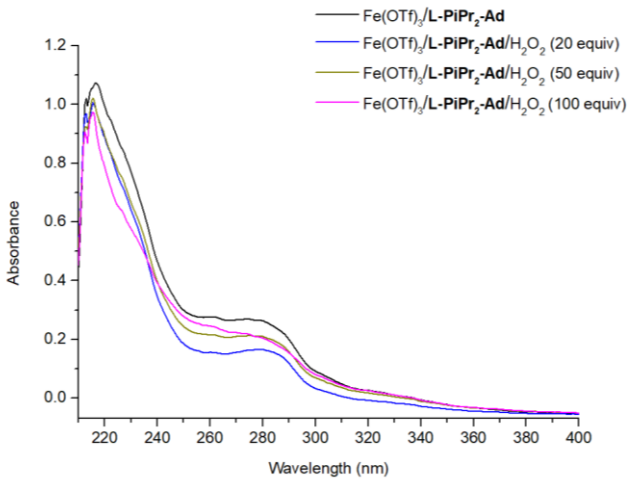


Figure S3. UV-vis spectrum of **L-PiPr$_2$-Ad**-Fe(OTf)$_3$ (1:1.2) with 20–100 equivalents of 35% aq. H_2O_2 in THF. Conditions: [**L-PiPr$_2$-Ad-**Fe(OTf)$_3$] = 5 x 10^{-6} M; temperature, 298 K.
The addition of H_2O_2 did not lead to new peaks along with decay of the 284 nm absorption.

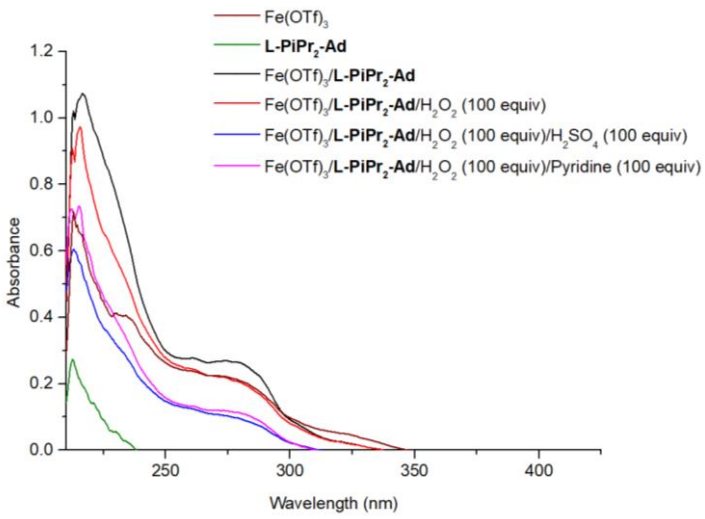
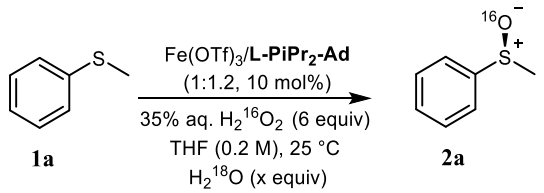
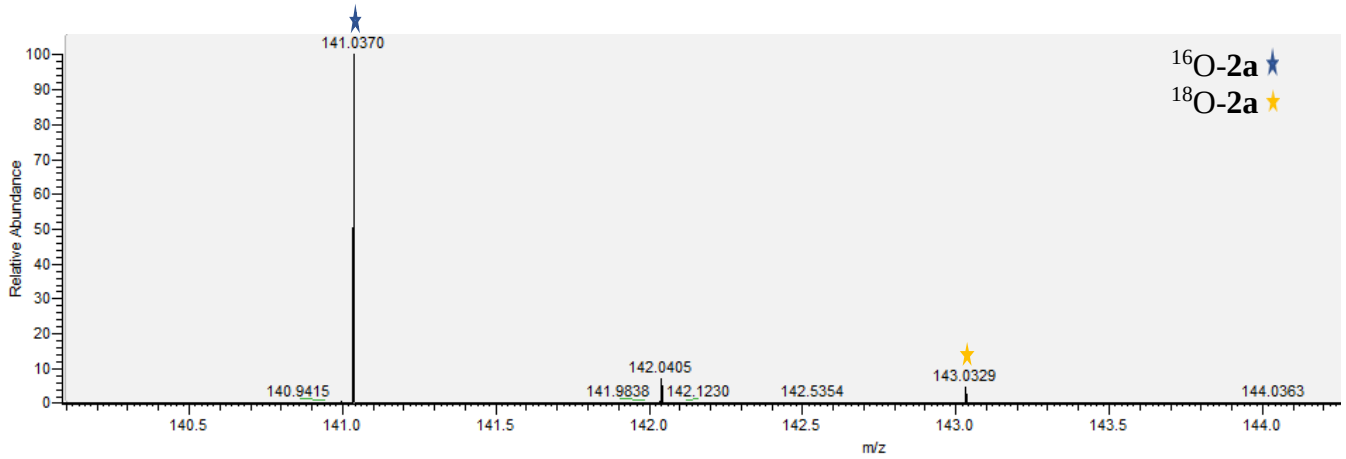


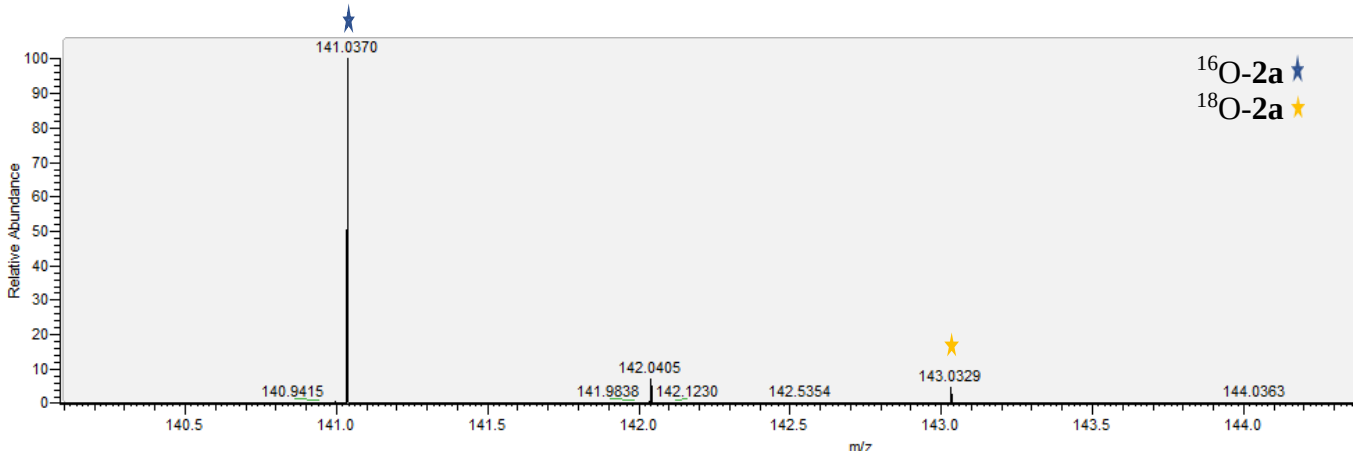
Figure S4: UV-Vis spectrum of **L-PiPr$_2$-Ad-Fe(OTf)$_3$ (**1:1.2) with 100 equiv. 35% aq. H_2O_2 with additive of H_2SO_4 or pyridine in THF. Conditions: [**L-PiPr$_2$-Ad**-Fe^{III}] = 5 x 10^{-6} M; temperature, 298 K.
Addition of acid or base did not lead to new peaks along with decay of the 284 nm absorption.

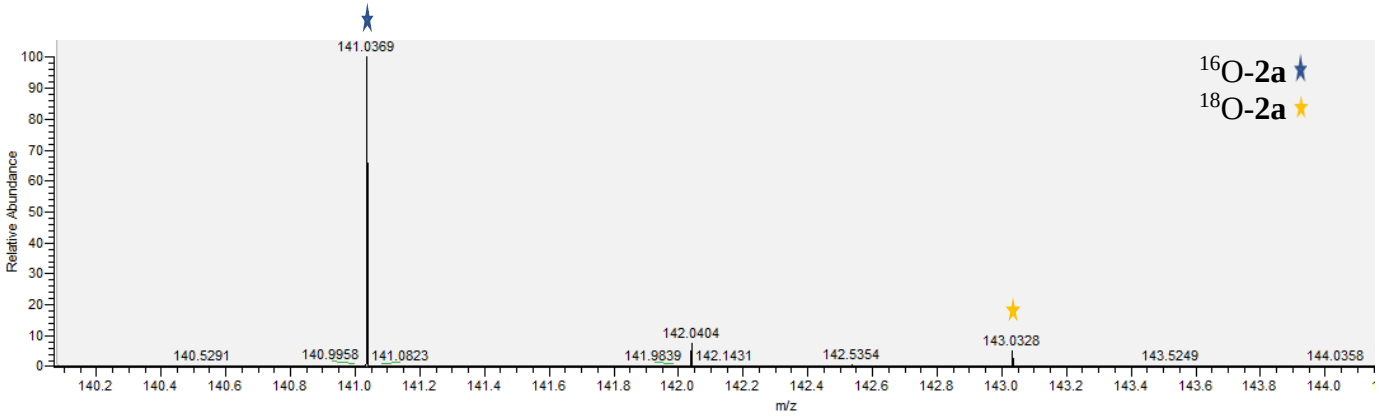
8.2 ^{18}O-Labeling of Sulfoxide



$H_2{}^{18}O$ (x equiv)	Time (h)	$^{18}O/^{16}O$
0	17	4.55/100
275	4	4.76/100
275	17	4.76/100



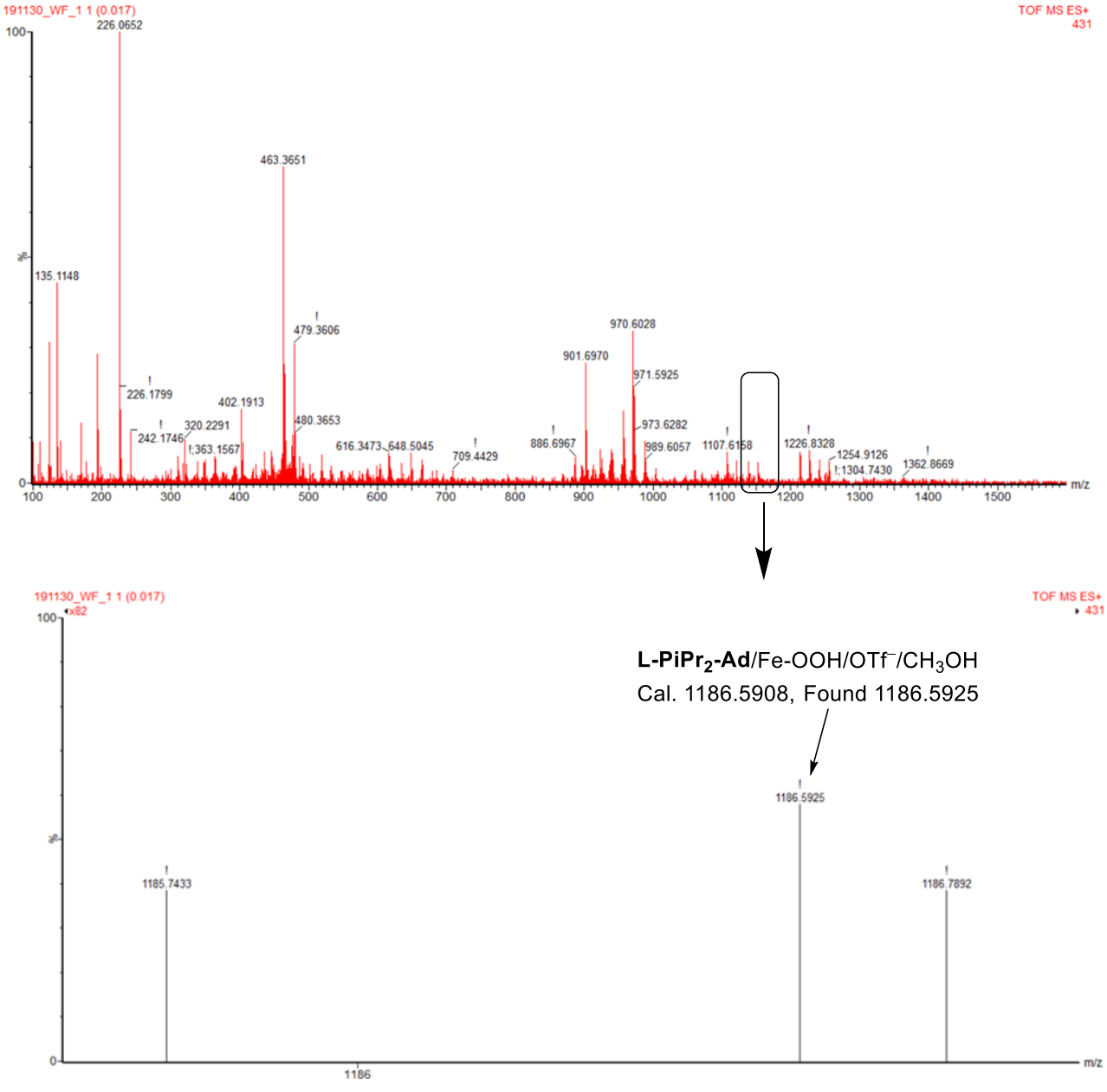




The reaction was conducted with $Fe(OTf)_3$ (10 mol%, 0.005 mmol), **L-PiPr$_2$-Ad**(12 mol%, 0.006 mmol) and sulfide **1a** (0.05 mmol) in 0.25 mL of THF. The mixture was stirred at 35 °C for 30 min and then cooled to 25 °C. $H_2{}^{18}O$ (13.75 mmol) and 35 % aq. H_2O_2 (0.30 mmol) was added and the resulting mixture was stirred at 25 °C for t h. The reaction mixture was subjected to HRMS.

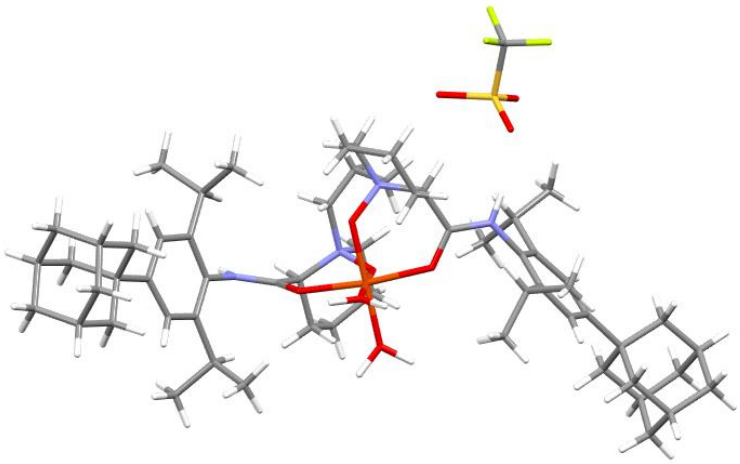
8.3 HRMS

The mixture of $Fe(OTf)_3$, **L-PiPr$_2$-Ad**, **1a** and 35% aq. H_2O_2 (1:1.2:1:6) in THF



8.4 X-ray crystal structure

The colourless and block-shape crystals were selected and mounted for the single-crystal X-ray diffraction. The data set was collected by a Bruker D8 Venture Photon II at 192K equipped with micro-focus Mo radiation source (K_α = 0.71073Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package.[2][3][4] Since attempts to refine peaks of residual election density attributed by partial-occupancy or disordered trifluoromethanesulfonic acid and solvent tetrahydrofuran molecules were unsuccessful, the data were corrected for unsolvable electron density using the SQUEEZE procedure as implemented in PLATON suite.[5] The value observed herein is indicative of racemic twinning and was accommodated during the refinement (using the SHELXL-2014 TWIN instruction). In this case, the relatively large standard uncertainty indicates that the structural data alone should not be used to confirm absolute stereochemistry, but should be used in conjunction with the established stereochemistry of the precursor compound. The structure was analyzed by ADDSYM routine in PLATON suite and no higher symmetry was suggested.[5]



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) waf00a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: waf00a

```
Bond precision:  C-C = 0.0107 A          Wavelength=0.71073

Cell:            a=28.876(2)     b=28.876(2)     c=11.5084(11)
                 alpha=90        beta=90         gamma=90
Temperature:     192 K

                 Calculated                Reported
Volume           9596.0(16)                9596.0(18)
Space group      P 42 21 2                 P 42 21 2
Hall group       P 4n 2n                   P 4n 2n
Moiety formula   C59 H92 Fe N4 O6, 2(C F3  C59 H92 Fe N4 O6, 2(C F3
                 O3 S) [+ solvent]         O3 S)
Sum formula      C61 H92 F6 Fe N4 O12 S2 [+ C61 H92 F6 Fe N4 O12 S2
                 solvent]
Mr               1307.36                   1307.35
Dx,g cm-3        0.905                     0.905
Z                4                         4
Mu (mm-1)        0.254                     0.254
F000             2776.0                    2776.0
F000'            2779.82
h,k,lmax         34,34,13                  34,34,13
Nref             8794[ 4945]               8775
Tmin,Tmax        0.952,0.966               0.834,0.960
Tmin'            0.952

Correction method= # Reported T Limits: Tmin=0.834 Tmax=0.960
AbsCorr = NUMERICAL

Data completeness= 1.77/1.00      Theta(max)= 25.343

R(reflections)= 0.0860( 5081)     wR2(reflections)= 0.2327( 8775)

S = 1.012                 Npar= 386
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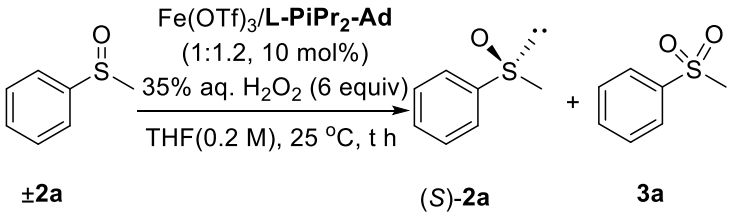
9. Kinetic resolution[a]



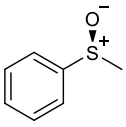
entry	t (h)	yield of **3a** (%)[b]	*ee* of **2a** (%)[c]
1	0.5	57	16
2	2	59	22
3	9	74	37

[a] Unless otherwise noted, all reactions were carried out with race-**2a** (0.10 mmol), 35% aq. H_2O_2 (0.60 mmol), **L-PiPr$_2$-Ad** (12 mol%), $Fe(OTf)_3$ (10 mol%) in THF (0.5 mL) at 25 °C for x h. [b] Yield of isolated product. [c] Determined by chiral HPLC.

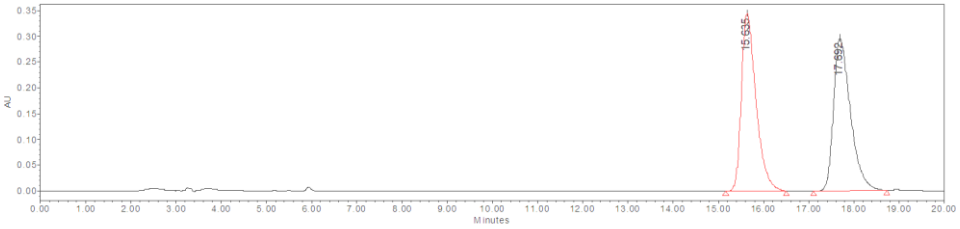
An experiment was performed under standard asymmetric sulfide oxidation condition using racemic sulfoxide **2a** as substrate. After 9 h reaction time the conversion of sulfoxide **2a** to sulfone **3a** was 74% and the enantiselectivation was 37%, which revealed that the kinetic resolution of asymmetric sulfoxidation.

10. Characterization of typical sulfoxide products

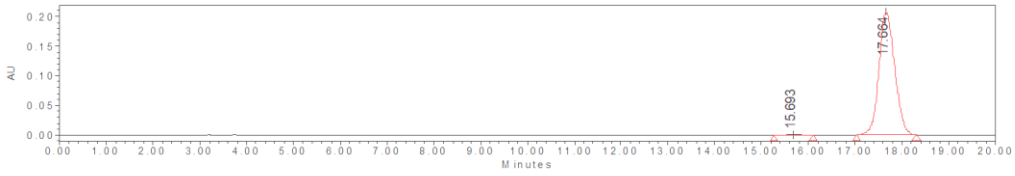
(*S*)-Phenyl methyl sulfoxide (2a)



25 °C, 4 h, 5 mo% catalyst loading; 11.2 mg, 80% yield; colorless oil; R_f = 0.30 (petroleum ether/ethyl acetate = 1/4). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel IC, hexane/*i*PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm): t_r (minor) = 15.693 min, t_r (major) = 17.664 min, *ee* = 99%. $[\alpha]^{22}_D$ = –153.3 (*c* = 0.2 in acetone). lit: $[\alpha]_D$ = –130.1 (*c* = 1.7 in acetone) for (*S*), 90% *ee*.[6] ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.70 – 7.60 (m, 2H), 7.56 – 7.46 (m, 3H), 2.72 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-d) δ= 145.7, 131.0, 129.3, 123.5, 43.9 ppm.

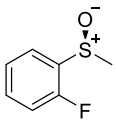


Peak	Retention Time	Area	% Area
1	15.635	7737131	50.19
2	17.692	7679599	49.81

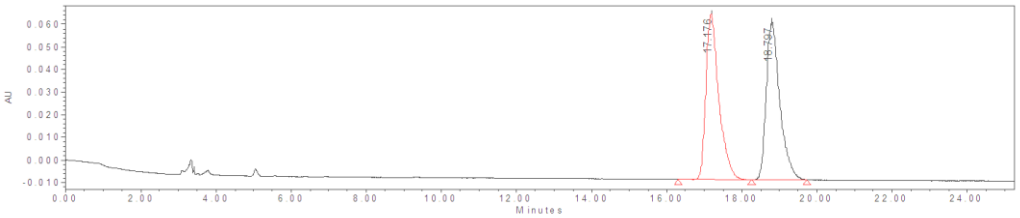


Peak	Retention Time	Area	% Area
1	15.693	20203	0.42
2	17.664	4812786	99.58

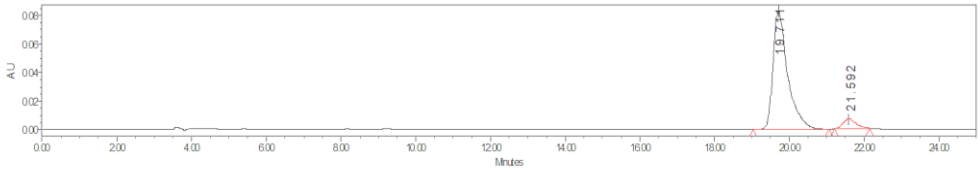
(*S*)-2-Fluorophenyl methyl sulfoxide (2b)



25 °C, 4 h, 5 mo% catalyst loading; 14.4 mg, 91% yield; colorless oil; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel ID, hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) major isomer: t_r (major) = 19.711 min, t_r (minor) = 21.592 min, *ee* = 87%. $[\alpha]^{22}_D$ = –135.2 (*c* = 0.3 in $CHCl_3$). lit: $[\alpha]_D$ = +163 (*c* = 1.6 in $CHCl_3$) for (*R*), >98% *ee*.[7] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.86 (m, 1H), 7.53 – 7.44 (m, 1H), 7.39 (m, 1H), 7.12 (m, 1H), 2.84 (s, 3H) ppm.^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 158.6 (*J* = 245 Hz), 132.8 (*J* = 17 Hz), 132.7 (*J* = 8 Hz), 125.4 (*J* = 9 Hz), 125.38 (*J* = 2 Hz),115.7 (*J* = 20 Hz), 42.3 – 41.9 (m) ppm. ^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ = –114.7 ppm.

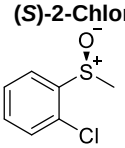


Peak	Retention Time	Area	% Area
1	17.176	1744868	50.00
2	18.797	1744810	50.00

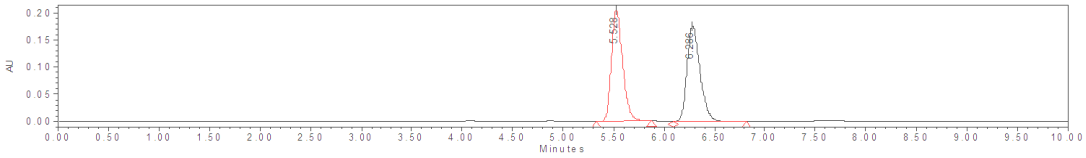


Peak	Retention Time	Area	% Area
1	19.711	2249923	93.31
2	21.592	161345	6.69

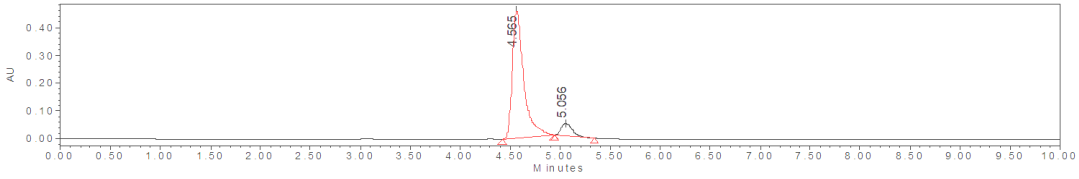
(*S*)-2-Chlorophenyl methyl sulfoxide (2c)



25 °C, 4 h, 10 mo% catalyst loading; 17.1mg, 98% yield; pale yellow oil; R_f = 0.50 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel ADH, hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) major isomer: t_r (major) = 4.565 min, t_r (minor) = 5.056 min, *ee* = 84%. $[\alpha]^{22}_D$ = –230.2 (*c* = 0.3 in $CHCl_3$). lit: $[\alpha]_D$ = +116 (*c* = 1.2 in $CHCl_3$) for (*R*), 41% *ee*.[7] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.79 (d, *J* = 4 Hz, 1H), 7.61 (m, 1H), 7.53 (m, 1H), 7.40 (t, *J* = 8 Hz, 1H), 2.73 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 147.9, 134.0, 130.8, 126.4, 123.5, 122.0, 43.9 (d, *J* = 3 Hz) ppm.

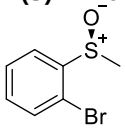


Peak	Retention Time	Area	% Area
1	5.528	1558749	49.87
2	6.286	1567064	50.13

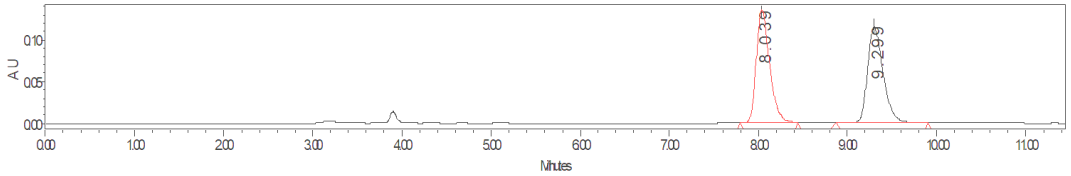


Peak	Retention Time	Area	% Area
1	4.565	3629711	91.76
2	5.056	325826	8.24

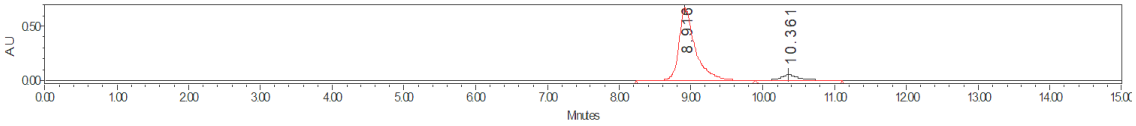
(*S*)-2-Bromophenyl methyl sulfoxide (2d)



25 °C, 4 h, 5 mo% catalyst loading; 21.5 mg, 98% yield; pale yellow oil; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel IA, hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm): t_r (major) = 8.916 min, t_r (minor) = 10.361 min, *ee* = 84%. $[\alpha]^{22}_D$ = –210.7 (*c* = 0.4 in $CHCl_3$). lit: $[\alpha]^{22}_D$ = –174.9 (*c* = 1.3 in $CHCl_3$) for (*S*), 66% *ee*.[6] ^{1}H NMR (400 MHz, Chloroform-*d*) δ =7.97 – 7.90 (m, 1H), 7.62 – 7.52 (m, 2H), 7.41 – 7.32 (m, 1H), 2.81 (s, 3H) ppm.^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 145.3, 132.9, 132.2, 128.7, 125.7, 118.4, 41.9 (d, *J* = 2.0 Hz) ppm.

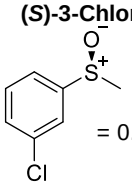


Peak	Retention Time	Area	% Area
1	8.039	1397498	50.02
2	9.299	1398645	49.98

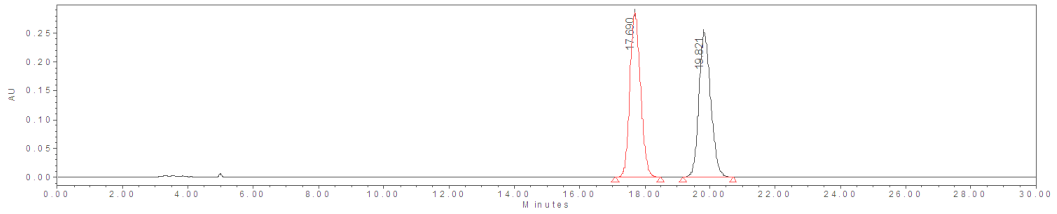


Peak	Retention Time	Area	% Area
1	8.916	10466762	92.14
2	10.361	893289	7.86

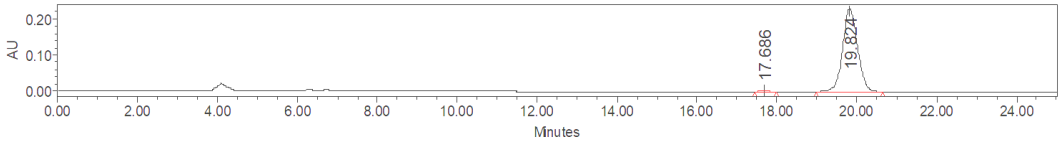
(*S*)-3-Chlorophenyl methyl sulfoxide (2e)



25 °C, 4 h, 5 mo% catalyst loading; 15.7 mg, 90% yield; colorless oil; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel IC, hexane/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) major isomer: t_r (minor) = 17.686 min, t_r (major) = 19.824 min, *ee* = 99%. $[\alpha]^{22}_D$ = –80.4 (*c* = 0.3 in acetone). lit: $[\alpha]^{25}_D$ = +98.1 (*c* = 0.6 in acetone) for (*R*), 99% *ee*.[8] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.79 (d, *J* = 4 Hz, 1H), 7.61 (m, 1H), 7.53 (m, 1H), 7.39 (d, *J* = 8 Hz, 1H), 2.73 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-d) δ = 147.8, 135.7, 131.2, 130.6, 123.6, 121.6, 44.0 ppm.

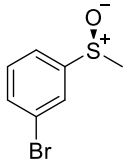


Peak	Retention Time	Area	% Area
1	17.690	6397186	50.01
2	19.821	6395591	49.99

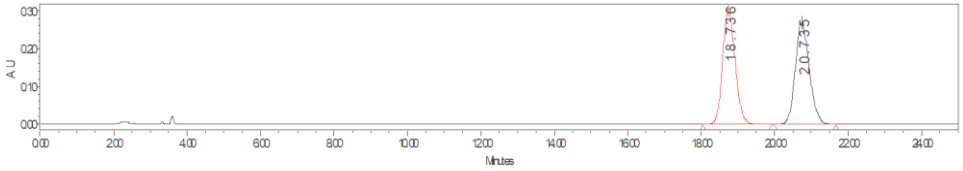


Peak	Retention Time	Area	% Area
1	17.686	13422	0.23
2	19.824	5928284	99.77

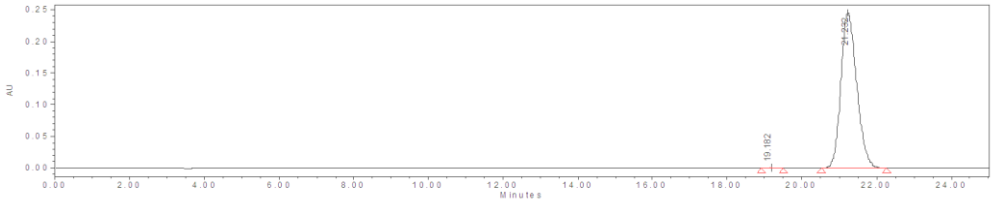
(*S*)-3-Bromophenyl methyl sulfoxide (2f)



25 °C, 4 h, 2.5 mo% catalyst loading; 20.1 mg, 92% yield; pale yellow oil; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel IC, hexane/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 18.942 min, t_r (major) = 20.957 min, *ee* = 99%. $[\alpha]^{22}_D$ = –121.1 (*c* = 0.4 in acetone). lit: $[\alpha]_D$ = +116.3 (*c* = 1.2 in acetone) for (*R*), 97% *ee*.[9] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.79 (d, *J* = 4 Hz, 1H), 7.61 (m, 1H), 7.55 – 7.51 (m, 1H), 7.38 (t, *J* = 8 Hz, 1H), 2.72 (s, 3H). ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-d) δ = 147.9, 134.1, 130.8, 126.5, 123.6, 122.1, 44.0 (d, *J* = 2 Hz) ppm.

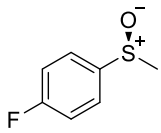


Peak	Retention Time	Area	% Area
1	18.736	7210032	50.05
2	20.735	7194955	49.95

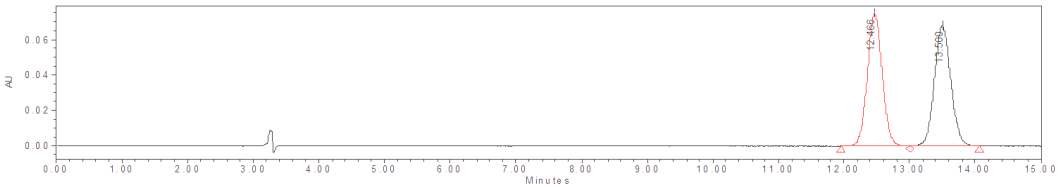


Peak	Retention Time	Area	% Area
1	18.942	15107	0.21
2	20.957	7219420	99.79

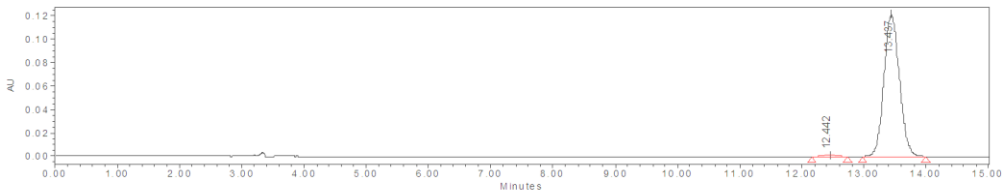
(*S*)-4-Fluorophenyl methyl sulfoxide (2g)



25 °C, 4 h, 5 mo% catalyst loading; 11.1 mg, 70% yield; colorless oil; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel IC, hexane/*i*PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 12.442 min, t_r (major) =13.437 min, *ee* = 98%. $[\alpha]^{22}_D$ = –125.1 (*c* = 0.3 in $CHCl_3$). lit: $[\alpha]^{25}_D$ = +120.1 (*c* = 2.0 in $CHCl_3$) for (*R*), 99% *ee*.[10] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.66 (m, 2H), 7.24 (t, *J* = 8 Hz, 2H), 2.72 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 165.5 (*J* = 250 Hz), 141.1 (*J* = 3 Hz), 125.9 (*J* = 9 Hz), 116.8 (*J* = 20 Hz), 44.2 ppm. ^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ = –108.61 ppm.

