Supporting Information

Synthesis of Chiral β-Hydroxy Allylic Sulfides *via* Iridium-Catalyzed Asymmetric Cascade Allylation/Acyl Transfer Rearrangement

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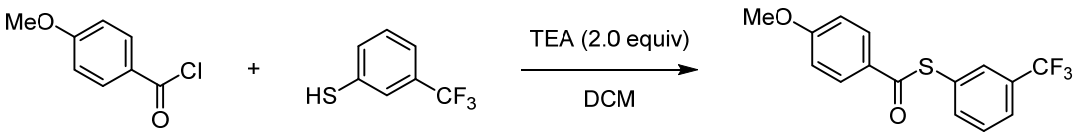
1. General remarks

^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = single, d = double, t = triple, q = quarte, m = multiple or unresolved, br s = broad single, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on a Bruker 101 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. ^{19}F NMR spectra were recorded on a Bruker 376 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal CF_3COOH signal at -76.55 ppm. High resolution mass spectra (HR-MS) were recorded on a LTQ-Orbitrap Elite mass spectrometer with CH_3CN/MeOH as solvent mixture for the measurements. Commercially obtained reagents were used without further purification. Solvents were purified prior to use according to the standard methods. Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. Enantiomeric excess was determined by chiral-phase HPLC analysis in comparison with authentic racemic materials. Optical rotations were measured on a Rudolph Research Analytical Autopol VI polarimeter with $[\alpha]_D$ values reported in degrees; concentration (*c*) is in g/100 mL. Substrates (**1a**, **1f**, **1j**, **1n**, **1p**, **1y**, **1z**),[1] (**1b**, **1d**, **1i**),[2] **1c**,[3] (**1e**, **1g**, **1m**),[4] **1h**,[5] (**1k**, **1l**),[6] **1o**,[7] **1q**,[8] (**1r**, **1C**),[9] **1s**,[10] (**1t**, **1v**, **1x**)[11], **1u**[12] were prepared according to the literature procedure. Chiral ligands,[13,14] dbcot,[15] and [Ir*]-**1-4** complexes[16,17] were prepared according to the literature procedure. X-ray diffraction was measured on XtaLAB PRO MM007HF Cu. The absolute configuration of *ent*-**5** was determined by X-ray analysis, and those of other adducts were deduced based on this result.

2. Preparation of aryl thioesters



To a round-bottomed flask with 3-(trifluoromethyl) thiophenol (1.0 equiv., 5 mmol), were added TEA (2.0 equiv.) and DCM (30 mL), the reaction was cooled to 0 °C, then the 4-methoxybenzoyl chloride was added slowly. Allow the reaction to proceed at room temperature overnight. When the

starting material was consumed, the reaction was quenched with sat. aq. $NaHCO_3$ and extracted three times with DCM. The combined organic layer was washed with brine, dried over Na_2SO_4, and then filtered. The filtrate was concentrated in vacuo and the residue was purified by column chromatography.

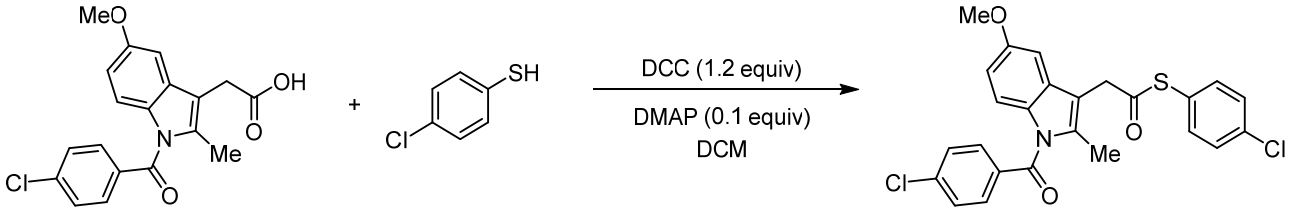
S-(3-(trifluoromethyl)phenyl) 4-methoxybenzothioate (1w): yield (70%); white solid, m.p. 65℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.96 (m, 2H), 7.78 (s, 1H), 7.74 – 7.66 (m, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.02 – 6.94 (m, 2H), 3.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.4, 164.3, 138.5, δ 131.8 (q, *J* = 3.8 Hz), 131.6 (q, *J* = 30.3 Hz), 131.4, 129.8, 129.5, 129.1, 128.9, 126.4 (q, *J* = 272.7 Hz), 126.1 (q, *J* = 3.8 Hz), 114.0, 55.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.7.

HRMS (ESI+) Calcd. For $C_{15}H_{13}F_3O_2S^+$ ($[M+H]^+$): 313.0505, found: 313.0504.



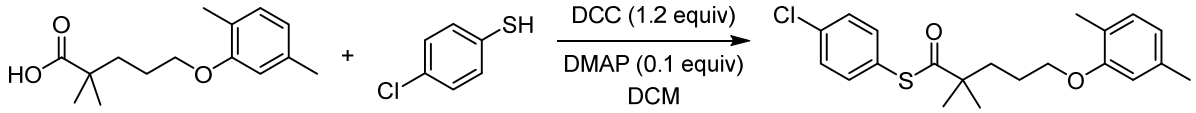
To a mixture of Indocin (1.0 equiv., 5 mmol), 4-chlorobenzenethiol (1.1 equiv., 5.5 mmol), dicyclohexylcarbodiimide (DCC, 1.2 equiv., 6.0 mmol), and 4- dimethyl-aminopyridine (DMAP, 0.1 equiv., 0.5mmol) into the flask, then dissolve with 10 mL dichloromethane (DCM), and stir the mixture at room temperature. Consumed alcohol completely determined by TLC analysis, then filter off the insoluble white solid on diatomaceous earth, wash the filter cake twice with DCM, concentrate the filtrate, the residue was purified by column chromatography on silica gel.

S-(4-chlorophenyl) 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)ethanethioate (1A): yield (55%); white solid, m.p. 135℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 2H), 7.52 – 7.44 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 – 7.27 (m, 2H), 6.98 (d, *J* = 2.5 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 6.71 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.96 (s, 2H), 3.85 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 168.3, 156.2, 139.5, 137.0, 135.9, 135.6, 133.7, 131.2, 130.9, 130.4, 129.4, 129.2, 126.1, 115.0, 111.9, 111.5, 101.1, 55.7, 39.1, 13.5.

HRMS (ESI+) Calcd. For $C_{25}H_{19}NCl_2O_3SNa^+$ ($[M+Na]^+$): 506.0355, found: 506.0353.



To a mixture of Gemfibrozil (1.0 equiv., 5 mmol), 4-chlorobenzenethiol (1.1 equiv., 5.5 mmol), dicyclohexylcarbodiimide (DCC, 1.2 equiv., 6.0 mmol), and 4- dimethyl-aminopyridine (DMAP, 0.1 equiv., 0.5mmol) into the flask, then dissolve with 10 mL dichloromethane (DCM), and stir the mixture at room temperature. Consumed alcohol completely determined by TLC analysis, then filter off the insoluble white solid on diatomaceous earth, wash the filter cake twice with DCM, concentrate the filtrate, the residue was purified by column chromatography on silica gel.

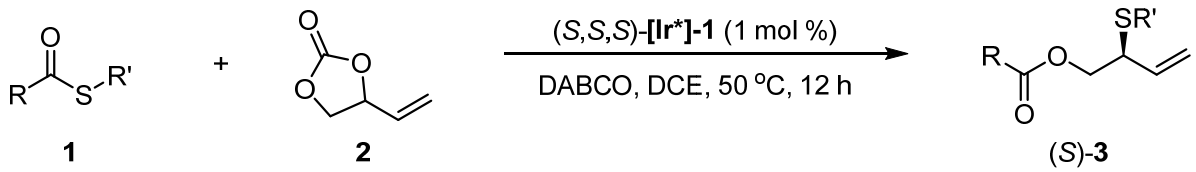
S-(4-chlorophenyl) 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanethioate (1B): yield (70%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.32 – 7.27 (m, 2H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.69 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.63 (d, *J* = 1.7 Hz, 1H), 3.97 (t, *J* = 5.7 Hz, 2H), 2.33 (s, 3H), 2.22 (s, 3H), 1.95 – 1.76 (m, 4H), 1.36 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6, 156.8, 136.4, 136.2, 135.5, 130.3, 129.3, 126.4, 123.6, 120.7, 111.9, 67.6, 50.1, 37.6, 25.3, 24.9, 21.4, 15.8.

HRMS (ESI+) Calcd. For $C_{21}H_{29}ClNO_2S^+$ ($[M+NH_4]^+$): 394.1602, found: 394.1597.

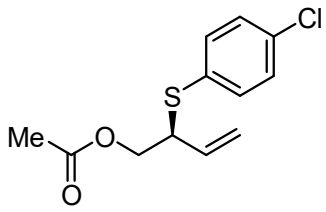
3. General procedure for chiral β-hydroxy allylic sulfides



A flame dried Schlenk tube was cooled to rt and evacuated and backfilled with argon for three times. To this Schlenk tube were added (*S*,*S*,*S*)-[Ir*]-**1** (0.01 mmol, 5 mol %), aryl thioesters **1** (0.20 mmol, 1.0 equiv.), VEC **2** (0.60 mmol, 3.0 equiv.), DABCO (0.2 mmol, 1.0 equiv.) and DCE (2 mL). The reaction was stirred at 50 °C for 12 hours. Once starting material was consumed (monitored by TLC), the solvent was evaporated under reduced pressure and the residue was purified by column chromatography to give the desired product **3**, which was then directly analyzed by HPLC to

determine the enantiomeric excess.

4. Spectral characterization data for the products



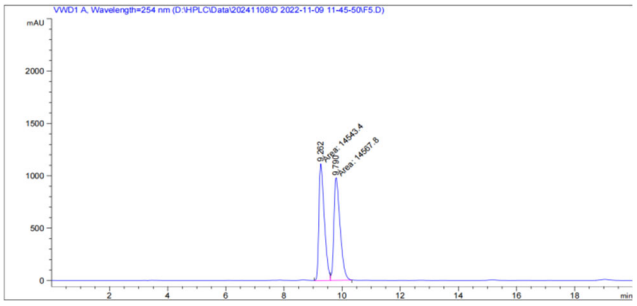
(*S*)-2-((4-chlorophenyl)thio)but-3-en-1-yl acetate (3a): yield (45.1 mg, 88%); colorless oil; $[\alpha]^{15}_{D}$ = -3.6 (*c* 1.34, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 254 nm); t_r = 9.26 and 9.79 min.

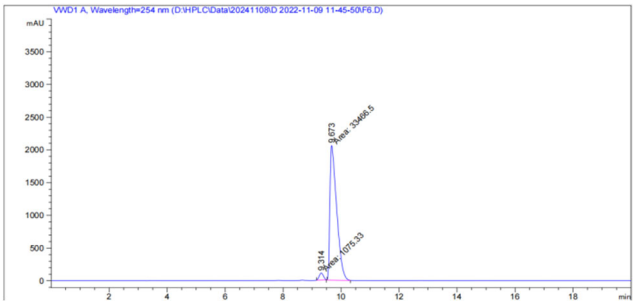
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.33 (m, 2H), 7.30 – 7.24 (m, 2H), 5.73 (ddd, *J* = 17.1, 10.3, 8.3 Hz, 1H), 5.19 – 4.98 (m, 2H), 4.23 (d, *J* = 1.6 Hz, 1H), 4.21 (d, *J* = 2.1 Hz, 1H), 3.92 – 3.77 (m, 1H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 134.5, 134.4, 134.0, 131.6, 129.1, 118.3, 65.2, 50.3, 20.8.

HRMS (ESI+) Calcd. For $C_{12}H_{13}ClO_2SNa^+$ ($[M+Na]^+$): 279.0217, found: 279.0228.

HPLC chromatogram of compound 3a





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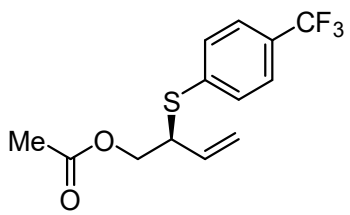
1	9.262	MF	0.2170	1.45434e4	1117.06531	49.9582
2	9.790	FM	0.2474	1.45678e4	981.38940	50.0418

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.314	MM	0.1668	1075.33337	107.47681	3.1131
2	9.673	MM	0.2712	3.34665e4	2056.40405	96.8869



(*S*)-2-((4-(trifluoromethyl)phenyl)thio)but-3-en-1-yl acetate (3b): yield (47.6 mg, 82%); colorless oil; $[\alpha]^{15}_{D}$ = +10.9 (*c* 0.70, CH_2Cl_2);The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 250 nm); t_r = 9.27 and 9.99 min.

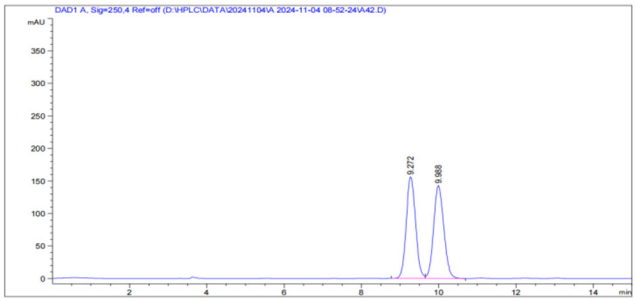
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.46 (m, 4H), 5.78 (ddd, *J* = 17.1, 10.2, 8.1 Hz, 1H), 5.26 – 5.15 (m, 2H), 4.33 – 4.19 (m, 2H), 4.09 – 3.99 (m, 1H), 2.04 (s, 3H).

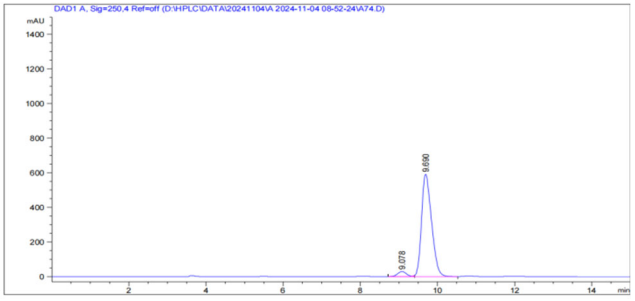
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 139.0, 134.1, 131.1, 129.0 (q, *J* = 33.0 Hz), 125.7 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.1 Hz), 118.8, 65.2, 49.2, 20.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.6 (s).

HRMS (ESI+) Calcd. For $C_{13}H_{13}F_3O_2SNa^+$ ($[M+Na]^+$): 313.0481, found: 313.0480.

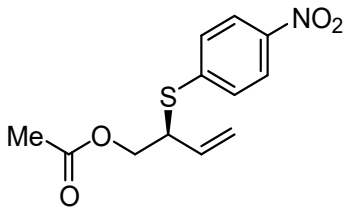
HPLC chromatogram of compound 3b





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.272	BV	0.2612	2611.55371	156.10199	49.9170
2	9.988	VB	0.2880	2620.23975	142.85268	50.0830

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.078	BV E	0.2429	442.07013	28.50359	4.0009
2	9.690	VB R	0.2794	1.06072e4	591.04260	95.9991



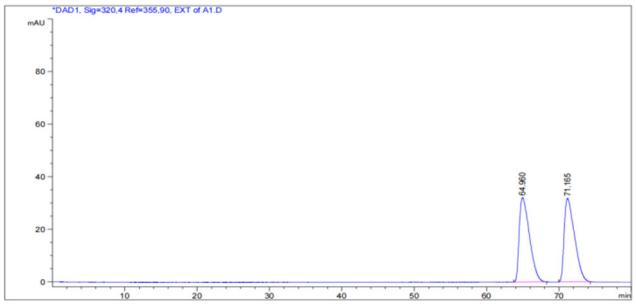
(*S*)-2-((4-nitrophenyl)thio)but-3-en-1-yl acetate (3c): yield (40.6 mg, 76%); $[\alpha]^{15}_{D}$ = +23.3 (*c* 1.33, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 88% ee (Chiralpak AS-H, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 320 nm); t_r = 64.96 and 71.17 min.

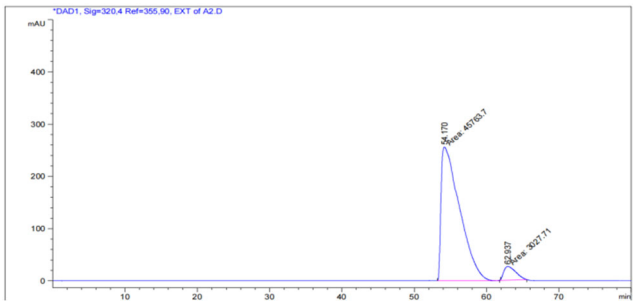
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.08 (m, 2H), 7.47 (d, *J* = 8.9 Hz, 2H), 5.80 (ddd, *J* = 17.1, 10.3, 7.9 Hz, 1H), 5.32 – 5.21 (m, 2H), 4.37 – 4.21 (m, 2H), 4.20 – 4.13 (m, 1H), 2.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 146.0, 144.4, 133.5, 129.2, 123.9, 119.4, 65.0, 48.6, 20.7.

HRMS (ESI+) Calcd. For $C_{12}H_{13}NO_4SNa^+$ ([M+Na]$^+$): 290.0458, found: 290.0460.

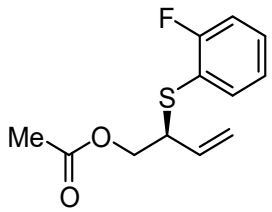
HPLC chromatogram of compound 3c





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	64.960	BB	1.2926	3146.98267	32.13282	50.0006
2	71.165	BB	1.3390	3146.91064	31.73078	49.9994

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	54.170	MM	2.9770	4.57637e4	256.20563	93.7946
2	62.937	MM	1.9194	3027.70923	26.29001	6.2054



(*S*)-2-((2-fluorophenyl)thio)but-3-en-1-yl acetate (3d): yield (33.1 mg, 69%); colorless oil; $[\alpha]^{15}_D$ = +1.1 (*c* 0.6, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 88% ee (Chiralpak ID, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 8.22 and 9.45 min.

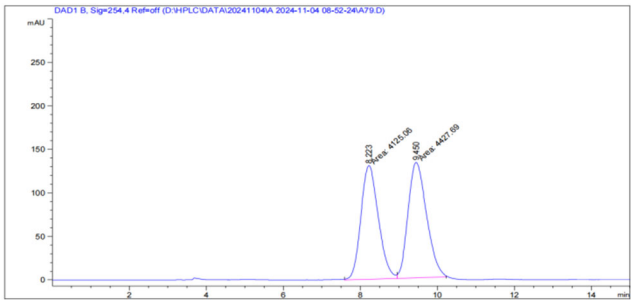
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.41 (m, 1H), 7.33 – 7.27 (m, 1H), 7.13 – 7.03 (m, 2H), 5.74 (ddd, 1H), 5.14 – 5.05 (m, 2H), 4.30 – 4.17 (m, 2H), 4.03 – 3.93 (m, 1H), 2.03 (s, 3H).

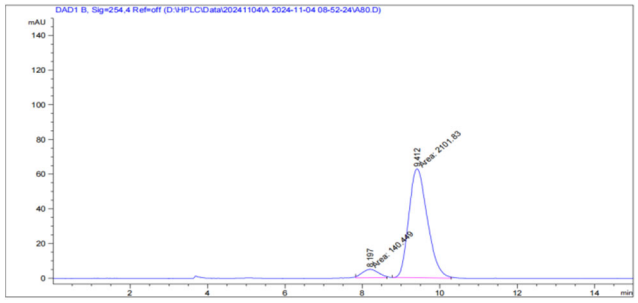
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 162.7 (d, *J* = 246.4 Hz), 136.0, 134.3, 130.3 (d, *J* = 8.0 Hz), 124.4 (d, *J* = 3.9 Hz), 120.0 (d, *J* = 18.0 Hz), 118.3, 115.9 (d, *J* = 23.2 Hz), 65.5, 49.4 (d, *J* = 2.6 Hz), 20.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -106.69 – -106.74 (m).

HRMS (ESI+) Calcd. For $C_{12}H_{13}FO_2SNa^+$ ([M+Na]$^+$): 263.0513, found: 263.0515.

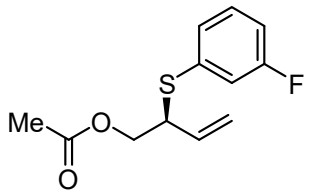
HPLC chromatogram of compound 3d





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.223	MF	0.5263	4125.06348	130.62331	48.2308
2	9.450	FM	0.5565	4427.69434	132.60344	51.7692

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.197	FM	0.4793	140.44933	4.88334	6.2637
2	9.412	MF	0.5570	2101.82861	62.88615	93.7363



(*S*)-2-((3-fluorophenyl)thio)but-3-en-1-yl acetate (3e): yield (32.6 mg, 68%); colorless oil; $[\alpha]^{15}_{D}$ = -9.4 (*c* 2.1, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralpak OD-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 250 nm); t_r = 6.51 and 7.77 min.

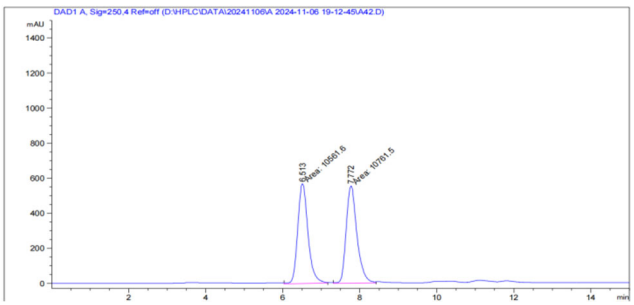
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 1H), 7.21 – 7.09 (m, 2H), 6.99 – 6.89 (m, 1H), 5.76 (ddd, *J* = 17.2, 10.1, 8.2 Hz, 1H), 5.21 – 5.10 (m, 2H), 4.30 – 4.18 (m, 2H), 3.99 – 3.89 (m, 1H), 2.04 (s, 3H).

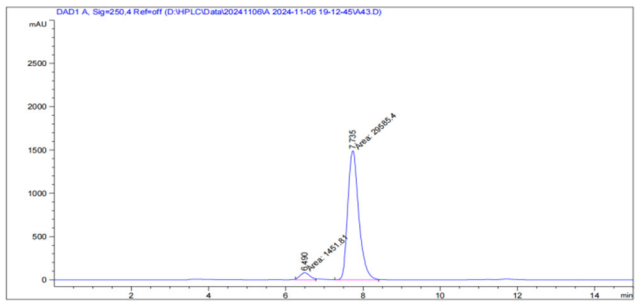
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 162.5 (d, *J* = 248.7 Hz), 135.7 (d, *J* = 8.0 Hz), 134.3, 130.1 (d, *J* = 8.5 Hz), 127.8 (d, *J* = 2.9 Hz), 118.9 (d, *J* = 22.2 Hz), 118.4, 114.4 (d, *J* = 21.2 Hz), 65.3, 49.8, 20.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -112.1 – -112.2 (m).

HRMS (ESI+) Calcd. For $C_{12}H_{13}FO_2SNa^+$ ([M+Na]$^+$): 263.0513, found: 263.0519.

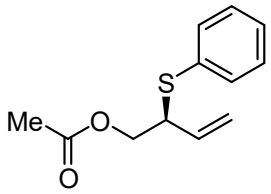
HPLC chromatogram of compound 3e





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.513	MM	0.3091	1.05616e4	569.46771	49.5313
2	7.772	MM	0.3236	1.07615e4	554.19232	50.4687

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.490	FM	0.2989	1451.81177	80.94463	4.6776
2	7.735	MF	0.3308	2.95854e4	1490.64099	95.3224



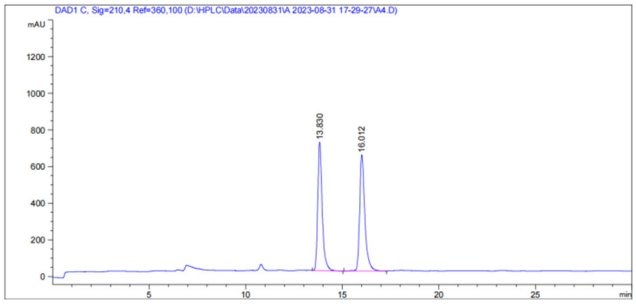
(*S*)-2-(phenylthio)but-3-en-1-yl acetate (3f): yield (38.9 mg, 88%); colorless oil; $[\alpha]^{15}_{D}$ = +29.7 (*c* 0.1, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak IF, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 13.83 and 16.01 min.

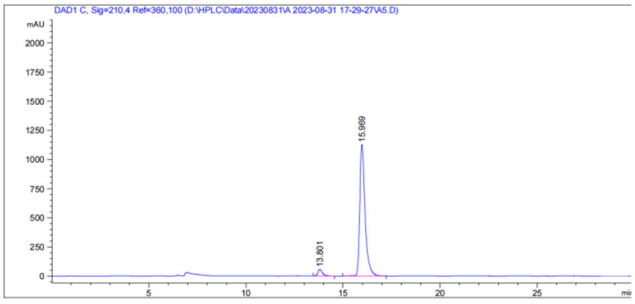
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 2H), 7.28 – 7.14 (m, 3H), 5.73-5.63 (m, 1H), 5.11 – 5.00 (m, 2H), 4.23 – 4.10 (m, 2H), 3.88 – 3.78 (m, 1H), 1.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 134.7, 133.1, 133.0, 128.9, 127.7, 118.0, 65.4, 50.0, 20.8.

HRMS (ESI+) Calcd. For $C_{12}H_{14}O_2SNa^+$ ($[M+Na]^+$): 245.0607, found: 245.0616.

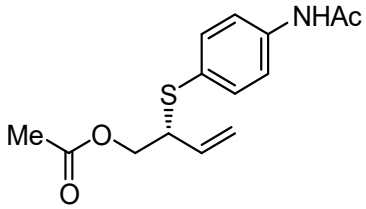
HPLC chromatogram of compound 3f





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.830	BB	0.2441	1.13043e4	701.07544	48.7537
2	16.012	BB	0.2826	1.18823e4	634.07996	51.2463

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.801	BB	0.2421	918.56689	56.38351	4.1313
2	15.969	VB R	0.2817	2.13155e4	1129.28015	95.8687



(*R*)-2-((4-acetamidophenyl)thio)but-3-en-1-yl acetate (3g): using (*R*,*R*,*R*)-**[Ir*]-1** as the catalyst, yield (39.1 mg, 70%); colorless oil; $[\alpha]^{15}_{D}$ = -6.8 (*c* 0.8, CH_2Cl_2); The product was analyzed by HPLC

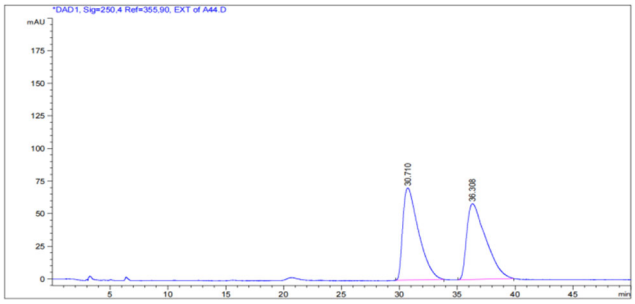
to determine the enantiomeric excess: 81% ee (Chiralpak OD-H, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 220 nm); t_r = 9.26 and 9.79 min.

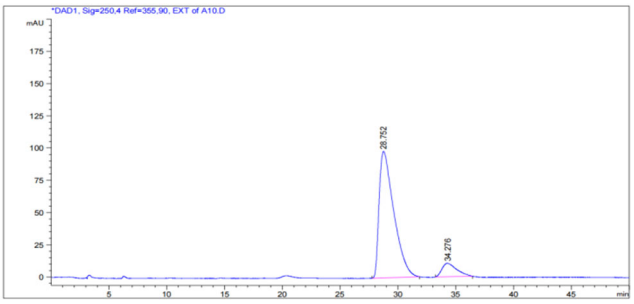
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 5.78 (ddd, *J* = 17.3, 10.1, 8.2 Hz, 1H), 5.29 – 5.12 (m, 2H), 4.34 – 4.14 (m, 2H), 4.07 – 3.92 (m, 1H), 2.27 (s, 6H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 170.7, 138.4, 135.2, 134.3, 133.1, 129.2, 118.4, 65.3, 49.8, 26.9, 20.8.

HRMS (ESI+) Calcd. For $C_{14}H_{17}NO_3SNa^+$ ($[M+Na]^+$): 302.0821, found: 302.0825.

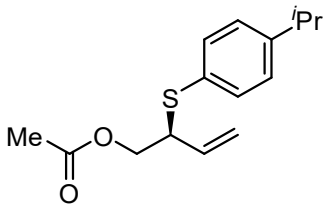
HPLC chromatogram of compound 3g





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.710	BB	1.1186	6697.73730	70.54850	50.2232
2	36.308	BB	1.3358	6638.20801	58.19339	49.7768

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.752	BB	1.0327	8643.37793	98.12006	90.3584
2	34.276	BV R	1.0382	922.28339	10.39418	9.6416



(*S*)-2-((4-isopropylphenyl)thio)but-3-en-1-yl acetate (3h): yield (34.9 mg, 85%); colorless oil; $[\alpha]^{15}_D$ = +4.3 (*c* 1.30, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 0.5 mL/min, λ = 220 nm); t_r = 15.38 and 16.32 min.

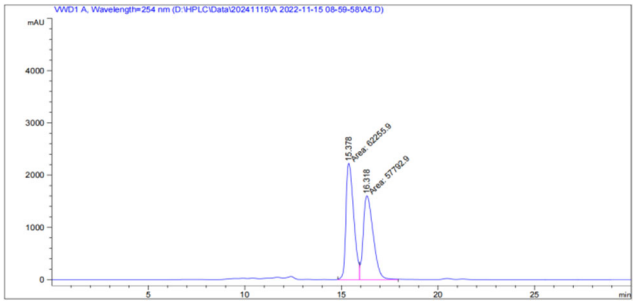
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 7.21 – 7.10 (m, 2H), 5.77 (ddd, *J* = 17.4, 9.9, 8.3 Hz, 1H), 5.18 – 5.07 (m, 2H), 4.28 – 4.16 (m, 2H), 3.89 – 3.79 (m, 1H), 2.96 – 2.81 (m, 1H), 2.02 (s, 3H), 1.23 (d, *J* = 7.0 Hz, 6H).

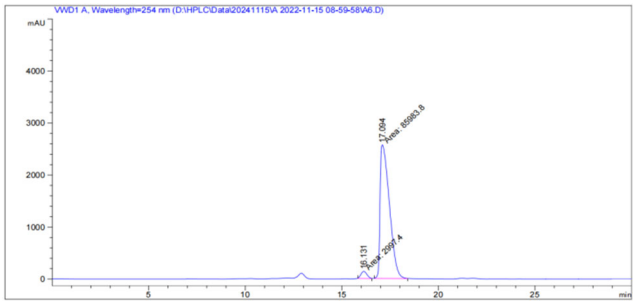
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 148.8, 134.9, 133.6, 129.6, 127.0, 117.8, 65.5, 50.1, 33.7,

23.8, 20.8.

HRMS (ESI+) Calcd. For $C_{15}H_{20}O_2SNa^+$ ([M+Na]$^+$): 287.1076, found: 287.1078.

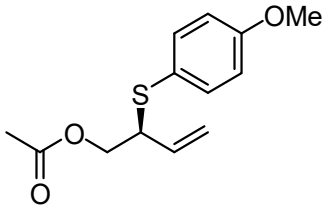
HPLC chromatogram of compound 3h





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.378	MF	0.4660	6.22559e4	2226.71997	51.8588
2	16.318	FM	0.6002	5.77929e4	1604.94336	48.1412

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.131	MM	0.3609	2997.40088	138.41592	3.3686
2	17.094	MM	0.5579	8.59838e4	2568.54980	96.6314



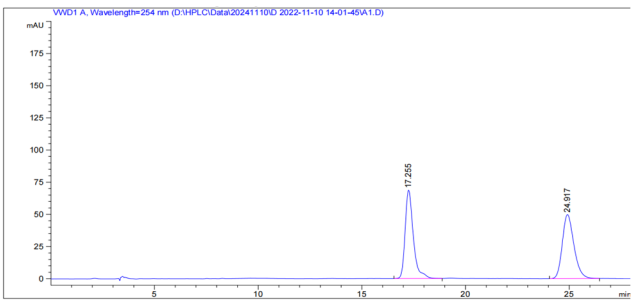
(*S*)-2-((4-methoxyphenyl)thio)but-3-en-1-yl acetate (3i): yield (43.6 mg, 86%); colorless oil; $[\alpha]^{15}_D$ = -2.0 (*c* 0.81, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 17.26 and 24.92 min.

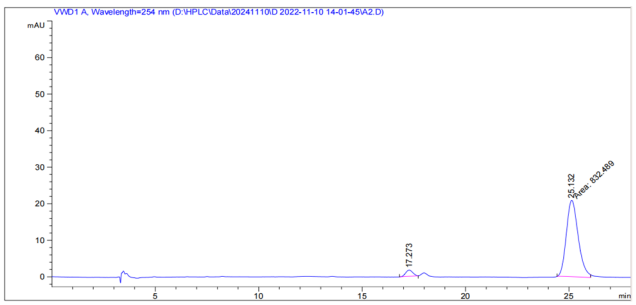
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 6.88 – 6.79 (m, 2H), 5.72 (ddd, *J* = 17.1, 10.3, 8.4 Hz, 1H), 5.13 – 4.98 (m, 2H), 4.25 – 4.12 (m, 2H), 3.80 (s, 3H), 3.76 – 3.66 (m, 1H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 159.9, 136.5, 134.9, 122.8, 117.6, 114.4, 65.3, 55.3, 50.9, 20.8.

HRMS (ESI+) Calcd. For $C_{13}H_{16}O_3SNa^+$ ([M+Na]$^+$): 275.0712, found: 275.0716.

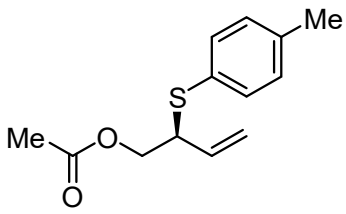
HPLC chromatogram of compound 3i





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.255	BB	0.4140	1882.38403	68.62749	49.2953
2	24.917	BB	0.5943	1936.20618	49.72767	50.7047

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.273	BB	0.3649	40.37965	1.70767	4.6261
2	25.132	MM	0.6634	832.48859	20.91449	95.3739



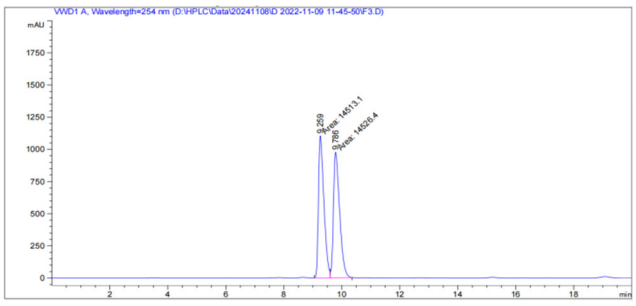
(*S*)-2-(p-tolylthio)but-3-en-1-yl acetate (3j): yield (36.6 mg, 77%); colorless oil; $[\alpha]^{15}_{D}$ = +6.0 (*c* 0.3, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 254 nm); t_r = 9.26 and 9.79 min.

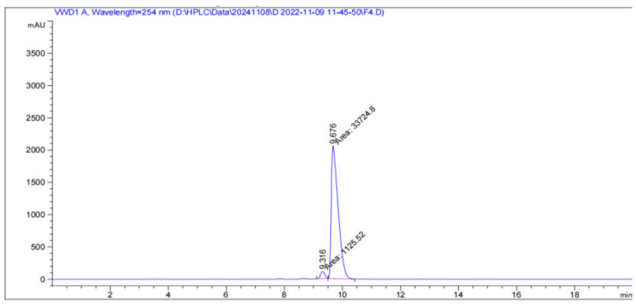
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 2H), 7.07 – 7.01 (m, 2H), 5.68 (ddd, *J* = 17.0, 10.3, 8.3 Hz, 1H), 5.09 – 4.97 (m, 2H), 4.15 (d, *J* = 1.2 Hz, 1H), 4.13 (d, *J* = 1.9 Hz, 1H), 3.79 – 3.70 (m, 1H), 2.26 (s, 3H), 1.96 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 138.0, 134.9, 133.8, 129.7, 129.1, 117.8, 65.4, 50.3, 21.1, 20.8.

HRMS (ESI+) Calcd. For $C_{13}H_{16}O_2SNa^+$ ([M+Na]$^+$): 259.0763, found: 259.0766.

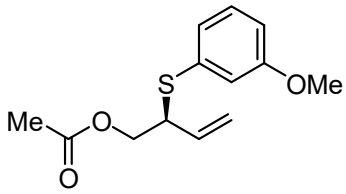
HPLC chromatogram of compound 3j





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.259	MF	0.2189	1.45131e4	1105.12683	49.9770
2	9.786	FM	0.2478	1.45264e4	976.92548	50.0230

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.316	MM	0.1712	1125.52075	109.54490	3.2296
2	9.676	MM	0.2733	3.37248e4	2056.45654	96.7704



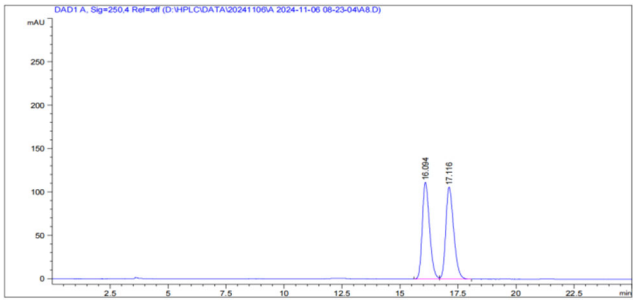
(*S*)-2-((3-methoxyphenyl)thio)but-3-en-1-yl acetate (3k): yield (40.3 mg, 80%); colorless oil; $[\alpha]^{15}_{D}$ = +10.6 (*c* 1.23, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 250 nm); t_r = 16.09 and 17.12 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 1H), 7.06 – 6.94 (m, 2H), 6.84 – 6.75 (m, 1H), 5.85-5.71 (ddd, 1H), 5.22 – 5.11 (m, 2H), 4.31 – 4.17 (m, 2H), 3.99 – 3.88 (m, 1H), 3.80 (s, 3H), 2.04 (s, 3H).

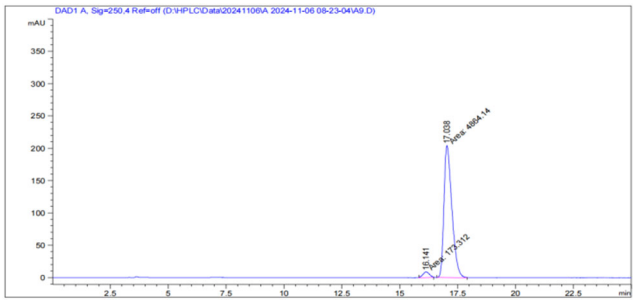
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 159.7, 134.7, 134.5, 129.7, 124.7, 118.1, 117.7, 113.4, 65.4, 55.3, 49.7, 20.8.

HRMS (ESI+) Calcd. For $C_{13}H_{16}O_3SNa^+$ ($[M+Na]^+$): 275.0712, found: 275.0703.

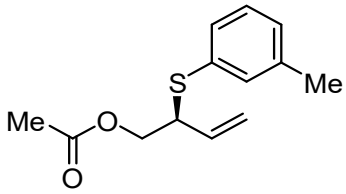
HPLC chromatogram of compound 3k



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.094	BV	0.3342	2433.33862	111.67866	49.1656
2	17.116	VB	0.3626	2515.93579	106.10332	50.8344



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.141	MM	0.3295	173.31224	8.76756	3.4405
2	17.038	MM	0.3973	4864.13525	204.06253	96.5595



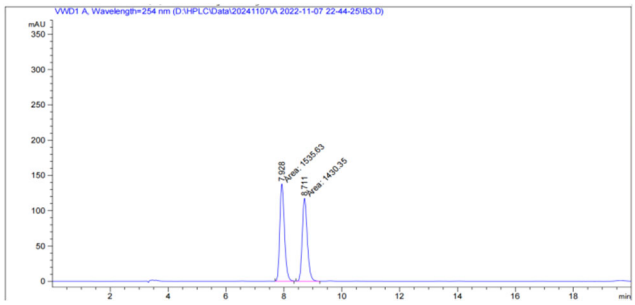
(*S*)-2-(m-tolylthio)but-3-en-1-yl acetate (3l): yield (34.5 mg, 73%); colorless oil; $[\alpha]^{15}_{D}$ = +7.0 (*c* 0.52, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 7.93 and 8.71 min.

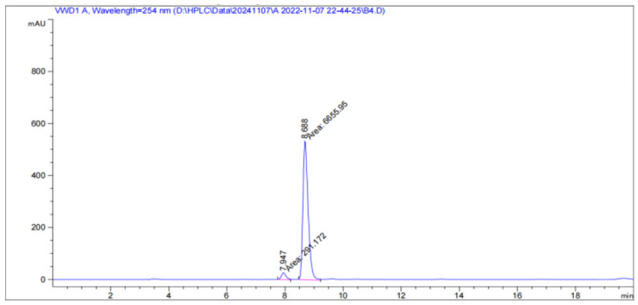
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 7.23 – 7.13 (m, 1H), 7.10 – 7.03 (m, 1H), 5.77 (ddd, *J* = 17.2, 10.0, 8.2 Hz, 1H), 5.26 – 5.04 (m, 2H), 4.29 – 4.15 (m, 2H), 3.95 – 3.84 (m, 1H), 2.33 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 138.7, 134.8, 133.5, 132.8, 129.9, 128.7, 128.5, 117.9, 65.5, 49.8, 21.2, 20.8.

HRMS (ESI+) Calcd. For $C_{13}H_{16}O_2SNa^+$ ($[M+Na]^+$): 259.0763, found: 259.0761.

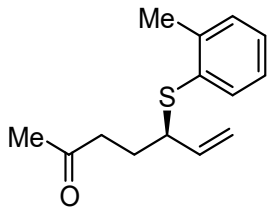
HPLC chromatogram of compound 3l





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.928	MM	0.1856	1535.62573	137.87798	51.7747
2	8.711	MM	0.2027	1430.35254	117.60011	48.2253

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.947	MM	0.1893	291.17233	25.63072	4.1913
2	8.688	MM	0.2078	6655.94580	533.75629	95.8087



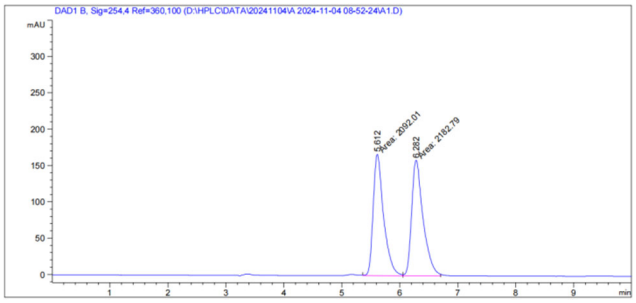
(*S*)- 2-(o-tolylthio)but-3-en-1-yl acetate (3m): yield (29.3 mg, 62%); colorless oil; $[\alpha]^{15}_D$ = +4.5 (*c* 0.6, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak OD-H, *i*-propanol/hexane = 3/97, flow rate 1 mL/min, λ = 254 nm); t_r = 5.61 and 6.28 min.

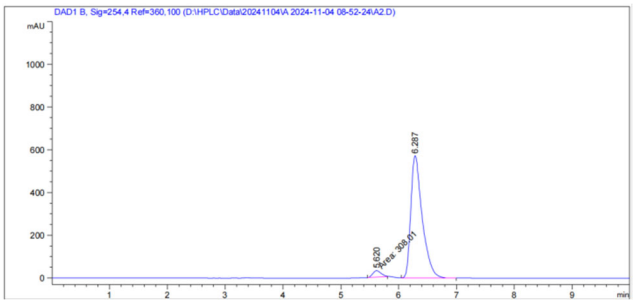
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.22 – 7.10 (m, 3H), 5.78 (ddd, *J* = 17.3, 10.1, 8.3 Hz, 1H), 5.18 – 5.07 (m, 2H), 4.33 – 4.17 (m, 2H), 3.92 – 3.82 (m, 1H), 2.44 (s, 3H), 2.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 140.5, 134.7, 133.3, 132.6, 130.4, 127.7, 126.4, 117.9, 65.5, 49.6, 20.9, 20.8.

HRMS (ESI+) Calcd. For $C_{13}H_{16}O_2SNa^+$ ($[M+Na]^+$): 259.0764, found: 259.0774.

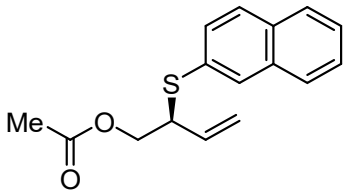
HPLC chromatogram of compound 3m





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.612	FM	0.2086	2092.01196	167.11705	48.9382
2	6.282	MF	0.2286	2182.79443	159.12639	51.0618

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.620	MM	0.1692	308.01038	30.33475	3.7639
2	6.287	VB	0.2025	7875.28418	572.52356	96.2361



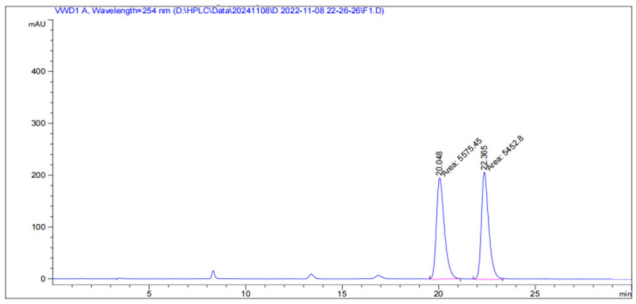
(*S*)-2-(naphthalen-2-ylthio)but-3-en-1-yl acetate (3n): yield (45.2 mg, 83%); colorless oil; $[\alpha]^{15}_{D}$ = +11.2 (*c* 1.98, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 20.05 and 22.37 min.

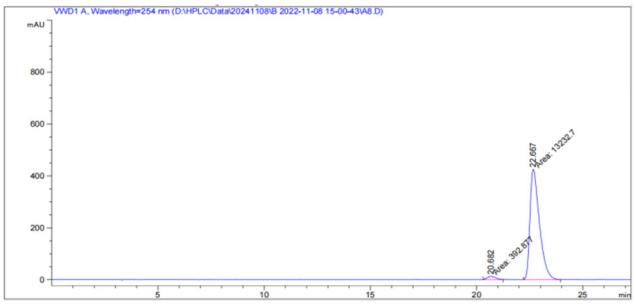
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 1.7 Hz, 1H), 7.85 – 7.74 (m, 3H), 7.54 – 7.43 (m, 3H), 5.82 (ddd, *J* = 17.0, 10.3, 8.3 Hz, 1H), 5.21 – 5.10 (m, 2H), 4.36 – 4.23 (m, 2H), 4.08 – 3.98 (m, 1H), 2.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 134.6, 133.6, 132.5, 131.8, 130.5, 130.0, 128.4, 127.7, 127.5, 126.5, 126.3, 118.1, 65.5, 49.9, 20.8.

HRMS (ESI+) Calcd. For $C_{16}H_{16}O_2SNa^+$ ($[M+Na]^+$): 295.0763, found: 295.0754.

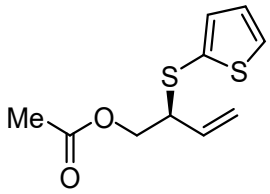
HPLC chromatogram of compound 3n





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.048	MM	0.4758	5575.45166	195.30965	50.5561
2	22.365	MM	0.4401	5452.80420	206.51262	49.4439

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.682	MF	0.4989	392.87747	13.12354	2.8834
2	22.667	MF	0.5183	1.32327e4	425.55124	97.1166



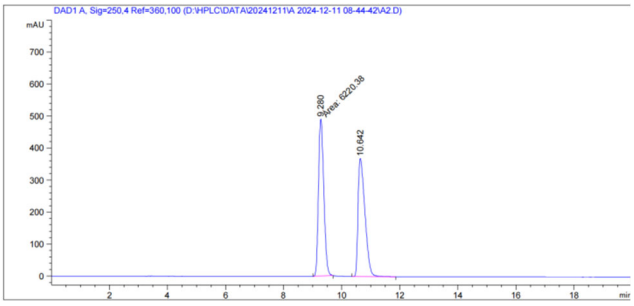
(*S*)-2-(thiophen-2-ylthio)but-3-en-1-yl acetate (3o): yield (27.4 mg, 60%); colorless oil; $[\alpha]^{15}_{D}$ = +5.86 (*c* 1.00, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak AS-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 250 nm); t_r = 9.28 and 10.64 min.

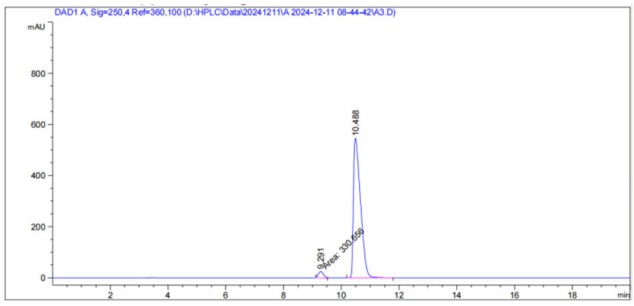
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 6.99 (dd, *J* = 5.4, 3.5 Hz, 1H), 5.74 (ddd, *J* = 17.0, 10.3, 8.4 Hz, 1H), 5.17 – 5.02 (m, 2H), 4.23 (d, *J* = 6.8 Hz, 2H), 3.73 – 3.63 (m, 1H), 2.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 136.3, 134.2, 130.8, 130.2, 127.6, 118.3, 64.8, 52.2, 20.8.

HRMS (ESI+) Calcd. For $C_{10}H_{12}O_2S_2Na^+$ ($[M+Na]^+$): 251.0171, found: 251.0168.

