Electronic Supplementary Material (ESI) for ChemComm.


# Alkyl Radical Triggered *in situ* $SO_2$-Capture Cascades

Xiaolong Su,[‡] Honggui Huang,[‡] Wei Hong, Jianchao Cui, Menglin Yu and Yi Li*

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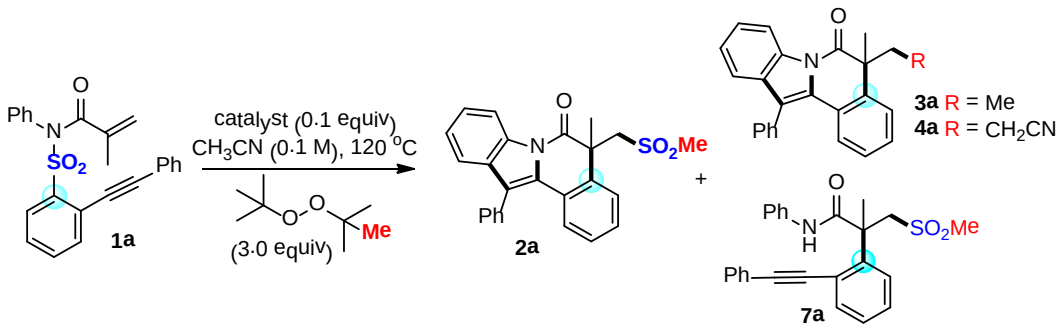
## 1. General

Unless otherwise noted, all reactions were carried out in flame-dried glassware under argon. All solvents were purified and dried according to standard methods prior to use. $^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded on a BRUKER 400 MHz spectrometer in deuterated solvent. $^{1}$H NMR chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration). $^{13}$C NMR spectra were recorded in deuterated solvent. Chemical shifts are reported in ppm with the internal solvent signal as a standard. $^{19}$F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard. GC-MS measurements were conducted on a Shimadzu QP2010SE. HRMS were obtained on Waters GCT-TOF. IR measurements were conducted on Nicolet is 50 KBr pelleting method.

## 2. Optimization details:

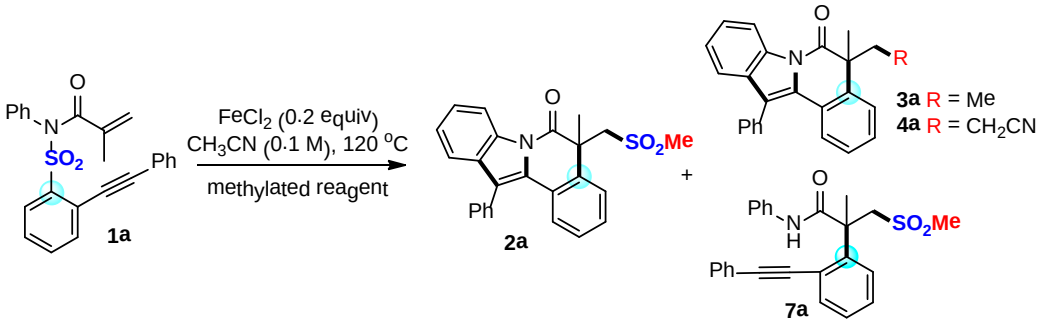
### 2.1 Optimization of catalysts




| entry[a, b] | catalyst (equiv) | **2a** (%) | **3a** (%) | **4a** (%) | **7a** (%) |
|---|---|---|---|---|---|
| 1 | $FeCl_2$ (0.1) | 71 | 13 | 7 | - |
| 2 | $FeCl_3$ (0.1) | 57 | 16 | 13 | - |
| 3 | CuCl (0.1) | 39 | 16 | 14 | 29 |
| 4 | $CuCl_2$ (0.1) | 48 | 20 | 13 | 20 |
| 5 | $AgNO_3$ (0.1) | 34 | 17 | 9 | - |
| 6 | $AlCl_3$ (0.1) | 22 | 12 | 19 | - |
| 7 | $MgCl_2$ (0.1) | 52 | 14 | 21 | - |
| 8 | $I_2$ (0.1) | 47 | 25 | 13 | - |
| 9 | TBAI (0.1) | 53 | 18 | 14 | trace |
| 10 | $Fe(OTf)_2$ (0.1) | 73 | 9 | 7 | - |
| 11 | $Fe(acac)_2$ (0.1) | 68 | 10 | 6 | - |
| 12 | $FeCl_2$ (0.05) | 65 | 10 | 8 | - |
| 13 | $FeCl_2$ (0.2) | 71 | 8 | 7 | - |
| 14 | $FeCl_2$ (0.3) | 70 | 7 | 6 | - |

[a]*Reaction conditions*: **1a** (0.2 mmol), DTBP (0.6 mmol, 3.0 equiv), catalyst (0.02 mmol, 0.1 equiv), 2 mL $CH_3CN$ in sealed tube at 120 °C for 12 h. [b]Isolated yields.

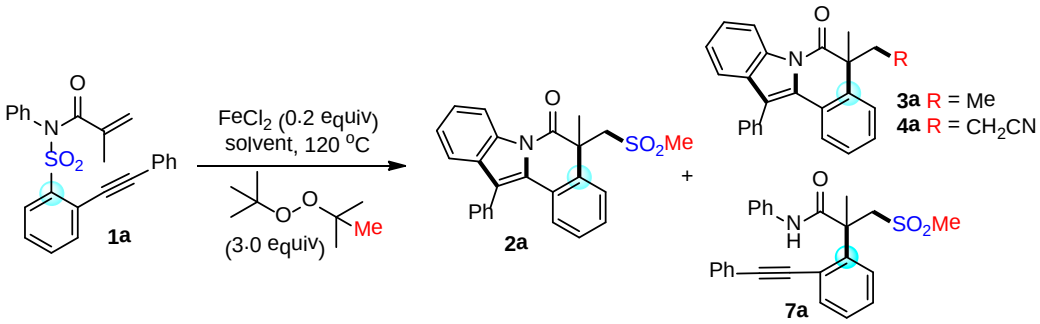
## **2.2** Optimization of methylated reagents




| entry[a, b] | methylated reagent (equiv) | **2a** (%) | **3a** (%) | **4a** (%) | **7a** (%) |
|---|---|---|---|---|---|
| 1 | DTBP (3.0) | 71 | 13 | 7 | - |
| 2 | TBHP (3.0) | trace | trace | trace | trace |
| 3 | DCP (3.0) | 57 | 25 | - | - |
| 4 | TBP (3.0) | 58 | 13 | 21 | - |
| 5 | DTBP (2.0) | 69 | 11 | 15 | - |
| 6 | DTBP (4.0) | 68 | 12 | 20 | - |

[a]*Reaction conditions*: **1a** (0.2 mmol), methylated reagent, $FeCl_2$ (0.04 mmol) in 2 mL $CH_3CN$ in sealed tube at 120 °C for 12 h. [b]Isolated yields.

