Electronic Supplementary Information (ESI)

Thiophene insertion for continuously modulating photoelectronic property of triphenylamine-based metal-organic framework for photocatalytic sulfonylation-cyclisation of activated alkenes†

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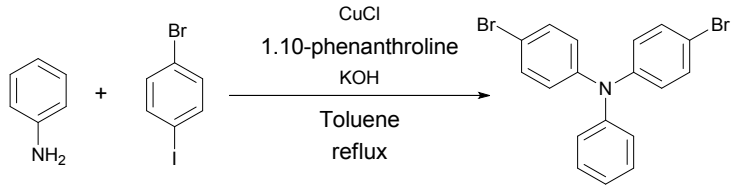
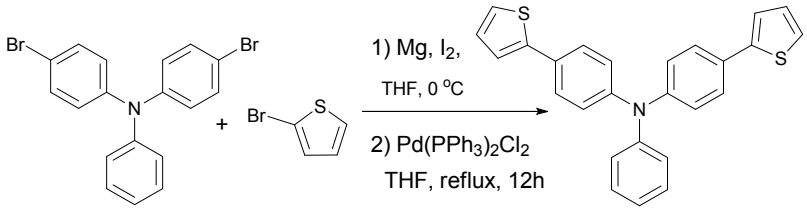
Syntheses and Characterization of Ligands

4-Bromo-*N*-(4-bromophenyl)-*N*-phenylaniline



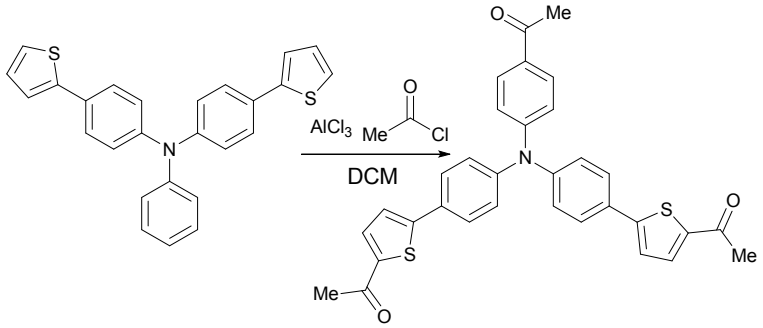
The title compound was prepared according to the literature protocol.[1] To a 100 mL oven-dried flask was added aniline (1.022 g, 10.97 mmol), 1-bromo-4-iodobenze (6.98 g, 24.67 mmol), phenanthroline (74 mg, 0.4 mmol), cuprous chloride (43 mg, 0.4 mmol) and KOH flakes (4.83 g, 86.14 mmol) under N_2, then degassed toluene (11 mL) was added by syringe. The mixture was heated to reflux within 30 min, then stirred under reflux for 48 h. After cooling to 75 °C, toluene (15 mL) and distilled water (10 mL) were added, the organic phase was collected and dried with anhydrous $MgSO_4$, the filtrate was evaporated under vacuum and the crude product was purified by flash column chromatography to obtain the product. (3.53 g, 78 %). ^{1}H NMR (400 MHz, CDCl3) δ 7.33 (d, J = 8.8 Hz, 4H), 7.26 (dd, J = 9.7, 6.1 Hz, 2H), 7.08 – 7.03 (m, 3H), 6.93 (d, J = 8.8 Hz, 4H). ^{13}C NMR (101 MHz, CDCl3) δ 147.1, 146.7, 132.5, 129.7, 125.6, 124.8, 123.9, 115.6. The NMR spectrum were in compliance with the reported data.[1]

***N*-Phenyl-4-(thiophen-2-yl)-*N*-(4-(thiophen-2-yl)phenyl)aniline**



The title compound was prepared according to the literature protocol.[2] 2-bromothiophene (1.43 mL, 14.79 mmol) was added dropwise to the mixture of fresh magnesium turnings (0.72 g, 29.58 mmol), I_2 (catalytic amount) and THF (15 mL) at 0 °C under N_2, after being stirred under reflux for 2 h. the solution of Grignard reagent was added dropwise to a mixture of 4-bromo-*N*-(4-bromphenyl)-*N*-phenylaniline (1.99 g, 4.93 mmol) and $Pd(PPh_3)_2Cl_2$ (394 mg) in THF (15 mL), the reaction was reflux for 12 h and then cooled to room temperature. Saturated aqueous solution of NH_4Cl was added to quench the reaction at 0 °C, then chloroform was added, the combined organic phase was collected and dried over $NaSO_4$, the filtrate was evaporated under vacuum and the crude product was purified by flash column chromatography to get the product. (0.93 g, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.7 Hz, 4H), 7.31 – 7.26 (m, 2H), 7.23 – 7.21 (m, 4H), 7.17 – 7.13 (m, 2H), 7.10 (d, J = 8.7 Hz, 4H), 7.08 – 7.04 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3, 147.0, 144.3, 129.5, 129.1, 128.1, 127.0, 124.8, 124.27 (overlapped), 124.25 (overlapped), 123.5, 122.5. The NMR spectrum were in compliance with the reported data.[2]

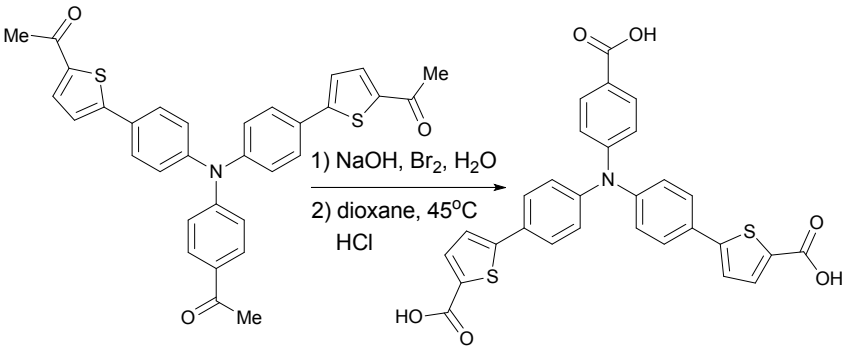
1,1'-((((4-Acetylphenyl)azanediyl)bis(4,1-phenylene))bis(thiophene-5,2-diyl))bis(ethan-1-one)



N-phenyl-4-(thiophen-2-yl)-*N*-(4-(thiophen-2-yl)phenyl)aniline (2.05 g, 5.00 mmol), $AlCl_3$ (2.20 g, 16.50 mmol) and anhydrous DCM (100 mL) were added to a three-neck flask under N_2, the mixture was cooled to 0 °C by ice-water bath. Acetyl chloride (2.44 mL, 34.50 mmol) was then added dropwise to the

stirred reaction mixture at 0 °C. The reaction was allowed to warm to room temperature and continued for overnight. The resulting mixture was poured to ice water and the organic phase was collected and dried over $NaSO_4$, the filtrate was evaporated under vacuum and the crude product was purified by flash column chromatography to get the product. (2.04 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 3.9 Hz, 2H), 7.61 (d, J = 8.6 Hz, 4H), 7.29 (d, J = 3.9 Hz, 2H), 7.18 (d, J = 8.5 Hz, 4H), 7.13 (d, J = 8.7 Hz, 2H), 2.571 (s, 6H, overlapped), 2.566 (s, 3H, overlapped). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 190.6, 152.0, 151.0, 147.0, 143.0, 133.7, 131.6, 130.2, 129.5, 127.6, 125.6, 123.7, 122.0, 26.6, 26.4. HRMS (ESI) m/z calcd for $C_{32}H_{26}NO_3S_2^+$ $[M + H]^+$ 536.1349, found 536.1350.

Bis[4-(5-carboxy-2-thienyl)phenyl](4-carboxyphenyl)amine (H_3BCTA, 2)



Br_2 (1.7 mL, 33.18 mmol) was added dropwise to the solution of NaOH (3.9 g, 97.51 mmol) in water (16 mL) on ice bath, the mixture was further stirred for 20 min, then it was transferred to a constant pressure funnel and added dropwise to a solution of 1,1'-((((4-acetylphenyl)azanediyl)bis(4,1-phenylene))bis(thiophene-5,2-diyl))bis(ethan-1-one) (1.61 g, 3.00 mmol) in 1,4-dioxane (30 mL), the reaction mixture was heated at 45 °C for 5 h, after that it was put on ice bath and saturated hydroxylamine HCl was added to deoxidize the excessive sodium hypobromite. The solution was acidified by diluted hydrochloric acid and the solid product was filtered, the crude product was recrystallized from acetic acid to afford pure product as yellow powder. (1.48 g, 91%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.32 (br s, 3H), 7.87 (d, J = 8.6 Hz, 2H), 7.75 (d, J = 8.5 Hz, 4H), 7.70 (d, J = 3.8 Hz, 2H), 7.53 (d, J = 3.8 Hz, 2H), 7.17 (d, J = 8.5 Hz, 4H), 7.09 (d, J = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 166.8, 162.8, 150.2, 149.3, 146.4, 134.4, 132.8, 131.0, 128.7, 127.4, 125.4, 124.4, 124.2, 121.6. FTIR (KBr pellet; cm^{-1}): 3269, 2675, 2549, 1677, 1594, 1536, 1508, 1448, 1320, 1275, 1178, 1104, 810, 752 cm^{-1}. HRMS (ESI) m/z calcd for $C_{29}H_{18}NO_6S_2^-$ $[M - H]^-$ 540.0581, found 540.0579.

Mono[4-(5-carboxy-2-thienyl)phenyl]bis(4-carboxyphenyl)amine (H_3MCTA, 1) was prepared in a similar protocol as H_3**BCTA**, the yellow powder like product was obtained in a yield of 86 % (1.18 g). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.84 (br s, 3H), 7.89 (d, J = 8.8 Hz, 4H), 7.76 (d, J = 8.7 Hz, 2H), 7.72 (d, J = 3.9 Hz, 1H), 7.55 (d, J = 3.9 Hz, 1H), 7.18 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 8.8 Hz, 4H). ^{13}C NMR (101 MHz, DMSO) δ 166.8, 162.8, 150.0, 149.2, 146.2, 134.5, 133.0, 131.1, 129.2, 127.5, 126.0, 125.3, 124.4, 122.9. FTIR (KBr pellet; cm^{-1}): 2964, 2659, 2539, 1690, 1672, 1613, 1593, 1536, 1508, 1450, 1413, 1316, 1281, 1175, 1106, 772 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{25}H_{16}NO_6S^-$ $[M - H]^-$ 458.0704, found 458.0701.

Tris[4-(5-carboxy-2-thienyl)phenyl]amine (H_3TCTA, 3) was prepared was prepared in a similar protocol as H_3**BCTA**, the yellow powder was obtained as the product in a yield of 88 % (1.64 g). The NMR spectrum of **3** were in compliance with the reported data.[3,4] ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.10 (br s, 3H), 7.74–7.70 (m, 9H), 7.51 (d, J = 3.9 Hz, 3H), 7.15 (d, J = 8.7 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.8, 149.4, 146.7, 134.4, 132.6, 128.0, 127.3, 124.4, 123.9.

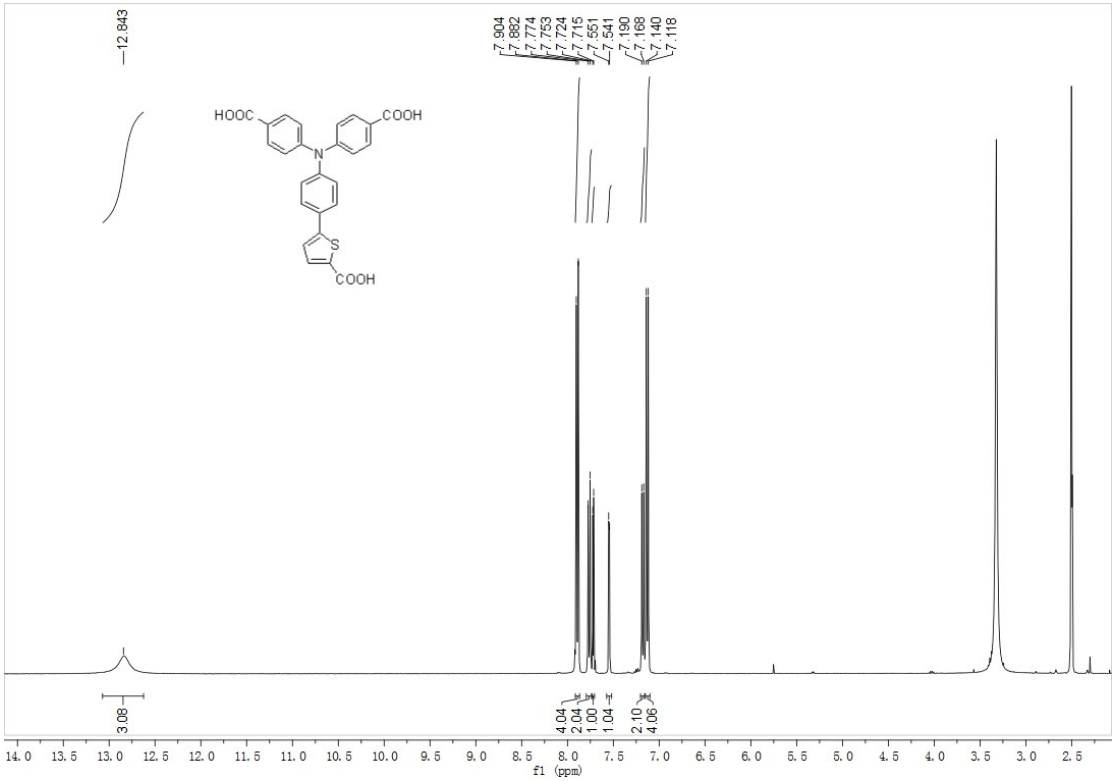


Figure S.1. ^{1}H NMR spectra of H_3**MCTA**, **1**.

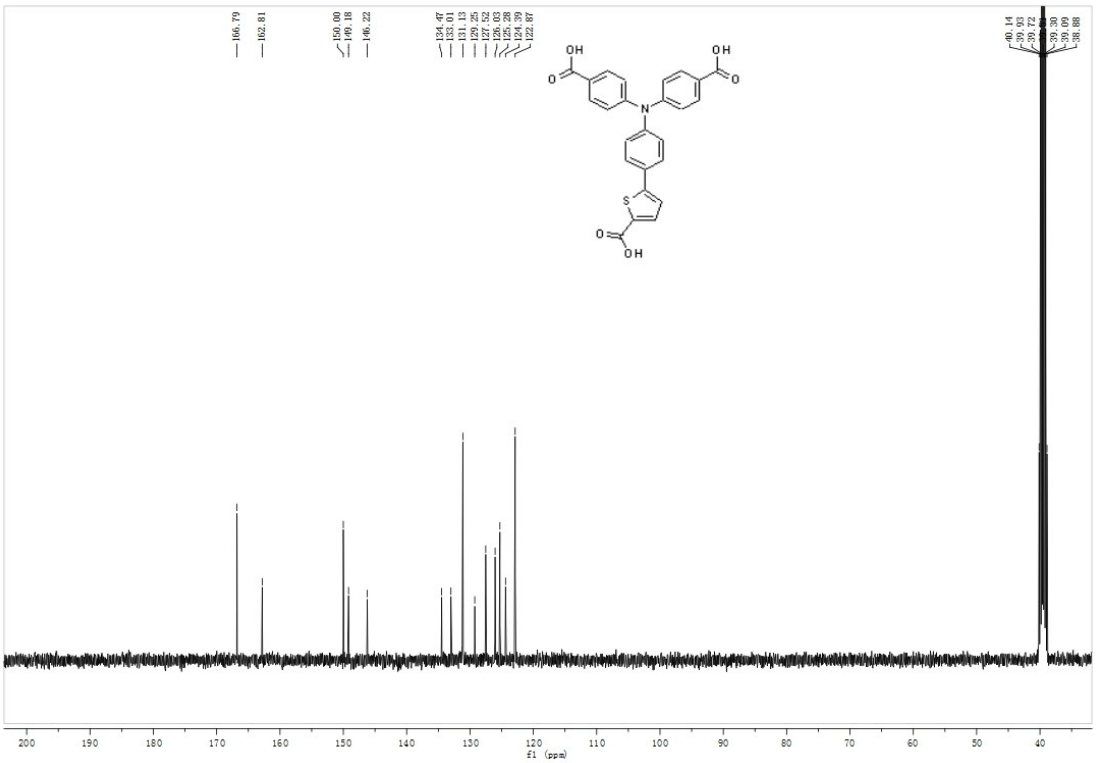


Figure S.2. ^{13}C NMR spectra of H_3**MCTA**, **1**.

