Supporting Information

for

Visible-light-driven thio-carboxylation of alkynes with CO_2:

facile synthesis of thiochromones

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Supplementary Methods

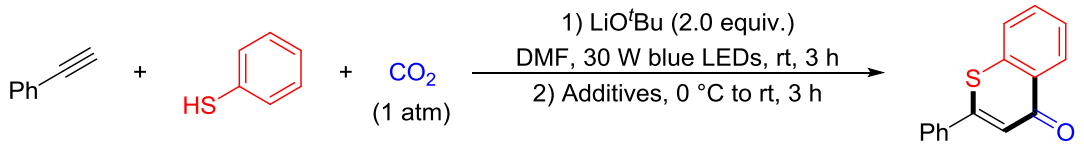
1. General information

All reactions were set up using standard Schlenk techniques and carried out under a carbon dioxide (CO_2) atmosphere with dry solvents. Commercially available chemicals were obtained from Adamas-beta, Acros Organics, Aldrich Chemical Co., Alfa Aesar, ABCR and TCI and used as received unless otherwise stated. Anhydrous *N*,*N*-dimethylformamide (DMF) was purchased from www.jkchemical.com. Lithium *tert*-butoxide (LiO^{t}Bu) was purchased from Asta Tech. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.2±0.03 mm using UV light as a visualizing agent.

^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Brüker Advance 400 spectrometer (^{1}H: 400 MHz, ^{19}F: 376 MHz, ^{13}C: 101 MHz). Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS, The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm).

Exact ESI mass spectra were recorded on a SHIMADZU LCMS-IT-TOF. LRMS was obtained using Thermo-Fisher LTQ-ESI-MS. GC-MS was obtained using electron ionization (Agilent Technologies 7890B/GC-System and 5977A/MSD). Metal element contents were obtained on a thermo ICP-AES (IRIS Adv). Melting points were determined with a melting point apparatus. UV-Vis measurements were performed with a UV-3600 UV/Vis spectrophotometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm.

2. Additional optimization[a)]



1a **2a**, 0.3 mmol **3aa**

Entry	Additives	Yield[b)]
1	TfOH (7.5 equiv.), DCM (1 mL)	44%
2	TfOH (10.0 equiv.), DCM (1 mL)	79% (77%)
3	TfOH (1 mL)	80% (77%)
3	Tf_2O (1 mL)	38%
4	TFAA (3.0 equiv.), TFA (1 mL)	60%

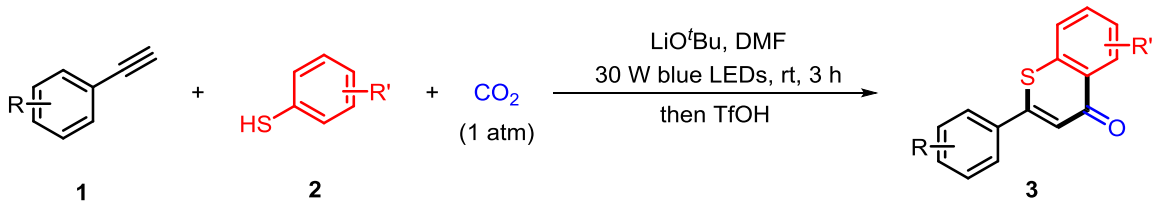
a) Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv.), LiO^{t}Bu (2.0 equiv.), DMF (2 mL), irradiation by 30 W blue LEDs at room temperature (rt) under CO_2 (1 atm) for 3 h. After removing the solvent, additives were added into the residue at 0 ℃, then stirred at rt for 3 h. b) Yields were determined by ^{1}H NMR with CH_2Br_2 as internal standard, and isolated yields were provided in parentheses. TFAA = Trifluoroacetic anhydride, TFA = Trifluoroacetic acid.

Procedure:

To an oven-dried Schlenk tube (10 mL) containing a magnetic stirring bar was charged with LiO^{t}Bu (32.0 mg, 0.4 mmol, 2.0 equiv.) in the glovebox. The tube was sealed and then evacuated and back-filled with CO_2 atmosphere for 3 times, subsequently, anhydrous DMF (2 mL) was added followed by thiophenol **2a** (33.1 mg, 0.3 mmol, 1.5 equiv.), alkyne **1a** (20.4 mg, 0.2 mmol, 1.0 equiv.) via syringe under CO_2. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The reaction was stirred and irradiated with a 30 W blue light-emitting diode (LED) lamp (1-2 cm away, with cooling fan to keep the reaction temperature at 22-25 ℃) for 3 hours. The resulting mixture was then removed the solvent with vacuum, and additives were added into the residue at 0 ℃, then stirred at room temperature for 3 h. After the reaction was completed, reaction mixture was diluted with 3 mL EtOAc and quenched by saturated $NaHCO_3$ aqueous solution (pH was justified to >7) at 0 ℃, then stirred for 3 min. The reaction mixture was extracted by EtOAc with five times and the combined organic phases were concentrated *in vacuo*. The residue was analyzed by ^{1}H NMR with CH_2Br_2 as internal standard.

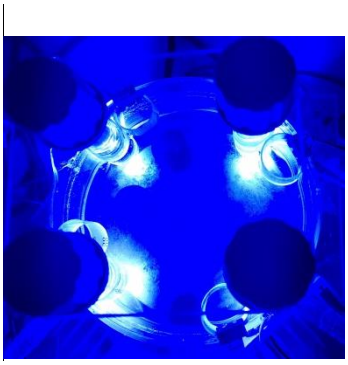
3. Experimental procedures and characterizations data

3.1 Substrate scope for the synthesis of thiochromones

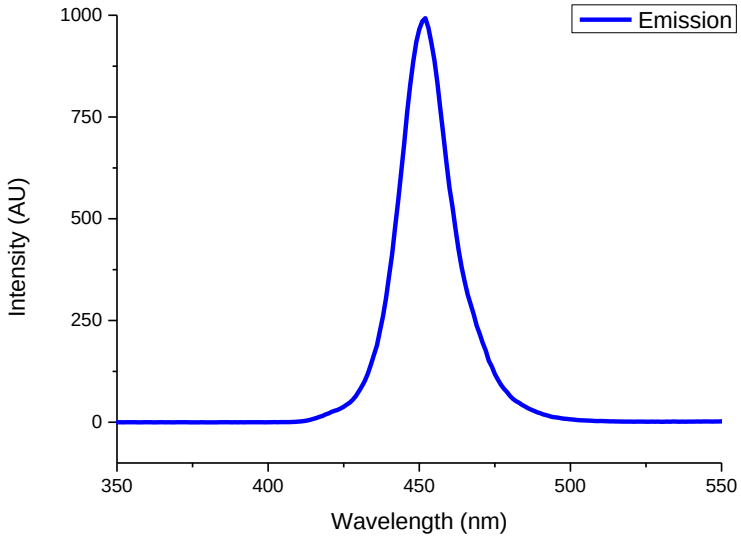


General procedure:

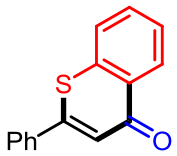
To an oven-dried Schlenk tube (10 mL) containing a magnetic stirring bar was added thiophenol **2** (0.3 mmol, 1.5 equiv., for non-liquid substrates), alkyne **1** (0.2 mmol, 1.0 equiv., for non-liquid substrates). Then, the tube was moved into a glovebox and was charged with LiO^{t}Bu (32.0 mg, 0.4 mmol, 2.0 equiv.). The tube was sealed and then evacuated and back-filled with CO_2 atmosphere for 3 times, subsequently, anhydrous DMF (2 mL) was added followed by thiophenol **2** (0.3 mmol, 1.5 equiv., for liquid substrates), alkyne **1** (0.2 mmol, 1.0 equiv., for liquid substrates) via syringe under CO_2. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The reaction was stirred and irradiated with a 30 W blue LED lamp (1-2 cm away, with cooling fan to keep the reaction temperature at 22-25 ℃) for 3 hours. The resulting mixture was then removed the solvent with vacuum, and the residue was resolved in DCM (1 mL), and added TfOH (10.0 equiv.) or TfOH (1 mL) at 0 ℃, then stirred at room temperature for 3 h. After the reaction was completed, reaction mixture was diluted with 3 mL EtOAc and quenched by saturated $NaHCO_3$ aqueous solution (pH was justified to >7) at 0 ℃, then stirred for 3 min. The reaction mixture was extracted by EtOAc with five times and the combined organic phases were concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc= 20/1 ~ 1/2) to give the pure desired product.



The emission spectrum of 30 W blue LED:



2-phenyl-4*H*-thiochromen-4-one (3aa)[1]

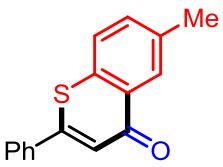


Following the general procedure, the title compound was obtained (36.6 mg, 77% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.75 – 7.60 (m, 4H), 7.59 – 7.46 (m, 4H), 7.25 (s, 1H); **^{13}C NMR** (101 MHz, CDCl3) δ 181.5, 153.7, 138.3, 137.2, 132.2, 131.50, 131.4, 129.9, 129.2, 128.4, 127.6, 127.1, 124.0; **LRMS (ESI$^+$):** calculated for $C_{15}H_{11}OS^+$ $[M+H]^+$ 239.05, found 239.09. All analytical data are consistent with those reported in the literature.

6-methyl-2-phenyl-4*H*-thiochromen-4-one (3ab)[1]

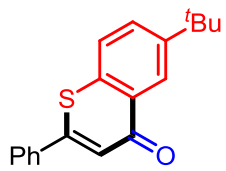


Following the general procedure, the title compound was obtained (38.2 mg, 76% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (t, *J* = 1.4 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.50 (dd, *J* = 5.2, 2.0 Hz, 3H), 7.45 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.24 (s, 1H), 2.50 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.0, 153.0, 138.1, 136.7, 134.7, 133.0, 130.8, 129.3, 128.3, 127.0, 126.4, 123.3, 21.3; **LRMS (ESI$^+$):** calculated for $C_{16}H_{13}OS^+$ $[M+H]^+$ 253.07, found 253.13. All analytical data are consistent with those reported in the literature.

6-(*tert*-butyl)-2-phenyl-4*H*-thiochromen-4-one (3ac)



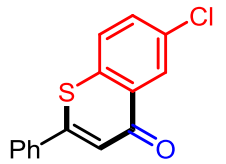
General procedure with the following changes：4-*tert*-butylthiophenol (33.3 mg, 0.2 mmol, 1.0 equiv.), phenylacetylene (30.6 mg, 0.3 mmol, 1.5 equiv.), LiO^{t}Bu (24.0 mg, 0.3 mmol, 1.5 equiv.), the title compound was obtained (39.6 mg, 67% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

MP 97-99 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 2.2 Hz, 1H), 7.72 – 7.66 (m, 3H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.25 (s, 1H), 1.40 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 181.1, 152.8, 151.3, 136.6, 134.8, 130.7, 130.5, 129.6, 129.2, 126.9, 126.3, 124.6, 123.3, 35.1, 31.2; **HRMS (ESI$^+$):** calculated for $C_{19}H_{18}NaOS^+$ $[M+Na]^+$ 317.0971, found 317.0966.

6-chloro-2-phenyl-4*H*-thiochromen-4-one (3ad)[1]

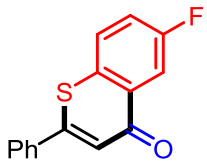


Following the general procedure, the title compound was obtained (40.6 mg, 74% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.3~0.4;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 2.1, 0.8 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.62 – 7.55 (m, 2H), 7.55 – 7.46 (m, 3H), 7.23 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.6, 153.2, 136.2, 135.8, 134.3, 132.03, 131.96, 131.0, 129.3, 128.2, 127.9, 126.9, 123.2; **LRMS (ESI$^+$):** calculated for $C_{15}H_{10}ClO_3S^+$ $[M+H]^+$ 273.01, found 273.10; $C_{15}H_{10}{}^{37}ClO_3S^+$ $[M+H]^+$ 275.01, found 275.07. All analytical data are consistent with those reported in the literature.

6-fluoro-2-phenyl-4*H*-thiochromen-4-one (3ae)



Following the general procedure, the title compound was obtained (39.0 mg, 76% yield, yellow solid);

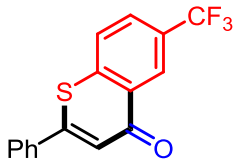
R_f (PE/EA 10:1) = 0.2~0.3;

MP 153-155 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dt, *J* = 9.4, 2.2 Hz, 1H), 7.74 – 7.62 (m, 3H), 7.51 (d, *J* = 6.7 Hz, 3H), 7.43 – 7.34 (m, 1H), 7.23 (s, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.3; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.9 (d, *J* = 2.3 Hz), δ 162.1 (d, *J* = 249.7 Hz), 153.4, 136.3, 133.0 (d, *J* = 2.5 Hz),

132.9 (d, *J* = 6.9 Hz), 131.0, 129.3, 128.6 (d, *J* = 7.6 Hz), 127.0, 122.5, 120.4 (d, *J* = 24.4 Hz), 114.2 (d, *J* = 22.9 Hz); **HRMS (ESI$^+$):** calculated for $C_{15}H_{10}FOS^+$ $[M+H]^+$ 257.0431, found 257.0435.

2-phenyl-6-(trifluoromethyl)-4*H*-thiochromen-4-one (3af)[2]

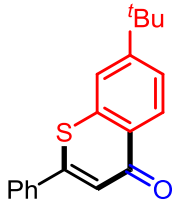


Following the general procedure, the title compound was obtained (38.8 mg, 63% yield, pale brown solid);

R_f (PE/EA 10:1) = 0.3~0.4;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 – 8.79 (m, 1H), 7.87 – 7.76 (m, 2H), 7.74 – 7.66 (m, 2H), 7.59 – 7.48 (m, 3H), 7.27 (s, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.7; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.8, 153.2, 141.2, 136.0, 131.3, 131.0, δ 130.1 (q, *J* = 33.5 Hz), 129.5, 127.6 (q, *J* = 3.5 Hz), 127.5, 127.0, 126.1 (q, *J* = 4.0 Hz), 123.7, 123.5 (q, *J* = 273.6 Hz); **LRMS (ESI$^+$):** calculated for $C_{16}H_{10}F_3OS^+$ $[M+H]^+$ 307.04, found 307.09. All analytical data are consistent with those reported in the literature.

7-(*tert*-butyl)-2-phenyl-4*H*-thiochromen-4-one (3ag)



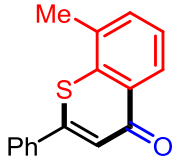
Following the general procedure, the title compound was obtained (47.0 mg, 80% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

MP 136-138 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.7 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.63 – 7.57 (m, 2H), 7.53 – 7.45 (m, 3H), 7.22 (s, 1H), 1.39 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.8, 155.4, 152.9, 137.7, 136.7, 130.7, 129.2, 128.7, 128.3, 126.9, 125.9, 123.4, 122.6, 35.2, 31.0; **HRMS (ESI$^+$):** calculated for $C_{19}H_{18}NaOS^+$ $[M+Na]^+$ 317.0971, found 317.0968.

8-methyl-2-phenyl-4*H*-thiochromen-4-one (3ah)[1]



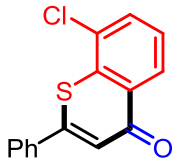
Following the general procedure, the title compound was obtained (36.6 mg, 73% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.57 – 7.48 (m,

3H), 7.48 – 7.42 (m, 2H), 7.25 (s, 1H), 2.57 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.4, 152.1, 137.2, 136.9, 134.7, 132.8, 131.3, 130.7, 129.3, 127.10, 127.06, 126.5, 123.3, 19.6; **LRMS (ESI$^+$):** calculated for $C_{16}H_{13}OS^+$ $[M+H]^+$ 253.07, found 253.11. All analytical data are consistent with those reported in the literature.

8-chloro-2-phenyl-4*H*-thiochromen-4-one (3ai)



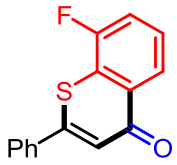
Following the general procedure, the title compound was obtained (38.5 mg, 71% yield, yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

MP 158-160 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.77 – 7.63 (m, 3H), 7.57 – 7.43 (m, 4H), 7.23 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.5, 152.9, 136.9, 136.5, 132.8, 132.0, 131.00, 130.98, 129.3, 127.7, 127.2, 127.1, 123.0; **HRMS (ESI$^+$):** calculated for $C_{15}H_{10}ClO_3S^+$ $[M+H]^+$ 273.0135, found 273.0137; $C_{15}H_{10}{}^{37}ClO_3S^+$ $[M+H]^+$ 275.0106, found 275.0107.

8-fluoro-2-phenyl-4*H*-thiochromen-4-one (3aj)[1]

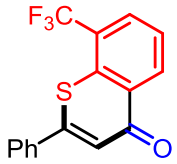


Following the general procedure, the title compound was obtained (41.8 mg, 82% yield, yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.55 – 7.43 (m, 4H), 7.40 – 7.32 (m, 1H), 7.20 (s, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.3; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.9 (d, *J* = 3.6 Hz), 157.9 (d, *J* = 247.7 Hz), 152.0, 136.5, 132.5, 131.1, 129.4, 127.8 (d, *J* = 7.9 Hz), 127.1, 126.3 (d, *J* = 16.2 Hz), 124.2 (d, *J* = 3.0 Hz), 123.5, 117.1 (d, *J* = 19.6 Hz); **LRMS (ESI$^+$):** calculated for $C_{15}H_{10}FOS^+$ $[M+H]^+$ 257.04, found 257.07. All analytical data are consistent with those reported in the literature.

2-phenyl-8-(trifluoromethyl)-4*H*-thiochromen-4-one (3ak)



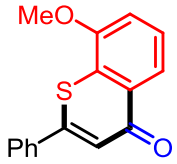
Following the general procedure, the title compound was obtained (42.7 mg, 70% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

MP 142-144 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.02 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.78 – 7.68 (m, 2H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.60 – 7.49 (m, 3H), 7.26 (s, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -60.9; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.8, δ 152.6 (q, *J* = 1.9 Hz), 136.0, 135.9, 132.7, 132.3, 131.2, 130.1 (q, *J* = 5.6 Hz), 129.4, 127.2, 127.1, 126.8, 123.4 (q, *J* = 275.5 Hz), 122.9; **HRMS (ESI$^+$):** calculated for $C_{16}H_{10}F_3OS^+$ $[M+H]^+$ 307.0399, found 307.0396.

8-methoxy-2-phenyl-4*H*-thiochromen-4-one (3al)



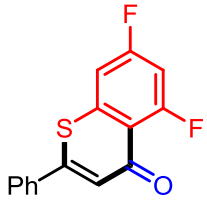
General procedure with the following changes：2-methoxybenzenethiol (28.0 mg, 0.2 mmol, 1.0 equiv.), phenylacetylene (30.6 mg, 0.3 mmol, 1.5 equiv.), LiO^tBu (24.0 mg, 0.3 mmol, 1.5 equiv.), the title compound was obtained (36.7 mg, 68% yield, pale yellow solid);

R_f (PE/EA 5:1) = 0.2~0.3;

MP 103-105 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.76 – 7.67 (m, 2H), 7.55 – 7.43 (m, 4H), 7.24 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 4.02 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.9, 154.9, 153.1, 137.1, 132.0, 130.7, 129.2, 128.0, 127.6, 127.0, 123.2, 120.3, 111.5, 56.5; **HRMS (ESI$^+$):** calculated for $C_{16}H_{13}O_2S^+$ $[M+H]^+$ 269.0631, found 269.0625.

5,7-difluoro-2-phenyl-4*H*-thiochromen-4-one (3am)



General procedure with the following changes：reaction time 12 h of step 1, the title compound was obtained (41.1 mg, 75% yield, white solid);

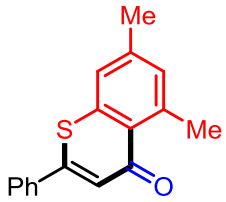
R_f (PE/EA 10:1) = 0.2~0.3;

MP 140-142 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.60 (m, 2H), 7.57 – 7.45 (m, 3H), 7.17 (dd, *J* = 6.9, 2.5 Hz, 1H), 7.11 (s, 1H), 6.99 – 6.88 (m, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.1, -102.15, -102.16,

-102.20; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.0 (d, *J* = 2.7 Hz), 164.2 (dd, *J* = 272.2, 14.1 Hz), 163.3 (dd, *J* = 258.3, 14.5 Hz), 150.2, 141.8 (dd, *J* = 11.0, 2.4 Hz), 135.3, 131.1, 129.4, 126.8, 124.7, 117.6 (dd, *J* = 5.8, 3.3 Hz), 108.7 (dd, *J* = 23.0, 5.9 Hz), 104.8 (t, *J* = 25.6 Hz); **HRMS (ESI$^+$):** calculated for $C_{15}H_9F_2OS^+$ $[M+H]^+$ 275.0337, found 275.0334.

5,7-dimethyl-2-phenyl-4*H*-thiochromen-4-one (3an)



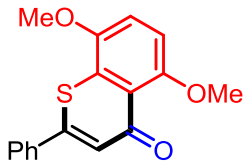
Following the general procedure, the title compound was obtained (36.3 mg, 68% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.3~0.4;

MP 102-104 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 2H), 7.53 – 7.42 (m, 3H), 7.26 (d, *J* = 4.5 Hz, 1H), 7.08 (s, 1H), 7.06 (s, 1H), 2.87 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.4, 149.6, 142.9, 141.2, 139.5, 136.2, 132.8, 130.5, 129.1, 127.2, 126.7, 125.0, 124.5, 24.6, 21.3; **HRMS (ESI$^+$):** calculated for $C_{17}H_{15}OS^+$ $[M+H]^+$ 267.0838, found 267.0833.

5,8-dimethoxy-2-phenyl-4*H*-thiochromen-4-one (3ao)



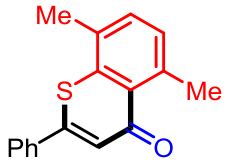
General procedure with the following changes：2,5-dimethoxythiophenol (34.0 mg, 0.2 mmol, 1.0 equiv.), phenylacetylene (30.6 mg, 0.3 mmol, 1.5 equiv.), LiO^tBu (24.0 mg, 0.3 mmol, 1.5 equiv.), the title compound was obtained (54.7 mg, 92% yield, yellow solid;

R_f (PE/EA 1:2) = 0.2;

MP 191-193 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 2H), 7.54 – 7.43 (m, 3H), 7.14 (s, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.8, 155.6, 149.7, 148.4, 136.5, 130.58, 130.55, 129.1, 127.0, 125.1, 121.8, 112.7, 109.9, 57.0, 56.9; **HRMS (ESI$^+$):** calculated for $C_{17}H_{14}NaO_3S^+$ $[M+Na]^+$ 321.0556, found 321.0561.

5,8-dimethyl-2-phenyl-4*H*-thiochromen-4-one (3ap)



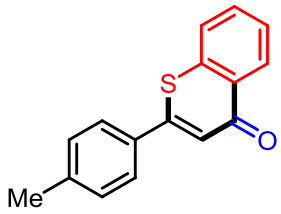
Following the general procedure, the title compound was obtained (36.2 mg, 68% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.3~0.4;

MP 119-121 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.67 (m, 3H), 7.55 – 7.44 (m, 4H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.15 (s, 1H), 2.87 (s, 4H), 2.52 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.2, 149.2, 140.7, 138.5, 136.5, 132.3, 132.0, 130.6, 130.5, 129.8, 129.2, 126.9, 125.0, 24.7, 19.9; **HRMS (ESI$^+$):** calculated for $C_{17}H_{15}OS^+$ $[M+H]^+$ 267.0838, found 267.0831.

2-(*p*-tolyl)-4*H*-thiochromen-4-one (3ba)[1]

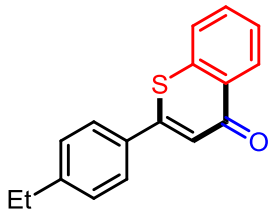


Following the general procedure, the title compound was obtained (37.2 mg, 74% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.56 (m, 4H), 7.56 – 7.51 (m, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.9, 153.1, 141.4, 137.7, 133.7, 131.5, 130.9, 130.0, 128.6 127.7, 126.8, 126.5, 122.8, 21.4; **LRMS (ESI$^+$):** calculated for $C_{16}H_{13}OS^+$ $[M+H]^+$ 253.07, found 253.10. All analytical data are consistent with those reported in the literature.

2-(4-ethylphenyl)-4*H*-thiochromen-4-one (3ca)[3]

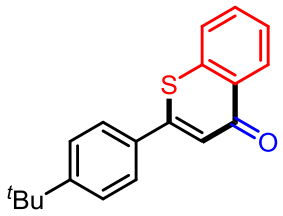


Following the general procedure, the title compound was obtained (41.1 mg, 77% yield, yellow solid;

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.68 – 7.56 (m, 4H), 7.55 – 7.48 (m, 1H), 7.35 – 7.28 (m, 2H), 7.23 (s, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.9, 153.1, 147.5, 137.7, 133.8, 131.5, 130.9, 128.8, 128.5, 127.6, 126.9, 126.4, 122.8, 28.7, 15.3; **LRMS (ESI$^+$):** calculated for $C_{17}H_{15}OS^+$ $[M+H]^+$ 267.08, found 267.13. All analytical data are consistent with those reported in the literature.

2-(4-(*tert*-butyl)phenyl)-4*H*-thiochromen-4-one (3da)[4]

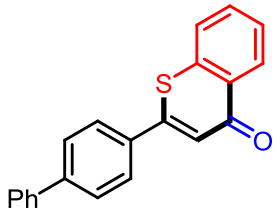


General procedure with the following changes：TfOH (300.2 mg， 2.0 mmol，10.0 equiv.) and DCM (1 mL) instead of TfOH (1 mL), the title compound was obtained (43.7 mg, 74% yield, pale yellow oil;

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (ddd, *J* = 8.0, 1.5, 0.6 Hz, 1H), 7.67 – 7.57 (m, 4H), 7.56 – 7.49 (m, 3H), 7.25 (s, 1H), 1.36 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.9, 154.4, 153.0, 137.7, 133.6, 131.5, 130.9, 128.5, 127.6, 126.6, 126.4, 126.2, 122.8, 34.9, 31.1; **LRMS (ESI$^+$):** calculated for $C_{19}H_{19}OS^+$ $[M+H]^+$ 295.12, found 295.18. All analytical data are consistent with those reported in the literature.

2-([1,1'-biphenyl]-4-yl)-4*H*-thiochromen-4-one (3ea)[1]

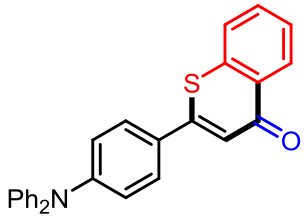


General procedure with the following changes：TfOH (300.2 mg， 2.0 mmol，10.0 equiv.) and DCM (1 mL) instead of TfOH (1 mL), the title compound was obtained (33.2 mg, 53% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.1~0.2;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.73 – 7.69 (m, 2H), 7.68 – 7.59 (m, 4H), 7.57 – 7.51 (m, 1H), 7.51 – 7.44 (m, 2H), 7.43 – 7.36 (m, 1H), 7.29 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.9, 152.6, 143.8, 139.7, 137.6, 135.3, 131.6, 131.0, 129.0, 128.6, 128.1, 127.9, 127.8, 127.4, 127.1, 126.5, 123.2; **LRMS (ESI$^+$):** calculated for $C_{21}H_{15}OS^+$ $[M+H]^+$ 315.08, found 315.17. All analytical data are consistent with those reported in the literature.

2-(4-(diphenylamino)phenyl)-4*H*-thiochromen-4-one (3fa)



Following the general procedure, the title compound was obtained (47.8 mg, 59% yield, yellow solid);

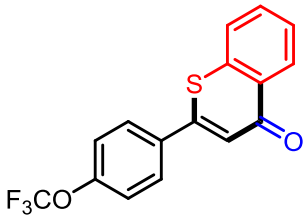
R_f (PE/EA 5:1) = 0.4~0.5;

MP 178-180 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.70 – 7.58 (m, 2H), 7.58 – 7.50 (m, 3H), 7.38 – 7.28 (m, 4H), 7.25 (s, 1H), 7.20 – 7.05 (m, 8H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.9, 152.6, 150.5, 146.7, 137.5, 131.4, 130.9, 129.6, 128.51, 128.48, 127.7, 127.6, 126.4, 125.6, 124.3,

121.54, 121.47; **HRMS (ESI$^+$):** calculated for $C_{27}H_{20}NOS^+$ $[M+H]^+$ 406.1260, found 406.1264.

2-(4-(trifluoromethoxy)phenyl)-4*H*-thiochromen-4-one (3ga)[1]

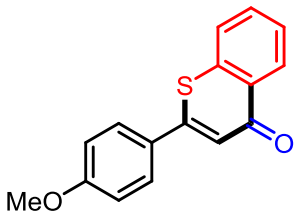


Following the general procedure, the title compound was obtained (43.0 mg, 67% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.49 (m, 1H), 7.76 – 7.69 (m, 2H), 7.67 – 7.59 (m, 2H), 7.59 – 7.51 (m, 1H), 7.38 – 7.30 (m, 2H), 7.19 (s, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.7; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.6, 151.2, δ 151.0 (q, *J* = 1.9 Hz), 137.3, 135.0, 131.8, 130.8, 128.6, 128.0, 126.5, 123.8, 121.4, 120.3 (q, *J* = 258.6 Hz); **LRMS (ESI$^+$):** calculated for $C_{16}H_{10}F_3O_2S^+$ $[M+H]^+$ 323.03, found 323.09. All analytical data are consistent with those reported in the literature.

2-(4-methoxyphenyl)-4*H*-thiochromen-4-one (3ha)[1]

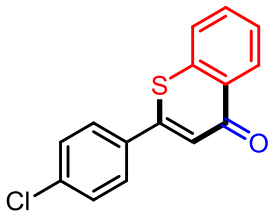


General procedure with the following changes: 7.5 wt% P_2O_5-MsOH (2 mL) instead of TfOH (1 mL), the title compound was obtained (36.2 mg, 67% yield, yellow solid);

R_f (PE/EA 5:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.68 – 7.62 (m, 3H), 7.62 – 7.57 (m, 1H), 7.56 – 7.50 (m, 1H), 7.20 (s, 1H), 7.04 – 6.96 (m, 2H), 3.87 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.9, 161.9, 152.9, 137.7, 131.5, 130.9, 128.8, 128.6, 128.3, 127.7, 126.4, 122.1, 114.7, 55.5; **LRMS (ESI$^+$):** calculated for $C_{16}H_{13}O_2S^+$ $[M+H]^+$ 269.06, found 269.13. All analytical data are consistent with those reported in the literature.

2-(4-chlorophenyl)-4*H*-thiochromen-4-one (3ia)[3]



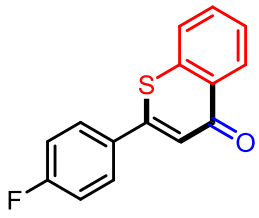
Following the general procedure, the title compound was obtained (30.0 mg, 55% yield, pale brown solid);

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.70 – 7.60 (m, 4H), 7.60 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 7.22 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.8,

151.6, 137.4, 137.1, 135.0, 131.8, 130.8, 129.6, 128.7, 128.2, 128.0, 126.5, 123.6; **LRMS (ESI$^+$):** calculated for $C_{15}H_{10}ClO_3S^+$ $[M+H]^+$ 273.01, found 273.09; $C_{15}H_{10}{}^{37}ClO_3S^+$ $[M+H]^+$ 275.01, found 275.10. All analytical data are consistent with those reported in the literature.

2-(4-fluorophenyl)-4*H*-thiochromen-4-one (3ja)[1]

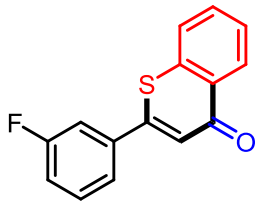


Following the general procedure, the title compound was obtained (42.7 mg, 81% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.74 – 7.60 (m, 4H), 7.59 – 7.52 (m, 1H), 7.23 – 7.13 (m, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.1; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.9, δ 164.3 (d, *J* = 252.0 Hz), 151.8, 137.4, 132.7 (d, *J* = 3.4 Hz), 131.7, 130.9, 129.0 (d, *J* = 8.6 Hz), 128.6, 127.9, 126.5, 123.5, 116.5 (d, *J* = 22.0 Hz); **LRMS (ESI$^+$):** calculated for $C_{15}H_{10}FOS^+$ $[M+H]^+$ 257.04, found 257.07. All analytical data are consistent with those reported in the literature.

2-(3-fluorophenyl)-4*H*-thiochromen-4-one (3ka)[1]

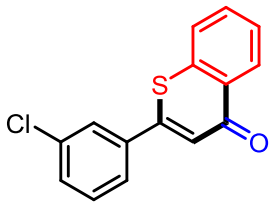


General procedure with the following changes：TfOH (300.2 mg， 2.0 mmol，10.0 equiv.) and DCM (1 mL) instead of TfOH (1 mL), the title compound was obtained (30.0 mg, 59% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.51 (m, 1H), 7.70 – 7.59 (m, 2H), 7.59 – 7.52 (m, 1H), 7.52 – 7.44 (m, 2H), 7.43 – 7.36 (m, 1H), 7.25 – 7.17 (m, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.0; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.7, δ 162.9 (d, *J* = 248.5 Hz), 151.3 (d, *J* = 2.4 Hz), 138.6 (d, *J* = 8.0 Hz), 137.3, 131.8, 130.9 (d, *J* = 8.4 Hz), 130.8, 128.6, 127.9, 126.5, 123.8, 122.7 (d, *J* = 3.1 Hz), 117.7 (d, *J* = 21.0 Hz), 114.1 (d, *J* = 23.4 Hz); **LRMS (ESI$^+$):** calculated for $C_{15}H_{10}FOS^+$ $[M+H]^+$ 257.04, found 257.06. All analytical data are consistent with those reported in the literature.

2-(3-chlorophenyl)-4*H*-thiochromen-4-one (3la)



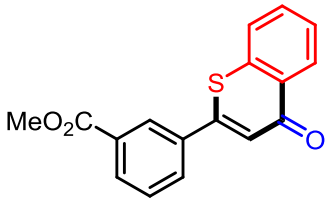
Following the general procedure, the title compound was obtained (27.4 mg, 50% yield, pale brown solid);

R_f (PE/EA 10:1) = 0.2~0.3;

MP 124-126 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.51 (m, 1H), 7.72 – 7.61 (m, 3H), 7.61 – 7.53 (m, 2H), 7.52 – 7.41 (m, 2H), 7.22 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.8, 151.3, 138.3, 137.4, 135.4, 131.8, 130.9, 130.8, 130.6, 128.7, 128.0, 127.1, 126.5, 125.2, 124.0; **HRMS (ESI$^+$):** calculated for $C_{15}H_9ClNaOS^+$ $[M+Na]^+$ 294.9955, found 294.9951; $C_{15}H_9{}^{37}ClNaOS^+$ $[M+Na]^+$ 296.9925, found 296.9925.

methyl 3-(4-oxo-4*H*-thiochromen-2-yl)benzoate (3ma)



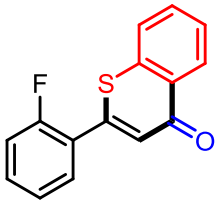
Following the general procedure, the title compound was obtained (24.3 mg, 41% yield, pink solid);

R_f (PE/EA 5:1) = 0.2~0.3;

Mp 147-149 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.51 (m, 1H), 8.38 (t, *J* = 1.9 Hz, 1H), 8.18 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.92 – 7.84 (m, 1H), 7.72 – 7.60 (m, 2H), 7.64 – 7.52 (m, 2H), 7.28 (s, 1H), 3.98 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.8, 166.1, 151.8, 137.4, 136.9, 131.8, 131.7, 131.3, 131.1, 130.9, 129.5, 128.7, 128.1, 128.0, 126.6, 123.9, 52.5; **HRMS (ESI$^+$):** calculated for $C_{17}H_{12}NaO_3S^+$ $[M+Na]^+$ 319.0399, found 319.0395.

2-(2-fluorophenyl)-4*H*-thiochromen-4-one (3na)[4]



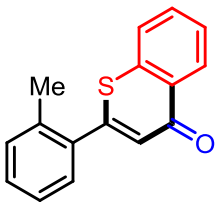
General procedure with the following changes：reaction time 12 h of step 1, the title compound was obtained (28.2 mg, 55% yield, pale yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.60 – 7.52 (m, 2H), 7.52 – 7.44 (m, 1H), 7.31 – 7.26 (m, 1H), 7.25 – 7.20 (m, 1H), 7.19 (d, *J* = 1.2 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.9; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.5, δ 159.2 (d, *J* = 252.6 Hz), 147.1, 138.0, 132.1 (d, *J* = 8.7 Hz), 131.7, 130.8, 130.1 (d, *J* = 2.1 Hz), 128.7, 127.9,

126.9 (d, *J* = 3.7 Hz), 126.3, 124.8 (d, *J* = 4.2 Hz), 124.4 (d, *J* = 13.1 Hz), 116.8 (d, *J* = 22.4 Hz); **LRMS (ESI$^+$):** calculated for $C_{15}H_{10}FOS^+$ $[M+H]^+$ 257.04, found 257.09. All analytical data are consistent with those reported in the literature.

2-(*o*-tolyl)-4*H*-thiochromen-4-one (3oa)[1]

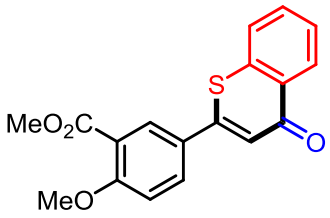


General procedure with the following changes: NMP instead of DMF, reaction time 12 h of step 1, the title compound was obtained (23.1 mg, 46% yield, yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.68 – 7.58 (m, 2H), 7.62 – 7.51 (m, 1H), 7.42 – 7.27 (m, 4H), 6.92 (s, 1H), 2.39 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.6, 153.6, 138.4, 136.2, 135.7, 131.6, 131.0, 130.9, 129.8, 129.1, 128.7, 127.8, 126.3, 126.1, 19.9; **LRMS (ESI$^+$):** calculated for $C_{16}H_{13}OS^+$ $[M+H]^+$ 253.07, found 253.07. All analytical data are consistent with those reported in the literature.

methyl 2-methoxy-5-(4-oxo-4*H*-thiochromen-2-yl)benzoate (3pa)



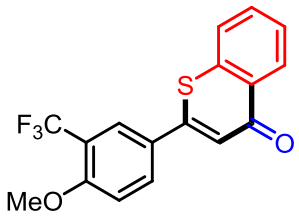
Following the general procedure, the title compound was obtained (41.7 mg, 64% yield, pale yellow solid);

R_f (PE/EA 3:1) = 0.1~0.2;

Mp 137-139 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.49 (m, 1H), 8.17 (d, *J* = 2.5 Hz, 1H), 7.81 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.59 – 7.50 (m, 1H), 7.21 (s, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.8, 165.6, 161.1, 151.5, 137.3, 131.8, 131.7, 130.8, 130.4, 128.6, 128.3, 127.8, 126.5, 122.6, 120.7, 112.8, 56.4, 52.4; **HRMS (ESI$^+$):** calculated for $C_{18}H_{15}O4S^+$ $[M+H]^+$ 327.0686, found 327.0681.

2-(4-methoxy-3-(trifluoromethyl)phenyl)-4*H*-thiochromen-4-one (3qa)



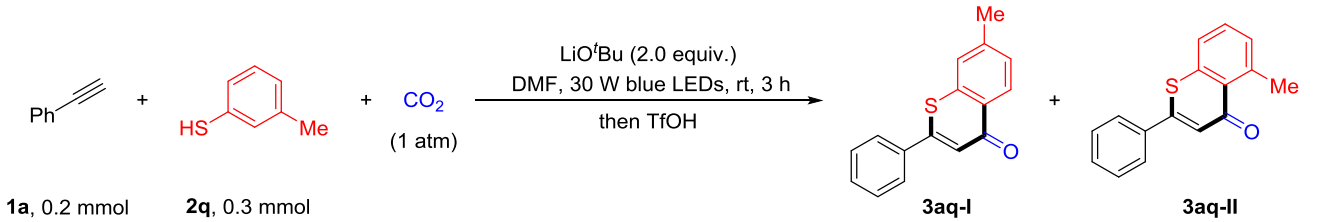
General procedure with the following changes：TfOH (300.2 mg， 2.0 mmol，10.0 equiv.) and DCM (1 mL) instead of TfOH (1 mL), the title compound was obtained (41.6 mg, 62% yield, white solid);

R_f (PE/EA 3:1) = 0.2~0.3;

Mp 133-135 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.49 (m, 1H), 7.91 (d, *J* = 2.4 Hz, 1H), 7.84 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.58 – 7.52 (m, 1H), 7.18 (s, 1H), 7.13 (d, *J* = 8.7 Hz, 1H), 3.98 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.8; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 180.7, 159.4, 151.2, 137.2, 131.9, 131.8, 130.7, 128.6, 128.3, 127.9, 126.5, δ 125.9 (q, *J* = 5.4 Hz), 123.1 (q, *J* = 272.8 Hz), 122.9, 119.6 (q, *J* = 31.5 Hz), 112.7, 56.3; **HRMS (ESI$^+$):** calculated for $C_{17}H_{11}F_3NaO_2S^+$ $[M+Na]^+$ 359.0324, found 359.0321.

Reaction of thiophenol 2q:

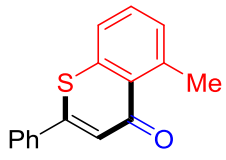


1a, 0.2 mmol　　**2q**, 0.3 mmol　　**3aq-I**　　**3aq-II**

81%

3aq-I: 3aq-II = 1:1.3, determined by crude ^{1}H NMR

5-methyl-2-phenyl-4*H*-thiochromen-4-one (3aq-I)



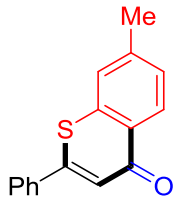
Following the general procedure, the title compound was obtained (24.5 mg, 49% yield, brownish yellow solid;

R_f (PE/EA 10:1) = 0.4~0.5;

MP 113-115 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.54 – 7.45 (m, 4H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 6.8 Hz, 1H), 7.12 (s, 1H), 2.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.6, 150.0, 143.2, 139.3, 136.1, 131.3, 130.6, 130.5, 129.5, 129.2, 126.8, 125.0, 124.7, 24.7; **HRMS (ESI$^+$):** calculated for $C_{16}H_{13}OS^+$ $[M+H]^+$ 253.0682, found 253.0682.

7-methyl-2-phenyl-4*H*-thiochromen-4-one (3aq-II)[1]

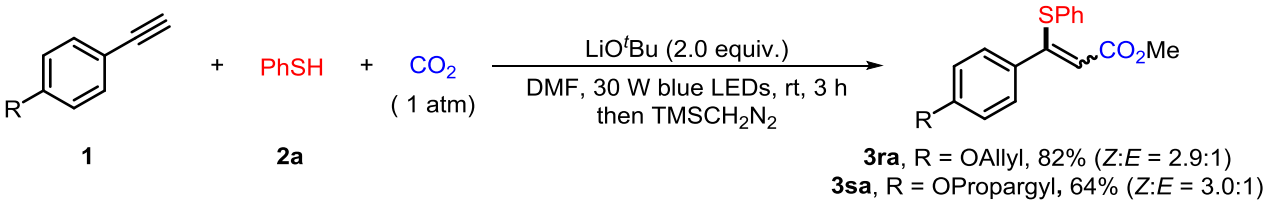


Following the general procedure, the title compound was obtained (16.3 mg, 32% yield, brownish yellow solid);

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$)δ 8.43 (d, *J* = 8.2 Hz, 1H), 7.69 (dd, *J* = 6.7, 2.8 Hz, 2H), 7.56 – 7.47 (m, 3H), 7.45 (s, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.21 (s, 1H), 2.48 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.8, 152.6, 142.5, 137.8, 136.6, 130.7, 129.3, 129.2, 128.7, 128.5, 126.9, 126.2, 123.4, 21.6. **LRMS (ESI$^+$)**: calculated for $C_{16}H_{13}OS^+[M+H]^+$ 253.07, found: 253.06. All analytical data are consistent with those reported in the literature.

3.2 The exploration of other alkyne substrates in visible-light-driven thio-carboxylation:



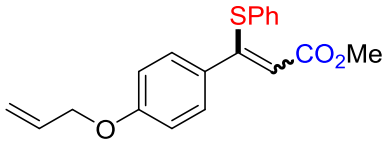
1 **2a**

3ra, R = OAllyl, 82% (*Z*:*E* = 2.9:1)
3sa, R = OPropargyl, 64% (*Z*:*E* = 3.0:1)

General procedure:

To an oven-dried Schlenk tube (10 mL) containing a magnetic stirring was moved into a glovebox and was charged with LiO^{t}Bu (32.0 mg, 0.4 mmol, 2.0 equiv.). The tube was sealed and then evacuated and back-filled with CO_2 atmosphere for 3 times, subsequently, anhydrous DMF (2 mL) was added followed by thiophenol **2a** (33.1 mg, 0.3 mmol, 1.5 equiv.) and alkyne (0.2 mmol, 1.0 equiv.) via syringe under CO_2. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 The reaction was stirred and irradiated with a 30 W blue LED lamp (1-2 cm away, with cooling fan to keep the reaction temperature at 22-25 ℃) for 3 hours. The resulting mixture was diluted with EtOAc (3 mL) and quenched by 2 N HCl (2 mL), then stirred for 5 min. The reaction mixture was extracted by EtOAc four times and the combined organic phases were concentrated *in vacuo*. The residue was then dissolved in a 1:1 MeOH:Et_2O (3 mL) mixture and cooled down to 0 ℃. $TMSCHN_2$ (1.0 mL of a 2 M solution in hexane, 10.0 equiv.) was added dropwise. Then after 1 h the mixture was concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc= 50/1 ~ 10/1) to give the pure desired product.

methyl 3-(4-(allyloxy)phenyl)-3-(phenylthio)acrylate (3ra)

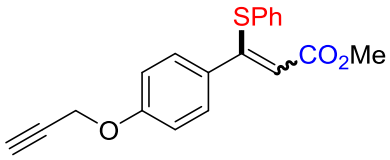


Following the general procedure, the title compound was obtained (53.5 mg, 82% yield (*Z*:*E* = 2.9:1, determined by crude ^{1}H NMR), pale yellow oil);

R_f (PE/EA 10:1) = 0.1~0.2;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.31 (m, 2.45H-*E*), 7.21 – 6.97 (m, 7H), 6.91 (d, *J* = 8.3 Hz, 0.7H-*E*), 6.64 (d, *J* = 8.3 Hz, 2H-*Z*), 6.08 (s, 1H-*Z*), 6.03 – 5.87 (m, 1.35H), 5.49 – 5.16 (m, 3.05H), 4.55 (d, *J* = 5.2 Hz, 0.7H-*E*), 4.42 (d, *J* = 5.3 Hz, 2H-*Z*), 3.79 (s, 3H-*Z*), 3.49 (s, 1.05H-*E*); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 165.1, 161.1, 159.4, 158.8, 158.8, 135.2, 133.6, 133.0, 132.8, 130.8, 130.3, 130.1, 130.0, 129.8, 128.7, 128.4, 127.5, 117.7, 115.4, 114.1, 114.0, 110.9, 110.0, 68.8, 68.7, 51.4, 50.9; **HRMS (ESI$^+$)**: calculated for $C_{19}H_{17}O_3S^+[M+H]^+$ 327.1049, found: 327.1045.

methyl 3-(phenylthio)-3-(4-(prop-2-yn-1-yloxy)phenyl)acrylate (3sa)

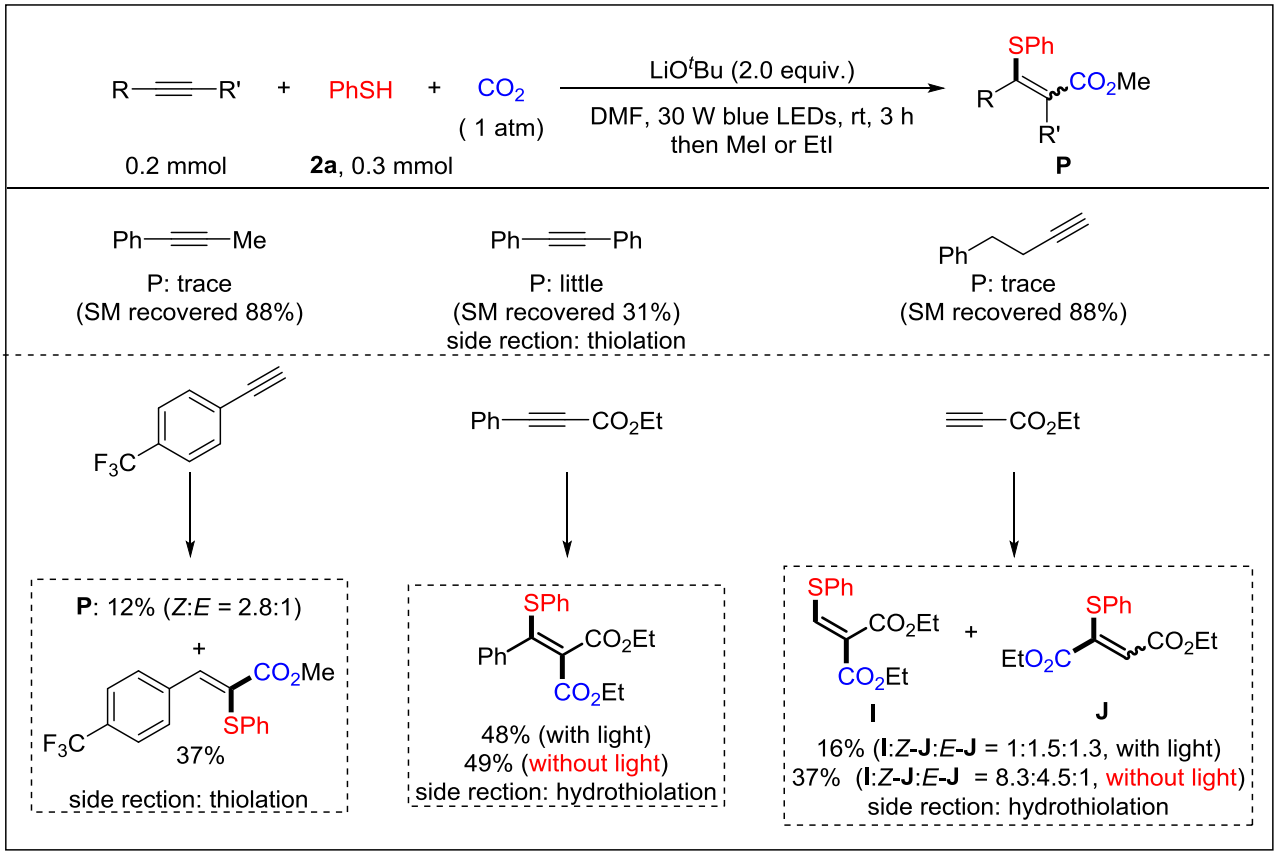


Following the general procedure, the title compound was obtained (41.5 mg, 64% yield (*Z*:*E* = 3.0:1, determined by crude ^{1}H NMR), pale yellow oil);

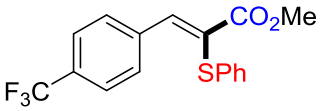
R_f (PE/EA 10:1) = 0.1~0.2;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.5, 3.0 Hz, 0.7H-*E*), 7.45 – 7.41 (m, 1.05H-*E*), 7.40 – 7.36 (m, 0.7H-*E*), 7.19 – 7.10 (m, 4H-*Z*), 7.06 (dd, *J* = 5.0, 1.8 Hz, 3H-*Z*), 6.97 (d, *J* = 8.6 Hz, 0.70H-*E*), 6.70 (d, *J* = 8.7 Hz, 2H-*Z*), 6.08 (s, 1H-*Z*), 5.38 (s, 0.35H-*E*), 4.70 (d, *J* = 2.4 Hz, 0.7H-*E*), 4.57 (d, *J* = 2.4 Hz, 2H-*Z*), 3.79 (s, 3H-*Z*), 3.48 (s, 0.70H-*E*), 2.53 (t, *J* = 2.4 Hz, 0.35H-*E*), 2.48 (t, *J* = 2.4 Hz, 1H-*Z*); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 165.0, 160.9, 158.6, 158.4, 157.7, 135.3, 133.6, 132.6, 131.5, 130.2, 130.1, 130.0, 129.9, 129.8, 129.5, 128.4, 127.6, 115.6, 114.3, 114.2, 111.0, 78.3, 78.1, 75.71, 75.69, 55.8, 55.7, 51.4, 50.9; **HRMS (ESI$^+$)**: calculated for $C_{19}H_{17}O_3S^+[M+H]^+$ 325.0893, found: 325.0890.

Unsuccessful Substrates:



methyl (*Z*)-2-(phenylthio)-3-(4-(trifluoromethyl)phenyl)acrylate

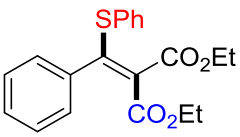


25.0 mg, 37% yield, pale yellow oil;

R_f (PE/EA 10:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.69 (d, J = 8.1 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.42 – 7.31 (m, 3H), 3.76 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 146.7, 138.5, 133.5, 131.1, 130.1 (q, *J* = 32.9 Hz), 130.0, 129.6, 128.5, 127.0, δ 125.3 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 3.8 Hz), 52.3; **HRMS (ESI$^+$):** calculated for $C_{17}H_{14}F_3O_2S^+$ $[M+H]^+$ 339.0661, found 339.0661.

diethyl 2-(phenyl(phenylthio)methylene)malonate



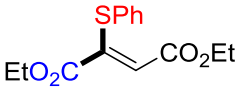
25.4 mg, 48% yield (with light), 49% yield(without light), pale yellow oil;

R_f (PE/EA 20:1) = 0.1~0.2;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.13 (m, 2H), 7.12 – 7.07 (m, 1H), 7.06 – 6.96 (m, 7H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.88 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 163.9, 161.1, 135.5, 135.4, 130.7, 128.9,

128.6, 128.4, 128.2, 127.3, 121.8, 61.3, 61.1, 14.2, 13.5; **HRMS (ESI$^+$):** calculated for $C_{20}H_{21}O_4S^+$ $[M+H]^+$ 357.1155, found 357.1153.

diethyl 2-(phenylthio)fumarate (*Z*-J)[5]

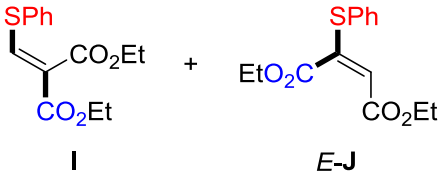


7.7 mg, 14% yield, pale yellow oil (without light);

R_f (PE/EA 20:1) = 0.2~0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.38 – 7.29 (m, 3H), 6.39 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.80 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 164.4, 149.4, 133.2, 132.4, 129.0, 128.7, 119.6, 62.1, 60.9, 14.2, 13.5; **GCMS**: 280.2. All analytical data are consistent with those reported in the literature.

diethyl 2-((phenylthio)methylene)malonate (I)[6] **and diethyl 2-(phenylthio)maleate (*E*-J)**



I *E*-J

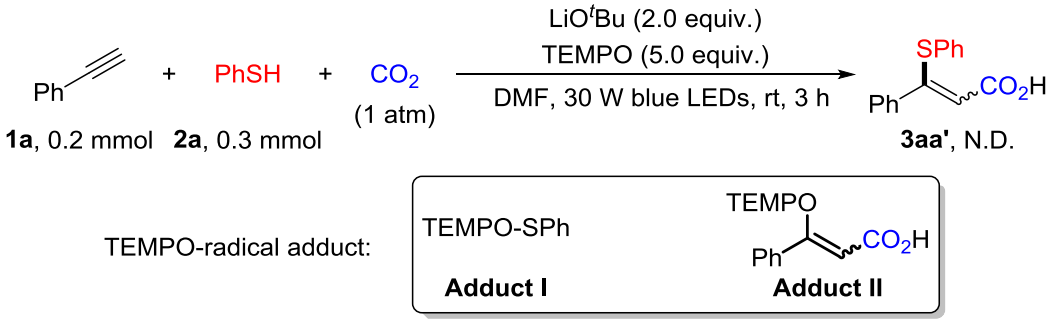
12.7 mg, 23% yield (**I**: *E*-**J** = 8.3:1, determined by crude ^{1}H NMR), pale yellow oil (without light);

R_f (PE/EA 20:1) = 0.1~0.2;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H-**I**), 7.58 – 7.49 (m, 2.28H), 7.47 – 7.37 (m, 3.42H), 5.54 (s, 0.14H-*E*-**J**), 4.36 (q, *J* = 7.1 Hz, 2H-**I**), 4.25 (q, *J* = 7.1 Hz, 2H-**I**), 4.14 (dq, *J* = 10.4, 7.1 Hz, 0.56H- *E*-**J**), 1.38 (t, *J* = 7.1 Hz, 3H-**I**), 1.30 (t, *J* = 7.1 Hz, 3H-**I**), 1.22 (q, *J* = 7.0 Hz, 0.84H-*E*-**J**); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.6, 163.3, 160.3, 135.7, 135.1, 131.3, 130.4, 129.7, 129.6, 129.0, 118.7, 114.4, 62.2, 61.4, 61.2, 60.8, 14.3, 14.2, 14.1, 13.8; **HRMS (ESI$^+$):** calculated for $C_{17}H_{14}O_4S^+$ $[M+H]^+$ 281.0842, found 281.0844. All analytical data of **I** are consistent with those reported in the literature.

