Supporting Information

Nickel-catalysed chelation-assisted reductive defluorinative sulfenylation of trifluoropropionic acid derivatives

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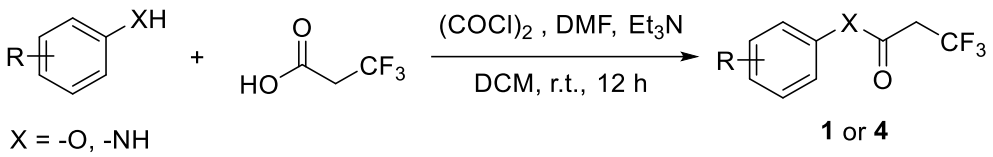
1. General remarks

^{1}H NMR, ^{13}C NMR data were obtained on AVANCE III Bruker 500 MHz nuclear resonance spectrometers unless otherwise noted. Chemical shifts (in ppm) were referenced to tetramethylsilane (TMS) (δ = 0.00 ppm) in $CDCl_3$ or dimethyl sulfoxide (δ = 2.50 ppm) in DMSO-d_6 as an internal standard. The data of ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (J values) in Hz and integration. ^{13}C NMR spectra were obtained by the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.16 ppm) or DMSO-d_6 (δ = 39.50 ppm). Flash chromatography was performed using 300-400 mesh silica gel with the indicated eluent according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) unless otherwise noted. High-resolution mass spectral (HRMS) data were recorded on Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionization (ESI) mode.

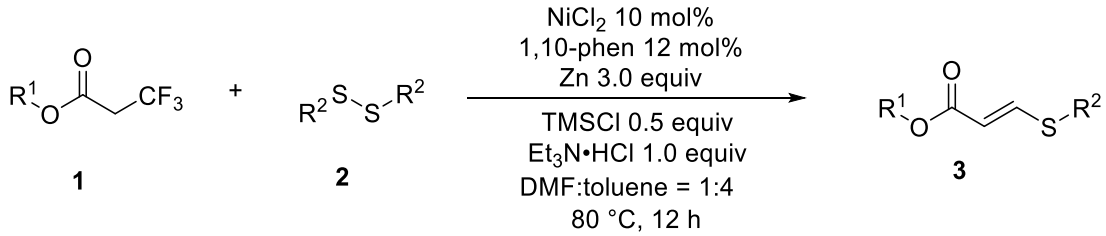
2. General procedure



X = -O, -NH

1 or **4**

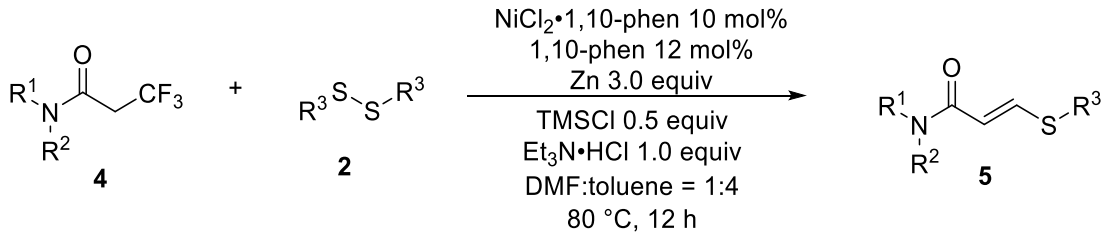
General procedure for the synthesis of trifluoropropanesters/amides 1 or 4: [1] To a stirred suspension of 3,3,3-trifluoropropionic acid (0.58 mL, 6.5 mmol) in dichloromethane (20 mL) was added oxalyl chloride (0.52 mL, 6 mmol) followed by three drops of DMF at 0 °C. The reaction mixture was stirred at room temperature for 3 h. To this solution was added a solution of anilines (5 mmol) or phenols (5 mmol) in dichloromethane (10 mL) followed by triethylamine (1.74 mL, 12.5 mmol) at 0 °C. The reaction mixture was stirred for 12 h and then washed with water (15 mL) and 1 N HCl (15 mL). The organic layer was dried over Na_2SO_4 and evaporated to afford a residue, which was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford trifluoropropanamides/esters.



1 **2** **3**

General procedure for the Ni-catalysed reductive cross-coupling of Product 3: To a 10 mL Schlenk tube was added sequentially $NiCl_2$ (2.59 mg, 0.02 mmol), 1,10-Phenanthroline (4.32 mg, 0.024 mmol), Zn power (32.90 mg, 0.6 mmol), $Et_3N{\cdot}HCl$ (27.53 mg, 0.2 mmol) and disulfides **2** (0.30 mmol). The vessel was evacuated and filled with argon (three times), toluene (0.40 mL) was added via syringe and the mixture was stirred at room temperature for 10 min. The trifluoropropanesters **1** (0.20 mmol) was added, followed by the chlorotrimethylsilane (10.86 mg, 12.68 μL, 0.10 mmol) in one portion. DMF (0.10 mL) was subsequently added via syringe. The resulting solution was stirred for 12 h at 80 ˚C. After this time, the crude reaction mixture was diluted with ethyl acetate (5 mL) and washed with water (2.0 mL). The organic layer

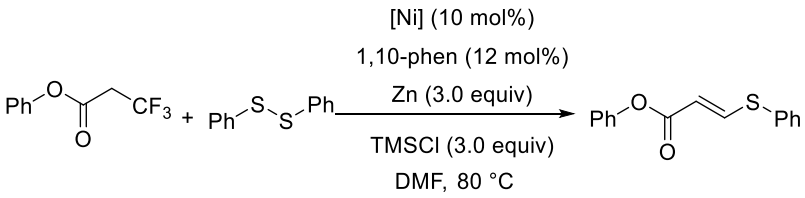
was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography.



General procedure for the Ni-catalysed reductive cross-coupling of Product 5: To a 10 mL Schlenk tube was added sequentially $NiCl_2$·1,10-phen (6.20 mg, 0.02 mmol), 1,10-phenanthroline (4.32 mg, 0.024 mmol), Zn power (32.90 mg, 0.6 mmol), Et_3N·HCl (27.53 mg, 0.2 mmol) and disulfides **2** (0.30 mmol). The vessel was evacuated and filled with argon (three times), toluene (0.40 mL) was added via syringe and the mixture was stirred at room temperature for 10 min. The trifluoropropanamides **4** (0.20 mmol) was added, followed by the chlorotrimethylsilane (10.86 mg, 12.68 μL, 0.10 mmol) in one portion. DMF (0.10 mL) was subsequently added via syringe. The resulting solution was stirred for 12 h at 80 ˚C. After this time, the crude reaction mixture was diluted with ethyl acetate (5 mL) and washed with water (2.0 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography.

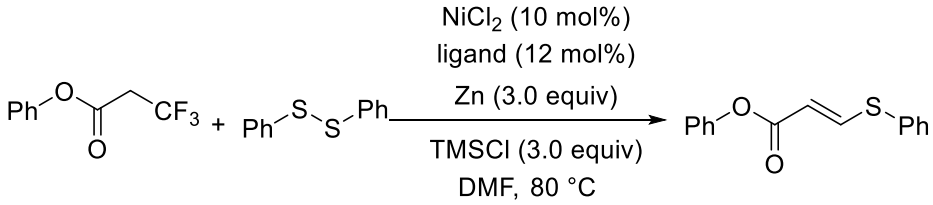
3. Optimization of the reaction conditions

Table S1. Optimization of the catalysts

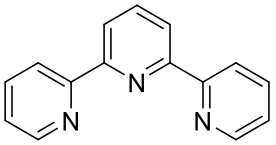


entry	conditions	yield
1	NiF_2	<10%
2	$NiCl_2$	32%
3	$NiBr_2$	12%
4	NiI_2	<10%
5	$NiCl_2$•DME	15%
6	$NiBr_2$•DME	<10%
7	$NiCl_2$•$6H_2O$	<10%
8	$NiCl_2$•1,10-phen	30%
9	$Ni(OTf)_2$	<10%
10	$NiBr_2$•bpy	20%
11	$NiBr_2$•diglyme	15%
12	$Ni(acac)_2$	20%
13	$NiCl_2$•dppe	23%
14	$Fe(OTf)_3$	trace
15	$CoBr_2$	trace
16	$CrCl_3$	trace

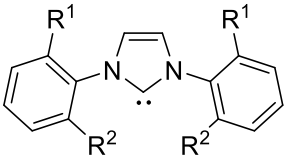
Table S2. Optimization of the ligands



entry	ligand	yield
1	1,10-phen	32% (*E*:*Z* = 85:15)
2	bpy	20% (*E*:*Z* = 80:20)
3	L1	<10%
4	L2	18%
5	L3	10%
6	L4	<20%
7	L5	20%
8	L6	trace
9	L7	10%
10	L8	18%
11	dppe	n.d.
12	PCy_3	trace
13	L9	trace
14	L10	n.d.

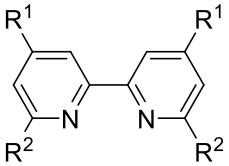


L1



L9: $R^1 = R^2 = {}^i$Pr

L10: $R^1 = R^2$ = Cy

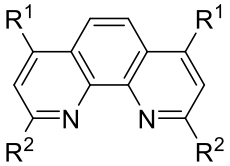


L2: $R^1 = {}^t$Bu, R^2 = H

L3: R^1 = H, R^2 = Me

L4: R^1 = OMe, R^2 = H

L5: R^1 = Me, R^2 = H

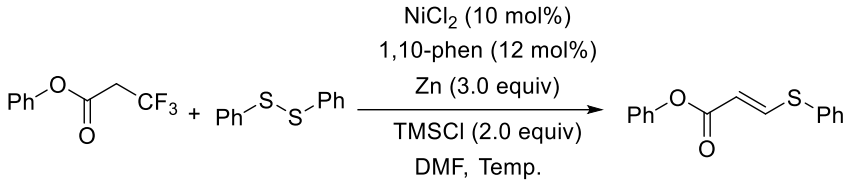


L6: R^1 = H, R^2 = Me

L7: R^1 = Ph, R^2 = H

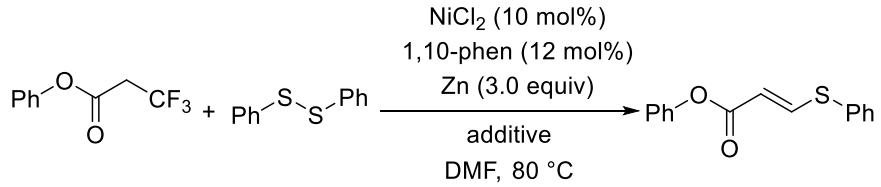
L8: R^1 = Me, R^2 = H

Table S3. Optimization of reaction temperature



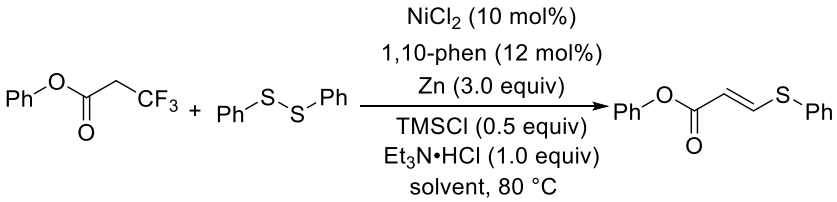
entry	Temp.	yield
1	100 °C	15 % (*E*:*Z* = 72:28)
2	80 °C	32 % (*E*:*Z* = 70:30)
3	60 °C	20 % (*E*:*Z* = 49:51)
4	40 °C	n.d.
5	r.t.	n.d.

Table S4. Optimization of the additive



entry	additive	yield
1	none	<10%
2	CsF	11%
3	$MgCl_2$	<10%
4	LiBr	<10%
5	NaI	<10%
6	TMEDA	<10%
7	pyridine	11%
8	TMSCl (0.5 equiv)	20%
9	TMSCl (2.0 equiv)	32%
10	TMSCl (3.0 equiv)	30%
11	TESCl (2.0 equiv)	12%
12	TIPSCl (2.0 equiv)	10%
13	DEMS (2.0 equiv)	trace
14	Et_3N•HCl (1.0 equiv)	35 % (*E*:*Z* = 84:16)
15	TMSCl 2.0 eq. and Et_3N•HCl 1.0 eq.	61 % (*E*:*Z* = 80:20)
16	TMSCl 1.0 eq. and Et_3N•HCl 1.0 eq.	68 % (*E*:*Z* = 82:18)
17	TMSCl 0.5 eq. and Et_3N•HCl 1.0 eq.	74 % (*E*:*Z* = 83:17)
18	TMSCl 1.0 eq. and Et_3N•HCl 2.0 eq.	71 % (*E*:*Z* = 60:40)

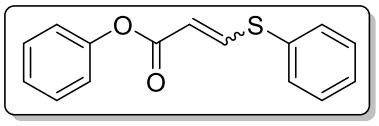
Table S5. Optimization of the solvents



entry	solvent	yield
1	DMF	64% (*E*:*Z* = 83:17)
2	DMA	63% (*E*:*Z* = 80:20)
3	DMSO	58% (*E*:*Z* = 75:25)
4	THF	trace
5	DCE	n.d.
6	MeCN	n.d.
7	toluene	n.d.
8	dioxane	n.d.
9	DMF:THF = 1:1	trace
10	DMF:MeCN = 1:1	trace
11	DMF:toluene = 1:1	76% (*E*:*Z* = 81:19)
12	DMF:dioxane = 1:1	59% (*E*:*Z* = 80:20)
13	DMF:toluene = 9:1	72% (*E*:*Z* = 80:20)
14	DMF:toluene = 4:1	69% (*E*:*Z* = 83:17)
15	DMF:toluene = 1:4	85% (*E*:*Z* = 84:16)
16	DMF:toluene = 1:9	50% (*E*:*Z* = 70:30)
17[a]	DMF:toluene = 1:4	83% (*E*:*Z* = 84:16)

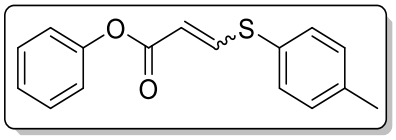
[a] With $NiCl_2 \cdot$1,10-phen as catalyst

4. Characterization data

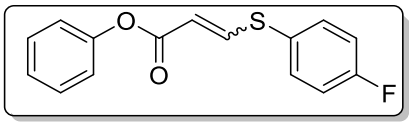


Phenyl 3-(phenylthio)acrylate[2] (3aa). The representative procedure was followed using phenyl 3,3,3-trifluoropropanoate (**1a**) (40.83 mg, 0.20 mmol) and 1,2-diphenyldisulfane (**2a**) (65.45 mg, 0.30 mmol). Isolation by column chromatography

(*n*-hexane : EtOAc = 20 : 1) yielded **3aa** (43.57 mg, 85 %) as a white solid, *E*:*Z* = 84:16. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 8.00 (d, *J* = 15.0 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.43 – 7.41 (m, 2H), 7.38 – 7.33 (m, 3H), 7.22 – 7.18 (m, 1H), 7.09 – 7.07 (m, 2H), 6.13 (d, *J* = 10.0 Hz, 0.19H), 5.80 (d, *J* = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, CDCl$_3$) δ** 163.53, 150.60, 149.49, 133.19, 131.12, 129.77, 129.42, 129.31, 125.62, 121.54, 114.26. **MS** (EI) *m*/*z* (relative intensity): 256 (**M**$^+$, 20), 163 (100), 135 (20), 109 (40), 91 (30).

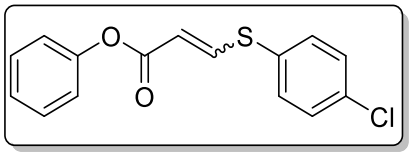


Phenyl 3-(*p*-tolylthio)acrylate (3ab). The representative procedure was followed using phenyl 3,3,3-trifluoropropanoate (**1a**) (40.83 mg, 0.20 mmol) and 1,2-*di*-*p*-tolyldisulfane (**2b**) (73.92 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **3ab** (40.56 mg, 83 %) as a white solid, *E*:*Z* = 95:5. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.99 (d, *J* = 15.0 Hz, 1H), 7.42 – 7.41 (m, 2H), 7.37 – 7.34 (m, 2H), 7.26 – 7.24 (m, 2H), 7.22 – 7.20 (m, 1H), 7.08 – 7.06 (m, 2H), 6.10 (d, *J* = 10.0 Hz, 0.05H), 5.73 (d, *J* = 15.0 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$) δ** 163.64, 150.65, 150.19, 139.93, 133.55, 130.60, 129.33, 125.95, 125.62, 121.58, 113.82, 21.27. **MS** (EI) *m*/*z* (relative intensity): 270 (**M**$^+$, 20), 177 (100), 149 (10), 134 (20), 123 (30).

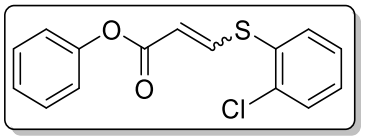


Phenyl 3-((4-fluorophenyl)thio)acrylate (3ac). The representative procedure was followed using phenyl 3,3,3-trifluoropropanoate (**1a**) (40.83 mg, 0.20 mmol) and 1,2-bis(4-fluorophenyl)disulfane (**2c**) (76.29 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **3ac** (35.66 mg, 65 %) as a white solid, *E*:*Z* = 95:5. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.94 (d, *J* = 15.0 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.38 – 7.35 (m, 2H), 7.23 – 7.21 (m, 1H), 7.17 – 7.13 (m, 2H), 7.09 – 7.06 (m,

2H), 6.12 (d, J = 10.0 Hz, 0.05H), 5.72 (d, J = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.46, 150.60, 149.46, 135.88, 135.81, 129.36, 125.70, 121.54, 117.24, 117.06, 114.30. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -110.33. **MS** (EI) m/z (relative intensity): 274 ($\mathbf{M}^+$, 20), 181 (100), 153 (10), 127 (50), 109 (40).

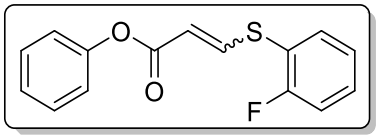


Phenyl 3-[(4-chlorophenyl)thio]acrylate (3ad). The representative procedure was followed using phenyl 3,3,3-trifluoropropanoate (**1a**) (40.83 mg, 0.20 mmol) and 1,2-bis(4-chlorophenyl)disulfane (**2d**) (86.16 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 10 : 1) yielded **3ad** (39.54 mg, 68 %) as a white solid, E:Z = 91:9. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.90 (d, J = 15.0 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.42 – 7.41 (m, 1H), 7.40 – 7.35 (m, 4H), 7.24 – 7.20 (m, 1H), 7.10 – 7.07 (m, 2H), 6.15 (d, J = 10.0 Hz, 0.1H), 5.79 (d, J = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.37, 150.57, 148.64, 137.48, 135.91, 134.51, 130.05, 129.35, 125.70, 121.51, 114.78. **MS** (EI) m/z (relative intensity): 290 ($\mathbf{M}^+$, 10), 197 (100), 143 (30), 134 (30), 108 (30).

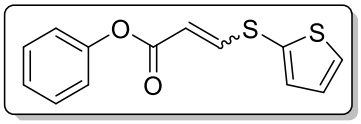


Phenyl 3-[(2-chlorophenyl)thio]acrylate (3ae). The representative procedure was followed using phenyl 3,3,3-trifluoropropanoate (**1a**) (40.83 mg, 0.20 mmol) and 1,2-bis(2-chlorophenyl)disulfane (**2e**) (86.16 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 10 : 1) yielded **3ae** (40.71 mg, 70 %) as a white solid, E:Z = 91:9. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 (d, J = 15.0 Hz, 1H), 7.62 – 7.60 (m, 1H), 7.55 – 7.53 (m, 1H), 7.40 – 7.37 (m, 4H), 7.24 – 7.20 (m, 1H), 7.10 – 7.09 (m, 2H), 6.20 (d, J = 10.0 Hz, 0.1H), 5.78 (d, J = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.39, 150.58, 146.92, 137.48, 135.05, 130.93, 130.62, 129.37, 129.10,

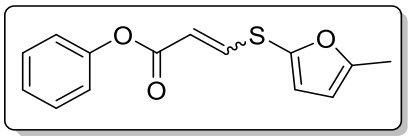
127.96, 125.72, 121.56, 115.20. **MS** (EI) *m*/*z* (relative intensity): 290 ($\mathbf{M}^+$, 10), 197 (100), 143 (30), 134 (30), 108 (40).



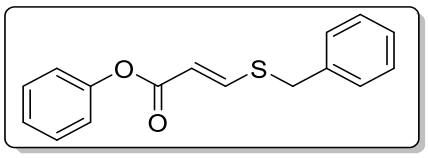
Phenyl 3-[(2-fluorophenyl)thio]acrylate (3af). The representative procedure was followed using phenyl 3,3,3-trifluoropropanoate (**1a**) (40.83 mg, 0.20 mmol) and 1,2-bis(2-fluorophenyl)disulfane (**2f**) (76.29 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **3af** (32.91 mg, 60 %) as a white solid, *E*:*Z* = 83:17. **^{1}H NMR (500 MHz, $CDCl_3$)** $\boldsymbol{\delta}$ 7.89 (d, *J* = 15.0 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.48 – 7.43 (m, 1H), 7.38 – 7.34 (m, 2H), 7.23 – 7.20 (m, 3H), 7.09 – 7.07 (m, 2H), 6.16 (d, *J* = 10.0 Hz, 0.2H), 5.75 (d, *J* = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** $\boldsymbol{\delta}$ 163.30, 150.58, 147.26, 135.62, 132.25, 129.36, 125.68, 125.33, 125.30, 121.54, 116.75, 116.57, 114.88. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -106.89, -108.38. **MS** (EI) *m*/*z* (relative intensity): 274 ($\mathbf{M}^+$, 10), 181 (100), 127 (30), 109 (30).



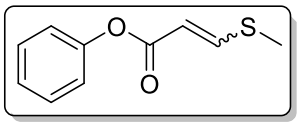
Phenyl 3-(thiophen-2-ylthio)acrylate (3ag). The representative procedure was followed using phenyl 3,3,3-trifluoropropanoate (**1a**) (40.83 mg, 0.20 mmol) and 1,2-di(thiophen-2-yl)disulfane (**2g**) (69.11 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded 3ag (37.77 mg, 72 %) as a white solid, *E*:*Z* = 85:15. **^{1}H NMR (500 MHz, $CDCl_3$)** $\boldsymbol{\delta}$ 7.84 (d, *J* = 15.0 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.29 – 7.28 (m, 1H), 7.22 – 7.18 (m, 1H), 7.11 – 7.10 (m, 1H), 7.07 – 7.06 (m, 2H), 6.07 (d, *J* = 10.0 Hz, 0.2H), 5.74 (d, *J* = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** $\boldsymbol{\delta}$ 163.25, 150.50, 149.90, 136.48, 132.33, 129.28, 128.31, 125.74, 125.63, 121.47, 114.65. **MS** (EI) *m*/*z* (relative intensity): 262 ($\mathbf{M}^+$, 10), 168 (100), 140 (10), 114 (30).



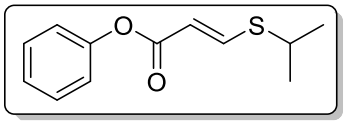
Phenyl 3-[(5-methylfuran-2-yl)thio]acrylate (3ah). The representative procedure was followed using phenyl 3,3,3-trifluoropropanoate (**1a**) (40.83 mg, 0.20 mmol) and 1,2-bis(5-methylfuran-2-yl)disulfane (**2h**) (67.89 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **3ah** (36.44 mg, 70 %) as a white solid, *E*:*Z* = 81:19. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.80 (d, *J* = 15.0 Hz, 1H), 7.40 – 7.39 (m, 1H), 7.37 – 7.34 (m, 2H), 7.24 – 7.18 (m, 1H), 7.09 – 7.07 (m, 2H), 6.40 – 6.39 (m, 1H), 6.08 (d, *J* = 10.0 Hz, 0.25H), 5.69 (d, *J* = 15.0 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$) δ** 163.48, 156.71, 150.60, 148.68, 141.73, 129.31, 125.61, 121.56, 121.53, 114.41, 113.91, 11.78. **MS** (EI) *m*/*z* (relative intensity): 260 (**M**$^+$, 20), 167 (100), 134 (10), 113 (30).



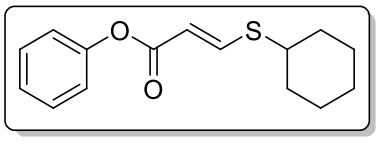
Phenyl (*E*)-3-(benzylthio)acrylate (3ai). The representative procedure was followed using phenyl 3,3,3-trifluoropropanoate (**1a**) (40.83 mg, 0.20 mmol) and 1,2-dibenzyldisulfane (**2i**) (73.92 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **3ai** (23.25 mg, 43 %) as a white solid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.91 (d, *J* = 15.0 Hz, 1H), 7.38 – 7.36 (m, 6H), 7.34 – 7.29 (m, 1H), 7.24 – 7.20 (m, 1H), 7.10 – 7.09 (m, 2H), 5.99 (d, *J* = 15.0 Hz, 1H), 4.08 (s, 2H). **^{13}C NMR (125 MHz, CDCl$_3$) δ** 163.50, 150.67, 148.53, 135.15, 129.32, 128.88, 128.78, 127.84, 125.62, 121.59, 113.25, 36.65. **MS** (EI) *m*/*z* (relative intensity): 270 (**M**$^+$, 20), 177 (70), 91 (100), 65 (20).



Phenyl 3-(methylthio)acrylate (3aj). The representative procedure was followed using phenyl 3,3,3-trifluoropropanoate (**1a**) (40.83 mg, 0.20 mmol) and 1,2-dimethyldisulfane (**2j**) (28.26 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **3aj** (32.24 mg, 83 %) as a colorless liquid, *E*:*Z* = 95:5. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 15.0 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.24 – 7.21 (m, 1H), 7.13 – 7.11 (m, 2H), 6.07 (d, *J* = 10.0 Hz, 0.05H), 5.85 (d, *J* = 15.0 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.53, 150.72, 149.46, 129.34, 125.61, 121.62, 112.10, 14.43. **MS** (EI) *m*/*z* (relative intensity): 194 (**M**$^+$, 20), 101 (100), 73 (30).