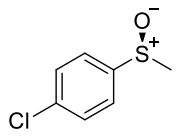


Peak	Retention Time	Area	% Area
1	12.466	1173215	50.00
2	13.500	1173095	50.00

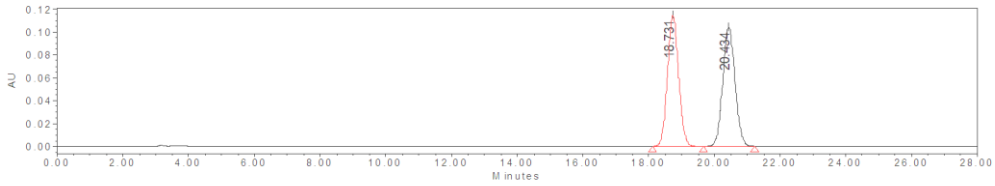


Peak	Retention Time	Area	% Area
1	12.442	18612	0.88
2	13.437	2097386	99.12

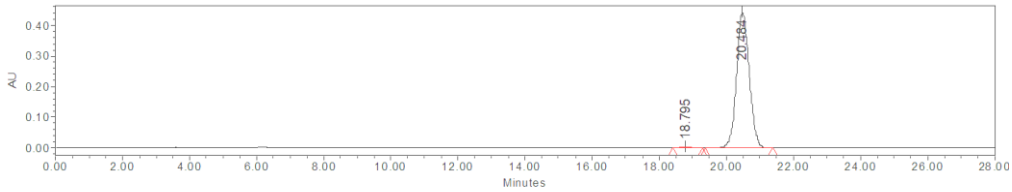
(*S*)-4-Chlorophenyl methyl sulfoxide (2h)



25 °C, 4 h, 2.5 mo% catalyst loading; 14.1 mg, 81% yield; colorless oil; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel IC, hexane/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 18.795 min, t_r (major) = 20.484 min, *ee* = 98%. $[\alpha]^{22}_D$ = –120.8 (*c* = 0.4 in acetone). lit: $[\alpha]_D$ = –109.7 (*c* = 2.0 in acetone) for (*S*), 92% *ee*.[6] ^{1}H NMR (400 MHz, Chloroform-*d*) δ =7.56 – 7.54 (m, 2H), 7.50 – 7.44 (m, 2H), 2.68 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 144.1, 137.3, 129.6, 124.9, 44.0 (d, *J* = 2 Hz) ppm.

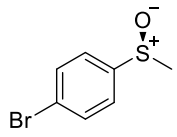


Peak	Retention Time	Area	% Area
1	18.731	2717230	50.02
2	20.434	2715142	49.98

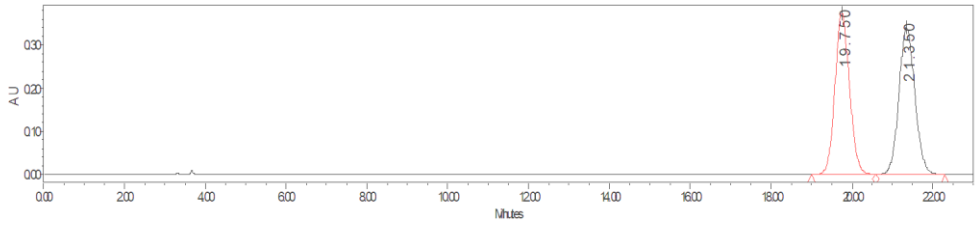


Peak	Retention Time	Area	% Area
1	18.795	110001	0.94
2	20.484	11650428	99.06

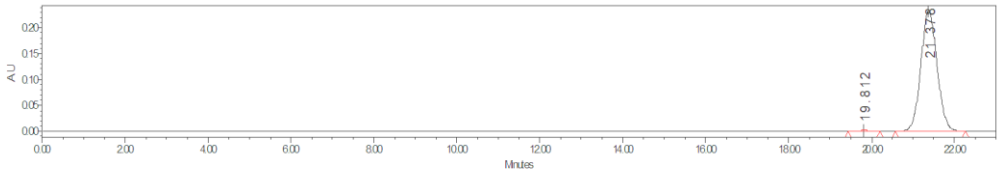
(*S*)-4-Bromophenyl methyl sulfoxide (2i)



25 °C, 4 h, 10 mo% catalyst loading; 17.3 mg, 79% yield; white solid; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel IC, hexane/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 19.812 min, t_r (major) = 21.378 min, *ee* = 99%. $[\alpha]^{22}_D$ = –100.3 (*c* = 0.3 in acetone). lit: $[\alpha]_D$ = –97.5 (*c* = 1.8 in acetone) for (*S*), 94% *ee*.[6] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.66 (m, 2H), 7.51 (m, 2H), 2.71 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-d) δ = 144.8, 132.5, 125.4, 125.1, 43.9 (d, *J* = 3 Hz) ppm.

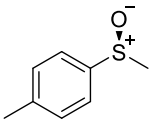


Peak	Retention Time	Area	% Area
1	19.750	9356922	50.01
2	21.350	9354913	49.99

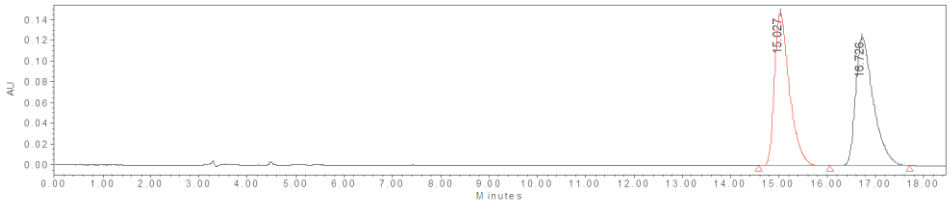


Peak	Retention Time	Area	% Area
1	19.812	36903	0.58
2	21.378	6331529	99.42

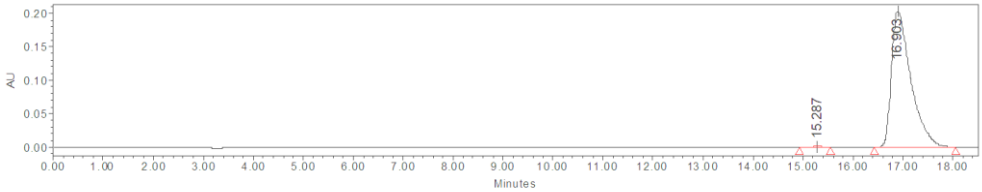
(*S*)-4-Tolyl methyl sulfoxide (2j)



0 °C, 12 h, 5 mo% catalyst loading; 14.9 mg, 97% yield; white solid; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel ID, hexane/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) major isomer: t_r (minor) = 15.287 min, t_r (major) = 16.903 min, *ee* = 99%. $[\alpha]^{22}_D$ = –132.2 (*c* = 0.3 in acetone). lit: $[\alpha]_D$ = –126.9 (*c* = 2.0 in acetone) for (*S*), 92% *ee*.[6] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.56 – 7.51 (m, 2H), 7.35 – 7.30 (m, 2H), 2.70 (s, 3H), 2.41 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 142.4, 141.5, 130.0, 123.5, 43.9 (d, *J* = 2 Hz), 21.4 (d, *J* = 2 Hz) ppm.

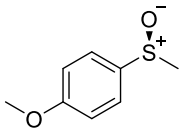


Peak	Retention Time	Area	% Area
1	15.027	3147133	49.97
2	16.726	3150455	50.03

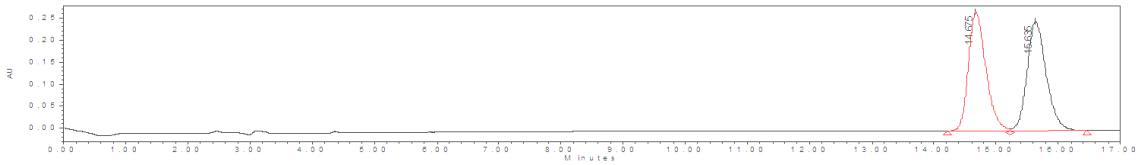


Peak	Retention Time	Area	% Area
1	15.287	13193	0.24
2	16.903	5457511	99.76

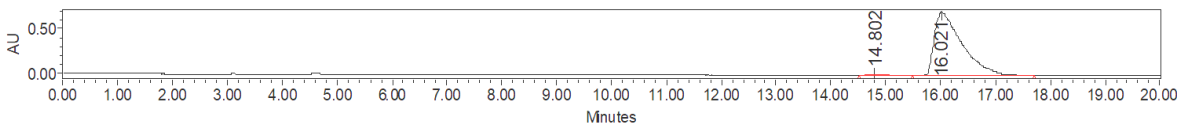
(*S*)-4-Methoxyphenyl methyl sulfoxide (2k)



0 °C, 12 h, 5 mo% catalyst loading; 16.3 mg, 96% yield; pale yellow oil; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel IE, hexane/*i*PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 14.802 min, t_r (major) = 16.021 min, *ee* = 99%. $[\alpha]^{22}_D$ = –138.3 (*c* = 0.3 in $CHCl_3$). lit: $[\alpha]_D$ = –129.7 (*c* = 2.0 in $CHCl_3$) for (*S*), 86% *ee*.[6] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.63 – 7.56 (m, 2H), 7.05 – 7.00 (m, 2H), 3.85 (s, 3H), 2.70 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 161.9, 136.6, 125.4, 114.8, 55.5 (d, *J* = 2 Hz), 44.0 ppm.

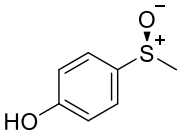


Peak	Retention Time	Area	% Area
1	14.675	5275505	49.92
2	15.635	5291816	50.08

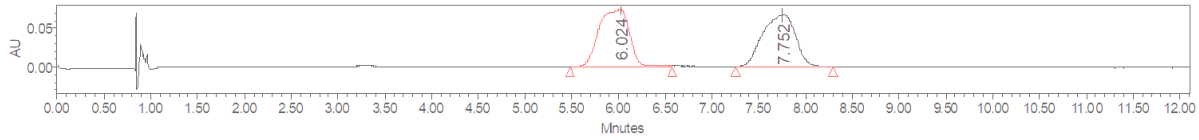


Peak	Retention Time	Area	% Area
1	14.802	127396	0.52
2	16.021	24480056	99.48

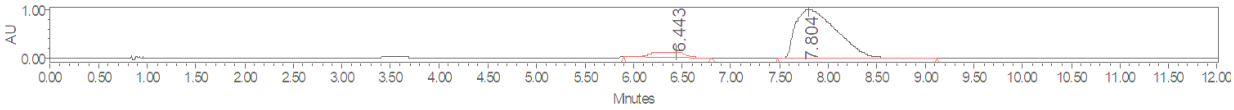
(*S*)-4-(Methylsulfinyl)phenol (2l)



25 °C, 12 h, 5 mo% catalyst loading; 14.0 mg, 90% yield; white solid; R_f = 0.20 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for UPC^2; UPC^2 (Chiralcel AS, CO_2/EtOH = 90/10, flow rate 1.5 mL/min, λ = 254 nm) t_r (minor) = 6.443 min, t_r (major) = 7.804 min, *ee* = 83%. $[\alpha]^{22}_D$ = –90.3 (*c* = 0.3 in acetone). lit: $[\alpha]^{20}_D$ = +67 (*c* = 1 in acetone) for (*R*), 50% *ee*.[11] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.99 (s, 1H), 7.55 – 7.45 (m, 2H), 7.02 – 6.90 (m, 2H), 2.73 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 160.4, 133.7, 125.9, 116.7, 43.3 ppm.

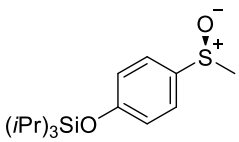


Peak	Retention Time	Area	% Area
1	6.024	1691260	50.33
2	7.752	1669399	49.67

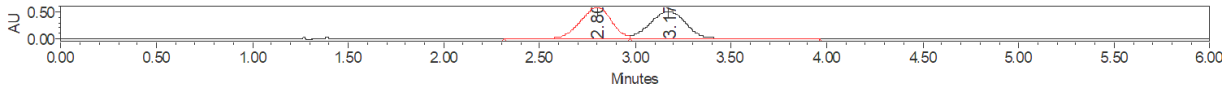


Peak	Retention Time	Area	% Area
1	6.443	2703058	8.44
2	7.804	29322662	91.56

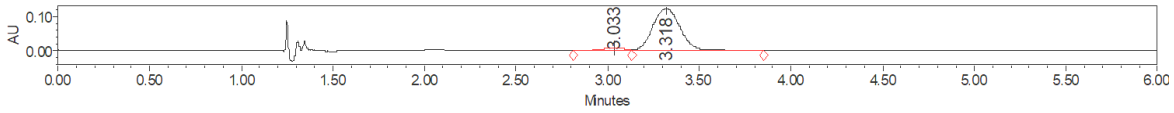
(*S*)-Triisopropyl(4-(methylsulfinyl)phenoxy)silane (2m)



35 °C, 14 h, 5 mo% catalyst loading; 19.0 mg, 61% yield; colorless oil; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for UPC^2; UPC^2 (Chiralcel AS, CO_2/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 3.033 min, t_r (major) = 3.318 min, *ee* = 89%. $[\alpha]^{22}_D$ = –130.6 (*c* = 0.3 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.53 (m, 2H), 7.00 (m, 2H), 2.80 – 2.63 (m, 3H), 1.27 (m, 3H), 1.10 (d, *J* = 8 Hz, 18H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 158.9, 136.9, 125.4, 120.8, 43.9, 17.8, 12.6 ppm. HRMS (ESI-TOF) calcd for $C_{16}H_{29}O_2SSi^+$ ([M]+H$^+$) = 313.1652, Found 313.1649.

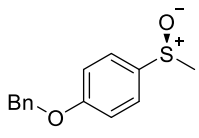


Peak	Retention Time	Area	% Area
1	2.801	7037170	50.78
2	3.174	6820062	49.22

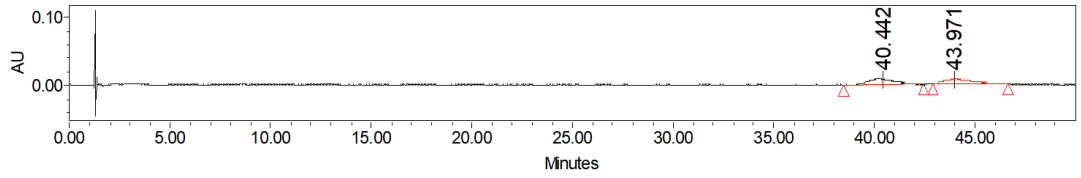


Peak	Retention Time	Area	% Area
1	3.033	73396	5.41
2	3.318	1282894	94.59

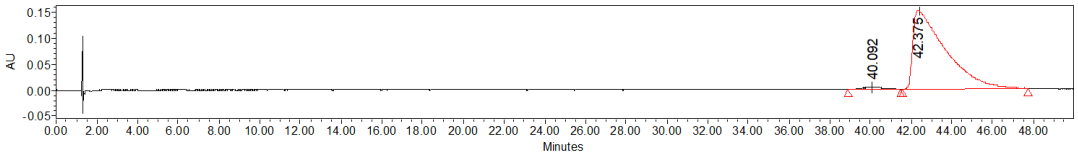
(*S*)-1-(Benzyloxy)-4-(methylsulfinyl)benzene (2n)



35 °C, 8 h, 5 mo% catalyst loading; 19.9 mg, 86% yield; white solid; R_f = 0.20 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for UPC^2; UPC^2 (Chiralcel OJ, CO_2/*i*PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 40.092 min, t_r (major) = 42.375 min, *ee* = 96%. $[\alpha]^{22}_D$ = –118.6 (*c* = 0.4 in $CHCl_3$). lit: $[\alpha]^{25}_D$ = +117.6 (*c* = 0.5 in $CHCl_3$) for (*S*), 96% *ee*.[12] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.63 – 7.54 (m, 2H), 7.46 – 7.31 (m, 5H), 7.15 – 7.08 (m, 2H), 5.12 (s, 2H), 2.70 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 161.1, 136.9, 136.2, 128.7, 128.2, 127.4, 125.5, 115.7, 70.3, 44.0 ppm.

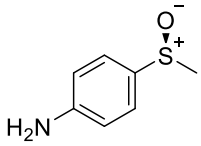


Peak	Retention Time	Area	% Area
1	40.442	687598	51.02
2	43.971	660182	48.98

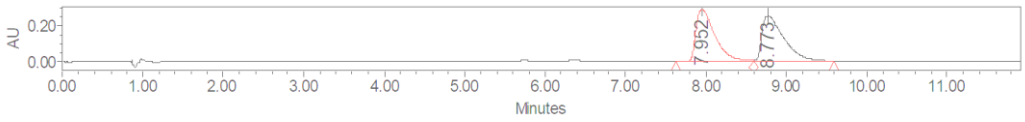


Peak	Retention Time	Area	% Area
1	40.092	293935	1.72
2	42.375	16780964	98.28

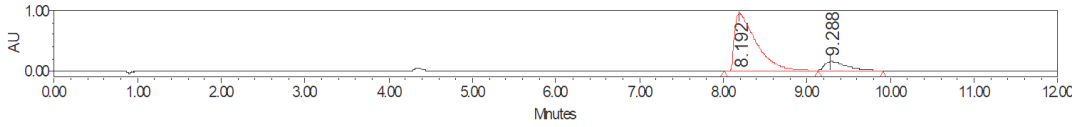
(*S*)-4-(Methylsulfinyl)aniline (2o)



25 °C, 15 h, 5 mo% catalyst loading; 13.9 mg, 90% yield; pale yellow oil; R_f = 0.20 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for UPC²; UPC² (Chiralcel ID, CO_2/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 8.192 min, t_r (minor) = 9.288 min, *ee* = 72%. $[\alpha]^{22}_D$ = –70.2 (*c* = 0.2 in EtOH). lit: $[\alpha]^{25}_D$ = –85.1 (*c* = 0.8 in EtOH) for (*S*), 95% *ee*.[13] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.53 – 7.37 (m, 2H), 6.78 – 6.71 (m, 2H), 4.03 (s, 1.65H), 2.67 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 149.5, 133.3, 125.6, 115.0, 43.8 ppm.

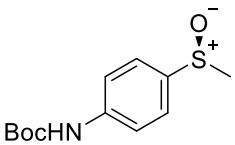


Peak	Retention Time	Area	% Area
1	7.952	4742021	49.92
2	8.773	4756911	50.08

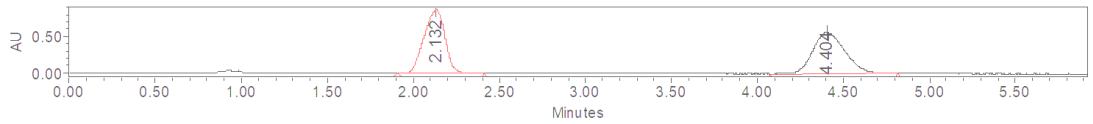


Peak	Retention Time	Area	% Area
1	8.192	17388027	85.90
2	9.288	2854554	14.10

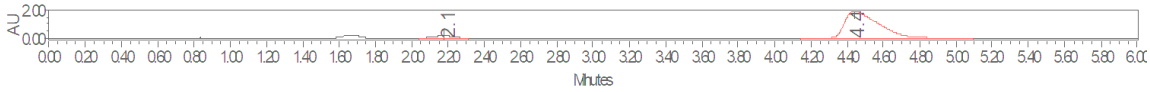
(*S*)-Tert-butyl [4-(methylsulfinyl)phenyl]carbamate (2p)



0 °C, 4 h, 5 mo% catalyst loading; 23.4 mg, 92% yield; white solid; R_f = 0.20 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for UPC²; UPC² (Chiralcel AS, CO_2/EtOH = 80/20, flow rate 1.5 mL/min, λ = 254 nm) t_r (minor) = 2.181 min, t_r (major) = 4.442 min, *ee* = 92%. $[\alpha]^{22}_D$ = –93.1 (*c* = 0.3 in acetone). ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.70 – 7.50 (m, 4H), 6.80 (s, 1H), 2.69 (s, 3H), 1.52 (s, 9H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 152.4, 141.3, 138.9, 124.7, 118.8, 81.2, 44.0, 28.3 ppm. HRMS (ESI-TOF) calcd for $C_{12}H_{18}F_3NO_3S^+$ ([M]+H$^+$) = 256.1001, Found 256.1006.

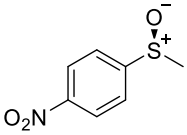


Peak	Retention Time	Area	% Area
1	2.132	7285232	50.11
2	4.404	7252596	49.89

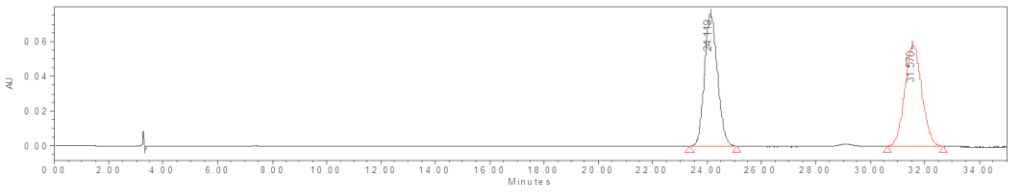


Peak	Retention Time	Area	% Area
1	2.181	1042898	4.11
2	4.442	24357590	95.89

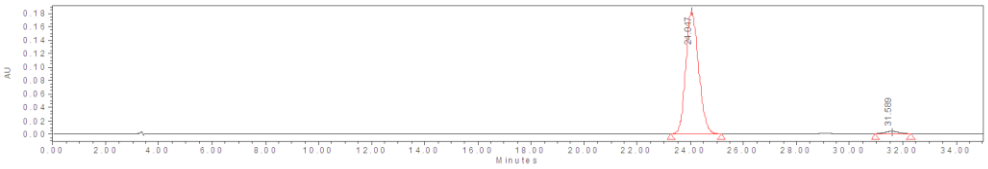
(*S*)-4-Nitrophenyl methyl sulfoxide (2q)



35 °C, 20 h, 10 mo% catalyst loading; 12.3 mg, 66% yield; pale yellow solid; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel IC, hexane/*i*PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 24.047 min, t_r (minor) = 31.589 min, *ee* = 96%. $[\alpha]^{22}_D$ = –130.6 (*c* = 0.2 in $CHCl_3$). lit: $[\alpha]_D$ = –128.5 (*c* = 0.75 in $CHCl_3$) for (*S*), 96% *ee*.[6] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.43 – 8.37 (m, 2H), 7.91 – 7.80 (m, 2H), 2.79 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 153.2, 149.5, 124.6, 124.5, 43.9 (d, *J* = 2 Hz) ppm.

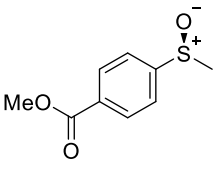


Peak	Retention Time	Area	% Area
1	24.119	2548499	50.15
2	31.570	2533728	49.85

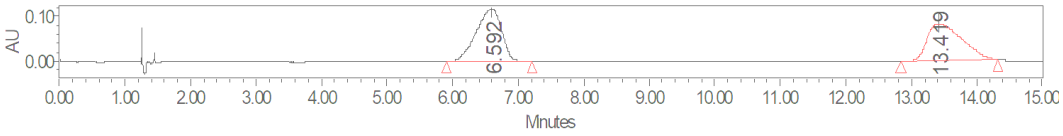


Peak	Retention Time	Area	% Area
1	24.047	6159117	97.96
2	31.589	149749	2.04

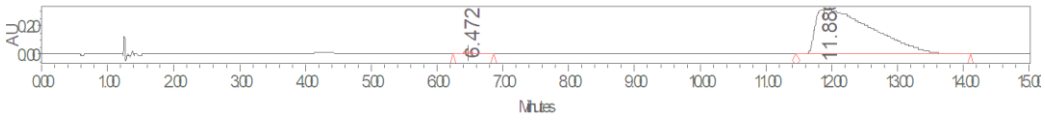
(*S*)-Methyl-4-methylsulfinylbenzoate (2r)



35 °C, 18 h, 5 mo% catalyst loading; 15.8 mg, 80% yield; white solid; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for UPC^2; UPC^2 (Chiralcel OJ, CO_2/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 6.472 min, t_r (major) = 11.886 min, *ee* = 98%. $[\alpha]^{22}_D$ = –220.6 (*c* = 0.3 in $CHCl_3$). lit: $[\alpha]^{20}_D$ = +260 (*c* = 0.5 in $CHCl_3$) for (*R*), 91% *ee*.[11] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.18 (m, 2H), 7.71 (m, 2H), 3.94 (s, 3H), 2.74 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 166.0, 150.9, 132.6, 130.5, 123.5, 52.5, 43.8 ppm.

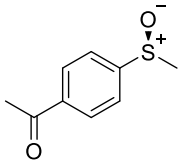


Peak	Retention Time	Area	% Area
1	6.592	3157925	50.86
2	13.419	3051417	49.14

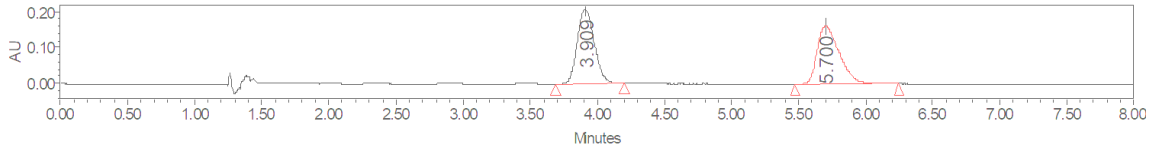


Peak	Retention Time	Area	% Area
1	6.472	181982	0.94
2	11.886	19280485	99.06

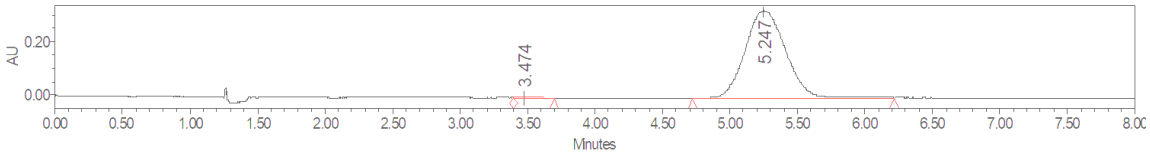
(*S*)-1-(4-Methylsulfinylphenyl)ethan-1-one (2s)



35 °C, 20 h, 5 mo% catalyst loading; 11.0 mg, 60% yield; white solid; R_f = 0.20 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for UPC^2; UPC^2 (Chiralcel OJ, CO_2/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 3.474 min, t_r (major) = 5.247 min, *ee* = 99%. $[\alpha]^{22}_D$ = –89.6 (*c* = 0.2 in acetone). lit: $[\alpha]^{25}_D$ = +90.2 (*c* = 1.0 in acetone) for (*R*), 87% *ee*.[14] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.13 – 8.08 (m, 2H), 7.76 – 7.72 (m, 2H), 2.75 (s, 3H), 2.64 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 197.0, 150.9, 139.1, 129.1, 123.7, 43.8, 26.8 ppm.

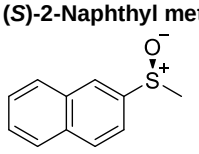


Peak	Retention Time	Area	% Area
1	3.909	1833317	49.68
2	5.700	1856971	50.32

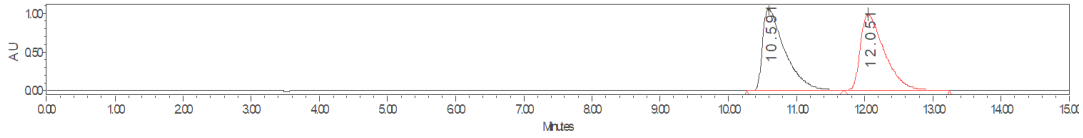


Peak	Retention Time	Area	% Area
1	3.474	11027	0.16
2	5.247	6750797	99.84

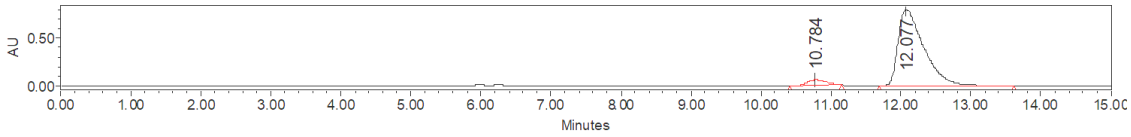
(*S*)-2-Naphthyl methyl sulfoxide (2t)



35 °C, 22 h, 5 mo% catalyst loading; 14.5mg, 76% yield; white solid; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel ODH, hexane/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 10.784 min, t_r (major) = 12.077 min, *ee* = 90%. $[\alpha]^{22}_D$ = –141.6 (*c* = 0.3 in $CHCl_3$). lit: $[\alpha]_D$ = –133.1 (*c* = 2.0 in $CHCl_3$) for (*S*), 95% *ee*.[6] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.20 (m, 1H), 7.97 (d, *J* = 8 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.61 – 7.56 (m, 3H), 2.78 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 142.7, 134.4, 132.9, 129.6, 128.5, 128.0, 127.8, 127.3, 124.0, 119.4, 43.8 (d, *J* = 2 Hz) ppm.

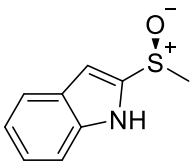


Peak	Retention Time	Area	% Area
1	10.591	23858499	49.99
2	12.051	23870522	50.01

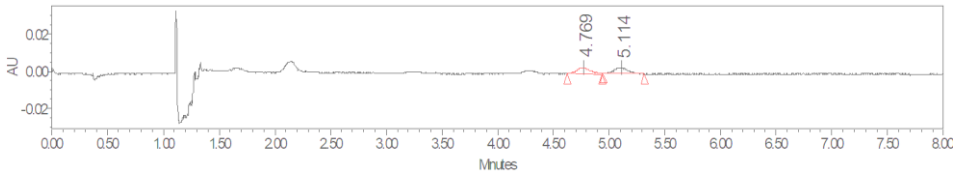


Peak	Retention Time	Area	% Area
1	10.784	1078433	5.05
2	12.077	20264954	94.95

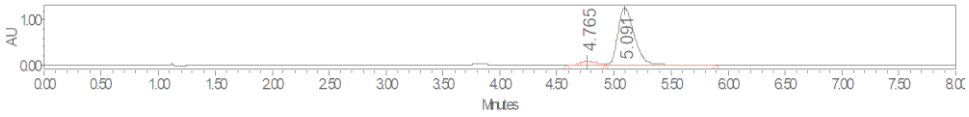
(*S*)-2-Methyl(sulfinyl)indole (2u)



-40 °C, 18 h, 5 mo% catalyst loading; 15.7 mg, 88% yield; white solid; R_f = 0.20 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for UPC^2; UPC^2 (Chiralcel IA, CO_2/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 4.765 min, t_r (major) = 5.091 min, *ee* = 90%. $[\alpha]^{22}_D$ = –46.1 (*c* = 0.3 in acetone). lit: $[\alpha]^{20}_D$ = –39.1 (*c* = 0.4 in acetone) for (*S*), 69% *ee*.[15] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 11.06 (s, 1H), 7.63 – 7.58 (m, 1H), 7.43 (m, 1H), 7.27 – 7.21 (m, 1H), 7.14 – 7.08 (m, 1H), 6.84 (m, 1H), 3.08 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 138.0, 135.6, 126.8, 124.5, 121.6, 120.7, 112.4, 105.0, 41.6 ppm.

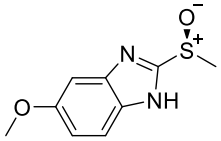


Peak	Retention Time	Area	% Area
1	4.769	28329	49.91
2	5.114	28431	50.09

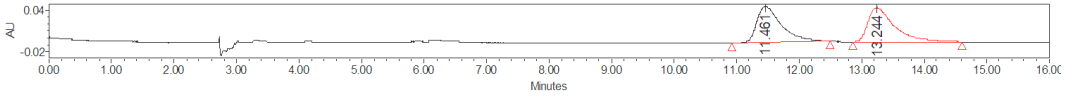


Peak	Retention Time	Area	% Area
1	4.765	707354	5.28
2	5.091	12691516	94.72

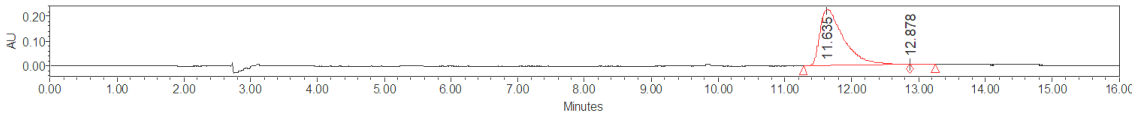
(*S*)-2-Methyl(sulfinyl)-5-methoxybenzimidazole (2v)



35 °C, 48 h, 5 mo% catalyst loading; 6.7 mg, 32% yield; white solid; R_f = 0.20 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for UPC^2; UPC^2 (Chiralcel OXH, CO_2/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 11.635 min, t_r (minor) = 12.878 min, *ee* = 99%. $[\alpha]^{22}_D$ = +50.4 (*c* = 0.3 in acetone). lit: $[\alpha]^{20}_D$ = +45.7 (*c* = 1.0 in acetone) for (*S*), 94% *ee*.[15] ^{1}H NMR (400 MHz, DMSO-d_6) δ = 13.46 (s, 0.9H), 7.60 (s, 1H), 7.12 (s, 1H), 6.95 (d, *J* = 8, 1H), 3.84 (s, 3H), 3.10 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ = 156.8, 154.1, 137.0, 135.6, 113.2, 120.5, 94.6, 55.5, 40.2 ppm.

