Iodine-Enabled Organoelectrocatalysis: Enantioselective Cross Dehydrogenative Coupling of Sulfides and Aldehydes

Zhen Wang, Marcel Gausmann, Jan-Hendrik Dickoff and Mathias Christmann*

*M. Sc. Z. Wang, M. Sc. M. Gausmann, M. Sc. J. -H. Dickoff, Prof. Dr. M. Christmann Freie Universität Berlin Institute of Chemistry and Biochemistry Takustr. 3, 14195 Berlin (Germany) E-mail: mathias.christmann@fu-berlin.de

Table of Contents

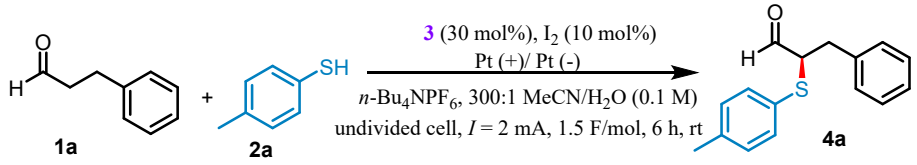
1. General information

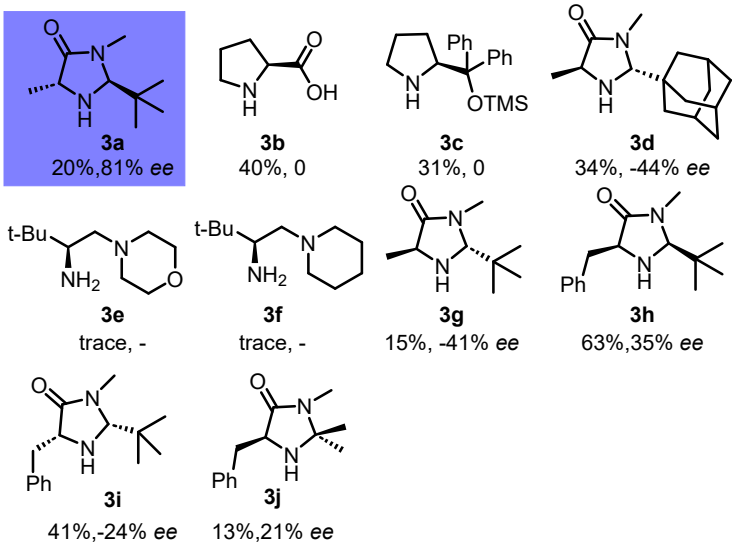
All the electrochemical reactions were performed in an undivided cell equipped with two Pt electrodes (1.0 × 1.0 cm^2) unless otherwise noted. Room temperature (rt) refers to 23 °C. Solvents such as THF, MeCN and DMF were purchased from Fischer Scientific. Products were purified by flash column chromatography on silica gel 60 M (0.040-0.063 mm, 230-400 mesh, *Macherey-Nagel*). As eluents, cyclohexane (99.5%+ quality) and EtOAc (HPLC grade) were used. Visualization of spots on TLC plate was accomplished with UV light (254 nm) or phosphomolybdic acid stain (5 g phosphomolybdic acid in 100 mL ethanol). All commercial reagents were purchased from Acros, TCI, Sigma-Aldrich. They were used without further purification unless specified.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 700 (700 MHz), *JEOL* ECZ600 S (600 MHz), *JEOL* (ECX 400, Eclipse 500) and *Bruker* Avance 500 (500 MHz) spectrometers. All ^{1}H NMR and ^{13}C NMR chemical shifts were reported in ppm relative the corresponding residual solvent signal ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). NMR yields were determined using dibromomethane as an internal standard. Reported integrals are in accordance with assignments; coupling constants (*J*) are given in Hz. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), etc. Cyclic voltammetry was performed on an Interface 1010 B Potentiostat/Galvanostat/ZRA from *Gamry Instruments*. The measurements were performed in anhydrous and oxygen free solvents under argon atmosphere. Platinum wires were used as working-, counter-, and quasi-reference electrodes. High resolution mass spectrometry (HRMS) was performed on a *Finnigan* MA T 95 (EI), *Bruker* APEX III FTMS (ESI) or *Agilent* 6210 (ESI). Enantiomeric ratios were determined by chiral HPLC (Agilent Series 1200 with DAD) on a chiral column.

2. Optimization details

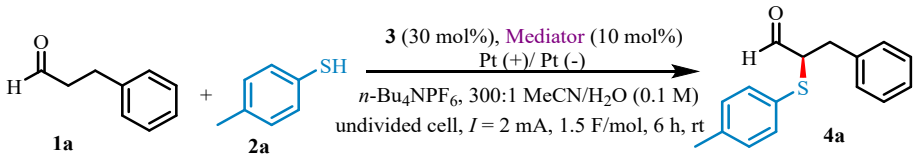
Table S1 Screening of organocatalyst[a, b]

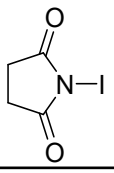




[a]Reaction conditions: **1a** (0.90 mmol, 3.00 equiv.), **2a** (0.30 mmol, 1.00 equiv.), **3** (30 mol%), I_2 (10 mol%), *n*-Bu_4NPF_6 (0.2 M), MeCN (3 mL) and H_2O (10 μL) in an undivided cell with two platinum electrodes (each 1.0 × 1.0 cm^2) under 2 mA at room temperature for 6 h. [b]Yields were determined by ^1H NMR analysis with CH_2Br_2 as an internal standard. The product was reduced by $NaBH_4$ to the corresponding alcohol and its enantioselectivities were determined by chiral HPLC analysis.

Table S2 Screening of mediator [a, b]

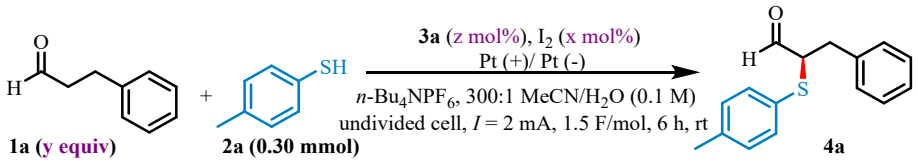


Entry	**Mediator**	Yield (%)	*ee*[b] (%)
1	**I_2**	**63**	**83**
2	NaI	30	25
3		7	-

[a]Reaction conditions: **1a** (0.90 mmol, 3.00 equiv.), **2a** (0.30 mmol, 1.00 equiv.), **3** (30 mol%), mediatior (10 mol%), *n*-Bu_4NPF_6 (0.2 M), MeCN (3 mL) and H_2O (10 μL) in an undivided cell with two platinum electrodes (each 1.0 × 1.0 cm^2) under 2 mA at

room temperature for 6 h. [b]Yields were determined by ^{1}H NMR analysis with CH_2Br_2 as an internal standard. The product was reduced by $NaBH_4$ to the corresponding alcohol and its enantioselectivities were determined by chiral HPLC analysis.

Table S3 Screening the amount of 1a, I_2, and organocatalyst[a, b]

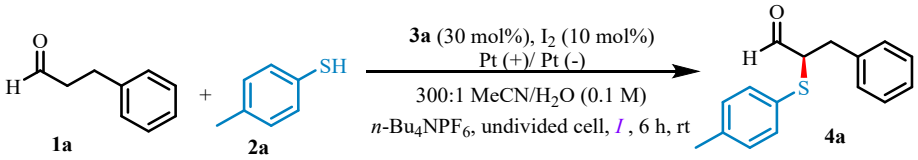


1a (y equiv) **2a (0.30 mmol)** **4a**

Entry	**1a (y equiv.)**	**I_2 (x mol%)**	**3a (z mol%)**	Yield (%)	*ee*[b] (%)
1	1.5	10	30	45	81
2	**3**	**10**	**30**	**63**	**83**
3	5	10	30	66	83
4	3	20	30	trace	-
5	3	100	30	0	-
6	3	5	30	21	45
7	3	1	30	16	53
8	3	10	20	21	48
9	3	10	10	10	54

[a]Reaction conditions: **1a** (y equiv.), **2a** (0.30 mmol, 1.00 equiv.), **3** (z mol%), I_2 (x mol%), *n*-Bu_4NPF_6 (0.2 M), MeCN (3 mL) and H_2O (10 μL) in an undivided cell with two platinum electrodes (each 1.0 × 1.0 cm^2) under 2 mA at room temperature for 6 h. [b]Yields were determined by ^{1}H NMR analysis with CH_2Br_2 as an internal standard. The product was reduced by $NaBH_4$ to the corresponding alcohol and its enantioselectivities were determined by chiral HPLC analysis.

Table S4 Screening of current[a, b]

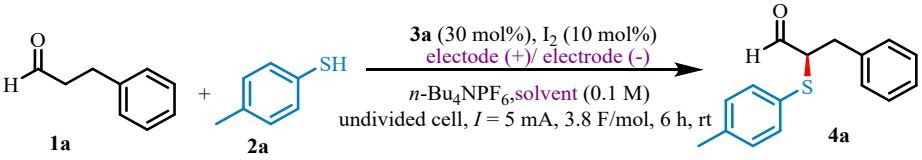


1a **2a** **4a**

Entry	**Current (mA)**	Yield of **4a** (%)	*ee*[b] (%)
1	4	63	54
2	**5**	**84**	**85**
3	6	52	74
4	8	55	34

[a]Reaction conditions: **1a** (0.90 mmol, 3.00 equiv.), **2a** (0.30 mmol, 1.00 equiv.), **3** (30 mol%), I_2 (10 mol%), *n*-Bu_4NPF_6 (0.2 M), MeCN (3 mL) and H_2O (10 μL) in an undivided cell with two platinum electrodes (each 1.0 × 1.0 cm^2) electrolysis under the corresponding current at room temperature for 6 h. [b]Yields were determined by ^{1}H NMR analysis with CH_2Br_2 as an internal standard. The product was reduced by $NaBH_4$ to the corresponding alcohol and its enantioselectivities were determined by chiral HPLC analysis.

Table S5 Screening of solvent and electodes[a, b]



1a **2a** **4a**

Entry	**Solvent**	Electrodes	Yield of 4a [b] (%)	*ee* [b] (%)
1	**300:1 MeCN/H_2O**	**Pt**	**84**	**85**
2	Toluene	Pt	0	-
3	DMF	Pt	Trace	-
4	MeCN	Pt	86	37
5	400:1 MeCN/H_2O	Pt	84	75
6	200:1 MeCN/H_2O	Pt	40	89
7	100:1 MeCN/H_2O	Pt	21	86
8	300:1 MeCN/H_2O	Graphite	63	79

[a] Reaction conditions: **1a** (0.90 mmol, 3.00 equiv.), **2a** (0.30 mmol, 1.00 equiv.), **3** (30 mol%), I_2 (10 mol%), *n*-Bu_4NPF_6 (0.2 M), solvent (HPLC level, 3 mL) in an undivided cell with two electrodes (each 1.0 × 1.0 × 0.01 cm^3 for platinum electrodes and each 1.0 × 1.0 × 0.3 cm^3 for graphite electrodes) electrolysis under 5 mA at room temperature for 6 h. [b] Yields were determined by ^1H NMR analysis with CH_2Br_2 as an internal standard. The product was reduced by $NaBH_4$ to the corresponding alcohol and its enantioselectivities were determined by chiral HPLC analysis.

3. Cyclic voltammetry studies and dynamic voltage measuring

3.1. Cyclic voltammetry studies

Cyclic voltammetry experiments were performed on an Interface 1010 B Potential/Galvanostat/ZRA from Gamry Instruments in anhydrous and oxygen-free MeCN under argon at room temperature. *n*-Bu_4NPF_6 (0.05 M) was used as the supporting electrolyte. Platinum wires were used as working-, counter- and quasi-reference electrodes. The voltammograms were adjusted relative to Fc/Fc^+. The scan rate was 100 mV/s.

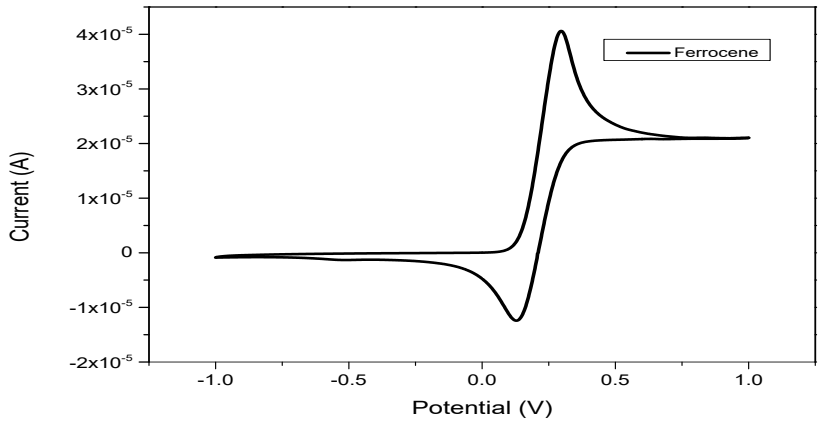


Fig. S1. CV of ferrocene (1 mM) in MeCN with *n*-Bu_4NPF_6 (0.05 M) as supporting electrolyte.

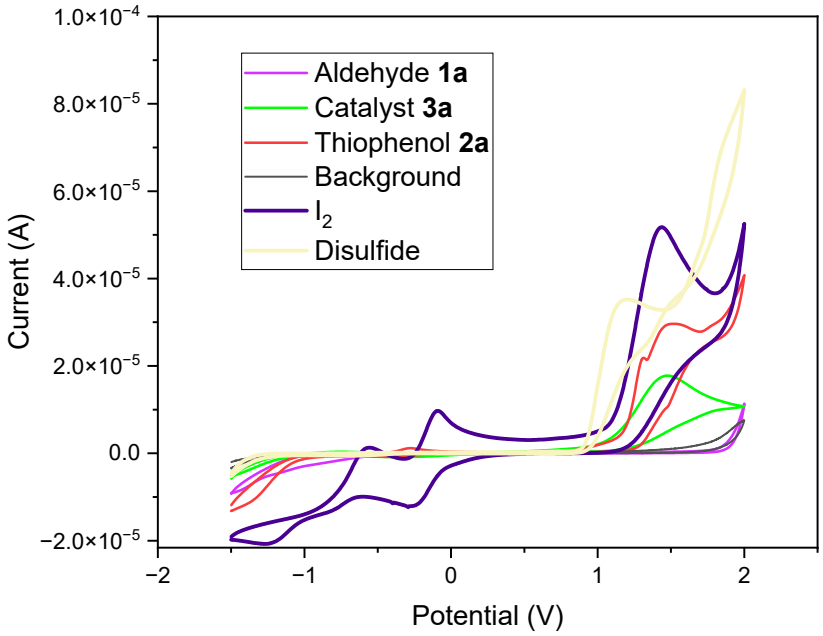


Fig. S2. CVs of substrates (1 mM) in MeCN with *n*-Bu_4NPF_6 (0.05 M) as supporting electrolyte.

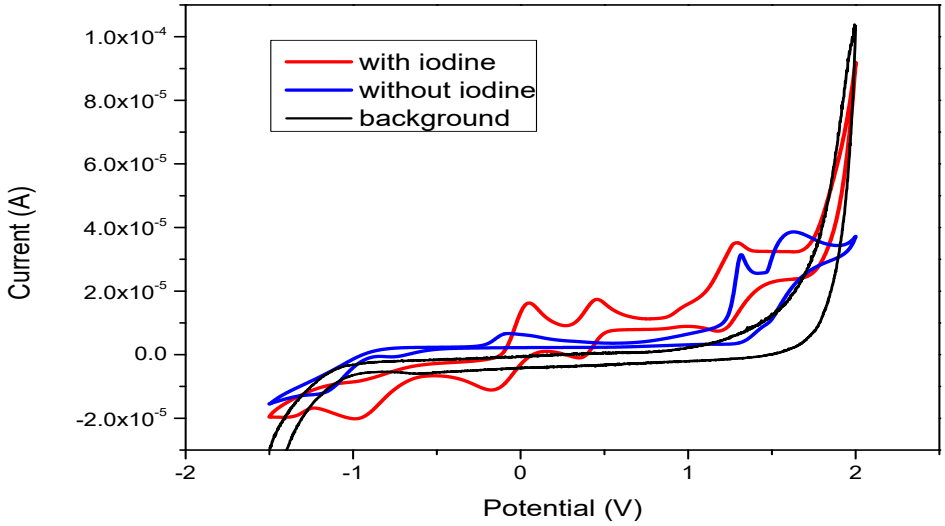


Fig. S3. CVs of the interaction of I_2 with other substrates (50 mM) in MeCN with *n*-Bu_4NPF_6 (0.05 M) as supporting electrolyte.

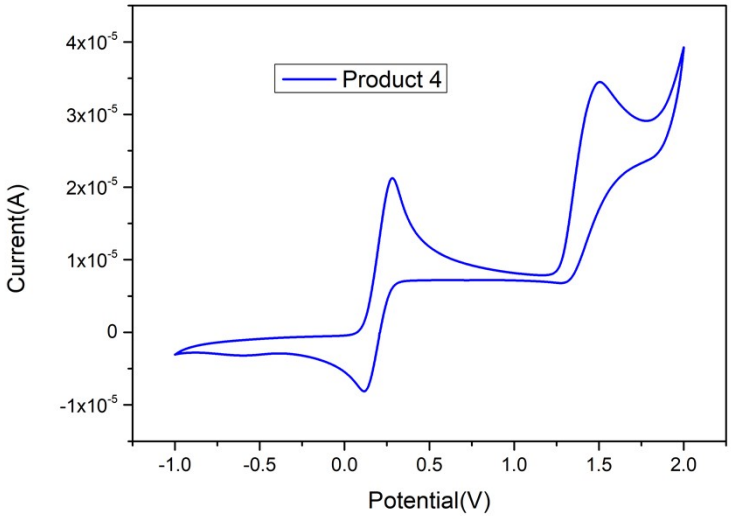


Fig. S4. CV of product **4a** (50 mM) in MeCN with *n*-Bu_4NPF_6 (0.1 M) as supporting electrolyte. Ferrocene was added as an internal reference.

3.2. Dynamic voltage measuring

The experiments were performed on 2460 SourceMeter from company *Keithley* under our standard conditions.

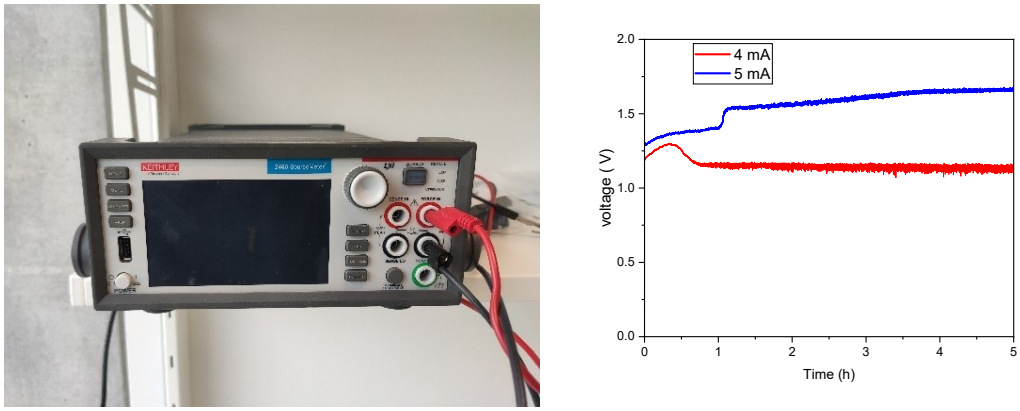


Fig. S5. 2460 SourMeter (left) and dynamic changes of voltage during 5 h of electrolysis under the electricity of 4 mA and 5 mA, separately (right)

4. Mechanism studying experiments

4.1 ^{1}H NMR analysis of the reaction mixture

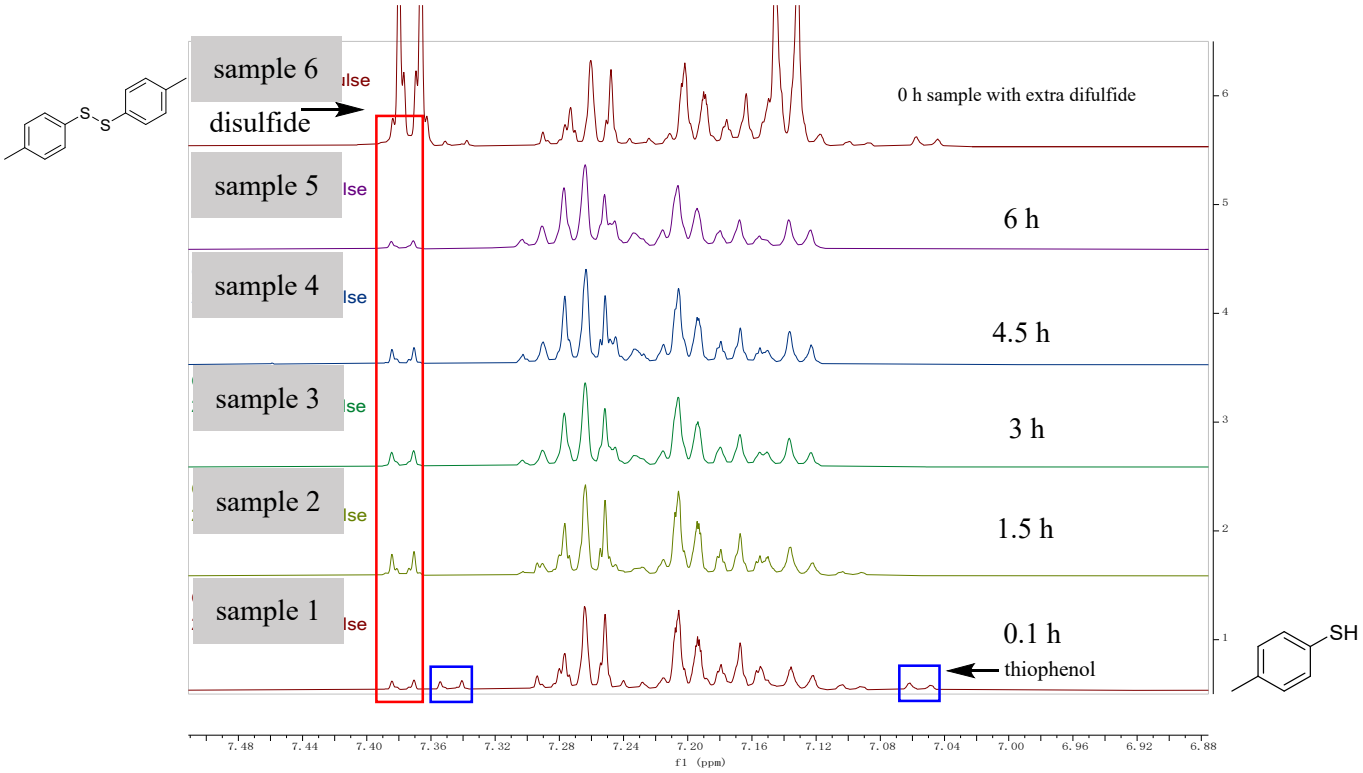


Fig. S6. Using ^{1}H NMR to monitor the variation of disulfide during the reaction.Throughout the duration of the reaction, a 50 μL mixture was collected at different time points (from sample 1 to sample **5**, 0.1 h, 1.5 h, 3 h, 4.5 h, 6 h). Sample **6** was prepared by adding 8.0 mg extra disulfide into the sample **1**.

4.2 Control experiments

Control experiments with ArSI as the reagent: S-(4-bromophenyl)-*N*-(4-nitrophenyl)thiohydroxylamine was prepared according to the established method.[1] Anhydrous HI gas was prepared according to the literature.[2] And the HI gas was used directly by bubbling into the mixture. First, sulfenamide **8** was mixed with 1.5 equivalent of concentrated hydriodic acid (57 wt.% in H_2O). By comparison of ^{1}H NMR spectrum, the final products were disulfide **2ii′** and 4-nitroaniline. It demonstrates the specie ArSI can be generated by the reaction of sulfenamide and hydriodic acid. Furthermore, a 10 mL round ground flask was charged with **1a** (0.90 mmol, 3.00 equiv.), **8** (0.30 mmol, 1.00 equiv.), **3a** (0.09 mmol, 15.32 mg, 30 mol%), MeCN (3 mL), H_2O (10 μL) and a proper PTFE coated stir bar. The mixture was stirred under argon for 30 minutes. There was no reaction observed by TLC monitoring. The freshly prepared anhydrous HI gas was then injected into the above mixture slowly and bubbled at a constant rate. TLC monitored the reaction until the starting material **8** consumed completely. Then the mixture was diluted with dichloromethane (3 mL). $NaBH_4$ (28.37 mg, 0.75 mmol, 5.00 equiv.) was added and the mixture was stirred at room temperature for 3 h. The reaction mixture was treated with water (2 mL) and extracted with dichloromethane (3×3 mL). The combined organic layers were washed with brine (3 mL), dried over Na_2SO_4,

filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography, furnishing the desired product **5i**. (42.30 mg, yield 55%).

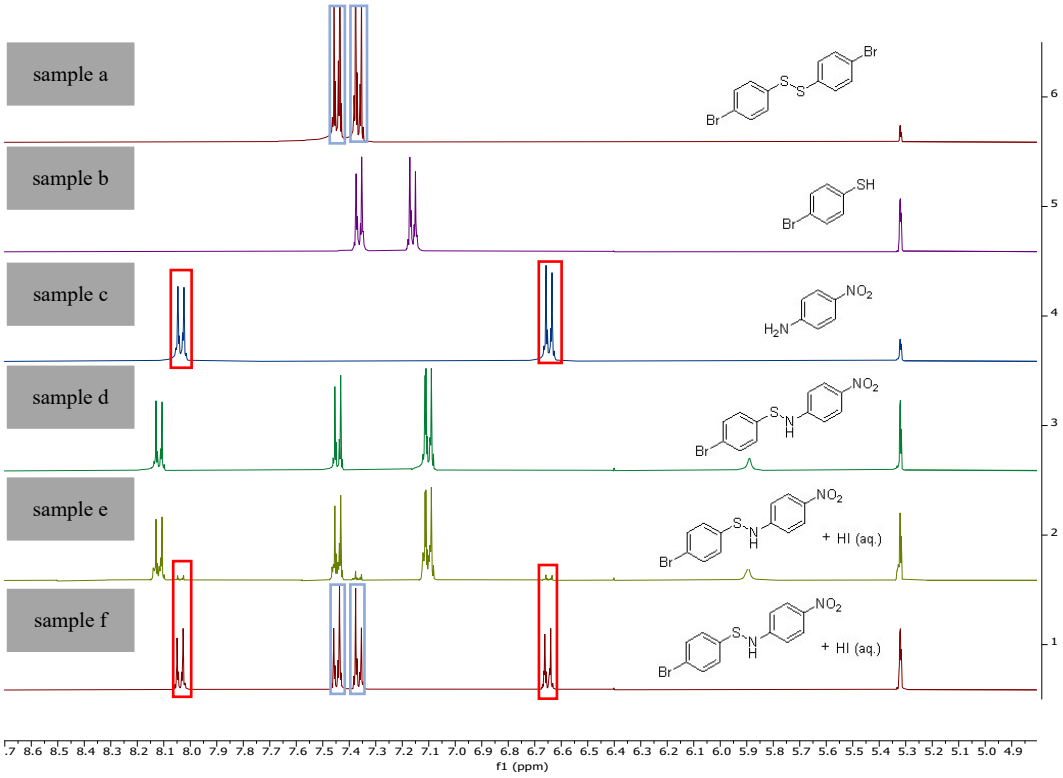
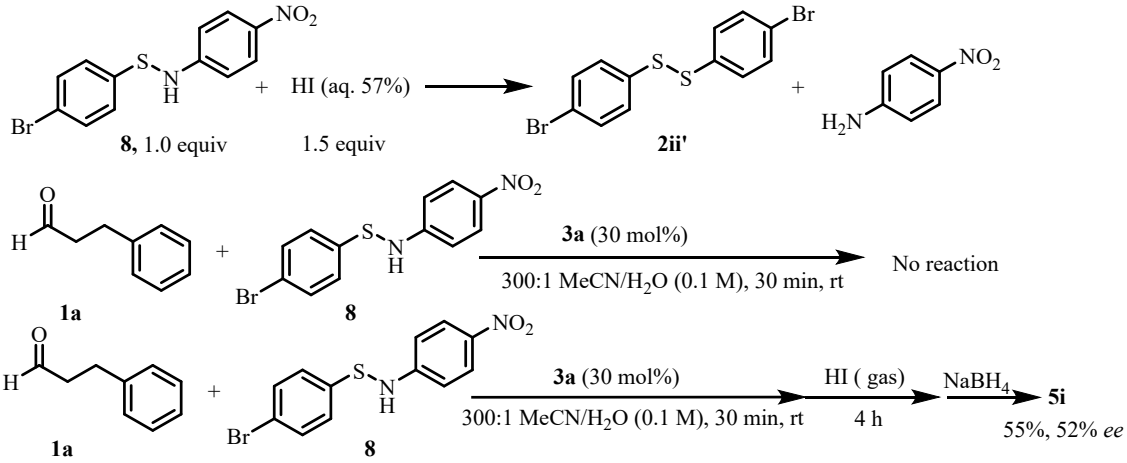
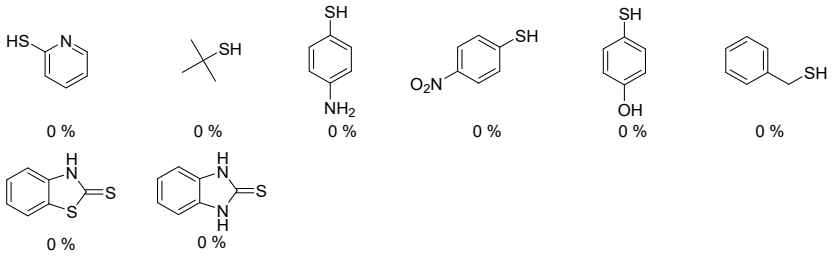


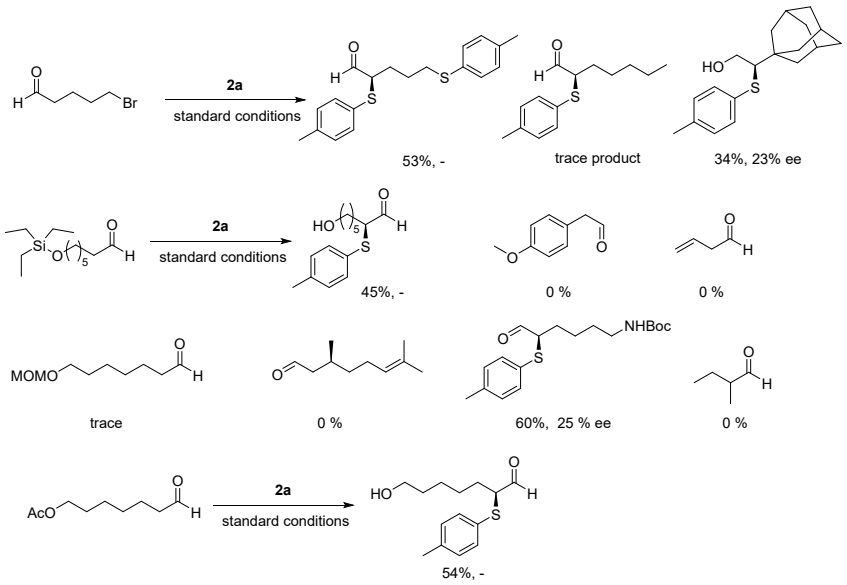
Fig. S7. Using ^{1}H NMR to monitor the reaction between sulfenamide and hydriodic acid. Sample **a** is 4-bromophenyl disulfide. Sample **b** is 4-bromothiophenol. Sample **c** is 4-nitrolaniline. Sample **d** is *S*-(4-bromophenyl)-*N*-(4-nitrophenyl)thiohydroxylamine. Sample **e** is the mixture of sample **d** with 1.5 equivalent of hydriodic acid. Sample **f** is the result of sample **e** after standing for 5 h.



5. Unsuccessful substrates

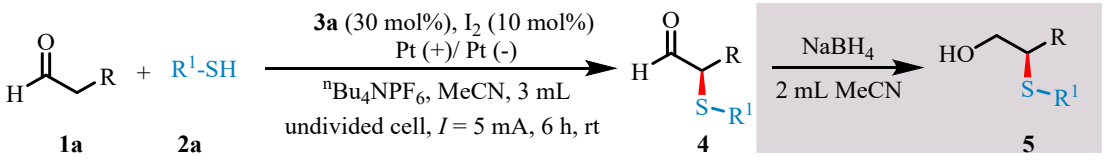


Scheme S1 Unsuccessful thiols



Scheme S2 Unsuccessful aldehydes and byproducts

6. Synthetic procedures and characterization data



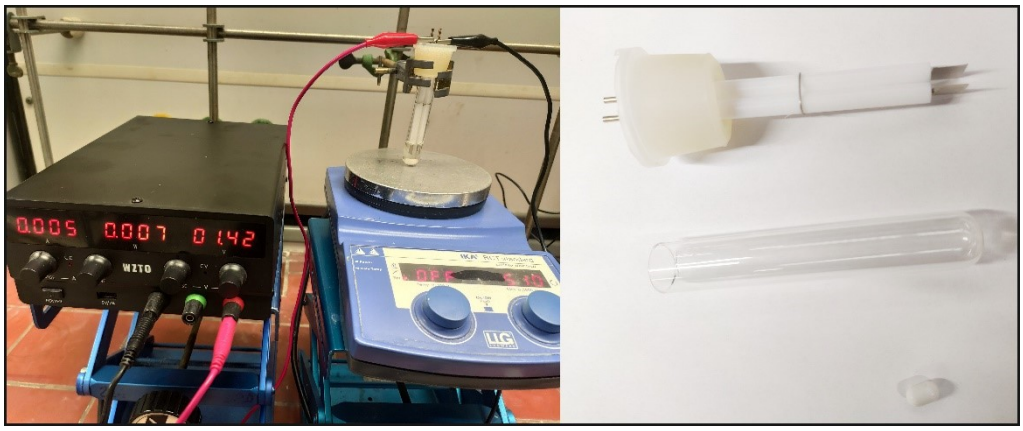
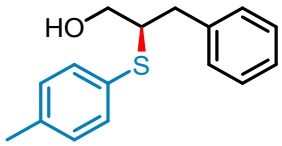


Fig. S8 Reaction setup α-sulfenylation of aldehydes (left) using a platinum electrode arrangement (right).

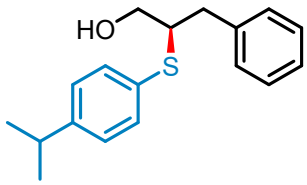
An 18 mL tube (diameter: 13 mm) was charged with **1** (0.90 mmol, 3.00 equiv.), **2** (0.30 mmol, 1.00 equiv.), I_2 (7.61 mg, 10 mol%), **3a** (15.30 mg, 30 mol%), *n*-Bu_4NPF_6 (232.0 mg, 0.2 M), MeCN (3 mL), H_2O (10 μL) and a proper PTFE coated stir bar. The tube was sealed with a septum equipped with two Pt electrodes (1×1 cm^2, approx. 5 mm interelectrode gap) and the reaction mixture was electrolyzed under a constant current of 5 mA for 6 h. Then the mixture was diluted with MeCN (2 mL). $NaBH_4$ (56.75 mg, 1.50 mmol, 5.00 equiv.) was added and the mixture was stirred at room temperature for 3 h. TLC monitored the reaction until it completed. The reaction mixture was treated with water (20 mL) and extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography, furnishing the desired product **5**.

(*R*)-3-phenyl-2-(*p*-tolylthio)propan-1-ol (5a)



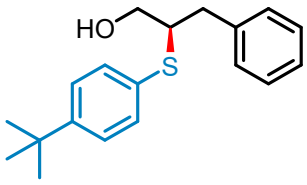
Purification: flash column chromatography (cyclohexane/EtOAc = 10:1, $\mathbf{R}_f$ = 0.2). Colorless liquid (62.10 mg, 80%). The enantiomeric excess (86% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 3:97, 38 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 18.03 min. t_r(minor) = 15.97 min. $[\alpha]_D^{24}$ = - 0.63 (c = 0.59, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.29 – 7.25 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 2H), 3.64 (dt, *J* = 10.6 Hz, 5.2 Hz, 1H), 3.56 (dt, *J* = 11.4, 5.7 Hz, 1H), 3.44 – 3.38 (m, 1H), 2.99 – 2.86 (m, 2H), 2.55 (t, *J* = 6.2 Hz, 1H), 2.37 (s, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.8, 137.8, 133.5, 129.9, 129.5, 129.2, 128.5, 126.5, 62.5, 53.9, 37.6, 21.1.
HRMS (ESI, m/z) calcd. for $C_{16}H_{18}NaOS^+$ $[M+Na]^+$: 281.0971, found: 281.0972.

(*R*)-2-((4-isopropylphenyl)thio)-3-phenylpropan-1-ol (5b)



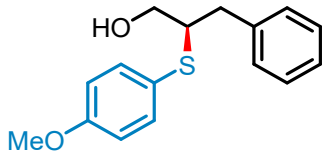
Purification: flash column chromatography (cyclohexane/EtOAc = 10:1, $\mathbf{R}_f$ = 0.22). Colorless liquid (39.60 mg, 47%). The enantiomeric excess (91% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 1:4, 31 bar, flow rate: 0.8 mL/min, λ_{max} = 254 nm): t_r(major) = 9.74 min. t_r(minor) = 8.64 min. $[\alpha]_D^{24}$ = 0.26 (c = 3.68, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.34 (m, 2H), 7.33 – 7.29 (m, 2H), 7.25 – 7.22 (m, 3H), 7.18 – 7.15 (m, 2H), 3.61 (dd, *J* = 11.5, 4.4 Hz, 1H), 3.51 (dd, *J* = 11.5, 5.7 Hz, 1H), 3.39 (dddd, *J* = 8.3, 6.6, 5.7, 4.3 Hz, 1H), 2.98 – 2.87 (m, 3H), 2.25 (s, 1H), 1.25 (s, 3H), 1.24 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.9, 138.8, 133.5, 129.9, 129.3, 128.6, 127.4, 126.7, 62.6, 54.1, 37.8, 33.8, 24.0.
HRMS (ESI, m/z) calcd. for $C_{18}H_{22}NaOS^+$ $[M+Na]^+$: 309.1284, found: 309.1287.

(*R*)-2-((4-(*tert*-butyl)phenyl)thio)-3-phenylpropan-1-ol (5c)



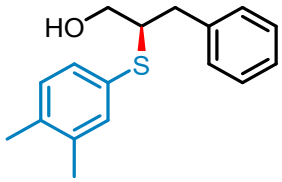
Purification: flash column chromatography (cyclohexane/EtOAc = 10:1, $\mathbf{R}_f$ = 0.21). Colorless liquid (37.90 mg, 42%). The enantiomeric excess (73% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 1:49, 37 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 16.00 min. t_r(minor) = 13.67 min. $[\alpha]_D^{24}$ = -0.66 (c = 0.64, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 2H), 7.32 – 7.28 (m, 4H), 7.25 – 7.21 (m, 3H), 3.60 (dd, *J* = 11.6, 4.3 Hz, 1H), 3.50 (dd, *J* = 11.6, 5.8 Hz, 1H), 3.39 (dddd, *J* = 8.4, 6.6, 5.8, 4.4 Hz, 1H), 2.96 (dd, *J* = 13.8, 6.6 Hz, 1H), 2.90 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.16 (s, 1H), 1.31 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 151.2, 138.9, 133.2, 129.7, 129.4, 128.6, 126.7, 126.3, 62.6, 54.0, 37.9, 34.7, 31.4.
HRMS (ESI, m/z) calcd. for $C_{19}H_{24}NaOS^+$ $[M+Na]^+$: 323.1440, found: 323.1445.

(*R*)-2-((4-methoxyphenyl)thio)-3-phenylpropan-1-ol (5d)



Purification: flash column chromatography (cyclohexane/EtOAc = 10:1, $\mathbf{R}_f$ = 0.18). Colorless liquid (66.30 mg, 78%). The enantiomeric excess (91% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 1:4, 38 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 17.43 min. t_r(minor) = 13.05 min. $[\alpha]_D^{24}$ = 3.17 (c = 0.54, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.31 – 7.28 (m, 2H), 7.24 – 7.19 (m, 3H), 6.86 – 6.83 (m, 2H), 3.80 (s, 3H), 3.56 (dd, *J* = 11.6, 4.2 Hz, 1H), 3.45 (dd, *J* = 11.6, 6.0 Hz, 1H), 3.28 – 3.23 (m, 1H), 2.92 (dd, *J* = 14.0, 6.6 Hz, 1H), 2.84 (dd, *J* = 14.0, 8.4 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.0, 138.9, 136.3, 129.3, 128.6, 126.7, 123.1, 114.8, 62.4, 55.5, 54.8, 37.8.
HRMS (ESI, m/z) calcd. for $C_{16}H_{18}NaO_2S^+$ $[M+Na]^+$: 297.0920, found: 297.0934.

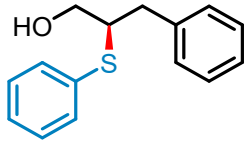
(*R*)-2-((3,4-dimethylphenyl)thio)-3-phenylpropan-1-ol (5e)



Purification: flash column chromatography (cyclohexane/EtOAc = 10:1, $\mathbf{R}_f$ = 0.18). Colorless liquid (64.70 mg, 79%). The enantiomeric excess (91% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 1:4, 31 bar, flow rate: 0.8 mL/min, λ_{max} = 254 nm): t_r(major) = 9.15 min. t_r(minor) = 11.36 min. $[\alpha]_D^{25}$ = -1.10 (c = 1.61, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.25 – 7.22 (m, 3H), 7.20 – 7.16 (m, 2H), 7.07 (d, *J* = 7.7 Hz, 1H), 3.60 (dd, *J* = 11.5, 4.4 Hz, 1H), 3.50 (dd, *J* = 11.5, 5.7 Hz, 1H), 3.37 (dddd, *J* = 8.3, 6.6, 5.7, 4.4 Hz, 1H), 2.96 (dd, *J* = 13.9, 6.6 Hz, 1H), 2.90 (dd, *J* = 13.9, 8.3 Hz,

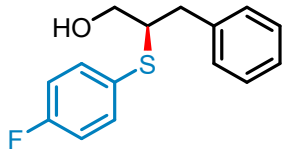
1H), 2.25 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.9, 137.6, 136.8, 134.8, 131.1, 130.4, 129.7, 129.4, 128.6, 126.7, 62.6, 54.2, 37.9, 19.8, 19.5.
HRMS (ESI, m/z) calcd. for $C_{17}H_{20}NaOS^+$ $[M+Na]^+$: 295.1127, found: 295.1135.

