Supporting information

Organic base-promoted formal [4+1] cycloaddition of vinylethylene carbonates with elemental sulfur to facile access to thiophenones

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1. General information

All reactions were performed using flame-dried glassware under an atmosphere of dry Nitrogen, and all commercial materials and solvents were used directly without further purification, unless otherwise noted.

Chromatography: Flash column chromatography was performed using silica gel plates (Silica gel 200−300 mesh) from Qingdao Haiyang Chemical Co., Ltd.. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60-F254 from Yantai Jiangyou Silicone Development Co., Ltd., which was visualized with ultraviolet light.

^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{19}F NMR: ^{1}H NMR spectra were recorded on a Bruker Avance III instrument (500 MHz). ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance III instrument (125 MHz) and were fully decoupled by broad band proton decoupling. ^{19}F NMR spectra were recorded on a Bruker Avance III instrument (471 MHz). NMR spectra were recorded in $CDCl_3$. All NMR spectra were referenced to the solvent peaks (^{1}H NMR: residual $CDCl_3$ = 7.26 ppm, DMSO-d_6 = 2.50 ppm, ^{13}C{^{1}H} NMR: residual $CDCl_3$ = 77.16 ppm, DMSO-d_6 = 39.53 ppm) with tetramethylsilane (TMS, 0.00 ppm) as internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are reported in hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

High-resolution mass spectra (HRMS) were recorded on an Agilent 1290 mass spectrometer using ESI-TOF (electrospray ionization time-of-flight). The solution was directly infused via 20% mobile phase A (water) and 80% mobile phase B (Methanol) at 0.4 mL/min. All samples were analyzed in positive ion mode.

X-ray Crystallography data were collected and processed using Agilent Gemini E.

Electron paramagnetic resonance (EPR) spectra were performed on Bruker EMXplus-9.5/12.

Melting points were determined microscopic melting point detector using Gongyi City Yuhua Instrument Co., Ltd. (X-4, X-5).

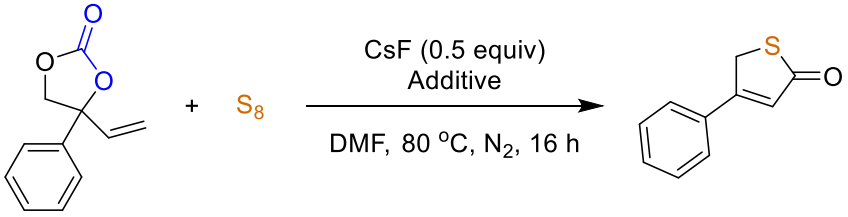
Vinylethylene carbonates (VECs) **1** were prepared according to reported literature procedures.[1-4]

Notice: *The water content in commercial DMA could vary to a certain extent, which would lead to different amounts of H_2O loadings, and thus affects reproducibility of experimental results. Therefore, to improve the accuracy, we consistently applied dried DMA as the solvent with the same equivalent of H_2O as an additive in the following substrate screenings and mechanistic studies.*

2. Optimization of reaction conditions

We examined and optimized the reaction conditions for this [4 +1] annulation of vinylethylene carbonate **1a** and S_8 (**2**), including additive, base, solvent, concentration of substrates, and reaction temperature and time as shown in **Table S1**−**7**.

Table S1 Screening of additives[a]



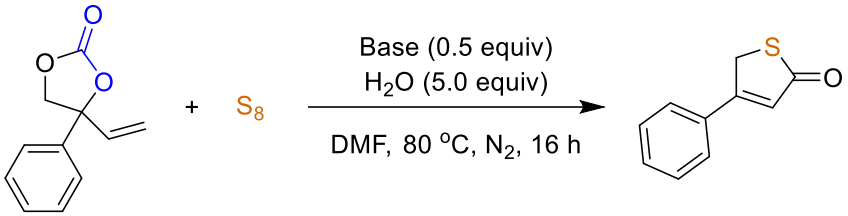
1a **2** **3a**

Entry	Additive (equiv.)	**3a** (%)[b]

1	–	34
2	$Pd(PPh)_3$ (0.1)	0
3	H_2O (5.0)	42
4	KPF_6 (2.0)	30

[a] Reaction conditions: **1a** (0.1 mmol), S_8 (**2**, 0.2 mmol), CsF (0.5 equiv.), additive (0.1−5.0 equiv.), DMF (1.0 mL) under N_2 at 80 °C for 16 h. [b] Isolated yields.

Table S2 Screening of bases[a]

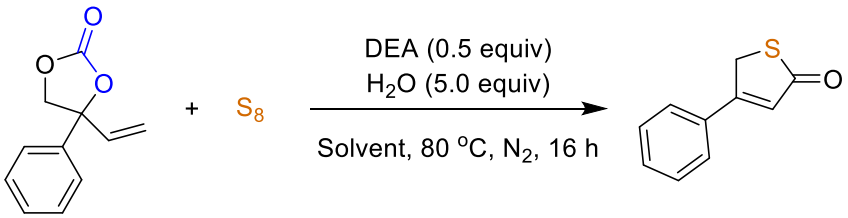


1a **2** **3a**

Entry	Base	**3a** (%)[b]
1	CsF	42
2	KF	65
3	K_3PO_4	31
4	Na_2CO_3	39
5	$KHCO_3$	45
6	DBU	0
7	IPA	49
8	DIPEA	71
9	DEA	77

[a] Reaction conditions: **1a** (0.1 mmol), S_8 (**2**, 0.2 mmol), base (0.5 equiv.), H_2O (5.0 equiv.), DMF (1.0 mL) under N_2 at 80 °C for 16 h. [b] Isolated yields.

Table S3 Screening of solvents[a]



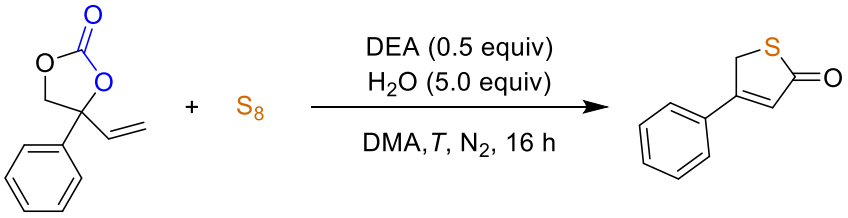
1a **2** **3a**

Entry	Solvent	**3a** (%)[b]
1	DMF	77
2	H_2O	0

3	DMA	91
4	NMP	0
5	DMSO	0
6	1,4-dioxane	0
7	DCE	0
8	MeOH	0
9	EtOH	0

[a] Reaction conditions: **1a** (0.1 mmol), S_8 (**2**, 0.2 mmol), DEA (0.5 equiv.), H_2O (5.0 equiv.), solvent (1.0 mL) under N_2 at 80 °C for 16 h. [b] Isolated yields. NMP = *N*-methylpyrrolidone. DCE = 1,2-dichloroethane.

Table S4 Screening of reaction temperature[a]

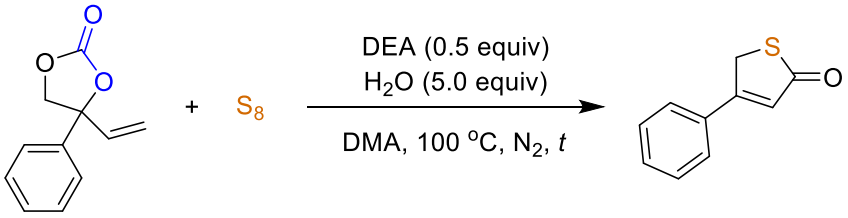


1a **2** **3a**

Entry	*T* (°C)	**3a** (%)[b]
1	100	86
2	80	91
3	60	69
4	r.t. (23)	0

[a] Reaction conditions: **1a** (0.1 mmol), S_8 (**2**, 0.2 mmol), DEA (0.5 equiv.), H_2O (5.0 equiv.), solvent (1.0 mL) under N_2 for 16 h. [b] Isolated yields.

Table S5 Screening of reaction time[a]

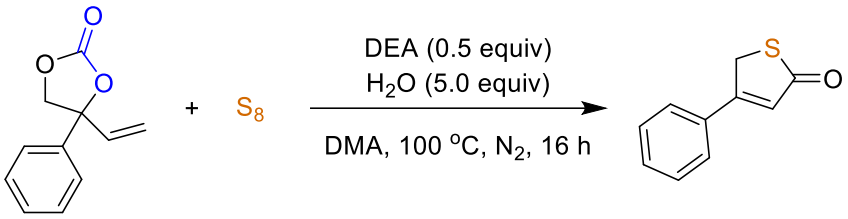


1a **2** **3a**

Entry	*t* (h)	**3a** (%)[b]
1	12	76
2	14	87
3	16	91
4	18	87

[a] Reaction conditions: **1a** (0.1 mmol), S_8 (**2**, 0.2 mmol), DEA (0.5 equiv.), H_2O (5.0 equiv.), DMA (1.0 mL) under N_2 at 80 °C. [b] Isolated yields.

Table S6 Effect of substrate concentration[a]

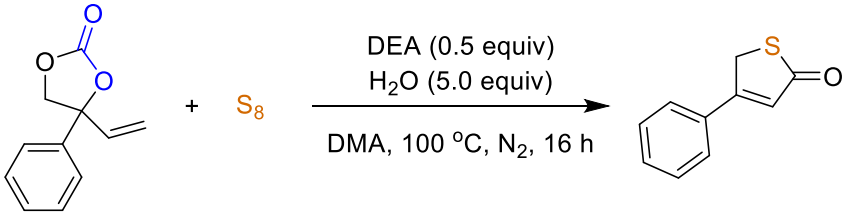


1a **2** **3a**

Entry	**1a** (mmol)	**3a** (%)[b]
1	0.1	91
2	0.2	85
3	0.4	57

[a] Reaction conditions: **1a** (0.1 mmol), S_8 (**2**, 0.2 equiv.), DEA (0.5 equiv.), H_2O (5.0 equiv.), DMA (1.0 mL) under N_2 at 80 °C for 16 h. [b] Isolated yields.

Table S7 Screening of S_8 Loadings[a]

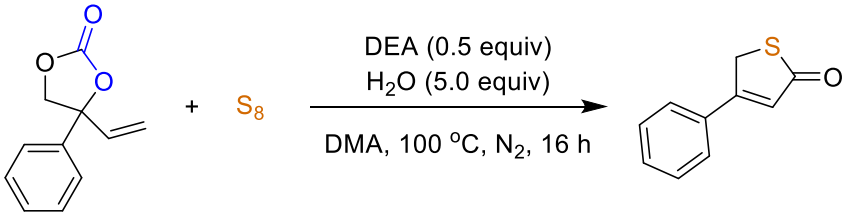


1a **2** **3a**

Entry	**S8** (mmol)	**3a** (%)[b]
1	0.1	76
2	0.2	91
3	0.3	92

[a] Reaction conditions: **1a** (0.1 mmol), S_8 (**2**, 0.1−0.3 equiv.), DEA (0.5 equiv.), H_2O (5.0 equiv.), DMA (1.0 mL) under N_2 at 80 °C for 16 h. [b] Isolated yields.

Table S8 Control experiments[a]



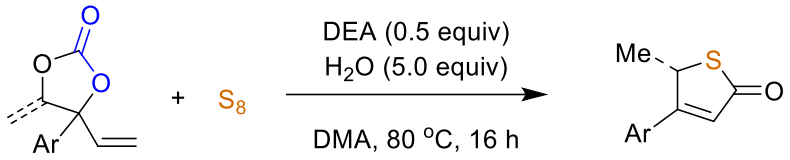
1a **2** **3a**

Entry	Deviate from above	**3a** (%)[b]

1	None	91
2	w/o H_2O	46
3	w/o DEA	0
4	Under air	0

[a] Reaction conditions: **1a** (0.1 mmol), S_8 (**2**, 0.2 equiv.), DEA (0.5 equiv.), H_2O (5.0 equiv.), DMA (1.0 mL) under N_2 at 80 °C. [b] Isolated yields.

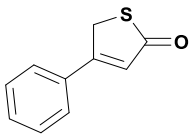
3. General procedure for the [4 + 1] annulation of VECs 1 with S_8 (2)



1 **2** **3**

To a 15 mL Schlenk tube containing a stir bar were added vinylethylene carbonate **1** (0.2 mmol, 1.0 equiv.), elemental sulfur (S_8, **2**; 102.6 mg, 0.4 mmol, 2.0 equiv.), DEA (15 μL, 0.1 mmol, 0.5 equiv.), H_2O (18 μL, 10.0 mmol, 5.0 equiv.) and dry DMA (1.0 mL). Then the tube was evacuated and charged with N_2 three times. The mixture was stirred at 80 °C for 16 h. After cooling to ambient temperature, the mixture was quenched by the addition of H_2O (10 mL). The aqueous phase was extracted with ethyl acetate (3 × 10 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (v/v) afforded the corresponding 2(5*H*)-thiophenone products **3**.

4. Characterization data of the thiophenone compounds 3



4-phenylthiophen-2(5*H*)-one (3a)

Following the general procedure, the title compound **3a** was isolated as a purple-brown solid (16.0 mg, 91%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

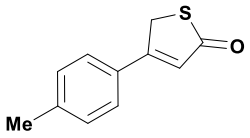
M. p. 133−135 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64−7.56 (m, 2H), 7.52−7.43 (m, 3H), 6.70 (t, J = 1.6 Hz, 1H), 4.45 (d, J = 1.7 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.0, 165.3, 133.4, 131.2, 129.2, 126.9, 126.4, 37.6.

HRMS (ESI) *m/z* calcd for $C_{10}H_9OS^+$ $[M + H]^+$: 177.0369, found 177.0377.

The spectral data were in accordance with those reported in the literature.[5]



4-(*p*-tolyl)thiophen-2(5*H*)-one (3b)

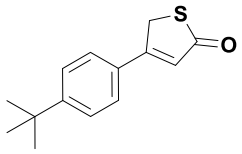
Following the general procedure, the title compound **3b** was isolated as a purple-brown solid (13.8 mg, 73%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 132−134 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 7.8 Hz, 2H), 7.29−7.18 (m, 2H), 6.65 (t, J = 1.6 Hz, 1H), 4.42 (d, J = 1.7 Hz, 2H), 2.41 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.2, 165.3, 141.8, 130.6, 129.9, 126.3, 126.0, 37.5, 21.5.

HRMS (ESI) *m/z* calcd for $C_{11}H_{11}OS^+$ $[M + H]^+$: 191.0525, found 191.0527.



4-{4-(*tert*-butyl)phenyl}thiophen-2(5*H*)-one (3c)

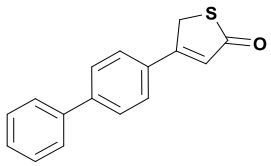
Following the general procedure, the title compound **3c** was isolated as a light-brown solid (14.1 mg, 61%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 150−153 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dt, J = 8.5, 2.0 Hz, 2H), 7.50 (dt, J = 8.5, 2.0 Hz, 2H), 6.69 (t, J = 1.6 Hz, 1H), 4.45 (d, J = 1.5 Hz, 2H), 1.37 (s, 9H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.2, 165.3, 154.9, 130.6, 126.2, 126.2, 126.1, 37.5, 35.0, 31.1.

HRMS (ESI) *m/z* calcd for $C_{14}H_{17}OS^+$ $[M + H]^+$: 233.0995, found 233.0989.



4-([1,1'-biphenyl]-4-yl)thiophen-2(5*H*)-one (3d)

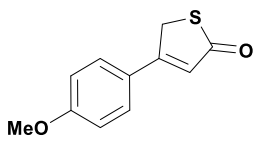
Following the general procedure, the title compound **3d** was isolated as a light-brown solid (16.5 mg, 65%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 205−208 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73−7.68 (m, 4H), 7.67−7.63 (m, 2H), 7.50 (dd, J = 7.8, 7.2 Hz, 2H), 7.43 (ddt, J = 7.4, 7.2, 1.2 Hz, 1H), 6.76 (t, J = 1.6 Hz, 1H), 4.50 (d, J = 1.6 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.0, 164.7, 143.9, 139.7, 132.2, 129.0, 128.2, 127.8, 127.1, 126.9, 126.7, 37.5.

HRMS (ESI) *m/z* calcd for $C_{16}H_{13}OS^+$ $[M + H]^+$: 253.0682, found 253.0670.



4-(4-methoxyphenyl)thiophen-2(5*H*)-one (3e)

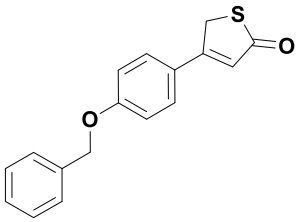
Following the general procedure, the title compound **3e** was isolated as a purple-brown solid (14.7 mg, 71%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 134−135 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dt, J = 8.8, 3.0 Hz, 2H), 6.98 (dt, J = 8.8, 3.0 Hz, 2H), 6.61 (t, J = 1.5 Hz, 1H), 4.43 (d, J = 1.5 Hz, 2H), 3.89 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.1, 164.9, 162.0, 128.1, 126.0, 124.7, 114.6, 55.5, 37.4.

HRMS (ESI) *m/z* calcd for $C_{11}H_{10}NaO_2S^+$ $[M + Na]^+$: 229.0294, found 207.0299.



4-{4-(benzyloxy)phenyl}thiophen-2(5*H*)-one (3f)

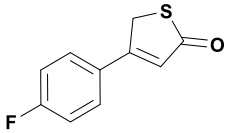
Following the general procedure, the title compound **3f** was isolated as a light-brown solid (18.6 mg, 66%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 183−186 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dt, J = 8.8, 2.1 Hz, 2H), 7.47−7.40 (m, 4H), 7.37 (ddt, J = 7.1, 6.7, 1.9 Hz, 1H), 7.05 (dt, J = 8.8, 2.1 Hz, 2H), 6.62 (t, J = 1.5 Hz, 1H), 5.15 (s, 2H), 4.43 (d, J = 1.5 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 199.1, 164.8, 161.1, 136.2, 128.7, 128.3, 128.1, 127.5, 126.2, 124.9, 115.4, 70.2, 37.4.

HRMS (ESI) *m/z* calcd for $C_{17}H_{15}O_2S^+$ $[M + H]^+$: 283.0787, found 283.0792.



4-(4-fluorophenyl)thiophen-2(5*H*)-one (3g)

Following the general procedure, the title compound **3g** was isolated as a black-brown solid (14.4 mg, 74%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

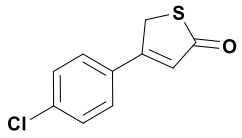
M. p. 133−134 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63−7.58 (m, 2H), 7.16 (dd, J = 8.5, 8.5 Hz, 2H), 6.65 (t, J = 1.6 Hz, 1H), 4.42 (d, J = 1.6 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.7, 164.4 (d, $^1J_{C–F}$ = 251.7 Hz), 163.9, 129.4 (d, $^4J_{C–F}$ = 3.5 Hz), 128.4 (d, $^3J_{C–F}$ = 8.9 Hz), 126.7, 116.4 (d, $^2J_{C–F}$ = 22.9 Hz), 37.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ −108.01.

HRMS (ESI) *m/z* calcd for $C_{10}H_7FNaOS^+$ $[M + Na]^+$: 217.0094, found 217.0101.



4-(4-chlorophenyl)thiophen-2(5*H*)-one (3h)

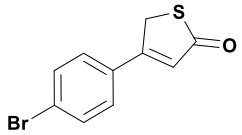
Following the general procedure, the title compound **3h** was isolated as a yellow-brown solid (15.1 mg, 72%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 134−136 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 6.68 (t, J = 1.6 Hz, 1H), 4.41 (d, J = 1.7 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.7, 163.7, 137.3, 131.8, 129.5, 127.6, 127.2, 37.46.

HRMS (ESI) *m/z* calcd for $C_{10}H_7ClNaOS^+$ $[M + Na]^+$: 232.9798, found 232.9806.



4-(4-bromophenyl)thiophen-2(5*H*)-one (3i)

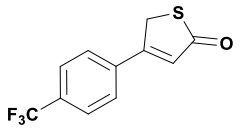
Following the general procedure, the title compound **3i** was isolated as a light-brown solid (17.8 mg, 70%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 134−136 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 6.72 (t, J = 1.6 Hz, 1H), 4.43 (d, J = 1.6 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.6, 163.7, 132.5, 132.2, 127.8, 127.4, 125.7, 37.4.

HRMS (ESI) *m/z* calcd for $C_{10}H_7BrNaOS^+$ $[M + Na]^+$: 276.9293, found 276.9300.



4-(4-(trifluoromethyl)phenyl)thiophen-2(5*H*)-one (3j)

Following the general procedure, the title compound **3j** was isolated as a black-brown solid (18.8 mg, 77%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

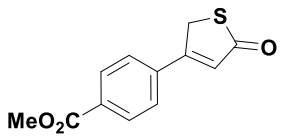
M. p. 135−137 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79−7.68 (m, 4H), 6.77 (s, 1H), 4.46 (d, J = 1.7 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.4, 163.2, 136.6, 132.8 (q, $^2J_{C–F}$ =34.1 Hz), 128.9, 126.7, 126.3 (q, $^3J_{C–F}$ = 11.2 Hz), 126.3 (q, $^1J_{C–F}$ = 272.4 Hz), 37.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ −63.00.

HRMS (ESI) *m/z* calcd for $C_{11}H_7F_3NaOS^+$ $[M + Na]^+$: 267.0062, found 267.0067.



methyl 4-(5-oxo-2,5-dihydrothiophen-3-yl)benzoate (3k)

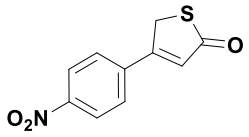
Following the general procedure, the title compound **3k** was isolated as a light-brown solid (16.2 mg, 69%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 197−201 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dt, J = 8.5, 2.0 Hz, 2H), 7.68 (dt, J = 8.5, 2.0 Hz, 2H), 6.79 (t. J = 1.6 Hz, 1H), 4.48 (d, J = 1.6 Hz, 2H), 3.97 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.5, 166.1, 163.6, 137.3, 132.2, 130.4, 128.7, 126.3, 52.5, 37.6.

HRMS (ESI) *m/z* calcd for $C_{12}H_{11}O_3S^+$ [M + H]$^+$: 235.0423, found 235.0413.



4-(4-nitrophenyl)thiophen-2(5*H*)-one (3l)

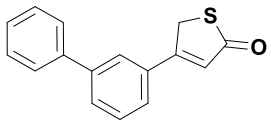
Following the general procedure, the title compound **3l** was isolated as a light-brown solid (5.8 mg, 26%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1→2:1, v/v).

M. p. 169−172 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dt, J = 8.6, 2.0 Hz, 2H), 6.71 (dt, J = 8.6, 2.0 Hz, 2H), 6.55 (t, J = 1.5 Hz, 1H), 4.40 (d, J = 1.5 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 199.3, 165.4, 149.4, 128.1, 123.4, 123.0, 114.8, 37.2.