## **2.3** Optimization of solvents

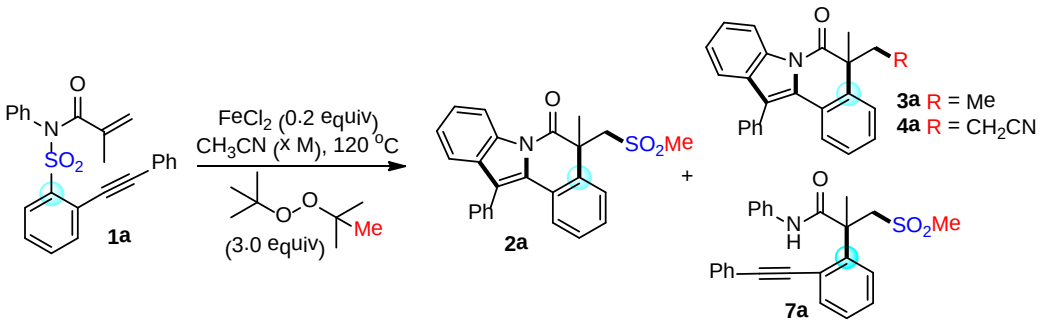



| entry[a, b] | solvent (M) | **2a** (%) | **3a** (%) | **4a** (%) | **7a** (%) |
|---|---|---|---|---|---|
| 1 | $CH_3CN$ (0.1) | 71 | 13 | 7 | - |
| 2 | toluene (0.1) | 12 | trace | - | - |
| 3 | $CH_2Cl_2$ (0.1) | 25 | 6 | - | - |
| 4 | $H_2O$ (0.1) | trace | trace | - | - |

| | | | | | |
|---|---|---|---|---|---|
| 5 | THF (0.1) | - | - | - | - |
| 6 | DMF (0.1) | - | trace | - | - |
| 7 | DMSO (0.1) | trace | 38 | - | - |
| 8 | dioxane (0.1) | trace | trace | - | - |
| 9 | $CH_3CN$ (0.1) | 62 | 18 | - | - |

[a]*Reaction conditions*: **1a** (0.2 mmol), DTBP (0.6 mmol, 3.0 equiv), $FeCl_2$ (0.04 mmol, 0.2 equiv), 2 mL solvent in sealed tube at 120 $^oC$ for 12 h. [b]Isolated yields.

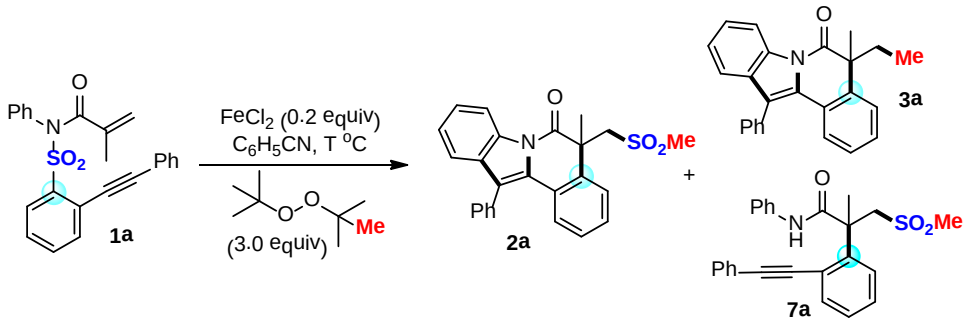
## **2.4** Optimization of concentrations




| Entry[a, b] | x (M) | **2a** (%) | **3a** (%) | **4a** (%) | **7a** (%) |
|---|---|---|---|---|---|
| 1 | $CH_3CN$ (0.1) | 71 | 13 | 7 | - |
| 2 | $C_6H_5CN$ (0.1) | 62 | 18 | - | - |
| 3 | $CH_3CN$ (0.05) | 81 | 8 | 7 | - |
| 4 | $C_6H_5CN$ (0.05) | 82 | 14 | - | - |
| 5 | $CH_3CN$ (0.025) | 60 | 7 | 22 | - |
| 6 | $C_6H_5CN$ (0.025) | 76 | 24 | - | - |

[a]*Reaction conditions*: **1a** (0.2 mmol), DTBP (0.6 mmol, 3.0 equiv), $FeCl_2$ (0.04 mmol, 0.2 equiv), $CH_3CN$ or $C_6H_5CN$ in sealed tube at 120 $^oC$ for 12 h. [b]Isolated yields.

**2.5** Optimization of temperatures



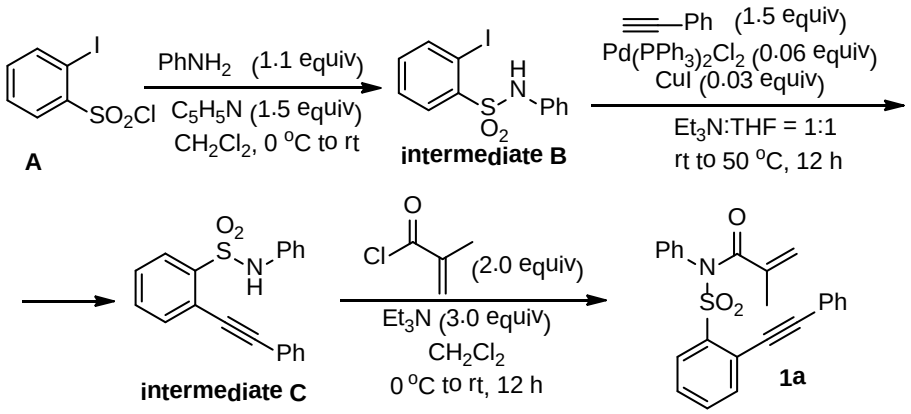

| entry[a, b] | T (°C) | **2a** (%) | **3a** (%) | **7a** (%) |
|---|---|---|---|---|
| 1 | 100 | 52 | 22 | - |
| 2 | 120 | 82 | 14 | - |
| 3 | 140 | 77 | 20 | - |
| 4 | 160 | 73 | 23 | - |

[a]*Reaction conditions*: **1a** (0.2 mmol), DTBP (0.6 mmol, 3.0 equiv), $FeCl_2$ (0.04 mmol, 0.2 equiv), 4 mL $C_6H_5CN$ in sealed tube at 120 °C for 12 h. [b]Isolated yields.

## 3. Synthesis of starting materials: 1a-1ae, peroxides and peroxybenzoate

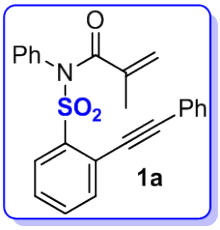
**3.1** Synthesis of **1a-1ae**: General procedure A

A typical procedure A (synthesis of **1a**) is shown as below[1]:



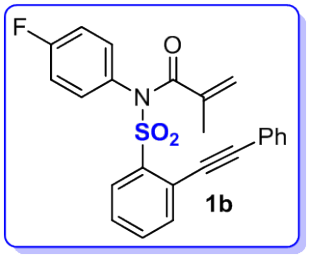

To a solution of 2-iodobenzene-1-sulfonyl chloride **A** (2.0 mmol) in $CH_2Cl_2$ (10 mL) at 0 °C were added pyridine (3 mmol, 1.5 equiv) and aniline (2.2 mmol, 1.1 equiv). The reaction mixture was warmed to room temperature until the disappearance of **A** confirmed by TLC. The mixture was then diluted with water, extracted with $CH_2Cl_2$, and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (8:1, v:v) as the eluent to give intermediate **B**, which was dissolved directly in a mixture of $Et_3N$:THF (8 mL, 1:1, v:v). Phenylacetylene (3.0 mmol, 1.5 equiv), $Pd(PPh_3)_2Cl_2$ (0.12 mmol, 0.06 equiv) and CuI (0.06 mmol, 0.03 equiv) were added subsequently to this mixture. The reaction mixture was warmed to 50 °C, stirred for 12 hours, diluted with saturated aqueous $NH_4Cl$, extracted with ethyl acetate, and dried over anhydrous $Na_2SO_4$. The combined organic layers were concentrated under reduced pressure and purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as the eluent to give intermediate **C**, which was dissolved in $CH_2Cl_2$ (10 mL) and cooled to 0 °C. $Et_3N$ (6 mmol, 3.0 equiv) and methacryloyl chloride (4 mmol, 2.0 equiv) were added to the reaction mixture. The reaction mixture was then warmed to room temperature until full consumption of **C** detected by TLC. The reaction was quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with $CH_2Cl_2$ (3 x 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as the eluent to give **1a** in 72% yield (578 mg, brown solid, three steps).

