Supporting Information

Copper-Assisted Oxidative Trifluoromethylthiolation of 2,3-Allenoic Acids with $AgSCF_3$

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Contents

1. General Remarks

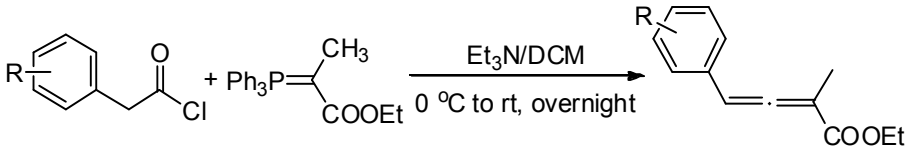
^{1}H and ^{19}F NMR ($CFCl_3$ as external standard and low field is positive) spectra were recorded on a Bruker AM 400 spectrometer or 600 spectrometer. ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer or Bruker AM 600 spectrometer. Chemical shifts (δ) were reported in ppm, and coupling constants (*J*) were in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The NMR yield was determined by ^{19}F NMR using (trifluoromethyl)benzene as an internal standard before working up the reaction. High resolution mass spectra (HRMS) were performed using a GC/MS TOF high-resolution mass spectrometer equipped with a liquid chromatography system or as electron spray ionization using a Thermo Fischer Scientific LTQ FT Ultra instrument in DART-positive mode.

Materials: Unless otherwise noted, all reagents were obtained commercially and used without further purification. CH_3CN was distilled from CaH_2 and stored with 4 Å molecular sieves. Reactions were performed under an atmosphere of N_2 using glassware that was flame-dried under vacuum. $AgSCF_3$ was prepared following the literature[1].

2. Preparation of 2,3-Allenoic Acids

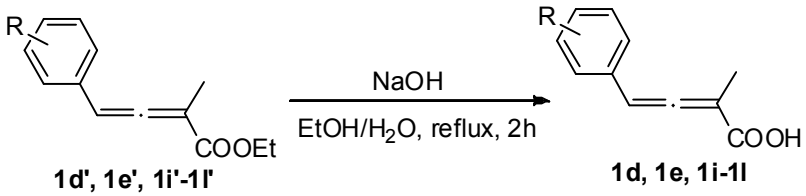
The 2,3-allenoic acids **1a-1c**,[2] **1f-1h**,[2] **1m**,[2] **1n-1q**,[3] **1r-1t**,[4] **1v**,[5] and **1w**[6] were prepared in accordance with methods described in the references.

General methods for preparation of 2,3-allenoic acids (1d, 1e, 1i-1l)[2]



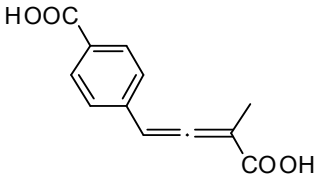
1d'', 1e'', 1i''-1l'' **1d', 1e', 1i'-1l'**

Typical Procedure. The mixture of ethyl 2-(triphenylphosphoranylidene) propanoate (2.90 g, 8 mmol, 1.0 equiv) and Et_3N (0.81 g, 8 mmol, 1.0 equiv) in DCM (80 mL) was stirred at 0 °C for 20 minutes. Then, a solution of **1d'', 1e'', 1i''-1l''** (10 mmol, 1.25 equiv) in DCM (15 mL) was added dropwise and the reaction mixture was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc, and extracted with saturated aqueous NaCl solution, and extracted with EtOAc. The combined organic layers were dried with Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel (PE/EA = 20:1) to give **1d', 1e', 1i'-1l'**.



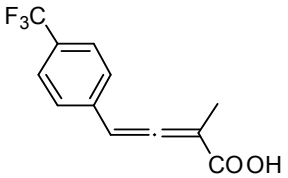
1d', 1e', 1i'-1l' **1d, 1e, 1i-1l**

Typical Procedure. To a round-bottom flask, **1d', 1e', 1i'-1l'** (5 mmol, 1.0 equiv), EtOH (15 mL), H_2O (15 mL), and NaOH (0.3 g, 7.5 mmol, 1.5 equiv) were added sequentially and the resulting solution was heated to reflux. After 2 h, the reaction was completed as monitored by TLC. The reaction mixture was diluted with EtOAc, and extracted with saturated aqueous $NaHCO_3$ solution. The aqueous layer was separated, acidified to pH 2.0 by addition of HCl (1 N), and extracted with DCM. The combined organic layers were dried with Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel (PE/EA = 5:1 with HOAc (1 %, v/v)) to give **1d, 1e, 1i-1l**.



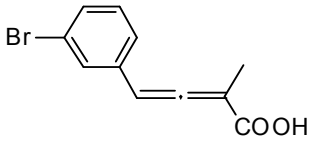
4-(3-Carboxybuta-1,2-dien-1-yl)benzoic acid (1d)

Compound **1d** was obtained as a white solid (228.2 mg, 21%), PE/EA = 5:1 with HOAc (1 %, v/v) as eluent for the column chromatography. Mp 188-190 ^{o}C. ^{1}H NMR (600 MHz, DMSO) δ 12.83 (s, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.82 (q, *J* = 2.9 Hz, 1H), 1.91 (d, *J* = 3.0 Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ 212.9, 167.9, 167.5, 137.7, 130.4, 130.1, 127.6, 99.7, 96.4, 15.2. MS (ESI) m/z: 219 $[M+H]^+$. HRMS (ESI) m/z: Calcd for $C_{12}H_{11}O_4$ 219.0652; found $[M+H]^+$: 219.0651.



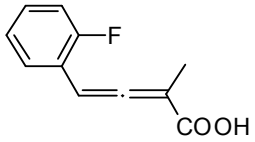
2-Methyl-4-(4-(trifluoromethyl)phenyl)buta-2,3-dienoic acid (1e)

Compound **1e** was obtained as a white solid (678.8 mg, 56%), PE/EA = 5:1 with HOAc (1 %, v/v) as eluent for the column chromatography. Mp 123-125 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.24 (s, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.49 (q, *J* = 2.7 Hz, 1H), 1.93 (d, *J* = 2.9 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.1, 172.2, 135.8, 129.9 (q, *J* = 32.5 Hz), 127.6, 125.8 (q, *J* = 7.6 Hz), 124.0 (q, *J* = 273.8 Hz), 99.6, 96.9, 14.5. MS (ESI) m/z: 243 $[M+H]^+$. HRMS (ESI) m/z: Calcd for $C_{12}H_{10}F_3O_2$ 243.0627; found $[M+H]^+$: 243.0626.



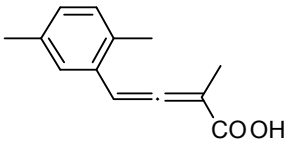
4-(3-Bromophenyl)-2-methylbuta-2,3-dienoic acid (1i)

Compound **1i** was obtained as a white solid (810.1 mg, 64%), PE/EA = 5:1 with HOAc (1 %, v/v) as eluent for the column chromatography. Mp 103-105 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.56 (s, 1H), 7.45 (d, *J* = 1.4 Hz, 1H), 7.42-7.39 (m, 1H), 7.25-7.21 (m, 2H), 6.51 (q, *J* = 2.9 Hz, 1H), 2.03 (d, *J* = 3.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 213.7, 172.4, 134.1, 130.9, 130.3, 130.2, 126.1, 123.0, 99.6, 96.7, 14.7. MS (ESI) m/z: 253 $[M+H]^+$. HRMS (ESI) m/z: Calcd for $C_{11}H_{10}BrO_2$ 252.9859, found $[M+H]^+$: 252.9856.



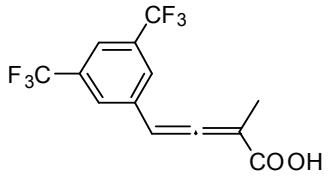
4-(2-Fluorophenyl)-2-methylbuta-2,3-dienoic acid (1j)

Compound **1j** was obtained as a white solid (729.3 mg, 76%), PE/EA = 5:1 with HOAc (1 %, v/v) as eluent for the column chromatography. Mp 107-109 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.61 (s, 1H), 7.25-7.21 (m, 1H), 7.19-7.10 (m, 1H), 7.03-6.94 (m, 2H), 6.65 (q, *J* = 2.8 Hz, 1H), 1.91 (d, *J* = 3.0 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -117.2--117.4 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.2, 171.6, 158.8 (d, *J* = 251.5 Hz), 128.4 (d, *J* = 8.1 Hz), 128.0 (d, *J* = 3.0 Hz), 123.3 (d, *J* = 3.0 Hz), 118.5, 114.8 (d, *J* = 21.2 Hz), 97.9, 89.5 (d, *J* = 6.1 Hz), 13.6. MS (ESI) m/z: 193 $[M+H]^+$. HRMS (ESI) m/z: Calcd for $C_{11}H_{10}FO_2$ 193.0659; found $[M+H]^+$: 193.0659.



4-(2,5-Dimethylphenyl)-2-methylbuta-2,3-dienoic acid (1k)

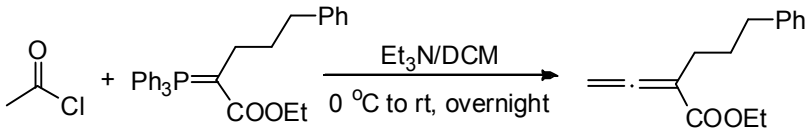
Compound **1k** was obtained as a white solid (858.7 mg, 85%), PE/EA = 5:1 with HOAc (1 %, v/v) as eluent for the column chromatography. Mp 126-128 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.17 (s, 1H), 7.13 (s, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.73 (q, *J* = 3.0 Hz, 1H), 2.37 (s, 3H), 2.34 (s, 3H), 2.03 (d, *J* = 3.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 214.2, 173.0, 135.8, 132.8, 130.7, 130.0, 128.8, 97.9, 95.4, 20.9, 19.6, 15.0. MS (ESI) m/z: 203 $[M+H]^+$. HRMS (ESI) m/z: Calcd for $C_{13}H_{15}O_2$ 203.1067; found $[M+H]^+$: 203.1066.



4-(3,5-Bis(trifluoromethyl)phenyl)-2-methylbuta-2,3-dienoic acid (1l)

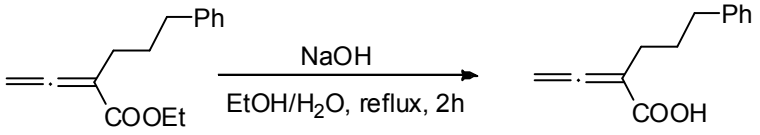
Compound **1l** was obtained as a white solid (434.1 mg, 28%), PE/EA = 5:1 with HOAc (1 %, v/v) as eluent for the column chromatography. Mp 147-149 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.89 (s, 1H), 7.68 (s, 1H), 7.61 (s, 2H), 6.55 (q, J = 2.8 Hz, 1H), 1.97 (d, J = 3.0 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.0 (s, 6F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.7, 170.6, 133.6, 131.3 (q, J = 33.5 Hz), 126.1 (q, J = 3.7 Hz), 122.1 (q, J = 271.8 Hz), 120.5 (q, J = 3.8 Hz), 99.6, 95.1, 13.5. MS (ESI) m/z: 311 $[M+H]^+$. HRMS (ESI) m/z: Calcd for $C_{13}H_9F_6O_2$ 311.0501; found $[M+H]^+$: 311.0499.

Preparation of 5-phenyl-2-vinylidenepentanoic acid (1u)[4]



1u" **1u'**

The mixture of **1u''** (3.73 g, 8 mmol, 1.0 equiv) and Et_3N (0.81 g, 8 mmol, 1.0 equiv) in DCM (80 mL) was stirred 0 ^{o}C 20 minutes. Then, a solution of acetyl chloride (0.79 g, 10 mmol, 1.25 equiv) in DCM (15 mL) was added dropwise and the reaction mixture was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc, and extracted with saturated aqueous NaCl solution, and extracted with EtOAc. The combined organic layers were dried with Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel (PE/EA = 20:1) to give **1u'** (1.58 g, 86% yield).



1u' **1u**

To a round-bottom flask, **1u'** (1.15 g, 5 mmol, 1.0 equiv), EtOH (15 mL), H_2O (15 mL), and NaOH (0.3 g, 7.5 mmol, 1.5 equiv) were added sequentially and the resulting solution was heated to reflux. After 2 h, the reaction was completed as monitored by TLC. The reaction mixture was diluted with EtOAc, and extracted with saturated aqueous $NaHCO_3$ solution. The aqueous layer was separated, acidified to pH 2.0 by addition of HCl (1 N), and extracted with DCM. The combined organic layers were dried with Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel (PE/EA = 5:1 with HOAc (1 %, v/v)) to give **1u** as a white solid (678.8 mg, 67% yield). Mp 67-69 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.36 (s, 1H), 7.18-7.23 (m, 2H),

7.10-7.13 (m, 3H), 5.14 (t, J = 3.0 Hz, 2H), 2.62-2.55 (m, 2H), 2.30-2.09 (m, 2H), 1.82-1.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.8, 172.8, 142.0, 128.5, 128.4, 125.8, 99.8, 79.6, 35.3, 29.6, 27.3. MS (ESI) m/z: 203 $[M+H]^+$. HRMS (ESI) m/z: Calcd for $C_{13}H_{15}O_2$ 203.1067; found $[M+H]^+$: 203.1066.

References:

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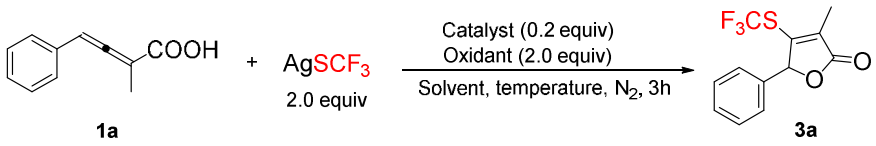
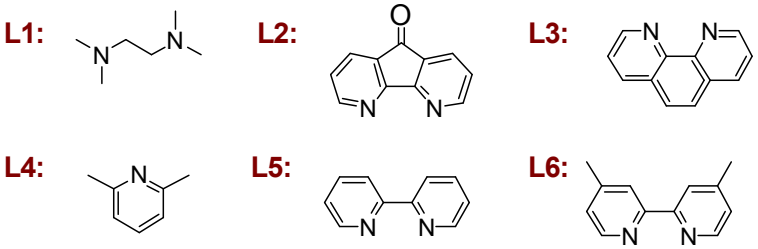
3. Optimization of Reaction Conditions

Optimization of reaction conditions for cyclic oxytrifluoromethylthiolation [a]



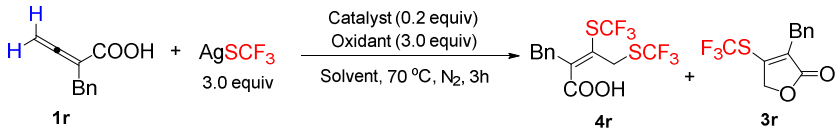


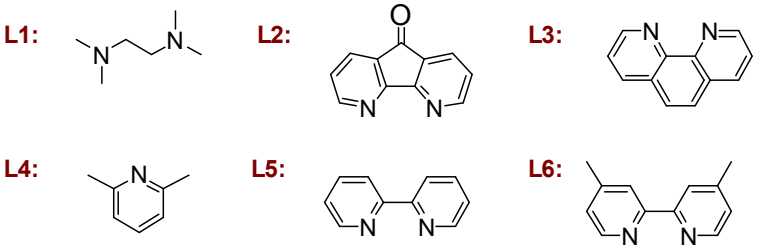
Entry	Catalyst	Oxidant	Solvent (x:y)	Tem (^{o}C)	Yield (%)[b]
1	---	$(NH_4)_2S_2O_8$	CH_3CN	70	22
2	---	$(NH_4)_2S_2O_8$	DMF	70	Trace
3	---	$(NH_4)_2S_2O_8$	THF	70	NR
4	---	$(NH_4)_2S_2O_8$	CH_3CN/H_2O (1:1)	70	7
5	---	$(NH_4)_2S_2O_8$	CH_3CN/TFA (1:1)	70	NR
6	---	$(NH_4)_2S_2O_8$	CH_3CN/TfOH (1:1)	70	NR
7	---	$(NH_4)_2S_2O_8$	CH_3CN/ HCOOH (1:1)	70	15
8	---	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (1:1)	70	38
9	---	$(NH_4)_2S_2O_8$	CH_3CN/ HOAc (2:1)	70	60
10	---	$(NH_4)_2S_2O_8$	CH_3CN/HOAc (1:2)	70	6
11	---	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	65
12	---	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (8:1)	70	58

13	---	$(NH_4)_2S_2O_8$	THF / HOAc (4:1)	70	NR
14	---	$(NH_4)_2S_2O_8$	DCE / HOAc (4:1)	70	NR
15	---	$(NH_4)_2S_2O_8$	toluene / HOAc (4:1)	70	NR
16	$CuSO_4$	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	68
17	CuTC	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	76
18	$Cu(OAc)_2$	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	77
19	$Cu(OTf)_2$	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	71
20	CuI	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	67
21	Cu	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	70
22	**CuCN**	**$(NH_4)_2S_2O_8$**	**CH_3CN /HOAc (4:1)**	**70**	**85**
23	CuCN	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	50	36
24	CuCN	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	90	75
25	CuCN	$K_2S_2O_8$	CH_3CN /HOAc (4:1)	70	48
26	CuCN	$Na_2S_2O_8$	CH_3CN /HOAc (4:1)	70	39
27	CuCN	PIDA	CH_3CN /HOAc (4:1)	70	NR
28	CuCN	TBHP	CH_3CN /HOAc (4:1)	70	Trace
29[c]	CuCN	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	61
30[d]	CuCN	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	85
31	CuCN + L1	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	70
32	CuCN + L2	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	74
33	CuCN + L3	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	68
34	CuCN + L4	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	59
35	CuCN + L5	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	83
36	CuCN + L6	$(NH_4)_2S_2O_8$	CH_3CN /HOAc (4:1)	70	40

[a]Reaction conditions: **1a** (0.1 mmol), $AgSCF_3$ (0.2 mmol), catalyst (0.02 mmol), oxidant (0.2 mmol), solvent (2.0 mL), under N_2, 70 °C, 3 h. [b]Yields determined by ^{19}F NMR spectroscopy using trifluoromethylbenzene as an internal standard. [c]$AgSCF_3$ (1.5 mmol). [d]$AgSCF_3$ (3.0 mmol).

Optimization of reaction conditions for bis-trifluoromethylthiolation[a]



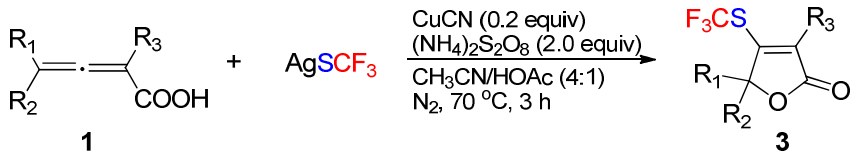


Entry	Catalyst	Oxidant	Solvent (x:y)	**4r**/**3r** Yield (%)[b]
1	CuCN	$(NH_4)_2S_2O_8$	CH_3CN/HOAc (4:1)	16/trace
2	$Cu(OAc)_2$	$(NH_4)_2S_2O_8$	CH_3CN/HOAc (4:1)	24/trace
3	$CuCl_2$	$(NH_4)_2S_2O_8$	CH_3CN/HOAc (4:1)	19/trace

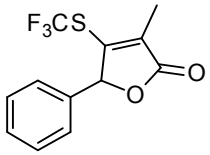
4	CuI	$(NH_4)_2S_2O_8$	CH_3CN/HOAc (4:1)	12/trace
5	$Cu(OAc)_2$	$(NH_4)_2S_2O_8$	CH_3CN/HCOOH (4:1)	28 trace
6	$Cu(OAc)_2$	$(NH_4)_2S_2O_8$	CH_3CN/HCOOH (9:1)	23/trace
7	$Cu(OAc)_2$	$(NH_4)_2S_2O_8$	CH_3CN/HCOOH (2:1)	21/trace
8	$Cu(OAc)_2$	$(NH_4)_2S_2O_8$	CH_3CN/HCOOH (1:1)	17/trace
9	$Cu(OAc)_2$	$(NH_4)_2S_2O_8$	CH_3CN/H_2O/HCOOH (4 :0.5: 1)	35/2
10	$Cu(OAc)_2$	$(NH_4)_2S_2O_8$	CH_3CN/H_2O/HCOOH (4 :1.0: 1)	38/2
11	$Cu(OAc)_2$	$(NH_4)_2S_2O_8$	CH_3CN/H_2O/HCOOH (4 :1.5: 1)	45/3
12	**$Cu(OAc)_2$**	**$(NH_4)_2S_2O_8$**	**CH_3CN/H_2O/HCOOH (4 :2.0: 1)**	**51/5**
13	$Cu(OAc)_2$	$(NH_4)_2S_2O_8$	CH_3CN/H_2O/HCOOH (4 :3.0: 1)	45/5
14	---	$(NH_4)_2S_2O_8$	CH_3CN/H_2O/HCOOH (4 :2.0: 1)	NR
15	$Cu(OAc)_2$	$K_2S_2O_8$	CH_3CN/H_2O/HCOOH (4 :2.0: 1)	45/4
16	$Cu(OAc)_2$	$Na_2S_2O_8$	CH_3CN/H_2O/HCOOH (4 :2.0: 1)	41/4
17	$Cu(OAc)_2$	PIDA	CH_3CN/H_2O/HCOOH (4 :2.0: 1)	NR
18	$Cu(OAc)_2$	TBHP	CH_3CN/H_2O/HCOOH (4 :2.0: 1)	trace
19	$Cu(OAc)_2$ + L1	$(NH_4)_2S_2O_8$	CH_3CN/H_2O/HCOOH (4 :2.0: 1)	35/5
20	$Cu(OAc)_2$ + L2	$(NH_4)_2S_2O_8$	CH_3CN/H_2O/HCOOH (4 :2.0: 1)	45/6
21	$Cu(OAc)_2$ + L3	$(NH_4)_2S_2O_8$	CH_3CN/H_2O/HCOOH (4 :2.0: 1)	39/5
22	$Cu(OAc)_2$ + L4	$(NH_4)_2S_2O_8$	CH_3CN/H_2O/HCOOH (4 :2.0: 1)	38/6
23	$Cu(OAc)_2$ + L5	$(NH_4)_2S_2O_8$	CH_3CN/H_2O/HCOOH (4 :2.0: 1)	12/3
24	$Cu(OAc)_2$ + L6	$(NH_4)_2S_2O_8$	CH_3CN/H_2O/HCOOH (4 :2.0: 1)	14/3

[a]Reaction conditions: **1r** (0.1 mmol), $AgSCF_3$ (0.3 mmol), catalyst (0.02 mmol), oxidant (0.3 mmol), solvent (2.8 mL), under N_2, 70 °C, 3 h. [b]Yields determined by ^{19}F NMR spectroscopy using trifluoromethylbenzene as an internal standard.

4. Cyclic Oxytrifluoromethylthiolation of 2,3-Allenoic Aicds with $AgSCF_3$

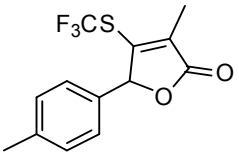


A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 2,3-allenoic acid (0.2 mmol, 1.0 equiv), CuCN (3.6 mg, 0.04 mmol, 0.2 equiv), $AgSCF_3$ (83.6 mg, 0.4 mmol, 2.0 equiv), and $(NH_4)_2S_2O_8$ (91.3 mg, 0.4 mmol, 2.0 equiv). The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Then CH_3CN (3.2 mL) and HOAc (0.8 mL) was added by a syringe. The mixture was stirred at 70 °C for 3 h. A saturated ammonium chloride aqueous solution (5 mL) was added. The resulting mixture was filtered by Celite, eluted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced vacuum. The residue was purified with silica gel column chromatography to provide the pure product.



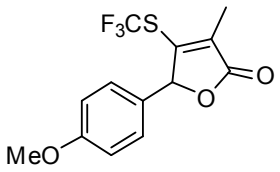
3-Methyl-5-phenyl-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3a)

Compound **3a** was obtained as a yellow oil (44.3 mg, 81%), with PE/EA = 30:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 3H), 7.15-7.12 (m, 2H), 5.81 (d, *J* = 1.8 Hz, 1H), 2.06 (d, *J* = 1.9 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 144.5, 137.5, 132.0, 128.9, 128.0, 127.1 (q, *J* = 311.2 Hz), 126.3, 84.2 (d, *J* = 0.7 Hz), 9.6. IR (KBr): ν 2960, 2923, 2858, 1767, 1507, 1448, 1301, 1139, 1098, 1045, 989, 757, 697, 516 cm^{-1}. MS (EI) m/z: 274 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{12}H_9F_3O_2S$ 274.0275; found: 274.0276.



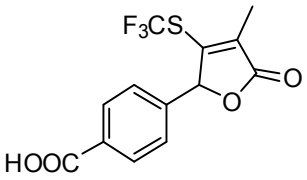
3-Methyl-5-(*p*-tolyl)-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3b)

Compound **3b** was obtained as a yellow oil (43.3 mg, 75%), with PE/EA = 30:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 5.77 (d, *J* = 1.6 Hz, 1H), 2.25 (s, 3H), 2.04 (d, *J* = 1.8 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.9 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 145.6 (d, *J* = 1.7 Hz), 140.0, 138.3, 130.0, 129.8, 128.2 (q, *J* = 311.1 Hz), 127.3, 85.2, 21.3, 10.6. IR (KBr): ν 2962, 2920, 2878, 1668, 1516, 1488, 1301, 1261, 1140, 1100, 987, 815, 745, 632, 517 cm^{-1}. MS (EI) m/z: 288 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{13}H_{11}F_3O_2S$ 288.0432; found: 288.0437.



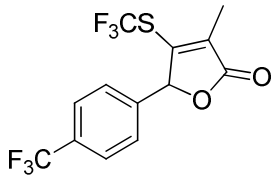
5-(4-Methoxyphenyl)-3-methyl-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3c)

Compound **3c** was obtained as a yellow oil (31.6 mg, 52%), with PE/EA = 30:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.79 (d, *J* = 1.7 Hz, 1H), 3.74 (s, 3H), 2.07 (d, *J* = 1.9 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.8 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.0, 159.8, 144.6 (d, *J* = 1.8 Hz), 137.2, 127.8, 127.1 (q, *J* = 311.1 Hz), 123.7, 113.5, 84.1, 54.3, 9.6. IR (KBr): ν 2960, 2925, 2872, 1767, 1624, 1515, 1306, 1250, 1140, 1100, 983, 830, 797, 613, 539 cm^{-1}. MS (EI) m/z: 304 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{13}H_{11}F_3O_3S$ 304.0381; found: 304.0383.



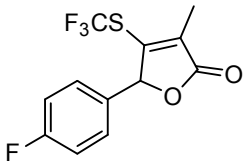
4-(4-Methyl-5-oxo-3-((trifluoromethyl)thio)-2,5-dihydrofuran-2-yl)benzoic acid (3d)

Compound **3d** was obtained as a white solid (25.7 mg, 40%), with PE/EA = 10:1 as eluent for the column chromatography. Mp 150-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 8.09 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 5.90 (d, *J* = 1.6 Hz, 1H), 2.10 (d, *J* = 1.8 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 170.7, 145.1 (d, *J* = 1.9 Hz), 139.2, 138.8, 130.9, 130.7, 128.0 (q, *J* = 311.2 Hz), 127.3, 84.3, 10.8. IR (KBr): ν 2958, 2920, 2873, 2567, 1772, 1695, 1425, 1286, 1143, 1101, 1047, 999, 860, 734, 704, 513 cm^{-1}. MS (ESI) m/z: 319 $[M+H]^+$. HRMS (ESI) m/z: Calcd for $C_{13}H_{10}F_3O_4S$ 319.0246; found $[M+H]^+$: 319.0245.



3-Methyl-5-(4-(trifluoromethyl)phenyl)-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3e)

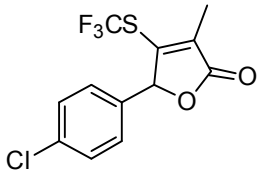
Compound **3e** was obtained as a yellow oil (36.2 mg, 53%), with PE/EA = 30:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.87 (d, *J* = 1.7 Hz, 1H), 2.09 (d, *J* = 1.9 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.8 (s, 3F), -62.9 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 144.0 (d, *J* = 1.6 Hz), 138.2, 136.1, 131.1 (q, *J* = 32.8 Hz), 127.0 (q, *J* = 311.4 Hz), 126.6, 125.1 (q, *J* = 3.8 Hz), 122.7 (q, *J* = 272.4 Hz), 83.1, 9.7. IR (KBr): ν 2961, 2924, 2865, 1773, 1634, 1422, 1325, 1101, 1065, 1003, 910, 830, 739, 636 cm^{-1}. MS (EI) m/z: 342 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{13}H_8F_6O_2S$ 342.0149; found: 342.0142.



5-(4-Fluorophenyl)-3-methyl-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3f)

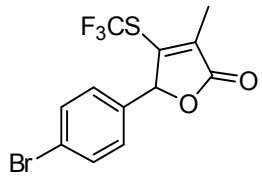
Compound **3f** was obtained as a white solid (40.3 mg, 69%), with PE/EA = 30:1 as eluent for the column chromatography. Mp 69-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.10 (m, 2H), 7.06-6.99 (m, 2H), 5.81 (d, *J* = 1.7 Hz, 1H), 2.07 (d, *J* = 1.9 Hz,

3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.8 (s, 3F), -110.7--110.8 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 163.5 (d, *J* = 249.2 Hz), 145.4 (d, *J* = 1.4 Hz), 138.6, 129.3, 129.2, 128.8 (d, *J* = 4.5 Hz), 128.1 (q, *J* = 311.3 Hz), 116.3, 116.1, 84.4, 10.7. IR (KBr): ν 2960, 2921, 2852, 1770, 1616, 1512, 1301, 1234, 1141, 1099, 997, 834, 796, 524 cm^{-1}. MS (EI) m/z: 292 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{12}H_8F_4O_2S$ 292.0181; found: 292.0175.



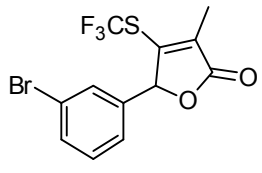
5-(4-Chlorophenyl)-3-methyl-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3g)

Compound **3g** was obtained as a yellow oil (44.4 mg, 72%), with PE/EA = 30:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 5.78 (d, *J* = 1.6 Hz, 1H), 2.05 (d, *J* = 1.9 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.8 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 145.2 (d, *J* = 1.7 Hz), 138.8, 135.9, 131.6, 129.3, 128.6, 128.1 (q, *J* = 311.3 Hz), 84.3, 10.7. IR (KBr): ν 2979, 2925, 2852, 1769, 1613, 1493, 1347, 1169, 1100, 1082, 992, 821, 733, 647, 513 cm^{-1}. MS (EI) m/z: 308 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{12}H_8ClF_3O_2S$ 307.9886; found: 307.9889.



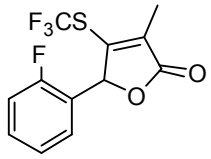
5-(4-Bromophenyl)-3-methyl-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3h)

Compound **3h** was obtained as a white solid (52.0 mg, 74%), with PE/EA = 30:1 as eluent for the column chromatography. Mp 40-42 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 5.78 (d, *J* = 1.7 Hz, 1H), 2.07 (d, *J* = 1.9 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.7 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 145.2 (d, *J* = 1.7 Hz), 138.8, 132.3, 132.1, 128.8, 128.1 (q, *J* = 311.4 Hz), 124.2, 84.4, 10.7. IR (KBr): ν 2980, 2963, 2858, 1770, 1667, 1535, 1490, 1301, 1260, 1140, 1100, 1068, 1004, 780, 747, 624, 505 cm^{-1}. MS (EI) m/z: 352 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{12}H_8BrF_3O_2S$ 351.9380; found: 351.9366.



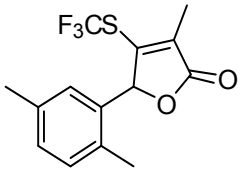
5-(3-Bromophenyl)-3-methyl-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3i)

Compound **3i** was obtained as a yellow oil (42.8 mg, 61%), with PE/EA = 30:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (ddd, *J* = 8.0, 1.7, 1.0 Hz, 1H), 7.27 (t, *J* = 1.7 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 5.76 (d, *J* = 1.8 Hz, 1H), 2.06 (d, *J* = 1.9 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.8 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 145.0 (d, *J* = 1.7 Hz), 139.1, 135.3, 133.1, 130.6, 130.0, 128.1 (q, *J* = 311.4 Hz), 126.1, 123.0, 84.2, 10.7. IR (KBr): ν 2962, 2932, 2856, 1769, 1546, 1431, 1296, 1140, 1098, 997, 876, 784, 697, 646 cm^{-1}. MS (EI) m/z: 352 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{12}H_8BrF_3O_2S$ 351.9380; found: 351.9375.



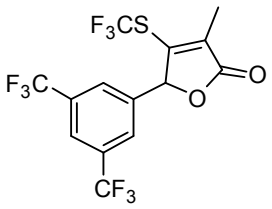
5-(2-Fluorophenyl)-3-methyl-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3j)

Compound **3j** was obtained as a yellow oil (38.0 mg, 65%), with PE/EA = 30:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 1H), 7.13-6.99 (m, 3H), 6.11 (d, *J* = 1.9 Hz, 1H), 2.07 (d, *J* = 2.0 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -38.1 (s, 3F), -117.63--117.98 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 160.7 (d, *J* = 251.5 Hz), 143.4 (d, *J* = 1.6 Hz), 138.2, 130.9 (d, *J* = 9.1 Hz), 127.8 (d, *J* = 3.0 Hz), 127.0 (q, *J* = 311.2 Hz), 123.7 (d, *J* = 1.6 Hz), 119.4 (d, *J* = 12.1 Hz), 115.3 (d, *J* = 21.2 Hz), 78.7 (d, *J* = 2.3 Hz), 9.6. IR (KBr): ν 2961, 2931, 2856, 1770, 1534, 1493, 1459, 1301, 1142, 1100, 1046, 994, 908, 910, 811, 757, 640 cm^{-1}. MS (EI) m/z: 292 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{12}H_8F_4O_2S$ 292.0181; found: 292.0180.



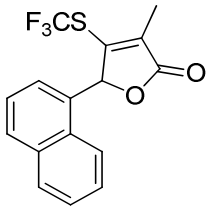
5-(2,5-Dimethylphenyl)-3-methyl-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3k)

Compound **3k** was obtained as a yellow solid (47.1 mg, 78%), with PE/EA = 30:1 as eluent for the column chromatography. Mp 65-67 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07-7.01 (m, 2H), 6.58 (s, 1H), 6.12 (q, *J* = 1.9 Hz, 1H), 2.34 (s, 3H), 2.20 (s, 3H), 2.11 (d, *J* = 1.9 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -38.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 144.1 (d, *J* = 1.9 Hz), 138.3, 135.3, 133.5, 130.2, 129.6, 129.5, 127.2 (q, *J* = 311.1 Hz), 125.9, 81.1, 19.9, 17.6, 9.7. IR (KBr): ν 2961, 2923, 2856, 1768, 1505, 1477, 1296, 1260, 1138, 1100, 981, 805, 749, 651, 541 cm^{-1}. MS (EI) m/z: 302 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{14}H_{13}F_3O_2S$ 302.0588; found: 302.0583.



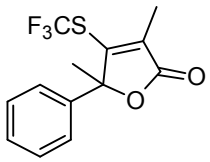
5-(3,5-Bis(trifluoromethyl)phenyl)-3-methyl-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3l)

Compound **3l** was obtained as a yellow oil (32.9 mg, 40%), with PE/EA = 30:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.63 (s, 2H), 5.93 (d, *J* = 1.8 Hz, 1H), 2.12 (d, *J* = 1.9 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.7 (s, 3F), -63.0 (s, 6F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 143.3 (d, *J* = 1.7 Hz), 139.1, 135.0, 131.7 (q, *J* = 34.0 Hz), 126.9 (q, *J* = 311.6 Hz), 126.3 (d, *J* = 3.1 Hz), 122.9 (dt, *J* = 7.6, 3.8 Hz), 121.8 (q, *J* = 272.9 Hz), 82.3, 9.9. IR (KBr): ν 2963, 2928. 2864, 1779, 1657, 1484, 1380, 1239, 1278, 1135, 1099, 1013, 905, 797, 733, 681 cm^{-1}. MS (EI) m/z: 410 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{14}H_7F_9O_2S$ 410.0023; found: 410.0018.



3-Methyl-5-(naphthalen-1-yl)-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3m)

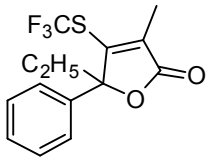
Compound **3m** was obtained as a yellow oil (31.0 mg, 48%), with PE/EA = 30:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.56-7.44 (m, 2H), 7.39-7.33 (m, 1H), 7.10 (dd, *J* = 7.2, 0.6 Hz, 1H), 6.69 (d, *J* = 1.9 Hz, 1H), 2.13 (d, *J* = 1.8 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -38.0 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 145.2 (d, *J* = 1.8 Hz), 139.6, 134.0, 131.9, 130.8, 129.1, 128.8, 128.2 (q, *J* = 311.3 Hz), 127.3, 126.4, 125.4, 125.2, 122.4, 81.4, 10.9. IR (KBr): ν 2962, 2919, 2853, 1766, 1628, 1554, 1356, 1295, 1140, 1098, 1016, 976, 795, 774, 641, 540 cm^{-1}. MS (EI) m/z: 324 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{16}H_{11}F_3O_2S$ 324.0432; found: 324.0435.