HRMS (ESI) *m/z* calcd for $C_{10}H_6NO_3S^-$ [M − H]$^-$: 220.0074, found 220.0064.



4-([1,1'-biphenyl]-3-yl)thiophen-2(5*H*)-one (3m)

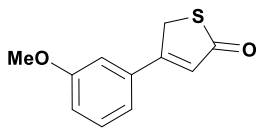
Following the general procedure, the title compound **3m** was isolated as a light-brown solid (13.5 mg, 54%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 134−136 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (t, J = 1.8 Hz, 1H), 7.71 (dt, J = 7.5, 1.5 Hz, 1H), 7.64−7.58 (m, 3H), 7.56 (dd, J = 7.7, 7.5 Hz, 1H), 7.51 (dd, J = 7.8, 7.3 Hz, 2H), 7.43 (dt, J = 7.3, 2.0 Hz, 1H), 6.78 (t, J = 1.6 Hz, 1H), 4.51 (d, J = 1.6 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.9, 165.2, 142.4, 140.1, 133.9, 130.0, 129.7, 129.0, 128.0, 127.2, 127.2, 125.2, 125.2, 37.7.

HRMS (ESI) *m/z* calcd for $C_{16}H_{13}OS^+$ [M + H]$^+$: 253.0682, found 253.0669.



4-(3-methoxyphenyl)thiophen-2(5*H*)-one (3n)

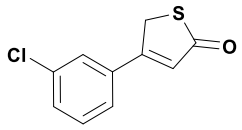
Following the general procedure, the title compound **3n** was isolated as a purple-brown solid (12.9 mg, 63%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 134−136 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, J = 8.0 Hz, 8.0 Hz 1H), 7.21−7.02 (m, 3H), 6.69 (q, J = 1.4 Hz, 1H), 4.45−4.42 (m, 2H), 3.87 (d, J = 0.8 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.0, 165.2, 160.0, 134.7, 130.3, 127.2, 118.8, 116.3, 112.2, 55.5, 37.6.

HRMS (ESI) *m/z* calcd for $C_{11}H_{10}NaO_2S^+$ $[M + Na]^+$: 229.0294, found 229.0306.



4-(3-chlorophenyl)thiophen-2(5*H*)-one (3o)

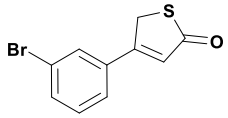
Following the general procedure, the title compound **3o** was isolated as a yellow-brown solid (14.3 mg, 68%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 133−135 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (t, J = 1.9 Hz, 1H), 7.52−7.41 (m, 3H), 6.72 (t, J = 1.7 Hz, 1H), 4.43 (d, J = 1.7 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.5, 163.4, 135.3, 133.9, 130.8, 129.3, 128.0, 125.0, 123.4, 37.5.

HRMS (ESI) *m/z* calcd for $C_{10}H_7ClNaOS^+$ $[M + Na]^+$: 232.9798, found 232.9802.



4-(3-chlorophenyl)thiophen-2(5*H*)-one (3p)

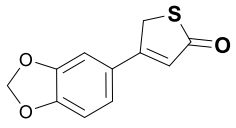
Following the general procedure, the title compound **3p** was isolated as a light-brown solid (17.4 mg, 65%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 134−136 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (t, J = 1.9 Hz, 1H), 7.62 (ddd, J = 7.9, 2.0, 1.0 Hz, 1H), 7.55 (ddd, J = 7.9, 1.8, 1.0 Hz, 1H), 7.37 (t, J = 7.9 Hz, 1H), 6.71 (t, J = 1.7 Hz, 1H), 4.43 (d, J = 1.7 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.5, 163.4, 135.3, 133.9, 130.8, 129.3, 128.0, 125.0, 123.4, 37.5.

HRMS (ESI) *m/z* calcd for $C_{10}H_7BrNaOS^+$ $[M + Na]^+$: 276.9293, found 276.9302.



4-(benzo[*d*][1,3]dioxol-5-yl)thiophen-2(5*H*)-one (3q)

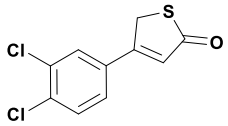
Following the general procedure, the title compound **3q** was isolated as a light-brown solid (11.3 mg, 51%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 204−207 ℃.

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.46 (d, J = 1.8 Hz, 1H), 7.36 (dd, J = 8.2, 1.8 Hz, 1H), 7.04 (d, J = 8.2 Hz, 1H), 6.90 (t, J = 1.5 Hz, 1H), 6.12 (s, 2H), 4.66 (d, J = 1.5 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 199.0, 166.8, 150.2, 148.5, 127.9, 124.9, 122.4, 109.0, 107.5, 102.3, 37.6.

HRMS (ESI) *m/z* calcd for $C_{11}H_9O_3S^+$ [M + Na]$^+$: 221.0267, found 221.0277.



4-(3,4-dichlorophenyl)thiophen-2(5*H*)-one (3r)

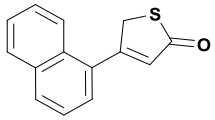
Following the general procedure, the title compound **3r** was isolated as a purple-brown solid (13.9 mg, 57%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 134−136 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 2.2 Hz, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.45 (dd, J = 8.4, 2.1 Hz, 1H), 6.71 (t, J = 1.6 Hz, 1H), 4.42 (d, J = 1.6 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.2, 162.3, 135.4, 133.8, 133.2, 131.3, 128.2, 128.1, 125.5, 37.4.

HRMS (ESI) *m/z* calcd for $C_{10}H_7Cl_2OS^+$ [M + H]$^+$: 244.9589, found 244.9582.



4-(naphthalen-1-yl)thiophen-2(5*H*)-one (3s)

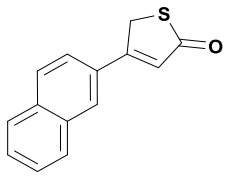
Following the general procedure, the title compound **3s** was isolated as a light-brown solid (15.3 mg, 68%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 130−132 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01−7.93 (m, 3H), 7.61−7.57 (m, 2H), 7.56 (dd, J = 8.3, 7.0 Hz, 1H), 7.48 (dd, J = 7.2, 1.2 Hz, 1H), 6.61 (t, J = 1.7 Hz, 1H), 4.49 (d, J = 1.7 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.1, 166.1, 133.8, 133.0, 132.4, 130.2, 130.1, 128.8, 127.3, 126.6, 125.1, 125.0, 124.5, 41.1.

HRMS (ESI) *m/z* calcd for $C_{14}H_{11}OS^+$ [M + H]$^+$: 227.0525, found 227.0518.



4-(naphthalen-2-yl)thiophen-2(5*H*)-one (3t)

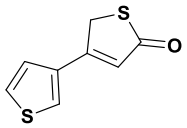
Following the general procedure, the title compound **3t** was isolated as a light-brown solid (18.1 mg, 80%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 135−137 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 1.9 Hz, 1H), 7.95−7.86 (m, 3H), 7.68 (dd, J = 8.7, 1.9 Hz, 1H), 7.64−7.55 (m, 2H), 6.83 (q, J = 1.4 Hz, 1H), 4.57 (t, J = 1.3 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.0, 165.0, 134.4, 133.0, 130.7, 129.1, 128.9, 127.9, 127.9, 127.2, 127.1, 126.3, 123.5, 37.6.

HRMS (ESI) *m/z* calcd for $C_{14}H_{10}NaOS^+$ [M + Na]$^+$: 249.0345, found 249.0357.



(3,3'-bithiophen)-5(2*H*)-one (3u)

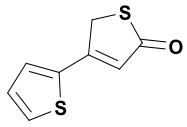
Following the general procedure, the title compound **3u** was isolated as a purple-brown solid (13.7 mg, 75%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 136−138 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, J = 3.0, 1.3 Hz, 1H), 7.45 (dd, J = 5.2, 2.8 Hz, 1H), 7.33 (dd, J = 5.1, 1.3 Hz, 1H), 6.56 (t, J = 1.5 Hz, 1H), 4.43 (d, J = 1.5 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.1, 159.7, 136.0, 127.5, 125.8, 125.7, 125.6, 37.6.

HRMS (ESI) *m/z* calcd for $C_8H_6NaOS_2^+$ [M + Na]$^+$: 204.9752, found 204.9762.



(2,3'-bithiophen)-5'(2'*H*)-one (3v)

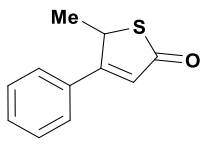
Following the general procedure, the title compound **3v** was isolated as a purple-brown solid (12.7 mg, 71%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 134−136 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 5.1 Hz, 1H), 7.43 (d, J = 3.8 Hz, 1H), 7.15 (dd, J = 5.1, 3.7 Hz, 1H), 6.54 (d, J = 1.5 Hz, 1H), 4.45 (d, J = 1.5 Hz, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.3, 158.4, 137.4, 129.8, 128.5, 127.9, 124.8, 37.4.

HRMS (ESI) *m/z* calcd for $C_8H_6NaOS_2^+$ [M + Na]$^+$: 204.9752, found 204.9753.



5-methyl-4-phenylthiophen-2(5*H*)-one (3w)

Following the general procedure, the title compound **3w** was isolated as a yellow-brown solid (11.6 mg, 61%) by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1→5:1, v/v).

M. p. 134−136 ℃.

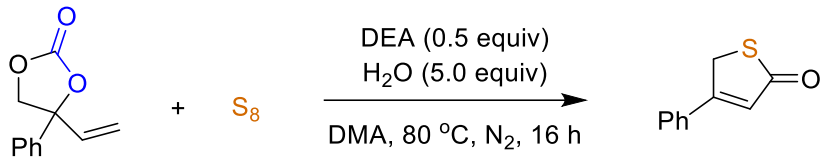
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 1.1 Hz, 5H), 6.50 (s, 1H), 4.99−4.95 (m, 1H), 1.57 (d, J = 7.2 Hz, 3H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 197.7, 171.3, 132.7, 130.7, 129.2, 127.5, 127.3, 47.6, 21.0.

HRMS (ESI) *m/z* calcd for $C_{11}H_{10}NaOS^+$ $[M + Na]^+$: 213.0345, found 213.0356.

5. Gram-scale and late-stage functionalization experiments

5.1 Gram scale synthesis of the thiophenone product 3a

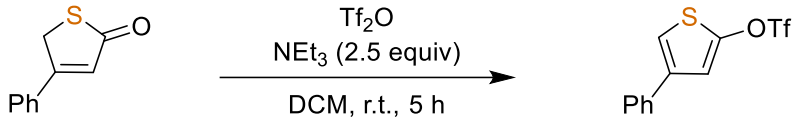


1a **2** **3a**

To a 50 mL round-bottom flask containing a stir bar were added vinylethylene carbonate **1a** (0.95 g, 5.0 mmol, 1.0 equiv.), elemental sulfur (S_8, **2**; 2.56 g, 10.0 mmol, 2.0 equiv.), DEA (375 μL, 12.5 mmol, 0.5 equiv.), H_2O (2.2 mL, 125 mmol, 5.0 equiv.), and dry DMA (25.0 mL). Then the tube was evacuated and charged with N_2 three times. The mixture was stirred at 80°C for 16 h. After cooling to ambient temperature, the solvent was removed under reduced pressure, and the residue was quenched by the addition of H_2O (50 mL). The aqueous phase was extracted with ethyl acetate (3×50 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (15:1→5:1, v/v) afforded the corresponding 2(5*H*)-thiophenone product **3a** in 76% yield (0.67 g) as a purple-brown solid.

Notice: *Due to the high boiling point of DMA (165 °C), the large amount of solvent could not be completely removed by rotary evaporation, resulting in impure target product* ***3a*** *during subsequent column chromatography, and therefore a solvent-reduced approach (halved solvent volume, 25 mL) was adopted for the gram-scale reaction.*

5.2 Synthesis of 2-thiophenyl trifluoromethanesulfonate (4)



3a **4**

To a 15 mL Schlenk tube containing a stir bar were added 2(5*H*)-thiophenone **3a** (17.6.0 mg, 0.1 mmol, 1.0 equiv.), Tf_2O (28.2 mg, 0.1 mmol, 1.0 equiv.), Et_3N (35 μL, 0.25 mmol, 2.5 equiv.), and DCM (1.0 mL). Then the tube was evacuated and charged with N_2 three times. The mixture was stirred at ambient temperature for 5 h and then was quenched by the addition of H_2O (15 mL). The aqueous phase was extracted with ethyl acetate (3×15 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (65:1→35:1, v/v) afforded 2-thiophenyl trifluoromethanesulfonate (**4**) in 37% yield (11.3 mg) as a colorless-brown oil.

4-phenylthiophen-2-yl trifluoromethanesulfonate (4)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 7.5 Hz, 2H), 7.44 (dd, J = 7.5, 7.4 Hz, 2H), 7.37 (dd, J

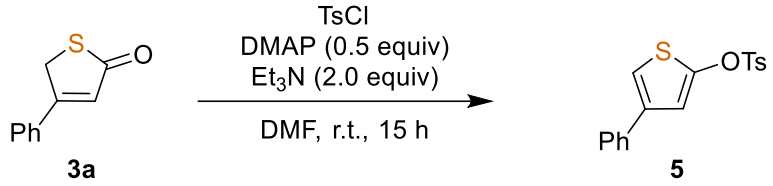
= 7.5, 7.4 Hz, 1H), 7.22 (d, J = 1.9 Hz, 1H), 7.17 (d, J = 1.9 Hz, 1H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 149.5, 139.5, 134.7, 129.0, 128.0, 126.1, 117.9, 117.5, 115.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ −71.46.

HRMS (ESI) *m/z* calcd for $C_{11}H_7F_3NaO_3S_2^+$ $[M + Na]^+$: 330.9681, found 330.9686.

5.3 Synthesis of 2-thiophenyl 4-methylbenzenesulfonate (5)



3a **5**

To a 15 mL Schlenk tube containing a stir bar were added 2(5*H*)-thiophenone **3a** (22.9 mg, 0.13 mmol, 1.3 equiv.), TsCl (28.2 mg, 0.1 mmol, 1.0 equiv.), 4-dimethylaminopyridine (DMAP, 6.1 mg, 0.05 mmol, 0.5 equiv.), Et_3N (28 μL, 0.2 mmol, 2.0 equiv.), and DMF (1.0 mL). Then the tube was evacuated and charged with N_2 three times. The mixture was stirred at ambient temperature for 15 h and then was quenched by the addition of H_2O (15 mL). The aqueous phase was extracted with ethyl acetate (3×15 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (15:1→5:1, v/v) afforded 2-thiophenyl 4-methylbenzenesulfonate (**5**) in 45% yield (14.8 mg) as a yellow-brown oil.

4-phenylthiophen-2-yl 4-methylbenzenesulfonate (**5**)

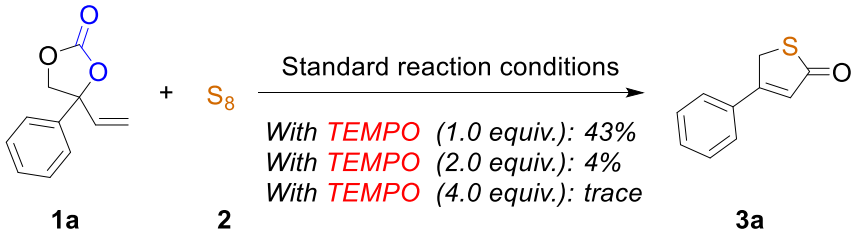
^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 7.6 Hz, 2H), 7.41−7.35 (m, 4H), 7.31 (dd, J = 7.6, 7.0 Hz, 1H), 7.01 (d, J = 1.9 Hz, 1H), 6.91 (d, J = 1.9 Hz, 1H), 2.49 (s, 3H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 151.1, 146.2, 139.0, 135.2, 130.9, 129.9, 129.0, 128.9, 127.6, 126.0, 117.3, 114.27, 21.8.

HRMS (ESI) *m/z* calcd for $C_{17}H_{15}O_3S_2^+$ $[M + H]^+$: 331.0457, found 331.0452.

6. Mechanistic studies

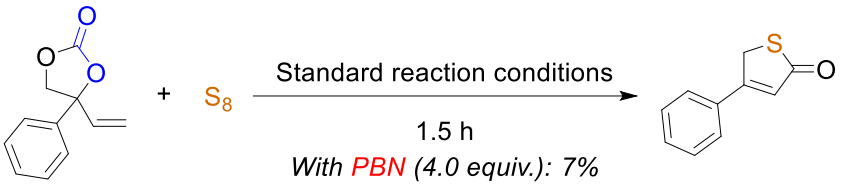
6.1 Radical inhibition experiment



1a **2** **3a**

To a 15 mL Schlenk tube containing a stir bar were added vinylethylene carbonate **1a** (0.2 mmol, 1.0 equiv.), elemental sulfur (S_8, **2**; 102.6 mg, 0.4 mmol, 2.0 equiv.), DEA (15 μL, 0.1 mmol, 0.5 equiv.), H_2O (18 μL, 10.0 mmol, 5.0 equiv.), TEMPO (31.2/62.5/125.0 mg, 0.2/0.4/0.8 mmol, 1.0/2.0/4.0 equiv.), and dry DMA (1.0 mL). Then the tube was evacuated and charged with N_2 three times. The mixture was stirred at 80°C for 16 h. After cooling to ambient temperature, the target product **3a** was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (15:1→5:1, v/v).

6.2 EPR experiments



1a **2** **3a**

To a 15 mL Schlenk tube containing a stir bar were added vinylethylene carbonate **1a** (19.0 mg, 0.1 mmol, 1.0 equiv.), elemental sulfur (S_8, **2**; 51.3 mg, 0.2 mmol, 2.0 equiv.), DEA (7 μL, 0.05 mmol, 0.5 equiv.), H_2O (9 μL, 5.0 mmol, 5.0 equiv.), PBN (72 μL, 0.4 mmol, 4.0 equiv.), and dry DMA (1.0 mL). Then the tube was evacuated and charged with N_2 three times. The mixture was stirred at 80 °C for 1.5 h. The resulting reaction mixture was measured by EPR, and no diagnostic signal was observed by EPR measurements (Fig. S1; the EPR spectrum was recorded at 77 K on Bruker EMXplus-9.5/12). Meanwhile, the target product **3a** was isolated in 7% yield by column chromatography on silica gel with petroleum ether/ethyl acetate (15:1→5:1, v/v).

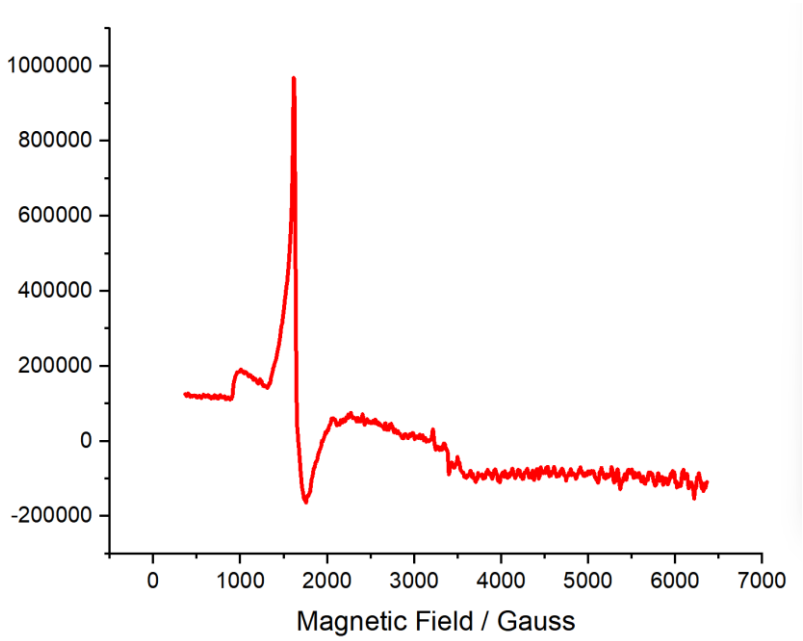
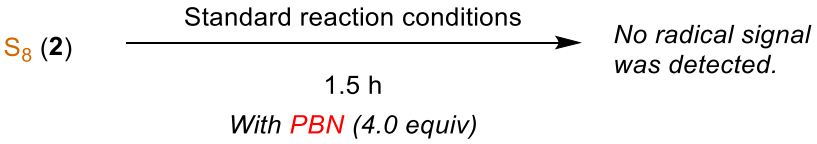


Fig. S1 EPR experiment under the standard reaction conditions.



To a 15 mL Schlenk tube containing a stir bar were added elemental sulfur (S_8, **2**; 51.3 mg, 0.2 mmol, 2.0 equiv.), DEA (7 μL, 0.05 mmol, 0.5 equiv.), H_2O (9 μL, 5.0 mmol, 5.0 equiv.), PBN (72 μL, 0.4 mmol, 4.0 equiv.), and dry DMA (1.0 mL). Then the tube was evacuated and charged with N_2 three times. The mixture was stirred at 80 °C for 1.5 h, and no diagnostic signal was observed by EPR analysis ((Fig. S2; the EPR spectrum was recorded at 77 K on Bruker EMXplus-9.5/12).