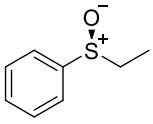


Peak	Retention Time	Area	% Area
1	11.461	1379121	49.28
2	13.244	1419551	50.72

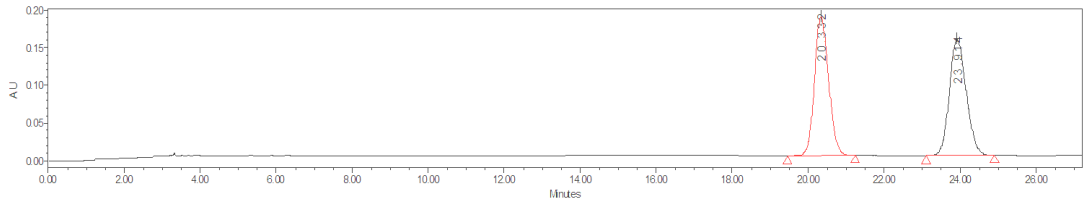


Peak	Retention Time	Area	% Area
1	11.635	5740134	99.55
2	12.878	25782	0.45

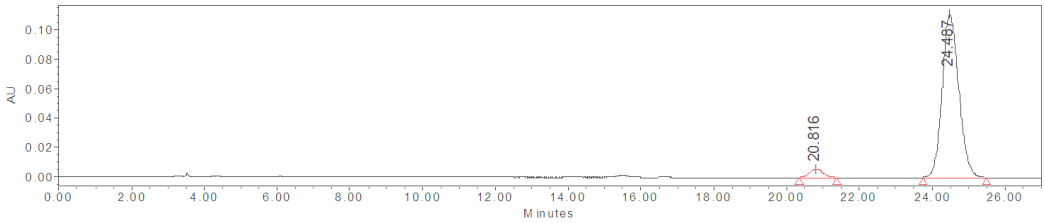
(*S*)-Phenyl ethyl sulfoxide (2w)



25 °C, 5 h, 10 mo% catalyst loading; 12.9 mg, 84% yield; colorless oil; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel IC, hexane/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 20.816 min, t_r (major) = 24.487 min, *ee* = 92%. $[\alpha]^{22}_D$ = –192.1 (*c* = 0.2 in EtOH). lit: $[\alpha]_D$ = –169.1 (*c* = 1.4 in EtOH) for (*S*), 82% *ee*.[6] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.62 – 7.55 (m, 2H), 7.53 – 7.44 (m, 3H), 2.88 (m, 1H), 2.74 (m, 1H), 1.17 (t, *J* = 8 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 144.13, 137.29, 129.68, 124.98, 44.04, 31.05 ppm.

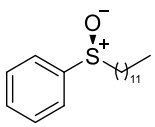


Peak	Retention Time	Area	% Area
1	20.332	4760804	50.00
2	23.914	4760940	50.00

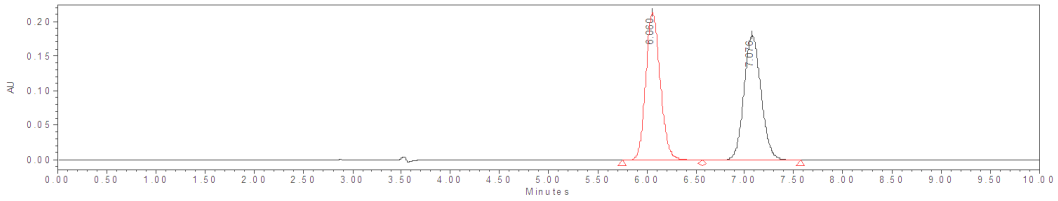


Peak	Retention Time	Area	% Area
1	20.816	144854	3.93
2	24.487	3536676	96.07

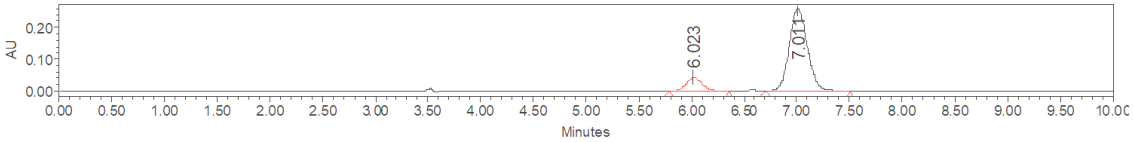
(*S*)-Phenyl dodecyl sulfoxide (2x)



25 °C, 8 h, 10 mo% catalyst loading; 17.6 mg, 60% yield; white solid; R_f = 0.50 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel ODH, hexane/*i*PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 6.023 min, t_r (major) = 7.011 min, *ee* = 76%. $[\alpha]^{22}_D$ = –81.7 (*c* = 0.3 in $CHCl_3$). lit: $[\alpha]^{25}_D$ = +123.0 (*c* = 0.5 in $CHCl_3$) for (*R*), 95% *ee*.[12] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.65 – 7.59 (m, 2H), 7.54 – 7.46 (m, 3H), 2.78 (m, 2H), 1.73 (m, 1H), 1.67 – 1.53 (m, 1H), 1.24 (m, 18H), 0.87 (t, *J* = 8 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 137.0, 128.54, 128.51, 125.3, 53.2, 33.3, 31.8, 29.5, 29.5, 29.4, 29.2, 29.1, 29.0, 28.7, 28.0, 22.6, 14.0 ppm.

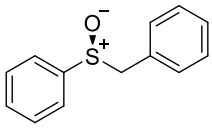


Peak	Retention Time	Area	% Area
1	6.060	2189340	50.01
2	7.076	2188286	49.99

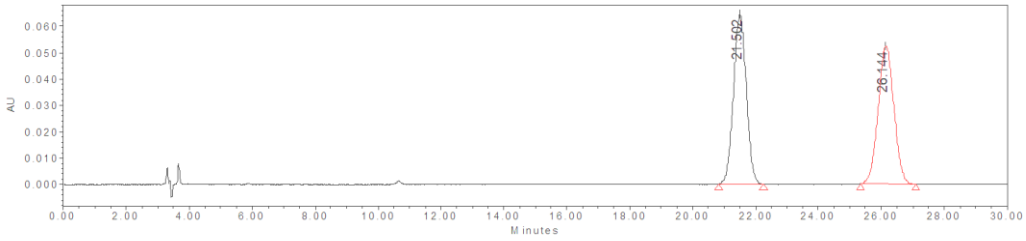


Peak	Retention Time	Area	% Area
1	6.023	417335	12.01
2	7.011	3057917	87.99

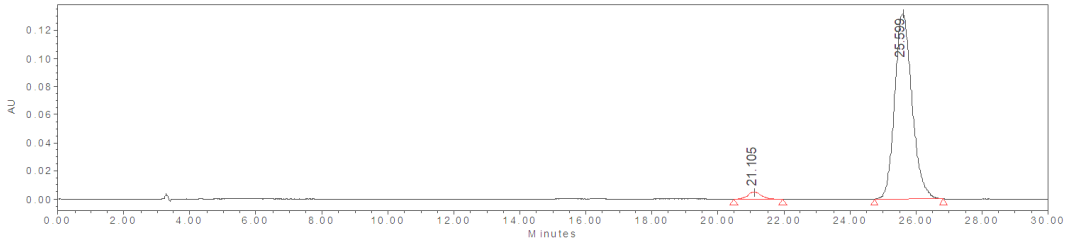
(*S*)-Phenyl benzyl sulfoxide (2y)



0 °C, 24 h, 10 mo% catalyst loading; 16.2 mg, 75% yield; white solid; R_f = 0.40 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel IC, hexane/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 21.105 min, t_r (major) = 25.599 min, *ee* = 94%. $[\alpha]^{22}_D$ = –191.9 (*c* = 0.3 in acetone). lit: $[\alpha]_D$ = –169.8 (*c* = 1.0 in acetone) for (*S*), 79% *ee*.[6] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.51 – 7.36 (m, 5H), 7.33 – 7.22 (m, 3H), 7.06 – 6.94 (m, 2H), 4.11 (d, *J* = 12 Hz, 1H), 4.00 (d, J = 12 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 142.7, 131.1, 130.3, 129.1, 128.8, 128.4, 128.2, 124.4, 63.6 ppm.

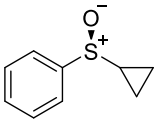


Peak	Retention Time	Area	% Area
1	21.502	1823158	50.04
2	26.144	1820281	49.96

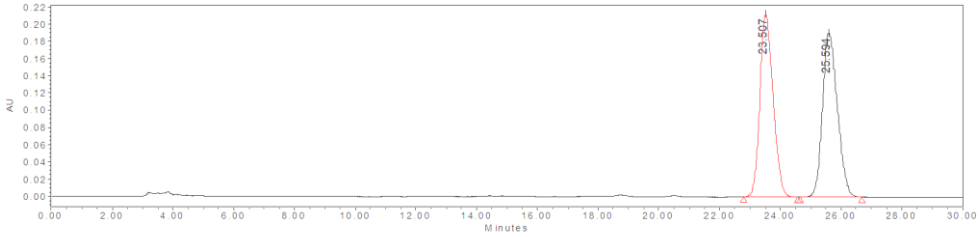


Peak	Retention Time	Area	% Area
1	21.105	149271	3.02
2	25.599	4796417	96.98

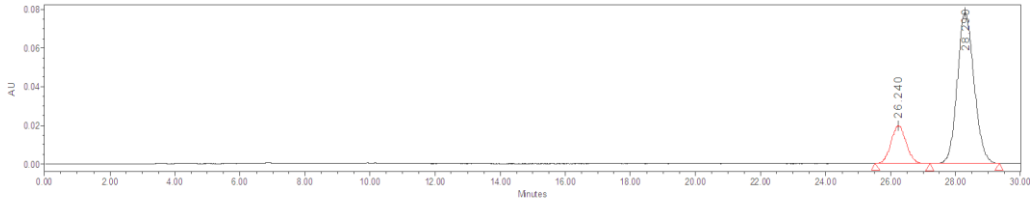
(*S*)-Phenyl cyclopropyl sulfoxide (2z)



25 °C, 8 h, 10 mo% catalyst loading; 10.0 mg, 60% yield; colorless oil; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel IC, hexane/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 26.240 min, t_r (major) = 28.290 min, *ee* = 63%. $[\alpha]^{22}_D$ = –82.1 (*c* = 0.3 in acetone). lit: $[\alpha]^{20}_D$ = –131.6 (*c* = 1.1 in acetone) for (*S*), 92% *ee*.[16] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.70 – 7.63 (m, 2H), 7.55 – 7.46 (m, 3H), 2.26 (m, 1H), 1.24 – 1.19 (m, 1H), 1.08 – 0.99 (m, 1H), 0.98 – 0.89 (m, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 144.8, 130.9, 129.2, 124.0, 33.8, 3.4, 2.9 ppm.

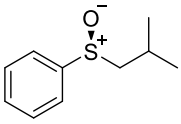


Peak	Retention Time	Area	% Area
1	23.507	6451699	49.93
2	25.594	6471049	50.07

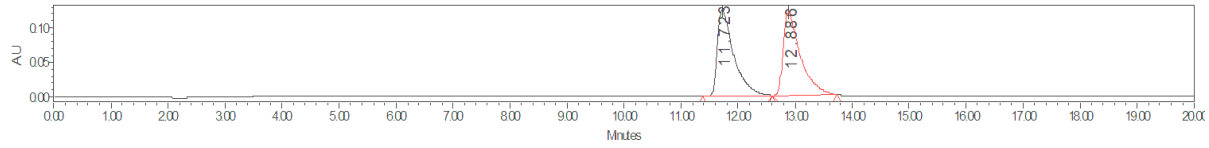


Peak	Retention Time	Area	% Area
1	26.240	639292	18.57
2	28.290	2803745	81.43

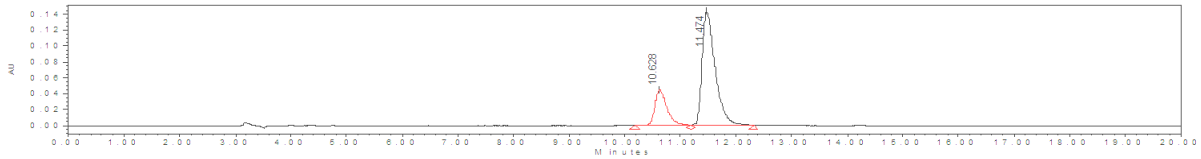
(*S*)-Isobutyl phenyl sulfoxide (2aa)



25 °C, 8 h, 10 mo% catalyst loading; 11.8 mg, 65% yield; colorless oil; R_f = 0.50 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel IB, hexane/*i*PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 10.628 min, t_r (major) = 11.474 min, *ee* = 56%. $[\alpha]^{22}_D$ = –134.7(*c* = 0.2 in $CHCl_3$).lit: $[\alpha]^{20}_D$ = +129.0 (*c* = 1.0 in $CHCl_3$) for (*R*), 48% *ee*.[17] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.65 – 7.58 (m, 2H), 7.53 – 7.44 (m, 3H), 2.81 (q, *J* = 8, 4 Hz, 1H), 2.45 (q, *J* = 8, 4 Hz, 1H), 2.22 (m, 1H), 1.14 (d, *J* = 8 Hz, 3H), 1.05 (d, *J* = 8 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 144.7, 130.9, 129.2, 123.9, 67.6, 24.2, 22.8, 21.7 ppm.

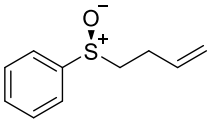


Peak	Retention Time	Area	% Area
1	11.723	2508460	49.63
2	12.886	2546178	50.37

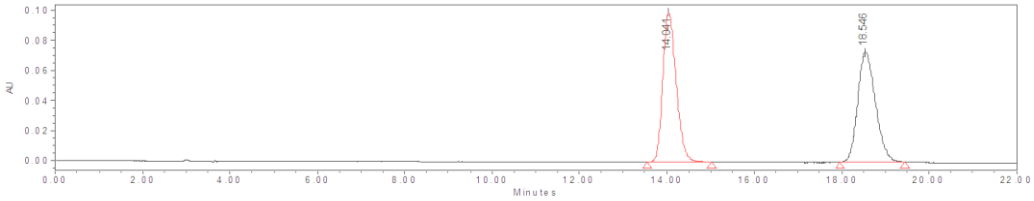


Peak	Retention Time	Area	% Area
1	10.628	665440	22.27
2	11.474	2322028	77.73

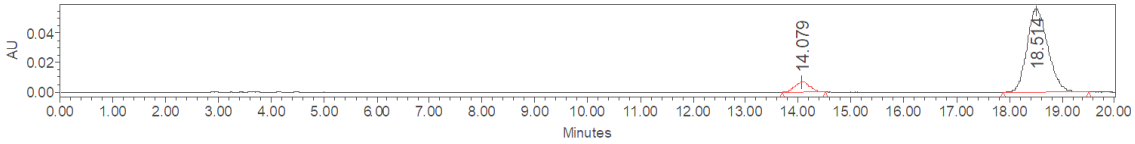
(*S*)-4-(Phenylsulfinyl)but-1-ene (2ab)



25 °C, 5 h, 10 mo% catalyst loading; 12.2 mg, 68% yield; colorless oil; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for HPLC; HPLC (Chiralcel ODH, hexane/*i*PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) =14.079 min, t_r (major) =18.514 min, *ee* = 84%. $[\alpha]^{22}_D$ = –164.1 (*c* = 0.3 in CH_2Cl_2). lit: $[\alpha]^{20}_D$ = –131 (*c* = 1.0 in CH_2Cl_2) for (*S*), 70% *ee*.[18] ^{1}H NMR (400 MHz, Chloroform-*d*) δ =7.59 – 7.53 (m, 2H), 7.49 – 7.38 (m, 3H), 5.72 (m, 1H), 5.11 – 4.92 (m, 2H), 2.85 – 2.75 (m, 2H), 2.53 – 2.40 (m, 1H), 2.31 – 2.20 (m, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 143.7, 134.8, 131.0, 129.2, 124.0, 117.0, 56.1, 26.2 ppm.

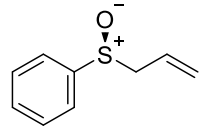


Peak	Retention Time	Area	% Area
1	14.041	2096633	50.13
2	18.546	2085886	49.87

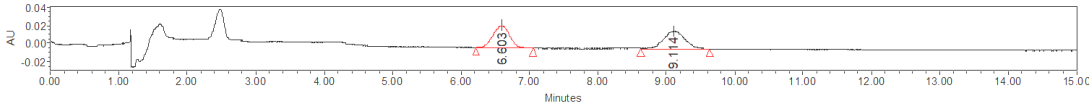


Peak	Retention Time	Area	% Area
1	14.079	135042	8.01
2	18.514	1550197	91.99

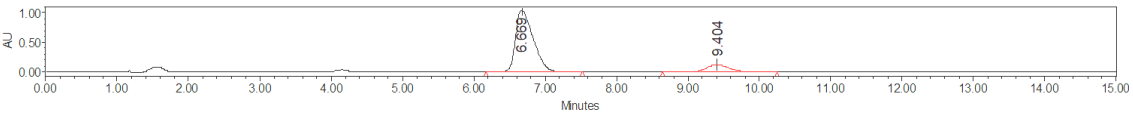
(*S*)-Phenyl allyl sulfoxide (2ac)



25 °C, 20 h, 5 mo% catalyst loading; 13.4 mg, 81% yield; colorless oil; R_f = 0.50 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for UPC^2; UPC^2 (Chiralcel OX, CO_2/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 6.669 min, t_r (minor) = 9.404 min, *ee* = 74%. $[\alpha]^{22}_D$ = –150.6 (*c* = 0.3 in acetone). lit: $[\alpha]_D$ = –143.0 (*c* = 1.0 in acetone) for (*S*), 71% *ee*.[6] ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.70 – 7.45 (m, 5H), 5.65 (m, 1H), 5.33 (d, *J* = 8 Hz, 1H), 5.23 – 5.16 (d, *J* = 8 Hz, 1H), 3.54 (m, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ = 143.0, 131.1, 129.0, 125.2, 124.3, 123.8, 60.9 ppm.

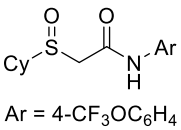


Peak	Retention Time	Area	% Area
1	6.603	431598	49.81
2	9.114	434910	50.19



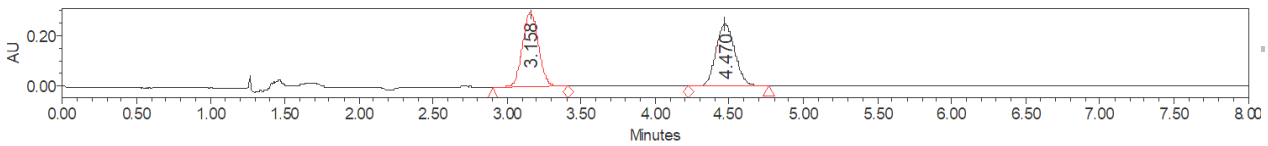
Peak	Retention Time	Area	% Area
1	6.669	18022708	86.80
2	9.404	2740230	13.20

2-(Cyclohexylsulfinyl)-*N*-(4-(trifluoromethoxy)phenyl)acetamide(2ad)[19]



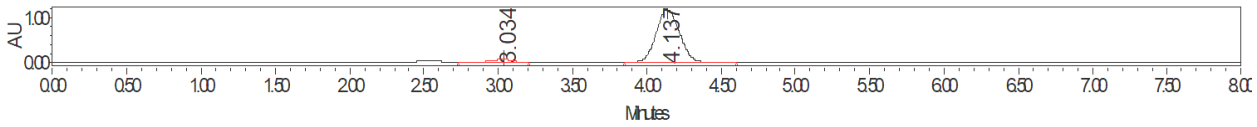
Ar = 4-$CF_3OC_6H_4$

25 °C, 8 h, 5 mo% catalyst loading; 26.5 mg, 76% yield; white solid; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). Dissolved in *i*PrOH for UPC^2; UPC^2 (Chiralcel IC, CO_2/*i*PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 3.034 min, t_r (major) = 4.137 min, *ee* = 90%. $[\alpha]^{22}_D$ = –61.0 (*c* = 0.3 in acetone). ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 9.51 (s, 1H), 7.60 – 7.50 (m, 2H), 7.11 (d, *J* = 8 Hz, 2H), 3.78 (m, 1H), 3.53 (m, 1H), 3.05 – 2.78 (m, 1H), 2.25 – 2.14 (m, 1H), 1.99 – 1.84 (m, 3H), 1.72 (m, 1H), 1.53 (m, 3.5 Hz, 1H), 1.45 – 1.31 (m, 3H),



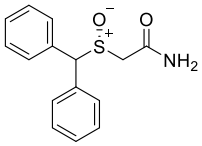
0.98 – 0.70 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ = 162.7, 145.3 (m), 136.3, 121.7 (*J* = 255 Hz), 121.6, 121.1, 59.1, 51.1, 26.3, 25.6, 25.3, 25.0, 24.9 ppm. $^{19}F\{^1H\}$ NMR (376 MHz, Chloroform-d) δ = –58.13 ppm. HRMS (ESI-TOF) calcd for $C_{15}H_{19}F_3NO_3S^+$ ([M]+H$^+$) = 350.1032, Found 350.1029.

Peak	Retention Time	Area	% Area
1	3.158	2210777	50.26
2	4.470	2187863	49.74

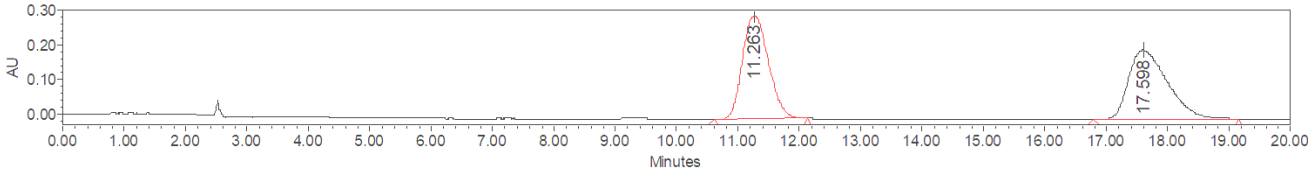


Peak	Retention Time	Area	% Area
1	3.034	678010	4.97
2	4.137	12969882	95.03

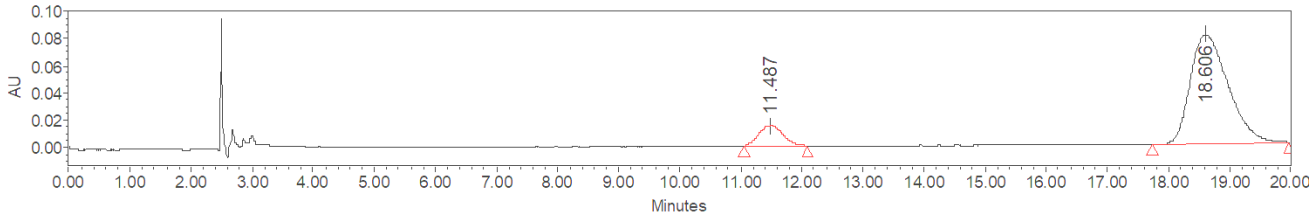
(*R*)-2-(Benzhydrylsulfinyl)acetamide (2ae)



25.6 mg, 94% yield; white solid; R_f = 0.30 (petroleum ether/ethyl acetate = 1/4). Dissolved in EtOH for UPC^2; UPC^2 (Chiralcel AS, CO_2/EtOH = 80/20, flow rate 0.5 mL/min, λ = 230 nm) t_r (minor) = 11.487 min, t_r (major) = 18.606 min, *ee* = 87%. $[\alpha]^{22}_D$ = –53.7 (*c* = 0.5 in $CHCl_3$). lit: $[\alpha]^{22}_D$ = –79.0 (*c* = 1.0 in $CHCl_3$) for (*R*), 99% *ee*.[20] ^1H NMR (400 MHz, Chloroform-*d*) δ = 7.72 – 7.43 (m, 10H), 6.47 (s, 1H), 5.45 (s, 1H), 3.57 (d, *J* = 16 Hz, 1H), 3.43 (d, *J* = 12 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ = 167.2, 134.6, 134.2, 129.4, 129.0 – 128.5 (m), 71.4, 52.8 ppm.

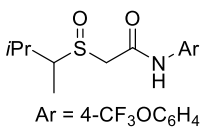


Peak	Retention Time	Area	% Area
1	11.263	8850073	50.01
2	17.598	8848240	49.99



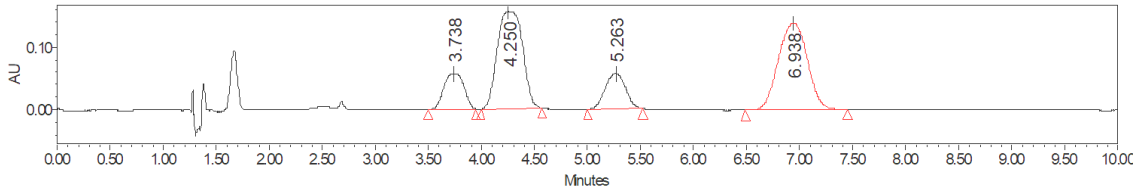
Peak	Retention Time	Area	% Area
1	11.487	246776	6.65
2	18.606	3460174	93.35

2-((1,2-Dimethylpropanyl)sulfinyl)-*N*-(4-(trifluoromethoxy)phenyl)acetamide (2af)[19]

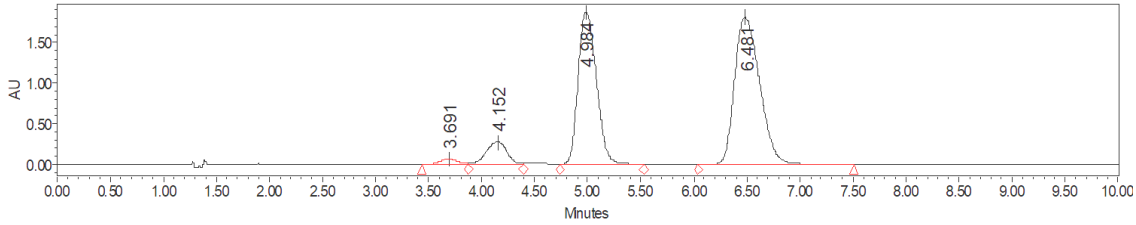


25 °C, 8 h, 5 mo% catalyst loading; 32.0 mg, 95% yield; white solid; R_f = 0.30 (petroleum ether/ethyl acetate = 1/1). The d.r. was determined by NMR analysis while *ee* were determined by UPC^2 analysis. Dissolved in *i*PrOH for UPC^2; UPC^2 (Chiralcel IC, CO_2/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) major isomer: t_r(minor) = 4.152 min, t_r(major) = 6.481 min, *ee* = 77%; minor isomer: t_r(minor) = 3.691min, t_r(major) = 4.984 min. *ee* = 83%. $[\alpha]^{22}_D$ = –130.6 (*c* = 0.3 in acetone). ^1H NMR (400 MHz, Chloroform-*d*) δ = 9.46 (s, 1.7H), 7.57 – 7.52

(m, 3.4H), 7.15 – 7.08 (m, 3.4H), 3.83 (m, 0.7H), 3.70 (m, 1H), 3.59 (m, 1H), 3.44 (m, 0.7H), 2.97 (m, 0.7H), 2.82 (m, 1H), 2.46 (m, 0.7H), 2.07 (m, 1H), 1.33 (d, *J* = 8 Hz, 3H), 1.15 – 1.05 (m, 7.3H), 1.02 (d, *J* = 8 Hz, 5H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ = 162.7, 145.4, 136.2 (d, *J* = 3 Hz), 121.7 (*J* = 255 Hz), 121.6, 121.2 (*J* = 9 Hz), 61.5, 61.3, 53.0, 50.7, 29.6, 26.1, 20.5, 20.4, 18.2, 16.1, 7.8, 7.3 ppm. $^{19}F\{^{1}H\}$ NMR (376 MHz, Chloroform-d) δ = –58.13 ppm. HRMS (ESI-TOF) calcd for $C_{14}H_{19}F_3NO_3S^+$ ([M]+H$^+$) = 338.1032, Found 338.1030.



Peak	Retention Time	Area	% Area
1	3.738	757633	11.14
2	4.250	2606232	38.34
3	5.263	765327	11.26
4	6.938	2669028	39.26



Peak	Retention Time	Area	% Area
1	3.691	755781	1.33
2	4.152	3751271	6.61
3	4.984	22440912	39.53
4	6.481	29823115	52.53

11. A comparision table of Fe-different ligands-H_2O_2-based asymmetric sulfoxidation

entry	catalyst	catalyst loading	substrate scope	result	drug
1[21]	diiron-(—)4,5-pinene-2,2'-bipyridine-CH_3CN	0.17 mol%	aryl alkyl (7 examples) sulfides	45-90% yield 11-40% *ee*	no
2[22]	Fe-Schiff base-DCM	20 mol%	aryl alkyl(9 examples) and dialkyl(1 example) sulfides	36-78% yield 66-96% *ee*	esomeprazole and related proton pump inhibitors[23]
3[24]	Fe-salan-H_2O	1 mol%	aryl alkyl(8 examples) and dialkyl(4 examples) sulfides	72-90% yield 81-96% *ee*	no
4[25]	Fe-porphyrin-MeOH/ H_2O	1 mol%	aryl alkyl (6 examples) sulfides	83-98% yield 34-87% *ee*	no
5[26]	Fe-bis(oxazolinyl)bipyridine-THF	8 mol%	aryl alkyl (10 examples) sulfides	21-61% yield 48-97% *ee*	no
6 (This work)	Fe-*N,N'*-dioxide-THF	2.5 or 5 mol%	aryl alkyl(29 examples) and dialkyl(1 example) sulfides	60-98% yield 56-99% *ee*	(*R*)-modafinil

From the table, we found that the main advantages of current strategy were wide substrate scope and practical gram-scale synthesis of drug molecular-(*R*)-modafinil.

