Electronic Supplementary Information

Iridium complex-linked porous organic polymers for recyclable, broad-scope photocatalysis of organic transformations

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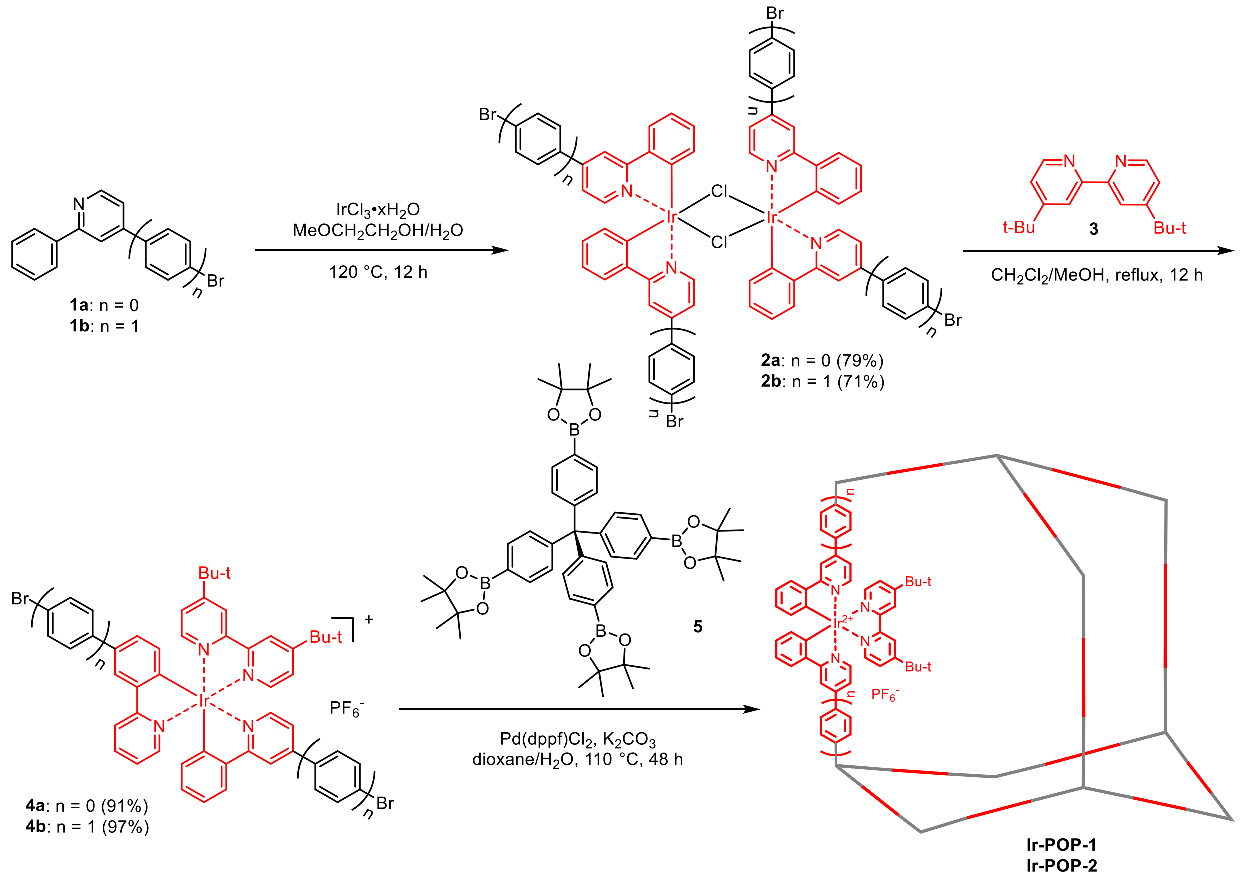
General methods. Commercial reactants were used without further purification. Solvents were dried according to standard methods. All reactions were conducted under the atmosphere of argon. ^{1}H and ^{13}C NMR spectra were recorded by Bruker AVANCE III HD 400 MHz (100 MHz) instrument, and were internally referenced to residual solvent signals (^{1}H NMR: $CDCl_3$ and DMSO-d_6 referenced at 7.26 and 2.49 ppm, respectively; ^{13}C NMR: $CDCl_3$ and DMSO-d_6 referenced at 77.2 and 39.5 ppm, respectively). Gas chromatography was conducted on a Shimadazu GC-2010 instrument. UV-visible spectra were recorded with a PerkinElmer LAMBDA 650 UV/Vis/NIR spectrometer. Fluorescence spectra were recorded with a PerkinElmer LS-55 fluorescence spectrometer. Fourier Transform Infrared spectra were recorded with a ThermoFisher Nicolet iS10 FT-IR spectrometer. Cyclic Voltammetric spectra were recorded on a CHI660E electrochemical workstation. Thermogravimetric analysis (TGA) profiles were recorded on a TGA 8000 thermogravimetric analyzer. Nitrogen adsorption experiments weres recorded on a Micromeritics Tristar II 3020 analyzer. X-ray photoelectron spectra (XPS) were recorded on a PHI 5000C&PHI5300 spectrometer. Scanning electron microscopic (SEM) images and energy dispersive spectra (EDS) were obtained on a Nova NanoSem 450 microscope. Single crystal X-ray diffraction was recorded on a Bruker SMART CCD diffractometer. Inductively coupled plasma-optical emission spectrometer (ICP-OES) experiments were performed on a PE ICP Optima 8000 instrument. Powder X-ray diffraction (PXRD) experiments were conducted on Bruker D8 Powder Diffractometer. High-resolution mass spectra (HRMS) were recorded on a Bruker McriOTOF11 analyzer. Compounds **1a**,[1] **5**,[2] **6a**,**b**[3] **8a-e**,[4] **8h**,[4] **8j**,[4] **8k**,[4] **8m**,[4] **10a,b**,[5, 6] and **11c**[7] were synthesized using reported methods. Compound **1b** was synthesized via successive Miyaura borylation reaction and Suzuki coupling reaction from **1a**.

The crystal data of complexes **4a**, **4b**, and **Ir-Ph-2** have been deposited in Cambridge Crystallographic Data Centre (CCDC deposit no. 1961159-1961161).

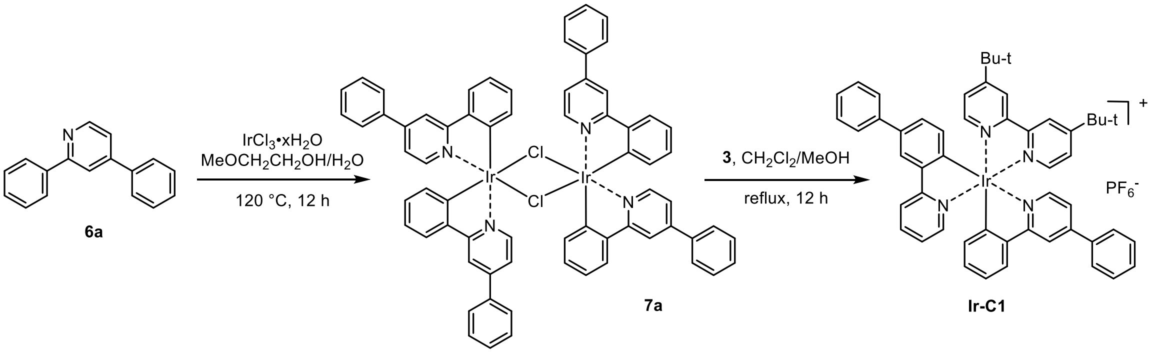


Compound 4a. A mixture of compound **1a** (2.3 g, 10 mmol), $IrCl_3{\cdot}xH_2O$ (1.4 g, 4.4 mmol), 2-methoxyethanol (170 mL) and water (60 mL) in a Schlenk tube was stirred for 12 hours at 120 °C and then cooled to room temperature. The yellowish precipitate formed was filtered and washed with water and dried *in vacuo* to afford **2a** as a crude product (2.4 g, 79%). The product was used in following steps without further purification. A mixture of **2a** (0.69 g, 0.50 mmol), **3** (0.34 g, 1.25 mmol) in dichloromethane (140 mL) and methanol (70 mL) in a Schlenk tube was stirred for 12 hours under reflux and then cooled to room temperature. NH_4PF_6 (1.6 g, 10 mmol) was added and the mixture was stirred for 15 minutes. The solution was filtered and concentrated *in vacuo*. The resulting crude product was washed with ether and dried and then subjected to flash column chromatography on silica gel (CH_2Cl_2/MeOH 20:1) to afford **4a** as a yellow solid (0.98 g, 91%). $R_f = 0.30$ (CH_2Cl_2:MeOH 20:1). M.p. >300 °C (decom.). ^1H NMR (400 MHz, DMSO-d_6): δ 8.86 (s, 2H), 8.58 (d, $J = 2.0$ Hz, 2H), 8.01 (d, $J = 7.2$ Hz, 2H), 7.70 (s, 4H), 7.45 (d, $J = 6.4$ Hz, 2H), 7.42-7.34 (m, 2H), 7.08-6.98 (m, 2H), 6.98-6.90 (m, 2H), 1.38 (s, 18H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.7, 164.1, 155.5, 151.8, 150.1, 150.0, 143.1, 135.2, 131.5, 131.4, 127.4, 126.3, 126.0, 123.6, 123.6, 122.8, 36.1, 30.4. IR (KBr) 2963, 1615, 1589, 1537, 1465, 1413, 1264, 1060, 838, 635 cm^{-1}. HRMS (ESI): Calcd for $C_{40}H_{38}Br_2IrN_4$ 927.1062 [M$^+$]. Found 927.1066.

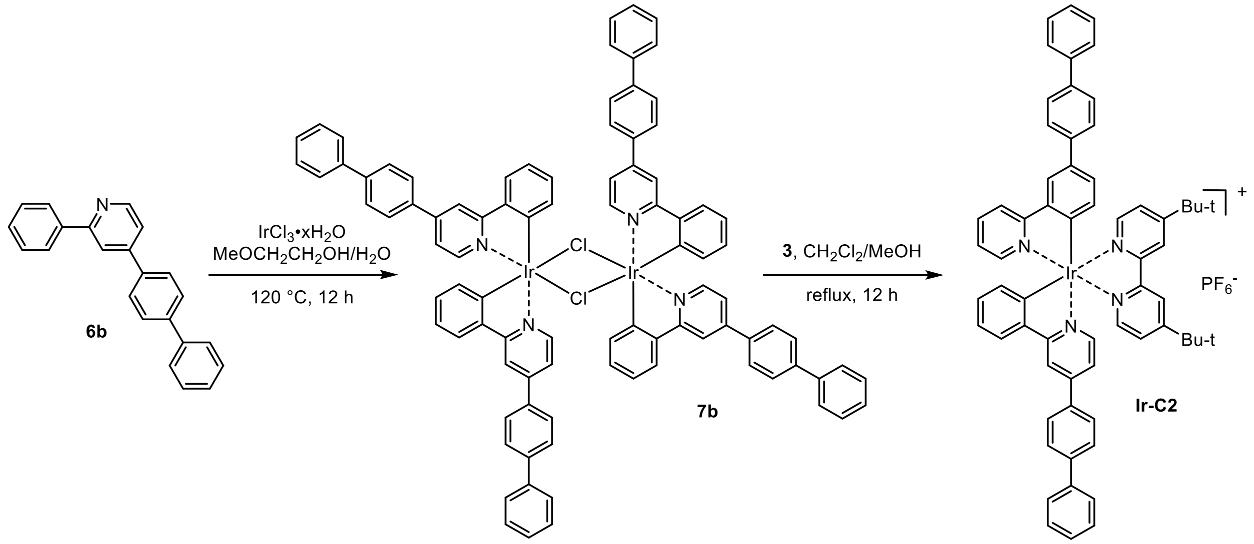
Compound 4b. A mixture of compound **1b** (3.1 g, 10 mmol), $IrCl_3{\cdot}xH_2O$ (1.4 g, 4.4 mmol), 2-methoxyethanol (340 mL) and water (60 mL) in a Schlenk tube was stirred for 12 hours at 120 °C and then cooled to room temperature. The yellowish precipitate formed was filtered and washed with water and dried *in vacuo* to afford **2b** as a crude product (2.7 g, 71%). The product was used in following steps without further purification. A mixture of **2b** (0.52 g, 0.30 mmol), **3** (0.20 g, 0.76 mmol) in dichloromethane (280 mL) and methanol (140 mL) in a Schlenk tube was stirred for 12 hours under reflux and then cooled to room temperature. NH_4PF_6 (0.98 g, 6 mmol) was added and the mixture was stirred for 15 minutes. The solution was filtered and concentrated *in vacuo*. The resulting crude product was washed with ether and dried and then subjected to flash column chromatography on silica gel (CH_2Cl_2/MeOH 25:1) to afford **4b** as a yellow solid (0.74 g, 97%). R_f = 0.26 (CH_2Cl_2:MeOH 20:1). M.p. >300 °C (decom.). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.88 (s, 2H), 8.59 (s, 2H), 8.17 (d, *J* = 8.0, 2H), 7.96 (d, *J* = 8.4 Hz, 4H), 7.88-7.64 (m, 8H), 7.63-7.57 (m, 2H), 7.56-7.49 (m, 2H), 7.03 (t, *J* = 7.2 Hz, 2H), 6.93 (t, *J* = 7.2 Hz, 2H), 6.29 (d, *J* = 7.2 Hz, 2H), 1.39 (s, 18H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.0, 164.1, 155.7, 151.6, 150.1, 149.3, 148.2, 144.3, 135.1, 132.6, 131.5, 130.9, 129.9, 126.1, 126.0, 124.5, 122.8, 122.6, 121.5, 117.3, 36.2, 30.5. IR (KBr) 2965, 1613, 1584, 1531, 1472, 1413, 1247, 1074, 1003, 842, 641 cm^{-1}. HRMS (ESI): Calcd for $C_{52}H_{46}Br_2IrN_4$: 1077.1673 [M$^+$]. Found 1077.1694.

Ir-POP-1. Compounds **4a** (0.46 g, 0.50 mmol), **5** (0.21 g, 0.25 mmol) and $Pd(PPh_3)_4$ (60 mg, 0.05 mmol) were dissolved in 1,4-dioxane (15 mL). To the mixture was added a solution of K_2CO_3 (0.28 g, 2.0 mmol) in water (1.0 mL) and the mixture was stirred at 80 °C for 12 hours. after cooling to room temperature, the precipitate formed was filtered and washed successively with 1,4-dioxane, MeCN, water and MeOH. The solid was further extracted in a Soxhlet extractor with acetone to afford **Ir-POP-1** as a yellow powder (0.48 g, 90% calculated on the basis of).

Ir-POP-2. Compounds **4b** (0.68 g, 0.56 mmol), **5** (0.23 g, 0.28 mmol) and $Pd(PPh_3)_4$ (40 mg, 0.056 mmol) were dissolved in 1,4-dioxane (33 mL). To the mixture was added a solution of K_2CO_3 (0.30 g, 2.2 mmol) in water (1.1 mL) and the mixture was stirred at 80 °C for 12 hours. After cooling to room temperature, the precipitate formed was filtered and washed successively with 1,4-dioxane, MeCN, water and MeOH. The solid was further extracted in a Soxhlet extractor with acetone to afford **Ir-POP-2** as a yellow powder (0.64 g, 93%).



Compound Ir-Ph-1. A mixture of compound **6a** (0.92 g, 4.0 mmol), $IrCl_3 \cdot xH_2O$ (0.56 g, 1.8 mmol), 2-methoxyethanol (68 mL) and water (24 mL) in a Schlenk tube was stirred for 12 hours at 120 °C and then cooled to room temperature. The yellowish precipitate formed was filtered and washed with water and dried *in vacuo* to afford **7a** as a crude product (0.92 g, 76%). The product was used in the next reaction without further purification. A mixture of **7a** (0.42 g, 0.30 mmol), **3** (0.20 g, 0.60 mmol) in dichloromethane (64 mL) and methanol (32 mL) in a Schlenk tube was stirred for 12 hours under reflux and then cooled to room temperature. NH_4PF_6 (1.0 g, 6.0 mmol) was added and the mixture was stirred for 15 minutes. The solution was filtered and concentrated *in vacuo*. The resulting crude product was washed with ether and dried and then subjected to flash column chromatography on silica gel (CH_2Cl_2/MeOH 20:1) to afford **Ir-Ph-1** as a yellow solid (0.48 g, 86%). R_f = 0.32 (CH_2Cl_2:MeOH 20:1). M.p. >300 °C (decom.).^{1}H NMR (400 MHz, DMSO-d_6): δ 8.89 (d, *J* = 2.0 Hz, 2H), 8.57 (d, *J* = 2.0 Hz, 2H), 8.17 (d, *J* = 8.0 Hz, 2H), 8.05-7.93 (m, 4H), 7.83 (d, *J* = 6.0 Hz, 2H), 7.79-7.71 (m, 2H), 7.65-7.46 (m, 10H), 7.10-6.99 (m, 2H), 6.98-6.88 (m, 2H), 1.39 (s, 18H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.9, 164.0, 155.6, 151.6, 150.1, 149.4, 149.2, 144.3, 135.9, 131.5, 130.7, 129.7, 127.8, 126.0, 122.8, 122.6, 121.6, 117.3, 36.2, 30.4. IR (KBr) 2961, 1615, 1582, 1536, 1474, 1406, 1252, 1076, 1033, 838 cm^{-1}. HRMS (ESI): Calcd for $C_{52}H_{48}IrN_4$: 921.3506 [M$^+$]. Found: 927.3508.



Compound Ir-Ph-2. A mixture of compound **6b** (0.93 g, 3.0 mmol), $IrCl_3·xH_2O$ (0.39 g, 1.2 mmol), 2-methoxyethanol (48 mL) and water (18 mL) in a Schlenk tube was stirred for 12 hours at 120 °C and then cooled to room temperature. The yellowish precipitate formed was filtered and washed with water and dried *in vacuo* to afford **7b** as a crude product (0.93 g, 91%). The product was used in the next reaction without further purification. A mixture of **7b** (0.72 g, 0.44 mmol), **3** (0.29 g, 1.1 mmol) in dichloromethane (120 mL) and methanol (60 mL) in a Schlenk tube was stirred for 12 hours under reflux and then cooled to room temperature. NH_4PF_6 (1.4 g, 8.8 mmol) was added and the mixture was stirred for 15 minutes. The solution was filtered and concentrated *in vacuo*. The resulting crude product was washed with ether and dried and then subjected to flash column chromatography on silica gel (CH_2Cl_2/MeOH 20:1) to afford **Ir-Ph-2** as a yellow solid (0.80 g, 77%). R_f = 0.27 (CH_2Cl_2:MeOH 20:1). M.p. >300 °C (decom.). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.47 (d, *J* = 1.6 Hz, 2H), 8.16 (d, *J* = 2.0 Hz, 2H), 7.92 (d, *J* = 6.0 Hz, 2H), 7.75-7.74 (m, 10H), 7.71-7.64 (m, 6H), 7.54-7.48 (m, 4H), 7.47-7.36 (m, 6H), 7.13-7.05 (m, 2H), 7.01-6.93 (m, 2H), 6.50-6.43 (m, 2H), 1.48 (s, 18H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.9, 164.1, 155.6, 151.6, 150.1, 149.2, 148.8, 144.3, 142.2, 139.4, 134.8, 131.5, 130.8, 129.5, 128.5, 128.4, 127.8, 127.2, 126.8, 126.0, 122.8, 122.6, 121.4, 117.1, 36.2, 30.5. IR (KBr) 2963, 1613, 1582, 1544, 1470, 1404, 1253, 1080, 1033, 833 cm^{-1}. HRMS (ESI): Calcd for $C_{64}H_{56}IrN_4$: 1073.4134 [M$^+$]. Found: 1073.4116.

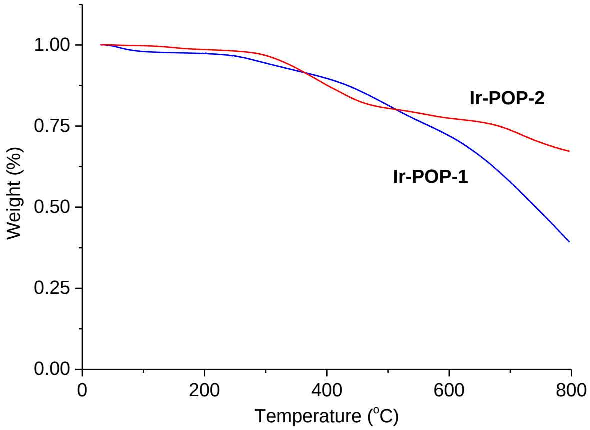


Fig. S1 Thermogravimetric profile of polymers **Ir-POP-1** and **Ir-POP-2**.

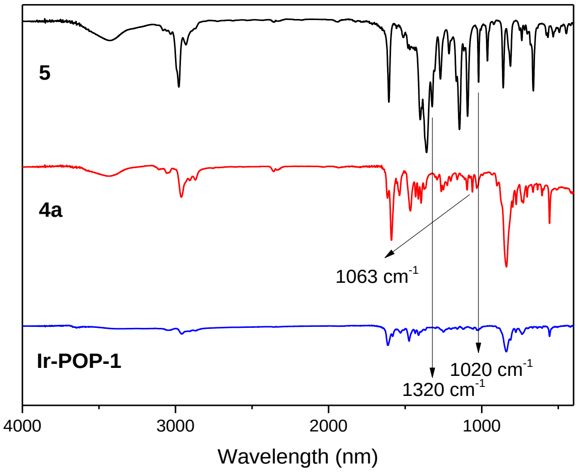


Fig. S2 FT-IR spectrum of compounds **5** and **4a** and polymer **Ir-POP-1**.

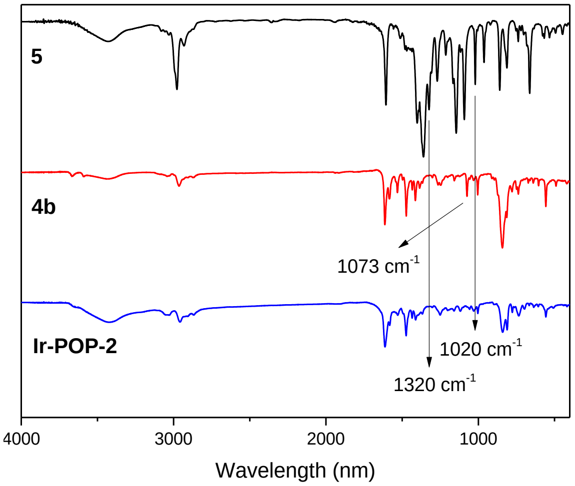


Fig S3 FT-IR spectrum of compounds **5** and **4b** and polymer **Ir-POP-2**.

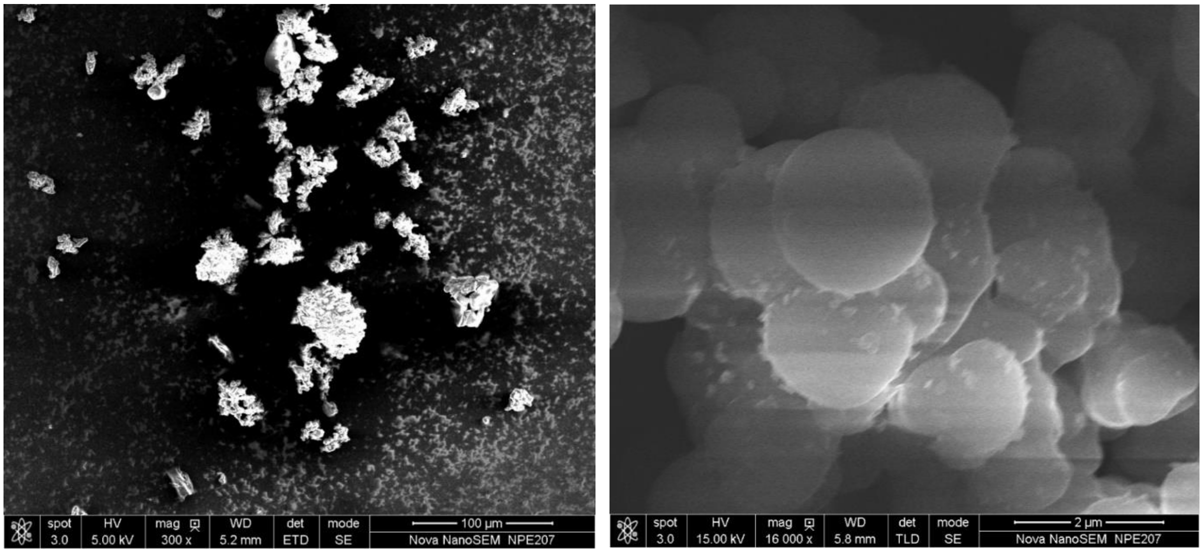


Fig. S4 SEM images of polymers **Ir-POP-1** (left) and **Ir-POP-2** (right).

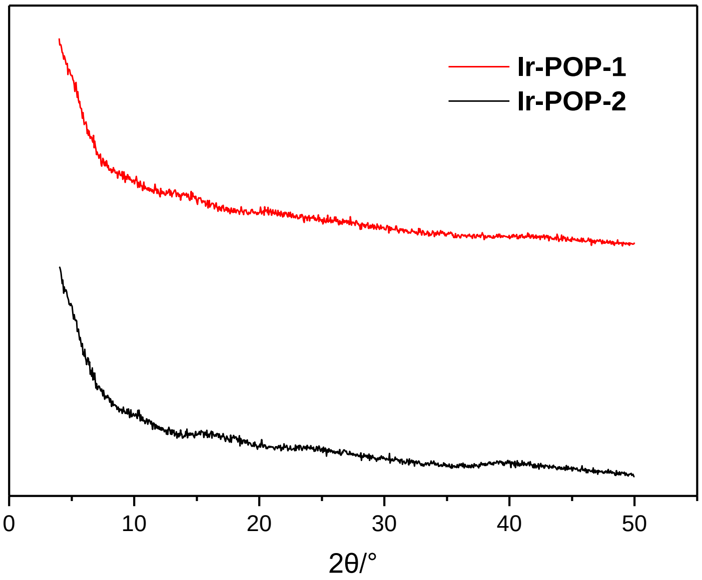


Fig. S5 Powder X-ray diffraction (PXRD) of **Ir-POP-1** and **Ru-POP-2**. The weak, broad peaks indicate the amorphous nature of the two polymers.

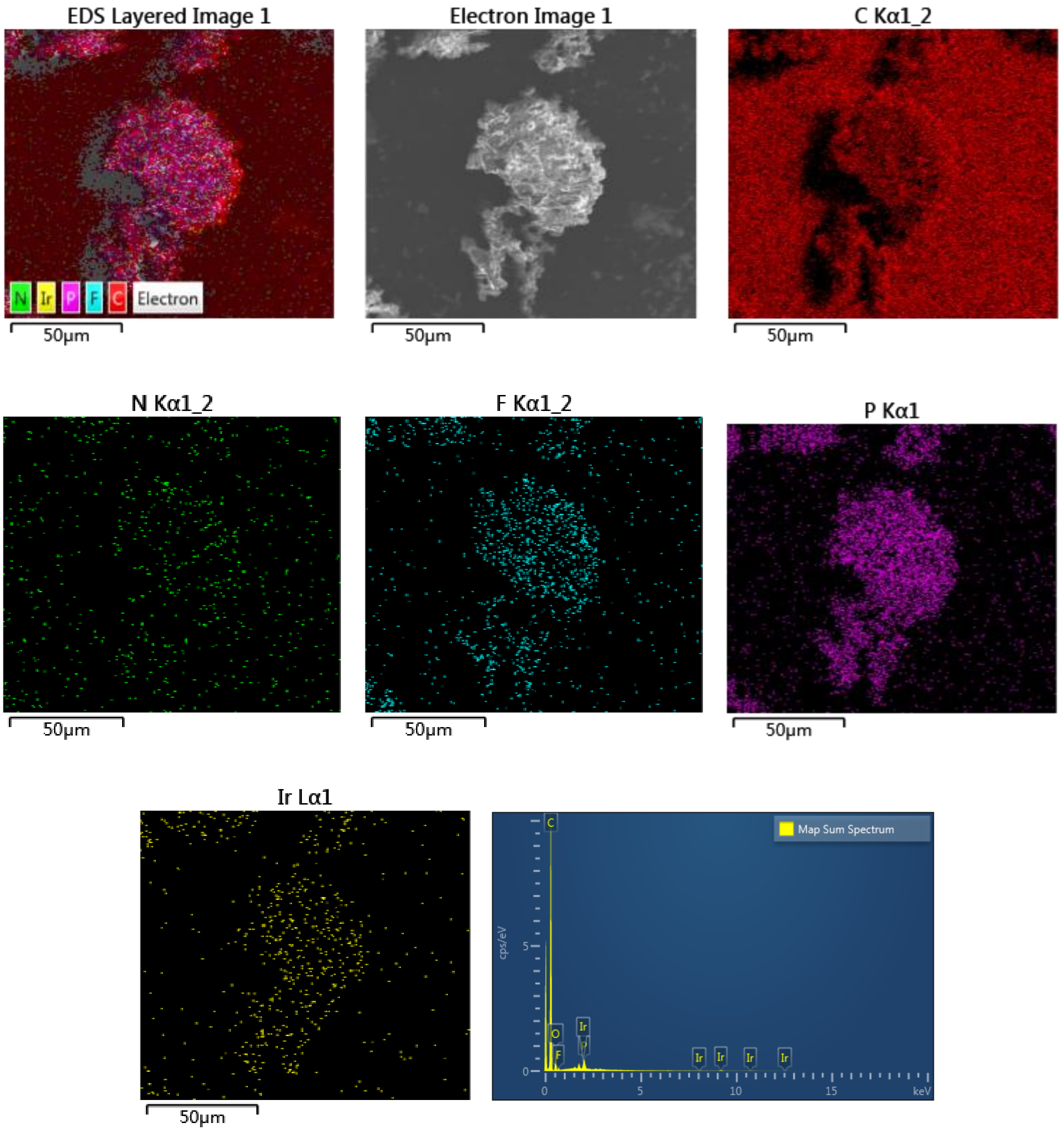


Fig. S6 Energy dispersive spectroscopic (EDS) images of polymer **Ir-POP-1**.

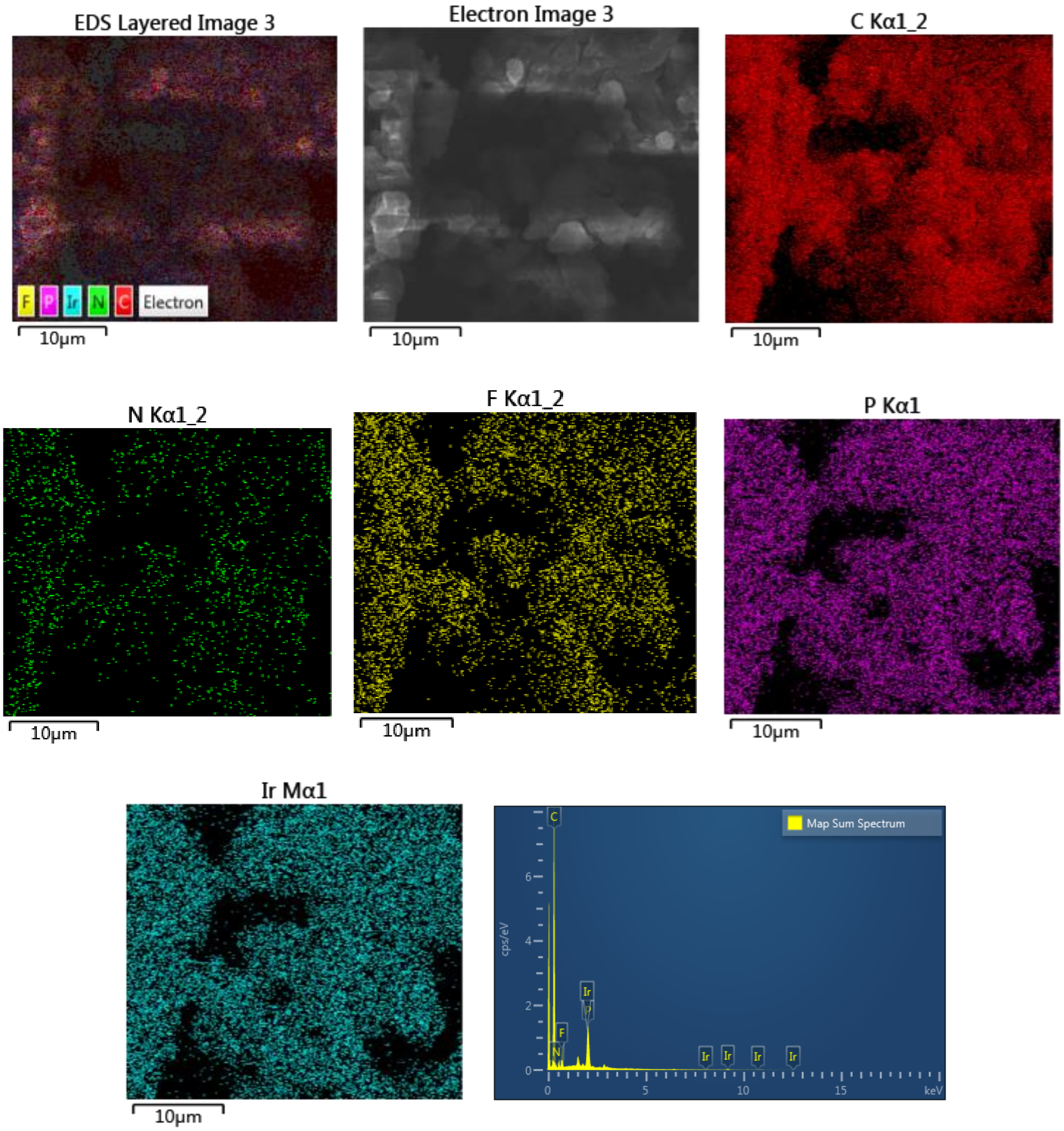


Fig. S7 EDS images of polymer **Ir-POP-2**.