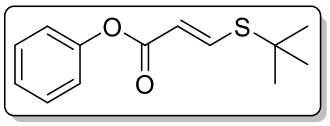


Phenyl (*E*)-3-(isopropylthio)acrylate (3ak). The representative procedure was followed using phenyl 3,3,3-trifluoropropanoate (**1a**) (40.83 mg, 0.20 mmol) and 1,2-diisopropyldisulfane (**2k**) (45.09 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **3ak** (29.79 mg, 67 %) as a colorless liquid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 15.0 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.23 – 7.20 (m, 1H), 7.12 – 7.10 (m, 2H), 5.98 (d, *J* = 15.0 Hz, 1H), 3.35 (sept, *J* = 7.0 Hz, 1H), 1.40 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.68, 150.68, 148.85, 129.26, 125.51, 121.57, 113.00, 36.80, 22.88. **MS** (EI) *m*/*z* (relative intensity): 222 (**M**$^+$, 10), 129 (100), 87 (90).

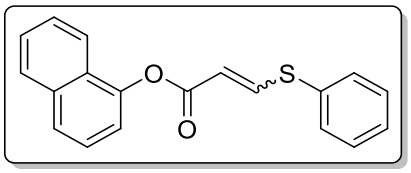


Phenyl (*E*)-3-(cyclohexylthio)acrylate (3al). The representative procedure was followed using phenyl 3,3,3-trifluoropropanoate (**1a**) (40.83 mg, 0.20 mmol) and 1,2-dicyclohexyldisulfane (**2l**) (69.14 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **3al** (32.53 mg, 62 %) as a

colorless liquid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.86 (d, *J* = 15.0 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.16 – 7.13 (m, 1H), 7.05 – 7.02 (m, 2H), 5.92 (d, *J* = 15.0 Hz, 1H), 3.09 – 3.04 (m, 1H), 1.75 – 1.70 (m, 2H), 1.45 – 1.18 (m, 6H). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 163.76, 150.71, 149.00, 129.28, 125.53, 121.61, 112.81, 45.16, 32.97, 25.70, 25.36. **MS** (EI) *m*/*z* (relative intensity): 262 (**M**$^+$, 10), 169 (90), 87 (100).

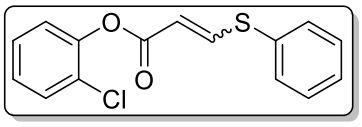


Phenyl (*E*)-3-(*tert*-butylthio)acrylate (3am). The representative procedure was followed using phenyl 3,3,3-trifluoropropanoate (**1a**) (40.83 mg, 0.20 mmol) and 1,2-*di*-*tert*-butyldisulfane (**2m**) (53.51 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **3am** (37.81 mg, 80 %) as a colorless liquid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.05 (d, *J* = 15.0 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.24 – 7.21 (m, 1H), 7.12 – 7.10 (m, 2H), 6.12 (d, *J* = 15.0 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 163.85, 150.77, 147.96, 129.31, 125.58, 121.66, 114.26, 45.62, 31.02. **MS** (EI) *m*/*z* (relative intensity): 236 (**M**$^+$, 20), 143 (50), 94 (30), 87 (100), 57 (40).

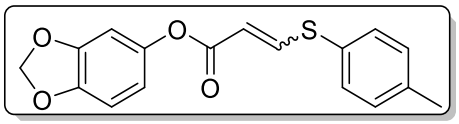


Naphthalen-1-yl 3-(phenylthio)acrylate (3ba). The representative procedure was followed using naphthalen-1-yl 3,3,3-trifluoropropanoate (**1b**) (50.84 mg, 0.20 mmol) and 1,2-diphenyldisulfane (**2a**) (65.45 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **3ba** (42.89 mg, 70 %) as a white solid, *E*:*Z* = 95:5. **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.96 (d, *J* = 15.0 Hz, 1H), 7.74 – 7.71 (m, 2H), 7.69 – 7.67 (m, 1H), 7.46 – 7.42 (m, 3H), 7.37 – 7.35 (m, 2H), 7.34 – 7.32 (m, 3H), 7.15 – 7.12 (m, 1H), 6.40 – 6.39 (m, 1H), 6.08 (d, *J* = 10.0 Hz, 0.05H), 5.76 (d, *J* = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 163.70, 149.71, 148.26, 133.66, 133.18,

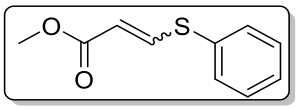
131.31, 129.80, 129.77, 129.43, 129.26, 127.67, 127.55, 126.42, 125.55, 121.14, 118.46, 114.21. **MS** (EI) *m*/*z* (relative intensity): 306 ($\mathbf{M}^+$, 20), 163 (100), 143 (10), 135 (20).



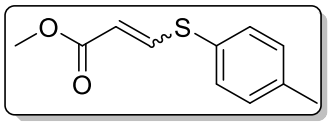
2-Chlorophenyl 3-(phenylthio)acrylate (3ca). The representative procedure was followed using 2-chlorophenyl 3,3,3-trifluoropropanoate (**1c**) (50.84 mg, 0.20 mmol) and 1,2-diphenyldisulfane (**2a**) (65.45 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **3ca** (41.87 mg, 72 %) as a white solid, *E*:*Z* = 88:12. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.08 (d, *J* = 15.0 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.44 – 7.40 (m, 4H), 7.27 – 7.23 (m, 1H), 7.17 – 7.12 (m, 2H), 6.18 (d, *J* = 10.0 Hz, 0.14H), 5.83 (d, *J* = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.48, 150.54, 146.89, 133.19, 131.11, 130.18, 129.78, 129.62, 129.48, 127.62, 126.83, 123.73, 113.26. **MS** (EI) *m*/*z* (relative intensity): 290 ($\mathbf{M}^+$, 10), 163 (100), 154 (30), 135 (30).



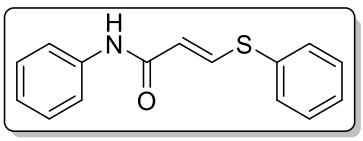
Benzo[*d*][1,3]dioxol-5-yl 3-(*p*-tolylthio)acrylate (3da). The representative procedure was followed using benzo[*d*][1,3]dioxol-5-yl 3,3,3-trifluoropropanoate (**1d**) (49.63 mg, 0.20 mmol) and 1,2-*di*-*p*-tolyldisulfane (**2b**) (73.92 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 10 : 1) yielded **3da** (45.90 mg, 73 %) as a white solid, *E*:*Z* = 80:20. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.89 (d, *J* = 15.0 Hz, 1H), 7.34 – 7.32 (m, 2H), 7.18 – 7.16 (m, 2H), 6.70 – 6.67 (m, 1H), 6.53 – 6.52 (m, 1H), 6.44 – 6.42 (m, 1H), 5.90 -5.89 (m, 2H), 5.62 (d, *J* = 15.0 Hz, 1H), 2.32 (s, 3H), 2.19 (s, 0.82H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 163.93, 150.27, 147.89, 145.19, 144.96, 139.94, 133.55, 130.59, 125.94, 113.93, 113.64, 107.89, 103.78, 101.61, 21.25. **MS** (EI) *m*/*z* (relative intensity): 314 ($\mathbf{M}^+$, 20), 177 (100), 123 (20), 105 (10).



Methyl 3-(phenylthio)acrylate (3ea). The representative procedure was followed using methyl 3,3,3-trifluoropropanoate (**1e**) (28.42 mg, 0.20 mmol) and 1,2-diphenyldisulfane (**2a**) (65.45 mg, 0.30 mmol). Isolation by column chromatography (n-hexane : EtOAc = 20 : 1) yielded **3ea** (26.42 mg, 68 %) as a colorless oil, *E*:*Z* = 75:25. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 15.0 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.34 – 7.30 (m, 3H), 5.84 (d, *J* = 10.0 Hz, 0.30H), 5.59 (d, *J* = 15.0 Hz, 1H), 3.71 (s, 0.93H), 3.62 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 166.88, 165.62, 150.07, 147.19, 136.02, 132.93, 131.08, 130.40, 129.65, 129.13, 128.22, 115.12, 112.87, 51.46. **MS** (EI) *m*/*z* (relative intensity): 194 ($\mathbf{M}^+$, 80), 163 (70), 135 (100), 109 (70), 91 (50).

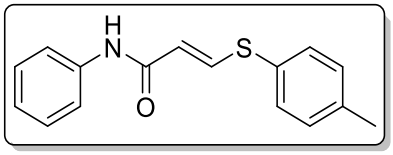


Methyl 3-(*p*-tolylthio)acrylate (3eb). The representative procedure was followed using methyl 3,3,3-trifluoropropanoate (**1e**) (28.42 mg, 0.20 mmol) and 1,2-*di*-*p*-tolyldisulfane (**2b**) (73.92 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 20 : 1) yielded **3eb** (29.58 mg, 71 %) as a colorless oil, *E*:*Z* = 75:25. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 15.0 Hz, 1H), 7.30 – 7.28 (m, 2H), 7.14 – 7.13 (m, 2H), 5.81 (d, *J* = 10.0 Hz, 0.3H), 5.51 (d, *J* = 15.0 Hz, 1H), 3.71 (s, 0.88H), 3.6 (s, 3H), 2.30 (s, 3H), 2.28 (s, 0.88H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 166.92, 165.69, 150.91, 147.88, 139.57, 133.30, 131.29, 130.44, 130.06, 126.49, 114.61, 112.50, 51.40, 21.20. **MS** (EI) *m*/*z* (relative intensity): 208 ($\mathbf{M}^+$, 90), 177 (80), 149 (100), 123 (20).

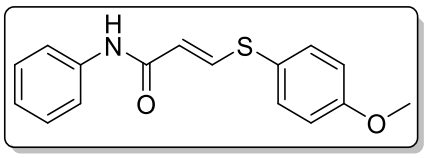


(*E*)-*N*-Phenyl-3-(phenylthio)acrylamide (5aa). The representative procedure was

followed using 3,3,3-trifluoro-*N*-phenylpropanamide (**4a**) (40.63 mg, 0.20 mmol) and 1,2-diphenyldisulfane (**2a**) (65.45 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **5aa** (44.43 mg, 87 %) as a white solid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.83 (d, *J* = 15.0 Hz, 1H), 7.53 – 7.48 (m, 4H), 7.43 – 7.39 (m, 3H), 7.32 – 7.28 (m, 2H), 7.15 (br, 1H), 7.11 – 7.08 (m, 1H), 5.78 (d, *J* = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, CDCl$_3$) δ** 162.59, 144.14, 137.94, 132.52, 131.14, 129.58, 128.93, 128.82, 124.23, 119.92, 118.34. **MS** (EI) *m*/*z* (relative intensity): 255 (**M**$^+$, 30), 163 (100), 135 (10), 109 (30), 91 (20).

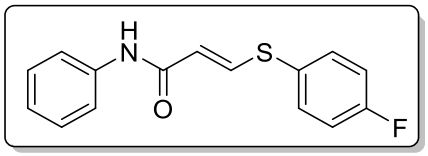


(*E*)-*N*-Phenyl-3-(*p*-tolylthio)acrylamide (5ab). The representative procedure was followed using 3,3,3-trifluoro-*N*-phenylpropanamide (**4a**) (40.63 mg, 0.20 mmol) and 1,2-di-*p*-tolyldisulfane (**2b**) (73.92 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **5ab** (40.94 mg, 76 %) as a white solid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, DMSO-d_6) δ** 9.90 (s, 1H), 7.63 (d, *J* = 15.0 Hz, 1H), 7.61 – 7.59 (m, 2H), 7.45 – 7.43 (m, 2H), 7.34 – 7.32 (m, 2H), 7.31 – 7.29 (m, 1H), 7.27 – 7.26 (m, 1H), 7.25 – 7.24 (m, 1H), 7.03 – 7.00 (m, 1H), 5.93 (d, *J* = 15.0 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR (125 MHz, DMSO-d_6) δ** 162.49, 142.17, 139.72, 139.50, 135.18, 133.37, 131.10, 129.17, 126.98, 123.59, 119.55, 21.26. **MS** (EI) *m*/*z* (relative intensity): 269 (**M**$^+$, 30), 177 (100), 123 (10).

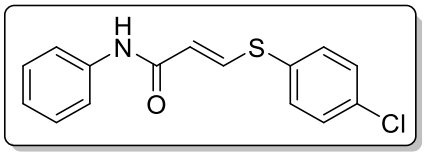


(*E*)-3-[(4-Methoxyphenyl)thio]-*N*-phenylacrylamide (5an). The representative procedure was followed using 3,3,3-trifluoro-*N*-phenylpropanamide (**4a**) (40.63 mg, 0.20 mmol) and 1,2-bis(4-methoxyphenyl)disulfane (**2n**) (83.51 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 3 : 1) yielded **5an** (41.66

mg, 73 %) as a white solid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.76 (d, *J* = 15.0 Hz, 1H), 7.50 – 7.49 (m, 1H), 7.44 – 7.42 (m, 2H), 7.30 – 7.27 (m, 2H), 7.15 – 7.13 (m, 1H), 7.10 – 7.06 (m, 1H), 6.95 – 6.93 (m, 2H), 5.70 (d, *J* = 15.0 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$) δ** 160.55, 146.91, 145.75, 137.98, 135.43, 128.94, 124.11, 120.72, 119.74, 117.20, 115.25, 55.41. **MS** (EI) *m*/*z* (relative intensity): 285 (**M**$^+$, 30), 165 (100), 146 (20), 139 (30).

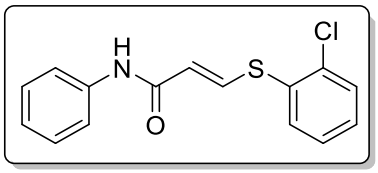


(*E*)-3-[(4-Fluorophenyl)thio]-*N*-phenylacrylamide (5ac). The representative procedure was followed using 3,3,3-trifluoro-*N*-phenylpropanamide (**4a**) (40.63 mg, 0.20 mmol) and 1,2-bis(4-fluorophenyl)disulfane (**2c**) (76.29 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 10 : 1) yielded **5ac** (41.55 mg, 76 %) as a white solid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ** 9.92 (s, 1H), 7.66 (d, *J* = 15.0 Hz, 1H), 7.64 – 7.60 (m, 4H), 7.41 – 7.37 (m, 2H), 7.31 – 7.27 (m, 2H), 7.05 – 7.01 (m, 1H), 5.92 (d, *J* = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ** 164.14, 162.37, 141.93, 139.67, 136.07, 129.18, 126.14, 123.64, 119.79, 119.57, 117.72.; **^{19}F NMR (377 MHz, DMSO-*d*$_6$) δ** -111.82. **MS** (EI) *m*/*z* (relative intensity): 273 (**M**$^+$, 20), 181 (100), 153 (20), 133 (30).

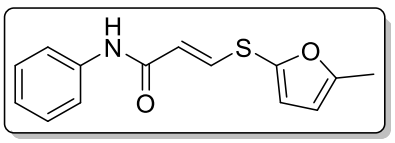


(*E*)-3-[(4-Chlorophenyl)thio]-*N*-phenylacrylamide (5ad). The representative procedure was followed using 3,3,3-trifluoro-*N*-phenylpropanamide (**4a**) (40.63 mg, 0.20 mmol) and 1,2-bis(4-chlorophenyl)disulfane (**2d**) (86.17 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 10 : 1) yielded **5ad** (41.73 mg, 72 %) as a white solid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ** 9.93 (s, 1H), 7.66 (d, *J* = 15.0 Hz, 1H), 7.62 – 7.59 (m, 6H), 7.31 – 7.28 (m, 2H), 7.05 – 7.02 (m,

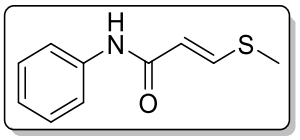
1H), 6.01 (d, *J* = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, DMSO-*d*$_6$) *δ*** 162.30, 140.85, 139.62, 134.77, 134.50, 130.44, 129.84, 129.19, 123.69, 120.49, 119.59. **MS** (EI) *m*/*z* (relative intensity): 289 (**M**$^+$, 20), 169 (100), 156 (10), 146 (20).



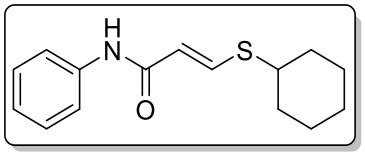
(*E*)-3-[(2-Chlorophenyl)thio]-*N*-phenylacrylamide (5ae). The representative procedure was followed using 3,3,3-trifluoro-*N*-phenylpropanamide (**4a**) (40.63 mg, 0.20 mmol) and 1,2-bis(2-chlorophenyl)disulfane (**2e**) (86.17 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 10 : 1) yielded **5ae** (41.15 mg, 71 %) as a white solid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, CDCl$_3$) *δ*** 7.67 (d, *J* = 15.0 Hz, 1H), 7.48 – 7.44 (m, 4H), 7.26 – 7.19 (m, 5H), 7.04 – 7.01 (m, 1H), 5.78 (d, *J* = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, CDCl$_3$) *δ*** 162.24, 141.62, 137.82, 137.81, 136.49, 133.79, 130.67, 130.34, 130.05, 129.00, 127.81, 124.38, 119.88. **MS** (EI) *m*/*z* (relative intensity): 289 (**M**$^+$, 20), 169 (100), 156 (10), 146 (20).



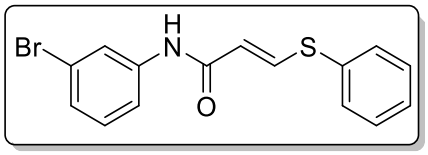
(*E*)-3-[(5-Methylfuran-2-yl)thio]-*N*-phenylacrylamide (5ah). The representative procedure was followed using 3,3,3-trifluoro-*N*-phenylpropanamide (**4a**) (40.63 mg, 0.20 mmol) and 1,2-bis(5-methylfuran-2-yl)disulfane (**2h**) (67.89 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 10 : 1) yielded **5ah** (37.34 mg, 72 %) as a yellow solid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, DMSO-*d*$_6$) *δ*** 9.92 (s, 1H), 7.79 – 7.78 (m, 1H), 7.62 – 7.60 (m, 2H), 7.50 (d, *J* = 15.0 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.04 – 7.01 (m, 1H), 6.60 – 6.59 (m, 1H), 5.82 (d, *J* = 15.0 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR (125 MHz, DMSO-*d*$_6$) *δ*** 162.45, 156.38, 143.07, 141.18, 139.76, 129.15, 123.54, 119.52, 119.12, 115.08, 105.34, 12.06. **MS** (EI) *m*/*z* (relative intensity): 259 (**M**$^+$, 20), 146 (70), 139 (100), 113 (20).



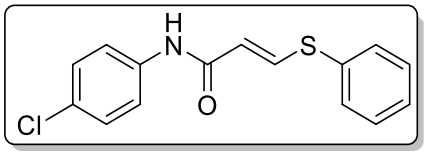
(*E*)-3-(Methylthio)-*N*-phenylacrylamide (5aj). The representative procedure was followed using 3,3,3-trifluoro-*N*-phenylpropanamide (**4a**) (40.63 mg, 0.20 mmol) and 1,2-dimethyldisulfane (**2j**) (28.26 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 10 : 1) yielded **5aj** (23.96 mg, 62 %) as a colorless oil, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 15.0 Hz, 1H), 7.49 – 7.48 (m, 3H), 7.25 – 7.22 (m, 2H), 7.04 – 7.00 (m, 1H), 5.74 (d, *J* = 15.0 Hz, 1H), 2.24 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 162.75, 144.70, 138.10, 128.97, 124.18, 119.96, 115.85, 14.67. **MS** (EI) *m*/*z* (relative intensity): 193 (**M**$^+$, 40), 146 (10), 101 (100), 93 (60), 73 (40).



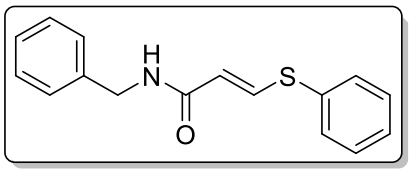
(*E*)-3-(Cyclohexylthio)-*N*-phenylacrylamide (5al). The representative procedure was followed using 3,3,3-trifluoro-*N*-phenylpropanamide (**4a**) (40.63 mg, 0.20 mmol) and 1,2-dicyclohexyldisulfane (**2l**) (69.13 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **5al** (33.98 mg, 65 %) as a colorless oil, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 15.0 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.25 – 7.22 (m, 2H), 7.03 – 7.00 (m, 1H), 5.92 (d, *J* = 15.0 Hz, 1H), 2.96 – 2.92 (m, 1H), 1.96 – 1.92 (m, 2H), 1.71 – 1.67 (m, 2H), 1.37 – 1.32 (m, 2H), 1.30 – 1.23 (m, 2H), 1.22 – 1.17 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 162.96, 146.64, 144.10, 138.13, 128.94, 124.10, 119.87, 45.59, 33.28, 25.76, 25.37. **MS** (EI) *m*/*z* (relative intensity): 261 (**M**$^+$, 20), 169 (70), 93 (80), 87 (100), 55 (30).



(*E*)-*N*-(3-Bromophenyl)-3-(phenylthio)acrylamide (5ba). The representative procedure was followed using *N*-(3-bromophenyl)-3,3,3-trifluoropropanamide (**4b**) (56.41 mg, 0.20 mmol) and 1,2-diphenyldisulfane (**2a**) (65.45 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **5ba** (38.10 mg, 57 %) as a white solid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.82 (d, *J* = 15.0 Hz, 1H), 7.76 (s, 1H), 7.49 – 7.48 (m, 2H), 7.42 – 7.39 (m, 4H), 7.35 – 7.33 (m, 1H), 7.22 – 7.19 (m, 1H), 5.75 (d, *J* = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, CDCl$_3$) δ** 162.55, 145.27, 139.20, 132.73, 130.82, 130.22, 129.66, 129.03, 127.18, 122.57, 118.32, 117.54. **MS** (EI) *m*/*z* (relative intensity): 334 (**M**$^+$, 20), 223 (60), 198 (100), 135 (30).

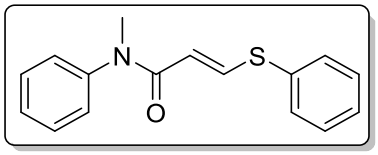


(*E*)-*N*-(4-Chlorophenyl)-3-(phenylthio)acrylamide (5ca). The representative procedure was followed using *N*-(4-chlorophenyl)-3,3,3-trifluoropropanamide (**4c**) (47.52 mg, 0.20 mmol) and 1,2-diphenyldisulfane (**2a**) (65.45 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **5ca** (35.93 mg, 62 %) as a white solid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.82 (d, *J* = 15.0 Hz, 1H), 7.50 – 7.45 (m, 4H), 7.42 – 7.40 (m, 3H), 7.26 – 7.24 (m, 3H), 5.75 (d, *J* = 15.0 Hz, 1H). **^{13}C NMR (125 MHz, CDCl$_3$) δ** 162.40, 145.07, 136.48, 133.11, 132.82, 130.85, 129.68, 129.05, 129.00, 121.19, 117.58. **MS** (EI) *m*/*z* (relative intensity): 289 (**M**$^+$, 50), 127 (100), 123 (40), 109 (30).



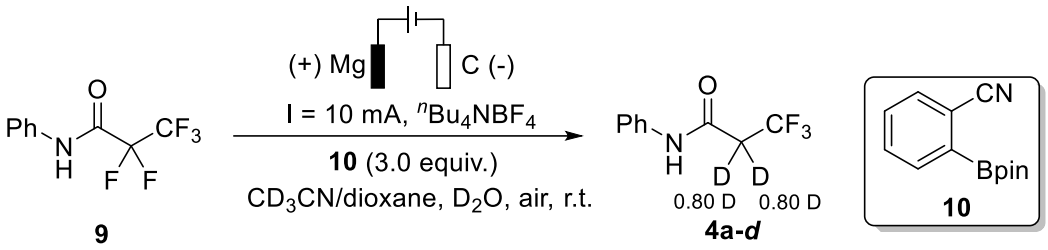
(*E*)-*N*-Benzyl-3-(phenylthio)acrylamide (5da). The representative procedure was

followed using *N*-benzyl-3,3,3-trifluoropropanamide (**4d**) (43.44 mg, 0.20 mmol) and 1,2-diphenyldisulfane (**2a**) (65.45 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **5da** (46.87 mg, 87 %) as a colorless oil, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.69 (d, *J* = 15.0 Hz, 1H), 7.46 – 7.44 (m, 2H), 7.37 – 7.34 (m, 3H), 7.30 – 7.28 (m, 2H), 7.26 – 7.23 (m, 3H), 5.85 (br, 1H), 5.67 (d, *J* = 15.0 Hz, 1H), 4.42 (d, *J* = 5.5 Hz, 2H). **^{13}C NMR (125 MHz, CDCl$_3$) δ** 164.21, 142.64, 138.15, 132.48, 129.48, 128.66, 128.60, 127.79, 127.42, 121.78, 118.06, 43.57. **MS** (EI) *m*/*z* (relative intensity): 269 (**M**$^+$, 10), 160 (100), 109 (20), 91 (30).

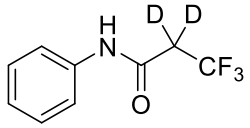


(*E*)-*N*-Methyl-*N*-phenyl-3-(phenylthio)acrylamide (5ea). The representative procedure was followed using 3,3,3-trifluoro-*N*-methyl-*N*-phenylpropanamide (**4e**) (43.44 mg, 0.20 mmol) and 1,2-diphenyldisulfane (**2a**) (65.45 mg, 0.30 mmol). Isolation by column chromatography (*n*-hexane : EtOAc = 5 : 1) yielded **5ea** (36.09 mg, 67 %) as a white solid, *E*:*Z* > 99:1. **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.72 (d, *J* = 15.0 Hz, 1H), 7.38 – 7.35 (m, 4H), 7.31 – 7.30 (m, 1H), 7.29 – 7.26 (m, 3H), 7.13 – 7.11 (m, 2H), 5.71 (d, *J* = 15.0 Hz, 1H), 3.32 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$) δ** 164.54, 143.39, 142.99, 131.95, 131.80, 129.48, 129.27, 128.25, 127.39, 127.28, 116.90, 37.22. **MS** (EI) *m*/*z* (relative intensity): 269 (**M**$^+$, 20), 163 (30), 135 (100), 109 (20).

