Supplementary Information

for

A Solvent-dependent Chirality-switchable Thia-Michael Addition to α,β-Unsaturated Carboxylic Acids using a Chiral Multifunctional Thiourea Catalyst

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CONTENTS

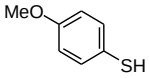
1. General information

All non-aqueous reactions were carried out under a positive atmosphere of argon in dried glassware unless otherwise noted. Solvents and materials were obtained from commercial suppliers and used without further purification. Column chromatography was performed on Cica silica gel 60 (230−400 mesh) or Fuji Silysia silica gel (NH, 100−200 mesh), gel permeation chromatography was performed with LC-9201, and flash column chromatography was performed on Cica silica gel 60 (spherical/40−100 μm). Reactions and chromatography fractions were analyzed using pre-coated silica gel plate (Merck Silica Gel 60 F_{254}). All melting points were measured on BÜCHI M-565 melting point apparatus and are uncorrected. IR spectra were measured on JASCO FT/IR-4100. Unless otherwise noted, NMR spectra were obtained in $CDCl_3$. ^{1}H NMR (400 MHz) spectra were recorded with JEOL ECP-400 spectrometers and chemical shifts are reported in δ (ppm) relative to TMS (in $CDCl_3$) as internal standard. Unless otherwise noted, ^{13}C NMR (100 MHz) spectra were also recorded using JEOL ECP-400 spectrometers and referenced to the residual $CHCl_3$ or CHD_2CN signals. ^{11}B NMR (128 MHz) spectra were recorded using JEOL ECP-400 spectrometers using quarts NMR tubes. ^{1}H NMR multiplicities are reported as follows: br = broad; m = multiplet; s = singlet; d = doublet; t = triplet; q = quartet. High-resolution mass spectra were obtained on a JMS-HX/MS700 (FAB) or a Shimadzu LCMS-IT-TOF fitted with an ESI. Optical rotations were recorded on a JASCO P-2200 polarimeter with a path length of 0.5 cm; concentrations are quoted in grams per 100 mL. $[\alpha]_D$ values are measured in 10^{-1} deg cm^2g^{-1}. Enantiomeric excess was determined by high performance liquid chromatography (HPLC) analyses using a Shimadzu Prominence HPLC System fitted with Daicel chiral column. Unless otherwise noted, all materials and solvents were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used without purification. All non-commercially available substrates were prepared according to the literature procedure as indicated below.

2. Preparation of benzenethiols

Benzenethiols **2a-g** were commercially available.

2a



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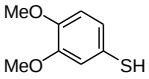

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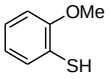
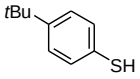
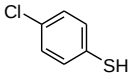


2d



2e



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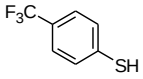


2g

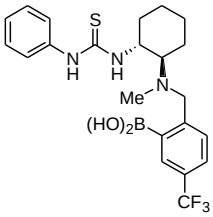
3. Preparation of α,β-unsaturated carboxylic acids

α,β-Unsaturated carboxylic acids **3a**, **3b**, **3d-f**, and **3n** were commercially available. The carboxylic acids **3c**,[S1] **3g**,[S1] **3h**,[S2] **3i -l**,[S1]and **3m**[S3] were prepared according to the literatures.

4. Preparation of multifunctional thiourea catalysts

Catalysts **1a–c**[S1] were prepared according to the literature. Catalysts **1d-h** were prepared by a similar procedure according to the literature[S1] as described below.

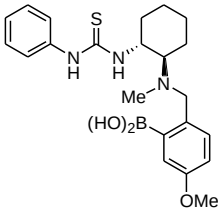
2-[[*N*-Methyl-(1*R*,2*R*)-2-(3-phenylthioureido)cyclohexan-1-yl]-(2-aminomethyl)]-5-(trifluoromethyl)phenylboronic Acid (1d)



1d

White amorphous; ^{1}H NMR (CD_3CN, 400 MHz) δ 8.82 (br s, 1H), 8.18 (br s, 1H), 7.95 (s, 1H), 7.61 (dd, J_1 = 8.1 Hz, J_2 = 1.7 Hz, 1H), 7.39–7.29 (m, 5H), 7.21–7.15 (m, 1H), 6.32 (br s, 1H), 4.60–4.47 (m, 1H), 3.81 (d, J = 12.8 Hz, 1H), 3.73 (d, J = 12.8 Hz, 1H), 2.39 (ddd, J_1 = J_2 = 11.3 Hz, J_3 = 3.1 Hz, 1H), 2.28 (s, 3H), 2.06–1.97 (m, 2H), 1.80–1.72 (m, 1H), 1.66–1.57 (m, 1H), 1.40–1.18 (m, 2H), 1.12–0.95 (m, 2H), one *O*-H or *N*-H proton was not observed; ^{13}C NMR (CD_3CN, 100 MHz) δ 181.3, 147.1, 139.2, 132.8 (q, J = 3.8 Hz), 131.6, 129.7 (2C), 129.2 (q, J = 31.9 Hz), 127.2 (q, J = 3.8 Hz), 126.2, 125.8 (2C), 124.2 (q, J = 271 Hz), 62.1, 59.7, 55.5, 35.7, 33.4, 25.5, 25.3, 22.8, One carbon peak (<u>*C*</u>-B(OH)$_2$) could not be observed; IR (ATR): 2938, 1535 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{28}BF_6N_3O_2S$ $[M+H]^+$ 466.1946, found 466.1943; $[\alpha]_D^{25}$ +34.8 (*c* 1.03, $CHCl_3$).

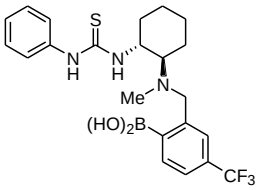
2-[[*N*-Methyl-(1*R*,2*R*)-2-(3-phenylthioureido)cyclohexan-1-yl]-(2-aminomethyl)]-5-(methoxy)phenylboronic Acid (1e)



1e

White amorphous; ^{1}H NMR (CD_3CN, 400 MHz) δ 8.25 (br s, 1H), 7.31 (d, J = 7.5 Hz, 2H), 7.26 (t, J = 7.8 Hz, 2H), 7.18 (d, J = 2.9 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 8.1 Hz, 1H), 6.79 (dd, J_1 = 8.1 Hz, J_2 = 2.9 Hz, 1H), 6.32 (br s, 1H), 4.54–4.43 (m, 1H), 3.71 (s, 3H), 3.64 (d, J = 12.8 Hz, 1H), 3.56 (d, J = 12.8 Hz, 1H), 2.40 (ddd, J_1 = J_2 = 11.3 Hz, J_3 = 3.3 Hz, 1H), 2.19 (s, 3H), 1.98–1.90 (m, 2H), 1.72–1.65 (m, 1H), 1.60–1.53 (m, 1H), 1.33–1.10 (m, 2H), 1.16–0.93 (m, 2H), two *O*-H or *N*-H protons were not observed; ^{13}C NMR (CD_3CN, 100 MHz) δ 181.4, 159.4, 139.4, 134.3, 132.7, 129.7 (2C), 126.1, 125.6 (2C), 121.8, 115.5, 61.7, 59.5, 55.6, 55.4, 35.3, 33.5, 25.6, 25.4, 22.7, one carbon peak (<u>*C*</u>-B(OH)$_2$) could not be observed; IR (ATR): 3278, 2934, 1536 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{31}BN_3O_3S$ $[M+H]^+$ 428.2178, found 428.2175; $[\alpha]_D^{21}$ +50.5 (*c* 0.97, $CHCl_3$).

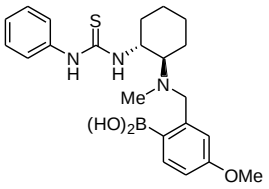
2-[[*N*-Methyl-(1*R*,2*R*)-2-(3-phenylthioureido)cyclohexan-1-yl]-(2-aminomethyl)]-4-(trifluoromethyl)phenylboronic Acid (1f)



1f

White amorphous; ^{1}H NMR (CD_3CN, 400 MHz) δ 8.20 (br s, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.52 (s, 1H), 7.39–7.29 (m, 4H), 7.20–7.14 (m, 1H), 6.38 (br s, 1H), 4.60–4.43 (m, 1H), 3.82 (d, *J* = 12.8 Hz, 1H), 3.74 (d, *J* = 12.8 Hz, 1H), 2.41 (ddd, $J_1 = J_2$ = 11.3 Hz, J_3 = 2.7 Hz, 1H), 2.26 (s, 3H), 2.07–1.98 (m, 2H), 1.80–1.73 (m, 1H), 1.66–1.57 (m, 1H), 1.40–1.17 (m, 2H), 1.14–0.95 (m, 2H), two *O*-H or *N*-H protons were not observed; ^{13}C NMR (CD_3CN, 100 MHz) δ 181.4, 143.9, 139.4, 137.0, 131.5 (q, *J* = 32.3 Hz), 129.7 (2C), 127.1 (q, *J* = 2.9 Hz), 126.1, 125.7 (2C), 126.6 (q, *J* = 272 Hz), 124.2 (q, *J* = 3.8 Hz), 62.2, 59.7, 55.5, 35.5, 33.4, 25.6, 25.4, 22.7, one carbon peak (*C*-B(OH)$_2$) could not be observed; IR (ATR): 3268, 2936, 1534 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{28}BF_3N_3O_2S$ $[M+H]^+$ 466.1946, found 466.1945; $[\alpha]_D^{26}$ +14.2 (*c* 1.04, $CHCl_3$).

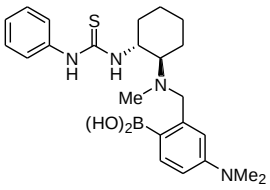
2-[[*N*-Methyl-(1*R*,2*R*)-2-(2phenylthioureido)cyclohexan-1-yl]-(2-aminomethyl)]-4-(methoxyl)phenylboronic Acid (1g)



1g

White amorphous; ^{1}H NMR (CD_3CN, 400 MHz) δ 8.72 (br s, 2H), 8.37 (br s, 1H), 7.70–7.64 (m, 1H), 7.42–7.35 (m, 2H), 7.34–7.25 (m, 2H), 7.17–7.09 (m, 1H), 6.89–6.77 (m, 2H), 6.48 (br s, 1H), 4.62–4.48 (m, 1H), 3.78 (s, 3H), 3.80–3.70 (m, 1H), 3.62 (d, *J* = 12.2 Hz, 1H), 2.45 (ddd, $J_1 = J_2$ = 9.4 Hz, J_3 = 3.1 Hz, 1H), 2.27 (s, 3H), 2.08–1.97 (m, 2H), 1.81–1.71 (m, 1H), 1.68–1.58 (m, 1H), 1.40–1.18 (m, 2H), 1.13–0.97 (m, 2H), one *O*-H or *N*-H proton was not observed; ^{13}C NMR (CD_3CN, 100 MHz) δ 181.4, 161.9, 144.7, 139.6, 138.7, 129.6 (2C), 125.9, 125.5 (2C), 117.4, 112.5, 61.8, 60.3, 55.7, 55.5, 35.6, 33.5, 25.6, 25.4, 22.6, one carbon peak could not be observed; IR (ATR): 3271, 2935, 1538 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{31}BN_3O_3S$ $[M+H]^+$ 428.2178, found 428.2179; $[\alpha]_D^{25}$ +27.5 (*c* 1.03, $CHCl_3$).

2-[[*N*-Methyl-(1*R*,2*R*)-2-(2phenylthioureido)cyclohexan-1-yl]-(2-aminomethyl)]-4-(dimethylamino)phenylboronic Acid (1h)

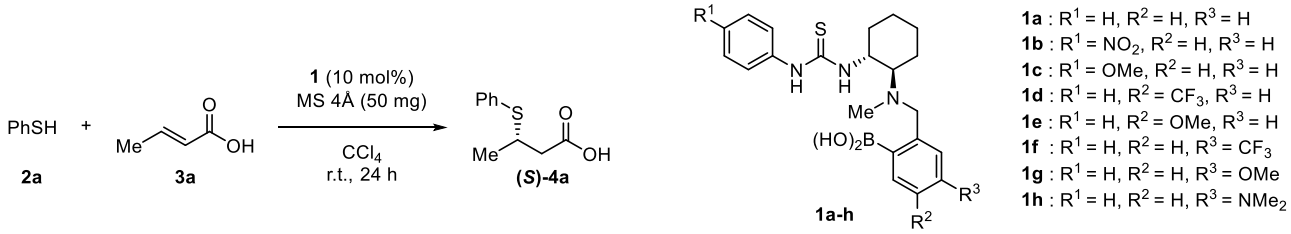


1h

White amorphous; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (br s, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.40–7.28 (m, 4H), 7.24–7.20 (m, 1H), 6.58 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1H), 6.44 (d, J = 1.8 Hz, 1H), 6.17 (br s, 1H), 4.70–4.60 (m, 1H), 3.66 (d, J = 12.4 Hz, 1H), 3.62 (d, J = 12.4 Hz, 1H), 3.06–2.96 (m, 1H), 2.97 (s, 6H), 2.59 (dd, J_1 = 9.6 Hz, J_2 = 1.6 Hz, 1H), 2.38–2.28 (m, 1H), 2.31 (s, 3H), 2.08–2.00 (m, 1H), 1.88–1.80 (m, 1H), 1.75–1.67 (m, 1H), 1.45–1.31 (m, 2H), 1.29–1.15 (m, 2H), two *O*-H or *N*-H protons was not observed; ^{13}C NMR (CD_3CN, 100 MHz) δ 180.2, 151.7, 137.7, 137.4, 129.4 (2C), 129.0. 126.0, 124.9 (2C), 114.4, 110.5, 62.1, 61.1, 55.6, 40.1 (2C), 34.3, 33.2, 24.9, 24.7, 22.0, one carbon peak could not be observed; IR (ATR): 3269, 2936, 1601, 1353 cm^{-1}; HRMS (ESI): calcd for $C_{23}H_{34}BN_4O_2S$ $[M+H]^+$ 441.2494, found 441.2483; $[\alpha]_D^{28}$ +23.2 (*c* 0.98, $CHCl_3$).

5. Optimization of the reaction condition

Table S1. Optimization in CCl_4[a]



Entry	catalyst	concentration (M)	yield[b] (%)	ee[c] (%)
1	**1a**	0.1	90	41 (*S*)
2	**1b**	0.1	78	22 (*S*)
3	**1c**	0.1	96	69 (*S*)
4	**1d**	0.1	81	41 (*S*)
5	**1e**	0.1	87	40 (*S*)
6	**1f**	0.1	76	11 (*S*)
7	**1g**	0.1	83	28 (*S*)
8	**1h**	0.1	69	6 (*R*)
9	**1a**	0.02	46	24 (*S*)
10	**1a**	0.05	63	38 (*S*)
11	**1a**	0.2	91	57 (*S*)
12	**1a**	0.4	86	72 (*S*)
13	**1a**	1	88	76 (*S*)
14[d]	**1a**	2	91	81 (*S*)
15[d]	**1g**	2	78	75 (*S*)

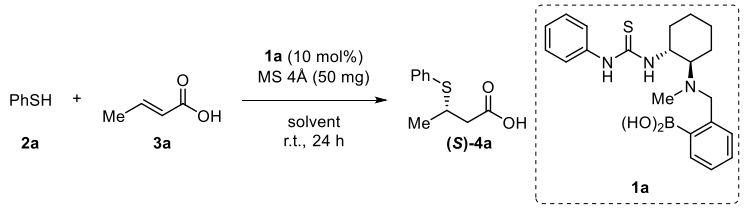
[a] Unless otherwise noted, the reaction was carried out with **2a** (0.1 mmol), **3a** (1.0 equiv), catalyst (0.1 equiv), and 4Å MS (50 mg) in CCl_4 at room temperature for 24 h.

[b] Isolated yield after treatment with $TMSCHN_2$.

[c] Estimated by chiral HPLC after treatment with $TMSCHN_2$. Absolute configuration is shown in the brackets.

[d] 4Å MS (20 mg)

Table S2. Optimization in hexane and CH_2Cl_2[a]



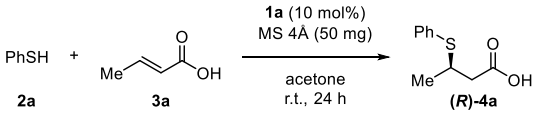
Entry	solvent	concentration (M)	yield[b] (%)	ee[c] (%)
1	*n*-hexane	0.02	16	19 (*R*)
2	*n*-hexane	0.05	25	23 (*S*)
3	*n*-hexane	0.1	28	48 (*S*)
4	*n*-hexane	0.2	36	61 (*S*)
5	*n*-hexane	0.4	34	70 (*S*)
6	CH_2Cl_2	1	72	64 (*S*)
7	*n*-hexane/CH_2Cl_2	1	56	74 (*S*)

[a] Unless otherwise noted, the reaction was carried out with **2a** (0.1 mmol), **3a** (1.0 equiv), catalyst (0.1 equiv), and 4Å MS (50 mg) in solvent at room temperature for 24 h.

[b] Isolated yield after treatment with $TMSCHN_2$.

[c] Estimated by chiral HPLC after treatment with $TMSCHN_2$. Absolute configuration is shown in the brackets.

Table S3. Optimization in acetone[a]



Entry	concentration (M)	yield[b] (%)	ee[c] (%)
1	0.02	33	75 (*R*)
2	0.05	57	82 (*R*)
3	0.1	68	82 (*R*)
4	0.2	86	57 (*R*)
5	0.4	85	41 (*R*)
6[d]	0.1	83	81 (*R*)

[a] Unless otherwise noted, the reaction was carried out with **2a** (0.1 mmol), **3a** (1.0 equiv), catalyst (0.1 equiv), and 4Å MS (50 mg) in acetone at room temperature for 24 h.

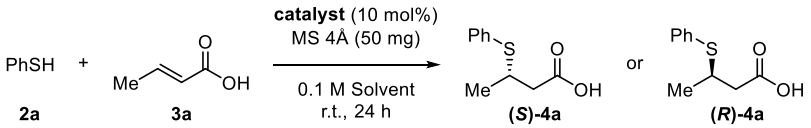
[b] Isolated yield after treatment with $TMSCHN_2$.

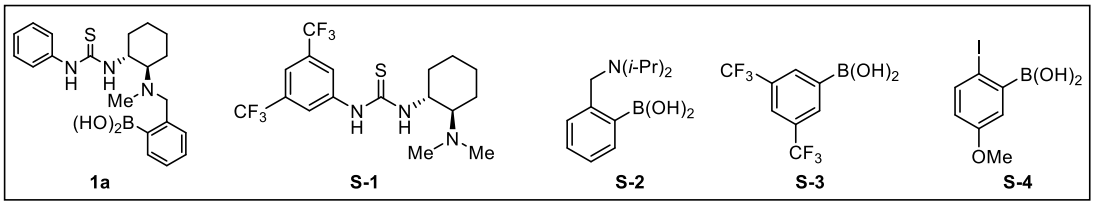
[c] Estimated by chiral HPLC after treatment with $TMSCHN_2$. Absolute configuration is shown in the brackets.

[d] 4Å MS (100 mg)

6. Control experiments

Table S4. Screening of mono- and bi-functional catalyst[a]





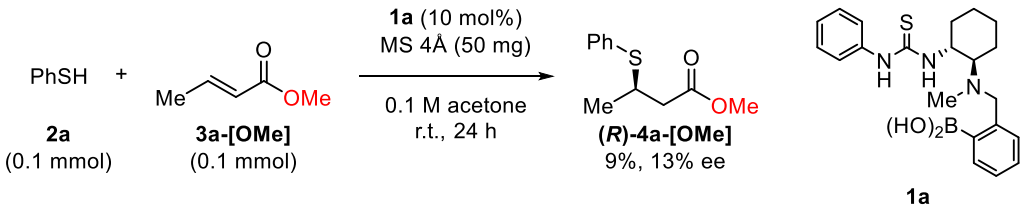
Entry	catalyst	solvent	yield[b] (%)	ee[c] (%)
1	**1a**	acetone	68	81 (*R*)
2[d]	**1a**	acetone	11	15 (*R*)
3	**S-1**	acetone	13	12 (*R*)
4	**S-2**	acetone	28	-
5	**S-3**	acetone	ND	-
6	**S-4**	acetone	ND	-
7	**1a**	CCl_4	90	41 (*S*)
8[d]	**1a**	CCl_4	ND	-
9	**S-1**	CCl_4	3	5 (*R*)
10	**S-2**	CCl_4	90	-
11	**S-3**	CCl_4	ND	-
12	**S-4**	CCl_4	ND	-

[a] Unless otherwise noted, the reaction was carried out with **2a** (0.1 mmol), **3a** (1.0 equiv), catalyst (0.1 equiv), and 4Å MS in solvent (1.0 mL) at room temperature for 24 h.

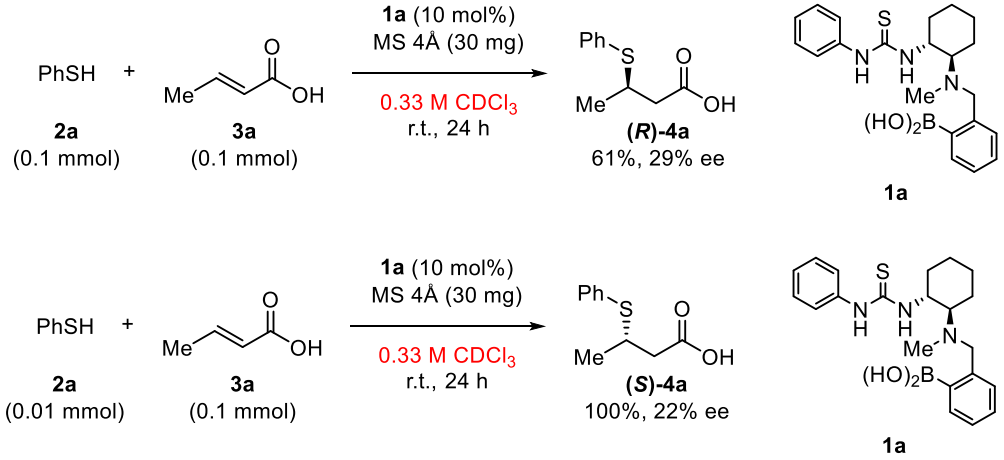
[b] Isolated yield after treatment with $TMSCHN_2$.

[c] Estimated by chiral HPLC after treatment with $TMSCHN_2$. Absolute configuration is shown in the brackets.

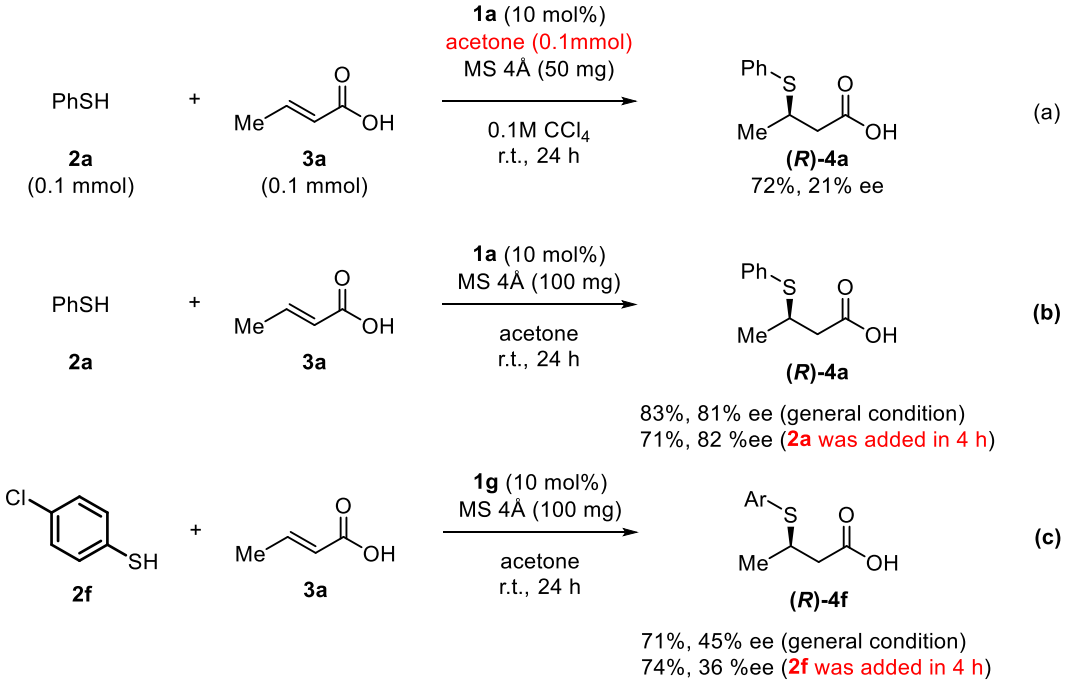
[d] Without 4Å MS.



Scheme S1. A control experiment using α,β-unsaturated ester **3a**-[OMe]



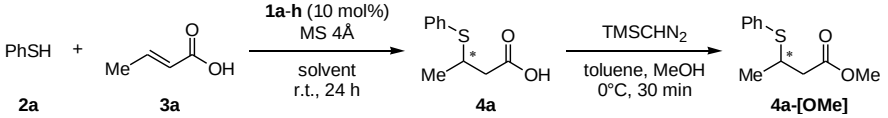
Scheme S2. Effect of the concentration of thiol **2a**



Scheme S3. (a) The reaction with 1 equiv of acetone in CCl_4 (b)(c) Effect of pre-mixing of catalyst and **3a**

7. Asymmetric thia-Michael addition

General procedure for the synthesis of 4a and their methyl esters 4a-[OMe] as described in Table 1.



To a stirred suspension of (*E*)-crotonic acid **3a** (0.10 mmol), boronic acid catalyst **1a-h** (10 mol%), and activated MS 4Å in an appropriate solvent, was added benzenethiol **2a** (100 mol%) in the same solvent at room temperature. The reaction mixture was stirred at room temperature for 24 h, and directly purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 4:1 to ethyl acetate/methanol = 7:3) to afford the crude product **4a**. To the solution of crude **4a** in toluene/methanol (0.75 mL/0.25 mL) was slowly added a solution of $TMSCHN_2$ in Et_2O (2.0 M, 0.25 mL, 0.5 mmol) at 0°C. The resulting mixture was stirred at 0°C for 30 min, before being quenched with AcOH, until yellow color of the solution disappeared. After evaporation of the reaction mixture, the residue was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 20:1) to afford methyl esters **4a-[OMe]** as a colorless oil; The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: 5.5 min 6.5 min].

(entry 1): The reaction with **3a** (8.6 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), **2a** (10 μL, 0.10 mmol), and activated MS 4Å (50 mg) in CCl_4 (1.0 mL) gave the crude product **(*S*)-4a**. The same treatment as described in general procedure afford the desired product **(*S*)-4a-[OMe]** (18.9 mg, 90%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (41% ee).

(entry 2): The reaction with **3a** (8.7 mg, 0.10 mmol), **1a** (3.9 mg, 0.01 mmol), **2a** (10 μL, 0.10 mmol), and activated MS 4Å (50 mg) in CH_2Cl_2 (1.0 mL) gave the crude product **(*S*)-4a**. The same treatment as described in general procedure afford the desired product **(*S*)-4a-[OMe]** (4.4 mg, 21%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (22% ee).

(entry 3): The reaction with **3a** (8.6 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), **2a** (10 μL, 0.10 mmol), and activated MS 4Å (50 mg) in *n*-hexane (1.0 mL) gave the crude product **(*S*)-4a**. The same treatment as described in general procedure afford the desired product **(*S*)-4a-[OMe]** (5.9 mg, 28%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (49% ee).

(entry 4): The reaction with **3a** (8.8 mg, 0.10 mmol), **1a** (4.1 mg, 0.01 mmol), **2a** (10 μL, 0.10 mmol), and activated MS 4Å (50 mg) in CH_3CN (1.0 mL) gave the crude product **(*R*)-4a**. The same treatment as described in general procedure afford the desired product **(*R*)-4a-[OMe]** (7.6 mg, 36%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (39% ee).

(entry 5): The reaction with **3a** (8.7 mg, 0.10 mmol), **1a** (4.1 mg, 0.01 mmol), **2a** (10 μL, 0.10 mmol), and activated MS 4Å (50 mg) in acetone (1.0 mL) gave the crude product **(*R*)-4a**. The same treatment as described in general procedure afford the desired product **(*R*)-4a-[OMe]** (14.3 mg, 68%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (82% ee).

(entry 6): The reaction with **3a** (8.7 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), **2a** (10 μL, 0.10 mmol), and activated MS 4Å (50 mg) in MeOH (1.0 mL) gave not the desired product **4a**.

(entry 7): The reaction with **3a** (8.8 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol) and **2a** (10 μL, 0.10 mmol) without activated MS 4Å in CCl_4 (1.0 mL) gave not the desired product **4a**.

(entry 8): The reaction with **3a** (8.6 mg, 0.10 mmol), **1a** (4.1 mg, 0.01 mmol) and **2a** (10 μL, 0.10 mmol) without activated MS 4Å in acetone (1.0 mL) gave the crude product **(*R*)-4a**. The same treatment as described in general procedure afford the desired product **(*R*)-4a-[OMe]** (2.3 mg, 11%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (15% ee).

(entry 9): The reaction with **3a** (8.7 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), **2a** (10 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) gave the crude product **(*S*)-4a**. The same treatment as described in general procedure afford the desired product **(*S*)-4a-[OMe]** (19.1 mg, 91%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (81% ee).

(entry 10): The reaction with **3a** (8.7 mg, 0.10 mmol), **1b** (4.3 mg, 0.01 mmol), benzenethiol **2a** (10 μL, 0.10 mmol), and activated MS 4Å (50 mg) in acetone (1.0 mL) gave the crude product **(*R*)-4a**. The same treatment as described in general procedure afford **(*R*)-4a-[OMe]** (7.4 mg, 35%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (33% ee).

(entry 11): The reaction with **3a** (8.7 mg, 0.10 mmol), **1c** (4.5 mg, 0.01 mmol), benzenethiol **2a** (10 μL, 0.10 mmol), and activated MS 4Å (50 mg) in acetone (1.0 mL) gave the crude product **(*R*)-4a**. The same treatment as described in general procedure afford **(*R*)-4a-[OMe]** (14.1 mg, 67%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (78% ee).

(entry 12): The reaction with **3a** (8.7 mg, 0.10 mmol), **1d** (4.6 mg, 0.01 mmol), benzenethiol **2a** (10 μL, 0.10 mmol), and activated MS 4Å (50 mg) in acetone (1.0 mL) gave the crude product **(*R*)-4a**. The same treatment as described in general procedure afford **(*R*)-4a-[OMe]** (12.0 mg, 57%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (80% ee).

(entry 13): The reaction with **3a** (8.7 mg, 0.10 mmol), **1e** (4.4 mg, 0.01 mmol), benzenethiol **2a** (10 μL, 0.10 mmol), and activated MS 4Å (50 mg) in acetone (1.0 mL) gave the crude product **(*R*)-4a**. The same treatment as described in general procedure afford **(*R*)-4a-[OMe]** (12.9 mg, 61%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (68% ee).

(entry 14): The reaction with **3a** (8.7 mg, 0.10 mmol), **1f** (4.7 mg, 0.01 mmol), benzenethiol **2a** (10 μL, 0.10 mmol), and activated MS 4Å (50 mg) in acetone (1.0 mL) gave the crude product **(*R*)-4a**. The same treatment as described in general procedure afford **(*R*)-4a-[OMe]** (7.3 mg, 35%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (45% ee).

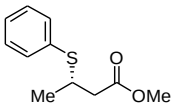
(entry 15): The reaction with **3a** (8.7 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), benzenethiol **2a** (10 μL, 0.10 mmol), and activated MS 4Å (50 mg) in acetone (1.0 mL) gave the crude product **(*R*)-4a**. The same treatment as described in general procedure afford **(*R*)-4a-[OMe]** (15.4 mg, 73%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (92% ee).

(entry 16): The reaction with **3a** (8.6 mg, 0.10 mmol), **1h** (4.5 mg, 0.01 mmol), benzenethiol **2a** (10 μL, 0.10 mmol), and activated MS 4Å (50 mg) in acetone (1.0 mL) gave the crude product **(*R*)-4a**. The same treatment as described in general procedure afford **(*R*)-4a-[OMe]** (11.1 mg, 53%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (45% ee).

(entry 17): The reaction with **3a** (8.6 mg, 0.10 mmol), **1g** (4.4 mg, 0.01 mmol), benzenethiol **2a** (10 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) gave the crude product **(*R*)-4a**. The same treatment as described in general procedure afford **(*R*)-4a-[OMe]** (16.8 mg, 80%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (92% ee).

(entry 18): The reaction with **3a** (8.6 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), **2a** (10 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) gave the crude product **(*S*)-4a**. The same treatment as described in general procedure afford the desired product **(*S*)-4a-[OMe]** (16.4 mg, 78%). The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (75% ee).

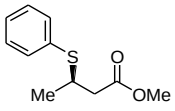
Methyl (*S*)-3-(phenylthio)butanoate ((*S*)-4a-[OMe])



(*S*)-4a-[OMe]

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.5 Hz, 2H), 7.35–7.23 (m, 3H), 3.67 (s, 3H), 3.67–3.57 (m, 1H), 2.65 (dd, J_1 = 15.7 Hz, J_2 = 5.8 Hz, 1H), 2.44 (dd, J_1 = 15.7 Hz, J_2 = 8.1 Hz, 1H), 1.33 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 139.7, 130.7 (2C), 128.9 (2C), 128.7, 51.7, 41.6, 39.4, 20.8; IR (ATR): 1738 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{14}NaO_2S$ $[M+Na]^+$ 233.0607, found 233.0608; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 6.2 min (minor) 5.2 min]; $[\alpha]_D^{28}$ +20.9 (*c* 0.97, $CHCl_3$) for 81% ee. (Lit [S4]: $[\alpha]_D^{25}$ +24.9 (*c* 1.09, $CHCl_3$) for 97% ee, (*S*) enantiomer)

Methyl (*R*)-3-(phenylthio)butanoate ((*R*)-4a-[OMe])

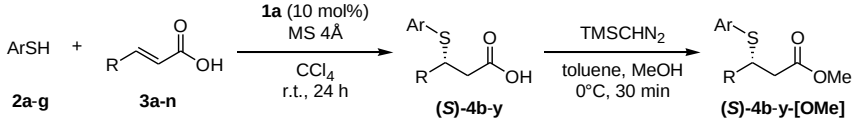


(*R*)-4a-[OMe]

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 5.6 min (minor) 6.6 min]; $[\alpha]_D^{24}$ –25.9 (*c* 0.98, $CHCl_3$) for 92% ee.

General procedure for the synthesis of 4 and their methyl esters 4-[OMe] as described in Figure 2, 3.

(in CCl_4)

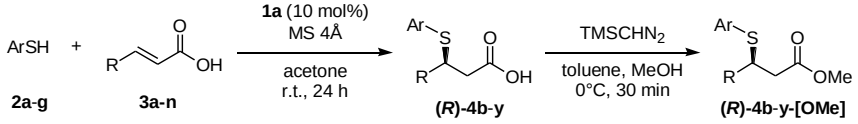


2a-g **3a-n** **(*S*)-4b-y** **(*S*)-4b-y-[OMe]**

To a stirred suspension of α,β-unsaturated carboxylic acid **3** (0.10 mmol), boronic acid catalyst **1a** (10 mol%), and activated MS 4Å (20 mg) in CCl_4 (25 μL), was added arylthiol **2** (100 mol%) in the same solvent (25 μL) at room temperature. The reaction mixture was stirred at room temperature for 24 h, and directly purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 4:1 to ethyl acetate/methanol = 7:3) to afford the crude product **4**. To the solution of crude **4** in toluene/methanol (0.75 mL/0.25 mL) was slowly added a solution of $TMSCHN_2$ in Et_2O (2.0 M, 0.25 mL, 0.5 mmol) at 0°C. The resulting mixture was stirred at 0°C for 30 min, before being quenched

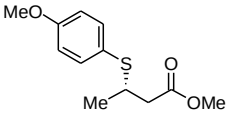
with AcOH, until yellow color of the solution disappeared. After evaporation of the reaction mixture, the residue was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 20:1) to afford methyl esters **4-[OMe].** The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis.

(in acetone)



To a stirred suspension of α,β-unsaturated carboxylic acid **3** (0.10 mmol), boronic acid catalyst **1g** (10 mol%), and activated MS 4Å (100 mg) in acetone (0.50 mL), was added arylthiol **2** (100 mol%) in the same solvent (0.50 mL) at room temperature. The reaction mixture was stirred at room temperature for 24 h, and directly purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 4:1 to ethyl acetate/methanol = 7:3) to afford the crude product **4**. To the solution of crude **4** in toluene/methanol (0.75 mL/0.25 mL) was slowly added a solution of $TMSCHN_2$ in Et_2O (2.0 M, 0.25 mL, 0.5 mmol) at 0°C. The resulting mixture was stirred at 0°C for 30 min, before being quenched with AcOH, until yellow color of the solution disappeared. After evaporation of the reaction mixture, the residue was purified by flash chromatography on silica gel to afford methyl esters **4-[OMe]**. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis.

Methyl (*S*)-3-((4-methoxyphenyl)thio)butanoate ((*S*)-4b-[OMe])

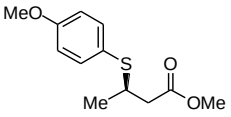


(*S*)-4b-[OMe]

(Figure 2): The reaction with (*E*)-crotonic acid **3a** (8.8 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4b**. The same treatment as described in general procedure afford **(*S*)-4b-[OMe]** (21.1 mg, 88%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (82% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 3.67 (s, 3H), 3.49–3.38 (m, 1H), 2.59 (dd, J_1 = 15.7 Hz, J_2 = 6.4 Hz, 1H), 2.40 (dd, J_1 = 15.7 Hz, J_2 = 8.1 Hz, 1H), 1.28 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 159.8, 136.4 (2C), 123.4, 114.4 (2C), 55.3, 51.7, 41.6, 40.4, 20.8; IR (ATR): 1738, 1247 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{17}O_3S$ $[M+H]^+$ 241.0893, found 241.0895; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 11.9 min (minor) 9.8 min]; $[\alpha]_D^{28}$ +17.5 (*c* 0.94, $CHCl_3$) for 82% ee.

Methyl (*R*)-3-((4-methoxyphenyl)thio)butanoate ((*R*)-4b-[OMe])



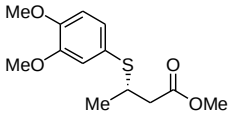
(*R*)-4b-[OMe]

(Figure 2): The reaction with (*E*)-crotonic acid **3a** (8.7 mg, 0.10 mmol), **1g** (4.4 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4b**. The same treatment as described in general procedure afford **(*R*)-4b-[OMe]** (20.5 mg, 85%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (91% ee).

(Scheme 1): The reaction with (*E*)-crotonic acid **3a** (8.6 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4b**. The same treatment as described in general procedure afford **(*R*)-4b-[OMe]** (17.8 mg, 74%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (90% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 10.3 min (minor) 12.2 min]; $[\alpha]_D^{28}$ −18.5 (*c* 0.95, $CHCl_3$) for 91% ee.

Methyl (*S*)-3-((3,4-dimethoxyphenyl)thio)butanoate ((*S*)-4c-[OMe])

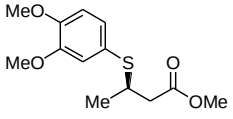


(*S*)-4c-[OMe]

(Figure 2): The reaction with (*E*)-crotonic acid **3a** (8.7 mg, 0.10 mmol), **1a** (4.1 mg, 0.01 mmol), 3,4-dimethoxybenzenethiol **2c** (14 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4c**. The same treatment as described in general procedure afford **(S)-4c-[OMe]** (21.4 mg, 79%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (84% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (dd, J_1 = 8.1 Hz, J_2 = 2.2 Hz, 1H), 7.01 (d, J = 2.2 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.68 (s, 3H), 3.53–3.44 (m, 1H), 2.61 (dd, J_1 = 15.6 Hz, J_2 = 6.4 Hz, 1H), 2.42 (dd, J_1 = 15.6 Hz, J_2 = 8.2 Hz, 1H), 1.30 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 149.3, 148.9, 127.6, 123.8, 117.6, 111.3, 55.94, 55.88, 51.7, 41.6, 40.4, 20.8; IR (ATR): 1734, 1254 cm^{-1}; HRMS (FAB): calcd for $C_{13}H_{18}NaO_4S$ $[M+Na]^+$ 293.0824, found 293.0819; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 12.4 min (minor) 11.2 min]; $[\alpha]_D^{28}$ +21.0 (*c* 1.03, $CHCl_3$) for 84% ee.

Methyl (*R*)-3-((3,4-dimethoxyphenyl)thio)butanoate ((*R*)-4c-[OMe])



(*R*)-4c-[OMe]

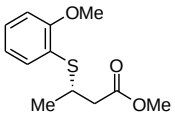
(Figure 2): The reaction with (*E*)-crotonic acid **3a** (8.6 mg, 0.10 mmol), **1g** (4.2 mg, 0.01 mmol), 3,4-dimethoxybenzenethiol **2c** (14 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4c**. The same treatment as described in general procedure afford **(*R*)-4c-[OMe]** (20.6 mg, 76%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was

determined by chiral stationary phase HPLC analysis (90% ee).

(Scheme 1): The reaction with (*E*)-crotonic acid **3a** (8.6 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 3,4-dimethoxybenzenethiol **2c** (14 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4c**. The same treatment as described in general procedure afford **(*R*)-4c-[OMe]** (22.2 mg, 82%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (90% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 10.6 min (minor) 11.7 min]; $[\alpha]_D^{25}$ –21.5 (*c* 1.04, $CHCl_3$) for 90% ee.

Methyl (*S*)-3-((2-methoxyphenyl)thio)butanoate ((*S*)-4d-[OMe])

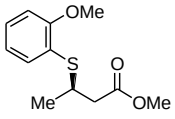


(*S*)-4d-[OMe]

(Figure 2): The reaction with (*E*)-crotonic acid **3a** (8.7 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 2-methoxybenzenethiol **2d** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4d**. The same treatment as described in general procedure afford **(*S*)-4d-[OMe]** (15.4 mg, 64%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (84% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J_1 = 7.2 Hz, J_2 = 1.7 Hz, 1H), 7.29–7.23 (m, 1H), 6.92 (dd, J_1 = J_2 = 7.2 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 3.89 (s, 3H), 3.80–3.70 (m, 1H), 3.65 (s, 3H), 2.66 (dd, J_1 = 15.7 Hz, J_2 = 5.2 Hz, 1H), 2.43 (dd, J_1 = 15.7 Hz, J_2 = 9.3 Hz, 1H), 1.33 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 158.8, 133.6, 128.9, 121.9, 120.9, 110.8, 55.7, 51.6, 41.6, 37.3, 20.6; IR (ATR): 1738, 1246 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{17}O_3S$ $[M+H]^+$ 241.0893, found 241.0891; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 16.6 min (minor) 13.2 min]; $[\alpha]_D^{27}$ +2.4 (*c* 0.95, $CHCl_3$) for 84% ee.

Methyl (*R*)-3-((2-methoxyphenyl)thio)butanoate ((*R*)-4d-[OMe])

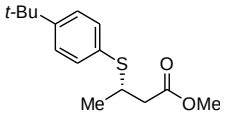


(*R*)-4d-[OMe]

(Figure 2): The reaction with (*E*)-crotonic acid **3a** (8.8 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), 2-methoxybenzenethiol **2d** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 48 h gave the crude product **(*R*)-4d**. The same treatment as described in general procedure afford **(*R*)-4d-[OMe]** (17.6 mg, 73%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (86% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 12.8 min (minor) 15.9 min]; $[\alpha]_D^{25}$ –3.3 (*c* 1.01, $CHCl_3$) for 86% ee.