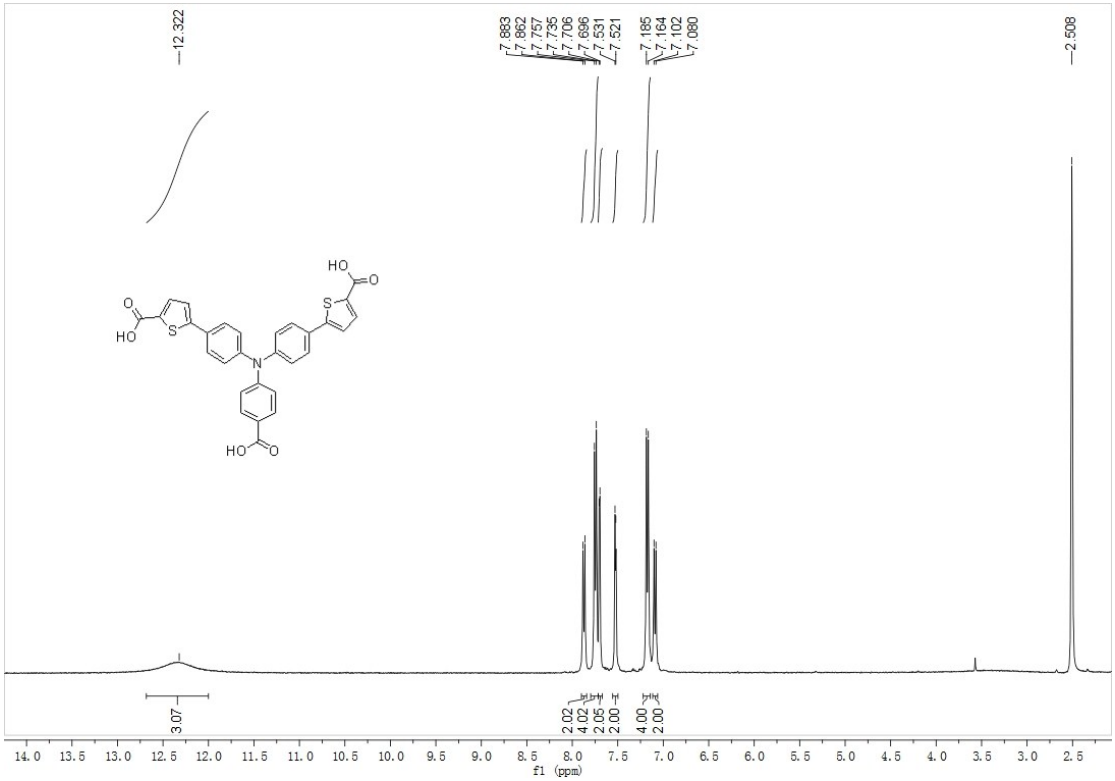


Figure S.3. ^{1}H NMR spectra of H_3**BCTA**, **2**.

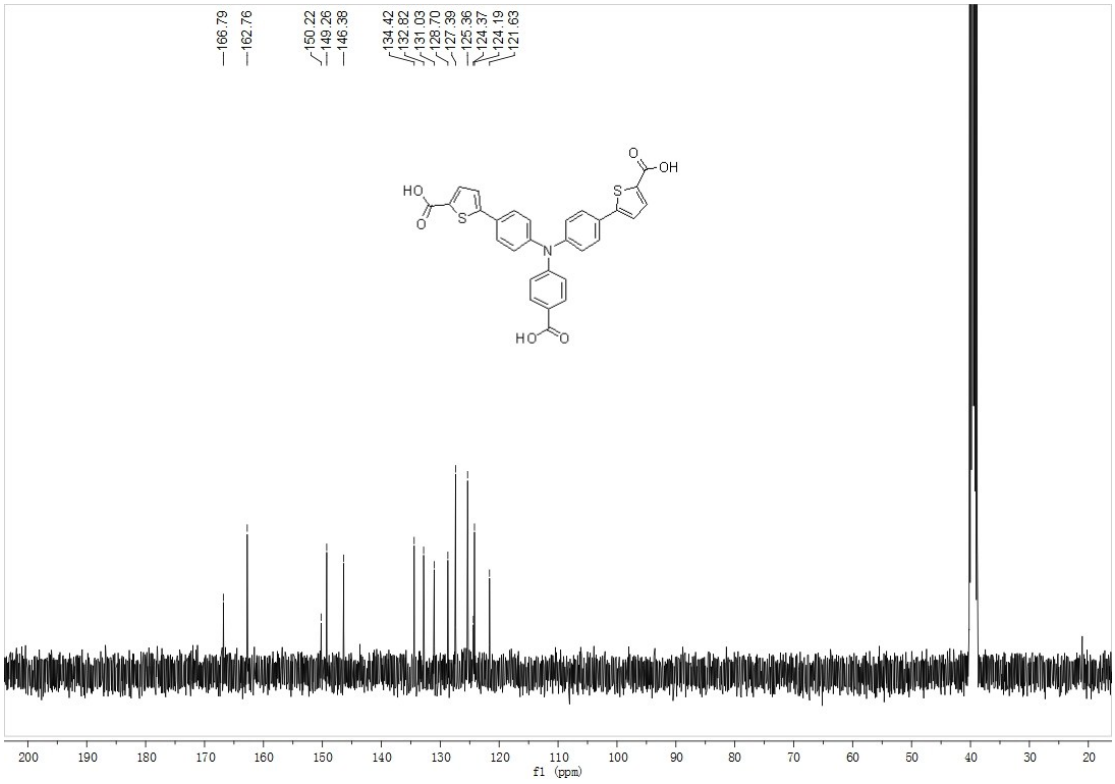


Figure S.4. ^{13}C NMR spectra of H_3**BCTA**, **2**.

Structures of Catalyst

Table S.1. Crystal data and structure refinement for Zn-**BCTA**.

Empirical formula	$C_{64}H_{46}N_4O_{15}S_4Zn_4$	
Formula weight	1500.77	
Temperature	220(2) K	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 32.7017(17) Å	α = 90°
	b = 54.218(3) Å	β = 132.2510(10)°
	c = 23.843(2) Å	γ = 90°
Volume	31292(4) Å^3	
Z	8	
Density (calculated)	0.637 g/cm^3	
Absorption coefficient	0.688 mm^{-1}	
F(000)	6096	
Reflections collected	431251	
Independent reflections	27556	
$R_{(int)}$	0.0717	
Data/restraints/parameters	27556 / 108 / 823	
Goodness-of-fit on F2	1.018	
R_1[a] [I>2σ(I)]	0.0473	
wR_2[b] [I>2σ(I)]	0.1302	
R_1[a] (all data)	0.0878	
wR_2[b] (all data)	0.1438	
Largest diff. peak and hole	0.344 and -0.235 e.Å^{-3}	
CCDC number	1861320	

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$

[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

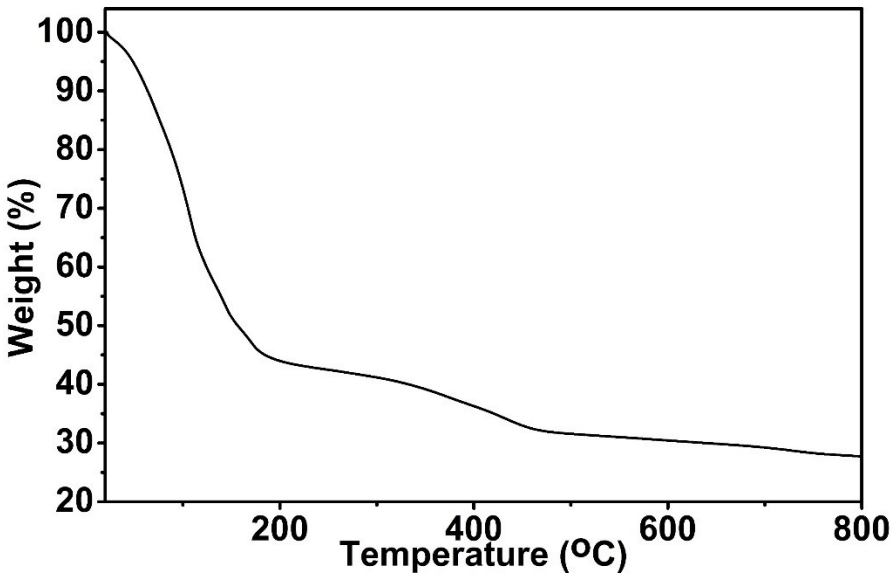


Figure S.5. Thermogravimetric analysis (TGA) curve of Zn-**BCTA** in the flowing N_2 atmosphere.

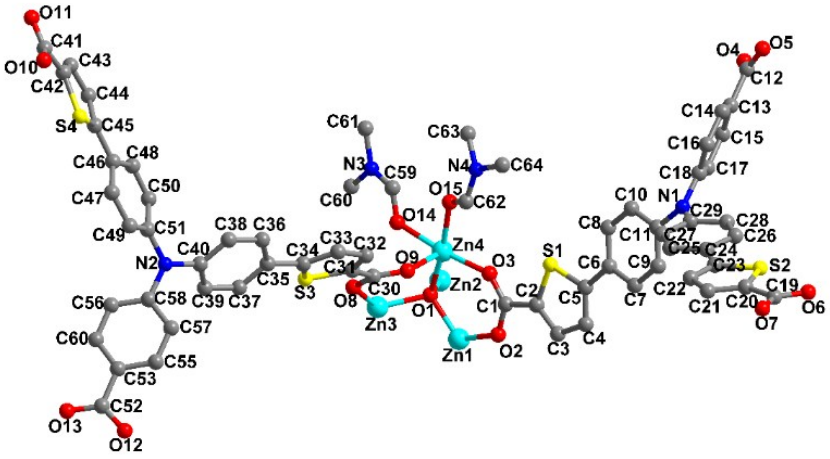


Figure S.6. Ball-and-stick representation of Zn-**BCTA** in an asymmetric unit with atomic-numbering scheme. Hydrogen atoms are omitted for clarity.

Selective bond distance (Å): Zn1−O1 1.9197(16), Zn1−O2 1.9423(18), Zn1−O12$^{\#4}$ 1.945(2), Zn1−O10$^{\#3}$ 1.950(2), Zn2−O1 1.9161(16), Zn2−O4$^{\#1}$ 1.9301(18), Zn2−O11$^{\#3}$ 1.966(2), Zn2−O6$^{\#2}$ 1.9675(19), Zn3−O1 1.9262(16), Zn3−O7$^{\#2}$ 1.9588(18), Zn3−O8 1.9551(19), Zn3−O13$^{\#4}$ 1.971(2), Zn4−O1 2.0267(16), Zn4−O3 2.0854(19), Zn4−O5$^{\#1}$ 2.103(2), Zn4−O9 2.1034(19), Zn4−O14 2.1725(19), Zn4−O15 2.0980(19).

Selective angles (°): O1−Zn1−O2 118.05(8), O1−Zn1−O12$^{\#4}$ 112.64(8), O2−Zn1−O12$^{\#4}$ 103.69(9), O1−Zn1−O10$^{\#3}$ 112.14(8), O2−Zn1−O10$^{\#3}$ 105.33(9), O12−Zn1−O10$^{\#3}$ 103.64(9), Zn2−O1−Zn1 109.57(7), Zn2−O1−Zn3 109.53(7), Zn1−O1−Zn3 108.15(9), Zn2−O1−Zn4 108.87(8), Zn1−O1−Zn4 112.10(7), Zn3−O1−Zn4 108.59(7), O1−Zn2−O4$^{\#1}$ 123.07(8), O1−Zn2−O11$^{\#3}$ 111.70(8), O4$^{\#1}$−Zn2−O11$^{\#3}$ 104.00(9), O1−Zn2−O6$^{\#2}$ 109.71(8), O4$^{\#1}$−Zn2−O6$^{\#2}$ 100.68(8), O11$^{\#3}$−Zn2−O6$^{\#2}$ 106.10(9), C1−O2−Zn1 122.95(18), O1−Zn3−O8 115.61(7), O1−Zn3−O7$^{\#2}$ 114.05(8), O8−Zn3−O7$^{\#2}$ 109.17(8), O1−Zn3−O13$^{\#4}$ 111.82(8), O8−Zn3−O13$^{\#4}$ 98.13(9), O7$^{\#2}$−Zn3−O13$^{\#4}$ 106.62(9), C1−O3−Zn4 140.37(18), O1−Zn4−O3 99.16(7), O1−Zn4−O15 172.63(7), O3−Zn4−O15 88.17(8), O1−Zn4−O5$^{\#1}$ 94.51(7), O3−Zn4−O5$^{\#1}$ 88.78(8), O15−Zn4−O5$^{\#1}$ 84.79(8), O1−Zn4−O9 93.49(8), O3−Zn4−O9 90.47(8), O15−Zn4−O9 87.22(8), O5$^{\#1}$−Zn4−O9 171.99(8), O1−Zn4−O14 85.16(7), O3−Zn4−O14 173.73(8), O15−Zn4−O14 87.48(8), O5$^{\#1}$−Zn4−O14 86.34(8), O9−Zn4−O14 93.82(8), C12$^{\#1}$−O4$^{\#1}$−Zn2 116.38(18), C12$^{\#1}$−O5$^{\#1}$−Zn4 135.70(18), C19$^{\#2}$−O6$^{\#2}$−Zn2 132.70(18), C19$^{\#2}$−O7$^{\#2}$−Zn3 126.50(19), C30−O8−Zn3 120.10(18), C30−O9−Zn4 130.91(18), C41$^{\#3}$−O10$^{\#3}$−Zn1 129.2(2), C41$^{\#3}$−O11$^{\#3}$−Zn2 129.3(2), C52$^{\#4}$−O12$^{\#4}$−Zn1 129.9(2), C52$^{\#4}$−O13$^{\#4}$−Zn3 129.3(2), C59−O14−Zn4 123.5(2), C62−O15−Zn4 123.1(2).

Symmetry code: #1 0.5+*x*, 0.5-*y*, 0.5+*z*; #2 1+*x*, *y*, 1+*z*; #3 *x*, *y*, 1+*z*; #4 *x*, -*y*, 0.5+*z*

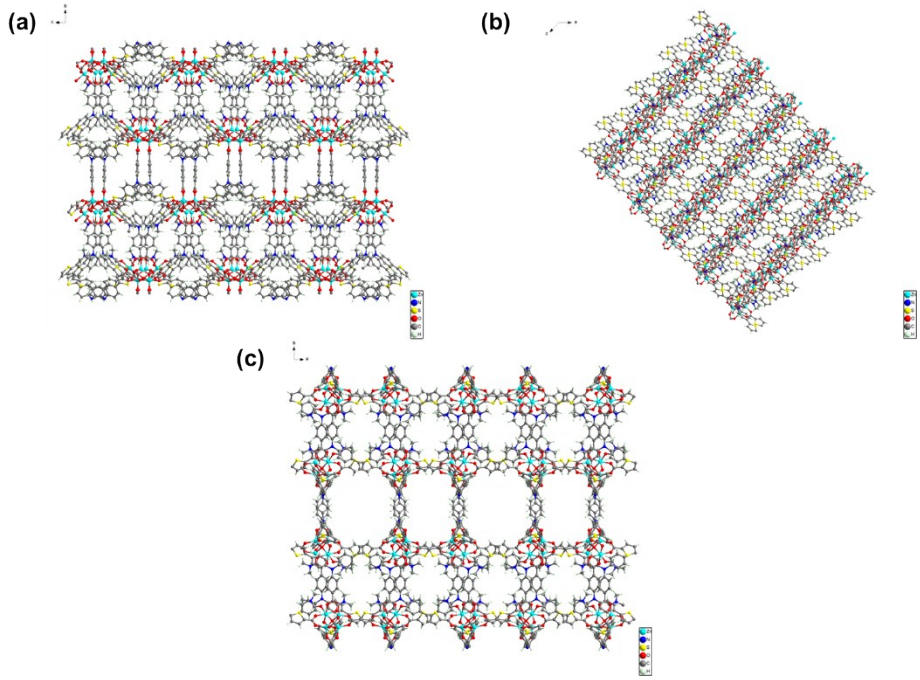


Figure S.7. View of the crystal packing of Zn-**BCTA** along (a) the *a* direction; (b) the *b* direction; (c) the *c* direction.

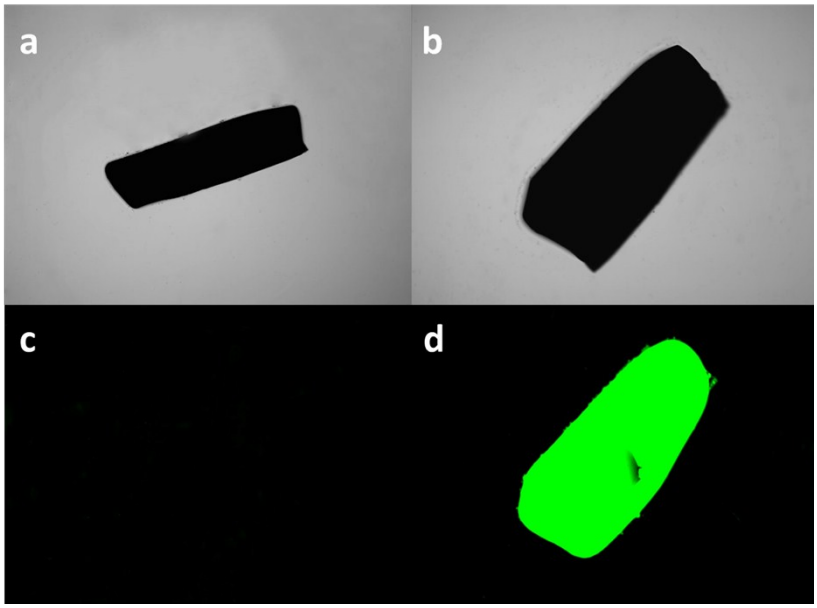
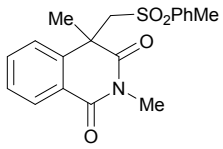


Figure S.8. Confocal images of empty MOF Zn-**BCTA** crystals (a and c) and the ones soaked with methylene blue (b and d). Brightfield images (a and b) and confocal images (c and d).