***N*-phenyl-*N*-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamide (1a)**[2]



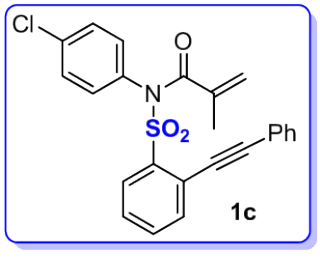

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 8.0, 1.4 Hz, 1H; Ar-*H*), 7.70 (dd, *J* = 7.7, 1.5 Hz, 1H; Ar-*H*), 7.61 (td, *J* = 7.6, 1.5 Hz, 1H; Ar-*H*), 7.54 (td, *J* = 7.7, 1.5 Hz, 1H; Ar-*H*), 7.41 (dd, *J* = 6.8, 2.8 Hz, 2H; 2(Ar-*H*)), 7.38-7.29 (m, 5H; 5(Ar-*H*)), 7.23-7.16 (m, 3H; 3(Ar-*H*)), 5.33 (s, 1H; C=CH*H*), 5.19 (d, *J* = 1.9 Hz, 1H; C=CH*H*), 1.66 (s, $CH_2$=CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 139.5, 139.1, 136.1, 134.7, 133.2, 132.9, 131.9, 130.6, 129.1, 129.0, 128.9, 128.2, 128.0, 123.4, 122.4, 122.4, 97.3, 86.3, 19.3.

***N*-(4-fluorophenyl)-*N*-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamide (1b)**[2]



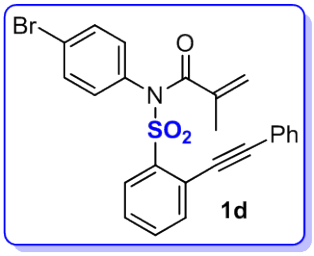

According to general procedure A with 4-fluoroaniline, **1b** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 62% yield (520 mg, white solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 8.1 Hz, 1.5 Hz, 1H; Ar-*H*), 7.70 (dd, *J* = 7.7, 1.5 Hz, 1H; Ar-*H*), 7.62 (td, *J* = 7.5, 1.4 Hz, 1H; Ar-*H*), 7.55 (ddd, *J* = 8.2, 7.4, 1.5 Hz, 1H; Ar-*H*), 7.42-7.34 (m, 7H; 7(Ar-*H*)), 6.89-6.80 (m, 2H; 2(Ar-*H*)), 5.32 (d, *J* = 0.9 Hz, 1H; C=CH*H*), 5.23 (d, *J* = 1.0 Hz, 1H; C=CH*H*), 1.67 (t, *J* = 1.3 Hz, 3H; $CH_2$=CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.7, 162.7 (d, *J* = 250.4 Hz), 139.5, 139.0, 134.7, 133.3, 132.9, 132.4 (d, *J* = 8.9 Hz), 132.1 (d, *J* = 3.4 Hz), 131.8, 129.2, 128.3, 128.0, 123.5, 122.3, 122.3, 116.0 (d, *J* = 23.0 Hz), 97.3, 86.3, 19.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -111.30 (s).

***N*-(4-chlorophenyl)-*N*-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamide (1c)**[3]



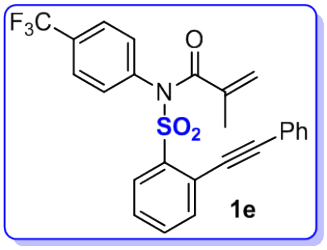

According to general procedure A with 4-chloroaniline, **1c** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 67% yield (600 mg, white solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 8.1, 1.4 Hz, 1H; Ar-*H*), 7.69 (dd, *J* = 7.6, 1.5 Hz, 1H; Ar-*H*), 7.62 (td, *J* = 7.5, 1.5 Hz, 1H; Ar-*H*), 7.55 (td, *J* = 7.7, 1.6 Hz, 1H; Ar-*H*), 7.41-7.28 (m, 7H; 7(Ar-*H*)), 7.16-7.10 (m, 2H; 2(Ar-*H*)), 5.32 (s, 1H; C=CH*H*), 5.24 (d, *J* = 1.8 Hz, 1H; C=CH*H*), 1.68 (s, 3H; $CH_2$=CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.6, 139.3, 139.0, 135.3, 134.9, 134.7, 133.3, 133.0, 131.7, 131.7, 129.2, 129.2, 128.3, 128.0, 123.8, 122.3, 122.2, 97.3, 86.2, 19.2.

***N*-(4-bromophenyl)-*N*-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamide (1d)**[3]



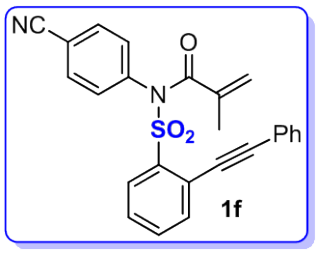

According to general procedure A with 4-bromoaniline, **1d** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 70% yield (668 mg, light yellow solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.0 Hz, 1H; Ar-*H*), 7.68 (d, *J* = 7.6 Hz, 1H; Ar-*H*), 7.61 (t, *J* = 7.5 Hz, 1H; Ar-*H*), 7.54 (t, *J* = 7.7 Hz, 1H; Ar-*H*), 7.43-7.24 (m, 9H; 9(Ar-*H*)), 5.31 (s, 1H; C=CH*H*), 5.23 (s, 1H; C=CH*H*), 1.67 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.5, 139.3, 139.0, 135.5, 134.7, 133.4, 132.9, 132.2, 132.0, 131.8, 129.2, 128.4, 128.1, 123.9, 123.5, 122.3, 122.1, 97.4, 86.2, 19.3.

***N*-((2-(phenylethynyl)phenyl)sulfonyl)-*N*-(4-(trifluoromethyl)phenyl)methacryla mide (1e)**[2]




According to general procedure A with 4-(trifluoromethyl)aniline, **1e** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 53% yield (500 mg, white solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 8.0, 1.3 Hz, 1H; Ar-*H*), 7.69 (dd, *J* = 7.7, 1.5 Hz, 1H; Ar-*H*), 7.63 (td, *J* = 7.5, 1.4 Hz, 1H; Ar-*H*), 7.59-7.49 (m, 3H; 3(Ar-*H*)), 7.42 (d, *J* = 8.3 Hz, 2H; 2(Ar-*H*)), 7.39-7.34 (m, 1H; Ar-*H* ), 7.34-7.22 (m, 4H; 4(Ar-*H*)), 5.30 (s, 1H; C=C*H*H), 5.25 (d, *J* = 1.6 Hz, 1H; C=C*H*H), 1.68 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.4, 139.7 (q, *J* = 1.0 Hz), 139.2, 139.0, 134.7, 133.5, 133.0, 131.6, 130.8 (q, *J* = 33.0 Hz), 130.8, 130.4 (q, *J* = 288.0 Hz), 129.3, 128.3, 128.1, 126.0 (q, *J* = 3.7 Hz), 124.2, 122.3, 122.0, 97.5, 86.1, 19.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.70 (s).

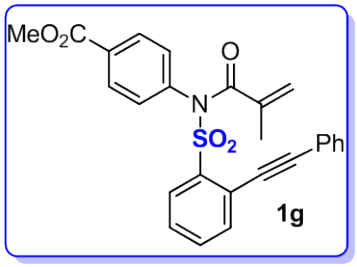
***N*-(4-cyanophenyl)-*N*-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamide (1f)**




According to general procedure A with 4-aminobenzonitrile, **1f** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 50% yield (426 mg, white solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 8.0, 1.4 Hz, 1H; Ar-*H*), 7.70-7.58 (m, 2H; 2(Ar-*H*)), 7.54 (ddd, *J* = 8.8, 7.2, 1.7 Hz, 1H; Ar-*H*), 7.48-7.29 (m, 7H; 7(Ar-*H*)), 7.25-7.17 (m, 2H; 2(Ar-*H*)), 5.27 (d, *J* = 1.2 Hz,

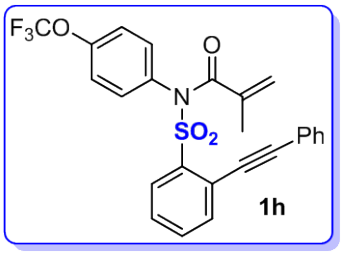
1H; C=CH*H*), 5.25 (d, *J* = 1.6 Hz, 1H; C=C*H*H ), 1.66 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.2, 140.8, 139.2, 139.1, 134.6, 133.6, 133.0, 132.6, 131.6, 131.0, 129.6, 128.4, 128.2, 124.6, 122.2, 121.9, 117.6, 112.6, 97.4, 86.1, 19.1; HRMS (ESI) exact mass calculated for $C_{24}H_{20}NO_3S^+$ [M+H$^+$]: 427.1111, found: 427.1108; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1698, 1365, 1176, 1119, 757, 732, 690, 674; m.p. 137-139 $^o$C.

