Supporting Information

$RhCl_3 \cdot 3H_2O$-Catalyzed Ligand-Enabled Highly Regioselective Thiolation of Acrylic Acids

Can Liu,[†,‡] Yi Fang,[†,‡] Shun-Yi Wang,*[,†,‡] and Shun-Jun Ji*[,†,‡]

[†]*Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, China.*
[‡]*Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou, 215123, China.*

Email: shunyi@suda.edu.cn; shunjun@suda.edu.cn

Table of Contents

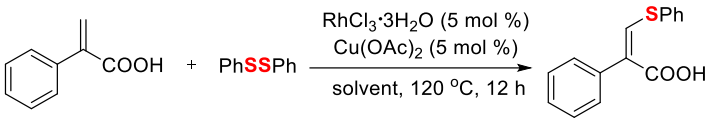
General information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Acrylic acids **1** and **1a**-d_2 were prepared according to the literature procedures.[1] Solvents for chromatography were analytical grade and used without further purification. Anhydrous MeCN, DMF, DMA, DMSO, THF (99.9%, Extra Dry with molecular sieves, Water≤50 ppm, in resealable bottle under Ar) were purchased from Adamas-beta®. Analytical thin-layer chromatography (TLC) was performed on silica gel, visualized by I_2 or irradiation with UV light. For column chromatography, 200-300 mesh silica gel was used. Flash chromatography was performed with SepaBean® machine of Santai Technologies. ^{1}H-NMR and ^{13}C-NMR were recorded on a BRUKER 400 MHz spectrometer. Chemical shifts (δ) were reported referenced to an internal tetramethylsilane standard or the $CDCl_3$ residual peak (δ 7.26) for ^{1}H NMR. Chemical shifts of ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.16). Data were reported in the following order: chemical shift (δ) in ppm; multiplicities were indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (*J*) were in Hertz (Hz). IR spectra were recorded on a BRUKER VERTEX 70 spectrophotometer and were reported in terms of frequency of absorption (cm^{-1}). In situ IR spectroscopy was performed on Mettler-Toledo ReactIR 15 equipped with a diamond ATR probe and a MCT detector. Spectra were acquired using Mettler-Toledo iC IR software version 7.0.297 in the range of 650–2200 cm^{-1} with a 4 cm^{-1} resolution. HRMS spectra were obtained by using GCT Premier TOF-MS with CI source or BRUKER microTOF-Q III instrument with ESI source. Standard XPS spectra of Cu is accessable from website of Thermo Scientific (https://xpssimplified.com/elements/copper.php#opennewwindow).

Experimental section

Optimization of the Rh-catalyzed thiolation of 1a with 2a.

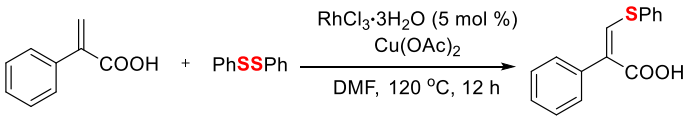
Table S1. Optimization of solvents.



1a (1 equiv) **2a** (1 equiv) **4a**

Entry	Solvent (1 mL)	LC-yield (%)
1	DMF	10
2	DMA	N.D.
3	NMP	7
4	DMSO	N.D.
5	1,4-dioxane	N.D.
6	THF	trace
7	MeCN	7
8	DCE	N.D.
9	Toluene	N.D.
10	$PhCF_3$	N.D.
11	HFIP	trace
12	EtOH	N.D.
13	t-AmOH	N.D.
14	AcOH	N.D.

Table S2. Optimization of amount of $Cu(OAc)_2$.

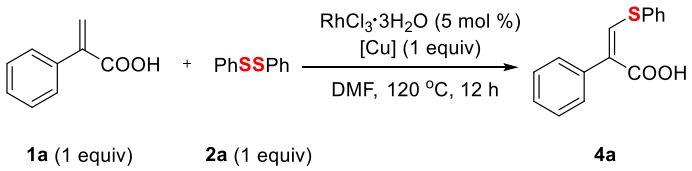


1a (1 equiv) **2a** (1 equiv) **4a**

Entry	$Cu(OAc)_2$	LC-yield (%)
1	-	N.D.
2	10 mol%	17
3	15 mol%	17
4	20 mol%	27
5	25 mol%	32
6	50 mol%	40
7	75 mol%	40

8	1 equiv	49
9	1.5 equiv	38

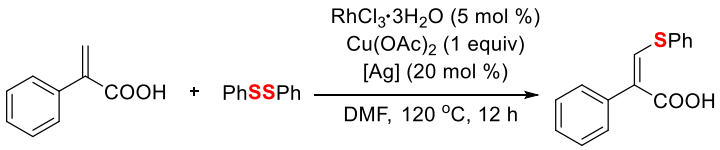
Table S3. Optimization of sort of Cu salts.



1a (1 equiv) **2a** (1 equiv) **4a**

Entry	[Cu]	LC-yield (%)
1	$CuCl_2$	Trace
2	$Cu(OTf)_2$	17
3	CuO	22
4	$CuSO_4$	16
5	$Cu(TFA)_2$	34
6	$Cu(NO_3)_2$	Trace
7	CuCl	19
8	$Cu(acac)_2$	32
9	CuI	23
10	CuBr	29

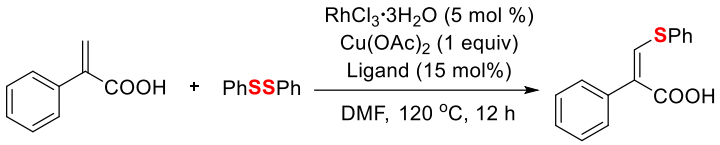
Table S4. Optimization of sort of Ag salts.



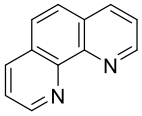
1a (1 equiv) **2a** (1 equiv) **4a**

Entry	[Ag]	LC-yield (%)
1	$AgSbF_6$	30
2	$AgBF_4$	45
3	AgOTf	28
4	AgOTs	39
5	AgTFA	46
6	AgOAc	45
7	Ag_2O	49
8	Ag_2CO_3	45

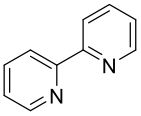
Table S5. Optimization of sort of ligands.



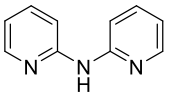
1a (1 equiv) **2a** (1 equiv) **4a**



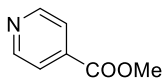
L1, 37%



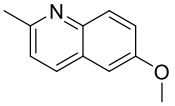
L2, 25%



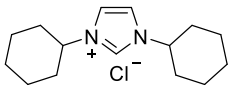
L3, 24%



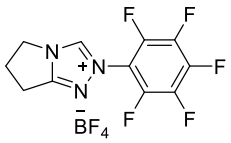
L4, 21%



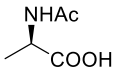
L5, 43%



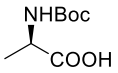
L6, 52%



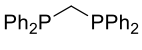
L7, 27%



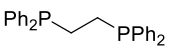
L8, 25%



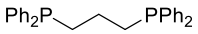
L9, 39%



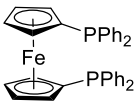
L10, 53%



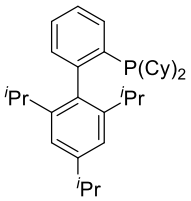
L11, 54%



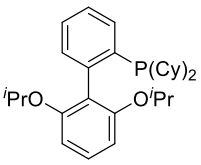
L12, 51%



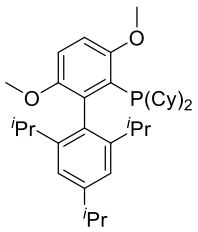
L13, 49%



L14, 51%

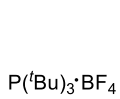


L15, 48%

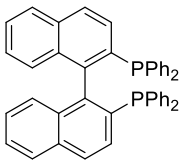


L16, 48%

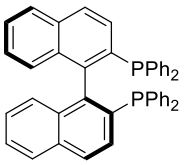
L17, 43%



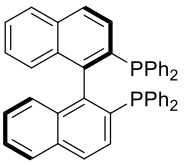
L18, 41%



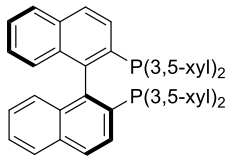
L19, 52%



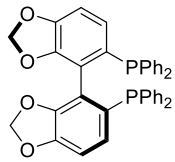
L20, 58%



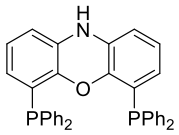
L21, 50%



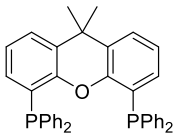
L22, 51%



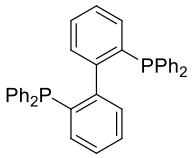
L23, 57%



L24, 49%

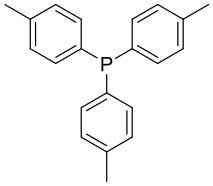


L25, 46%

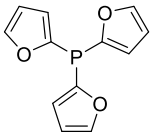


L26, 52%

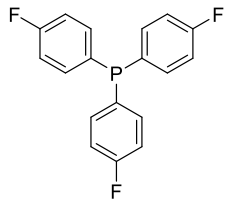
L27, 48%



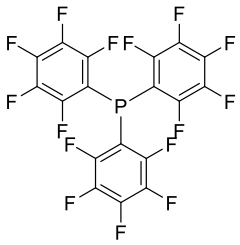
L28, 41%



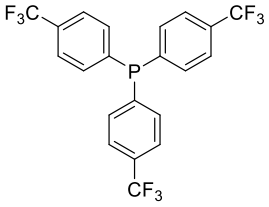
L29, 39%



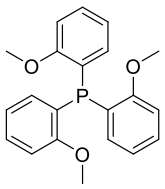
L30, 49%



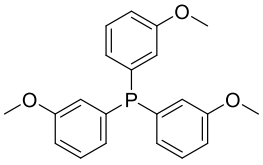
L31, 41%



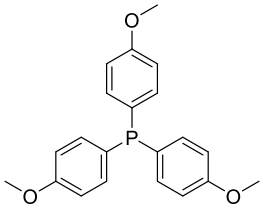
L32, 43%



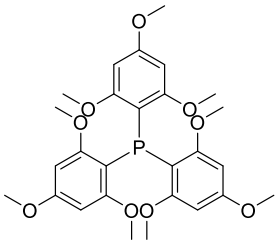
L33, 57%



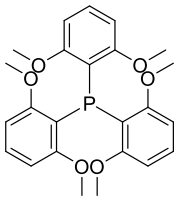
L34, 59%



L35, 37%



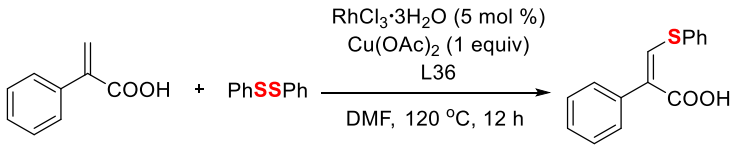
L36, 71%, 80%[a]



L37, 79%[a]

[a]PhSSPh: 2 equiv, 6 h.

Table S6. Optimization of amount of L36.

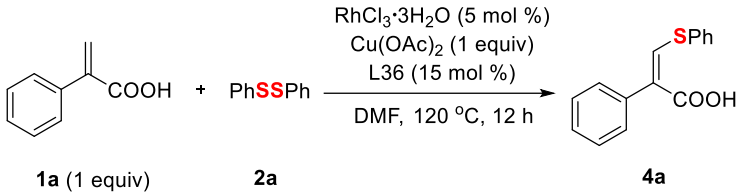


1a (1 equiv) **2a** (1 equiv) **4a**

Entry	Amount of **L36**	Isolated yield (%)
1	5 mol %	54
2	10 mol %	64

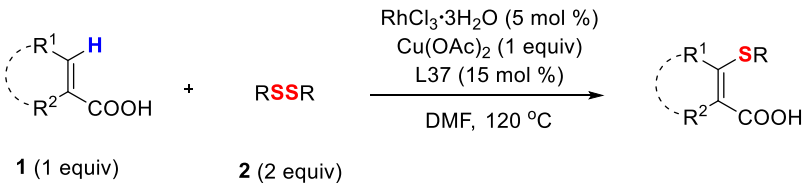
3	15 mol %	69
4	20 mol %	66
5	25 mol %	65
6	30 mol %	68

Table S7. Optimization of amount of PhSSPh.



Entry	Amount of PhSSPh	Isolated yield (%)
1	50 mol %	34
2	1 equiv	66
3	1.25 equiv	70
4	1.5 equiv	67
5	2 equiv	75

General procedure for the preparation of alkenyl sulfides



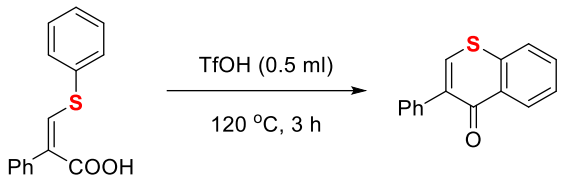
An oven-dried screw-capped 8-mL vial equipped with a magnetic stir bar was charged with **1** (0.3 mmol), **2** (0.6 mmol), $RhCl_3·3H_2O$ (5 mol %, 3.9 mg), $Cu(OAc)_2$ (1 equiv, 54 mg), L37 (15 mol %, 19.9 mg). DMF (3 mL) was added via syringe and the mixture was stirred at 120 °C for 6 h. The crude reaction mixture was filtered to remove the PhSCu(0, I) powder. The filtrate was diluted with ethyl acetate (50 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography with EtOAc and DCM or PE.

Large scale reaction

An oven-dried round-bottomed 25-mL flask equipped with a magnetic stir bar was charged with Atropic acid **1a** (6 mmol, 0.8890 g), PhSSPh **2a** (12 mmol, 2.6200 g), $RhCl_3·3H_2O$ (5 mol %, 80 mg), $Cu(OAc)_2$ (1 equiv, 1.0898 g), L37 (15 mol %, 398 mg). DMF (10 mL) was added via syringe and the mixture was stirred at 120 °C for 24 h. The crude reaction mixture was filtered to remove the PhSCu(0, I) powder. The filtrate was diluted with ethyl acetate (150 mL) and washed with water (50 mL × 3). The

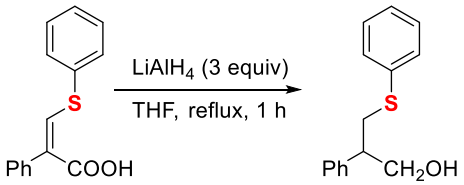
organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by auto flash chromatography with EtOAc and PE (EA : PE = 1 : 10). Isolated yield: 60%, 0.9260 g.

Derivative reaction



4a **der1**, 88%

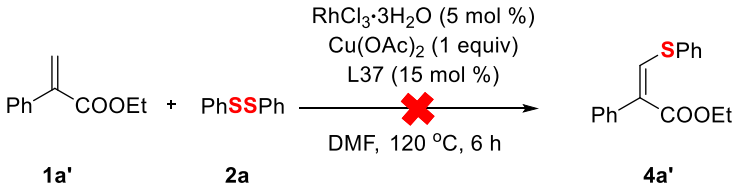
The procedure was adapted from the literature.[2]An oven-dried screw-capped 8-mL vial equipped with a magnetic stir bar was charged with **4a** (0.2 mmol, 51.3 mmg), TfOH (0.5 mL) was added via syringe and the mixture was stirred at 120 °C for 3 h. The reaction was quenched by H_2O and diluted with DCM (10 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography with EtOAc and PE (EA : PE = 1 : 20).



4a **der2**, 50%

The procedure was adapted from the literature.[3] An oven-dried round bottom tube equipped with a magnetic stir bar was charged with $LiAlH_4$ in THF (1 mol/L, 1.5 mL, 1.5 mmol) and cooled to 0 °C. **4a** (128.2 mg, 0.5 mmol) was carefully added in portions at this temperature then the mixture was warmed up to room temperature and refluxed for 1 h. At this point, the mixture was cooled to 0 °C and reaction was quenched by slow addition of Sat. Rochelle's salt (5 mL) was added and the aqueous layer was extracted using EtOAc (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography with EtOAc and PE (EA : PE = 1 : 5).

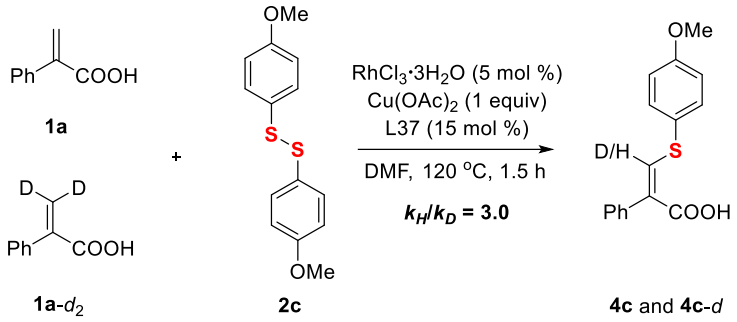
Controlled experiment



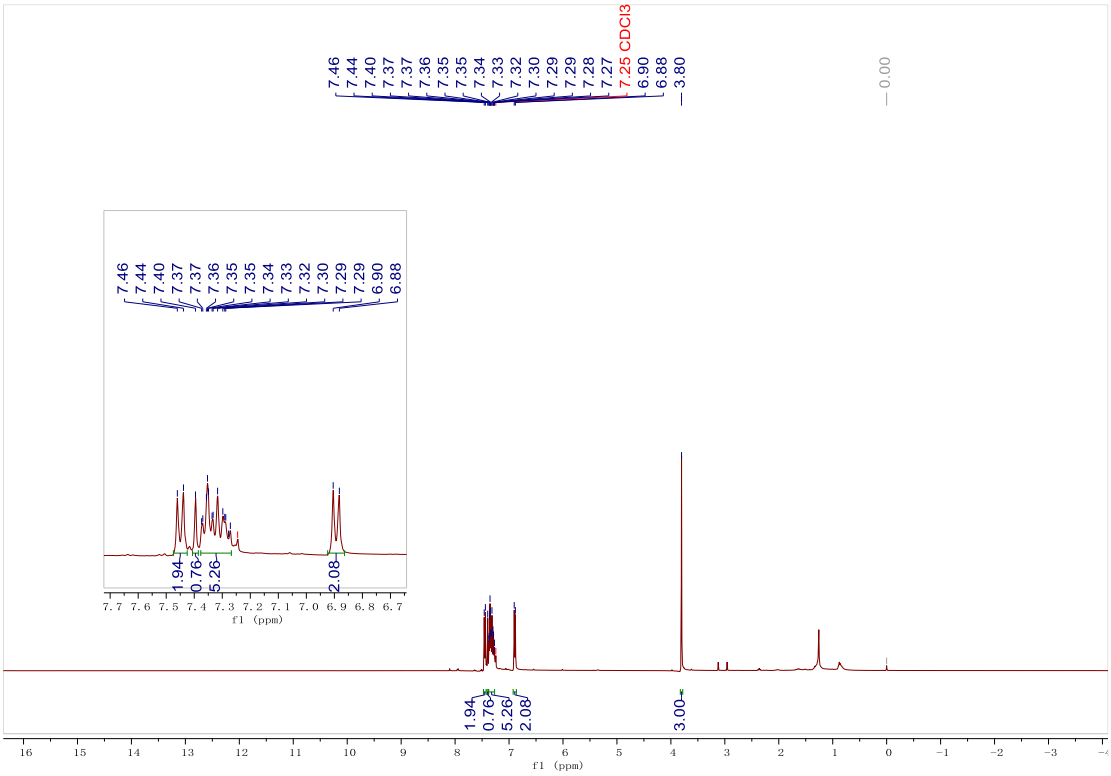
1a' **2a** **4a'**

An oven-dried screw-capped 8-mL vial equipped with a magnetic stir bar was charged with **1a'** (0.3 mmol), **2a** (0.6 mmol), $RhCl_3 \cdot 3H_2O$ (5 mol %, 3.9 mg), $Cu(OAc)_2$ (1 equiv, 54 mg), L37 (15 mol %, 19.9 mg). DMF (3 mL) was added via syringe and the mixture was stirred at 120 °C for 6 h. Corresponding product **4a'** was not detected.

Competitive experiment

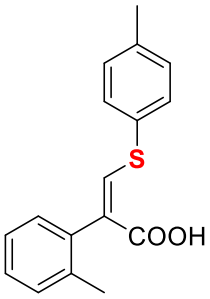


An oven-dried screw-capped 8-mL vial equipped with a magnetic stir bar was charged with **1a** (29.6 mg, 0.2 mmol), **1a-**d_2 (99% D, 30.0 mg, 0.2 mmol)**, 2c** (111.4 mg, 0.4 mmol), $RhCl_3 \cdot 3H_2O$ (5 mol %, 2.6 mg), $Cu(OAc)_2$ (1 equiv, 36 mg), L37 (15 mol %, 13.4 mg). DMF (2 mL) was added via syringe and the mixture was stirred at 120 °C for 1.5 h. The crude reaction mixture was filtered to remove the PhSCu(0, I) powder. The filtrate was diluted with ethyl acetate (50 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography with EtOAc and DCM (EA: DCM = 1 : 5). The ratio was identified by ^{1}HNMR to give the KIE value of 3.0.



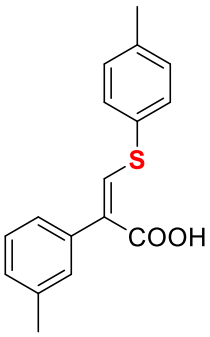
Characterization of structurally novel compounds

(*Z*)-2-(*o*-tolyl)-3-(*p*-tolylthio)acrylic acid 3a



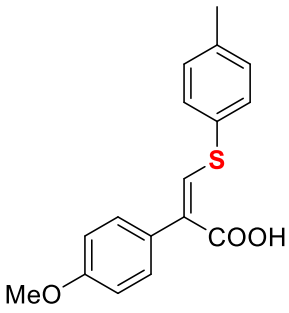
Following general procedure, **3a** was obtained as a yellow solid (50.2 mg, 59%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.92 (s, 1H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.31 (s, 1H), 7.22 – 7.12 (m, 6H), 2.33 (s, 3H), 2.30 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 152.67, 138.69, 137.26, 137.22, 133.05, 131.44, 130.30, 130.22, 130.10, 128.26, 125.85, 125.81, 21.24, 20.20.; **FT-IR (ATR):** 2924, 1660, 1536, 1486, 1419, 1318, 1234 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{17}H_{16}O_2S$ $[M+Na]^+$: 307.0769, found: 307.0765. **Mp**: 167.3-168.3 °C.

(*Z*)-2-(*m*-tolyl)-3-(*p*-tolylthio)acrylic acid 3b



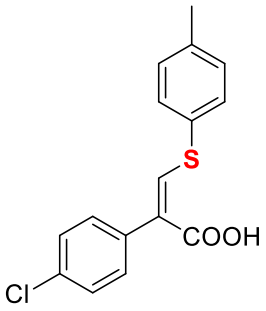
Following general procedure, **3b** was obtained as a yellow solid (67.3 mg, 56%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.95 (s, 1H), 7.52 – 7.37 (m, 3H), 7.19 (dd, *J* = 7.6, 14.8 Hz, 5H), 7.10 (d, *J* = 7.3 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.73, 137.84, 133.27, 131.52, 130.32, 130.26, 129.72, 128.44, 128.12, 126.14, 21.53, 21.26; **FT-IR (ATR):** 2923, 1656, 1532, 1232, 1239 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{17}H_{16}O_2S$ $[M+Na]^+$: 307.0769, found: 307.0767. **Mp**: 151.3-152.2 °C.

(*Z*)-2-(4-methoxyphenyl)-3-(*p*-tolylthio)acrylic acid 3c



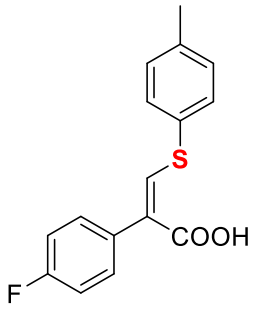
Following general procedure, **3c** was obtained as a yellow solid (65.4 mg, 76%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.43 – 7.36 (m, 3H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.89 – 6.82 (m, 2H), 3.79 (s, 3H), 2.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.11, 151.45, 138.60, 133.25, 131.38, 130.17, 130.12, 130.03, 113.57, 55.35, 21.18; **FT-IR (ATR):** 2956, 1670, 1508, 1286, 1241, 1182 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{17}H_{16}O_3S$ $[M+Na]^+$:323.0718, found: 323.0722. **Mp**: 148.9-149.9 °C.