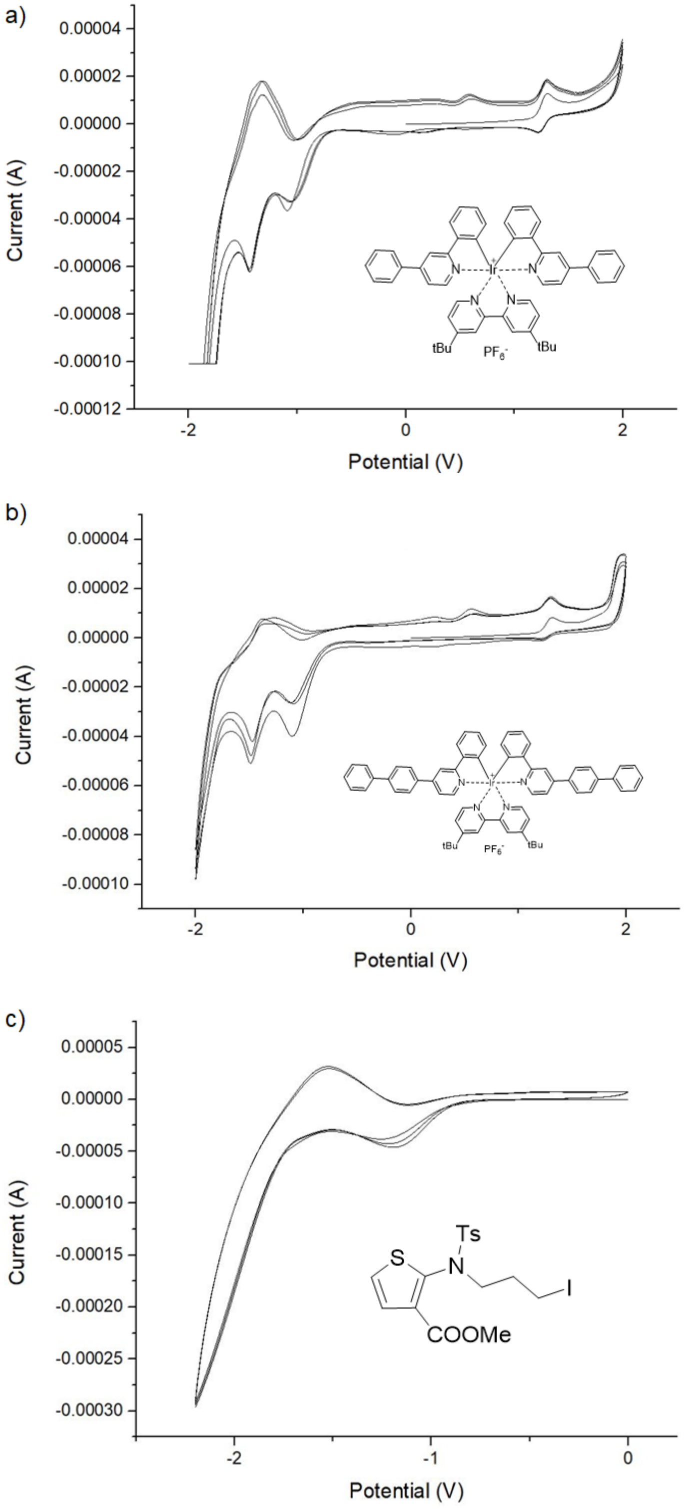


Fig. S8 Cyclic Voltammetry (CV) curve of a) **Ir-Ph-1**, b) **Ir-Ph-2** and c) **8a** in acetonitrile ($E_{1/2}^{red}$= -1.217 V vs. (Ag/AgCl) (-1.262 V vs. SCE)).

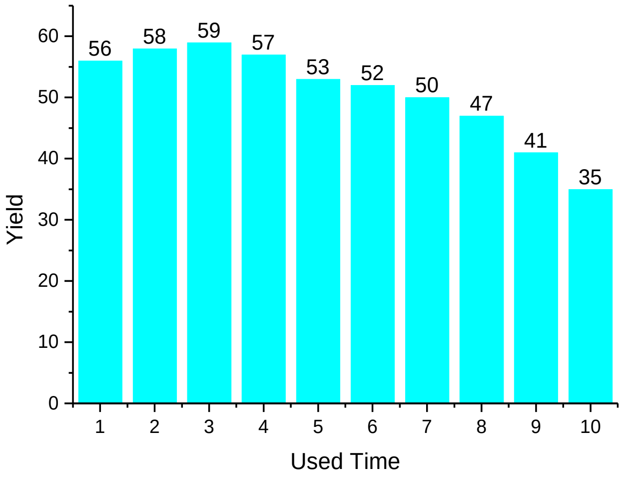


Fig. S9 Recyclability of **Ir-POP-2** in the reactions for the generation of **9a**. Conditions: **8a** (0.1 mmol, 1 equiv.), **Ir-POP-2** (1 μmol, 1.0 mol%), DIPEA (85 μL, 0.5 mmol, 5.0 equiv.), two 34 W blue LED lamps, room temperature, 6 h.

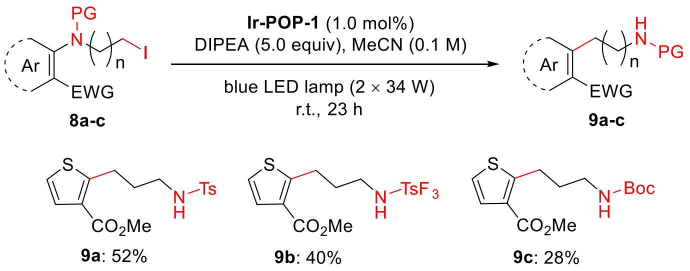


Fig. S10 Substrate scope for **Ir-POP-1**-catalyzed rearrangements of alkyliodides **8a-c** to form the related alkylamines **9a-c**. The yields were determined by GC.

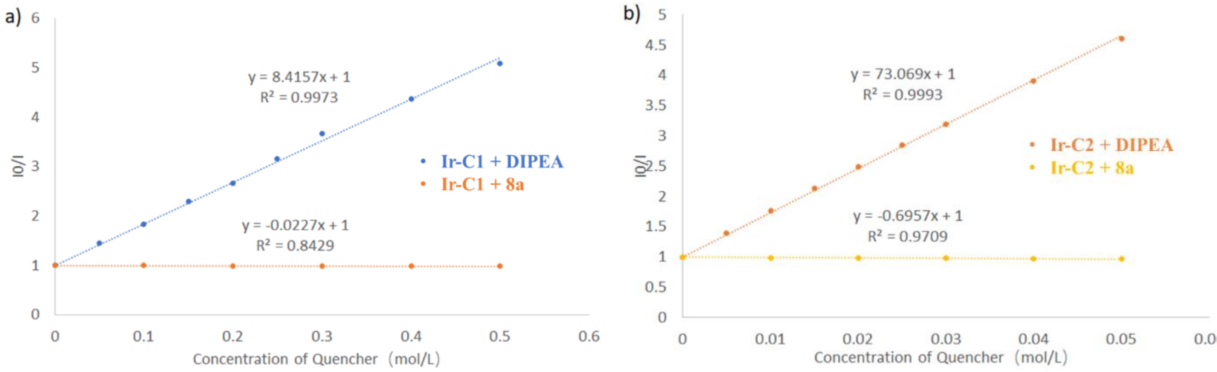


Fig. S11. Stern-Volmer fluorescent quenching experiments. a) **Ir-Ph-1** or b) **Ir-Ph-2** was used as photosensitizer while DIPEA and **8a** were used as quencher separately.

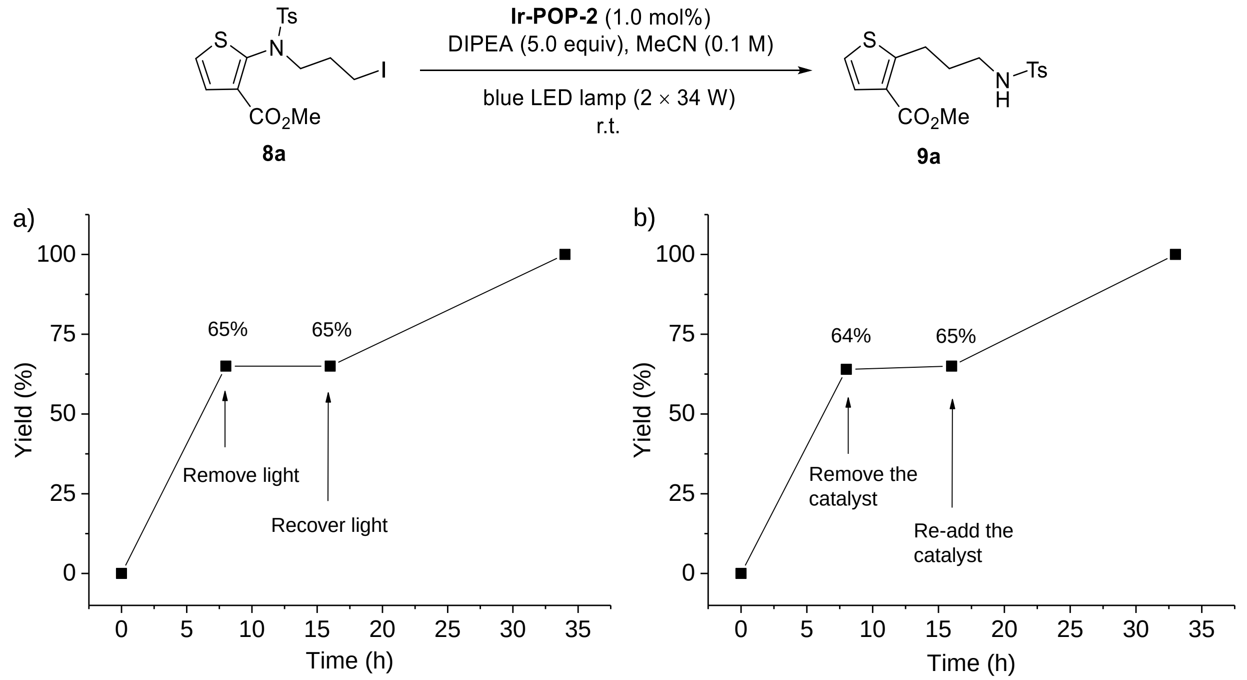


Fig. S12 a) On-off experiment and b) leaching experiment for the rearrangement of **8a** to produce **9a** in acetonitrile in the presence of **Ir-POP-2**.

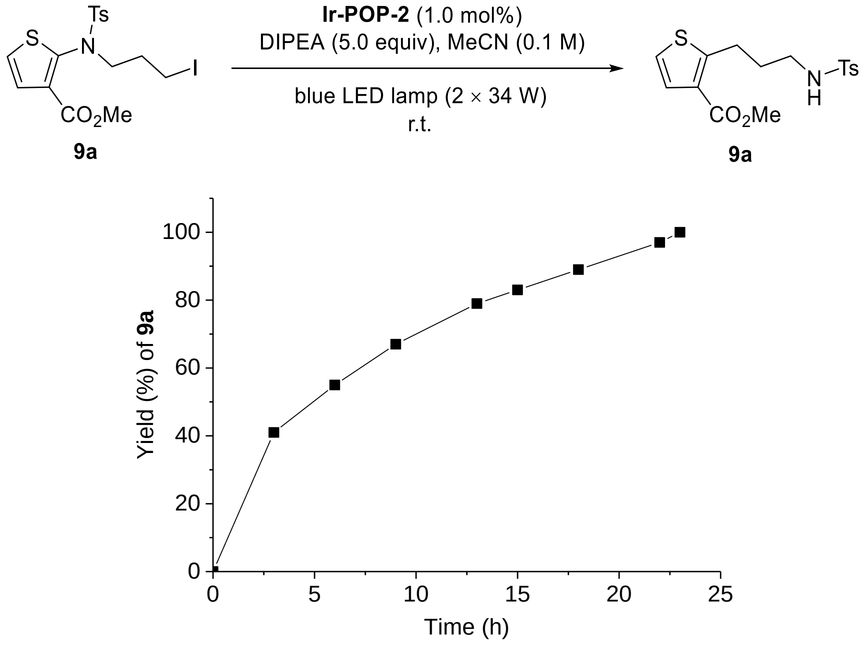
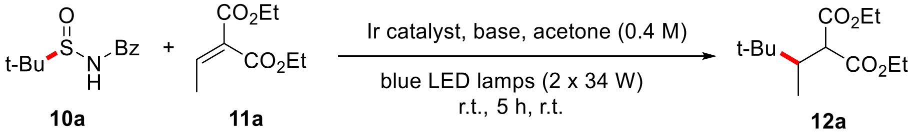


Fig. S13 The reaction progress of **Ir-POP-2**-mediated visible light photoredox rearrangement of **8a** to form **9a** in MeCN.

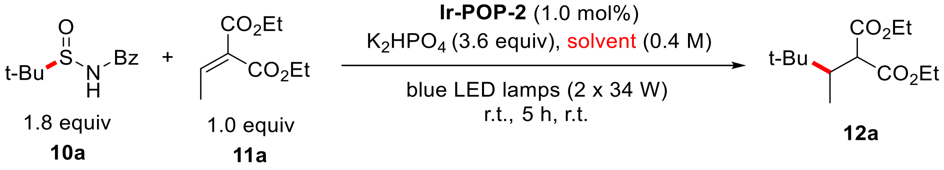
Table S1. Photocatalytic desulfurative conjugate addition of **10a** and **11a** to afford **12a**



Entry	Catalyst [mol%]	Base [equiv]	Yield[a] [%]
1[b]	**Ir-Ph-1** (1.0)	K_2HPO_4 (3.6)	95
2[b]	**Ir-Ph-2** (1.0)	K_2HPO_4 (3.6)	96
3	**Ir-POP-1** (1.0)	K_2HPO_4 (3.6)	19
4	**Ir-POP-2** (1.0)	K_2HPO_4 (3.6)	92
5	**Ir-POP-2** (0.5)	K_2HPO_4 (3.6)	74
6	—	K_2HPO_4 (3.6)	n.d.
7	**Ir-POP-2** (1.0)	K_2HPO_4 (1.8)	65
8	**Ir-POP-2** (1.0)	—	n.d.
9[c]	**Ir-POP-2** (1.0)	K_2HPO_4 (3.6)	13
10[d]	**Ir-POP-2** (1.0)	K_2HPO_4 (3.6)	n.d.
11[e]	**Ir-POP-2** (1.0)	K_2HPO_4 (3.6)	n.d.

[a]Reactions were conducted on a 0.5 mmol scale (**10a**) with 1.8 equiv of **10a** and 1.0 equiv of **11a**. Yields were determined by GC with n-dodecane as internal standard. [b]Reaction time: 3 h. [c]Using a 23 W CFL bulb as light source. [d]No light source. [e]2,2,6,6-Tetramethylpiperidinyl-1-oxide (TEMPO, 1.0 equiv) was added as free radical scavenger.

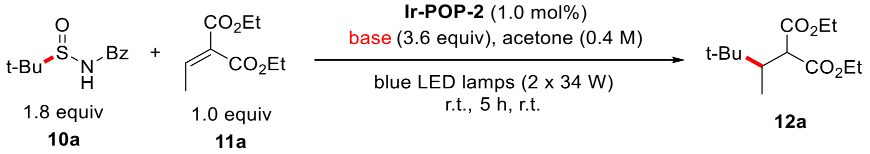
Table S2. Solvent optimization for heterogeneous photocatalytic desulfurative conjugate addition of **10a** and **11a** to afford **12a** in the presence of **Ir-POP-2**



Entry[a]	solvent	Yield[b] [%]
1	MeCN	37
2	DMF	53
3	DMAC	45
4	DMSO	36
5	Acetone	92
6	DMPU	7

[a]Reactions were conducted on a 0.5 mmol scale (**10a**). [b] Yields were determined by GC with n-dodecane as internal standard.

Table S3. Base optimization the reaction of **10a** and **11a** to afford **12a** in the presence of **Ir-POP-2**



Entry	Base	Yield (%)[a]
1	K_2HPO_4	92
2	Cs_2CO_3	39
3	NaOAc	28
4	Na_2CO_3	31
5	K_3PO_4	36
6	K_2CO_3	47

[a]Reactions were conducted on a 0.5 mmol scale (**10a**). [b] Yields were determined by GC with n-dodecane as internal standard.

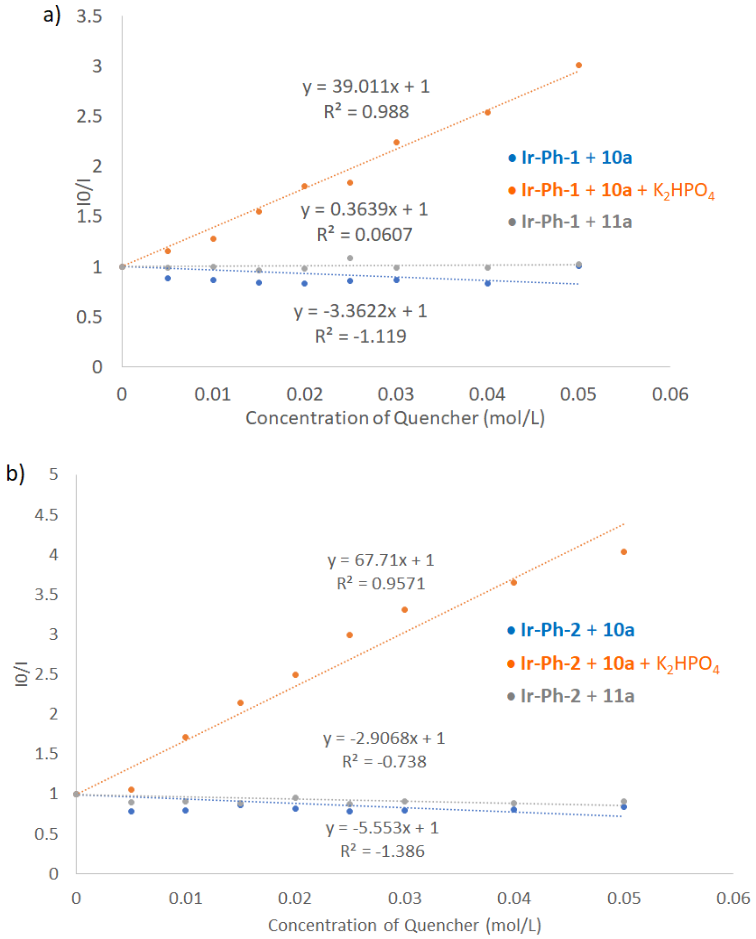


Fig. S14 Stern-Volmer fluorescent quenching experiments. a) **Ir-Ph-1** or b) **Ir-Ph-2** was used as photosensitizer while **10a**, **10a** + K_2HPO_4 and **11a** were used as quencher separately.

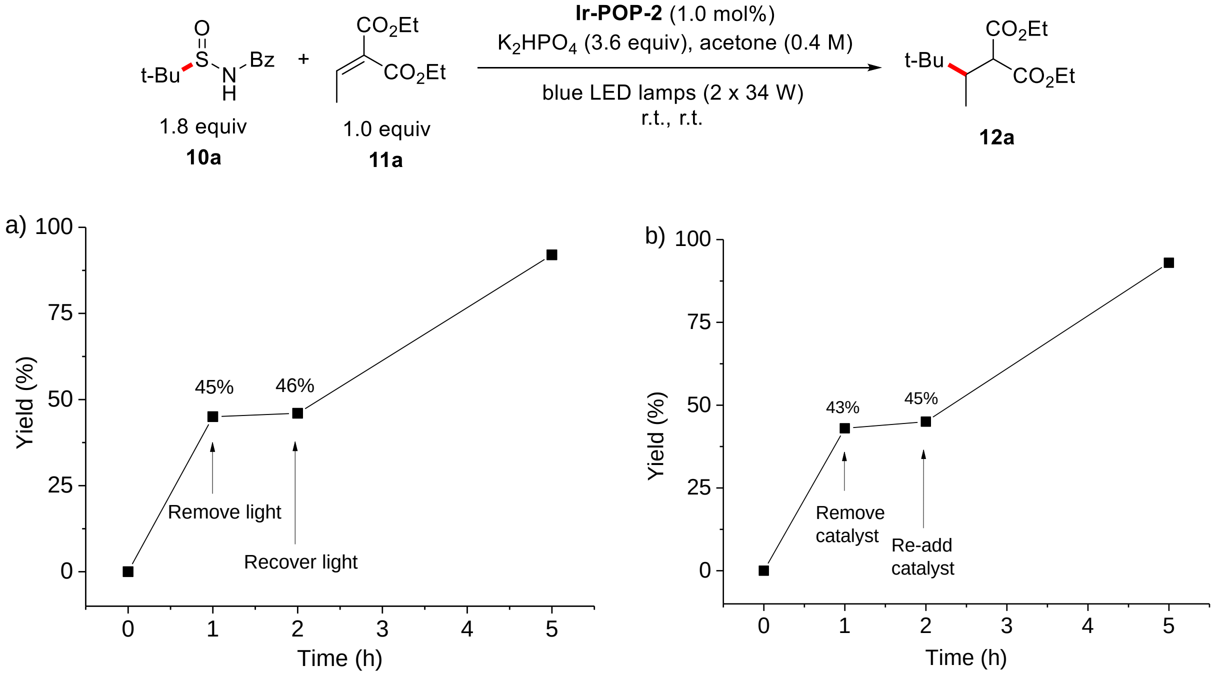


Fig. S15 a) On-off experiment and b) leaching experiment for the intermolecular coupling reaction in the presence of **Ir-POP-2**.

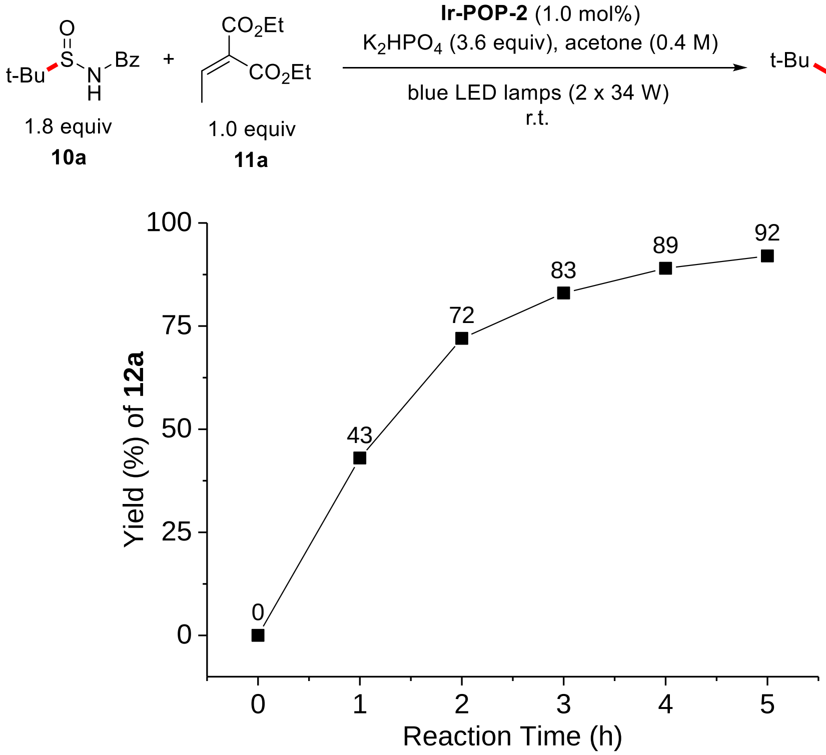
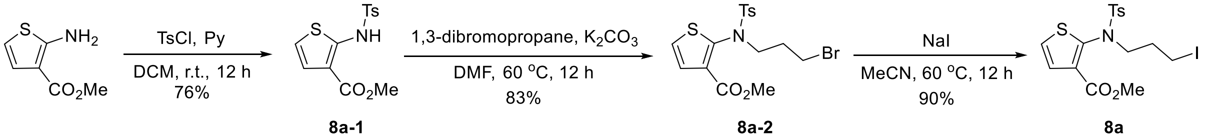


Fig. S16 The reaction progress of **Ir-POP-2**-mediated visible light photoredox reaction of **10a** and **11a** to form **12a** in acetonitrile.

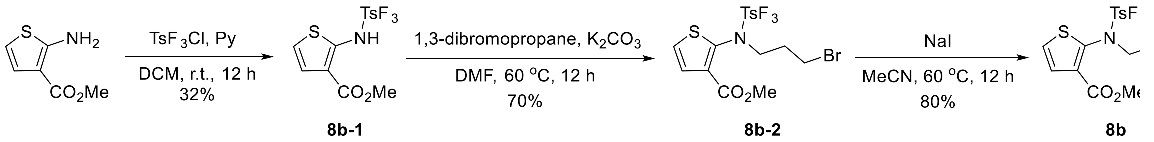
The preparation of starting materials:



Compound 8a-1. Methyl 2-aminothiophene-3-carboxylate (15.2 g, 96.7 mmol), tosyl chloride (27.7 g, 145 mmol) and pyridine (38.2 g, 38.9 mL, 483 mmol) were dissolved in DCM (250 mL). The mixture was stirred for 12 h at room temperature. This organic solution was washed with 1N HCl, water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8a-1** as white solid (23.09 g, 76%). R_f = 0.67 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 5.6 Hz, 1H), 6.65 (d, *J* = 5.6 Hz, 1H), 3.80 (s, 3H), 2.39 (s, 3H).

Compound 8a-2. Compound **8a-1** (11.5 g, 36.93 mmol), 1,3-dibromopropane (74.5 g, 37.5 mL, 369.3 mmol) and K_2CO_3 (20.5 g, 184.5 mmol) were dispersed in DMF (529 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM and this organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8a-2** as white solid (13.40 g, 83%). R_f = 0.46 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 6.0 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 5.6 Hz, 1H), 3.79 (t, *J* = 6.8 Hz, 2H), 3.64 (s, 3H), 3.50 (t, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 2.21-2.10 (m, 2H).

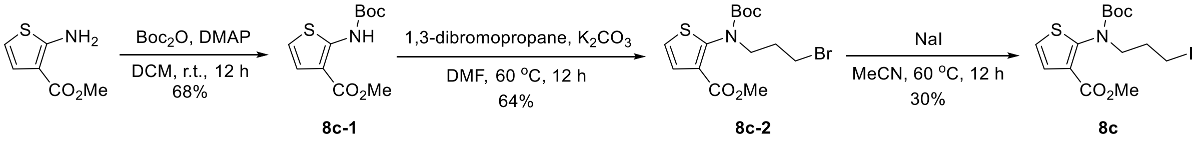
Compound 8a. Compound **8a-2** (0.49 g, 1.13 mmol) and NaI (0.85 g, 5.67 mmol) were dissolved in MeCN (11 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8a** as white solid (0.49 g, 90%). R_f=0.46 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 5.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 5.6 Hz, 1H), 3.74 (t, *J* = 6.4 Hz, 2H), 3.64 (s, 3H), 3.26 (t, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 2.18-2.06 (m, 2H).



Compound 8b-1. Methyl 2-aminothiophene-3-carboxylate (2.37 g, 15.0 mmol), 4-(trifluoromethyl)benzene-1-sulfonyl chloride (4.03 g,16.5 mmol) and pyridine (3.56 g, 3.63 mL, 45.0 mmol) were dissolved in DCM (38 mL). The mixture was stirred for 12 h at room temperature. This organic solution was washed with hydrochloric acid (1N), water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8b-1** as white solid (1.80 g, 32%). R_f = 0.46 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.28 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 6.0 Hz, 1H), 6.73 (d, *J* = 6.0 Hz, 1H), 3.84 (s, 3H).

Compound 8b-2. Compound **8b-1** (1.10 g, 3.0 mmol), 1,3-dibromopropane (6.06 g, 3.1 mL, 30.0 mmol) and K_2CO_3 (2.07 g, 15.0 mmol) were dispersed in DMF (43 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM and this organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8b-2** as white solid (1.03 g, 70%). R_f=0.37 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 6.0 Hz, 1H), 7.22 (d, *J* = 6.0 Hz, 1H), 3.87 (t, *J* = 6.8 Hz, 2H), 3.57 (s, 3H), 3.49 (t, *J* = 6.4 Hz, 2H), 2.23-2.13 (m, 2H).

Compound 8b. Compound **8b-2** (1.03 g, 2.12 mmol) and NaI (1.59 g, 10.59 mmol) were dissolved in MeCN (21 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8b** as white solid (0.91 g, 80%). R_f = 0.37 (hexane/ethyl acetate 5:1). M.p. 59-61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 6.4 Hz, 1H), 7.23 (d, *J* = 6.0 Hz, 1H), 3.81 (t, *J* = 6.8 Hz, 2H), 3.57 (s, 3H), 3.25 (t, *J* = 6.8 Hz, 2H), 2.20-2.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=161.4, 145.2, 141.6, 134.7, 134.4, 129.3, 128.2, 128.0, 125.9, 124.4, 53.8, 51.6, 32.6, 1.6. IR (KBr): 2953, 1717, 1354, 1323, 1267, 1171, 1131, 1061 cm^{-1}. HRMS (ESI): Calcd for $C_{16}H_{15}F_3INO_4S_2Na$: 555.9331 $[M + Na]^+$. Found: 555.9317.

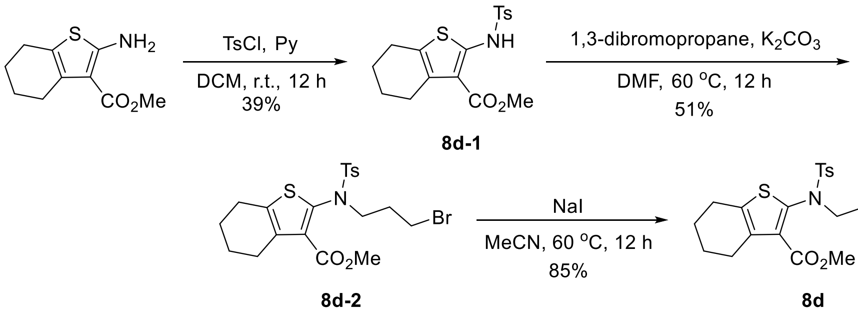


Compound 8c-1. Methyl 2-aminothiophene-3-carboxylate (0.94 g, 6.0 mmol), Boc_2O (1.44 g, 6.6 mmol) and DMAP (0.07 g, 0.6 mmol) were dissolved in DCM (20 mL). The mixture was stirred for 12 h at room temperature. This organic solution was washed with hydrochloric acid (1N), water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8c-1** as colourless oil (1.05 g, 68%). R_f = 0.86 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 7.14 (d, *J* = 6.0 Hz, 1H), 6.65 (d, *J* = 5.6 Hz, 1H), 3.86 (s, 3H), 1.53 (s, 9H).