3,5-Dimethyl-5-phenyl-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3n)

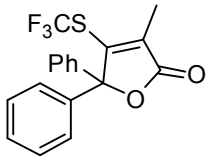
Compound **3n** was obtained as a yellow oil (40.6 mg, 70%), with PE/EA = 30:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (m,

5H), 2.03 (d, J = 0.9 Hz, 3H), 1.86 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.4 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 150.0 (d, J = 1.3 Hz), 138.6, 136.7, 129.0, 128.8, 128.2 (q, J = 311.4 Hz), 125.4, 89.4, 23.5, 11.2 (d, J = 1.5 Hz). IR (KBr): ν 2962, 2923, 2856, 1763, 1505, 1474, 1292, 1142, 1097, 1063, 1023, 923, 800, 769, 696, 660 cm^{-1}. MS (EI) m/z: 288 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{13}H_{11}F_3O_2S$ 288.0432; found: 288.0437.



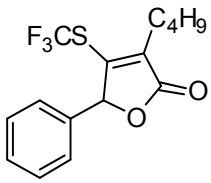
5-Ethyl-3-methyl-5-phenyl-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3o)

Compound **3o** was obtained as a yellow oil (52.6 mg, 87%), with PE/EA = 30:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.21 (m, 5H), 2.38 (dq, J = 14.7, 7.4 Hz, 1H), 2.05 (dq, J = 14.4, 7.2 Hz, 1H), 2.00 (d, J = 0.9 Hz, 3H), 0.81 (t, J = 7.3 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.0 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 149.2 (d, J = 1.4 Hz), 138.7, 136.1, 128.8, 128.7, 128.2 (q, J = 311.6 Hz), 125.4, 91.9, 29.2, 11.1 (d, J = 1.5 Hz), 7.5. IR (KBr): ν 2958, 2920, 2861, 1766, 1521, 1495, 1290, 1167, 1097, 1030, 975, 801, 767, 698, 498 cm^{-1}. MS (EI) m/z: 302 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{14}H_{13}F_3O_2S$ 302.0588; found: 302.0579.



3-Methyl-5,5-diphenyl-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3p)

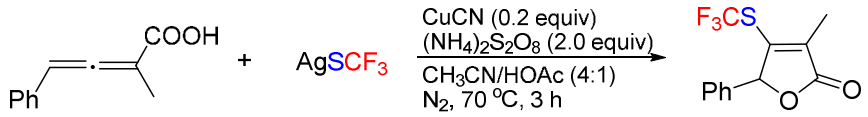
Compound **3p** was obtained as a yellow solid (63.0 mg, 90%), with PE/EA = 30:1 as eluent for the column chromatography. Mp 67-69 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 6H), 7.21-7.17 (m, 4H), 2.12 (d, J = 1.2 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.2 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 148.4 (d, J = 1.2 Hz), 139.4, 137.4, 129.3, 128.6, 127.8, 127.7 (q, J = 312.7 Hz), 94.0, 11.6 (d, J = 1.9 Hz). IR (KBr): ν 2960, 2927, 2850, 1771, 1515, 1448, 1290, 1152, 1099, 985, 759, 698, 652 cm^{-1}. MS (EI) m/z: 350 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{18}H_{13}F_3O_2S$ 350.0588; found: 350.0580.



3-Butyl-5-phenyl-4-((trifluoromethyl)thio)furan-2(5*H*)-one (3q)

Compound **3q** was obtained as a yellow oil (48.1 mg, 76%), with PE/EA = 30:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 3H), 7.14-7.08 (m, 2H), 5.82 (s, 1H), 2.54-2.40 (m, 2H), 1.60-1.46 (m, 2H), 1.30 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -37.8 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 145.5 (d, *J* = 1.7 Hz), 142.1, 133.3, 129.9, 129.1, 128.0 (q, *J* = 311.1 Hz), 127.3, 84.9, 29.8, 25.0, 22.5, 13.7. IR (KBr): ν 2962, 2931. 2860, 1769, 1543, 1457, 1315, 1263, 1140, 1104, 1003, 944, 802, 757, 697, 645 cm^{-1}. MS (EI) m/z: 316 $[M]^+$. HRMS (EI) m/z: Calcd for $C_{15}H_{15}F_3O_2S$ 316.0745; found $[M]^+$: 316.0740.

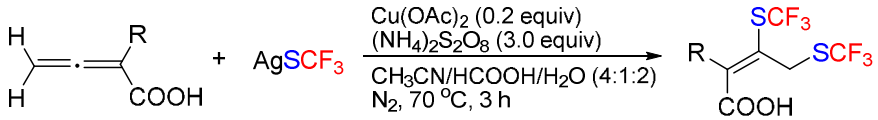
Cyclic Oxytrifluoromethylthiolation of 2,3-Allenoic Acid 1a on a 1.0 mmol Scale:



1a (1.0 mmol) **3a** (197.8 mg)

2-Methyl-4-phenylbuta-2,3-dienoic acid (174.2 mg, 1.0 mmol, 1.0 equiv), CuCN (17.9 mg, 0.2 mmol, 0.2 equiv), $AgSCF_3$ (417.9 mg, 2.0 mmol, 2.0 equiv), and $(NH_4)_2S_2O_8$ (456.4 mg, 2.0 mmol, 2.0 equiv) were added to a Schlneck tube. The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Then CH_3CN (16 mL) and HOAc (4 mL) was added by a syringe. The mixture was stirred at 70 °C for 3 h. A saturated ammonium chloride aqueous solution (15 mL) was added. The resulting mixture was filtered by Celite, eluted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced vacuum. The residue was purified with silica gel column chromatography (PE/EA = 30:1) to give **3a** (197.8 mg, 72%) as a yellow oil.

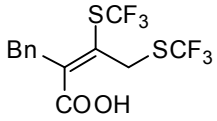
5. Bis-Trifluoromethylthiolation of 2,3-Allenoic Acids with $AgSCF_3$



1 **4**

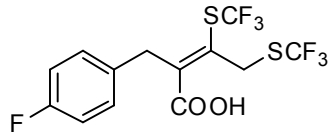
A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with 2,3-allenoic acid (0.2 mmol, 1.0 equiv), $Cu(OAc)_2$ (7.3 mg, 0.04 mmol, 0.2 equiv), $AgSCF_3$ (125.4 mg, 0.6 mmol, 3.0 equiv), and $(NH_4)_2S_2O_8$ (136.9 mg, 0.6 mmol, 3.0 equiv). The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Then CH_3CN (3.2 mL), HCOOH (0.8 mL) and H_2O (1.6 mL) were added

by a syringe. The mixture was stirred at 70 °C for 3 h. A saturated ammonium chloride aqueous solution (5 mL) was added. The resulting mixture was filtered by Celite, eluted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced vacuum. The residue was purified with silica gel column chromatography to provide the pure product.



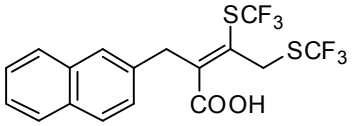
(*E*)-2-Benzyl-3,4-bis((trifluoromethyl)thio)but-2-enoic acid (4r)

Compound **4r** was obtained as a yellow solid (37.6 mg, 50%), with PE/EA = 5:1 as eluent for the column chromatography. Mp 73-75 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 2H), 4.28 (s, 2H), 4.17 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -39.3 (s, 3F), -40.8 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 145.3, 136.1, 134.1, 130.4 (q, *J* = 307.4 Hz), 129.0 (q, *J* = 310.8 Hz), 128.8, 128.3, 127.1, 38.8, 34.9. IR (KBr): ν 2962, 2921, 2861, 1764, 1586, 1454, 1352, 1251, 1119, 1095, 1036, 958, 752, 697, 467 cm^{-1}. MS (ESI) m/z: 375 [M-H]$^-$. HRMS (ESI) m/z: Calcd for $C_{13}H_9F_6O_2S_2$ 374.9973, found [M-H]$^-$: 374.9953.



(*E*)-2-(4-Fluorobenzyl)-3,4-bis((trifluoromethyl)thio)but-2-enoic acid (4s)

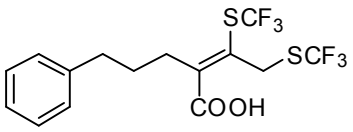
Compound **4s** was obtained as a yellow oil (49.6 mg, 63%), with PE/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.11-7.09 (m, 2H), 7.03-6.99 (m, 2H), 4.27 (s, 2H), 4.12 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -38.5 (s, 3F), -41.1 (s, 3F), -115.3--115.4 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.1, 161.9 (d, *J* = 246.1 Hz), 145.1, 134.2, 131.7 (d, *J* = 3.0 Hz), 130.3 (q, *J* = 307.4 Hz), 129.9 (d, *J* = 7.5 Hz), 128.9 (q, *J* = 311.1 Hz), 115.7 (d, *J* = 37.8 Hz), 38.1, 35.0. IR (KBr): ν 2960, 2927, 2857, 1701, 1605, 1510, 1405, 1260, 1159, 1096, 1016, 954, 802, 756 cm^{-1}. MS (ESI) m/z: 393 [M-H]$^-$. HRMS (ESI) m/z: Calcd for $C_{13}H_8F_7O_2S_2$ 392.9859, found [M-H]$^-$: 392.9866.



(*E*)-2-(Naphthalen-2-ylmethyl)-3,4-bis((trifluoromethyl)thio)but-2-enoic acid (4t)

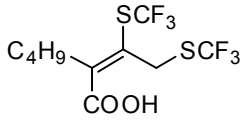
Compound **4t** was obtained as a yellow solid (38.3 mg, 45%), with PE/EA = 5:1 as eluent for the column chromatography. Mp 117-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.74-7.63 (m, 3H), 7.43 (s, 1H), 7.41-7.34 (m, 2H), 7.15 (dd, *J* = 8.4,

1.7 Hz, 1H), 4.20 (s, 2H), 4.18 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -38.4 (s, 3F), -41.0 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.3, 144.9, 134.6, 133.6, 133.5, 132.4, 130.3 (q, *J* = 307.4 Hz), 129.0 (q, *J* = 314.2 Hz), 128.6, 127.7, 127.6, 126.8, 126.5, 126.3, 125.9, 38.9, 35.0. IR (KBr): ν 2960, 2925, 2855, 1704, 1522, 1463, 1261, 1160, 1099, 974, 907, 807, 732, 649 cm^{-1}. MS (ESI) m/z: 425 $[M-H]^-$. HRMS (ESI) m/z: Calcd for $C_{17}H_{11}F_6O_2S_2$ 425.0114, found $[M-H]^-$: 425.0110.



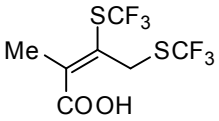
(*E*)-2-(1,2-Bis((trifluoromethyl)thio)ethylidene)-5-phenylpentanoic acid (4u)

Compound **4u** was obtained as a yellow oil (36.4 mg, 45%), with PE/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.23-7.09 (m, 5H), 4.11 (s, 2H), 2.75-2.66 (m, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 1.78-1.68 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -38.9 (s, 3F), -41.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 146.3, 140.0, 131.4, 129.3 (q, *J* = 307.4 Hz), 128.0 (q, *J* = 310.5 Hz), 127.4, 127.3, 125.1, 34.4, 34.1, 32.1, 28.9. IR (KBr): ν 2961, 2926, 2849, 1717, 1633, 1426, 1323, 1264, 1154, 1099, 971, 908, 754, 698, 646 cm^{-1}. MS (ESI) m/z: 403 $[M-H]^-$. HRMS (ESI) m/z: Calcd for $C_{15}H_{13}F_6O_2S_2$ 403.0277; found $[M-H]^-$: 403.0269.



(*E*)-2-(1,2-Bis((trifluoromethyl)thio)ethylidene)hexanoic acid (4v)

Compound **4v** was obtained as a colorless oil (27.3 mg, 40%), with PE/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 4.11 (s, 2H), 2.80-2.47 (m, 2H), 1.47-1.24 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -38.7 (s, 3F), -40.9 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 147.2, 130.2, 129.4 (q, *J* = 306.9 Hz), 128.1 (q, *J* = 310.4 Hz), 34.2, 32.3, 29.3, 21.4, 12.7. IR (KBr): ν 2953, 2921, 2846, 1681, 1260, 1100, 905, 796, 657 cm^{-1}. MS (ESI) m/z: 341 $[M-H]^-$. HRMS (ESI) m/z: Calcd for $C_{10}H_{11}F_6O_2S_2$ 341.0110; found $[M-H]^-$: 341.0104.

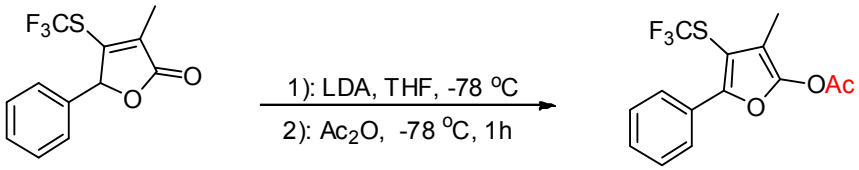


(*E*)-2-Methyl-3,4-bis((trifluoromethyl)thio)but-2-enoic acid (4w)

Compound **4w** was obtained as a colorless oil (31.4 mg, 48%), with PE/EA = 5:1 as eluent for the column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 4.19 (s, 2H), 2.27 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -39.1 (s, 3F), -41.2 (s, 3F).

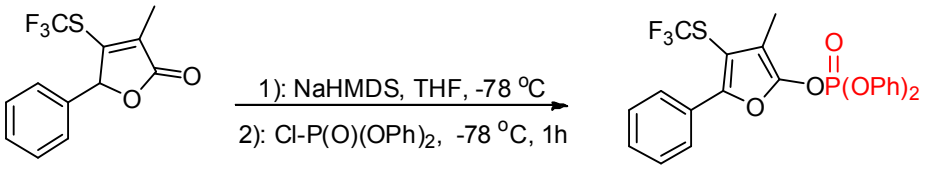
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 142.3, 132.2 (d, J = 1.1 Hz), 129.4 (q, J = 307.4 Hz), 128.3 (q, J = 310.4 Hz), 34.5, 19.0. IR (KBr): ν 2960, 2927, 2859, 1703, 1278, 1103, 1007, 807, 757 cm^{-1}. MS (ESI) m/z: 299 [M-H]$^-$. HRMS (ESI) m/z: Calcd for $C_7H_5F_6O_2S_2$ 298.9641; found [M-H]$^-$: 298.9639.

6. Transformation of Compound 3a



3a (1.0 equiv) **5a** yield:68%

3-Methyl-5-phenyl-4-((trifluoromethyl)thio)furan-2-yl acetate (5a): A solution of LDA (1.5M in THF, 0.16 mL, 1.2 equiv) in THF (2.0 mL) was slowly added a solution of **3a** (54.9 mg, 0.2 mmol, 1.0 equiv) in dry THF (1.0 mL) at -78 °C. After the reaction mixture was stirred for 0.5 h at -78 °C, Ac_2O (40.9 mg, 0.4 mmol, 2.0 equiv) was added slowly. The mixture was stirred at -78 °C for 1 h. Then, saturated ammonium chloride aqueous solution was added. The resulting mixture was eluted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced vacuum. The residue was purified with silica gel column chromatography (PE/EA = 40:1) to give product **5a** as a yellow oil (42.9 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.3 Hz, 2H), 7.38-7.27 (m, 3H), 2.29 (s, 3H), 1.90 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -42.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 145.5, 141.6, 127.9, 127.5, 127.4, 127.2, 126.2 (q, J = 310.0 Hz), 125.6, 107.8, 34.8, 19.2. IR (KBr): ν 2968, 2922, 2840, 1767, 1531, 1432, 1267, 1139, 1100, 1014, 843, 793, 697, 565 cm^{-1}. MS (ESI) m/z: 317 [M+H]$^+$. HRMS (ESI) m/z: Calcd for $C_{14}H_{12}F_3O_3S$ 317.0454; found [M+H]$^+$: 317.0453.

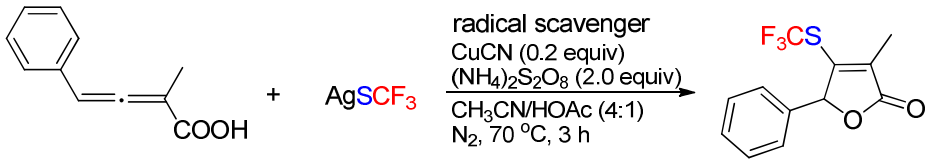


3a (1.0 equiv) **6a** yield:87%

3-Methyl-5-phenyl-4-((trifluoromethyl)thio)furan-2-yl diphenyl phosphate (6a): A solution of NaHMDS (2.0 M in THF, 0.12 mL, 1.2 equiv) in THF (2.0 mL) was slowly added a solution of **3a** (54.9 mg, 0.2 mmol, 1.0 equiv) in dry THF (1.0 mL) at -78 °C. After the reaction mixture was stirred for 0.5 h at -78 °C, aqueous Cl-P(O)(OPh)$_2$ (88.1 mg, 0.4 mmol, 2.0 equiv) solution was added slowly. The mixture was stirred at -78 °C for 1 h. Then, saturated ammonium chloride aqueous solution was added. The resulting mixture was eluted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under

reduced vacuum. The residue was purified with silica gel column chromatography (PE/EA = 20:1) to give product **6a** as a yellow oil (107.5 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.76 (m, 2H), 7.35-7.26 (m, 7H), 7.25-7.14 (m, 6H), 1.86 (d, J = 2.5 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -42.7 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 149.1, 149.1, 144.6, 144.5, 129.0, 128.1 (q, J = 310.9 Hz), 128.0, 127.5, 125.5, 125.1, 125.0, 119.1, 119.0, 105.3, 105.2, 102.8, 5.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ -18.3 (s, 1P). IR (KBr): ν 2966, 2925, 2857, 1762, 1549, 1433, 1259, 1099, 1032, 845, 759, 667, 482 cm^{-1}. MS (ESI) m/z: 524 $[M+NH_4]^+$. HRMS (ESI) m/z: Calcd for $C_{24}H_{12}F_3NO_5PS$ 524.0900; found $[M+NH_4]^+$: 524.0900.

7. Mechanistic Investigation.



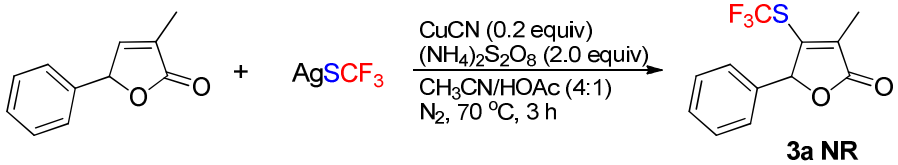
1a **3a**

The experimental procedures for radical capture with 1,4-benzoquinone:

2-Methyl-4-phenylbuta-2,3-dienoic acid **1a** (34.8 mg, 0.2 mmol, 1.0 equiv), CuCN (3.6 mg, 0.04 mmol, 0.2 equiv), $AgSCF_3$ (83.6 mg, 0.4 mmol, 2.0 equiv), $(NH_4)_2S_2O_8$ (91.3 mg, 0.4 mmol, 2.0 equiv), and 1,4-benzoquinone (21.6 mg, 0.2 mmol, 1.0 equiv) were added to a Schlenk tube. The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Then CH_3CN (3.2 mL) and HOAc (0.8 mL) was added by a syringe. The mixture was stirred at 70 °C for 3 h. Only trace of the desired product **3a** was detected.

The experimental procedures for radical capture with BHT:

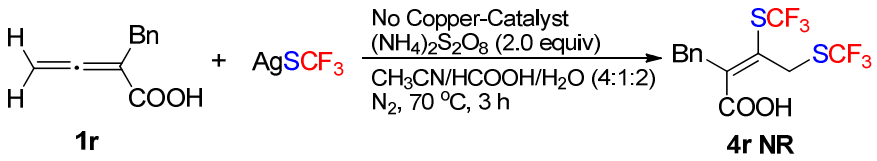
2-Methyl-4-phenylbuta-2,3-dienoic acid **1a** (34.8 mg, 0.2 mmol, 1.0 equiv), CuCN (3.6 mg, 0.04 mmol, 0.2 equiv), $AgSCF_3$ (83.6 mg, 0.4 mmol, 2.0 equiv), $(NH_4)_2S_2O_8$ (91.3 mg, 0.4 mmol, 2.0 equiv), and BHT (40.5 mg, 0.2 mmol, 1.0 equiv) were added to a Schlenk tube. The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Then CH_3CN (3.2 mL) and HOAc (0.8 mL) was added by a syringe. The mixture was stirred at 70 °C for 3 h. Only trace of the desired product **3a** was detected.



3a NR

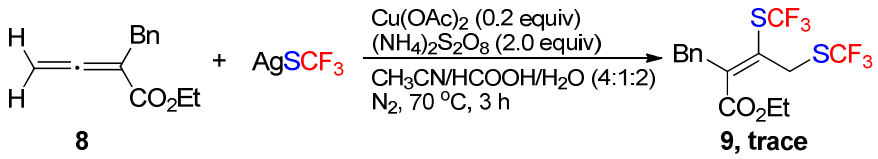
3-Methyl-5-phenylfuran-2(5*H*)-one (34.8 mg, 0.2 mmol, 1.0 equiv), CuCN (3.6 mg, 0.04 mmol, 0.2 equiv), $AgSCF_3$ (83.6 mg, 0.4 mmol, 2.0 equiv) and $(NH_4)_2S_2O_8$ (91.3 mg, 0.4 mmol, 2.0 equiv) were added to a Schlenk tube. The tube was sealed

with a septum, evacuated, and backfilled with nitrogen three times. Then CH_3CN (3.2 mL) and HOAc (0.8 mL) was added by a syringe. The mixture was stirred at 70 °C for 3 h. The desired product **3a** was not detected.



1r **4r NR**

2-Benzylbuta-2,3-dienoic acid **1r** (34.8 mg, 0.2 mmol, 1.0 equiv), $AgSCF_3$ (125.3 mg, 0.6 mmol, 3.0 equiv) and $(NH_4)_2S_2O_8$ (136.9 mg, 0.6 mmol, 3.0 equiv) were added to a Schlenk tube. The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Then CH_3CN (3.2 mL), HCOOH (0.8 mL) and H_2O (1.6 ml) was added by a syringe. The mixture was stirred at 70 °C for 3 h. The desired product **4r** was not detected.

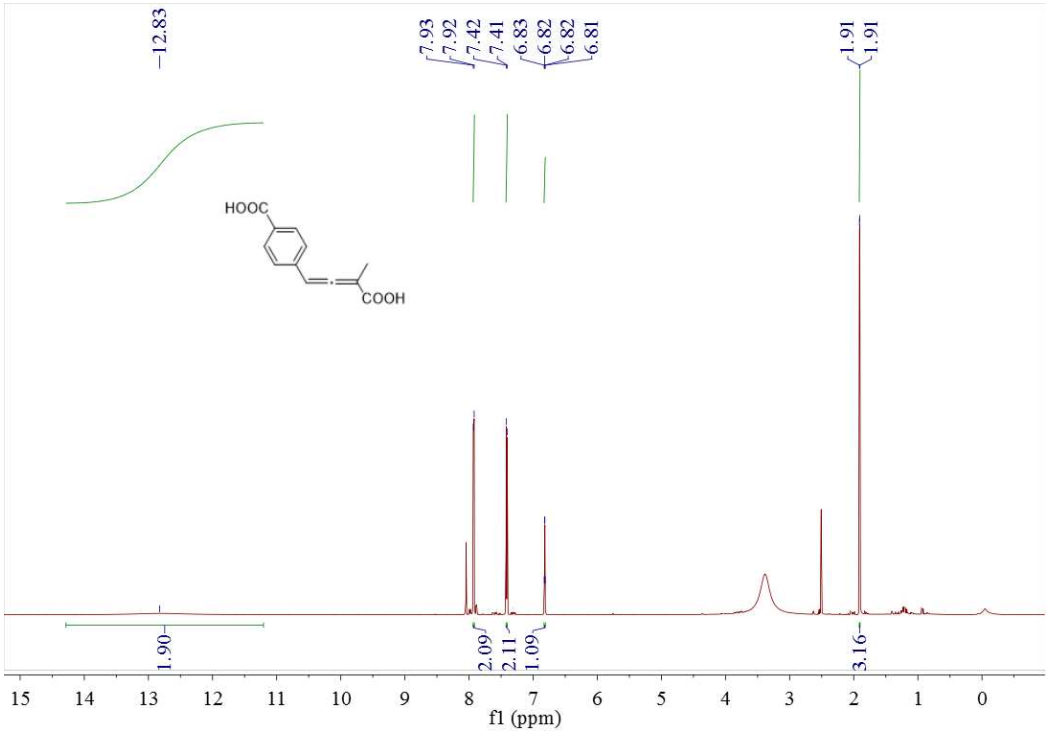


8 **9, trace**

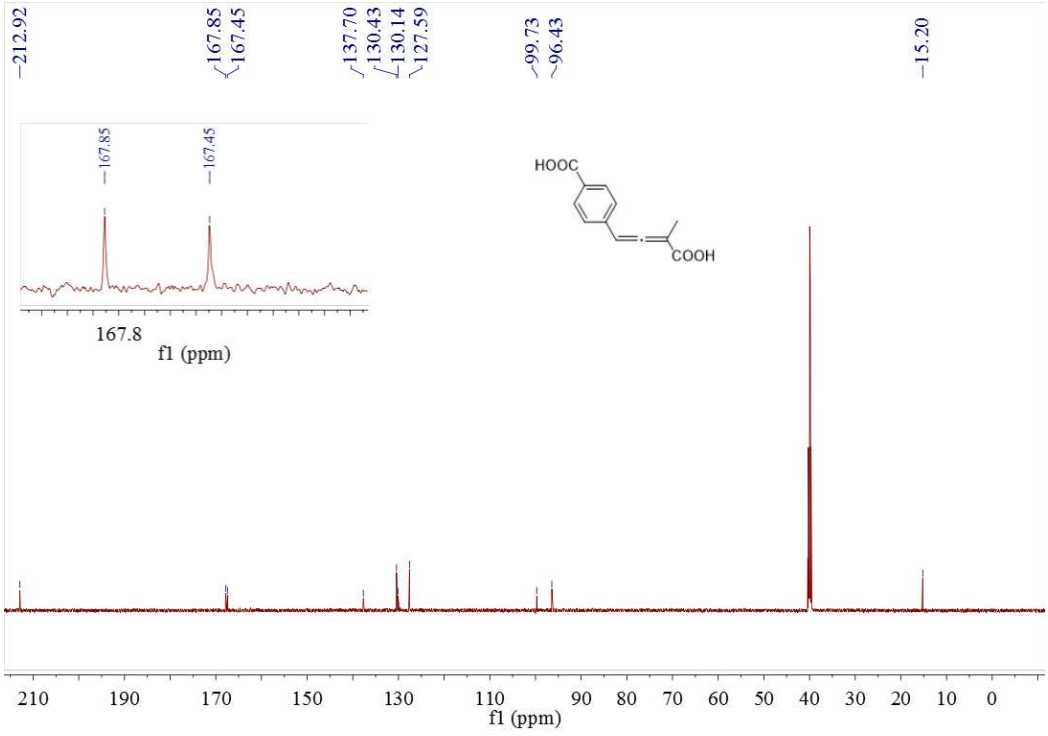
A 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **8** (40.4 mg, 0.2 mmol, 1.0 equiv), $Cu(OAc)_2$ (7.3 mg, 0.04 mmol, 0.2 equiv), $AgSCF_3$ (125.4 mg, 0.6 mmol, 3.0 equiv), and $(NH_4)_2S_2O_8$ (136.9 mg, 0.6 mmol, 3.0 equiv). The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Then CH_3CN (3.2 mL), HCOOH (0.8 mL) and H_2O (1.6 mL) were added by a syringe. The mixture was stirred at 70 °C for 3 h. Only trace of the desired product **9** was detected.

8. Copies of ^{1}H, ^{19}F, and ^{13}C NMR Spectra for the Products

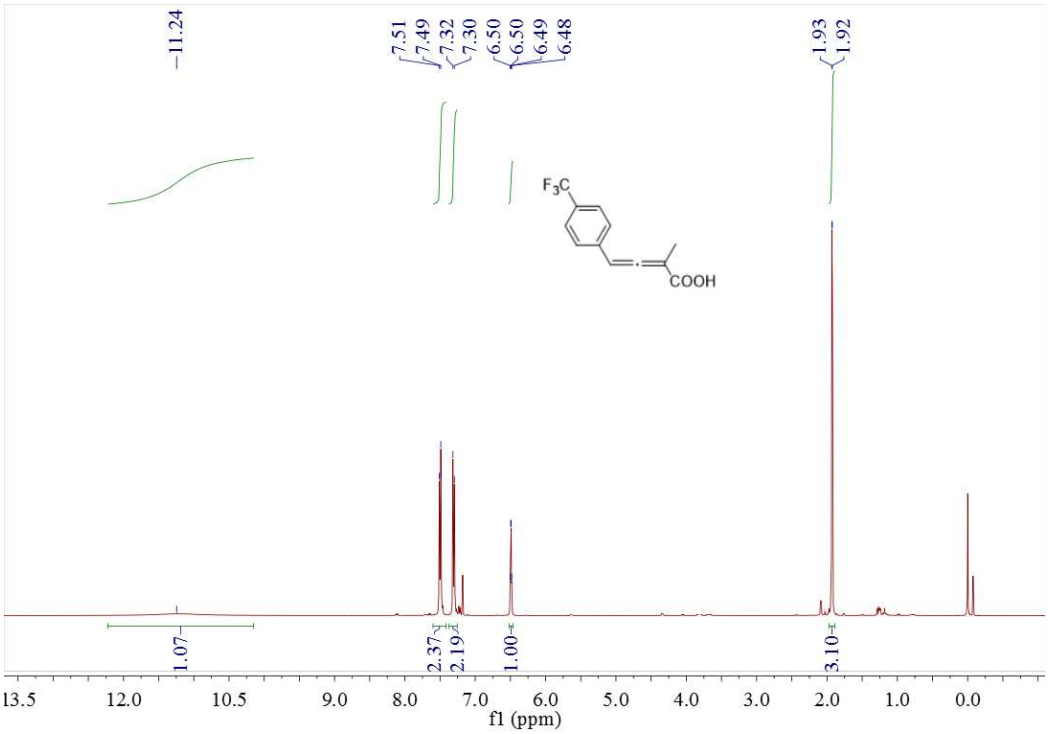
^{1}H NMR spectrum of **1d** in DMSO



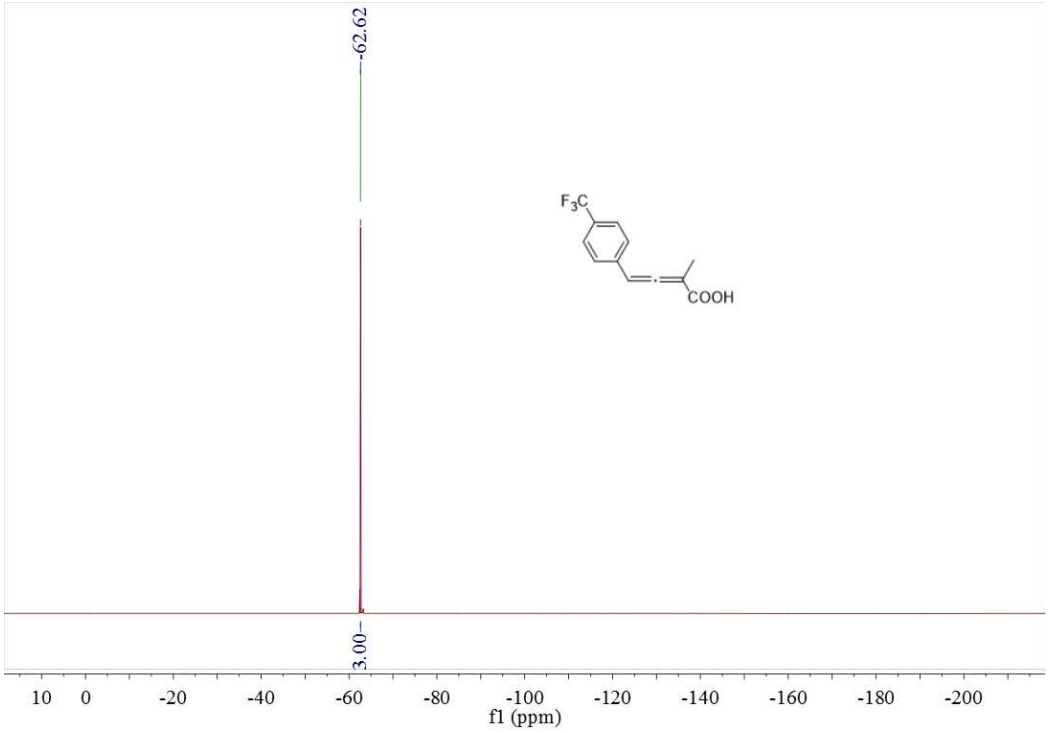
^{13}C NMR spectrum of **1d** in DMSO



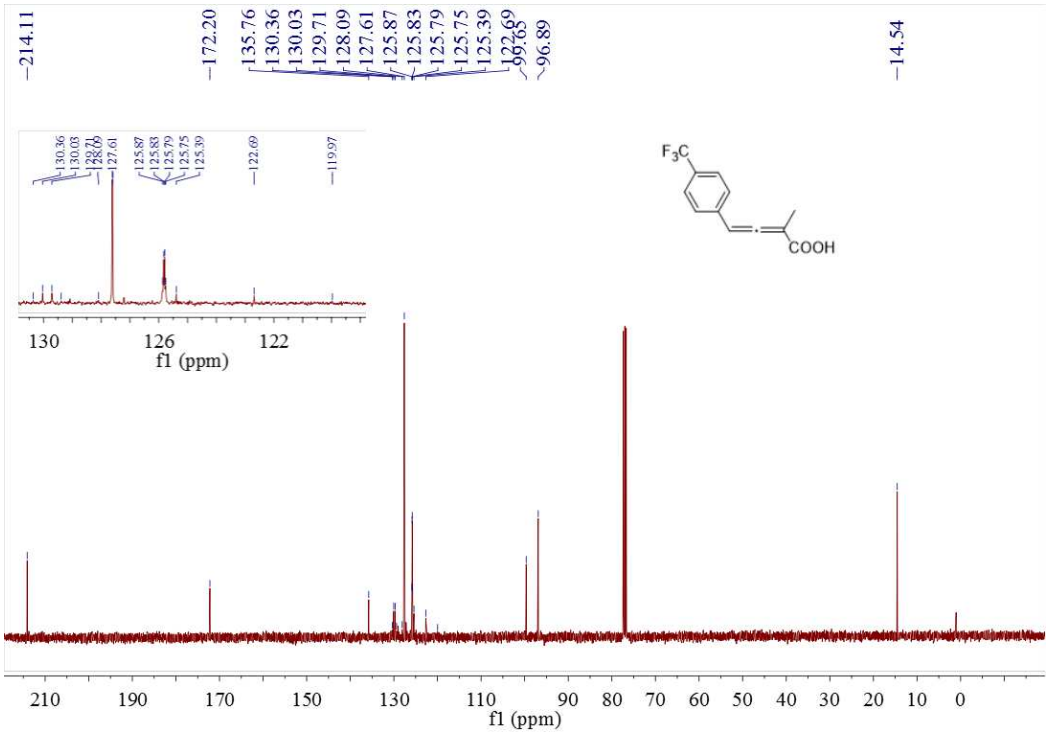
^{1}H NMR spectrum of **1e** in $CDCl_3$