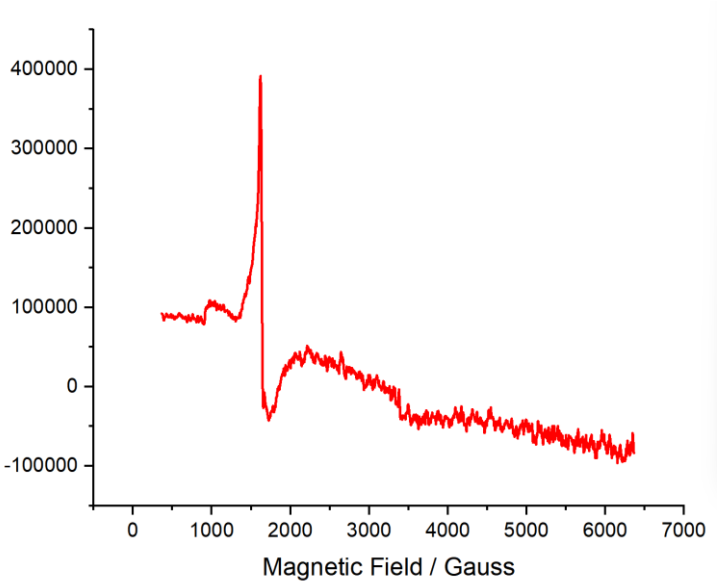
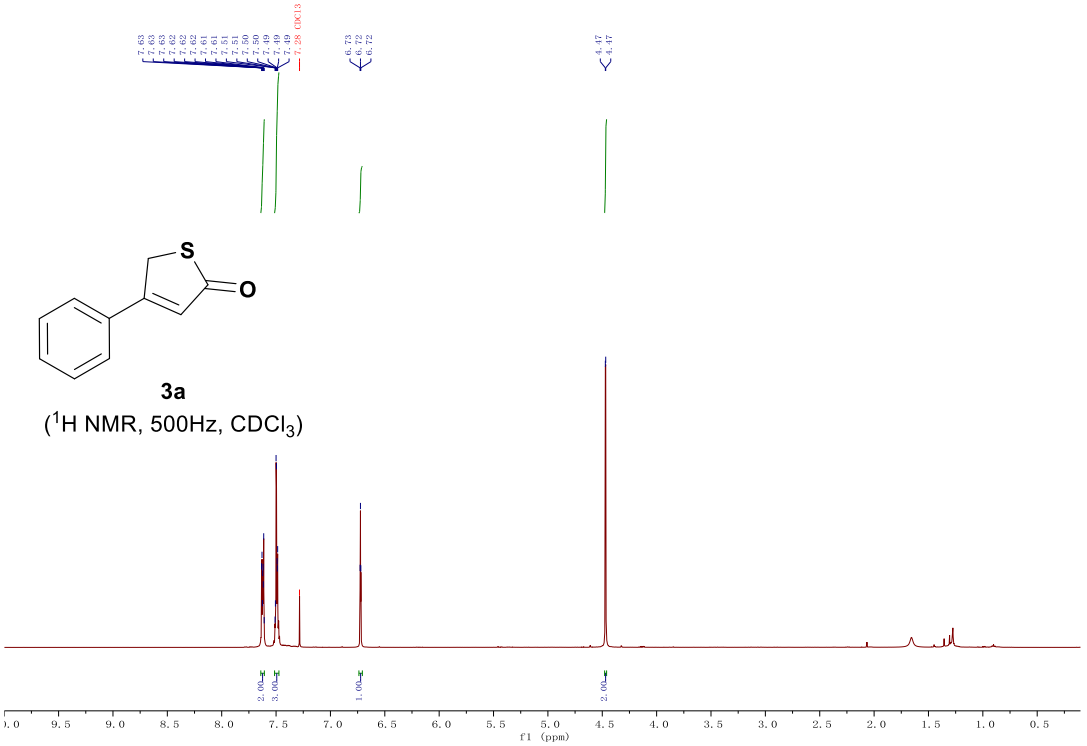


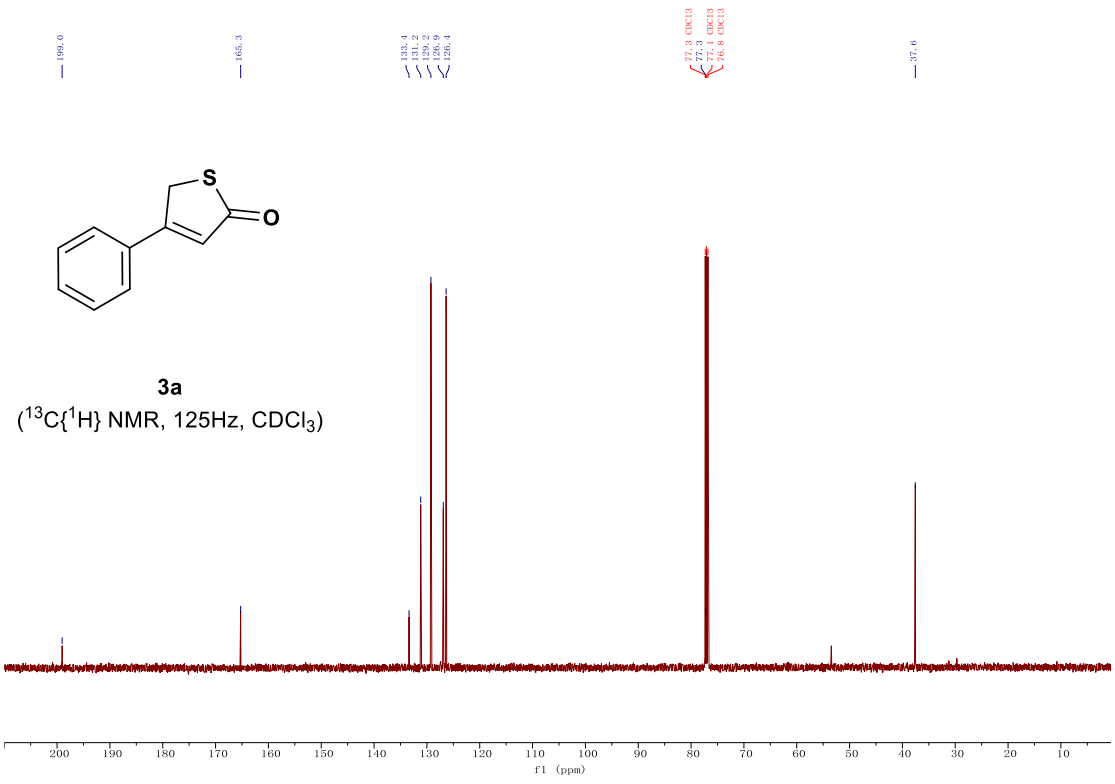
Fig. S2 EPR experiment by mixing S_8 and DIPEA upon heating.

7. NMR spectra of compounds 3−5



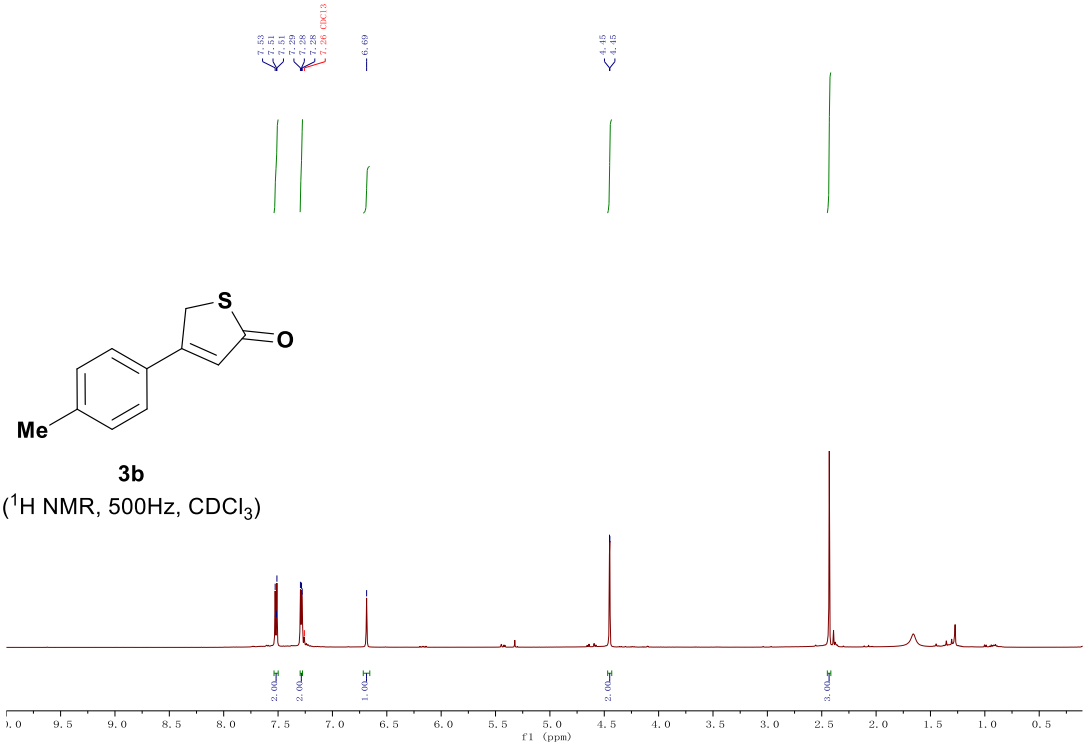
3a

(^{1}H NMR, 500Hz, $CDCl_3$)



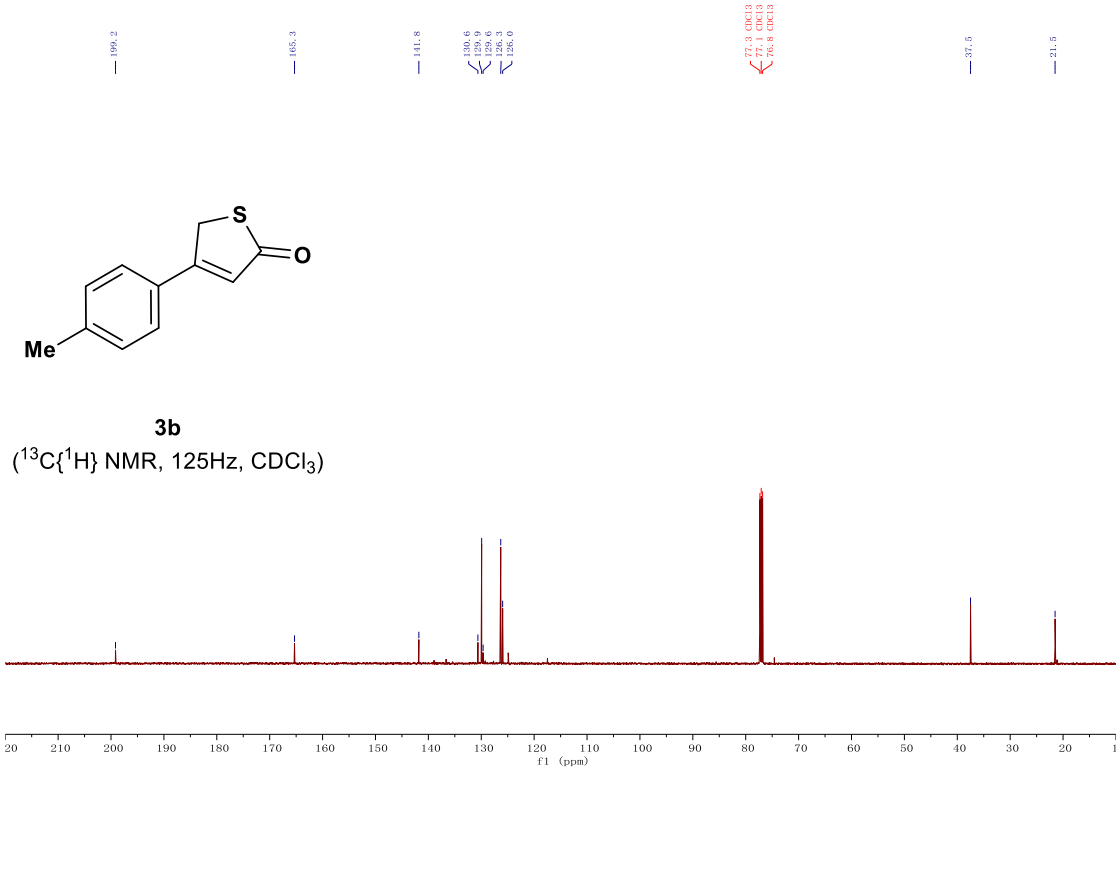
3a

($^{13}C\{^{1}H\}$ NMR, 125Hz, $CDCl_3$)



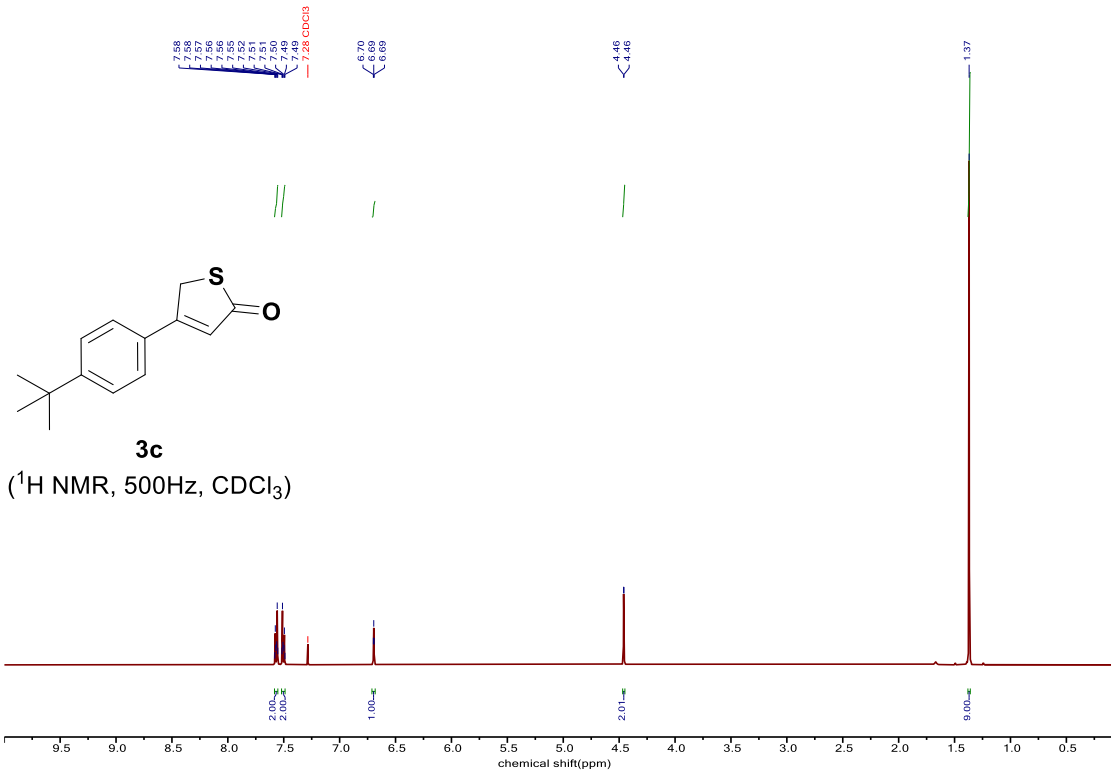
3b

(^{1}H NMR, 500Hz, $CDCl_3$)



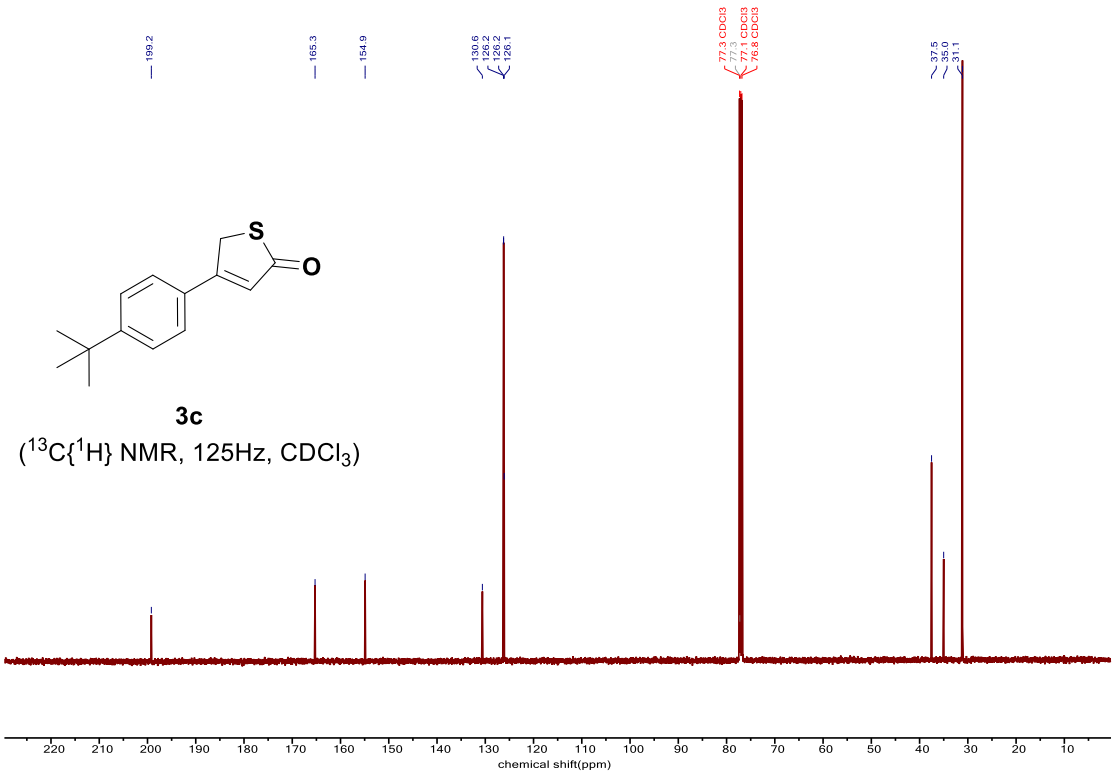
3b

($^{13}C\{^1H\}$ NMR, 125Hz, $CDCl_3$)



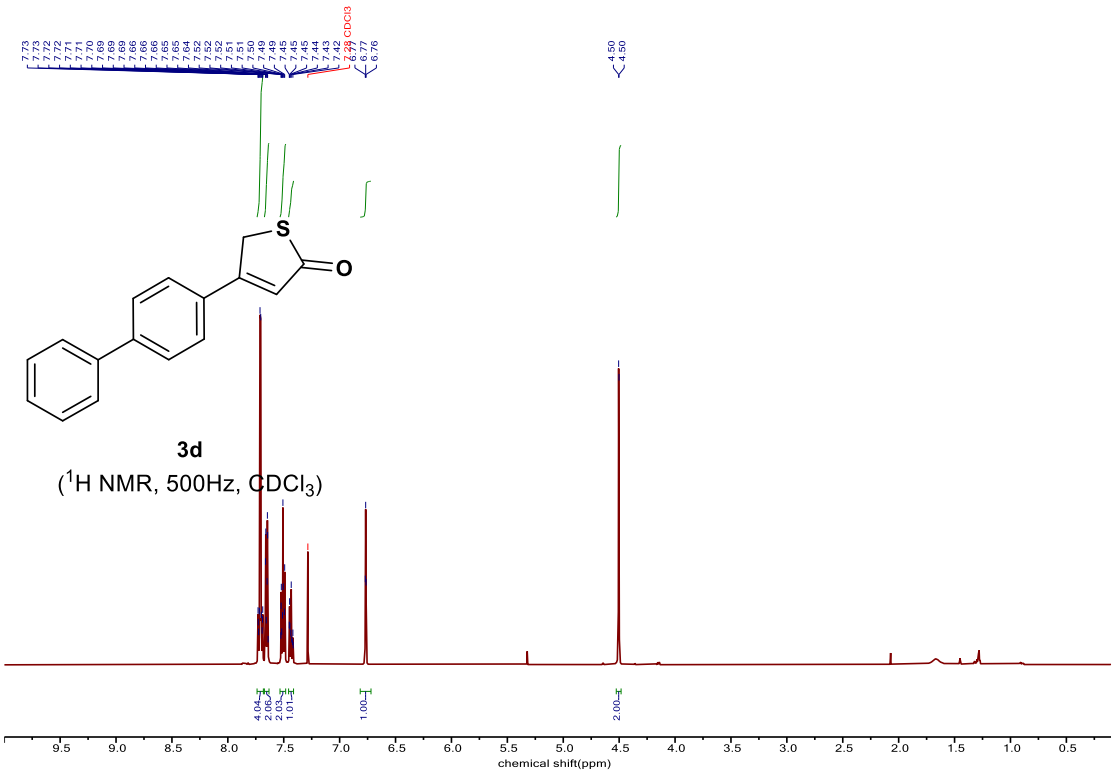
3c

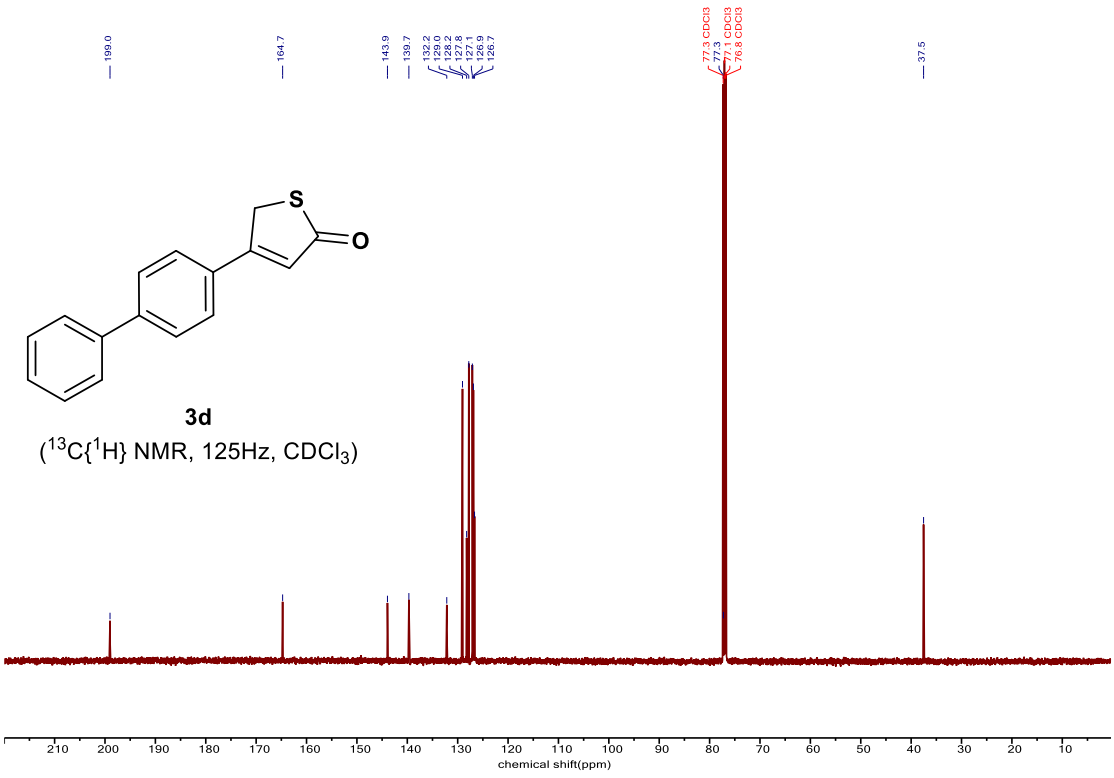
(^{1}H NMR, 500Hz, $CDCl_3$)