**Methyl-4-(*N*-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamido)benzoate (1g)**[2]



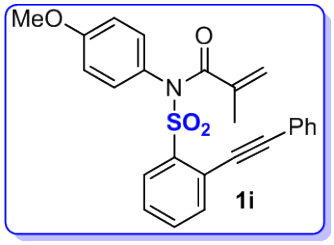

According to general procedure A with 4-aminobenzoate, **1g** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 57% yield (520 mg, white solid, three steps). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 8.0, 1.4 Hz, 1H; Ar-*H* ), 7.84-7.76 (m, 2H; 2(Ar-*H*)), 7.66-7.68 (m, 1H; Ar-*H*), 7.59-7.63 (m, 1H; Ar-*H*), 7.52-7.56 (m, 1H; Ar-*H*), 7.47-7.39 (m, 2H; 2(Ar-*H*)), 7.35-7.30 (m, 1H; Ar-*H*), 7.26 (td, *J* = 7.9, 6.0 Hz, 4H; 4(Ar-*H*)), 5.33 (s, 1H; C=CH*H*), 5.23 (q, *J* = 1.7 Hz, 1H; C=CH*H*), 3.85 (s, 3H; $CO_2CH_3$), 1.67 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.5, 165.7, 140.8, 139.2, 134.6, 133.4, 132.9, 131.7, 130.3, 130.1, 128.9, 128.1, 128.0, 124.3, 122.4, 122.1, 97.3, 86.2, 52.2, 19.2.

***N*-((2-(phenylethynyl)phenyl)sulfonyl)-*N*-(4-(trifluoromethoxy)phenyl)methacryl amide (1h)**



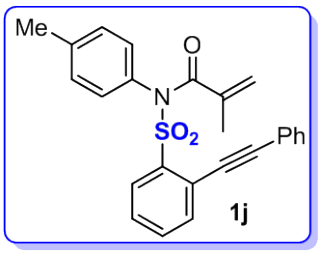

According to general procedure A with 4-(trifluoromethoxy)aniline, **1h** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 49% yield (475 mg, white solid, three steps). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H; Ar-*H*), 7.72 (d, *J* = 1.4 Hz, 1H; Ar-*H*), 7.63 (td, *J* = 7.6, 1.4 Hz, 1H; Ar-*H*), 7.55 (td, *J* = 7.8, 1.4 Hz, 1H; Ar-*H*), 7.47-7.33 (m, 7H; 7(Ar-*H*)), 7.00 (d, *J* = 8.4 Hz, 2H; 2(Ar-*H*)), 5.32 (s, 1H; C=C*H*H), 5.25 (d, *J* = 1.8 Hz, 1H; C=CH*H*), 1.68 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.5, 149.4 (q, *J* = 1.9 Hz), 139.3, 138.8, 134.7, 134.4, 133.4, 132.9, 132.1, 131.7, 129.2, 128.3, 128.1, 123.7, 122.3, 122.2, 120.8 (q, *J* = 1.0 Hz), 120.2 (q, *J* = 258.5 Hz), 97.4, 86.2, 19.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -57.87 (s); HRMS (ESI) exact mass calculated for $C_{25}H_{19}F_3NO_4S^+$ [M+H$^+$]: 486.0981, found: 486.0974; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1697, 1503, 1249, 1172, 757, 689, 592, 543; m.p. 90-92 $^o$C.

***N*-(4-methoxyphenyl)-*N*-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamide (1i)**[2]



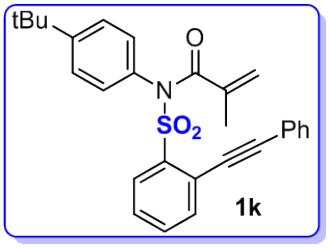

According to general procedure A with 4-methoxyaniline, **1i** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 50% yield (420 mg, brown solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.48-8.34 (m, 1H; Ar-*H*), 7.78-7.66 (m, 1H; Ar-*H*), 7.61 (td, *J* = 7.5, 1.5 Hz, 1H; Ar-*H*), 7.58-7.48 (m, 1H; Ar-*H*), 7.38-7.26 (m, 7H; 7(Ar-*H*)), 6.66 (d, *J* = 8.7 Hz, 2H; 2(Ar-*H*)), 5.34 (s, 1H; C=C*H*H), 5.20 (s, 1H; C=CH*H*), 3.63 (s, Ar-OC$H_3$), 1.66 (s, 3H, $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.0, 159.9, 139.6, 139.2, 134.6, 133.1, 132.9, 131.9, 131.8, 128.9, 128.6, 128.1, 128.0, 123.2, 122.5, 122.3, 114.1, 97.0, 86.5, 55.2, 19.3.

***N*-((2-(phenylethynyl)phenyl)sulfonyl)-*N*-(*p*-tolyl)methacrylamide (1j)**[2]




According to general procedure A with *p*-toluidine, **1j** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 78% yield (648 mg, brown solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 8.0, 1.4 Hz, 1H; Ar-*H*), 7.68 (dd, *J* = 7.7, 1.4 Hz, 1H; Ar-*H*), 7.60 (td, *J* = 7.5, 1.5 Hz, 1H; Ar-*H*), 7.53 (td, *J* = 7.7, 1.5 Hz, 1H; Ar-*H*), 7.37-7.30 (m, 5H; 5(Ar-*H*)), 7.27-7.24 (m, 2H; 2(Ar-*H*)), 6.97 (d, *J* = 8.1 Hz, 2H; 2(Ar-*H*)), 5.41-5.31 (m, 1H; C=CH*H*), 5.19 (d, *J* = 2.1 Hz, 1H; C=CH*H*), 2.17 (s, 3H; Ar-C$H_3$), 1.66 (s, $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 180.0, 139.5, 139.4, 139.2, 134.7, 133.6, 133.1, 132.9, 131.9, 130.4, 129.7, 128.9, 128.1, 127.9, 123.4, 122.5, 122.4, 97.1, 86.5, 21.1, 19.3.

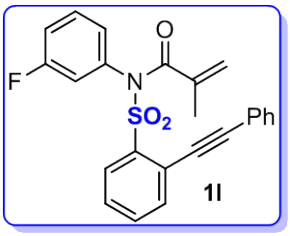
***N*-(4-(*tert*-butyl)phenyl)-*N*-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamide (1k)**[3]




According to general procedure A with 4-(*tert*-butyl)aniline, **1k** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 50% yield (453 mg, brown solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.45-8.33 (m, 1H; Ar-*H*), 7.74-7.66 (m, 1H; Ar-*H*), 7.60 (dt, *J* = 7.6, 4.5 Hz, 1H; Ar-*H*), 7.57-7.48 (m, 1H; Ar-*H*), 7.43-7.28 (m, 7H; 7(Ar-*H*)), 7.20 (d, *J* =

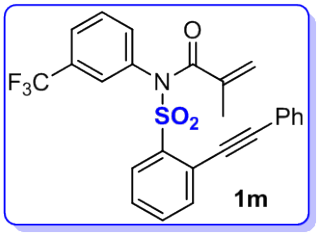
8.2 Hz, 2H; 2(Ar-*H*)), 5.34 (s, 1H; C=CH*H*), 5.19 (s, 1H; C=CH*H*), 1.64 (s, 3H; $CH_2$=CC$H_3$), 1.19 (s, 9H; Ar-C-($CH_3$)$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.0, 152.3, 139.5, 139.1, 134.7, 133.1, 133.1, 132.8, 132.0, 130.1, 128.9, 128.2, 127.9, 125.9, 123.3, 122.6, 122.4, 97.1, 86.4, 34.6, 31.1, 19.3.