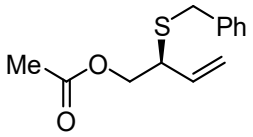
HPLC chromatogram of compound 3o





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.280	MM	0.2115	6220.38232	490.27914	50.6062
2	10.642	BB	0.2561	6071.36279	368.79669	49.3938

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.291	MM	0.2102	330.65588	26.22366	3.4258
2	10.488	BB	0.2672	9321.19922	545.92517	96.5742



(*S*)-2-(benzylthio)but-3-en-1-yl acetate (3p): yield (34.0 mg, 72%); colorless oil; $[\alpha]^{15}_{D}$ = +41.2 (*c*

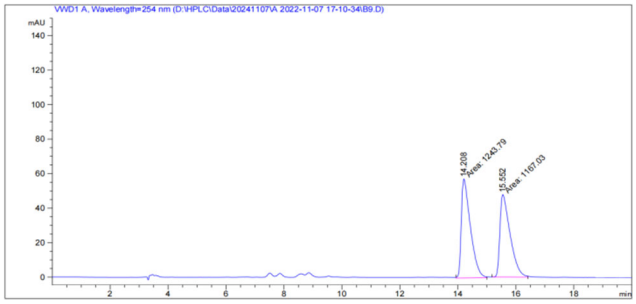
1.80, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 14.21 and 15.56 min.

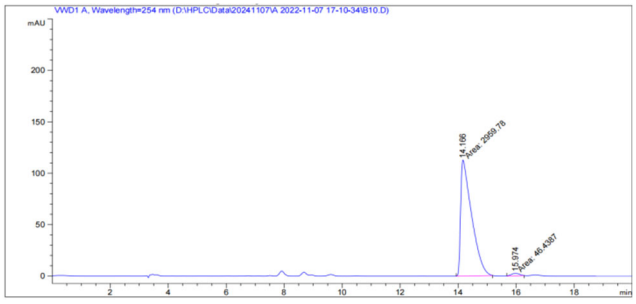
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 7.26 – 7.20 (m, 1H), 5.73 (ddd, *J* = 17.0, 10.2, 8.7 Hz, 1H), 5.24 – 5.08 (m, 2H), 4.25 – 4.12 (m, 2H), 3.80 – 3.63 (m, 2H), 3.45 – 3.35 (m, 1H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 137.8, 135.2, 128.9, 128.5, 127.1, 117.5, 65.3, 46.4, 34.8, 20.8.

HRMS (ESI+) Calcd. For $C_{13}H_{16}O_2SNa^+$ ($[M+Na]^+$): 259.0763, found: 259.0760.

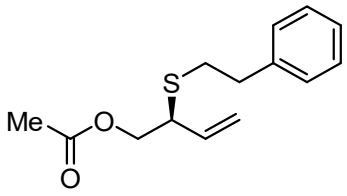
HPLC chromatogram of compound 3p





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.208	MM	0.3615	1243.78821	57.33702	51.5920
2	15.552	MF	0.4070	1167.02661	47.79437	48.4080

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.166	MM	0.4373	2959.77783	112.79761	98.4552
2	15.974	MM	0.3255	46.43865	2.37799	1.5448



(*S*)-2-(phenethylthio)but-3-en-1-yl acetate (3q): yield (38 mg, 76%); colorless oil; $[\alpha]^{15}_D$ = -2.7 (*c* 3.00, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (Chiralpak OD-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 10.37 and 11.42 min.

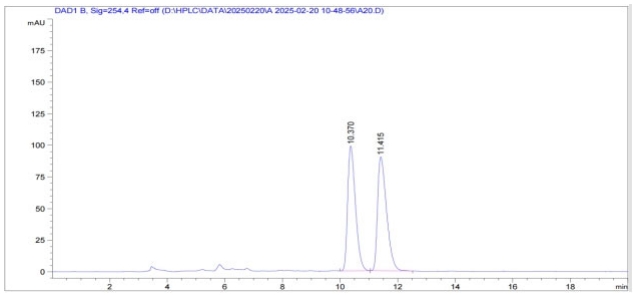
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 5.69 (ddd, *J* = 17.0, 10.2, 8.8 Hz, 1H), 5.21 – 5.10 (m, 2H), 4. 26 – 4.12 (m, 2H), 3.56 – 3.46 (m, 1H), 2.92 – 2.83 (m, 2H), 2.80 – 2.72 (m, 2H), 2.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 140.3, 135.4, 128.49, 128.46, 126.4, 117.4, 65.4, 47.1, 36.2,

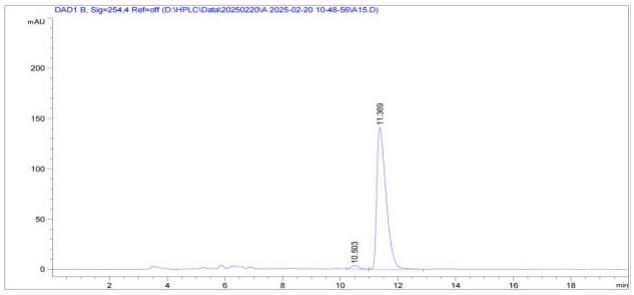
31.9, 20.8.

HRMS (ESI+) Calcd. For $C_{14}H_{18}O_2SNa^+$ ([M+Na]$^+$): 273.0920, found: 273.0925.

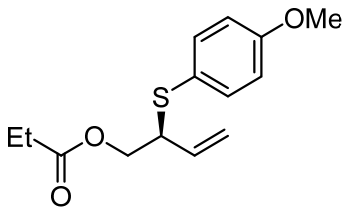
HPLC chromatogram of compound 3q



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.370	BB	0.2902	1863.20654	98.71007	48.7579
2	11.415	BB	0.3316	1958.13733	90.09667	51.2421



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.503	BB	0.2424	64.29920	3.60041	2.0110
2	11.369	BB	0.3395	3133.07056	140.86646	97.9890



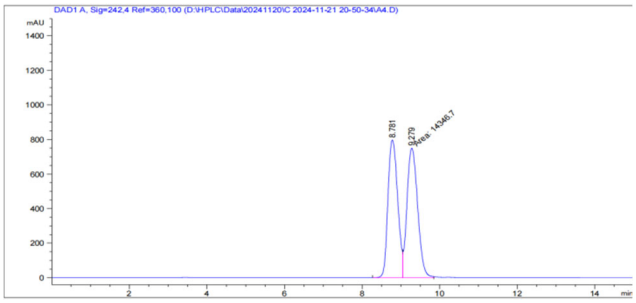
(*S*)-2-((4-methoxyphenyl)thio)but-3-en-1-yl propionate (3r): yield (41.5 mg, 78%); colorless oil; $[\alpha]^{15}_D$ = -4.3 (*c* 1.01, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak AS-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 242 nm); t_r = 8.78 and 9.23 min.

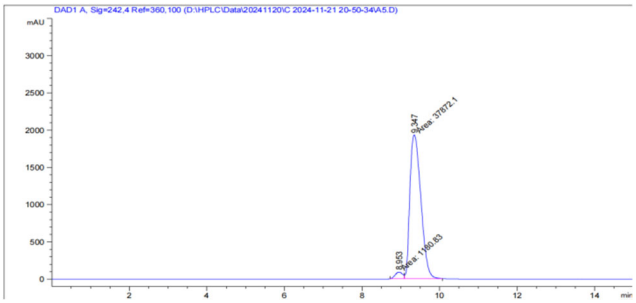
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 6.87 – 6.79 (m, 2H), 5.72 (ddd, *J* = 17.1, 10.3, 8.4 Hz, 1H), 5.12 – 4.97 (m, 2H), 4.26 – 4.14 (m, 2H), 3.79 (s, 3H), 3.77 – 3.66 (m, 1H), 2.31 (q, *J* = 7.6 Hz, 2H), 1.12 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 159.9, 136.4, 135.0, 122.9, 117.6, 114.4, 65.1, 55.3, 50.9, 27.4, 9.1.

HRMS (ESI+) Calcd. For $C_{14}H_{18}O_3SNa^+$ ([M+Na]$^+$): 289.0869, found: 289.0865.

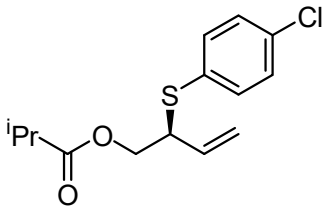
HPLC chromatogram of compound 3r





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.781	BV	0.2791	1.38788e4	797.21942	49.1711
2	9.279	MF	0.3189	1.43467e4	749.73743	50.8289

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.953	MF	0.2239	1180.82593	87.90112	3.0237
2	9.347	FM	0.3272	3.78721e4	1929.37695	96.9763



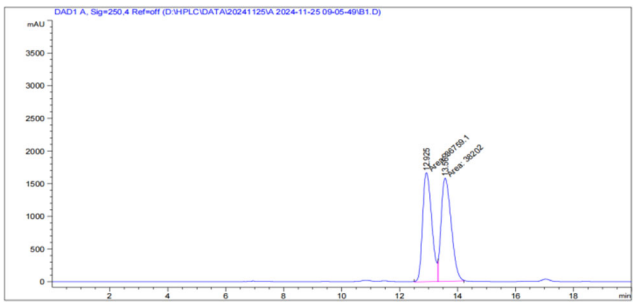
(*S*)-2-((4-chlorophenyl)thio)but-3-en-1-yl isobutyrate (3s): yield (45.4 mg, 80%); colorless oil; $[\alpha]^{15}_{D}$ = +8.9 (*c* 2.39, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 87% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 0.5 mL/min, λ = 250 nm); t_r = 12.93 and 13.57 min.

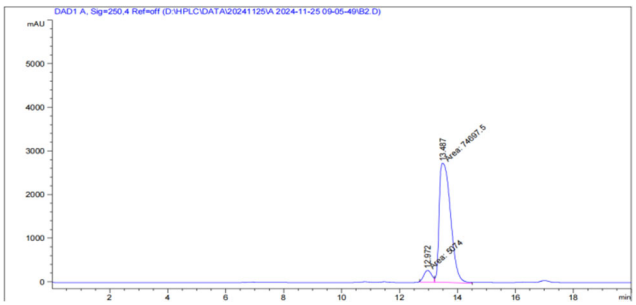
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 2H), 7.22 – 7.17 (m, 2H), 5.65 (ddd, *J* = 17.0, 10.3, 8.4 Hz, 1H), 5.09 – 4.96 (m, 2H), 4.22 – 4.07 (m, 2H), 3.84 – 3.72 (m, 1H), 2.46 (p, *J* = 7.0 Hz, 1H), 1.08 (d, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 134.5, 134.4, 133.9, 131.6, 129.0, 118.2, 64.8, 50.4, 33.9, 18.9.

HRMS (ESI+) Calcd. For $C_{14}H_{17}ClO_2SNa^+$ ($[M+Na]^+$): 307.0530, found: 307.0532.

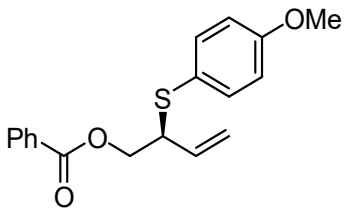
HPLC chromatogram of compound 3s





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.925	MF	0.3671	3.67591e4	1669.07141	49.0376
2	13.569	FM	0.4031	3.82020e4	1579.51050	50.9624

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.972	MF	0.3144	5074.00391	268.96637	6.3607
2	13.487	FM	0.4553	7.46975e4	2734.43652	93.6393



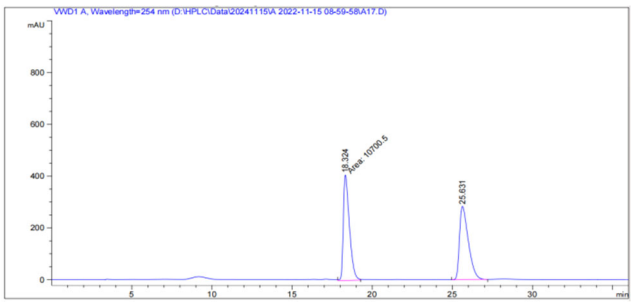
(*S*)-2-((4-methoxyphenyl)thio)but-3-en-1-yl benzoate (3t): yield (45.2 mg, 72%); colorless oil; $[\alpha]^{15}_{D}$ = +1.2 (*c* 1.17, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 89% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 18.32 and 25.63 min.

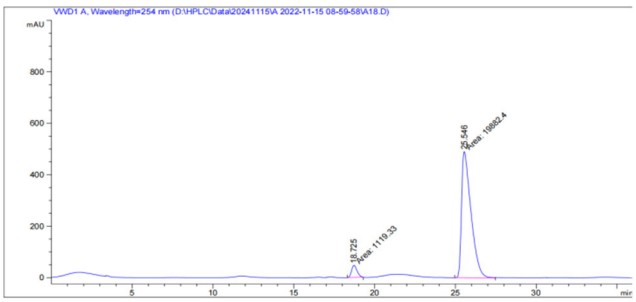
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 2H), 7.60 – 7.51 (m, 1H), 7.50 – 7.37 (m, 4H), 6.89 – 6.79 (m, 2H), 5.84 (ddd, *J* = 17.0, 10.4, 8.4 Hz, 1H), 5.17 – 5.05 (m, 2H), 4.52 – 4.38 (m, 2H), 3.93 – 3.83 (m, 1H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 159.9, 136.5, 134.9, 133.0, 129.9, 129.6, 128.3, 122.8, 117.7, 114.5, 65.7, 55.2, 51.0.

HRMS (ESI+) Calcd. For $C_{18}H_{18}O_3SNa^+$ ($[M+Na]^+$): 337.0869, found: 337.0878.

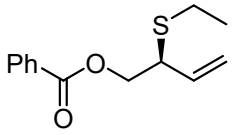
HPLC chromatogram of compound 3t





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.324	MM	0.4381	1.07005e4	407.04385	49.6900
2	25.631	BB	0.5794	1.08340e4	283.15814	50.3100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.725	MM	0.3961	1119.33130	47.10273	5.3297
2	25.546	MM	0.6762	1.98824e4	490.07321	94.6703



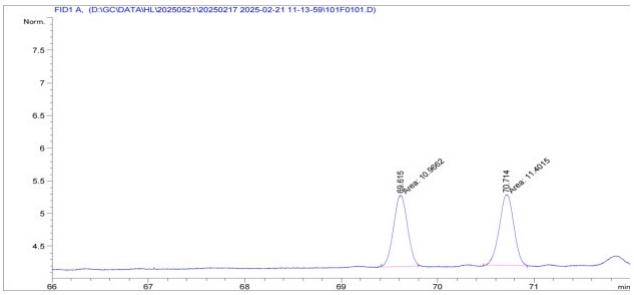
(*S*)-2-(ethylthio)but-3-en-1-yl benzoate (3u): yield (33 mg, 68%); colorless oil; $[\alpha]^{15}_D$ = -2.8 (*c* 1.50, CH_2Cl_2); The product was analyzed by GC to determine the enantiomeric excess: >99% ee (Beta DEX-390, N_2 flow rate 1.0 mL/min, 80 min at 150 °C); t_r = 69.62 and 70.71 min.

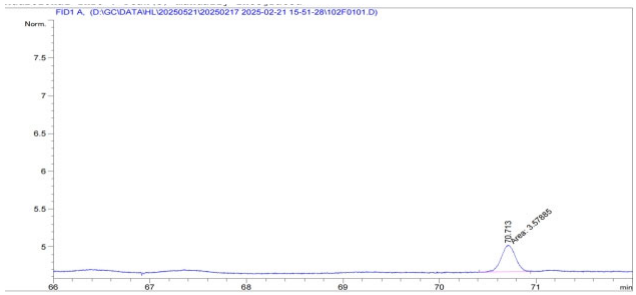
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.99 (m, 2H), 7.62 – 7.51 (m, 1H), 7.50 – 7.39 (m, 2H), 5.79 (ddd, *J* = 17.0, 10.2, 8.7 Hz, 1H), 5.27 – 5.14 (m, 2H), 4.50 (dd, *J* = 11.1, 5.8 Hz, 1H), 4.40 (dd, *J* = 11.1, 7.8 Hz, 1H), 3.72 – 3.62 (m, 1H), 2.58 (q, *J* = 7.4 Hz, 2H), 1.27 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 135.6, 133.0, 130.0, 129.7, 128.4, 117.2, 66.0, 46.7, 24.5, 14.7.

HRMS (ESI+) Calcd. For $C_{13}H_{12}O_2SNa^+$ ($[M+Na]^+$): 259.0763, found: 259.0774.

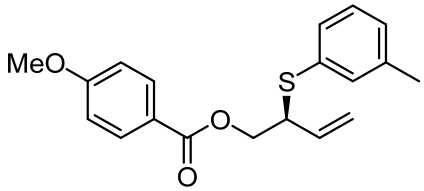
GC chromatogram of compound 3u





Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	69.615	MM	0.1674	10.96617	1.09172	49.02676
2	70.714	MM	0.1752	11.40155	1.08455	50.97324

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	70.713	MM	0.1690	3.57885	3.53018e-1	1.000e2



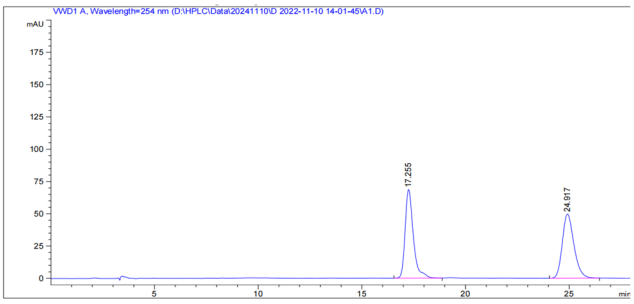
(*S*)-2-(m-tolylthio)but-3-en-1-yl 4-methoxybenzoate (3v): yield (35.4 mg, 54%); colorless oil; $[\alpha]^{15}_D$ = +11.0 (*c* 0.20, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 17.26 and 24.92 min.

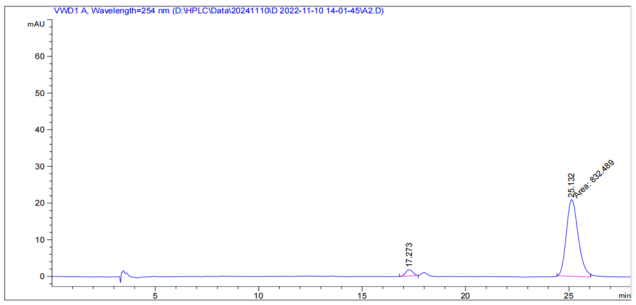
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.90 (m, 2H), 7.32 – 7.25 (m, 2H), 7.24 – 7.14 (m, 1H), 7.10 – 7.03 (m, 1H), 6.97 – 6.86 (m, 2H), 5.86 (ddd, *J* = 17.1, 10.3, 8.2 Hz, 1H), 5.24 – 5.12 (m, 2H), 4.58 – 4.37 (m, 2H), 4.09 – 3.98 (m, 1H), 3.86 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 163.4, 138.7, 134.9, 133.6, 132.9, 131.7, 129.9, 128.7, 128.4, 122.3, 117.9, 113.6, 65.7, 55.4, 50.1, 21.2.

HRMS (ESI+) Calcd. For $C_{19}H_{20}O_3SNa^+$ ([M+Na]$^+$): 351.1025, found: 351.1018.

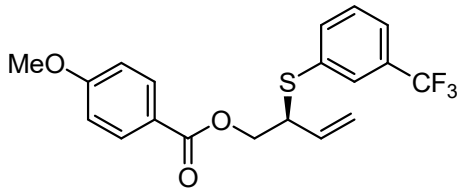
HPLC chromatogram of compound 3v





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.255	BB	0.4140	1882.38403	68.62749	49.2953
2	24.917	BB	0.5943	1936.20618	49.72767	50.7047

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.273	BB	0.3649	40.37965	1.70767	4.6261
2	25.132	MM	0.6634	832.48859	20.91449	95.3739



(*S*)-2-((3-(trifluoromethyl)phenyl)thio)but-3-en-1-yl 4-methoxybenzoate (3w): yield (39.7mg, 58%); colorless oil; $[\alpha]^{15}_D$ = -10.1 (*c* 1.32, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 15.46 and 16.72 min.

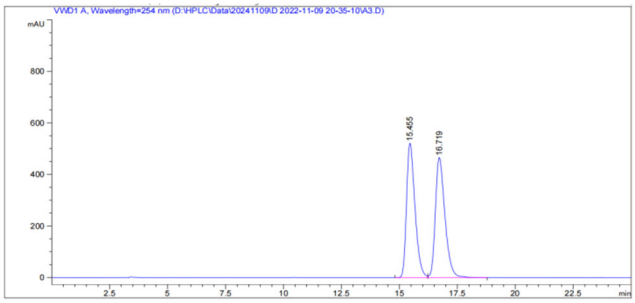
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 2H), 7.70 (d, *J* = 1.8 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 6.97 – 6.87 (m, 2H), 5.85 (ddd, *J* = 17.2, 10.1, 8.3 Hz, 1H), 5.23 – 5.14 (m, 2H), 4.58 – 4.41 (m, 2H), 4.16 – 4.06 (m, 1H), 3.86 (s, 3H).

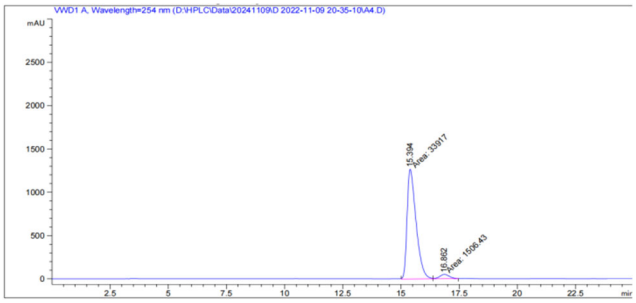
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 163.6, 135.5, 135.1, 134.3, 131.7, 131.3 (q, *J* = 20.2 Hz), 129.3, 129.0 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 272.7 Hz), 124.1 (q, *J* = 3.7 Hz), 122.1, 118.6, 113.7, 65.5, 55.4, 50.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.8.

HRMS (ESI+) Calcd. For $C_{19}H_{17}F_3O_3SNa^+$ ([M+Na]$^+$): 405.0743, found: 405.0738.

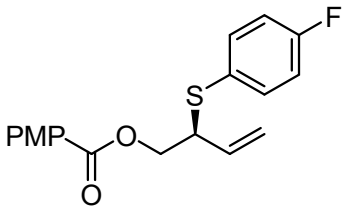
HPLC chromatogram of compound 3w





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.455	BV	0.3864	1.32085e4	521.71149	49.6741
2	16.719	VB	0.4360	1.33818e4	466.03995	50.3259

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.394	MF	0.4460	3.39170e4	1267.43433	95.7474
2	16.862	FM	0.4920	1506.42871	51.02662	4.2526



(*S*)-2-((4-fluorophenyl)thio)but-3-en-1-yl 4-methoxybenzoate (3x): yield (45.2 mg, 68%); colorless oil; $[\alpha]^{15}_{D}$ = +11.9 (*c* 0.60, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 254 nm); t_r = 25.23 and 33.48 min.

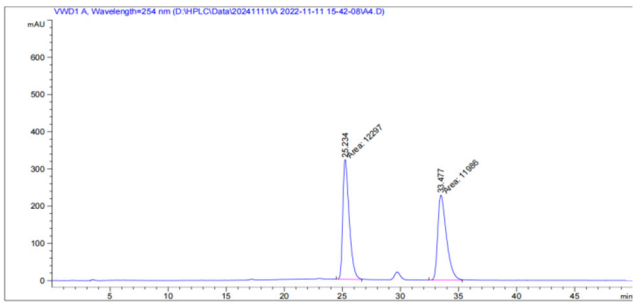
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.91 (m, 2H), 7.52 – 7.42 (m, 2H), 7.05 – 6.95 (m, 2H), 6.95 – 6.87 (m, 2H), 5.82 (ddd, *J* = 17.0, 8.3, 1.7 Hz, 1H), 5.18 – 5.06 (m, 2H), 4.51 – 4.36 (m, 2H), 3.99 – 3.90 (m, 1H), 3.86 (s, 1H).

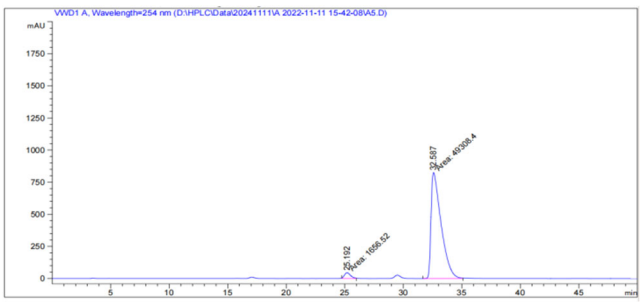
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 163.5, 162.8(d, *J* = 252.5 Hz), 136.2 (d, *J* = 8.4 Hz), 134.7, 131.7, 127.9(d, *J* = 3 Hz), 122.2, 118.1, 116.0 (d, *J* = 21.8 Hz), 113.6, 65.4, 55.4, 51.0.

^{19}F NMR (377 MHz, $CDCl_3$) δ -113.2.

HRMS (ESI+) Calcd. For $C_{18}H_{17}FO_3SNa^+$ ($[M+Na]^+$): 355.0775, found: 355.0777.

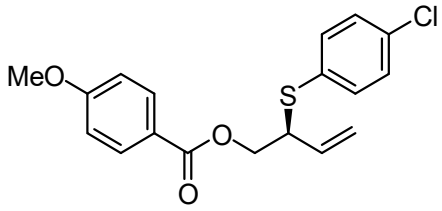
HPLC chromatogram of compound 3x





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.234	MF	0.6366	1.22970e4	321.93414	50.6402
2	33.477	MF	0.8739	1.19860e4	228.58730	49.3598

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.192	FM	0.6060	1656.52222	45.55738	3.2503
2	32.587	MF	0.9958	4.93084e4	825.24530	96.7497



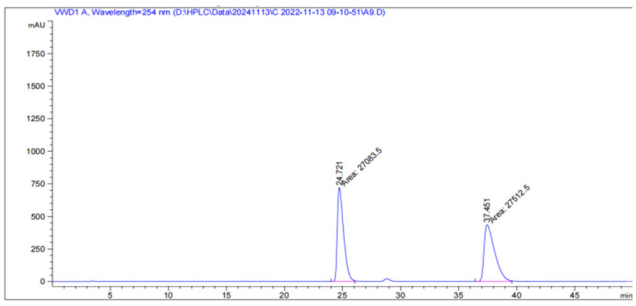
(*S*)-2-((4-chlorophenyl)thio)but-3-en-1-yl 4-methoxybenzoate (3y): yield (42.5 mg, 61%); colorless oil; $[\alpha]^{15}_{D}$ = +22.6 (*c* 2.84, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 24.72 and 37.45 min.

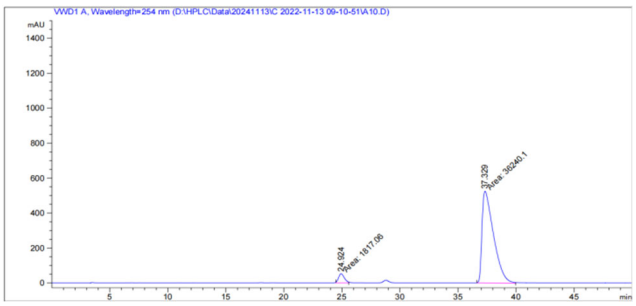
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.43 – 7.35 (m, 2H), 7.31 – 7.22 (m, 2H), 6.96 – 6.86 (m, 2H), 5.83 (ddd, *J* = 17.3, 10.1, 8.3 Hz, 1H), 5.21 – 5.11 (m, 2H), 4.51 – 4.37 (m, 2H), 4.06 – 3.96 (m, 1H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 163.5, 134.5, 134.4, 133.9, 131.7, 131.7, 129.1, 122.1, 118.3, 113.6, 65.5, 55.4, 50.5.

HRMS (ESI+) Calcd. For $C_{18}H_{17}ClO_3SNa^+$ ($[M+Na]^+$): 371.0479, found: 371.0488.

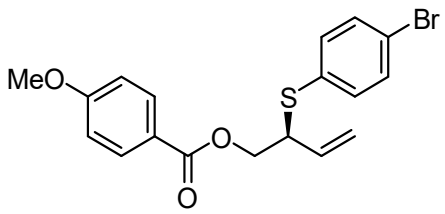
HPLC chromatogram of compound 3y





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.721	MF	0.6255	2.70835e4	721.65460	49.6072
2	37.451	MF	1.0532	2.75125e4	435.38403	50.3928

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.924	FM	0.5775	1817.06287	52.43667	4.7746
2	37.329	MM	1.1503	3.62401e4	525.06512	95.2254



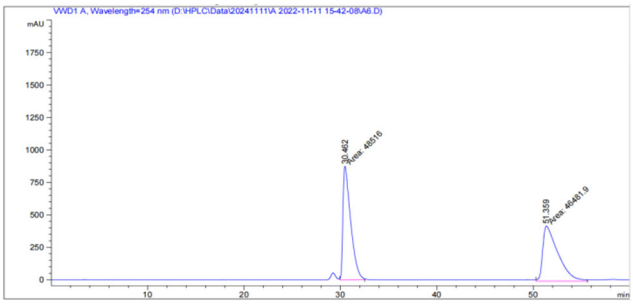
(*S*)-2-((4-bromophenyl)thio)but-3-en-1-yl 4-methoxybenzoate (3z): yield (50.2 mg, 64%); colorless oil; $[\alpha]^{15}_{D}$ = +18.1 (*c* 0.40, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 30.46 and 51.36 min.

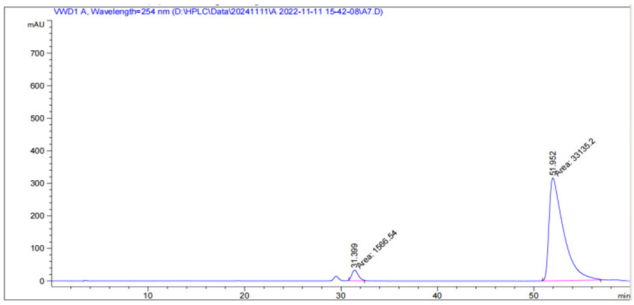
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 2H), 7.46 – 7.37 (m, 2H), 7.36 – 7.29 (m, 2H), 6.97 – 6.87 (m, 2H), 5.83 (ddd, *J* = 17.2, 10.1, 8.2 Hz, 1H), 5.22 – 5.12 (m, 2H), 4.51 – 4.38 (m, 2H), 4.07 – 3.97 (m, 1H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 163.5, 134.6, 134.5, 132.5, 132.0, 131.7, 122.1, 121.9, 118.4, 113.6, 65.6, 55.4, 50.4.

HRMS (ESI+) Calcd. For $C_{18}H_{17}BrO_3SNa^+$ ([M+Na]$^+$): 414.9974, found: 414.9972.

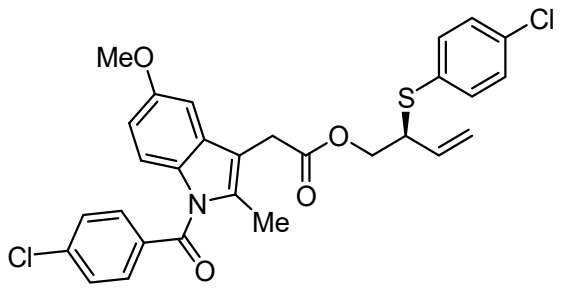
HPLC chromatogram of compound 3z





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.462	MF	0.9244	4.85160e4	874.77277	51.0706
2	51.359	MM	1.8306	4.64819e4	423.18808	48.9294

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.399	FM	0.7894	1566.54163	33.07469	4.5143
2	51.952	MM	1.7477	3.31352e4	315.99356	95.4857



(*S*)-2-((4-chlorophenyl)thio)but-3-en-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-

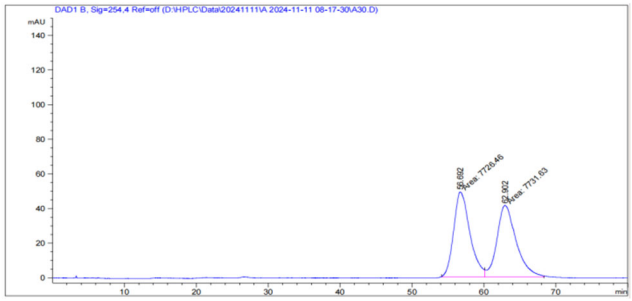
indol-3-yl)acetate (3A): yield (55.3 mg, 50%); white solid (m.p. 90 ℃); $[\alpha]^{15}_{D}$ = +2.9 (*c* 1.42, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (Chiralpak IA, *i*-propanol/hexane = 3/97, flow rate 1 mL/min, λ = 254 nm); t_r = 56.69 and 62.90 min.

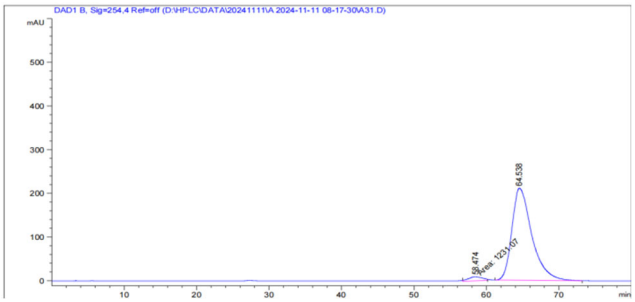
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.61 (m, 2H), 7.50 – 7.40 (m, 2H), 7.32 – 7.19 (m, 4H), 6.96 (d, *J* = 2.6 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.67 (ddd, *J* = 17.0, 10.3, 8.4 Hz, 1H), 5.07 – 4.94 (m, 2H), 4.24 (dd, *J* = 6.7, 0.8 Hz, 2H), 3.83 (s, 3H), 3.67 (s, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 168.2, 156.0, 139.2, 136.0, 134.6, 134.2, 134.0, 133.8, 131.2, 131.1, 130.8, 130.5, 129.1, 118.2, 114.9, 112.2, 111.6, 101.4, 65.4, 55.7, 50.4, 30.2, 13.3.

HRMS (ESI+) Calcd. For $C_{29}H_{25}Cl_2NO_4SNa^+$ ($[M+Na]^+$): 576.0774, found: 576.0780.

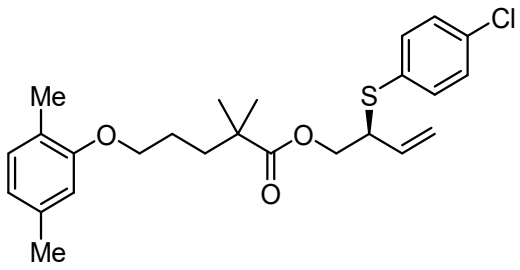
HPLC chromatogram of compound 3A





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	56.692	MF	2.6188	7726.46387	49.17360	49.9833
2	62.902	FM	3.1100	7731.63037	41.43445	50.0167

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	58.474	MM	2.2773	1231.07300	9.00971	2.9615
2	64.538	BB	2.2610	4.03382e4	210.94702	97.0385



(*S*)-2-((4-chlorophenyl)thio)but-3-en-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3B): yield (28.4 mg, 33%); colorless oil; $[\alpha]^{15}_{D}$ = +1.1 (*c* 0.3, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 89% ee (Chiralpak OD-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 7.86 and 8.86 min.

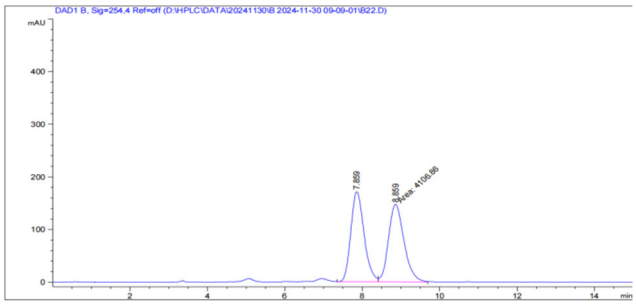
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.31 – 7.21 (m, 1H), 7.00 (d, *J* = 7.4 Hz, 1H),

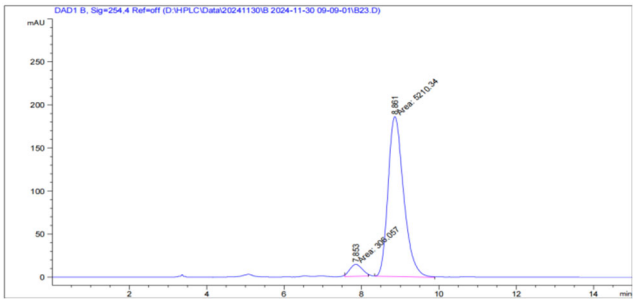
6.66 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 5.73 (ddd, *J* = 17.0, 10.3, 8.4 Hz, 1H), 5.15 – 5.03 (m, 2H), 4.29 – 4.15 (m, 2H), 3.94 – 3.81 (m, 3H), 2.30 (s, 3H), 2.17 (s, 3H), 1.75-1.71 (m, 4H), 1.22 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 156.9, 136.4, 134.6, 134.4, 133.9, 131.6, 130.3, 129.1, 123.5, 120.7, 118.2, 111.9, 67.9, 64.9, 50.5, 42.2, 36.9, 29.7, 25.2, 25.1, 21.4, 15.8.

HRMS (ESI+) Calcd. For $C_{25}H_{35}ClO_3S^+$ ($[M+NH_4]^+$): 464.2021, found: 464.2014.

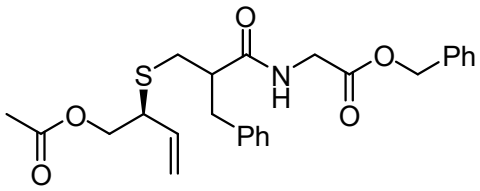
HPLC chromatogram of compound 3B





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.859	VV	0.3685	4082.22266	170.99350	49.8495
2	8.859	MF	0.4642	4106.86475	147.44647	50.1505

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.853	MF	0.3687	306.05737	13.83628	5.5481
2	8.861	MM	0.4676	5210.34473	185.73134	94.4519



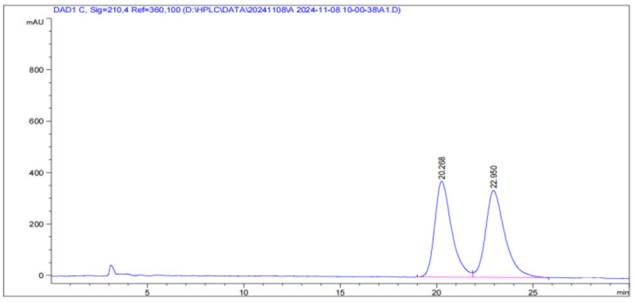
Benzyl (3-(((*S*)-1-acetoxybut-3-en-2-yl)thio)-2-benzylpropanoyl)glycinate (3C): yield (70 mg, 67%); colorless oil; $[\alpha]^{15}_D$ = +7.3 (*c* 1.35, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (Chiralpak IA, *i*-propanol/hexane = 10/90, flow rate 1 mL/min, λ = 210 nm); t_r = 20.27 and 22.95 min.

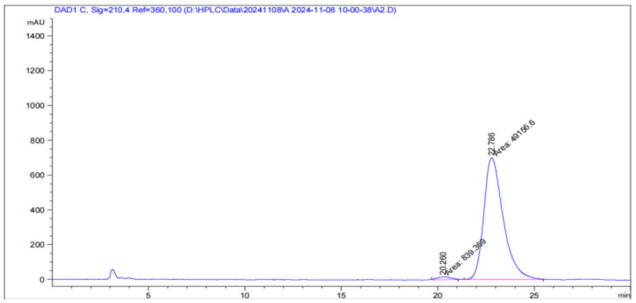
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 5H), 7.29 – 7.24 (m, 2H), 7.23 – 7.11 (m, 3H), 6.10 – 6.03 (m, 1H), 5.61 (ddd, *J* = 17.1, 10.2, 8.7 Hz, 1H), 5.16 (s, 2H), 5.09 – 4.87 (m, 2H), 4.23 – 4.10 (m, 2H), 4.10 – 4.04 (m, 1H), 4.01 – 3.92 (m, 1H), 3.47 – 3.36 (m, 1H), 3.03 – 2.90 (m, 1H), 2.88 – 2.77 (m, 2H), 2.64 – 2.52 (m, 2H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 170.7, 169.5, 138.8, 135.1, 135.0, 128.9, 128.9, 128.6, 128.5, 128.3, 126.5, 117.6, 67.1, 65.3, 49.6, 47.2, 41.4, 38.2, 31.9, 20.8.

HRMS (ESI+) Calcd. For $C_{25}H_{29}NO_5SNa^+$ ($[M+Na]^+$): 478.1659, found: 478.1654.

HPLC chromatogram of compound 3C

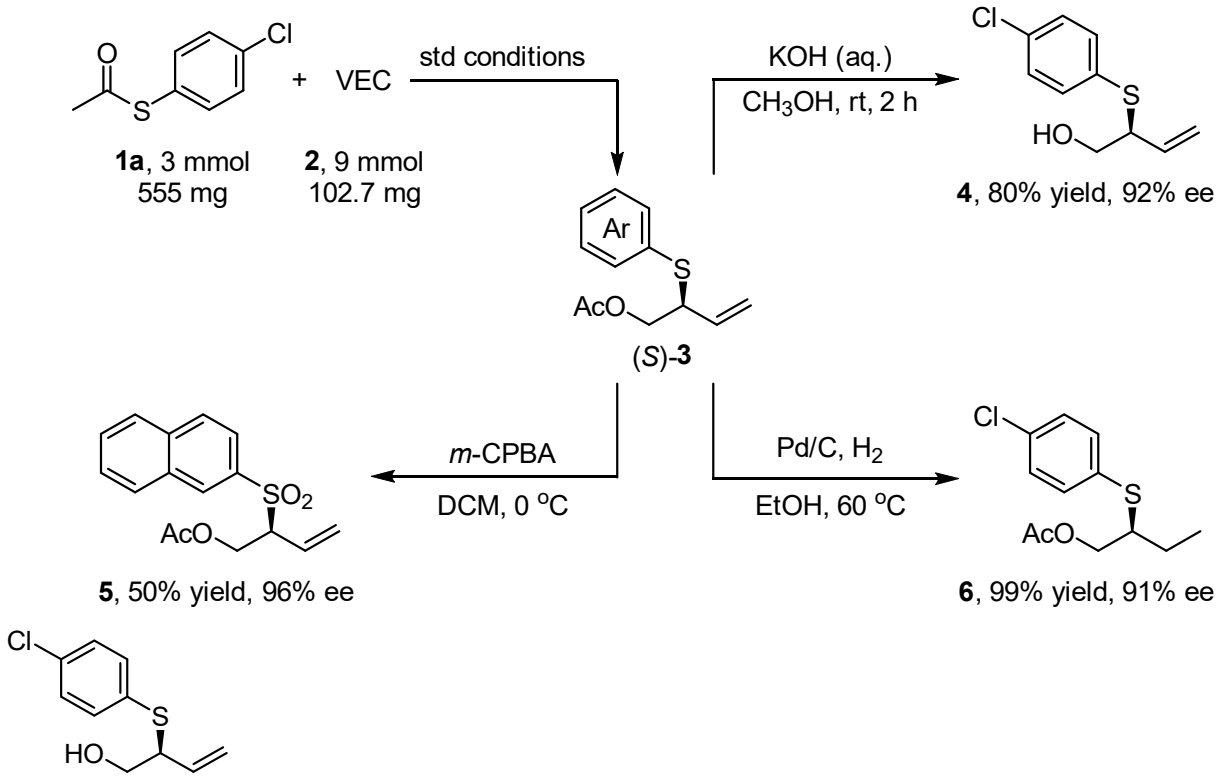




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.268	BV	0.7910	2.25928e4	372.81296	49.0707
2	22.950	VB	0.9211	2.34485e4	338.09265	50.9293

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.260	MF	0.8413	839.36859	16.62812	1.6789
2	22.786	MF	1.1693	4.91566e4	700.62561	98.3211

5. Synthetic transformation



A 10 mL dried flask equipped with magnetic stirring bar. Then, (*S*)-**3a** (25.6 mg, 0.1 mmol) and MeOH (1.0 mL) were added, respectively. Add KOH (1 mL, aq., 1 M) to solution slowly at room temperature. The mixture was allowed to react at this temperature and stir for 2 h. After completion, the aqueous phase was extracted with ethyl acetate. the combined organic layers were washed with brine, dried by Na_2SO_4 and concentrate in vacuo. The mixture was purified by column chromatography to give the desired product **4**.

(*S*)-2-((4-chlorophenyl)thio)but-3-en-1-ol (4): yield (17.1 mg, 80%); colorless oil; $[\alpha]^{15}_D = 20.4$ (*c* 0.32, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee

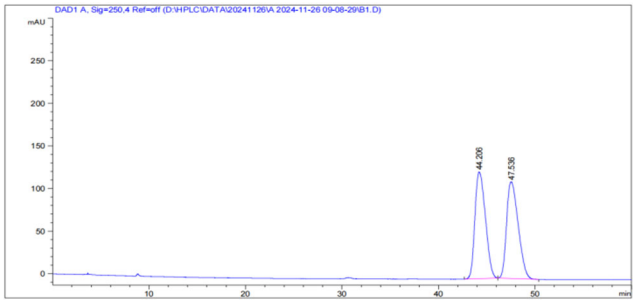
(Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 250 nm); t_r = 44.21 and 47.54 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 2H), 7.30 – 7.26 (m, 2H), 5.84 – 5.70 (m, 1H), 5.21 – 5.09 (m, 2H), 3.78 – 3.59 (m, 3H).

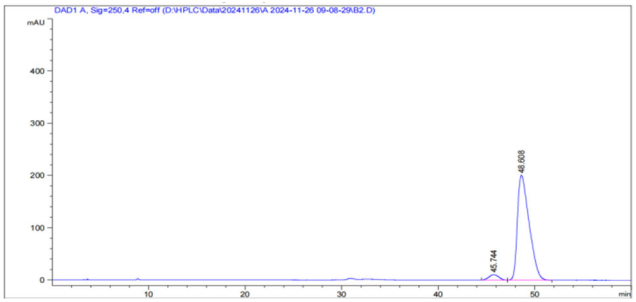
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9, 134.6, 134.0, 131.3, 129.1, 118.5, 63.6, 54.9.

HRMS (ESI+) Calcd. For $C_{10}H_{11}ClOSNa^+$ ([M+Na]$^+$): 237.0122, found: 237.0111.

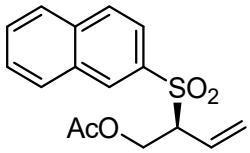
HPLC chromatogram of compound 4



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.206	BB	1.1115	9469.42773	125.32547	49.9682
2	47.536	BB	1.2143	9481.48145	113.53406	50.0318



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.744	BB	0.8259	715.29138	10.20342	4.0671
2	48.608	BB	1.2102	1.68718e4	200.80637	95.9329



To a solution of sulfide (*S*)-**3n** (0.1 mmol) in DCM (0.5 mL) was added *m*-CPBA (45.2 mg, 0.22 mmol, 70% wt). The resulting mixture was stirred at 0℃ for 20 min, then quenched with $NaHCO_3$ (2 mL), and extracted with DCM (2 mL × 3). The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. After flash chromatography on silica gel, the desired sulfone was analyzed by HPLC to determine the ee value.

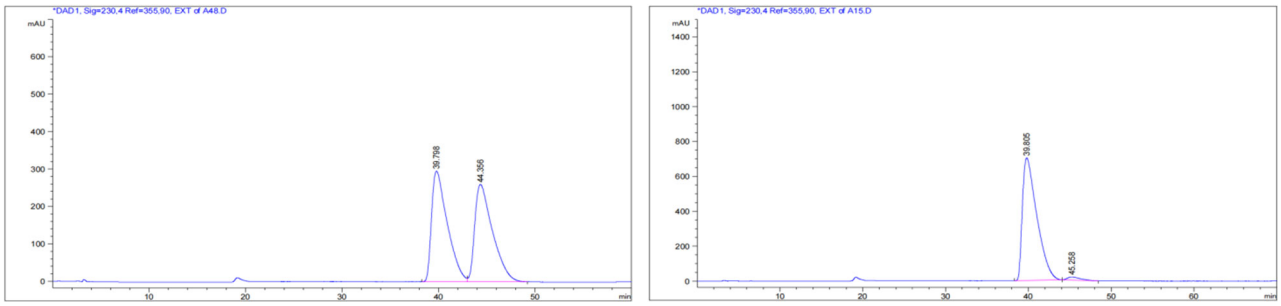
(*S*)-2-(naphthalen-2-ylsulfonyl)but-3-en-1-yl acetate (5): yield (15.2 mg, 50%); white solid, m.p. 60℃; $[\alpha]^{15}_D$ = -13.0 (*c* 0.26, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (Chiralpak OD-H, *i*-propanol/hexane = 6/94, flow rate 1 mL/min, λ = 230 nm); t_r = 30.46 and 51.36 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 – 8.42 (m, 1H), 8.04 – 7.90 (m, 3H), 7.83 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.74 – 7.55 (m, 2H), 5.79 (ddd, *J* = 17.1, 10.3, 9.0 Hz, 1H), 5.44 – 5.16 (m, 2H), 4.61 – 4.38 (m, 2H), 4.12 – 4.02 (m, 1H), 1.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 135.4, 134.7, 131.9, 131.1, 129.5, 129.2, 127.9, 127.7, 127.0, 124.9, 123.6, 68.0, 60.9, 20.5.

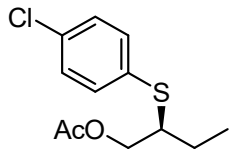
HRMS (ESI+) Calcd. For $C_{16}H_{16}O_4SNa^+$ ([M+Na]$^+$): 327.0662, found: 327.0667.

HPLC chromatogram of compound 5



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.798	BV	1.5119	3.36685e4	295.80704	50.2101
2	44.356	VB	1.5393	3.33867e4	260.48270	49.7899

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.805	BB	1.6435	8.50057e4	702.59009	97.7731
2	45.258	BB	1.2654	1936.13892	17.93511	2.2269



To a vial equipped with a magnetic stirring rod was added successively: Pd/C (0.1 mmol, 1 equiv.), (*S*)-**3a** (0.1 mmol, 1 equiv.), EtOH (1 mL). The vial was subsequently transferred into an autoclave and then hydrogen gas was charged. The reaction was then stirred under H_2 (50 atm) at 60 ℃ for 12 h. The hydrogen gas was released slowly and carefully. The solution was passed through a short column of silica gel to remove the metal complex. The conversion of products was determined by ^{1}H NMR analysis. The crude products were concentrated and purified by column chromatography, and the ee values were determined by HPLC on a chiral stationary phase.

