Supporting Information

CoH-Catalyzed Asymmetric Remote Hydroalkylation of Heterocyclic Alkenes: A Rapid Approach to Chiral Five-Membered S- and O-Heterocycles

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Table of Contents

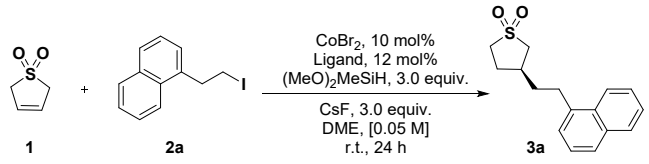
General Information

Unless noted otherwise, all solvents were dried by filtration through a Pure–Solv MD–5 Solvent Purification System (Innovative Technology). Sensitive reagents and solvents were transferred under nitrogen into a nitrogen–filled glovebox with standard techniques. Analytical thin–layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, Leyan chemical). High resolution mass spectra (HRMS) were recorded on Thermo Scientific Exactive Plus (EMR) with a quadrupole mass analyzer. Nuclear magnetic resonance spectra (^{1}H NMR, ^{2}H NMR, ^{13}C NMR and ^{19}F NMR) were recorded with a Bruker Model DMX 500 (500 MHz, ^{1}H at 500 MHz, ^{13}C at 126 MHz,). Chemical shifts were reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ=0.00ppm) and were referenced to residual solvent ($CDCl_3$, δ=7.26 ppm (^{1}H) and 77.00 ppm (^{13}C), or DMSO-d_6, δ=2.50 ppm (^{1}H)). All the ^{19}F chemical shifts were not referenced. Coupling constants were reported in Hertz (Hz). Data for ^{1}H NMR spectra were reported as follows: chemical shift (ppm, referenced to protium, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). Commercially available materials were obtained from Rhawn Corporation, Leyan, Aladdin Bio–Chem Technology or Energy chemical and were used as received.

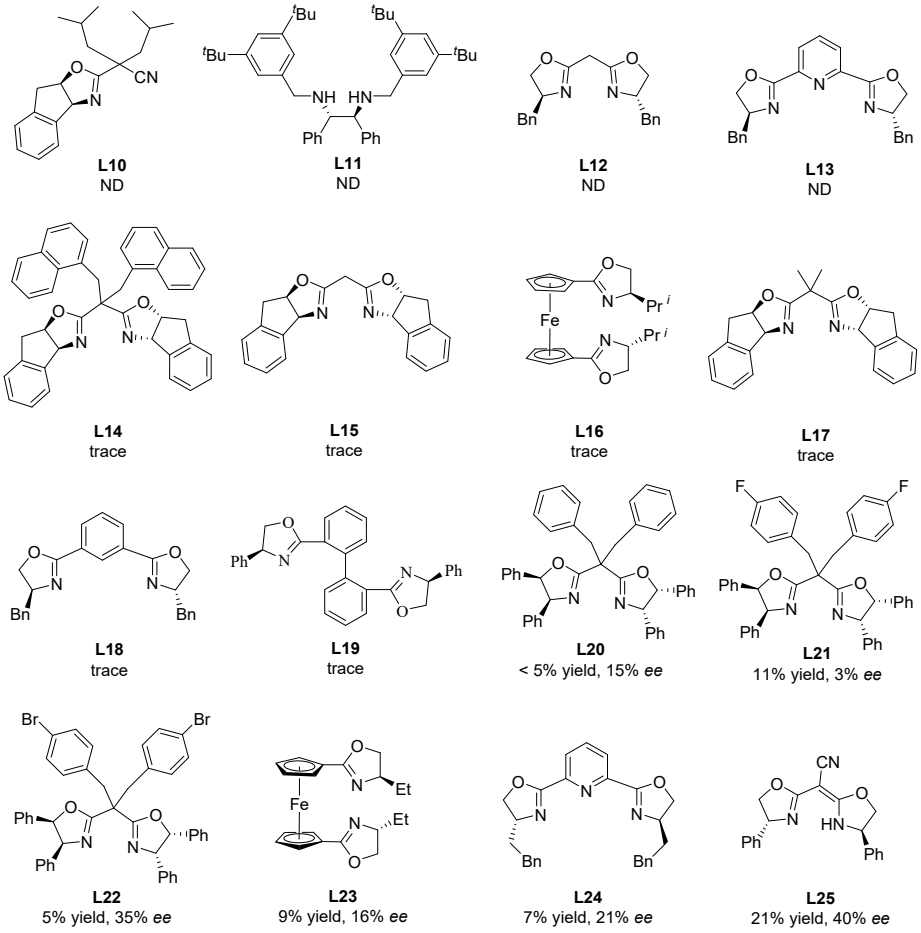
Optimization of the reaction conditions

<u>Cobalt-catalyzed enantioselective hydroalkylation of 2,5-dihydrothiophene 1,1-dioxide:</u>

Table S1. Screening of chiral ligands[a,b,c]



1 2a 3a



L10 ND

L11 ND

L12 ND

L13 ND

L14 trace

L15 trace

L16 trace

L17 trace

L18 trace

L19 trace

L20 < 5% yield, 15% *ee*

L21 11% yield, 3% *ee*

L22 5% yield, 35% *ee*

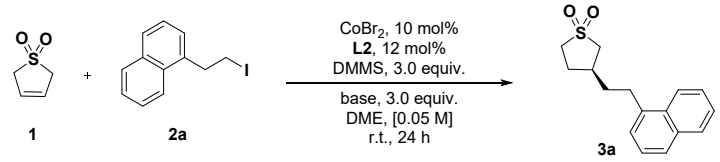
L23 9% yield, 16% *ee*

L24 7% yield, 21% *ee*

L25 21% yield, 40% *ee*

[a]Conditions: **1** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), $CoBr_2$ (10 mol%), Ligand (12 mol%), DMMS (0.3 mmol, 3.0 equiv.), CsF (0.3 mmol, 3.0 equiv.), DME (2.0 mL, 0.05 M), r.t., 24 h. [b]Isolated yields. [c]The enantiomeric ratio were determined by HPLC analysis with a chiral column. Abbreviations: DME, 1,2-dimethoxyethane. DMMS, dimethoxymethylsilane. ND, no detected.

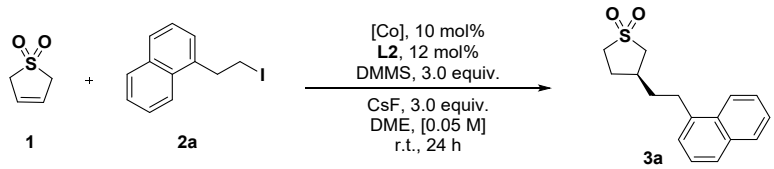
Table S2. Screening of base[a,b,c]



entry	Base	yield (%)	*ee* (%)
1	KF	32	66
2	Cs_2CO_3	28	69
3	K_3PO_4	19	38
4	$K_3PO_4·H_2O$	19	38
5	NaF	trace	-
6	K_2HPO_4	trace	-
7	KH_2PO_4	trace	-

[a]Conditions: **1** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), $CoBr_2$ (10 mol%), Ligand (12 mol%), DMMS (0.3 mmol, 3.0 equiv.), base (0.3 mmol, 3.0 equiv.), DME (2.0 mL, 0.05 M), r.t., 24 h. [b]Isolated yields. [c]The enantiomeric ratio were determined by HPLC analysis with a chiral column. Abbreviations: DME, 1,2-dimethoxyethane. DMMS, dimethoxymethylsilane.

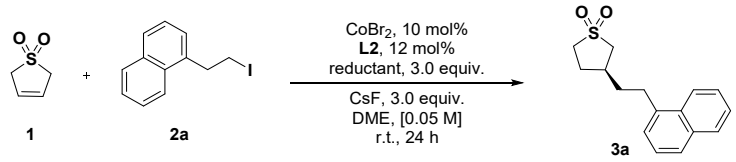
Table S3. Screening of [Co][a,b,c]



entry	[Co]	yield (%)	*ee* (%)
1	CoI_2	33	65
2	$CoBr_2$·glyme	27	56
3	$CoCl_2$	19	27
4	$CoCl_2(PPh_3)_2$	<10	17
5	$Co(OAc)_2$	trace	-
6	Bis(acetylacetonato)cobalt	trace	-
7	$(PPh_3)_3CoCl_2$	trace	-
8	$Co(OAc)_2(H_2O)_4$	trace	-

[a]Conditions: **1** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), [Co] (10 mol%), L2 (12 mol%), DMMS (0.3 mmol, 3.0 equiv.), CsF (0.3 mmol, 3.0 equiv.), DME (2.0 mL, 0.05 M), r.t., 24 h. [b]Isolated yields. [c]The enantiomeric ratio were determined by HPLC analysis with a chiral column. Abbreviations: DME, 1,2-dimethoxyethane. DMMS, dimethoxymethylsilane.

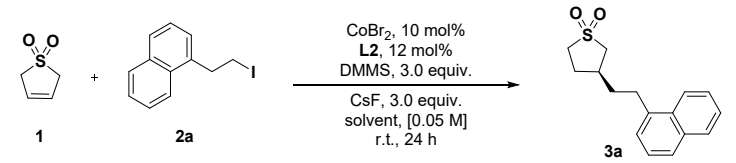
Table S4. Screening of reductant[a,b,c]



entry	reductant	yield (%)	*ee* (%)
1	$(EtO)_2MeSiH$	34	80
2	$(MeO)_3SiH$	23	81
3	$(EtO)_3SiH$	trace	-
4	Me_2PhSiH	trace	-
5	Et_3SiH	trace	-
6	Ph_3SiH	trace	-
7	Cl_3SiH	trace	-
8	HBpin	trace	-

[a]Conditions: **1** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), $CoBr_2$ (10 mol%), L2 (12 mol%), reductant (0.3 mmol, 3.0 equiv.), CsF (0.3 mmol, 3.0 equiv.), DME (2.0 mL, 0.05 M), r.t., 24 h. [b]Isolated yields. [c]The enantiomeric ratio were determined by HPLC analysis with a chiral column. Abbreviations: HBpin, Pinacolborane. DME, 1,2-dimethoxyethane.

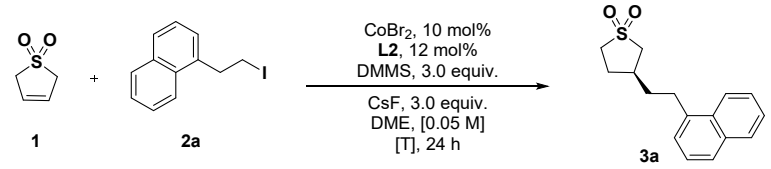
Table S5. Screening of solvent[a,b,c]



entry	solvent	yield (%)	*ee* (%)
1	1,4-dioxane	33	80
2	THF	trace	-
3	CPME	trace	-
4	TBME	trace	-
5	PhOMe	trace	-
6	Isopropyl ether	trace	-

[a]Conditions: **1** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), $CoBr_2$ (10 mol%), L2 (12 mol%), DMMS (0.3 mmol, 3.0 equiv.), CsF (0.3 mmol, 3.0 equiv.), solvent (2.0 mL, 0.05 M), r.t., 24 h. [b]Isolated yields. [c]The enantiomeric ratio were determined by HPLC analysis with a chiral column. Abbreviations: CPME, Cyclopentyl methyl ether. TBME, *tert*-butyl methyl ether. DMMS, dimethoxymethylsilane.

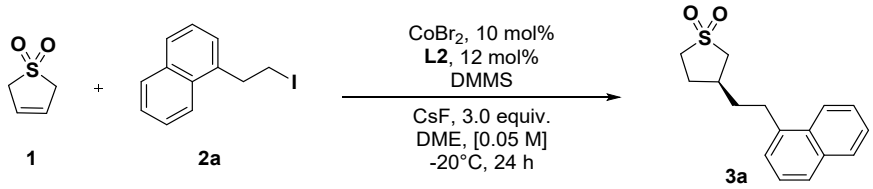
Table S6. Screening of amount of the temperature[a,b,c]



entry	T(°C)	yield (%)	*ee* (%)
1	40	12	52
2	25	39	83
3	0	32	91
4	-20	73	96
5	-40	49	90

[a]Conditions: **1** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), $CoBr_2$ (10 mol%), L2 (12 mol%), DMMS (0.3 mmol, 3.0 equiv), DME (2.0 mL, 0.05 M), T. 24 h. [b]Isolated yields. [c]The enantiomeric ratio were determined by HPLC analysis with a chiral column. Abbreviations: DME, 1,2-dimethoxyethane. DMMS, dimethoxymethylsilane.

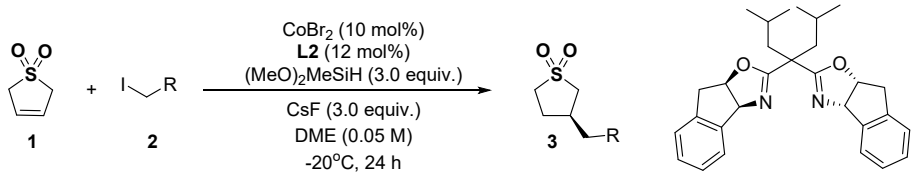
Table S7. Screening of amount of the silane[a,b,c]



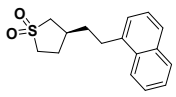
entry	DMMS	yield (%)	*ee* (%)
1	1.0 equiv.	22	92
2	2.0 equiv.	21	92
3	3.0 equiv.	73	96
4	4.0 equiv.	45	93

[a]Conditions: **1** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv), $CoBr_2$ (10 mol%), L2 (12 mol%), CsF (0.3 mmol, 3.0 equiv.), DME (2.0 mL, 0.05 M), -20 °C, 24 h. [b]Isolated yields. [c]The enantiomeric ratio were determined by HPLC analysis with a chiral column. Abbreviations: DME, 1,2-dimethoxyetha. DMMS, dimethoxymethylsilane.

General procedures for cobalt-catalyzed enantioselective hydroalkylation of 2,5-dihydrothiophene 1,1-dioxide



To an oven-dried 10 mL Schlenk tube containing a stirring bar was charged with $CoBr_2$ (4.4 mg, 0.02 mmol, 10 mol%), (*S*, *R*)-**L9** (13.1 mg, 0.024 mmol, 12 mol%) and 2.0 mL dry 1,2-dimethoxyethane in a nitrogen-filled glovebox, the mixture was stirred for 10 min at room temperature. Then 2,5-dihydrothiophene 1,1-dioxide **1** (0.2 mmol, 1.0 equiv.), alkyl iodides **2** (0.4 mmol, 2.0 equiv.), CsF (91.1 mg, 0.6 mmol, 3.0 equiv.) and another 2.0 mL dry 1,2-dimethoxyethane were added sequentially. The tube was sealed and removed from the glovebox, $(MeO)_2MeSiH$ (63.7 mg, 0.6 mmol, 3.0 equiv.) was added dropwise at -20°C and the reaction was stirred at -20 °C for 24 h. After the reaction was completed, the reaction mixture was diluted with saturated NH_4Cl (aq., 2.0 mL) and EtOAc (5 mL). The aqueous phase was extracted with EtOAc (2 × 5 mL). The organic phase was dried over Na_2SO_4, filtered, and the solvent removed in vacuo. The crude mixture was purified by flash column chromatography on silica gel using a mixture of Hexane/EtOAc as eluent to obtain the desired product.



3a

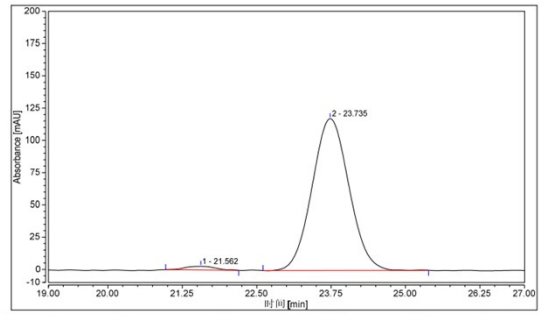
The title compound was synthesized according to general procedure A, the product **3a** was purified by flash column chromatography (PE: EA = 3:1) as a yellow oil（73% yield) with 96% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95-7.93 (m, 1H), 7.88-7.86 (m, 1H), 7.75-7.73 (m, 1H), 7.54-7.47 (m, 2H), 7.42-7.38 (m, 1H), 7.29-7.28 (m, 1H), 3.29 (dd, J = 13.1, 7.6 Hz, 1H), 3.23-3.17 (m, 1H), 3.13-3.10 (m, 2H), 3.05-2.99 (m, 1H), 2.74-2.69 (m, 1H), 2.55-2.44 (m, 1H), 2.41-2.35(m, 1H), 2.00-1.94 (m, 2H), 1.94 – 1.83 (m, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.8, 134.0, 131.5, 129.1, 127.3, 126.1, 126.0, 125.7, 125.6, 123.3, 56.9, 52.2, 36.6, 35.6, 30.9, 29.2.

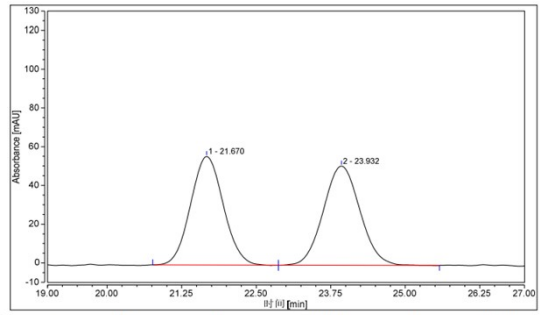
HRMS (ESI): Calculated for ($C_{16}H_{19}O_2S^+$) $[M+H]^+$: 275.1100, found: 275.1100.

$[\alpha]^{25}_D = -14.8^o$ (c = 1.0, $CHCl_3$).

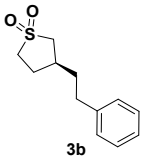
HPLC (UltiMate 3000): Daicel Chiralpak IC Column (*n*-Hexane/*i*-PrOH = 30 : 70, 1.0 mL/min), 30 °C, 220 nm, R*t* = 21.562 min (minor) and 23.735 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	21.562	1.700	2.854	1.97	2.37
2	23.735	84.429	117.622	98.03	97.63



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	21.670	35.693	55.985	49.50	52.25
2	23.932	36.414	51.171	50.50	47.75



3b

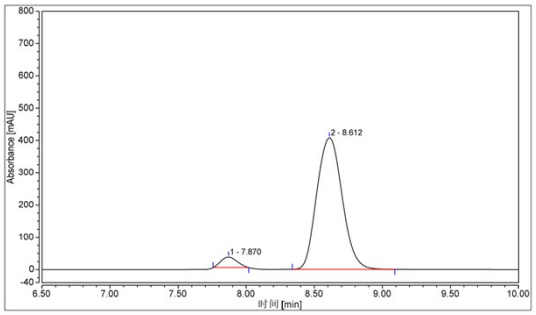
The title compound was synthesized according to general procedure A, the product **3b** was purified by flash column chromatography (PE: EA = 3:1) as a white solid (56% yield) with 90% *ee*. m.p. 49-52 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 2H), 7.23 – 7.20 (m, 1H), 7.18 – 7.12 (m, 2H), 3.27 – 3.15 (m, 2H), 3.04 – 2.97 (m, 1H), 2.70 – 2.63 (m, 3H), 2.45 – 2.31 (m, 2H), 1.90 – 1.81 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.7, 128.7, 128.2, 126.4, 56.9, 52.2, 36.3, 36.2, 33.6, 29.2.

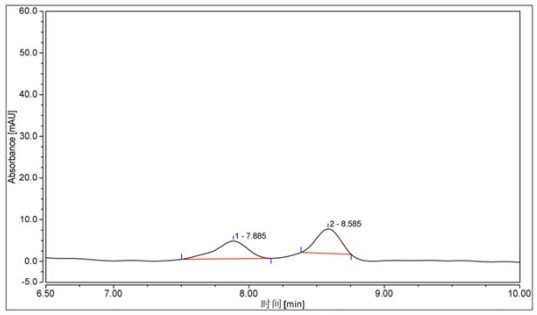
HRMS (ESI): Calculated for ($C_{12}H_{16}NaO_2S^+$) $[M+Na]^+$: 247.0763, found: 247.0767.

$[\alpha]^{25}_D = -12.9^o$ (c = 1.0, $CHCl_3$).

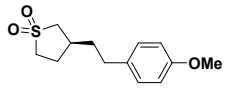
HPLC (UltiMate 3000): Daicel Chiralpak AD-H Column (*n*-Hexane/*i*-PrOH = 80 : 20, 1.0 mL/min), 30 °C, 220 nm, R*t* = 7.870 min (minor) and 8.612 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	7.870	4.517	32.672	4.90	7.43
2	8.612	87.674	407.072	95.10	92.57



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	7.885	1.177	4.233	50.21	41.84
2	8.585	1.167	5.883	49.79	58.16



3c

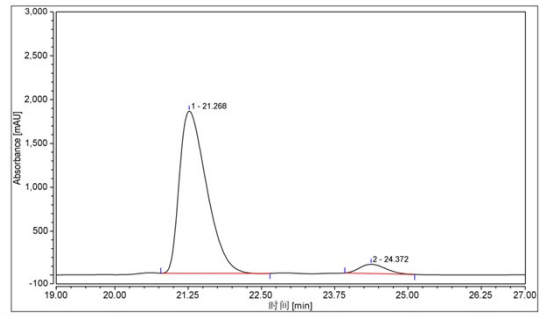
The title compound was synthesized according to general procedure A, the product **3c** was purified by flash column chromatography (PE: EA = 3:1) as a colorless oil (70% yield) with 89% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 – 7.02 (m, 2H), 6.88 – 6.79 (m, 2H), 3.79 (s, 3H), 3.24 – 3.15 (m, 2H), 3.02 – 2.96 (m, 1H), 2.69 – 2.58 (m, 3H), 2.43 – 2.29 (m, 2H), 1.89 – 1.74 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.2, 132.7, 129.1, 114.1, 56.9, 55.3, 52.2, 36.5, 36.1, 32.7, 29.1.

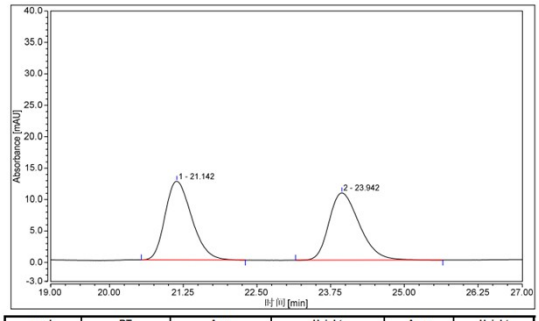
HRMS (ESI): Calculated for ($C_{13}H_{18}NaO_3S^+$) $[M+Na]^+$: 277.0869, found 277.0868.

$[\alpha]^{25}_D$ = −30.2° (c = 1.0, $CHCl_3$).

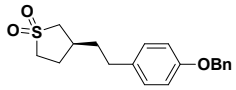
HPLC (UltiMate 3000): Daicel Chiralpak IE Column (*n*-Hexane/*i*-PrOH = 70 : 30, 1.0 mL/min), 30 °C, 220 nm, R*t* = 21.268 min (major) and 24.372 min (minor).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	21.268	990.667	1849.467	94.76	94.58
2	24.372	54.760	105.969	5.24	5.42



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	21.142	6.554	12.509	50.65	53.93
2	23.942	6.387	10.686	49.35	46.07



3d

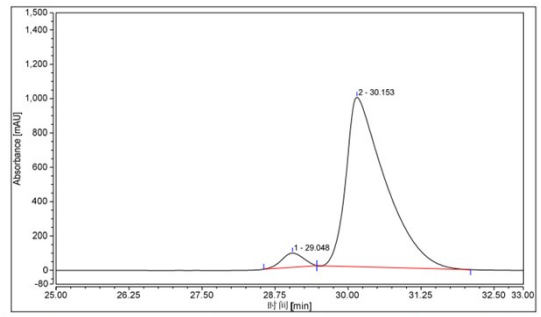
The title compound was synthesized according to general procedure A, the product **3d** was purified by flash column chromatography (PE: EA = 3:1) as a white solid (96% yield) with 91% *ee*. m.p. 102-104 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.1 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.35 – 7.30 (m, 1H), 7.11 – 7.02 (m, 2H), 6.96 – 6.86 (m, 2H), 5.04 (s, 2H), 3.25 – 3.14 (m, 2H), 3.03-2.97 (m, 1H), 2.69 – 2.55 (m, 3H), 2.44 – 2.29 (m, 2H), 1.87-1.78 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.4, 137.1, 133.0, 129.2, 128.6, 128.0, 127.5, 115.1, 70.1, 56.9, 52.2, 36.5, 36.2, 32.7, 29.2.

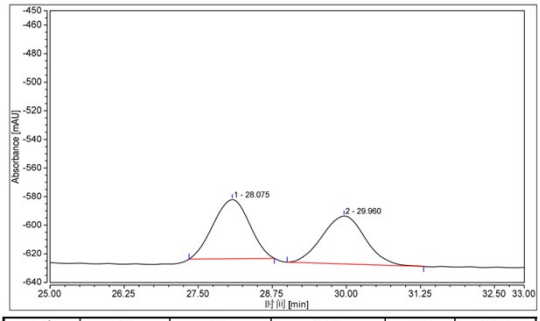
HRMS (ESI): Calculated for ($C_{19}H_{22}NaO_3S^+$) $[M+Na]^+$: 353.1182, found 353.1191.

$[\alpha]^{25}_D$ = -101.2 (c = 1.0, $CHCl_3$).

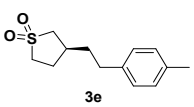
HPLC (UltiMate 3000): Daicel Chiralpak IF-3 Column (*n*-Hexane/*i*-PrOH = 70 : 30, 1.0 mL/min), 30 °C, 220 nm, R*t* = 29.048 min (minor) and 30.153 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	29.048	35.870	82.923	4.43	7.75
2	30.153	773.887	986.970	95.57	92.25



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	28.075	29.380	41.303	51.03	55.22
2	29.960	28.195	33.499	48.97	44.78



3e

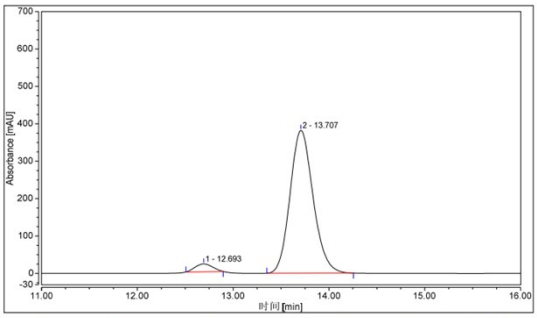
The title compound was synthesized according to general procedure A, the product **3e** was purified by flash column chromatography (PE: EA = 3:1) as a yellow solid (60% yield) with 92% *ee*. m.p. 88-90 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, J = 7.8 Hz, 2H), 7.04 (d, J = 7.7 Hz, 2H), 3.27-3.11 (m, 2H), 3.02-2.96 (m, 1H), 2.70-2.56 (m, 3H), 2.43-2.37 (m, 1H), 2.32 (s, 4H), 1.88-1.79 (m, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.5, 135.9, 129.3, 128.1, 56.9, 52.2, 36.4, 36.2, 33.2, 29.1, 21.0.

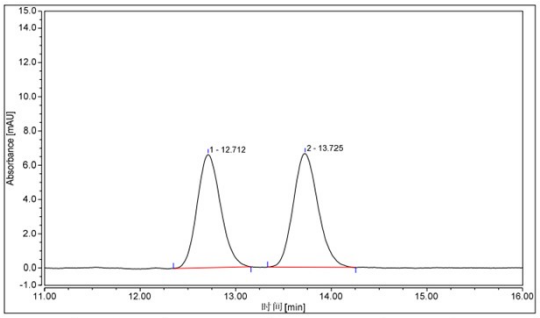
HRMS (ESI): Calculated for ($C_{13}H_{18}NaO_2S^+$) $[M+Na]^+$: 261.0920, found 261.0929.

$[\alpha]^{25}_D$ = –20.3° (c = 1.0, $CHCl_3$).

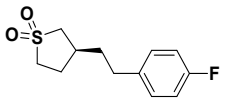
HPLC (UltiMate 3000): Daicel Chiralpak AD-H Column (*n*-Hexane/*i*-PrOH = 90 : 10, 1.0 mL/min), 30 °C, 220 nm, R*t* = 12.693 min (minor) and 13.707 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	12.693	4.366	20.878	3.94	5.18
2	13.707	106.552	381.789	96.06	94.82



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	12.712	1.880	6.606	48.45	49.87
2	13.725	2.000	6.640	51.55	50.13



3f

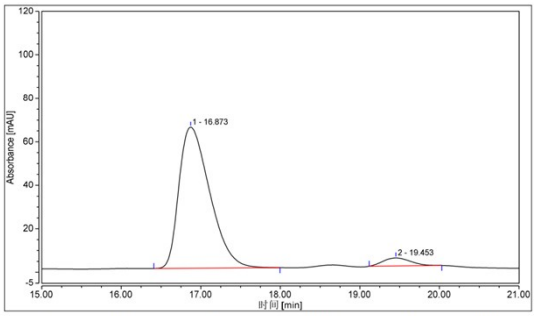
The title compound was synthesized according to general procedure A, the product **3f** was purified by flash column chromatography (PE: EA = 3:1) as a yellow oil (56% yield) with 91% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 8.4, 5.3 Hz, 2H), 6.98 (t, *J* = 8.5 Hz, 2H), 3.29 – 3.15 (m, 2H), 3.04-2.98 (m, 1H), 2.72 – 2.59 (m, 3H), 2.46 – 2.30 (m, 2H), 1.88-1.79 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.5 (d, *J* = 244.5 Hz), 136.3 (d, *J* = 3.1 Hz), 129.6 (d, *J* = 7.8 Hz), 115.4 (d, *J* = 21.2 Hz), 56.8, 52.2, 36.4, 36.2, 32.8, 29.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.8.

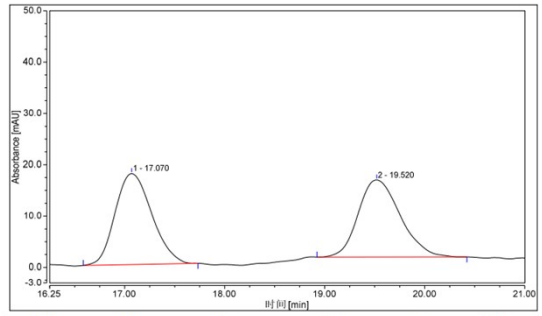
HRMS (ESI): Calculated for ($C_{12}H_{15}NaFO_2S^+$) $[M+Na]^+$: 265.0669, found 265.0674.

$[\alpha]^{25}_D$ = –11.2° (c = 1.0, $CHCl_3$).

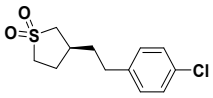
HPLC (UltiMate 3000): Daicel Chiralpak IE Column (*n*-Hexane/*i*-PrOH = 70 : 30, 1.0 mL/min), 30 °C, 220 nm, R*t* = 16.873 min (major) and 19.453 min (minor).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	16.873	29.127	64.905	95.21	94.62
2	19.453	1.466	3.688	4.79	5.38



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	17.070	7.522	17.706	50.71	54.09
2	19.520	7.312	15.027	49.29	45.91



3g

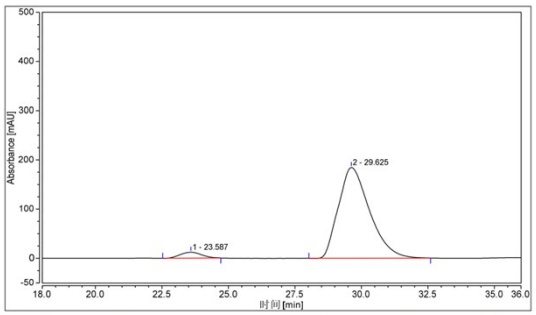
The title compound was synthesized according to general procedure A, the product **3g** was purified by flash column chromatography (PE: EA = 3:1) as a white solid (46% yield) with 91% *ee*. m.p. 101-103 ^{o}C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 3.26 – 3.17 (m, 2H), 3.05 – 2.97 (m, 1H), 2.71 – 2.61 (m, 3H), 2.44 – 2.33 (m, 2H), 1.92 – 1.78 (m, 3H). 2.71 – 2.48 (m, 2H), 2.30 – 1.98 (m, 2H), 1.80 – 1.75 (m, 1H), 1.71 – 1.51 (m, 2H), 1.30 (d, *J* = 11.3 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.2, 137.5, 127.9, 125.6, 56.9, 52.3, 36.2, 34.4, 33.1, 29.1.

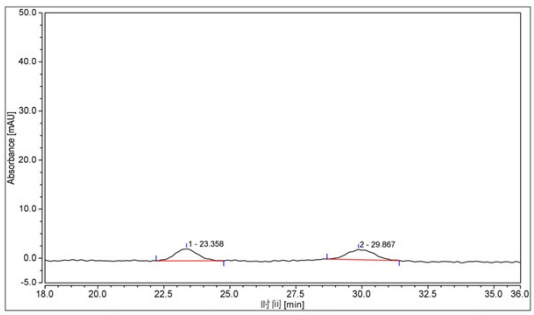
HRMS (ESI): Calculated for ($C_{12}H_{16}ClO_2S^+$) $[M+H]^+$: 259.0554, found 259.0556.

$[\alpha]^{25}_{D}$ = –2.9^{o} (c = 1.0, $CHCl_3$).

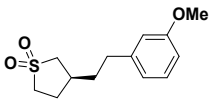
HPLC (UltiMate 3000): Daicel Chiralcel OD-H Column (*n*-Hexane/*i*-PrOH = 90 : 10, 1.0 mL/min), 30 ^{o}C, 220 nm, R*t* = 23.587 min (minor) and 29.625 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	23.587	11.337	12.057	4.33	6.14
2	29.625	250.555	184.361	95.67	93.86



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	23.358	2.437	2.438	49.88	54.25
2	29.867	2.449	2.056	50.12	45.75



3h

The title compound was synthesized according to general procedure A, the product **3h** was purified by flash column chromatography (PE: EA = 3:1) as a yellow oil (70% yield) with 93% *ee*.

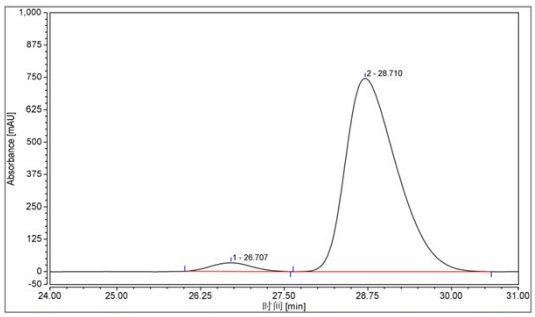
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.9 Hz, 1H), 6.79 – 6.72 (m, 2H), 6.70 (t, *J* = 2.1 Hz, 1H), 3.80 (s,

3H), 3.25-3.17 (m, 2H), 3.06 – 2.93 (m, 1H), 2.66 – 2.61 (m, 2H), 2.48 – 2.38 (m, 1H), 2.38 – 2.32 (m, 1H), 1.89 – 1.81 (m, 3H), 1.30 – 1.21 (m, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 142.3, 129.7, 120.6, 114.2, 111.4, 56.9, 55.2, 52.2, 36.2, 36.1, 33.6, 29.1.

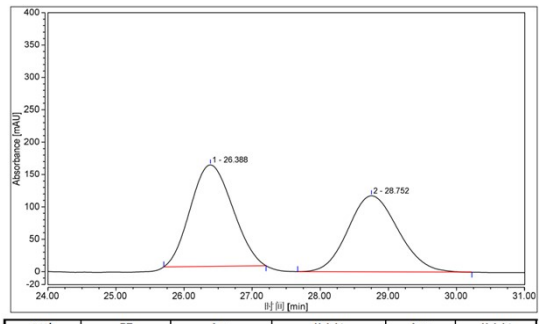
HRMS (ESI): Calculated for ($C_{13}H_{19}O_3S^+$) $[M+H]^+$: 255.1049, found 255.1057.

$[\alpha]^{25}_D$ = –15.1° (c = 1.0, $CHCl_3$).

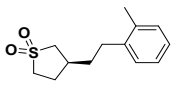
HPLC (UltiMate 3000): Daicel Chiralpak IC Column (*n*-Hexane/*i*-PrOH = 70 : 30, 1.0 mL/min), 30 °C, 220 nm, R*t* = 26.707 min (minor) and 28.710 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	26.707	23.603	33.148	3.43	4.25
2	28.710	663.647	746.631	96.57	95.75



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	26.388	112.394	156.773	52.83	57.16
2	28.752	100.357	117.481	47.17	42.84



3i

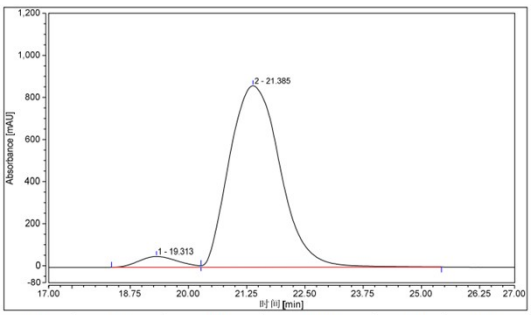
The title compound was synthesized according to general procedure A, the product **3i** was purified by flash column chromatography (PE: EA = 3:1) as a yellow oil (54% yield) with 91% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15-7.12 (m, 3H), 7.08 (dd, *J* = 6.6, 2.5 Hz, 1H), 3.30 – 3.26 (m, 1H), 3.24-3.19 (m, 1H), 3.07-3.01 (m, 1H), 2.74 – 2.62 (m, 3H), 2.52 – 2.44 (m, 1H), 2.42 – 2.36 (m, 1H), 2.30 (s, 3H), 1.93 – 1.83 (m, 1H), 1.81 – 1.78 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.9, 135.6, 130.5, 128.6, 126.5, 126.2, 56.9, 52.2, 36.7, 35.1, 31.1, 29.2, 19.3.