(*Z*)-2-(4-chlorophenyl)-3-(*p*-tolylthio)acrylic acid 3d



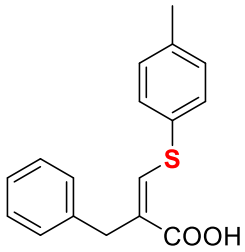
Following general procedure, **3d** was obtained as a light yellow solid (69.0 mg, 72%). **^{1}H NMR (400 MHz, DMSO-d_6):** δ 13.03 (s, 1H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.42 – 7.32 (m, 4H), 7.21 (d, *J* = 7.7 Hz, 2H), 2.29 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d_6):** δ 166.85, 146.62, 137.74, 136.62, 132.74, 131.83, 130.40, 130.28, 130.11, 127.85, 126.48, 20.61; **FT-IR (ATR):** 2926, 1651, 1522, 1487, 1422, 1315, 1236 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{16}H_{13}ClO_2S$ $[M+H]^+$: 305.0403, found: 305.0406. **Mp**: 177.1-178.2 °C.

(*Z*)-2-(4-fluorophenyl)-3-(*p*-tolylthio)acrylic acid 3e



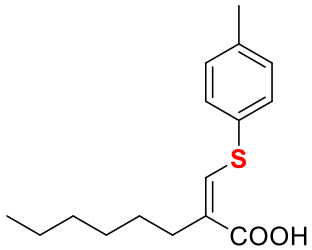
Following general procedure, **3e** was obtained as a light yellow solid (63.9 mg, 78%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.48 (s, 1H), 7.43 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.33 (dd, *J* = 5.4, 8.5 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.01 (t, *J* = 8.5 Hz, 2H), 2.35 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.60, 162.55(d, J_{C-F}= 245.0 Hz),153.01, 138.85, 133.48(d, J_{C-F}= 3.0 Hz), 132.94, 131.46, 130.66(d, J_{C-F}= 3.0 Hz),130.25, 115.14, 114.93, 21.17; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -114.57. **FT-IR (ATR):** 2919, 1662, 1492, 1219 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{16}H_{13}FO_2S$ $[M+Na]^+$: 311.0518, found: 311.0517. **Mp**: 150.7-151.8 °C.

(*Z*)-2-benzyl-3-(*p*-tolylthio)acrylic acid 3f



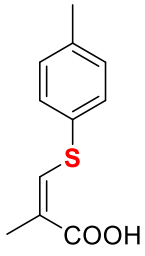
Following general procedure, **3f** was obtained as a light yellow solid (51.6 mg, 76%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.29 (dd, *J* = 7.7, 18.0 Hz, 4H), 7.23 – 7.18 (m, 3H), 7.17 – 7.10 (m, 3H), 3.67 (s, 2H), 2.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 172.32, 149.92, 139.34, 138.43, 133.39, 131.15, 130.21, 128.82, 128.59, 126.49, 123.80, 38.83, 21.25; **FT-IR (ATR):** 2909, 1664, 1557, 1430, 1249 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{17}H_{16}O_2S$ $[M+Na]^+$: 307.0769, found: 307.0763. **Mp**: 138.3-139.2 °C.

(*Z*)-2-((*p*-tolylthio)methylene)octanoic acid 3g



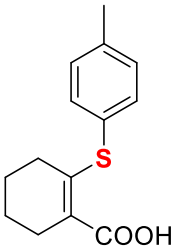
Following general procedure, **3g** was obtained as a white solid (62.1 mg, 52%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.07 (s, 1H), 2.34 (d, *J* = 15.8 Hz, 5H), 1.49 (p, *J* = 7.0, 7.5 Hz, 2H), 1.29 (d, *J* = 9.1 Hz, 6H), 0.87 (t, *J* = 6.5 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 172.49, 147.82, 138.40, 133.74, 131.48, 130.19, 125.13, 33.37, 31.75, 29.55, 29.02, 22.76, 21.26, 14.21; **FT-IR (ATR):** 2919, 2851, 1665, 1556, 1251, 941 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{16}H_{22}O_2S$ $[M+H]^+$: 279.1419, found: 279.1414. **Mp**: 58.9-59.8 °C.

(*Z*)-2-methyl-3-(*p*-tolylthio)acrylic acid 3h



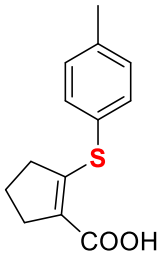
Following general procedure, **3h** was obtained as a yellow solid (36.7 mg, 48%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.59 (s, 1H), 7.42 – 7.35 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.10 (s, 1H), 2.36 (s, 3H), 1.99 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 147.96, 138.45, 133.52, 131.54, 130.18, 21.26, 19.23, 19.23; **FT-IR (ATR):** 2918, 1672, 1540, 1418, 1250 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{11}H_{12}O_2S$ $[M+Na]^+$: 231.0456, found: 231.0450. **Mp**: 134.7-135.8 °C.

2-(*p*-tolylthio)cyclohex-1-ene-1-carboxylic acid 3i



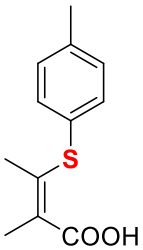
Following general procedure, **3i** was obtained as a yellow solid (55.2 mg, 39%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.98 (s, 1H), 7.43 – 7.36 (m, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 2.43 (td, *J* = 2.9, 6.2 Hz, 2H), 2.37 (s, 3H), 2.00 (td, *J* = 3.0, 5.9 Hz, 2H), 1.63 – 1.49 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 172.72, 154.19, 139.39, 136.09, 129.86, 128.23, 120.52, 32.35, 27.25, 23.14, 21.95, 21.40; **FT-IR (ATR):** 2926, 1662, 1552, 1414, 1249 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{14}H_{16}O_2S$ $[M+Na]^+$: 271.0769, found: 271.0771. **Mp**: 191.9-192.6 °C.

2-(*p*-tolylthio)cyclopent-1-ene-1-carboxylic acid 3j



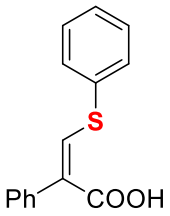
Following general procedure, **3j** was obtained as a yellow solid (55.2 mg, 35%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46 – 7.40 (m, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 2.72 (tt, *J* = 2.1, 7.0 Hz, 2H), 2.37 (s, 3H), 2.35 – 2.30 (m, 2H), 1.81 (p, *J* = 7.6 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.50, 160.22, 139.67, 135.45, 129.87, 128.22, 122.78, 39.29, 33.48, 21.99, 21.39; **FT-IR (ATR):** 2924, 1698, 1639, 1427, 1274 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{13}H_{14}O_2S$ $[M+H]^+$: 235.0793, found: 235.0789. **Mp**: 204.0-205.0 °C.

(*Z*)-2-methyl-3-(*p*-tolylthio)but-2-enoic acid 3k



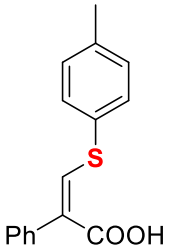
Following general procedure, **3k** was obtained as a yellow solid (55.2 mg, 26%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.96 (s, 1H), 7.40 – 7.34 (m, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 2.37 (s, 3H), 2.01 (s, 3H), 1.84 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 152.21, 139.25, 135.45, 129.97, 129.53, 119.19, 21.60, 21.39, 16.53; **FT-IR (ATR):** 2922, 2852, 1659, 1540, 1412, 1282, 1196 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{12}H_{14}O_2S$ $[M+Na]^+$: 245.0612, found: 245.0611. **Mp**: 172.2-173.3 °C.

(*Z*)-2-phenyl-3-(phenylthio)acrylic acid 4a



Following general procedure, **4a** was obtained as a light yellow solid (77.1 mg, 77%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.51 (s, 1H), 7.55 – 7.47 (m, 3H), 7.40 – 7.29 (m, 8H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 151.94, 137.50, 136.64, 131.35, 129.58, 129.05, 128.56, 128.27, 127.75, 126.36; **FT-IR (ATR):** 2920, 1656, 1534,1419, 1234 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{15}H_{13}O_2S$ $[M+H]^+$:257.0636, found: 257.0638. **Mp**: 150.4-151.4 °C.

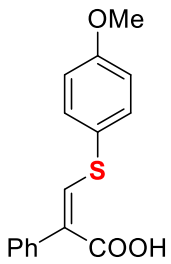
(*Z*)-2-phenyl-3-(*p*-tolylthio)acrylic acid 4b



Following general procedure, **4b** was obtained as a light yellow solid (73.0 mg, 77%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.82 (s, 1H), 7.46 (s, 1H), 7.43 – 7.25 (m, 7H), 7.16 (d, *J* = 7.8 Hz, 2H), 2.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 152.84, 138.77, 137.56, 133.19, 131.49, 130.27, 129.02, 128.20, 127.63, 126.04, 21.25; **FT-IR (ATR):** 2875, 1652, 1526, 1488, 1418, 1231 cm^{-1}. **HRMS (ESI, m/z):** calcd for

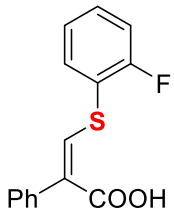
$C_{16}H_{14}O_2S$ [M+Na]$^+$: 293.0612, found: 293.0608. **Mp**: 168.6-169.5 ^oC.

(*Z*)-3-((4-methoxyphenyl)thio)-2-phenylacrylic acid 4c



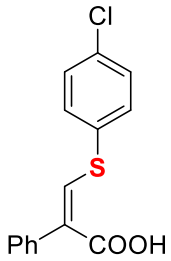
Following general procedure, **4c** was obtained as a light yellow solid (76.1 mg, 73%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.92 (s, 1H), 7.47 – 7.43 (m, 2H), 7.40 (s, 1H), 7.38 – 7.25 (m, 5H), 6.93 – 6.85 (m, 2H), 3.80 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.25, 153.84, 137.54, 133.60, 129.00, 128.19, 127.60, 127.35, 125.66, 115.08, 55.53; **FT-IR (ATR):** 2832, 1662, 1541, 1490, 1234, 1173 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{16}H_{14}O_3S$ [M+Na]$^+$: 309.0561, found: 309.0561. **Mp**: 134.0-135.0 ^oC.

(*Z*)-3-((2-fluorophenyl)thio)-2-phenylacrylic acid 4d



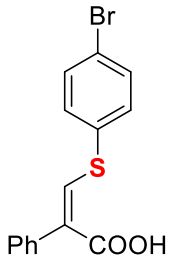
Following general procedure, **4d** was obtained as a light yellow solid (68.0 mg, 75%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.76 (s, 1H), 7.53 (td, *J* = 1.8, 7.6 Hz, 1H), 7.33 (tt, *J* = 6.6, 16.4 Hz, 7H), 7.19 – 7.09 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.90, 161.55 (d, $J_{C\text{-}F}$ = 246 Hz), 150.77 (d, $J_{C\text{-}F}$ = 1 Hz), 137.16 (d, $J_{C\text{-}F}$ = 7 Hz), 134.19, 131.16, 129.03, 128.26, 127.83, 127.03, 125.05 (d, $J_{C\text{-}F}$ = 4 Hz), 123.27 (d, $J_{C\text{-}F}$ = 17 Hz), 116.57 (d, $J_{C\text{-}F}$ = 22 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -108.44; **FT-IR (ATR):** 2929, 1655, 1532, 1473, 1249, 1222 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{15}H_{11}FO_2S$ [M+Na]$^+$: 297.0361, found: 297.0358. **Mp**: 124.0-124.9 ^oC.

(*Z*)-3-((4-chlorophenyl)thio)-2-phenylacrylic acid 4e



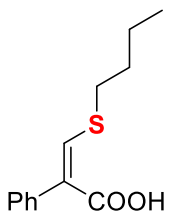
Following general procedure, **4e** was obtained as a yellow solid (81.3 mg, 73%). **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 13.09 (s, 1H), 7.74 – 7.18 (m, 10H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$):** δ 167.25, 143.67, 137.51, 135.32, 132.70, 131.83, 129.38, 128.83, 128.51, 127.95, 127.24.; **FT-IR (ATR):** 2824, 1650, 1522, 1476, 1421, 1250, 1093 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{15}H_{11}ClO_2S$ [M+Na]$^+$: 313.0066, found: 313.0059. **Mp**: 164.7-165.5 ^oC.

(*Z*)-3-((4-bromophenyl)thio)-2-phenylacrylic acid 4f



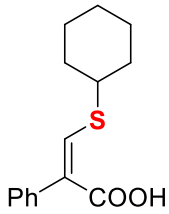
Following general procedure, **4f** was obtained as a light brown solid (75.4 mg, 62%). **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 13.01 (s, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 7.4 Hz, 2H), 7.31 (dt, *J* = 6.8, 12.8 Hz, 4H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$):** δ 143.39, 137.51, 135.82, 132.25, 132.01, 128.47, 127.93, 127.22, 121.13; **FT-IR (ATR):** 2918, 1651, 1471, 1421, 1248 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{15}H_{11}BrO_2S$ [M+H]$^+$: 334.9741, found: 334.9745. **Mp**: 192.4-193.3 ^oC.

(*Z*)-3-(butylthio)-2-phenylacrylic acid 4g



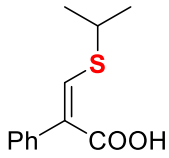
Following general procedure, **4g** was obtained as a light brown solid (61.6 mg, 22%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.28 (d, *J* = 919.5 Hz, 1H), 7.37 – 7.26 (m, 6H), 2.79 (t, *J* = 7.4 Hz, 2H), 1.68 (p, *J* = 7.6 Hz, 2H), 1.45 (dq, *J* = 7.4, 14.8 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.75, 152.57, 138.03, 128.88, 128.09, 127.37, 36.44, 32.40, 21.68, 13.64; **FT-IR (ATR):** 2957, 2927, 2855, 1724, 1666, 1418, 1250,1217 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{13}H_{16}O_2S$ $[M+Na]^+$: 259.0769, found: 259.0765. **Mp**: 66.7-67.6 °C.

(*Z*)-3-(cyclohexylthio)-2-phenylacrylic acid 4h



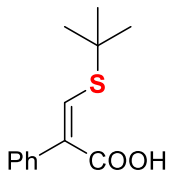
Following general procedure, **4h** was obtained as an orange solid (61.4 mg, 52%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.00 (s, 1H), 7.42 – 7.25 (m, 6H), 2.84 (tt, *J* = 3.8, 10.8 Hz, 1H), 2.04 (dd, *J* = 4.1, 13.2 Hz, 2H), 1.80 (dd, *J* = 4.1, 9.0 Hz, 2H), 1.67 – 1.59 (m, 1H), 1.53 – 1.41 (m, 2H), 1.41 – 1.18 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.62, 138.27, 128.93, 128.07, 127.32, 48.30, 33.64, 25.93, 25.41; **FT-IR (ATR):** 2919, 2850, 1655, 1531, 1426, 1328, 1238, 1206 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{15}H_{18}O_2S$ $[M+Na]^+$: 285.0925, found: 285.0920. **Mp**: 155.5-156.5 °C.

(*Z*)-3-(isopropylthio)-2-phenylacrylic acid 4i



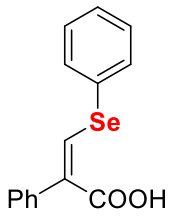
Following general procedure, **4i** was obtained as a yellow solid (61.4 mg, 36%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.77 (s, 1H), 7.38 (s, 1H), 7.36 – 7.25 (m, 5H), 3.12 (hept, *J* = 6.8 Hz, 1H), 1.38 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.81, 150.41, 138.26, 128.98, 128.16, 127.44, 39.80, 23.61; **FT-IR (ATR):** 2963, 1657, 1526, 1419, 1325,1233 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{12}H_{14}O_2S$ $[M+Na]^+$: 245.0612, found: 245.0617. **Mp**: 106.9-107.8 °C.

(*Z*)-3-(tert-butylthio)-2-phenylacrylic acid 4j



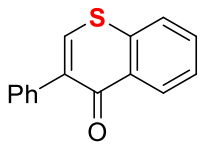
Following general procedure, **4j** was obtained as a yellow solid (42.6 mg, 31%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.80 (s, 1H), 7.45 (s, 1H), 7.37 – 7.29 (m, 5H), 1.42 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.69, 147.96, 138.55, 129.03, 128.23, 127.45, 125.69, 44.75, 30.87; **FT-IR (ATR):** 2960, 2927, 1655, 1524, 1419, 1325, 1248, 1149 cm^{-1}. **HRMS (ESI, m/z):** calcd for 245.0612 $[M+Na]^+$: 259.0769, found: 259.0763. **Mp**: 151.7-152.9 °C.

(*Z*)-2-phenyl-3-(phenylselanyl)acrylic acid 4k



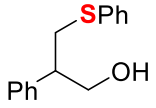
Following general procedure, **4k** was obtained as an orange solid (45.2 mg, 22%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.94 (s, 1H), 7.63 (dd, *J* = 2.9, 6.5 Hz, 2H), 7.42 – 7.26 (m, 8H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 172.05, 152.28, 137.74, 133.39, 133.16, 129.49, 128.79, 128.45, 128.17, 127.70; **^{77}Se NMR (76 MHz, $CDCl_3$)** δ 508.96; **FT-IR (ATR):** 2922, 2851, 1656, 1421, 1307, 1324, 1217 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{15}H_{12}O_2Se$ $[M+Na]^+$: 326.9900, found: 326.9902. **Mp**: 158.0-159.0 °C.

3-phenyl-4H-thiochromen-4-one der1



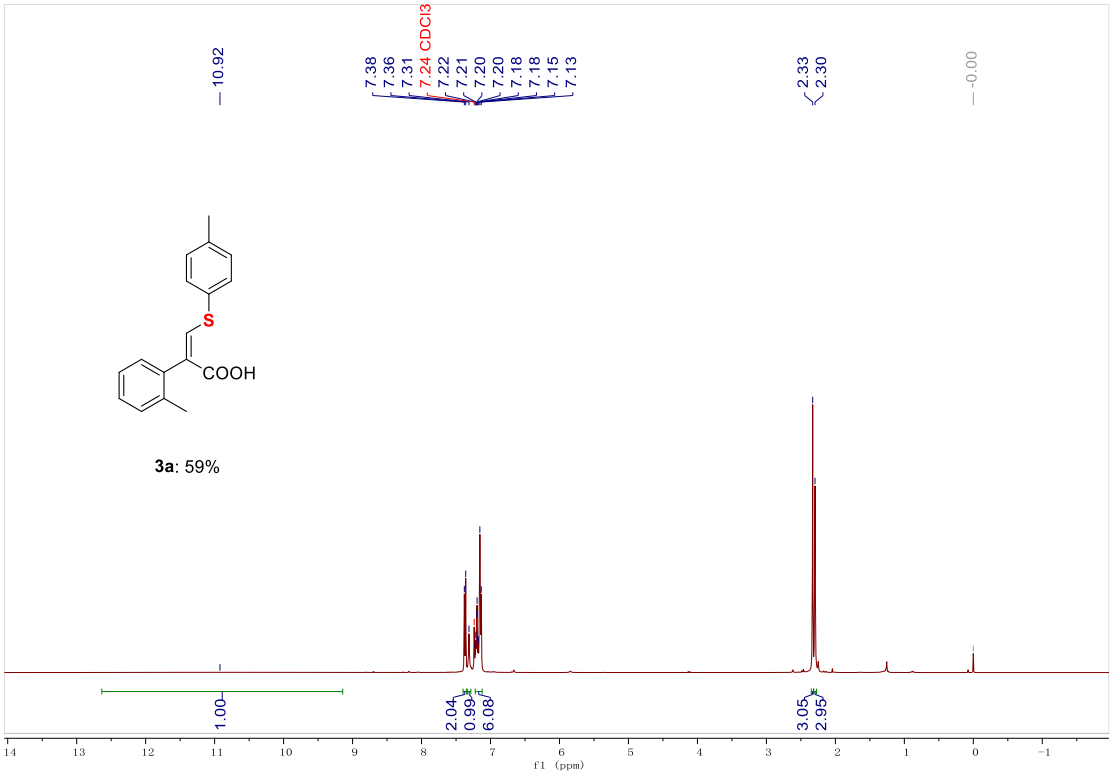
Following general procedure, **der1** was obtained as a light yellow solid (45.2 mg, 88%). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.62 (dt, *J* = 1.2, 7.9 Hz, 1H), 7.85 (s, 1H), 7.61 – 7.57 (m, 2H), 7.56 – 7.49 (m, 3H), 7.44 – 7.38 (m, 2H), 7.38 – 7.32 (m, 1H); **^{13}C NMR (100 MHz, CDCl$_3$):** δ 178.27, 137.51, 136.85, 136.78, 135.61, 132.80, 131.28, 129.50, 129.00, 128.31, 128.08, 127.81, 126.57; **FT-IR (ATR):** 1609, 1589, 1531,1437, 1355 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{15}H_{10}OS$ [M+Na]$^+$: 261.0350, found: 261.0353. **Mp**: 167.3-168.3 ºC.