4. Mechanistic studies

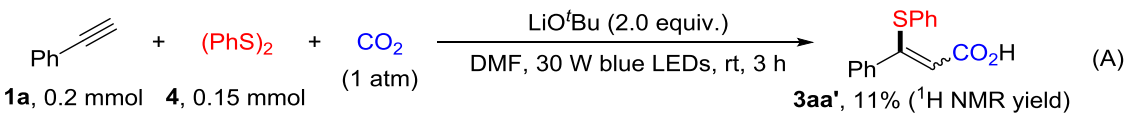
4.1 Radical trapping experiments



Procedure:

To an oven-dried Schlenk tube (10 mL) containing a magnetic stirring bar was added radical scavenger TEMPO (156.2 mg, 1.0 mmol, 5.0 equiv.). Then the tube was moved into a glovebox and was charged with LiO^{t}Bu (32.0 mg, 0.4 mmol, 2.0 equiv.). The tube was sealed and then evacuated and back-filled with CO_2 atmosphere for 3 times, subsequently, anhydrous DMF (2 mL) was added followed by thiophenol **2a** (33.1 mg, 0.3 mmol, 1.5 equiv.), alkyne **1a** (20.4 mg, 0.2 mmol, 1.0 equiv.) via syringe under CO_2. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The reaction was stirred and irradiated with a 30 W blue LED lamp (1-2 cm away, with cooling fan to keep the reaction temperature at 22-25 ℃) for 3 hours. The resulting mixture then was subjected to HRMS analysis. The thio-carboxylation product **3aa'** was fully suppressed when radical scavenger TEMPO was subjected to the standard conditions. And when using TEMPO as radical scavenger, two TEMPO-radical adducts was detected, **Adduct I**: **HRMS (ESI$^+$):** calculated for $C_{15}H_{24}NOS^+$ $[M+H]^+$ 266.1573, found 266.1573; **Adduct II**: **HRMS (ESI$^+$):** calculated for $C_{18}H_{26}NO_3^+$ $[M+H]^+$ 304.1907, found 304.1912.

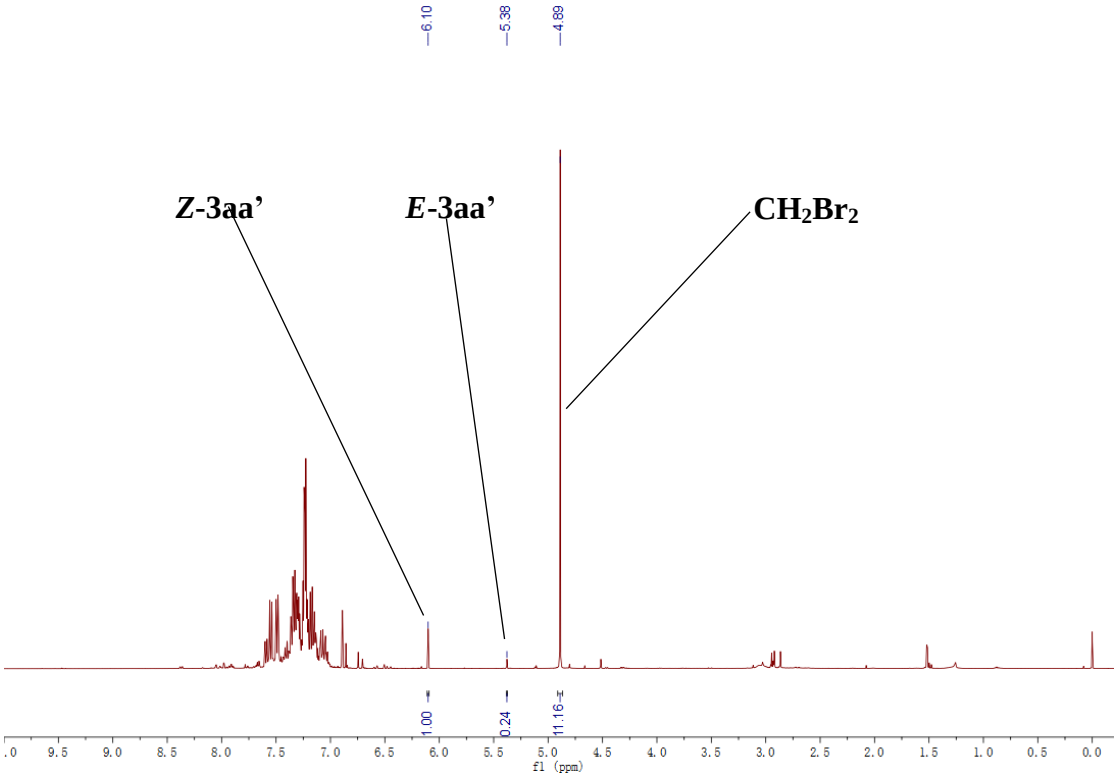
4.2 The possibility of 4 and 1a' acted as reaction intermediates



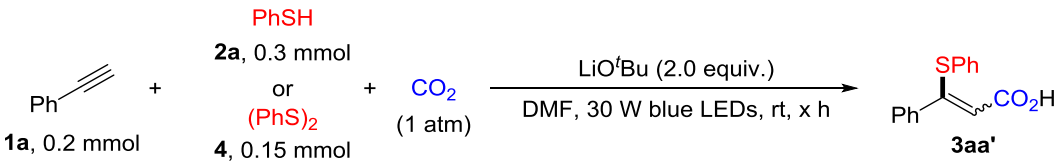
Procedure:

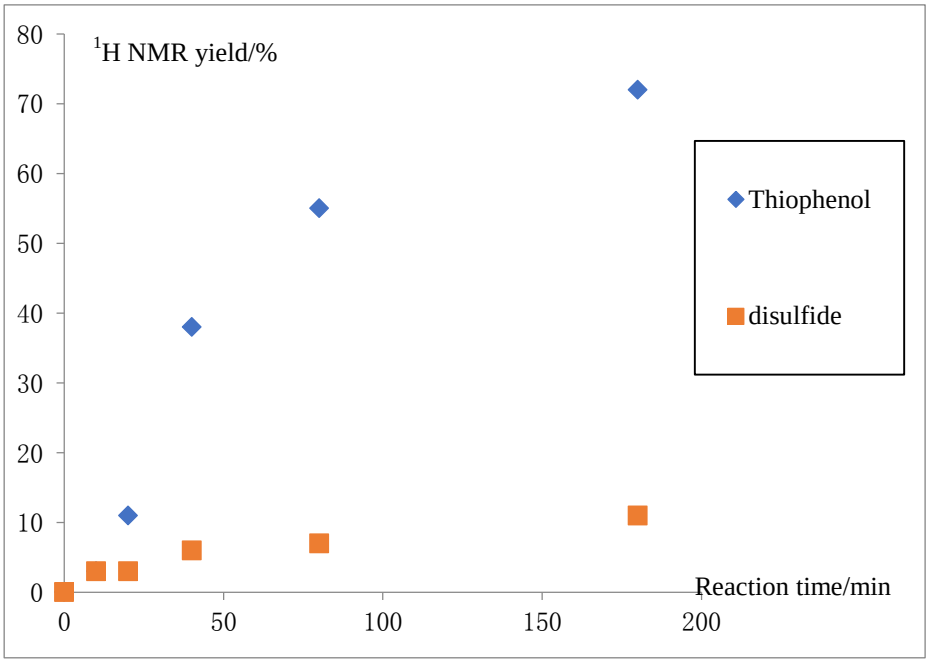
For (A): To an oven-dried Schlenk tube (10 mL) containing a magnetic stirring bar was added

disulfide **4** (37.0 mg, 0.15 mmol, 0.75 equiv.). Then the tube was moved into a glovebox and charged with LiO^tBu (32.0 mg, 0.4 mmol, 2.0 equiv.). The tube was sealed and then evacuated and back-filled with CO_2 atmosphere for 3 times, subsequently, anhydrous DMF (2 mL) was added followed by alkyne **1a** (20.4 mg, 0.2 mmol, 1.0 equiv.) via syringe under CO_2. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The reaction was stirred and irradiated with a 30 W blue LED lamp (1-2 cm away, with cooling fan to keep the reaction temperature at 22-25 ℃) for 3 hours. The resulting mixture was diluted with EtOAc (3 mL) and quenched by 2 N HCl (2 mL), then stirred for 5 min. The reaction mixture was extracted by EtOAc four times and the combined organic phases were concentrated *in vacuo*. The residue was analyzed by ^{1}H NMR with CH_2Br_2 as internal standard. The thio-carboxylation product **3aa'** was given in only 11% NMR yield, showing that disulfide was not the reaction intermediate.

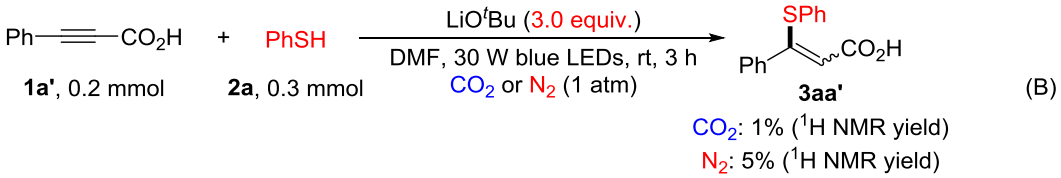


Kinetic experiments:





The kinetic experiments with thiophenol **2a** was conducted according to the standard reaction with reaction time 0 min, 10 min, 20 min, 40 min, 80 min and 180 min. The kinetic experiments with disulfide **4** was performed according to the procedure (A) with reaction time 0 min, 10 min, 20 min, 40 min, 80 min and 180 min. The resulting mixture was diluted with EtOAc (3 mL) and quenched by 2 N HCl (2 mL), then stirred for 5 min. The reaction mixture was extracted by EtOAc four times and the combined organic phases were concentrated *in vacuo*. The residue was analyzed by ^{1}H NMR with CH_2Br_2 as internal standard. The kinetic experiments further showed that disulfide was not the reaction intermediate of thio-carboxylation reaction.

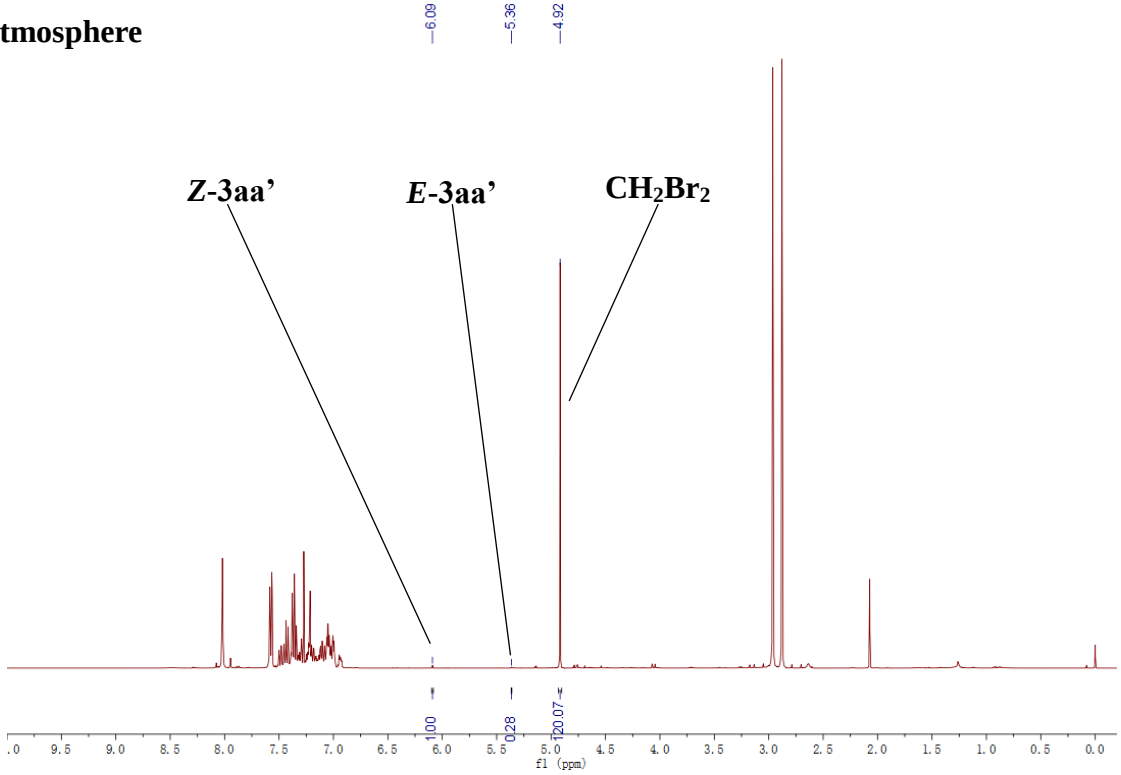


Procedure:

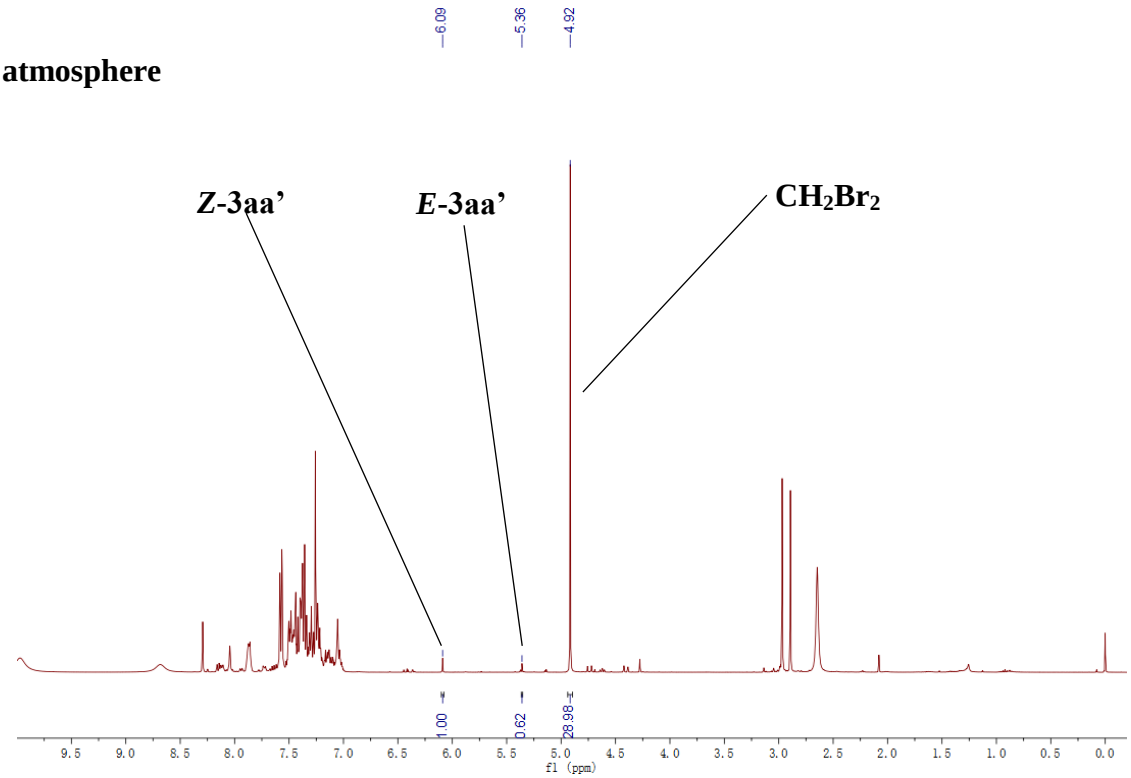
For (B): To an oven-dried Schlenk tube (10 mL) containing a magnetic stirring bar was added **1a'** (29.2 mg, 0.2 mmol, 1.0 equiv.). Then the tube was moved into a glovebox and was charged with LiO^{t}Bu (48.0 mg, 0.6 mmol, 3.0 equiv.). The tube was sealed and then evacuated and back-filled with CO_2 or N_2 atmosphere for 3 times, subsequently, anhydrous DMF (2 mL) was added followed by thiophenol **2a** (33.1 mg, 0.3 mmol, 1.5 equiv.) via syringe under CO_2 or N_2. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 or N_2 (1 atm). The reaction was stirred and irradiated with a 30 W blue LED lamp (1-2 cm away, with cooling fan to

keep the reaction temperature at 22-25 ℃) for 3 hours. The resulting mixture was diluted with EtOAc (3 mL) and quenched by 2 N HCl (2 mL), then stirred for 5 min. The reaction mixture was extracted by EtOAc four times and the combined organic phases were concentrated *in vacuo*. The residue was analyzed by ^{1}H NMR with CH_2Br_2 as internal standard, the yield of thio-carboxylation product **3aa'** is only 1% under CO_2, 5% yield of **3aa'** was afforded under N_2, which indicated that **1a'** is not the intermediate of the reaction.

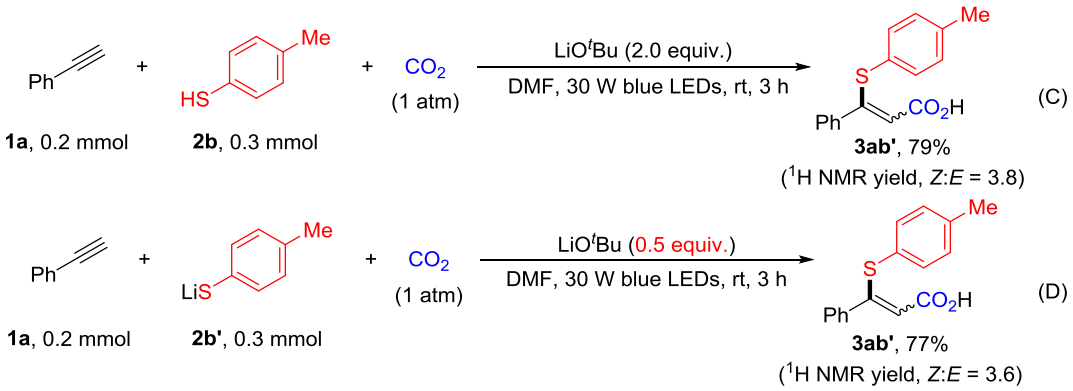
CO_2 atmosphere



N_2 atmosphere



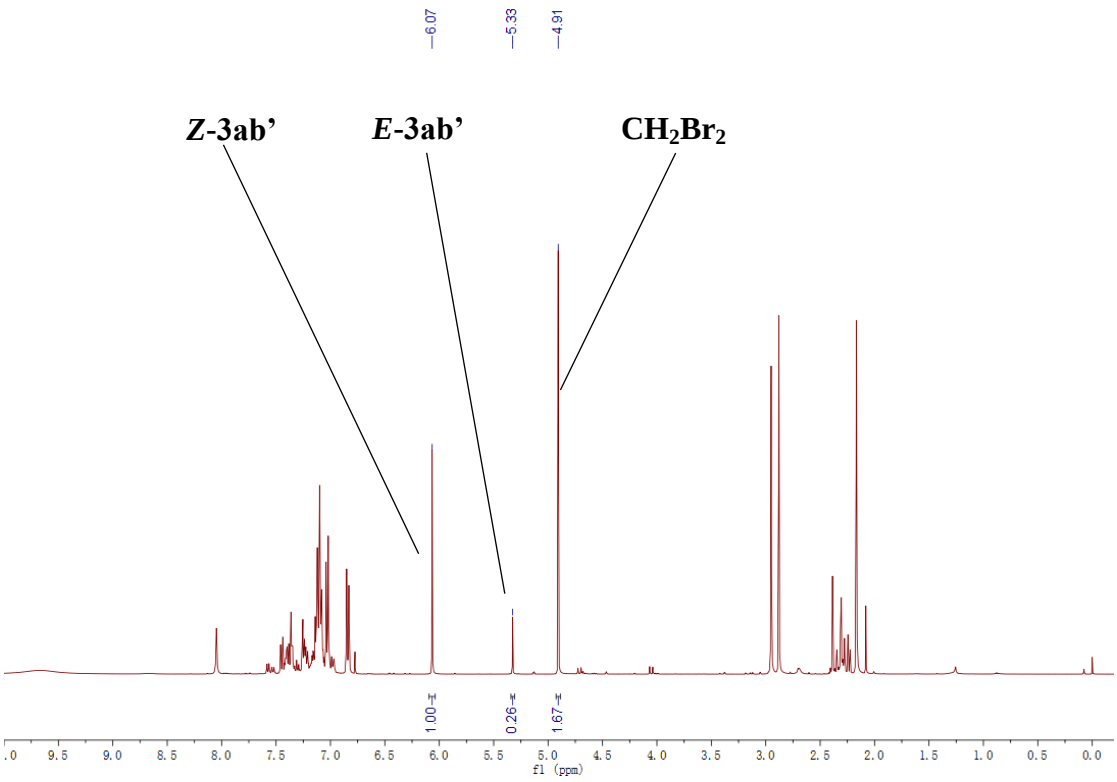
4.3 The exploration for the role of LiO^{t}Bu



Procedure:

For (C): To an oven-dried Schlenk tube (10 mL) containing a magnetic stirring bar was added **2b** (37.3 mg, 0.3 mmol, 1.5 equiv.). Then the tube was moved into a glovebox and was charged with LiO^{t}Bu (32.0 mg, 0.4 mmol, 2.0 equiv.).The tube was sealed and then evacuated and back-filled with CO_2 atmosphere for 3 times, subsequently, anhydrous DMF (2 mL) was added followed by alkyne (20.4 mg, 0.2 mmol, 1.0 equiv.) via syringe under CO_2. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The reaction was stirred and irradiated with a 30 W

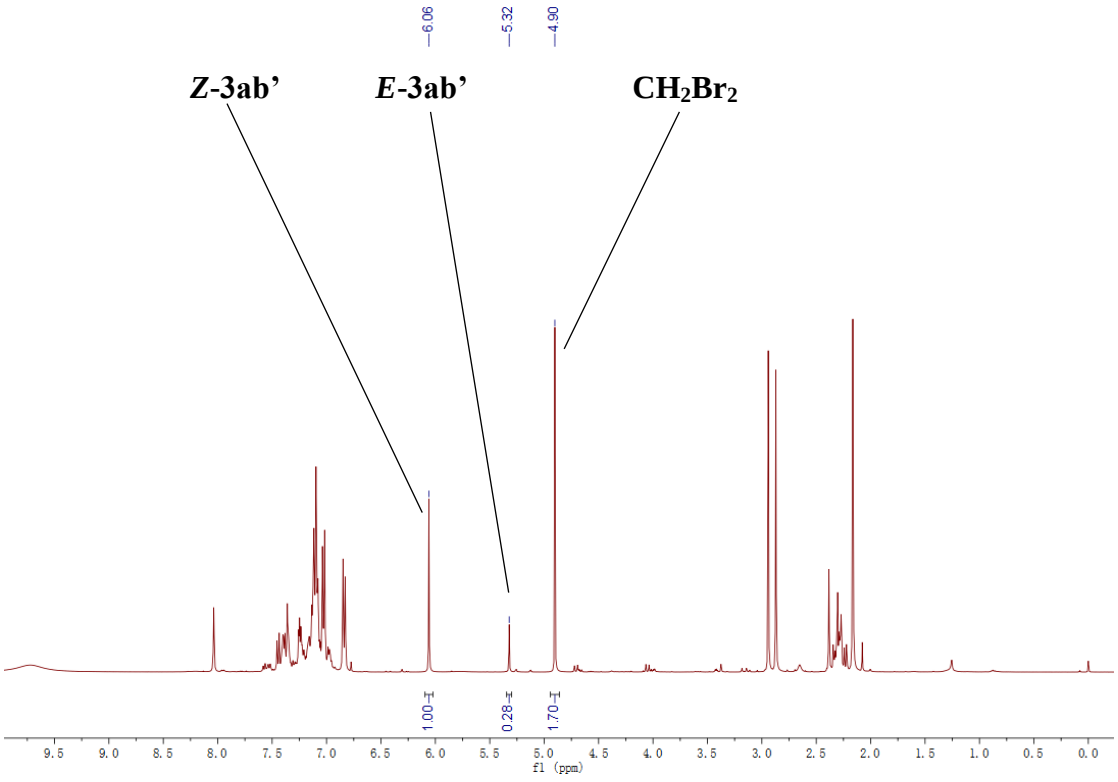
blue LED lamp (1-2 cm away, with cooling fan to keep the reaction temperature at 22-25 ℃) for 3 hours. The resulting mixture was diluted with EtOAc (3 mL) and quenched by 2 N HCl (2 mL), then stirred for 5 min. The reaction mixture was extracted by EtOAc four times and the combined organic phases were concentrated *in vacuo*. The residue was analyzed by ^{1}H NMR with CH_2Br_2 as internal standard. The thio-carboxylation product was given in 79% yield (*Z*/*E* = 3.8).



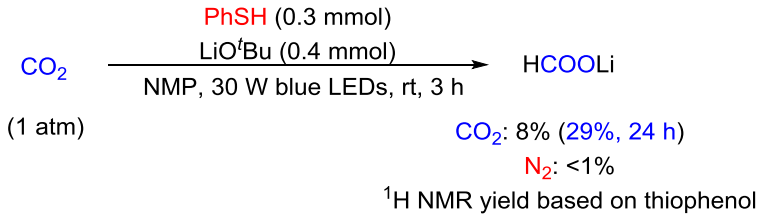
Procedure:

For (D): To an oven-dried Schlenk tube (10 mL) containing a magnetic stirring bar was charged with LiO^tBu (8.0 mg, 0.1 mmol, 0.5 equiv.) and thiolate 2b' (39.0 mg, 0.3 mmol, 1.5 equiv.) in the glovebox. The tube was sealed and then evacuated and back-filled with N_2 atmosphere for 3 times, subsequently, anhydrous DMF (2 mL) was added followed by alkyne **1a** (20.4 mg, 0.2 mmol, 1.0 equiv.) via syringe under CO_2. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The reaction was stirred and irradiated with a 30 W blue LED lamp (1-2 cm away, with cooling fan to keep the reaction temperature at 22-25 ℃) for 3 hours. The resulting mixture was diluted with EtOAc (3 mL) and quenched by 2 N HCl (2 mL), then stirred for 5 min. The reaction mixture was extracted by EtOAc four times and the combined organic phases were concentrated *in vacuo*. The residue was analyzed by ^{1}H NMR with CH_2Br_2 as internal standard.

Thiolate **2b'** was subjected to the reaction conditions to take place of thiophenol **2b**, the thio-carboxylation product was given in comparative yield and *Z*/*E* value, indicating that the main role of LiO^{t}Bu is acted as base to abstract the proton from thiophenol.



4.4 Detection of formate in the absence of alkyne

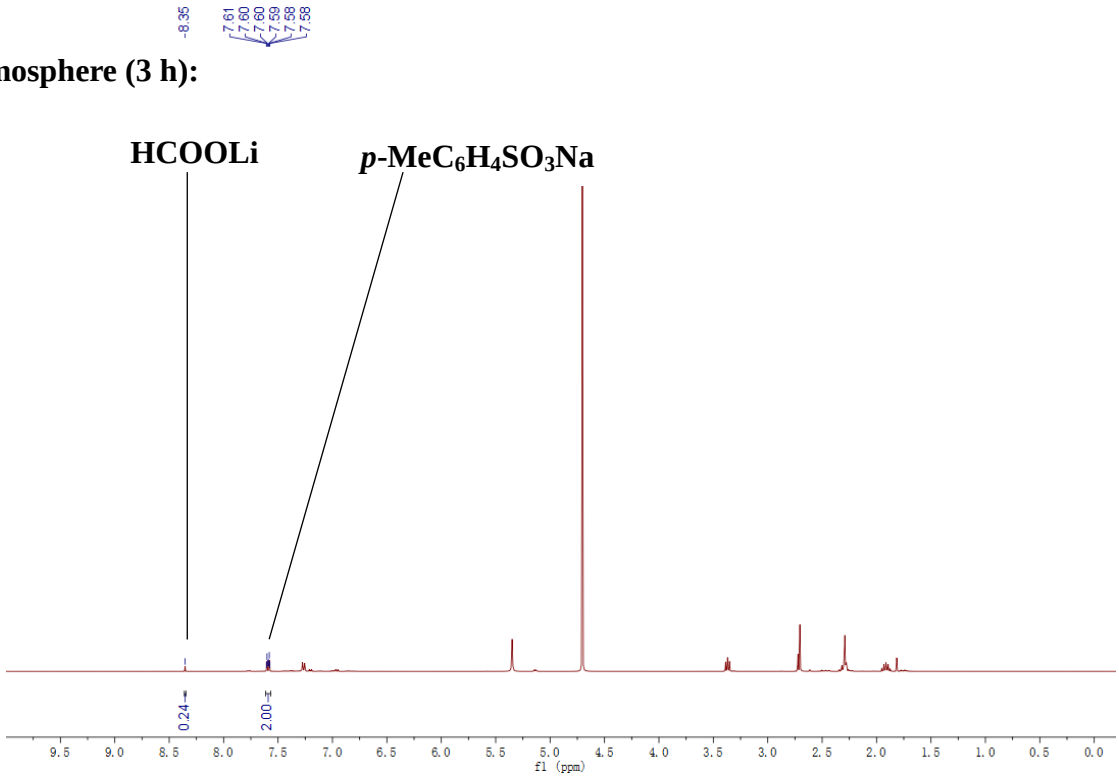


Procedure:

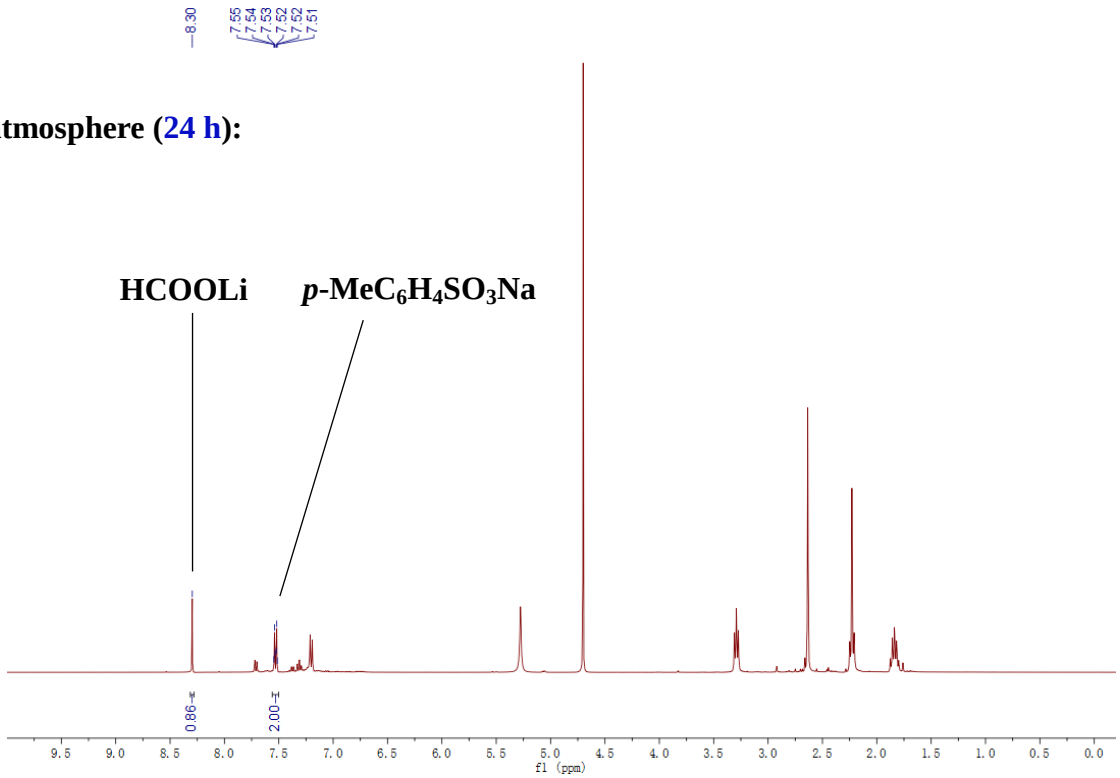
To an oven-dried Schlenk tube (10 mL) containing a magnetic stirring was moved into a glovebox and was charged with LiO^{t}Bu (32.0 mg, 0.4 mmol, 2.0 equiv.). The tube was sealed and then evacuated and back-filled with CO_2 or N_2 atmosphere for 3 times, subsequently, anhydrous NMP (2 mL) was added followed by thiophenol **2a** (33.1 mg, 0.3 mmol, 1.5 equiv.) via syringe under CO_2 or N_2. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 or N_2 (1

atm). The reaction was stirred and irradiated with a 30 W blue LED lamp (1-2 cm away, with cooling fan to keep the reaction temperature at 22-25 ℃) for 3 hours. The resulting mixture was quenched by 2 mL aqueous sodium *p*-methylbenzene sulfonate (0.1 mmol) and transferred to 50 mL round bottom flask. After concentrating *in vacuo* carefully, 1.5 mL D_2O and 5 mL CH_2Cl_2 were added to make the mixture dissolved sufficiently. The aqueous phase was analyzed by crude ^{1}H-NMR with sodium *p*-methylbenzene sulfonate as internal standard. The 8% (in CO_2) or < 1% (in N_2) yield of lithium formate was observed based on thiophenol **2a**. We also performed same reaction at CO_2 atmosphere with prolonging reaction time to 24 h, The 29% yield of lithium formate was observed based on thiophenol **2a**. The detection of lithium formate at CO_2 atmosphere indicated the generation of CO_2 radical anion.

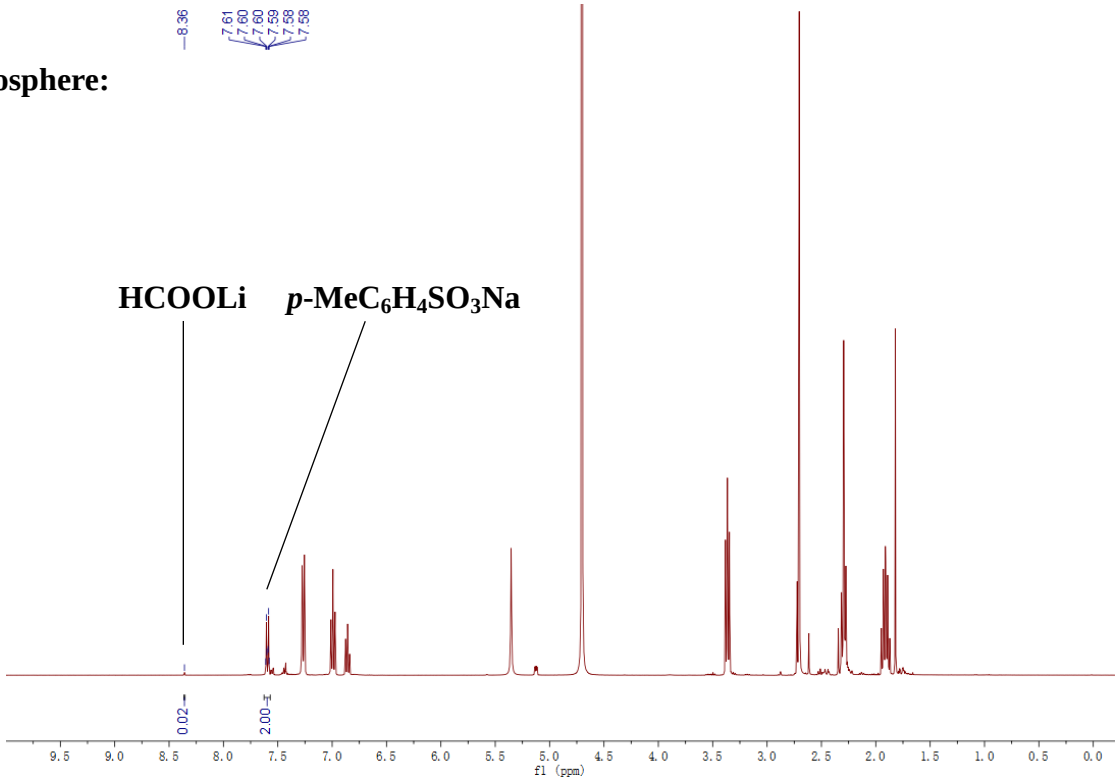
CO_2 atmosphere (3 h):



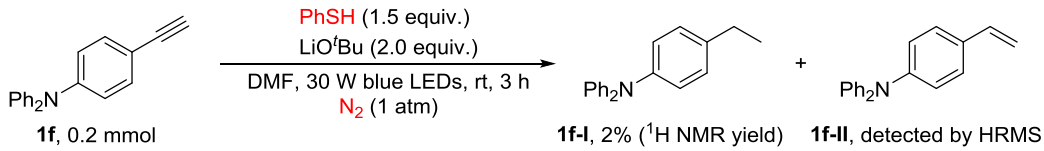
CO_2 atmosphere (24 h):



N_2 atmosphere:



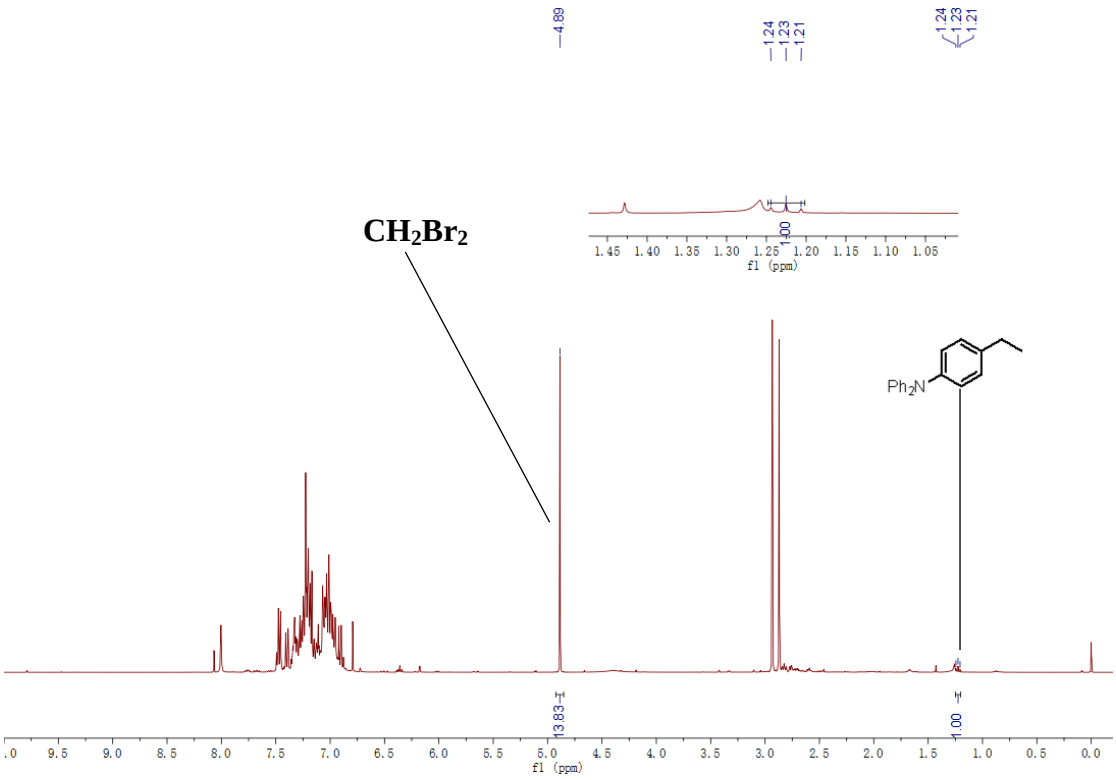
4.5 Detection of the reduction products of alkyne



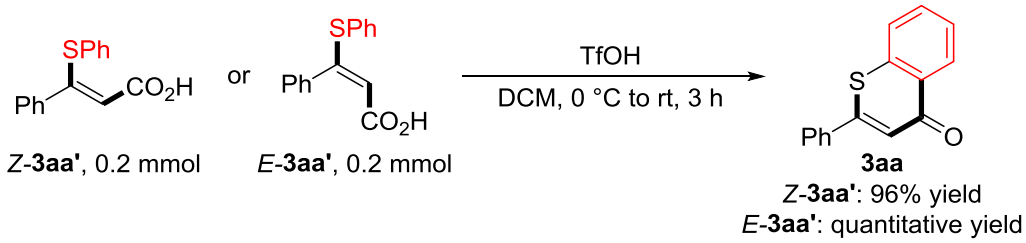
1f, 0.2 mmol **1f-I**, 2% (^{1}H NMR yield) **1f-II**, detected by HRMS

Procedure:

To an oven-dried Schlenk tube (10 mL) containing a magnetic stirring was charged with alkyne **1f** (53.9 mg, 0.2 mmol, 1.0 equiv.). Then the tube was moved into a glovebox and was charged with LiO^{t}Bu (32.0 mg, 0.4 mmol, 2.0 equiv.). The tube was sealed and then evacuated and back-filled with N_2 atmosphere for 3 times, subsequently, anhydrous DMF (2 mL) was added followed by thiophenol **2a** (33.1 mg, 0.3 mmol, 1.5 equiv.) via syringe under N_2. Once added, the Schlenk tube was sealed at atmospheric pressure of N_2 (1 atm). The reaction was stirred and irradiated with a 30 W blue LED lamp (1-2 cm away, with cooling fan to keep the reaction temperature at 22-25 ℃) for 3 hours. The resulting mixture was diluted with Et_2O (3 mL) and quenched by 2 N HCl (2 mL), then stirred for 5 min. The organic base then was subjected to HRMS analysis. The reduction products of alkyne **1f** were detected, **1f-I**: **HRMS (ESI$^+$):** calculated for $C_{20}H_{20}N^+$ $[M+H]^+$ 274.1590, found 274.1590; **1f-II**: **HRMS (ESI$^+$):** calculated for $C_{20}H_{18}N^+$ $[M+H]^+$ 272.1434, found 272.1437. The reaction mixture then was extracted by Et_2O four times and the combined organic phases were concentrated *in vacuo*. The residue was analyzed by ^{1}H NMR with CH_2Br_2 as internal standard, 2% yield of **1f-I** was afforded. The detection of reduction products of alkyne indicated the single electron reduction of alkyne was possible under the reaction conditions.



4.6 The cyclizing acylation of *Z* or *E* type of thio-carboxlation product



Z-**3aa'**, 0.2 mmol *E*-**3aa'**, 0.2 mmol

3aa

Z-**3aa'**: 96% yield

E-**3aa'**: quantitative yield

Procedure:

To an oven-dried Schlenk tube (10 mL) containing a magnetic stirring was charged with *Z*-or *E*-**3aa'** (51.3 mg, 0.2 mmol, 1.0 equiv.). Then the tube was sealed and then evacuated and back-filled with N_2 atmosphere for 3 times, subsequently, anhydrous DCM (1 mL) was added followed by TfOH (300.2 mg, 2.0 mmol, 10.0 equiv.) via syringe under N_2 at 0 ℃. Once added, the Schlenk tube was sealed at atmospheric pressure of N_2 (1 atm). The reaction was moved to room temperature and stirred for 3 hours. After the reaction was completed, reaction mixture was diluted with 3 mL DCM and quenched by saturated $NaHCO_3$ aqueous solution (pH was justified to >7) at 0 ℃, then stirred for 3 min. The reaction mixture was extracted by DCM with five times and the combined organic phases were concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc= 10:1) to give the pure desired product. Both *Z*-

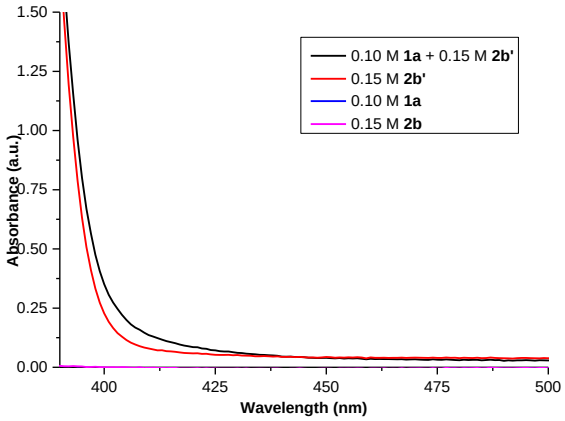
and *E*-**3aa'** could be converted to the same desired cyclizing product **3aa**, which further explained the high efficiency of the transformation.

4.7 UV-vis spectroscopic measurements

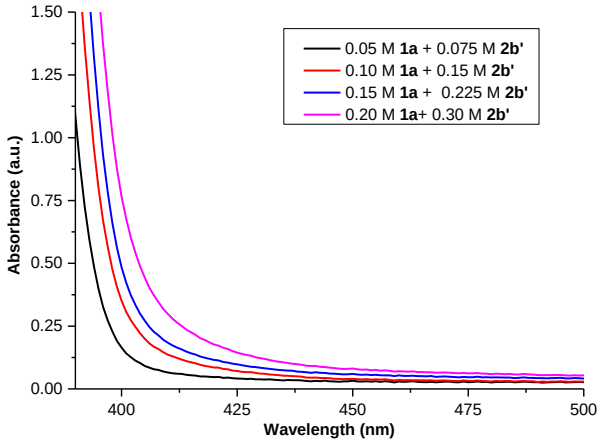
The UV-vis spectroscopy analysis concentration of Supplementary Figure 1A: **1a** (0.10 M), **2b** (0.15 M), **2b'** (0.15 M) in anhydrous DMF solution (with N_2 bubbling 30 min). The concentrations of Supplementary Figure 1B: (1) **1a** (0.05 M), **2b'** (0.075 M) in anhydrous DMF solution (with N_2 bubbling 30 min); (2) **1a** (0.10 M), **2b** (0.15 M) in anhydrous DMF solution (with N_2 bubbling 30 min); (3) **1a** (0.15 M), **2b'** (0.0.225 M) in anhydrous DMF solution (with N_2 bubbling 30 min); (4) **1a** (0.20 M), **2b'** (0.30 M) in anhydrous DMF solution (with N_2 bubbling 30 min). All solutions of different combinations were prepared under N_2 atmosphere in the glovebox. The concentrations of Supplementary Figure 1D: (1) **2b'** (0.15 M) in anhydrous DMF solution (with N_2 bubbling 30 min); (2) **2b'** (0.15 M) in anhydrous DMF solution with N_2 bubbling 30 min, then CO_2 bubbling 30 min.

The single component **1a** and **2b** had no absorption of the visible light. Compared to thiolate **2b'**, the bathochromic-shift was observed with the mixture of **1a** and thiolate **2b'** in reaction concentration. We also found red-shift became more obvious as the concentration of mixture of **1a** and **2b'** increased, and the correlation between absorbance and concentration at same wavelength (400 nm) is quadratic function, which might support the formation of CTC (charge-transfer complex) between alkyne and thiolate. We also explored the possibility of the formation of CTC between CO_2 and thiolate (Supplementary Figure 1C). The thiolate **2b'** (0.10 M) in anhydrous DMF solution was bubbling with CO_2 for 1 min, then the solution was subjected to conduct the UV-vis test and no red shift was observed

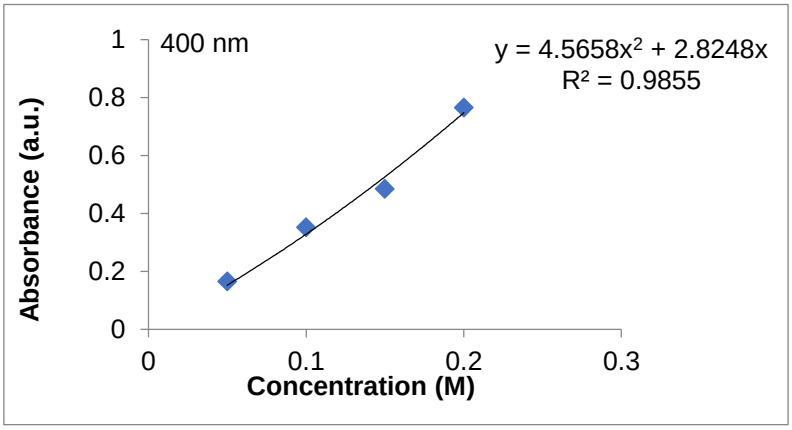
(A)


0.10 M 1a + 0.15 M 2b'
0.15 M 2b'
0.10 M 1a
0.15 M 2b
Absorbance (a.u.)
Wavelength (nm)
1.50
1.25
1.00
0.75
0.50
0.25
0.00
400
425
450
475
500

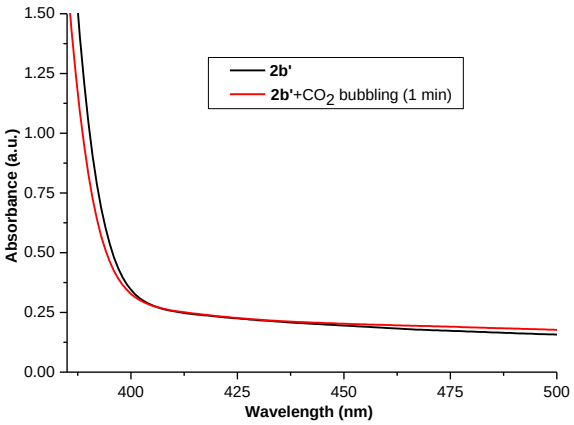
(B)


0.05 M 1a + 0.075 M 2b'
0.10 M 1a + 0.15 M 2b'
0.15 M 1a + 0.225 M 2b'
0.20 M 1a+ 0.30 M 2b'
Absorbance (a.u.)
Wavelength (nm)
1.50
1.25
1.00
0.75
0.50
0.25
0.00
400
425
450
475
500

(C)


400 nm
y = 4.5658x² + 2.8248x
R² = 0.9855
Absorbance (a.u.)
Concentration (M)
1
0.8
0.6
0.4
0.2
0
0
0.1
0.2
0.3

(D)



Supplementary Figure 1.. UV-vis spectroscopic measurements (A) UV-vis absorption spectra of different components at the stadard reaction concentration (path length = 1 cm); (B) UV-vis absorption spectra of the mixture of **1a** and **2b'** at different concentrations (path length = 1 cm); (C) Plot of absorbance as a function of the mixture of **1a** and **2b'** at different concentrations at 400 nm ; (4) UV-vis absorption spectra of **2b'** (0.1 M) and **2b'** (0.1 M) with CO_2 bubbling 1 min (path length = 1 cm).

5. General computational calculation details

5.1 Complete reference for Gaussian 16

Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J.

B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

5.2 Computational methods

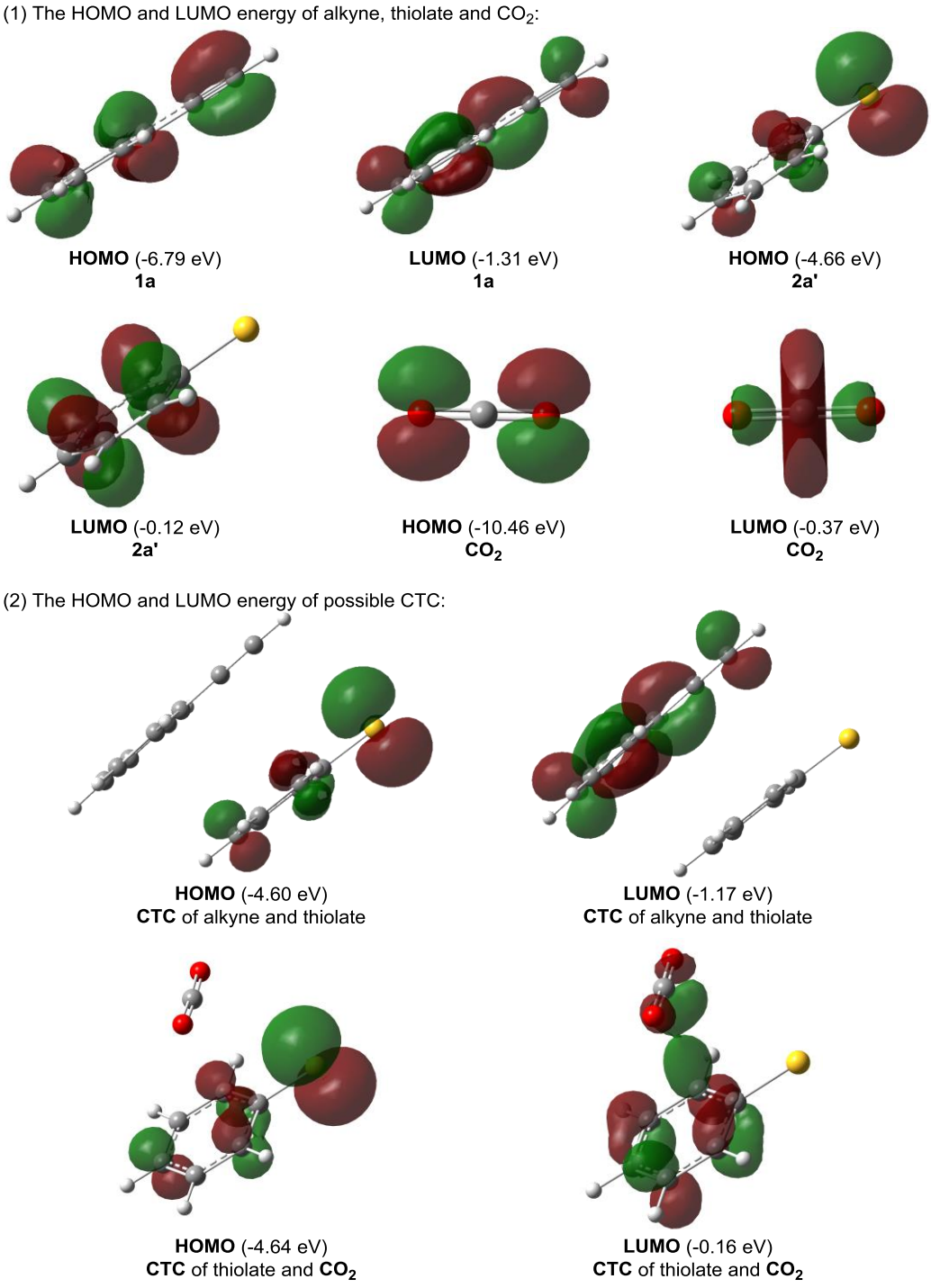
All the DFT calculations were carried out with the GAUSSIAN 16 series of programs. DFT method B3LYP-D3[1] with a standard 6–31G(*d*) basis set was used for geometry optimizations. Harmonic vibrational frequency calculations were performed for all of the stationary points to confirm them as a local minima or transition structures, and to derive the thermochemical corrections for the enthalpies and free energies. The large basis set 6–311+G(*d*,*p*) was used to calculate the single point energies to give more accurate energy information. The solvent effects were considered by an SMD[2] solvation model in *N*,*N*-dimethylformamide solvent. The singlet diradical species were calculated by first performing a single-point energy calculation on a triplet surface, and reading that wavefunction into the singlet geometry optimization as the initial guess. The molecular orbital diagram and electrostatic potential surface were conducted at B3LYP-D3/6-31G(*d*) level of theory in *N*,*N*-dimethylformamide solvent.