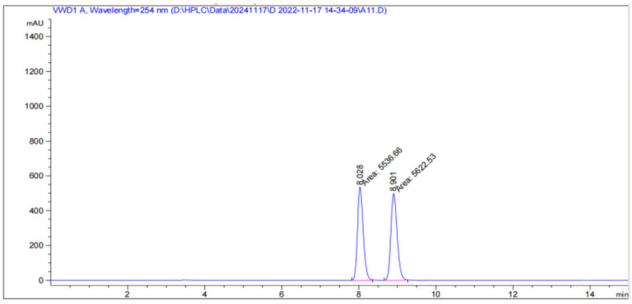
(*S*)-2-((4-chlorophenyl)thio)butyl acetate (6): yield (25.5 mg, 99%); colorless oil; $[\alpha]^{15}_D$ = 2.9 (*c* 1.42, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 8.03 and 8.90 min.

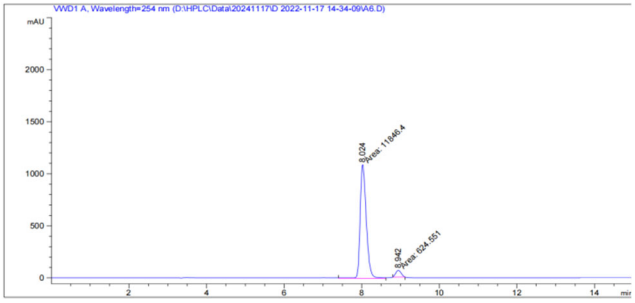
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 2H), 7.30 – 7.22 (m, 2H), 4.18 (dd, *J* = 11.4, 5.8 Hz, 1H), 4.09 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.24 – 3.13 (m, 1H), 2.01 (s, 3H), 1.85 – 1.70 (m, 1H), 1.58 – 1.47 (m, 1H), 1.08 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 133.5, 133.3, 132.8, 129.1, 66.2, 49.3, 24.4, 20.8, 11.3.

HRMS (ESI+) Calcd. For $C_{18}H_{17}ClO_3SNa^+$ ([M+Na]$^+$): 371.0479, found: 371.0488.

HPLC chromatogram of compound 6



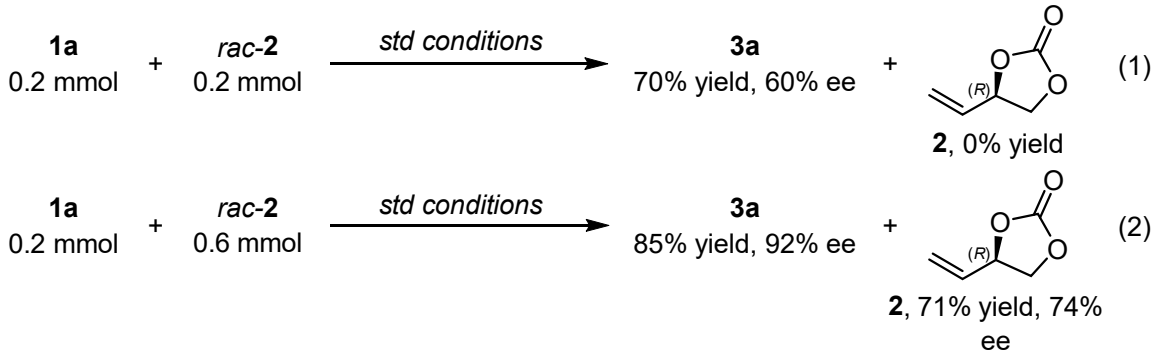


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.028	MM	0.1723	5536.65869	535.49731	49.6152
2	8.901	MM	0.1884	5622.53418	497.34482	50.3848

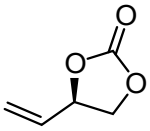
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.024	MM	0.1809	1.18464e4	1091.30139	94.9919
2	8.942	MM	0.1621	624.55127	64.20832	5.0081

6. Control experiments and mechanistic investigations

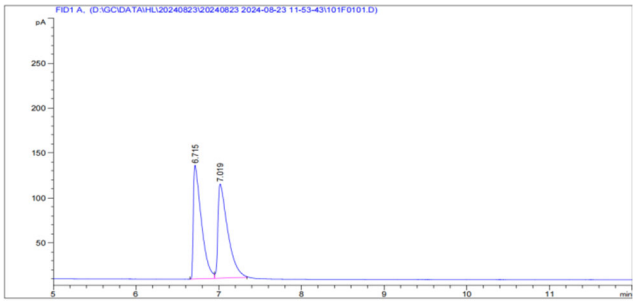
a) Investigation of kinetic resolution

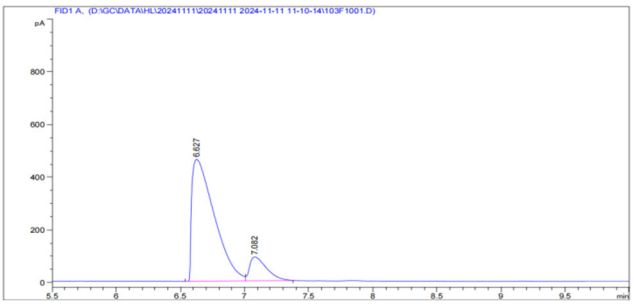


A flame dried Schlenk tube was cooled to rt, and it was then evacuated and backfilled with argon for three times. To this Schlenk tube was added (*S*,*S*,*S*)-**[Ir*]-1** (0.01 mmol, 5 mol %), aryl thioester **1a** (0.20 mmol, 1 equiv.), *rac*-**2** (0.2 mmol, 1 equiv.) and DCE (2 mL). The reaction was stirred at 50 °C for 12 hours. Once starting material was consumed (monitored by TLC), the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography to give the desired product, which was then directly analyzed by HPLC to determine the enantiomeric excess. And recovered **2** in eq. 2 was then directly analyzed by GC to determine the enantiomeric excess.



(*R*)-4-vinyl-1,3-dioxolan-2-one (2): yield (71%); colorless oil; The product was analyzed by GC to determine the enantiomeric excess: 74% ee (Beta DEX-390, N_2 flow rate 1.0 mL/min, 20 min at 150 °C); t_r = 6.72 and 7.02 min.

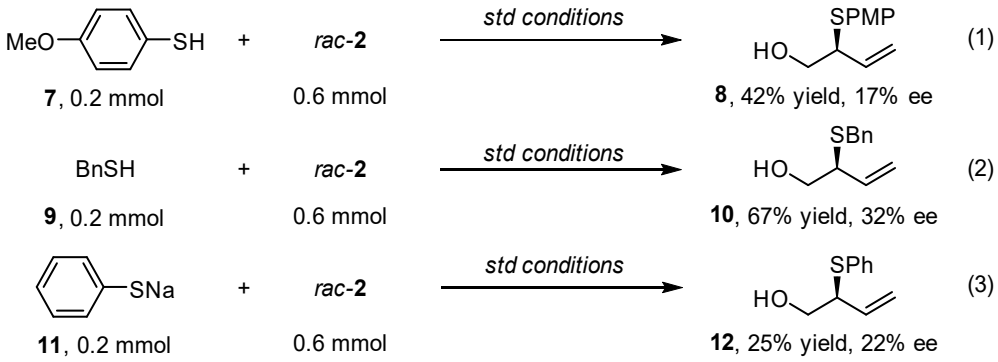




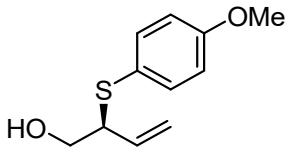
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	6.715	BV	0.0914	851.26074	126.64633	49.67344
2	7.019	VB	0.1100	862.45337	104.76733	50.32656

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	6.627	BV	0.1671	5637.26318	462.86511	87.05190
2	7.082	VB	0.1299	838.48639	90.69037	12.94810

b) Control experiments of thioalcohol as the nucleophile



A flame dried Schlenk tube was cooled to rt, and it was then evacuated and backfilled with argon for three times. To this Schlenk tube was added (*S*,*S*,*S*)-**[Ir*]-1** (0.02 mmol, 10 mol %), *p*-methoxythiophenol **7** , benzylmercaptan **9** or sodium thiophenolate **11** (0.20 mmol, 1.0 equiv.), VEC **2** (1.2 mmol, 3 equiv.), DABCO (0.2 mmol, 1 equiv.) and DCE (2 mL). The reaction was stirred at 50 °C for 12 hours. Once starting material was consumed (monitored by TLC), the solvent was evaporated under reduced pressure and the residue was purified by column chromatography to give **8**, **10** or **12**.



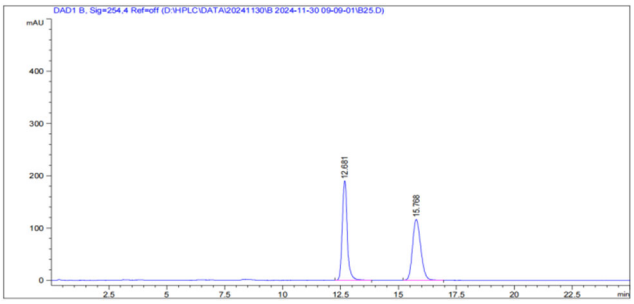
(*S*)-2-((4-methoxyphenyl)thio)but-3-en-1-ol (8): yield (17.6 mg, 42%); colorless oil; $[\alpha]^{15}_{D}$ = +2.1 (*c* 1.80, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 17% ee (Chiralpak AS-H, *i*-propanol/hexane = 10/90, flow rate 1 mL/min, λ = 254 nm); t_r = 12.68 and 15.77 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 6.88 – 6.80 (m, 2H), 5.75 (ddd, *J* = 17.1, 10.4, 7.9 Hz, 1H), 5.17 – 5.03 (m, 2H), 3.80 (s, 3H), 3.70 – 3.54 (m, 3H).

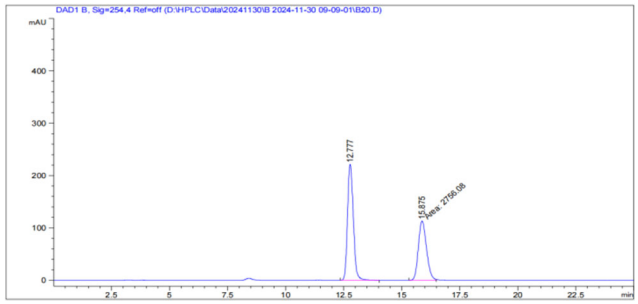
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 136.5, 135.3, 122.4, 117.9, 114.5, 63.2, 55.4, 55.3.

HRMS (ESI+) Calcd. For $C_{11}H_{14}O_2SNa^+$ ($[M+Na]^+$): 233.0607, found: 233.0610.

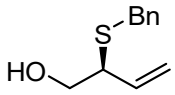
HPLC chromatogram of compound 8



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.681	BB	0.2322	2839.15430	190.19125	49.9367
2	15.768	BB	0.3839	2846.35571	116.13731	50.0633



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.777	BB	0.2732	3848.20166	220.89803	58.2683
2	15.875	MF	0.4067	2756.08228	112.94962	41.7317



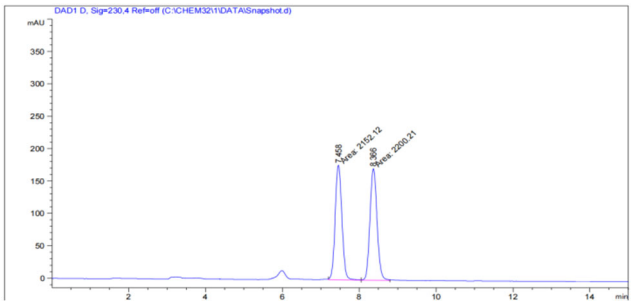
(*S*)-2-(benzylthio)but-3-en-1-ol (10): yield (26.0 mg, 67%); colorless oil; $[\alpha]^{15}_{D}$ = +35.9 (*c* 1.00, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 32% ee (Chiralpak AS-H, *i*-propanol/hexane = 10/90, flow rate 1 mL/min, λ = 230 nm); t_r = 7.46 and 8.37 min.

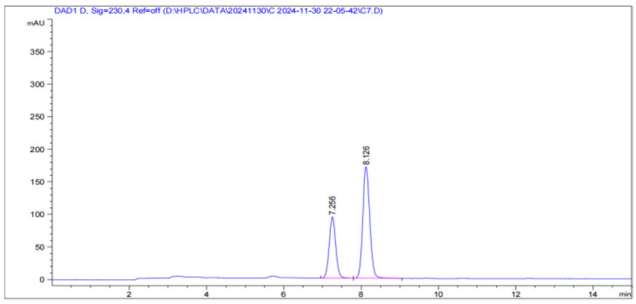
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 4H), 7.25 – 7.21 (m, 1H), 5.75 (ddd, *J* = 17.0, 10.2, 8.5 Hz, 1H), 5.27 – 5.14 (m, 2H), 3.71 (q, *J* = 13.4 Hz, 2H), 3.67 – 3.59 (m, 2H), 3.38 – 3.26 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 135.7, 128.9, 128.6, 127.1, 117.9, 63.7, 50.7, 34.5.

HRMS (ESI+) Calcd. For $C_{11}H_{14}OSNa^+$ ([M+Na]$^+$): 217.0658, found: 217.0605.

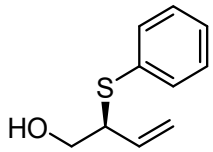
HPLC chromatogram of compound 10





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.458	FM	0.2027	2152.12085	176.96689	49.4476
2	8.366	MF	0.2133	2200.20654	171.93277	50.5524

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.256	BB	0.1841	1111.64160	93.94337	34.0488
2	8.126	BB	0.1949	2153.20874	170.97652	65.9512



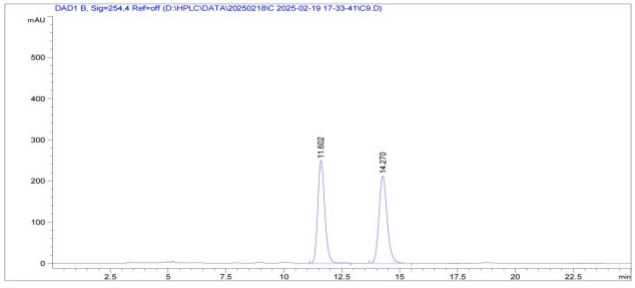
(*S*)-2-(phenylthio)but-3-en-1-ol (12): yield (9 mg, 25%); colorless oil; $[\alpha]^{15}_D$ = -4.5 (*c* 0.5, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 22% ee (Chiralpak OD-H, *i*-propanol/hexane = 6/94, flow rate 1 mL/min, λ = 254 nm); t_r = 11.60 and 14.27 min.

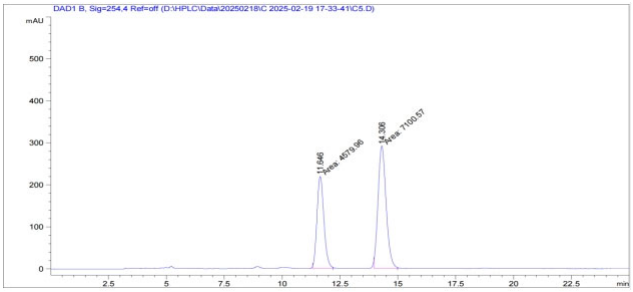
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 2H), 7.36 – 7.27 (m, 3H), 5.80 (ddd, *J* = 17.7, 10.0, 7.8 Hz, 1H), 5.22 – 5.13 (m, 2H), 3.81 – 3.63 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 133.2, 132.8, 128.9, 127.7, 118.2, 63.6, 54.6.

HRMS (ESI+) Calcd. For $C_{10}H_{12}OSNa^+$ ([M+Na]$^+$): 203.0501, found: 203.0501.

HPLC chromatogram of compound 12

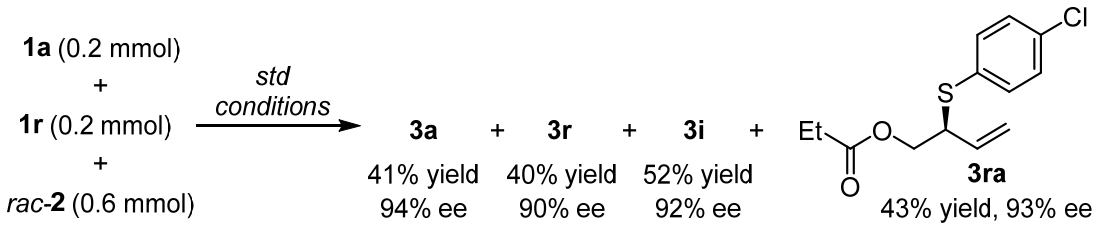




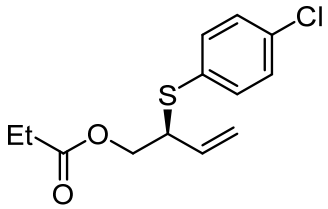
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.602	BB	0.3236	5203.80615	249.23286	50.1081
2	14.270	BB	0.3768	5181.34863	212.27002	49.8919

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.646	MF	0.3479	4579.96045	219.42577	39.2102
2	14.306	MF	0.4051	7100.56592	292.10580	60.7898

c) Cross-over experiments



A flame dried Schlenk tube was cooled to rt, and it was then evacuated and backfilled with argon for three times. To this Schlenk tube was added (*S*,*S*,*S*)-**[Ir*]-1** (0.02 mmol, 10 mol %), thioester **1a** (0.20 mmol, 1.0 equiv.), **1r** (0.20 mmol, 1.0 equiv.), VEC **2** (1.2 mmol, 6 equiv.), DABCO (0.2 mmol, 2 equiv.) and DCE (4 mL). The reaction was stirred at 50 ºC for 12 hours. Once starting material was consumed (monitored by TLC), the solvent was evaporated under reduced pressure and the residue was purified by column chromatography to give the products **3a**, **3q**, **3i** and **3ra**, which were then directly analyzed by HPLC to determine the enantiomeric excess.



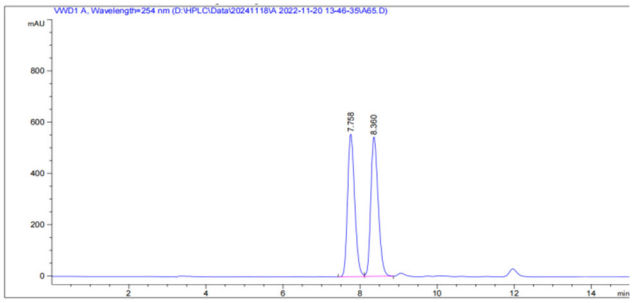
(*S*)-2-((4-chlorophenyl)thio)but-3-en-1-yl propionate (3ra): yield (23.0 mg, 43%); colorless oil; $[\alpha]^{15}_{D}$ = +8.04 (*c* 2.00, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak OJ-H, *i*-propanol/hexane = 2/98, flow rate 1 mL/min, λ = 254 nm); t_r = 7.76 and 8.36 min.

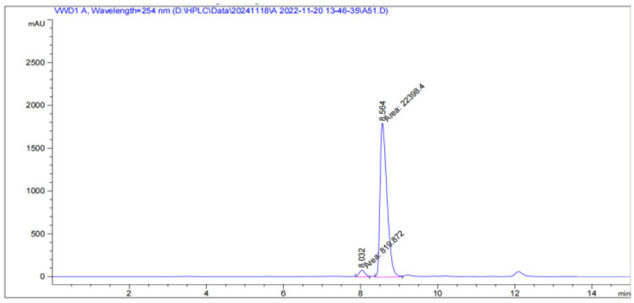
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 2H), 7.30 – 7.22 (m, 2H), 5.73 (ddd, *J* = 17.0, 10.3, 8.3 Hz, 1H), 5.16 – 5.03 (m, 2H), 4.29 – 4.16 (m, 2H), 3.92 – 3.77 (m, 1H), 2.31 (q, *J* = 7.6 Hz, 2H), 1.12 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 134.5, 134.4, 133.9, 131.6, 129.0, 118.2, 65.0, 50.4, 27.4, 9.0.

HRMS (ESI+) Calcd. For $C_{13}H_{15}ClO_2SNa^+$ ($[M+Na]^+$): 293.0373, found: 293.0375.

HPLC chromatogram of compound 3ra





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.758	BV	0.1998	7135.50342	555.88275	49.6349
2	8.360	VB	0.2063	7240.47412	543.97180	50.3651

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.032	MM	0.1775	819.87244	76.99979	3.5312
2	8.564	MM	0.2077	2.23984e4	1797.26355	96.4688

7. X-ray structure of *ent*-5

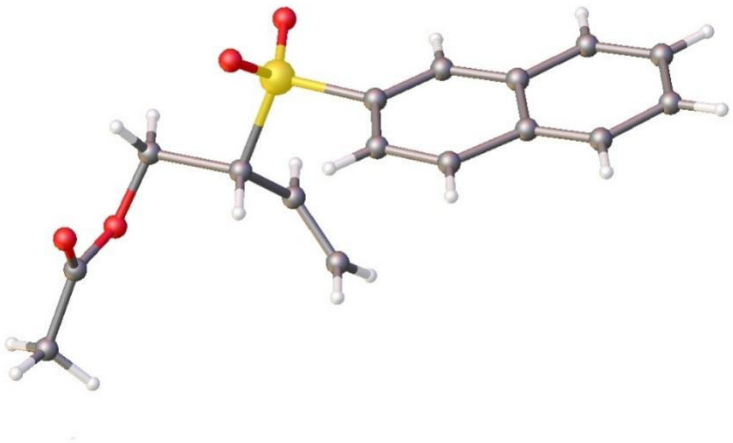


Figure S1. X-ray structure of *ent*-**5** (using (*R*,*R*,*R*)-**[Ir*]-1** as the catalyst)

Crystal data for *ent*-**5** (using (*R*,*R*,*R*)-**[Ir*]-1** as the catalyst): 16 ($C_{16}H_{16}O_4S$), M_r = 4855.44, T = 100 K, Monoclinic, space group *P1211*, a = 5.7878(1), b = 33.2044(6), c = 30.9443(5) Å, α = 90, β = 89.996(2), γ = 90, V = 5946.89(18) Å^3, Z = 1, 7005 unique reflections, final R_1 = 0.0733(21057) and wR_2 = 0.1909(21664) observed [I>2σ(I)] reflections, Flack = -0.009(7). CCDC 2411685 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

8. References

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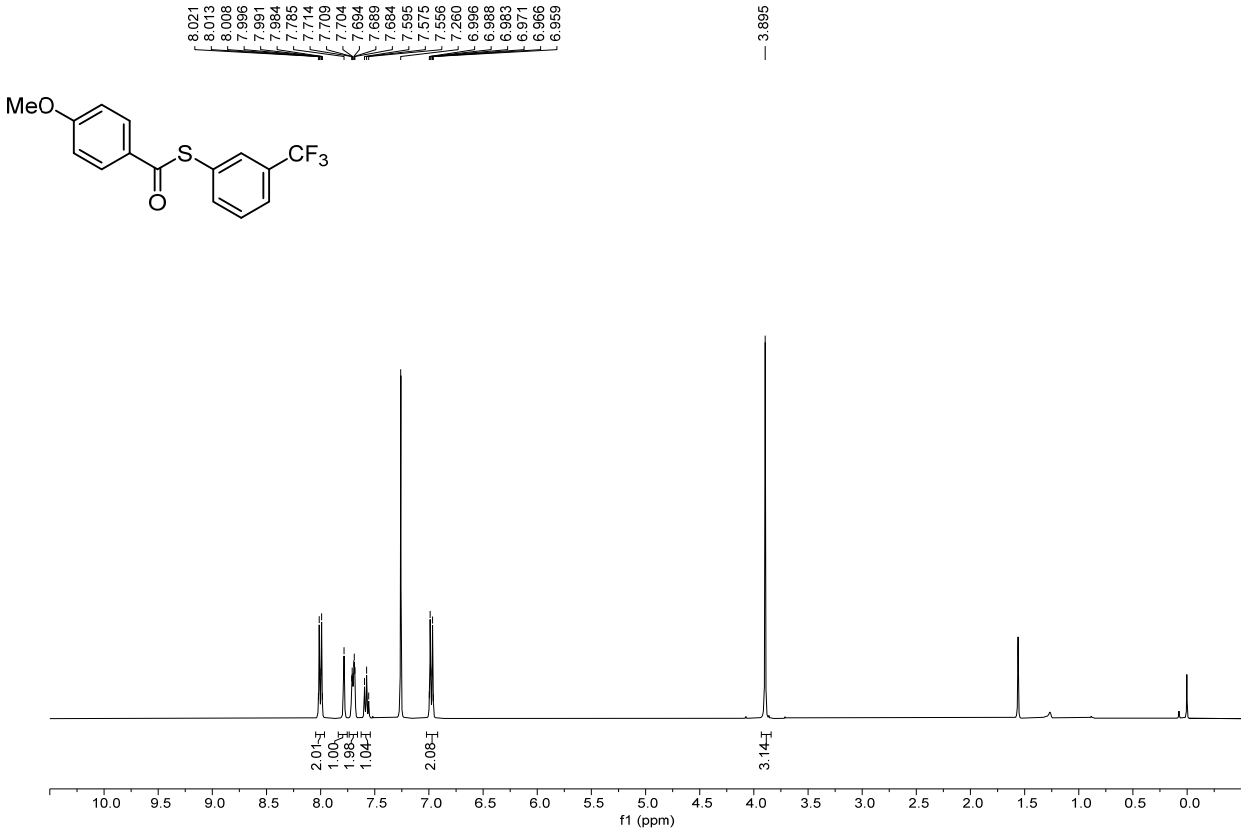
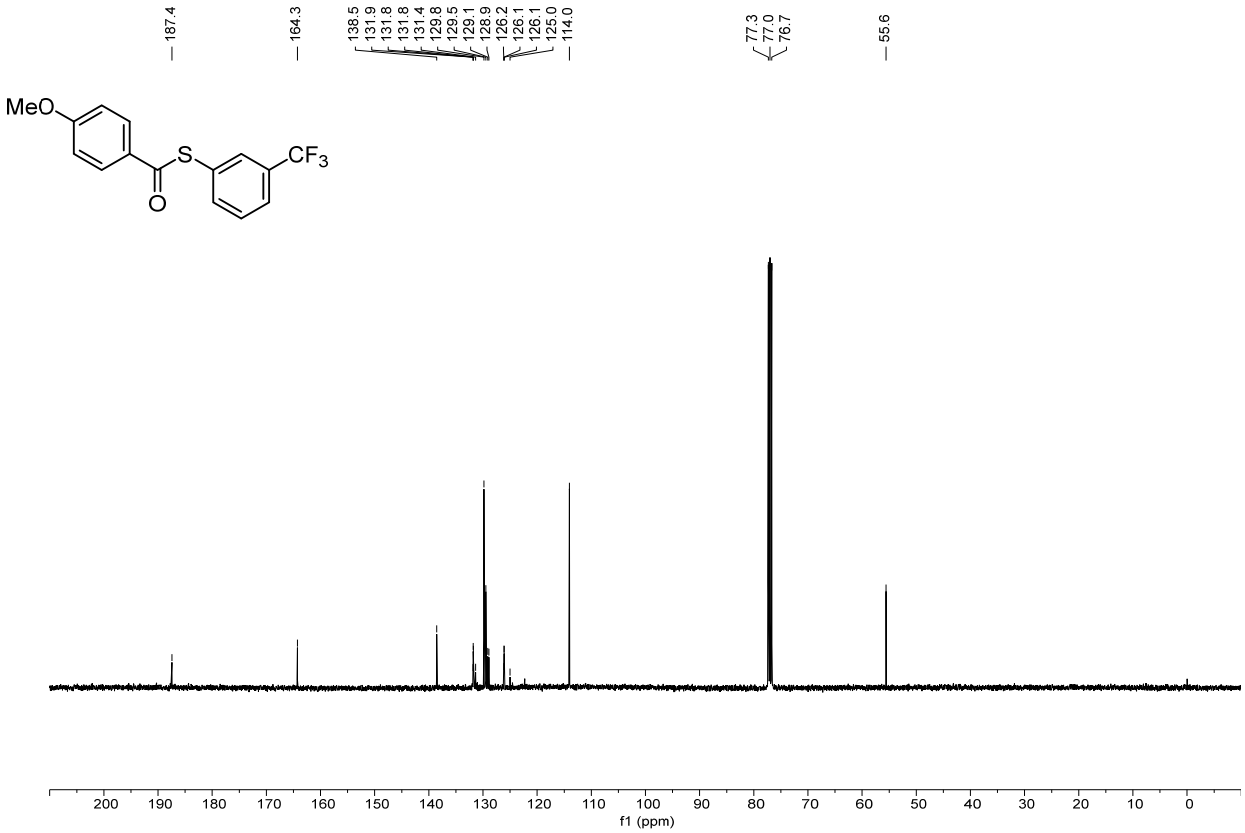
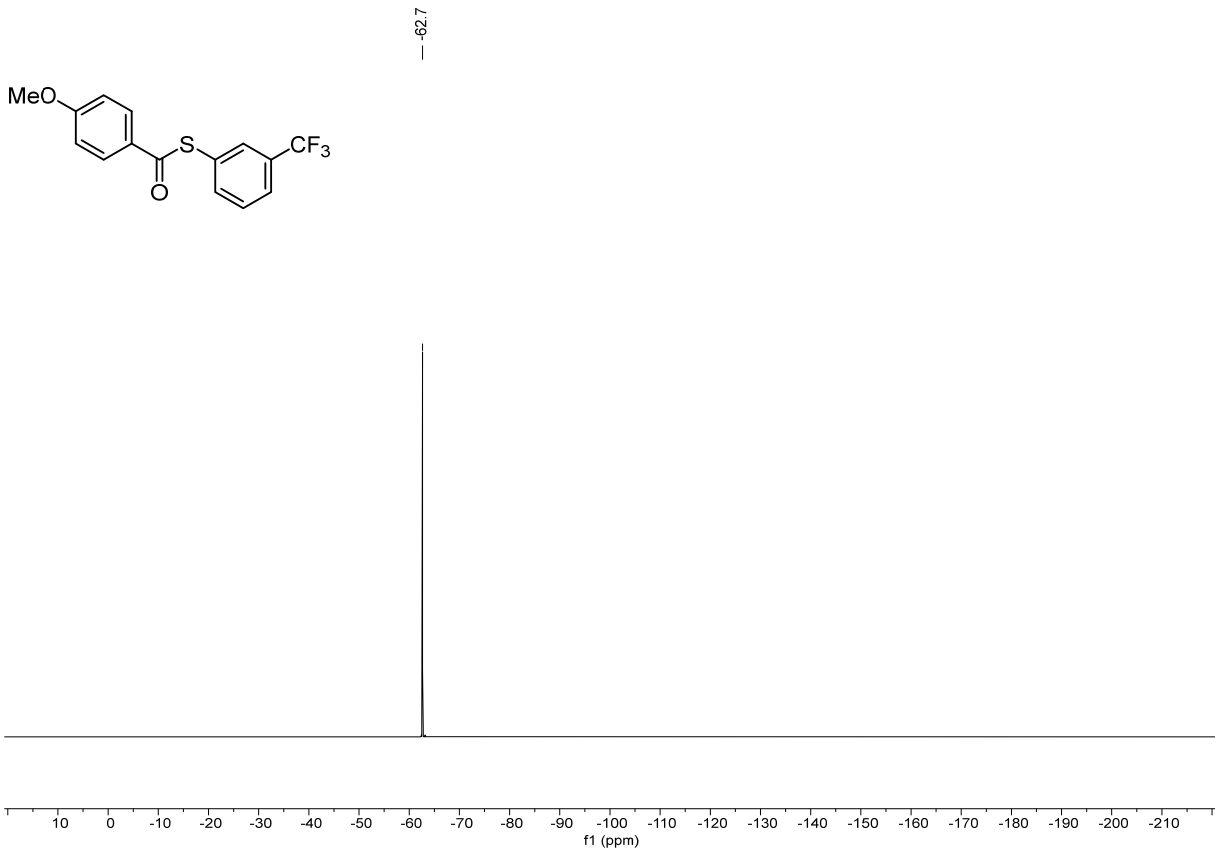
9. NMR spectra



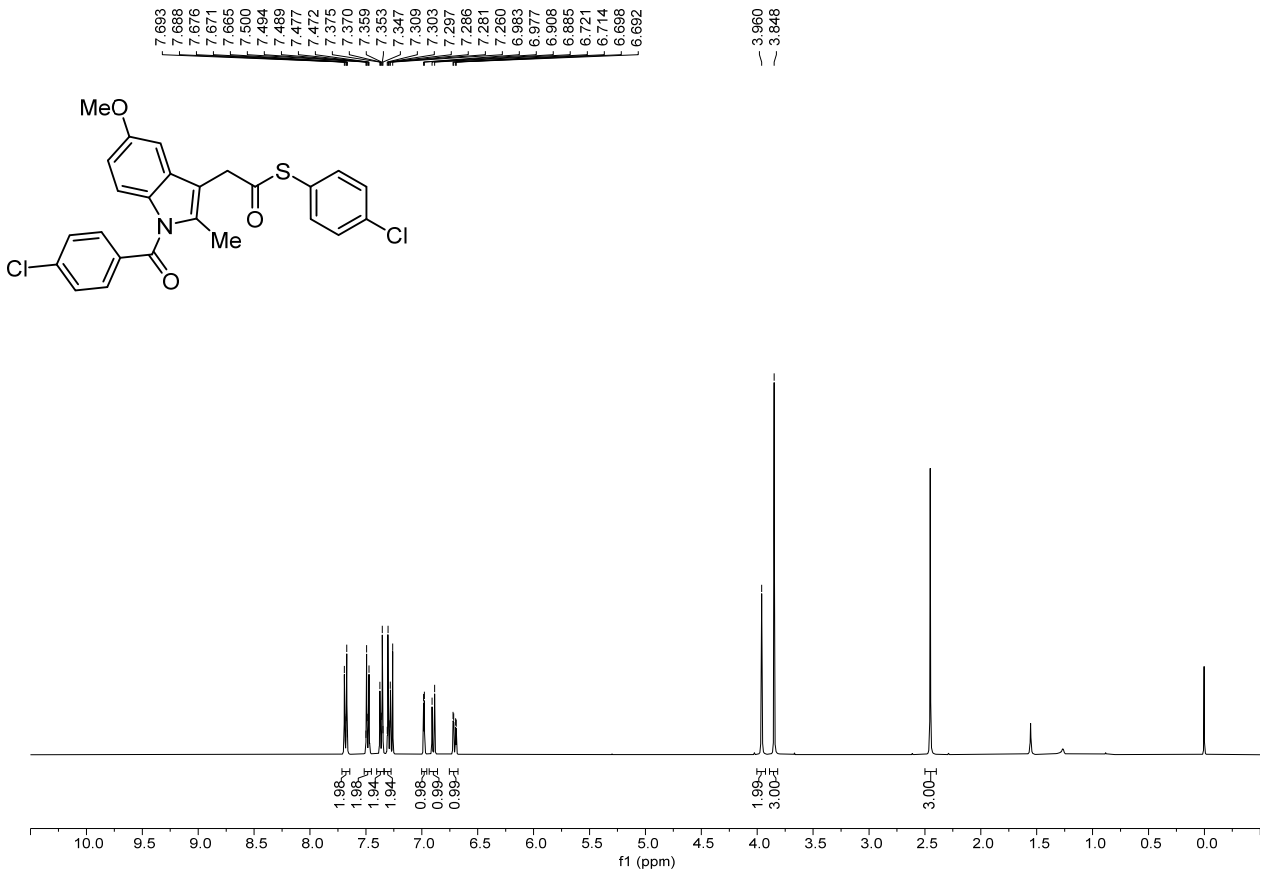
^{1}H NMR (400 MHz, $CDCl_3$) of **1w**



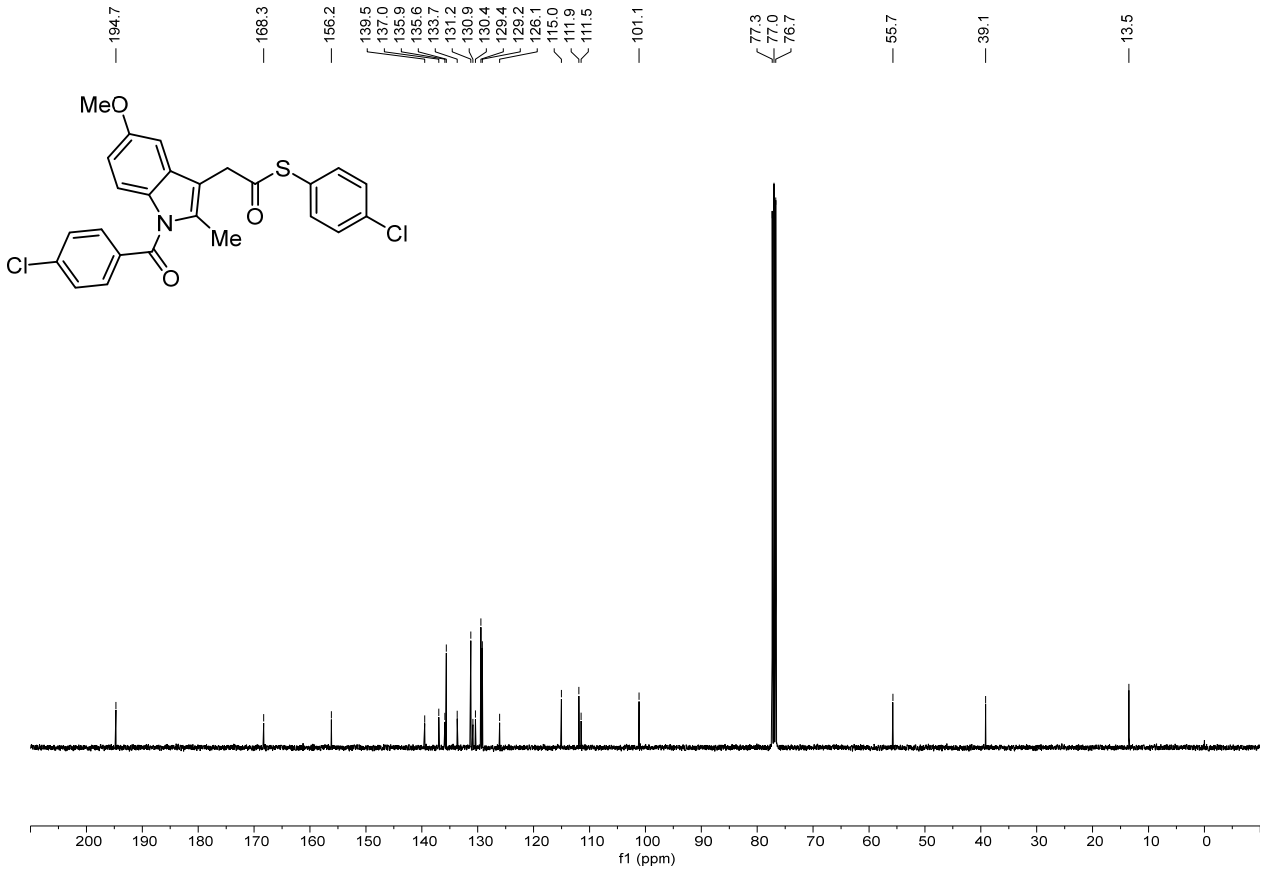
^{13}C NMR (101 MHz, $CDCl_3$) of **1w**



^{19}F NMR (377 MHz, $CDCl_3$) of **1w**



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



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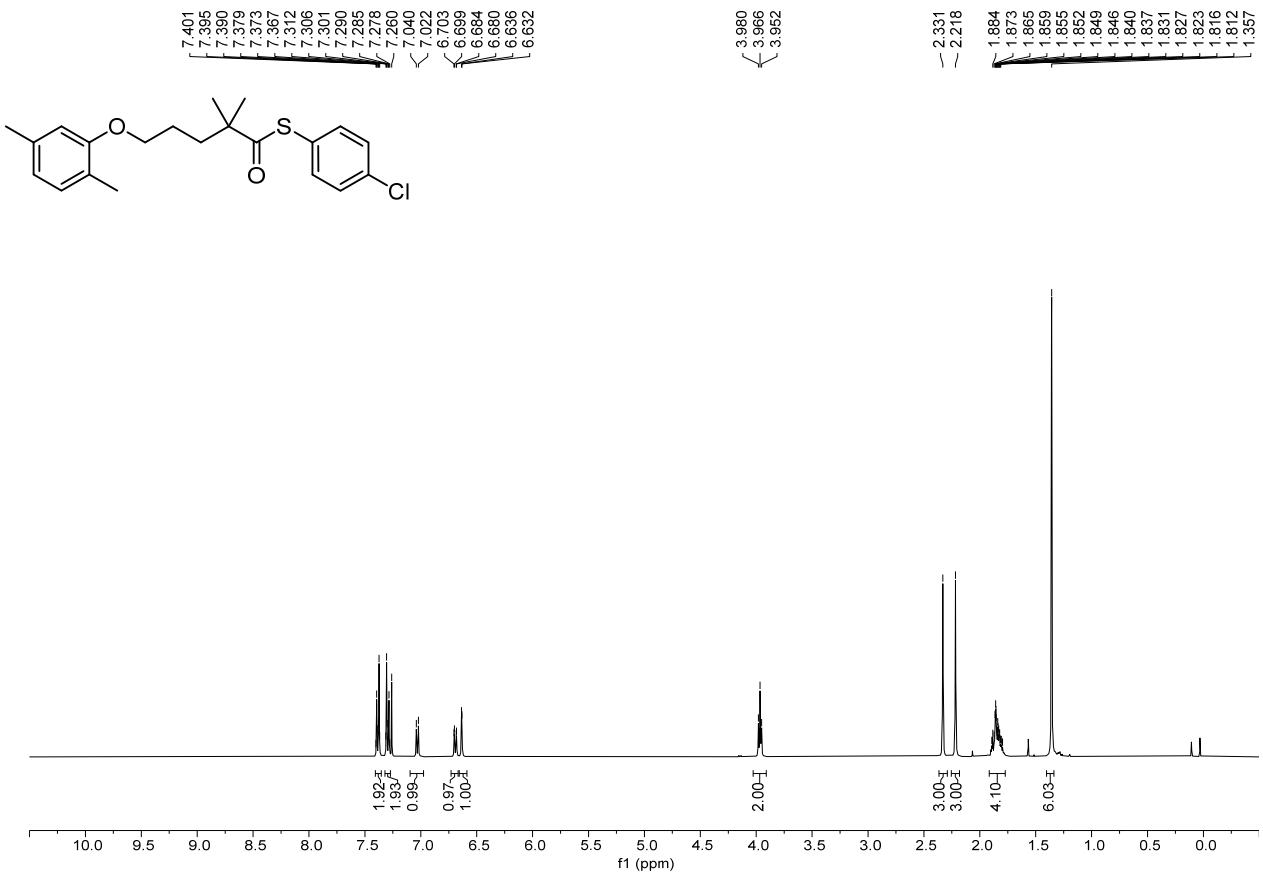
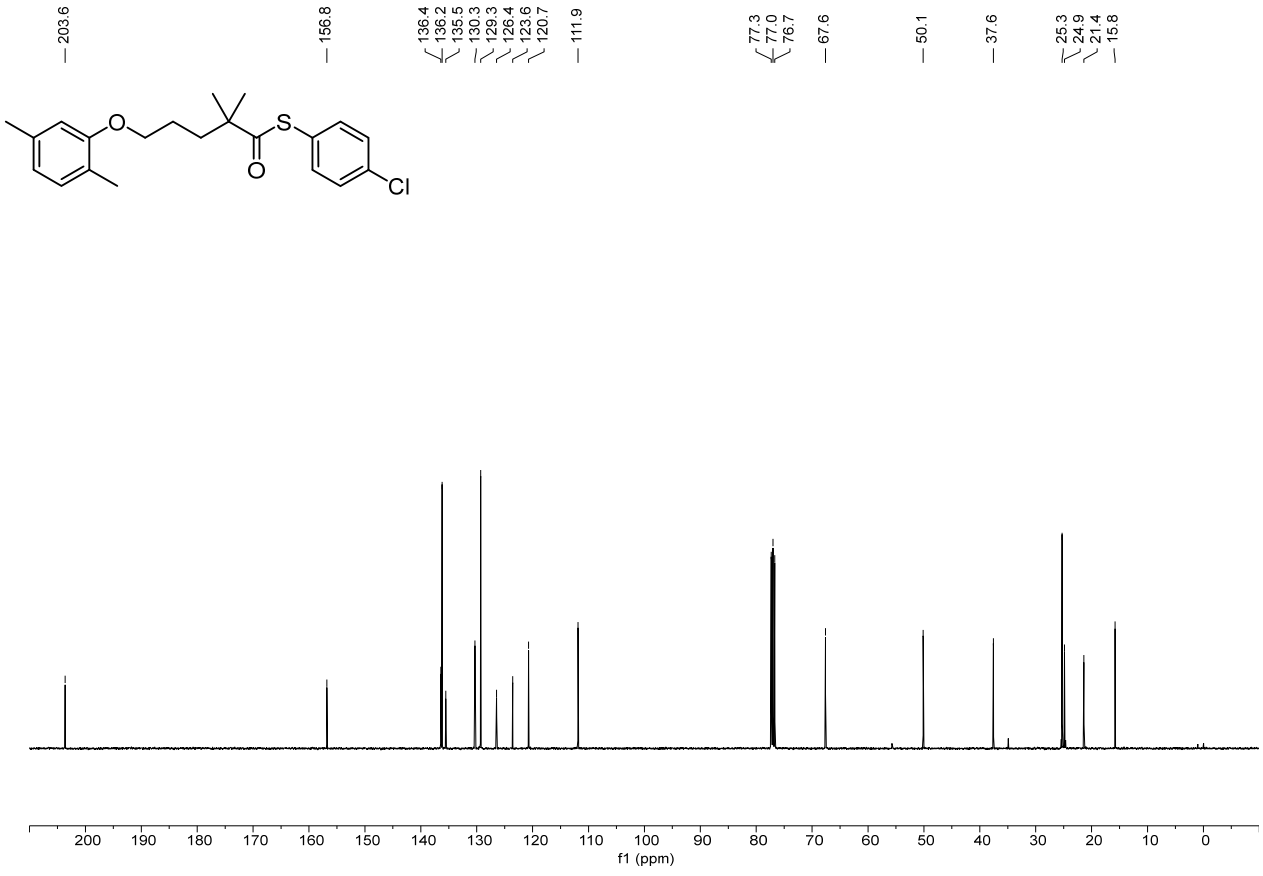
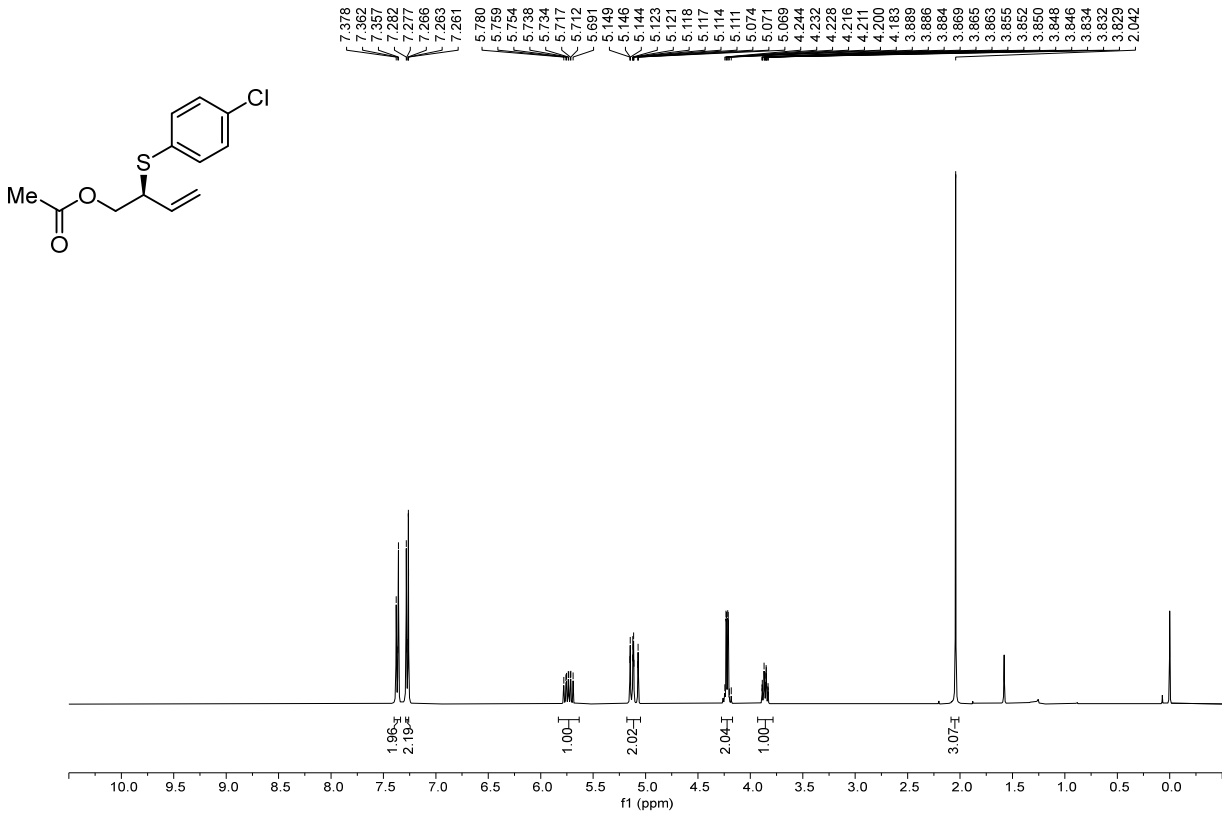