**_N_-(3-fluorophenyl)-_N_-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamide (1l)**[2]



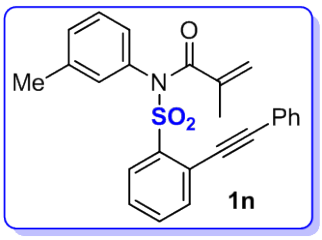

According to general procedure A with 3-fluoroaniline, **1l** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 50% yield (416 mg, brown solid, three steps). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.1 Hz, 1H; Ar-*H*), 7.70 (d, *J* = 7.5 Hz, 1H; Ar-*H*), 7.62 (t, *J* = 7.6 Hz, 1H; Ar-*H*), 7.55 (d, *J* = 7.9 Hz, 1H; Ar-*H*), 7.35 (dt, *J* = 14.3, 7.3 Hz, 5H; 5(Ar-*H*)), 7.15 (dd, *J* = 8.5, 7.4 Hz, 3H; 3(Ar-*H*)), 6.95-6.79 (m, 1H; Ar-*H*), 5.36 (s, 1H, C=CH*H*), 5.25 (s, 1H, C=CH*H*), 1.69 (s, 3H, $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.6, 162.3 (d, *J* = 248.6 Hz), 139.3, 138.9, 137.6, 134.7, 133.4, 132.9, 131.8, 129.8 (d, *J* = 8.9 Hz), 129.1, 128.2, 128.0, 126.3 (d, *J* = 3.5 Hz), 123.9, 122.4, 122.2, 118.1 (d, *J* = 23.1 Hz), 116.2 (d, *J* = 20.9 Hz), 97.4, 86.2, 19.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -111.14 (s).

**_N_-((2-(phenylethynyl)phenyl)sulfonyl)-_N_-(3-(trifluoromethyl)phenyl)methacrylamide (1m)**



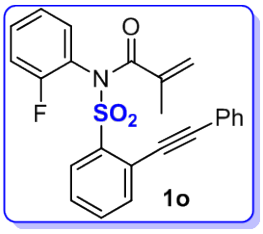

According to general procedure A with 3-(trifluoromethyl)aniline, **1m** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 33% yield (325 mg, white solid, three steps). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 8.0, 1.3 Hz, 1H; Ar-*H*), 7.69 (dd, *J* = 7.7, 1.5 Hz, 1H; Ar-*H*), 7.66-7.58 (m, 3H; 3(Ar-*H*)), 7.54 (td, *J* = 7.7, 1.5 Hz, 1H; Ar-*H*), 7.36 (ddt, *J* = 5.9, 4.4, 1.9 Hz, 2H; 2(Ar-*H*)), 7.32-7.23 (m, 5H; 5(Ar-*H*)), 5.36-5.32 (m, 1H; C=C*H*H), 5.26 (q, *J* = 1.6 Hz, 1H; C=CH*H*), 1.68 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.5, 139.3, 138.9, 137.2, 134.7, 133.8, 133.5, 132.9, 131.7, 131.4 (q, *J* = 33.1 Hz), 129.4, 129.1, 128.2, 128.1, 127.3 (q, *J* = 3.7 Hz), 125.6 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 273.7 Hz), 124.1, 122.4, 122.0, 97.5, 86.0, 19.1; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.79 (s); HRMS (ESI) exact mass calculated for $C_{25}H_{19}F_3NO_3S^+$ [M+H$^+$]: 470.1032, found: 470.1029; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1761, 1367, 1328, 1176, 1132, 759, 697, 592; m.p. 89-91 $^o$C.

***N*-((2-(phenylethynyl)phenyl)sulfonyl)-*N*-(*m*-tolyl)methacrylamide (1n)**[2]



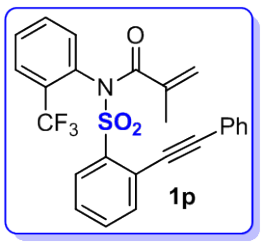

According to general procedure A with *m*-toluidine, **1n** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 50% yield (412 mg, brown solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H; Ar-*H*), 7.67 (dd, *J* = 7.9, 2.8 Hz, 1H; Ar-*H*), 7.58-7.51 (m, 1H; Ar-*H*), 7.52-7.43 (m, 1H; Ar-*H*), 7.39-7.26 (m, 5H; 5(Ar-*H*)), 7.23 (s, 1H; Ar-*H*), 7.18 (d, *J* = 8.1 Hz, 1H; Ar-*H*), 7.08 (td, *J* = 7.8, 2.2 Hz, 1H; Ar-*H*), 6.97 (d, *J* = 7.5 Hz, 1H; Ar-*H*), 5.32 (s, 1H; C=CH*H*), 5.15 (s, 1H; C=CH*H*), 2.03 (s, Ar-C$H_3$), 1.64 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 139.4, 139.2, 139.2, 135.9, 134.7, 133.3, 132.8, 131.9, 131.2, 130.1, 129.1, 128.7, 128.3, 128.0, 127.7, 123.3, 122.4, 122.3, 97.3, 86.4, 20.9, 19.3.

***N*-(2-fluorophenyl)-*N*-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamide (1o)**[2]




According to general procedure A with 2-fluoroaniline, **1o** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 37% yield (311 mg, brown solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 8.1, 1.4 Hz, 1H; Ar-*H*), 7.68 (dd, *J* = 7.7, 1.5 Hz, 1H; Ar-*H*), 7.65-7.47 (m, 3H; 3(Ar-*H*)), 7.38-7.31 (m, 1H; Ar-*H*), 7.30-7.21 (m, 4H; 4(Ar-*H*)), 7.10-7.02 (m, 1H; Ar-*H*), 6.95 (td, *J* = 7.8, 1.4 Hz, 1H; Ar-*H*), 6.88 (ddd, *J* = 9.7, 8.2, 1.4 Hz, 1H; Ar-*H*), 5.22 (s, 1H; C=CH*H*), 5.19 (d, *J* = 1.9 Hz, 1H; C=CH*H*), 1.73 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.5, 158.8 (d, *J* = 251.5 Hz), 139.5, 138.7, 138.7, 134.6, 133.3, 133.1, 132.8, 131.8, 130.9, 128.9, 128.0, 127.9, 125.2 (d, *J* = 12.8 Hz), 124.3 (d, *J* = 3.9 Hz), 122.8, 122.4 (d, *J* = 11.3 Hz), 116.2 (d, *J* = 20.2 Hz), 96.9, 86.3, 19.0; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -118.40 (s).