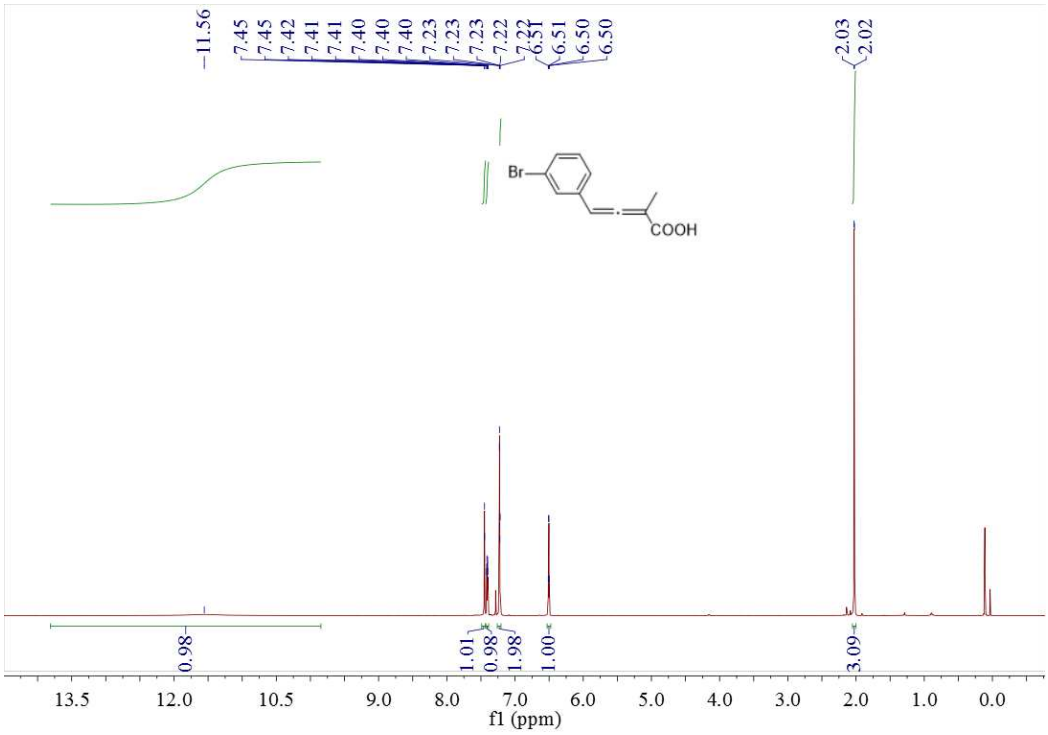
^{19}F NMR spectrum of **1e** in $CDCl_3$



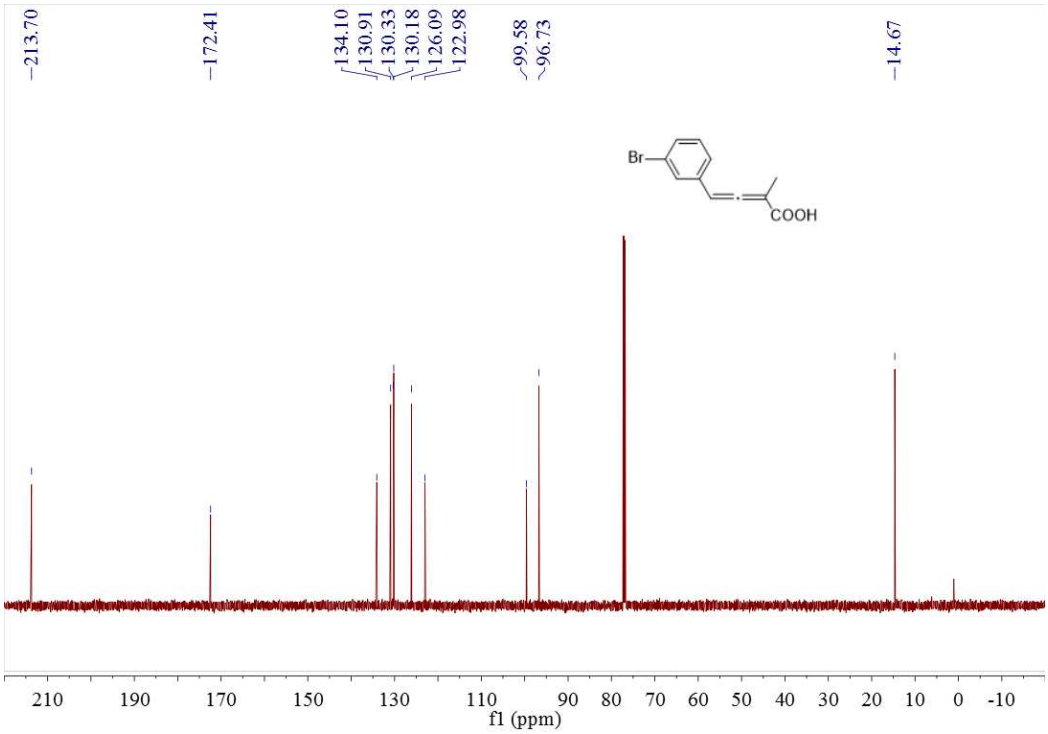
^{13}C NMR spectrum of **1e** in $CDCl_3$



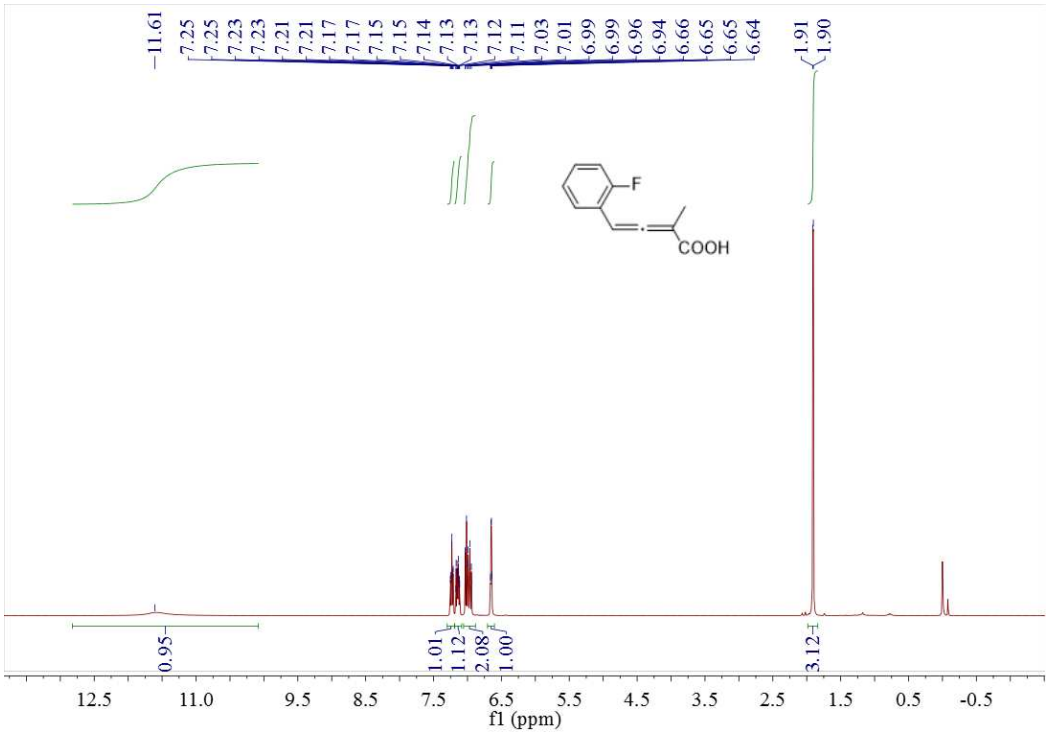
^{1}H NMR spectrum of **1i** in $CDCl_3$



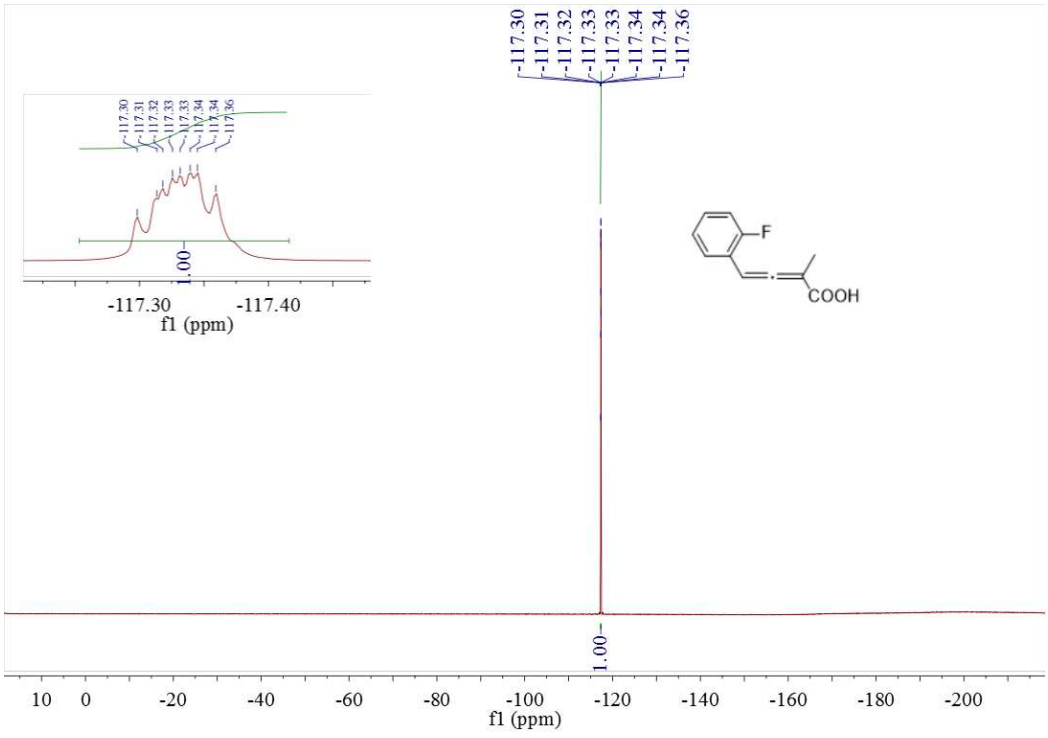
^{13}C NMR spectrum of **1i** in $CDCl_3$



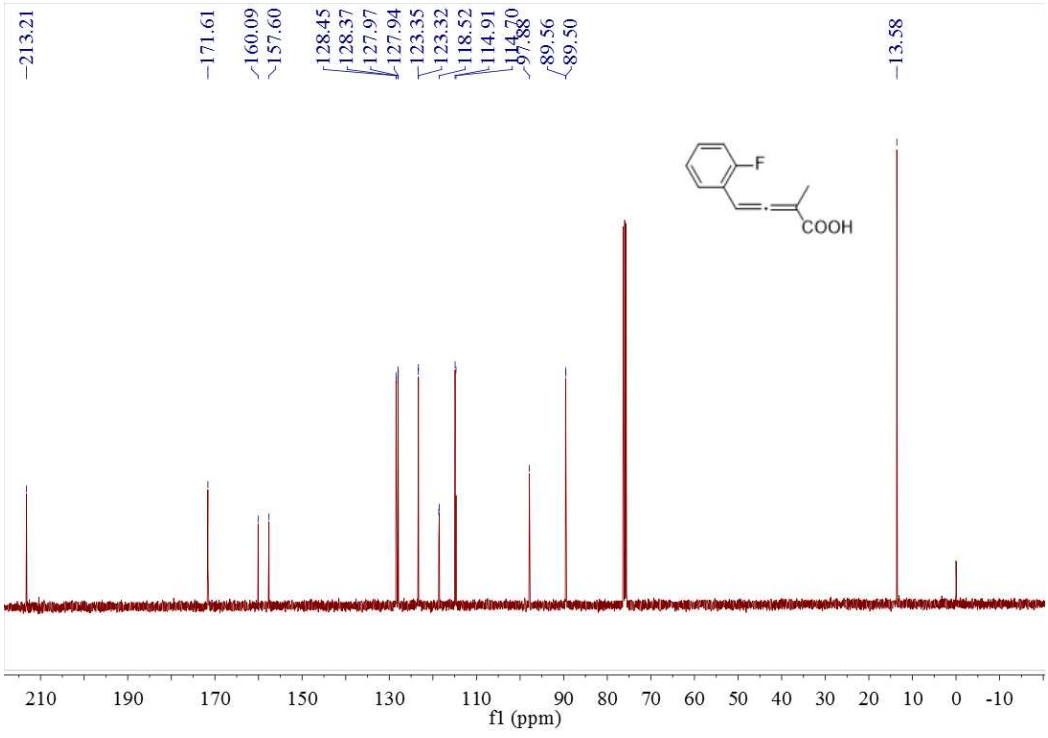
^{1}H NMR spectrum of **1j** in $CDCl_3$



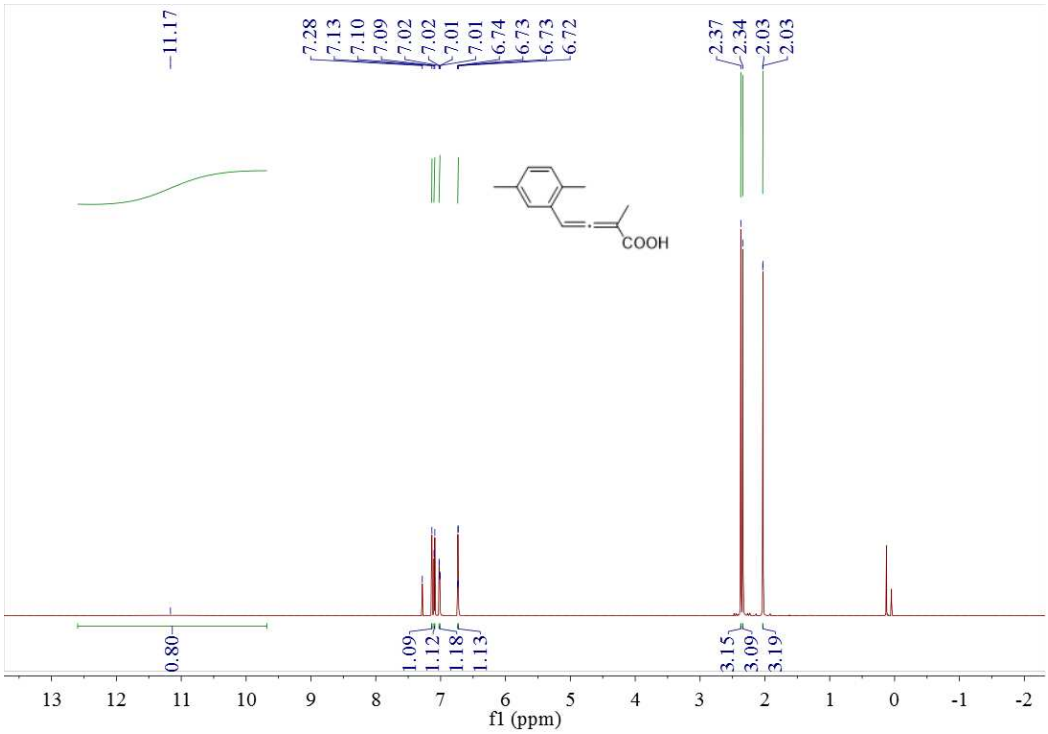
^{19}F NMR spectrum of **1j** in $CDCl_3$



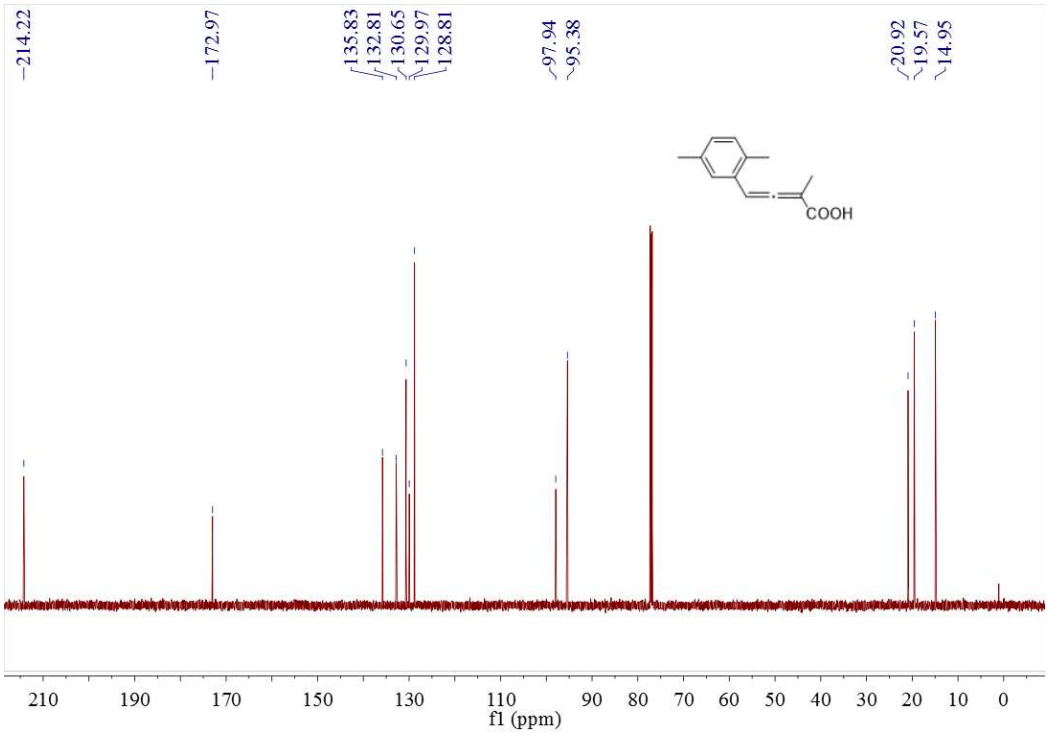
^{13}C NMR spectrum of **1j** in $CDCl_3$



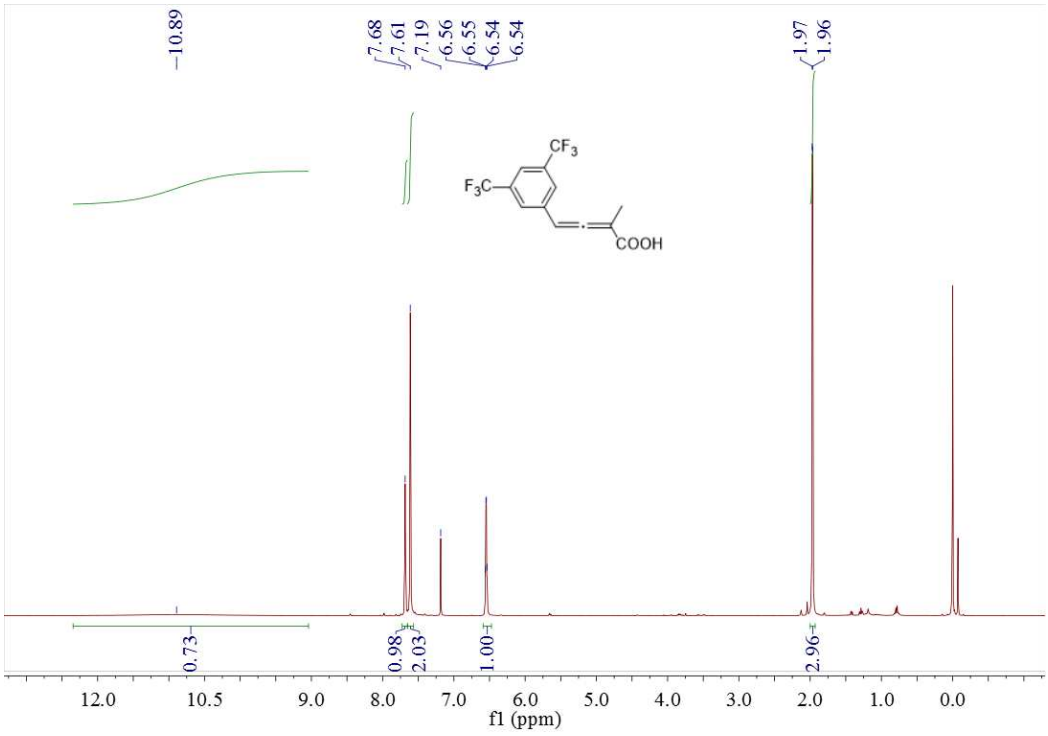
^{1}H NMR spectrum of **1k** in $CDCl_3$



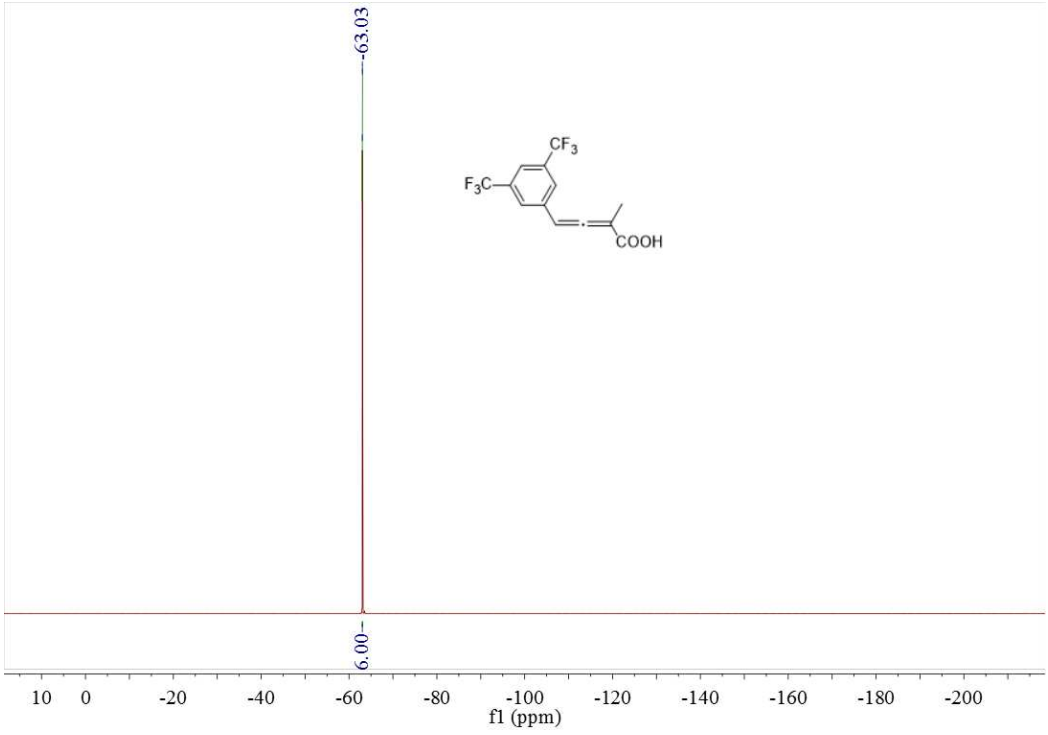
^{13}C NMR spectrum of **1k** in $CDCl_3$



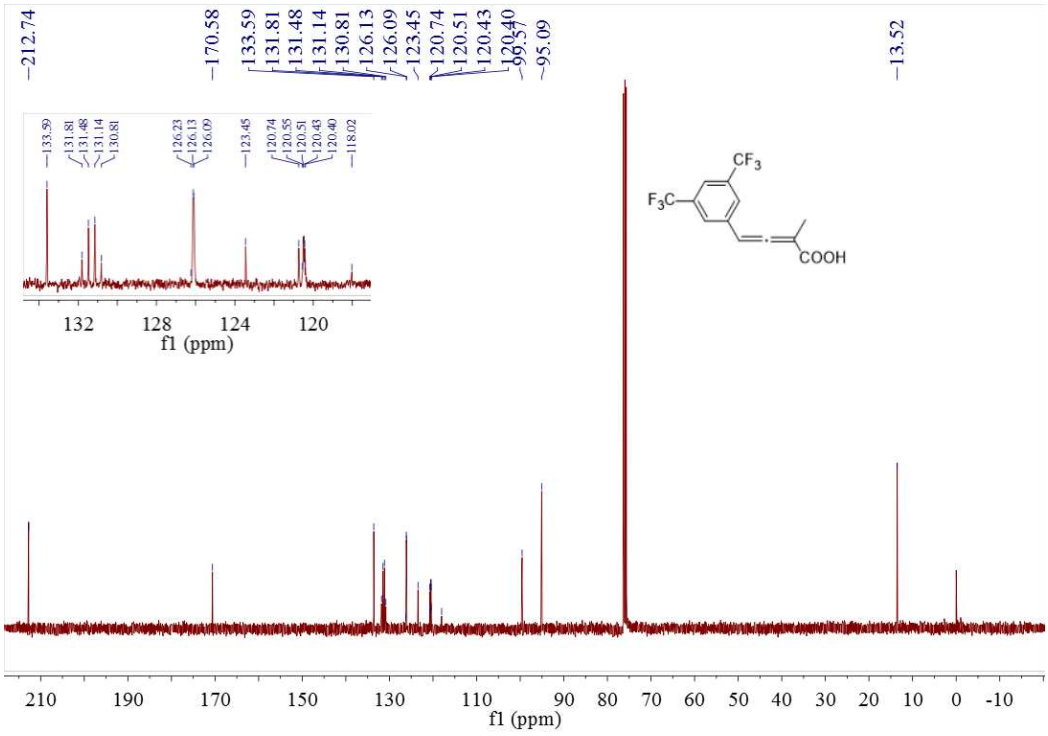
^{1}H NMR spectrum of **1l** in $CDCl_3$



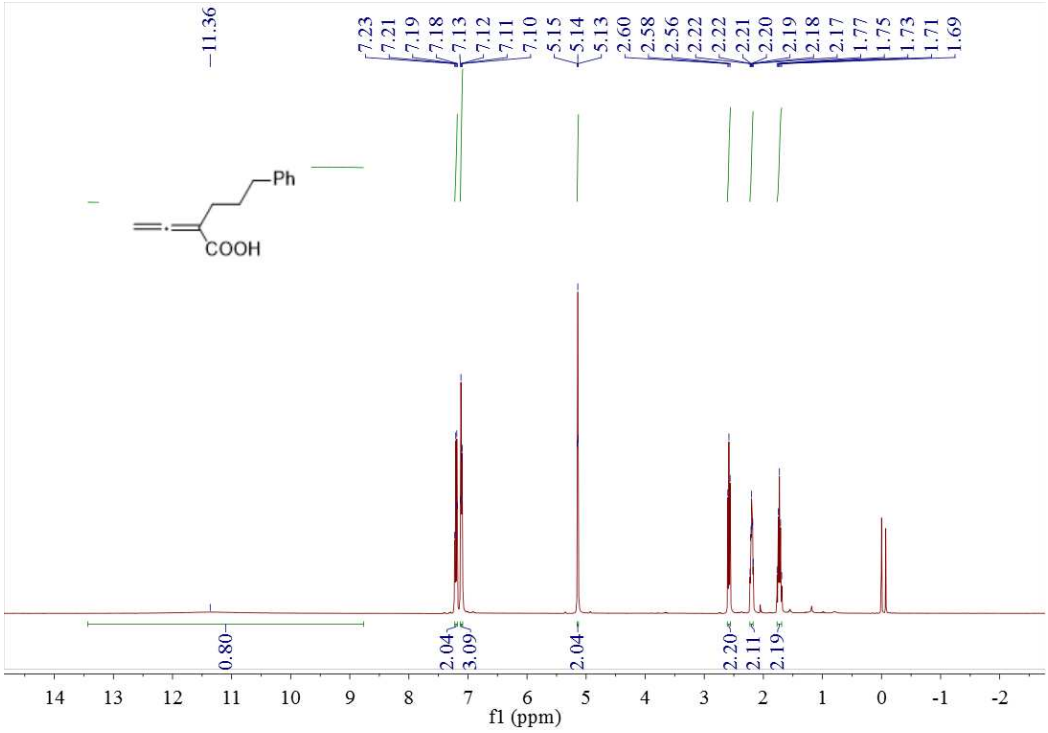
^{19}F NMR spectrum of **1l** in $CDCl_3$



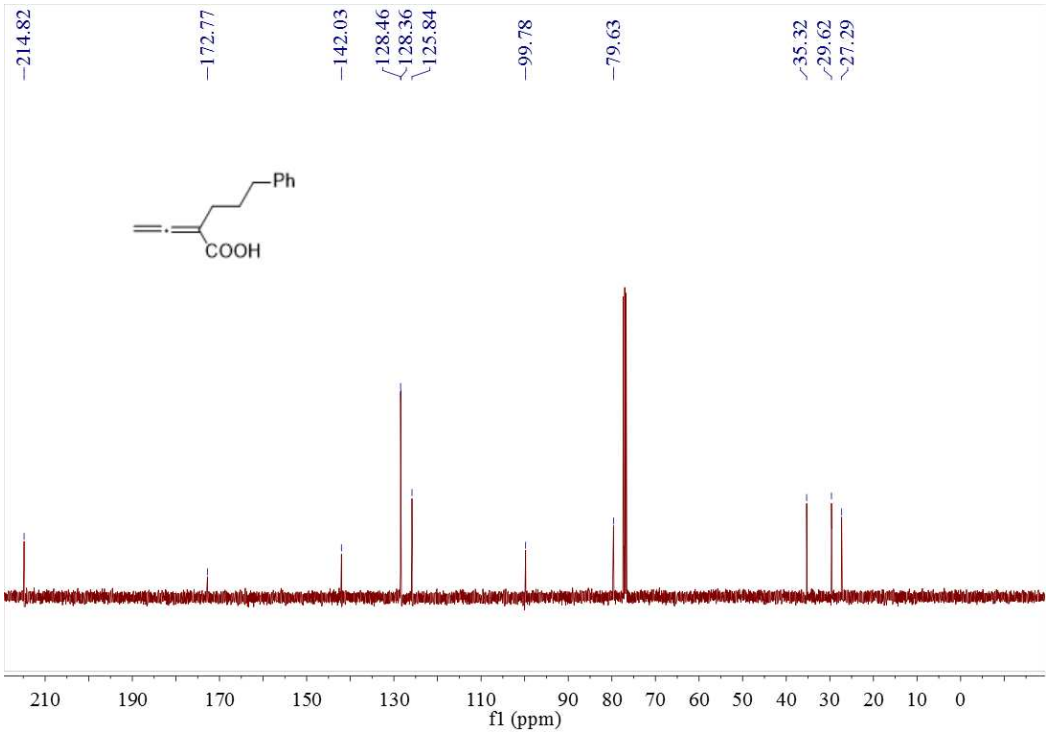
^{13}C NMR spectrum of **1l** in $CDCl_3$



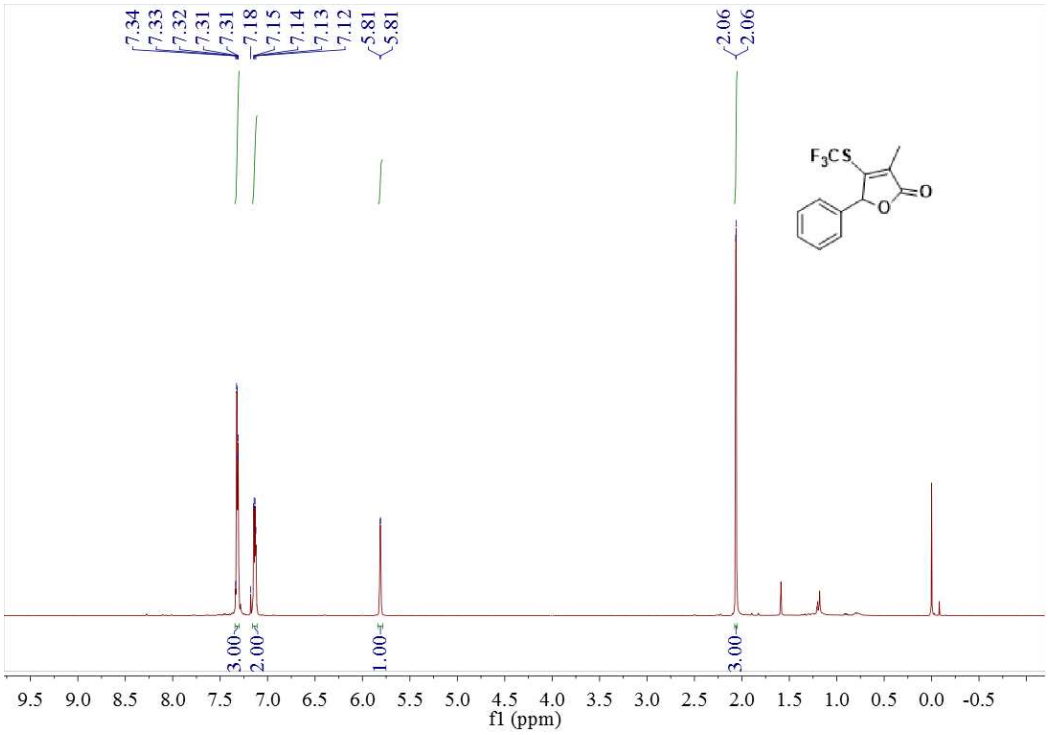
^{1}H NMR spectrum of **1u** in $CDCl_3$



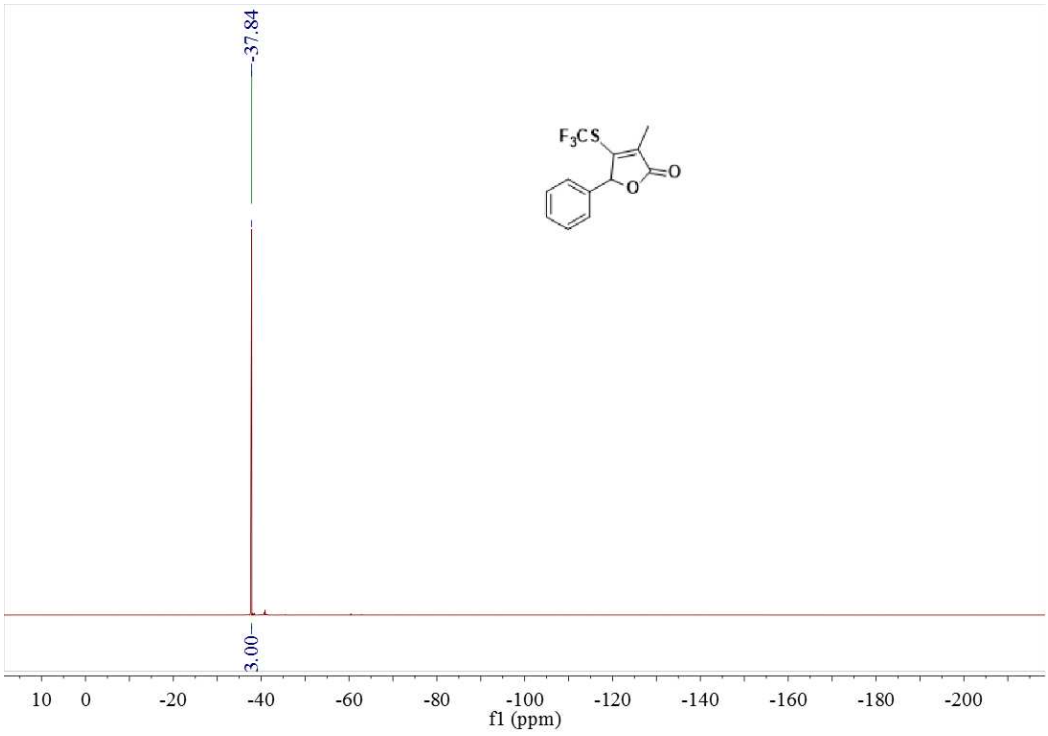
^{13}C NMR spectrum of **1u** in $CDCl_3$



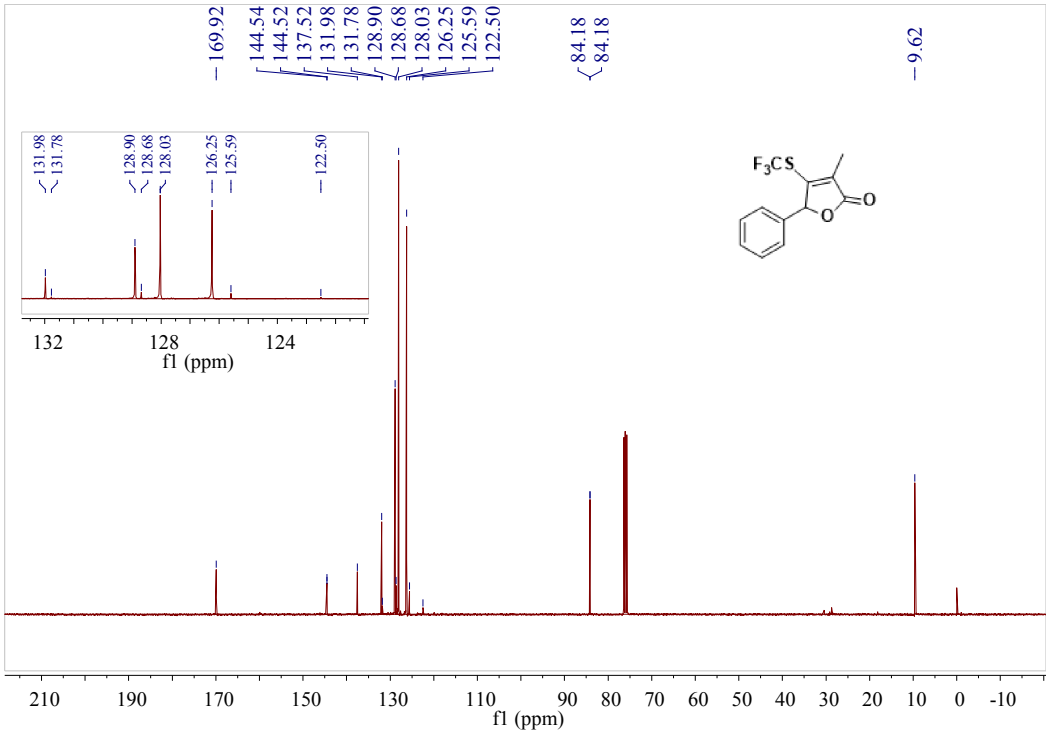
^{1}H NMR spectrum of **3a** in $CDCl_3$