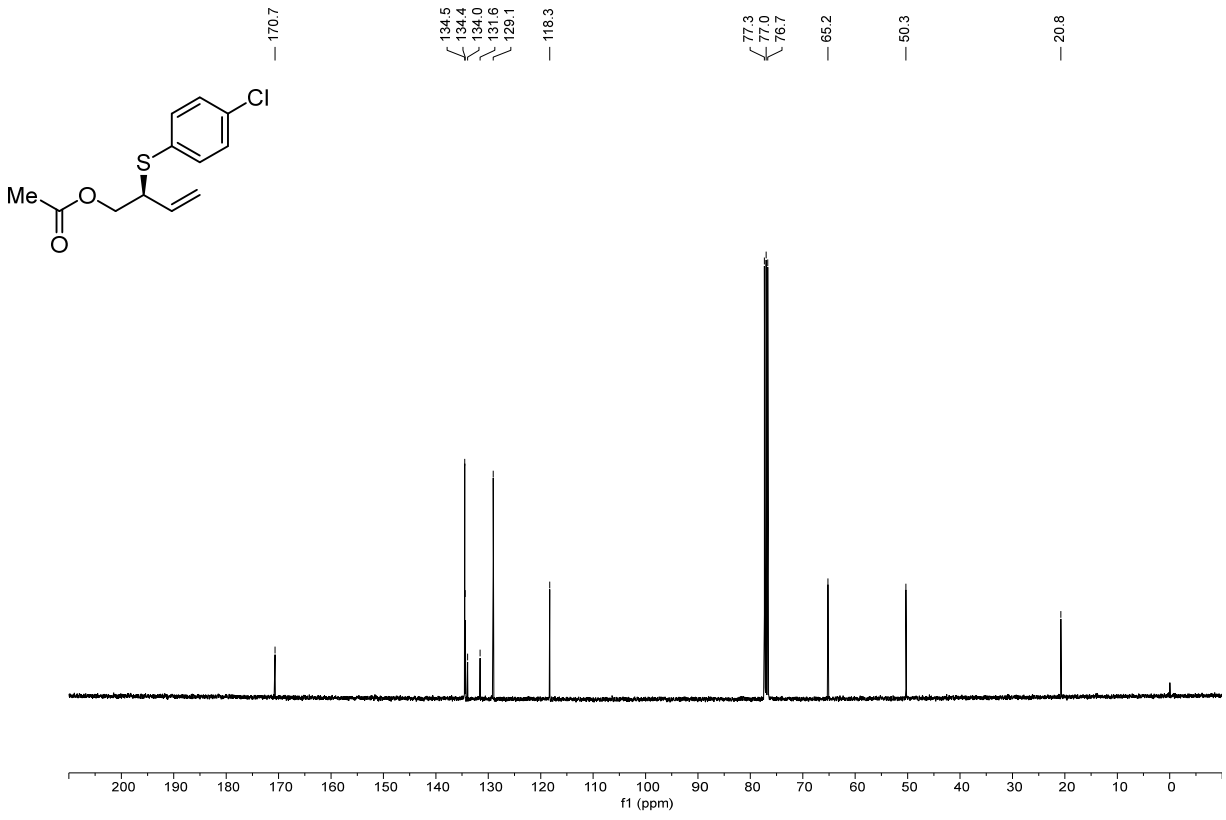
^{1}H NMR (400 MHz, $CDCl_3$) of **1B**



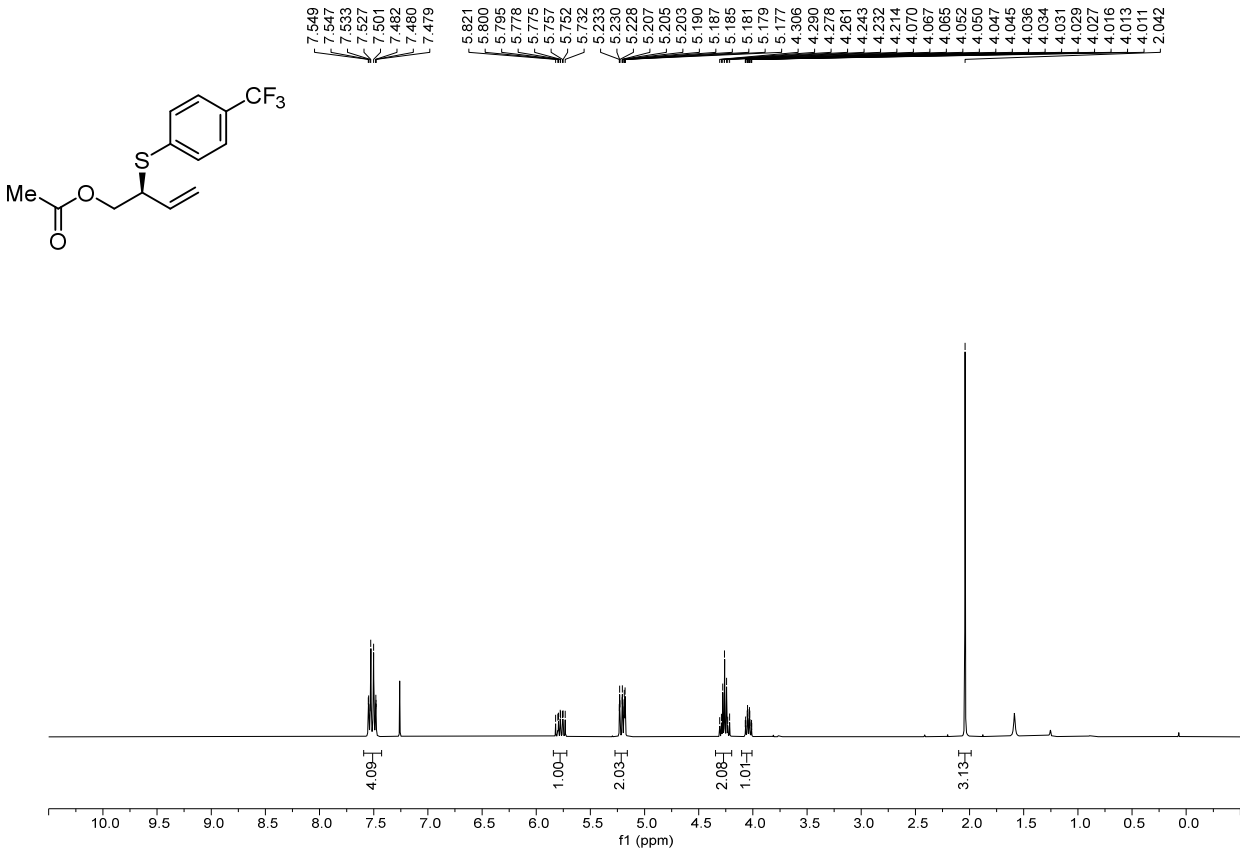
^{13}C NMR (101 MHz, $CDCl_3$) of **1B**



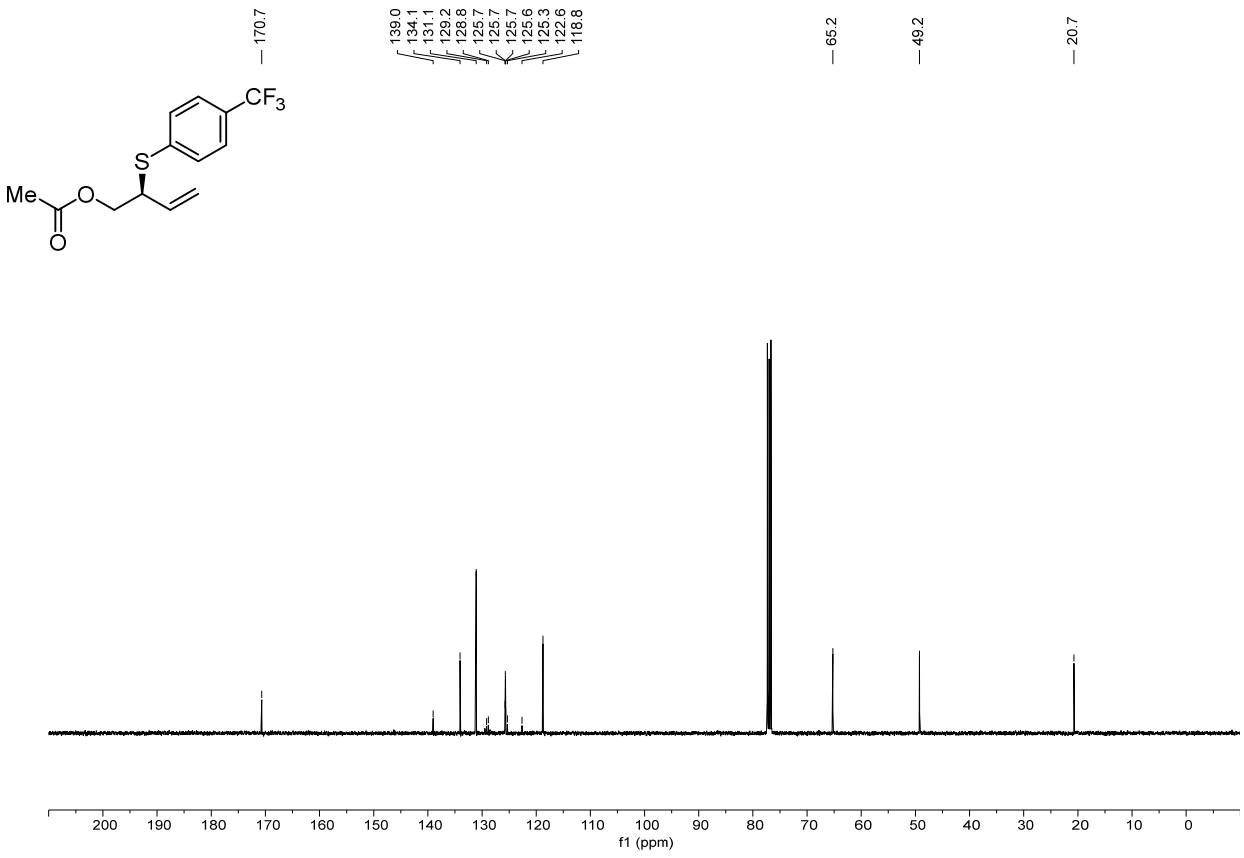
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



^{13}C NMR (101 MHz, $CDCl_3$) of **3a**



^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



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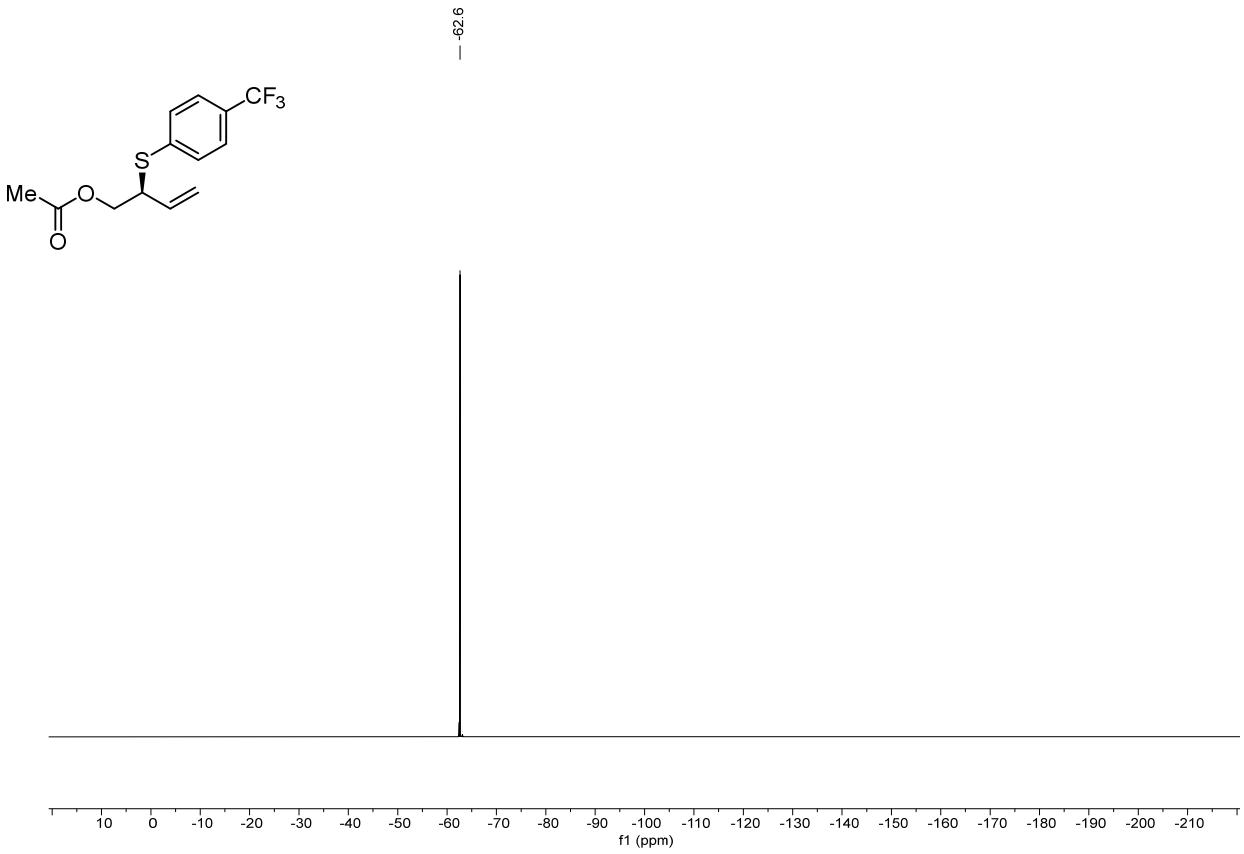
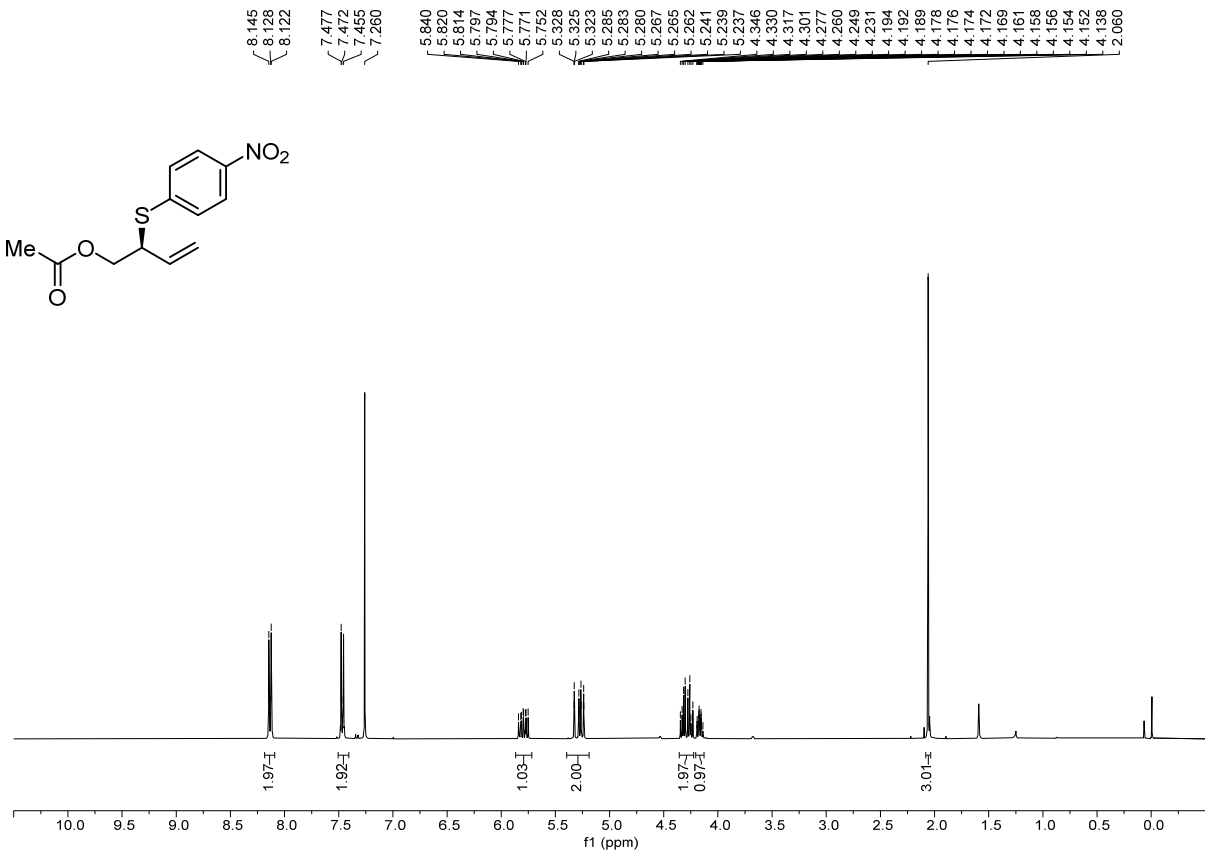


^{19}F NMR (377 MHz, $CDCl_3$) of **3b**



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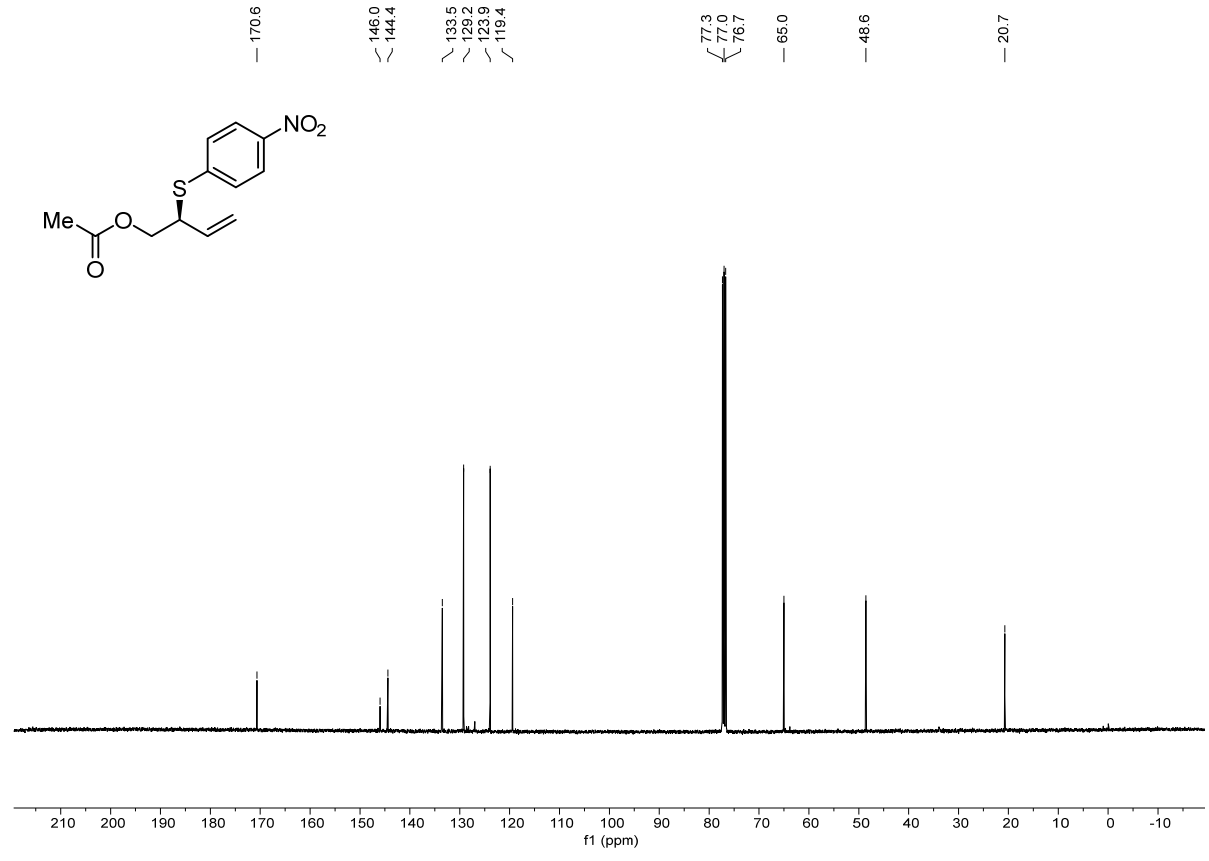

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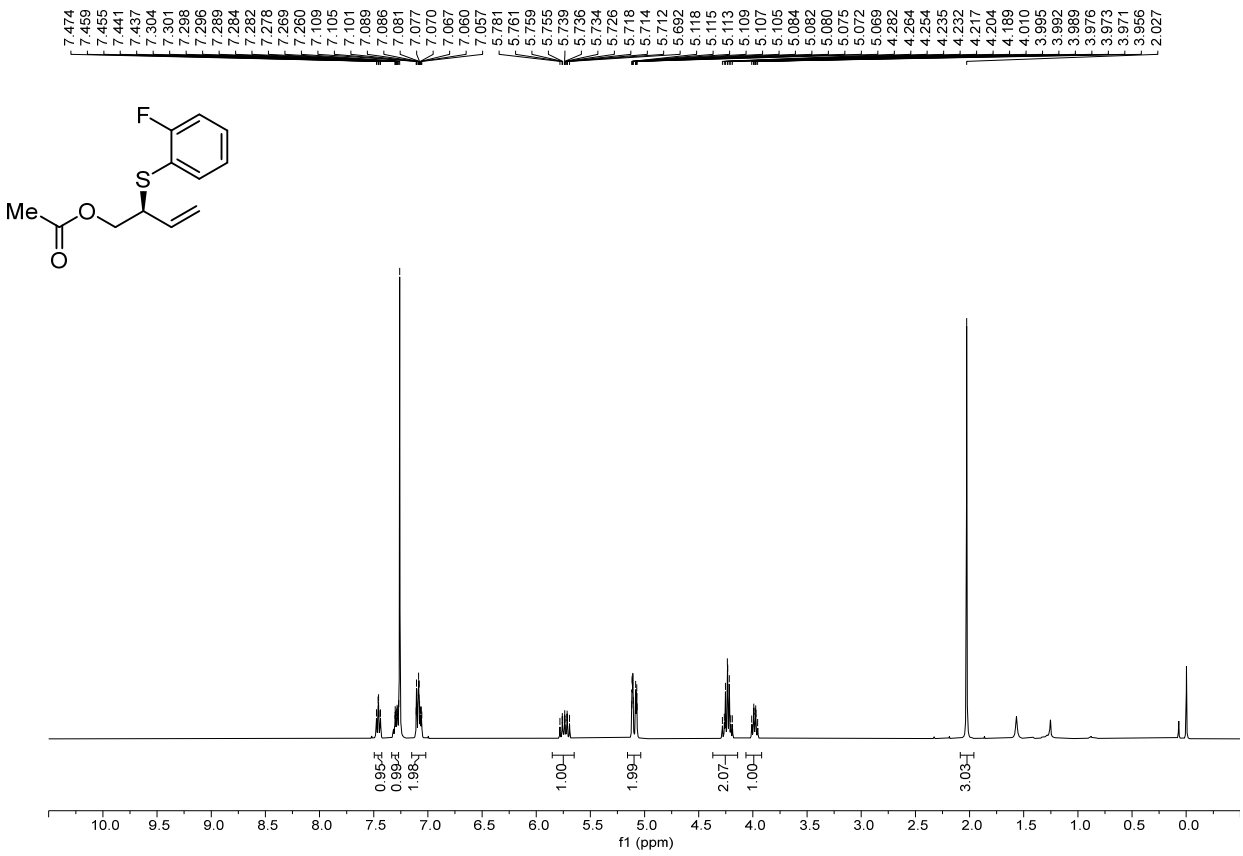
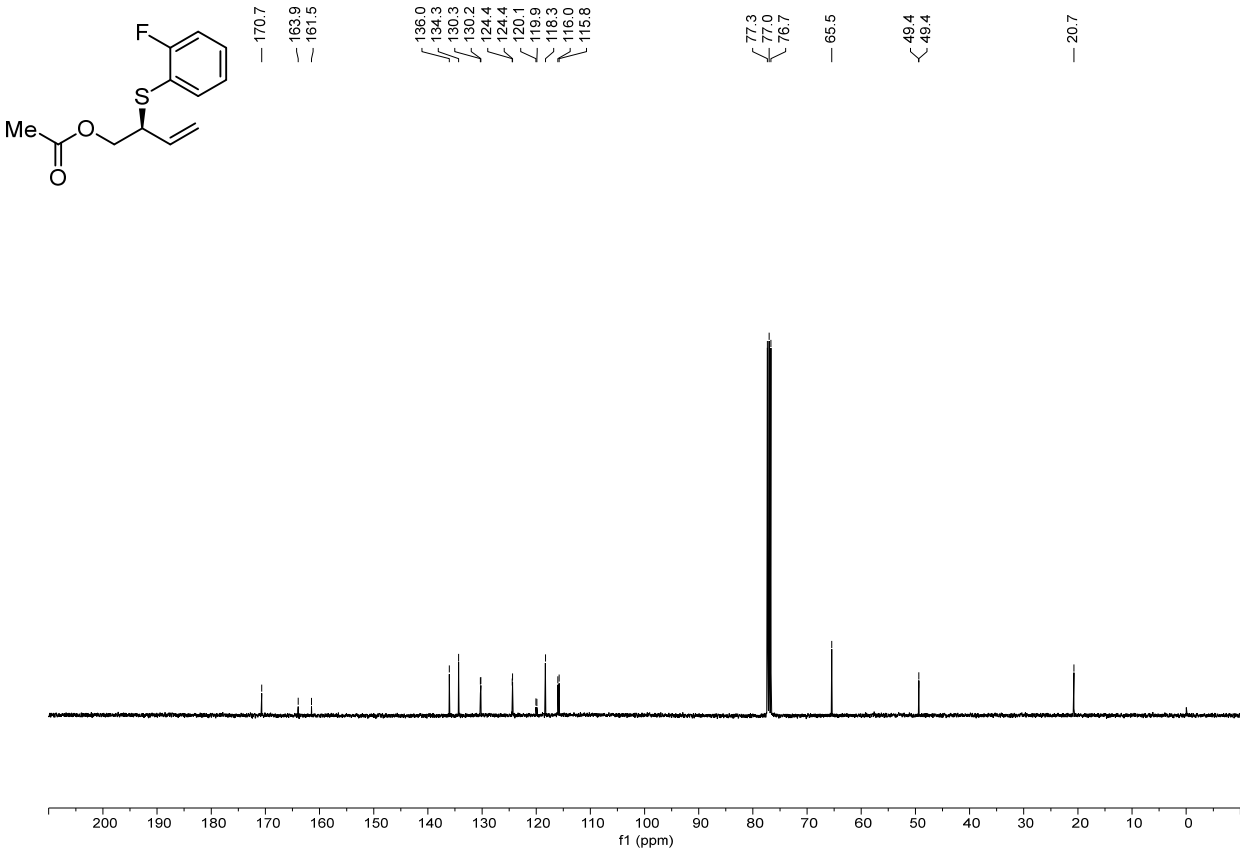
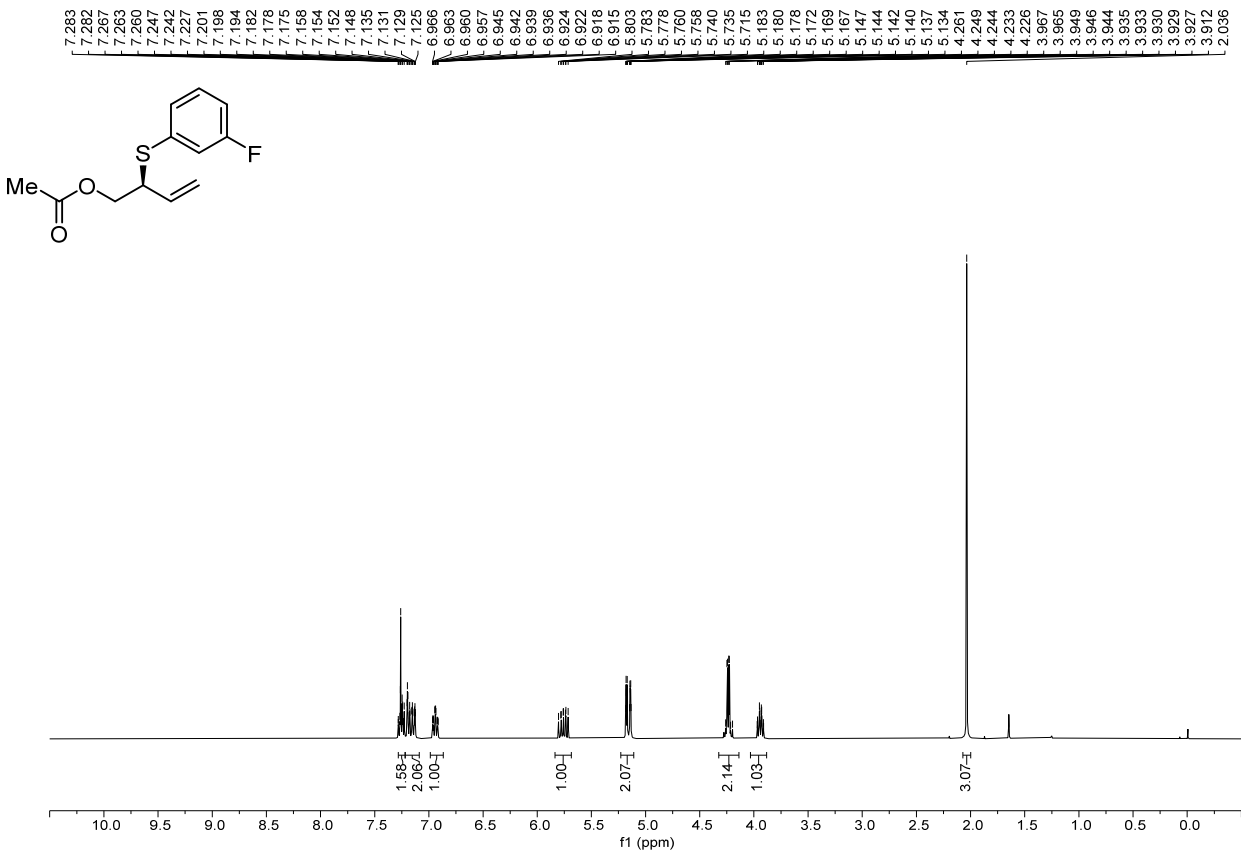


^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



^{13}C NMR (101 MHz, $CDCl_3$) of **3d**

^{19}F NMR (377 MHz, $CDCl_3$) of **3d**



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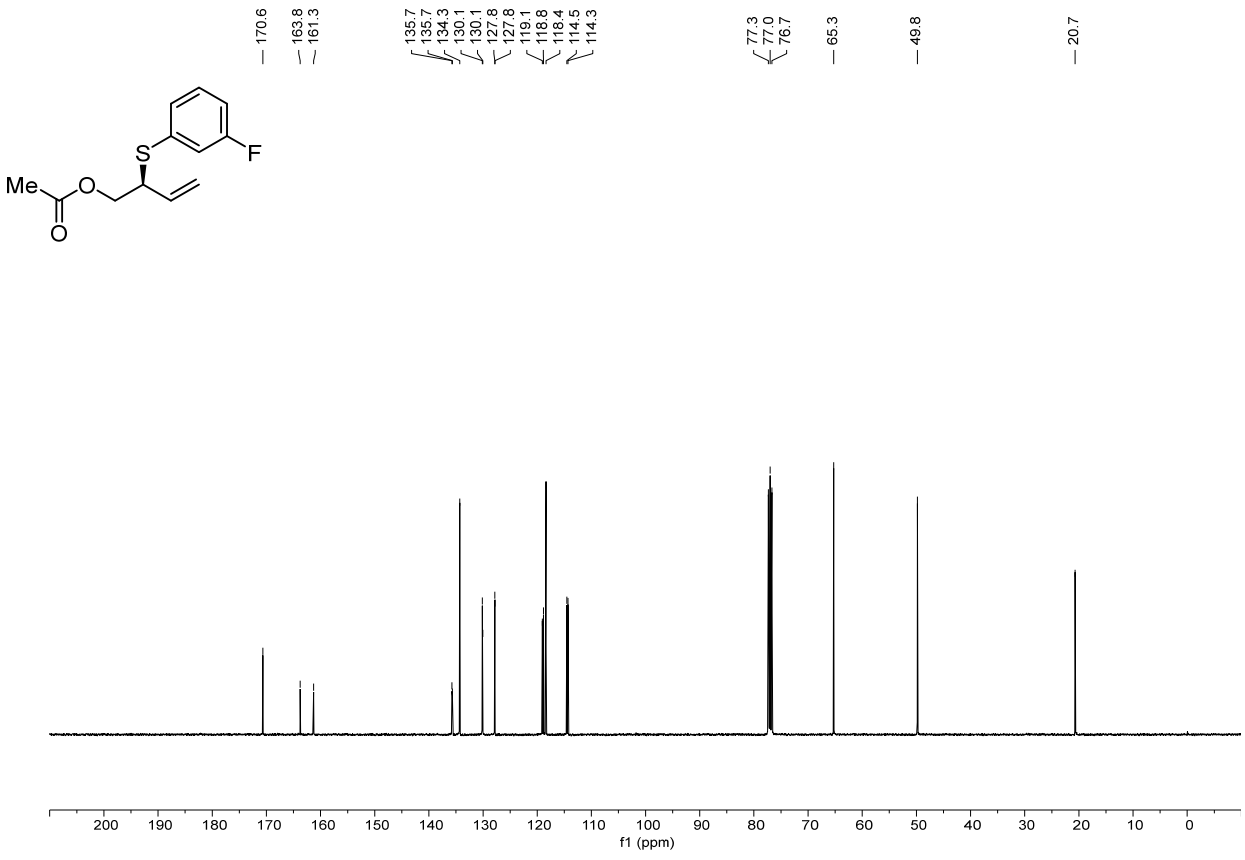

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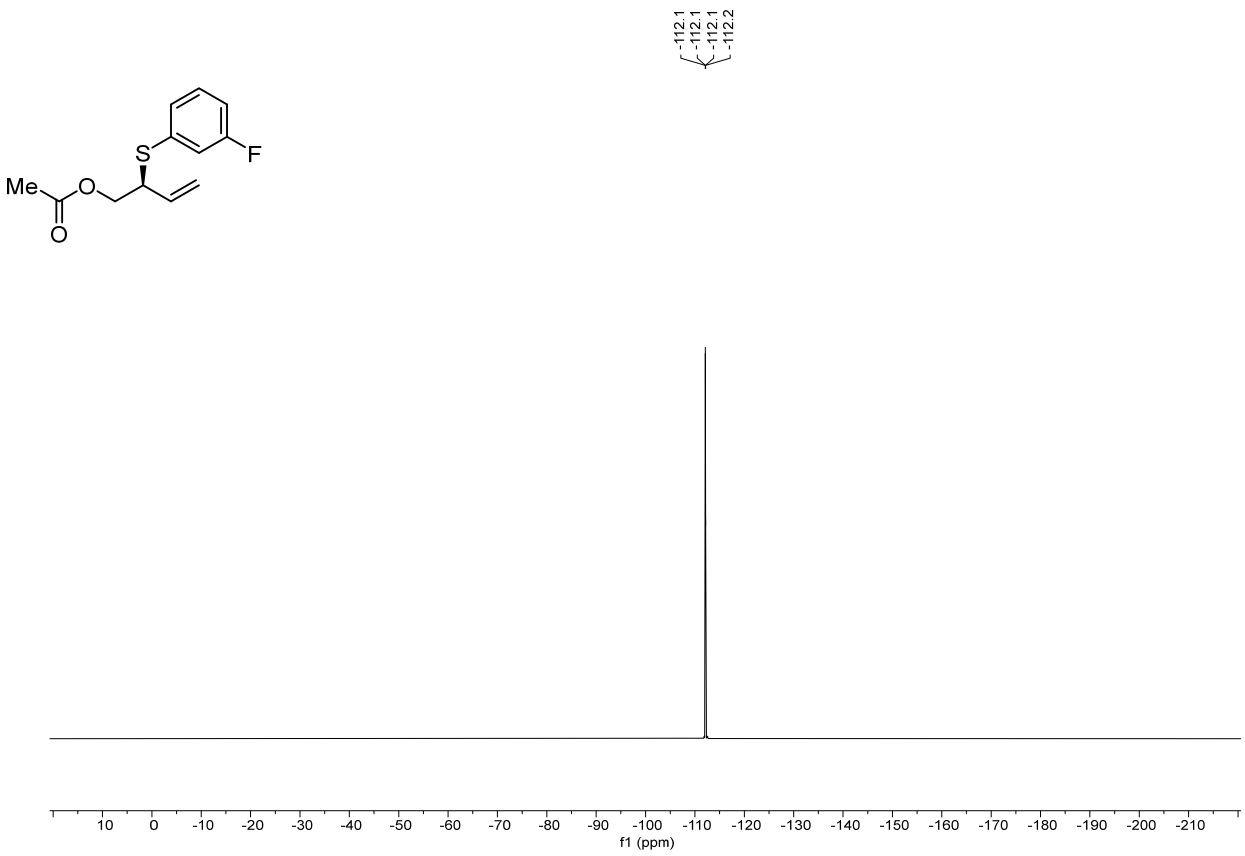

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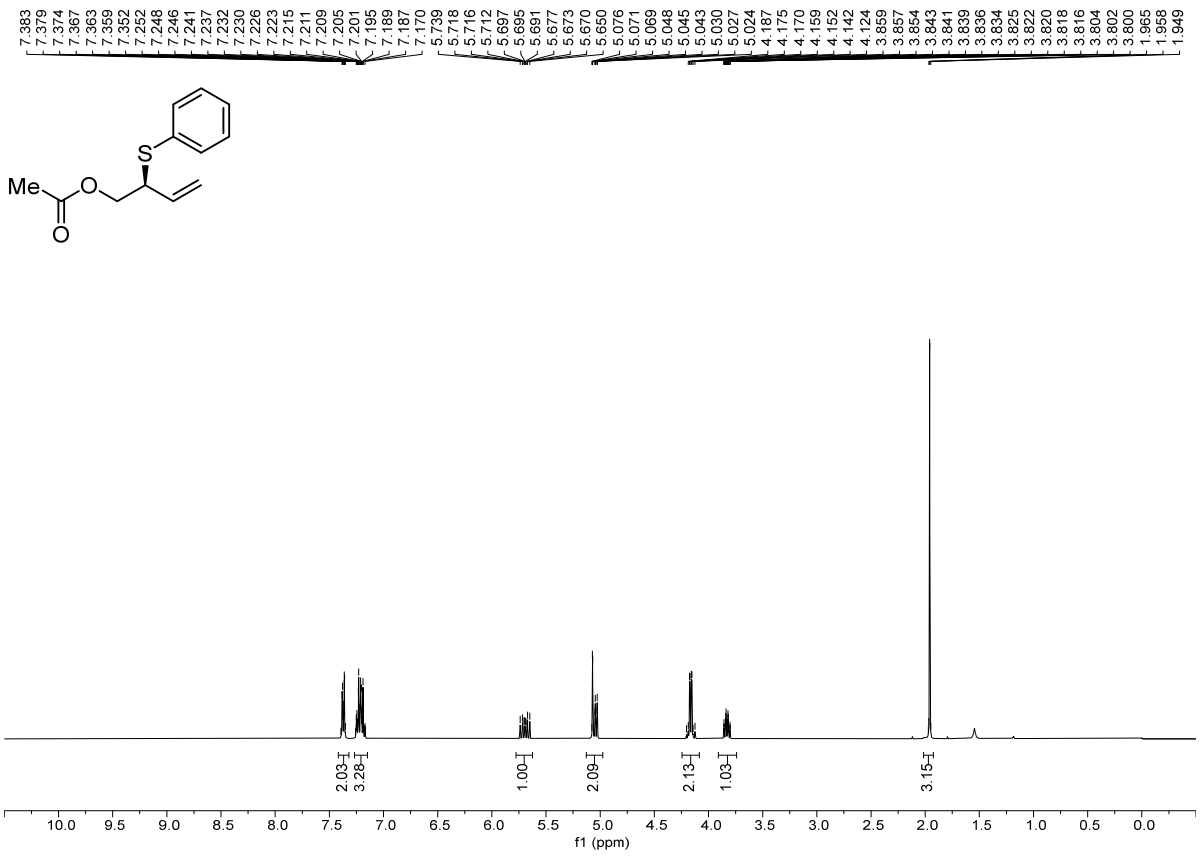

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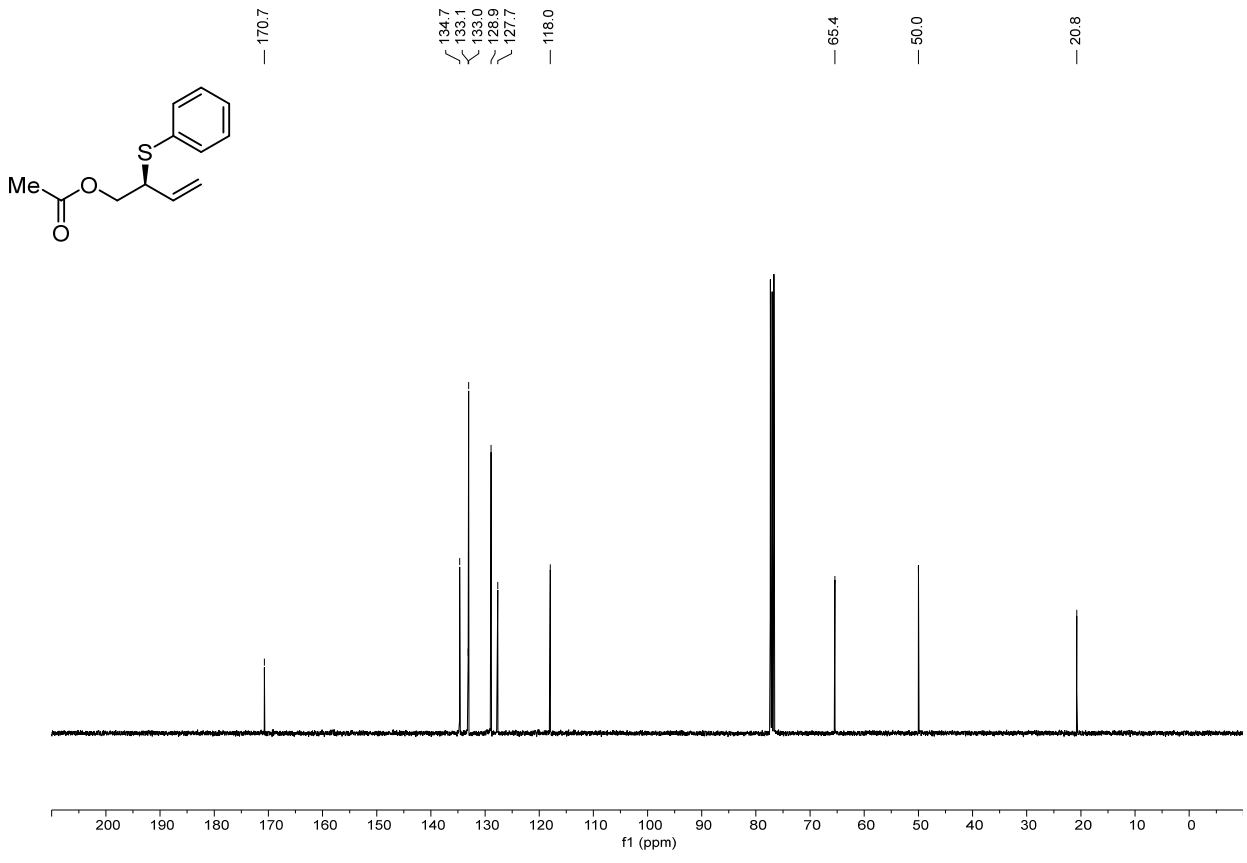

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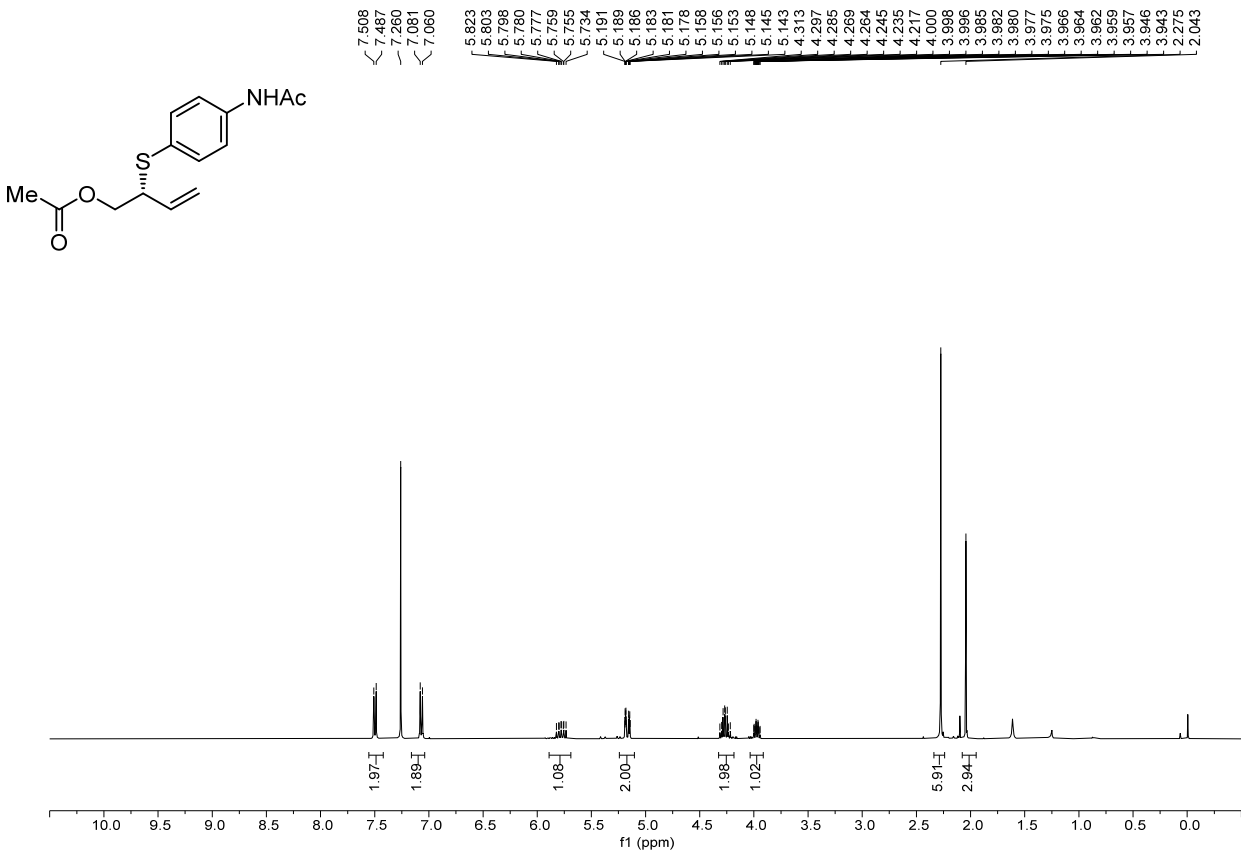
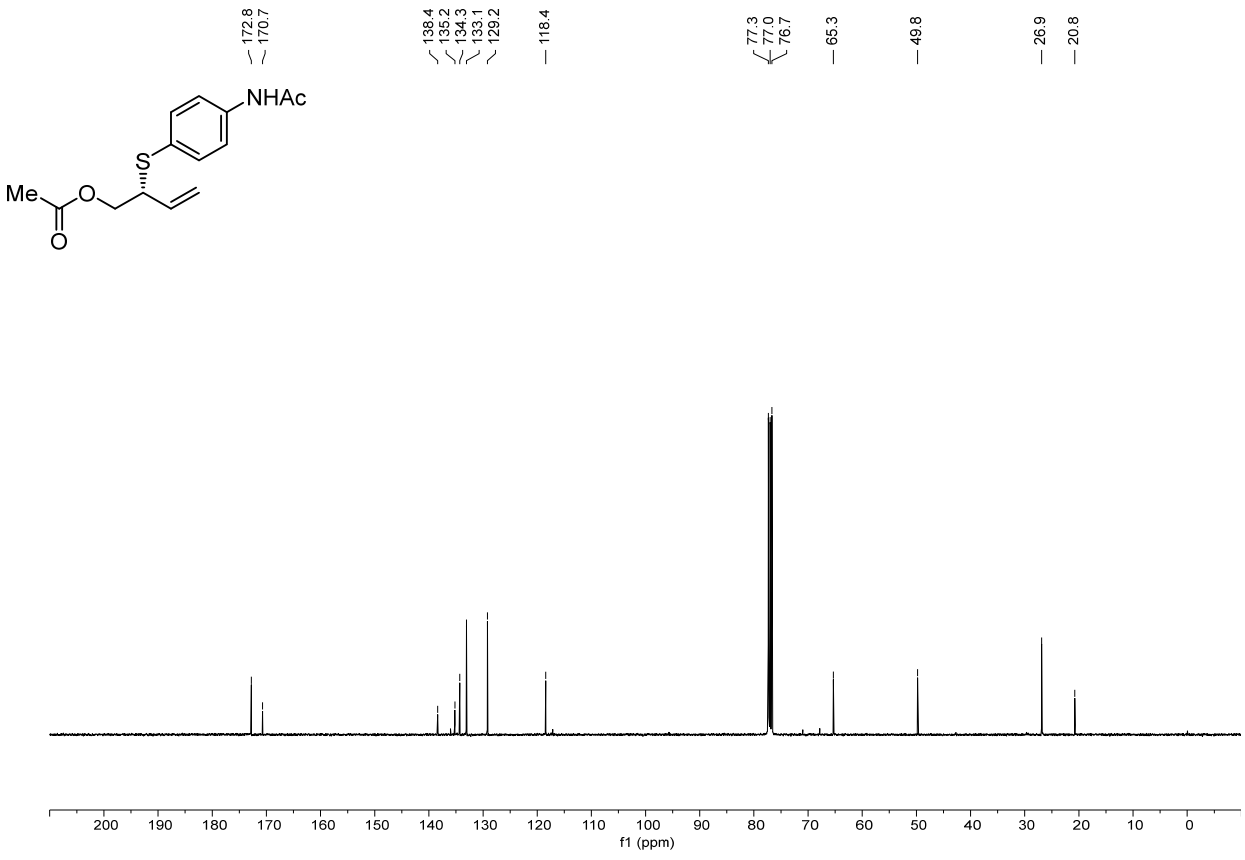