Compound 8c-2. Compound **8c-1** (1.05 g, 4.08 mmol), 1,3-dibromopropane (8.24 g, 4.2 mL, 40.8 mmol) and K_2CO_3 (2.82 g, 20.4 mmol) was dispersed in DMF (58 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM and this organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8c-2** as colourless oil (0.99 g, 64%). R_f = 0.83 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 5.6 Hz, 1H), 7.07 (d, *J* = 6.0 Hz, 1H), 3.83 (s, 3H), 3.77 (t, *J* = 6.8 Hz, 2H), 3.46 (t, *J* = 6.8 Hz, 2H), 2.23-2.10 (m, 2H), 1.34 (s, 9H).

Compound 8c. Compound **8c-2** (1.00 g, 2.6 mmol) and NaI (1.98 g, 13.2 mmol) were dissolved in

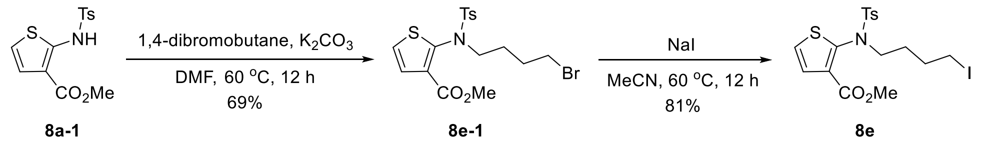
MeCN (26 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8c** as colorless oil (0.34 g, 30%). R_f = 0.38 (hexane/ethyl acetate 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 5.6 Hz, 1H), 7.09 (d, J = 5.6 Hz, 1H), 3.85 (s, 3H), 3.73 (t, J = 7.2 Hz, 2H), 3.23 (t, J = 7.2 Hz, 2H), 2.24-2.09 (m, 2H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 153.7, 150.9, 127.4, 126.4, 121.3, 80.9, 52.1, 51.6, 32.1, 27.9, 2.5. IR (KBr): 2959, 1706, 1341, 1268, 1162 cm^{-1}. HRMS (ESI): Calcd for $C_{14}H_{20}F_3INO_4SNa$: 448.0050 [M + Na]$^+$. Found: 448.0042.



Compound 8d-1. Methyl 2-amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylate (2.1 g, 10 mmol), tosyl chloride (2.2 g, 11.5 mmol) and pyridine (2.37 g, 2.41 mL, 30 mmol) were dissolved in DCM (20 mL). The mixture was stirred for 12 h at room temperature. This organic solution was washed with 1N HCl, water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8d-1** as white solid (1.45 g, 39%). R_f=0.30 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.38 (s, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 3.77 (s, 3H), 2.71-2.52 (m, 4H), 2.39 (s, 3H), 1.82-1.65 (m, 4H).

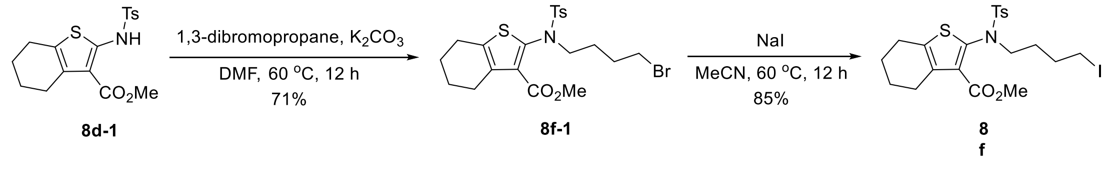
Compound 8d-2. Compounds **8d-1** (1.44 g, 3.94 mmol), 1,3-dibromopropane (8.5 g, 4.27 mL, 39.4 mmol) and K_2CO_3 (2.72 g, 19.7 mmol) were dispersed in DMF (58 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM and this organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8d-2** as white solid (0.99 g, 51%). R_f = 0.41 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 3.76-3.60 (m, 5H), 3.51 (t, J = 6.4 Hz, 2H), 2.80-2.69 (m, 2H), 2.69-2.61 (m, 2H), 2.43 (s, 3H), 2.23-2.11 (m, 2H), 1.88-1.72 (m, 4H).

Compound 8d. Compound **8d-2** (0.99 g, 2.04 mmol) and NaI (1.53 g, 10.18 mmol) were dissolved in MeCN (20 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8d** as white solid (0.94 g, 85%). R_f= 0.30 (hexane/ethyl acetate 5:1). M.p. 110-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 3.76-3.50 (m, 5H), 3.26 (t, J = 6.4 Hz, 2H), 2.79-2.58 (m, 4H), 2.43 (s, 3H), 2.20-2.07 (m, 2H), 1.89-1.71 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 143.8, 141.3, 135.3, 134.6, 130.5, 129.5, 127.9, 53.6, 51.5, 32.5, 25.7, 25.2, 22.8, 22.4, 21.6, 2.2. IR (KBr): 2929, 1708, 1354, 1268, 1239, 1167, 1089 cm^{-1}. HRMS (ESI): Calcd for $C_{20}H_{25}INO_4S_2$: 534.0264 [(M+H)$^+$]. Found: 534.0259.



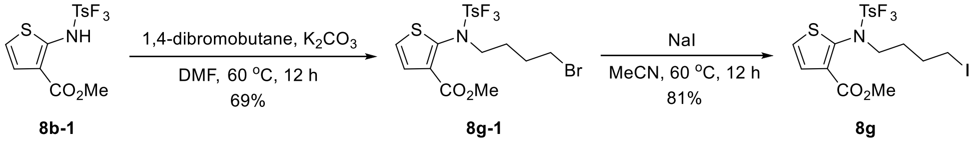
Compound 8e-1. Compounds **8a-1** (1.0 g, 3.21 mmol), 1,4-dibromobutane (6.93 g, 32.1 mmol) and K_2CO_3 (2.2 g, 16.1 mmol) were dispersed in DMF (46 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM and this organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8e-1** as white solid (0.99 g, 69%). R_f = 0.43 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 5.6 Hz, 1H), 7.26 (d, J = 7.6 Hz, 2H), 7.17 (d, J = 5.6 Hz, 1H), 3.70 (t, J = 6.8 Hz, 2H), 3.62 (s, 3H), 3.42 (t, J = 6.4 Hz, 2H), 2.42 (s, 3H), 2.03-1.91 (m, 2H), 1.78-1.66 (m, 2H).

Compound 8e. Compound **8e-1** (1.0 g, 2.24 mmol) and NaI (1.68 g, 11.20 mmol) were dissolved in MeCN (22 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8e** as white solid (0.89 g, 81%). R_f= 0.43 (hexane/ethyl acetate 5:1). M.p. 65-67 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 6.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 5.6 Hz, 1H), 3.69 (t, J = 7.2 Hz, 2H), 3.62 (s, 3H), 3.18 (t, J = 7.2 Hz, 2H), 2.42 (s, 3H), 1.97-1.87 (m, 2H), 1.73-1.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9, 145.7, 143.7, 135.2, 129.8. 129.4, 127.9, 127.7, 123.7, 51.5, 29.9, 29.3, 21.5, 6.0. IR (KBr): 2945, 1726, 1444, 1347, 1252, 1155, 1087 cm^{-1}. HRMS (ESI): Calcd for $C_{17}H_{20}INO_4S_2Na$: 515.9771 [M + Na]$^+$. Found: 515.9779.



Compound 8f-1. Compounds **8d-1** (1.50 g, 4.10 mmol), 1,4-dibromobutane (8.86 g, 4.90 mL, 41.0 mmol) and K_2CO_3 (2.84 g, 20.5 mmol) were dispersed in DMF (60 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM and this organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8f-1** as white solid (1.46 g, 71%). R_f = 0.30 (hexane/ethyl acetate 5:1). M.p. 100-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 3.64 (s, 3H), 3.58 (t, J = 6.8 Hz, 3H), 3.42 (t, J = 6.8 Hz, 2H), 2.78-2.59 (m, 4H), 2.43 (s, 3H), 2.03-1.90 (m, 2H), 1.89-1.66 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 143.6, 141.4, 135.6, 134.6, 130.3, 129.5, 127.9, 52.0, 51.4, 33.2, 29.5, 27.0, 25.7, 25.2, 22.8, 22.4, 21.5. IR (KBr): 2950, 1723, 1355, 1253, 1244, 1160, 1090 cm^{-1}. HRMS (ESI): Calcd for $C_{21}H_{26}BrNO_4S_2Na$: 524.0359 [M + Na]$^+$. Found: 524.0362.

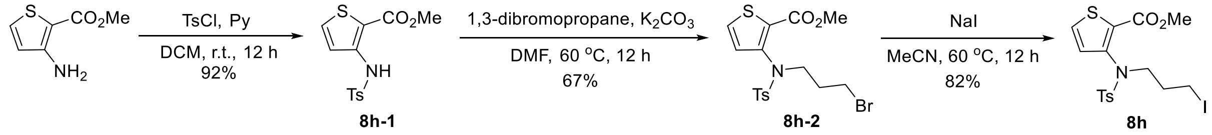
Compound 8f. Compound **8f-1** (1.46 g, 2.90 mmol) and NaI (2.19 g, 14.60 mmol) were dissolved in MeCN (29 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8f** as colourless oil (1.36 g, 85%). R_f = 0.30 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.64 (s, 3H), 3.57 (t, *J* = 6.4 Hz, 2H), 3.19 (t, *J* = 6.4 Hz, 2H), 2.82-2.61 (m, 4H), 2.43 (s, 3H), 2.01-1.88 (m, 2H), 1.88-1.74 (m, 4H) 1.74-1.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 143.6, 141.3, 135.5, 135.2, 134.6, 130.2, 129.5, 127.8, 51.7, 51.4, 30.2, 29.3, 25.7, 25.1, 22.7, 22.4, 21.5, 6.1. IR (KBr): 2937, 1717, 1354, 1277, 1243, 1166, 1090 cm^{-1}. HRMS (ESI): Calcd for $C_{21}H_{26}INO_4S_2Na$: 570.0240 [M + Na]$^+$. Found: 570.0240.



8b-1 **8g-1** **8g**

Compound 8g-1. Compounds **8b-1** (1.83 g, 5.0 mmol), 1,4-dibromobutane (10.80 g, 6.0 mL, 50.0 mmol) and K_2CO_3 (3.46 g, 25.0 mmol) were dispersed in DMF (74 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM and this organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8g-1** as white solid (0.99 g, 40%). R_f = 0.48 (hexane/ethyl acetate 5:1). M.p. 46-48 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 6.0 Hz, 1H), 7.22 (d, *J* = 6.0 Hz, 1H), 3.78 (t, *J* = 6.8 Hz, 2H), 3.54 (s, 3H), 3.42 (t, *J*=6.4 Hz, 2H), 2.03-1.92 (m, 2H), 1.80-1.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 145.1, 141.9, 129.2, 129.2, 128.2, 128.0, 125.9, 125.8, 124.5, 52.1, 51.5, 33.0, 29.3, 27.1. IR (KBr): 2952, 1717, 1433, 1347, 1251, 1224, 1159, 1085 cm^{-1}. HRMS (ESI): Calcd for $C_{17}H_{20}BrF_3NO_4S_2Na$: 523.9606 [M + Na]$^+$. Found: 523.9618.

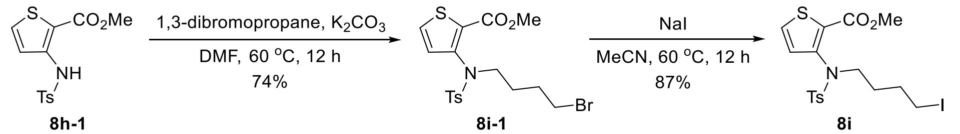
Compound 8g. Compound **8g-1** (0.23 g, 0.47 mmol) and NaI (0.35 g, 2.34 mmol) were dissolved in MeCN (4.5 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8g** as white solid (0.24 g, 91%). R_f = 0.48 (hexane/ethyl acetate 5:1). M.p. 52-53 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 6.0 Hz, 1H), 7.22 (d, *J* = 6.0 Hz, 1H), 3.77 (t, *J* = 6.0 Hz, 2H), 3.54 (s, 3H), 3.19 (t, *J* = 6.8 Hz, 2H), 2.00-1.87 (m, 2H), 1.77-1.62 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 145.1, 141.9, 134.7, 134.3, 129.2, 128.2, 128.0, 125.9, 124.4, 51.9, 51.5, 30.0, 29.5, 5.7. IR (KBr): 2953, 1725, 1357, 1320, 1261, 1177, 1130, 1060 cm^{-1}. HRMS (ESI): Calcd for $C_{17}H_{20}F_3INO_4S_2Na$: 569.9488 [M + Na]$^+$. Found: 569.9498.



Compound 8h-1. Methyl 3-aminothiophene-2-carboxylate (1.57 g, 10.0 mmol), tosyl chloride (2.19 g, 11.48 mmol) and pyridine (3.97 g, 4.04 mL, 50.0 mmol) were dissolved in DCM (25 mL). The mixture was stirred for 12 h at room temperature. This organic solution was washed with 1N HCl, water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8h-1** as white solid (2.88g, 92%). R_f=0.37 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.59 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.39 (s, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H).

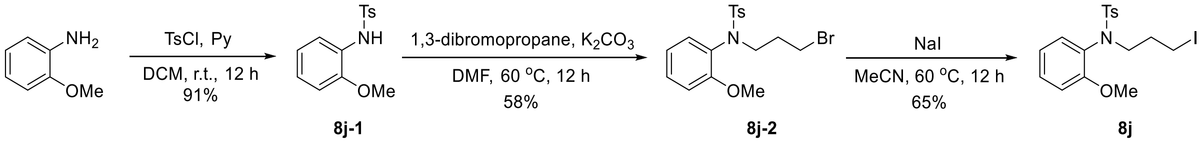
Compound 8h-2. Compounds **8h-1** (1.0 g, 3.2 mmol), 1,3-dibromopropane (6.93 g, 3.5 mL, 32.1 mmol) and K_2CO_3 (2.22 g, 16.1 mmol) were dispersed in DMF (46 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM and this organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8h-2** as white solid (0.96 g, 67%). R_f = 0.31 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 5.6 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 5.2 Hz, 1H), 3.77 (t, *J* = 6.8 Hz, 2H), 3.68 (s, 3H), 3.51 (t, *J* = 6.8 Hz, 2H), 2.44 (s, 3H), 2.18-2.06 (m, 2H).

Compound 8h. Compounds **8h-2** (0.96 g, 2.15 mmol) and NaI (1.61 g, 10.75 mmol) were dissolved in MeCN (21 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8h** as white solid (0.85 g, 82%). R_f = 0.37 (hexane/ethyl acetate 5:1). M.p. 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* 8.0 Hz, 2H), 7.46 (d, *J* 5.2 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 5.2 Hz, 1H), 3.77-3.57 (m, 5H), 3.24 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 2.13-1.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 143.4, 140.7, 135.8, 129.8, 129.4, 129.3, 128.6, 127.5, 52.0, 33.2, 21.4, 2.4. IR (KBr): 2946, 1734, 1433, 1347, 1261, 1230, 1159, 1086 cm^{-1}. HRMS (ESI): Calcd for $C_{16}H_{18}INO_4S_2Na$: 501.9614 $[M + Na]^+$. Found: 501.9647.



Compound 8i-1. Compounds **8h-1** (1.56 g, 5.0 mmol), 1,4-dibromobutane (10.80 g, 6.0 mL, 50.0 mmol) and K_2CO_3 (3.46 g, 25.0 mmol) were dispersed in DMF (74 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM and this organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8i-1** as white solid (1.65 g, 74%). R_f= 0.32 (hexane/ethyl acetate 5:1). M.p. 80-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 5.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 5.2 Hz, 1H), 3.71-3.55 (m, 5H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 2.01-1.89 (m, 2H), 1.71-1.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 143.3, 140.5, 136.1, 130.2, 129.4, 128.6, 127.5, 51.9, 50.3, 33.2, 29.4, 27.5, 21.5. IR (KBr): 2950, 1727, 1433, 1343, 1251, 1221, 1159, 1089 cm^{-1}. HRMS (ESI): Calcd for $C_{17}H_{20}BrNO_4S_2Na$: 469.9889 $[M + Na]^+$. Found: 469.9876.

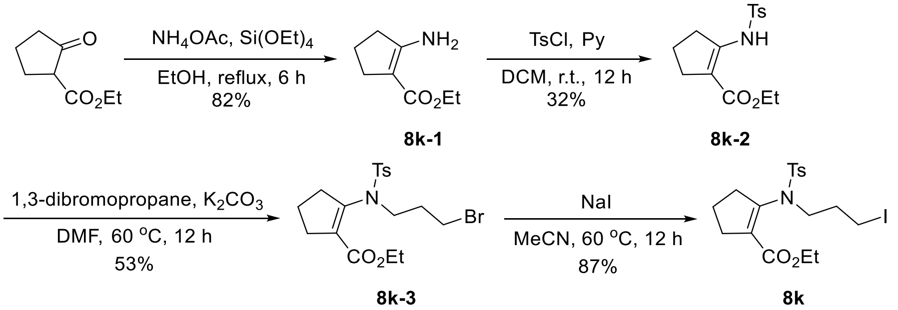
Compound 8i. Compounds **8i-1** (1.00 g, 2.24 mmol) and NaI (1.68 g, 11.20 mmol) were dissolved in MeCN (22 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8i** as white solid (0.97 g, 87%). R_f = 0.32 (hexane/ethyl acetate 5:1). M.p. 85-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J*=8.0 Hz, 2H), 7.46 (d, *J* = 5.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 5.2 Hz, 1H), 3.72-3.57 (m, 5H), 3.17 (t, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 1.97-1.84 (m, 2H), 1.67-1.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 143.3, 140.6, 136.3, 130.3, 129.3, 128.7, 127.9, 127.6, 52.0, 50.1, 30.2, 29.9, 21.5, 6.1. IR (KBr): 2944, 1723, 1359, 1250, 1167, 1088 cm^{-1}. HRMS (ESI): Calcd for $C_{17}H_{20}INO_4S_2Na$: 515.9771 $[M + Na]^+$. Found: 515.9771.



Compound 8j-1. Compounds *o*-anisidine (1.14 g, 9.28 mmol), tosyl chloride (2.03 g, 10.67 mmol) and pyridine (3.64 g, 3.7 mL, 46.4 mmol) were dissolved in DCM (23 mL). The mixture was stirred for 12 h at room temperature. This organic solution was washed with 1N HCl, water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8j-1** as white solid (2.35 g, 91%). R_f= 0.50 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.54 (dd, J_1 = 8.0, J_2 = 1.6 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.10-6.99 (m, 2H), 6.96-6.88 (m, 1H), 6.75 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 3.67 (s, 3H), 2.38 (s, 3H).

Compound 8j-2. Compounds **8j-1** (0.83 g, 3.0 mmol), 1,3-dibromopropane (6.06 g, 3.06 mL, 30.0 mmol) and K_2CO_3 (2.07 g, 15.0 mmol) were dispersed in DMF (43 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM and this organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8j-2** as white solid (0.69 g, 58%). R_f= 0.41 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.40-7.18 (m, 4H), 6.96 (t, *J*=7.6 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 3.79-3.66 (m, 2H), 3.50 (t, *J* = 6.8 Hz, 2H), 3.45 (s, 3H), 2.44 (s, 3H), 2.09-1.98 (m, 2H).

Compound 8j. Compounds **8j-2** (0.69 g, 1.47 mmol) and NaI (1.10 g, 7.33 mmol) were dissolved in MeCN (14 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8j** as white solid (0.51 g, 65%). R_f = 0.41 (hexane/ethyl acetate 5:1). M.p. 87-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.38-7.18 (m, 4H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 3.72-3.61 (m, 2H), 3.46 (s, 3H), 3.26 (t, *J* = 6.8 Hz, 2H), 2.44 (s, 3H), 2.07-1.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 142.8, 136.9, 132.5, 129.8, 128.9, 127.5, 126.6, 120.6, 111.7, 54.9, 50.5, 33.0, 21.4, 2.5. IR (KBr): 2936, 1497, 1346, 1259, 1161, 1097, 1030 cm^{-1}. HRMS (ESI): Calcd for $C_{17}H_{20}INO_3SNa$: 468.0101 $[M + Na]^+$. Found: 468.0103.



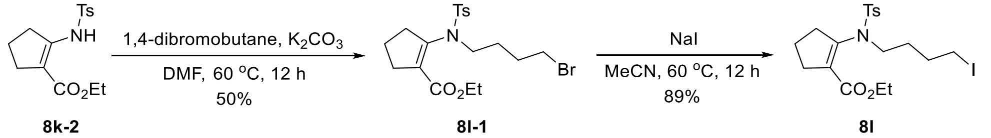
Compound 8k-1. Ethyl 2-oxocyclopentanecarboxylate (4.96 g, 32 mmol), NH_4OAc (12.32 g, 160 mmol) and $Si(OEt)_4$ (13.36 g, 14.24 mL, 64 mmol) were dissolved in Ethanol (160 mL). The mixture was stirred for 6 h under reflux with inert gas protection and the solvent was then removed *in vacuo*. The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8k-1** as white solid (4.07 g, 82%). R_f = 0.50 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): 4.16 (q, *J* = 7.2 Hz, 2H), 2.58-2.42 (m, 4H), 1.89-1.75 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

Compound 8k-2. Compounds **8k-1** (4.07 g, 26.21 mmol), tosyl chloride (5.75 g, 30.14 mmol) and pyridine (10.37 g, 10.5 mL, 131.04 mmol) were dissolved in DCM (69 mL). The mixture was stirred for 12 h at room temperature. This organic solution was washed with 1N HCl, water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8k-2** as white solid (2.64 g, 32%). R_f = 0.5 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ10.09 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.53-2.38 (m, 5H), 1.86-1.72 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

Compound 8k-3. Compounds **8k-2** (1.0 g, 3.23 mmol), 1,3-dibromopropane (6.52 g, 3.28 mL, 32.3 mmol) and K_2CO_3 (2.23 g, 16.2 mmol) were dispersed in DMF (47 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM and this organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8k-3** as white solid (0.74 g, 53%). R_f = 0.28 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.57 (t, *J* = 6.4 Hz, 2H), 3.493(t, *J* = 6.4 Hz, 2H), 2.77-2.61 (m, 2H), 2.50-2.34 (m, 5H), 2.11 (t, *J* = 6.4 Hz, 2H), 1.96-1.81 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).

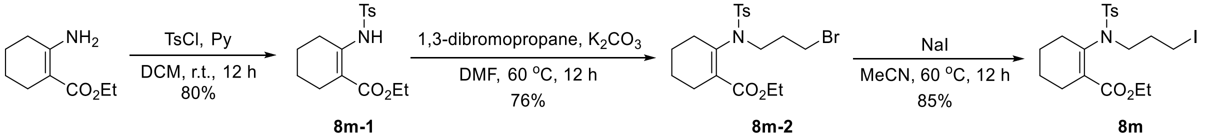
Compound 8k. Compounds **8k-3** (0.74 g, 1.72 mmol) and NaI (1.29 g, 8.60 mmol) were dissolved in MeCN (17 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*.

The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8k** as colorless oil (0.72 g, 87%). R_f = 0.55 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.44 (t, *J* = 6.4 Hz, 2H), 3.33 (t, *J* = 6.4 Hz, 2H), 2.70 (t, *J* = 6.8 Hz, 2H), 2.50-2.34 (m, 5H), 2.15-2.02 (m, 2H), 1.93-1.80 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 145.8, 143.5, 136.6, 131.5, 129.6, 127.2, 60.3, 49.4, 34.5, 33.2, 32.1, 21.5, 20.3, 14.1, 3.0. IR (KBr): 2950, 1717, 1341, 1235, 1163, 1090 cm^{-1}. HRMS (ESI): Calculated for $C_{18}H_{25}INO_4S$: 478.0453 [M + H]$^+$. Found: 478.0566.



Compound 8l-1. Compounds **8k-2** (1.0 g, 3.23 mmol), 1,4-dibromobutane (6.98 g, 3.86 mL, 32.3 mmol) and K_2CO_3 (2.23 g, 16.2 mmol) were dispersed in DMF (47 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM and this organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8l-1** as white solid (0.72 g, 50%). R_f = 0.38 (hexane/ethyl acetate 5:1). M.p. 53-54 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.44 (t, *J* = 6.8 Hz, 2H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.52-2.34 (m, 5H), 2.06-1.94 (m, 2H), 1.93-1.80 (m, 2H), 1.73-1.62 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 143.2, 138.1, 137.4, 133.2, 129.5, 127.3, 60.6, 47.2, 33.3, 29.8, 28.1, 27.3, 22.4, 21.5, 14.1. IR (KBr): 2953, 1717, 1356, 1222, 1155, 1086 cm^{-1}. HRMS (ESI): Calculated for $C_{19}H_{26}BrNO_4SNa$: 466.0658 [M + Na]$^+$. Found: 466.0641.

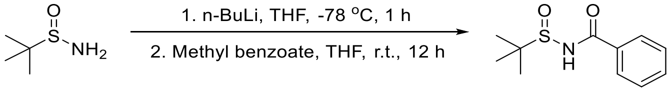
Compound 8l. Compounds **8l-1** (0.72 g, 1.62 mmol) and NaI (1.21 g, 8.10 mmol) were dissolved in MeCN (16 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8l** as white solid (0.72 g, 89%). R_f = 0.38 (hexane/ethyl acetate 5:1). M.p. 57-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.38 (t, *J*=6.8 Hz, 2H), 3.21 (t, *J* = 6.8 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.52-2.33 (m, 5H), 2.63-1.78 (m, 4H), 1.70-1.59 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 146.1, 143.4, 136.9, 131.3, 129.6, 127.3, 60.3, 47.8, 35.0, 32.2, 29.9, 29.8, 21.5, 20.4, 14.1, 6.5. IR (KBr): 2955, 1712, 1354, 1223, 1162, 1090 cm^{-1}. HRMS (ESI): Calcd for $C_{19}H_{26}INO_4SNa$: 514.0519 [M + Na]$^+$. Found: 514.0533.



Compound 8m-1. Ethyl 2-amino-1-cyclohexane-1-carboxylate (3.38 g, 20 mmol), tosyl chloride (4.38 g, 23 mmol) and pyridine (4.75 g, 4.83 mL, 60 mmol) were dissolved in DCM (40 mL). The mixture was stirred for 12 h at room temperature. This organic solution was washed with 1N HCl, water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8m-1** as white solid (5.19 g, 80%). R_f = 0.66 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.61 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.51-2.33 (m, 5H), 2.29-2.15 (m, 2H), 1.54-1.41 (m, 4H), 1.28 (t, *J* = 7.2 Hz, 3H).

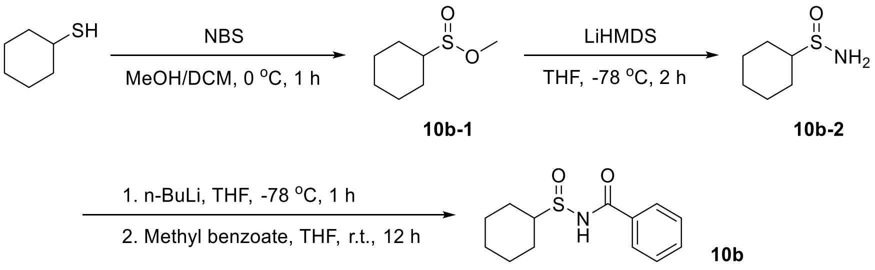
Compound 8m-2. Compounds **8m-1** (1.6 g, 5.0 mmol), 1,3-dibromopropane (10.8 g, 5.43 mL, 50.0 mmol) and K_2CO_3 (3.46 g, 25.0 mmol) were dispersed in DMF (74 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM and this organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8m-2** as white solid (1.69 g, 76%). R_f = 0.37 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.71-3.28 (m, 4H), 2.77-1.57 (m, 13H), 1.30 (t, *J* = 7.2 Hz, 3H).

Compound 8m. Compounds **8m-2** (1.69 g, 3.8 mmol) and NaI (2.85 g, 19.0 mmol) were dissolved in MeCN (37 mL). The mixture was stirred for 12 h at 60 °C and the solvent was then removed *in vacuo*. The residue was redissolved in DCM, filtered and this organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **8m** as white solid (1.60 g, 85%). R_f = 0.43 (hexane/ethyl acetate 5:1). M.p. 64-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.75-2.94 (m, 4H), 2.76-1.58 (m, 13H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 143.4, 137.9, 137.2, 133.4, 129.6, 127.3, 60.7, 48.3, 32.6, 27.7, 27.4, 22.4, 21.5, 14.1, 3.4. IR (KBr): 2944, 1724, 1341, 1235, 1159, 1085, 1045 cm^{-1}. HRMS (ESI): Calcd for $C_{19}H_{27}INO_4S$: 492.0700 [M + H]$^+$. Found: 492.0697.



10a

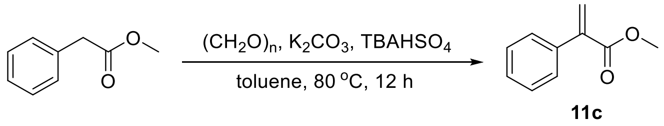
Compound 10a. tert-Butanesulfinamide (0.78 g, 6.40 mmol, 1.0 equiv.) was dissolved in dry THF (20 mL). n-BuLi (8.0 mL, 2.4 M, 19.2 mmol, 3 equiv.) was added dropwise at -78 °C under inert gas protection and the mixture was stirred for 1 h. Methyl benzoate (2.60 g, 2.4 mL, 19.20 mmol, 3 equiv.) was then added and the mixture was stirred at room temperature for another 12 h. The reaction was quenched by saturated aqueous solution of NH_4Cl. The organic phase was separated, washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **10a** as white solid (1.02 g, 70%). R_f=0.16 (hexane/ethyl acetate 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.63-7.56 (m, 1H), 7.53-7.45 (m, 3H), 1.34 (s, 9H).



Compound 10b-1. Cyclohexyl mercaptan (2.00 g, 2.1 mL, 17.2 mmol) was dissolved in a mixture of DCM and MeOH (30 mL+30 mL). NBS (6.12 g, 34.40 mmol) was added in small portions at 0 °C and the mixture was stirred at room temperature for 1 h. The reaction was quenched by saturated aqueous solution of $NaHCO_3$. The aqueous phase was extracted by DCM and the organic phase was combined, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give **10b-1** as colorless oil (2.79 g, 100 %). R_f= 0.27 (hexane/diethyl ether/DCM 18:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H), 2.61-2.47 (m, 1H), 2.05-1.92 (m, 2H), 1.92-1.79 (m, 2H), 1.75-1.61 (m, 1 H), 1.47-1.12 (m, 5H).

Compound 10b-2. Compound **10b-1** (2.79 g, 17.20 mmol) was dissolved in dry THF (44 mL). LiHMDS (26.0 mL, 1.0 M) was added dropwise at -78 °C under inert gas protection and the mixture was stirred at room temperature for 2 h. The reaction was quenched by saturated aqueous solution of NH_4Cl. The organic phase was separated, washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was recrystallized in hexane to give **10b-2** as white solid (1.50 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 2H), 2.54-2.39 (m, 1H), 2.12-1.98 (m, 2H), 1.96-1.81 (m, 2H), 1.75-1.65 (m, 1H), 1.53-1.16 (m, 5H).

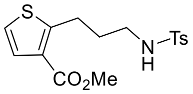
Compound 10b. Compound **10b-2** (1.00 g, 6.79 mmol) was dissolved in dry THF (21 mL). nBuLi (8.2 mL, 2.5 M, 20.40 mmol) was added dropwise at -78 °C under inert gas protection and the mixture was stirred for 1 h. Methyl benzoate (2.77 g, 3.0 mL, 20.40 mmol) was then added and the mixture was stirred at room temperature for another 12 h. The reaction was quenched by saturated aqueous solution of NH_4Cl. The organic phase was separated, washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give **10b** as white solid (1.28 g, 74%). R_f= 0.30 (hexane/ethyl acetate 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61-8.48 (m, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 3.06 (m, 1H), 2.10-1.95 (m, 2H), 1.95-1.82 (m, 2H), 1.76-1.64 (m, 1H), 1.53-1.15 (m, 5H).