(*R*)-3-phenyl-2-(phenylthio)propan-1-ol (5f)



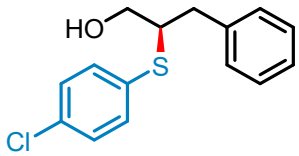
Purification: flash column chromatography (cyclohexane/EtOAc = 10:1, $\mathbf{R}_f$ = 0.18). Colorless liquid (50.59 mg, 65%). The enantiomeric excess (86% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 1:4, 37 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 11.42 min. t_r(minor) = 9.38 min. $[\alpha]_D^{24}$ = -8.53 (c = 0.10, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H), 7.32 – 7.26 (m, 5H), 7.25 – 7.22 (m, 3H), 3.62 (dd, *J* = 11.5, 4.3 Hz, 1H), 3.53 (dd, *J* = 11.5, 5.6 Hz, 1H), 3.46 – 3.41 (m, 1H), 2.98 – 2.90 (m, 2H), 1.58 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.7, 133.5, 133.0, 129.4, 129.2, 128.6, 127.8, 126.8, 62.7, 53.9, 37.9.
HRMS (ESI, m/z) calcd. for C15H16NaOS$^+$ $[M+Na]^+$: 267.0814, found: 267.0807.

(*R*)-2-((4-fluorophenyl)thio)-3-phenylpropan-1-ol (5g)



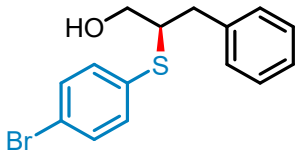
Purification: flash column chromatography (cyclohexane/EtOAc = 10:1, $\mathbf{R}_f$ = 0.12). Colorless liquid (59.32 mg, 75%). The enantiomeric excess (82% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 1:4, 38 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 11.91 min. t_r(minor) = 8.73 min. $[\alpha]_D^{25}$ = -1.65 (c = 0.48, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.32 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 7.02 – 6.96 (m, 2H), 3.60 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.51 (dd, *J* = 11.6, 5.9 Hz, 1H), 3.32 (tdd, *J* = 7.4, 5.9, 4.4 Hz, 1H), 2.91 (d, *J* = 7.4 Hz, 2H), 1.68 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.8 (d, *J* = 248.5 Hz), 138.6, 135.8 (d, *J* = 8.1 Hz), 129.3, 128.7, 128.4 (d, *J* = 4.1 Hz), 126.8, 116.3 (d, *J* = 21.8 Hz), 62.7, 54.8, 37.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.14.
HRMS (ESI, m/z) calcd. for $C_{15}H_{15}FNaOS^+$ $[M+Na]^+$: 285.0720, found: 285.0720.

(*R*)-2-((4-chlorophenyl)thio)-3-phenylpropan-1-ol (5h)



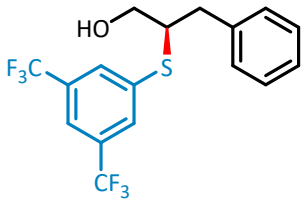
Purification: flash column chromatography (cyclohexane/EtOAc = 10:1, $\mathbf{R}_f$ = 0.2). Colorless oil (40.36 mg, 48%). The enantiomeric excess (87% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc /hexane = 1:4, 38 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 13.86 min. t_r(minor) = 8.82 min. $[\alpha]_D^{24}$ = 16.64 (c = 0.22, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 4H), 7.26 – 7.23 (m, 3H), 7.22 – 7.20 (m, 2H), 3.63 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.53 (dd, *J* = 11.6, 5.7 Hz, 1H), 3.44 – 3.34 (m, 1H), 2.96 – 2.89 (m, 2H), 2.15 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.5, 134.1, 133.9, 132.2, 129.34, 129.32, 128.7, 126.8, 62.8, 54.2, 37.8.
HRMS (ESI, m/z) calcd. for $C_{15}H_{15}ClNaOS^+$ $[M+Na]^+$: 301.0424, found: 301.0415.

(*R*)-2-((4-bromophenyl)thio)-3-phenylpropan-1-ol (5i)



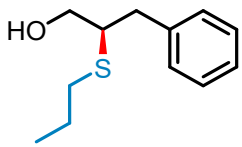
Purification: flash column chromatography (cyclohexane/EtOAc = 10:1, $\mathbf{R}_f$ = 0.2). Colorless liquid (82.01 mg, 84%). The enantiomeric excess (74% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/Hexane = 1:19, 38 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 15.45 min. t_r(minor) = 12.92 min. $[\alpha]_D^{24}$ = -5.83 (c = 2.13, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.41 (m, 1H), 7.40 – 7.39 (m, 1H), 7.33 – 7.29 (m, 2H), 7.26 – 7.20 (m, 5H), 3.68 – 3.60 (m, 1H), 3.57 – 3.51 (m, 1H), 3.44 – 3.37 (m, 1H), 2.99 – 2.88 (m, 2H), 2.14 (t, *J* = 5.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.4, 134.3, 132.9, 132.3, 129.3, 128.7, 126.8, 121.9, 62.8, 54.1, 37.8.
HRMS (ESI, m/z) calcd. for $C_{15}H_{15}BrNaOS^+$ $[M+Na]^+$: 344.9919, found: 344.9931.

(*R*)-2-((3,5-bis(trifluoromethyl)phenyl)thio)-3-phenylpropan-1-ol (5j)



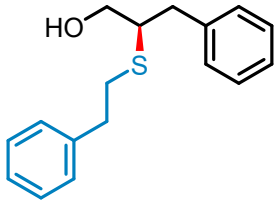
Purification: flash column chromatography (cyclohexane/EtOAc = 20:1, $\mathbf{R}_f$ = 0.1). Colorless liquid (59.20 mg, 52%). The enantiomeric excess (61% *ee*) was determined by HPLC with a *Diacel* Chiralpak IC column (EtOH/hexane = 1:99, 41bar, flow rate: 1.0 mL/min, λ_{max} = 254nm): t_r(major) = 6.34 min. t_r(minor) = 6.67 min. $[\alpha]_D^{25}$= -7.92 (c = 0.96, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (s, 3H), 7.32 – 7.28 (m, 2H), 7.25 – 7.21 (m, 3H), 3.83 – 3.74 (m, 1H), 3.74 – 3.65 (m, 1H), 3.58 – 3.54 (m, 1H), 3.10 (dd, *J* = 14.0, 7.0 Hz, 1H), 2.91 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.03 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.8, 137.8, 132.3 (q, *J* = 33.5 Hz), 130.66 (d, *J* = 4.2 Hz), 129.4, 128.8, 127.2, 123.04 (q, *J* = 273.2 Hz) 120.58 (p, *J* = 3.9 Hz), 63.8, 54.3, 38.2. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.91.
HRMS (ESI, m/z) calcd. for $C_{17}H_{14}F_6NaOS^+$ $[M+Na]^+$: 403.0562, found: 403.0586.

(*R*)-3-phenyl-2-(propylthio)propan-1-ol (5k)



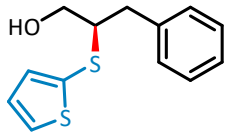
Purification: flash column chromatography (cyclohexane/EtOAc = 15:1, $\mathbf{R}_f$ = 0.2). Colorless liquid (34.32 mg, 54%). The enantiomeric excess (enantiopure, >99% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOH /hexane = 1:99, 39 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 11.77 min. t_r(minor) = 12.89 min. $[\alpha]_D^{25}$ = 15.70 (c = 0.47, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.25 – 7.21 (m, 3H), 3.65 (ddd, *J* = 11.2, 6.6, 4.3 Hz, 1H), 3.53 – 3.43 (m, 1H), 2.99 (tdd, *J* = 7.4, 6.2, 4.2 Hz, 1H), 2.94 – 2.81 (m, 2H), 2.49 – 2.39 (m, 2H), 2.26 (t, *J* = 6.2 Hz, 1H), 1.59 – 1.53 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.1, 129.4, 128.6, 126.6, 62.8, 50.9, 38.7, 32.9, 23.3, 13.6.
HRMS (ESI, m/z) calcd. for $C_{12}H_{18}NaOS^+$ $[M+Na]^+$: 233.0971, found:233.0990.

(*R*)-2-(phenethylthio)-3-phenylpropan-1-ol (5l)



Purification: flash column chromatography (cyclohexane/EtOAc = 15:1, $\mathbf{R}_f$ = 0.18). Colorless liquid (15.62 mg, 20%). The enantiomeric excess (91% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOH/hexane = 1:99, 39 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 16.41 min. t_r(minor) = 17.19 min. $[\alpha]_D^{25}$ = 11.44 (c = 0.32, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 4H), 7.26 – 7.19 (m, 4H), 7.19 – 7.11 (m, 2H), 3.64 (dd, *J* = 11.6, 4.2 Hz, 1H), 3.47 (dd, *J* = 11.6, 6.2 Hz, 1H), 3.01 – 2.96 (m, 1H), 2.89 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.88 – 2.77 (m, 3H), 2.75 – 2.68 (m, 2H), 2.17 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.3, 139.0, 129.4, 128.645, 128.635, 128.59, 126.69, 128.61, 63.0, 51.2, 38.6, 36.5, 32.4.
HRMS (ESI, m/z) calcd. for $C_{17}H_{20}NaOS^+$ $[M+Na]^+$: 295.1127, found: 295.1152.

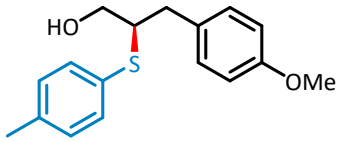
(*R*)-3-phenyl-2-(thiophen-2-ylthio)propan-1-ol (5m)



Purification: flash column chromatography (cyclohexane/EtOAc = 15:1, $\mathbf{R}_f$ = 0.12). Colorless liquid (56.60 mg, 76%). The enantiomeric excess (89% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 3:97, 44 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 16.18 min. t_r(minor) = 19.51 min. $[\alpha]_D^{24}$ = 4.4 (c = 0.25, $CHCl_3$).

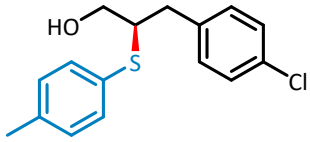
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, J = 5.4, 1.2 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.31 – 7.25 (m, 3H), 7.19 (dd, J = 3.6, 1.2 Hz, 1H), 7.06 (dd, J = 5.4, 3.6 Hz, 1H), 3.70 – 3.65 (m, 1H), 3.60 – 3.55 (m, 1H), 3.26 (dtd, J = 8.2, 6.4, 4.4 Hz, 1H), 3.00 (dd, J = 14.0, 6.8 Hz, 1H), 2.91 (dd, J = 14.0, 8.2 Hz, 1H), 2.26 (d, J = 6.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.5, 136.1, 130.7, 130.5, 129.3, 128.6, 127.9, 126.7, 62.4, 55.9, 37.4.
HRMS (ESI, m/z) calcd. for $C_{13}H_{14}NaOS_2^+$ $[M+Na]^+$: 273.0378, found: 273.0381.

(*R*)-3-(4-methoxyphenyl)-2-(*p*-tolylthio)propan-1-ol (5n)



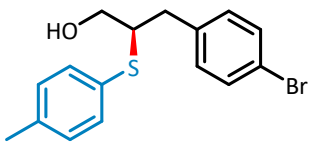
Purification: flash column chromatography (cyclohexane/EtOAc = 20:1, $\mathbf{R}_f$ = 0.13). Colorless liquid (38.72 mg, 45%). The enantiomeric excess (50% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 20:80, 40 bar, flow rate: 1.0 mL/min, λ_{max} = 270 nm): t_r(major) = 15.71 min. t_r(minor) = 13.74 min. $[\alpha]_D^{24}$ = -2.59 (c = 0.99, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 2H), 7.15 – 7.13 (m, 2H), 7.11 (d, J = 7.8 Hz, 2H), 6.86 – 6.83 (m, 2H), 3.79 (s, 3H), 3.61 – 3.56 (m, 1H), 3.52 – 3.47 (m, 1H), 3.34 – 3.30 (m, 1H), 2.89 (dd, J = 14.0, 6.6 Hz, 1H), 2.84 (dd, J = 14.0, 8.4 Hz, 1H), 2.34 (s, 3H), 2.24 (t, J = 6.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.4, 138.0, 133.6, 130.8, 130.3, 130.0, 129.5, 114.0, 62.5, 55.4, 54.3, 36.9, 21.2.
HRMS (ESI, m/z) calcd. for $C_{17}H_{20}NaO_2S^+$ $[M+Na]^+$: 311.1076, found: 311.1093.

(*R*)-3-(4-chlorophenyl)-2-(*p*-tolylthio)propan-1-ol (5o)



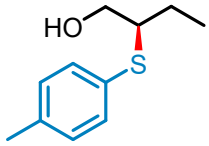
Purification: flash column chromatography (cyclohexane/EtOAc = 15:1, $\mathbf{R}_f$ = 0.2). Colorless liquid (30.50 mg, 35%). The enantiomeric excess (76% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (Ethyl acetate/hexane = 30:70, 41 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 7.77 min. t_r(minor) = 5.885 min. $[\alpha]_D^{23}$ = -5.2 (c = 0.74, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 2H), 7.28 – 7.25 (m, 2H), 7.17 – 7.14 (m, 2H), 7.11 (d, J = 7.8 Hz, 2H), 3.61 – 3.55 (m, 1H), 3.49 (dt, J = 11.8, 6.0 Hz, 1H), 3.30 (tdd, J = 7.4, 5.8, 4.4 Hz, 1H), 2.88 (d, J = 6.0 Hz, 2H), 2.34 (s, 3H), 2.17 (t, J = 6.0 Hz,1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.3, 137.3, 133.7, 132.5, 130.7, 130.1, 129.3, 128.7, 62.5, 54.1, 37.0, 21.3.
HRMS (ESI, m/z) calcd. for $C_{16}H_{17}ClNaOS^+$ $[M+Na]^+$: 315.0581, found: 315.0580.

(*R*)-3-(4-bromophenyl)-2-(p-tolylthio)propan-1-ol (5p)



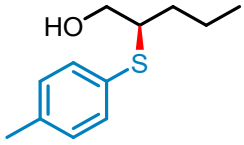
Purification: flash column chromatography (cyclohexane/EtOAc = 15:1, $\mathbf{R}_f$ = 0.2). Colorless liquid (35.32 mg, 35%). The enantiomeric excess (31% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (Ethyl acetate/hexane = 30:70, 41 bar, flow rate: 1.0 mL/min, λ_{max} = 270 nm): t_r(major) = 9.21 min. t_r(minor) = 6.05 min. $[\alpha]_D^{25}$ = -11 (c = 0.21, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 7.32 – 7.27 (m, 2H), 7.12 – 7.08 (m, 4H), 3.60 – 3.55 (m, 1H), 3.51 – 3.46 (m, 1H), 3.30 (tdd, *J* = 7.4, 5.6, 4.4 Hz, 1H), 2.87 (d, *J* = 4.2 Hz, 1H), 2.86 (d, *J* = 4.2 Hz, 1H), 2.33 (s, 3H), 2.19 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.3, 137.8, 133.7, 131.6, 131.1, 130.0, 129.2, 120.6, 62.5, 54.0, 37.1, 21.3.
HRMS (ESI, m/z) calcd. for $C_{16}H_{17}BrNaOS^+$ $[M+Na]^+$: 359.0076, found: 359.0091

(*R*)-2-(*p*-tolylthio)butan-1-ol (5q)



Purification: flash column chromatography (cyclohexane/EtOAc = 20:1, $\mathbf{R}_f$ = 0.18). Colorless liquid (39.30 mg, 67%). The enantiomeric excess (71% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 1:49, 40 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 14.70 min. t_r(minor) = 14.03 min. $[\alpha]_D^{25}$ = 40.47 (c = 0.3, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 3.61 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.49 (dd, *J* = 11.4, 6.4 Hz, 1H), 3.00 (dtd, *J* = 7.8, 6.4, 4.8 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 1H), 1.68 – 1.61 (m, 1H), 1.58 – 1.50 (m, 1H), 1.08 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 137.9, 133.8 (2**C**), 129.9 (2**C**), 129.5, 63.4, 55.05, 24.4, 21.2, 11.9.
HRMS (ESI, m/z) calcd. for $C_{11}H_{16}NaOS^+$ $[M+Na]^+$: 219.0814, found: 219.0810.

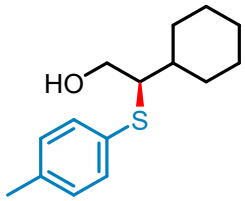
(*R*)-2-(*p*-tolylthio)pentan-1-ol (5r)



Purification: flash column chromatography (cyclohexane/EtOAc = 20:1, $\mathbf{R}_f$ = 0.2). Colorless oil (35.80 mg, 53%). The enantiomeric excess (84% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 1:48, 37 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 12.10 min. t_r(minor) = 13.19 min. $[\alpha]_D^{25}$ = 11.26 (c = 0.68, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 6.8 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 3.60 (dd, *J* = 11.4, 4.6 Hz, 1H), 3.47 (dd, *J* = 11.4, 6.6 Hz, 1H), 3.11 – 3.04 (m, 1H), 2.33 (s, 3H), 2.07 (s,

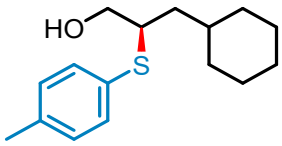
1H), 1.62 – 1.47 (m, 4H), 0.93 (t, J = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.0, 133.8 (2**C**), 129.9 (2**C**), 129.4, 63.7, 53.0, 33.4, 21.2, 20.4, 14.0.
HRMS (**ESI, m/z**) calcd. for $C_{12}H_{18}NaOS^+$ $[M+Na]^+$: 233.0971, found:. 233.0963.

(*R*)-2-cyclohexyl-2-(*p*-tolylthio)ethan-1-ol (5s)



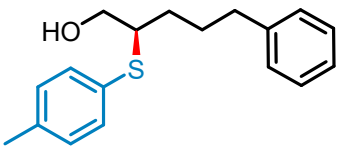
Purification: flash column chromatography (cyclohexane/EtOAc = 50:1, $\mathbf{R}_f$ = 0.2). Colorless liquid (51.2 mg, 64%). The enantiomeric excess (85% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 1:19, 39 bar, flow rate: 0.8 mL/min, λ_{max} = 254 nm): t_r(major) = 8.00 min. t_r(minor) = 7.43 min. $[\alpha]_D^{25}$ = -18.31 (c = 0.46, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 3.71 (dd, J = 11.5, 4.8 Hz, 1H), 3.58 (dd, J = 11.5, 7.0 Hz, 1H), 2.99 – 2.95 (m, 1H), 2.32 (s, 3H), 2.17 (s, 1H), 2.01 (d, J = 11.1 Hz, 1H), 1.80 – 1.72 (m, 3H), 1.69 – 1.59 (m, 2H), 1.27 – 1.12 (m, 5H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 137.5, 132.9 (2**C**), 131.3, 129.9 (2**C**), 62.0, 60.5, 39.5, 30.8, 30.7, 26.5, 26.44, 25.43, 21.2.
HRMS (**ESI, m/z**) calcd. for $C_{15}H_{22}NaOS^+$ $[M+Na]^+$: 273.1284, found: 273.1277.

(*R*)-3-cyclohexyl-2-(*p*-tolylthio)propan-1-ol (5t)



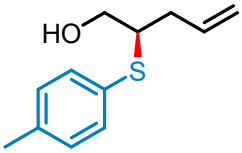
Purification: flash column chromatography (cyclohexane/EtOAc = 60:1, $\mathbf{R}_f$ = 0.15). Colorless liquid (71.00 mg, 84%). The enantiomeric excess (84% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOH/hexane = 1:99, 39 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 10.57 min. t_r(minor) = 10.10 min. $[\alpha]_D^{25}$ = 2.18 (c = 0.45, $CHCl_3$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.34 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 3.62 – 3.53 (m, 1H), 3.47 – 3.38 (m, 1H), 3.22 – 3.13 (m, 1H), 2.33 (s, 3H), 2.23 (t, J = 7.4 Hz, 1H), 1.77 – 1.58 (m, 5H), 1.41 – 1.37 (m, 1H), 1.29 – 1.18 (m, 4H), 1.18 – 1.10 (m, 1H), 0.96 – 0.83 (m, 2H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.1, 134.0, 129.9, 129.2, 63.9, 50.5, 38.8, 34.9, 33.8, 33.0, 26.7, 26.4, 26.3, 21.3.
HRMS (**ESI, m/z**) calcd. for $C_{16}H_{24}NaOS^+$ $[M+Na]^+$: 287.1440, found: 287.1456.

(*R*)-5-phenyl-2-(*p*-tolylthio)pentan-1-ol (5u)



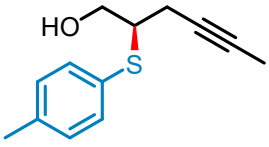
Purification: flash column chromatography (cyclohexane/EtOAc = 45:1, $\mathbf{R}_f$ = 0.15). Colorless liquid (76.87 mg, 85%). The enantiomeric excess (71% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 1:4, 36 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 9.69 min. t_r(minor) = 7.13 min. $[\alpha]_D^{25}$ = 1.33 (c = 0.45, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.4 Hz, 1H), 7.19 (d, J = 6.9 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 3.59 (dd, J = 11.4, 4.8 Hz, 1H), 3.48 (dd, J = 11.4, 6.2 Hz, 1H), 3.11 – 3.05 (m, 1H), 2.70 – 2.59 (m, 2H), 2.34 (s, 3H), 2.18 (s, 1H), 2.01 – 1.92 (m, 1H), 1.86 – 1.78 (m, 1H), 1.69 – 1.61 (m, 1H), 1.60 – 1.51 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.1, 138.0, 133.9, 129.9, 129.2, 128.6, 128.5, 125.9, 63.7, 53.1, 35.8, 30.8, 29.0, 21.2.
HRMS (ESI, m/z) calcd. for $C_{18}H_{22}NaOS^+$ $[M+Na]^+$: 309.1284, found: 309.1281.

(*R*)-2-(*p*-tolylthio)pent-4-en-1-ol (5v)



Purification: flash column chromatography (cyclohexane/EtOAc = 35:1, $\mathbf{R}_f$ = 0.16). Colorless liquid (40.50 mg, 65%). The enantiomeric excess (53% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOH/hexane = 1:99, 39 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 13.26 min. t_r(minor) = 12.72 min. $[\alpha]_D^{25}$ = 3.14 (c = 0.18, $CHCl_3$).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.35 (dd, J = 8.5, 2.3 Hz, 2H), 7.12 (dd, J = 8.6, 0.8 Hz, 2H), 5.89 (ddt, J = 17.2, 10.2, 7.0 Hz, 1H), 5.15 – 5.09 (m, 2H), 3.65 – 3.61 (m, 1H), 3.52 (dd, J = 11.5, 6.4 Hz, 1H), 3.17 – 3.12 (m, 1H), 2.38 – 2.35 (m, 2H), 2.34 (s, 3H). **^{13}C NMR** (176 MHz, $CDCl_3$) δ 138.1, 135.1, 133.8, 129.9, 129.1, 117.5, 63.2, 52.2, 35.8, 21.2.
HRMS (ESI, m/z) calcd. for $C_{12}H_{16}NaOS^+$ $[M+Na]^+$: 231.0814, found: 231.0815.

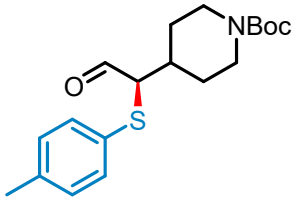
(*R*)-2-(*p*-tolylthio)hex-4-yn-1-ol (5w)



Purification: flash column chromatography (cyclohexane/EtOAc = 45:1, $\mathbf{R}_f$ = 0.22). Colorless oil (40.00 mg, 60%). The enantiomeric excess (38% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 1:66, 39 bar, flow rate: 0.8 mL/min, λ_{max} = 254 nm): t_r(major) = 25.31 min. t_r(minor) = 26.97 min. $[\alpha]_D^{25}$ = 0.24 (c = 0.38, $CHCl_3$).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.12 (d, J = 7.8 Hz, 2H), 3.78 (dd, J = 11.5, 5.1 Hz, 1H), 3.65 (dd, J = 11.5, 6.0 Hz, 1H), 3.21 (ddd, J = 10.8, 8.1, 6.0 Hz, 1H), 2.54 – 2.48

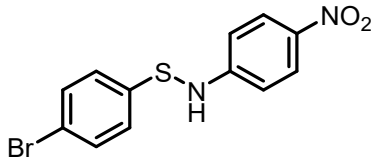
(m, 1H), 2.45 – 2.39 (m, 1H), 2.33 (s, 3H), 1.79 (t, *J* = 2.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 138.2, 133.7, 129.9, 129.0, 78.2, 75.7, 63.3, 51.4, 22.0, 21.2, 3.6.
HRMS (**ESI, m/z**) calcd. for $C_{13}H_{16}NaOS^+$ $[M+Na]^+$: 243.0814, found: 243.0803.

***tert*-butyl (*R*)-4-(2-oxo-1-(*p*-tolylthio)ethyl)piperidine-1-carboxylate (4x)**



Purification: flash column chromatography (cyclohexane/EtOAc = 20:1, $\mathbf{R}_f$ = 0.13). Colorless oil (51.00 mg, 48%). The enantiomeric excess (71% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH /hexane = 1:97, 37 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 7.99 min. t_r(minor) = 9.14 min. $[\alpha]_D^{25}$ = 13.34 (c = 0.81, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.36 (d, *J* = 4.6 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 4.13 (s, 2H), 3.25 (dd, *J* = 9.2, 4.6 Hz, 1H), 2.79 – 2.63 (m, 2H), 2.30 (s, 3H), 2.13 (d, *J* = 12.2 Hz, 1H), 1.94 – 1.83 (m, 1H), 1.72 – 1.62 (m, 1H), 1.44 (s, 9H), 1.38 – 1.23 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 193.9, 154.8, 138.8, 133.8, 130.2, 128.0, 79.7, 63.4, 35.0, 28.9, 28.5, 28.1, 21.3.
HRMS (**ESI, m/z**) calcd. for $C_{19}H_{27}NNaO_3S^+$ $[M+Na]^+$: 372.1604, found: 372.1644.

S-(4-bromophenyl)-*N*-(4-nitrophenyl)thiohydroxylamine (8)



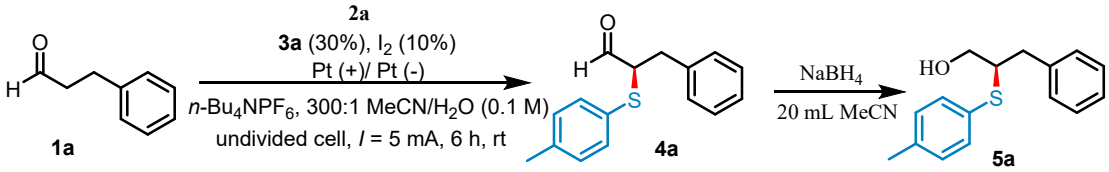
Purification: flash column chromatography (cyclohexane/EtOAc = 20:1, $\mathbf{R}_f$ = 0.12). Yellow solid (51.00 mg, 48%). m.p. 162.1 – 163. 5 °C. **^{1}H NMR** (600 MHz, DMSO-D6) δ 8.94 (s, 1H), 8.00 (d, J = 9.2 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.06 – 6.98 (m, 4H). **^{13}C NMR** (151 MHz, DMSO-D6) δ 153.9, 139.9, 139.4, 132.1, 126.0, 124.7, 118.8, 114.2.
HRMS (**ESI, m/z**) calcd. for $C_{12}H_{10}BrN_2O_2S^+$ $[M+H]^+$: 324.9641, found: 324.9685.

Cinnamaldehyde (9)

Purification: flash column chromatography (EtOAc/cyclohexane = 60:1, $\mathbf{R}_f$ = 0.2). Colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 9.71 – 9.68 (m, 1H), 7.58 – 7.55 (m, 2H), 7.49 – 7.42 (m, 4H), 6.75 – 6.68 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 193.8, 152.9, 134.1, 131.4, 129.2, 128.7, 128.6.

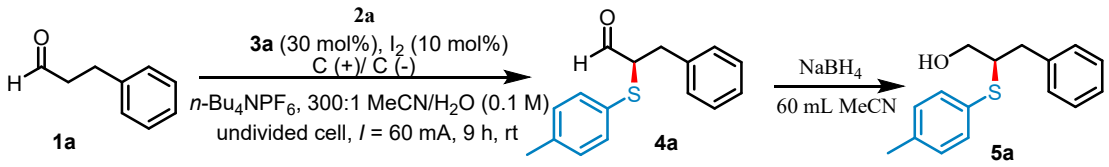
7. Large-scale synthesis and mechanistic studies

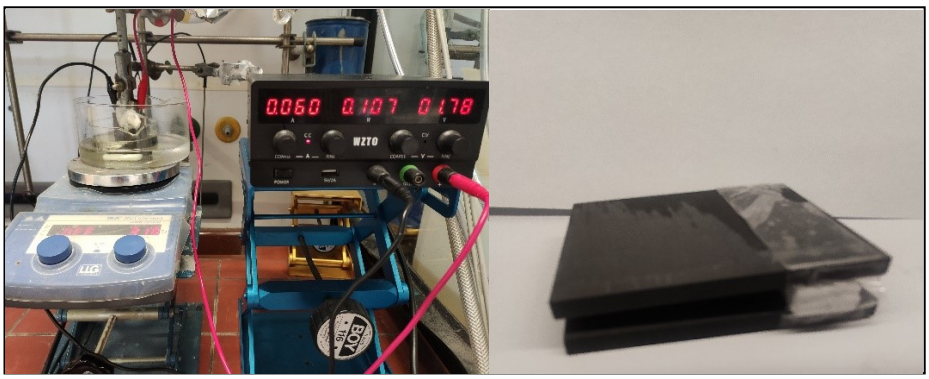
(a) 3 mmol-scale synthesis of **5a**



A 50 mL plastic centrifuge tube (inside diameter: 26 mm) was charged with **1a** (9.00 mmol, 1.21 g, 3.00 equiv.), **2a** (3.00 mmol, 372.60 mg, 1.00 equiv.), I_2 (0.30 mmol, 76.10 mg, 10 mol%), **3a** (0.90 mmol, 153.23 mg, 30 mol%), *n*-Bu_4NPF_6 (6.00 mmol, 2.32 g, 2.00 equiv.), MeCN (30 mL), H_2O (100 μL) and a proper stir bar. The tube was open to air with two groups of Pt electrodes (1×1 cm^2, approx. 5 mm interelectrode gap, each group worked separately with independent power supply) and the reaction mixture was electrolyzed under a constant current of 5 mA for 6 h. Then the mixture was diluted with MeCN (15 mL). $NaBH_4$ (15 mmol, 0.57 g, 5.0 equiv.) was added and the mixture was stirred at room temperature for 3 h. TLC monitored the reaction until it completed. The reaction mixture was treated with water (20 mL) and extracted with dichloromethane (3×40 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography, furnishing the desired product **5a**. Colorless liquid, 0.51 g. (yield 65%, 80% *ee*).

(b) 9 mmol-scale synthesis of **5a**

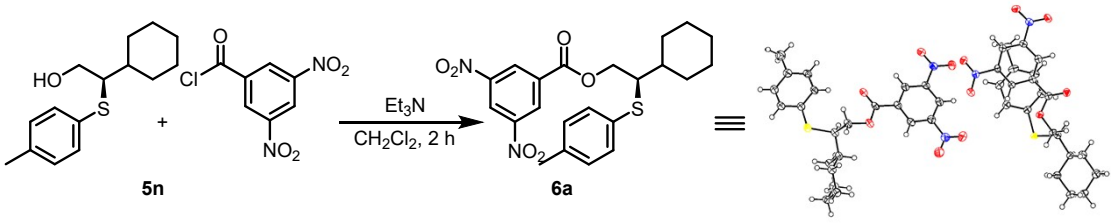




A 150 mL round electrolyzer (inside diameter: 75 mm) was charged with **1a** (27.00 mmol, 3.62 g, 3.00 equiv.), **2a** (9.00 mmol, 1.12 g, 1.00 equiv.), **3a** (2.70 mmol, 0.46 g, 30 mol%), I_2 (0.90 mmol, 228. 43 mg, 10 mol%), *n*-Bu_4NPF_6 (18.00 mmol, 6.97 g, 2.00 equiv.), MeCN (90 mL), H_2O (300 μL) and a proper stir bar. The electrolyzer was open to air with two graphite electrodes (40 × 25 × 3 mm, approx. 5 mm interelectrode gap) and the reaction mixture was electrolyzed under a constant current of 60 mA for 9 h. Then the mixture was diluted with MeCN (50 mL). $NaBH_4$ (45.00 mmol, 1.71 g, 5.00 equiv.) was added and the mixture was stirred at room temperature for 3 h. TLC monitored the reaction until it completed. The reaction mixture was treated with water (50 mL) and extracted with dichloromethane (3×40 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography, furnishing the desired product **5a**. Colorless liquid, 2.2 g. (yield 93%, 57% *ee*).

8. Preparation of compounds 6a, 6b and 6c.

Preparation of compound 6a



To a solution of **5n** (70.0 mg, 0.28 mmol, 1.00 equiv.) in dichloromethane (3 mL) was added 3,5-dinitrobenzoyl chloride (96.7 mg, 0.42 mmol, 1.50 equiv.), followed by the addition of Et_3N (58.5 μL, 0.42 mmol, 1.50 equiv.). The reaction mixture was stirred at room temperature for 2 h. Then the reaction mixture was treated with sat. aq. $NaHCO_3$ solution (2 mL). The phases were separated, and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic extracts were washed with brine (2 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, pentane/EtOAc = 20:1) to afford ester **6a** (47.00 mg, yield 38%) as a light-yellow oil. The major enantiomer (t = 7.25 min) was separated by chiral HPLC and crystallized from ether to give single crystals suitable for X-ray diffraction.

The enantiomeric excess (53% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (20% EtOAc /Hexane, 39 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 7.25 min. t_r(minor) = 6.74 min. $[\alpha]_D^{22}$ = - 12.71 (c = 1, $CHCl_3$).

^{1}H NMR (700 MHz, $CDCl_3$) δ 9.19 (t, *J* = 2.2 Hz, 1H), 8.97 (d, *J* = 2.2z Hz, 2H), 7.34 – 7.31 (m, 2H), 7.01 (d, *J* = 9.4 Hz, 2H), 4.68 (dd, *J* = 11.5, 6.4 Hz, 1H), 4.58 (dd, *J* = 11.5, 7.2 Hz, 1H), 3.37 (ddd, *J* = 7.2, 6.4, 4.7 Hz, 1H), 2.21 (s, 3H), 2.02 – 1.95 (m, 1H), 1.85 – 1.68 (m, 4H), 1.53 – 1.48 (m, 1H), 1.33 – 1.28 (m, 2H), 1.22 – 1.19 (m, 1H), 0.89 – 0.79 (m, 2H). **^{13}C**

NMR (151 MHz, $CDCl_3$) δ 162.4, 148.7, 137.5, 133.8, 132.4 (2**C**), 131.9, 130.0 (2**C**), 129.5 (2**C**), 122.4, 68.2, 54.7, 40.0, 30.8, 29.8, 26.49, 26.47, 26.4, 21.1.
HRMS (**ESI, m/z**) calcd. for $C_{22}H_{24}N_2NaO_6S^+$ $[M+Na]^+$: 467.1248, found: 467.1247.

Table S6 Crystal data and structure refinement for **6a**

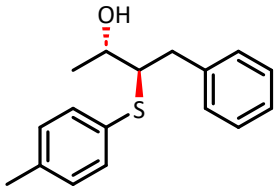
Crystal data and structure refinement of **6a**

Identification code	**ZW_CH119**
Empirical formula	$C_{22}H_{24}N_2O_6S$
Molecular weight	444.49
Temperature [K]	100
Wavelength [Å]	1.54178
Crystal system, space group	monoclinic, $P2_1$
Unit cell dimensions	a = 12.34031 (9) Å, alpha = 90 b = 7.13358 (5) Å, beta = 101.4062 (3) c = 24.66536 (18) Å, gamma = 90
Volume [Å^3]	2128.42 (3)
Z, Density (calculated)	4, 1.387 g/cm^3
Absorption coefficient [mm^{-1}]	1.716
F (000)	936.0
Crystal size [mm]	0.05 x 0.06 x 0.59
ϑ-range for data collection	3.654 – 68.209°
Index ranges	-14 ≤ h ≤ 14, –8 ≤ k ≤ 8, –29 ≤ l ≤ 29
Reflections collected	34981
Independent reflections	9212
Completeness to ϑ = 67.679°	98%
Absorption correction	multi-scan
Max. and min. transmission	0.753 and 0.445
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7622 / 1 / 561
Goodness-of-fit on F^2	1.124
Final R indices [I>2sigma(I)]	R_1 = 0.0552, wR_2 = 0.1228
R indices (all data)	R_1 = 0.0567, wR_2 = 0.1244
Largest diff. peak and hole	0.69 nd –0.53 e$^-$/Å^{-3}

Preparation of (2*S*,3*R*)-4-phenyl-3-(*p*-tolylthio)butan-2-ol (6b).[3]

An 18 mL tube (diameter: 13 mm) was charged with **1** (0.90 mmol, 3.00 equiv.), **2** (0.30 mmol, 1.00 equiv.), I_2 (7.61 mg, 10 mol%), **3a** (15.30 mg, 30 mol%), *n*-Bu_4NPF_6 (232.0 mg, 0.2 m), MeCN (3 mL), H_2O (10 μL) and a proper PTFE coated stir bar. The tube was sealed with a septum equipped with two Pt electrodes (1×1 cm^2, approx. 5 mm interelectrode gap) and the reaction mixture was electrolyzed under a constant current of 5 mA for 6 h. The reaction mixture was quickly filtered through a short pad of silica gel with toluene. The fractions containing the product were combined and used in the following step without further purification.

The toluene solution of the intermediate *α*-sulfenylaldehyde obtained was added dropwise to a solution of MeMgBr (5.0 equiv. based on 4-methyl thiophenol) cooled to -10 °C. The reaction was monitored by TLC and stirred until all the intermediate *α*-sulfenylaldehyde was consumed. The reaction was quenched with saturated NH_4Cl and partitioned between water and EtOAc. The aqueous layer was then extracted with EtOAc and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and evaporated to dryness. The mixture was purified by flash column chromatography (cyclohexane/EtOAc = 45:1, $\mathbf{R}_f$ = 0.1) to afford the secondary alcohol **6b** as a colorless oil (56.50 mg, two-step yield, 69%).



The diastereomeric ratio (94:6) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 3:97, 38 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 11.79 min. t_r(minor) = 16.02 min. $[\alpha]_D^{24}$ = -25.39 (c = 0.40, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.32 – 7.28 (m, 2H), 7.25 – 7.21 (m, 3H), 7.20 – 7.18 (m, 2H), 7.06 – 7.03 (m, 2H), 3.90 (pd, *J* = 6.4, 3.2 Hz, 1H), 3.36 (ddd, *J* = 9.0, 5.8, 3.2 Hz, 1H), 3.03 (dd, *J* = 14.4, 5.8 Hz, 1H), 2.81 (dd, *J* = 14.4, 9.0 Hz, 1H), 2.30 (s, 3H), 1.28 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 139.4, 137.6, 132.9, 131.2, 129.9, 129.3, 128.5, 126.6, 68.0, 60.8, 36.8, 21.2, 19.2.

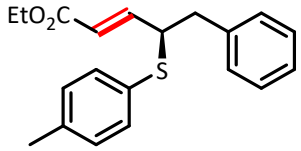
HRMS (ESI, m/z) calcd. for $C_{17}H_{20}NaOS^+$ $[M+Na]^+$: 295.1127, found: 295.1142.

Preparation of ethyl (*R*, *E)*-5-phenyl-4-(*p*-tolylthio)pent-2-enoate (6c).[4]

An 18 mL tube (diameter: 13 mm) was charged with **1** (0.90 mmol, 3.00 equiv.), **2** (0.30 mmol, 1.00 equiv.), I_2 (7.61 mg, 10 mol%), **3a** (15.30 mg, 30 mol%), *n*-Bu_4NPF_6 (232.0 mg, 0.2 m), MeCN (3 mL), H_2O (10 μL) and a proper PTFE coated stir bar. The tube was sealed with a septum equipped with two Pt electrodes (1×1 cm^2, approx. 5 mm interelectrode gap) and the reaction mixture was electrolyzed under a constant current of 5 mA for 6 h. The mixture was quickly filtered through a short pad of silica gel (cyclohexane/EtOAc = 10:1) and concentrated in vacuo.

The above mixture was dissolved in 3 mL anhydrous dichloromethane and cooled to -78 °C. A pre-mixed solution of *n*-BuLi (0.54 mL, 2.5 M, 4.5 equiv. based on 4-methyl thiophenol) and triethylphosphonoacetate (0.31 g, 4.5 equiv.) in dichloromethane (5 mL) at -78 °C was added to the aforementioned mixture. After stirring at -78 °C for 1 h, the solution was quenched with

NH_4Cl (sat), extracted (dichloromethane), dried (Na_2SO_4) and concentrated in vacuo. The mixture was purified by flash column chromatography (cyclohexane/EtOAc = 150:1, $\mathbf{R_f}$ = 0.1) to afford the title compound **6c** as a colorless oil. (63.80 mg, two steps, 65%).



The enantiomeric excess (83% *ee*) was determined by HPLC with a *Diacel* Chiralpak IC column (EtOH/hexane = 1:99, 40 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 9.24 min. t_r(minor) = 7.14 min. $[\alpha]_D^{24}$ = 48.28 (c = 0.86, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.27 – 7.25 (m, 2H), 7.24 – 7.21 (m, 1H), 7.19 – 7.16 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.82 (dd, *J* = 15.6, 9.2 Hz, 1H), 5.39 (dd, *J* = 15.6, 0.8 Hz, 1H), 4.13 (q, *J* = 7.0 Hz, 2H), 3.83 – 3.78 (m, 1H), 3.07 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.94 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.32 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.1, 146.9, 138.4, 138.0, 134.4, 129.9, 129.5, 129.3, 128.6, 126.9, 121.7, 60.4, 52.6, 40.3, 21.3, 14.3.