^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



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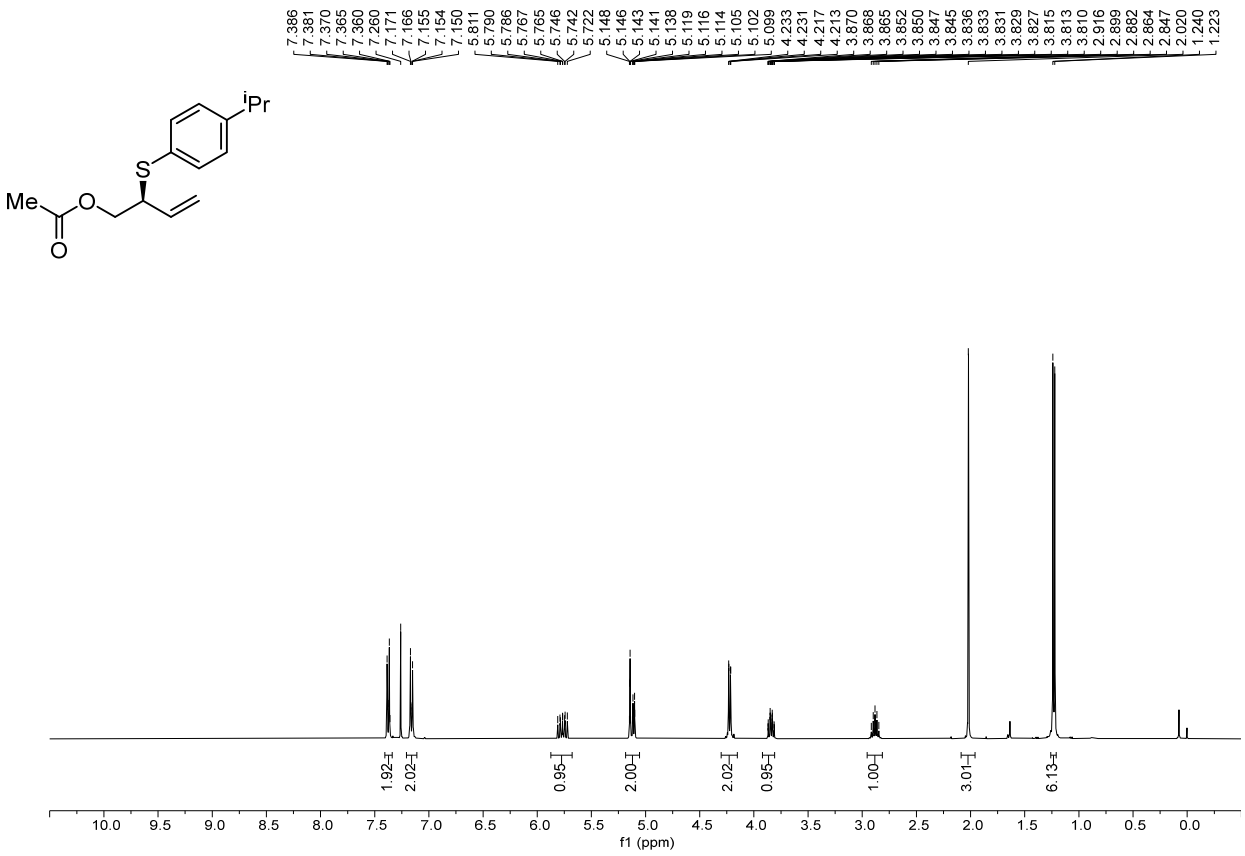
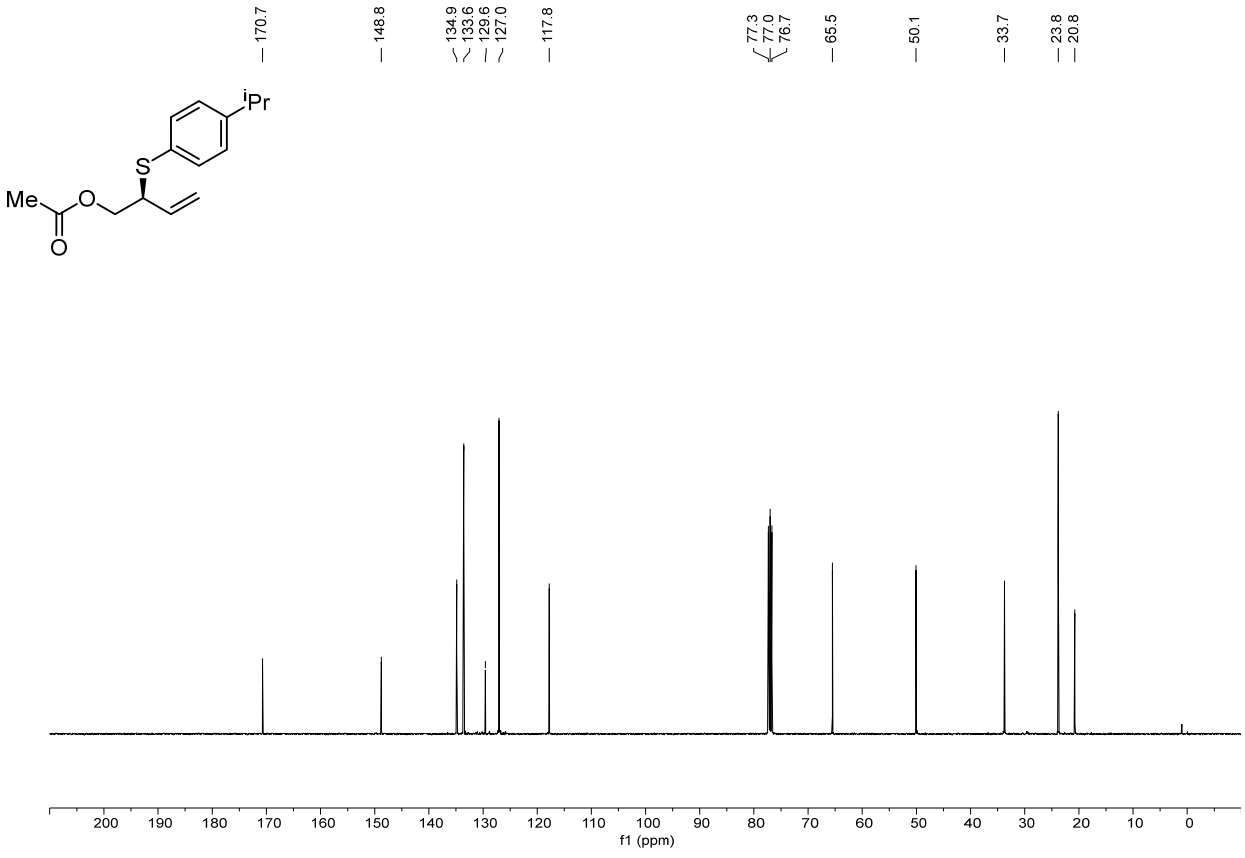


^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



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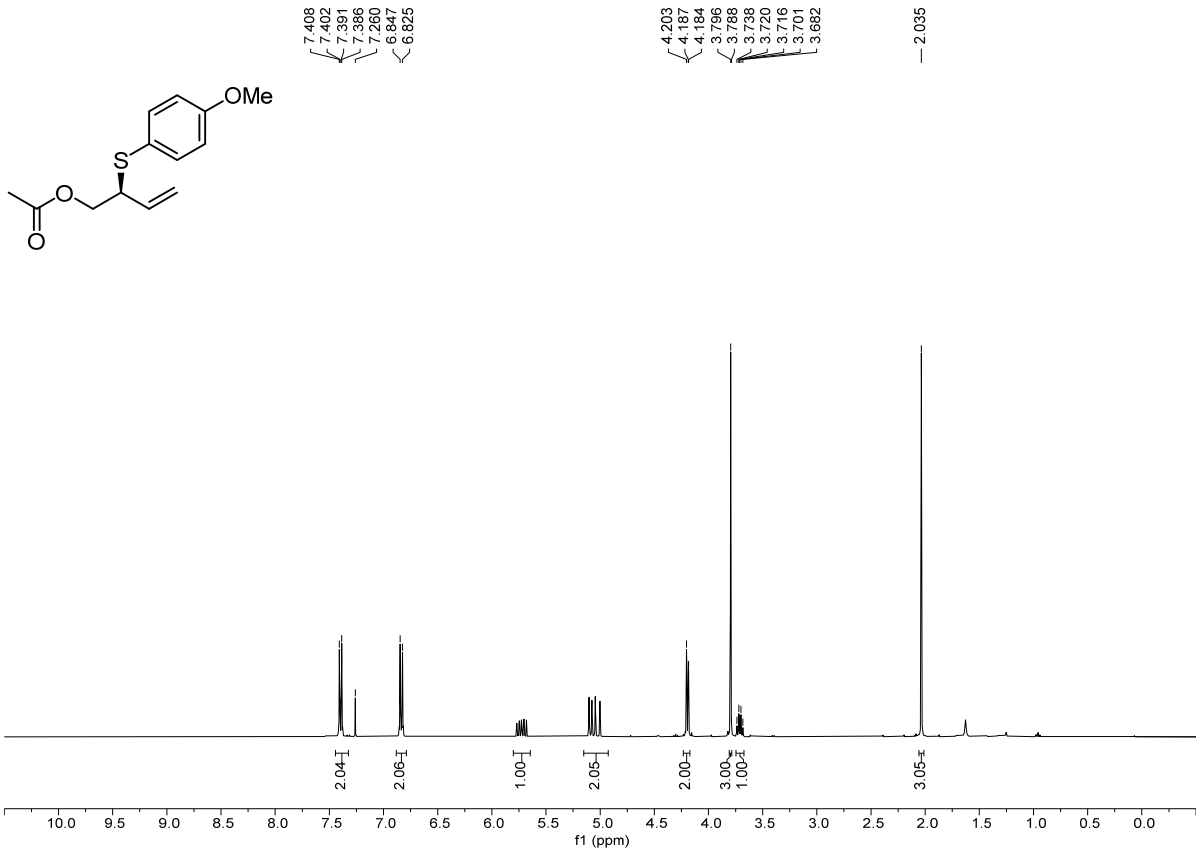
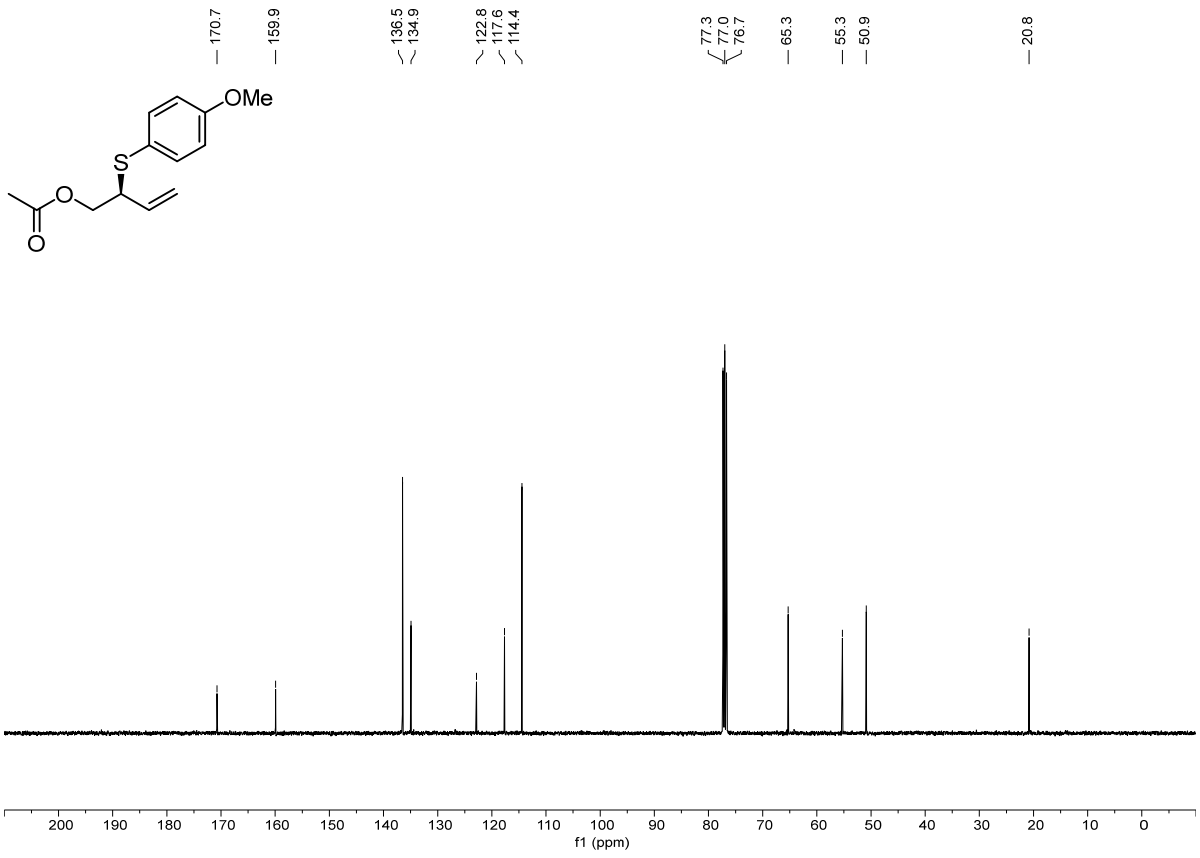


^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



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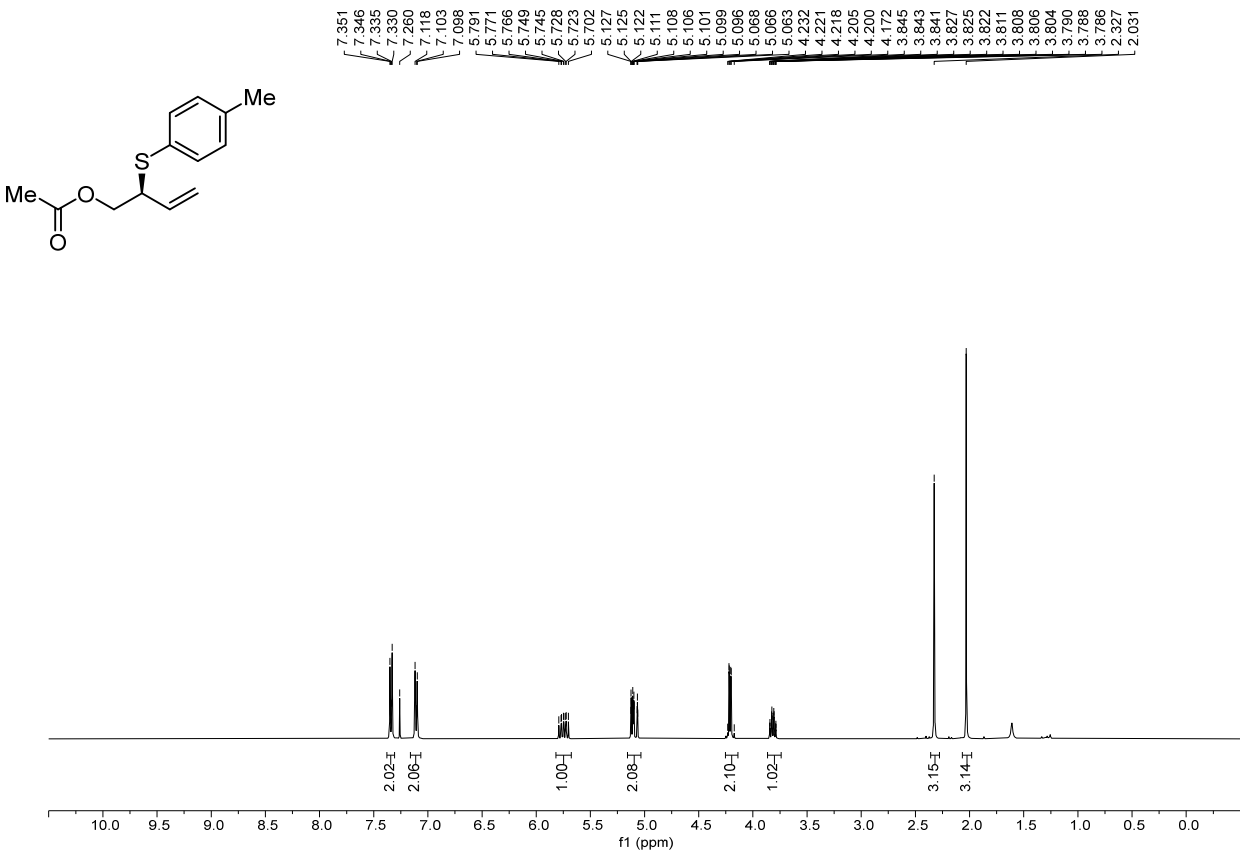

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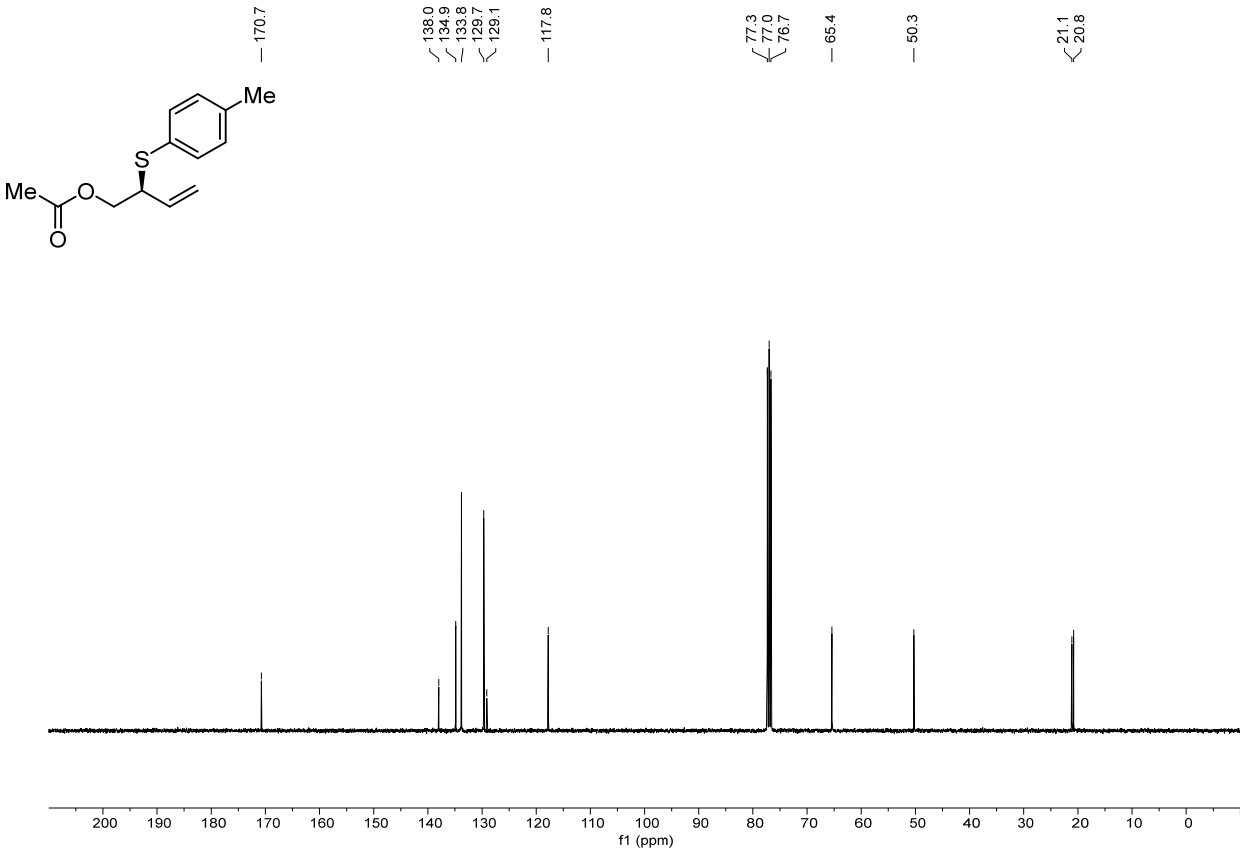

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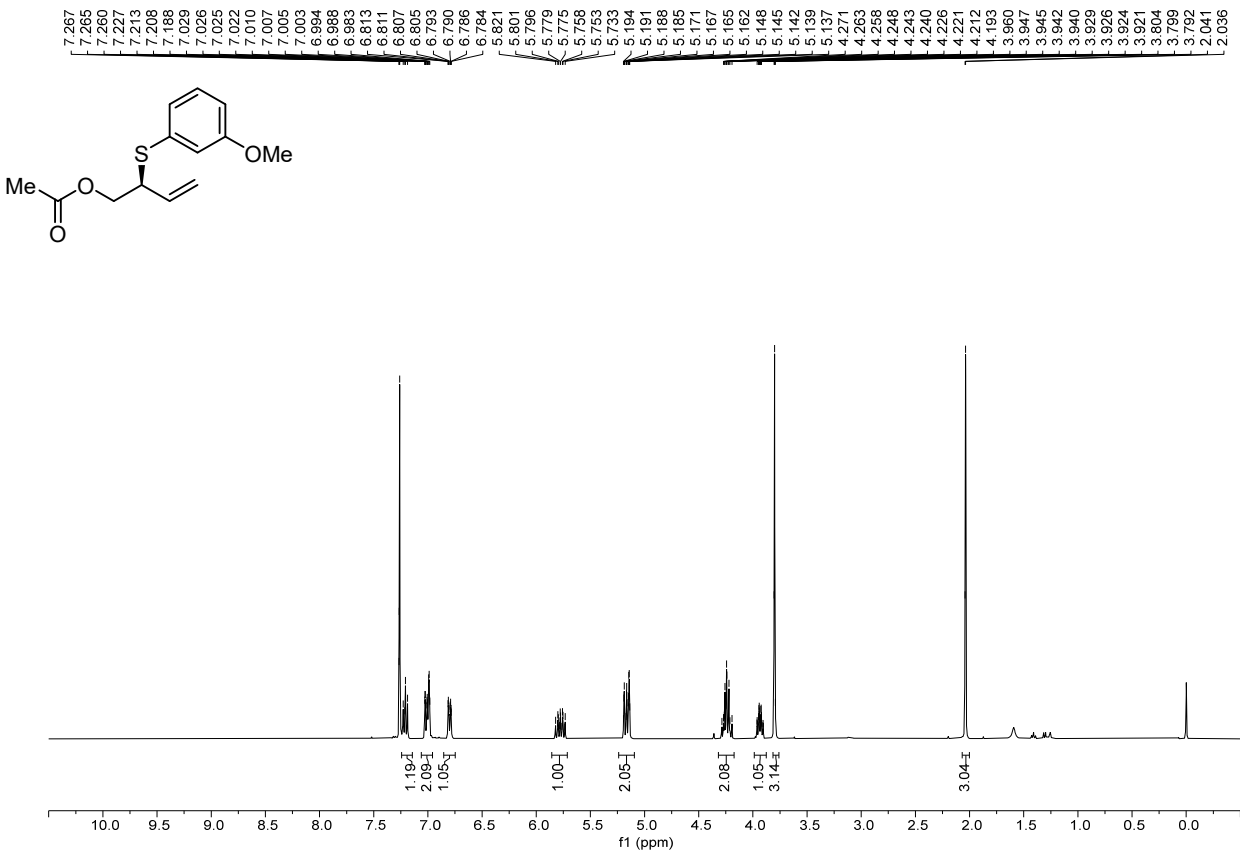

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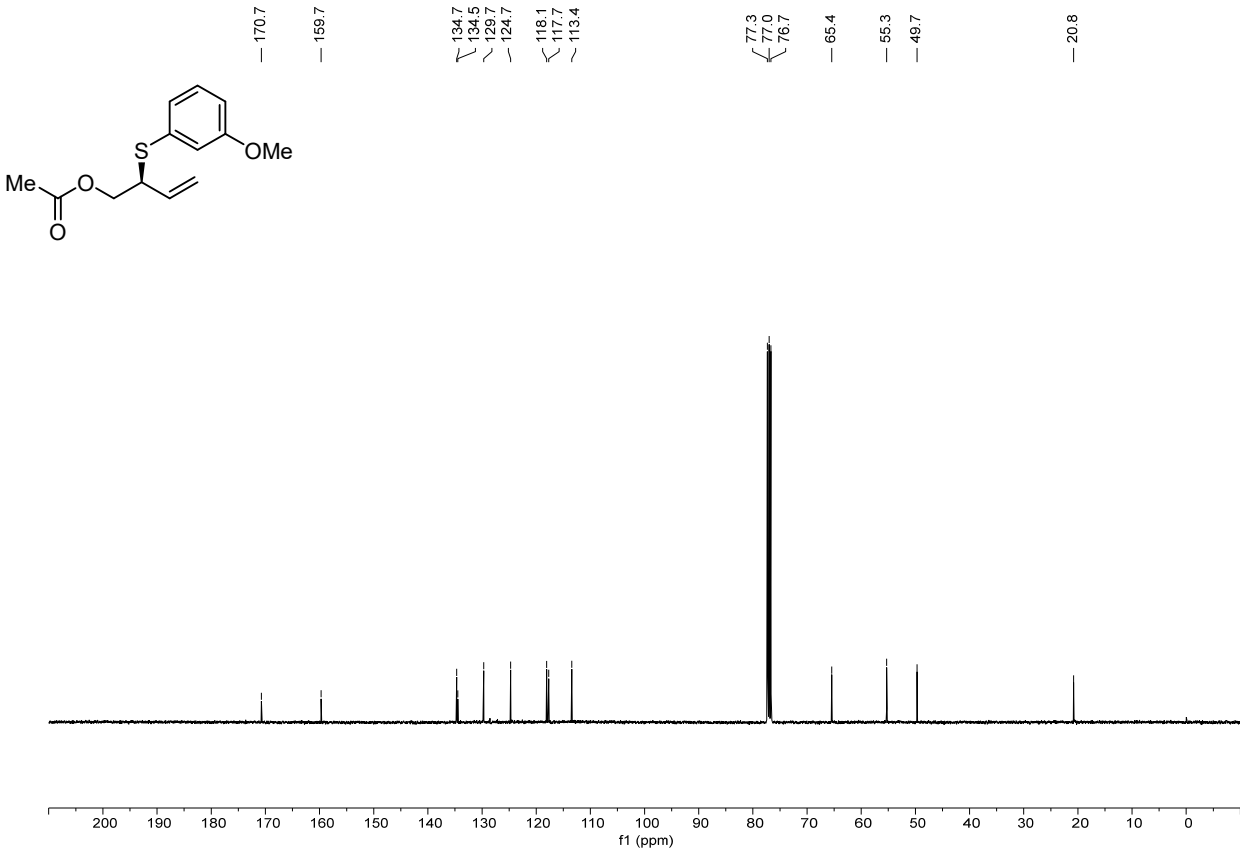

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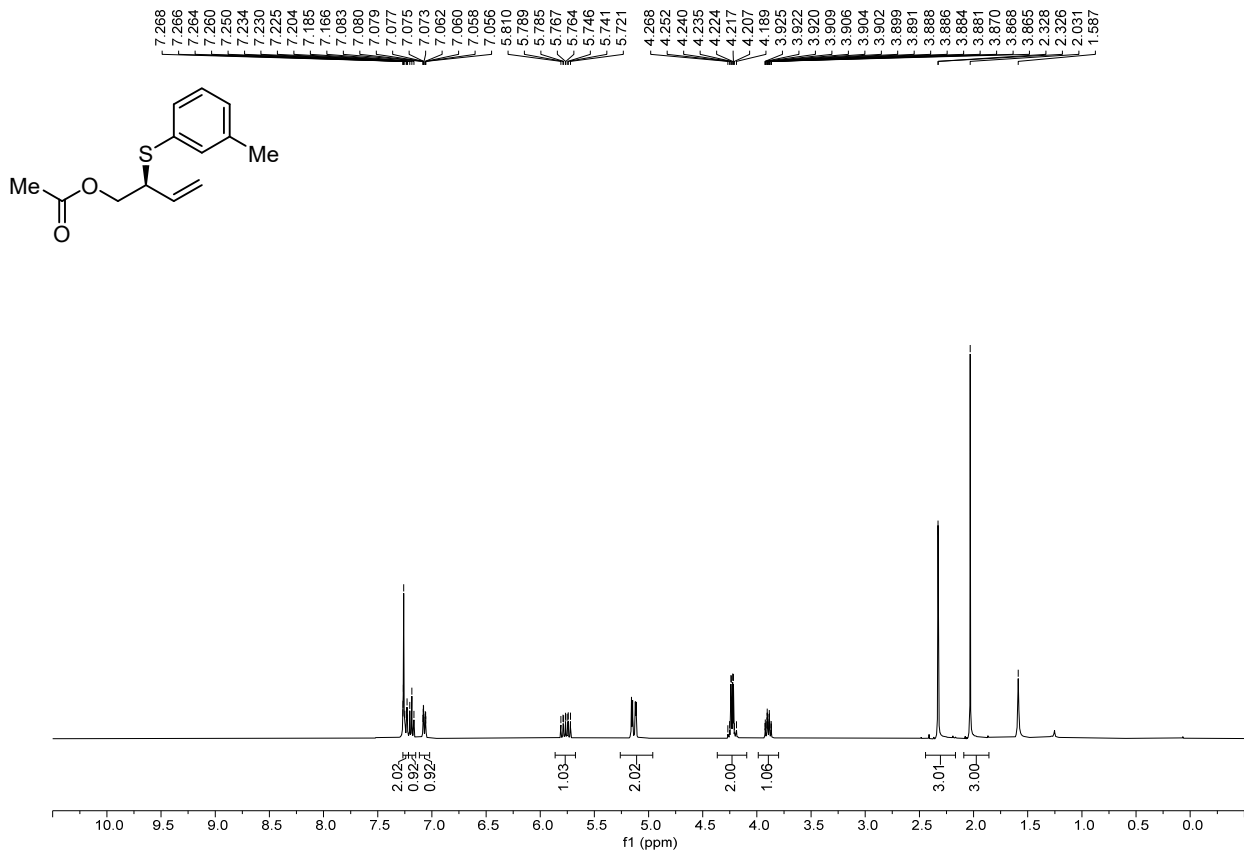
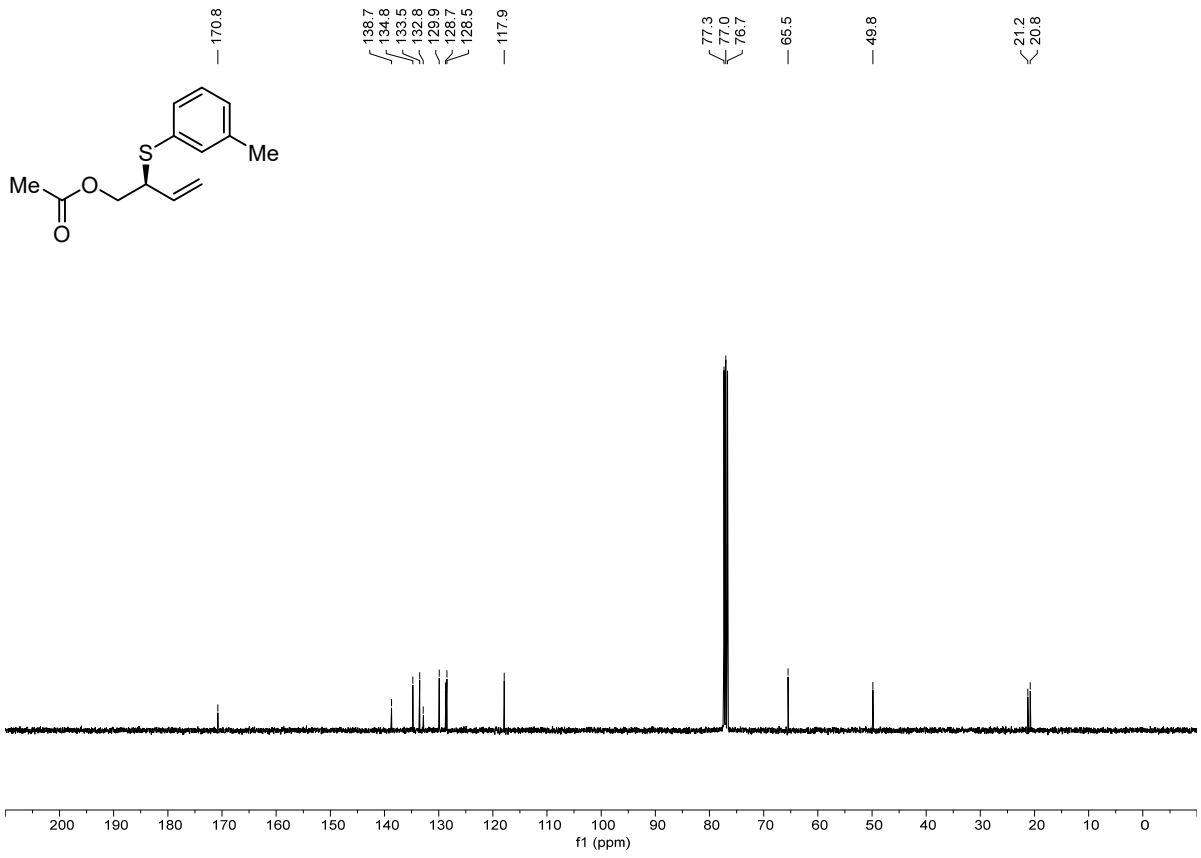
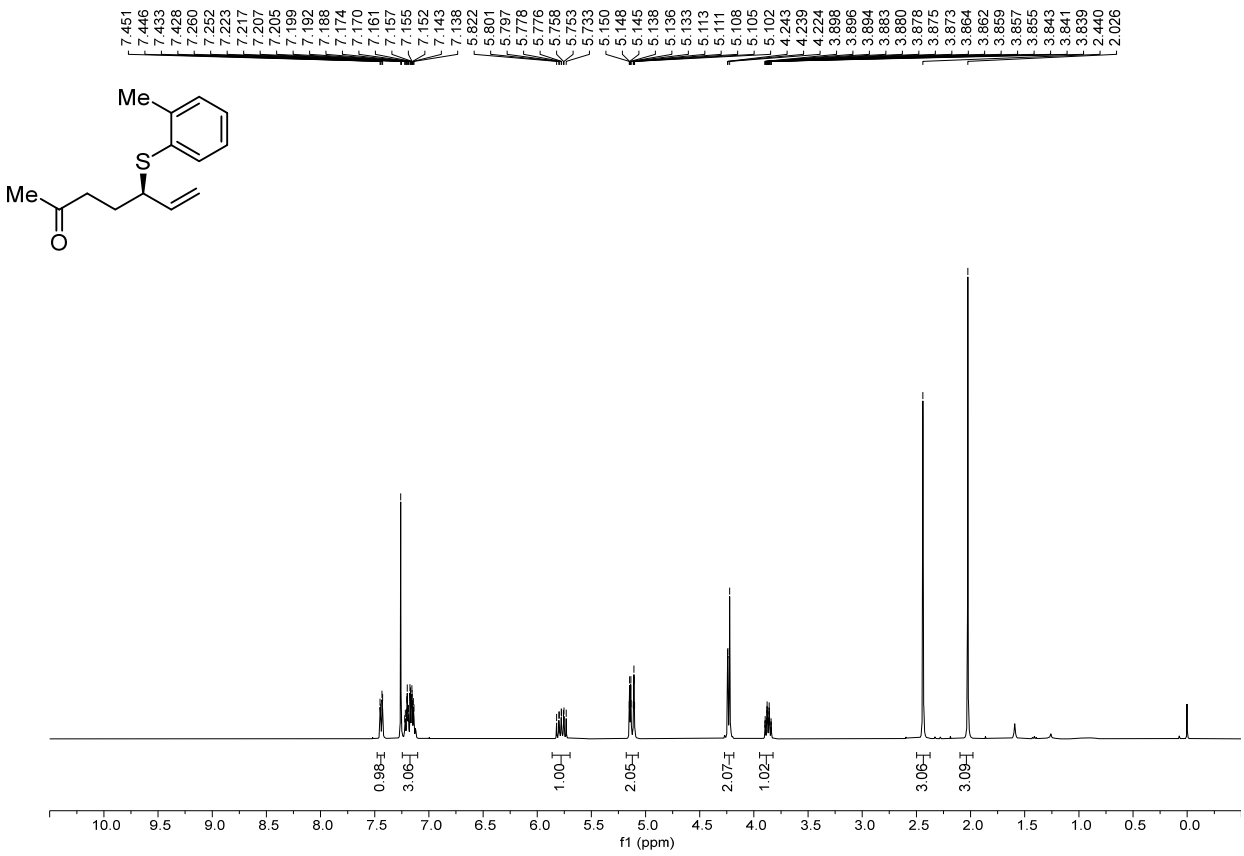


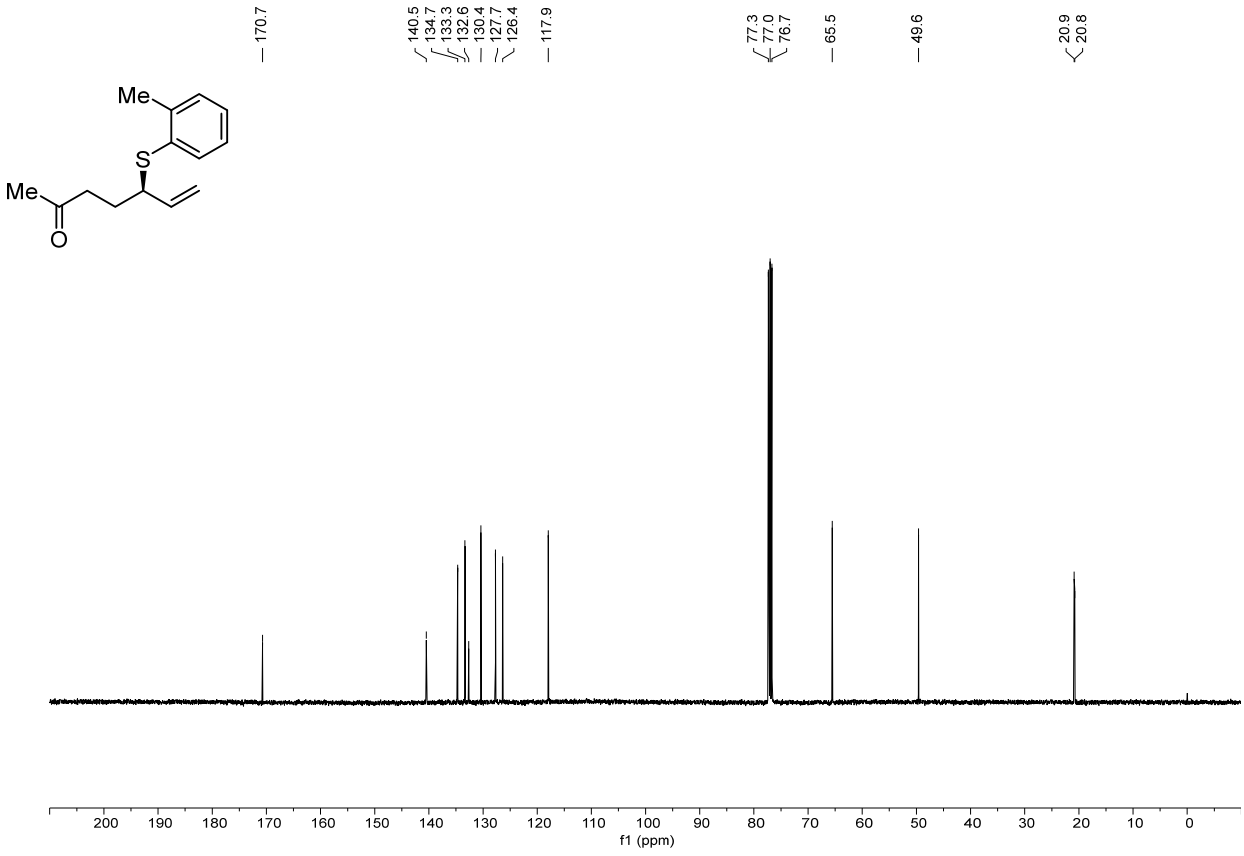
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



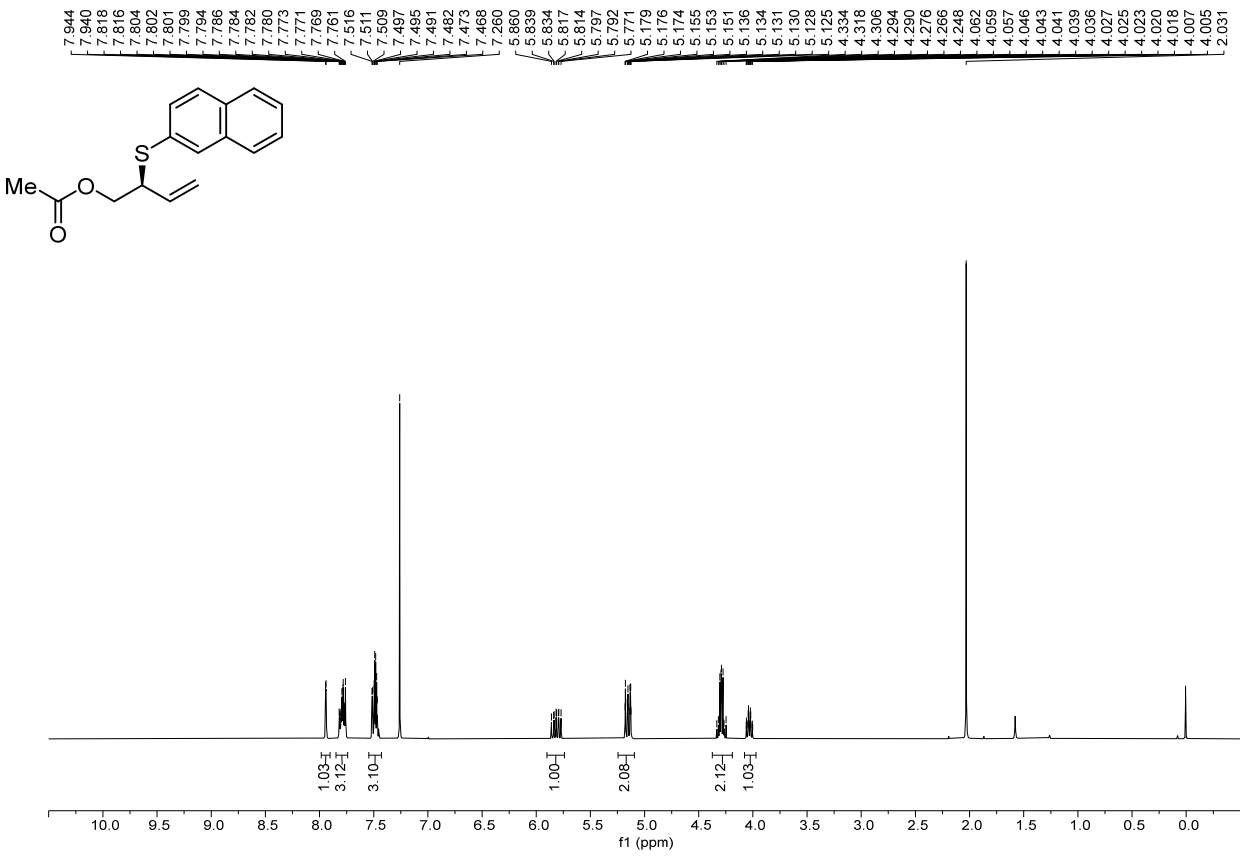
^{13}C NMR (101 MHz, $CDCl_3$) of **3l**



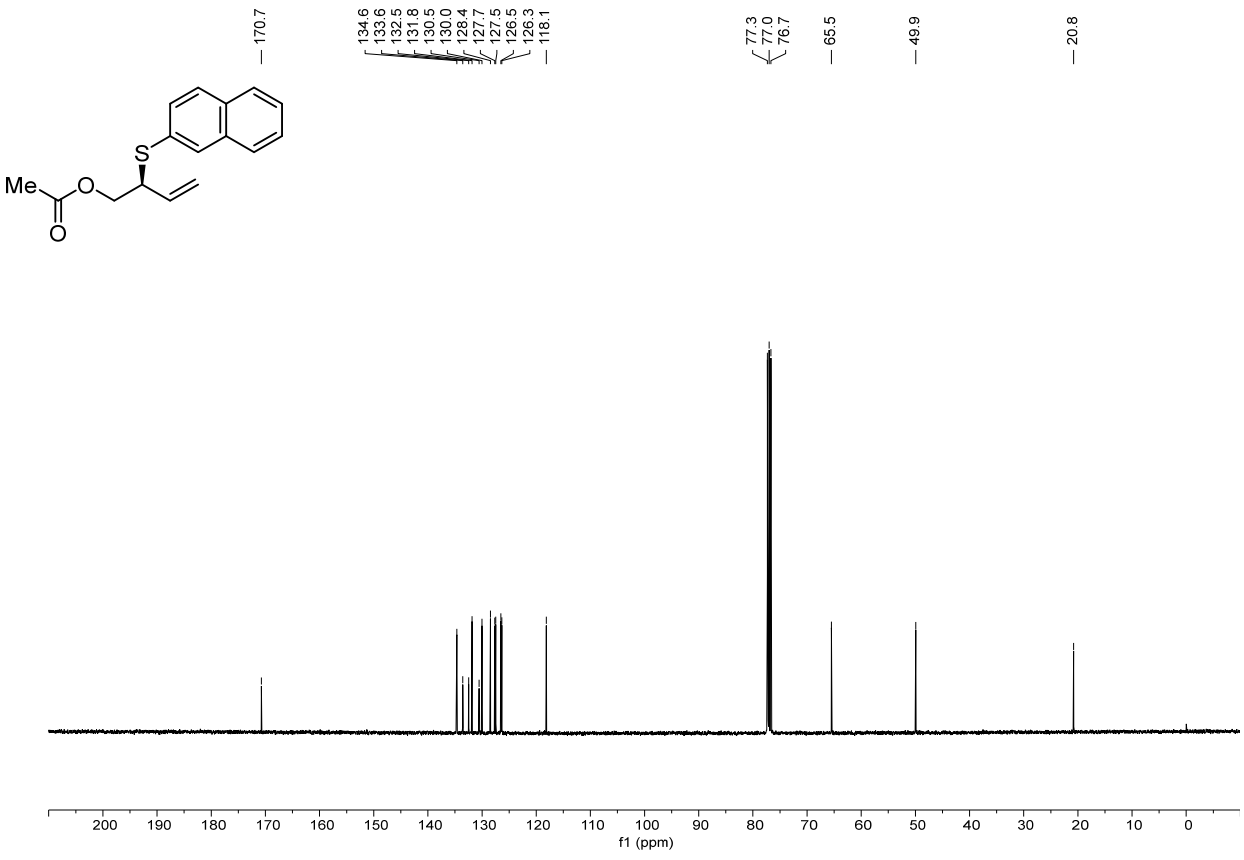
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



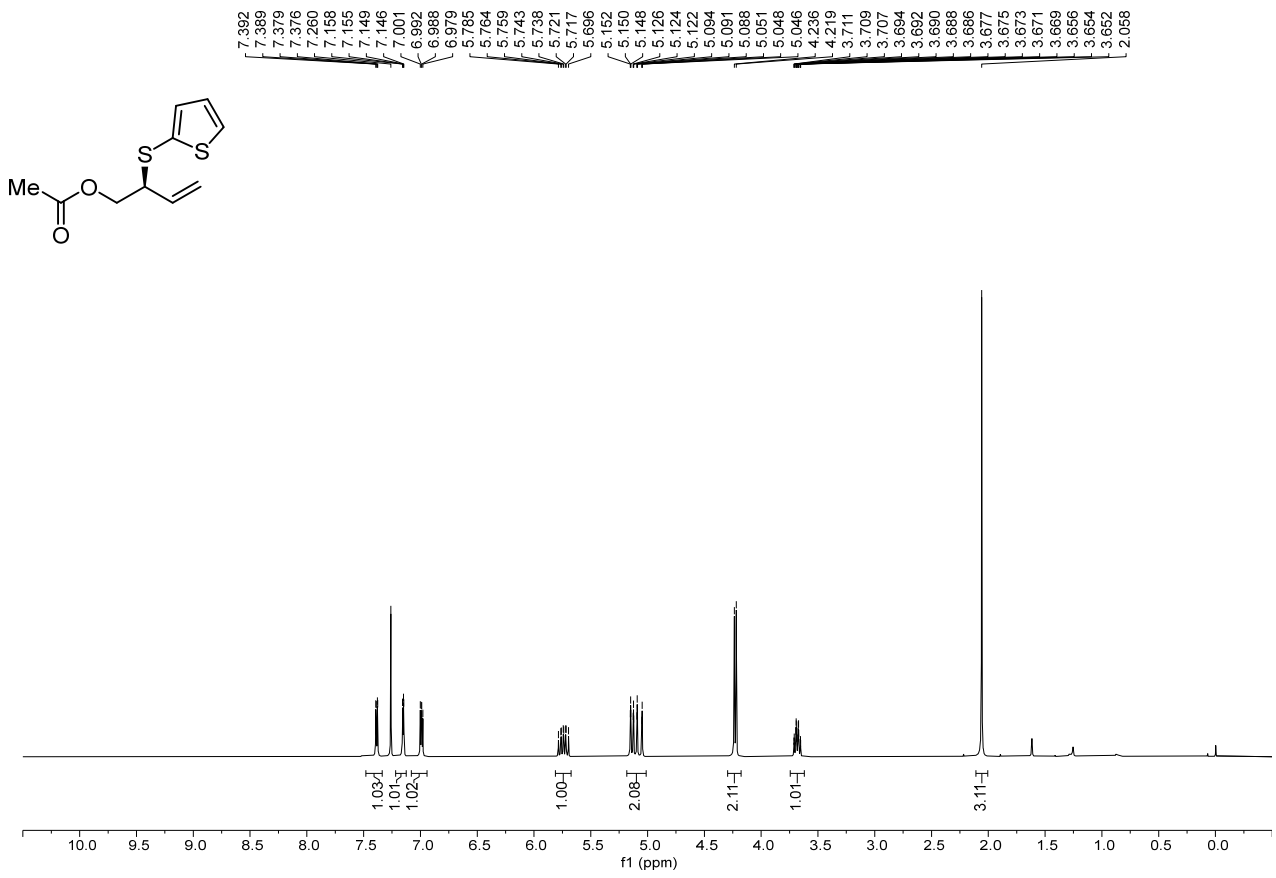
^{13}C NMR (101 MHz, $CDCl_3$) of **3m**