NMR Data of Photocatalytic Products

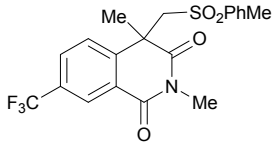
2,4-Dimethyl-4-(tosylmethyl)isoquinoline-1,3(2*H*,4*H*)-dione[5]



3a

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as white solid (76 mg, 85% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 – 8.26 (m, 1H), 7.45 – 7.40 (m, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.19 (m, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 4.44 (d, *J* = 14.6 Hz, 1H), 3.87 (d, *J* = 14.6 Hz, 1H), 3.39 (s, 3H), 2.39 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 164.0, 144.7, 139.4, 137.4, 133.6, 129.9, 129.5, 128.3, 127.9, 126.1, 125.0, 65.02, 45.61, 31.88, 27.73, 21.77.

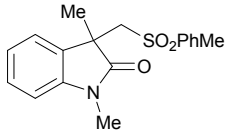
2,4-Dimethyl-4-(tosylmethyl)-7-(trifluoromethyl)isoquinoline-1,3(2*H*,4*H*)-dione



3b

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as sticky oil (89 mg, 84% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 4.47 (d, *J* = 14.7 Hz, 1H), 3.89 (d, *J* = 14.7 Hz, 1H), 3.44 (s, 3H), 2.38 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 162.8, 145.0, 142.8, 137.1, 130.9 (q, *J* = 33.5 Hz), 130.0, 129.6 (q, *J* = 3.1 Hz), 127.6, 127.0, 126.7 (q, *J* = 3.7 Hz), 125.8, 123.5 (q, *J* = 272.8 Hz), 64.9, 45.6, 31.4, 28.0, 21.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.0 (s). HRMS (ESI) *m/z* calcd for $C_{20}H_{18}F_3NNaO_4S^+$ $[M + Na]^+$ 448.0801, found 448.0805.

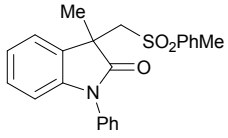
1,3-Dimethyl-3-(tosylmethyl)indolin-2-one[6]



3c

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as sticky oil (75 mg, 91% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.29 (td, *J* = 7.8, 1.0 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.3 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.85 (d, *J* = 14.5 Hz, 1H), 3.65 (d, *J* = 14.5 Hz, 1H), 3.16 (s, 3H), 2.40 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 144.5, 143.4, 137.2, 129.8, 129.6, 128.7, 128.0, 124.3, 122.6, 108.5, 62.1, 45.8, 26.7, 25.6, 21.7.

3-Methyl-1-phenyl-3-(tosylmethyl)indolin-2-one[6]

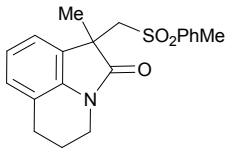


3d

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as white solid (64 mg, 66% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 4H), 7.43 – 7.41 (m, 3H), 7.21 – 7.16 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.01 (dd, *J* = 7.5, 0.8 Hz, 1H), 6.87 (td, *J* = 7.5, 0.9 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 3.97 (d, *J* = 14.5 Hz, 1H), 3.75 (d, *J* = 14.5 Hz, 1H), 2.37 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.5, 144.4, 143.7, 137.4, 134.6,

129.73 (partially overlapped), 129.70 (partially overlapped), 129.4, 128.5, 128.3, 127.8, 126.9, 124.1, 122.9, 109.8, 62.5, 45.9, 25.9, 21.7.

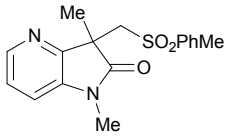
1-Methyl-1-(tosylmethyl)-5,6-dihydro-1*H*-pyrrolo[3,2,1-*ij*]quinolin-2(4*H*)-one[6]



3e

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as sticky oil (70 mg, 79% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.03 (dd, J = 7.7, 0.6 Hz, 1H), 6.98 (d, J = 7.4 Hz, 1H), 6.84 (t, J = 7.6 Hz, 1H), 3.81 (d, J = 14.5 Hz, 1H), 3.74 – 3.67 (m, 1H), 3.65 (d, J = 14.4 Hz, 1H), 3.63 – 3.58 (m, 1H), 2.84 – 2.72 (m, 2H), 2.40 (s, 3H), 2.09 – 1.93 (m, 2H), 1.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.7, 144.5, 139.2, 137.5, 129.7, 128.6, 128.1, 127.5, 122.3, 122.2, 120.6, 62.1, 47.1, 39.3, 25.3, 24.8, 21.8, 21.2.

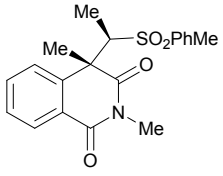
1,3-Dimethyl-3-(tosylmethyl)-1*H*-pyrrolo[3,2-*b*]pyridin-2(3*H*)-one



3f

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as sticky oil (71 mg, 86% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 5.0, 1.3 Hz, 1H), 7.40 (d, J = 8.3 Hz, 2H), 7.21 – 7.15 (m, 3H), 7.11 (dd, J = 7.9, 1.3 Hz, 1H), 3.93 (d, J = 14.3 Hz, 1H), 3.87 (d, J = 14.4 Hz, 1H), 3.29 (s, 3H), 2.40 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5, 151.3, 144.5, 142.9, 139.1, 137.4, 129.8, 127.8, 123.4, 114.7, 61.5, 46.0, 26.6, 23.7, 21.8. HRMS (ESI) *m/z* calcd for $C_{17}H_{19}N_2O_3S^+$ $[M + H]^+$ 331.1111, found 331.1113.

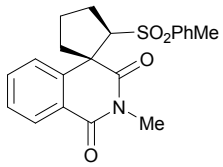
2,4-Dimethyl-4-(1-tosylethyl)isoquinoline-1,3(2*H*,4*H*)-dione



3g

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as sticky oil (59 mg, 63% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, J = 7.8, 1.0 Hz, 1H), 7.52 (td, J = 8.0, 1.4 Hz, 1H), 7.47 (d, J = 7.3 Hz, 1H), 7.43 (d, J = 8.2 Hz, 2H), 7.43 – 7.40 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 3.84 (q, J = 7.2 Hz, 1H), 3.41 (s, 3H), 2.39 (s, 3H), 1.82 (s, 3H), 1.52 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 164.2, 144.6, 141.6, 136.7, 133.6, 129.8, 129.2, 128.3, 128.1, 126.4, 125.5, 69.8, 48.1, 28.2, 27.7, 21.7, 12.4. HRMS (ESI) *m/z* calcd for $C_{20}H_{22}NO_4S^+$ $[M + H]^+$ 372.1264, found 372.1269.

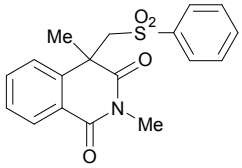
2'-Methyl-2-tosyl-1'*H*-spiro[cyclopentane-1,4'-isoquinoline]-1',3'(2'*H*)-dione



3h

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as sticky oil (58 mg, 61% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, J = 7.9, 1.3 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.36 (d, J = 8.3 Hz, 2H, overlapped), 7.38 – 7.32 (m, 1H, overlapped), 7.28 (d, J = 8.0 Hz, 1H, partially overlapped), 7.09 (d, J = 7.9 Hz, 2H), 3.93 (dd, J = 12.2, 7.3 Hz, 1H), 3.44 (s, 3H), 2.83 (tt, J = 12.4, 9.4 Hz, 1H), 2.69 (ddd, J = 13.9, 8.9, 5.8 Hz, 1H), 2.35 (s, 3H, overlapped), 2.44 – 2.22 (m, 3H, partially overlapped), 2.10 – 1.98 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 164.0, 144.7, 141.8, 136.3, 133.9, 129.8, 128.9, 127.8, 127.6, 125.8, 124.9, 78.5, 54.4, 43.8, 28.0, 27.7, 23.5, 21.7. HRMS (ESI) *m/z* calcd for $C_{21}H_{22}NO_4S^+$ $[M + H]^+$ 384.1264, found 384.1266.

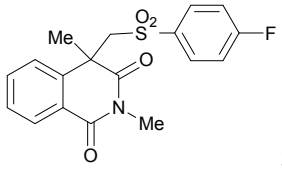
2,4-Dimethyl-4-((phenylsulfonyl)methyl)isoquinoline-1,3(2*H*,4*H*)-dione[5]



3i

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as white solid (70 mg, 82% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.45 (d, J = 7.7 Hz, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.36 - 7.31 (m, 3H), 7.15 (d, J = 7.8 Hz, 1H), 4.45 (d, J = 14.7 Hz, 1H), 3.94 (d, J = 14.7 Hz, 1H), 3.41 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 163.9, 140.2, 139.1, 133.6, 133.5, 129.3, 129.2, 128.2, 127.6, 126.0, 124.8, 64.9, 45.4, 31.6, 27.6.

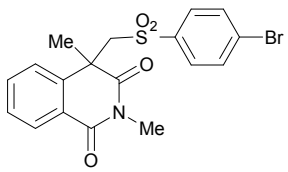
4-(((4-Fluorophenyl)sulfonyl)methyl)-2,4-dimethylisoquinoline-1,3(2*H*,4*H*)-dione[5]



3j

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as white solid (68 mg, 75% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 – 8.27 (m, 1H), 7.52 – 7.47 (m, 2H), 7.46 – 7.39 (m, 2H), 7.20 – 7.15 (m, 1H), 7.07 – 7.00 (m, 2H), 4.46 (d, J = 14.7 Hz, 1H), 3.90 (d, J = 14.7 Hz, 1H), 3.42 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 165.7 (q, J = 256.8 Hz), 163.9, 139.2, 136.49 (q, J = 3.1 Hz), 133.7, 130.7 (q, J = 9.7 Hz), 129.6, 128.4, 125.9, 125.0, 116.5 (q, J = 22.7 Hz), 65.1, 45.6, 31.7, 27.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -103.31 – -103.38 (m).

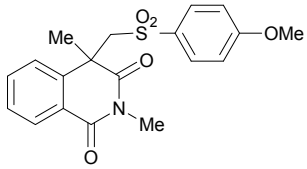
4-(((4-Bromophenyl)sulfonyl)methyl)-2,4-dimethylisoquinoline-1,3(2*H*,4*H*)-dione[5]



3k

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as white solid (86 mg, 82% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 7.7 Hz, 1H), 7.50 (d, J = 8.3 Hz, 2H), 7.45 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.3 Hz, 1H), 7.32 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 7.7 Hz, 1H), 4.45 (d, J = 14.7 Hz, 1H), 3.90 (d, J = 14.7 Hz, 1H), 3.42 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 163.8, 139.3, 139.1, 133.7, 132.6, 129.6, 129.3, 129.0, 128.4, 125.9, 125.0, 65.0, 45.6, 31.7, 27.8.

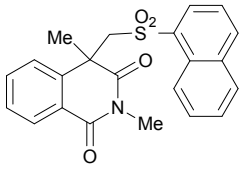
4-(((4-Methoxyphenyl)sulfonyl)methyl)-2,4-dimethylisoquinoline-1,3(2*H*,4*H*)-dione[7]



3l

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as sticky oil (82 mg, 88% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.27 (m, 1H), 7.45 – 7.36 (m, 4H), 7.23 – 7.18 (m, 2H), 6.81 (d, *J* = 8.9 Hz, 1H), 4.43 (d, *J* = 14.6 Hz, 1H), 3.87 (d, *J* = 14.6 Hz, 1H), 3.83 (s, 3H), 3.39 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 164.0, 163.8, 139.4, 133.6, 131.9, 130.0, 129.4, 128.2, 126.1, 125.0, 114.4, 65.2, 55.9, 45.6, 31.8, 27.7.

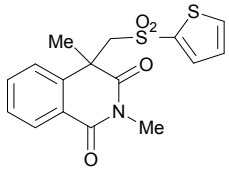
2,4-Dimethyl-4-((naphthalen-1-ylsulfonyl)methyl)isoquinoline-1,3(2*H*,4*H*)-dione



3m

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as sticky oil (83 mg, 84% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.6 Hz, 1H), 8.22 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.94 (t, *J* = 8.2 Hz, 2H), 7.78 – 7.72 (m, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.45 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.97 (td, *J* = 7.8, 1.3 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 4.59 (d, *J* = 14.7 Hz, 1H), 4.11 (d, *J* = 14.6 Hz, 1H), 3.43 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 164.0, 138.9, 135.0, 134.9, 134.1, 133.1, 130.2, 129.5, 129.2, 129.1, 128.3, 128.2, 127.2, 125.5, 124.9, 124.6, 123.9, 64.3, 45.4, 31.5, 27.7. HRMS (ESI) *m/z* calcd for $C_{22}H_{20}NO_4S^+$ $[M + H]^+$ 394.1108, found 394.1104.

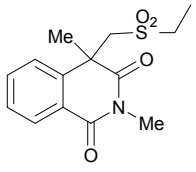
2,4-Dimethyl-4-((thiophen-2-ylsulfonyl)methyl)isoquinoline-1,3(2*H*,4*H*)-dione[8]



3n

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as sticky oil (81 mg, 93% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.25 (m, 1H), 7.57 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.24 – 7.18 (m, 1H), 7.11 (dd, *J* = 3.8, 1.2 Hz, 1H), 6.90 (dd, *J* = 4.8, 3.9 Hz, 1H), 4.56 (d, *J* = 14.7 Hz, 1H), 4.01 (d, *J* = 14.7 Hz, 1H), 3.42 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 163.9, 141.5, 139.2, 134.4, 134.2, 133.6, 129.5, 128.3, 127.9, 125.8, 125.0, 66.3, 45.6, 31.7, 27.7.

4-((Ethylsulfonyl)methyl)-2,4-dimethylisoquinoline-1,3(2*H*,4*H*)-dione



3o

This compound was synthesized according to the general procedure (GP) and isolated by column chromatography as sticky oil (64 mg, 87% yield) using petroleum ether/ethyl acetate (4:1 v:v) as the eluent system. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, J = 7.9, 1.2 Hz, 1H), 7.68 (td, J = 7.6, 1.4 Hz, 1H), 7.51 (m, 2H), 4.27 (d, J = 14.4 Hz, 1H), 3.74 (d, J = 14.4 Hz, 1H), 3.42 (s, 3H), 2.80 – 2.64 (m, 2H), 1.63 (s, 3H), 1.28 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 163.9, 140.1, 133.9, 129.7, 128.4, 125.4, 124.8, 60.6, 50.3, 45.5, 31.5, 27.6, 6.4. HRMS (ESI) *m/z* calcd. for $C_{14}H_{18}NO_4S^+$ $[M + H]^+$ 296.0951, found 296.0952.

NMR Spectrum of Photocatalytic Products

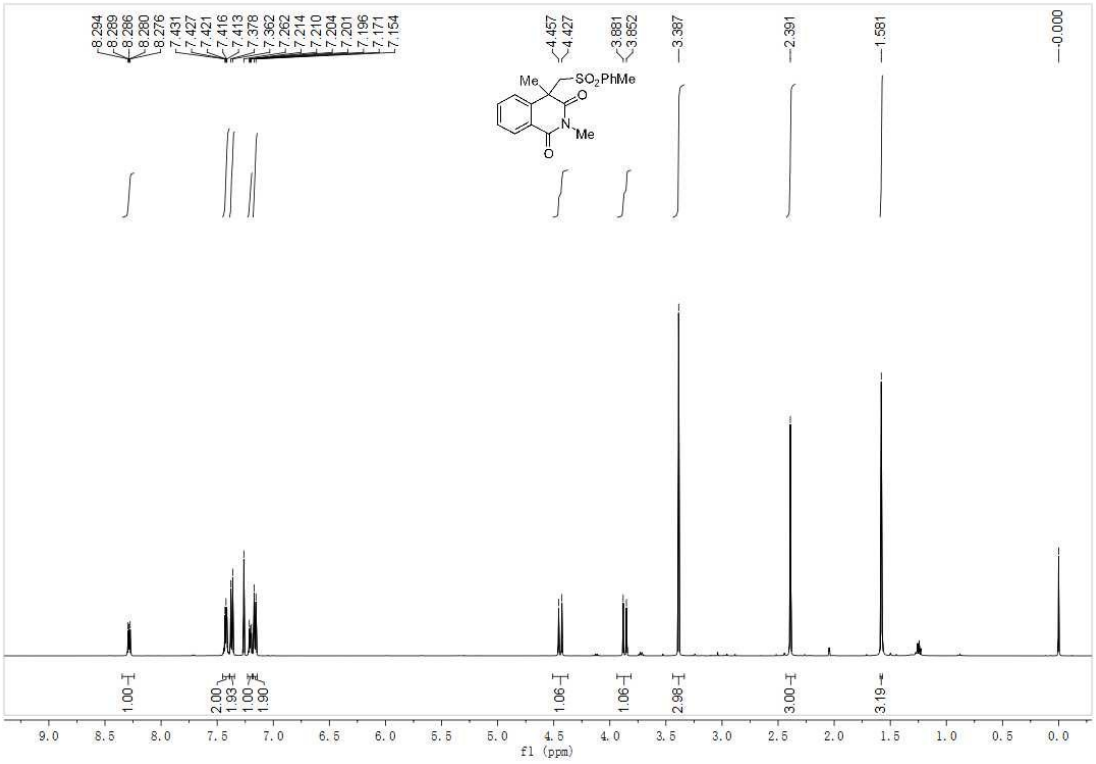


Figure S.9. ^{1}H NMR spectra of **3a**.