12. References

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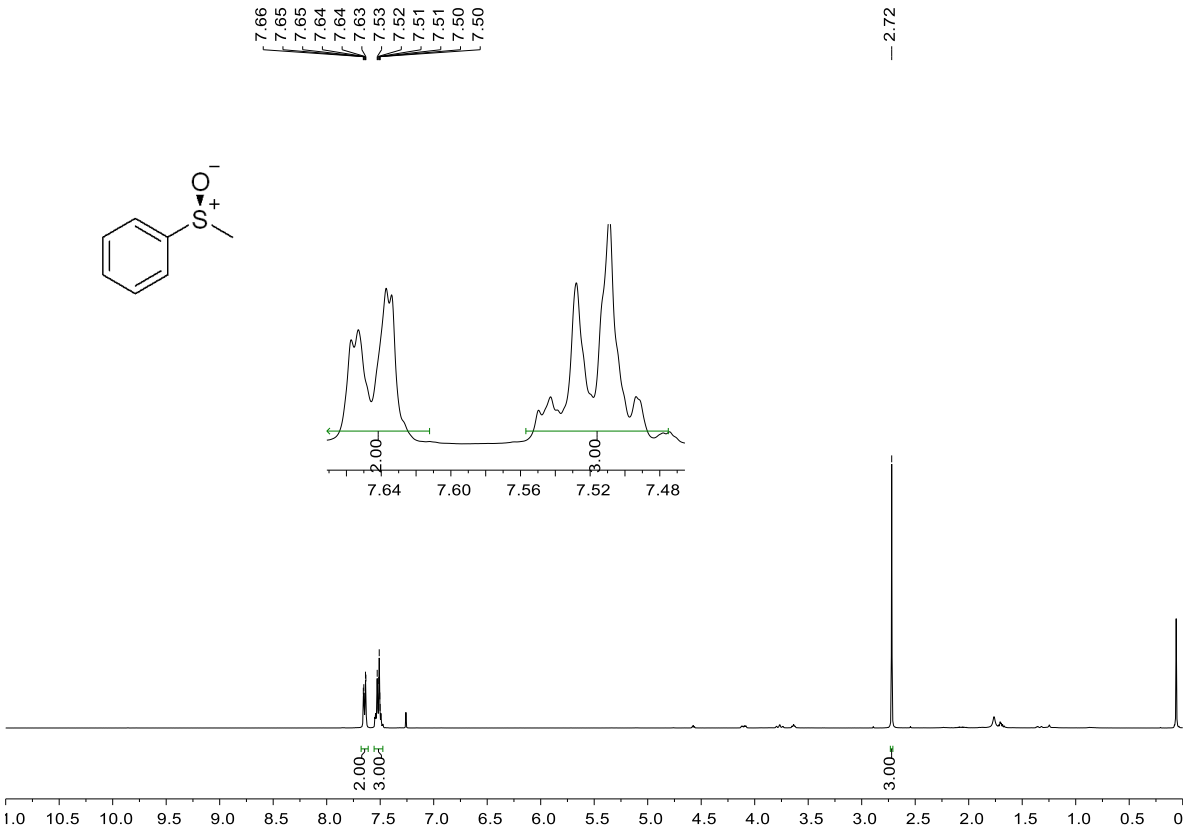
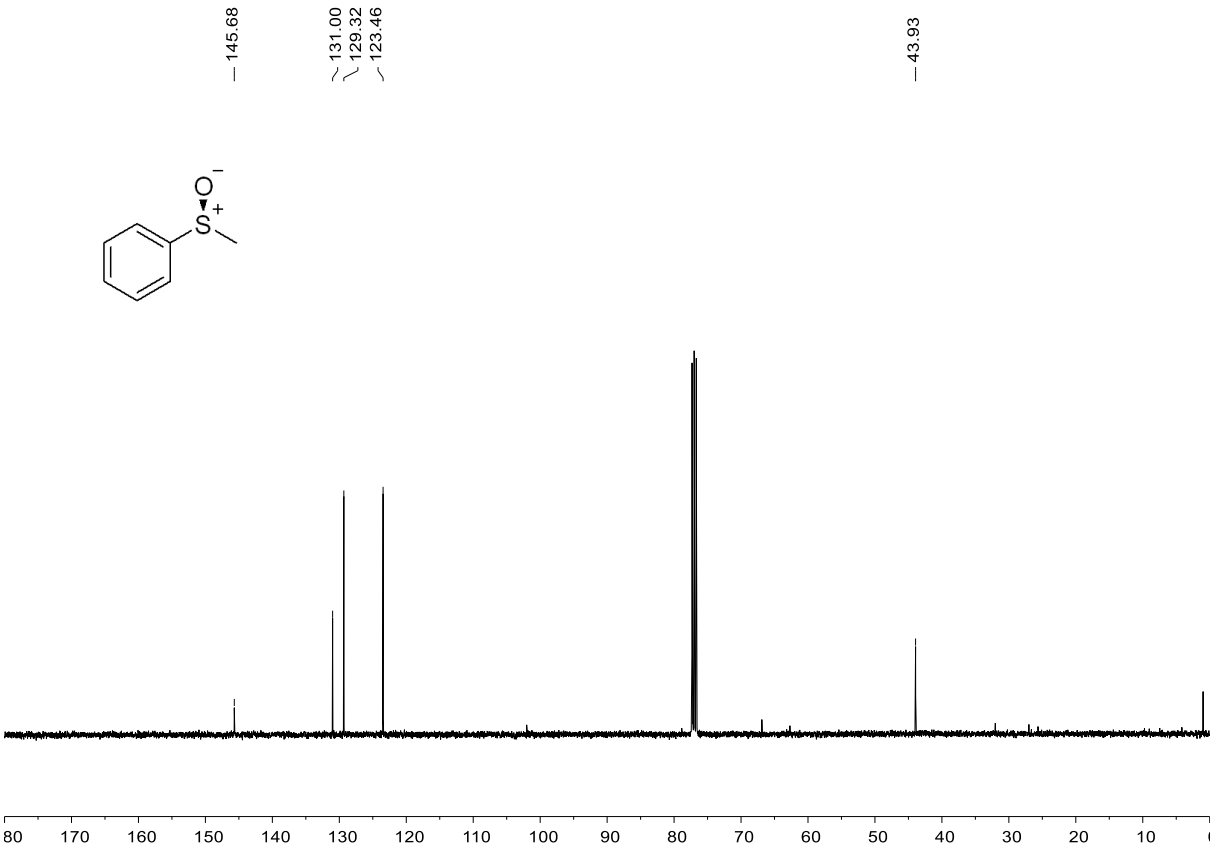
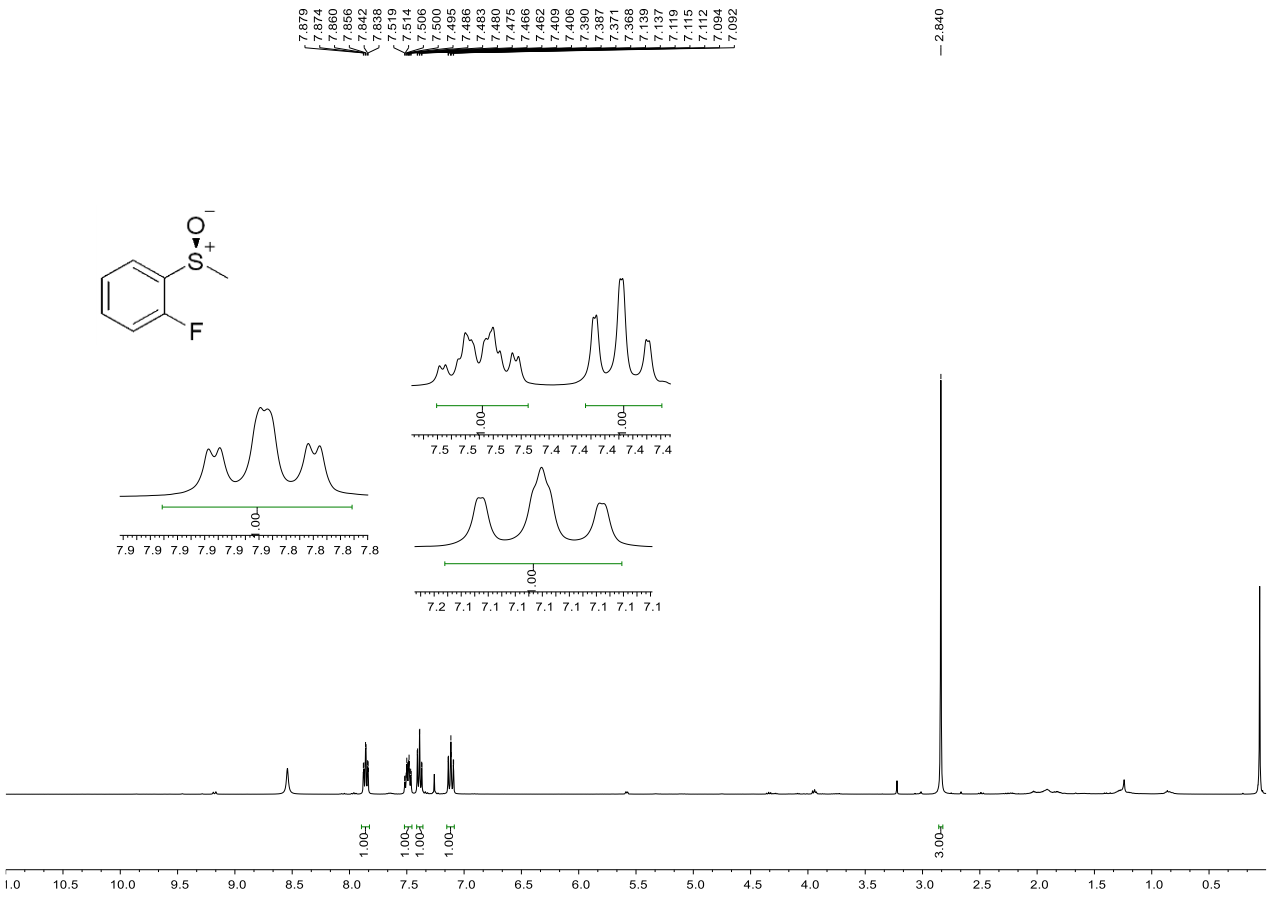
13. Copies of NMR spectra for products

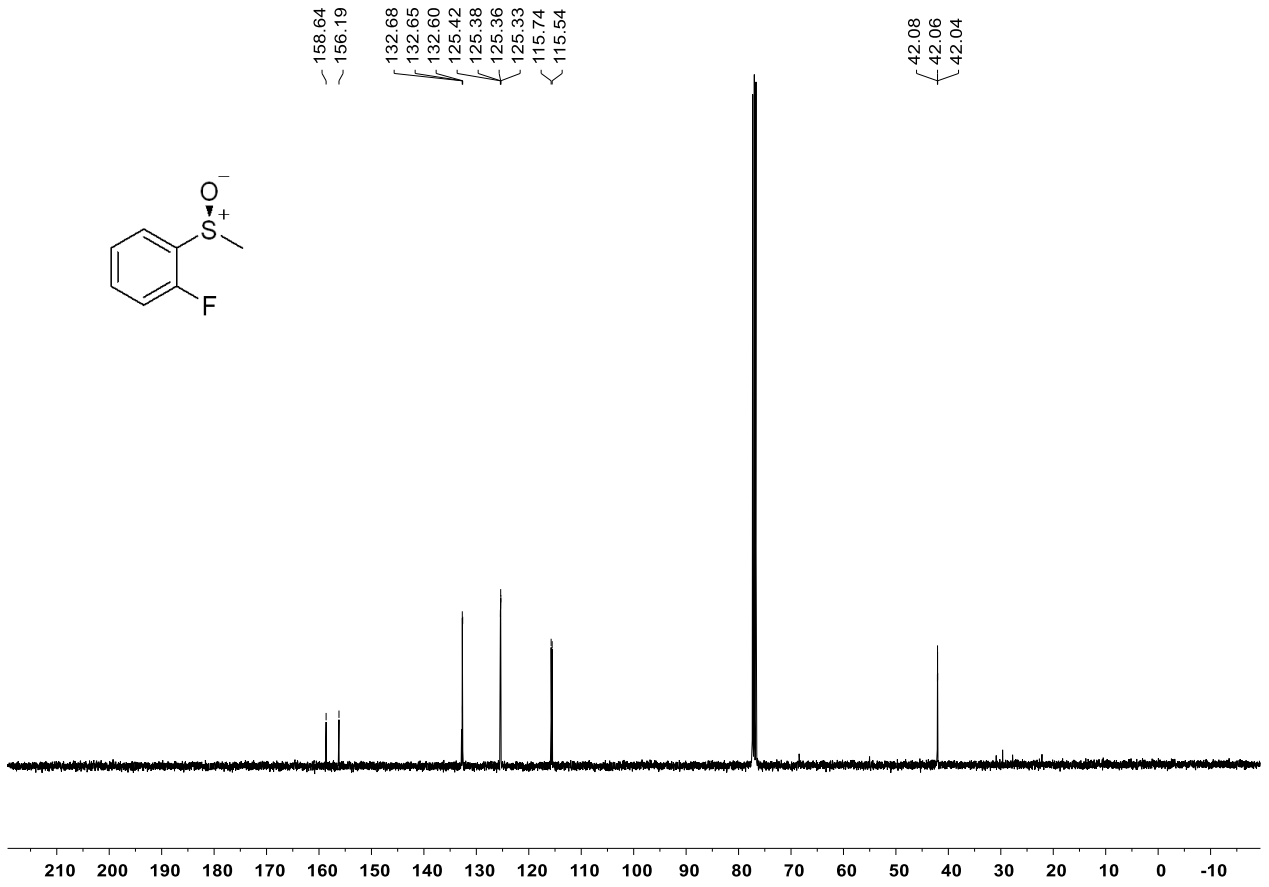
(*S*)-Phenyl methyl sulfoxide (2a)

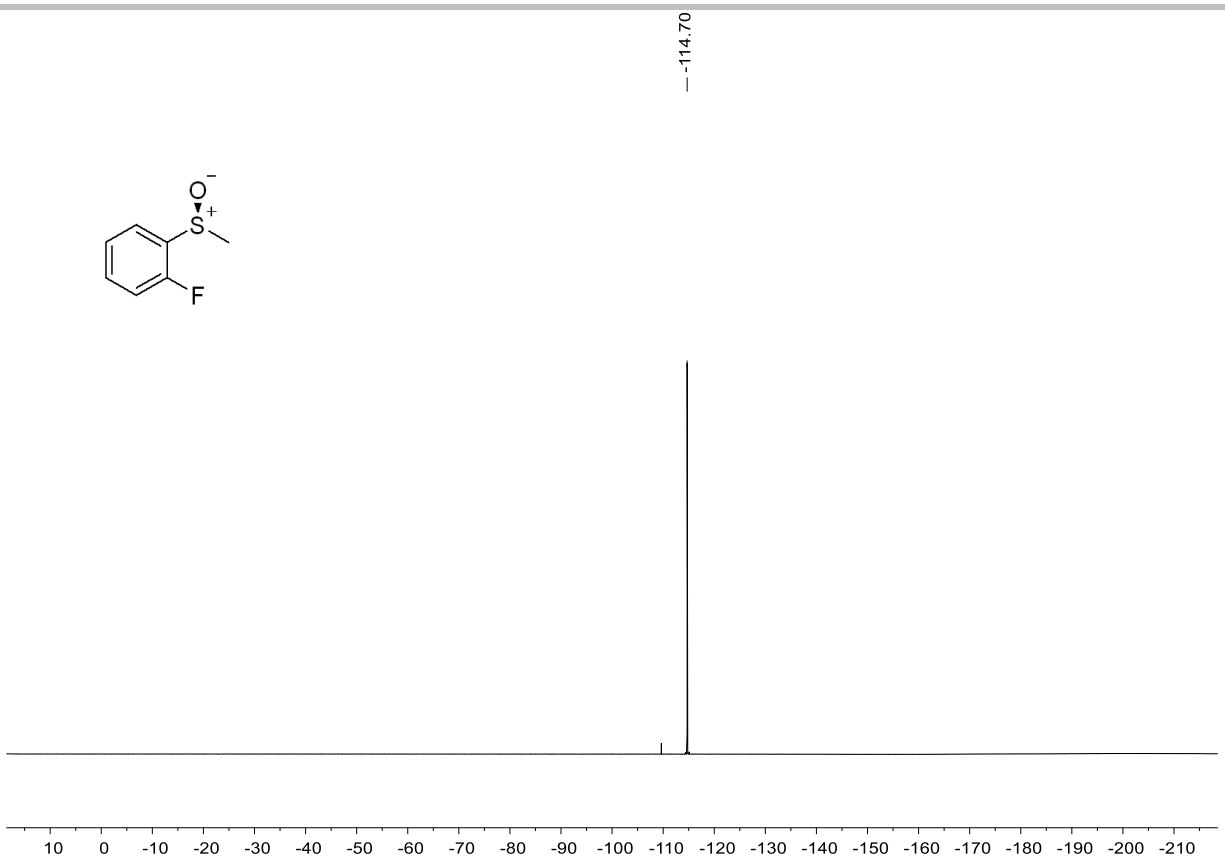




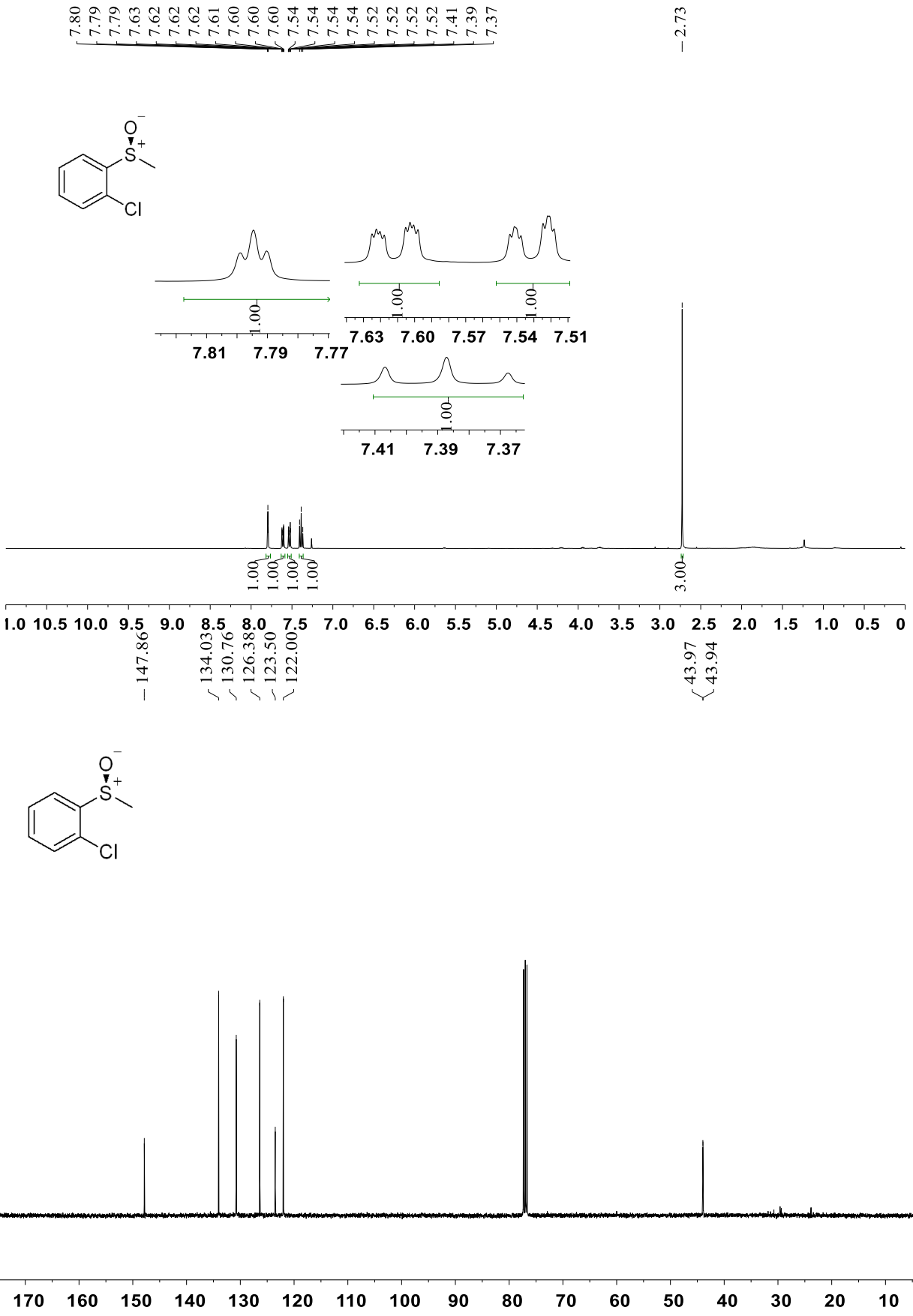
(*S*)-2-Fluorophenyl methyl sulfoxide (2b)



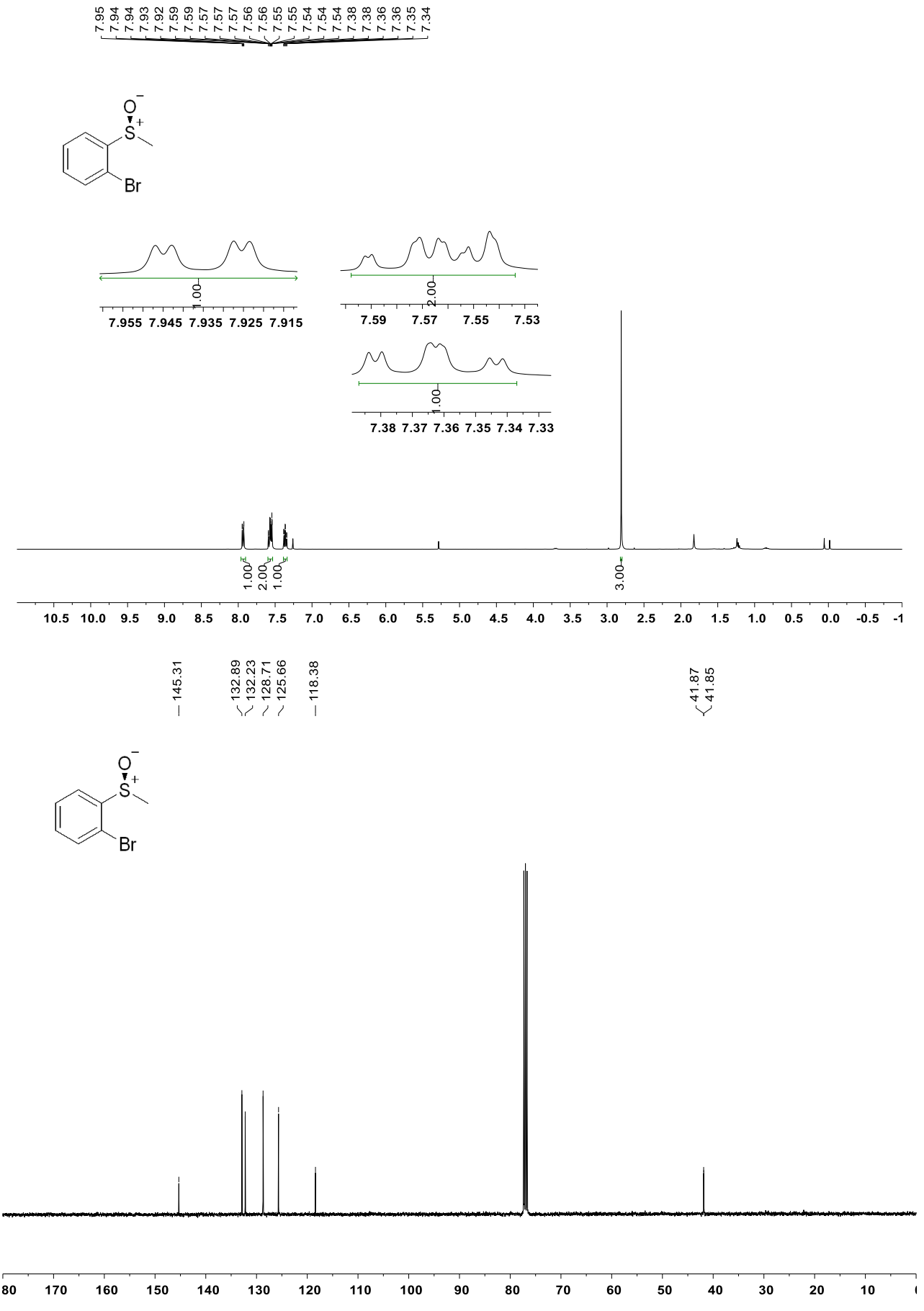



-114.70
O
S
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

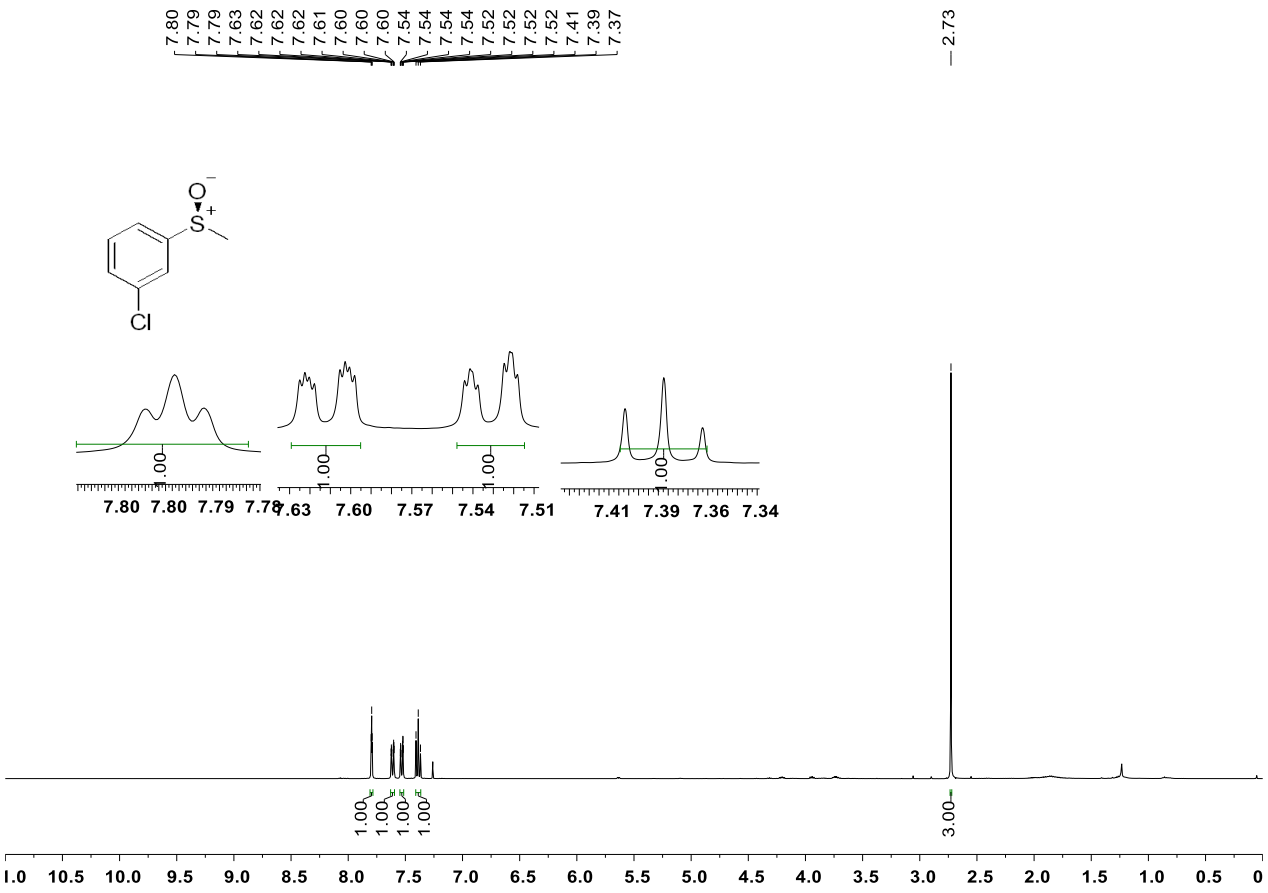
(*S*)-2-Chlorophenyl methyl sulfoxide (2c)

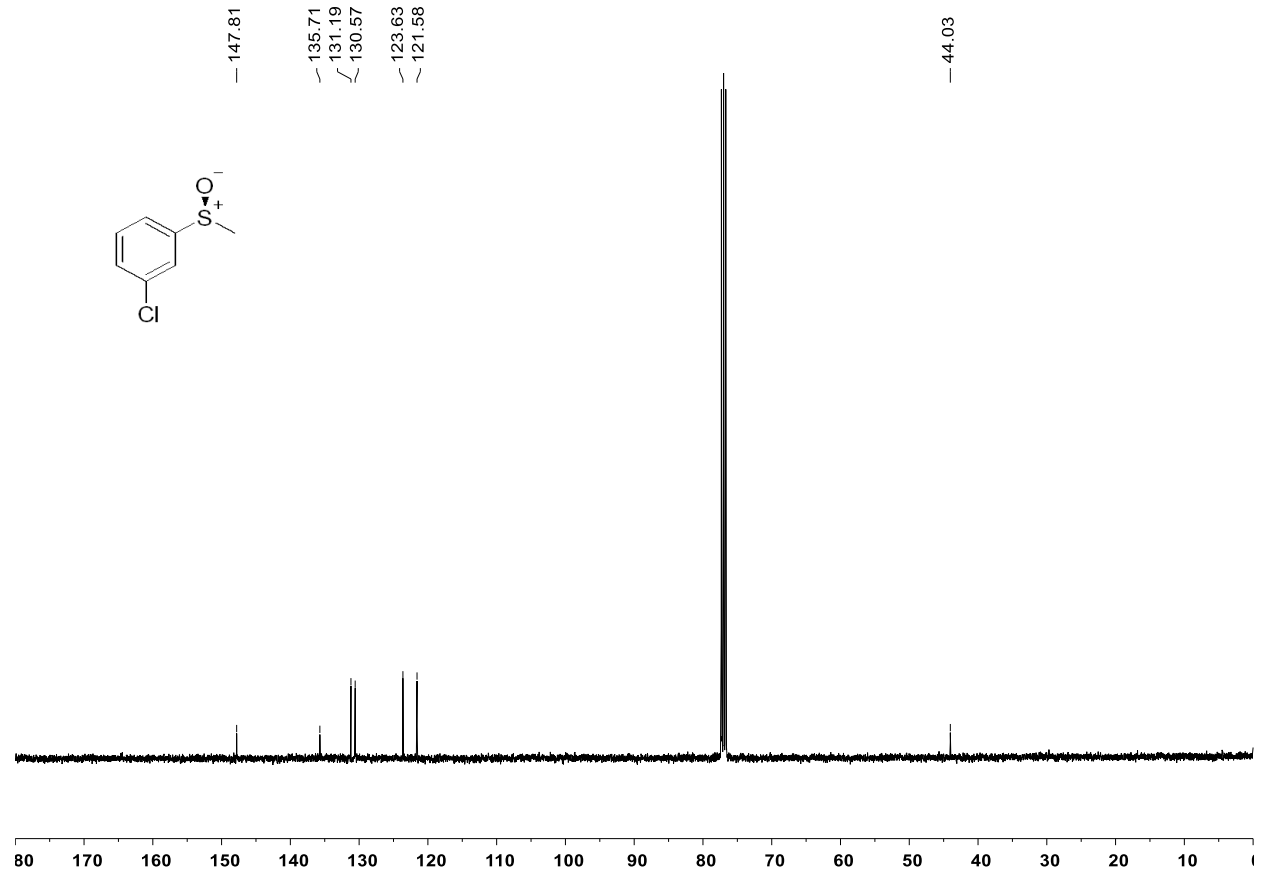


(*S*)-2-Bromophenyl methyl sulfoxide (2d)

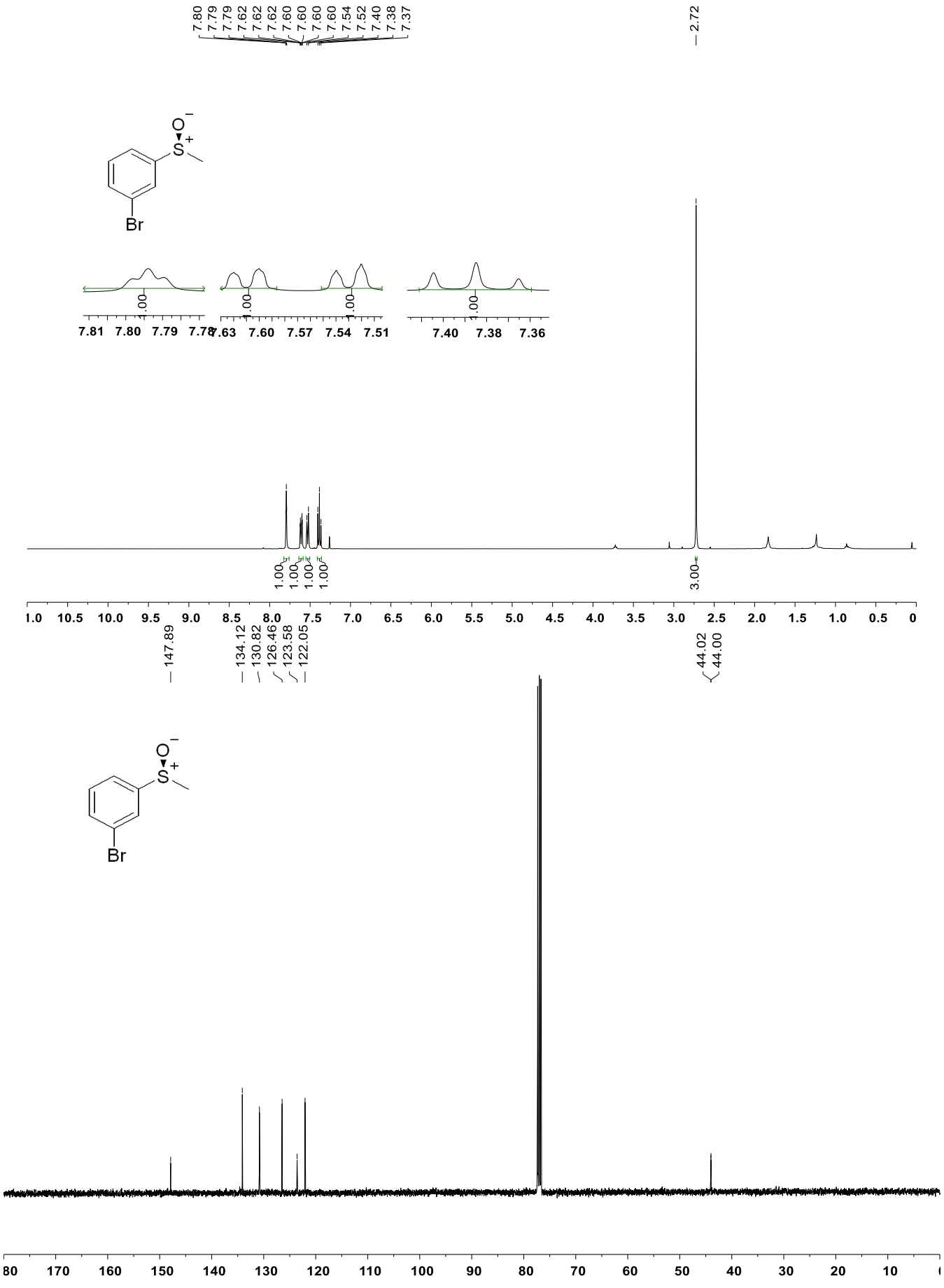


(*S*)-3-Chlorophenyl methyl sulfoxide (2e)

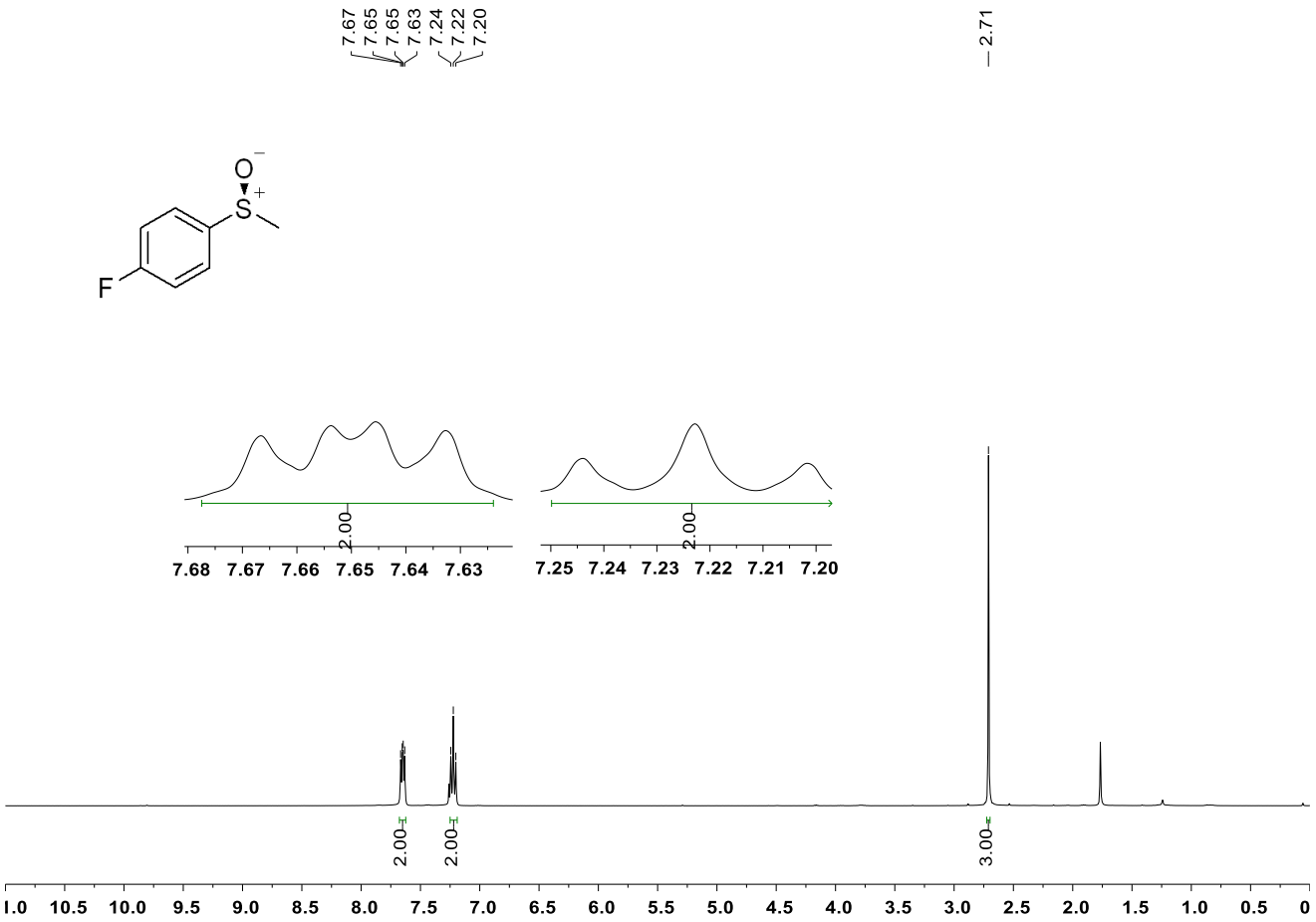


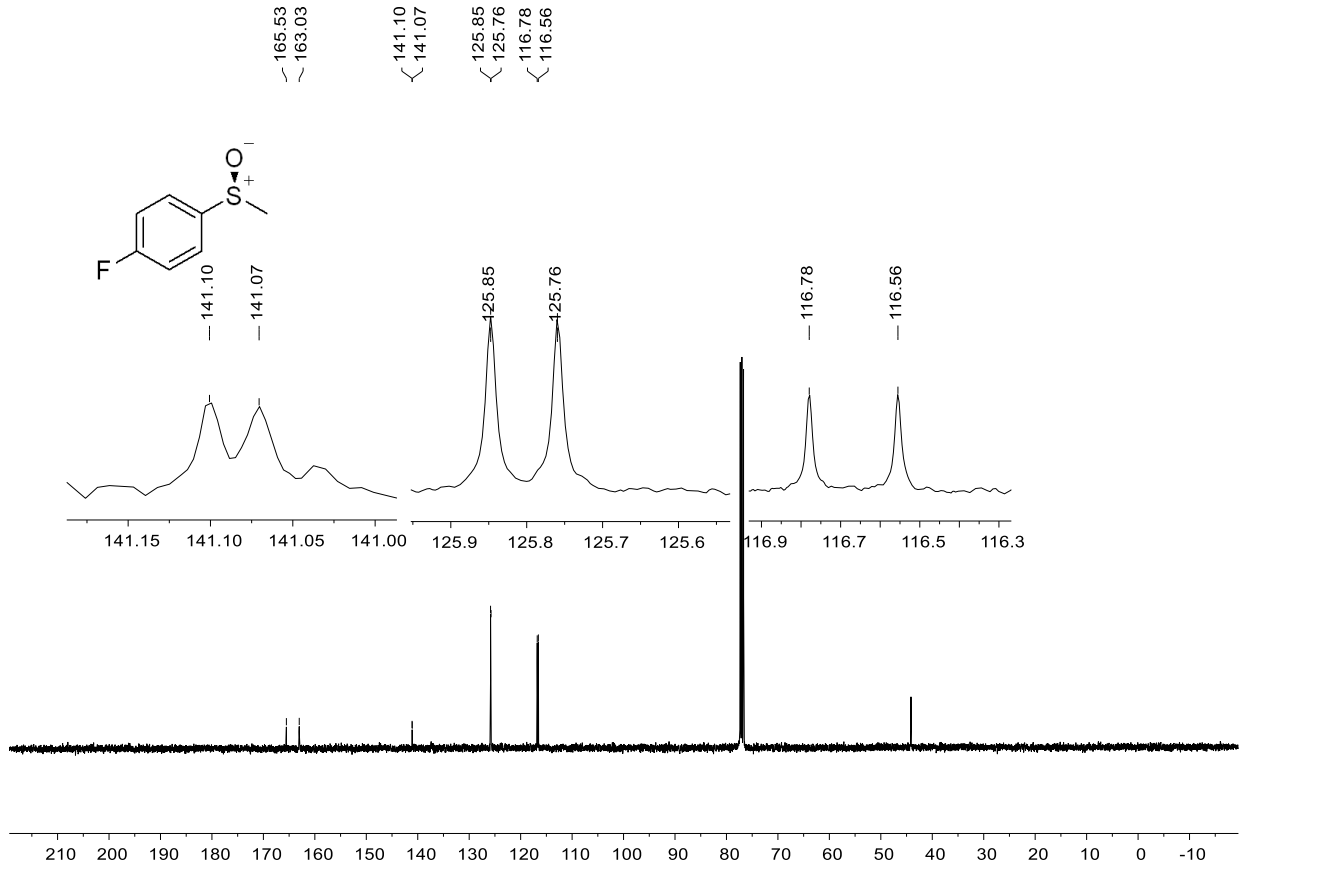


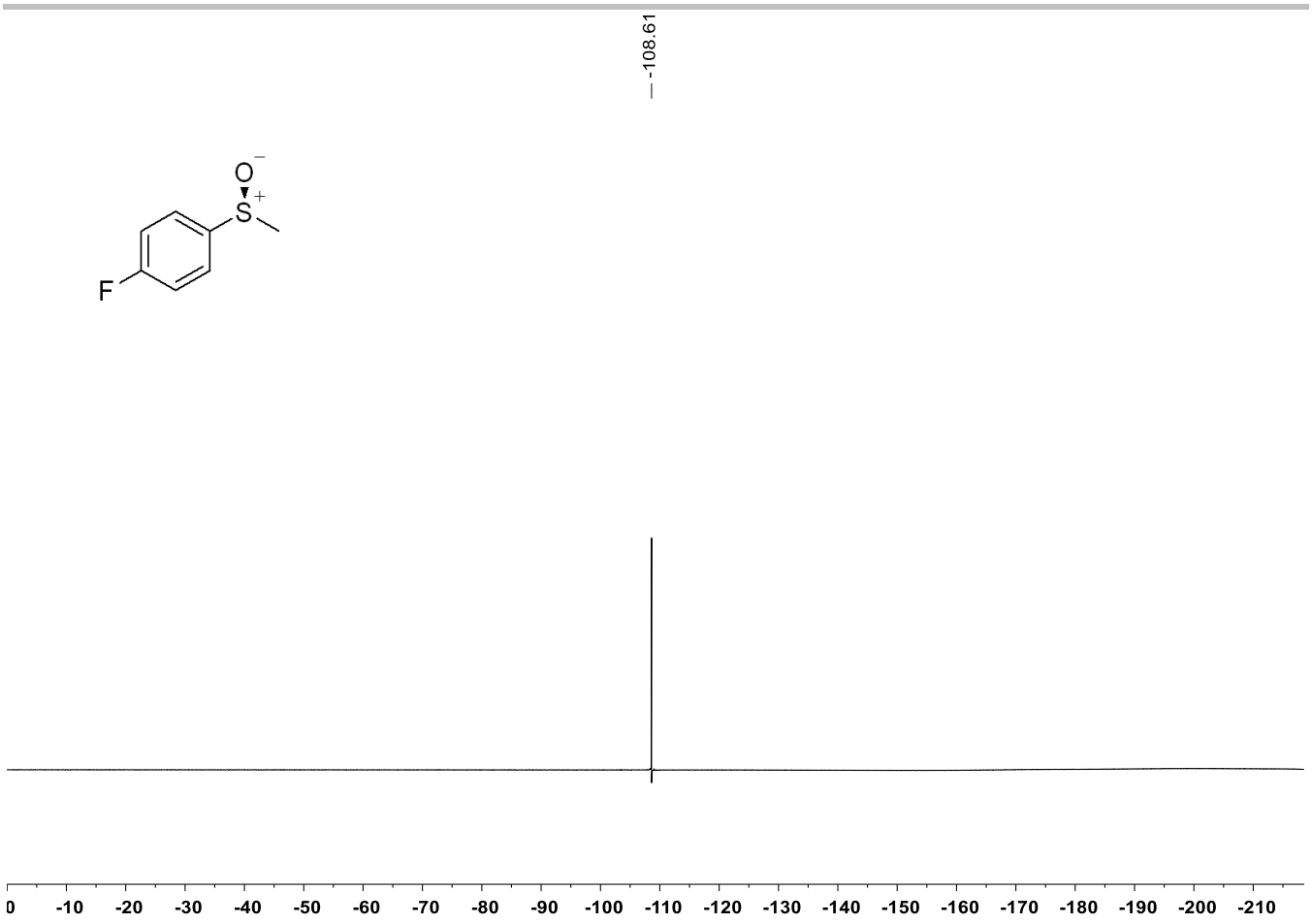
(*S*)-3-Bromophenyl methyl sulfoxide (2f)



(*S*)-4-Fluorophenyl methyl sulfoxide (2g)