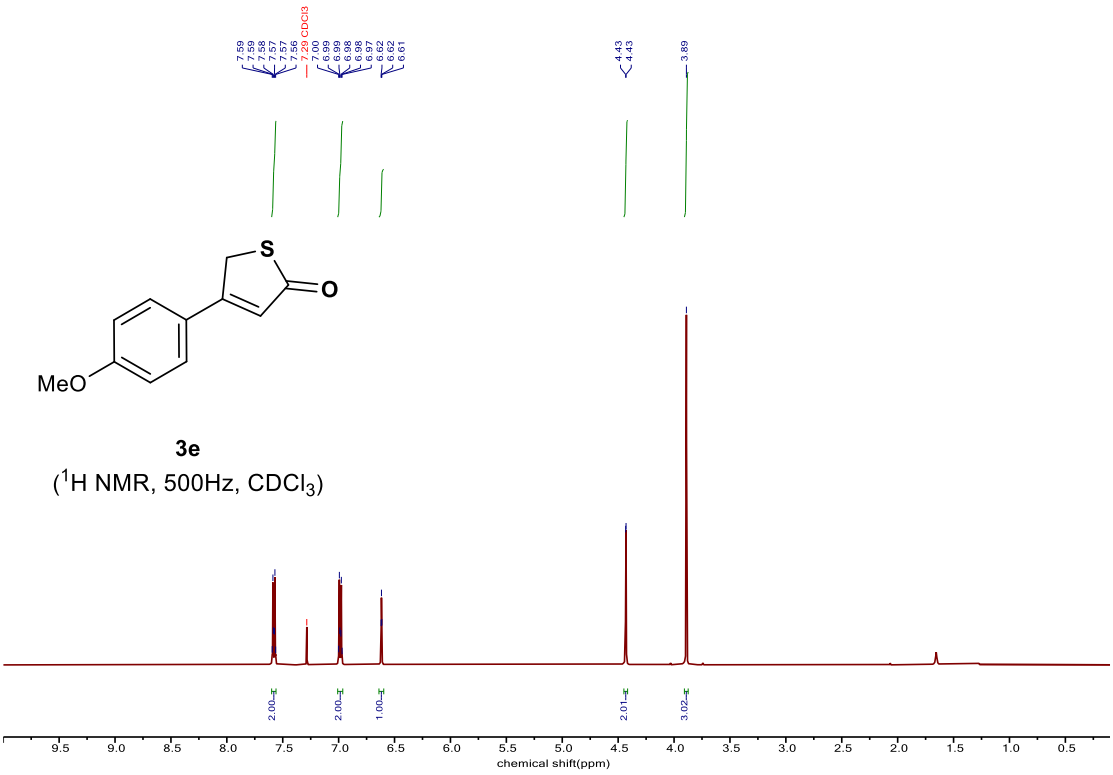


3c

(^{13}C{^{1}H} NMR, 125Hz, $CDCl_3$)

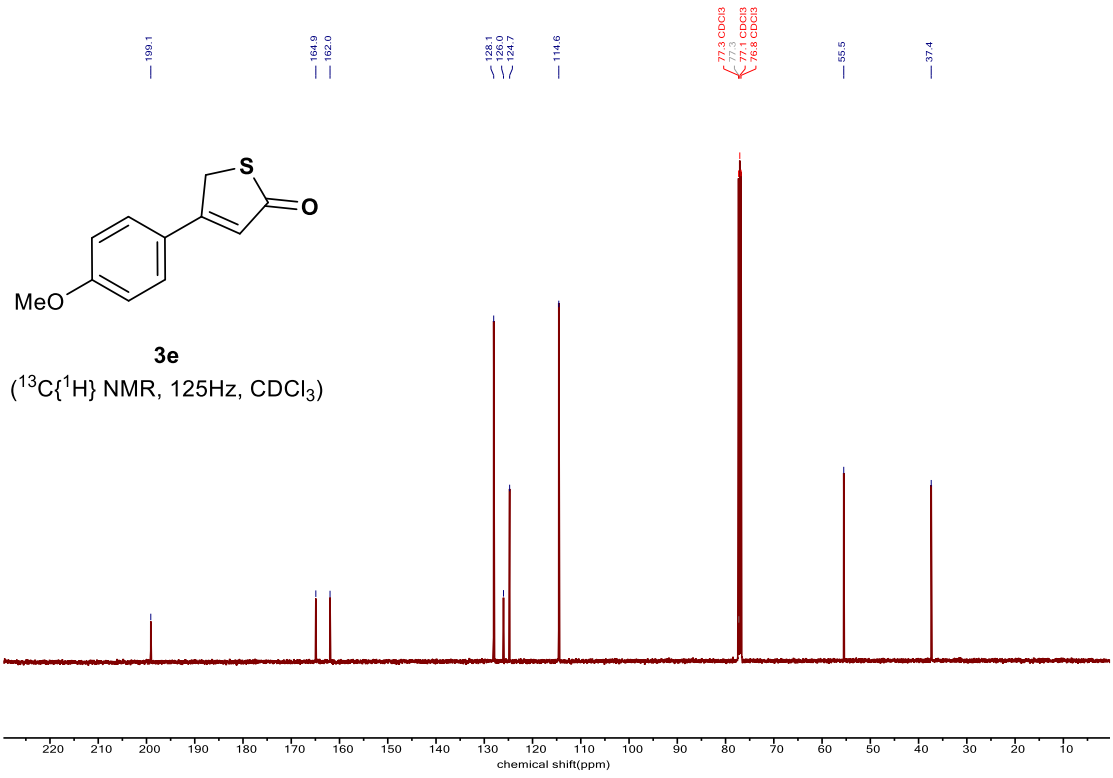

S
O
3d
(1H NMR, 500Hz, CDCl3)
chemical shift(ppm)


S
O
3d
(13C{1H} NMR, 125Hz, CDCl3)
chemical shift(ppm)



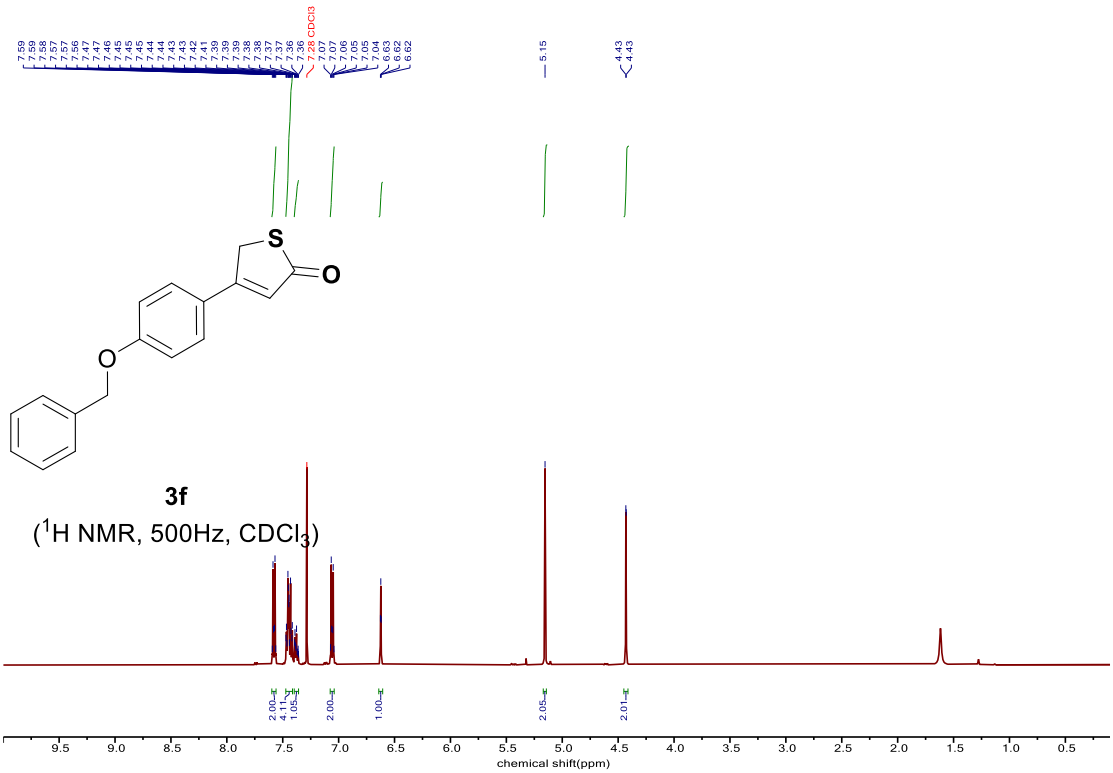
3e

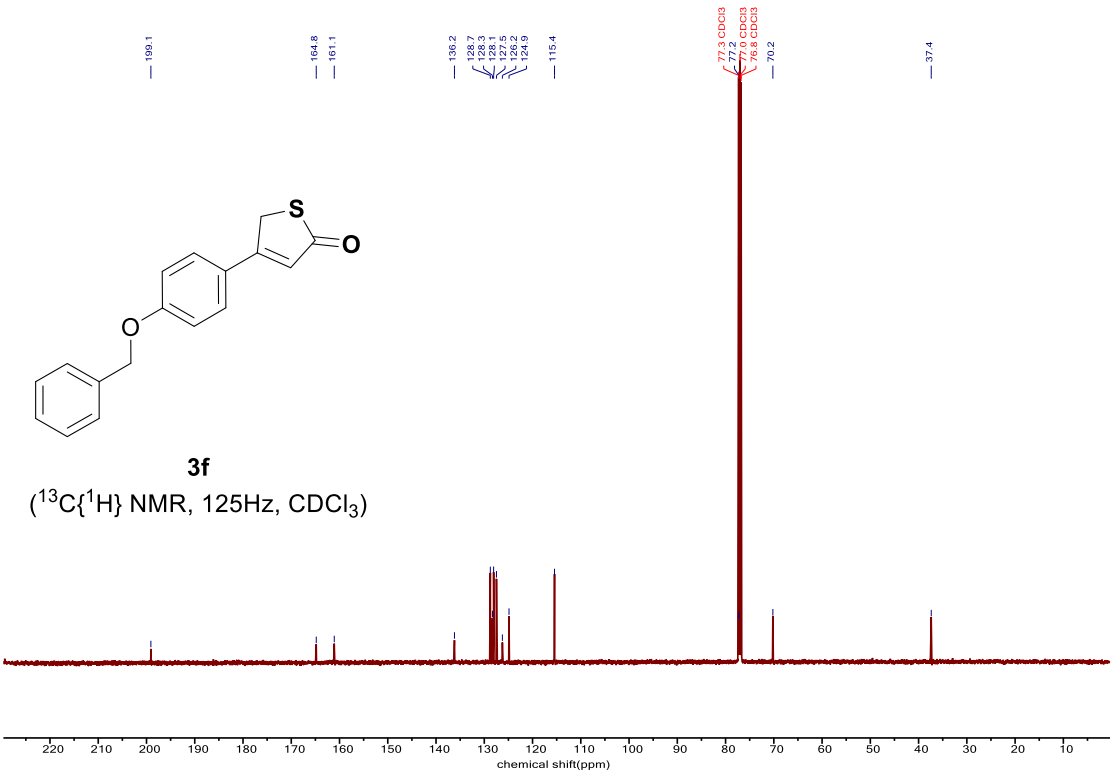
(^{1}H NMR, 500Hz, $CDCl_3$)

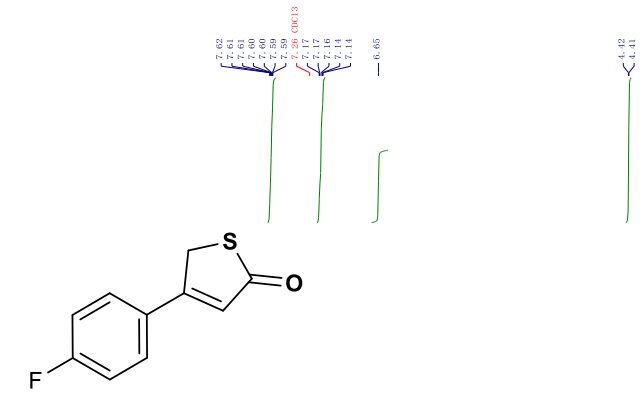


3e

(^{13}C{^{1}H} NMR, 125Hz, $CDCl_3$)

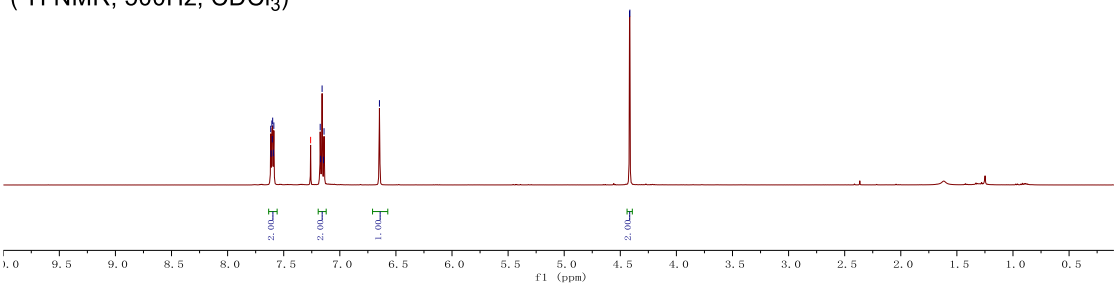

7.59
7.59
7.58
7.57
7.57
7.57
7.56
7.47
7.47
7.46
7.45
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.28 CDCl3
7.07
7.06
7.05
7.05
7.04
6.63
6.62
6.62
5.15
4.43
4.43
S
O
O
3f
(1H NMR, 500Hz, CDCl3)
2.00
4.11
1.05
2.00
1.00
2.05
2.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
chemical shift(ppm)

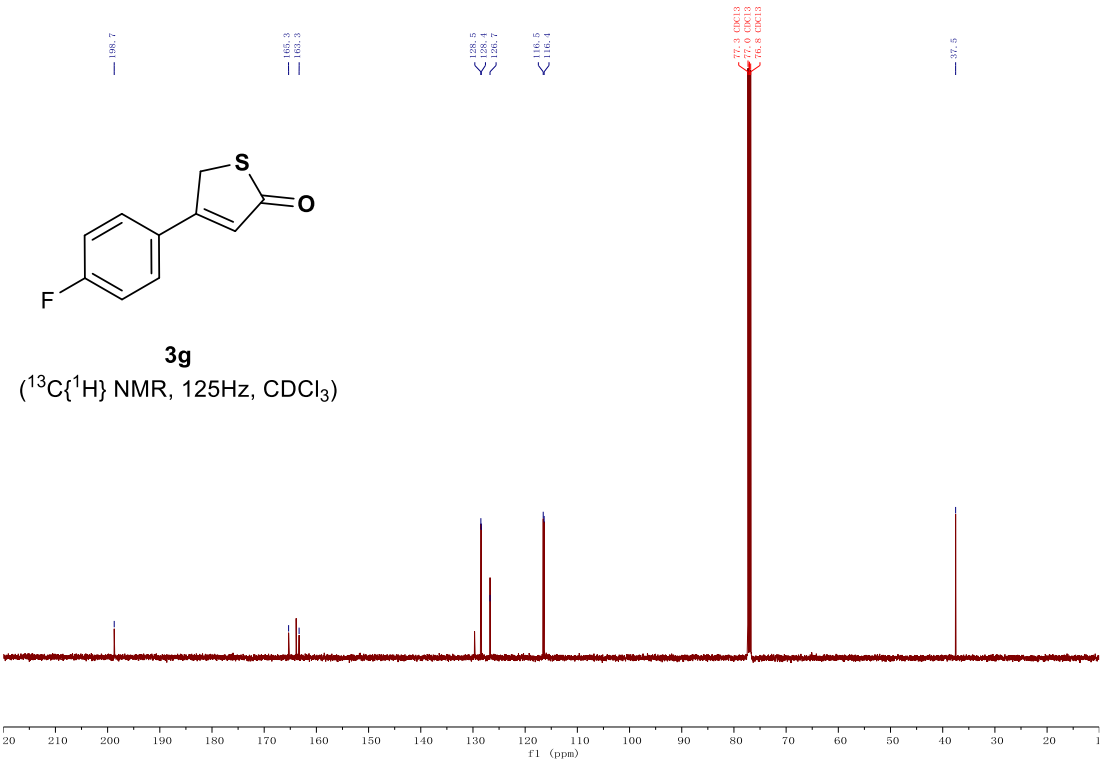

199.1
164.8
161.1
136.2
128.7
128.3
128.1
127.5
126.2
124.9
115.4
77.3 CDCl3
77.2
77.0 CDCl3
76.8 CDCl3
70.2
37.4
S
O
O
3f
(13C{1H} NMR, 125Hz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
chemical shift(ppm)



3g

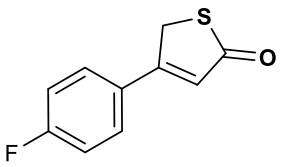
(^{1}H NMR, 500Hz, $CDCl_3$)





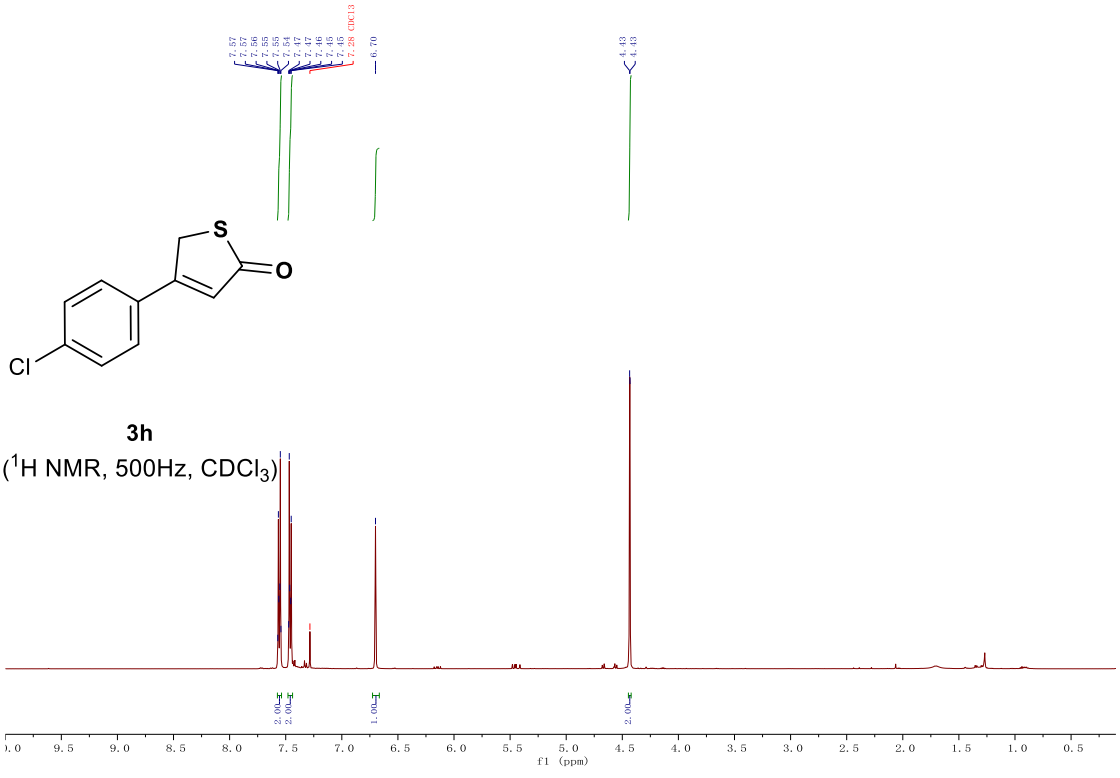
3g

($^{13}C\{^1H\}$ NMR, 125Hz, $CDCl_3$)



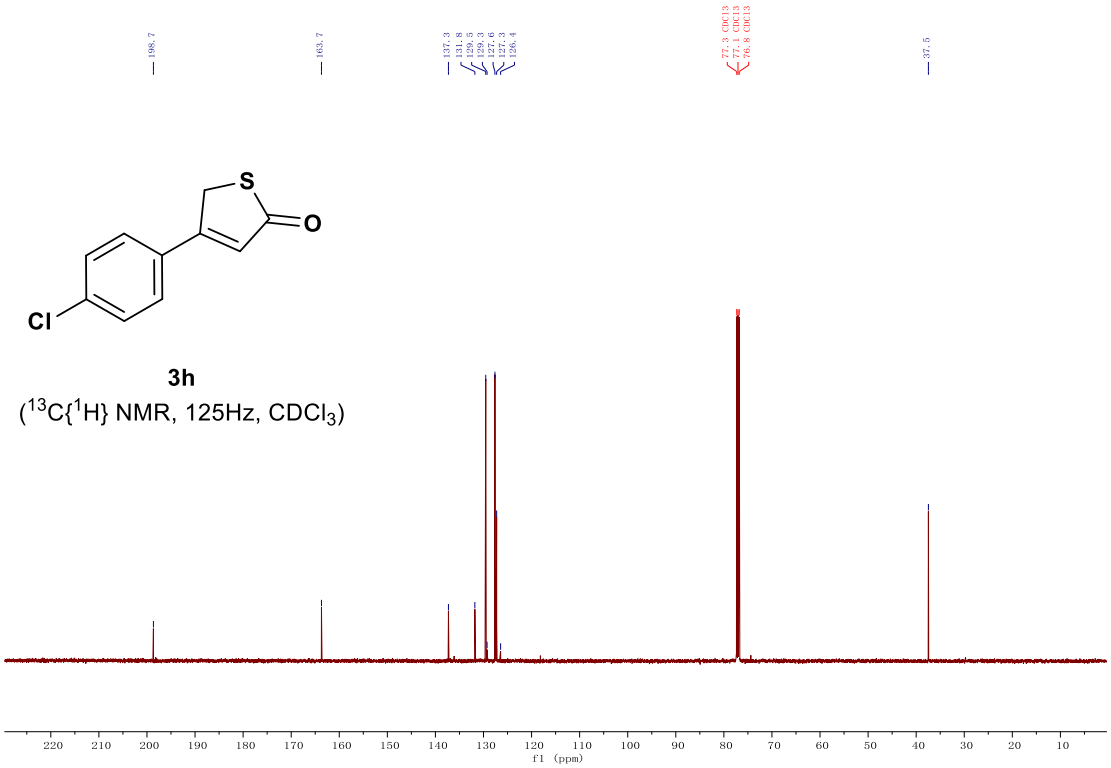
3g

(^{19}F NMR, 471Hz, $CDCl_3$)



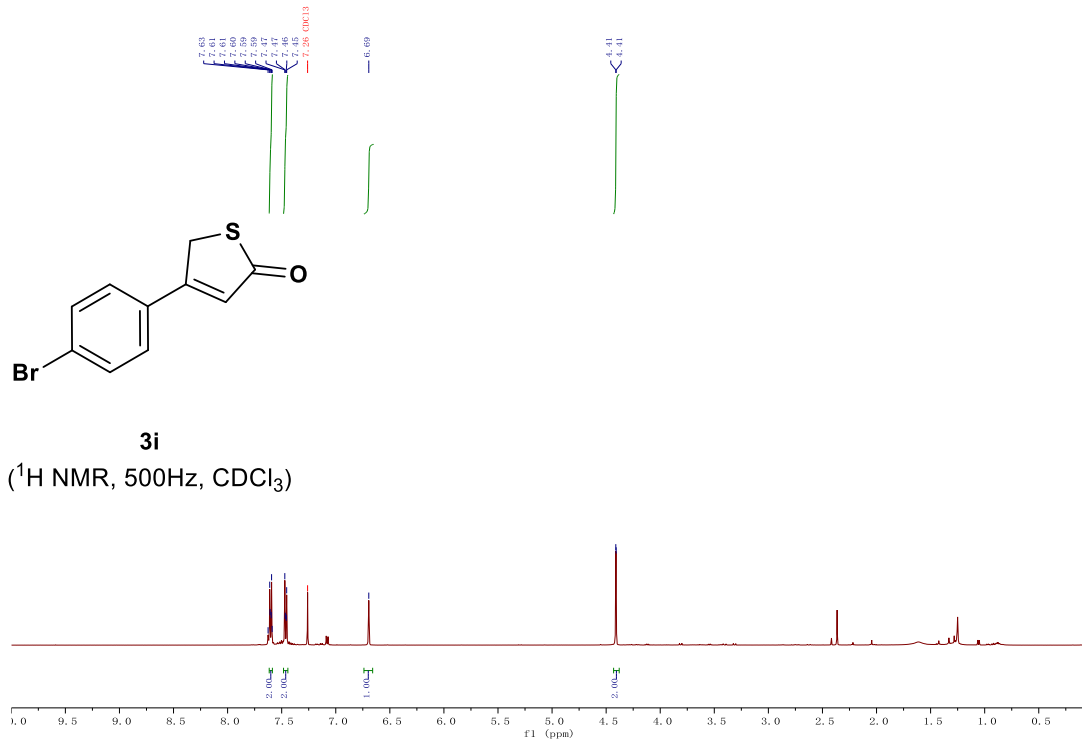
3h

(^{1}H NMR, 500Hz, $CDCl_3$)