5. Mechanistic studies



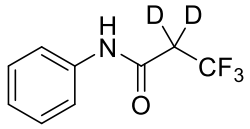
General procedure for the synthesis of trifluoropropanamides 4a-*d*[3]: Primarily, the flask was equipped with one magnesium rod electrodes (φ = 6 mm) and graphite rod electrode (φ = 6 mm), the distance between which was approximately 2 cm. We use the imported sealing film to stick the magnesium rod and the carbon rod together only at both ends of the three bottles for several rounds, and then add the reaction in the glove box. To a 10 mL three-necked flask was added 2,2,3,3,3-pentafluoro-N-phenylpropanamide **9** (81.2 mg, 0.4 mmol) and electrolyte $^{n}Bu_4NBF_4$ (0.5 mmol), followed by the reaction solvent (a mixture of 2.0 mL CD_3CN with 2.0 mL anhydrous 1,4-dioxane with 33 μL of D_2O) and boron reagent **10** (1.2 mmol). The constant current (10 mA) electrolysis was then performed at room temperature under nitrogen atmosphere with vigorous stirring for about 7 h (monitored by TLC analysis). Upon completion, the reaction mixture was poured into brine and extracted with DCM for three times. The combined organic layer was dried over anhydrous Na_2SO_4, and the solvent was then removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel to afford the desired product **4a-*d*** as a white solid; 80% deuterium incorporation was determined by **^{1}H NMR (500 MHz, $CDCl_3$)** ***δ*** 7.61 (br, 1H), 7.50 – 7.48 (m, 2H), 7.35 – 7.32 (m, 2H), 7.18 – 7.15 (m, 1H), 3.25 – 3.18 (m, 0.40H). **^{13}C NMR (125 MHz, $CDCl_3$)** ***δ*** 161.45, 136.78, 129.04, 125.36 125.03 (q, J = 273.75 Hz), 120.70. **MS** (EI) m/z (relative intensity): 205 (M^+, 30), 120 (100), 113 (10).



4a-*d*

^{1}H NMR, 500MHz

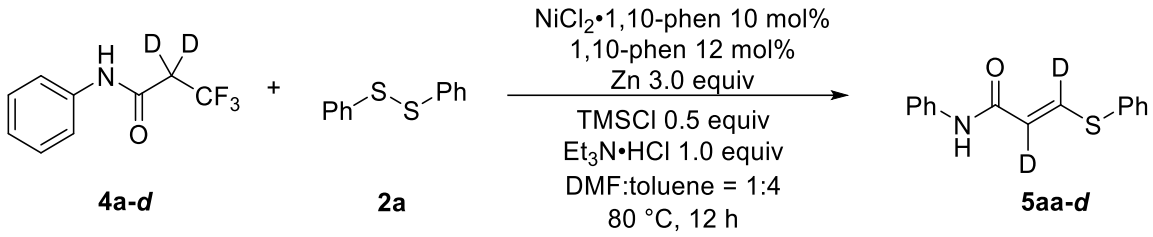
$CDCl_3$



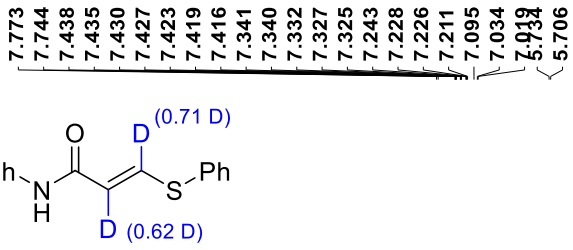
4a-*d*

^{13}C NMR, 125MHz

$CDCl_3$



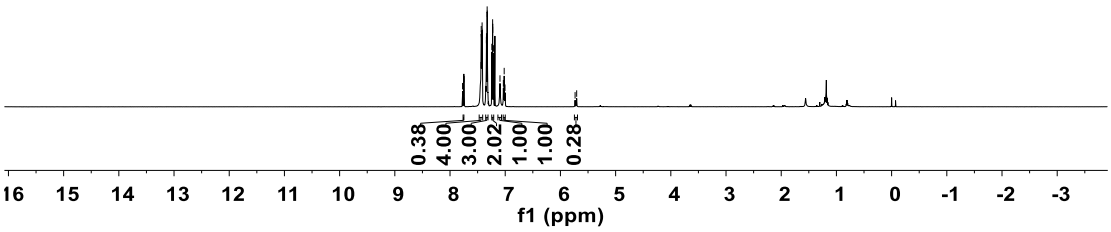
General procedure for the Ni-catalysed reductive cross-coupling of Product 5aa-*d*: To a 10 mL Schlenk tube was added sequentially $NiCl_2$·1,10-phen (6.20 mg, 0.02 mmol), 1,10-Phenanthroline (4.32 mg, 0.024 mmol), Zn power (32.90 mg, 0.6 mmol), Et_3N·HCl (27.53 mg, 0.2 mmol) and 1,2-diphenyldisulfane **2a** (0.30 mmol). The vessel was evacuated and filled with argon (three times), toluene (0.40 mL) was added via syringe and the mixture was stirred at room temperature for 10 min. The deuterated trifluoropropanamide **4a-*d*** (0.20 mmol) was added, followed by the chlorotrimethylsilane (10.86 mg, 12.68 μL, 0.10 mmol) in one portion. DMF (0.10 mL) was subsequently added via syringe. The resulting solution was stirred for 12 h at 80 ˚C. After this time, the crude reaction mixture was diluted with ethyl acetate (5 mL) and washed with water (2.0 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography. deuterium incorporation was determined by **^{1}H NMR (500 MHz, $CDCl_3$)** ***δ*** 7.75 (d, *J* = 15.0 Hz, 0.38H), 7.44 – 7.42 (m, 4H), 7.34 – 7.33 (m, 3H), 7.24 – 7.21 (m, 2H), 7.10 (br, 1H), 7.03 – 7.00 (m, 1H), 5.72 (d, *J* = 15.0 Hz, 0.29H). **^{13}C NMR (125 MHz, $CDCl_3$)** ***δ*** 162.39, 144.21, 137.92, 132.67, 131.12, 129.63, 128.98, 128.90, 124.27, 119.79, 118.15. **MS** (EI) *m*/*z* (relative intensity): 257 (M^+, 10), 137 (100), 120 (50).

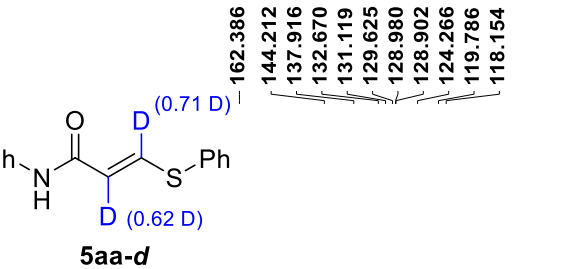


5aa-*d*

^{1}H NMR, 500MHz

$CDCl_3$

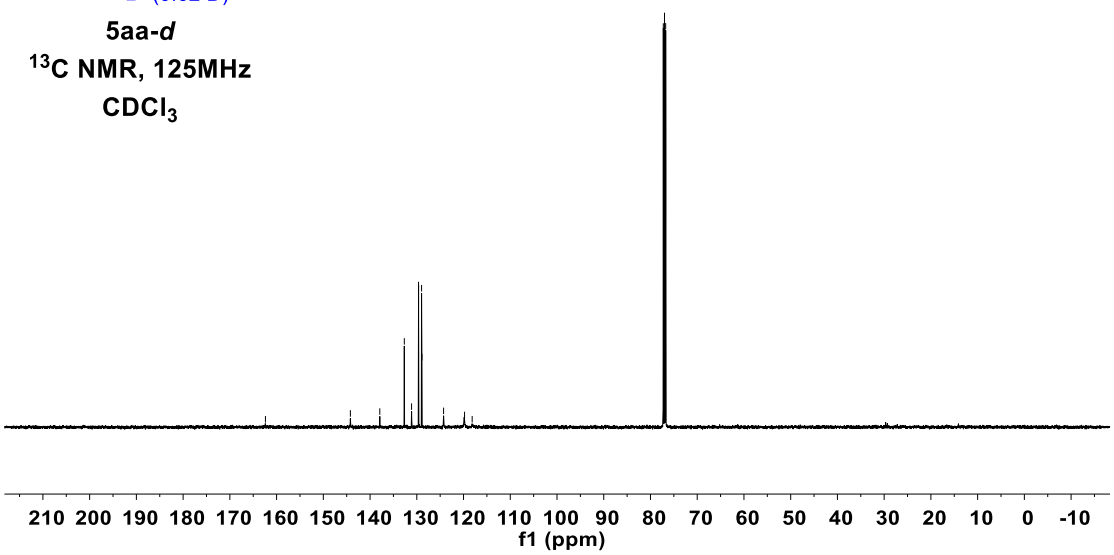




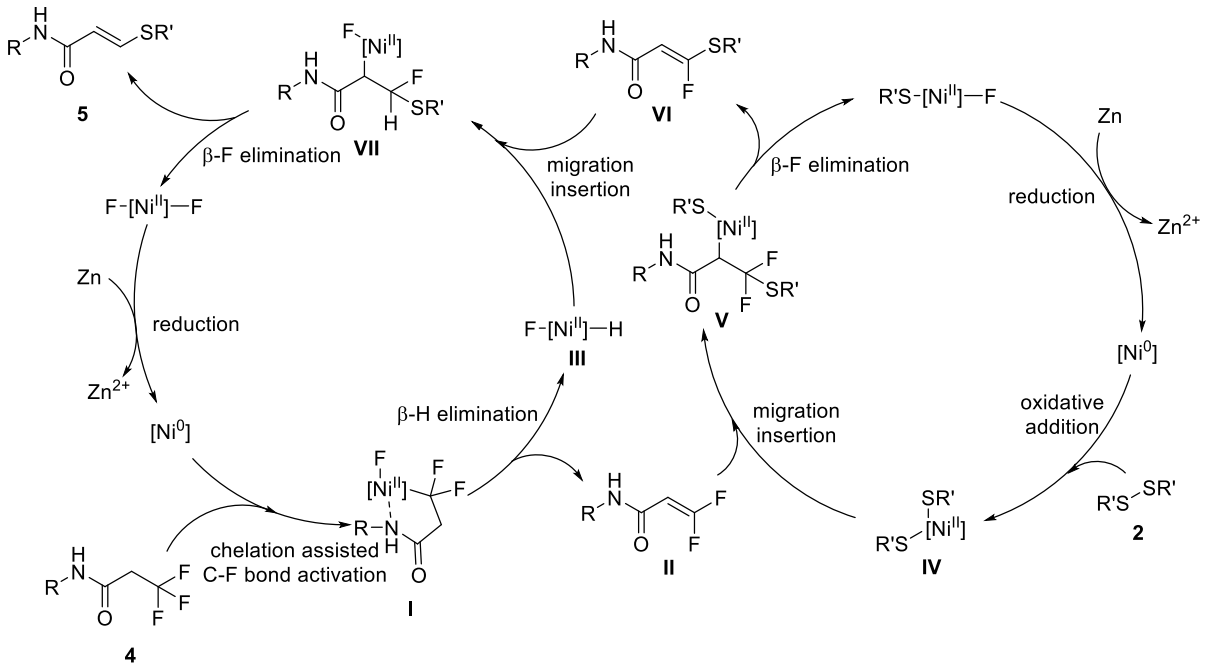
5aa-*d*

^{13}C NMR, 125MHz

$CDCl_3$



6. Proposed reaction mechanism for amides



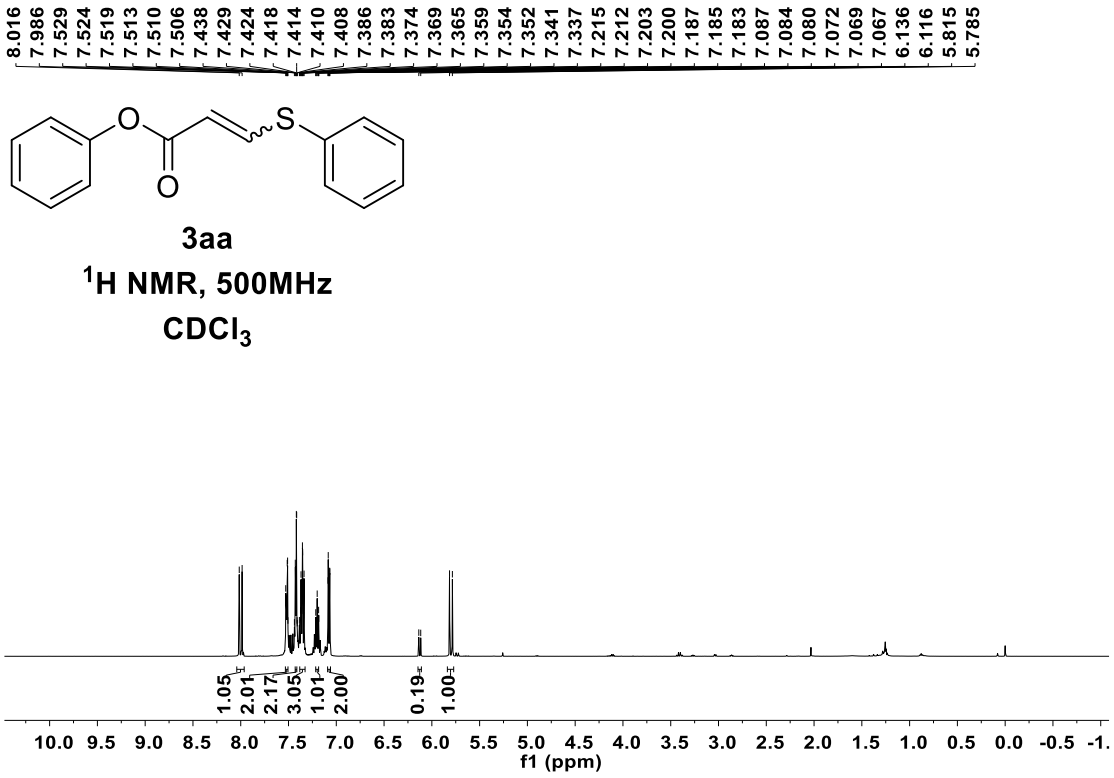
7. References

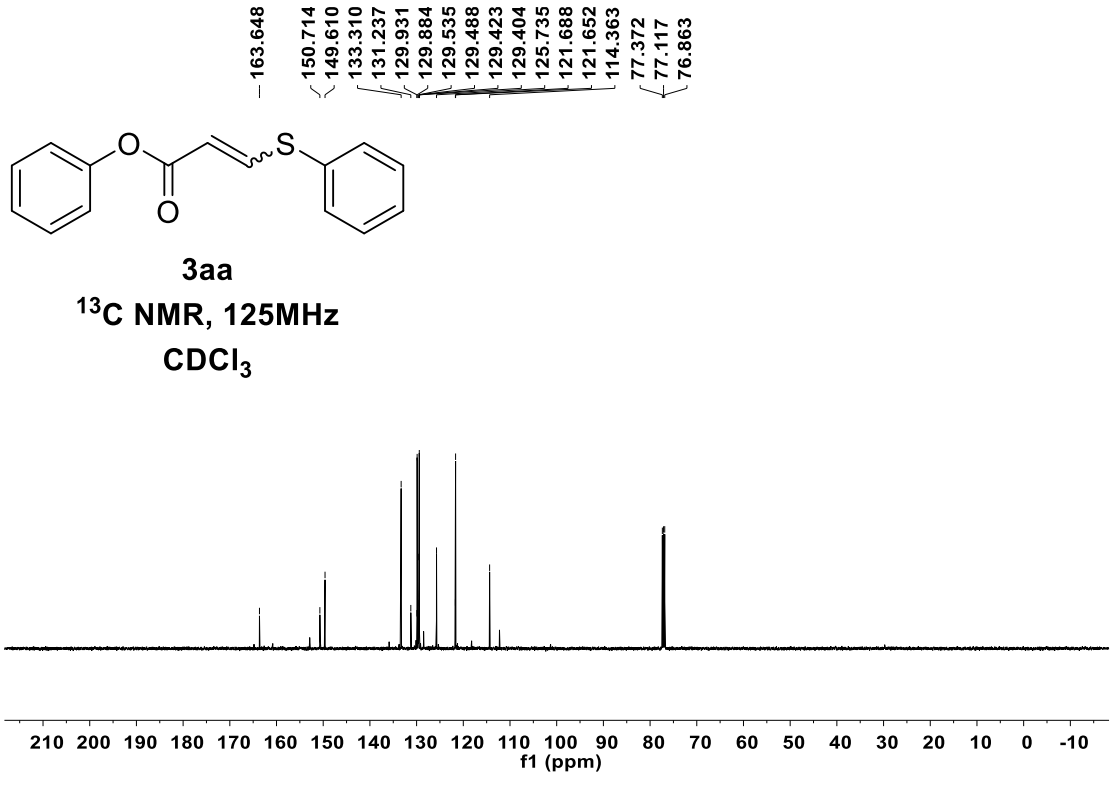
[1] P. V. Ramachandran, G. Parthasarathy and P. D. Gagare, *Org. Lett.,* 2010, **12**, 4474.

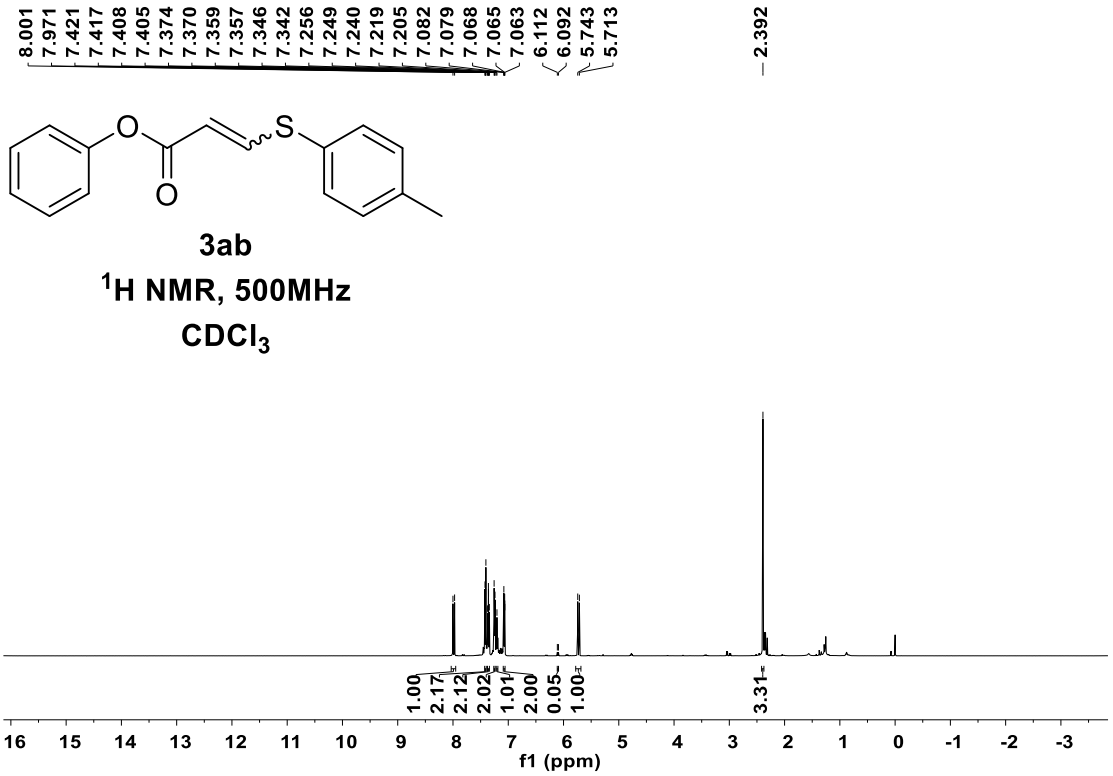
[2] C. K. W. Jim, A. Qin, J. W. Y. Lam, F. Mahtab, Y. Yu and B.-Z. Tang, *Adv. Funct. Mater*., 2010, **20**, 1319.

[3] Z.-J. Shen, C. Zhu, X. Zhang, C. Yang, M. Rueping, L. Guo and W. Xia, *Angew. Chem., Int. Ed*., 2023, **62**, e202217244.