5.3 DFT calculations of CTC between alkynes and thiolates (or CO_2 and thiolates)

DFT calculations are preformed to illuminate the formation of CTC. The energy gap of alkyne **1a** between HOMO (-6.79 eV) and LUMO (-1.31 eV) was calculated to be 5.48 eV. The energy gap of thiolates **2a'** between HOMO (-4.66 eV) and LUMO (-0.12 eV) was calculated to be 4.54 eV, the energy gap of CO_2 between HOMO (-10.46 eV) and LUMO (-0.37 eV) was calculated to be 10.09 eV (Supplementary Figure 2-1). The high energy gap lead to the difficulty in absorbing the visible light for these three compounds. The CTC between alkyne and thiolate displayed a reduced HOMO-LUMO gap with 3.43 eV (HOMO -4.60 eV, LUMO -1.17 eV,) compared to alkyne **1a** and thiolate **2a'**. The reduced HOMO-LUMO gap might arise from the electron donation from HOMO of thiolate **2a'** to the LUMO of **1a**. The reduced HOMO–LUMO gap explained well the bathochromic shift of absorption of CTC.

Since CO_2 could act as the electrophile, the possibility of the formation of CTC between CO_2 and thiolate **2a'** was also calculated. A reduced HOMO-LUMO gap was obtained in 4.48 eV (HOMO -4.64 eV, LUMO -0.16 eV (Supplementary Figure 2-2). Therefore, the formation of CTC

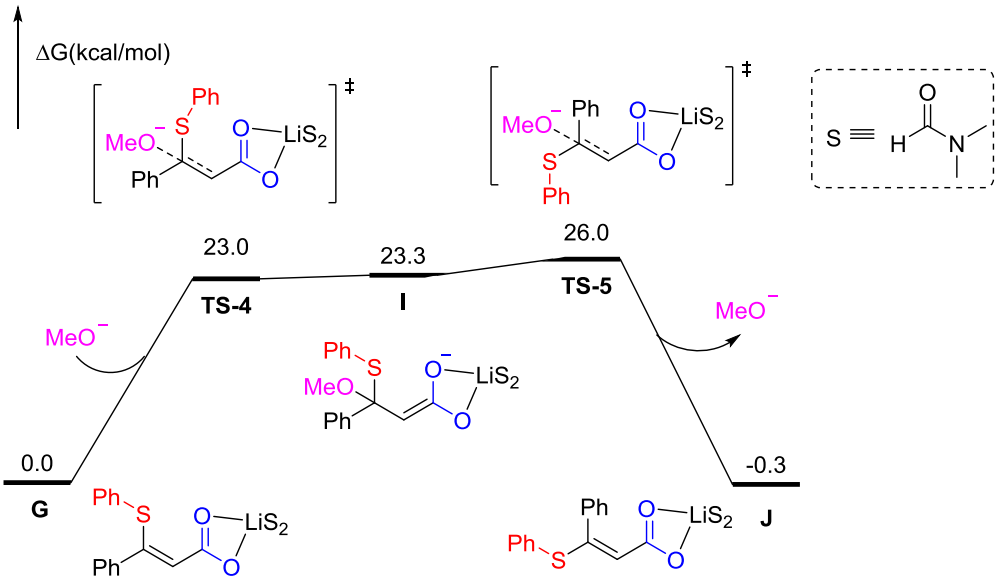
between CO_2 and thiolate is more difficult because of its higher energy gap than alkyne/thiolate in our reaction system.



Supplementary Figure 2. The energy of HOMO and LUMO of **1a**, **2a'**, CO_2 and possible CTC.

5.4 DFT calculations of the *Z*/*E* isomerization of thio-carboxylated products

We also evaluated the isomerization of generated thio-carboxylated product **G**. As shown in Supplementary Figure 3, the methylate anion was employed as the model reaction instead of tert-butoxide anion. Calculated results indicate that the overall free energy barrier of this isomerization is 26.0 kcal/mol (via **TS-5**). It suggests that the isomerization between **G** and **J** could proceed smoothly in the reaction system. Moreover, photo-induced isomerization and thiophenol radical mediated isomerization might also occur in this reaction system.



Supplementary Figure 3. DFT calculations of *Z*/*E* isomerization under reaction conditions.

5.5 Absolute calculation energies, enthalpies, and free energies

Geometry	$E_{(B3LYP\text{-}D3/6\text{–}31G(d))}$[1]	$G_{(corre)}$[2]	$H_{(corre))}$[3]	$E_{(B3LYP\text{-}D3/6\text{–}311+G(d,p))}$[4]	IF[5]
1a	-308.41145	0.079193	0.117058	-308.510289	-
2b	-630.451166	0.068928	0.10694	-630.560635	-
A*	-938.237172	0.153093	0.212118	-938.517745	-
B	-308.380781	0.073743	0.112778	-308.577640	-
C	-629.825726	0.060503	0.097467	-629.929799	-
D	-188.528781	-0.015409	0.012520	-188.723058	-
E	-693.230983	0.17005	0.241984	-693.474779	-

F	-1001.705402	0.274925	0.362454	-1002.034569	-
G	-1631.639507	0.364692	0.464809	-1632.060957	-
H	-1002.379251	0.290175	0.376509	-1002.709639	-
I	-1746.787946	0.405996	0.508074	-1747.306826	-
J	-1631.642779	0.363827	0.464804	-1632.069125	-
TS-1	-1001.653676	0.272026	0.360116	-1001.985511	358.58*i*
TS-2	-1631.548276	0.359356	0.461001	-1631.975247	77.98*i*
TS-3	-1632.174575	0.366796	0.468356	-1632.598965	416.48*i*
TS-4	-1746.772979	0.402576	0.505909	-1747.303876	92.47*i*
TS-5	-1746.777424	0.403317	0.506666	-1747.29986	266.51*i*
LiS_4^+	-1001.631931	0.354232	0.45242	-1001.999752	-
S	-248.521214	0.07404	0.110167	-248.61508	-
MeO-	-115.071478	0.012429	0.038491	-115.245648	-

[1]The electronic energy calculated by B3LYP-D3/6–31G(d) in gas phase. [2]The thermal correction to Gibbs free energy calculated by B3LYP-D3/6–31G(d) in gas phase. [3]The thermal correction to enthalpy calculated by B3LYP-D3/6–31G(d) in gas phase. [4]The electronic energy calculated by B3LYP-D3/6–311+G(d,p) in solvent. [5]The B3LYP-D3 calculated imaginary frequencies for the transition states.

5.6 Geometries for all the optimized compounds

1a

C -1.51144800 1.20869100 -0.00000900
C -0.11920000 1.21320700 0.00000400
C 0.59346800 -0.00003300 0.00006300
C -0.11923500 -1.21322900 0.00000400
C -1.51149600 -1.20865700 -0.00001000
C -2.21151100 0.00002300 -0.00000500
H -2.05201500 2.15086200 -0.00003500
H 0.43068900 2.14873800 -0.00000300
H 0.43059500 -2.14879600 -0.00000200
H -2.05208400 -2.15081600 -0.00003500
H -3.29769700 0.00004700 -0.00002600
C 2.02175600 -0.00002700 0.00001200
C 3.23152400 0.00001900 -0.00004100
H 4.29736700 0.00000000 -0.00001000

2b

S 2.29061500 -0.08359200 -0.00008400
C 0.50701000 -0.00087700 0.00010700
C -0.19420300 1.21065200 0.00001500
C -0.20098600 -1.20995700 0.00006400

C	-1.58904400	1.20818600	-0.00002300
H	0.34412900	2.15424500	-0.00006200
C	-1.59439400	-1.20149000	-0.00002000
H	0.33730200	-2.15354700	0.00008600
C	-2.29609900	0.00553800	-0.00000400
H	-2.12208800	2.15491600	-0.00016200
H	-2.13283400	-2.14505600	-0.00001800
H	-3.38183200	0.00829900	-0.00005500
H	2.51177700	1.24630600	0.00072100

A*

C	-2.32896500	0.05546200	-1.18985500
C	-1.15440400	0.74910700	-1.35332000
C	-0.62122900	1.58980900	-0.29827400
C	-1.39392200	1.63506000	0.93032300
C	-2.57427300	0.93594700	1.06079100
C	-3.07436700	0.12973900	0.01357800
H	-2.68746200	-0.57761100	-2.00092100
H	-0.58647800	0.66794100	-2.27523500
H	-1.01672600	2.24409900	1.74762300
H	-3.12713500	0.99977800	1.99834100
H	-4.00069400	-0.42625700	0.13055700
C	-0.58622700	-2.67033700	0.03543700
C	-0.47911900	-1.85546100	1.16491600
C	0.56458900	-0.94608000	1.28140400
C	1.54299600	-0.81848000	0.26592400
C	1.40131000	-1.63658800	-0.88103000
C	0.36076800	-2.55225500	-0.98796200
H	-1.41261300	-3.37035400	-0.05877100
H	-1.23466900	-1.90696200	1.94380200
H	0.63859300	-0.30274700	2.15088600
H	2.12967300	-1.53157000	-1.67963700
H	0.27483300	-3.16890900	-1.88082600
S	2.86423200	0.30265200	0.41982900
C	0.55861700	2.26895300	-0.44154700
C	1.54626200	3.03836400	-0.64445500
H	2.62276200	2.99070100	-0.52866800

B

C	1.51151500	-1.21037800	0.00248500
C	0.13206500	-1.22399700	-0.00143400
C	-0.64344000	-0.00017400	-0.00105700
C	0.13177100	1.22385200	-0.00144800
C	1.51121600	1.21058300	0.00247800
C	2.24597000	0.00018800	0.00664000
H	2.04808000	-2.16121300	0.00081500
H	-0.40660200	-2.16968800	-0.00751800
H	-0.40714900	2.16940000	-0.00749200
H	2.04755700	2.16154300	0.00083600
H	3.33326600	0.00032600	0.01109200
C	-2.02758100	-0.00033900	0.02075000
C	-3.27890900	0.00014900	-0.12458200
H	-4.11079300	0.00033200	0.57927200

C

C	2.23493600	0.00001800	-0.00000300
C	1.53699200	1.21510300	-0.00001200
C	0.14938400	1.21987900	0.00000800
C	-0.57827400	-0.00000400	0.00011400
C	0.14938600	-1.21990500	0.00000200
C	1.53698200	-1.21510000	-0.00001200
H	3.32111500	-0.00002900	-0.00003500
H	2.08278300	2.15407300	-0.00005800

H	-0.40453600	2.15269800	-0.00002000
H	-0.40452800	-2.15272600	-0.00003000
H	2.08283400	-2.15403500	-0.00002900
S	-2.30338200	0.00000500	-0.00002500

D

C	0.00000000	0.35818200	0.00000000
O	1.15132100	-0.13428900	0.00000000
O	-1.15132100	-0.13434800	0.00000000

E

C	0.14668600	1.90490000	-0.56430300
O	0.43857500	1.11276200	-1.48353800
O	-0.11495300	1.66443100	0.64138900
N	-3.71145500	-0.28234000	0.07307300
C	-5.13254400	-0.49695400	-0.14240200
H	-5.30206800	-1.49425300	-0.55589100
H	-5.68061500	-0.40926300	0.80352500
H	-5.52935000	0.24735700	-0.84294500
C	-3.31901400	1.00870100	0.62920200
H	-3.77374400	1.13585900	1.61906600
H	-2.23446400	1.07875600	0.71382600
H	-3.67497800	1.81230500	-0.02554800
C	-2.81544400	-1.23957100	-0.22400500
H	-3.28063600	-2.15305800	-0.62864000
O	-1.59362300	-1.17328200	-0.07753300
Li	0.04409100	-0.24304700	-0.03146000
N	3.62536800	-0.32610200	0.16859900
C	3.20334100	1.03263200	0.49529100
H	2.23978400	1.00912100	1.00233400
H	3.95410000	1.48946800	1.14875300
H	3.09925500	1.63002900	-0.41608400
C	5.00326600	-0.50765800	-0.25557000
H	5.69153700	-0.18557900	0.53465400
H	5.18890300	-1.56167800	-0.47700800
H	5.20770300	0.08215100	-1.15714500
C	2.75739200	-1.35102300	0.16646200
H	3.22571500	-2.31450300	-0.09242600
O	1.55463800	-1.28949200	0.43820000

F

C	4.91633100	-0.54234000	-0.17528300
C	3.79101400	-0.91559900	-0.89533200
C	2.70062800	-1.56920700	-0.25146100
C	2.81308400	-1.84531100	1.14135100
C	3.94555300	-1.46192600	1.84468800
C	5.00435700	-0.80922400	1.19739300
H	5.73498100	-0.03942700	-0.68309100
H	3.72312000	-0.71285500	-1.95949700
H	1.98300300	-2.33141400	1.64197400
H	4.00711500	-1.66529800	2.91040500
H	5.88817800	-0.51565700	1.75580400
C	1.57069400	-1.95368300	-0.96965600
C	0.32604800	-1.83788400	-1.35860000
H	-0.13049700	-2.52394900	-2.07206400
C	-0.55759400	-0.68628000	-0.90014700
O	-0.31257600	-0.12678500	0.20436900
O	-1.50034800	-0.34295600	-1.67819700
N	-4.97609000	-0.68723200	0.45816300
C	-6.20101500	-1.24308200	1.00768300
H	-6.68490300	-0.51126500	1.65938800
H	-6.89476700	-1.51110700	0.20182600
H	-5.98423600	-2.14563300	1.59199200

C	-4.20616100	-1.54694200	-0.43489200
H	-4.85476400	-1.89704600	-1.24627900
H	-3.35861700	-1.00575400	-0.85914900
H	-3.83596200	-2.41963300	0.11720100
C	-4.57090600	0.55235900	0.78883500
H	-5.27167100	1.06539700	1.46776900
O	-3.54493900	1.11755300	0.40785500
Li	-1.80513000	1.11315400	-0.34757400
N	1.39424900	2.41446100	-0.07068900
C	1.51247300	1.95075400	-1.44543800
H	0.59810300	2.20492900	-1.98014200
H	2.37223000	2.43625000	-1.92048100
H	1.65229700	0.86750700	-1.46466500
C	2.52466500	2.16352800	0.81050100
H	3.43711400	2.59088900	0.38156900
H	2.34029100	2.62754200	1.78310100
H	2.66740300	1.08761200	0.94941100
C	0.20225500	2.77532700	0.42676300
H	0.24758000	3.06521200	1.48948000
O	-0.86417200	2.81727500	-0.20309700

G

C	4.70370000	-1.85141900	-1.85507000
C	3.37240000	-1.46835800	-1.70972300
C	2.75568900	-1.46791400	-0.44655900
C	3.52272700	-1.83684500	0.66969200
C	4.85401100	-2.22073700	0.52374900
C	5.45040100	-2.23236300	-0.73852400
H	5.16295800	-1.83716600	-2.83965900
H	2.80488300	-1.14020600	-2.57493300
H	3.06382700	-1.82232500	1.65230900
H	5.42804100	-2.51115700	1.39946500
H	6.49088200	-2.52430300	-0.84981500
C	1.33351200	-1.06675200	-0.32649800
C	0.41873000	-1.36612100	-1.26937200
H	0.71002400	-2.04032000	-2.07257400
C	-0.99880800	-0.87679700	-1.34647700
O	-1.89856600	-1.71715300	-1.63809000
O	-1.23438400	0.35098500	-1.13613000
S	0.85200700	-0.20643300	1.18217100
C	1.62729900	1.38517400	0.90964200
C	1.33374800	2.11286500	-0.25168700
C	2.49118600	1.91228300	1.87391500
C	1.92547800	3.36128200	-0.44462000
H	0.63323400	1.69418300	-0.96802300
C	3.05948000	3.17322300	1.68121600
H	2.72322800	1.33316400	2.76243100
C	2.78395100	3.89675400	0.52035200
H	1.70995700	3.92171300	-1.35086600
H	3.73096600	3.58103000	2.43182000
H	3.23839100	4.87135200	0.36560400
N	-2.70314200	2.96481900	-0.19446500
C	-1.89919000	4.17476900	-0.14116900
H	-2.02050100	4.73989900	-1.06905200
H	-2.21361200	4.80463000	0.69958300
H	-0.84022400	3.92244700	-0.01620300
C	-2.62376700	2.07314400	0.95786800
H	-3.43837900	1.34982600	0.90947700
H	-1.66953100	1.53811100	0.95568700
H	-2.72015000	2.66895200	1.87181500
C	-3.34994300	2.60589000	-1.31529100

H	-3.31846500	3.38066000	-2.09858000
O	-3.95625000	1.54331200	-1.49829400
Li	-3.15085600	-0.17870000	-1.16109600
N	-3.21555300	-2.94125800	1.08521300
C	-2.00213800	-2.27333900	1.53343100
H	-2.11925800	-1.19920300	1.40927200
H	-1.82075900	-2.50657300	2.58861900
H	-1.14903900	-2.60495400	0.93444600
C	-3.25128400	-4.38863200	1.19976200
H	-3.12796600	-4.69102100	2.24619200
H	-4.20945900	-4.76618700	0.83412700
H	-2.44591300	-4.83719200	0.60606400
C	-4.18311100	-2.26899000	0.44316700
H	-5.02355200	-2.91096900	0.13316100
O	-4.19488800	-1.05251800	0.21828000

H

C	-5.65987900	-0.27192300	-0.73570900
C	-4.29510400	-0.10404300	-0.94410900
C	-3.35478900	-0.80365700	-0.16429000
C	-3.83688100	-1.67320100	0.82944600
C	-5.20410800	-1.84262900	1.03947500
C	-6.12232100	-1.14173800	0.25716200
H	-6.36892200	0.27664500	-1.34969600
H	-3.95151200	0.57403000	-1.71910600
H	-3.12268900	-2.22117100	1.43915200
H	-5.55207900	-2.52181100	1.81287600
H	-7.18903700	-1.27041000	0.41702200
C	-1.90708700	-0.65942200	-0.33630200
C	-1.25853300	0.10847900	-1.22783600
H	-1.77742400	0.72286600	-1.95861500
C	0.23239700	0.20791300	-1.25755100
O	0.74444200	1.05217500	-2.05604200
O	0.92890900	-0.49673900	-0.45747500
N	4.28220400	-1.74203700	0.33787600
C	4.66757300	-3.08784300	0.72663400
H	5.20709100	-3.56938100	-0.09282900
H	5.31770800	-3.05985100	1.60873300
H	3.78189000	-3.68981600	0.96353300
C	3.53514400	-0.94439700	1.30874200
H	3.66774700	0.11565900	1.08698900
H	2.46683600	-1.17361900	1.25772800
H	3.92514500	-1.15882200	2.30830400
C	4.47280100	-1.29747000	-0.91570800
H	5.05595000	-1.99059700	-1.54263800
O	4.07672100	-0.21759400	-1.36624900
Li	2.42189800	0.68335300	-1.09868100
N	0.42376400	2.53112500	1.04411400
C	0.58272300	1.47449700	2.03760400
H	1.64426900	1.36783600	2.26104400
H	0.03844300	1.75402700	2.94481000
H	0.21021100	0.52448100	1.64467500
C	-0.90600900	3.09394900	0.87104300
H	-1.24171400	3.57438900	1.79734200
H	-0.88634800	3.83791700	0.07105800
H	-1.61586100	2.30536700	0.59731800
C	1.41521900	2.79899100	0.17778900
H	1.16952700	3.59495900	-0.54038900
O	2.51625700	2.22873200	0.16443300
H	-1.28421800	-1.24400100	0.33914500

I

C	4.25365800	0.23826500	1.93080400
C	3.05533000	-0.34426800	1.51706100
C	1.92326600	0.43857500	1.25620200
C	2.02896900	1.82622600	1.42408900
C	3.22407600	2.41213900	1.83823600
C	4.34642500	1.62023900	2.09399700
H	5.12033500	-0.39261400	2.11543300
H	2.99056900	-1.41354800	1.36407000
H	1.15624300	2.43529300	1.21699500
H	3.28074600	3.49222600	1.95765900
H	5.28167600	2.07651300	2.41107500
C	0.63133400	-0.17028300	0.72855100
C	-0.56100600	0.46369200	1.26898100
H	-0.46146700	0.93002700	2.24431400
C	-1.87367700	0.31046400	0.75692800
O	-2.91424200	0.67248100	1.46469100
O	-2.08670800	-0.14139100	-0.44959700
S	0.69980100	-0.03470400	-1.21371900
C	2.41621700	-0.41707100	-1.52232300
C	2.87665600	-1.74318100	-1.47232100
C	3.33473600	0.59999500	-1.82276500
C	4.21874300	-2.03924100	-1.70458200
H	2.16986200	-2.52432400	-1.21437600
C	4.67633000	0.30300100	-2.06208100
H	2.98821500	1.62863200	-1.83510900
C	5.12545800	-1.01770000	-2.00178500
H	4.56112000	-3.07085900	-1.65210700
H	5.37641900	1.10650600	-2.28062000
H	6.17311300	-1.24909400	-2.18011700
N	-3.13853100	-2.88862100	0.06058000
C	-1.81486400	-3.30980600	-0.38824700
H	-1.81493800	-3.38086300	-1.47933700
H	-1.05278000	-2.58070000	-0.09496600
H	-1.58311100	-4.29723600	0.02932600
C	-3.34167400	-2.72367200	1.49849200
H	-2.77130800	-3.49690800	2.02048800
H	-3.01957300	-1.72839600	1.82474400
H	-4.40474400	-2.83488800	1.72481700
C	-3.90598600	-2.16042100	-0.76534000
H	-3.61503400	-2.24638300	-1.82386500
O	-4.88574300	-1.48061900	-0.41572000
Li	-3.97819700	0.27065300	-0.05732600
N	-2.52400300	3.07583300	-0.85875300
C	-3.07406300	3.58530500	0.39617400
H	-4.14965900	3.72616100	0.27397400
H	-2.90145700	2.85618700	1.19666200
H	-2.59791200	4.54559800	0.62117000
C	-1.07857700	3.15590400	-1.02513800
H	-0.58576500	2.58744200	-0.22741300
H	-0.79072800	2.70029700	-1.97425600
H	-0.75819300	4.20534900	-1.01001400
C	-3.22664400	2.17088600	-1.56050500
H	-2.68537300	1.77893000	-2.43342700
O	-4.38693800	1.81162000	-1.29671200
O	0.72436200	-1.65233200	0.87686400
C	0.41051500	-2.09915700	2.18003600
H	0.37556700	-3.19401700	2.13394800
H	1.17392000	-1.80018100	2.91710500
H	-0.55742500	-1.70374600	2.50952400

J

C	-1.16515200	2.00379800	1.44707800
C	-0.89112400	0.78689600	0.82470400
C	-1.58434600	0.40642400	-0.33752100
C	-2.56566500	1.27241400	-0.84653000
C	-2.83695500	2.48830000	-0.22299700
C	-2.14119200	2.85835600	0.93141400
H	-0.62493400	2.27273800	2.35083100
H	-0.14645200	0.11877500	1.24247300
H	-3.12073200	0.97938300	-1.73120800
H	-3.60325700	3.14196200	-0.63088300
H	-2.37310400	3.79381100	1.43396000
C	-1.31632900	-0.91065900	-0.96763100
C	-0.10328000	-1.48111300	-1.07803900
H	-0.02896500	-2.48967300	-1.47727200
C	1.20317400	-0.82660700	-0.70689400
O	1.71708700	-1.12833900	0.41216600
O	1.72402900	-0.01536400	-1.52393600
S	-2.70734100	-1.78711700	-1.68861600
C	-3.87502000	-1.79948200	-0.33395900
C	-3.45793900	-1.93061300	0.99611800
C	-5.23976600	-1.70191400	-0.62828800
C	-4.40273300	-1.94961000	2.02041700
H	-2.39997500	-2.01076800	1.22289200
C	-6.18033900	-1.74534200	0.40105300
H	-5.56032100	-1.58335200	-1.65939900
C	-5.76583000	-1.86217600	1.72861400
H	-4.07115300	-2.04161000	3.05112300
H	-7.23824200	-1.67094300	0.16416500
H	-6.49866300	-1.88231500	2.53010800
N	1.18392100	3.77371800	-0.16817000
C	0.57175600	5.07612800	0.02811200
H	0.92656800	5.52087700	0.96148900
H	0.82725600	5.74648900	-0.80122900
H	-0.51767800	4.97149200	0.07437300
C	0.79366400	3.04742300	-1.37294300
H	1.19592100	2.03506100	-1.36052800
H	-0.29787900	2.99236700	-1.41648200
H	1.16266400	3.57922500	-2.25854500
C	2.02384000	3.26243000	0.74362600
H	2.18457000	3.93337000	1.60325400
O	2.59705100	2.17036000	0.69283300
Li	2.92006100	0.45674400	-0.01286200
N	5.89210700	-2.22466500	0.35067900
C	7.19200700	-1.58593600	0.21666600
H	7.03615600	-0.51725800	0.07234600
H	7.79204400	-1.75272700	1.11939500
H	7.73109400	-1.99947300	-0.64414600
C	5.86448800	-3.66265700	0.54952100
H	6.40031900	-3.93619700	1.46690900
H	4.82914000	-4.00124400	0.63348200
H	6.33716100	-4.17869000	-0.29533000
C	4.75408200	-1.50380700	0.28973000
H	3.82914400	-2.08742600	0.40104400
O	4.71062500	-0.27754700	0.12300500

TS-1

C	-1.58361000	3.16731400	1.80410500
C	-1.21820400	2.51271400	2.97970000
C	-0.46138900	1.32664600	2.93065700
C	-0.08450200	0.80587900	1.67445500
C	-0.45276900	1.46927700	0.50676900

C	-1.19977400	2.65041900	0.56459600
H	-2.17004100	4.08062700	1.85570200
H	-1.51481600	2.90838100	3.94637100
H	0.49871400	-0.10959600	1.65019200
H	-0.15862800	1.05976900	-0.45636700
H	-1.48707500	3.16049700	-0.35079800
C	-0.05643700	0.65633700	4.12647600
C	0.52774500	-0.09802900	4.90350800
H	0.76364300	-0.53395100	5.85020600
C	2.21366200	-1.28400500	3.78799000
O	1.92067700	-1.61297900	2.62008800
O	3.33554400	-1.09632700	4.30619300
N	4.38717500	-4.70896600	2.29166100
C	4.33698200	-6.10646100	1.89528200
H	4.86941500	-6.24497400	0.95098200
H	4.80410100	-6.73723200	2.66049500
H	3.29780700	-6.43091100	1.76339400
C	3.71063500	-4.34225400	3.53291400
H	3.94791100	-5.08955200	4.29693100
H	4.04691800	-3.36042900	3.86442000
H	2.62669900	-4.30320700	3.38339700
C	4.95266900	-3.78331600	1.49995000
H	5.43357000	-4.21149100	0.60590300
O	4.98178700	-2.56614400	1.70586000
Li	3.87555600	-1.16216900	2.31926600
N	2.92776200	2.41957300	2.26792100
C	3.21055200	2.20418000	3.68274800
H	3.67572900	1.23028400	3.82257400
H	3.87265200	2.99639600	4.05310500
H	2.27308600	2.21889100	4.24543700
C	2.16209700	3.60714800	1.92372200
H	2.71325500	4.51073200	2.21184400
H	1.97504400	3.62944900	0.84837100
H	1.19833600	3.59268900	2.43970900
C	3.32475600	1.55560300	1.32471100
H	3.01748400	1.85249200	0.30997100
O	3.98291400	0.52399400	1.50726600

TS-2

C	-4.52615400	-0.83253200	1.98447400
C	-3.20362000	-1.21389100	2.09939900
C	-2.49880700	-1.73879600	0.96654500
C	-3.20079200	-1.85434400	-0.27295900
C	-4.52967800	-1.48454700	-0.35673000
C	-5.19640200	-0.95678200	0.75734100
H	-5.04536100	-0.42384300	2.84659400
H	-2.66842800	-1.11053300	3.03707300
H	-2.66434500	-2.21291700	-1.14303600
H	-5.04667900	-1.56464800	-1.30732300
H	-6.23214500	-0.64323000	0.67034500
C	-1.17332300	-2.05008000	1.11838400
C	0.03171800	-2.33272600	1.51398200
H	0.29553400	-3.32925300	1.87392300
C	1.16608500	-1.31001200	1.52156400
O	2.34306700	-1.76432600	1.50886100
O	0.86838200	-0.08491000	1.55755700
S	-0.34195100	-0.34435800	-1.70452500
C	-1.77089700	0.58148500	-1.39352100
C	-1.97465500	1.19959700	-0.13088200
C	-2.79448100	0.70404800	-2.36757400
C	-3.14832200	1.89081800	0.13605000

H	-1.21097500	1.07146900	0.62990200
C	-3.95281800	1.42171800	-2.09939200
H	-2.65050100	0.22482300	-3.33099500
C	-4.14405600	2.00663400	-0.84181100
H	-3.30040400	2.33041500	1.11804100
H	-4.72239100	1.51119200	-2.86195400
H	-5.05979800	2.55012000	-0.62650900
N	2.20465100	3.46944900	0.35428700
C	2.12421700	4.83784700	-0.12618300
H	2.68769400	5.49906200	0.53744100
H	2.54182800	4.91923800	-1.13754200
H	1.08088800	5.17258300	-0.15449300
C	1.51547300	2.43557000	-0.42029300
H	2.16801600	2.02883800	-1.20067700
H	1.19119700	1.62352900	0.23007400
H	0.62983400	2.87284800	-0.88664300
C	2.97980000	3.14775500	1.40492100
H	3.43669700	4.02359200	1.89377200
O	3.19121300	2.00985200	1.83279800
Li	2.81345500	0.22288900	1.24463900
N	4.06236900	-2.09593500	-1.15741700
C	2.69342600	-1.98635100	-1.64278700
H	2.38172200	-0.94551800	-1.58886200
H	2.64424300	-2.33579300	-2.67940200
H	2.02203800	-2.58152000	-1.01736100
C	4.70463400	-3.39284700	-1.27117400
H	4.74938400	-3.70461700	-2.32106600
H	5.72198300	-3.33971600	-0.87495300
H	4.14487300	-4.14587300	-0.70341600
C	4.62546300	-1.10040600	-0.45743200
H	5.65049500	-1.33122100	-0.12274800
O	4.10427100	-0.00630300	-0.20563200

TS-3

C	5.40347200	1.28332200	1.11758500
C	4.02524400	1.11832100	1.19577300
C	3.43223200	-0.11793400	0.85332600
C	4.26791300	-1.16782000	0.40443300
C	5.64529700	-0.99330600	0.33267400
C	6.21872100	0.23187100	0.68706200
H	5.84614700	2.23712400	1.38963500
H	3.38939400	1.93645900	1.51601100
H	3.81553100	-2.11609700	0.13240000
H	6.27573900	-1.81272500	-0.00128400
H	7.29436000	0.36793100	0.62315600
C	2.01578700	-0.30152500	0.90020600
C	1.12461100	-1.14685900	1.38374200
H	1.43830100	-1.91495300	2.09732300
C	-0.33228500	-1.22018100	0.96452600
O	-0.90343900	-2.31424600	1.15770700
O	-0.82031400	-0.17210900	0.43245900
N	0.17862700	-2.22011300	-2.12307700
C	1.46697600	-2.80225100	-1.78849000
H	2.25263400	-2.05247100	-1.90723200
H	1.45985500	-3.13944500	-0.74620200
H	1.68190000	-3.65646900	-2.44150100
C	-0.99813400	-3.06796600	-1.94935400
H	-1.16165900	-3.24981200	-0.88216500
H	-1.86221700	-2.55175900	-2.36761900
H	-0.83856600	-4.01418100	-2.47794000
C	0.05287600	-0.91681100	-2.41365900

H	1.00866900	-0.37916300	-2.49369400
O	-1.02853400	-0.32977000	-2.58010300
Li	-2.00395500	0.09162800	-0.95770500
N	-3.82174200	-1.22557500	1.59246900
C	-3.63961800	0.16836300	1.97835700
H	-2.57450900	0.39843500	2.08152300
H	-4.05489800	0.80992000	1.20097400
H	-4.16232600	0.34659000	2.92273400
C	-3.64442600	-2.23328100	2.62773500
H	-4.32987500	-2.03650800	3.45862600
H	-3.85987100	-3.22141800	2.21461800
H	-2.60719800	-2.23128000	2.97661700
C	-3.76836800	-1.56934300	0.30000900
H	-3.85375500	-2.65161900	0.12825500
O	-3.67450400	-0.77578600	-0.65272400
S	1.34824000	2.19672500	-0.78670100
C	-0.36382800	2.62585800	-0.54551600
C	-1.23578400	2.65788100	-1.64459300
C	-0.85309700	2.94409000	0.72975800
C	-2.58489800	2.97861900	-1.46127700
H	-0.86442400	2.39194700	-2.62738900
C	-2.19809300	3.26034500	0.90720100
H	-0.17754800	2.92103200	1.57811500
C	-3.07074400	3.27513300	-0.18500900
H	-3.25415600	2.98933100	-2.31709800
H	-2.56830800	3.49407100	1.90178200
H	-4.11956400	3.52032900	-0.04463200
H	1.39936600	1.00820400	0.03391900

TS-4

C	-3.76649400	0.26217100	-3.05663700
C	-2.57631000	-0.17960800	-2.47734700
C	-2.14320400	0.34804100	-1.25450900
C	-2.93604800	1.31944300	-0.62407400
C	-4.12815800	1.75451600	-1.20007200
C	-4.54965300	1.22929600	-2.42385600
H	-4.09013200	-0.16207500	-4.00520800
H	-1.97017900	-0.96585000	-2.90963800
H	-2.61250000	1.72562300	0.32929300
H	-4.73009400	2.50423400	-0.69073200
H	-5.48174300	1.56510000	-2.87359900
C	-0.80908900	-0.02448500	-0.68007100
C	0.29233100	0.58200700	-1.26104200
H	0.17116700	0.94370400	-2.27757600
C	1.59848200	0.78087500	-0.66901800
O	2.52452800	1.36888000	-1.34278500
O	1.82193600	0.43314300	0.55617100
S	-0.75425400	-0.35607000	1.10349000
C	-2.38757300	-1.01523100	1.43376000
C	-2.95837800	-2.04983900	0.67568700
C	-3.06796600	-0.52390100	2.55627400
C	-4.20403900	-2.55856200	1.03951600
H	-2.39471000	-2.41084500	-0.18616900
C	-4.30453300	-1.05712000	2.92480200
H	-2.62802000	0.28634200	3.13258500
C	-4.88206400	-2.07308100	2.16225700
H	-4.64923300	-3.35172200	0.44192100
H	-4.82289500	-0.66518200	3.79771100
H	-5.85202000	-2.48121800	2.43856700
N	4.59204400	-2.55294100	-0.07623400
C	3.69828600	-3.67743700	-0.28994300

H	2.66691900	-3.37079500	-0.10161300
H	3.76860700	-4.03501200	-1.32535800
H	3.95566900	-4.50676200	0.38246100
C	6.00926000	-2.75660700	-0.30417900
H	6.52258600	-1.81205100	-0.12278500
H	6.40119000	-3.52731400	0.37277000
H	6.18977000	-3.07946800	-1.33811200
C	4.10506800	-1.33343000	0.24512500
H	3.01342800	-1.27557800	0.36222000
O	4.80882900	-0.32184100	0.39899500
Li	3.58727800	1.24002400	0.28265100
N	1.35539000	3.59726400	0.76554800
C	1.00202300	2.99066000	2.04359900
H	1.92333000	2.75958700	2.57659100
H	0.39832200	3.70101500	2.62368000
H	0.44544600	2.06392700	1.88120700
C	0.25578000	3.91553400	-0.13262100
H	-0.43562900	4.61609300	0.35205900
H	0.64957100	4.37399400	-1.04337700
H	-0.27732400	2.99874900	-0.41063200
C	2.62072800	3.57777700	0.31657400
H	2.73276100	4.02844400	-0.67953600
O	3.59917700	3.12772500	0.93880700
O	-0.88612200	-2.01638600	-1.36792300
C	0.37644400	-2.51005100	-1.30109300
H	0.59296400	-3.25968100	-2.09901400
H	1.15283600	-1.71473900	-1.43007400
H	0.61795300	-3.01972000	-0.33155200

TS-5

C	0.47701200	-0.84669000	2.96139700
C	0.54161000	-0.43904900	1.62945800
C	0.67319600	-1.37264400	0.59273400
C	0.76248100	-2.73170200	0.93335900
C	0.69569100	-3.14119700	2.26501700
C	0.55030200	-2.20173900	3.28872200
H	0.36593500	-0.10120400	3.74623100
H	0.46472900	0.60756200	1.37493100
H	0.86595900	-3.44943400	0.13087900
H	0.75779100	-4.20110600	2.50378300
H	0.49996400	-2.52098700	4.32767100
C	0.82881100	-0.90491400	-0.82944400
C	0.21832500	0.25864200	-1.32771500
H	0.61412900	0.66289700	-2.25347800
C	-1.12056400	0.71459900	-0.99736700
O	-1.72747400	0.35549300	0.08321400
O	-1.72306900	1.52413500	-1.81085100
S	2.55364300	-1.22055200	-1.42195400
C	3.56977200	0.00179000	-0.61390200
C	3.09105300	1.22141600	-0.11270800
C	4.94263600	-0.27904600	-0.49567600
C	3.96017900	2.12553800	0.49565000
H	2.03535300	1.43898500	-0.22709800
C	5.80929100	0.63741200	0.09609500
H	5.32379900	-1.22841600	-0.86407400
C	5.32421000	1.84605500	0.60318300
H	3.56588600	3.06405300	0.88120800
H	6.86809800	0.39924000	0.17518700
H	5.99893600	2.55603800	1.07529100
N	-3.51304200	-1.96957700	0.15626600
C	-2.90803100	-2.61205300	1.31250100

H	-3.45621700	-2.33448900	2.21777000
H	-2.94343300	-3.70148600	1.19665200
H	-1.86666400	-2.29444400	1.40875900
C	-2.91443800	-2.28318300	-1.13793600
H	-3.22112500	-1.52527300	-1.85710200
H	-1.82139600	-2.29287400	-1.05970200
H	-3.26307900	-3.26974600	-1.47178700
C	-4.28356000	-0.88935600	0.31518300
H	-4.57749700	-0.72199700	1.36589700
O	-4.67324800	-0.12225600	-0.58293500
Li	-3.27000500	1.26952100	-0.70068400
N	-1.44147100	3.67464300	0.52468100
C	-1.65008700	4.36499200	-0.74493300
H	-2.70773200	4.61743500	-0.82911200
H	-1.04595000	5.27923300	-0.75441000
H	-1.37781500	3.69558000	-1.56784400
C	-0.06165600	3.42895000	0.90792100
H	0.47552000	4.37813900	1.02230700
H	-0.03358300	2.88777300	1.85687900
H	0.43460200	2.81685200	0.14638700
C	-2.42818900	2.91706200	1.04154500
H	-2.12994000	2.37581400	1.95122500
O	-3.57752700	2.83846800	0.58295000
O	0.28474200	-2.44883100	-1.69509500
C	-0.10481500	-2.18301800	-2.99801500
H	-0.45154100	-1.13826800	-3.11596500
H	0.70328900	-2.34752000	-3.73822800
H	-0.95147900	-2.83481800	-3.28425100

LiS4+

N	-3.05197200	1.68204400	1.72646900
C	-4.18627000	2.23648200	2.45541200
H	-3.96736100	2.24427200	3.52557800
H	-4.38473100	3.26320500	2.13025200
H	-5.08383200	1.63212500	2.28532400
C	-3.13361600	1.57515900	0.26743300
H	-2.28475500	2.08318900	-0.19822100
H	-3.11755500	0.52628900	-0.04375600
H	-4.06340400	2.03956300	-0.06395400
C	-1.95490500	1.25124300	2.35739300
H	-1.98804500	1.37222900	3.45012500
O	-0.96266100	0.75184600	1.80472300
Li	-0.24277100	0.30850300	0.07356500
N	1.84888100	2.48226400	-2.26641600
C	2.71633200	1.38687600	-1.85109300
H	2.22328000	0.79338000	-1.08239100
H	2.95042000	0.74931500	-2.71175000
H	3.65348000	1.79287600	-1.45372800
C	2.39251400	3.42225200	-3.23816400
H	2.66050500	2.90004600	-4.16341300
H	1.65054700	4.18973600	-3.46922000
H	3.28947800	3.90683100	-2.83695600
C	0.60153200	2.61525600	-1.79201200
H	0.07324000	3.49083600	-2.19776700
O	0.04566800	1.86780500	-0.97821600
O	1.40753800	-0.62891600	0.57791400
C	1.77688100	-0.63873700	1.76578300
N	2.92746600	-1.16821400	2.20476500
H	1.14811900	-0.19370000	2.54868600
C	3.28826700	-1.13971900	3.61595700
C	3.86993900	-1.79546600	1.28671300

H	2.50120600	-0.64341600	4.18787500
H	3.41501000	-2.15902300	3.99730300
H	4.22746000	-0.59363100	3.75773900
H	4.03278900	-2.84056500	1.57235400
H	3.45838900	-1.74964700	0.27927400
H	4.83105200	-1.27032400	1.31746400
O	-1.26486300	-1.02015400	-0.88258500
C	-0.89316500	-2.19401300	-1.03363800
N	-1.58481700	-3.14145500	-1.68415500
H	0.06880100	-2.53827500	-0.62624100
C	-1.08217400	-4.50207900	-1.80919500
C	-2.87707300	-2.84756400	-2.29192000
H	-0.11180400	-4.58468800	-1.31418500
H	-1.77756200	-5.21006600	-1.34450500
H	-0.96488700	-4.76964900	-2.86526600
H	-3.66022200	-3.45526100	-1.82501100
H	-3.09727200	-1.79063900	-2.14881700
H	-2.84596700	-3.07577700	-3.36284000

S

N	0.34832300	-0.01975100	0.00011500
C	0.41228400	1.43012600	-0.00001600
H	-0.60966600	1.81036100	0.00004200
H	0.94071400	1.79450100	0.89044900
H	0.94054100	1.79436100	-0.89064500
C	1.59553500	-0.75378000	-0.00002600
H	2.19395200	-0.51488100	0.88937500
H	1.38920400	-1.82787100	-0.00033700
H	2.19398600	-0.51437700	-0.88926700
C	-0.86255100	-0.65092200	0.00000500
H	-0.75069700	-1.75313400	-0.00004400
O	-1.95098800	-0.10040600	-0.00002000

MeO-

O	-0.78794700	0.00003100	-0.00001200
C	0.51987400	0.00005000	-0.00000300
H	1.06115900	-0.45927000	0.92224300
H	1.06132700	-0.56954300	-0.85852200
H	1.06184900	1.02826800	-0.06360800

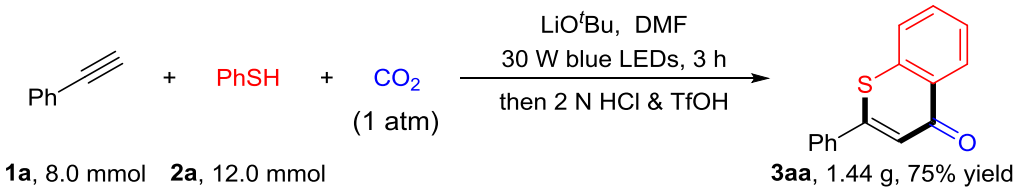
5.7 Reference

1. (a) Becke AD. *J Chem Phys*, 1993, 98: 5648–5652; (b) Grimme S, Antony J, Ehrlich S, Krieg H. *J Chem Phys*, 2010, 132: 154104

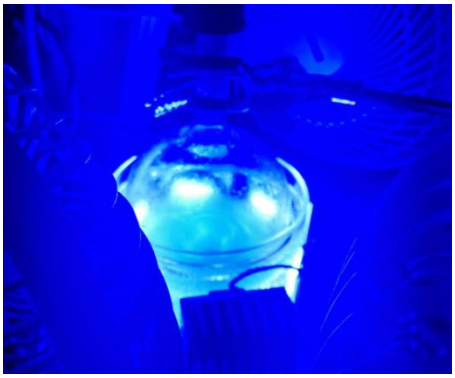
2. Marenich AV, Cramer CJ, Truhlar DG. *J Phys Chem B*, 2009, 113: 6378–6396

6. The application of the reaction

6.1 Synthesis of 3aa in gram scale



1a, 8.0 mmol **2a**, 12.0 mmol **3aa**, 1.44 g, 75% yield

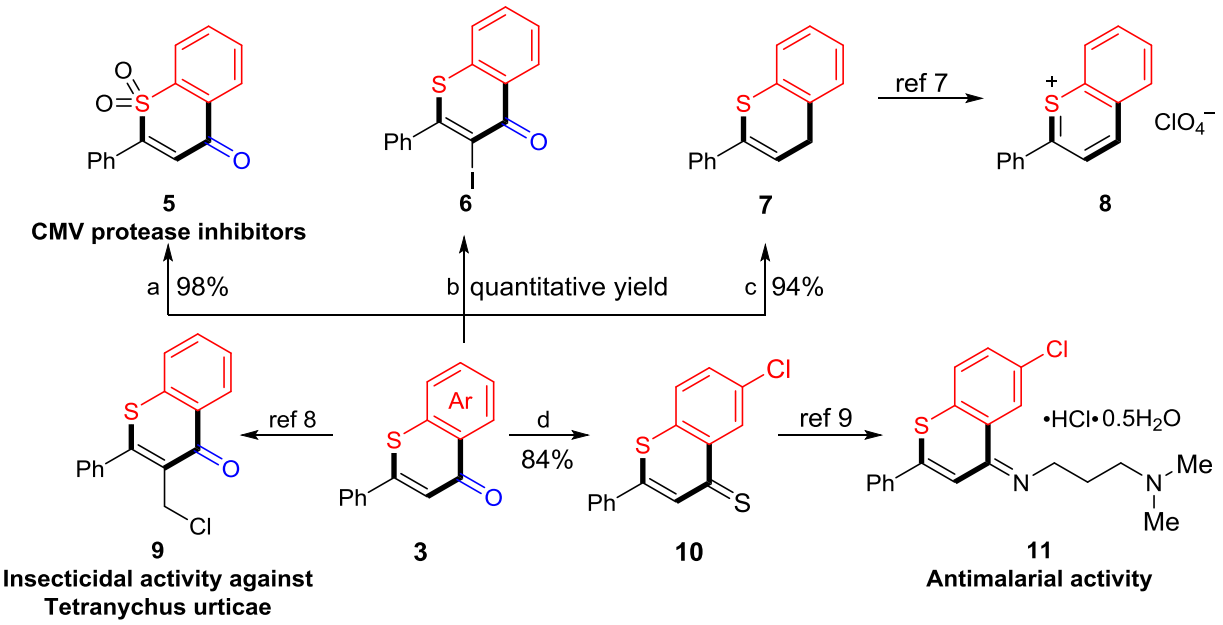


Procedure:

To an oven-dried Schlenk flask (250 mL) containing a magnetic stirring bar was moved into a glovebox and was charged with LiO^{t}Bu (1.28 g, 16 mmol, 2.0 equiv.). The tube was sealed and then evacuated and back-filled with CO_2 atmosphere for 3 times, subsequently, anhydrous DMF (80 mL) was added followed by thiophenol **2a** (1.32 g, 12 mmol, 1.5 equiv.), alkyne **1a** (817 mg, 8 mmol, 1.0 equiv.) via syringe under CO_2. Once added, the Schlenk flask was sealed at atmospheric pressure of CO_2 (1 atm). The reaction was stirred and irradiated with six 30 W blue LED lamps (2 cm away, with cooling fan, the temperature of water bath is at 20-40 ℃ and keeping the reaction region located in the center of LED lamp) for 3 hours. The resulting mixture was diluted with EtOAc and quenched by 2 N HCl (80 mL), then stirred for 5 min. The reaction mixture was

extracted by EtOAc four times and the combined organic phases were concentrated *in vacuo*. Then at 0 ℃, TfOH (8 mL) was added into the residue, followed by stirring at room temperature for 8 h. After the reaction was completed, reaction mixture was diluted with DCM and quenched by saturated $NaHCO_3$ aqueous solution (pH was justified to >7) at 0 ℃, then stirred for 10 min. The reaction mixture was extracted by DCM with five times and the combined organic phases were concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc= 15/1 ~ 8:1) to give the pure desired product (1.44 g, 75% isolated yield, pale brown solid).

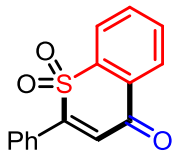
6.2 Synthetic applications of thiochromones



Synthesis of 5:

To a Schlenk tube (10 mL) equipped with a magnetic stir bar was added **3aa** (47.7 mg, 0.2 mmol, 1.0 equiv.) and *m*-CPBA (103.5 mg, 0.6 mmol, 3.0 equiv.) and DCM (2 mL). Then the reaction mixture was stirred at room temperature for 3 h. After completing reaction, the mixture was concentrated *in vacuum*. The residue was purified by silica gel flash column chromatography to give the pure desired product (98% yield, pale yellow solid).

2-phenyl-4*H*-thiochromen-4-one 1,1-dioxide (5)[2]



52.9 mg, 98% yield, pale yellow solid;

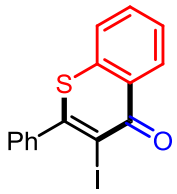
R_f (PE/EA 10:1) = 0.1~0.2;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 7.9, 1.3 Hz, 1H), 8.12 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.93 – 7.84 (m, 3H), 7.78 (td, *J* = 7.7, 1.2 Hz, 1H), 7.62 – 7.48 (m, 3H), 6.84 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.3, 153.2, 141.8, 134.9, 133.0, 131.9, 129.3, 128.9, 128.8, 128.6, 128.1, 123.6; **LRMS (ESI$^+$)** $[M+H]^+$ calculated for $[C_{15}H_{11}O_3S]^+$: 271.04, found: 271.08. All analytical data are consistent with those reported in the literature.

Synthesis of 6:

To an oven-dried Schlenk tube (25 mL) equipped with a magnetic stir bar was added **3aa** (47.7 mg, 0.2 mmol, 1.0 equiv.), I_2 (60.9 mg, 0.24 mmol, 1.2 equiv.) and $(NH_4)_2Ce(NO_3)_6$ (116.6 mg, 0.22 mmol, 1.1 equiv.). The tube was sealed and then evacuated and back-filled with N_2 atmosphere for 3 times. Subsequently, anhydrous MeCN (2 mL) was added via syringe under N_2 atmosphere. Then the reaction mixture was heated at 55 ℃ for 20 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (3 mL) and quenched by saturated $Na_2S_2O_3$ aqueous solution. The mixture was extracted by EtOAc (3 mL) five times and the combined organic phase were concentrated *in vacuum*. The residue was purified by silica gel flash column chromatography to give the pure desired product (quantitative yield, yellow solid).

3-iodo-2-phenyl-4*H*-thiochromen-4-one (6)[2]



72.7 mg, quantitative yield, yellow solid;

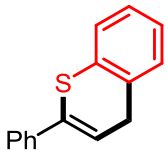
R_f (PE/EA 10:1) = 0.3~0.4;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.58 (m, 1H), 7.70 – 7.56 (m, 3H), 7.56 – 7.47 (m, 3H), 7.46 – 7.38 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.3, 154.2, 140.8, 137.4, 132.0, 130.12, 130.09, 128.7, 128.6, 128.5, 127.4, 125.1, 103.2; **LRMS (ESI$^+$)** $[M+H]^+$ calculated for $[C_{15}H_{10}IOS]^+$: 364.95, found 364.99;. All analytical data are consistent with those reported in the literature.

Synthesis of 7:

To an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was added $AlCl_3$ (26.7 mg, 0.2 mmol, 1.0 equiv.) in the glovebox. The tube was sealed and then evacuated and back-filled with N_2 atmosphere for 3 times. Subsequently, anhydrous THF (1 mL) was added via syringe under N_2 atmosphere. After adding $LiAlH_4$ (7.6 mg, 0.2 mmol, 1.0 equiv.), the reaction mixture was stirred at room temperature for 10 min. To this slurry was slowly added a solution of **3aa** (47.7 mg, 0.2 mmol, 1.0 equiv.) in anhydrous THF (3 mL), the resulting mixture was stirred for 2 h at room temperature. After the reaction was completed, the mixture was diluted with EtOAc (3 mL) and quenched by water (2 mL). The mixture was extracted by EtOAc (3 mL) five times and the combined organic phase were concentrated *in vacuum*. The residue was purified by silica gel flash column chromatography to give the pure desired product (94% yield, pale yellow solid).

2-phenyl-4*H*-thiochromene (7)[3]



42.2 mg, 94% yield, pale yellow solid;

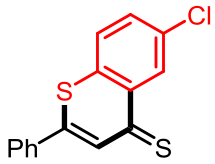
R_f (PE) = 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.43 – 7.37 (m, 1H), 7.37 – 7.26 (m, 3H), 7.21 – 7.14 (m, 3H), 6.25 (t, *J* = 5.1 Hz, 1H), 3.52 (d, *J* = 5.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.1, 136.7, 134.0, 133.4, 128.5, 128.3, 128.0, 126.8, 126.73, 126.70, 126.3, 119.0, 33.6; **GCMS** calculated for [$C_{15}H_{12}S$]: 224.1, found 224.1. All analytical data are consistent with those reported in the literature.

Synthesis of 10:

To an oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was added **3ad** (54.6 mg, 0.2 mmol, 1.0 equiv.) and Lawesson's reagent (161.8 mg, 0.4 mmol, 2.0 equiv.). The tube then was evacuated and back-filled with N_2 atmosphere for 3 times. Subsequently, anhydrous MeCN (2 mL) was added via syringe under N_2 atmosphere. Then the reaction mixture was heated at 110 ℃ to reflux for 6 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuum*. The residue was purified by silica gel flash column chromatography to give the pure desired product (84% yield, brown solid).

6-chloro-2-phenyl-4*H*-thiochromene-4-thione (10)



47.4 mg, 82% yield, brown solid;

R_f (PE/EA 10:1) = 0.5~0.6;

Mp 150-152 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 2.1 Hz, 1H), 8.29 (s, 1H), 7.74 – 7.69 (m, 2H), 7.62 – 7.55 (m, 2H), 7.54 – 7.47 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.1, 143.0, 138.0, 135.9, 135.8, 135.7, 131.6, 131.4, 131.2, 131.1, 129.4, 128.4, 127.0; **HRMS (ESI$^+$)**: calculated m/z for $C_{15}H_{10}ClS^+$ $[M+H]^+$ 288.9907, found: 288.9910; $C_{15}H_{10}{}^{37}ClS^+$ $[M+H]^+$ 290.9877, found: 290.9873.