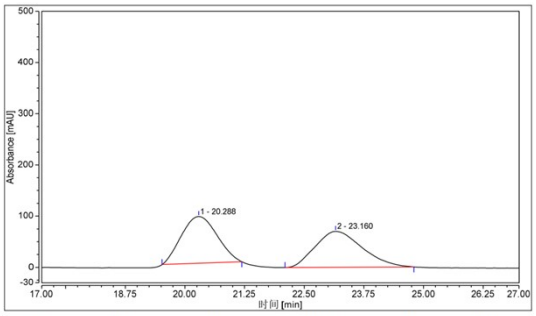
HRMS (ESI): Calculated for ($C_{13}H_{18}NaO_2S^+$) $[M+Na]^+$: 261.0920, found 261.0925.

$[\alpha]^{25}_D$ = –9.2° (c = 1.0, $CHCl_3$).

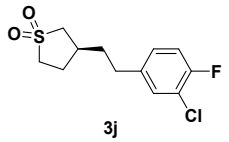
HPLC (UltiMate 3000): Daicel Chiralcel OD-H Column (*n*-Hexane/*i*-PrOH = 70 : 30, 1.0 mL/min), 30 °C, 220 nm, R*t* = 19.313 min (minor) and 21.385 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	19.313	49.607	51.148	4.36	5.60
2	21.385	1088.548	861.928	95.64	94.40



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	20.288	79.199	91.253	49.69	56.53
2	23.160	80.200	70.160	50.31	43.47



3j

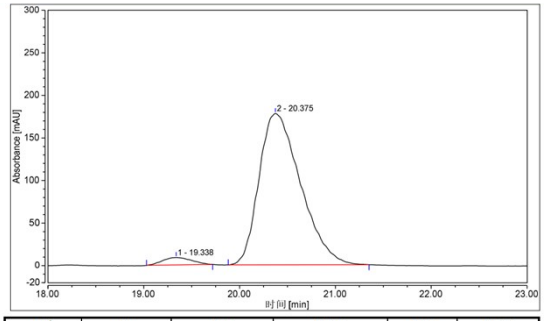
The title compound was synthesized according to general procedure A, the product **3j** was purified by flash column chromatography (PE: EA = 3:1) as a yellow solid (46% yield) with 93% *ee*. m.p. 67-69 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 7.0, 2.2 Hz, 1H), 7.07 (t, *J* = 8.6 Hz, 1H), 7.02-6.99 (m, 1H), 3.27 – 3.19 (m, 2H), 3.06-3.00 (m, 1H), 2.69 (dd, *J* = 13.0, 10.5 Hz, 1H), 2.64 – 2.60 (m, 2H), 2.44 – 2.34 (m, 2H), 1.98 – 1.72 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.8 (d, *J* = 247.4 Hz), 137.7 (d, *J* = 3.9 Hz), 130.2, 127.8 (d, *J* = 6.9 Hz), 121.0 (d, *J* = 17.8 Hz), 116.7 (d, *J* = 20.9 Hz), 56.7, 52.1, 36.1, 36.1, 32.6, 29.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -119.0.

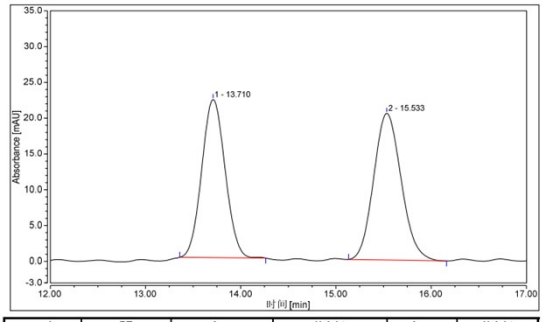
HRMS (ESI): Calculated for ($C_{12}H_{14}NaClFO_2S^+$) $[M+Na]^+$: 299.0279, found 299.0288.

$[\alpha]^{25}_D$ = –6.8° (c = 1.0, $CHCl_3$).

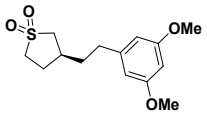
HPLC (UltiMate 3000): Daicel Chiralpak IB N-5 Column (*n*-Hexane/*i*-PrOH = 70: 30, 1.0 mL/min), 30 °C, 220 nm, R*t* = 19.338 min (minor) and 20.375 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	19.338	3.042	8.673	3.30	4.66
2	20.375	89.148	177.631	96.70	95.34



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	13.710	6.299	22.095	47.81	51.88
2	15.533	6.875	20.491	52.19	48.12



3k

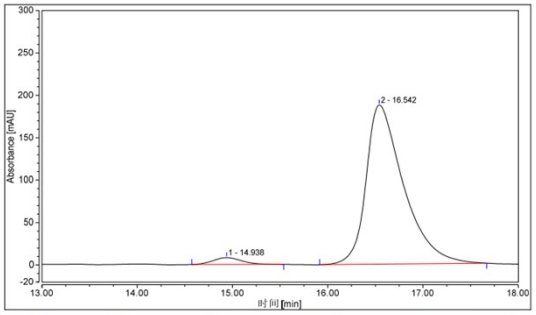
The title compound was synthesized according to general procedure A, the product **3k** was purified by flash column chromatography (PE: EA = 3:1) as a yellow oil (63% yield) with 93% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.39 – 6.26 (m, 3H), 3.78 (s, 6H), 3.16 (s, 2H), 3.04-2.98 (m,1H), 2.67 (dd, *J* = 13.1, 10.6 Hz, 1H), 2.64 – 2.55 (m, 2H), 2.47 – 2.30 (m, 2H), 1.90 – 1.78 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.0, 143.0, 106.5, 98.0, 56.8, 55.3, 52.2, 36.2, 36.0, 33.9, 29.1.

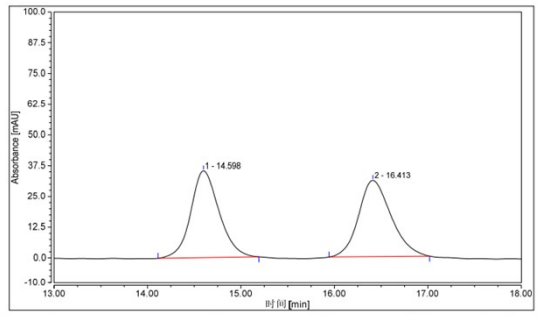
HRMS (ESI): Calculated for ($C_{14}H_{14}NaO_4S^+$) $[M+Na]^+$: 307.0975, found 307.0984

$[\alpha]^{25}_D$ = –18.5° (c = 1.0, $CHCl_3$).

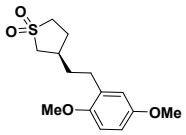
HPLC (UltiMate 3000): Daicel Chiralpak IA Column (*n*-Hexane/*i*-PrOH = 80 : 20, 1.0 mL/min), 30 °C, 220 nm, R*t* = 14.938 min (minor) and 16.542 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	14.938	2.804	8.046	3.17	4.11
2	16.542	85.603	187.689	96.83	95.89



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	14.598	12.438	35.275	49.81	53.22
2	16.413	12.535	31.000	50.19	46.78



3l

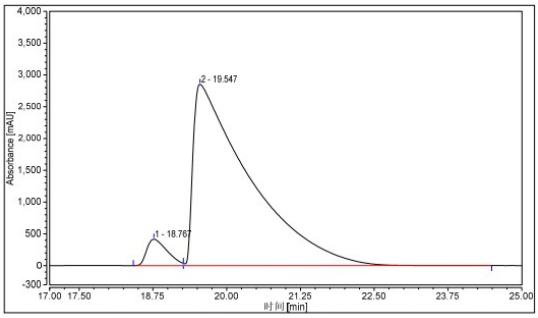
The title compound was synthesized according to general procedure A, the product **3l** was purified by flash column chromatography (PE: EA = 3:1) as a yellow oil (56% yield) with 90% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (d, *J* = 8.8 Hz, 1H), 6.75 – 6.64 (m, 2H), 3.77 (d, *J* = 9.6 Hz, 6H), 3.33 – 3.24 (m, 1H), 3.21 – 3.16 (m, 1H), 3.04 – 2.97 (m, 1H), 2.70 – 2.57 (m, 3H), 2.46 – 2.30 (m, 2H), 1.89 – 1.74 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.5, 151.6, 130.4, 116.4, 111.20, 111.18, 57.0, 55.8, 55.7, 52.3, 36.4, 35.0, 29.2, 28.1.

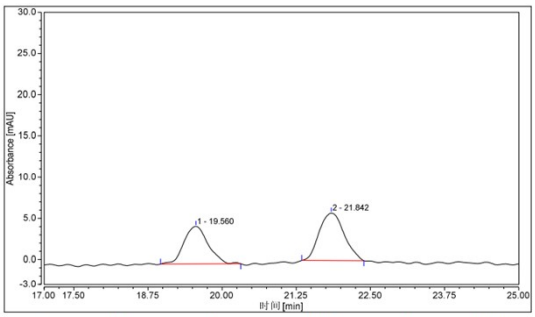
HRMS (ESI): Calculated for ($C_{14}H_{21}O_4S^+$) $[M+H]^+$: 285.1155, found 285.1163.

$[\alpha]^{25}_D$ = –21.6° (c = 1.0, $CHCl_3$).

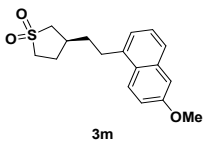
HPLC (UltiMate 3000): Daicel Chiralpak IB N-5 Column (*n*-Hexane/*i*-PrOH = 70 : 30, 1.0 mL/min), 30 °C, 220 nm, R*t* = 18.757 min (minor) and 19.547 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	18.767	165.818	414.843	5.00	12.71
2	19.547	3153.675	2850.130	95.00	87.29



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	19.560	2.164	4.566	43.45	44.20
2	21.842	2.816	5.764	56.55	55.80



3m

The title compound was synthesized according to general procedure A, the product **3m** was purified by flash column chromatography (PE: EA = 3:1) as a white solid (71% yield) with 92% *ee*. m.p. 96-98

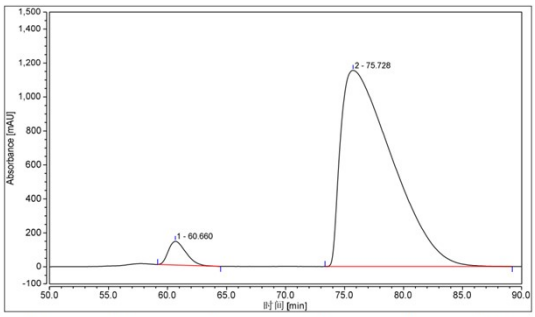
°C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.99(m, 2H), 7.51 (d, *J* = 1.7 Hz, 1H), 7.17 – 7.08 (m, 2H), 3.91 (s, 3H), 3.27 – 3.14 (m, 2H), 3.02-2.96 (m, 1H), 2.78 (t, *J* = 7.7 Hz, 2H), 2.69 (dd, *J* = 13.1, 10.7 Hz, 1H), 2.50 – 2.38 (m, 1H), 2.37-2.32 (m, , 1H), 1.93-1.94 (m, 3H), 1.25 (d, *J* = 3.3 Hz, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.4, 135.8, 133.2, 129.1, 128.9, 127.3, 127.2, 126.3, 119.0, 105.7, 56.9, 55.3, 52.2, 36.3, 36.2, 33.6, 29.2.

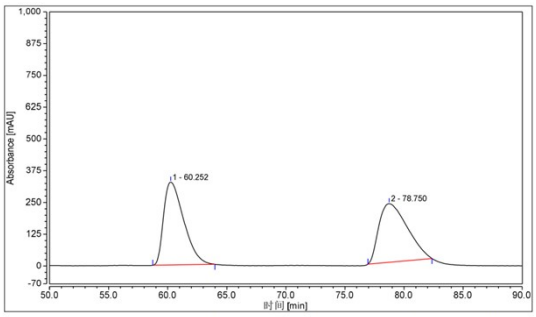
HRMS (ESI): Calculated for ($C_{17}H_{20}NaO_3S^+$) $[M+Na]^+$: 327.1025, found 327.1024.

$[\alpha]^{25}_D$ = –81.0° (c = 1.0, $CHCl_3$).

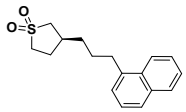
HPLC (UltiMate 3000): Daicel Chiralpak IH-3 Column (*n*-Hexane/*i*-PrOH = 70 : 30, 1.0 mL/min), 30 °C, 220 nm, R*t* = 60.660 min (major) and 75.728 min (minor).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	60.660	239.315	139.110	3.93	10.75
2	75.728	5845.689	1155.158	96.07	89.25



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	60.252	643.729	326.367	50.09	58.60
2	78.750	641.318	230.559	49.91	41.40



3n

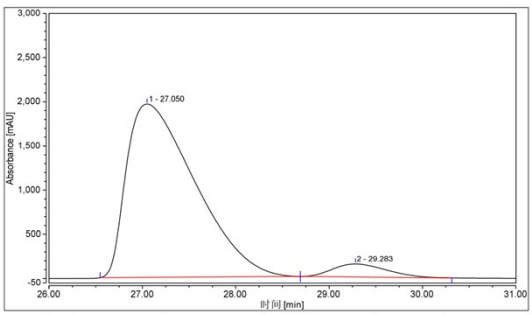
The title compound was synthesized according to general procedure A, the product **3n** was purified by flash column chromatography (PE: EA = 3:1) as a white solid (52% yield) with 89% *ee*. m.p. 63-65 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 3.25 – 3.14 (m, 2H), 3.09 (t, *J* = 7.6 Hz, 2H), 3.03 - 2.97 (m, 1H), 2.64 (dd, *J* = 13.0, 10.8 Hz, 1H), 2.44 - 2.40 (m, 1H), 2.32 - 2.28 (m, 1H), 1.84 -1.75 (m, 3H), 1.64 – 1.58 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.6, 134.0, 131.7, 128.9, 126.9, 126.0, 125.9, 125.6, 125.5, 123.5, 57.0, 52.3, 36.8, 34.5, 32.8, 29.1, 28.5.

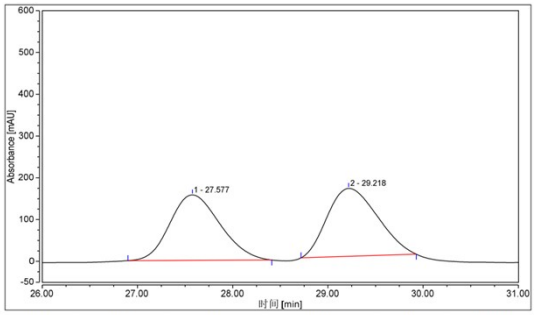
HRMS (ESI): Calculated for ($C_{17}H_{20}NaO_2S^+$) $[M+Na]^+$: 311.1076, found 311.1086.

$[\alpha]^{25}_D$ = –13.7° (c = 1.0, $CHCl_3$).

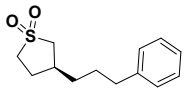
HPLC (UltiMate 3000): Daicel Chiralpak IH-3 Column (*n*-Hexane/*i*-PrOH = 70 : 30, 1.0 mL/min), 30 °C, 220 nm, R*t* = 9.682 min (major) and 11.195 min (minor).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	27.050	1667.887	1962.499	94.41	93.01
2	29.283	98.796	147.472	5.59	6.99



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	27.577	95.341	156.625	49.11	49.05
2	29.218	98.795	162.712	50.89	50.95



3o

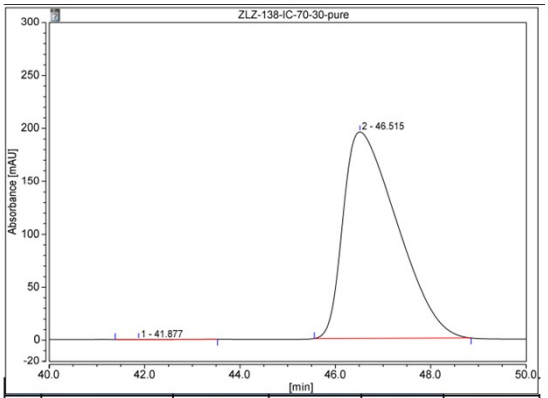
The title compound was synthesized according to general procedure A, the product **3o** was purified by flash column chromatography (PE: EA = 1:1) as a colorless oil (84% yield) with 99% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.18 (m, 1H), 7.15 (d, *J* = 7.0 Hz, 2H), 3.24 – 3.15 (m, 2H), 3.05 – 2.98 (m, 1H), 2.67v2.60 (m, 3H), 2.46-2.38 (m, 1H), 2.36 – 2.29 (m, 1H), 1.84 – 1.75 (m, 1H), 1.69 – 1.60 (m, 2H), 1.55 – 1.49 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.5, 128.5, 128.3, 126.1, 57.0, 52.3, 36.8, 35.6, 34.1, 29.1.

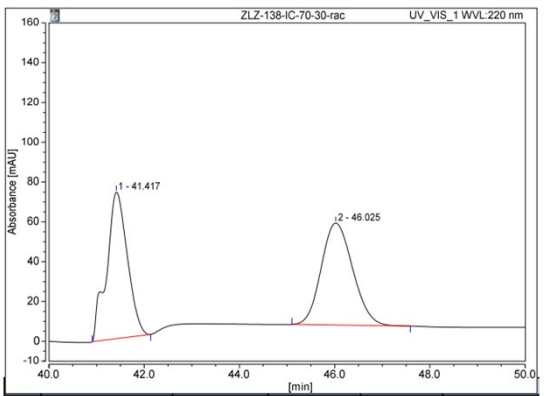
HRMS (ESI): Calculated for ($C_{13}H_{19}O_2S^+$) $[M+H]^+$: 239.1100, found 239.1108.

$[\alpha]^{25}_D$ = –-21.6° (c = 1.0, $CHCl_3$).

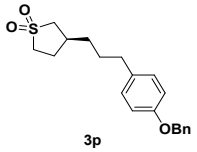
HPLC (UltiMate 3000): Daicel Chiralpak IC Column (*n*-Hexane/*i*-PrOH = 70 : 30, 1.0 mL/min), 30 °C, 220 nm, R*t* = 41.877 min (minor) and 46.515 min (major).



Peak	RT min	Area mAU*min	HEIGHT mAU	Area %	Height %
1	41.877	0.128	0.064	0.05	0.03
2	46.515	255.164	194.955	99.95	99.97



Peak	RT min	Area mAU*min	HEIGHT mAU	Area %	Height %
1	41.417	37.143	73.689	48.68	59.00
2	46.025	39.153	51.204	51.32	41.00



3p

The title compound was synthesized according to general procedure A, the product **3p** was purified by

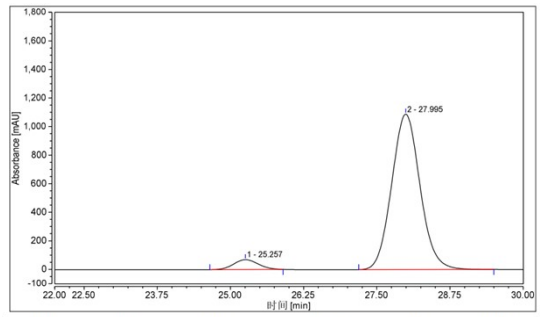
flash column chromatography (PE: EA = 3:1) as a white solid (74% yield) with 89% *ee*. m.p. 60-62 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.44 (m, 2H), 7.44-7.38 (m, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 5.07 (s, 2H), 3.27-3.18 (m, 2H), 3.07-3.00 (m, 1H), 2.70-2.56 (m, 3H), 2.45-2.40 (m, 1H), 2.38-2.28 (m, 1H), 1.84-1.77 (m, 1H), 1.68-1.62 (m, 2H), 1.56-1.50 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.2, 137.2, 133.9, 129.3, 128.6, 128.0, 127.5, 114.9, 70.1, 57.0, 52.4, 36.8, 34.7, 34.0, 29.3, 29.1.

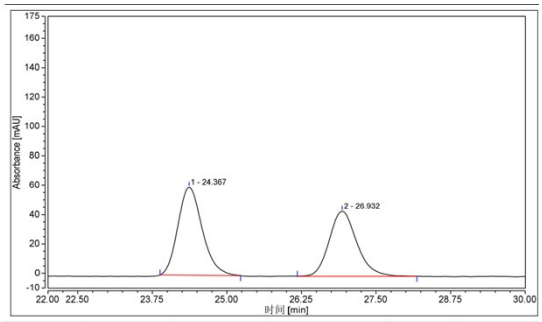
HRMS (ESI): Calculated for ($C_{20}H_{24}NaO_3S^+$) $[M+Na]^+$: 367.1338 found 367.1347.

$[\alpha]^{25}_D$ = –25.4° (c = 1.0, $CHCl_3$).

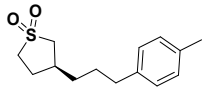
HPLC (UltiMate 3000): Daicel Chiralpak IG-3 Column (*n*-Hexane/*i*-PrOH = 90 : 10, 1.0 mL/min), 30 °C, 220 nm, R*t* = 25.257 min (minor) and 27.995 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	25.257	33.871	69.152	5.24	5.97
2	27.995	612.558	1088.618	94.76	94.03



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	24.367	28.338	59.870	54.33	57.47
2	26.932	23.818	44.310	45.67	42.53



3q

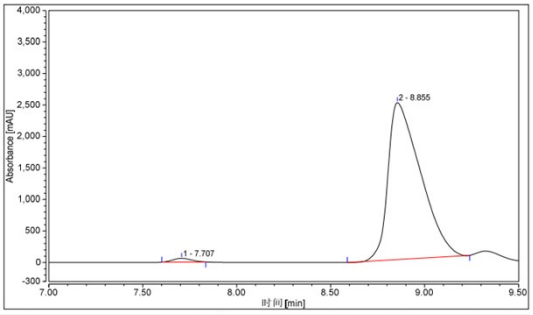
The title compound was synthesized according to general procedure A, the product **3q** was purified by flash column chromatography (PE: EA = 3:1) as a yellow oil (65% yield) with 97% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.7 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 3.25 – 3.15 (m, 2H), 3.04 – 2.98 (m, 1H), 2.65 – 2.56 (m, 3H), 2.45 – 2.36 (m, 1H), 2.32 (s, 3H), 1.83 – 1.73 (m, 1H), 1.69 – 1.58 (m, 3H), 1.54 – 1.49 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.4, 135.5, 129.1, 128.2, 57.0, 52.4, 36.8, 35.2, 34.1, 29.2, 29.1, 21.0.

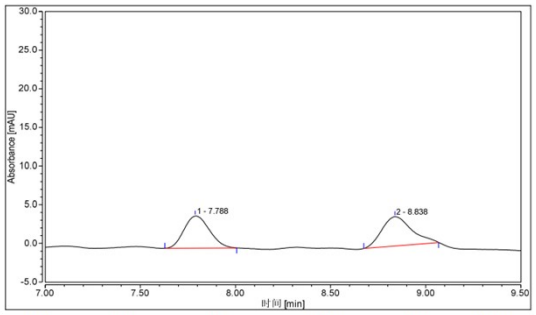
HRMS (ESI): Calculated for ($C_{14}H_{20}NaO_2S^+$) $[M+Na]^+$: 275.1076, found 275.1083.

$[\alpha]^{25}_D$ = –3.3° (c = 1.0, $CHCl_3$).

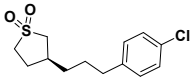
HPLC (UltiMate 3000): Daicel Chiralpak IB-3 Column (*n*-Hexane/*i*-PrOH = 90 : 10, 1.0 mL/min), 30 °C, 220 nm, R*t* = 7.707 min (minor) and 8.855 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	7.707	6.758	59.630	1.34	2.34
2	8.855	498.200	2490.691	98.66	97.66



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	7.788	0.644	4.159	48.31	52.32
2	8.838	0.689	3.790	51.69	47.68



3r

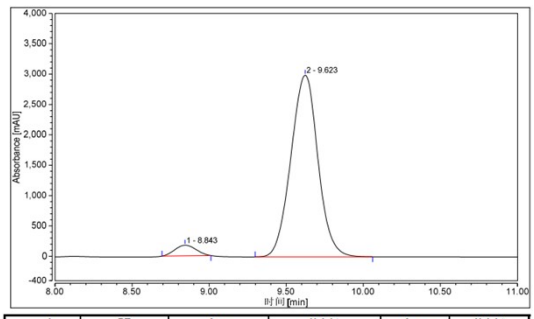
The title compound was synthesized according to general procedure A, the product **3r** was purified by flash column chromatography (PE: EA = 3:1) as a colorless oil (46% yield) with 91% *ee*.

^{1}H NMR (500 MHz,$CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 3.24 – 3.16 (m, 2H), 3.05 – 2.99 (m, 1H), 2.66 – 2.58 (m, 3H), 2.46 – 2.37 (m, 1H), 2.35 – 2.28 (m, 1H), 1.84 – 1.75 (m, 1H), 1.68 – 1.59 (m, 2H), 1.53 – 1.48 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.9, 131.8, 129.7, 128.6, 56.9, 52.3, 36.7, 34.9, 33.9, 29.1, 29.0.

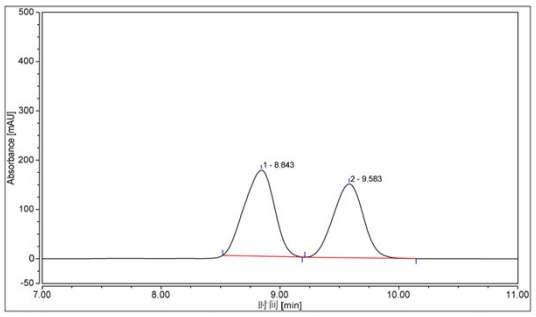
HRMS (ESI): Calculated for ($C_{13}H_{18}ClO_2S^+$) $[M+H]^+$: 273.0711, found 273.0706.

$[\alpha]^{25}_D = -5.5^o$ (c = 1.0, $CHCl_3$).

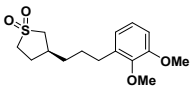
HPLC (UltiMate 3000): Daicel Chiralpak AD-H Column (*n*-Hexane/*i*-PrOH = 80 : 20, 1.0 mL/min), 30 °C, 220 nm, R*t* = 8.843 min (minor) and 9.623 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	8.843	27.849	175.098	4.37	5.53
2	9.623	609.847	2991.353	95.63	94.47



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	8.843	50.959	174.307	53.75	53.81
2	9.583	43.845	149.618	46.25	46.19



3s

The title compound was synthesized according to general procedure A, the product **3s** was purified by flash column chromatography (PE: EA = 3:1) as a yellow oil (60% yield) with 89% *ee*.

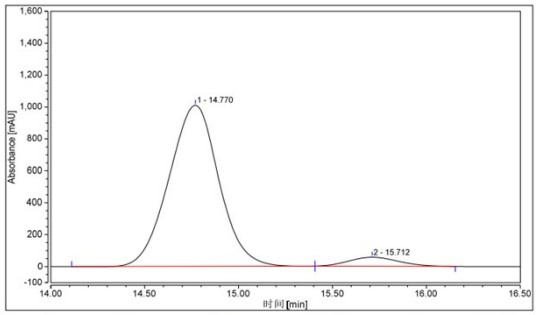
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.77 (m, 2H), 7.76 – 7.64 (m, 2H), 7.58 – 7.45 (m, 2H), 7.44 – 7.31 (m, 3H), 3.89 – 3.69 (m, 2H), 3.66 (t, *J* = 7.1 Hz, 1H), 3.63 – 3.39 (m, 2H), 3.23 – 3.00 (m, 1H), 2.32 – 2.02 (m,

2H), 1.80 – 1.38 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.6, 168.4, 137.0, 134.0, 132.1, 132.0, 129.8, 128.3, 128.2, 127.1, 123.2, 55.0, 51.7, 49.3, 45.9, 39.4, 37.8, 37.4, 32.3, 30.4, 29.9, 29.7, 27.3, 27.2.

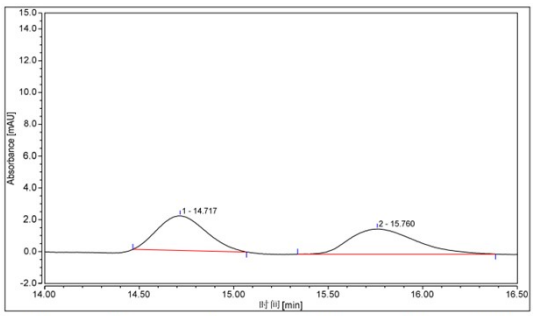
HRMS (ESI): Calculated for ($C_{15}H_{22}NaO_4S^+$) $[M+Na]^+$: 321.1131, found 321.1136.

$[\alpha]^{25}_D$ = –10.5° (c = 1.0, $CHCl_3$).

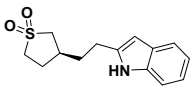
HPLC (UltiMate 3000): Daicel Chiralpak AD-H Column (*n*-Hexane/*i*-PrOH = 90 : 10, 1.0 mL/min), 30 °C, 220 nm, R*t* = 14.770 min (minor) and 15.712 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	14.770	311.078	1009.481	94.69	94.68
2	15.712	17.447	56.703	5.31	5.32



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	14.717	0.645	2.173	50.26	57.93
2	15.760	0.638	1.578	49.74	42.07



3t

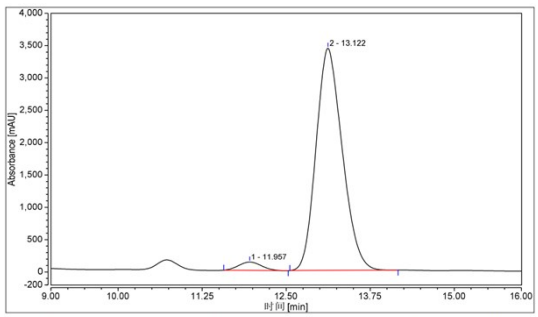
The title compound was synthesized according to general procedure A, the product **3t** was purified by flash column chromatography (PE: EA = 5:1) as a yellow oil (57% yield) with 93% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.15 – 7.09 (m, 1H), 6.96 (d, *J* = 2.2 Hz, 1H), 3.24 (dd, *J* = 13.8, 6.8 Hz, 1H), 3.21 – 3.14 (m, 1H), 3.02 – 2.95 (m, 1H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.72 – 2.64 (m, 1H), 2.50 – 2.40 (m, 1H), 2.33 (dt, *J* = 13.1, 7.1 Hz, 1H), 1.98 – 1.82 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.5, 127.1, 122.2, 121.4, 119.4, 118.6, 114.9, 111.4, 56.9, 52.3, 36.4, 34.9, 29.2, 23.1.

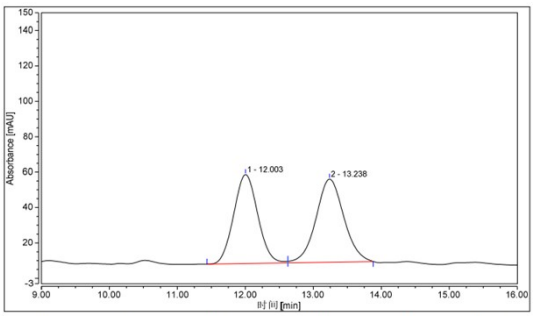
HRMS (ESI): Calculated for ($C_{14}H_{18}NO_2S^+$) $[M+H]^+$: 264.1053, found 264.1057.

$[\alpha]^{25}_D$ = –8.1° (c = 1.0, $CHCl_3$).

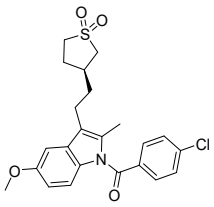
HPLC (UltiMate 3000): Daicel Chiralpak IC Column (*n*-Hexane/*i*-PrOH = 30: 70, 1.0 mL/min), 30 °C, 220 nm, R*t* = 11.957 min (minor) and 13.122 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	11.957	50.257	128.643	3.14	3.61
2	13.122	1552.243	3436.544	96.86	96.39



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	12.003	20.610	50.255	48.07	51.72
2	13.238	22.268	46.915	51.93	48.28



3u

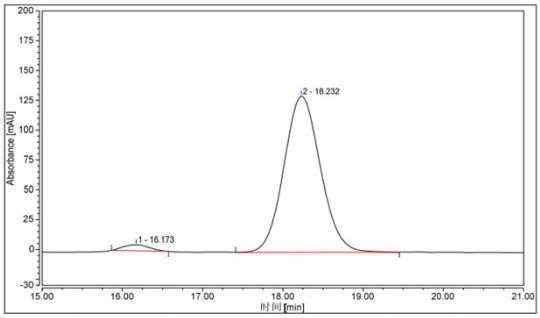
The title compound was synthesized according to general procedure A, the product **3u** was purified by flash column chromatography (PE: EA = 2:1) as a brown oil (72% yield) with 92% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 6.90 – 6.83 (m, 2H), 6.67 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.84 (s, 3H), 3.29 (dd, *J* = 13.7, 6.8 Hz, 1H), 3.21 (dd, *J* = 16.2, 8.1 Hz, 1H), 3.04 (d, *J* = 7.8 Hz, 1H), 2.77 – 2.65 (m, 3H), 2.53 – 2.45 (m, 1H), 2.41 (dd, *J* = 17.6, 7.1 Hz, 1H), 2.34 (s, 3H), 1.93 – 1.81 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.3, 156.0, 139.2, 134.2, 134.0, 131.1, 131.0, 130.6, 129.2, 118.3, 115.1, 111.0, 101.4, 56.8, 55.8, 52.1, 36.5, 34.5, 29.2, 22.0, 13.3.

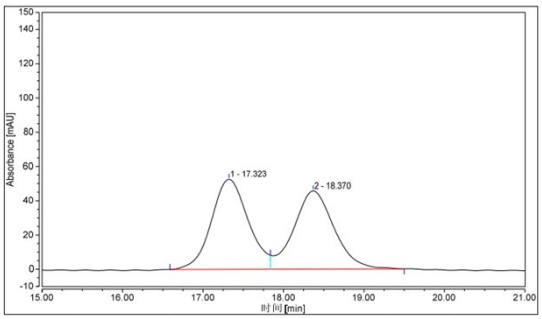
HRMS (ESI): Calculated for ($C_{23}H_{25}ClNO_4S^+$) $[M+H]^+$: 446.1187, found 446.1189.

$[\alpha]^{25}_D$ = -14.7° (c = 1.0, $CHCl_3$).

HPLC (UltiMate 3000): Daicel Chiralpak IA Column (*n*-Hexane/*i*-PrOH = 70 : 30, 1.0 mL/min), 30 °C, 220 nm, R*t* = 16.173 min (major) and 18.232 min (minor).

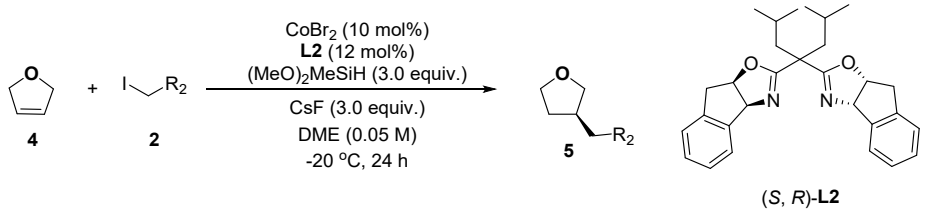


peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	16.173	1.905	5.049	2.68	3.72
2	18.232	69.071	130.754	97.32	96.28

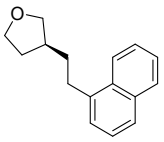


peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	17.323	27.825	52.569	51.23	53.51
2	18.370	26.487	45.664	48.77	46.49

General procedures for cobalt-catalyzed enantioselective hydroalkylation of 2,5-Dihydrofuran



To an oven-dried 10 mL Schlenk tube containing a stirring bar was charged with $CoBr_2$ (4.4 mg, 0.02 mmol, 10 mol%), (*S*, *R*)-**L2** (10.7 mg, 0.024 mmol, 12 mol%) and 2.0 mL dry 1,2-dimethoxyethane in a nitrogen-filled glovebox, the mixture was stirred for 10 min at room temperature. Then 2,5-Dihydrofuran (0.2 mmol, 1.0 equiv.), alkyl iodides (0.4 mmol, 2.0 equiv.), CsF (91.1 mg, 0.6 mmol, 3.0 equiv.) and another 2.0 mL dry 1,2-dimethoxyethane were added sequentially. The tube was sealed and removed from the glove box, $(MeO)_2MeSiH$ (63.7 mg, 0.6 mmol, 3.0 equiv.) was added dropwise at -20°C and the reaction was stirred at -20°C for 24 h. After the reaction was completed, the reaction mixture was diluted with saturated NH_4Cl (aq., 2.0 mL) and EtOAc (5 mL). The aqueous phase was extracted with EtOAc (2 × 5 mL). The organic phase was dried over Na_2SO_4, filtered, and the solvent removed in vacuo. The crude mixture was purified by flash column chromatography on silica gel using a mixture of Hexane/EtOAc as eluent to obtain the desired product.