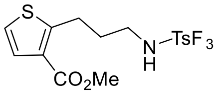
Compound 11c. Methyl phenylacetate (2.50 g, 16.62 mmol), paraformaldehyde (0.75 g, 24.90 mmol), K_2CO_3 (3.45 g, 24.96 mmol) and TBAHSO4 (0.56 g, 1.66 mmol) were separated in dry toluene (33 mL) and the mixture was stirred at 80 °C for 12 h. The solvent was removed *in vacuo* and the residue was redissolved in ethyl acetate, washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography on silica gel

(hexane/ethyl acetate) to give **11c** as colorless oil (1.06 g, 39%). R_f=0.74 (hexane/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.30 (m, 5H), 6.37 (s, 1H), 5.90 (s, 1H), 3.83 (s, 3H).

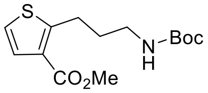
General method for visible light induced intramolecular rearrangement (Method A): Alkyliodide (0.1 mmol, 1 equiv.), heterogeneous photocatalyst (1.1 mg for **Ir-POP-2** and 1.0 mg for **Ir-POP-1**, 0.01 equiv.) and DIPEA (0.066 g, 85 µL, 0.5 mmol, 5 equiv.) was dispersed in MeCN (915 µL or 3915 µL). The mixture was stirred with irradiation of two blue LED light under inert gas protection for 23 h. A fan was used to keep the system cool. After the reaction, the solvent was removed in vacuo and the product was purified by column chromatography on silica gel.



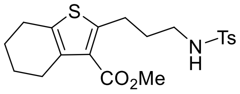
Compound 9a. According to Method A, **8a** (0.048 g) and MeCN (915 µL) were used. Yield 95%. Recorded spectroscopic data matched previous report in literature.



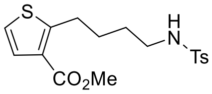
Compound 9b. According to Method A, **8b** (0.053 g) and MeCN (3915 µL) were used. Yield 77%. Recorded spectroscopic data matched previous report in literature.



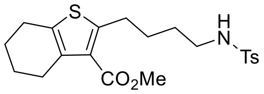
Compound 9c. According to Method A, **8c** (0.043 g) and MeCN (3915 µL) were used. Yield 64%. Recorded spectroscopic data matched previous report in literature.



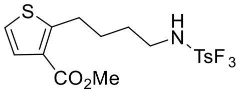
Compound 9d. According to Method A, **8d** (0.053 g) and MeCN (915 µL) were used. Yield 97%. Recorded spectroscopic data matched previous report in literature.



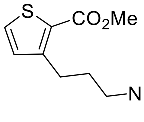
Compound 9e. According to Method A, **8e** (0.049 g) and MeCN (3915 µL) were used. Yield 70%. Recorded spectroscopic data matched previous report in literature.



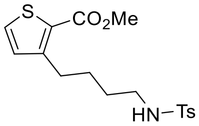
Compound 9f. According to Method A, **8f** (0.055 g) and MeCN (3915 μL) were used. Yield 89%. ^{1}H NMR (400 MHz, CDCl$_3$): δ=7.75 (d, *J*=8.0 Hz, 2H), 7.28 (d, *J*=8.0 Hz, 2H), 4.63 (t, *J*=6.4 Hz, 1H), 3.82 (s, 3H), 3.04-2.91 (m, 4H), 2.79-2.71 (m, 2H), 2.70-2.62 (m, 2H), 2.42 (s, 3H), 1.86-1.70 (m, 4H) 1.68-1.59 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ=164.8, 150.8, 143.2, 137.0, 135.8, 132.8, 129.6, 127.0, 126.7, 51.7, 51.1, 42.5, 28.8, 28.4, 26.5, 25.0, 23.0, 22.7, 21.5. IR (KBr) 3277, 2944, 1705, 1323, 1159, 1099 cm^{-1}. HRMS (ESI): Calcd for $C_{21}H_{27}NO_4S_2$: 422.1454 [M + H]$^+$. Found: 422.1450.



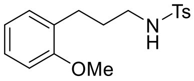
Compound 9g. According to Method A, **8g** (0.055 g) and MeCN (3915 μL) were used. Yield 76%. ^{1}H NMR (400 MHz, CDCl$_3$): δ=8.01 (d, *J*=8.0 Hz, 2H), 7.78 (d, *J*=8.4 Hz, 2H), 7.37 (d, *J*=5.6 Hz, 1H), 7.02 (d, *J*=5.2 Hz, 1H), 5.05 (t, *J*=6.4 Hz, 1H), 3.85 (s, 3H), 3.14-3.03 (m, 4H), 1.75-1.67 (m, 2H), 1.64-1.57 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ=164.0, 154.4, 143.9, 129.1, 128.2, 128.0, 127.5, 126.2, 125.8, 121.5, 51.5, 42.3, 28.6, 28.0, 1.0. IR (KBr) 3273, 2930, 1710, 1326, 1258, 1155, 1131, 1048 cm^{-1}. HRMS (ESI): Calcd for $C_{17}H_{18}F_3NO_4S_2Na$: 444.0522 [M + Na]$^+$. Found: 444.0530.



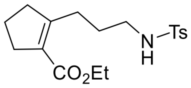
Compound 9h. According to Method A, **8h** (0.048 g) and MeCN (915 μL) were used. Yield 78%. Recorded spectroscopic data matched previous report in literature.



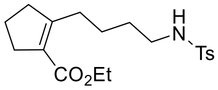
Compound 9i. According to Method A, **8i** (0.049 g) and MeCN (3915 μL) were used. Yield 82%. ^{1}H NMR (400 MHz, CDCl$_3$): δ=7.78 (d, *J*=8.0 Hz, 2H), 7.42 (d, *J*=5.2 Hz, 1H), 7.32 (d, *J*=8.0 Hz, 2H), 6.92 (d, *J*=4.8 Hz, 1H), 4.68 (t, *J*=6.4 Hz, 1H), 3.89 (s, 3H), 3.08-2.99 (m, 2H), 2.99-2.90 (m, 2H), 2.45 (s, 3H), 1.68-1.61 (m, 2H), 1.32-1.27 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ=163.0, 150.8, 142.2, 137.1, 130.8, 130.5, 129.6, 129.3, 127.0, 51.8, 42.5, 28.9, 28.5, 27.1, 21.5. IR (KBr) 3276, 2945, 1717, 1433, 1324, 1263, 1155, 1086 cm^{-1}. HRMS (ESI): Calcd for $C_{17}H_{21}O_4S_2$: 368.0985 [M + H]$^+$. Found: 368.0994.



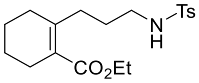
Compound 9j. According to Method A, **8j** (0.045 g) and MeCN (915 μL) were used. Yield 41%. Recorded spectroscopic data matched previous report in literature.



Compound 9k. According to Method A, **8k** (0.048 g) and MeCN (915 μL) were used. Yield 89%. Recorded spectroscopic data matched previous report in literature.

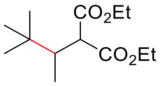


Compound 9l. According to Method A, **8l** (0.044 g) and MeCN (3915 μL) were used. Yield 79%. ^{1}H NMR (400 MHz, CDCl$_3$): δ=7.75 (d, *J*=7.6 Hz, 2H), 7.30 (d, *J*=8.0 Hz, 2H), 4.68 (t, *J*=6.4 Hz, 1H), 4.17 (q, *J*=7.6 Hz, 2H), 3.98 (q, *J*=6.0 Hz, 2H), 2.65-2.56 (m, 2H), 2.53-2.47 (m, 2H), 2.47-2.39 (m, 5H), 1.85-1.74 (m, 2H), 1.52-1.44 (m, 4H), 1.28 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ=166.1, 159.4, 143.2, 137.1, 129.6, 127.5, 127.0, 60.0, 42.6, 38.2, 33.5, 29.1, 28.8, 24.7, 21.4, 14.3. IR (KBr) 3275, 2929, 1675, 1336, 1259, 1162, 1086 cm^{-1}. HRMS (ESI): Calcd for $C_{19}H_{27}NO_4S$: 366.1734 [M + H]$^+$. Found: 366.1742.

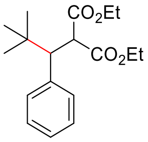


Compound 9m. According to Method A, **8m** (0.049 g) and MeCN (915 μL) were used. Yield 79%. Recorded spectroscopic data matched previous report in literature.

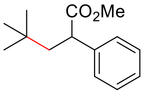
General method for visible light induced coupling of sulfonamide and Michael acceptor (Method B). Sulfonamide (0.72 mmol, 1.8 equiv.), heterogeneous photocatalyst (3.6 mg for **Ir-POP-2** and 3.3 mg for **Ir-POP-1**, 0.01 equiv.) and K_2HPO_4 (0.125 g, 0.72 mmol, 1.8 equiv.) was dispersed in acetone (1 mL). The system was protected by inert gas, and Michael acceptor (0.4 mmol, 1 equiv.) was added. The mixture was stirred with irradiation of two blue LED light for 5 h unless otherwise mentioned. A fan was used to keep the system cool. After the reaction, the solvent was removed in vacuo and the product was purified by column chromatography on silica gel.



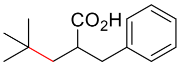
Compound 12a. According to Method B, **10a** (0.081 g) and Diethyl Ethylidenemalonate (0.037 g, **11a**) were used. Yield 87%. Recorded spectroscopic data matched previous report in literature.



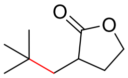
Compound 12b. According to Method B, **10a** (0.081 g) and Diethyl Benzylidenemalonate (0.050 g, **11b**) were used. Reaction time: 10 h. Yield 92%. Recorded spectroscopic data matched previous report in literature.



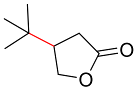
Compound 12c. According to Method B, **10a** (0.081 g) and **11c** (0.032 g) were used. Yield 90%. Recorded spectroscopic data matched previous report in literature.



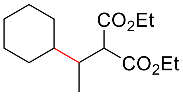
Compound 12d. According to Method B, **10a** (0.081 g) and 2-Benzylacrylic Acid (0.032 g, **11d**) were used. Yield 76%. Recorded spectroscopic data matched previous report in literature.



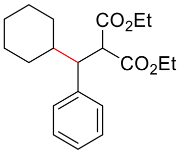
Compound 12e. According to Method B, **10a** (0.082 g) and α-methylene-γ-butyrolactone (0.020 g, **11e**) was used. Yield 70%. ^1H NMR (400 MHz, $CDCl_3$): δ=4.36 (t, *J*=5.2 Hz, 1H), 4.27-4.11 (m, 1H), 2.63-2.410 (m, 2H), 2.12-1.89 (m, 2H), 1.37-1.25 (m, 1H), 0.98 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=180.3, 66.2, 45.0, 36.4, 31.5, 30.5, 29.6. IR (KBr) 2976, 2894, 1770, 1385, 1199, 1048 cm^{-1}. HRMS (ESI): Calcd for $C_{19}H_{16}O_2K$: 195.0782 $[M + K]^+$. Found: 195.0796.



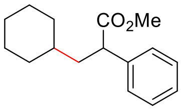
Compound 12f. According to Method B, **10a** (0.081 g) and 2-buten-4-olide (0.017 g, **11f**) were used. Yield 53%. Recorded spectroscopic data matched previous report in literature.



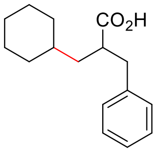
Compound 12g. According to Method B, **10b** (0.090 g) and Diethyl Ethylidenemalonate (0.037 g, **11a**) were used. Yield 79%. Recorded spectroscopic data matched previous report in literature.



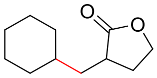
Compound 12h. According to Method B, **10b** (0.090 g) and Diethyl Benzylidenemalonate (0.050 g, **11b**) were used. Reaction time: 10 h. Yield 83%. Recorded spectroscopic data matched previous report in literature.



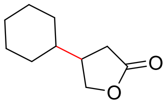
Compound 12i. According to Method B, **10b** (0.090 g) and **11c** (0.032 g) were used. Yield 84%. Recorded spectroscopic data matched previous report in literature.



Compound 12j. According to Method B, **10b** (0.090 g) and 2-benzylacrylic acid (0.032 g, **11d**) were used. Yield 51%. Recorded spectroscopic data matched previous report in literature.



Compound 12k. According to Method B, **10b** (0.090 g) and α-methylene-γ-butyrolactone (0.020 g, **11e**) was used. Yield 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.35 (t, *J* = 5.2 Hz, 1H), 4.26-4.09 (m, 1H), 2.71-2.51 (m, 1H), 2.51-2.32 (m, 1H), 2.03-1.63 (m, 7H), 1.44-1.12 (m, 5H), 1.08-0.82 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.1, 66.4, 38.1, 36.8, 35.5, 33.8, 32.1, 29.2, 26.3, 26.1, 26.0. IR (KBr): 2924, 2852, 1771, 1449, 1374, 1163, 1024 cm^{-1}. HRMS (ESI): Calcd for $C_{11}H_{19}O_2$: 183.1380 [M + H]$^+$. Found: 183.1369.



Compound 12l. According to Method B, **10b** (0.090 g) and 2-buten-4-olide (0.017 g, **11f**) were used. Yield 32%. Recorded spectroscopic data matched previous report in literature.

General method for visible light induced selective oxidization of sulfide reactions (Method C). Sulfide (0.5 mmol, 1 equiv.) and heterogeneous photocatalyst (5.5 mg for **Ir-POP-2**, 0.01 equiv.) was dispersed in methanol (0.5 mL). The system was opened to air with a needle outlet. The mixture was stirred with irradiation of two blue LED light. A fan was used to keep the system cool. After the reaction, the solvent was removed *in vacuo*. Conversion and selectivity were identified by ^{1}H NMR.

General method for visible light induced selective oxidization of sulfide reactions (Method D). Boronic acid (0.1 mmol, 1 equiv.) (0.05 mmol, 0.5 equiv. for Benzene-1,4-diboronic acid), heterogeneous photocatalyst (1.1 mg for **Ir-POP-2**, 0.01 equiv.) and DIPEA (was dispersed in MeCN (1 mL). The system was opened to air with a needle outlet. The mixture was stirred with irradiation of two blue LED light. A fan was used to keep the system cool. After the reaction, yield was identified by ^{1}H NMR.

References

(1) Zhou, Q.-Z.; Zhang, B.; Su, L.-J.; Jiang, T.-S.; Chen, R.-E.; Du, T.-Q.; Ye, Y.-Y.; Shen, J.-F.; Dai, G.-L.; Han, D.-M.; Jiang, H.-J. Palladium-Catalyzed Highly Regioselective 2-Arylation of 2,x-Dibromopyridines and Its Application in the Efficient Synthesis of a 17β-HSD1 Inhibitor. *Tetrahedron* **2013**, *69*, 10996-11003.

(2) Baldwin, L. A.; Crowe, J. W.; Pyles, D. A.; McGrier, P. L. Metalation of a Mesoporous Three-Dimensional Covalent Organic Framework. *J. Am. Chem. Soc.* **2016**, *138*, 15134-15137.

(3) Sicre, C.; Braga, A. A. C.; Maseras, F.; Cid, M. M. Mechanistic Insights into the Transmetalation Step of a Suzuki–Miyaura Reaction of 2(4)-Bromopyridines: Characterization of an Intermediate. *Tetrahedron* **2008**, *64*, 7437-7443.

(4) Alpers, D.; Cole, K. P.; Stephenson, C. R. J. Visible Light Mediated Aryl Migration by Homolytic C—N Cleavage of Aryl Amines. *Angew. Chem. Int. Ed.* **2018**, *57*, 12167-12170.

(5) Lujan-Montelongo, J. A.; Estevez, A. O.; Fleming, F. F. Alkyl Sulfinates: Formal Nucleophiles for Synthesizing TosMIC Analogs. *Eur. J. Org. Chem.* **2015**, *2015,* 1602-1605.

(6) Xue, F.; Wang, F.-L.; Liu, J.-Z.; Di, J.-M.; Liao, Q.; Lu, H.-F.; Zhu, M.; He, L.-P.; He, H.; Zhang, D.; Song, H.; Liu, X.-Y.; Qin, Y. A Desulfurative Strategy for the Generation of Alkyl Radicals Enabled by Visible-Light Photoredox Catalysis. *Angew. Chem. Int. Ed.* **2018**, *57*, 6667-6671.

(7) Felpin, F.-X.; Jean-Marc Sotiropoulos, K. M.; Oier Ibarguren, E. F.; Laudien, J. Room-Temperature, Ligand- and Base-Free Heck Reactions of Aryl Diazonium Salts at Low Palladium Loading: Sustainable Preparation of Substituted Stilbene Derivatives. *Chem. Eur. J.* **2010**, *16*, 5191-5204.

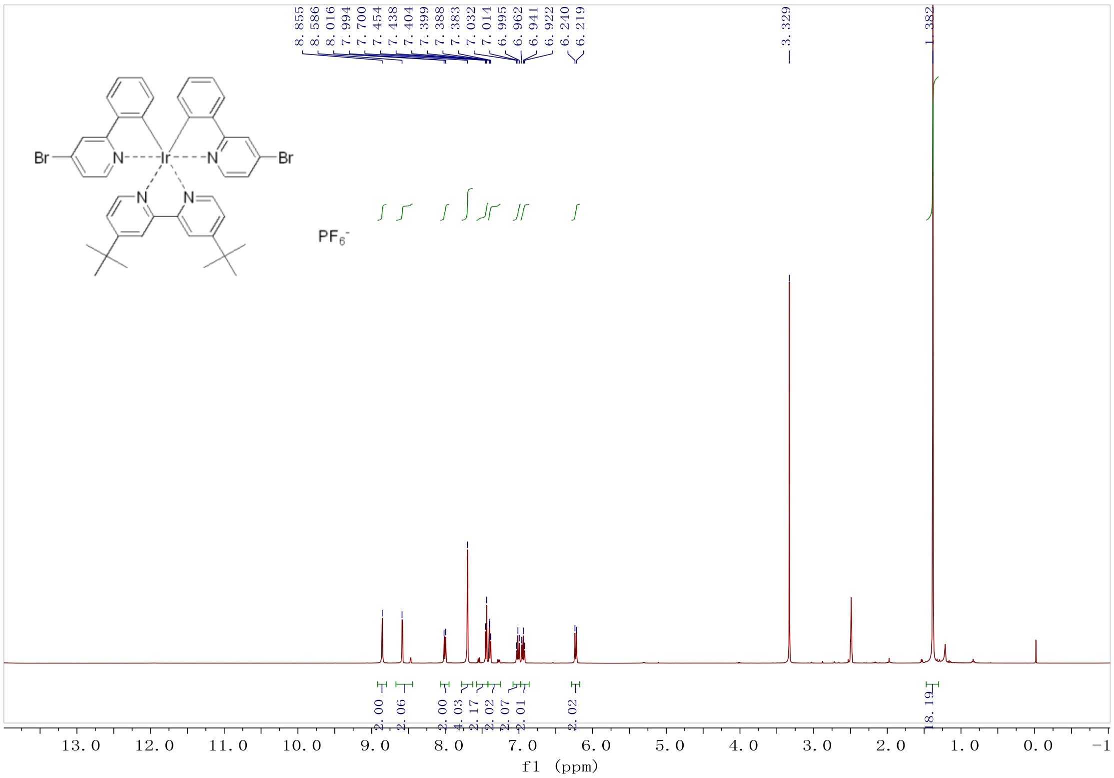


Fig. S17 ^{1}H NMR of compound **4a** in DMSO-d_6.

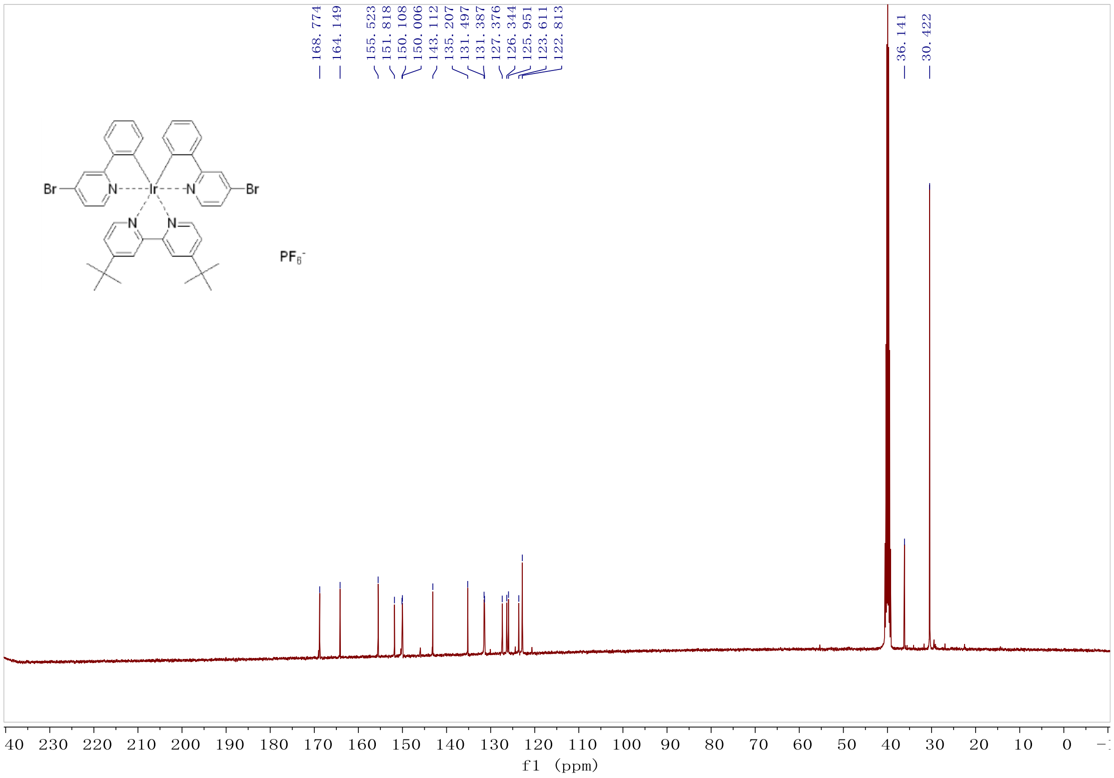


Fig. S18 ^{13}C NMR of compound **4a** in DMSO-d_6.

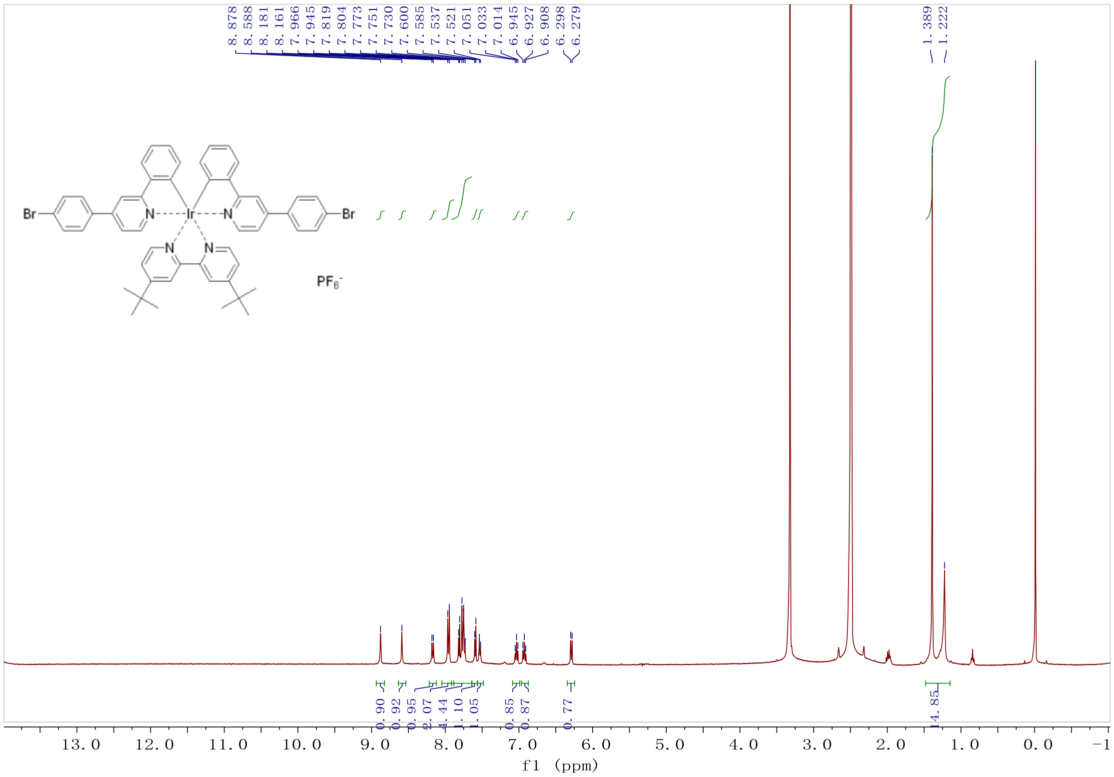


Fig. S19 ^{1}H NMR of compound **4b** in DMSO-d_6.

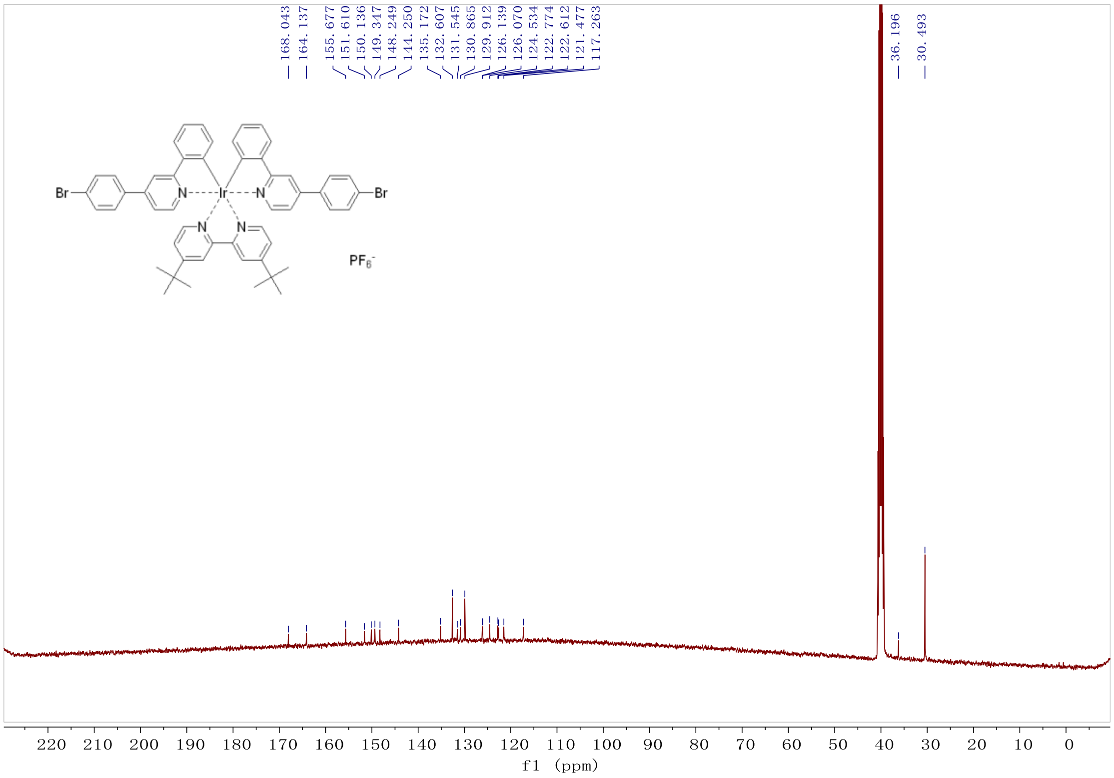


Fig. S20 ^{13}C NMR of compound **4b** in DMSO-d_6.

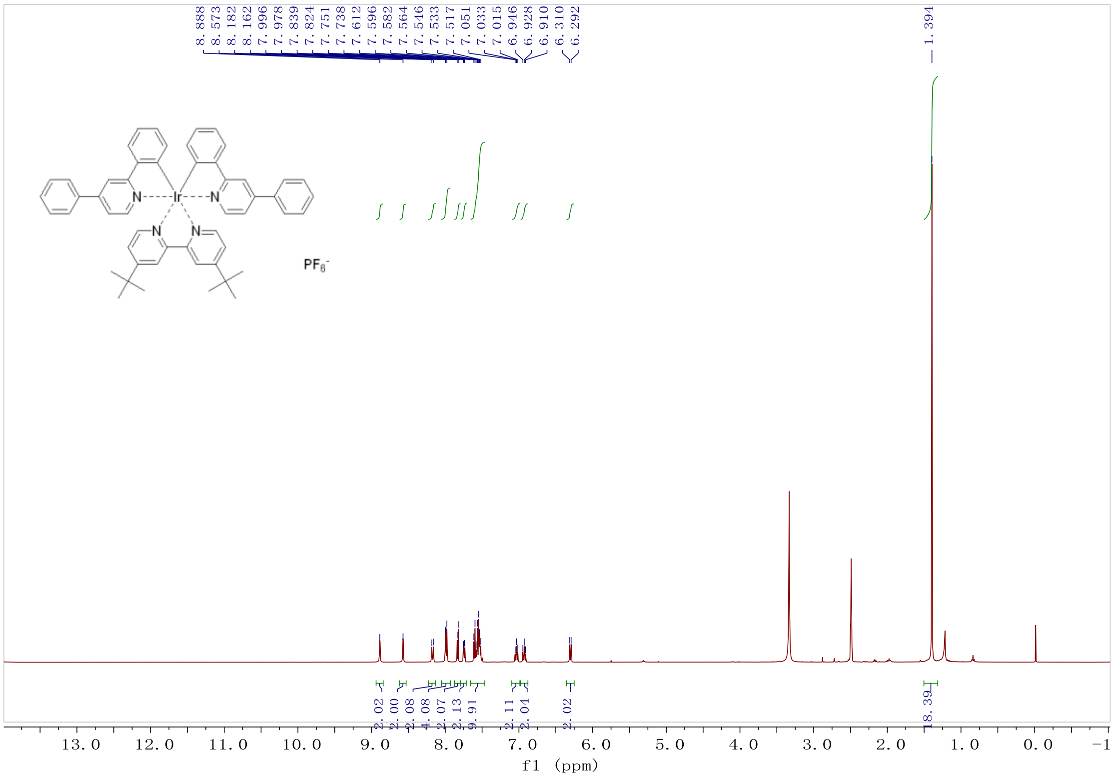


Fig. S21 ^{1}H NMR of compound **Ir-C1** in DMSO-d_6.

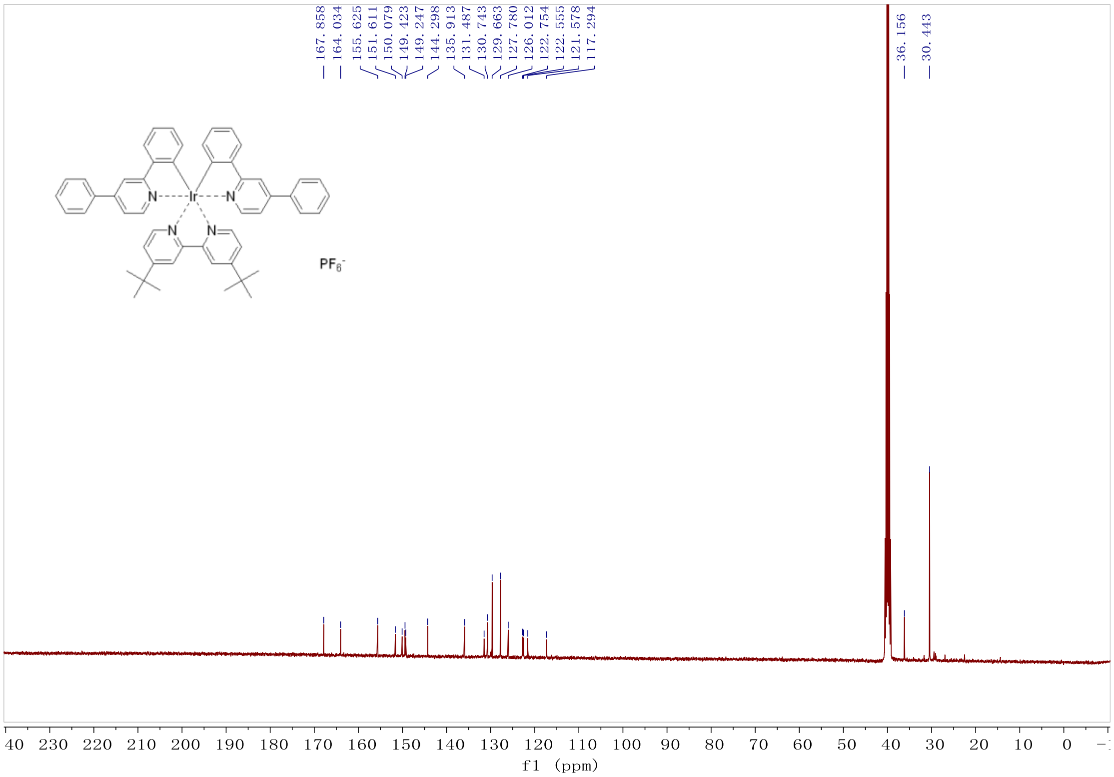


Fig. S22 ^{13}C NMR of compound **Ir-C1** in DMSO-d_6.