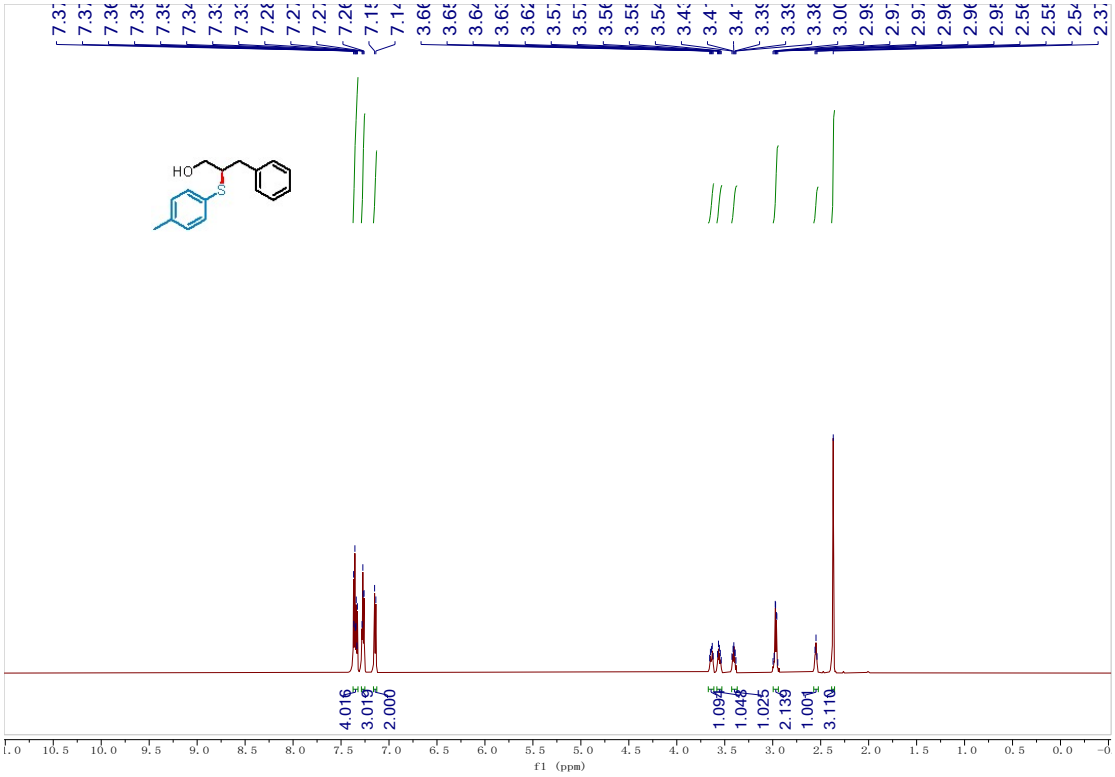
HRMS (**ESI, m/z**) calcd. for $C_{20}H_{22}NaO_2S^+$ $[M+Na]^+$: 349.1233, found: 349.1218.

Reference

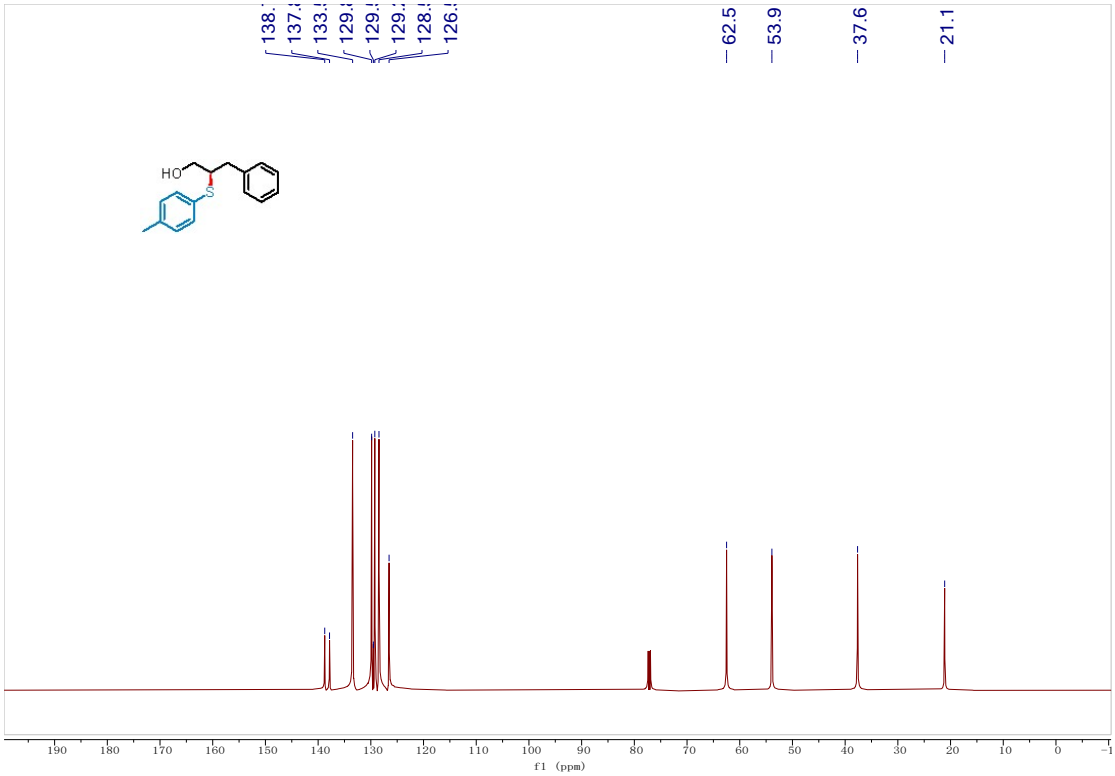
(1) Zhou, Q.; Li, J.; Wang, T.; Yang, X. Base-Promoted S-Arylation of Sulfenamides for the Synthesis of Sulfilimines. *Org.Lett.* **2023**, *25*, 4335-4339.
(2) Dillon, R. T.; Young, W. G. The Preparation of Anhydrous Hydrogen Iodide. *J. Am. Chem. Soc.* **1929**, *51*, 2389-2391.
(3) Sheppard, T.; Rota, F.; Benhamou, L. Asymmetric Synthesis of Secondary Alcohols and 1,2-Disubstituted Epoxides via Organocatalytic Sulfenylation. *Synlett* **2015**, *27*, 33-36.
(4) Armstrong, A.; Challinor, L.; Moir, J. H. Exploiting Organocatalysis: Enantioselective Synthesis of Vinyl Glycines by Allylic Sulfimide [2,3] Sigmatropic Rearrangement. *Angew. Chem. Int. Ed.* **2007**, *46*, 5369-5372.

9. Copies of NMR spectra

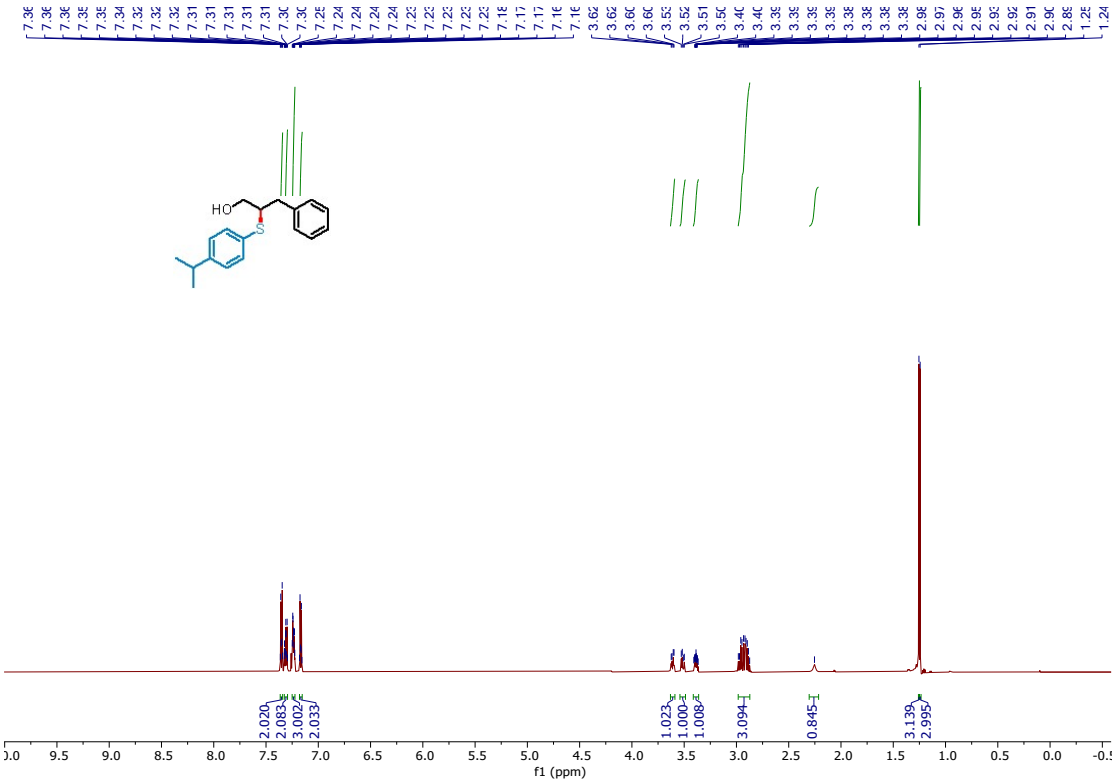
^{1}H NMR spectrum of compound **5a**



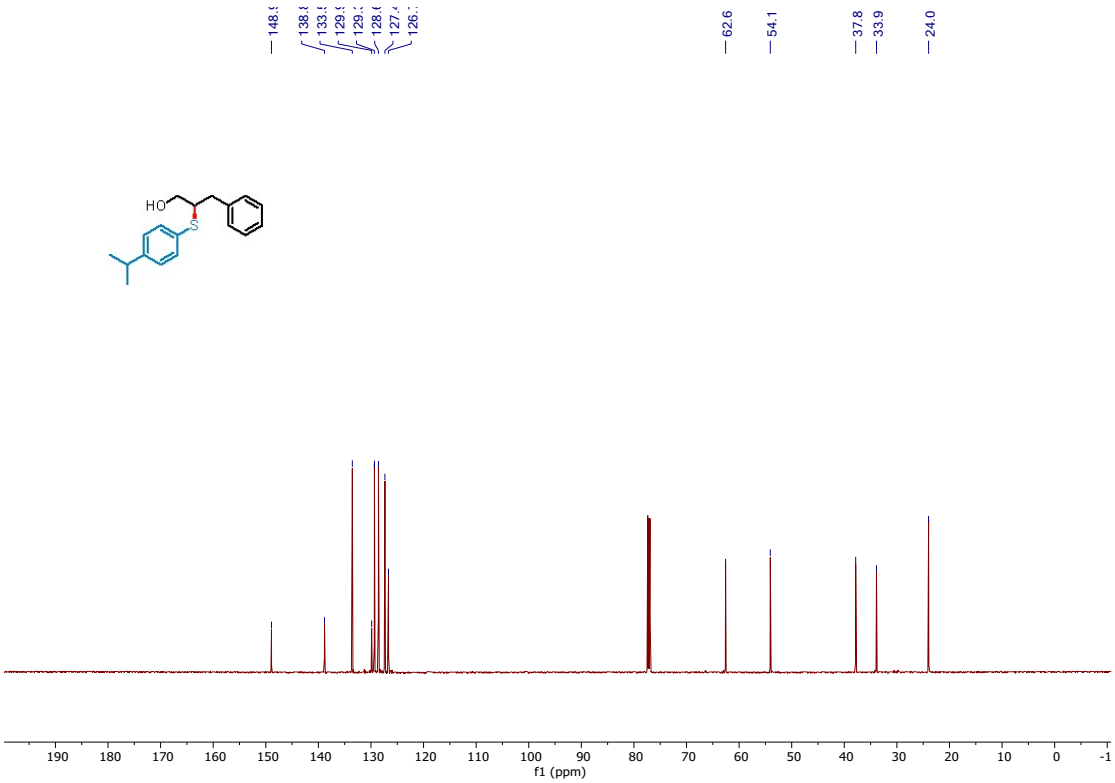
^{13}C NMR spectrum of compound **5a**



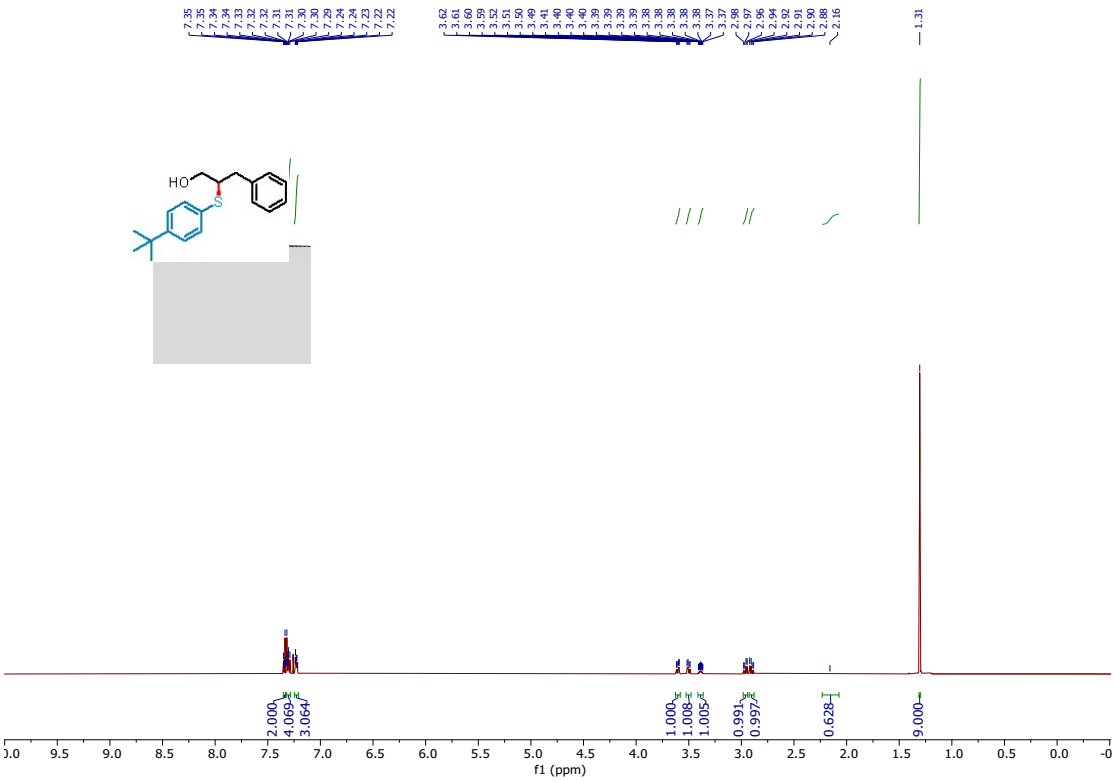
^{1}H NMR spectrum of compound **5b**



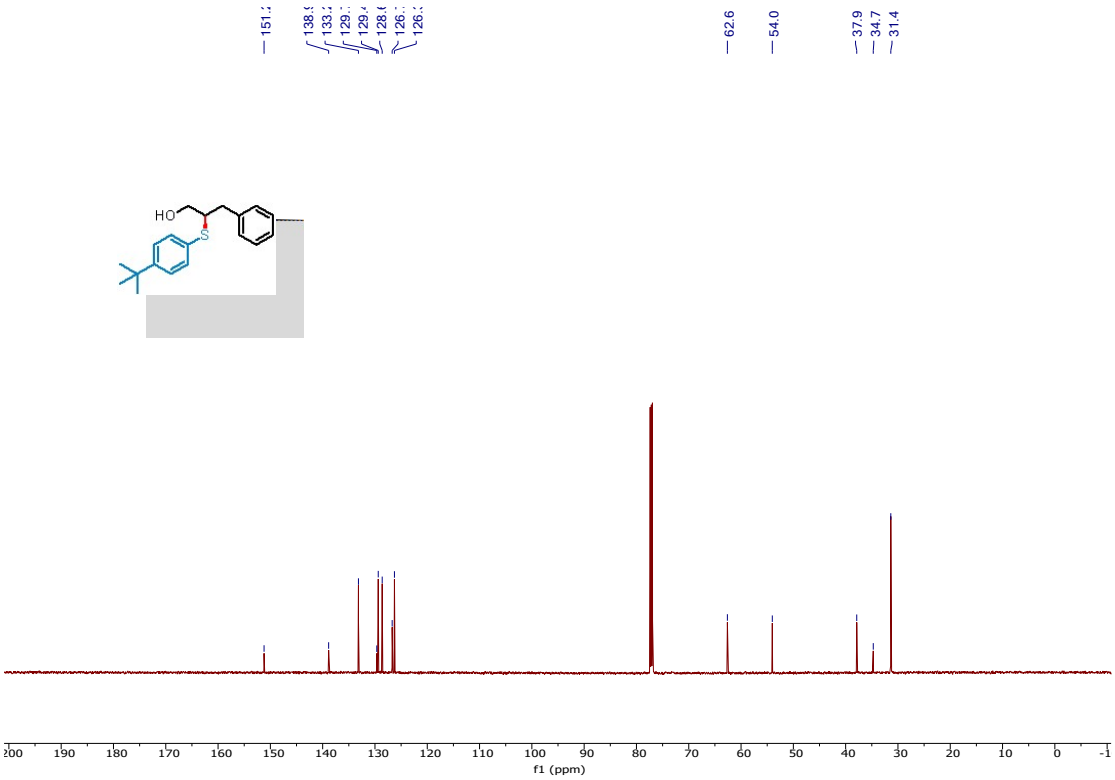
^{13}C NMR spectrum of compound **5b**



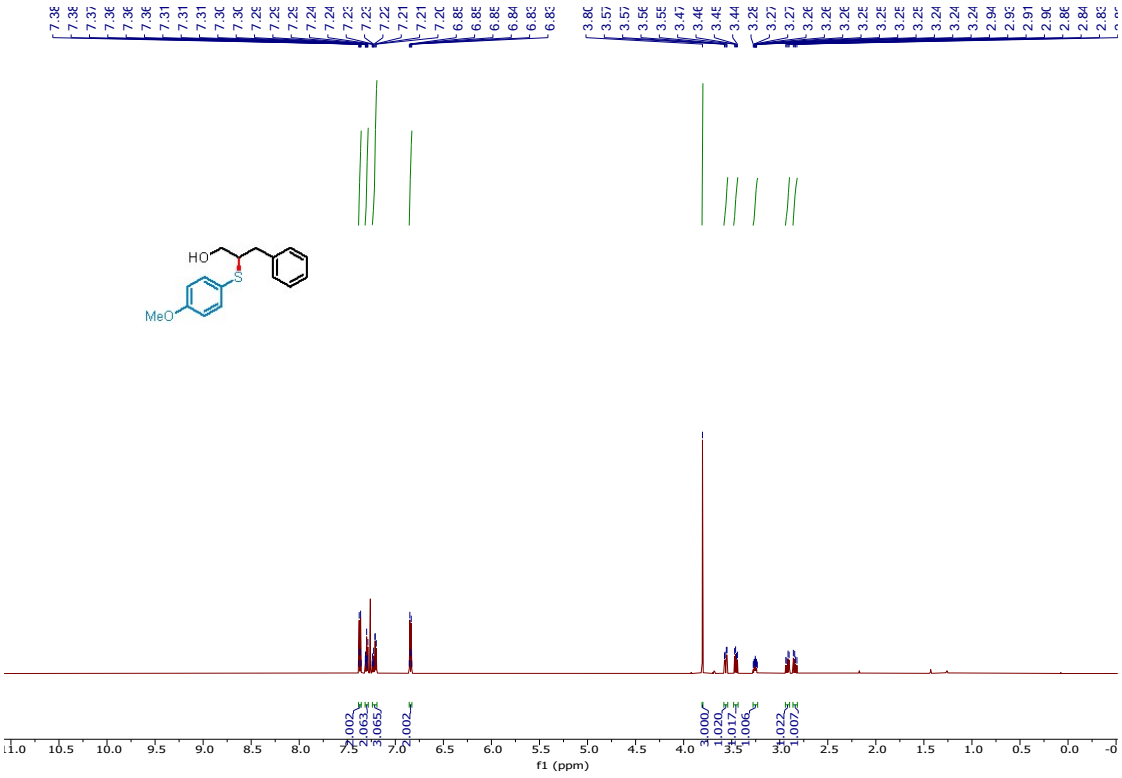
^{1}H NMR spectrum of compound **5c**



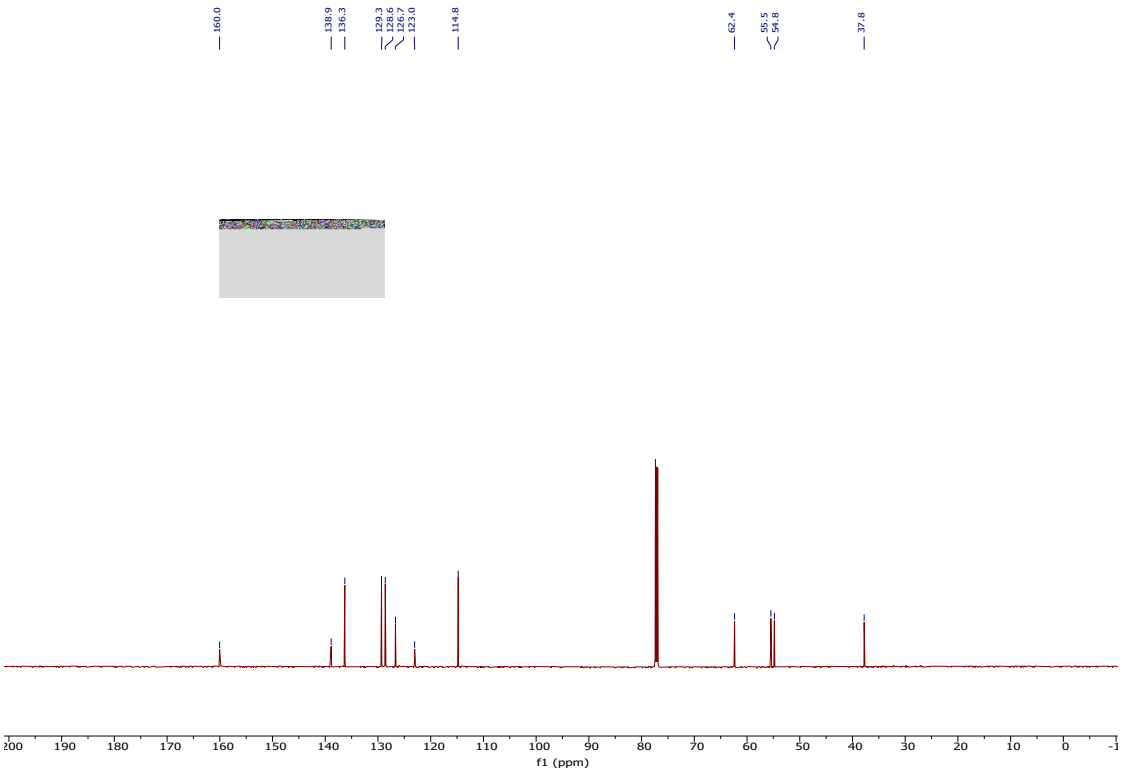
^{13}C NMR spectrum of compound **5c**



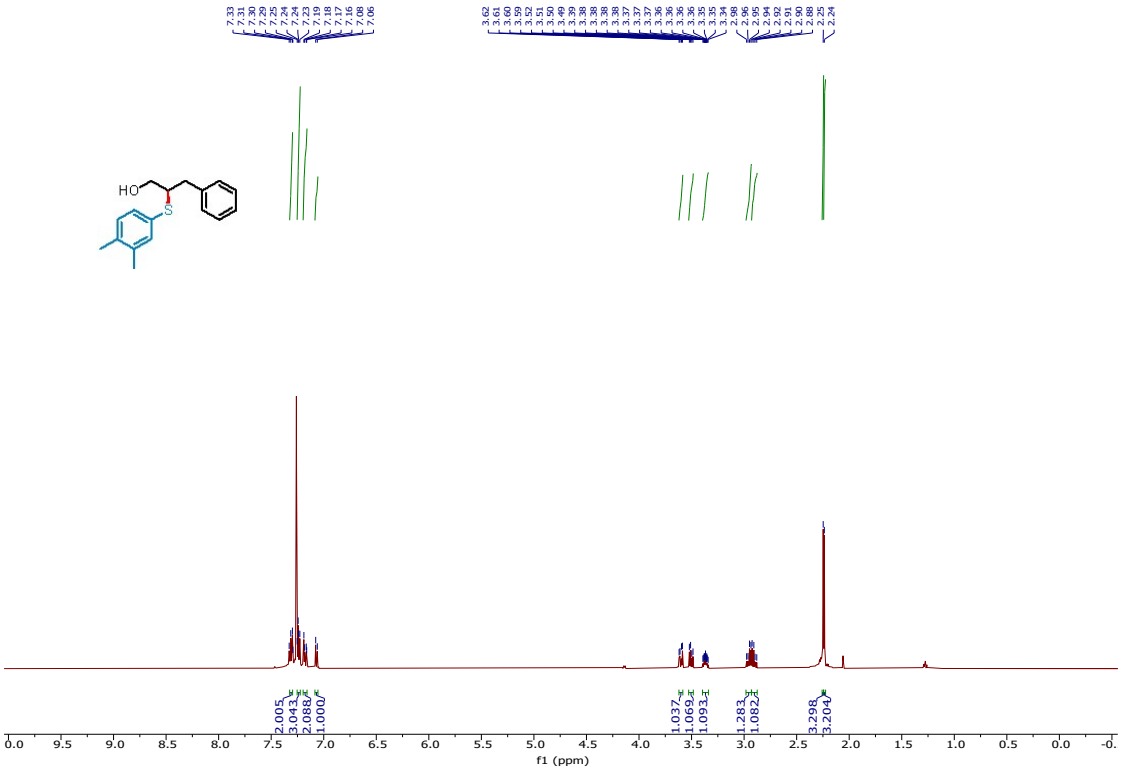
^{1}H NMR spectrum of compound **5d**



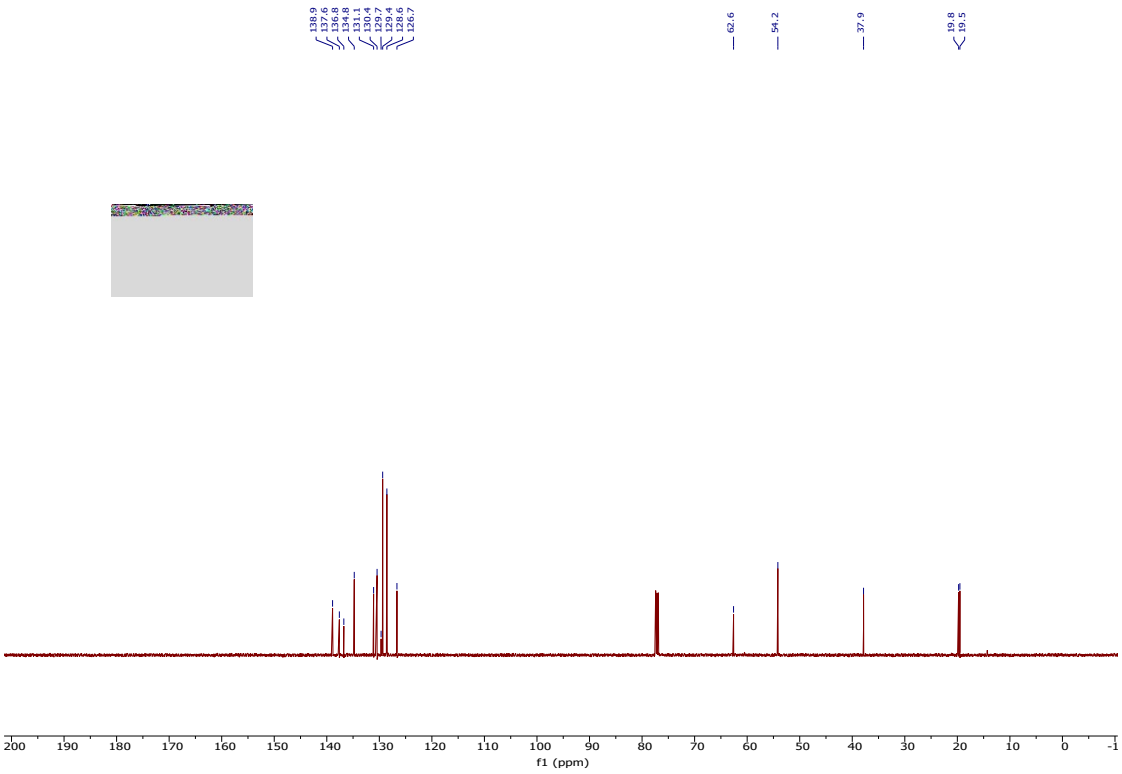
^{13}C NMR spectrum of compound **5d**


160.0
138.9
136.3
129.3
128.6
126.7
123.0
114.8
62.4
55.5
54.8
37.8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

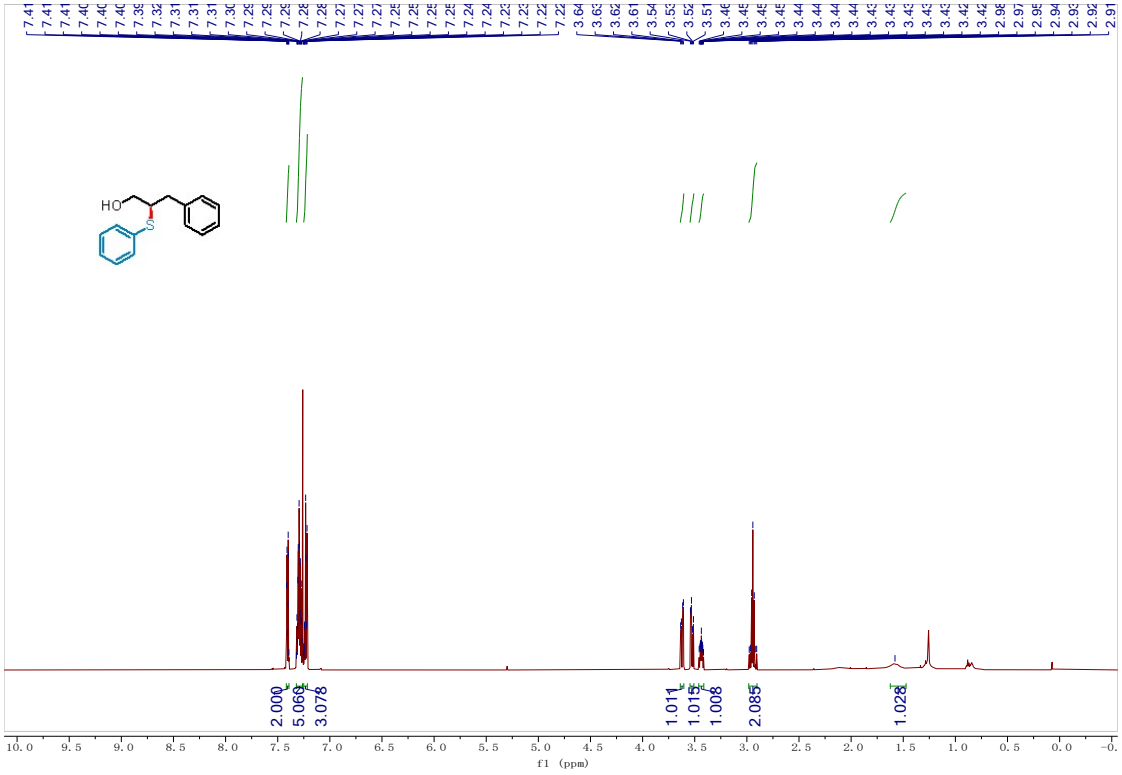
^{1}H NMR spectrum of compound **5e**



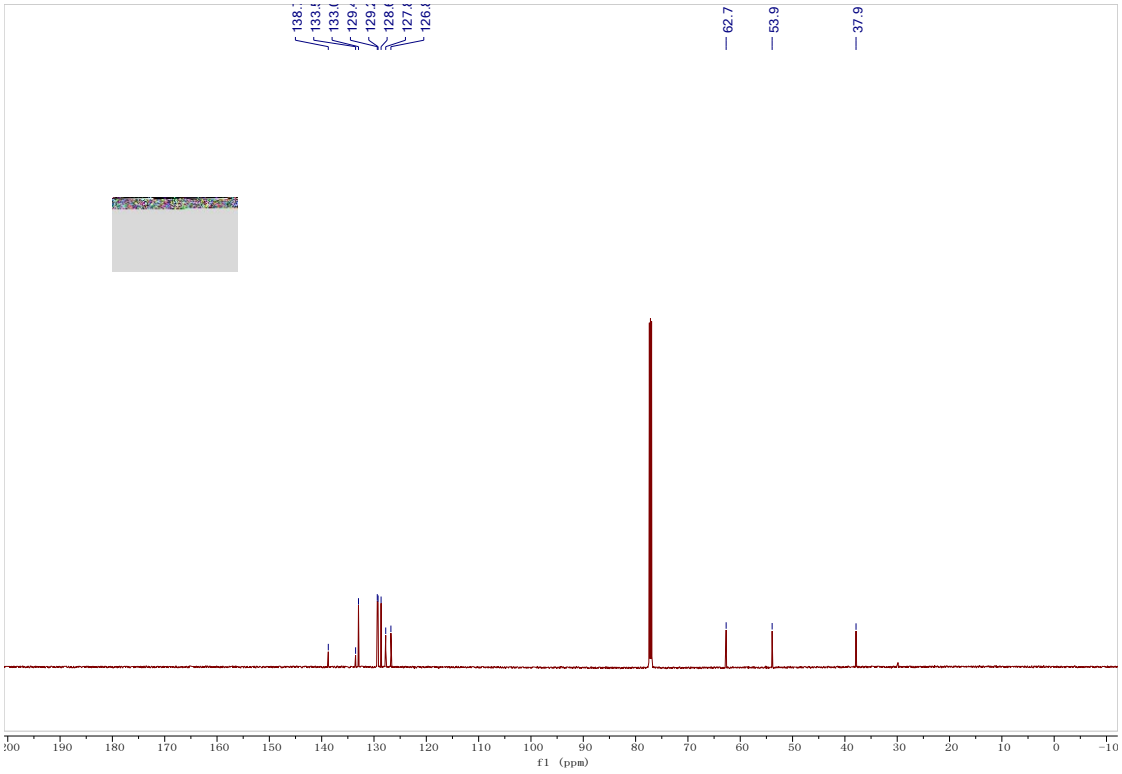
^{13}C NMR spectrum of compound **5e**


138.9
137.6
136.8
134.8
131.1
130.4
129.7
129.4
128.6
126.7
62.6
54.2
37.9
19.8
19.5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

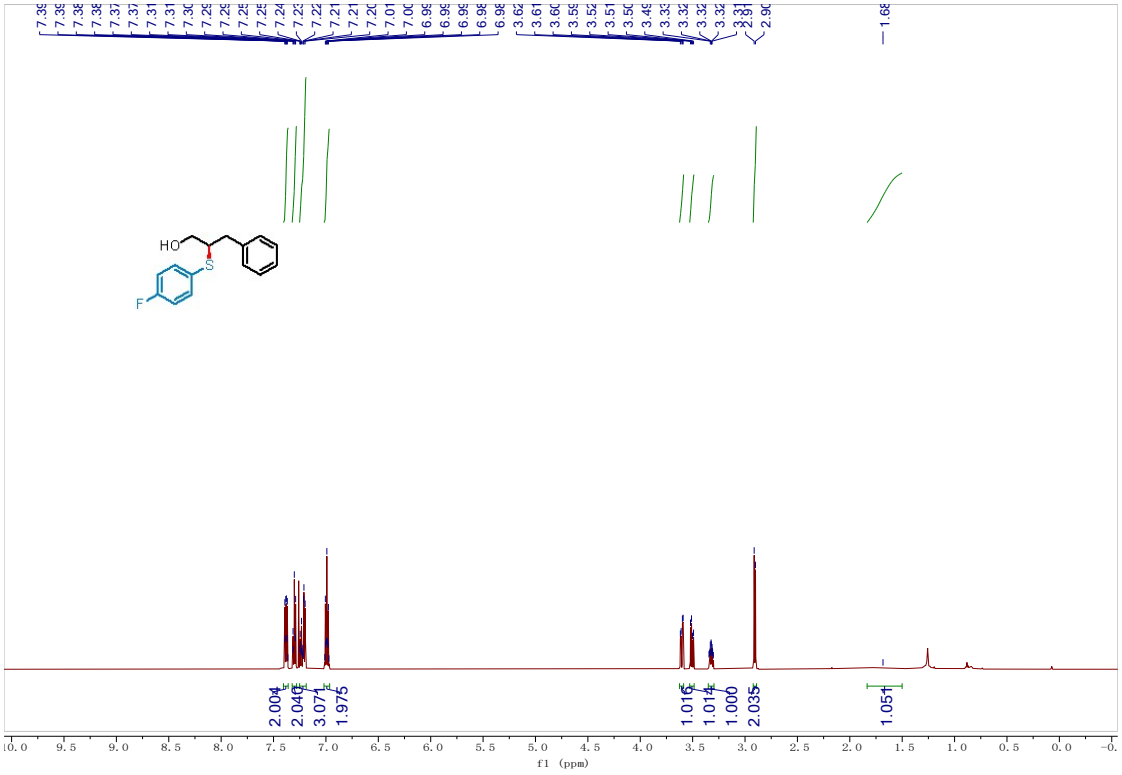
^{1}H NMR spectrum of compound **5f**



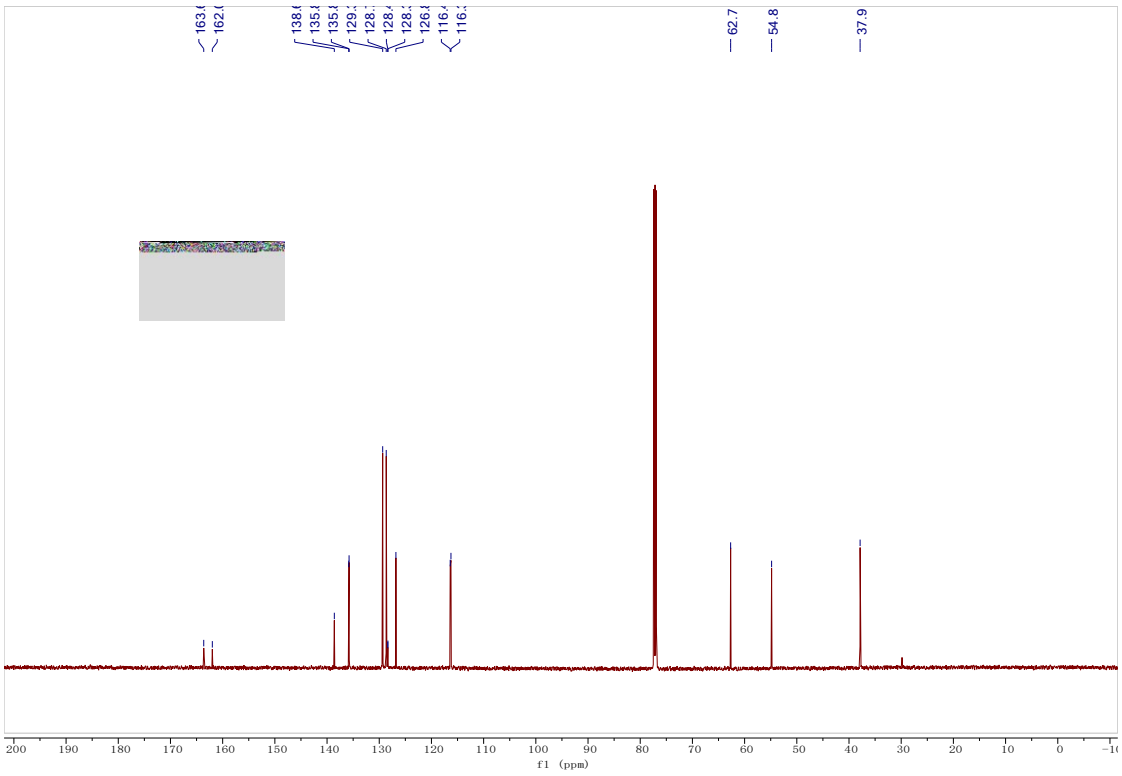
^{13}C NMR spectrum of compound **5f**


62.7
53.9
37.9
f1 (ppm)