8. NMR Spectra



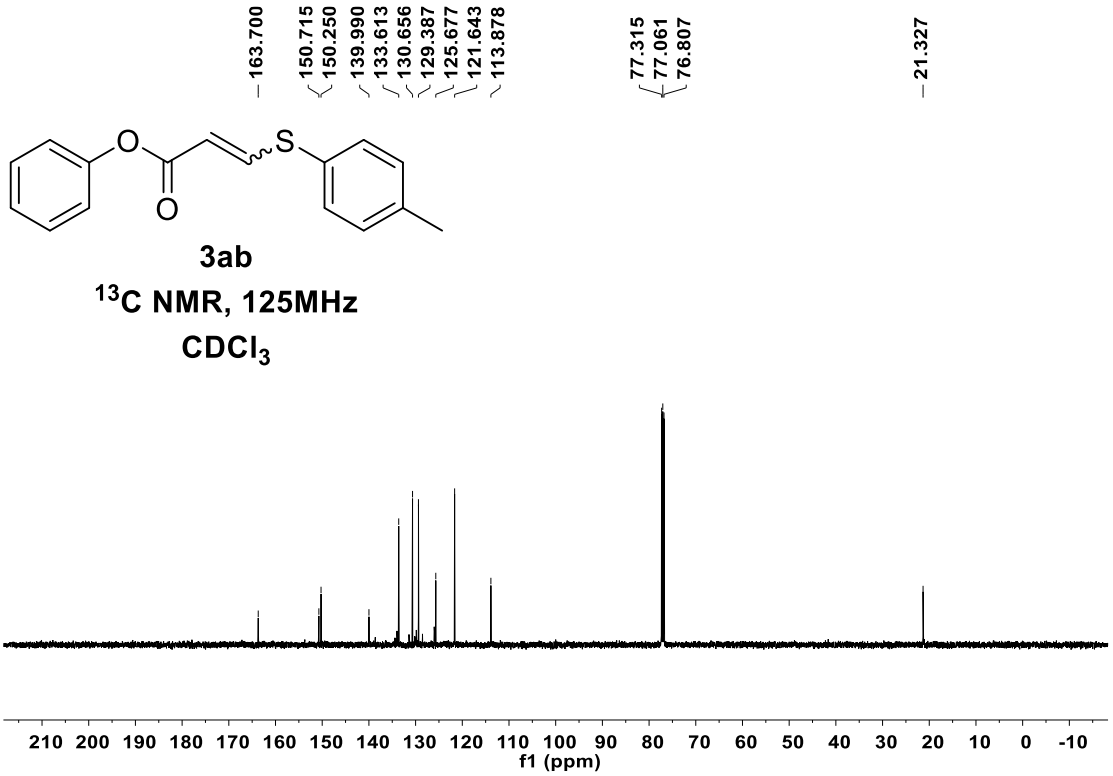




3ab

^{1}H NMR, 500MHz

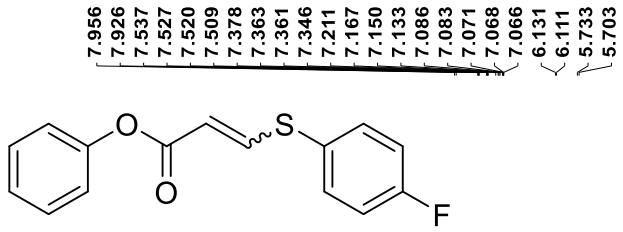
$CDCl_3$



3ab

^{13}C NMR, 125MHz

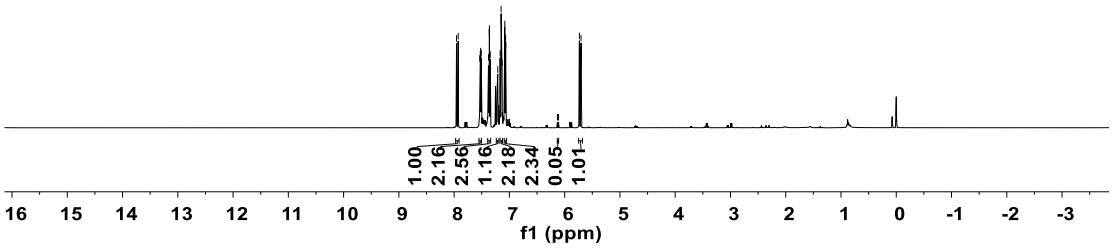
$CDCl_3$

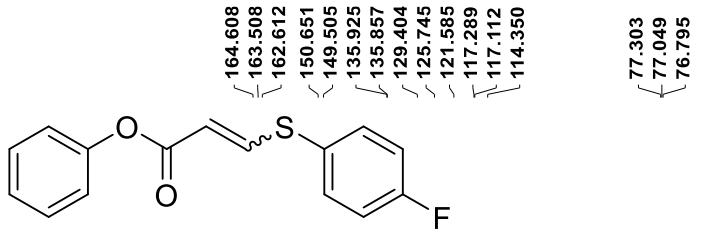


3ac

^{1}H NMR, 500MHz

$CDCl_3$

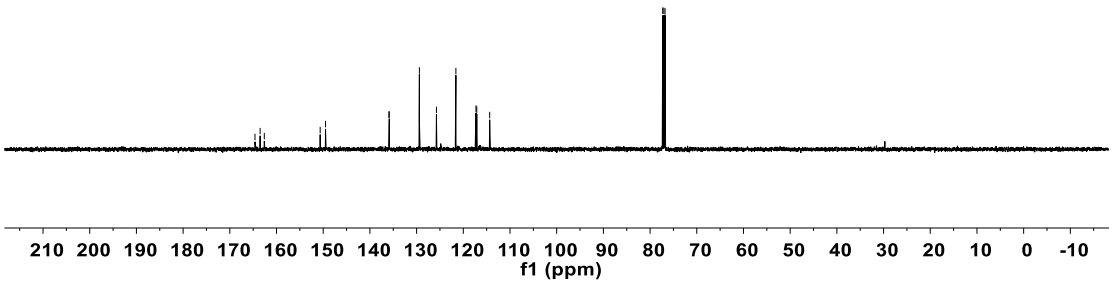


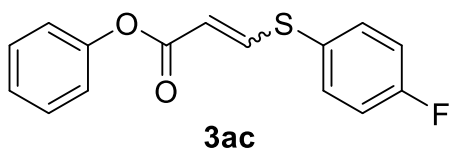


3ac

^{13}C NMR, 125MHz

$CDCl_3$

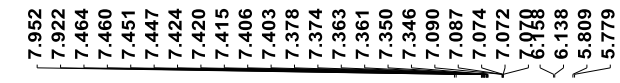


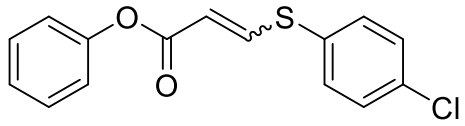


3ac

^{19}F NMR, 377MHz

$CDCl_3$

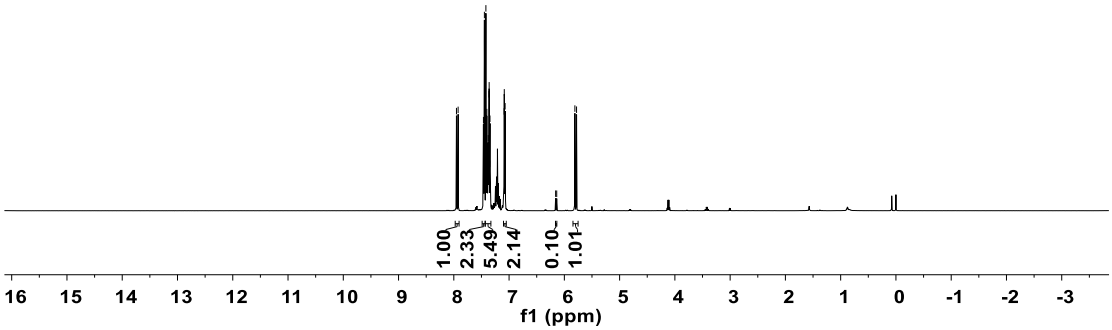


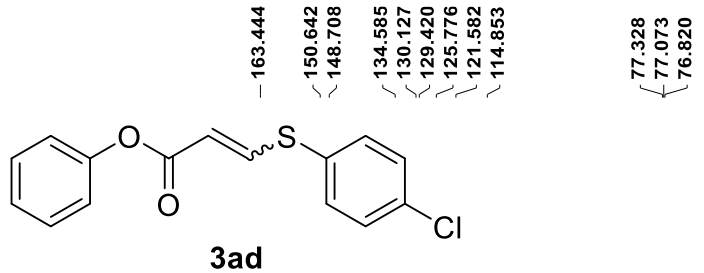


3ad

^{1}H NMR, 500MHz

$CDCl_3$

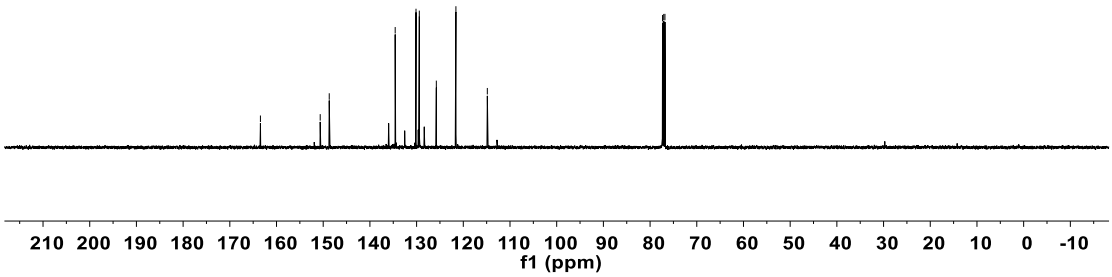


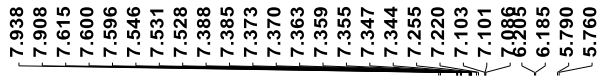


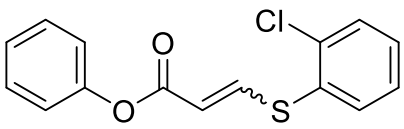
3ad

^{13}C NMR, 125MHz

$CDCl_3$



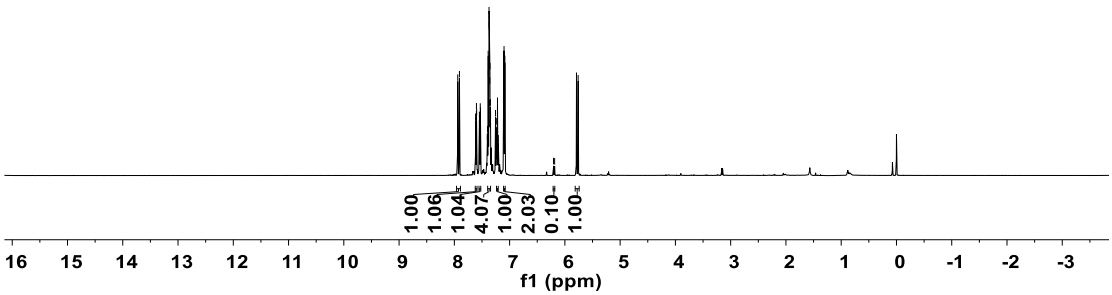


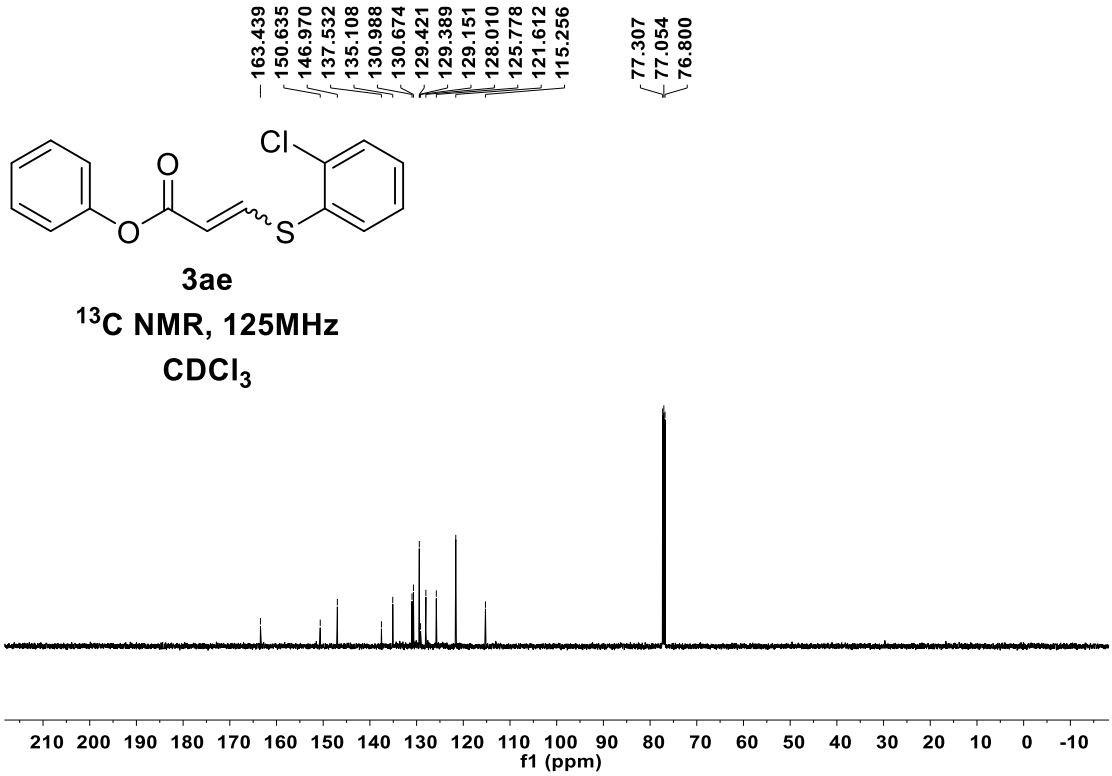


3ae

^{1}H NMR, 500MHz

$CDCl_3$

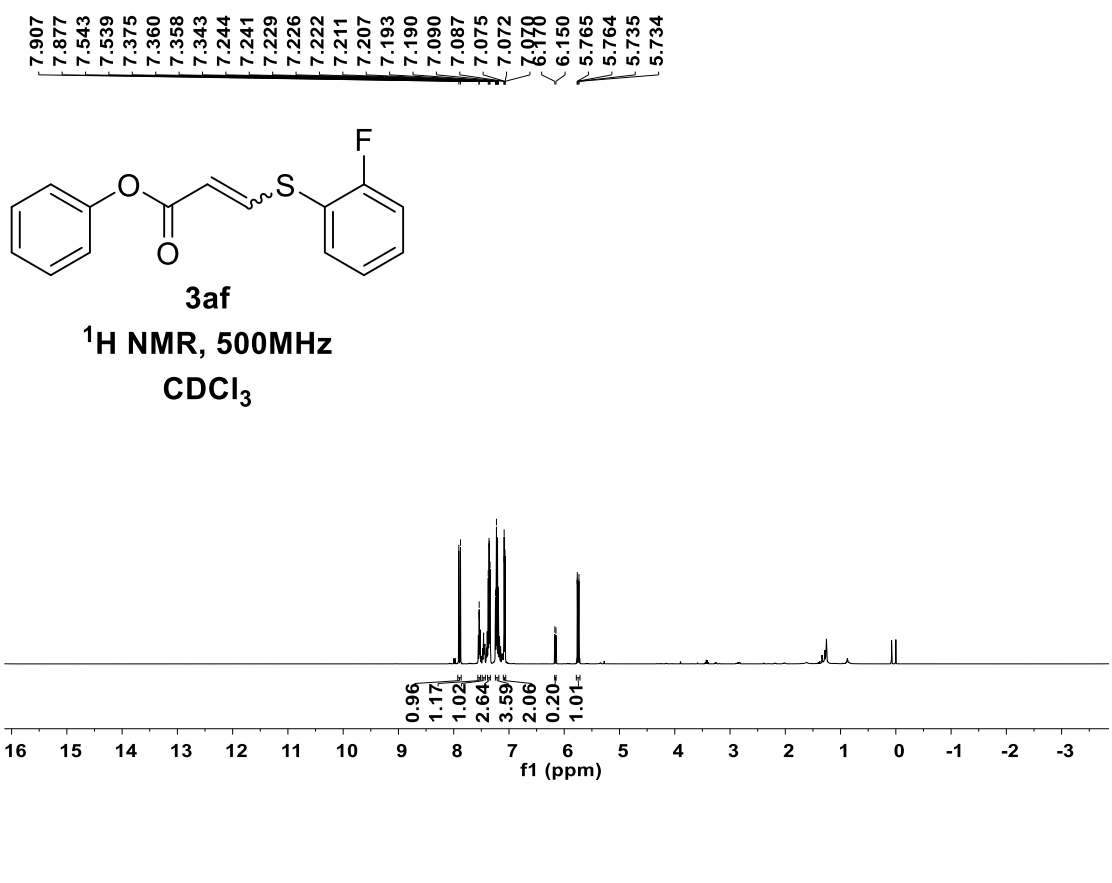




3ae

^{13}C NMR, 125MHz

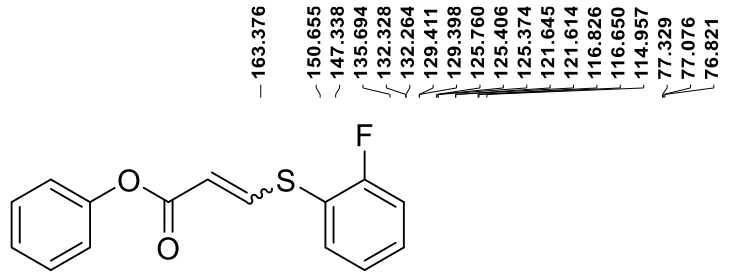
$CDCl_3$



3af

^{1}H NMR, 500MHz

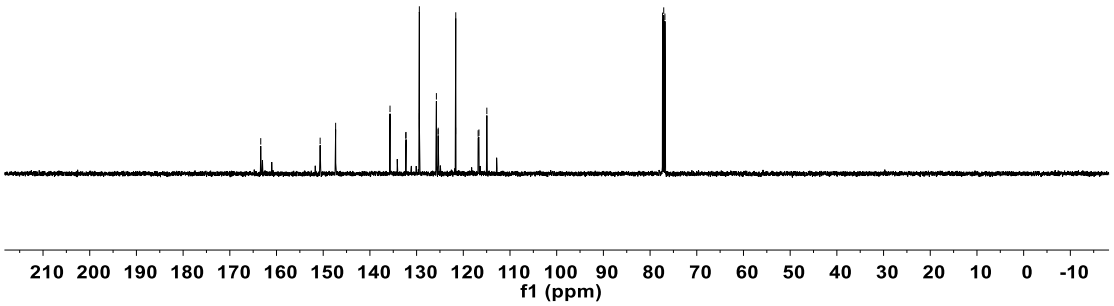
$CDCl_3$

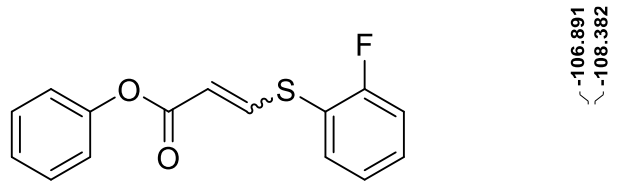


3af

^{13}C NMR, 125MHz

$CDCl_3$

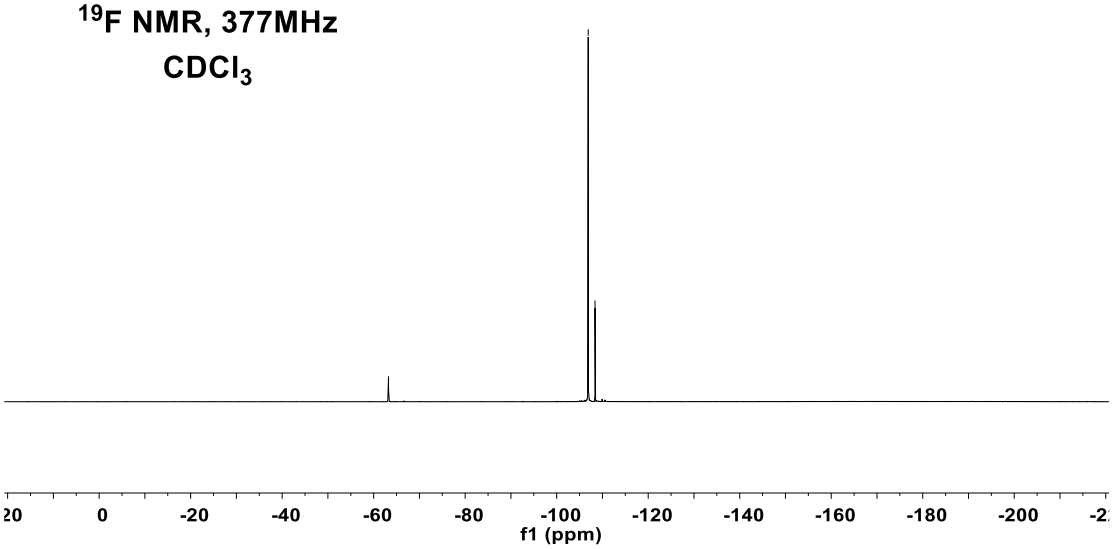


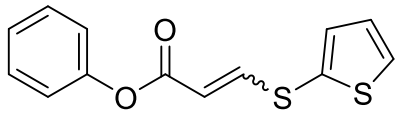


3af

^{19}F NMR, 377MHz

$CDCl_3$

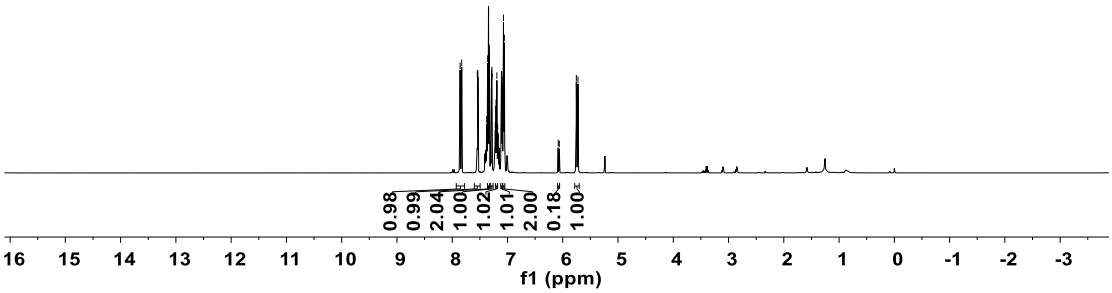


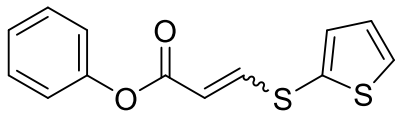


3ag

^{1}H NMR, 500MHz

$CDCl_3$





3ag

^{13}C NMR, 125MHz

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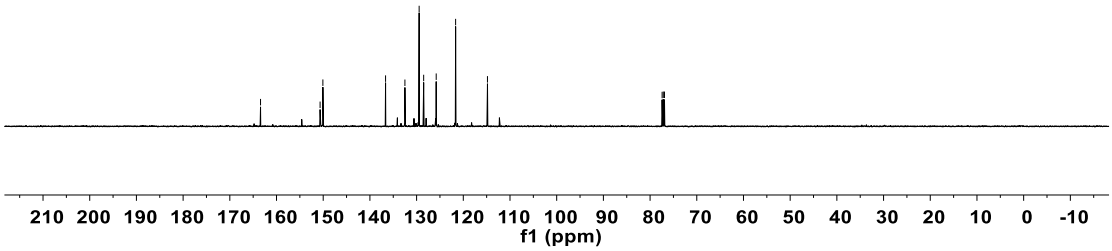
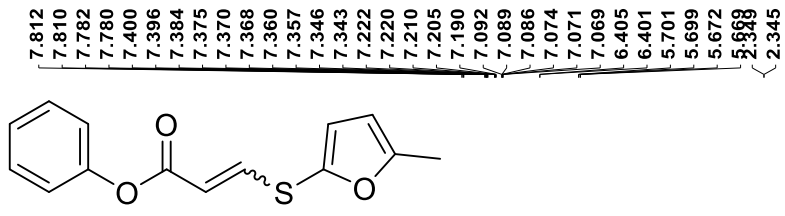
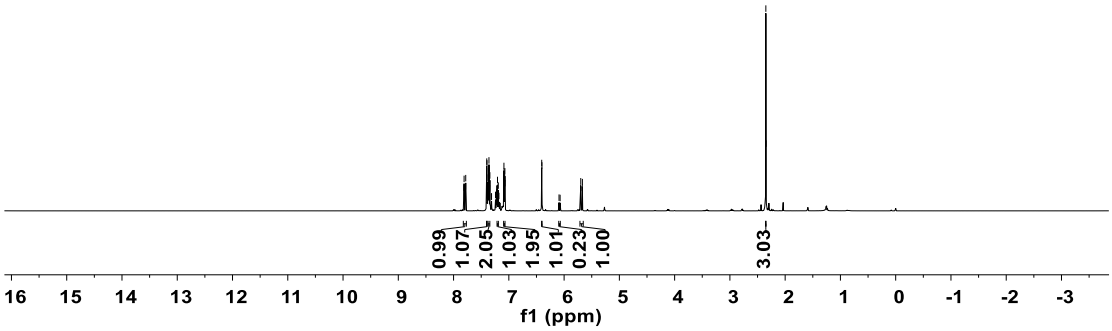


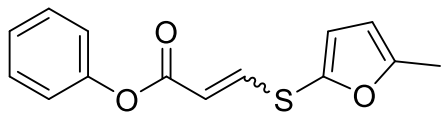


3ah

^{1}H NMR, 500MHz

$CDCl_3$





3ah

^{13}C NMR, 125MHz

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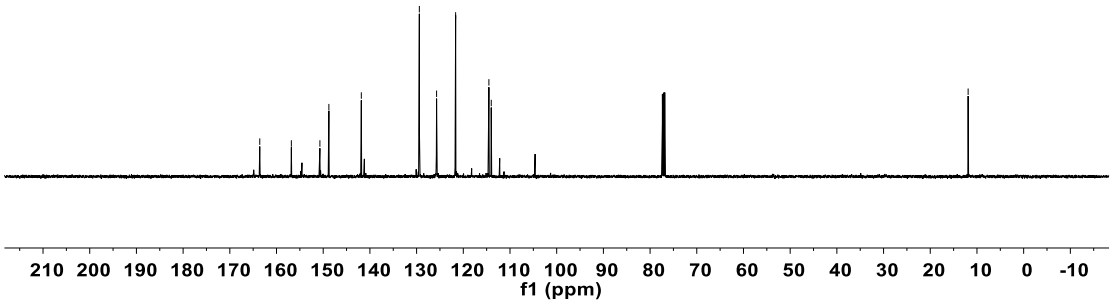
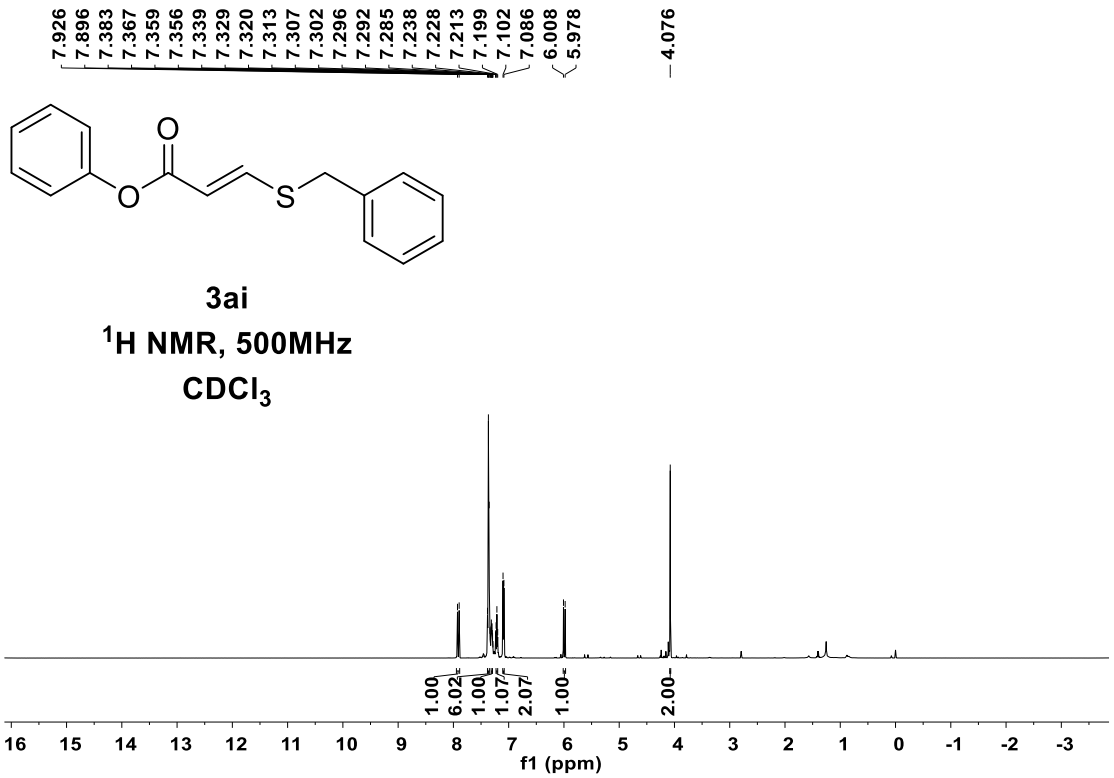
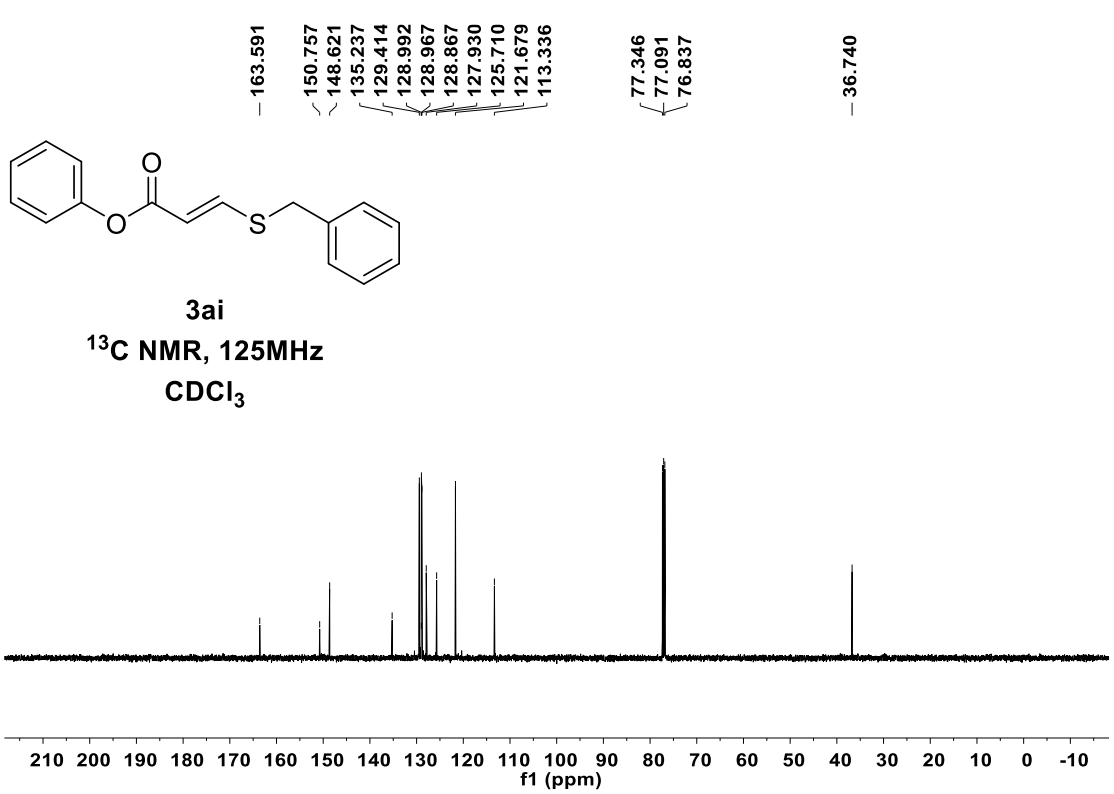