Methyl (*S*)-3-((4-(*tert*-butyl)phenyl)thio)butanoate ((*S*)-4e-[OMe])

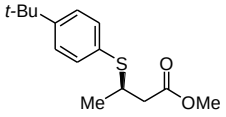


(*S*)-4e-[OMe]

(Figure 2): The reaction with (*E*)-crotonic acid **3a** (8.6 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 4-*tert*-butylbenzenethiol **2e** (17 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4e**. The same treatment as described in general procedure afford **(*S*)-4e-[OMe]** (24.7 mg, 93%) after flash chromatography using *n*-hexane/ethyl acetate = 20:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (80% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 3.66 (s, 3H), 3.62–3.52 (m, 1H), 2.65 (dd, J_1 = 15.7 Hz, J_2 = 5.8 Hz, 1H), 2.43 (dd, J_1 = 15.7 Hz, J_2 = 8.1 Hz, 1H), 1.34–1.29 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 150.8, 133.1 (2C), 129.9, 126.0 (2C), 51.7, 41.7, 39.5, 34.5, 31.2 (3C), 20.8; IR (ATR): 1739 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{23}O_2S$ $[M+H]^+$ 267.1413, found 267.1414; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 6.9 min (minor) 5.5 min]; $[\alpha]_D^{20}$ +9.9 (*c* 0.96, $CHCl_3$) for 80% ee.

Methyl (*R*)-3-((4-(*tert*-butyl)phenyl)thio)butanoate ((*R*)-4e-[OMe])

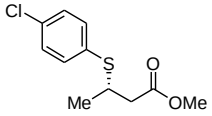


(*R*)-4e-[OMe]

(Figure 2): The reaction with (*E*)-crotonic acid **3a** (8.6 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), 4-*tert*-butylbenzenethiol **2e** (17 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4e**. The same treatment as described in general procedure afford **(*R*)-4e-[OMe]** (23.4 mg, 88%) after flash chromatography using *n*-hexane/ethyl acetate = 20:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (90% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 5.6 min (minor) 6.9 min]; $[\alpha]_D^{20}$ –11.9 (*c* 0.94, $CHCl_3$) for 90% ee.

Methyl (*S*)-3-((4-chlorophenyl)thio)butanoate ((*S*)-4f-[OMe])



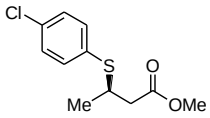
(*S*)-4f-[OMe]

(Figure 2): The reaction with (*E*)-crotonic acid **3a** (8.7 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 4-chlorobenzenethiol **2f** (14.5 mg, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4f**. The same treatment as described in general procedure afford **(*S*)-4f-[OMe]** (17.3 mg, 71%) after flash chromatography using *n*-hexane/ethyl acetate = 20:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (83% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 3.68 (s, 3H), 3.63–3.54

(m, 1H), 2.61 (dd, J_1 = 15.6 Hz, J_2 = 6.0 Hz, 1H), 2.44 (dd, J_1 = 15.6 Hz, J_2 = 8.2 Hz, 1H), 1.32 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 134.3 (2C), 132.7, 132.2, 129.1 (2C), 51.8, 41.5, 39.8, 20.9; IR (ATR): 1739, 1096 cm^{-1}; HRMS (FAB): calcd for $C_{11}H_{13}ClNaO_2S$ $[M+Na]^+$ 267.0222, found 267.0218; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 7.4 min (minor) 6.0 min]; $[\alpha]_D^{28}$ +13.6 (*c* 1.04, $CHCl_3$) for 83% ee.

Methyl (*R*)-3-((4-chlorophenyl)thio)butanoate ((*R*)-4f-[OMe])

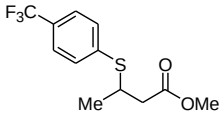


(*R*)-4f-[OMe]

(Figure 2): The reaction with (*E*)-crotonic acid **3a** (8.8 mg, 0.10 mmol), **1g** (4.4 mg, 0.01 mmol), 4-chlorobenzenethiol **2f** (14.5 mg, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4f**. The same treatment as described in general procedure afford **(*R*)-4f-[OMe]** (17.4 mg, 71%) after flash chromatography using *n*-hexane/ethyl acetate = 20:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (45% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 6.1 min (minor) 7.3 min]; $[\alpha]_D^{25}$ –9.3 (*c* 0.88, $CHCl_3$) for 45% ee.

Methyl 3-((4-(trifluoromethyl)phenyl)thio)butanoate (4g-[OMe])

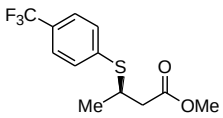


4g-[OMe]

(Figure 2): The reaction with (*E*)-crotonic acid **3a** (8.8 mg, 0.10 mmol), **1a** (3.9 mg, 0.01 mmol), 4-(trifluoromethyl)benzenethiol **2g** (14 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **4g**. The same treatment as described in general procedure afford **4g-[OMe]** (25.1 mg, 90%) after flash chromatography using *n*-hexane/ethyl acetate = 20:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (0% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 3.81–3.70 (m, 1H), 3.68 (s, 3H), 2.67 (dd, J_1 = 15.7 Hz, J_2 = 5.8 Hz, 1H), 2.49 (dd, J_1 = 15.7 Hz, J_2 = 8.1 Hz, 1H), 1.38 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 139.7, 136.7 (2C), 128.7 (q, J = 32.9 Hz), 125.8 (q, J = 3.8 Hz, 2C), 124.0 (q, J = 272 Hz), 51.8, 41.4, 38.6, 20.8; IR (ATR): 1739, 1327, 772 cm^{-1}; HRMS (ESI): calcd for $C_{12}H_{14}F_3O_2S$ $[M+H]^+$ 279.0661, found 279.0659; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: 5.8 min, 7.4 min]

Methyl (*R*)-3-((4-(trifluoromethyl)phenyl)thio)butanoate ((*R*)-4g-[OMe])

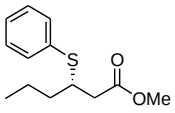


(*R*)-4g-[OMe]

(Figure 2): The reaction with (*E*)-crotonic acid **3a** (8.6 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), 4-(trifluoromethyl)benzenethiol **2g** (14 μL, 0.10 mmol), activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4g**. The same treatment as described in general procedure afford **(*R*)-4g-[OMe]** (20.9 mg, 75%) after flash chromatography using *n*-hexane/ethyl acetate = 20:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (15% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 5.8 min (minor) 7.4 min]; $[\alpha]_D^{24}$ –3.1 (*c* 0.90, $CHCl_3$) for 15% ee.

Methyl (*S*)-3-(phenylthio)hexanoate ((*S*)-4h-[OMe])

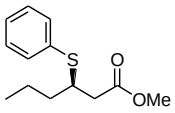


(*S*)-4h-[OMe]

(Figure 3): The reaction with (*E*)-hexe-2-noic acid **3b** (11.4 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), benzenethiol **2a** (10 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) gave the desired product **(*S*)-4h**. The same treatment as described in general procedure afford **(*S*)-4h-[OMe]** (20.8 mg, 87%) after flash chromatography using *n*-hexane/ethyl acetate = 20:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (81% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.42 (m, 2H), 7.33–7.22 (m, 3H), 3.66 (s, 3H), 3.55–3.45 (m, 1H), 2.60 (dd, J_1 = 15.7 Hz, J_2 = 7.0 Hz, 1H), 2.53 (dd, J_1 = 15.7 Hz, J_2 = 7.5 Hz, 1H), 1.63–1.40 (m, 4H), 0.92 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 133.9, 132.9 (2C), 128.9 (2C), 127.3, 51.7, 44.8, 40.4, 36.7, 20.1, 13.8; IR (ATR): 1740 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{19}O_2S$ $[M+H]^+$ 239.1100, found 239.1100; HPLC [Chiralcel IC, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 7.5 min (minor) 6.7 min]; $[\alpha]_D^{19}$ +9.3 (*c* 0.98, $CHCl_3$) for 81% ee.

Methyl (*R*)-3-(phenylthio)hexanoate ((*R*)-4h-[OMe])

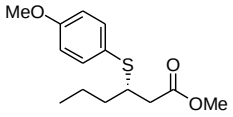


(*R*)-4h-[OMe]

(Figure 3): The reaction with (*E*)-hexe-2-noic acid **3b** (11.5 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), benzenethiol **2a** (10 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) gave the desired product **(*R*)-4h**. The same treatment as described in general procedure afford **(*R*)-4h-[OMe]** (18.3 mg, 77%) after flash chromatography using *n*-hexane/ethyl acetate = 20:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (80% ee).

Colorless oil; HPLC [Chiralcel IC, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 6.8 min (minor) 7.3 min]; $[\alpha]_D^{25}$ –9.6 (*c* 1.01, $CHCl_3$) for 80% ee.

Methyl (*S*)-3-((4-methoxyphenyl)thio)hexanoate ((*S*)-4i-[OMe])

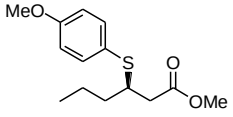


(*S*)-4i-[OMe]

(Figure 3): The reaction with (*E*)-hexe-2-noic acid **3b** (11.4 mg, 0.10 mmol), **1a** (4.1 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4i**. The same treatment as described in general procedure afford **(*S*)-4i-[OMe]** (22.3 mg, 83%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (82% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 3.67 (s, 3H), 3.34–3.25 (m, 1H), 2.54 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 2.47 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 1.62–1.41 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 159.7, 136.4 (2C), 123.5, 114.4 (2C), 55.3, 51.6, 45.7, 40.3, 36.5, 20.1, 13.8; IR (ATR): 1739, 1246 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{21}O_3S$ $[M+H]^+$ 269.1206, found 269.1204; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 16.4 min (minor) 13.0 min]; $[\alpha]_D^{27}$ +8.6 (*c* 1.01, $CHCl_3$) for 82% ee.

Methyl (*R*)-3-((4-methoxyphenyl)thio)hexanoate ((*R*)-4i-[OMe])

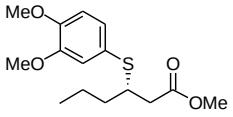


(*R*)-4i-[OMe]

(Figure 3): The reaction with (*E*)-hexe-2-noic acid **3b** (11.4 mg, 0.10 mmol), **1g** (4.2 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4i**. The same treatment as described in general procedure afford **(*R*)-4i-[OMe]** (21.4 mg, 80%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (94% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 13.0 min (minor) 16.5 min]; $[\alpha]_D^{25}$ –9.7 (*c* 1.01, $CHCl_3$) for 94% ee.

Methyl (*S*)-3-((3,4-dimethoxyphenyl)thio)hexanoate ((*S*)-4j-[OMe])



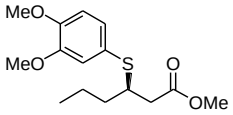
(*S*)-4j-[OMe]

(Figure 3): The reaction with (*E*)-hexe-2-noic acid **3b** (11.5 mg, 0.10 mmol), **1a** (3.9 mg, 0.01 mmol), 3,4-dimethoxybenzenethiol **2c** (14 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4j**. The same treatment as described in general procedure afford **(*S*)-4j-[OMe]** (25.5 mg, 85%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (81% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (dd, J_1 = 8.1 Hz, J_2 = 2.2 Hz, 1H), 7.02 (d, J = 2.2 Hz, 1H), 6.81

(d, J = 8.1 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.68 (s, 3H), 3.38–3.31 (m, 1H), 2.56 (dd, J_1 = 15.6 Hz, J_2 = 7.3 Hz, 1H), 2.50 (dd, J_1 = 15.6 Hz, J_2 = 7.3 Hz, 1H), 1.59–1.43 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 149.2, 148.8, 127.6, 123.7, 117.7, 111.3, 55.92, 55.87, 51.6, 45,7, 40.3, 36.6, 20.1, 13.8; IR (ATR): 1735, 1252 cm^{-1}; HRMS (FAB): calcd for $C_{15}H_{22}NaO_4S$ $[M+Na]^+$ 321.1137, found 321.1134; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 9.7 min (minor) 8.7 min]; $[\alpha]_D^{19}$ +10.5 (*c* 0.93, $CHCl_3$) for 81% ee.

Methyl (*R*)-3-((3,4-dimethoxyphenyl)thio)hexanoate ((*R*)-4j-[OMe])

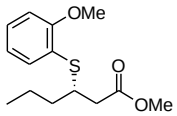


(*R*)-4j-[OMe]

(Figure 3): The reaction with (*E*)-hexe-2-noic acid **3b** (11.5 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), 3,4-dimethoxybenzenethiol **2c** (14 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4j**. The same treatment as described in general procedure afford **(*R*)-4j-[OMe]** (24.2 mg, 81%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (88% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 9.0 min (minor) 10.0 min]; $[\alpha]_D^{25}$ −10.9 (*c* 0.99, $CHCl_3$) for 88% ee.

Methyl (*S*)-3-((2-methoxyphenyl)thio)hexanoate ((*S*)-4k-[OMe])

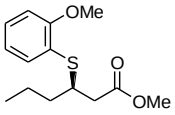


(*S*)-4k-[OMe]

(Figure 3): The reaction with (*E*)-hexe-2-noic acid **3b** (11.4 mg, 0.10 mmol), **1a** (4.1 mg, 0.01 mmol), 2-methoxybenzenethiol **2d** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4k**. The same treatment as described in general procedure afford **(*S*)-4k-[OMe]** (16.6 mg, 62%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (83% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J_1 = 7.5 Hz, J_2 = 1.6 Hz, 1H), 7.25 (ddd, J_1 = 8.2 Hz, J_2 = 7.5 Hz, J_3 = 1.6 Hz, 1H), 6.92 (ddd, J_1 = J_2 = 7.5 Hz, J_3 =1.2 Hz, 1H), 6.87 (dd, J_1 = 8.2 Hz, J_2 = 1.2 Hz, 1H), 3.89 (s, 3H), 3.68–3.59 (m, 1H), 3.62 (s, 3H), 2.63 (dd, J_1 = 15.7 Hz, J_2 = 5.9 Hz, 1H), 2.52 (dd, J_1 = 15.7 Hz, J_2 = 8.1 Hz, 1H), 1.65–1.45 (m, 4H), 0.92 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 158.8, 133.4, 128.6, 122.3, 120.9, 110.8, 55.7, 51.6, 42.5, 40.5, 36.7, 20.0, 13.8; IR (ATR): 1739, 1246 cm^{-1}; HRMS (FAB): calcd for $C_{14}H_{20}NaO_3S$ $[M+Na]^+$ 291.1031, found 291.1024; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 13.5 min (minor) 10.2 min]; $[\alpha]_D^{19}$ −8.5 (*c* 1.06, $CHCl_3$) for 83% ee.

Methyl (*R*)-3-((2-methoxyphenyl)thio)hexanoate ((*R*)-4k-[OMe])

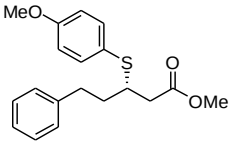


(*R*)-4k-[OMe]

(Figure 3): The reaction with (*E*)-hexe-2-noic acid **3b** (11.5 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), 2-methoxybenzenethiol **2d** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 48 h gave the crude product **(*R*)-4k**. The same treatment as described in general procedure afford **(*R*)-4k-[OMe]** (17.4 mg, 65%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (90% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 9.9 min (minor) 12.7 min]; $[\alpha]_D^{25}$ +9.1 (*c* 0.80, $CHCl_3$) for 90% ee.

Methyl (*S*)-3-((4-methoxyphenyl)thio)-5-phenylpentanoate ((*S*)-4l-[OMe])

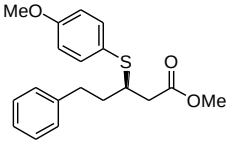


(*S*)-4l-[OMe]

(Figure 3): The reaction with (*E*)-5-Phenylpent-2-enoic acid **3c** (17.6 mg, 0.10 mmol), **1a** (4.1 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4l**. The same treatment as described in general procedure afford **(*S*)-4l-[OMe]** (30.1 mg, 91%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (82% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.7 Hz, 2H), 7.31–7.25 (m, 3H), 7.22–7.16 (m, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 3.66 (s, 3H), 3.34–3.24 (m, 1H), 2.97–2.88 (m, 1H), 2.82–2.73 (m, 1H), 2.59 (dd, J_1 = 15.7 Hz, J_2 = 7.0 Hz, 1H), 2.50 (dd, J_1 = 15.7 Hz, J_2 = 7.0 Hz, 1H), 1.91–1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 159.8, 141.4, 136.6 (2C), 128.40 (2C), 128.37 (2C), 125.9, 122.9, 114.5 (2C), 55.3, 51.7, 45.4, 40.3, 35.8, 33.0; IR (ATR): 1739, 1246 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{23}O_3S$ $[M+H]^+$ 331.1362, found 331.1358; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 19.0 min (minor) 21.3 min]; $[\alpha]_D^{28}$ –6.9 (*c* 0.95, $CHCl_3$) for 82% ee.

Methyl (*R*)-3-((4-methoxyphenyl)thio)-5-phenylpentanoate ((*R*)-4l-[OMe])



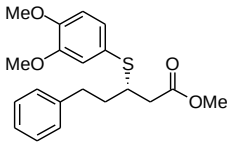
(*R*)-4l-[OMe]

(Figure 3): The reaction with (*E*)-5-Phenylpent-2-enoic acid **3c** (17.7 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4l**. The same treatment as described in general procedure afford **(*R*)-4l-[OMe]** (24.8 mg, 75%)

after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (88% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 21.0 min (minor) 19.5 min]; $[\alpha]_D^{29}$ +7.2 (*c* 0.97, $CHCl_3$) for 88% ee.

Methyl (*S*)-3-((3,4-dimethoxyphenyl)thio)-5-phenylpentanoate ((*S*)-4m-[OMe])

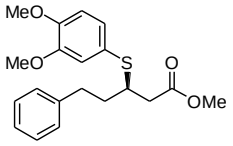


(*S*)-4m-[OMe]

(Figure 3): The reaction with (*E*)-5-Phenylpent-2-enoic acid **3c** (17.7 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 3,4-dimethoxybenzenethiol **2c** (14 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4m**. The same treatment as described in general procedure afford **(*S*)-4m-[OMe]** (31.4 mg, 87%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (84% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 2H), 7.23–7.15 (m, 3H), 7.07 (dd, J_1 = 8.2 Hz, J_2 = 2.0 Hz, 1H), 7.00 (d, J = 2.0 Hz, 1H), 6.81 (d, J = 8.2 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.67 (s, 3H), 3.37–3.28 (m, 1H), 2.97–2.88 (m, 1H), 2.84–2.75 (m, 1H), 2.60 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 2.53 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 1.95–1.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 149.4, 148.9, 141.3, 128.4 (4C), 127.8, 126.0, 123.3, 117.8, 111.3, 55.92, 55.90, 51.7, 45.4, 40.4, 35.8, 33.0; IR (ATR): 1734, 1501, 1251 cm^{-1}; HRMS (FAB): calcd for $C_{20}H_{24}NaO_4S$ $[M+Na]^+$ 383.1293, found 383.1290; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 18.4 min (minor) 23.0 min]; $[\alpha]_D^{19}$ –6.5 (*c* 0.92, $CHCl_3$) for 84% ee.

Methyl (*R*)-3-((3,4-dimethoxyphenyl)thio)-5-phenylpentanoate ((*R*)-4m-[OMe])

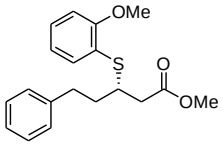


(*R*)-4m-[OMe]

(Figure 3): The reaction with (*E*)-5-Phenylpent-2-enoic acid **3c** (17.6 mg, 0.10 mmol), **1g** (4.4 mg, 0.01 mmol), 3,4-dimethoxybenzenethiol **2c** (14 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4m**. The same treatment as described in general procedure afford **(*R*)-4m-[OMe]** (26.3 mg, 73%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (90% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 22.3 min (minor) 18.1 min]; $[\alpha]_D^{19}$ +6.9 (*c* 1.00, $CHCl_3$) for 90% ee.

Methyl (*S*)-3-((2-methoxyphenyl)thio)-5-phenylpentanoate ((*S*)-4n-[OMe])

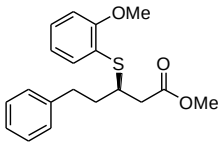


(*S*)-4n-[OMe]

(Figure 3): The reaction with (*E*)-5-Phenylpent-2-enoic acid **3c** (17.6 mg, 0.10 mmol), **1a** (4.1 mg, 0.01 mmol), 2-methoxybenzenethiol **2d** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*R*)-4n**. The same treatment as described in general procedure afford **(*R*)-4n-[OMe]** (19.2 mg, 58%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (80% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J_1 = 7.5 Hz, J_2 = 1.6 Hz, 1H), 7.30–7.23 (m, 3H), 7.21–7.15 (m, 3H), 6.91 (ddd, $J_1 = J_2$ = 7.5 Hz, J_3 =1.1 Hz, 1H), 6.87 (dd, J_1 = 8.4 Hz, J_2 = 1.1 Hz, 1H), 3.86 (s, 3H), 3.68–3.60 (m, 1H), 3.61 (s, 3H), 2.97–2.87 (m, 1H), 2.84–2.74 (m, 1H), 2.67 (dd, J_1 = 15.7 Hz, J_2 = 5.9 Hz, 1H), 2.56 (dd, J_1 = 15.7 Hz, J_2 = 8.1 Hz, 1H), 2.00–1.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 159.0, 141.6, 133.8, 128.9, 128.4 (2C), 128.3 (2C), 125.9, 121.8, 121.0, 110.8, 55.7, 51.6, 42.4, 40.4, 36.2, 32.9; IR (ATR): 1737, 1475, 1245 cm^{-1}; HRMS (FAB): calcd for $C_{19}H_{22}NaO_3S$ $[M+Na]^+$ 353.1187, found 353.1193; HPLC [Chiralcel AD-H, *n*-hexane/2-propanol = 97/3, 1.0 mL/min, λ = 254 nm, retention times: (major) 8.4 min (minor) 9.3 min]; $[\alpha]_D^{20}$ –2.7 (*c* 1.01, $CHCl_3$) for 80% ee.

Methyl (*R*)-3-((2-methoxyphenyl)thio)-5-phenylpentanoate ((*R*)-4n-[OMe])

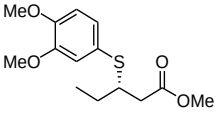


(*R*)-4n-[OMe]

(Figure 3): The reaction with (*E*)-5-Phenylpent-2-enoic acid **3c** (17.6 mg, 0.10 mmol), **1g** (4.4 mg, 0.01 mmol), 2-methoxybenzenethiol **2d** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 48 h gave the crude product **(*R*)-4n**. The same treatment as described in general procedure afford **(*R*)-4n-[OMe]** (22.1 mg, 67%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (87% ee).

Colorless oil; HPLC [Chiralcel AD-H, *n*-hexane/2-propanol = 97/3, 1.0 mL/min, λ = 254 nm, retention times: (major) 9.3 min (minor) 8.6 min]; $[\alpha]_D^{25}$ +2.8 (*c* 0.97, $CHCl_3$) for 87% ee.

Methyl (*S*)-3-((3,4-dimethoxyphenyl)thio)pentanoate ((*S*)-4o-[OMe])



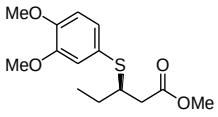
(*S*)-4o-[OMe]

(Figure 3): The reaction with (*E*)-pent-2-enoic acid **3d** (10.1 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 3,4-dimethoxybenzenethiol **2c** (14 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude

product **(*R*)-4o**. The same treatment as described in general procedure afford **(*S*)-4o-[OMe]** (23.6 mg, 83%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (89% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (dd, J_1 = 8.1 Hz, J_2 = 2.2 Hz, 1H), 7.02 (d, J = 2.2 Hz, 1H), 6.81 (d, J = 8.1 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.68 (s, 3H), 3.33–3.25 (m, 1H), 2.56 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 2.51 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 1.68–1.50 (m, 2H), 1.06 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 149.2, 148.8, 127.6, 123.8, 117.7, 111.3, 55.91, 55.85, 51.7, 47,5, 39.8, 27.3, 11.3; IR (ATR): 1738, 1254 cm^{-1}; HRMS (FAB): calcd for $C_{14}H_{20}NaO_4S$ $[M+Na]^+$ 307.0980, found 307.0977; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 11.8 min (minor) 10.6 min]; $[\alpha]_D^{19}$ +9.5 (*c* 1.01, $CHCl_3$) for 83% ee.

Methyl (*R*)-3-((3,4-dimethoxyphenyl)thio)pentanoate ((*R*)-4o-[OMe])

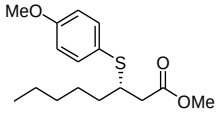


(*R*)-4o-[OMe]

(Figure 3): The reaction with (*E*)-pent-2-enoic acid **3d** (10.0 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), 3,4-dimethoxybenzenethiol **2c** (14 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4o**. The same treatment as described in general procedure afford **(*R*)-4o-[OMe]** (21.9 mg, 77%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (89% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 10.4 min (minor) 11.9 min]; $[\alpha]_D^{25}$ –10.3 (*c* 1.05, $CHCl_3$) for 89% ee.

Methyl (*S*)-3-((4-methoxyphenyl)thio)octanoate ((*S*)-4p-[OMe])

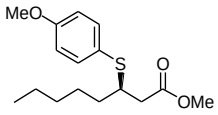


(*S*)-4p-[OMe]

(Figure 3): The reaction with (*E*)-oct-2-enoic acid **3e** (14.2 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4p**. The same treatment as described in general procedure afford **(*S*)-4p-[OMe]** (24.3 mg, 82%) after flash chromatography using *n*-hexane/ethyl acetate = 20:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (84% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 9.5 Hz, 2H), 6.85 (d, J = 9.5 Hz, 2H), 3.80 (s, 3H), 3.66 (s, 3H), 3.33–3.24 (m, 1H), 2.54 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 2.47 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 1.58–1.40 (m, 4H), 1.36–1.22 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 159.7, 136.4 (2C), 123.5, 114.4 (2C), 55.3, 51.6, 46.0, 40.3, 34.3, 31.5, 26.5, 22.5, 14.0; IR (ATR): 1739, 1246 cm^{-1}; HRMS (FAB): calcd for $C_{16}H_{24}NaO_3S$ $[M+Na]^+$ 319.1344, found 319.1339; HPLC [Chiralcel IC, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 13.8 min (minor) 11.1 min]; $[\alpha]_D^{19}$ +4.7 (*c* 0.96, $CHCl_3$) for 84% ee.

Methyl (*R*)-3-((4-methoxyphenyl)thio)octanoate ((*R*)-4p-[OMe])

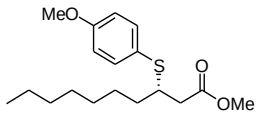


(*R*)-4p-[OMe]

(Figure 3): The reaction with (*E*)-oct-2-enoic acid **3e** (14.3 mg, 0.10 mmol), **1g** (4.4 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4p**. The same treatment as described in general procedure afford **(*R*)-4p-[OMe]** (24.5 mg, 83%) after flash chromatography using *n*-hexane/ethyl acetate = 20:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (91% ee).

Colorless oil; HPLC [Chiralcel IC, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: (major) 11.1 min (minor) 14.0 min]; $[\alpha]_D^{25}$ –5.0 (*c* 0.95, $CHCl_3$) for 91% ee.

Methyl (*S*)-3-((4-methoxyphenyl)thio)decanoate ((*S*)-4q-[OMe])

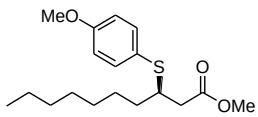


(*S*)-4q-[OMe]

(Figure 3): The reaction with (*E*)-dec-2-enoic acid **3f** (17.0 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4q**. The same treatment as described in general procedure afford **(*S*)-4q-[OMe]** (25.6 mg, 79%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (81% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 3.66 (s, 3H), 3.33–3.23 (m, 1H), 2.54 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 2.48 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 1.57–1.40 (m, 4H), 1.34–1.22 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 159.7, 136.4 (2C), 123.4, 114.4 (2C), 55.3, 51.7, 46.0, 40.3, 34.3, 31.8, 29.2, 29.1, 26.8, 22.6, 14.1; IR (ATR): 1739, 1246 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{29}O_3S$ $[M+H]^+$ 325.1832, found 325.2829; HPLC [Chiralcel AD-H, *n*-hexane/2-propanol = 95/5, 1.0 mL/min, λ = 254 nm, retention times: (major) 10.1 min (minor) 8.5 min]; $[\alpha]_D^{19}$ +5.0 (*c* 0.93, $CHCl_3$) for 81% ee.

Methyl (*R*)-3-((4-methoxyphenyl)thio)decanoate ((*R*)-4q-[OMe])

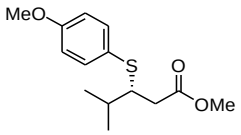


(*R*)-4q-[OMe]

(Figure 3): The reaction with (*E*)-dec-2-enoic acid **3f** (17.1 mg, 0.10 mmol), **1g** (4.2 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4q**. The same treatment as described in general procedure afford **(*R*)-4q-[OMe]** (24.7 mg, 76%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (88% ee).

Colorless oil; HPLC [Chiralcel AD-H, *n*-hexane/2-propanol = 95/5, 1.0 mL/min, λ = 254 nm, retention times: (major) 8.8 min (minor) 10.3 min]; $[\alpha]_D^{26}$ –5.2 (*c* 1.01 $CHCl_3$) for 88% ee.

Methyl (*S*)-3-((4-methoxyphenyl)thio)-4-methylpentanonate ((*R*)-4r-[OMe])



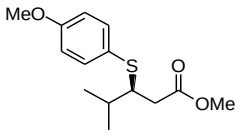
(*R*)-4r-[OMe]

(Figure 3): The reaction with (*E*)-4-methylpent-2-enoic acid **3g** (11.4 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4r**. The same treatment as described in general procedure afford **(*S*)-4r-[OMe]** (19.9 mg, 74%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (72% ee).

(Figure 3, Reaction with benzoic acid): The reaction with (*E*)-4-methylpent-2-enoic acid **3g** (11.5 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), benzoic acid (12.2 mg, 0.1 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4r**. The same treatment as described in general procedure afford **(*S*)-4r-[OMe]** (16.7 mg, 62%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (88% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 3.64 (s, 3H), 3.35–3.27 (m, 1H), 2.61 (dd, J_1 = 15.6 Hz, J_2 = 6.0 Hz, 1H), 2.49 (dd, J_1 = 15.6 Hz, J_2 = 8.6 Hz, 1H), 1.97–1.88 (m, 1H), 1.03 (d, J = 6.8 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 159.4, 135.4 (2C), 125.3, 114.5 (2C), 55.3, 53.8, 51.7, 37.6, 31.7, 19.5, 19.1; IR (ATR): 1739, 1494, 1247 cm^{-1}; HRMS (FAB): calcd for $C_{14}H_{21}O_3S$ $[M+H]^+$ 269.1215, found 269.1211; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 10.0 min (minor) 6.5 min]; $[\alpha]_D^{19}$ +3.3 (*c* 1.03, $CHCl_3$) for 88% ee.

Methyl (*R*)-3-((4-methoxyphenyl)thio)-4-methylpentanonate ((*S*)-4r-[OMe])

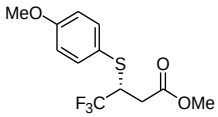


(*S*)-4r-[OMe]

(Figure 3): The reaction with (*E*)-4-methylpent-2-enoic acid **3g** (11.4 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 48 h gave the crude product **(*R*)-4r**. The same treatment as described in general procedure afford **(*R*)-4r-[OMe]** (16.0 mg, 60%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (91% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 6.7 min (minor) 10.9 min]; $[\alpha]_D^{27}$ –3.3 (*c* 1.00, $CHCl_3$) for 91% ee.

Methyl (*R*)-3-((4-methoxyphenyl)thio)-4,4,4-trifluorobutanoate ((*R*)-4s-[OMe])

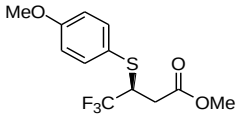


(*R*)-4s-[OMe]

(Figure 3): The reaction with (*E*)-4,4,4-trifluoro-but-2-enoic acid **3h** (14.0 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **4s**. The same treatment as described in general procedure afford **4s-[OMe]** (26.2 mg, 89%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (0% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H), 3.80–3.76 (m, 1H), 3.78 (s, 3H), 2.84 (dd, J_1 = 16.7 Hz, J_2 = 3.8 Hz, 1H), 2.62 (dd, J_1 = 16.7 Hz, J_2 = 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 160.6, 137.0 (2C), 126.3 (q, J = 279 Hz), 122.0, 114,7 (2C), 55.3, 52.3, 50.0 (q, J = 29.3 Hz), 34.1 (q, J = 2.1 Hz); IR (ATR): 1745, 1494, 1248 cm^{-1}; HRMS (FAB): calcd for $C_{12}H_{13}F_3NaO_3S$ $[M+Na]^+$ 317.0435, found 317.0431; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: 8.1 min 10.9 min].

Methyl (*R*)-3-((4-methoxyphenyl)thio)-4,4,4-trifluorobutanoate ((*S*)-4s-[OMe])

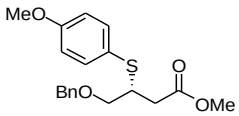


(*S*)-4s-[OMe]

(Figure 3): The reaction with (*E*)-4,4,4-trifluoro-but-2-enoic acid **3h** (14.1 mg, 0.10 mmol), **1g** (4.2 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **4s**. The same treatment as described in general procedure afford **4s-[OMe]** (25.0 mg, 85%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (0% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 99/1, 1.0 mL/min, λ = 254 nm, retention times: 7.3 min 9.8 min].

Methyl (*R*)-4-(benzyloxy)-3-((4-methoxyphenyl)thio)butanoate ((*R*)-4t-[OMe])

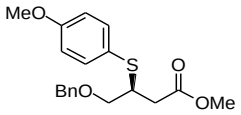


(*R*)-4t-[OMe]

(Figure 3): The reaction with (*E*)-4-(benzyloxy)but-2-enoic acid **3i** (19.3 mg, 0.10 mmol), **1a** (4.1 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*R*)-4t**. The same treatment as described in general procedure afford **(*R*)-4t-[OMe]** (26.7 mg, 77%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (82% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 10.1 Hz, 2H), 7.36–7.27 (m, 5H), 6.83 (d, J = 10.1 Hz, 2H), 4.49 (d, J = 12.0 Hz, 1H), 4.47 (d, J = 12.0 Hz, 1H), 3.80 (s, 3H), 3.65 (s, 3H), 3.65–3.61 (m, 1H), 3.57–3.49 (m, 1H), 3.47–3.43 (m, 1H), 2.77 (dd, J_1 = 15.8 Hz, J_2 = 6.3 Hz, 1H), 2.50 (dd, J_1 = 15.8 Hz, J_2 = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 159.9, 137.9, 136.3 (2C), 128.3 (2C), 127.7 (3C), 123.0, 114.5 (2C), 73.0, 71.8, 55.3, 51.8, 45.0, 37.0; IR (ATR): 1737, 1247 cm^{-1}; HRMS (ESI): calcd for $C_{19}H_{22}NaO_4S$ $[M+Na]^+$ 369.1131, found 369.1130; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 16.0 min (minor) 14.4 min]; $[\alpha]_D^{20}$ +20.0 (*c* 1.04, $CHCl_3$) for 82% ee.

Methyl (*S*)-4-(benzyloxy)-3-((4-methoxyphenyl)thio)butanoate ((*S*)-4t-[OMe])

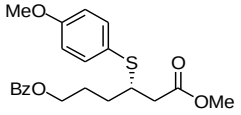


(*S*)-4t-[OMe]

(Figure 3): The reaction with (*E*)-4-(benzyloxy)but-2-enoic acid **3i** (19.3 mg, 0.10 mmol), **1g** (4.4 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*S*)-4t**. The same treatment as described in general procedure afford **(*S*)-4t-[OMe]** (25.0 mg, 72%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (94% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 15.4 min (minor) 17.2 min]; $[\alpha]_D^{28}$ –21.4 (*c* 1.00, $CHCl_3$) for 94% ee.

Methyl (*S*)-4-(benzyloxy)-3-((4-methoxyphenyl)thio)butanoate ((*S*)-4u-[OMe])

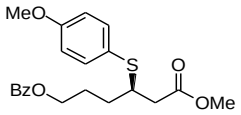


(*S*)-4u-[OMe]

(Figure 3): The reaction with (*E*)-6-(benzoyloxy)hex-2-enoic acid **3j** (23.5 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4u**. The same treatment as described in general procedure afford **(*S*)-4u-[OMe]** (31.9 mg, 82%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (87% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J_1 = 8.4 Hz, J_2 = 1.5 Hz, 2H), 7.57 (dd, J_1 = J_2 = 7.5 Hz, 1H), 7.48–7.38 (m, 4H), 6.81 (d, J = 8.8 Hz, 2H), 4.34 (t, J = 6.4 Hz, 2H), 3.78 (s, 3H), 3.66 (s, 3H), 3.39–3.29 (m, 1H), 2.60 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 2.50 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 2.17–2.07 (m, 1H), 1.99–1.89 (m, 1H), 1.78–1.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 166.5, 159.9, 136.7 (2C), 132.9, 130.3, 129.5 (2C), 128.3 (2C), 122.7, 114.5 (2C), 64.5, 55.3, 51.7, 45.5, 40.3, 30.6, 26.1; IR (ATR): 1722, 1278 cm^{-1}; HRMS (FAB): calcd for $C_{21}H_{24}NaO_5S$ $[M+Na]^+$ 411.1242, found 411.1248; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 26.3 min (minor) 20.8 min]; $[\alpha]_D^{20}$ +1.0 (*c* 1.04, $CHCl_3$) for 87% ee.

Methyl (*R*)-4-(benzyloxy)-3-((4-methoxyphenyl)thio)butanoate ((*R*)-4u-[OMe])

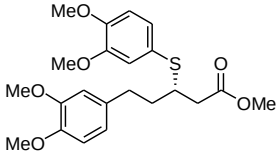


(*R*)-4u-[OMe]

(Figure 3): The reaction with (*E*)-6-(benzoyloxy)hex-2-enoic acid **3j** (23.4 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4u**. The same treatment as described in general procedure afford **(*R*)-4u-[OMe]** (31.5 mg, 81%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (80% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 20.3 min (minor) 25.0 min]; $[\alpha]_D^{26}$ –0.1 (*c* 1.01, $CHCl_3$) for 80% ee.

Methyl (*S*)-3-((3,4-dimethoxyphenyl)thio)-5-(3,4-dimethoxyphenyl)pentanoate ((*S*)-4v-[OMe])

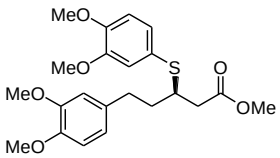


(*S*)-4v-[OMe]

(Figure 3): The reaction with (*E*)-5-(3,4-dimethoxyphenyl)pent-2-enoic acid **3k** (23.5 mg, 0.10 mmol), **1a** (4.1 mg, 0.01 mmol), 3,4-dimethoxybenzenethiol **2c** (14 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4v**. The same treatment as described in general procedure afford **(*S*)-4v-[OMe]** (28.2 mg, 67%) after flash chromatography using *n*-hexane/ethyl acetate = 2:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (84% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (dd, J_1 = 8.2 Hz, J_2 = 2.0 Hz, 1H), 7.00 (d, J = 2.0 Hz, 1H), 7.84–7.76 (m, 2H), 6.74–6.66 (m, 2H), 3.88 (s, 3H), 3.86 (s, 9H), 3.67 (s, 3H), 3.37–3.27 (m, 1H), 2.91–2.82 (m, 1H), 2.80–2.71 (m, 1H), 2.60 (dd, J_1 = 15.6 Hz, J_2 = 7.3 Hz, 1H), 2.56 (dd, J_1 = 15.6 Hz, J_2 = 7.3 Hz, 1H), 1.92–1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 149.4, 148.87, 148.82, 147.3, 133.9, 127.7, 123.4, 120.2, 117.7, 111.7, 111.3, 111.2, 55.91, 55.89, 55.88, 55.79, 51.7, 45.3, 40.3, 35.9, 32.5; IR (ATR): 1733, 1506, 1254 cm^{-1}; HRMS (FAB): calcd for $C_{22}H_{28}NaO_6S$ $[M+Na]^+$ 443.1504, found 443.1501; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm, retention times: (major) 17.3 min (minor) 21.3 min]; $[\alpha]_D^{20}$ –2.0 (*c* 1.05, $CHCl_3$) for 84% ee.

Methyl (*R*)-3-((3,4-dimethoxyphenyl)thio)-5-(3,4-dimethoxyphenyl)pentanoate ((*R*)-4v-[OMe])



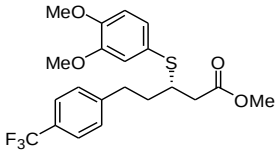
(*R*)-4v-[OMe]

(Figure 3): The reaction with (*E*)-5-(3,4-dimethoxyphenyl)pent-2-enoic acid **3k** (23.5 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), 3,4-dimethoxybenzenethiol **2c** (14 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL)

for 24 h gave the crude product **(*R*)-4v**. The same treatment as described in general procedure afford **(*R*)-4v-[OMe]** (35.3 mg, 84%) after flash chromatography using *n*-hexane/ethyl acetate = 2:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (94% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm, retention times: (major) 21.2 min (minor) 17.2 min]; $[\alpha]_D^{25}$ +2.4 (*c* 1.04, $CHCl_3$) for 94% ee.

Methyl (*S*)-3-((3,4-dimethoxyphenyl)thio)-5-(4-(trifluoromethyl)phenyl)pentanoate ((*S*)-4w-[OMe])

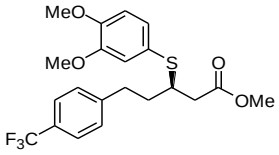


(*S*)-4w-[OMe]

(Figure 3): The reaction with (*E*)-5-(4-(trifluoromethyl)phenyl)pent-2-enoic acid **3l** (24.4 mg, 0.10 mmol), **1a** (4.0 mg, 0.01 mmol), 3,4-dimethoxybenzenethiol **3c** (14 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4w**. The same treatment as described in general procedure afford **(*S*)-4w-[OMe]** (36.0 mg, 84%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (82% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.06 (dd, J_1 = 8.2 Hz, J_2 = 2.0 Hz, 1H), 6.98 (d, *J* = 2.2 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.67 (s, 3H), 3.34–3.25 (m, 1H), 3.03–2.94 (m, 1H), 2.92–2.83 (m, 1H), 2.62 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 2.52 (dd, J_1 = 15.7 Hz, J_2 = 7.3 Hz, 1H), 1.97–1.88 (m, 1H), 1.86–1.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 149.5, 148.9, 145.4, 128.7 (2C), 128.4 (q, *J* = 32.5 Hz), 127.8, 125.3 (q, *J* = 3.7 Hz, 2C), 124.3 (q, *J* = 272 Hz), 123.1, 117.7, 111.4, 55.92, 55.90, 51.8, 45.3, 40.3, 35.3, 32.8; IR (ATR): 1737, 1504, 1326, 1253 cm^{-1}; HRMS (FAB): calcd for $C_{21}H_{23}F_3NaO_4S$ $[M+Na]^+$ 451.1167, found 451.1174; HPLC [Chiralcel IC, *n*-hexane/2-propanol = 95/5, 1.0 mL/min, λ = 254 nm, retention times: (major) 13.8 min (minor) 11.8 min]; $[\alpha]_D^{20}$ –8.5 (*c* 0.96, $CHCl_3$) for 82% ee.