-108.61
O
S
F
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-10
-20
-30
-40
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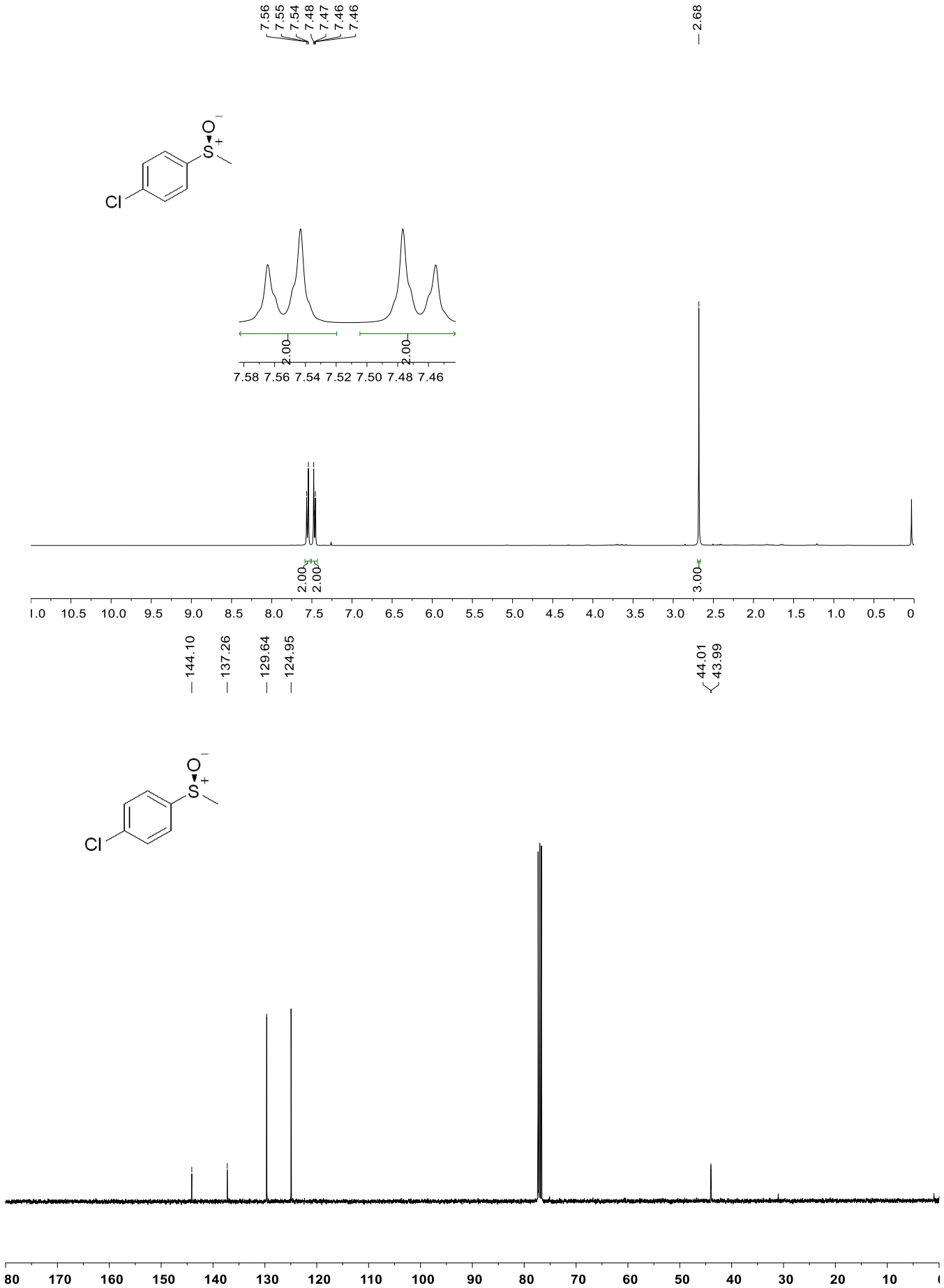
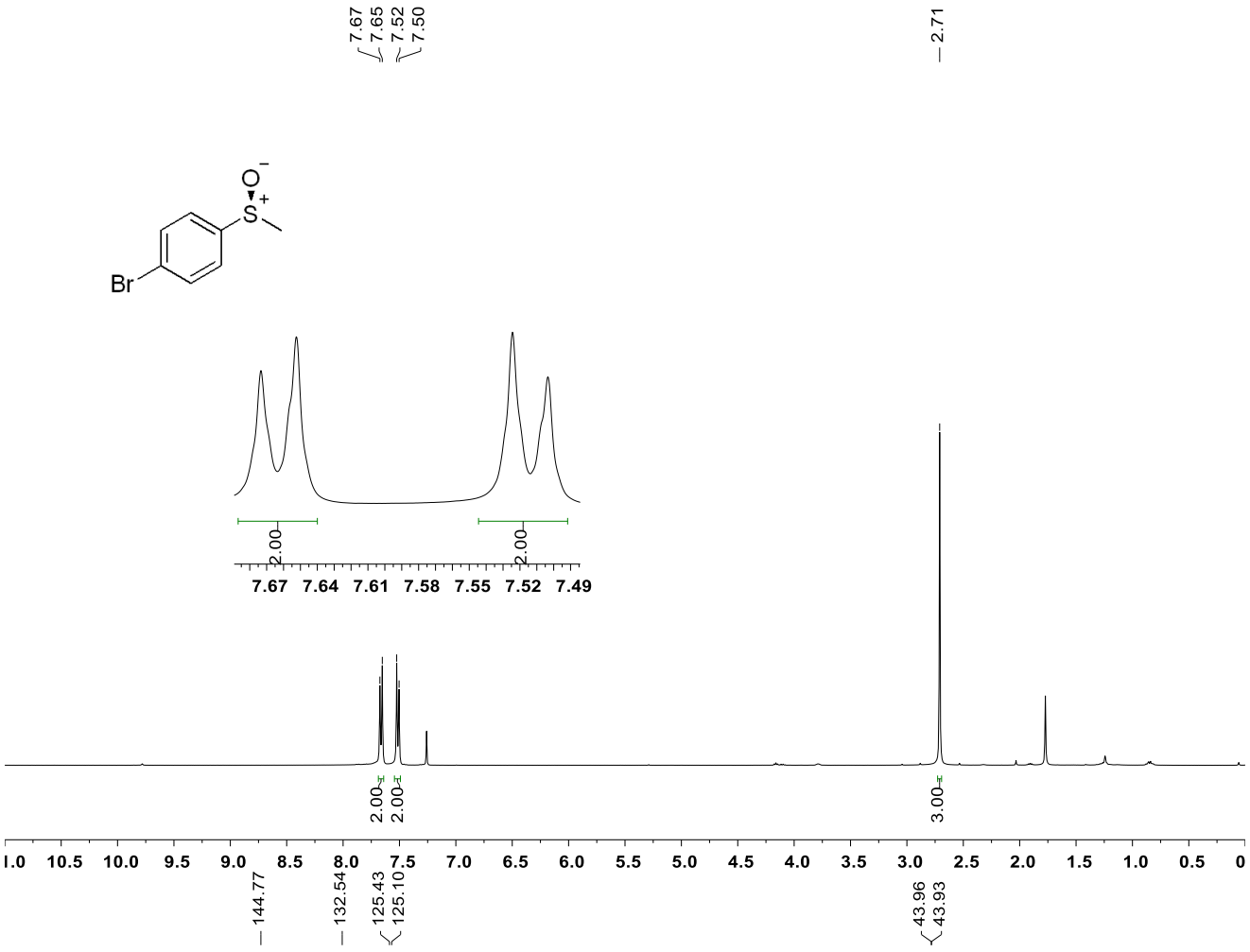
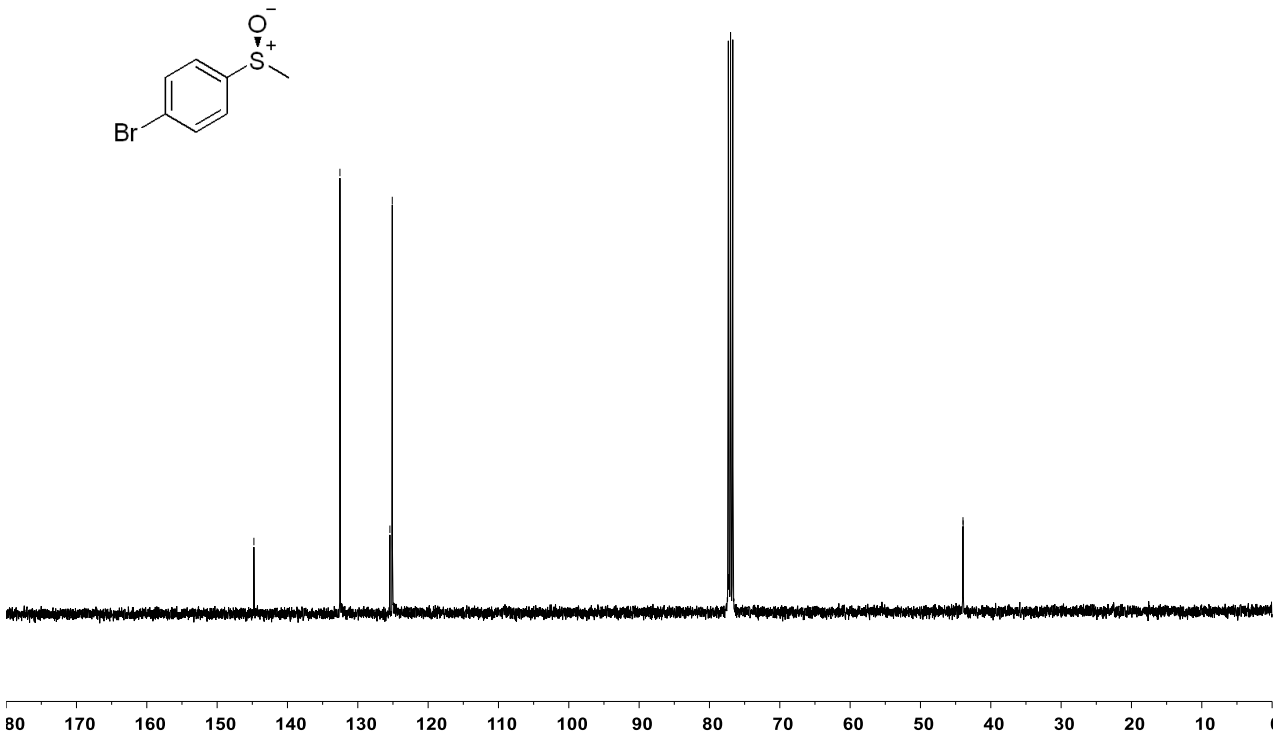
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

(*S*)-4-Chlorophenyl methyl sulfoxide (2h)

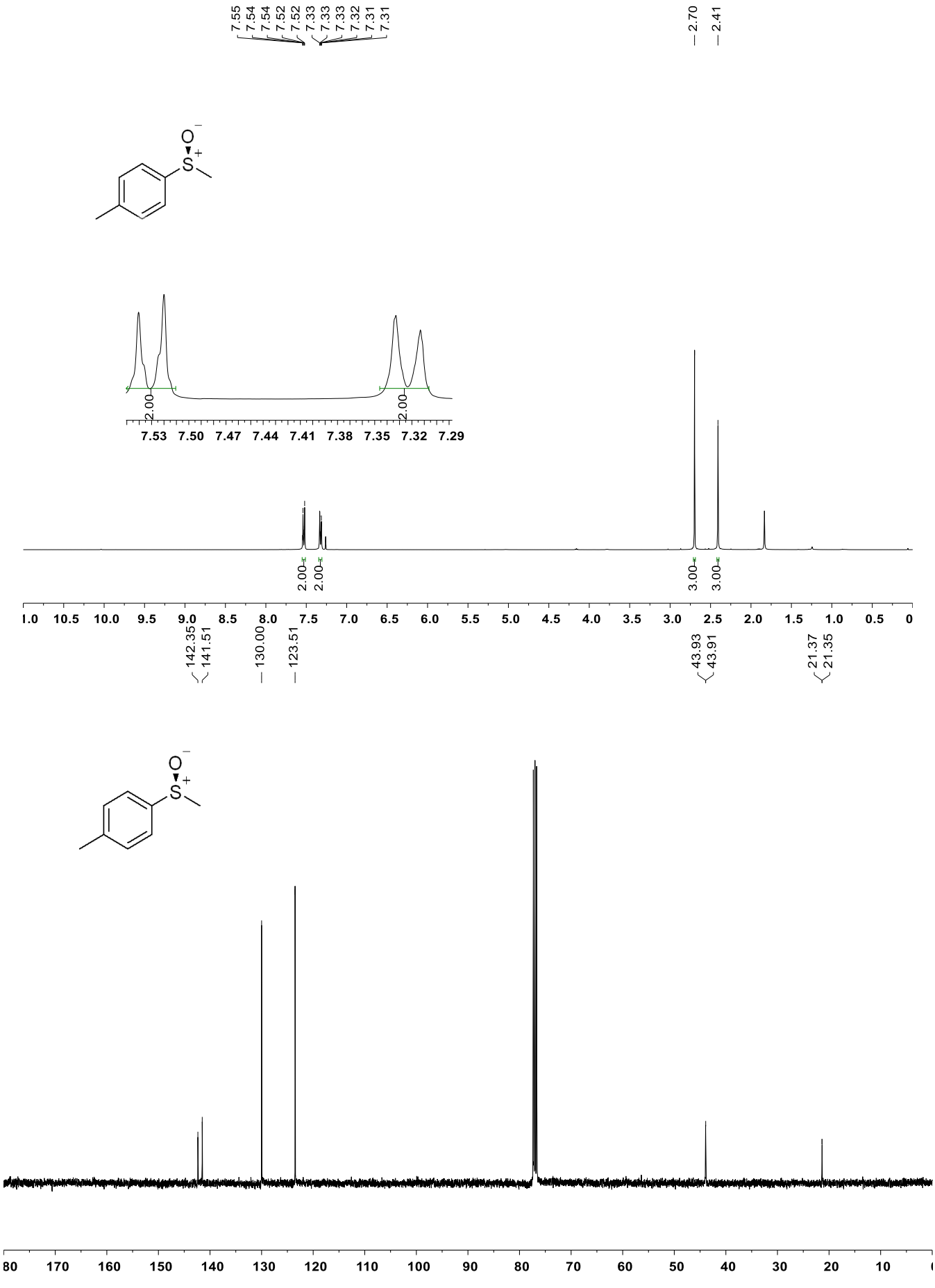


(*S*)-4-Bromophenyl methyl sulfoxide (2i)

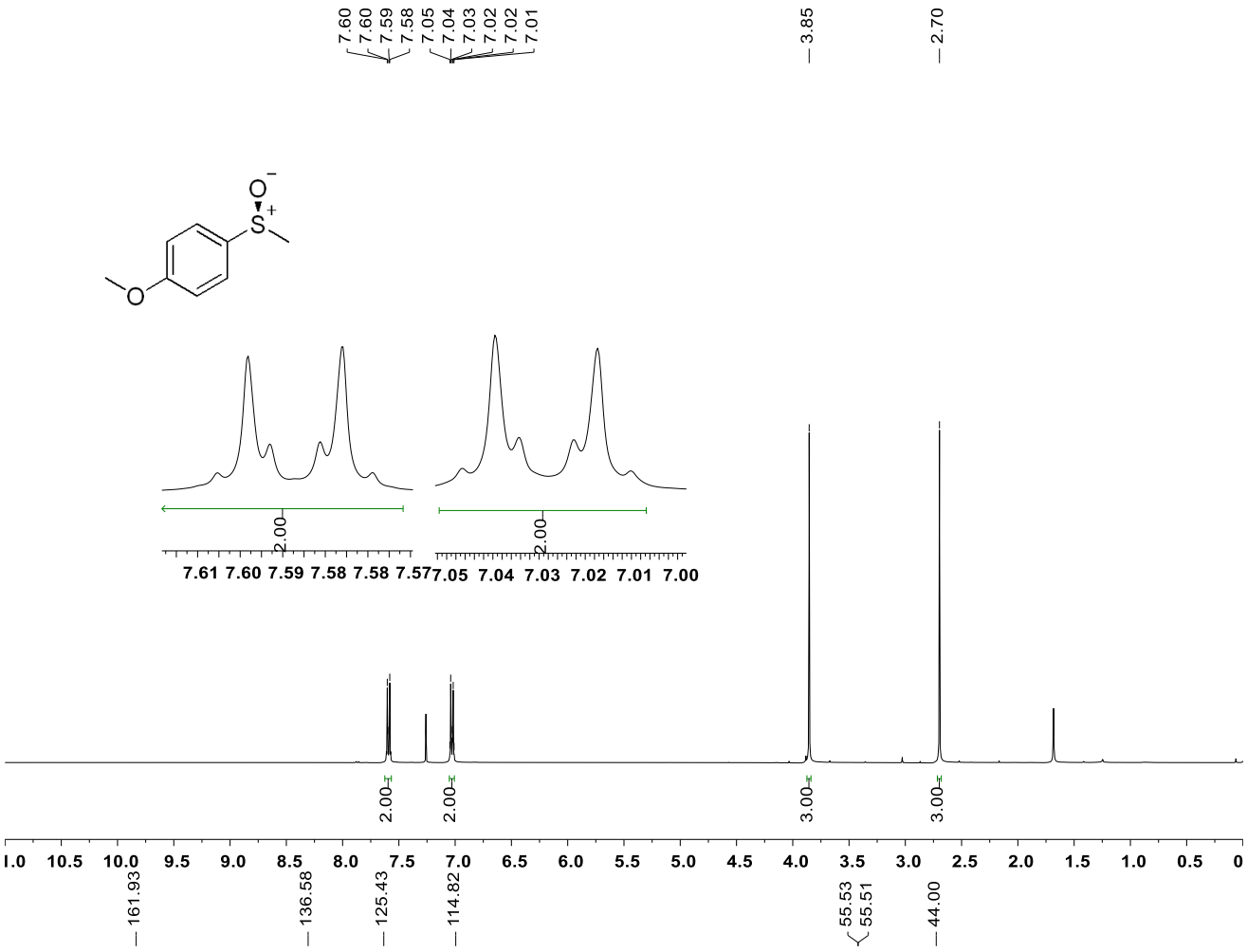


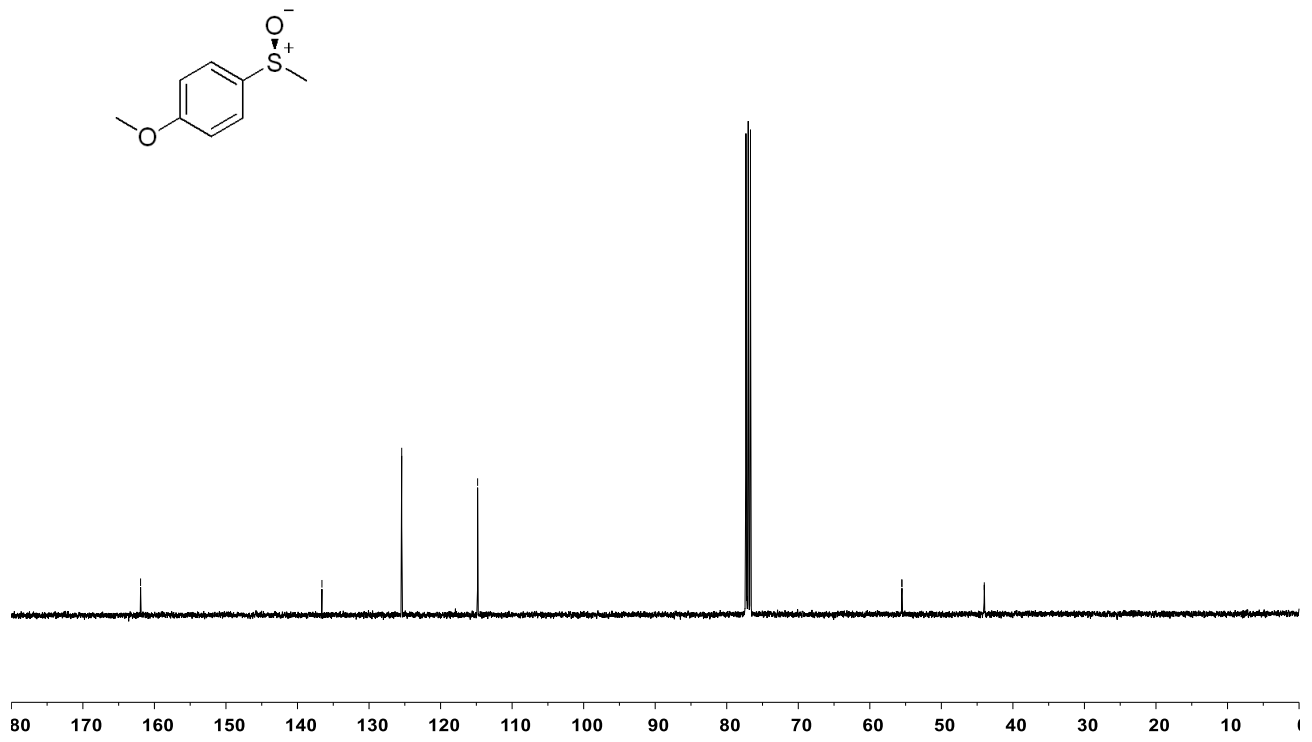


(*S*)-4-Tolyl methyl sulfoxide (2j)

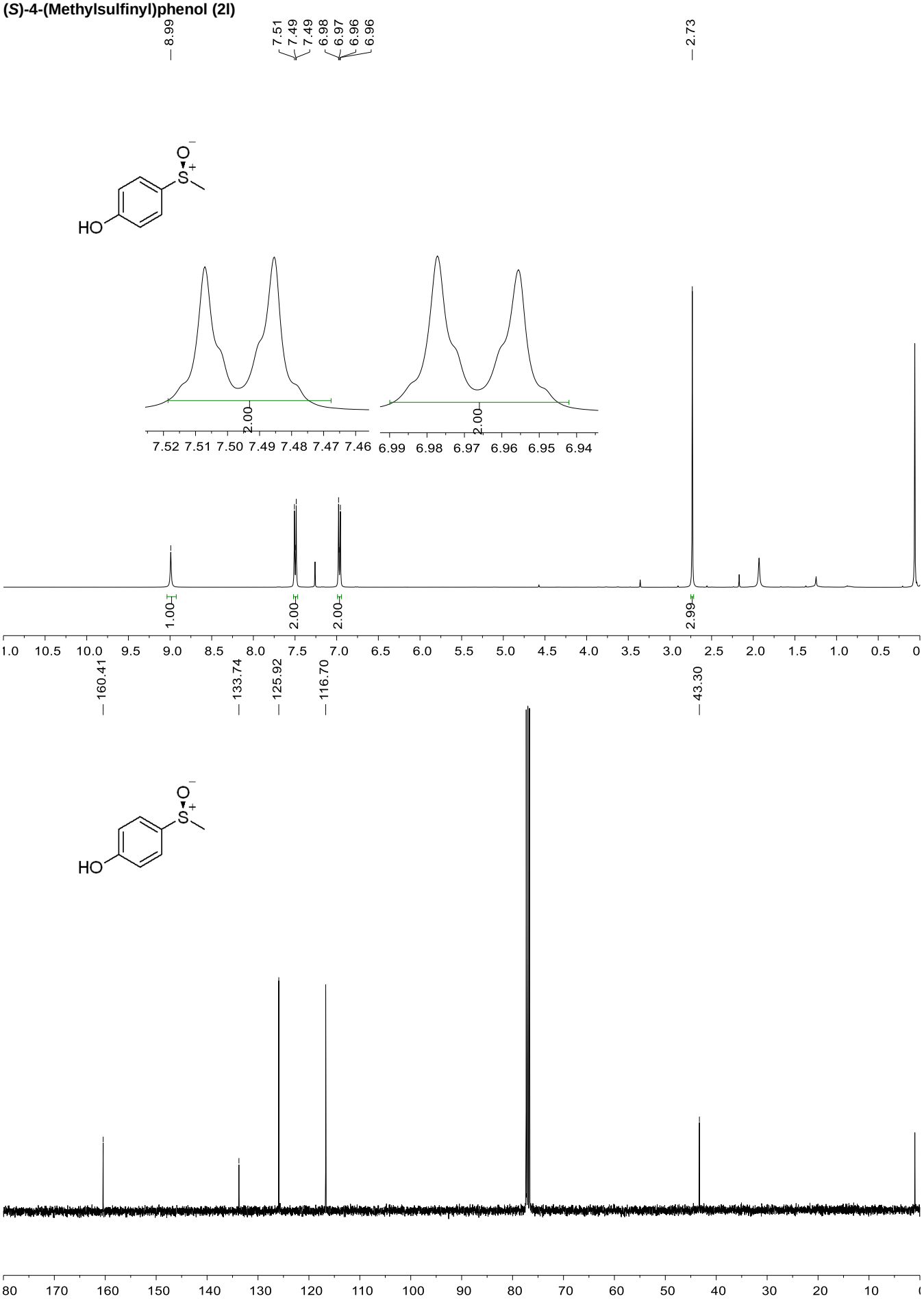


(*S*)-4-Methoxyphenyl methyl sulfoxide (2k)

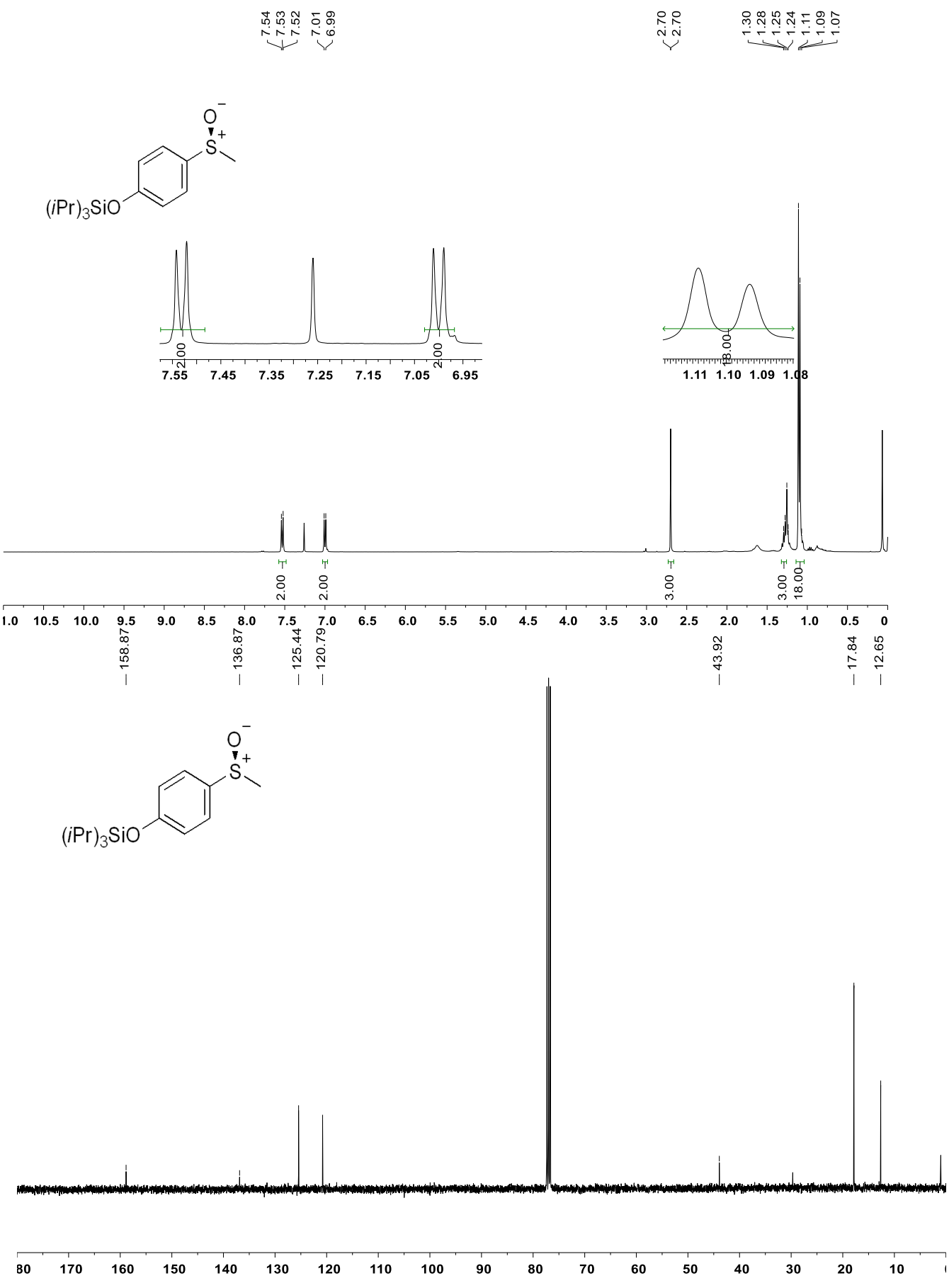




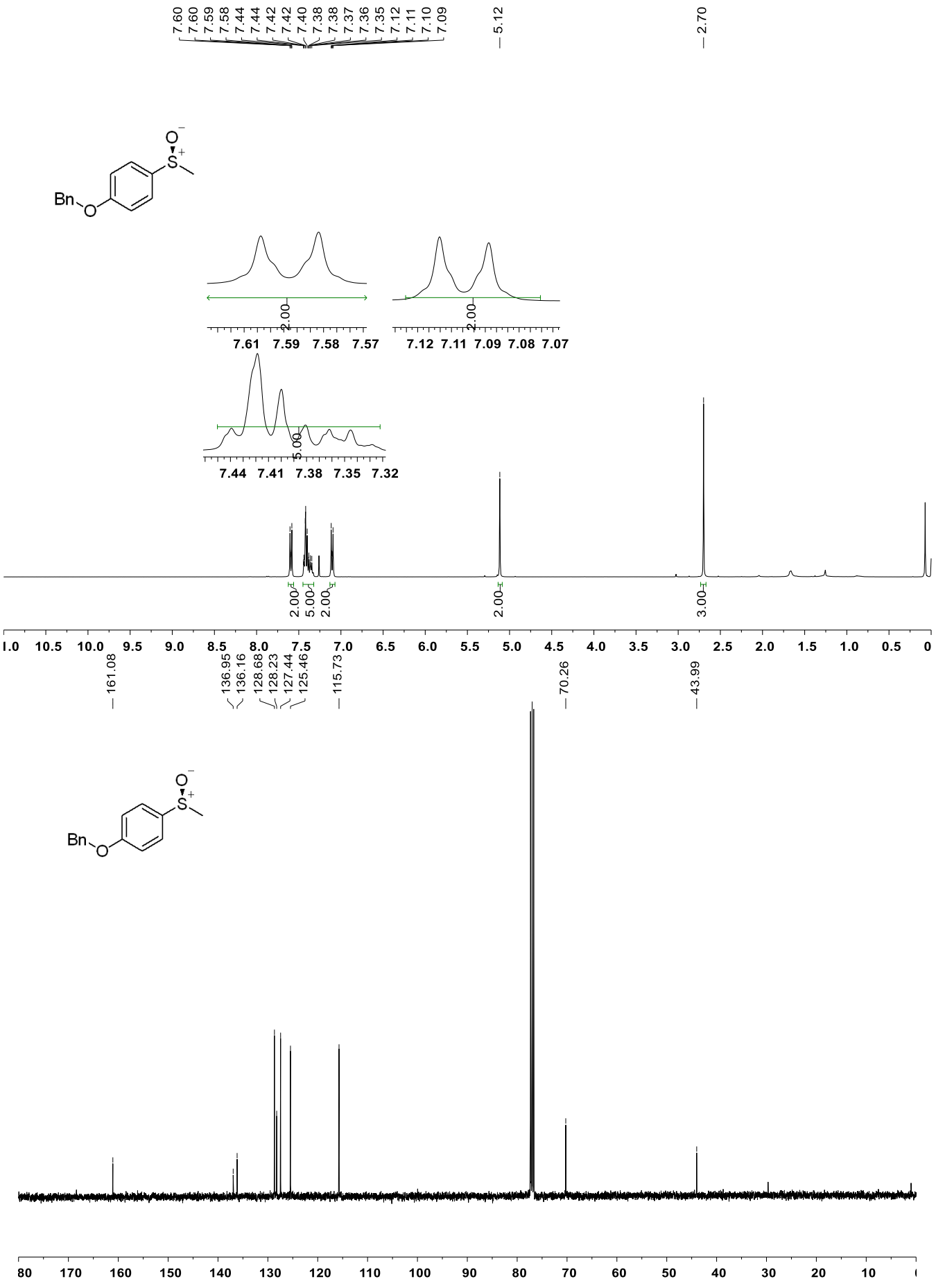
(*S*)-4-(Methylsulfinyl)phenol (2l)



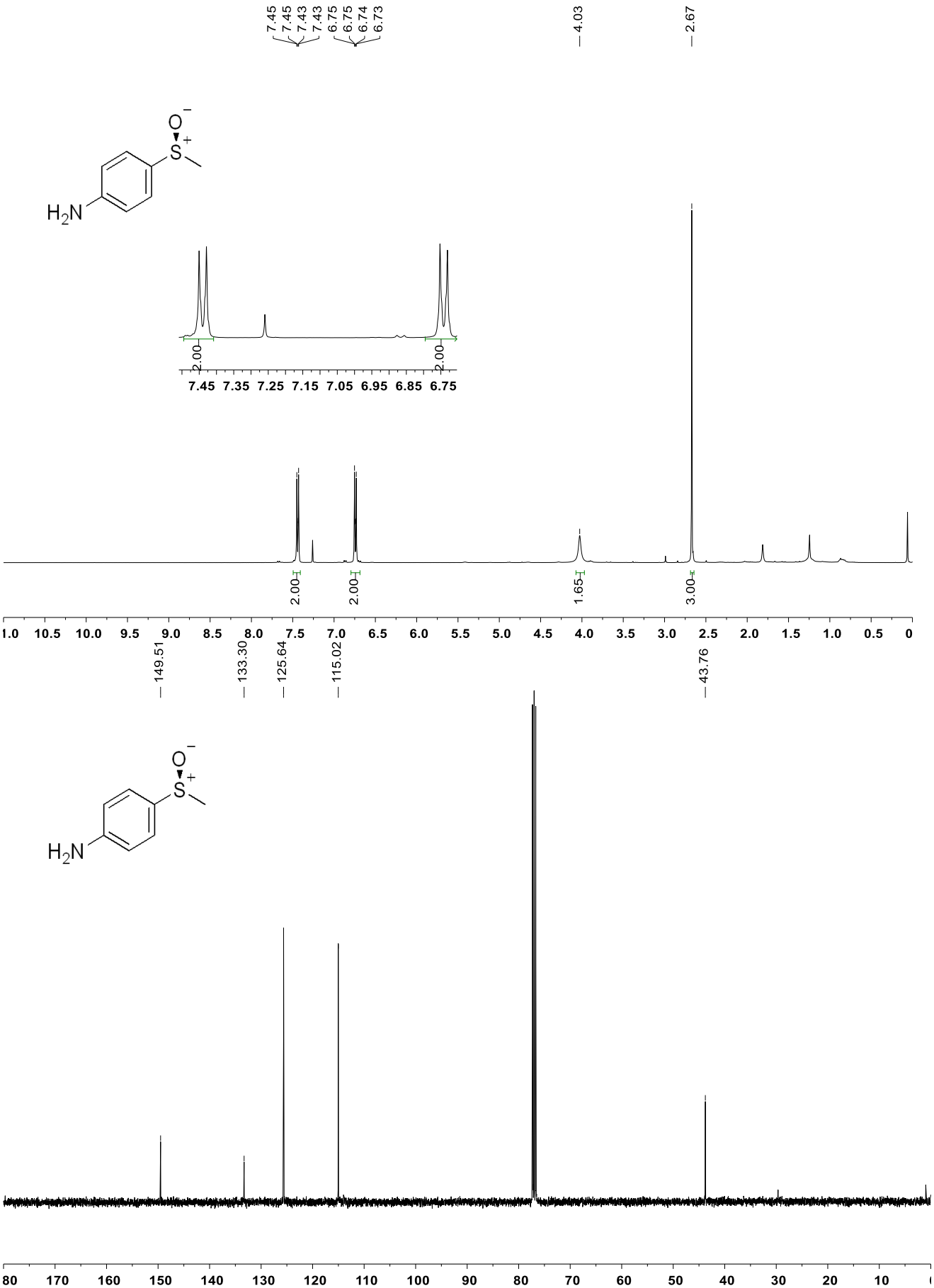
(*S*)-Triisopropyl(4-(methylsulfinyl)phenoxy)silane (2m)



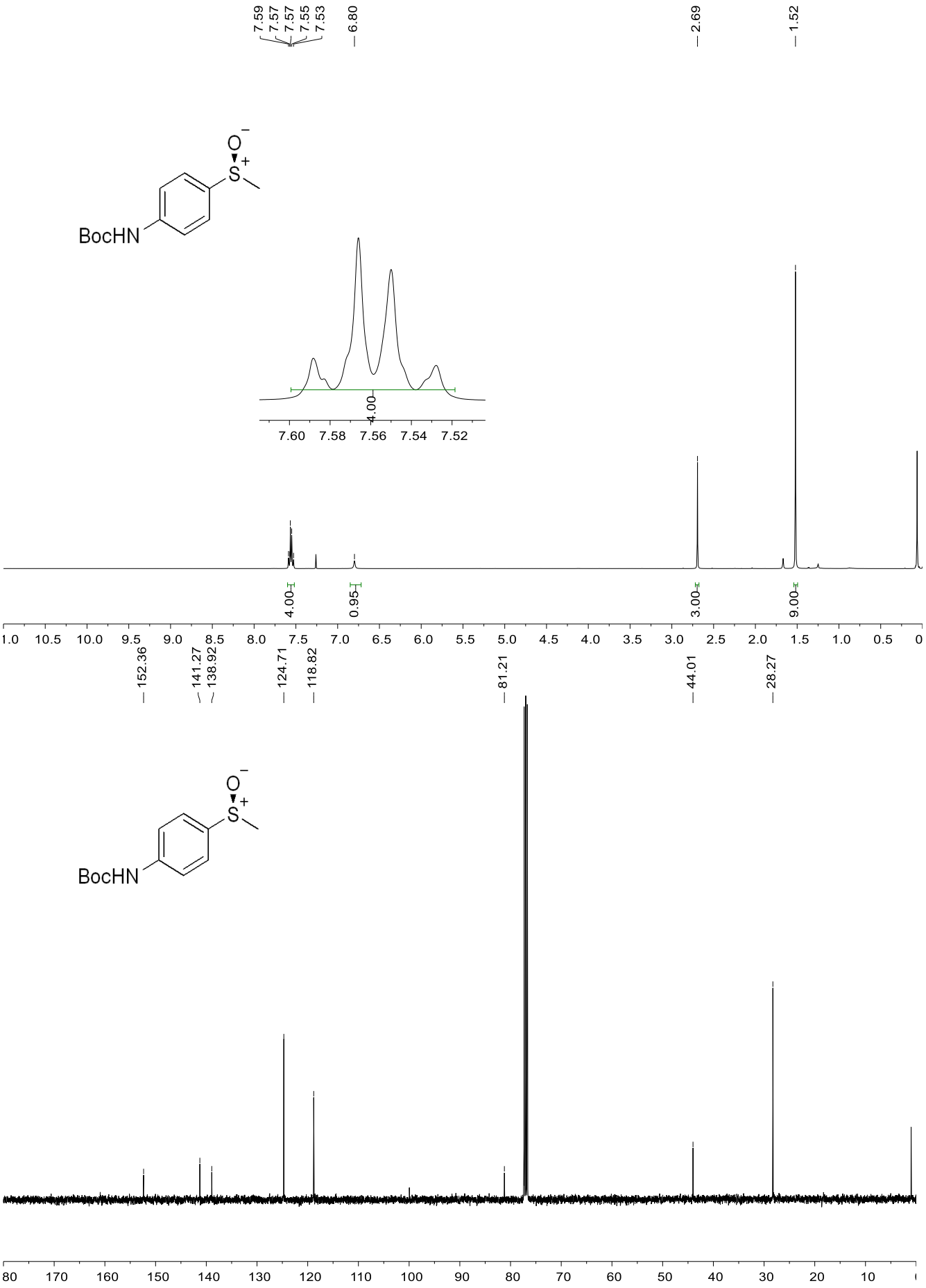
(*S*)-1-(Benzyloxy)-4-(methylsulfinyl)benzene (2n)



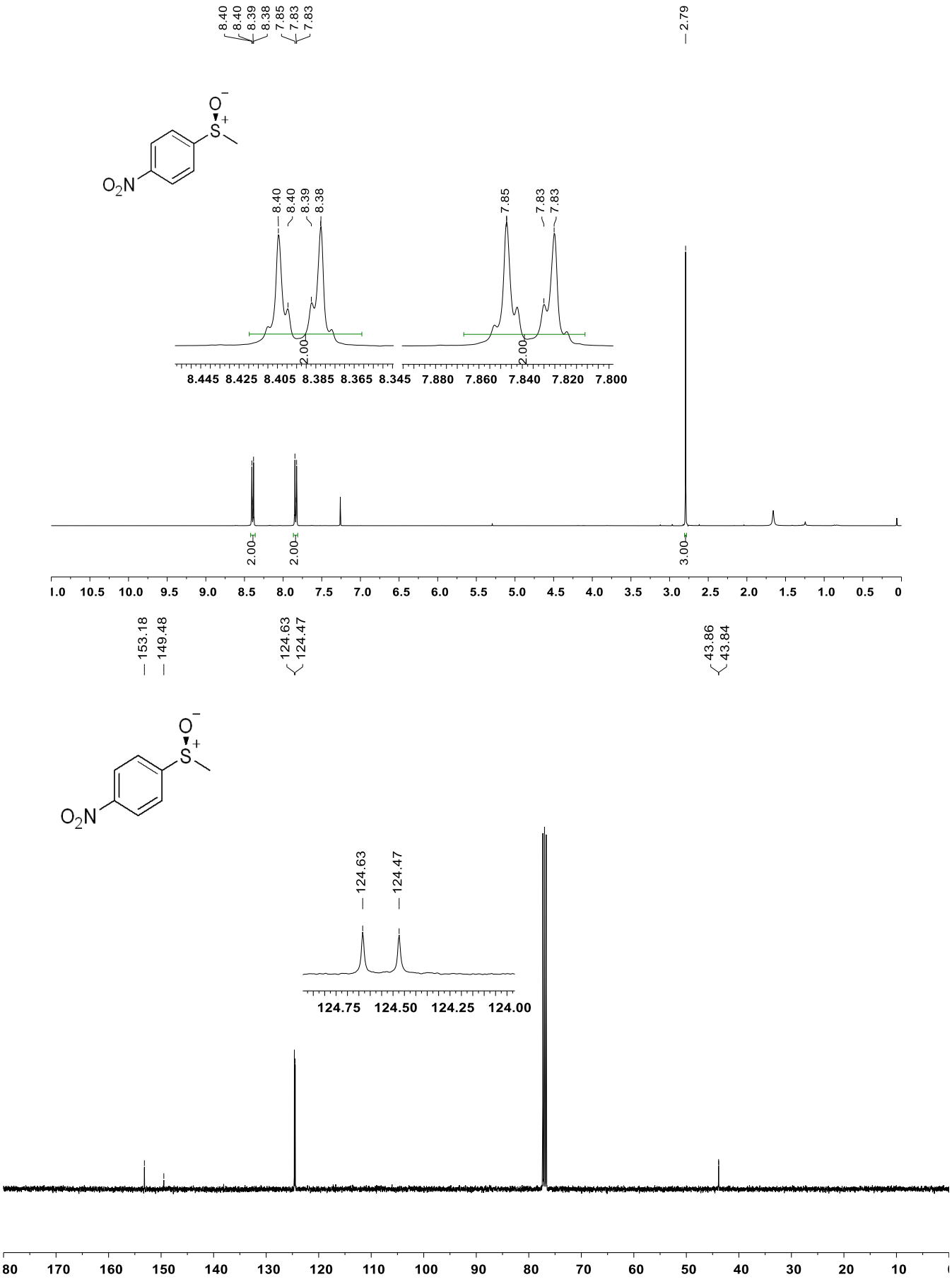