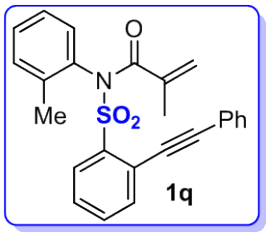
***N*-((2-(phenylethynyl)phenyl)sulfonyl)-*N*-(2-(trifluoromethyl)phenyl)methacrylamide (1p)**




According to general procedure A with 2-(trifluoromethyl)aniline, **1p** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 29% yield (290 mg, light yellow solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$)

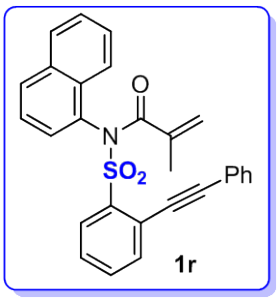
δ 8.42 (d, *J* = 8.0 Hz, 1H; Ar-*H*), 7.79-7.67 (m, 2H; 2(Ar-*H*)), 7.66-7.59 (m, 1H; Ar-*H*), 7.59-7.49 (m, 2H; 2(Ar-*H*)), 7.41-7.18 (m,7H; 7(Ar-*H*)), 5.25 (d, *J* = 1.9 Hz, 1H; C=C*H*H), 5.17 (s, 1H; C=CH*H*), 1.77 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 169.9, 139.1, 139.1, 134.7, 134.6, 133.7 (q, *J* = 1.8 Hz), 133.5, 133.4, 131.9, 131.9, 129.5, 129.2 (q, *J* = 30.5 Hz), 129.0, 128.1, 127.9, 127.9 (q, *J* = 4.5 Hz), 123.2, 123.2 (q, *J* = 274.1 Hz), 122.9, 122.3, 97.2, 86.7, 19.5; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -58.06 (s); HRMS (ESI) exact mass calculated for $C_{25}H_{19}F_3NO_3S^+$ [M+H$^+$]: 470.1032, found: 470.1026; IR (neat): $\nu_{max}$ ($cm^{-1}$) = 1699, 1370, 1315, 1176, 1138, 759, 595, 577; m.p. 122-123 °C.

***N*-((2-(phenylethynyl)phenyl)sulfonyl)-*N*-(*o*-tolyl)methacrylamide (1q)**[3]



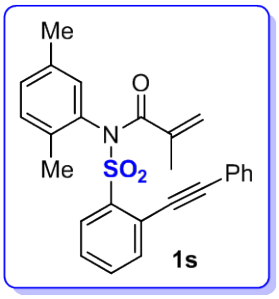

According to general procedure A with *o*-toluidine, **1q** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 50% yield (412 mg, brown solid, three steps). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.53-8.39 (m, 1H; Ar-*H*), 7.76-7.68 (m, 1H; Ar-*H*), 7.67-7.60 (m, 1H; Ar-*H*), 7.59-7.51 (m, 1H; Ar-*H*), 7.47 (d, *J* = 7.9 Hz, 1H; Ar-*H*), 7.39-7.33 (m, 1H; Ar-*H*), 7.32-7.23 (m, 4H; 4(Ar-*H*)), 7.11 (dt, *J* = 14.8, 7.5 Hz, 2H; 2(Ar-*H*)), 6.93 (t, *J* = 7.3 Hz, 1H; Ar-*H*), 5.24 (s, 1H; C=CH*H*), 5.17-5.06 (m, 1H; C=CH*H*), 2.37 (s, 3H; Ar-C$H_3$), 1.66 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.8, 139.5, 139.3, 138.6, 135.4, 134.6, 133.5, 133.2, 132.3, 132.0, 131.2, 129.3, 128.9, 128.1, 127.9, 126.3, 122.8, 122.5, 122.4, 97.3, 86.5, 19.3, 18.7.

***N*-(naphthalen-1-yl)-*N*-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamide (1r)**[3]



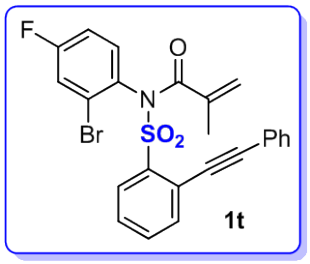

According to general procedure A with naphthalen-2-amine, **1r** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 62% yield (562 mg, light yellow solid, three steps). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.45 (dt, *J* = 8.1, 1.8 Hz, 1H; Ar-*H*), 7.85 (t, *J* = 2.4 Hz, 1H; Ar-*H*), 7.70 (dd, *J* = 7.8, 4.8 Hz, 2H; 2(Ar-*H*)), 7.63 (q, *J* = 8.0, 7.6 Hz, 2H; 2(Ar-*H*)), 7.59-7.52 (m, 3H; 3(Ar-*H*)), 7.44 (dt, *J* = 20.0, 7.1 Hz, 2H; 2(Ar-*H*)), 7.24 (tt, *J* = 8.5, 4.0 Hz, 1H; Ar-*H*), 7.18-7.06 (m, 4H; 4(Ar-*H*)), 5.40 (s, 1H; C=CH*H*), 5.16 (s, 1H; C=CH*H*), 1.67 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.1, 139.4, 139.3, 134.8, 133.7, 133.4, 133.1, 133.0, 131.7, 129.7, 128.9, 128.2, 128.1, 128.1, 128.1, 128.0, 127.7, 127.2, 126.7, 123.7, 122.4, 122.1, 97.4, 86.4, 86.4, 19.4.

***N*-(2,5-dimethylphenyl)-*N*-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamide (1s)**[3]



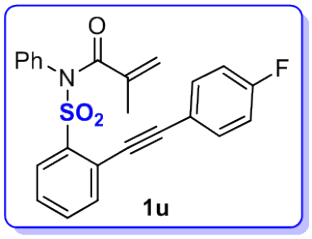

According to general procedure A with 2,5-dimethylaniline, **1s** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 77% yield (665 mg, brown solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 7.9, 1.4 Hz, 1H; Ar-*H*), 7.70 (dd, *J* = 7.7, 1.4 Hz, 1H; Ar-*H*), 7.61 (tt, *J* = 7.6, 1.3 Hz, 1H; Ar-*H*), 7.58-7.52 (m, 1H; Ar-*H*), 7.35 (ddd, *J* = 8.7, 5.2, 2.4 Hz, 1H; Ar-*H*), 7.31-7.21 (m, 5H; 5(Ar-*H*)), 7.04 (d, *J* = 7.7 Hz, 1H; Ar-*H*), 6.88 (dd, *J* = 7.8, 1.8 Hz, 1H; Ar-*H*), 5.23 (s, 1H; C=CH*H*), 5.13 (d, *J* = 1.9 Hz, 1H; C=CH*H*), 2.34 (s, 3H; Ar-C$H_3$), 1.88 (s, 3H; Ar-C$H_3$), 1.66 (s, $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.8, 139.7, 139.3, 136.3, 135.4, 135.2, 134.6, 133.5, 133.2, 132.6, 132.0, 130.9, 130.4, 128.9, 128.1, 127.8, 122.5, 122.4, 122.4, 97.2, 86.6, 20.3, 19.3, 18.3.

***N*-(2-bromo-4-fluorophenyl)-*N*-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamide (1t)**



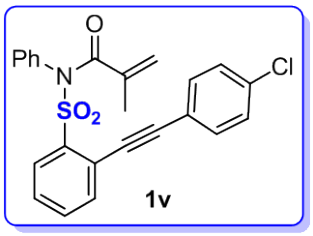

According to general procedure A with 2-bromo-4-fluoroaniline, **1t** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 67% yield (662 mg, brown solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 8.0, 1.5 Hz, 1H; Ar-*H*), 7.79-7.66 (m, 2H, 2(Ar-*H*)), 7.65-7.51 (m, 2H; 2(Ar-*H*)), 7.40-7.26 (m, 5H; 5(Ar-*H*)), 7.09 (dd, *J* = 7.8, 2.9 Hz, 1H; Ar-*H*), 6.80 (ddd, *J* = 8.9, 7.5, 2.9 Hz, 1H; Ar-*H*), 5.27 (q, *J* = 1.6 Hz, 1H; C=C*H*H), 5.25-5.19 (m, 1H; C=CH*H*), 1.83 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.0, 161.9 (d, *J* = 255.1 Hz), 139.5, 138.8, 135.1 (d, *J* = 9.2 Hz), 134.5, 133.5 (d, *J* = 2.1 Hz), 133.4, 132.9 (d, *J* = 3.8 Hz), 131.6, 129.1, 128.1, 127.9, 125.9 (d, *J* = 10.0 Hz), 123.8, 122.7, 122.2, 120.8, 120.5, 115.0 (d, *J* = 23.4 Hz), 97.0, 86.7, 19.4; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -(109.04-108.99) (m); HRMS (ESI) exact mass calculated for $C_{24}H_{18}BrFNO_3S^+$ [M+H$^+$]: 498.0169, found: 498.0168; IR (neat): $\nu_{max}$ ($cm^{-1}$) = 1700, 1483, 1370, 1180, 1120, 870, 759, 600; m.p. 102-104 $^{o}$C.