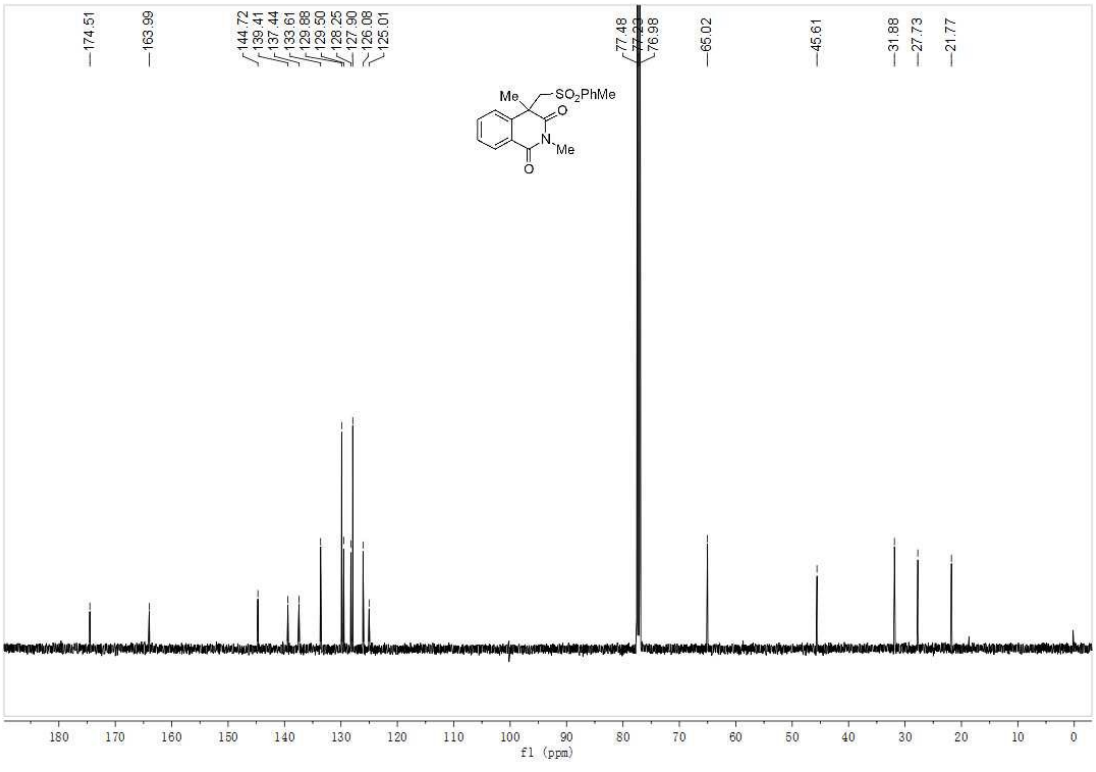


Figure S.10. ^{13}C NMR spectra of **3a**.

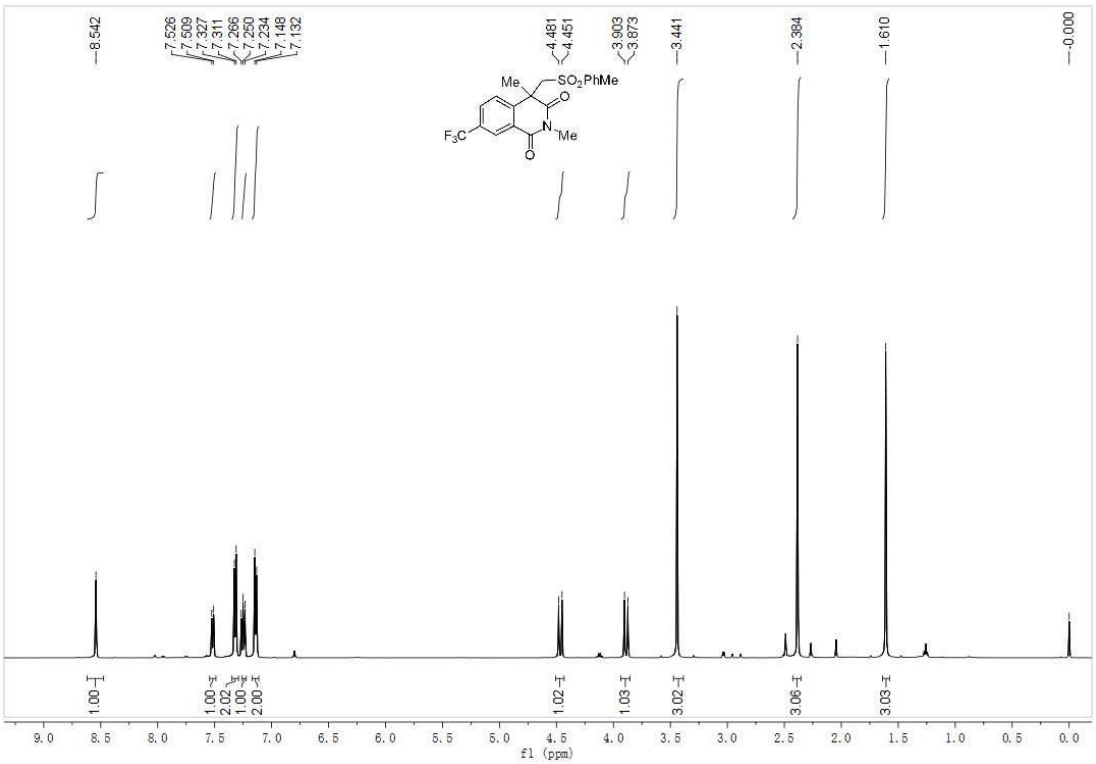


Figure S.11. ^{1}H NMR spectra of **3b**.

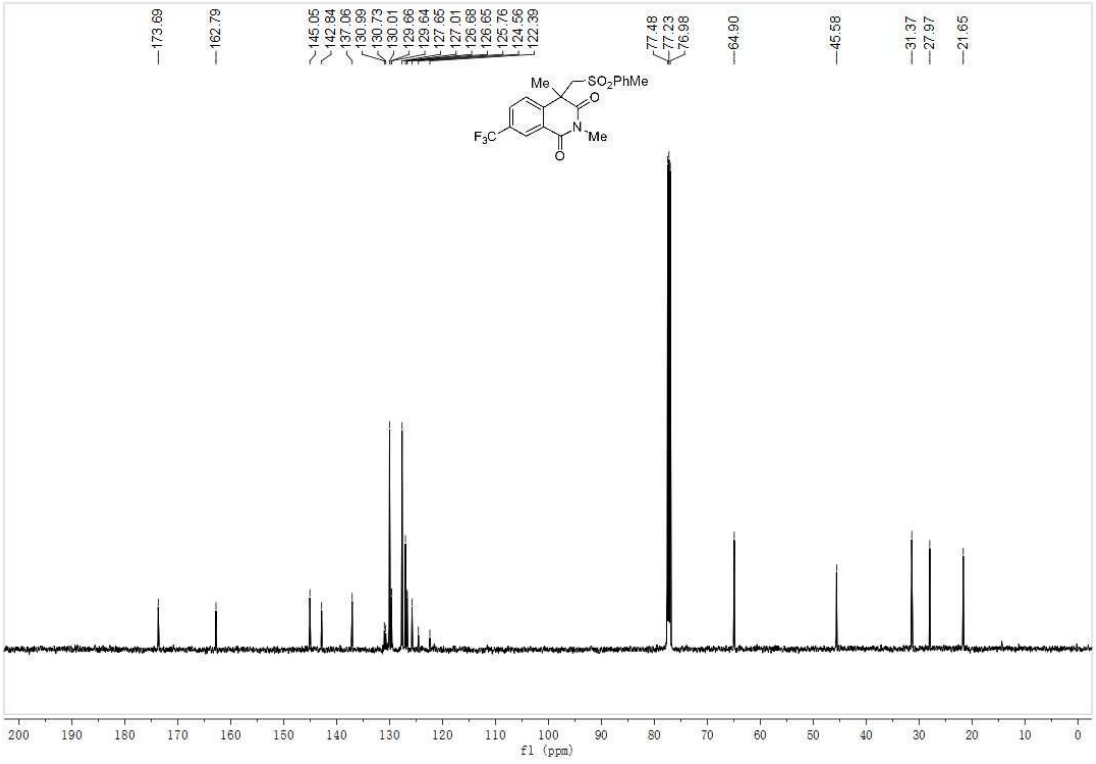


Figure S.12. ^{13}C NMR spectra of **3b**.

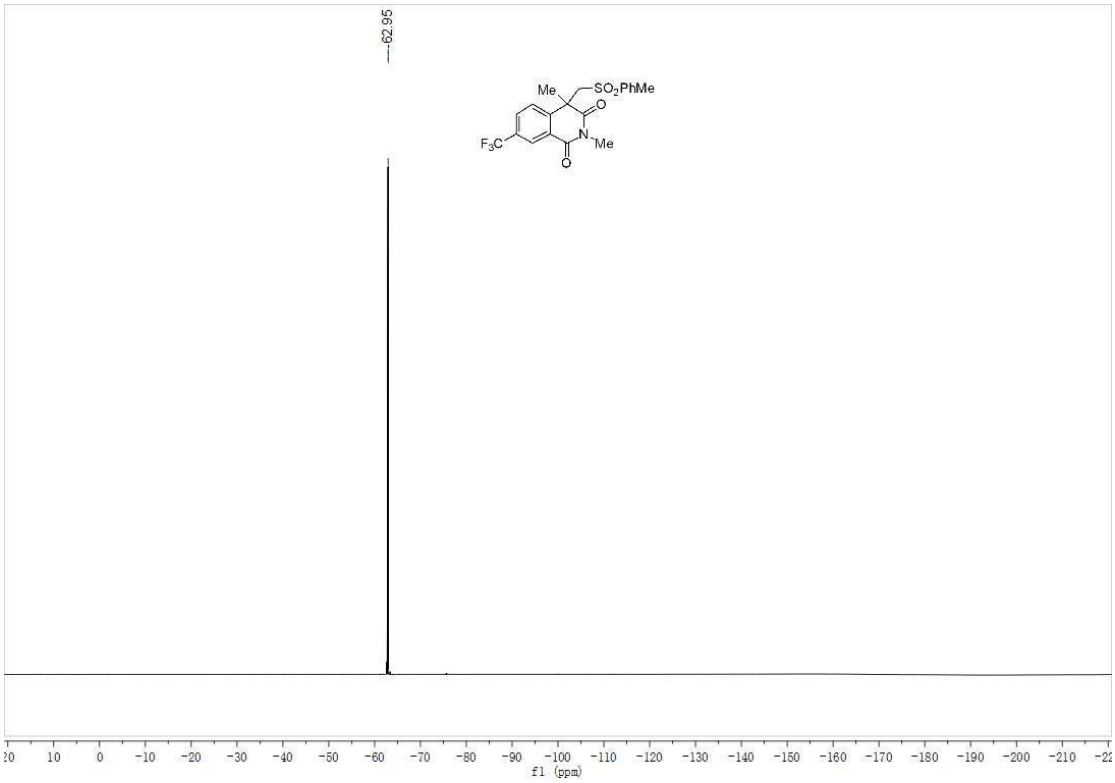


Figure S.13. ^{19}F NMR spectra of **3b**.

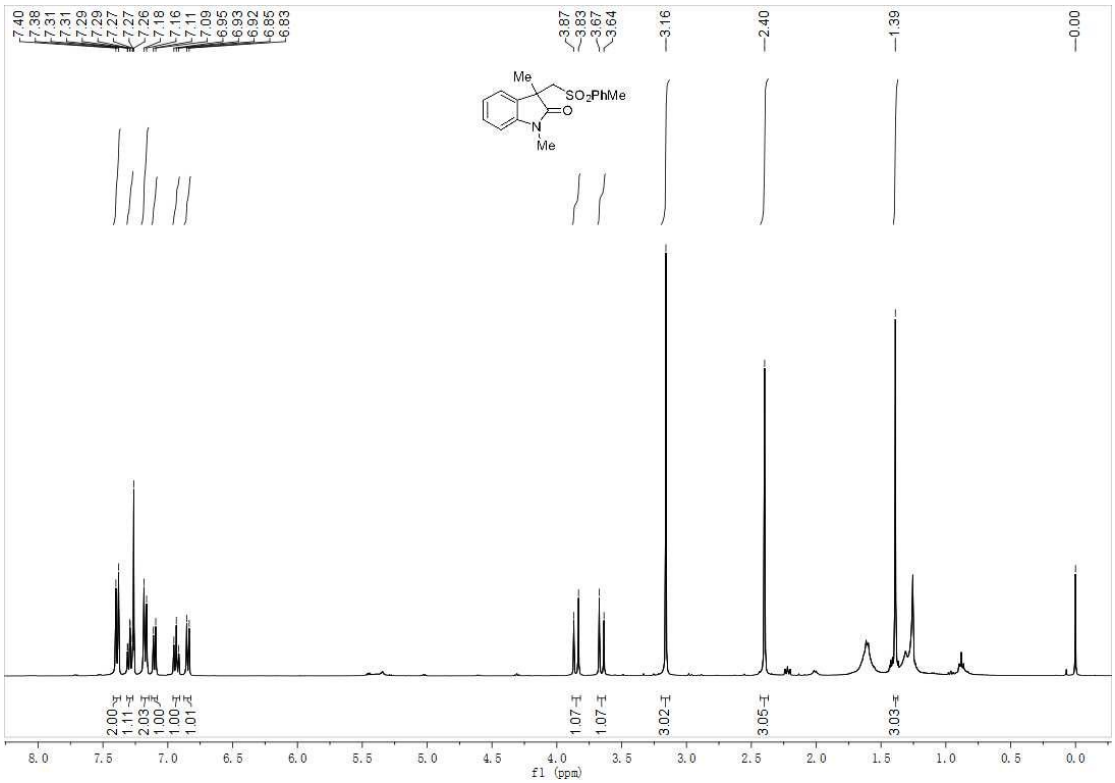


Figure S.14. ^{1}H NMR spectra of **3c**.

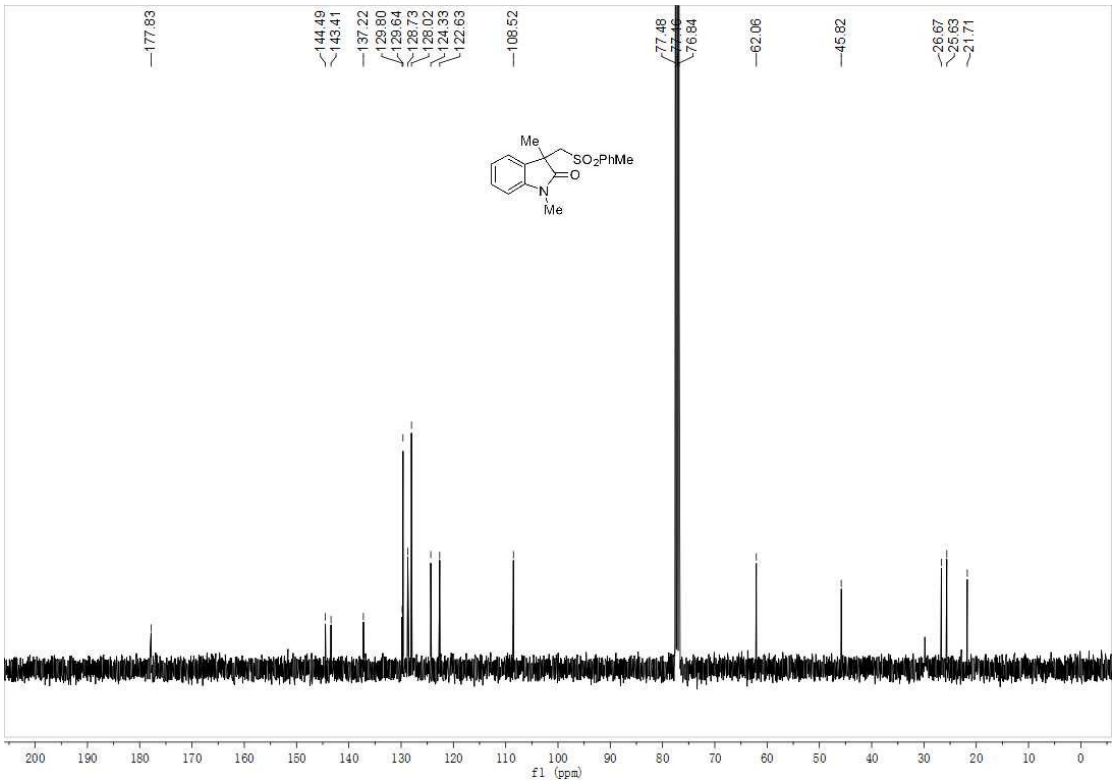


Figure S.15. ^{13}C NMR spectra of **3c**.