Methyl (*R*)-3-((3,4-dimethoxyphenyl)thio)-5-(4-(trifluoromethyl)phenyl)pentanoate ((*R*)-4w-[OMe])

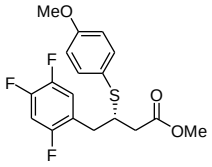


(*R*)-4w-[OMe]

(Figure 3): The reaction with (*E*)-5-(4-(trifluoromethyl)phenyl)pent-2-enoic acid **3l** (24.5 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), 3,4-dimethoxybenzenethiol **3c** (14 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4w**. The same treatment as described in general procedure afford **(*R*)-4w-[OMe]** (31.4 mg, 73%) after flash chromatography using *n*-hexane/ethyl acetate = 4:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (90% ee).

Colorless oil; HPLC [Chiralcel IC, *n*-hexane/2-propanol = 95/5, 1.0 mL/min, λ = 254 nm, retention times: (major) 12.1 min (minor) 14.0 min]; $[\alpha]_D^{25}$ +8.9 (*c* 1.02, $CHCl_3$) for 90% ee.

Methyl (*S*)-3-((4-methoxyphenyl)thio)-4-(2,4,5-trifluorophenyl)butanoate ((*S*)-4x-[OMe])



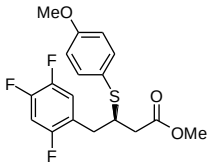
(*S*)-4x-[OMe]

(Figure 3): The reaction with (*E*)-4-(2,4,5-trifluorophenyl)but-2-enoic acid **3m** (21.6 mg, 0.10 mmol), **1g** (4.0 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4x**. The same treatment as described in general procedure afford **(*S*)-4x-[OMe]** (30.7 mg, 83%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (69% ee).

(Figure 3, Reaction with benzoic acid): The reaction with (*E*)-4-(2,4,5-trifluorophenyl)but-2-enoic acid **3m** (21.6 mg, 0.10 mmol), **1g** (4.0 mg, 0.01 mmol), benzoic acid (12.3 mg, 0.1 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (20 mg) in CCl_4 (50 μL) for 24 h gave the crude product **(*S*)-4x**. The same treatment as described in general procedure afford **(*S*)-4x-[OMe]** (24.0 mg, 65%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (77% ee).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 9.6 Hz, 2H), 7.04 (ddd, J_1 = 13.0 Hz, J_2 = 6.2 Hz, J_3 = 4.2 Hz, 1H), 6.91–6.80 (m, 3H), 3.81 (s, 3H), 3.66 (s, 3H), 3.60–3.51 (m, 1H), 2.91 (dd, J_1 = 14.3 Hz, J_2 = 7.3 Hz, 1H), 2.81 (dd, J_1 = 14.3 Hz, J_2 = 7.3 Hz, 1H), 2.60–2.44 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 159.3, 156.1 (ddd, J = 245, 9.6, 2.4 Hz), 148.9 (ddd, J = 250, 14.4, 12.8 Hz), 146.5 (ddd, J = 245, 12.0, 4.0 Hz), 136.2 (2C), 123.1, 121.9 (ddd, J = 18.1, 4.8, 4.8 Hz), 119.0 (ddd, J = 19.2, 4.8, 1.6 Hz), 114.6 (2C), 105.3 (dd, J = 28.0, 20.8 Hz), 55.3, 51.8, 45.9, 39.1, 33.7; IR (ATR): 1738, 1518, 1247 cm^{-1}; HRMS (FAB): calcd for $C_{18}H_{17}F_3NaO_3S$ $[M+Na]^+$ 393.0748, found 393.0752; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 11.1 min (minor) 7.8 min]; $[\alpha]_D^{19}$ +1.7 (*c* 0.94, $CHCl_3$) for 77% ee.

Methyl (*R*)-3-((4-methoxyphenyl)thio)-4-(2,4,5-trifluorophenyl)butanoate ((*R*)-4x-[OMe])



(*R*)-4x-[OMe]

The reaction with (*E*)-4-(2,4,5-trifluorophenyl)but-2-enoic acid **3m** (21.7 mg, 0.10 mmol), **1g** (4.3 mg, 0.01 mmol), 4-methoxybenzenethiol **2b** (12 μL, 0.10 mmol), and activated MS 4Å (100 mg) in acetone (1.0 mL) for 24 h gave the crude product **(*R*)-4x**. The same treatment as described in general procedure afford **(*R*)-4x-[OMe]** (29.6 mg, 80%) after flash chromatography using *n*-hexane/ethyl acetate = 10:1 as eluent. The enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis (90% ee).

Colorless oil; HPLC [Chiralcel OD-H, *n*-hexane/2-propanol = 98/2, 1.0 mL/min, λ = 254 nm, retention times: (major) 8.0 min (minor) 11.1 min]; $[\alpha]_D^{27}$ –2.2 (*c* 1.00, $CHCl_3$) for 90% ee.

8. ^{11}B NMR experiments of the catalyst-substrate complex

8-1. ^{11}B NMR titration experiment of **1a** with crotonic acid **3a** (10 equiv) and MS 4Å in $CDCl_3$ (0.033 M)

(a) A sample for ^{11}B NMR was prepared by decantation of a stirred suspension of **1a** (10.1 mg, 0.025 mmol) and activated MS 4Å (75 mg) in $CDCl_3$ (0.75 mL) at room temperature for 1 h.

(b) A sample for ^{11}B NMR was prepared by decantation of a stirred suspension of **1a** (10.1 mg, 0.025 mmol), crotonic acid **3a** (22.1 mg, 0.25 mmol, 10 equiv), and activated MS 4Å (75 mg) in $CDCl_3$ (0.75 mL) at room temperature for 1 h.

(c) A sample for ^{11}B NMR was prepared by decantation of a stirred suspension of **1a** (10.1 mg, 0.025 mmol), crotonic acid **3a** (22.1 mg, 0.25 mmol, 10 equiv), and activated MS 4Å (75 mg) in $CDCl_3$ (0.75 mL) at room temperature for 4 h.

(d) A sample for ^{11}B NMR was prepared by decantation of a stirred suspension of **1a** (10.1 mg, 0.025 mmol), crotonic acid **3a** (22.1 mg, 0.25 mmol, 10 equiv), and activated MS 4Å (75 mg) in $CDCl_3$ (0.75 mL) at room temperature for 24 h.

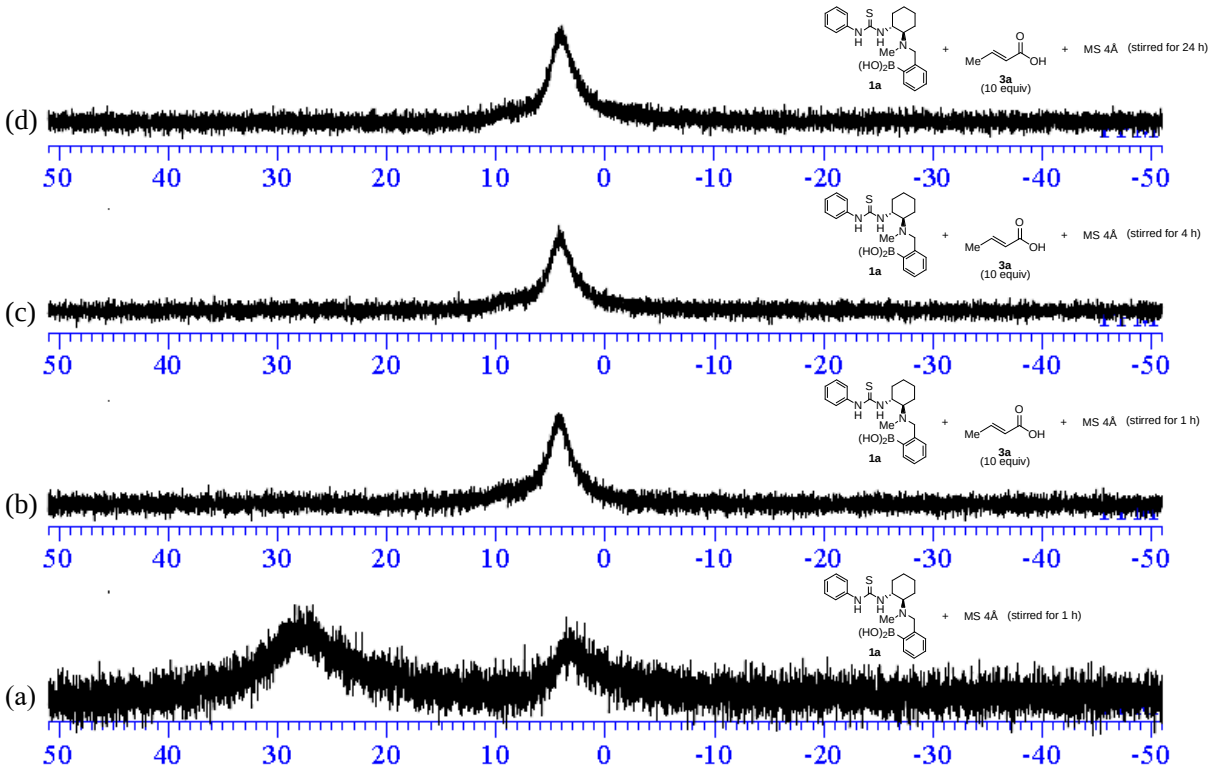


Figure S1. The time-course study of ^{11}B NMR spectra of **1a** and crotonic acid **3a** (10 equiv) in $CDCl_3$ (0.033 M). (a) *cat* **1a** with MS 4Å; (b) 1 h; (c) 4 h; (d) 24 h.

8-2. ^{11}B NMR titration experiment of **1a** (0.033 M) with benzenethiol **2a**, crotonic acid **3a** and MS 4Å in $CDCl_3$ (0.033 M)

(a) A sample for ^{11}B NMR was prepared by decantation of a stirred suspension of **1a** (10.1 mg, 0.025 mmol) and activated MS 4Å (75 mg) in $CDCl_3$ (0.75 mL) at room temperature for 4 h.

(b) A sample for ^{11}B NMR was prepared by decantation of a stirred suspension of **1a** (10.1 mg, 0.025 mmol), benzenethiol **2a** (26 μL, 0.25 mmol, 10 equiv), and activated MS 4Å (75 mg) in $CDCl_3$ (0.75 mL) at room temperature for 4 h.

(c) A sample for ^{11}B NMR was prepared by decantation of a stirred suspension of **1a** (10.1 mg, 0.025 mmol), crotonic acid **3a** (22.1 mg 0.25 mmol, 10 equiv), and activated MS 4Å (75 mg) in $CDCl_3$ (0.75 mL) at room temperature for 4 h.

(d) A sample for ^{11}B NMR was prepared by decantation of a stirred suspension of **1a** (10.1 mg, 0.025 mmol), benzenethiol **2a** (26 μL, 0.25 mmol, 10 equiv), crotonic acid **3a** (21.7 mg 0.25 mmol, 10 equiv), and activated MS 4Å (75 mg) in $CDCl_3$ (0.75 mL) at room temperature for 4 h.

(e) A sample for ^{11}B NMR was prepared by decantation of a stirred suspension of **1a** (10.0 mg, 0.025 mmol), benzenethiol **2a** (26 μL, 0.25 mmol, 10 equiv), crotonic acid **3a** (22.0 mg 0.25 mmol, 10 equiv), and activated MS 4Å (75 mg) in **CD_2Cl_2** (0.75 mL) at room temperature for 4 h.

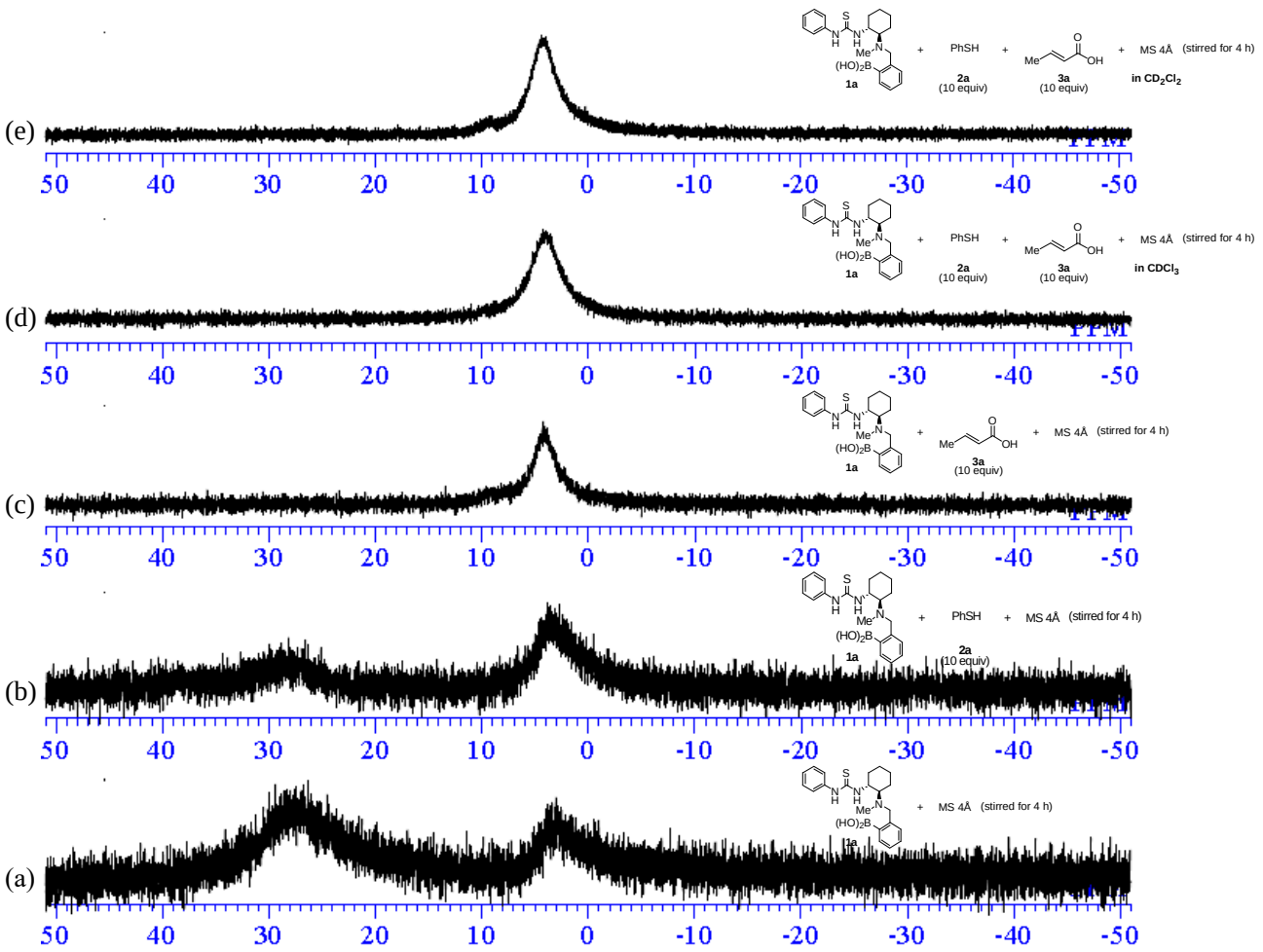


Figure S2. ^{11}B NMR titration experiments of **1a** with benzenethiol **2a** and crotonic acid **3a** in $CDCl_3$ (0.033 M). (a) *cat* **1a** with MS 4Å (b) *cat* **1a** with **2a** (10 equiv) and MS 4Å; (c) *cat* **1a** with **3a** (10 equiv) and MS 4Å; (d) *cat* **1a** with **2a** (10 equiv), **3a** (10 equiv) and MS 4Å; (e) *cat* **1a** with **2a** (10 equiv), **3a** (10 equiv) and MS 4Å in **CD_2Cl_2**.

8-3. ^{11}B NMR titration experiment of **1a** with crotonic acid **3a** (10 equiv) and MS 4Å in acetone-d_6 (0.033 M)

(a) A sample for ^{11}B NMR was prepared by decantation of a stirred suspension of **1a** (10.1 mg, 0.025 mmol) and activated MS 4Å (75 mg) in acetone-d_6 (0.75 mL) at room temperature for 1 h.

(b) A sample for ^{11}B NMR was prepared by decantation of a stirred suspension of **1a** (10.1 mg, 0.025 mmol), crotonic acid **3a** (21.7 mg, 0.25 mmol, 10 equiv), and activated MS 4Å (75 mg) in acetone-d_6 (0.75 mL) at room temperature for 1 h.

(c) A sample for ^{11}B NMR was prepared by decantation of a stirred suspension of **1a** (10.1 mg, 0.025 mmol), crotonic acid **3a** (21.7 mg, 0.25 mmol, 10 equiv), and activated MS 4Å (75 mg) in acetone-d_6 (0.75 mL) at room temperature for 4 h.

(d) A sample for ^{11}B NMR was prepared by decantation of a stirred suspension of **1a** (10.1 mg, 0.025 mmol), crotonic acid **3a** (21.7 mg, 0.25 mmol, 10 equiv), and activated MS 4Å (75 mg) in acetone-d_6 (0.75 mL) at room temperature for 24 h.

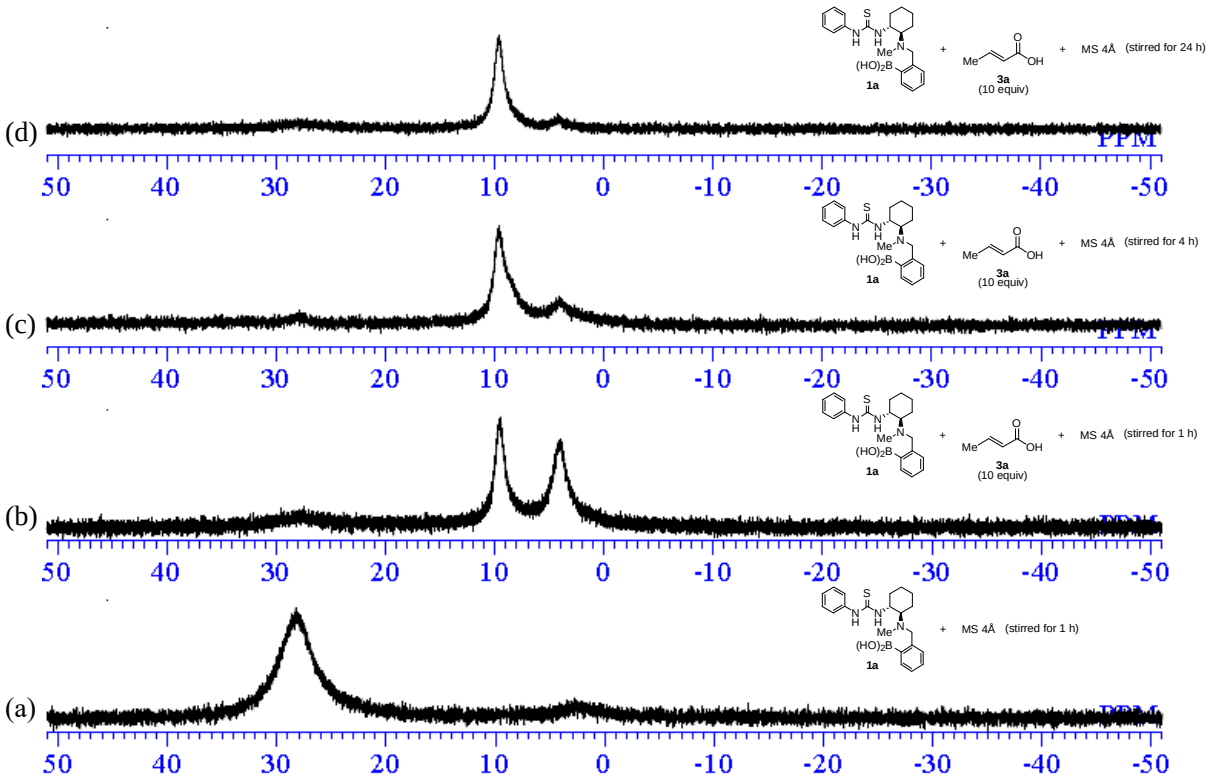


Figure S3. The time-course study of 11B NMR spectra of **1a** and crotonic acid **3a** (10 equiv) in acetone-*d6* (0.033 M). (a) *cat* **1a** with MS 4Å; (b) 1 h; (c) 4 h; (d) 24 h.

9. MS analysis

9-1. ESI-MS spectrum of the sample prepared in $CDCl_3$

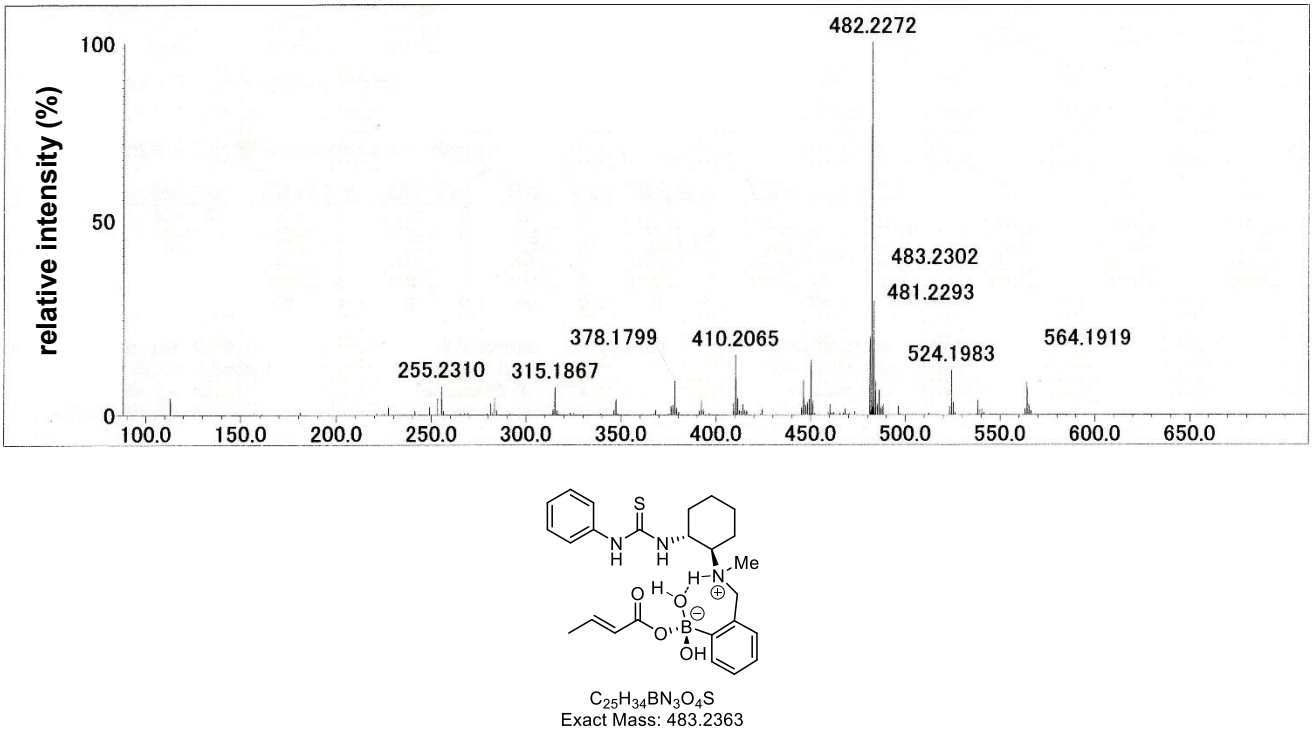


Figure S4. ESI-MS (negative) spectrum of the sample prepared in $CDCl_3$

9-2. ESI-MS spectrum of the sample prepared in acetone

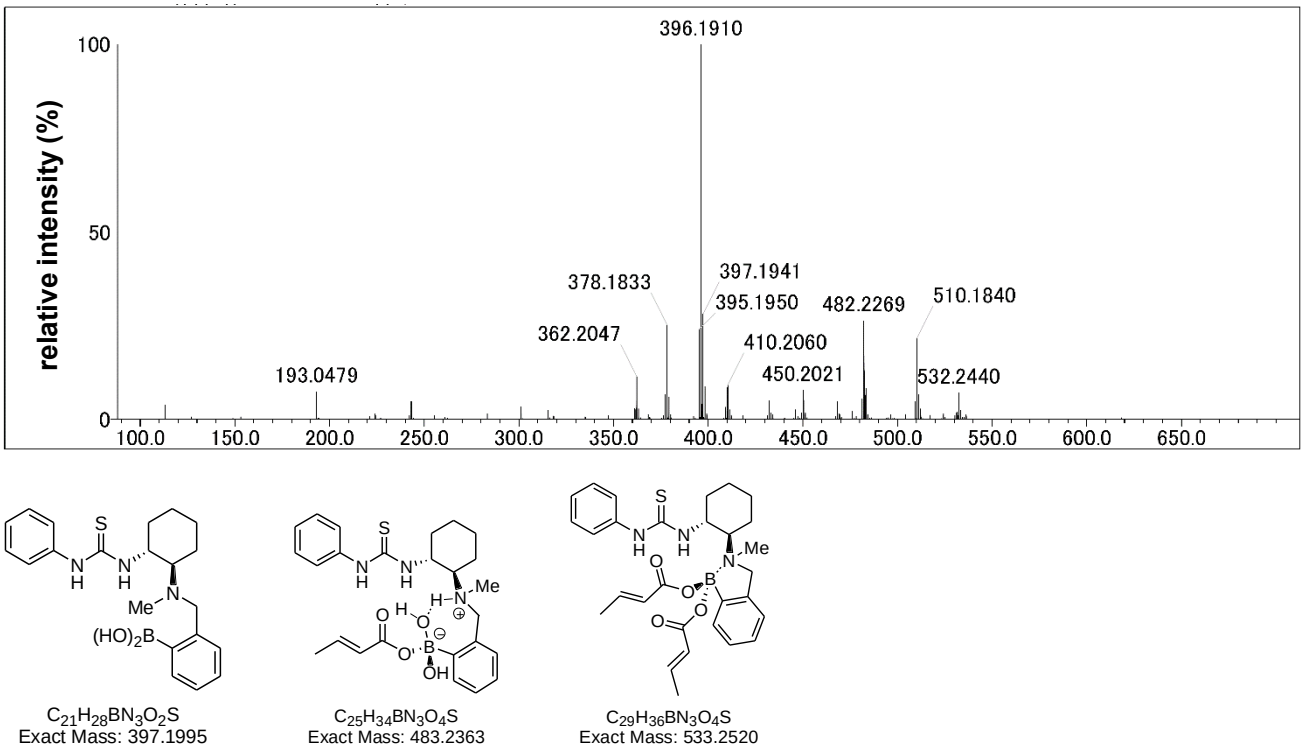


Figure S5. ESI-MS (negative) spectrum of the sample prepared in acetone-d_6 (Figure 4c)

10. Computational studies

The molecular geometries for the transition states were first estimated by Reaction plus software package, based on the nudged elastic band (NEB) method,[S5] and were subsequently re-optimized at B3LYP/6-31G(d,p) level using Gaussian09 software package.[S6] A single point energy calculation was further performed at wB97Xd/6-311+G(d,p) in acetone.

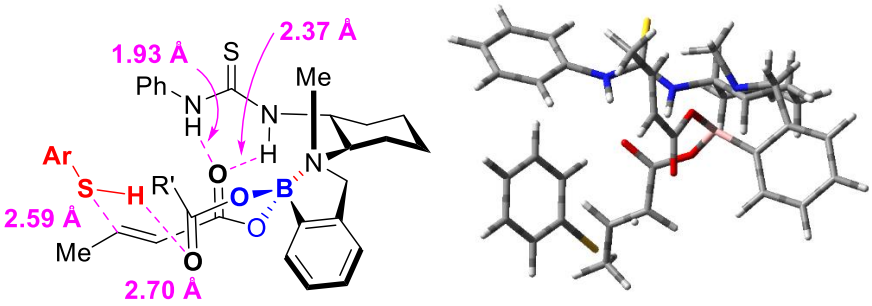


Figure S6. TS via s-*cis* configuration

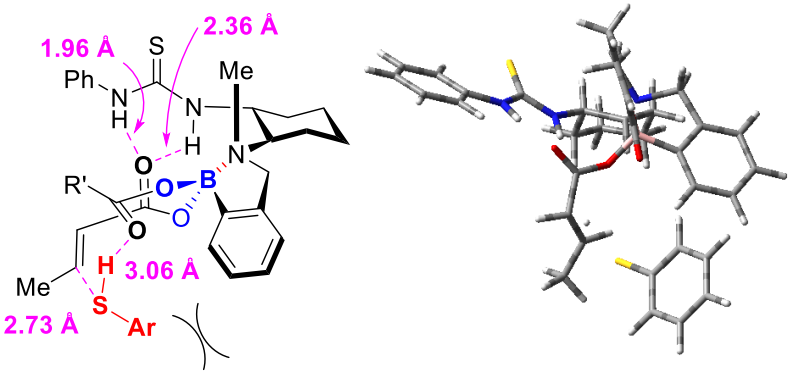


Figure S7. TS via s-*trans* configuration (+2.0 kcal/mol)

The coordinates of each structures

s-*cis*

Zero-point correction= 0.714040 (Hartree/Particle)

Thermal correction to Energy= 0.758435

Thermal correction to Enthalpy= 0.759379

Thermal correction to Gibbs Free Energy= 0.629623

Sum of electronic and zero-point Energies= -2644.802528

Sum of electronic and thermal Energies= -2644.758133

Sum of electronic and thermal Enthalpies= -2644.757189

Sum of electronic and thermal Free Energies= -2644.886945

E(RB3LYP)=-2645.51656802

E(RwB97XD)=-2645.39333936

Imaginary frequency = 1747i

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S	-3.47513600	-2.30504000	-2.28368600
H	-3.03427600	-0.34991700	-4.96682400

s-*trans*

Zero-point correction= 0.714675 (Hartree/Particle)
Thermal correction to Energy= 0.758979
Thermal correction to Enthalpy= 0.759923
Thermal correction to Gibbs Free Energy= 0.630985
Sum of electronic and zero-point Energies= -2644.802354
Sum of electronic and thermal Energies= -2644.758050
Sum of electronic and thermal Enthalpies= -2644.757106
Sum of electronic and thermal Free Energies= -2644.886044
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E(RwB97XD)=-2645.39149350
Imaginary frequency = 543i

0 1

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C	2.18054900	4.36176800	1.40646200
C	3.82218300	3.01858200	0.23076400
H	1.88784300	5.29604200	1.88015800
H	4.81183100	2.92195200	-0.20701400
H	4.15082200	5.05121600	0.87409000
C	-0.08065800	3.20173800	1.91925000
N	-0.84082400	2.16989600	1.09393100

B	0.45059100	1.02069600	0.81345200
H	-0.62649600	4.14376200	1.97309600
O	0.31921500	0.31518900	-0.49134200
O	0.34593400	0.16876200	1.98681200
C	0.10468800	-0.98109200	-0.71757000
O	-0.69649900	-1.66587800	-0.09670700
C	0.87229800	-1.55030000	-1.88330900
H	0.43066700	-2.48788900	-2.22454600
C	6.30862800	-2.45024800	-1.90528900
H	1.52318500	0.36148000	-2.62603900
H	-0.04033500	2.79149600	2.93268000
C	-1.33263800	2.74107600	-0.27544200
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C	-1.42068500	4.28201000	-0.31127700
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H	-2.22012200	2.31110500	-2.87706500
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H	-3.90363300	4.56588200	-1.65198700
H	-2.18563200	4.62938600	0.39660300
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N	-3.62949100	-1.34879700	-0.39525300
H	-2.64099900	-1.57185700	-0.29094300
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C	-6.52407700	-3.72792000	-0.44366900
C	-4.49372900	-4.88341100	0.12664400

H	-2.71834800	-3.66935100	0.21329900
H	-6.35386800	-1.60608700	-0.79310000
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H	-3.96161700	-5.79455800	0.38442300
H	-7.59359600	-3.73435700	-0.63417400
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C	1.29349300	-0.75124000	2.25981700
O	2.25087800	-0.95760200	1.53285700
C	1.07652800	-1.50697700	3.51222600
H	1.88875800	-2.18626200	3.75565900
C	-0.01763200	-1.42723500	4.27914300
H	-0.81211500	-0.74850200	3.97633100
C	-0.24935300	-2.22065300	5.52659300
H	-1.15173500	-2.83737500	5.43134600
H	0.59445600	-2.87683300	5.75562200
H	-0.41628600	-1.55813100	6.38524200
C	1.34423500	-0.67328500	-2.89926000
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C	5.56105400	-1.39393600	0.14818200
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H	7.04449800	-1.19511800	1.69036300
H	8.85984600	-2.21804300	0.33446100
H	8.38093000	-3.02209700	-1.96836700
S	3.64846200	-1.67753000	-1.82274500
H	2.22593700	-0.52292200	-4.85178500

11. Reference

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S5. G. Henkelman, H. Jónsson, *J. Chem*. *Phys*. **2000**, *113*, 9978–9985.

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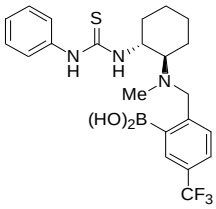
12. Copies of ^{1}H and ^{13}C NMR charts



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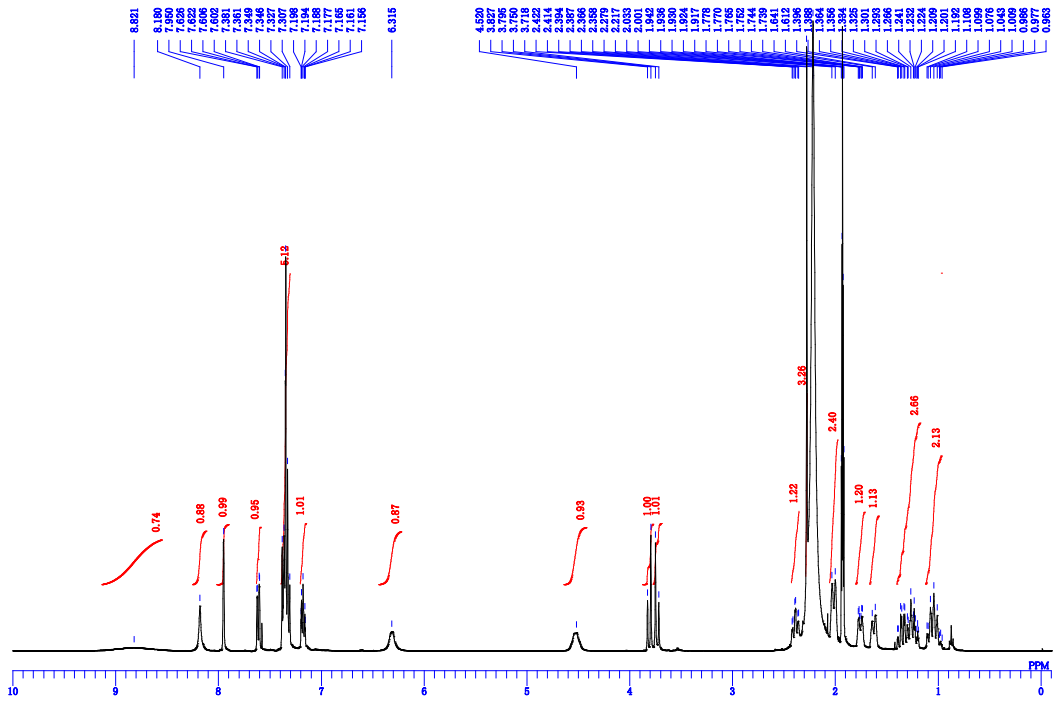

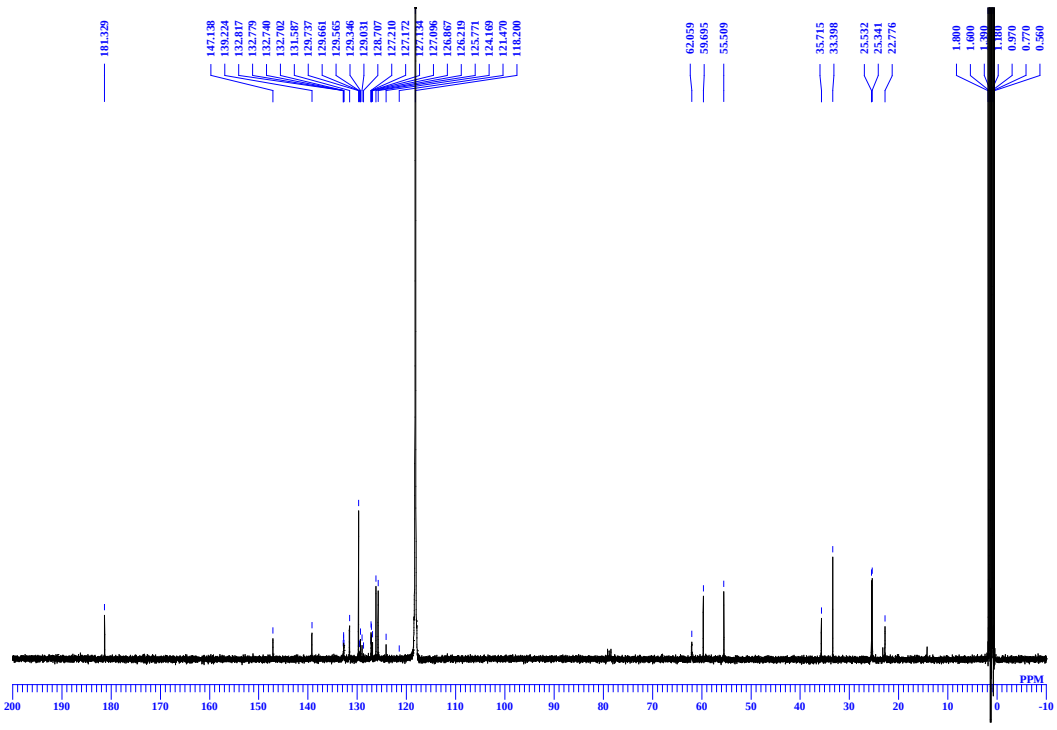

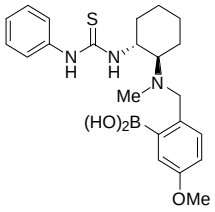

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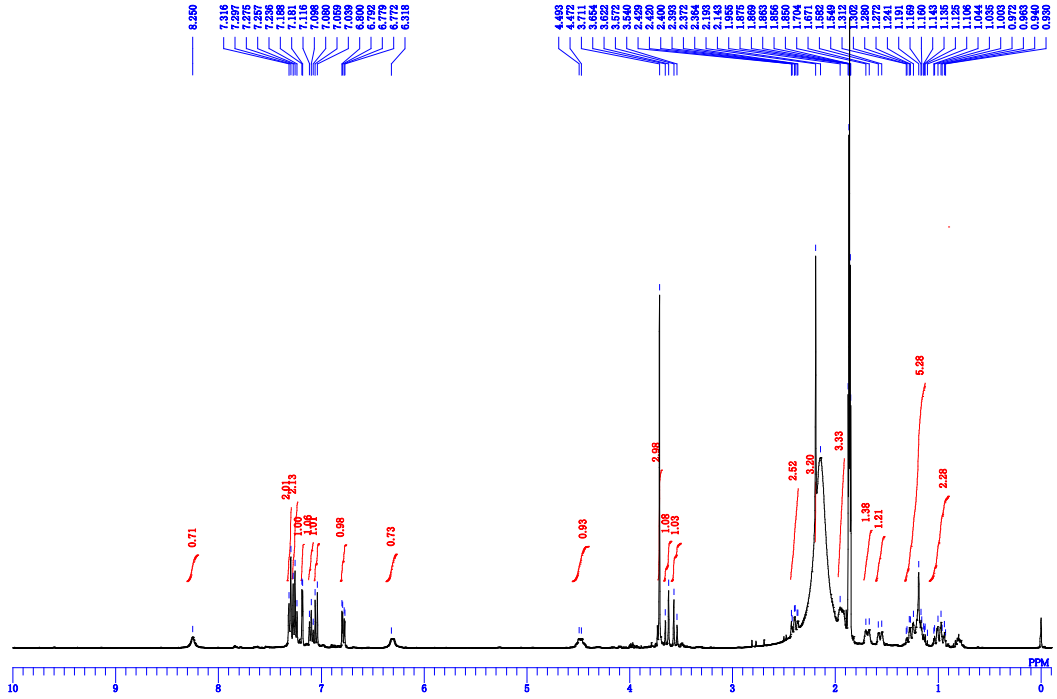

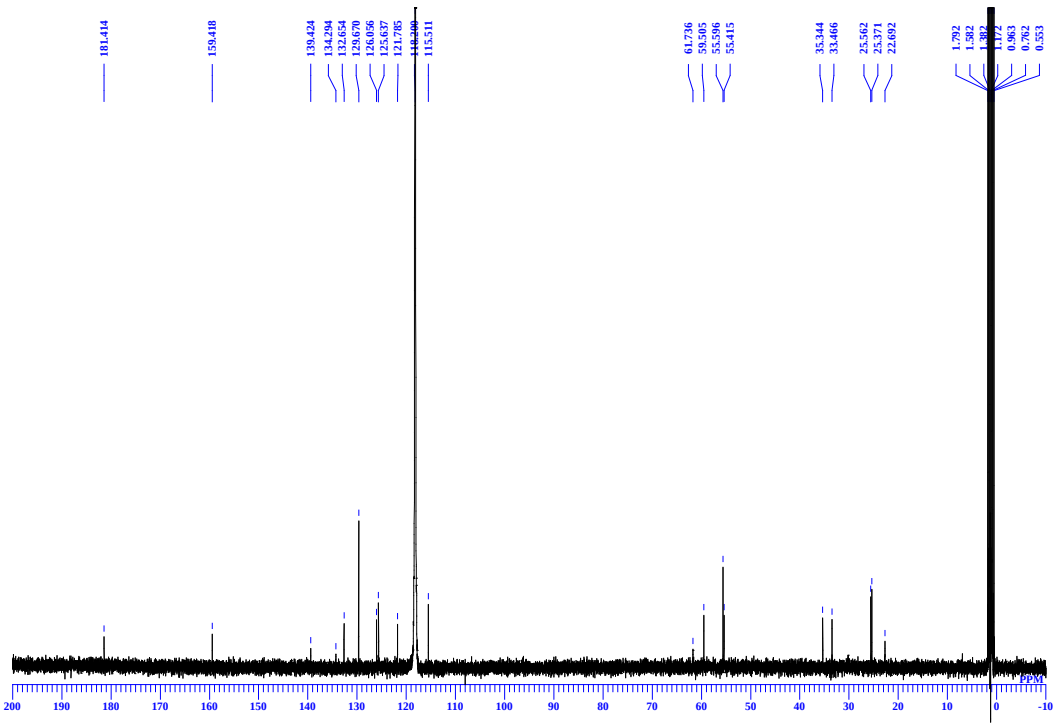

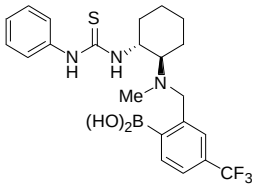

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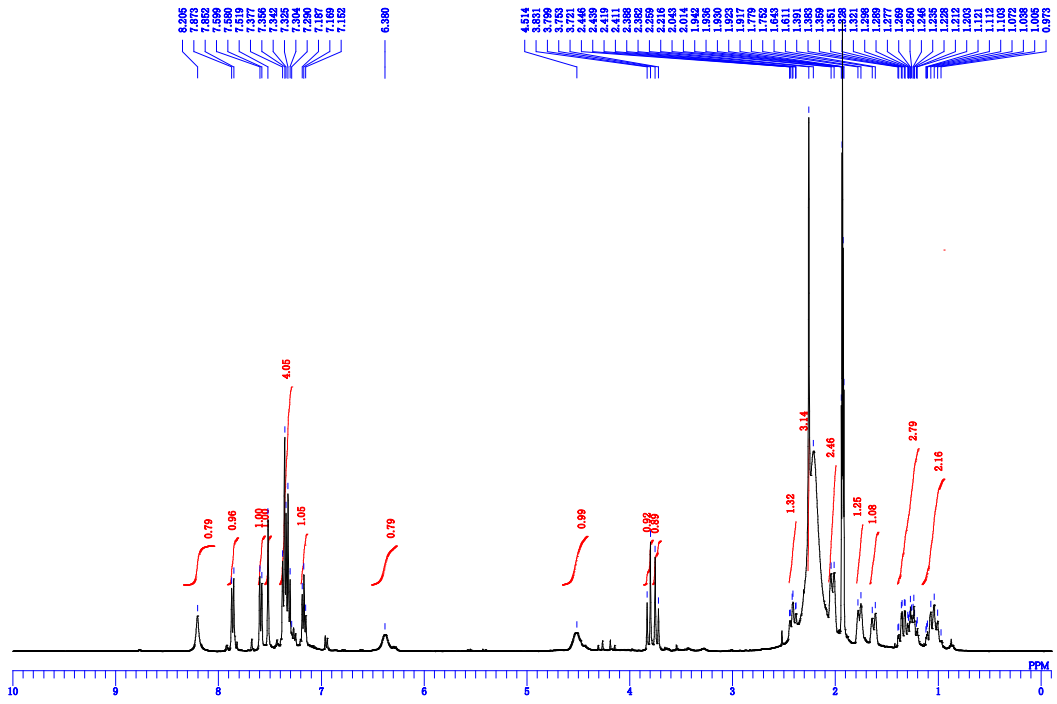