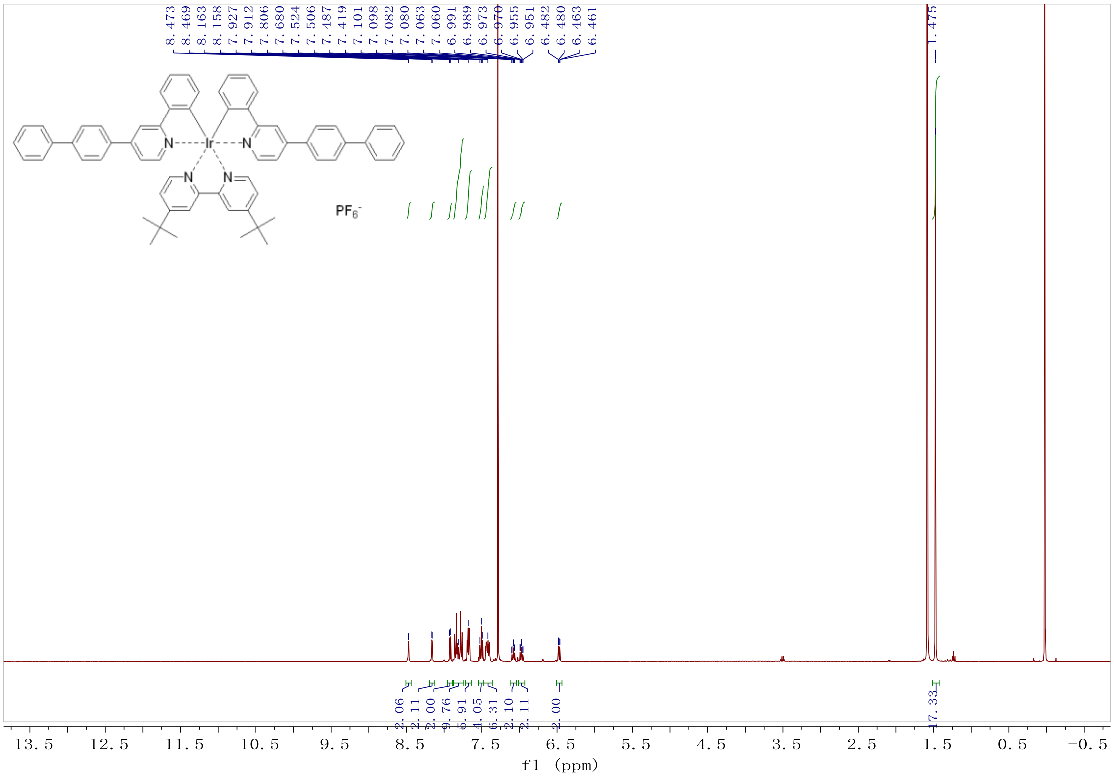


Fig. S23 ^{1}H NMR of compound **Ir-C2** in $CDCl_3$.

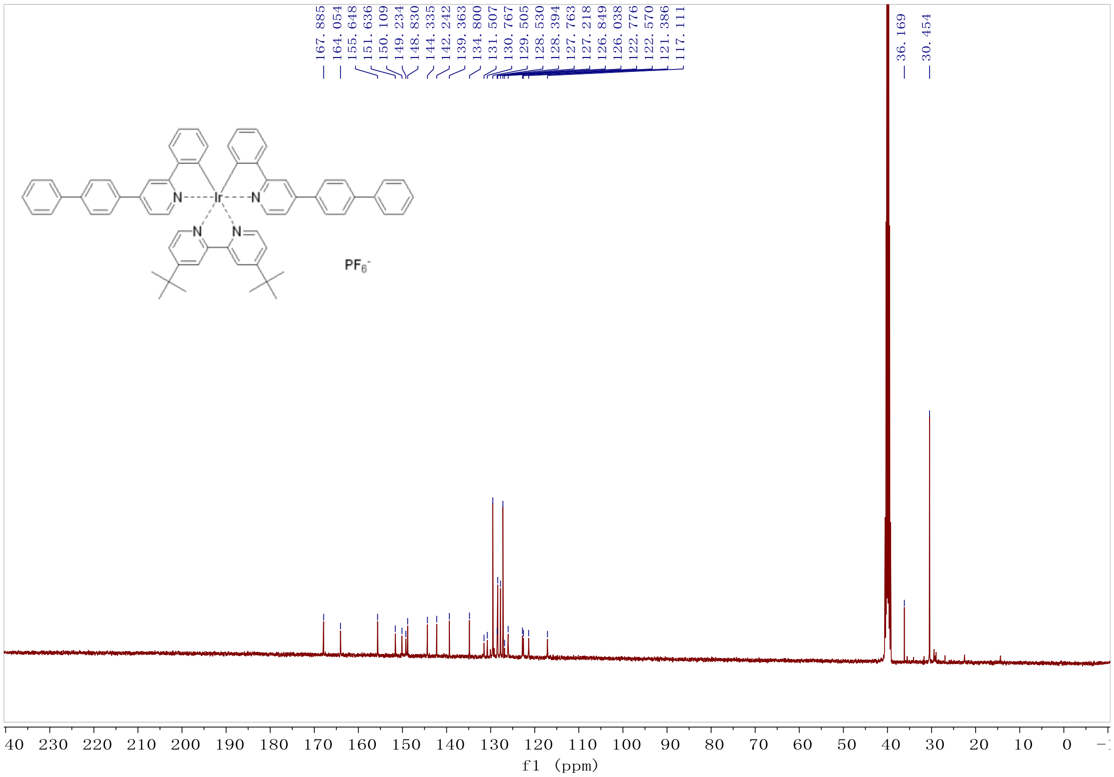


Fig. S24 ^{13}C NMR of compound **Ir-C2** in DMSO-d_6.

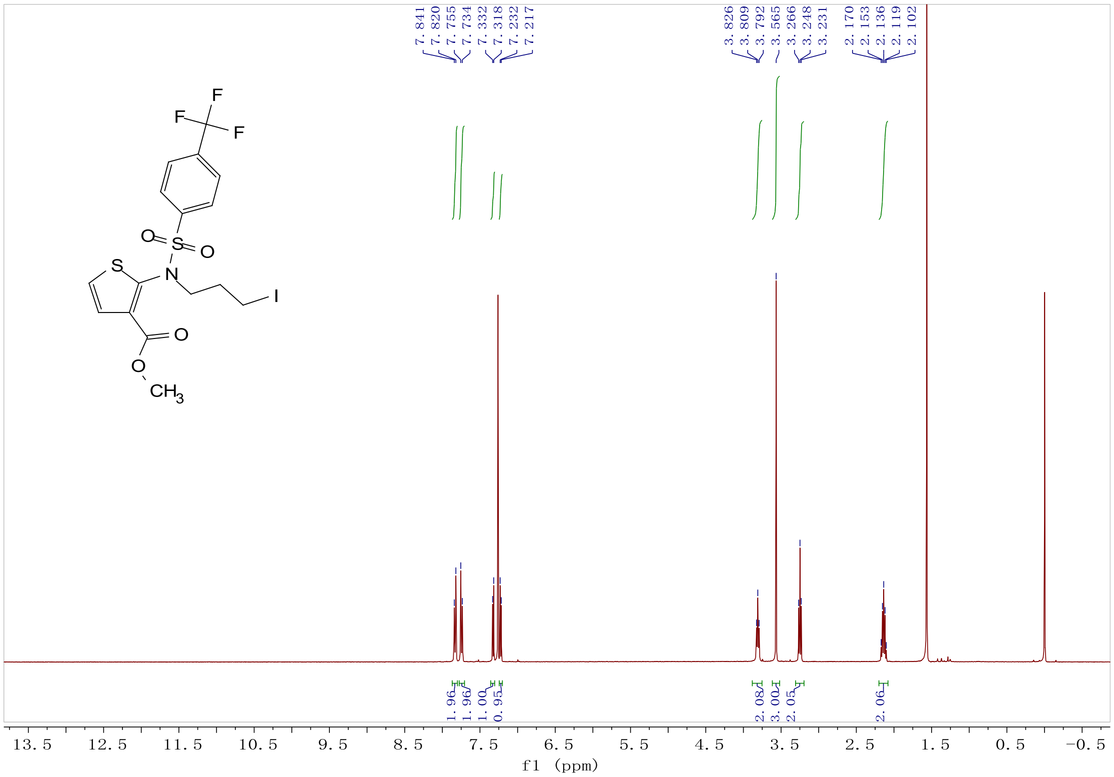


Fig. S25 ^{1}H NMR of compound **8b** in $CDCl_3$.

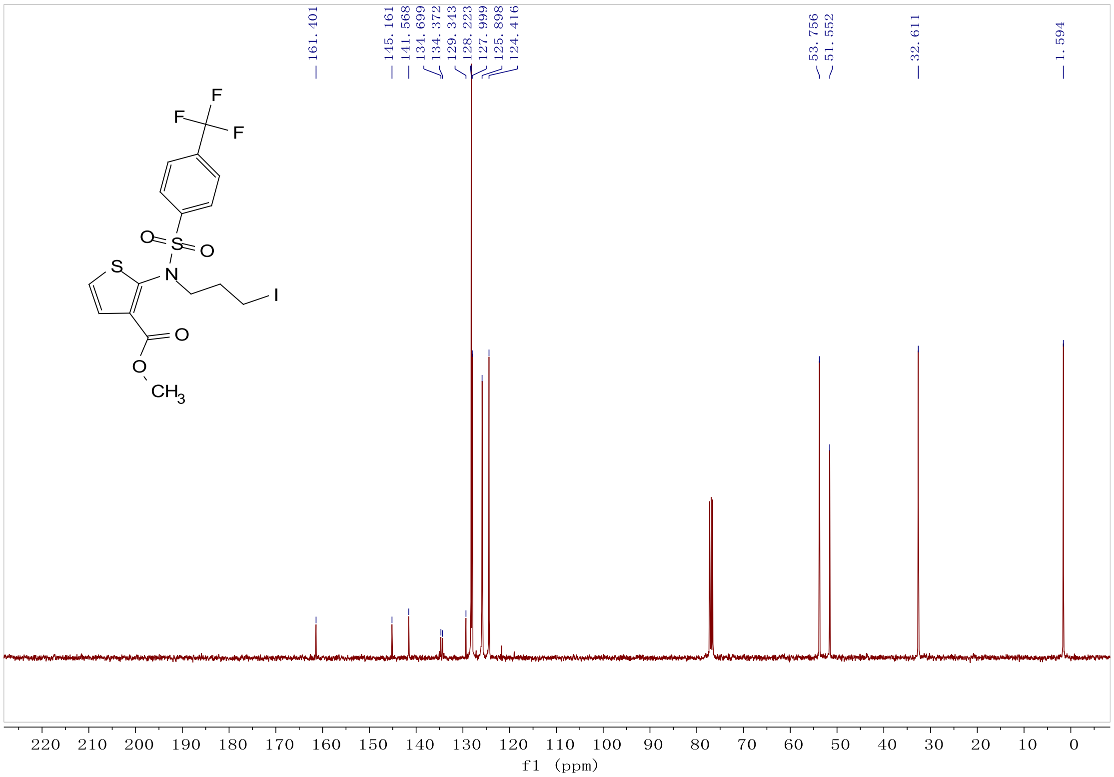


Fig. S26 ^{13}C NMR of compound **8b** in $CDCl_3$.

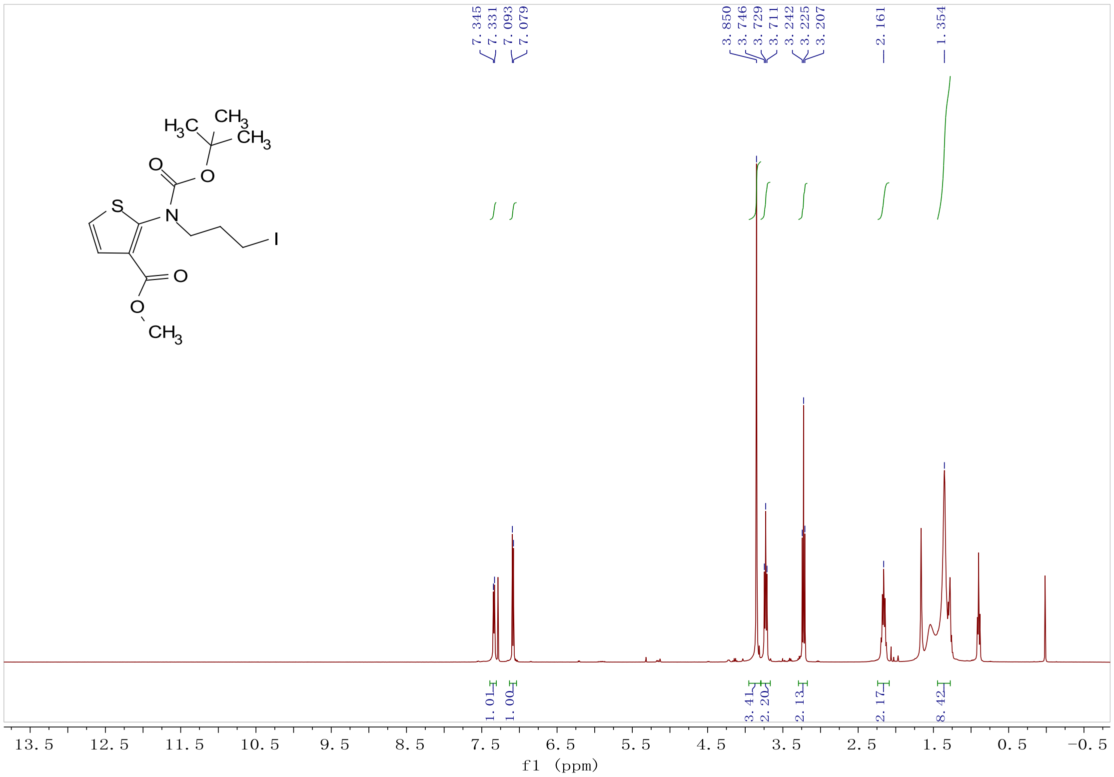


Fig. S27 ^{1}H NMR of compound **8c** in $CDCl_3$.

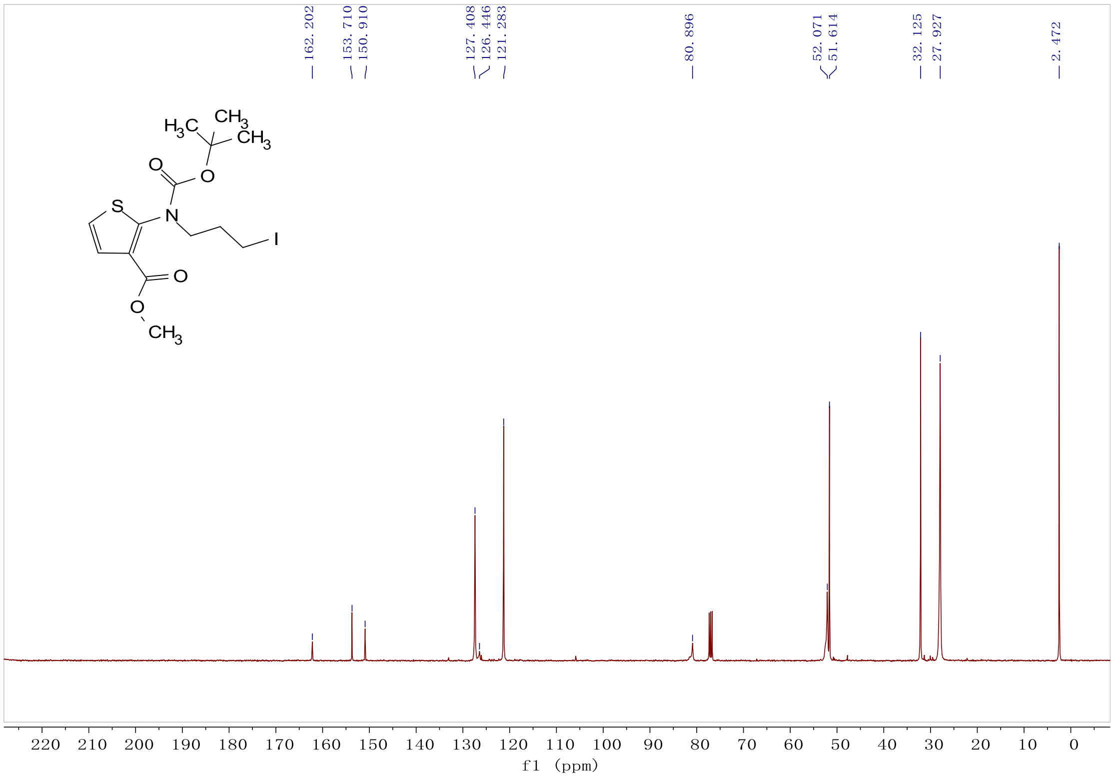


Fig. S28 ^{13}C NMR of compound **8c** in $CDCl_3$.

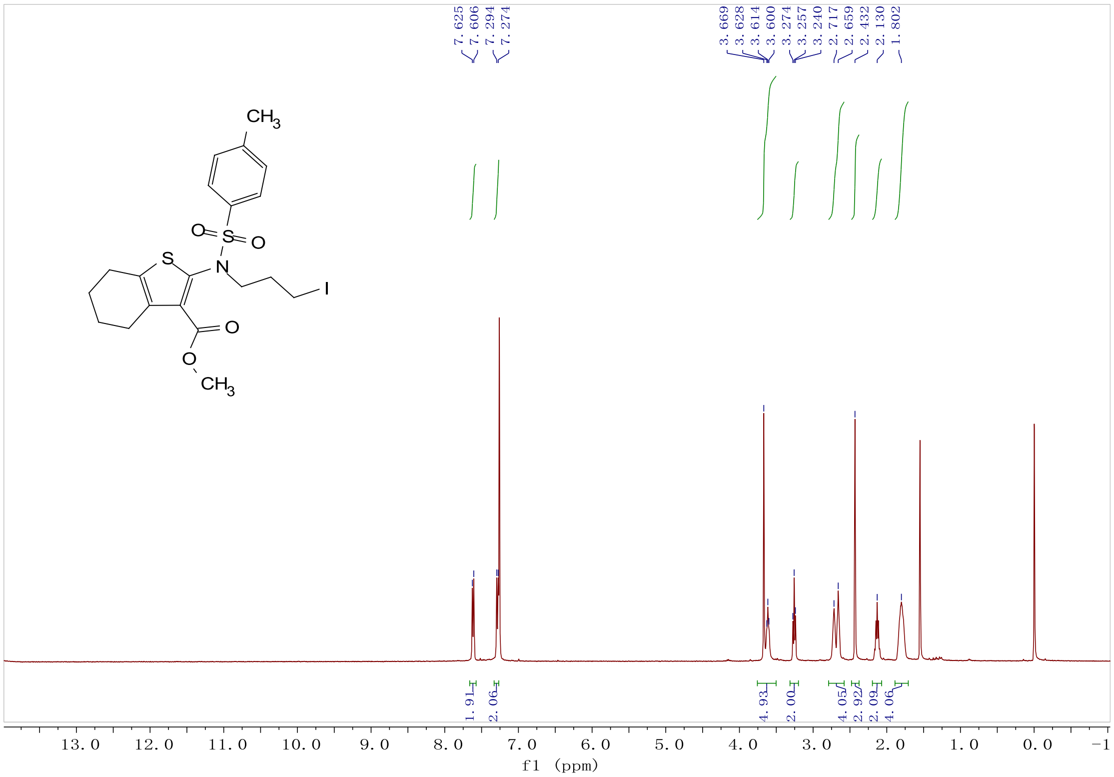


Fig. S29 ^{1}H NMR of compound **8d** in $CDCl_3$.

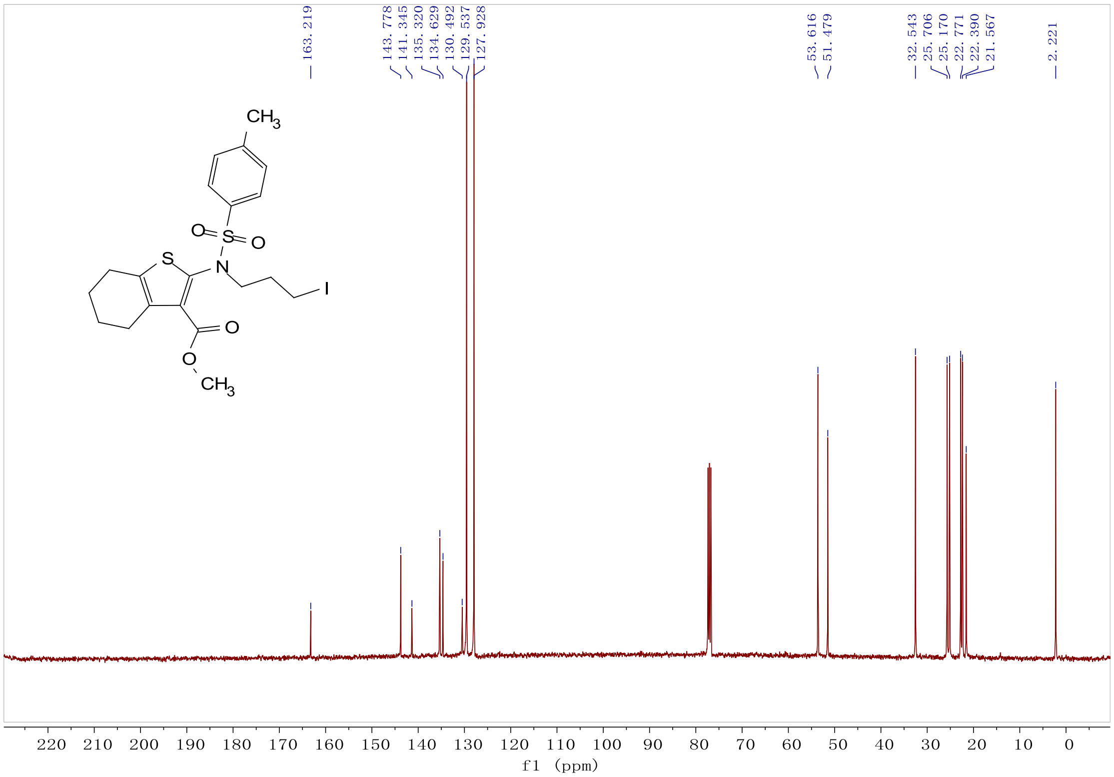


Fig. S30 ^{13}C NMR of compound **8d** in $CDCl_3$.

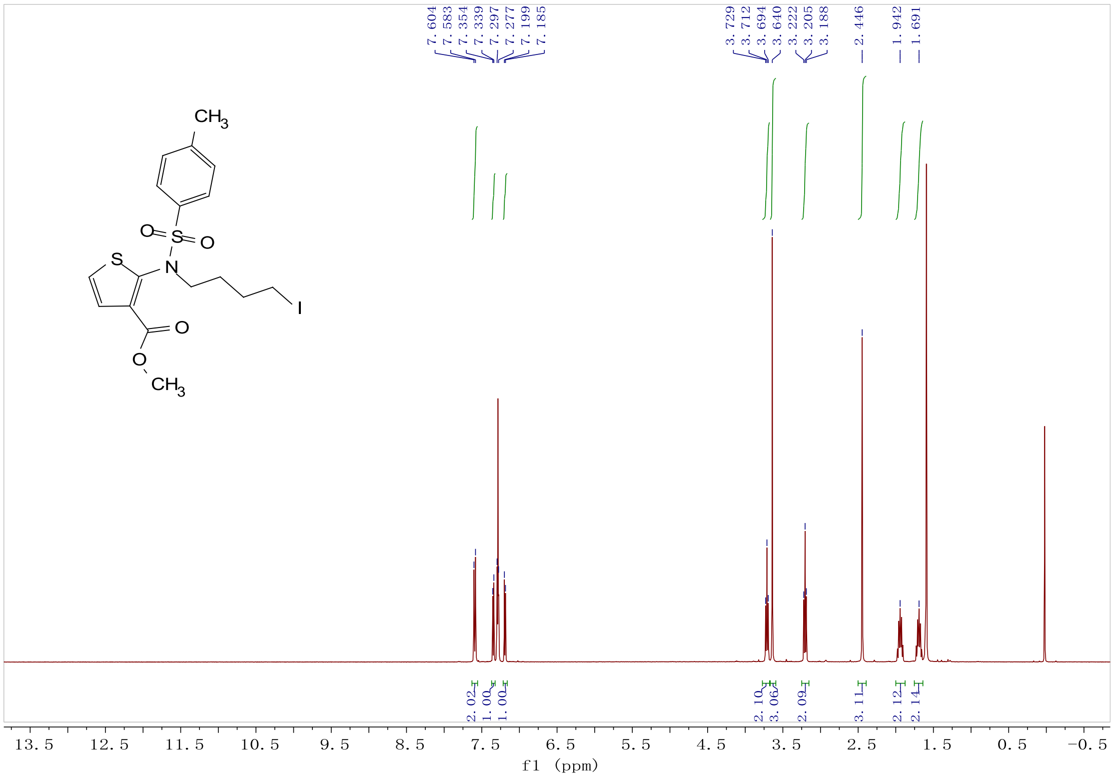


Fig. S31 ^{1}H NMR of compound **8e** in $CDCl_3$.

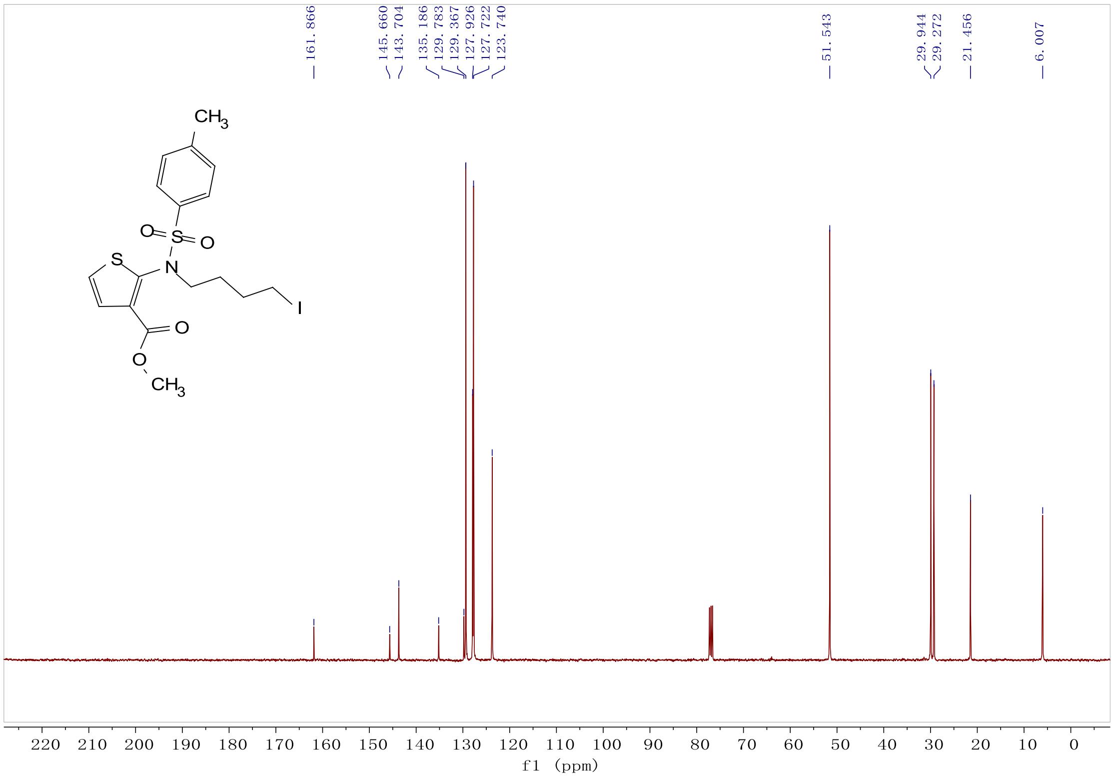


Fig. S32 ^{13}C NMR of compound **8e** in $CDCl_3$.

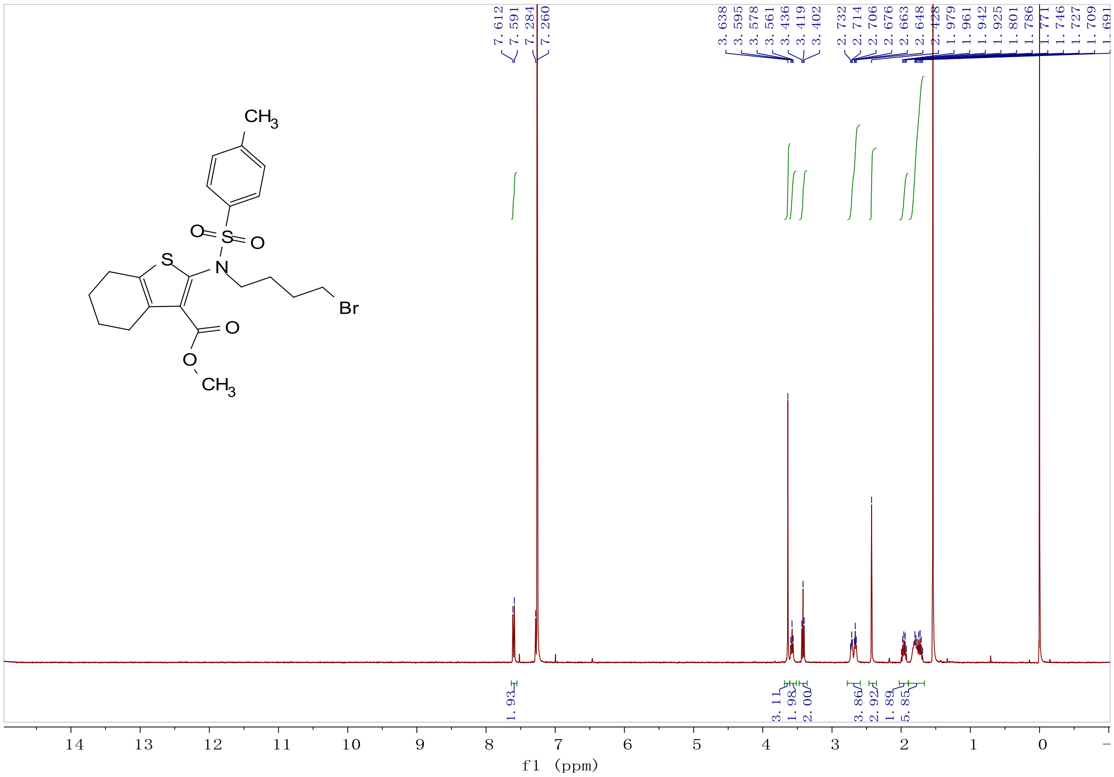


Fig. S33 ^{1}H NMR of compound **8f-1** in CDCl$_3$.