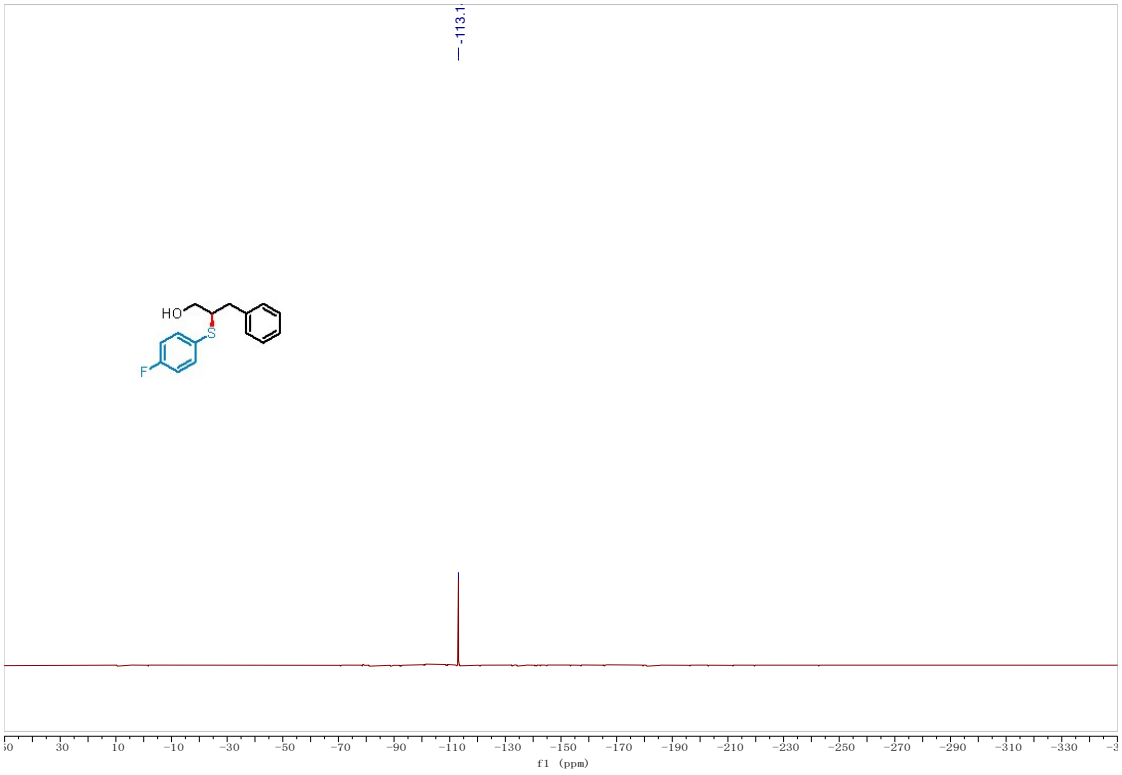
^{1}H NMR spectrum of compound **5g**



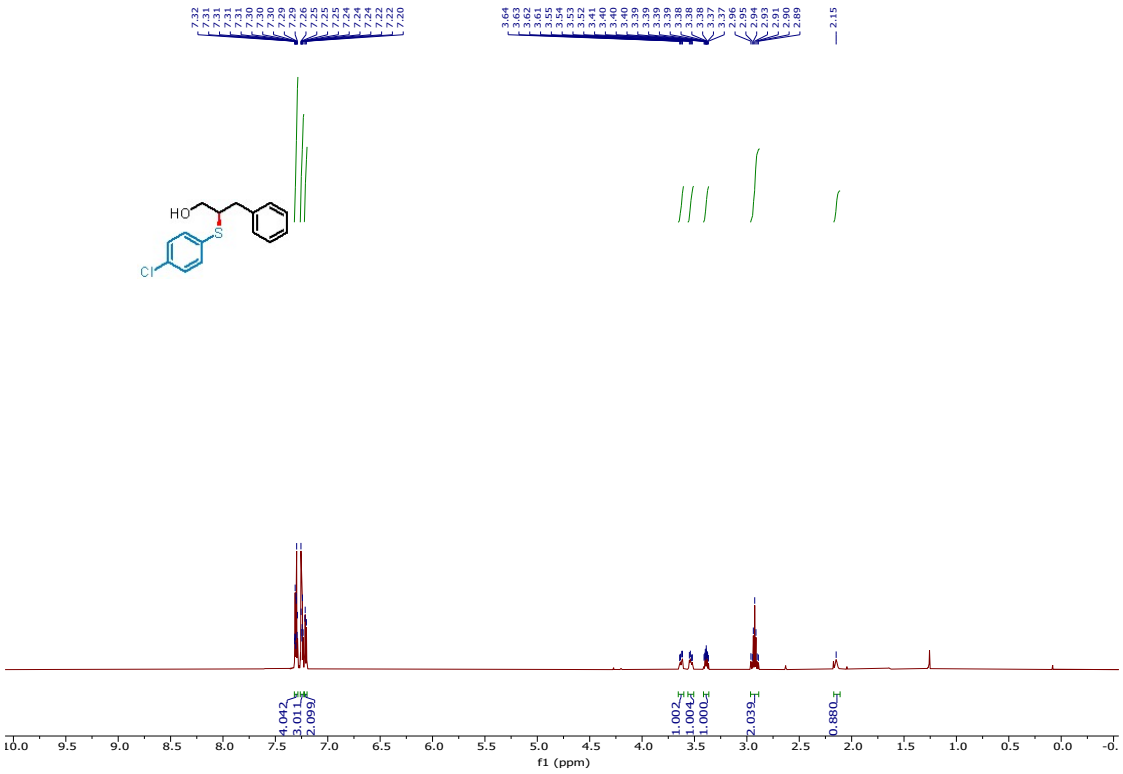
^{13}C NMR spectrum of compound **5g**


62.7
54.8
37.9
f1 (ppm)

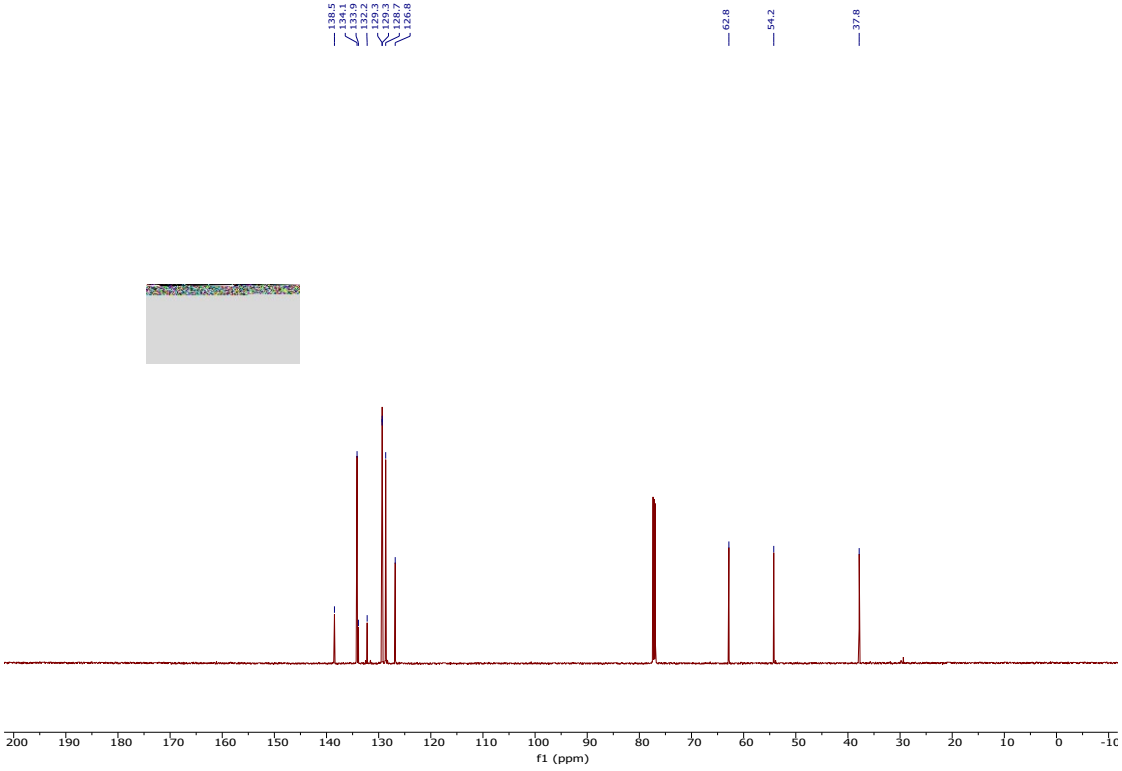
^{19}F NMR spectrum of compound **5g**



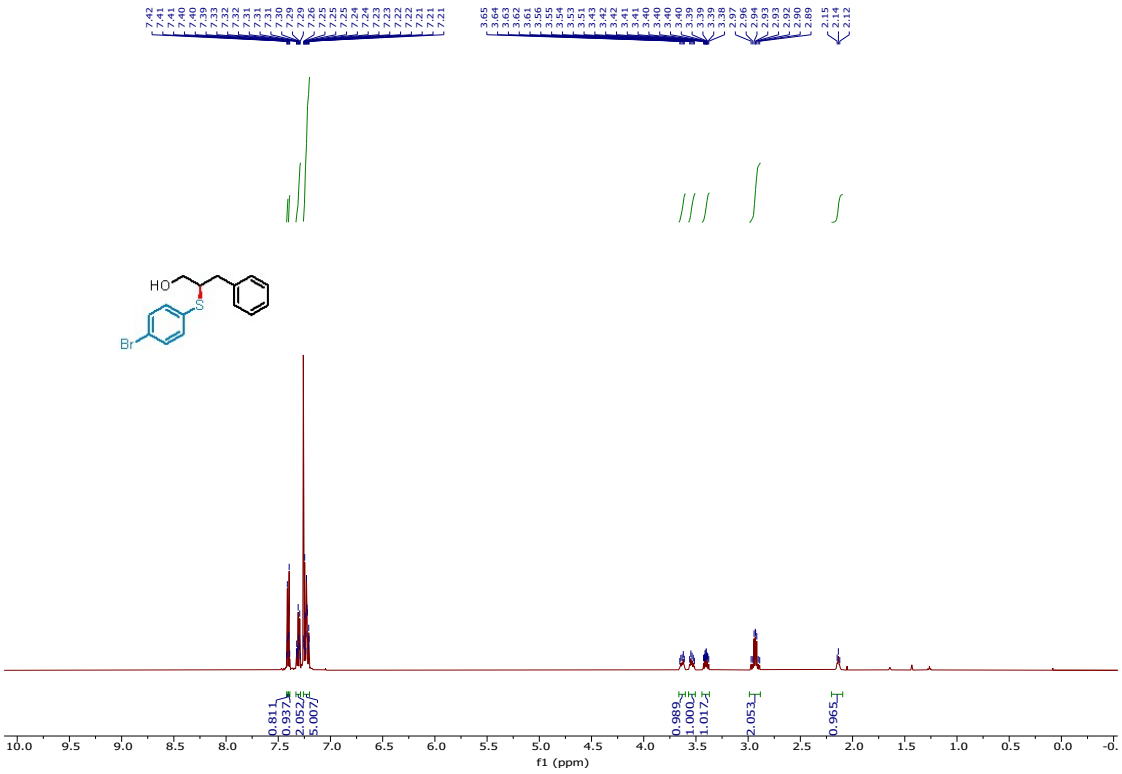
^{1}H NMR spectrum of compound **5h**


7.32
7.31
7.31
7.31
7.31
7.30
7.30
7.30
7.29
7.29
7.26
7.25
7.25
7.25
7.24
7.24
7.24
7.22
7.22
7.20
3.64
3.63
3.62
3.61
3.55
3.54
3.53
3.52
3.41
3.40
3.40
3.40
3.39
3.39
3.39
3.39
3.38
3.38
3.38
3.38
3.37
3.37
2.96
2.95
2.94
2.93
2.91
2.90
2.89
2.15
HO
S
Cl
4.042
3.011
2.099
1.002
1.004
1.000
2.039
0.880
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

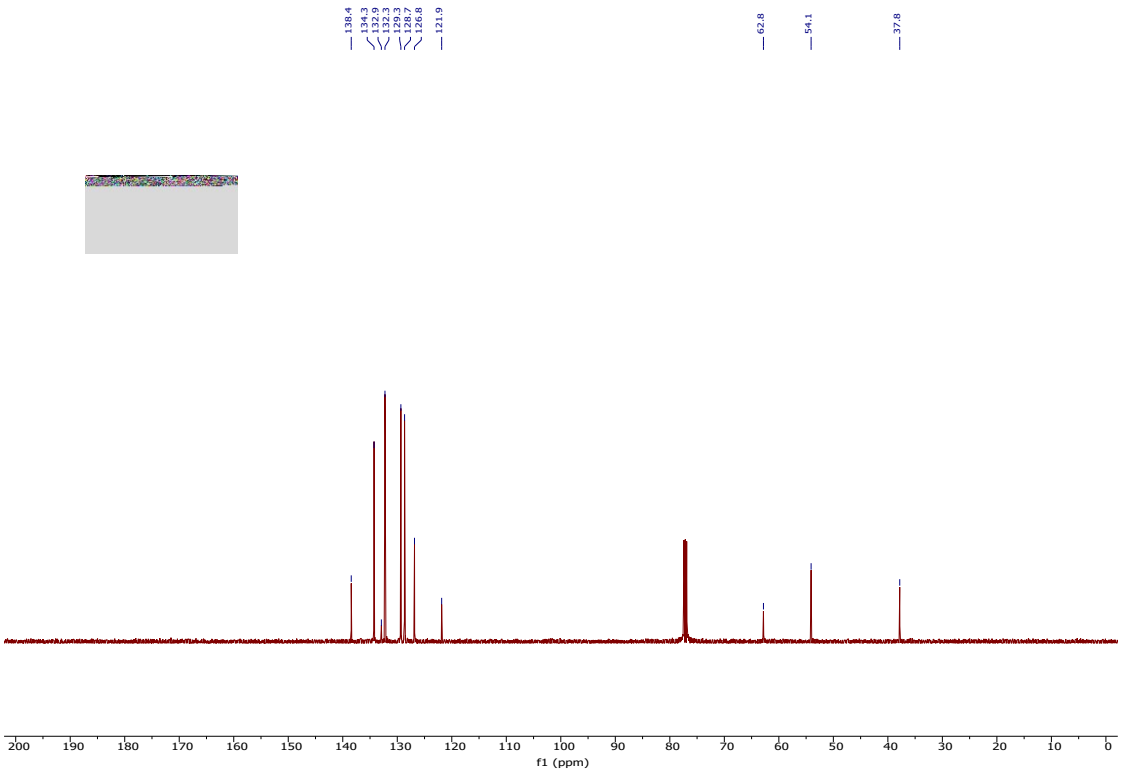
^{13}C NMR spectrum of compound **5h**



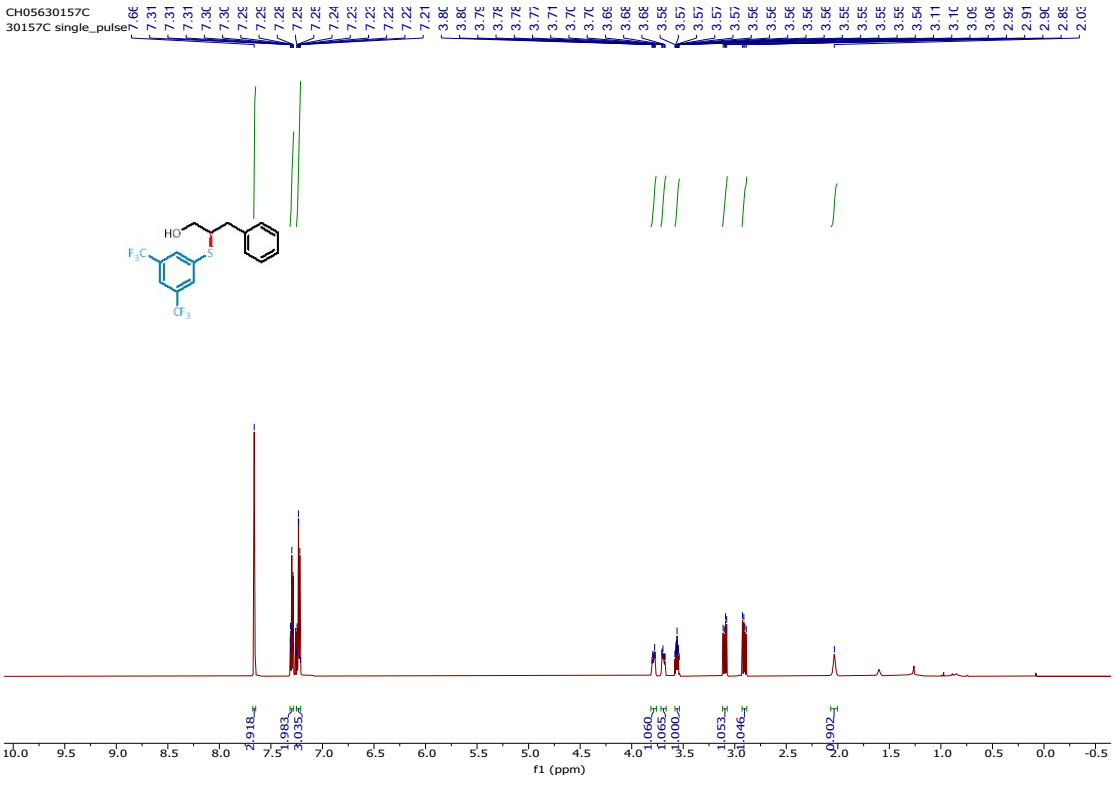
^{1}H NMR spectrum of compound **5i**


7.42 7.41 7.41 7.40 7.40 7.39 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.29 7.26 7.25 7.25 7.24 7.24 7.23 7.22 7.22 7.21 7.21
3.65 3.64 3.63 3.62 3.61 3.56 3.55 3.54 3.53 3.51 3.43 3.42 3.42 3.41 3.41 3.40 3.40 3.40 3.39 3.39 3.39 3.38 2.97 2.96 2.94 2.93 2.93 2.92 2.90 2.89 2.15 2.14 2.12
HO
S
Br
0.811 0.937 2.052 5.007 0.989 1.000 1.017 2.053 0.965
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

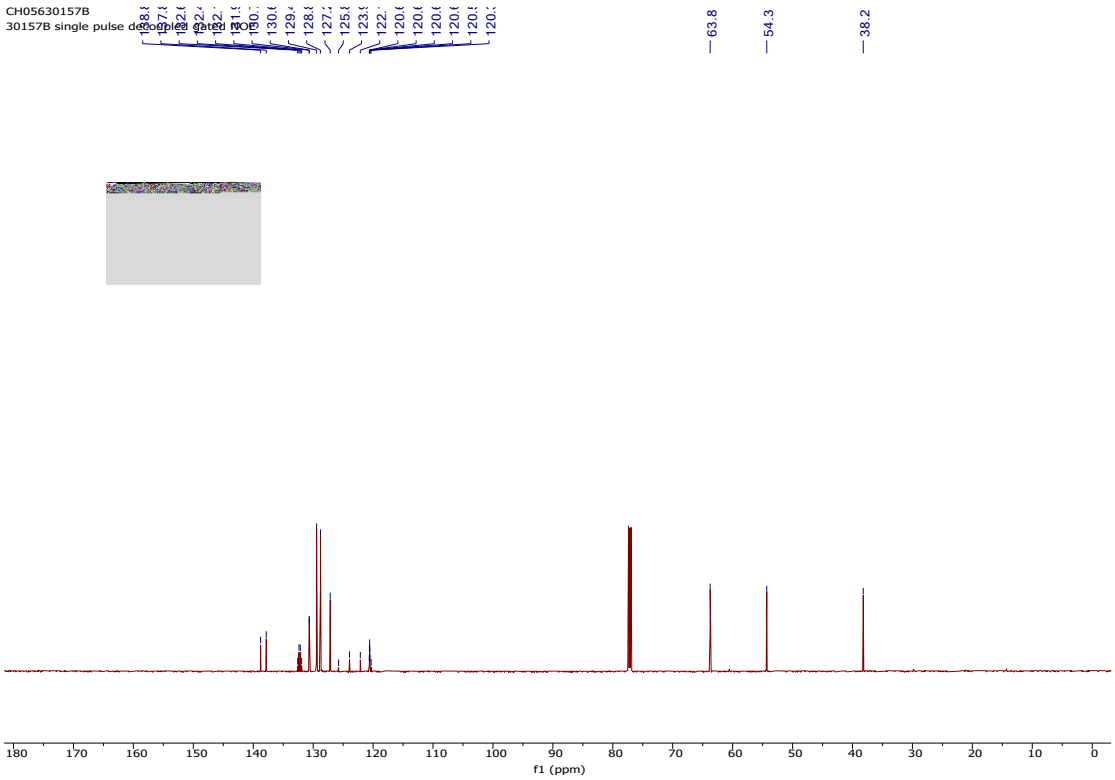
^{13}C NMR spectrum of compound **5i**



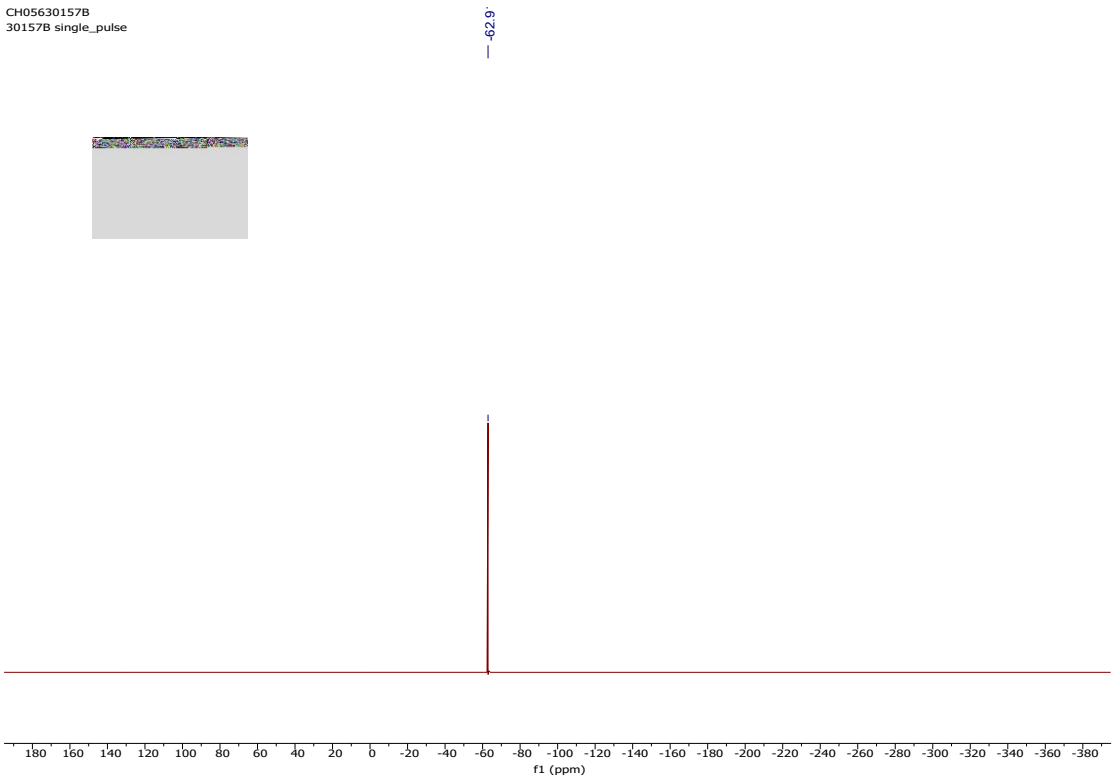
^{1}H NMR spectrum of compound **5j**



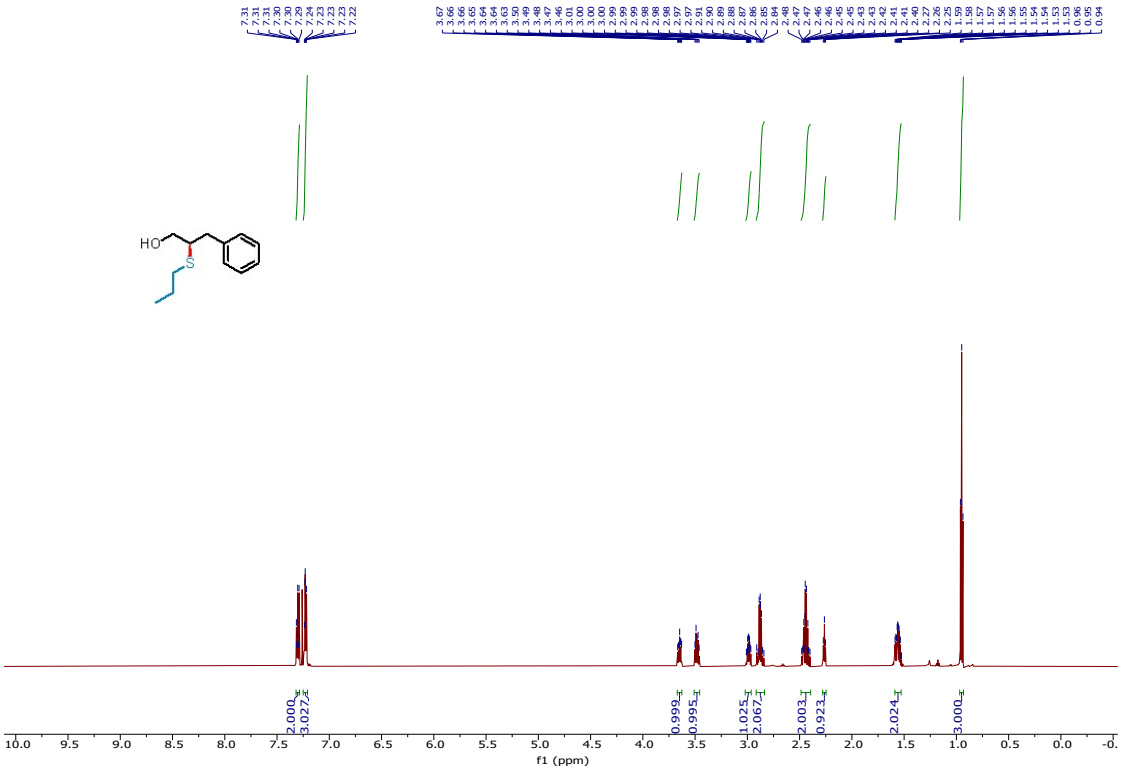
^{13}C NMR spectrum of compound **5j**



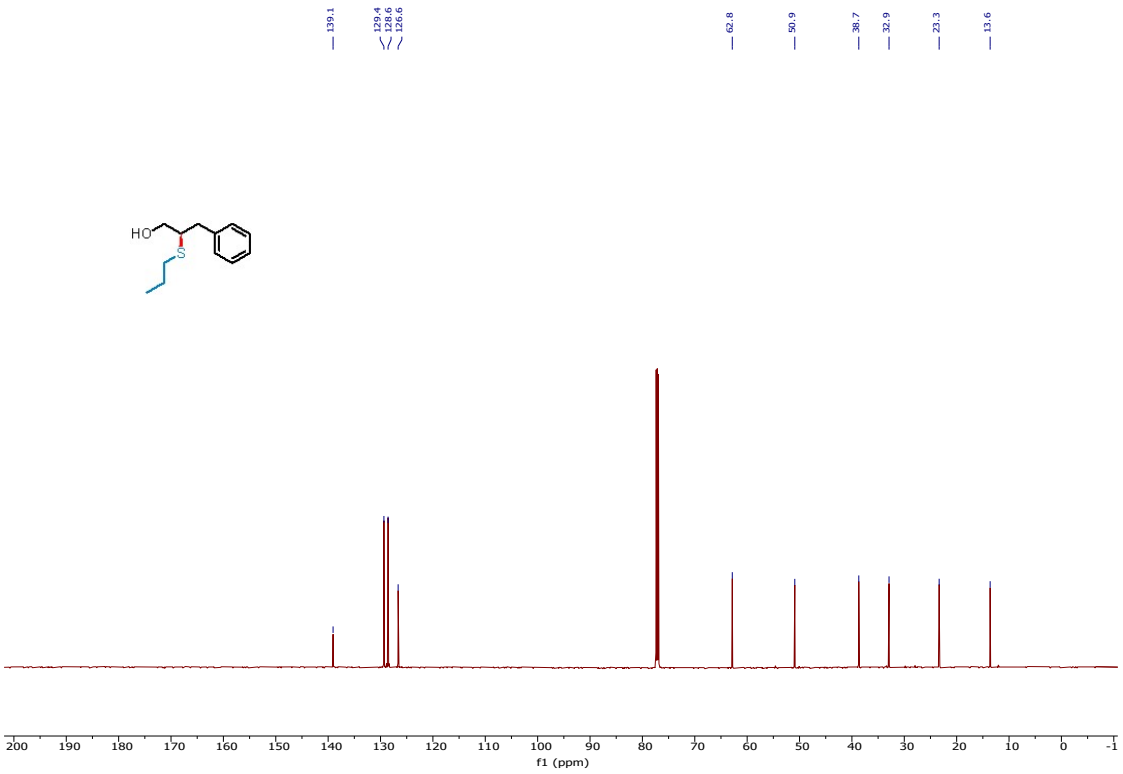
^{19}F NMR spectrum of compound **5j**



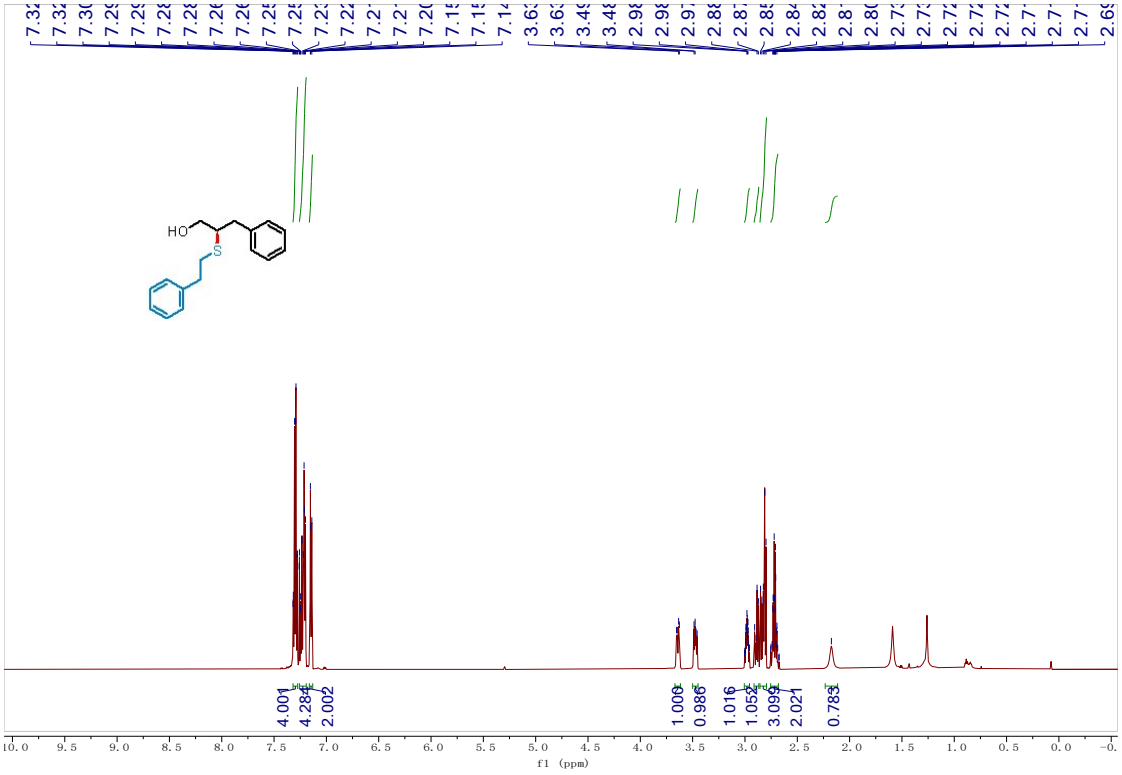
^{1}H NMR spectrum of compound **5k**



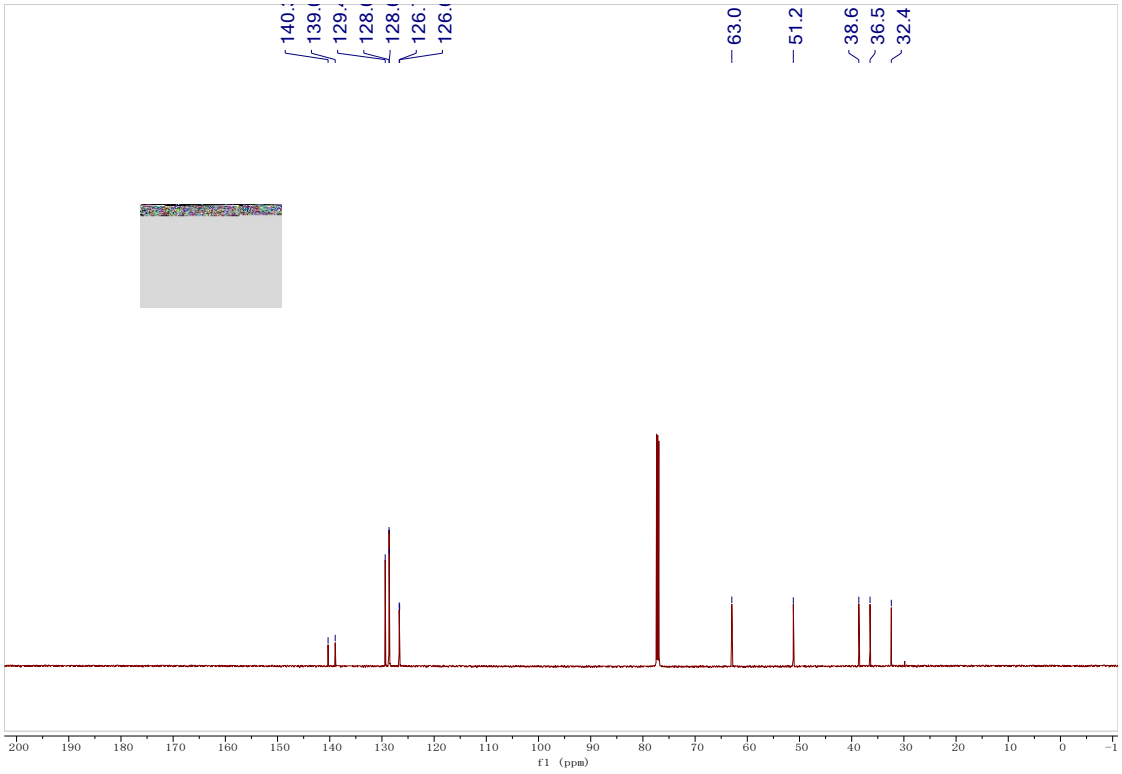
^{13}C NMR spectrum of compound **5k**


139.1
129.4
128.6
126.6
62.8
50.9
38.7
32.9
23.3
13.6
HO
S
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