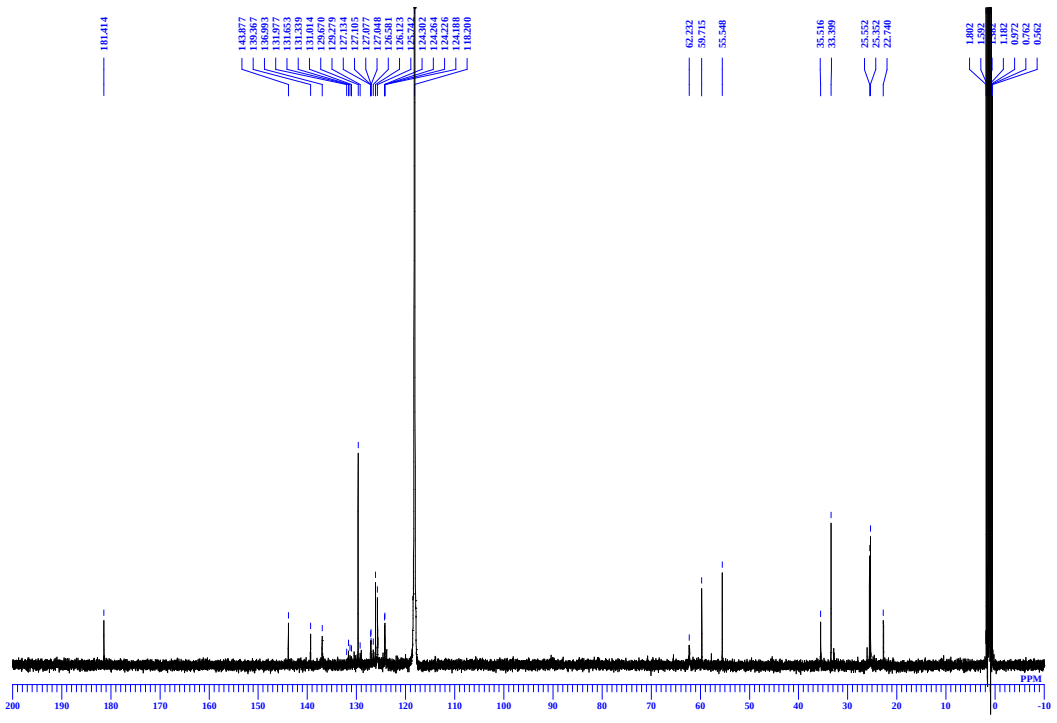

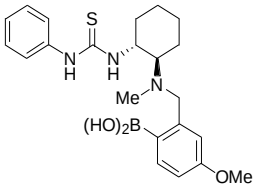
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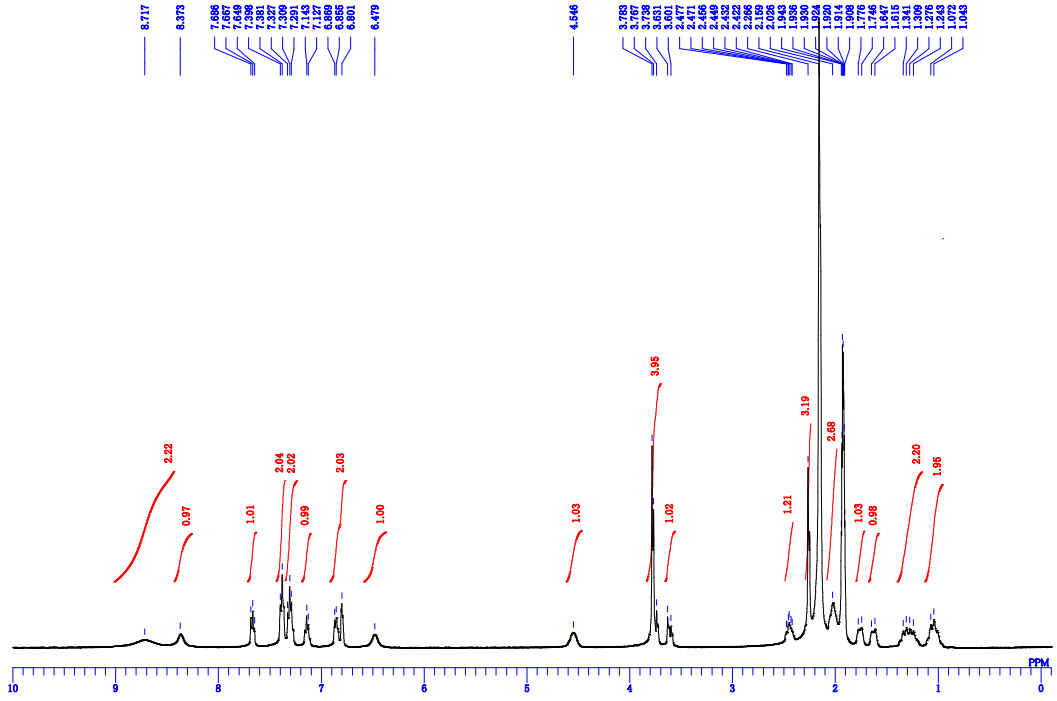
N
H
N
H
Me
N
(HO)2B
OMe

1g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6.869
6.855
6.801
6.479
4.546
3.783
3.767
3.738
3.651
3.601
2.477
2.471
2.456
2.449
2.432
2.422
2.266
2.159
2.026
1.945
1.936
1.930
1.924
1.920
1.914
1.908
1.776
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1.647
1.615
1.341
1.309
1.276
1.243
1.072
1.045
2.22
0.97
1.01
2.04
2.02
0.99
2.03
1.00
1.03
3.05
1.02
1.21
3.19
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2.20
1.96
PPM
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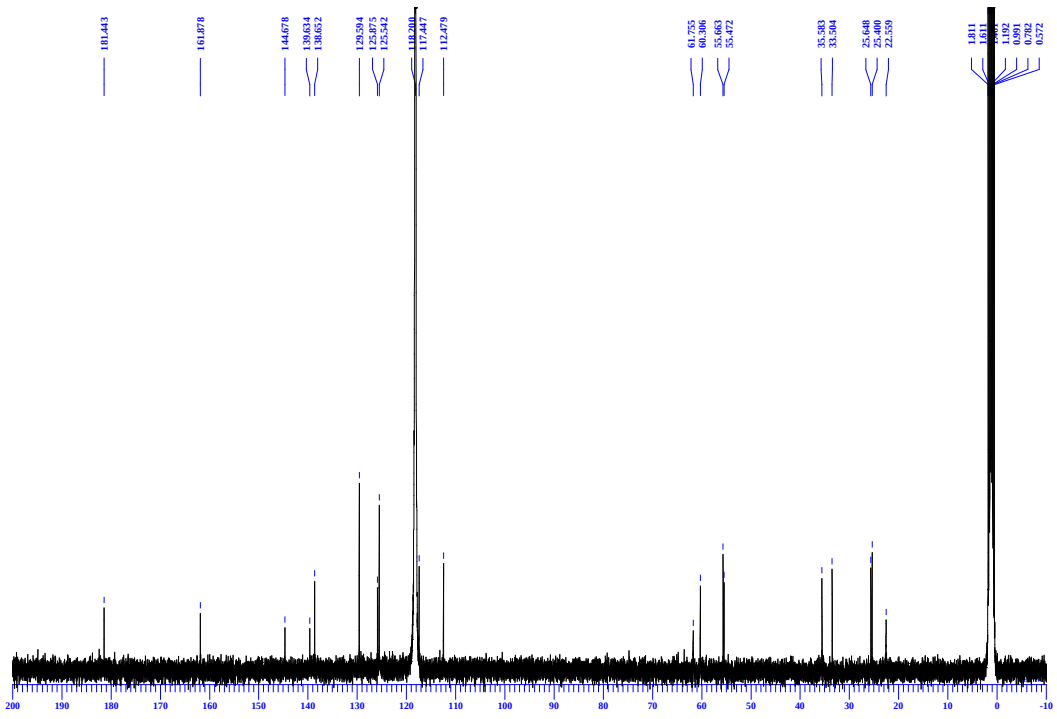
8
7
6
5
4
3
2
1
0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55.663
55.472
35.583
33.504
25.648
25.400
22.559
1.811
1.611
1.492
1.392
0.991
0.782
0.572
200
190
180
170
160
150
140
130
120
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100
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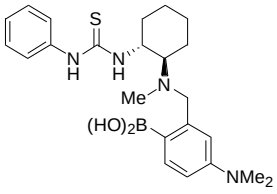
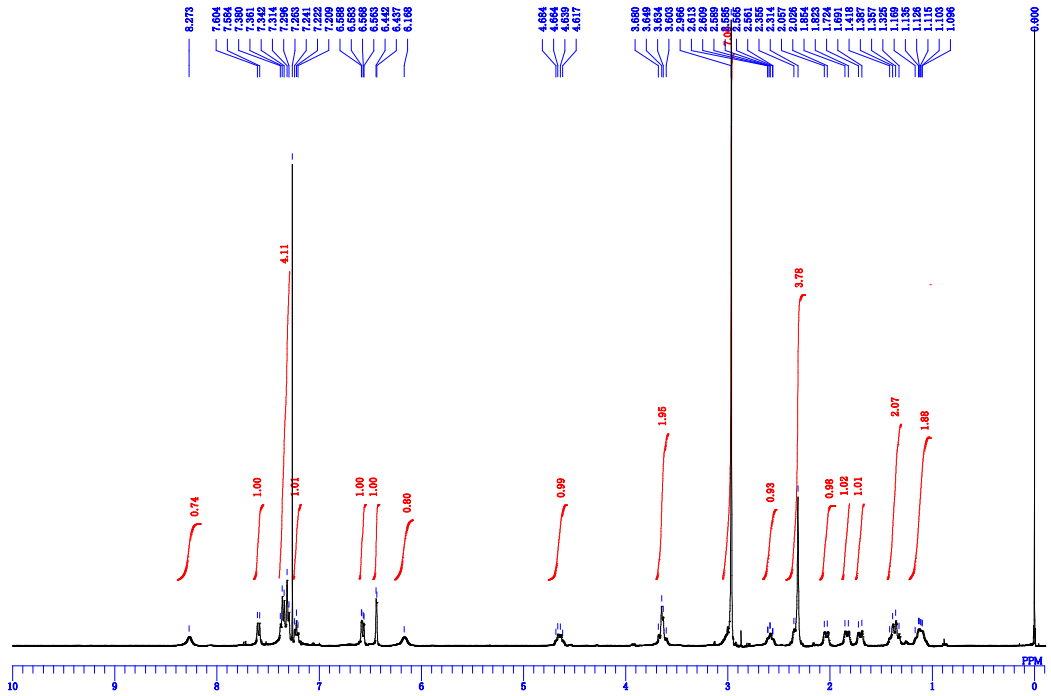
60
50
40
30
20
10
0
-10


S
N
H
N
H
Me
N
(HO)2B
NMe2

1h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6.442
6.437
6.188
4.684
4.664
4.639
4.617
3.680
3.649
3.634
3.605
2.966
2.613
2.609
2.589
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2.561
2.335
2.314
2.057
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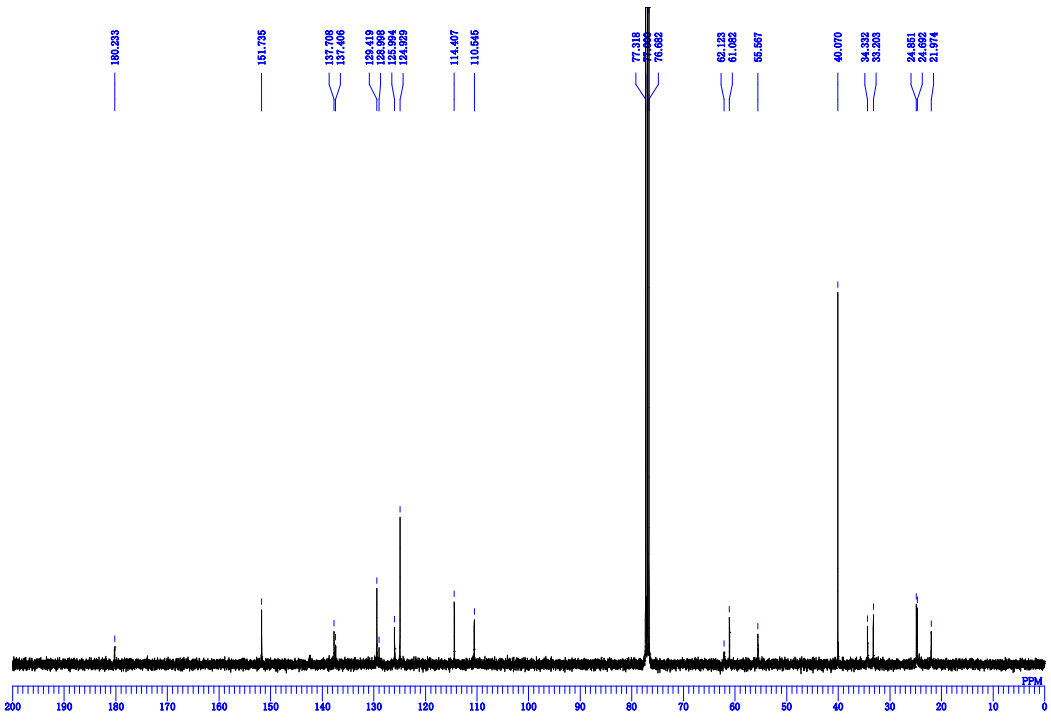
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40.070
34.332
33.203
24.851
24.692
21.974
PPM
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190
180
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150
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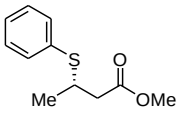
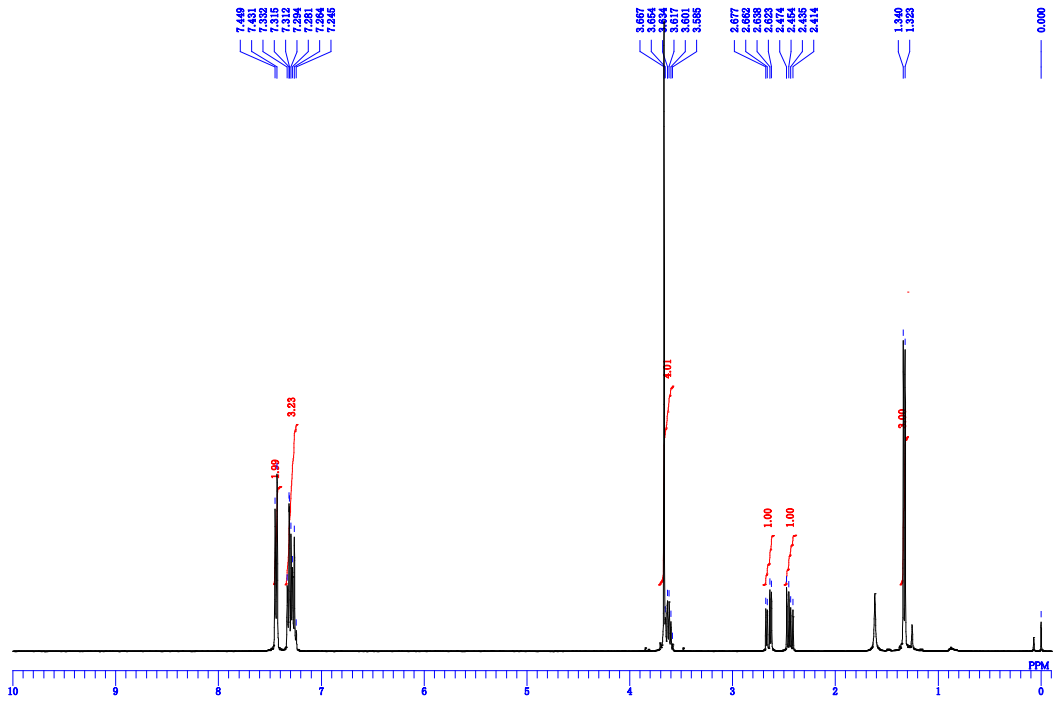

S
O
Me
OMe

(*S*)-4a-[OMe]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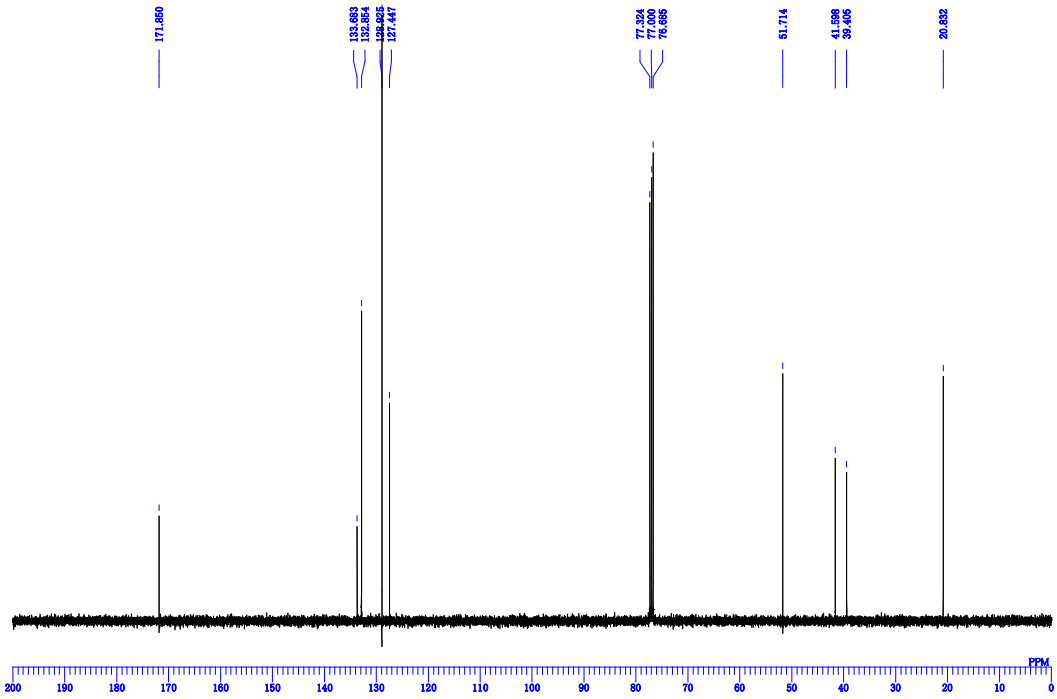
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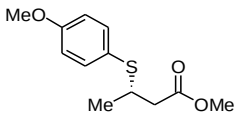
MeO
S
O
Me
OMe

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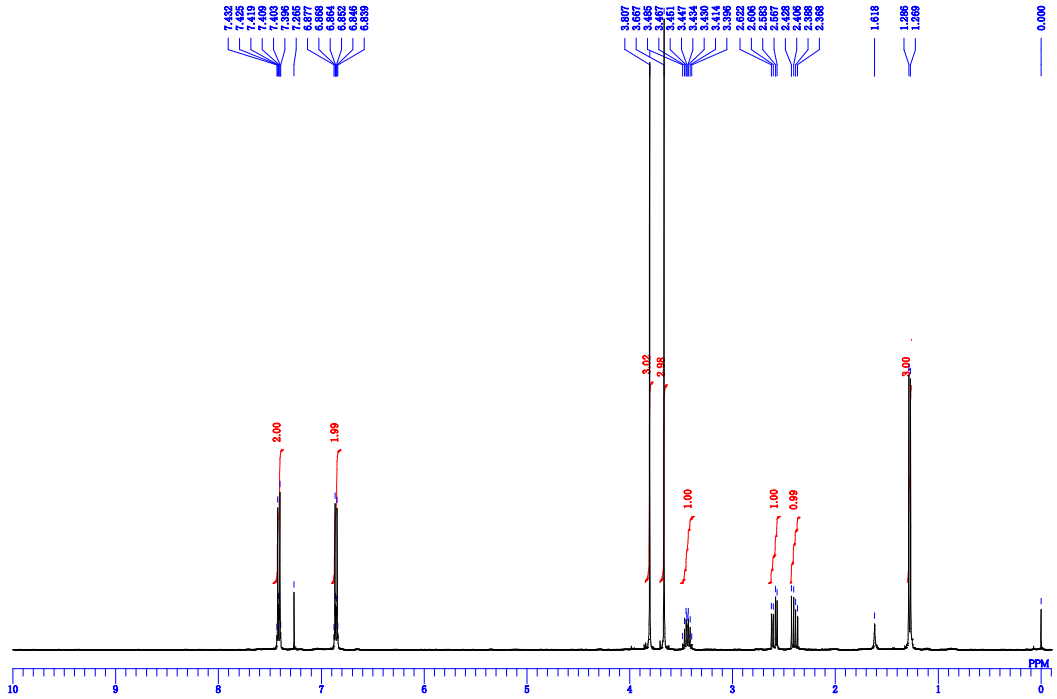
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6.839
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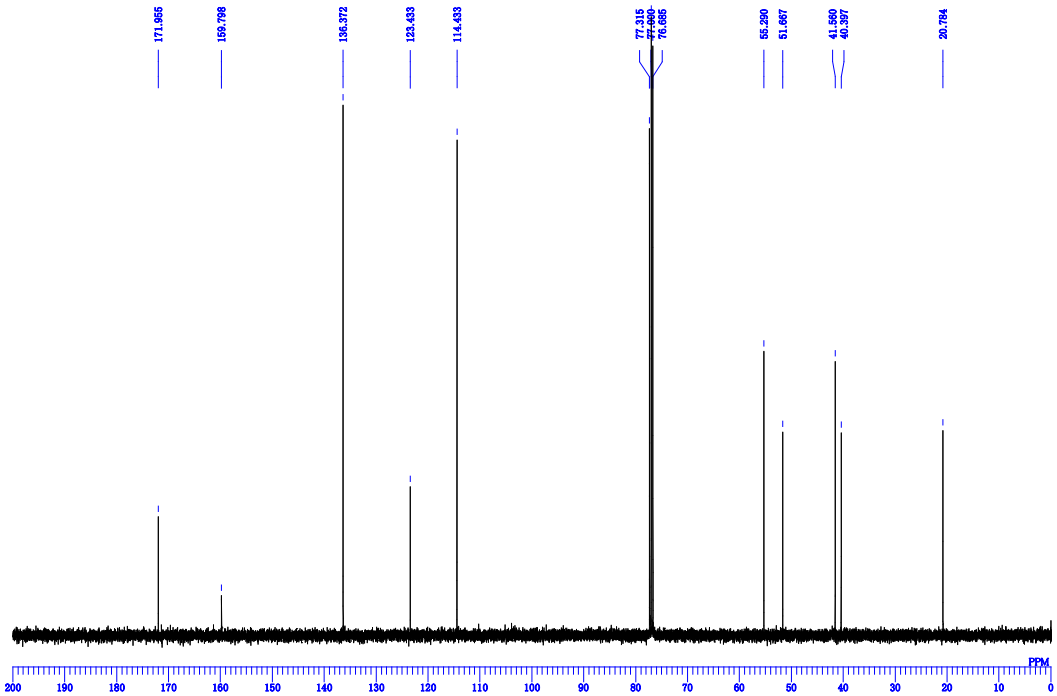
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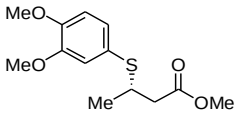
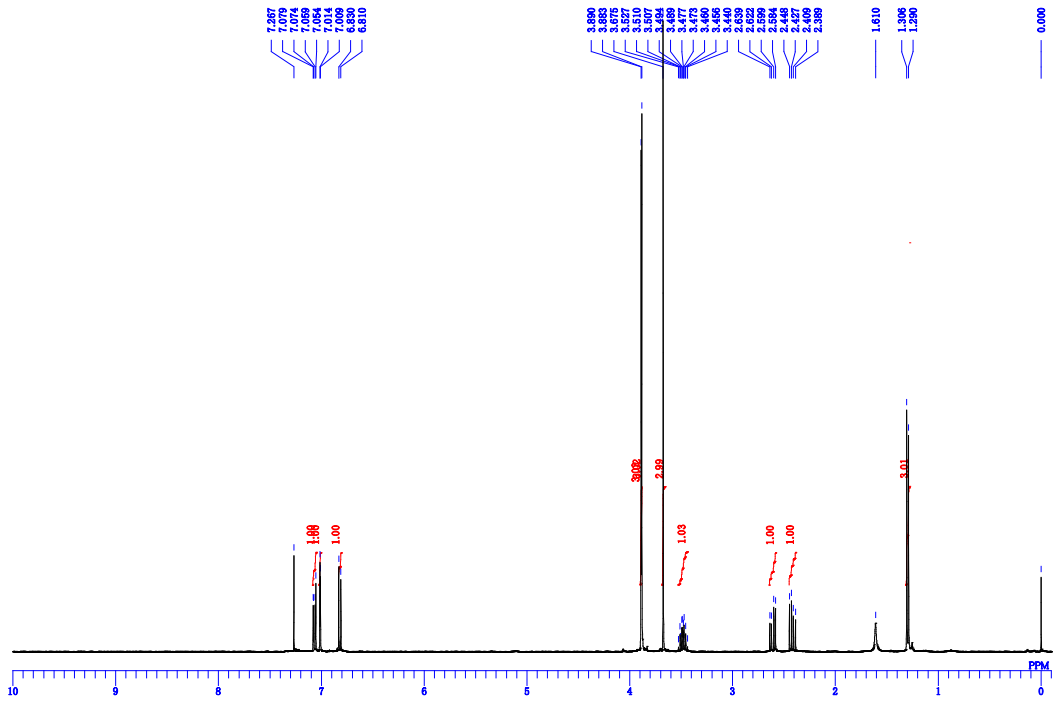

MeO
MeO
S
O
Me
OMe

(*S*)-4c-[OMe]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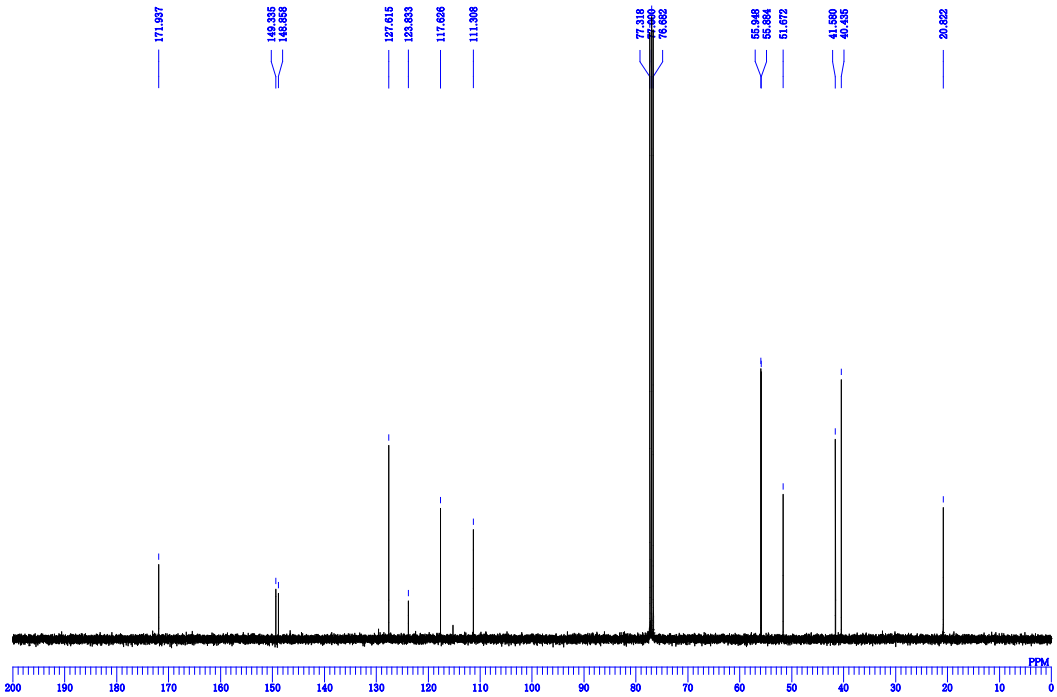
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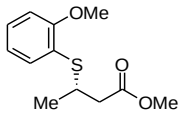
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Me
OMe

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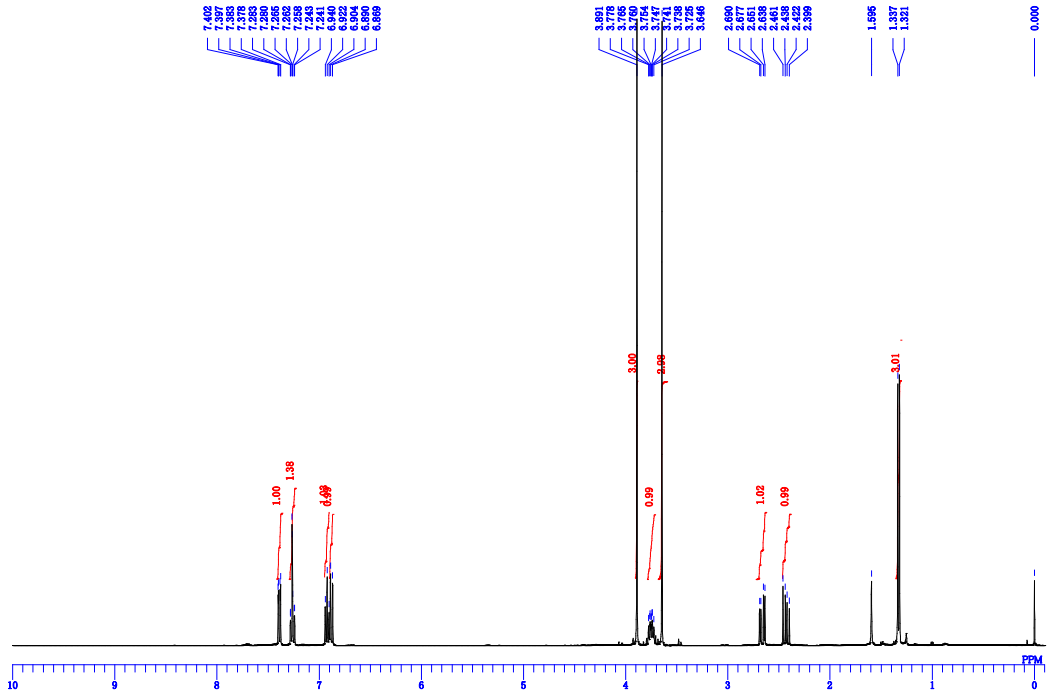
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7.241
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6.922
6.904
6.890
6.869
3.891
3.778
3.765
3.760
3.754
3.747
3.741
3.738
3.725
3.646
2.690
2.677
2.651
2.638
2.461
2.438
2.423
2.399
1.596
1.337
1.321
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3.00
2.98
3.01
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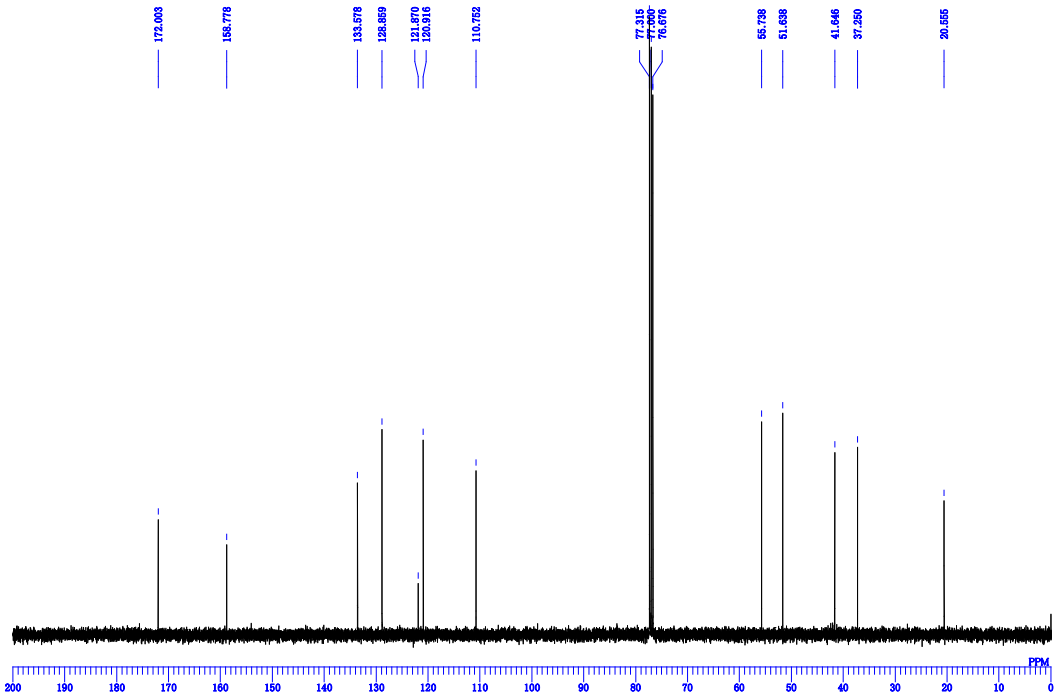
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77.000
76.676
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41.646
37.250
20.565
PPM
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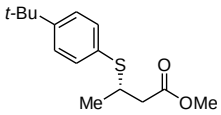
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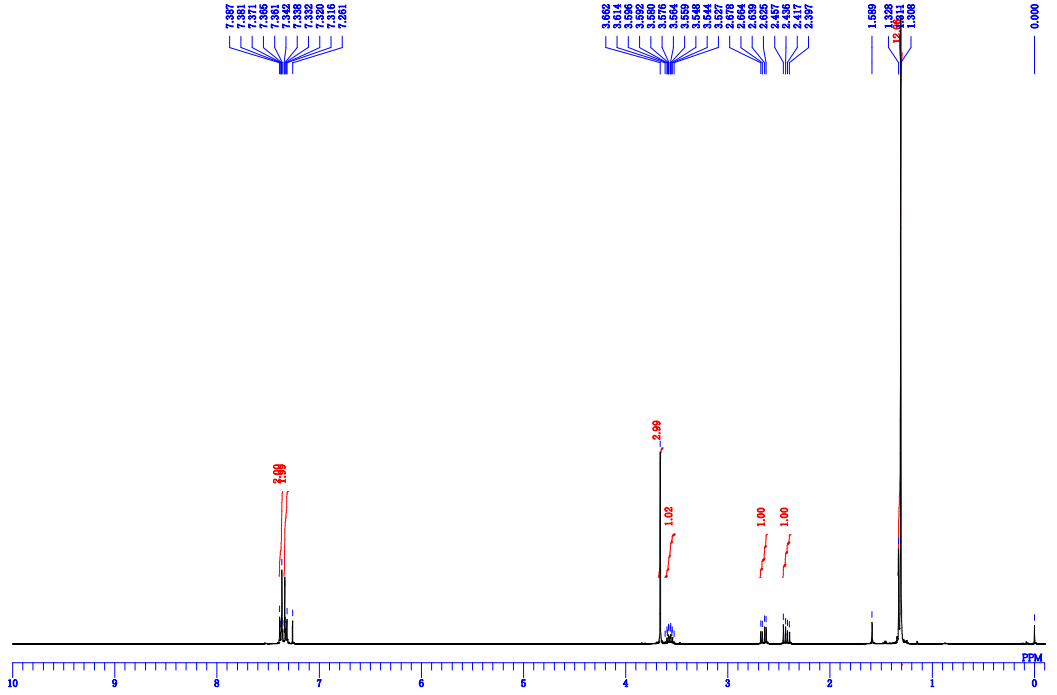
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7.332
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7.316
7.261
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3.614
3.595
3.592
3.580
3.576
3.564
3.559
3.548
3.544
3.527
2.678
2.654
2.639
2.625
2.457
2.436
2.417
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1.99
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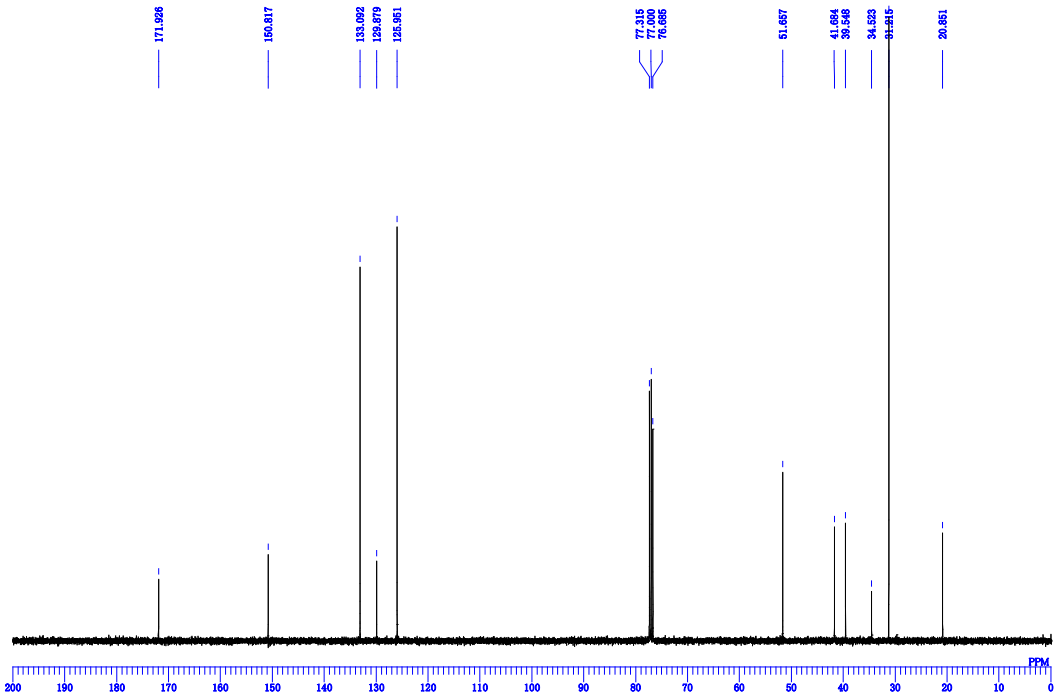
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77.000
76.686
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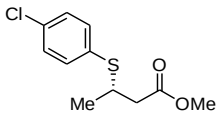
39.548
34.523
31.815
20.851
PPM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OMe