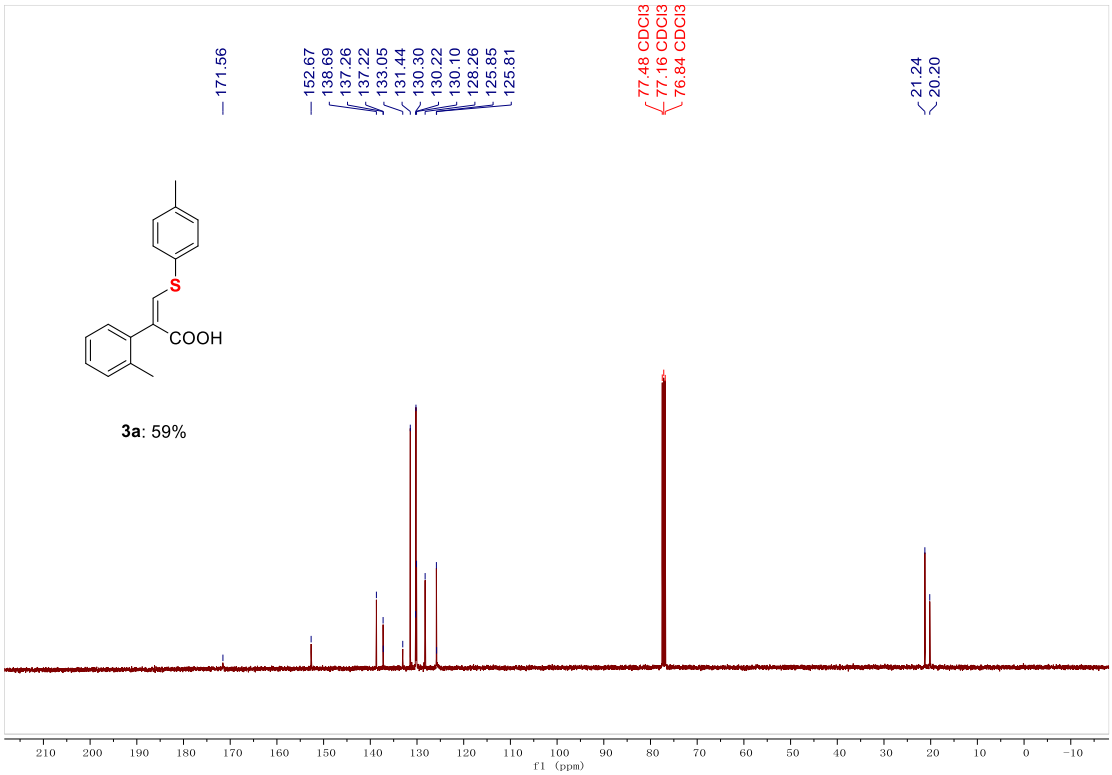
2-phenyl-3-(phenylthio)propan-1-ol der2

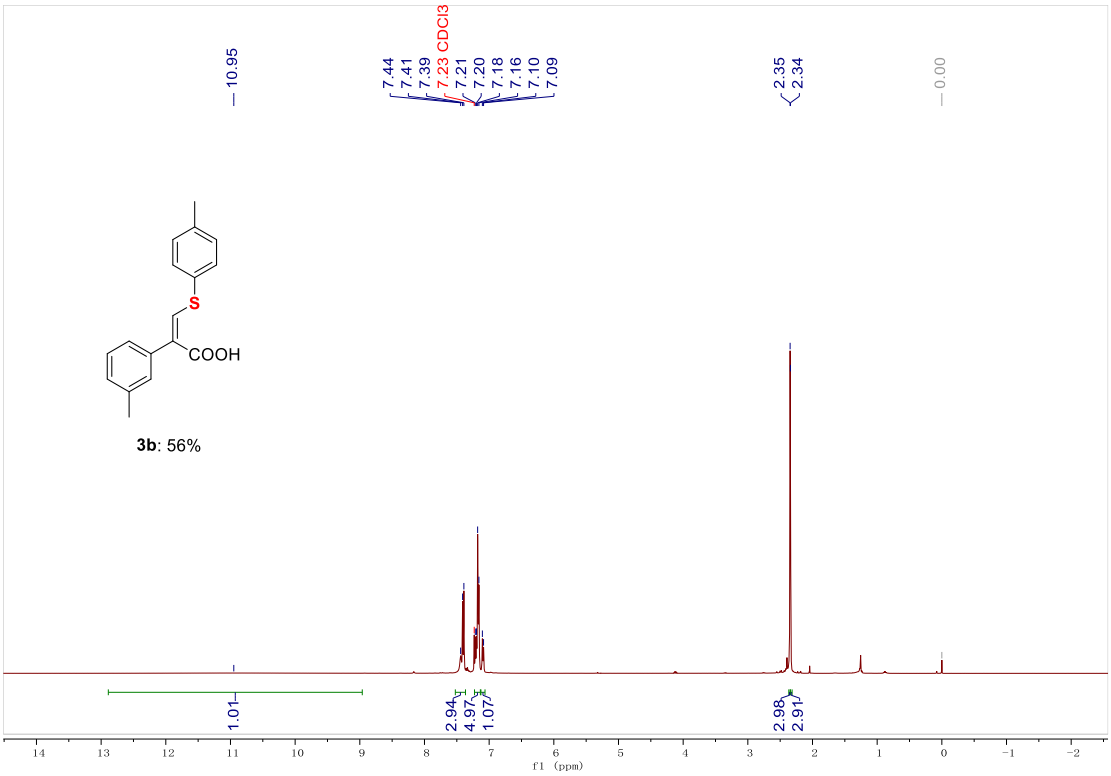


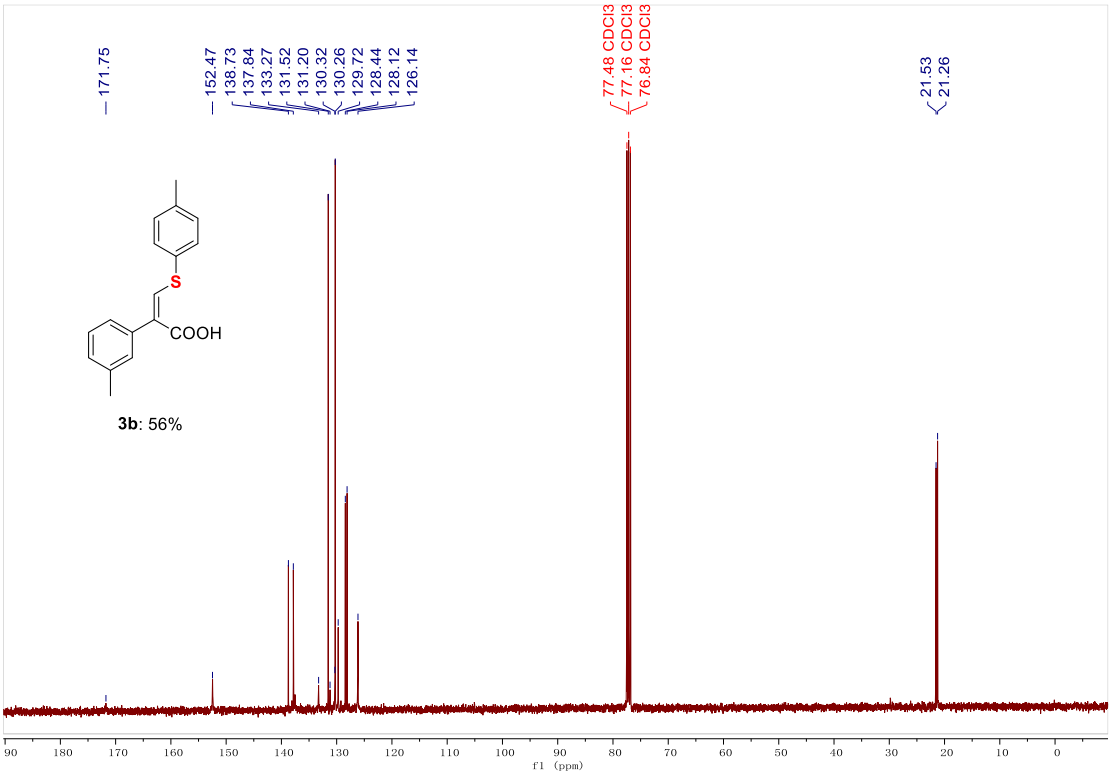
Following general procedure, **der2** was obtained as a colorless oil (45.2 mg, 50%). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.38 – 7.14 (m, 10H), 3.97 – 3.85 (m, 2H), 3.33 (dd, *J* = 7.7, 13.0 Hz, 1H), 3.22 (dd, *J* = 6.9, 13.0 Hz, 1H), 3.06 (p, *J* = 6.5 Hz, 1H); **^{13}C NMR (100 MHz, CDCl$_3$):** δ 141.08, 136.37, 129.51, 129.10, 128.94, 128.07, 127.44, 126.27, 66.23, 47.61, 36.41; **FT-IR (ATR):** 3559, 2923, 2873, 1582, 1479, 1438, 1053, 1024 cm^{-1}. **HRMS (ESI, m/z):** calcd for $C_{15}H_{16}OS$ [M+Na]$^+$: 267.0820, found: 267.0818.

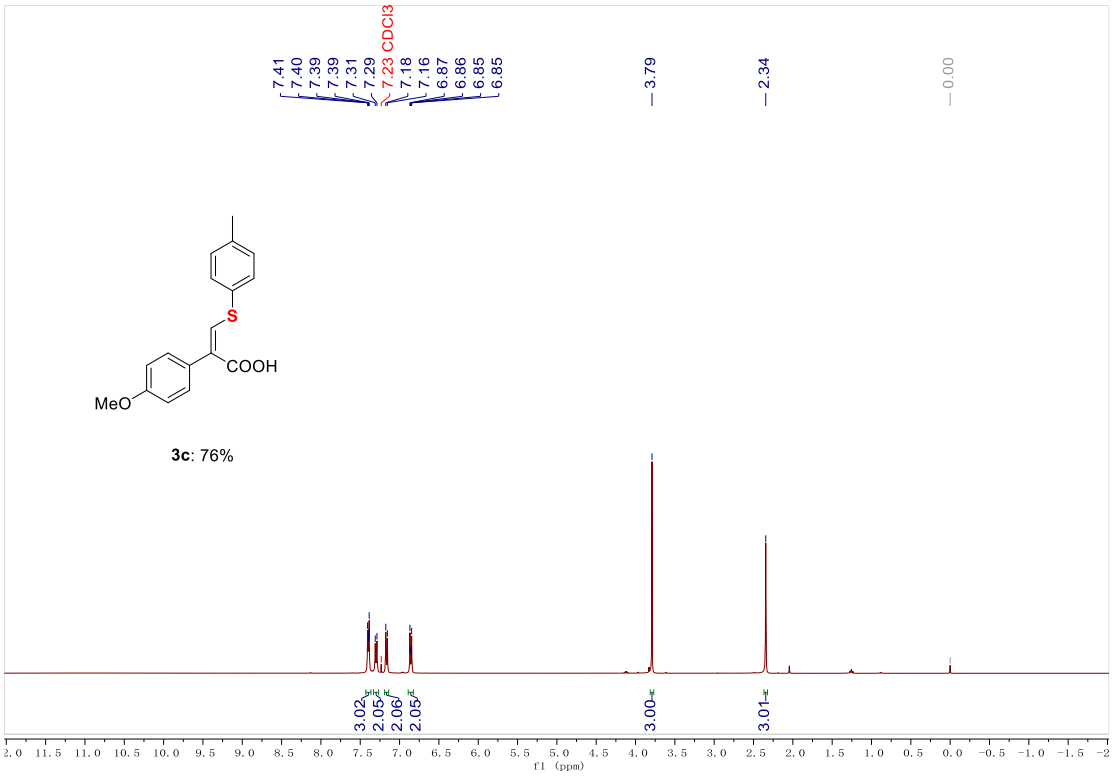
^{1}H and ^{13}C NMR Spectra of structurally novel compounds

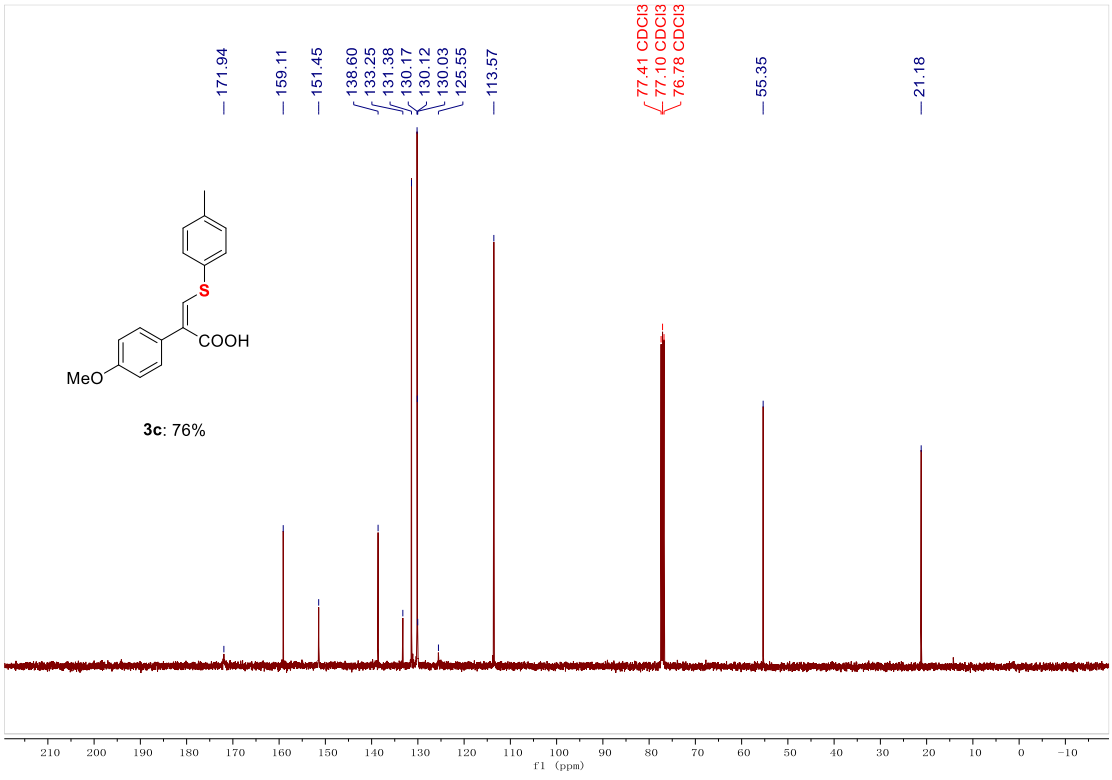


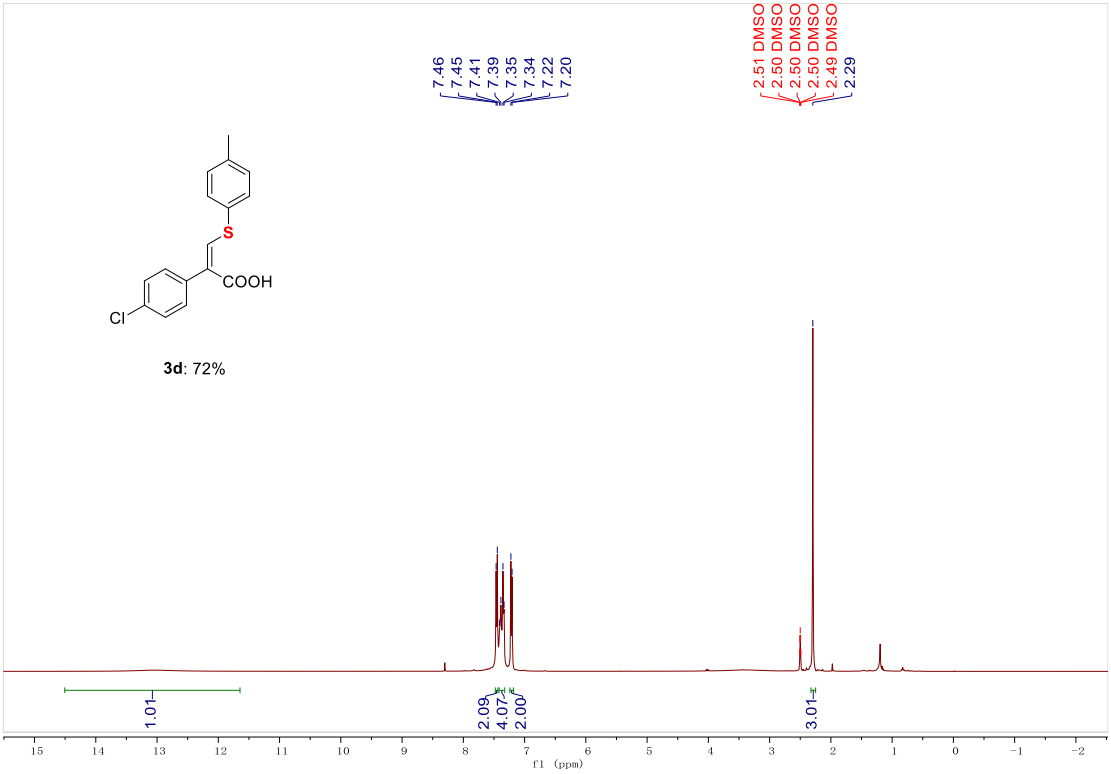


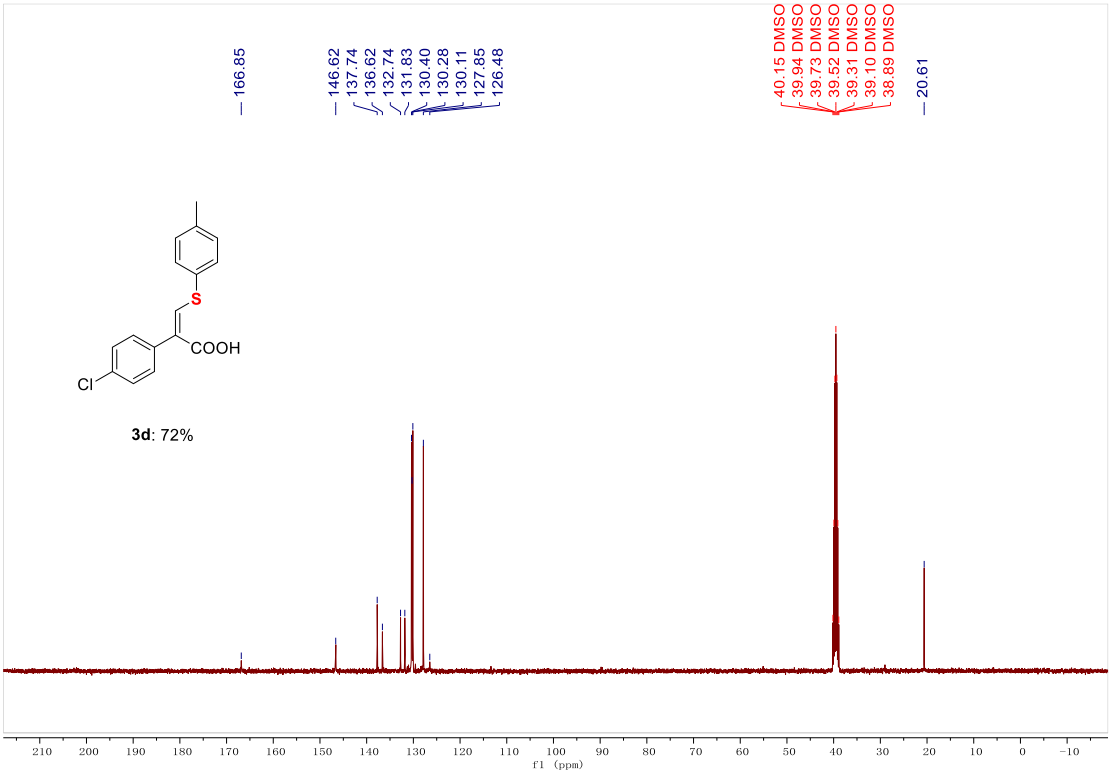

10.95
7.44
7.41
7.39
7.23 CDCl3
7.21
7.20
7.18
7.16
7.10
7.09
2.35
2.34
0.00
S
COOH
3b: 56%
1.01
2.94
4.97
1.07
2.98
2.91
f1 (ppm)

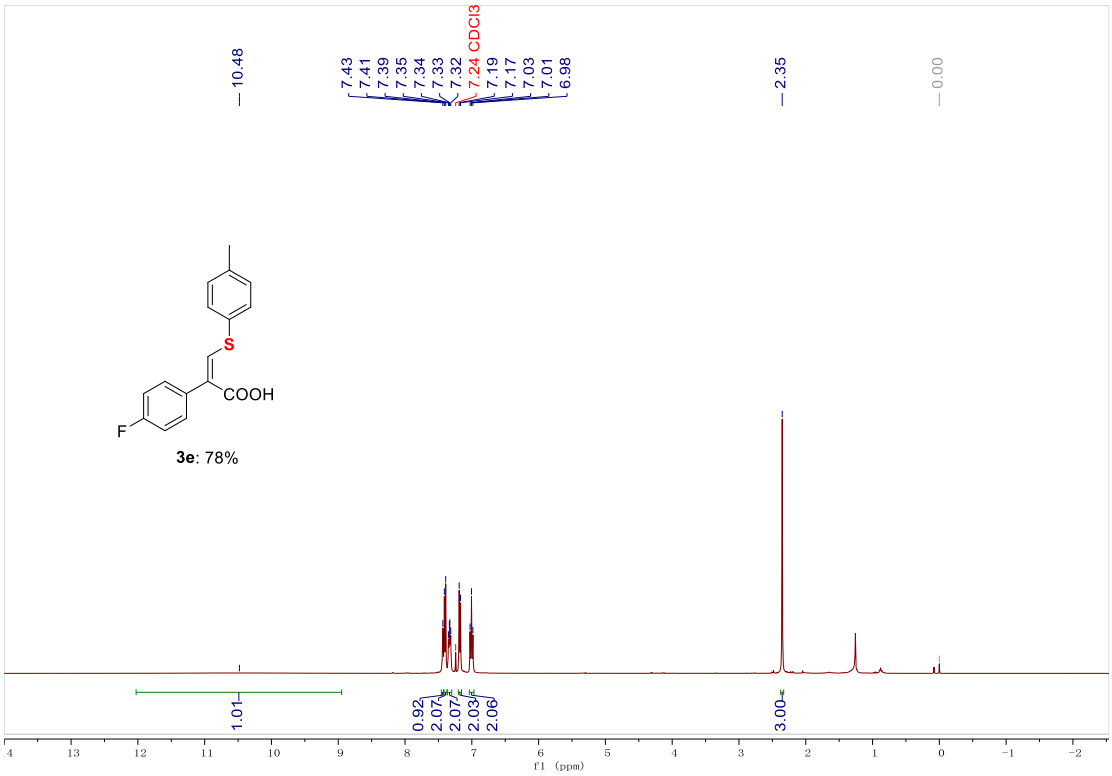

171.75
152.47
138.73
137.84
133.27
131.52
131.20
130.32
130.26
129.72
128.44
128.12
126.14
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.53
21.26
S
COOH
3b: 56%
f1 (ppm)

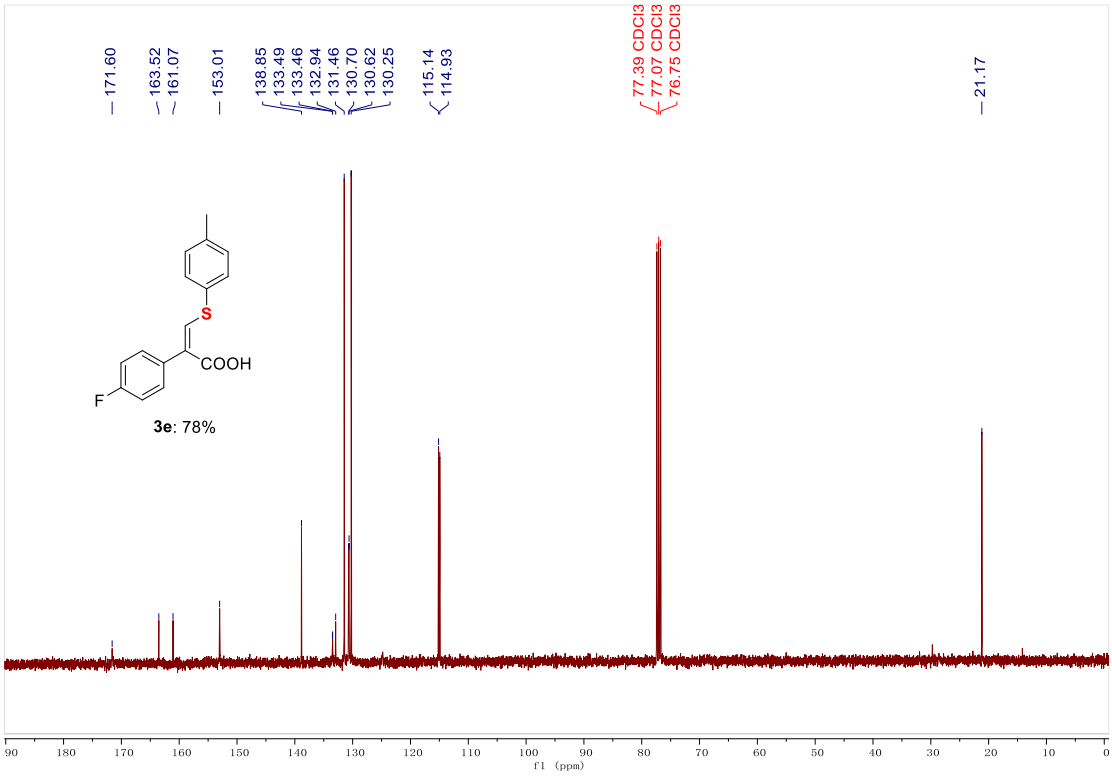

7.41
7.40
7.39
7.39
7.31
7.29
7.23 CDCl3
7.18
7.16
6.87
6.86
6.85
6.85
3.79
2.34
0.00
S
COOH
MeO
3c: 76%
3.02
2.05
2.06
2.05
3.00
3.01
f1 (ppm)

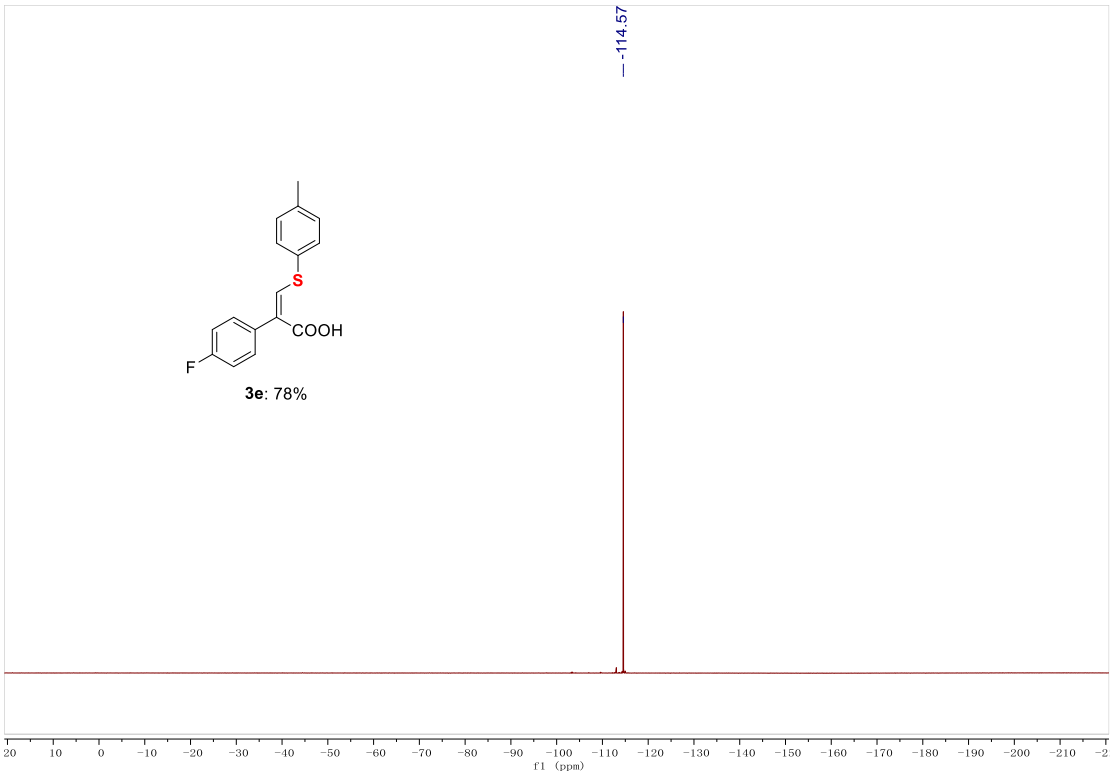

171.94
159.11
151.45
138.60
133.25
131.38
130.17
130.12
130.03
125.55
113.57
77.41 CDCl3
77.10 CDCl3
76.78 CDCl3
55.35
21.18
S
COOH
MeO
3c: 76%
f1 (ppm)