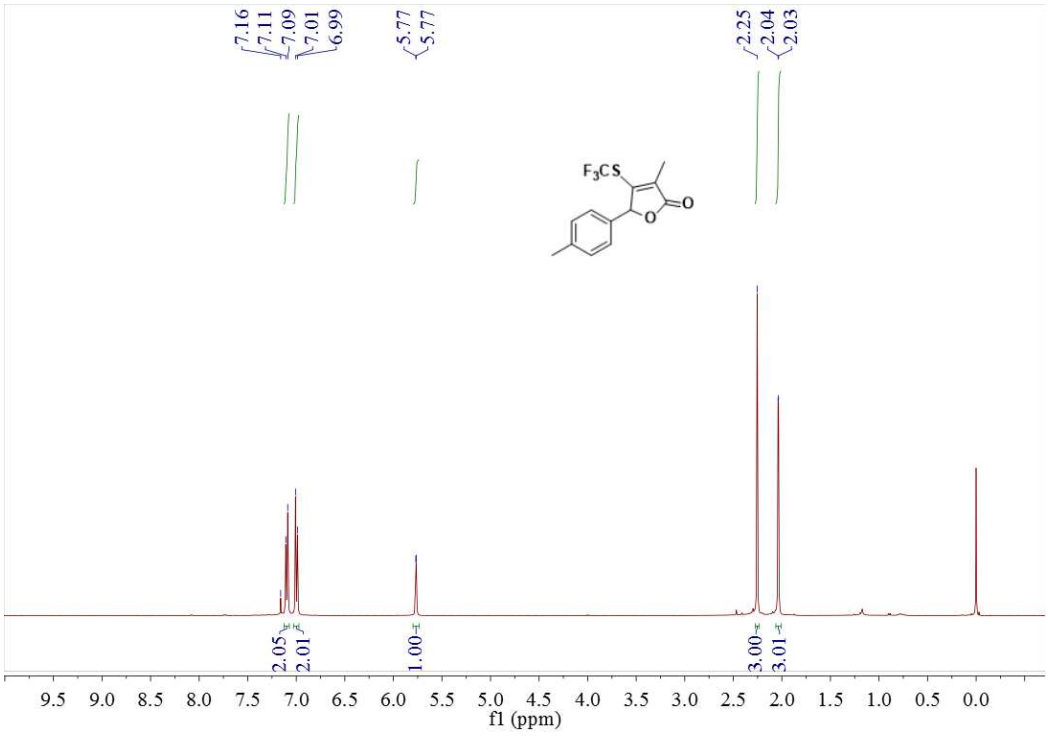
^{19}F NMR spectrum of **3a** in $CDCl_3$



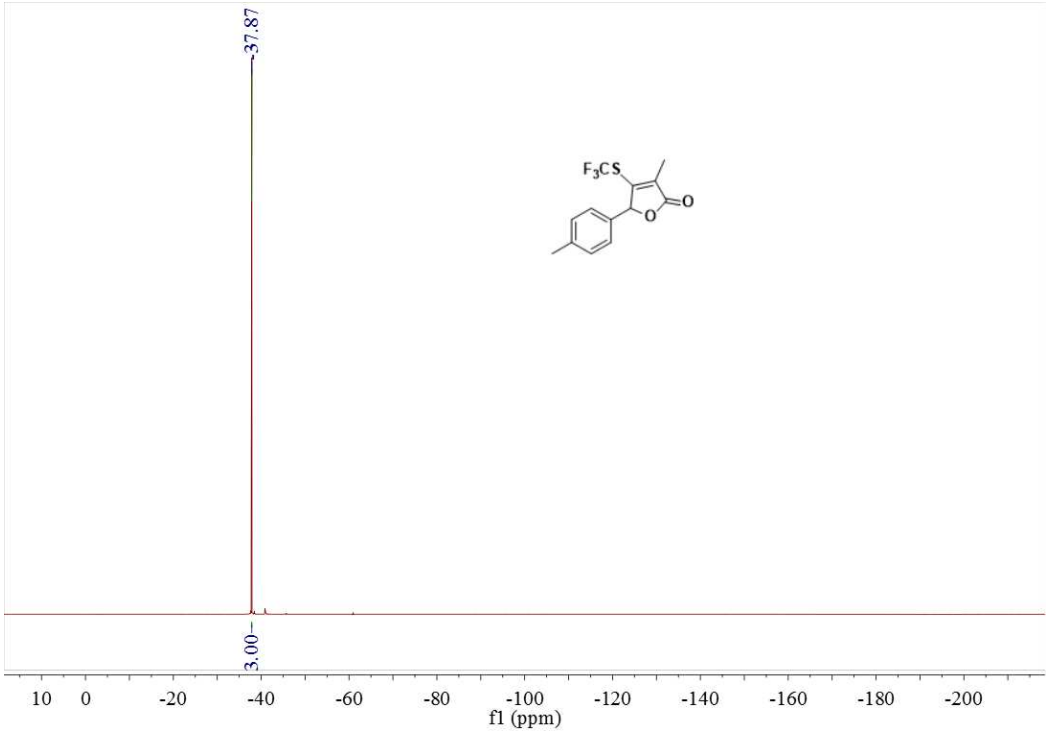
^{13}C NMR spectrum of **3a** in $CDCl_3$



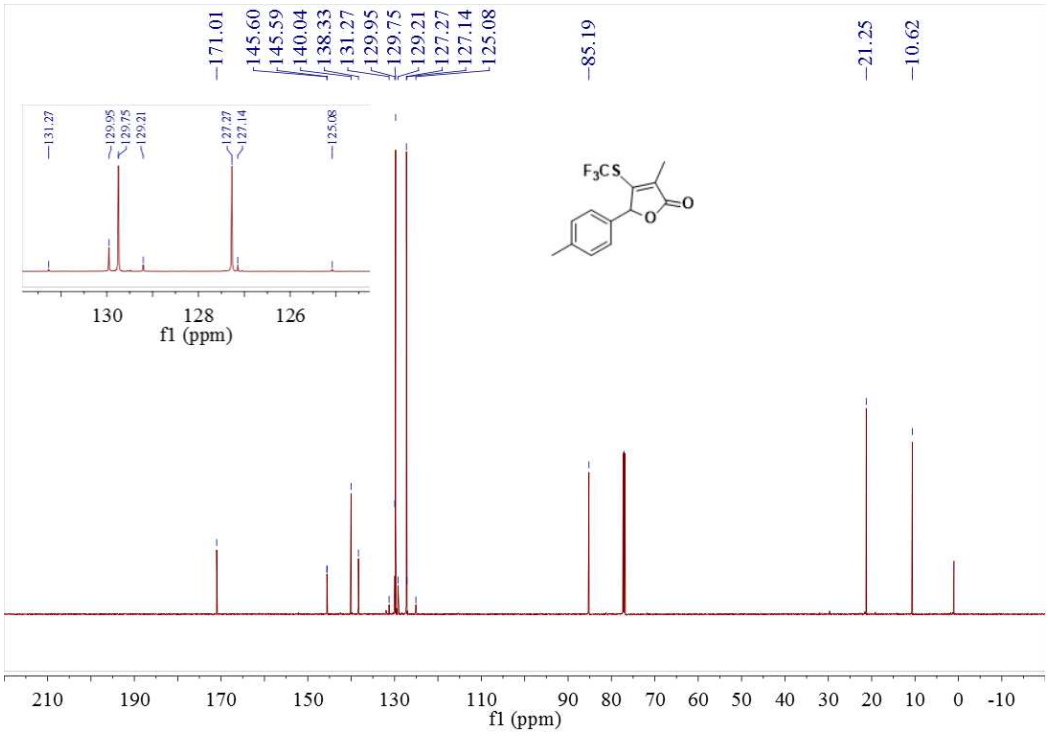
^{1}H NMR spectrum of **3b** in $CDCl_3$



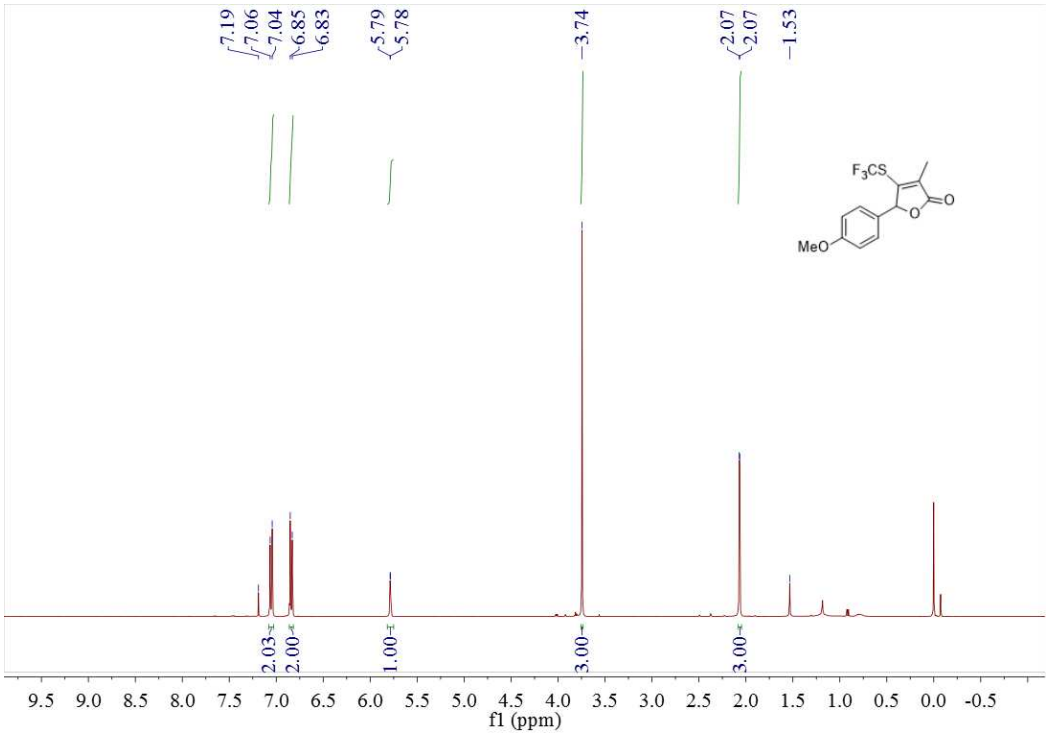
^{19}F NMR spectrum of **3b** in $CDCl_3$



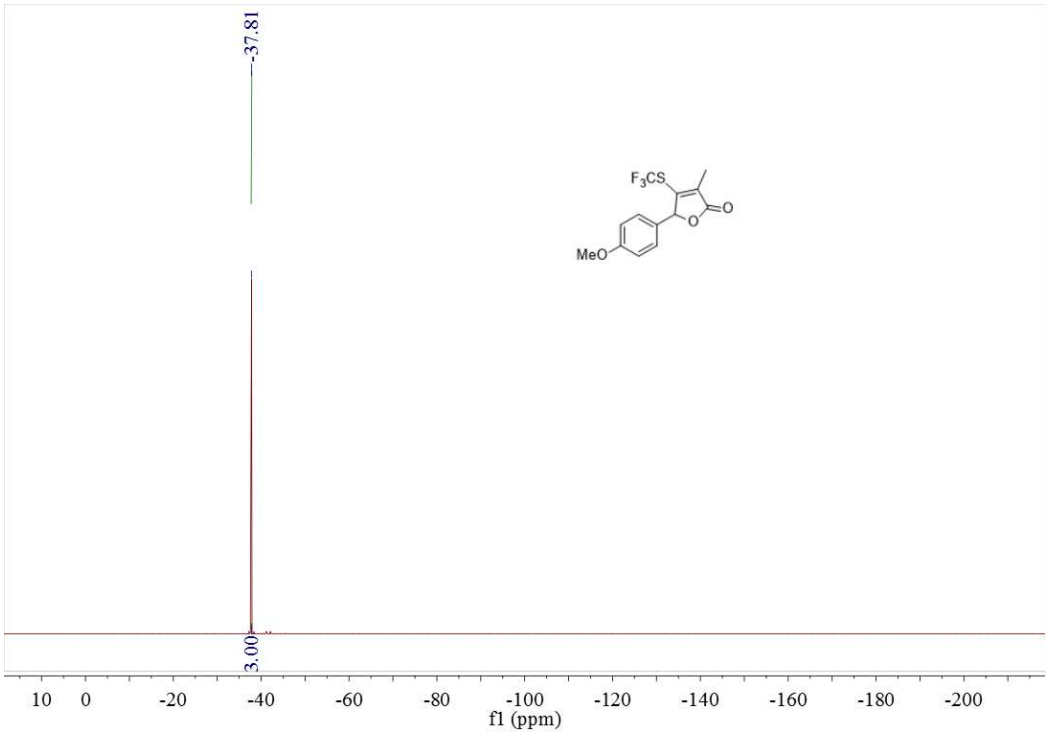
^{13}C NMR spectrum of **3b** in $CDCl_3$



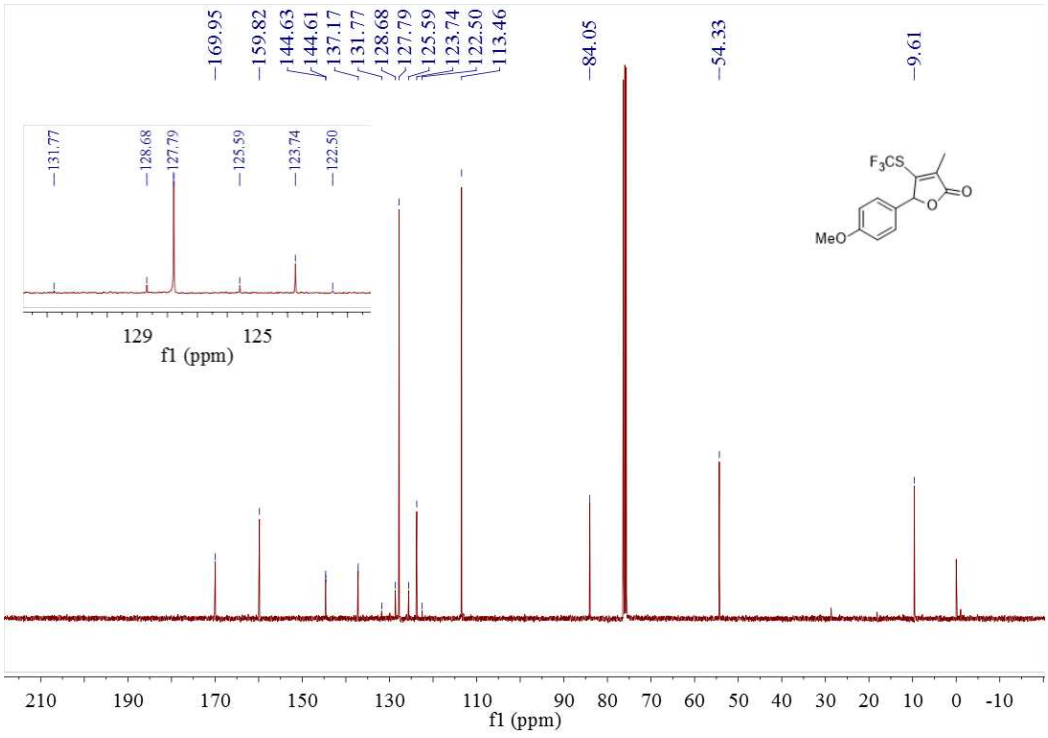
^{1}H NMR spectrum of **3c** in $CDCl_3$



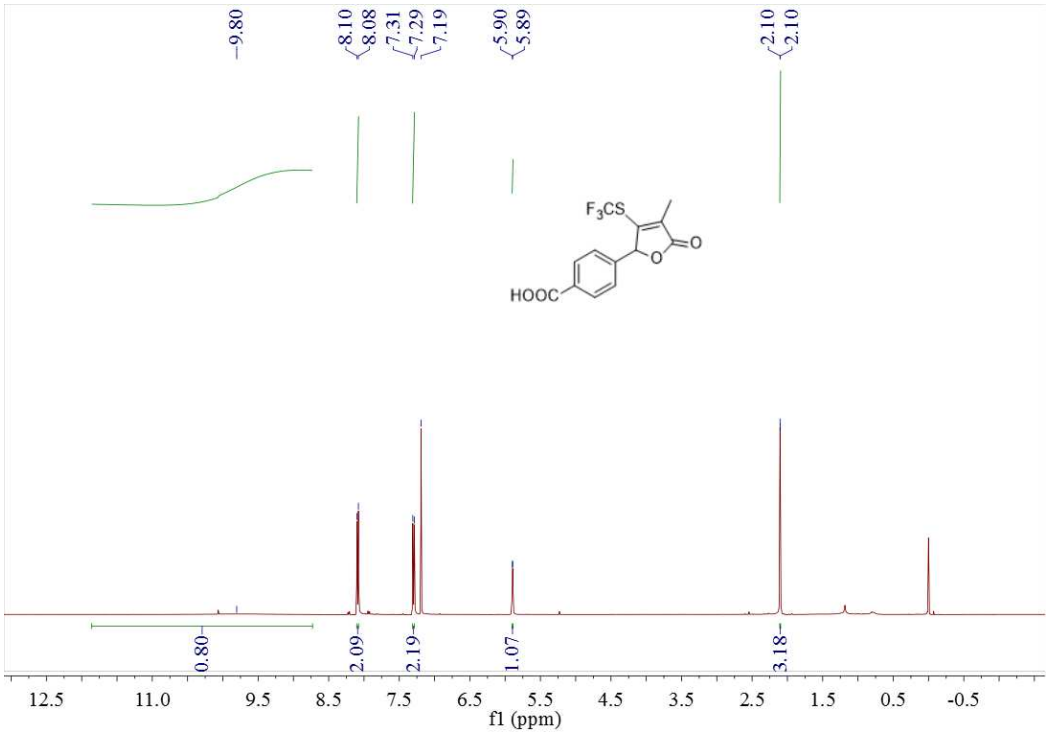
^{19}F NMR spectrum of **3c** in $CDCl_3$



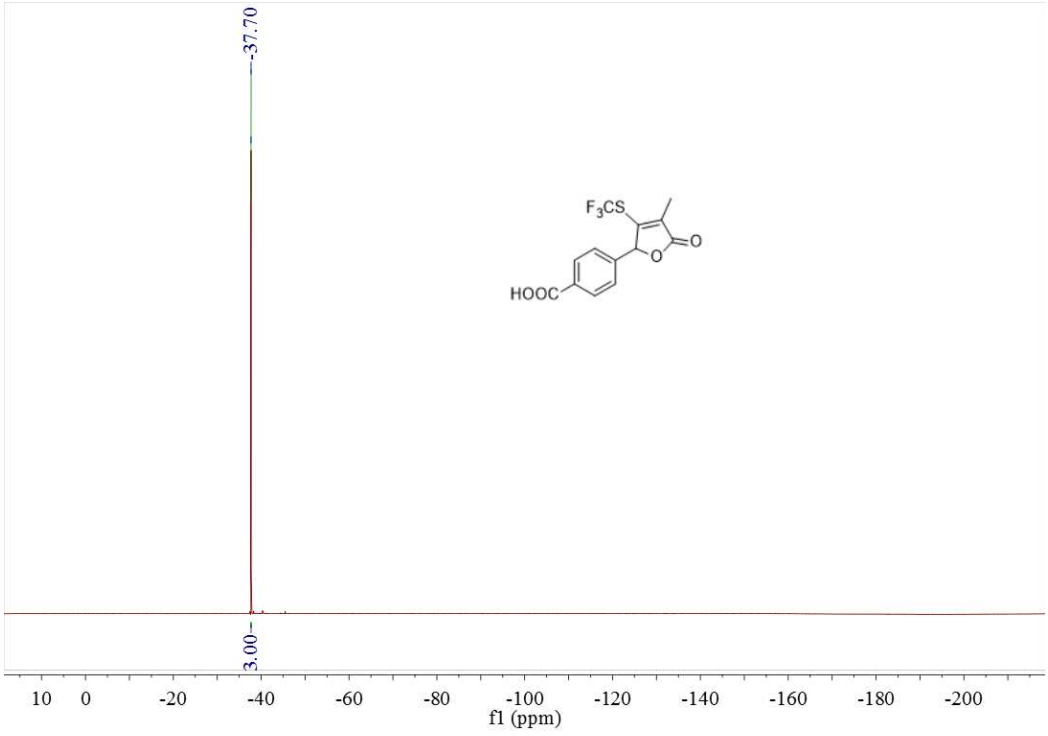
^{13}C NMR spectrum of **3c** in $CDCl_3$



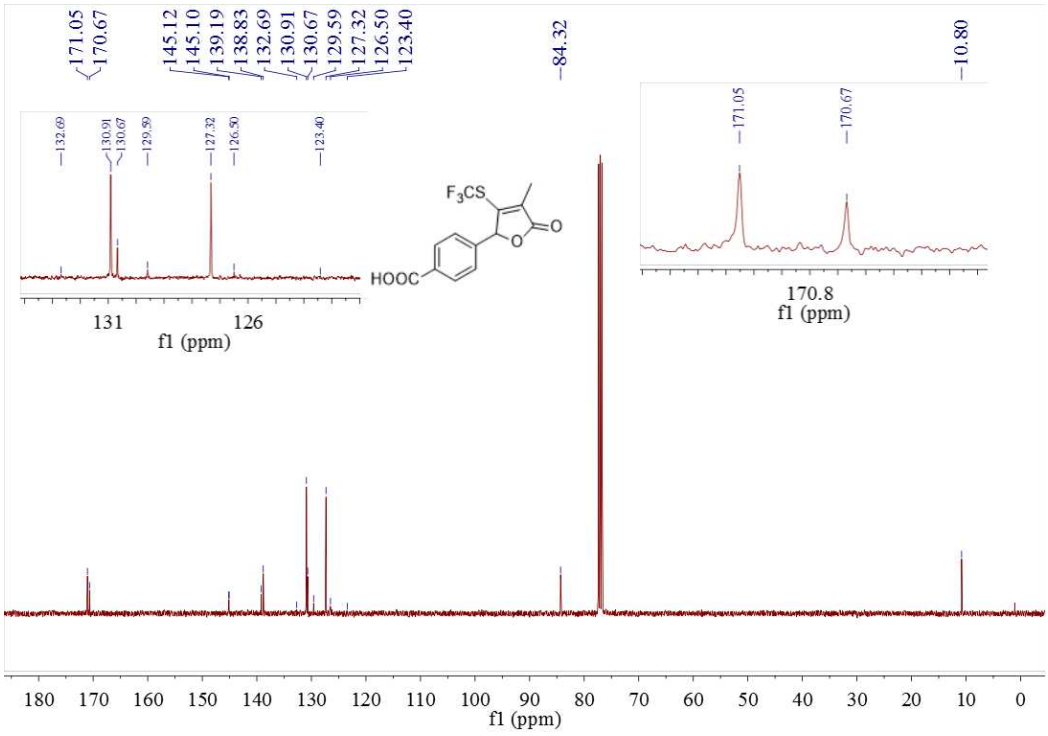
^{1}H NMR spectrum of **3d** in $CDCl_3$



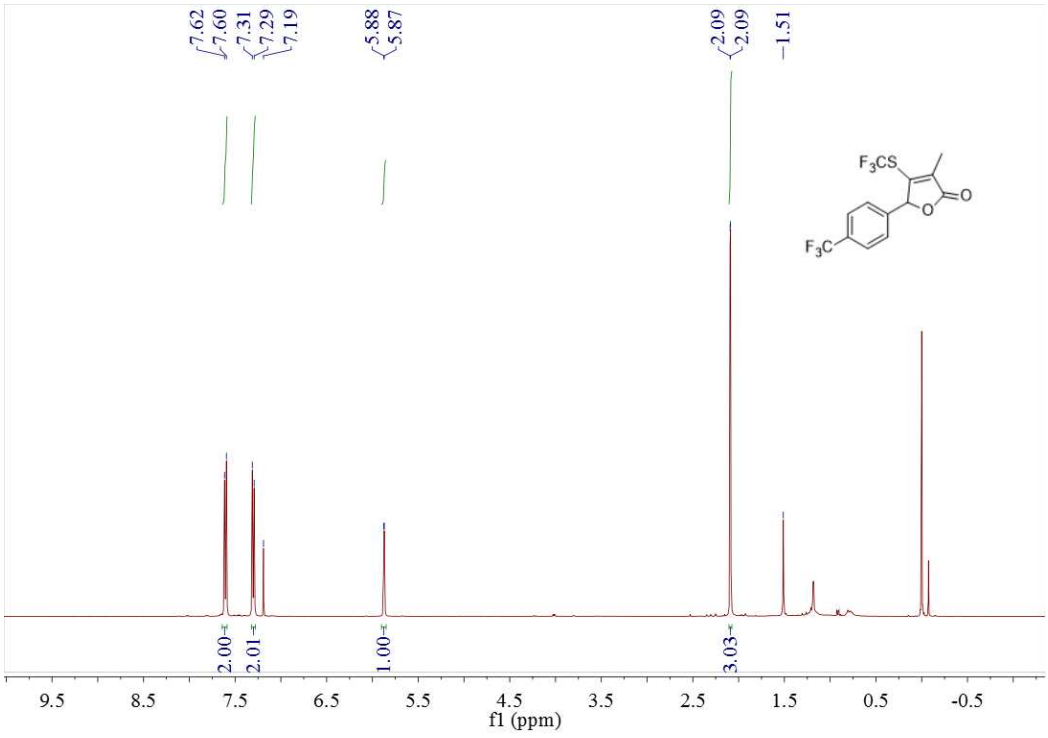
^{19}F NMR spectrum of **3d** in $CDCl_3$



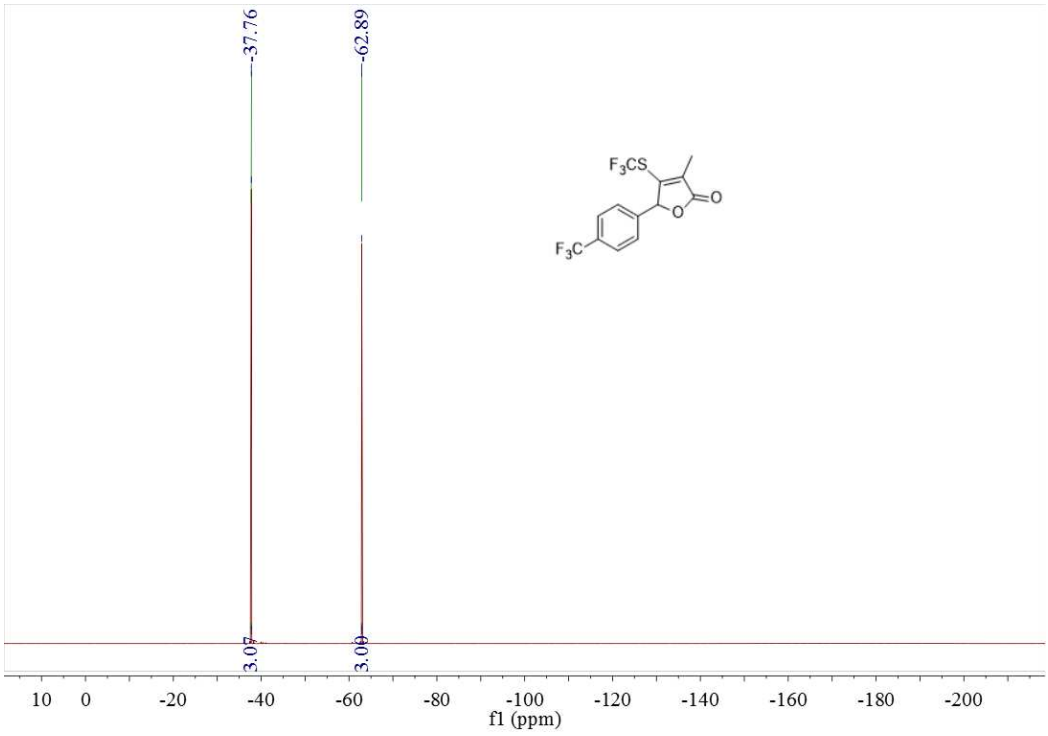
^{13}C NMR spectrum of **3d** in $CDCl_3$



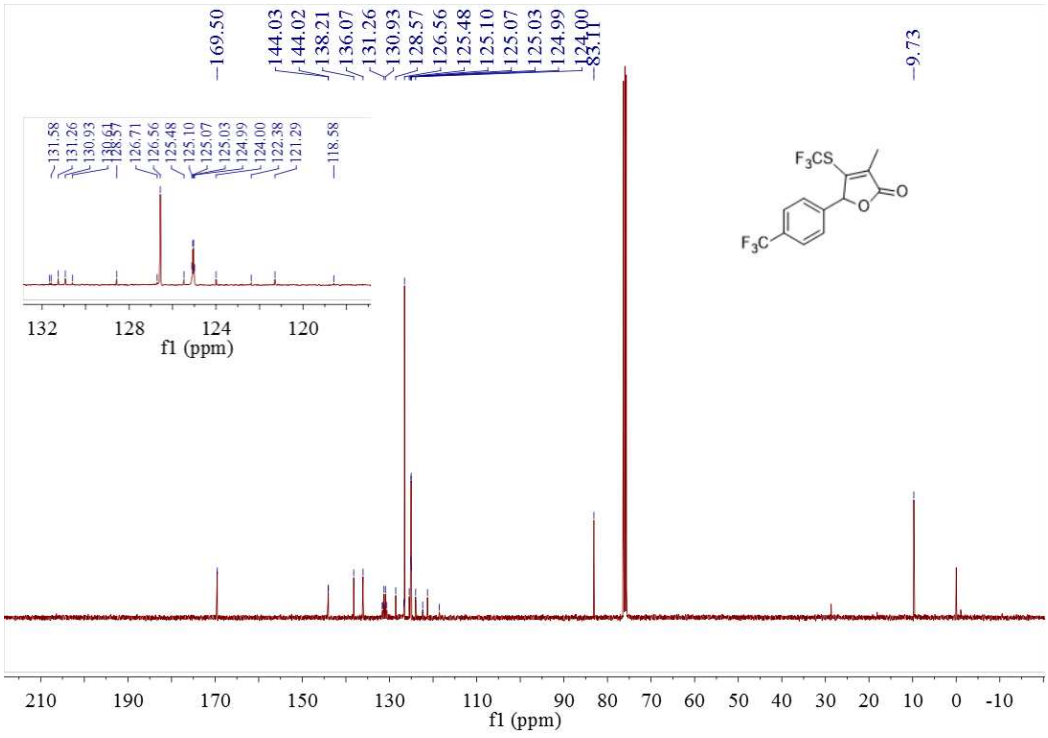
^{1}H NMR spectrum of **3e** in $CDCl_3$



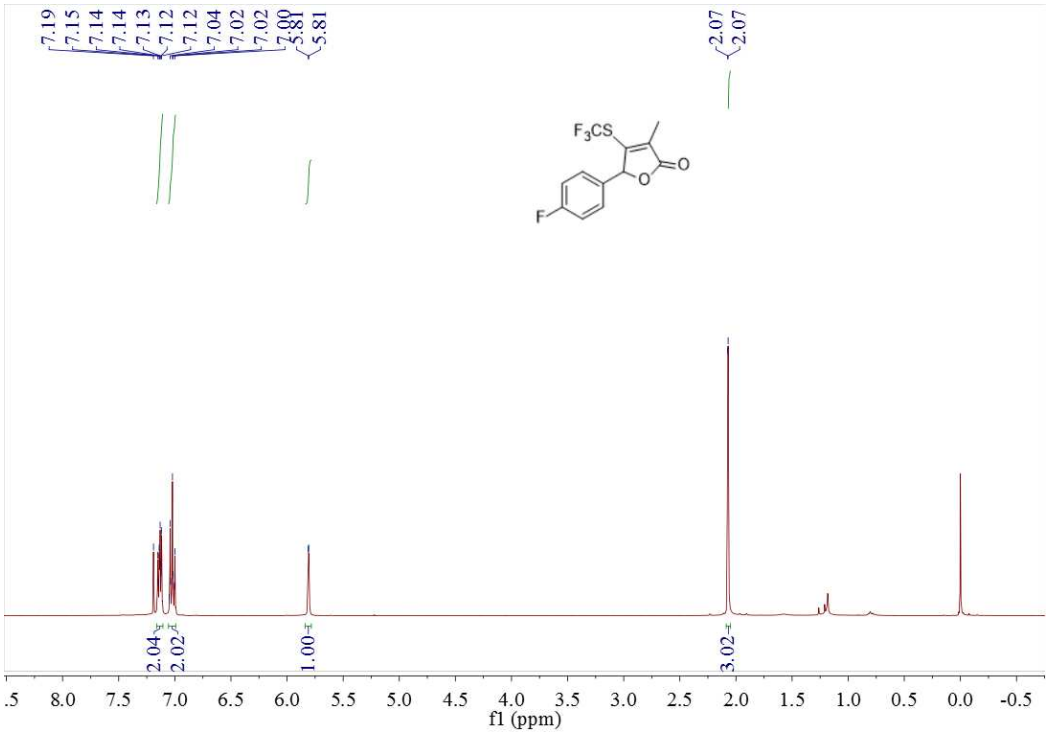
^{19}F NMR spectrum of **3e** in $CDCl_3$



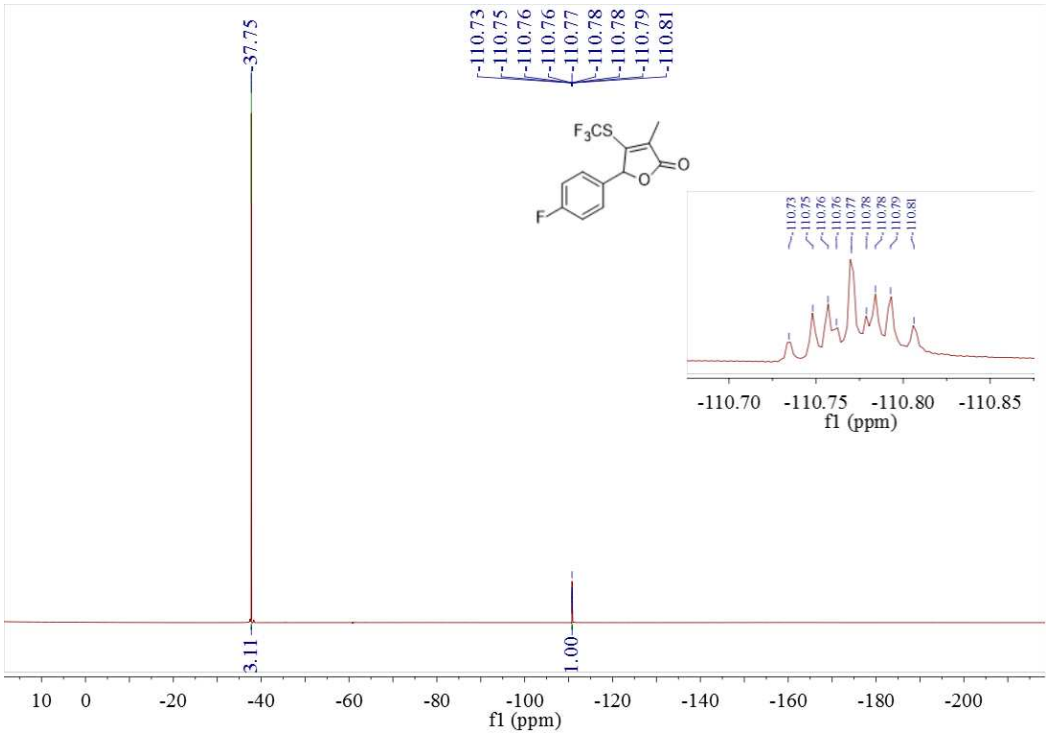
^{13}C NMR spectrum of **3e** in $CDCl_3$



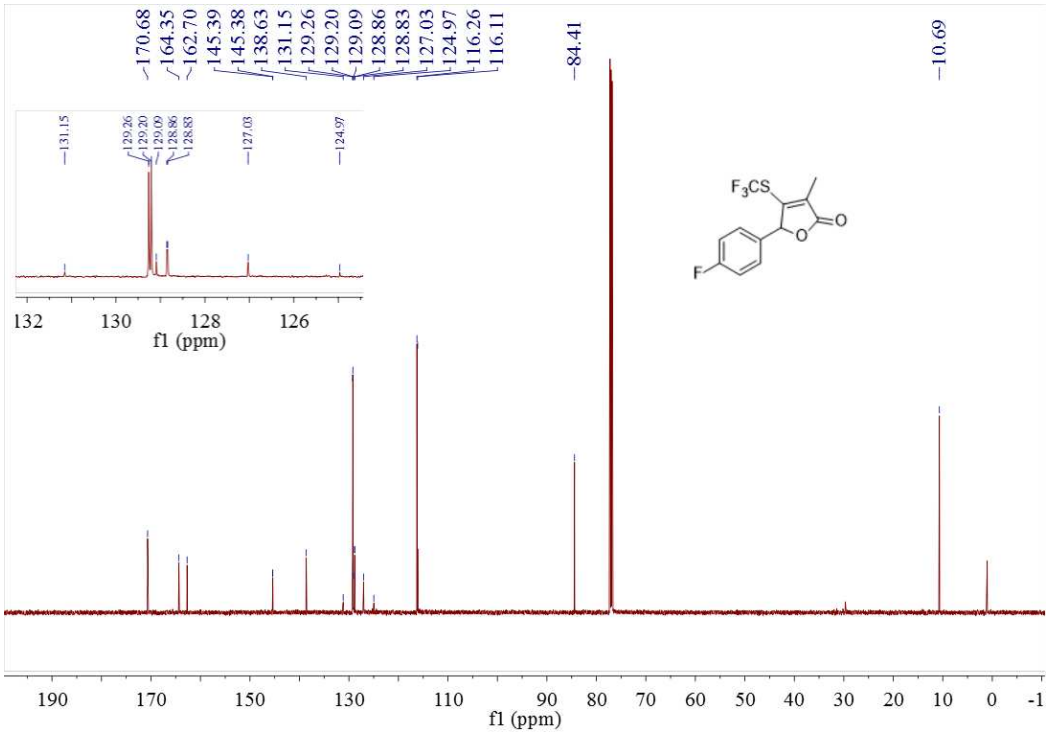
^{1}H NMR spectrum of **3f** in $CDCl_3$