3ai

^{1}H NMR, 500MHz

$CDCl_3$



3ai

^{13}C NMR, 125MHz

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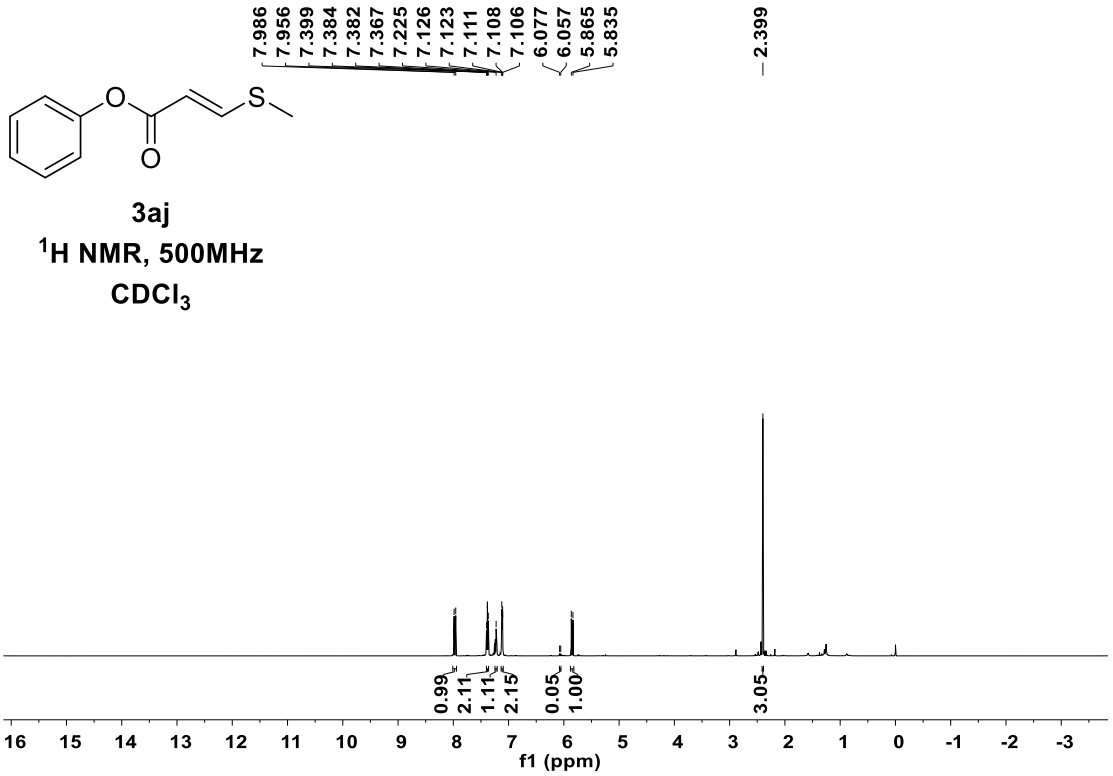

3aj

^{1}H NMR, 500MHz

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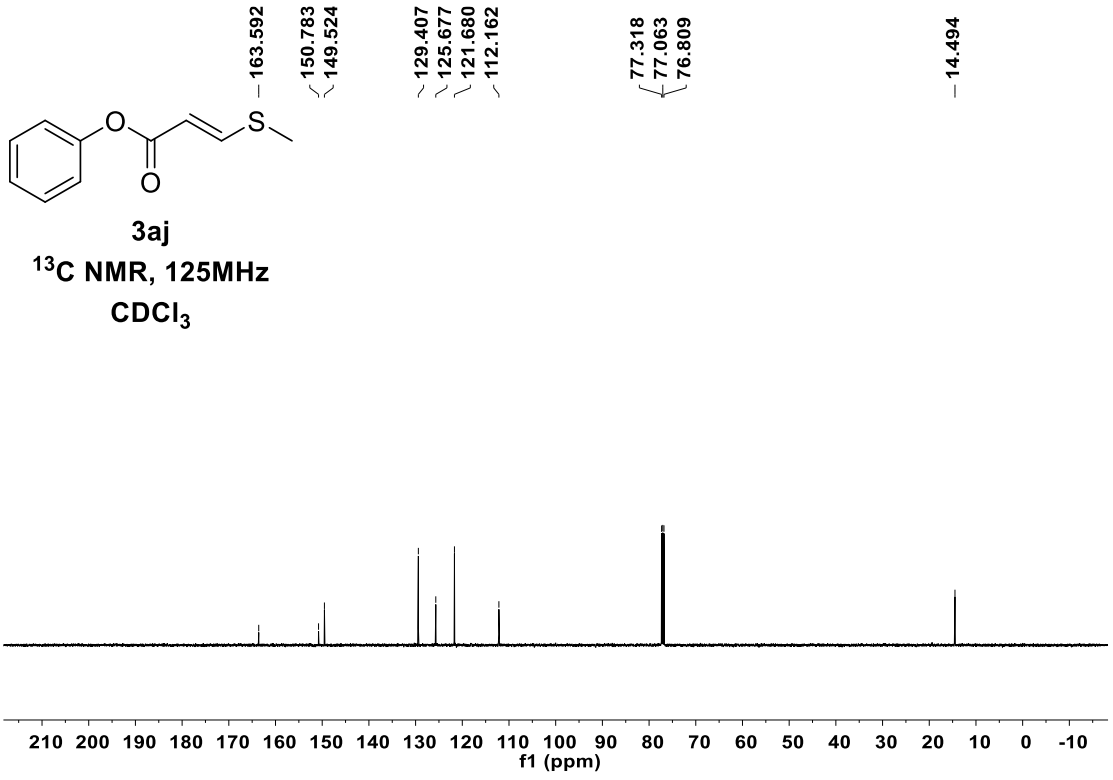

3aj

^{13}C NMR, 125MHz

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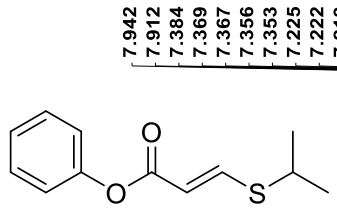

3ak

^{1}H NMR, 500MHz

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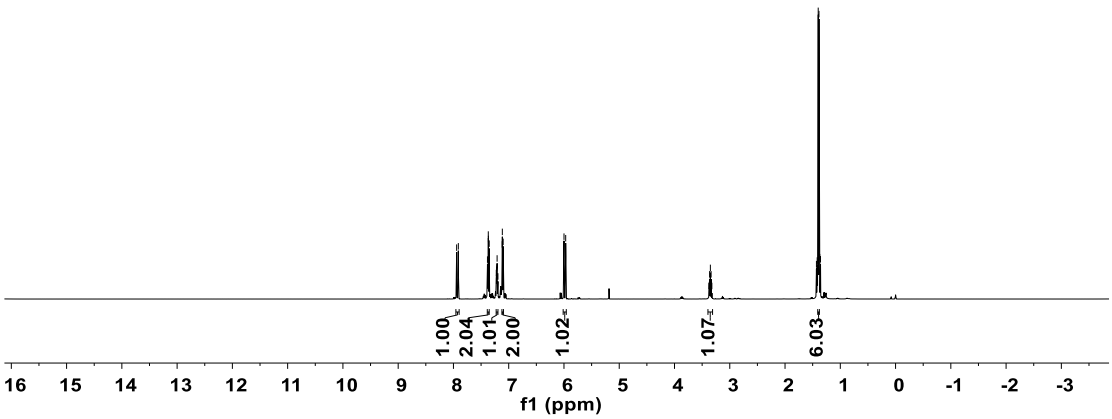

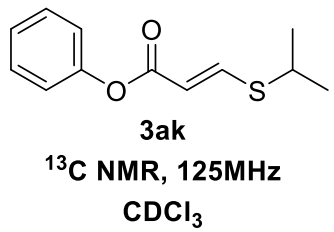

3ak

^{13}C NMR, 125MHz

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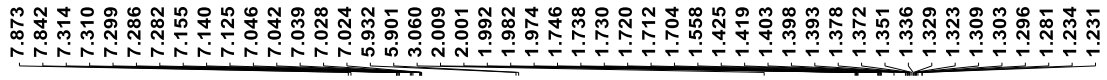
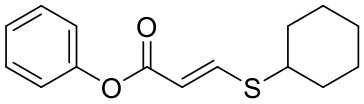
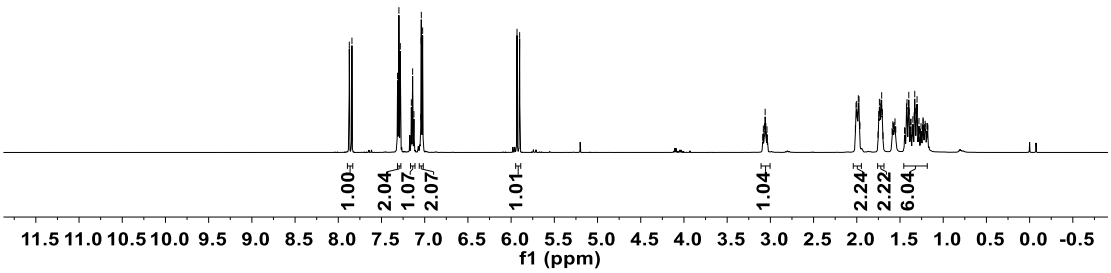