5a

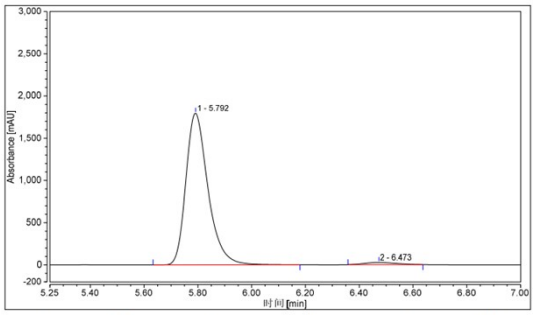
The title compound was synthesized according to general procedure A, the product **5a** was purified by flash column chromatography (PE: EA = 20:1) as a colorless oil (79% yield) with 96% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 1.6 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.40 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.0 Hz, 1H), 3.93 (t, *J* = 7.8 Hz, 1H), 3.88 – 3.79 (m, 1H), 3.73 (q, *J* = 7.8 Hz, 1H), 3.39 (t, *J* = 7.8 Hz, 1H), 3.12 – 2.96 (m, 2H), 2.28 – 2.22 (m, *J* = 7.4 Hz, 1H), 2.11 – 1.98 (m, 1H), 1.85 – 1.72 (m, 2H), 1.60 – 1.47 (m, 1H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.2, 134.0, 131.8, 128.9, 126.8, 126.0, 125.9, 125.6, 125.6, 123.7, 73.4, 68.0, 39.4, 34.6, 32.6, 32.1

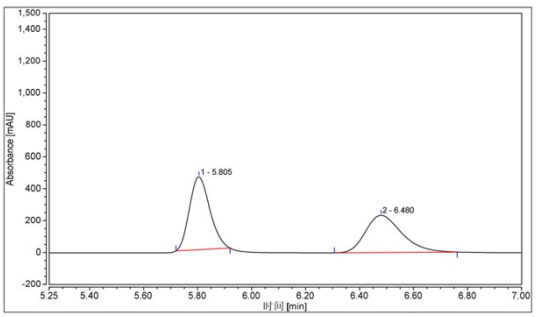
HRMS (ESI): Calculated for ($C_{16}H_{18}NaO^+$) $[M+Na]^+$: 249.1250, found 249.1242.

$[\alpha]^{25}_D$ = -12.4° (c = 1.0, $CHCl_3$).

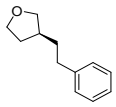
HPLC (UltiMate 3000): Daicel Chiralpak IH-3 Column (*n*-Hexane/*i*-PrOH = 70 : 30, 1.0 mL/min), 30 °C, 220 nm, R*t* = 5.792 min (major) and 6.473 min (minor).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	5.792	170.922	1796.261	97.98	98.57
2	6.473	3.519	25.980	2.02	1.43



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	5.805	39.898	456.369	52.36	66.20
2	6.480	36.308	232.980	47.64	33.80



5b

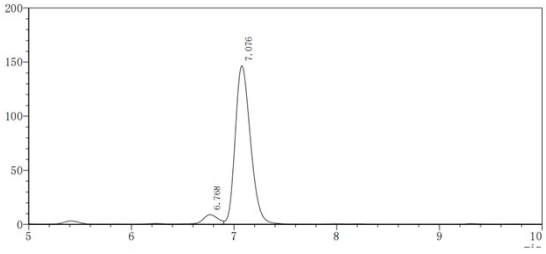
The title compound was synthesized according to general procedure A, the product **5b** was purified by flash column chromatography (PE: EA = 20:1) as a colorless oil (65% yield) with 89% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.21 – 7.13 (m, 3H), 3.91 (t, *J* = 7.8 Hz, 1H), 3.85 (td, *J* = 8.3, 4.6 Hz, 1H), 3.74 (q, *J* = 7.8 Hz, 1H), 3.37 (t, *J* = 7.8 Hz, 1H), 2.63 (q, *J* = 7.7 Hz, 2H), 2.19 (p, *J* = 7.4 Hz, 1H), 2.05 (d, *J* = 7.5 Hz, 1H), 1.74 – 1.69 (m, 2H), 1.57 – 1.51 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.1, 128.4, 128.3, 125.9, 73.3, 68.0, 38.9, 35.2, 34.9, 32.5.

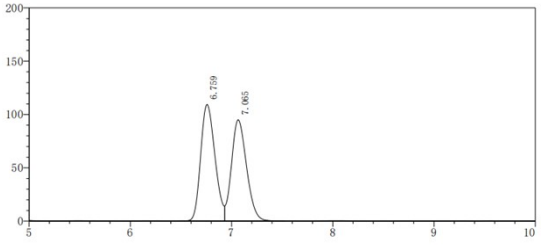
HRMS (ESI): Calculated for ($C_{12}H_{17}O^+$) $[M+H]^+$: 177.1247, found 177.1297.

$[\alpha]^{25}_D$ = -2.8° (c = 1.0, $CHCl_3$).

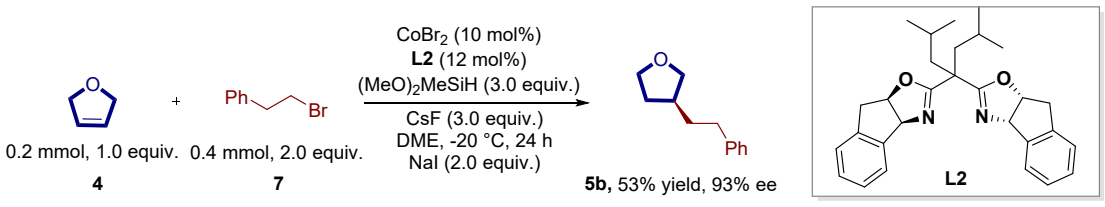
HPLC (UltiMate 3000): Daicel Chiralpak IE Column (*n*-Hexane/*i*-PrOH = 90 : 10, 0.8 mL/min), 30 °C, 220 nm, R*t* = 6.768 min (minor) and 7.076 min (major).



peak	RT/min	Area	Height	Area/ %
1	6.768	91189	8970	5.679
2	7.076	1514624	146576	94.321



peak	RT/min	Area	Height	Area/ %
1	6.759	1074297	109255	52.506
2	7.065	971766	94885	47.494



0.2 mmol, 1.0 equiv. **4** 0.4 mmol, 2.0 equiv. **7**

5b, 53% yield, 93% ee

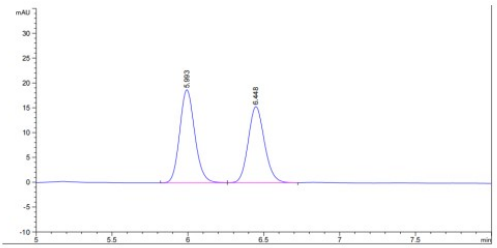
Alkyl bromide was used as the coupling partner under standard conditions, yielding the corresponding chiral furan compound **5b** with 53% yield and 93% ee. The addition of an equal amount of sodium iodide as an additive facilitated the reaction.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.20 – 7.11 (m, 3H), 3.91 – 3.88 (m, 1H), 3.84 (t, *J* = 8.3 Hz, 1H), 3.75 – 3.71 (m, 1H), 3.36 (t, *J* = 7.8 Hz, 1H), 2.60 (dd, *J* = 14.9, 7.3 Hz, 2H), 2.22 – 2.16 (m, 1H), 2.07 – 2.01 (m, 1H), 1.73 – 1.68 (m, 2H), 1.58 – 1.49 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.1, 128.4, 128.4, 125.9, 73.3, 68.0, 38.9, 35.2, 34.9, 32.5.

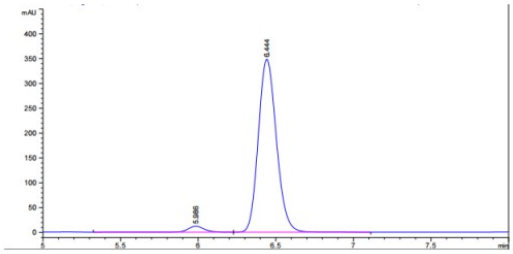
HRMS (ESI): Calculated for ($C_{12}H_{17}O^+$) $[M+H]^+$: 177.1247, found 177.1295.

$[\alpha]^{25}_D$ = -2.7° (c = 1.0, $CHCl_3$).

HPLC (UltiMate 3000): Daicel Chiralcel OD-H Column (*n*-Hexane/*i*-PrOH = 90 : 10, 0.8 mL/min), 30 °C, 220 nm, R*t* = 5.986 min (minor) and 6.444 min (major).



peak #	RT [min]		Time [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.993	BV	0.1090	129.64050	18.67953	53.1217
2	6.448	VB	0.1152	114.40389	15.31244	46.8783



Peak #	RT [min]		Time [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.986	BV	0.1162	95.32052	12.06427	3.2663
2	6.444	VB	0.1267	2822.94946	347.82584	96.7337

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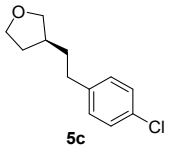


5c

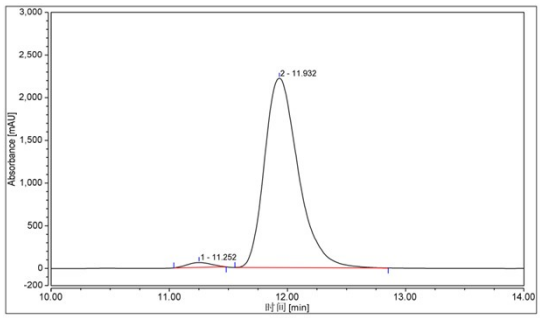
The title compound was synthesized according to general procedure A, the product **5c** was purified by flash column chromatography (PE: EA = 20:1) as a colorless oil (56% yield) with 96% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.92 – 3.82 (m, 2H), 3.77 – 3.70 (m, 1H), 3.38 – 3.33 (m, 1H), 2.65 – 2.55 (m, 2H), 2.21 – 2.14 (m, 1H), 2.07 (d, *J* = 7.4 Hz, 1H), 1.73 – 1.65 (m, 2H), 1.57 – 1.48 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.5, 131.6, 129.7, 128.5, 73.3, 67.9, 38.8, 35.1, 34.2, 32.4.

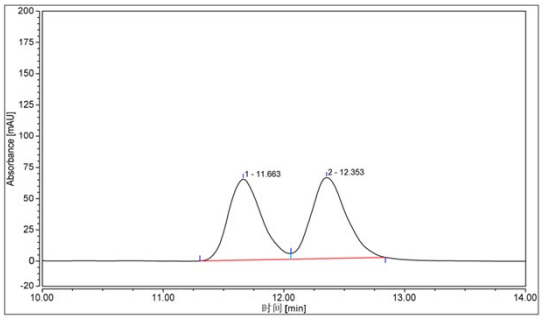
HRMS (ESI): Calculated for ($C_{12}H_{16}ClO^+$) $[M+H]^+$: 211.0884, found 211.0948.

$[\alpha]^{25}_D$ = -6.4° (c = 1.0, $CHCl_3$).

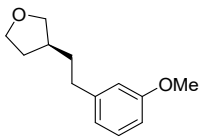
HPLC (UltiMate 3000): Daicel Chiralcel OD-H Column (*n*-Hexane/*i*-PrOH = 90 : 10, 0.5 mL/min), 30 °C, 220 nm, R*t* = 11.252 min (minor) and 11.932 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	11.252	13.542	57.206	1.81	2.51
2	11.932	734.337	2219.042	98.19	97.49



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	11.663	20.638	64.652	48.76	49.99
2	12.353	21.687	64.681	51.24	50.01



5d

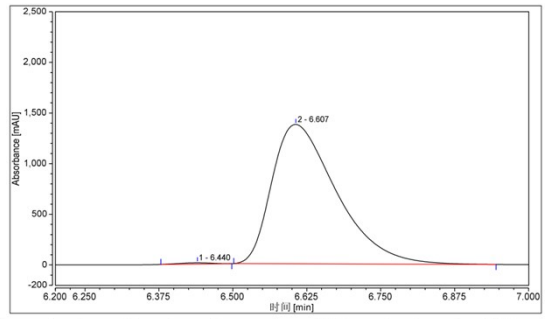
The title compound was synthesized according to general procedure A, the product **5d** was purified by flash column chromatography (PE: EA = 20:1) as a colorless oil (75% yield) with 99% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.18 (m, 1H), 6.80 – 6.69 (m, 3H), 3.93 – 3.89 (m, 1H), 3.86 (dd, *J* = 8.0, 3.4 Hz, 1H), 3.80 (s, 3H), 3.74 (q, *J* = 7.8 Hz, 1H), 3.40 – 3.34 (m, 1H), 2.61 (d, *J* = 8.1 Hz, 2H), 2.23 – 2.17 (m, 1H), 2.10 – 2.02 (m, 1H), 1.71 (t, *J* = 9.1 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.7, 143.7, 129.4, 120.8, 114.2, 111.1, 73.3, 67.9, 55.1, 38.9, 35.0, 34.9, 32.5.

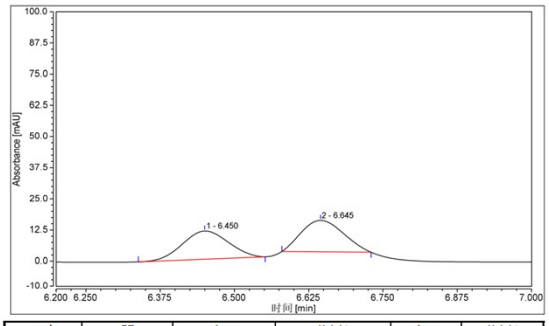
HRMS (ESI): Calculated for ($C_{13}H_{19}O_2^+$) $[M+H]^+$: 207.1380, found 207.1390.

$[\alpha]^{25}_D$ = –4.7° (c = 1.0, $CHCl_3$).

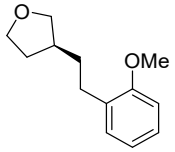
HPLC (UltiMate 3000): Daicel Chiralpak IH-3 Column (*n*-Hexane/*i*-PrOH = 90 : 10, 1.0 mL/min), 30 °C, 220 nm, R*t* = 6.440 min (minor) and 6.607 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	6.440	0.755	12.055	0.43	0.87
2	6.607	174.305	1375.375	99.57	99.13



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	6.450	1.006	11.285	49.39	47.28
2	6.645	1.031	12.584	50.61	52.72



5e

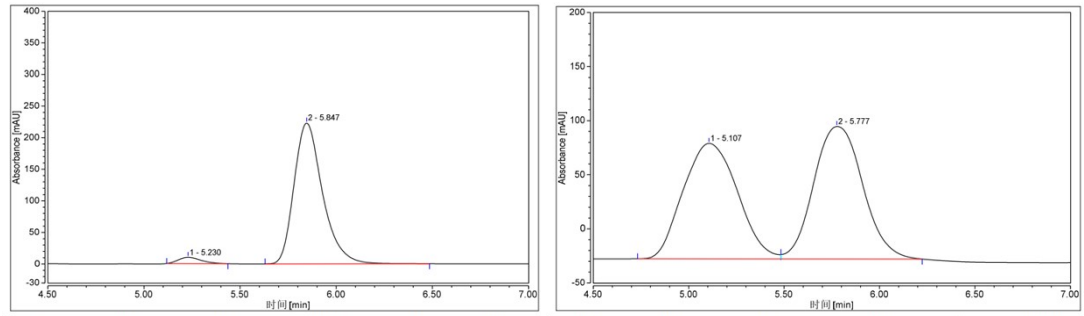
The title compound was synthesized according to general procedure A, the product **5e** was purified by flash column chromatography (PE: EA = 20:1) as a yellow oil (81% yield) with 93% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.14 (m, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 6.92 – 6.80 (m, 2H), 3.95 – 3.90 (m, 1H), 3.88 – 3.83 (m, 1H), 3.82 (s, 3H), 3.77 – 3.71 (m, 1H), 3.41 – 3.36 (m, 1H), 2.69 – 2.55 (m, 2H), 2.20 (dt, *J* = 14.8, 7.4 Hz, 1H), 2.10 – 2.03 (m, 1H), 1.72 – 1.63 (m, 2H), 1.57 – 1.51 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.4, 130.5, 129.7, 127.1, 120.4, 110.2, 73.5, 68.0, 55.2, 39.2, 33.7, 32.6, 29.2.

HRMS (ESI): Calculated for ($C_{13}H_{18}NaO_2^+$) $[M+Na]^+$: 229.1199, found 229.1208.

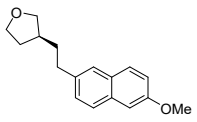
$[\alpha]^{25}_D$ = –1.5° (c = 1.0, $CHCl_3$).

HPLC (UltiMate 3000): Daicel Chiralcel OD Column (*n*-Hexane/*i*-PrOH = 90 : 10, 1.0 mL/min), 30 °C, 220 nm, R*t* = 5.230 min (minor) and 5.847 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	5.230	1.353	9.803	3.41	4.21
2	5.847	38.363	222.928	96.59	95.79

peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	5.107	35.168	106.817	49.07	46.58
2	5.777	36.495	122.497	50.93	53.42



5f

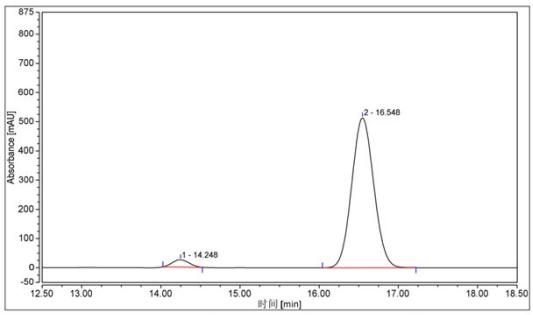
The title compound was synthesized according to general procedure A, the product **5f** was purified by flash column chromatography (PE: EA = 20:1) as a white solid (55% yield) with 93% *ee*. m.p. 47-49 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.53 (s, 1H), 7.28 (d, *J* = 10.2 Hz, 1H), 7.14 – 7.08 (m, 2H), 3.93 (d, *J* = 7.3 Hz, 1H), 3.91 (s, 3H), 3.89 – 3.84 (m, 1H), 3.77 – 3.71 (m, 1H), 3.42 – 3.37 (m, 1H), 2.79 – 2.71 (m, 2H), 2.26 – 2.20 (m, 1H), 2.11 – 2.03 (m, 1H), 1.82 – 1.76 (m, 2H), 1.60 – 1.53 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.2, 137.2, 133.0, 129.1, 128.9, 127.7, 126.8, 126.2, 118.8, 105.7, 73.4, 68.0, 55.3, 38.9, 35.1, 34.8, 32.5.

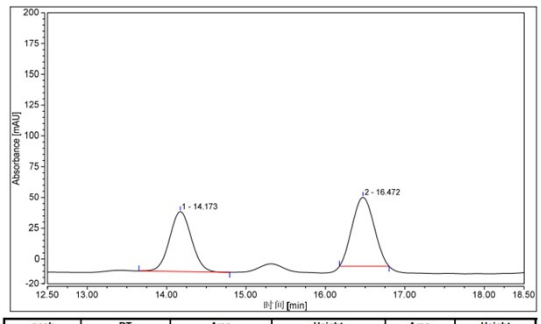
HRMS (ESI): Calculated for ($C_{17}H_{20}NNaO_2^+$) $[M+H]^+$: 279.1356, found 279.1360.

$[\alpha]^{25}_D$ =-7.4° (c = 1.0, $CHCl_3$).

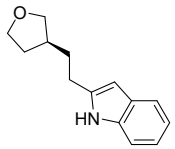
HPLC (UltiMate 3000): Daicel Chiralpak IC Column (*n*-Hexane/*i*-PrOH = 90:10, 1.0 mL/min), 30 °C, 220 nm, R*t* = 14.248 min (minor) and 16.548 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	14.248	6.131	25.119	3.56	4.67
2	16.548	166.045	513.302	96.44	95.33



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	14.173	15.541	48.596	46.73	46.49
2	16.472	17.714	55.926	53.27	53.51



5g

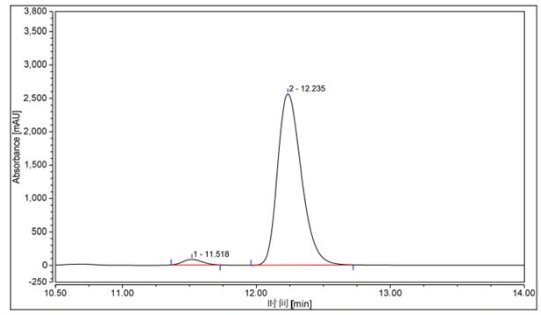
The title compound was synthesized according to general procedure A, the product **5g** was purified by flash column chromatography (PE: EA = 20:1) as a brown oil (67% yield) with 95% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.14 – 7.09 (m, 1H), 6.97 (d, *J* = 3.3 Hz, 1H), 3.97 – 3.91 (m, 1H), 3.90 – 3.84 (m, 1H), 3.78 – 3.72 (m, 1H), 3.44 – 3.38 (m, 1H), 2.78 (q, *J* = 7.1 Hz, 2H), 2.30 – 2.25 (m, 1H), 2.13 – 2.05 (m, 1H), 1.83 (s, 2H), 1.58 (d, *J* = 8.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.4, 127.4, 122.0, 121.1, 119.2, 118.9, 116.4, 111.1, 73.4, 68.0, 39.1, 33.9, 32.5, 24.2.

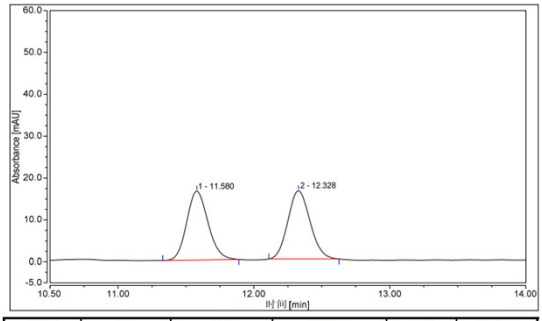
HRMS (ESI): Calculated for ($C_{14}H_{18}NO^+$) $[M+H]^+$: 216.1383, found 216.1384.

$[\alpha]^{25}_D$ = –9.5° (c = 1.0, $CHCl_3$).

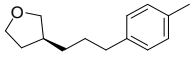
HPLC (UltiMate 3000): Daicel Chiralpak IA-3 Column (*n*-Hexane/*i*-PrOH = 90:10, 1.0 mL/min), 30 °C, 220 nm, R*t* = 11.518 min (minor) and 12.235 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	11.518	13.843	82.867	2.56	3.13
2	12.235	527.414	2562.613	97.44	96.87



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	11.580	2.997	16.470	49.23	50.28
2	12.328	3.090	16.284	50.77	49.72



5h

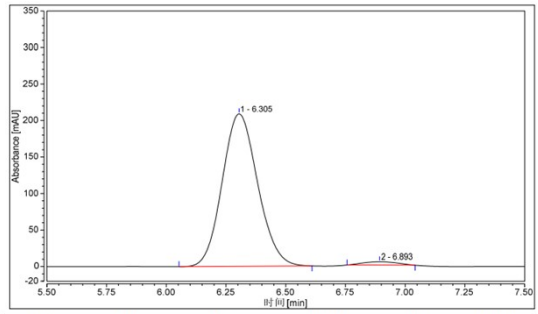
The title compound was synthesized according to general procedure A, the product **5h** was purified by flash column chromatography (PE: EA = 20:1) as a colorless oil (69% yield) with 96% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (q, *J* = 7.9 Hz, 4H), 3.89 (t, *J* = 7.8 Hz, 1H), 3.83 (td, *J* = 8.3, 4.6 Hz, 1H), 3.74 (t, *J* = 7.7 Hz, 1H), 3.30 (t, *J* = 7.8 Hz, 1H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.31 (s, 3H), 2.21 – 2.13 (m, 1H), 2.05 – 1.98 (m, 1H), 1.65 – 1.56 (m, 2H), 1.47 (d, *J* = 7.9 Hz, 1H), 1.43 – 1.38 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.3, 135.2, 129.0, 128.3, 73.4, 68.0, 39.4, 35.6, 32.9, 32.5, 30.6, 21.0.

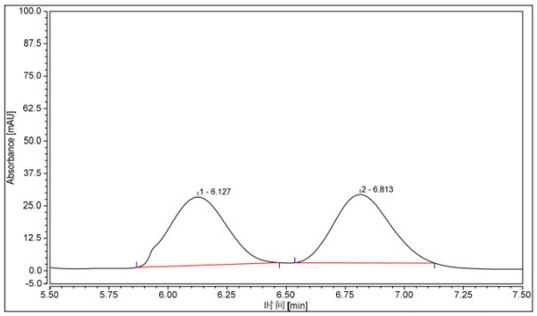
HRMS (ESI): Calculated for ($C_{14}H_{21}O^+$) $[M+H]^+$: 227.1406, found 227.1411.

$[\alpha]^{25}_D$ = –17.6° (c = 1.0, $CHCl_3$).

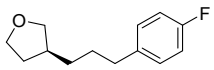
HPLC (UltiMate 3000): Daicel Chiralcel OB-H Column (*n*-Hexane/*i*-PrOH = 90 : 10, 1.0 mL/min), 30 °C, 220 nm, R*t* = 6.305 min (major) and 6.893 min (minor).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	6.305	35.964	208.815	97.93	97.85
2	6.893	0.760	4.587	2.07	2.15



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	6.127	7.291	26.325	50.20	50.01
2	6.813	7.231	26.310	49.80	49.99



5i

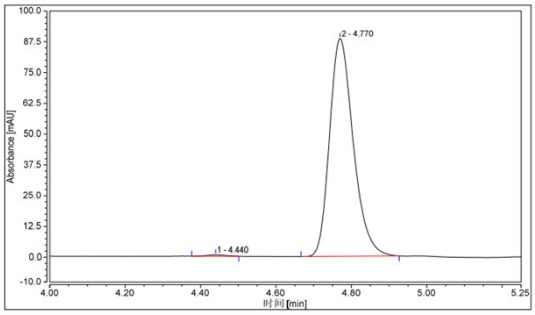
The title compound was synthesized according to general procedure A, the product **5i** was purified by flash column chromatography (PE: EA = 20:1) as a colorless oil (57% yield) with 99% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 – 7.09 (m, 2H), 7.00 – 6.89 (m, 2H), 3.89 (t, *J* = 7.8 Hz, 1H), 3.85 – 3.79 (m, 1H), 3.76 – 3.69 (m, 1H), 3.34 – 3.27 (m, 1H), 2.58 (t, *J* = 7.7 Hz, 2H), 2.21 – 2.13 (m, 1H), 2.06 – 1.98 (m, 1H), 1.65 – 1.56 (m, 2H), 1.51 – 1.45 (m, 1H), 1.43 – 1.36 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.2 (d, *J* = 243.2 Hz), 137.9 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 7.8 Hz), 115.0 (d, *J* = 21.1 Hz), 73.4, 70.0, 39.3, 35.2, 32.8, 32.5, 30.5. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -117.90.

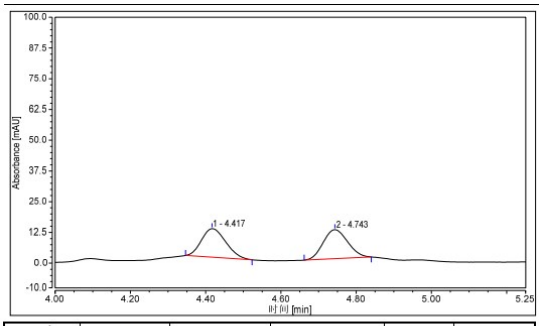
HRMS (ESI): Calculated for ($C_{13}H_{18}FO^+$) $[M+H]^+$: 209.1336, found 209.1338.

$[\alpha]^{25}_D$ = –164.2° (c = 1.0, $CHCl_3$).

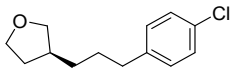
HPLC (UltiMate 3000): Daicel Chiralpak IA-3 Column (*n*-Hexane/*i*-PrOH = 90 : 10, 1.0 mL/min), 30 °C, 220 nm, R*t* = 4.440 min (minor) and 4.770 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	4.440	0.030	0.541	0.46	0.61
2	4.770	6.436	88.483	99.54	99.39



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	4.417	0.868	11.597	49.48	49.60
2	4.743	0.887	11.785	50.52	50.40



5j

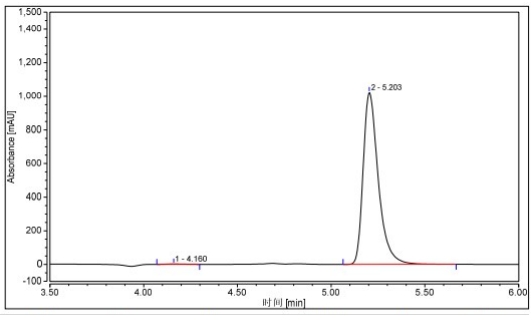
The title compound was synthesized according to general procedure A, the product **5j** was purified by flash column chromatography (PE: EA = 20:1) as a colorless oil (63% yield) with 99% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 3.91 – 3.86 (m, 1H), 3.86 – 3.80 (m, 1H), 3.74 (t, *J* = 8.1 Hz, 1H), 3.35 – 3.27 (m, 1H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.20 – 2.14 (m, 1H), 2.06 – 1.98 (m, 1H), 1.67 – 1.55 (m, 3H), 1.48 (s, 1H), 1.43 – 1.36 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.7, 131.5, 129.7, 128.4, 73.4, 68.0, 39.3, 35.4, 32.8, 32.4, 30.3.

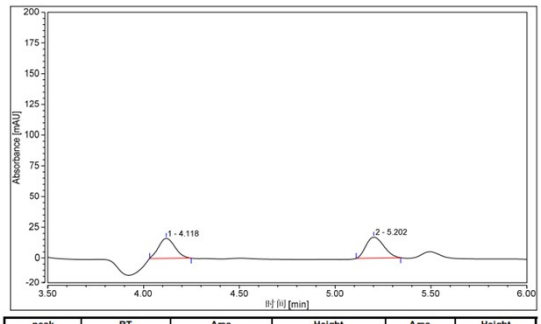
HRMS (ESI): Calculated for ($C_{13}H_{17}NaClO^+$) $[M+Na]^+$: 247.0860, found 247.0771.

$[\alpha]^{25}_D$ = –13.0° (c = 1.0, $CHCl_3$).

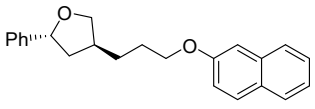
HPLC (UltiMate 3000): Daicel Chiralpak IH-3 Column (*n*-Hexane/*i*-PrOH = 95 : 5, 1.0 mL/min), 30 °C, 220 nm, R*t* = 4.160 min (minor) and 5.203 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	4.160	0.240	2.418	0.25	0.24
2	5.203	95.901	1021.975	99.75	99.76



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	4.118	1.613	16.271	46.65	48.81
2	5.202	1.844	17.061	53.35	51.19



5k

To an oven-dried 10 mL Schlenk tube containing a stirring bar was charged with $CoBr_2$ (4.4 mg, 0.02 mmol, 10 mol%), (*S*, *R*)-**L2** (10.7 mg, 0.024 mmol, 12 mol%) and 2.0 mL dry 1,2-dimethoxyethane in a nitrogen-filled glovebox, the mixture was stirred for 10 min at room temperature. Then 2-phenyl-2,5-

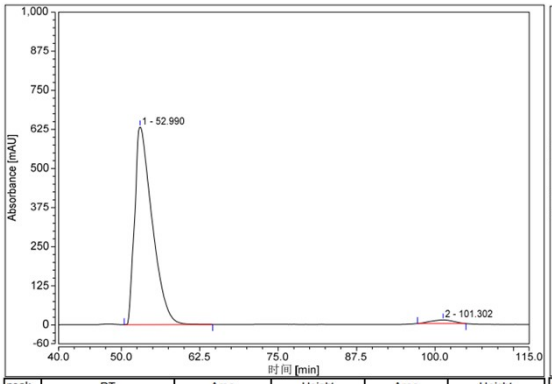
dihydrofuran (0.6 mmol, 3.0 equiv.), alkyl iodides (0.2 mmol, 1.0 equiv.), CsF (91.1 mg, 0.6 mmol, 3.0 equiv.) and another 2.0 mL dry 1,2-dimethoxyethane were added sequentially. The tube was sealed and removed from the glove box, $(MeO)_2MeSiH$ (63.7 mg, 0.6 mmol, 3.0 equiv.) was added dropwise at -20°C and the reaction was stirred at -20 °C for 24 h. After the reaction was completed, the reaction mixture was diluted with saturated NH_4Cl (aq., 2.0 mL) and EtOAc (5 mL). The aqueous phase was extracted with EtOAc (2 × 5 mL). The organic phase was dried over Na_2SO_4, filtered, and the solvent removed in vacuo. The crude mixture was purified by flash column chromatography on silica gel using a mixture of Hexane/EtOAc as eluent to obtain the desired product of **5k** as a colourless oil (51% yield) with 95% ee.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.69 (m, 3H), 7.43 (t, J = 7.6 Hz, 1H), 7.36 – 7.30 (m, 5H), 7.25 (d, J = 7.6 Hz, 1H), 7.13 – 7.11 (m, 2H), 5.04 (t, J = 6.8 Hz, 1H), 4.28 (t, J = 7.7 Hz, 1H), 4.08 (t, J = 6.3 Hz, 2H), 3.58 (t, J = 7.9 Hz, 1H), 2.44 – 2.38 (m, 1H), 2.06 (t, J = 7.1 Hz, 2H), 1.93 – 1.82 (m, 2H), 1.71 – 1.63 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.9, 143.8, 134.6, 129.4, 129.0, 128.3, 127.7, 127.1, 126.7, 126.4, 125.5, 123.6, 118.9, 106.6, 80.1, 74.2, 67.8, 40.7, 38.7, 29.8, 28.2.

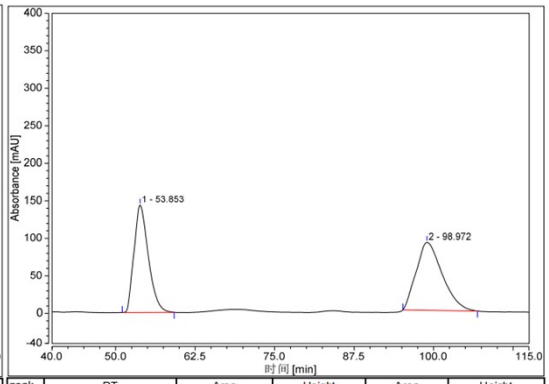
HRMS (ESI): Calculated for ($C_{23}H_{24}O_2Na^+$) [M+Na]$^+$: 355.1669, found 355.1672.

$[\alpha]^{25}_D$ = 0.73° (c = 1.0, $CHCl_3$).

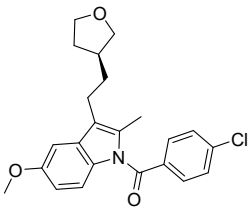
HPLC (UltiMate 3000): Daicel Chiralcel OD-H Column (*n*-Hexane/*i*-PrOH = 90 : 10, 1.0 mL/min), 30 °C, 214 nm, R*t* = 52.990 min (major) and 101.302 min (minor).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	52.990	2044.314	631.661	97.72	98.21
2	101.302	47.766	11.490	2.28	1.79



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	53.853	373.911	143.073	46.54	61.24
2	98.972	429.536	90.540	53.46	38.76



5l

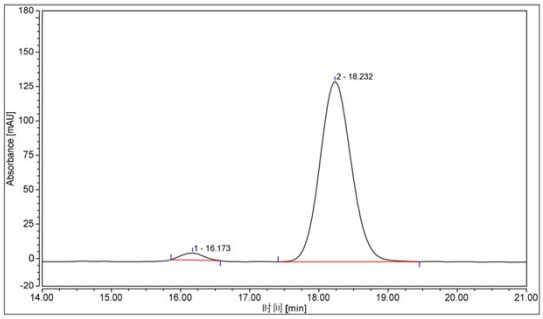
The title compound was synthesized according to general procedure A, the product **5l** was purified by flash column chromatography (PE: EA = 5:1) as a brown oil (80% yield) with 94% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.23 – 7.11 (m, 3H), 3.81 – 3.62 (m, 1H), 3.60 – 3.50 (m, 1H), 3.40 – 3.28 (m, 1H), 3.06 – 2.94 (m, 1H), 2.72 – 2.59 (m, 2H), 2.25 – 2.03 (m, 5H), 1.74 – 1.69 (m, 2H), 1.66 – 1.46 (m, 1H), 0.96 (d, *J* = 6.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.3, 155.9, 139.0, 134.3, 134.0, 131.1, 131.1, 131.1, 129.1, 119.5, 115.0, 110.8, 101.6, 73.4, 68.0, 55.8, 39.1, 33.5, 32.6, 23.0, 13.3.