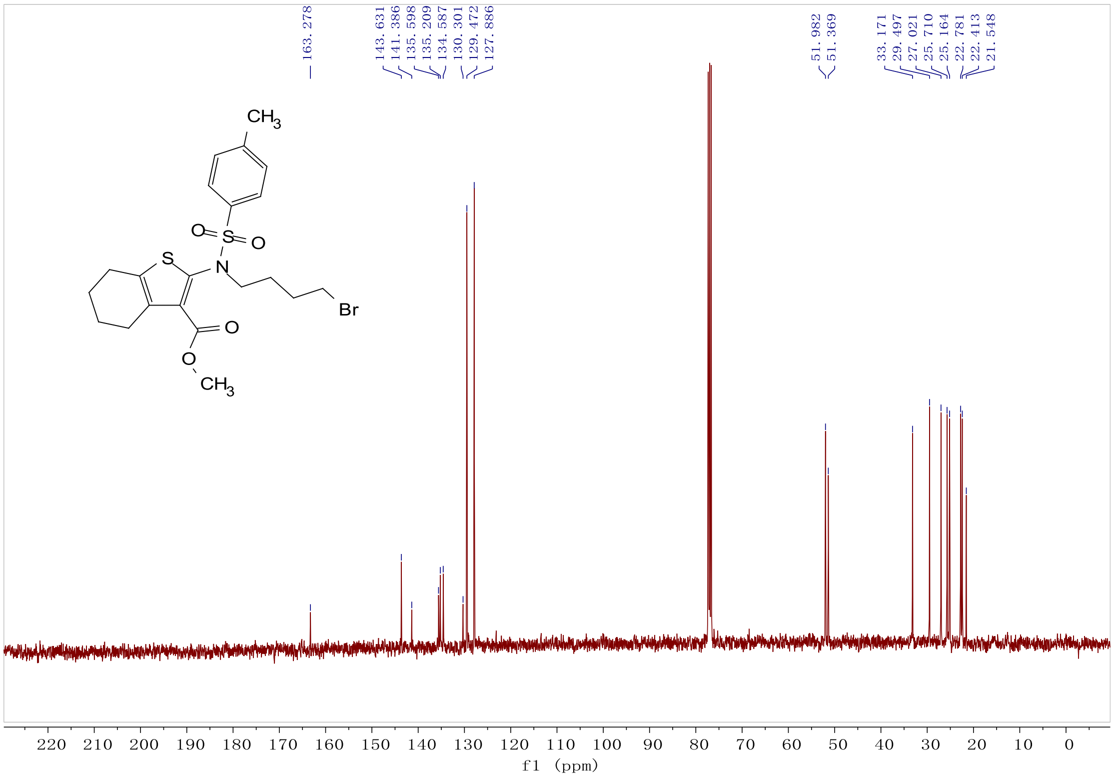


Fig. S34 ^{13}C NMR of compound **8f-1** in CDCl$_3$.

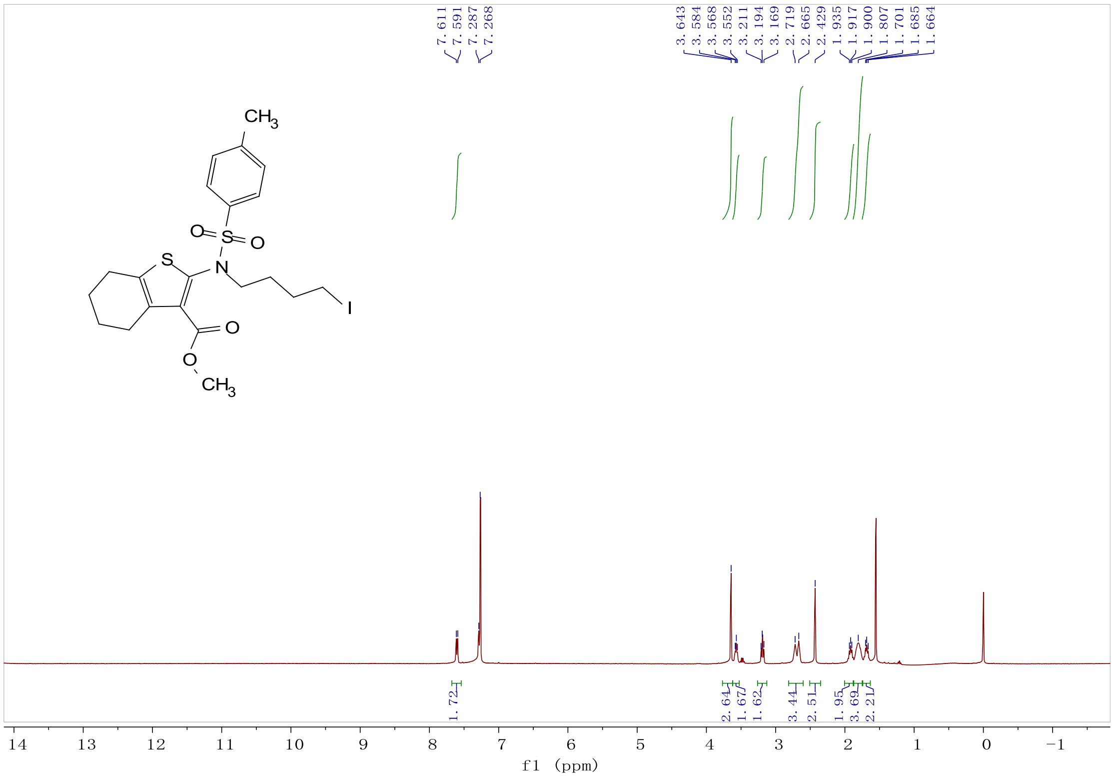


Fig. S35 ^{1}H NMR of compound **8f** in $CDCl_3$.

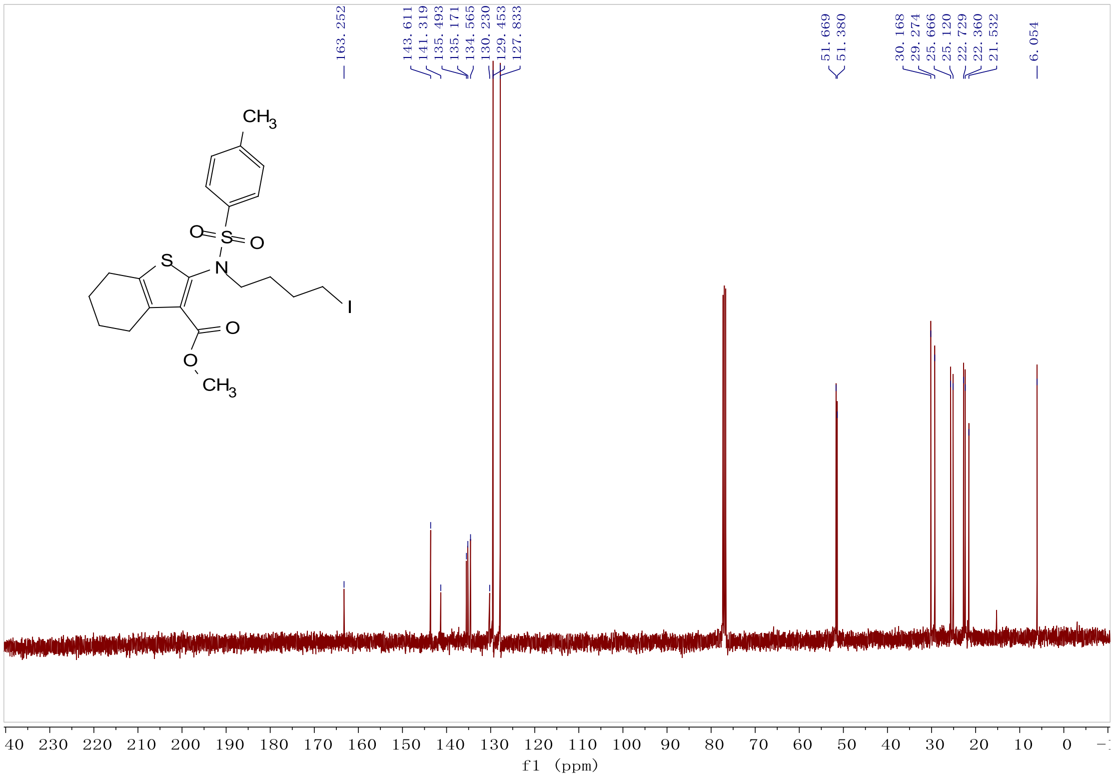


Fig. S36 ^{13}C NMR of compound **8f** in $CDCl_3$.

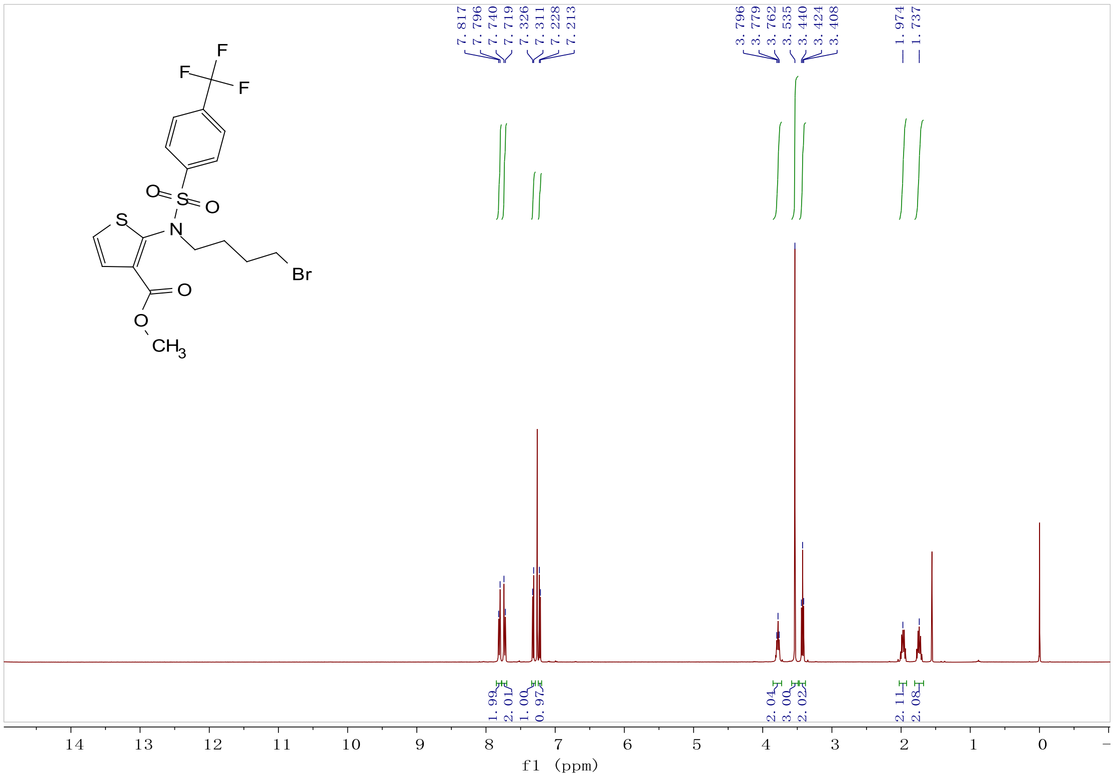


Fig. S37 ^{1}H NMR of compound **8g-1** in CDCl$_3$.

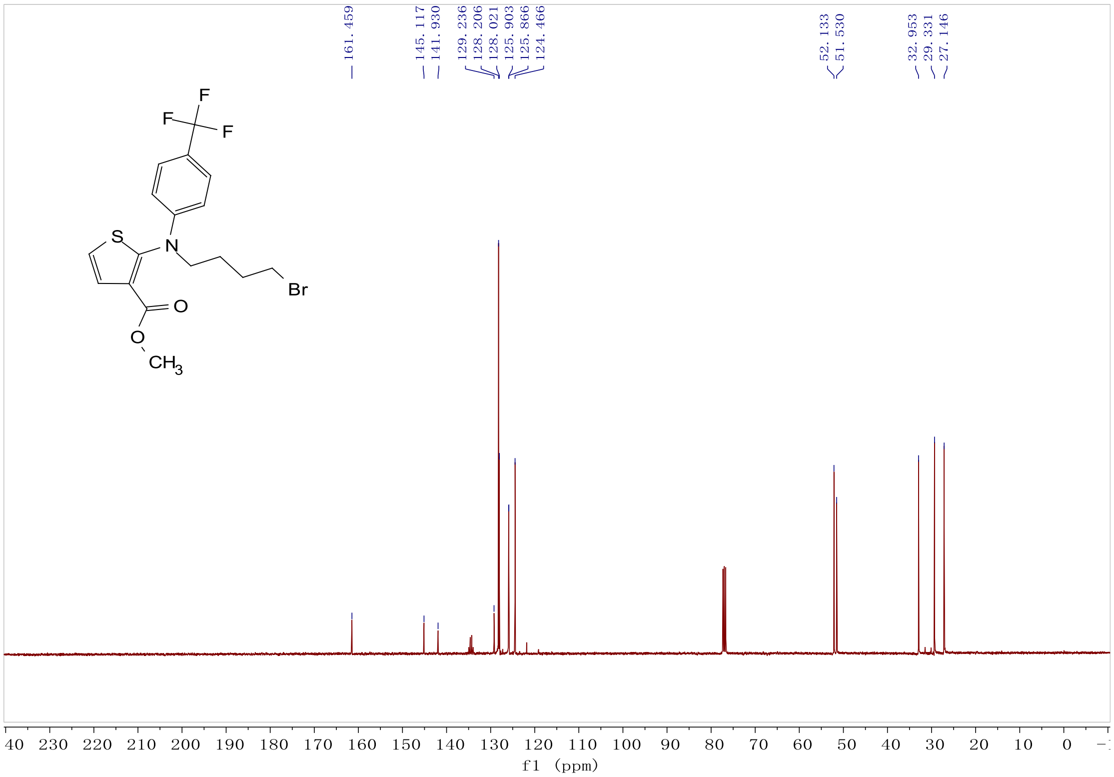


Fig. S38 ^{13}C NMR of compound **8g-1** in CDCl$_3$.

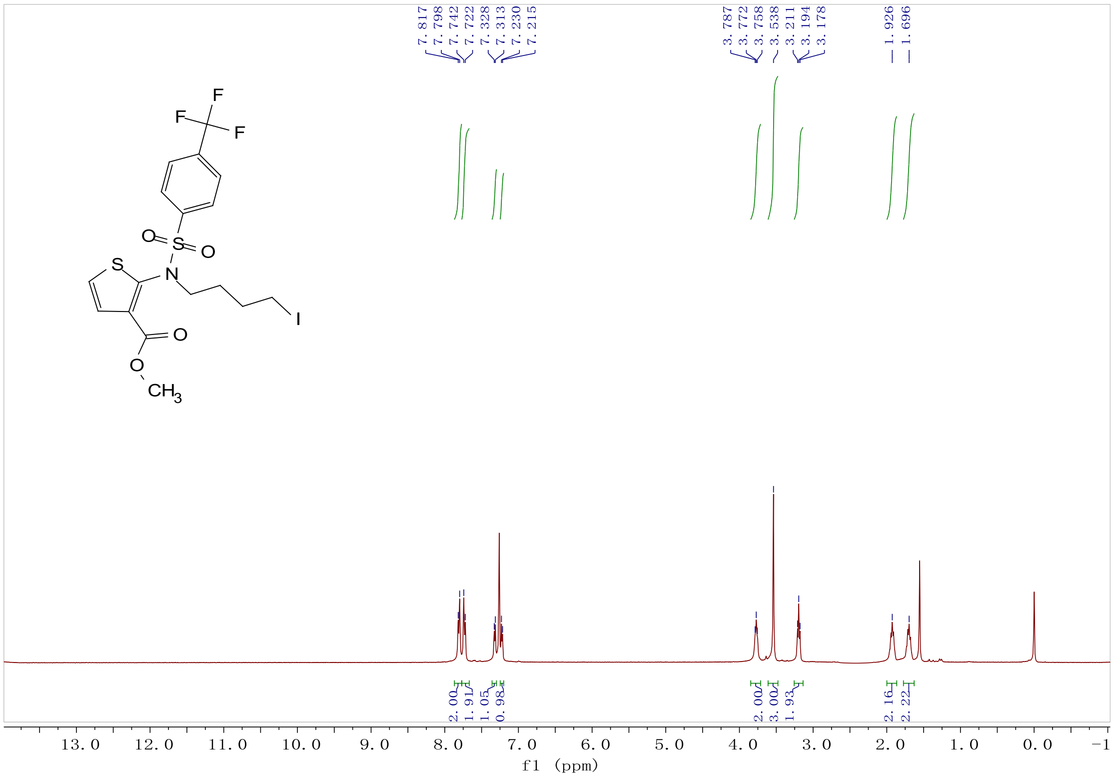


Fig. S39 ^{1}H NMR of compound **8g** in CDCl$_3$.

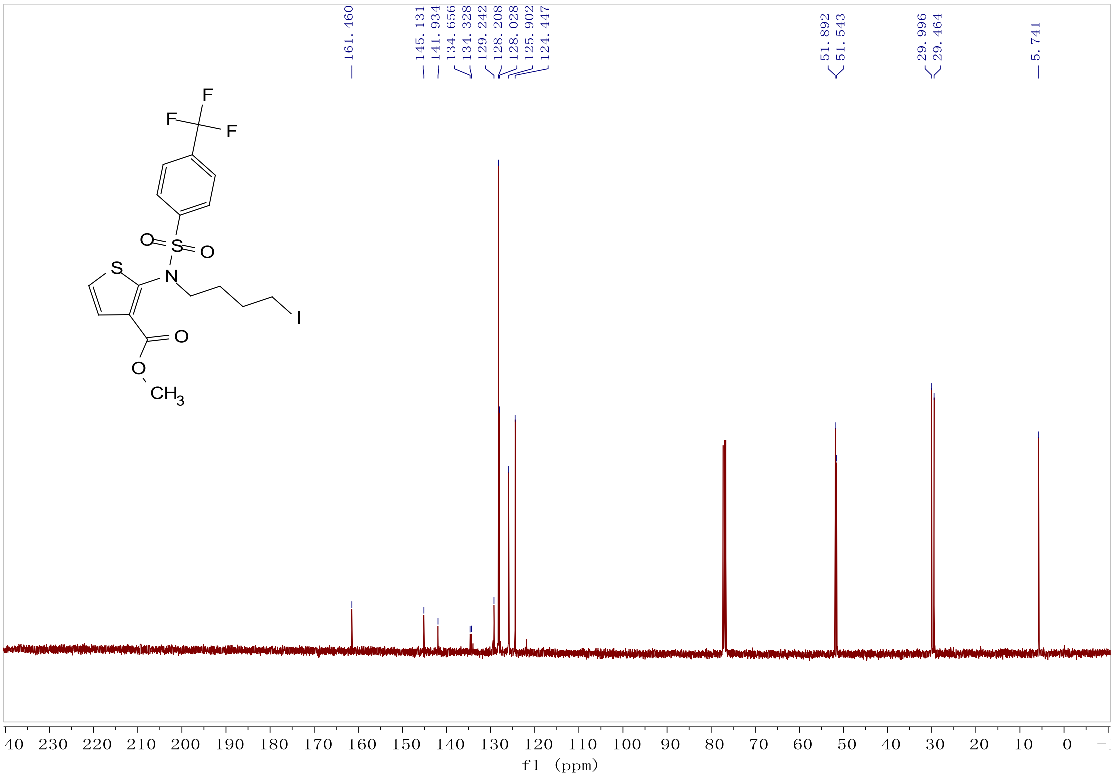


Fig. S40 ^{13}C NMR of compound **8g** in CDCl$_3$.

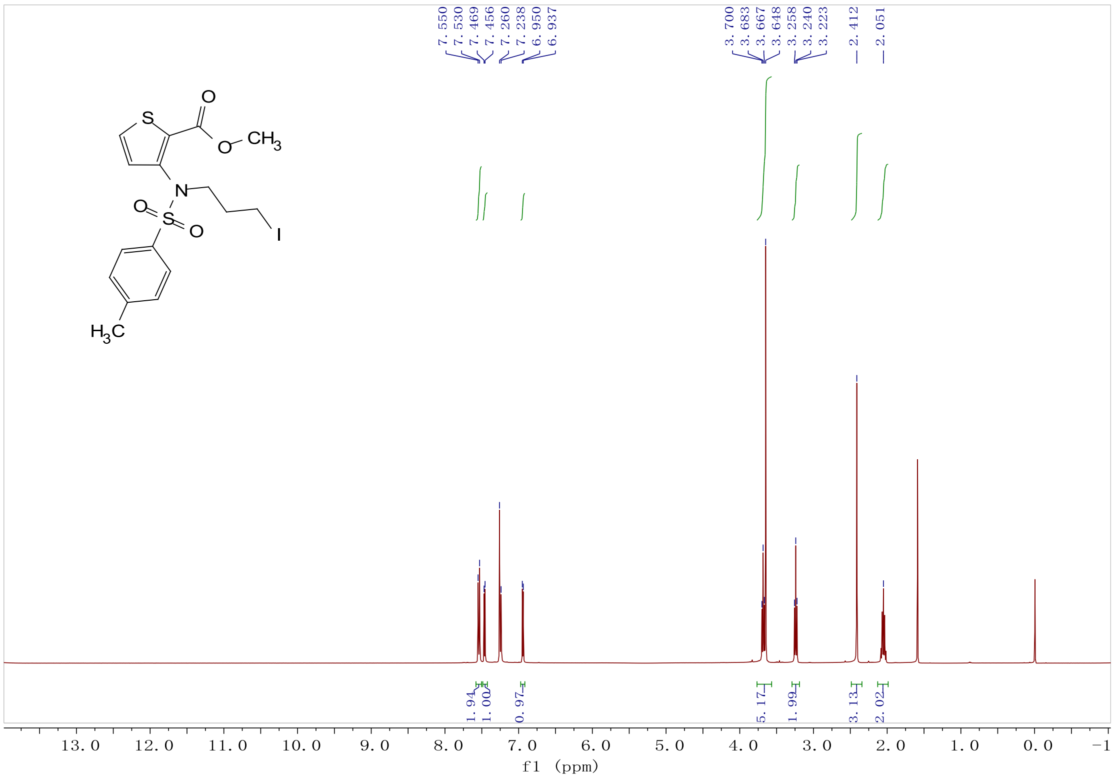


Fig. S41 ^{1}H NMR of compound **8h** in CDCl$_3$.

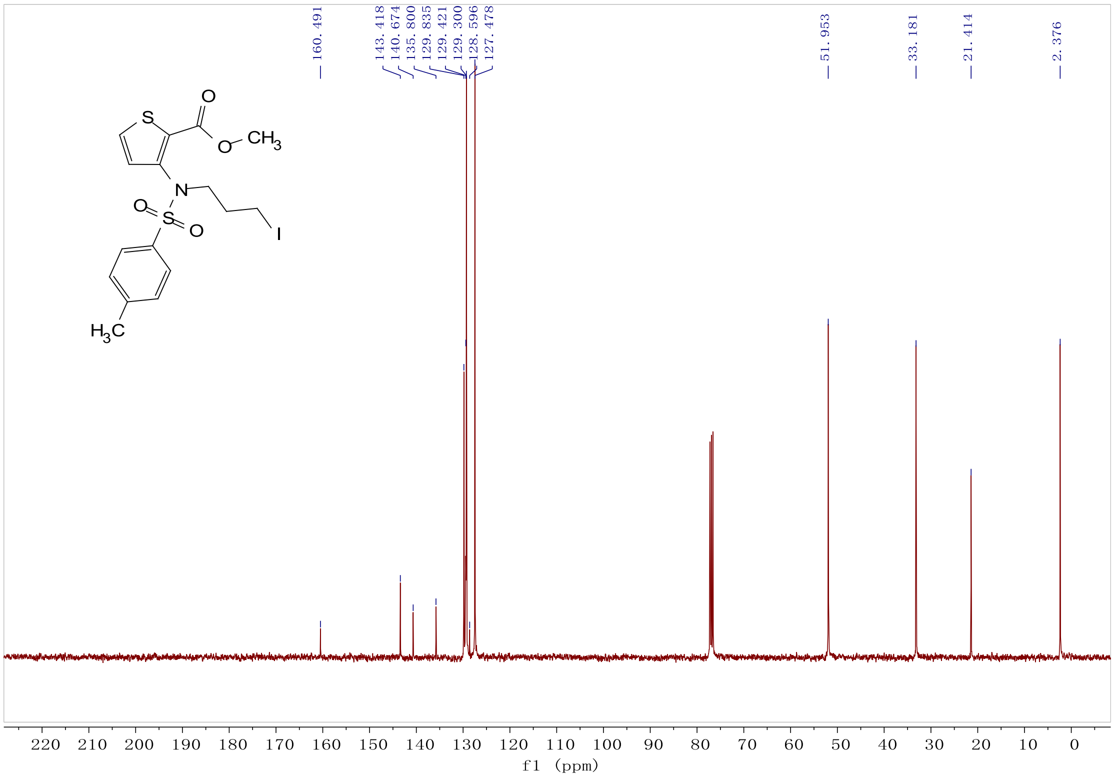


Fig. S42 ^{13}C NMR of compound **8h** in CDCl$_3$.

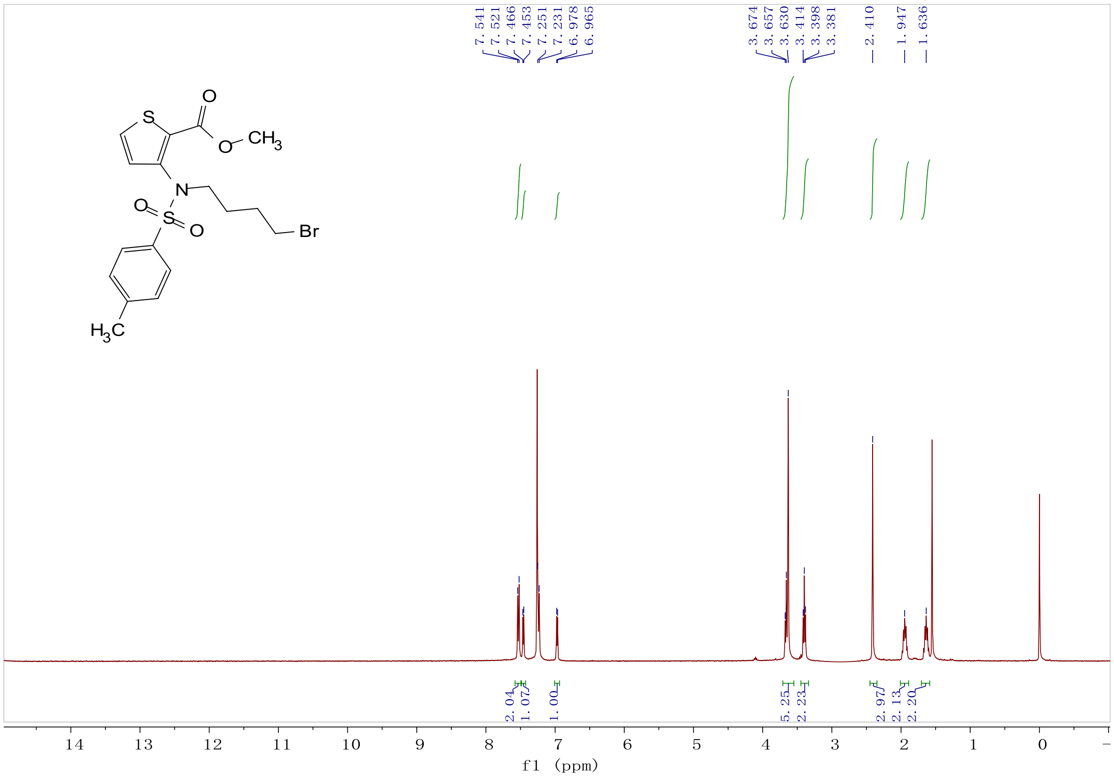


Fig. S43 ^{1}H NMR of compound **8i-1** in CDCl$_3$.

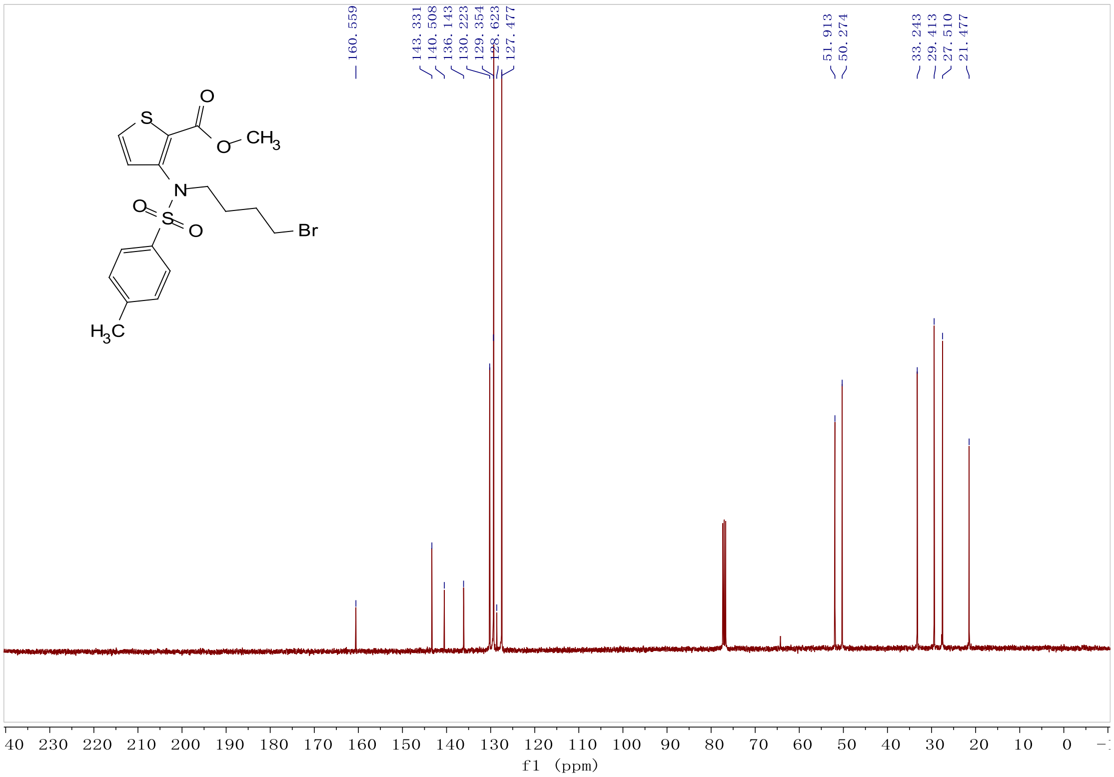


Fig. S44 ^{13}C NMR of compound **8i-1** in CDCl$_3$.

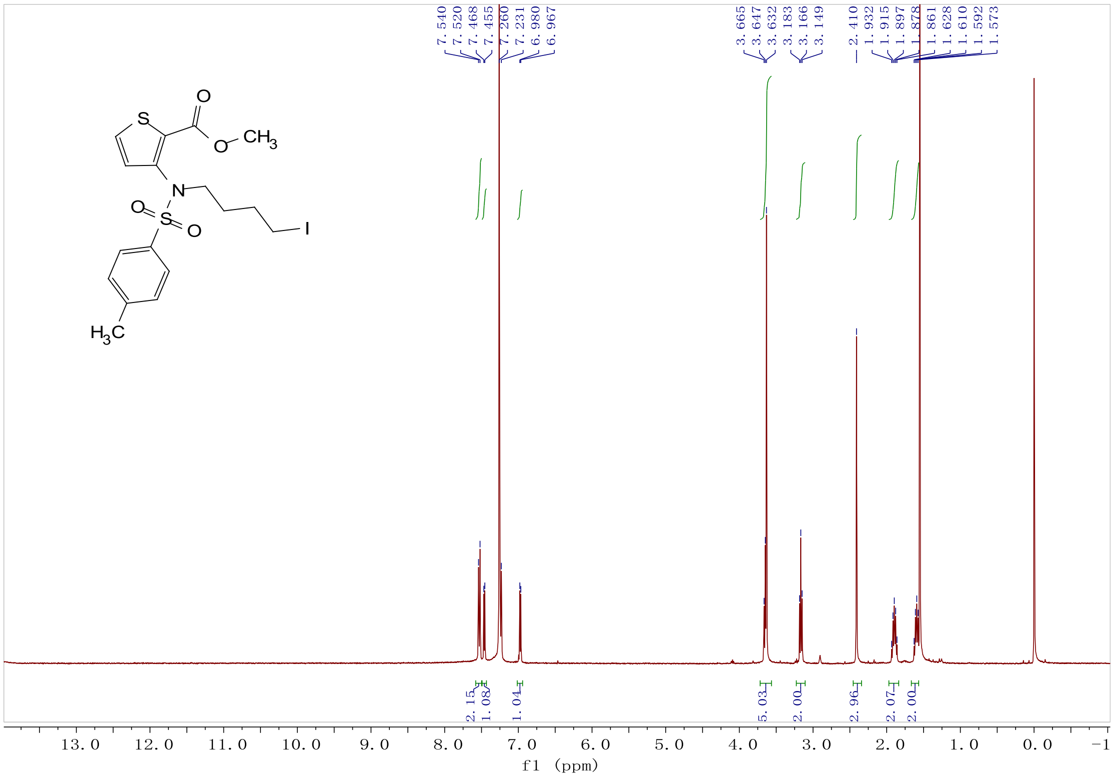


Fig. S45 ^{1}H NMR of compound **8i** in CDCl$_3$.