***N*-(naphthalen-1-yl)-*N*-((2-(phenylethynyl)phenyl)sulfonyl)methacrylamide (1u)**[3]



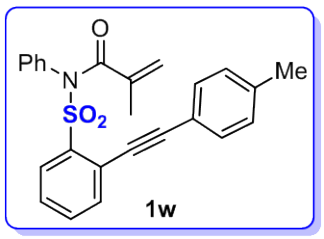

According to general procedure A with 1-ethynyl-4-fluorobenzene, **1u** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 59% yield (494 mg, yellow solid, three steps), $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.1 Hz, 1H; Ar-*H*), 7.71-7.64 (m, 1H; Ar-*H*), 7.60 (t, *J* = 7.2 Hz, 1H; Ar-*H* ), 7.57-7.49 (m, 1H; Ar-*H*), 7.37 (dd, *J* = 6.4, 3.2 Hz, 2H; 2(Ar-*H*)), 7.29 (dd, *J* = 8.6, 5.3 Hz, 2H; 2(Ar-*H*)), 7.25-7.13 (m, 3H; 3(Ar-*H*)), 7.00 (t, *J* = 8.6 Hz, 2H; 2(Ar-*H*)), 5.31 (s, 1H; C=CH*H*), 5.27 (s, 1H; C=CH*H*), 1.65 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR δ 170.9, 162.9 (d, *J* = 250.8 Hz), 139.5, 139.2, 136.4, 134.5, 133.9 (d, *J* = 8.5 Hz), 133.1 (d, *J* = 33.0 Hz), 130.6, 129.0, 128.9, 128.0, 123.4, 122.2, 118.5 (d, *J* = 3.7 Hz), 115.6, 115.4, 96.2, 86.2, 19.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -109.51 (s).

***N*-((2-((4-chlorophenyl)ethynyl)phenyl)sulfonyl)-*N*-phenylmethacrylamide (1v)**[3]




According to general procedure A with 1-chloro-4-ethynylbenzene, **1v** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 47% yield (406 mg, white solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 8.1, 1.4 Hz, 1H; Ar-*H*), 7.67 (dd, *J* = 7.7, 1.5 Hz, 1H; Ar-*H*), 7.60 (td, *J* = 7.5, 1.4 Hz, 1H; Ar-*H*), 7.53 (d, *J* = 1.5 Hz, 1H; Ar-*H*), 7.40-7.32 (m, 2H; 2(Ar-*H*)), 7.31-7.25 (m, 2H; 2(Ar-*H*)), 7.25-7.13 (m, 5H; 5(Ar-*H*)), 5.31 (s, 1H; C=C*H*H), 5.20 (d, *J* = 1.9 Hz, 1H; C=CH*H*), 1.65 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 139.5, 139.3, 136.4, 135.0, 134.5, 133.2, 133.1, 132.9, 130.6, 129.1, 128.9, 128.5, 128.2, 123.5, 122.1, 120.9, 95.9, 87.3, 19.2; HRMS (ESI) exact mass calculated for $C_{24}H_{19}ClNO_3S^+$ [M+H$^+$]: 436.0768, found: 436.0764; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1696, 1490, 1357, 1179, 1143, 763, 696, 586; m.p. 80-81 $^{o}$C.

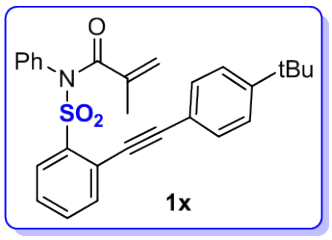
***N*-phenyl-*N*-((2-(p-tolylethynyl)phenyl)sulfonyl)methacrylamide (1w)**[3]




According to general procedure A with 1-ethynyl-4-methylbenzene, **1w** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 59% yield (490 mg, brown solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 8.1, 1.3 Hz, 1H; Ar-*H*), 7.69 (dd, *J* = 7.7, 1.4 Hz, 1H; Ar-*H*), 7.64-7.58 (m, 1H; Ar-*H*), 7.52 (td, *J* = 7.7, 1.5 Hz, 1H; Ar-*H*), 7.44-7.39

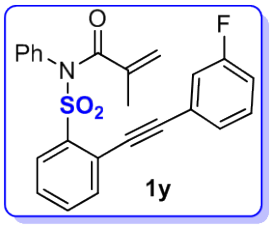
(m, 2H; 2(Ar-*H*)), 7.28 (d, *J* = 3.2 Hz, 1H; Ar-*H*), 7.26 (d, *J* = 1.7 Hz, 1H; Ar-*H*), 7.22 (dd, *J* = 5.3, 1.8 Hz, 3H; 3(Ar-*H*)), 7.15 (s, 1H; Ar-*H*), 7.13 (s, 1H; Ar-*H*), 5.37-5.20 (m, 1H; C=CH*H*), 5.19 (dd, *J* = 1.7, 0.8 Hz, 1H; C=CH*H*), 2.41 (s, 3H; Ar-C$H_3$), 1.67 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 139.5, 139.3, 138.8, 136.1, 134.7, 133.2, 132.8, 131.9, 130.7, 129.1, 129.0, 127.8, 123.3, 122.6, 119.4, 97.8, 85.8, 21.6, 19.3.

**_N_-((2-((4-(*tert*-butyl)phenyl)ethynyl)phenyl)sulfonyl)-_N_-phenylmethacrylamide (1x)**[3]




According to general procedure A with 1-(*tert*-butyl)-4-ethynylbenzene, **1x** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 68% yield (618 mg, white solid, three steps). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 8.1, 1.4 Hz, 1H; Ar-*H*), 7.70 (dd, *J* = 7.7, 1.4 Hz, 1H; Ar-*H*), 7.63-7.56 (m, 1H; Ar-*H*), 7.51 (td, *J* = 7.7, 1.4 Hz, 1H; Ar-*H*), 7.46-7.41 (m, 2H; 2(Ar-*H*)), 7.39-7.30 (m, 4H; 4(Ar-*H*)), 7.21 (dd, *J* = 5.2, 1.9 Hz, 3H; 3(Ar-*H*)), 5.34 (s, 1H, C=CH*H*), 5.19 (d, *J* = 1.9 Hz, 1H; C=CH*H*), 1.67 (s, 3H; $CH_2$=CC$H_3$), 1.37 (s, 9H; Ar-C(C$H_3$)$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 152.5, 139.5, 138.9, 136.1, 134.8, 133.2, 132.8, 131.7, 130.7, 129.1, 130.0, 127.8, 125.2, 123.3, 122.6, 119.4, 97.8, 85.8, 34.9, 31.2, 19.3.