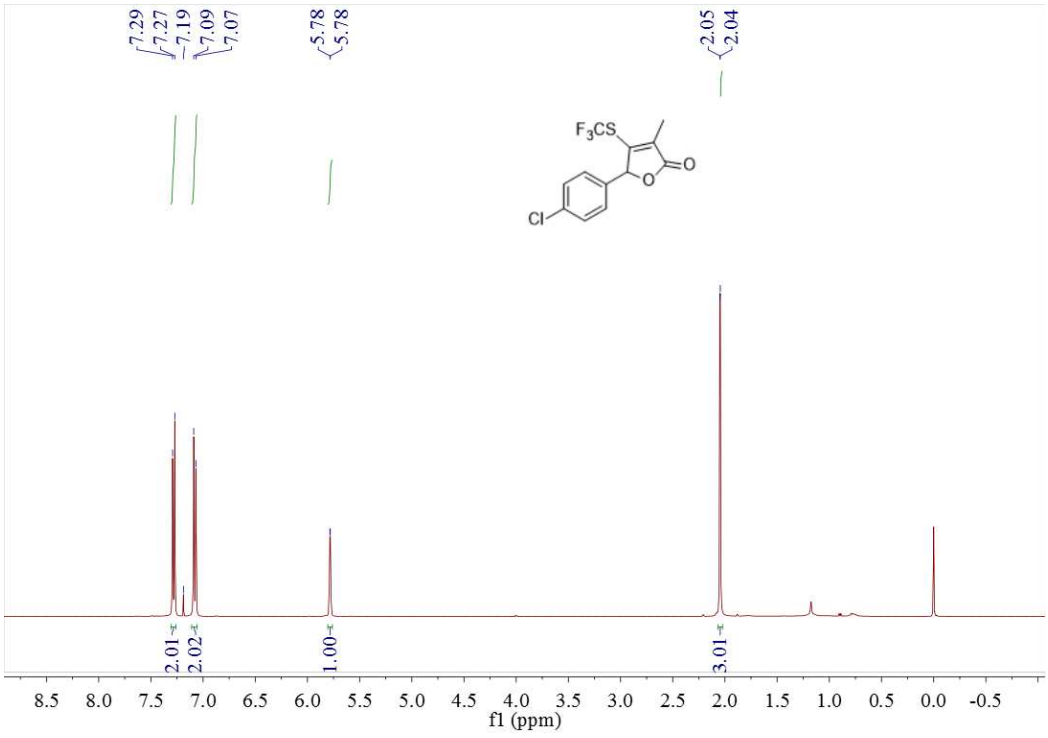
^{19}F NMR spectrum of **3f** in $CDCl_3$



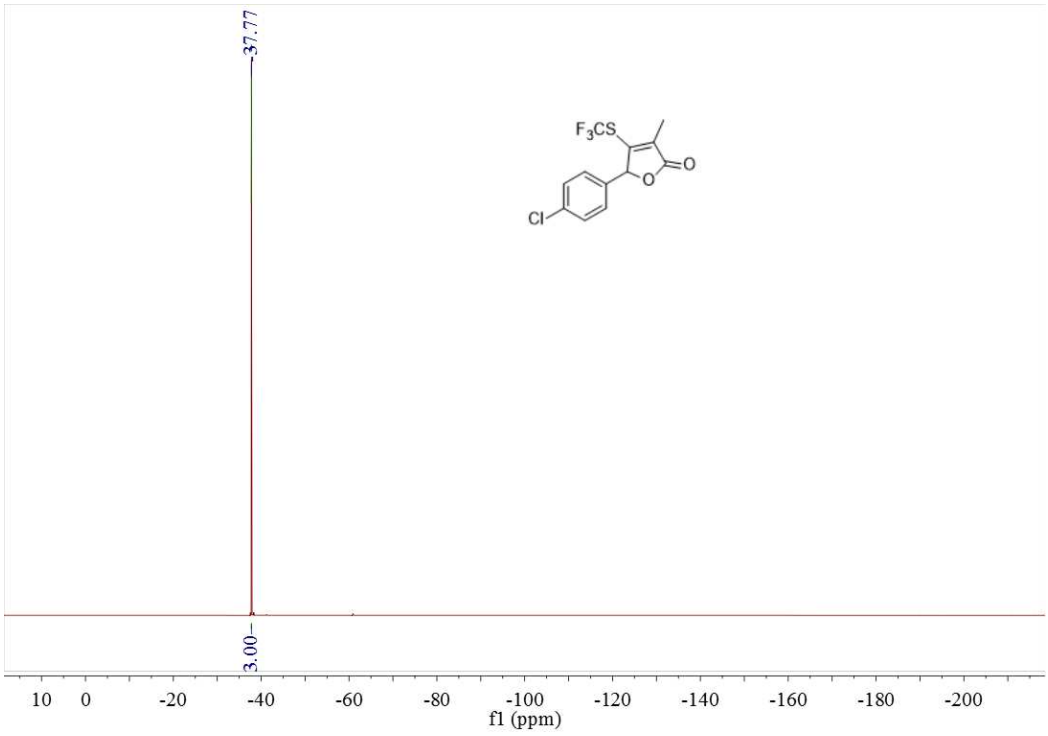
^{13}C NMR spectrum of **3f** in $CDCl_3$



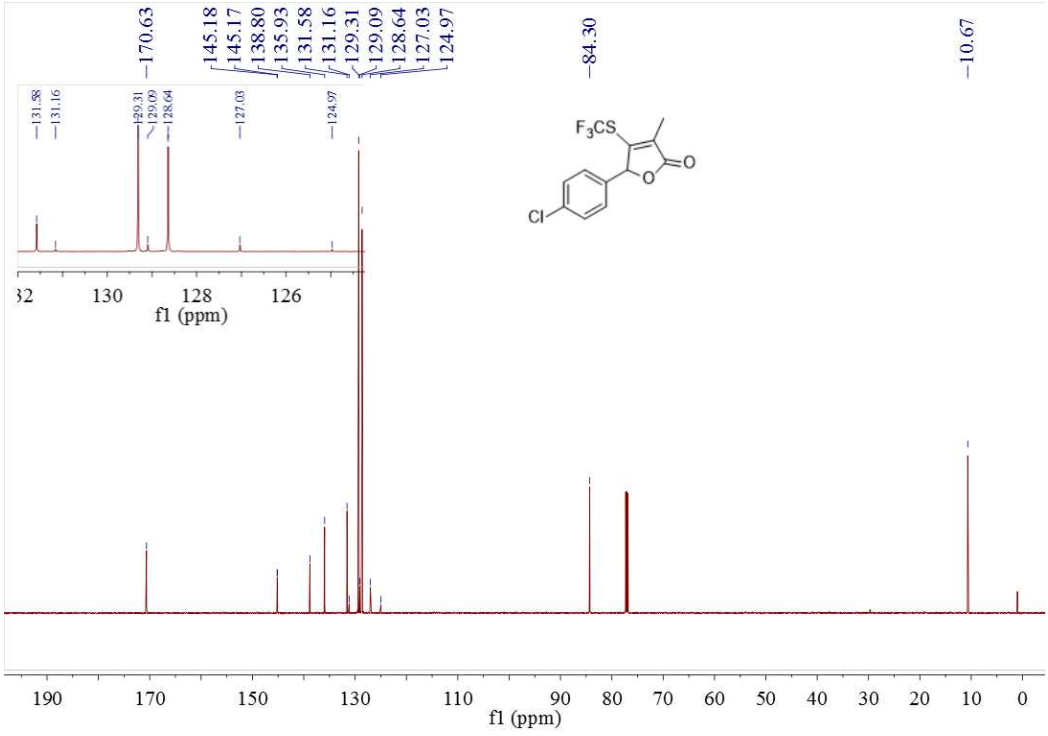
^{1}H NMR spectrum of **3g** in $CDCl_3$



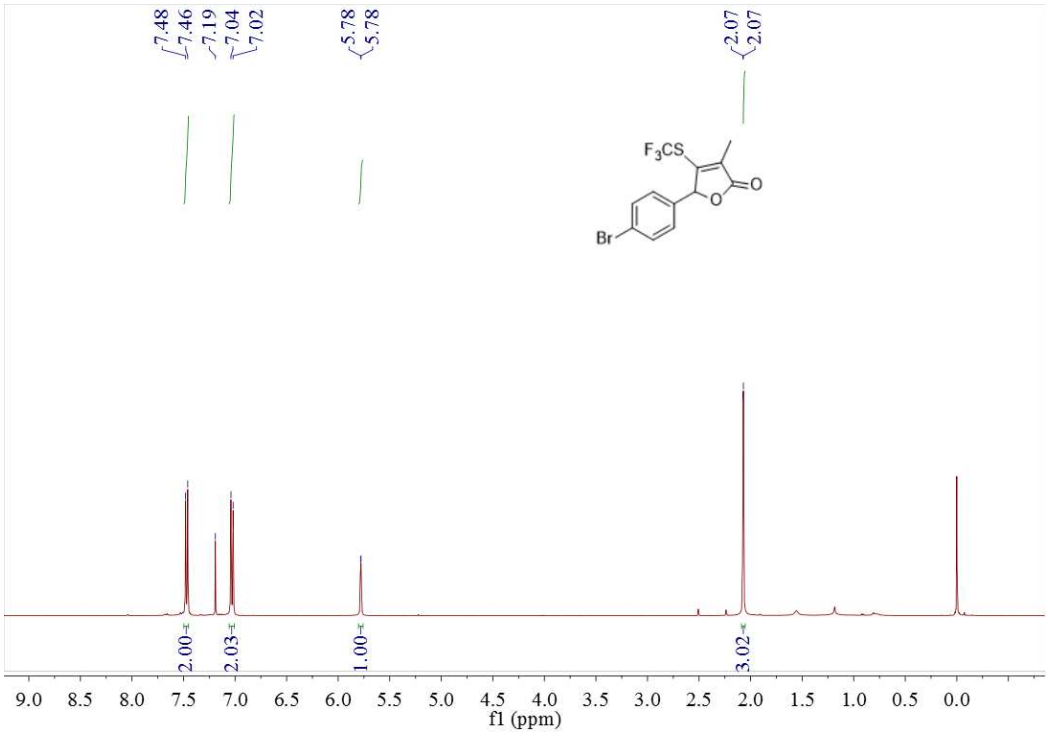
^{19}F NMR spectrum of **3g** in $CDCl_3$



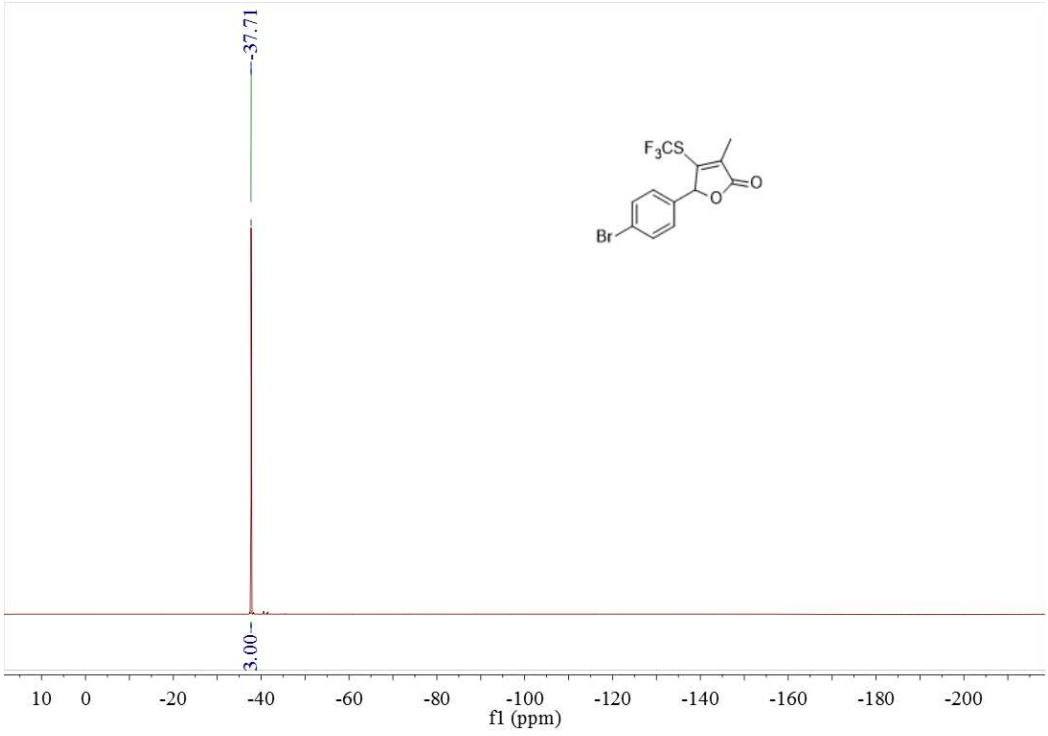
^{13}C NMR spectrum of **3g** in $CDCl_3$



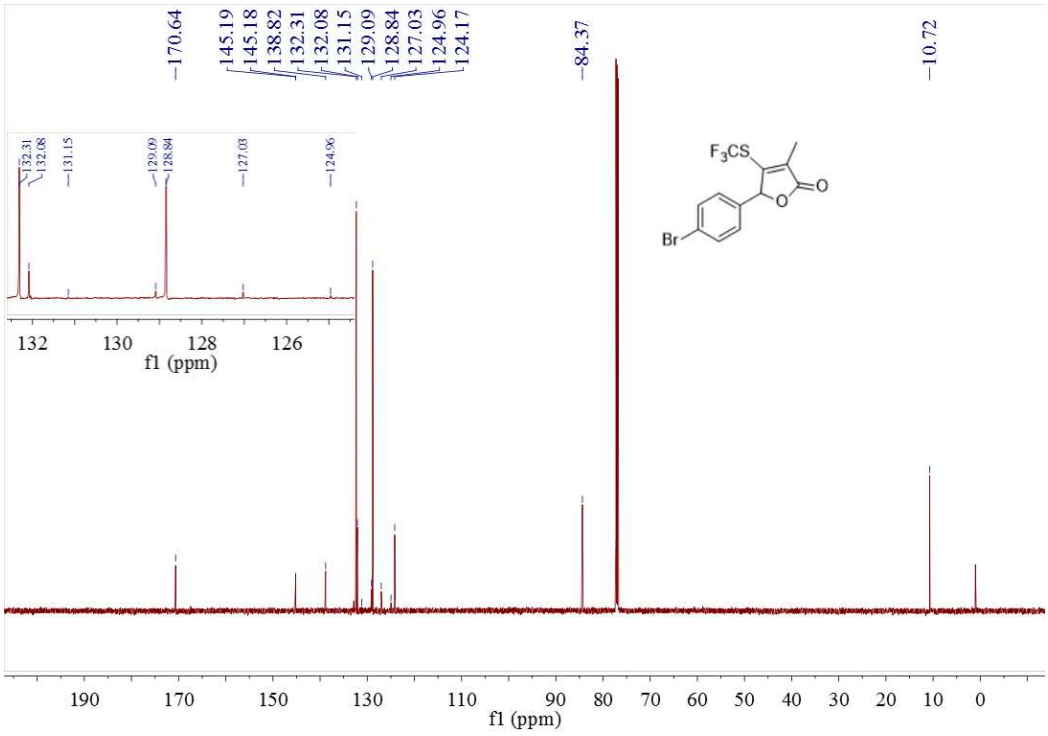
^{1}H NMR spectrum of **3h** in $CDCl_3$



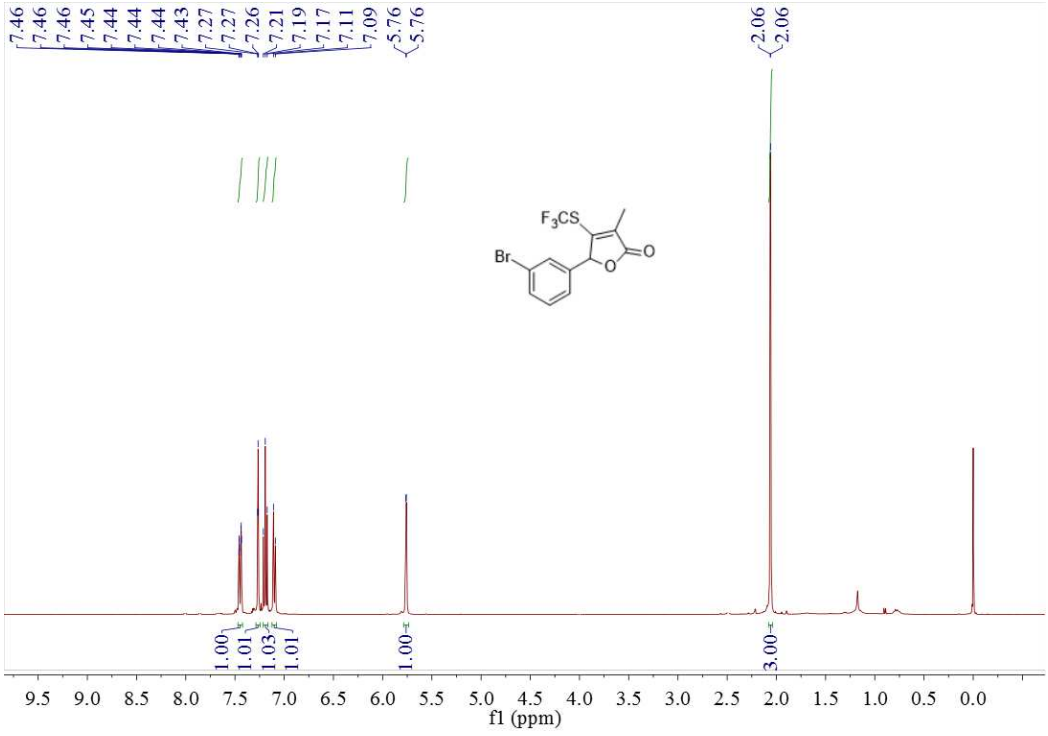
^{19}F NMR spectrum of **3h** in $CDCl_3$



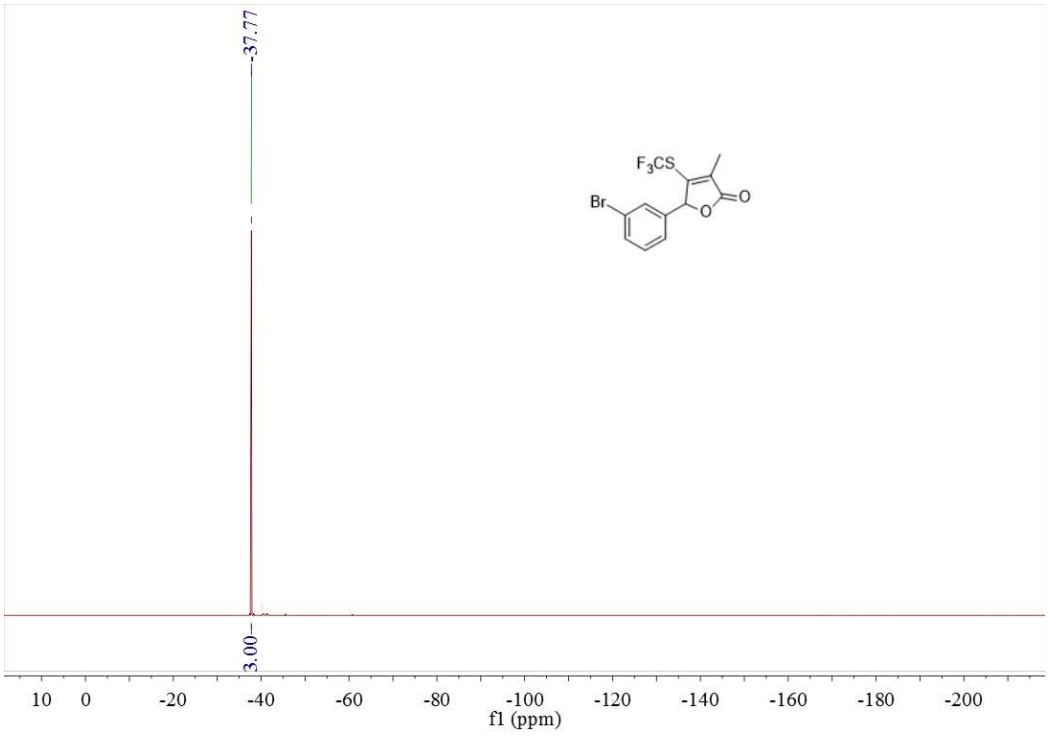
^{13}C NMR spectrum of **3h** in $CDCl_3$



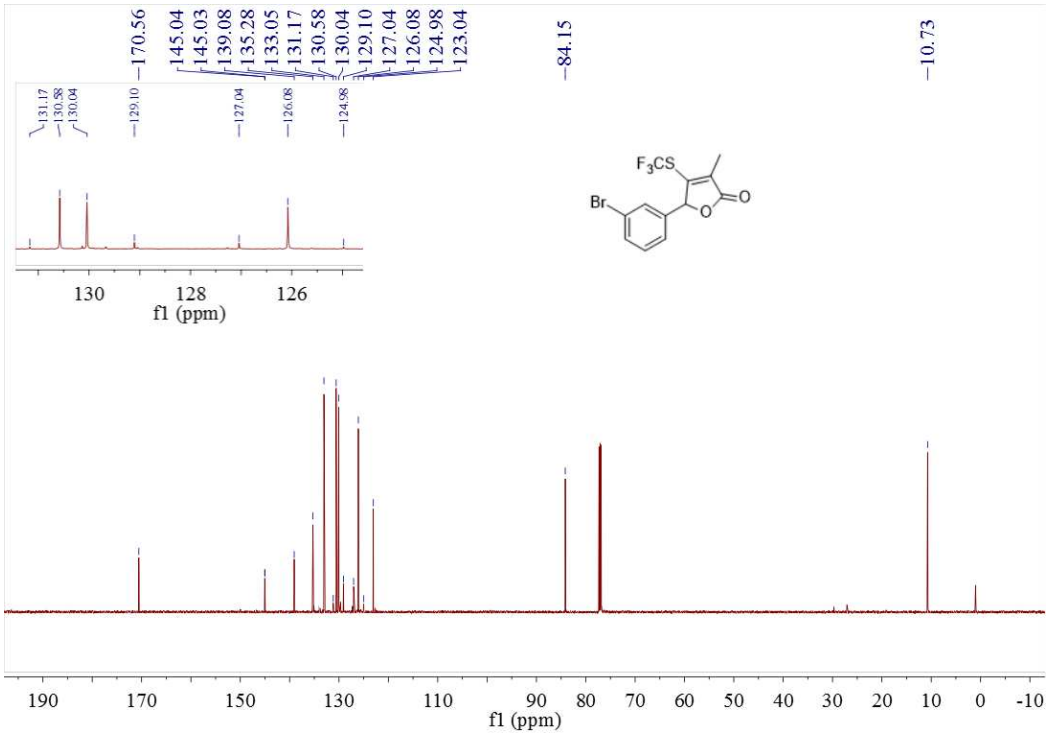
^{1}H NMR spectrum of **3i** in $CDCl_3$



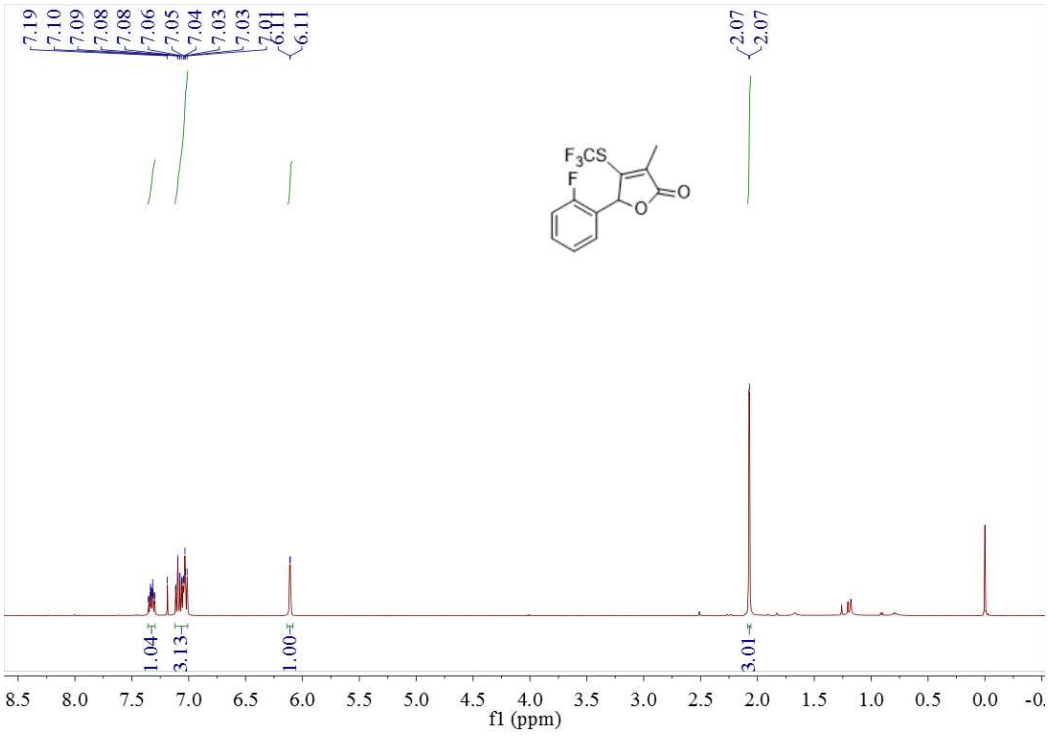
^{19}F NMR spectrum of **3i** in $CDCl_3$



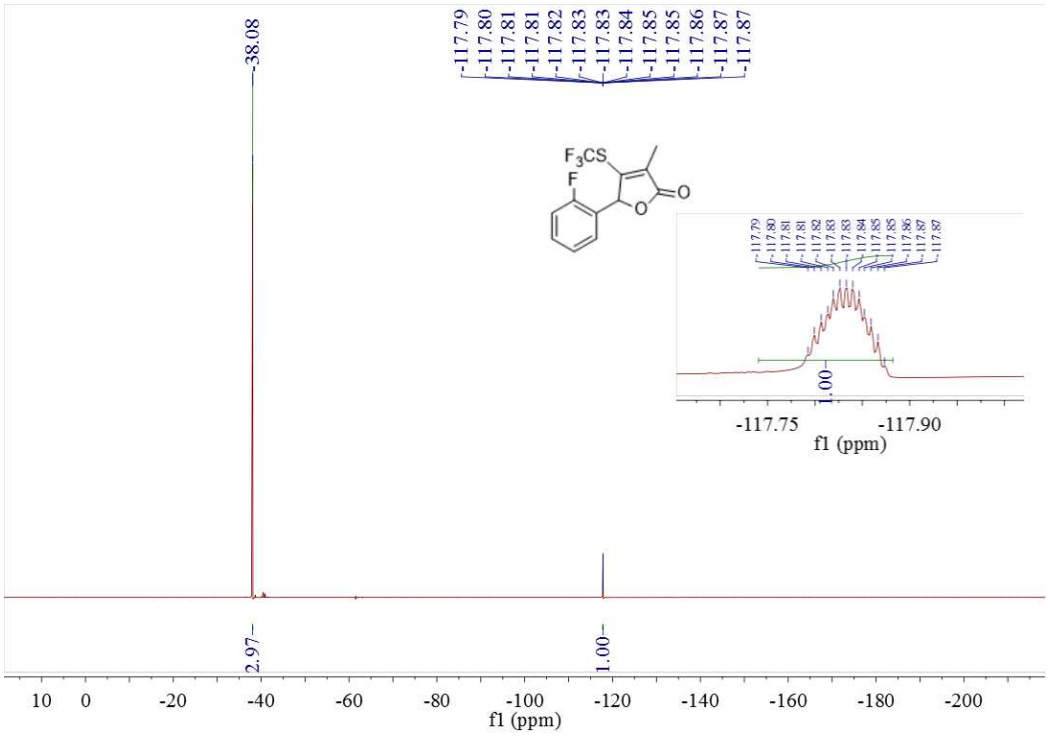
^{13}C NMR spectrum of **3i** in $CDCl_3$



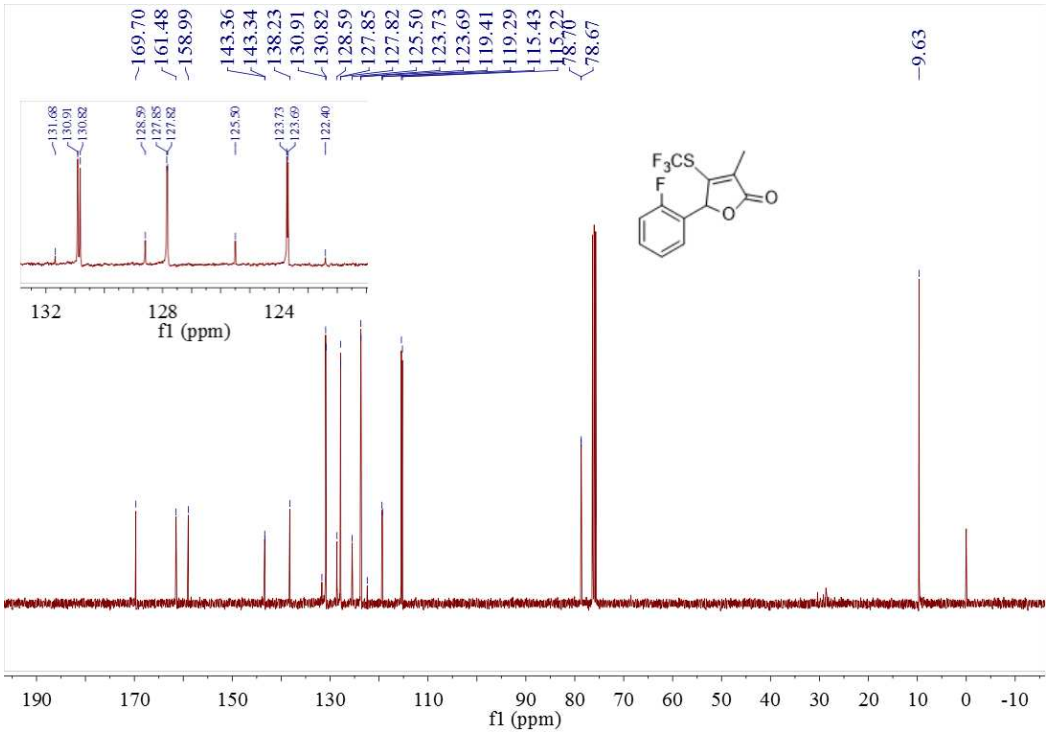
^{1}H NMR spectrum of **3j** in $CDCl_3$



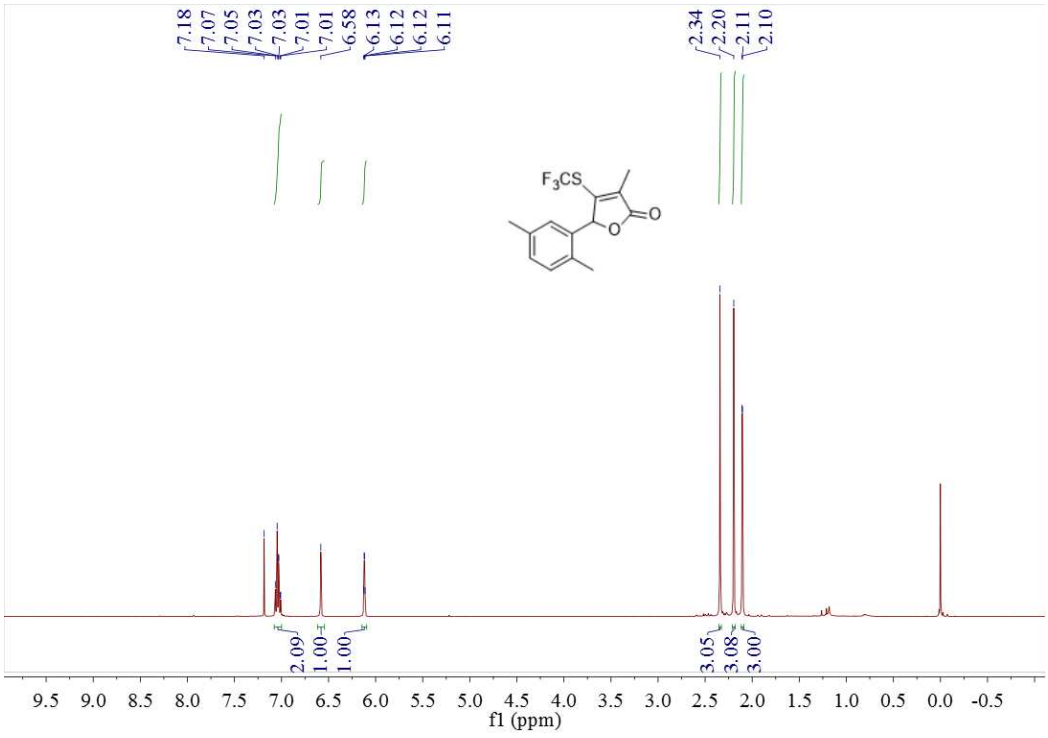
^{19}F NMR spectrum of **3j** in $CDCl_3$



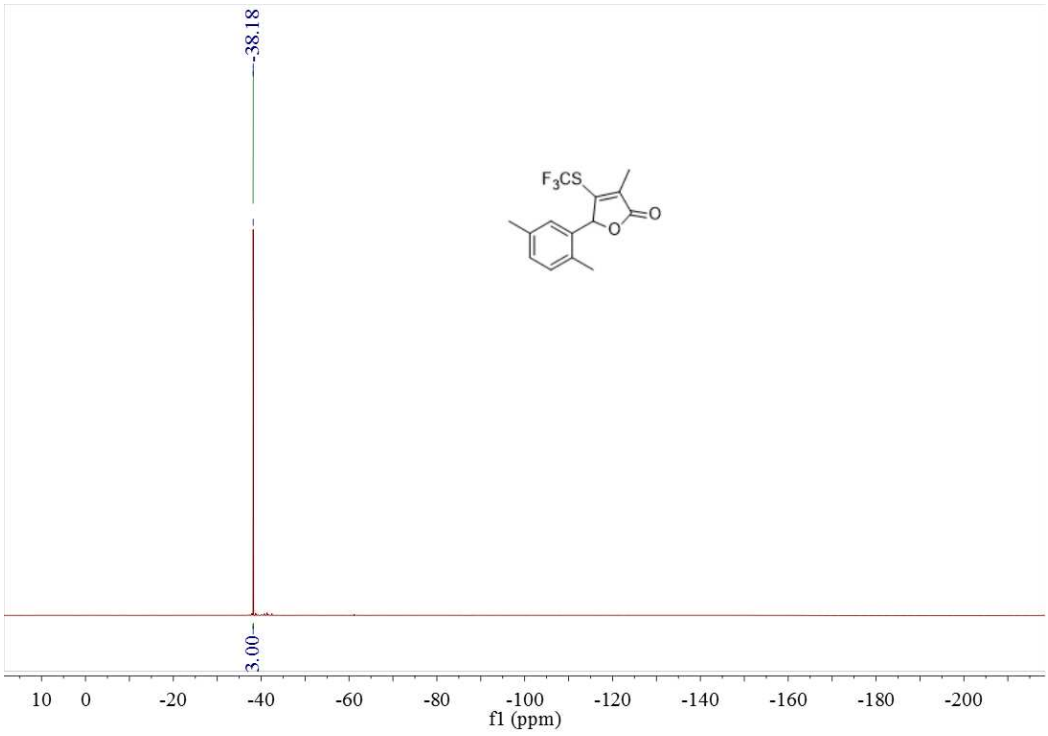
^{13}C NMR spectrum of **3j** in $CDCl_3$