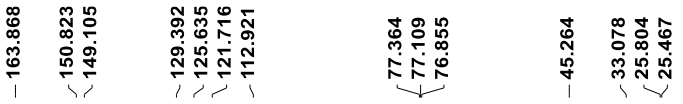


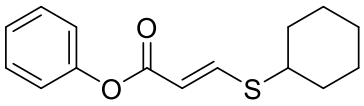
3al

^{1}H NMR, 500MHz

$CDCl_3$



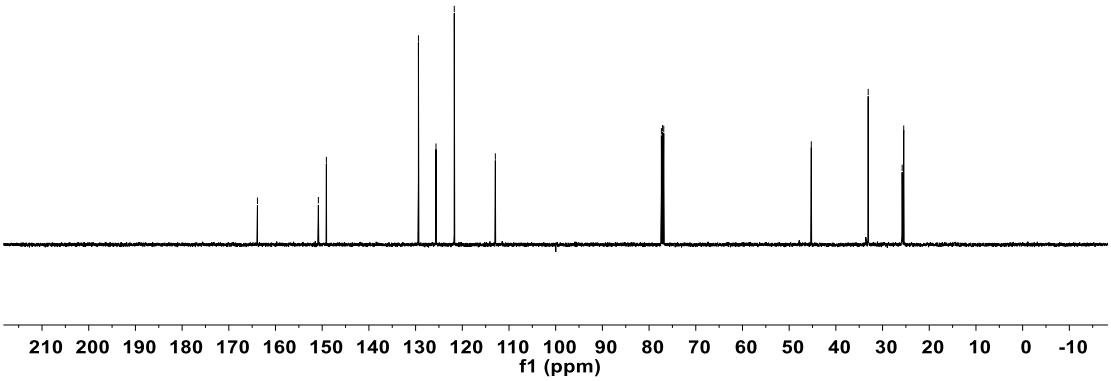


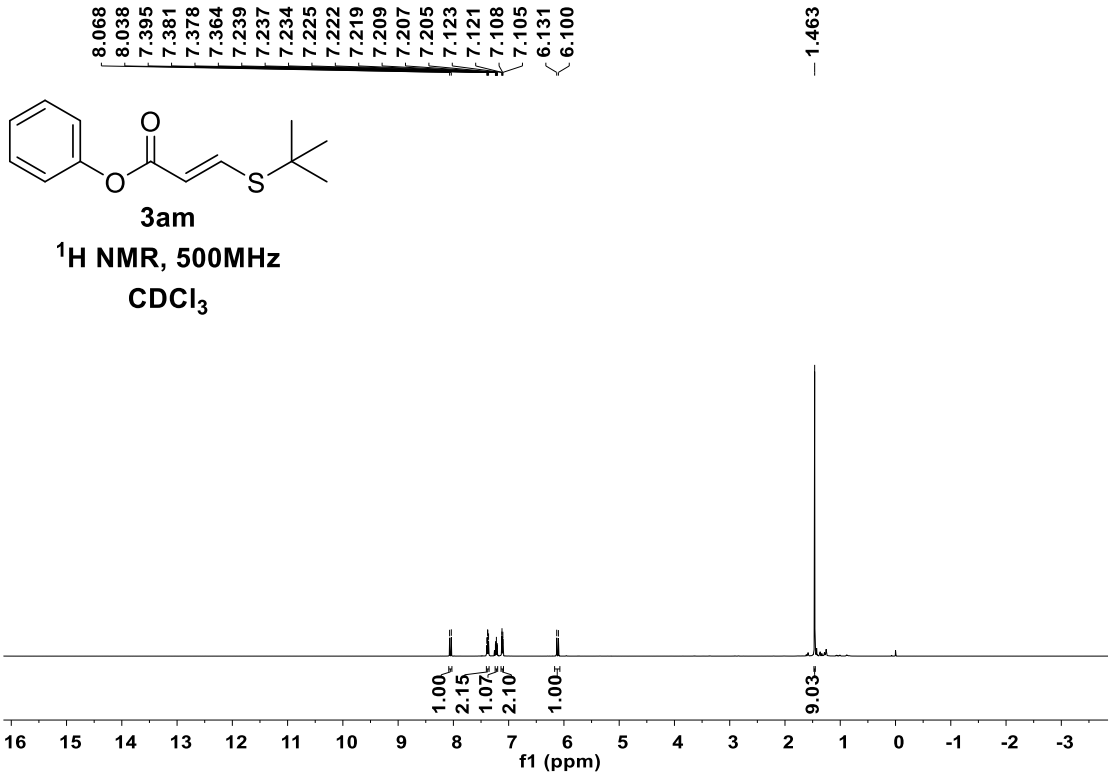


3al

^{13}C NMR, 125MHz

$CDCl_3$

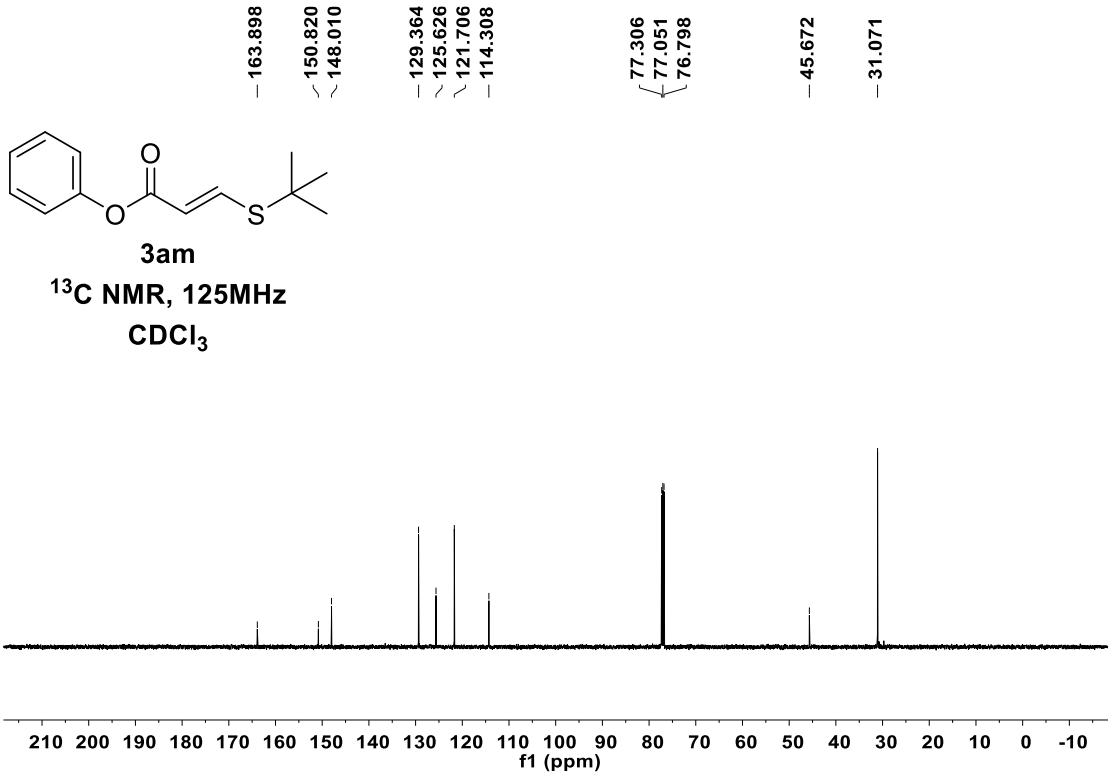




3am

^{1}H NMR, 500MHz

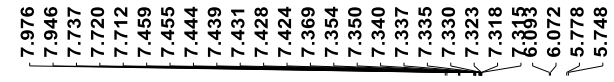
$CDCl_3$

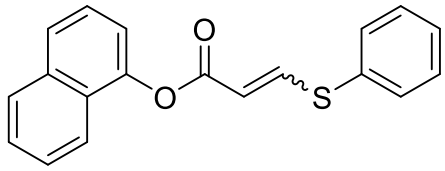


3am

^{13}C NMR, 125MHz

$CDCl_3$

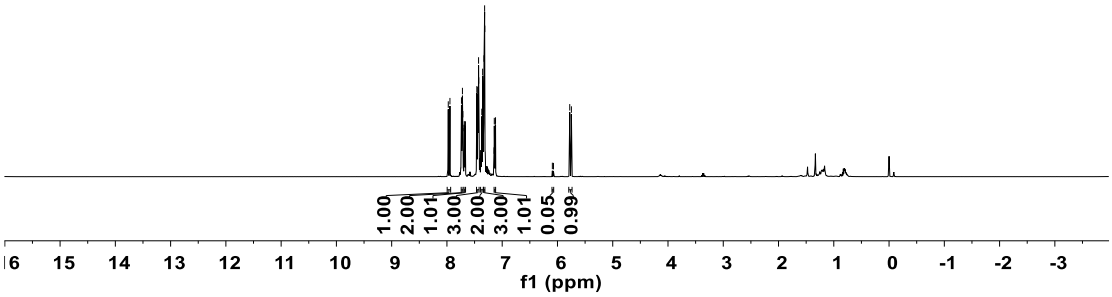


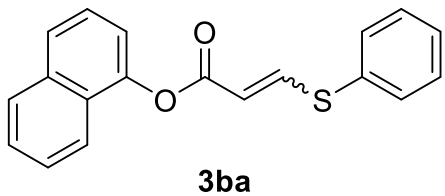


3ba

^{1}H NMR, 500MHz

$CDCl_3$

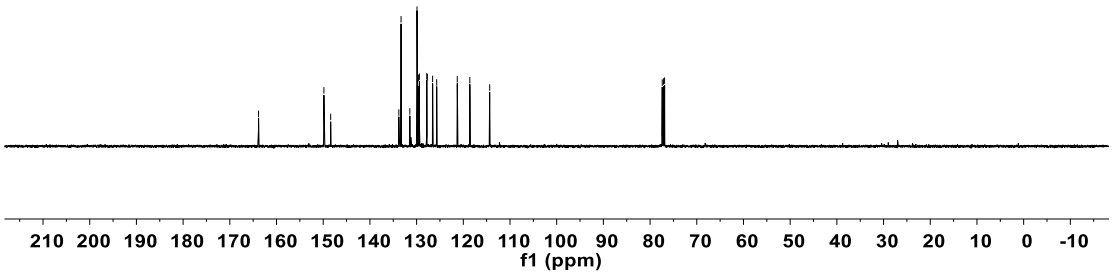


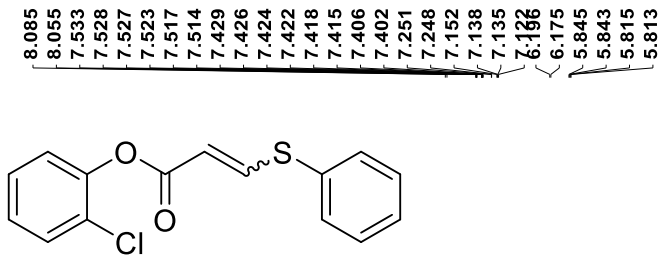


3ba

^{13}C NMR, 125MHz

$CDCl_3$

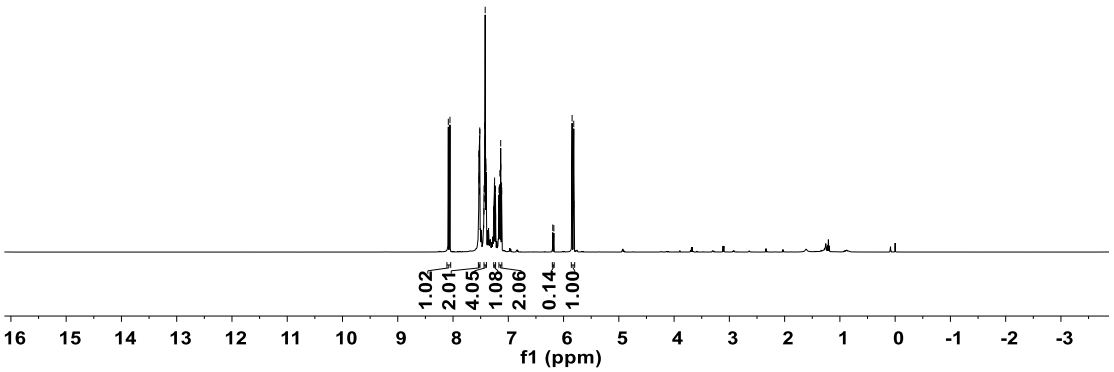


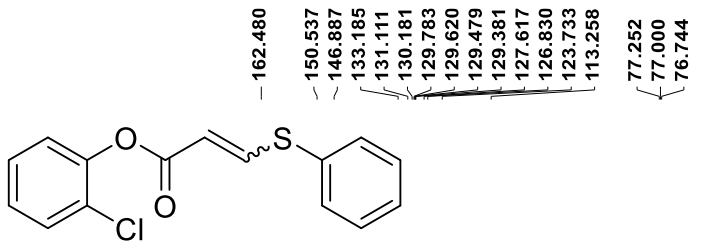


3ca

^{1}H NMR, 500MHz

$CDCl_3$

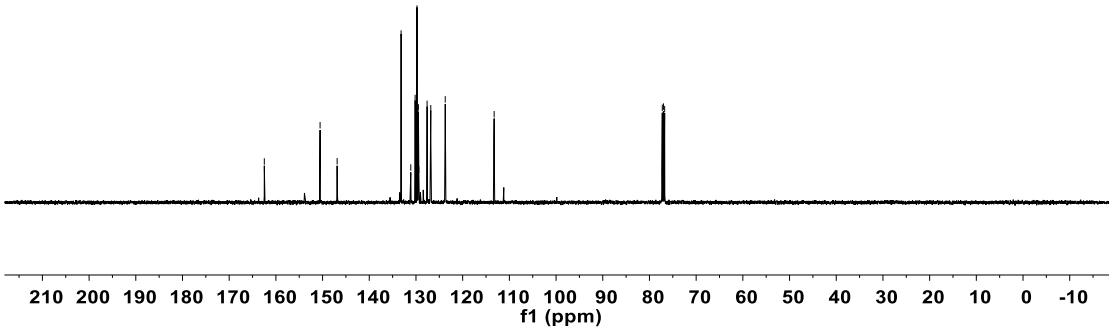


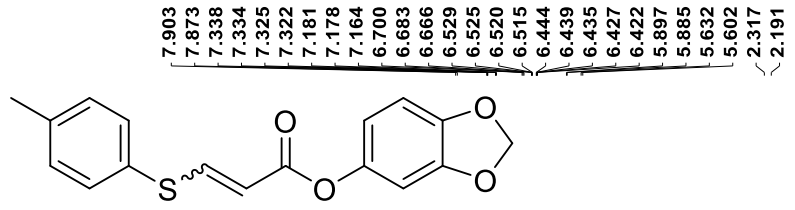


3ca

^{13}C NMR, 125MHz

$CDCl_3$

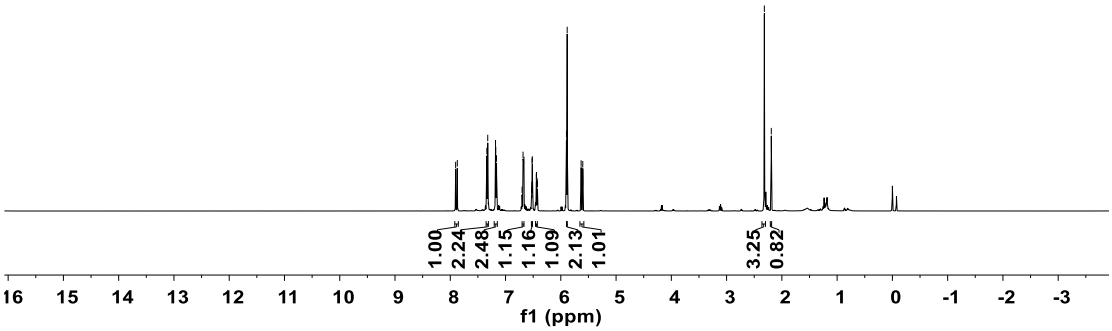


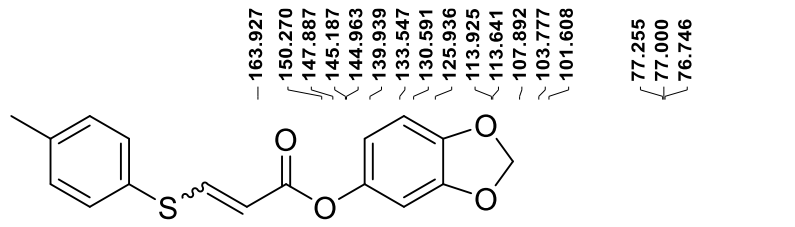


3da

^{1}H NMR, 500MHz

$CDCl_3$

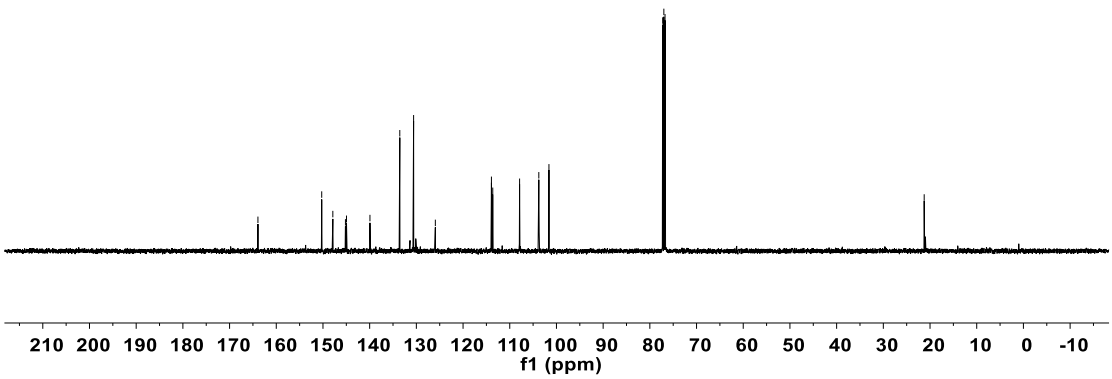


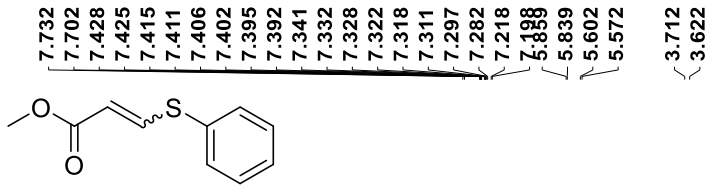


3da

^{13}C NMR, 125MHz

$CDCl_3$

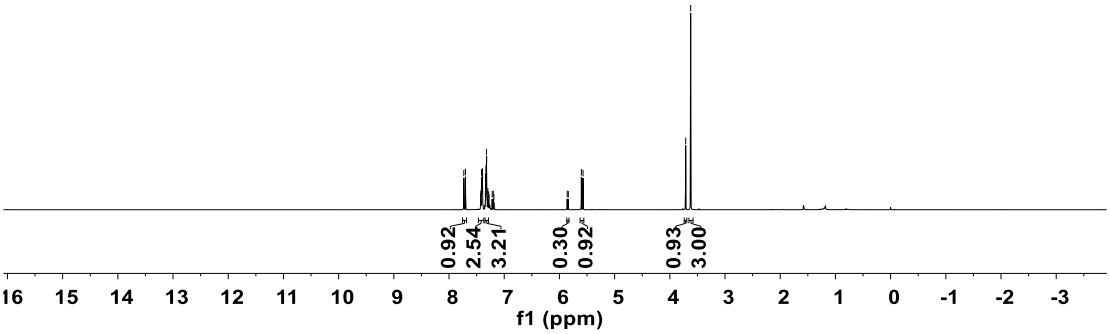


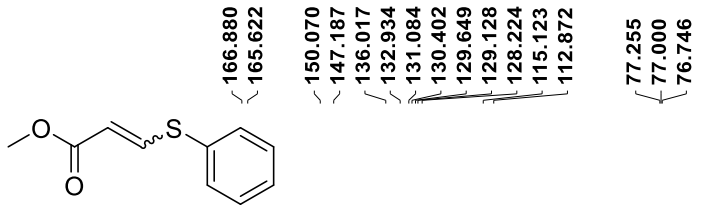


3ea

^{1}H NMR, 500MHz

$CDCl_3$

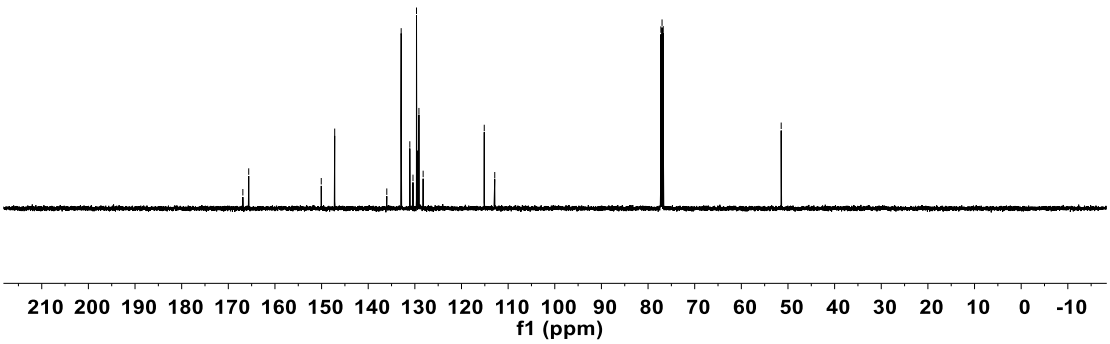


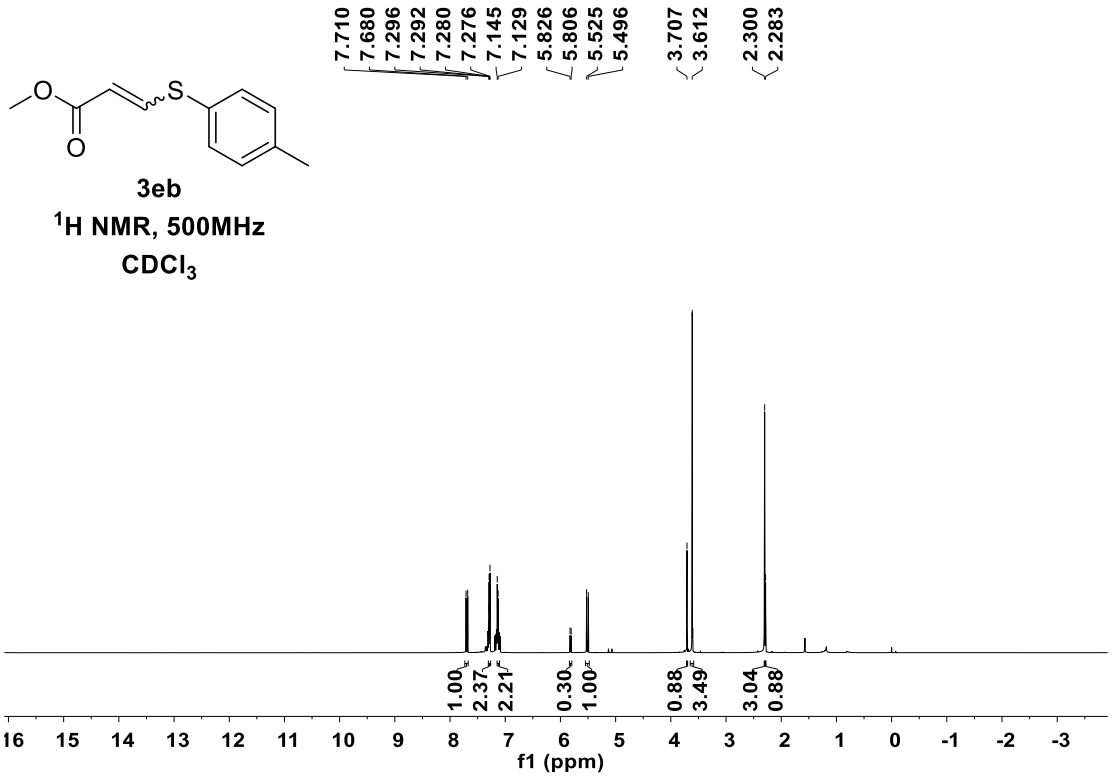


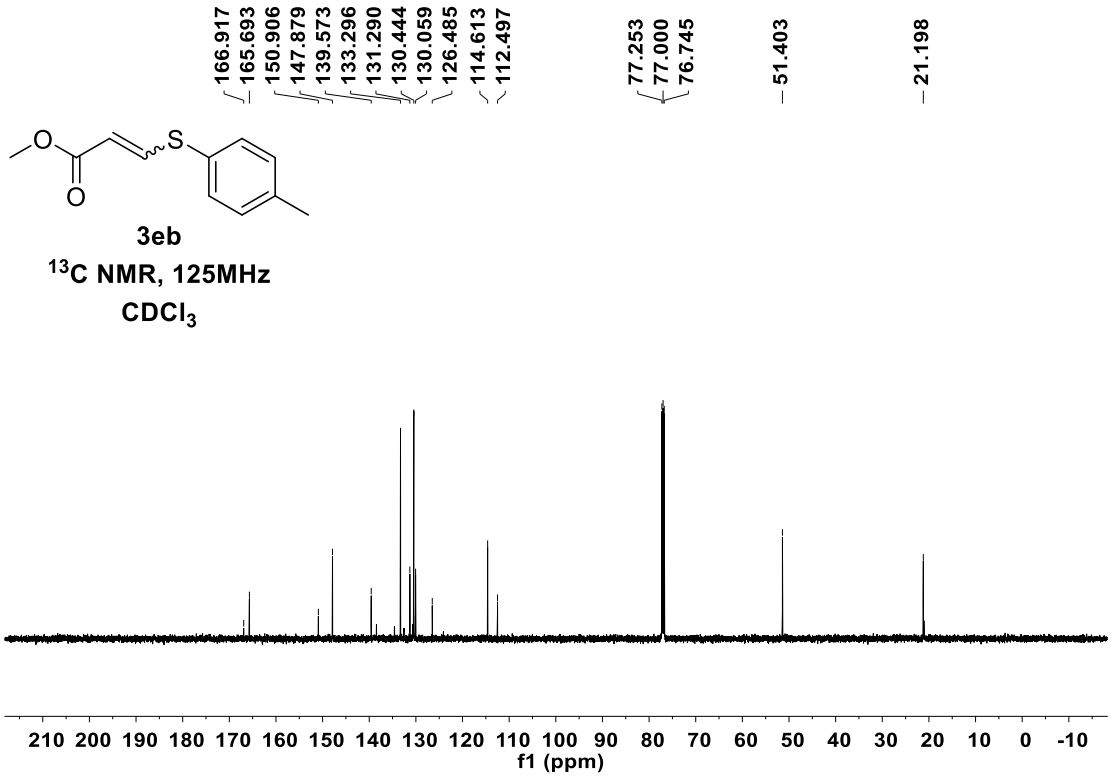
3ea

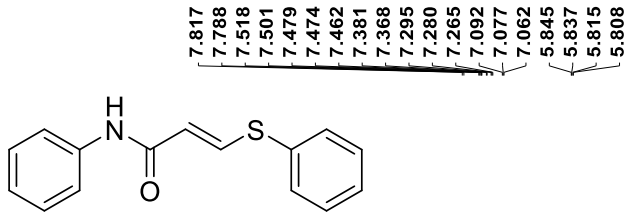
^{13}C NMR, 125MHz

$CDCl_3$




7.710
7.680
7.296
7.292
7.280
7.276
7.145
7.129
5.826
5.806
5.525
5.496
3.707
3.612
2.300
2.283
O
O
S
3eb
1H NMR, 500MHz
CDCl3
1.00
2.37
2.21
0.30
1.00
0.88
3.49
3.04
0.88
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

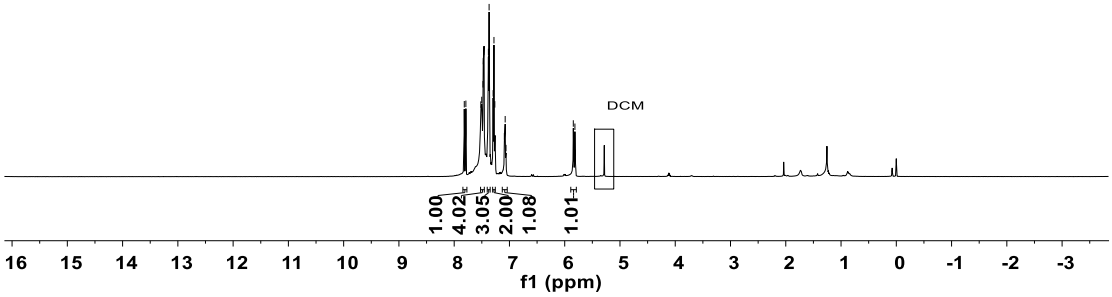

166.917
165.693
150.906
147.879
139.573
133.296
131.290
130.444
130.059
126.485
114.613
112.497
77.253
77.000
76.745
51.403
21.198
O
O
S
3eb
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