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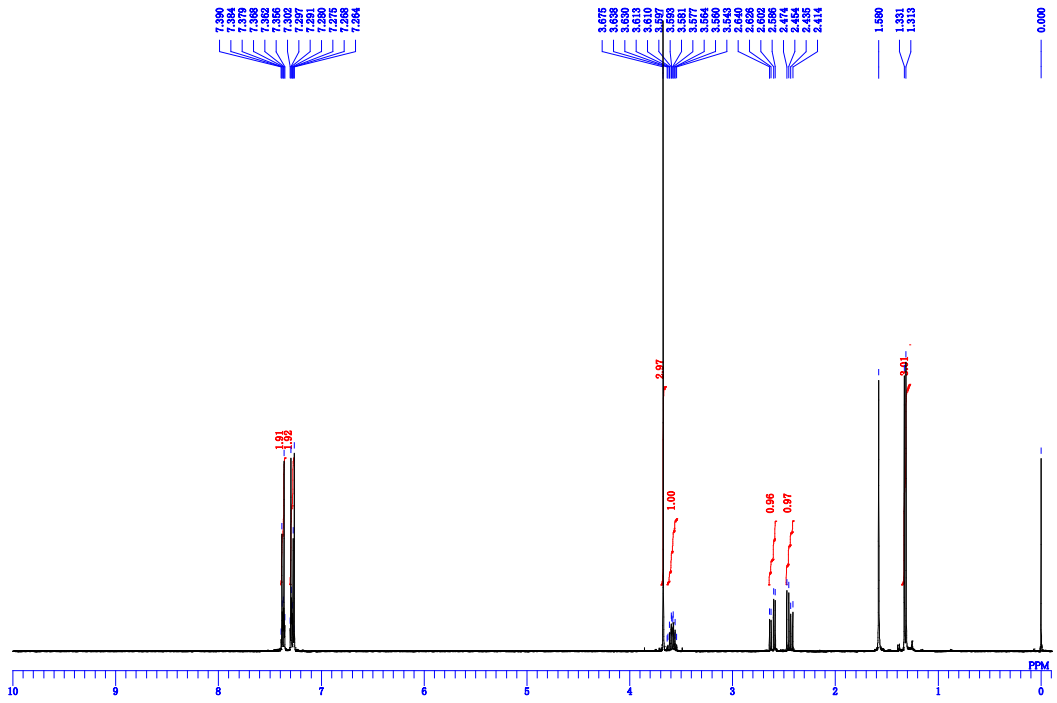
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7.297
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7.280
7.275
7.268
7.264
3.675
3.638
3.630
3.613
3.610
3.597
3.588
3.581
3.577
3.564
3.560
3.543
2.640
2.626
2.602
2.586
2.474
2.464
2.435
2.414
1.590
1.331
1.313
0.000
2.97
3.01
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0.96
0.97
PPM
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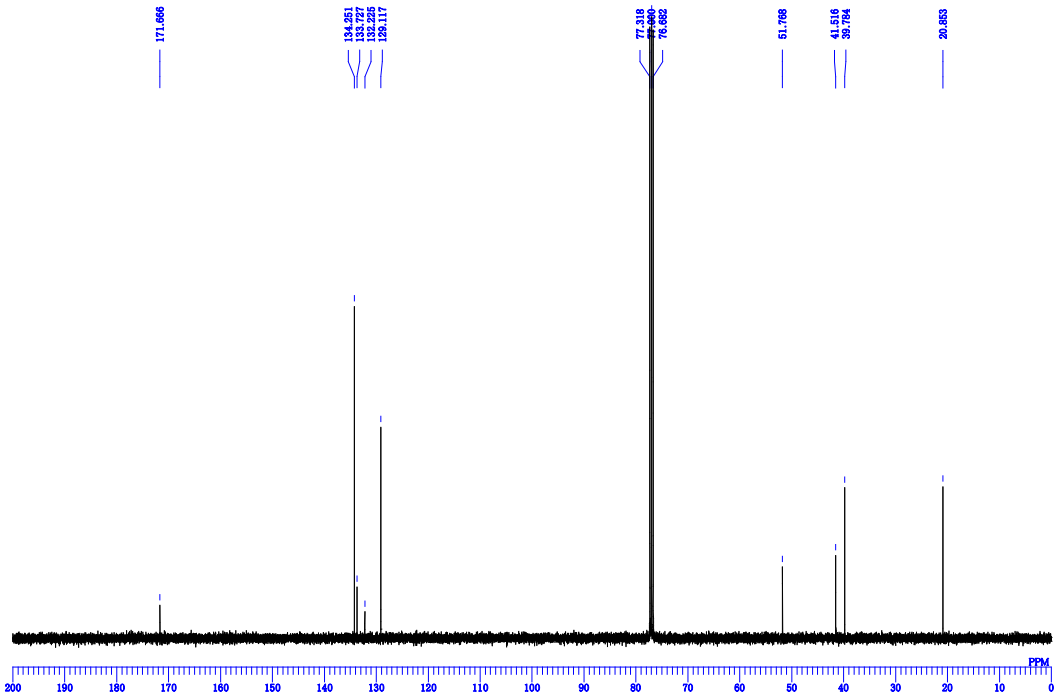
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77.000
76.682
51.768
41.516
39.784
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PPM
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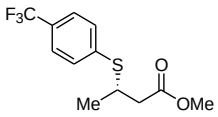
F3C
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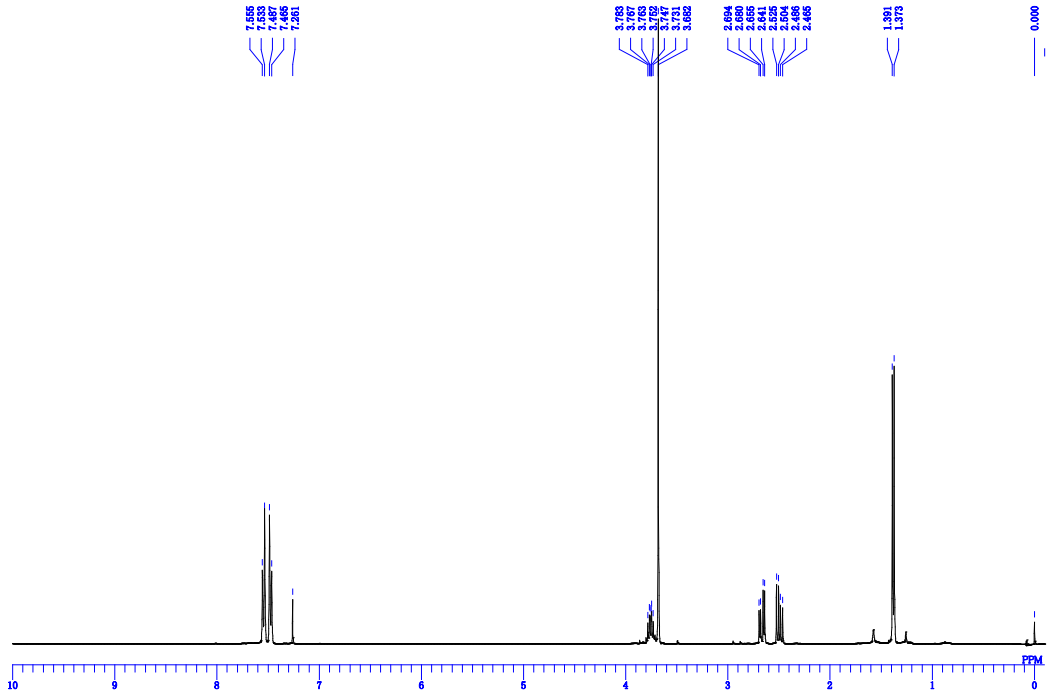
Me
OMe

(*S*)-4g-[OMe]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3.753
3.747
3.731
3.682
2.694
2.656
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2.625
2.494
2.466
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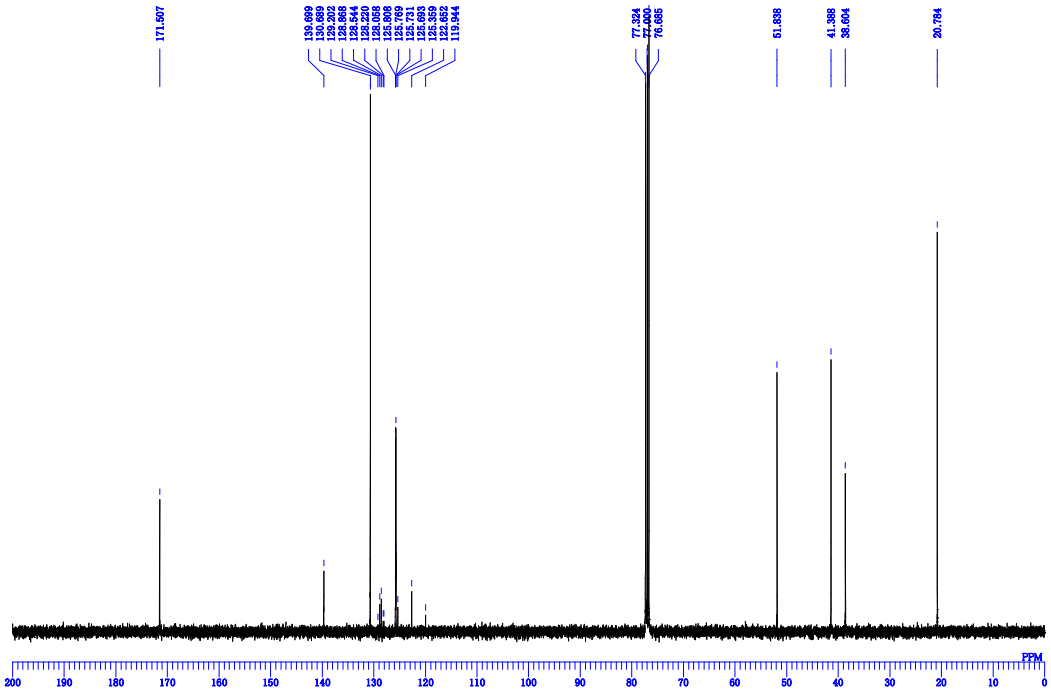
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128.544
128.220
126.056
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125.769
125.731
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125.369
122.652
119.944
77.324
77.000
76.685
51.838
41.388
38.604
20.784
PPM
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150
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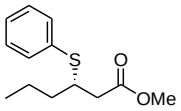
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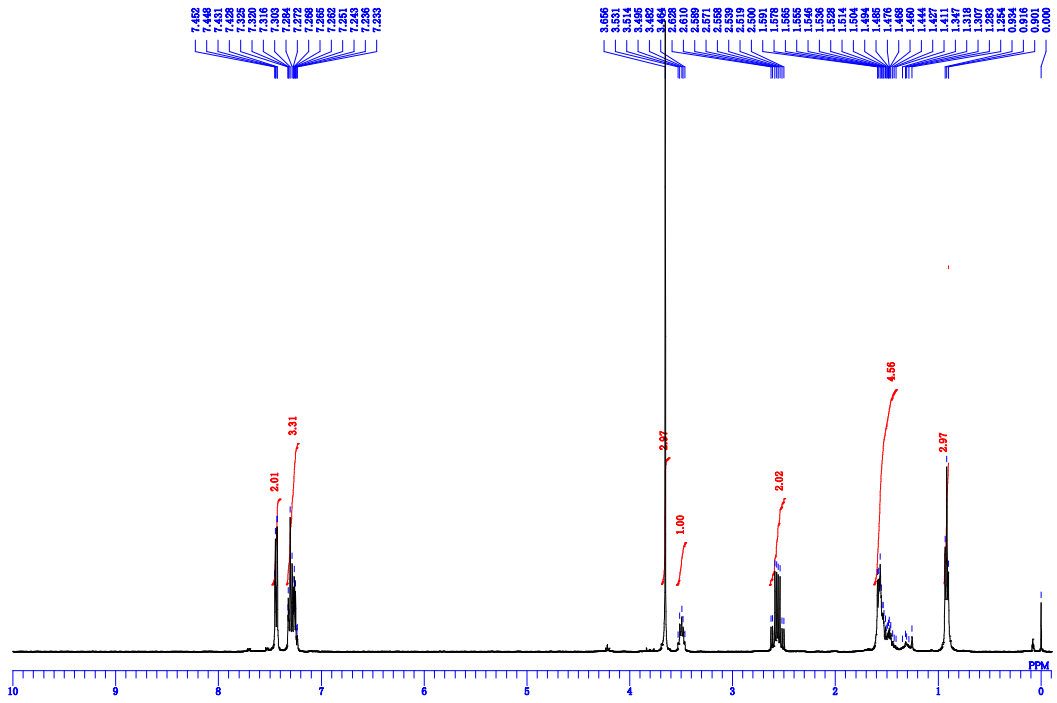
OMe

(*S*)-4h-[OMe]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7.272
7.268
7.265
7.262
7.251
7.243
7.236
7.233
3.656
3.531
3.514
3.496
3.482
3.464
3.428
2.610
2.589
2.571
2.568
2.539
2.519
2.500
1.591
1.578
1.565
1.555
1.546
1.536
1.528
1.514
1.504
1.494
1.486
1.476
1.468
1.460
1.444
1.427
1.411
1.347
1.318
1.307
1.283
1.254
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0.916
0.901
0.000
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3.31
2.97
1.00
2.02
4.56
2.97
PPM
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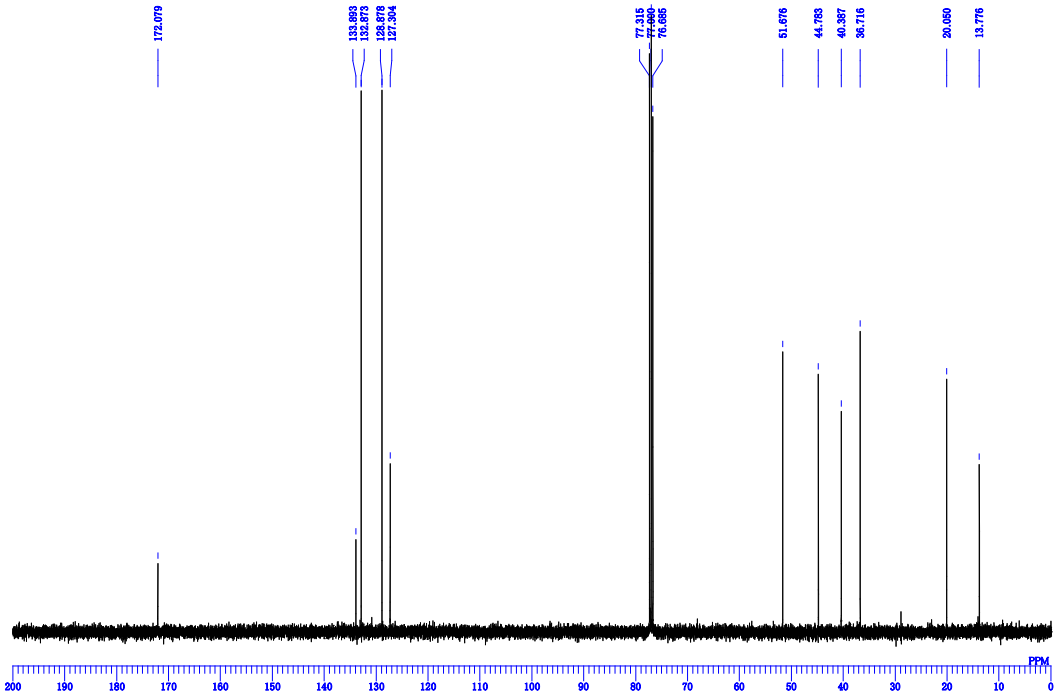
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77.000
76.685
51.676
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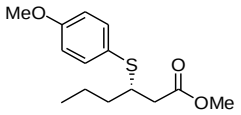
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OMe

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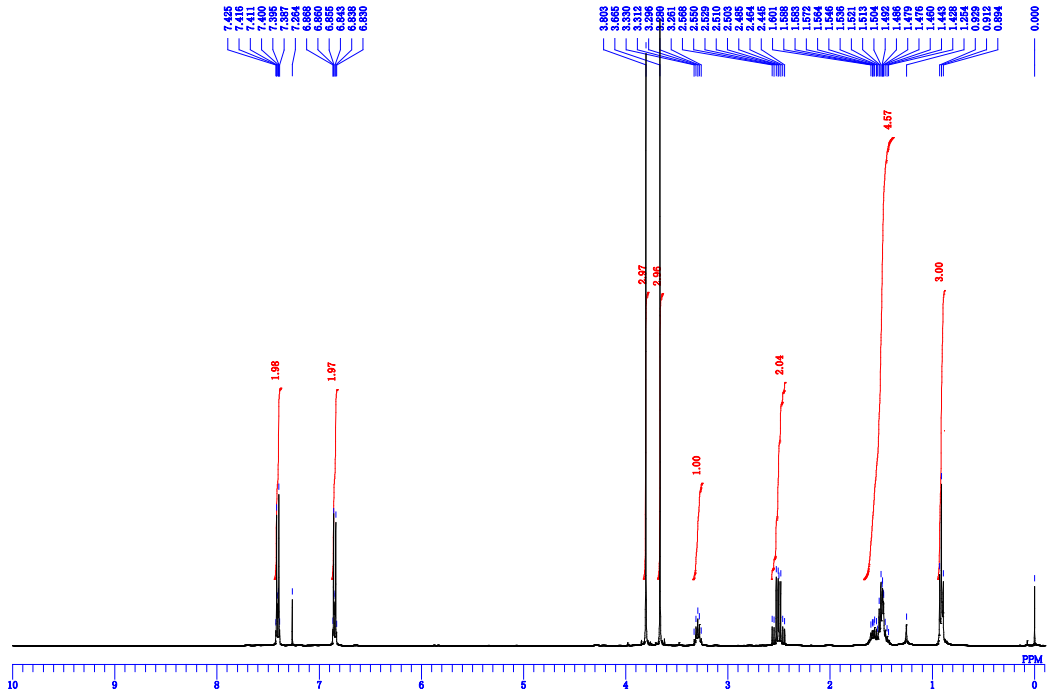
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6.830
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2.529
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2.493
2.465
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2.445
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1.572
1.564
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1.521
1.513
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1.460
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0.912
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0.000
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2.96
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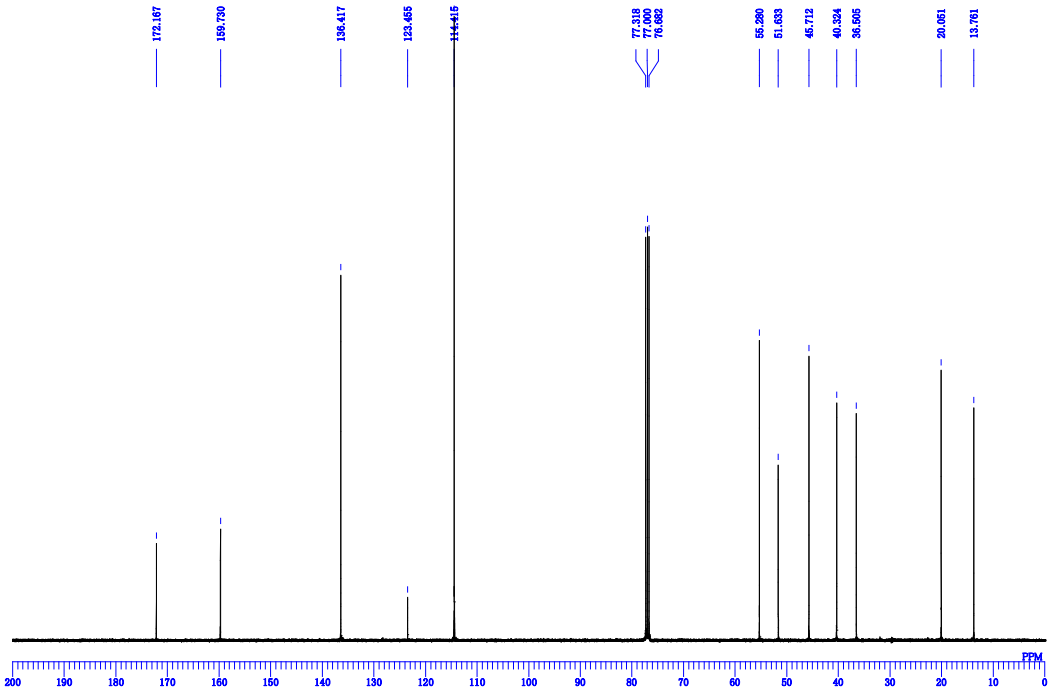
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76.682
55.280
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36.505
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PPM
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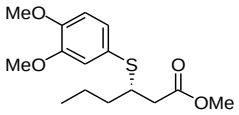
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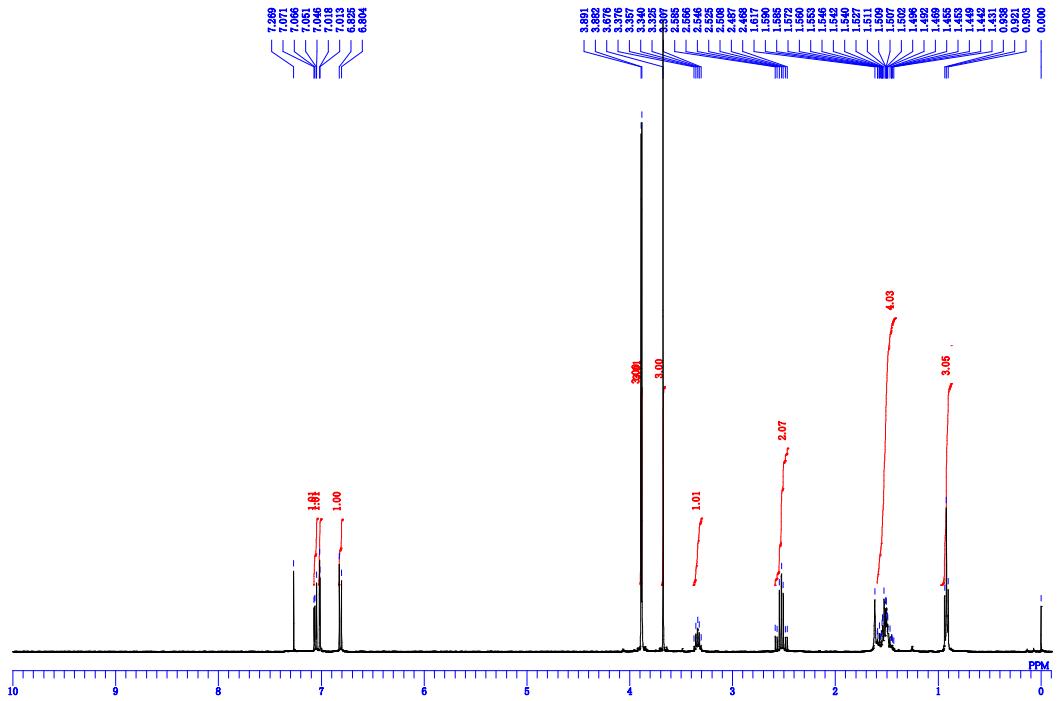
OMe

(*S*)-4j-[OMe]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3.340
3.325
3.307
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2.566
2.546
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1.590
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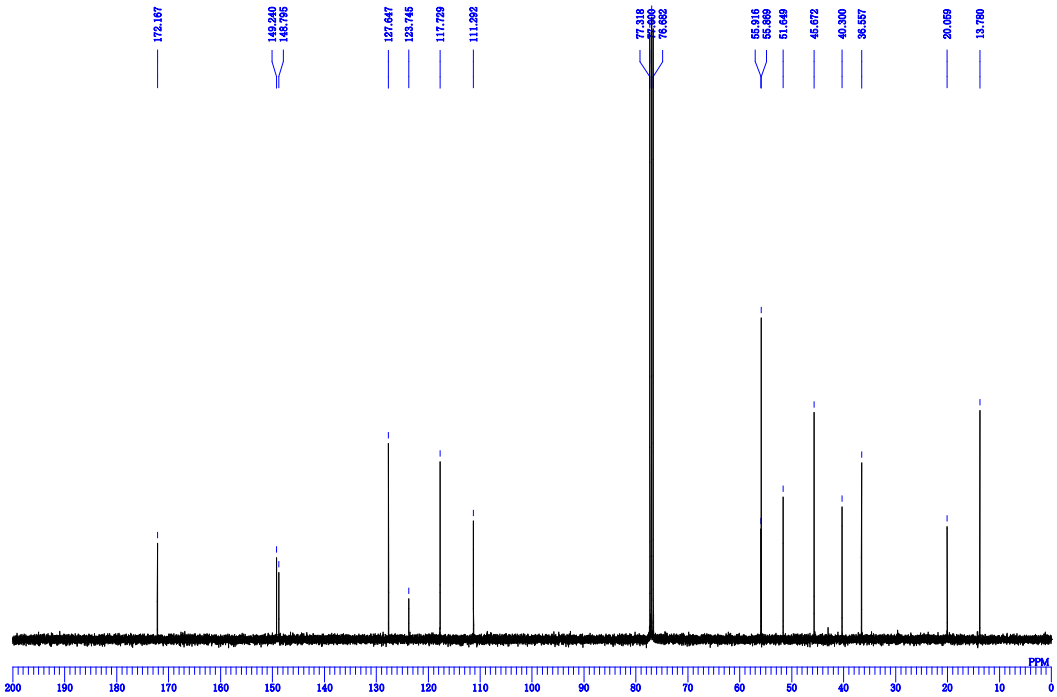
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76.682
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45.672
40.300
36.557
20.059
13.780
PPM
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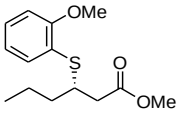
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OMe

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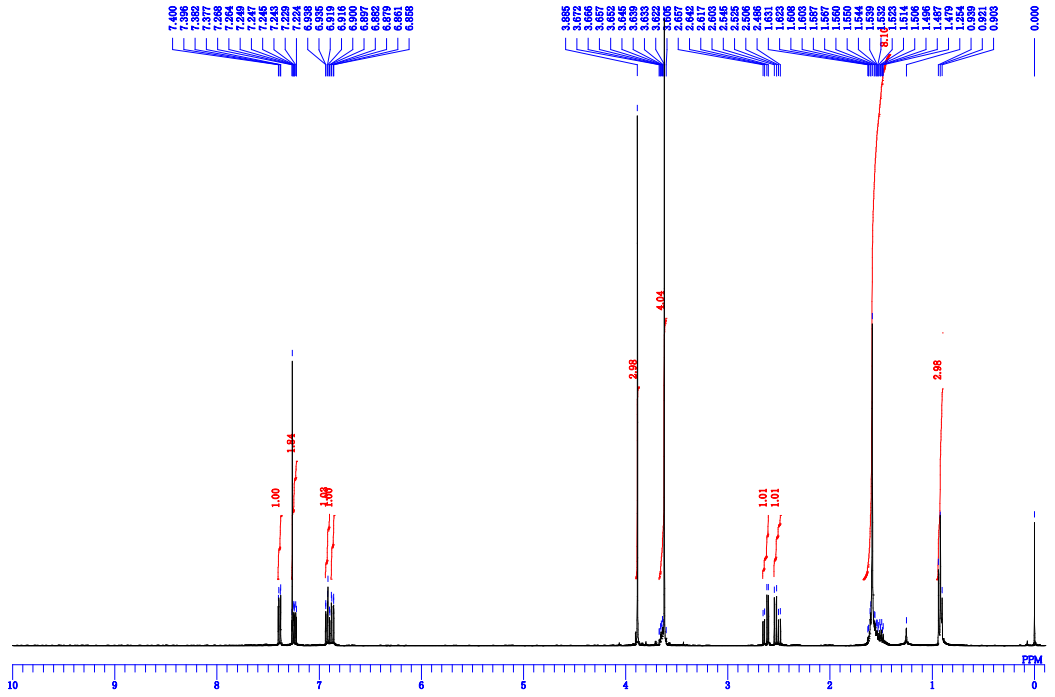
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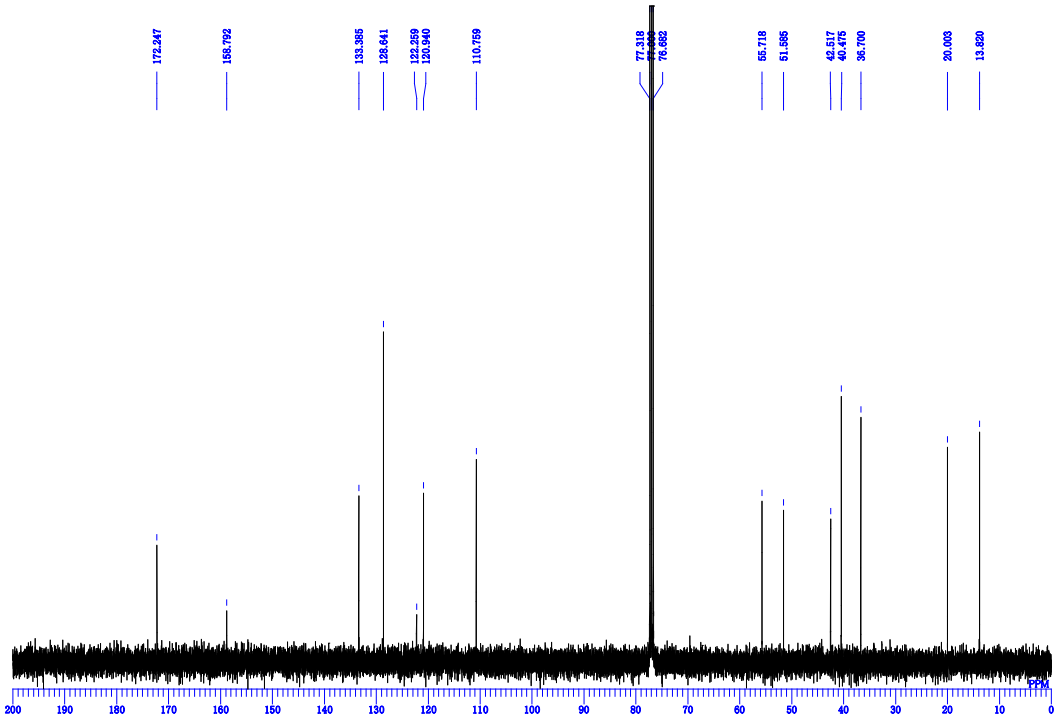
PPM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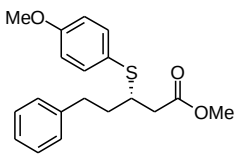
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OMe

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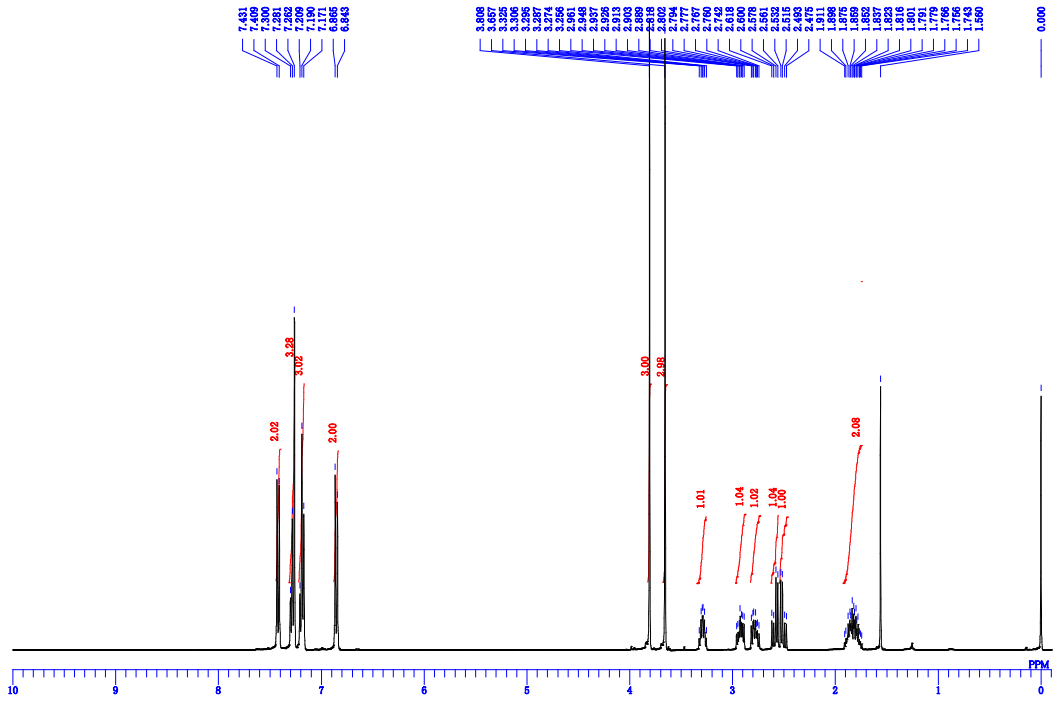
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1.02
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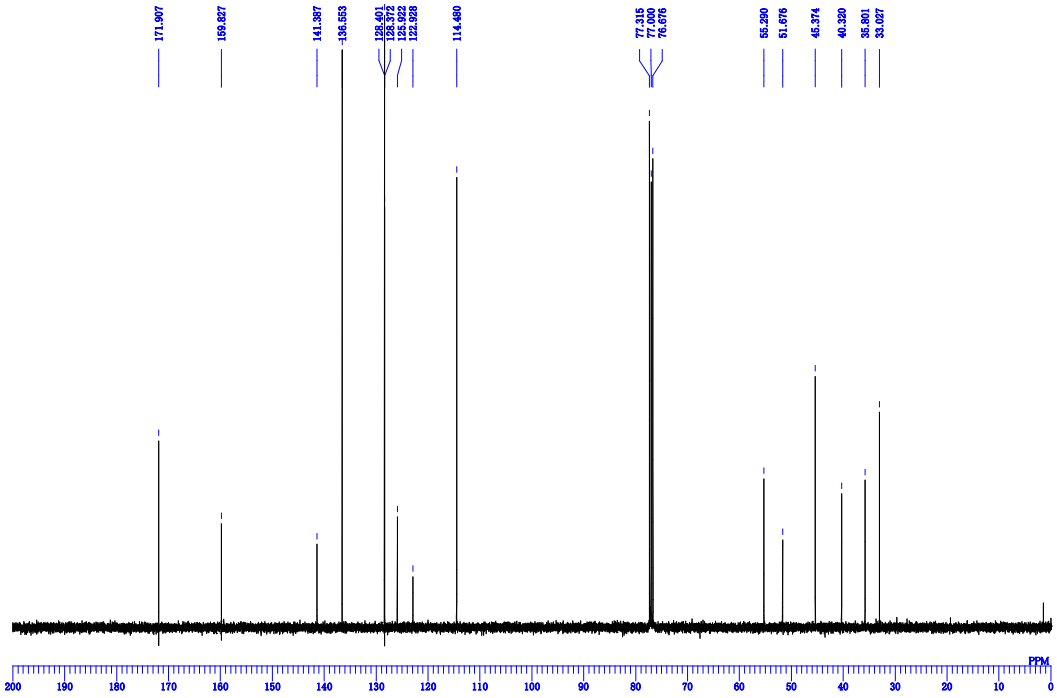
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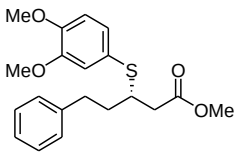
PPM



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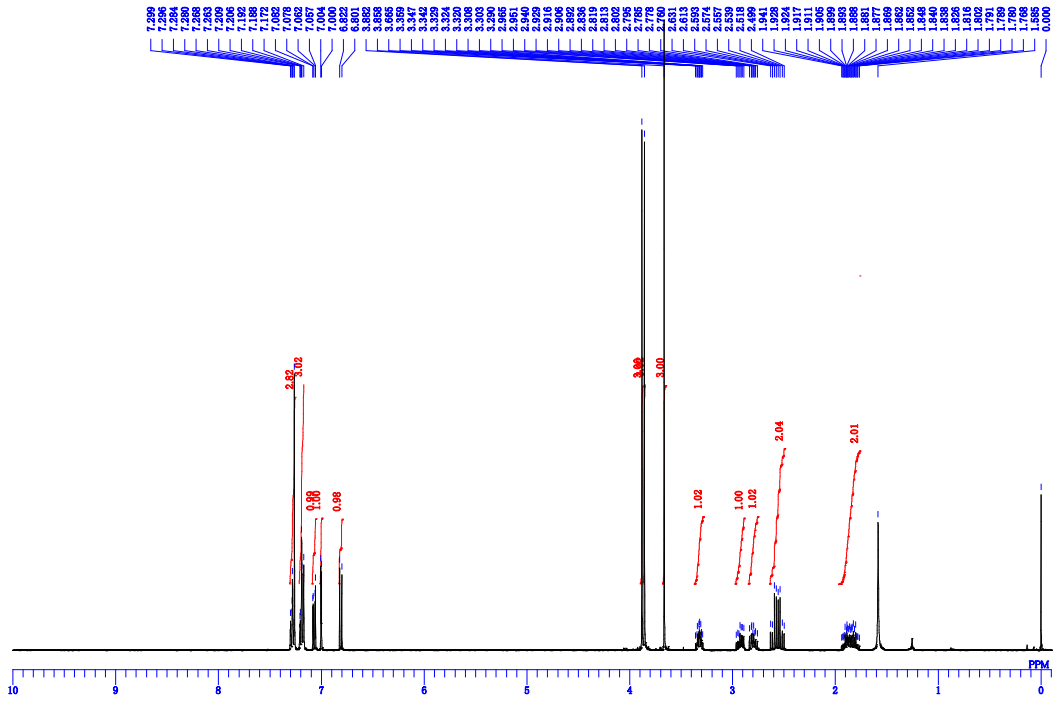

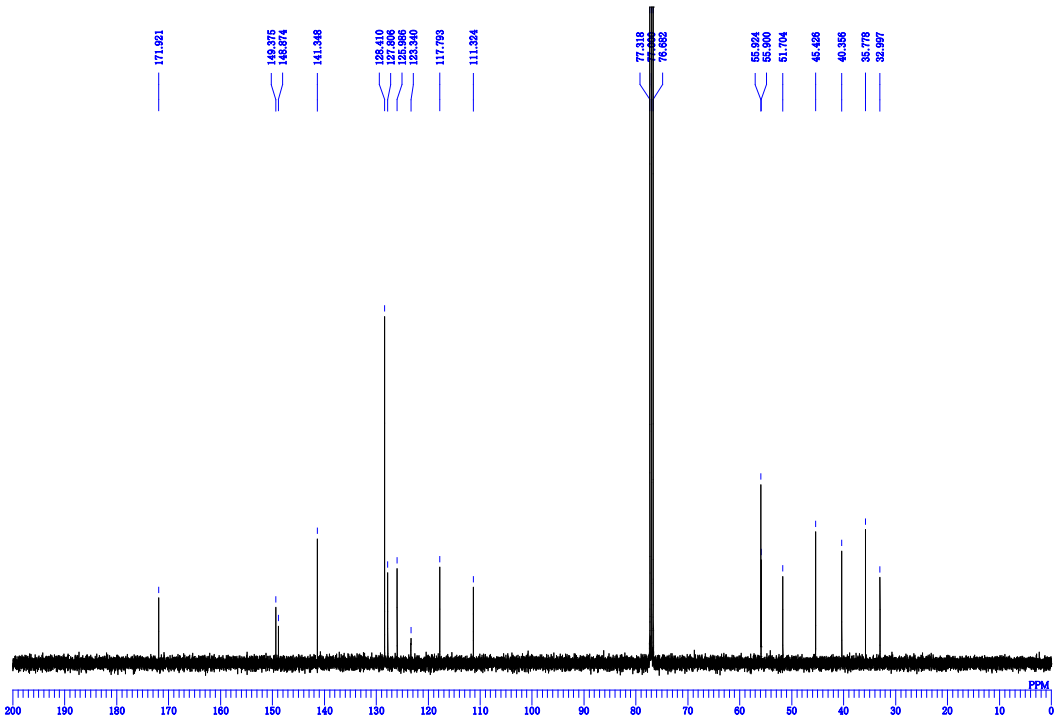

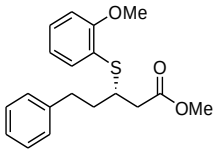
OMe
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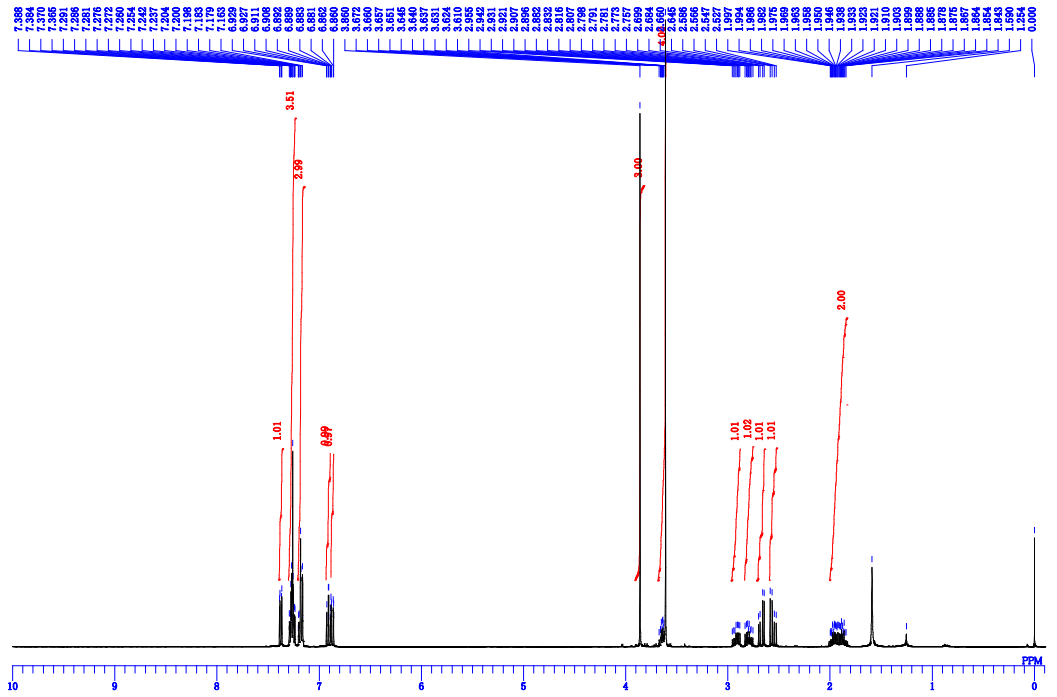
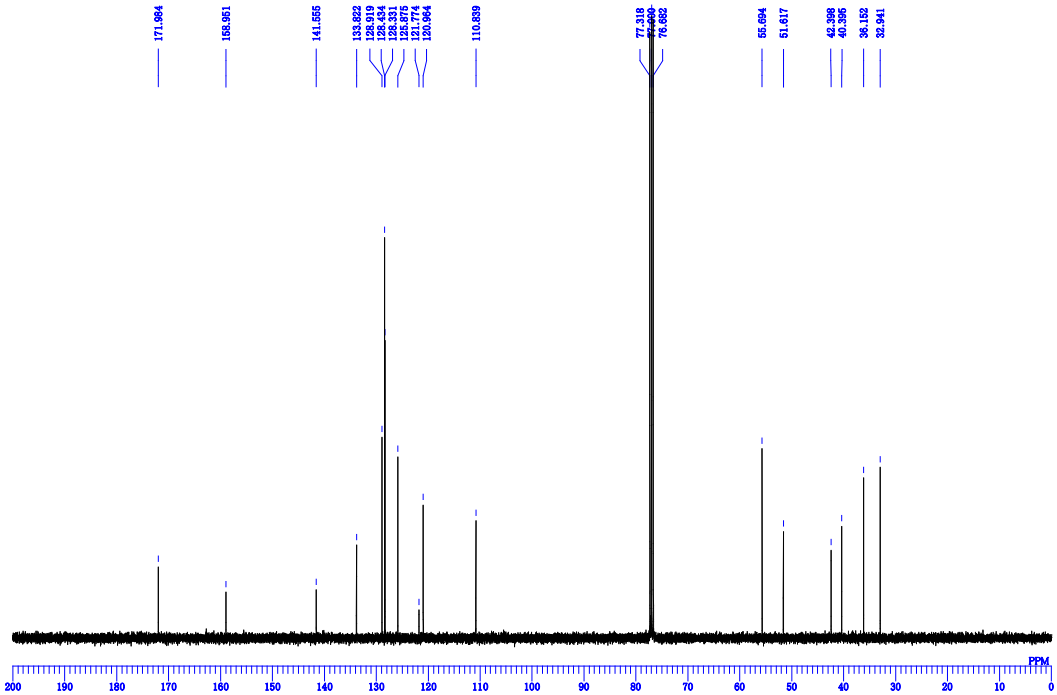
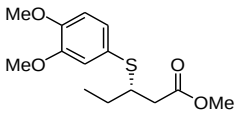
OMe

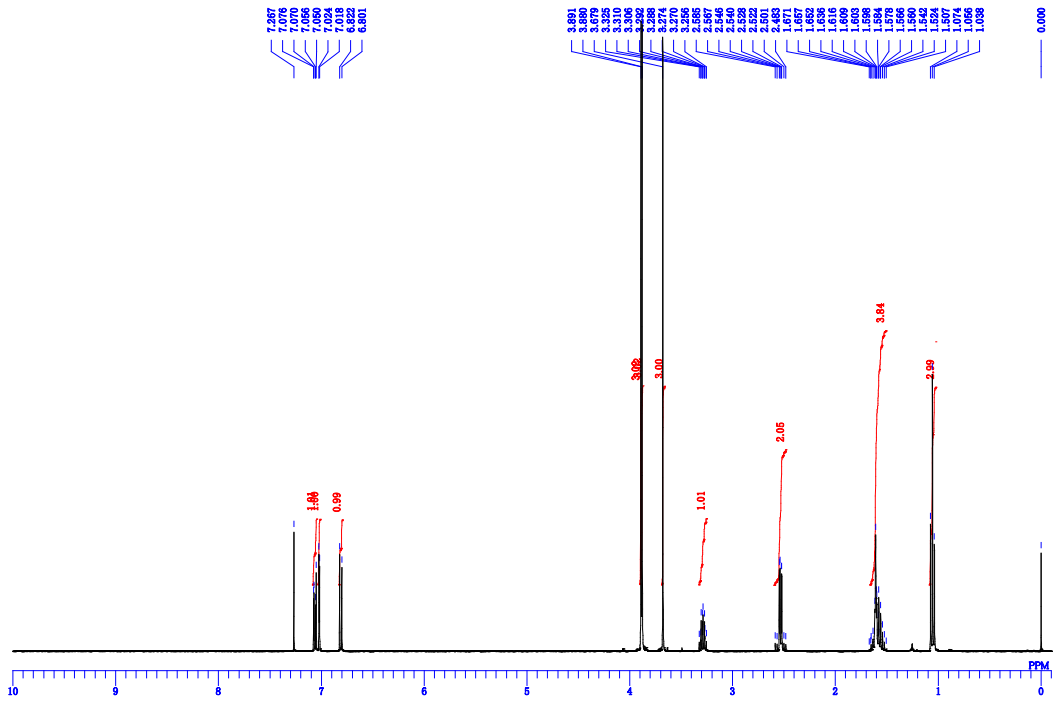
(*S*)-4n-[OMe]