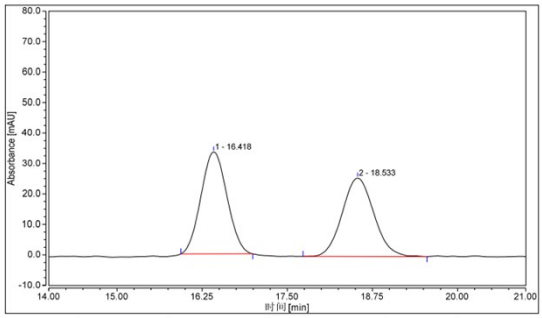
HRMS (ESI): Calculated for ($C_{23}H_{25}ClNO_3^+$) $[M+H]^+$: 398.1517, found 398.1522.

$[\alpha]^{25}_D$ = –7.9° (c = 1.0, $CHCl_3$).

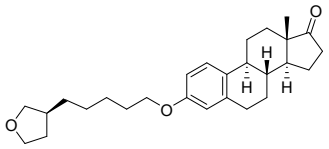
HPLC (UltiMate 3000): Daicel Chiralpak IC Column (*n*-Hexane/*i*-PrOH = 70 : 30, 1.0 mL/min), 30 °C, 220 nm, R*t* = 16.173 min (major) and 18.232 min (minor).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	16.173	1.905	5.049	2.68	3.72
2	18.232	69.071	130.754	97.32	96.28



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	16.418	14.847	33.470	51.68	56.53
2	18.533	13.881	25.735	48.32	43.47



5m

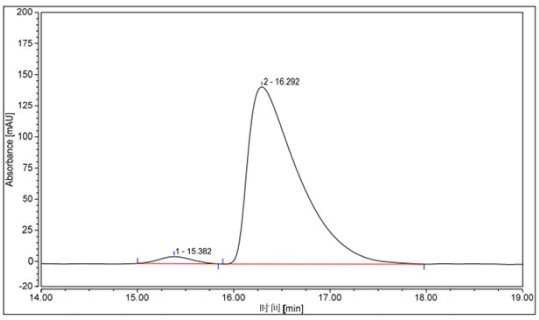
The title compound was synthesized according to general procedure A, the product **5m** was purified by flash column chromatography (PE: EA = 5:1) as a white solid (47% yield) with 95% *ee*. m.p. 44-46 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 8.5, 2.8 Hz, 1H), 6.63 (s, 1H), 3.92 (q, *J* = 6.9 Hz, 3H), 3.87 – 3.80 (m, 1H), 3.74 (q, *J* = 7.8 Hz, 1H), 3.32 (t, *J* = 7.8 Hz, 1H), 2.92 – 2.85 (m, 2H), 2.50 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.39 (d, *J* = 14.3 Hz, 1H), 2.25 (d, *J* = 10.6 Hz, 1H), 2.19 – 2.11 (m, 2H), 2.07 – 1.98 (m, 3H), 1.95 (d, *J* = 15.0 Hz, 1H), 1.76 (s, 2H), 1.59 (dd, *J* = 33.2, 11.3 Hz, 3H), 1.52 – 1.44 (m, 6H), 1.43 – 1.35 (m, 4H), 0.90 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 221.0, 157.1, 137.7, 131.9, 126.3, 114.6, 112.1, 73.5, 68.0, 67.8, 50.4, 48.0, 44.0, 39.4, 38.4, 35.9, 33.3, 32.6, 31.6, 29.7, 29.3, 28.4, 26.6, 26.2, 26.0, 21.6, 13.9.

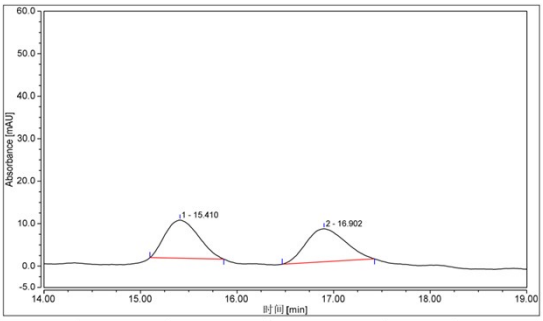
HRMS (ESI): Calculated for ($C_{27}H_{38}NaO_3^+$) $[M+Na]^+$: 433.2713, found 433.2782.

$[\alpha]^{25}_D$ = +131.1° (c = 1.0, $CHCl_3$).

HPLC (UltiMate 3000): Daicel Chiralpak IE Column (*n*-Hexane/*i*-PrOH = 50 : 50, 1.0 mL/min), 30 °C, 220 nm, R*t* = 15.382 min (major) and 16.292 min (minor).

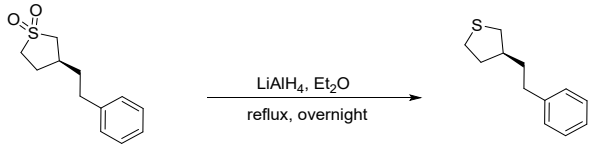


peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	15.382	2.197	5.563	2.48	3.76
2	16.292	86.551	142.201	97.52	96.24



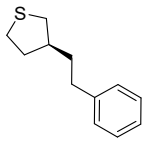
peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	15.410	3.589	8.973	49.51	53.60
2	16.902	3.659	7.767	50.49	46.40

Transformations of products



3b **6b**

To the stirring suspension of $LiAlH_4$ (68.3 mg, 1.8 mmol, 9.0 equiv.) and dry Et_2O (10 ml) was added **3b** (44.9 mg, 0.2 mmol, 1.0 equiv.) at 0 °C under N_2 atmosphere for reflux overnight. After the reaction was completed, the reaction was carefully quenched at 0 °C and then extracted with EtOAc (3x20 mL). The merged organic layer is dried with Na_2SO_4 and evaporated in vacuum.[1] The crude mixture was purified by flash column chromatography on silica gel to give desired **6b** in 74% as white solid. m.p. 70-72 °C.

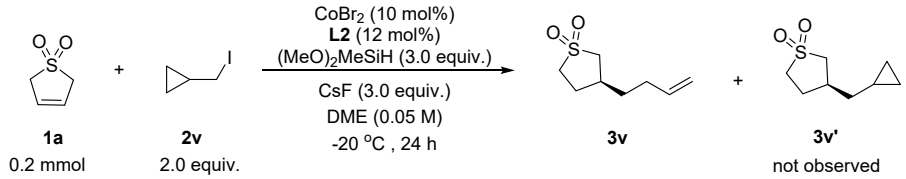


6b

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.22 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 3.28 – 3.12 (m, 2H), 3.00 (dd, *J* = 21.0, 11.1 Hz, 1H), 2.73 – 2.60 (m, 3H), 2.48 – 2.29 (m, 2H), 1.92 – 1.77 (m, 3H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.7, 128.7, 128.2, 126.4, 56.9, 52.2, 36.3, 36.2, 33.6, 29.1. **HRMS (ESI)**: Calculated for ($C_{12}H_{16}NaS^+$) $[M+Na]^+$: 215.0865, found 215.1014.

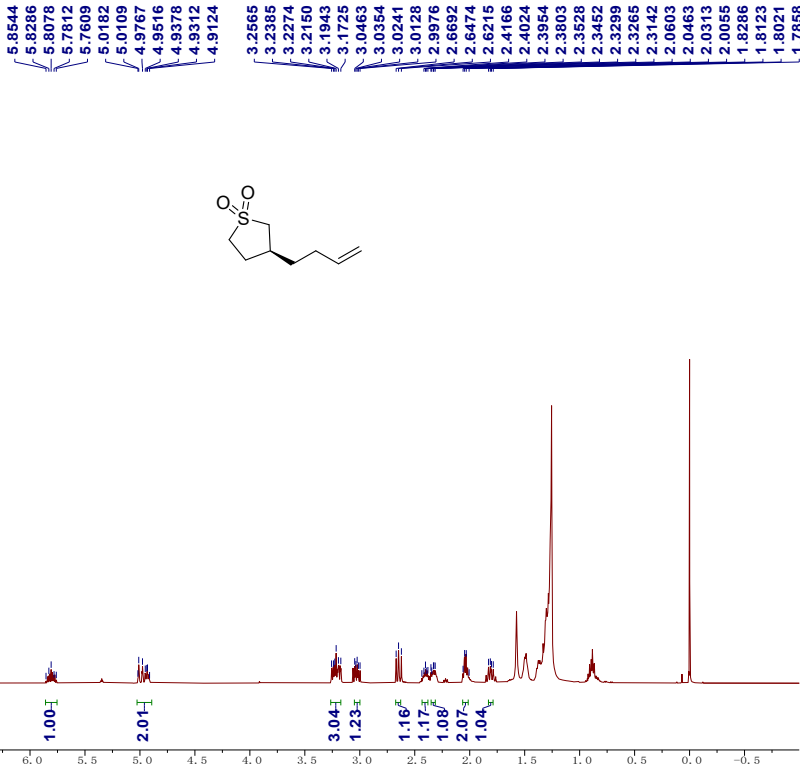
Mechanistic Experiments

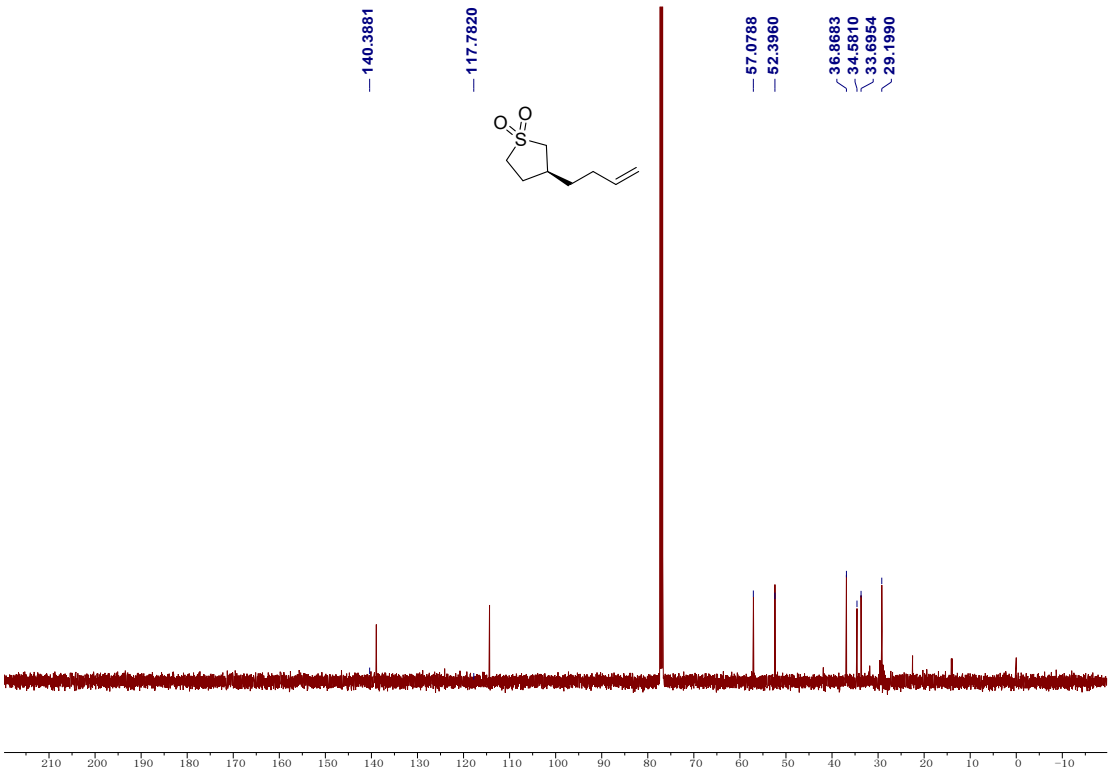
Radical Clock Experiment:



Following the general procedure A, the crude product was purified by flash column chromatography on silica gel to afford **3v** as a white solid (17% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 – 5.75 (m, 1H), 5.03 – 4.89 (m, 2H), 3.26 – 3.17 (m, 3H), 3.03 (dd, *J* = 11.2, 5.6 Hz, 1H), 2.66 (d, *J* = 10.9 Hz, 1H), 2.39 (d, *J* = 11.0 Hz, 1H), 2.35 – 2.31 (m, 1H), 2.05 (t, *J* = 7.2 Hz, 2H), 1.83 – 1.79 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.4, 117.8, 57.1, 52.4, 36.9, 34.6, 33.7, 29.2.

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33.6954
29.1990
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S
210
200
190
180
170
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150
140
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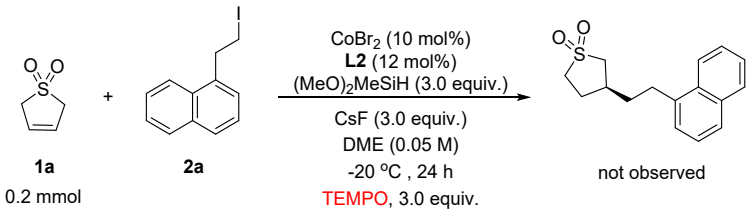
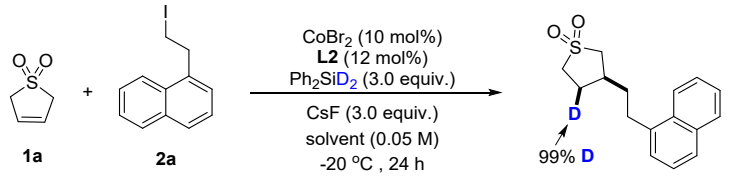
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

Radical Experiment:



To an oven-dried 10 mL Schlenk tube containing a stirring bar was charged with $CoBr_2$ (4.4 mg, 0.02 mmol, 10 mol%), (*S*, *R*)-**L2** (10.7 mg, 0.024 mmol, 12 mol%) and 2.0 mL dry 1,2-dimethoxyethane in a nitrogen-filled glove-box, the mixture was stirred for 10 min at room temperature. Then **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), CsF (91.1 mg, 0.6 mmol, 3.0 equiv.), 2,2,6,6-tetramethylpiperidinooxy (TEMPO) (0.6 mmol, 3.0 equiv.) and another 2.0 mL dry 1,2-dimethoxyethane were added sequentially. The tube was sealed and removed from the glove box, $(MeO)_2MeSiH$ (63.7 mg, 0.6 mmol, 3.0 equiv.) was added dropwise at -20 °C and the reaction was stirred at -20 °C for 24 h. No product was found by TLC monitoring and GC-MS was not detected the molecular weight of desired product.

Deuterium experiments with Ph_2SiD_2:

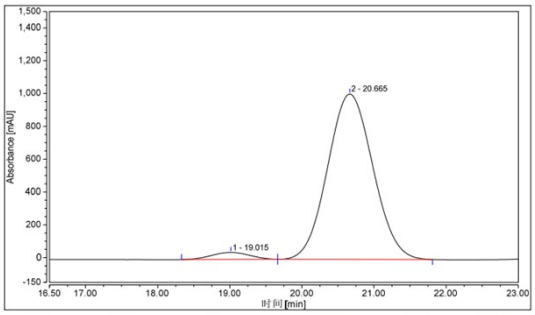


3a-*d*, 20% yield, 93% *ee*

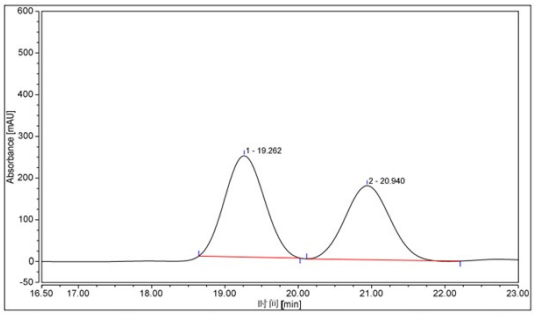
To an oven-dried 10 mL Schlenk tube containing a stirring bar was charged with $CoBr_2$ (4.4 mg, 0.02 mmol, 10 mol%), (*S*, *R*)-**L2** (10.7 mg, 0.024 mmol, 12 mol%) and 2.0 mL dry 1,2-dimethoxyethane in a nitrogen-filled glovebox, the mixture was stirred for 10 min at room temperature. Then **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv.), CsF (91.1 mg, 0.6 mmol, 3.0 equiv.) and another 2.0 mL dry 1,2-dimethoxyethane were added sequentially. The tube was sealed and removed from the glove box, Ph_2SiD_2[2] (111.8 mg, 0.6 mmol, 3.0 equiv.) was added dropwise at -20 °C and the reaction was stirred at -20 °C for 24 h. After the reaction was completed, the reaction mixture was diluted with saturated NH_4Cl (aq., 2.0 mL) and EtOAc (5 mL). The aqueous phase was extracted with EtOAc (2 × 5 mL). The organic phase was dried over Na_2SO_4, filtered, and the solvent removed in vacuo. The crude mixture was purified by flash column chromatography on silica gel using a mixture of Hexane/EtOAc as eluent to obtain the desired product **3a-*d*** in 20% isolated yield with 93% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.45 (m, 2H), 7.41 – 7.38 (m, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 3.30 (dd, *J* = 13.1, 7.4 Hz, 1H), 3.20 (d, *J* = 13.3 Hz, 1H), 3.12 (t, *J* = 7.8 Hz, 2H), 3.06 – 2.99 (m, 1H), 2.78 – 2.67 (m, 1H), 2.57 – 2.44 (m, 1H), 2.41 – 2.34 (m, 1H), 2.03 – 1.93 (m, 2H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.7, 134.0, 131.5, 129.1, 127.3, 126.1, 126.0, 125.7, 125.6, 123.3, 56.9, 52.2, 36.5, 35.6, 31.5, 30.9.

HPLC (UltiMate 3000): Daicel Chiralpak IC Column (*n*-Hexane/*i*-PrOH = 30 : 70, 1 mL/min), 30 °C, 220 nm, R*t* = 19.015 min (minor) and 20.665 min (major).



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	19.015	25.818	42.399	3.40	4.04
2	20.665	734.017	1007.375	96.60	95.96



peak	RT min	Area mAU*min	Height mAU	Area %	Height %
1	19.262	151.964	242.539	54.78	57.75
2	20.940	125.459	177.464	45.22	42.25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7.9372
7.8788
7.8644
7.7516
7.7353
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7.4919
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7.3845
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7.2846
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3.2107
3.1841
3.1390
3.1234
3.1077
3.0436
3.0169
3.0015
2.7423
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2.6948
2.5239
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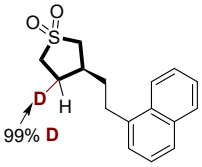
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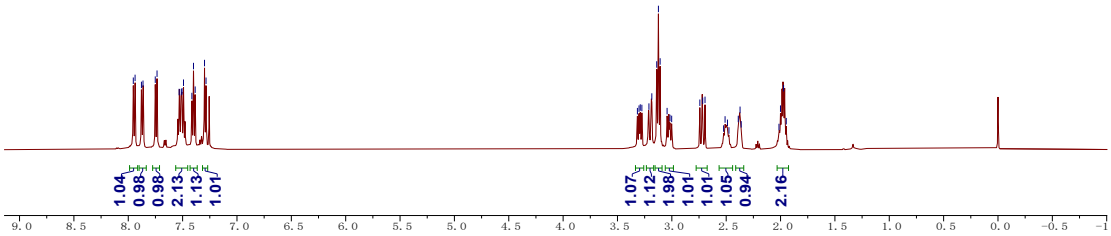
D
H
99% D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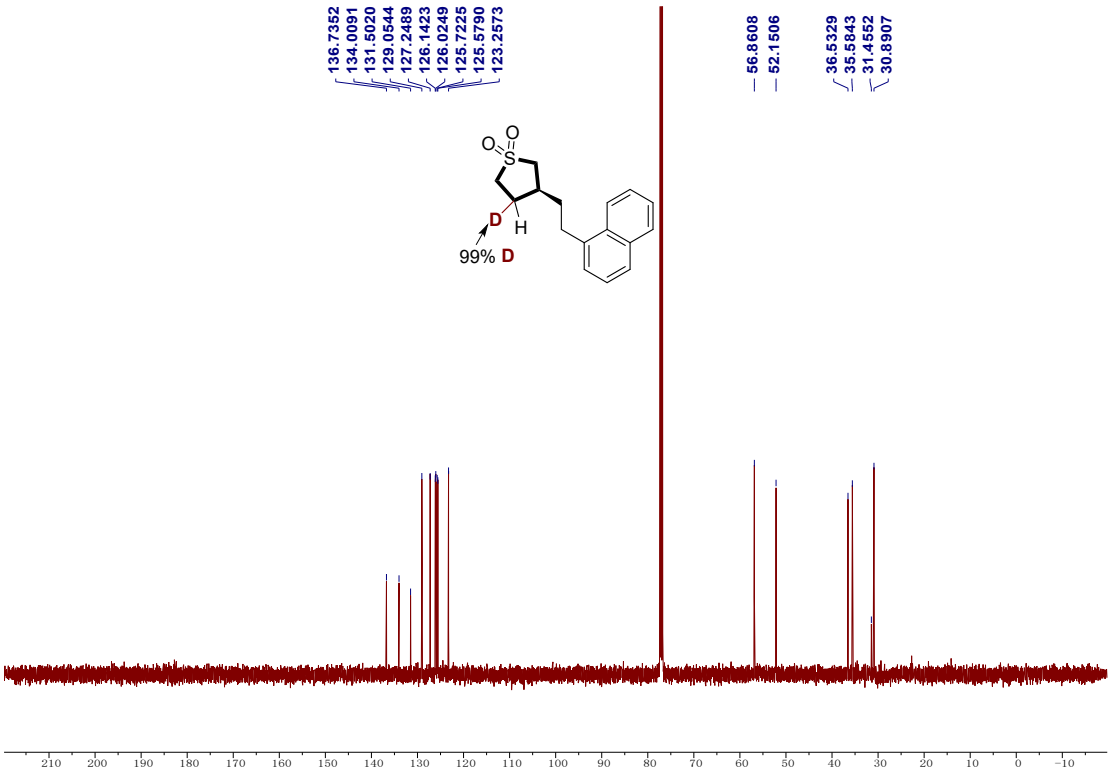
−1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36.5329
35.5843
31.4552
30.8907
O
O
S
D
H
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200
190
180
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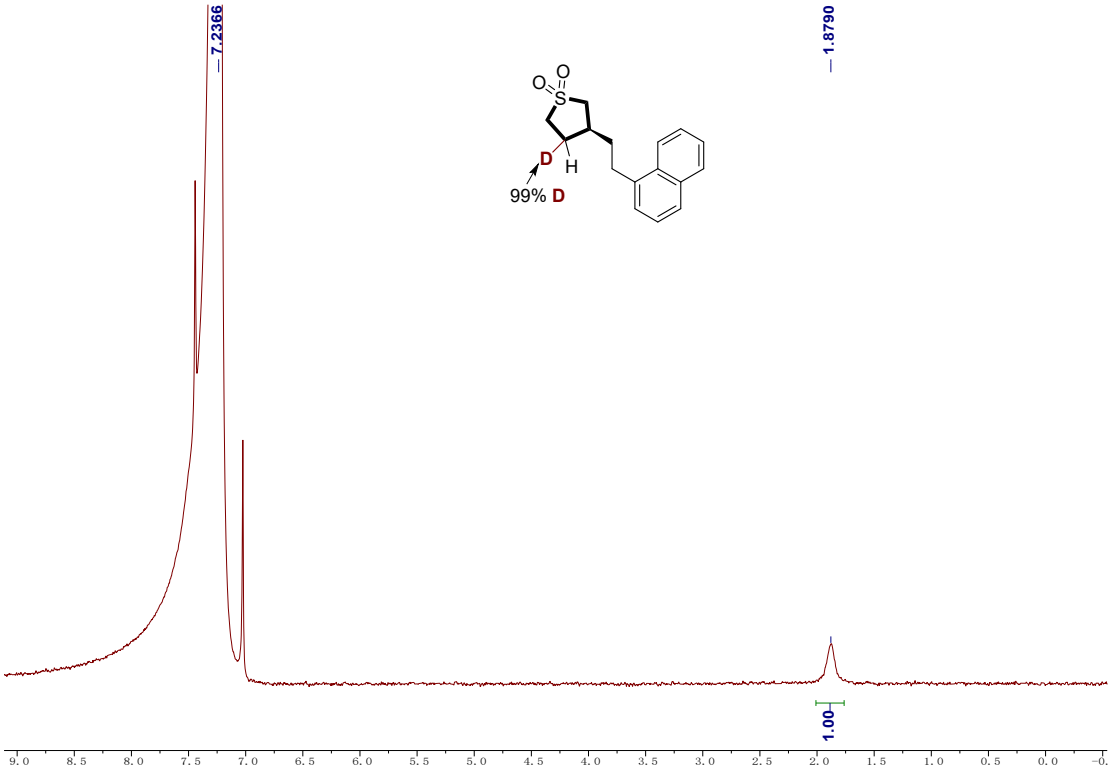
100
90
80
70
60
50
40
30
20
10
0
−10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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

References

[1] F. G. Bordwell, W. H. McKellin, *J. Am. Chem. Soc.* **1951**, *73*, 2251-2253.

[2] N. Gandhamsetty, S. Park, S. Chang, *J. Am. Chem. Soc.* **2015**, *137*, 15176-15184.

X-ray Crystallographic data for (S)-3p

Single crystals for X-ray studies were grown by slow evaporation of a solution of compound **3p** in a mixture of hexane and DCM at room temperature. X-Ray structural analysis of single crystal **3p** was obtained to confirm the absolute configuration. The X-ray data of **3p** is deposited in the Cambridge Crystallographic Data Centre with a number CCDC 2322228.

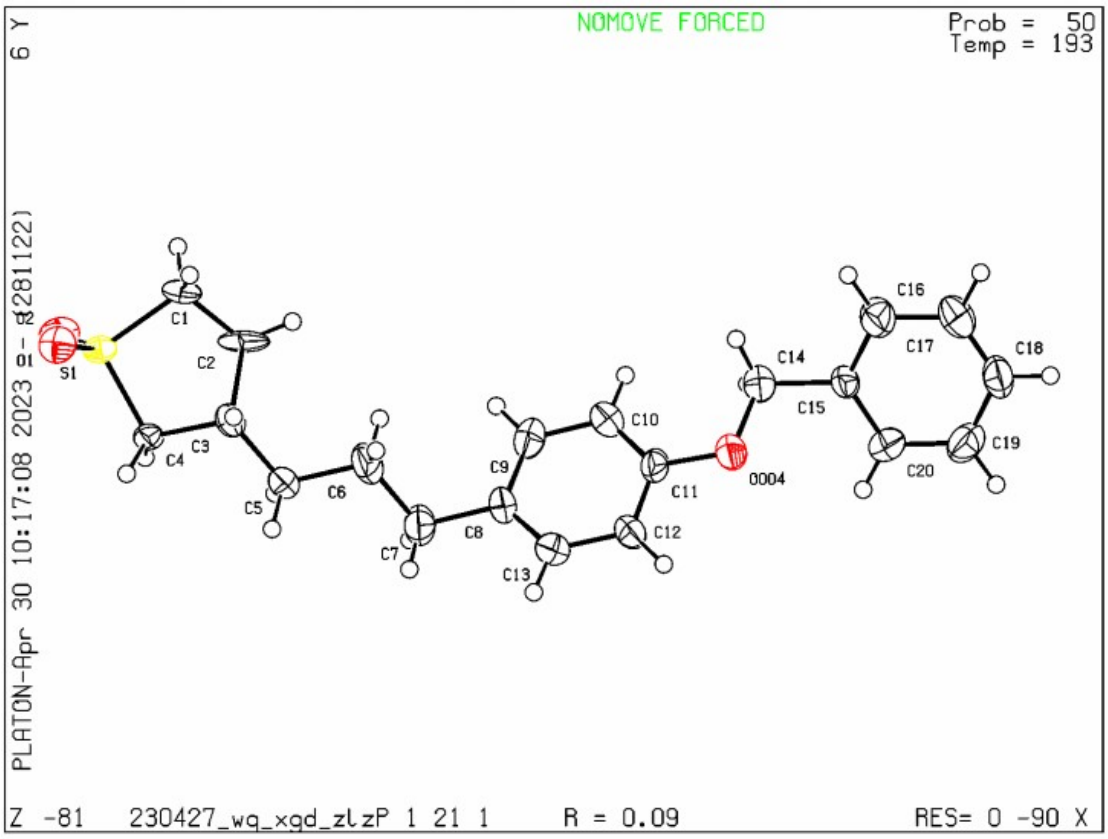


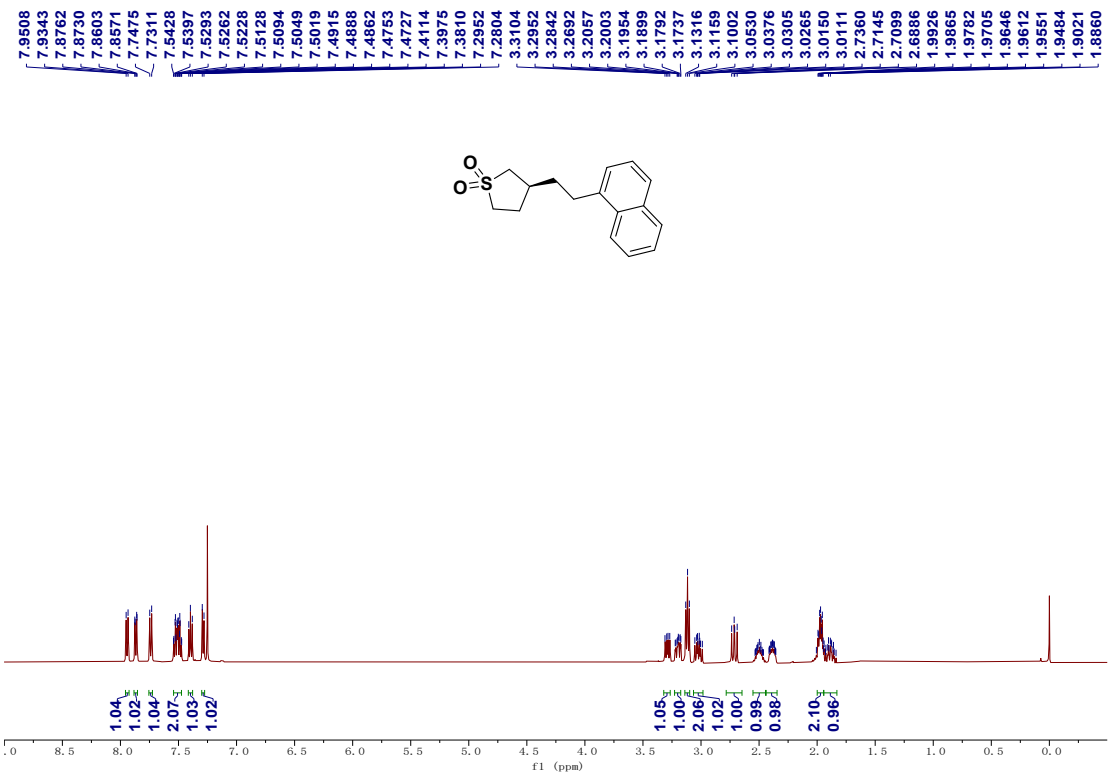
Figure S1. X-ray structure of **3p**

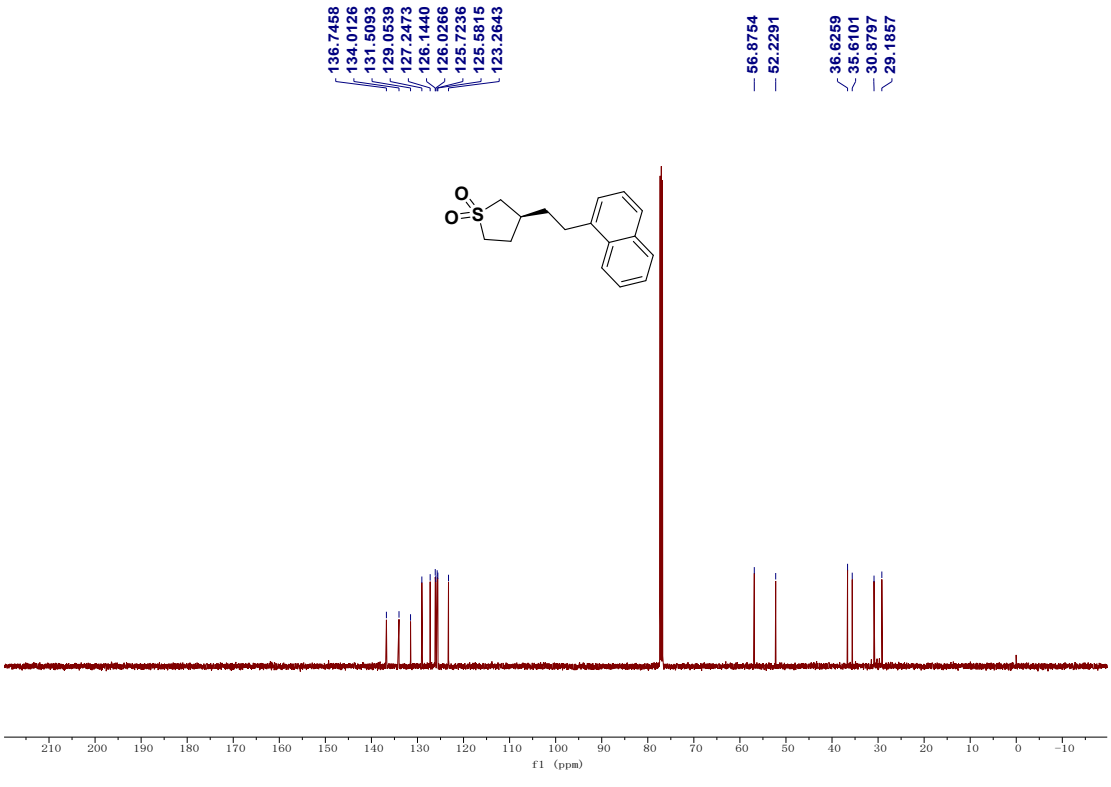
Table S8. Crystal data and structure refinement for 3p

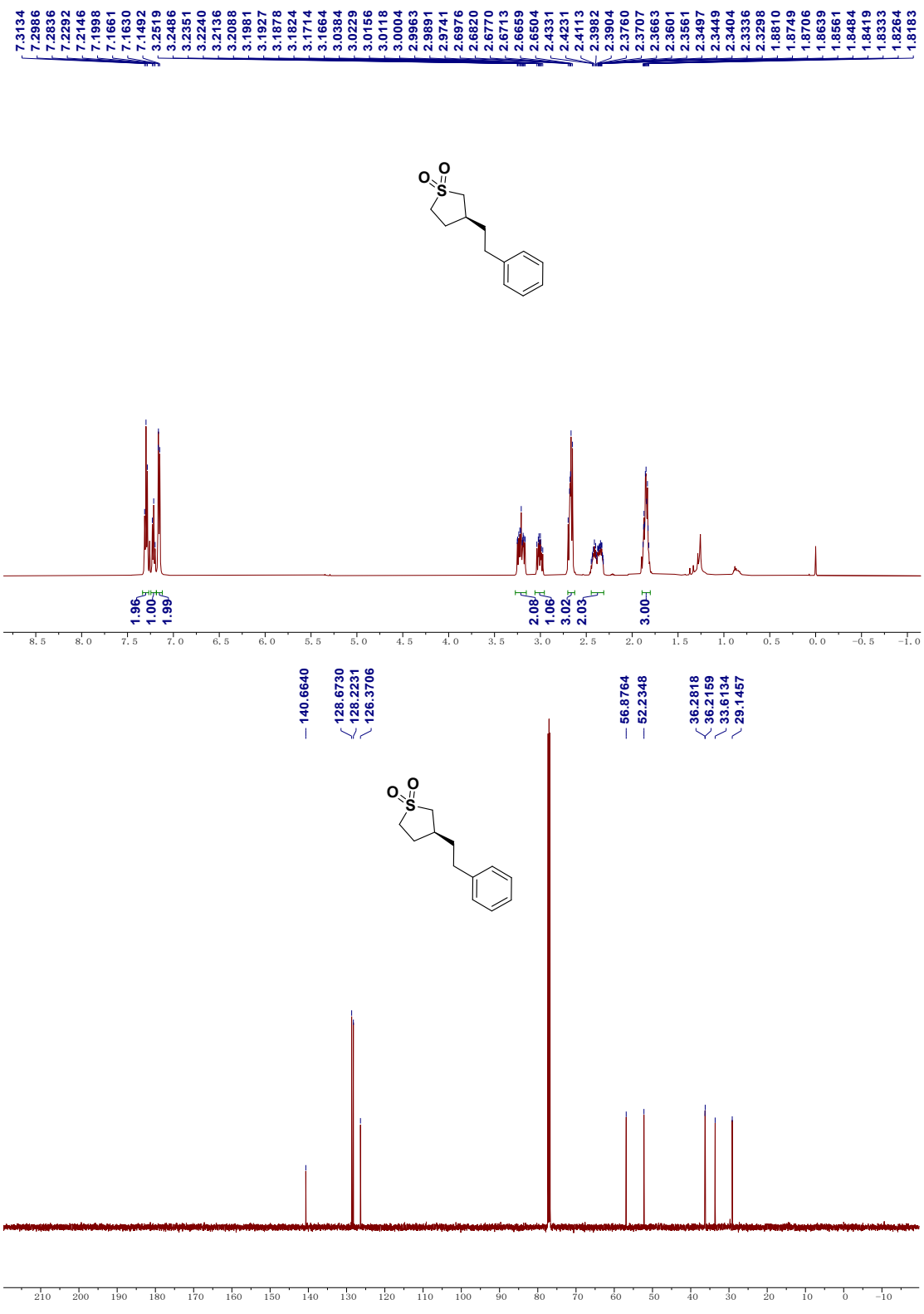
Identification code	230427_WQ_XGD_ZLZ_0m	
Empirical formula	$C_{20}H_{24}O_3S$	
Formula weight	344.45	
Temperature	193 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 6.243(2) Å	α = 90°.
	b = 8.030(3) Å	β = 94.875(10)°.
	c = 19.073(7) Å	γ = 90°.
Volume	952.7(6) $Å^3$	