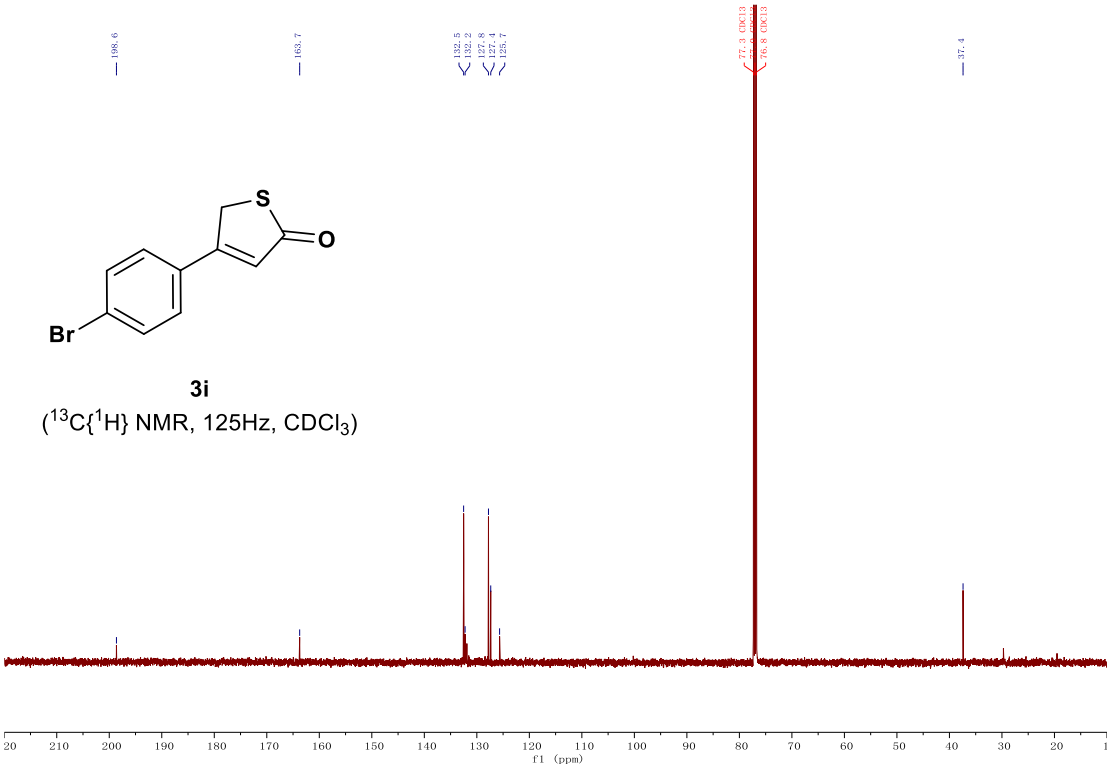
3h

($^{13}C\{^{1}H\}$ NMR, 125Hz, $CDCl_3$)



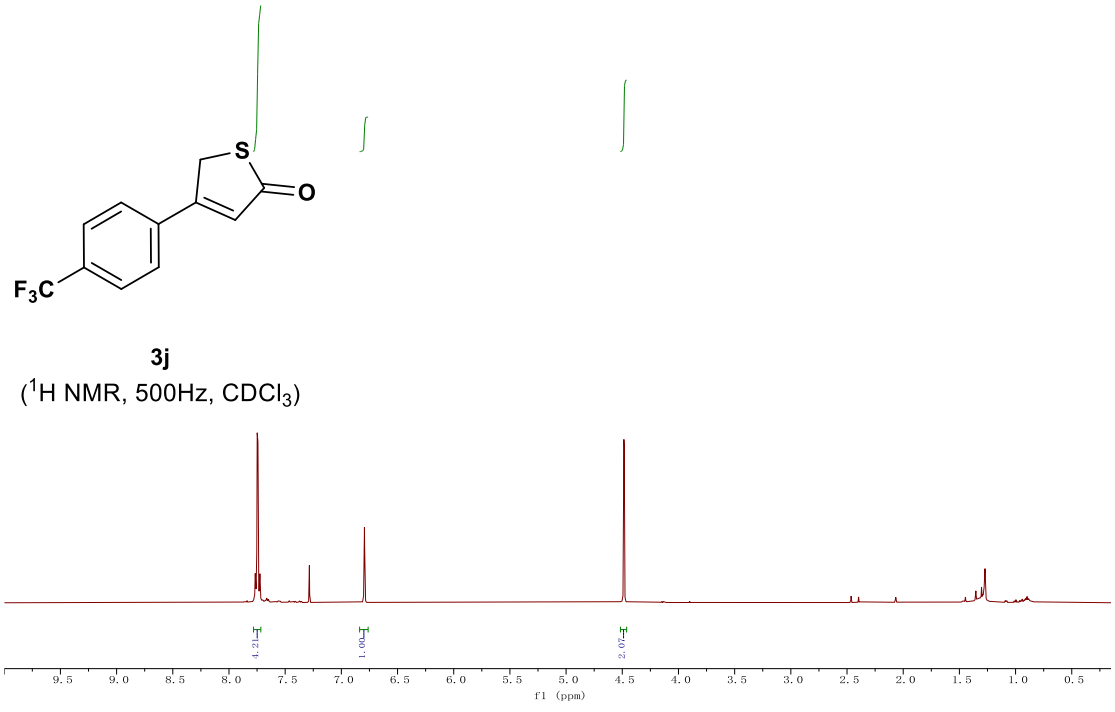
3i

(^{1}H NMR, 500Hz, $CDCl_3$)



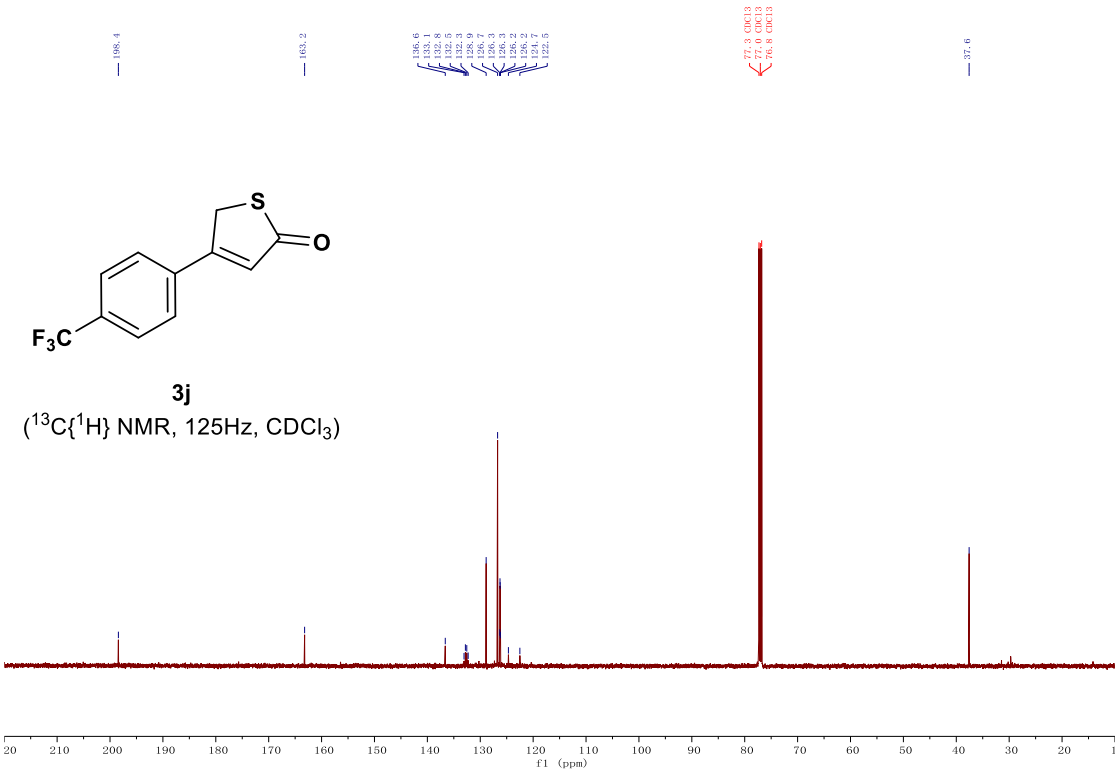
3i

($^{13}C\{^{1}H\}$ NMR, 125Hz, $CDCl_3$)



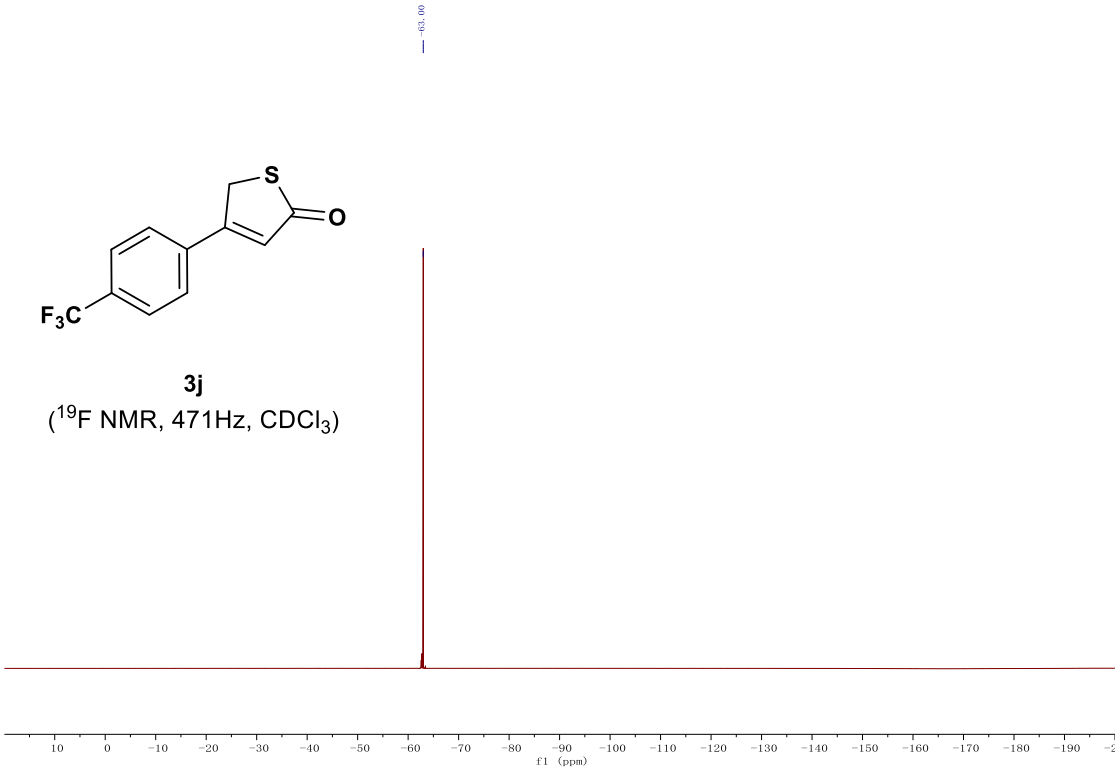
3j

(^{1}H NMR, 500Hz, $CDCl_3$)



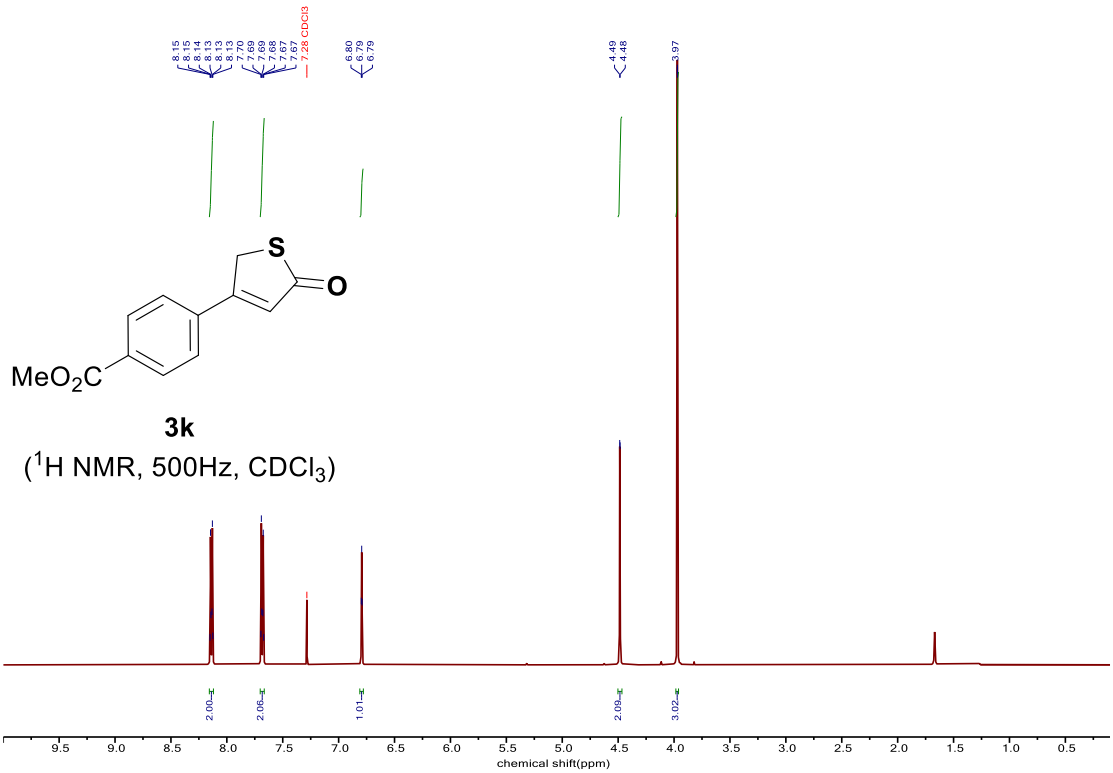
3j

($^{13}C\{^{1}H\}$ NMR, 125Hz, $CDCl_3$)



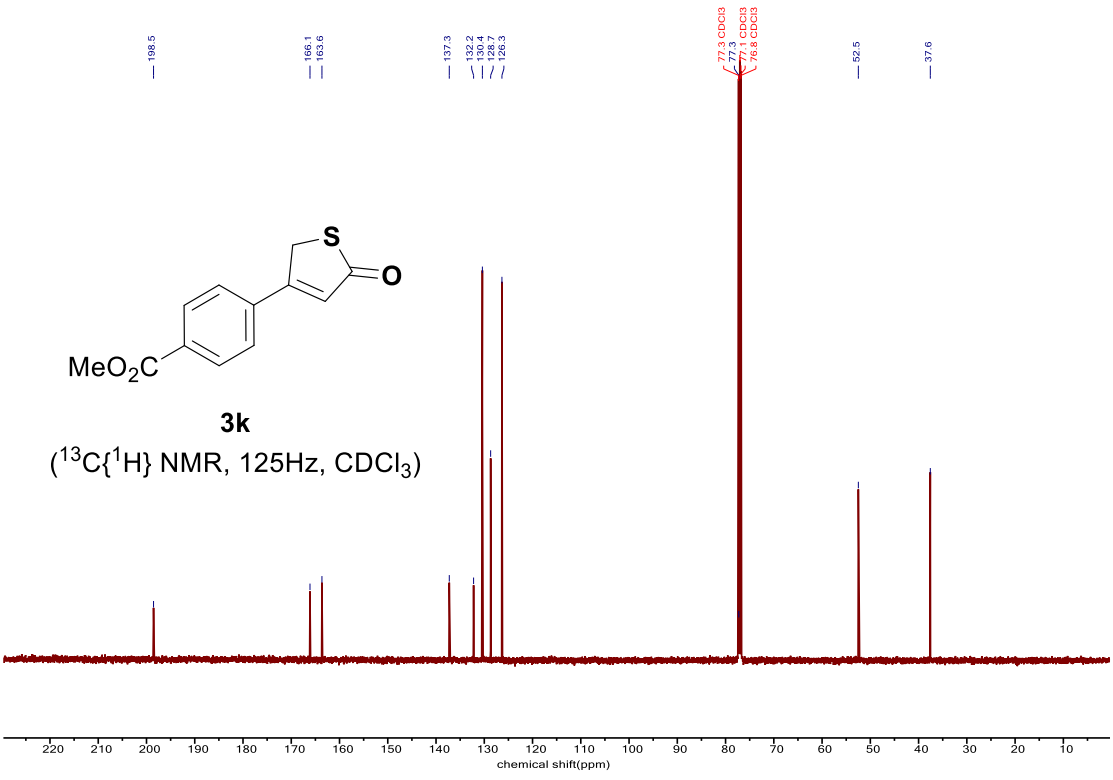
3j

(^{19}F NMR, 471Hz, $CDCl_3$)



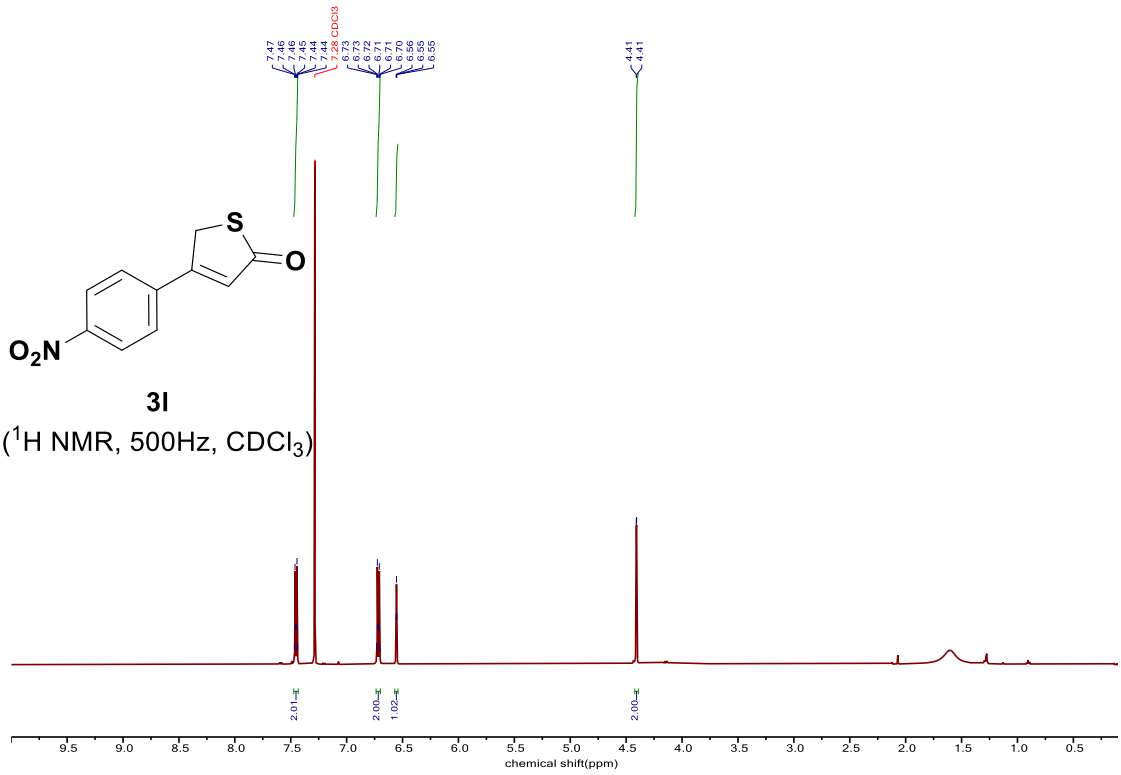
3k

(^{1}H NMR, 500Hz, $CDCl_3$)



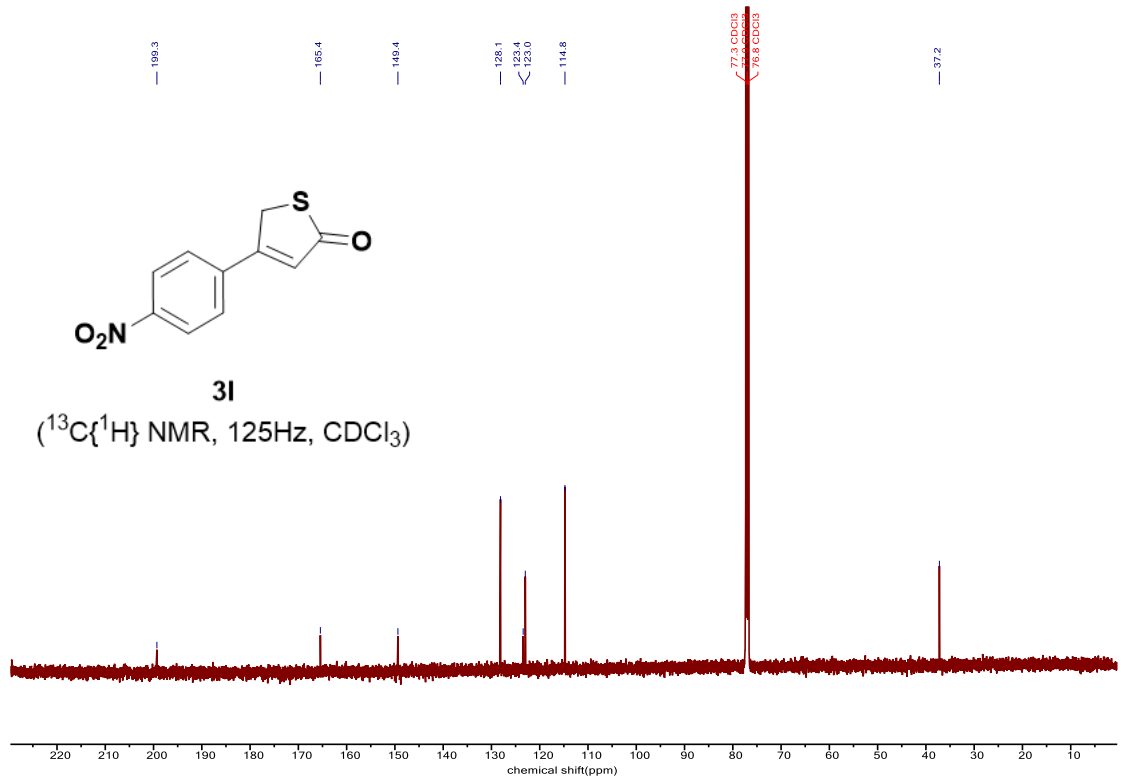
3k

(^{13}C{^{1}H} NMR, 125Hz, $CDCl_3$)