7.46
7.45
7.41
7.39
7.35
7.34
7.22
7.20
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.29
S
COOH
Cl
3d: 72%
1.01
2.09
4.07
2.00
3.01
f1 (ppm)

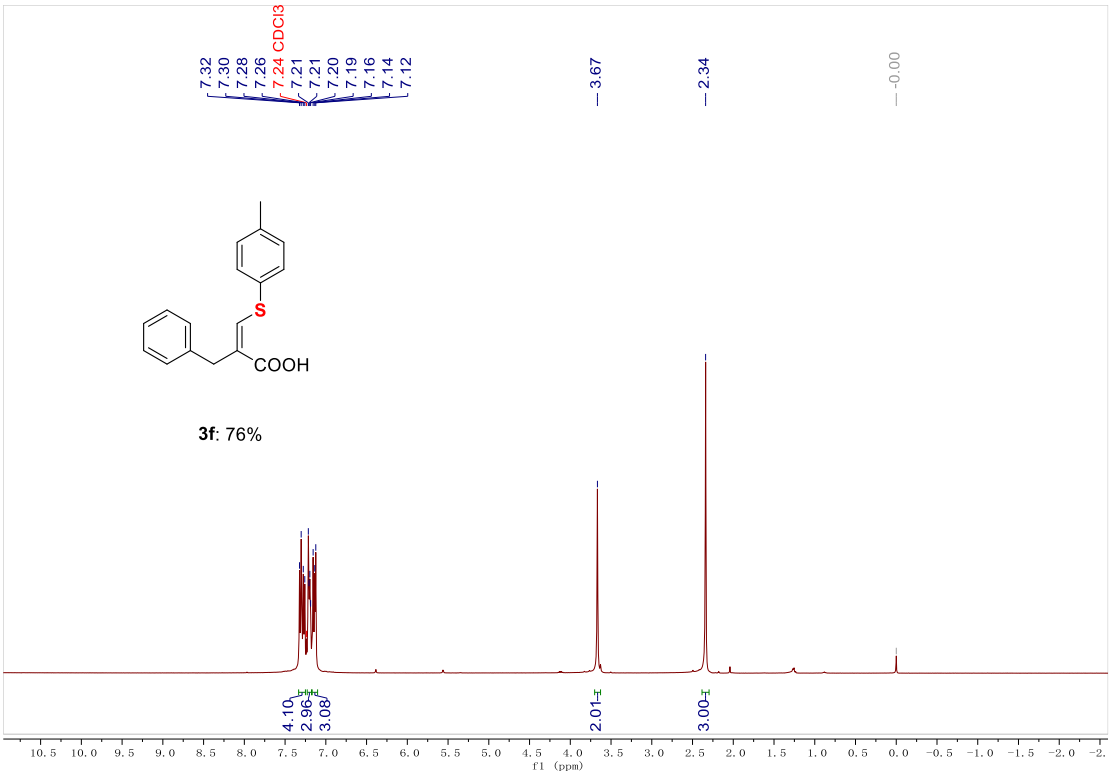

166.85
146.62
137.74
136.62
132.74
131.83
130.40
130.28
130.11
127.85
126.48
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
20.61
S
COOH
Cl
3d: 72%
f1 (ppm)

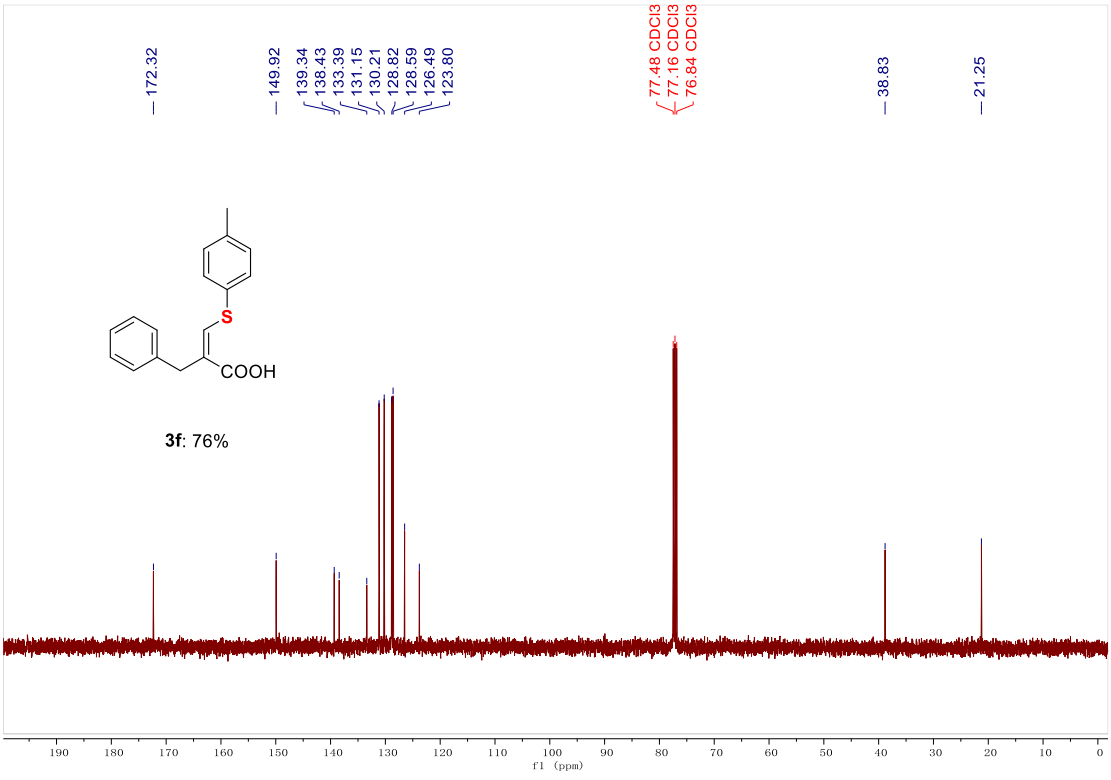

10.48
7.43
7.41
7.39
7.35
7.34
7.33
7.32
7.24 CDCl3
7.19
7.17
7.03
7.01
6.98
2.35
0.00
S
COOH
F
3e: 78%
1.01
0.92
2.07
2.07
2.03
2.06
3.00
f1 (ppm)

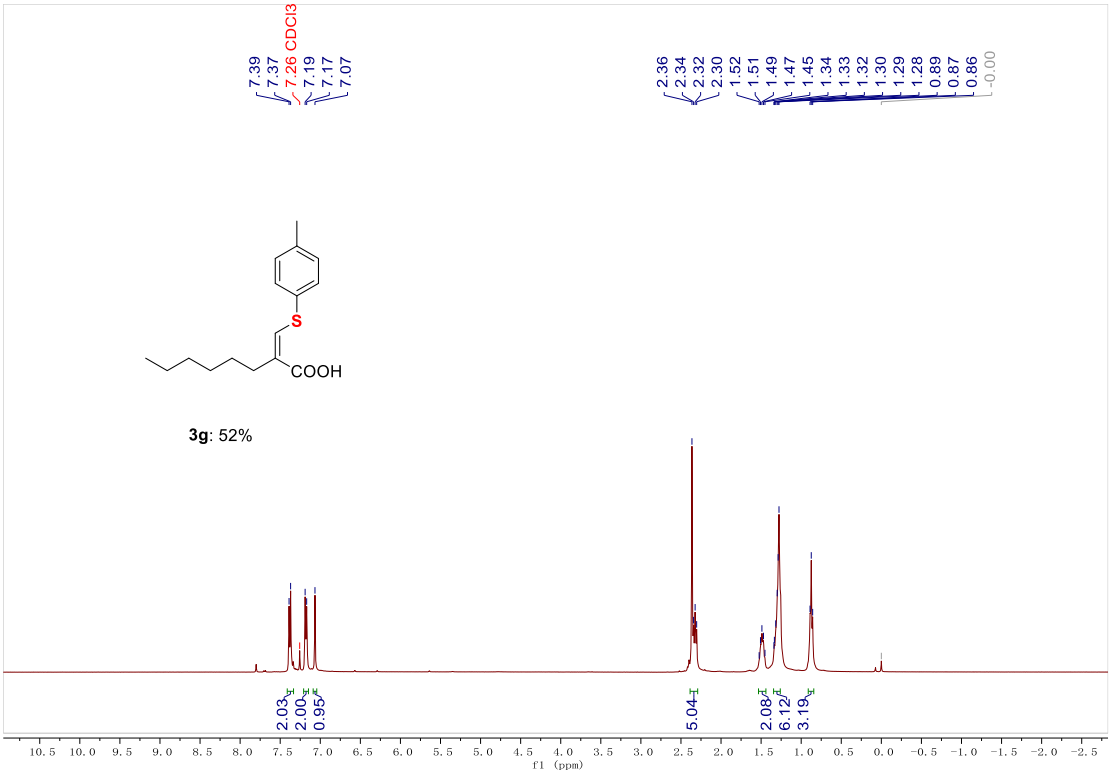

171.60
163.52
161.07
153.01
138.85
133.49
133.46
132.94
131.46
130.70
130.62
130.25
115.14
114.93
77.39 CDCl3
77.07 CDCl3
76.75 CDCl3
21.17
S
COOH
F
3e: 78%
f1 (ppm)

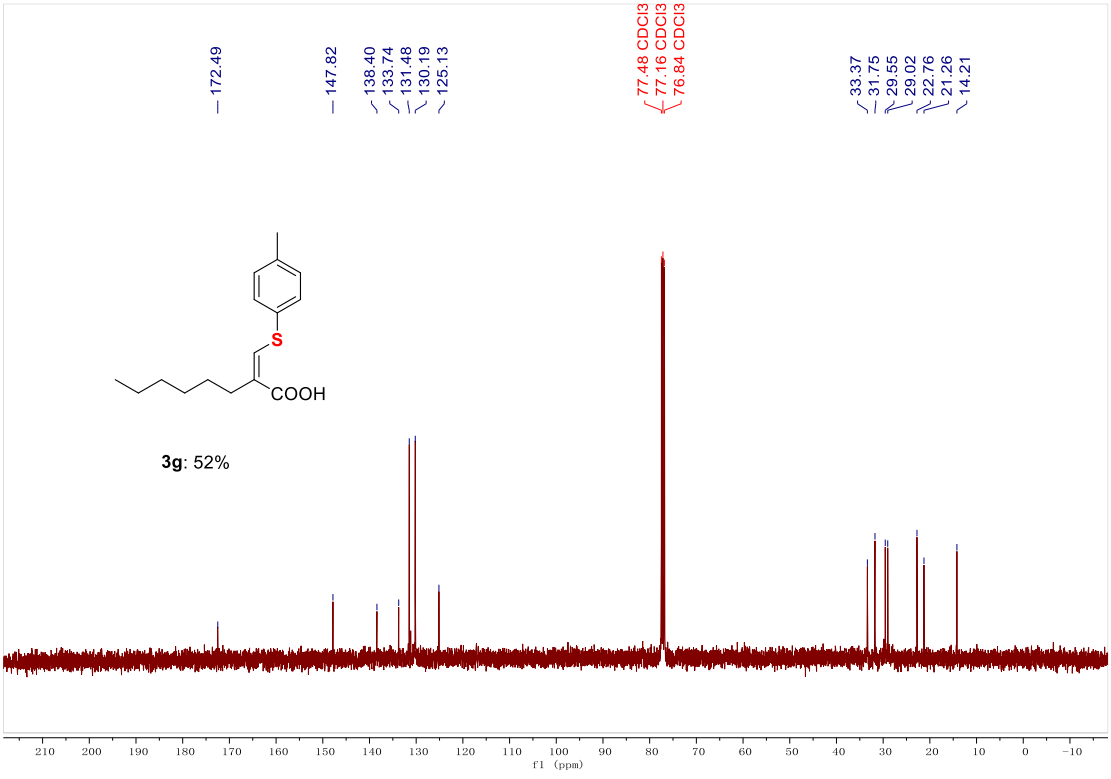

-114.57
S
COOH
F
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

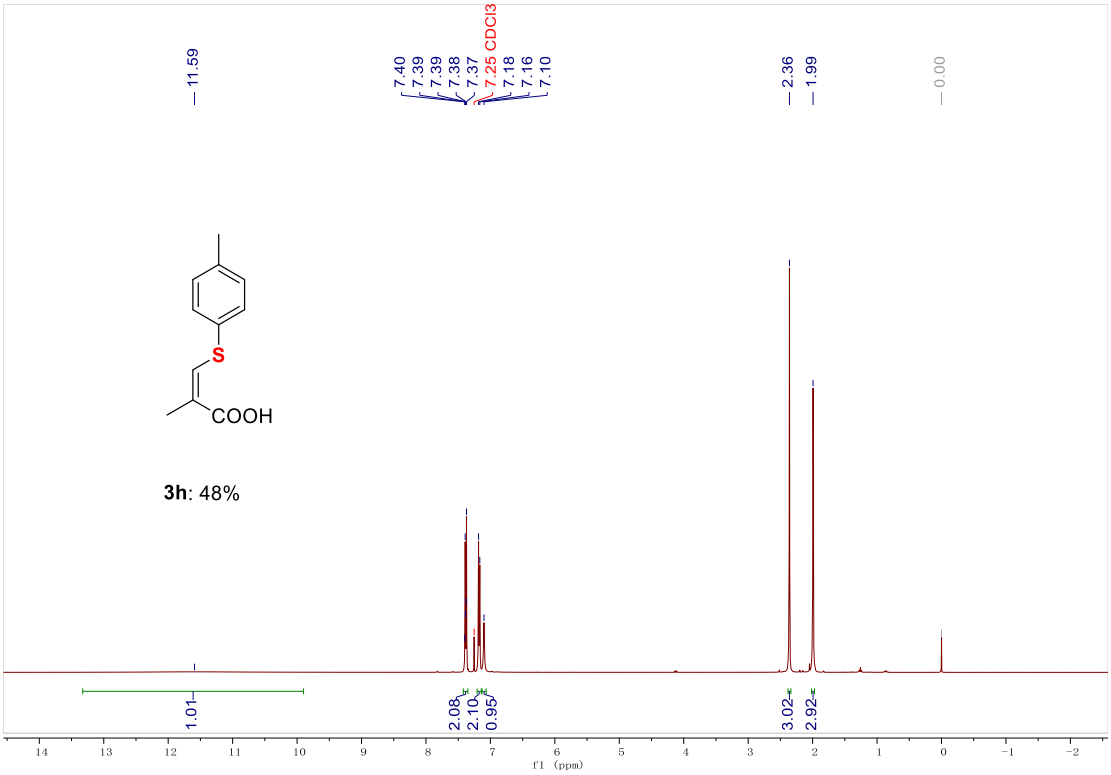
3e: 78%

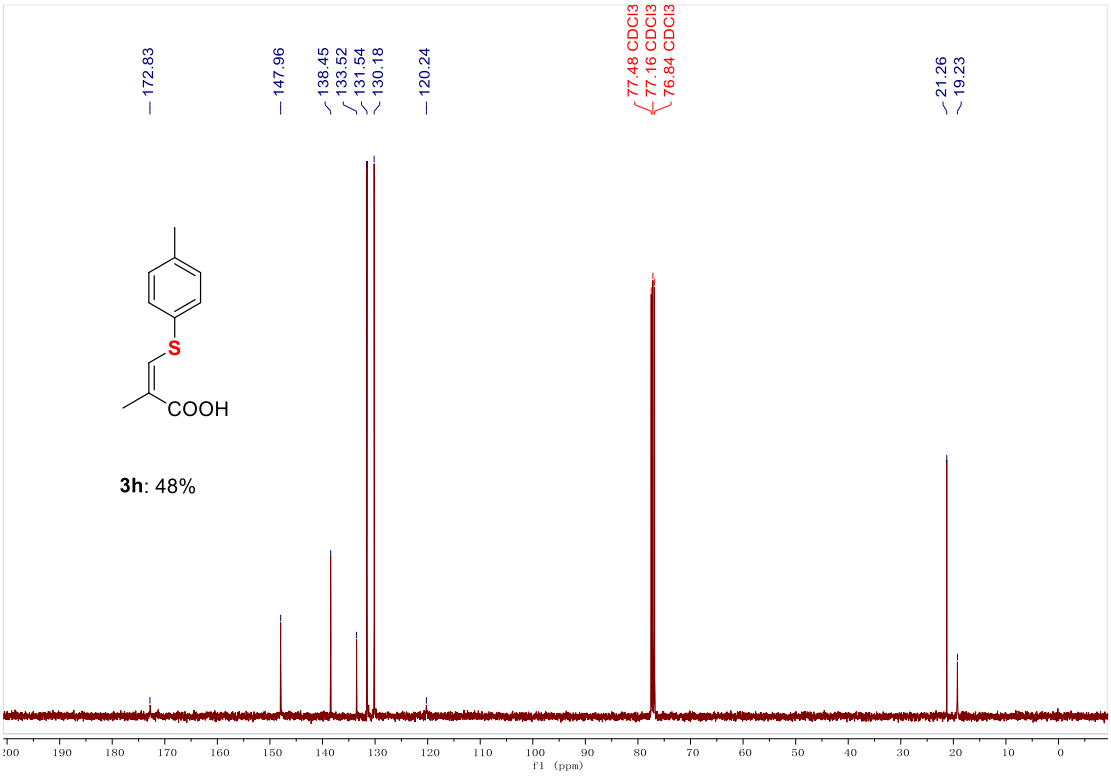

7.32
7.30
7.28
7.26
7.24 CDCl3
7.21
7.21
7.20
7.19
7.16
7.14
7.12
3.67
2.34
-0.00
S
COOH
3f: 76%
4.10
2.96
3.08
2.01
3.00
f1 (ppm)

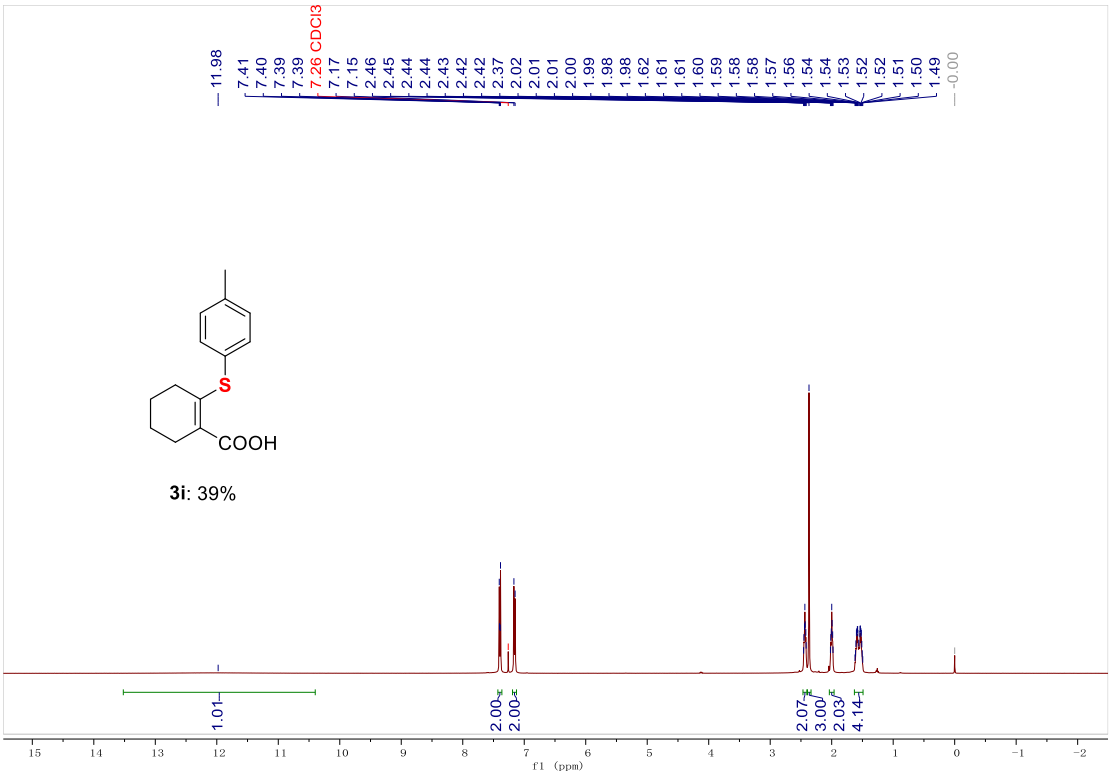

172.32
149.92
139.34
138.43
133.39
131.15
130.21
128.82
128.59
126.49
123.80
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
38.83
21.25
S
COOH
3f: 76%
f1 (ppm)

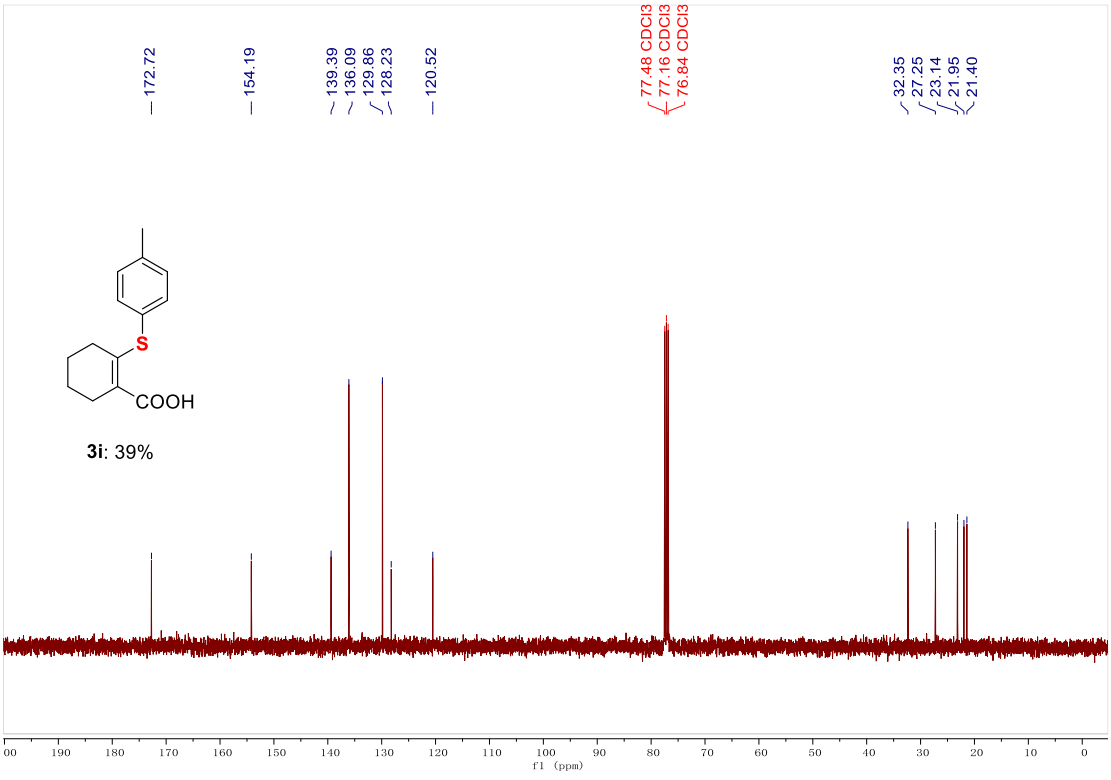

7.39
7.37
7.26 CDCl3
7.19
7.17
7.07
2.36
2.34
2.32
2.30
1.52
1.51
1.49
1.47
1.45
1.34
1.33
1.32
1.30
1.29
1.28
0.89
0.87
0.86
-0.00
S
COOH
3g: 52%
2.03
2.00
0.95
5.04
2.08
6.12
3.19
f1 (ppm)