Z	2
Density (calculated)	1.201 Mg/m^3
Absorption coefficient	0.184 mm^{-1}
F(000)	368.0
Crystal size	0.13 x 0.12 x 0.1 mm^3
Radiation	MoKα (λ = 0.71073)
Theta range for data collection	2.143 to 25.186°.
Index ranges	-7<=h<=6, -9<=k<=9, -22<=l<=22
Reflections collected	5375
Independent reflections	3180 [R(int) = 0.0497]
Data / restraints / parameters	3180 / 1 / 217
Goodness-of-fit on F^2	1.121
Final R indices [I>2sigma(I)]	R_1 = 0.0922, wR_2 = 0.2420
R indices (all data)	R_1 = 0.1040, wR_2 = 0.2547
Absolute structure parameter	0.19(10)
Largest diff. peak and hole	0.10 and -0.61 e.Å$^-$

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra



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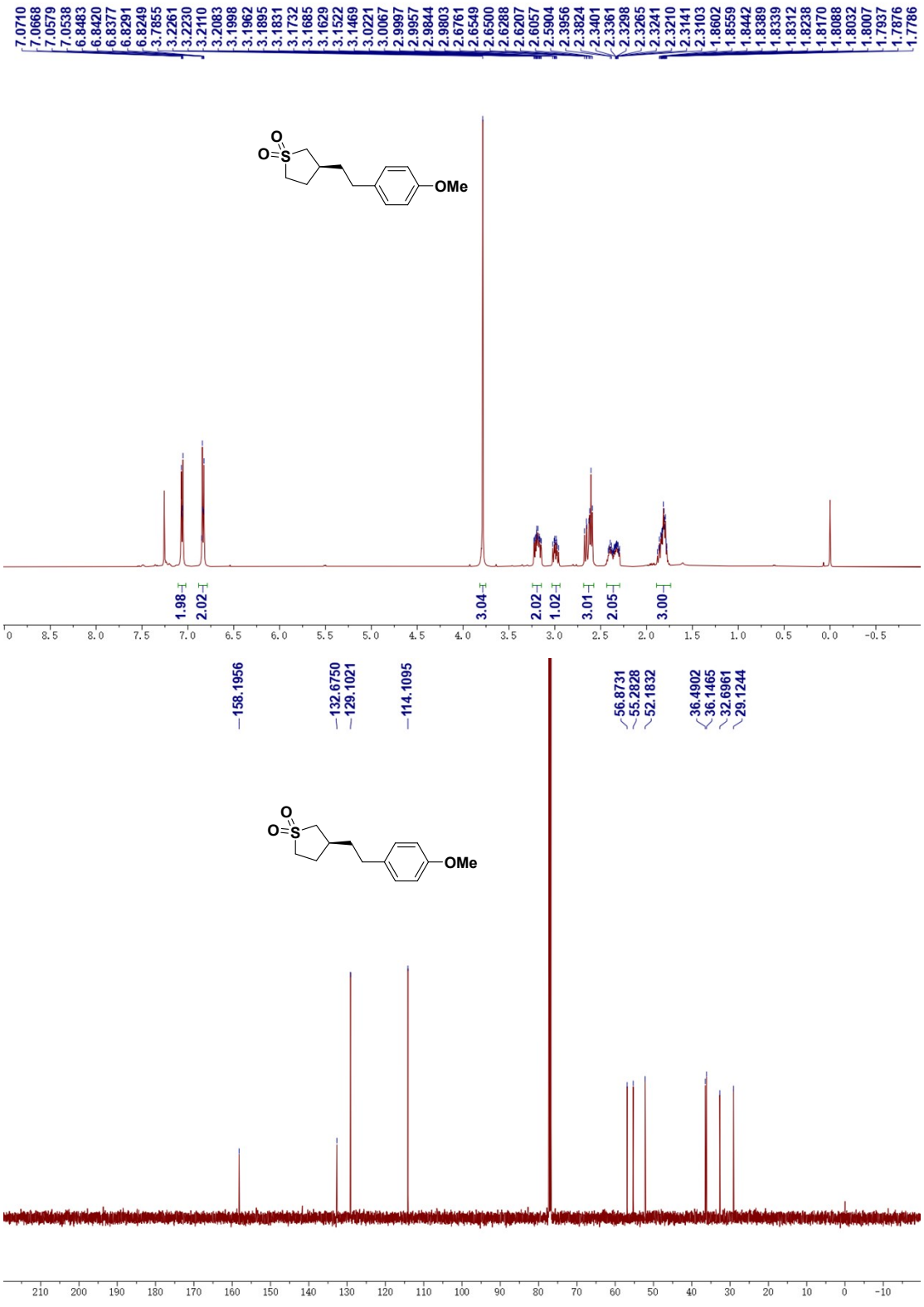
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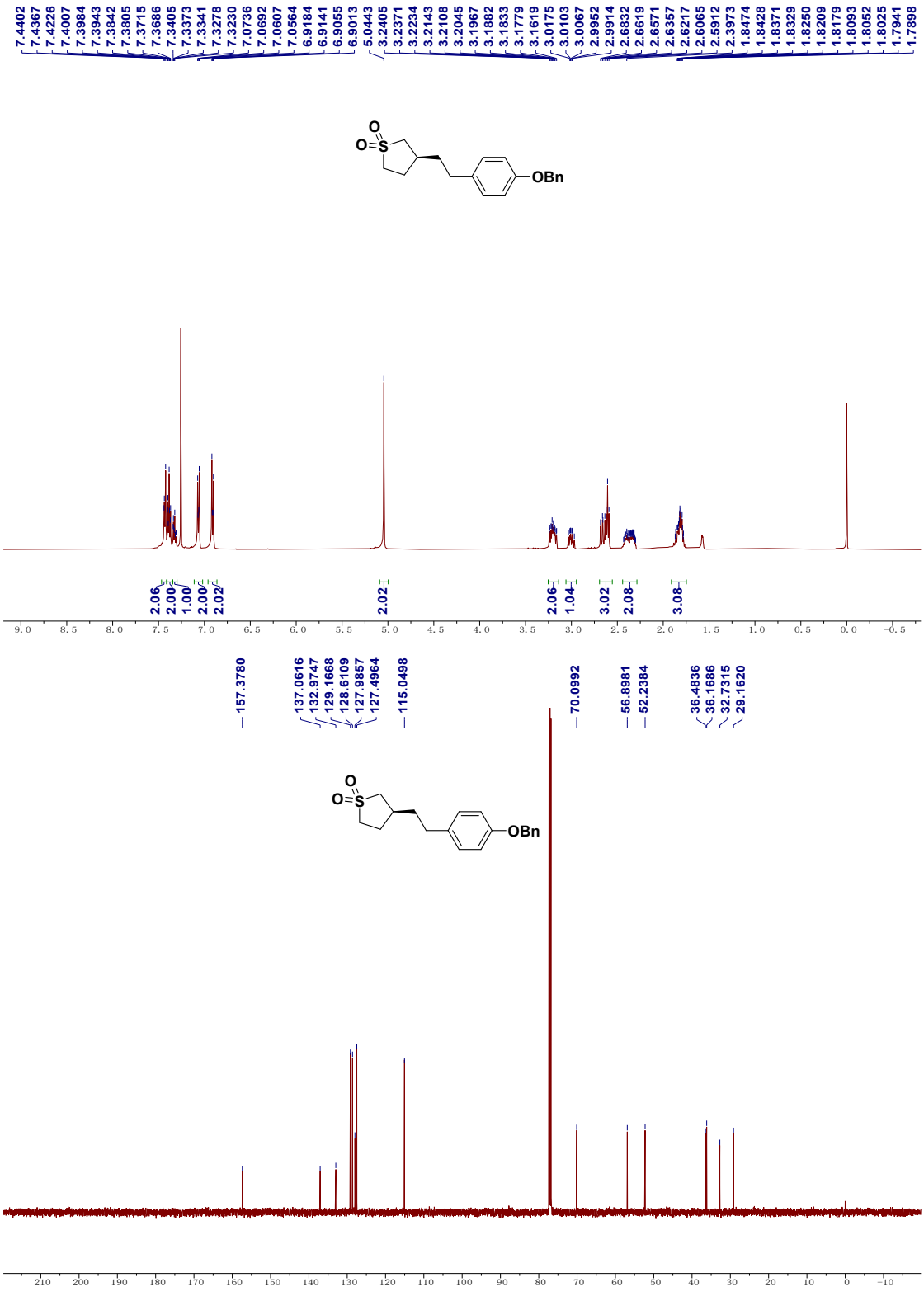
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1.04
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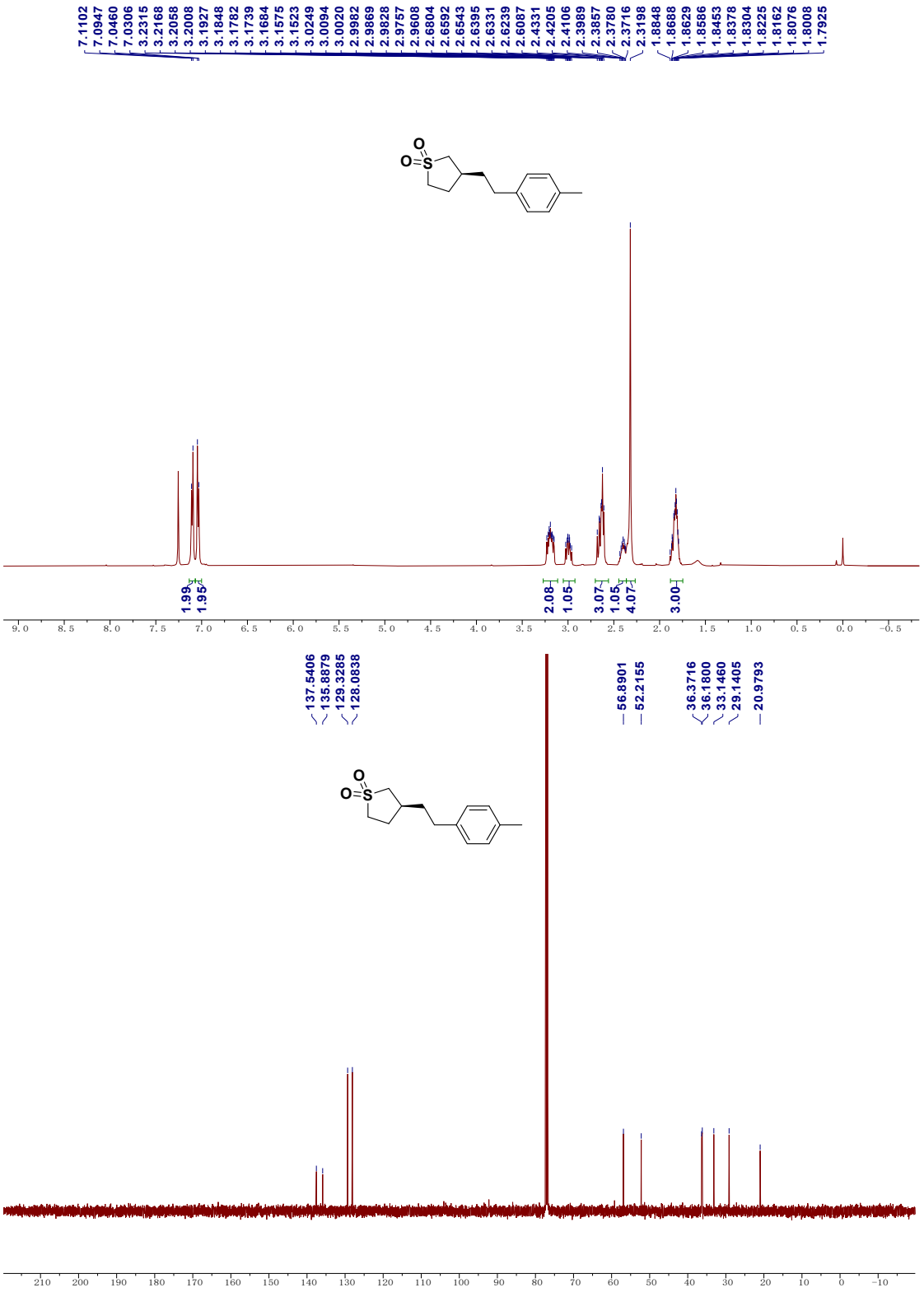
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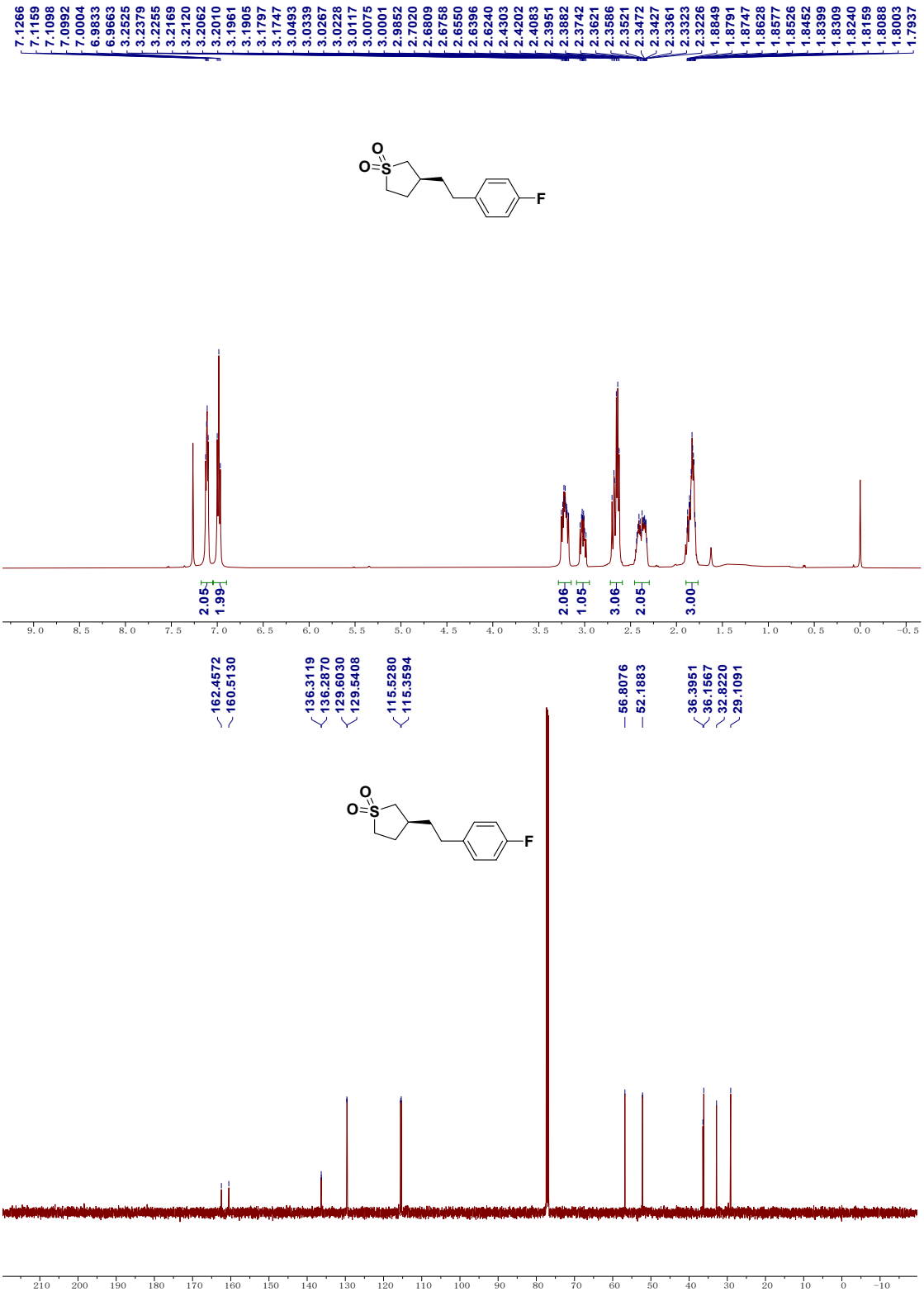
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F
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200
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80
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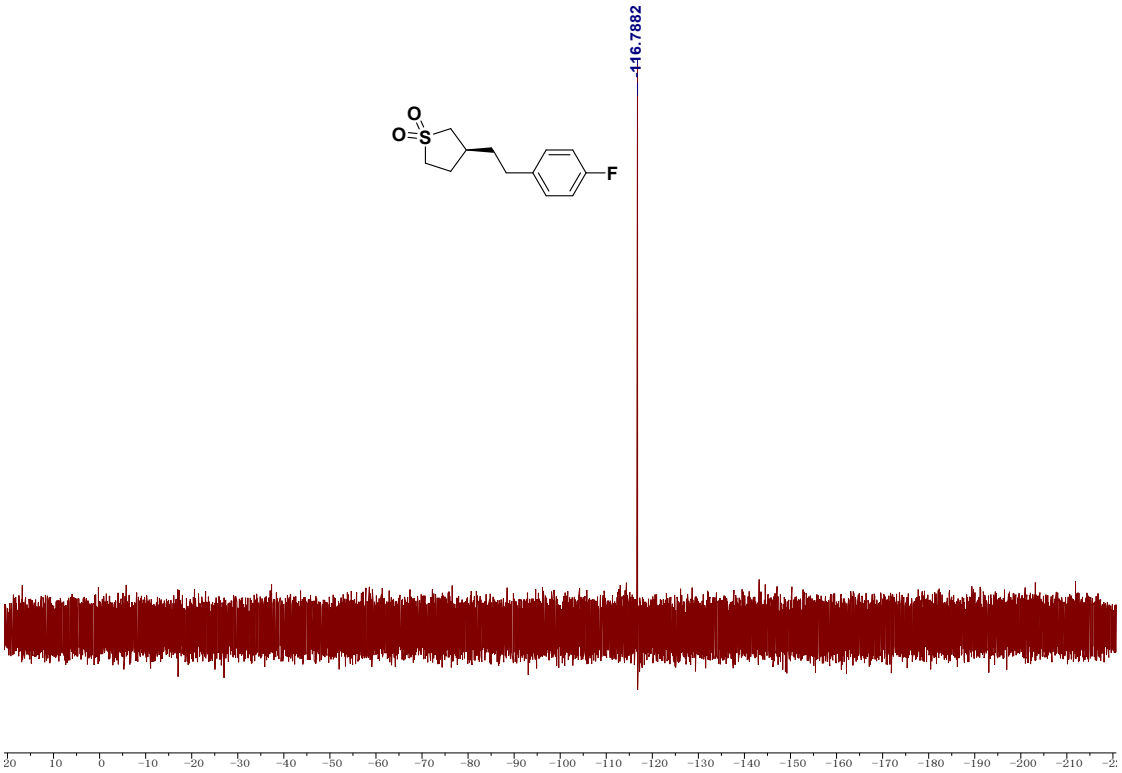
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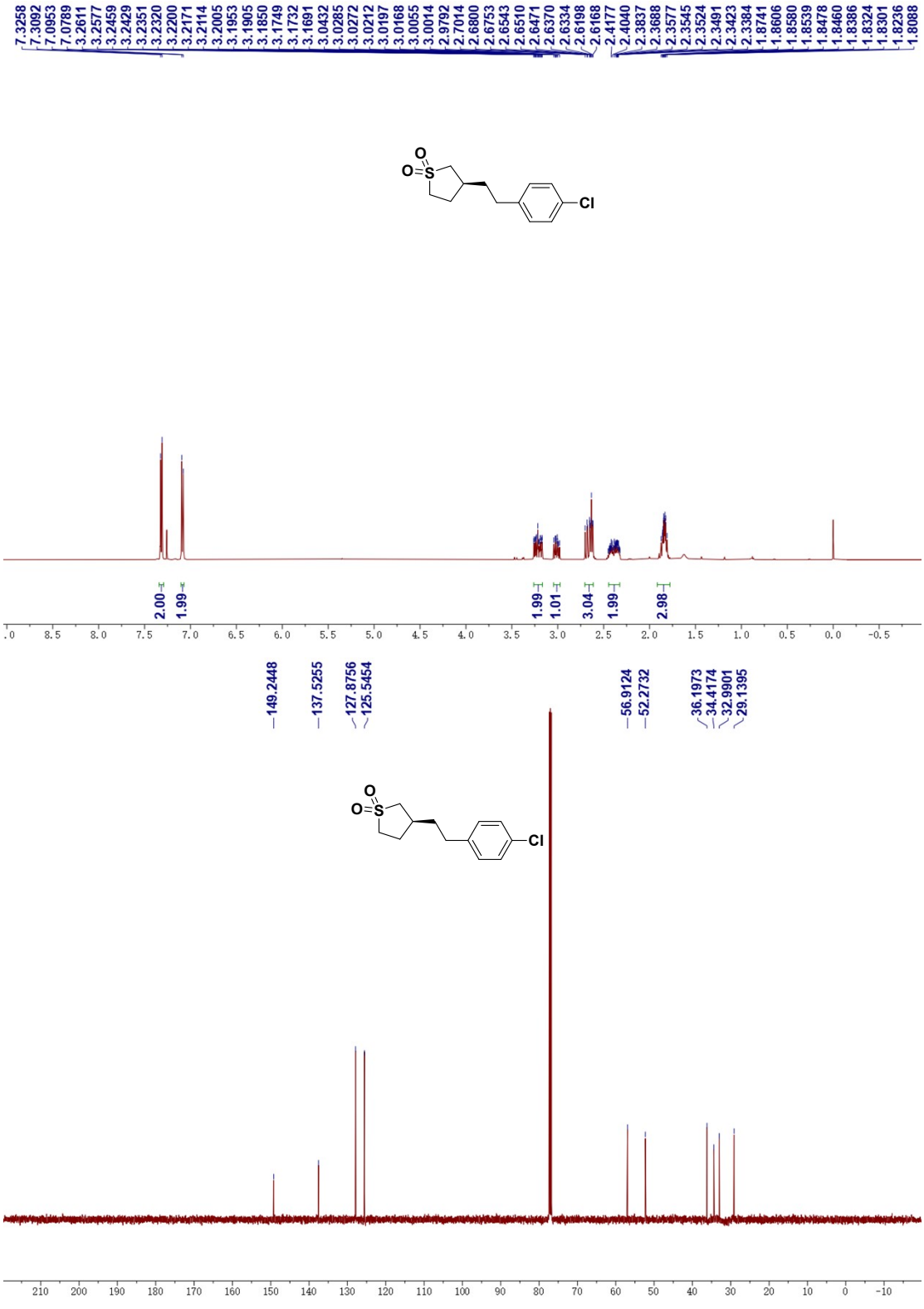