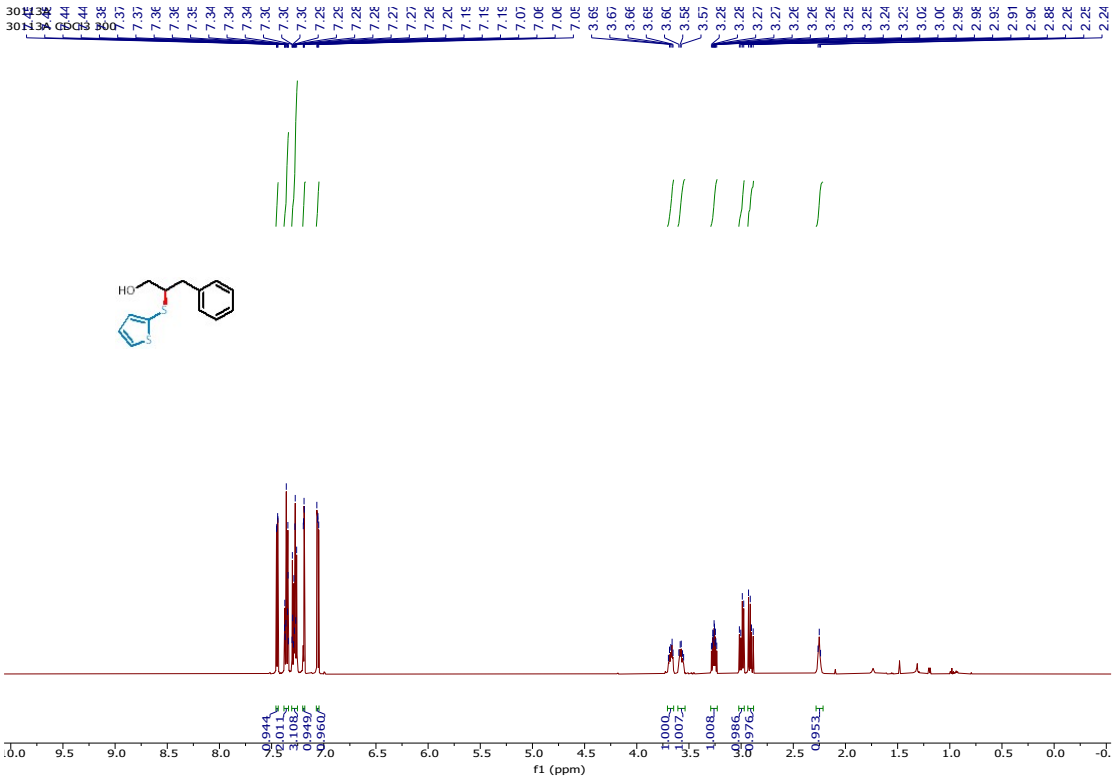
^{1}H NMR spectrum of compound **5l**



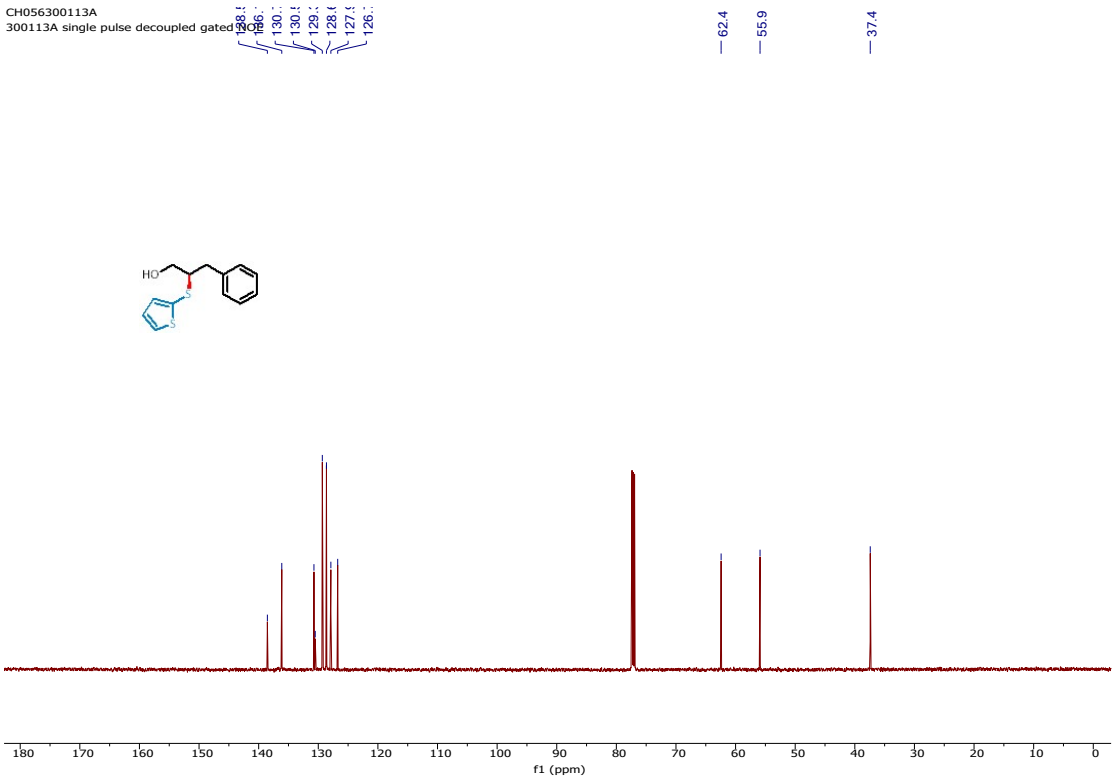
^{13}C NMR spectrum of compound **5l**


63.0
51.2
38.6
36.5
32.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

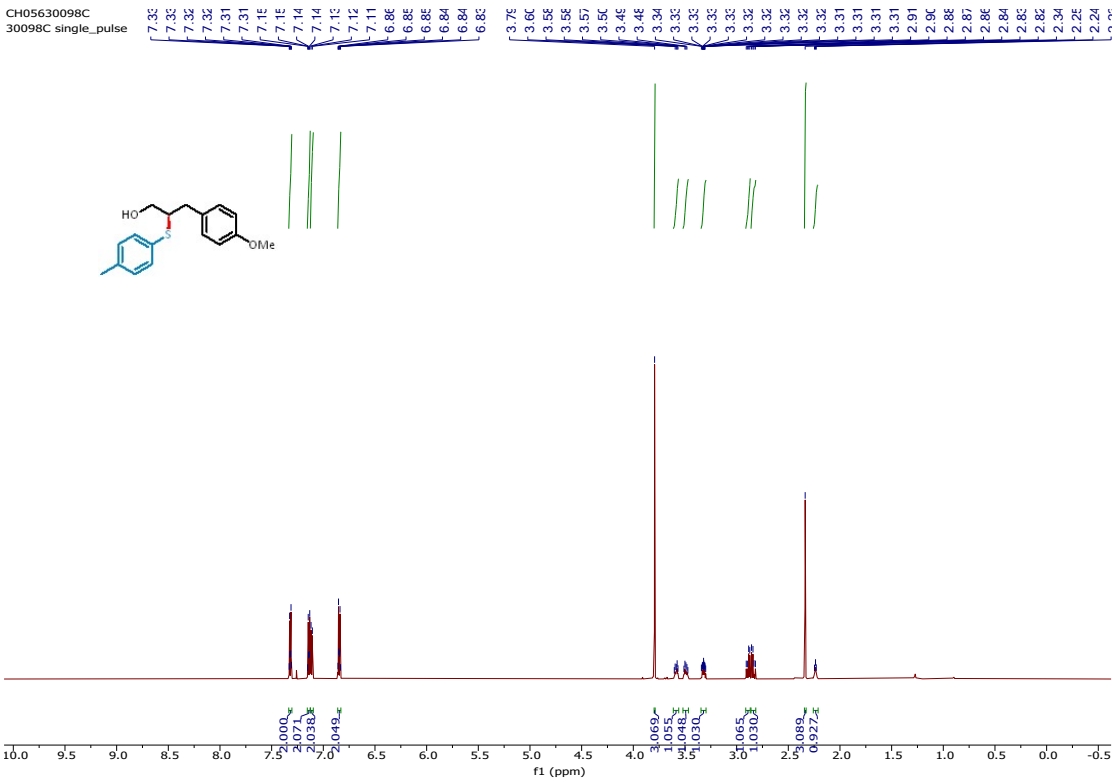
^{1}H NMR spectrum of compound **5m**



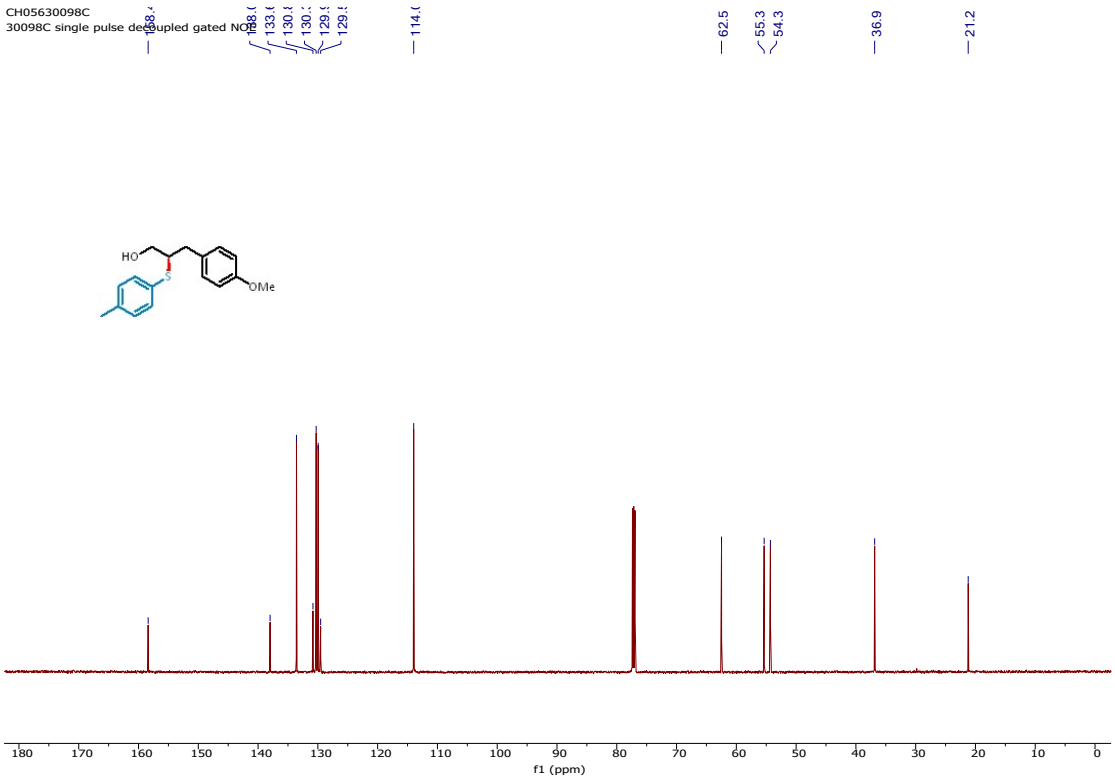
^{13}C NMR spectrum of compound **5m**



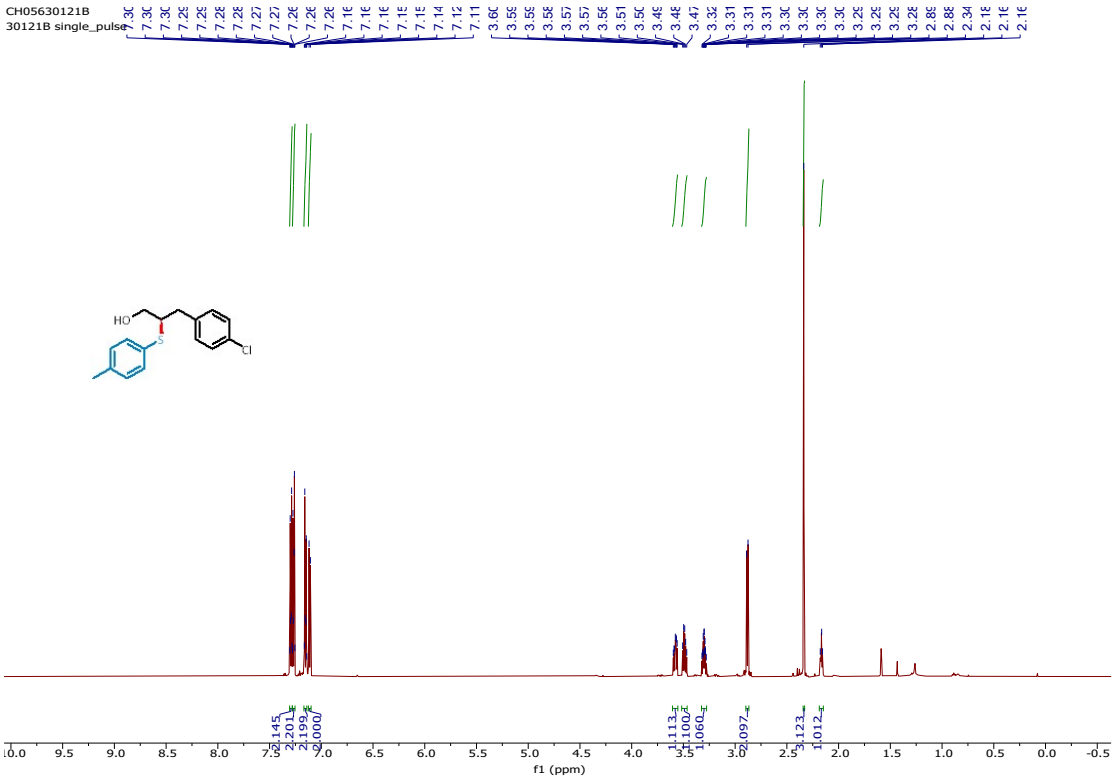
^{1}H NMR spectrum of compound **5n**



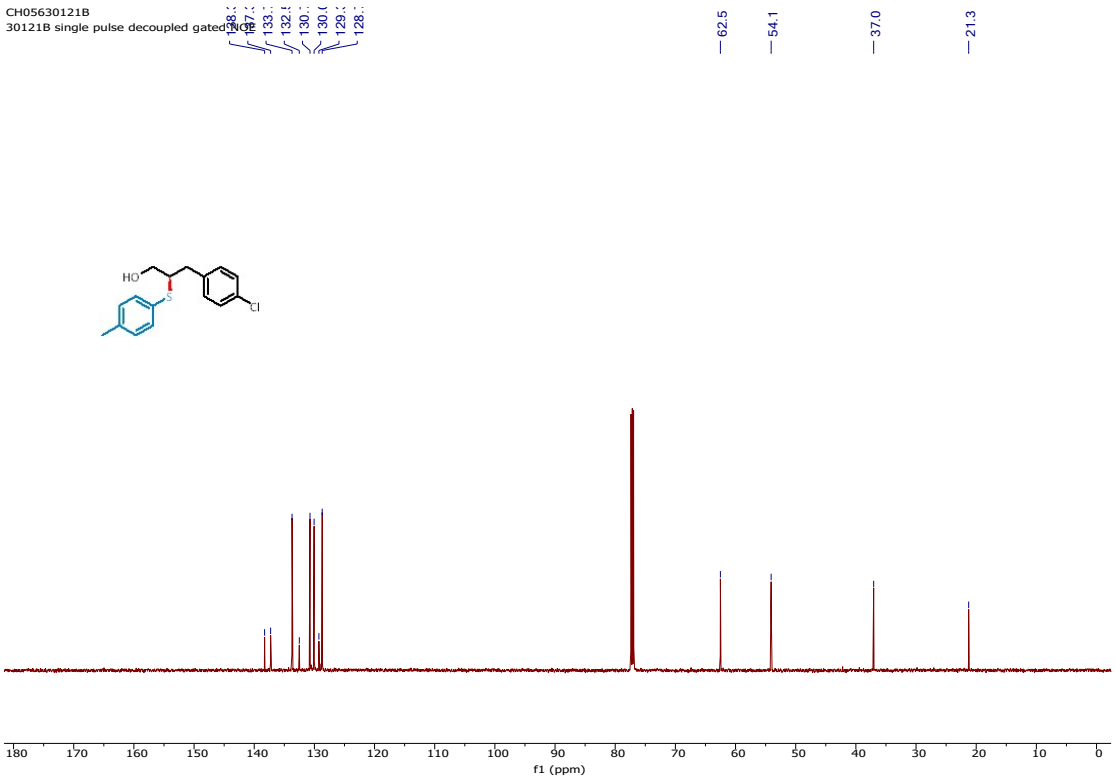
^{13}C NMR spectrum of compound **5n**



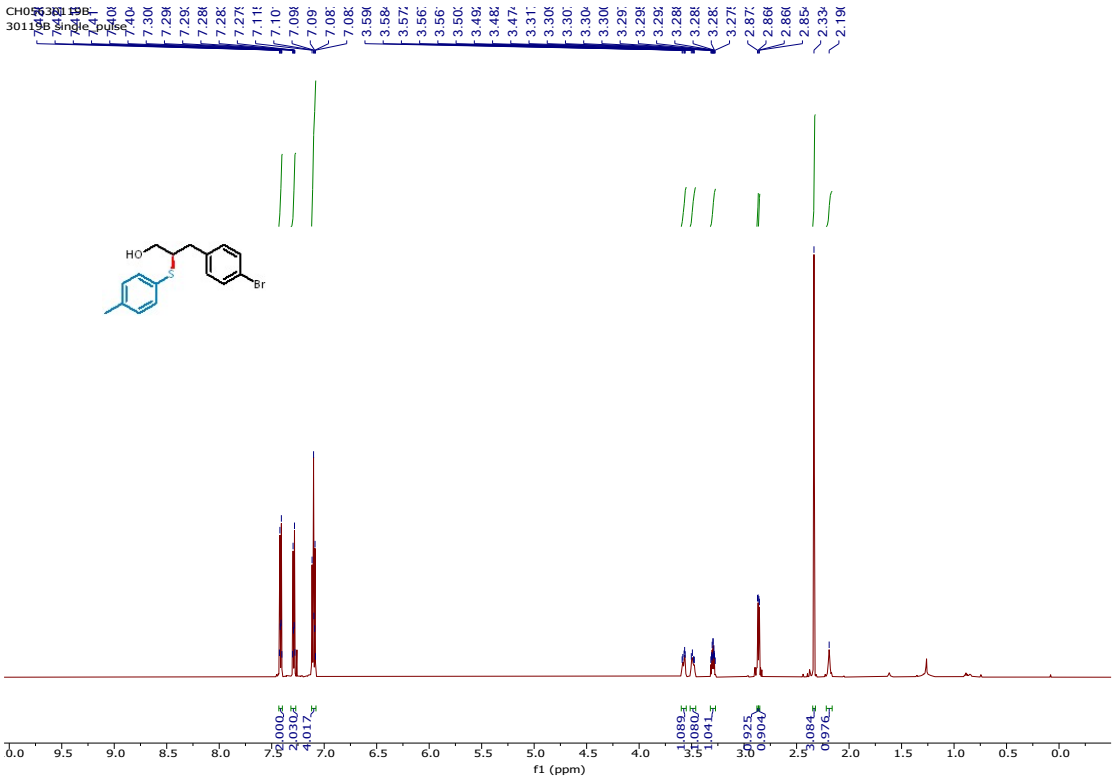
^{1}H NMR spectrum of compound **5o**



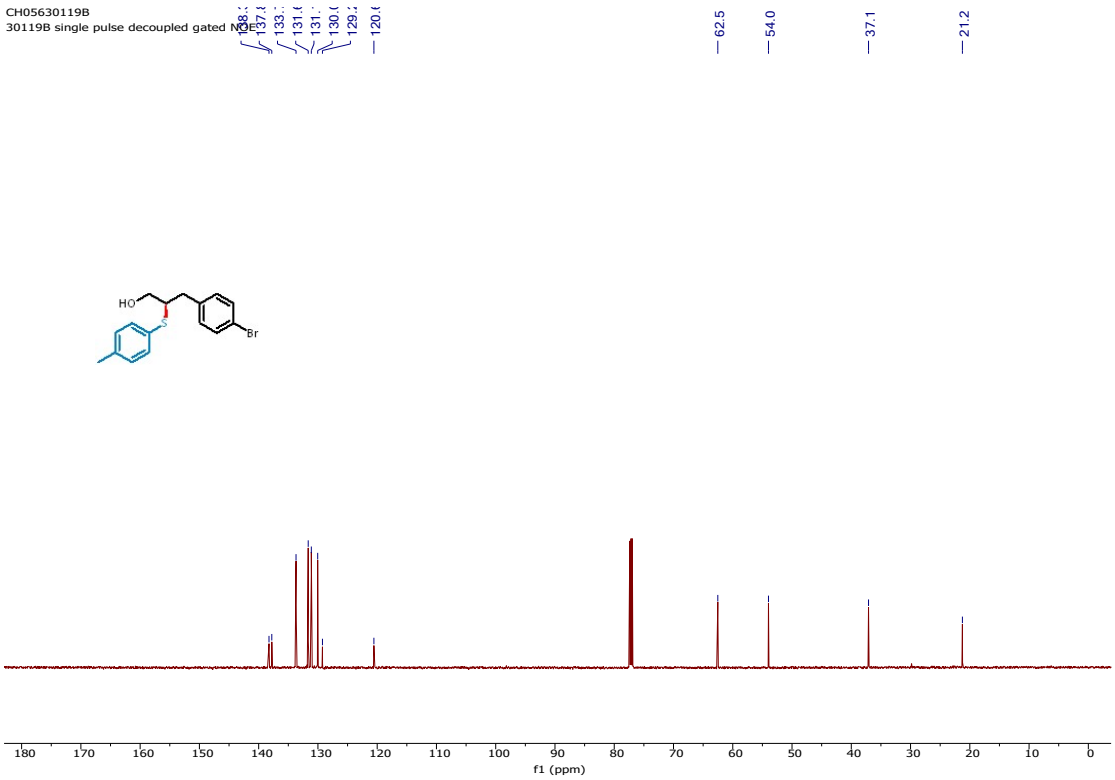
^{13}C NMR spectrum of compound **5o**



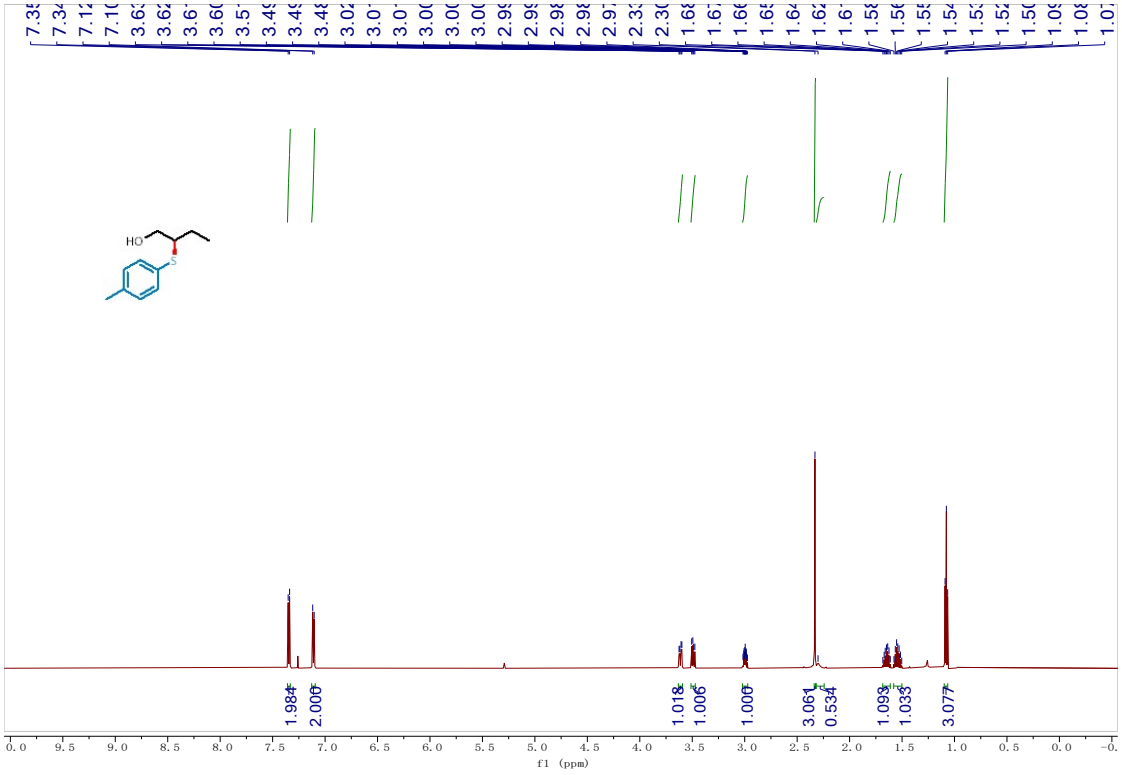
^{1}H NMR spectrum of compound **5p**



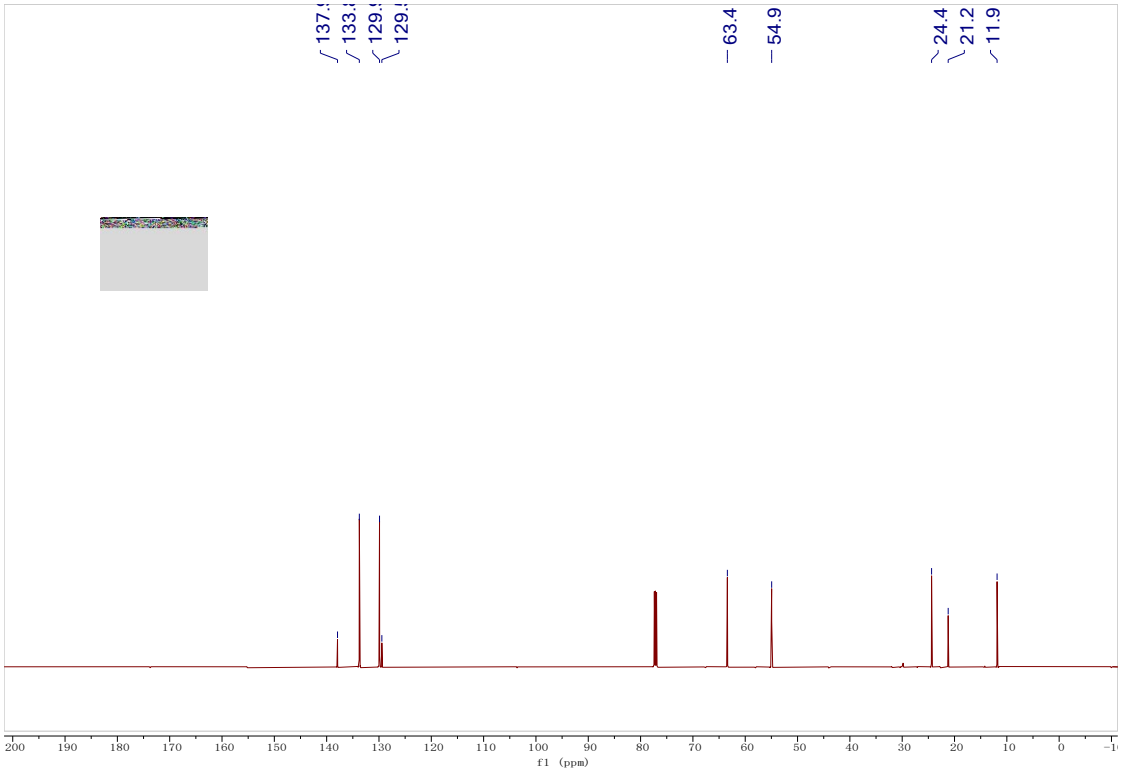
^{13}C NMR spectrum of compound **5p**



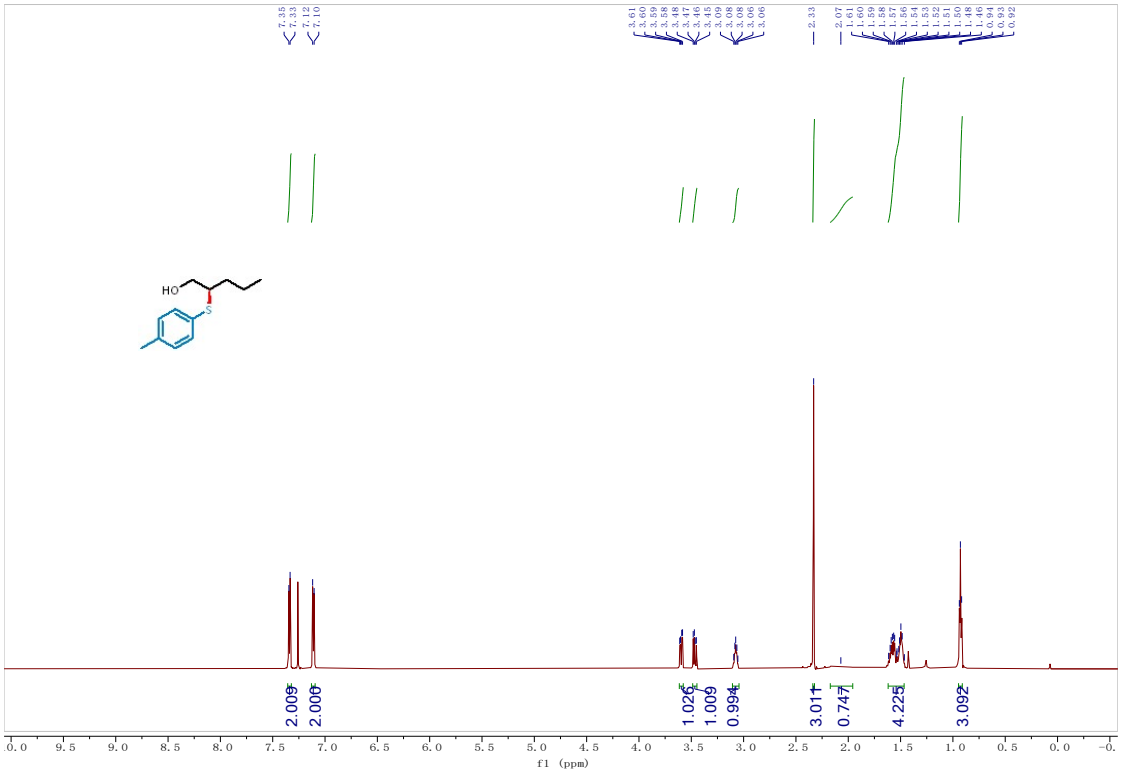
^{1}H NMR spectrum of compound **5q**



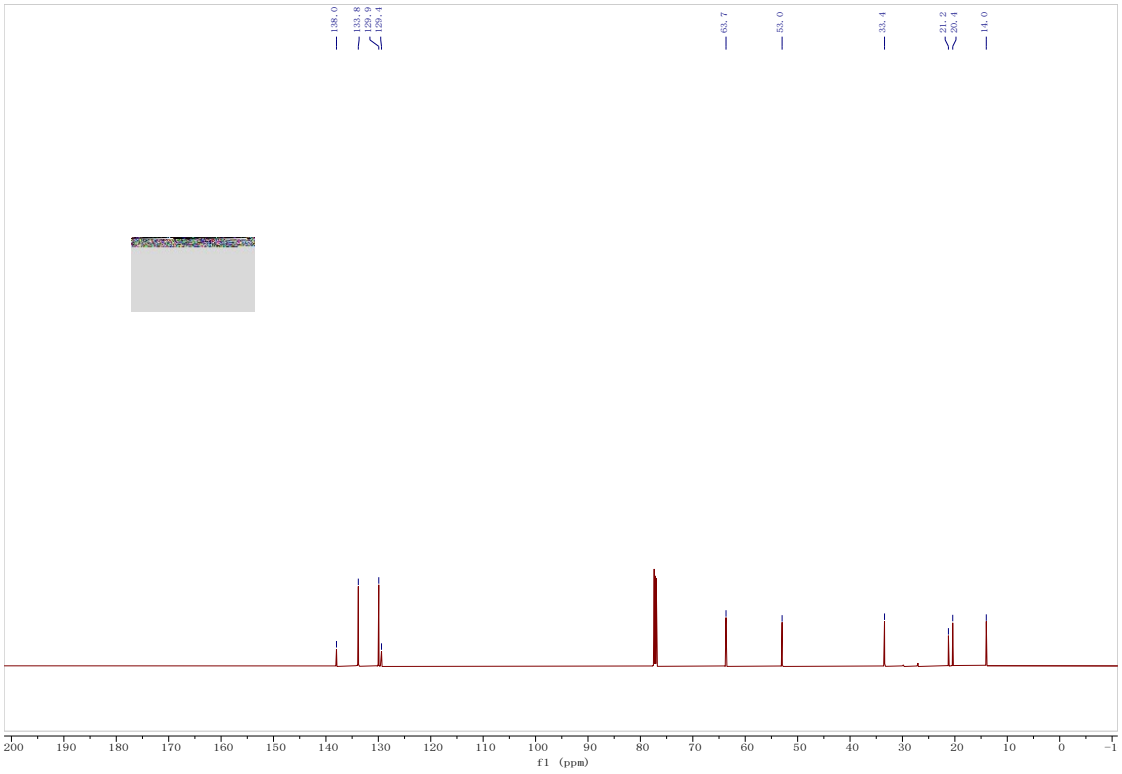
^{13}C NMR spectrum of compound **5q**


137.
133.
129.
129.
63.4
54.9
24.4
21.2
11.9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

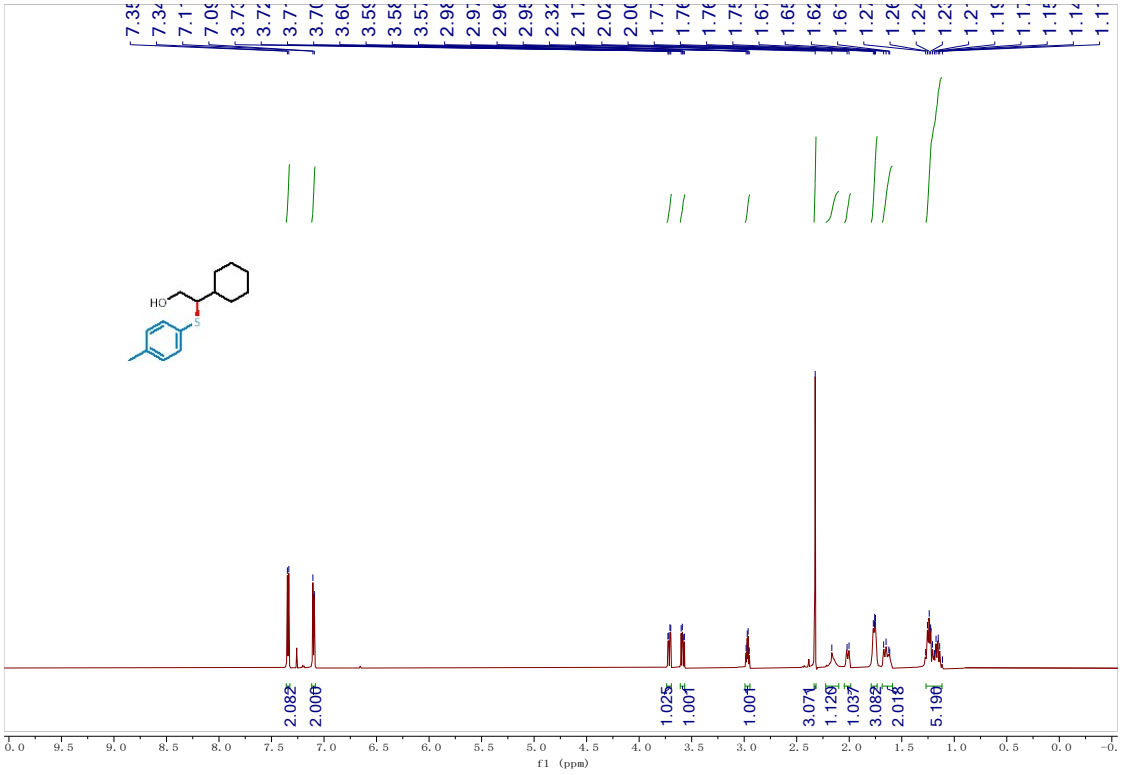
^{1}H NMR spectrum of compound **5r**



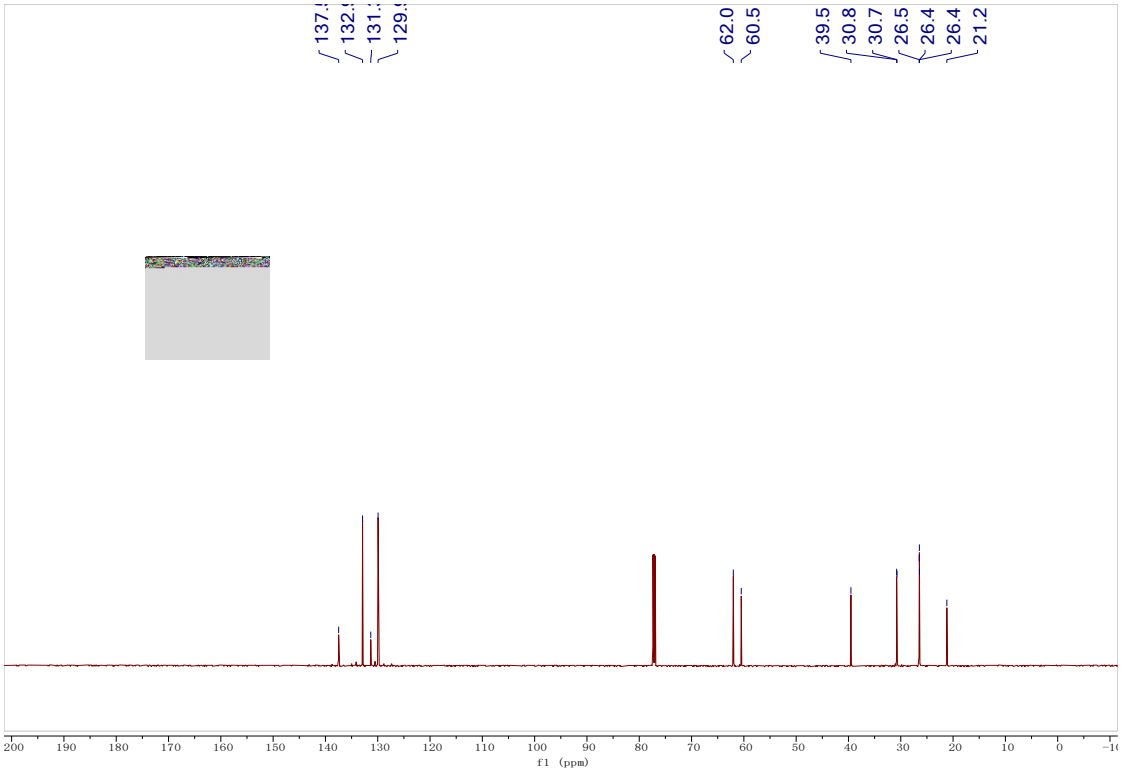
^{13}C NMR spectrum of compound **5r**


138.0
133.8
129.9
129.4
63.7
53.0
33.4
21.2
20.4
14.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

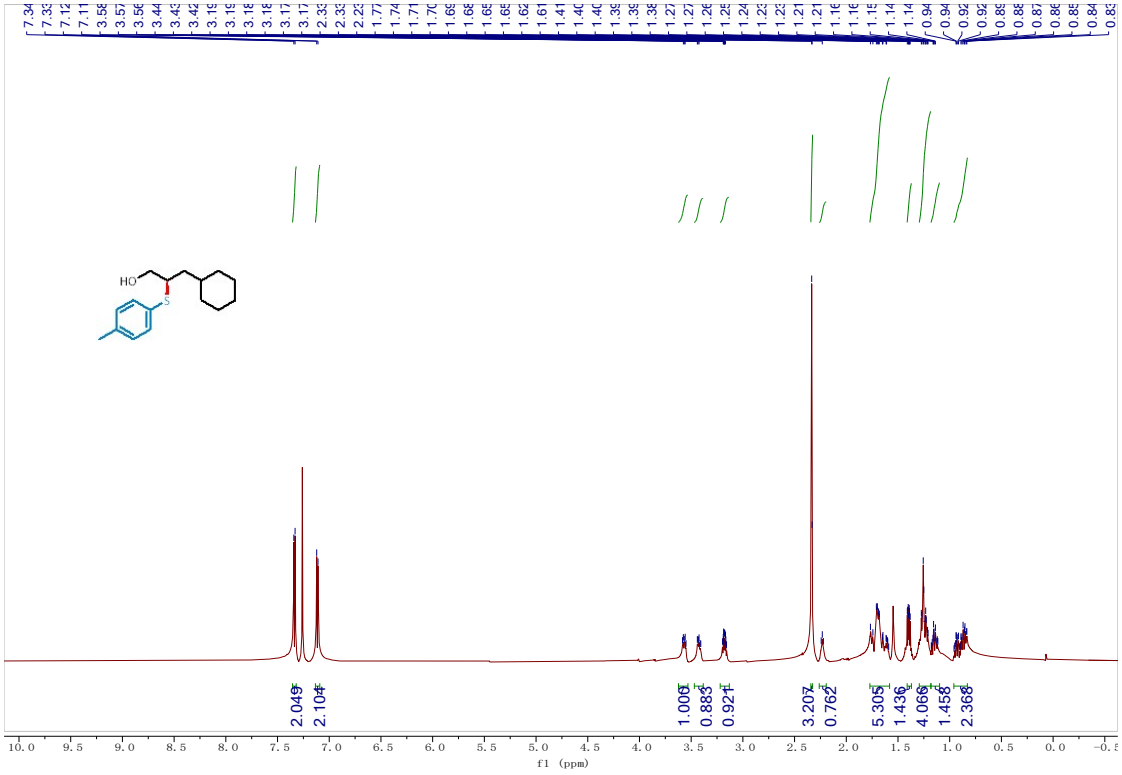
^{1}H NMR spectrum of compound **5s**



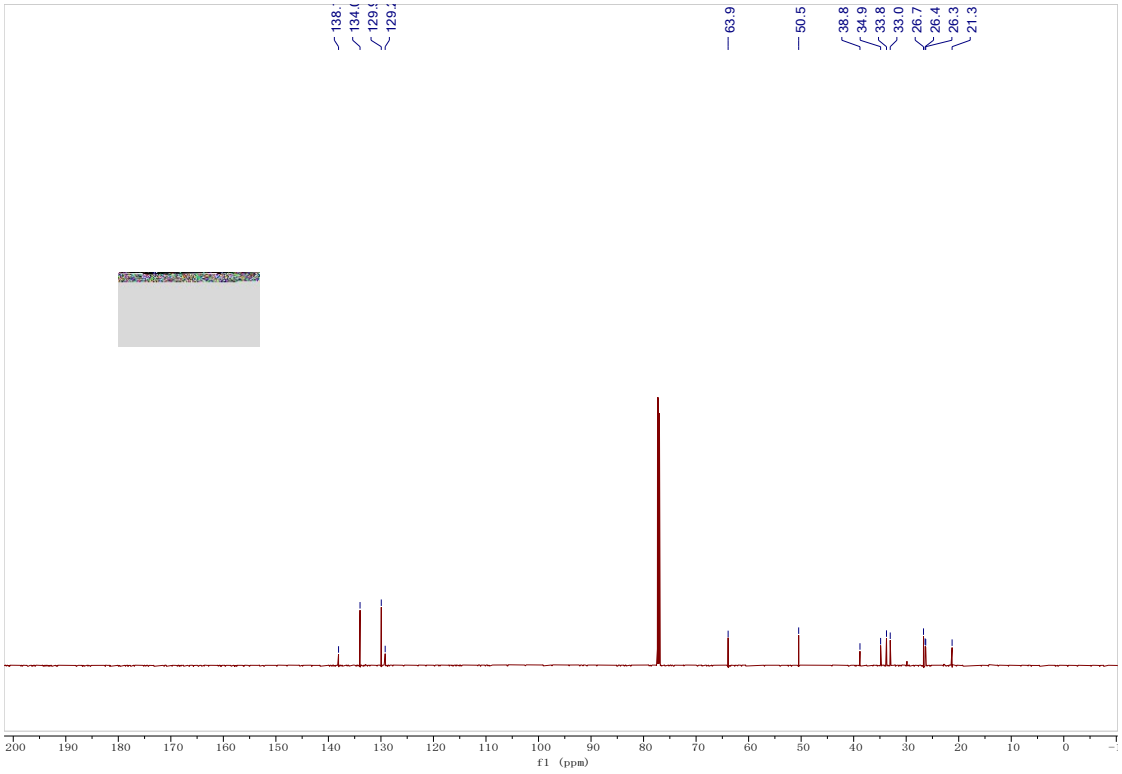
^{13}C NMR spectrum of compound **5s**


137.
132.
131.
129.
62.0
60.5
39.5
30.8
30.7
26.5
26.4
26.4
21.2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

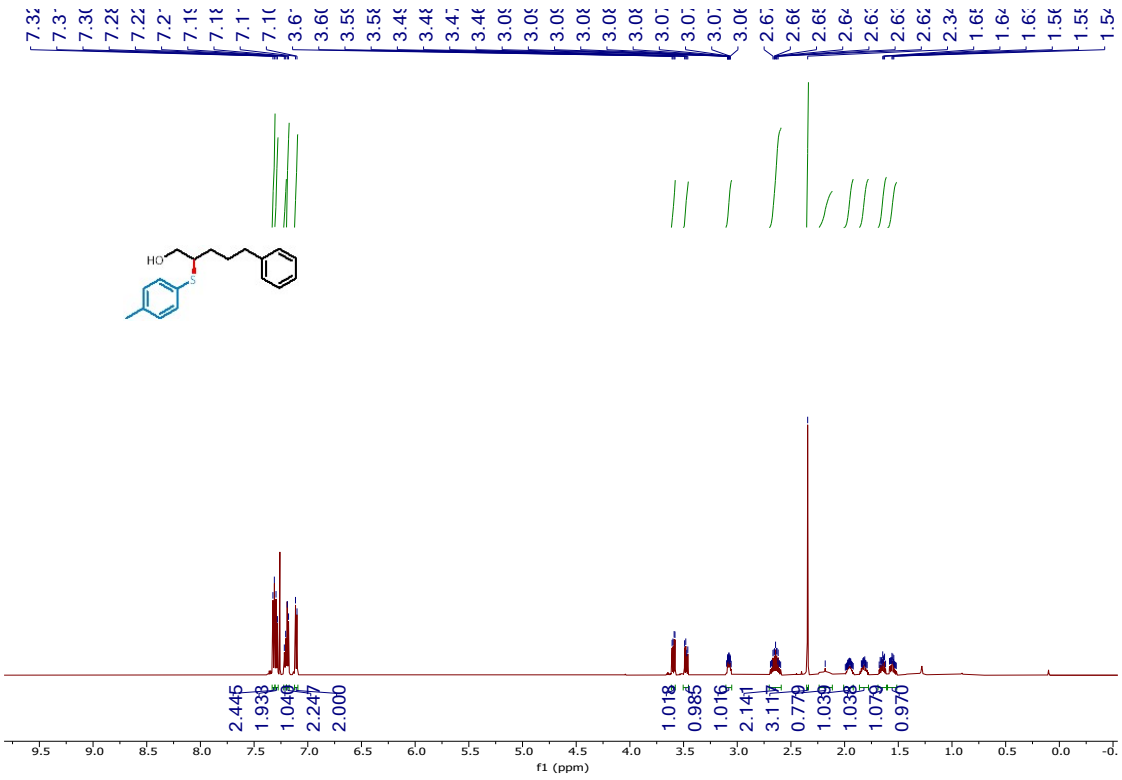
^{1}H NMR spectrum of compound **5t**



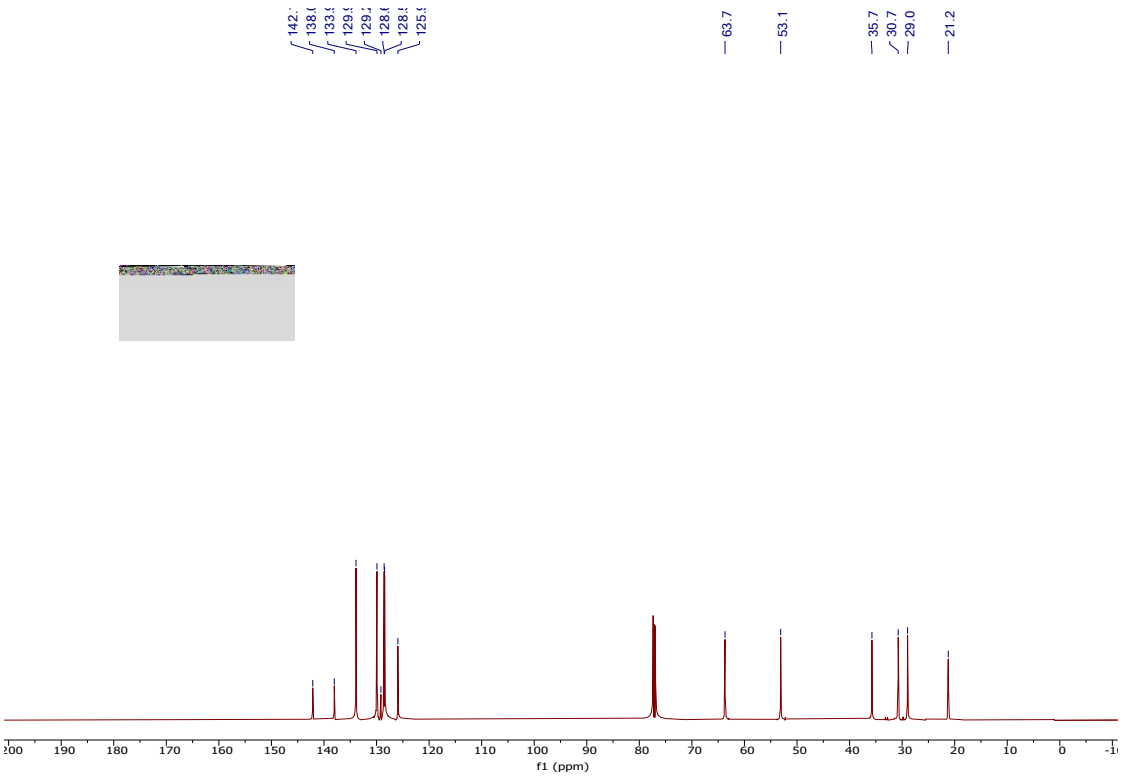
^{13}C NMR spectrum of compound **5t**


63.9
50.5
38.8
34.9
33.8
33.0
26.7
26.4
26.3
21.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