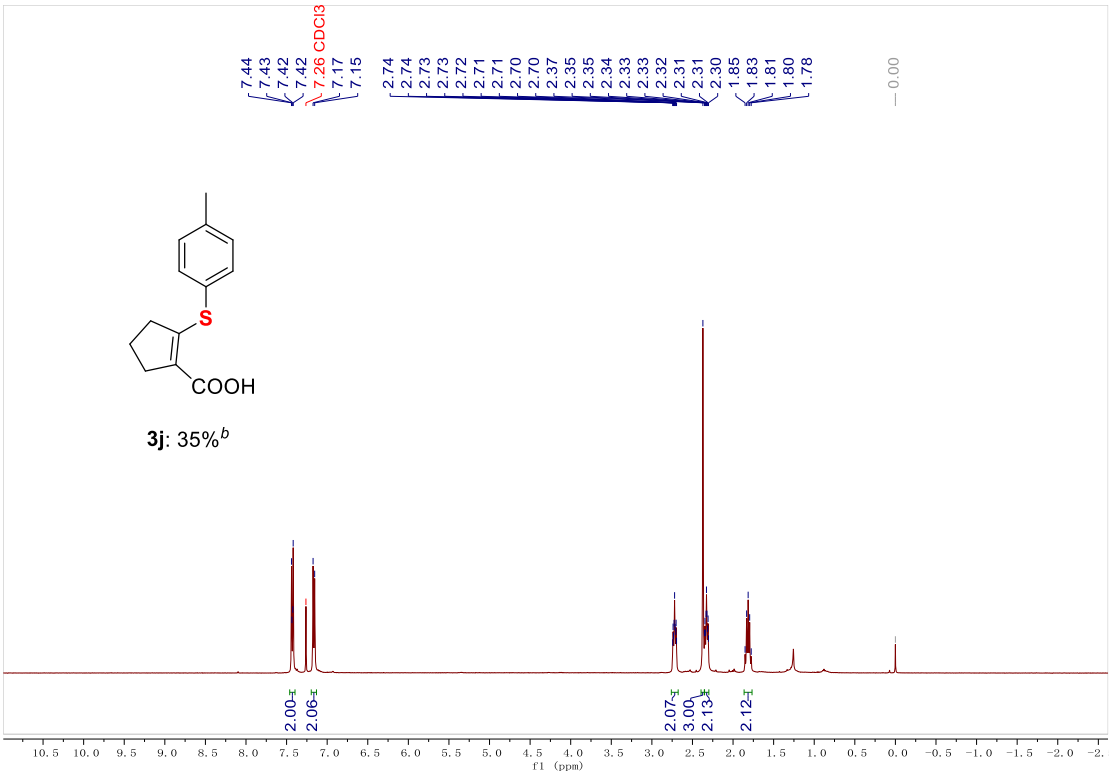

172.49
147.82
138.40
133.74
131.48
130.19
125.13
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
33.37
31.75
29.55
29.02
22.76
21.26
14.21
S
COOH
3g: 52%
f1 (ppm)

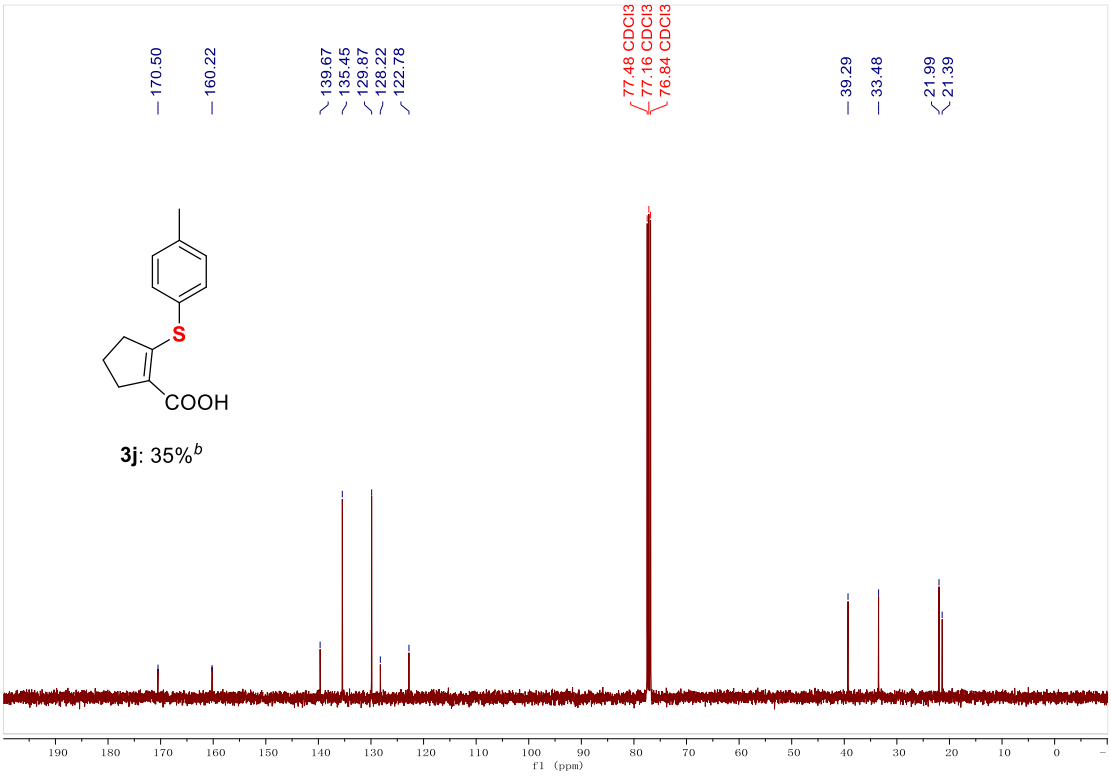

11.59
7.40
7.39
7.39
7.38
7.37
7.25 CDCl3
7.18
7.16
7.10
2.36
1.99
0.00
S
COOH
3h: 48%
1.01
2.08
2.10
0.95
3.02
2.92
f1 (ppm)

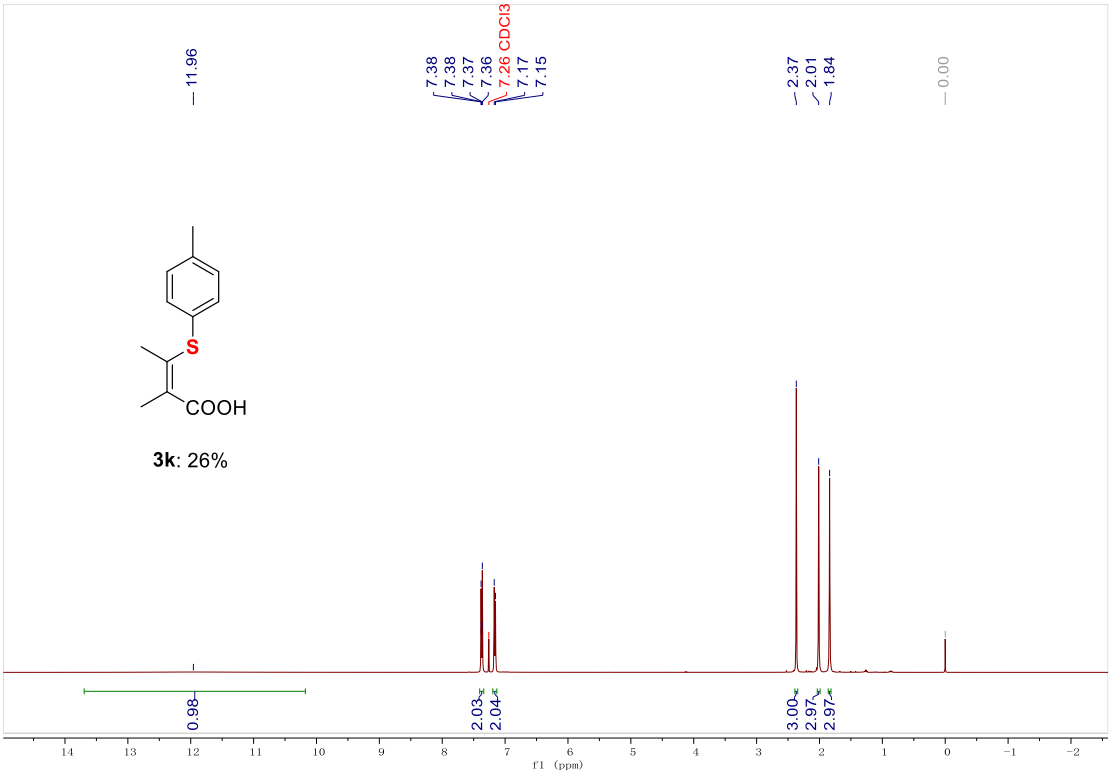

172.83
147.96
138.45
133.52
131.54
130.18
120.24
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.26
19.23
S
COOH
3h: 48%
f1 (ppm)

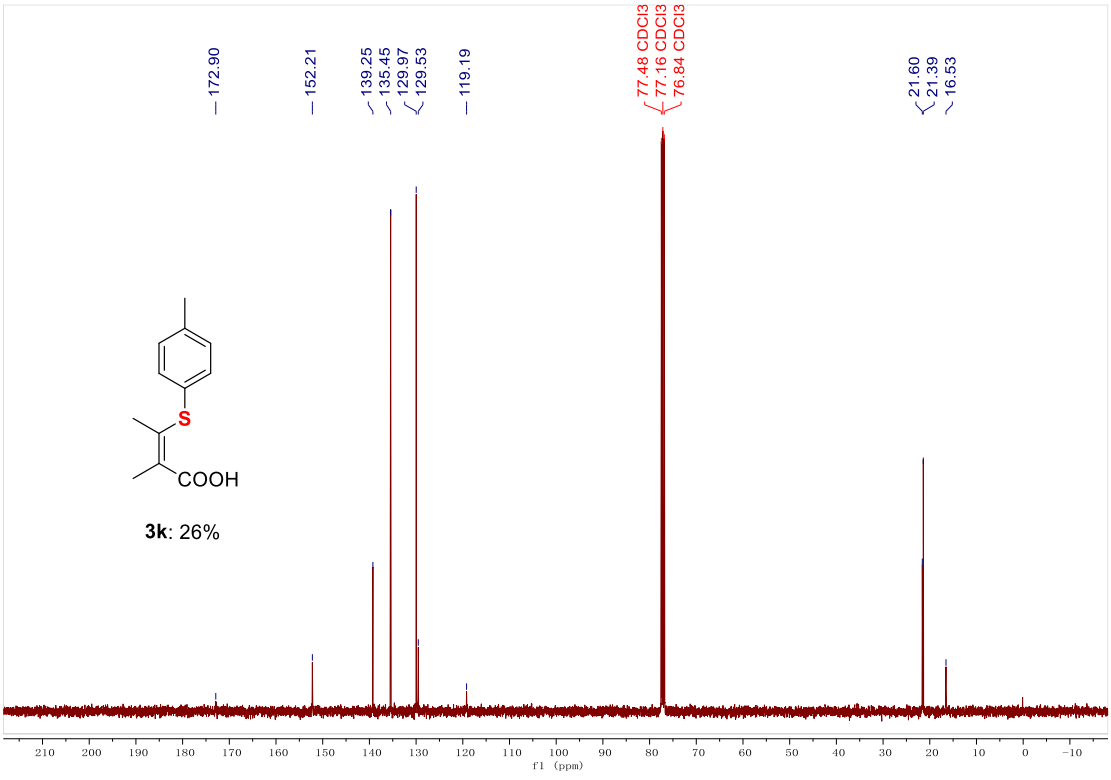

11.98
7.41
7.40
7.39
7.39
7.26 CDCl3
7.17
7.15
2.46
2.45
2.44
2.44
2.43
2.42
2.42
2.37
2.02
2.01
2.01
2.00
1.99
1.98
1.98
1.62
1.61
1.61
1.60
1.59
1.58
1.58
1.57
1.56
1.54
1.54
1.53
1.52
1.52
1.51
1.50
1.49
0.00
S
COOH
3i: 39%
1.01
2.00
2.00
2.07
3.00
2.03
4.14
f1 (ppm)

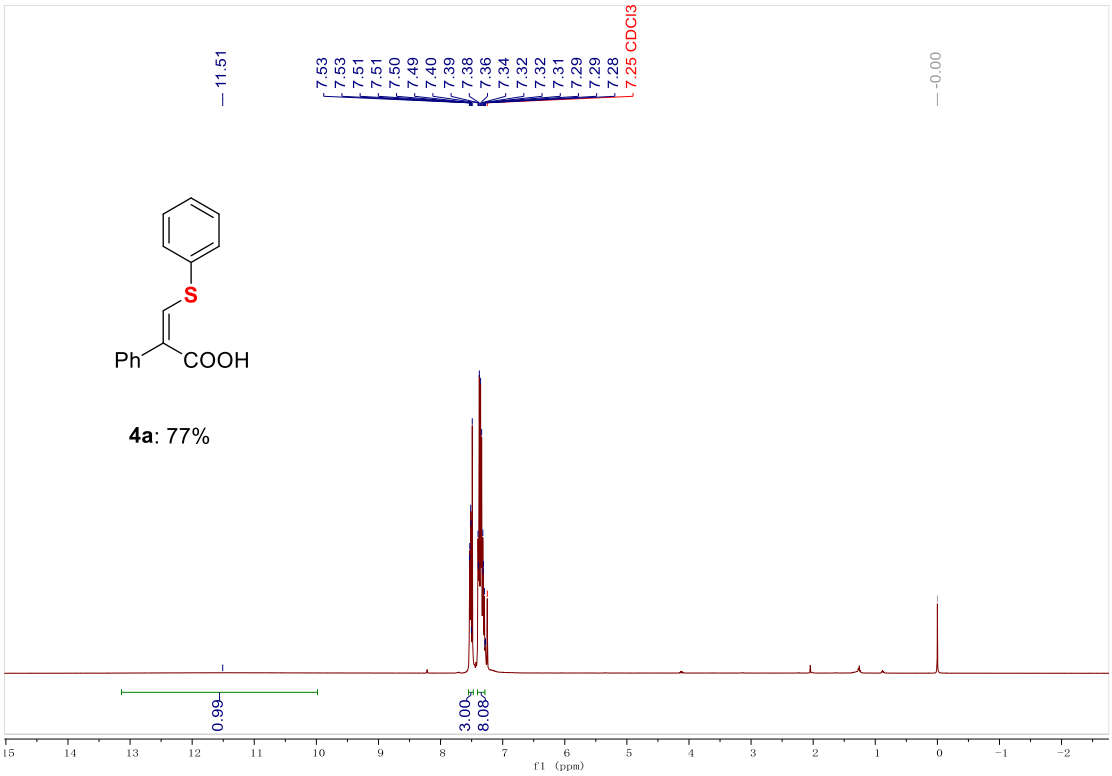

172.72
154.19
139.39
136.09
129.86
128.23
120.52
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
32.35
27.25
23.14
21.95
21.40
S
COOH
3i: 39%
f1 (ppm)

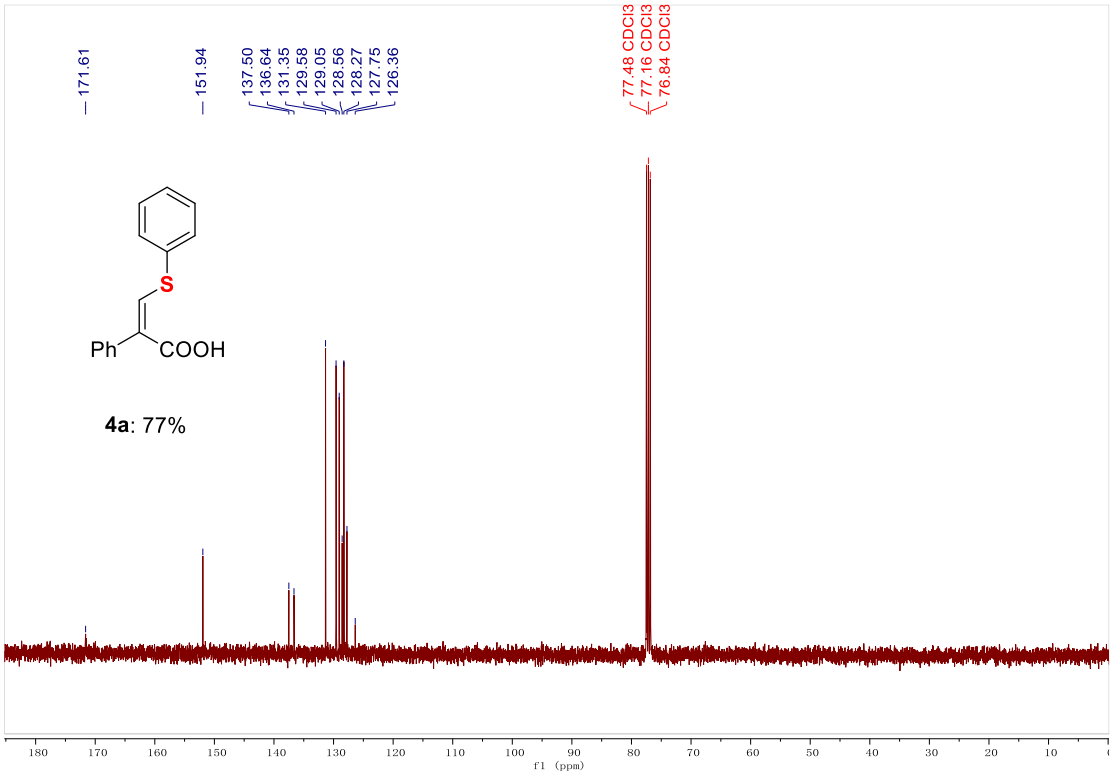

7.44
7.43
7.42
7.42
7.26 CDCl3
7.17
7.15
2.74
2.74
2.73
2.73
2.72
2.71
2.71
2.70
2.70
2.37
2.35
2.35
2.34
2.33
2.33
2.32
2.31
2.31
2.30
1.85
1.83
1.81
1.80
1.78
0.00
S
COOH
3j: 35%b
2.00
2.06
2.07
3.00
2.13
2.12
f1 (ppm)

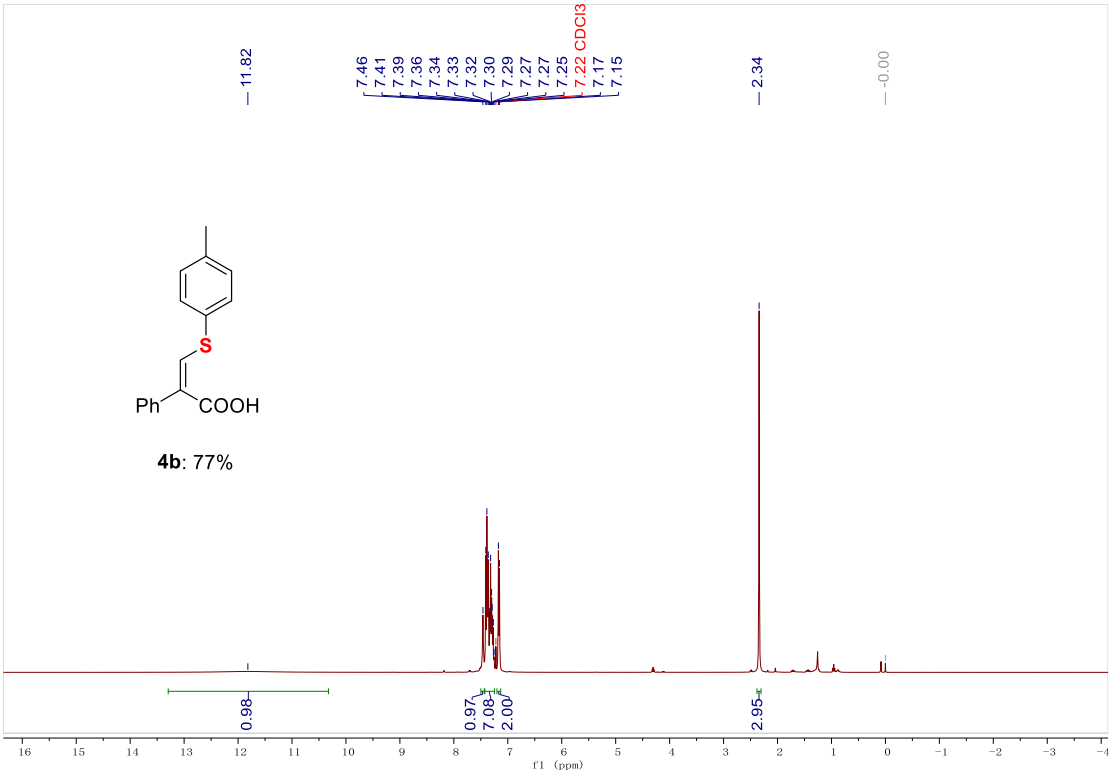

170.50
160.22
139.67
135.45
129.87
128.22
122.78
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
39.29
33.48
21.99
21.39
S
COOH
3j: 35%b
f1 (ppm)

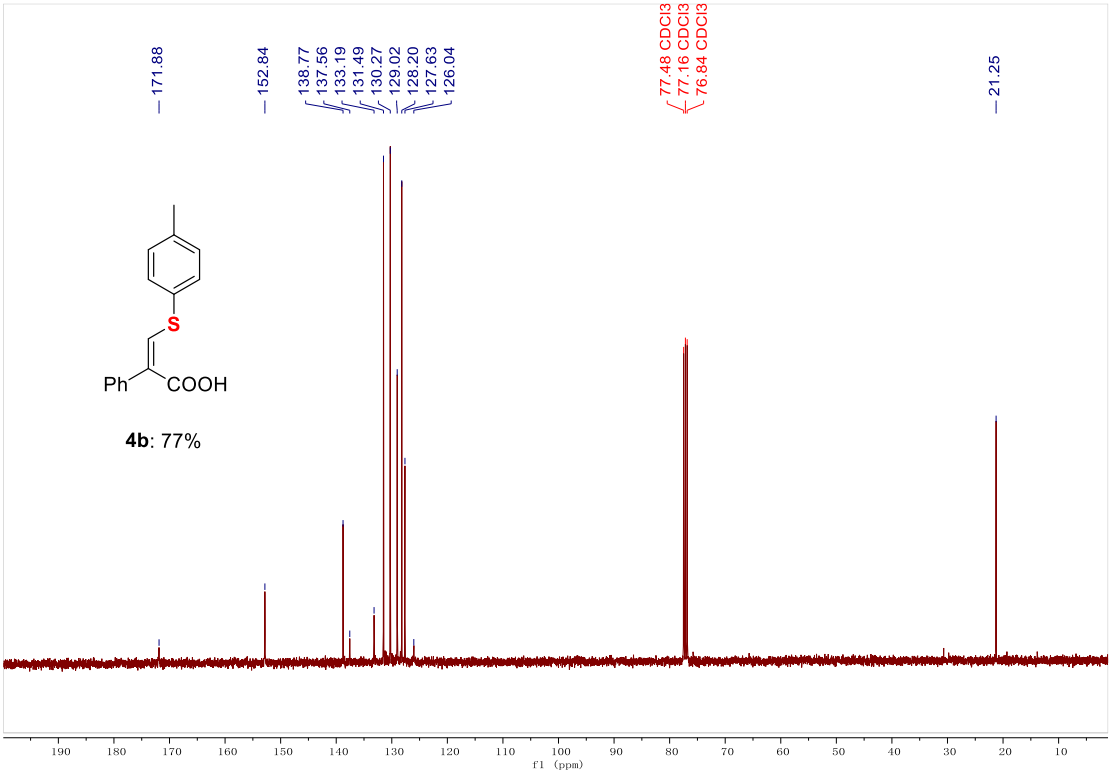

11.96
7.38
7.38
7.37
7.36
7.26 CDCl3
7.17
7.15
2.37
2.01
1.84
0.00
S
COOH
3k: 26%
0.98
2.03
2.04
3.00
2.97
2.97
f1 (ppm)