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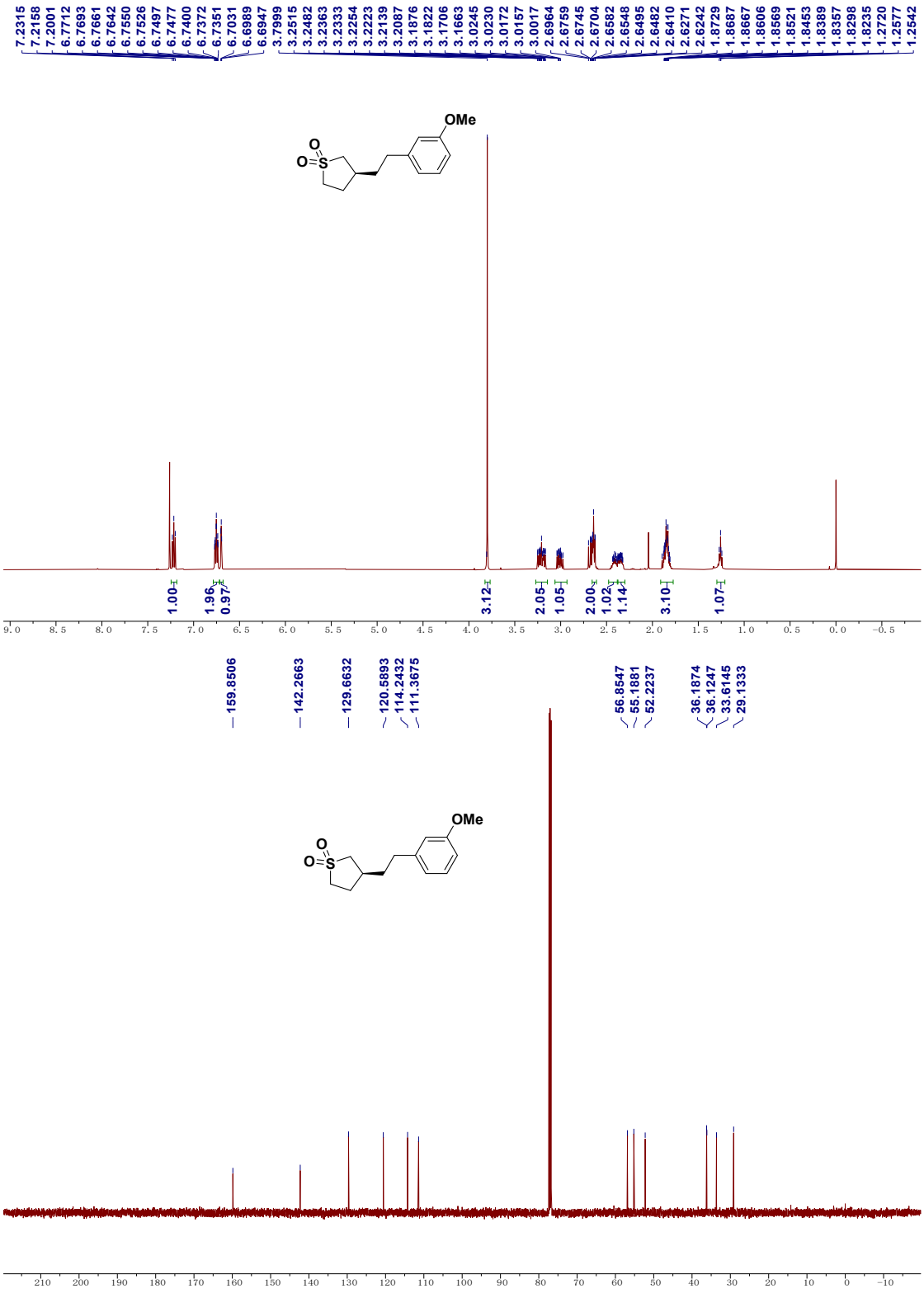
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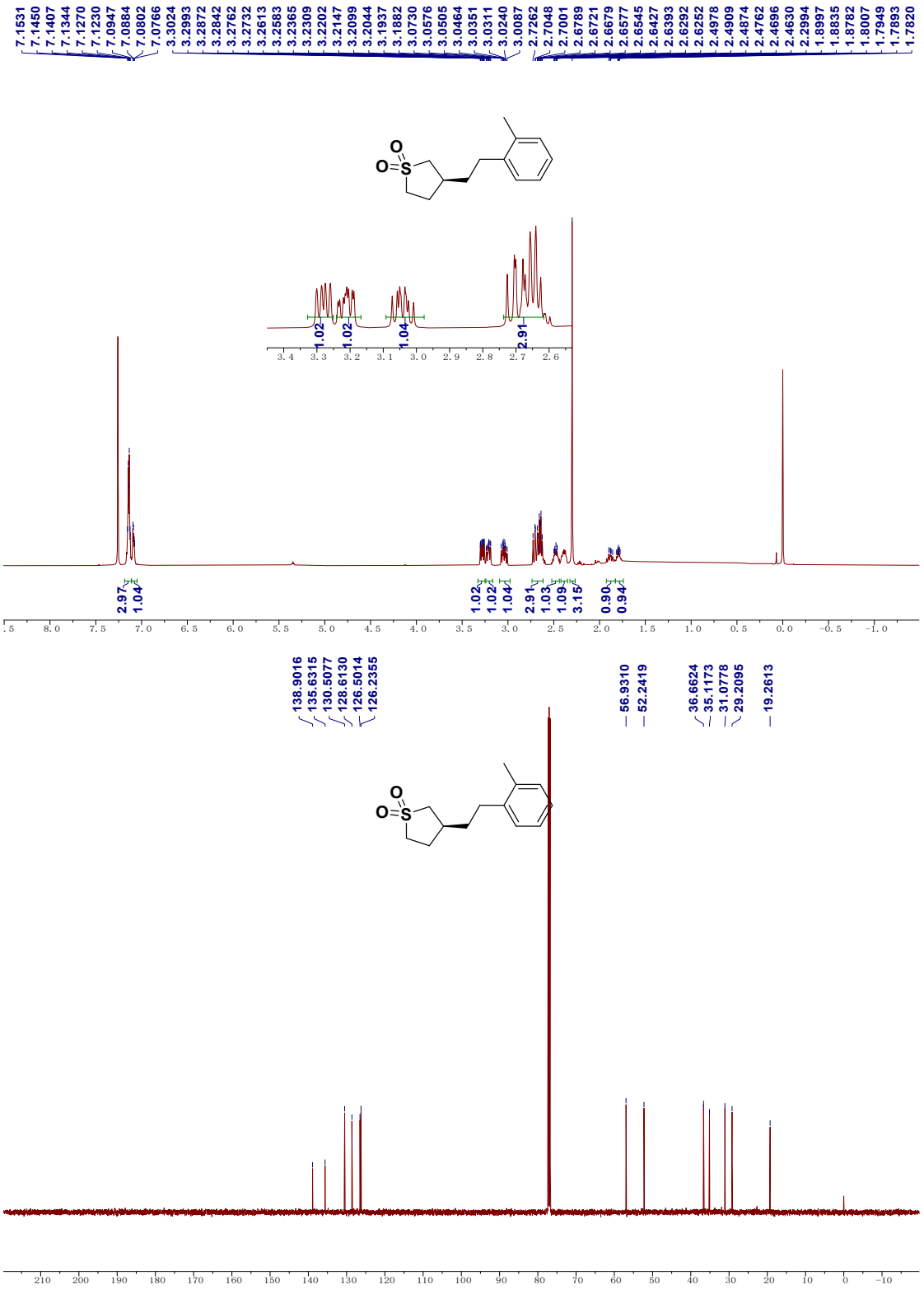
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2.97 1.04 1.02 1.02 1.04 2.91 1.03 1.09 3.15 0.90 0.94
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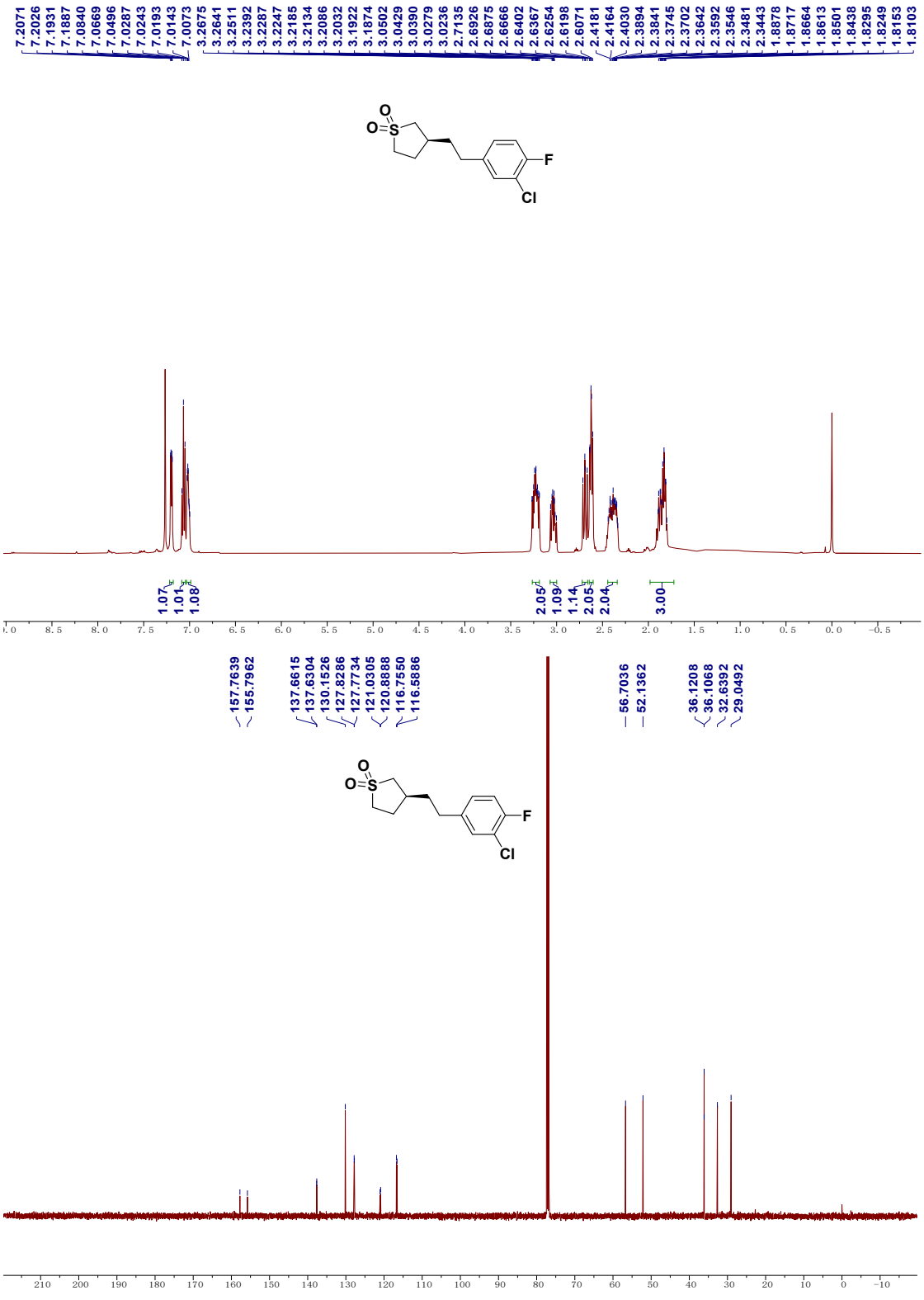
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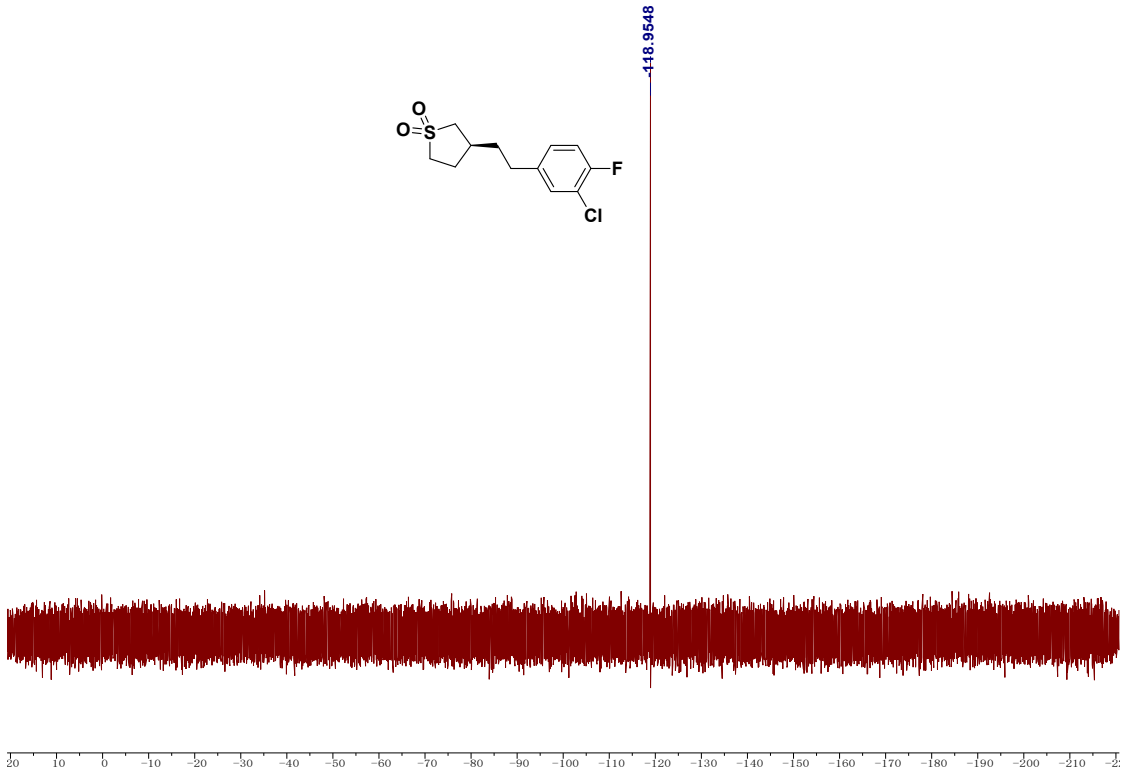
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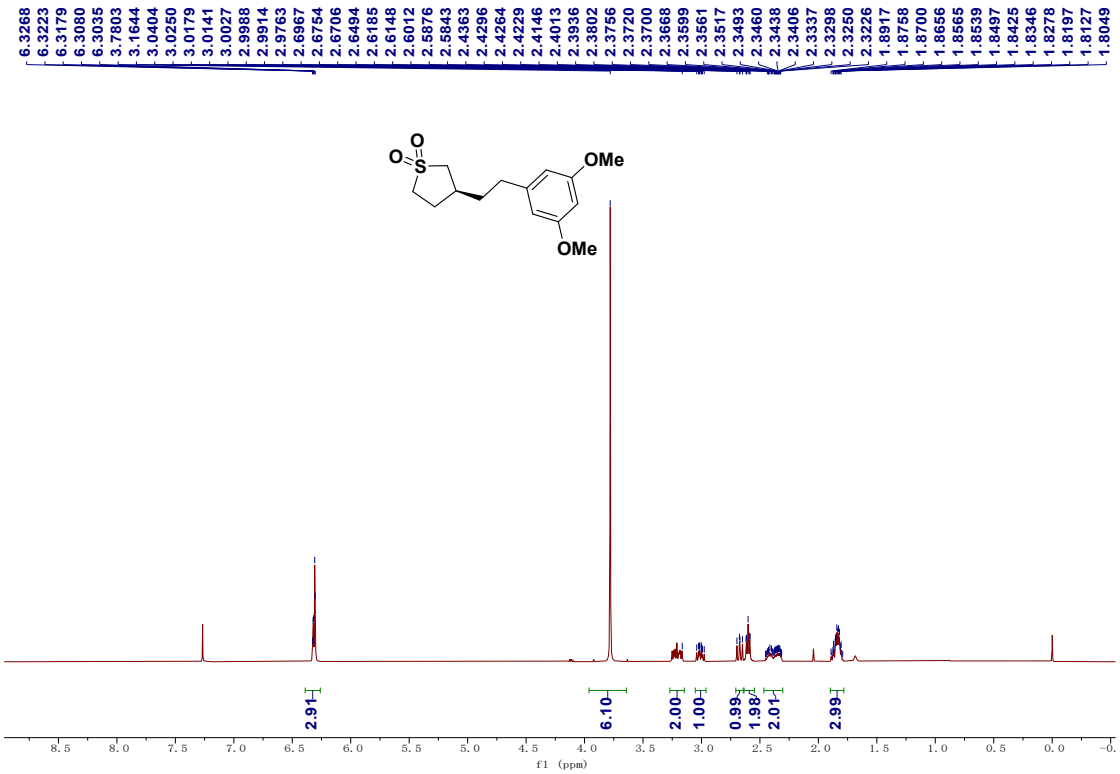
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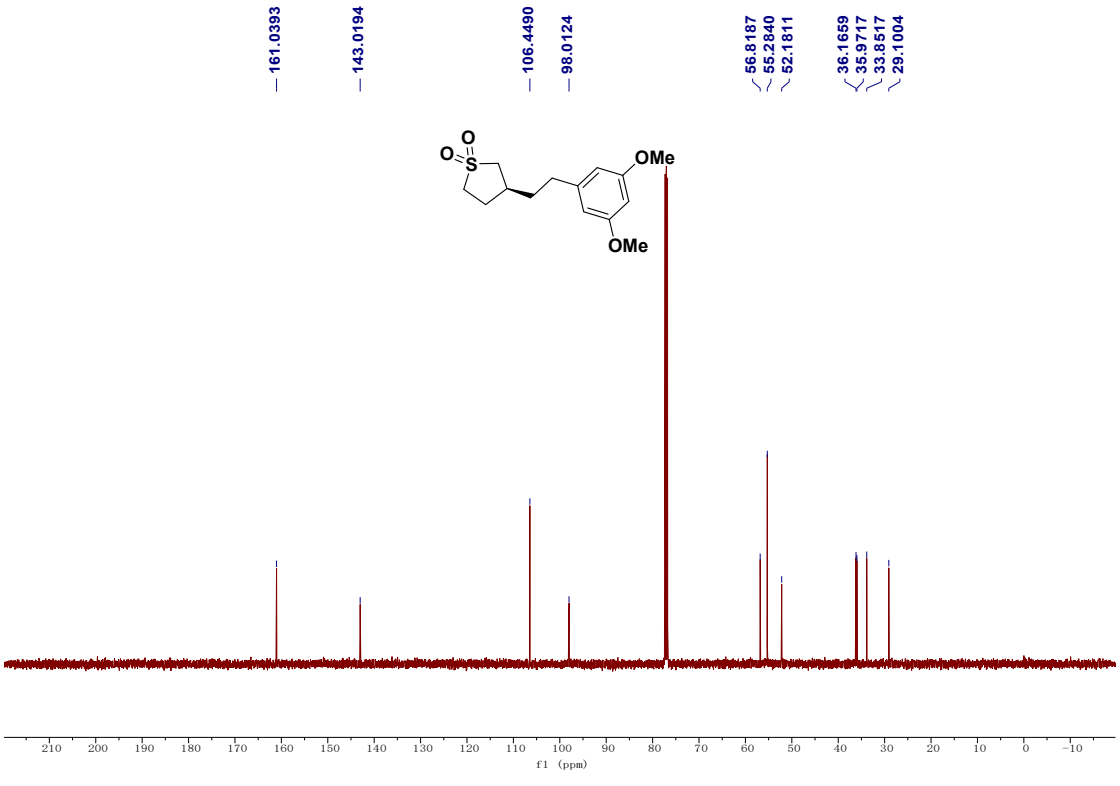
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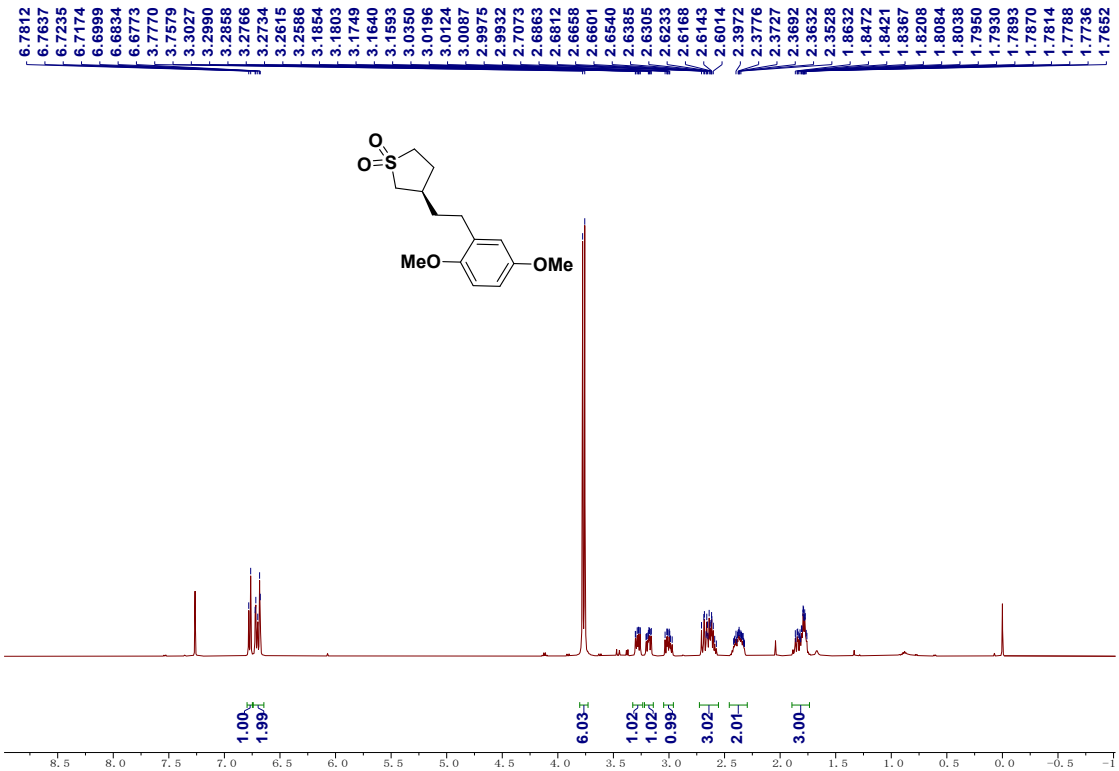
S
OMe
OMe
f1 (ppm)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3.00
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6.0
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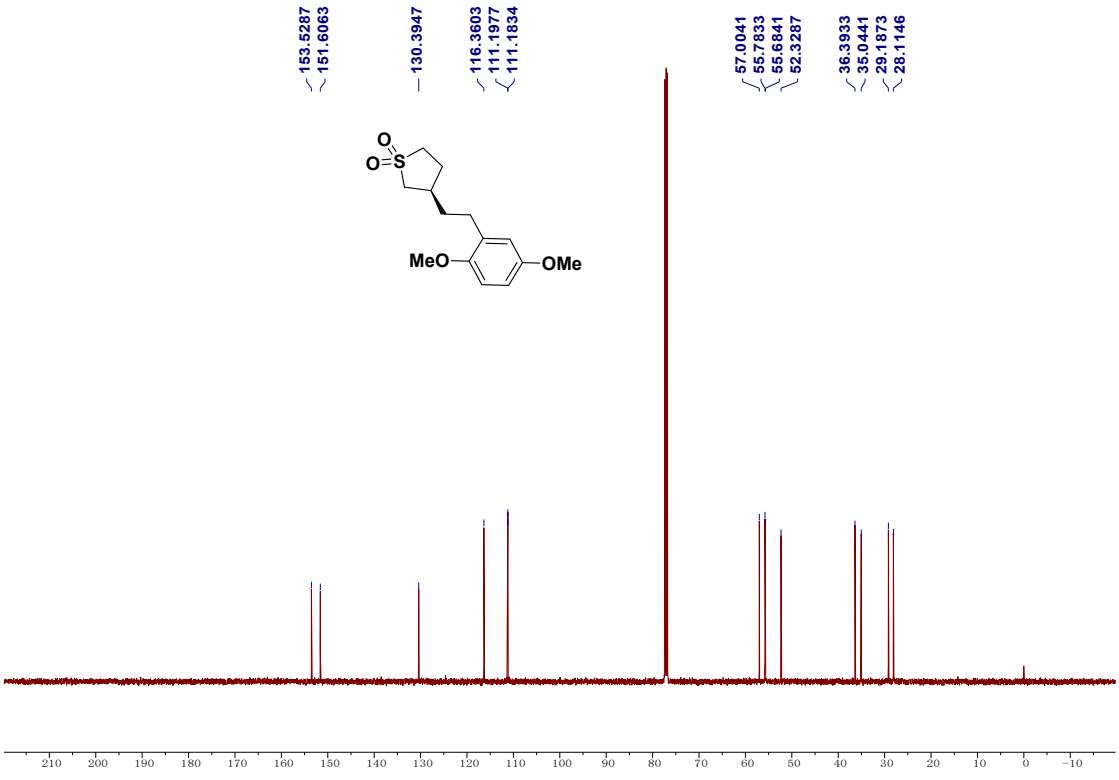
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OMe
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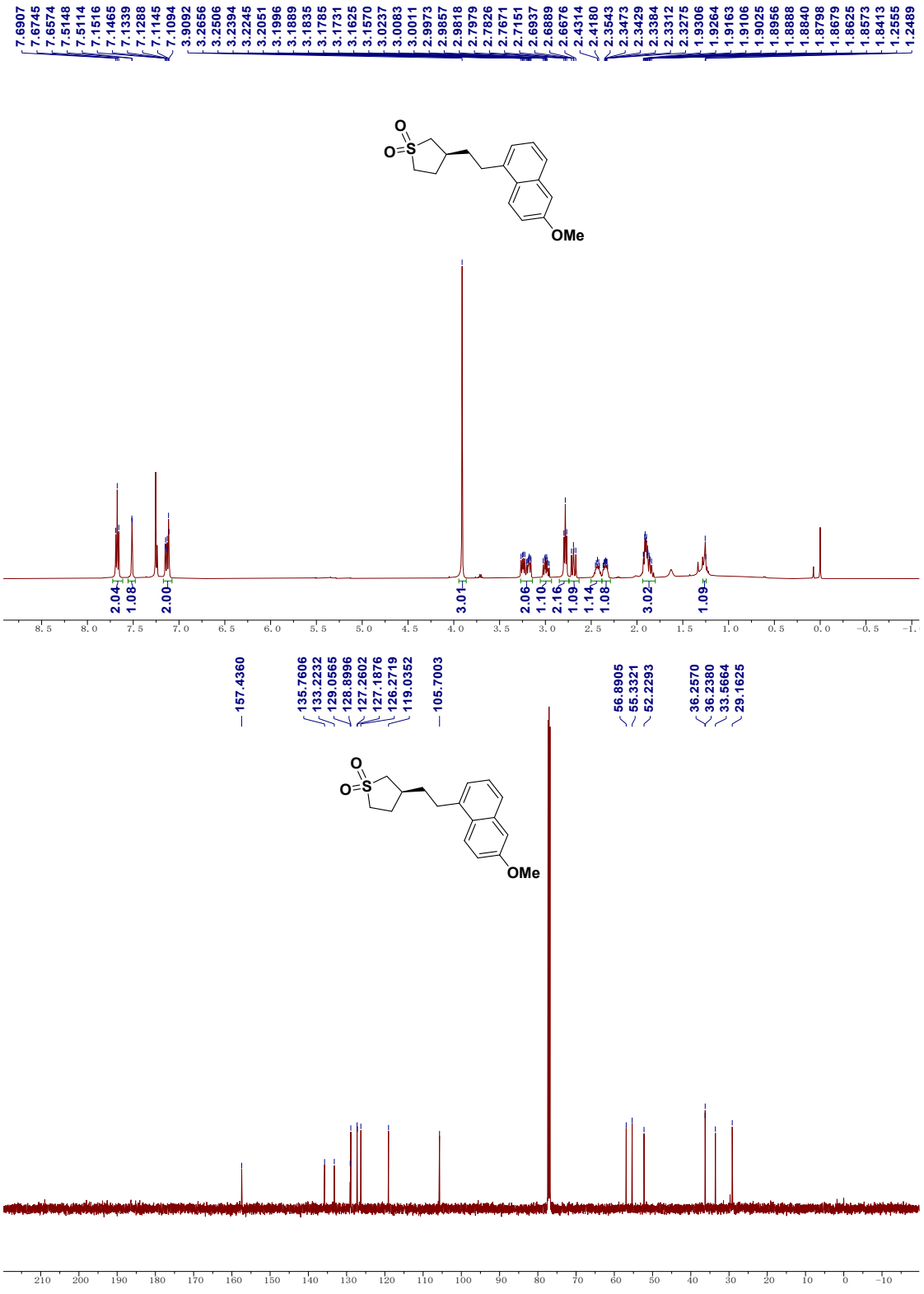
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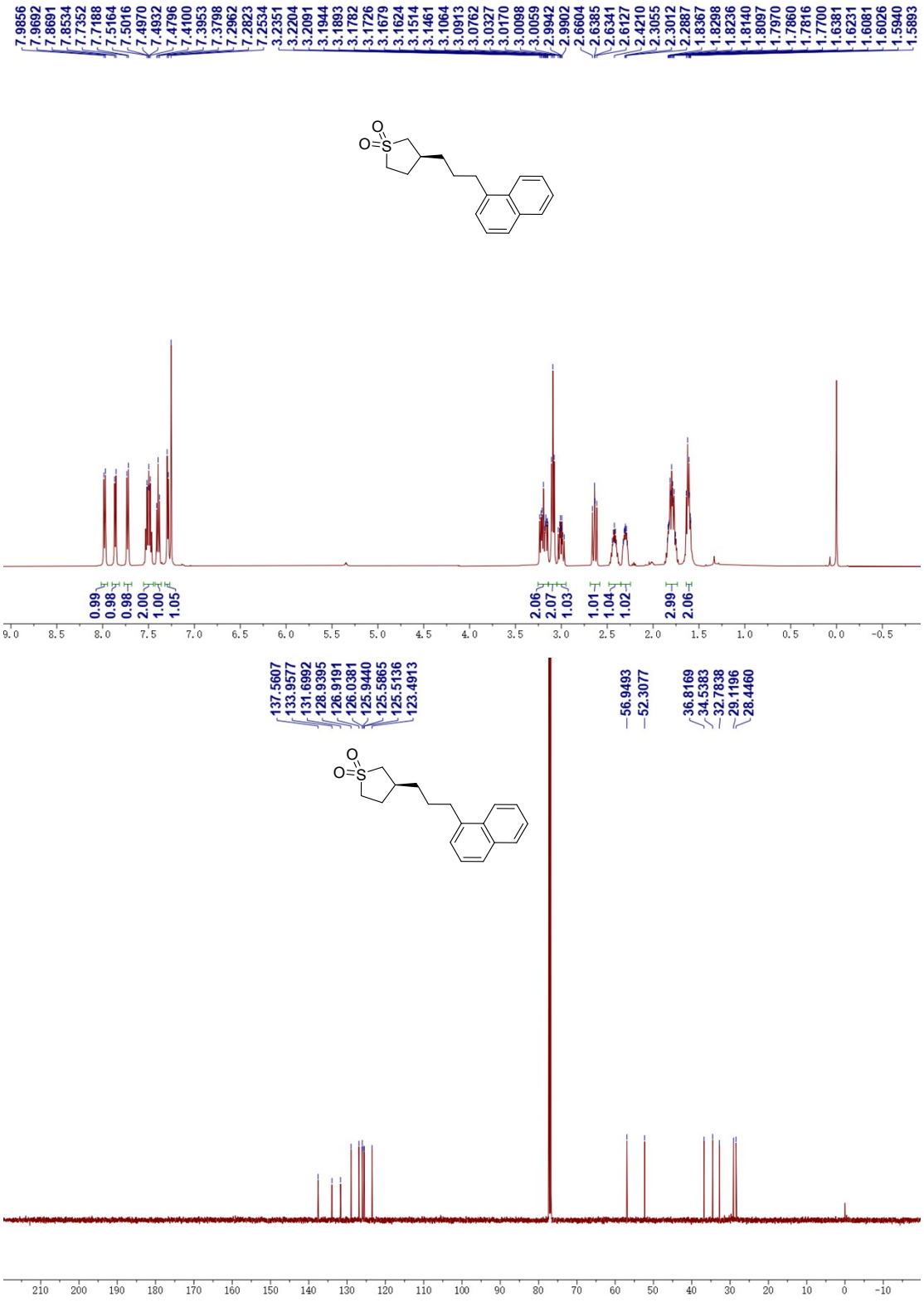
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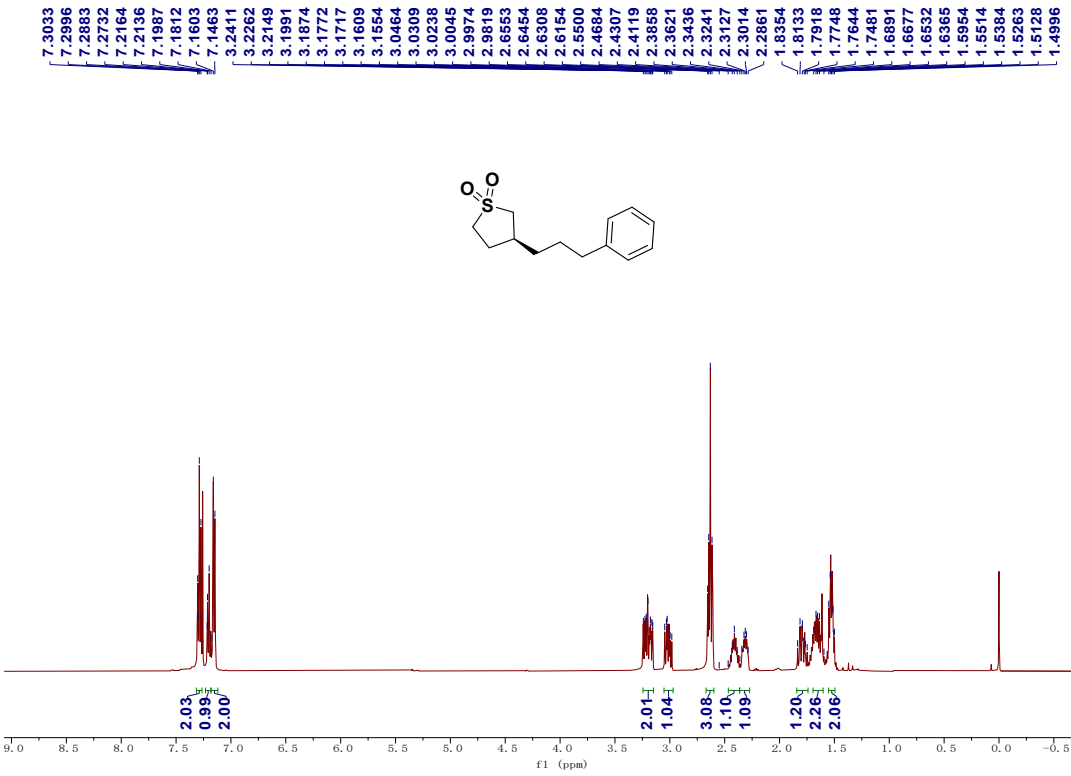