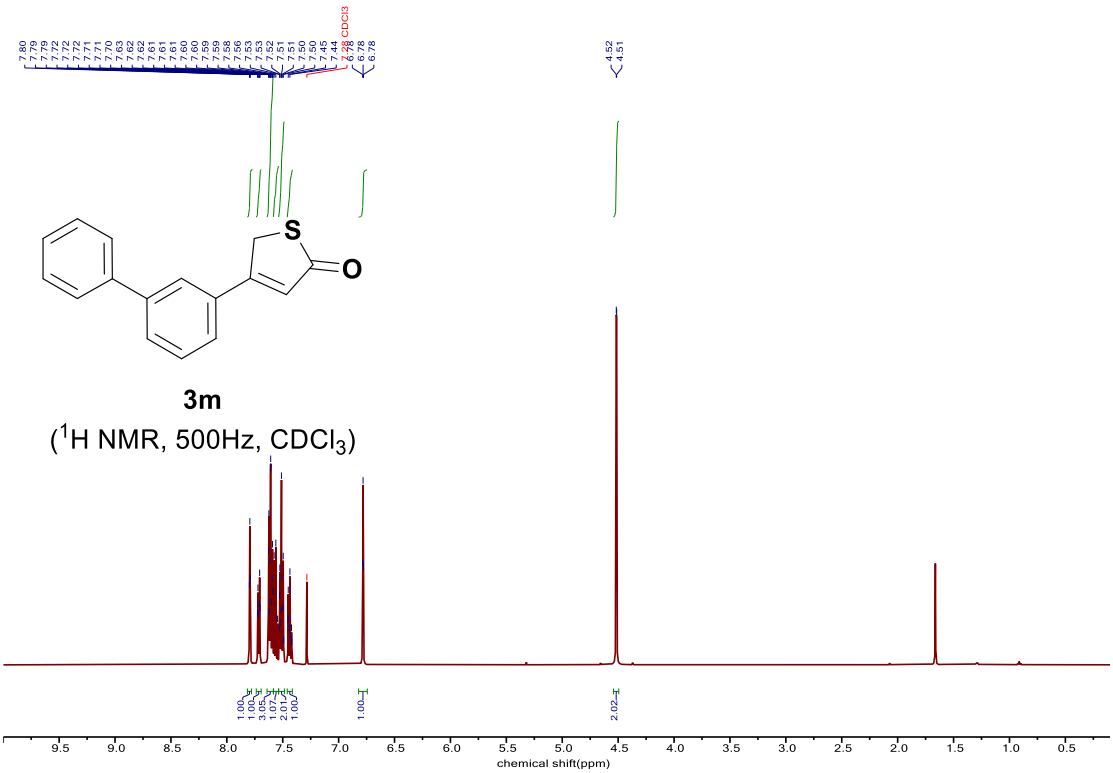
3l

(^{1}H NMR, 500Hz, $CDCl_3$)



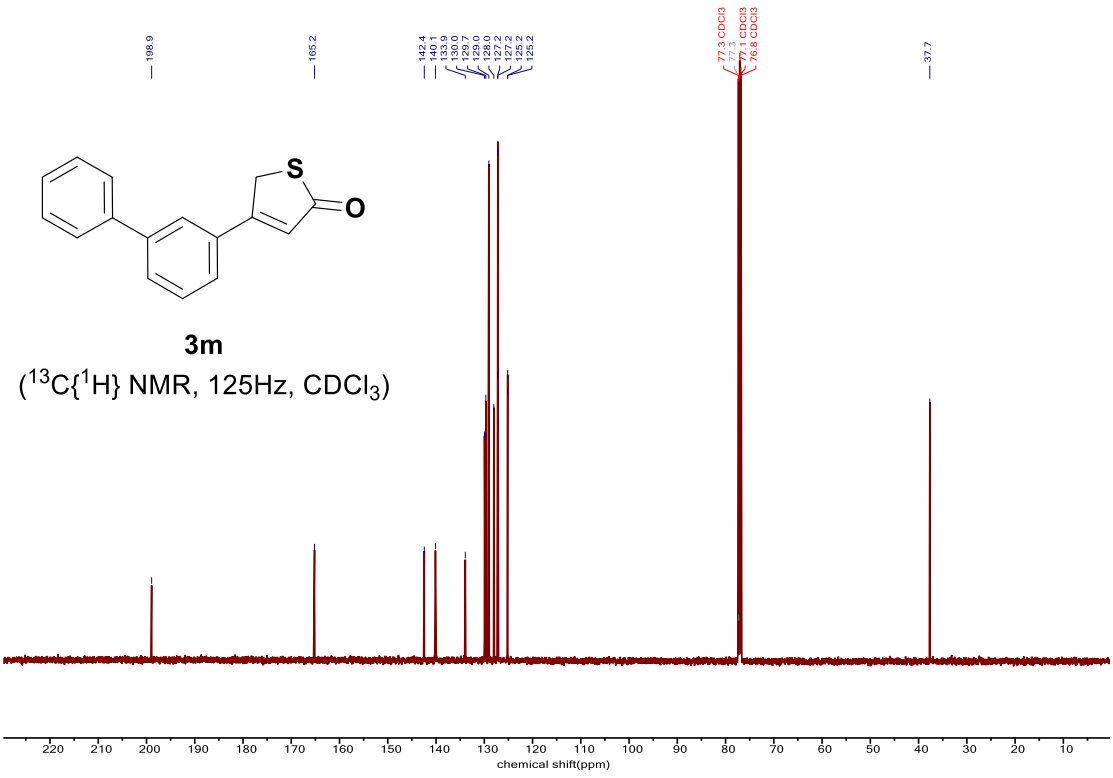
3l

(^{13}C{^{1}H} NMR, 125Hz, $CDCl_3$)



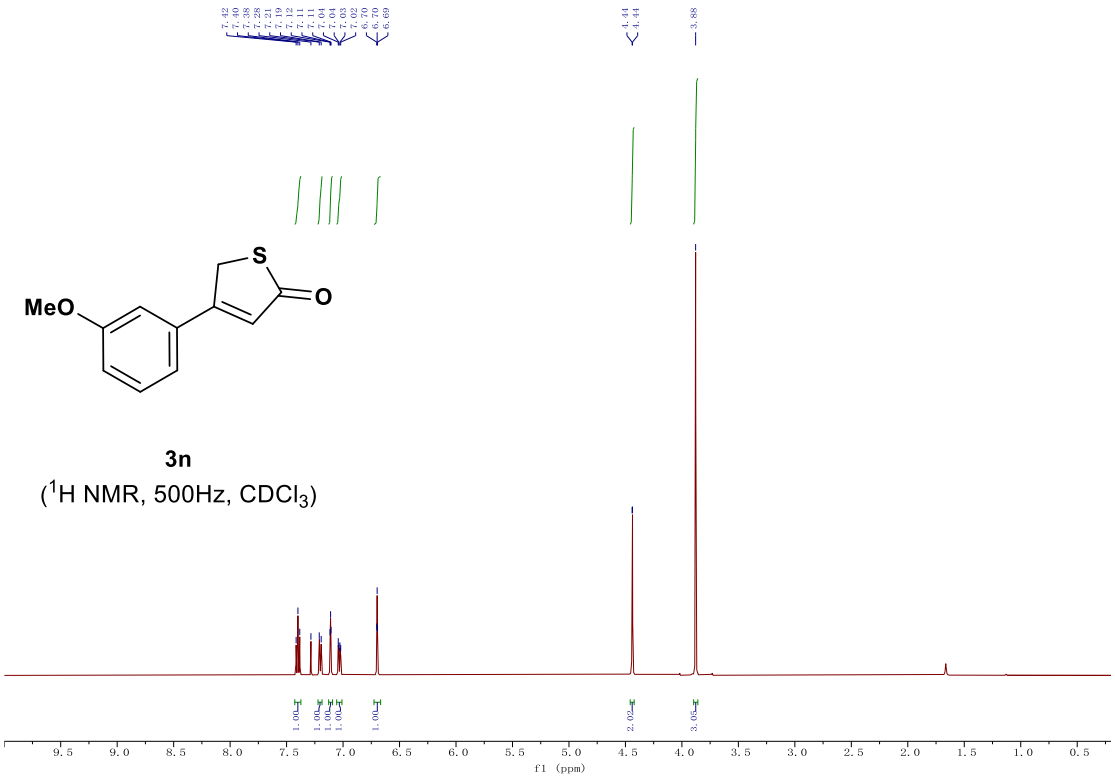
3m

(^{1}H NMR, 500Hz, $CDCl_3$)



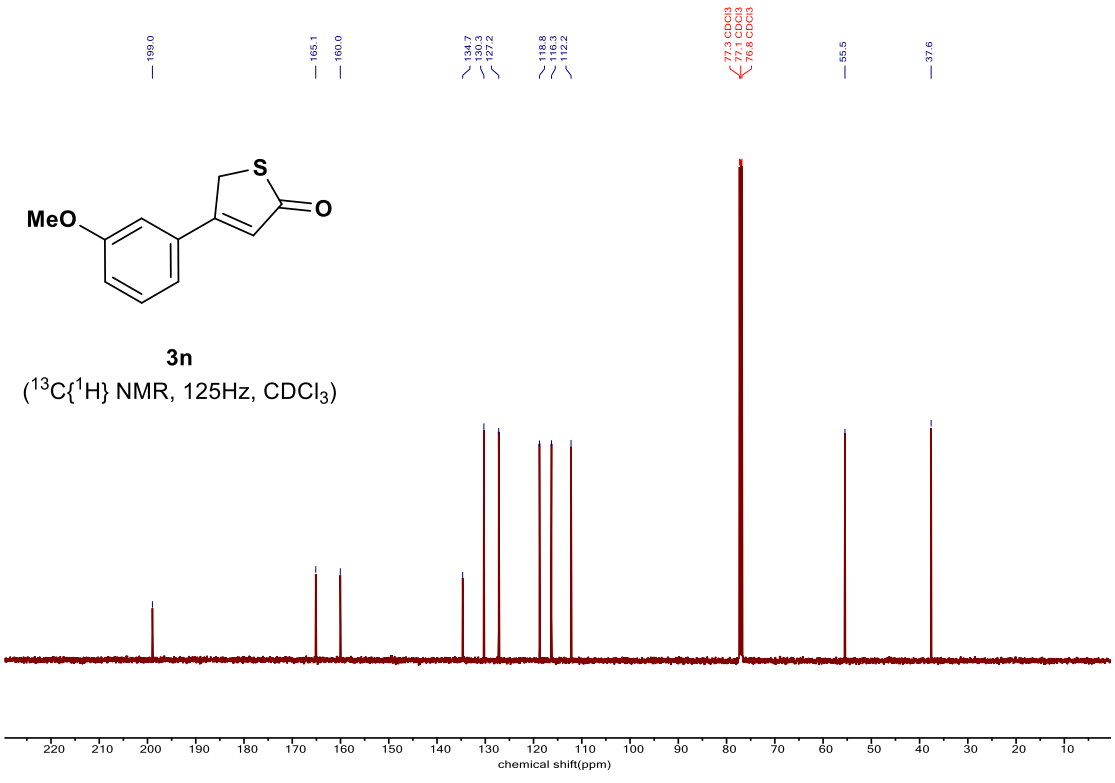
3m

(^{13}C{^{1}H} NMR, 125Hz, $CDCl_3$)



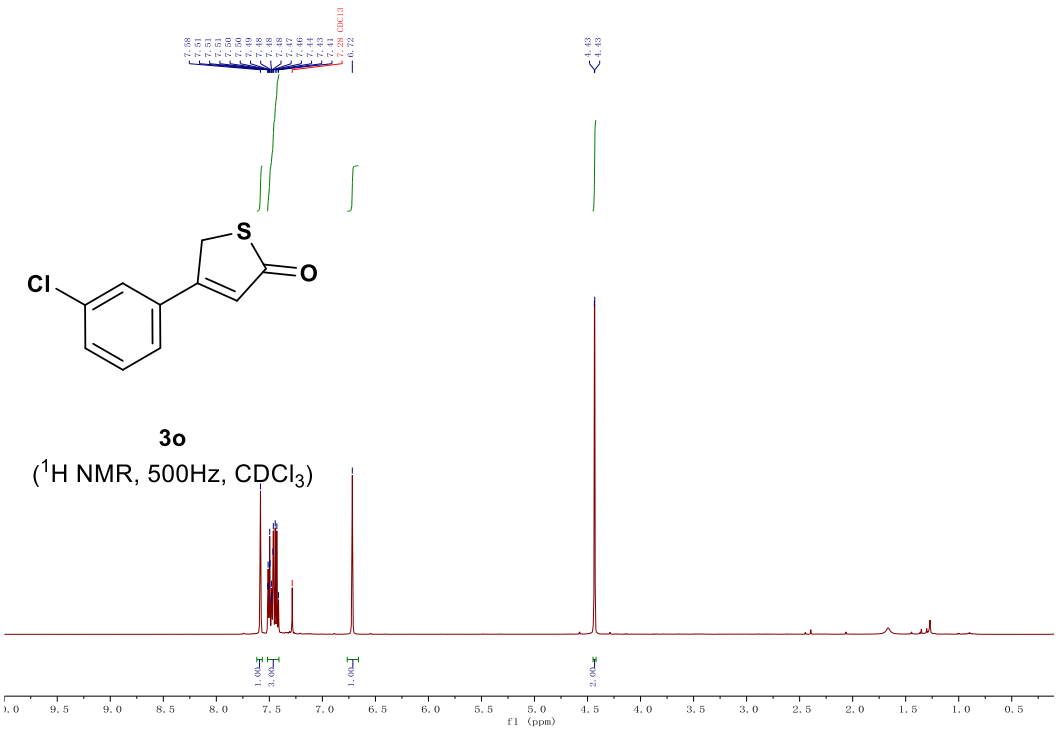
3n

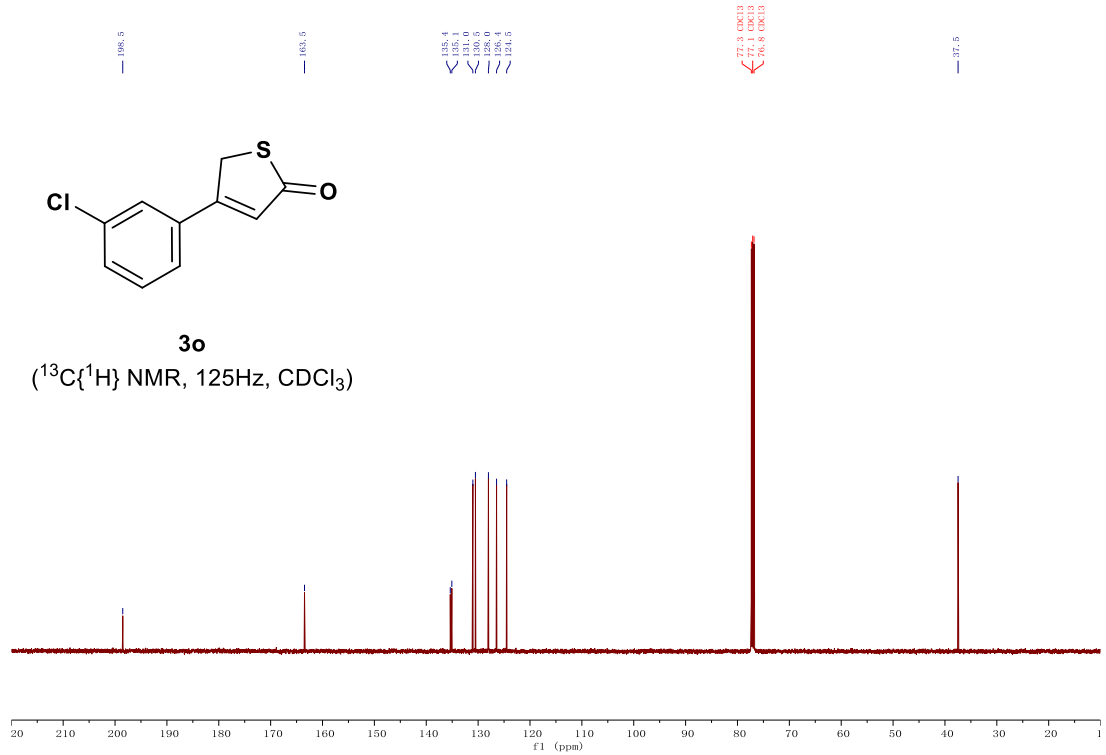
(^{1}H NMR, 500Hz, $CDCl_3$)

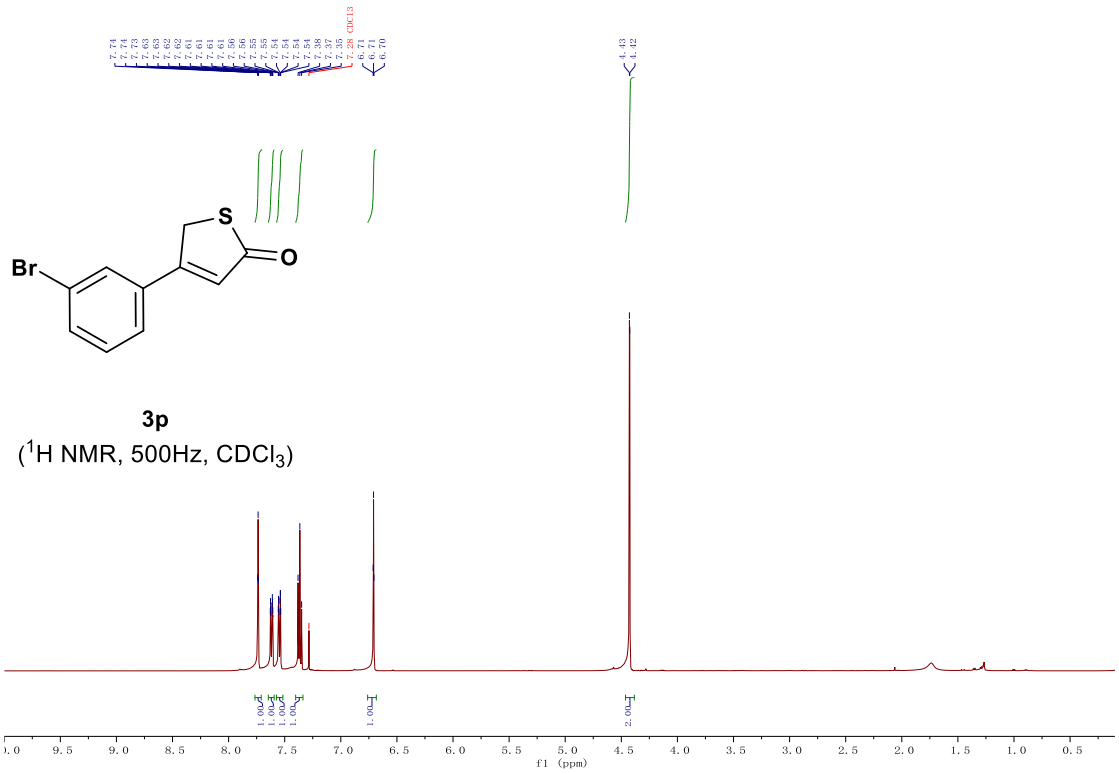


3n

($^{13}C\{^1H\}$ NMR, 125Hz, $CDCl_3$)

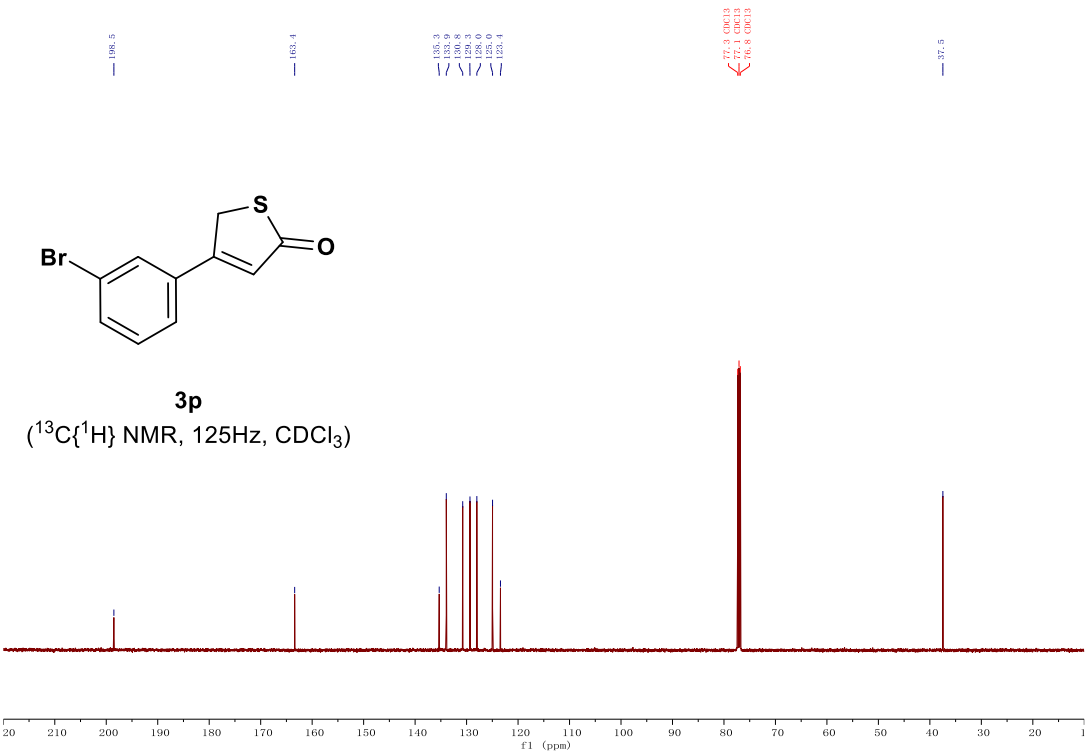

Cl
S
O
3o
(1H NMR, 500Hz, CDCl3)
f1 (ppm)


Cl
S
O
3o
(13C{1H} NMR, 125Hz, CDCl3)
f1 (ppm)