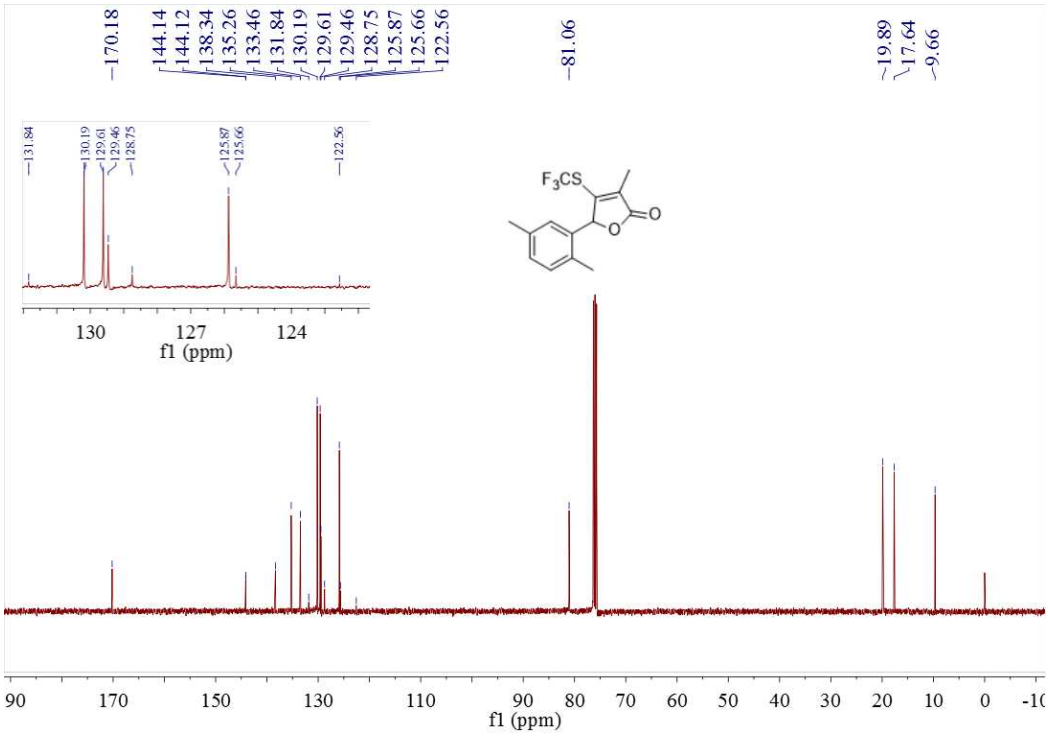
^{1}H NMR spectrum of **3k** in $CDCl_3$



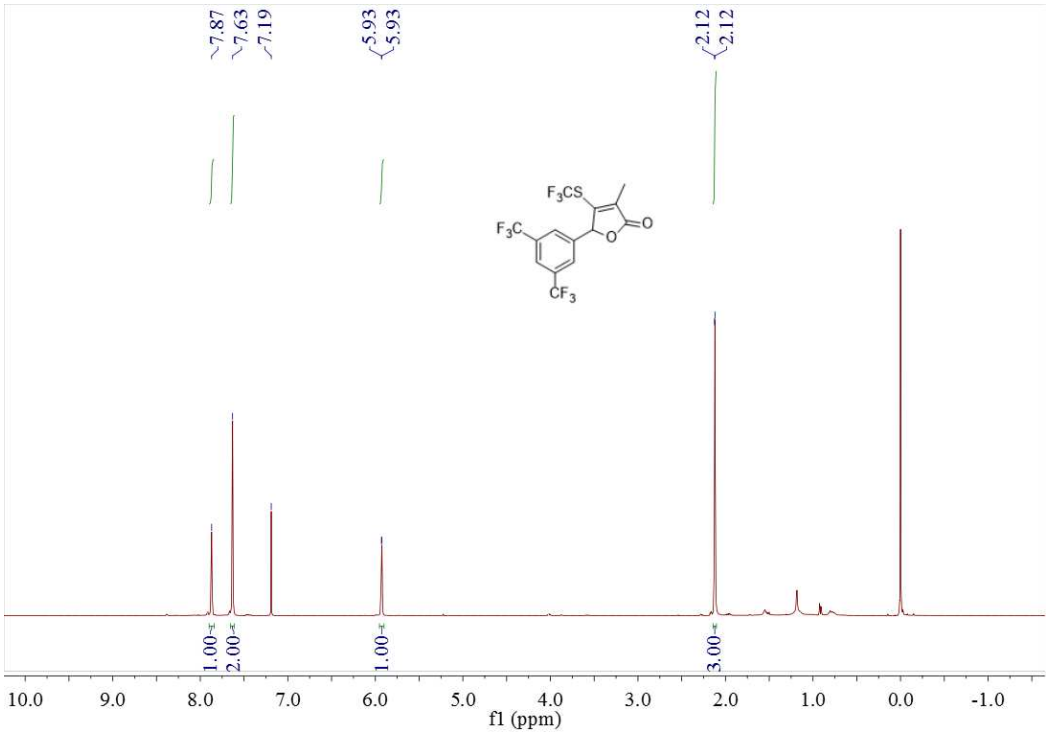
^{19}F NMR spectrum of **3k** in $CDCl_3$



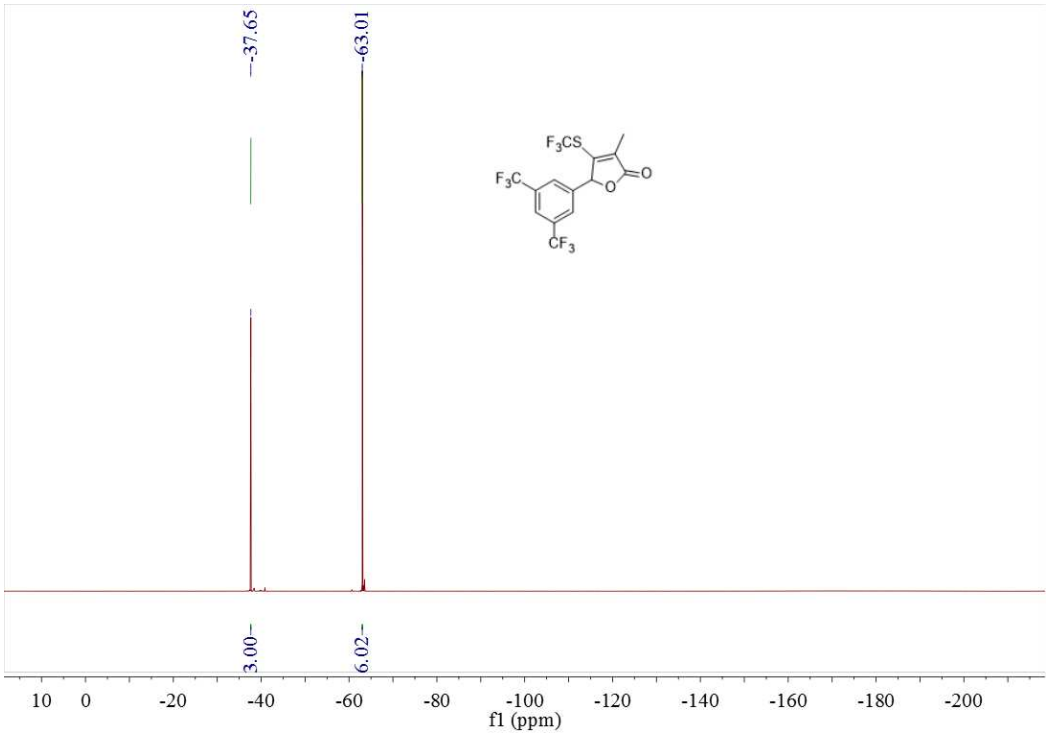
^{13}C NMR spectrum of **3k** in $CDCl_3$



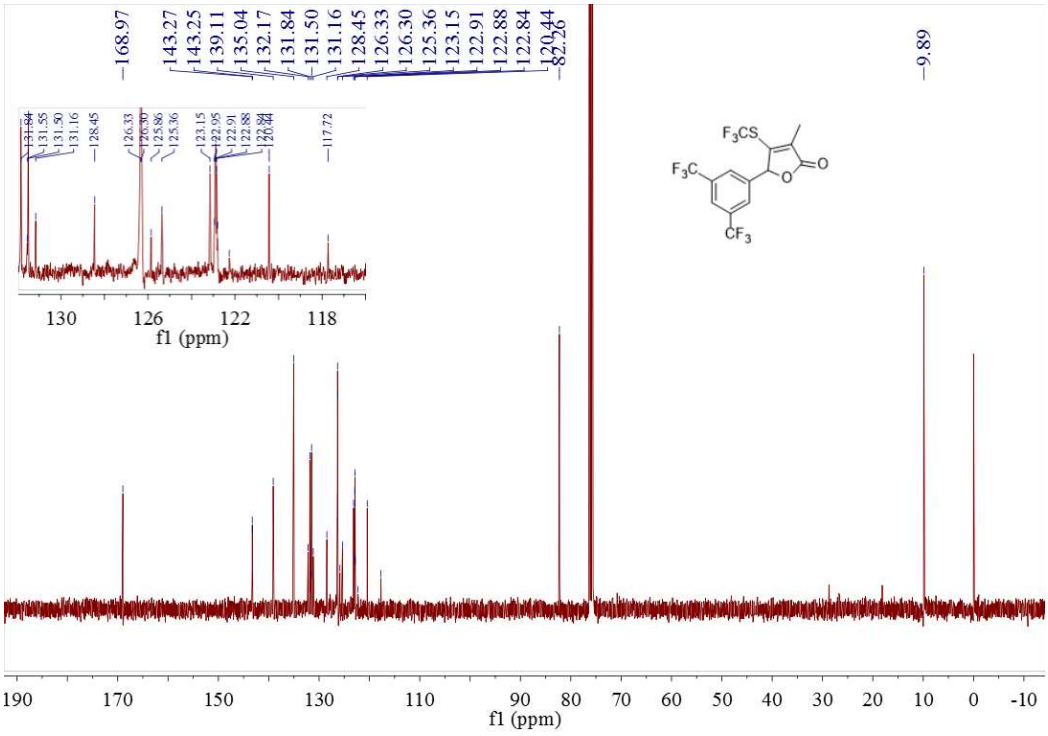
^{1}H NMR spectrum of **3l** in $CDCl_3$



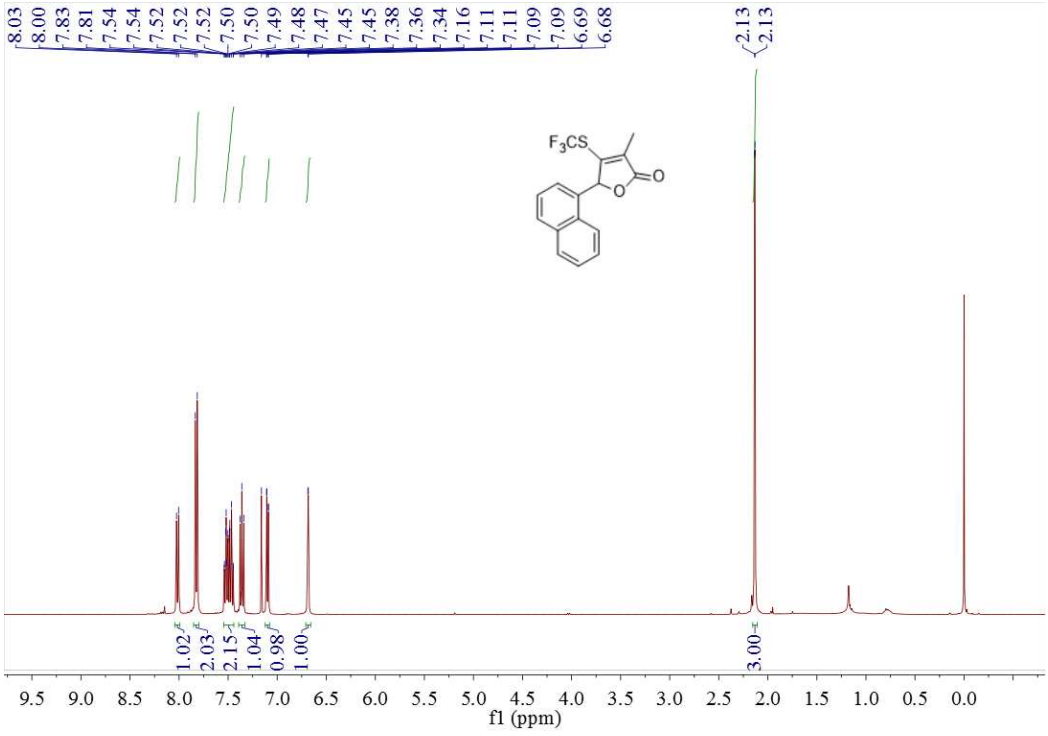
^{19}F NMR spectrum of **3l** in $CDCl_3$



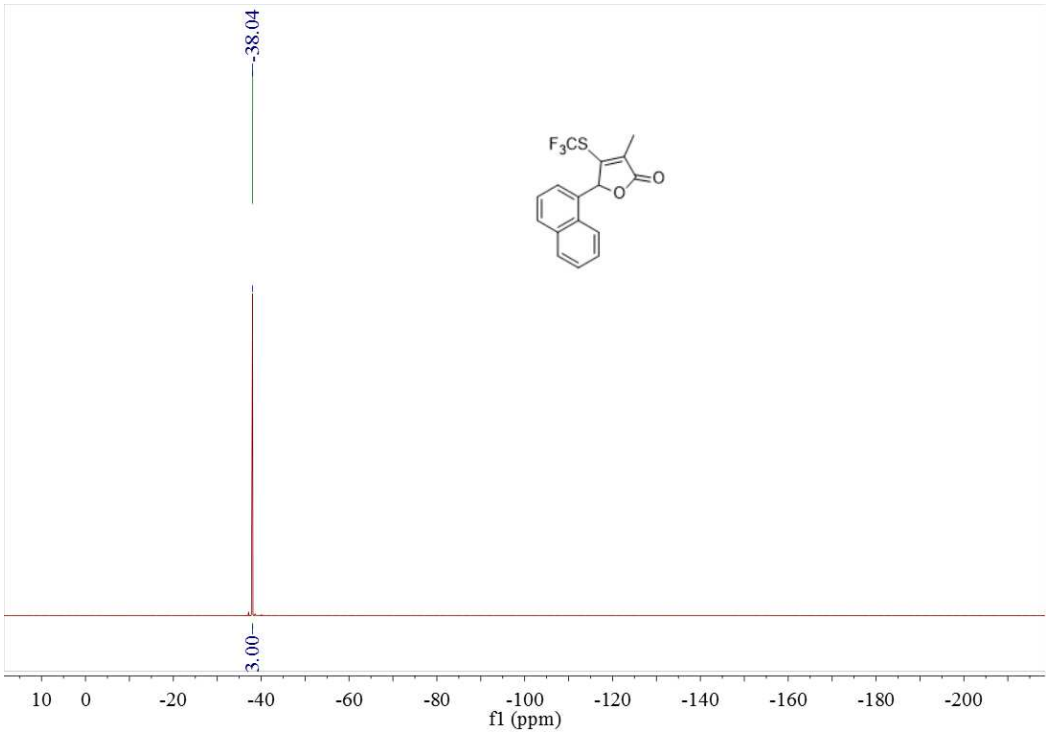
^{13}C NMR spectrum of **3l** in $CDCl_3$



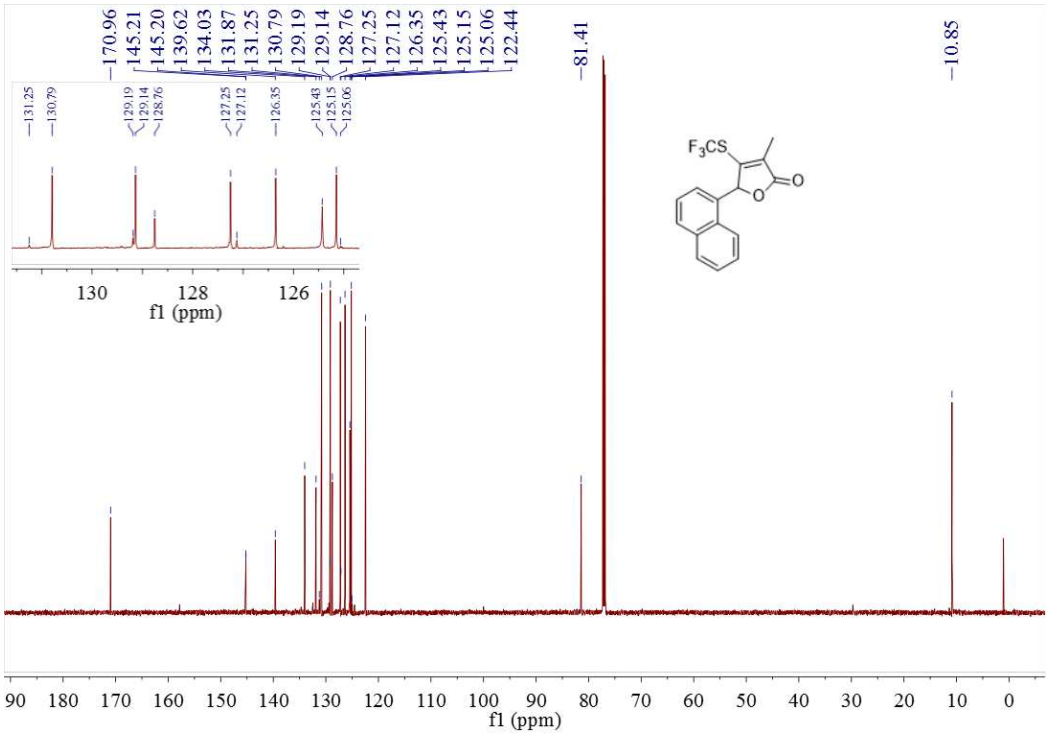
^{1}H NMR spectrum of **3m** in $CDCl_3$



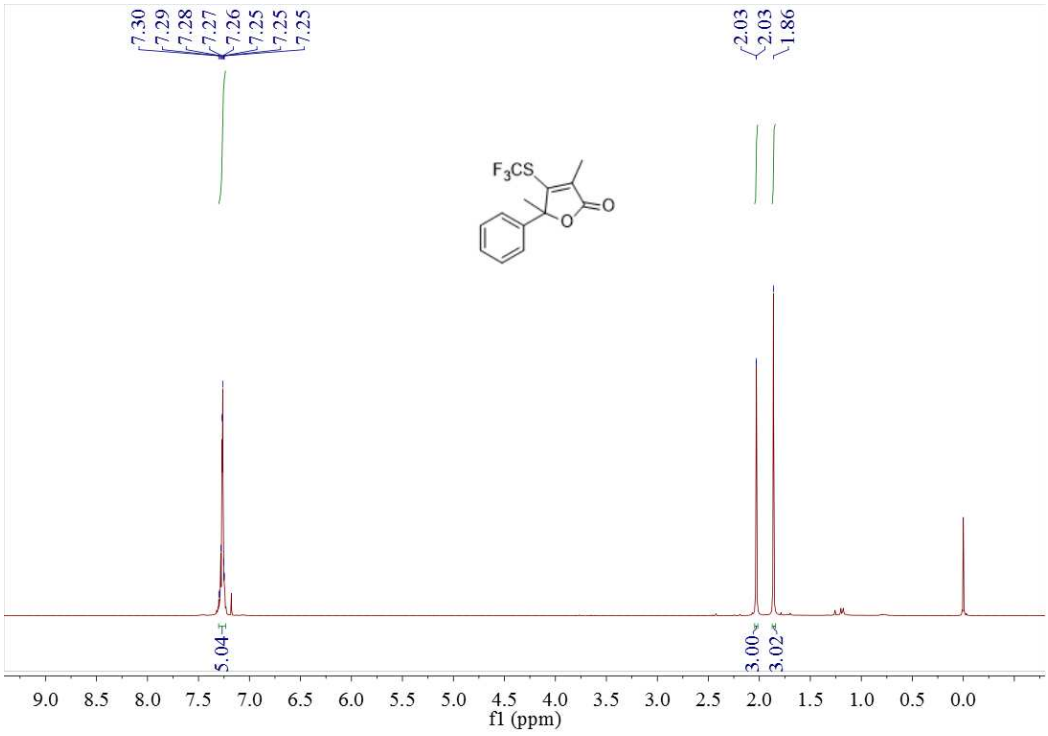
^{19}F NMR spectrum of **3m** in $CDCl_3$



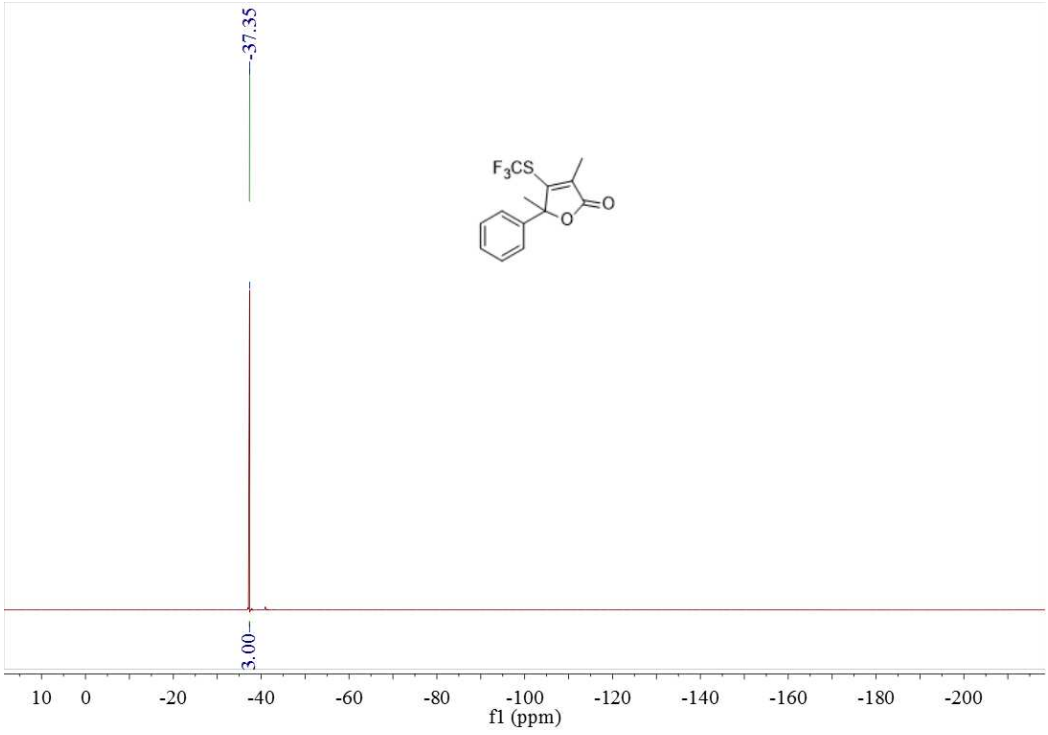
^{13}C NMR spectrum of **3m** in $CDCl_3$



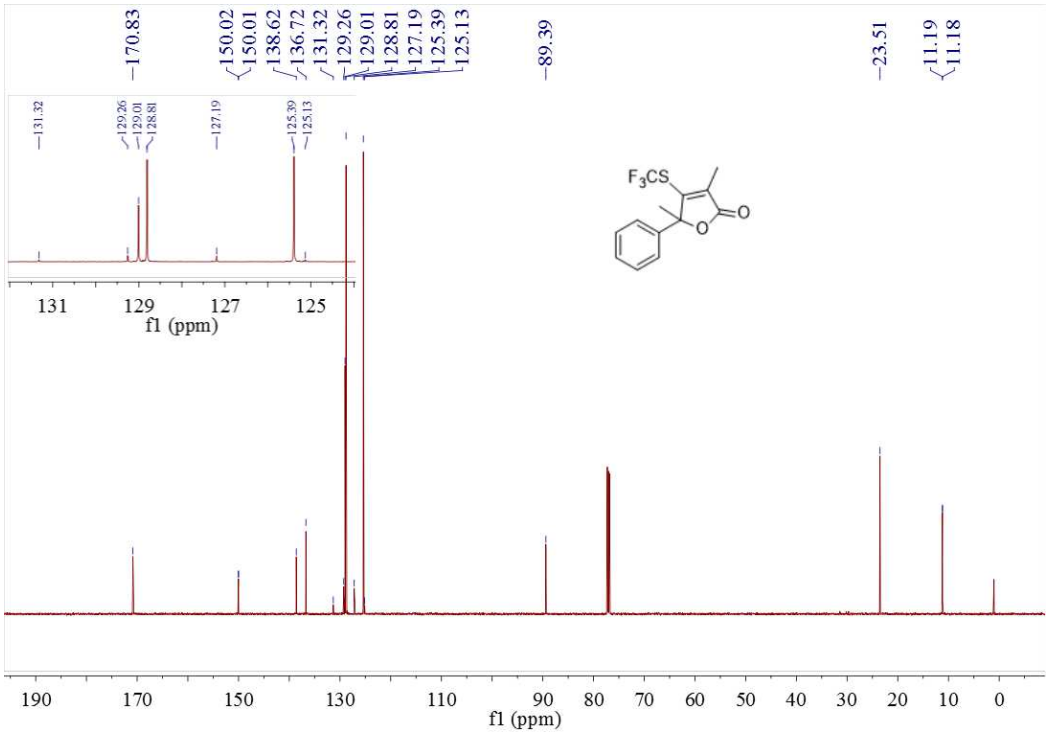
^{1}H NMR spectrum of **3n** in $CDCl_3$



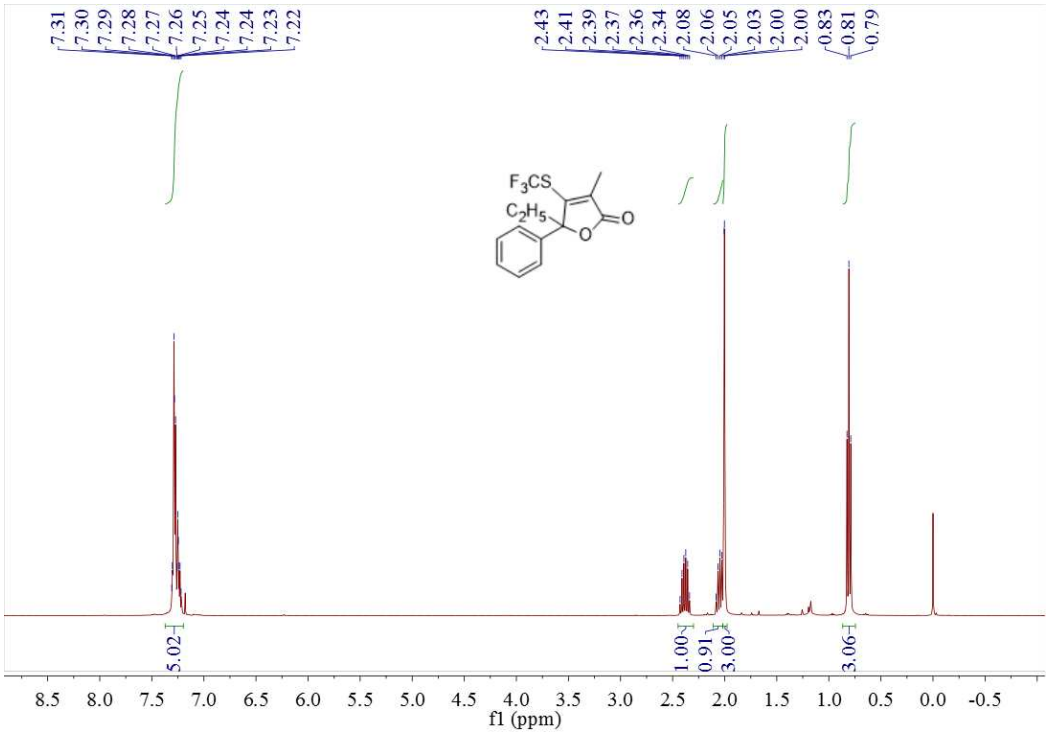
^{19}F NMR spectrum of **3n** in $CDCl_3$



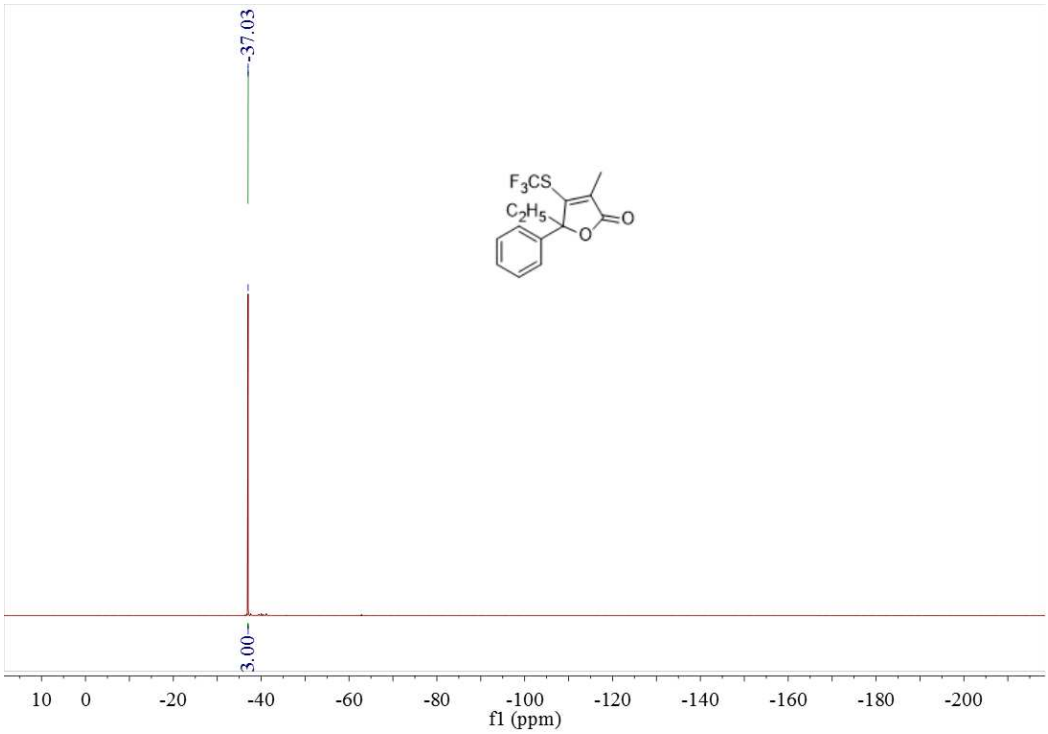
^{13}C NMR spectrum of **3n** in $CDCl_3$



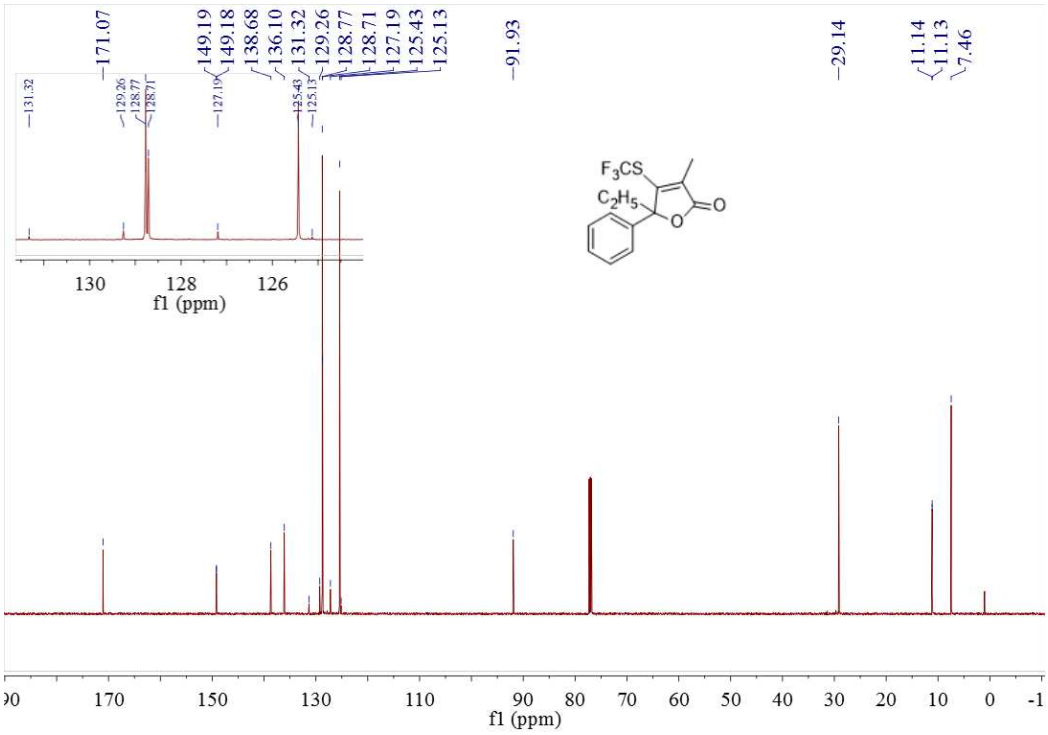
^{1}H NMR spectrum of **3o** in $CDCl_3$



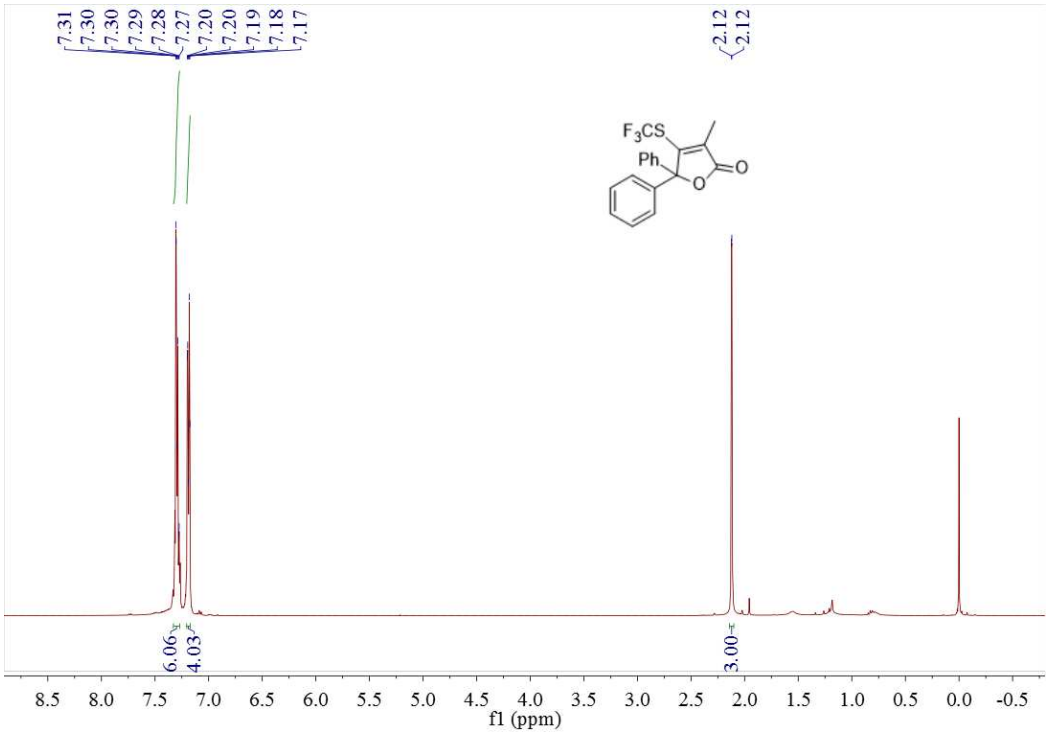
^{19}F NMR spectrum of **3o** in $CDCl_3$



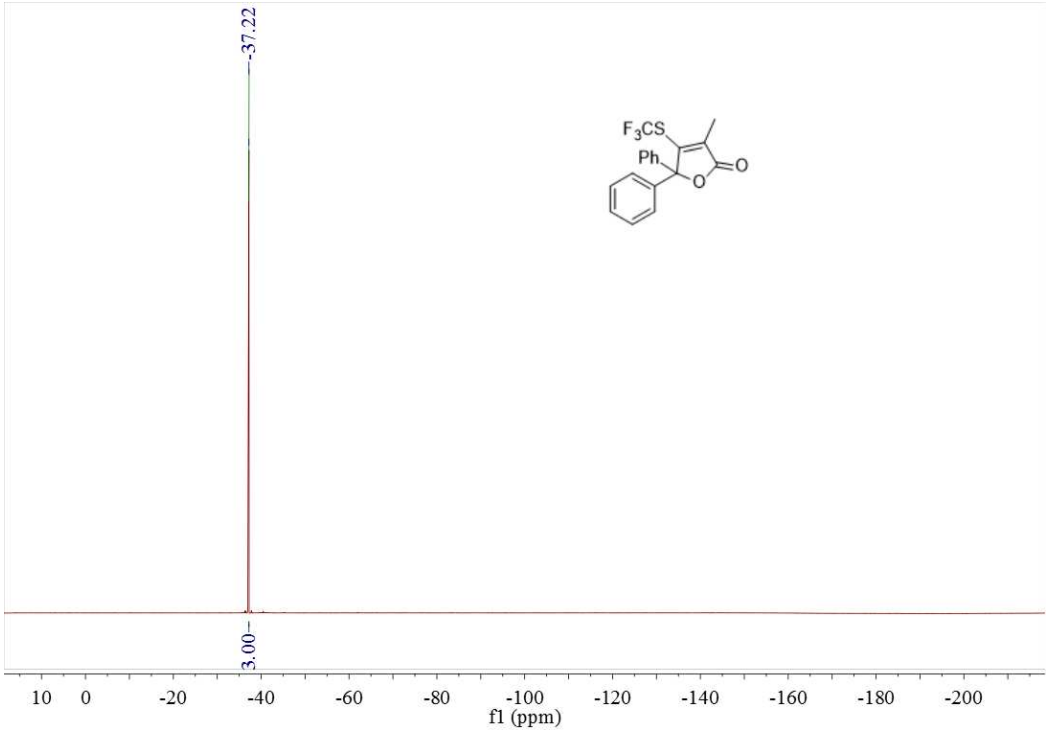
^{13}C NMR spectrum of **3o** in $CDCl_3$