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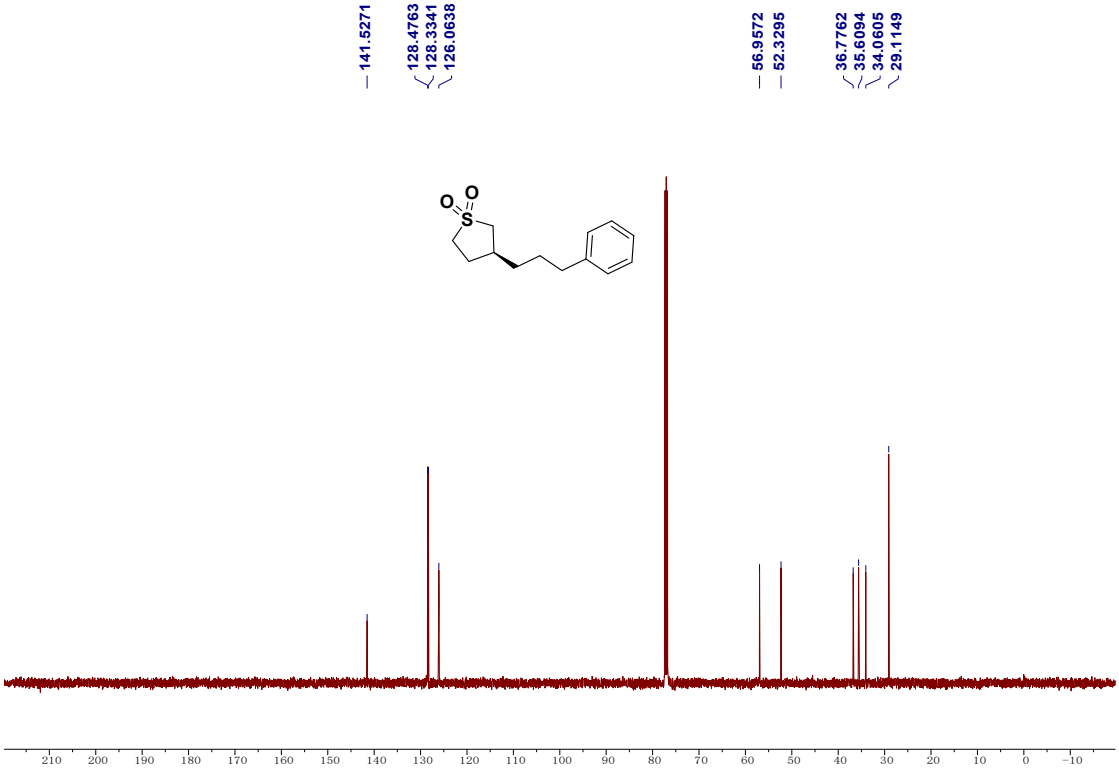
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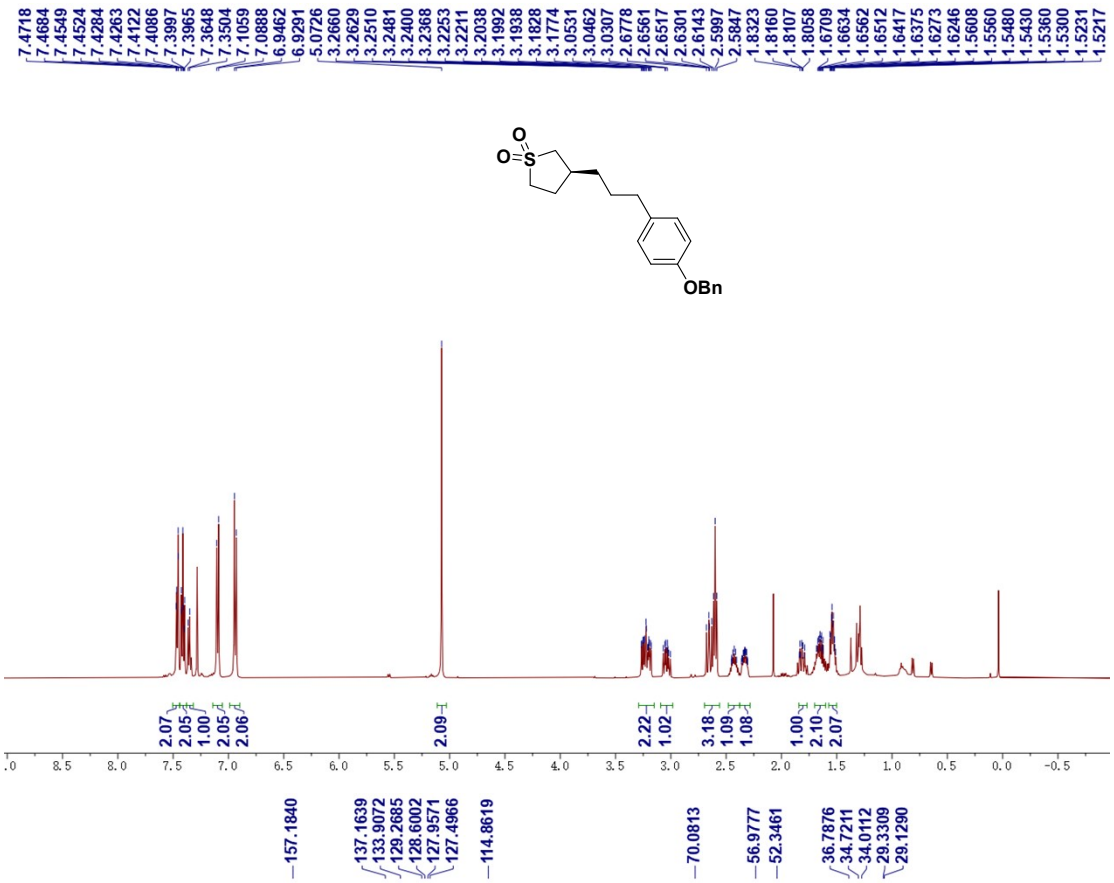
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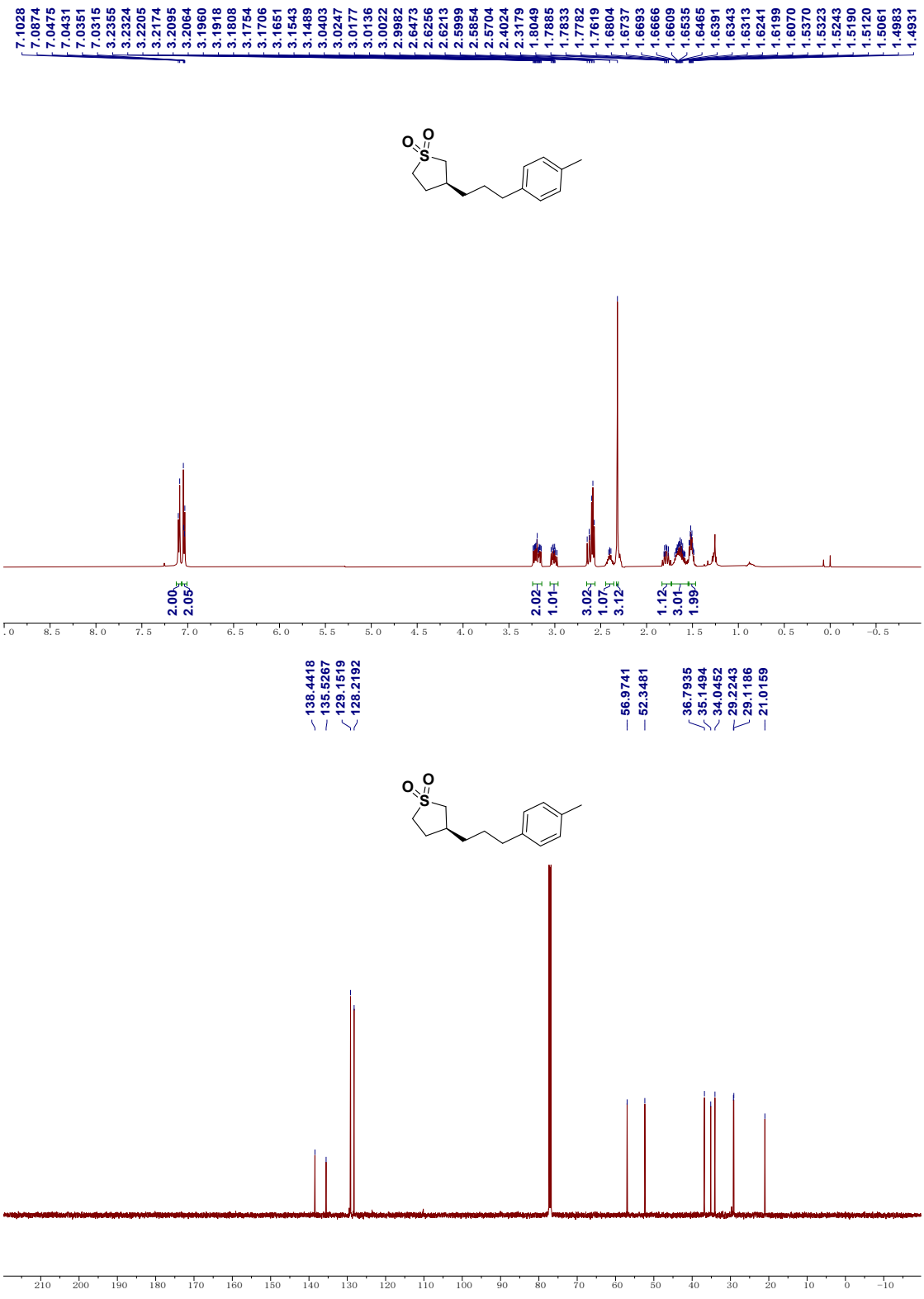
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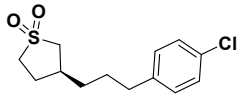
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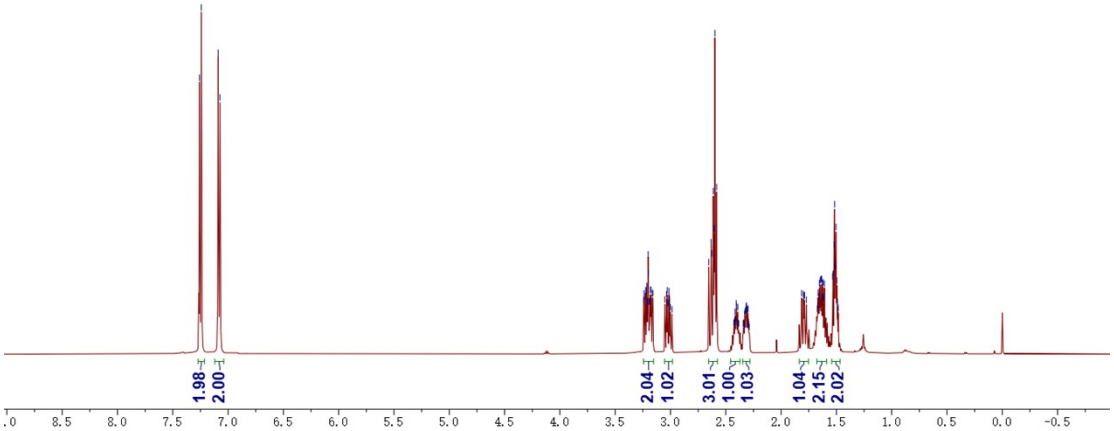
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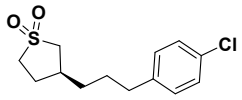
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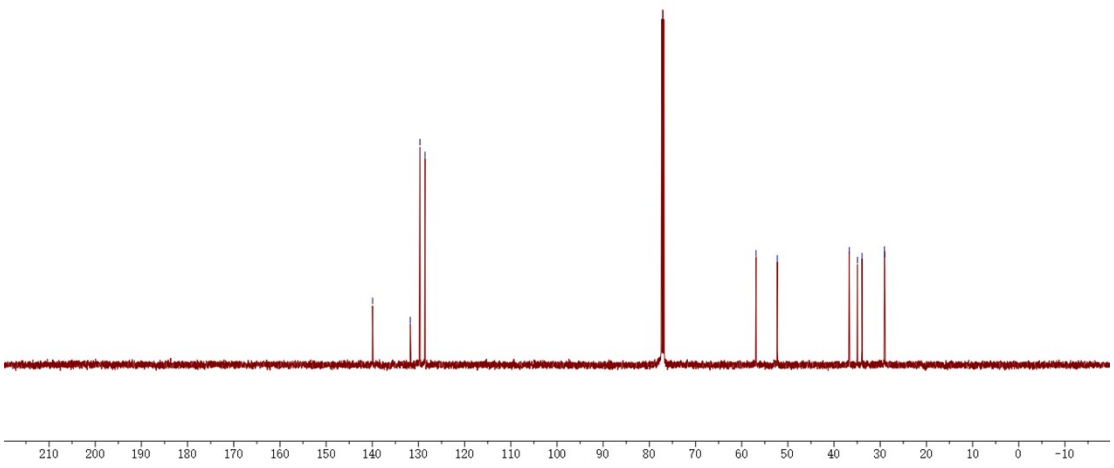
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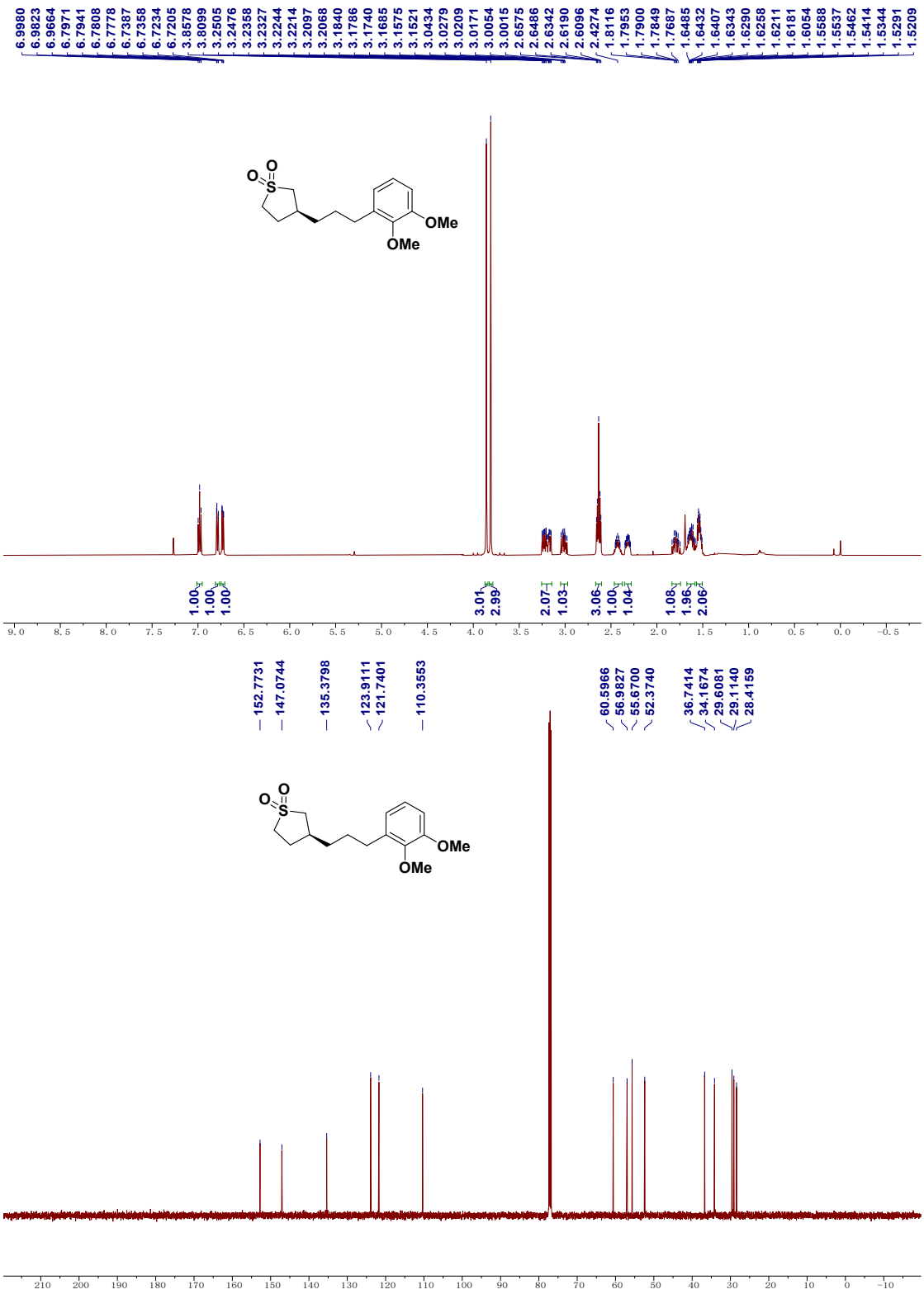
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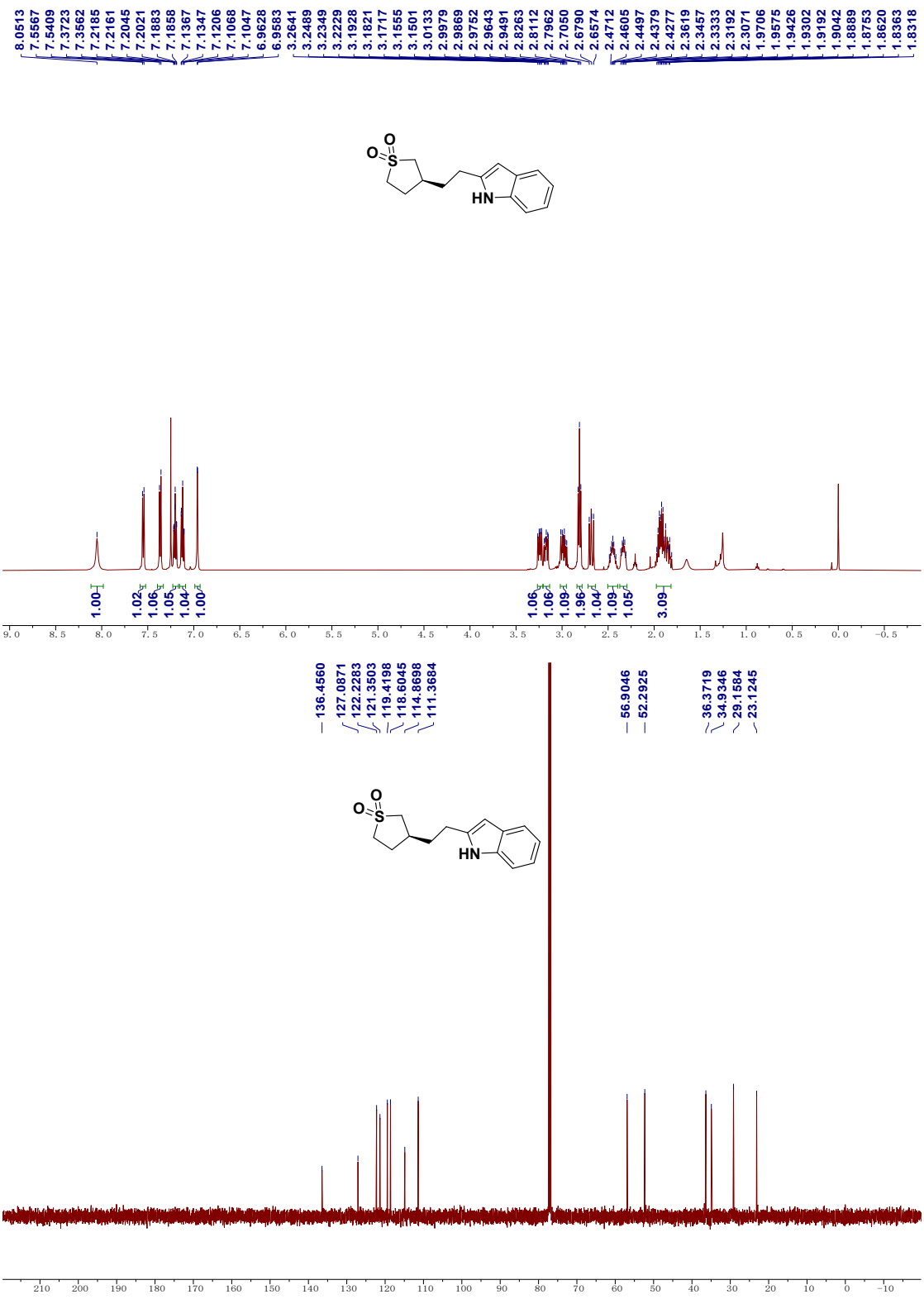
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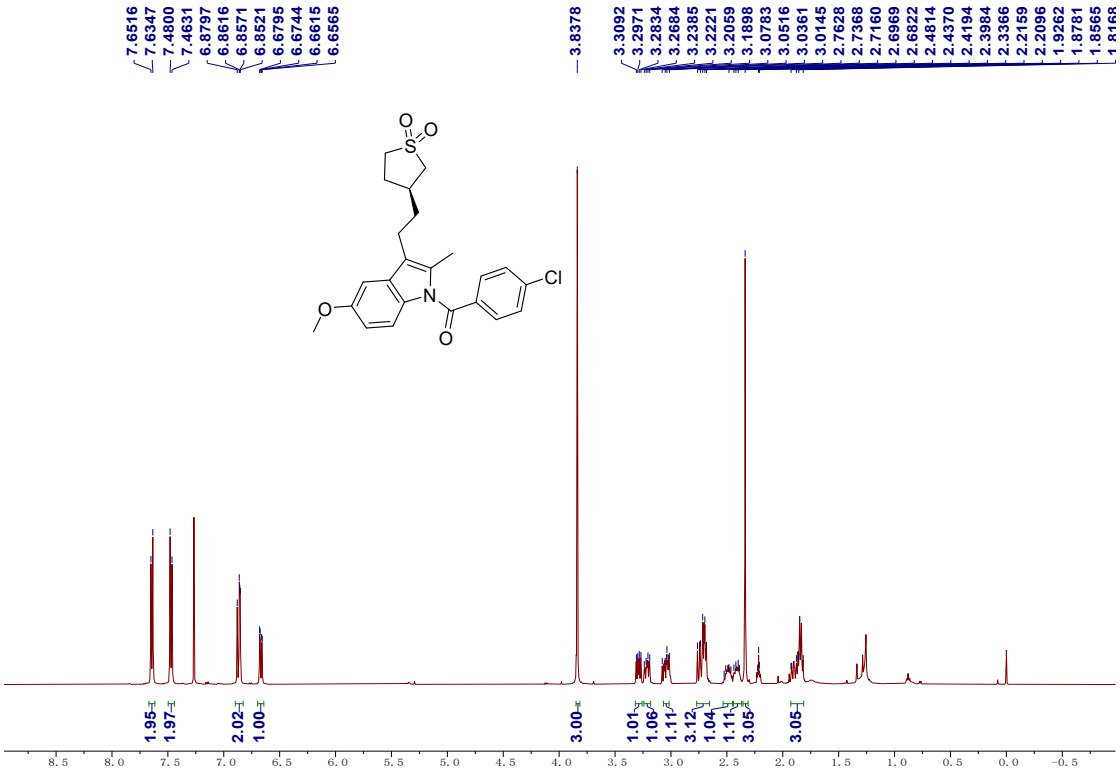
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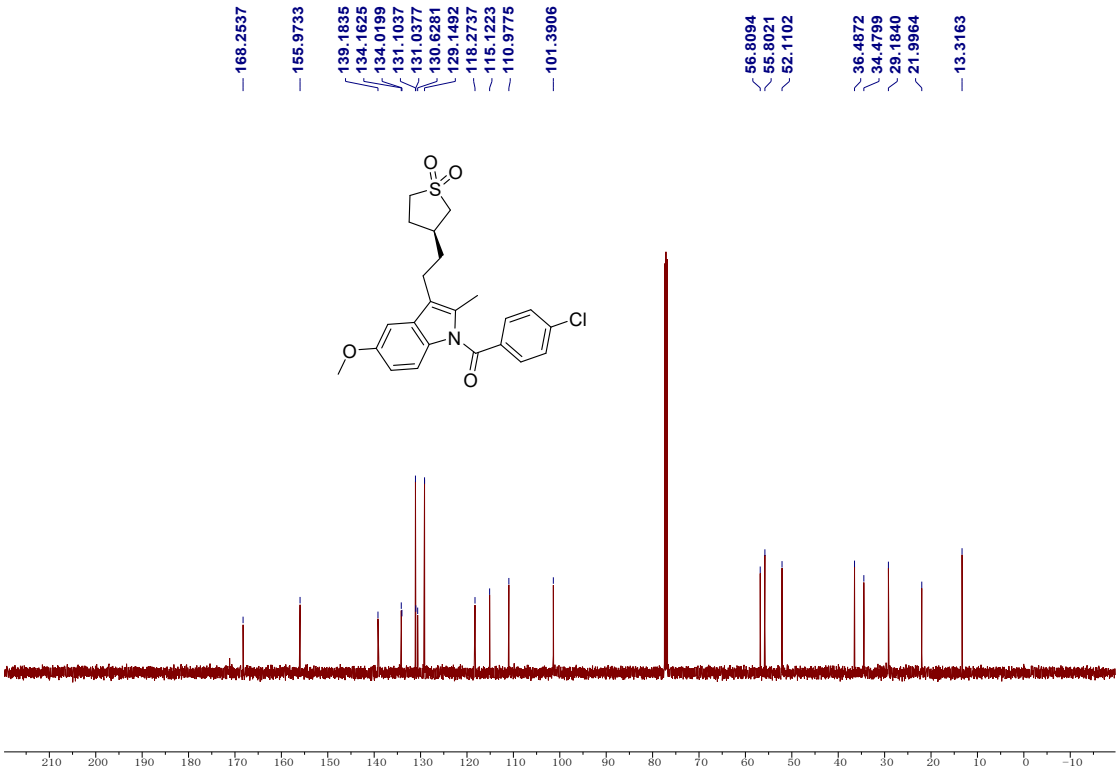
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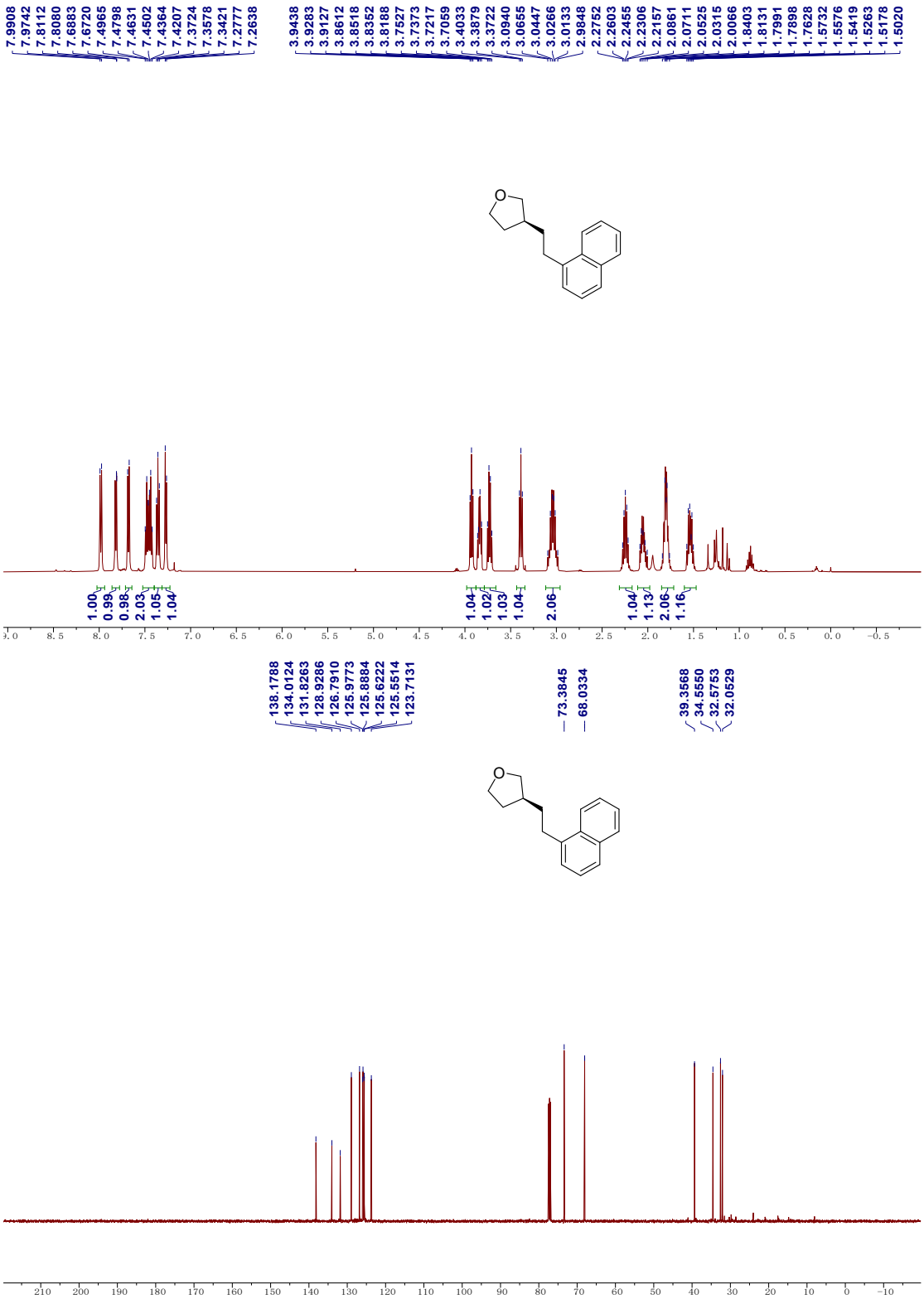
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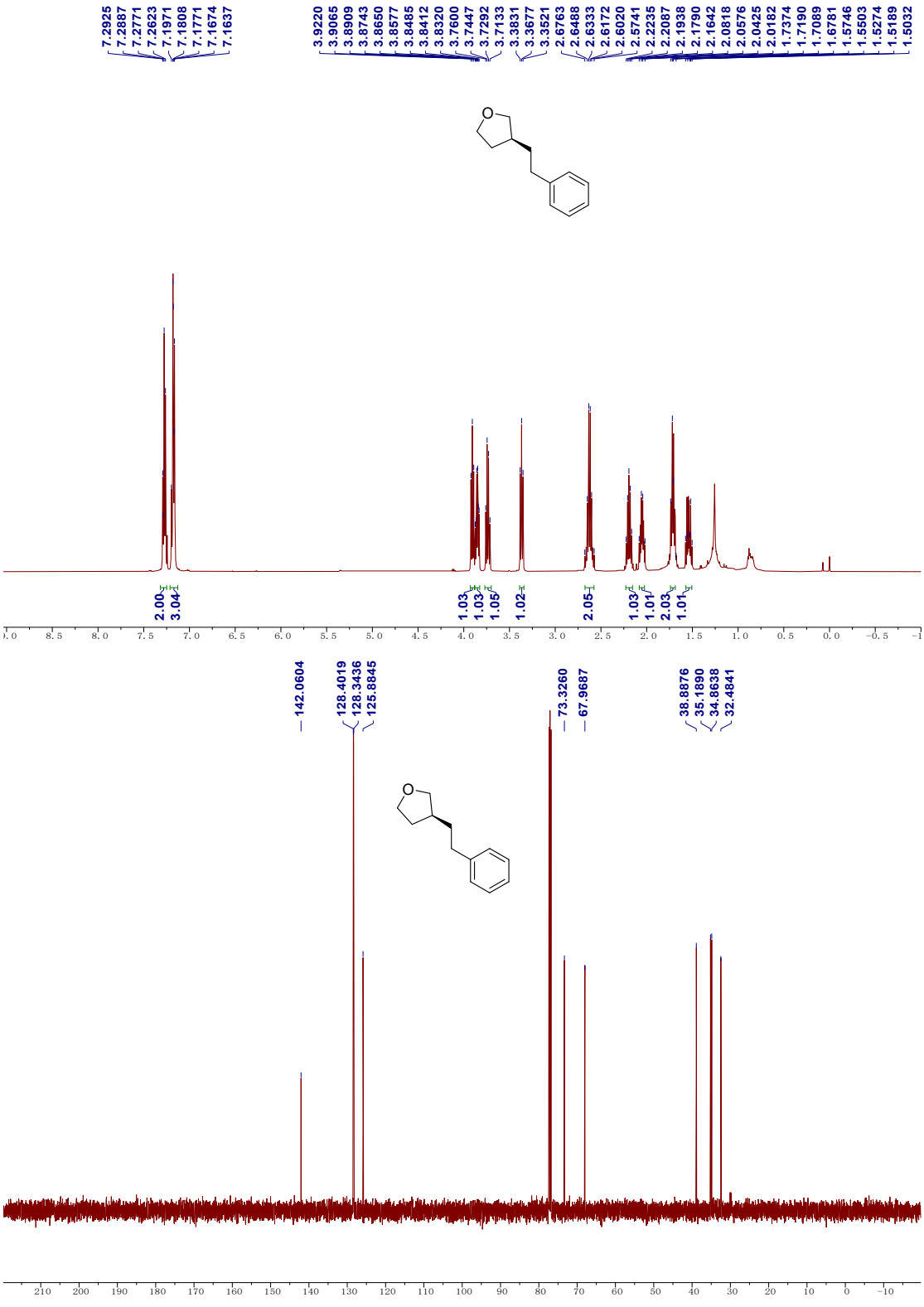
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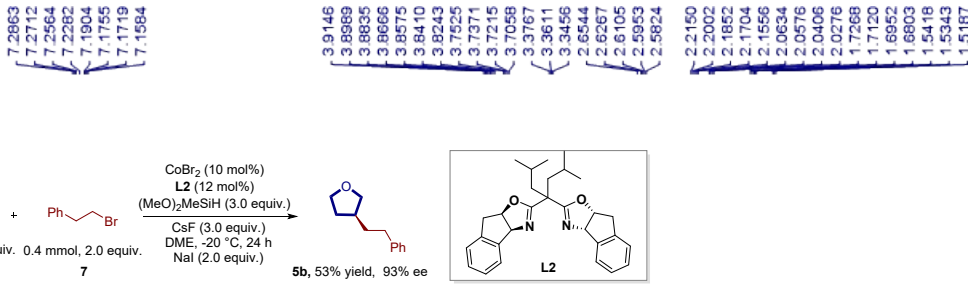
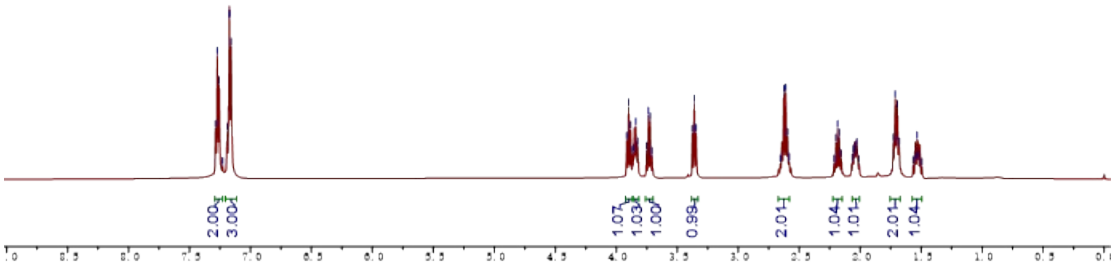
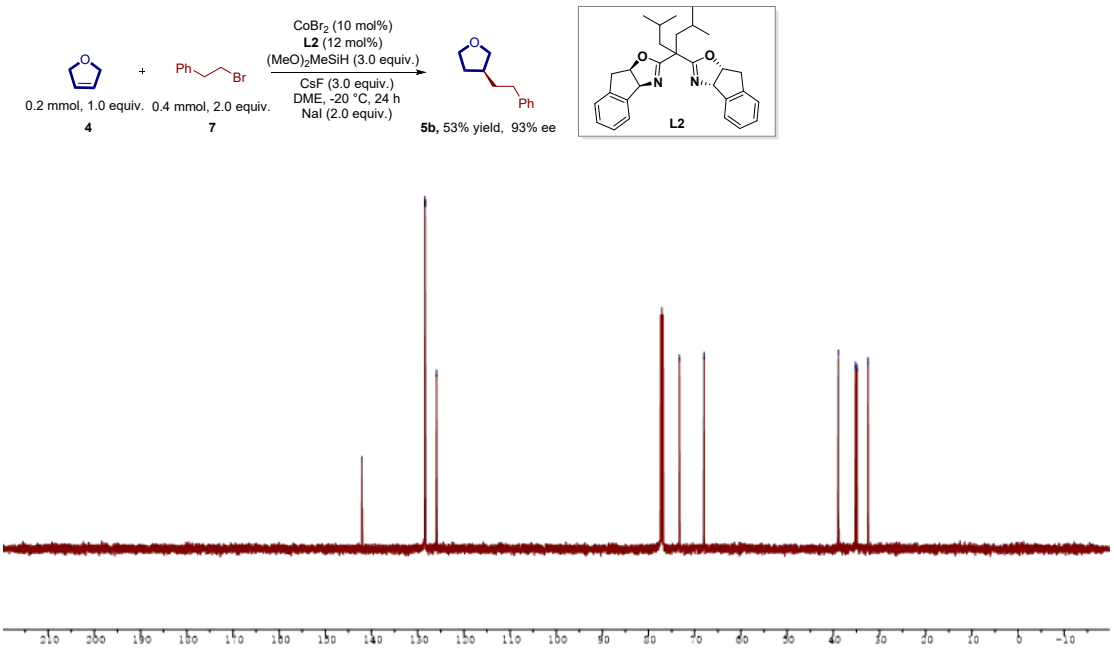
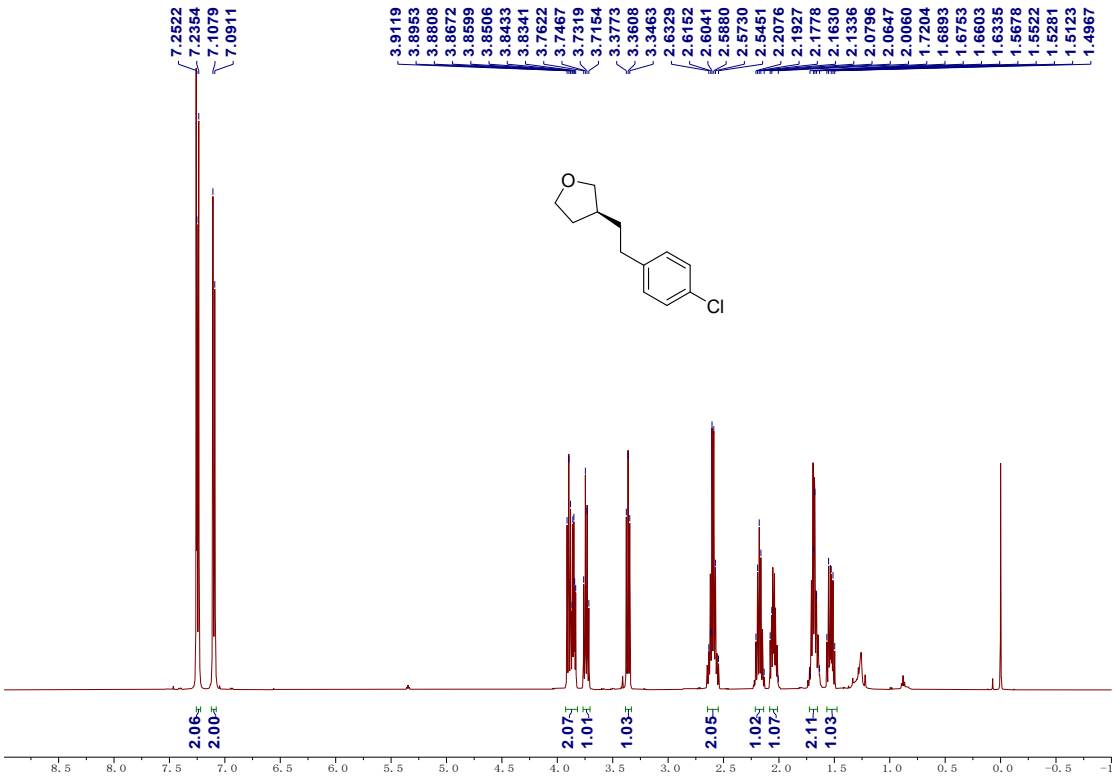