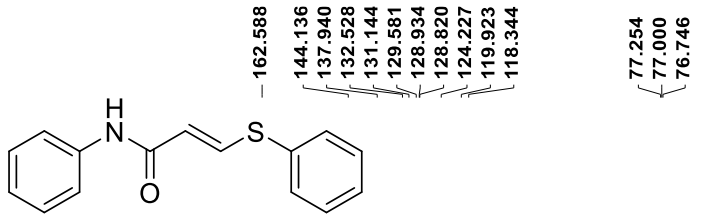


5aa

^{1}H NMR, 500MHz

$CDCl_3$

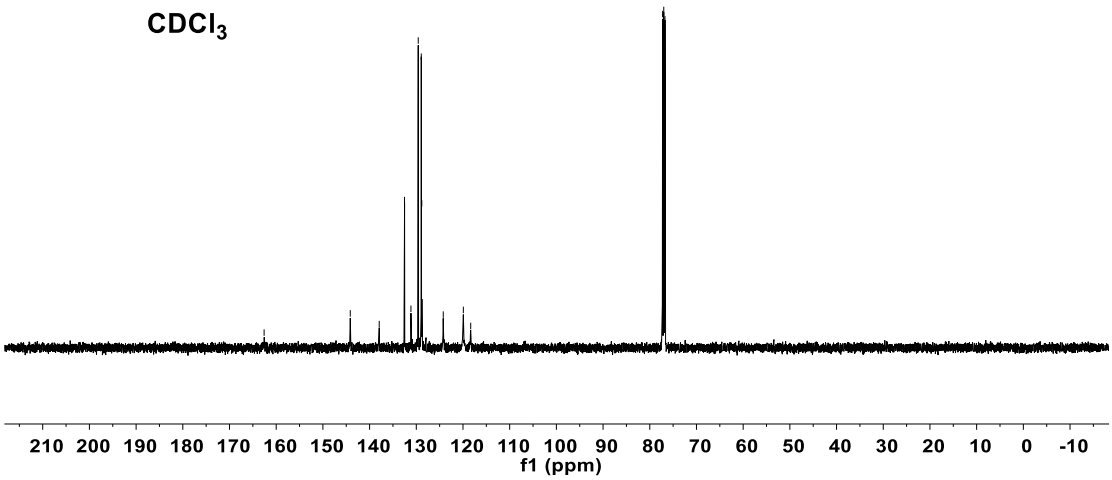


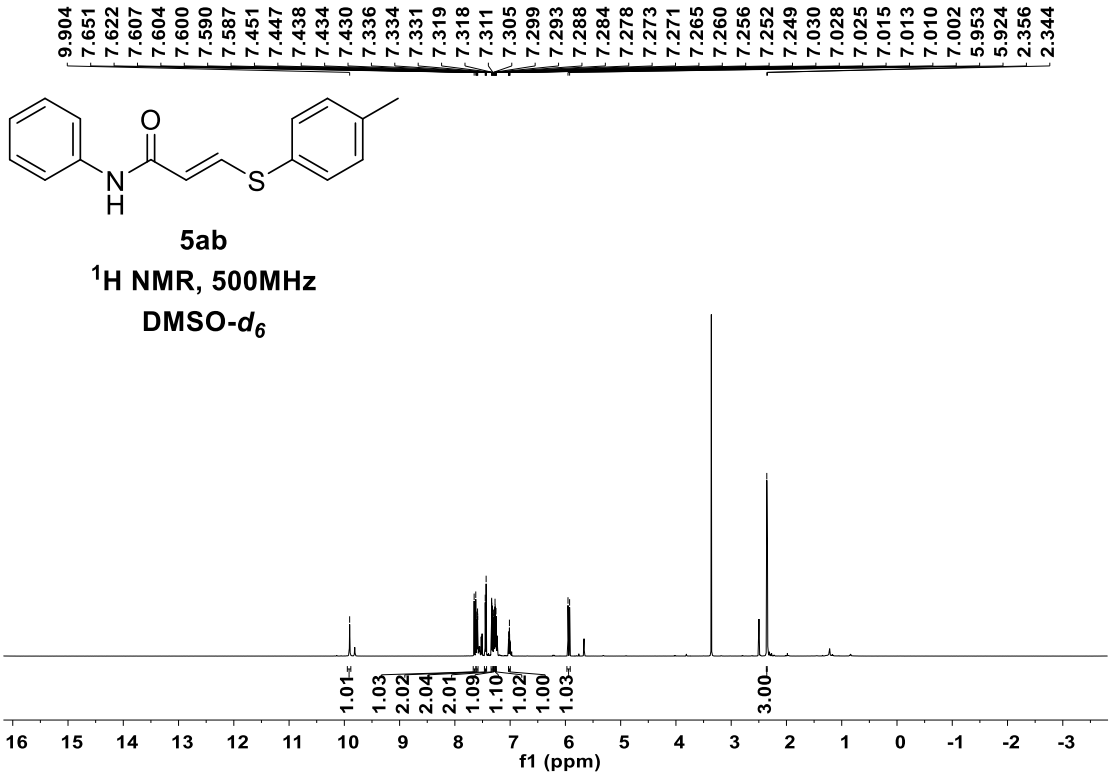


5aa

^{13}C NMR, 125MHz

$CDCl_3$

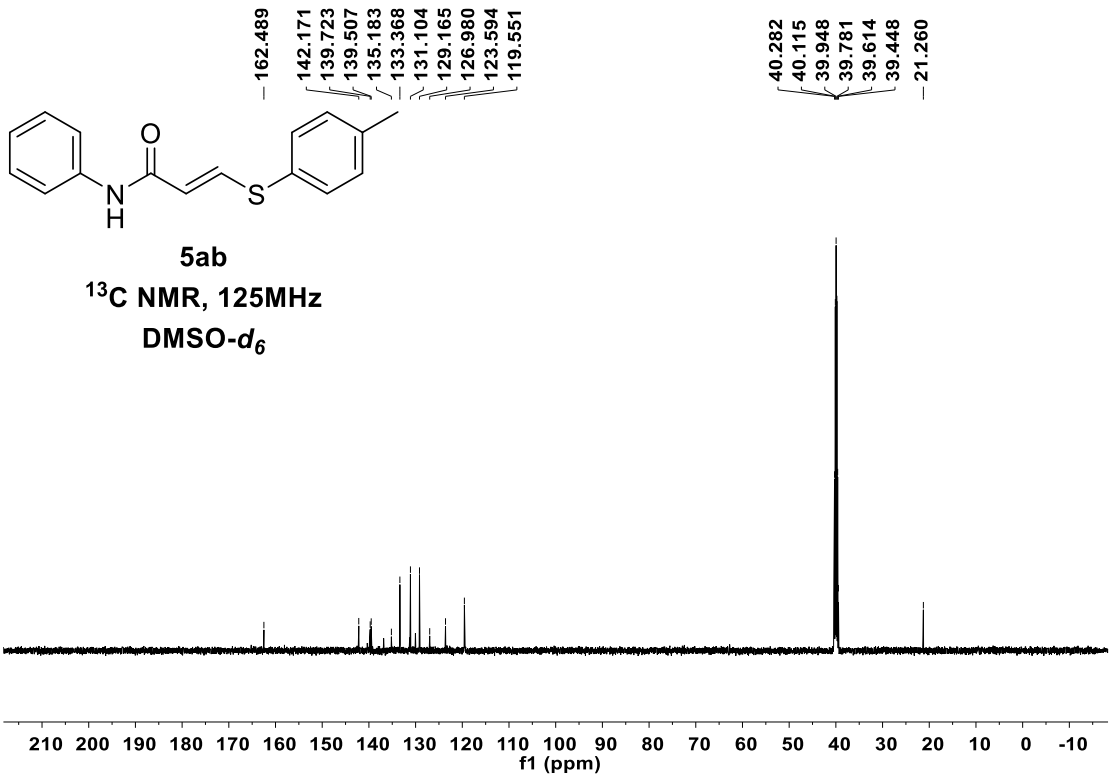




5ab

^{1}H NMR, 500MHz

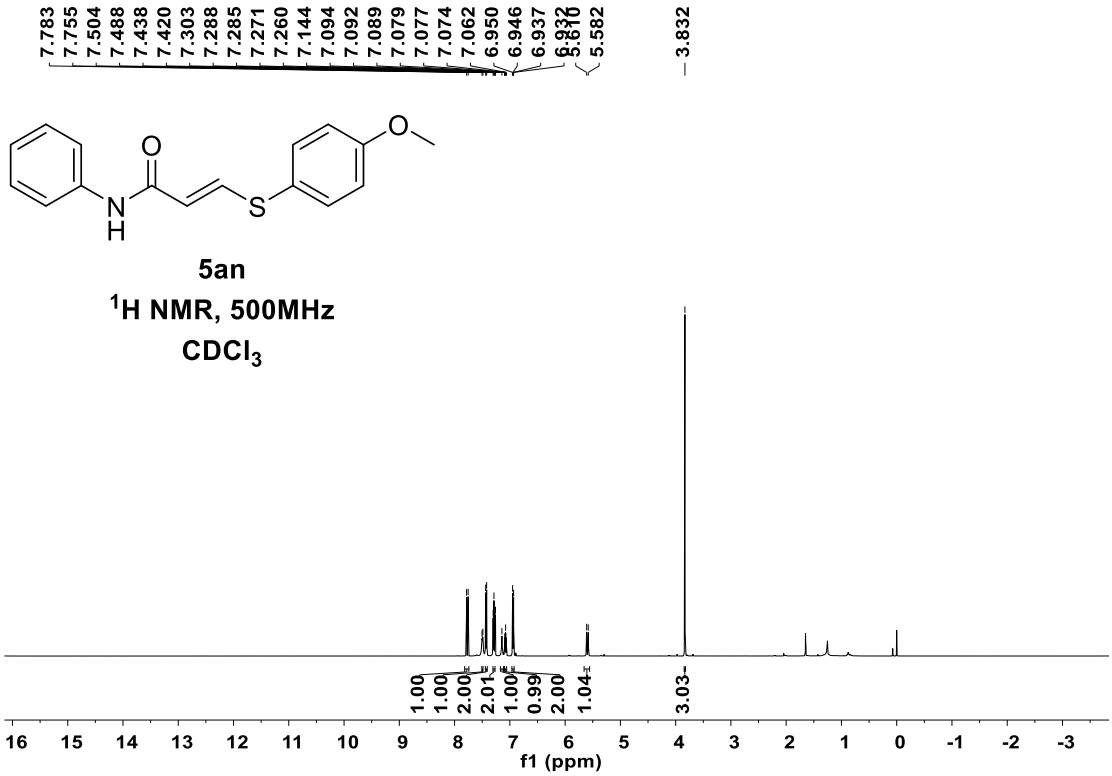
DMSO-*d*$_6$



5ab

^{13}C NMR, 125MHz

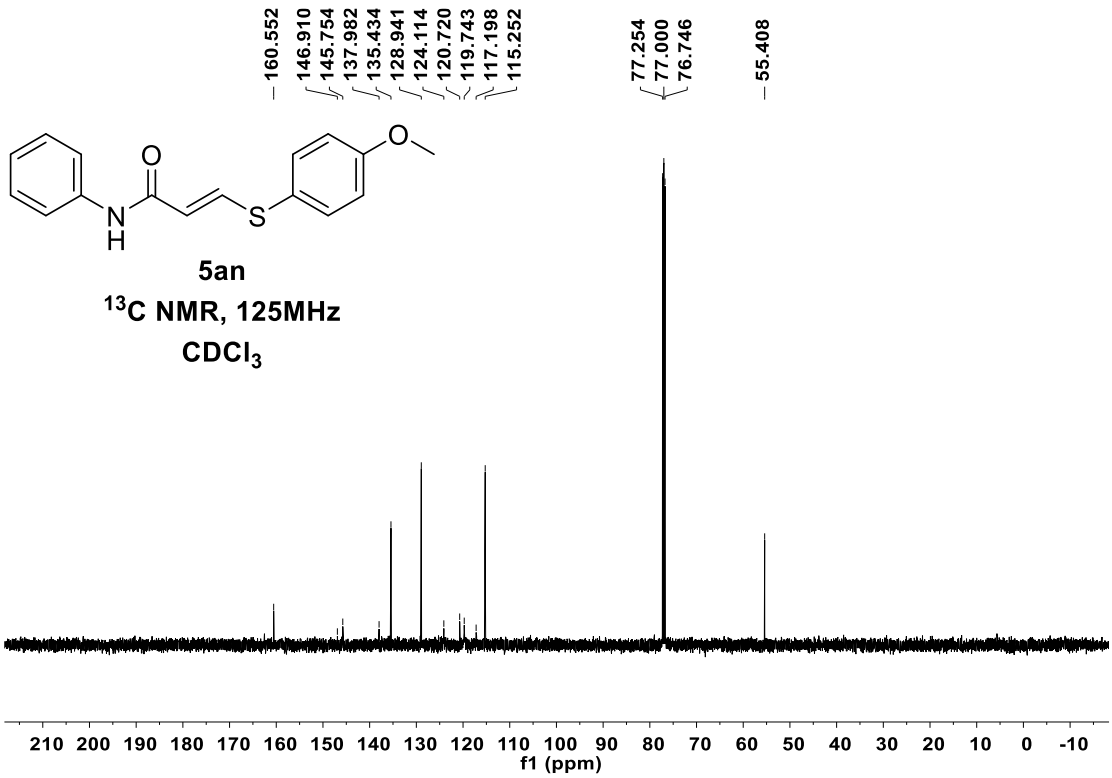
DMSO-*d*$_6$



5an

^{1}H NMR, 500MHz

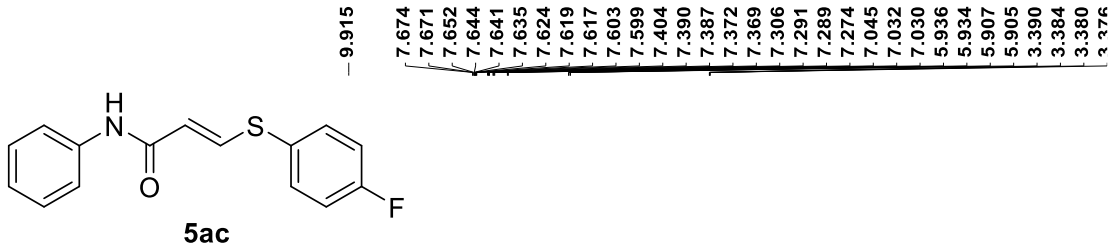
$CDCl_3$



5an

^{13}C NMR, 125MHz

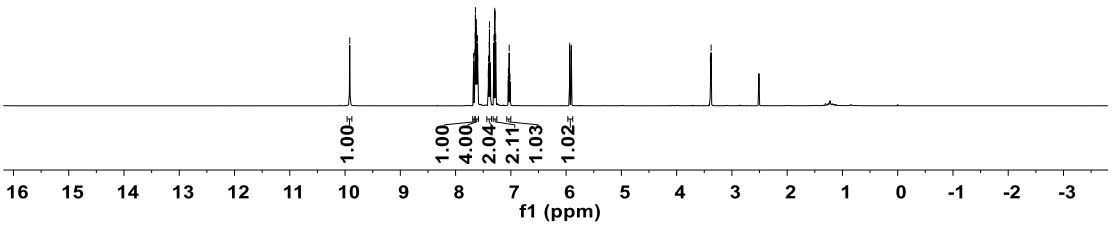
$CDCl_3$

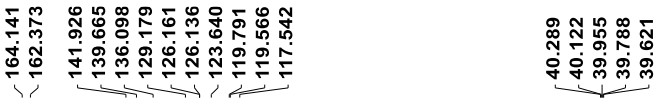


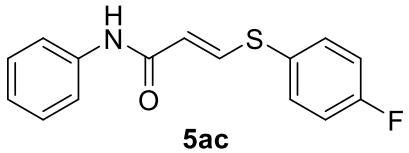
5ac

^{1}H NMR, 500MHz

DMSO-d_6



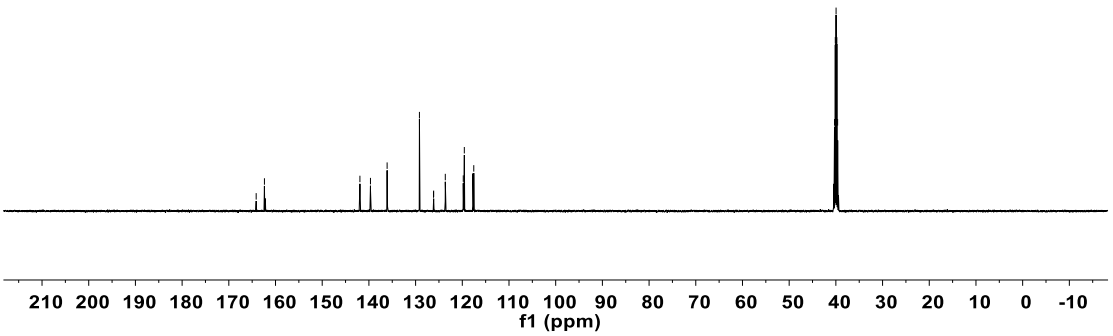


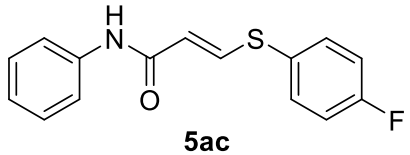


5ac

^{13}C NMR, 125MHz

DMSO-d_6

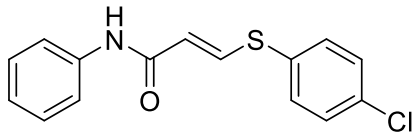




5ac

^{19}F NMR, 377MHz

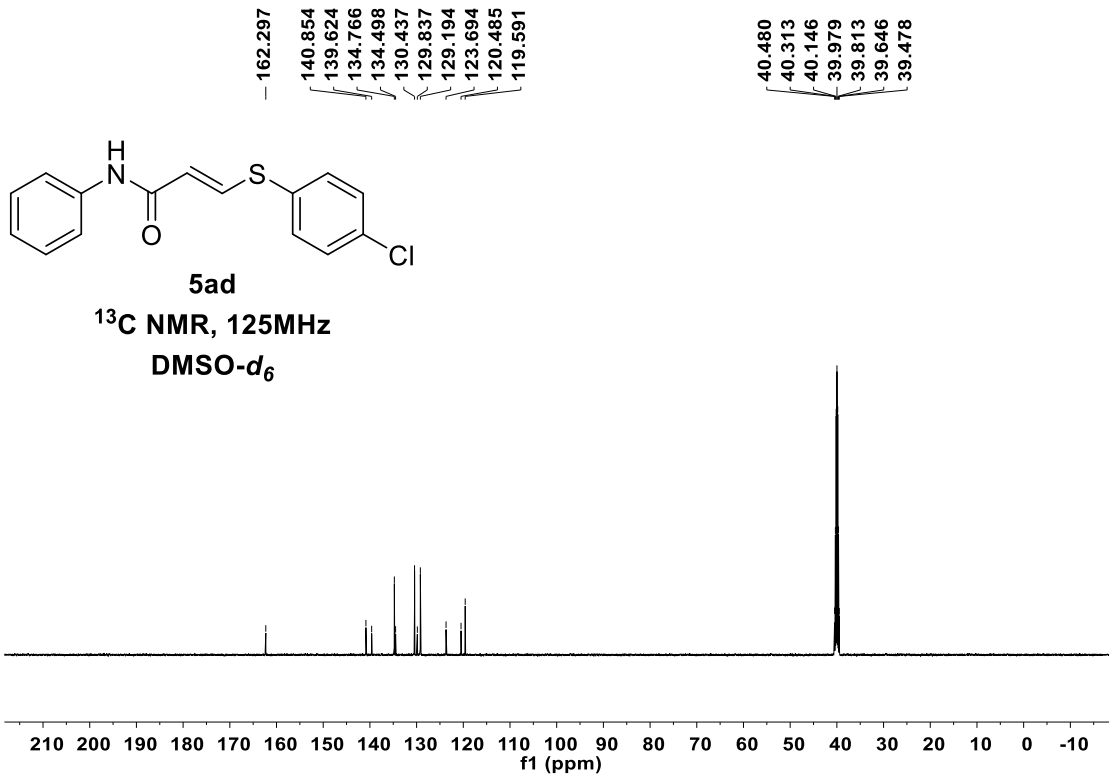
$CDCl_3$



5ad

^{1}H NMR, 500MHz

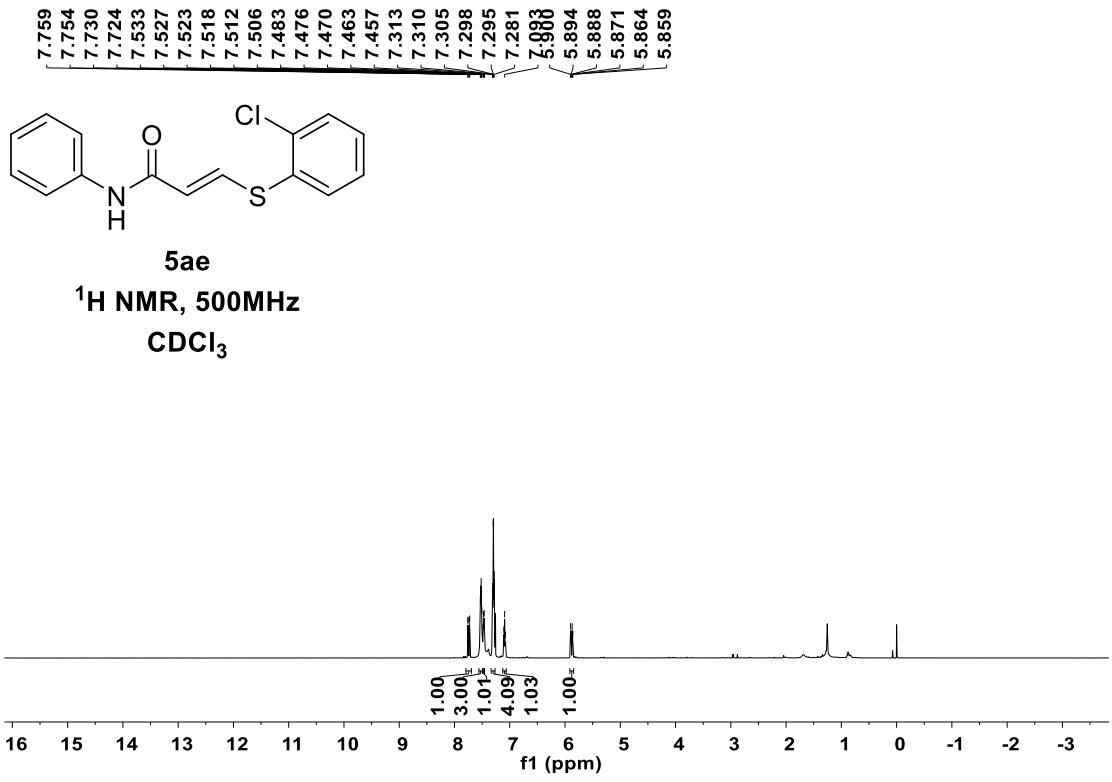
DMSO-d_6



5ad

^{13}C NMR, 125MHz

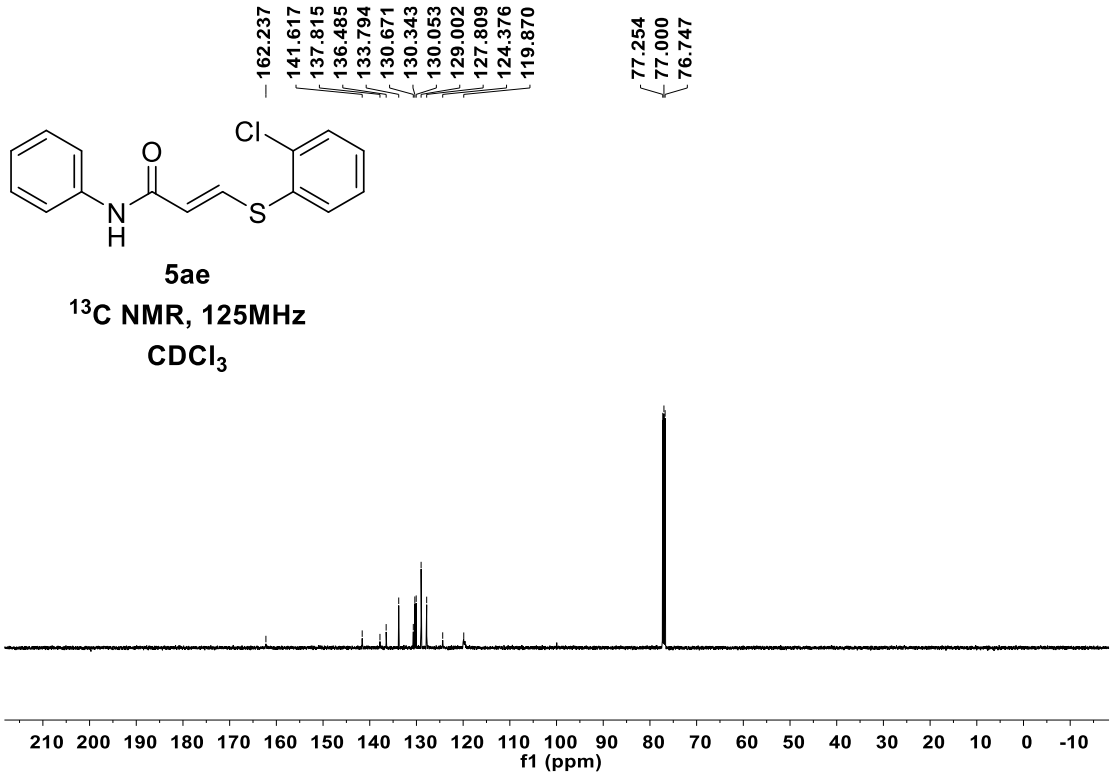
DMSO-d_6



5ae

^{1}H NMR, 500MHz

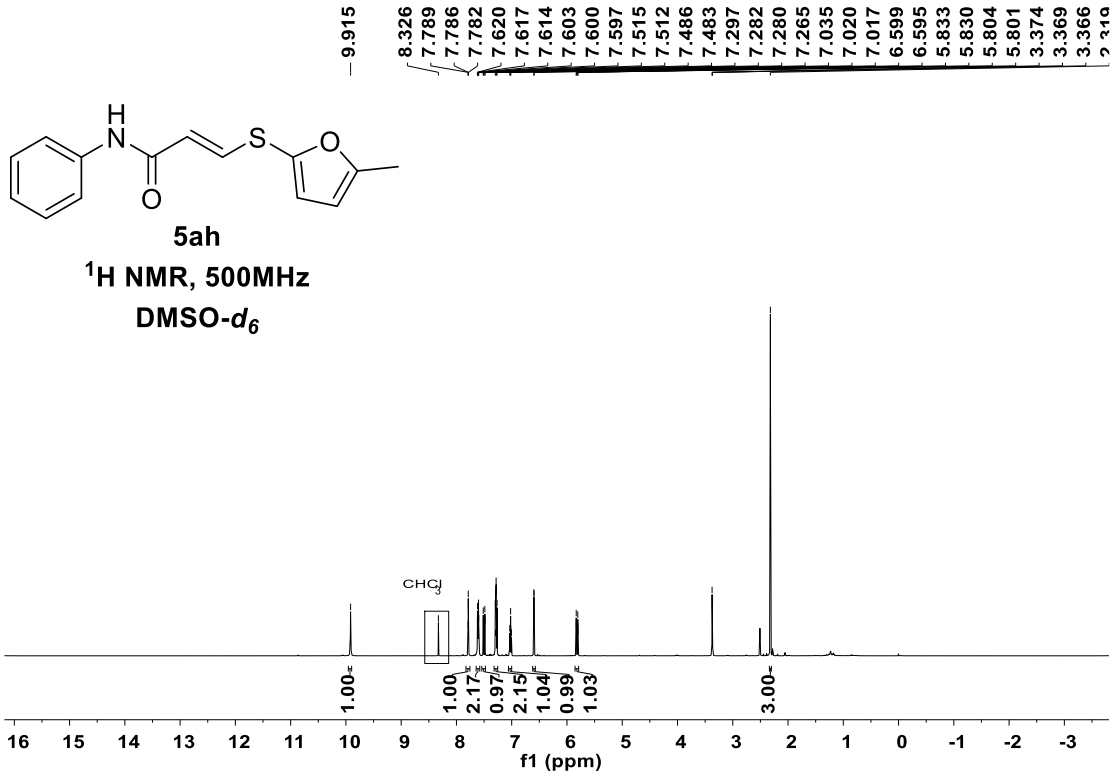
$CDCl_3$



5ae

^{13}C NMR, 125MHz

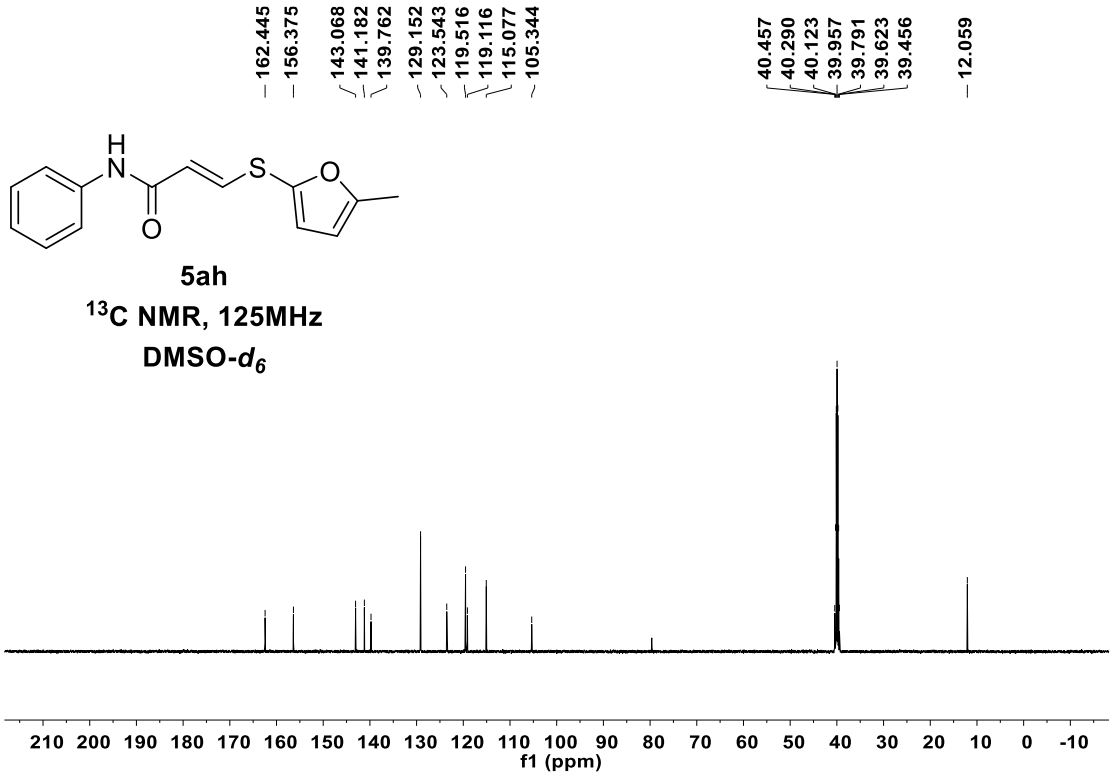
$CDCl_3$

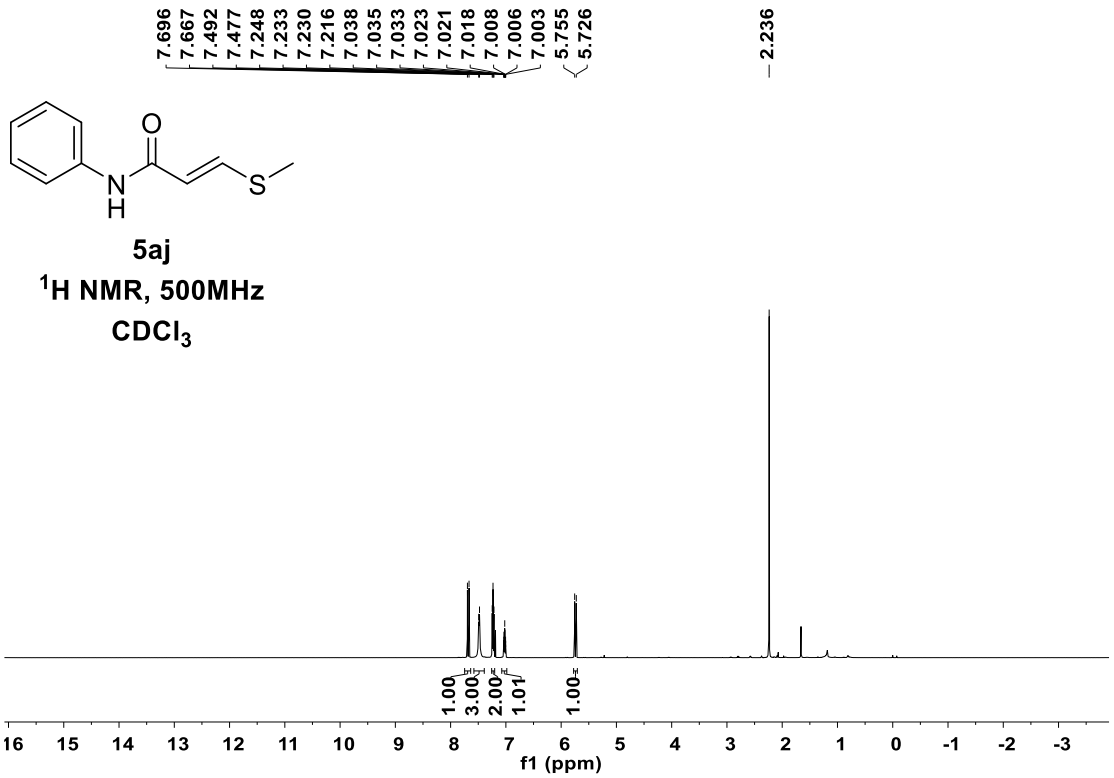


5ah

^{1}H NMR, 500MHz

DMSO-d_6


162.445
156.375
143.068
141.182
139.762
129.152
123.543
119.516
119.116
115.077
105.344
40.457
40.290
40.123
39.957
39.791
39.623
39.456
12.059
H
N
O
S
O
5ah
13C NMR, 125MHz
DMSO-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.696
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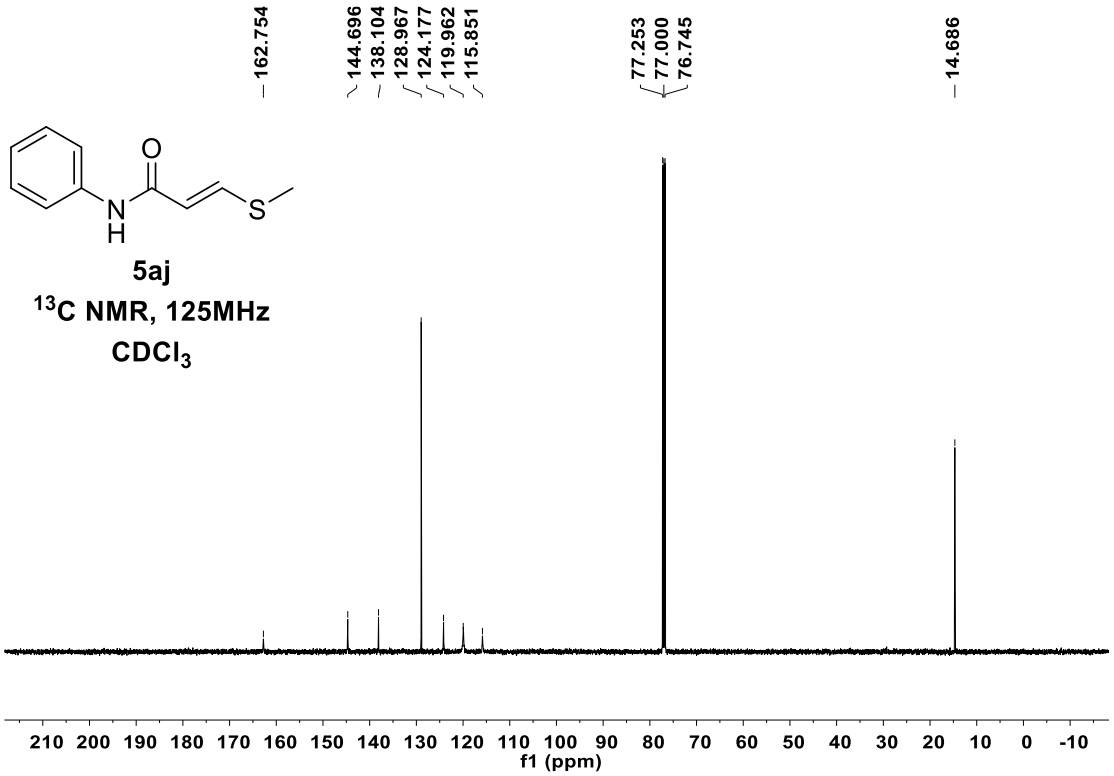
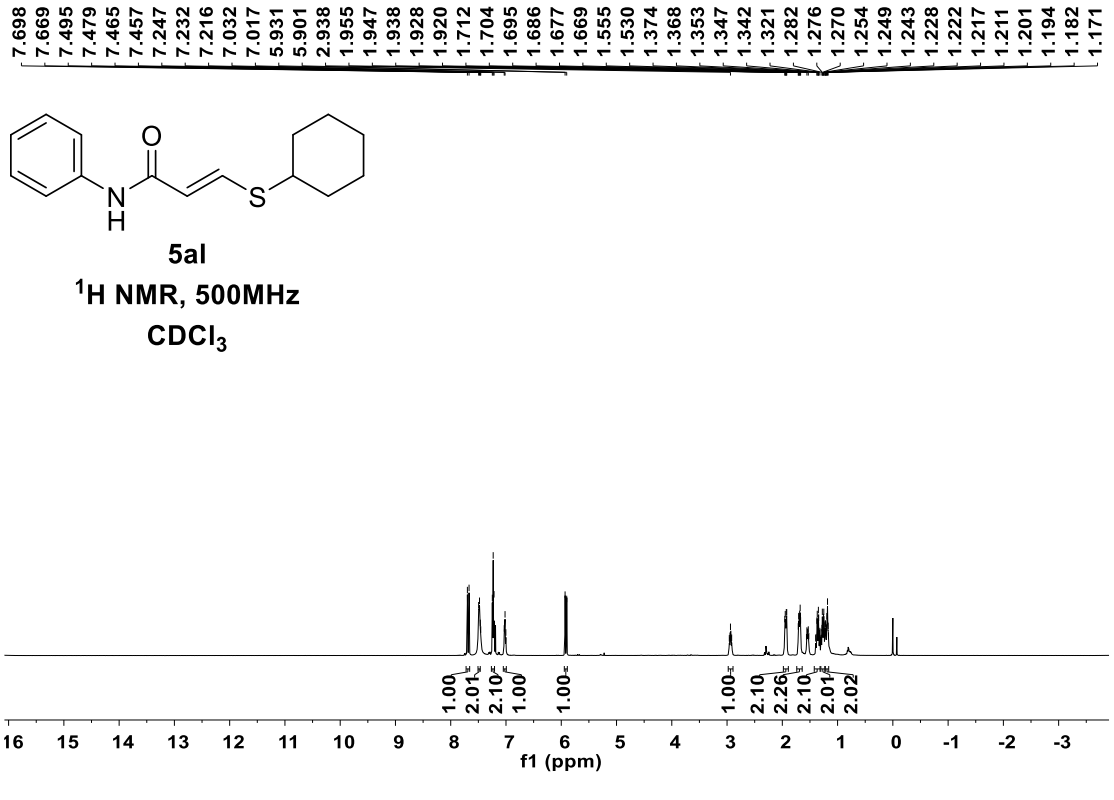
7.477
7.248
7.233
7.230
7.216
7.038
7.035
7.033
7.023
7.021
7.018
7.008
7.006
7.003
5.755
5.726
2.236
O
N
H
S
5aj
1H NMR, 500MHz
CDCl3
1.00
3.00
2.00
1.01
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)