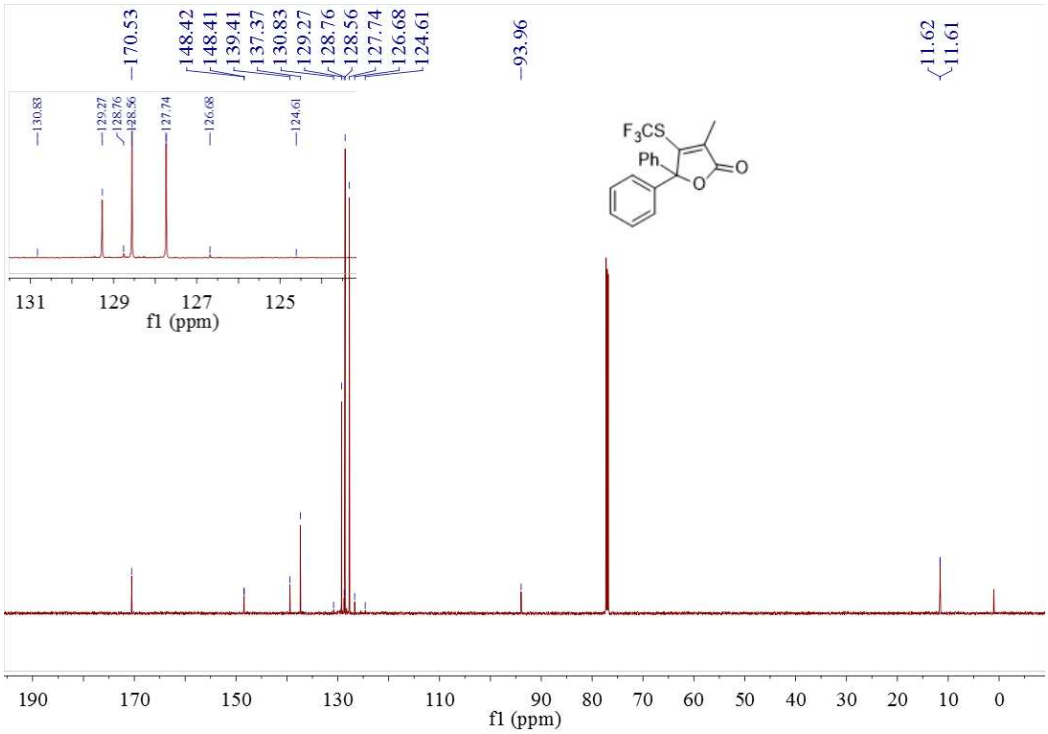
^{1}H NMR spectrum of **3p** in $CDCl_3$



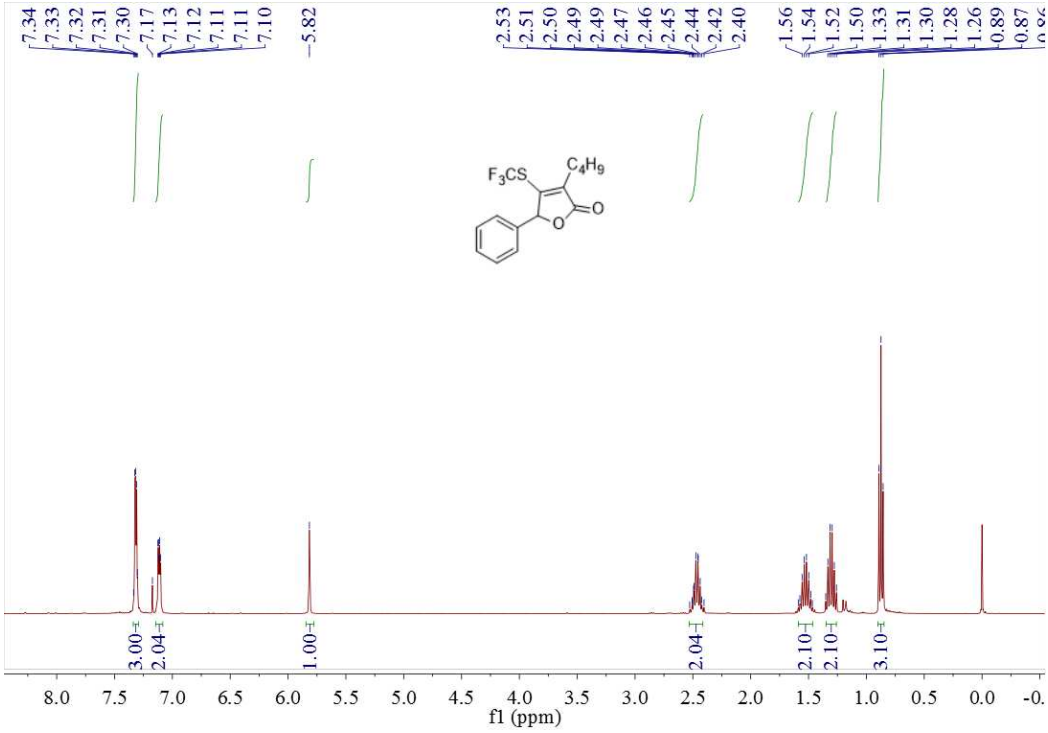
^{19}F NMR spectrum of **3p** in $CDCl_3$



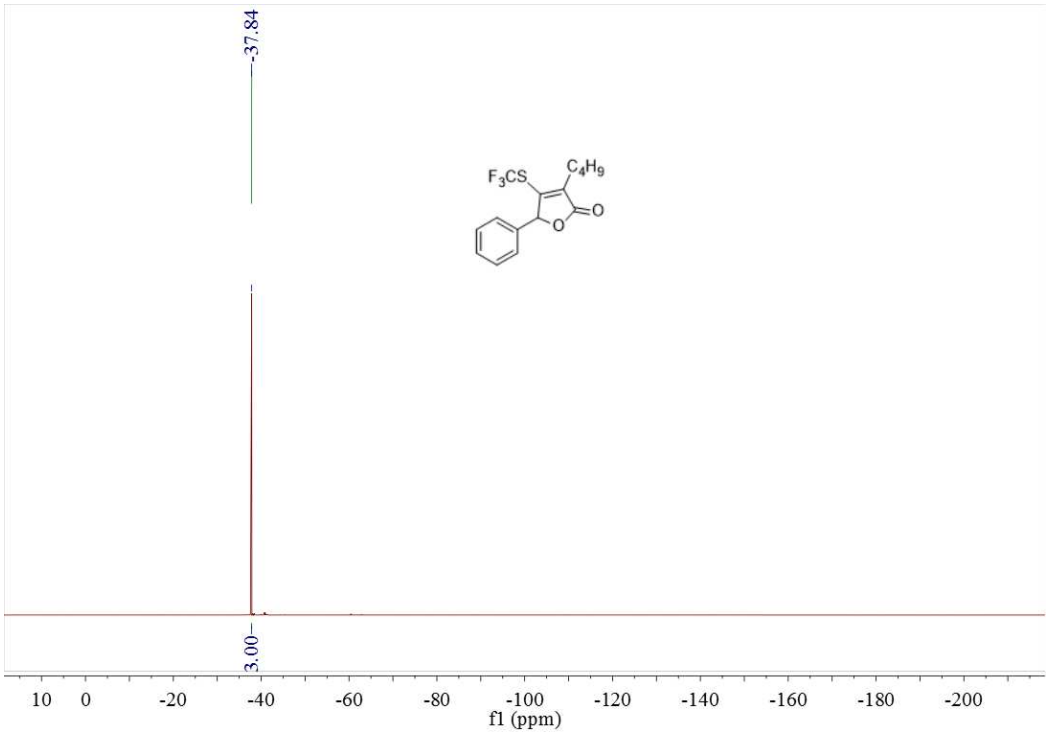
^{13}C NMR spectrum of **3p** in $CDCl_3$



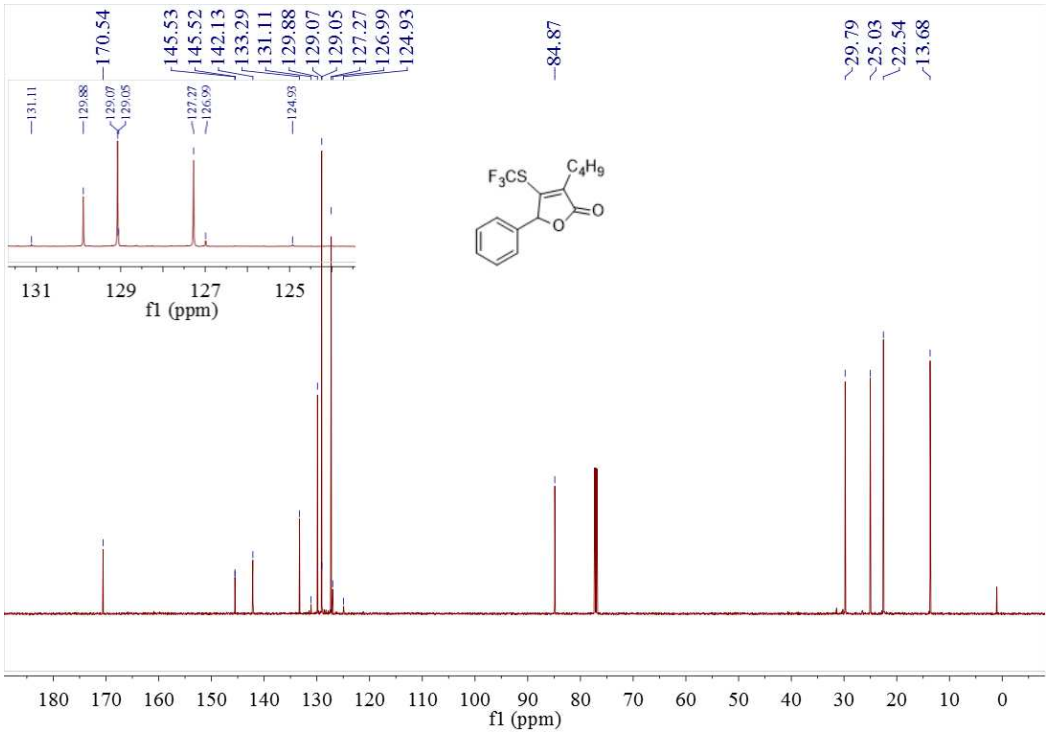
^{1}H NMR spectrum of **3q** in $CDCl_3$



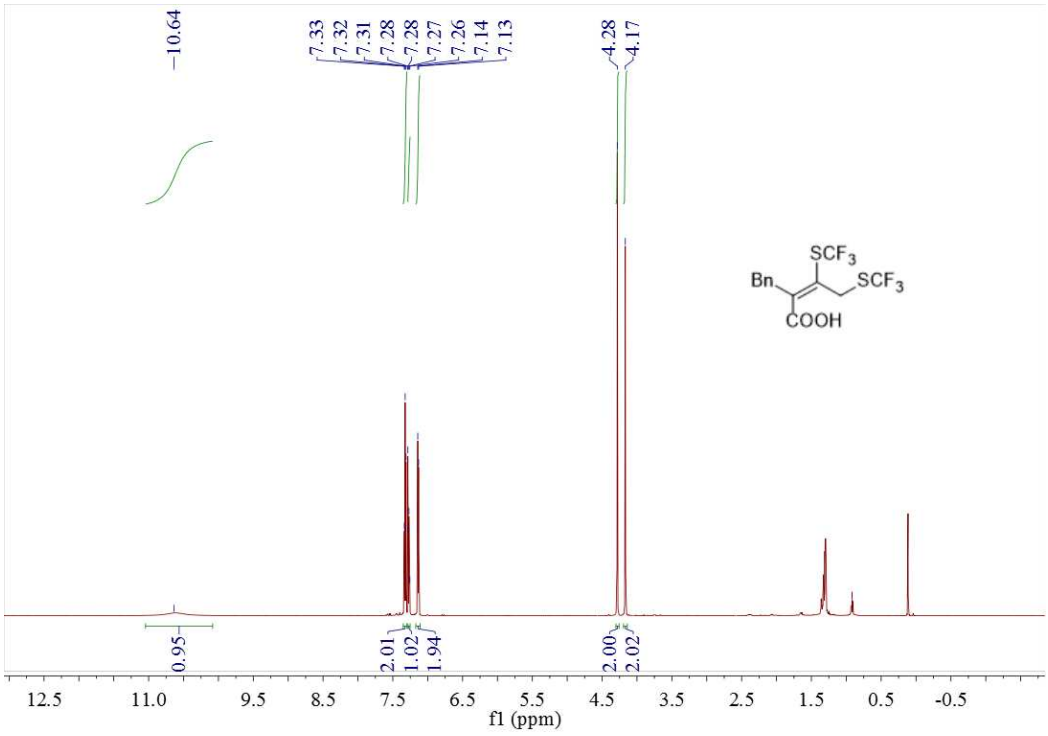
^{19}F NMR spectrum of **3q** in $CDCl_3$



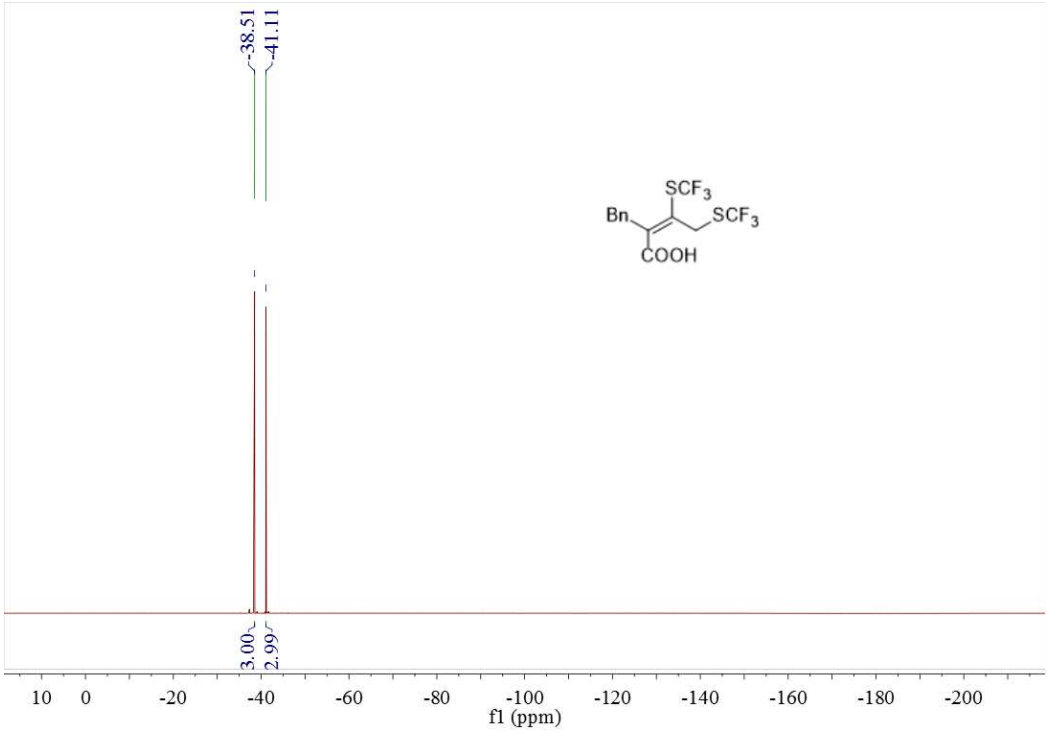
^{13}C NMR spectrum of **3q** in $CDCl_3$



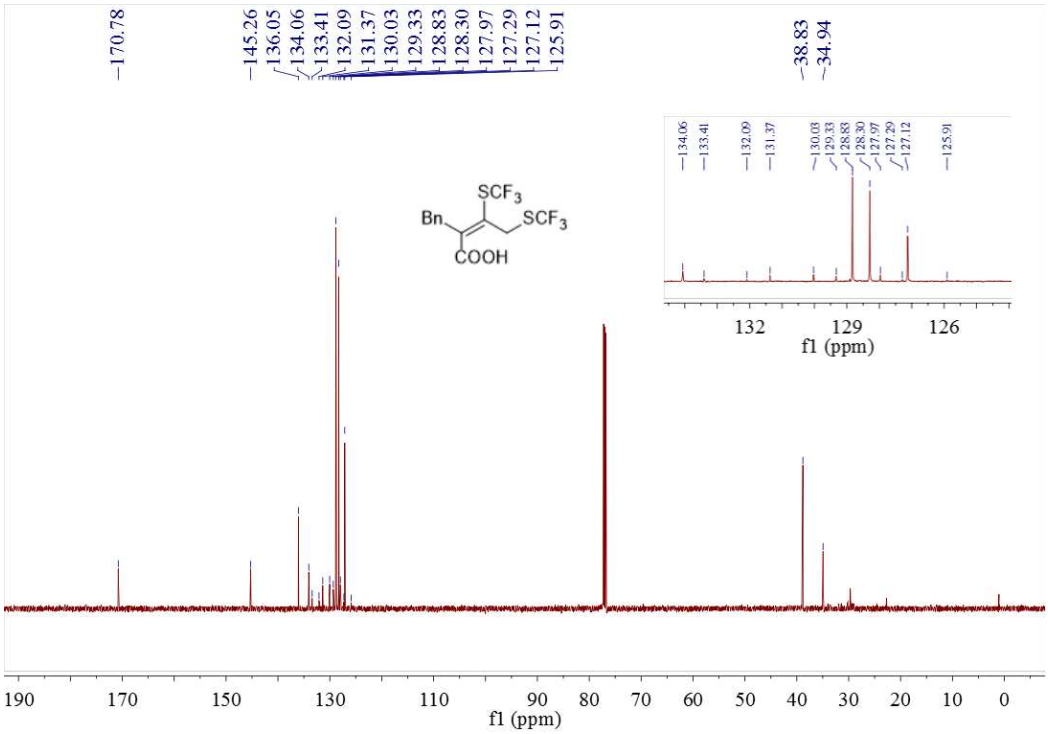
^{1}H NMR spectrum of **4r** in $CDCl_3$



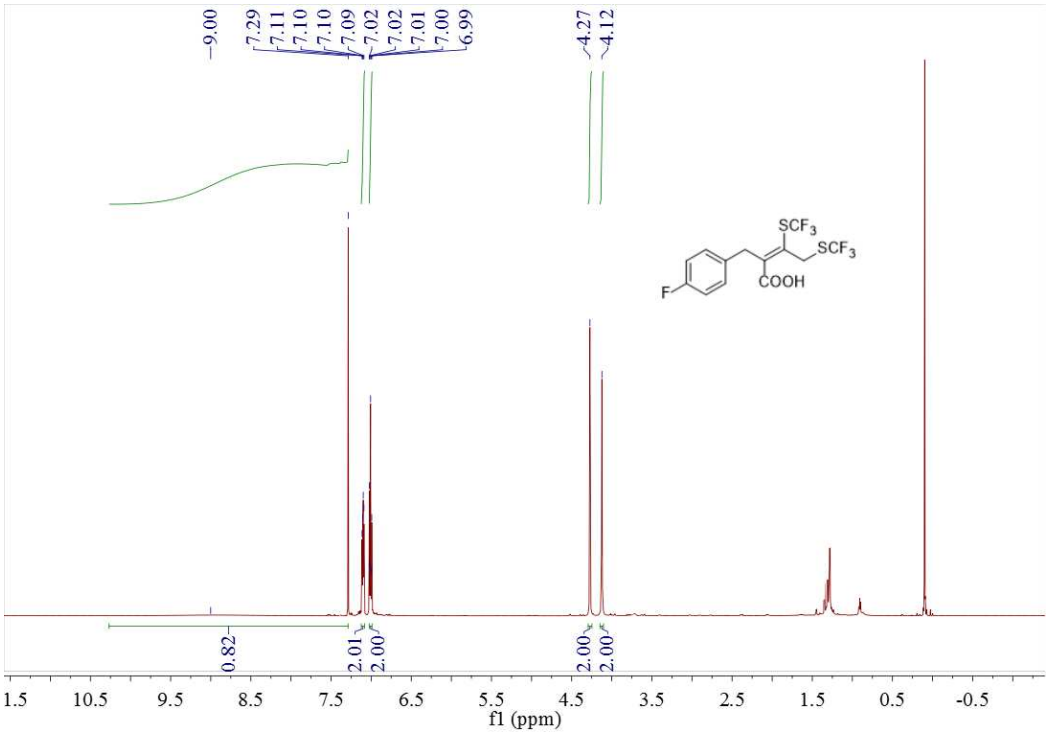
^{19}F NMR spectrum of **4r** in $CDCl_3$



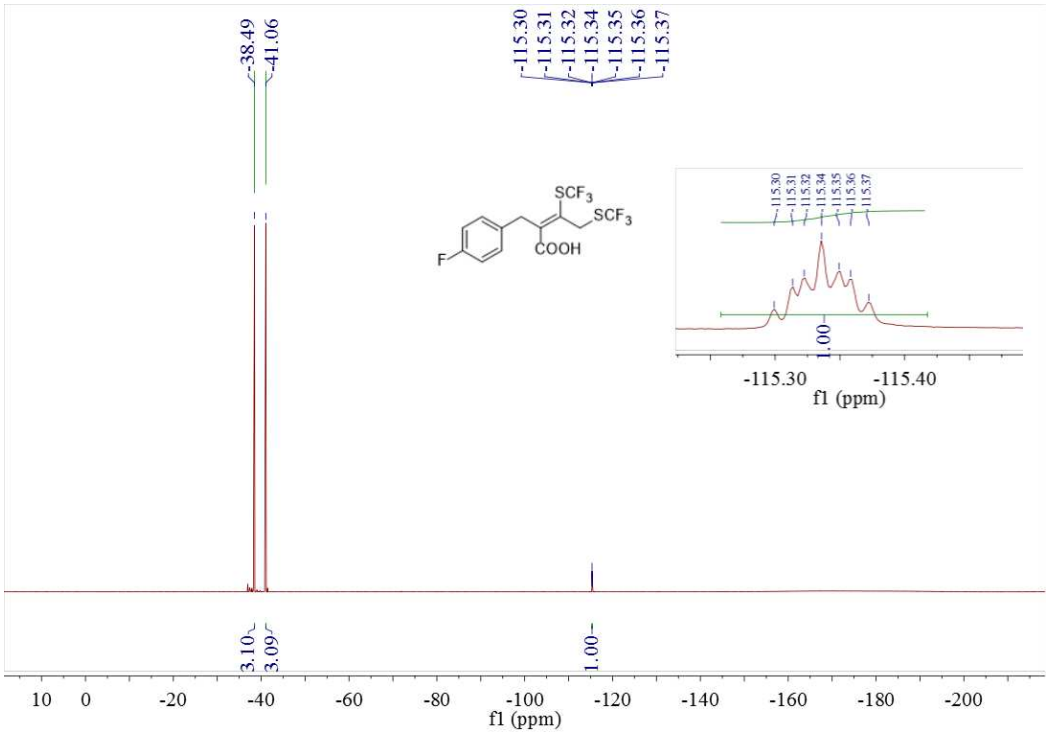
^{13}C NMR spectrum of **4r** in $CDCl_3$



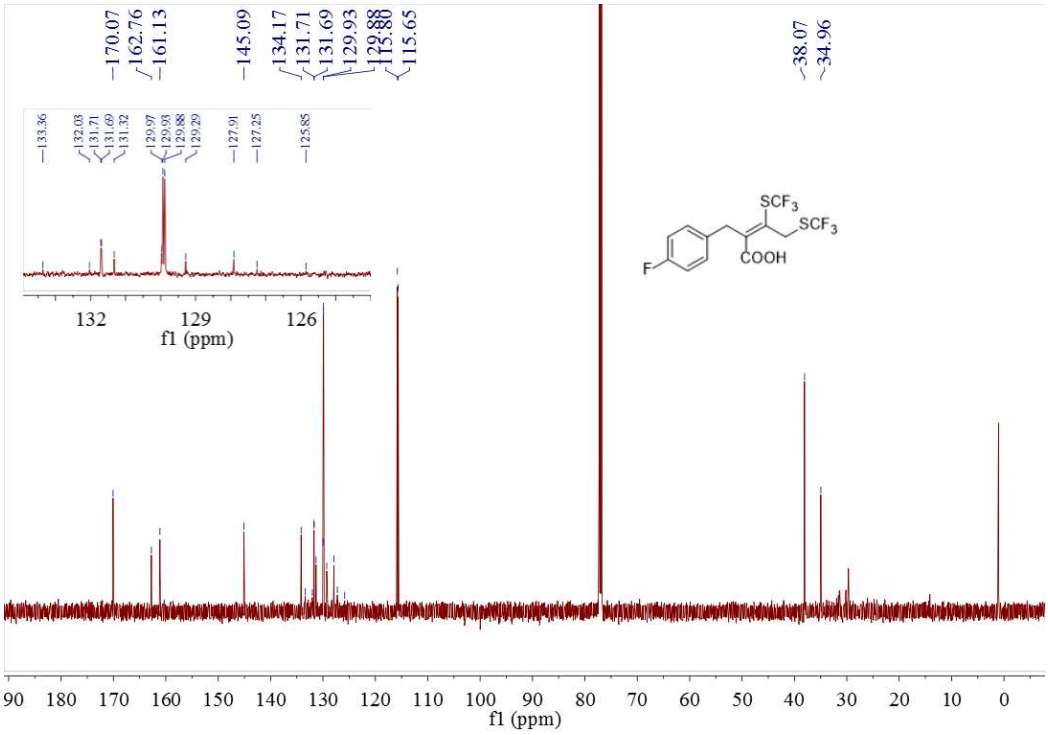
^{1}H NMR spectrum of **4s** in $CDCl_3$



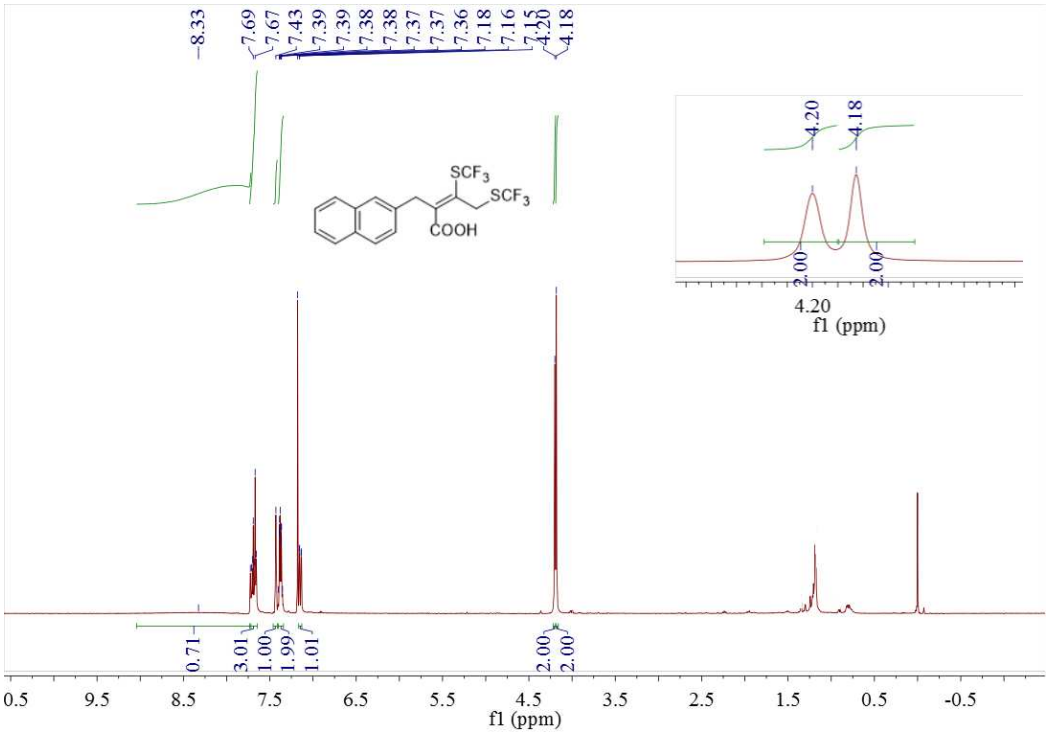
^{19}F NMR spectrum of **4s** in $CDCl_3$



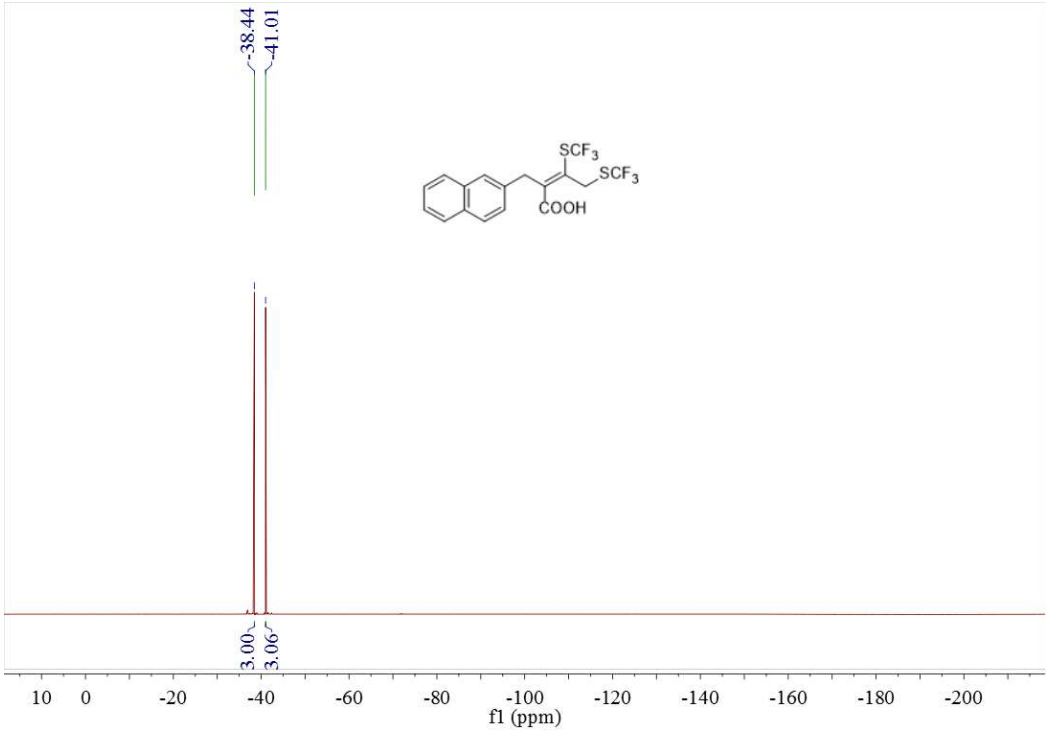
^{13}C NMR spectrum of **4s** in $CDCl_3$



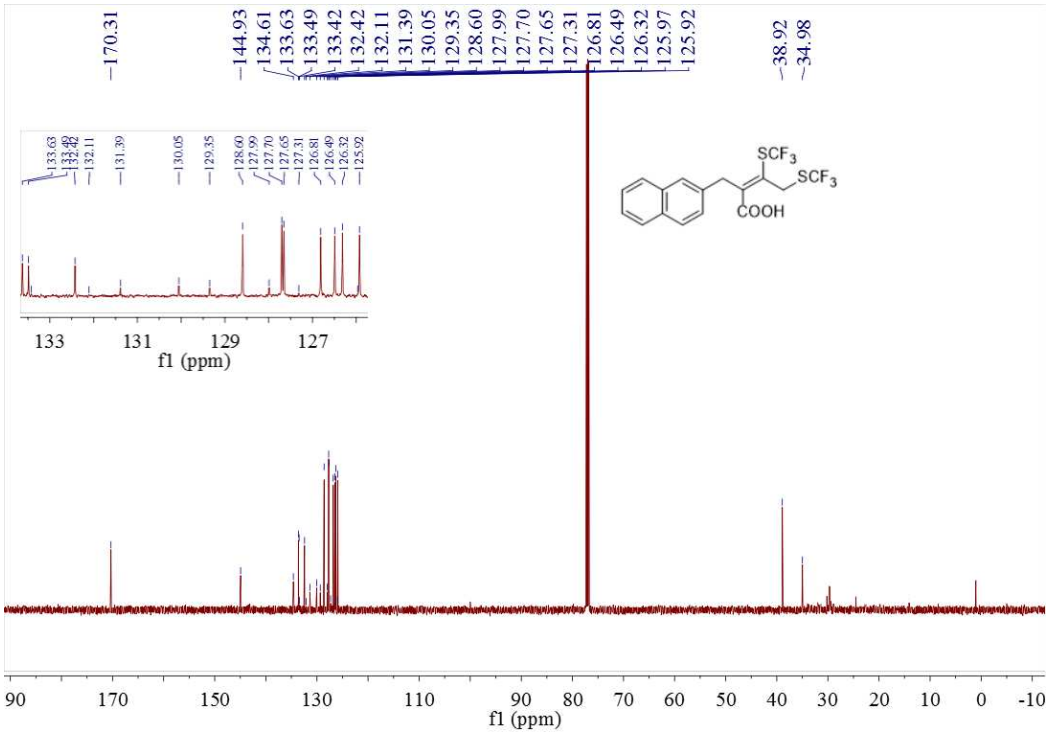
^{1}H NMR spectrum of **4t** in $CDCl_3$



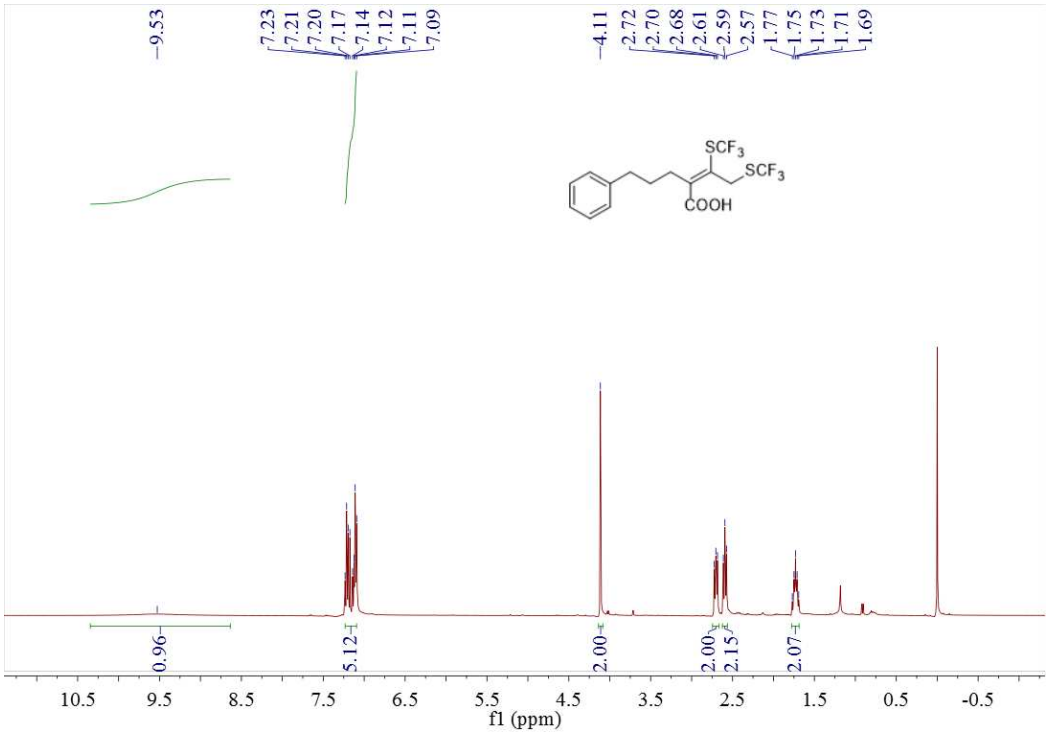
^{19}F NMR spectrum of **4t** in $CDCl_3$