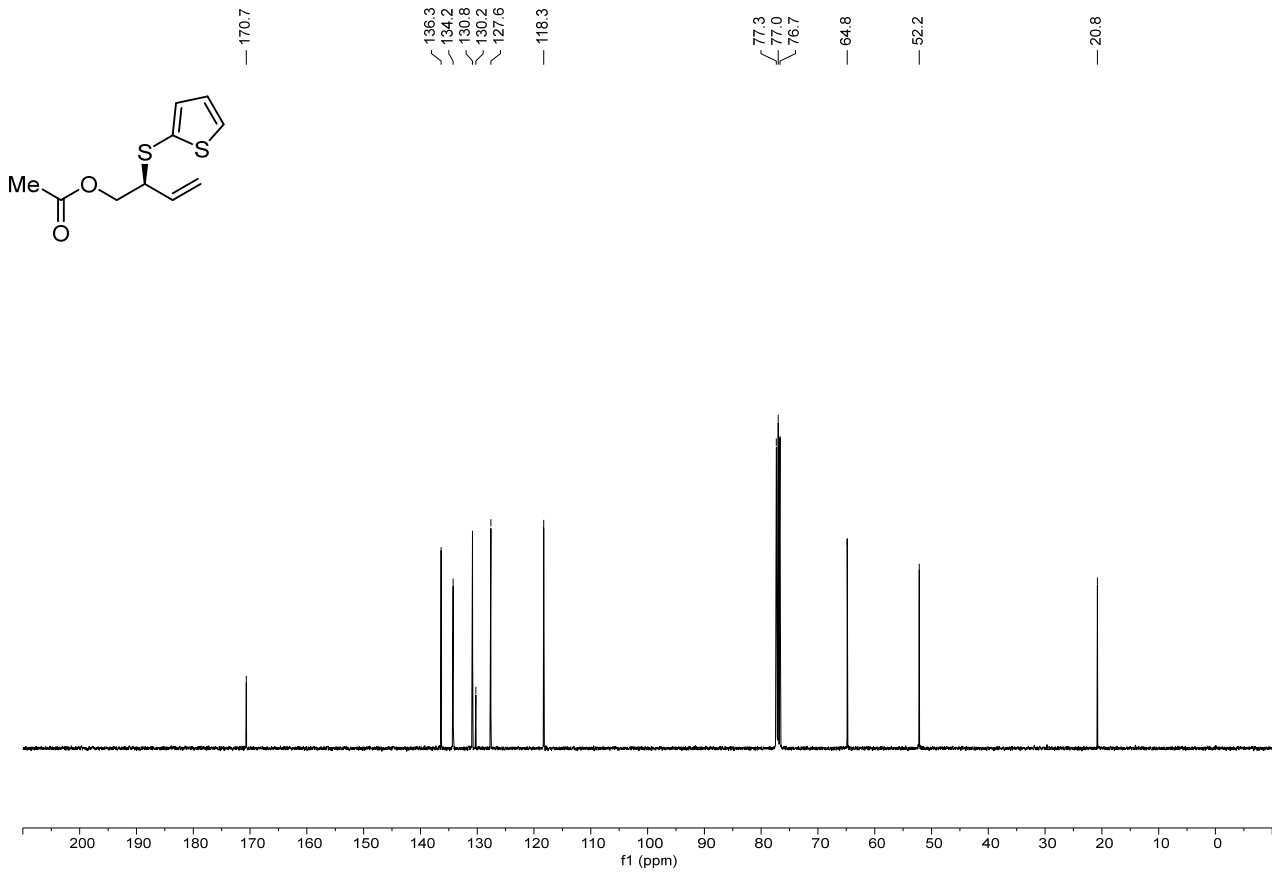
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



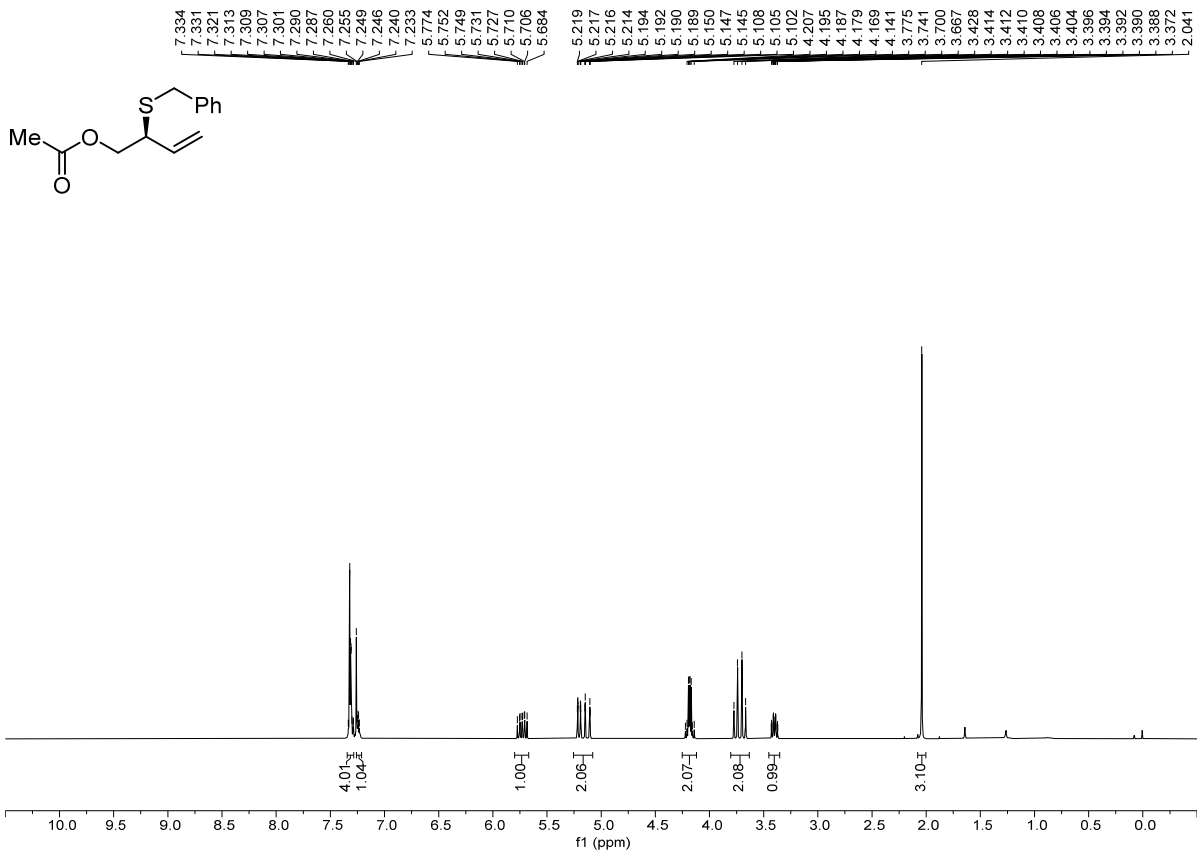
^{13}C NMR (101 MHz, $CDCl_3$) of **3n**



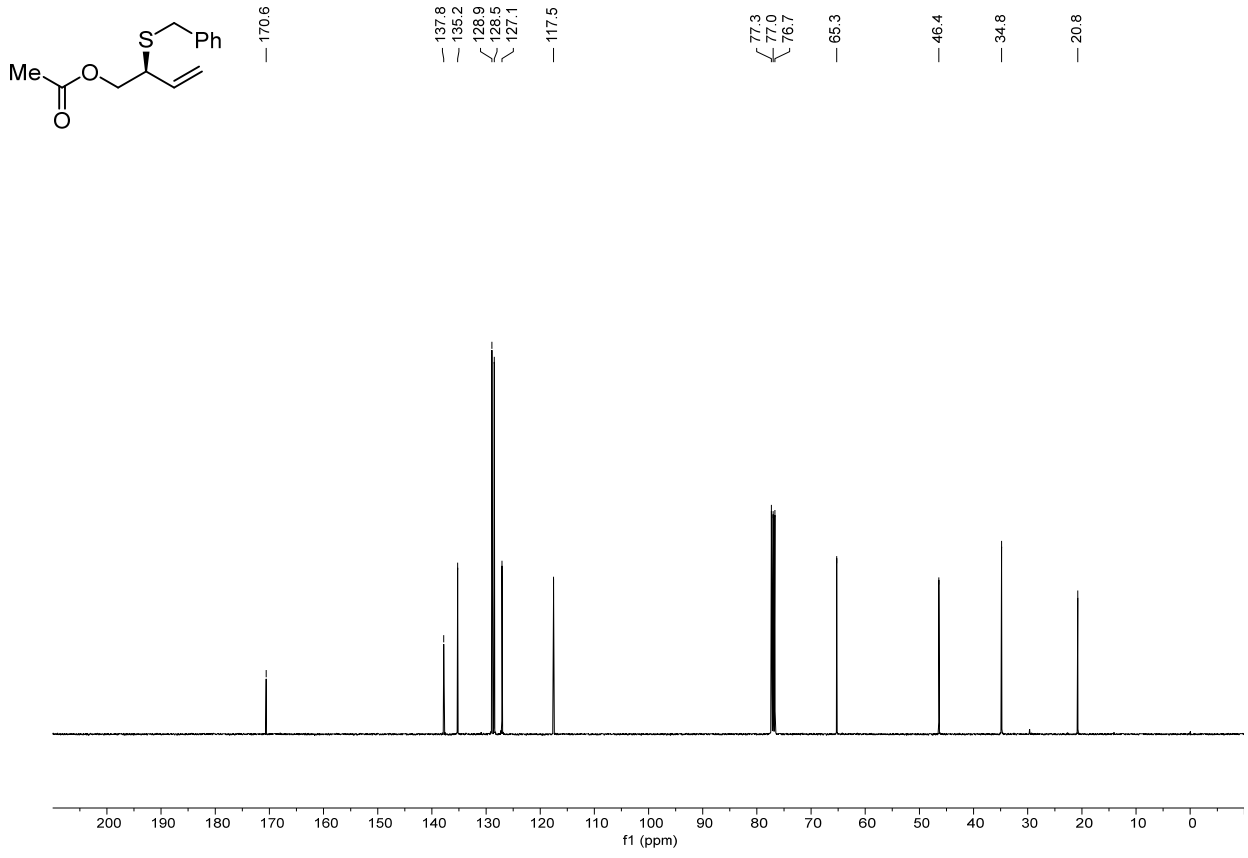
^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



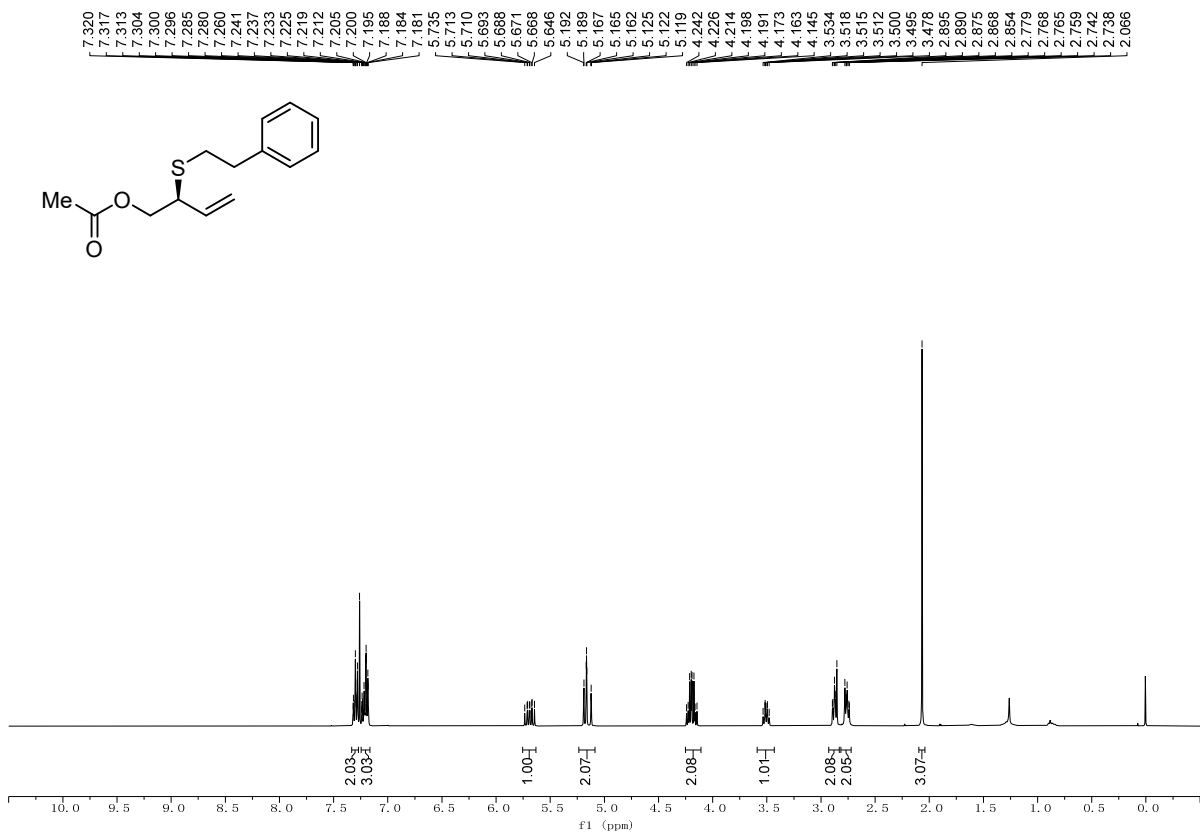
^{13}C NMR (101 MHz, $CDCl_3$) of **3o**



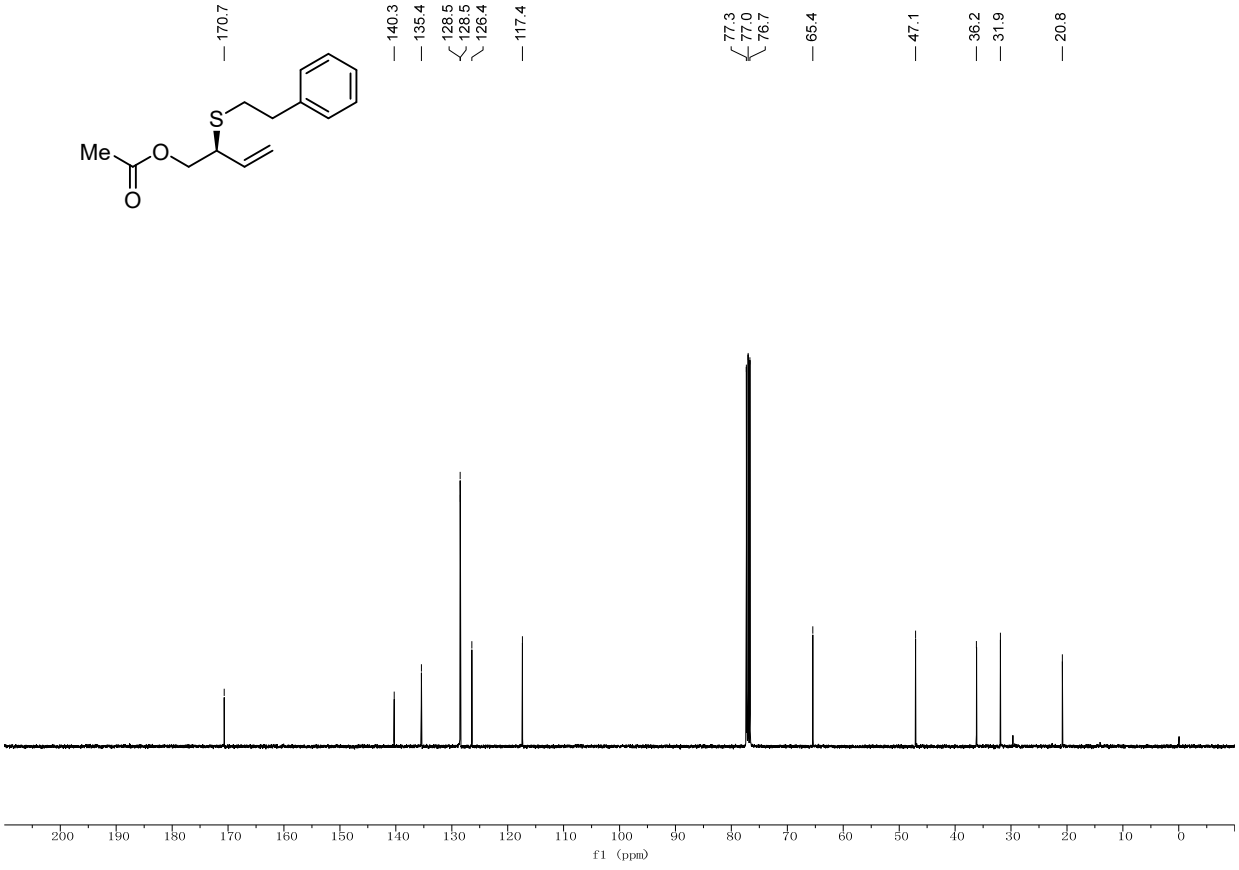
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



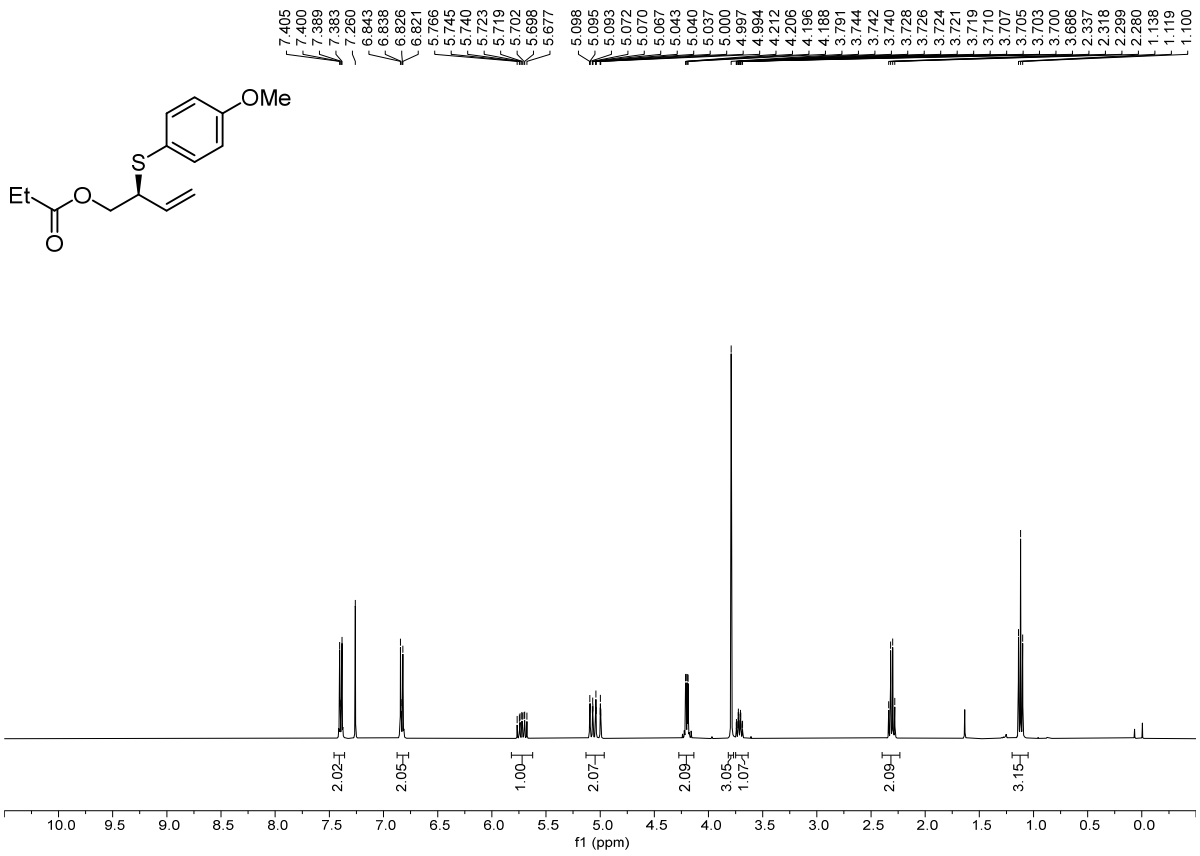
^{13}C NMR (101 MHz, $CDCl_3$) of **3p**



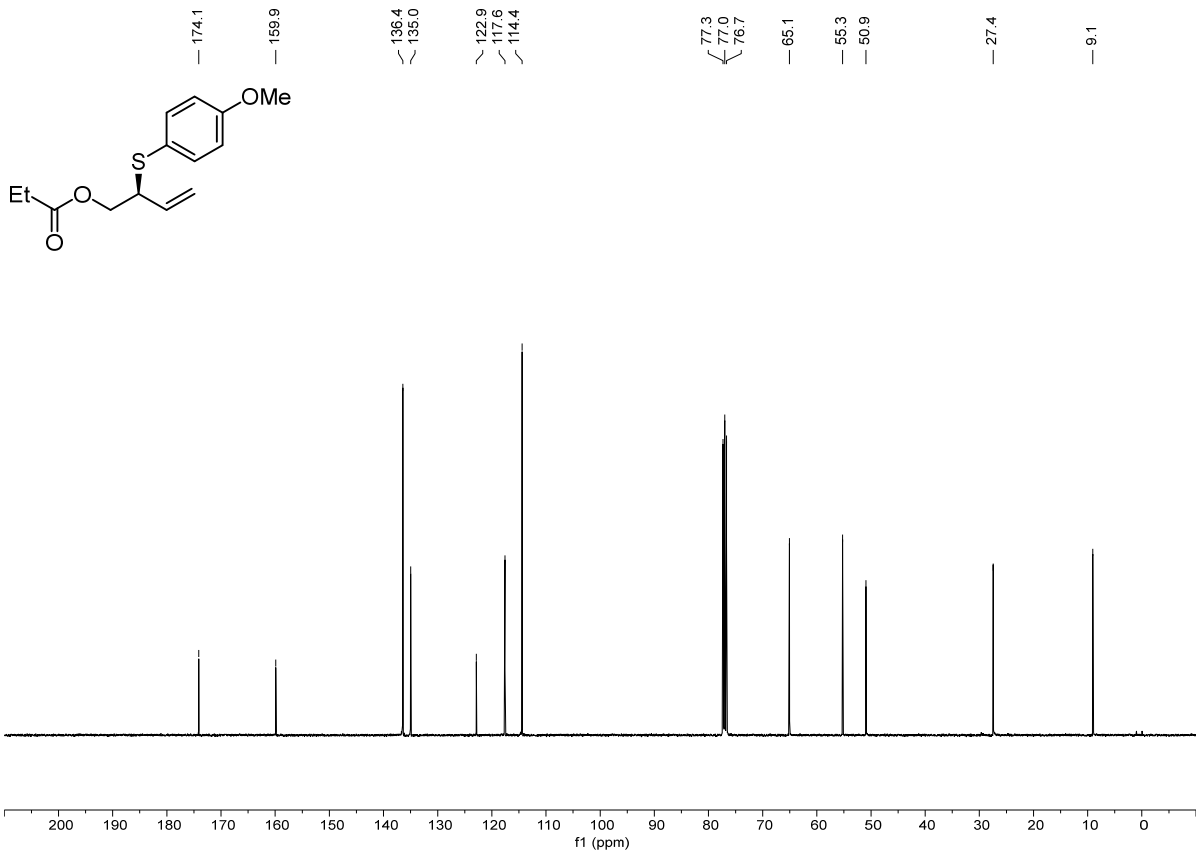
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



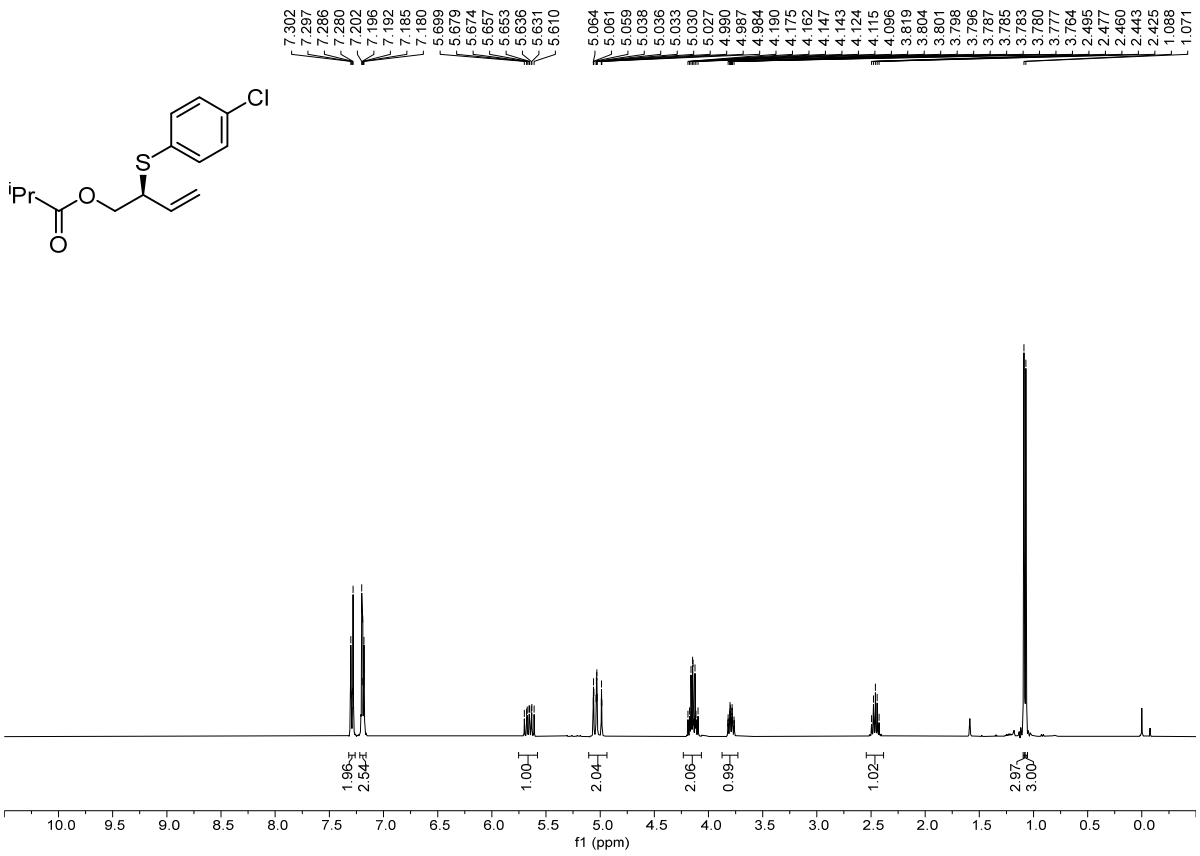
^{13}C NMR (101 MHz, $CDCl_3$) of **3q**



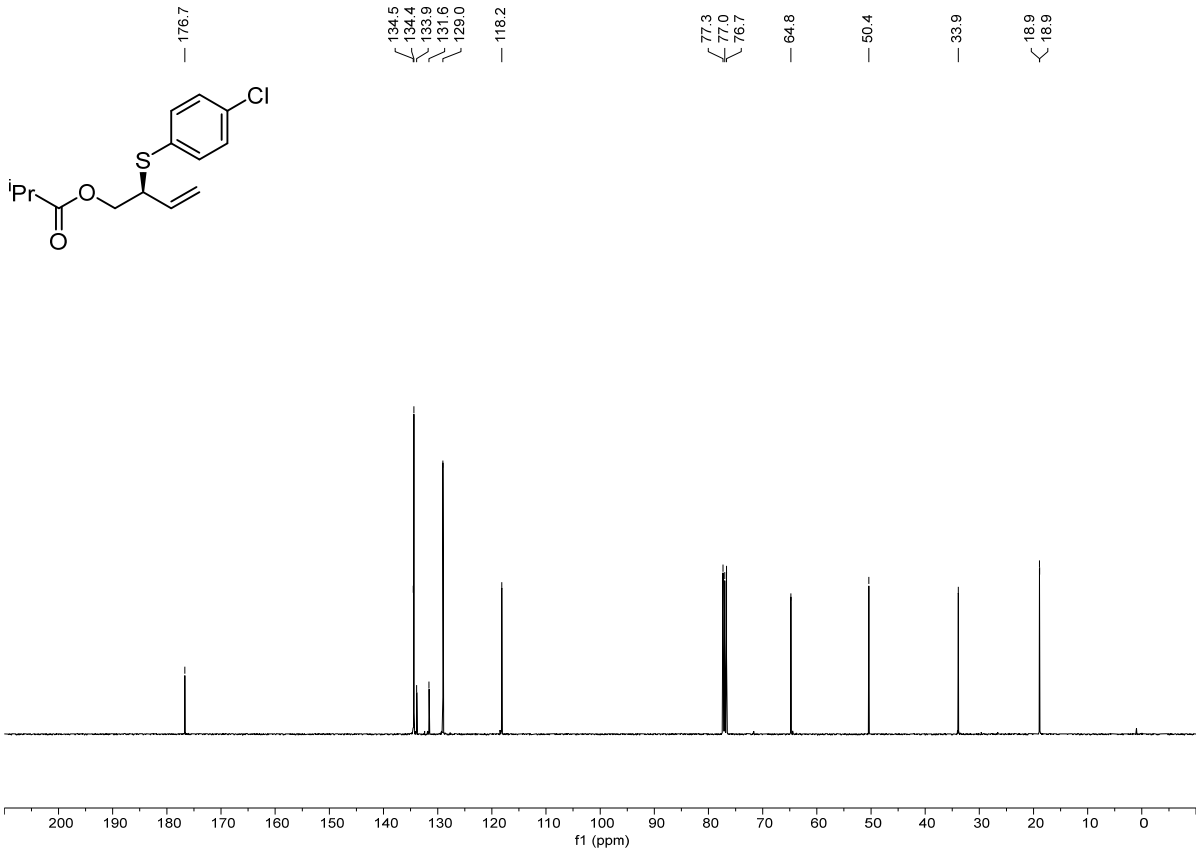
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



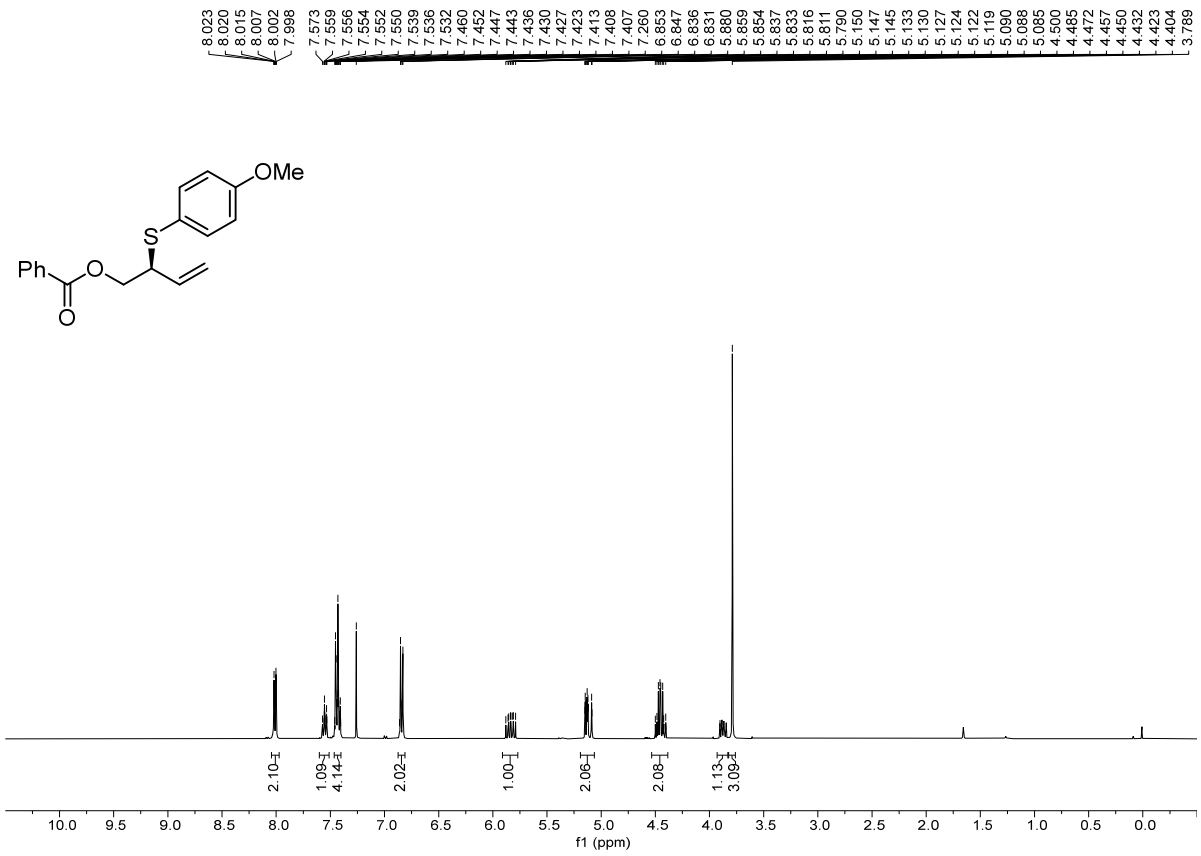
^{13}C NMR (101 MHz, $CDCl_3$) of **3r**



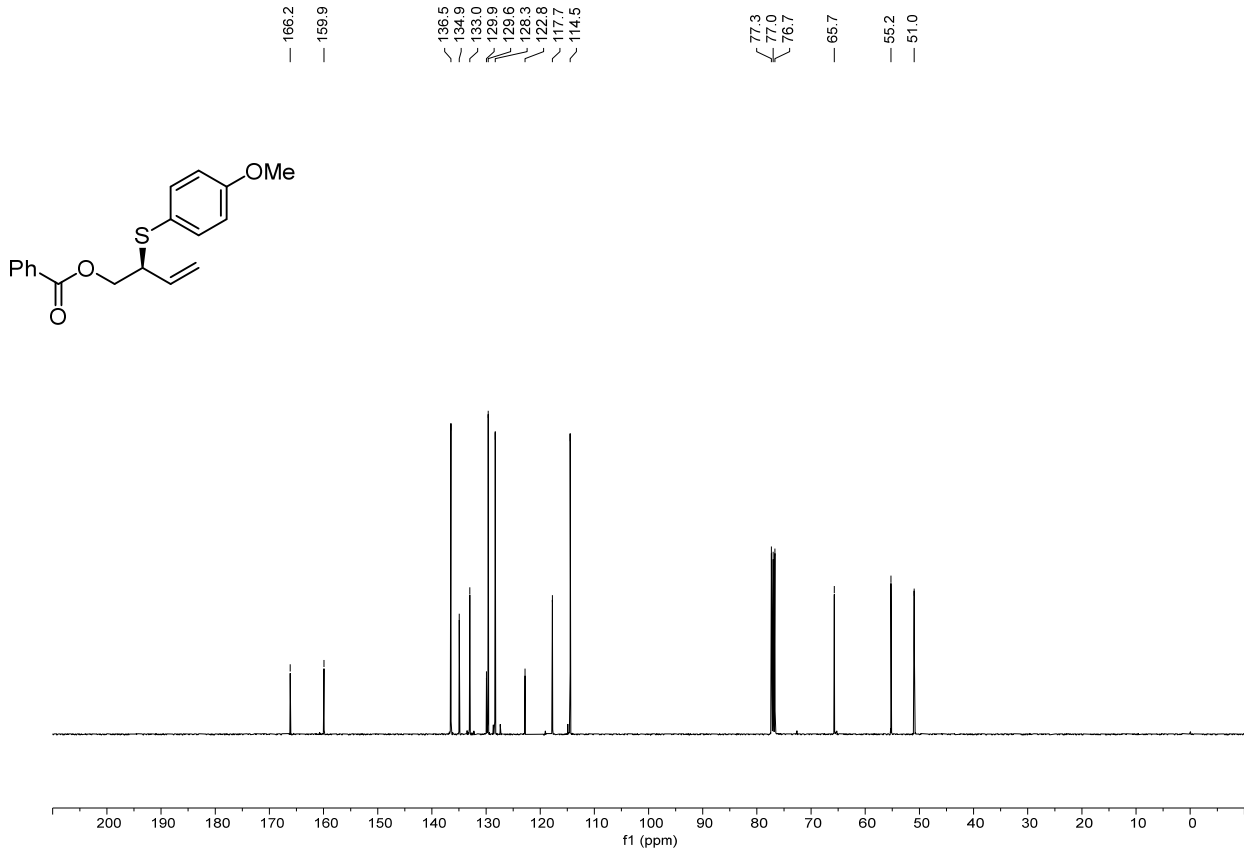
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**



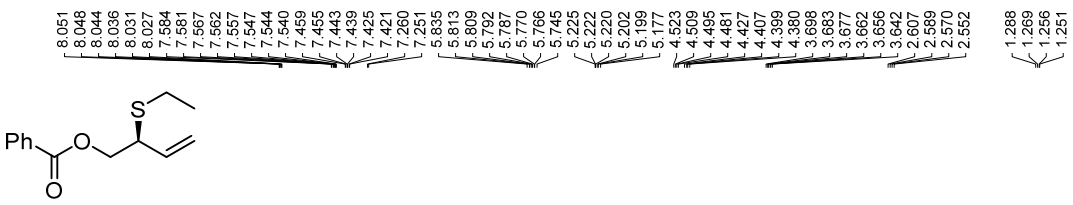
^{13}C NMR (101 MHz, $CDCl_3$) of **3s**

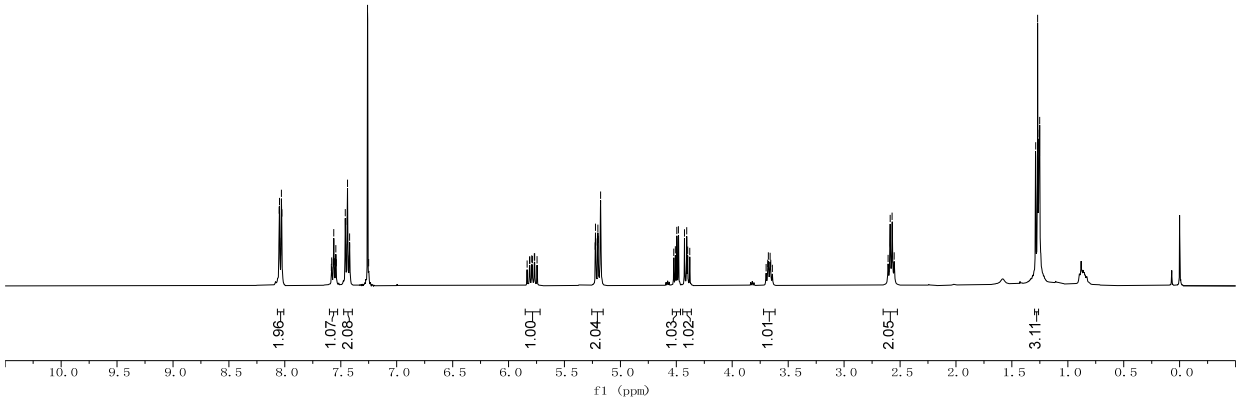


^{1}H NMR (400 MHz, $CDCl_3$) of **3t**

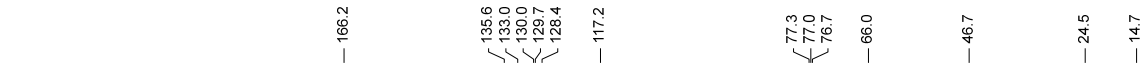


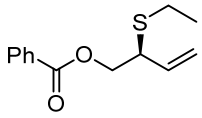
^{13}C NMR (101 MHz, $CDCl_3$) of **3t**

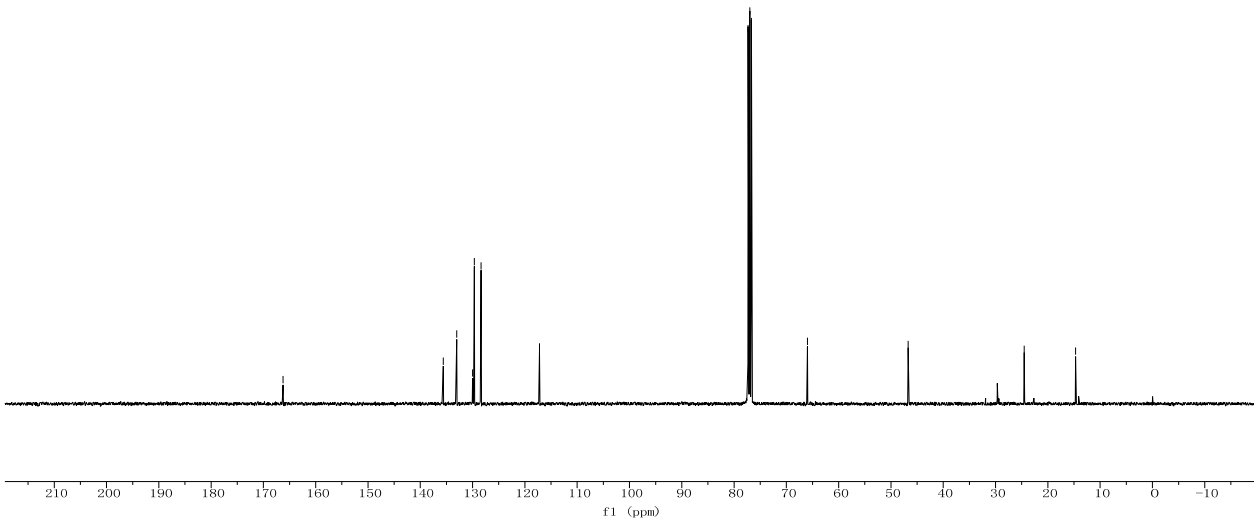




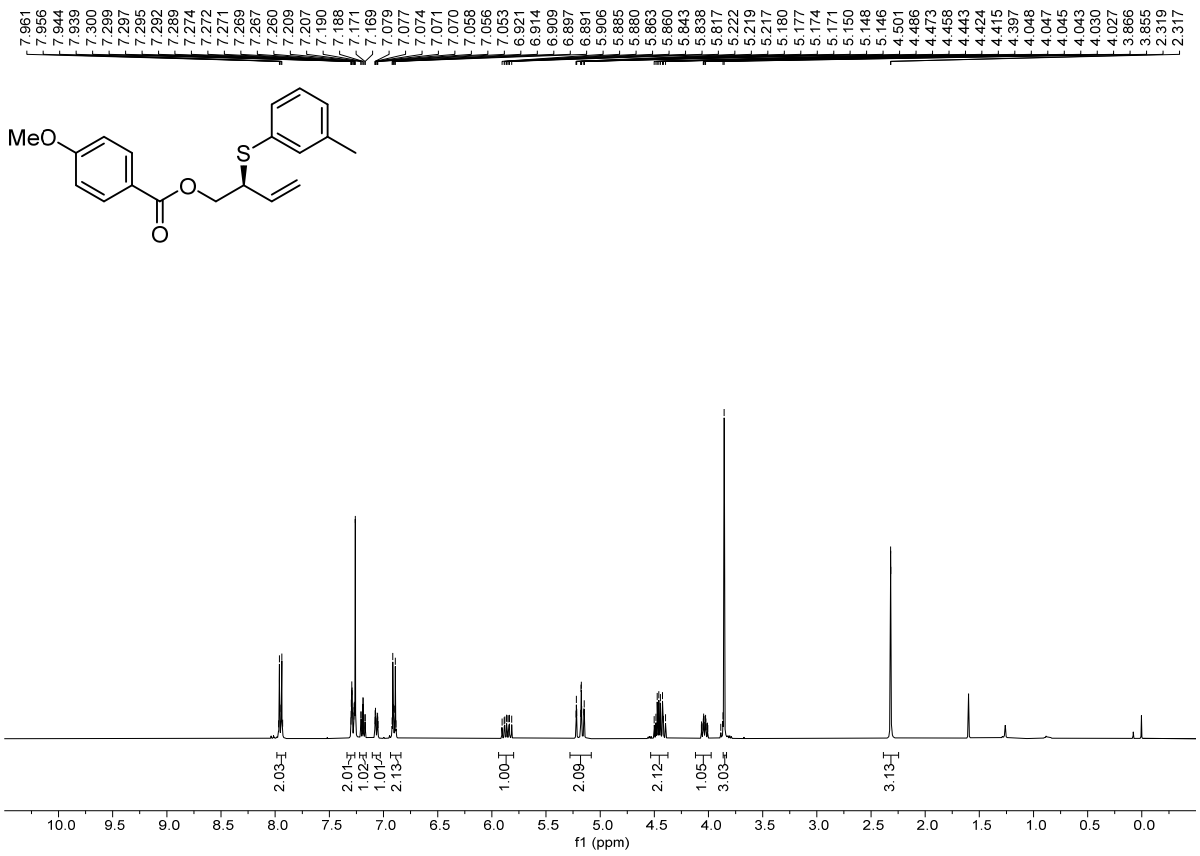
^{1}H NMR (400 MHz, $CDCl_3$) of **3u**



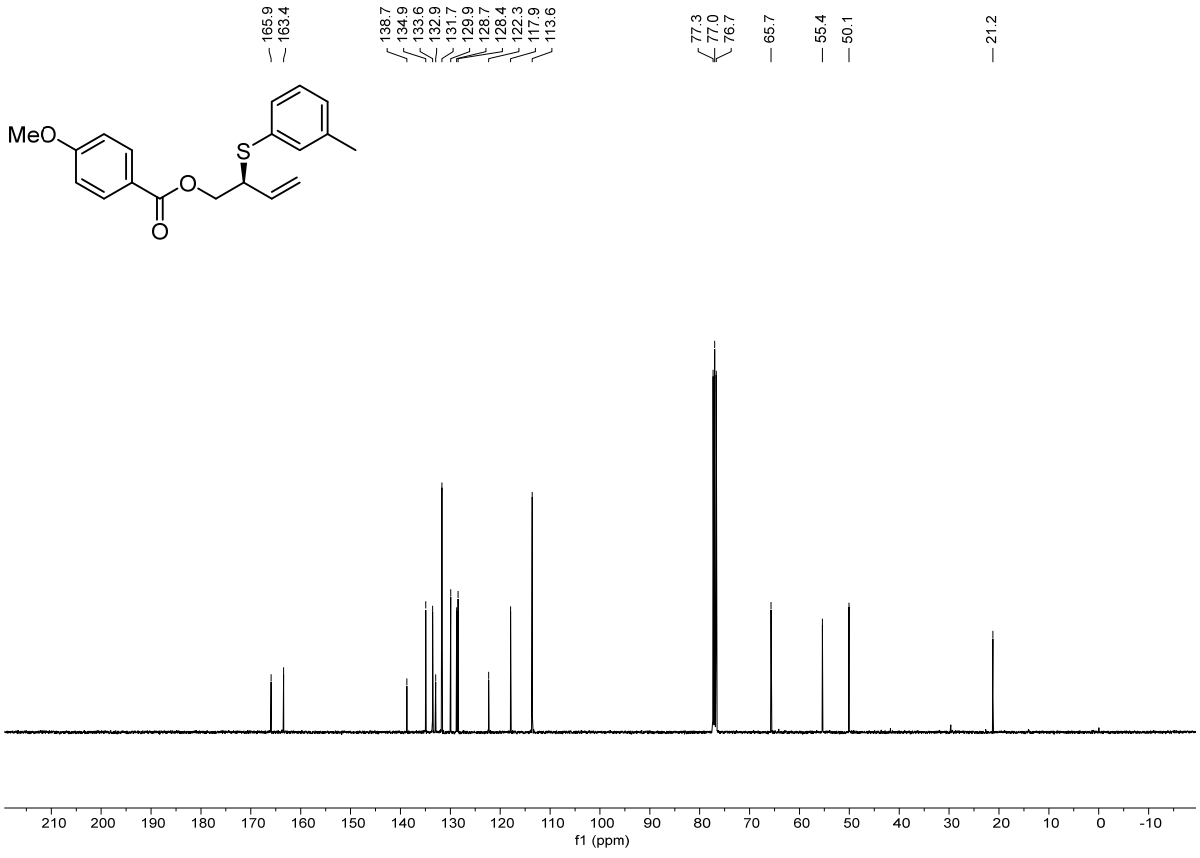




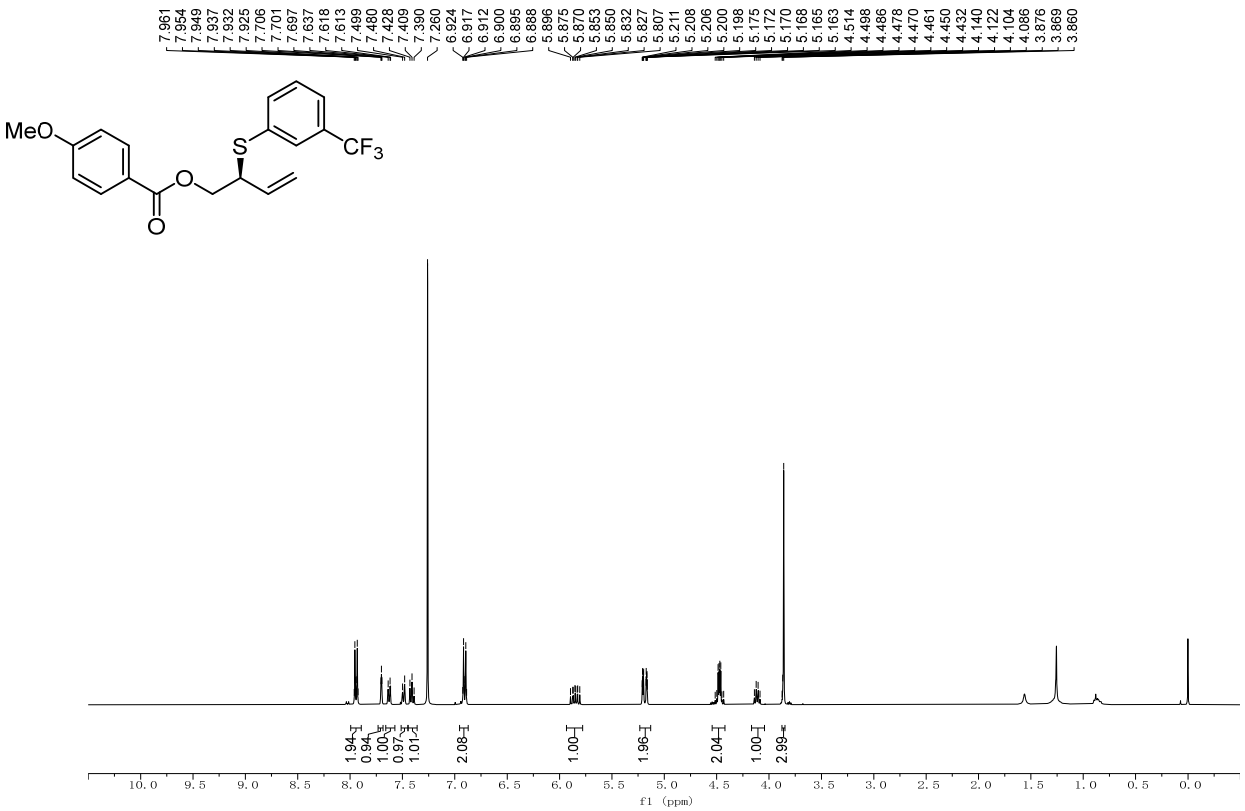
^{13}C NMR (101 MHz, $CDCl_3$) of **3u**