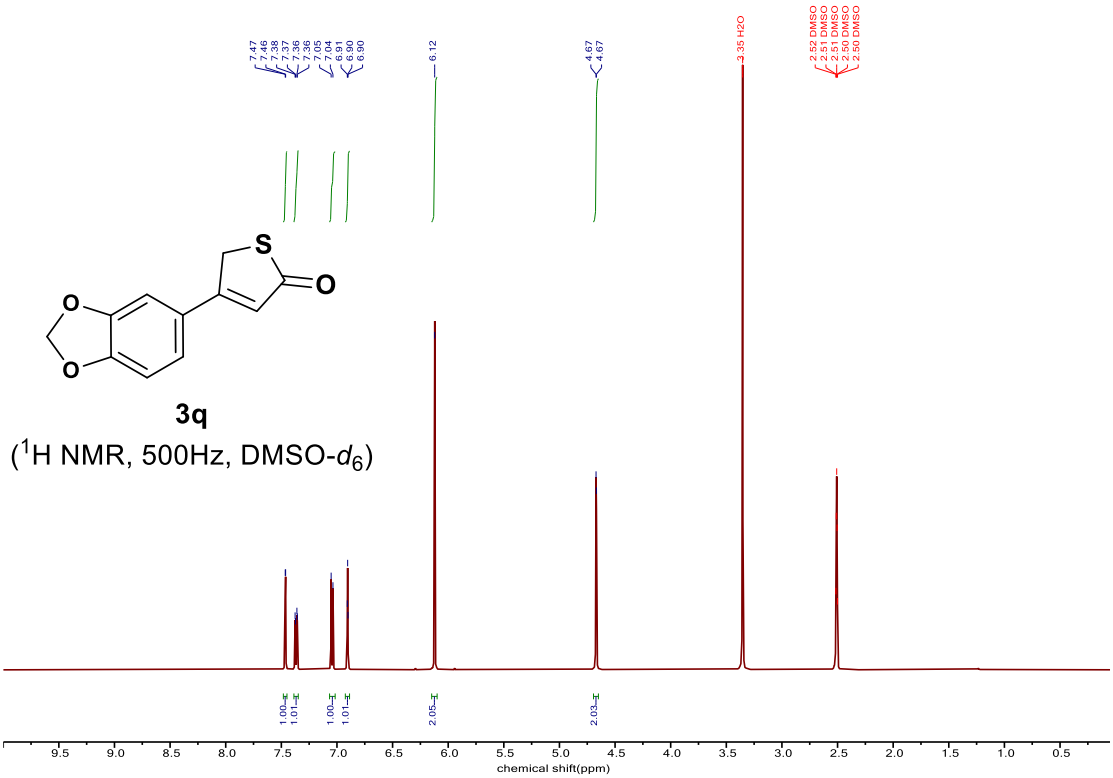
3p

(^{1}H NMR, 500Hz, $CDCl_3$)



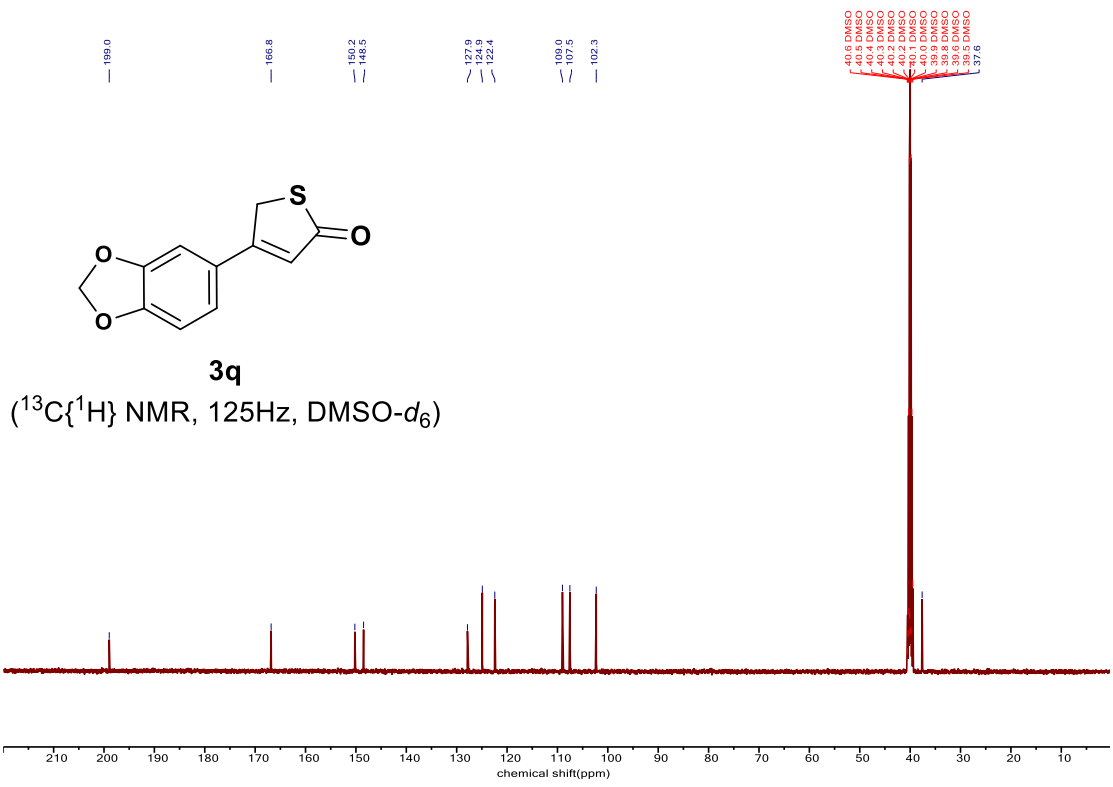
3p

($^{13}C\{^{1}H\}$ NMR, 125Hz, $CDCl_3$)



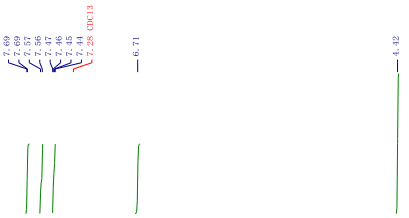
3q

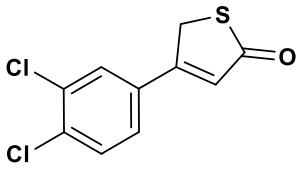
(^{1}H NMR, 500Hz, DMSO-d_6)



3q

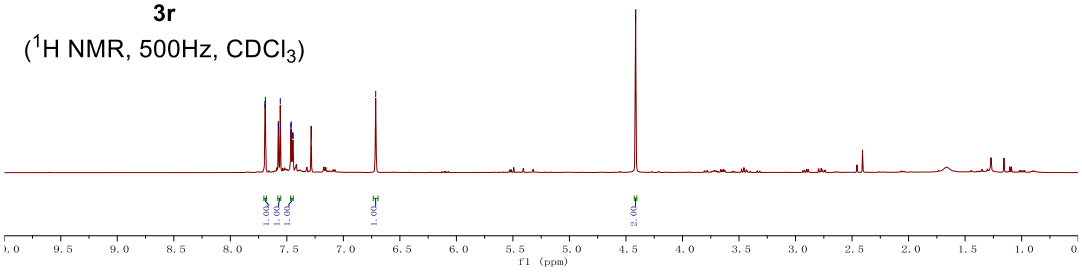
(^{13}C{^{1}H} NMR, 125Hz, DMSO-d_6)

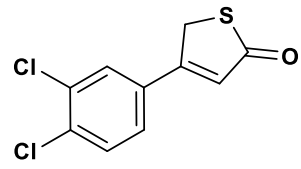




3r

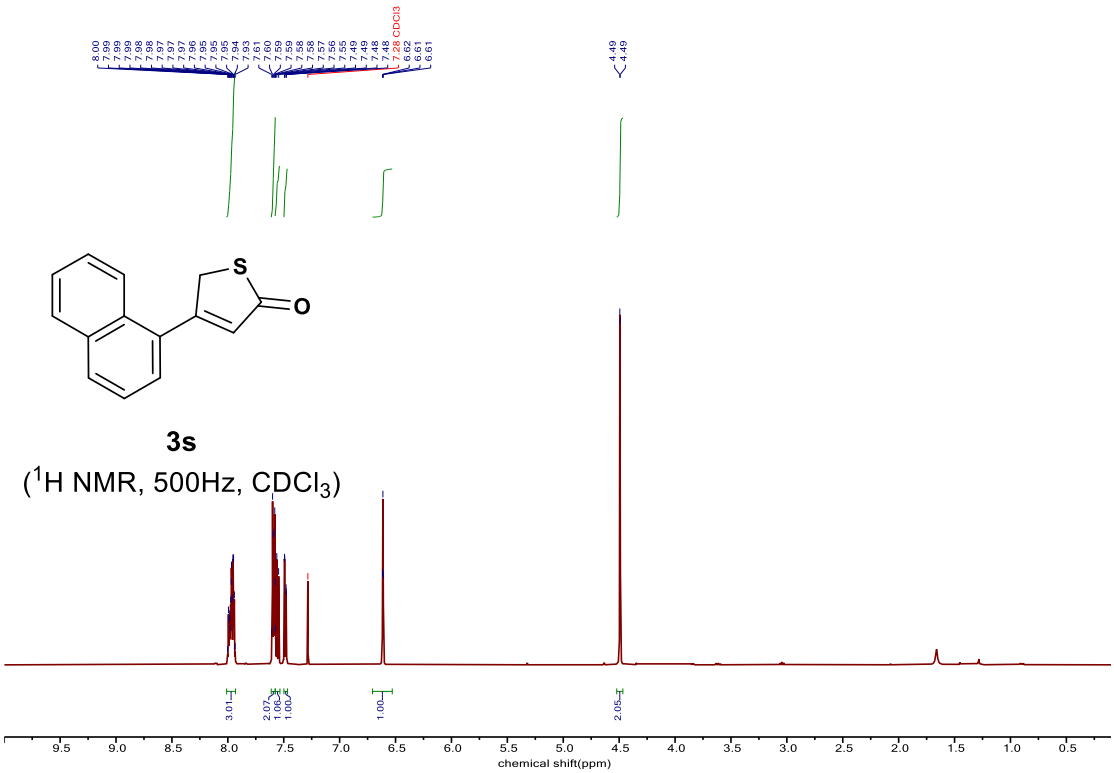
(^{1}H NMR, 500Hz, $CDCl_3$)





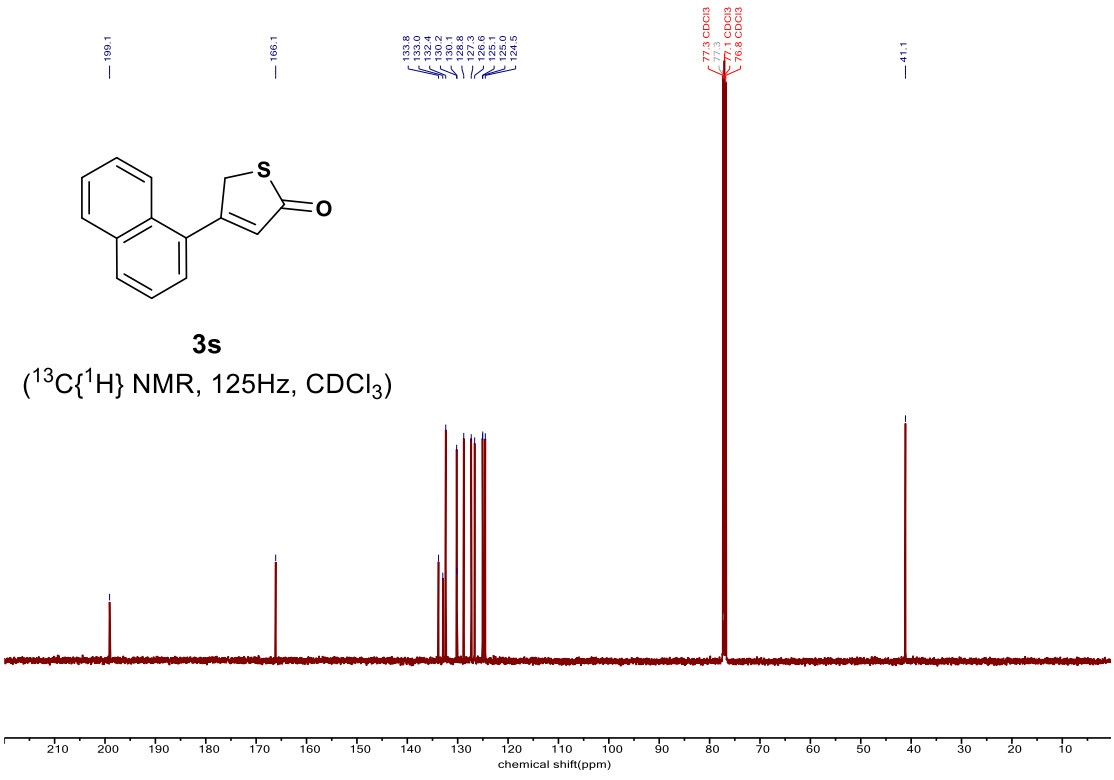
3r

($^{13}C\{^1H\}$ NMR, 125Hz, $CDCl_3$)



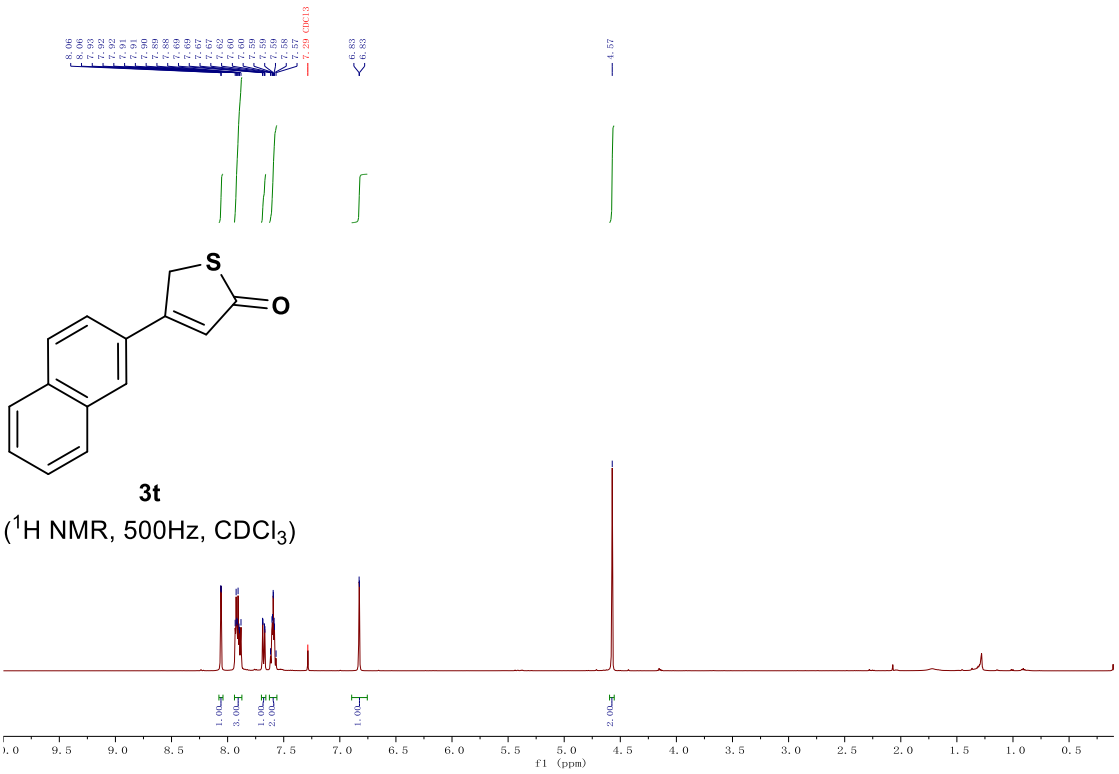
3s

(^{1}H NMR, 500Hz, $CDCl_3$)



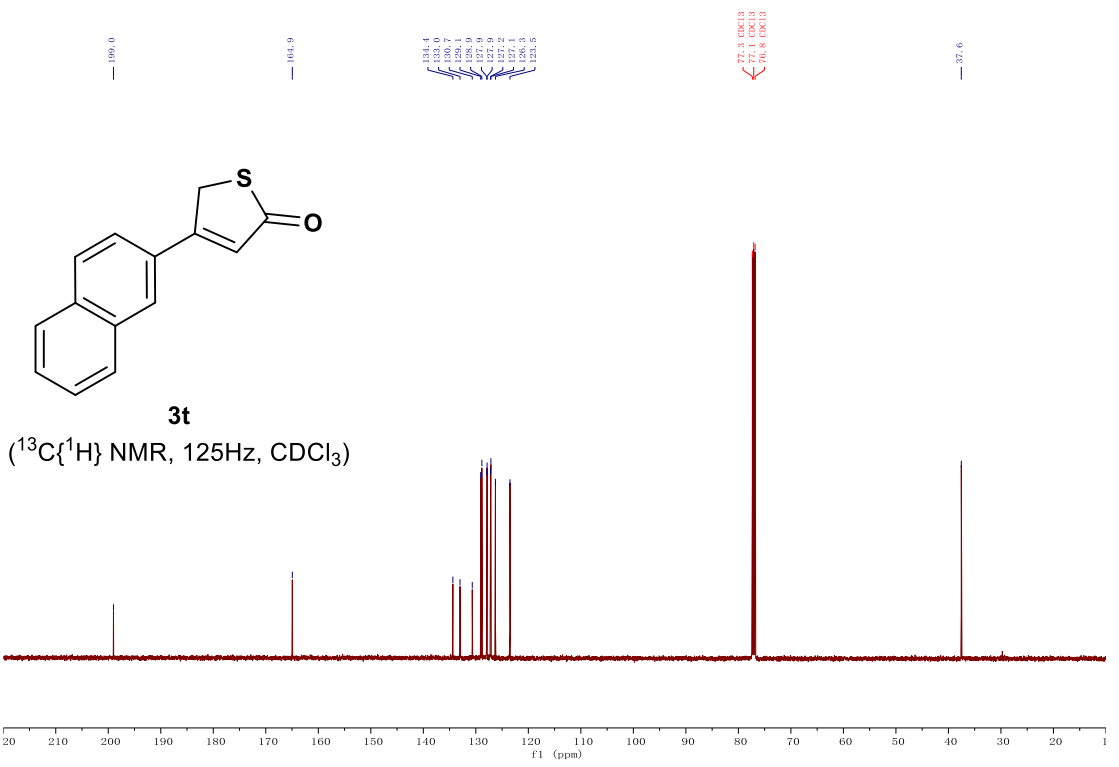
3s

(^{13}C{^{1}H} NMR, 125Hz, $CDCl_3$)



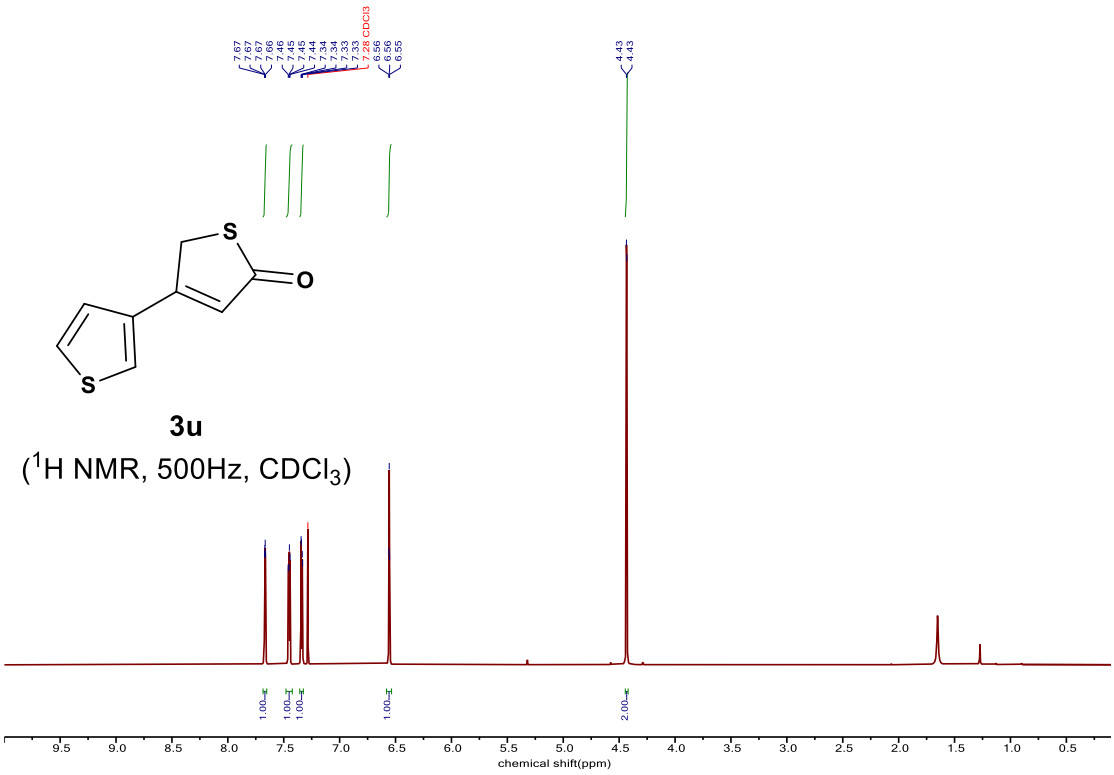
3t

(^{1}H NMR, 500Hz, $CDCl_3$)



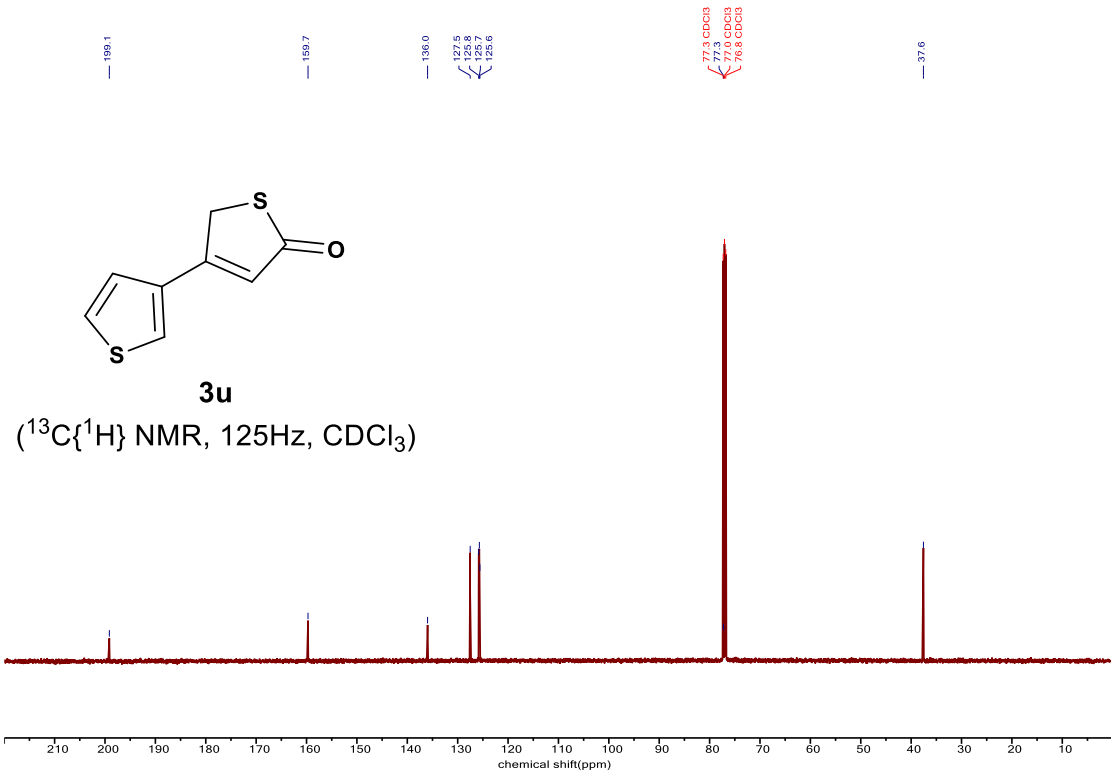
3t

(^{13}C{^{1}H} NMR, 125Hz, $CDCl_3$)