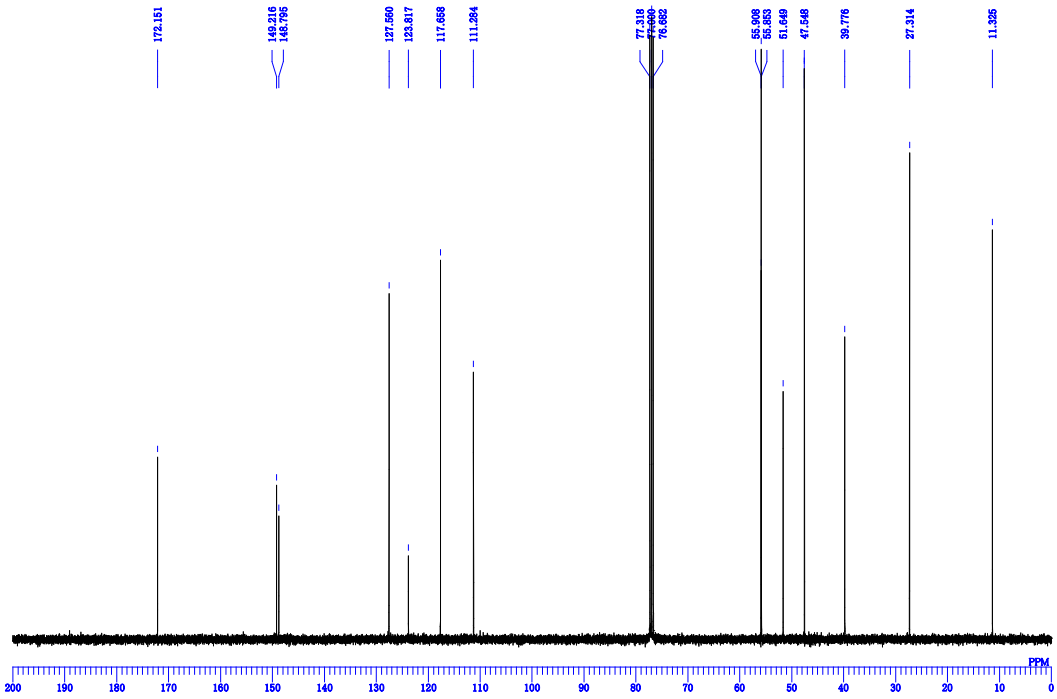

3.51
2.99
3.00
2.00
1.01
1.01
1.02
1.01
1.01
PPM

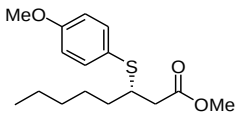

171.984
168.961
141.555
133.822
128.919
128.434
128.331
125.975
121.774
120.964
110.839
77.318
55.694
51.617
42.398
40.396
36.152
32.941
PPM


MeO
MeO
S
O
OMe

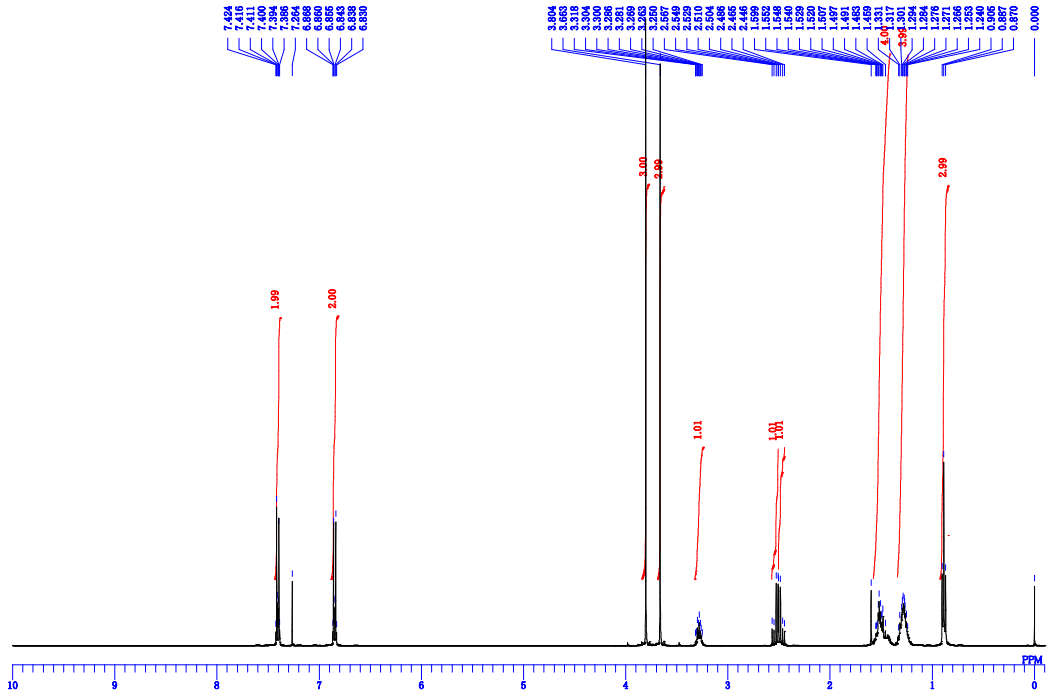
(*S*)-4o-[OMe]

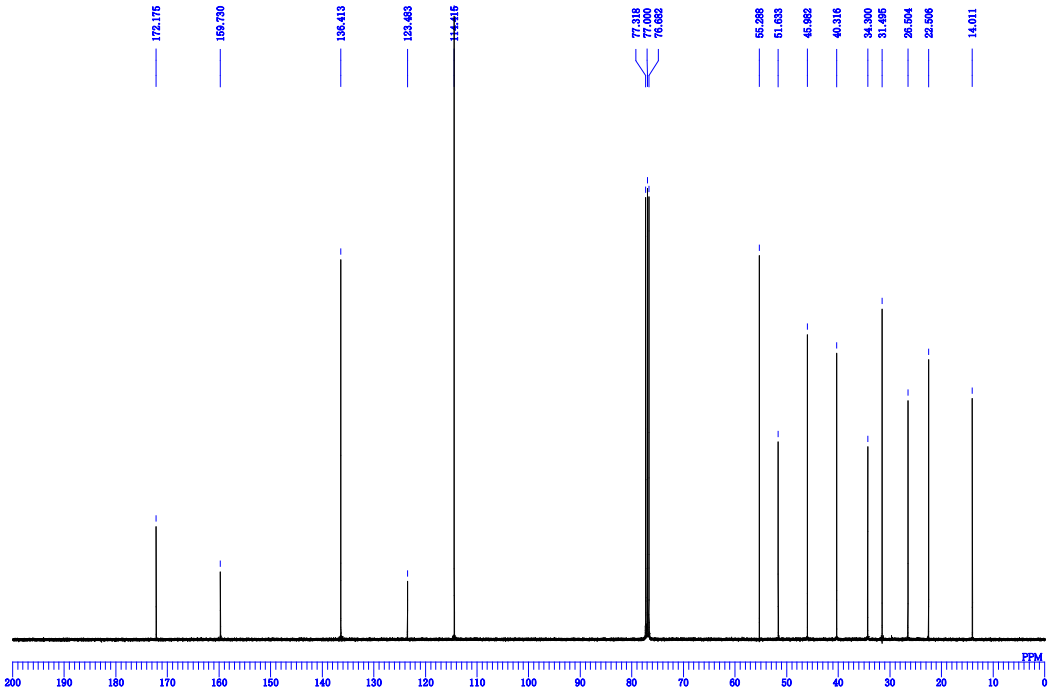

7.267
7.076
7.070
7.056
7.050
7.024
7.018
6.822
6.801
3.891
3.890
3.679
3.335
3.310
3.305
3.302
3.288
3.274
3.270
3.255
2.595
2.567
2.546
2.540
2.528
2.523
2.501
2.483
1.671
1.657
1.653
1.636
1.616
1.609
1.603
1.598
1.594
1.578
1.566
1.560
1.543
1.524
1.507
1.074
1.056
1.038
0.000
3.84
3.02
3.00
2.99
2.05
1.01
1.00
0.99
PPM
10
9
8
7
6
5
4
3
2
1
0


172.151
149.216
148.796
127.560
123.817
117.658
111.284
77.318
77.000
76.682
55.908
55.853
51.649
47.546
39.776
27.314
11.325
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


MeO
S
O
OMe

(*S*)-4p-[OMe]


7.424
7.416
7.411
7.400
7.394
7.386
7.284
6.868
6.860
6.855
6.843
6.838
6.830
3.804
3.663
3.318
3.304
3.300
3.286
3.251
3.269
3.263
3.250
2.567
2.549
2.529
2.510
2.504
2.496
2.465
2.446
1.599
1.559
1.548
1.540
1.529
1.507
1.497
1.491
1.483
1.469
1.331
1.317
1.301
1.294
1.284
1.276
1.271
1.266
1.253
1.240
0.905
0.887
0.870
0.000
3.00
3.00
2.99
1.99
2.00
1.01
1.01
1.01
4.01
3.99
PPM
10
9
8
7
6
5
4
3
2
1
0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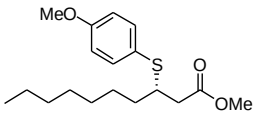
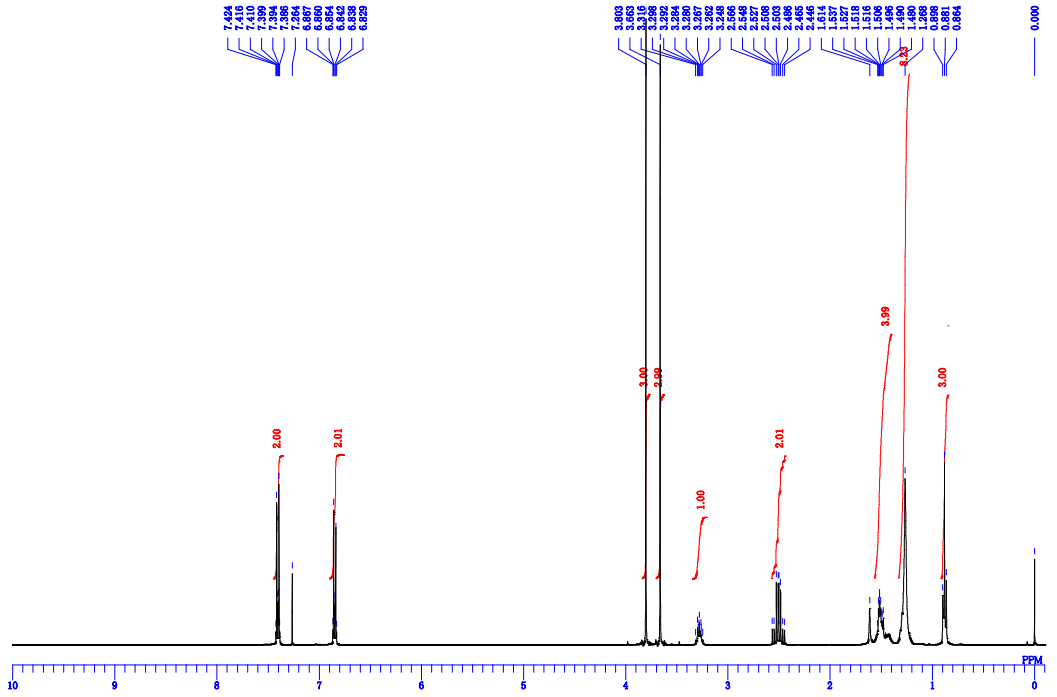
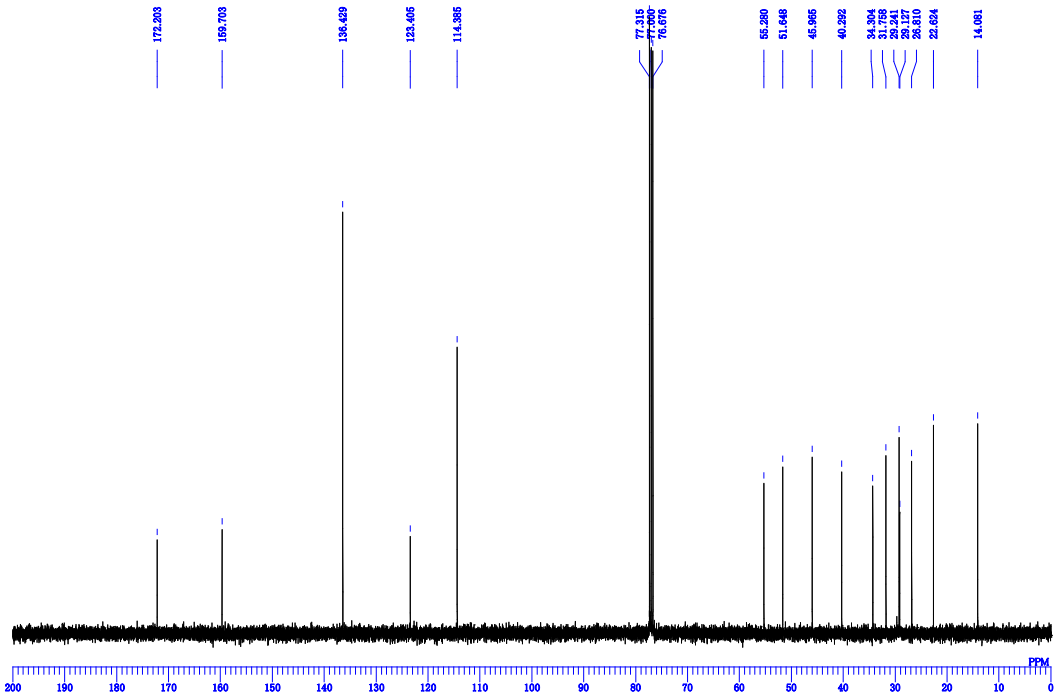
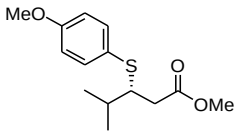
159.730
136.413
123.483
114.415
77.318
77.000
76.682
65.288
61.633
45.982
40.316
34.300
31.495
26.504
22.506
14.011
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


MeO
S
O
OMe

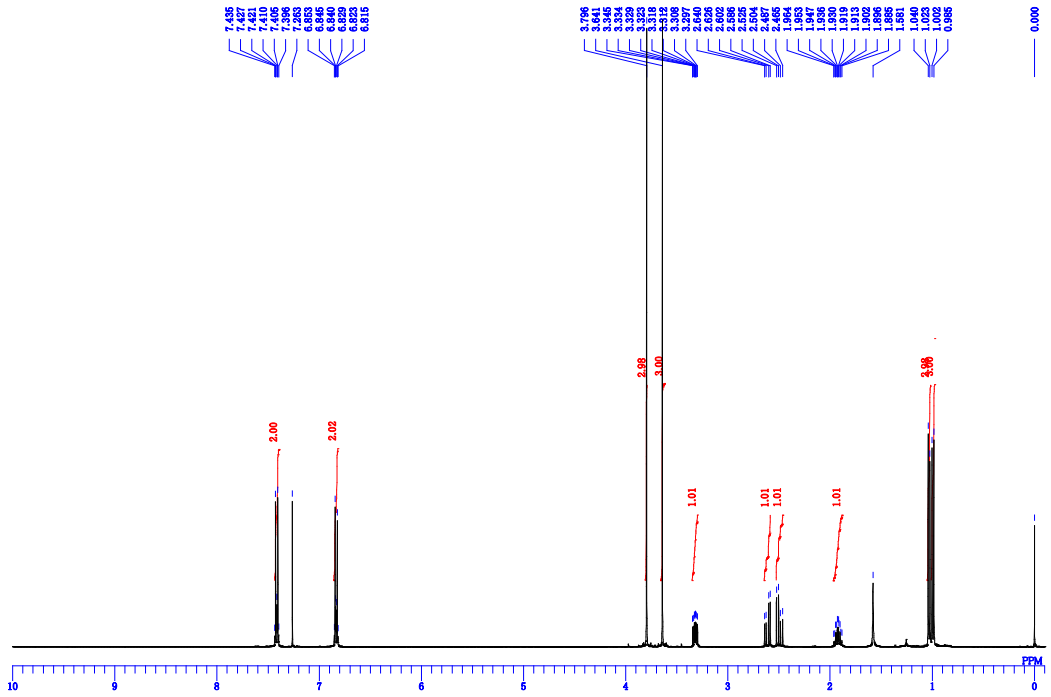
(*S*)-4q-[OMe]


7.424
7.416
7.410
7.399
7.394
7.386
7.264
6.857
6.850
6.854
6.842
6.838
6.829
3.803
3.653
3.315
3.298
3.292
3.284
3.280
3.267
3.262
3.248
2.566
2.548
2.527
2.508
2.503
2.496
2.495
2.444
1.614
1.537
1.527
1.518
1.514
1.506
1.496
1.490
1.480
1.398
0.898
0.881
0.864
0.000
2.00
2.01
3.00
2.89
1.00
2.01
3.59
8.33
3.00
PPM


172.203
159.703
136.429
123.405
114.385
77.315
77.000
76.676
55.280
51.648
45.965
40.392
34.304
31.758
29.341
29.127
26.810
22.624
14.081
PPM


MeO
S
O
OMe

(*R*)-4r-[OMe]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7.427
7.421
7.410
7.405
7.396
7.283
6.835
6.829
6.640
6.829
6.823
6.815
3.796
3.641
3.345
3.334
3.329
3.323
3.318
3.312
3.308
3.297
2.640
2.626
2.602
2.586
2.575
2.564
2.467
2.455
1.954
1.943
1.547
1.536
1.530
1.519
1.513
1.502
1.496
1.485
1.481
1.040
1.033
1.028
0.995
0.000
2.98
3.00
3.03
3.06
2.00
2.02
1.01
1.01
1.01
1.01
PPM
10
9
8
7
6
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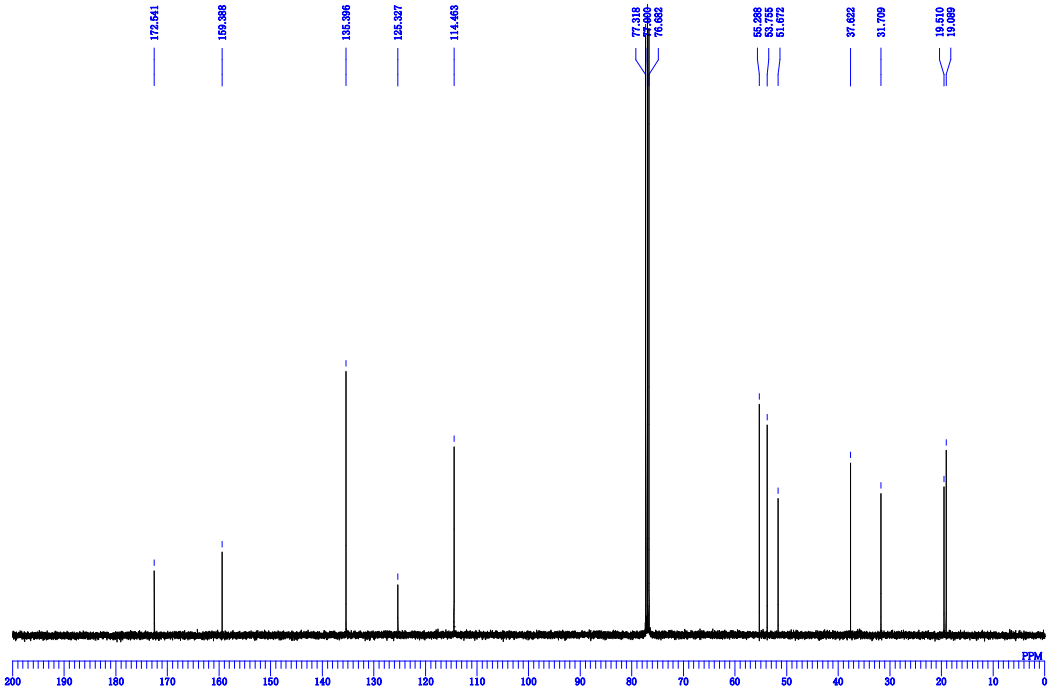
4
3
2
1
0


172.641
159.388
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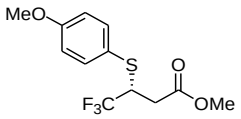
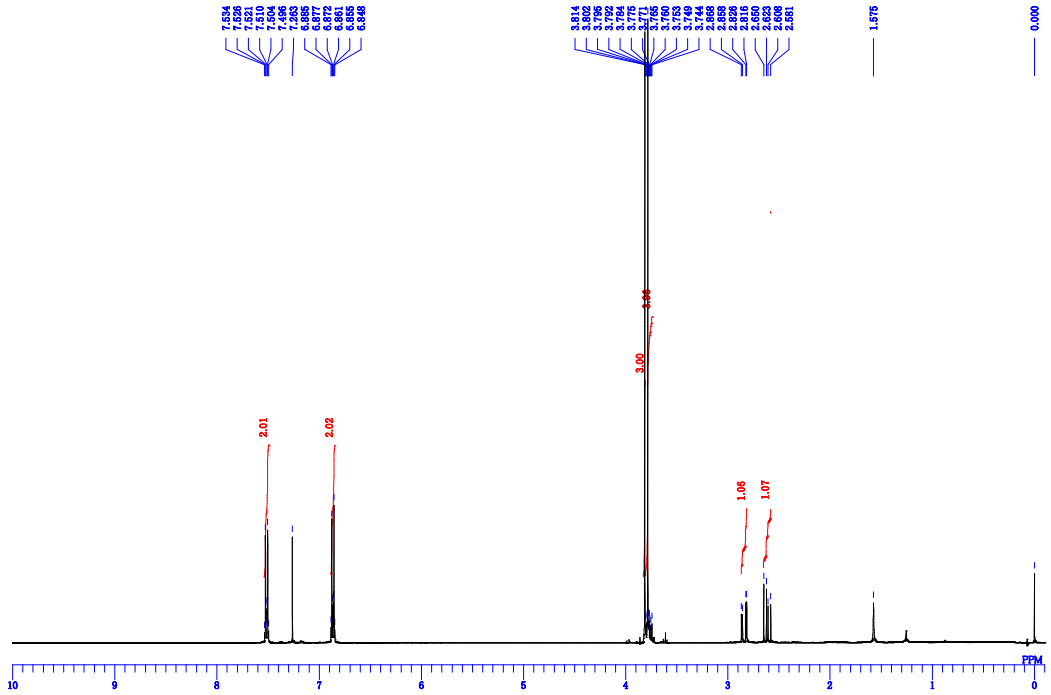
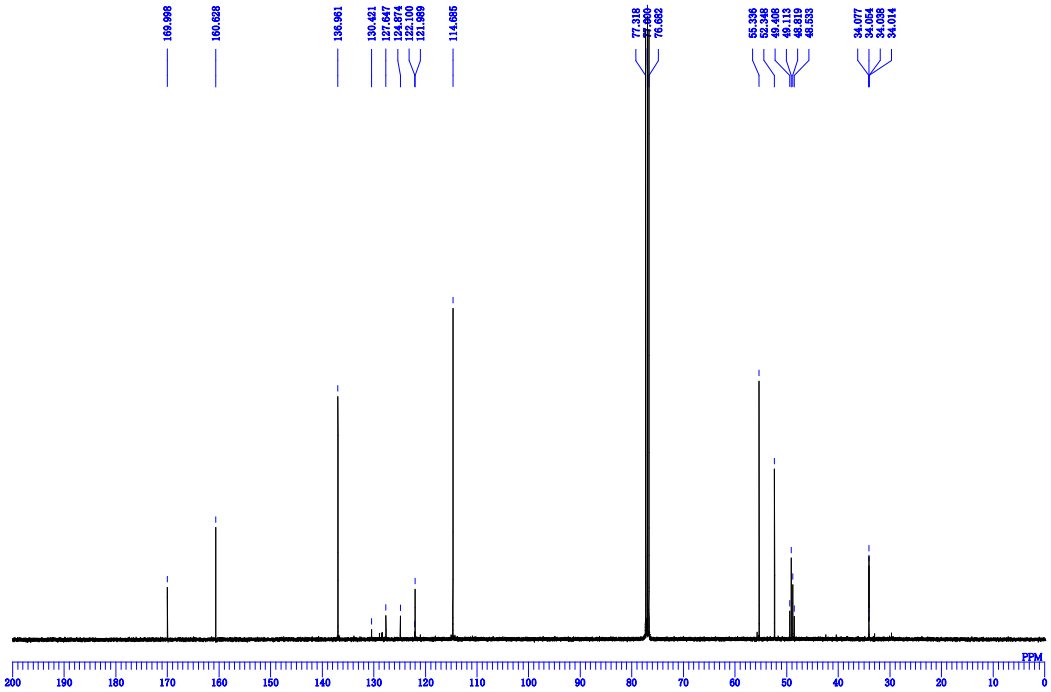
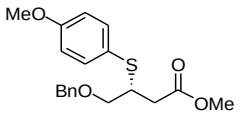
125.327
114.463
77.318
77.000
76.682
55.288
55.755
51.672
37.622
31.709
19.510
19.089
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


MeO
S
O
F3C
OMe

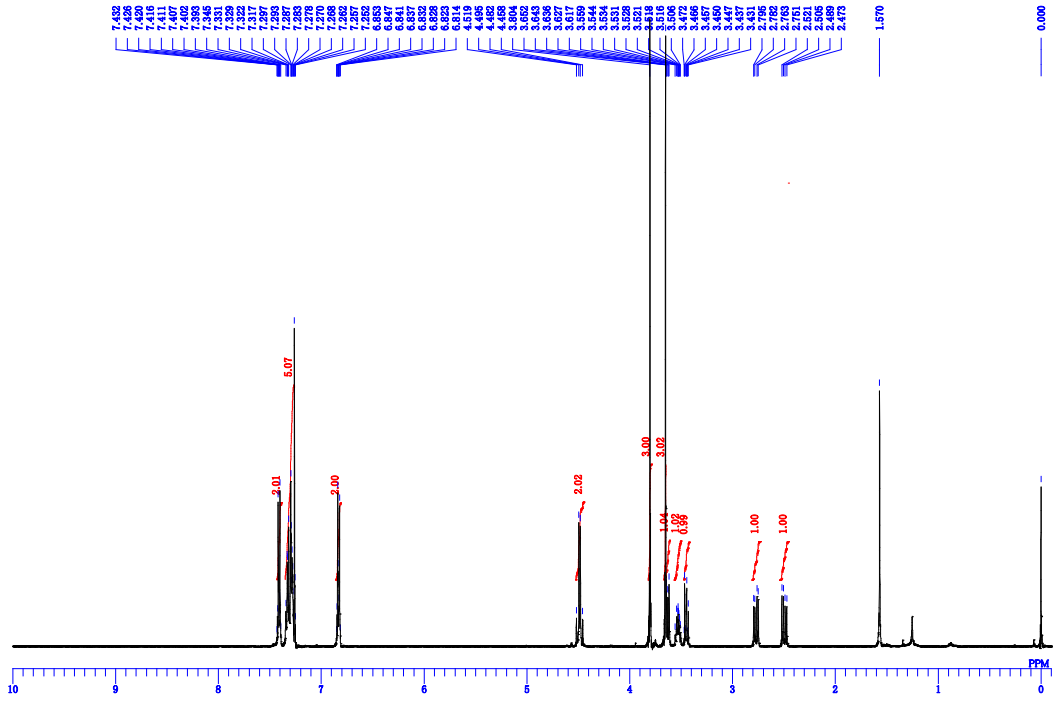
(*R*)-4s-[OMe]

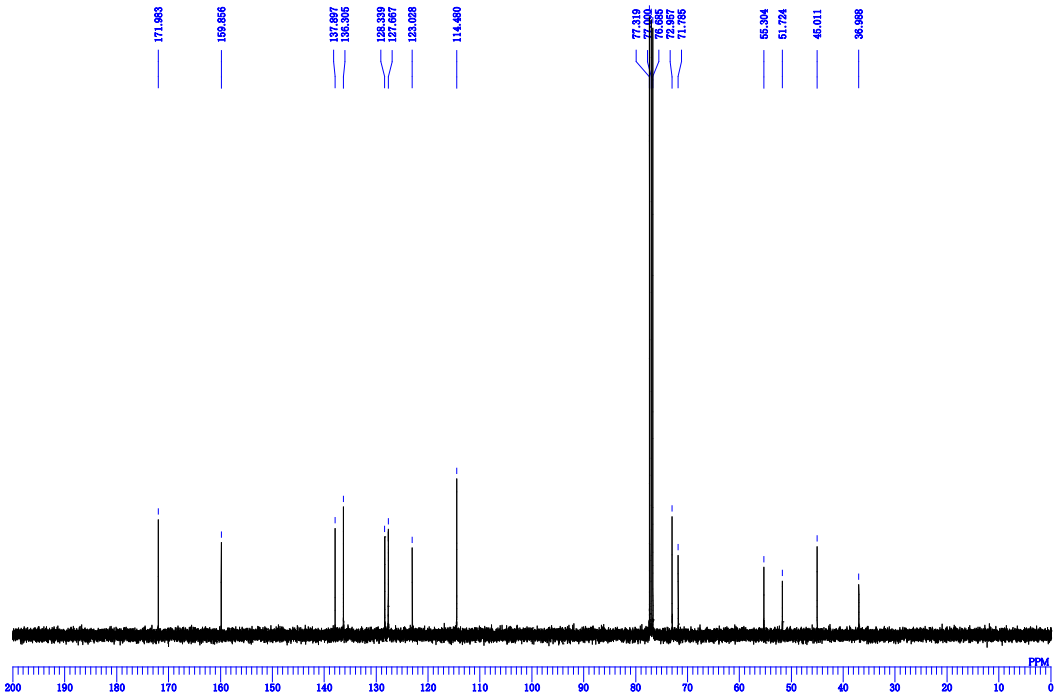

7.534
7.525
7.521
7.510
7.504
7.496
7.483
7.476
6.877
6.872
6.861
6.855
6.848
3.814
3.808
3.796
3.792
3.784
3.775
3.771
3.765
3.760
3.753
3.749
3.744
2.868
2.858
2.826
2.816
2.653
2.633
2.608
2.581
1.575
0.000
3.00
2.01
2.02
1.06
1.07
PPM

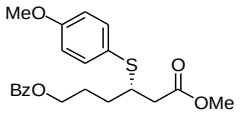

169.998
160.628
136.961
130.421
127.647
124.874
122.100
121.969
114.685
77.318
77.000
76.682
55.336
52.348
49.408
49.113
48.819
48.533
34.077
34.054
34.030
34.014
PPM



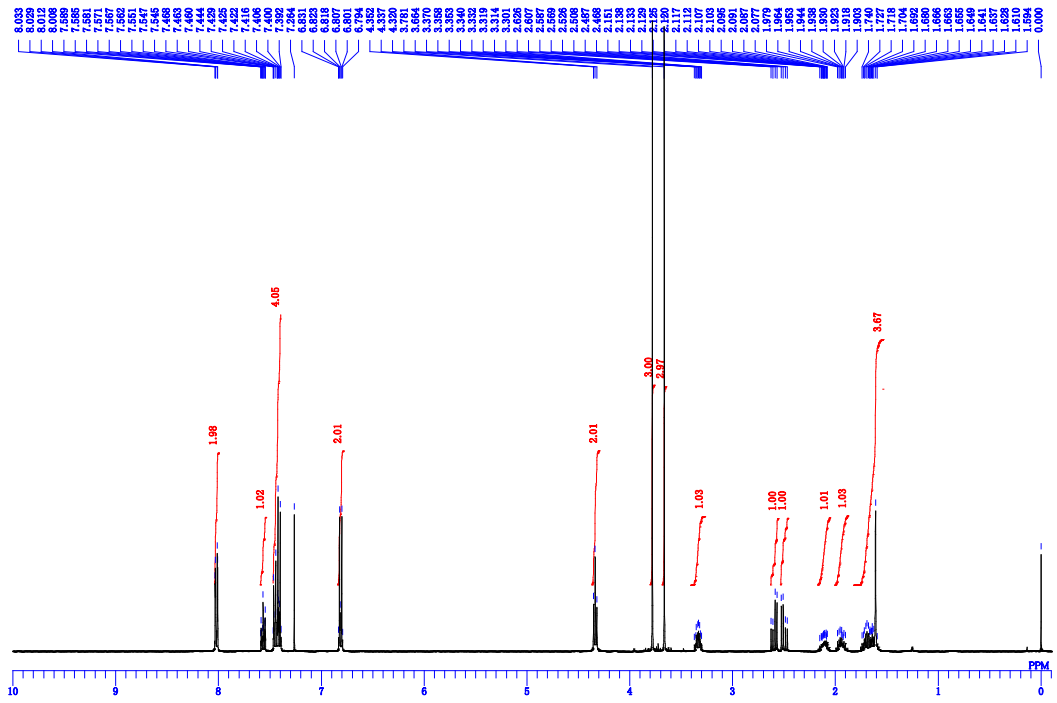
(*R*)-4t-[OMe]

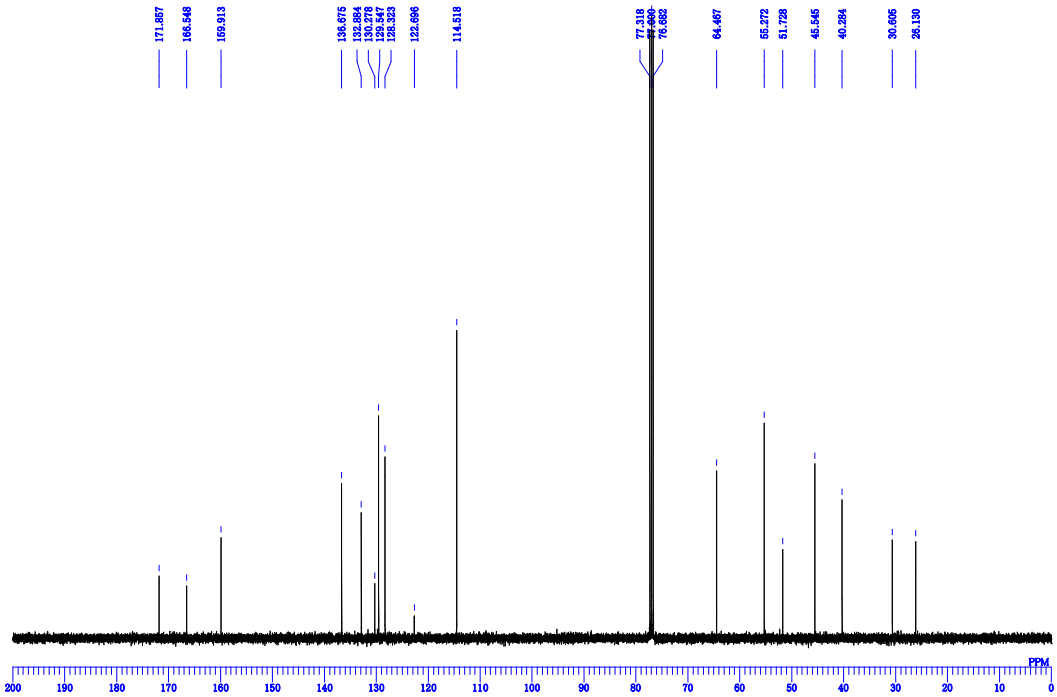


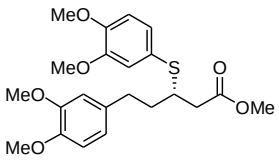



MeO
S
O
BzO
OMe

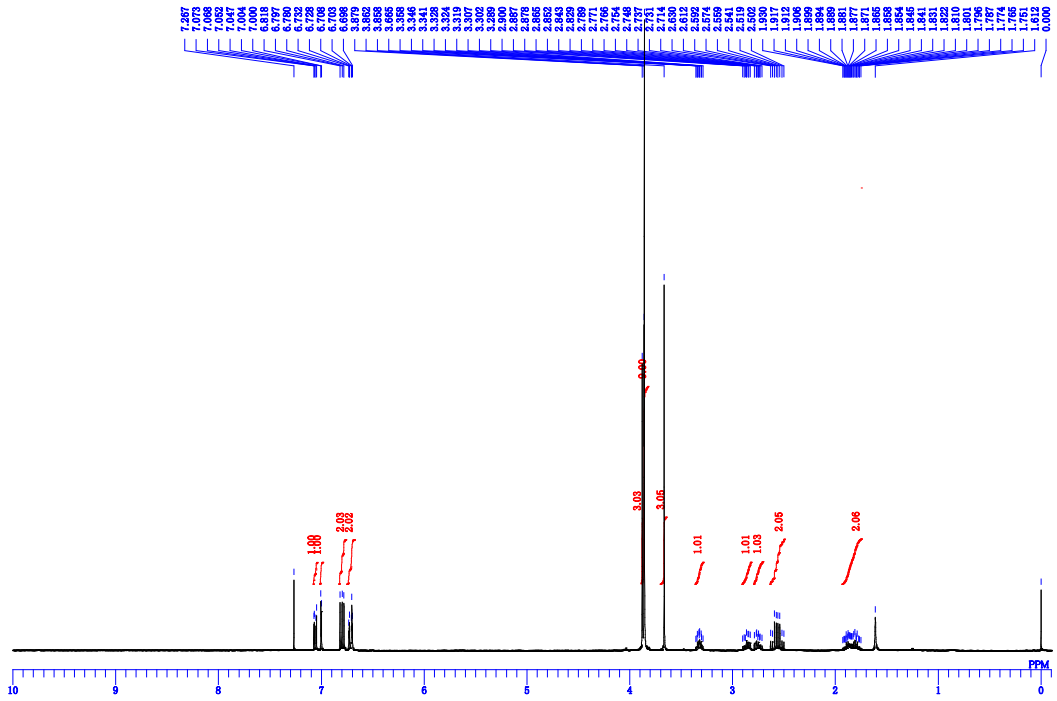
(*S*)-4u-[OMe]

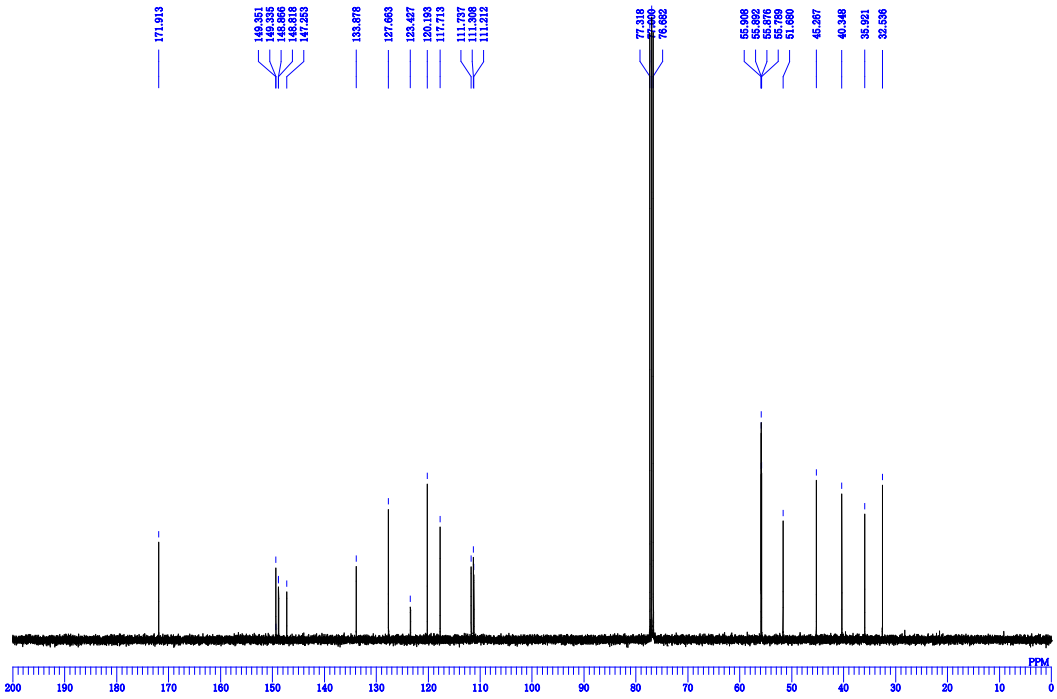

1.98
1.02
4.05
2.01
2.01
3.00
2.97
1.03
1.00
1.00
1.01
1.03
3.67
PPM

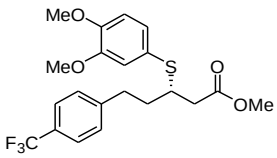

171.857
166.548
159.913
136.675
132.884
130.278
129.547
128.323
122.696
114.518
77.318
77.000
76.682
64.467
55.272
51.728
45.545
40.284
30.606
26.130
PPM



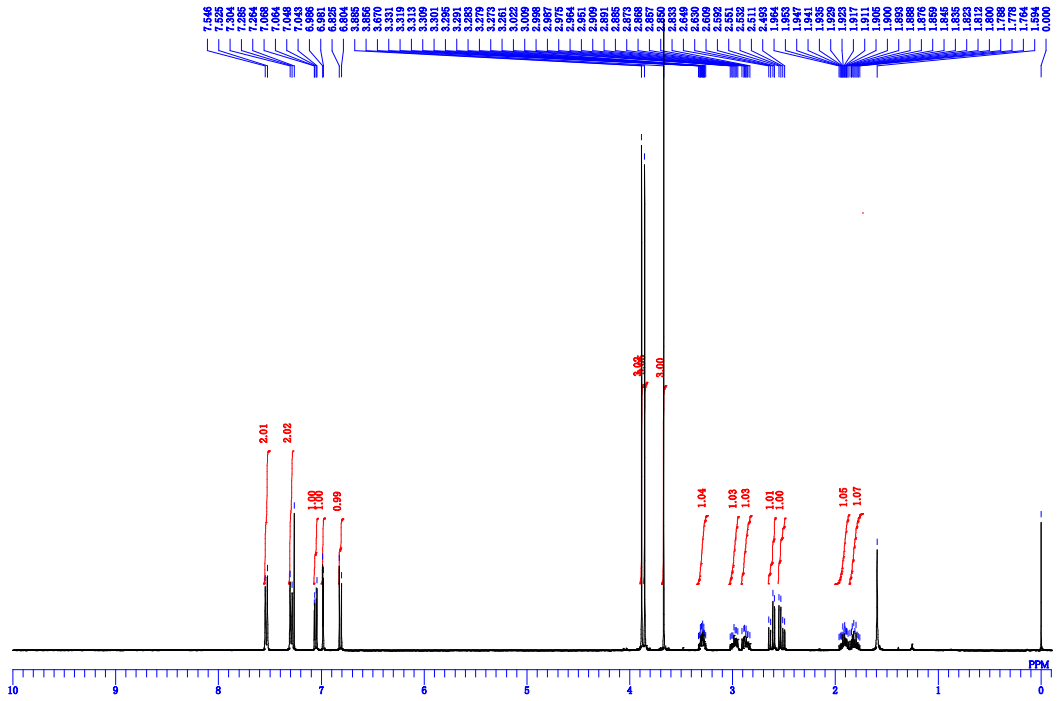
(*S*)-4v-[OMe]