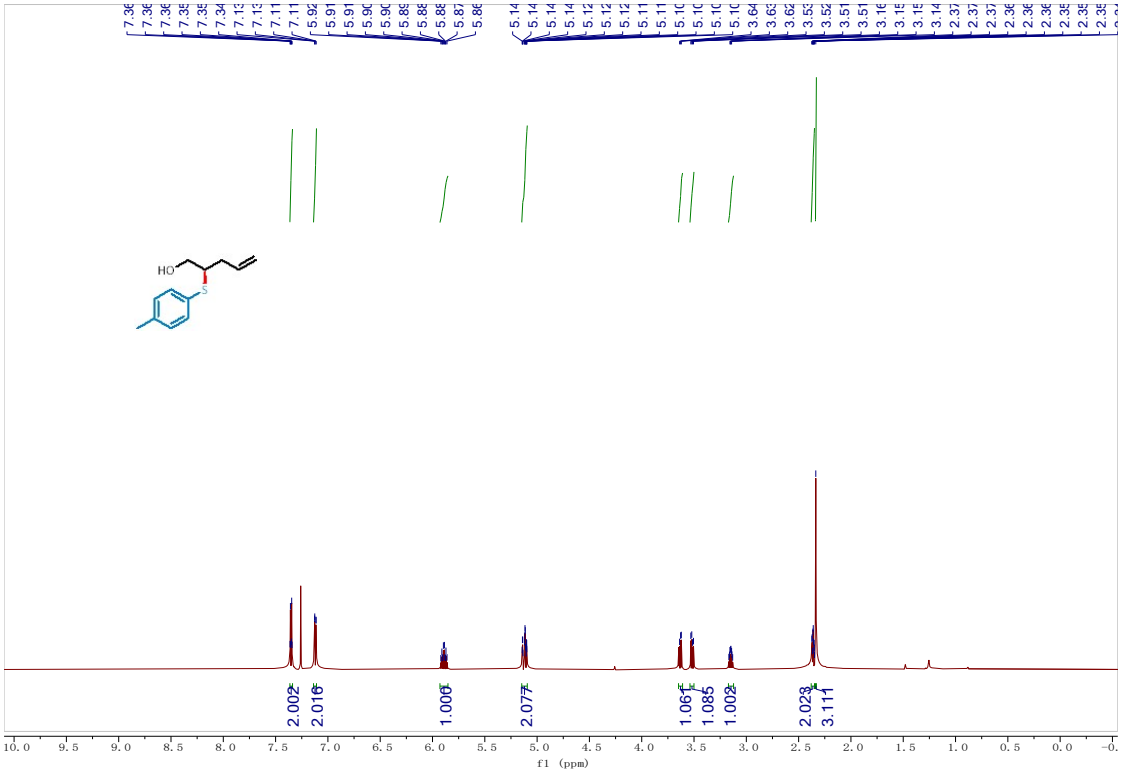
^{1}H NMR spectrum of compound **5u**



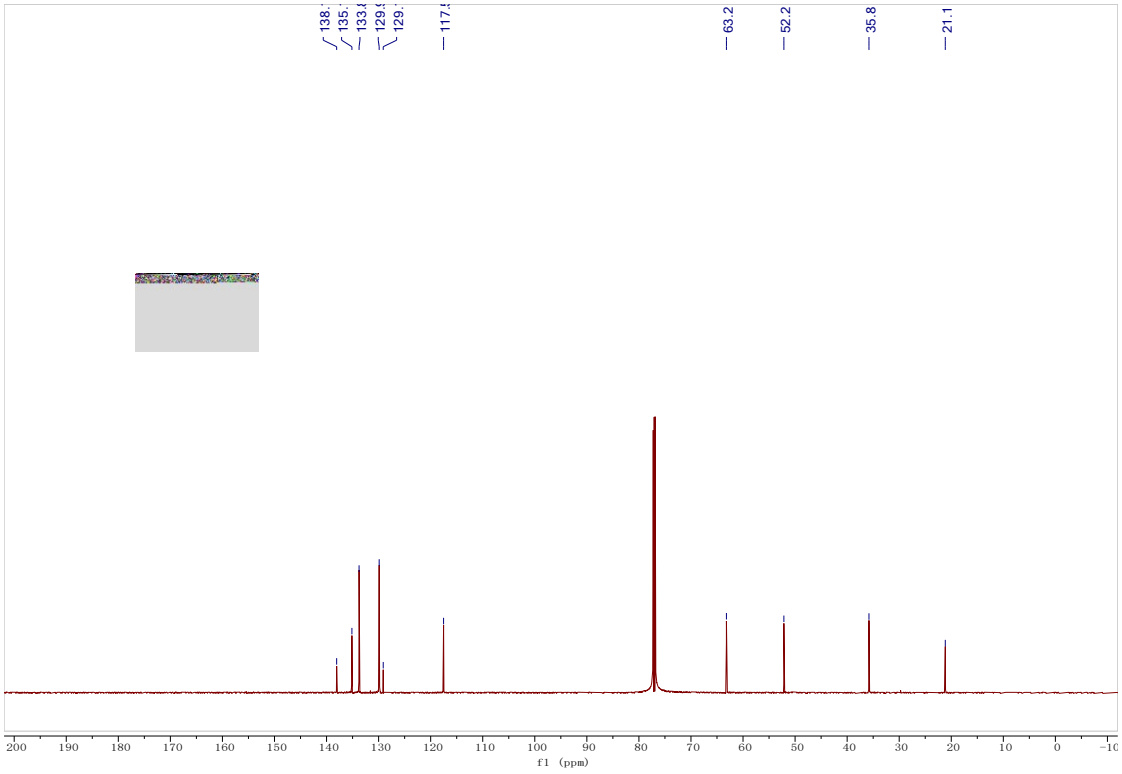
^{13}C NMR spectrum of compound **5u**


63.7
53.1
35.7
30.7
29.0
21.2
f1 (ppm)

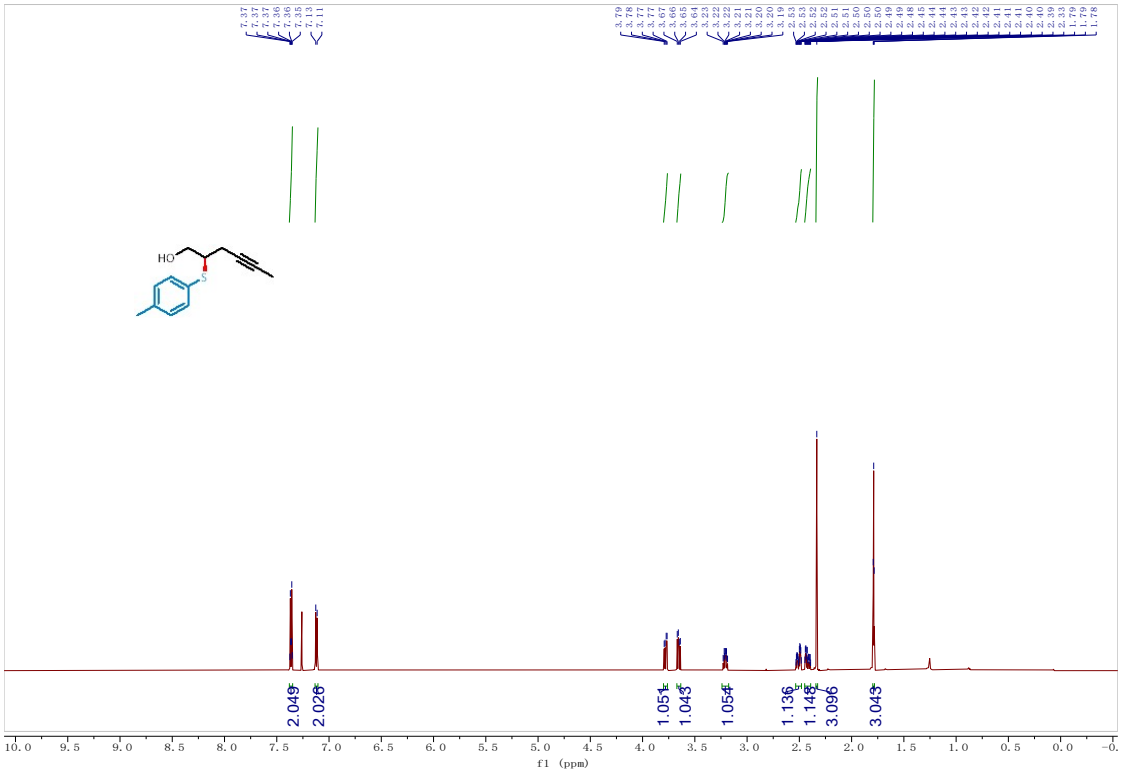
^{1}H NMR spectrum of compound **5v**



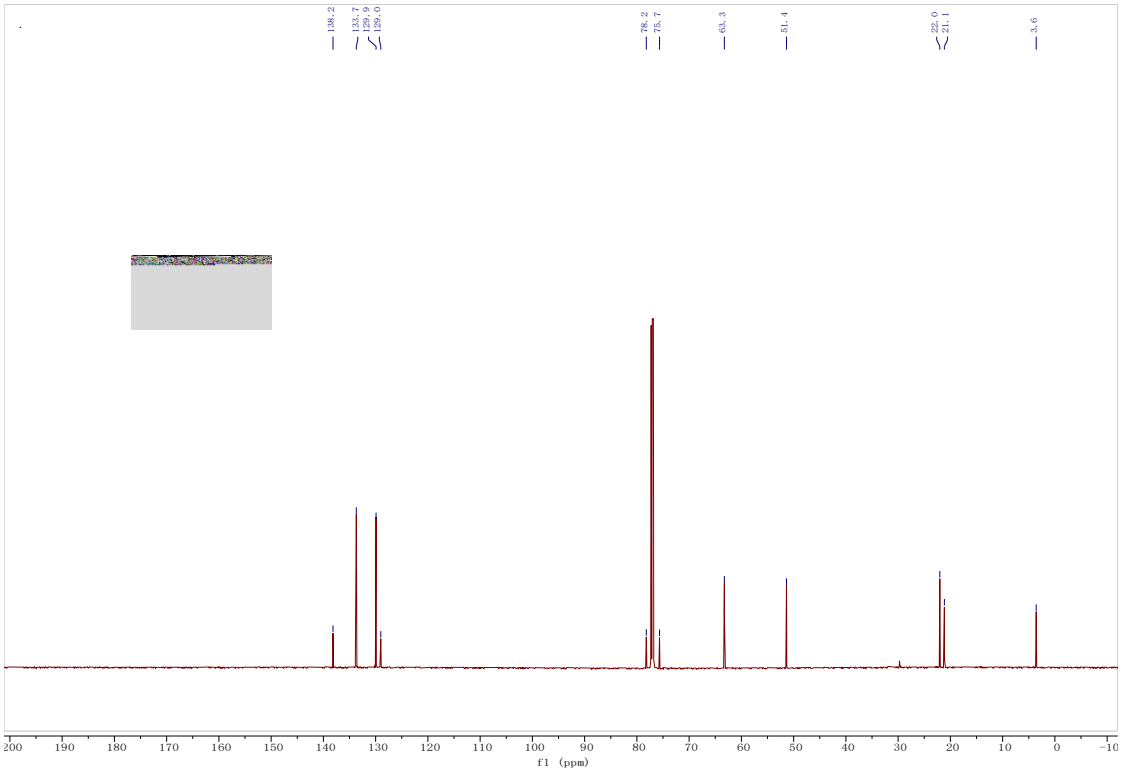
^{13}C NMR spectrum of compound **5v**


63.2
52.2
35.8
21.1
f1 (ppm)

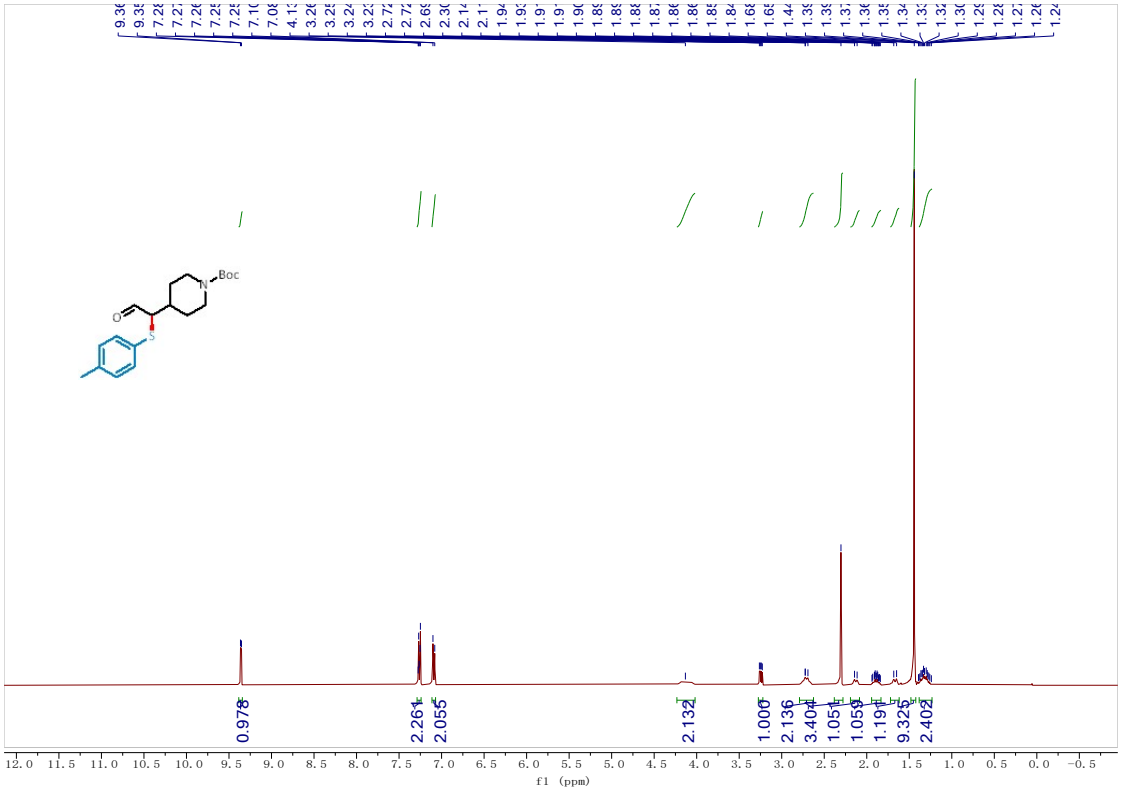
^{1}H NMR spectrum of compound **5w**



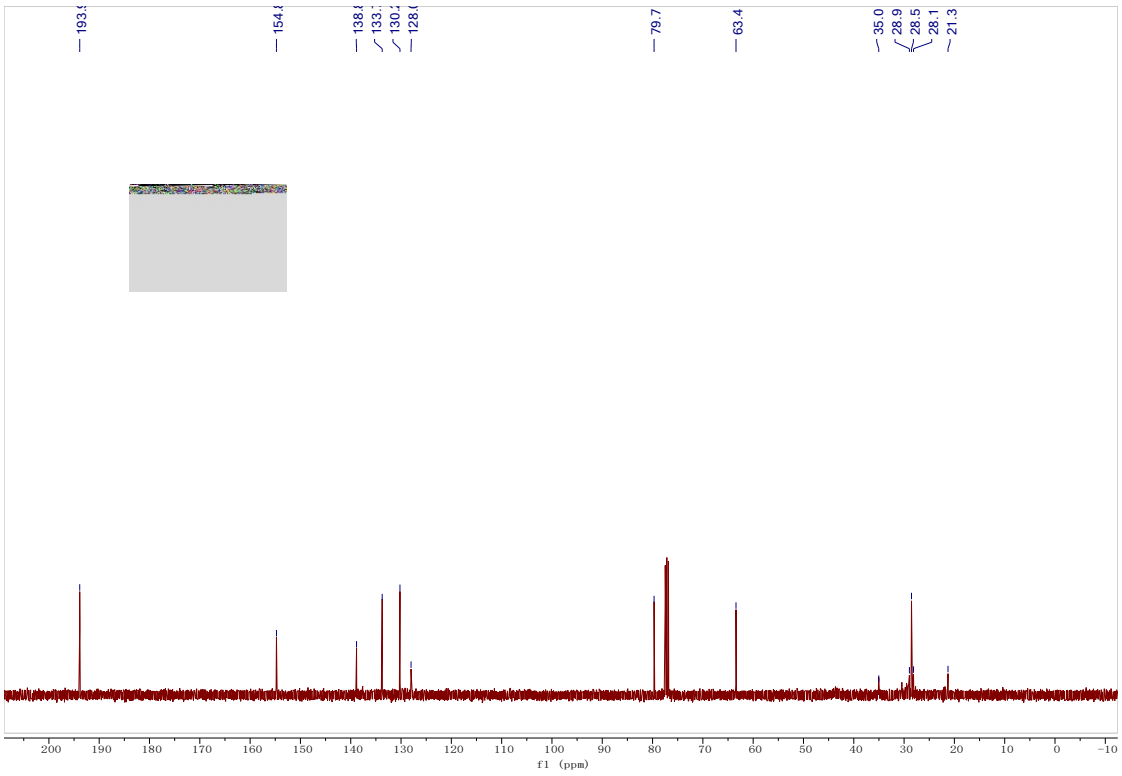
^{13}C NMR spectrum of compound **5w**


138.2
133.7
129.9
129.0
78.2
75.7
64.3
51.4
22.0
21.1
3.6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

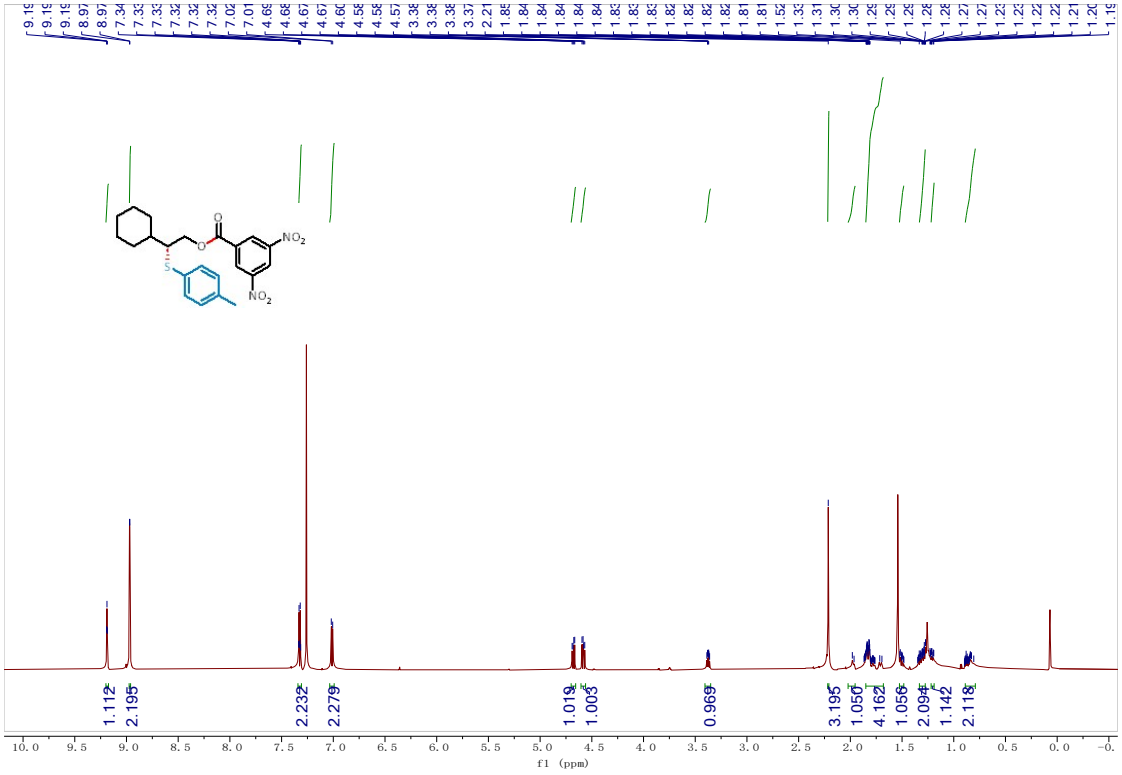
^{1}H NMR spectrum of compound **4x**



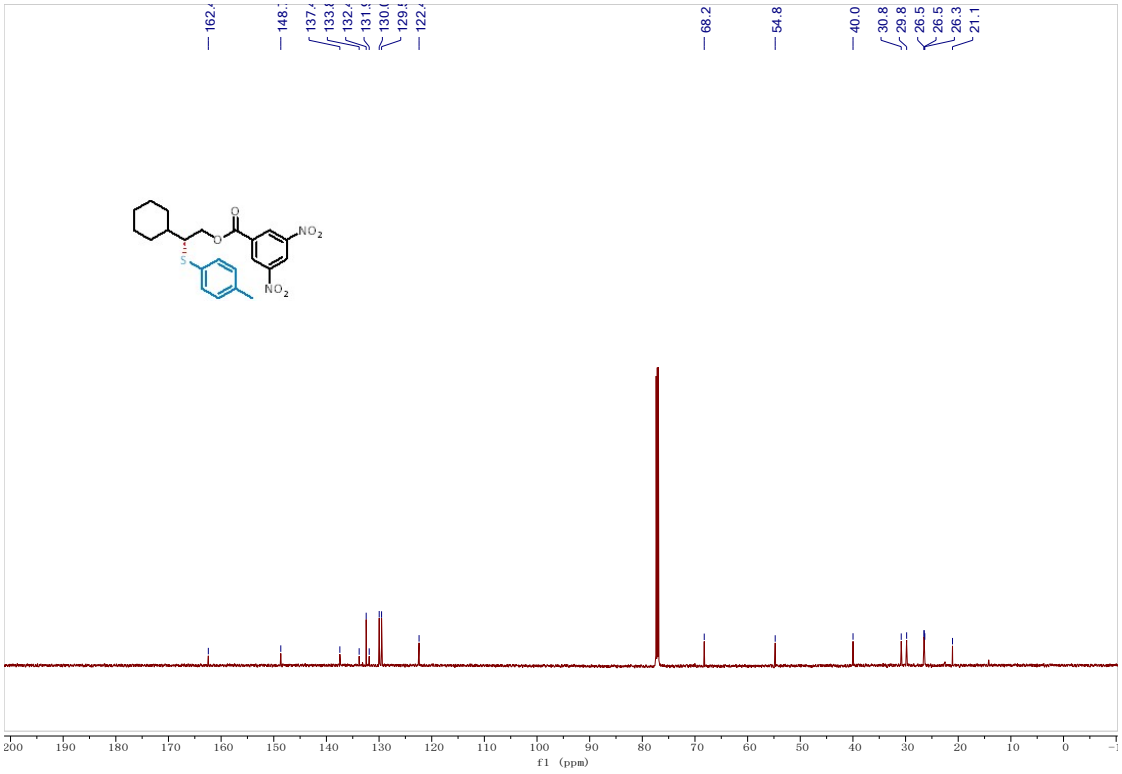
^{13}C NMR spectrum of compound **4x**


193.9
154.8
138.8
133.1
130.2
128.6
79.7
63.4
35.0
28.9
28.5
28.1
21.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

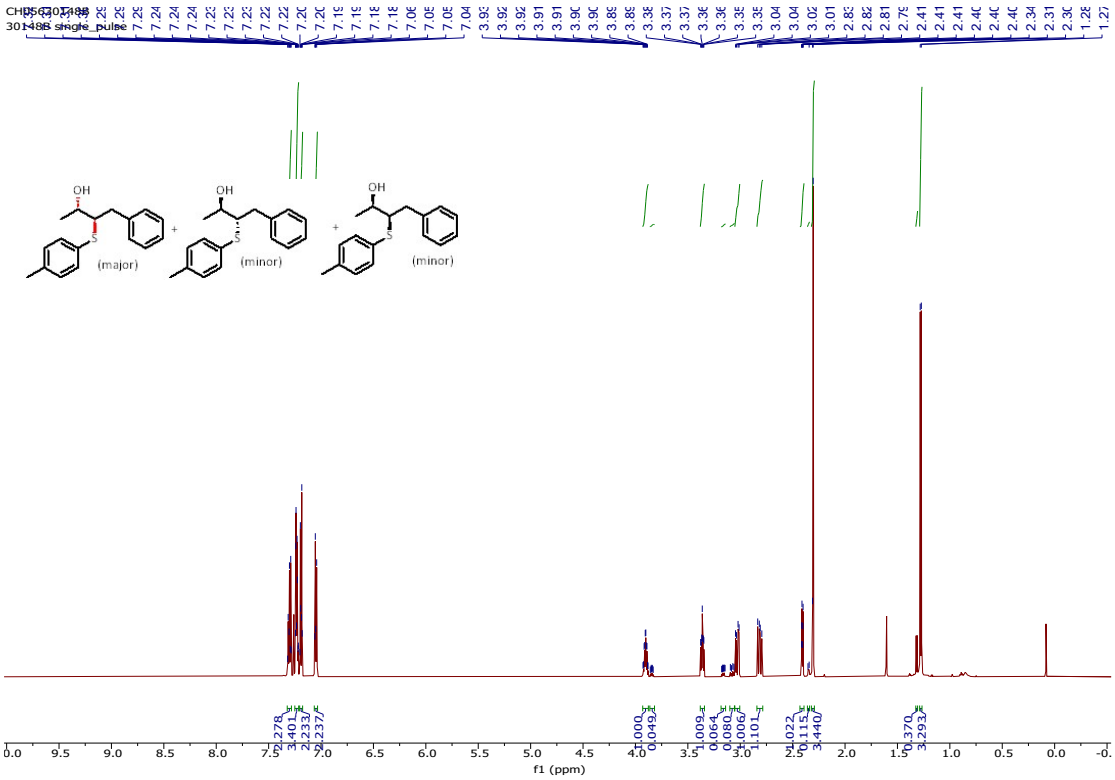
^{1}H NMR spectrum of compound **6a**



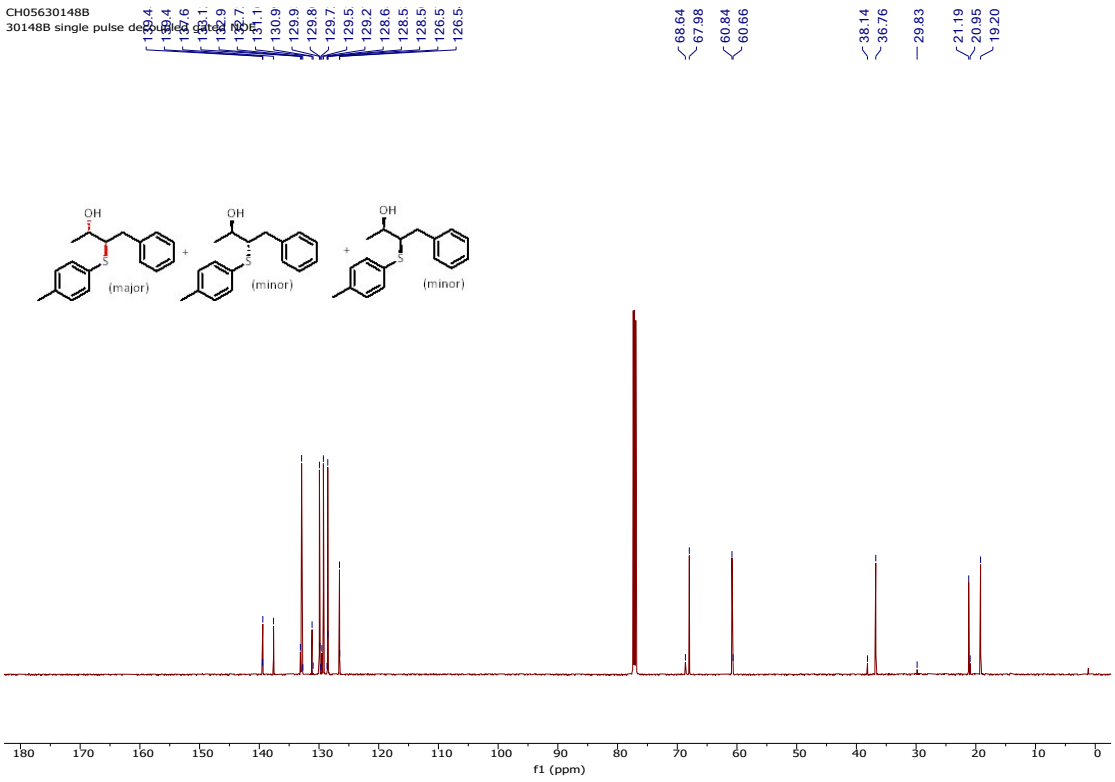
^{13}C NMR spectrum of compound **6a**


68.2
54.8
40.0
30.8
29.8
26.5
26.5
26.3
21.1
NO2
NO2
f1 (ppm)

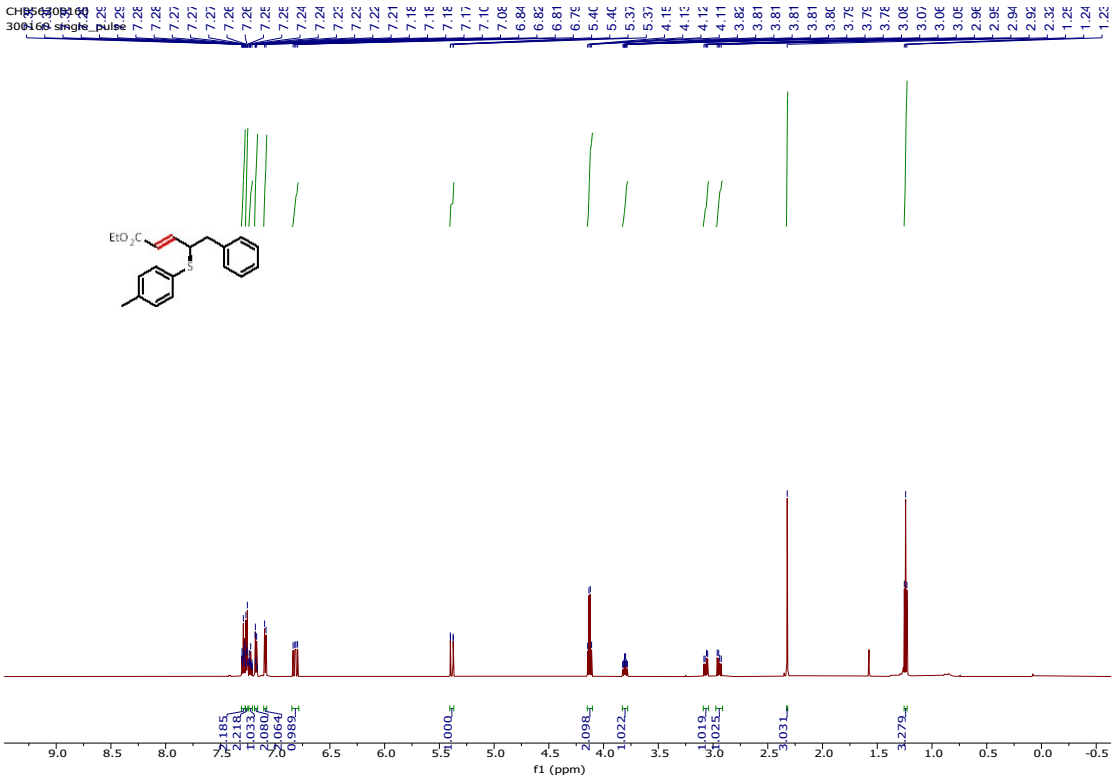
^{1}H NMR spectrum of compound **6b**



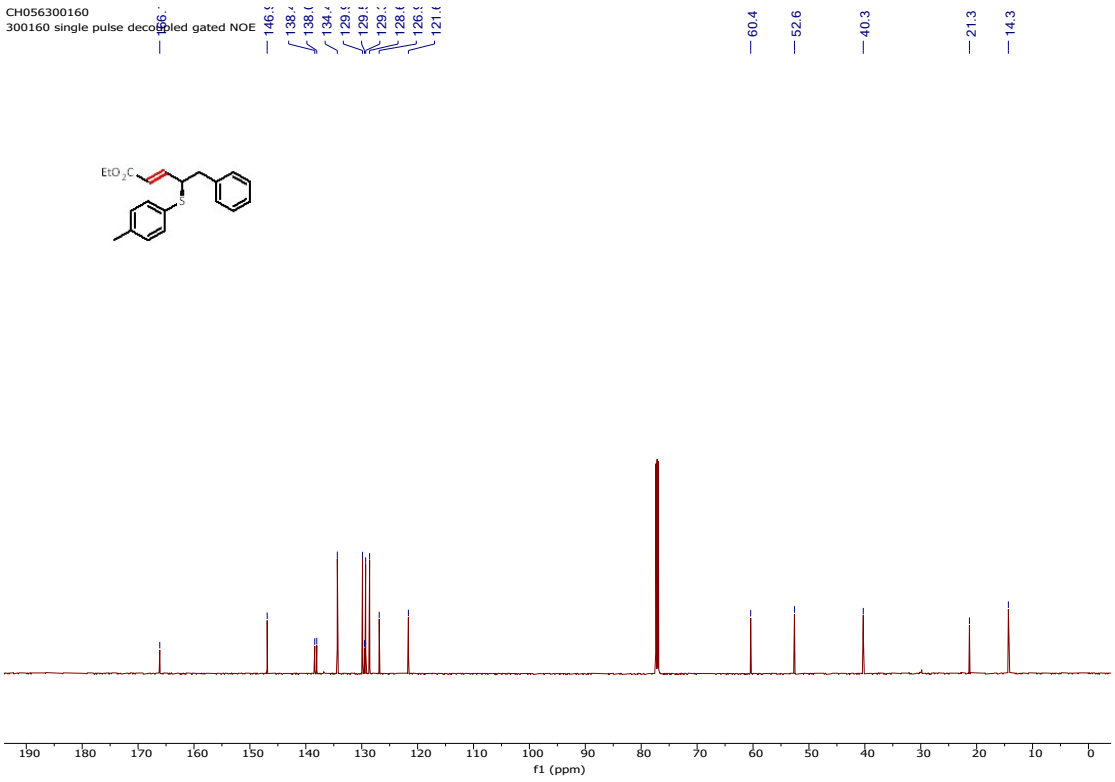
^{13}C NMR spectrum of compound **6b**



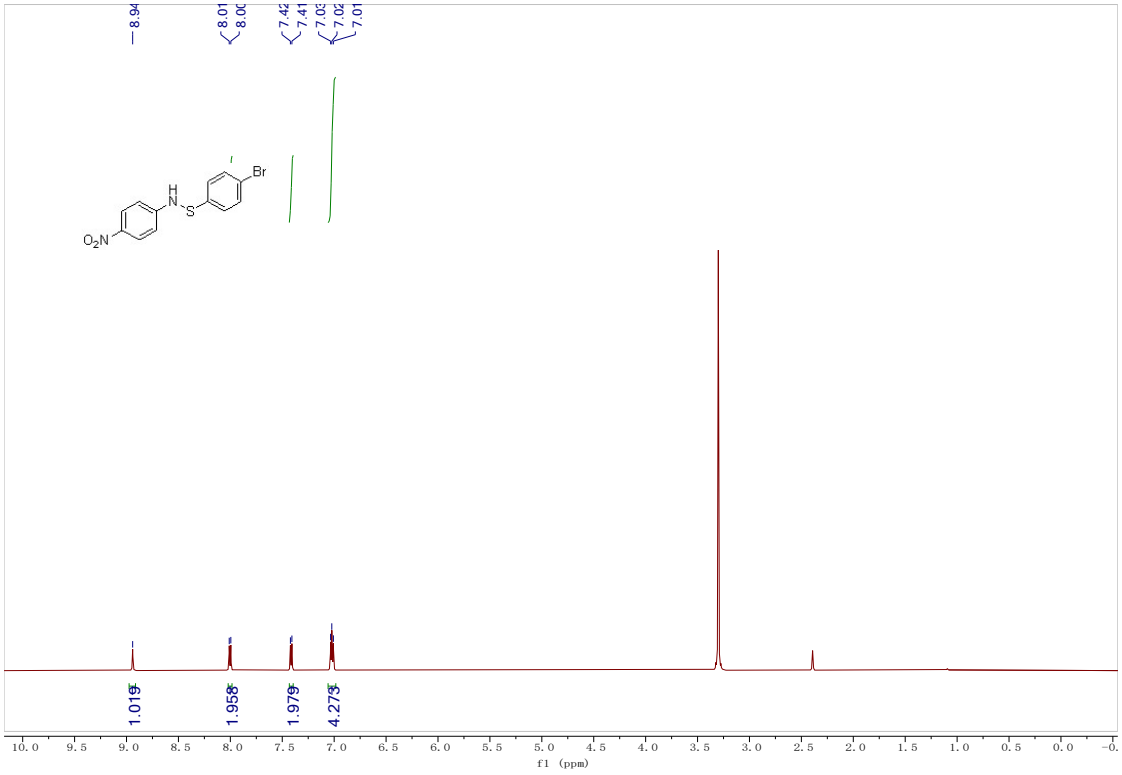
^{1}H NMR spectrum of compound **6c**



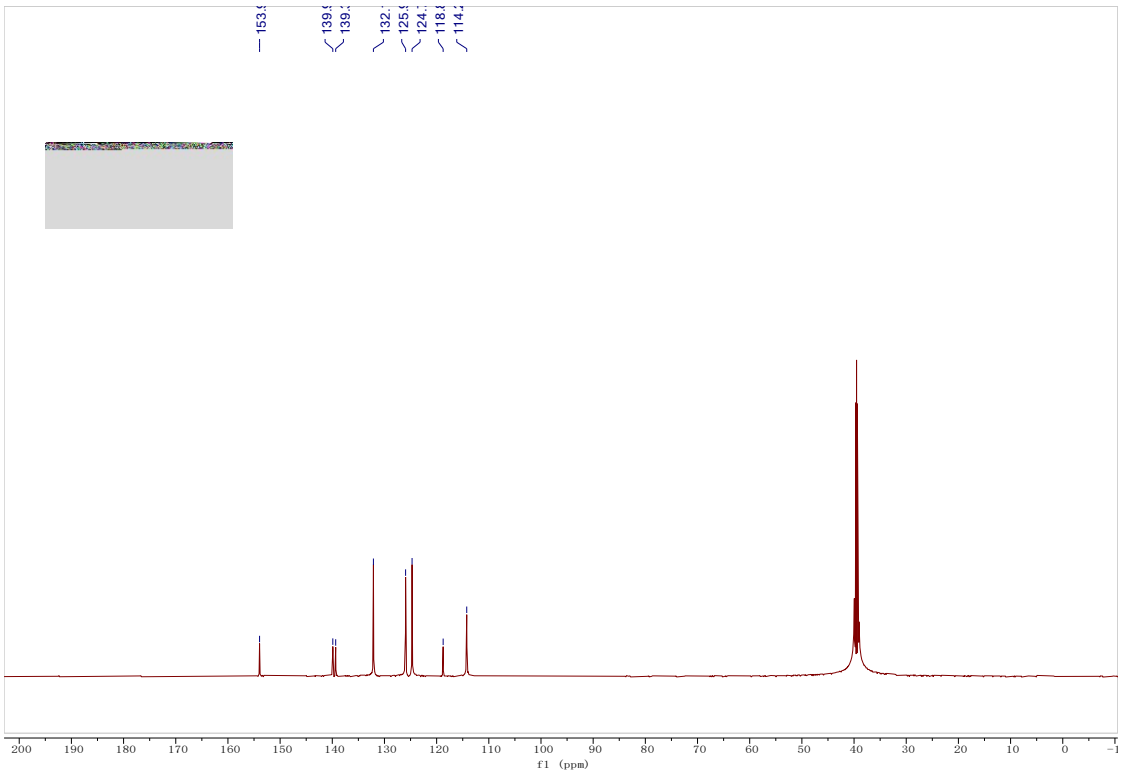
^{13}C NMR spectrum of compound **6c**



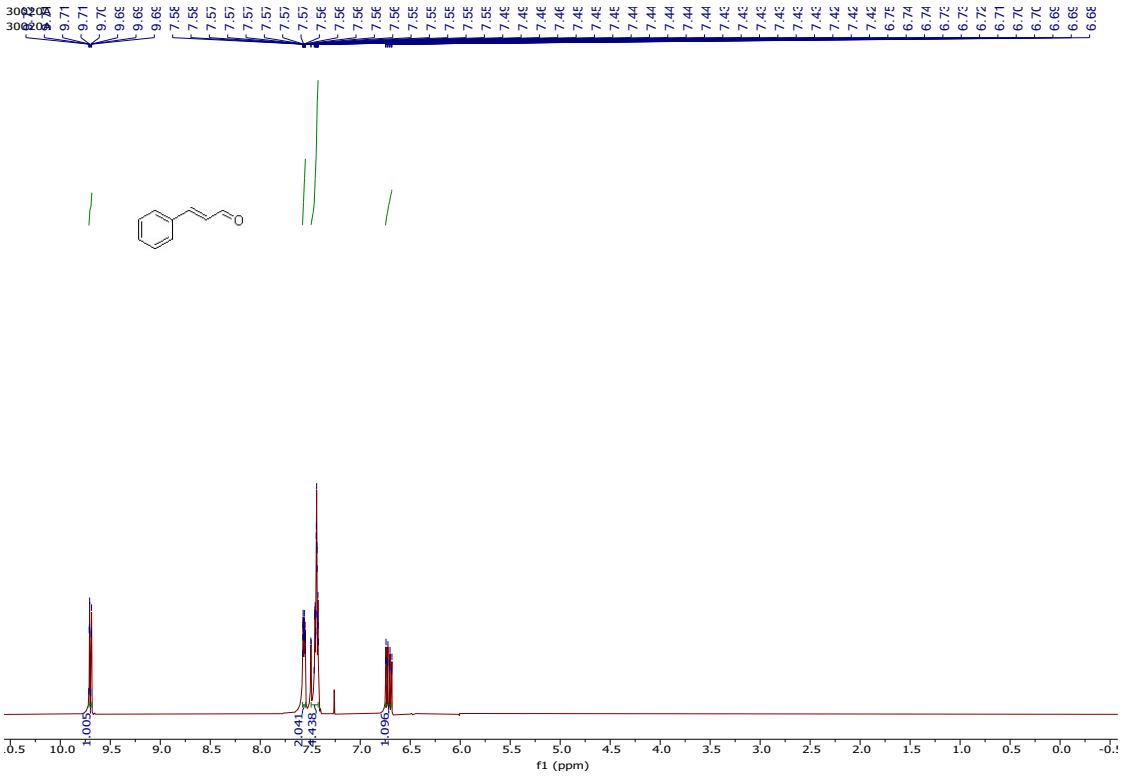
^{1}H NMR spectrum of compound **8**



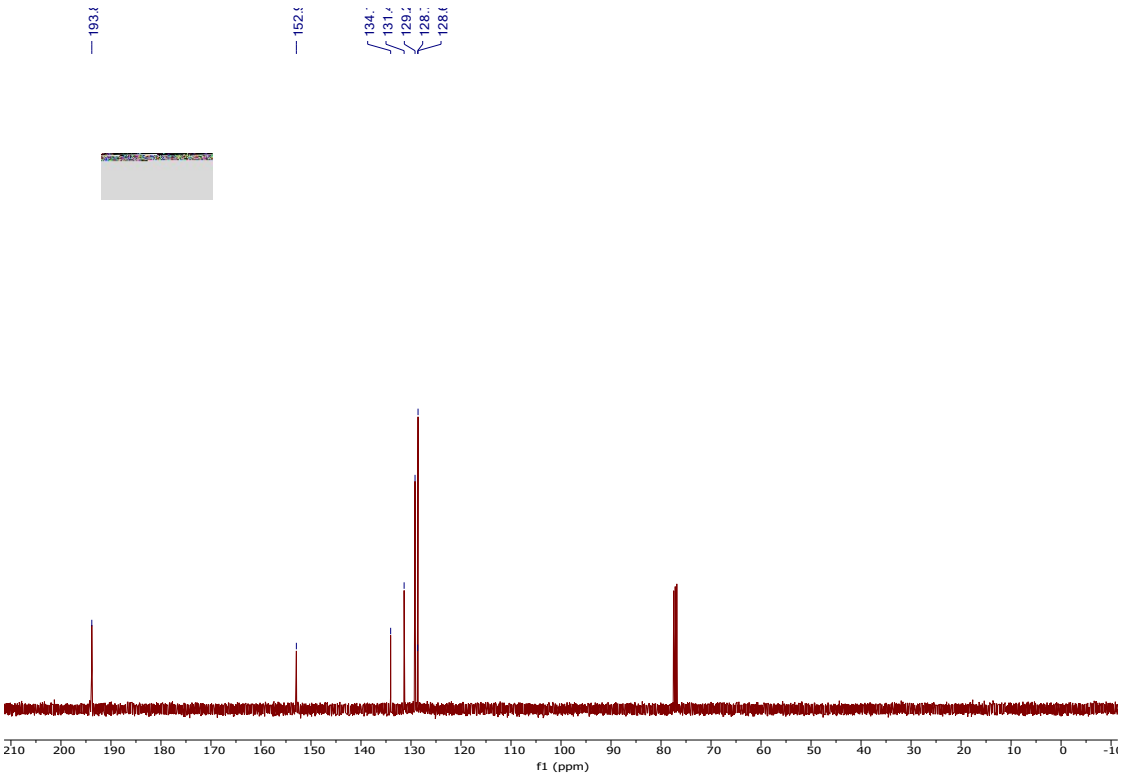
^{13}C NMR spectrum of compound **8**


153.9
139.5
139.2
132.7
125.9
124.7
118.8
114.2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR spectrum of compound **9**