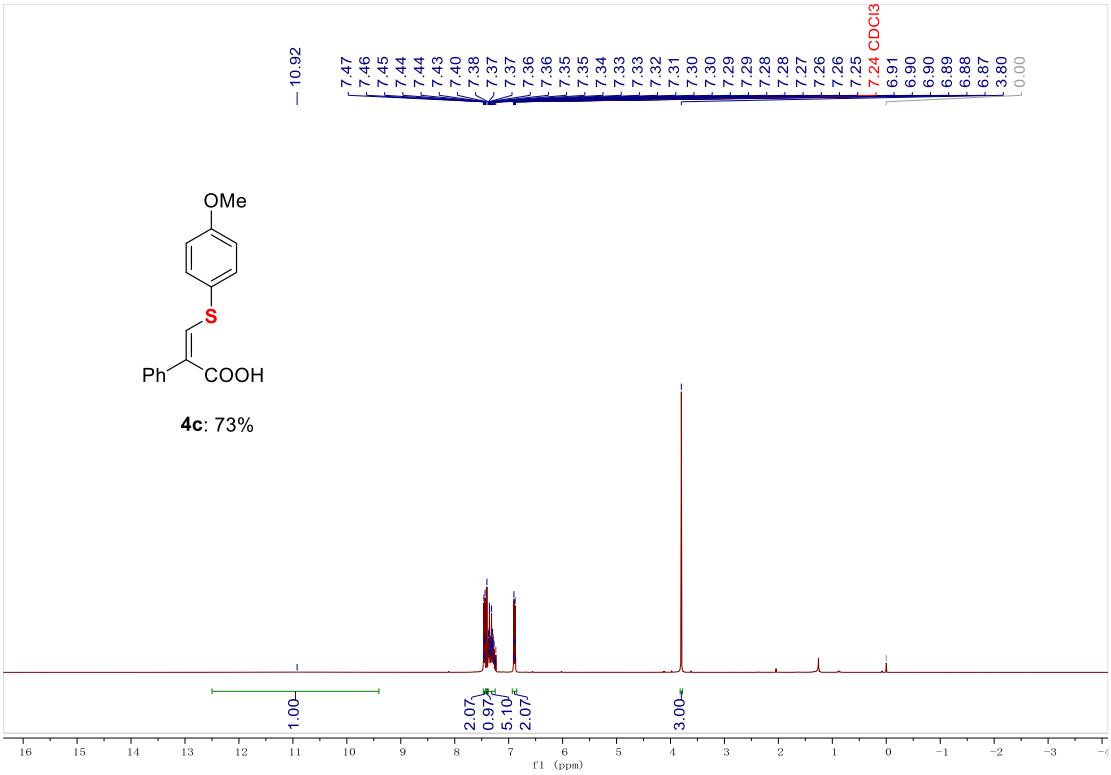

172.90
152.21
139.25
135.45
129.97
129.53
119.19
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.60
21.39
16.53
S
COOH
3k: 26%
f1 (ppm)

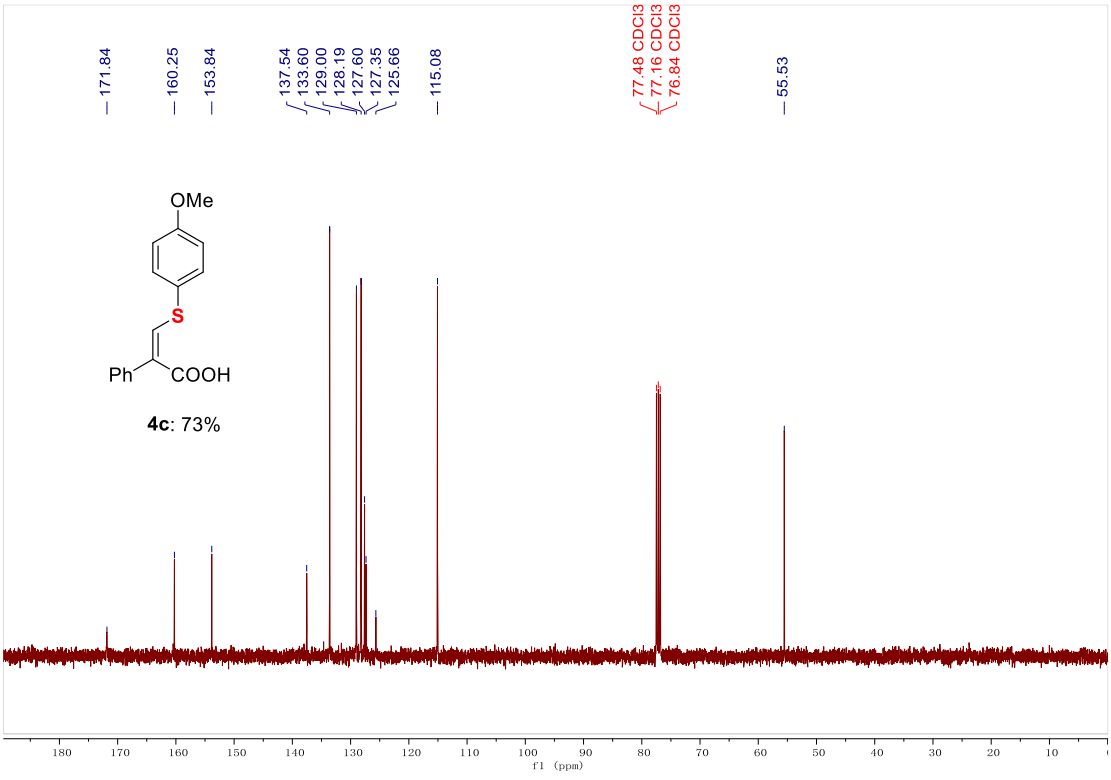

11.51
7.53
7.53
7.51
7.51
7.50
7.49
7.40
7.39
7.38
7.36
7.34
7.32
7.32
7.31
7.29
7.29
7.28
7.25 CDCl3
-0.00
S
Ph
COOH
4a: 77%
0.99
3.00
8.08
f1 (ppm)

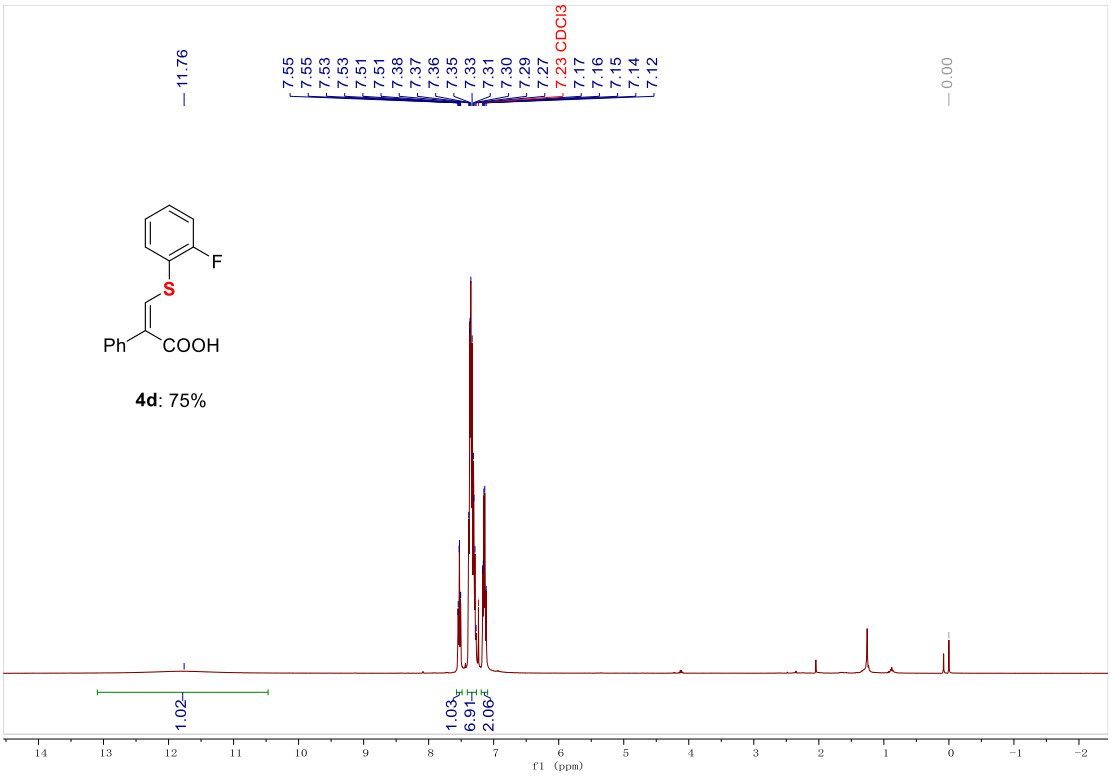

171.61
151.94
137.50
136.64
131.35
129.58
129.05
128.56
128.27
127.75
126.36
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
S
Ph
COOH
4a: 77%
f1 (ppm)

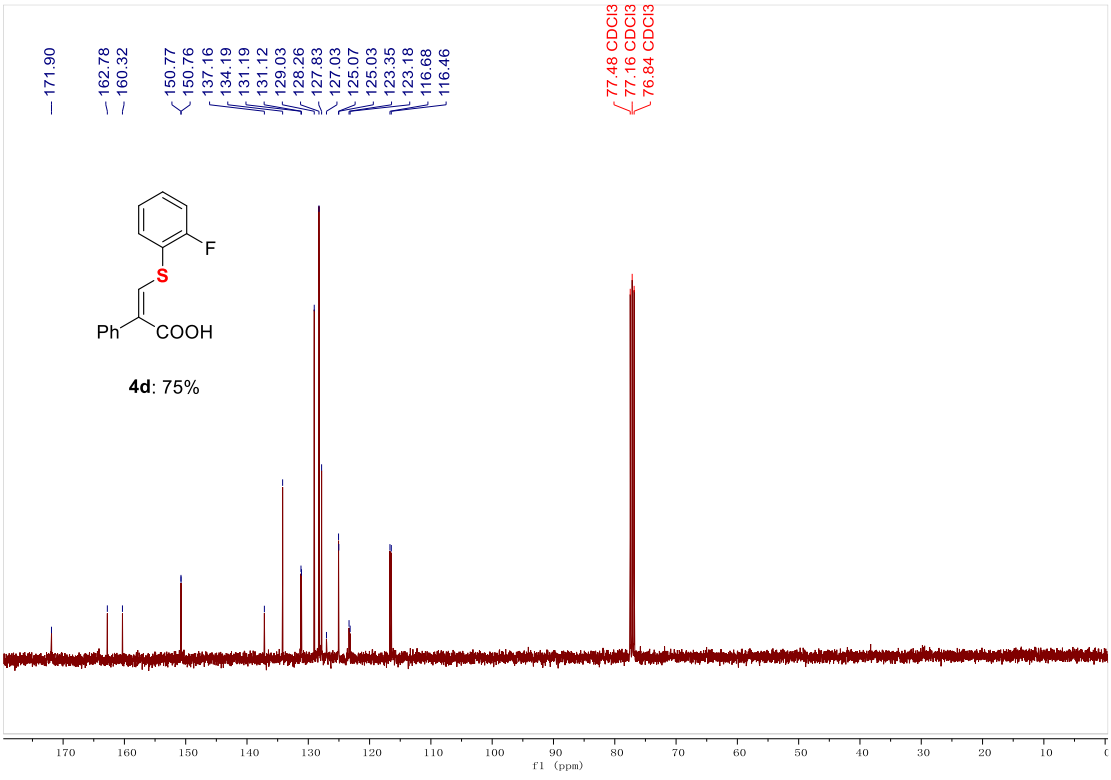

11.82
7.46
7.41
7.39
7.36
7.34
7.33
7.32
7.30
7.29
7.27
7.27
7.25
7.22 CDCl3
7.17
7.15
2.34
0.00
S
Ph
COOH
4b: 77%
0.98
0.97
7.08
2.00
2.95
f1 (ppm)

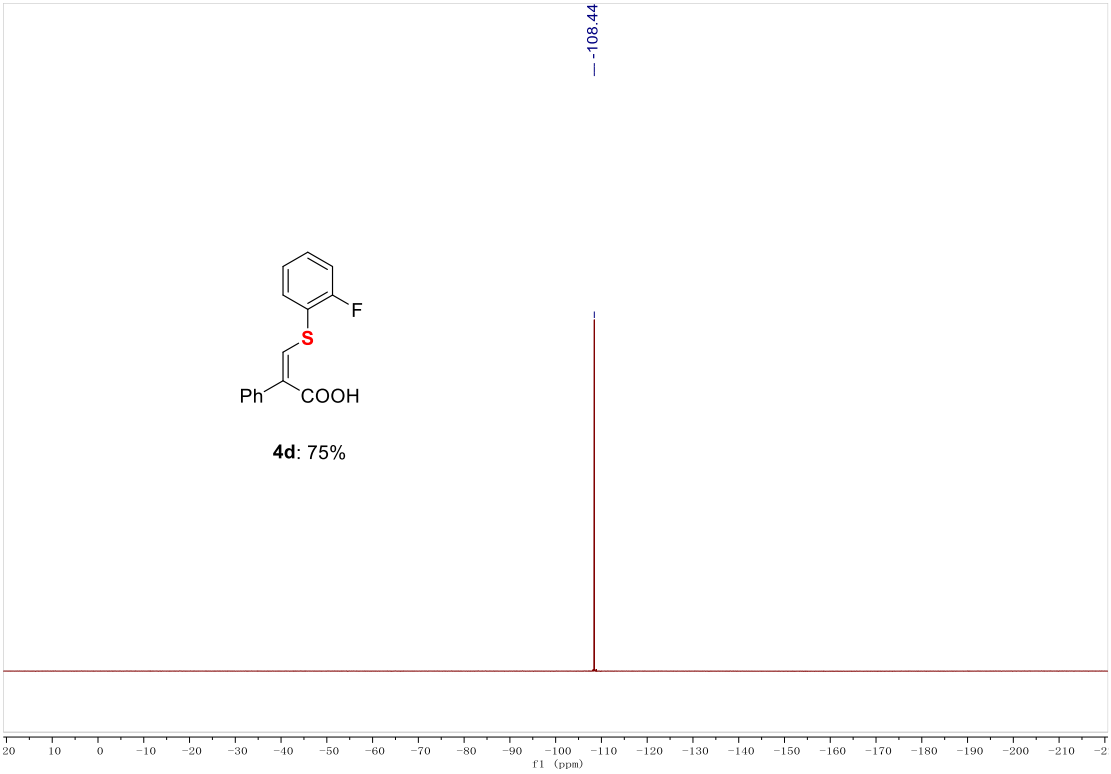

171.88
152.84
138.77
137.56
133.19
131.49
130.27
129.02
128.20
127.63
126.04
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.25
S
Ph
COOH
4b: 77%
f1 (ppm)

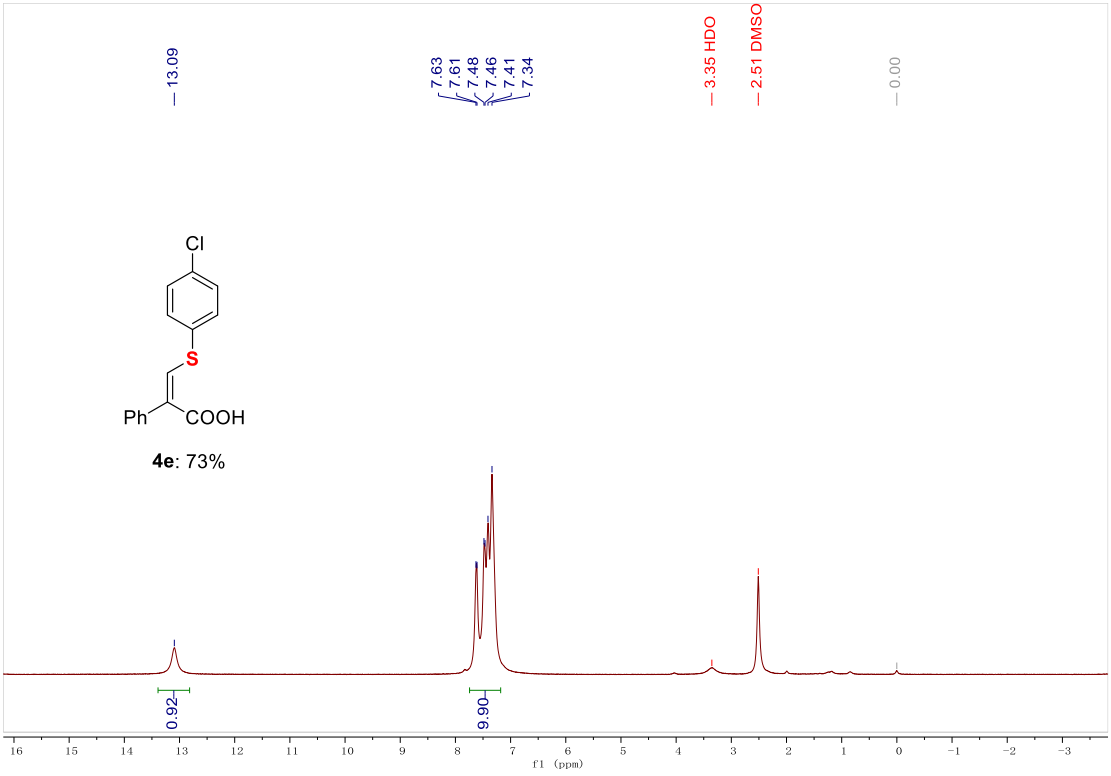

10.92
7.47
7.46
7.45
7.44
7.44
7.43
7.40
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.24 CDCl3
6.91
6.90
6.90
6.89
6.88
6.87
3.80
0.00
OMe
S
Ph
COOH
4c: 73%
1.00
2.07
0.97
5.10
2.07
3.00
f1 (ppm)

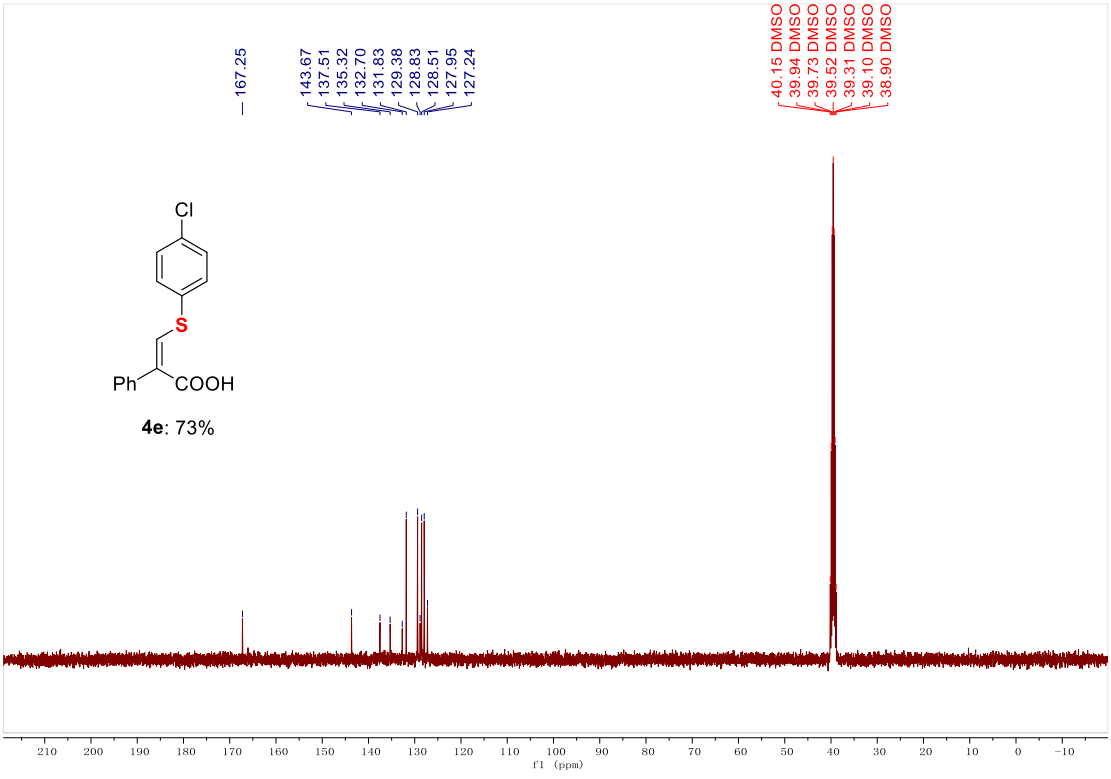

171.84
160.25
153.84
137.54
133.60
129.00
128.19
127.60
127.35
125.66
115.08
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.53
OMe
S
Ph
COOH
4c: 73%
f1 (ppm)

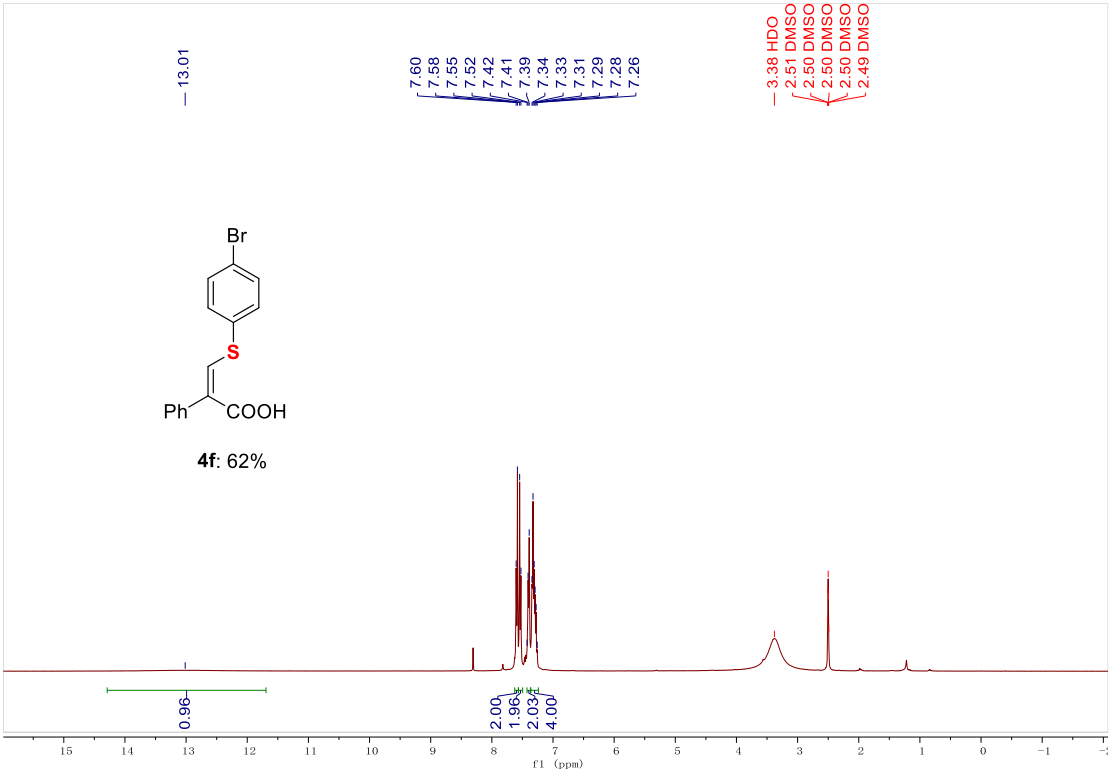

11.76
7.55
7.55
7.53
7.53
7.51
7.51
7.38
7.37
7.36
7.35
7.33
7.31
7.30
7.29
7.27
7.23 CDCl3
7.17
7.16
7.15
7.14
7.12
0.00
F
S
Ph
COOH
4d: 75%
1.02
1.03
6.91
2.06
f1 (ppm)

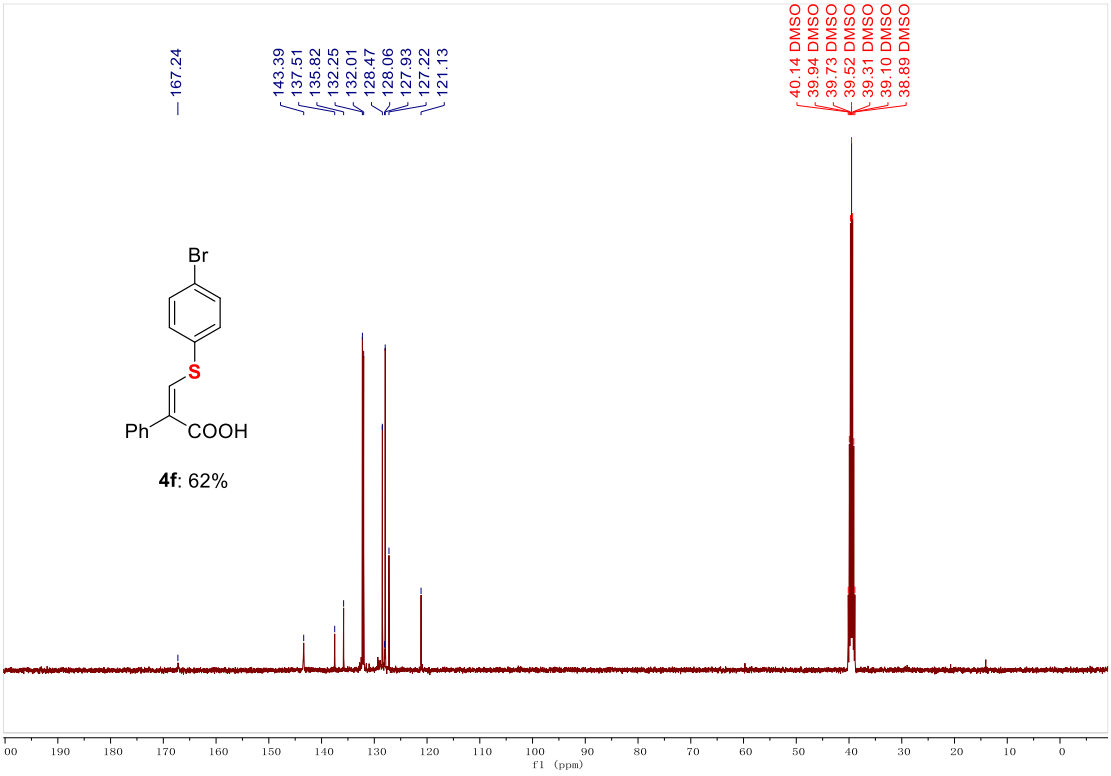

171.90
162.78
160.32
150.77
150.76
137.16
134.19
131.19
131.12
129.03
128.26
127.83
127.03
125.07
125.03
123.35
123.18
116.68
116.46
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
F
S
Ph
COOH
4d: 75%
f1 (ppm)