5aj

^{13}C NMR, 125MHz

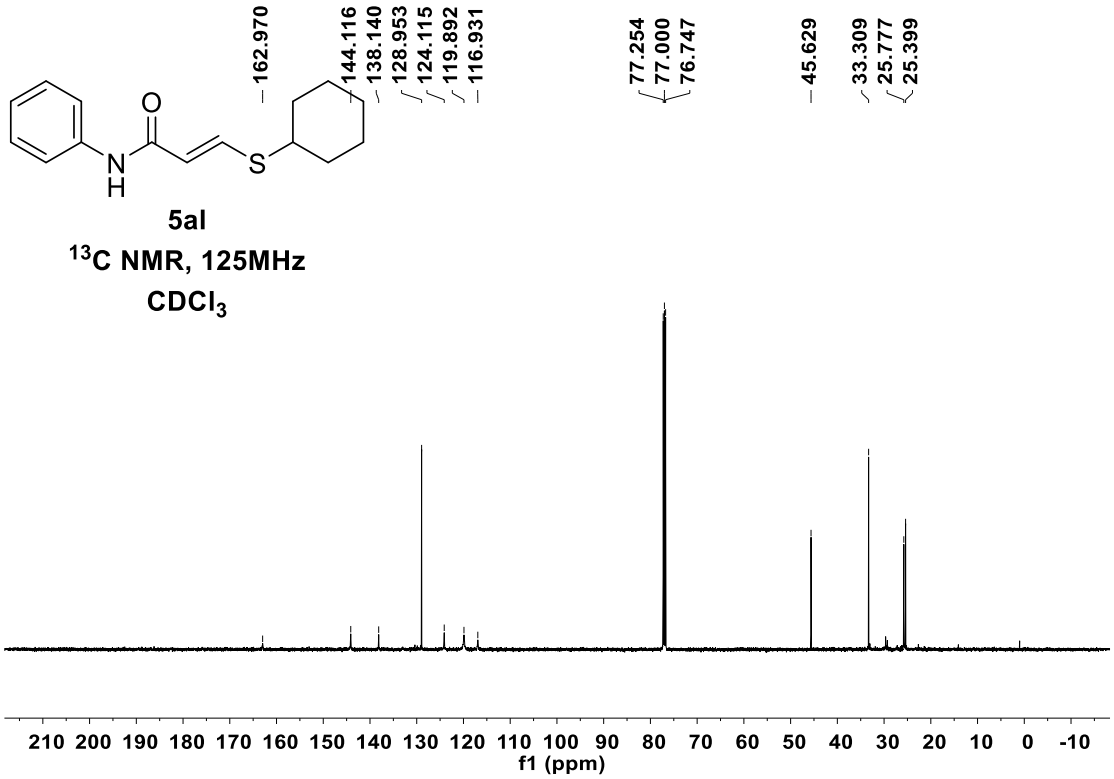
$CDCl_3$

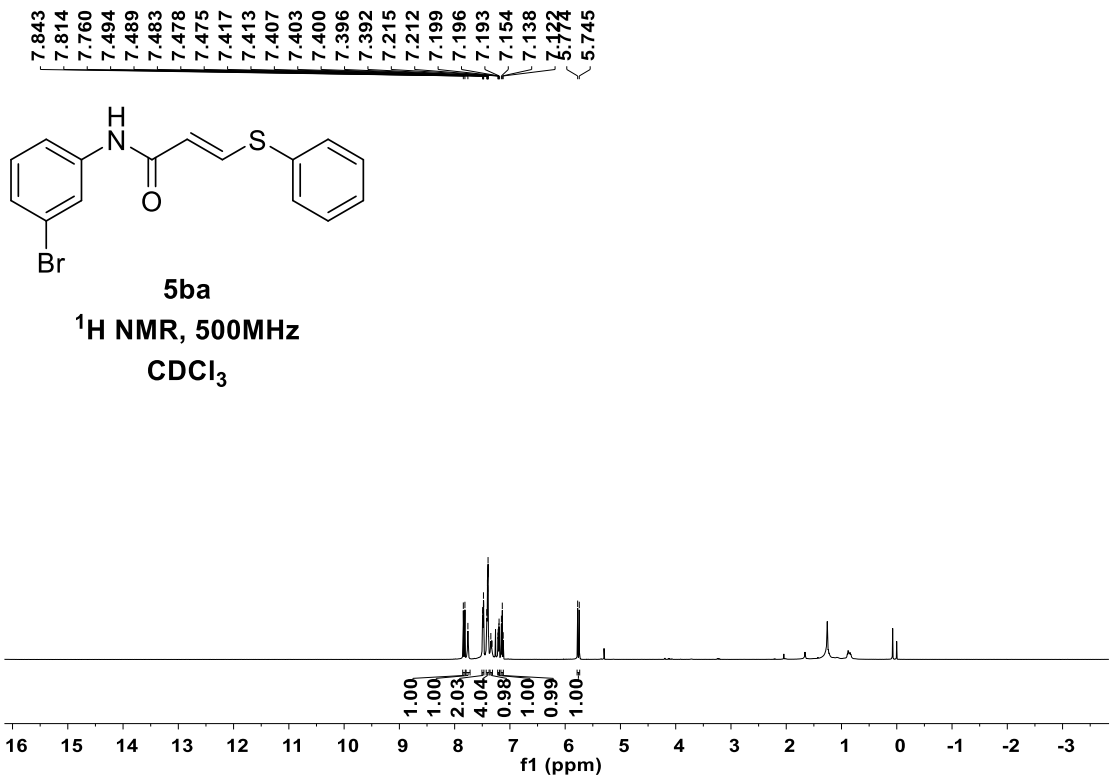


5al

^{1}H NMR, 500MHz

$CDCl_3$


162.970
144.116
138.140
128.953
124.115
119.892
116.931
77.254
77.000
76.747
45.629
33.309
25.777
25.399
O
N
H
S
5al
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.843
7.814
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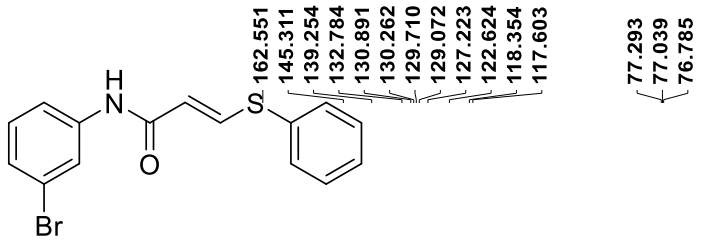
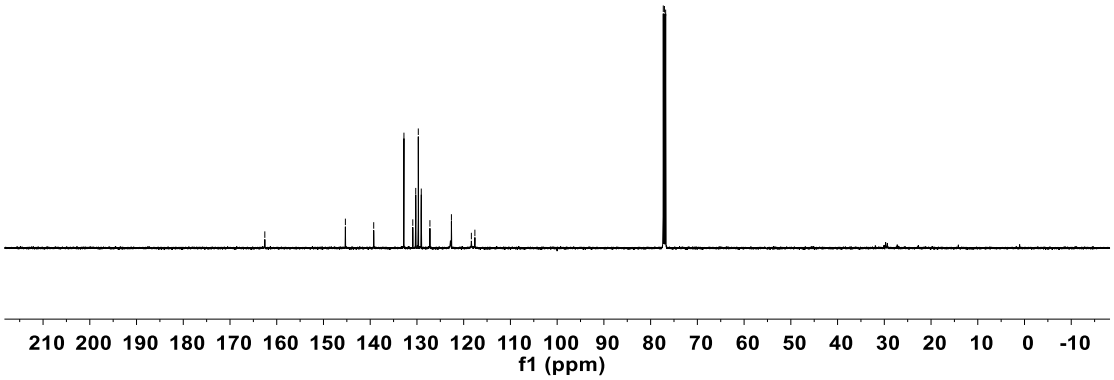
7.489
7.483
7.478
7.475
7.417
7.413
7.407
7.403
7.400
7.396
7.392
7.215
7.212
7.199
7.196
7.193
7.154
7.138
5.774
5.745
H
N
O
S
Br
5ba
1H NMR, 500MHz
CDCl3
1.00
1.00
2.03
4.04
0.98
1.00
0.99
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

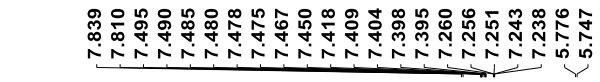


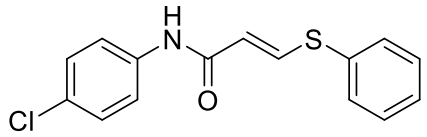
5ba

^{13}C NMR, 125MHz

$CDCl_3$



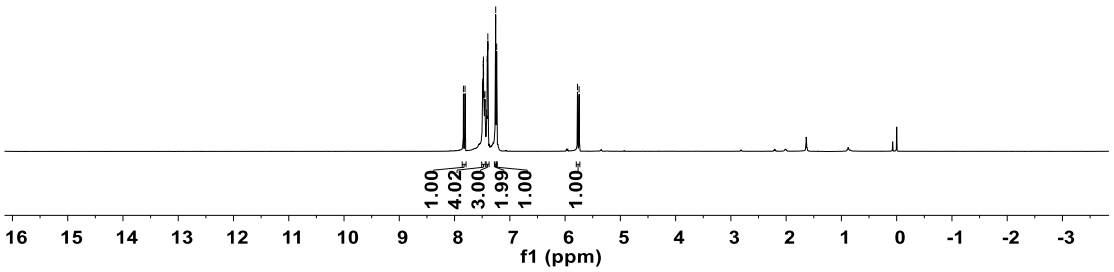


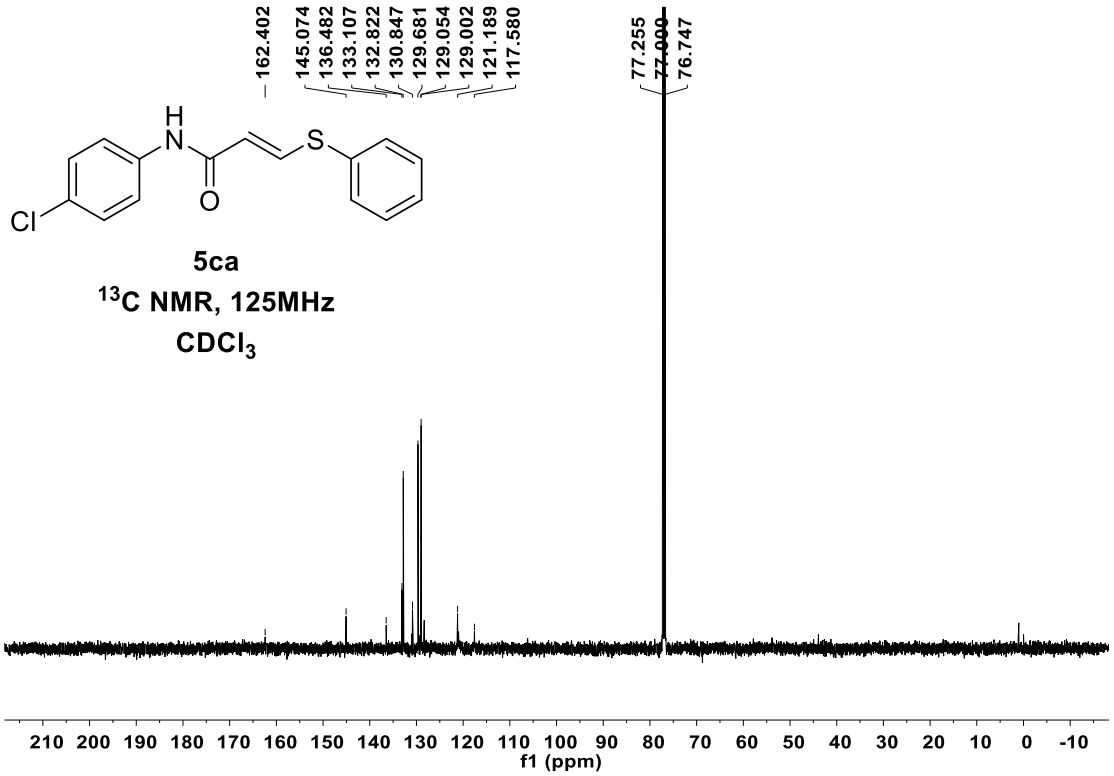


5ca

^{1}H NMR, 500MHz

$CDCl_3$

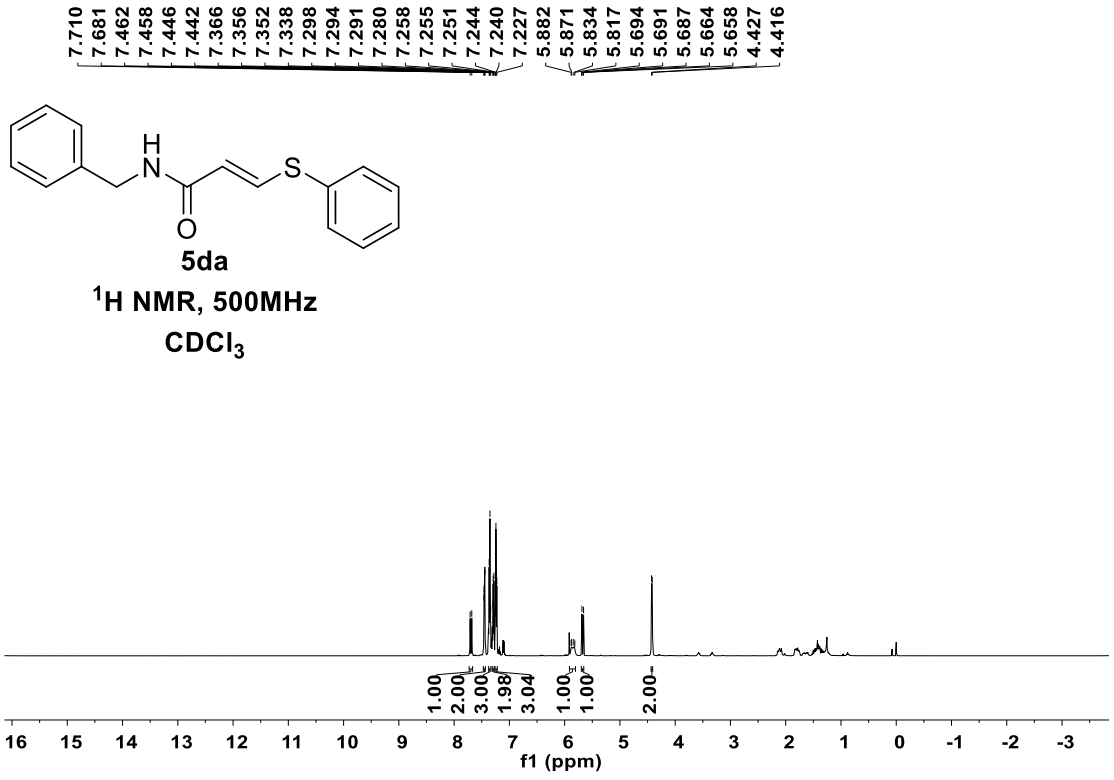




5ca

^{13}C NMR, 125MHz

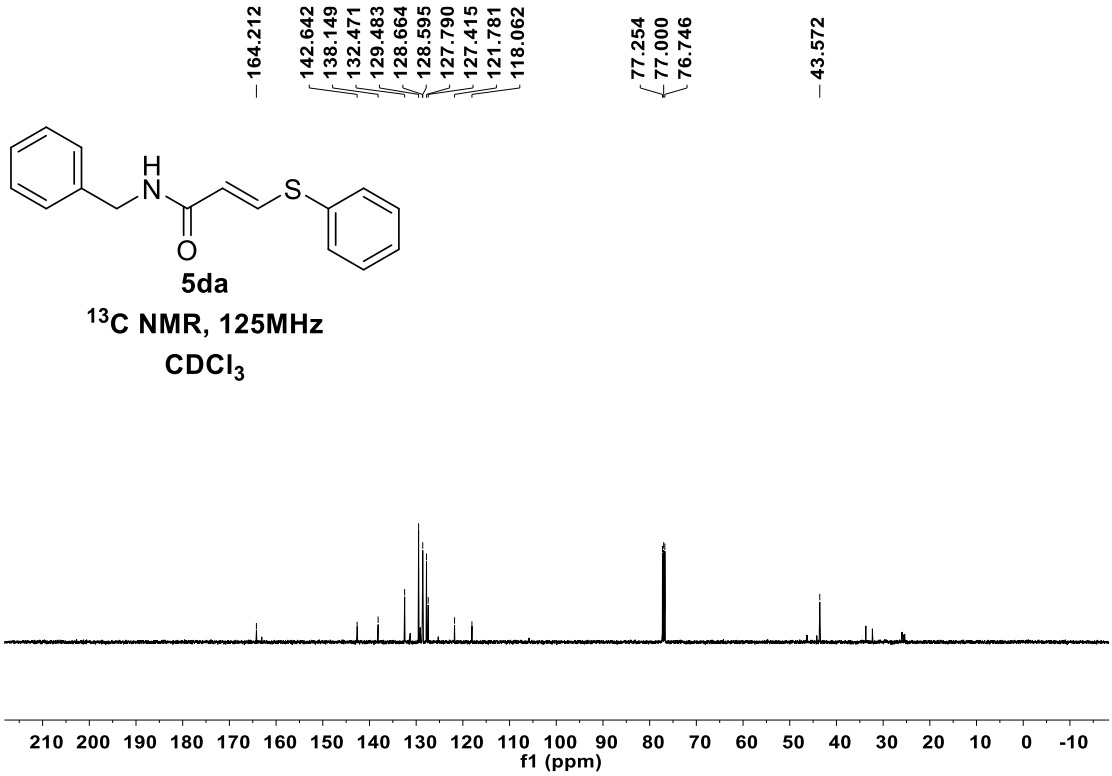
$CDCl_3$

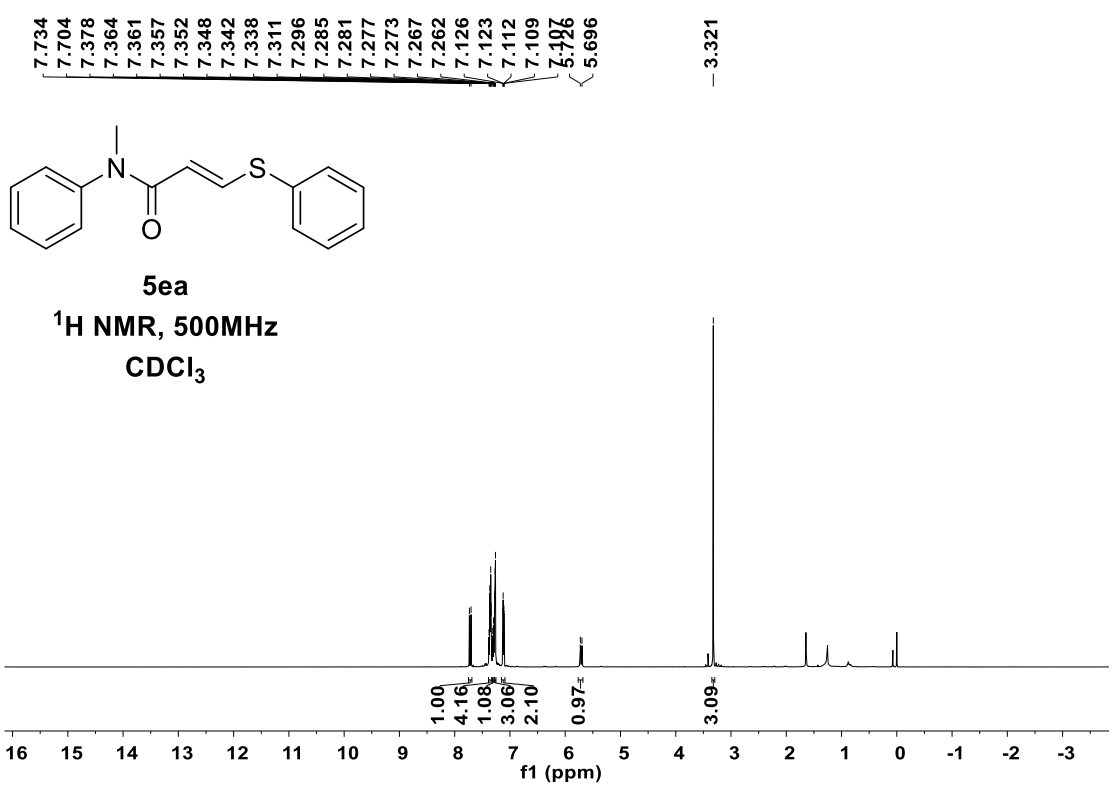


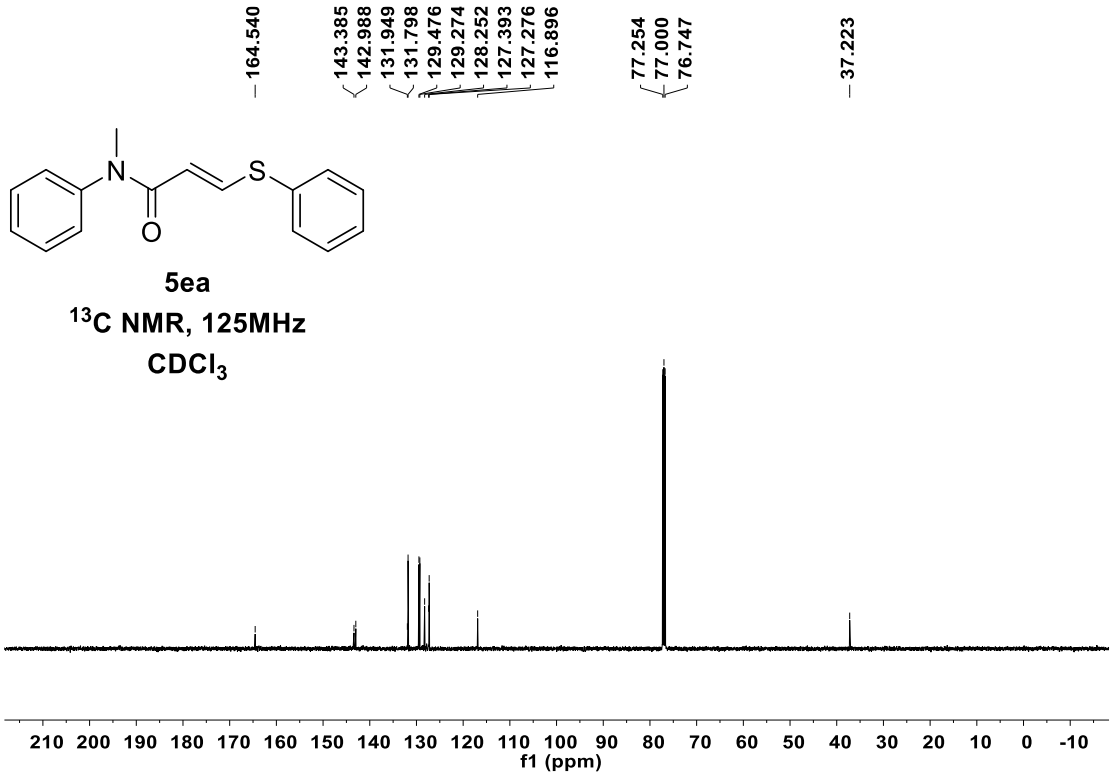
5da

^{1}H NMR, 500MHz

$CDCl_3$


164.212
142.642
138.149
132.471
129.483
128.664
128.595
127.790
127.415
121.781
118.062
77.254
77.000
76.746
43.572
H
N
S
O
5da
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.734
7.704
7.378
7.364
7.361
7.357
7.352
7.348
7.342
7.338
7.311
7.296
7.285
7.281
7.277
7.273
7.267
7.262
7.126
7.123
7.112
7.109
5.726
5.696
3.321
N
S
O
5ea
1H NMR, 500MHz
CDCl3
1.00
4.16
1.08
3.06
2.10
0.97
3.09
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


164.540
143.385
142.988
131.949
131.798
129.476
129.274
128.252
127.393
127.276
116.896
77.254
77.000
76.747
37.223
N
S
O
5ea
13C NMR, 125MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)