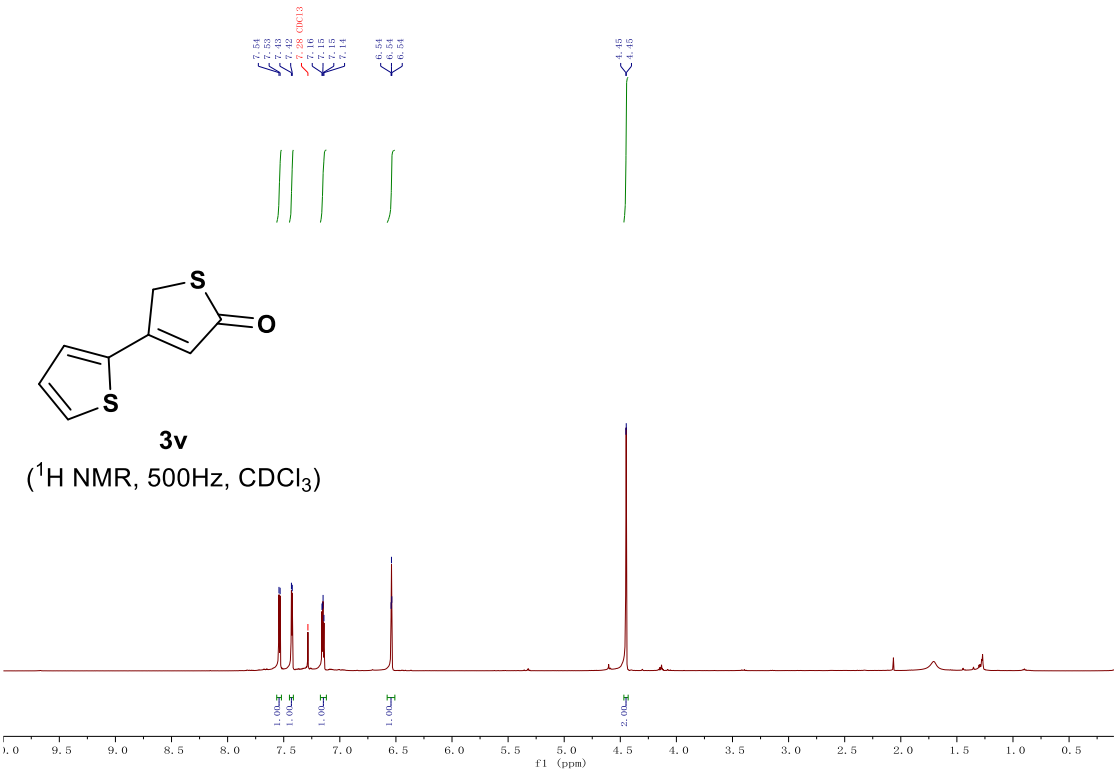
3u

(^{1}H NMR, 500Hz, $CDCl_3$)



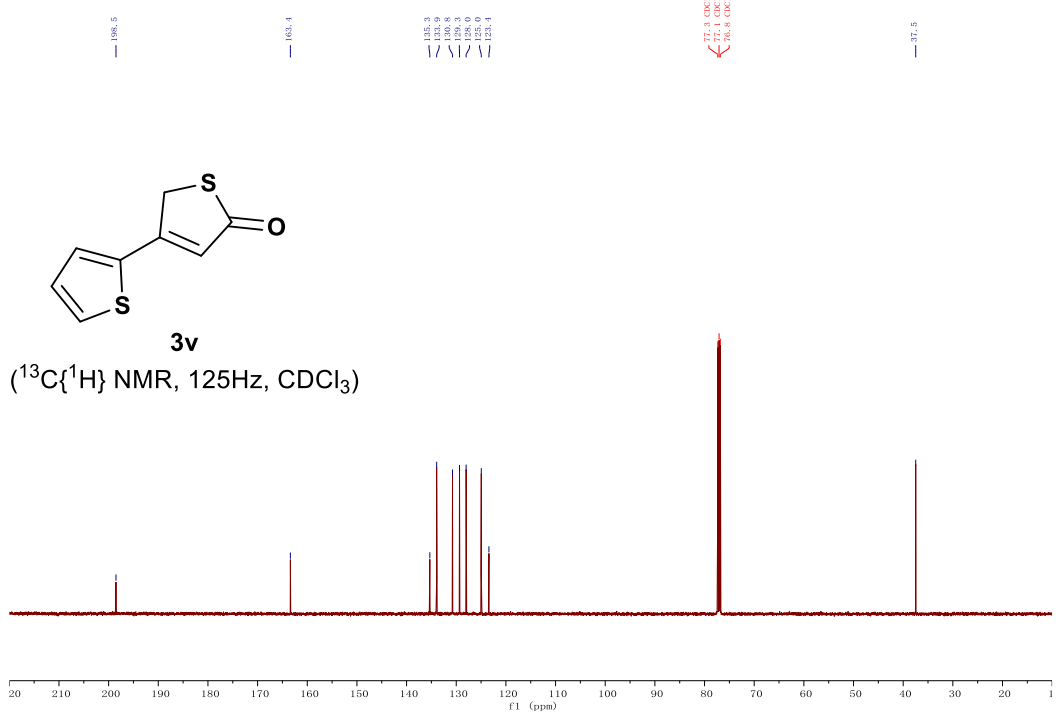
3u

(^{13}C{^{1}H} NMR, 125Hz, $CDCl_3$)



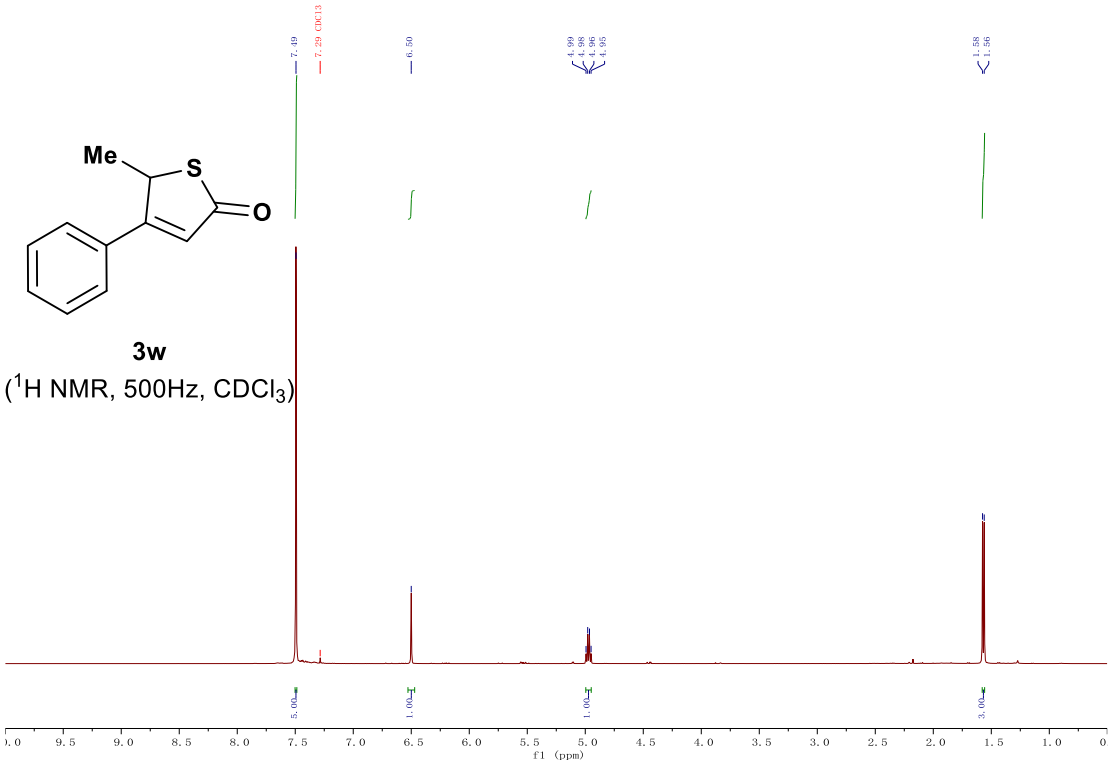
3v

(^{1}H NMR, 500Hz, $CDCl_3$)



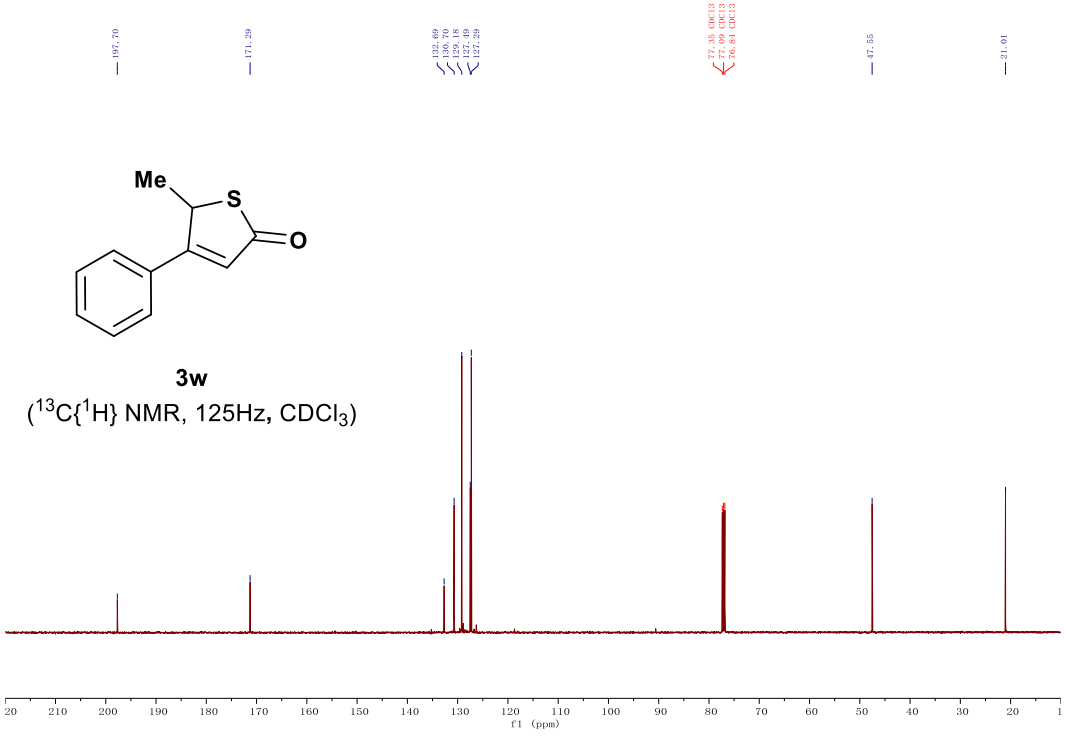
3v

(^{13}C{^{1}H} NMR, 125Hz, $CDCl_3$)



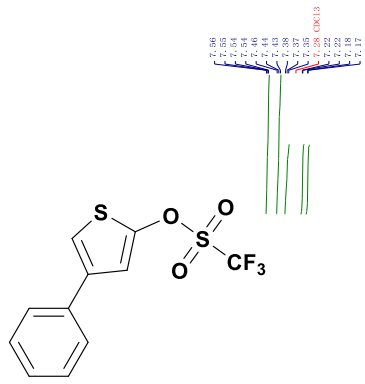
3w

(^{1}H NMR, 500Hz, $CDCl_3$)



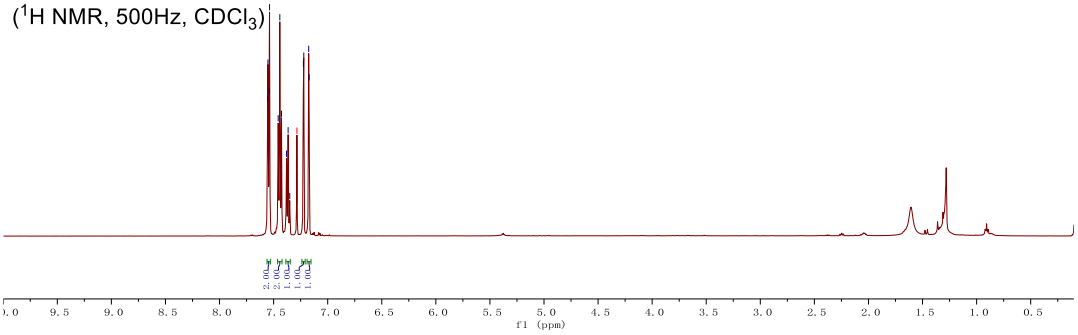
3w

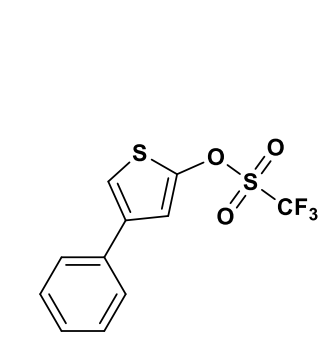
($^{13}C\{^1H\}$ NMR, 125Hz, $CDCl_3$)



4

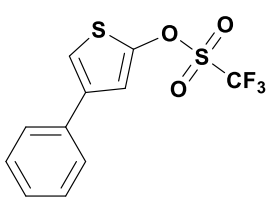
(^{1}H NMR, 500Hz, $CDCl_3$)





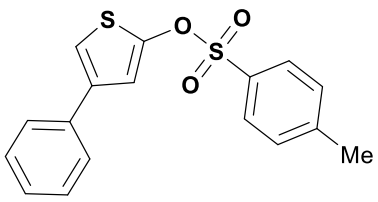
4

(^{13}C{^{1}H} NMR, 125Hz, $CDCl_3$)



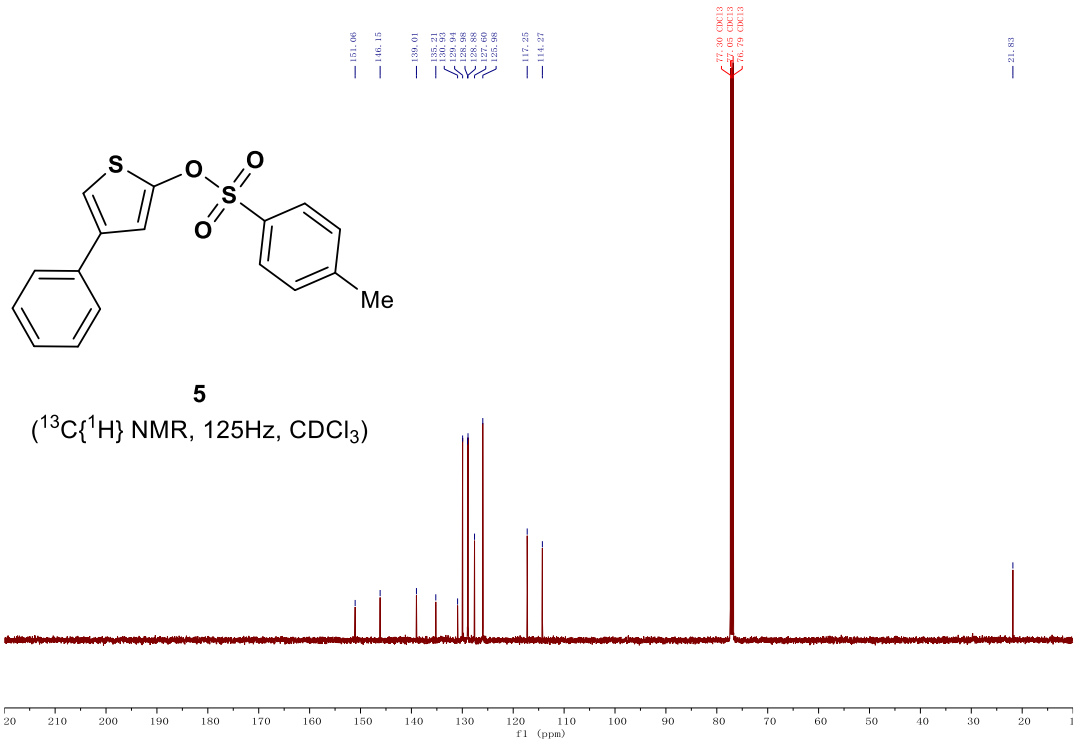
4

(^{19}F NMR, 471Hz, $CDCl_3$)



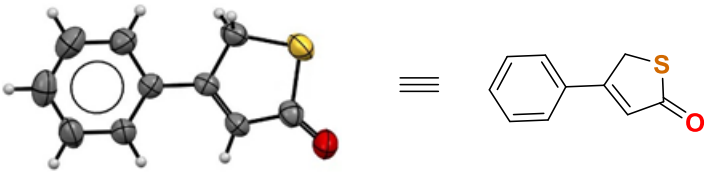
5

(^{1}H NMR, 500Hz, $CDCl_3$)


151.06
146.15
139.01
135.21
130.93
129.94
129.38
128.88
127.69
125.98
117.25
114.27
77.30 CDCl3
77.05 CDCl3
76.79 CDCl3
21.63
S
O
O
S
O
O
Me
5
(13C{1H} NMR, 125Hz, CDCl3)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 1
f1 (ppm)

8. Single-crystal X-ray diffraction data

Preparation of the single crystals of compound **3a**: 5.0 mg of pure compounds **3a** was respectively dissolved in the combined solvents of *n*-hexane and CH_2Cl_2 (16 mL, v/v = 15:1) at ambient temperature. The test tube was sealed by a piece of plastic film with several tiny holes, thus allowing the slow solvent evaporation. After about two weeks, several small crystals were observed at the bottom of the bottle. The crystals were collected and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **3a**. Single crystal X-ray crystallography data were collected by an Agilent Gemini E.



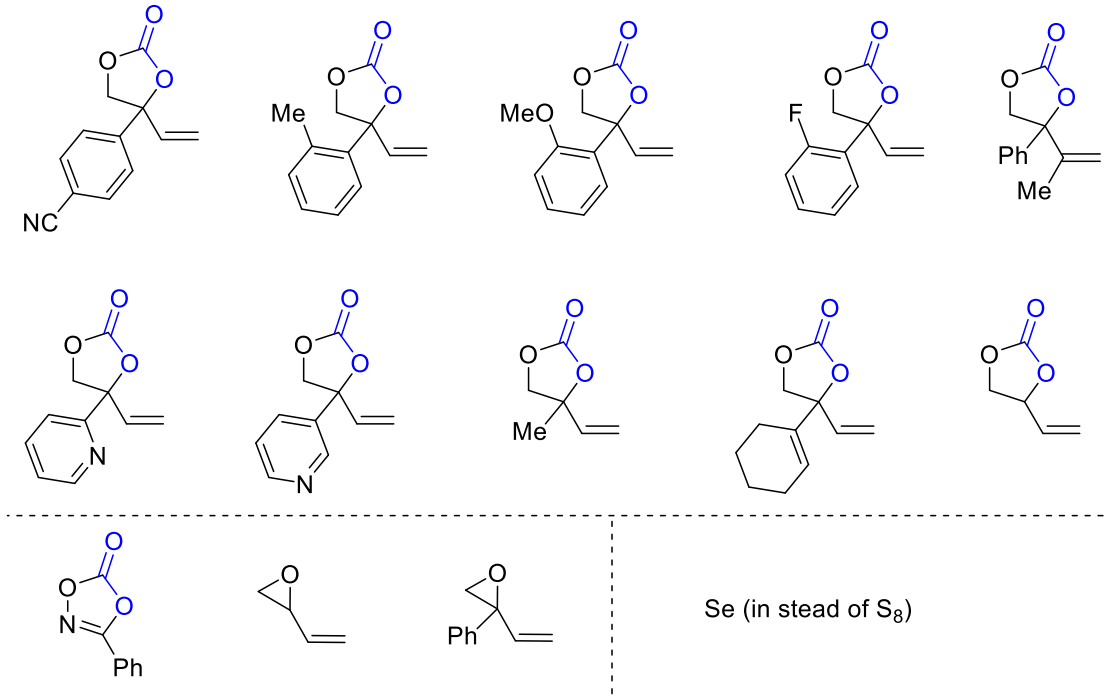
(CCDC 2499453) **3a**

Fig. S3 ORTEP plots for molecular structure of **3a** with the probability at 50% level.

Table S9 Crystal data and structure refinement for exp_9937 (**3a**)

Entry		
Bond precision	C–C = 0.0039 Å	Wavelength = 0.71073 Å
Cell	a = 8.1246(11) Å	α(alpha) = 90°
	b = 6.4322(6) Å	β(beta) = 95.607(12)°
	c = 16.443(2)Å	γ(gamma) = 90°
Temperature	296 K	
	Calculated	Reported
Volume	855.18(18)Å³	855.18(18)Å³
Space group	*P21/n*	*P21/n*
Hall group	-P 2yn	-P 2yn
Moiety formula	$C_{10}H_8OS$	$C_{10}H_8OS$
Sum formula	$C_{10}H_8OS$	$C_{10}H_8OS$
Mr	176.22	176.22
Dx (g/cm^{-3})	1.369	1.369
Z	4	4
Mu (mm-1)	0.320	0.320
F000	368.0	368.0
F000'	368.64	
h,k,l max	11,8,22	11,8,20
Nref	2295	1955
Tmin, Tmax	0.926,0.944	0.834,1.000
Tmin’	0.894	
Correction method = # Reported T Limits: Tmin = 0.834 Tmax = 1.000		
AbsCorr = MULTI-SCAN		
Data completeness = 0.852	Theta(max) = 29.097	
R(reflections) = 0.0631(1220)		wR2(reflections)= 0.1267(1955)
S = 1.065	Npar= 109	

9. Unsuccessful substrates



10. Reference

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