7. Determination of metal elements

Element	Co2388	Cu3247	Fe2599	Mn2576
Units	ppm	ppm	ppm	ppm
Avg	-0.0340[a]	-0.0053[a]	0.0013	-0.0011[a]
Element	Ni2316	Pd3242	Rh3434	Ru2402
Units	ppm	ppm	ppm	ppm
Avg	0.0347	-0.0020[a]	0.0303	0.0947

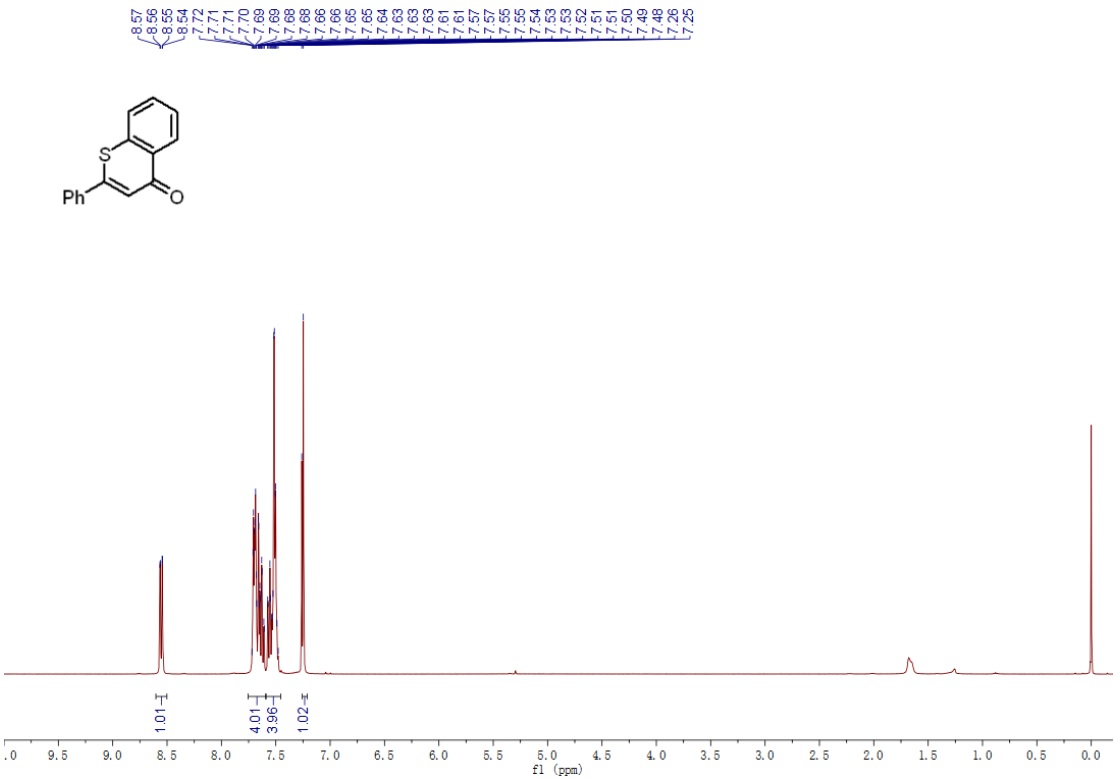
[a]The concertration of metal elements were below detection limit.

Procedure:

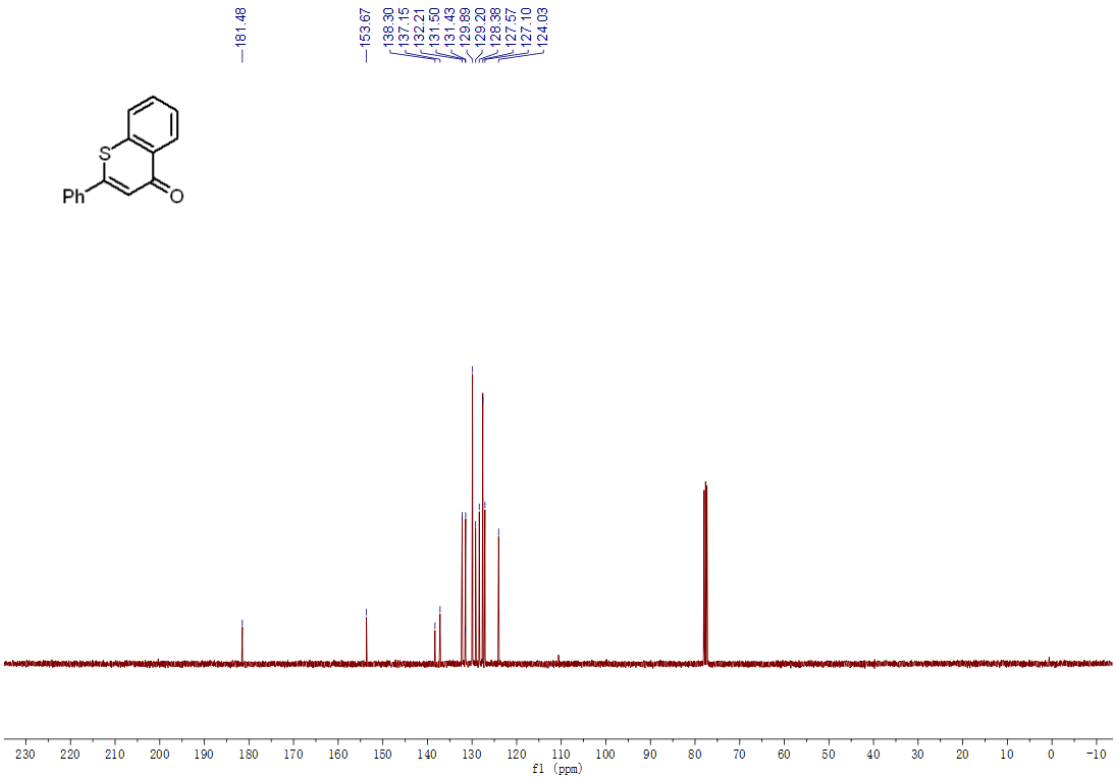
Reaction procedures: To an oven-dried Schlenk tube (10 mL) containing a magnetic stirring bar was charged with LiO^tBu (32.0 mg, 0.4 mmol, 2.0 equiv.) in the glovebox. The tube was sealed and then evacuated and back-filled with CO_2 atmosphere for 3 times. Subsequently, anhydrous DMF (2 mL) was added, followed by thiophenol **2h** (37.3 mg, 0.3 mmol, 1.5 equiv.), alkyne **1a** (33.1 mg, 0.2 mmol, 1.0 equiv.) via syringe under CO_2. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The reaction was stirred and irradiated with a 30 W blue LED lamp (1-2 cm away, with cooling fan to keep the reaction temperature at 22-25 ℃) for 3 hours. The resulting mixture was then treated with concentrated nitric acid (pH was justified to <7) and analyzed by ICP-AES.

8. The spectrums of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR

2-phenyl-4*H*-thiochromen-4-one (3aa, $CDCl_3$ as solvent)

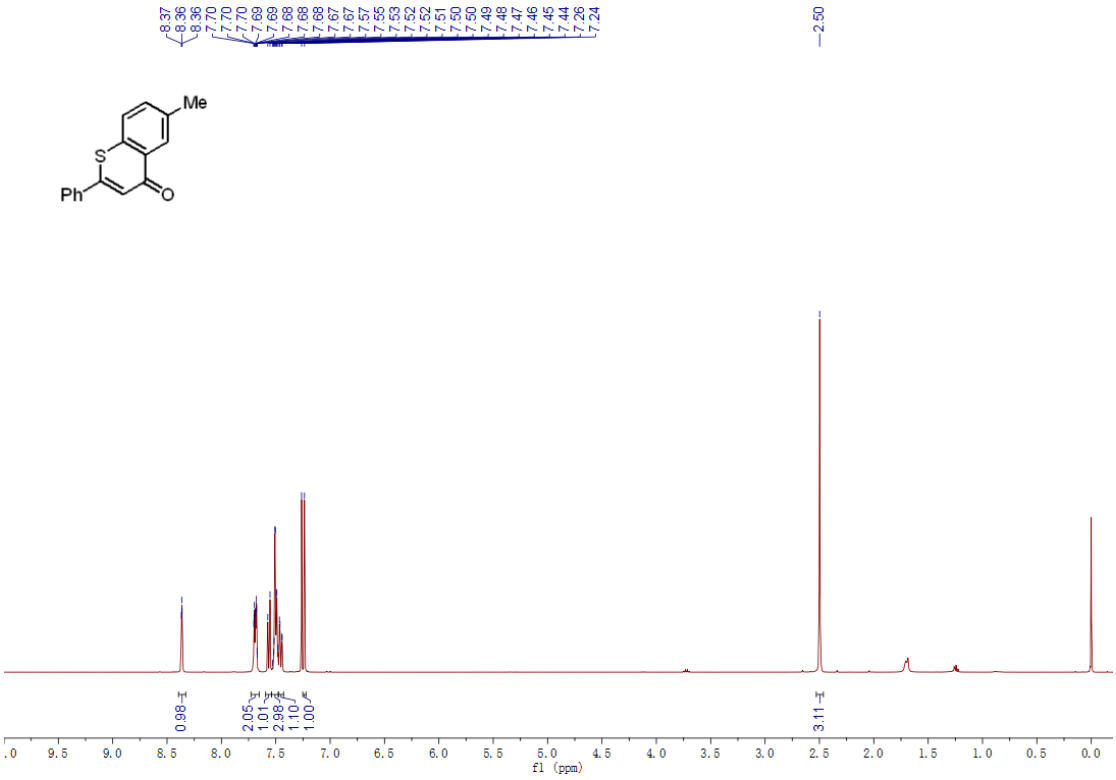


Supplementary Figure 4. ^{1}H NMR spectra of **3aa**

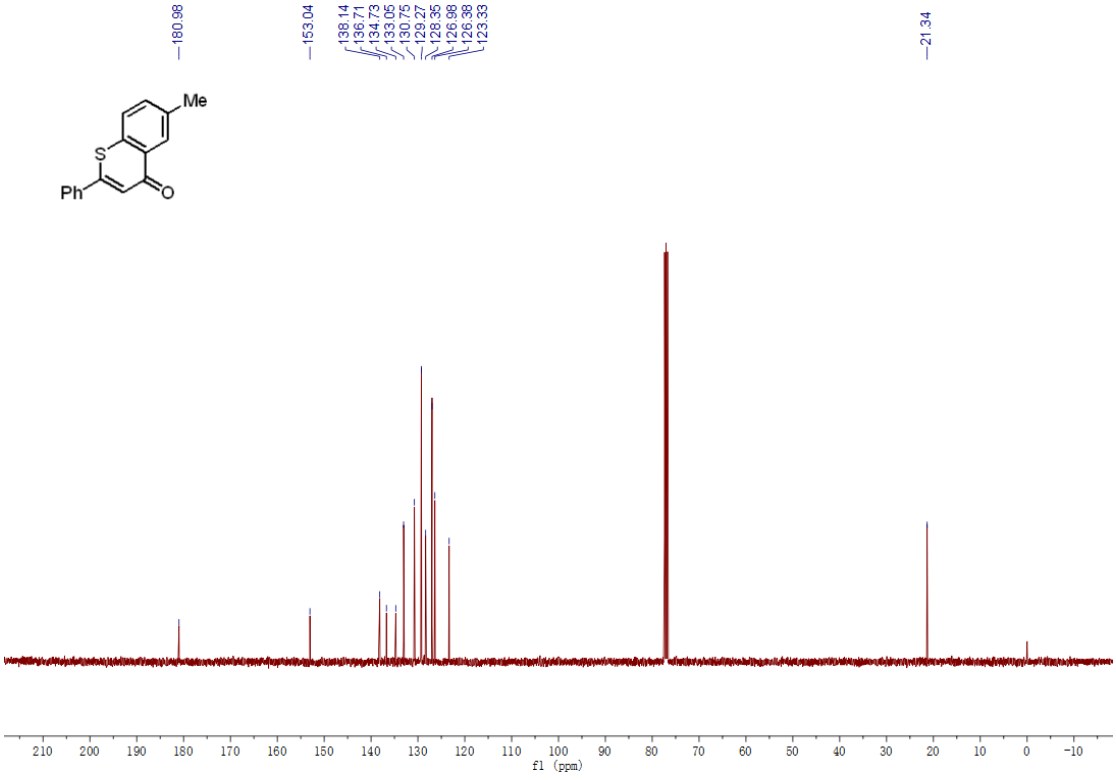


Supplementary Figure 5. ^{13}C NMR spectra of **3aa**

6-methyl-2-phenyl-4*H*-thiochromen-4-one (3ab, *$CDCl_3$* as solvent)

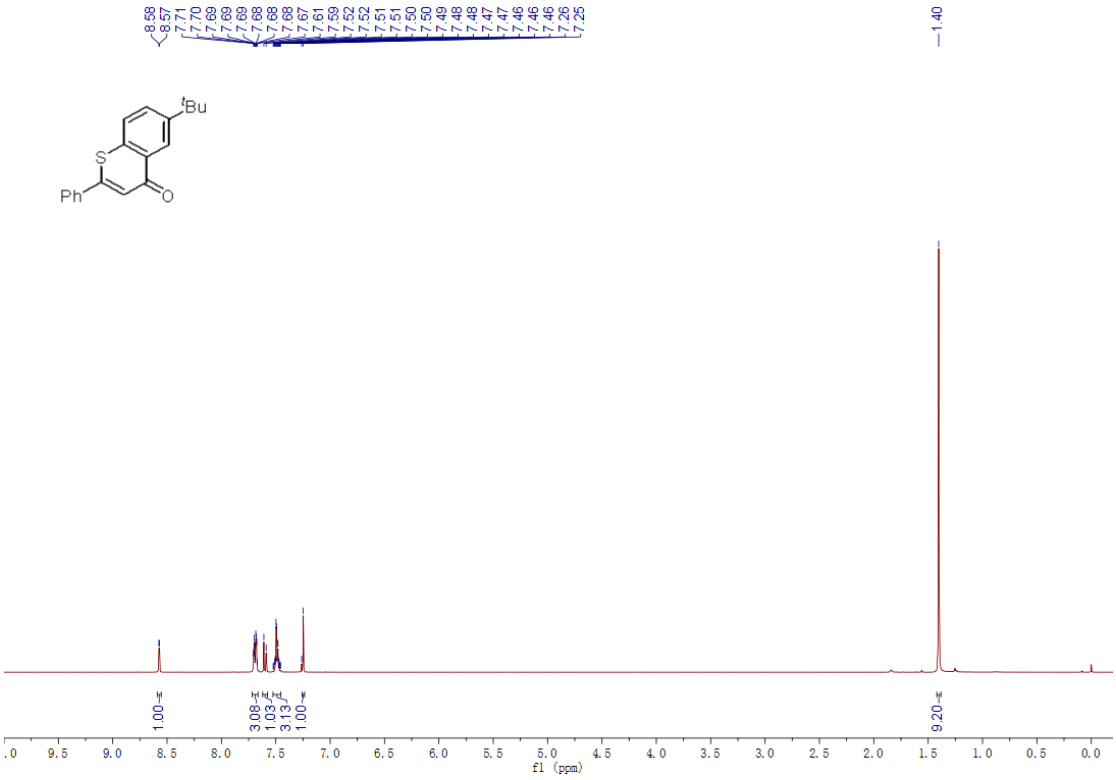


Supplementary Figure 6. ^{1}H NMR spectra of **3ab**

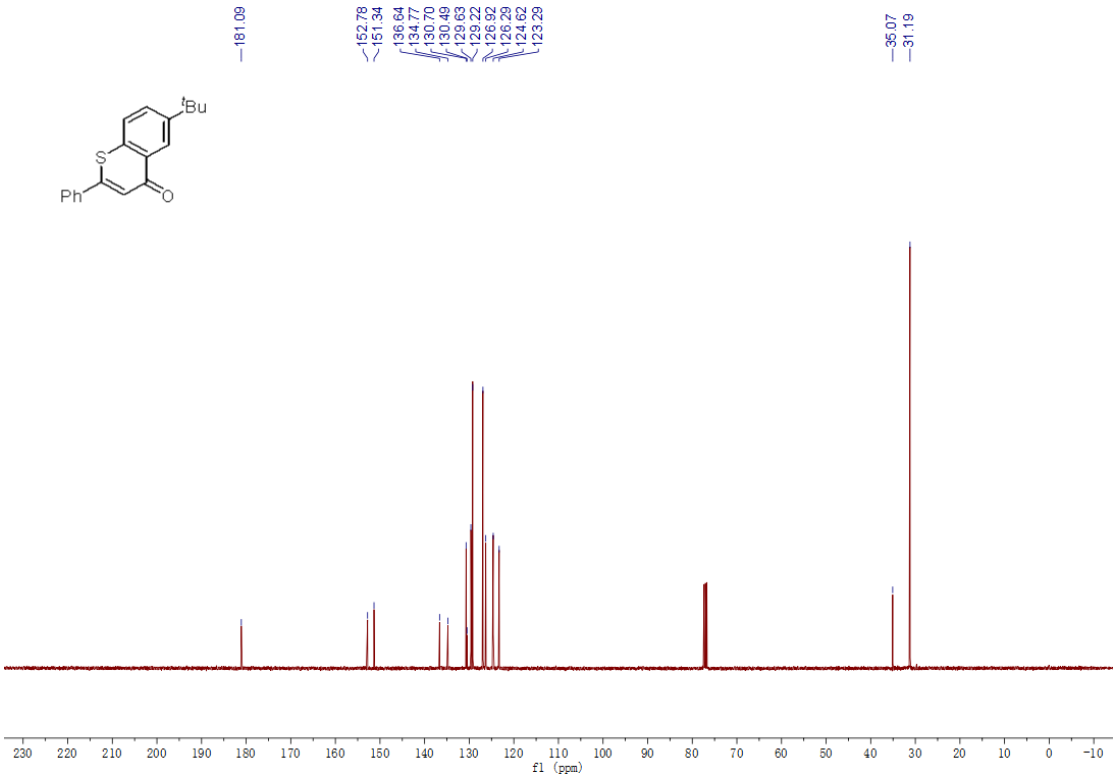


Supplementary Figure 7. ^{13}C NMR spectra of **3ab**

6-(*tert*-butyl)-2-phenyl-4*H*-thiochromen-4-one (3ac, $CDCl_3$ as solvent)

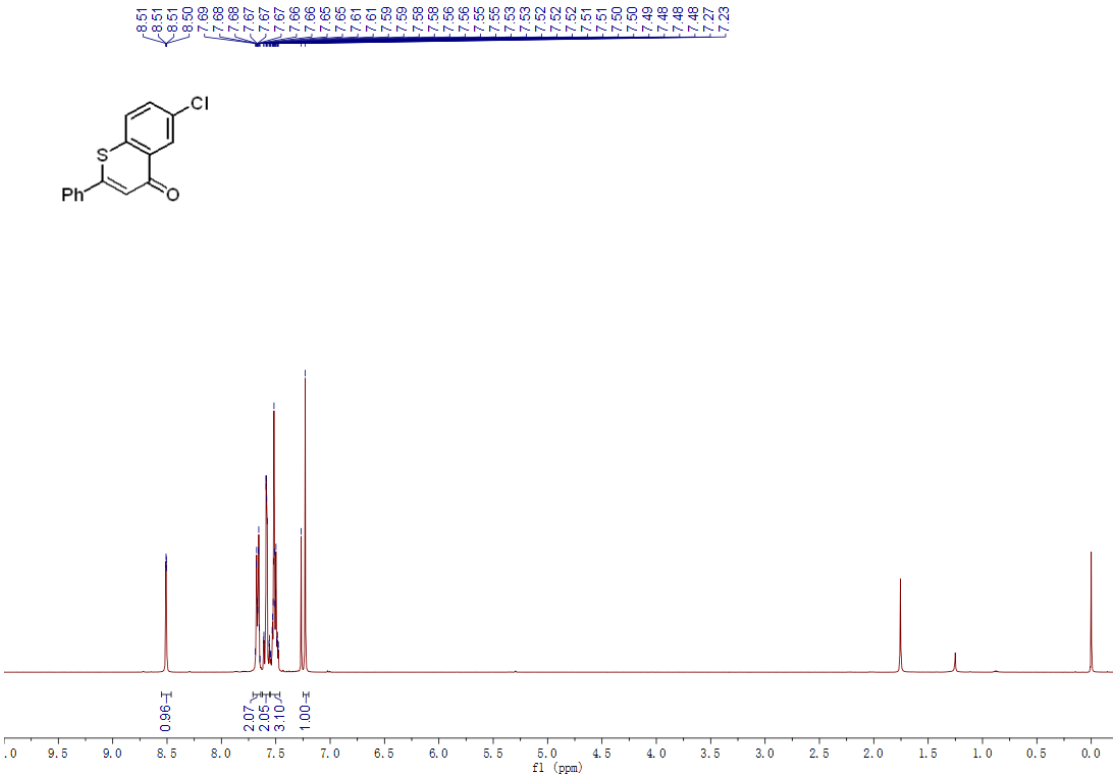


Supplementary Figure 8. ^{1}H NMR spectra of **3ac**

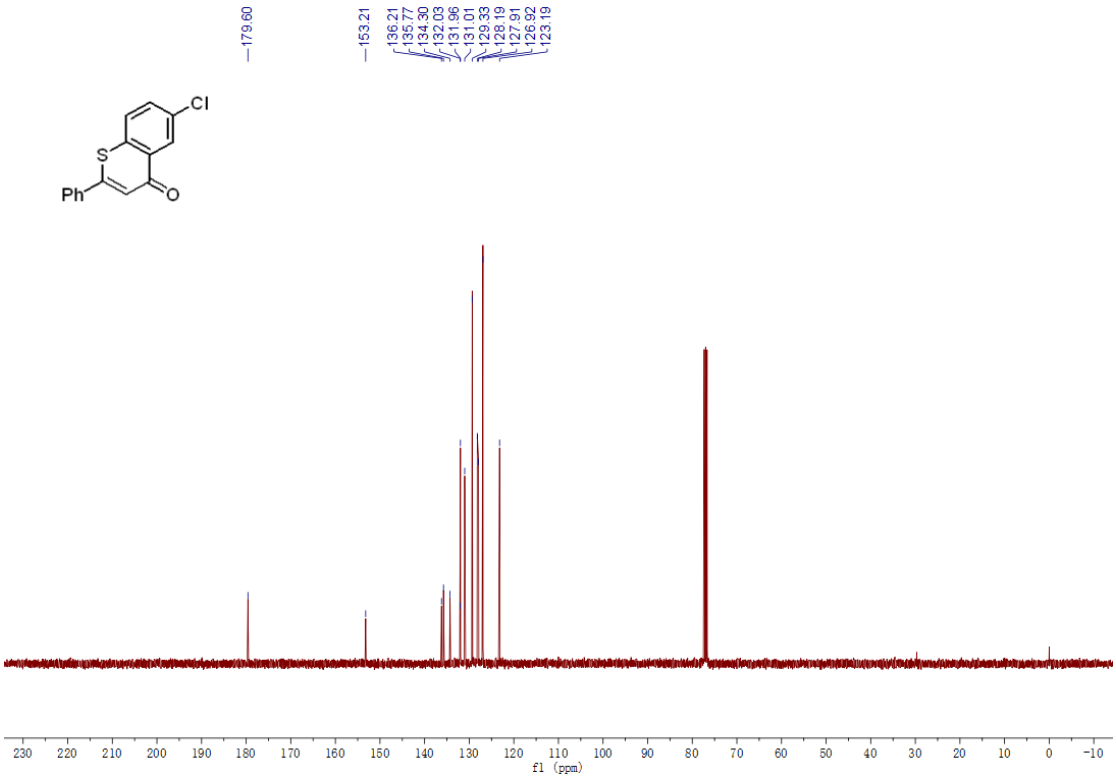


Supplementary Figure 9. ^{13}C NMR spectra of **3ac**

6-chloro-2-phenyl-4*H*-thiochromen-4-one (3ad, $CDCl_3$ as solvent)

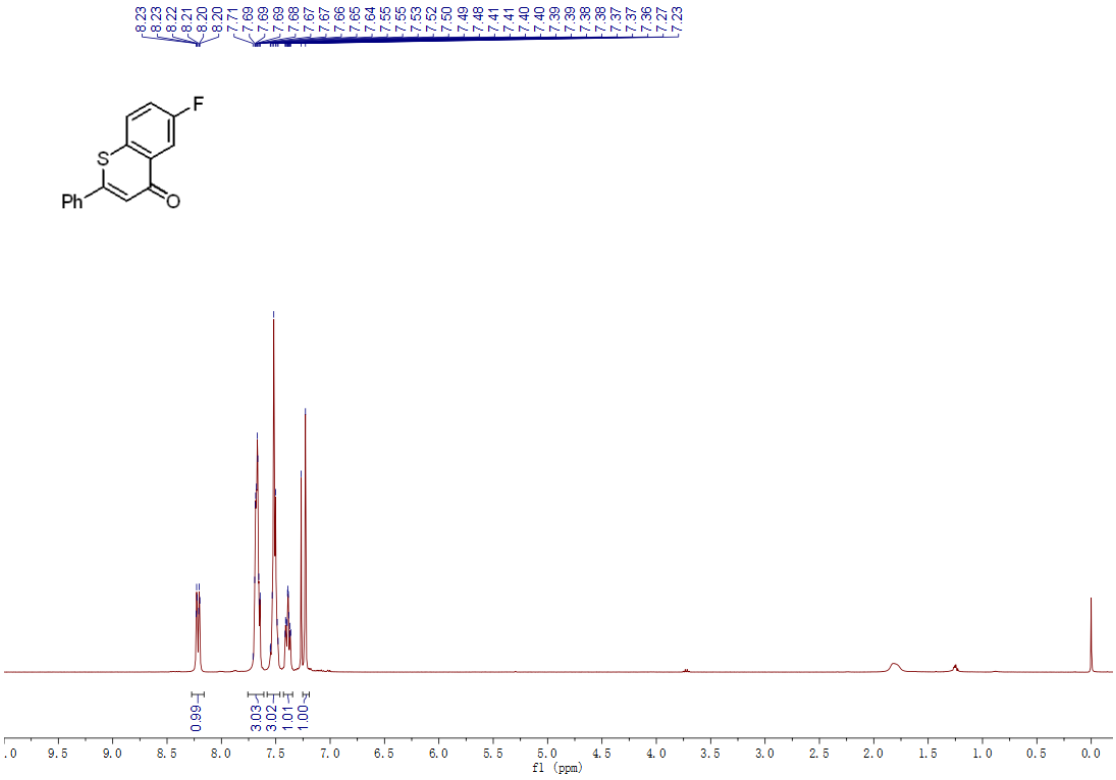


Supplementary Figure 10. ^{1}H NMR spectra of **3ad**

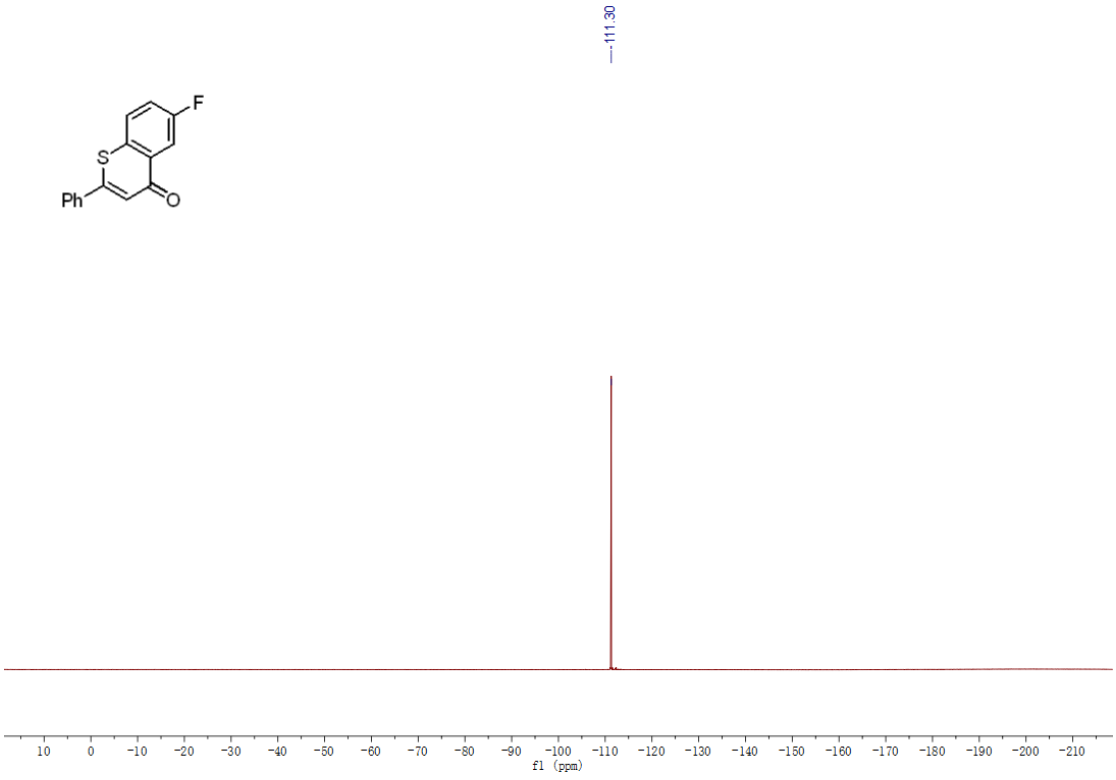


Supplementary Figure 11. ^{13}C NMR spectra of **3ad**

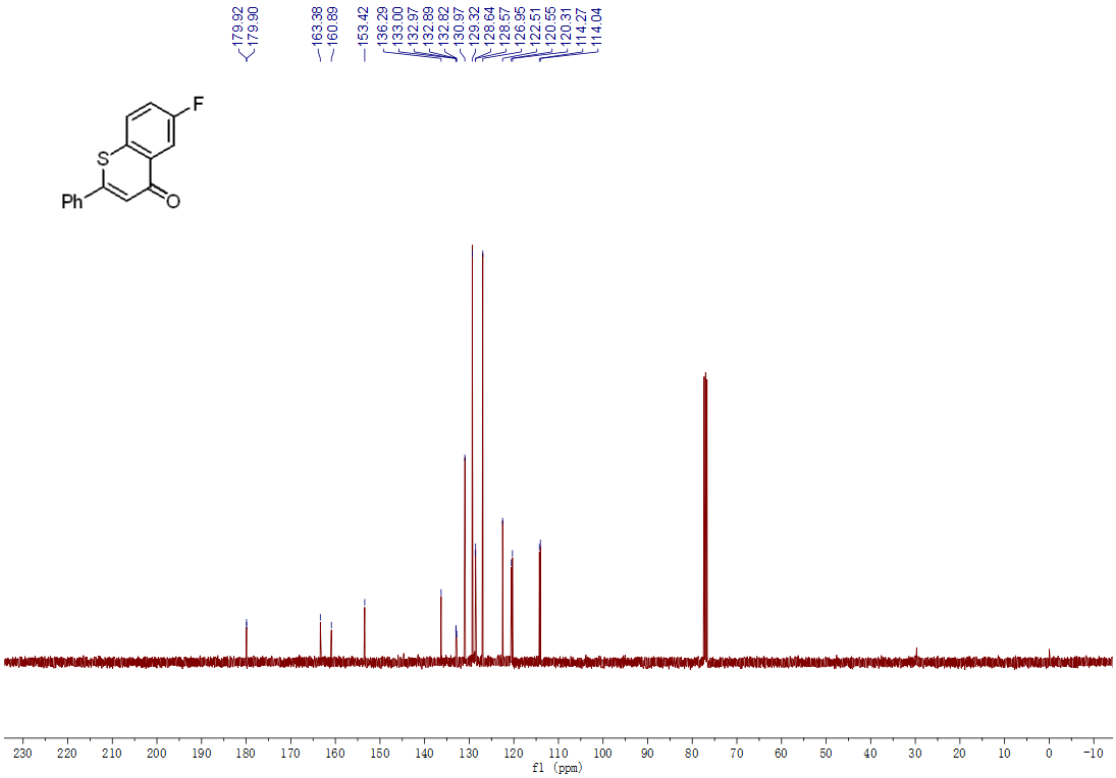
6-fluoro-2-phenyl-4*H*-thiochromen-4-one (3ae, $CDCl_3$ as solvent)



Supplementary Figure 12. ^{1}H NMR spectra of **3ae**

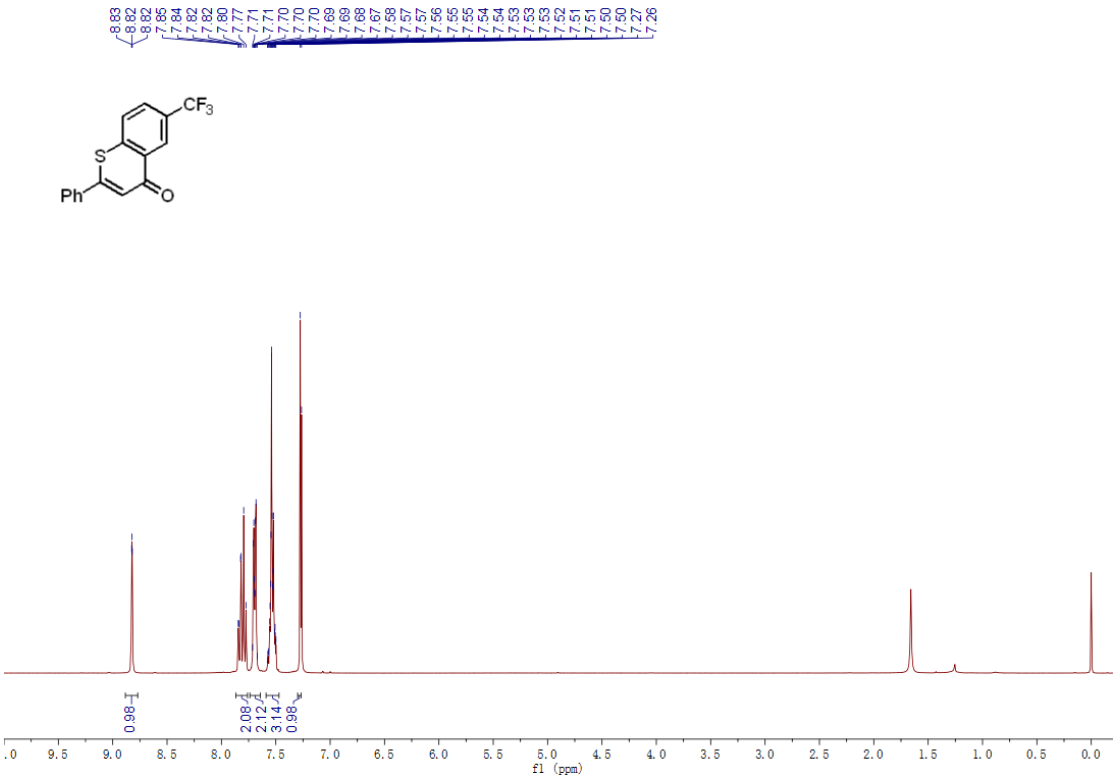


Supplementary Figure 13. ^{19}F NMR spectra of **3ae**

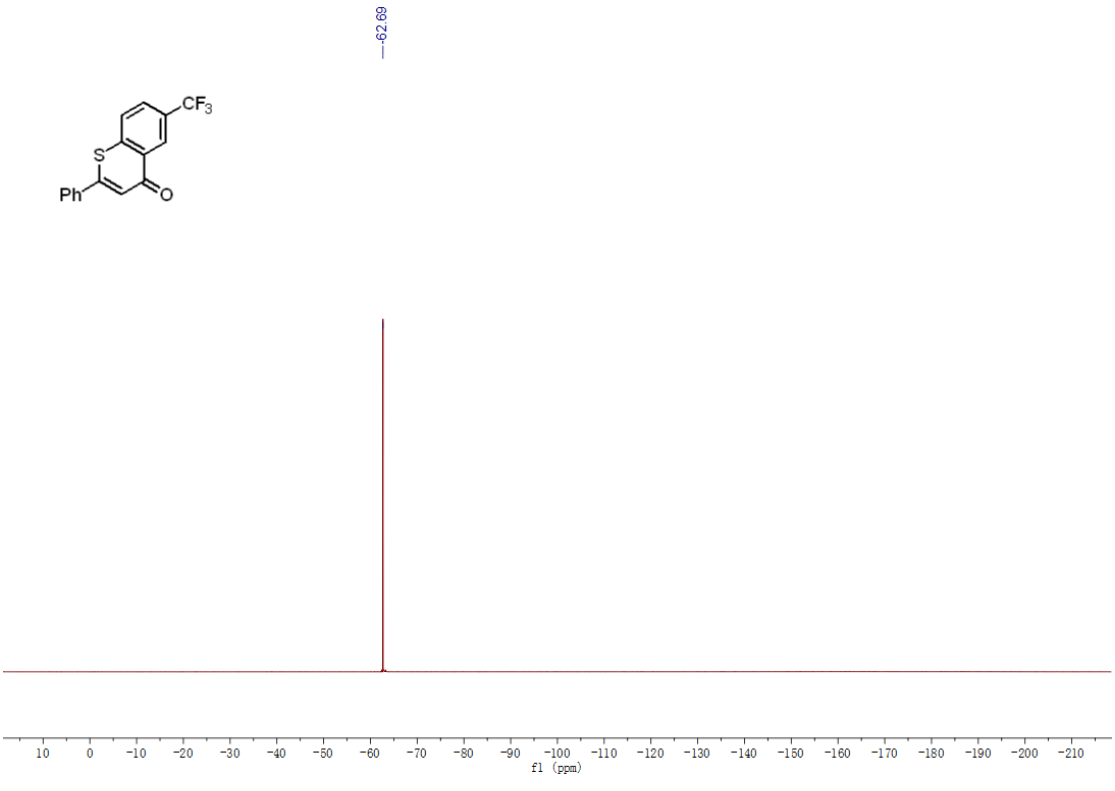


Supplementary Figure 14. ^{13}C NMR spectra of **3ae**

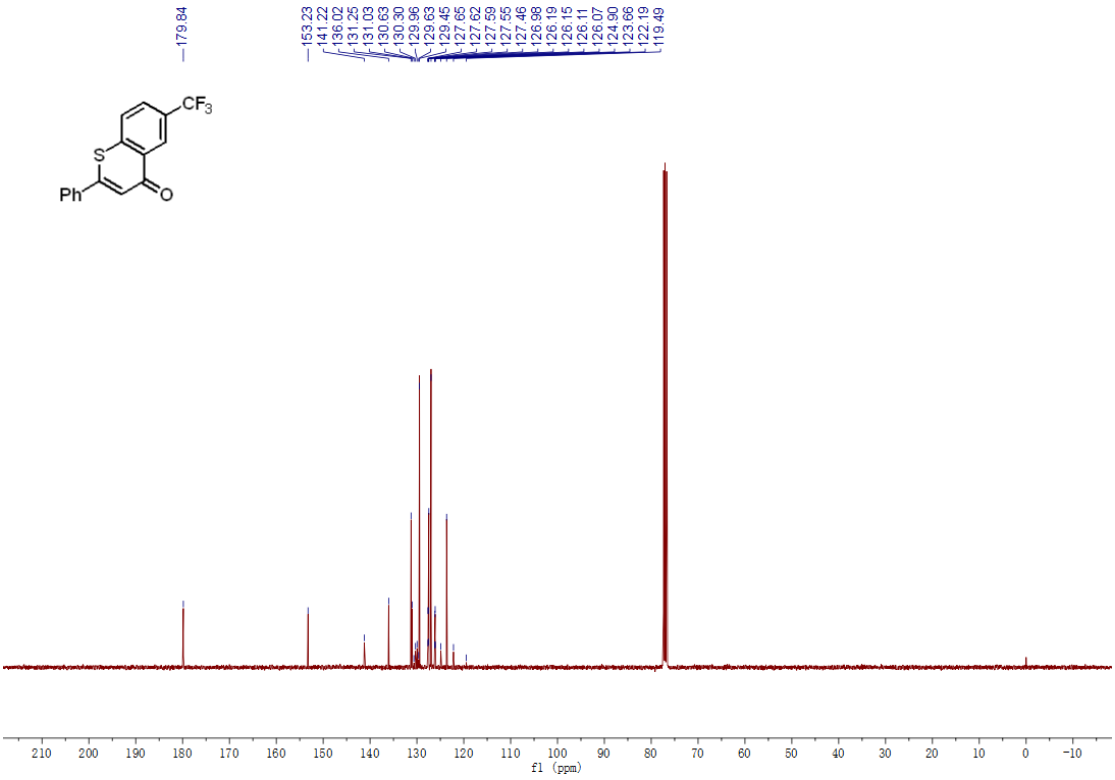
2-phenyl-6-(trifluoromethyl)-4*H*-thiochromen-4-one (3af, *$CDCl_3$* as solvent)



Supplementary Figure 15. ^{1}H NMR spectra of **3af**

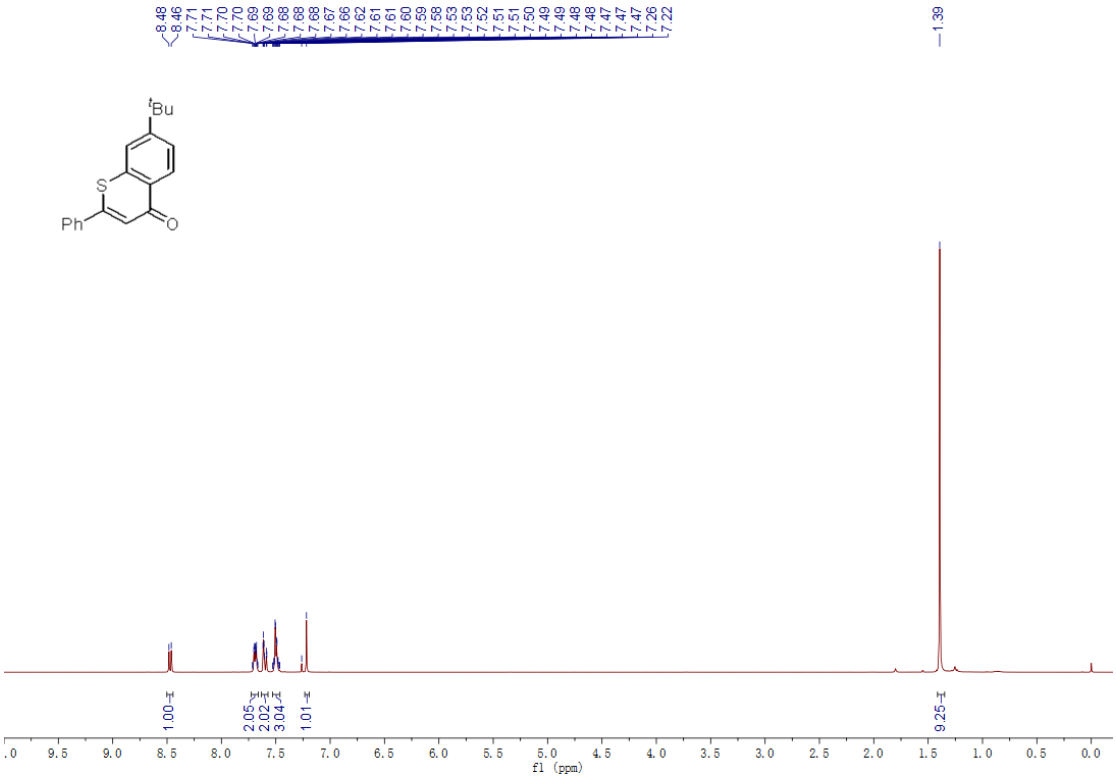


Supplementary Figure 16. ^{19}F NMR spectra of **3af**

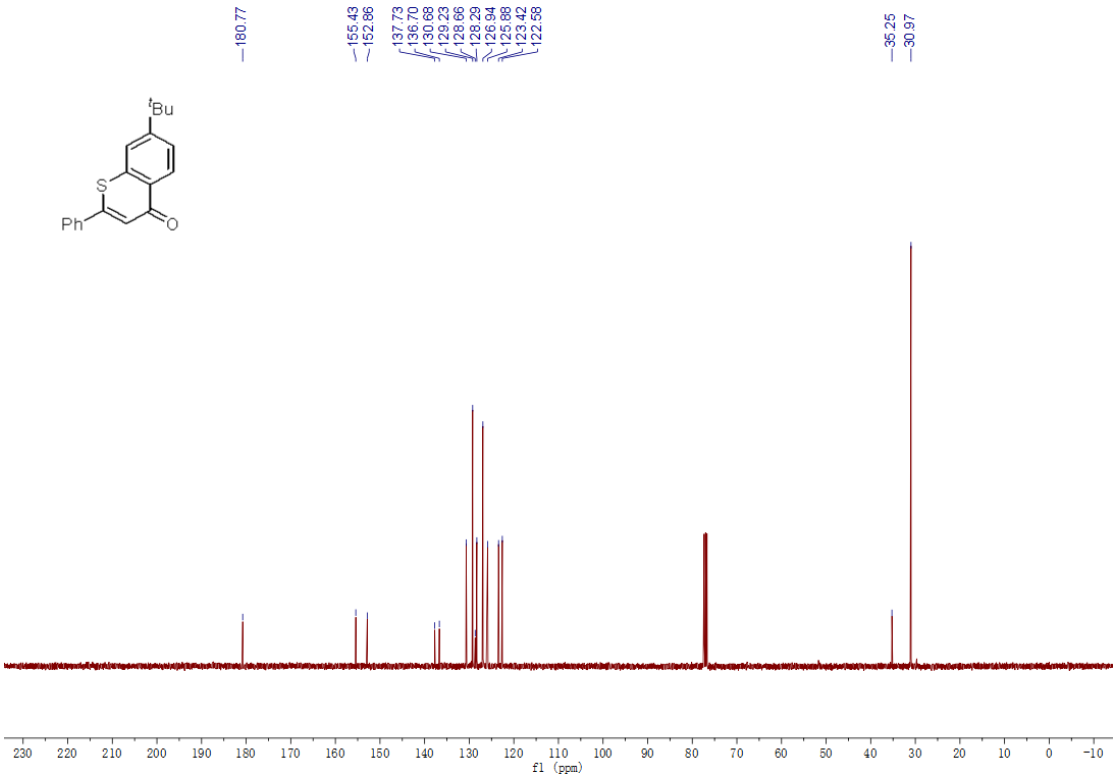


Supplementary Figure 17. ^{13}C NMR spectra of **3af**

7-(*tert*-butyl)-2-phenyl-4*H*-thiochromen-4-one (3ag, *$CDCl_3$* as solvent)

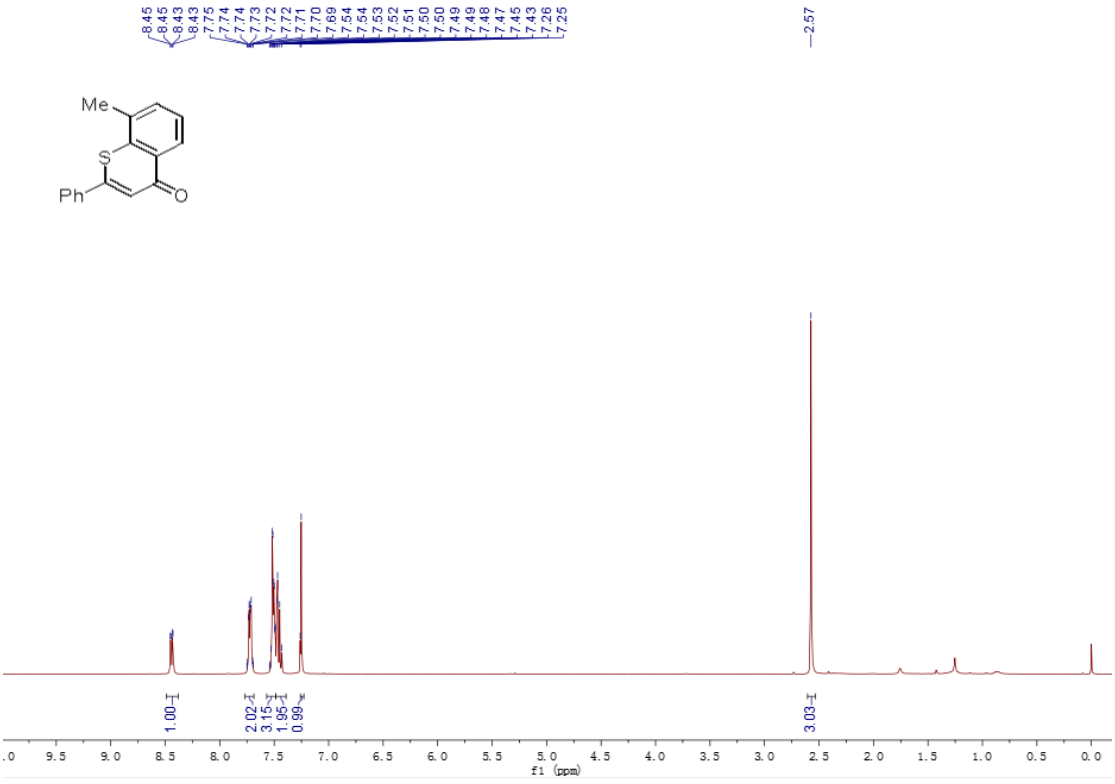


Supplementary Figure 18. ^{1}H NMR spectra of **3ag**

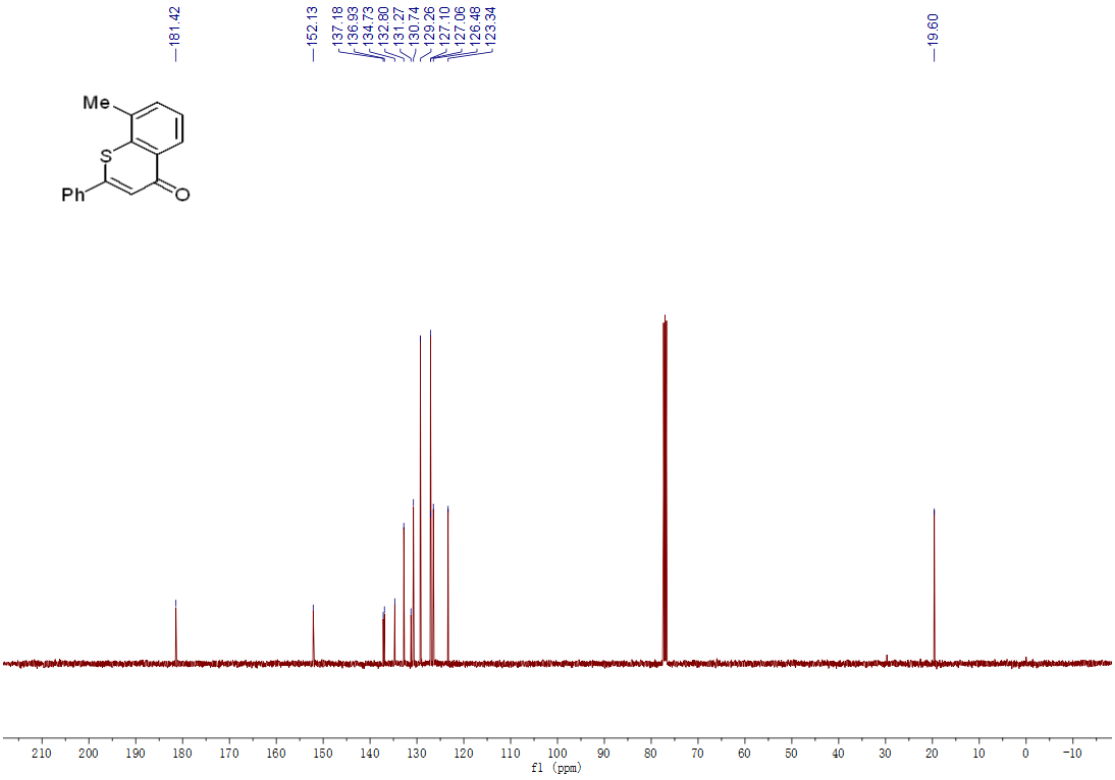


Supplementary Figure 19. ^{13}C NMR spectra of **3ag**

8-methyl-2-phenyl-4*H*-thiochromen-4-one (3ah, *$CDCl_3$* as solvent)

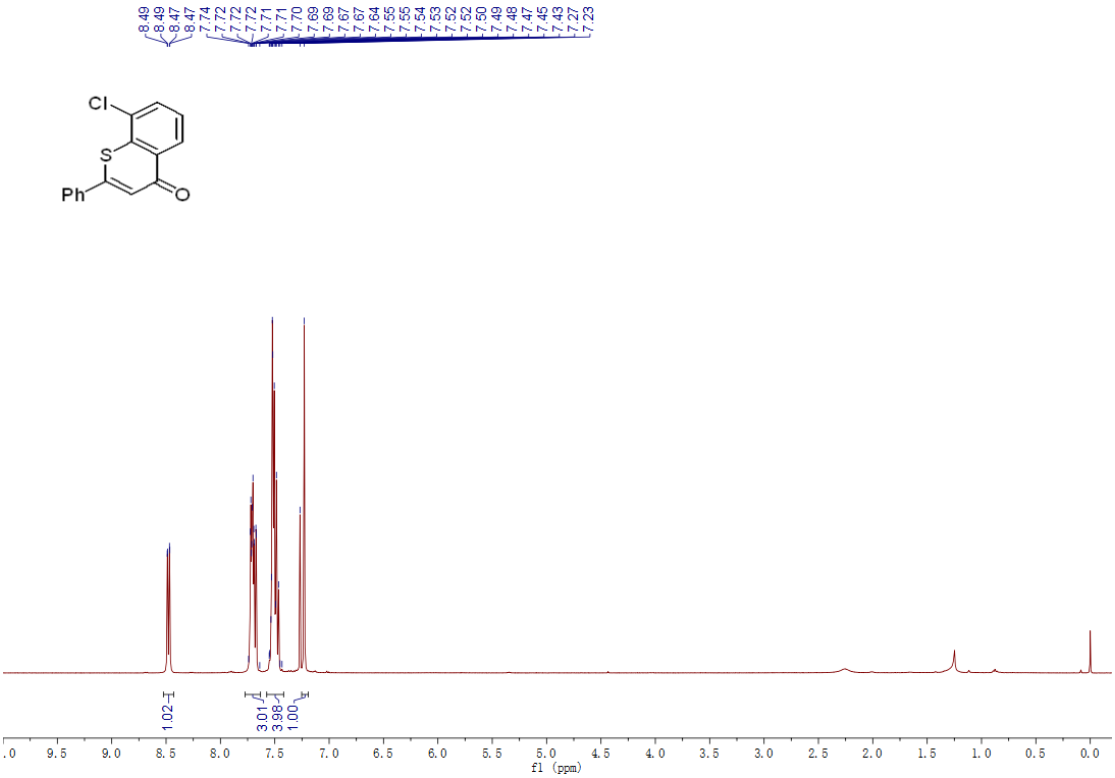


Supplementary Figure 20. ^{1}H NMR spectra of **3ah**

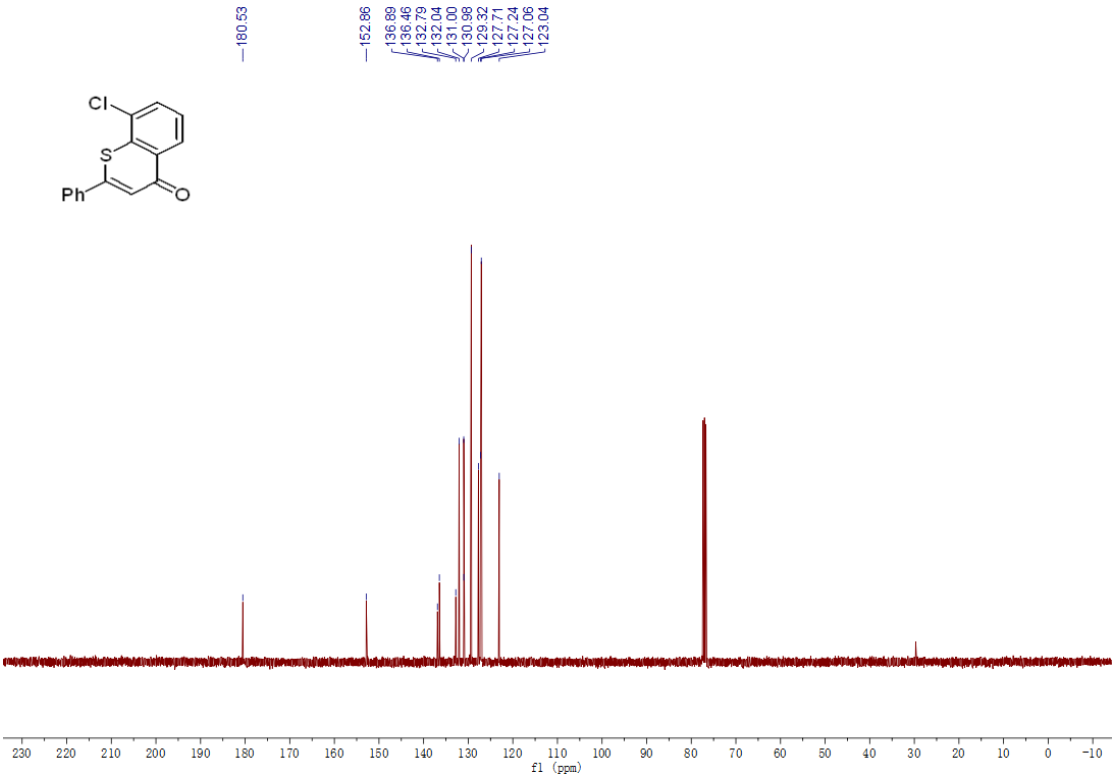


Supplementary Figure 21. ^{13}C NMR spectra of **3ah**

8-chloro-2-phenyl-4*H*-thiochromen-4-one (3ai, $CDCl_3$ as solvent)