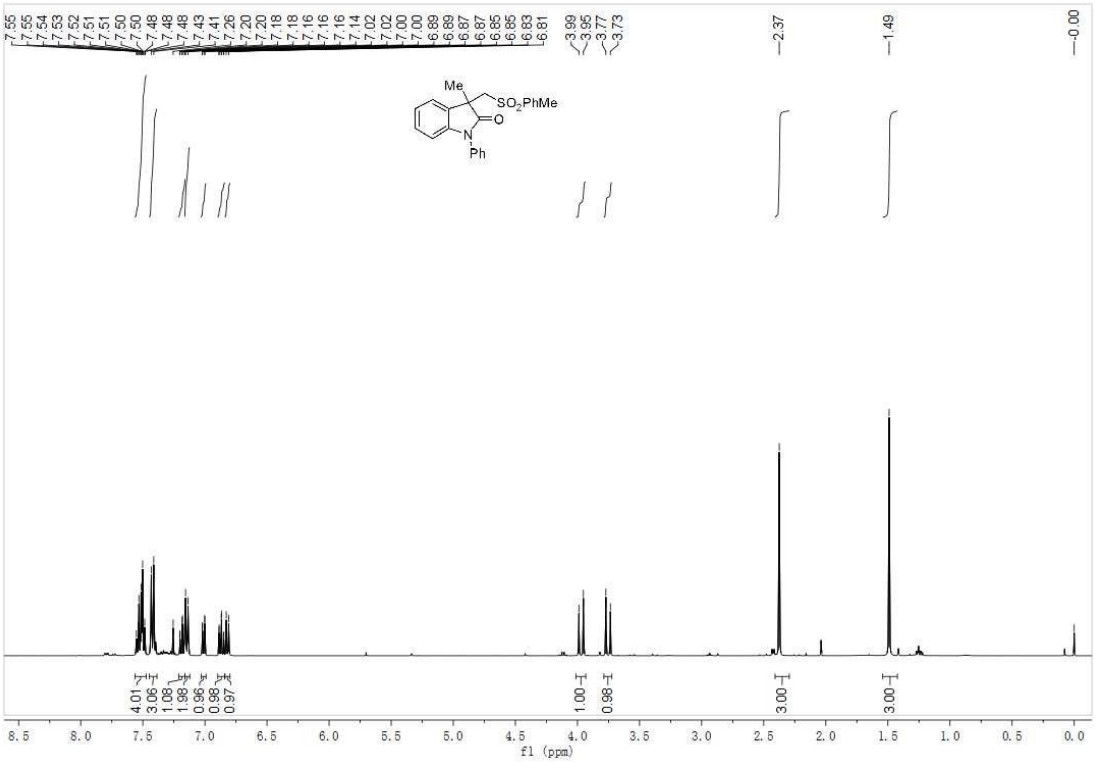


Figure S.16. ^{1}H NMR spectra of **3d**.

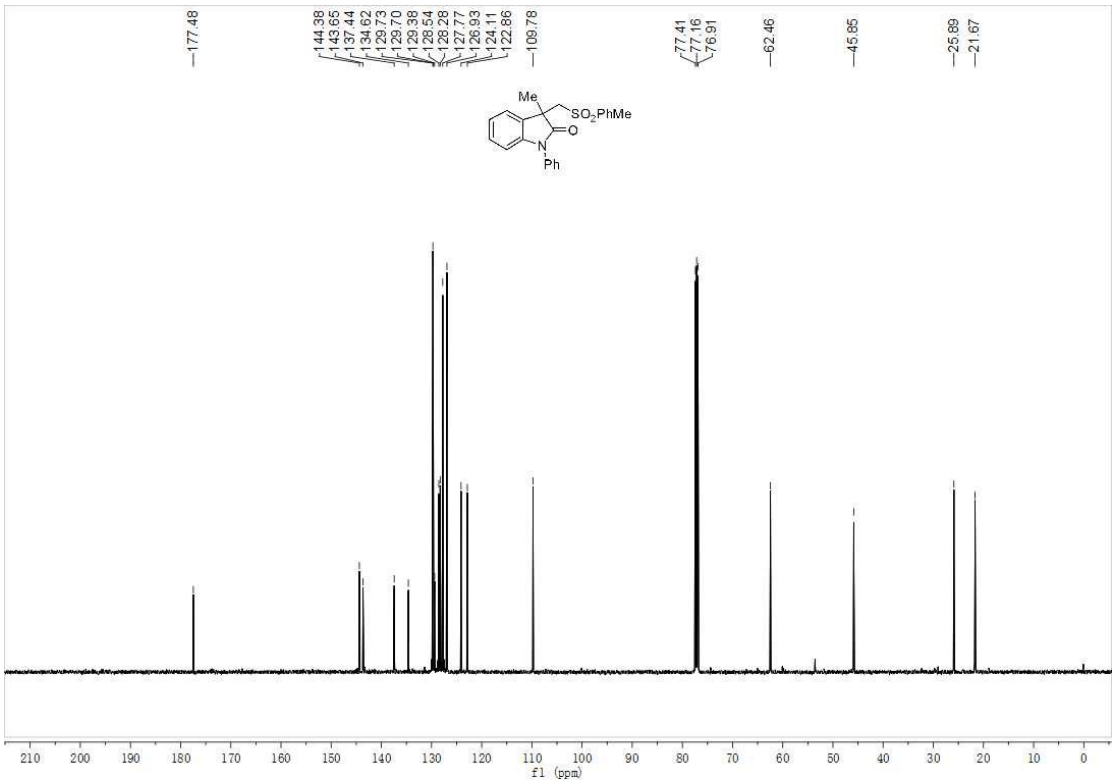


Figure S.17. ^{13}C NMR spectra of **3d**.

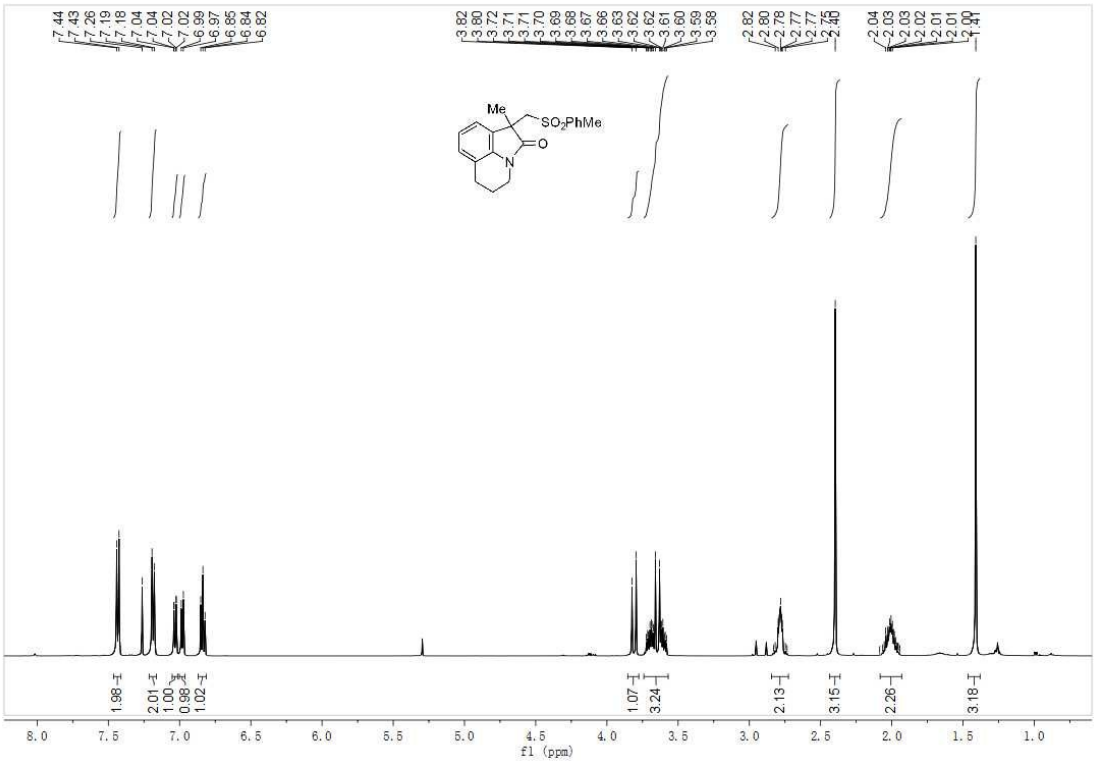


Figure S.18. ^{1}H NMR spectra of **3e**.

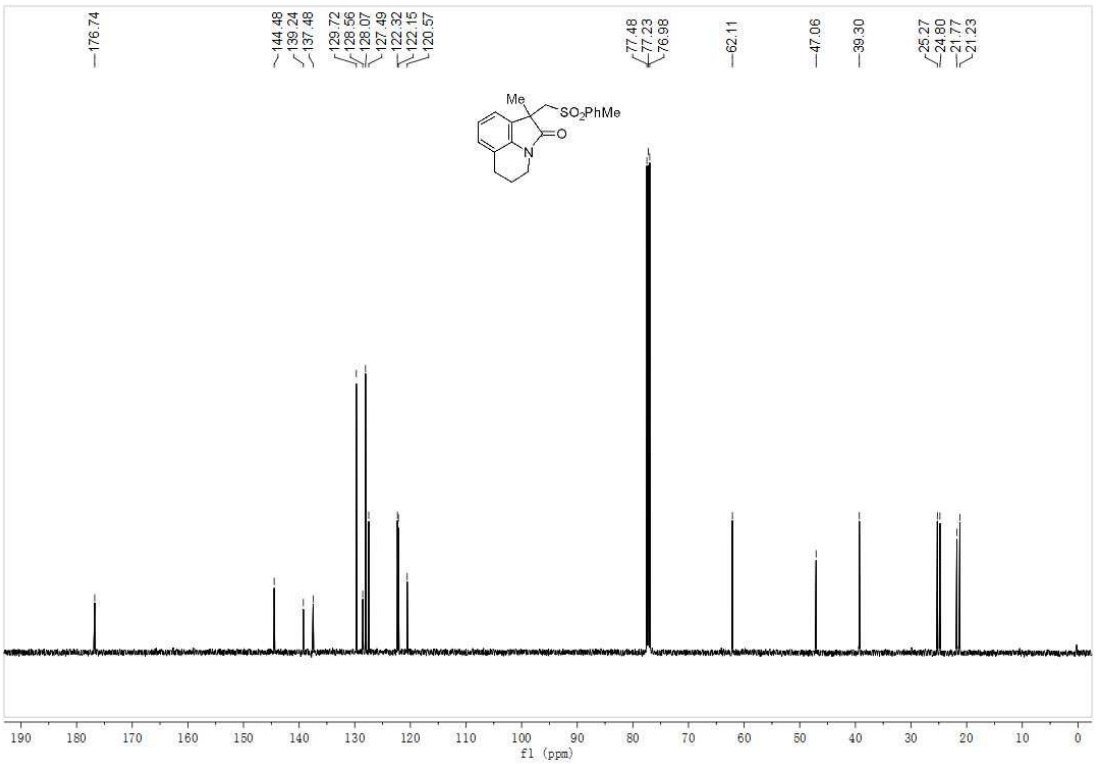


Figure S.19. ^{13}C NMR spectra of **3e**.

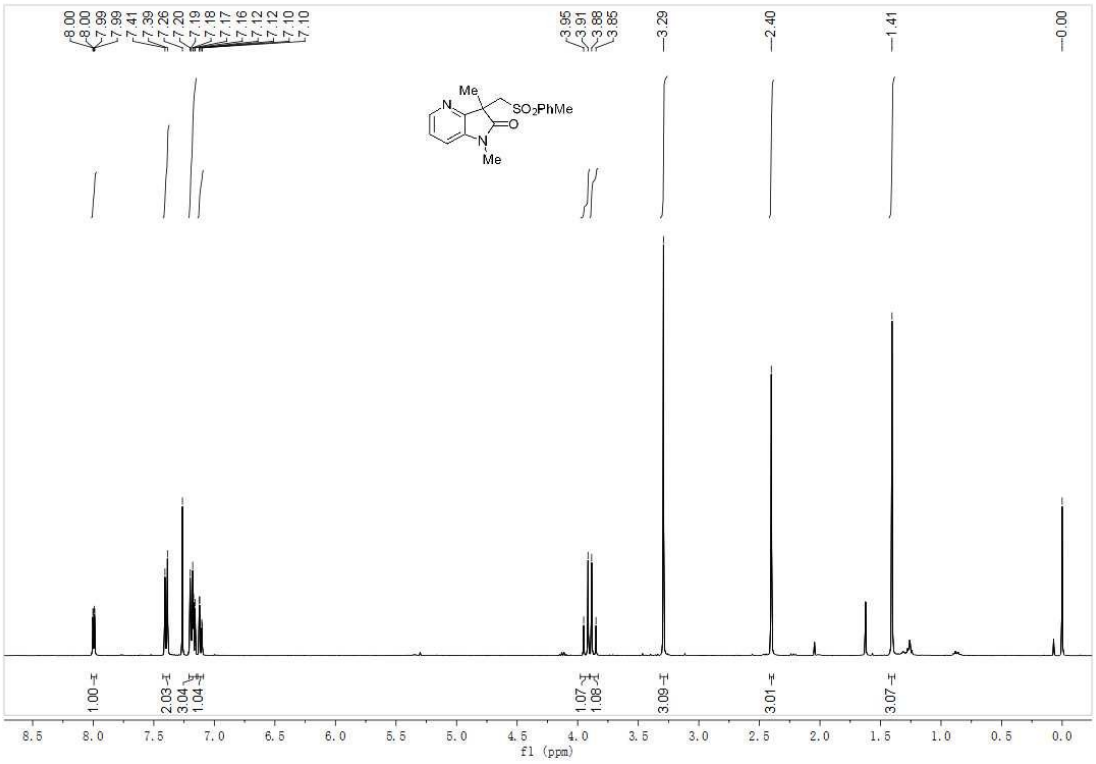


Figure S.20. ^{1}H NMR spectra of **3f**.

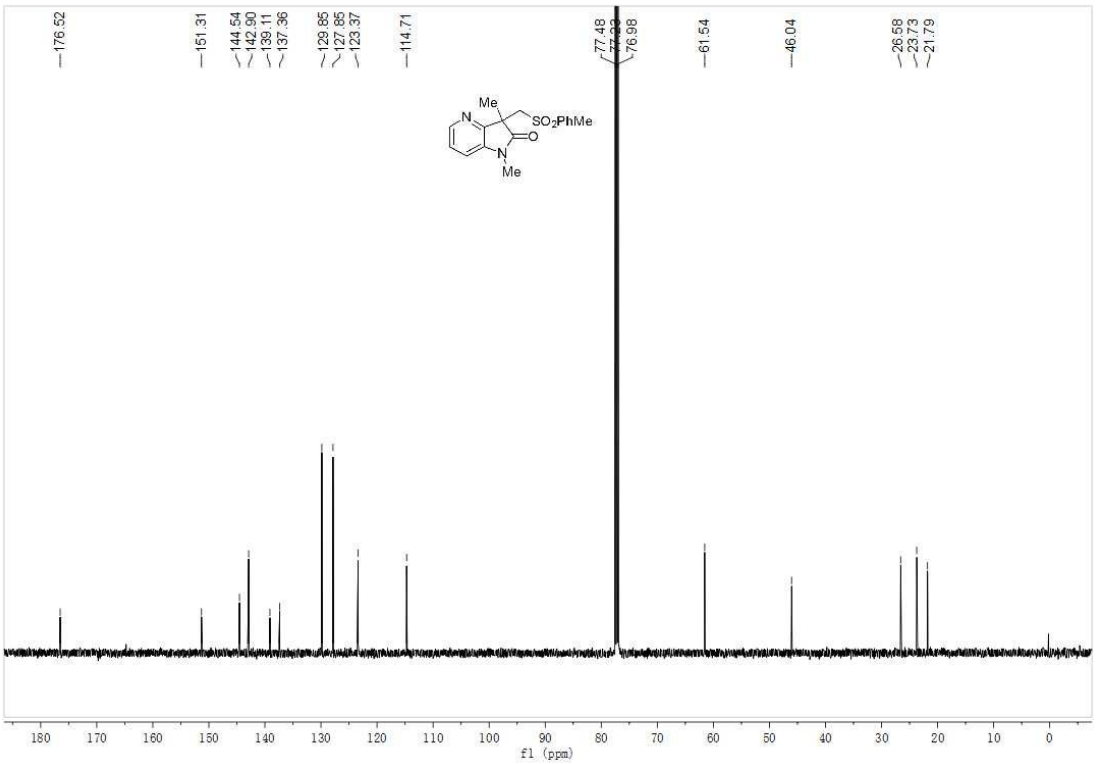


Figure S.21. ^{13}C NMR spectra of **3f**.