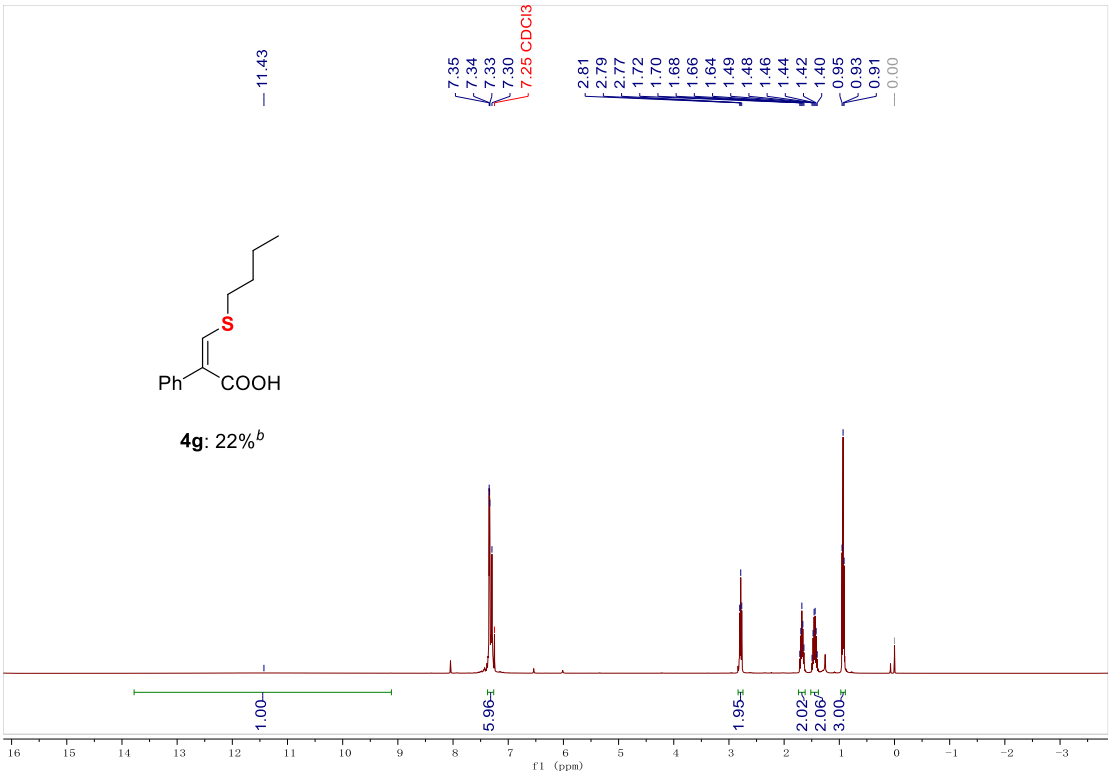

-108.44
F
S
Ph
COOH
4d: 75%
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

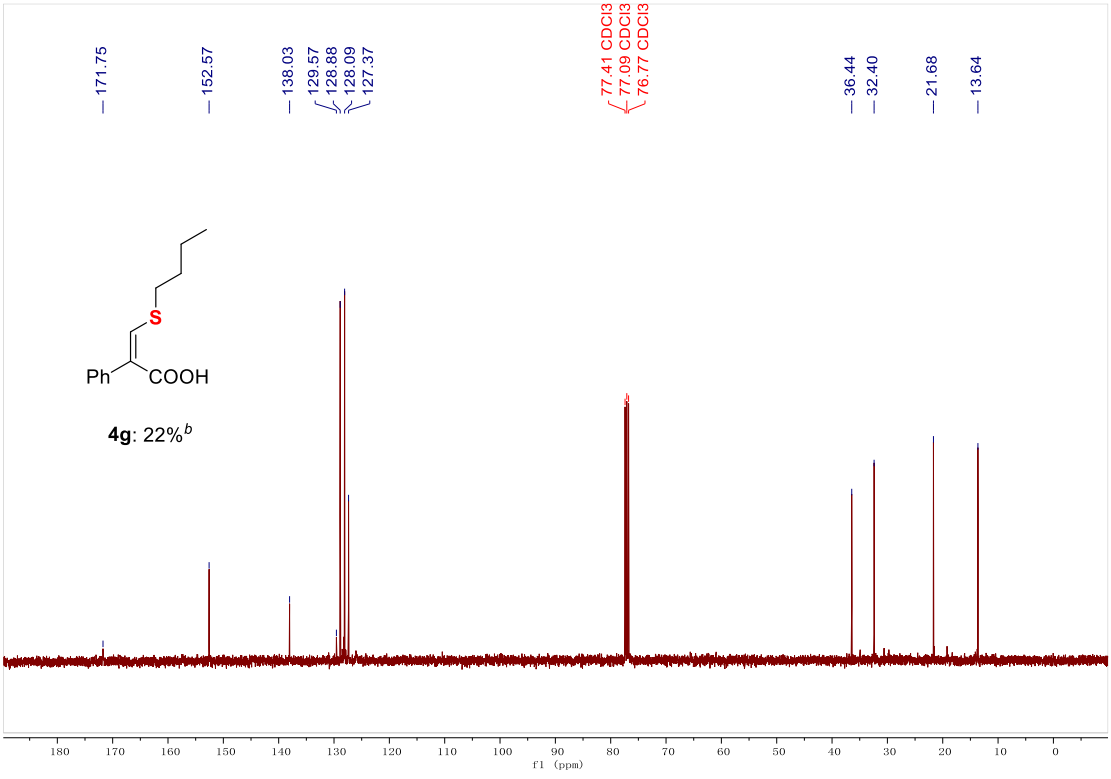

13.09
7.63
7.61
7.48
7.46
7.41
7.34
3.35 HDO
2.51 DMSO
0.00
Cl
S
Ph
COOH
4e: 73%
0.92
9.90
f1 (ppm)

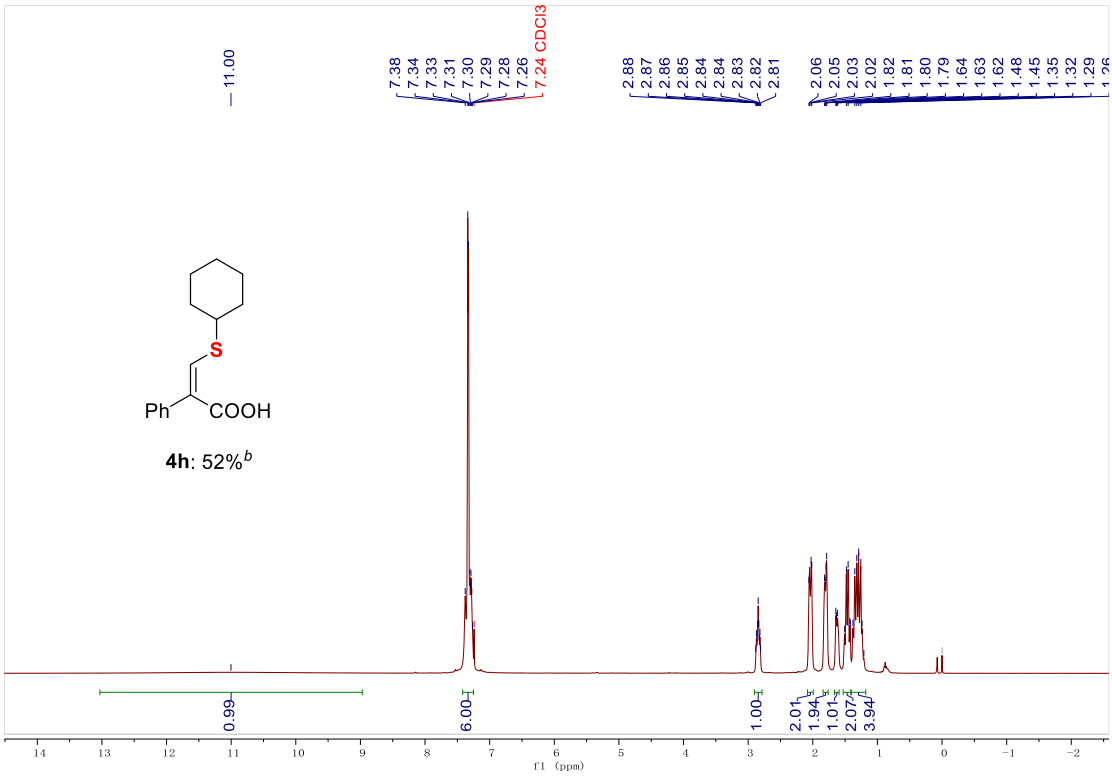

167.25
143.67
137.51
135.32
132.70
131.83
129.38
128.83
128.51
127.95
127.24
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.90 DMSO
Cl
S
Ph
COOH
4e: 73%
f1 (ppm)

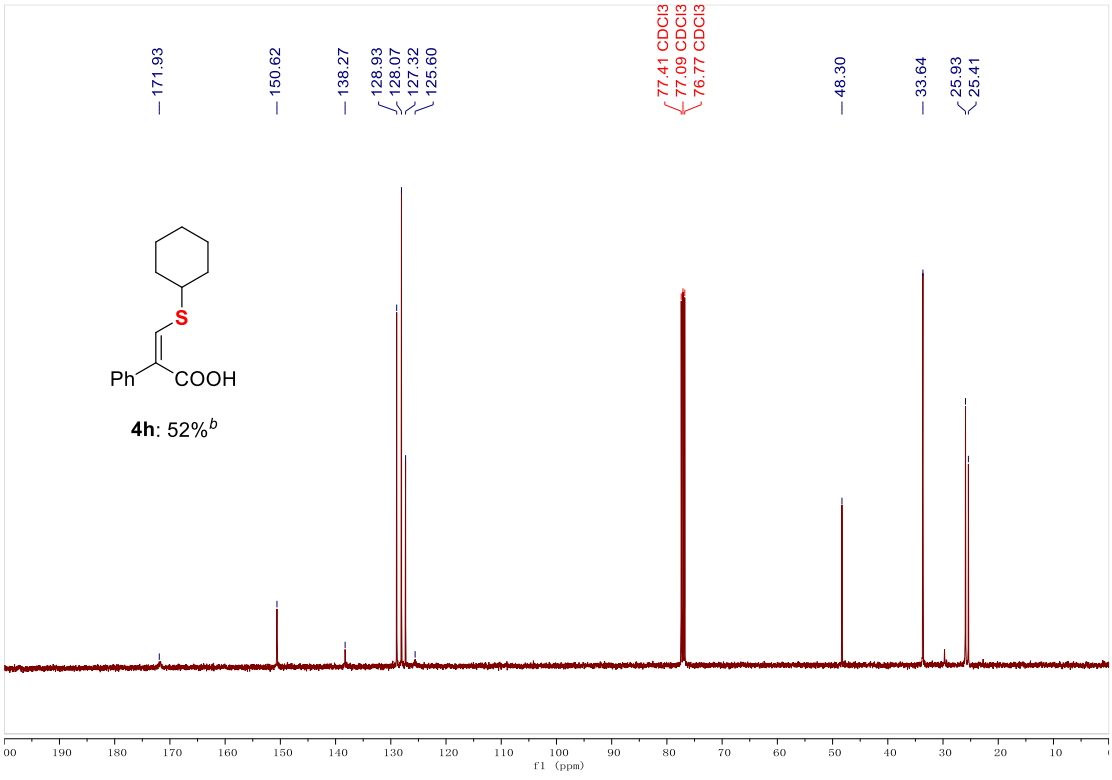

13.01
7.60
7.58
7.55
7.52
7.42
7.41
7.39
7.34
7.33
7.31
7.29
7.28
7.26
3.38 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
Br
S
Ph
COOH
4f: 62%
0.96
2.00
1.96
2.03
4.00
f1 (ppm)

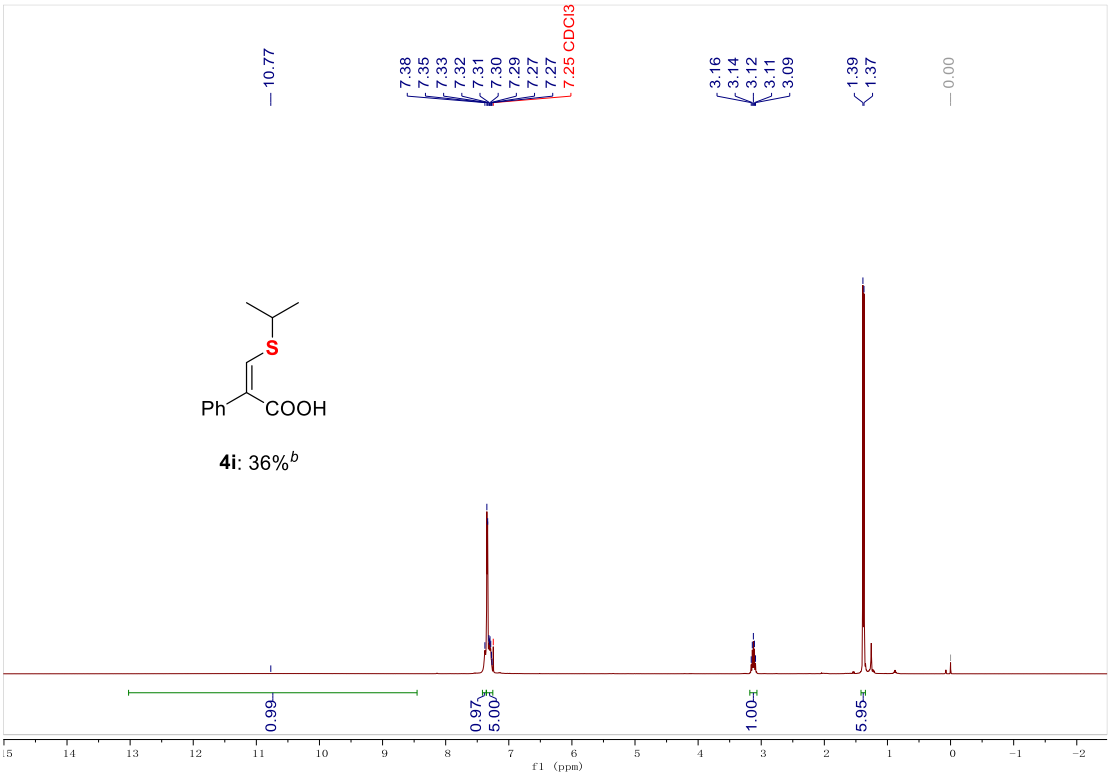

167.24
143.39
137.51
135.82
132.25
132.01
128.47
128.06
127.93
127.22
121.13
40.14 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
Br
S
Ph
COOH
4f: 62%
f1 (ppm)

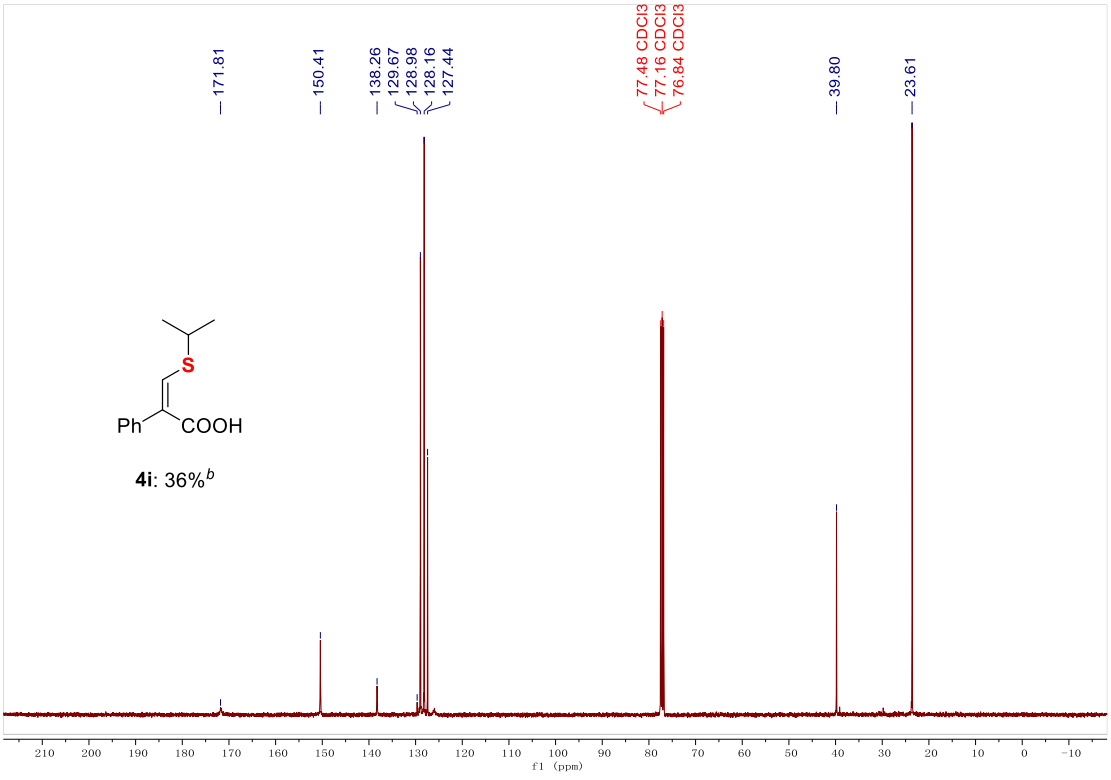

11.43
7.35
7.34
7.33
7.30
7.25 CDCl3
2.81
2.79
2.77
1.72
1.70
1.68
1.66
1.64
1.49
1.48
1.46
1.44
1.42
1.40
0.95
0.93
0.91
0.00
S
Ph
COOH
4g: 22%b
1.00
5.96
1.95
2.02
2.06
3.00
f1 (ppm)

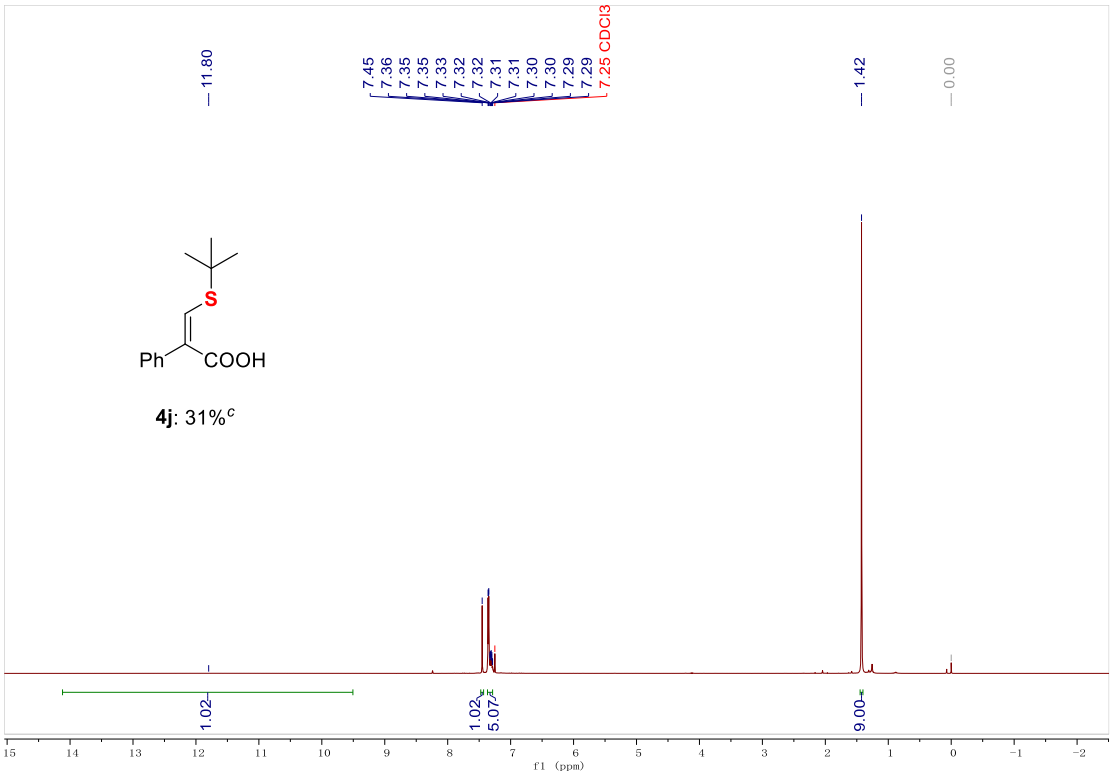

171.75
152.57
138.03
129.57
128.88
128.09
127.37
77.41 CDCl3
77.09 CDCl3
76.77 CDCl3
36.44
32.40
21.68
13.64
S
Ph
COOH
4g: 22%b
f1 (ppm)

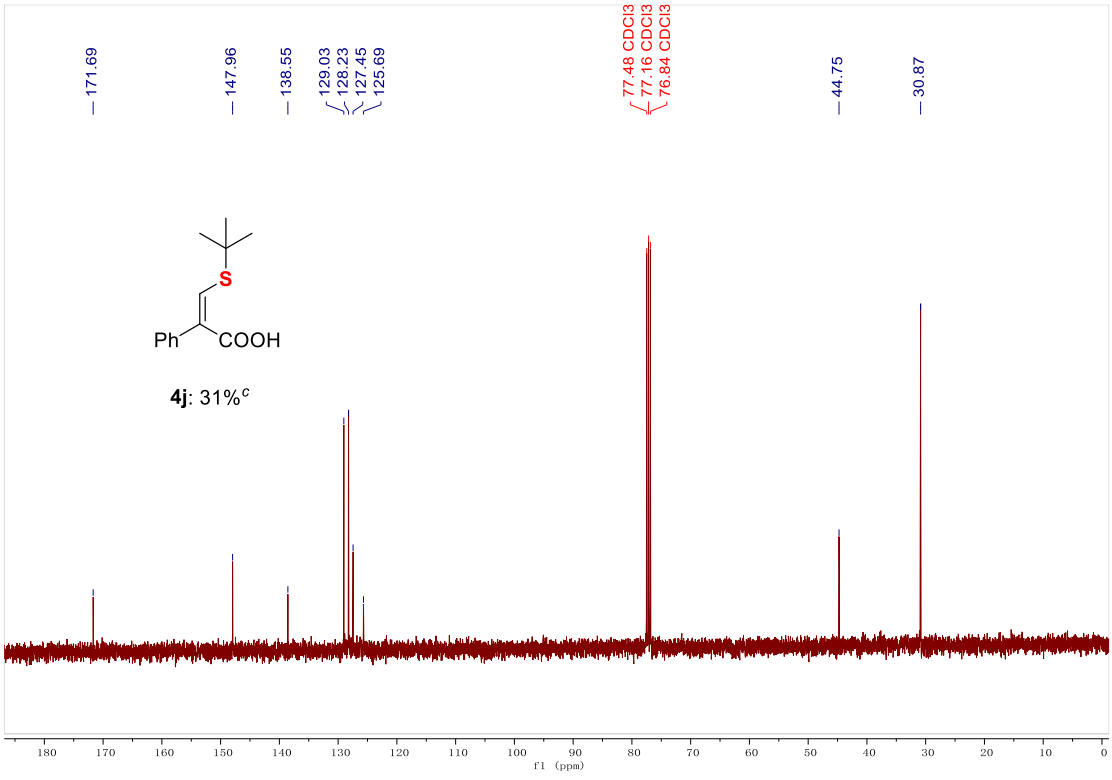

11.00
7.38
7.34
7.33
7.31
7.30
7.29
7.28
7.26
7.24 CDCl3
2.88
2.87
2.86
2.85
2.84
2.84
2.83
2.82
2.81
2.06
2.05
2.03
2.02
1.82
1.81
1.80
1.79
1.64
1.63
1.62
1.48
1.45
1.35
1.32
1.29
S
Ph
COOH
4h: 52%b
0.99
6.00
1.00
2.01
1.94
1.01
2.07
3.94
f1 (ppm)