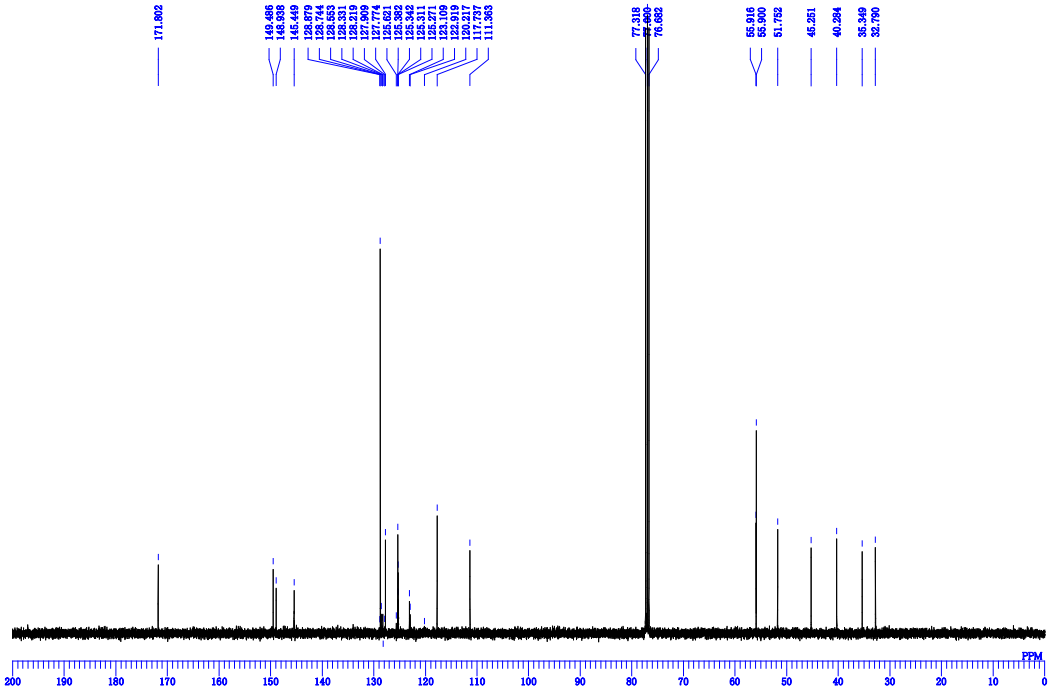





MeO
MeO
S
O
OMe
F3C

(*S*)-4w-[OMe]


2.01
2.02
1.00
1.00
0.99
3.02
3.00
1.04
1.03
1.03
1.01
1.00
1.06
1.07
PPM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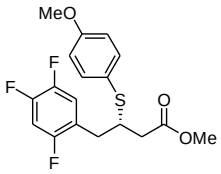
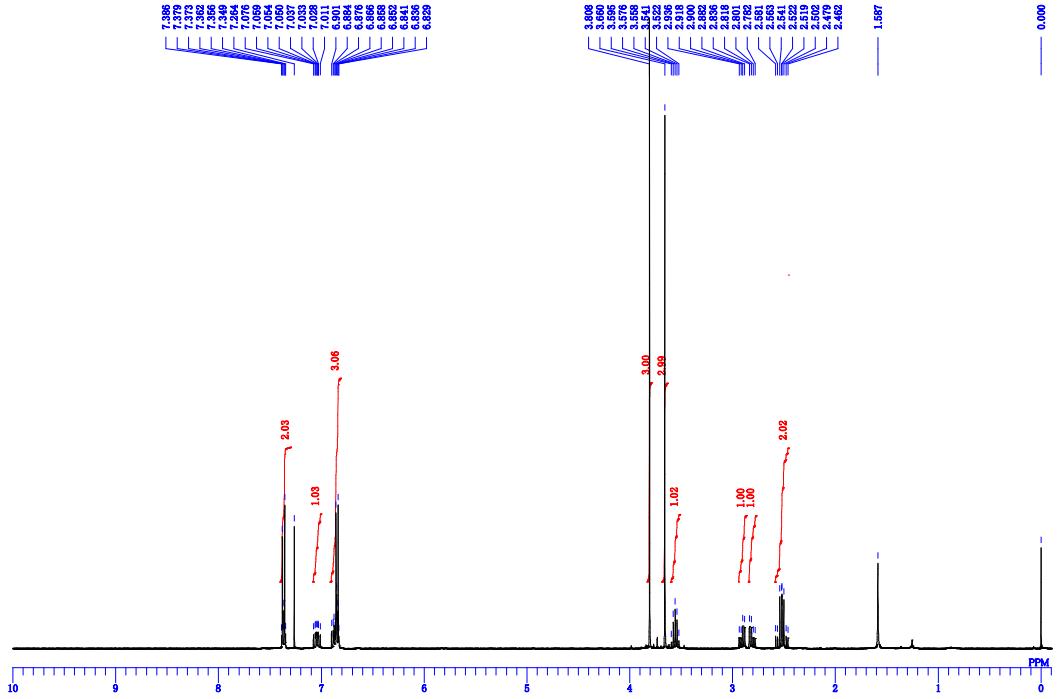
149.486
148.508
145.449
128.879
128.744
128.553
128.331
128.219
127.909
127.774
125.621
125.382
125.342
125.311
123.271
123.109
122.919
120.217
117.737
111.563
77.318
77.000
76.682
55.916
55.900
51.752
45.251
40.264
35.349
32.790
PPM


MeO
F
F
S
O
OMe
F

(*S*)-4x-[OMe]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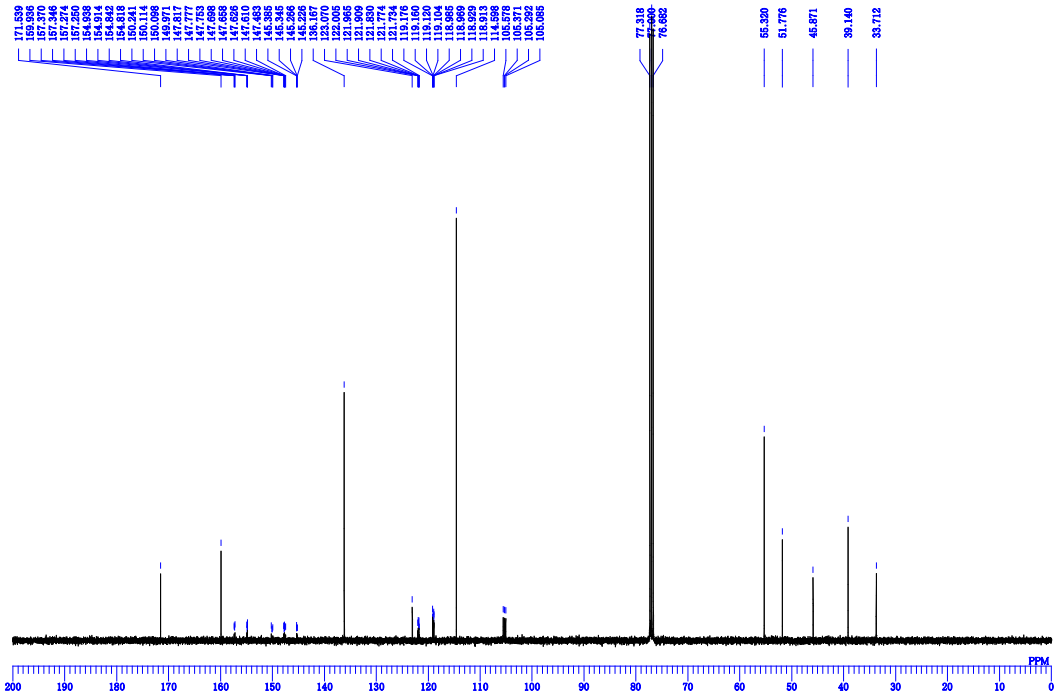
7.375
7.373
7.362
7.356
7.349
7.294
7.076
7.069
7.054
7.050
7.037
7.033
7.028
7.011
6.891
6.886
6.876
6.866
6.858
6.852
6.841
6.836
6.829
3.698
3.690
3.596
3.576
3.558
3.541
3.532
3.392
2.918
2.900
2.882
2.836
2.818
2.801
2.782
2.581
2.563
2.541
2.522
2.519
2.502
2.479
2.462
1.587
0.000
2.03
1.03
3.06
3.00
2.99
1.02
1.00
1.00
2.02
PPM
10
9
8
7
6
5
4
3
2
1
0


171.539
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157.370
157.346
157.274
157.250
154.938
154.914
154.844
154.818
150.241
150.114
150.088
149.977
147.817
147.777
147.753
147.698
147.658
147.626
147.610
147.483
145.385
145.345
145.286
145.226
136.167
123.070
122.995
122.965
121.909
121.830
121.774
121.734
119.175
119.160
119.120
119.104
118.965
118.949
118.929
118.913
114.598
105.578
105.571
105.392
105.086
77.318
77.000
76.682
55.320
51.776
45.671
39.140
33.712
PPM
200
190
180
170
160
150
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120
110
100
90
80
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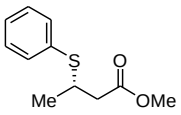
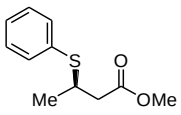
60
50
40
30
20
10
0

13. Copies of HPLC Chart



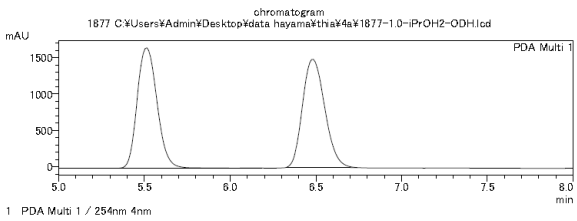
(*S*)-4a-[OMe]



(*R*)-4a-[OMe]

rac-**4a-[OMe]**

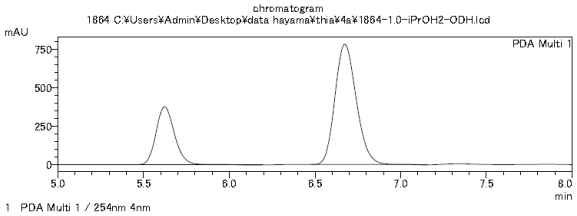
peak#	retention time (min)	area	area (%)
1	5.507	13359943	49.911
2	6.476	13407857	50.089



(*S*)-**4a-[OMe]** (table 1, entry 1)

reaction catalyzed by **1a** in CCl_4

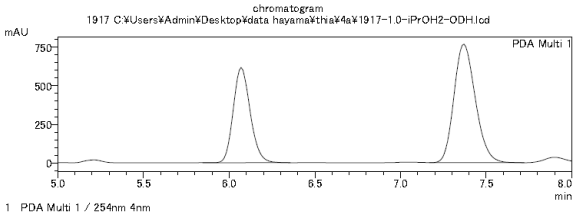
peak#	retention time (min)	area	area (%)
1	5.617	2819391	29.347
2	6.668	6787732	70.653



(*S*)-**4a-[OMe]** (table 1, entry 2)

reaction catalyzed by **1a** in CH_2Cl_2

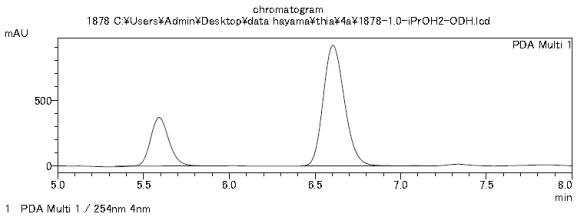
peak#	retention time (min)	area	area (%)
1	6.064	4258722	38.919
2	7.363	6683770	61.081



(*S*)-**4a-[OMe]** (table 1, entry 3)

reaction catalyzed by **1a** in hexane

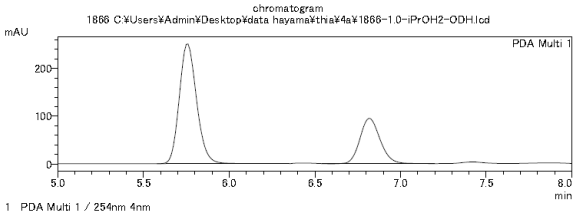
peak#	retention time (min)	area	area (%)
1	5.585	2739814	25.799
2	6.599	7879964	74.201



(*R*)-**4a-[OMe]** (table 1, entry 4)

reaction catalyzed by **1a** in CH_3CN

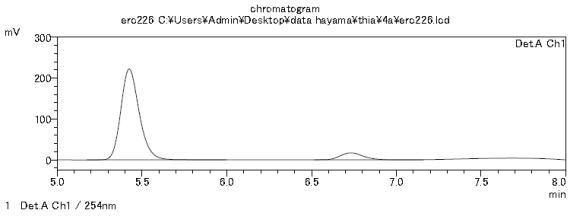
peak#	retention time (min)	area	area (%)
1	5.750	1757448	69.551
2	6.813	769396	30.449



(*R*)-**4a-[OMe]** (table 1, entry 5)

reaction catalyzed by **1a** in acetone

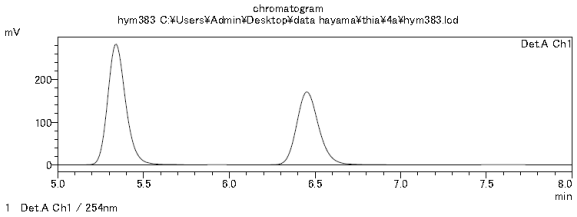
peak#	retention time (min)	area	area (%)
1	5.420	1678426	91.125
2	6.727	163478	8.875



(*R*)-**4a-[OMe]** (table 1, entry 8)

reaction catalyzed by **1a** in acetone without MS 4Å

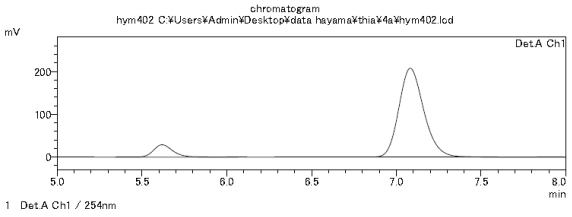
peak#	retention time (min)	area	area (%)
1	5.335	2062482	57.380
2	6.448	1531973	42.620



(*R*)-**4a-[OMe]** (table 1, entry 9)

reaction catalyzed by **1a** in CCl_4 (50 μL)

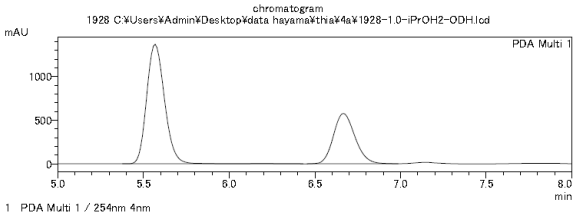
peak#	retention time (min)	area	area (%)
1	5.615	224892	9.602
2	7.078	2117302	90.398



(*R*)-**4a-[OMe]** (table 1, entry 10)

reaction catalyzed by **1b** in acetone

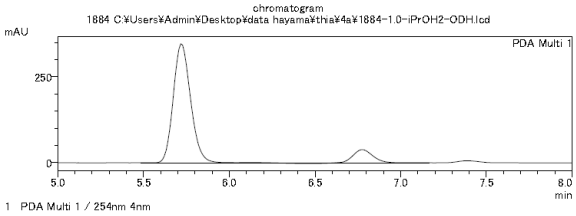
peak#	retention time (min)	area	area (%)
1	5.561	9939817	66.425
2	6.661	5024185	33.575



(*R*)-**4a-[OMe]** (table 1, entry 11)

reaction catalyzed by **1c** in acetone

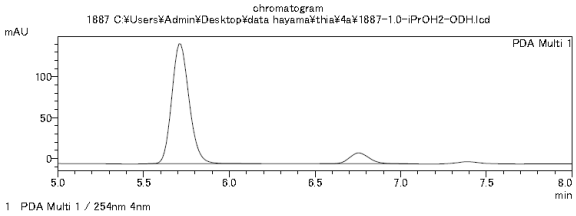
peak#	retention time (min)	area	area (%)
1	5.715	2442428	88.825
2	6.770	307284	11.175



(*R*)-**4a-[OMe]** (table 1, entry 12)

reaction catalyzed by **1d** in acetone

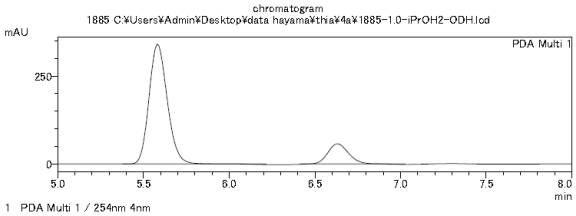
peak#	retention time (min)	area	area (%)
1	5.706	1032083	90.738
2	6.750	105349	9.262



(*R*)-**4a-[OMe]** (table 1, entry 13)

reaction catalyzed by **1e** in acetone

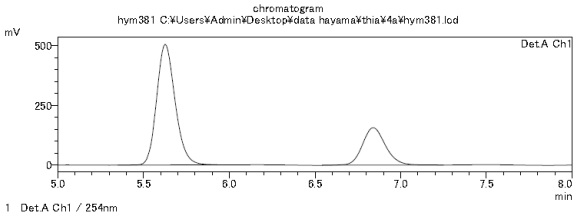
peak#	retention time (min)	area	area (%)
1	5.576	2525839	83.958
2	6.627	482614	16.042



(*R*)-**4a-[OMe]** (table 1, entry 14)

reaction catalyzed by **1f** in acetone

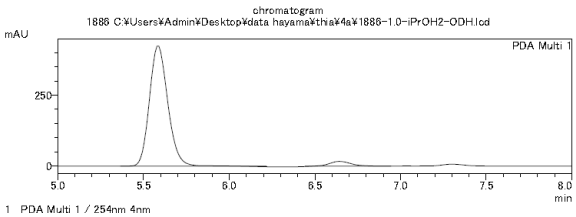
peak#	retention time (min)	area	area (%)
1	5.622	3791191	72.427
2	6.835	1443295	27.573



(*R*)-**4a-[OMe]** (table 1, entry 15)

reaction catalyzed by **1g** in acetone

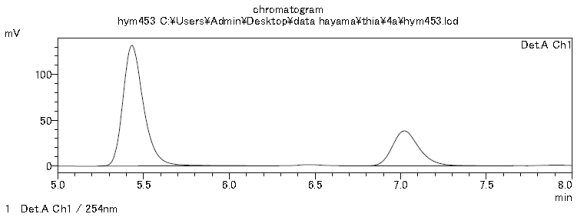
peak#	retention time (min)	area	area (%)
1	5.579	3154096	95.769
2	6.639	139351	4.231



(*R*)-**4a-[OMe]** (table 1, entry 16)

reaction catalyzed by **1h** in acetone

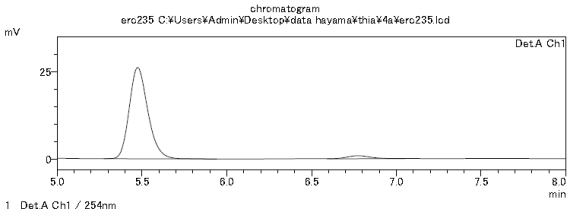
peak#	retention time (min)	area	area (%)
1	5.428	1105838	72.503
2	7.017	419310	27.497



(*R*)-**4a-[OMe]** (table 1, entry 17)

reaction catalyzed by **1g** with MS 4Å (100mg)

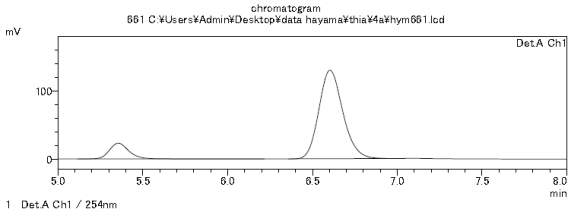
peak#	retention time (min)	area	area (%)
1	5.470	199853	96.015
2	6.768	8294	3.985



(*S*)-**4a-[OMe]** (table 1, entry 18)

reaction catalyzed by **1g** in CCl_4 (50 μL)

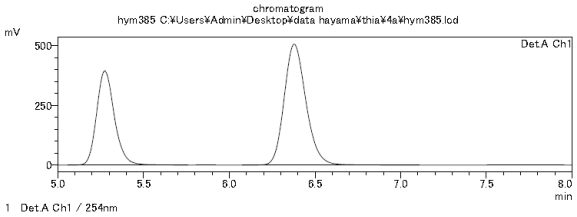
peak#	retention time (min)	area	area (%)
1	5.351	184731	12.597
2	6.599	1281780	87.403



(*S*)-**4a-[OMe]** (table s-1, entry 2)

reaction catalyzed by **1b** in CCl_4

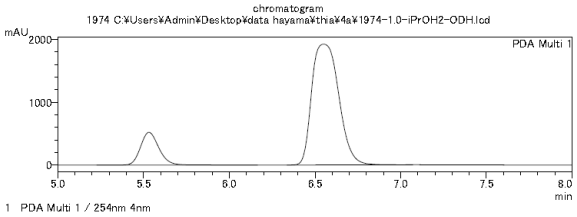
peak#	retention time (min)	area	area (%)
1	5.269	2837901	38.824
2	6.375	4471774	61.176



(*S*)-**4a-[OMe]** (table s-1, entry 3)

reaction catalyzed by **1c** in CCl_4

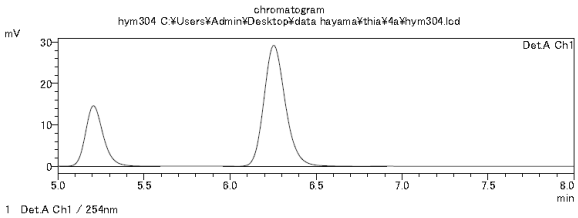
peak#	retention time (min)	area	area (%)
1	5.526	3858105	15.473
2	6.545	21075848	84.527



(*S*)-**4a-[OMe]** (table s-1, entry 4)

reaction catalyzed by **1d** in CCl_4

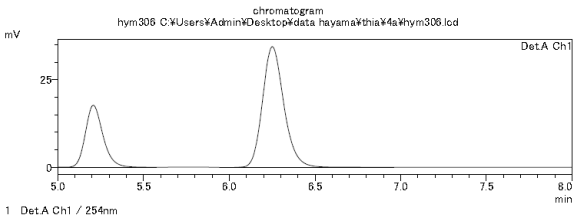
peak#	retention time (min)	area	area (%)
1	5.202	104987	29.282
2	6.250	253554	70.718



(*S*)-**4a-[OMe]** (table s-1, entry 5)

reaction catalyzed by **1e** in CCl_4

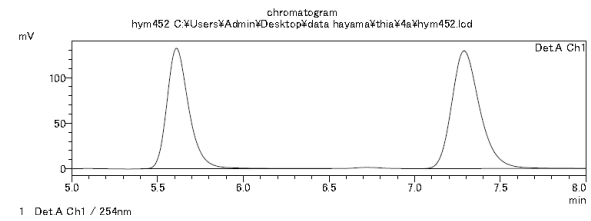
peak#	retention time (min)	area	area (%)
1	5.203	127232	29.835
2	6.247	299223	70.165



(*S*)-**4a-[OMe]** (table s-1, entry 6)

reaction catalyzed by **1f** in CCl_4

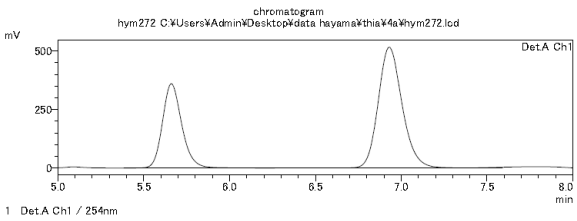
peak#	retention time (min)	area	area (%)
1	5.606	1175594	44.415
2	7.284	1471254	55.585



(*S*)-**4a-[OMe]** (table s-1, entry 7)

reaction catalyzed by **1g** in CCl_4

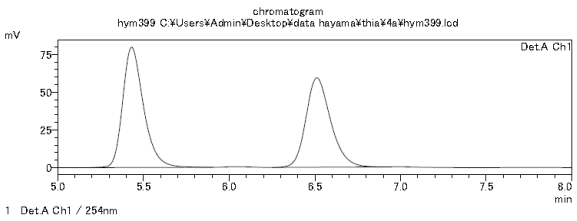
peak#	retention time (min)	area	area (%)
1	5.656	2801788	35.906
2	6.926	5001430	64.094



(*R*)-**4a-[OMe]** (table s-1, entry 8)

reaction catalyzed by **1h** in CCl_4

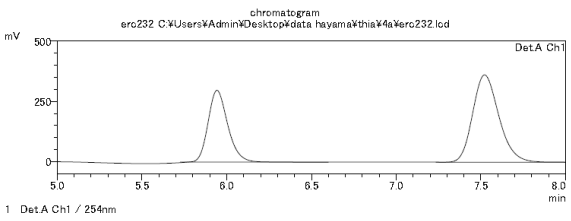
peak#	retention time (min)	area	area (%)
1	5.427	675912	53.141
2	6.508	596003	46.859



(*S*)-**4a-[OMe]** (table s-1, entry 9)

reaction catalyzed by **1a** in CCl_4 (5 mL)

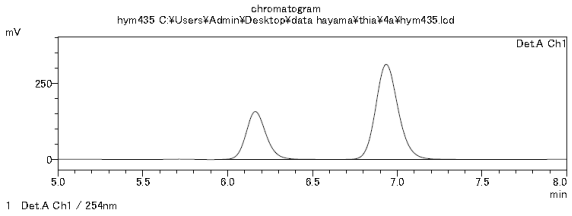
peak#	retention time (min)	area	area (%)
1	5.938	2408033	38.158
2	7.518	3902652	61.842



(*S*)-**4a-[OMe]** (table s-1, entry 10)

reaction catalyzed by **1a** in CCl_4 (2 mL)

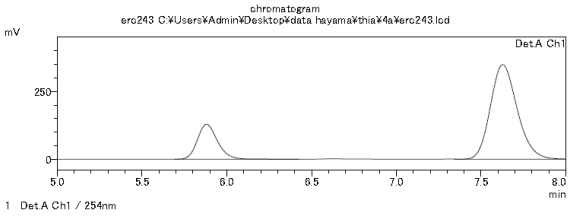
peak#	retention time (min)	area	area (%)
1	6.159	1278885	30.801
2	6.931	2873267	69.199



(*S*)-**4a-[OMe]** (table s-1, entry 11)

reaction catalyzed by **1a** in CCl_4 (0.5 mL)

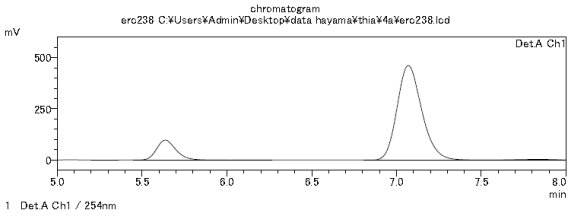
peak#	retention time (min)	area	area (%)
1	5.876	1059860	21.583
2	7.623	3850792	78.417



(*S*)-**4a-[OMe]** (table s-1, entry 12)

reaction catalyzed by **1a** in CCl_4 (0.25 mL)

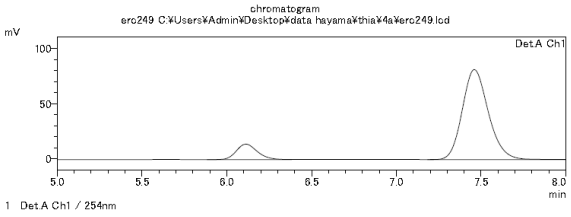
peak#	retention time (min)	area	area (%)
1	5.632	779326	14.229
2	7.065	4697522	85.771



(*S*)-**4a-[OMe]** (table s-1, entry 13)

reaction catalyzed by **1a** in CCl_4 (0.1 mL)

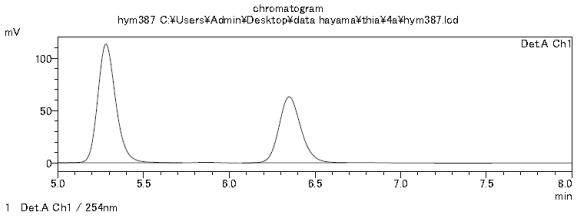
peak#	retention time (min)	area	area (%)
1	6.108	119369	12.046
2	7.456	871596	87.954



(*R*)-**4a-[OMe]** (table s-2, entry 1)

reaction catalyzed by **1a** in *n*-hexane (5 mL)

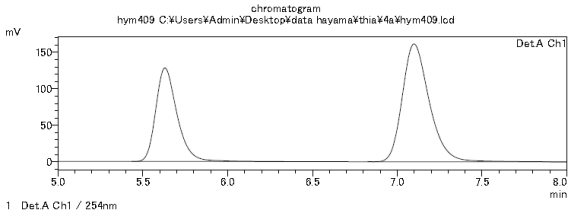
peak#	retention time (min)	area	area (%)
1	5.276	827642	59.643
2	6.345	560015	40.357



(*S*)-**4a-[OMe]** (table s-2, entry 2)

reaction catalyzed by **1a** in *n*-hexane (2 mL)

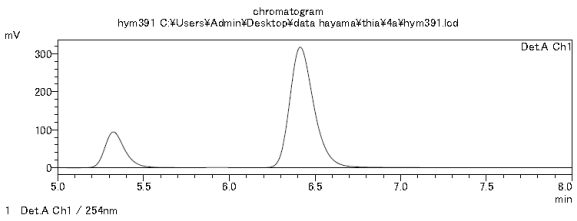
peak#	retention time (min)	area	area (%)
1	5.626	1122885	38.398
2	7.095	1801392	61.602



(*S*)-**4a-[OMe]** (table s-2, entry 4)

reaction catalyzed by **1a** in *n*-hexane (0.5 mL)

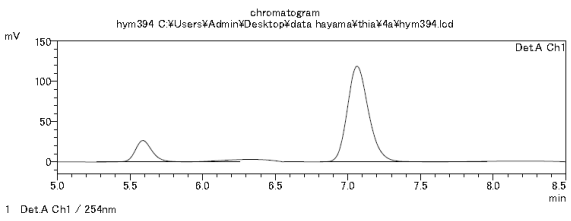
peak#	retention time (min)	area	area (%)
1	5.320	762686	19.658
2	6.410	3117903	80.342



(*S*)-**4a-[OMe]** (table s-2, entry 5)

reaction catalyzed by **1a** in *n*-hexane (0.25 mL)

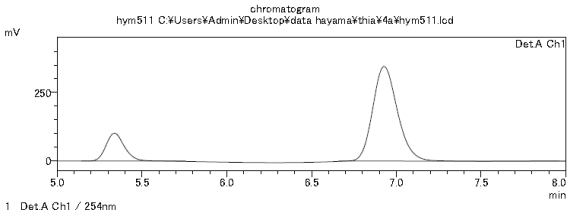
peak#	retention time (min)	area	area (%)
1	5.585	211133	14.900
2	7.059	1205890	85.100



(*S*)-**4a-[OMe]** (table s-2, entry 6)

reaction catalyzed by **1a** in CH_2Cl_2 (0.1 mL)

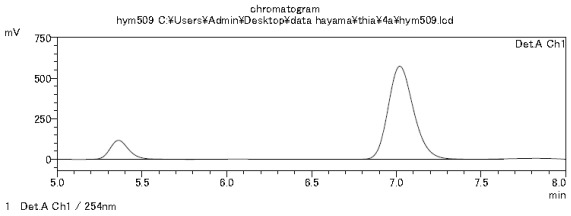
peak#	retention time (min)	area	area (%)
1	5.333	769070	18.030
2	6.924	3496345	81.970



(*S*)-**4a-[OMe]** (table s-2, entry 7)

reaction catalyzed by **1a** in *n*-hexane/CH_2Cl_2 (0.1 mL)

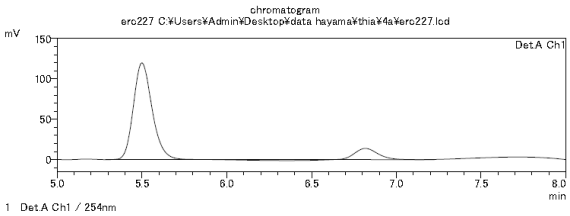
peak#	retention time (min)	area	area (%)
1	5.357	894921	13.049
2	7.016	5963293	86.951



(*R*)-**4a-[OMe]** (table s-3, entry 1)

reaction catalyzed by **1a** in acetone (5 mL)

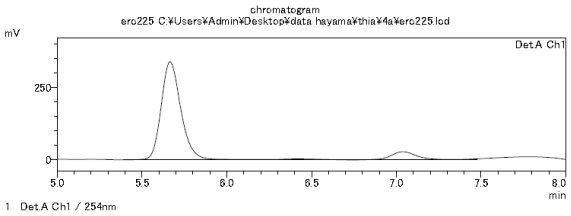
peak#	retention time (min)	area	area (%)
1	5.495	920869	87.371
2	6.813	133082	12.629



(*R*)-**4a-[OMe]** (table s-3, entry 2)

reaction catalyzed by **1a** in acetone (2 mL)

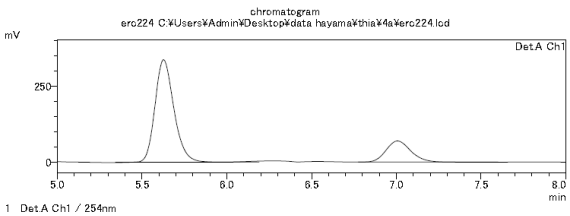
peak#	retention time (min)	area	area (%)
1	5.661	2703924	91.104
2	7.034	264038	8.896



(*R*)-**4a-[OMe]** (table s-3, entry 4)

reaction catalyzed by **1a** in acetone (0.5 mL)

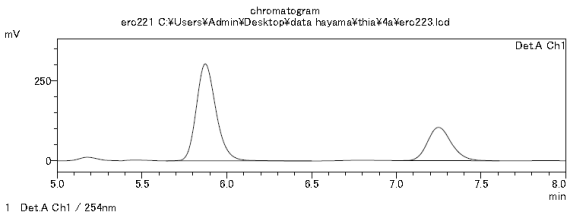
peak#	retention time (min)	area	area (%)
1	5.623	2603781	78.663
2	7.002	706253	21.337



(*R*)-**4a-[OMe]** (table s-3, entry 5)

reaction catalyzed by **1a** in acetone (0.25 mL)

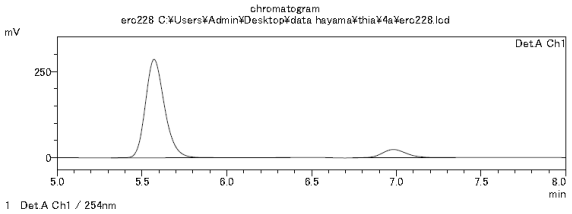
peak#	retention time (min)	area	area (%)
1	5.869	2438891	70.403
2	7.245	1025282	29.597



(*R*)-**4a-[OMe]** (table s-3, entry 6)

reaction catalyzed by **1a** with MS 4Å (100mg)

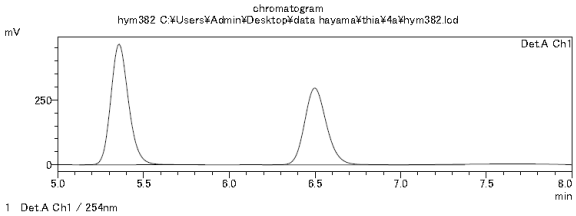
peak#	retention time (min)	area	area (%)
1	5.567	2241228	90.546
2	6.979	234022	9.454



(*S*)-**4a-[OMe]** (table s-4, entry 3)

reaction catalyzed by **S-1** in acetone

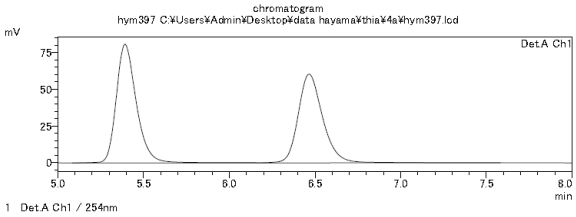
peak#	retention time (min)	area	area (%)
1	5.352	3352334	56.004
2	6.494	2633593	43.996



(*R*)-**4a-[OMe]** (table s-4, entry 9)

reaction catalyzed by **S-1** in CCl_4

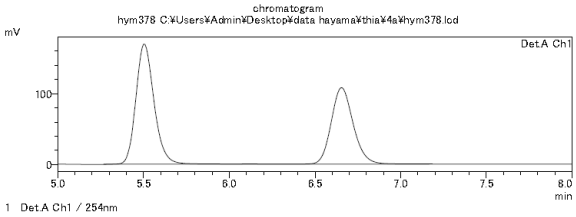
peak#	retention time (min)	area	area (%)
1	5.387	661975	52.343
2	6.461	602715	47.657



(*R*)-**4a-[OMe]** (table s-4, entry 13)

2a-[OMe] instead of **2a**

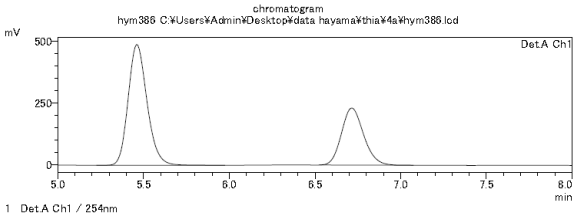
peak#	retention time (min)	area	area (%)
1	5.499	1247621	56.564
2	6.650	958054	43.436



(*R*)-**4a-[OMe]** (table s-4, entry 13)

3a (0.1 mmol) in $CDCl_3$ (0.3 mL)

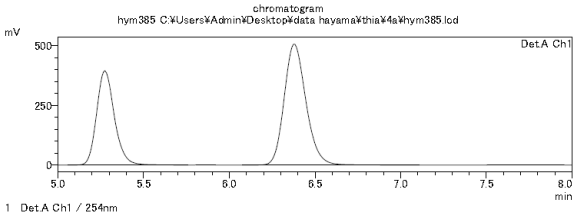
peak#	retention time (min)	area	area (%)
1	5.457	3728373	64.273
2	6.710	2072502	35.727



(*S*)-**4a-[OMe]** (table s-4, entry 14)

3a (0.01 mmol) in $CDCl_3$ (0.3 mL)

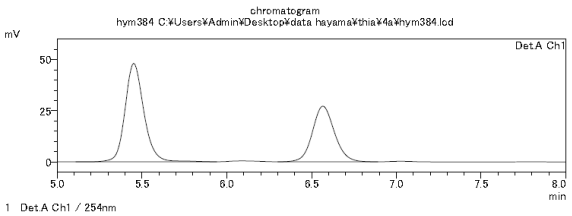
peak#	retention time (min)	area	area (%)
1	5.269	2837901	38.824
2	6.375	4471774	61.176

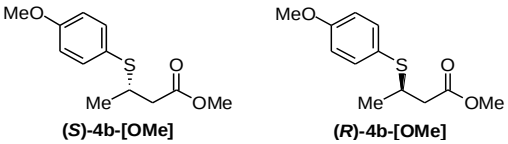


(*S*)-**4a-[OMe]** (table s-4, entry 16

reaction with acetone in CCl_4 (0.1mmol)

peak#	retention time (min)	area	area (%)
1	5.447	372777	60.288
2	6.563	245554	39.712

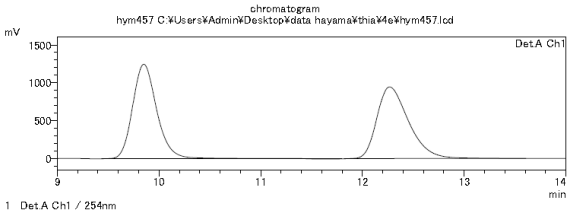




(*S*)-4b-[OMe] **(*R*)-4b-[OMe]**

rac-**4b-[OMe]**

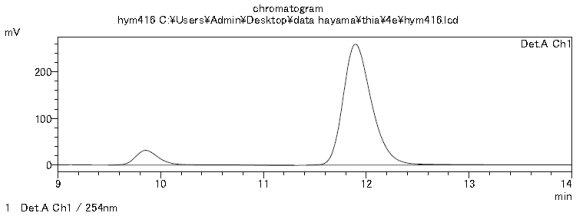
peak#	retention time (min)	area	area (%)
1	9.846	20566726	50.099
2	12.264	20485307	49.901



(*S*)-**4b-[OMe]**

reaction catalyzed by **1a** in CCl_4

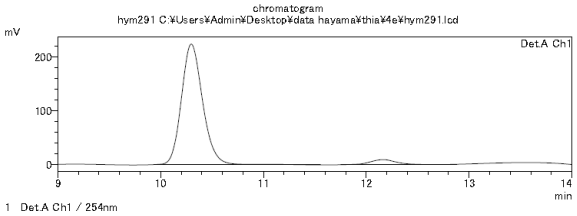
peak#	retention time (min)	area	area (%)
1	9.850	495481	9.031
2	11.891	4990693	90.969



(*R*)-**4b-[OMe]**

reaction catalyzed by **1g** in acetone

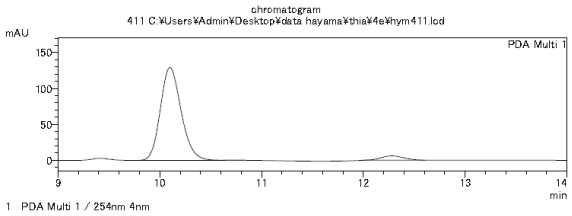
peak#	retention time (min)	area	area (%)
1	10.294	3196978	95.411
2	12.153	153750	4.589

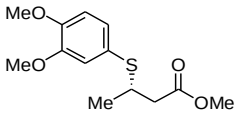


(*R*)-**4b-[OMe]**

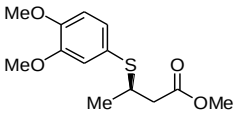
reaction catalyzed by **1a** in acetone

peak#	retention time (min)	area	area (%)
1	10.094	1835518	95.074
2	12.274	95097	4.926





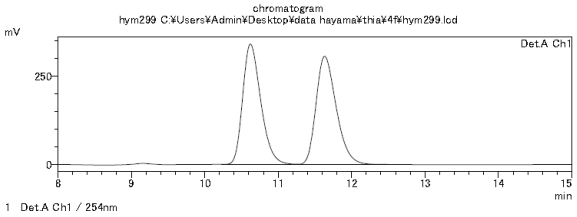
(*S*)-4c-[OMe]



(*R*)-4c-[OMe]

rac-**4c-[OMe]**

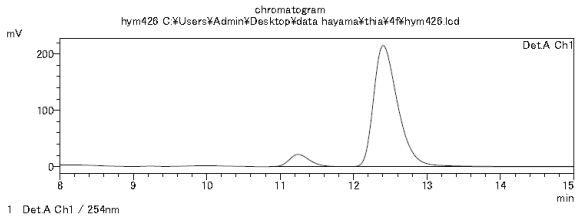
peak#	retention time (min)	area	area (%)
1	10.618	5850919	49.932
2	11.629	5866795	50.068



(*S*)-**4c-[OMe]**

reaction catalyzed by **1a** in CCl_4

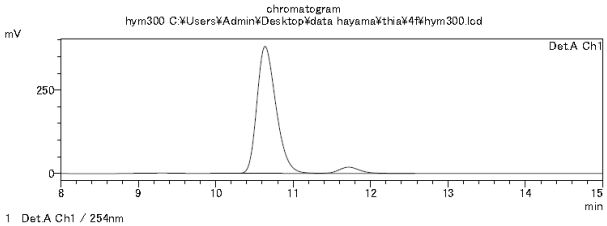
peak#	retention time (min)	area	area (%)
1	11.242	420081	7.855
2	12.399	4928024	92.145



(*R*)-**4c-[OMe]**

reaction catalyzed by **1g** in acetone

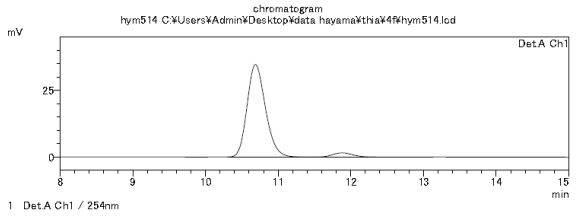
peak#	retention time (min)	area	area (%)
1	10.634	6487041	95.007
2	11.712	340913	4.993