(*S*)-4-(Methylsulfinyl)aniline (2o)



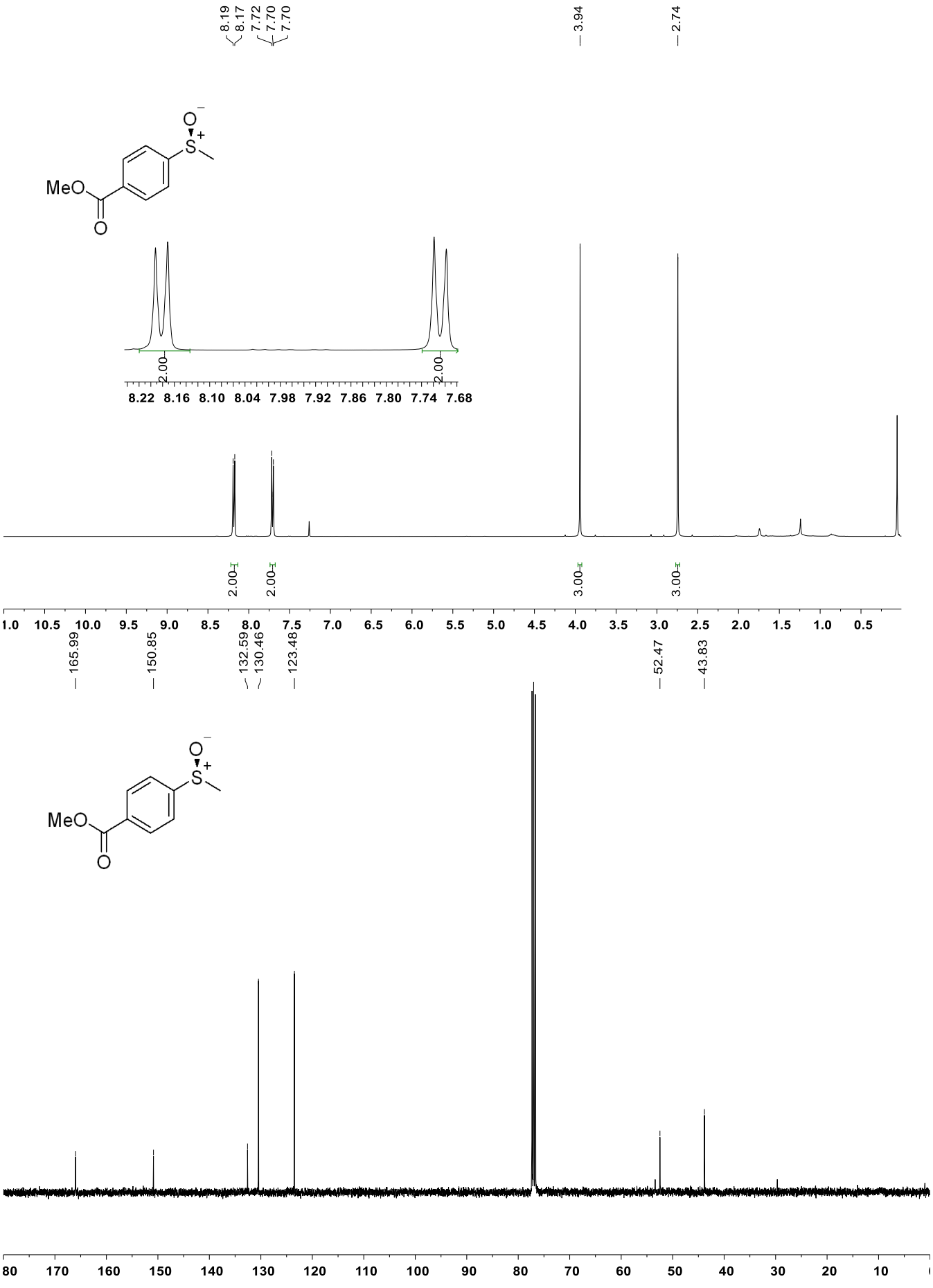
(*S*)-Tert-butyl [4-(methylsulfinyl)phenyl]carbamate (2p)



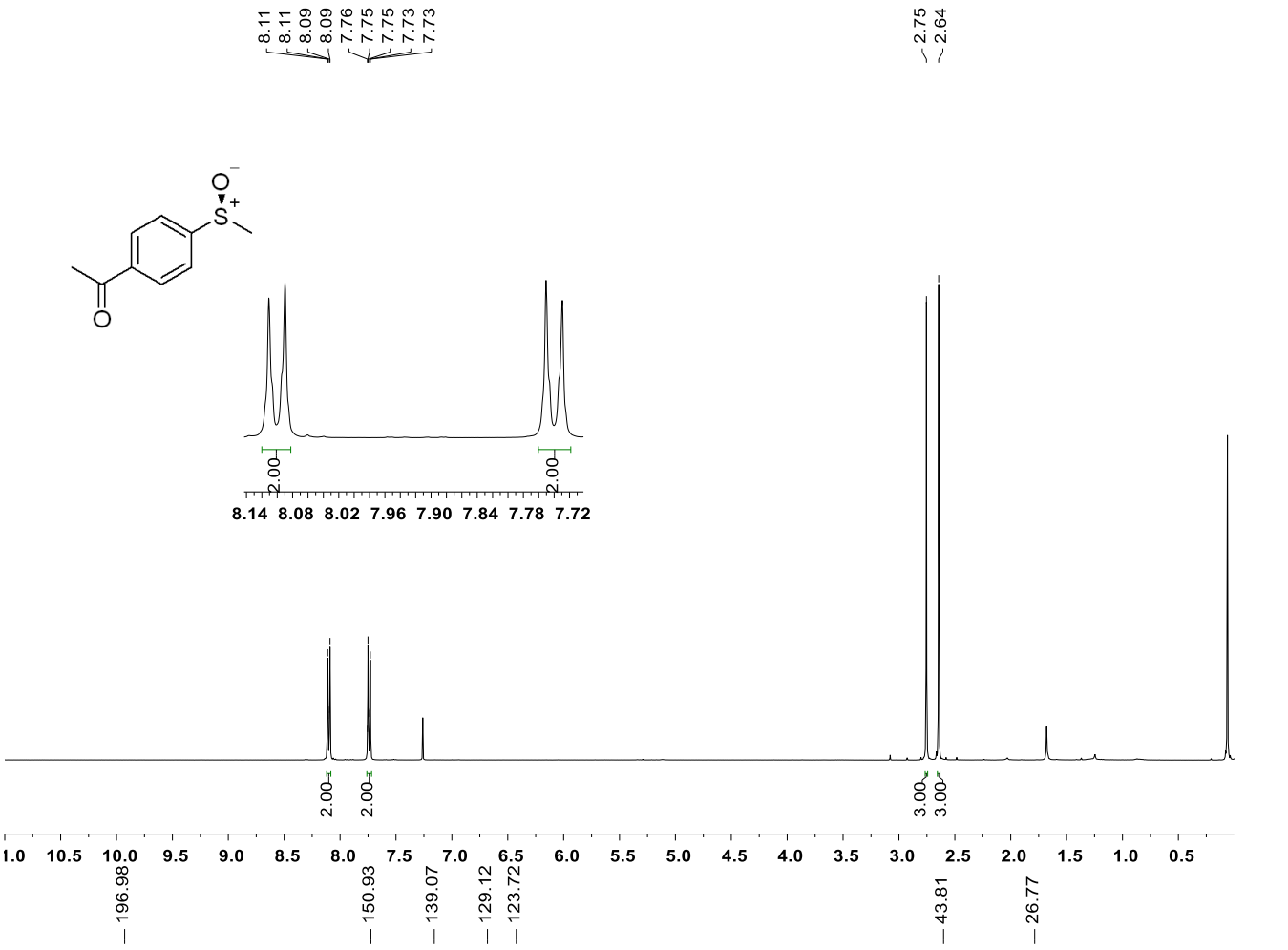
(S)-4-Nitrophenyl methyl sulfoxide (2q)

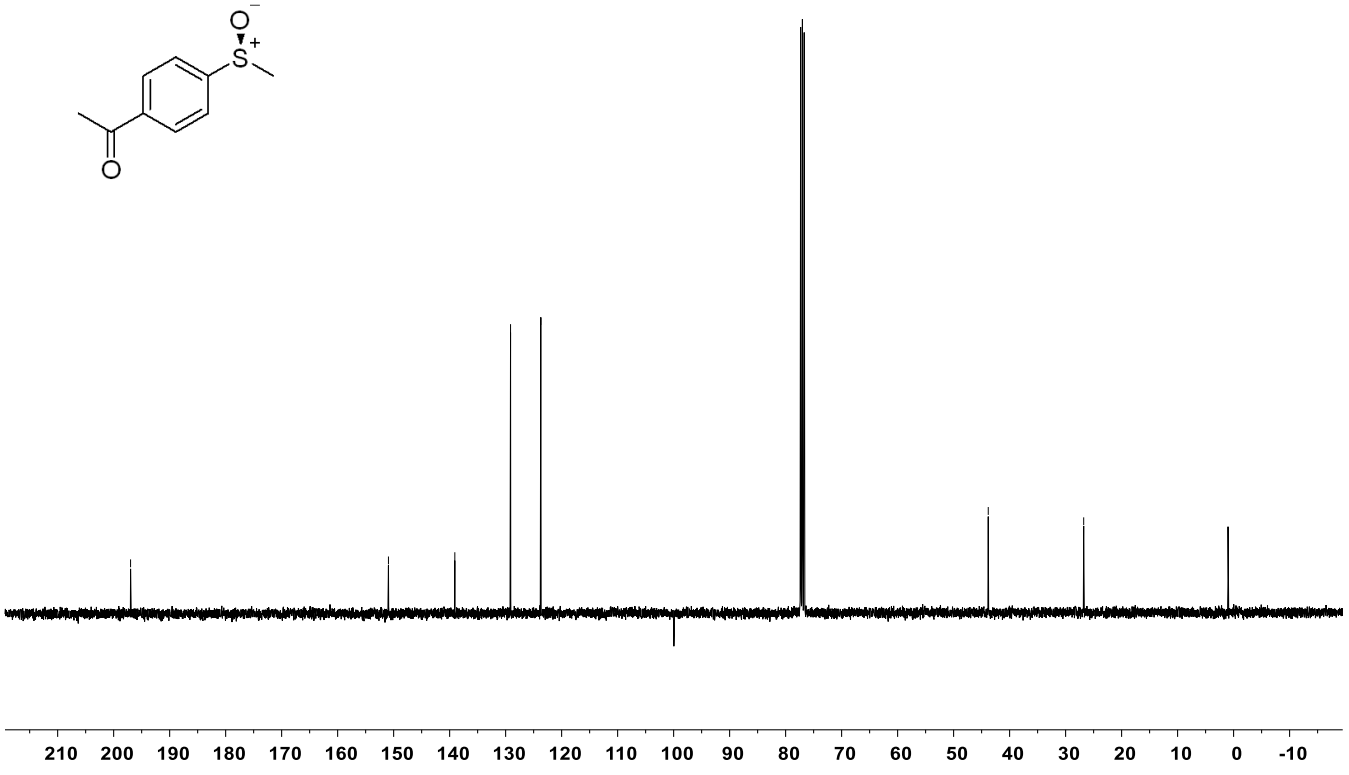


(S)-Methyl-4-methylsulfinylbenzoate (2r)

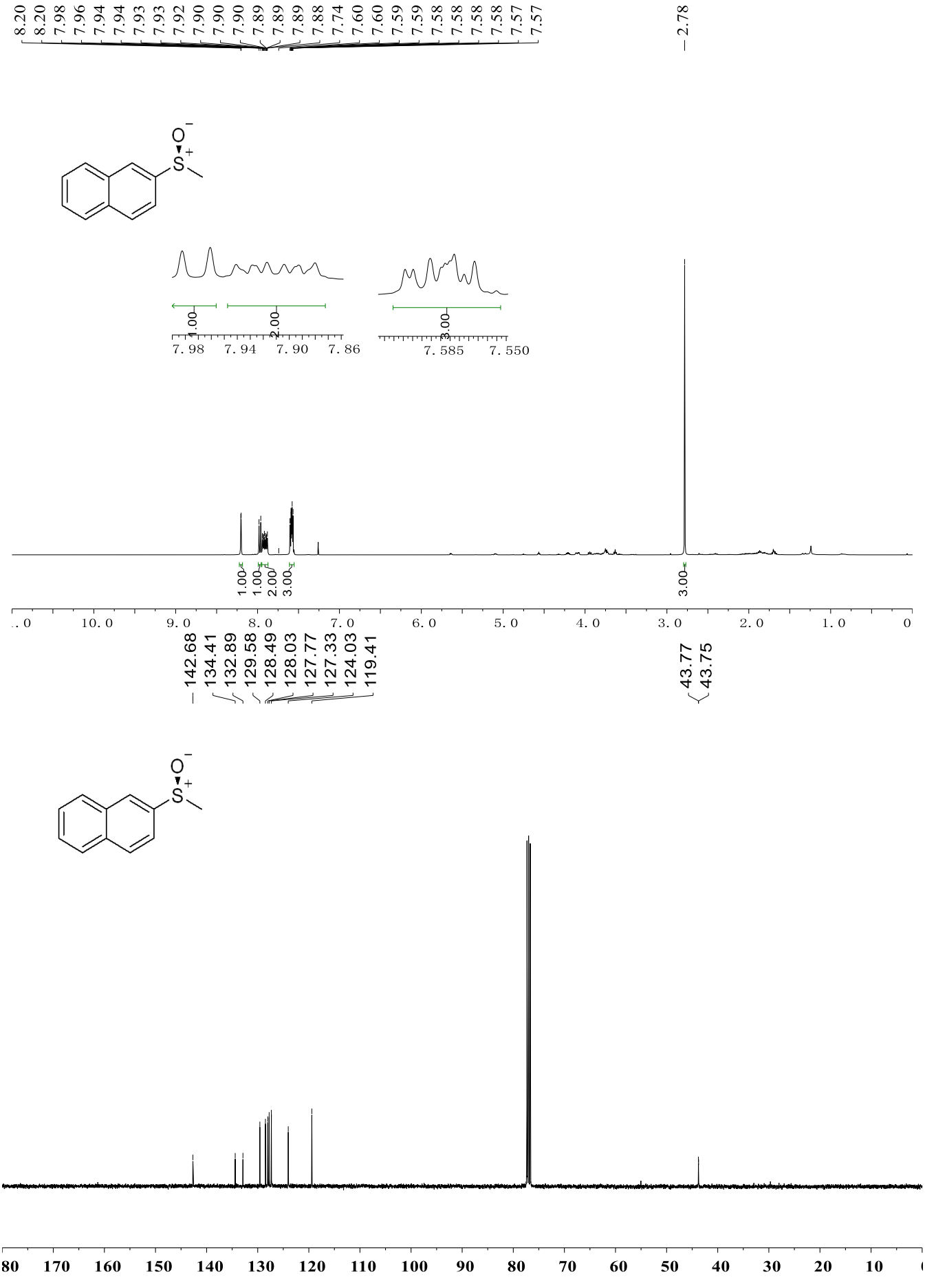


(S)-1-(4-(Methylsulfinyl)phenyl)ethan-1-one (2s)

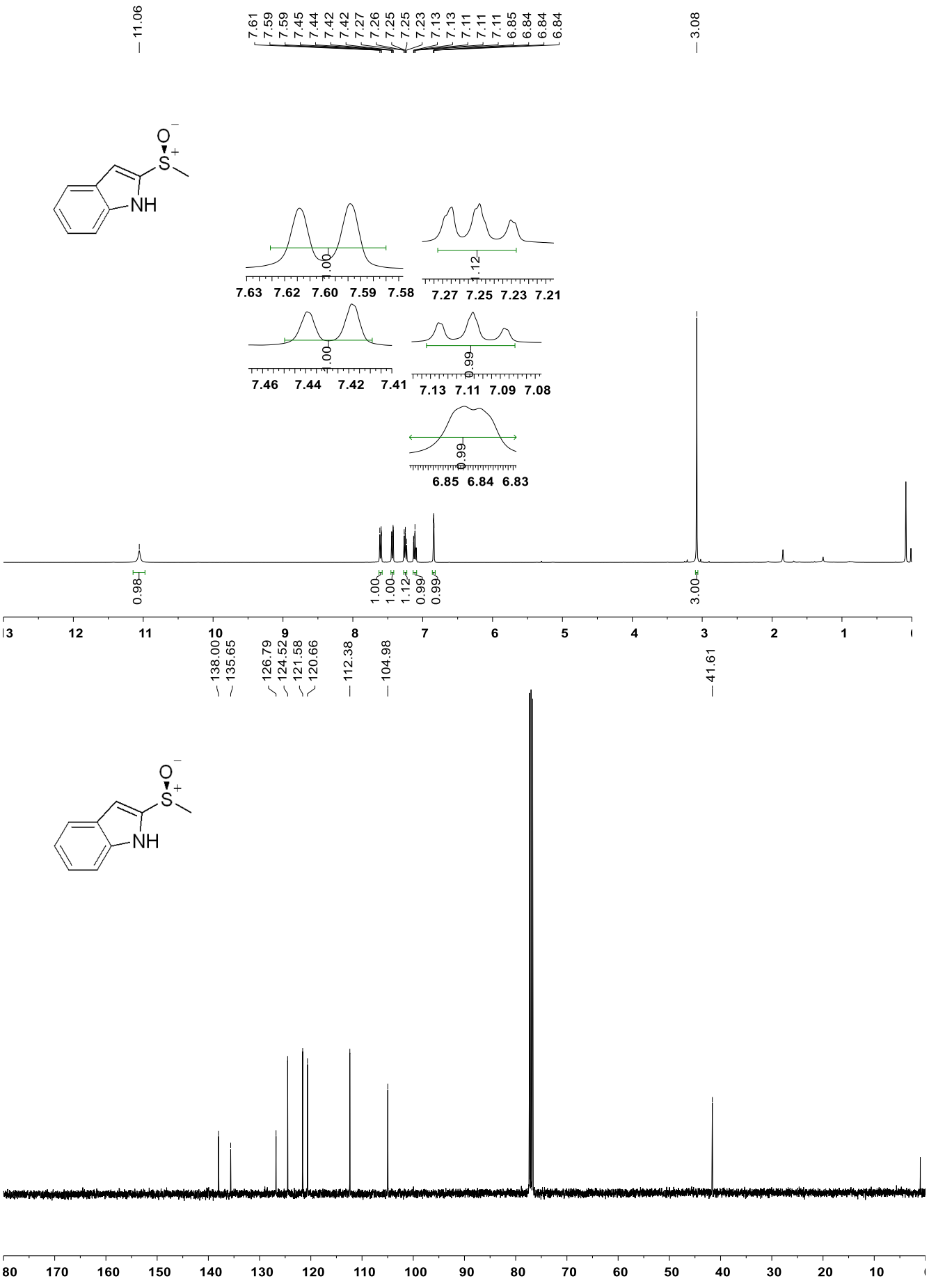




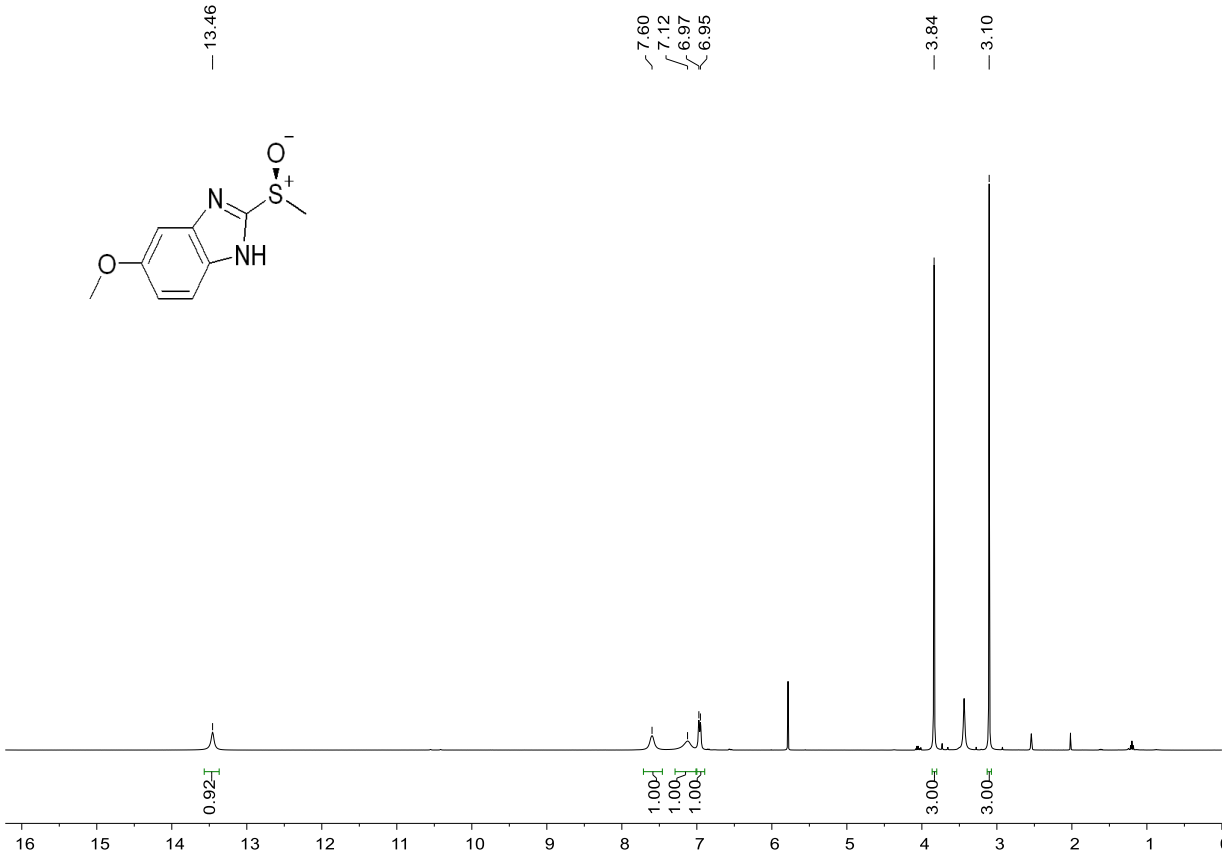
(S)-2-Naphthyl methyl sulfoxide (2t)

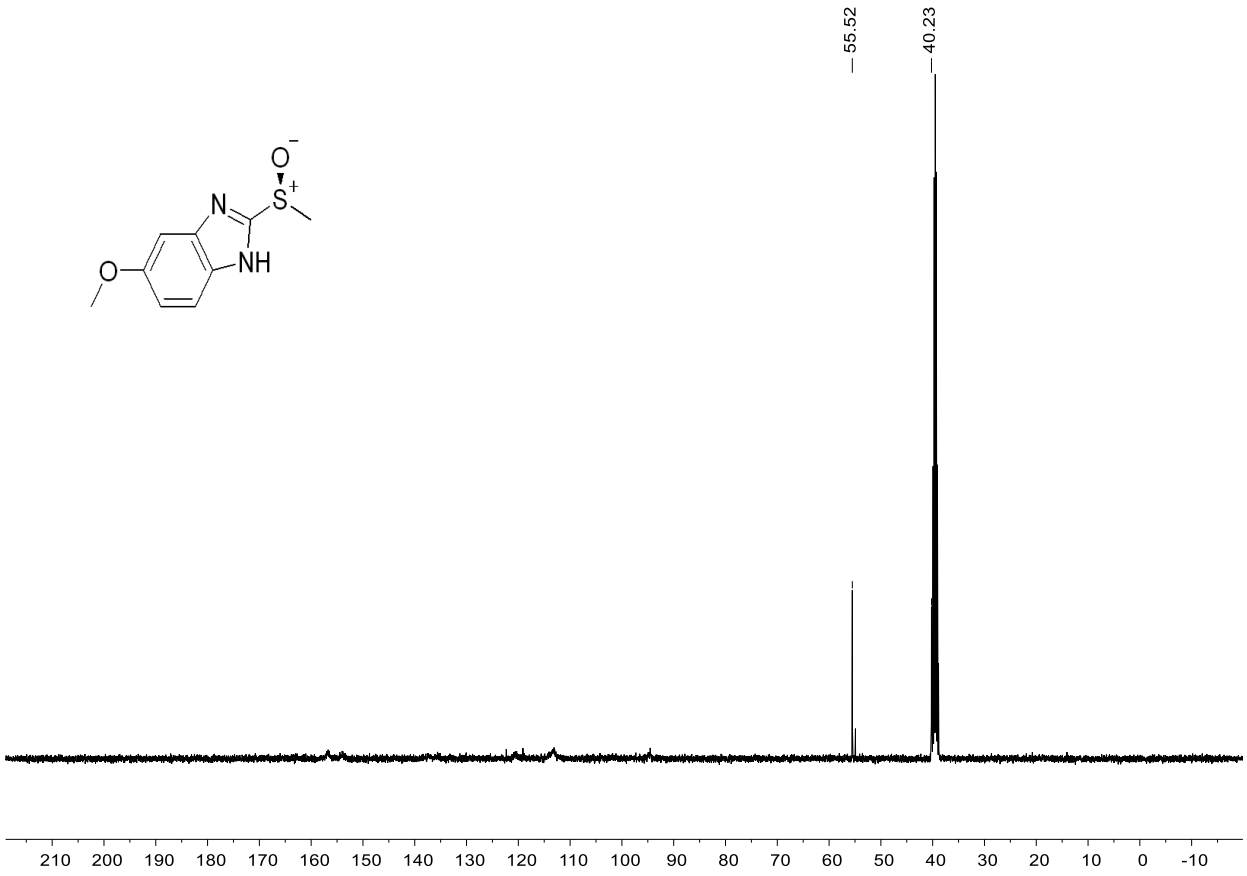


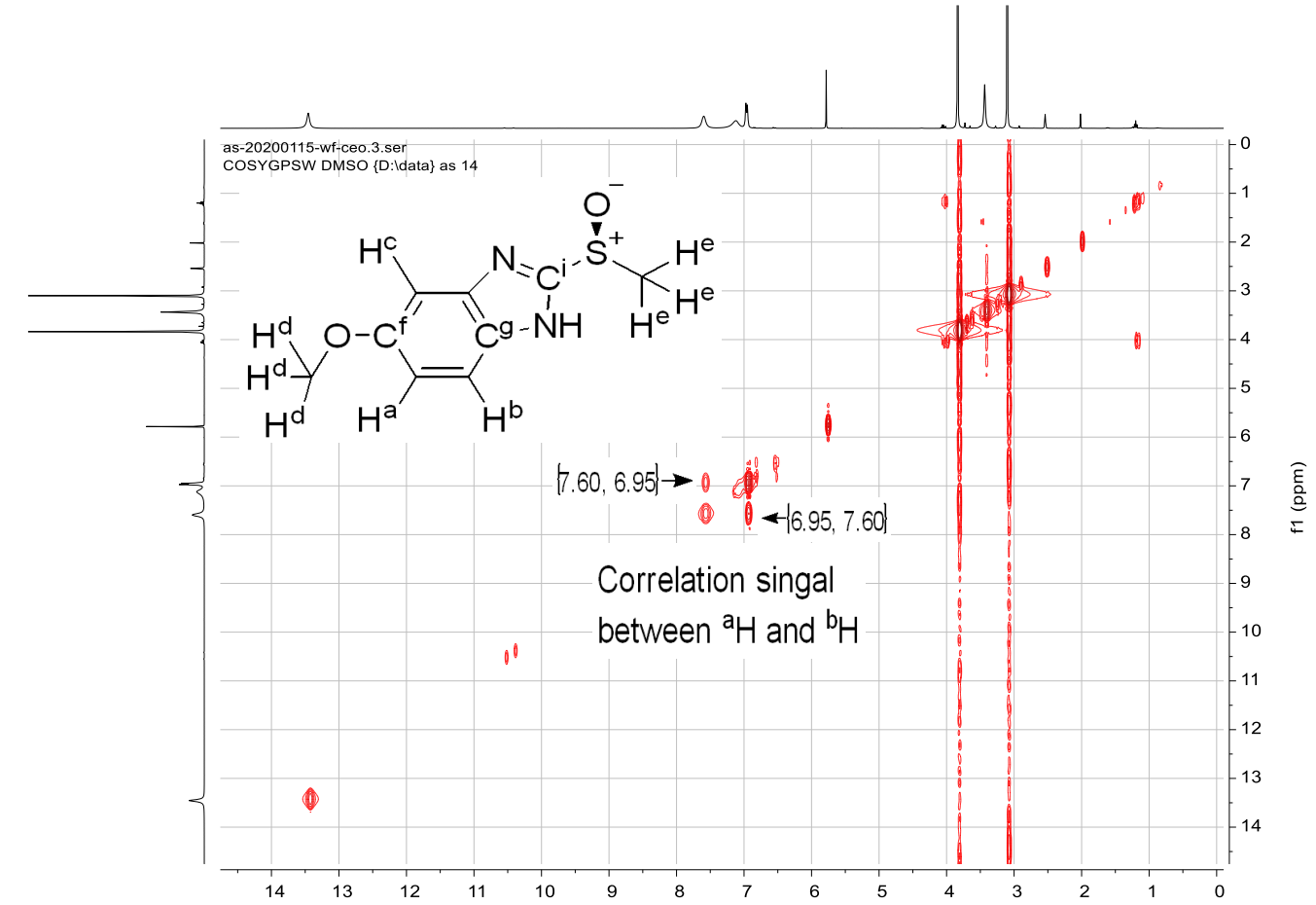
(S)-2-Methyl(sulfinyl)indole (2u)

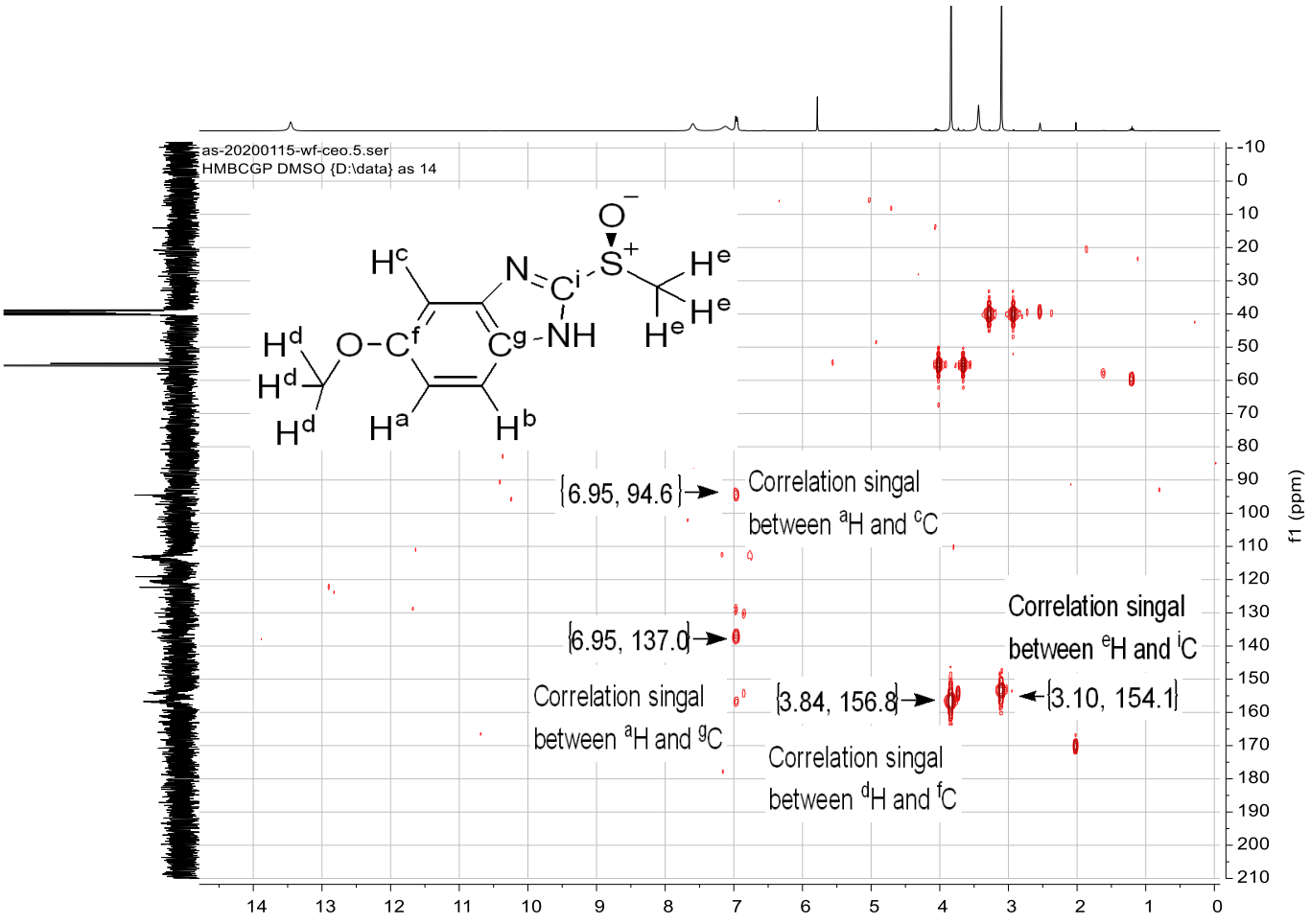


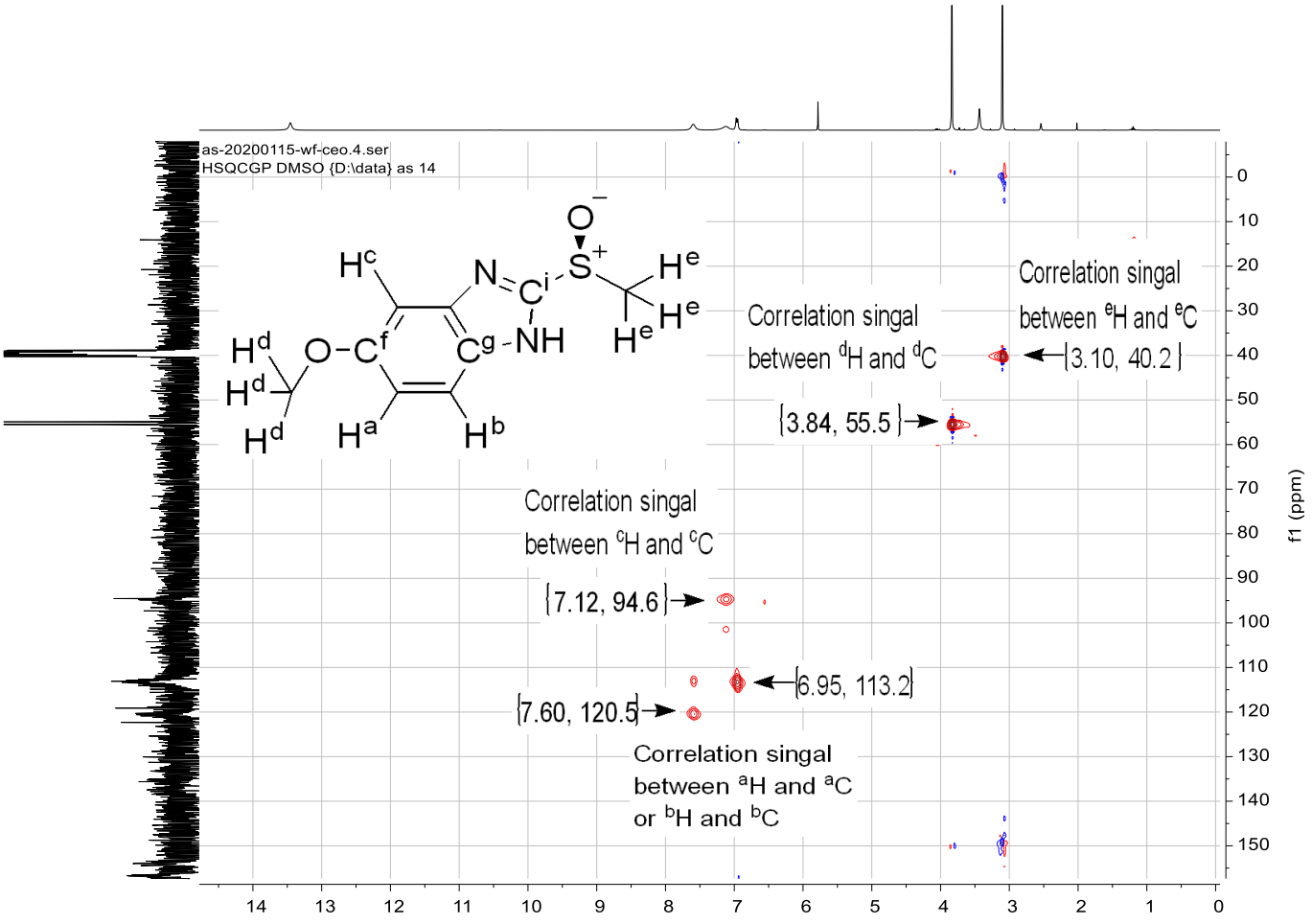
(S)-2-Methyl(sulfinyl)-5-methoxybenzimidazole (2v)



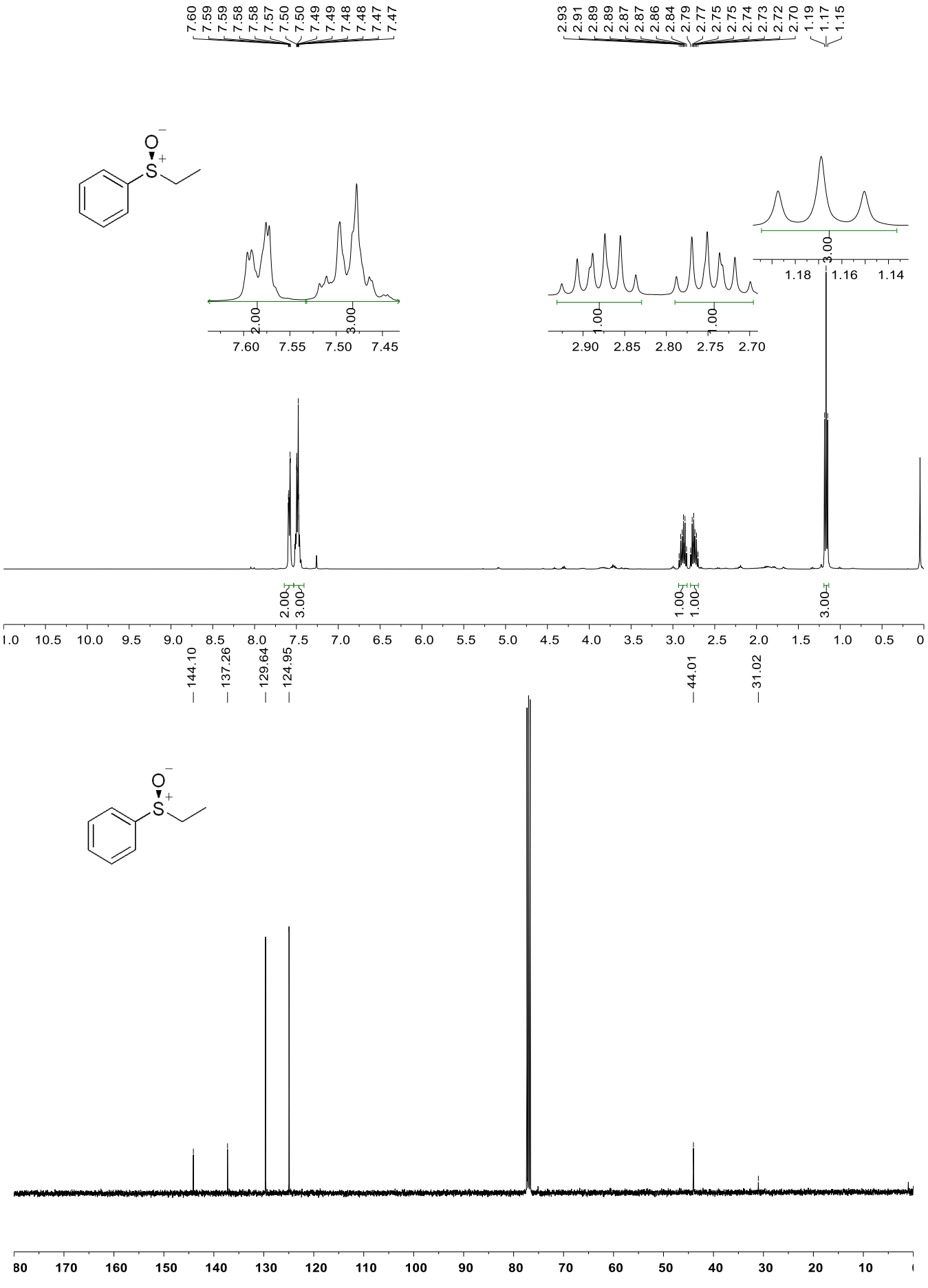



as-20200115-wf-ceo.3.ser
COSYGPSW DMSO {D:\data} as 14
{7.60, 6.95}
{6.95, 7.60}
Correlation singal
between aH and bH
f1 (ppm)

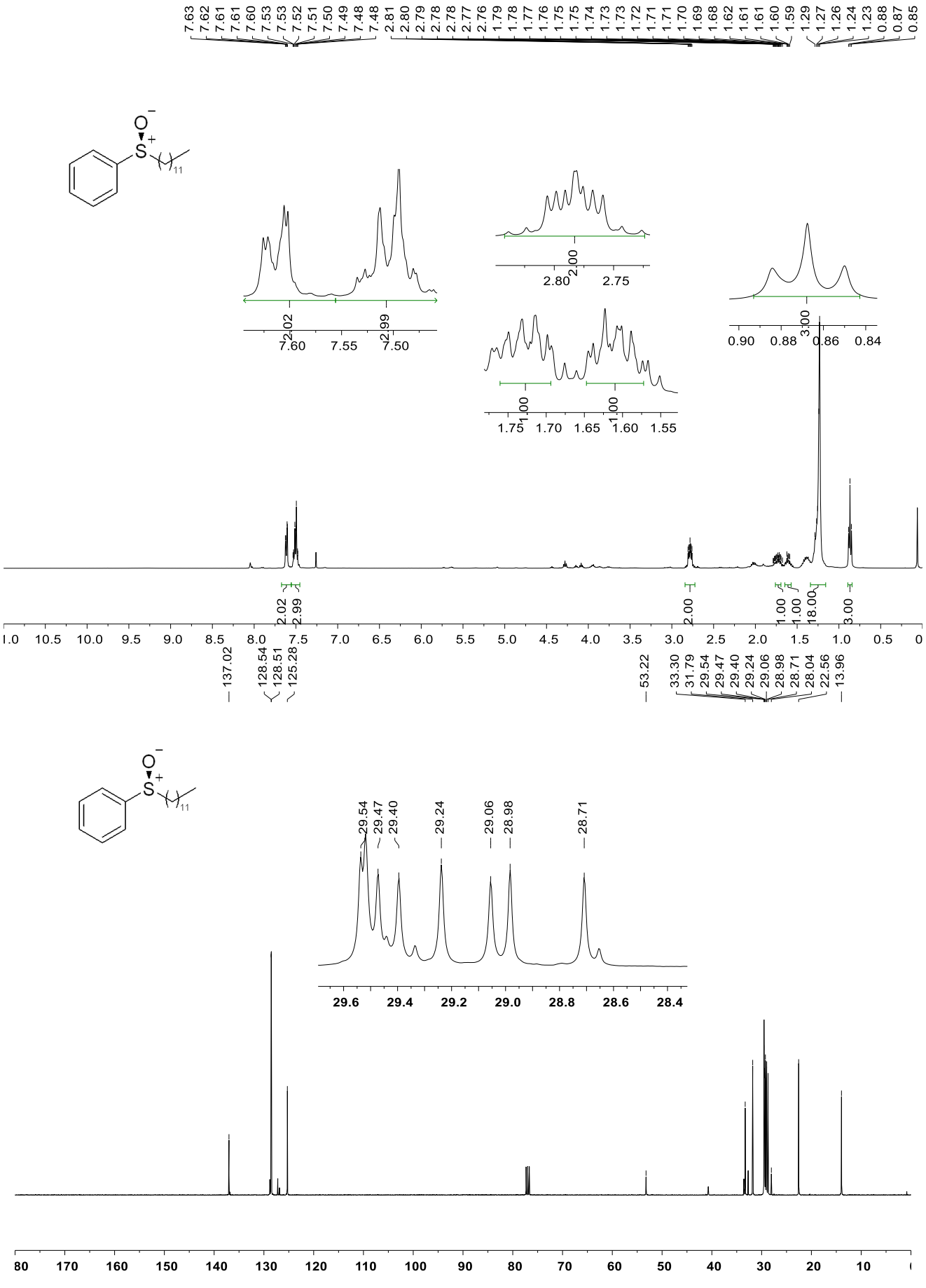

as-20200115-wf-ceo.5.ser
HMBCGP DMSO {D:\data} as 14