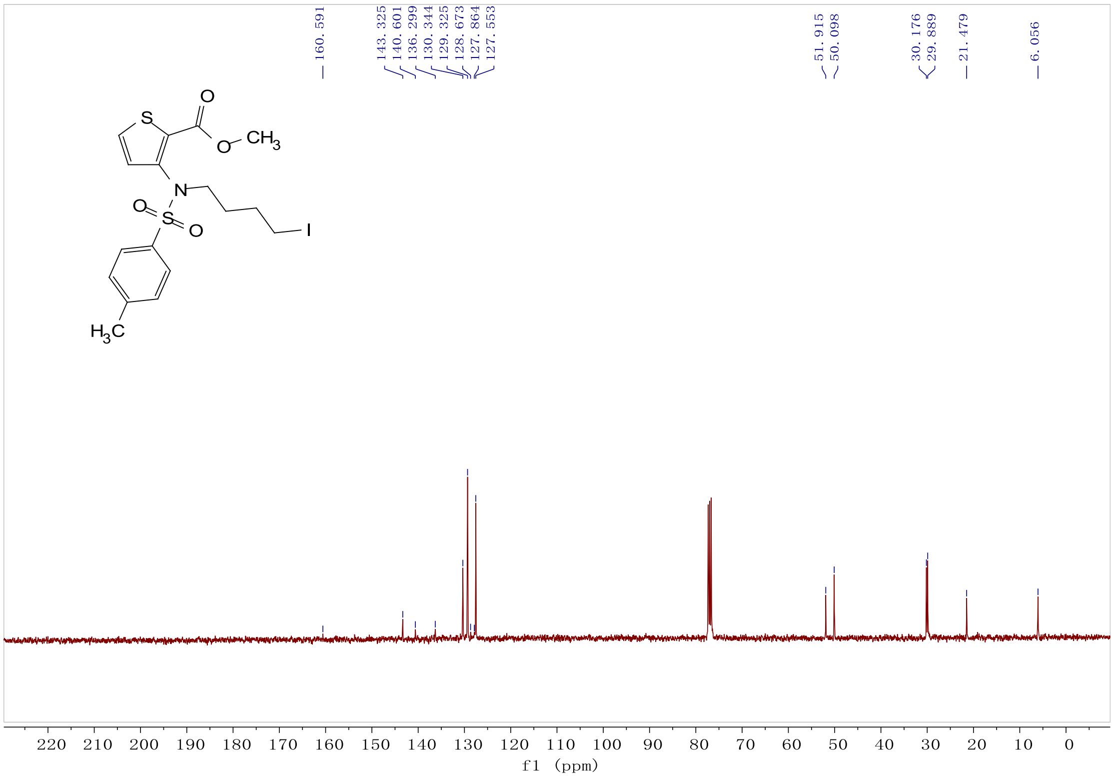


Fig. S46 ^{13}C NMR of compound **8i** in CDCl$_3$.

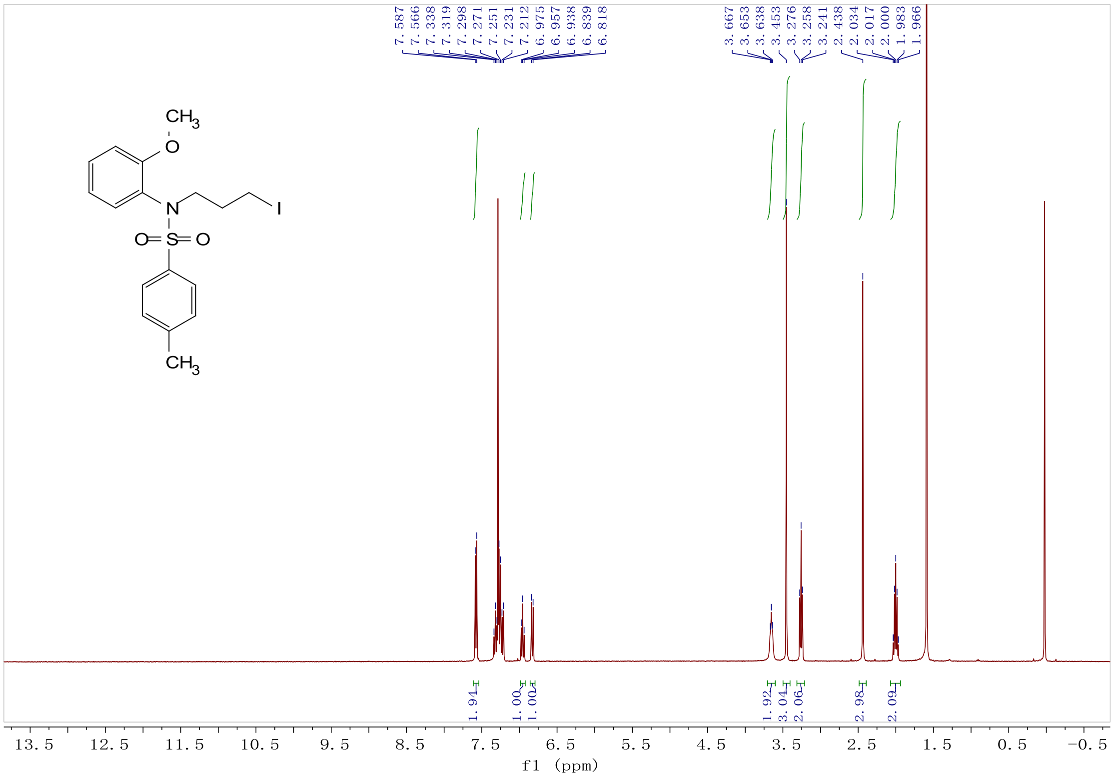


Fig. S47 ^{1}H NMR of compound **8j** in CDCl$_3$.

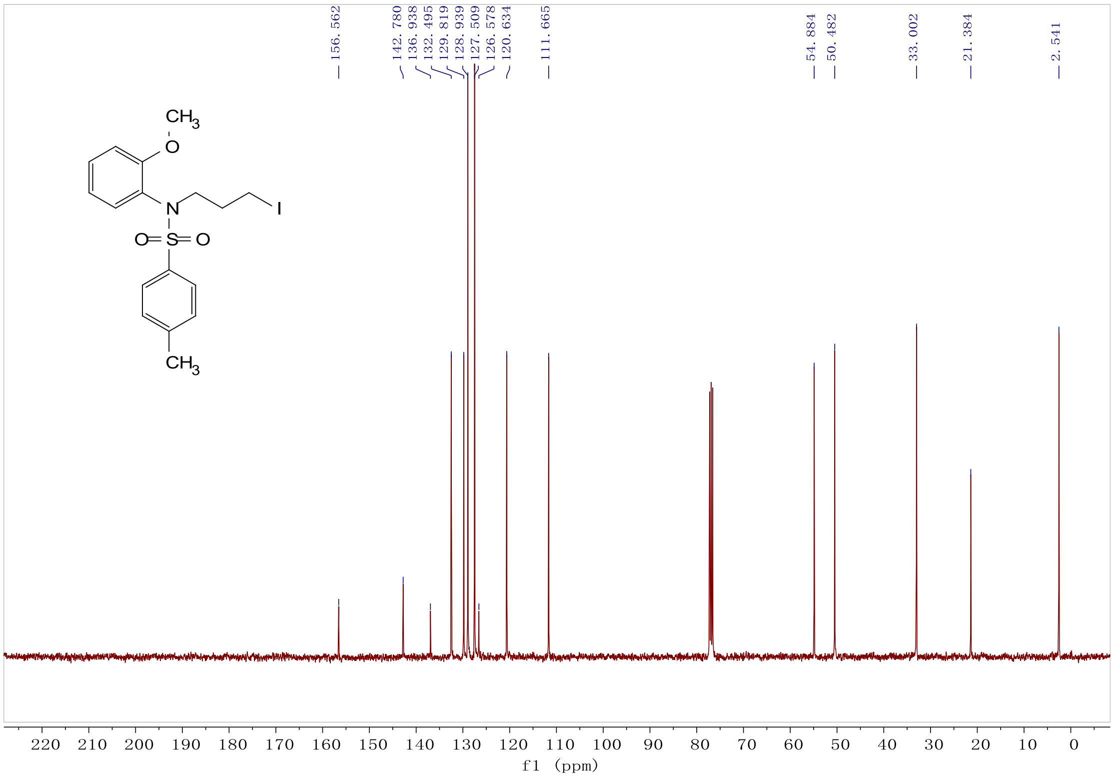


Fig. S48 ^{13}C NMR of compound **8j** in CDCl$_3$.

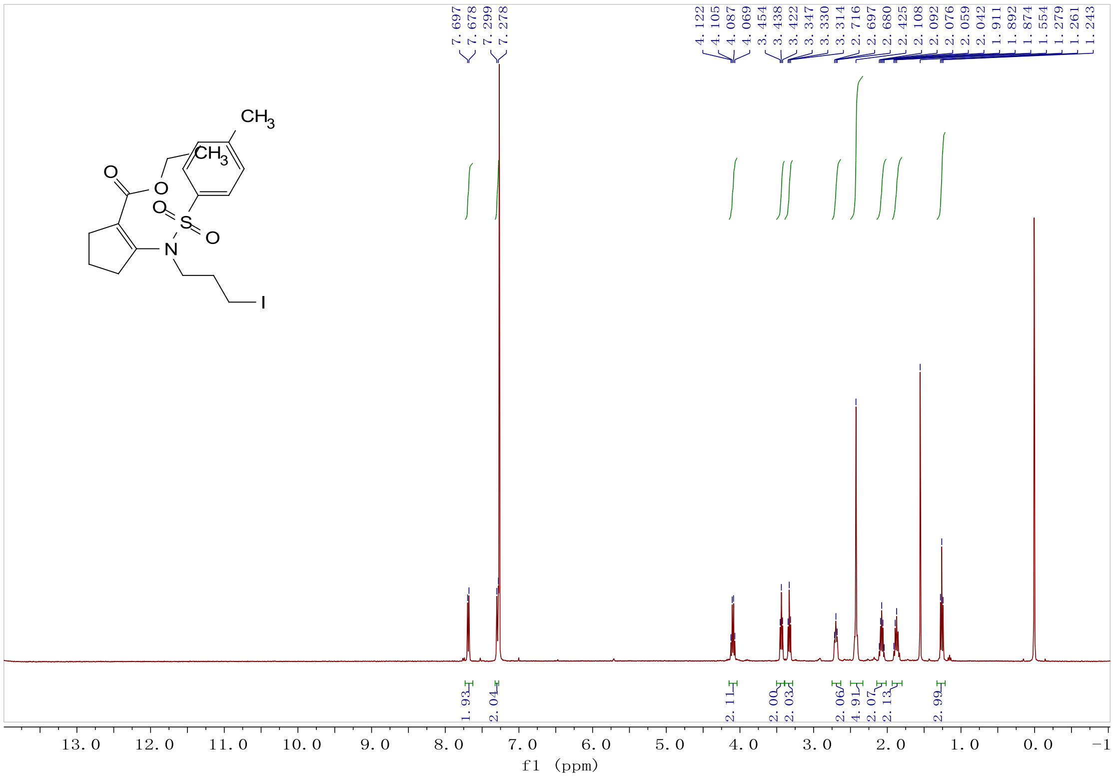


Fig. S49 ^{1}H NMR of compound **8k** in CDCl$_3$.

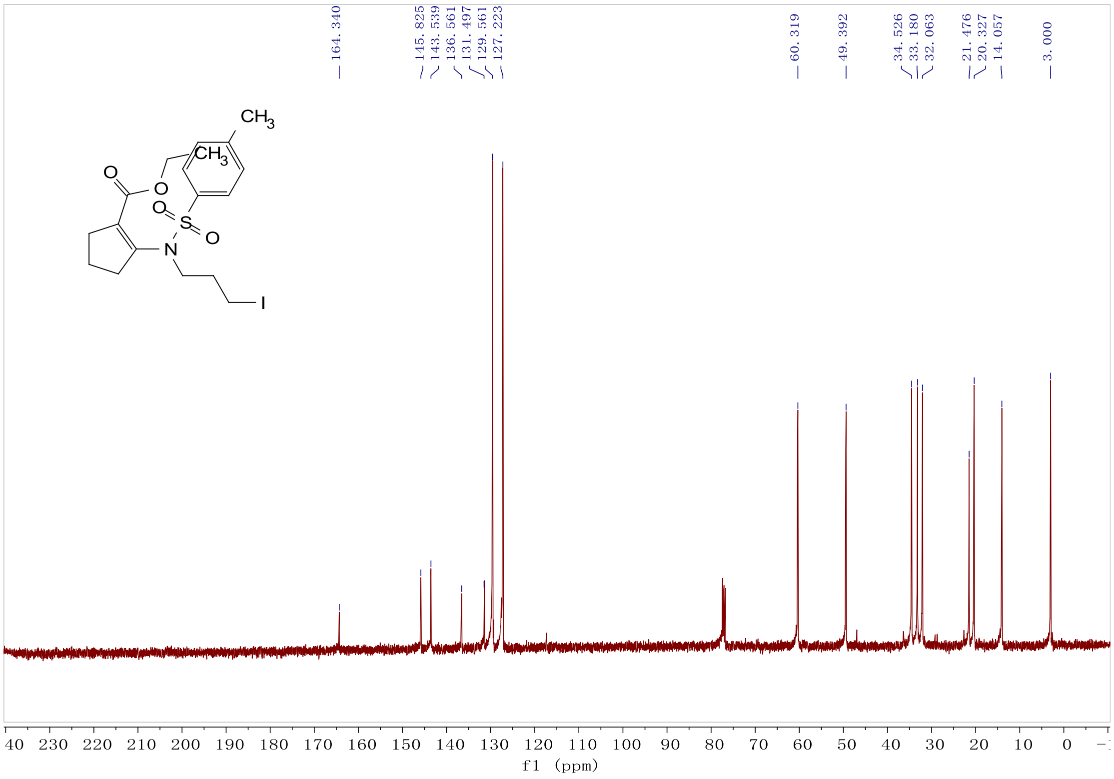


Fig. S50 ^{13}C NMR of compound **8k** in CDCl$_3$.

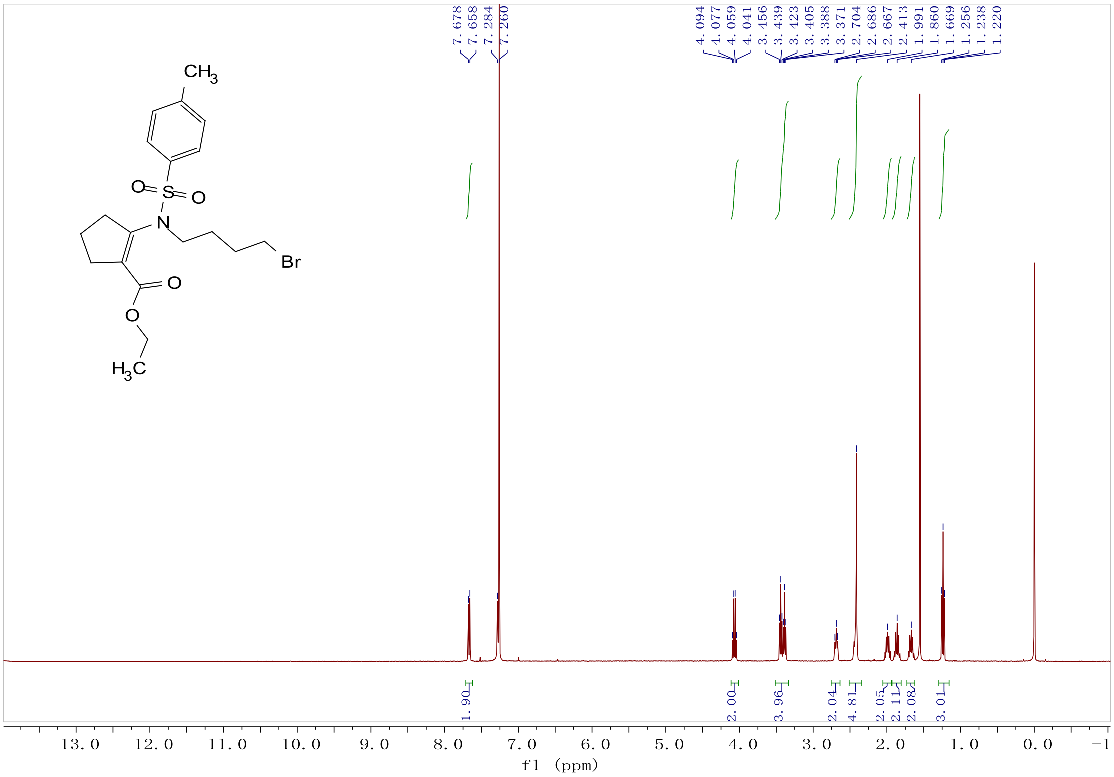


Fig. S51 ^{1}H NMR of compound **8l-1**in $CDCl_3$.

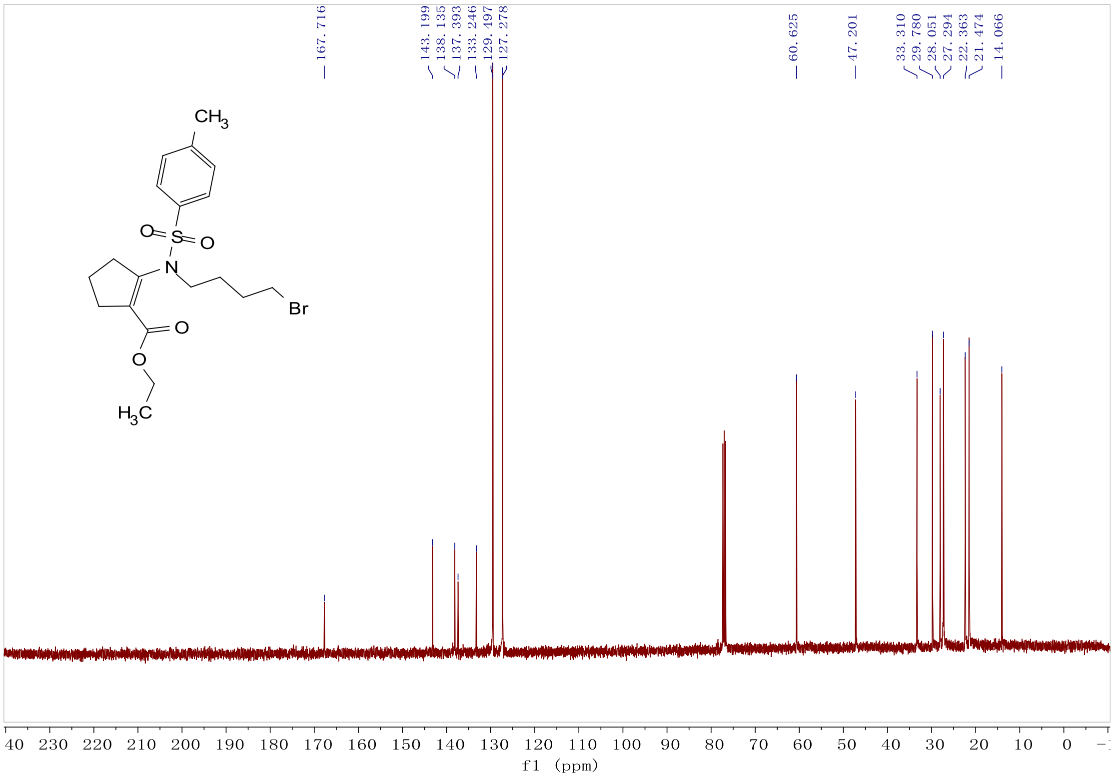


Fig. S52 ^{13}C NMR of compound **8l-1** in $CDCl_3$.

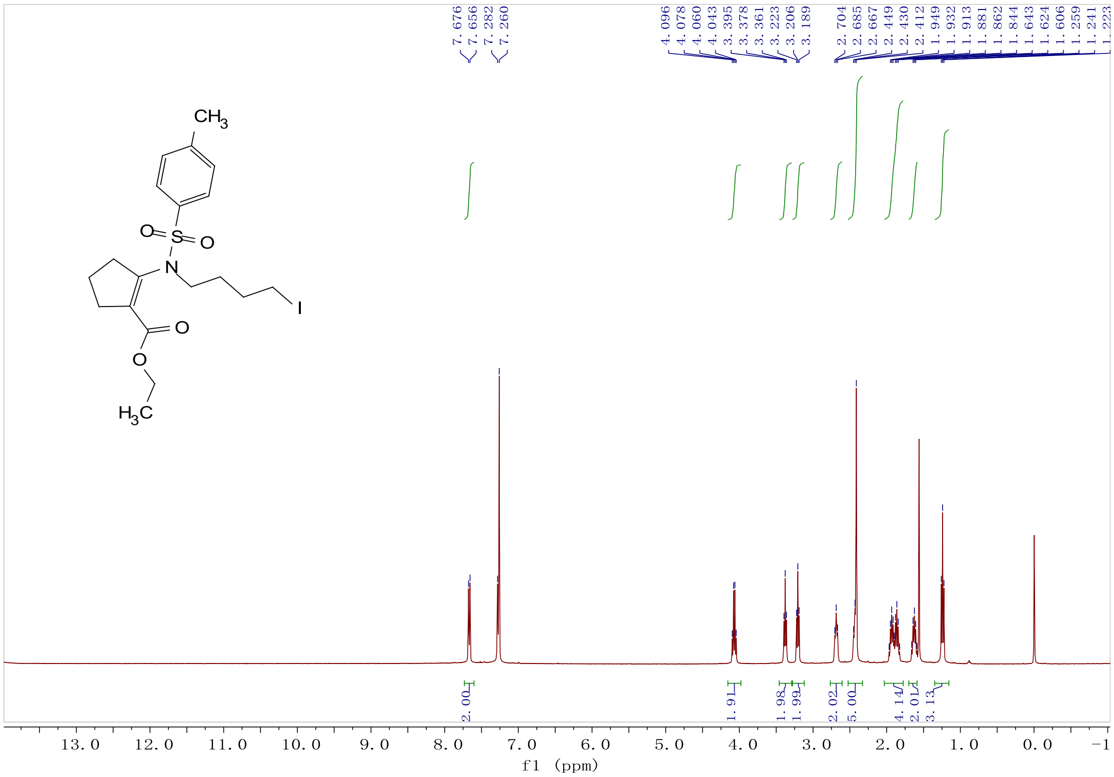


Fig. S53 ^{1}H NMR of compound **8l** in $CDCl_3$.

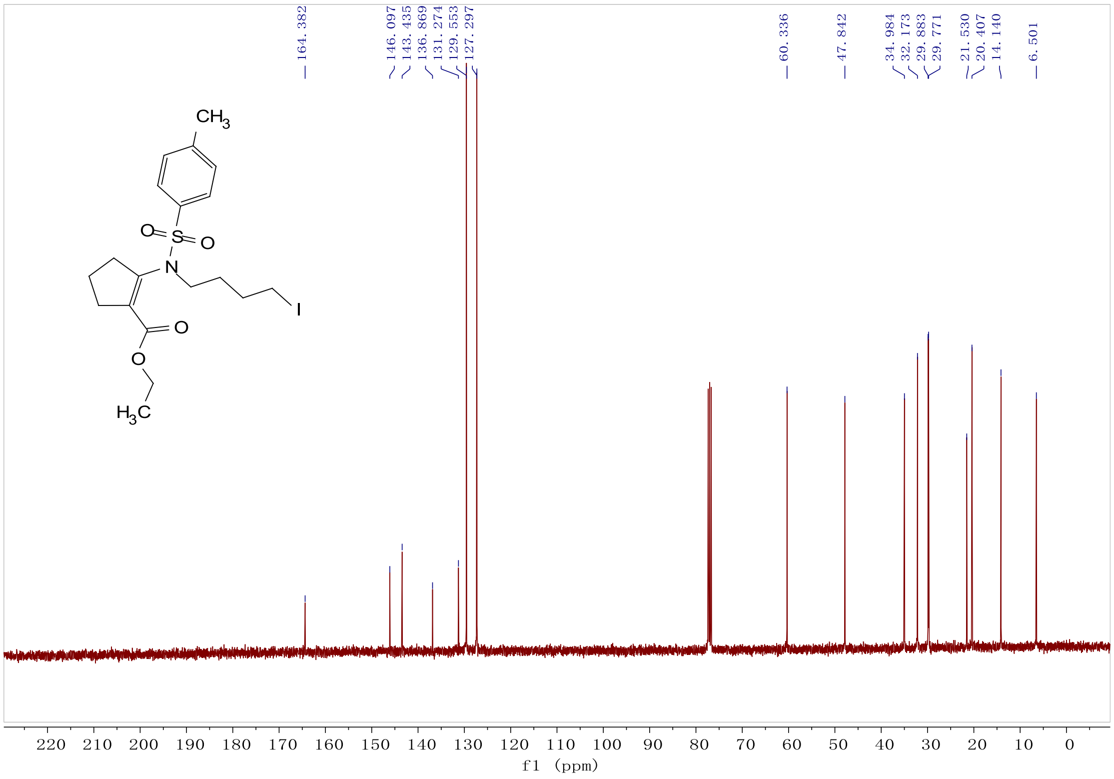


Fig. S54 ^{13}C NMR of compound **8l** in $CDCl_3$.

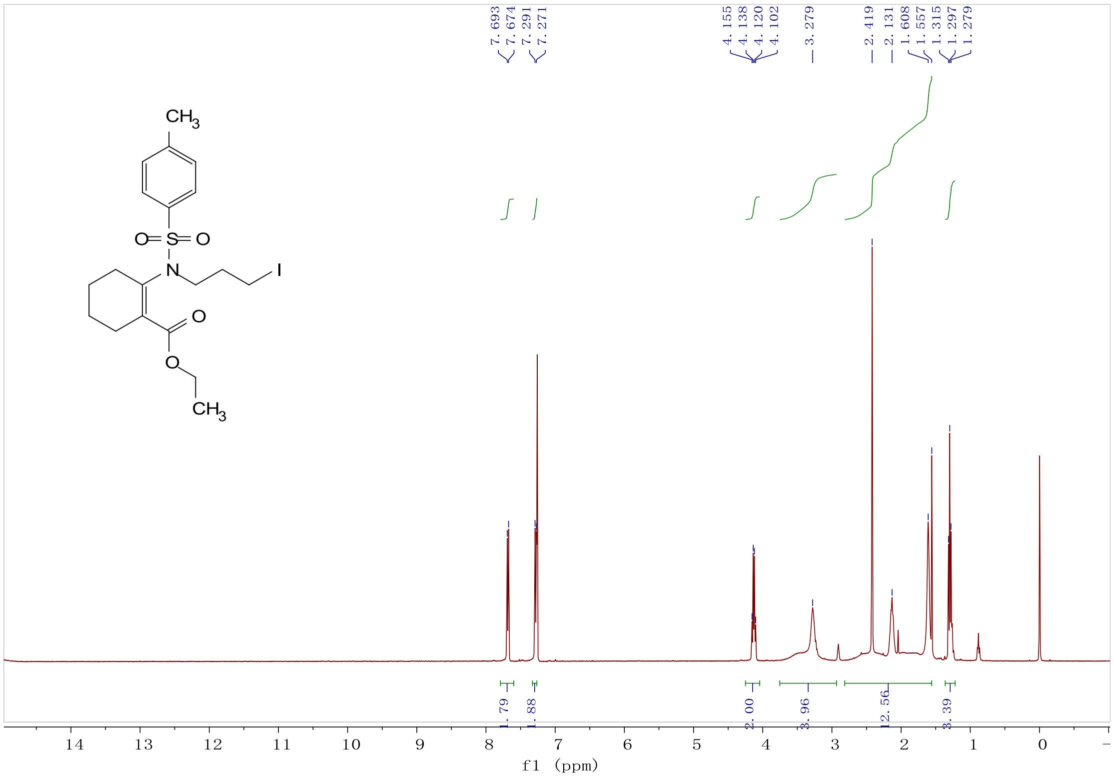


Fig. S55 ^{1}H NMR of compound **8m** in CDCl$_3$.

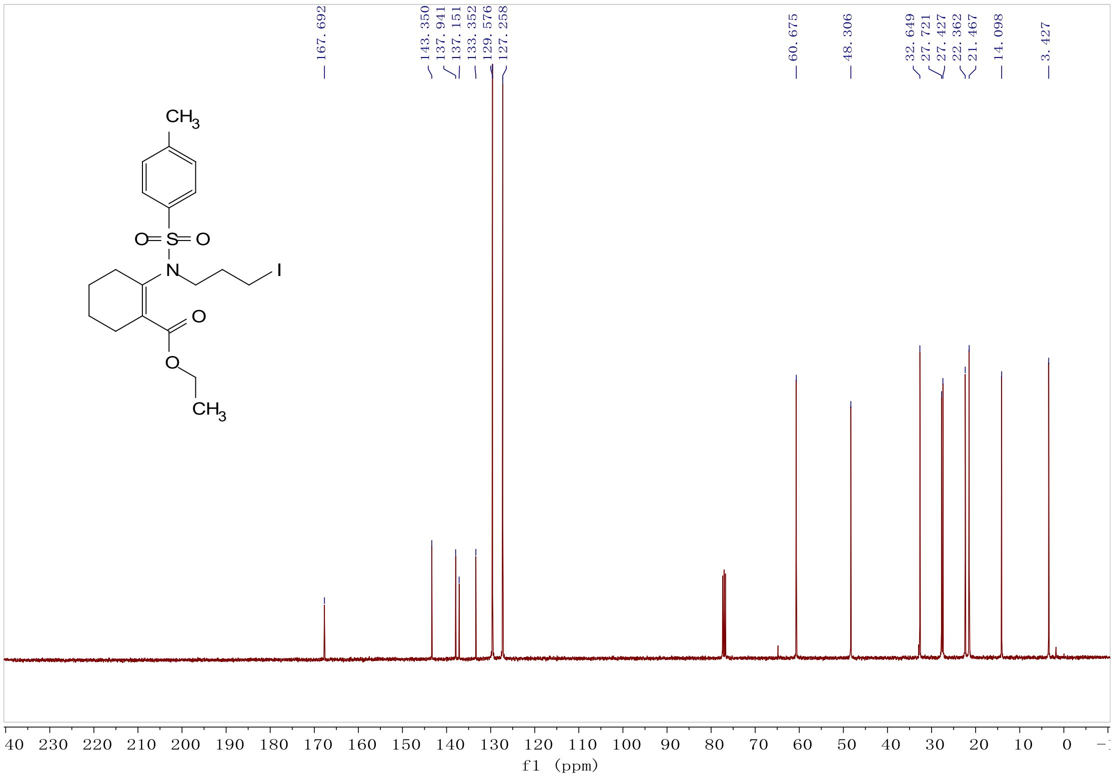


Fig. S56 ^{13}C NMR of compound **8m** in CDCl$_3$.