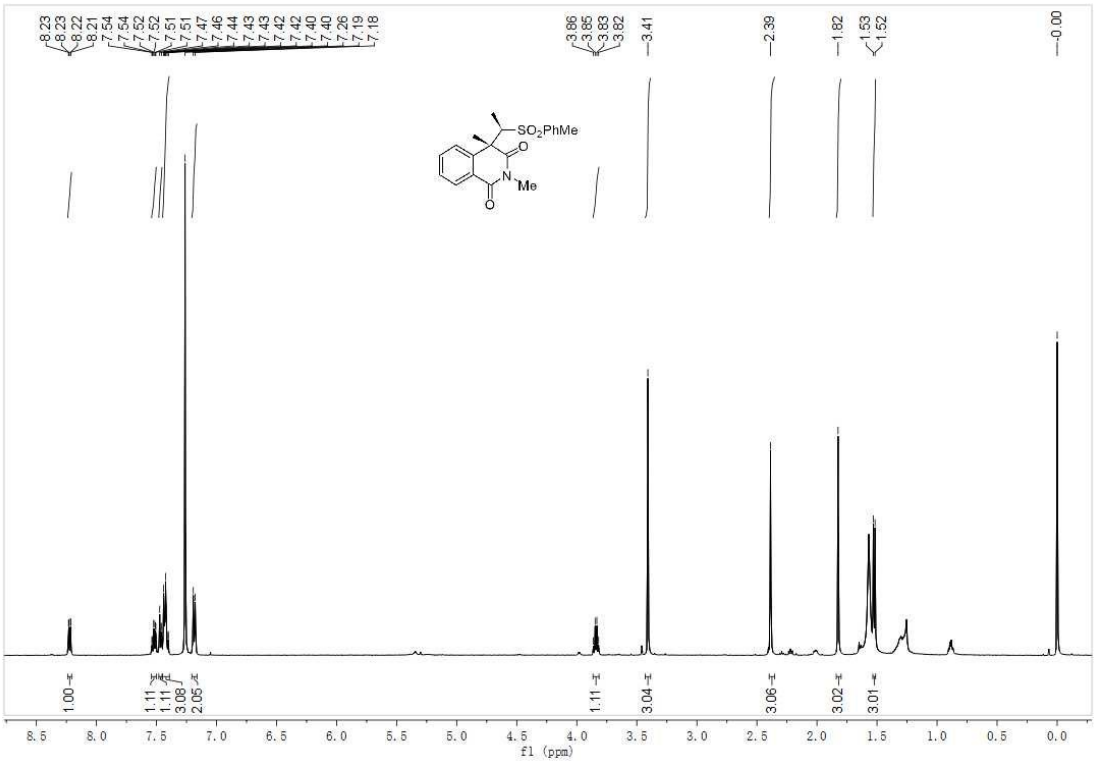


Figure S.22. ^{1}H NMR spectra of **3g**.

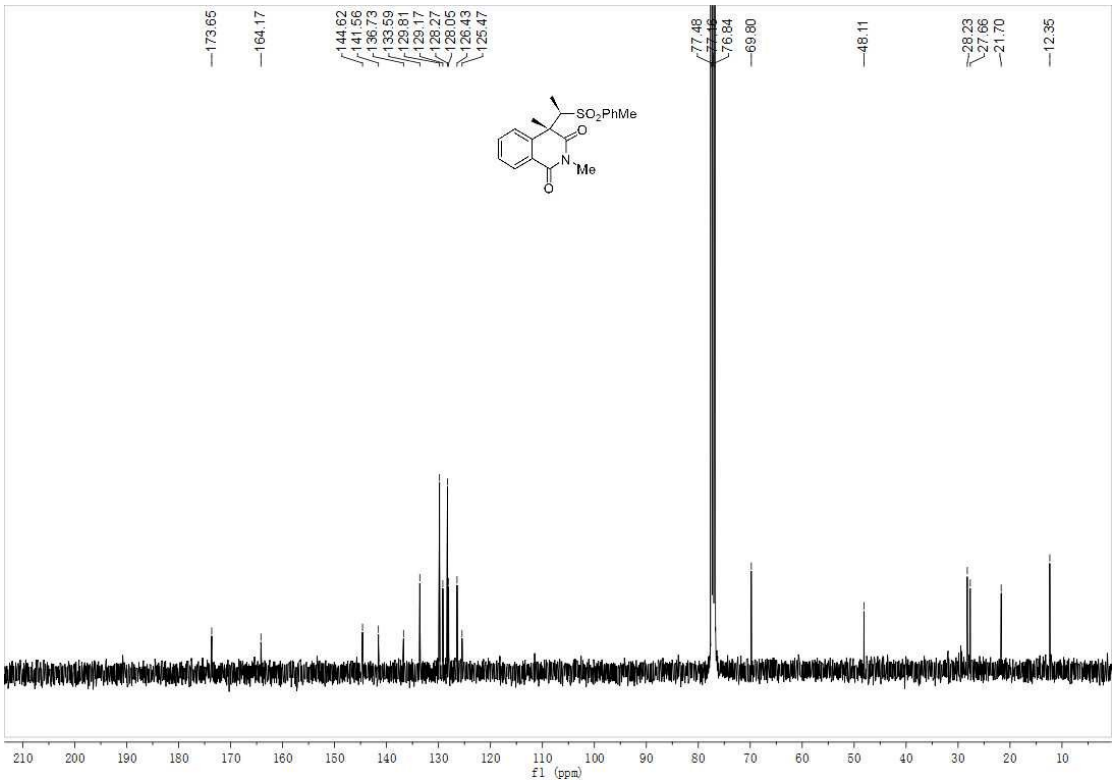


Figure S.23. ^{13}C NMR spectra of **3g**.

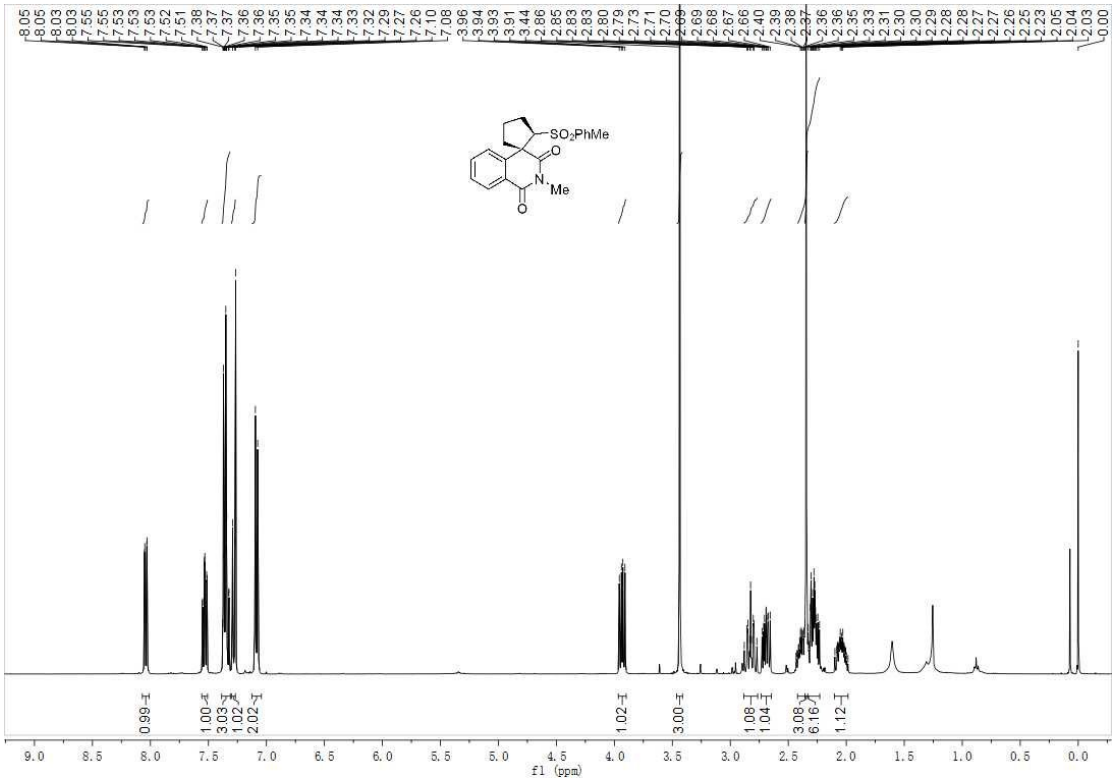


Figure S.24. ^{1}H NMR spectra of **3h**.

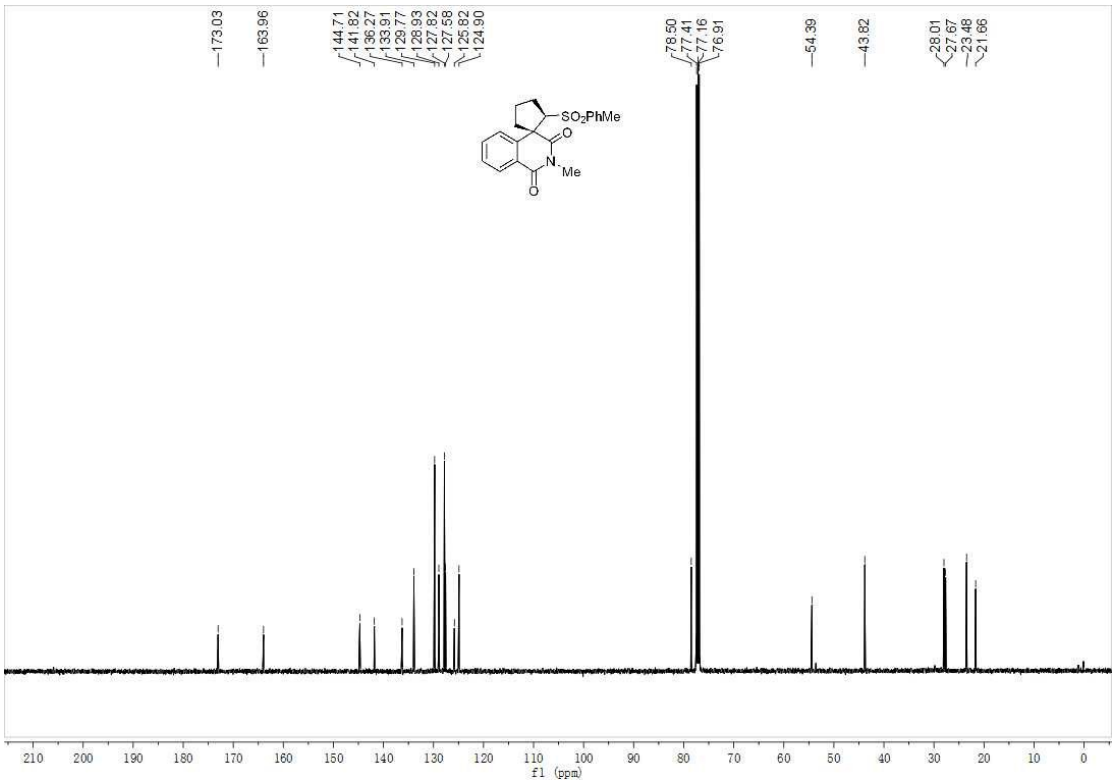


Figure S.25. ^{13}C NMR spectra of **3h**.

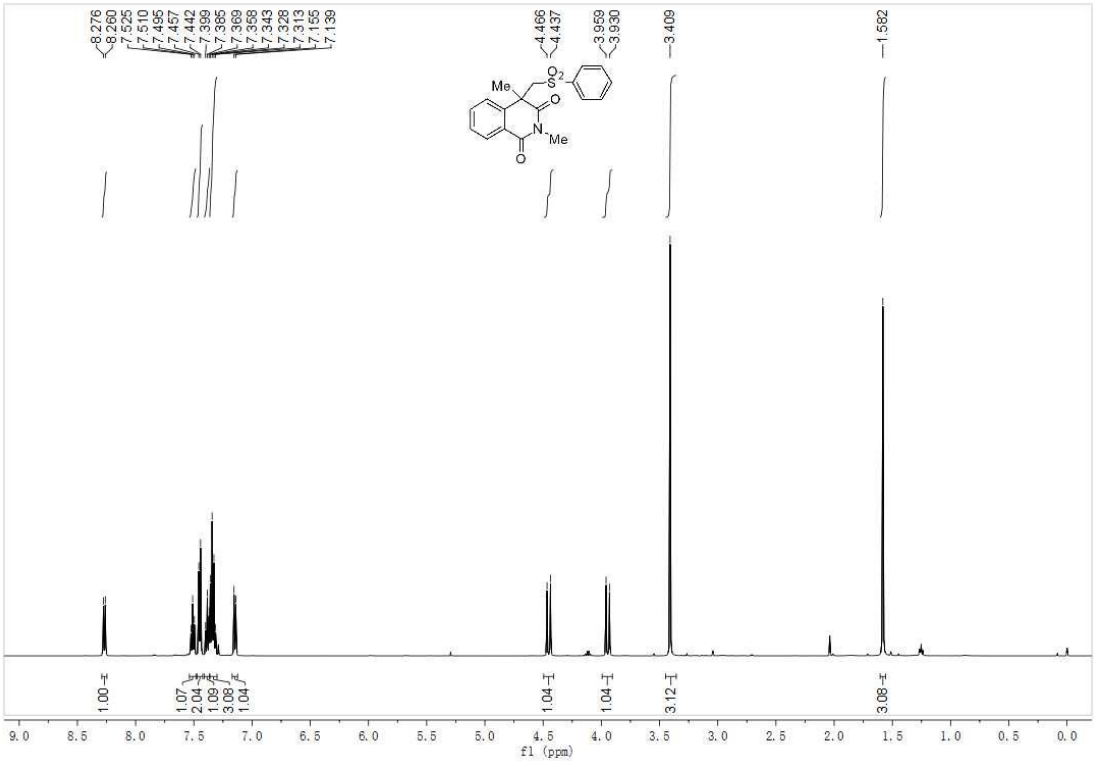


Figure S.26. ^{1}H NMR spectra of **3i**.

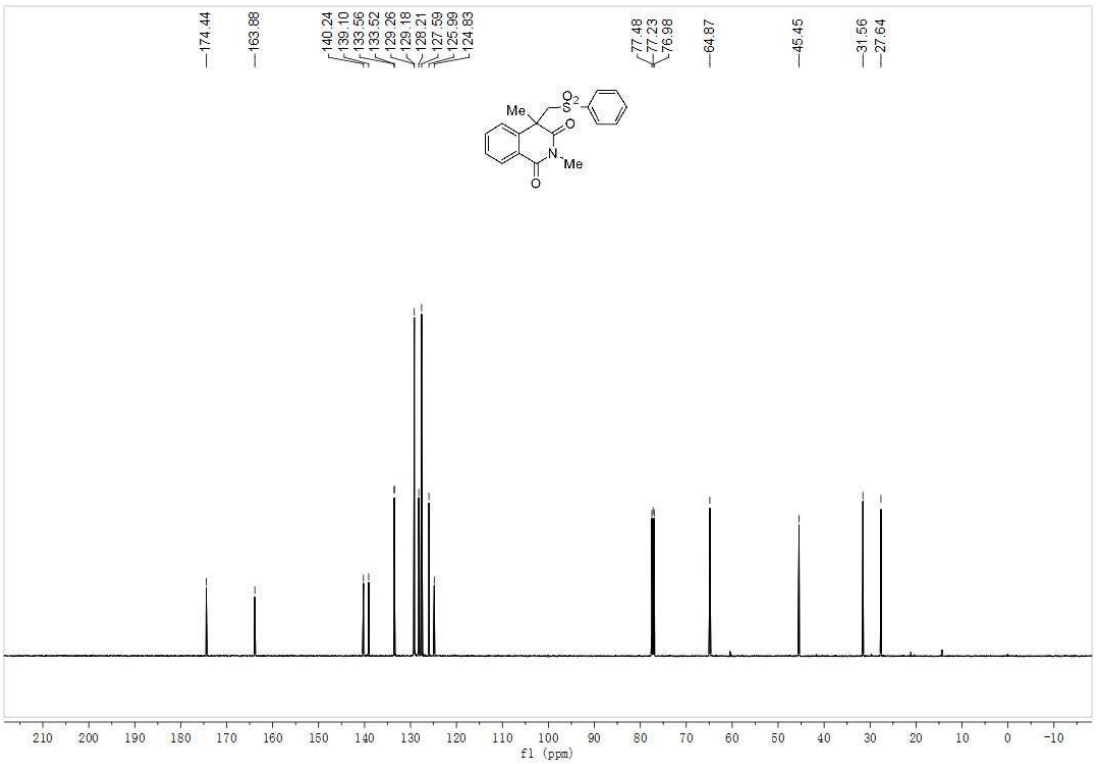


Figure S.27. ^{13}C NMR spectra of **3i**.

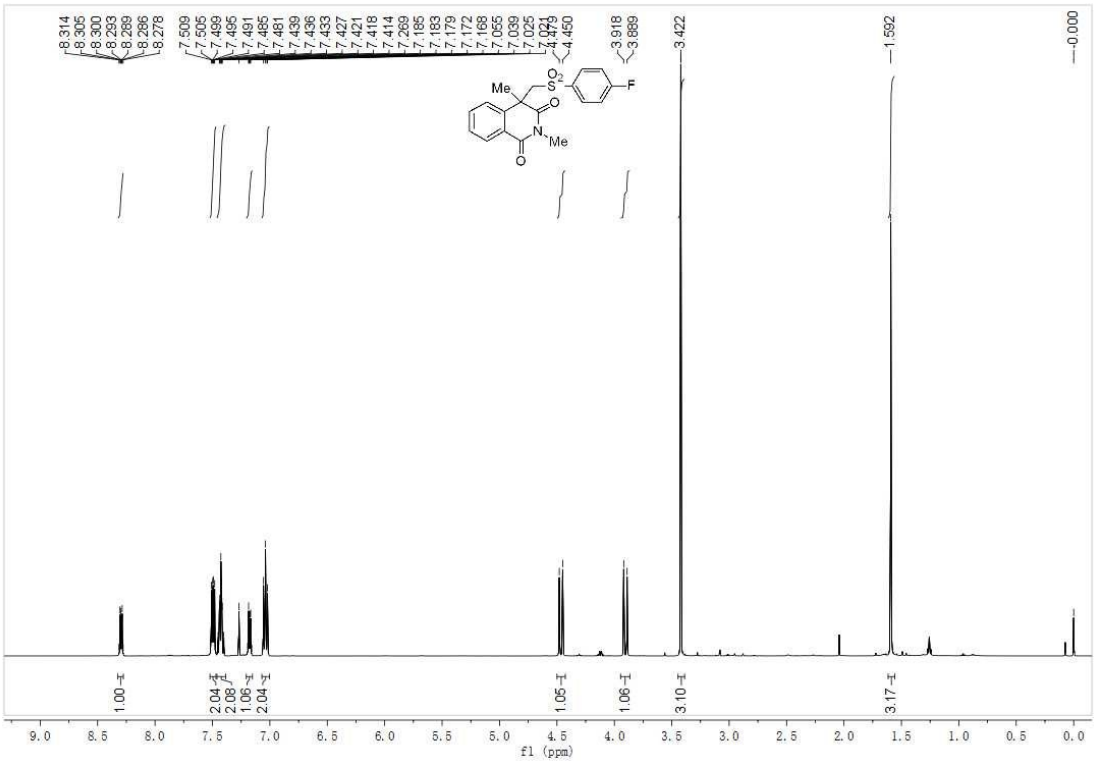


Figure S.28. ^{1}H NMR spectra of **3j**.