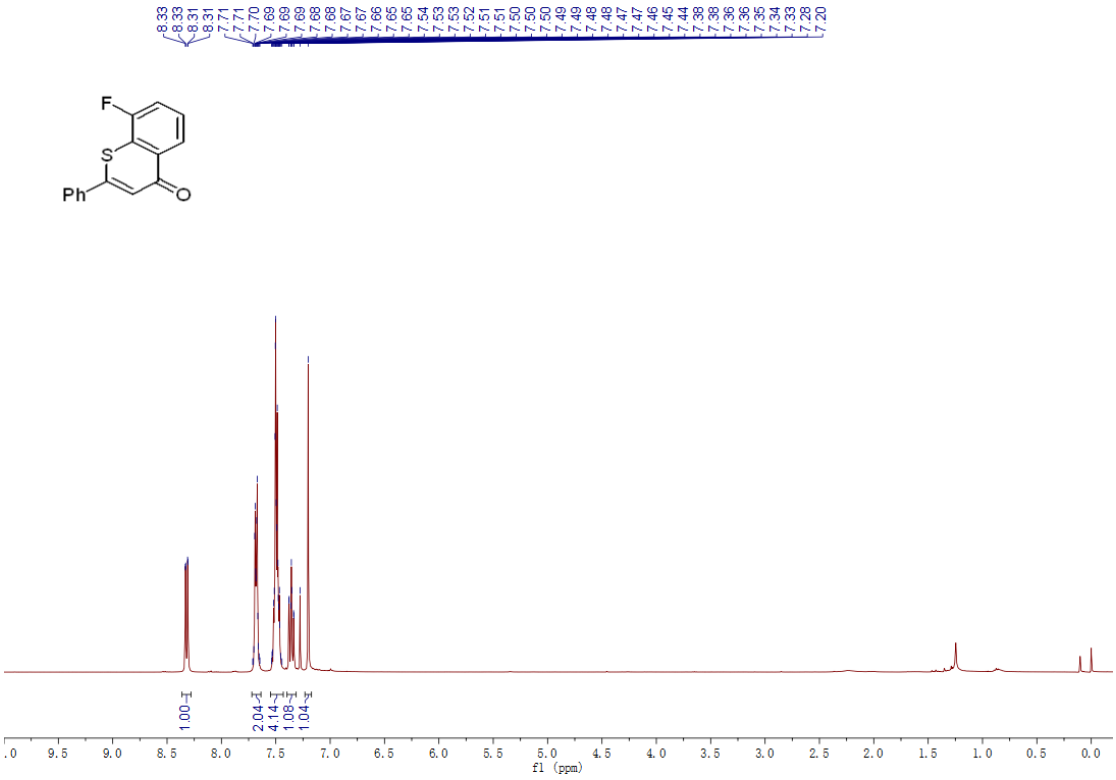


Supplementary Figure 22. ^{1}H NMR spectra of **3ai**

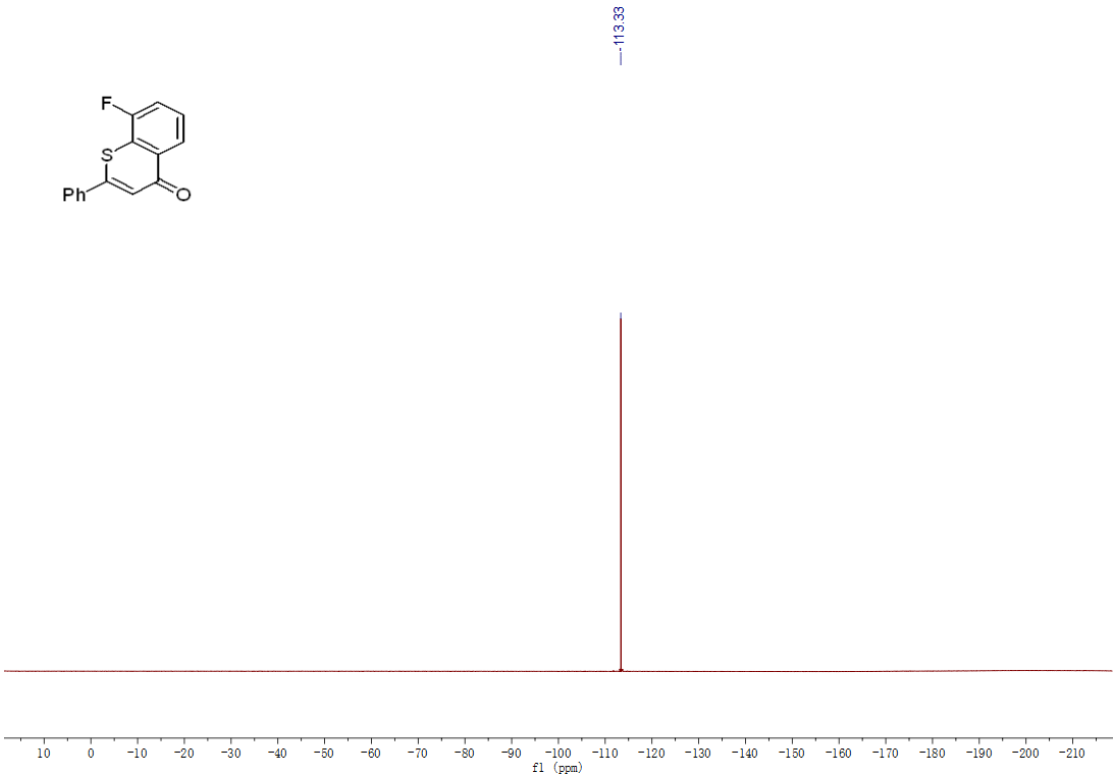


Supplementary Figure 23. ^{13}C NMR spectra of **3ai**

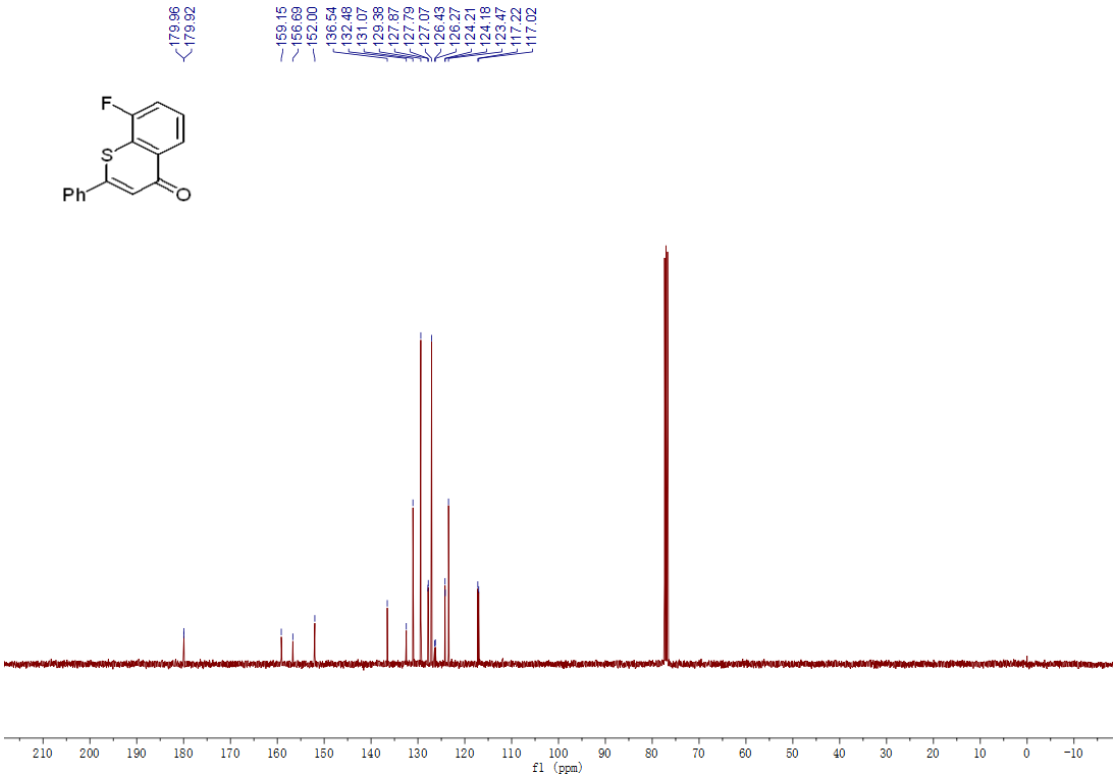
8-fluoro-2-phenyl-4*H*-thiochromen-4-one (3aj, $CDCl_3$ as solvent)



Supplementary Figure 24. ^{1}H NMR spectra of **3aj**

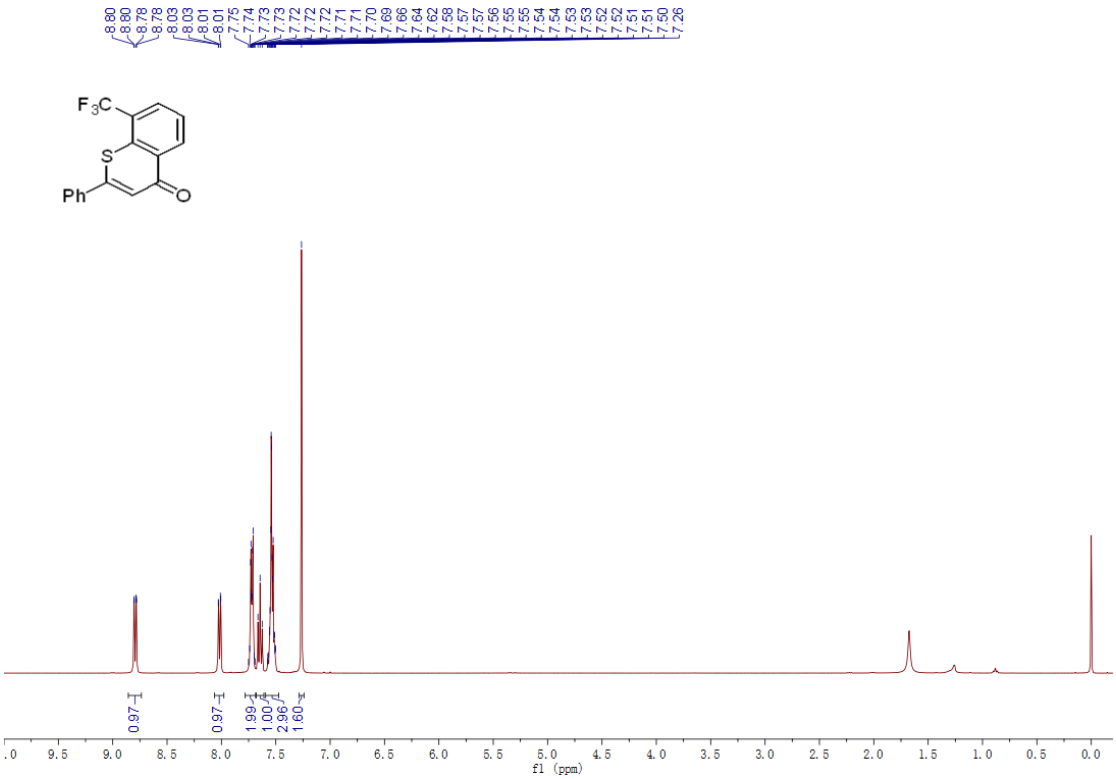


Supplementary Figure 25. ^{19}F NMR spectra of **3aj**

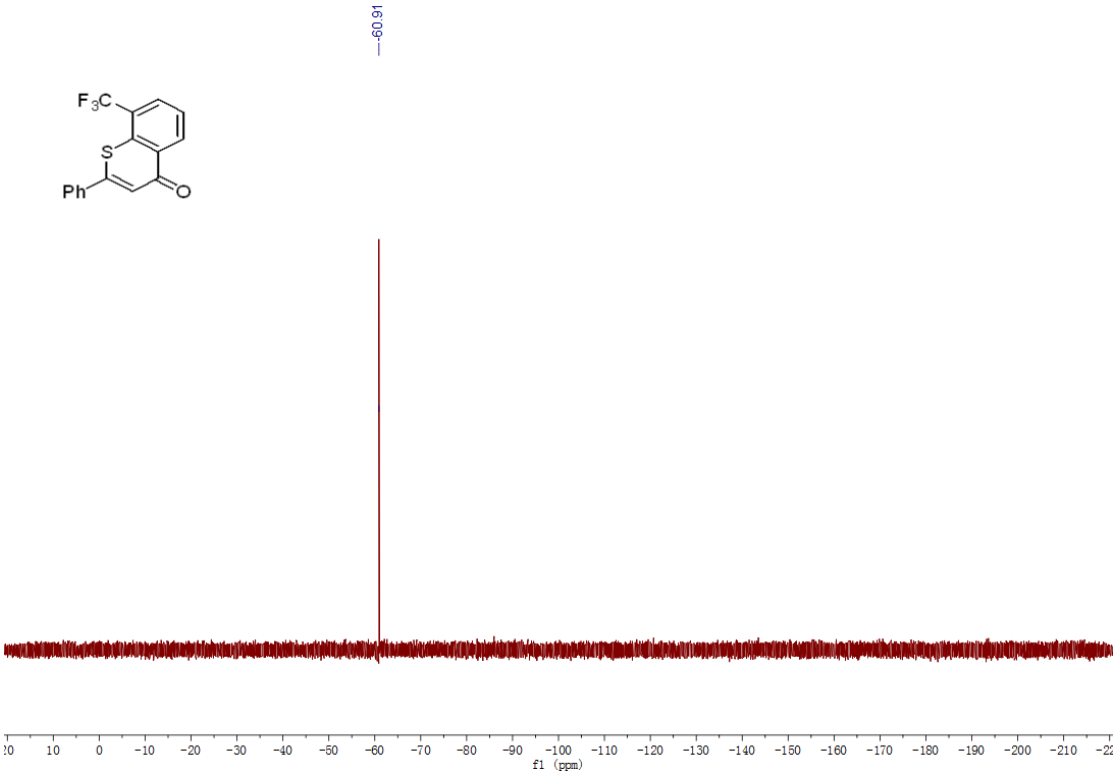


Supplementary Figure 26. ^{13}C NMR spectra of **3aj**

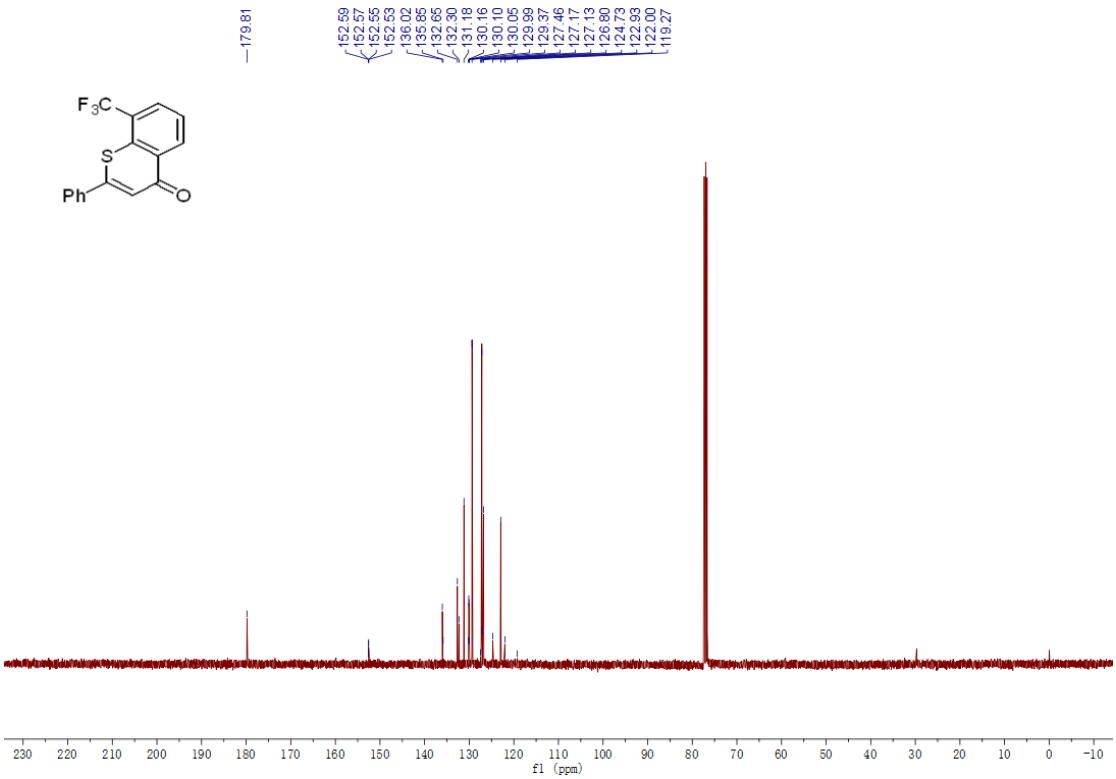
2-phenyl-8-(trifluoromethyl)-4*H*-thiochromen-4-one (3ak, *$CDCl_3$* as solvent)



Supplementary Figure 27. ^{1}H NMR spectra of **3ak**

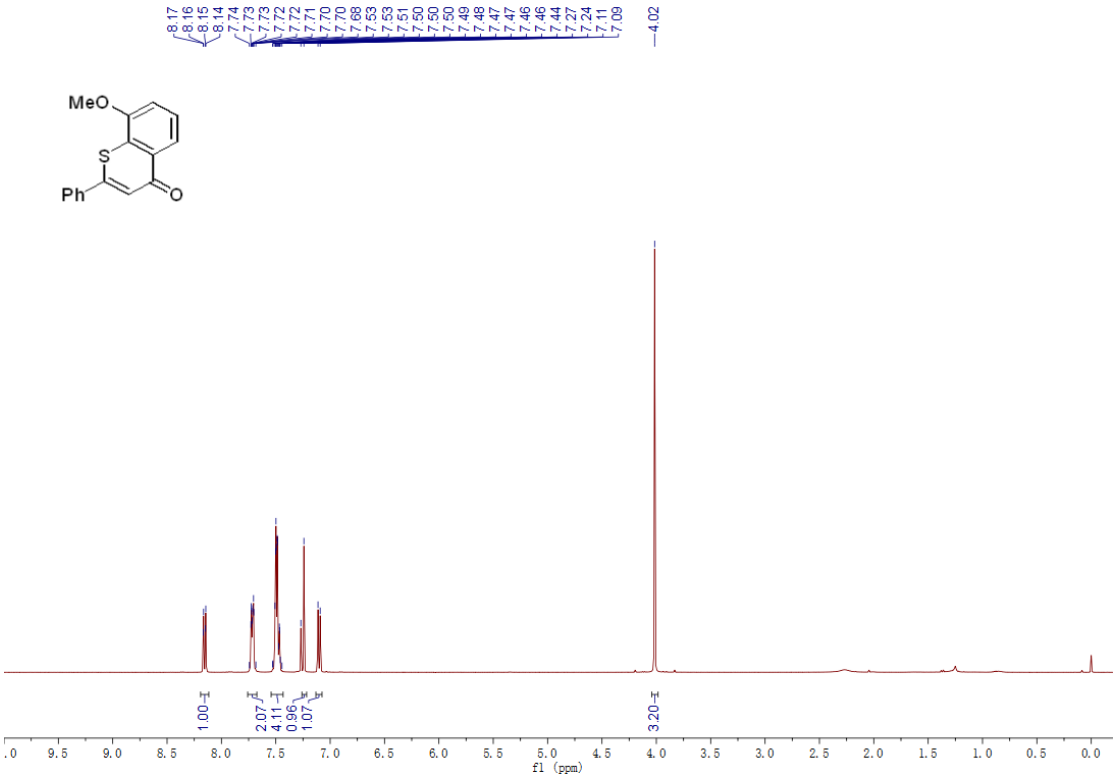


Supplementary Figure 28. ^{19}F NMR spectra of **3ak**

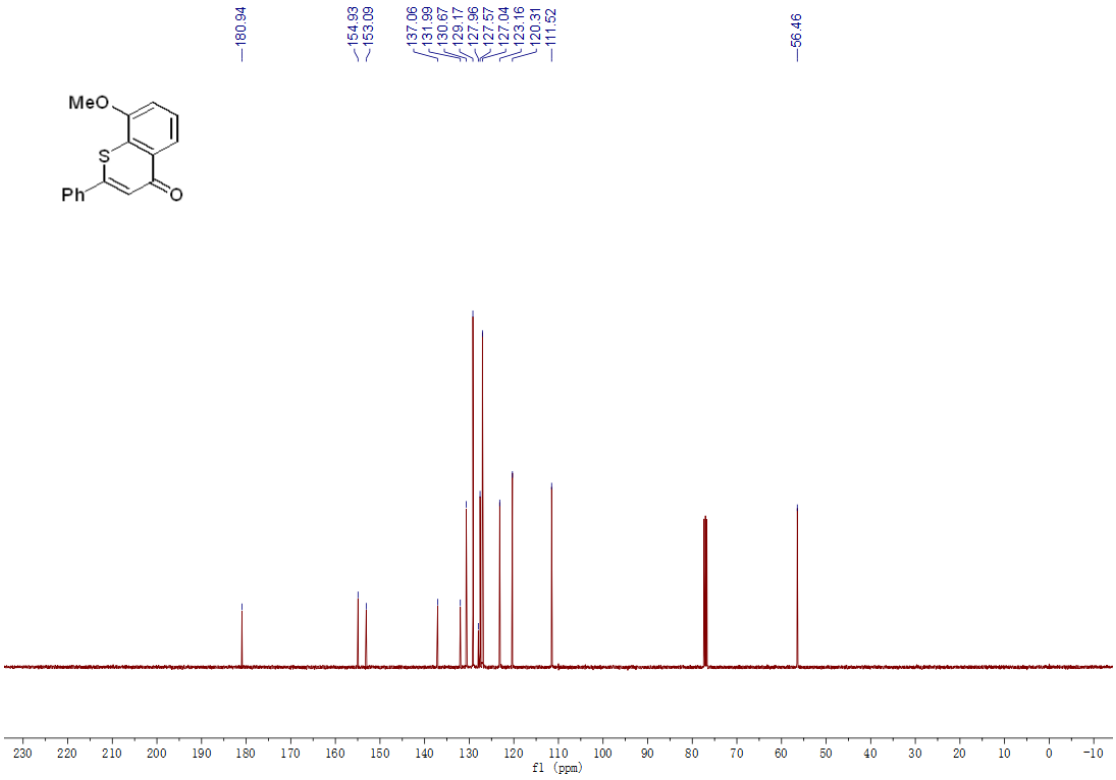


Supplementary Figure 29. ^{13}C NMR spectra of **3ak**

8-methoxy-2-phenyl-4H-thiochromen-4-one (3al, *$CDCl_3$* as solvent)

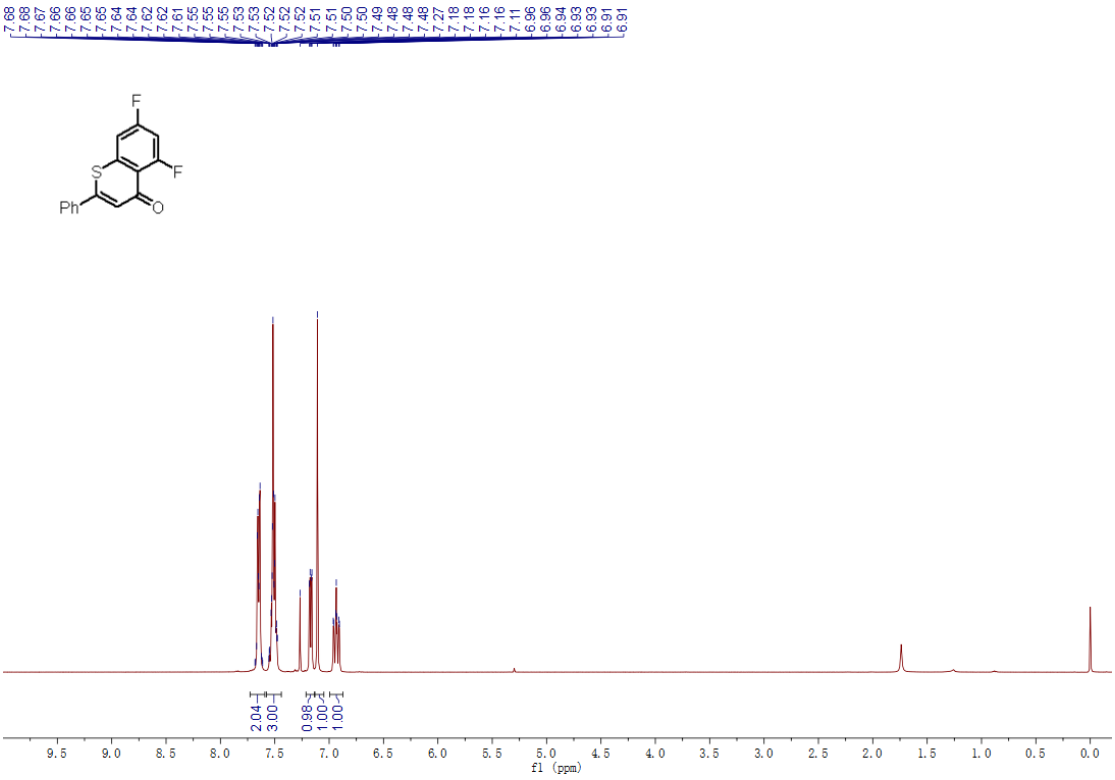


Supplementary Figure 30. ^{1}H NMR spectra of **3al**

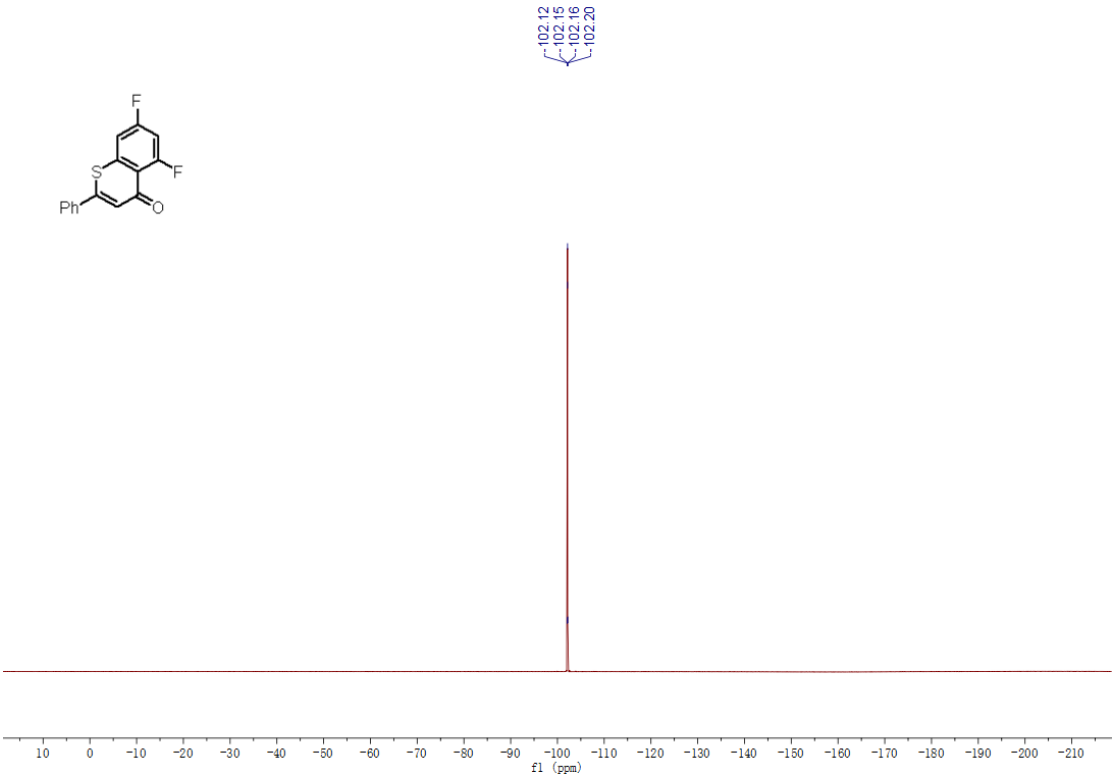


Supplementary Figure 31. ^{13}C NMR spectra of **3al**

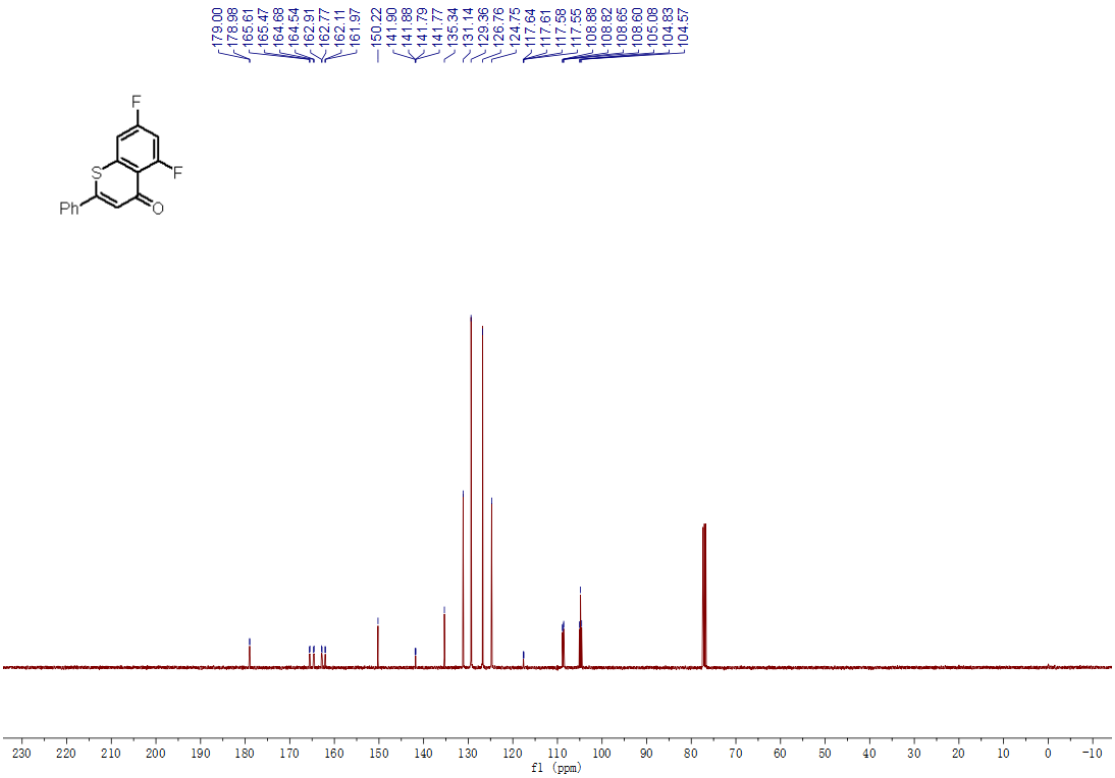
5,7-difluoro-2-phenyl-4*H*-thiochromen-4-one (3am, $CDCl_3$ as solvent)



Supplementary Figure 32. ^{1}H NMR spectra of **3am**

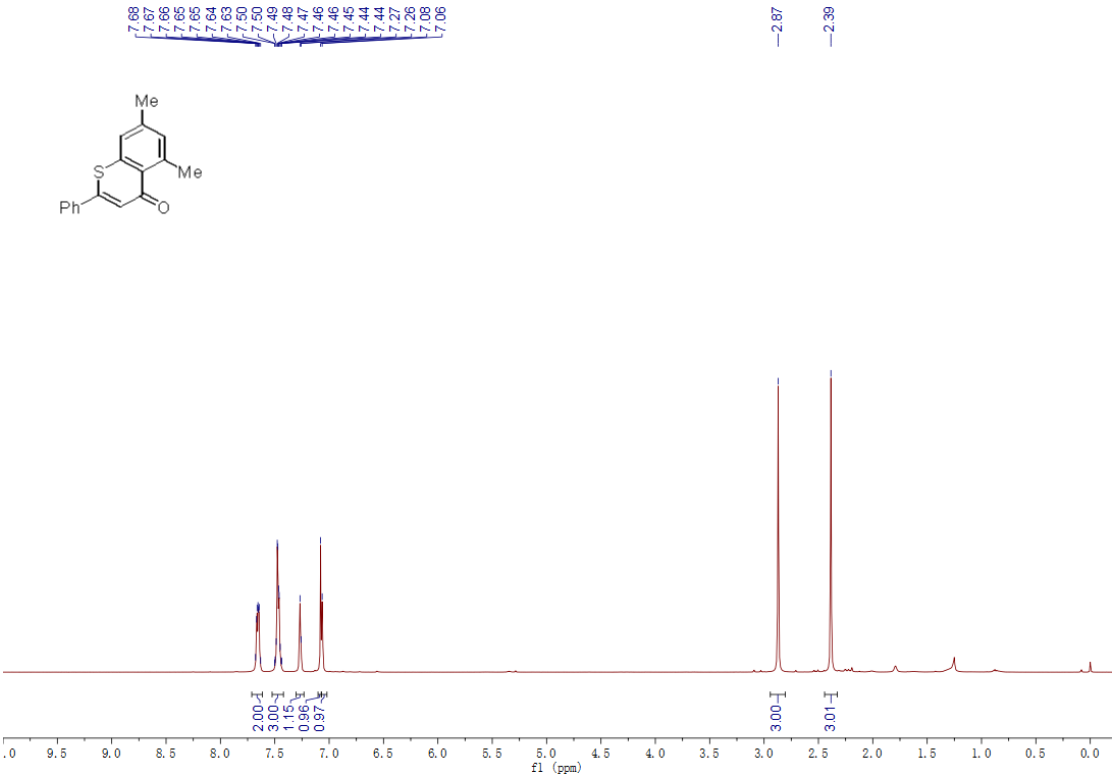


Supplementary Figure 33. ^{19}F NMR spectra of **3am**

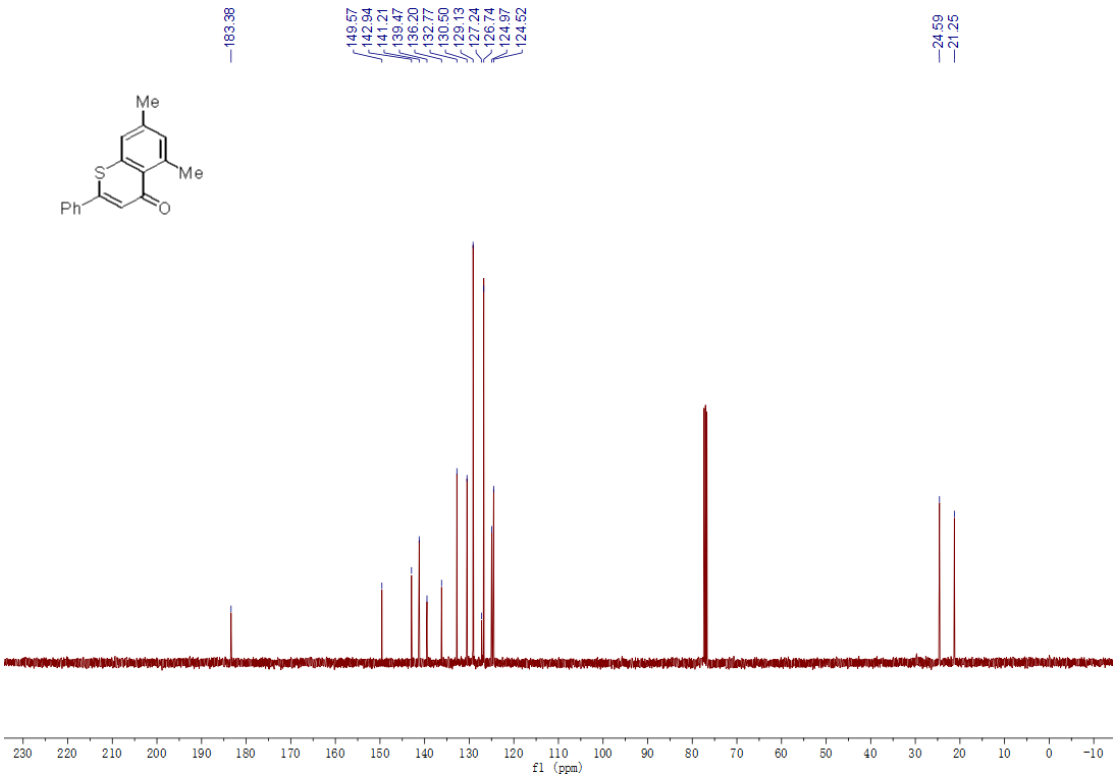


Supplementary Figure 34. ^{13}C NMR spectra of **3am**

5,7-dimethyl-2-phenyl-4*H*-thiochromen-4-one (3an, *CDCl$_3$* as solvent)

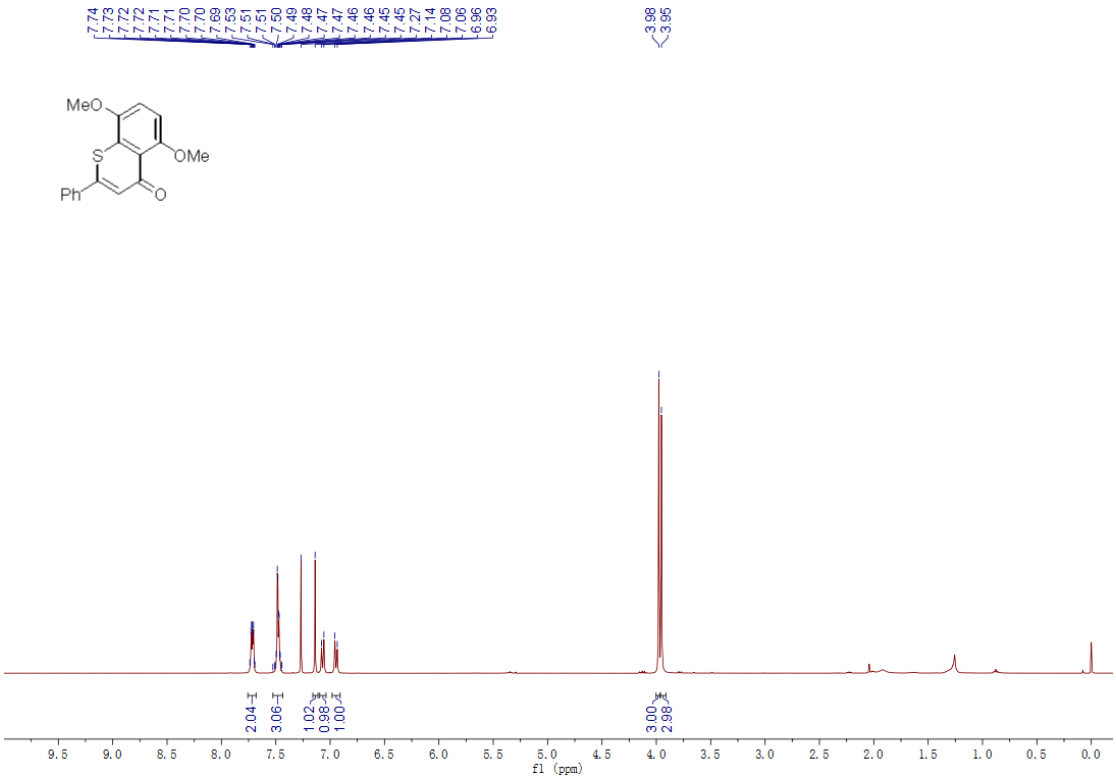


Supplementary Figure 35. ^{1}H NMR spectra of **3an**

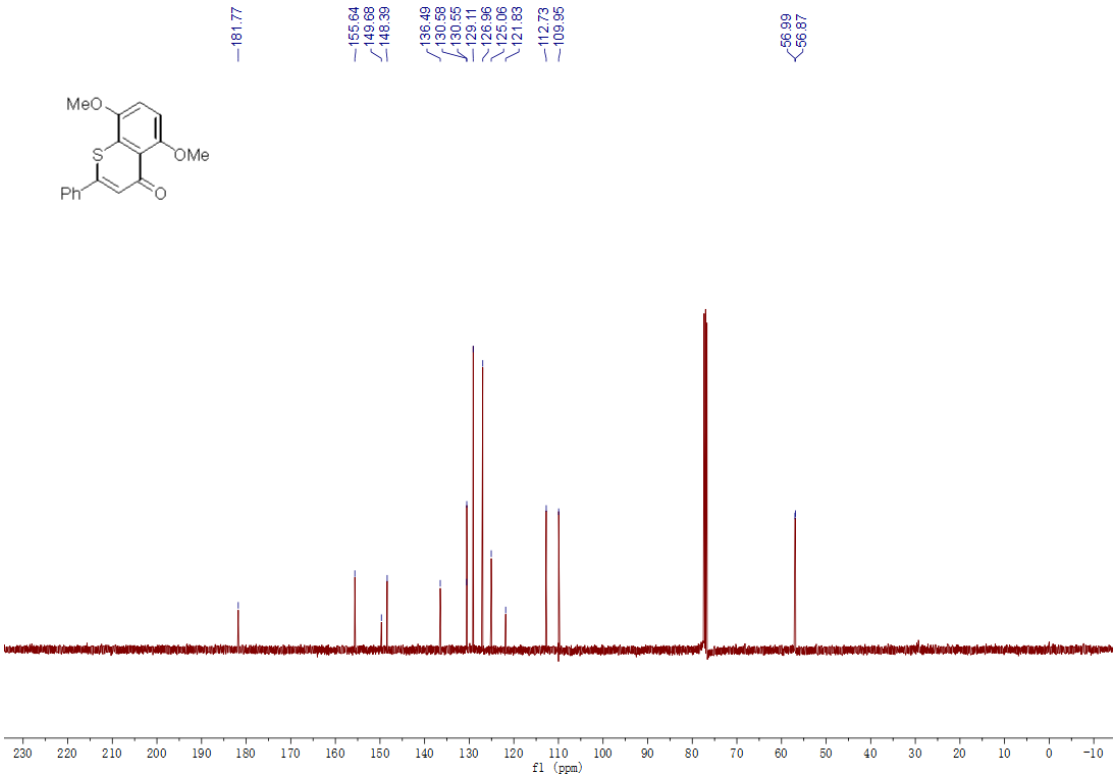


Supplementary Figure 36. ^{13}C NMR spectra of **3an**

5,8-dimethoxy-2-phenyl-4*H*-thiochromen-4-one (3ao, *$CDCl_3$* as solvent)

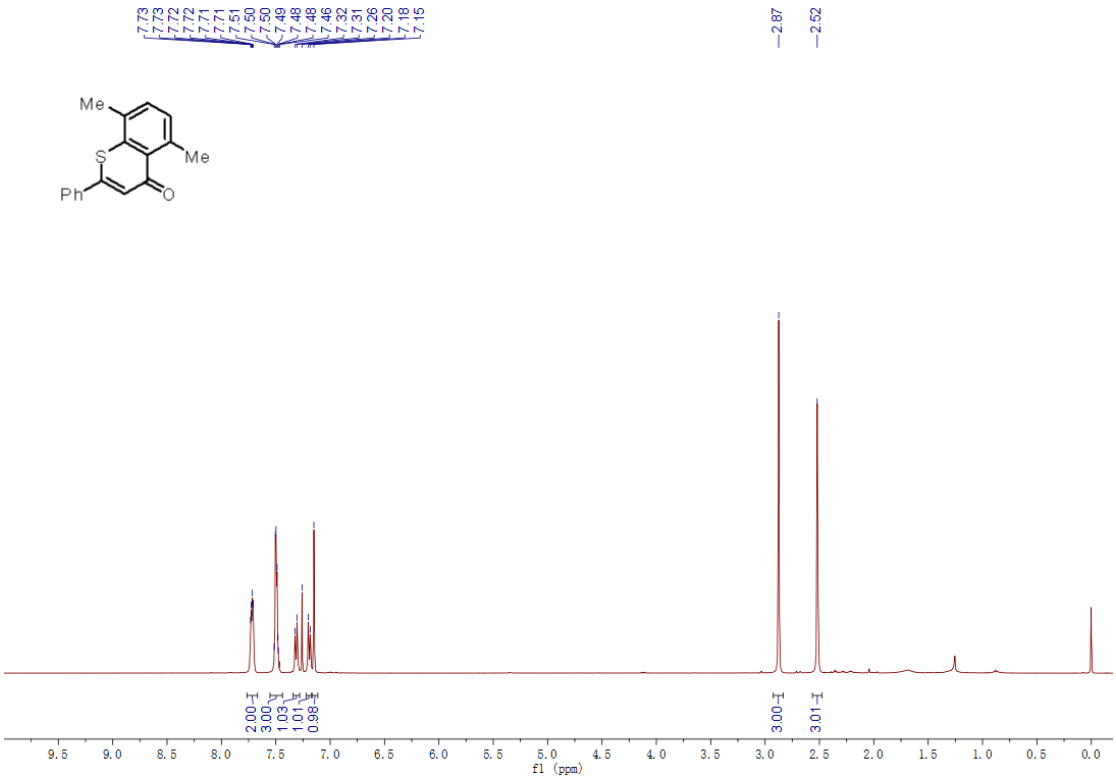


Supplementary Figure 37. ^{1}H NMR spectra of **3ao**

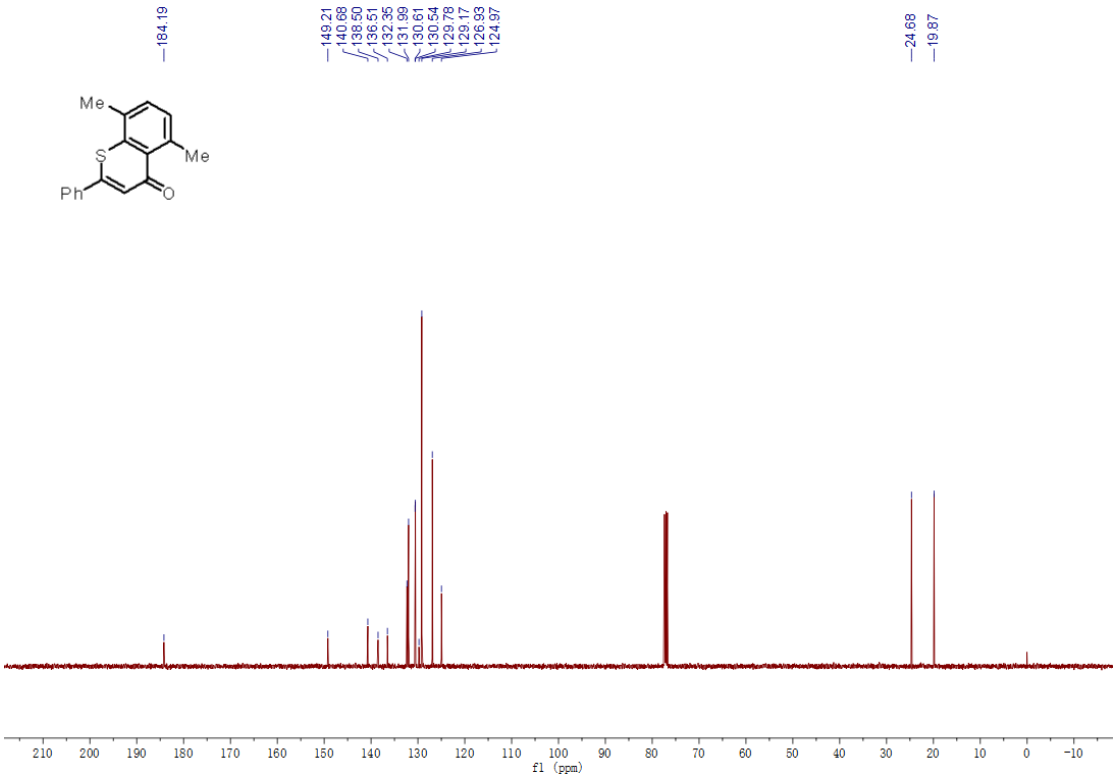


Supplementary Figure 38. ^{13}C NMR spectra of **3ao**

5,8-dimethyl-2-phenyl-4H-thiochromen-4-one (3ap, *CDCl$_3$* as solvent)

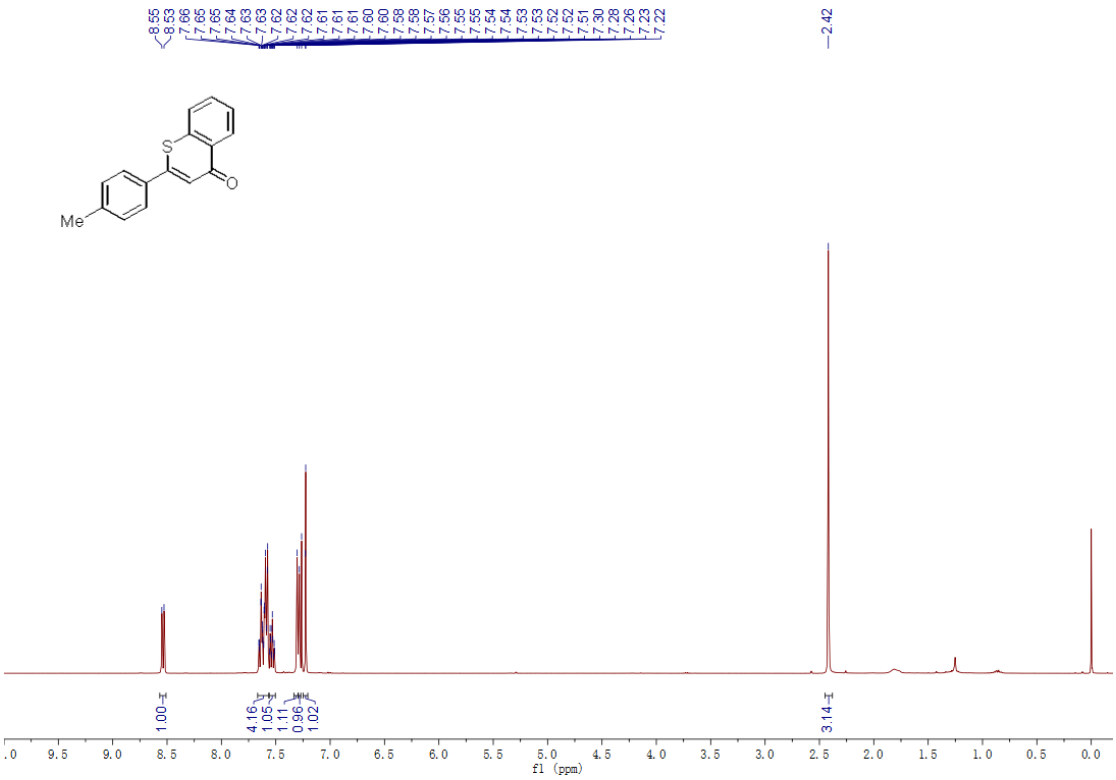


Supplementary Figure 39. ^{1}H NMR spectra of **3ap**

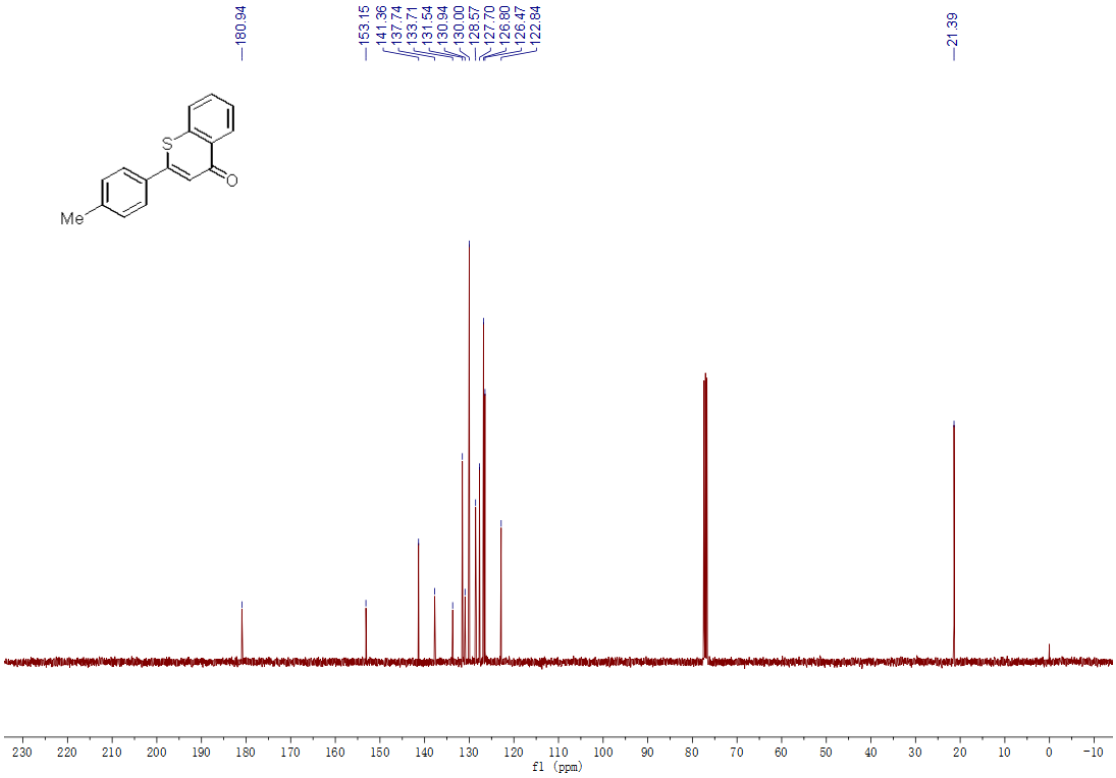


Supplementary Figure 40. ^{13}C NMR spectra of **3ap**

2-(*p*-tolyl)-4*H*-thiochromen-4-one (3ba, *CDCl*$_3$ as solvent)