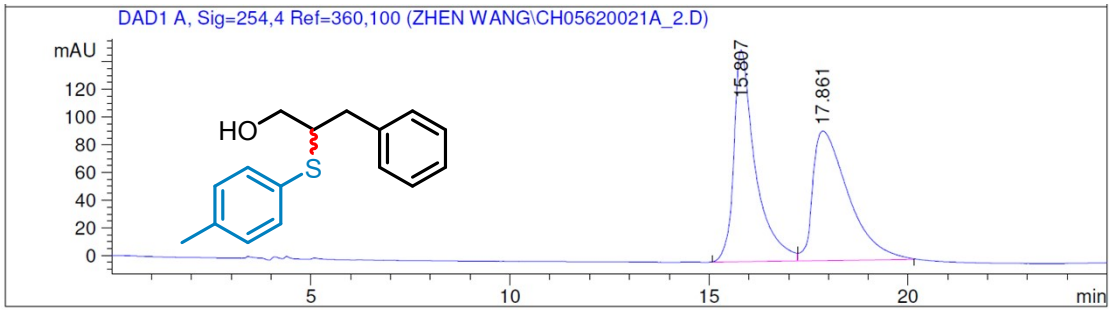


^{13}C NMR spectrum of compound **9**


193.8
152.5
134.7
131.4
129.2
128.1
128.6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

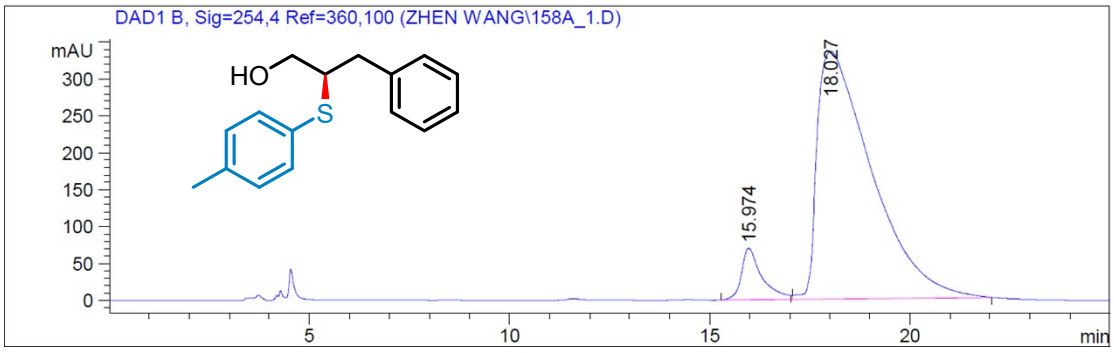
10. Copies of HPLC spectra

(*R*)-3-phenyl-2-(*p*-tolylthio)propan-1-ol (5a)



Signal 4: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.807	BB	0.5448	5781.57129	153.00375	49.6755
2	17.861	BB	0.9134	5857.11133	93.67904	50.3245

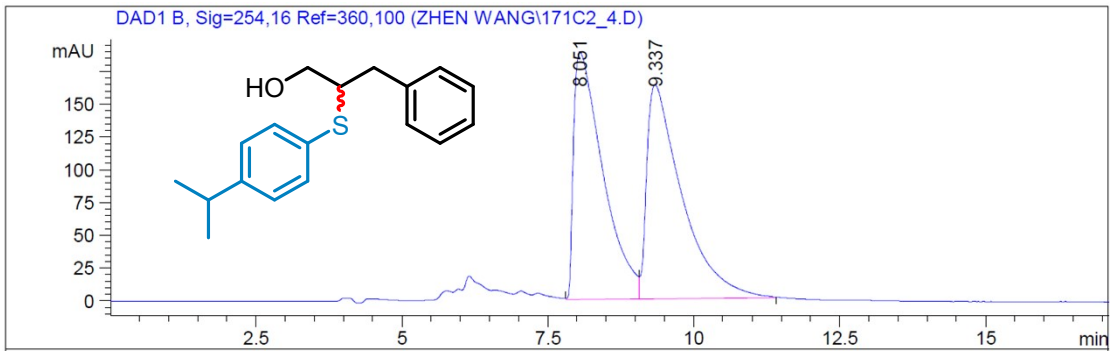


Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.974	BB	0.5093	2496.21704	70.11860	7.2290
2	18.027	BB	1.3168	3.20346e4	335.85004	92.7710

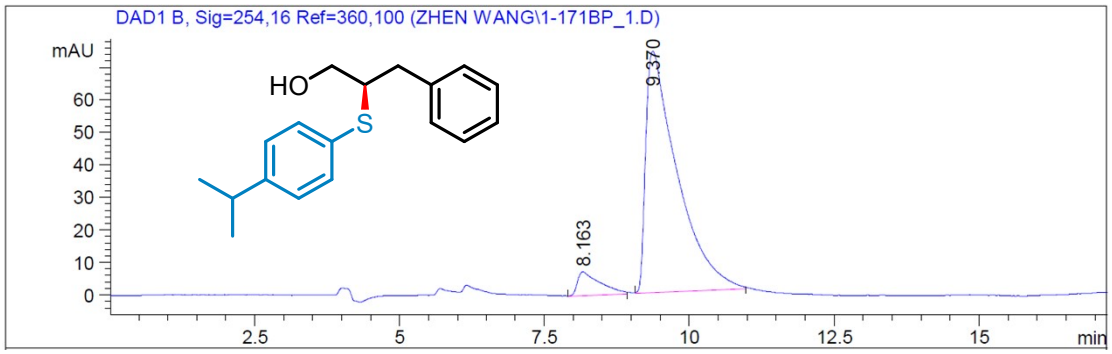
The enantiomeric excess (86% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 3:97, 38 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 18.03 min. t_r(minor) = 15.97 min. $[\alpha]_D^{24}$ = - 0.63 (c = 0.59, $CHCl_3$).

(*R*)-2-((4-isopropylphenyl)thio)-3-phenylpropan-1-ol (5b)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.051	BV	0.5037	6563.79590	188.75554	48.8581
2	9.337	VB	0.5958	6870.62354	162.98740	51.1419

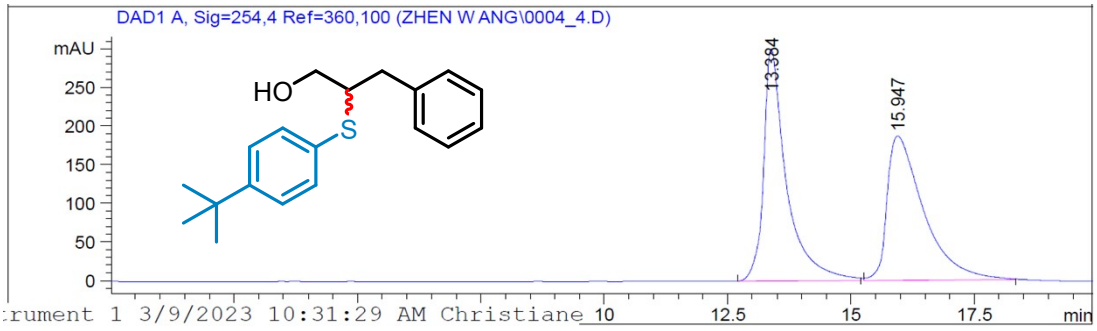


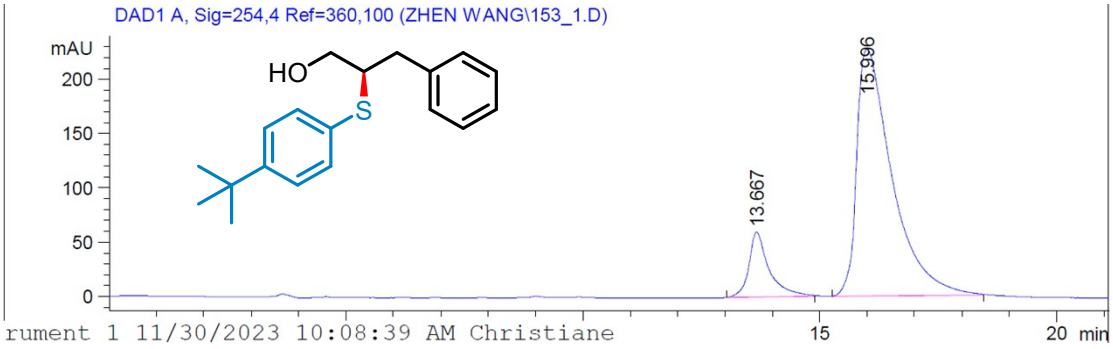
Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.163	BB	0.3566	195.03433	7.27883	6.4875
2	9.370	BB	0.5201	2811.28882	74.18294	93.5125

The enantiomeric excess (87% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 1:4, 29 bar, flow rate: 0.8 mL/min, λ_{max} = 254 nm): t_r(major) = 9.37 min. t_r(minor) = 8.16 min. $[\alpha]_D^{24}$ = 0.26 (c = 3.68, $CHCl_3$).

(*R*)-2-((4-(*tert*-butyl)phenyl)thio)-3-phenylpropan-1-ol (5c)



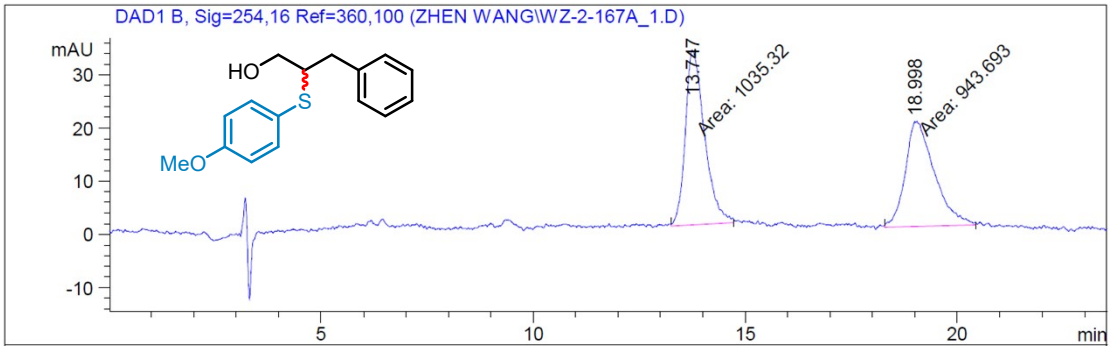


Signal 4: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.667	BB	0.4230	1784.82239	60.00216	13.1109
2	15.996	BB	0.7657	1.18284e4	227.84514	86.8891

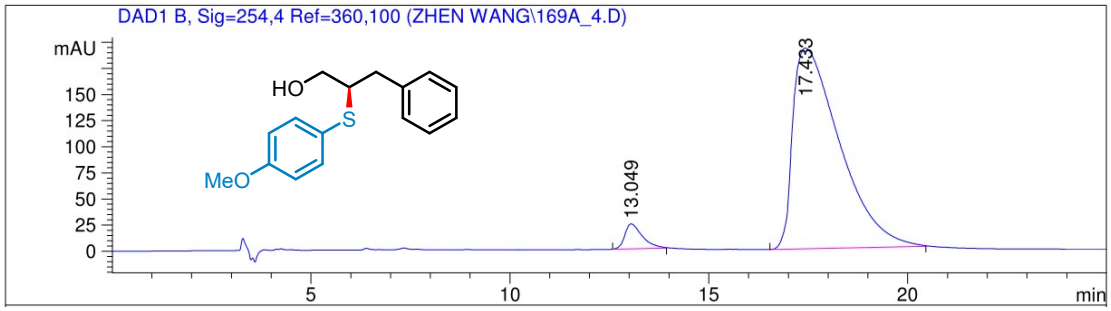
The enantiomeric excess (73% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 1:49, 37 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 16.00 min. t_r(minor) = 13.67 min. $[\alpha]_D^{24}$ = -0.66 (c = 0.64, $CHCl_3$).

(*R*)-2-((4-methoxyphenyl)thio)-3-phenylpropan-1-ol (5d)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.747	MM	0.5254	1035.32214	32.84340	52.3150
2	18.998	MM	0.7963	943.69330	19.75204	47.6850

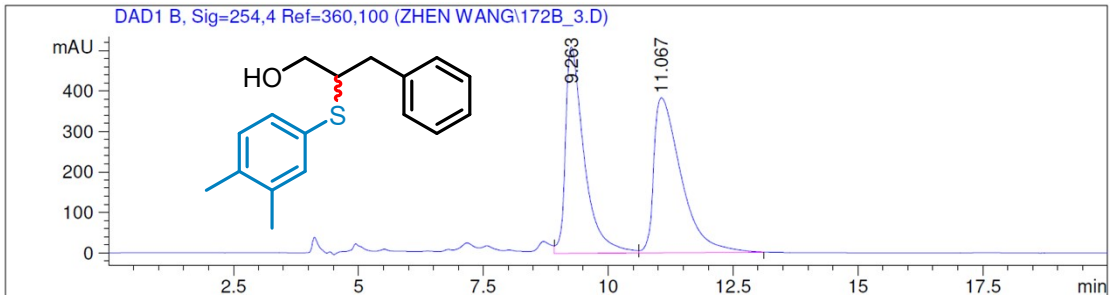


Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.049	BB	0.4515	739.15900	23.98428	4.4732
2	17.433	BB	1.1894	1.57851e4	191.95587	95.5268

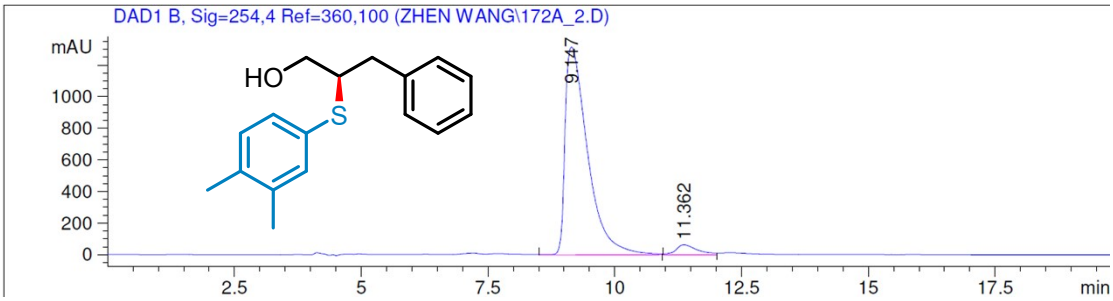
The enantiomeric excess (91% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 1:4, 38 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 17.43 min. t_r(minor) = 13.05 min. $[\alpha]_D^{24}$ = 3.17 (c = 0.54, $CHCl_3$).

(*R*)-2-((3,4-dimethylphenyl)thio)-3-phenylpropan-1-ol (5e)



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.263	VV	0.3873	1.33271e4	509.25266	47.7435
2	11.067	VB	0.5806	1.45868e4	382.76263	52.2565

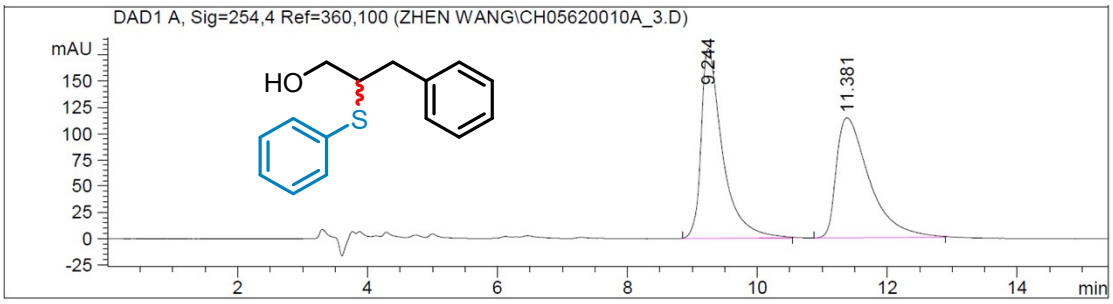


Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.147	VB	0.4713	4.07982e4	1317.36536	95.5910
2	11.362	BV	0.4254	1881.74158	63.56437	4.4090

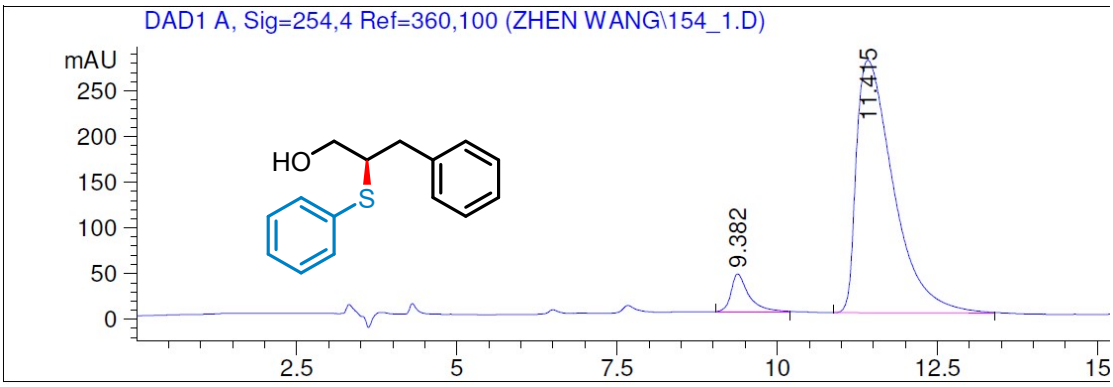
The enantiomeric excess (91% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 1:4, 31 bar, flow rate: 0.8 mL/min, λ_{max} = 254 nm): t_r(major) = 9.15 min. t_r(minor) = 11.36 min. $[\alpha]_D^{25}$ = -1.10 (c = 1.61, $CHCl_3$).

(*R*)-3-phenyl-2-(phenylthio)propan-1-ol (5f)



Signal 4: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.244	BB	0.3373	4150.03906	181.15094	50.6088
2	11.381	BB	0.5351	4050.19092	114.38026	49.3912

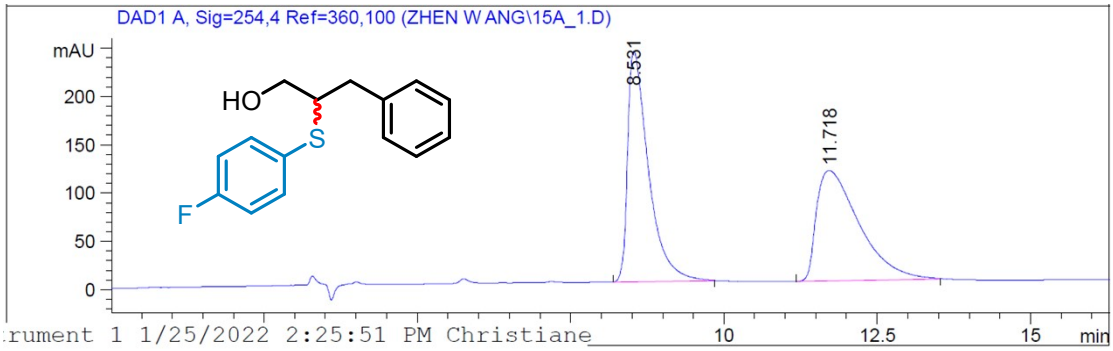


Signal 4: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.382	BB	0.2826	807.14862	41.55474	6.7539
2	11.415	BB	0.6222	1.11437e4	276.49271	93.2461

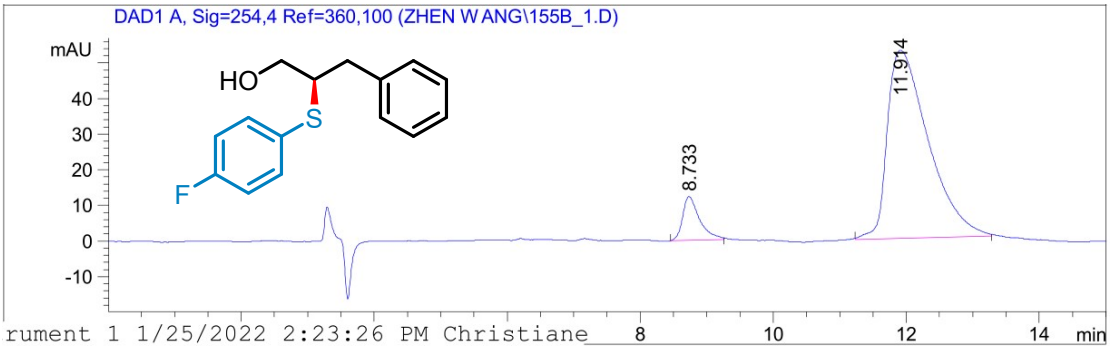
The enantiomeric excess (86% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 1:4, 37 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 11.42 min. t_r(minor) = 9.38 min. $[\alpha]_D^{24}$ = -8.53 (c = 0.10, $CHCl_3$).

(*R*)-2-((4-fluorophenyl)thio)-3-phenylpropan-1-ol (5g)



Signal 4: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.531	BB	0.3531	5672.29980	238.85959	50.4614
2	11.718	BB	0.7360	5568.56885	114.38321	49.5386

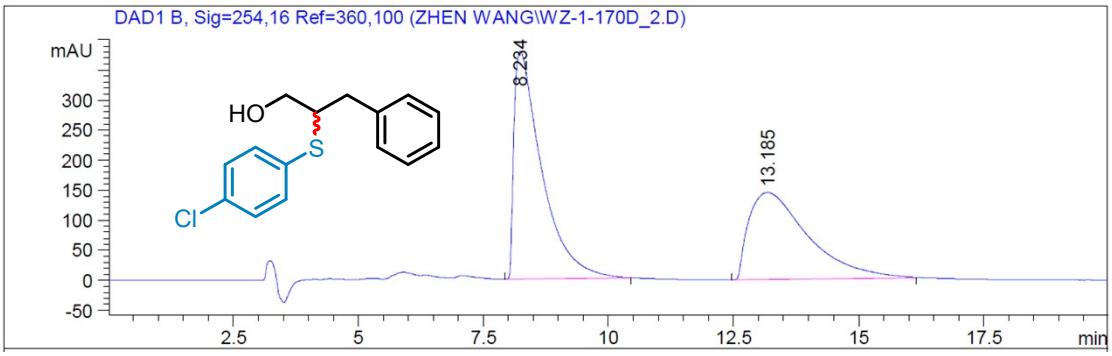


Signal 4: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.733	BB	0.2573	216.99179	12.33034	8.7518
2	11.914	BB	0.6386	2262.40527	52.72579	91.2482

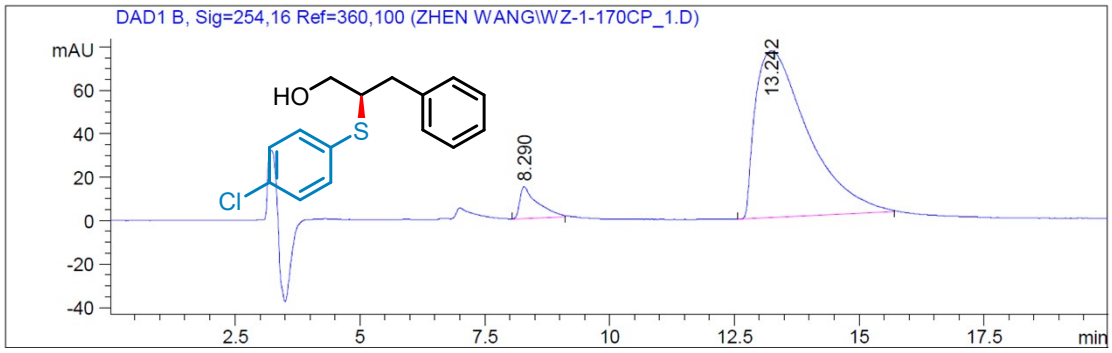
The enantiomeric excess (82% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 1:4, 38 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 11.91 min. t_r(minor) = 8.73 min. $[\alpha]_D^{25}$ = -1.65 (c = 0.48, $CHCl_3$).

(*R*)-2-((4-chlorophenyl)thio)-3-phenylpropan-1-ol (5h)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.234	BB	0.5570	1.47191e4	379.06180	55.2455
2	13.185	BB	1.2337	1.19240e4	144.65845	44.7545

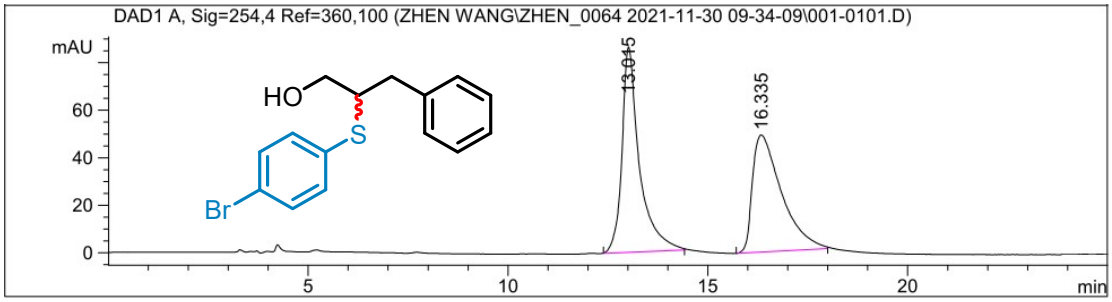


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.290	BB	0.3287	356.39877	14.60463	5.9347
2	13.242	BB	1.0629	5648.93652	76.73497	94.0653

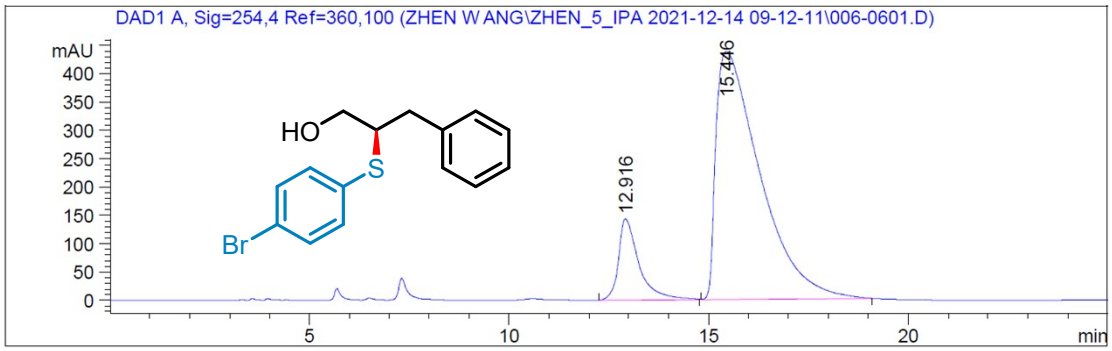
The enantiomeric excess (88% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc /hexane = 1:4, 38 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 13.24 min. t_r(minor) = 8.29 min. $[\alpha]_D^{24}$ = 16.64 (c = 0.22, $CHCl_3$).

(*R*)-2-((4-bromophenyl)thio)-3-phenylpropan-1-ol (5i)



Signal 4: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.015	BB	0.4313	2618.16675	86.45826	51.2571
2	16.335	BB	0.7533	2489.74854	49.29337	48.7429

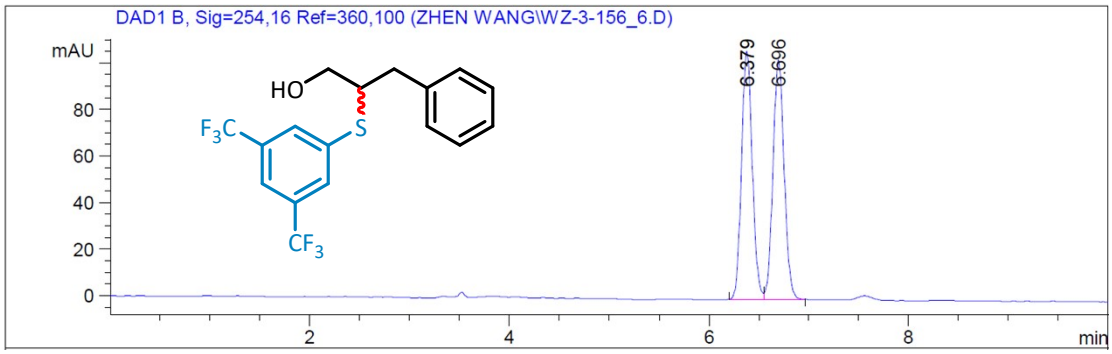


Signal 4: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.916	BB	0.5347	5119.92627	143.33904	13.1801
2	15.446	BB	1.1384	3.37259e4	437.95230	86.8199

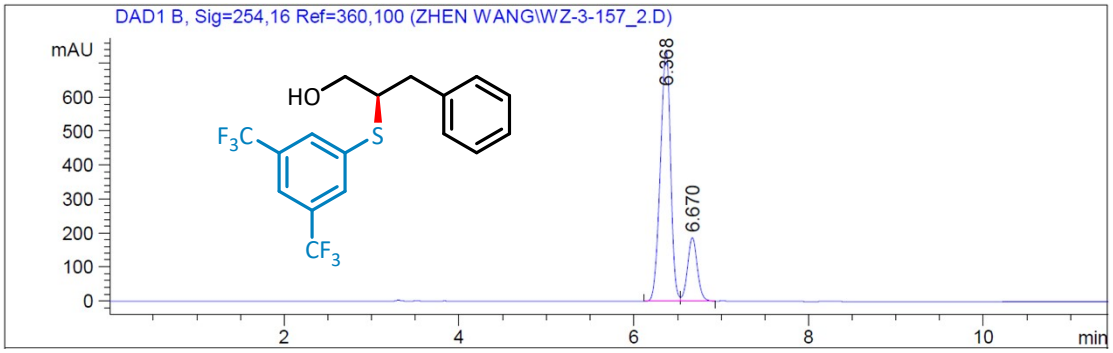
The enantiomeric excess (74% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/Hexane = 1:19, 38 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 15.45 min. t_r(minor) = 12.92 min. $[\alpha]_D^{24}$ = -5.83 (c = 2.13, $CHCl_3$).

(*R*)-2-((3,5-bis(trifluoromethyl)phenyl)thio)-3-phenylpropan-1-ol (5j)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.379	BV	0.1149	797.84601	107.06569	49.7455
2	6.696	VB	0.1211	806.01068	103.23490	50.2545

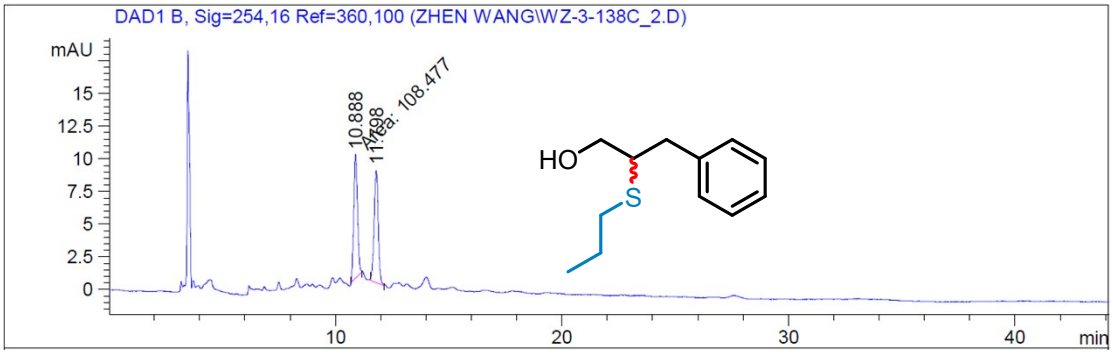


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.368	BV	0.1278	6066.08691	738.88824	80.4356
2	6.670	VV	0.1216	1475.45398	187.82895	19.5644

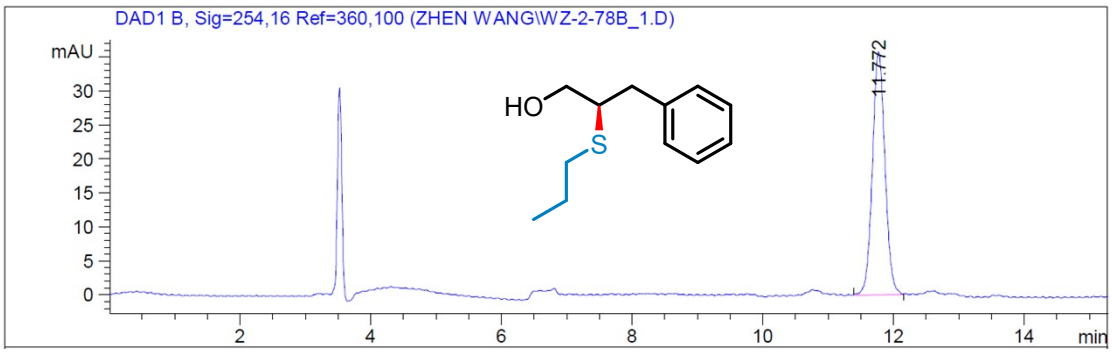
The enantiomeric excess (61% *ee*) was determined by HPLC with a *Diacel* Chiralpak IC column (EtOH/hexane = 1:99, 41bar, flow rate: 1.0 mL/min, λ_{max} = 254nm): t_r(major) = 6.34 min. t_r(minor) = 6.67 min. $[\alpha]_D^{25}$= -7.92 (c = 0.96, $CHCl_3$).

(*R*)-3-phenyl-2-(propylthio)propan-1-ol (5k)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.888	MM	0.1905	108.47723	9.49105	49.9953
2	11.798	BB	0.1977	108.49770	8.57241	50.0047

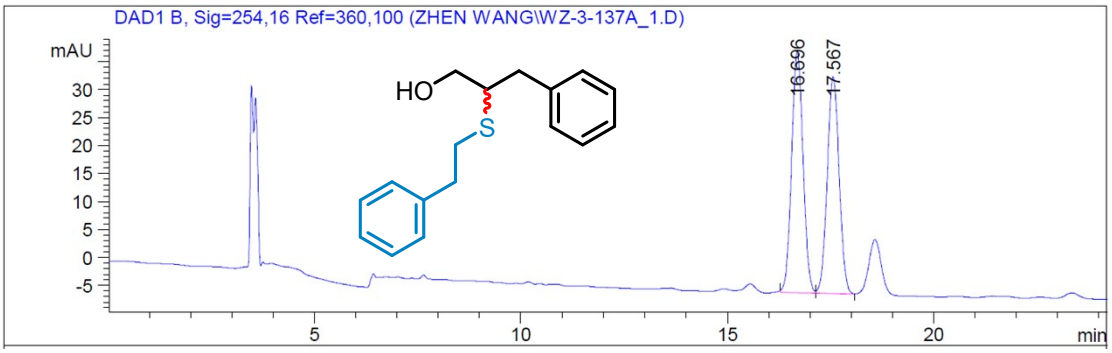


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.772	BB	0.2080	477.98386	35.75068	100.0000

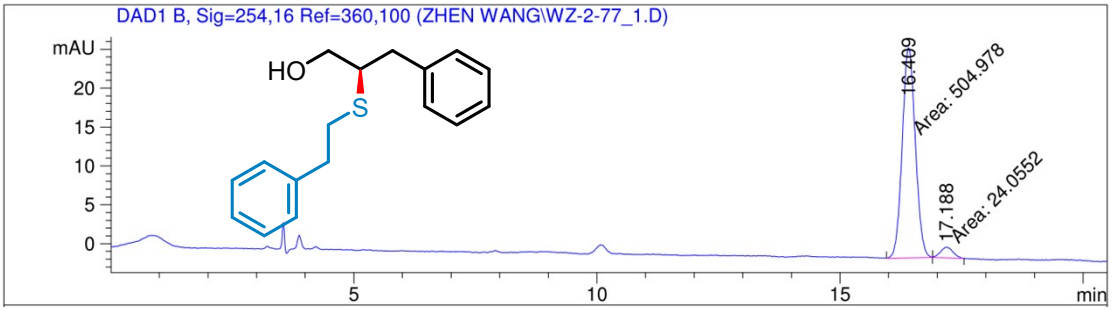
The enantiomeric excess (enantiopure, >99% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOH /hexane = 1:99, 39 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 11.77 min. t_r(minor) = 10.88 min. $[\alpha]_D^{25}$ = 15.70 (c = 0.47, $CHCl_3$).

(*R*)-2-(phenethylthio)-3-phenylpropan-1-ol (5l)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.696	BV	0.3006	831.88348	43.20303	51.5924
2	17.567	VB	0.3125	780.53119	38.82551	48.4076

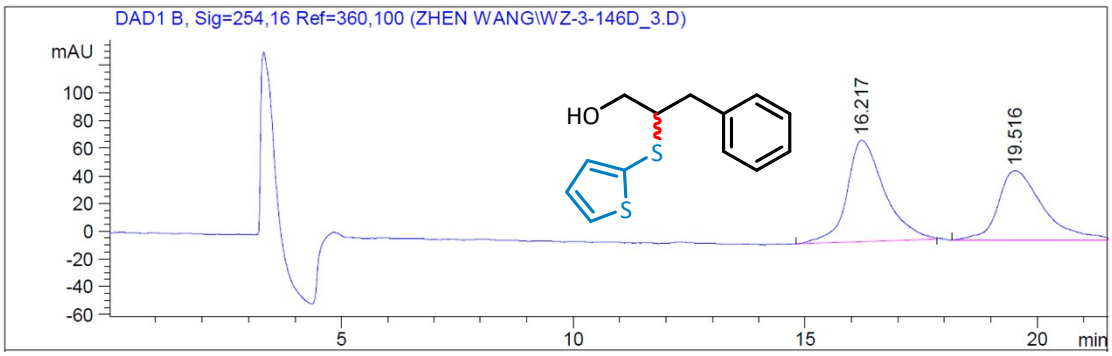


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.409	MM	0.3115	504.97800	27.02240	95.4530
2	17.188	MM	0.2940	24.05515	1.36358	4.5470

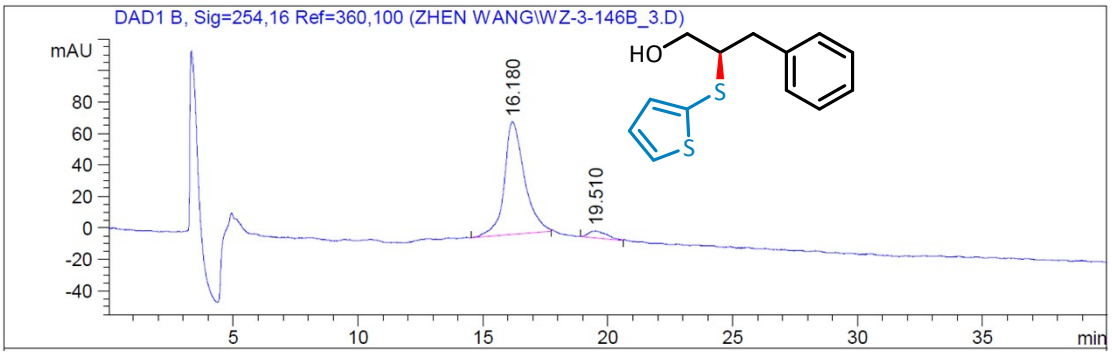
The enantiomeric excess (91% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOH /hexane = 1:99, 39 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 16.41 min. t_r(minor) = 17.19 min. $[\alpha]_D^{25}$ = 11.44 (c = 0.32, $CHCl_3$).

(*R*)-3-phenyl-2-(thiophen-2-ylthio)propan-1-ol (5m)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.217	BB	0.7303	4105.50830	73.20249	55.3668
2	19.516	BBA	0.7897	3309.60156	49.77993	44.6332

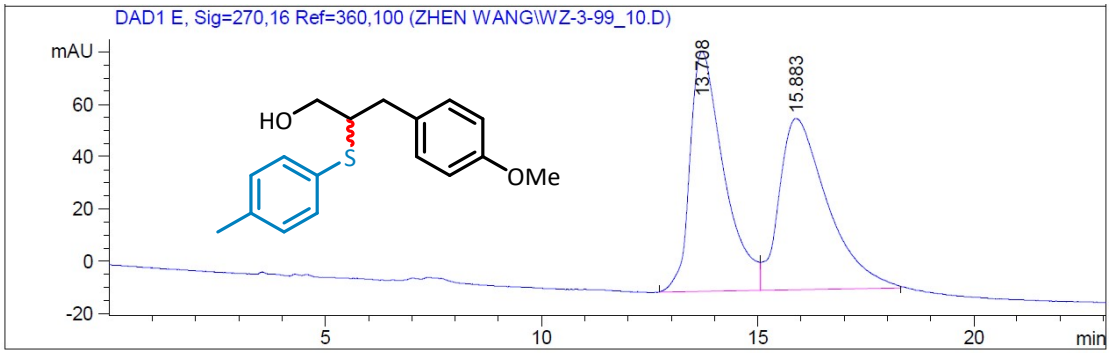


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.180	VB	0.7351	4018.52246	71.56213	94.5654
2	19.510	BV	0.6034	230.93935	4.52501	5.4346

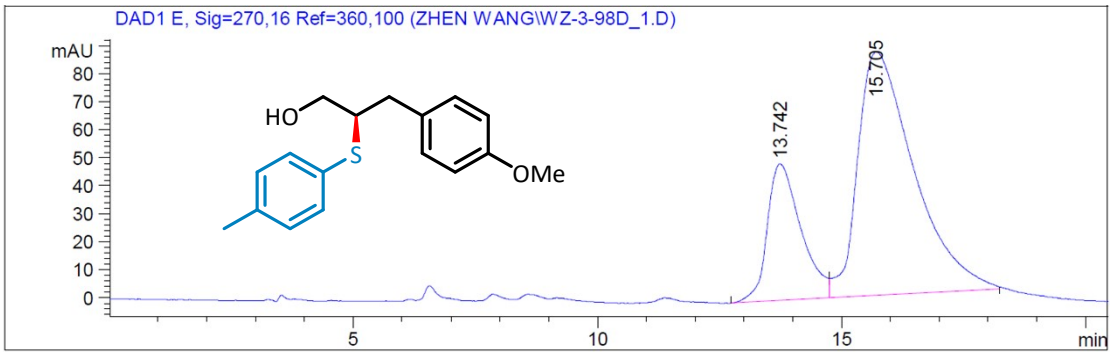
The enantiomeric excess (89% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 3:97, 44 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 16.18 min. t_r(minor) = 19.51 min. $[\alpha]_D^{24} = 4.4$ (c = 0.25, $CHCl_3$).