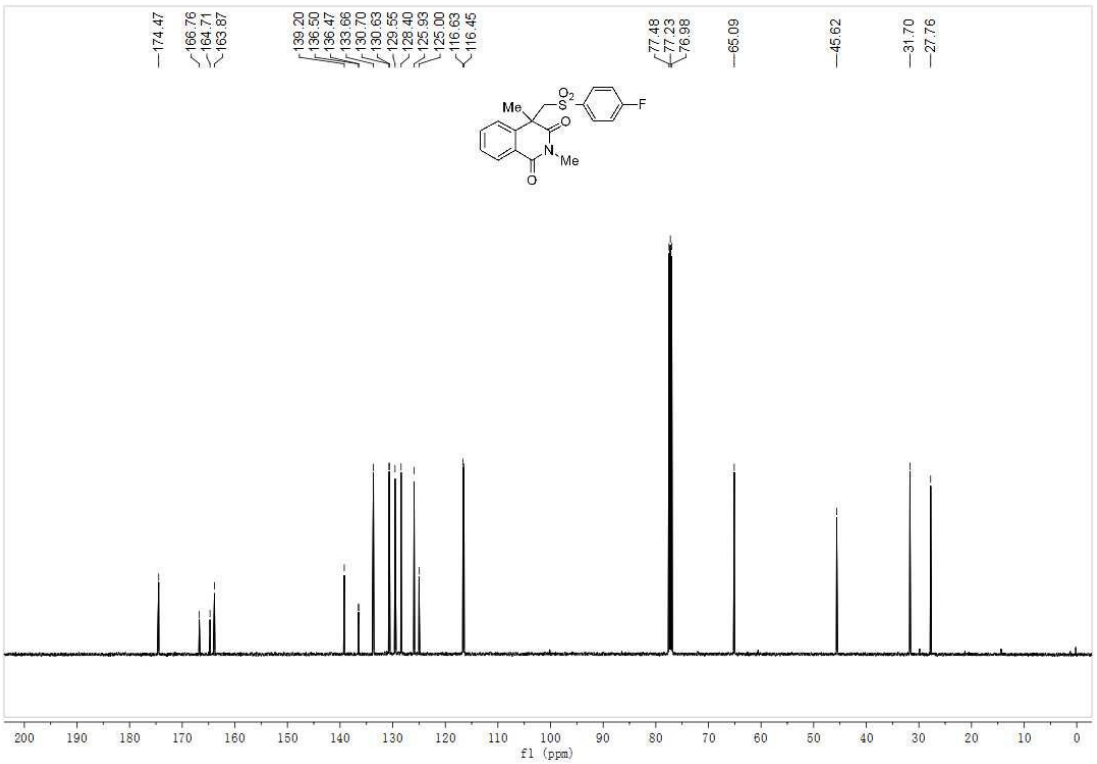


Figure S.29. ^{13}C NMR spectra of **3j**.

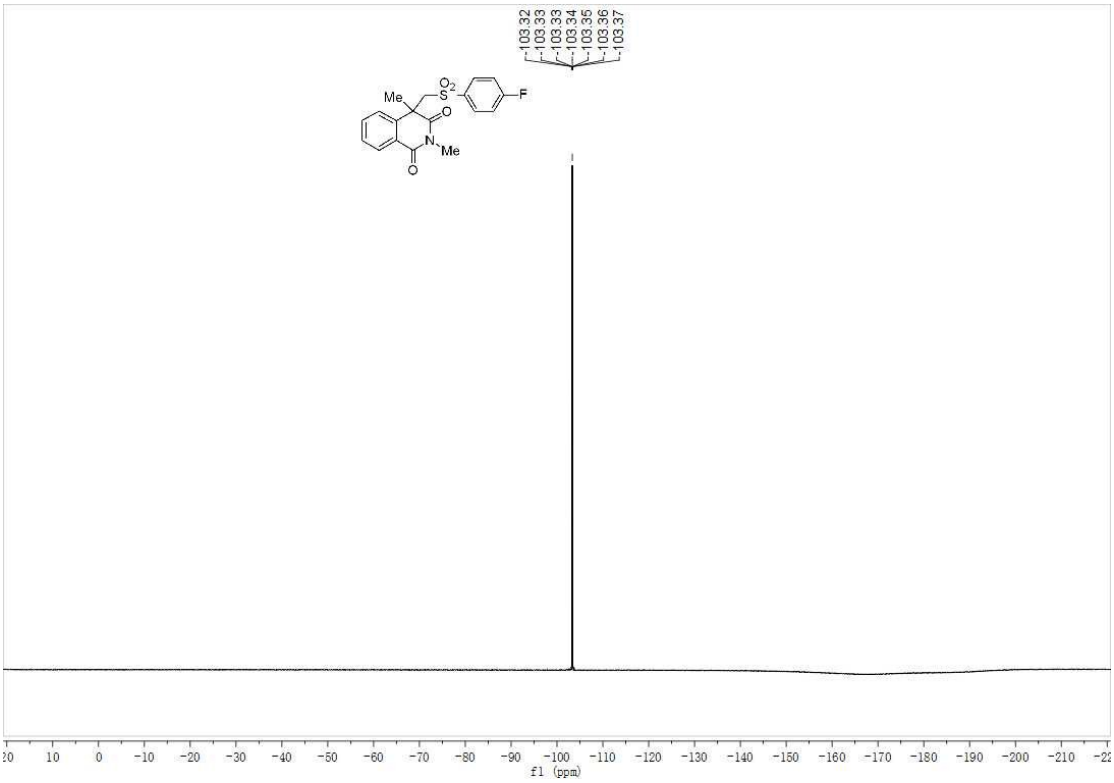


Figure S.30. ^{19}F NMR spectra of **3j**.

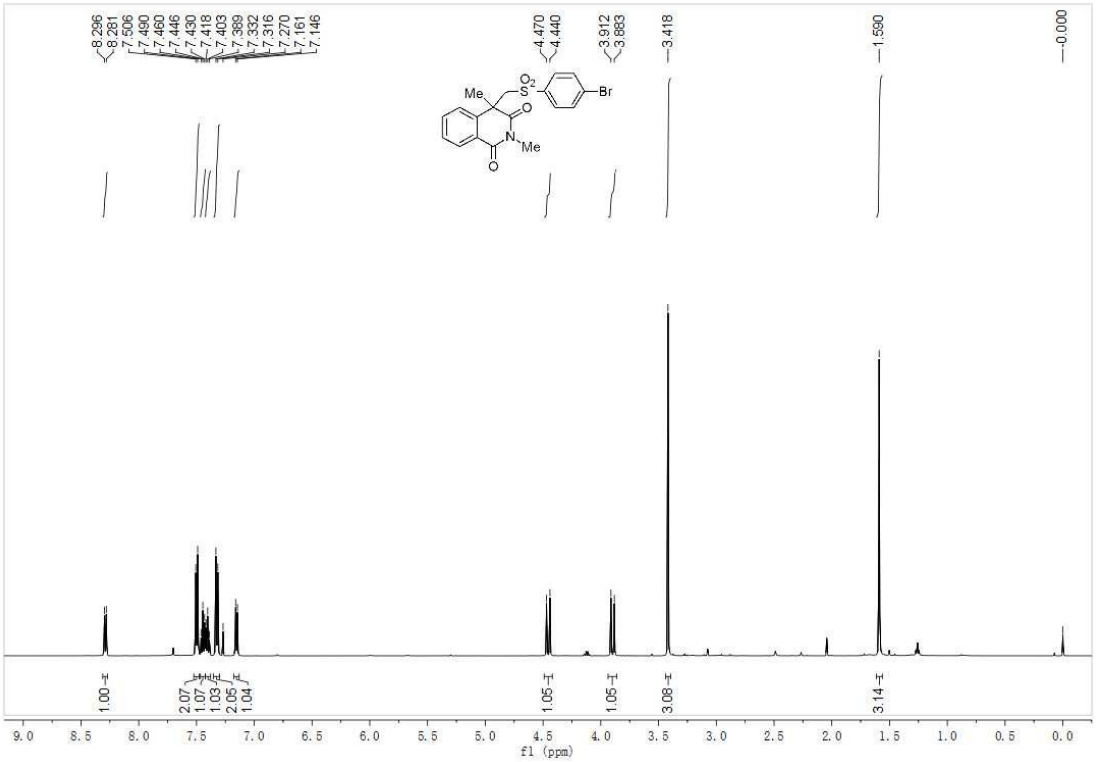


Figure S.31. ^{1}H NMR spectra of **3k**.

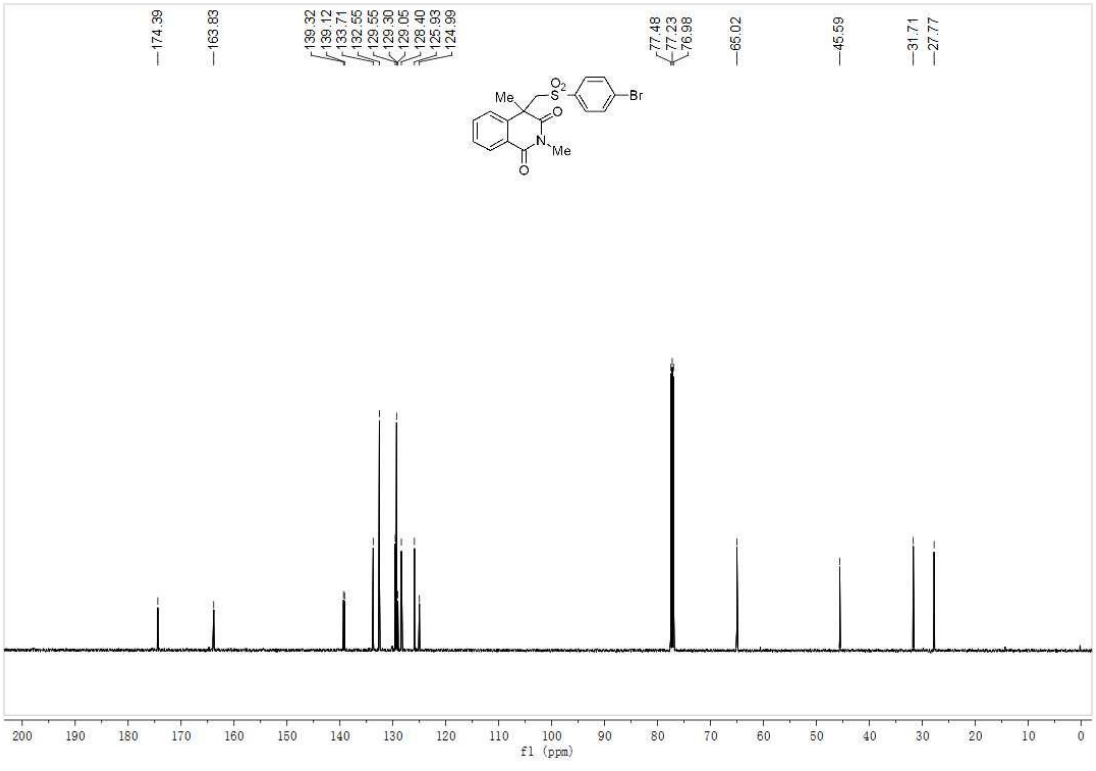


Figure S.32. ^{13}C NMR spectra of **3k**.

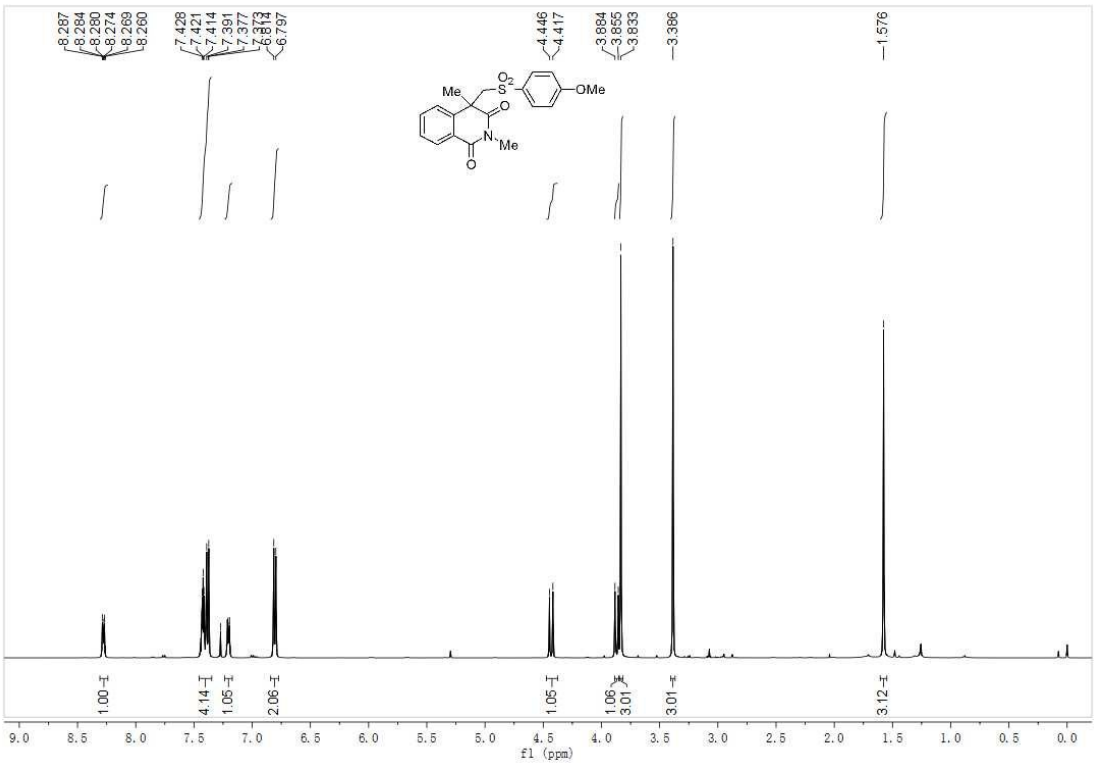


Figure S.33. ^{1}H NMR spectra of **3l**.

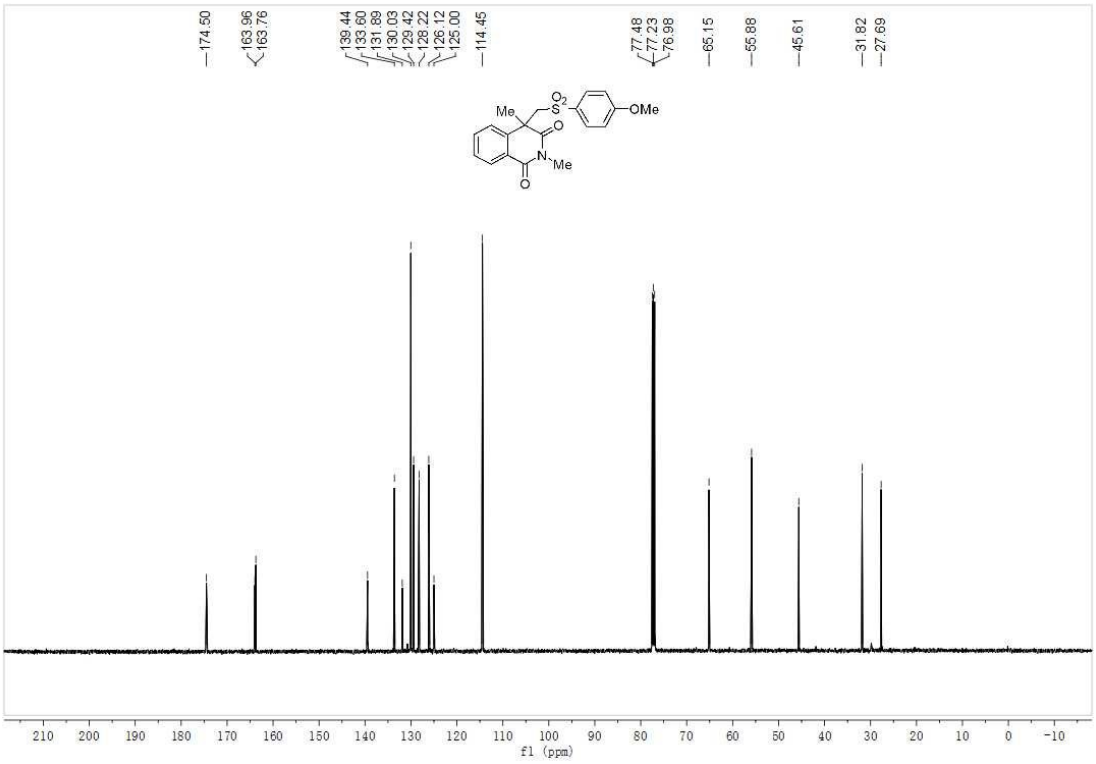


Figure S.34. ^{13}C NMR spectra of **3l**.