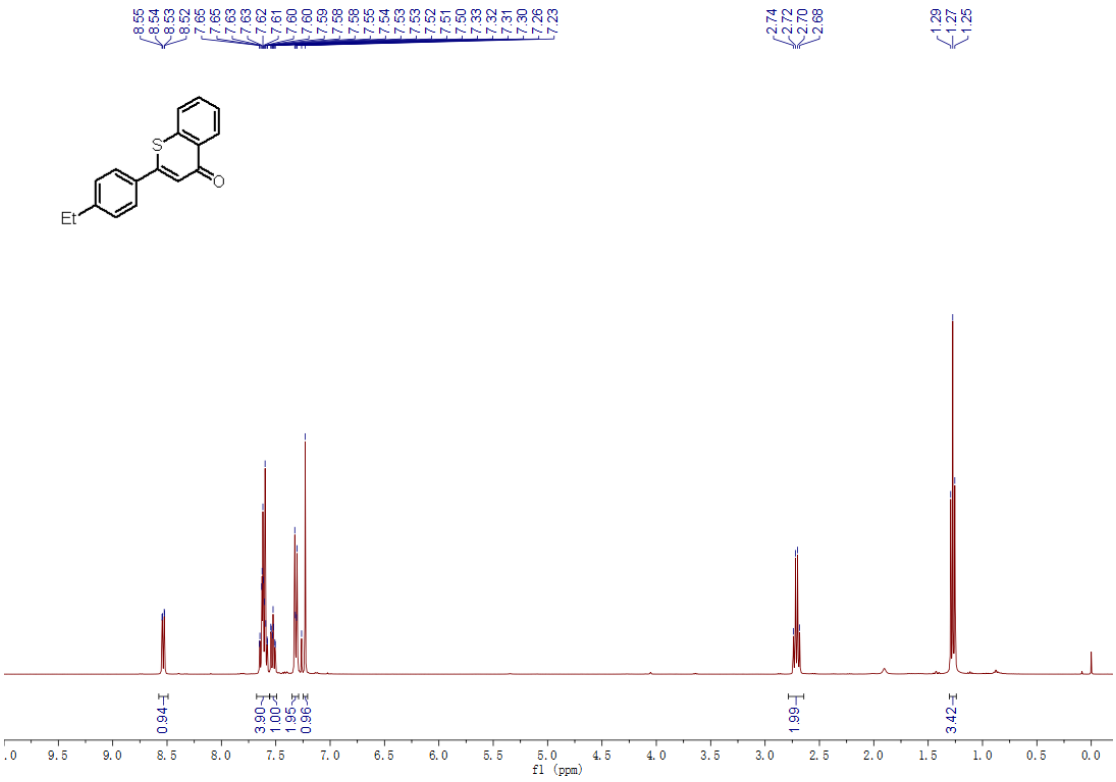


Supplementary Figure 41. ^{1}H NMR spectra of **3ba**

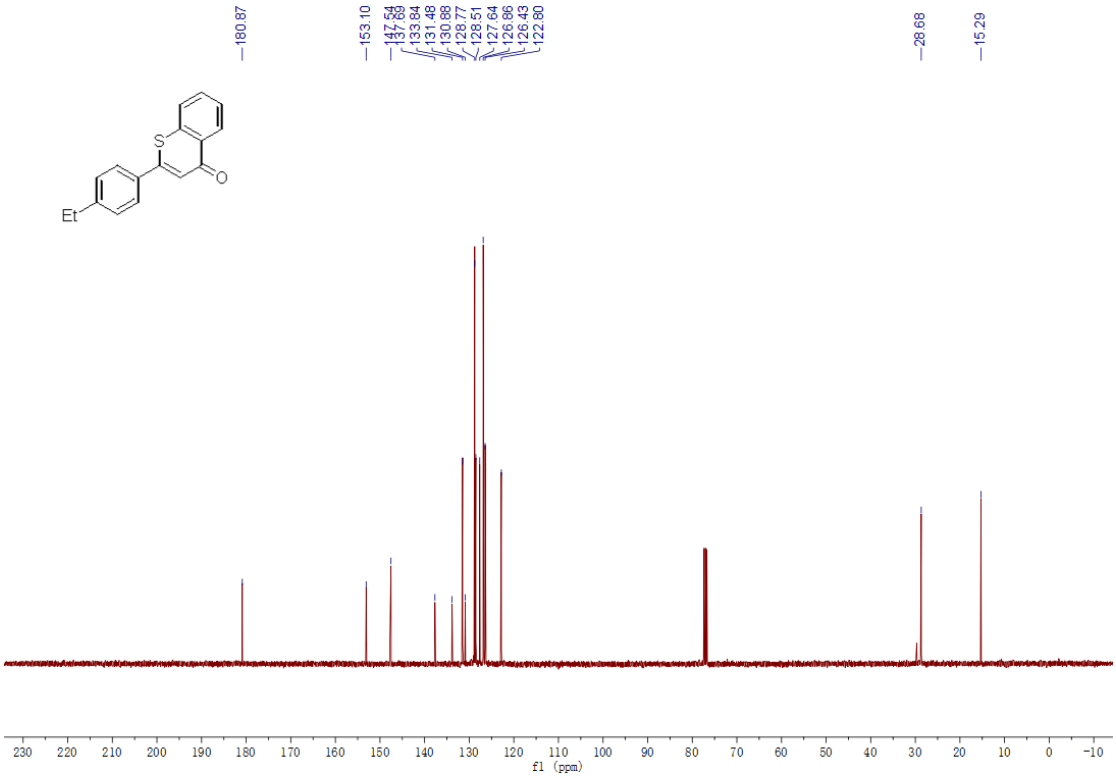


Supplementary Figure 42. ^{13}C NMR spectra of **3ba**

2-(4-ethylphenyl)-4*H*-thiochromen-4-one (3ca, $CDCl_3$ as solvent)

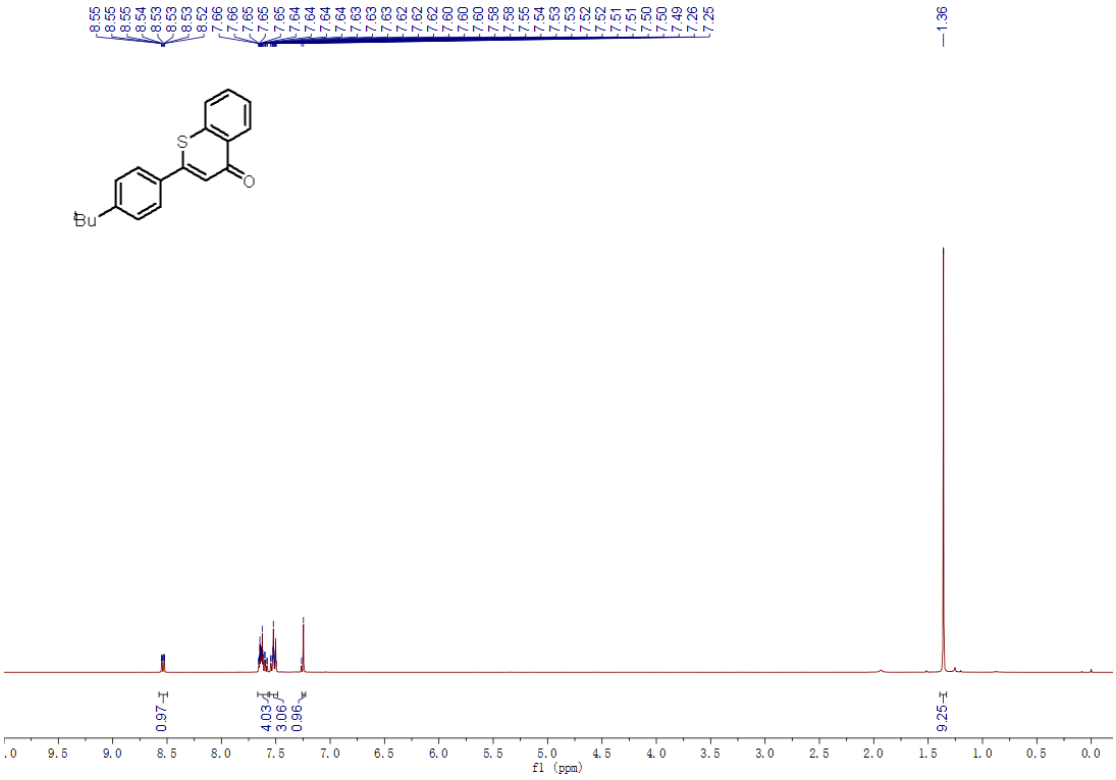


Supplementary Figure 43. ^{1}HNMR spectra of **3ca**

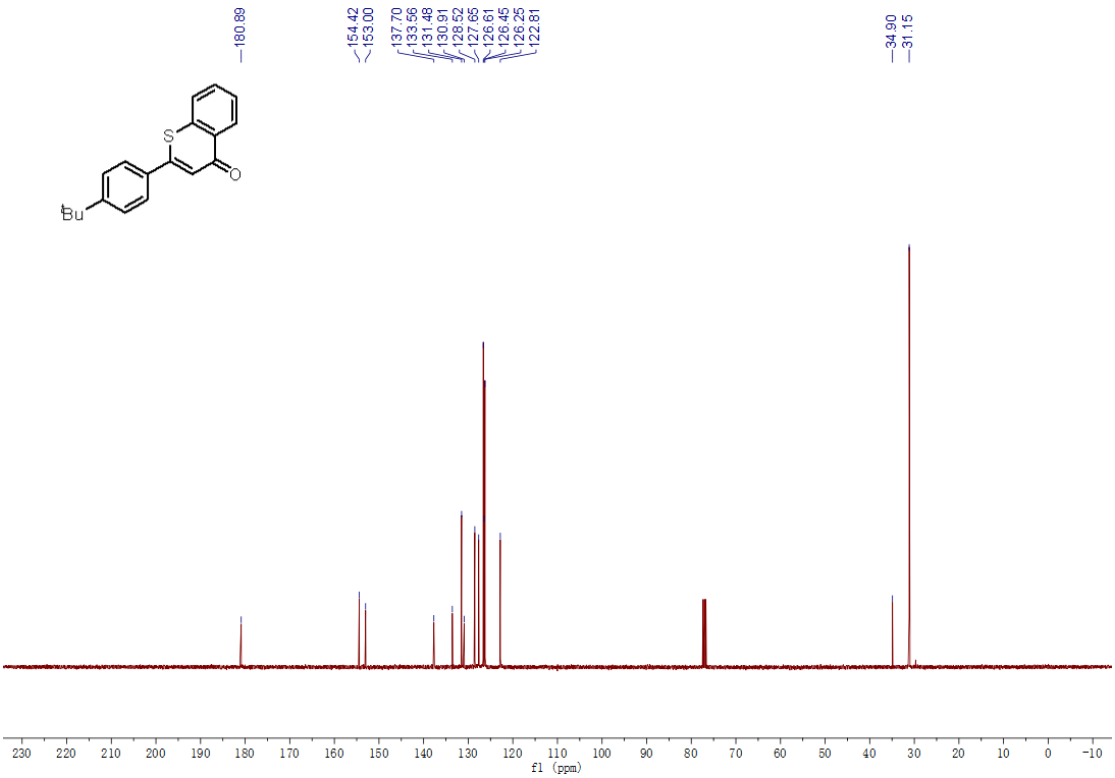


Supplementary Figure 44. ^{13}C NMR spectra of **3ca**

2-(4-(*tert*-butyl)phenyl)-4*H*-thiochromen-4-one (3da, $CDCl_3$ as solvent)

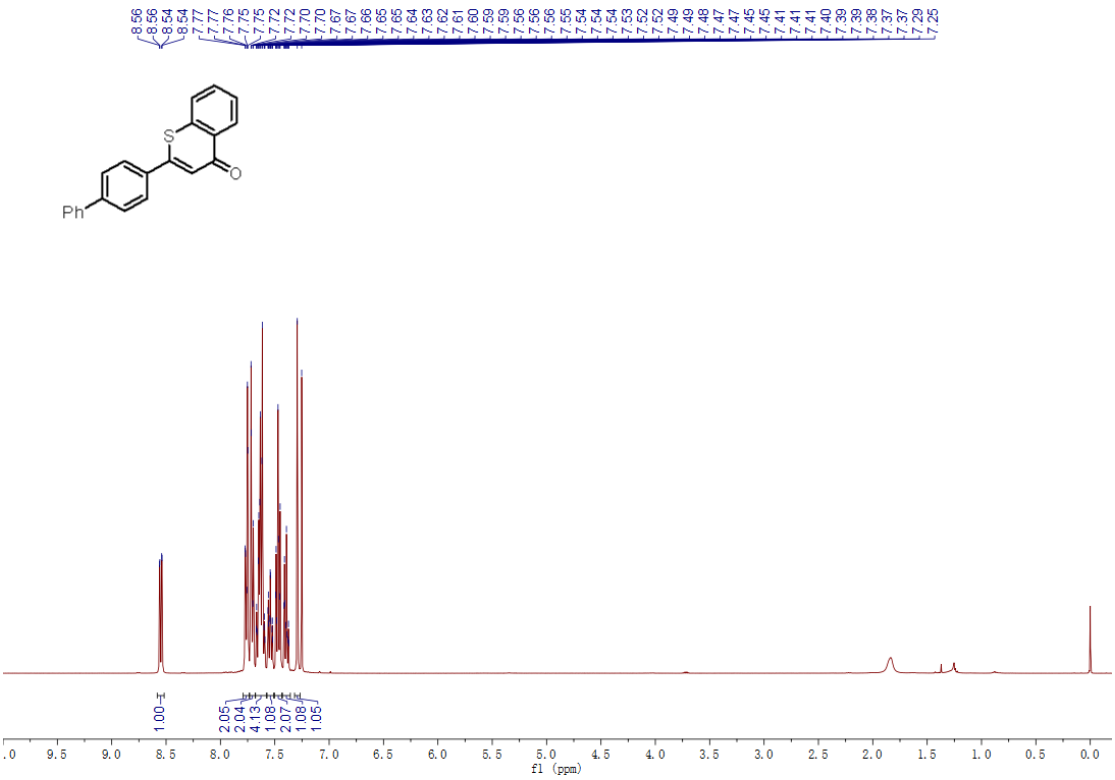


Supplementary Figure 45. ^{1}H NMR spectra of **3da**

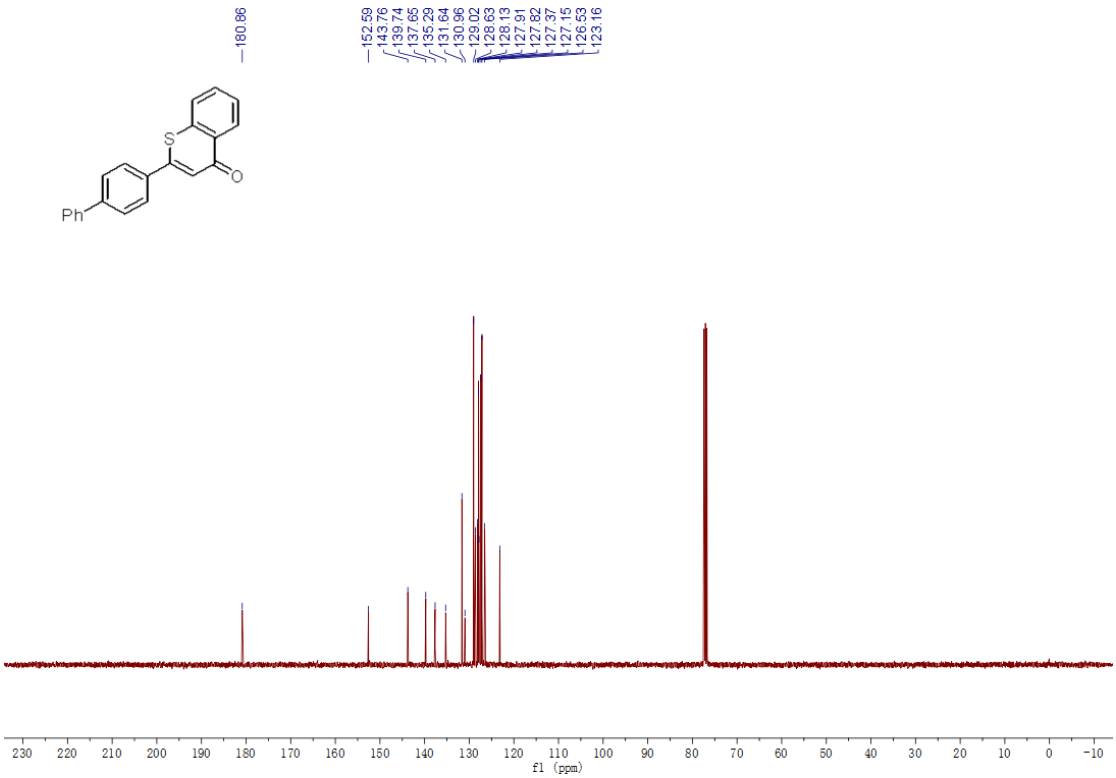


Supplementary Figure 46. ^{13}C NMR spectra of **3da**

2-([1,1'-biphenyl]-4-yl)-4*H*-thiochromen-4-one (3ea, *$CDCl_3$* as solvent)

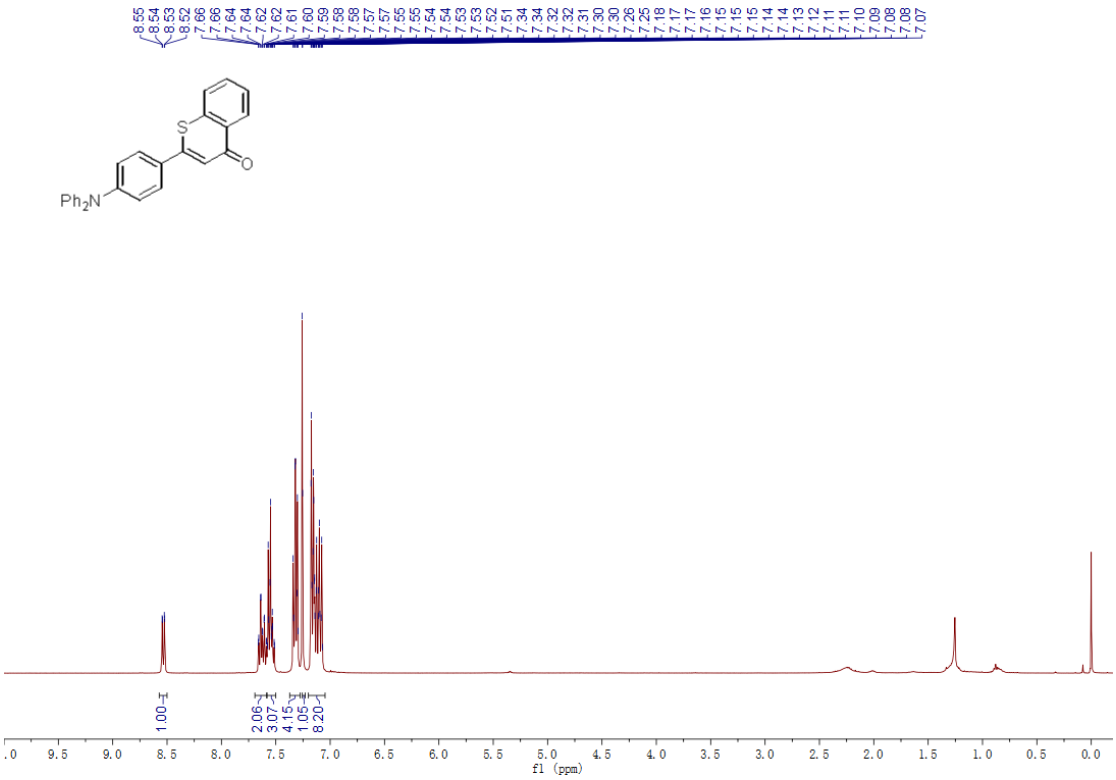


Supplementary Figure 47. ^{1}H NMR spectra of **3ea**

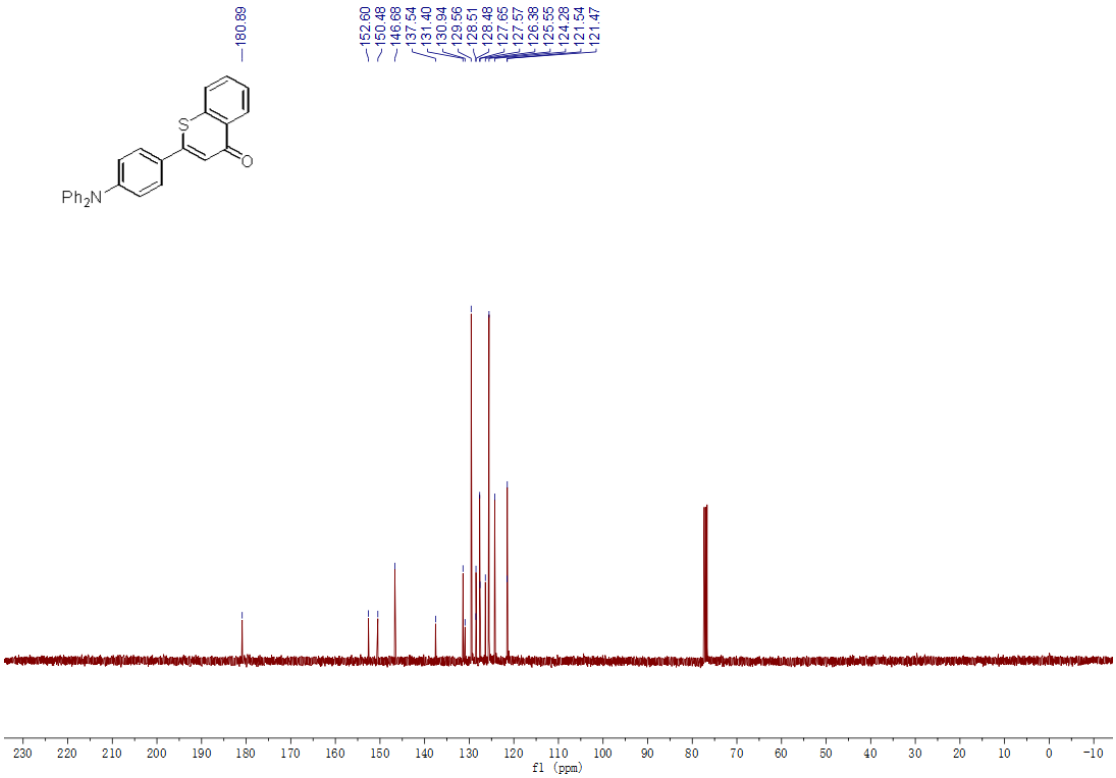


Supplementary Figure 48. ^{13}C NMR spectra of **3ea**

2-(4-(diphenylamino)phenyl)-4*H*-thiochromen-4-one (3fa, *CDCl$_3$* as solvent)

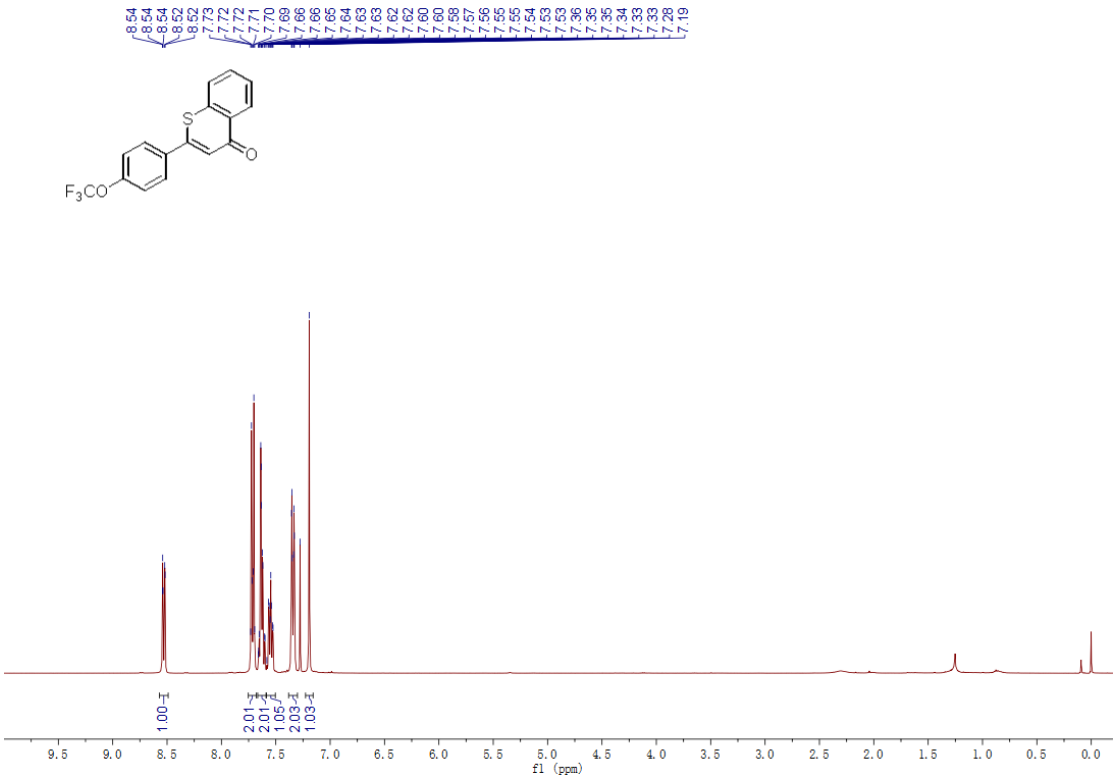


Supplementary Figure 49. ^{1}H NMR spectra of **3fa**

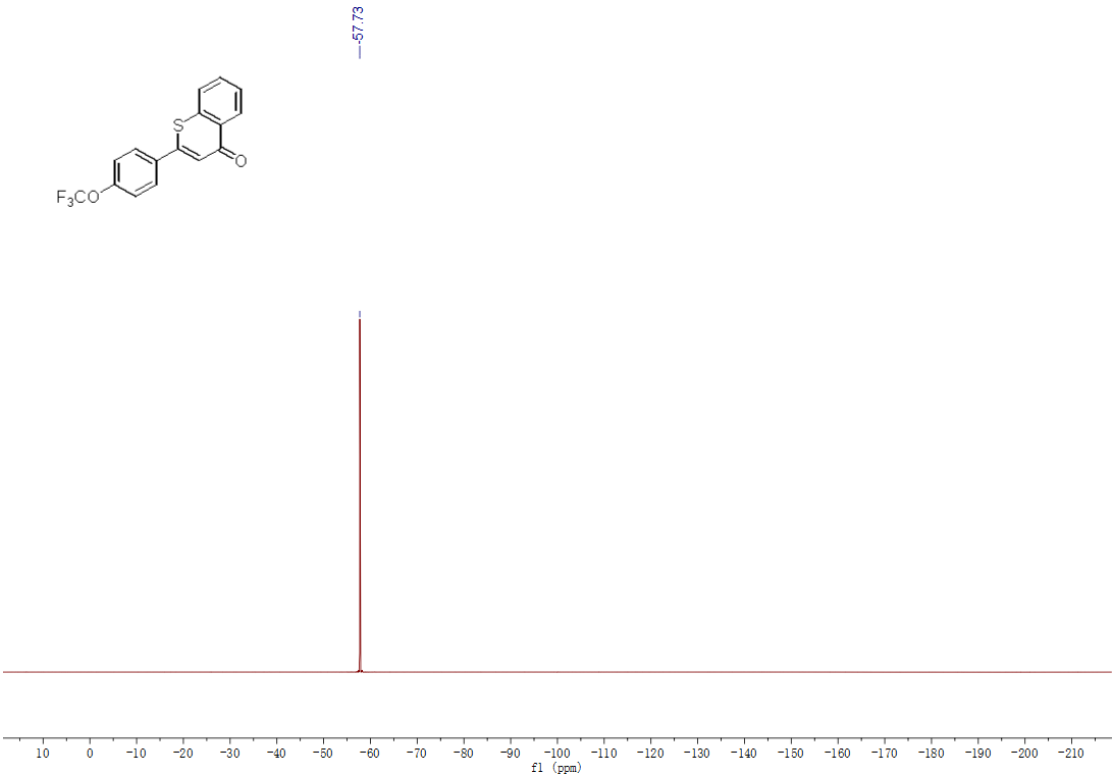


Supplementary Figure 50. ^{13}C NMR spectra of **3fa**

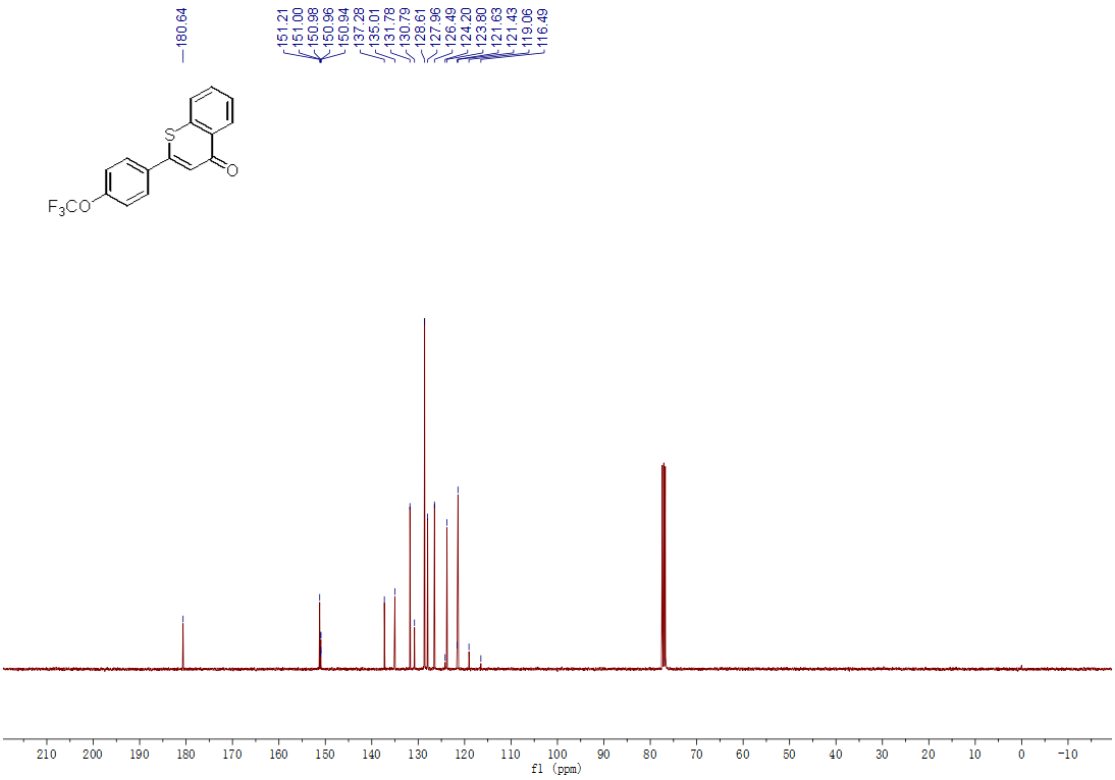
2-(4-(trifluoromethoxy)phenyl)-4*H*-thiochromen-4-one (3ga, *CDCl$_3$* as solvent)



Supplementary Figure 51. ^{1}H NMR spectra of **3ga**

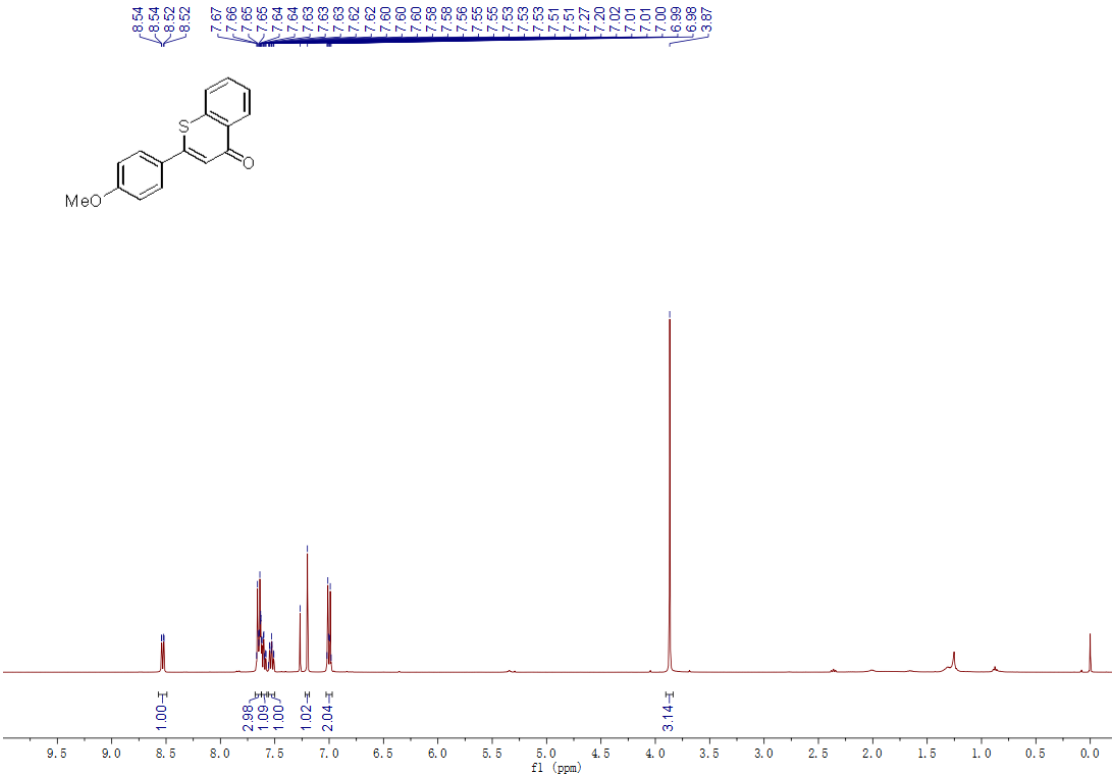


Supplementary Figure 52. ^{19}F NMR spectra of **3ga**

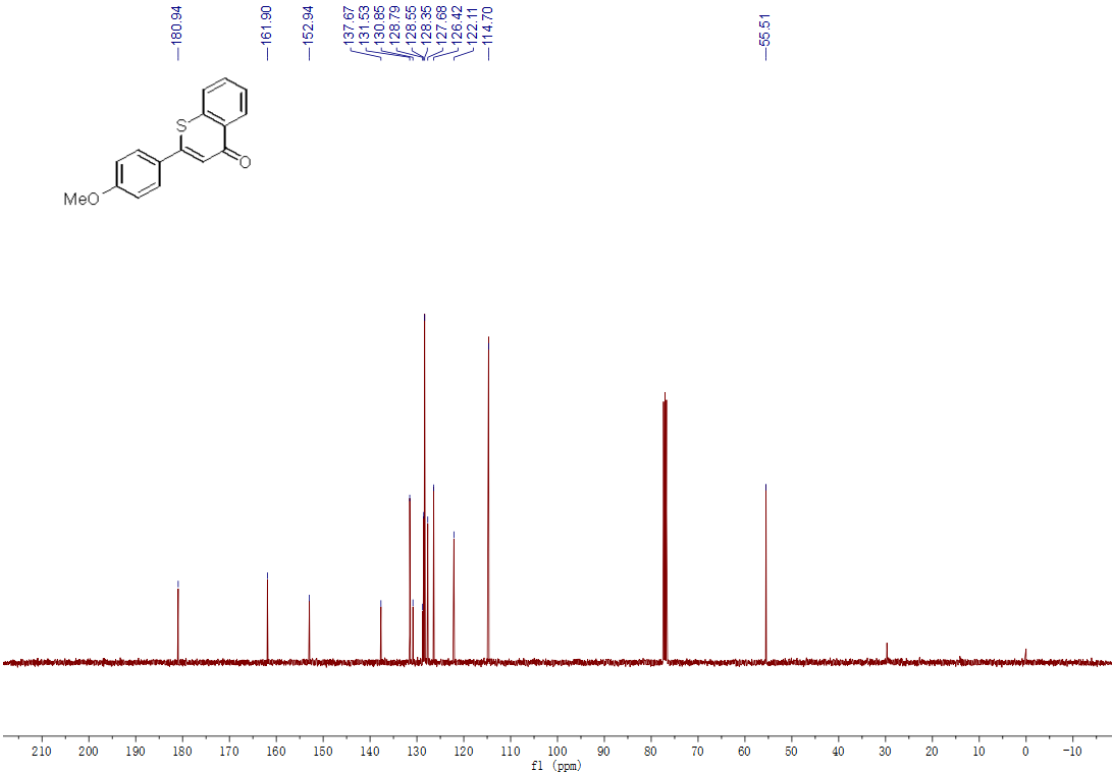


Supplementary Figure 53. ^{13}C NMR spectra of **3ga**

2-(4-methoxyphenyl)-4*H*-thiochromen-4-one (3ha, $CDCl_3$ as solvent)

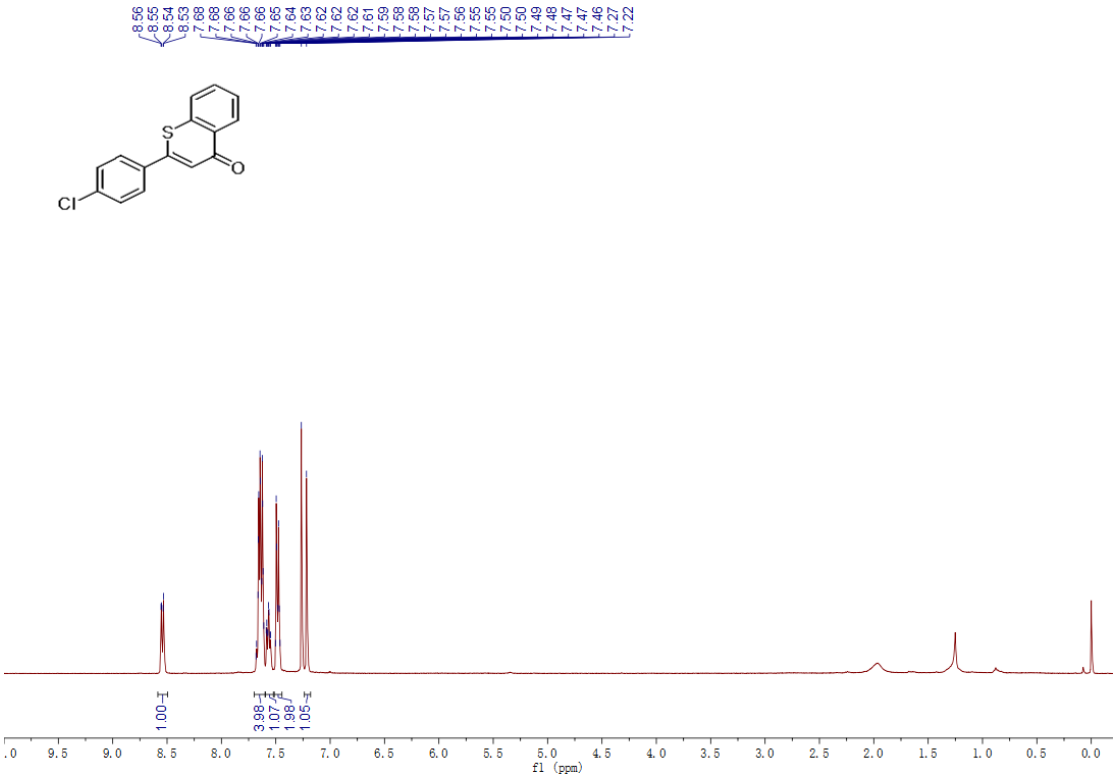


Supplementary Figure 54. ^{1}H NMR spectra of **3ha**

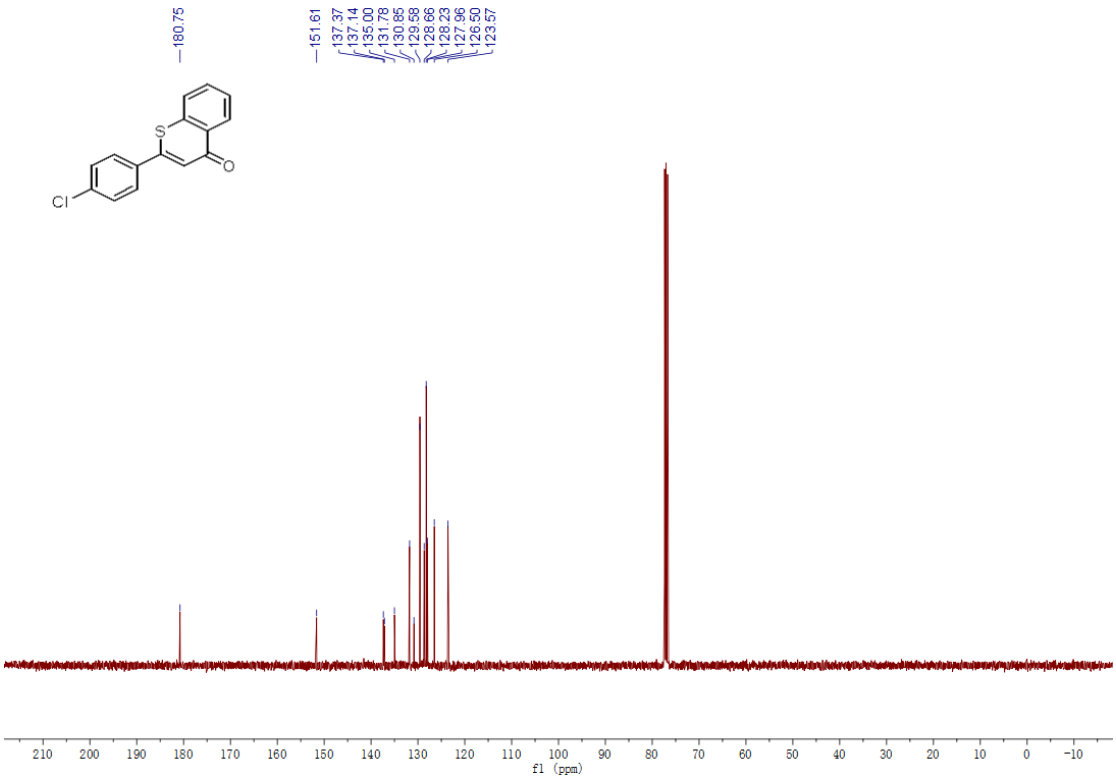


Supplementary Figure 55. ^{13}C NMR spectra of **3ha**

2-(4-chlorophenyl)-4*H*-thiochromen-4-one (3ia, $CDCl_3$ as solvent)

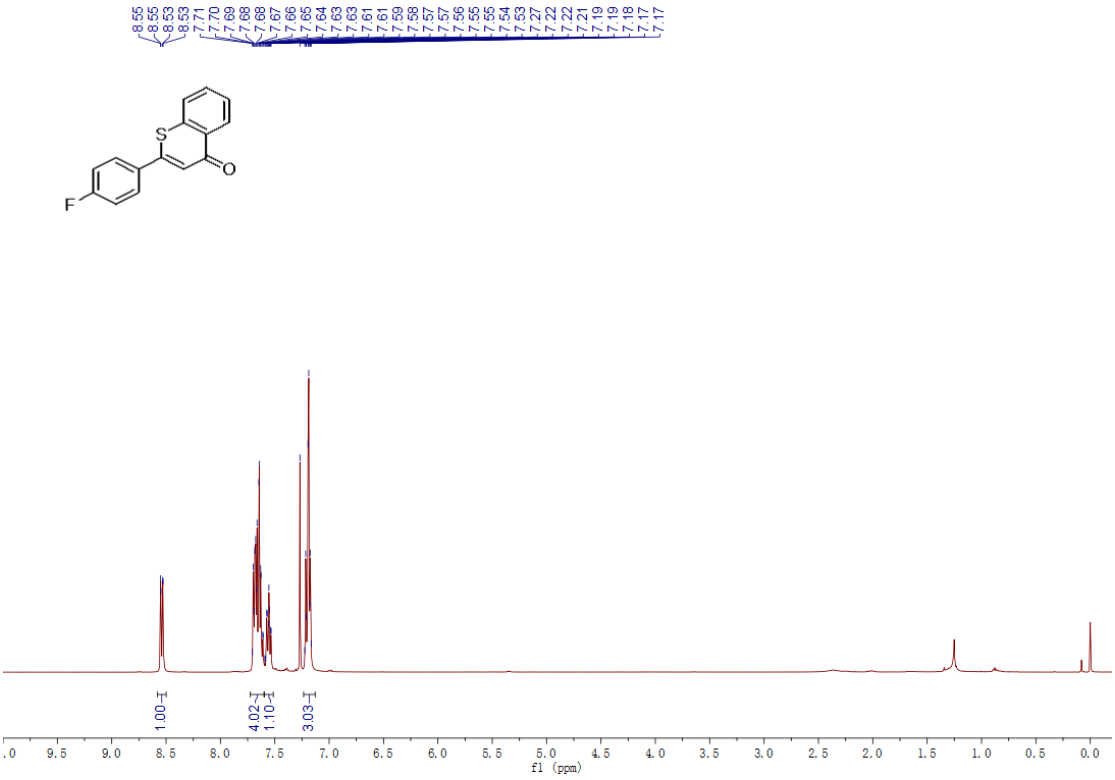


Supplementary Figure 56. ^{1}H NMR spectra of **3ia**

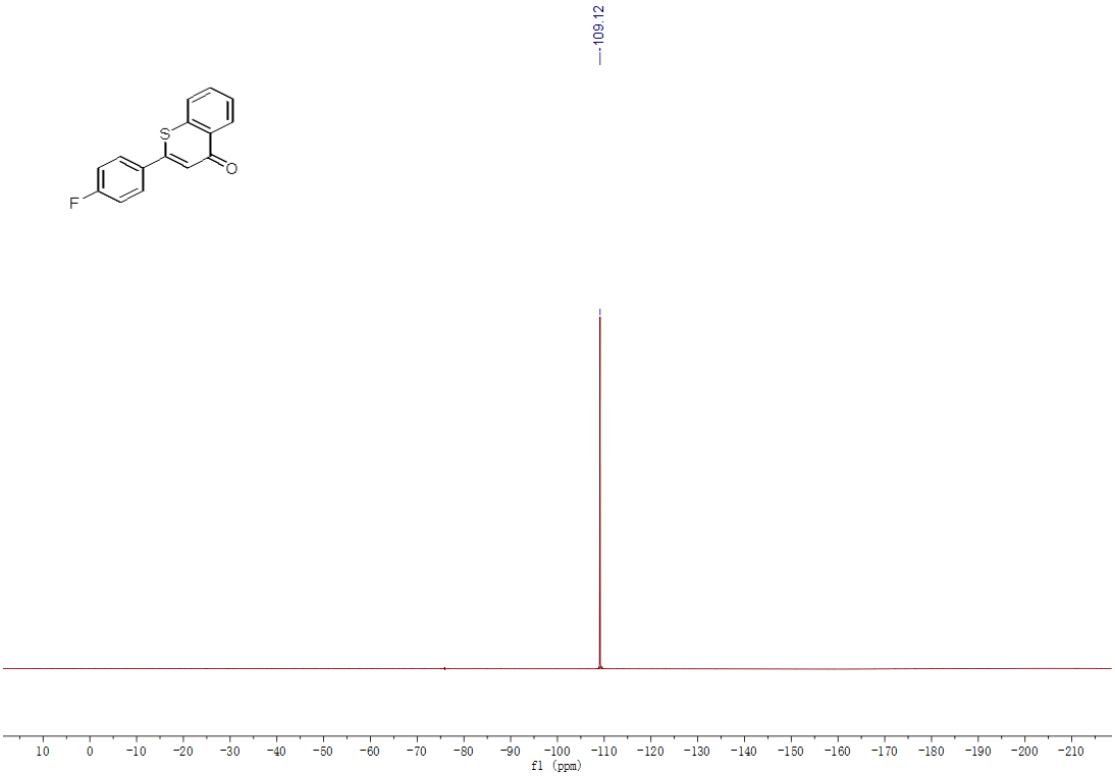


Supplementary Figure 57. ^{13}C NMR spectra of **3ia**

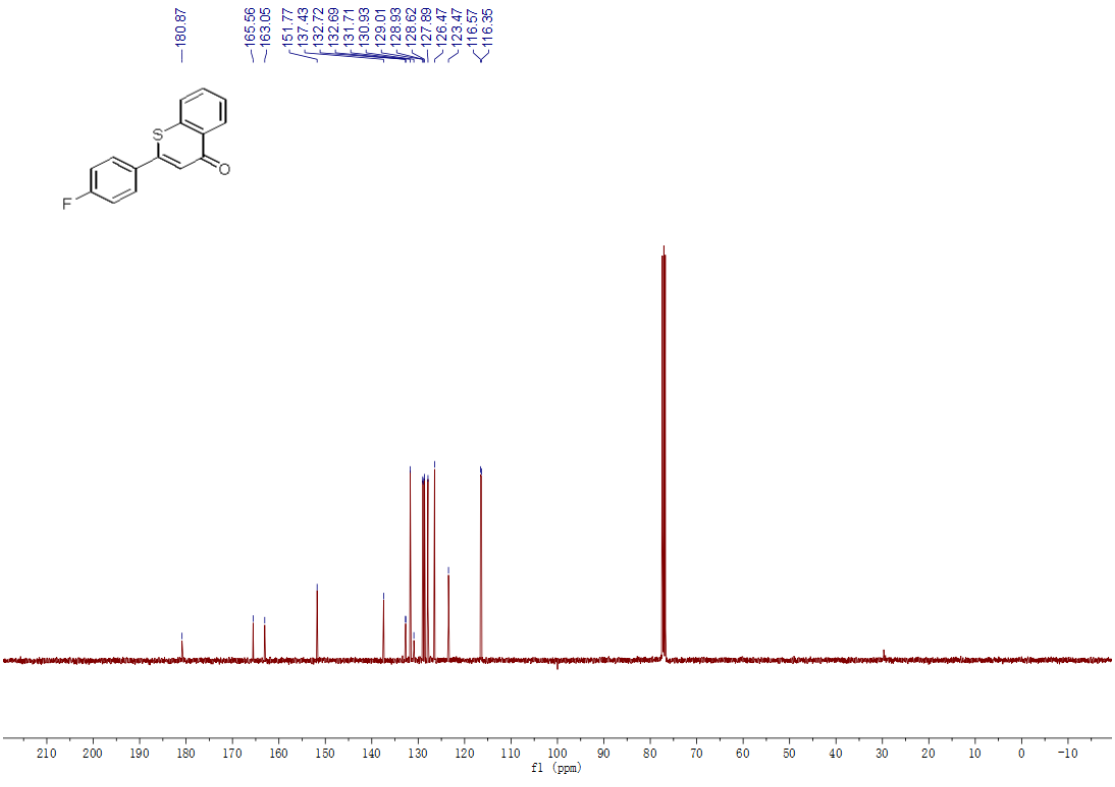
2-(4-fluorophenyl)-4*H*-thiochromen-4-one (3ja, *$CDCl_3$* as solvent)



Supplementary Figure 58. ^{1}H NMR spectra of **3ja**

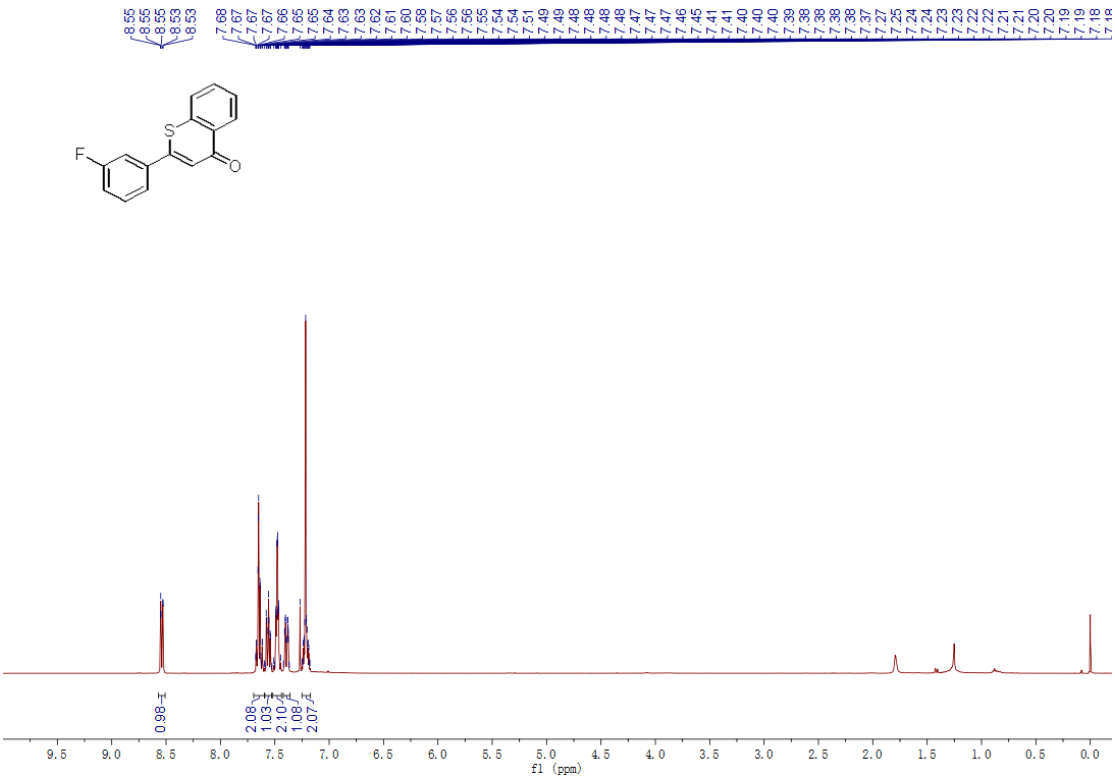


Supplementary Figure 59. ^{19}F NMR spectra of **3ja**



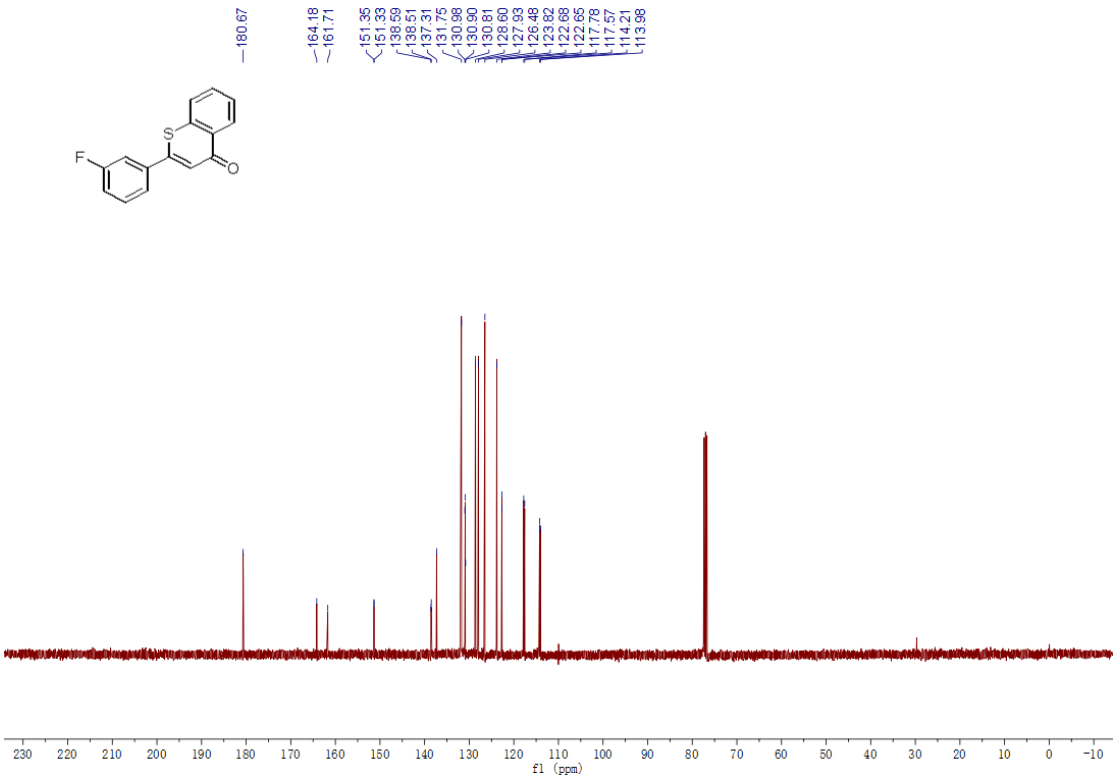
Supplementary Figure 60. ^{13}C NMR spectra of **3ja**