(*R*)-3-(4-methoxyphenyl)-2-(p-tolylthio)propan-1-ol (5n)



Signal 3: DAD1 E, Sig=270,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.708	BV	0.7893	5027.93652	91.75758	49.6252
2	15.883	VB	0.9985	5103.87500	65.53909	50.3748

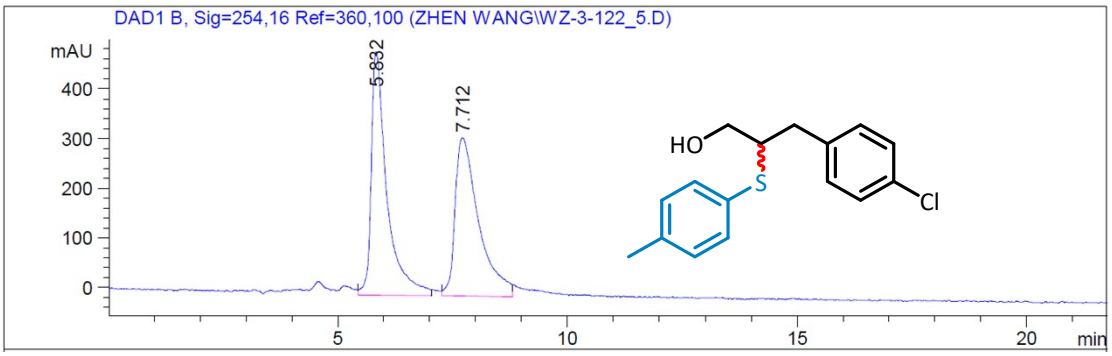


Signal 3: DAD1 E, Sig=270,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.742	BV	0.6644	2343.74390	48.79516	25.1247
2	15.705	VB	1.0750	6984.69287	86.97117	74.8753

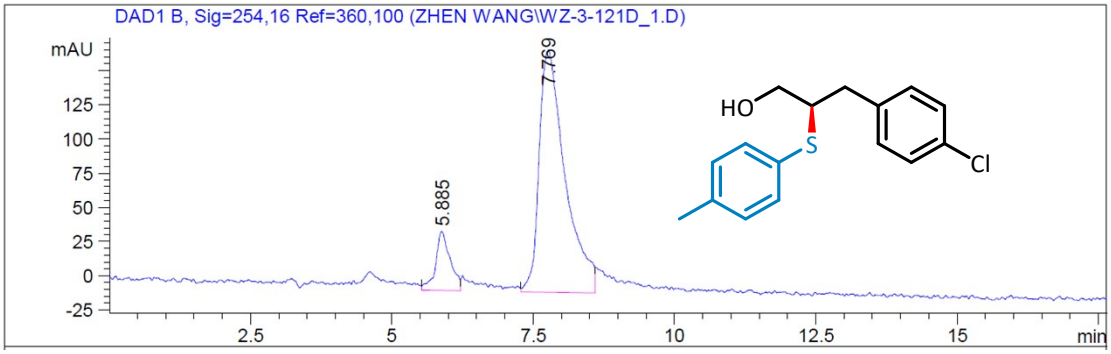
The enantiomeric excess (50% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 20:80, 40 bar, flow rate: 1.0 mL/min, λ_{max} = 270 nm): t_r(major) = 15.71 min. t_r(minor) = 13.74 min. $[\alpha]_D^{24}$ = -2.59 (c = 0.99, $CHCl_3$).

(*R*)-3-(4-chlorophenyl)-2-(p-tolylthio)propan-1-ol (5o)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.832	VV	0.3345	1.16017e4	489.43491	50.3442
2	7.712	VV	0.5212	1.14430e4	318.49640	49.6558

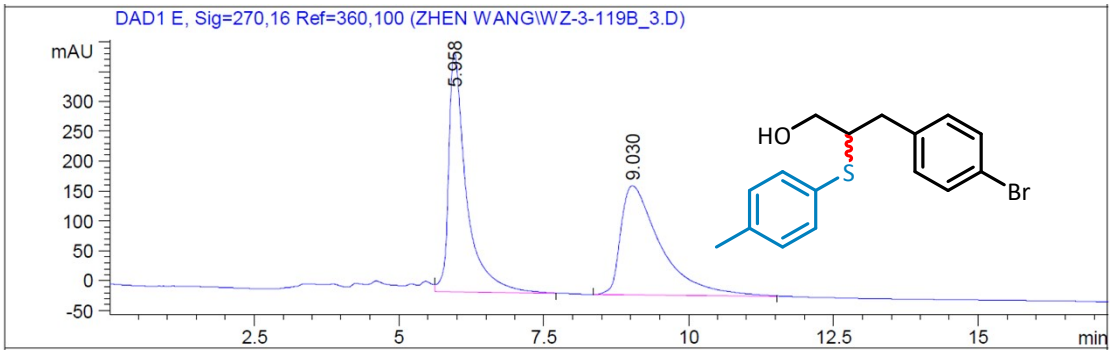


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.885	VV	0.2495	778.11145	42.92582	12.0918
2	7.769	VV	0.4448	5656.90283	177.02760	87.9082

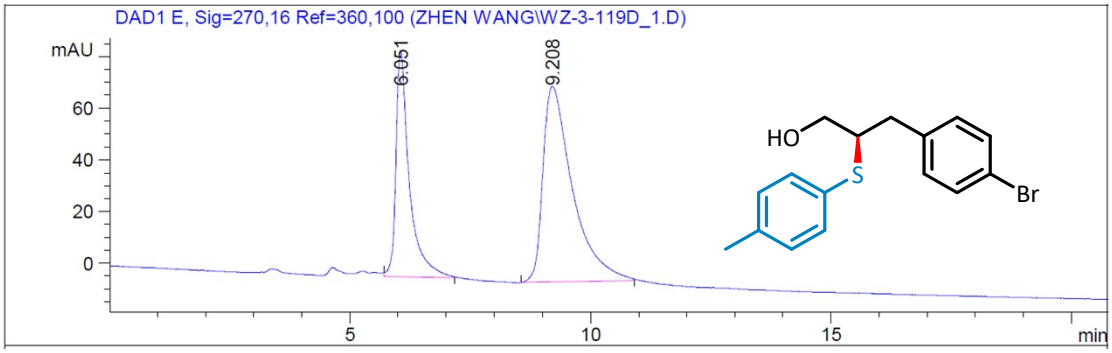
The enantiomeric excess (76% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (Ethyl acetate/hexane = 30:70, 41 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 7.77 min. t_r(minor) = 5.885 min. $[\alpha]_D^{23}$ = -5.2 (c = 0.74, $CHCl_3$).

(*R*)-3-(4-bromophenyl)-2-(p-tolylthio)propan-1-ol (5p)



Signal 3: DAD1 E, Sig=270,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.958	VB	0.3087	8536.28320	400.49347	49.3065
2	9.030	BB	0.7030	8776.42480	182.50995	50.6935

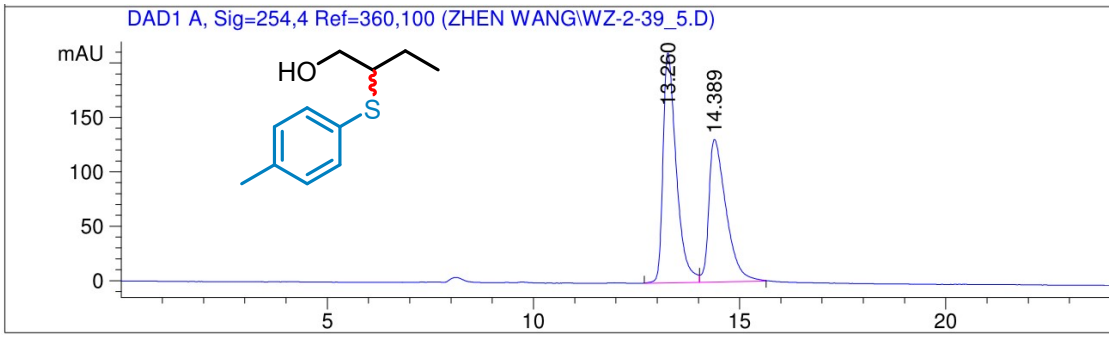


Signal 3: DAD1 E, Sig=270,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.051	BB	0.2794	1690.26074	87.49695	34.2521
2	9.208	BB	0.6074	3244.50049	75.79432	65.7479

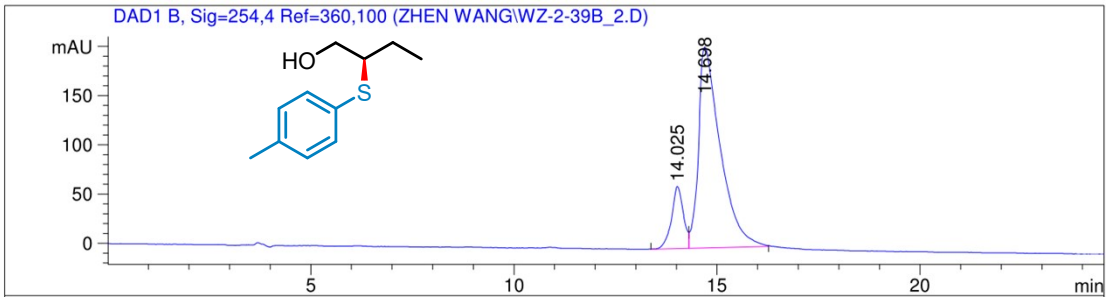
The enantiomeric excess (31% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (Ethyl acetate/hexane = 30:70, 41 bar, flow rate: 1.0 mL/min, λ_{max} = 270 nm): t_r(major) = 9.21 min. t_r(minor) = 6.05 min. $[\alpha]_D^{25}$ = -11 (c = 0.21, $CHCl_3$).

(*R*)-2-(*p*-tolylthio)butan-1-ol (5q)



Signal 4: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.260	BV	0.3388	4716.69385	211.01440	55.2938
2	14.389	VB	0.4335	3813.54565	131.04892	44.7062

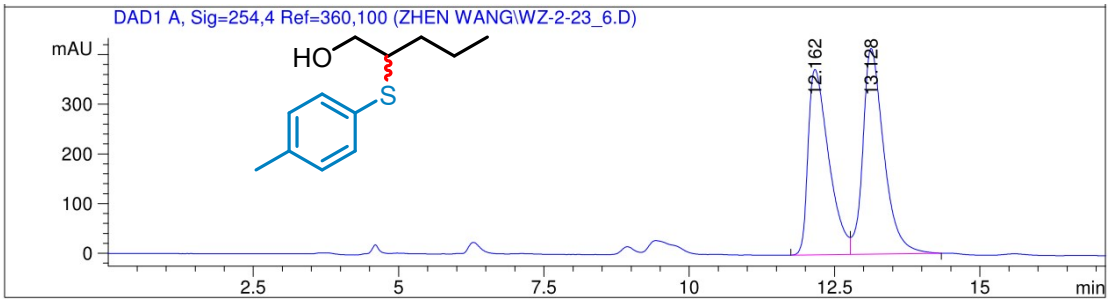


Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.025	VV	0.3033	1280.03809	62.93102	14.3887
2	14.698	VB	0.5159	7616.09229	203.81885	85.6113

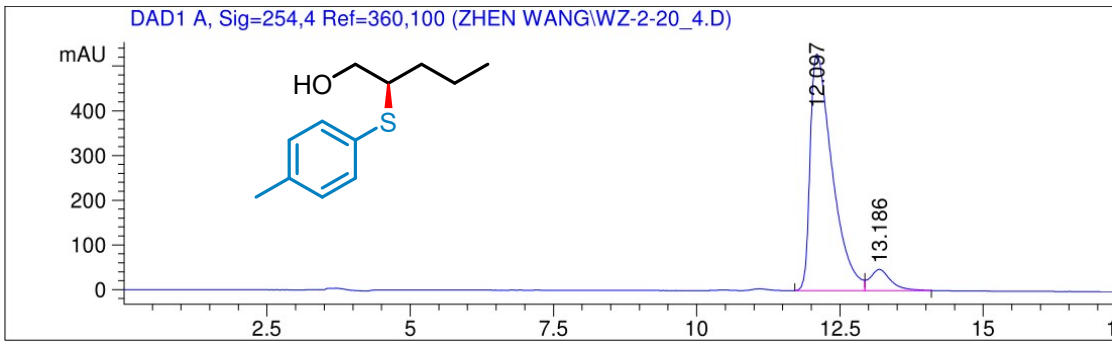
The enantiomeric excess (71% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 1:49, 40 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 14.70 min. t_r(minor) = 14.03 min. $[\alpha]_D^{25}$ = 40.47 (c = 0.3, $CHCl_3$).

(*R*)-2-(*p*-tolylthio)pentan-1-ol (5r)



Signal 4: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.162	BV	0.3745	9231.09570	373.31946	46.9662
2	13.128	VB	0.3776	1.04237e4	414.15805	53.0338

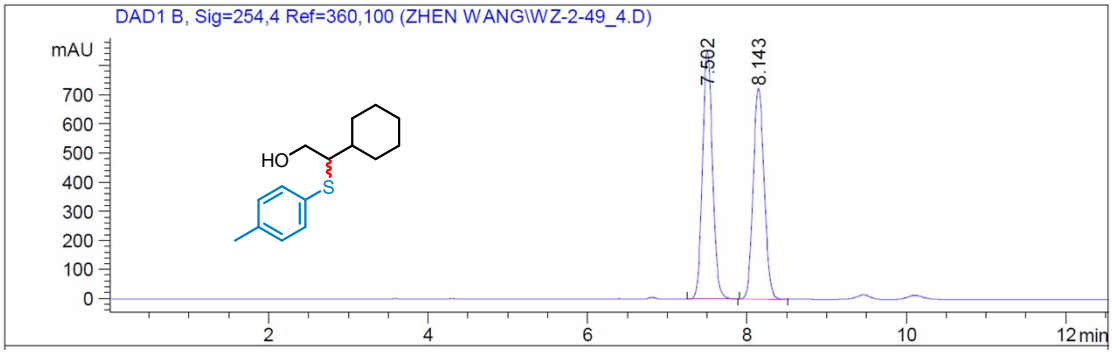


Signal 4: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.097	BV	0.3985	1.41784e4	529.27753	92.1055
2	13.186	VB	0.3680	1215.24854	47.57344	7.8945

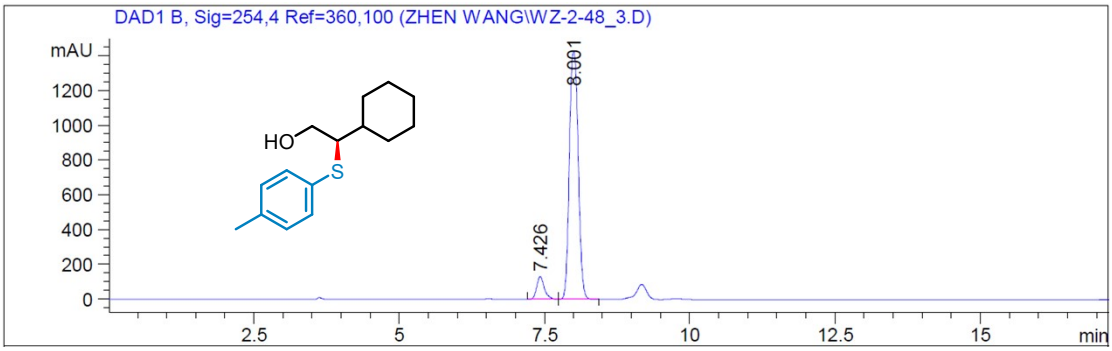
The enantiomeric excess (84% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 1:48, 37 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 12.10 min. t_r(minor) = 13.19 min. $[\alpha]_D^{25}$ = 11.26 (c = 0.68, $CHCl_3$).

(*R*)-2-cyclohexyl-2-(*p*-tolylthio)ethan-1-ol (5s)



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.502	BB	0.1363	7490.31934	854.62170	51.8691
2	8.143	BB	0.1499	6950.48535	724.77179	48.1309

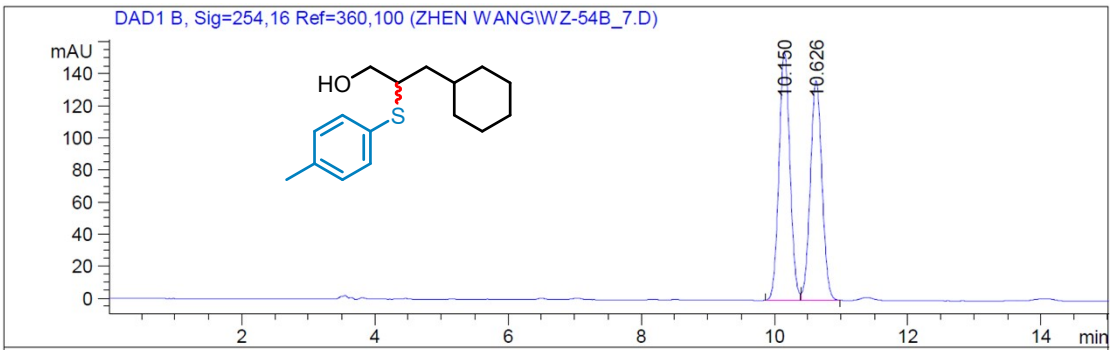


Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.426	VV	0.1373	1218.27478	132.46622	7.4758
2	8.001	VB	0.1691	1.50780e4	1429.36658	92.5242

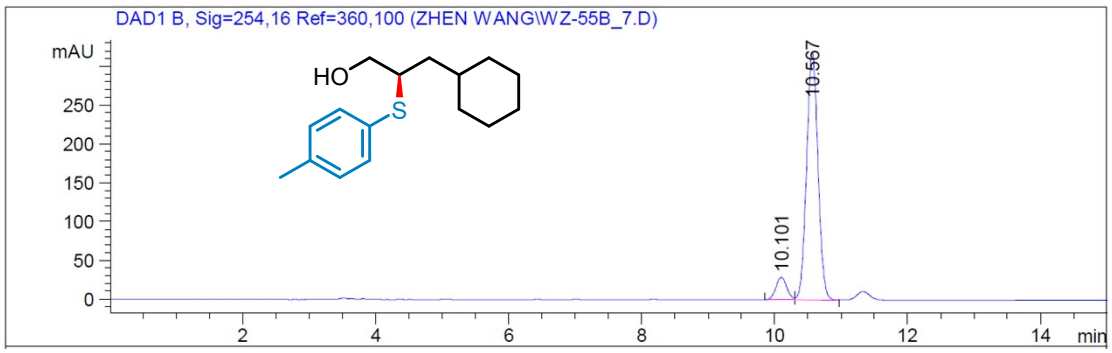
The enantiomeric excess (85% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 1:19, 39 bar, flow rate: 0.8 mL/min, λ_{max} = 254 nm): t_r(major) = 8.00 min. t_r(minor) = 7.43 min. $[\alpha]_D^{25}$ = -18.31 (c = 0.46, $CHCl_3$).

(*R*)-3-cyclohexyl-2-(*p*-tolylthio)propan-1-ol (5t)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.150	BV	0.1780	1781.37390	155.10416	51.6714
2	10.626	VB	0.1879	1666.12903	137.02281	48.3286

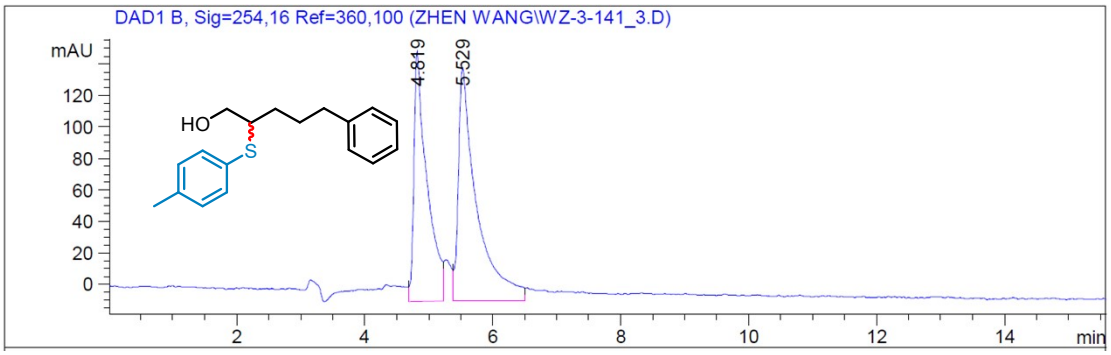


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.101	BV	0.1788	337.26382	29.17948	8.1406
2	10.567	VB	0.1869	3805.70312	319.71750	91.8594

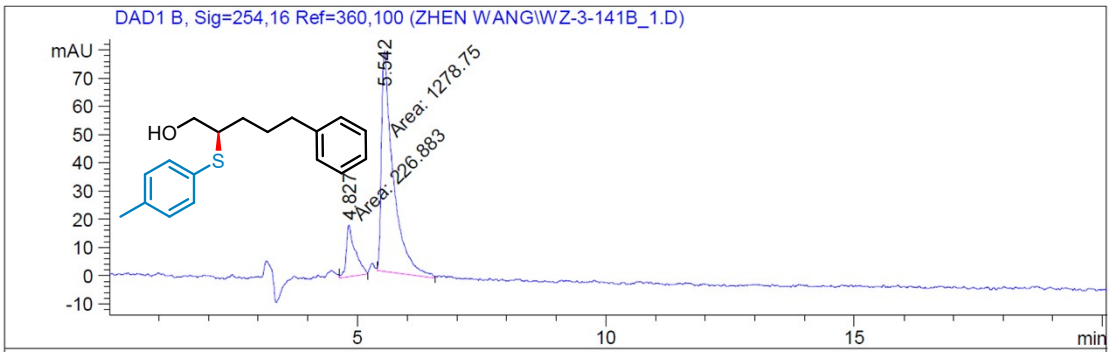
The enantiomeric excess (84% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOH/hexane = 1:99, 39 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 10.57 min. t_r(minor) = 10.10 min. $[\alpha]_D^{25}$ = 2.18 (c = 0.45, $CHCl_3$).

(*R*)-5-phenyl-2-(*p*-tolylthio)pentan-1-ol (5u)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.819	BV	0.1865	2241.29297	158.94128	43.0258
2	5.529	VV	0.2676	2967.88525	148.25380	56.9742

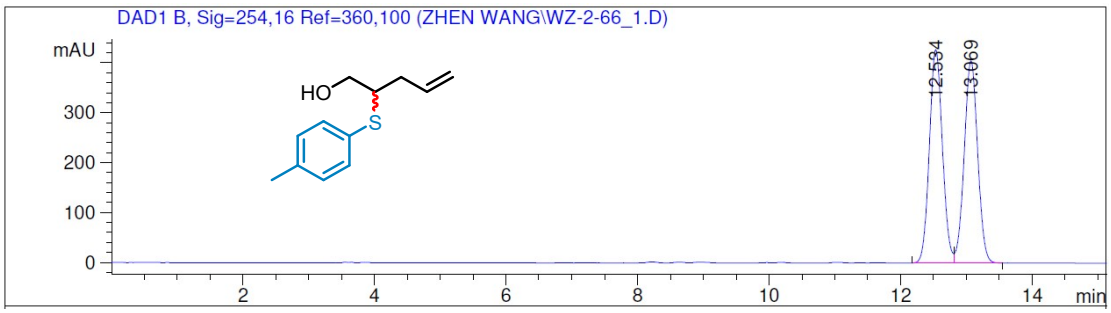


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.827	MM	0.2077	226.88287	18.20689	15.0689
2	5.542	MM	0.2732	1278.75061	78.00809	84.9311

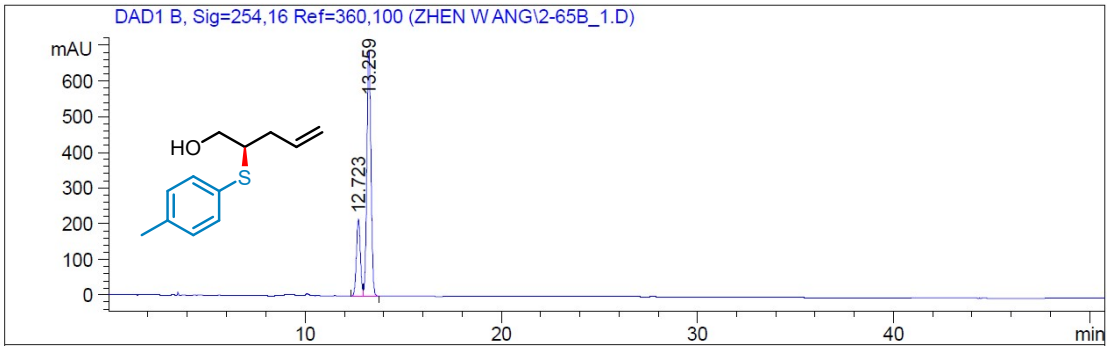
The enantiomeric excess (70% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 1:4, 36 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 5.54 min. t_r(minor) = 4.83 min. $[\alpha]_D^{25}$ = 1.33 (c = 0.45, $CHCl_3$).

(*R*)-2-(*p*-tolylthio)pent-4-en-1-ol (5v)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.534	BV	0.2147	5887.85205	427.40906	50.4962
2	13.069	VB	0.2202	5772.14160	405.19745	49.5038

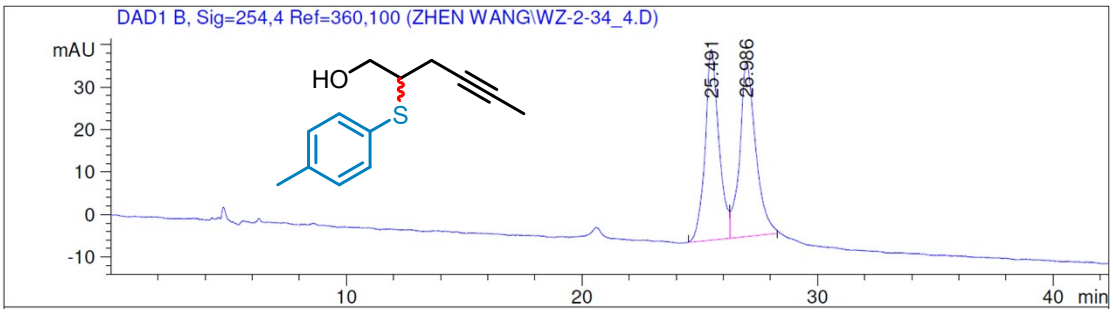


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.723	BV	0.2191	3018.86816	215.98494	23.1118
2	13.259	VB	0.2280	1.00432e4	689.30786	76.8882

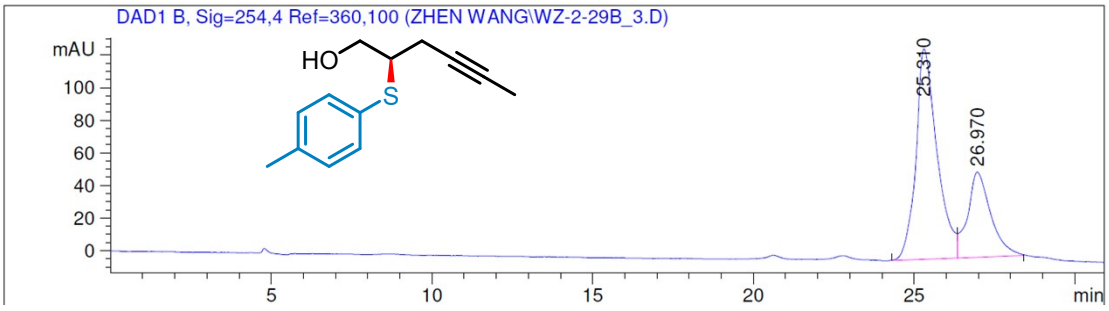
The enantiomeric excess (53% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOH/hexane = 1:99, 39 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 13.26 min. t_r(minor) = 12.72 min. $[\alpha]_D^{25}$ = 3.14 (c = 0.18, $CHCl_3$).

(*R*)-2-(*p*-tolylthio)hex-4-yn-1-ol (5w)



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.491	BV	0.5669	1840.78528	44.84558	48.6276
2	26.986	VB	0.6180	1944.69092	40.95383	51.3724

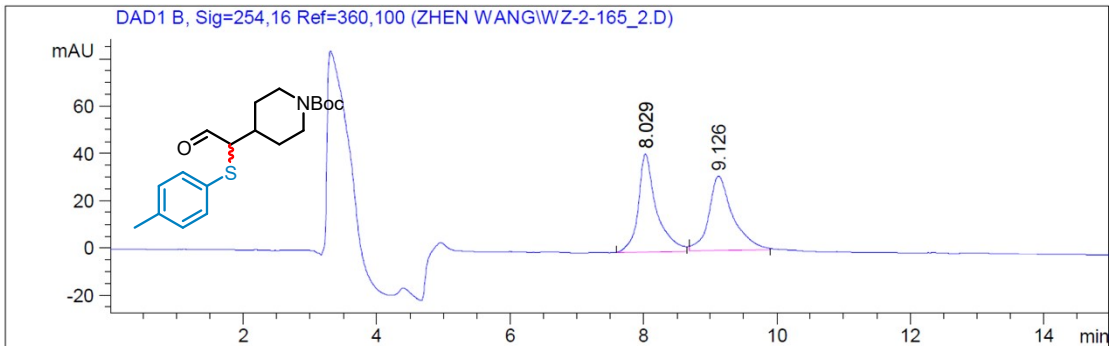


Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.310	BV	0.6541	5910.39697	129.09543	69.2105
2	26.970	VB	0.6846	2629.34766	52.29364	30.7895

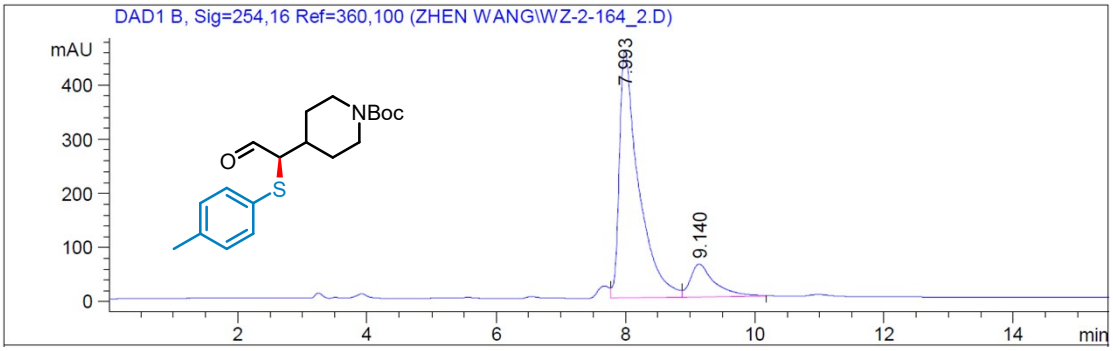
The enantiomeric excess (38% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 1:66, 39 bar, flow rate: 0.8 mL/min, λ_{max} = 254 nm): t_r(major) = 25.31 min. t_r(minor) = 26.97 min. $[\alpha]_D^{25} = 0.24$ (c = 0.38, $CHCl_3$).

***tert*-butyl (*R*)-4-(2-oxo-1-(*p*-tolylthio)ethyl)piperidine-1-carboxylate (4x)**



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.029	BB	0.2672	787.09473	41.51318	49.8923
2	9.126	BB	0.3635	790.49268	31.41918	50.1077

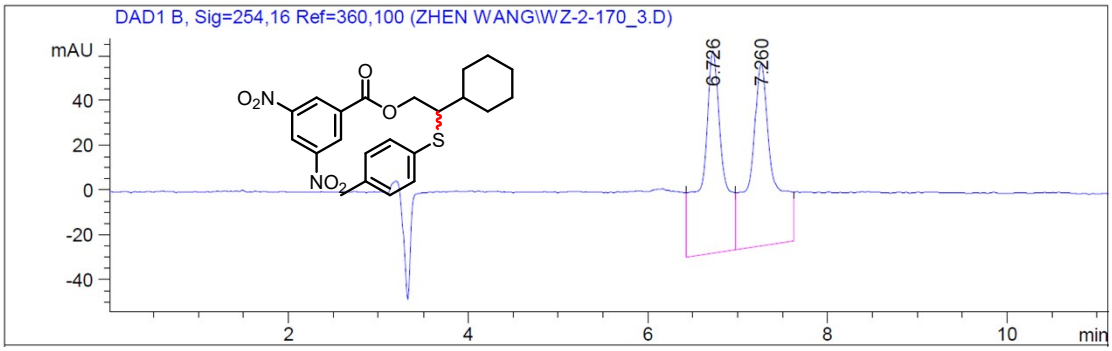


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.993	VV	0.2916	9486.58984	458.11786	85.5397
2	9.140	VB	0.3766	1603.69019	61.01978	14.4603

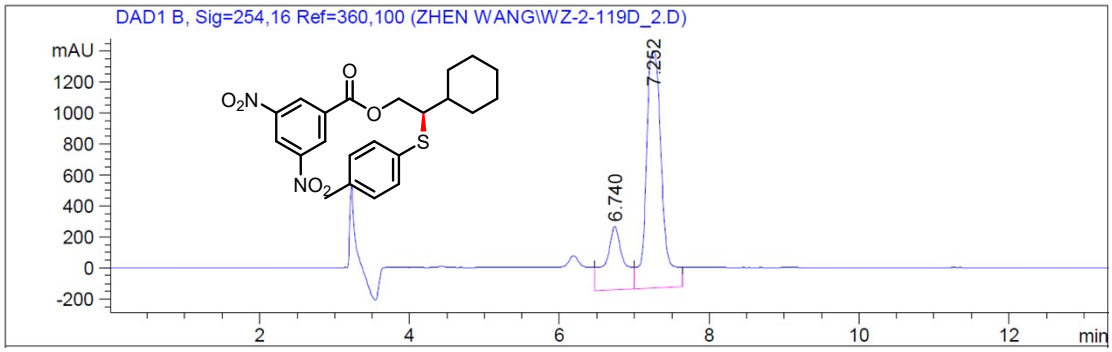
The enantiomeric excess (71% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH /hexane = 1:97, 37 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 7.99 min. t_r(minor) = 9.14 min. $[\alpha]_D^{25}$ = 13.34 (c = 0.81, $CHCl_3$).

(*R*)-2-cyclohexyl-2-(*p*-tolylthio)ethyl 3,5-dinitrobenzoate (6a)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.726	VV	0.2165	1431.34229	90.52164	49.5113
2	7.260	VV	0.2428	1459.59998	81.55550	50.4887

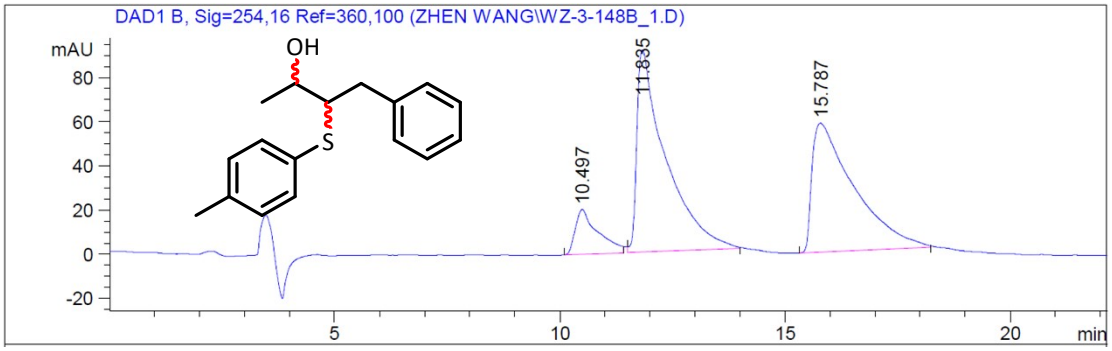


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.740	VV	0.2324	6909.79150	406.33820	23.7404
2	7.252	VV	0.2253	2.21959e4	1529.13855	76.2596

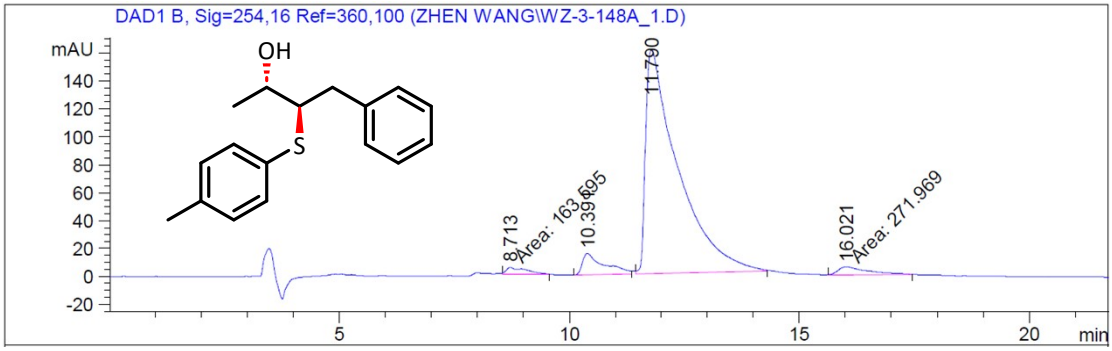
The enantiomeric excess (53% *ee*) was determined by HPLC with a *Diacel* Chiralpak IA column (EtOAc/hexane = 1:4, 39 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 7.25 min. t_r(minor) = 6.74 min. $[\alpha]_D^{22}$ = -90.76 (c = 0.11, $CHCl_3$).

(2*S*, 3*R*)-4-phenyl-3-(*p*-tolylthio)butan-2-ol (6b)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.497	BB	0.4913	707.26550	20.25642	8.2357
2	11.835	BB	0.6017	4104.86816	91.45319	47.7988
3	15.787	BB	0.8809	3775.66968	58.35501	43.9655

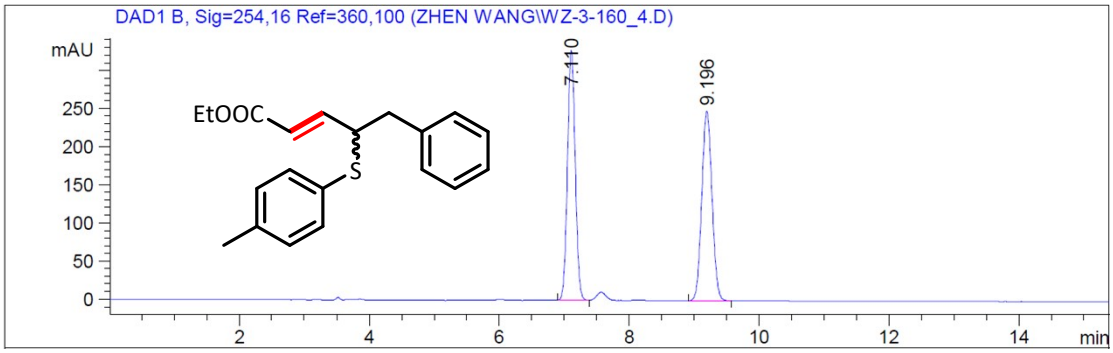


Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.713	MM	0.5356	163.59506	5.09035	1.8609
2	10.391	BB	0.4402	503.89758	15.46395	5.7319
3	11.790	BB	0.6640	7851.60205	160.14308	89.3135
4	16.021	MM	0.7743	271.96866	5.85391	3.0937

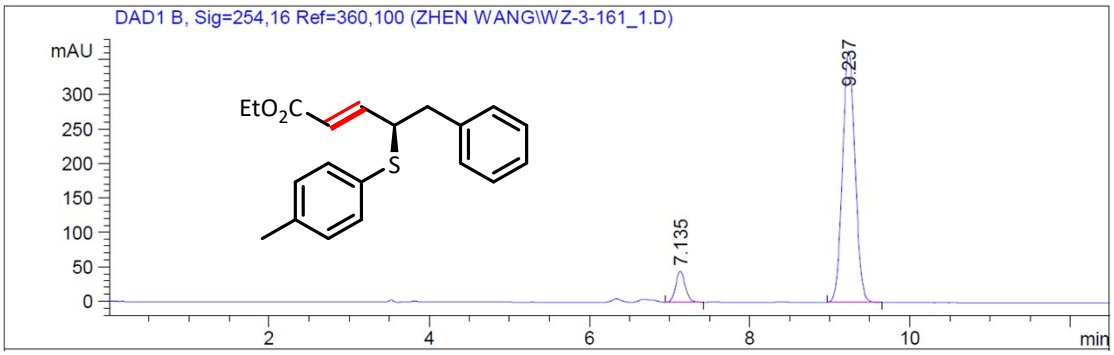
The diastereomeric ratio (94:6) was determined by HPLC with a *Diacel* Chiralpak IA column (*i*-PrOH/hexane = 3:97, 38 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 11.79 min. t_r(minor) = 16.02 min. $[\alpha]_D^{24}$ = -25.39 (c = 0.40, $CHCl_3$).

Ethyl (*R*, *E*)-5-phenyl-4-(*p*-tolylthio)pent-2-enoate (6c)



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.110	BV	0.1281	2696.32788	327.36337	49.8627
2	9.196	BB	0.1693	2711.17285	248.37793	50.1373



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.135	VB	0.1254	364.53772	44.58160	8.3888
2	9.237	BB	0.1696	3981.00415	364.02560	91.6112

The enantiomeric excess (83% *ee*) was determined by HPLC with a *Diacel* Chiralpak IC column (EtOH/hexane = 1:99, 40 bar, flow rate: 1.0 mL/min, λ_{max} = 254 nm): t_r(major) = 9.24 min. t_r(minor) = 7.14 min. $[\alpha]_D^{24}$ = 48.28 (c = 0.86, $CHCl_3$).