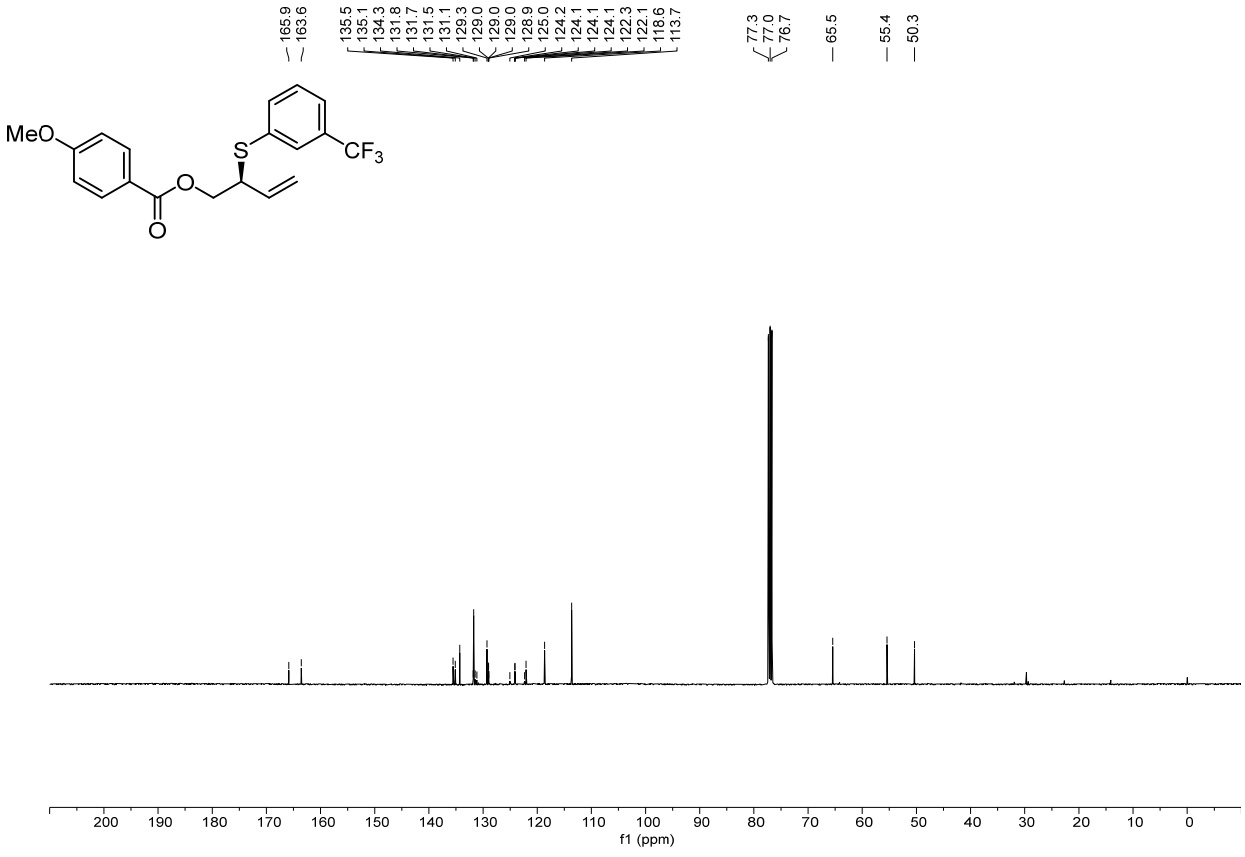
^{1}H NMR (400 MHz, $CDCl_3$) of **3v**



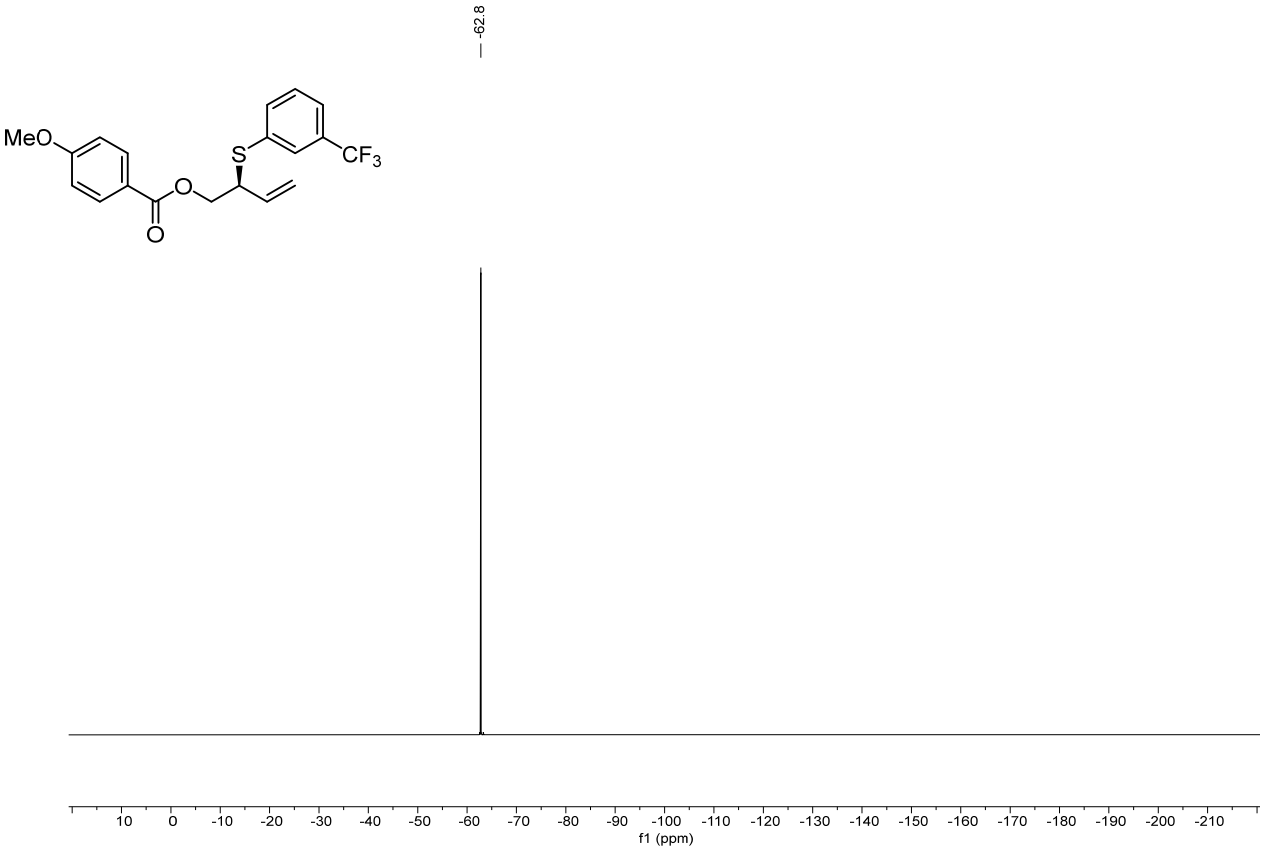
^{13}C NMR (101 MHz, $CDCl_3$) of **3v**



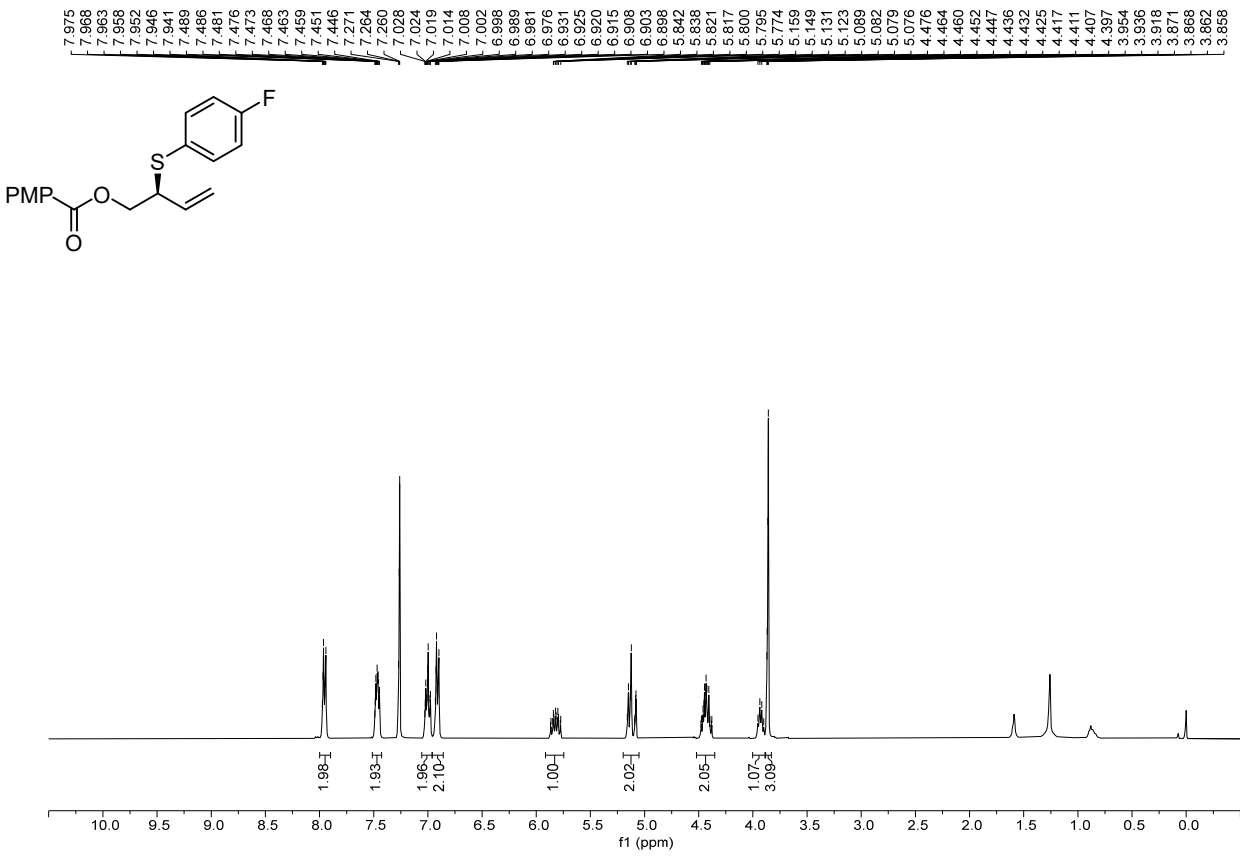
^{1}H NMR (400 MHz, $CDCl_3$) of **3w**



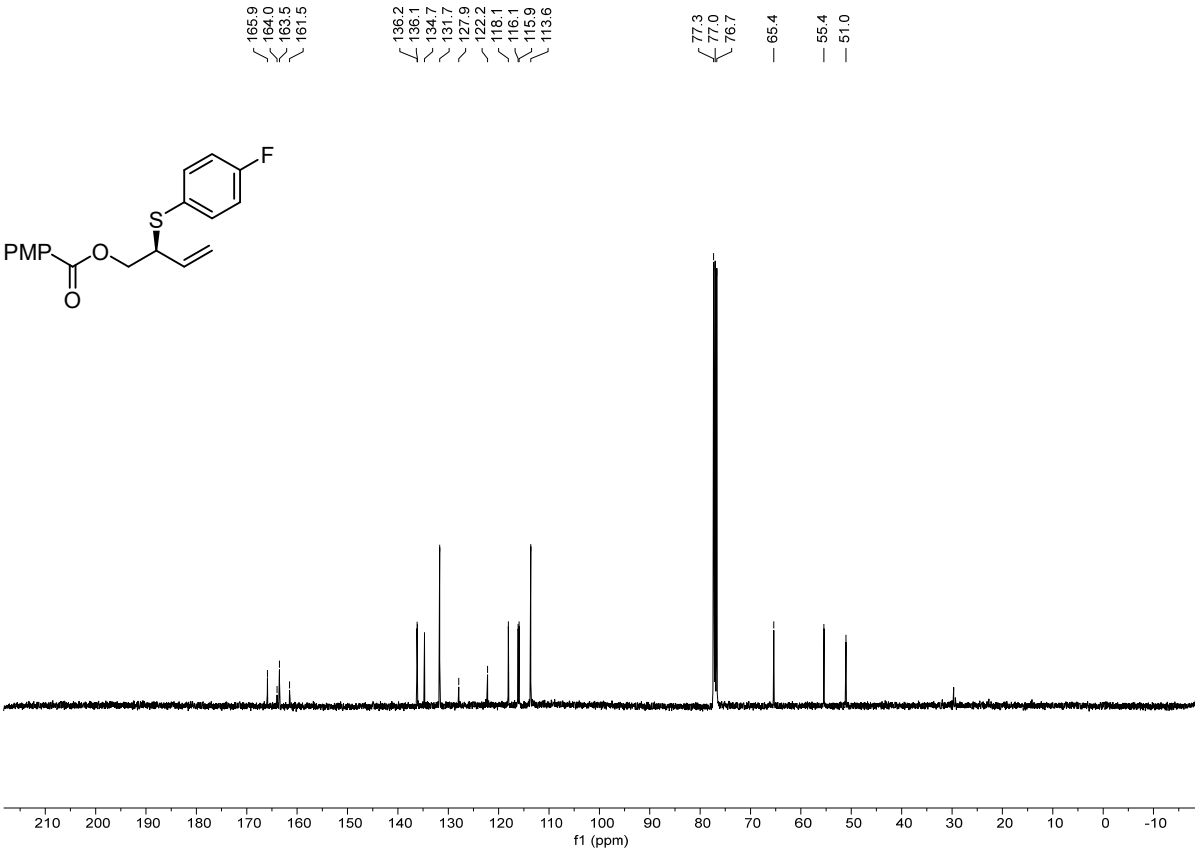
^{13}C NMR (101 MHz, $CDCl_3$) of **3w**



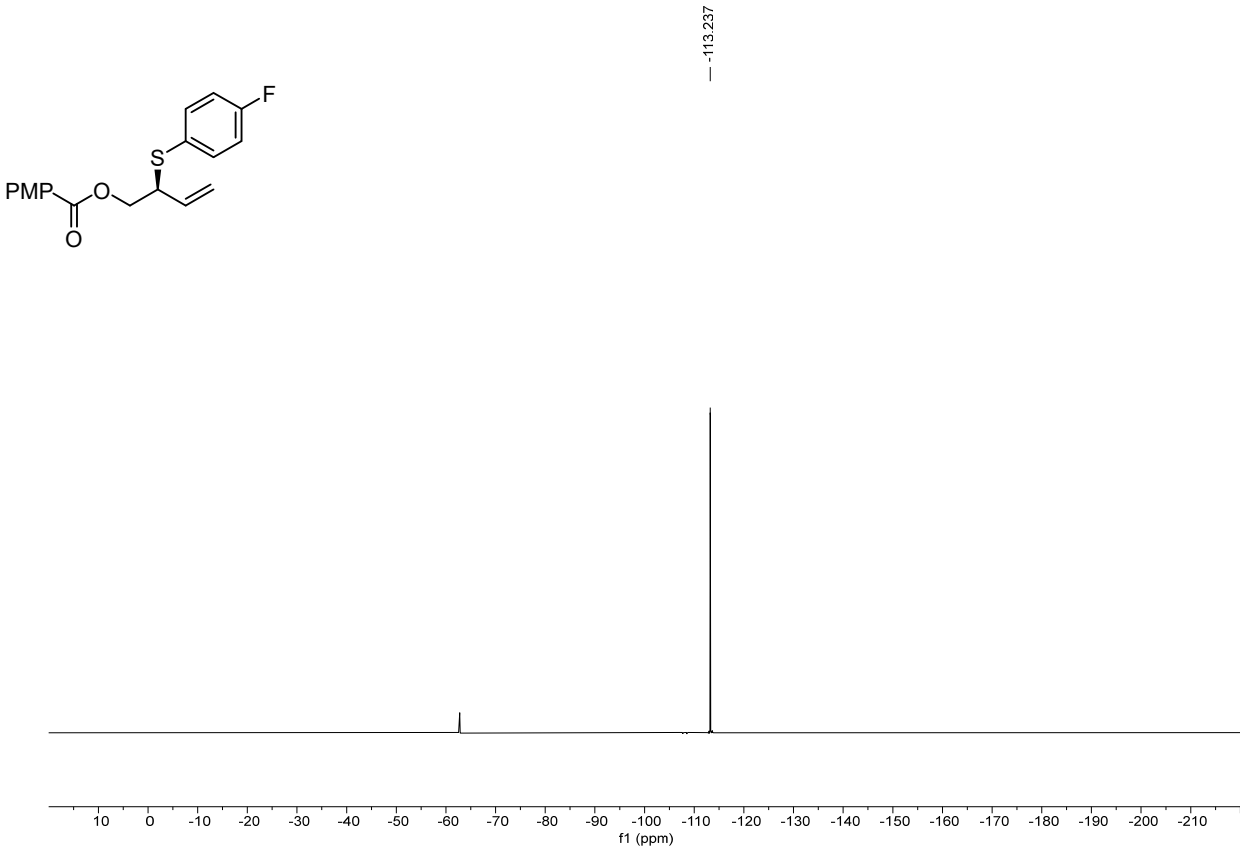
^{19}F NMR (377 MHz, $CDCl_3$) of **3w**



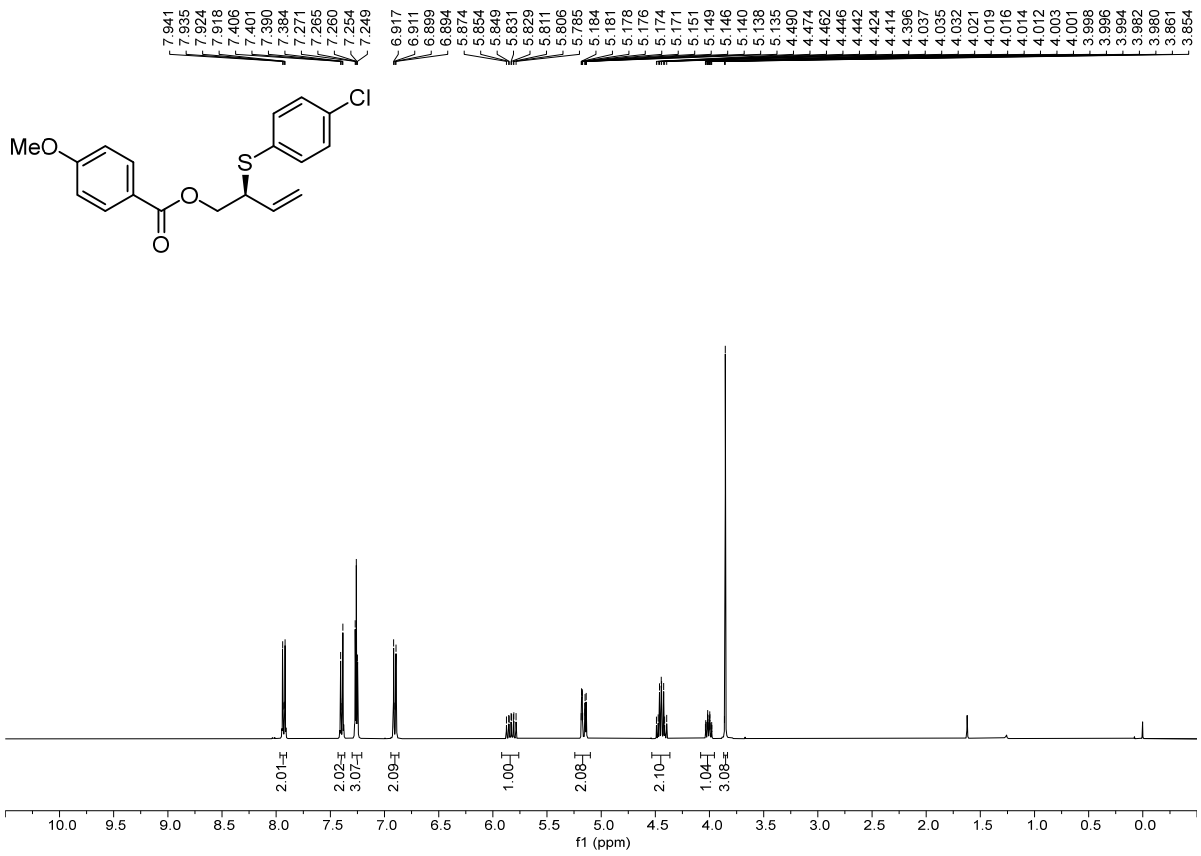
^{1}H NMR (400 MHz, $CDCl_3$) of **3x**



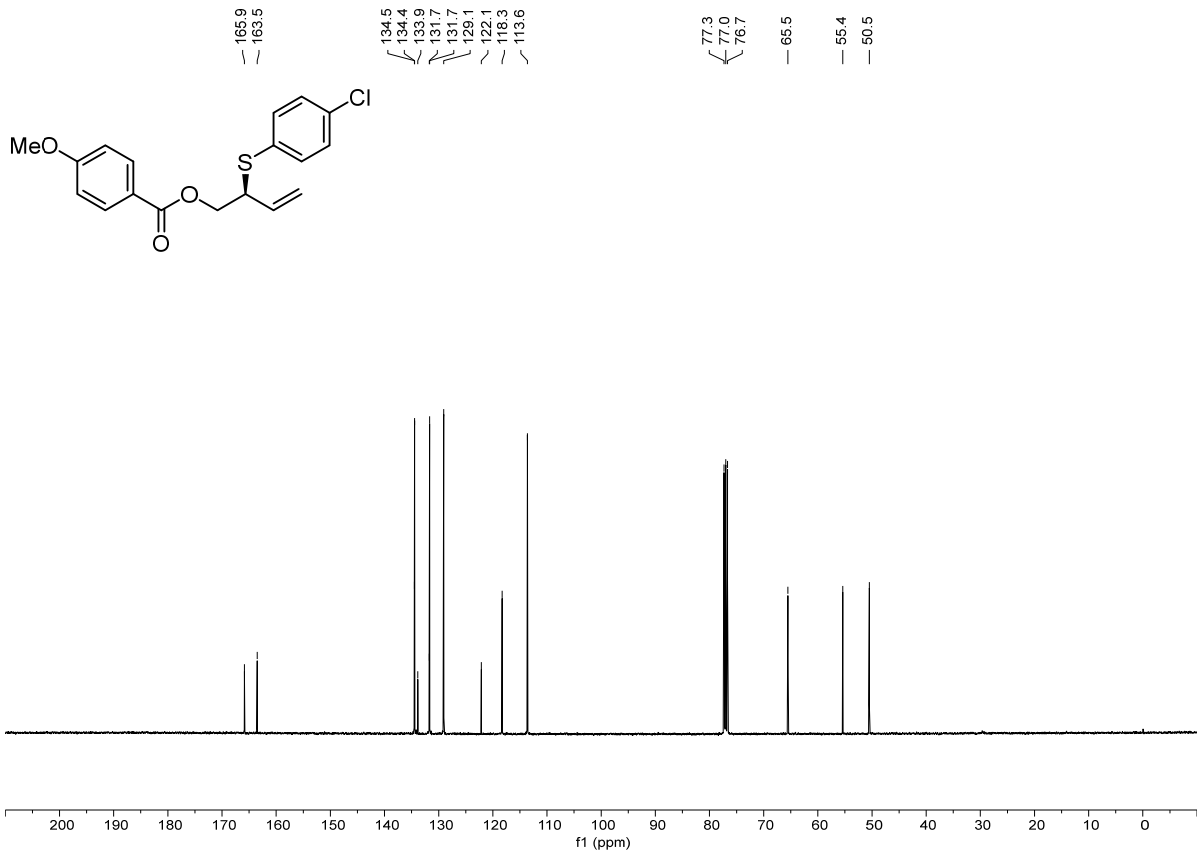
^{13}C NMR (101 MHz, $CDCl_3$) of **3x**



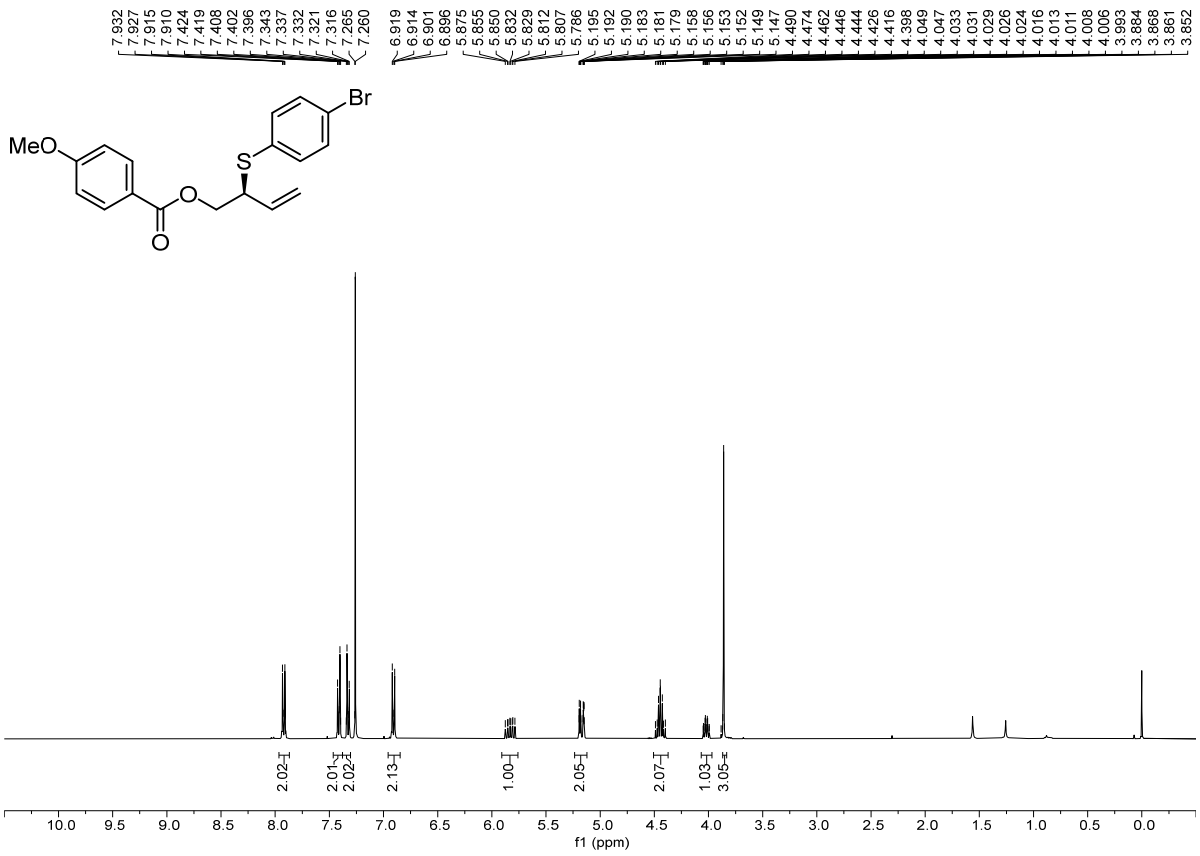
^{19}F NMR (377 MHz, $CDCl_3$) of **3x**



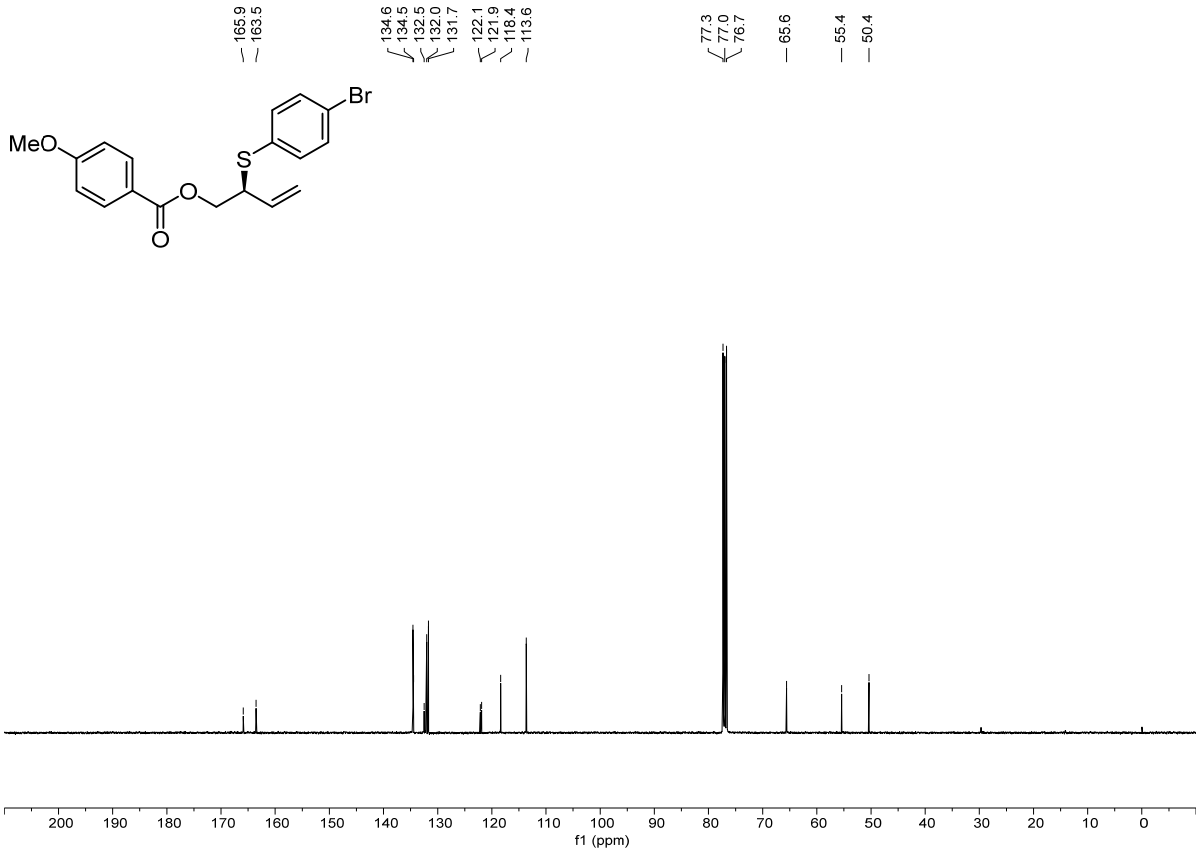
^{1}H NMR (400 MHz, $CDCl_3$) of **3y**



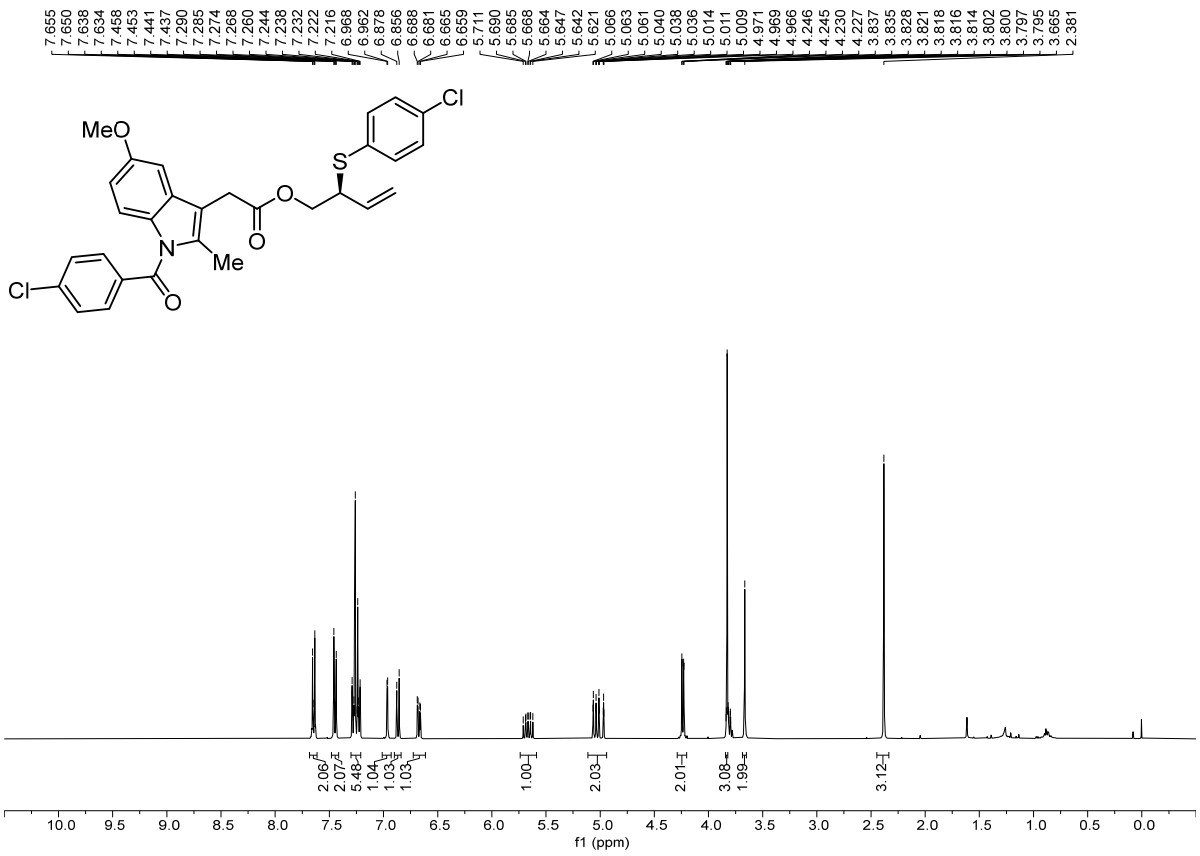
^{13}C NMR (101 MHz, $CDCl_3$) of **3y**



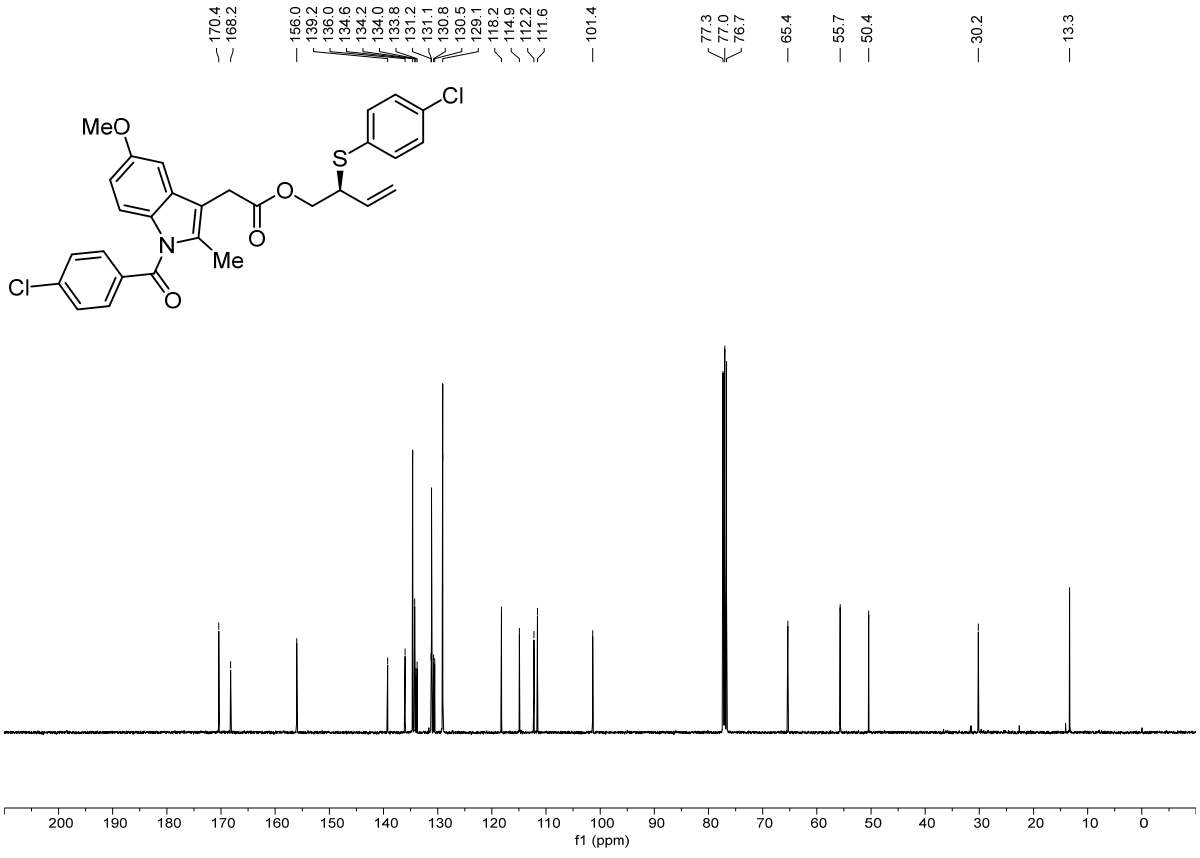
^{1}H NMR (400 MHz, $CDCl_3$) of **3z**



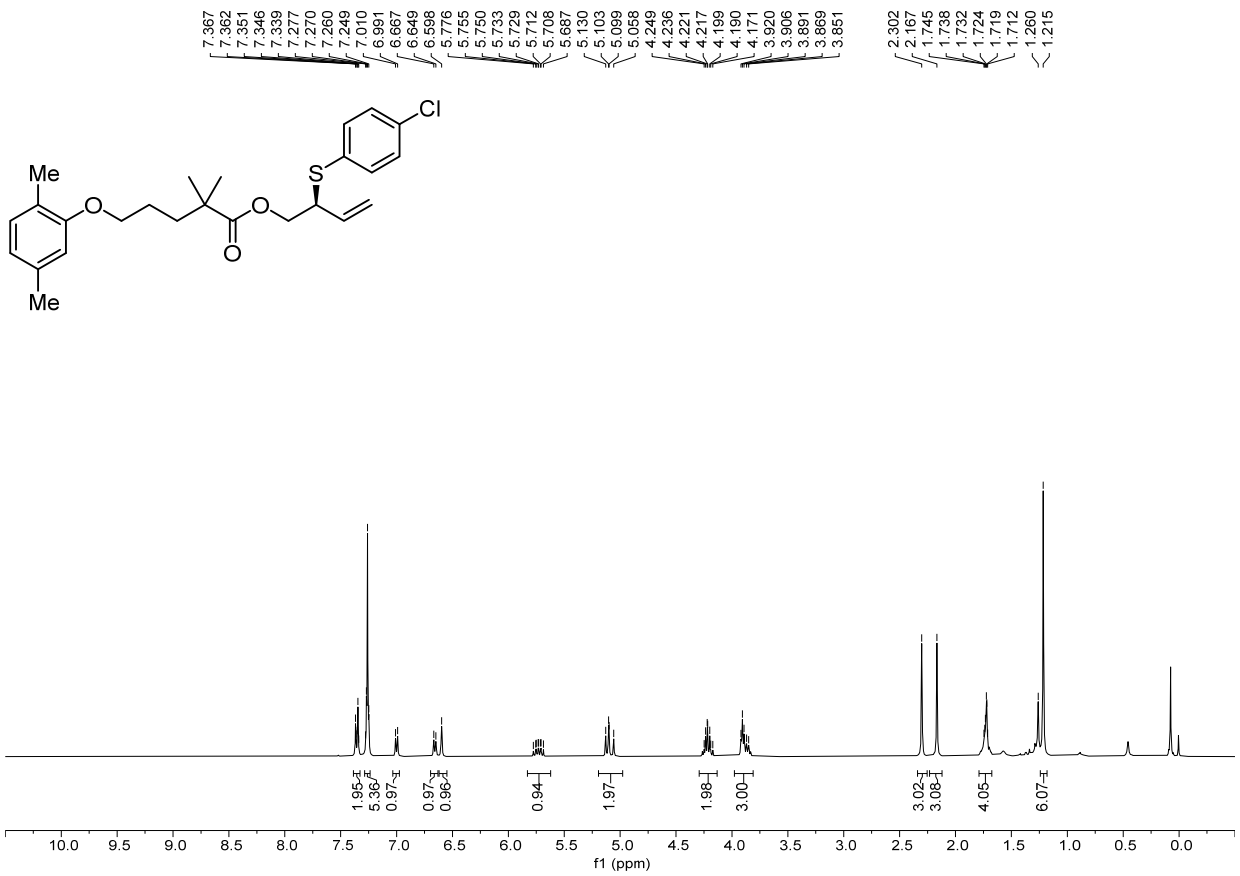
^{13}C NMR (101 MHz, $CDCl_3$) of **3z**



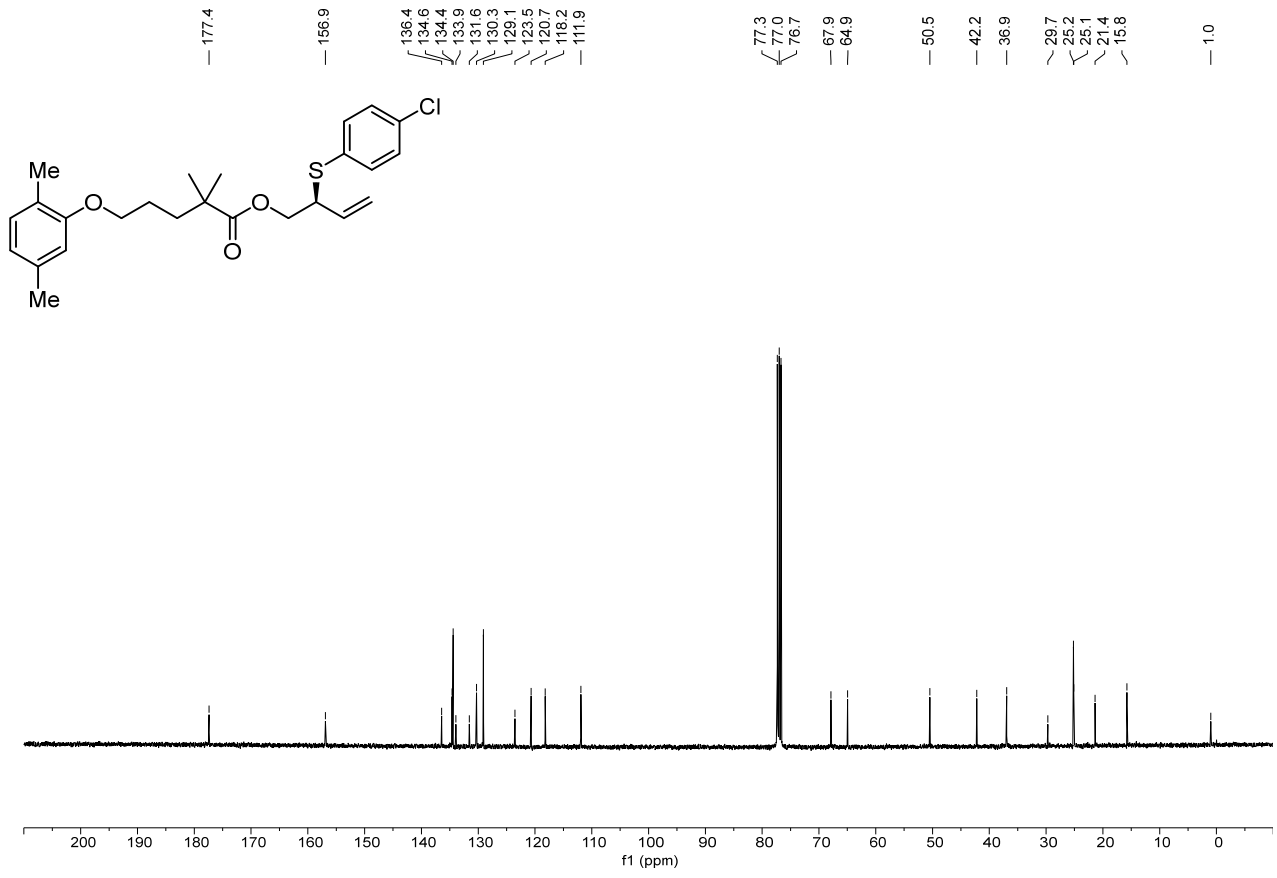
^{1}H NMR (400 MHz, $CDCl_3$) of **3A**



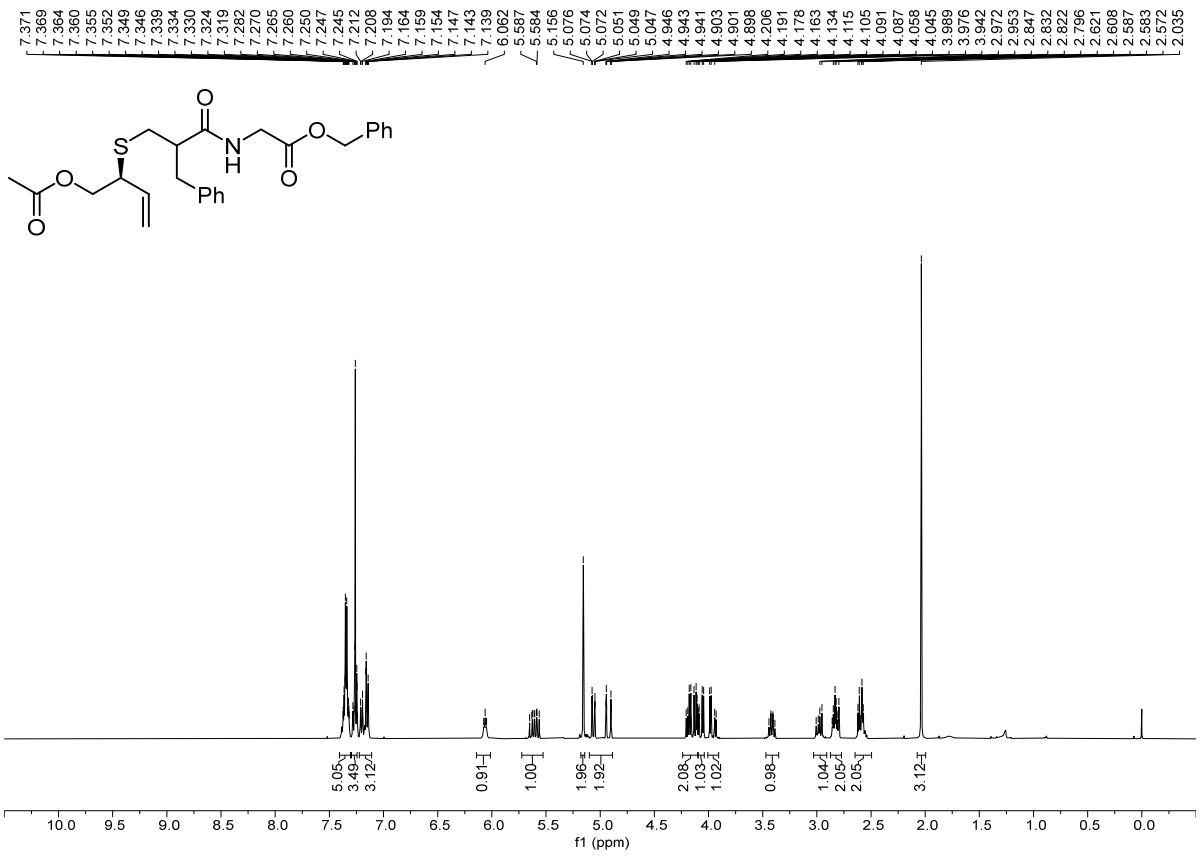
^{13}C NMR (101 MHz, $CDCl_3$) of **3A**