2-(3-fluorophenyl)-4*H*-thiochromen-4-one (3ka, *$CDCl_3$* as solvent)



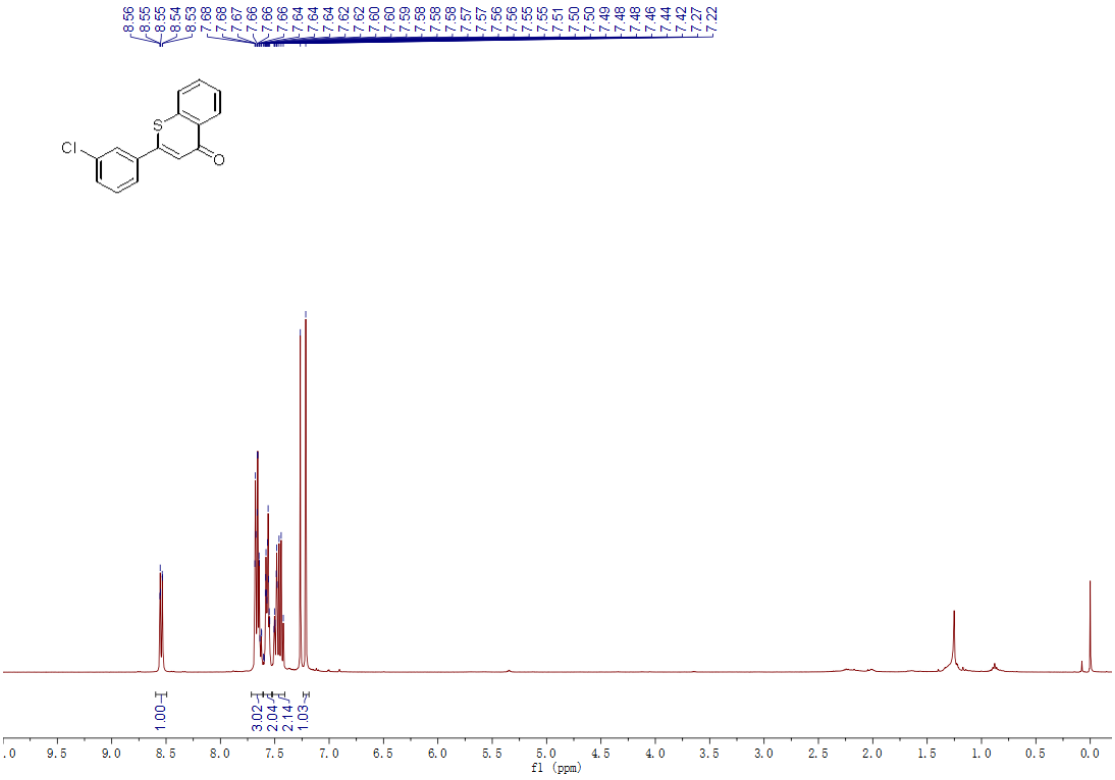
Supplementary Figure 61. ^{1}H NMR spectra of **3ka**

Supplementary Figure 62. ^{19}F NMR spectra of **3ka**

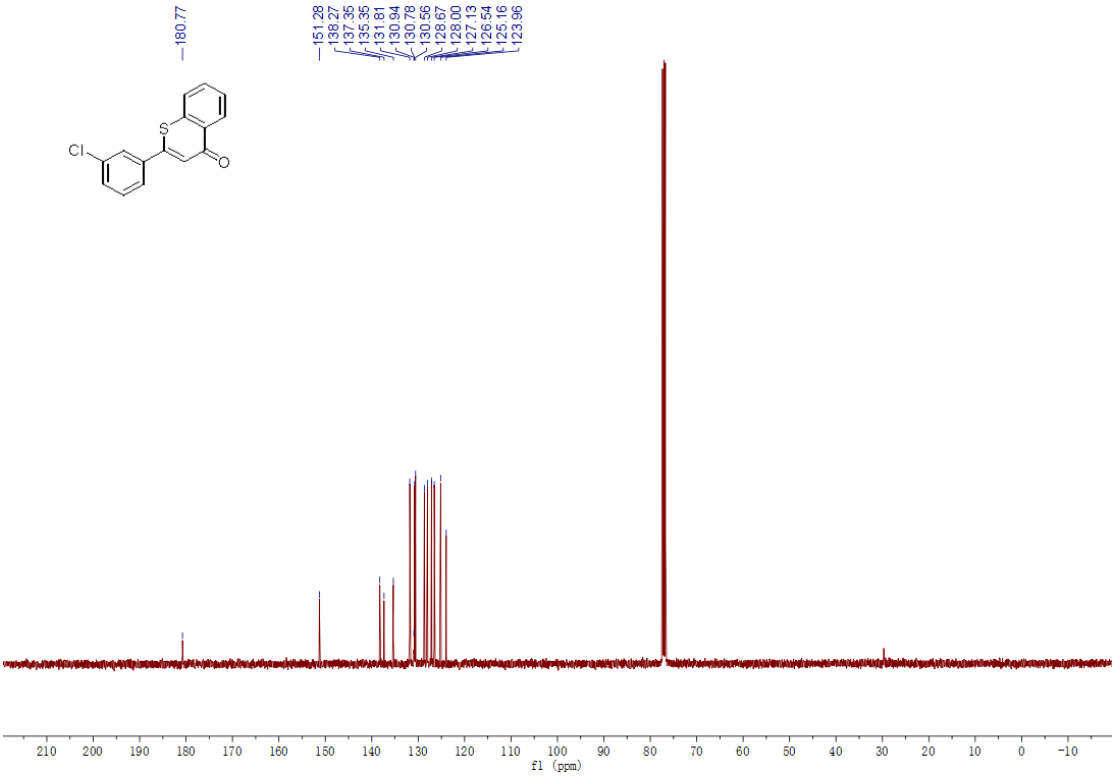


Supplementary Figure 63. ^{13}C NMR spectra of **3ka**

2-(3-chlorophenyl)-4*H*-thiochromen-4-one (3la, $CDCl_3$ as solvent)

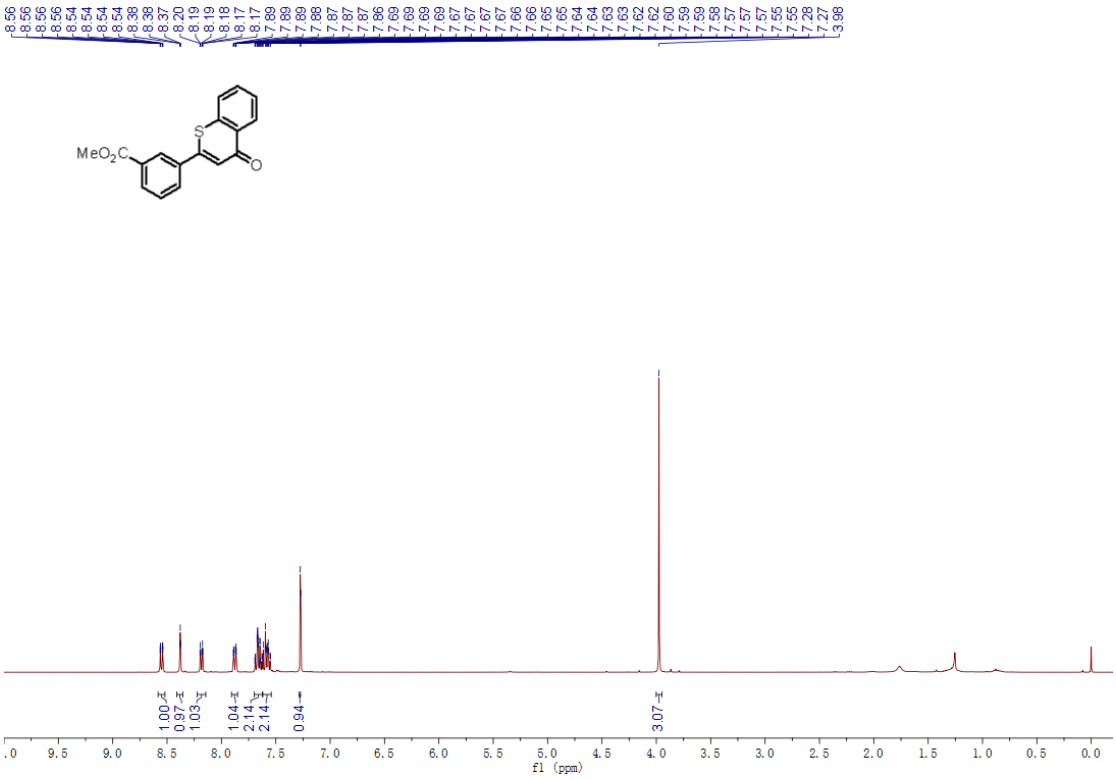


Supplementary Figure 64. ^{1}H NMR spectra of **3la**

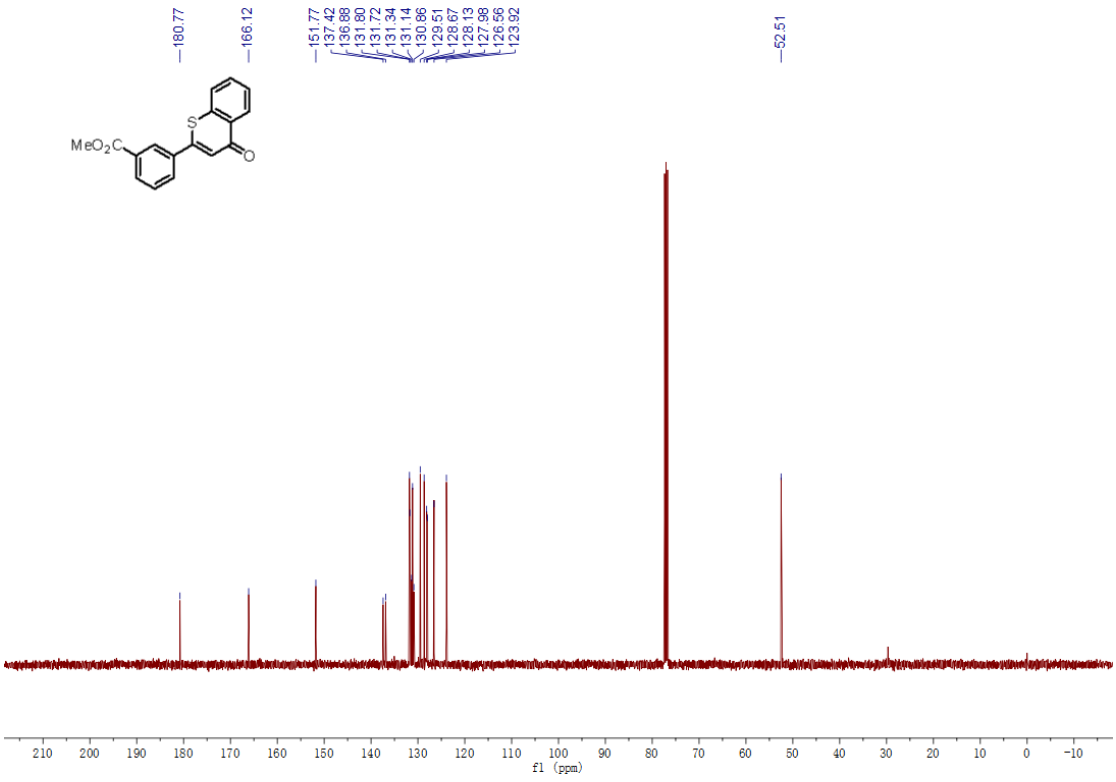


Supplementary Figure 65. ^{13}C NMR spectra of **3la**

methyl 3-(4-oxo-4*H*-thiochromen-2-yl)benzoate (3ma, *$CDCl_3$* as solvent)

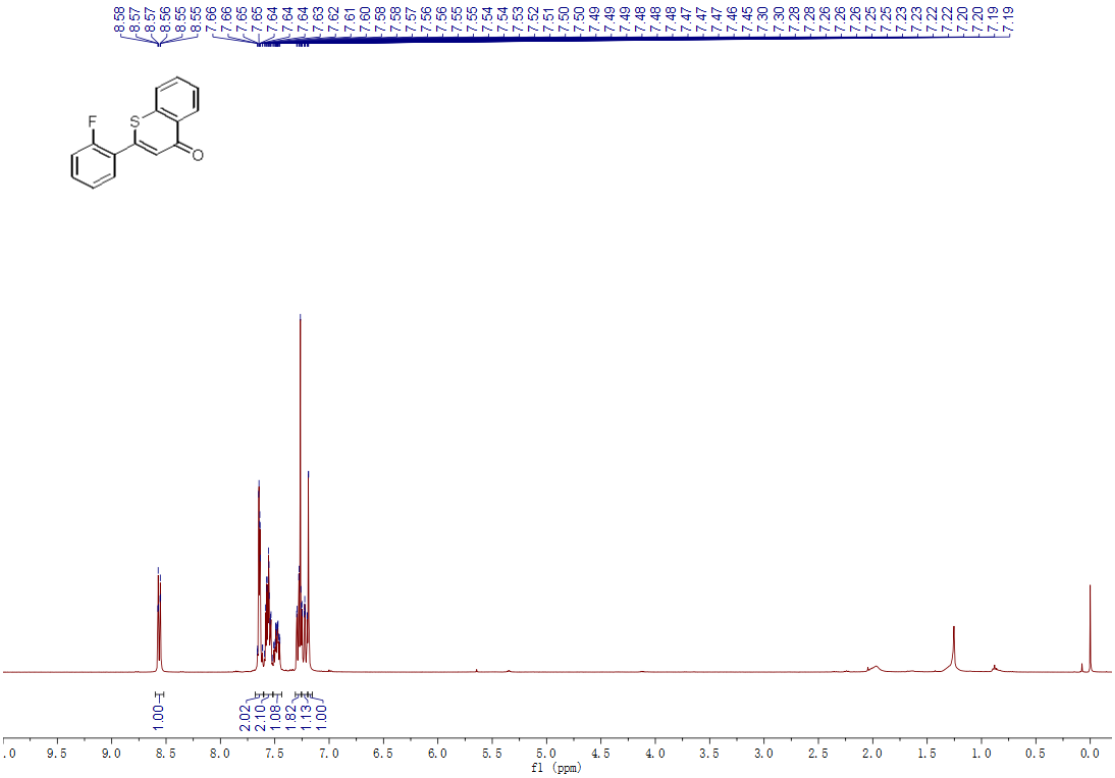


Supplementary Figure 66. ^{1}H NMR spectra of **3ma**

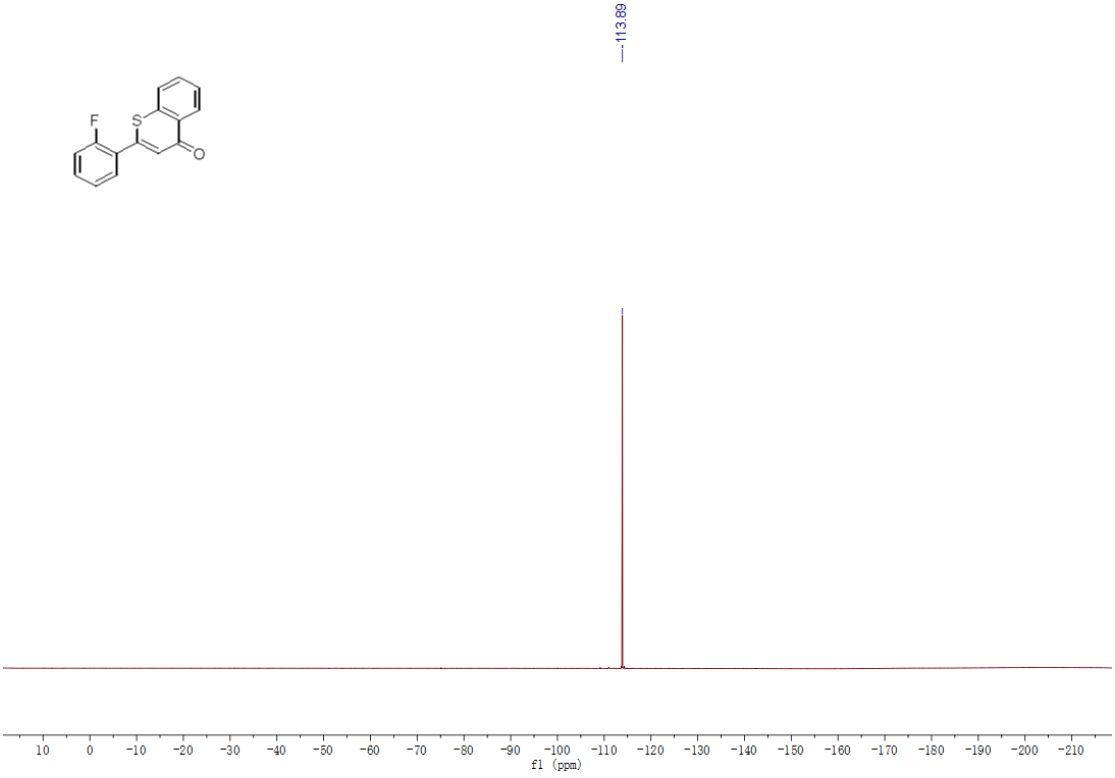


Supplementary Figure 67. ^{13}C NMR spectra of **3ma**

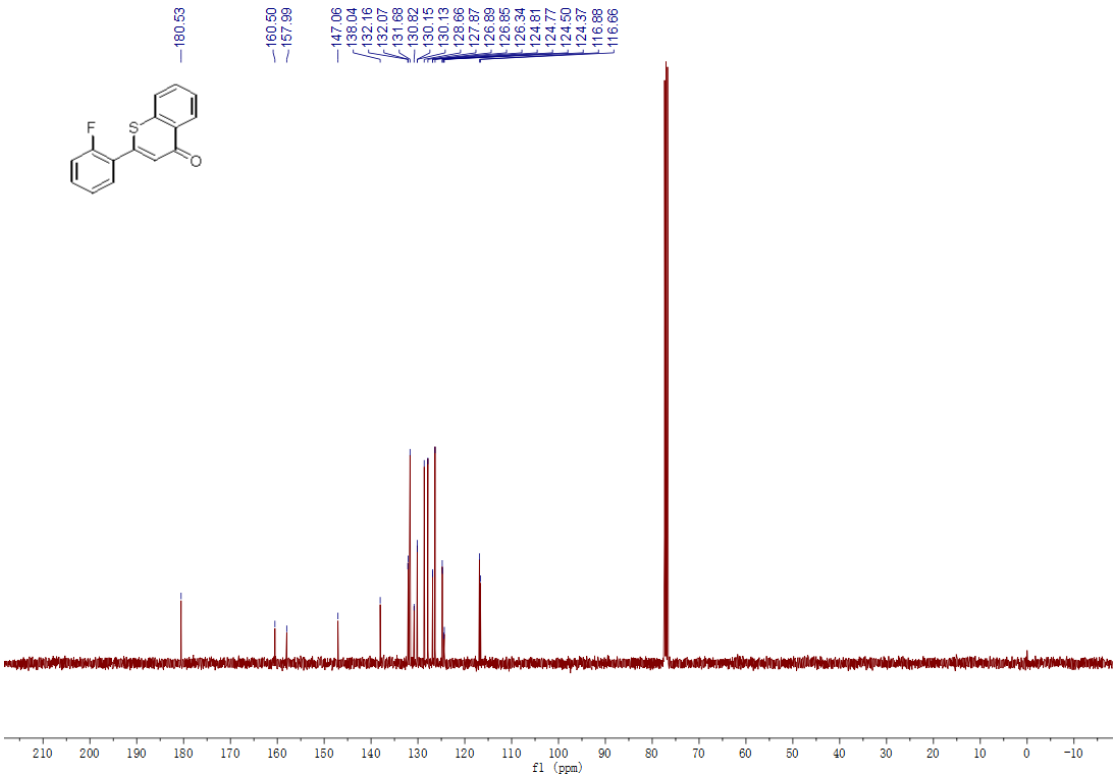
2-(2-fluorophenyl)-4*H*-thiochromen-4-one (3na, *CDCl$_3$* as solvent)



Supplementary Figure 68. ^{1}H NMR spectra of **3na**

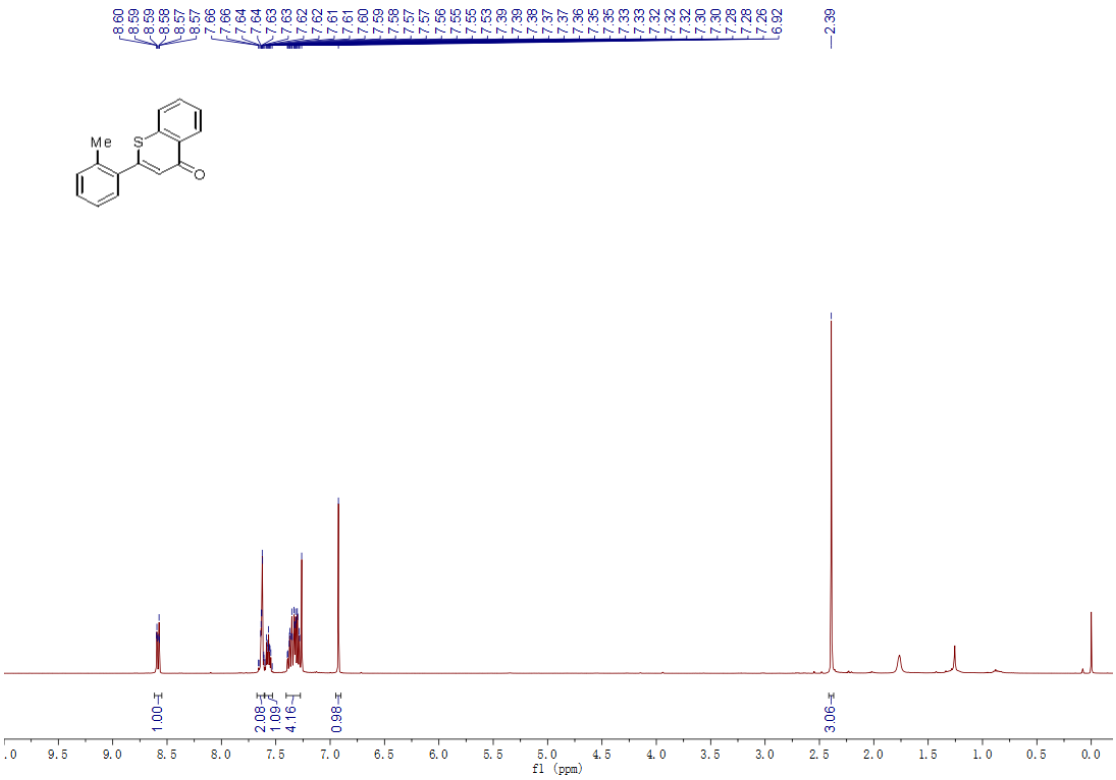


Supplementary Figure 69. ^{19}F NMR spectra of **3na**

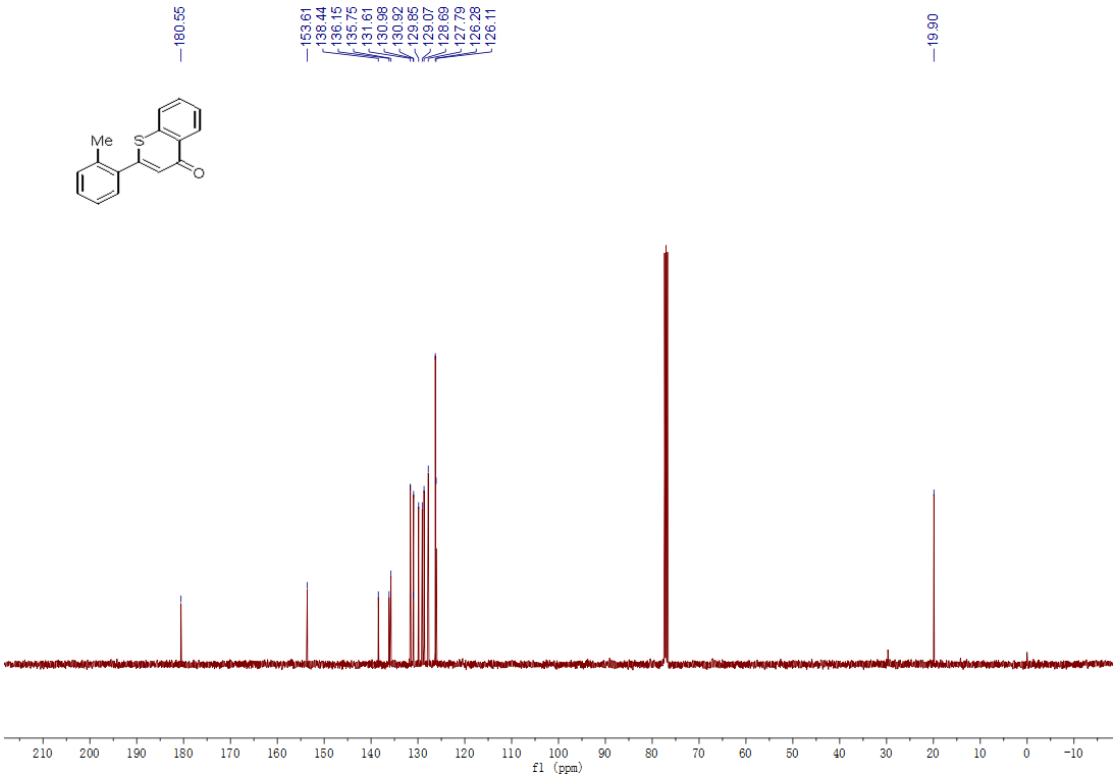


Supplementary Figure 70. ^{13}C NMR spectra of **3na**

2-(*o*-tolyl)-4*H*-thiochromen-4-one (3oa, *CDCl*$_3$ as solvent)

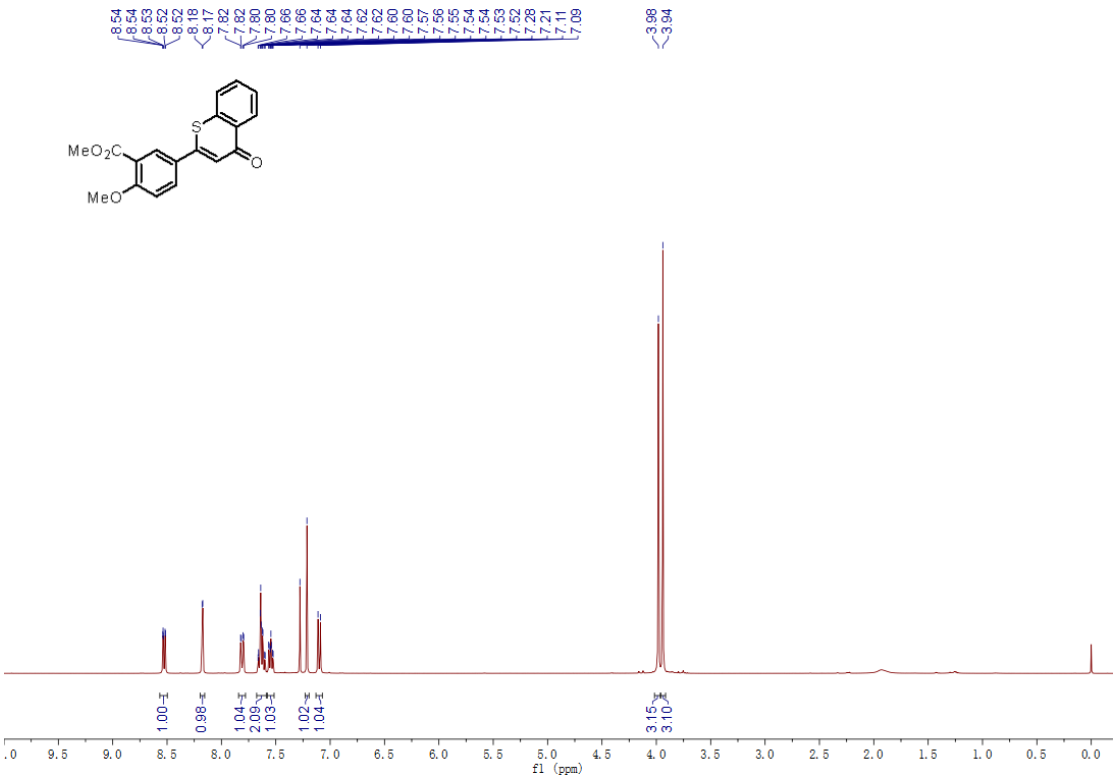


Supplementary Figure 71. ^{1}H NMR spectra of **3oa**

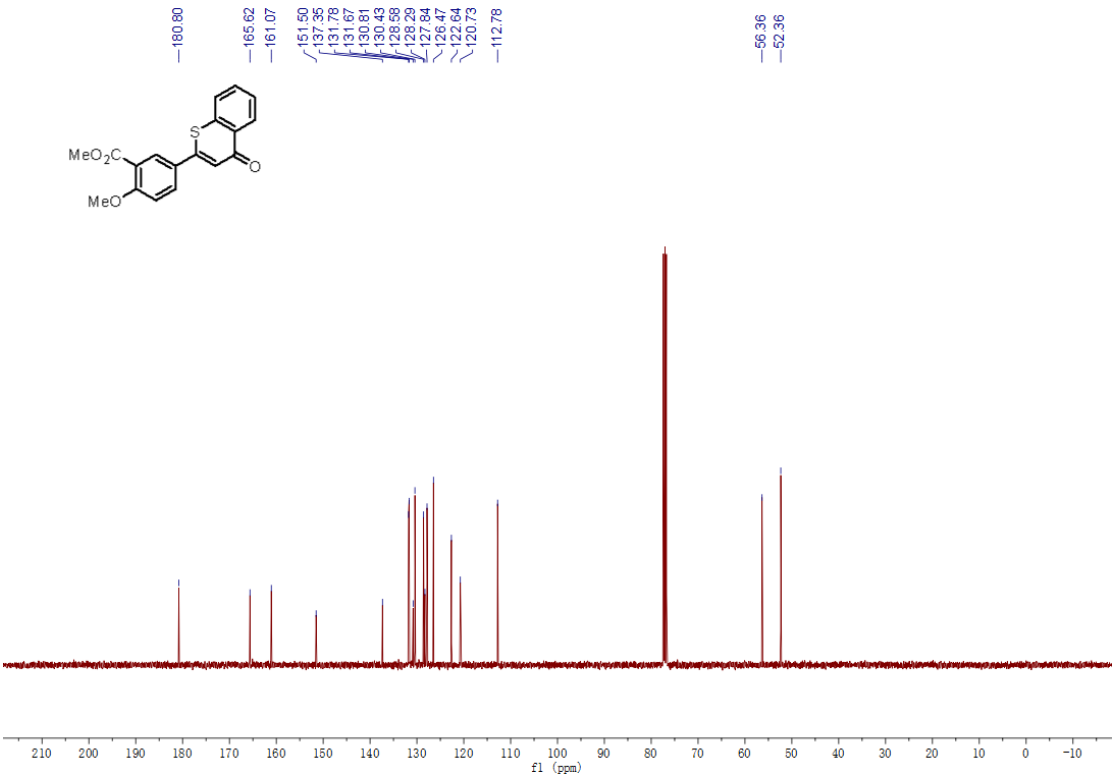


Supplementary Figure 72. ^{13}C NMR spectra of **3oa**

methyl 2-methoxy-5-(4-oxo-4*H*-thiochromen-2-yl)benzoate (3pa, *$CDCl_3$* as solvent)

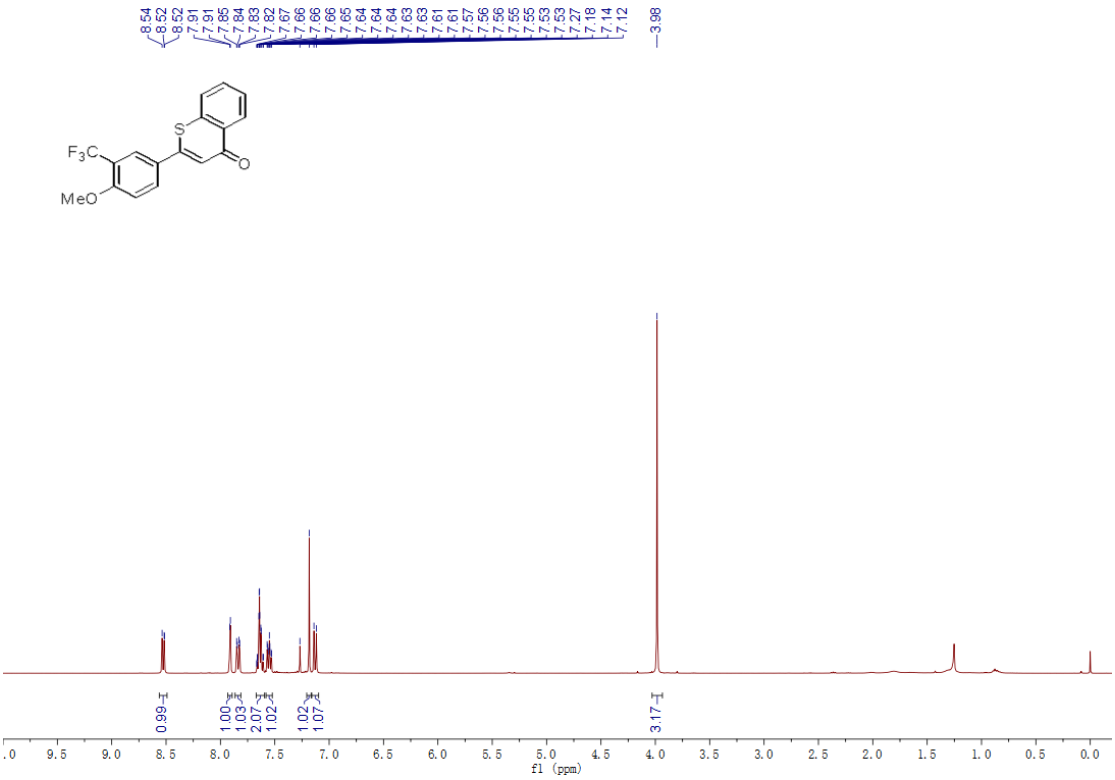


Supplementary Figure 73. ^{1}H NMR spectra of **3pa**

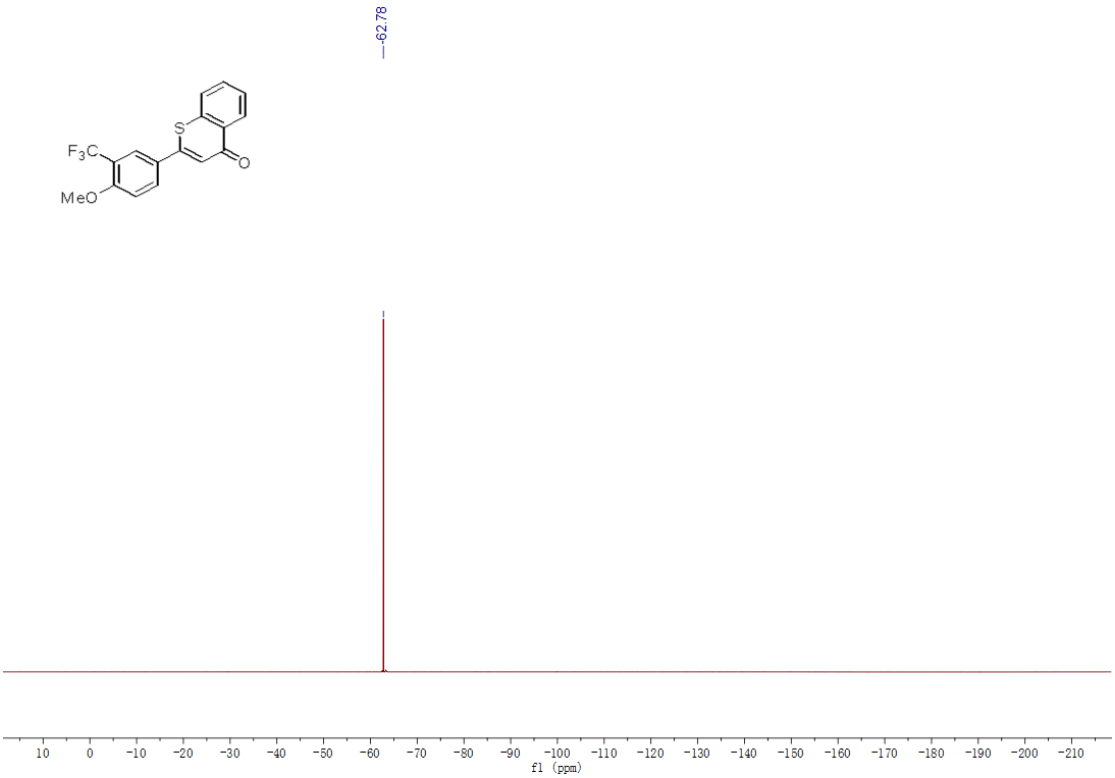


Supplementary Figure 74. ^{13}C NMR spectra of **3pa**

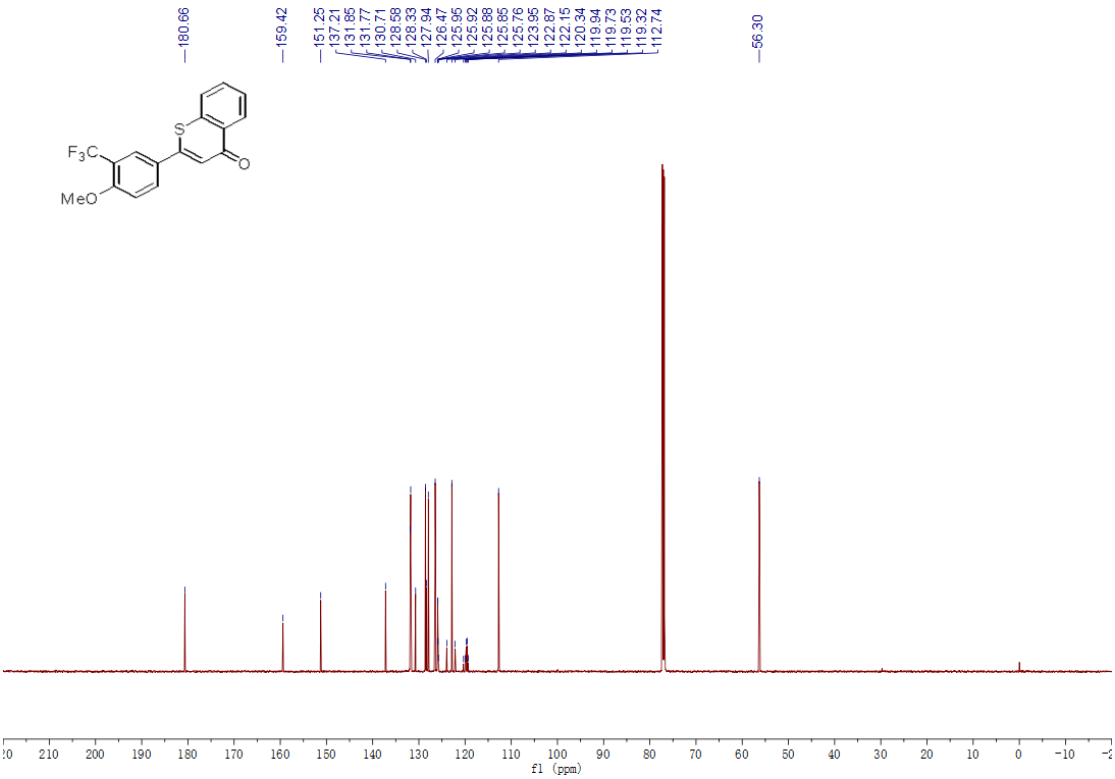
2-(4-methoxy-3-(trifluoromethyl)phenyl)-4*H*-thiochromen-4-one (3qa, *CDCl$_3$* as solvent)



Supplementary Figure 75. ^{1}H NMR spectra of **3qa**

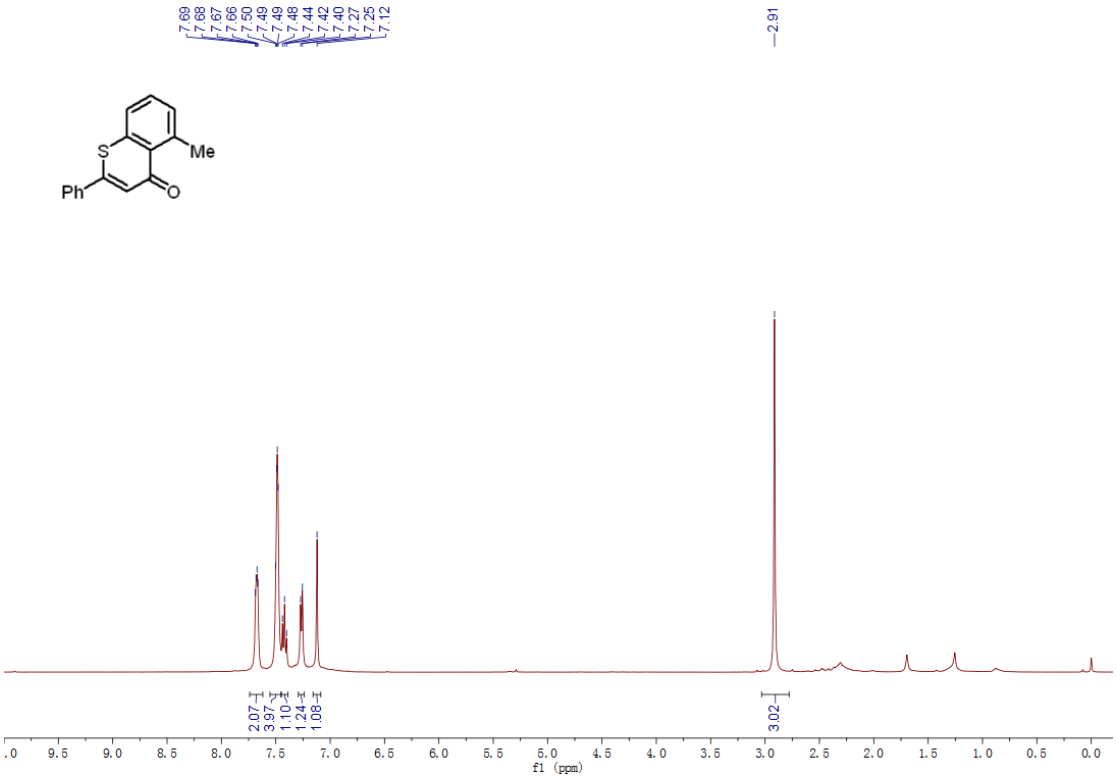


Supplementary Figure 76. ^{19}F NMR spectra of **3qa**

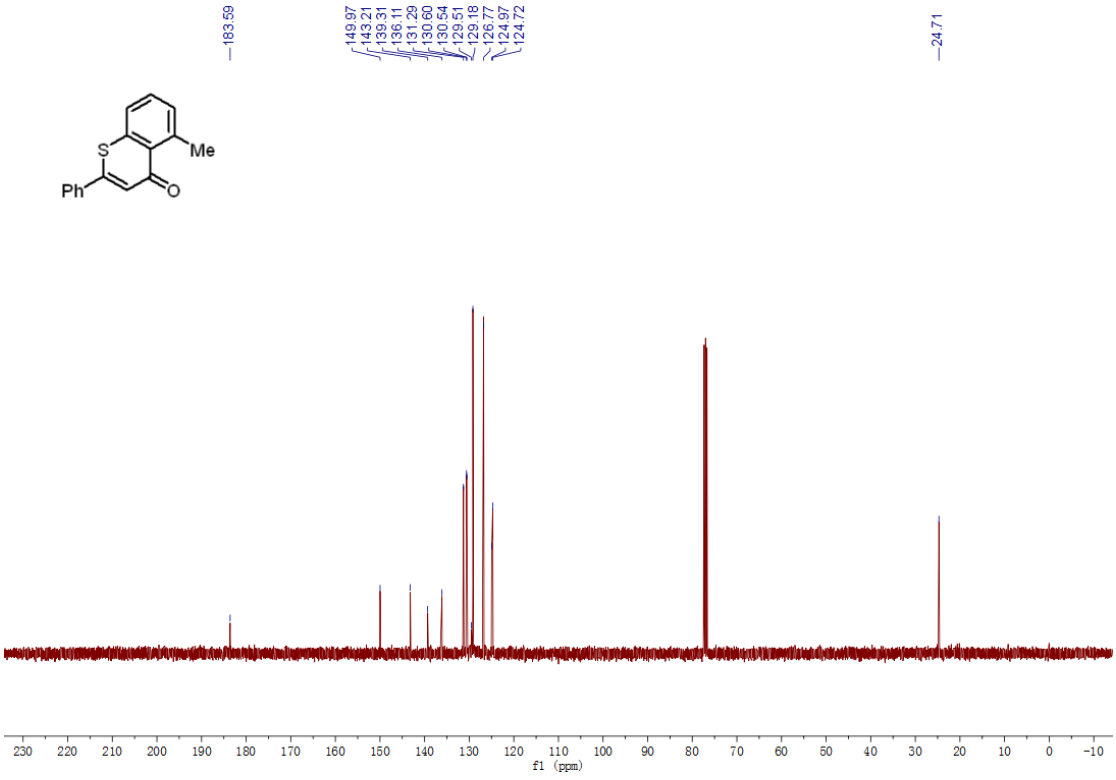


Supplementary Figure 77. ^{13}C NMR spectra of **3qa**

5-methyl-2-phenyl-4*H*-thiochromen-4-one (3aq-I, *$CDCl_3$* as solvent)

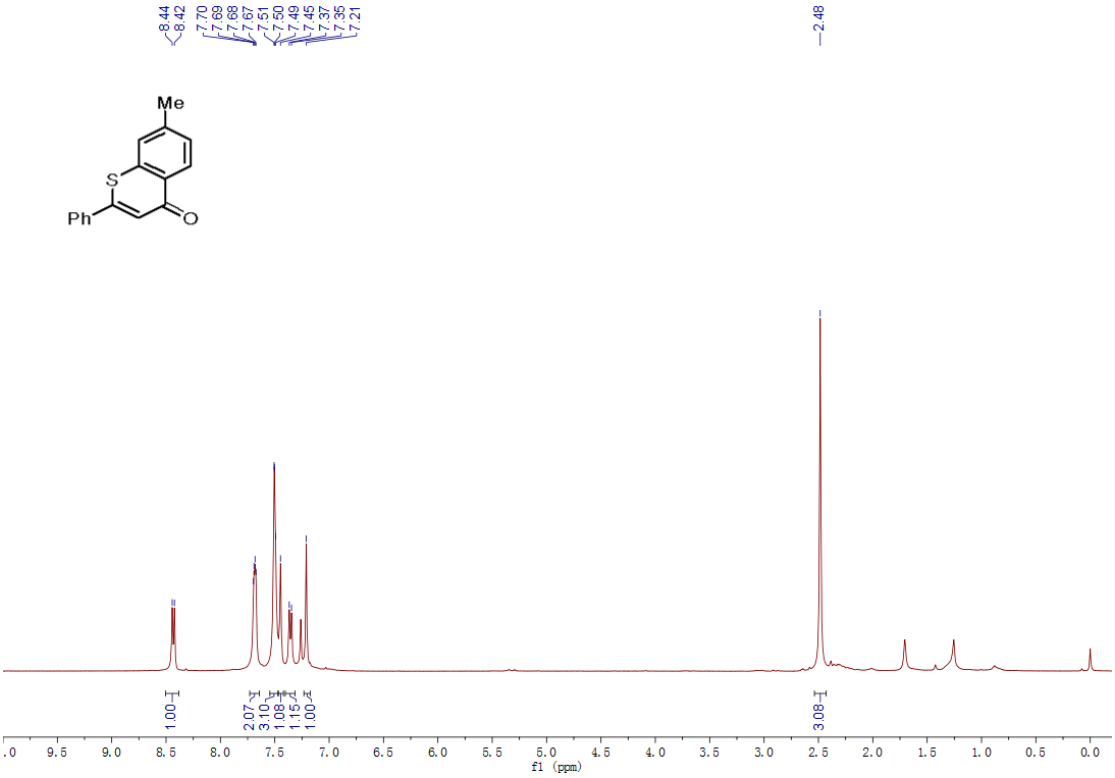


Supplementary Figure 78. ^{1}H NMR spectra of **3aq-I**

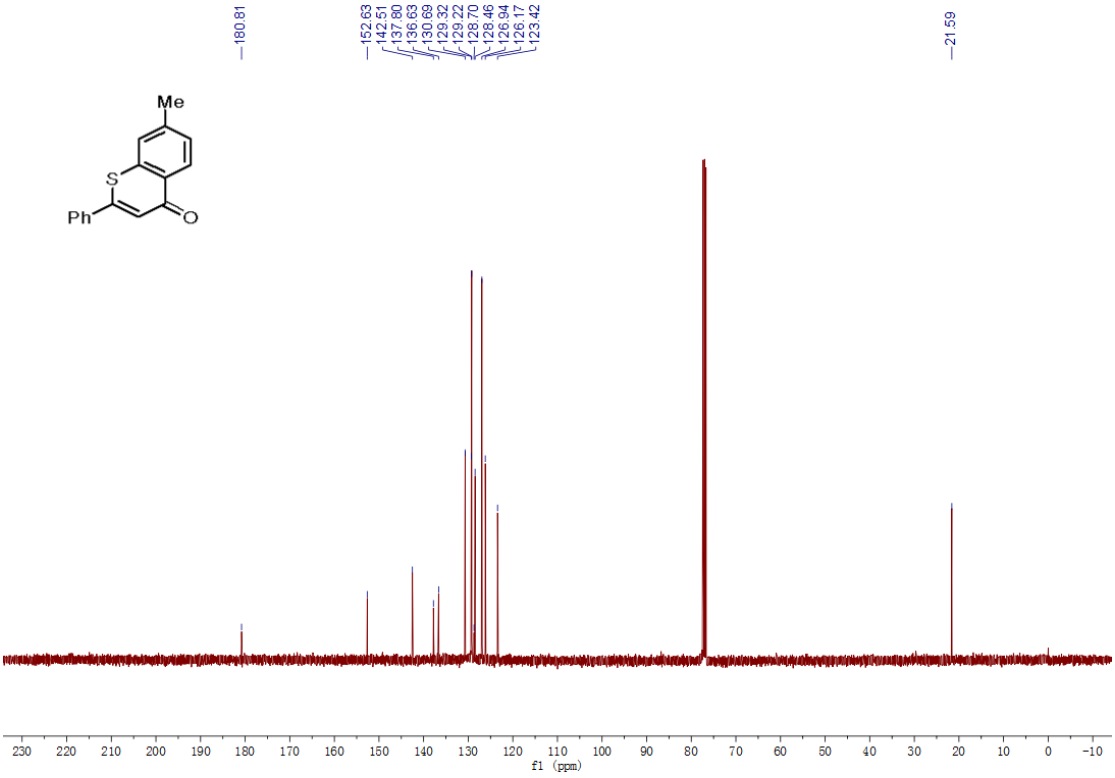


Supplementary Figure 79. ^{13}C NMR spectra of **3aq-I**

7-methyl-2-phenyl-4*H*-thiochromen-4-one (3aq-II, *$CDCl_3$* as solvent)

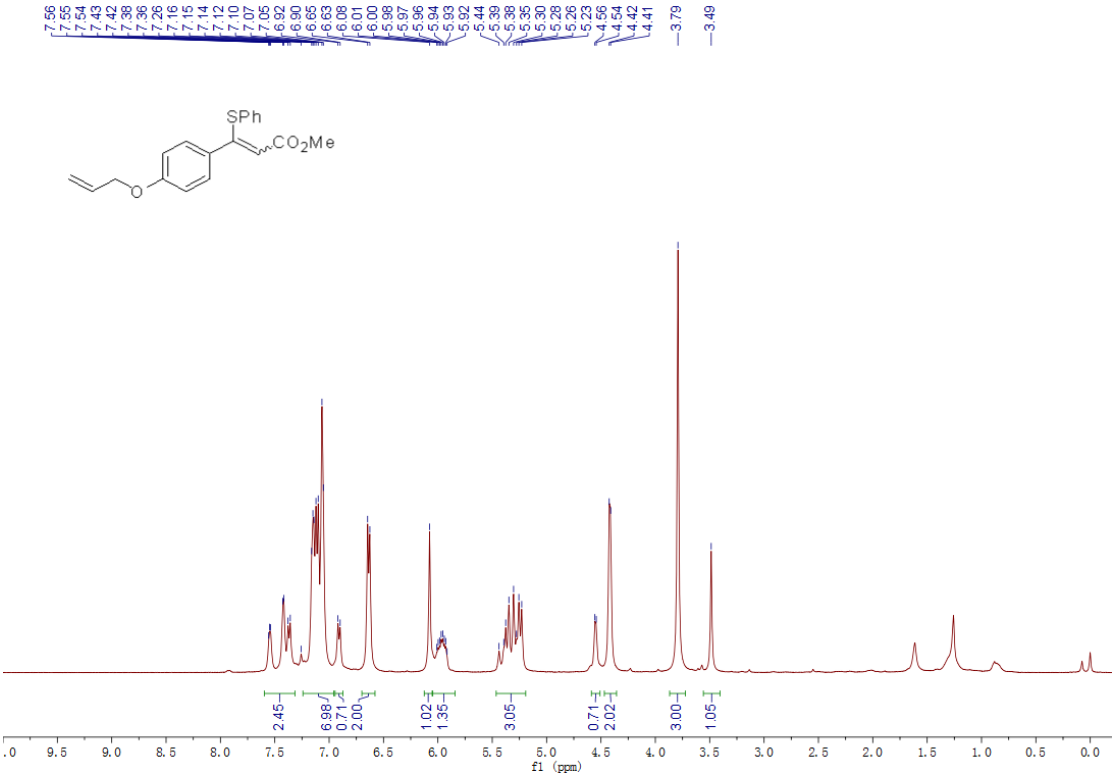


Supplementary Figure 80. ^{1}H NMR spectra of **3aq-II**

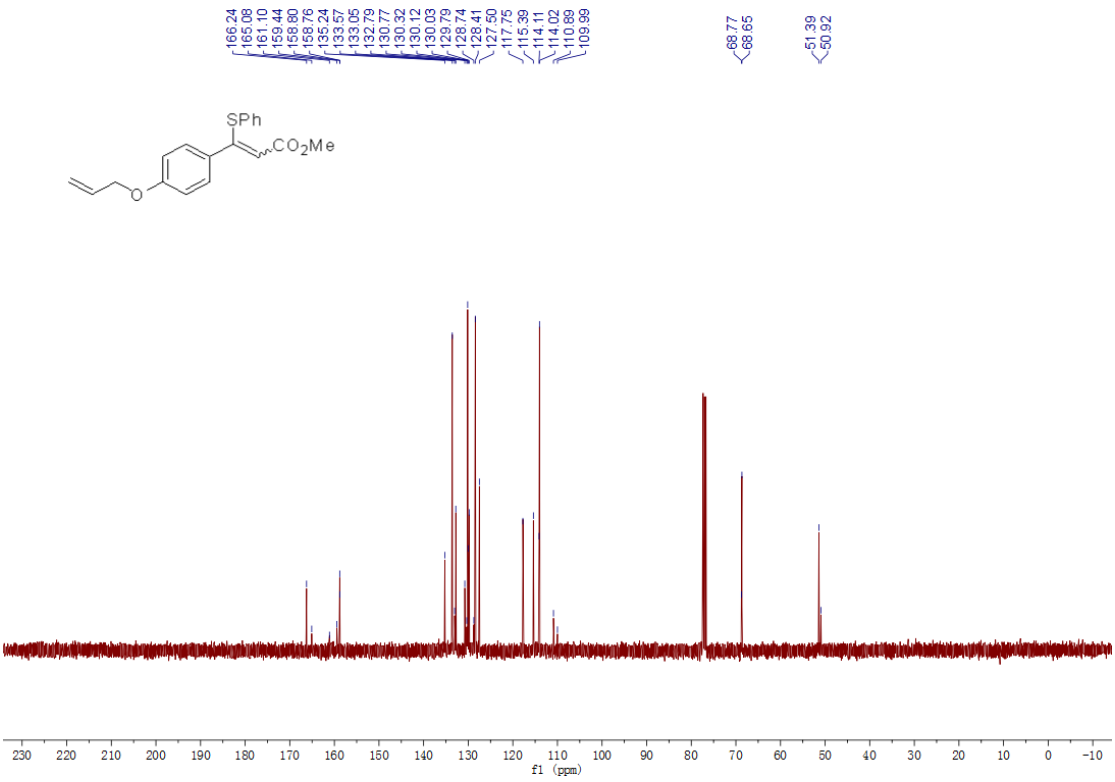


Supplementary Figure 81. ^{13}C NMR spectra of **3aq-II**

methyl 3-(4-(allyloxy)phenyl)-3-(phenylthio)acrylate (3ra, *CDCl$_3$* as solvent)