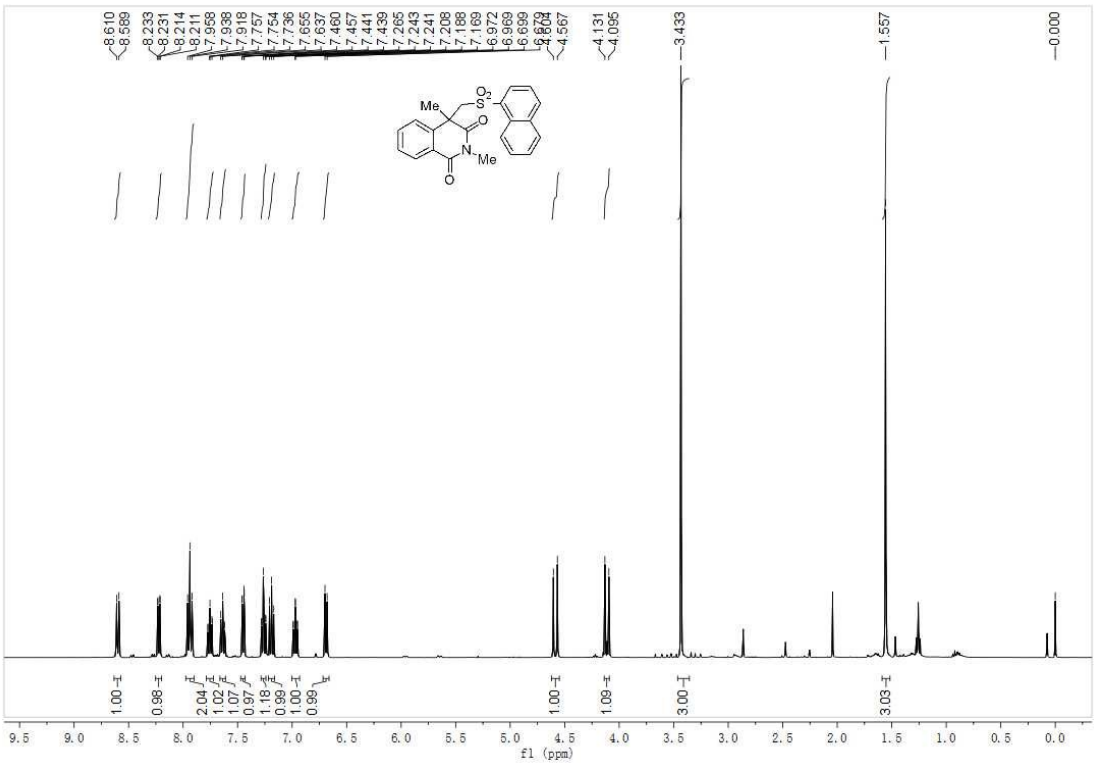


Figure S.35. ^{1}H NMR spectra of **3m**.

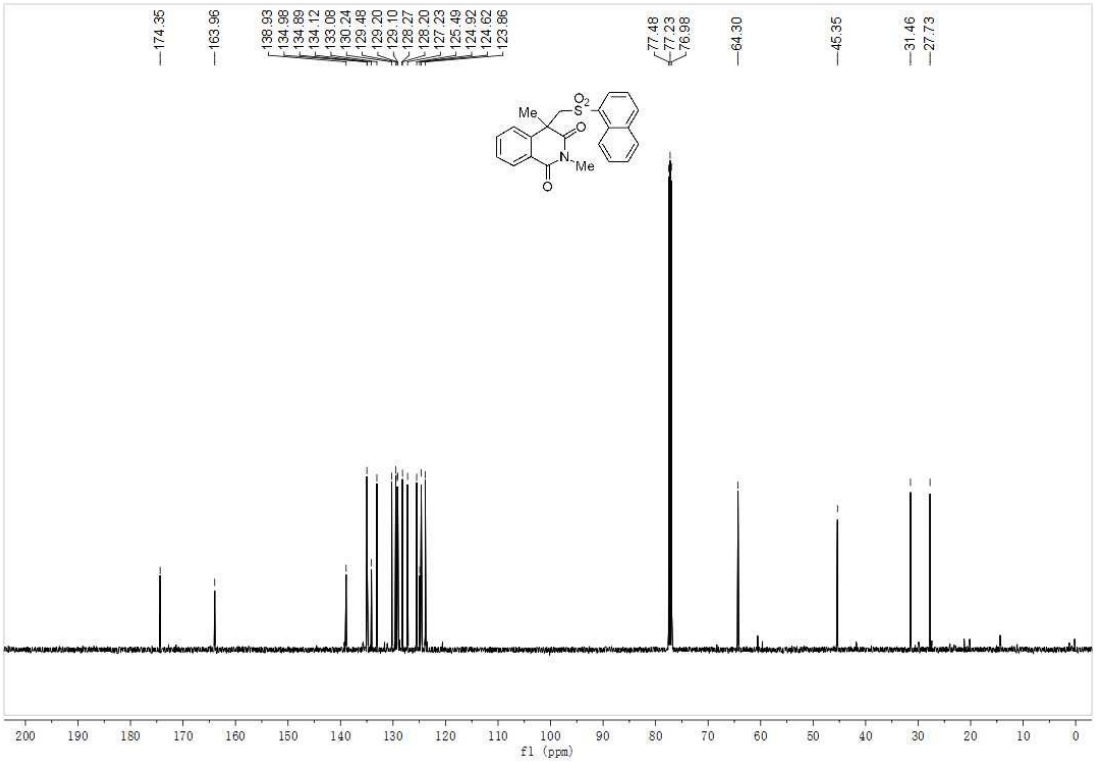


Figure S.36. ^{13}C NMR spectra of **3m**.

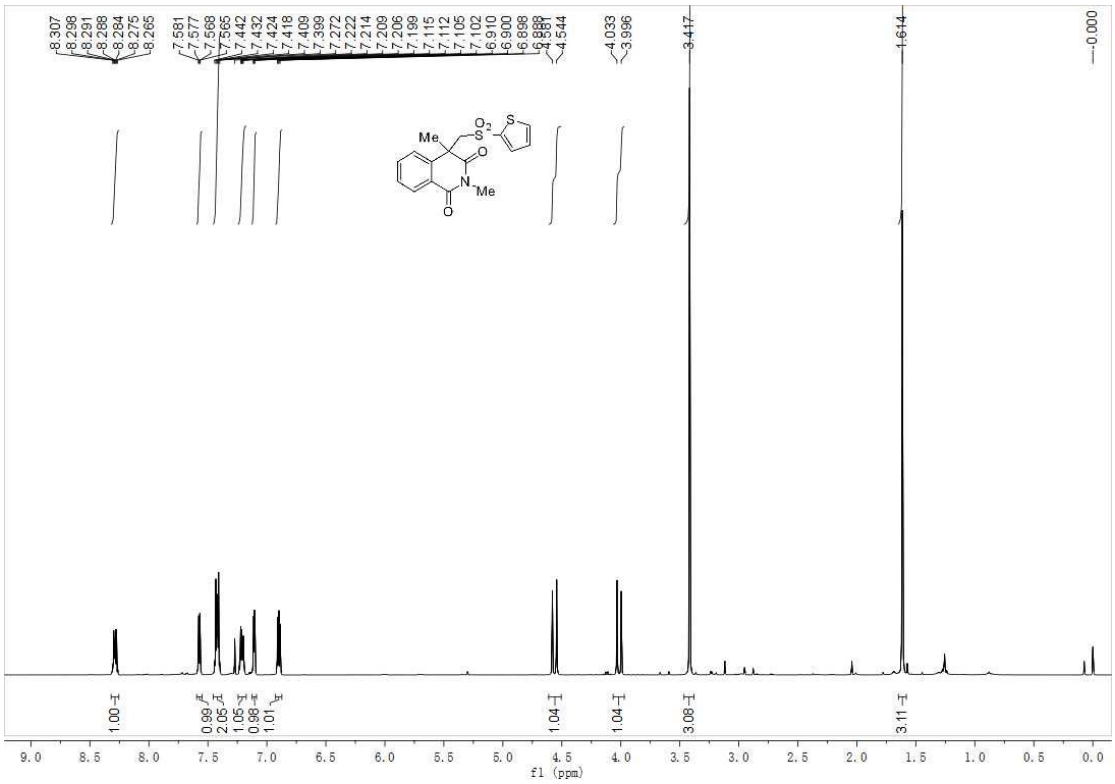


Figure S.37. ^{1}H NMR spectra of **3n**.

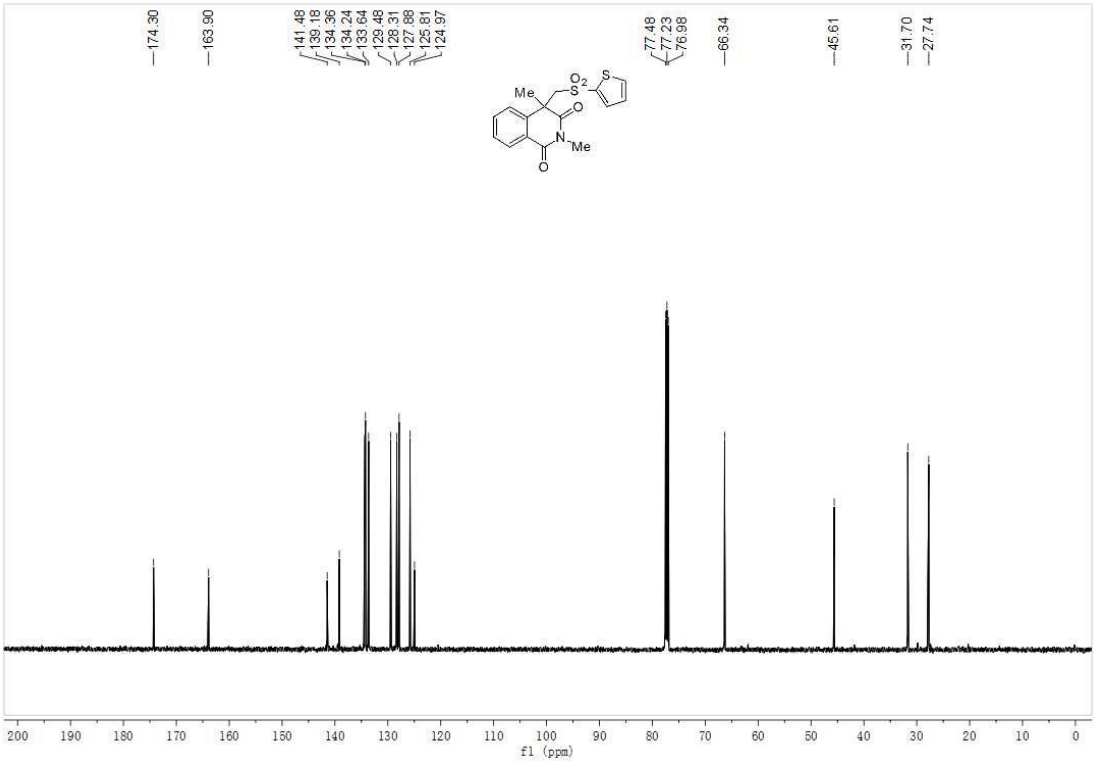


Figure S.38. ^{13}C NMR spectra of **3n**.

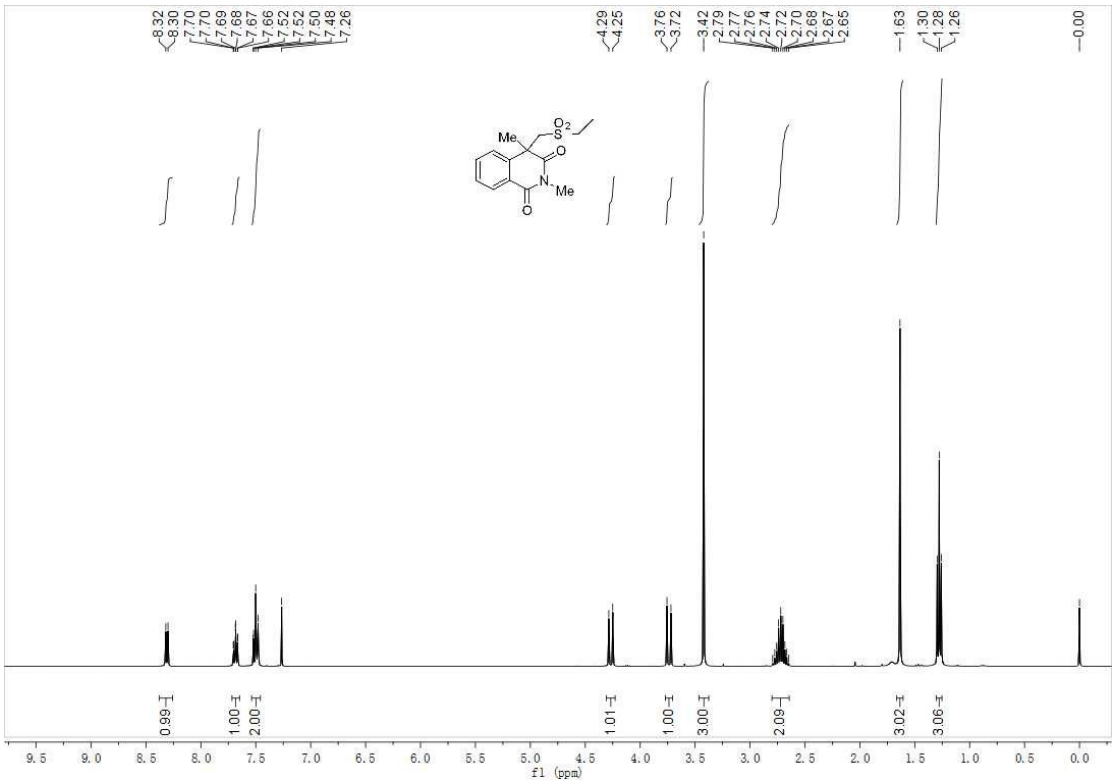


Figure S.39. ^{1}H NMR spectra of **3o**.

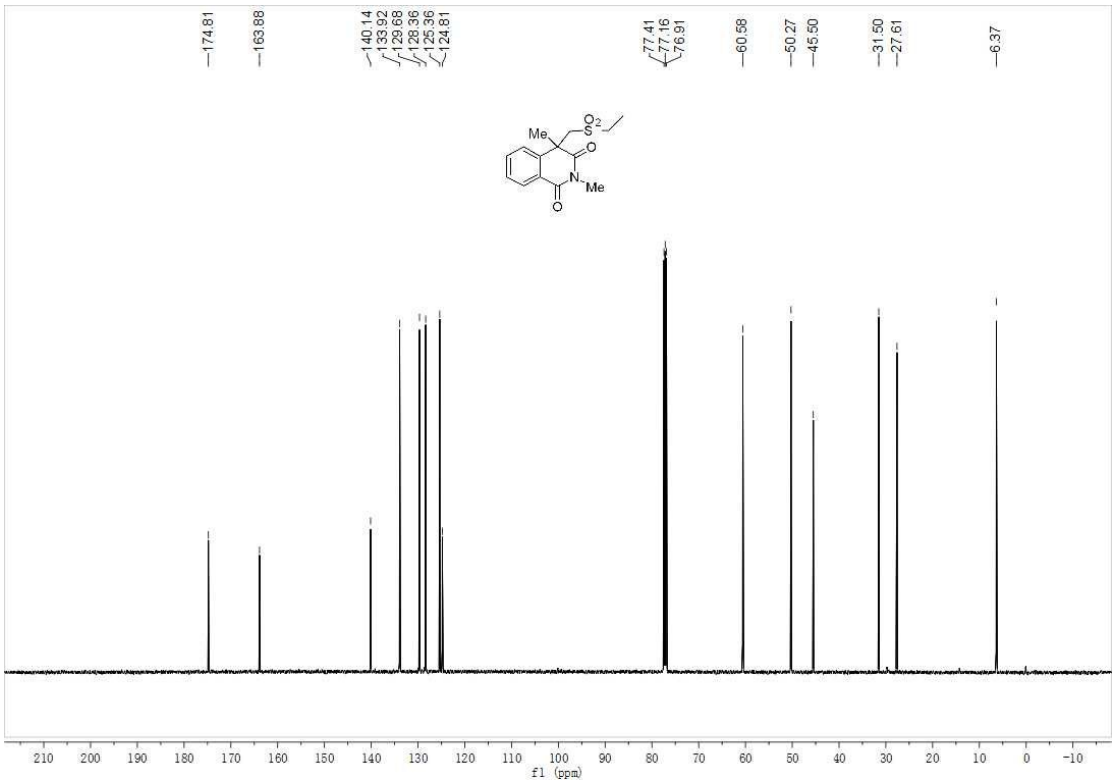


Figure S.40. ^{13}C NMR spectra of **3o**.

Supplementary Notes and references

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