{6.95, 94.6}
Correlation singal
between aH and cC
{6.95, 137.0}
Correlation singal
between aH and gC
Correlation singal
between eH and iC
{3.84, 156.8}
{3.10, 154.1}
Correlation singal
between dH and fC
f1 (ppm)


as-20200115-wf-ceo.4.ser
HSQCGP DMSO {D:\data} as 14
Correlation singal between dH and dC
{3.10, 40.2}
{3.84, 55.5}
Correlation singal between eH and eC
Correlation singal between cH and cC
{7.12, 94.6}
{6.95, 113.2}
{7.60, 120.5}
Correlation singal between aH and aC or bH and bC
f1 (ppm)

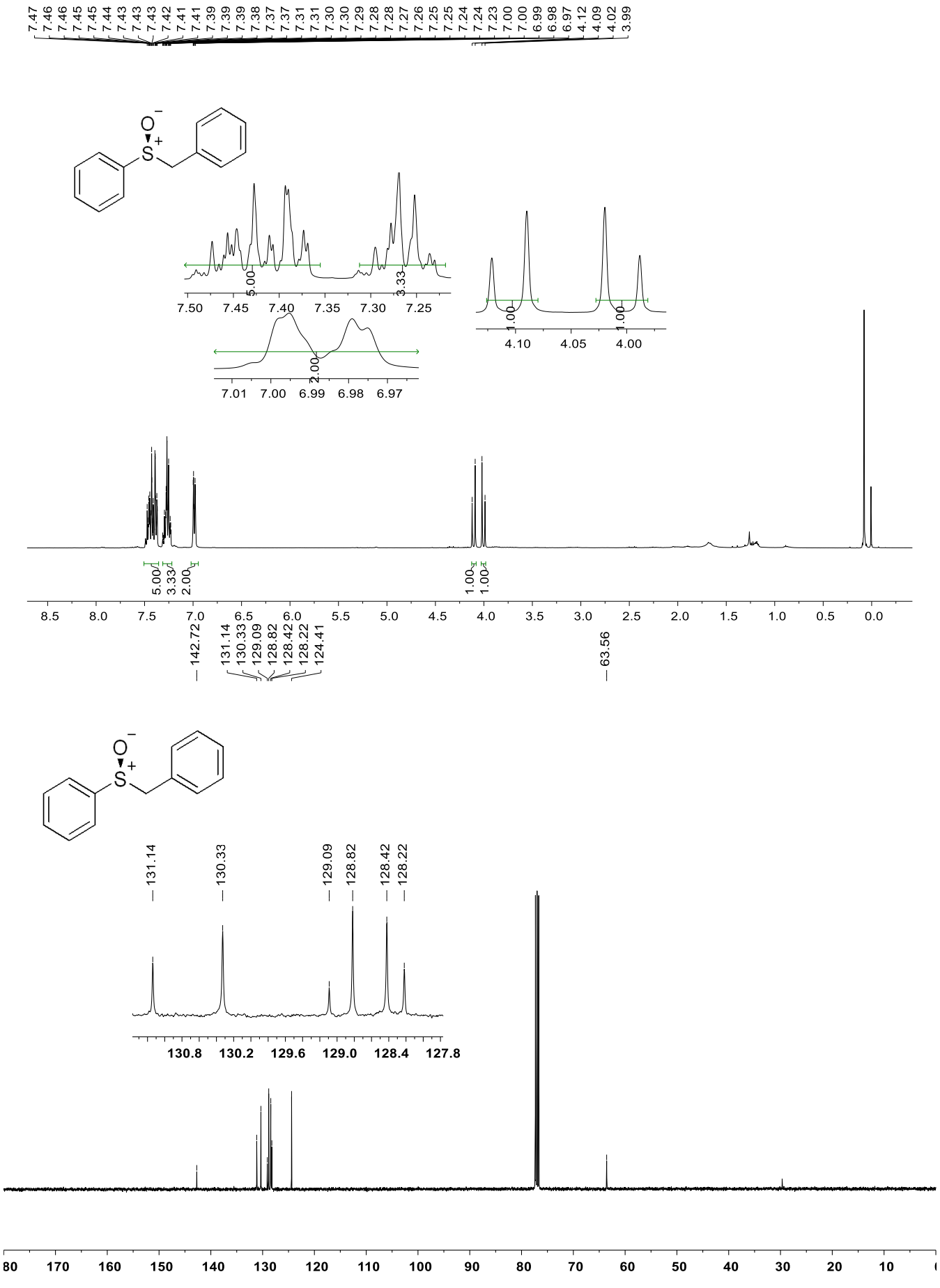
(S)-Phenyl ethyl sulfoxide (2w)



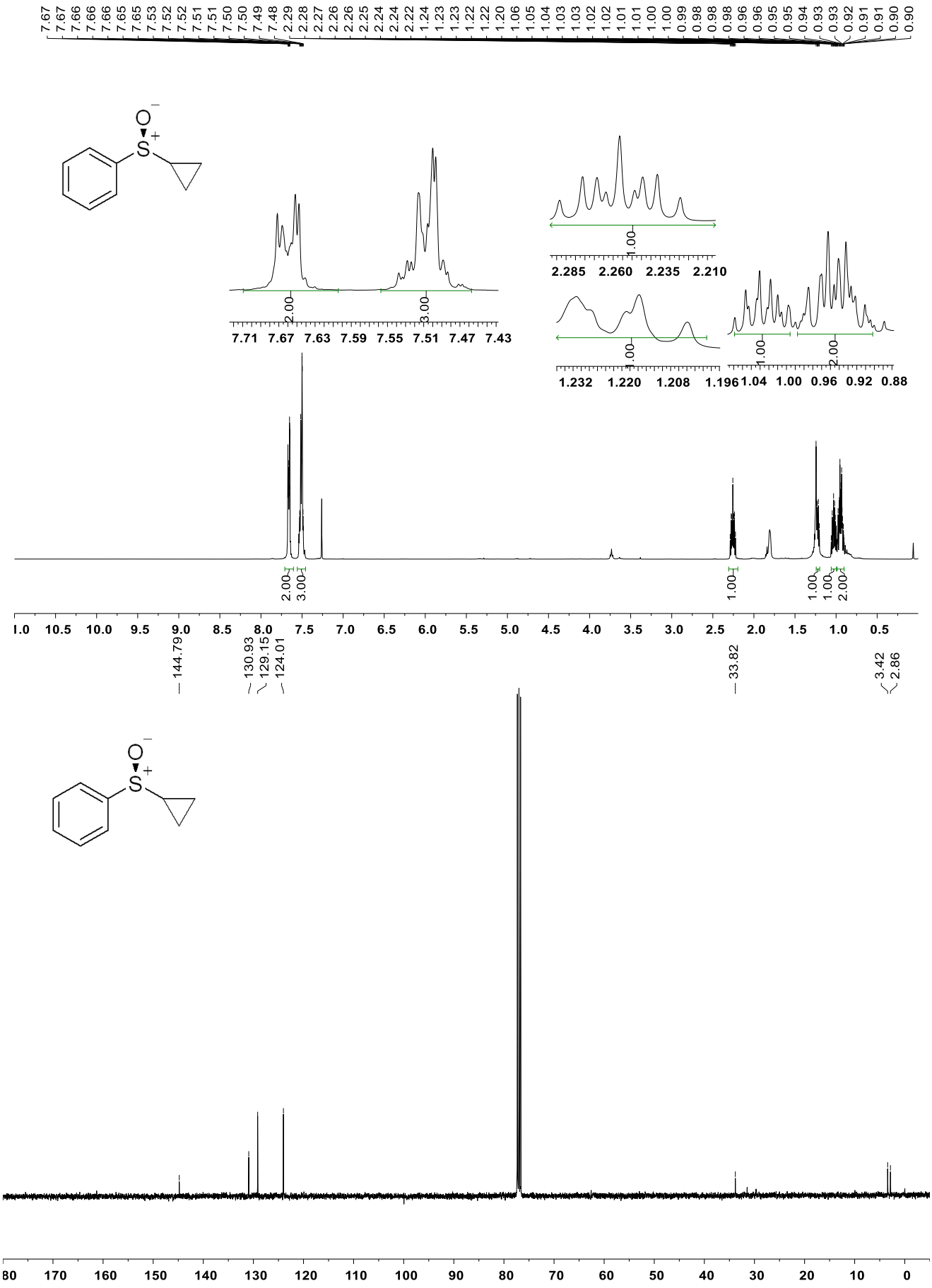
(*S*)-Phenyl dodecyl sulfoxide (2x)



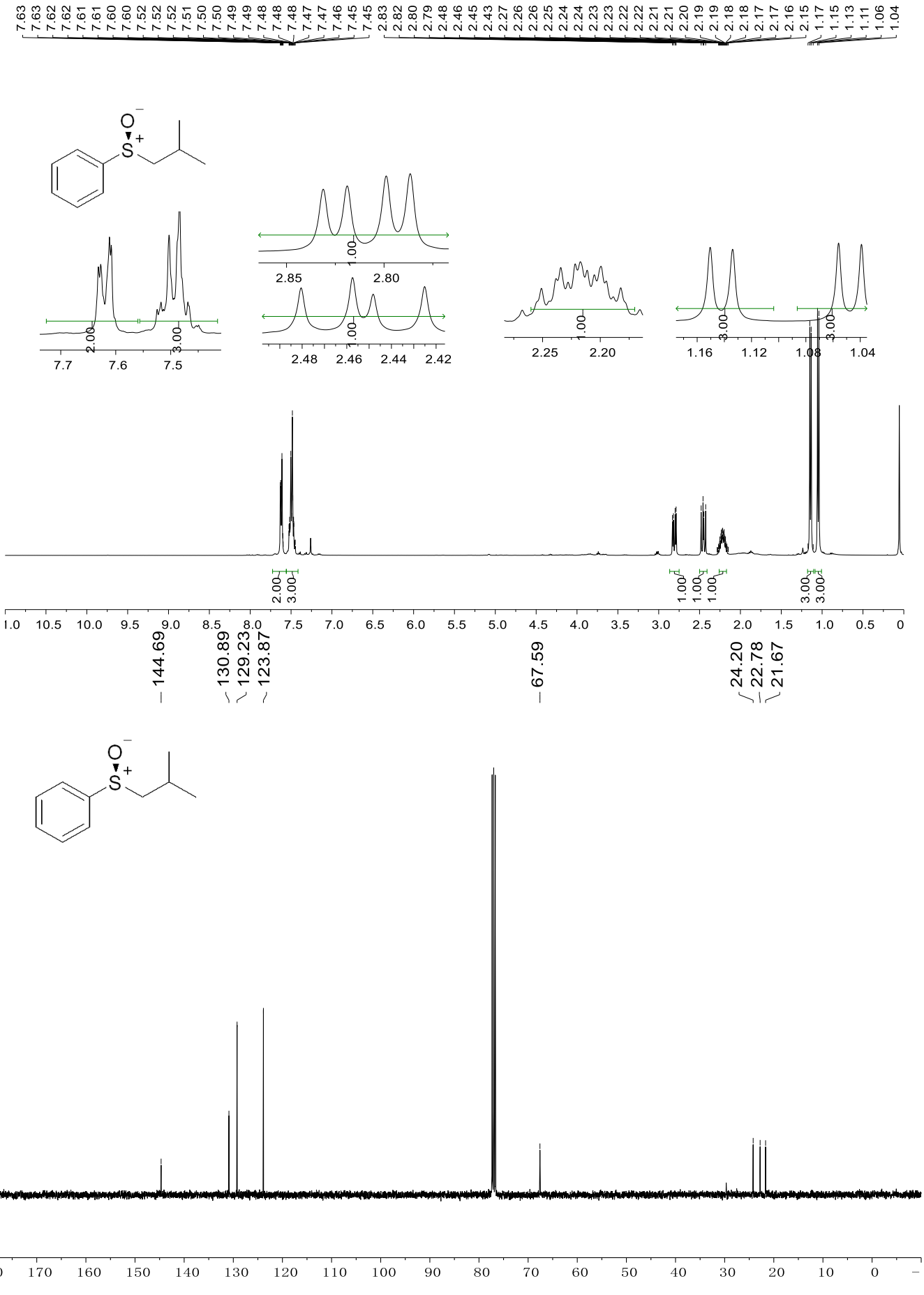
(*S*)-Phenyl benzyl sulfoxide (2y)



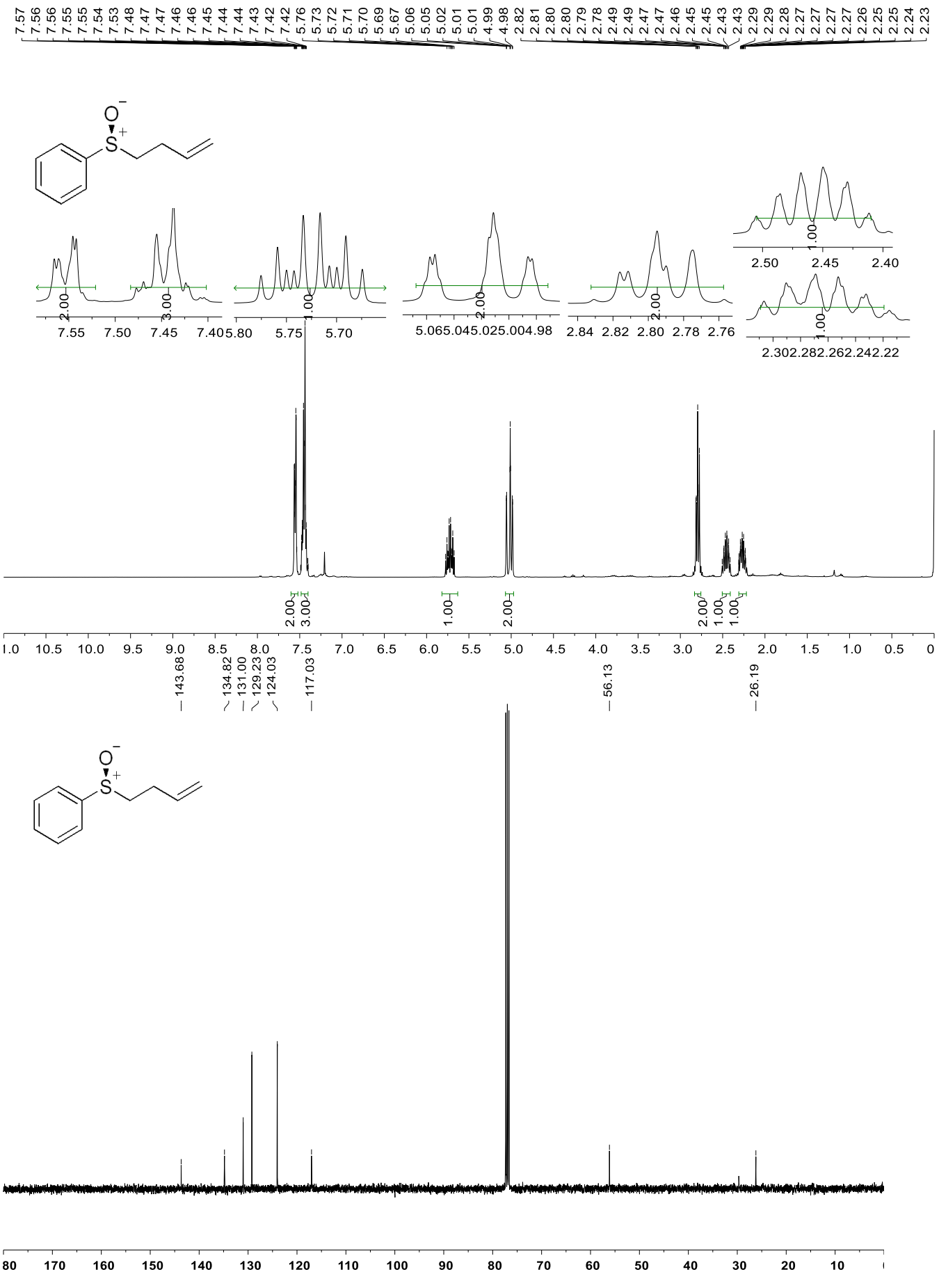
(*S*)-Phenyl cyclopropyl sulfoxide (2z)



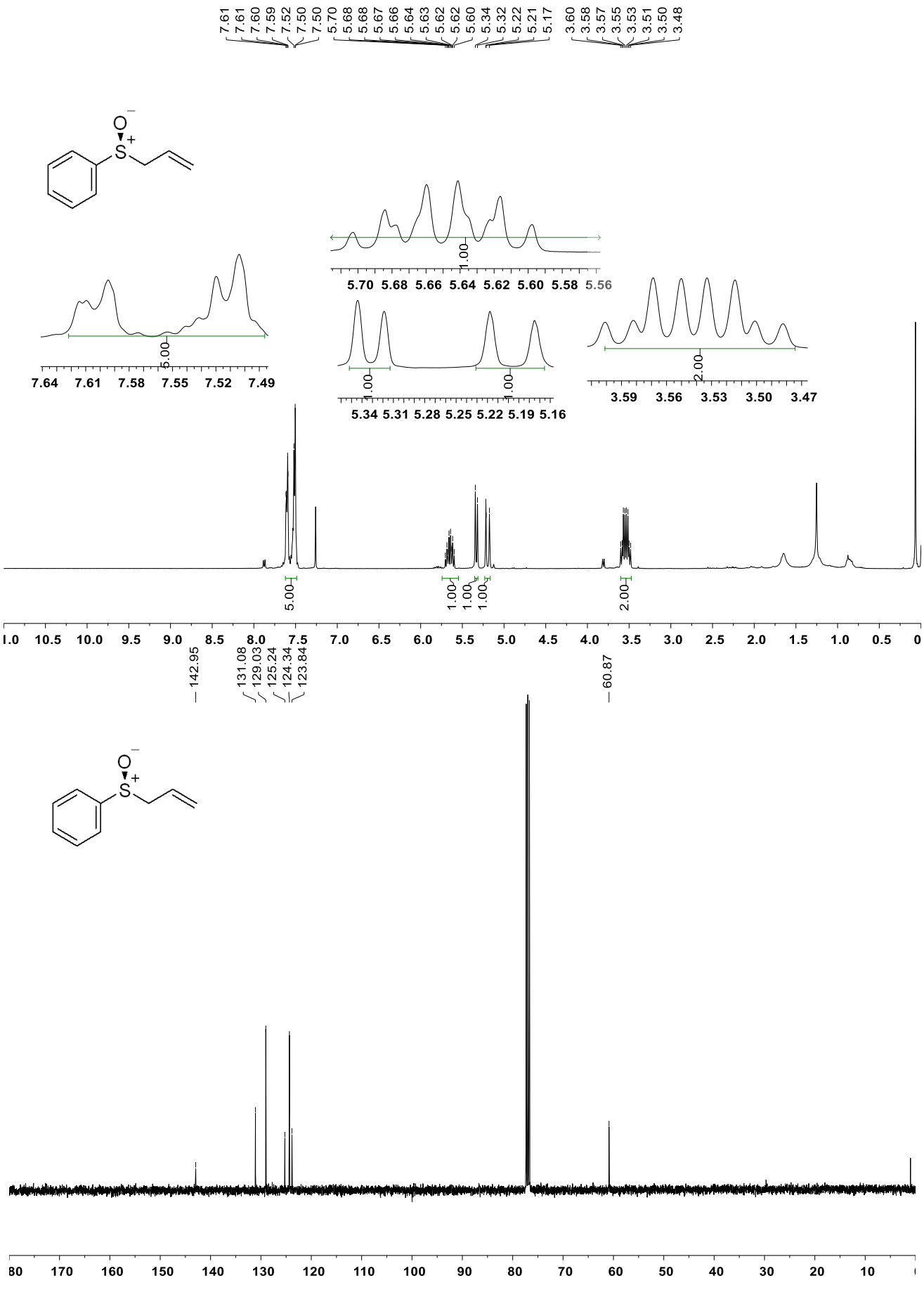
(*S*)-Isobutyl phenyl sulfoxide (2aa)



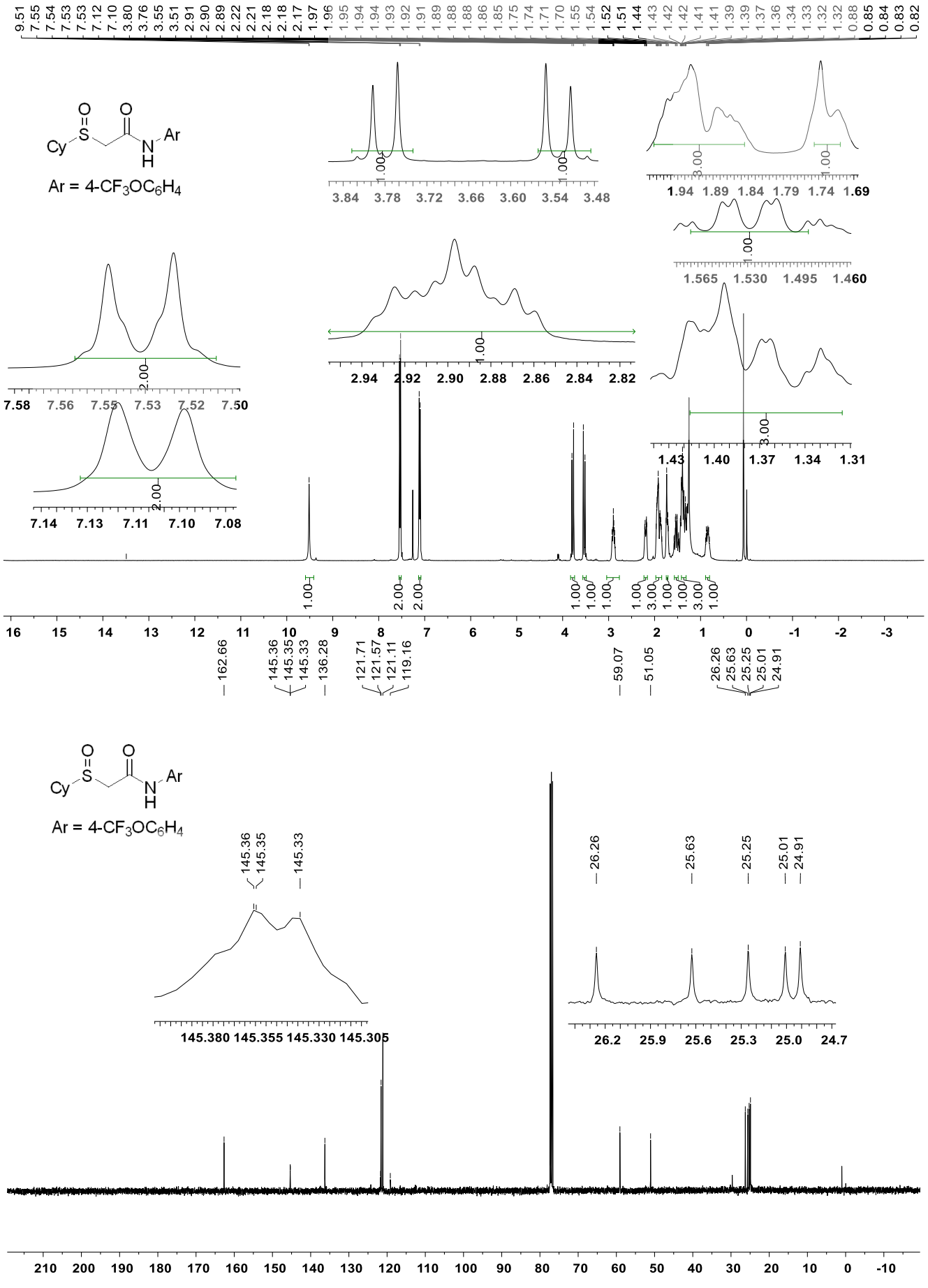
(*S*)-4-(Phenylsulfinyl)but-1-ene (2ab)

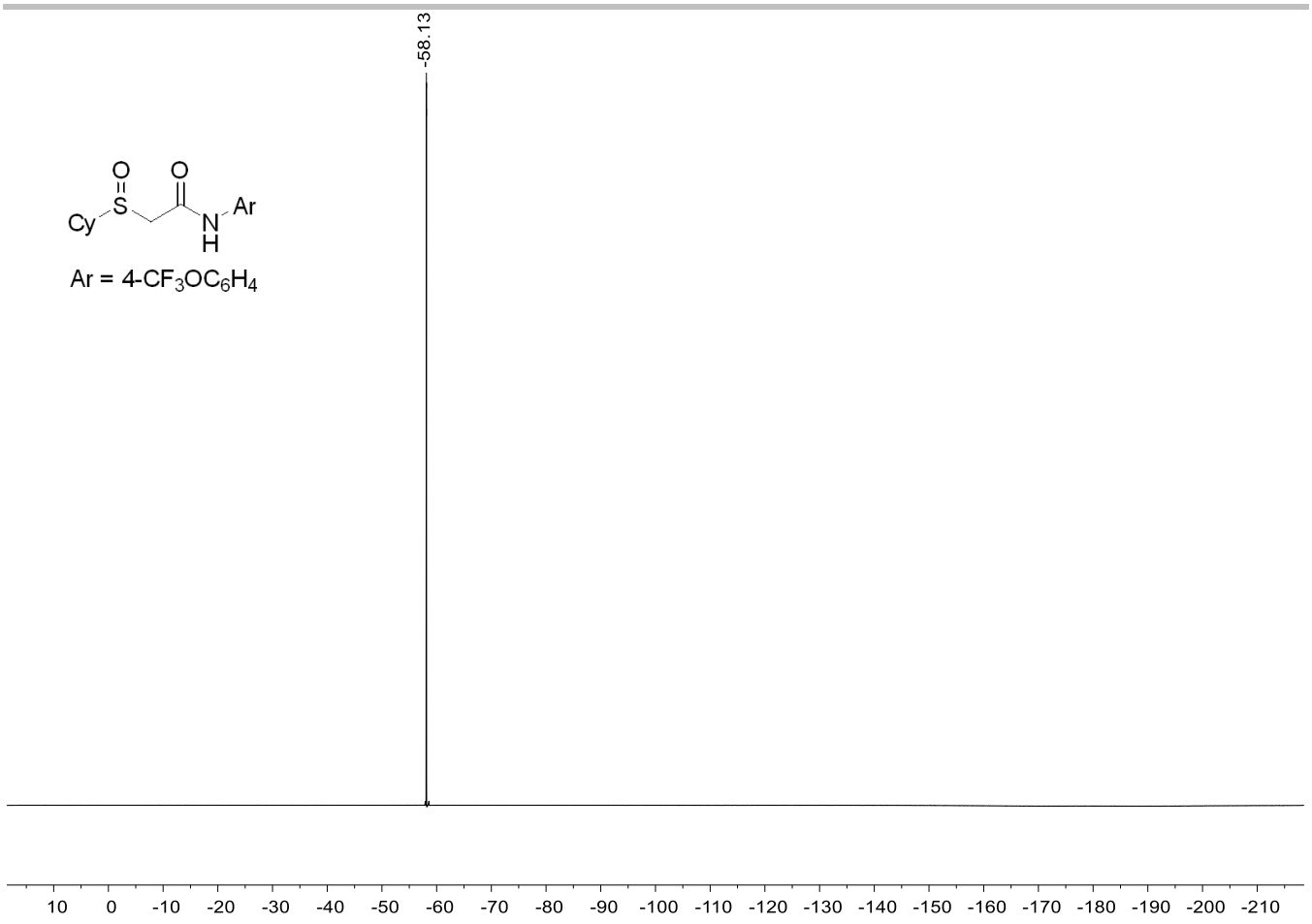