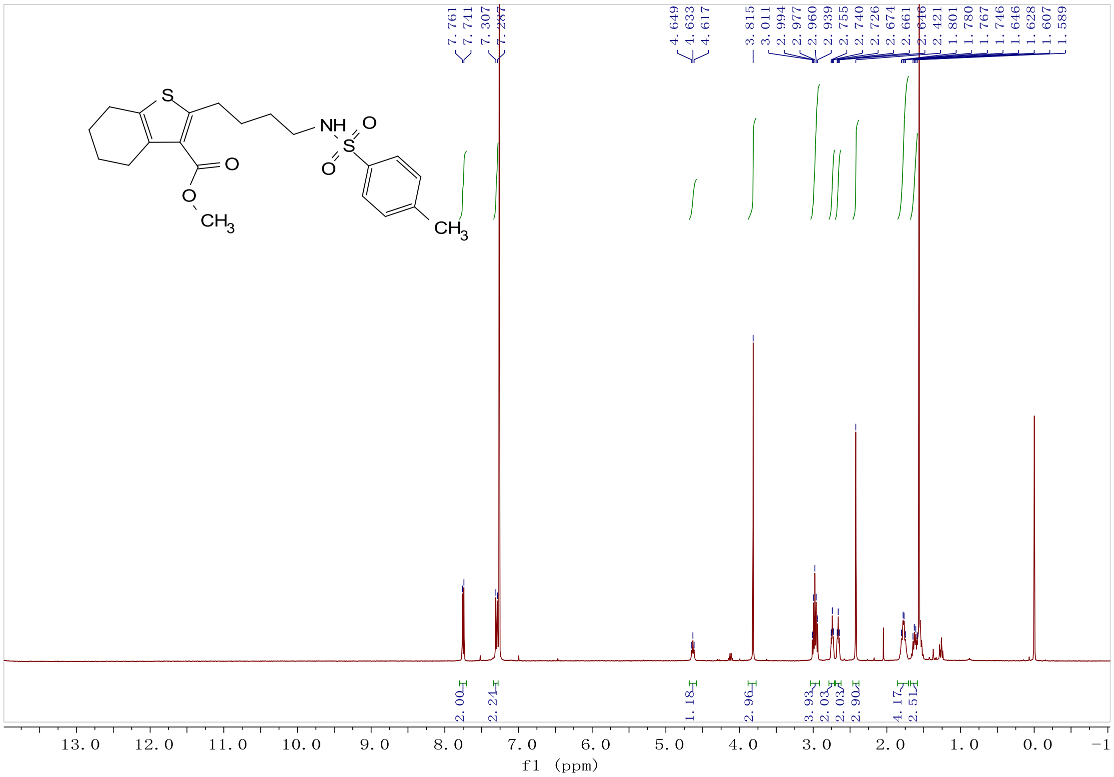


Fig. S57 ^{1}H NMR of compound **9f** in CDCl$_3$.

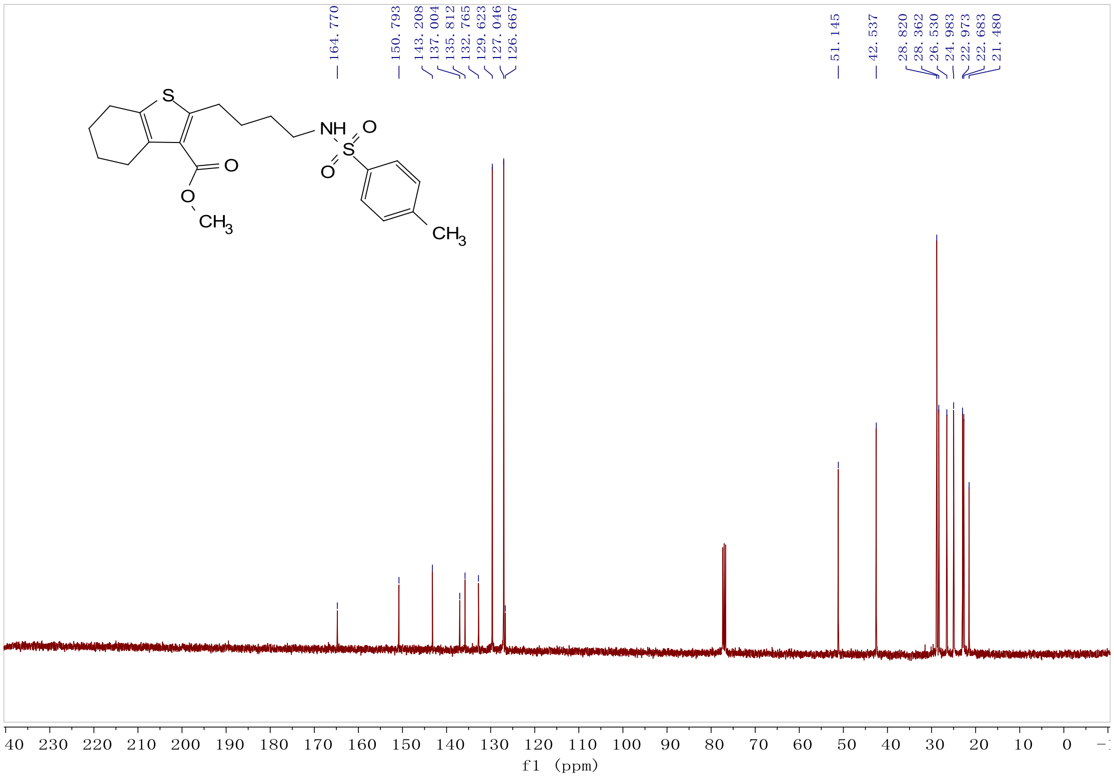


Fig. S58 ^{13}C NMR of compound **9f** in CDCl$_3$.

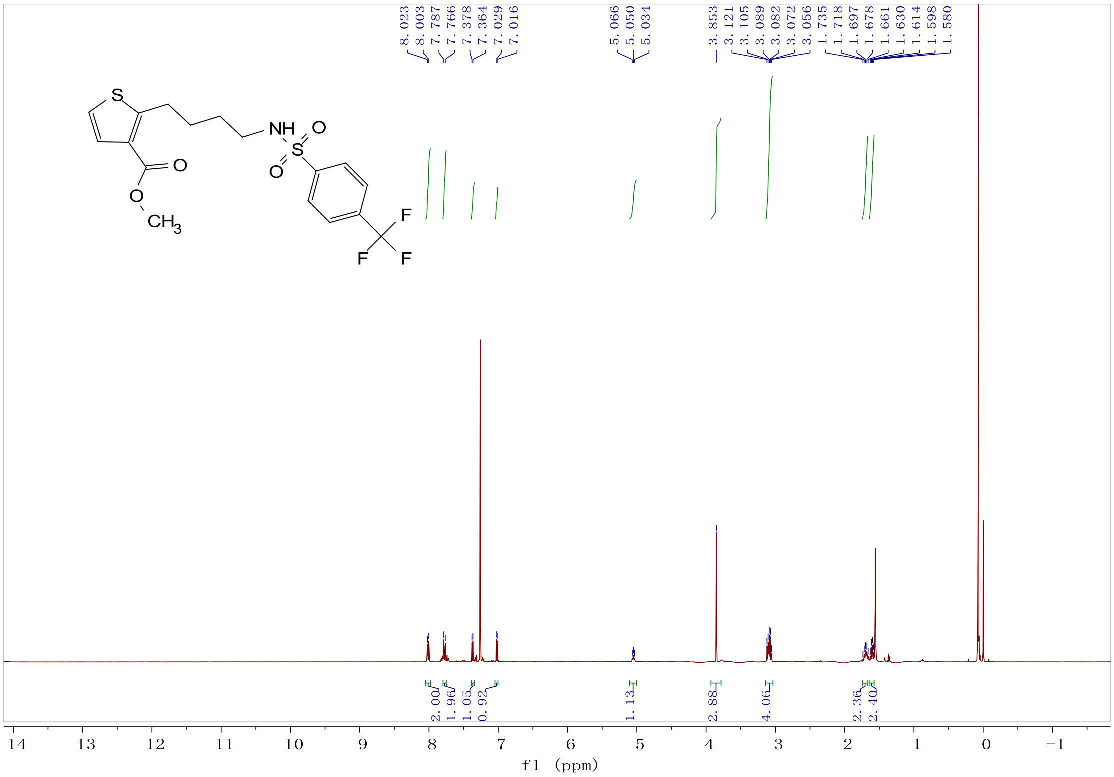


Fig. S59 ^{1}H NMR of compound **9g** in $CDCl_3$.

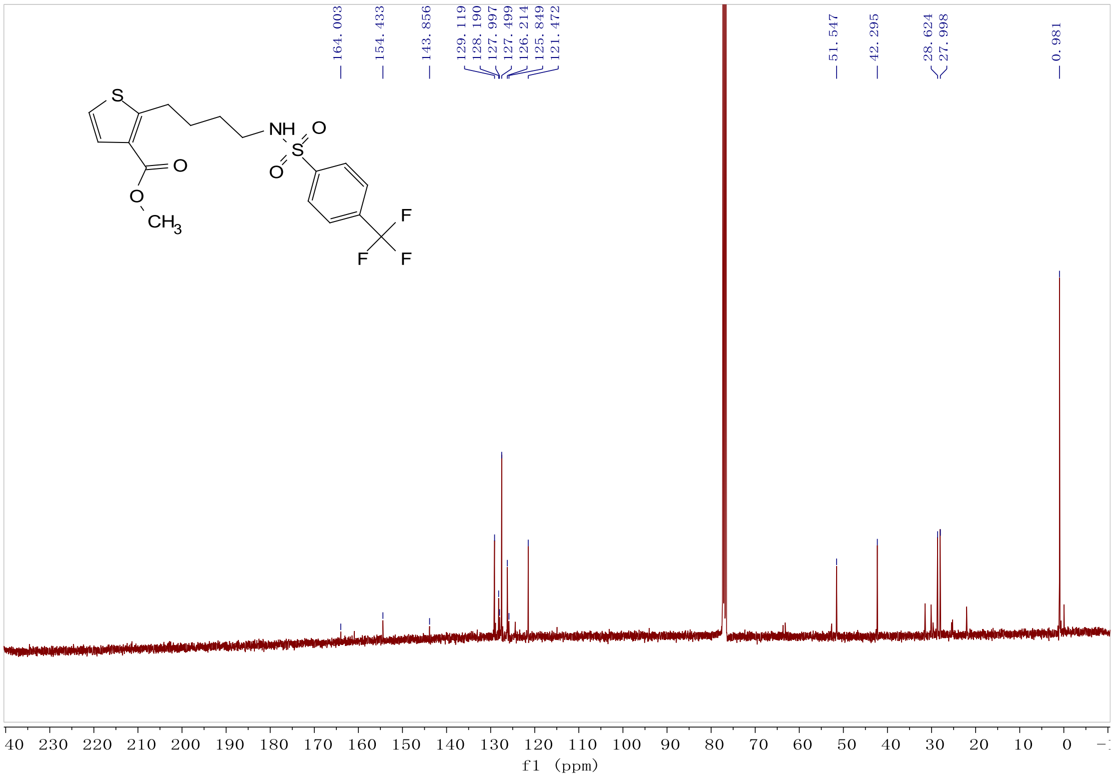


Fig. S60 ^{13}C NMR of compound **9g** in $CDCl_3$.

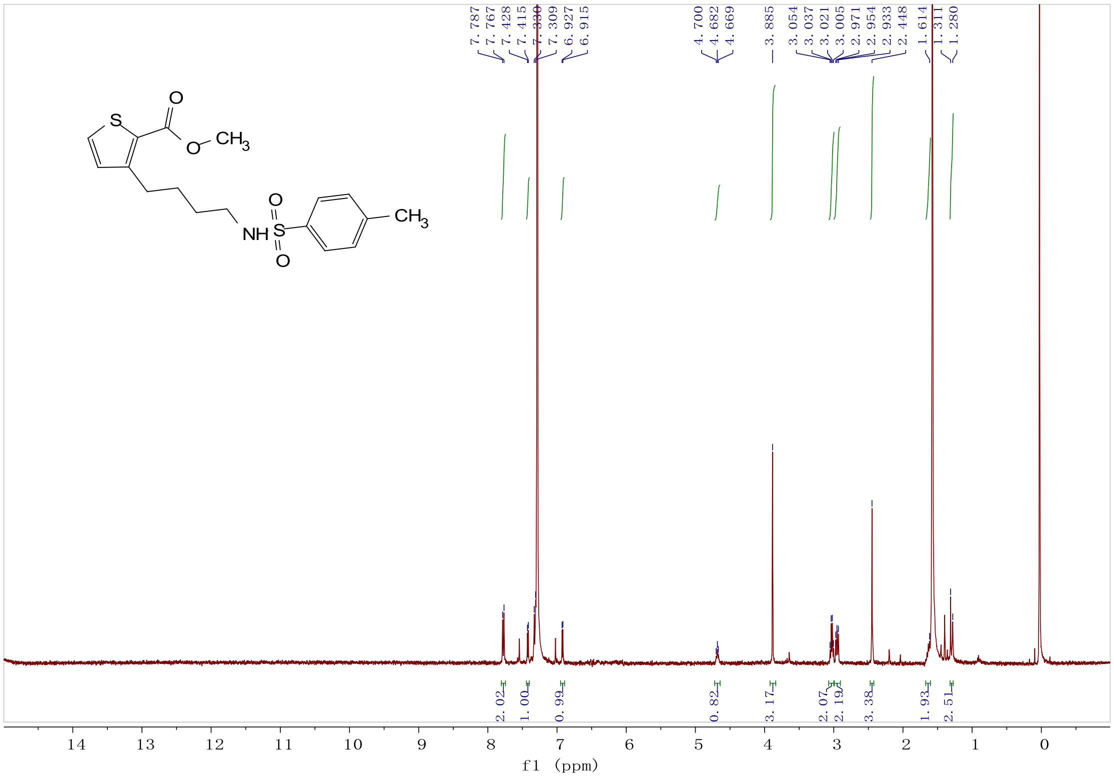


Fig. S61 ^{1}H NMR of compound **9i** in $CDCl_3$.

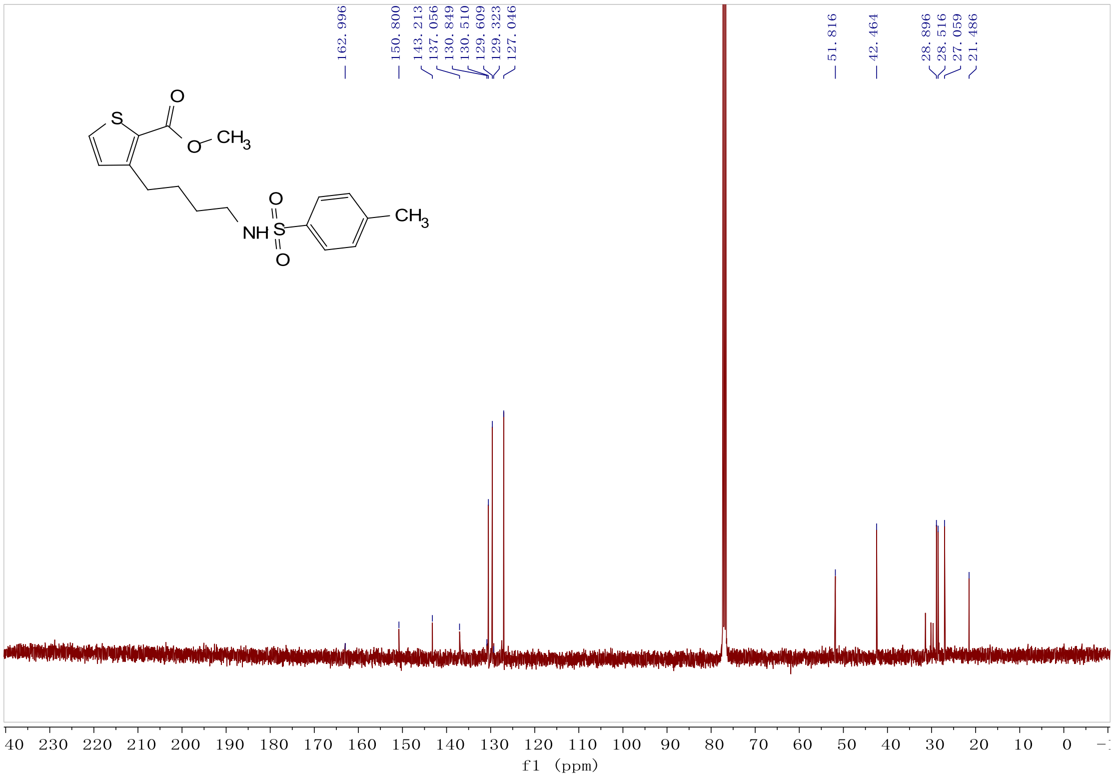


Fig. S62 ^{13}C NMR of compound **9i** in $CDCl_3$.

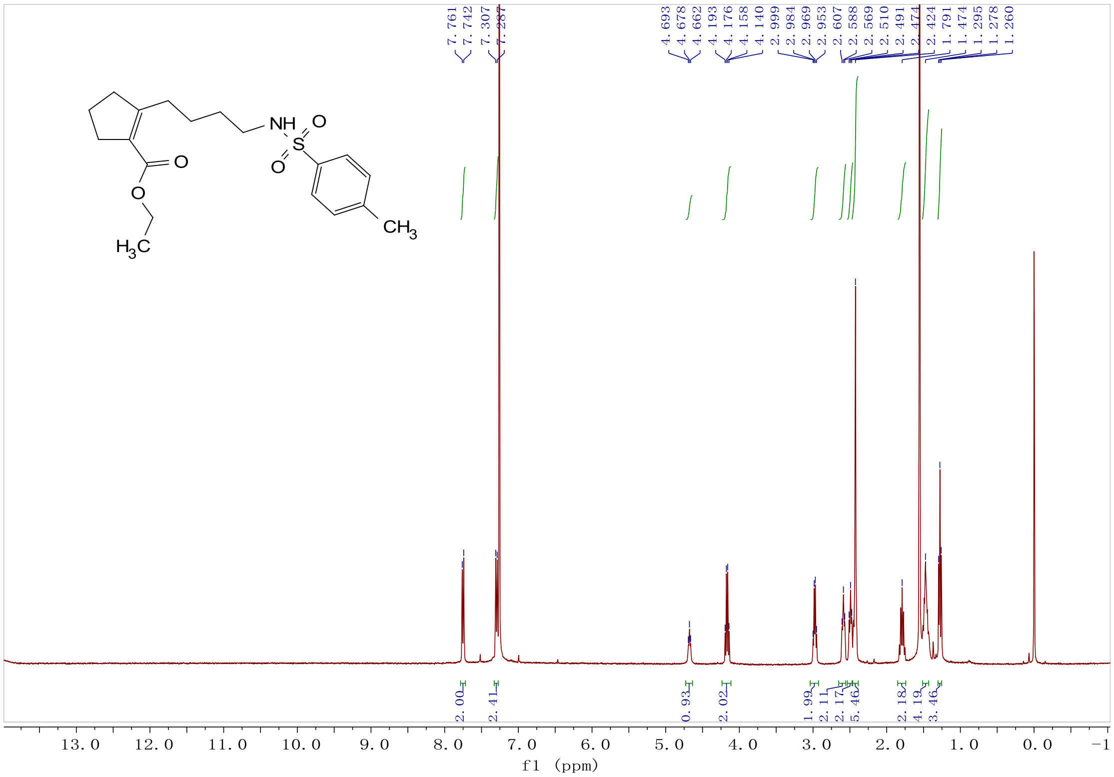


Fig. S63 ^{1}H NMR of compound **9l** in $CDCl_3$.

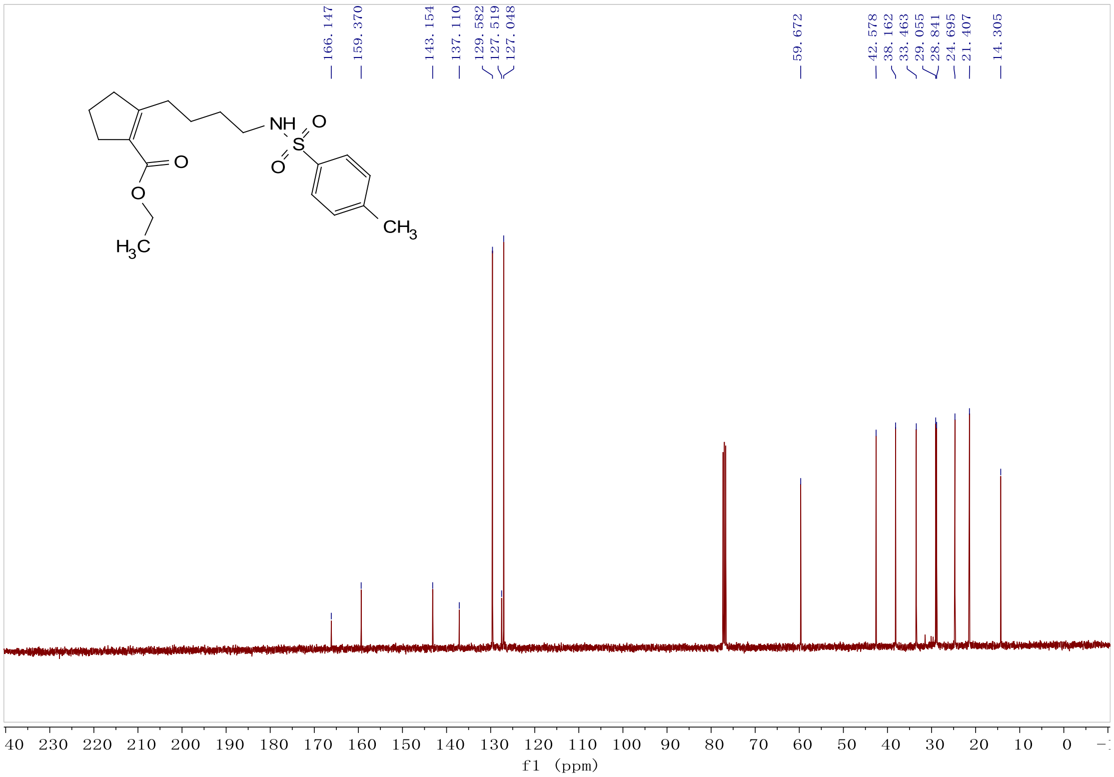


Fig. S64 ^{13}C NMR of compound **9l** in $CDCl_3$.

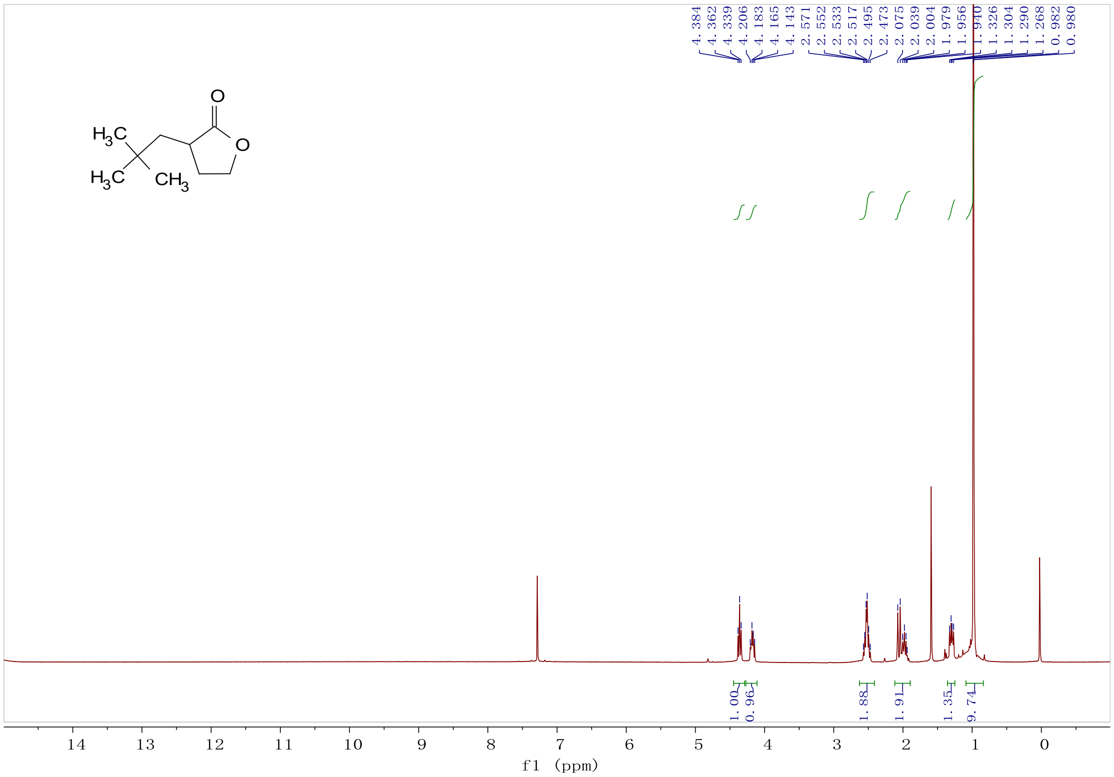


Fig. S65 ^{1}H NMR of compound **12e** in $CDCl_3$.

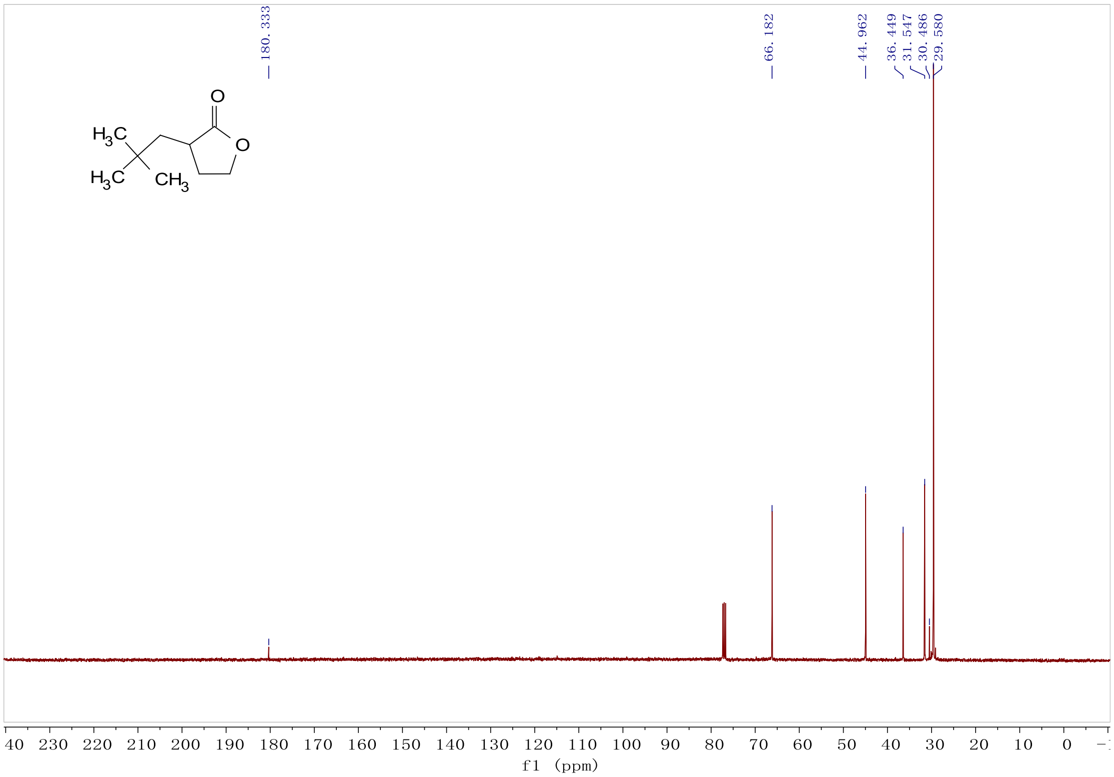


Fig. S66 ^{13}C NMR of compound **12e** in $CDCl_3$.

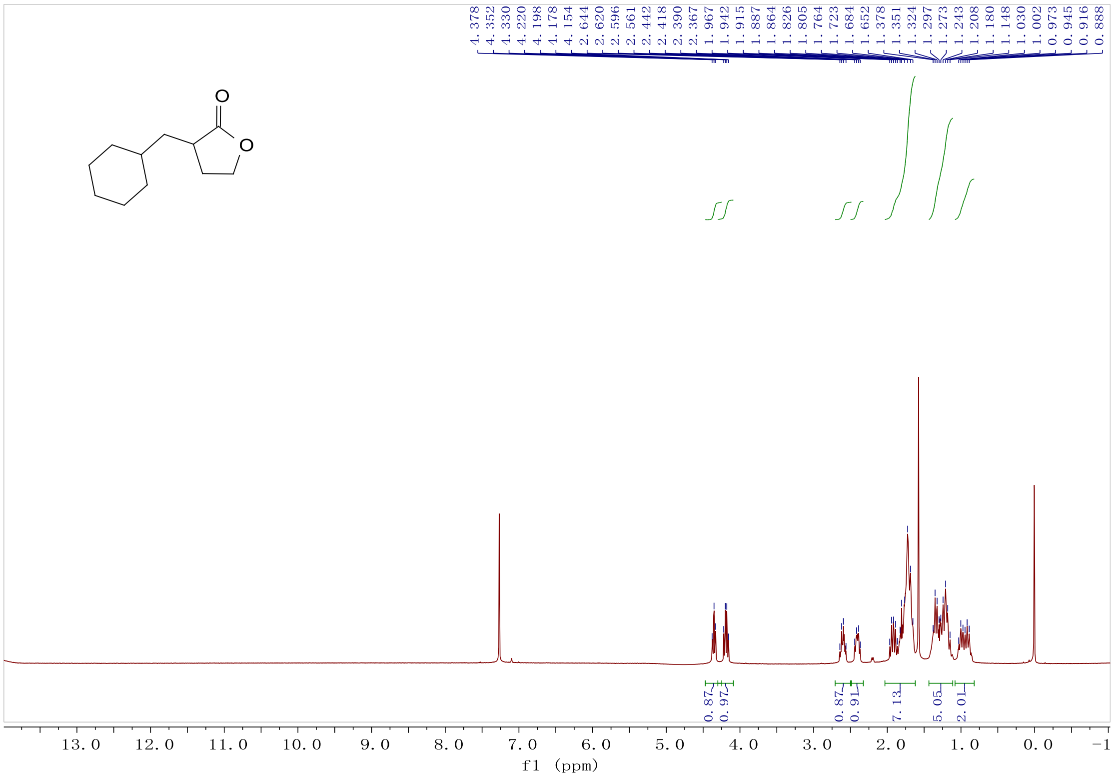


Fig. S67 ^{1}H NMR of compound **12k** in $CDCl_3$.

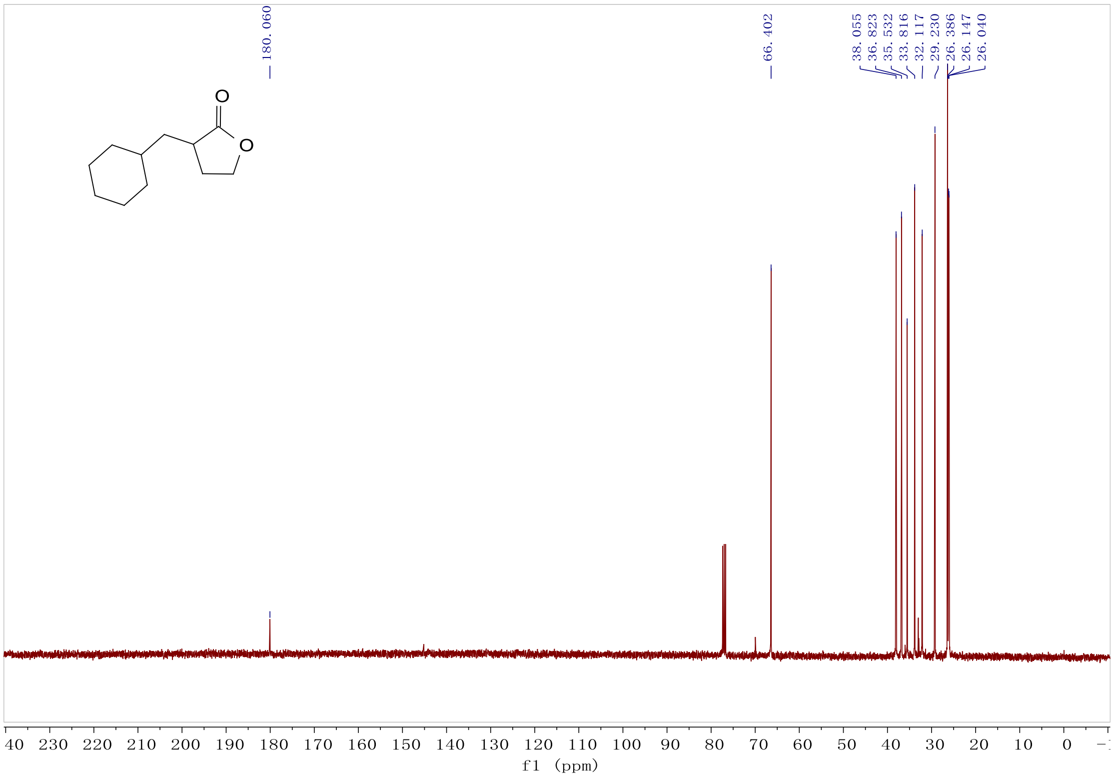


Fig. S68 ^{13}C NMR of compound **12k** in $CDCl_3$.