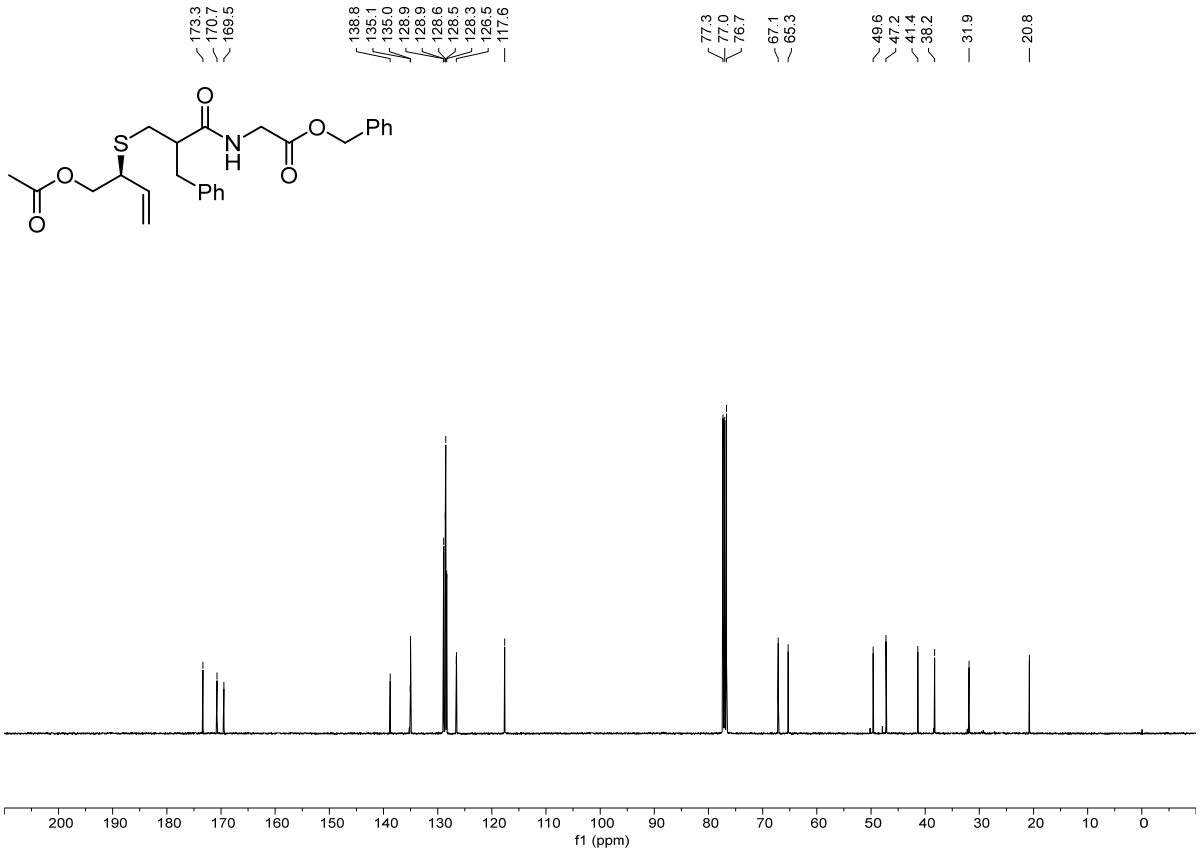
^{1}H NMR (400 MHz, $CDCl_3$) of **3B**



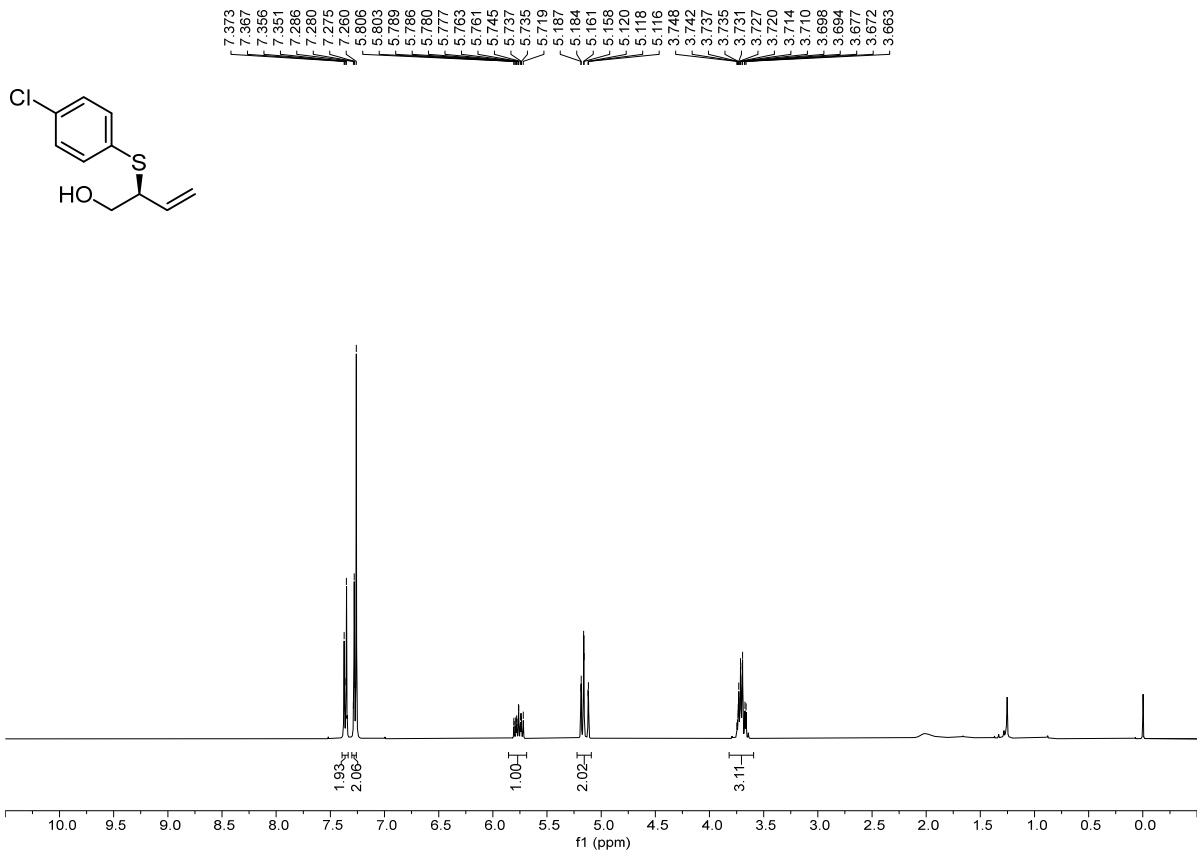
^{13}C NMR (101 MHz, $CDCl_3$) of **3B**



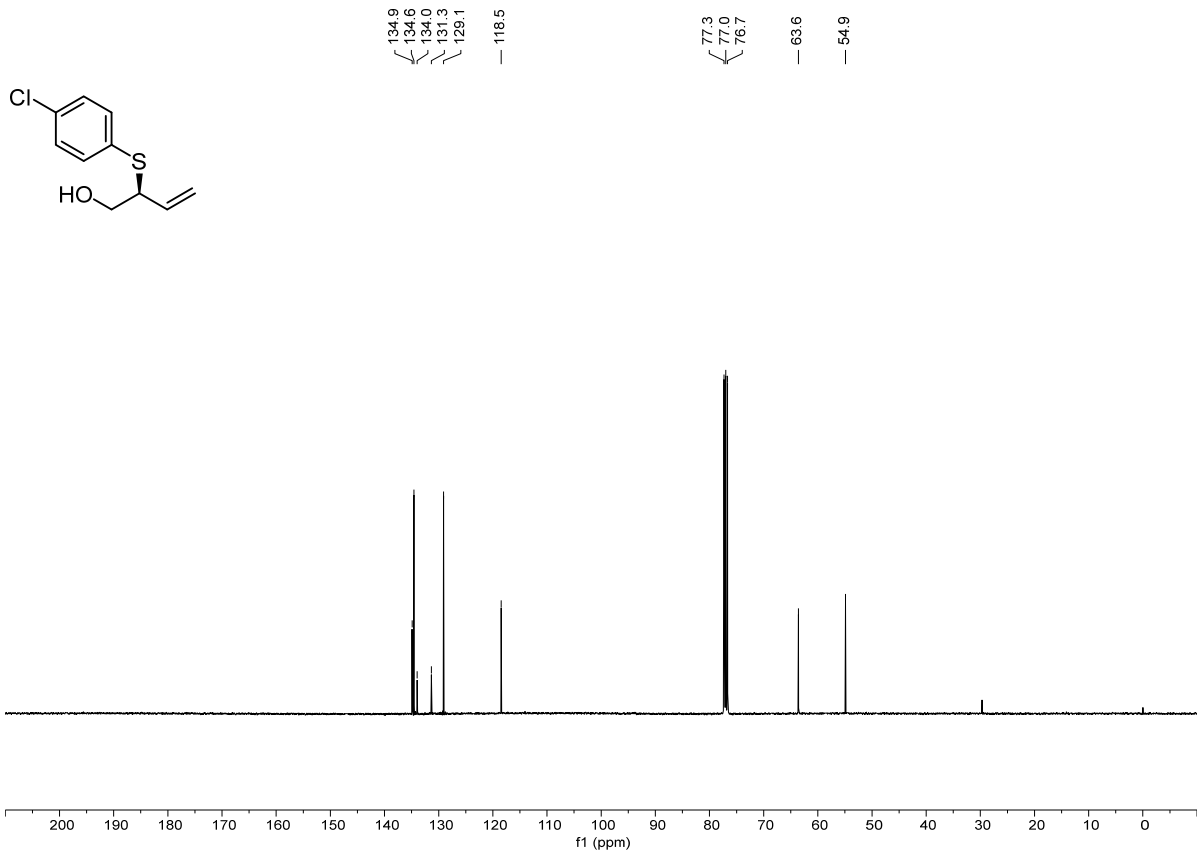
^{1}H NMR (400 MHz, $CDCl_3$) of **3C**



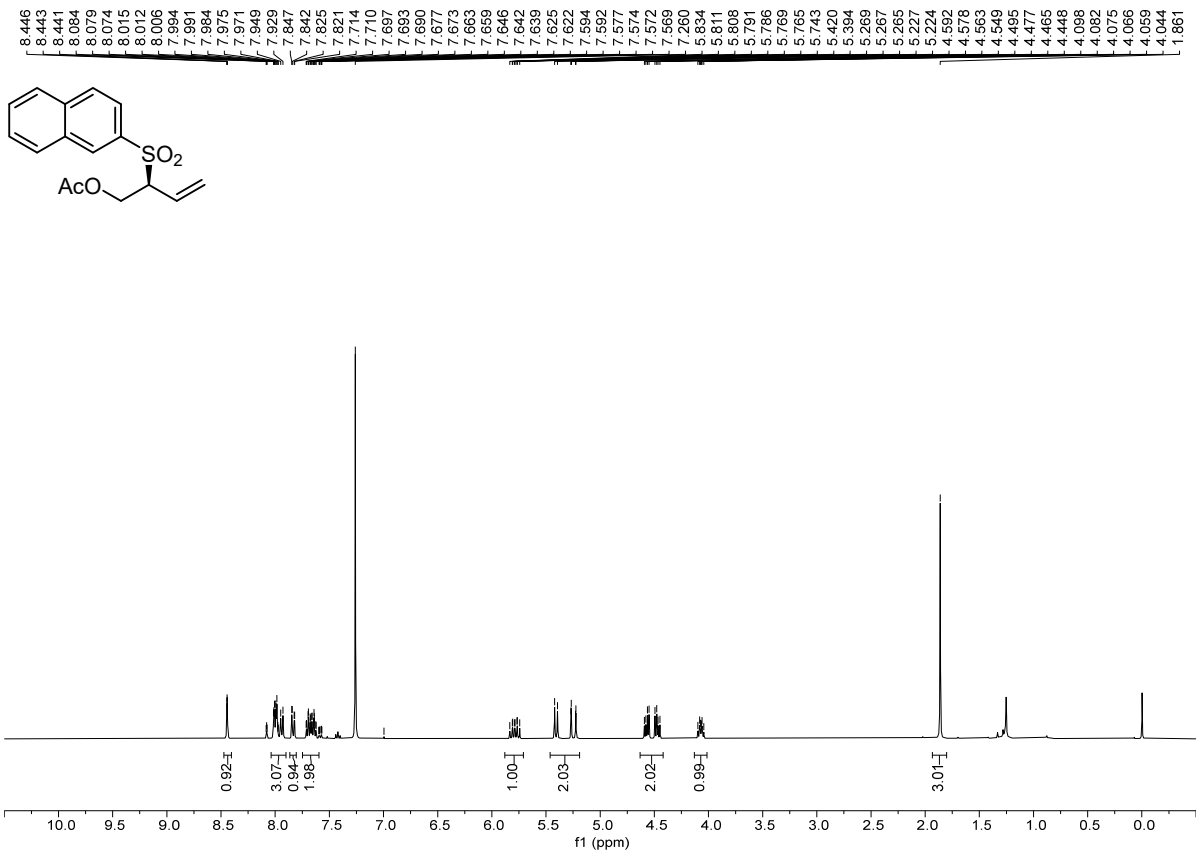
^{13}C NMR (101 MHz, $CDCl_3$) of **3C**



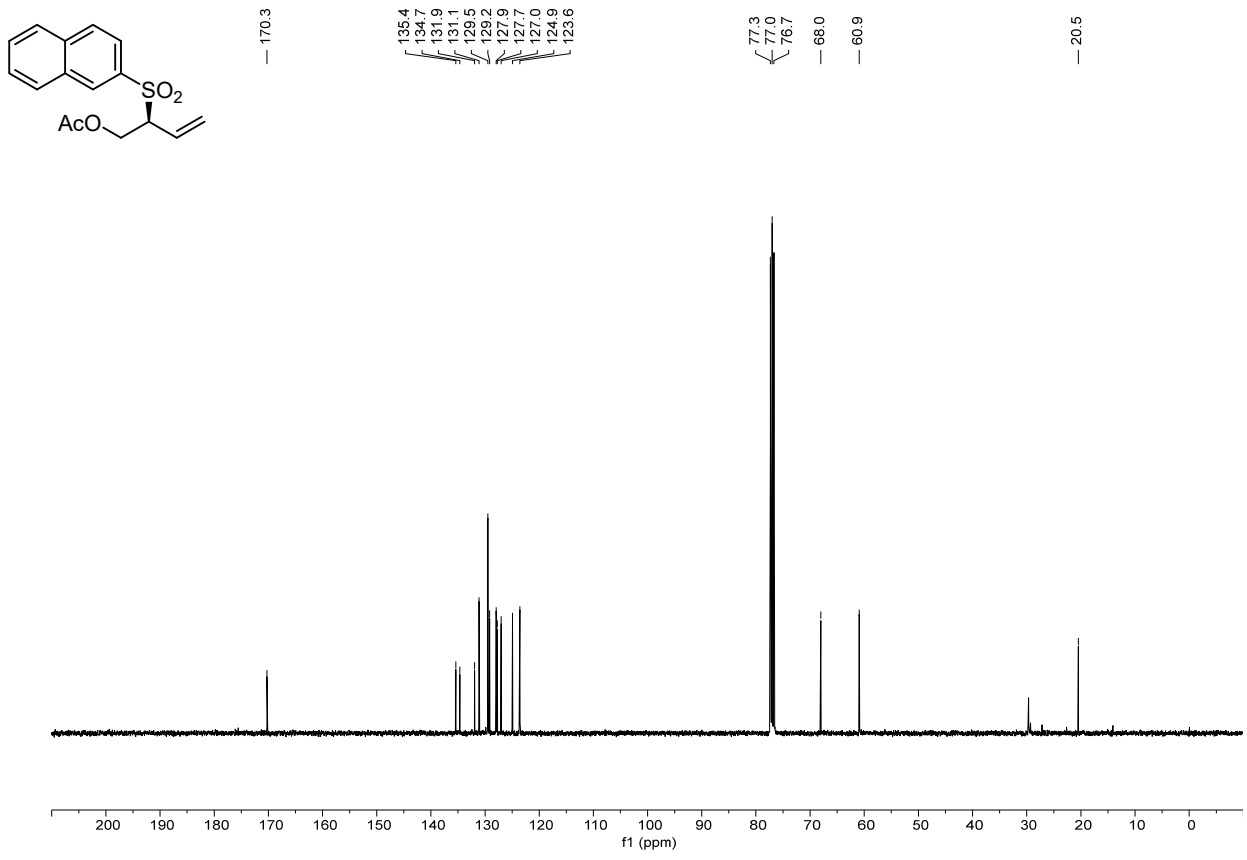
^{1}H NMR (400 MHz, $CDCl_3$) of **4**



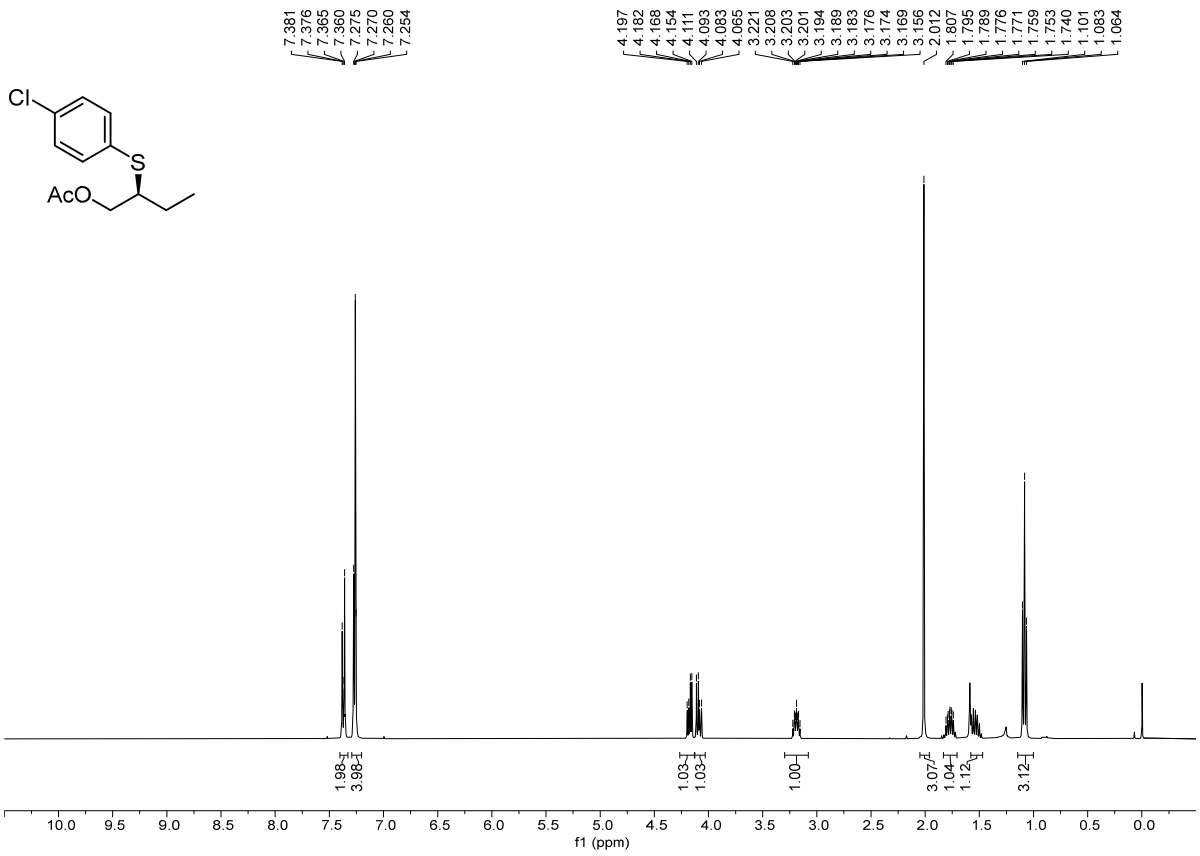
^{13}C NMR (101 MHz, $CDCl_3$) of **4**



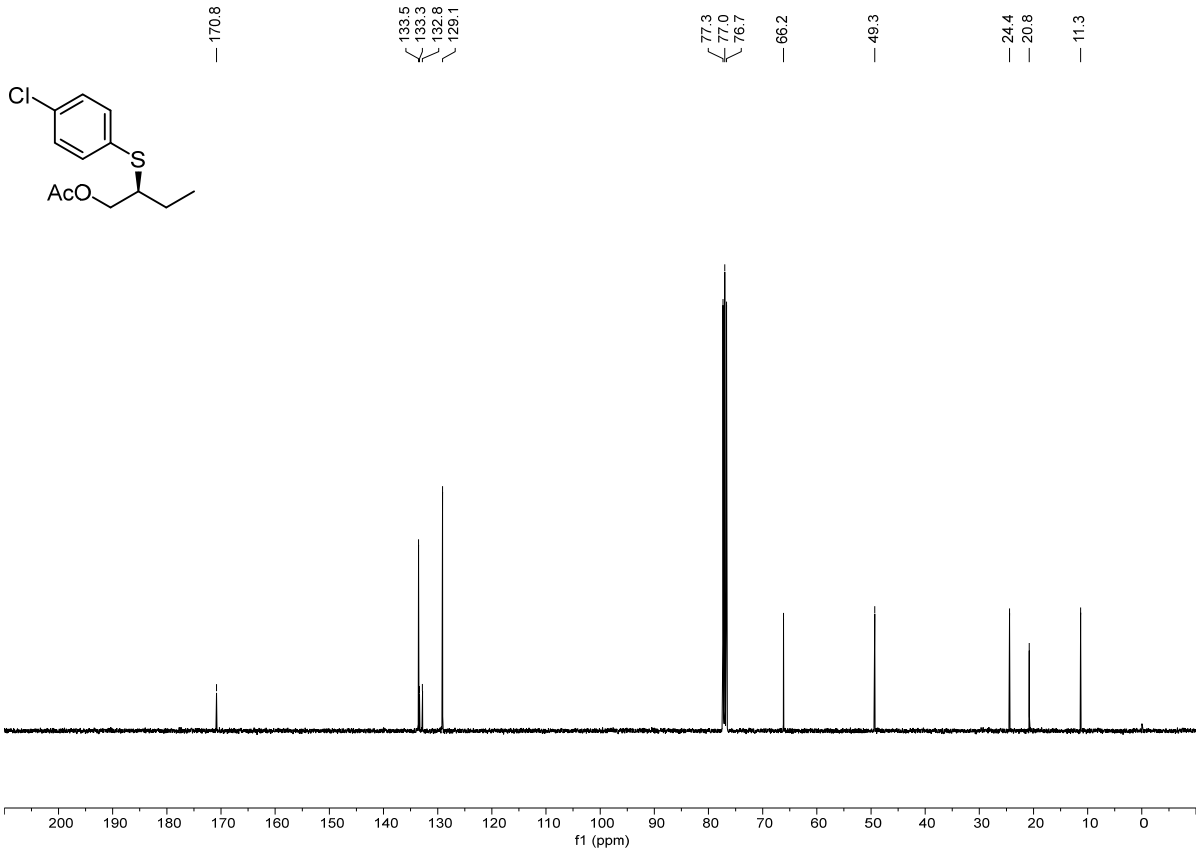
^{1}H NMR (400 MHz, $CDCl_3$) of **5**



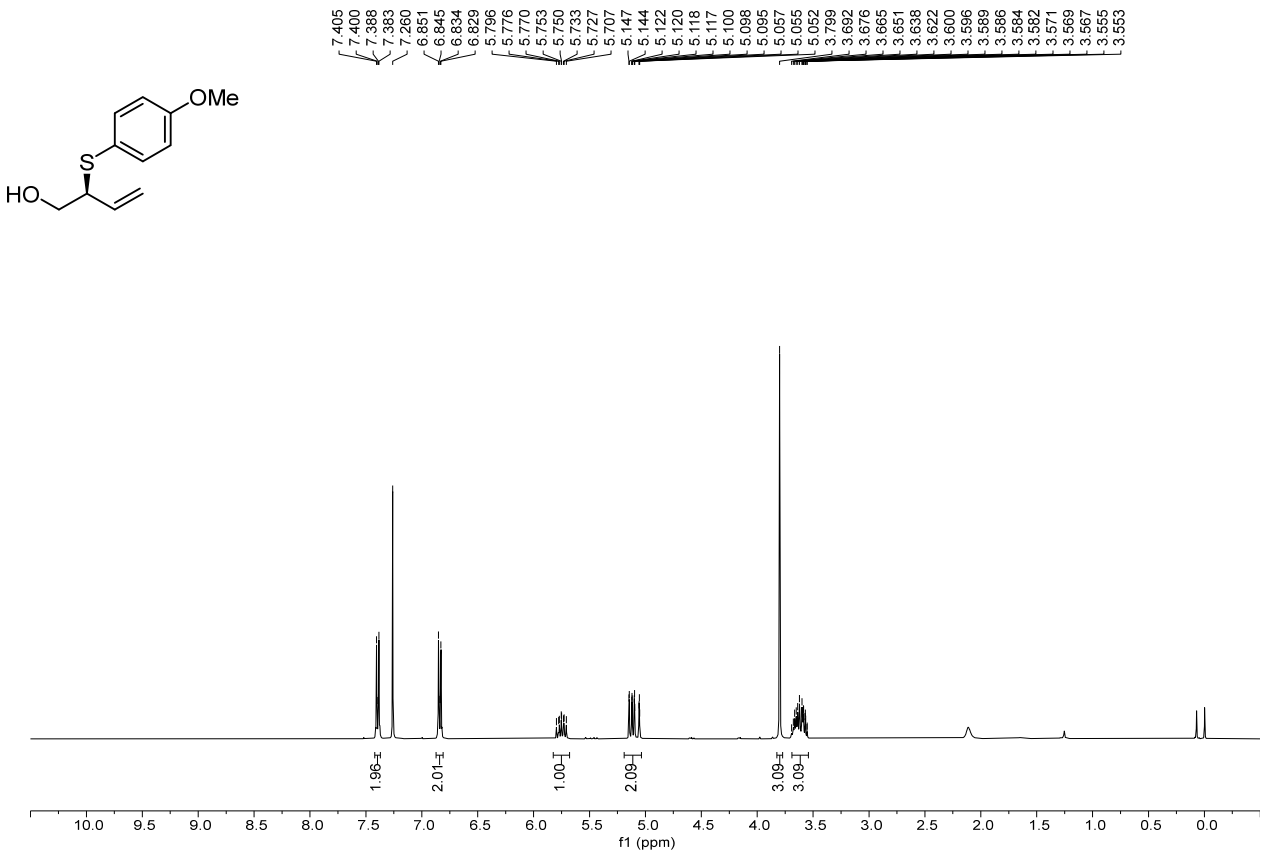
^{13}C NMR (101 MHz, $CDCl_3$) of **5**



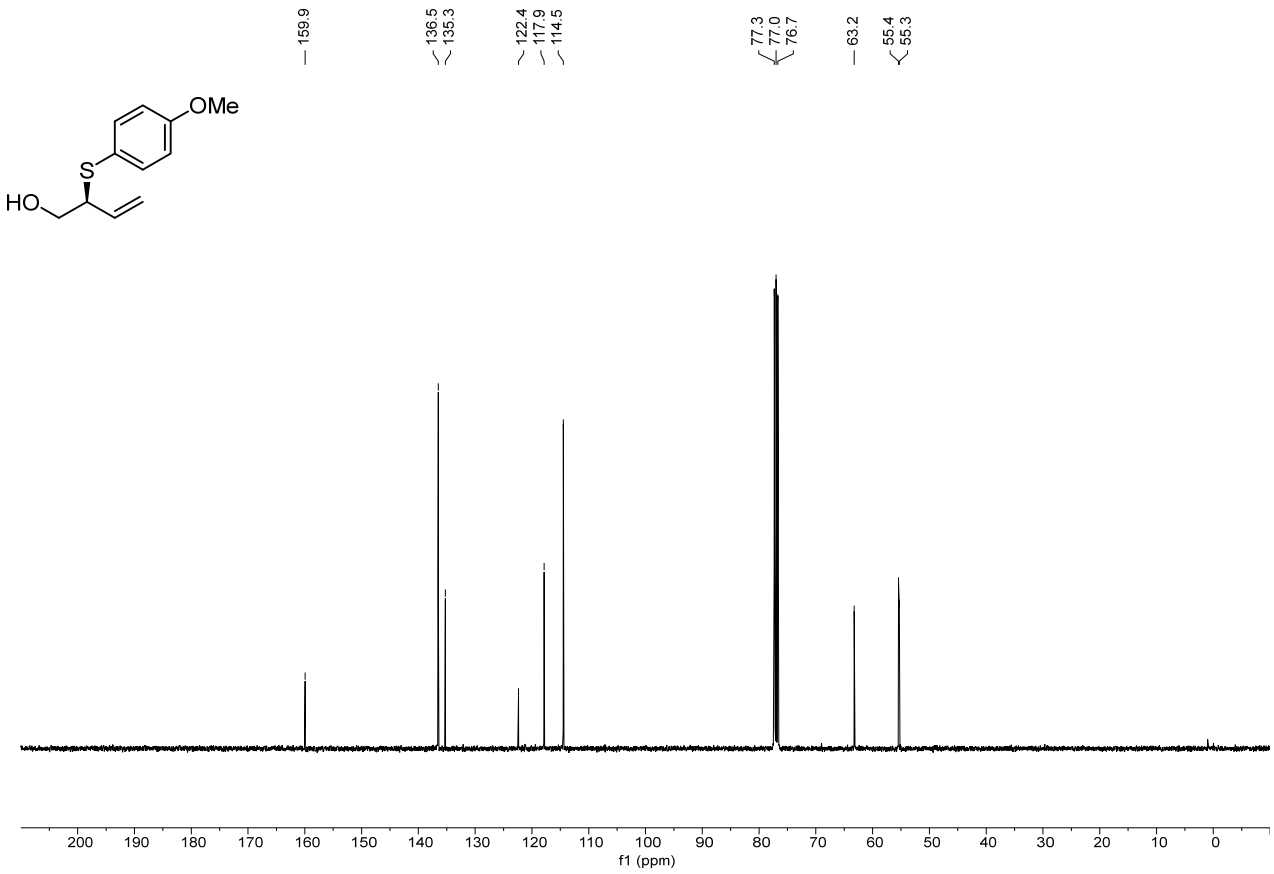
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



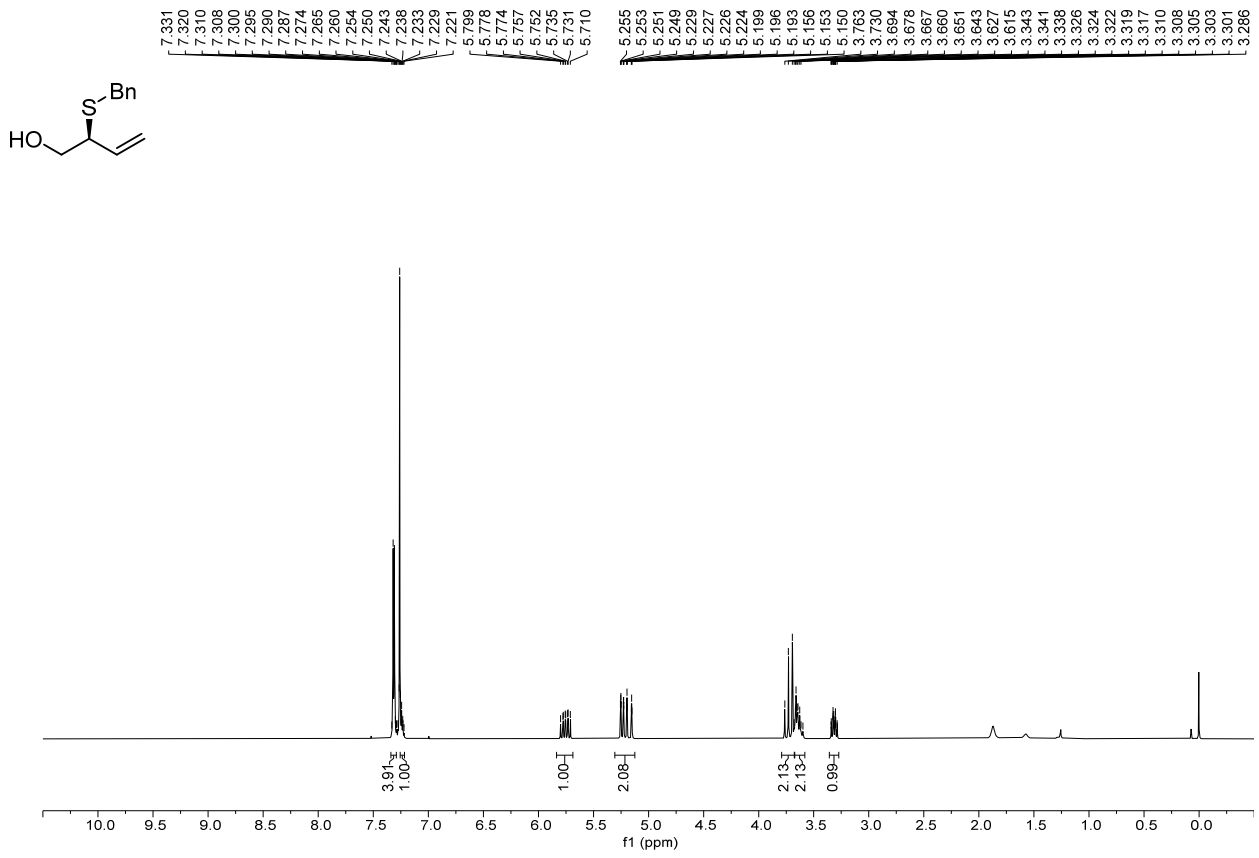
^{13}C NMR (101 MHz, $CDCl_3$) of **6**



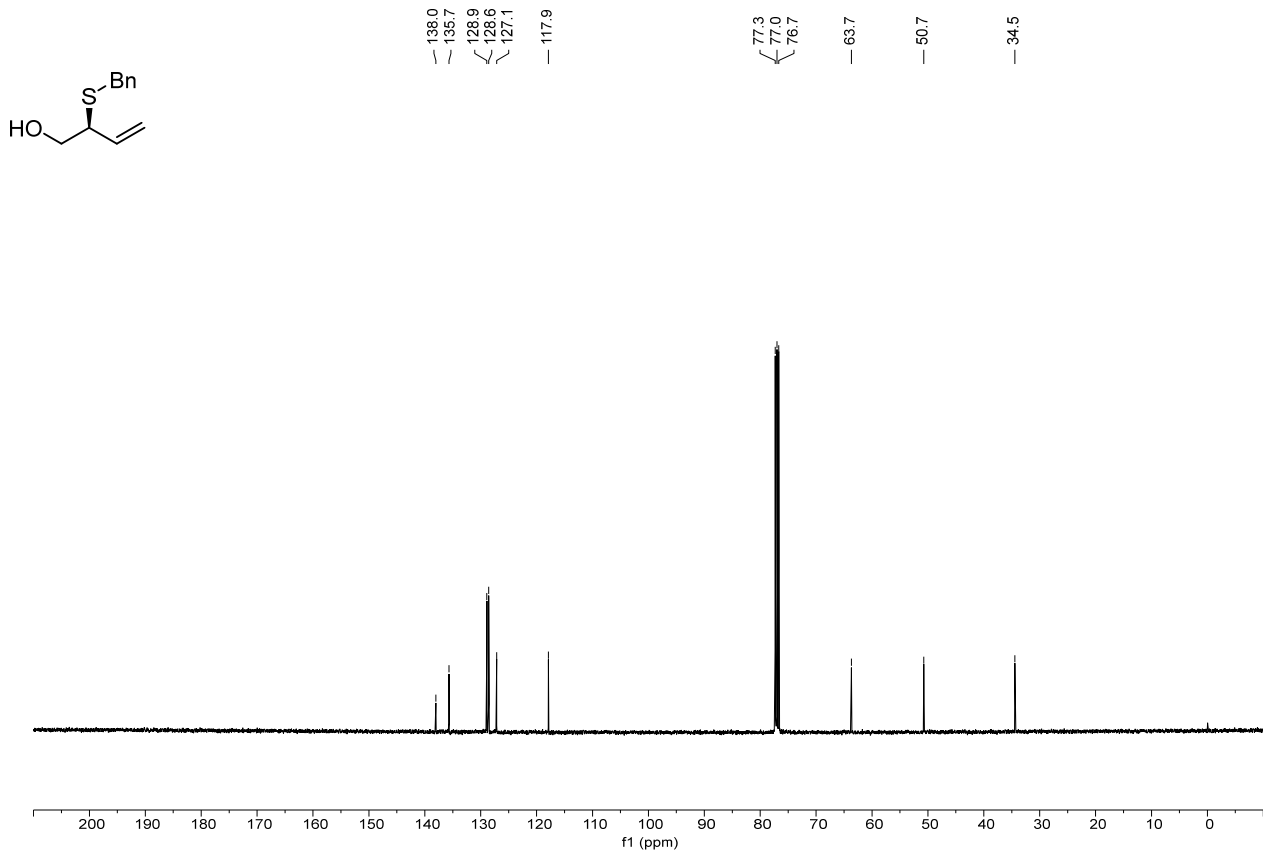
^{1}H NMR (400 MHz, $CDCl_3$) of **8**



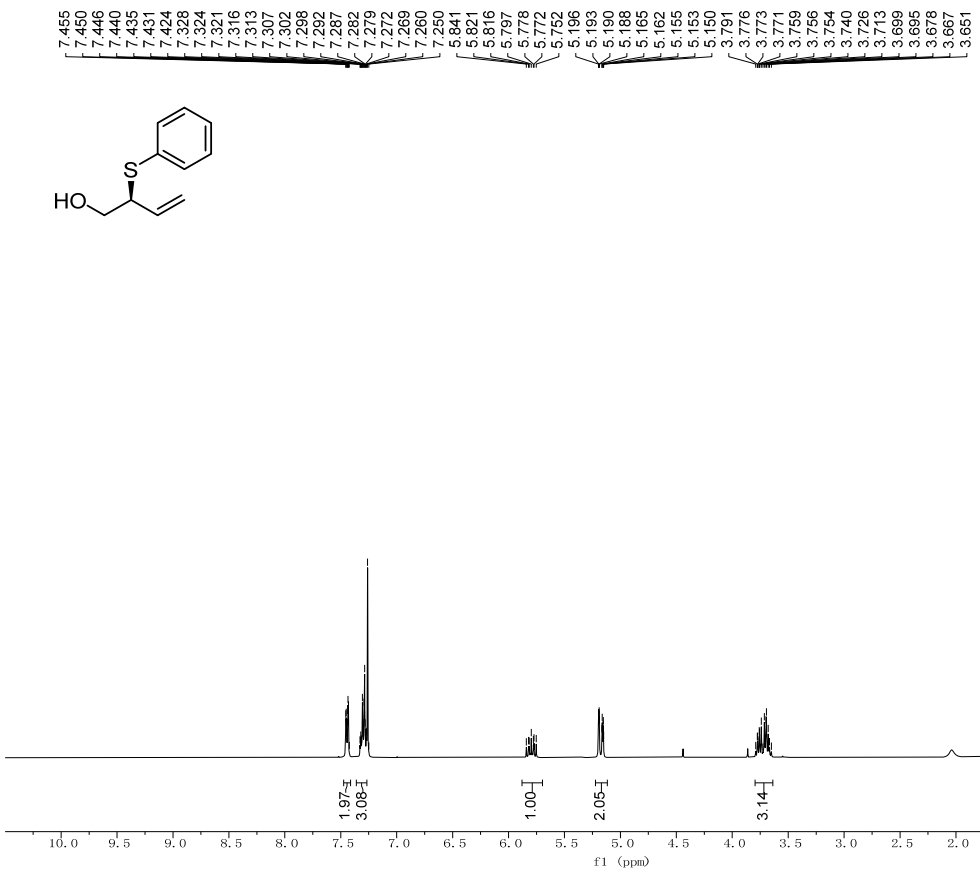
^{13}C NMR (101 MHz, $CDCl_3$) of **8**



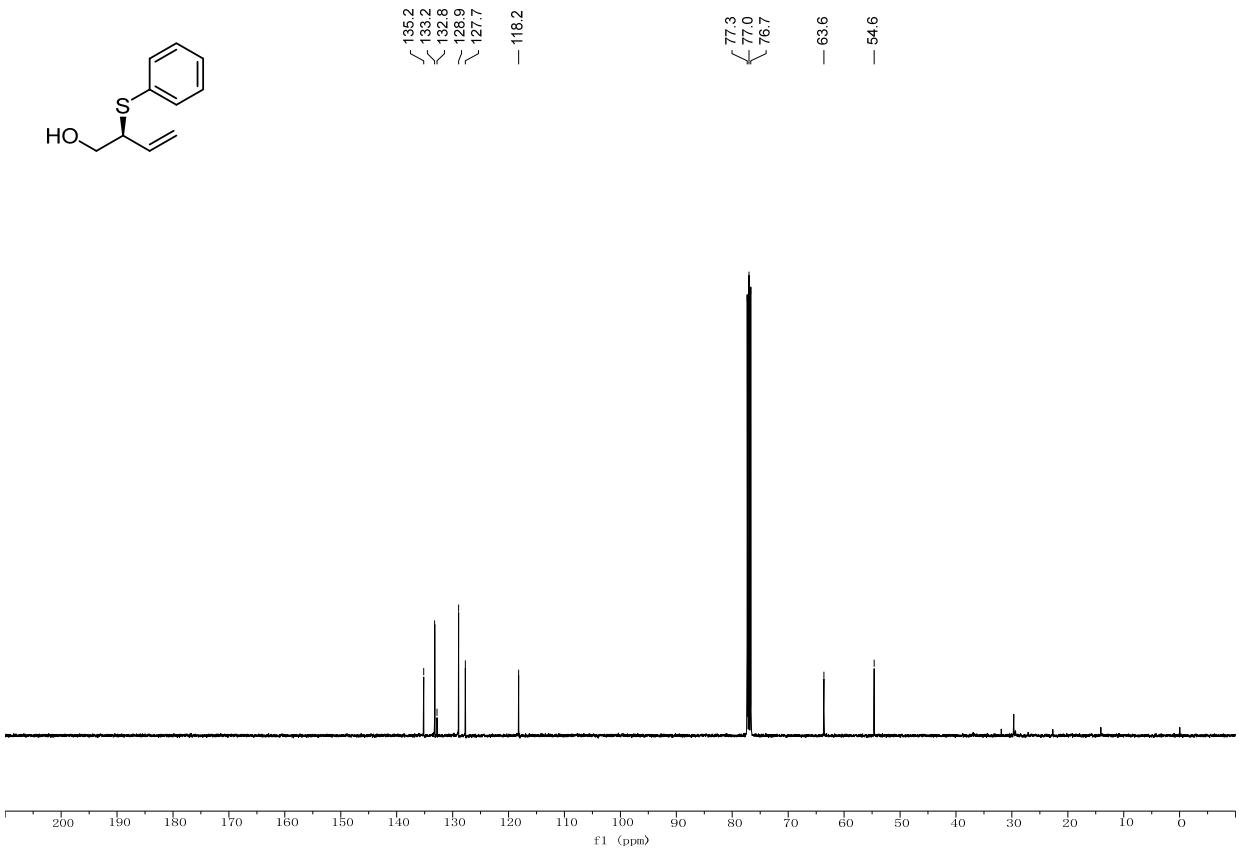
^{1}H NMR (400 MHz, $CDCl_3$) of **10**



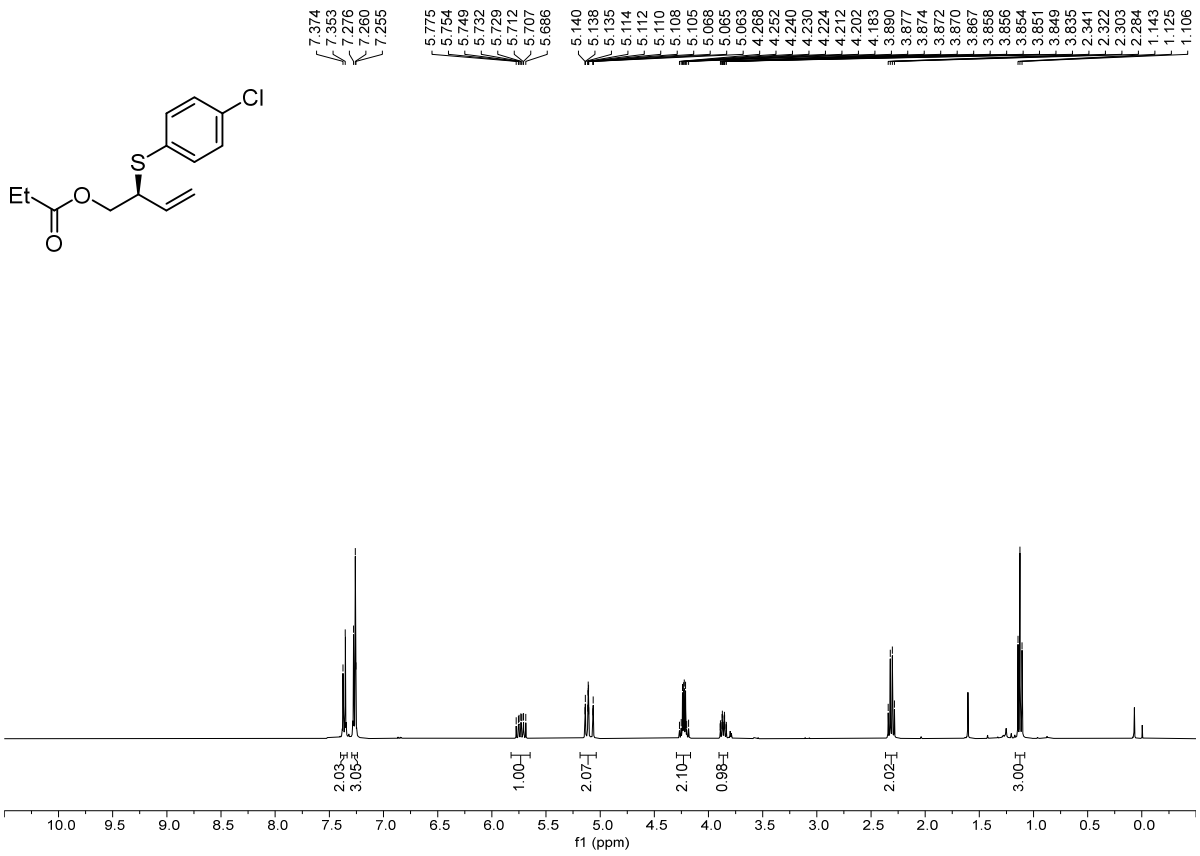
^{13}C NMR (101 MHz, $CDCl_3$) of **10**



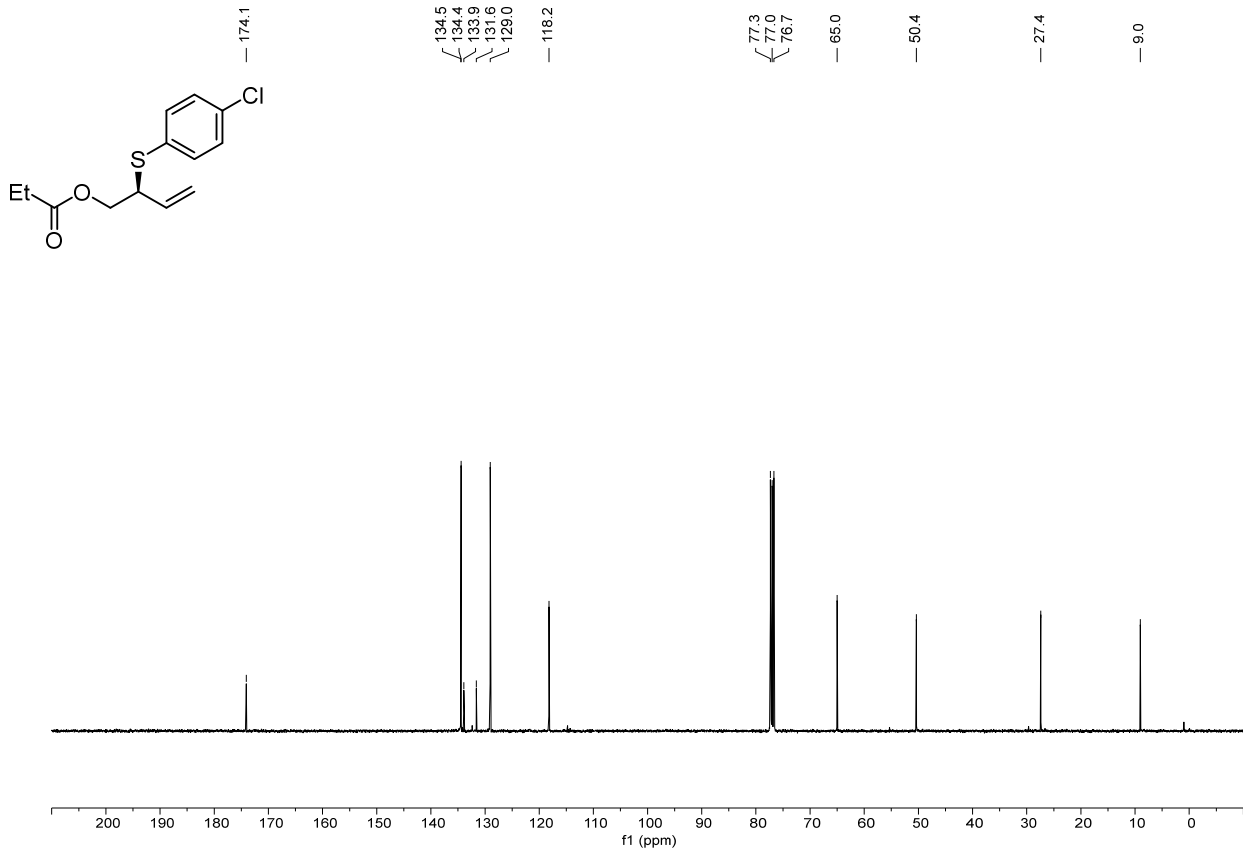
^{1}H NMR (400 MHz, $CDCl_3$) of **12**



^{13}C NMR (101 MHz, $CDCl_3$) of **12**



^{1}H NMR (400 MHz, $CDCl_3$) of **3ra**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ra**