(*S*)-Phenyl allyl sulfoxide (2ac)

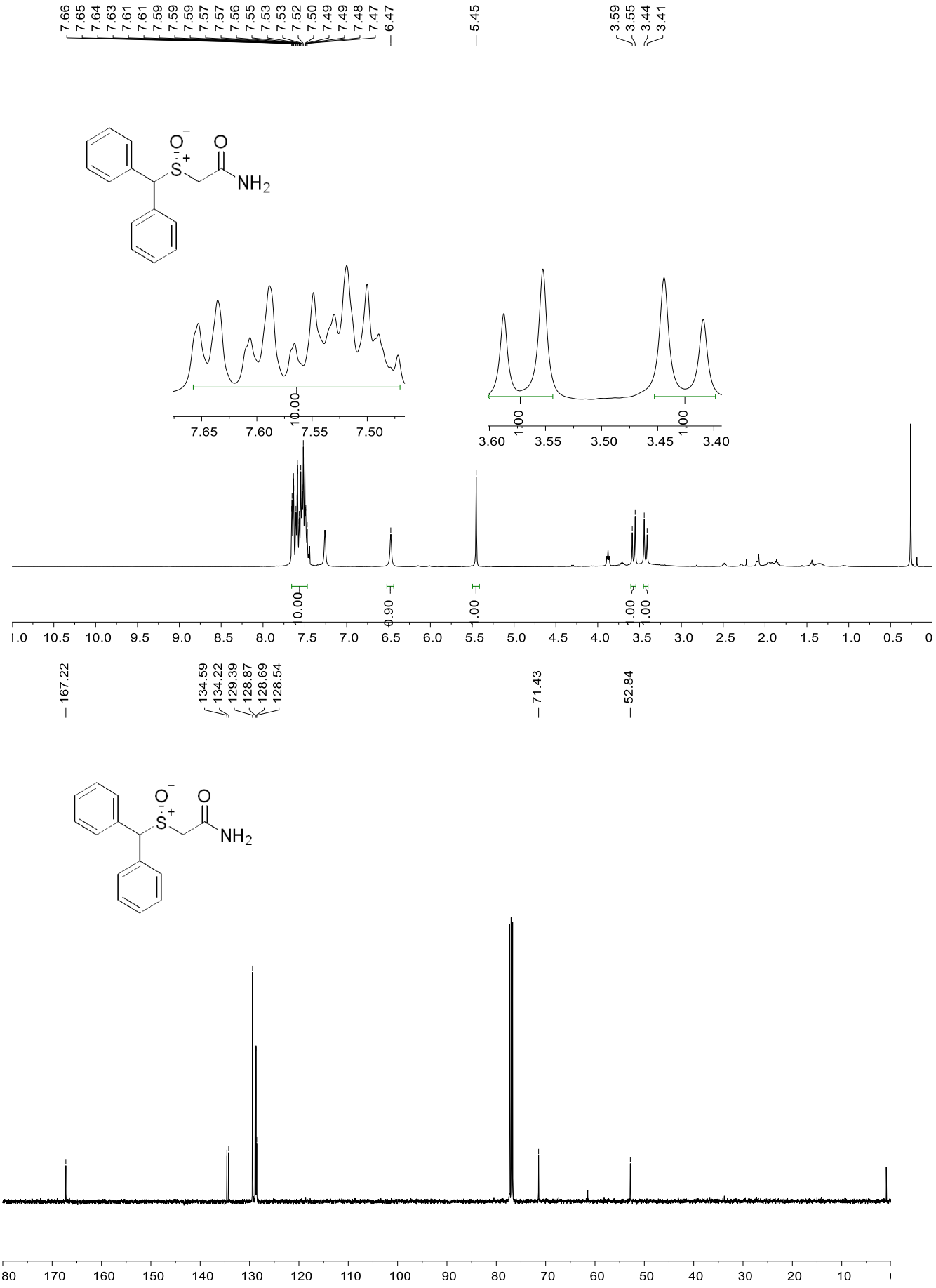


2-(Cyclohexylsulfinyl)-*N*-(4-(trifluoromethoxy)phenyl)acetamide (2ad)

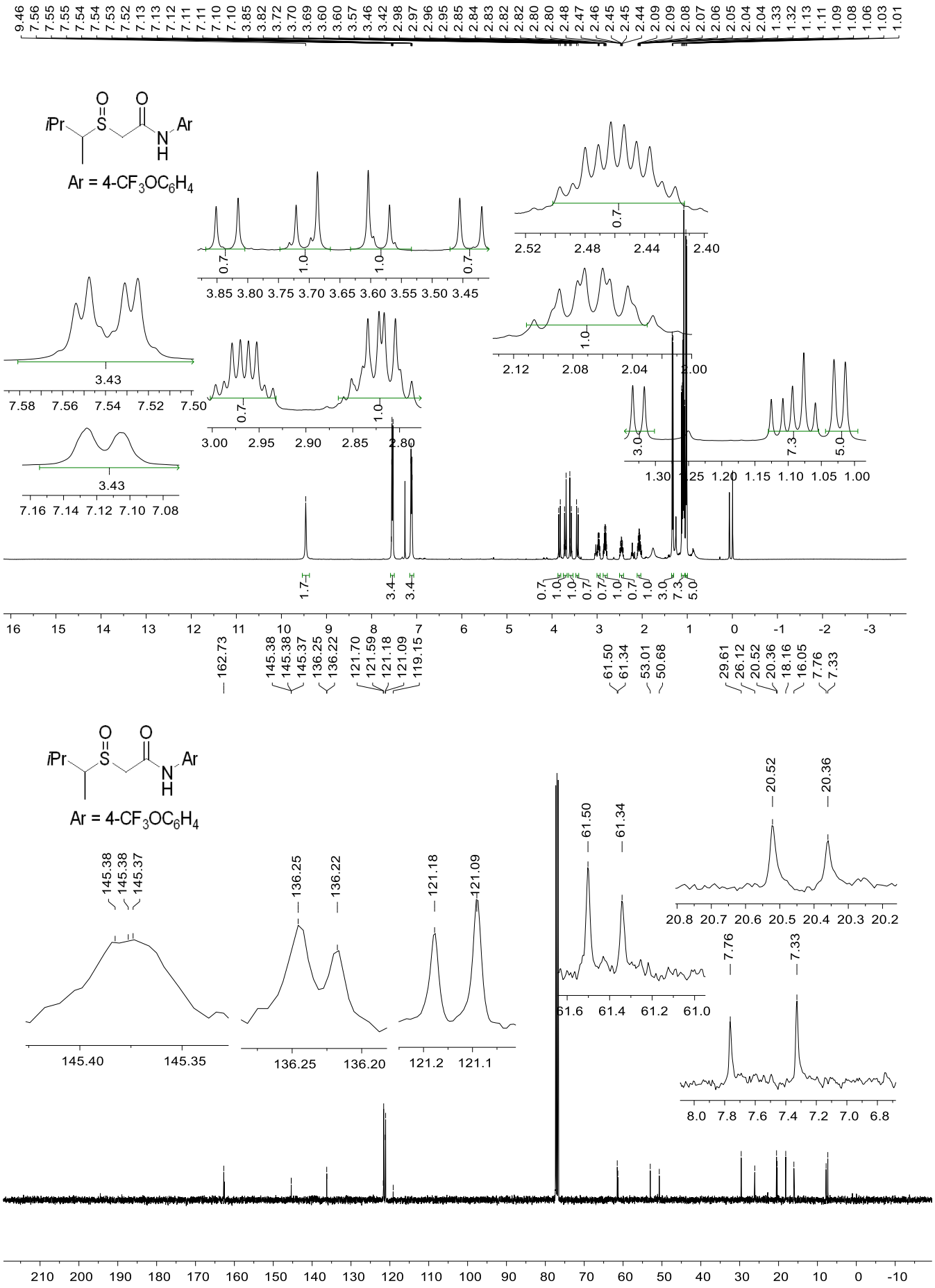


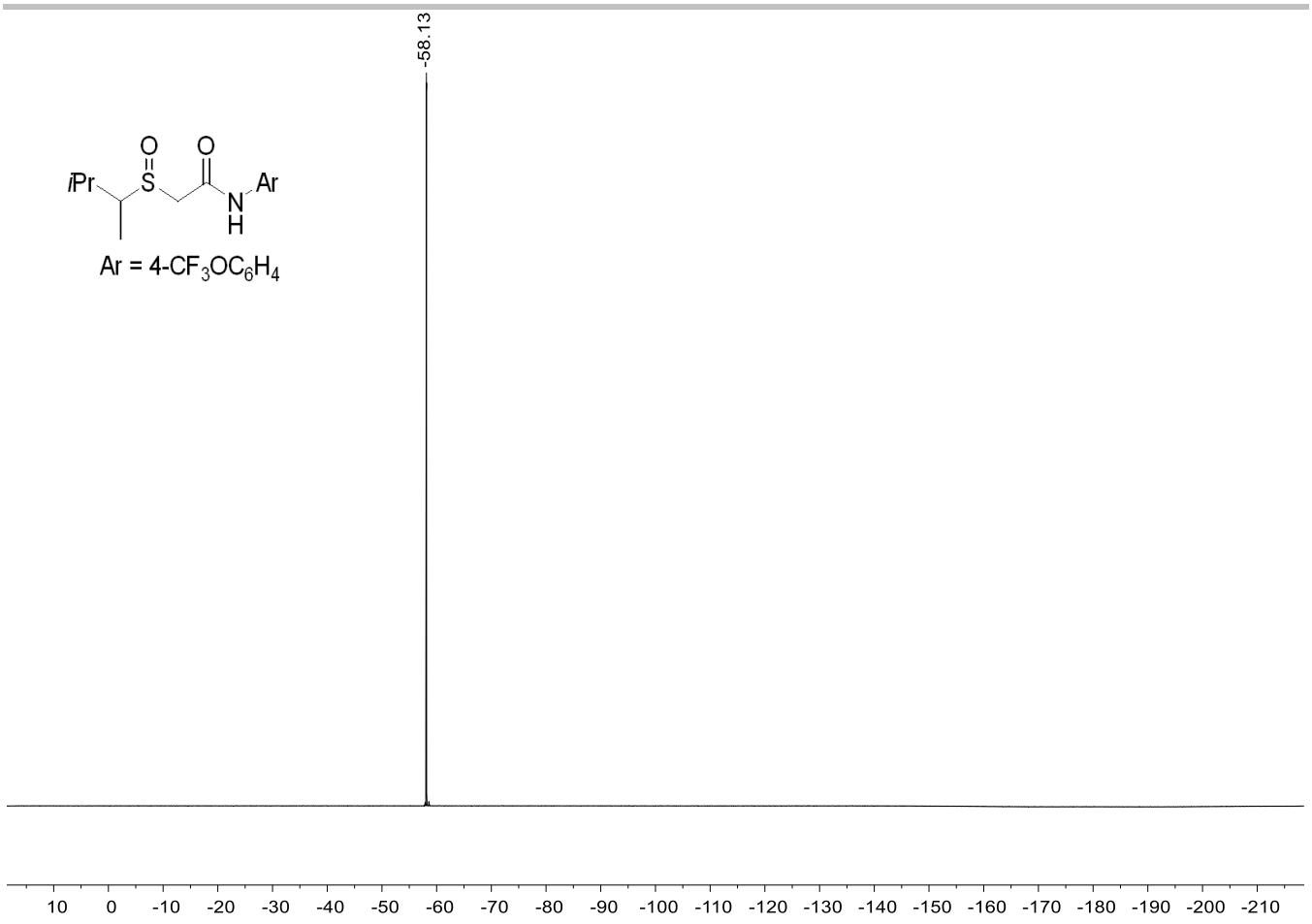

-58.13
Cy
S
O
O
N
H
Ar
Ar = 4-CF3OC6H4
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

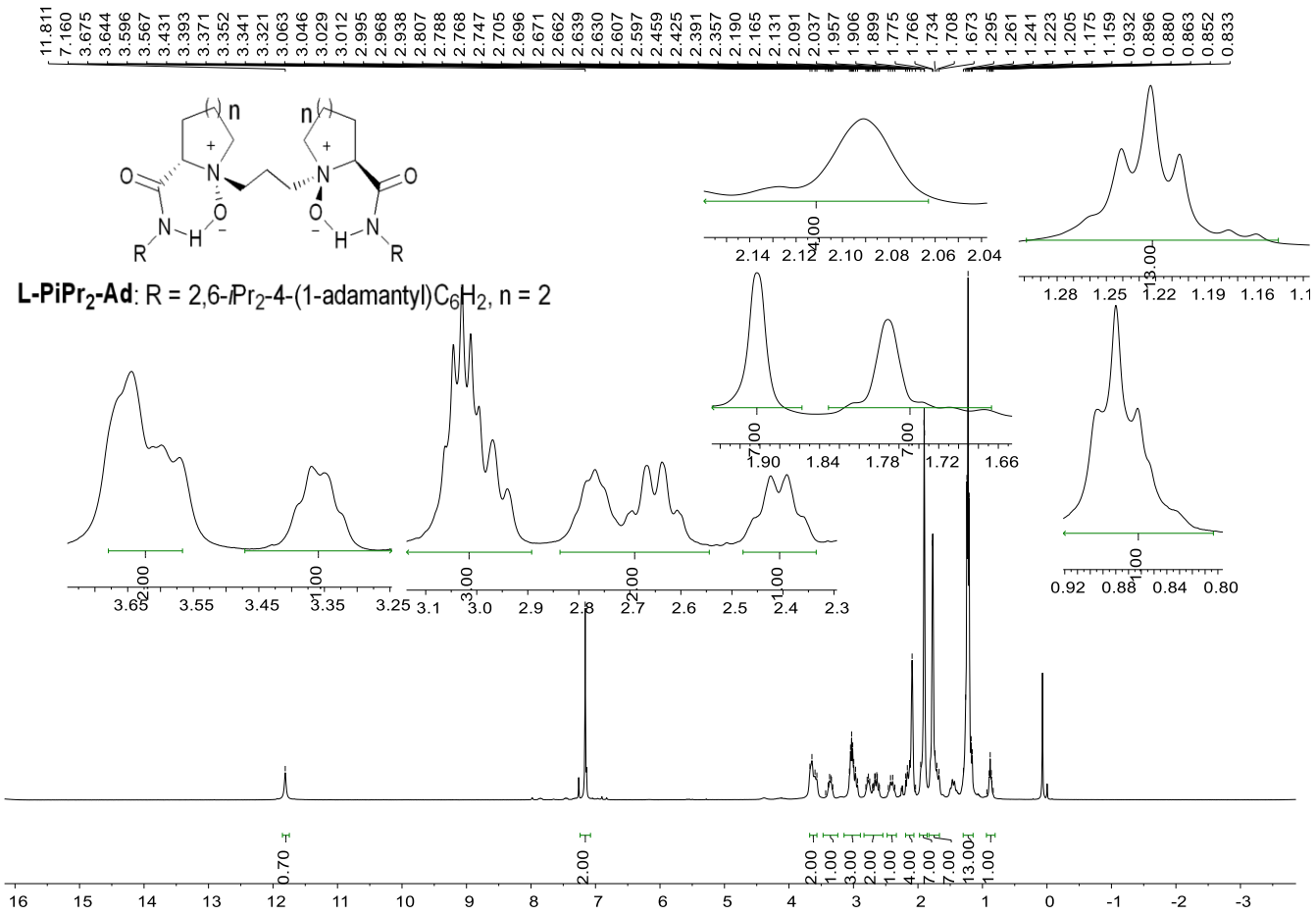
(*R*)-2-(Benzhydrylsulfinyl)acetamide (2ae)



2-((1,2-Dimethylpropanyl)sulfinyl)-*N*-(4-(trifluoromethoxy)phenyl)acetamide (2af)




-58.13
iPr
S
O
O
N
H
Ar
Ar = 4-CF3OC6H4
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


11.811
7.160
3.675
3.644
3.596
3.567
3.431
3.393
3.371
3.352
3.341
3.321
3.063
3.046
3.029
3.012
2.995
2.968
2.938
2.807
2.788
2.768
2.747
2.705
2.696
2.671
2.662
2.639
2.630
2.607
2.597
2.459
2.425
2.391
2.357
2.190
2.165
2.131
2.091
2.037
1.957
1.906
1.899
1.775
1.766
1.734
1.708
1.673
1.295
1.261
1.241
1.223
1.205
1.175
1.159
0.932
0.896
0.880
0.863
0.852
0.833
L-PiPr2-Ad: R = 2,6-iPr2-4-(1-adamantyl)C6H2, n = 2