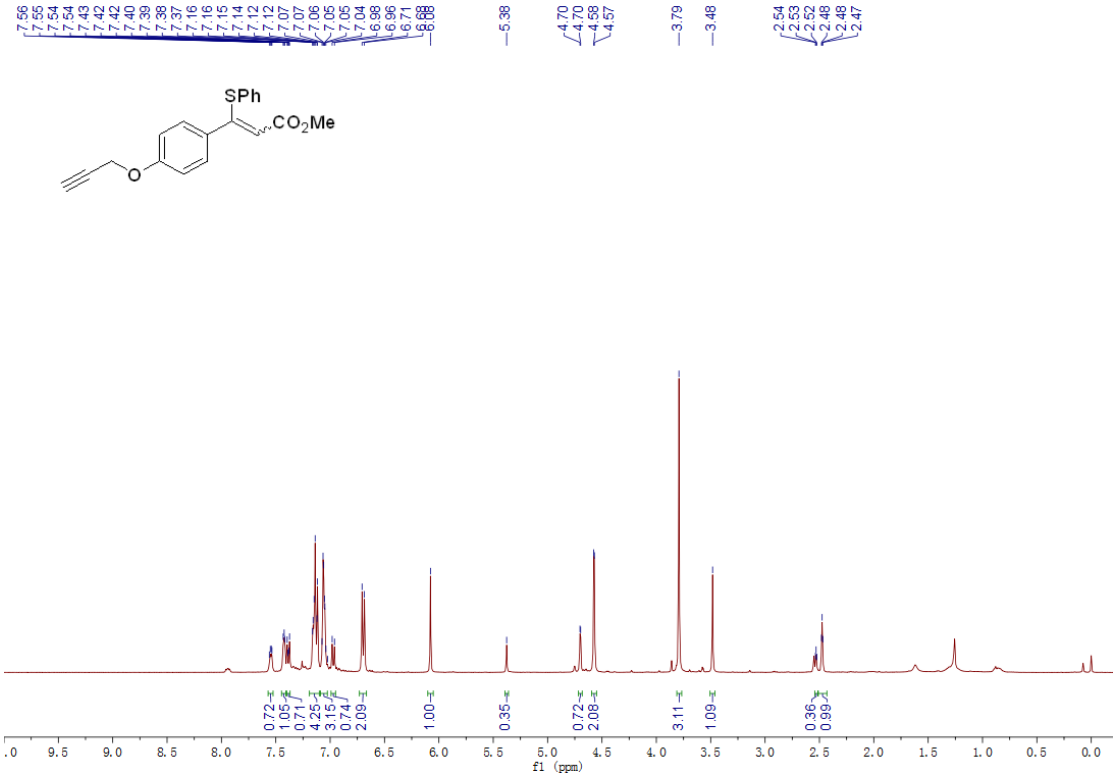


Supplementary Figure 82. ^{1}H NMR spectra of **3ra**

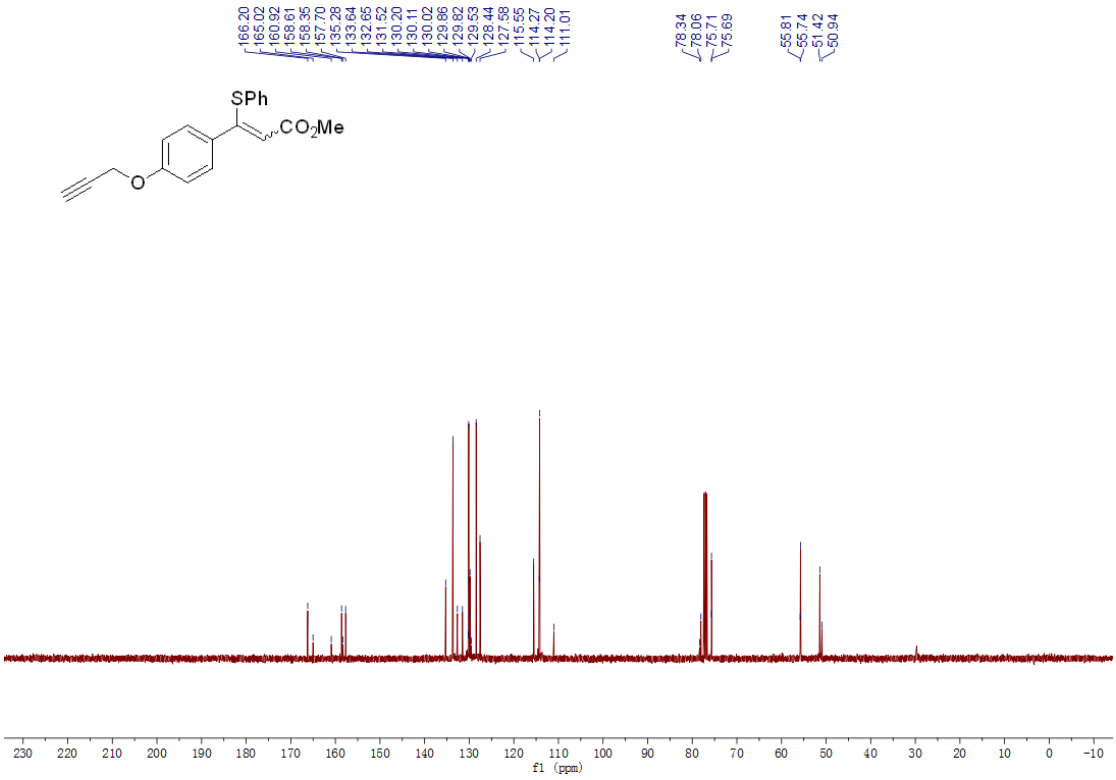


Supplementary Figure 83. ^{13}C NMR spectra of **3ra**

methyl 3-(phenylthio)-3-(4-(prop-2-yn-1-yloxy)phenyl)acrylate (3sa, *CDCl$_3$* as solvent)

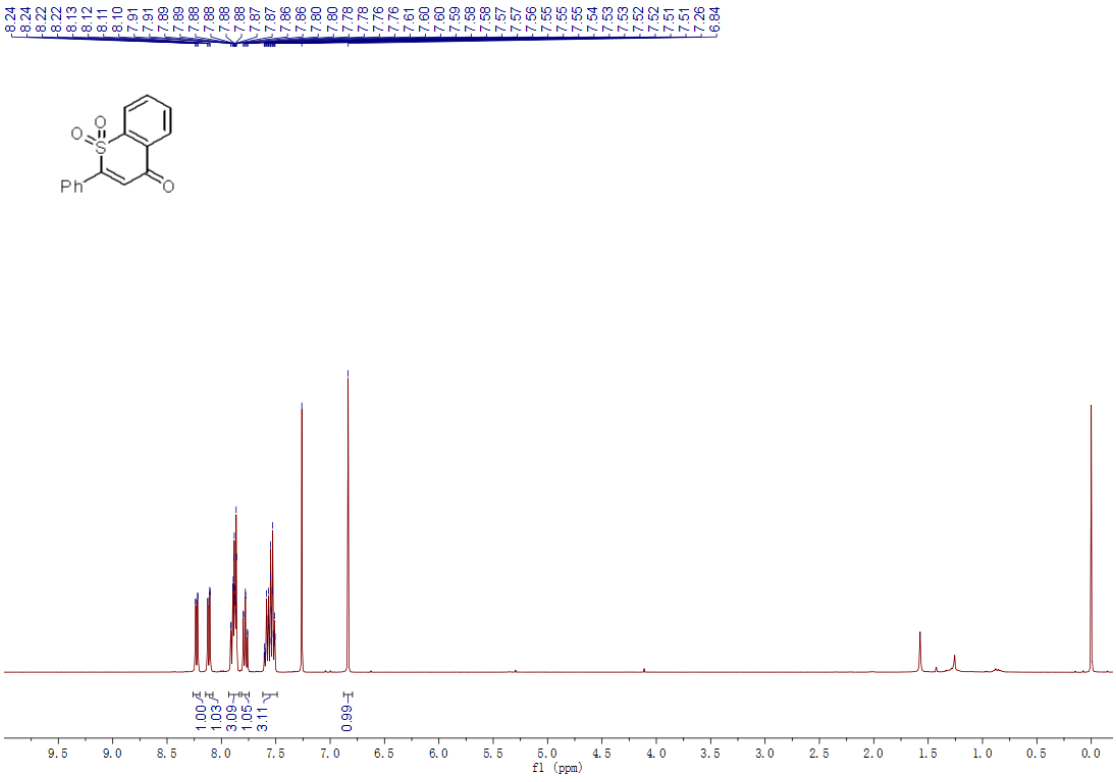


Supplementary Figure 84. ^{1}H NMR spectra of **3sa**

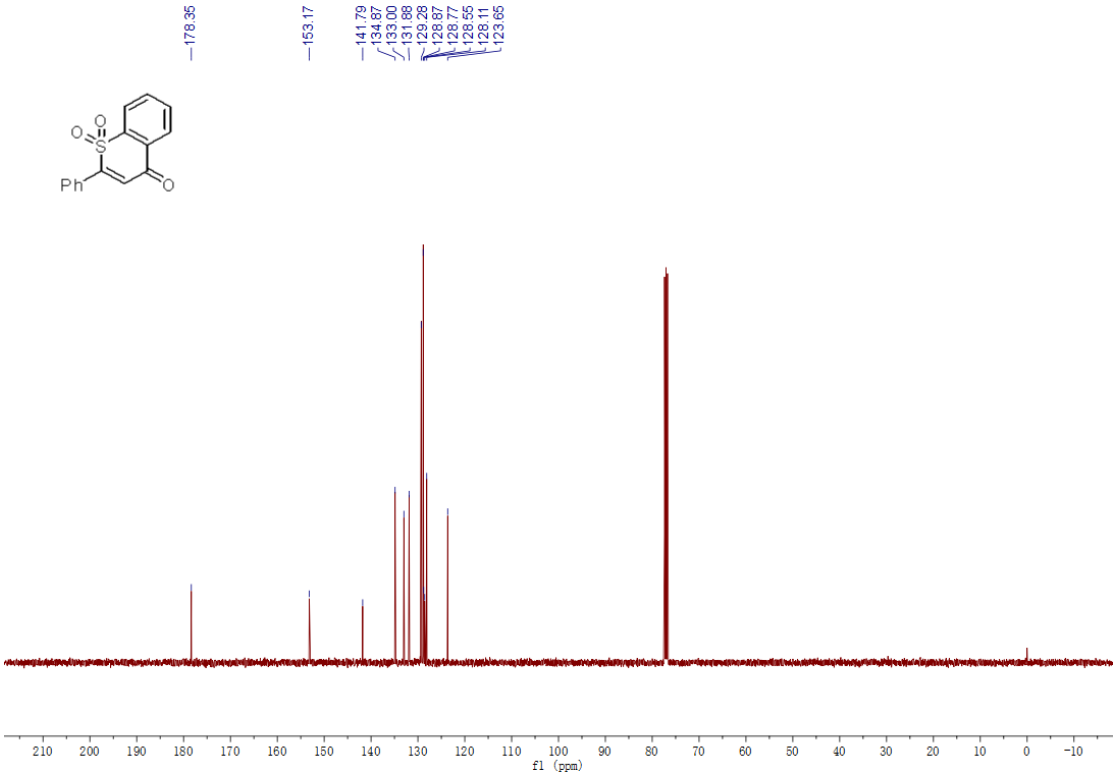


Supplementary Figure 85. ^{13}C NMR spectra of **3sa**

2-phenyl-4*H*-thiochromen-4-one 1,1-dioxide (5, $CDCl_3$ as solvent)

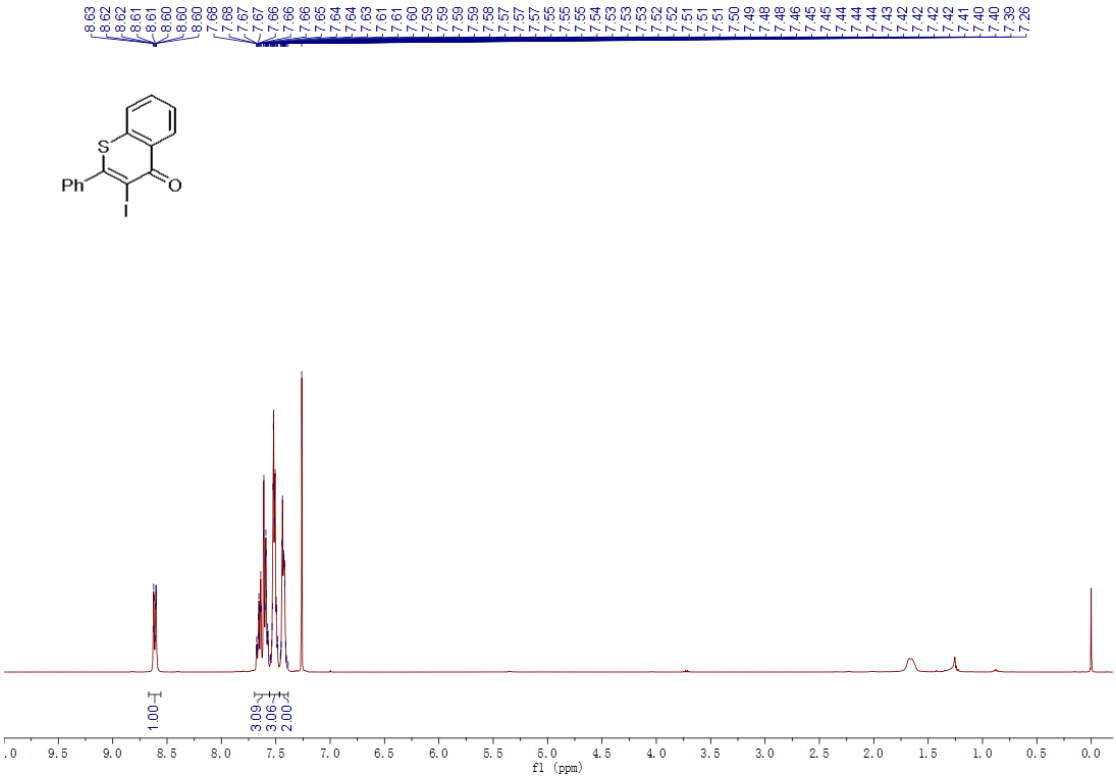


Supplementary Figure 86. ^{1}H NMR spectra of compound **5**

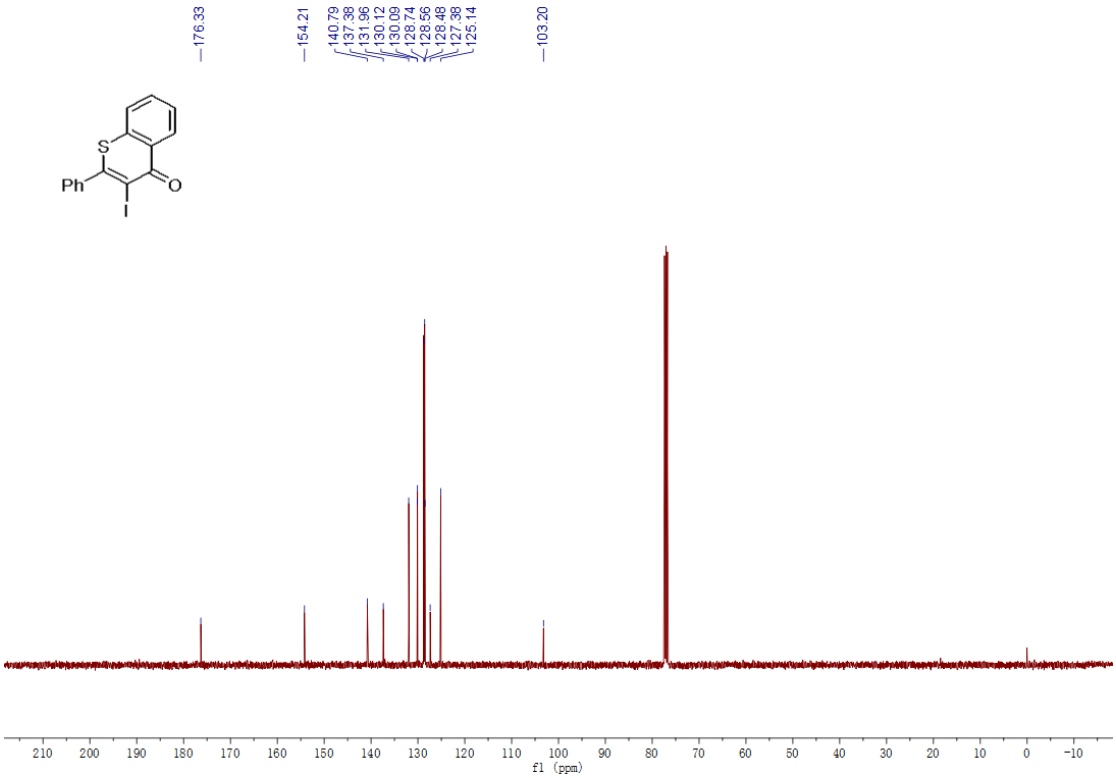


Supplementary Figure 87. ^{13}C NMR spectra of compound **5**

3-iodo-2-phenyl-4*H*-thiochromen-4-one (6, $CDCl_3$ as solvent)

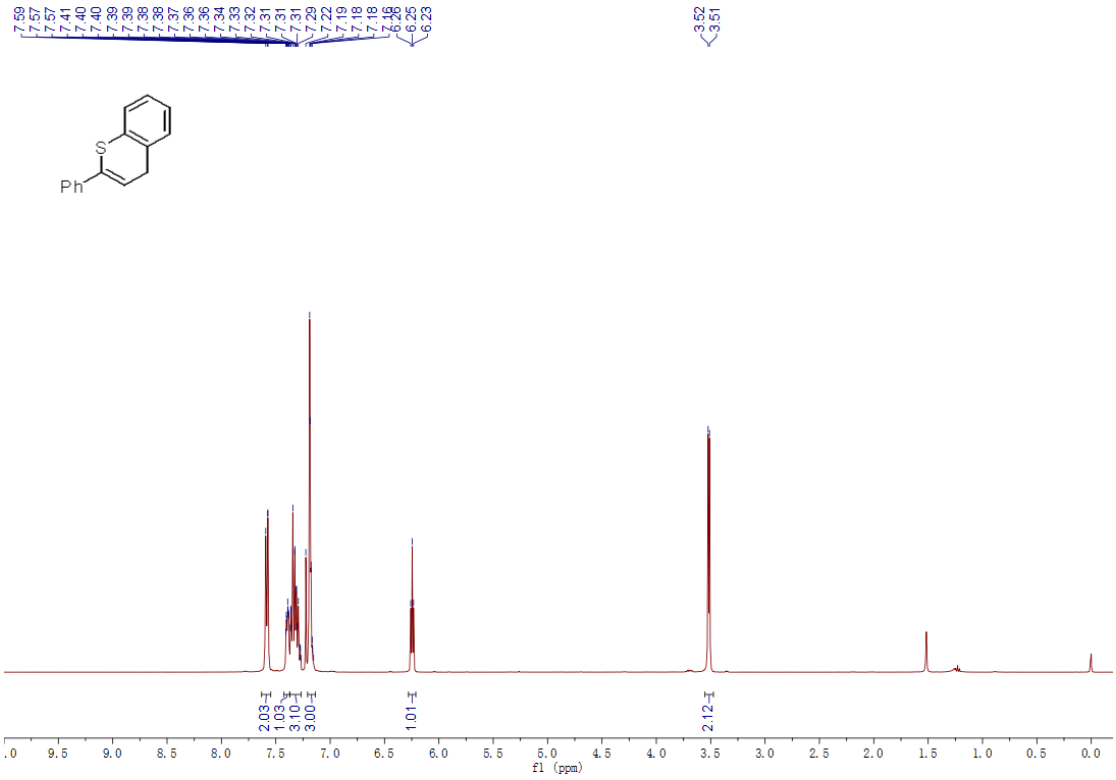


Supplementary Figure 88. ^{1}H NMR spectra of compound **6**

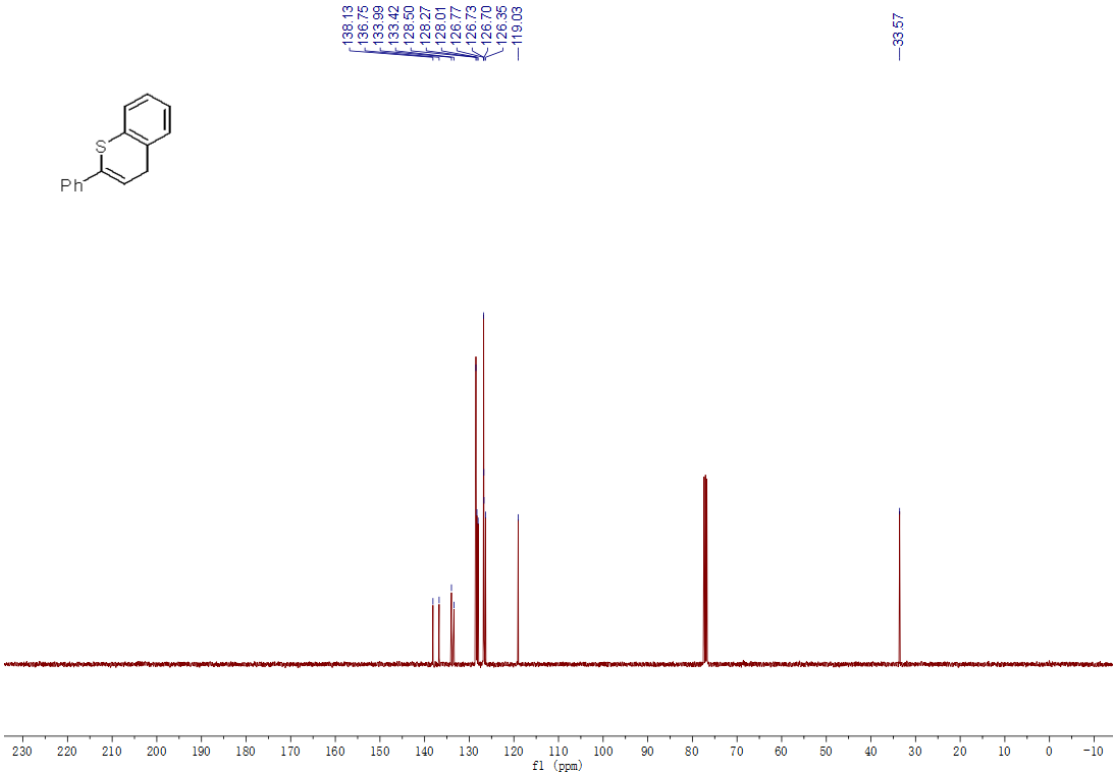


Supplementary Figure 89. ^{13}C NMR spectra of compound **6**

2-phenyl-4*H*-thiochromene (7, $CDCl_3$ as solvent)

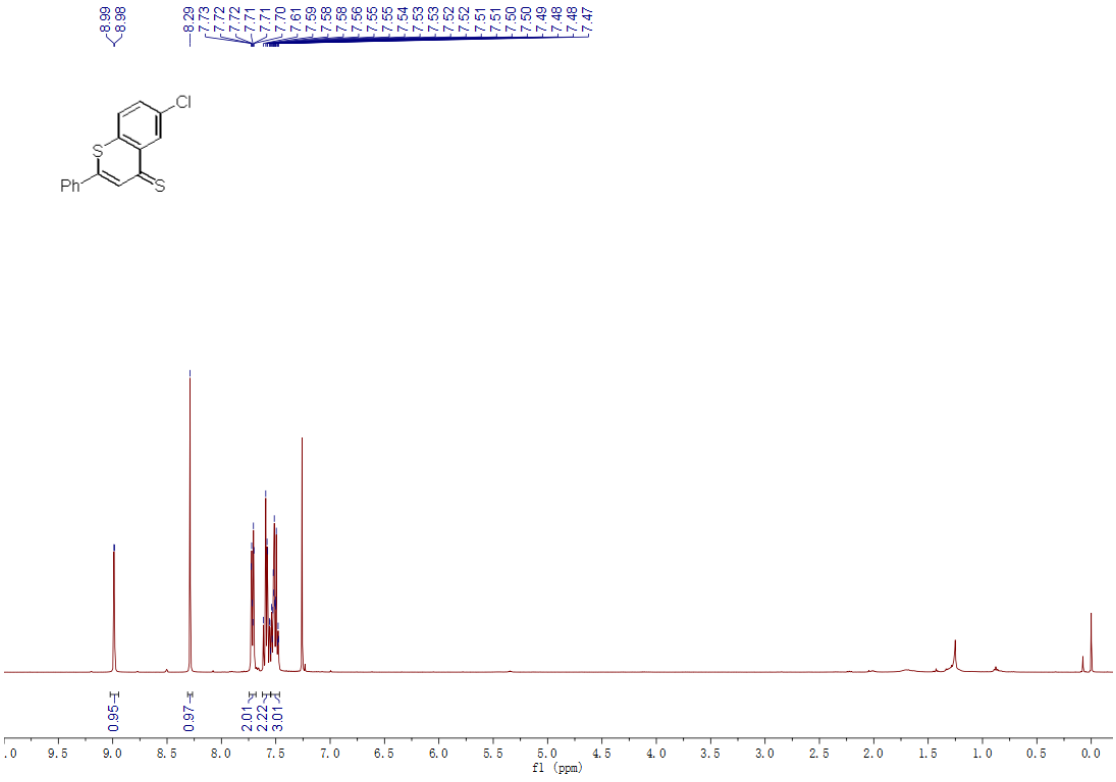


Supplementary Figure 90. ^{1}H NMR spectra of compound **7**

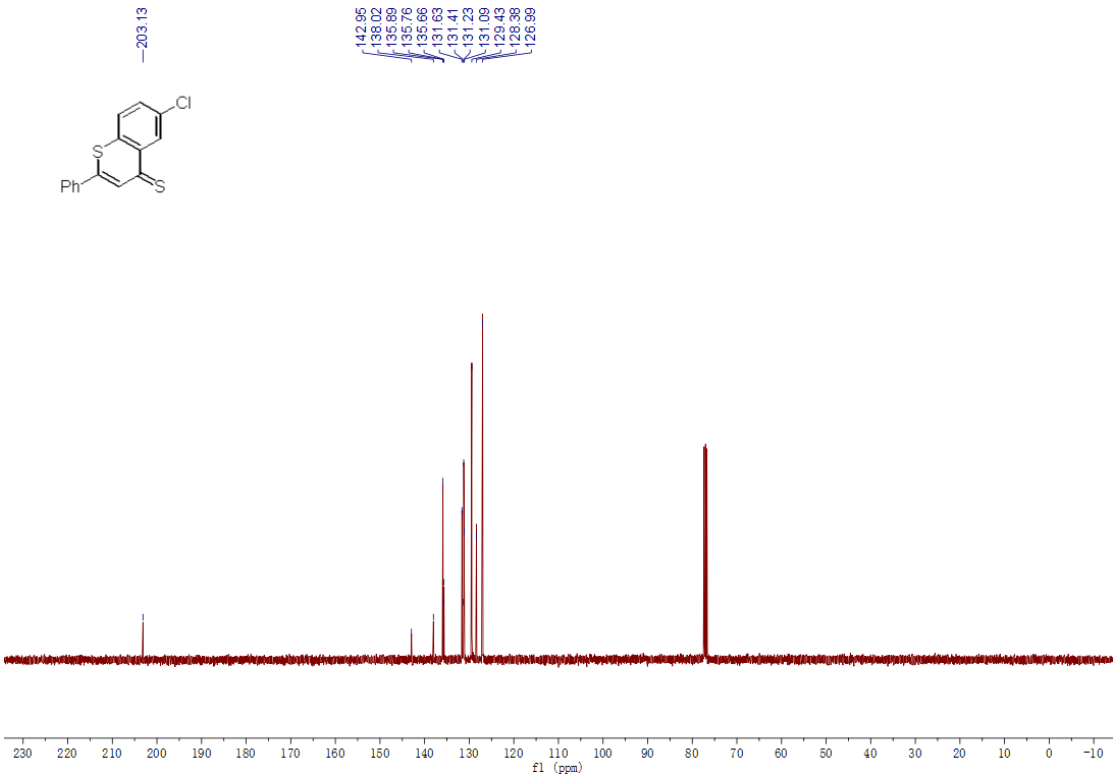


Supplementary Figure 91. ^{13}C NMR spectra of compound **7**

6-chloro-2-phenyl-4*H*-thiochromene-4-thione (10, $CDCl_3$ as solvent)

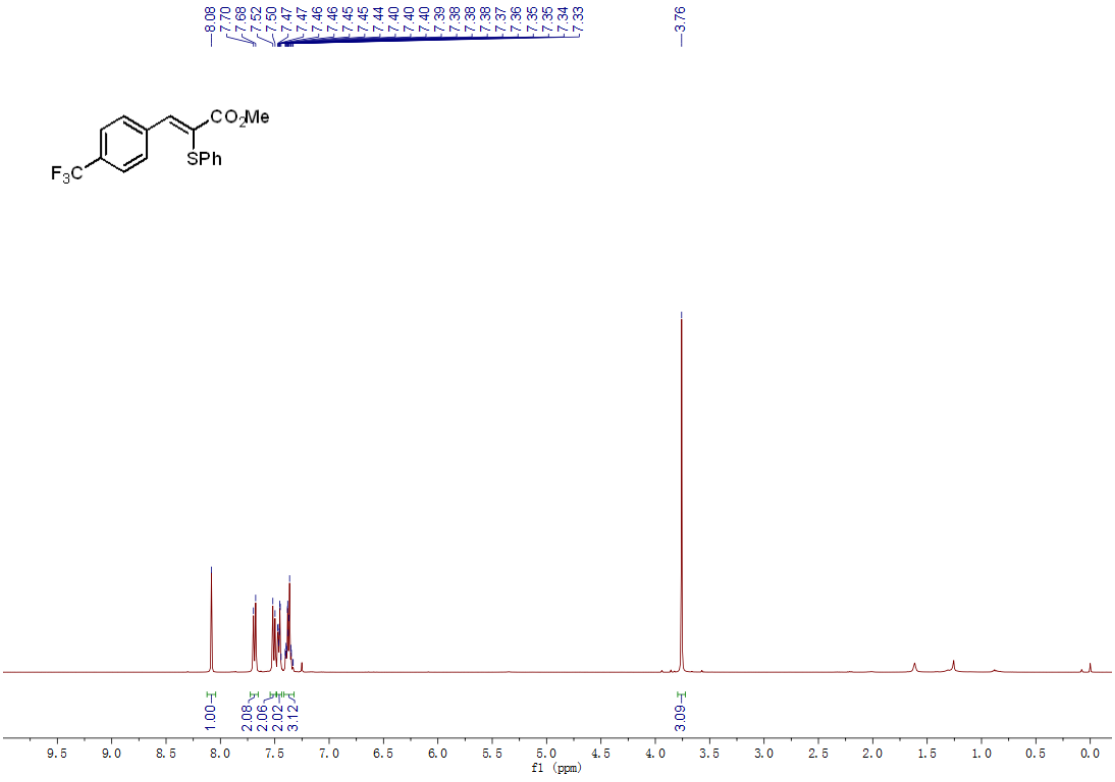


Supplementary Figure 92. ^{1}H NMR spectra of compound **10**

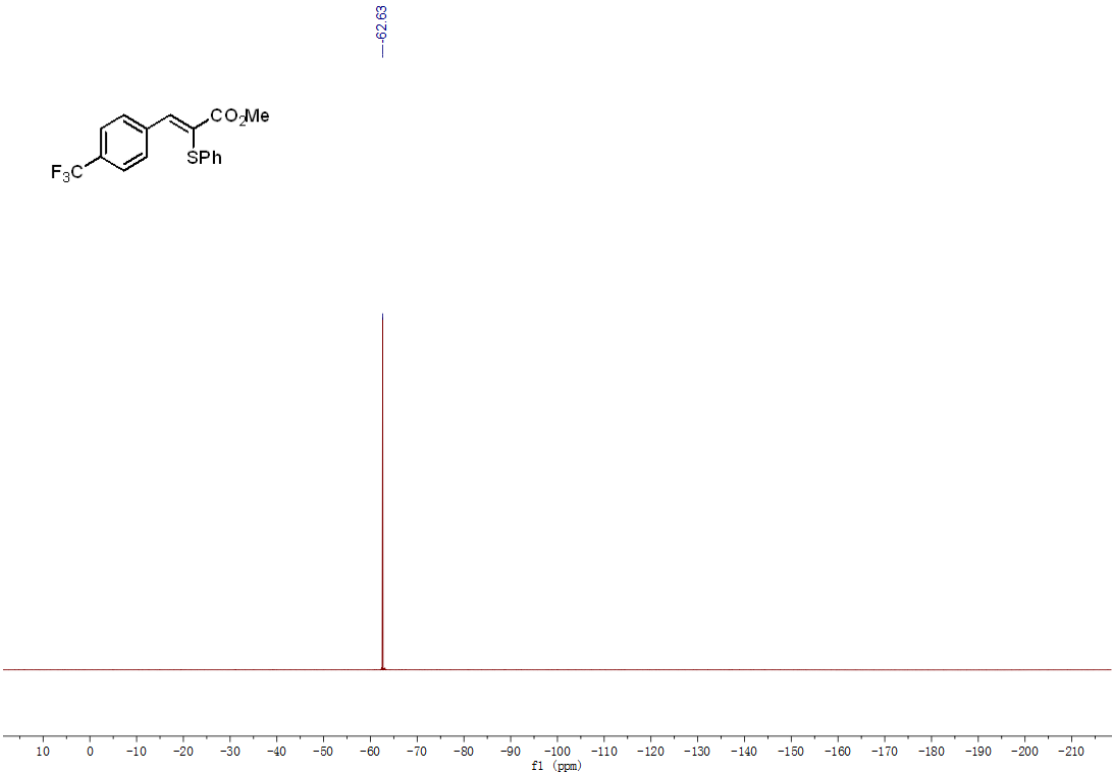


Supplementary Figure 93. ^{13}C NMR spectra of compound **10**

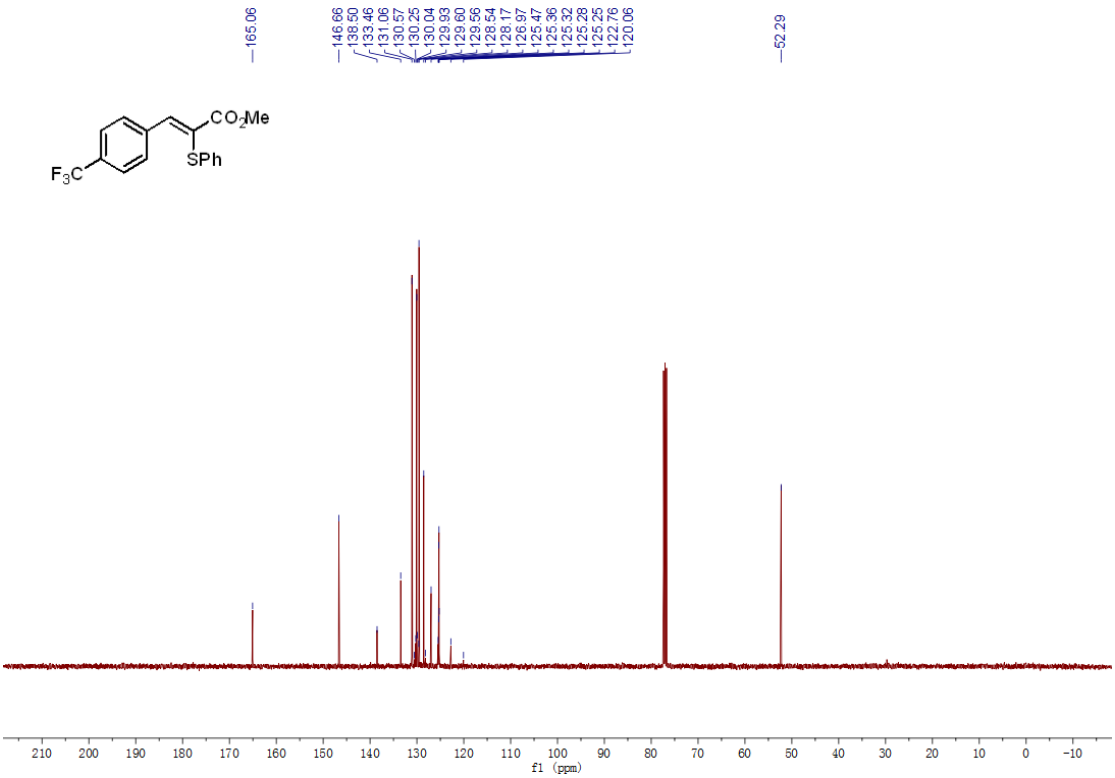
methyl (*Z*)-2-(phenylthio)-3-(4-(trifluoromethyl)phenyl)acrylate (*$CDCl_3$* as solvent)



Supplementary Figure 94. ^{1}H NMR spectra of the compound

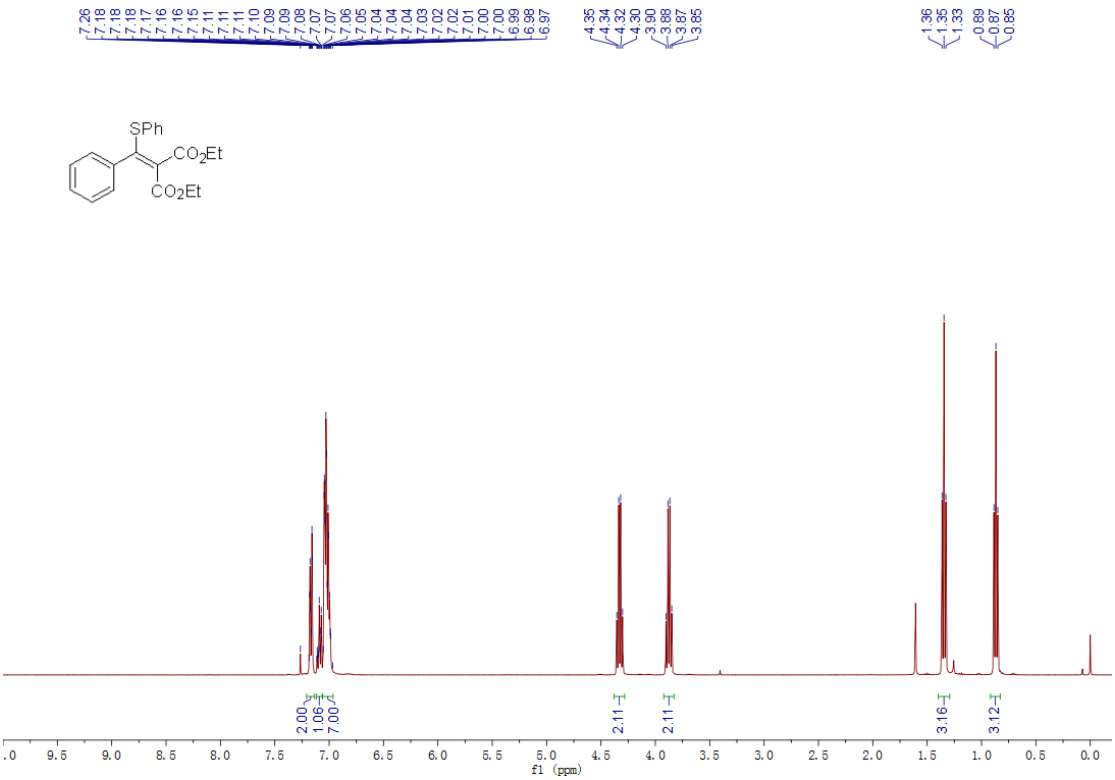


Supplementary Figure 95. ^{19}F NMR spectra of the compound

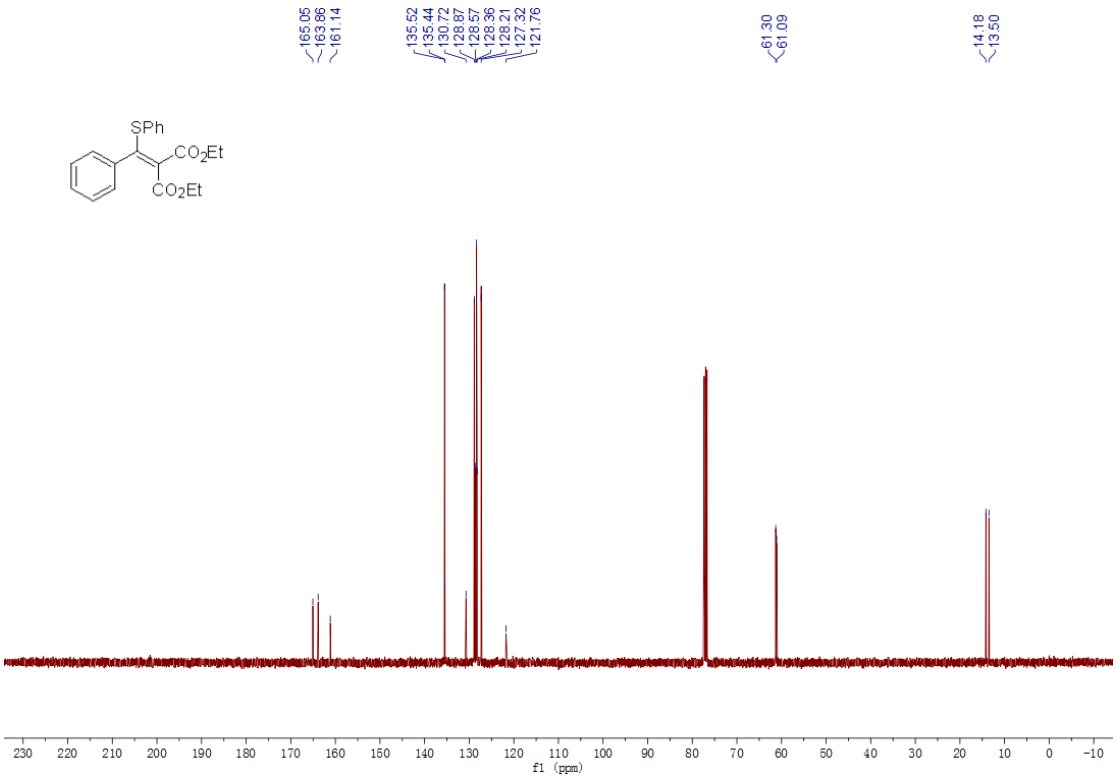


Supplementary Figure 96. ^{13}C NMR spectra of the compound

diethyl 2-(phenyl(phenylthio)methylene)malonate (*$CDCl_3$* as solvent)

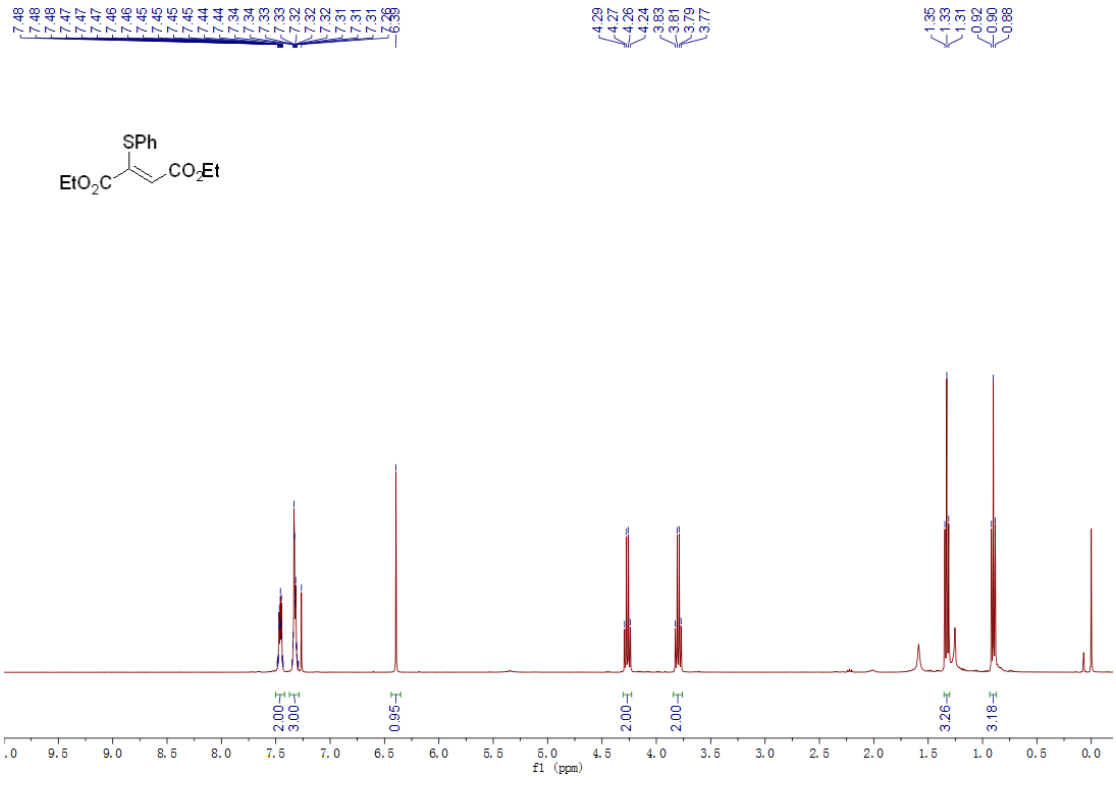


Supplementary Figure 97. ^{1}H NMR spectra of the compound

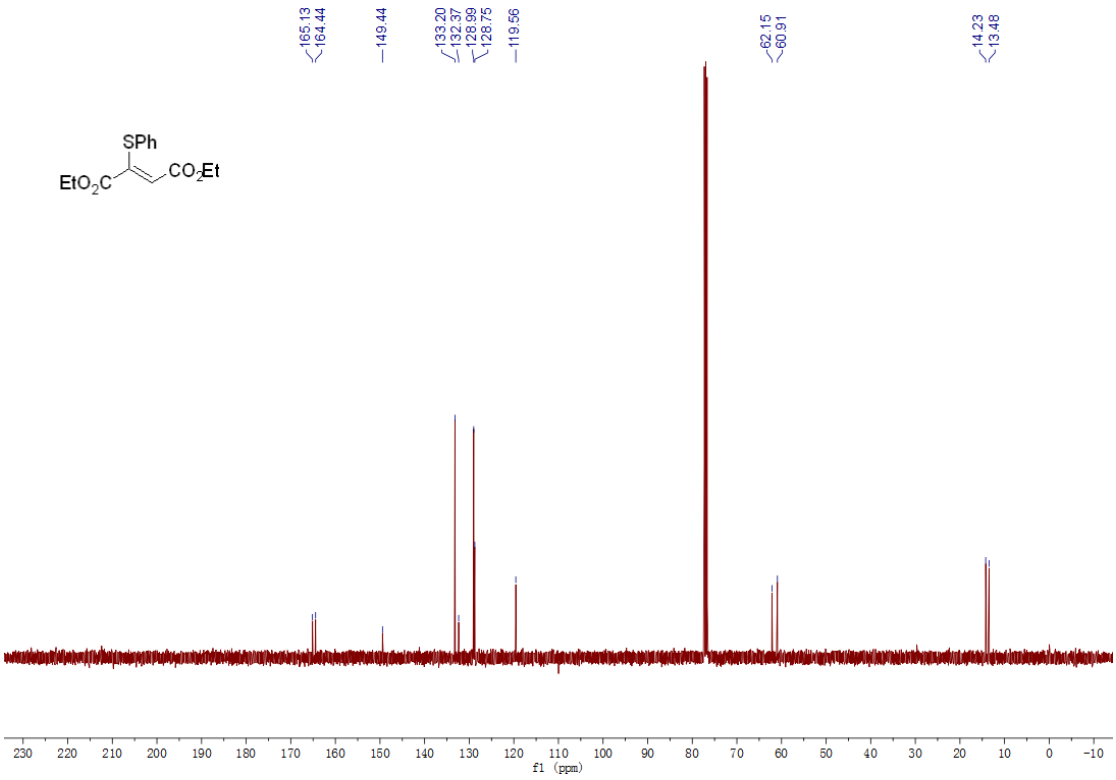


Supplementary Figure 98. ^{13}C NMR spectra of the compound

diethyl 2-(phenylthio)fumarate (*Z*-J, *CDCl$_3$* as solvent)

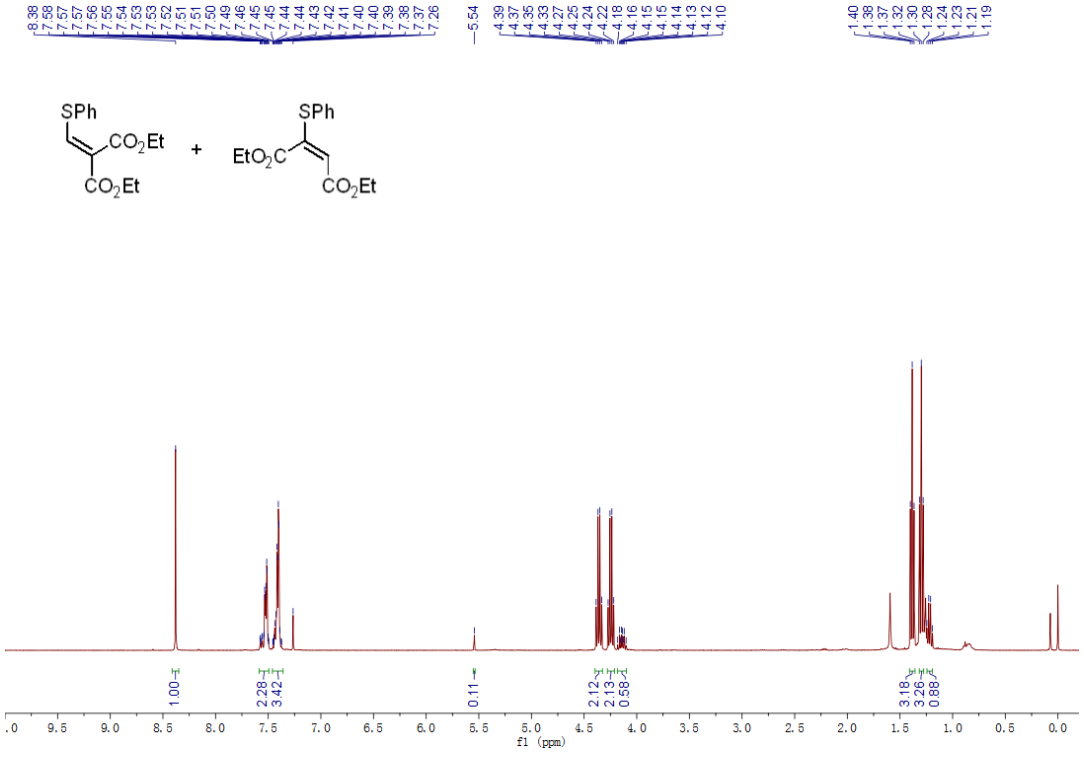


Supplementary Figure 99. ^{1}H NMR spectra of *Z*-**J**

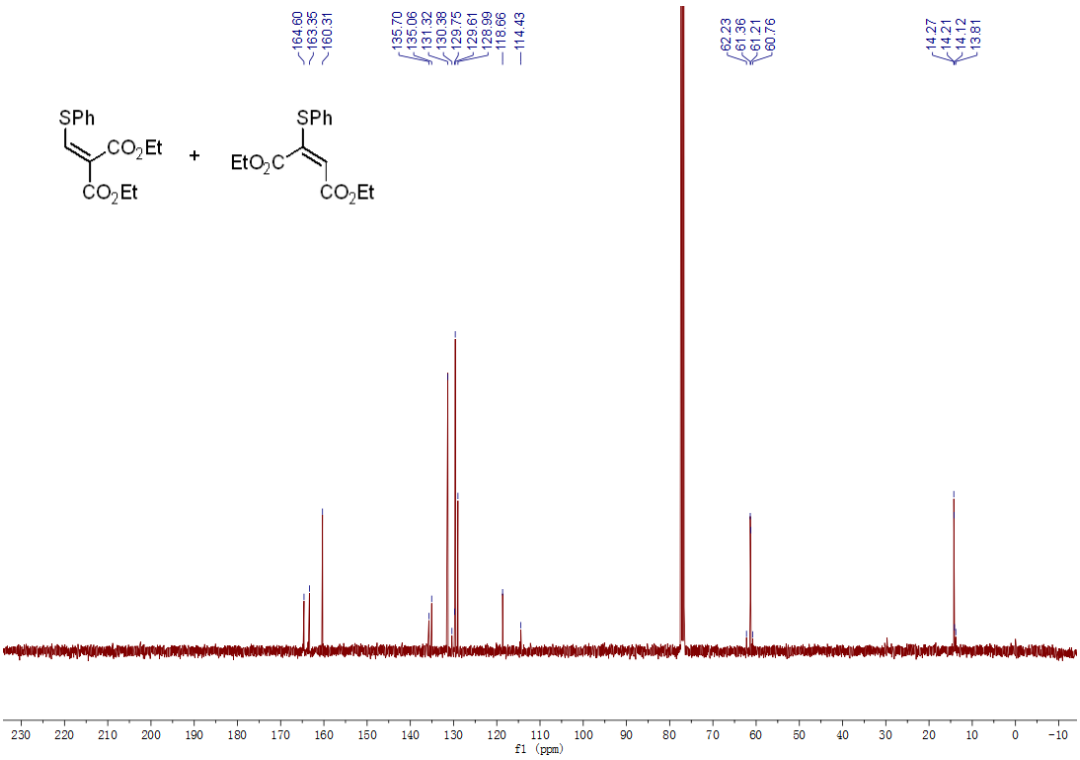


Supplementary Figure 100. ^{13}C NMR spectra of *Z*-**J**

diethyl 2-((phenylthio)methylene)malonate and diethyl 2-(phenylthio)maleate (I and *E*-J, *CDCl$_3$* as solvent)



Supplementary Figure 101. ^{1}H NMR spectra of **I** and *E*-**J**



Supplementary Figure 102. ^{13}C NMR spectra of **I** and *E*-**J**

Supplementary Reference

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