CoBr2 (10 mol%)
L2 (12 mol%)
(MeO)2MeSiH (3.0 equiv.)
CsF (3.0 equiv.)
DME, -20 °C, 24 h
NaI (2.0 equiv.)
0.2 mmol, 1.0 equiv.
4
0.4 mmol, 2.0 equiv.
7
5b, 53% yield, 93% ee
L2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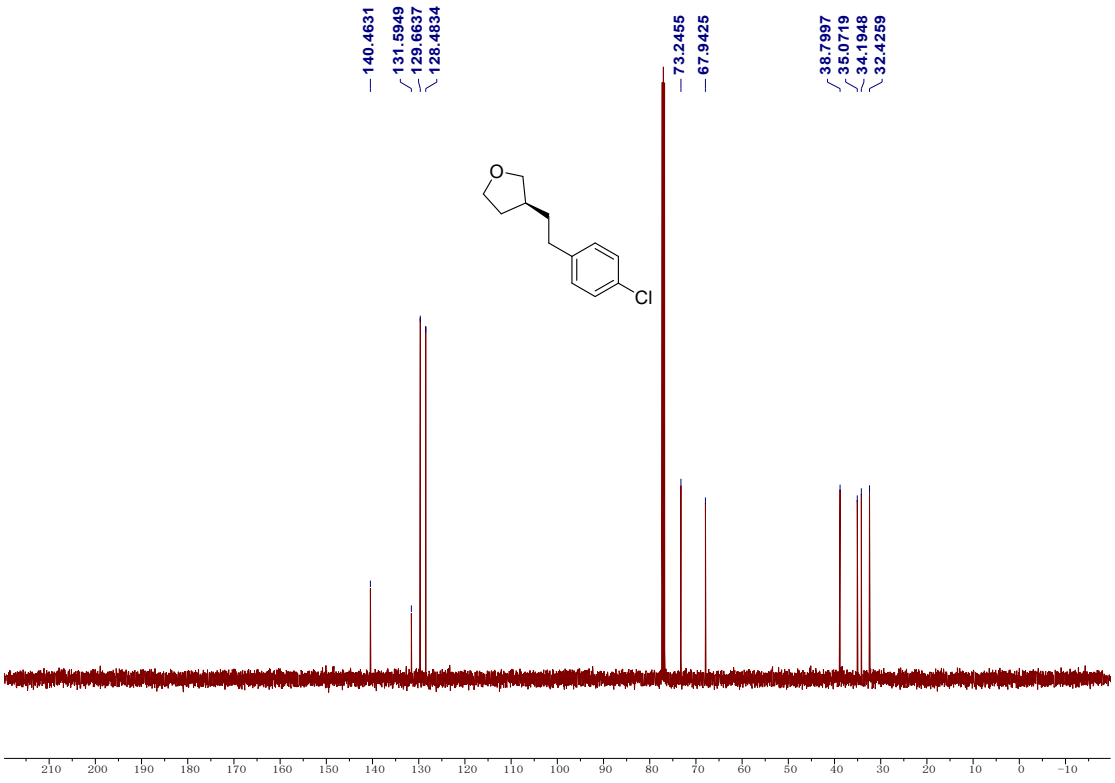
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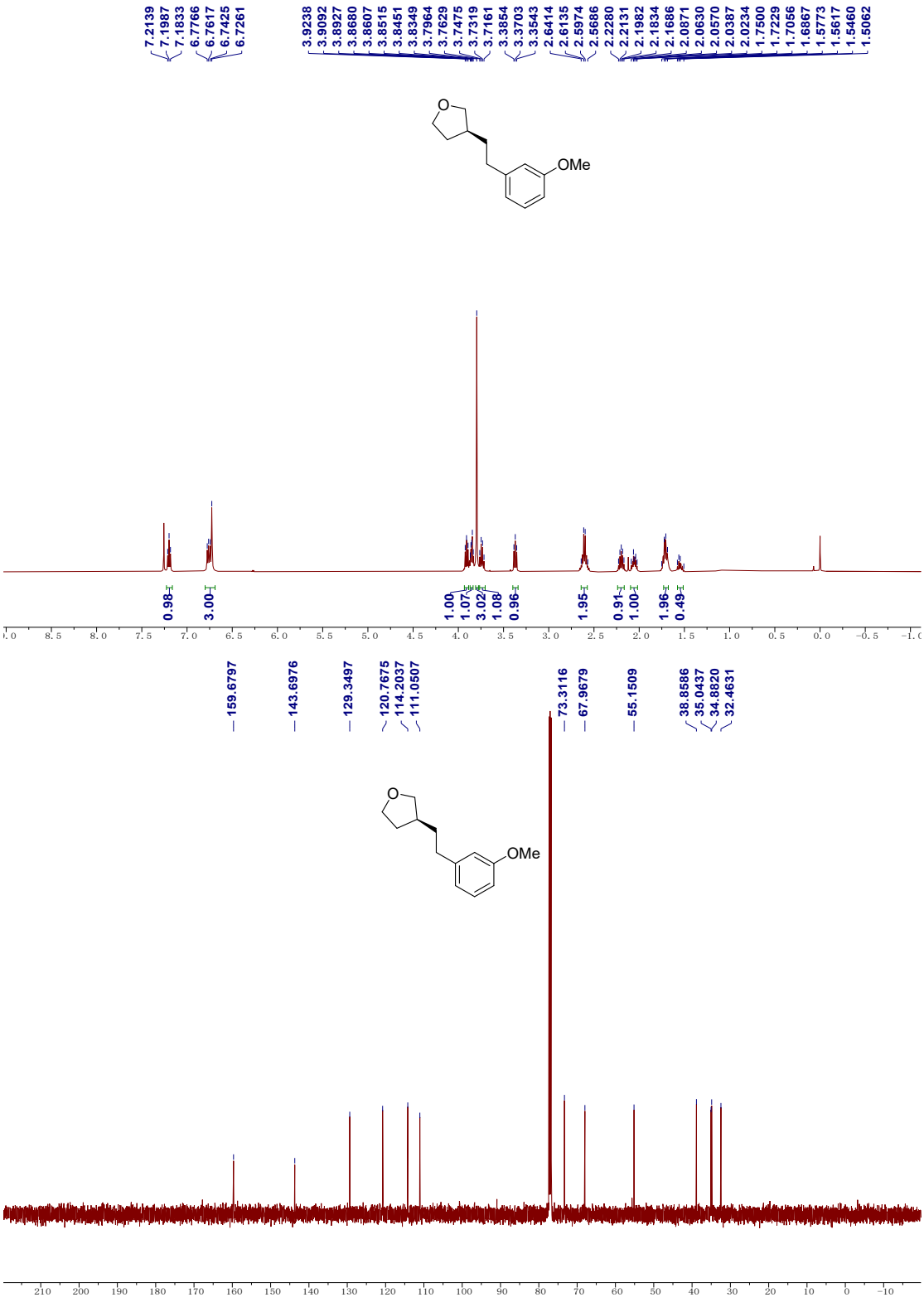
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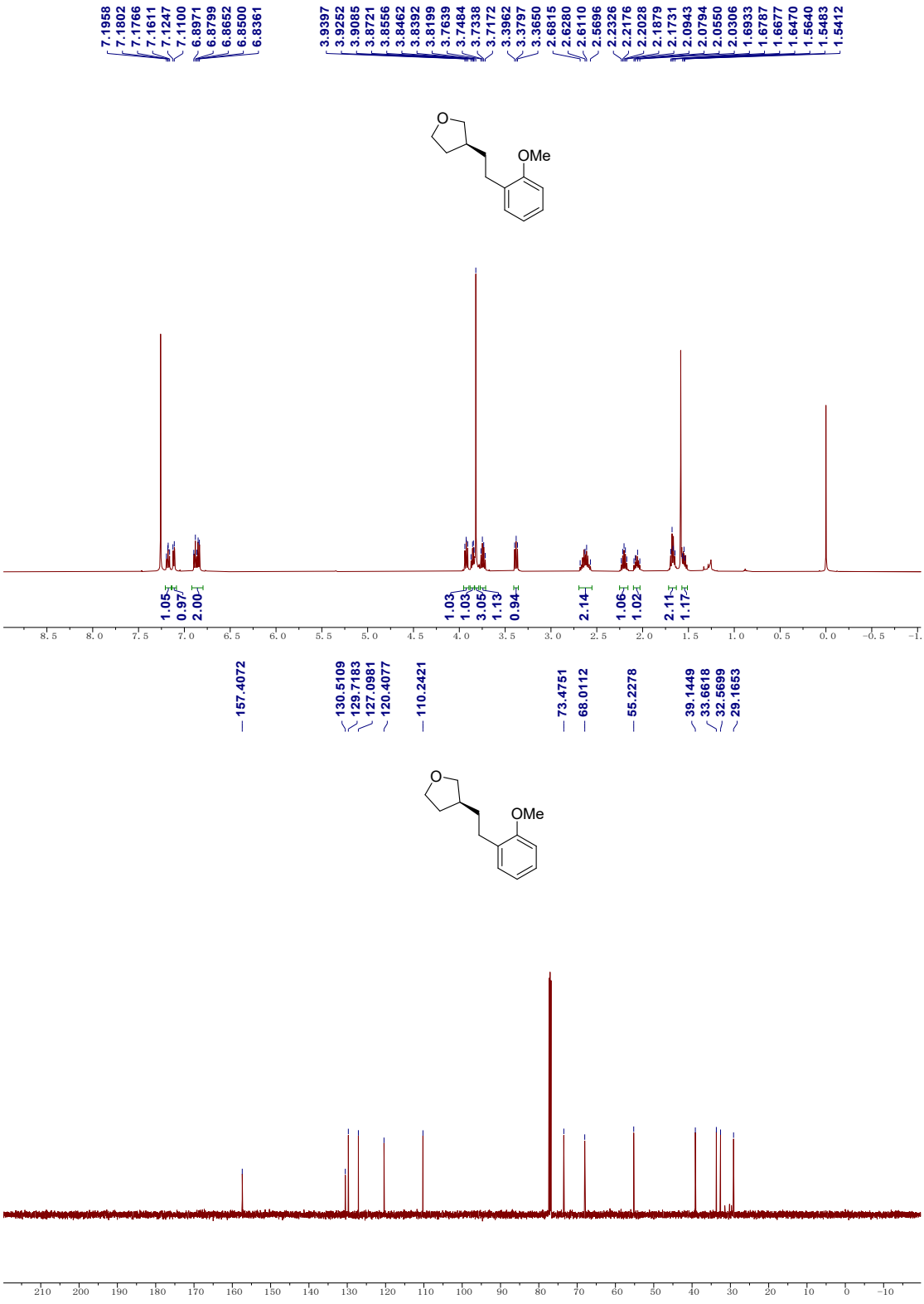
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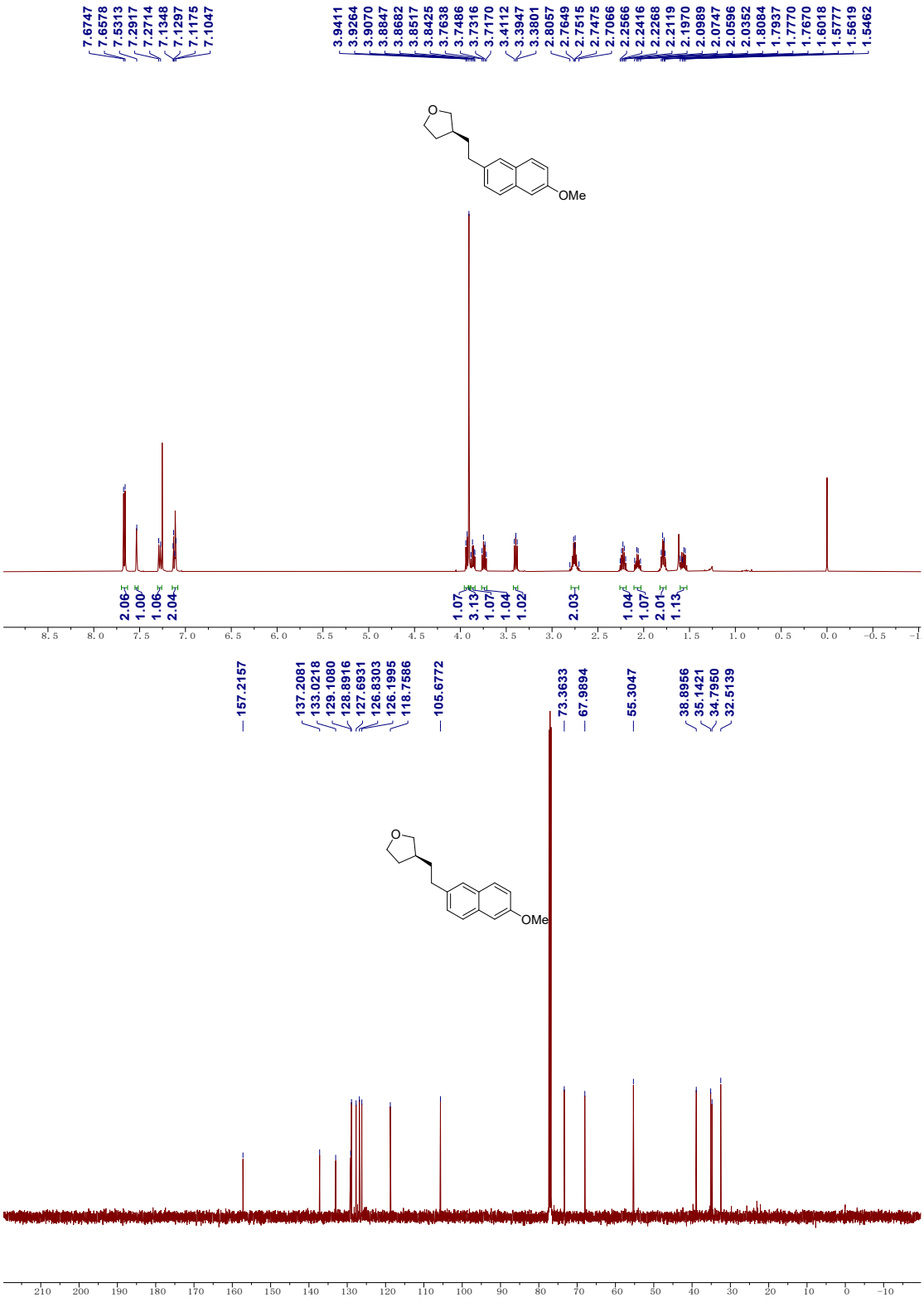
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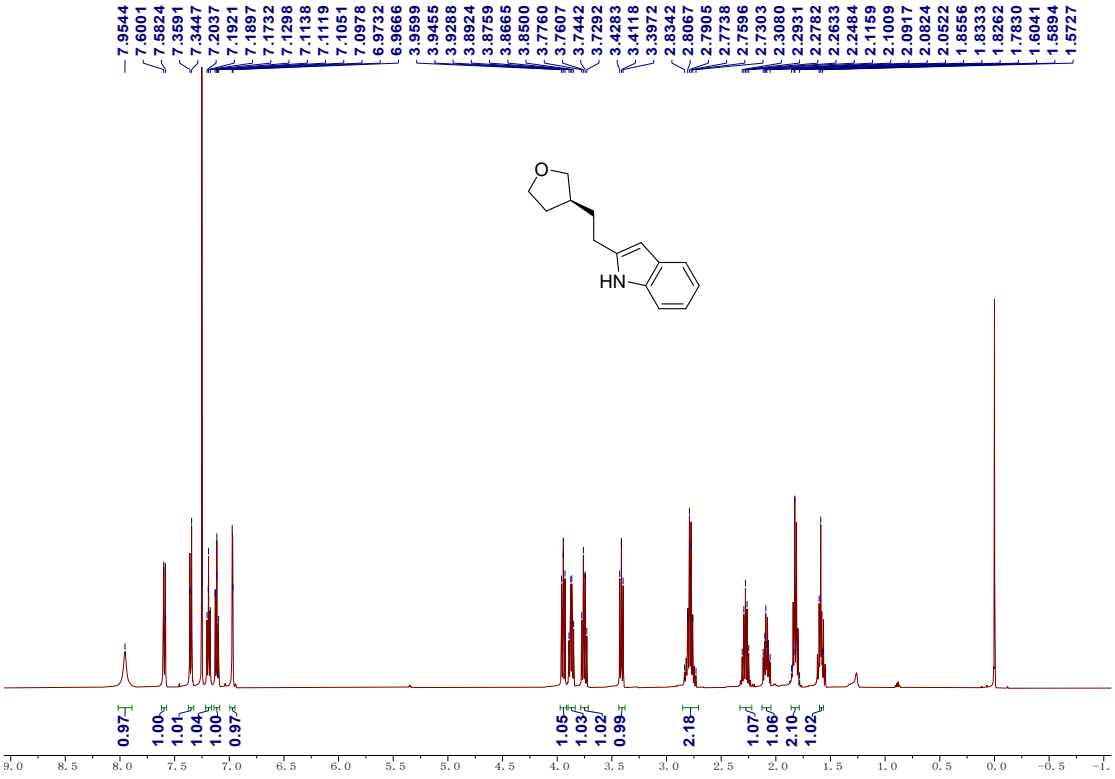
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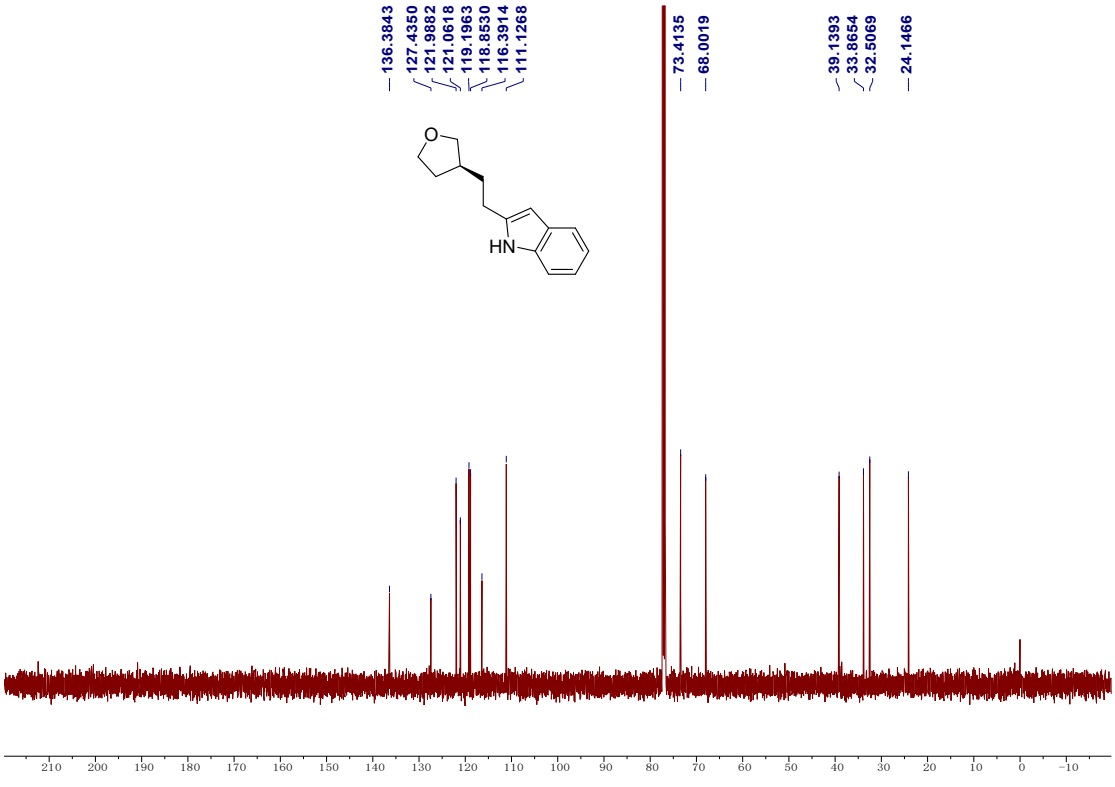
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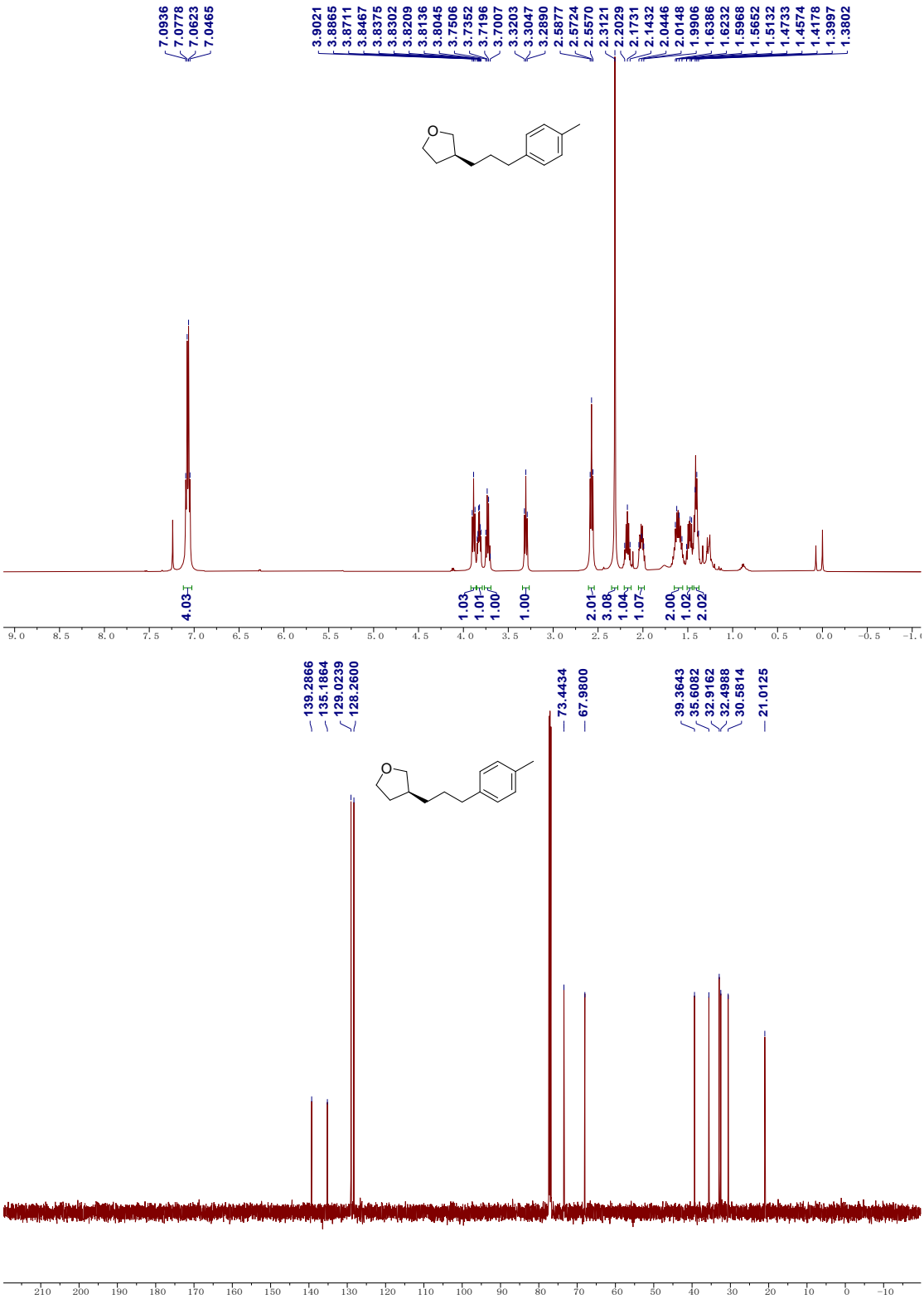
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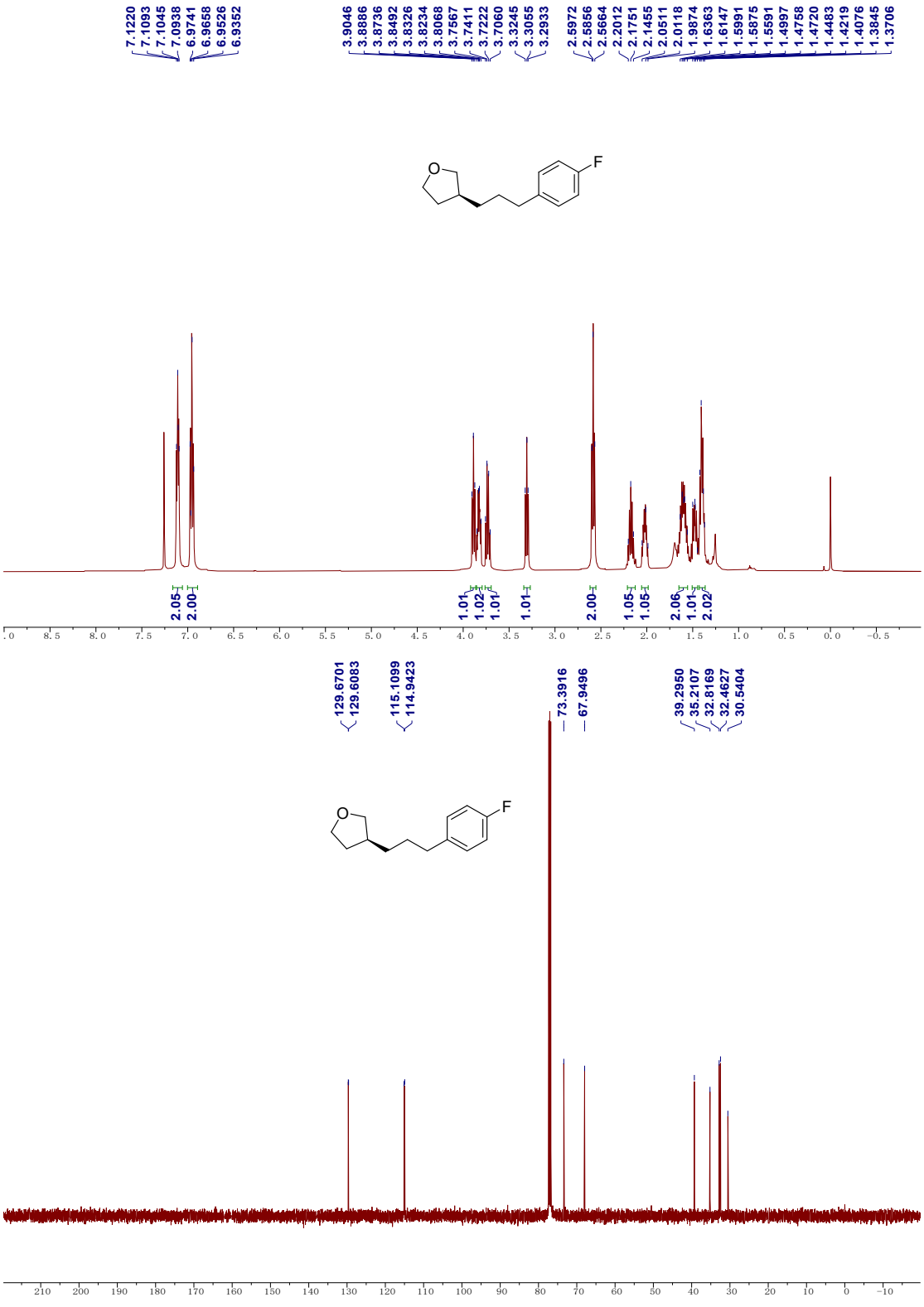
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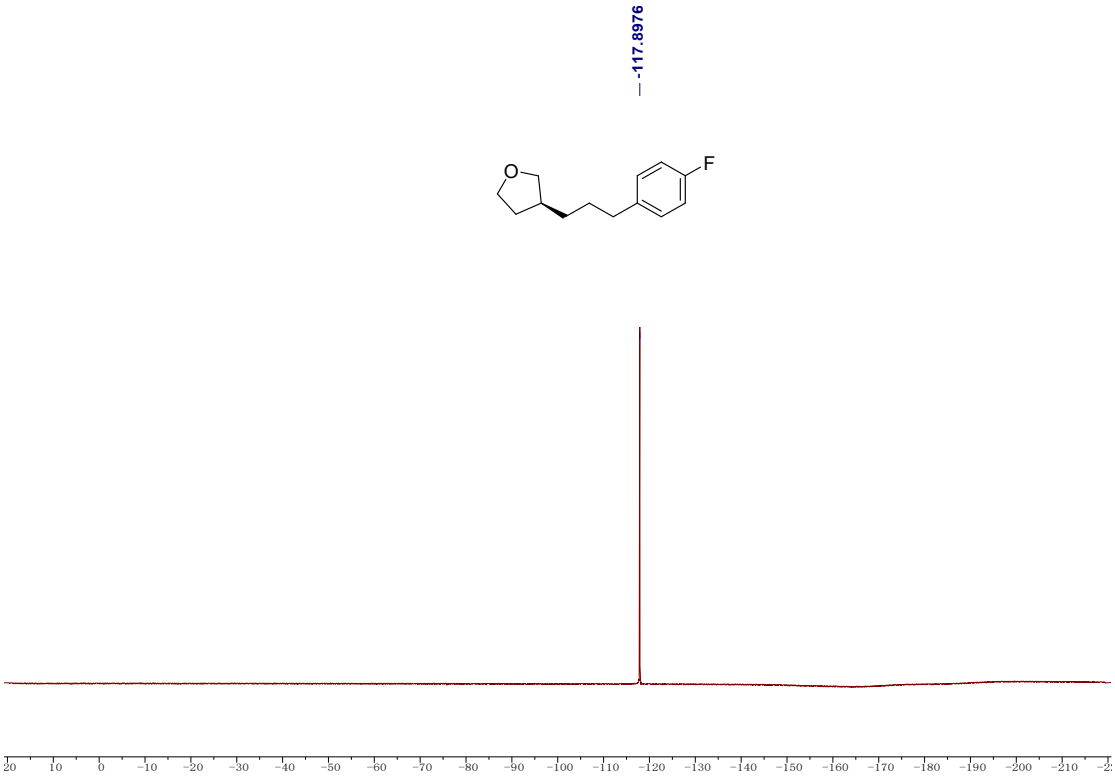
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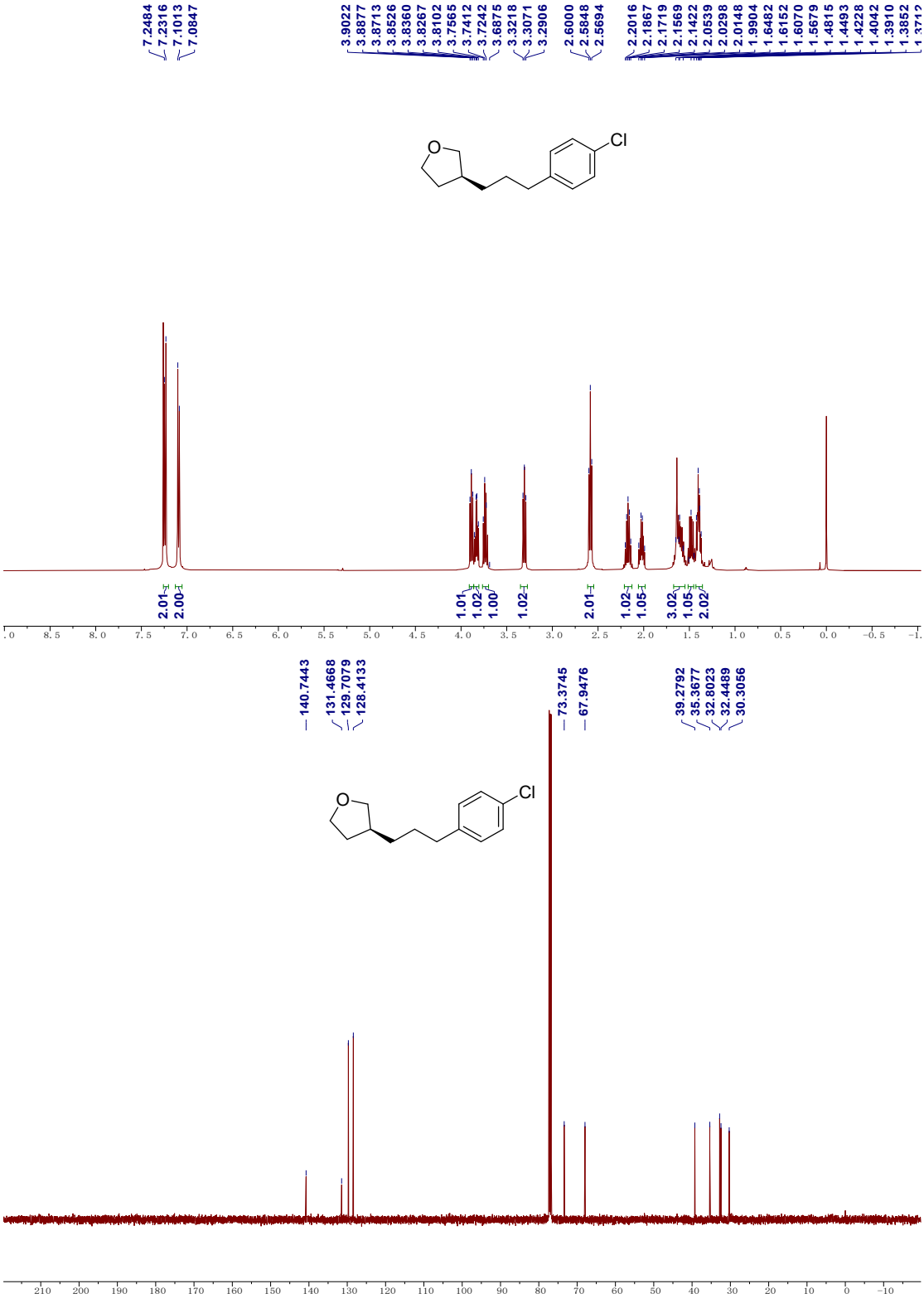
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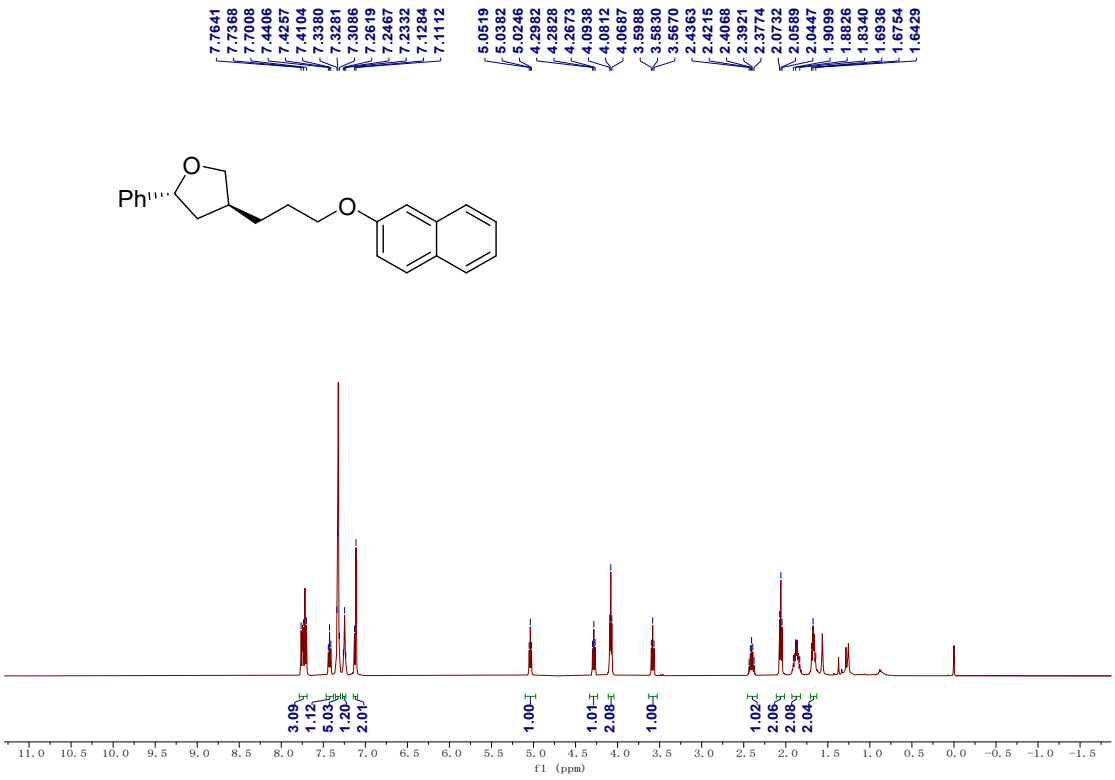
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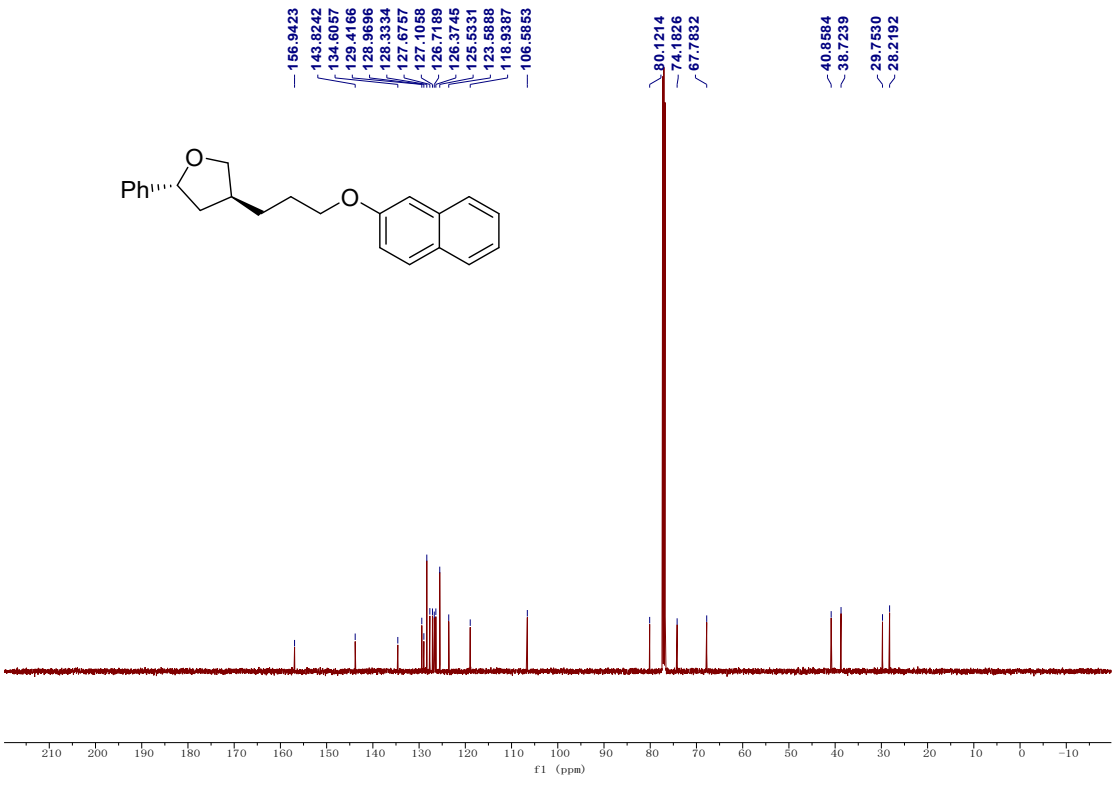
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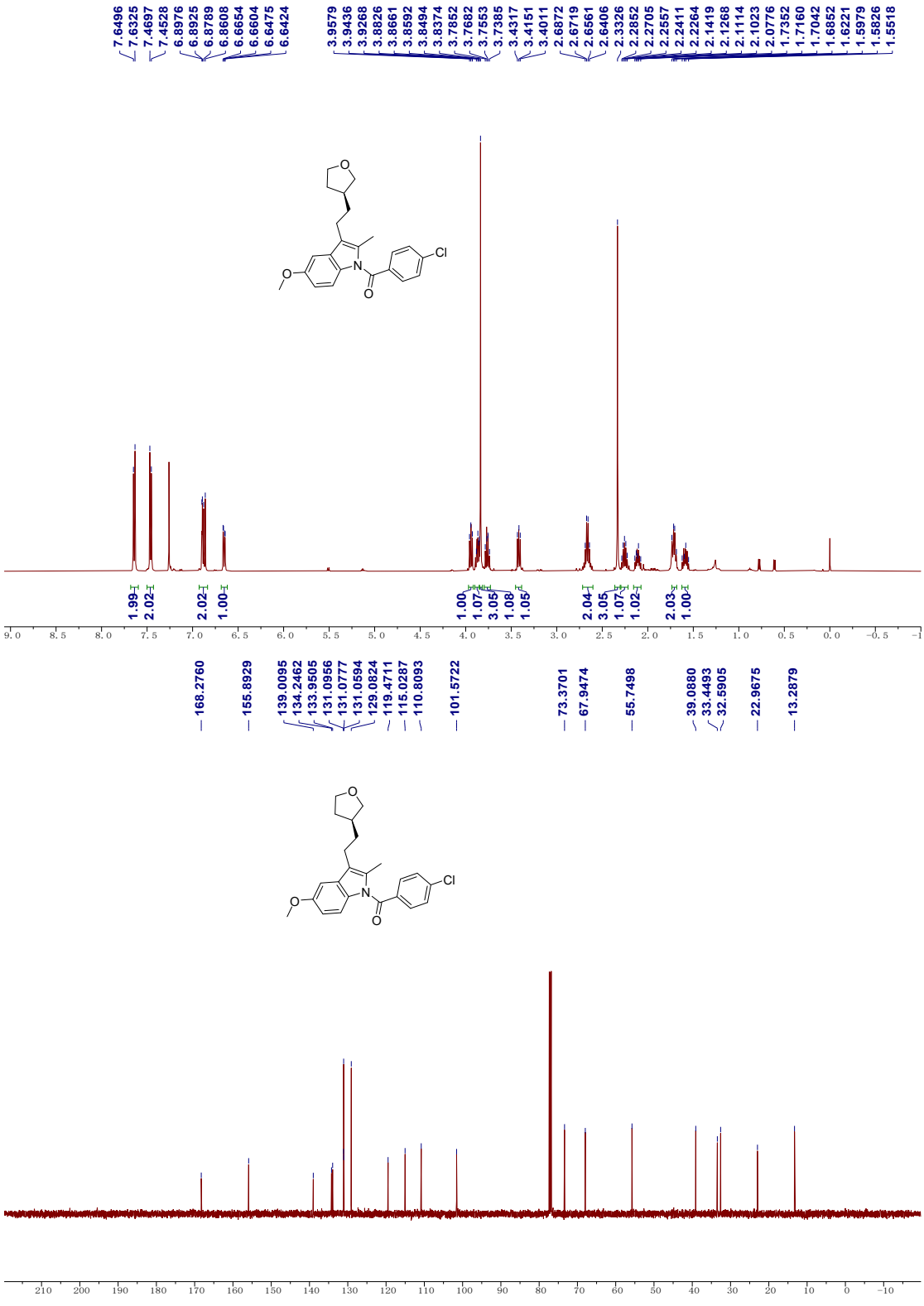
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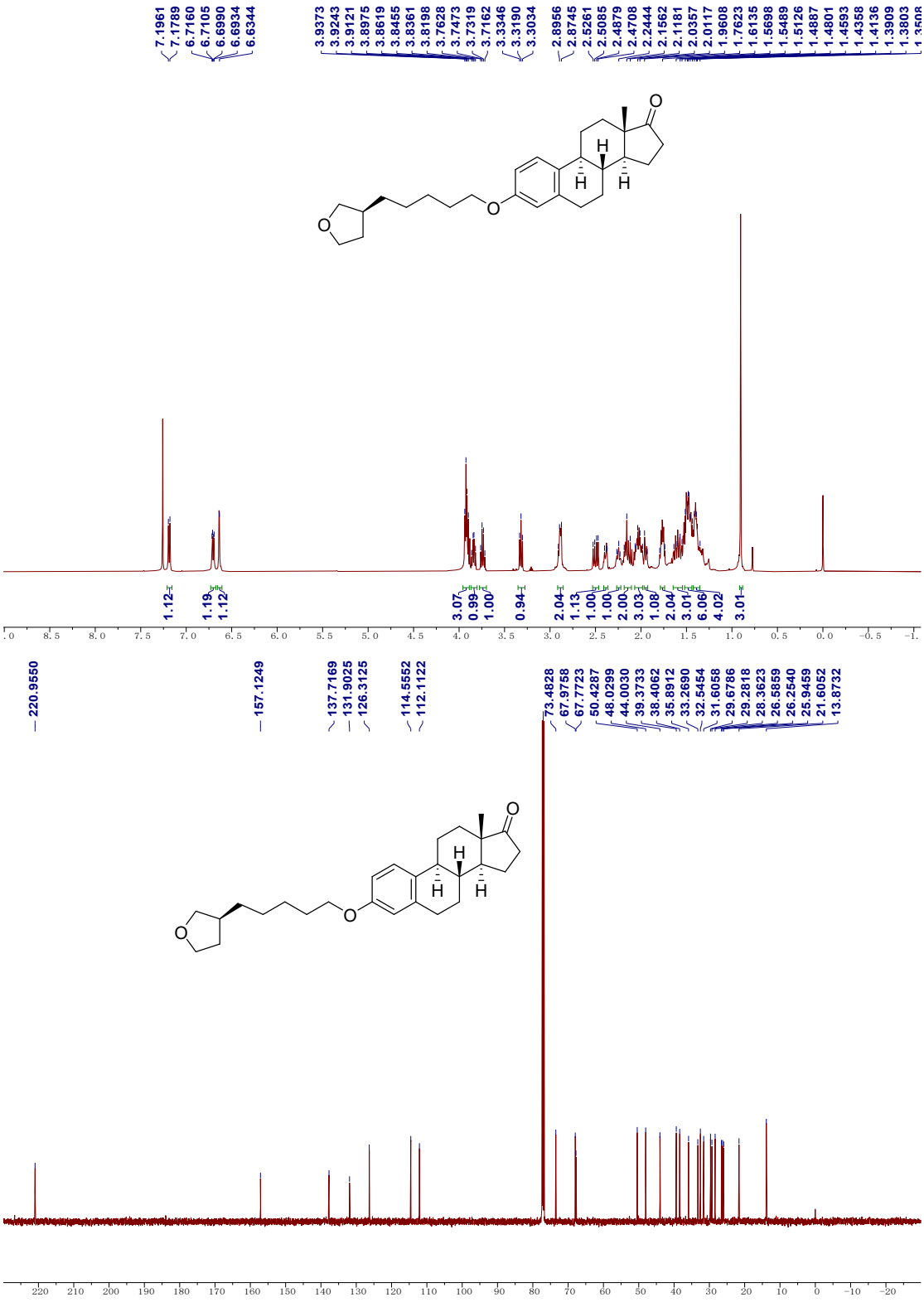
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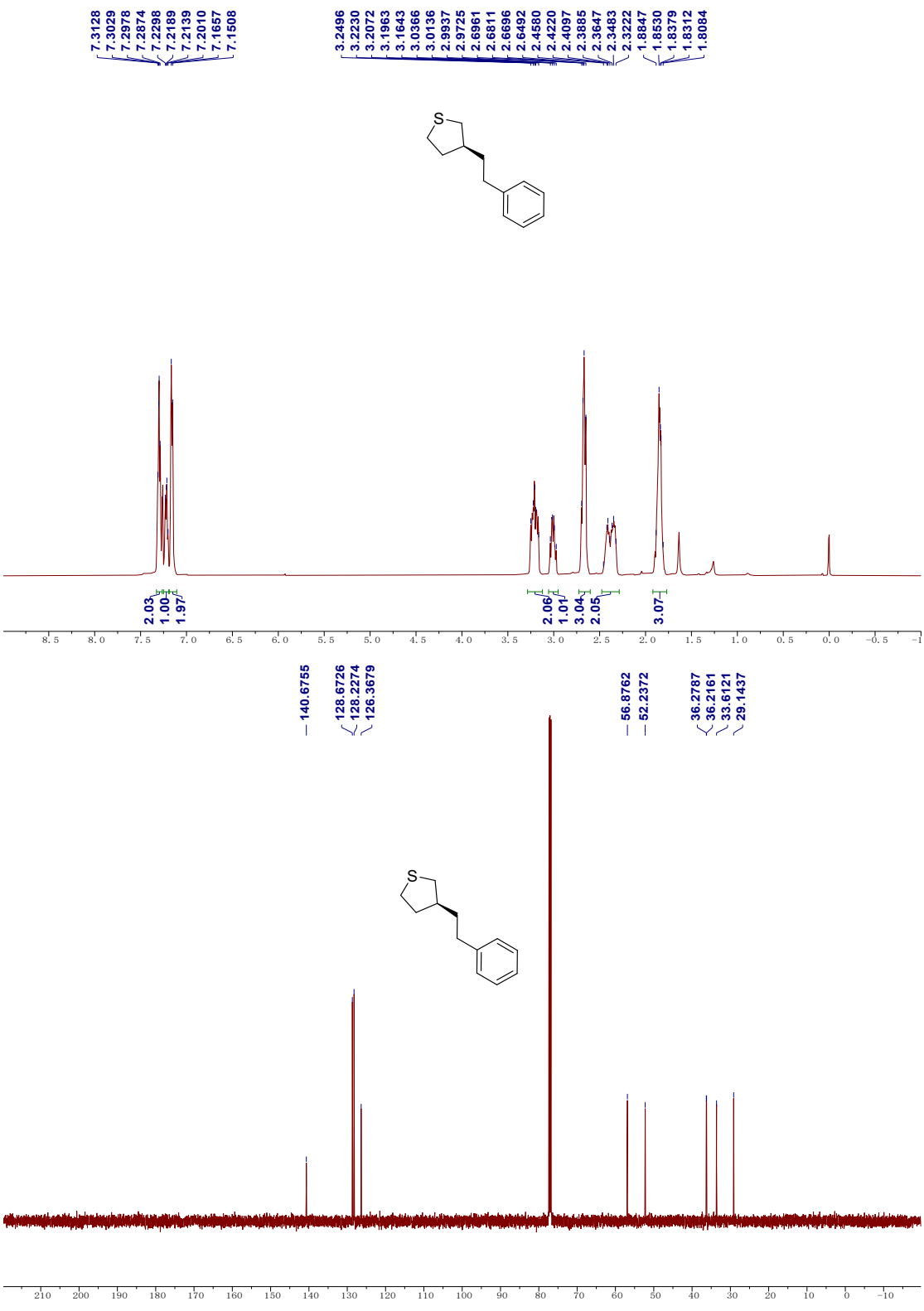
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