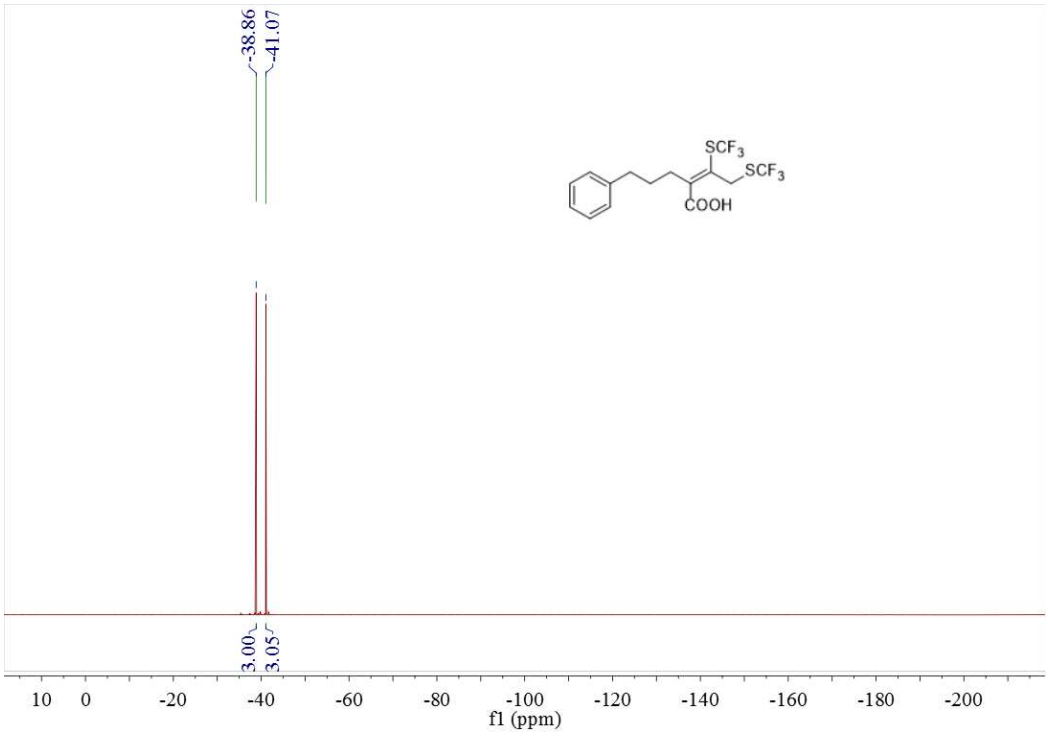
^{13}C NMR spectrum of **4t** in $CDCl_3$



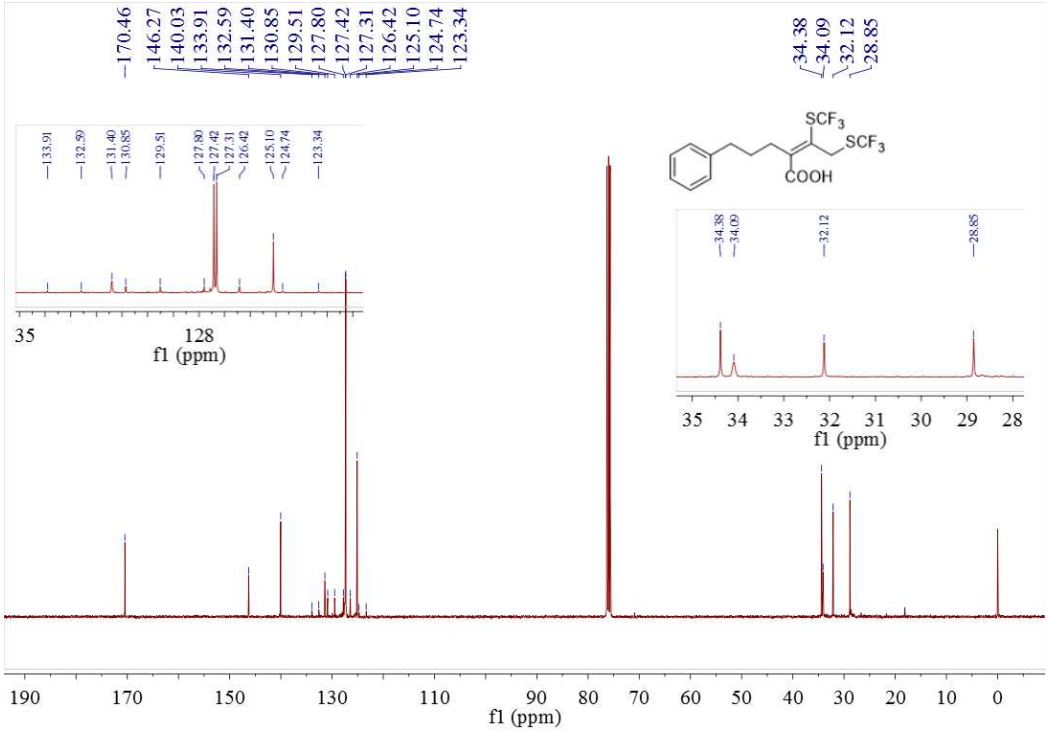
^{1}H NMR spectrum of **4u** in $CDCl_3$



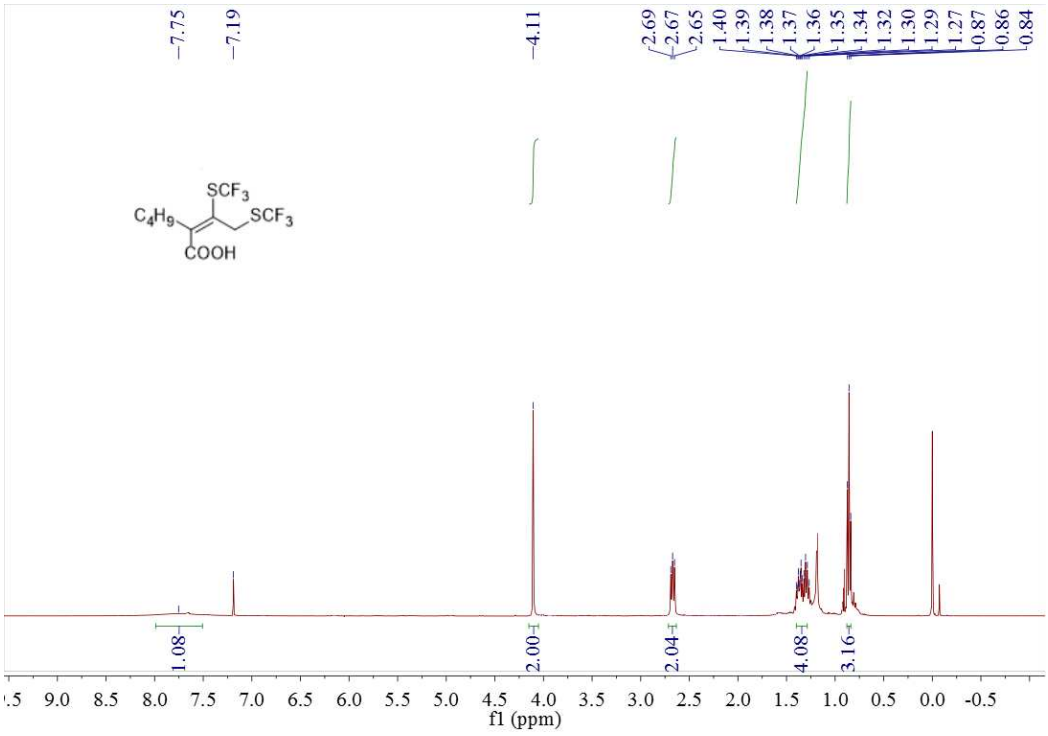
^{19}F NMR spectrum of **4u** in $CDCl_3$



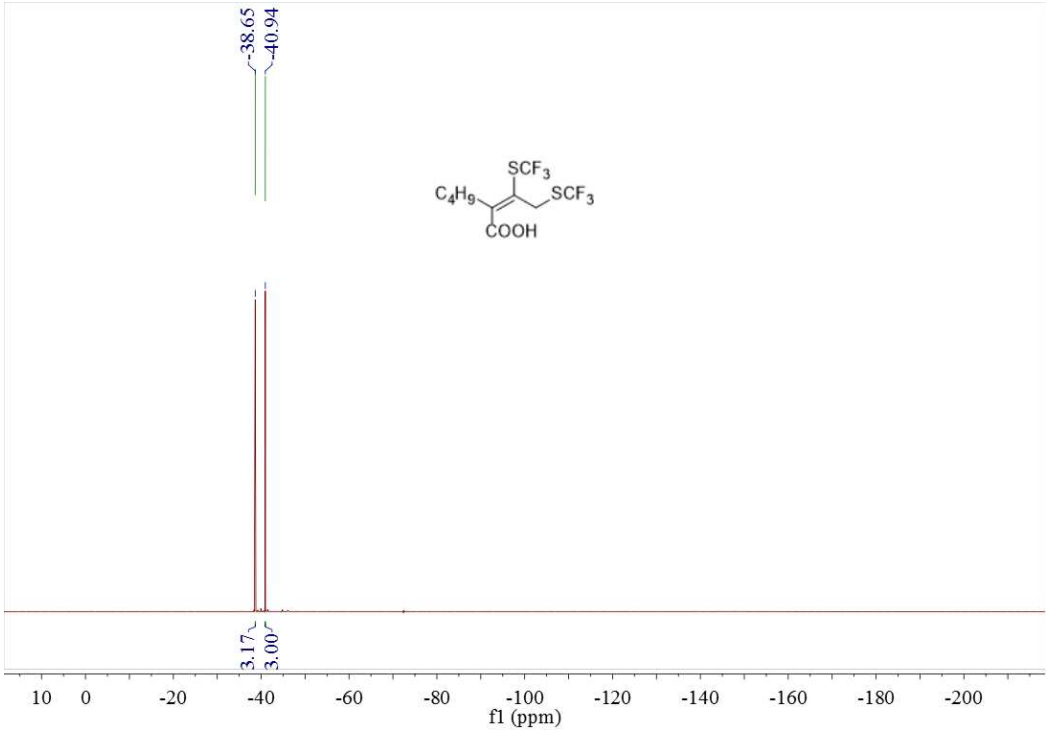
^{13}C NMR spectrum of **4u** in $CDCl_3$



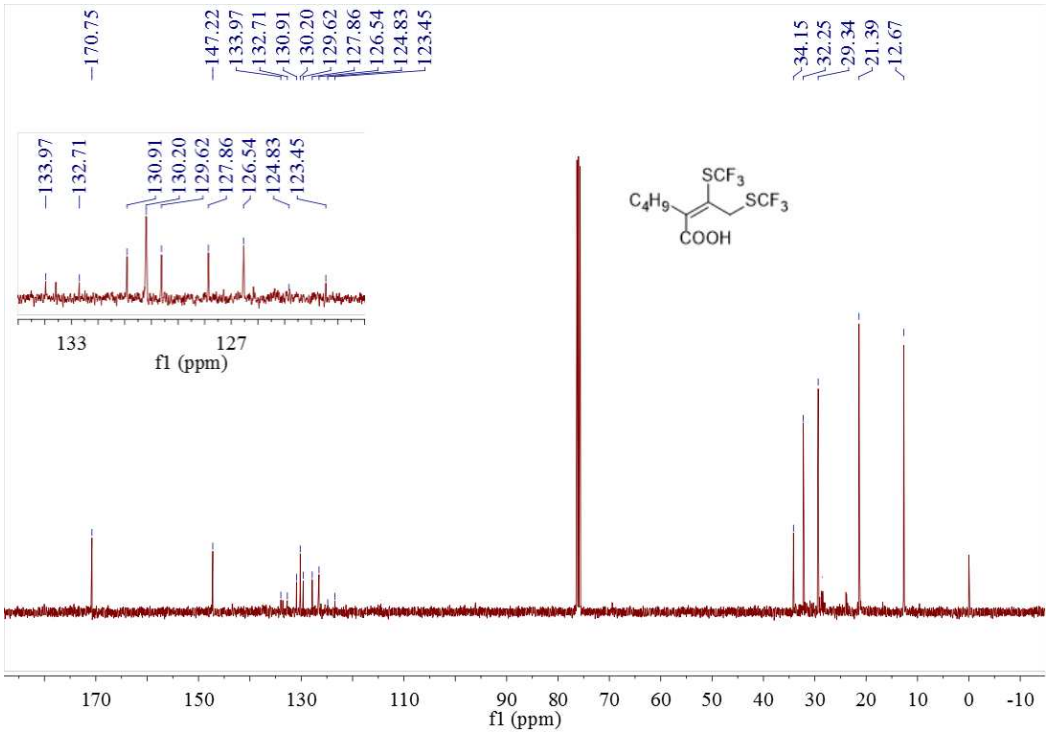
^{1}H NMR spectrum of **4v** in $CDCl_3$



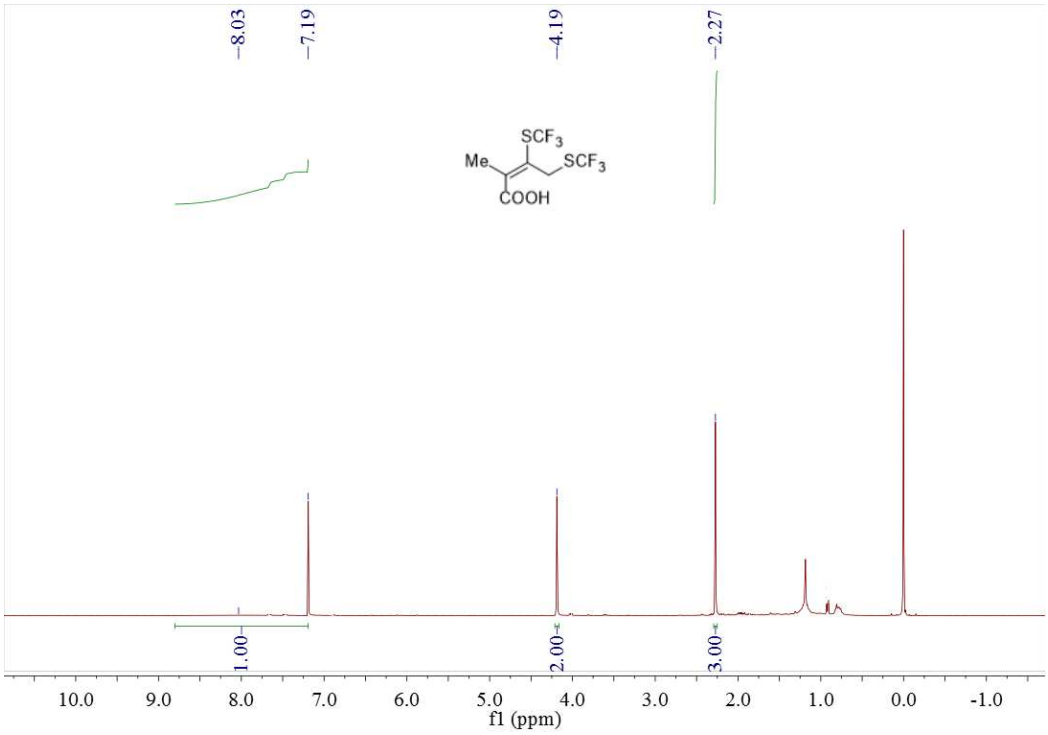
^{19}F NMR spectrum of **4v** in $CDCl_3$



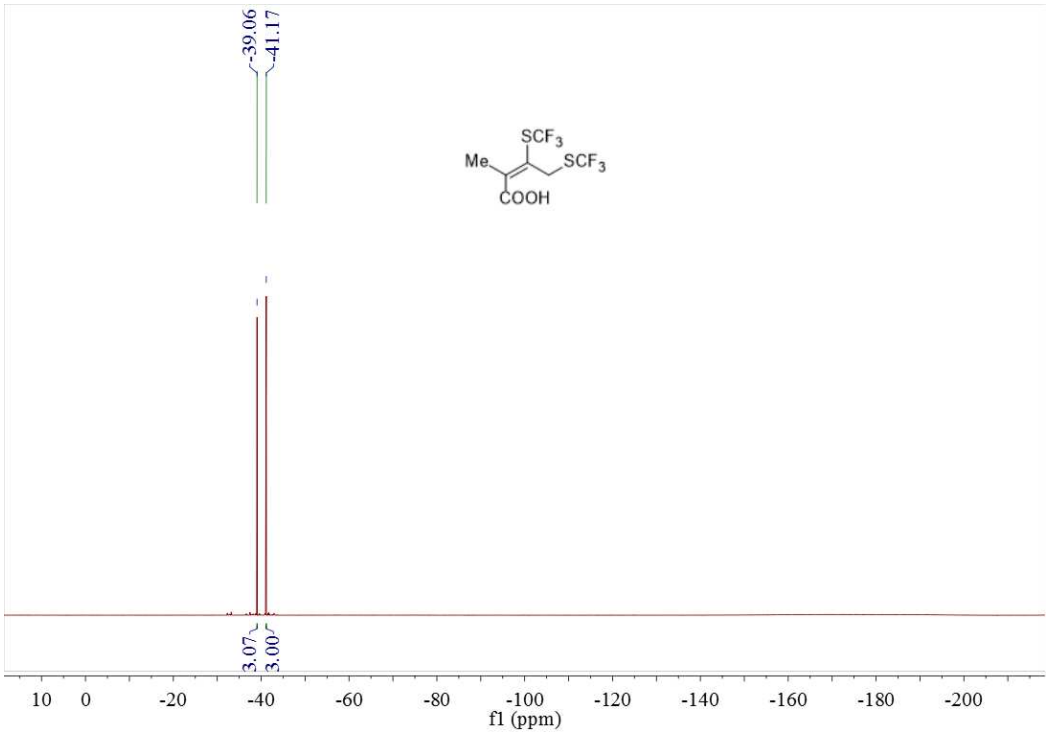
^{13}C NMR spectrum of **4v** in $CDCl_3$



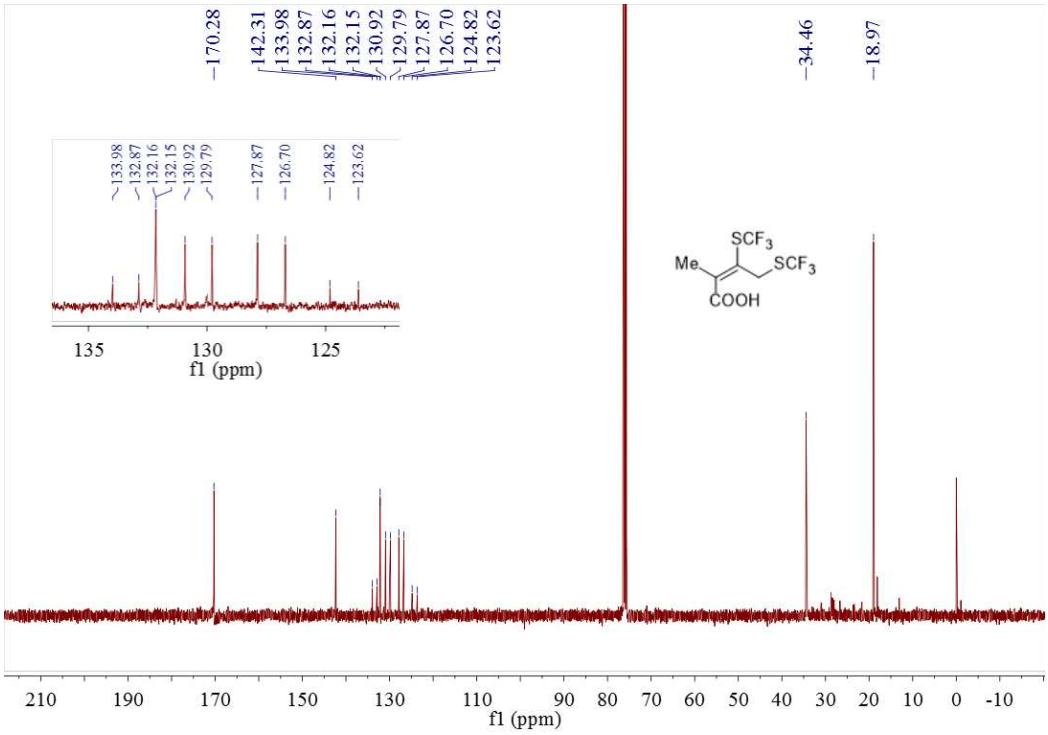
^{1}H NMR spectrum of **4w** in $CDCl_3$



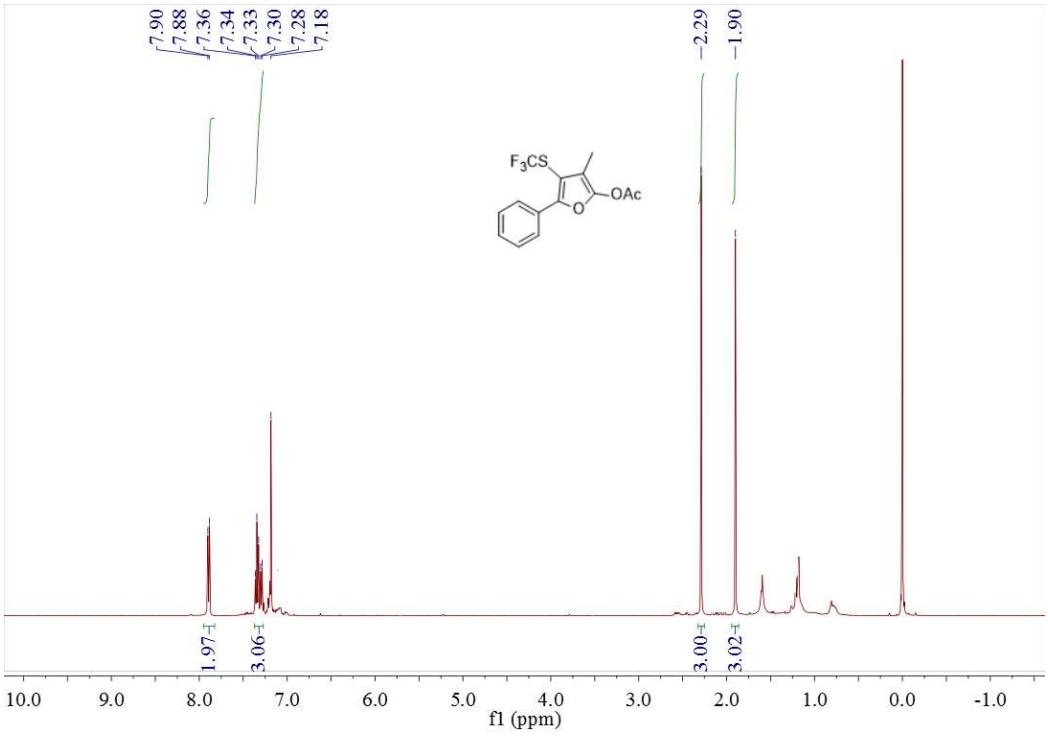
^{19}F NMR spectrum of **4w** in $CDCl_3$



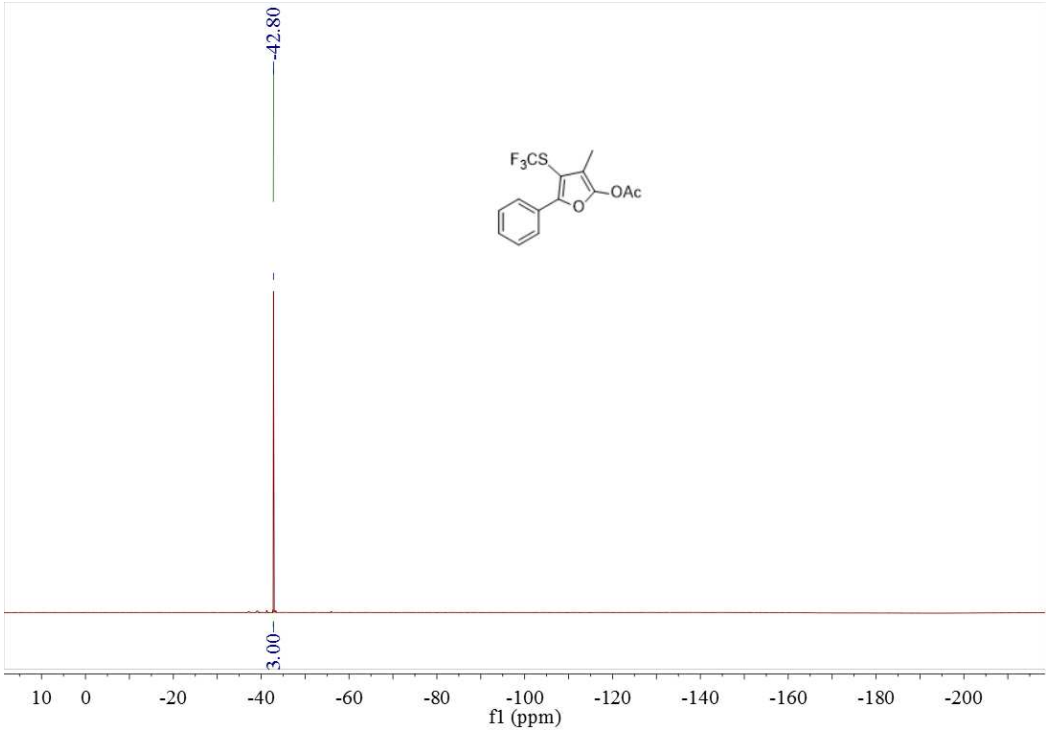
^{13}C NMR spectrum of **4w** in $CDCl_3$



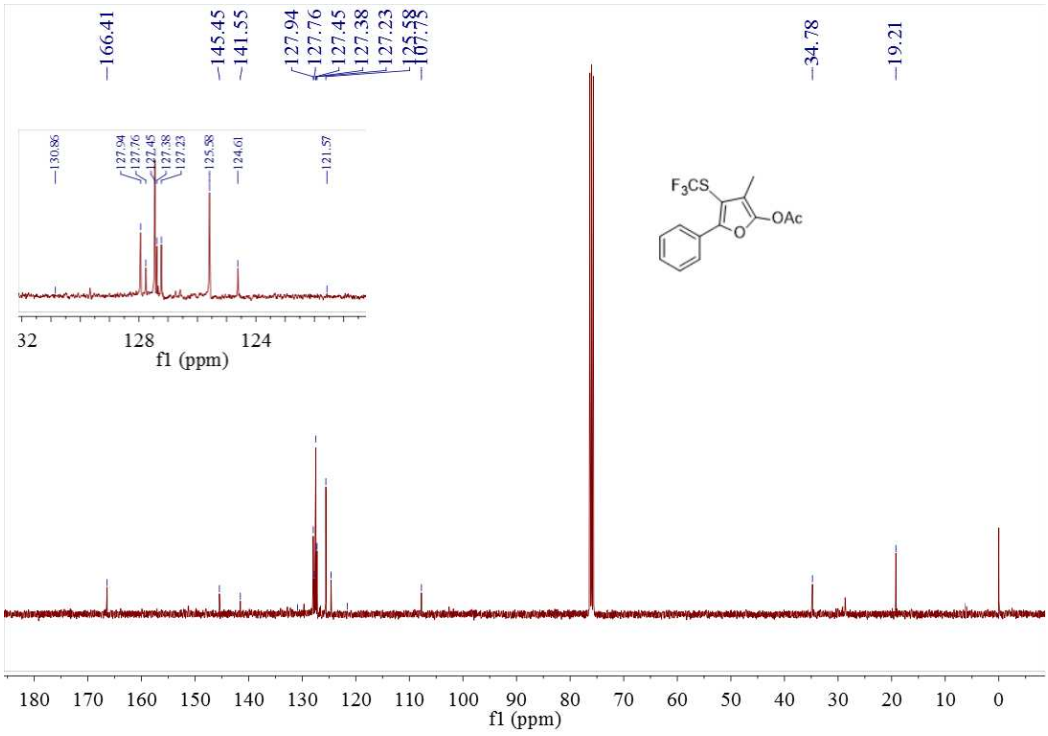
^{1}H NMR spectrum of **5a** in $CDCl_3$



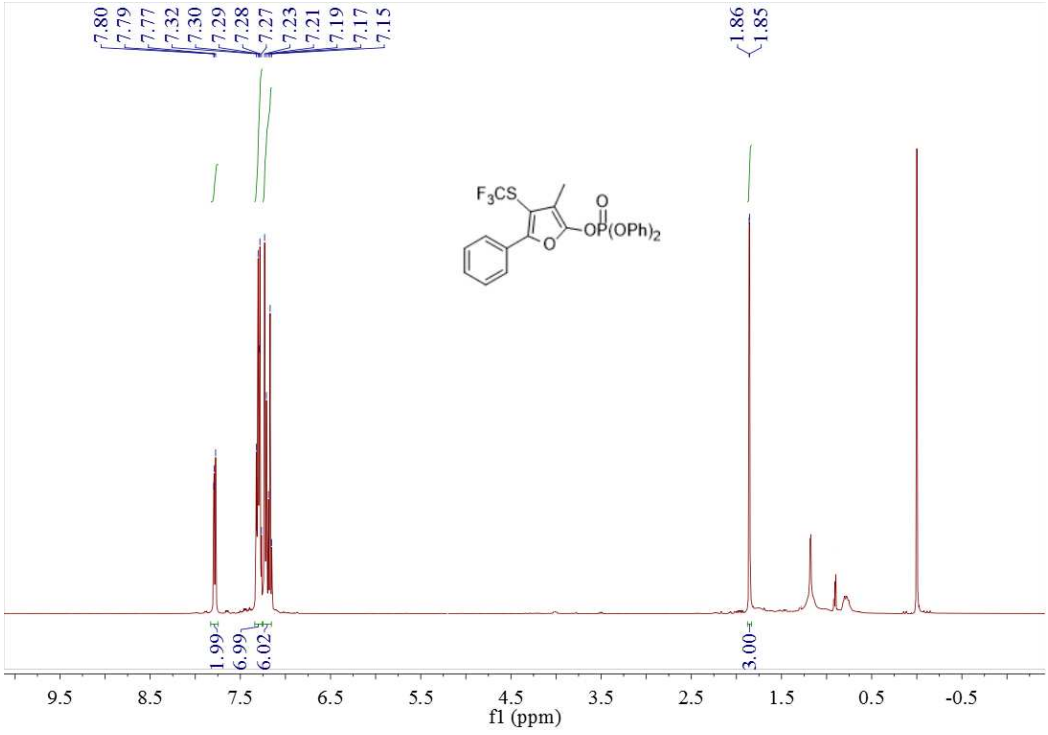
^{19}F NMR spectrum of **5a** in $CDCl_3$



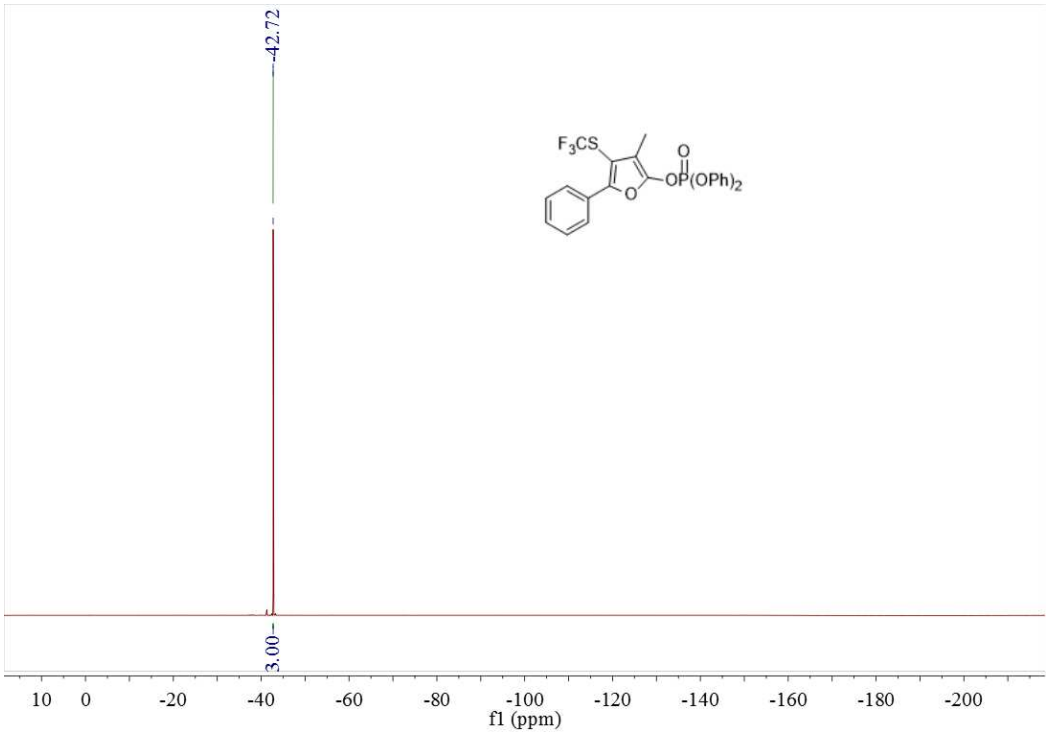
^{13}C NMR spectrum of **5a** in $CDCl_3$



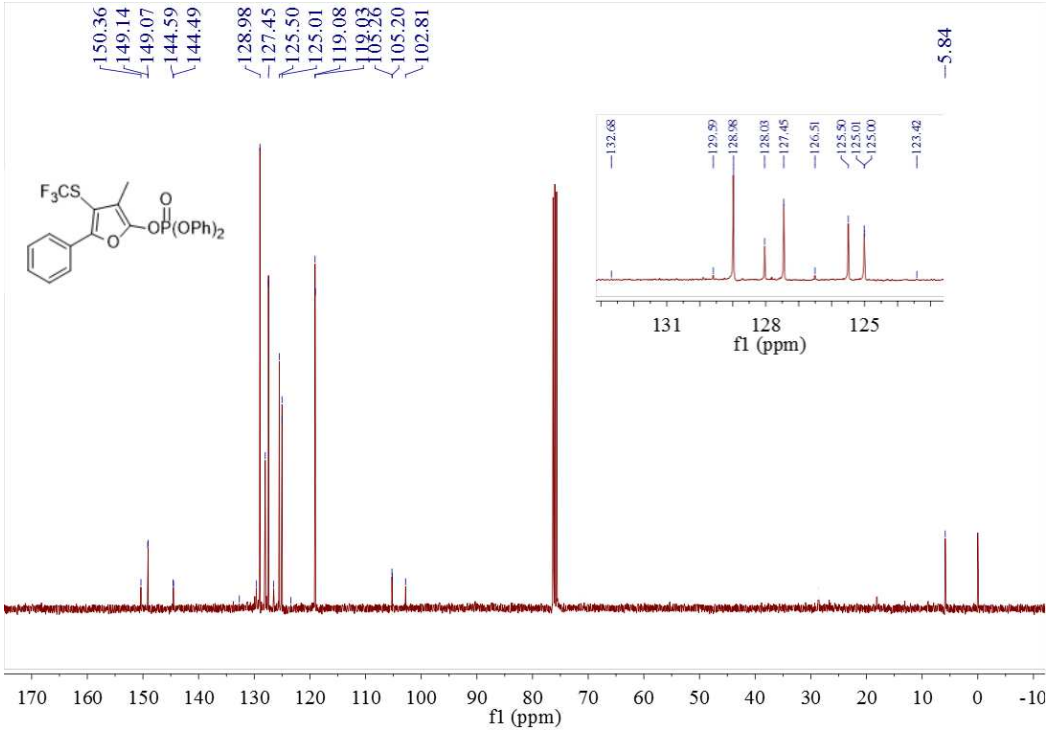
^{1}H NMR spectrum of **6a** in $CDCl_3$



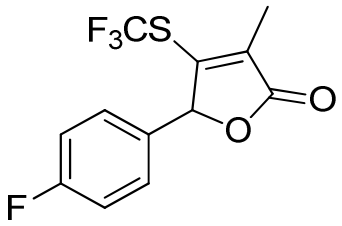
^{19}F NMR spectrum of **6a** in $CDCl_3$

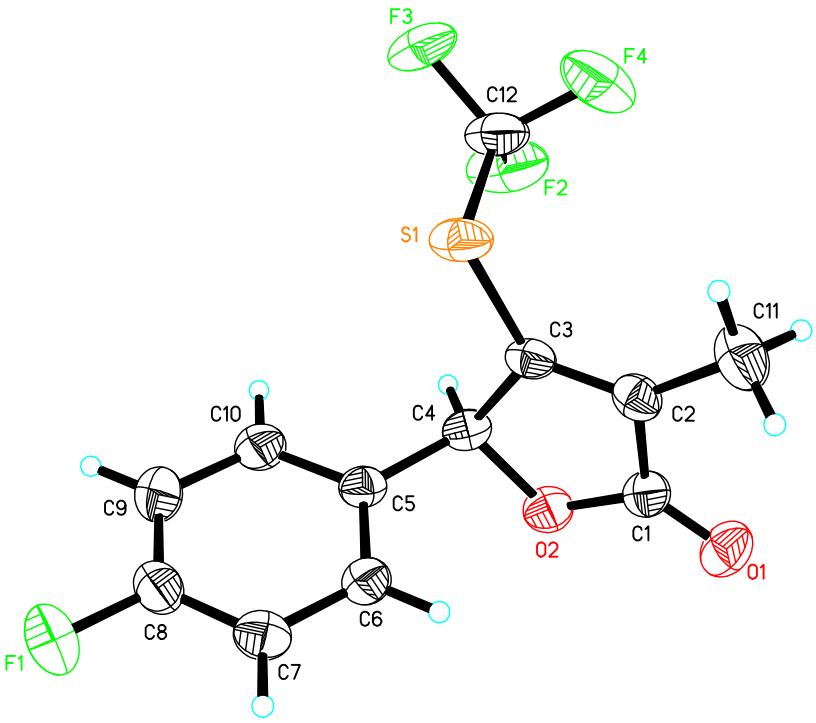


^{13}C NMR spectrum of **6a** in $CDCl_3$



9. ORTEP Drawing of the X-Ray Crystallographic Structure of 3f





CCDC 1559240 contains the supplementary crystallographic data for the target compound **3f**. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.