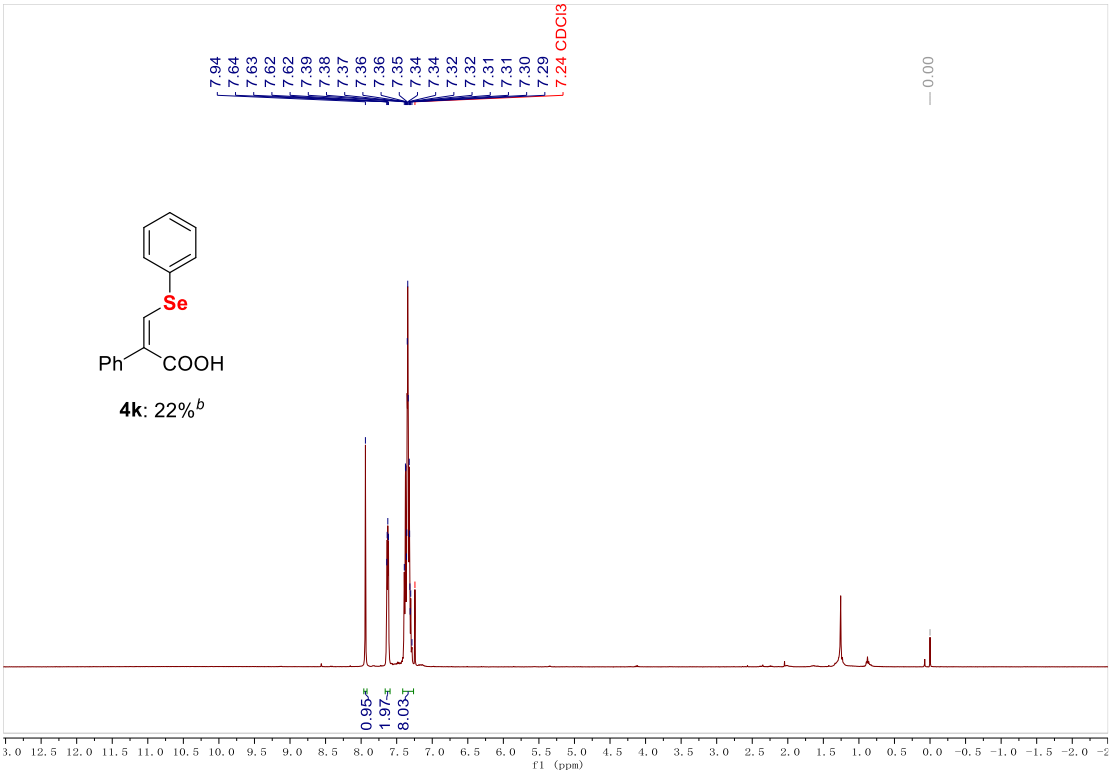

171.93
150.62
138.27
128.93
128.07
127.32
125.60
77.41 CDCl3
77.09 CDCl3
76.77 CDCl3
48.30
33.64
25.93
25.41
S
Ph
COOH
4h: 52%b
f1 (ppm)

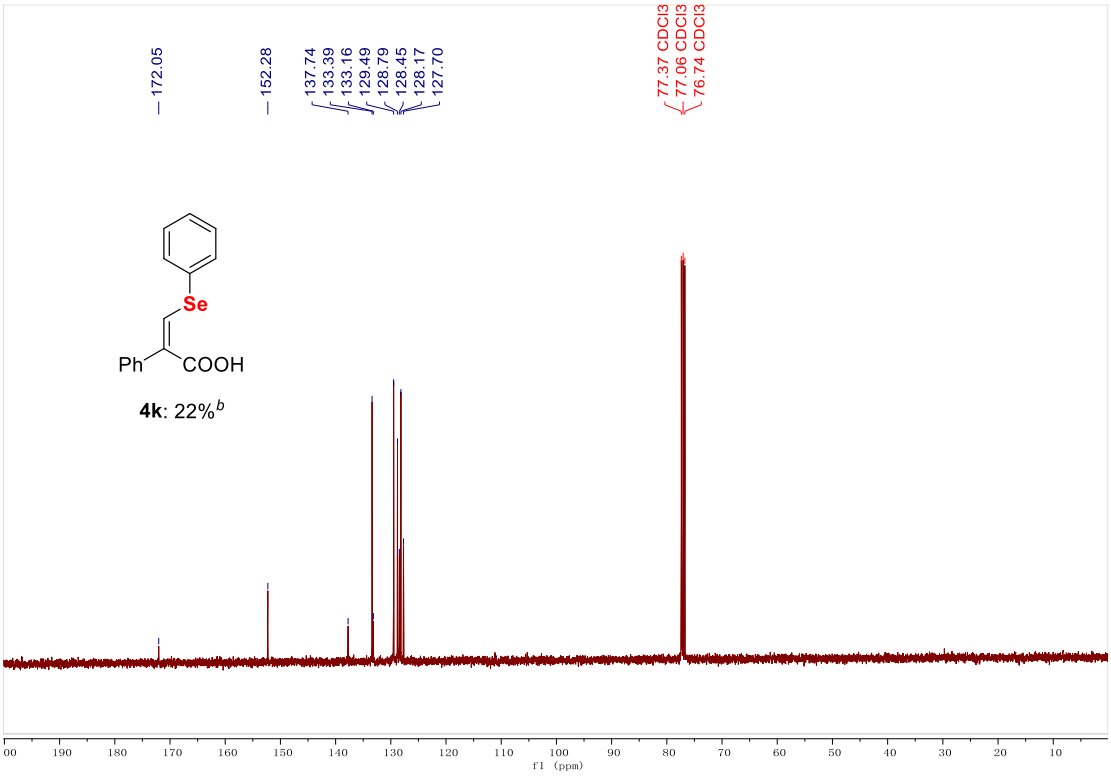

10.77
7.38
7.35
7.33
7.32
7.31
7.30
7.29
7.27
7.27
7.25 CDCl3
3.16
3.14
3.12
3.11
3.09
1.39
1.37
0.00
S
Ph
COOH
4i: 36%b
0.99
0.97
5.00
1.00
5.95
f1 (ppm)

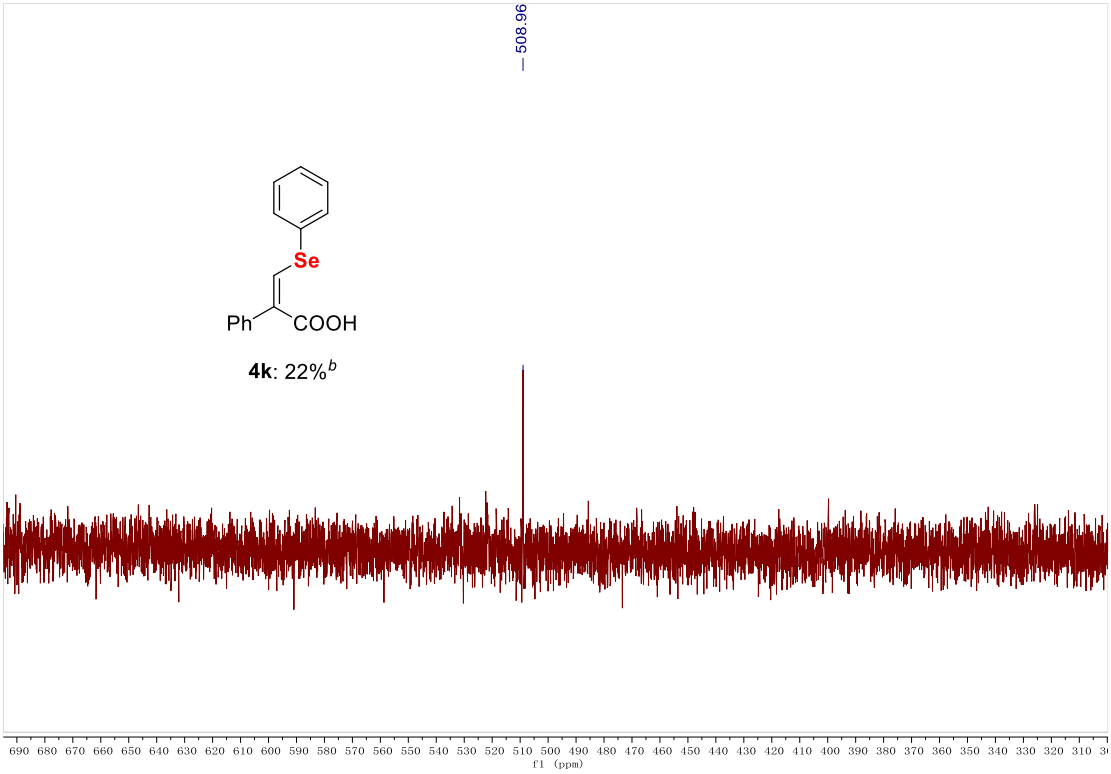

171.81
150.41
138.26
129.67
128.98
128.16
127.44
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
39.80
23.61
S
Ph
COOH
4i: 36%b
f1 (ppm)


11.80
7.45
7.36
7.35
7.35
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.25 CDCl3
1.42
0.00
S
Ph
COOH
4j: 31%c
1.02
1.02
5.07
9.00
f1 (ppm)

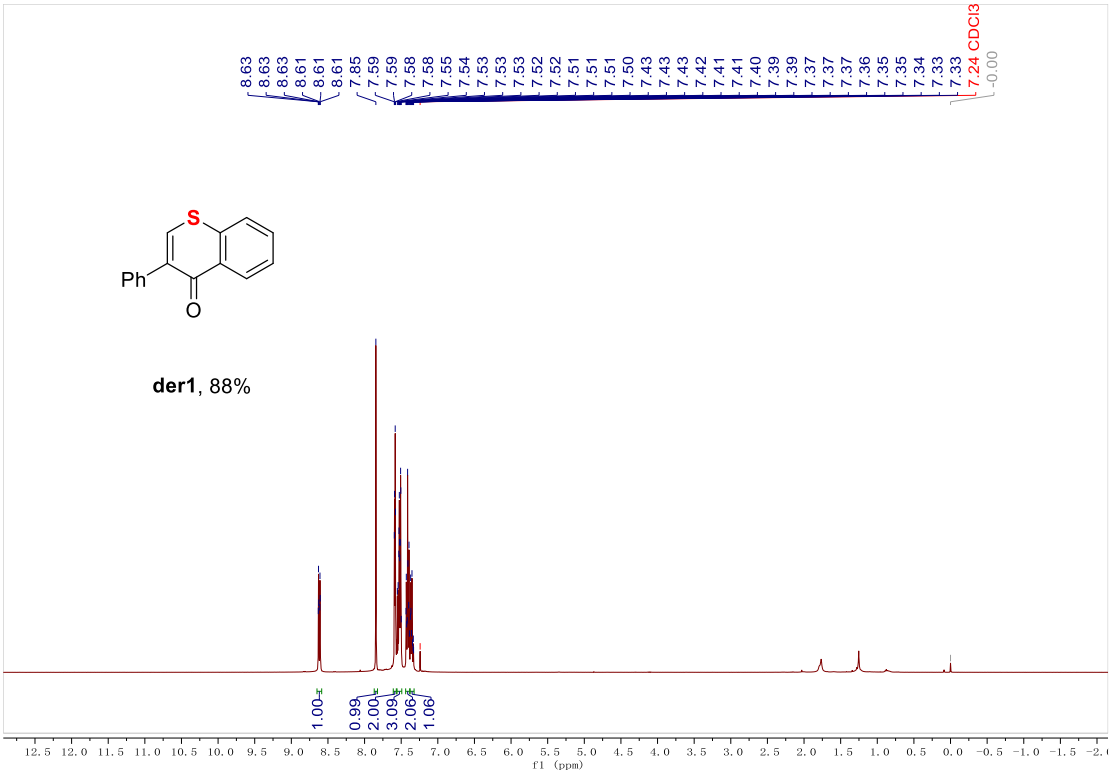

171.69
147.96
138.55
129.03
128.23
127.45
125.69
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
44.75
30.87
S
Ph
COOH
4j: 31%c
f1 (ppm)

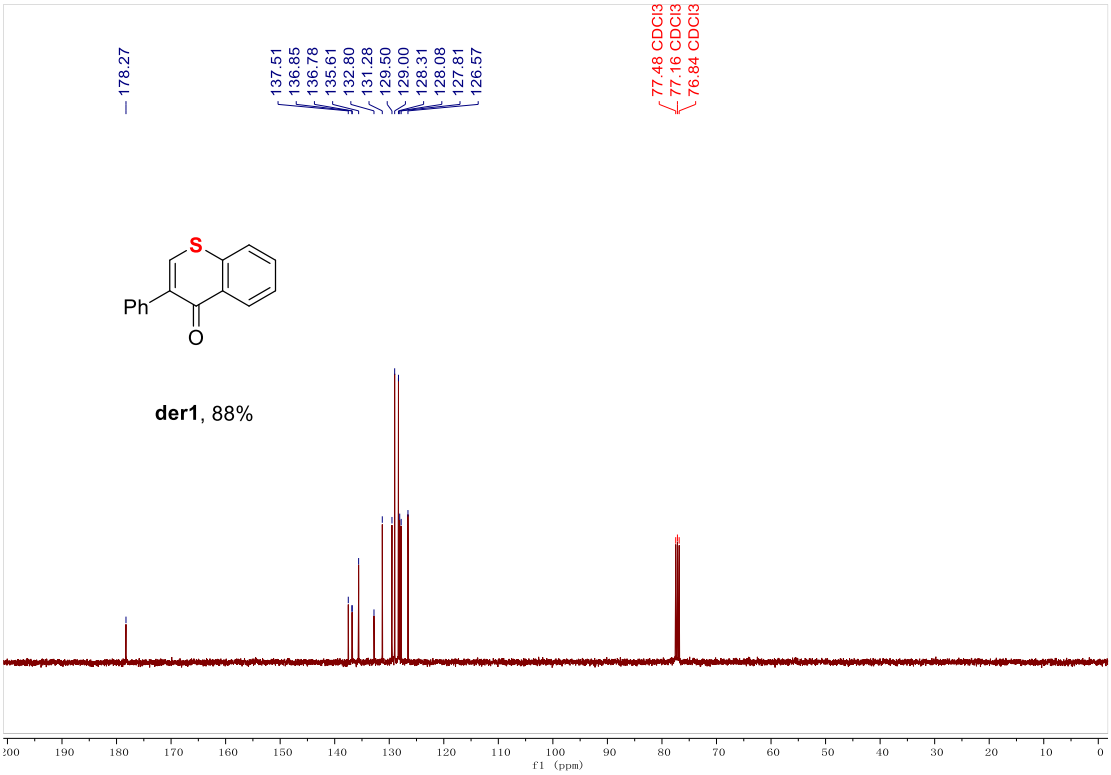

7.94
7.64
7.63
7.62
7.62
7.39
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.32
7.32
7.31
7.31
7.30
7.29
7.24 CDCl3
0.00
Se
Ph
COOH
4k: 22%b
0.95
1.97
8.03
f1 (ppm)

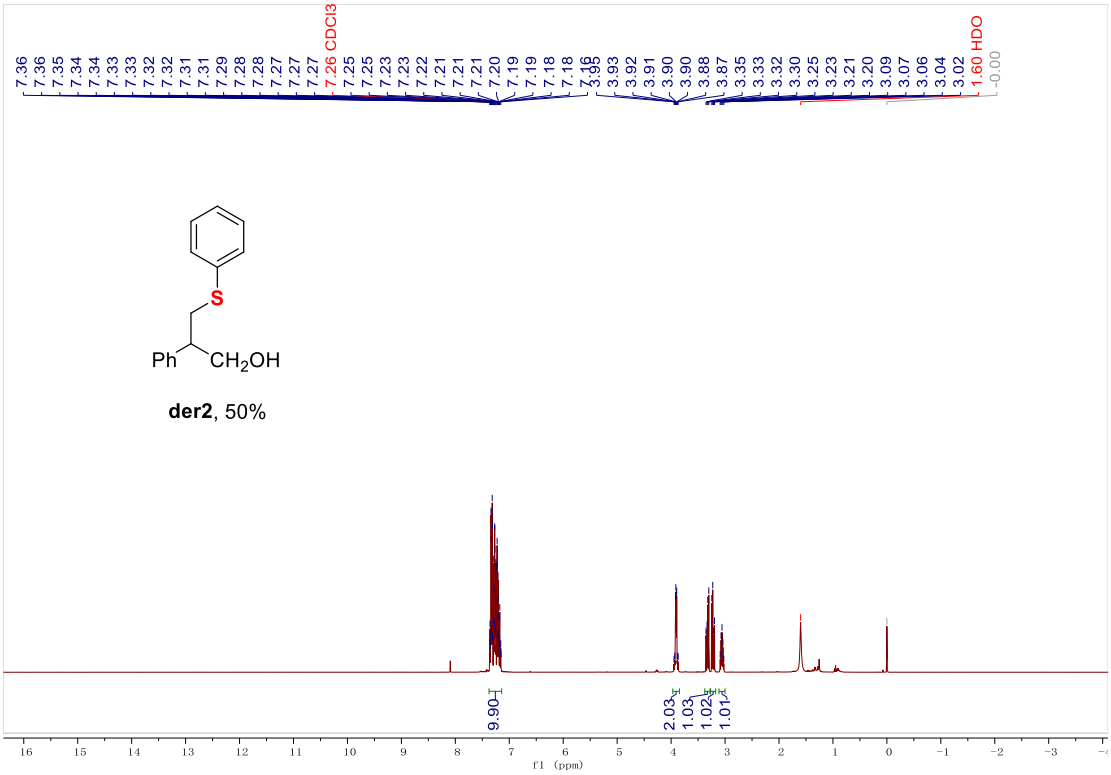

172.05
152.28
137.74
133.39
133.16
129.49
128.79
128.45
128.17
127.70
77.37 CDCl3
77.06 CDCl3
76.74 CDCl3
Se
Ph
COOH
4k: 22%b
f1 (ppm)

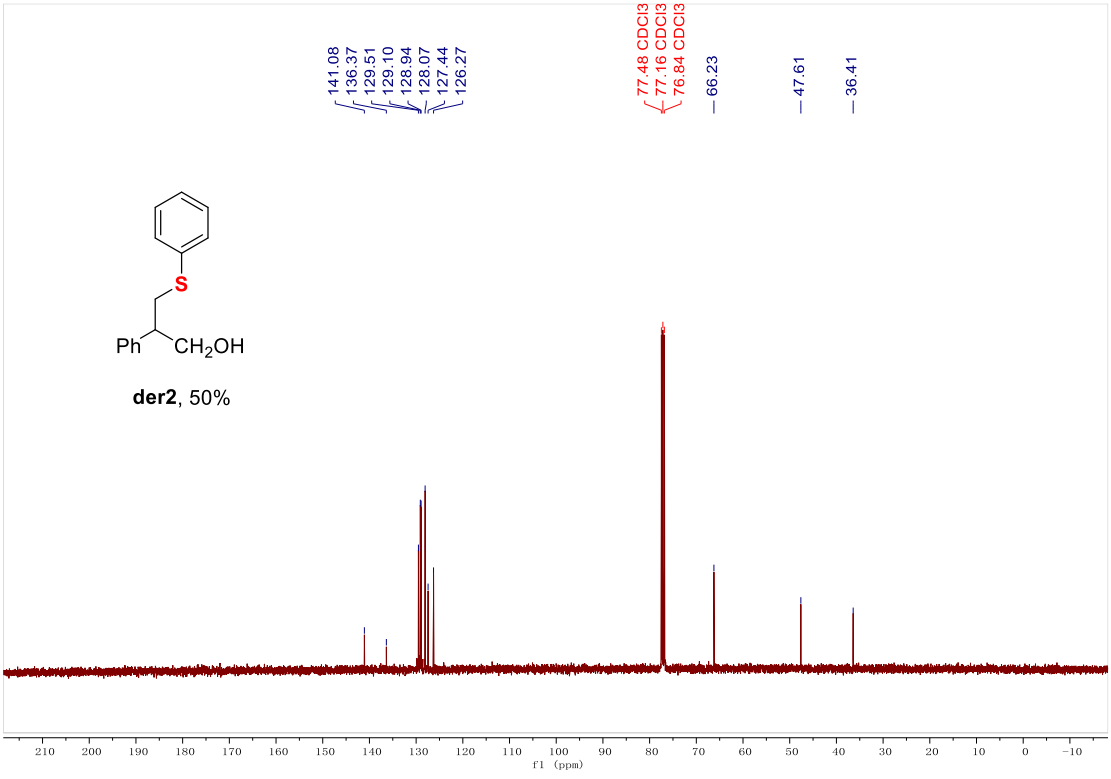

508.96
Se
Ph
COOH
690 680 670 660 650 640 630 620 610 600 590 580 570 560 550 540 530 520 510 500 490 480 470 460 450 440 430 420 410 400 390 380 370 360 350 340 330 320 310
f1 (ppm)

4k: 22%[b]

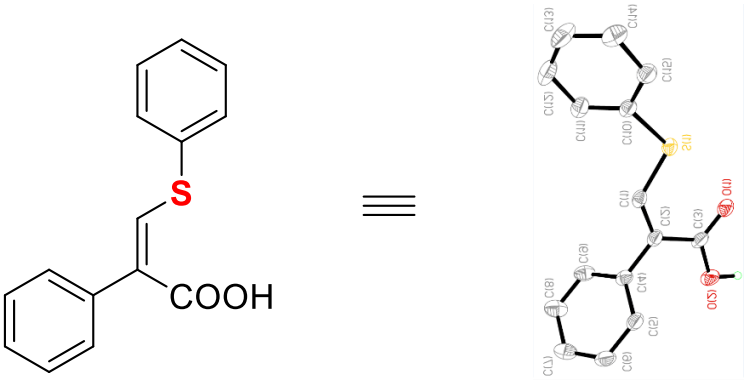

8.63
8.63
8.63
8.61
8.61
8.61
7.85
7.59
7.59
7.58
7.58
7.55
7.54
7.53
7.53
7.53
7.52
7.52
7.51
7.51
7.51
7.50
7.43
7.43
7.43
7.42
7.41
7.41
7.40
7.39
7.39
7.37
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.24 CDCl3
-0.00
S
Ph
O
der1, 88%
1.00
0.99
2.00
3.09
2.06
1.06
f1 (ppm)


178.27
137.51
136.85
136.78
135.61
132.80
131.28
129.50
129.00
128.31
128.08
127.81
126.57
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
S
Ph
O
der1, 88%
f1 (ppm)


7.26 CDCl3
1.60 HDO
S
Ph
CH2OH
der2, 50%
9.90
2.03
1.03
1.02
1.01
f1 (ppm)


141.08
136.37
129.51
129.10
128.94
128.07
127.44
126.27
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
66.23
47.61
36.41
S
Ph
CH2OH
der2, 50%
f1 (ppm)

X-ray Structure of 4a



Crystal Number: CCDC 1935976

Empirical formula: $C_{17}H_{14}O_2S$

Formula weight: 256.319

Unit cell parameters: a = 20.5001(11) Å, b = 9.8972(5) Å, c =14.0168(8) Å, α = 90.00, β = 114.293(2), γ = 90.00

Temperature: 150 K

Wavelength: 0.71073 Å

Crystal system: Monoclinic

Volume: 2592.1 (2) $Å^3$

F (000): 1072.0

h, k, l max: 26, 12, 18

Reference

(1) (a) Feng, C., Loh., T.-P. Directing-Group-Assisted Copper-Catalyzed Olefinic Trifluoromethylation of Electron-Deficient Alkenes. *Angew. Chem. Int. Ed.* **2013**, *52*, 12414−12417. (b) Sun, S., Yu, J.-T., Jiang, Y., Cheng, J. Cs_2CO_3-Promoted Carboxylation of N-Tosylhydrazones with Carbon Dioxide toward α-Arylacrylic Acids. *J. Org. Chem.* **2015**, *80*, 2855−2860.

(2) Anup, M.; Suman, D.; Harekrishna, S.; Gowri, S. G.; Mahiuddin, B. Ruthenium(II)-Catalyzed ortho-C–H Chalcogenation of Benzoic Acids via Weak O-Coordination: Synthesis of Chalcogenoxanthones. *Org. Lett.* **2017**, *19*, 2430−2433.

(3) (a) Xu, Y., Hong, Y.-J., Dean, J. T., M. Kevin, B. Intramolecular Chirality Transfer [2+2] Cycloadditions of Allenoates and Alkenes. *Org. Lett.* **2017**, *19*, 3703-3706. (b) Lei, Y., Xing, J.-J., Xu, Q., Shi, M. Synthesis of 5,6-Dihydropyrazolo[5,1-a]isoquinoline and Ethyl (Z)-3-Acetoxy-3-tosylpent-4-enoate through Tertiary-Amine-Catalyzed [3+2] Annulation. *Eur. J. Org. Chem*. **2016**, 3486–3490.