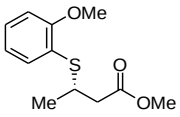


(*R*)-**4c-[OMe]**

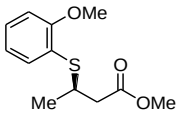
reaction catalyzed by **1a** in acetone

peak#	retention time (min)	area	area (%)
1	10.684	613350	95.075
2	11.876	31773	4.925





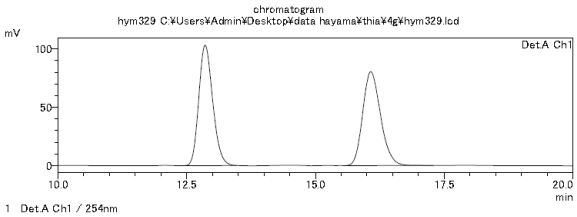
(*S*)-4d-[OMe]



(*R*)-4d-[OMe]

rac-**4d-[OMe]**

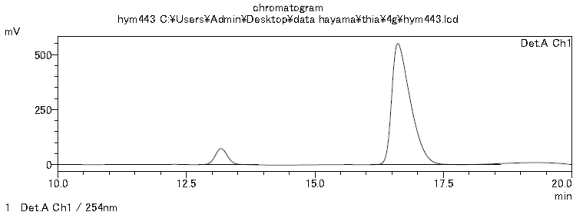
peak#	retention time (min)	area	area (%)
1	12.854	1946882	50.014
2	16.070	1945820	49.986



(*S*)-**4d-[OMe]**

reaction catalyzed by **1a** in CCl_4

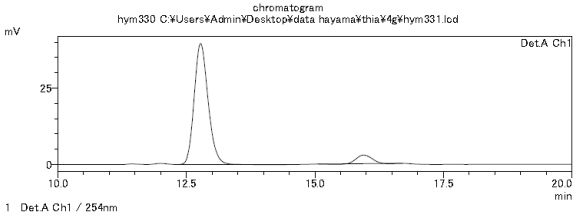
peak#	retention time (min)	area	area (%)
1	13.171	1222159	8.094
2	16.611	13878098	91.906

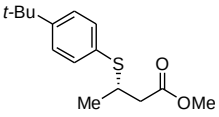


(*R*)-**4d-[OMe]**

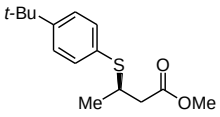
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	12.773	743851	93.024
2	15.949	55764	6.976





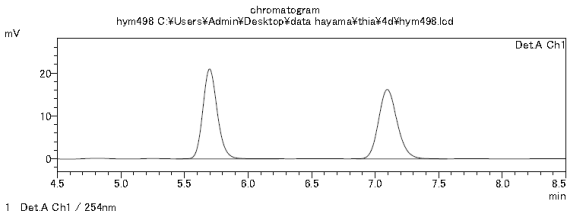
(*S*)-4e-[OMe]



(*R*)-4e-[OMe]

rac-**4e-[OMe]**

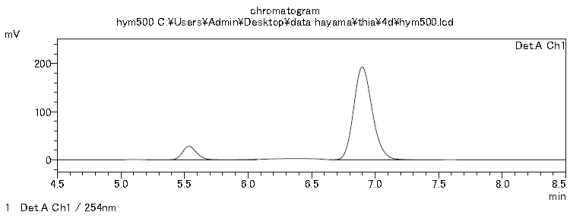
peak#	retention time (min)	area	area (%)
1	5.593	185304	49.979
2	7.091	185440	50.021



(*S*)-**4e-[OMe]**

reaction catalyzed by **1a** in CCl_4

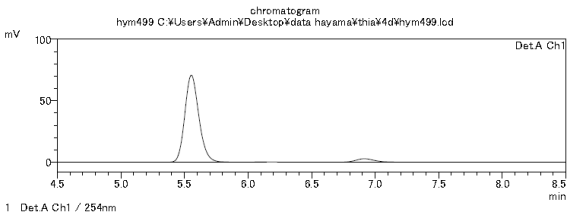
peak#	retention time (min)	area	area (%)
1	5.532	223491	10.233
2	6.894	1960560	89.767

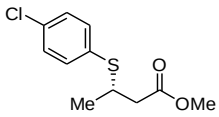


(*R*)-**4e-[OMe]**

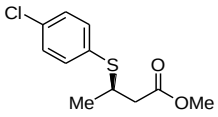
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	5.550	546731	94.892
2	6.911	29433	5.108





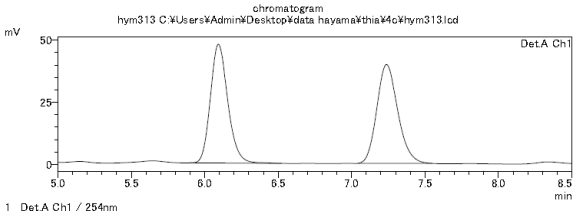
(*S*)-4f-[OMe]



(*R*)-4f-[OMe]

rac-**4f-[OMe]**

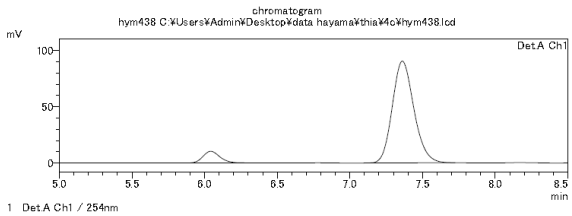
peak#	retention time (min)	area	area (%)
1	6.089	394984	49.959
2	7.234	395633	50.041



(*S*)-**4f-[OMe]**

reaction catalyzed by **1a** in CCl_4

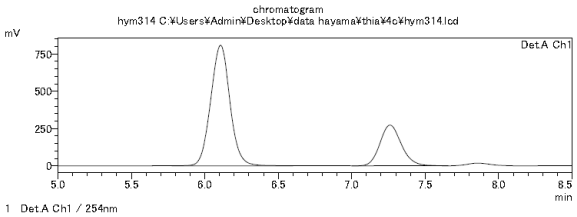
peak#	retention time (min)	area	area (%)
1	6.038	84787	8.303
2	7.357	936363	91.697

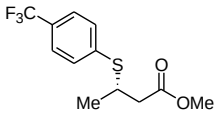


(*R*)-**4f-[OMe]**

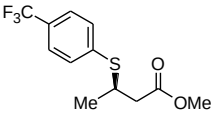
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	6.103	7372290	72.728
2	7.257	2764557	27.272





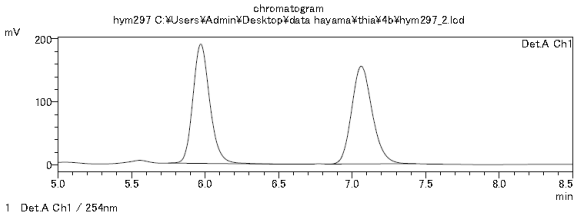
(*S*)-4g-[OMe]



(*R*)-4g-[OMe]

rac-**4g-[OMe]**

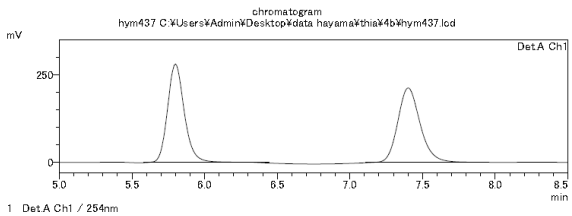
peak#	retention time (min)	area	area (%)
1	5.966	1513004	49.953
2	7.057	1515849	50.047



(*S*)-**4g -[OMe]**

reaction catalyzed by **1a** in CCl_4

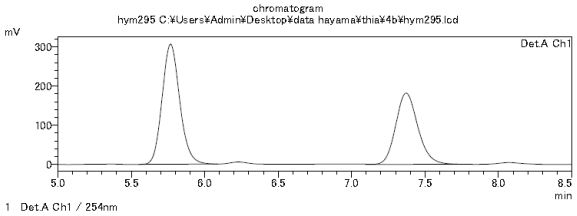
peak#	retention time (min)	area	area (%)
1	5.795	2257798	49.796
2	7.397	2276254	50.204

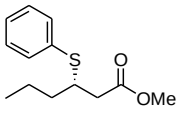


(*R*)-**4g-[OMe]**

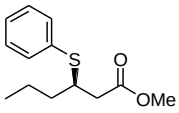
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	5.763	2566395	57.348
2	7.367	1908750	42.652





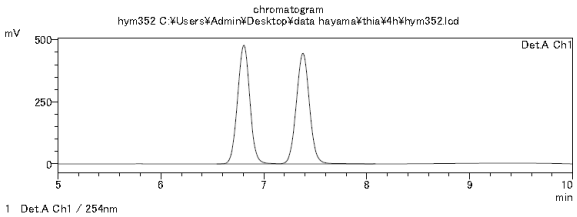
(*S*)-4h-[OMe]



(*R*)-4h-[OMe]

rac-**4h-[OMe]**

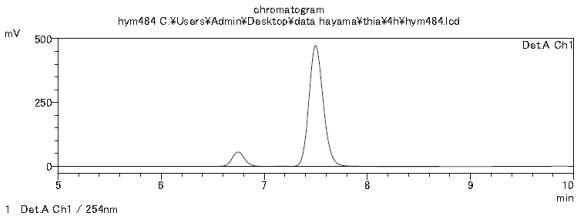
peak#	retention time (min)	area	area (%)
1	6.802	3971053	50.018
2	7.376	3968270	49.982



(*S*)-**4h-[OMe]**

reaction catalyzed by **1a** in CCl_4

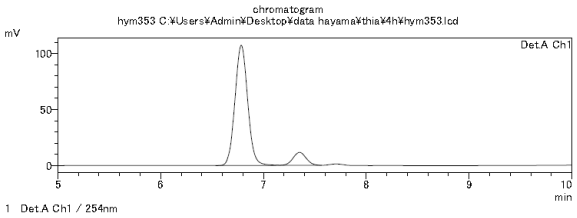
peak#	retention time (min)	area	area (%)
1	6.742	482347	9.532
2	7.494	4577960	90.468

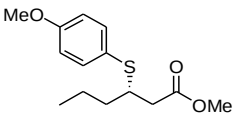


(*R*)-**4h-[OMe]**

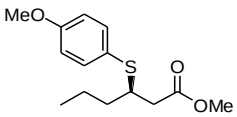
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	6.780	928297	89.982
2	7.347	103356	10.018





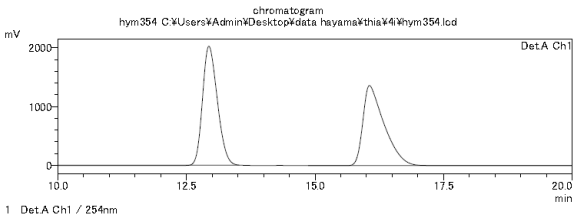
(*S*)-4i-[OMe]



(*R*)-4i-[OMe]

rac-**4i-[OMe]**

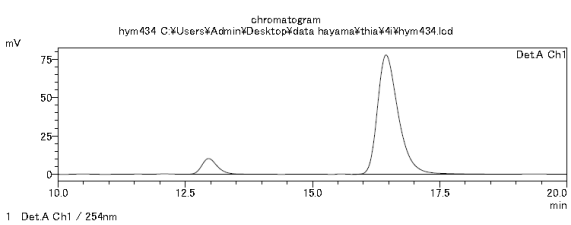
peak#	retention time (min)	area	area (%)
1	12.932	39085855	49.993
2	16.055	39096367	50.007



(*S*)-**4i-[OMe]**

reaction catalyzed by **1a** in CCl_4

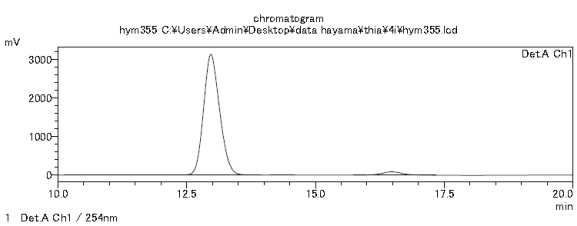
peak#	retention time (min)	area	area (%)
1	12.954	217766	8.961
2	16.442	2212516	91.039

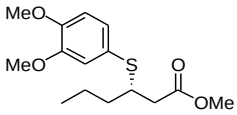


(*R*)-**4i-[OMe]**

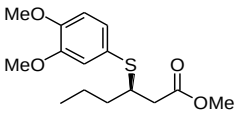
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	12.965	67767725	96.943
2	16.479	2137297	3.057





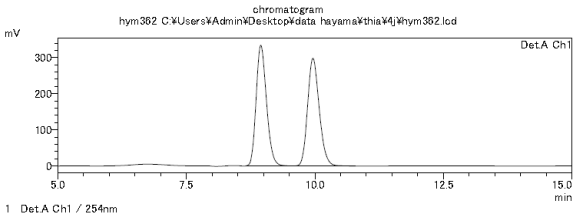
(*S*)-4j-[OMe]



(*R*)-4j-[OMe]

rac-**4j-[OMe]**

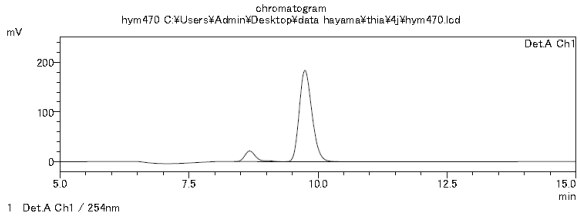
peak#	retention time (min)	area	area (%)
1	8.944	4667606	49.858
2	9.958	4694154	50.142



(*S*)-**4j-[OMe]**

reaction catalyzed by **1a** in CCl_4

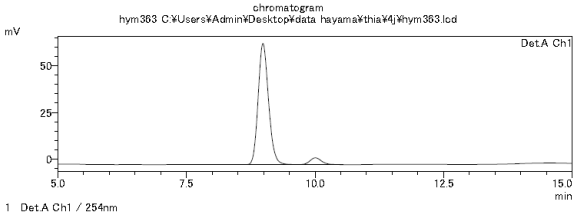
peak#	retention time (min)	area	area (%)
1	8.671	327119	9.424
2	9.743	3143957	90.576

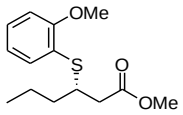


(*R*)-**4j-[OMe]**

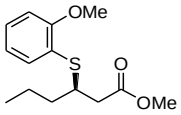
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	8.984	909856	94.136
2	10.003	56875	5.864





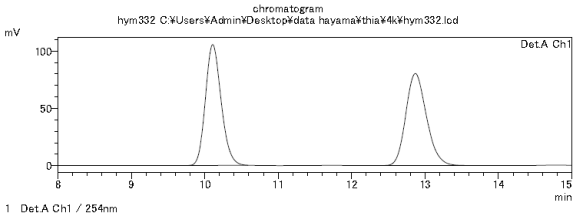
(*S*)-4k-[OMe]



(*R*)-4k-[OMe]

rac-**4k-[OMe]**

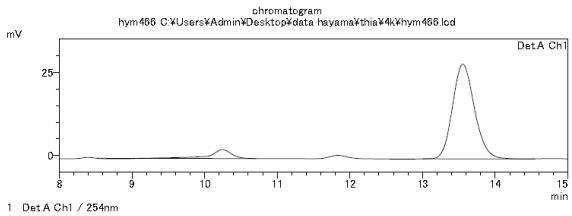
peak#	retention time (min)	area	area (%)
1	10.105	1572293	50.034
2	12.863	1570139	49.966



(*S*)-**4k-[OMe]**

reaction catalyzed by **1a** in CCl_4

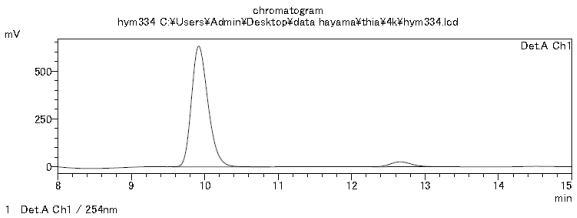
peak#	retention time (min)	area	area (%)
1	10.242	54779	8.381
2	13.549	598806	91.619

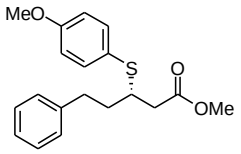


(*R*)-**4k-[OMe]**

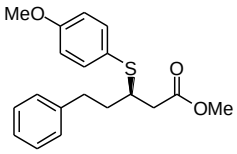
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	9.914	9859958	95.091
2	12.658	508985	4.909





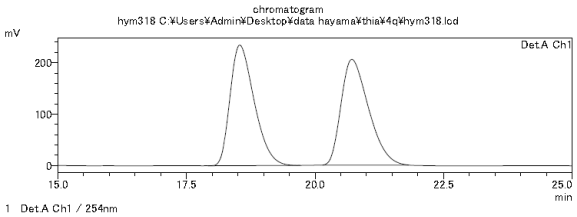
(*S*)-4l-[OMe]



(*R*)-4l-[OMe]

rac-**4l-[OMe]**

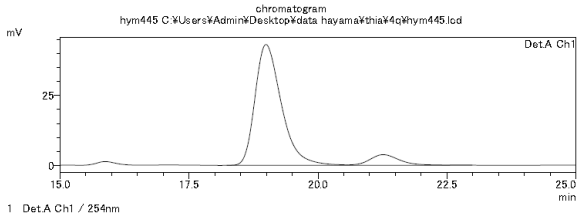
peak#	retention time (min)	area	area (%)
1	18.533	7666833	50.060
2	20.714	7648493	49.940



(*S*)-**4l-[OMe]**

reaction catalyzed by **1a** in CCl_4

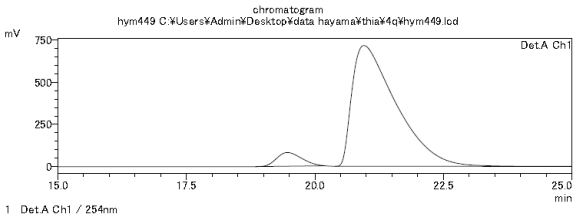
peak#	retention time (min)	area	area (%)
1	18.989	1526928	91.002
2	21.261	150977	8.998

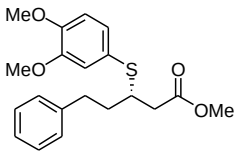


(*R*)-**4l-[OMe]**

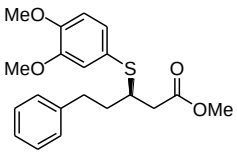
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	19.463	2757641	6.047
2	20.952	42848538	93.953





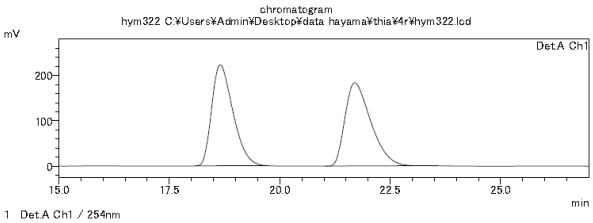
(*S*)-4m-[OMe]



(*R*)-4m-[OMe]

rac-**4m-[OMe]**

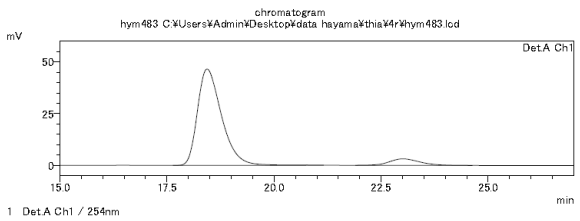
peak#	retention time (min)	area	area (%)
1	18.649	7449343	49.974
2	21.694	7457060	50.026



(*S*)-**4m-[OMe]**

reaction catalyzed by **1a** in CCl_4

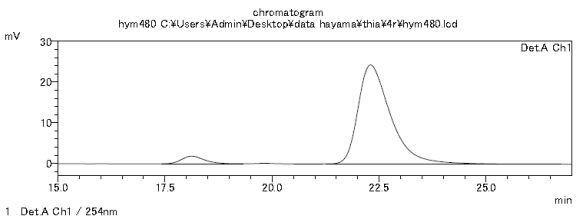
peak#	retention time (min)	area	area (%)
1	18.433	1824999	91.959
2	23.005	159587	8.041

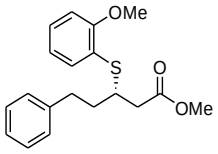


(*R*)-**4m-[OMe]**

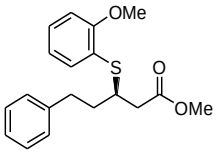
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	18.118	70229	5.184
2	22.295	1284436	94.816





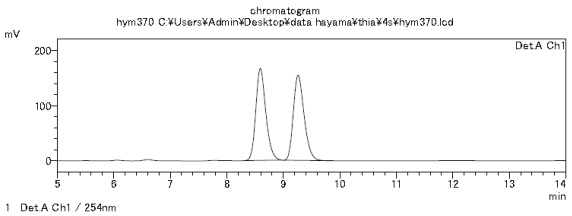
(*S*)-**4n-[OMe]**



(*R*)-**4n-[OMe]**

rac-**4n-[OMe]**

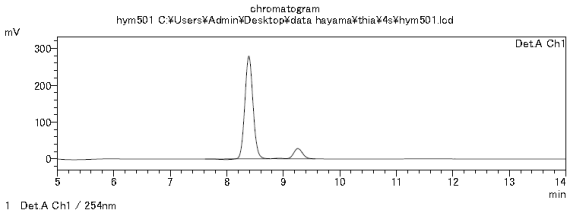
peak#	retention time (min)	area	area (%)
1	8.589	2055001	50.085
2	9.257	2048017	49.915



(*S*)-**4n-[OMe]**

reaction catalyzed by **1a** in CCl_4

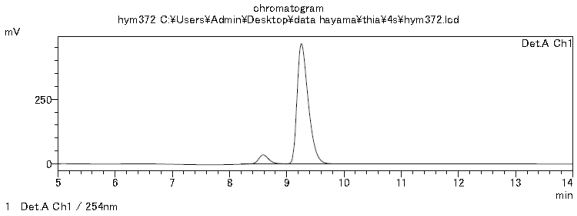
peak#	retention time (min)	area	area (%)
1	8.386	2785818	89.810
2	9.254	316079	10.190

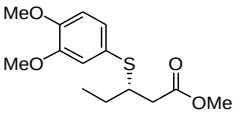


(*R*)-**4n-[OMe]**

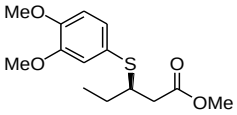
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	8.584	444353	6.574
2	9.251	6314790	93.426





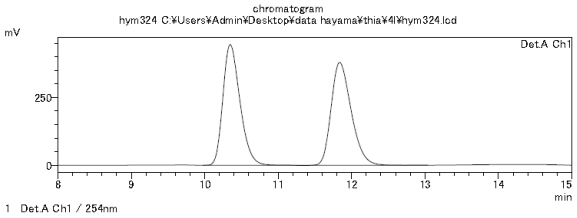
(*S*)-**4o-[OMe]**



(*R*)-**4o-[OMe]**

rac-**4o-[OMe]**

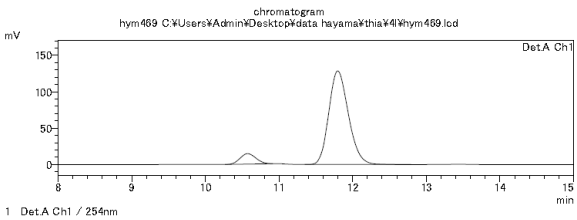
peak#	retention time (min)	area	area (%)
1	10.343	7211036	50.046
2	11.834	7197865	49.954



(*S*)-**4o-[OMe]**

reaction catalyzed by **1a** in CCl_4

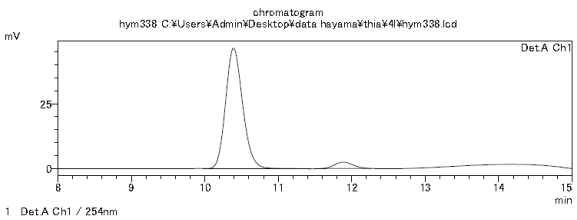
peak#	retention time (min)	area	area (%)
1	10.571	215319	8.290
2	11.793	2382030	91.710

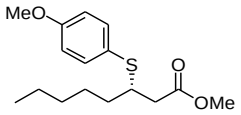


(*R*)-**4o-[OMe]**

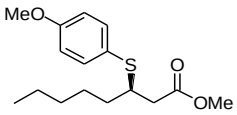
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	10.387	753451	94.517
2	11.881	43709	5.483





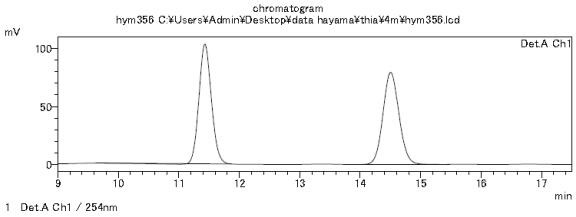
(*S*)-4p-[OMe]



(*R*)-4p-[OMe]

rac-**4p-[OMe]**

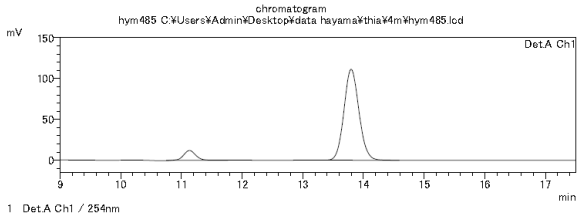
peak#	retention time (min)	area	area (%)
1	11.427	1463665	49.982
2	14.499	1464695	50.018



(*S*)-**4p-[OMe]**

reaction catalyzed by **1a** in CCl_4

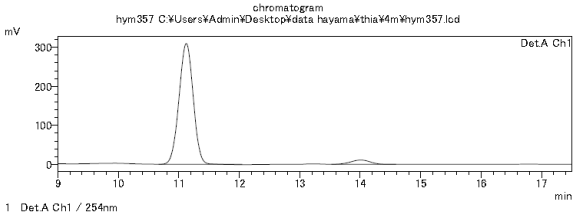
peak#	retention time (min)	area	area (%)
1	11.129	163143	7.855
2	13.793	1913737	92.145

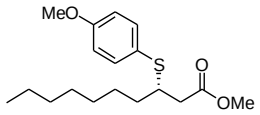


(*R*)-**4p-[OMe]**

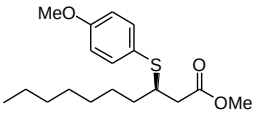
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	11.119	5049585	95.303
2	14.004	248891	4.697





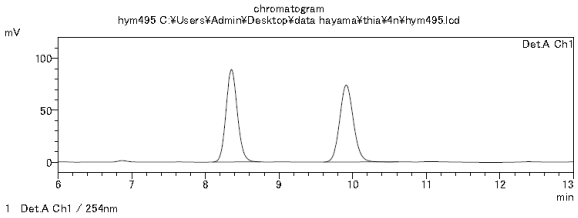
(*S*)-4q-[OMe]



(*R*)-4q-[OMe]

rac-**4q-[OMe]**

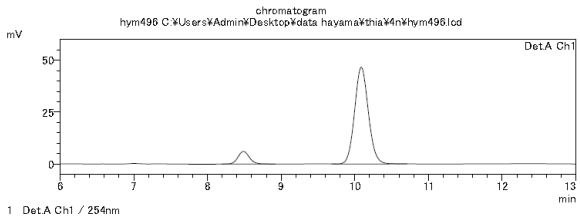
peak#	retention time (min)	area	area (%)
1	8.350	961822	50.029
2	9.909	960696	49.971



(*S*)-**4q-[OMe]**

reaction catalyzed by **1a** in CCl_4

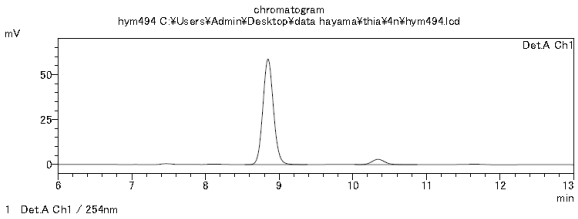
peak#	retention time (min)	area	area (%)
1	8.484	64970	9.663
2	10.083	607377	90.337

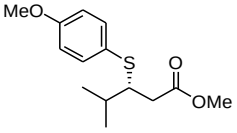


(*R*)-**4q-[OMe]**

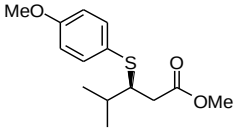
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	8.845	585052	94.233
2	10.339	35803	5.767





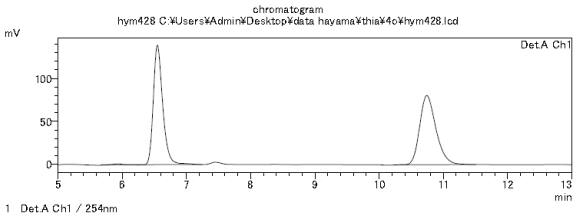
(*R*)-4r-[OMe]



(*S*)-4r-[OMe]

rac-**4r-[OMe]**

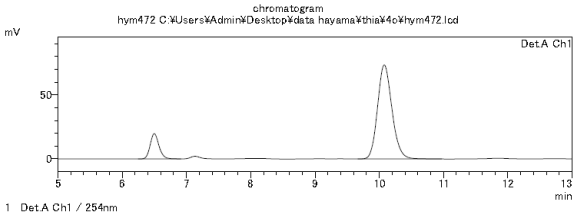
peak#	retention time (min)	area	area (%)
1	6.545	1421832	50.029
2	10.738	1420182	49.971



(*R*)-**4r-[OMe]**

reaction catalyzed by **1a** in CCl_4

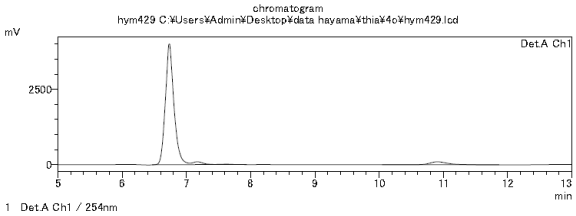
peak#	retention time (min)	area	area (%)
1	6.495	188558	14.136
2	10.074	1145320	85.864



(*S*)-**4r-[OMe]**

reaction catalyzed by **1g** in acetone

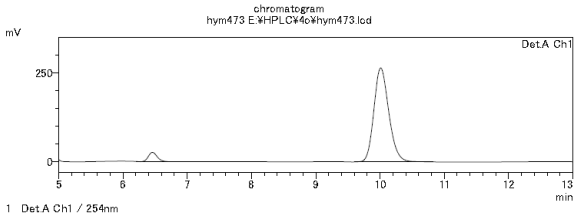
peak#	retention time (min)	area	area (%)
1	6.731	38435633	95.732
2	10.906	1713597	4.268

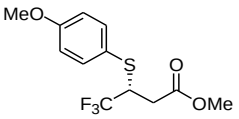


(*R*)-**4r-[OMe]**

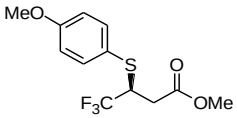
reaction catalyzed by **1a** in CCl_4 with benzoic acid

peak#	retention time (min)	area	area (%)
1	6.455	260851	5.773
2	10.006	4257764	94.227





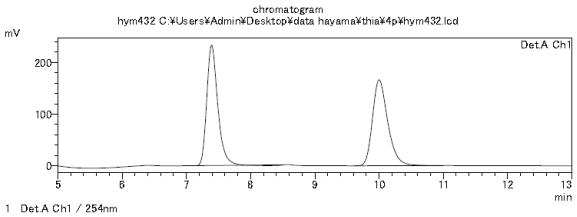
(*R*)-4s-[OMe]



(*S*)-4s-[OMe]

rac-**4s-[OMe]**

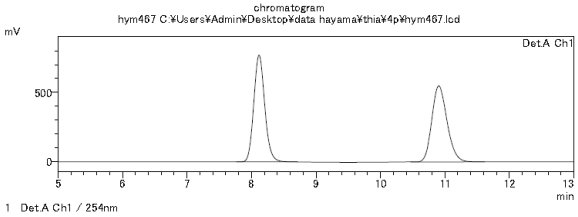
peak#	retention time (min)	area	area (%)
1	7.389	2747311	49.975
2	9.996	2750039	50.025



(*R*)-**4s-[OMe]**

reaction catalyzed by **1a** in CCl_4

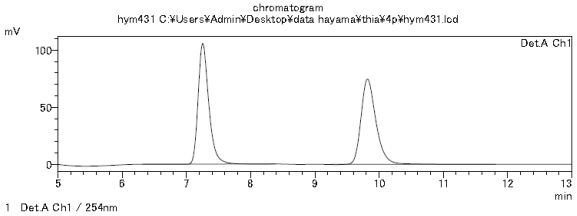
peak#	retention time (min)	area	area (%)
1	8.113	9084861	50.302
2	10.900	8975909	49.698

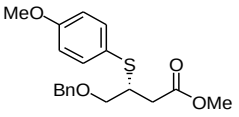


(*S*)-**4s-[OMe]**

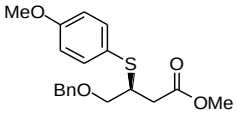
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	7.251	1208728	50.029
2	9.815	1207324	49.971





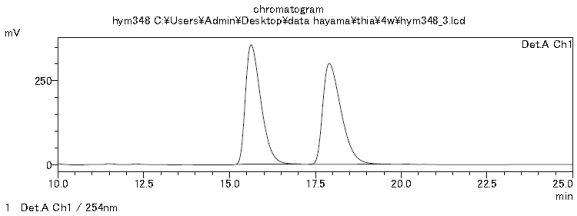
(*R*)-4t-[OMe]



(*S*)-4t-[OMe]

rac-**4t-[OMe]**

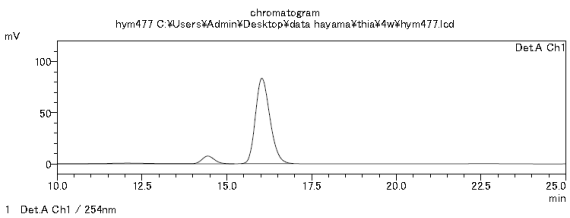
peak#	retention time (min)	area	area (%)
1	15.624	11141391	50.024
2	17.902	11130700	49.976



(*S*)-**4t-[OMe]**

reaction catalyzed by **1a** in CCl_4

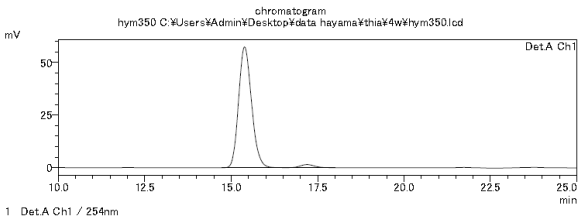
peak#	retention time (min)	area	area (%)
1	14.436	249965	9.082
2	16.031	2472327	90.918

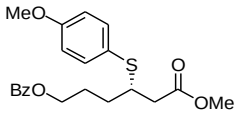


(*R*)-**4t-[OMe]**

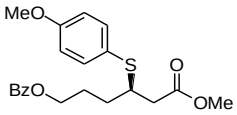
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	15.383	1503031	97.121
2	17.191	44558	2.879





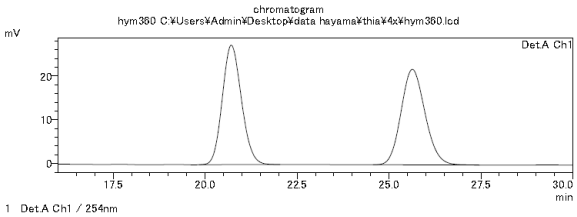
(*S*)-4u-[OMe]



(*R*)-4u-[OMe]

rac-**4u-[OMe]**

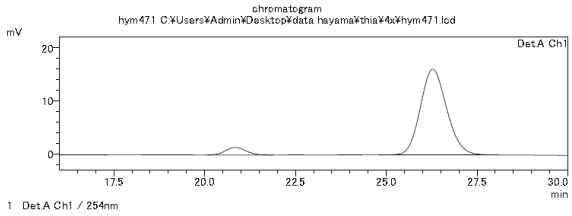
peak#	retention time (min)	area	area (%)
1	20.709	990647	49.986
2	25.631	991214	50.014



(*S*)-**4u-[OMe]**

reaction catalyzed by **1a** in CCl_4

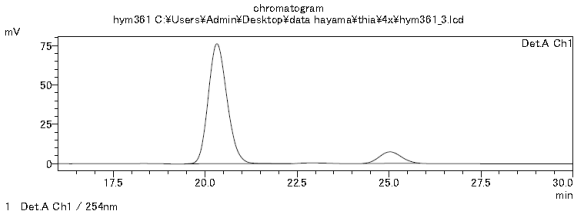
peak#	retention time (min)	area	area (%)
1	20.842	56103	6.462
2	26.275	812155	93.538

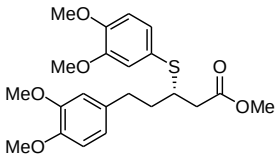


(*R*)-**4u-[OMe]**

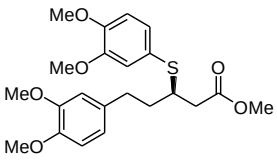
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	20.318	2718280	89.876
2	25.025	306197	10.124





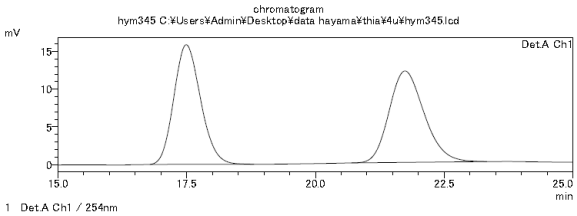
(*S*)-4v-[OMe]



(*R*)-4v-[OMe]

rac-**4v-[OMe]**

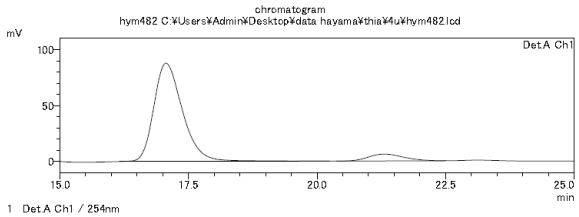
peak#	retention time (min)	area	area (%)
1	17.488	574032	49.973
2	21.735	574648	50.027



(*S*)-**4v-[OMe]**

reaction catalyzed by **1a** in CCl_4

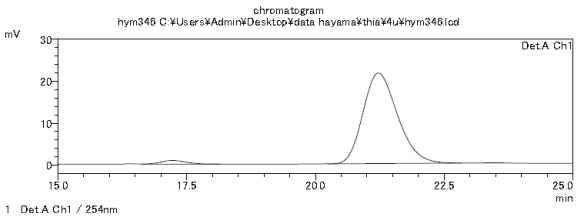
peak#	retention time (min)	area	area (%)
1	17.060	3385794	92.016
2	21.303	293761	7.984

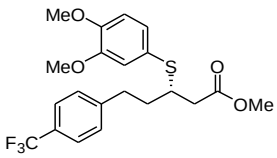


(*R*)-**4v-[OMe]**

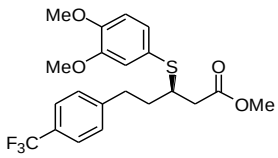
reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	17.227	30036	2.892
2	21.219	1008465	97.108





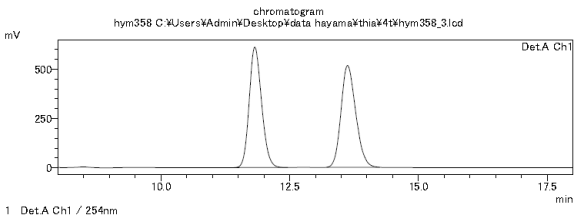
(*S*)-4w-[OMe]



(*R*)-4w-[OMe]

rac-**4w-[OMe]**

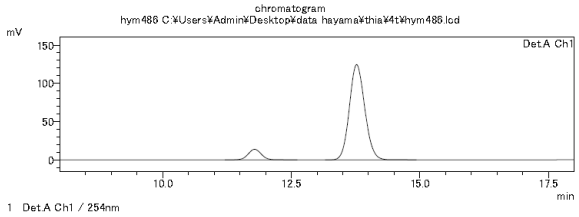
peak#	retention time (min)	area	area (%)
1	11.819	10281299	49.977
2	13.620	10290926	50.023



(*S*)-**4w-[OMe]**

reaction catalyzed by **1a** in CCl_4

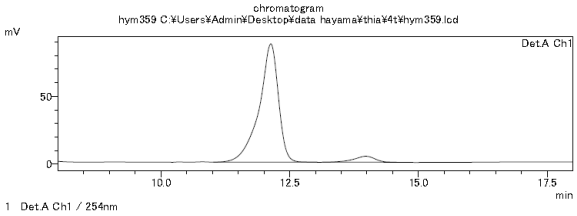
peak#	retention time (min)	area	area (%)
1	11.783	252266	8.866
2	13.767	2593043	91.134

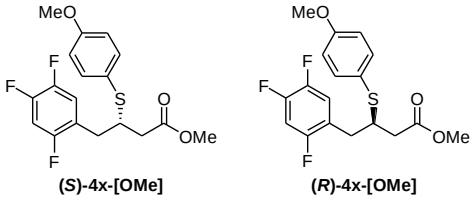


(*R*)-**4w-[OMe]**

reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	12.129	2272442	94.766
2	13.975	125518	5.234

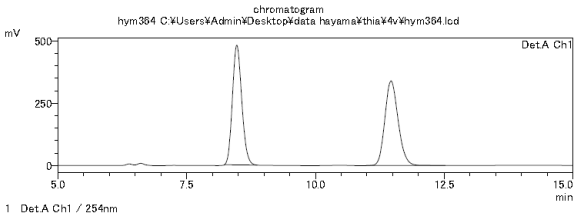




(*S*)-4x-[OMe] **(*R*)-4x-[OMe]**

rac-**4x-[OMe]**

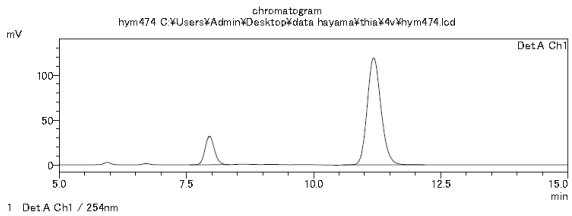
peak#	retention time (min)	area	area (%)
1	8.469	6077195	50.071
2	11.464	6059895	49.929



(*S*)-**4x-[OMe]**

reaction catalyzed by **1a** in CCl_4

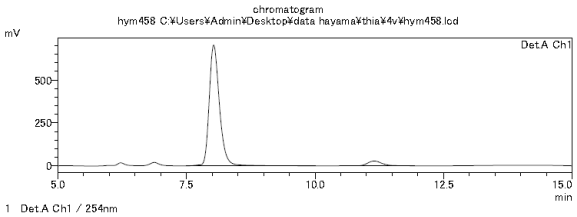
peak#	retention time (min)	area	area (%)
1	7.948	408900	15.369
2	11.177	2251690	84.631



(*R*)-**4x-[OMe]**

reaction catalyzed by **1g** in acetone

peak#	retention time (min)	area	area (%)
1	8.025	9771305	94.780
2	11.146	538203	5.220



(*S*)-**4x-[OMe]**

reaction catalyzed by **1a** in CCl_4 with benzoic acid

peak#	retention time (min)	area	area (%)
1	7.762	458477	11.566
2	11.085	3490349	88.434