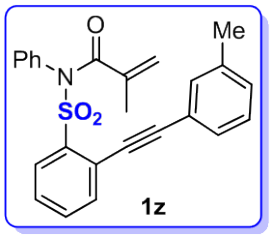
**_N_-((2-((3-fluorophenyl)ethynyl)phenyl)sulfonyl)-_N_-phenylmethacrylamide (1y)**[3]




According to general procedure A with 1-ethynyl-3-fluorobenzene, **1y** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 75% yield (629 mg, yellow solid, three steps). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 8.0, 1.4 Hz, 1H; Ar-*H*), 7.67 (dd, *J* = 7.7, 1.5 Hz, 1H; Ar-*H*), 7.60 (td, *J* = 7.6, 1.4 Hz, 1H; Ar-*H*), 7.53 (td, *J* = 7.7, 1.5 Hz, 1H; Ar-*H*), 7.36 (td, *J* = 6.1, 5.2, 3.3 Hz, 2H; 2(Ar-*H*)), 7.29-7.15 (m, 4H; 4(Ar-*H*)), 7.11 (d, *J* = 7.7 Hz, 1H; Ar-*H*), 7.05 (td, *J* = 8.5, 2.6 Hz, 1H; Ar-*H*), 6.95 (dt, *J* = 9.4, 1.9 Hz, 1H; Ar-*H*), 5.31 (s, 1H; C=CH*H*), 5.19 (d, *J* = 1.9 Hz, 1H, C=CH*H*), 1.65 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 162.1 (d, *J* = 246.6 Hz), 139.4 (d, *J* = 4.6 Hz), 136.4, 134.6, 133.3, 132.9, 130.5, 129.8 (d, *J* = 8.6 Hz), 129.1, 129.0, 128.3, 127.8 (d, *J* = 3.1 Hz),

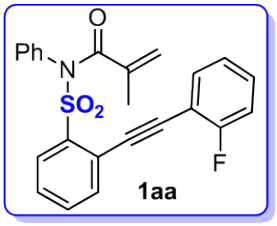
124.2 (d, *J* = 9.5 Hz), 123.6, 121.9, 118.8, 118.5, 116.3 (d, *J* = 21.2 Hz), 95.6, 87.2, 19.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -112.68 (s).

**_N_-phenyl-_N_-((2-(m-tolylethynyl)phenyl)sulfonyl)methacrylamide (1z)**[3]



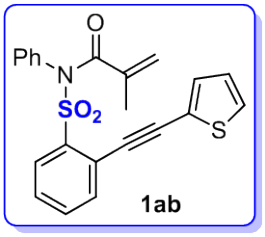

According to general procedure A with 1-ethynyl-3-methylbenzene, **1z** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 69% yield (574 mg, brown solid, three steps). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.0 Hz, 1H; Ar-*H*), 7.70 (d, *J* = 7.6 Hz, 1H; Ar-*H*), 7.60 (t, *J* = 7.5 Hz, 1H; Ar-*H*), 7.56-7.50 (m, 1H; Ar-*H*), 7.46-7.37 (m, 2H; 2(Ar-*H*)), 7.21 (dd, *J* = 6.8, 3.1 Hz, 6H; 6(Ar-*H*)), 7.15 (s, 1H; Ar-*H*), 5.32 (s, 1H, C=CH*H*), 5.26-5.11 (m, 1H, C=CH*H*), 2.35 (s, 3H; Ar-C$H_3$), 1.66 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 139.5, 139.1, 137.8, 136.2, 134.7, 133.2, 132.9, 132.5, 130.7, 129.9, 129.0, 123.0, 128.9, 128.1, 127.9, 123.3, 122.5, 122.2, 97.7, 86.0, 21.2, 19.3.

**_N_-((2-((2-fluorophenyl)ethynyl)phenyl)sulfonyl)-_N_-phenylmethacrylamide (1aa)**[3]



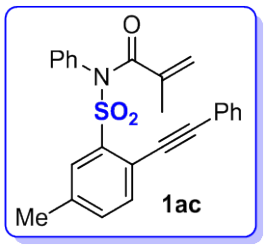

According to general procedure A with 1-ethynyl-2-fluorobenzene, **1aa** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 77% yield (644 mg, yellow solid, three steps). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 7.9, 1.7 Hz, 1H; Ar-*H*), 7.68 (dt, *J* = 7.0, 2.6 Hz, 1H; Ar-*H*), 7.58 (dt, *J* = 4.8, 3.1 Hz, 1H; Ar-*H*), 7.5 (qd, *J* = 7.1, 5.2, 2.6 Hz, 1H; Ar-*H*), 7.35 (ddd, *J* = 20.3, 6.8, 2.2 Hz, 3H; 3(Ar-*H*)), 7.23 (td, *J* = 7.4, 1.7 Hz, 1H; Ar-*H*), 7.20-7.10 (m, 3H; 3(Ar-*H*)), 7.06 (dt, *J* = 9.8, 5.4 Hz, 2H; 2(Ar-*H*)), 5.33 (s, 1H; C=CH*H*), 5.25-5.10 (m, 1H; C=CH*H*), 1.63 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 162.4 (d, *J* = 252.7 Hz), 139.4, 139.2, 136.3, 134.9, 134.0, 133.3, 132.7, 131.0 (d, *J* = 10.7 Hz), 130.5, 129.0 (d, *J* = 1.2 Hz), 128.9, 128.4, 124.0 (dd, *J* = 3.5 Hz, 2.3 Hz), 123.7, 121.9, 115.4 (d, *J* = 20.5 Hz), 111.1 (d, *J* = 16.2 Hz), 91.0, 90.6, 19.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -108.97 (s).

***N*-phenyl-*N*-((2-(thiophen-2-ylethynyl)phenyl)sulfonyl)methacrylamide (1ab)**[3]



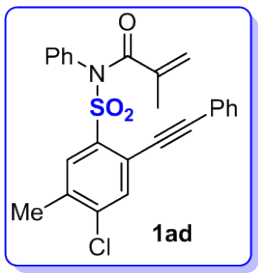

According to general procedure A with 2-ethynylthiophene, **1ab** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 41% yield (330 mg, white solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 8.1, 1.4 Hz, 1H; Ar-*H*), 7.68 (dd, *J* = 7.7, 1.4 Hz, 1H; Ar-*H*), 7.61 (td, *J* = 7.5, 1.4 Hz, 1H; Ar-*H*), 7.54 (td, *J* = 7.7, 1.5 Hz, 1H; Ar-*H*), 7.45-7.40 (m, 2H; 2(Ar-*H*)), 7.36 (dd, *J* = 5.2, 1.1 Hz, 1H; Ar-*H*), 7.31-7.25 (m, 3H; 3(Ar-*H*)), 7.17 (dd, *J* = 3.6, 1.1 Hz, 1H; Ar-*H*), 5.37 (s, 1H; C=CH*H*), 5.21 (d, *J* = 1.9 Hz, 1H; C=CH*H*), 1.68 (t, *J* = 1.2 Hz, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 139.4, 138.7, 136.0, 134.6, 133.3, 133.2, 132.7, 130.6, 129.1, 129.0, 128.5, 128.1, 127.1, 123.6, 122.3, 122.0, 90.7, 89.9, 19.3.

***N*-((5-methyl-2-(phenylethynyl)phenyl)sulfonyl)-*N*-phenylmethacrylamide (1ac)**[3]




According to general procedure A with 2-iodo-5-methylbenzene-1-sulfonyl chloride, **1ac** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 75% yield (621 mg, brown solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 1.8 Hz, 1H; Ar-*H*), 7.59 (d, *J* = 7.8 Hz, 1H; Ar-*H*), 7.42 (dd, *J* = 6.5, 3.7 Hz, 3H; 3(Ar-*H*)), 7.35 (q, *J* = 6.8, 6.2 Hz, 5H; 5(Ar-*H*)), 7.20 (dd, *J* = 5.2, 2.0 Hz, 3H; 3(Ar-*H*)), 5.33 (s, 1H; C=CH*H*), 5.24-5.15 (m, 1H; C=CH*H*), 2.50 (s, 3H; Ar-C$H_3$), 1.66 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.0, 139.5, 138.8, 138.7, 136.1, 134.7, 134.1, 133.1, 131.9, 1307, 129.1, 128.9, 128.8, 128.2, 123.2, 122.6, 119.3, 96.4, 86.4, 21.5, 19.3.

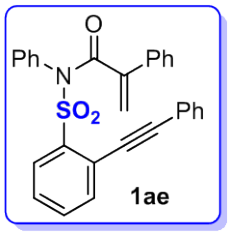
***N*-((4-chloro-5-methyl-2-(phenylethynyl)phenyl)sulfonyl)-*N*-phenylmethacrylamide (1ad)**[3]




According to general procedure A with 4-chloro-2-iodo-5-methylbenzene-1-sulfonyl chloride, **1ad** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 36% yield (326 mg, light yellow solid, three steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H; Ar-*H*), 7.68 (s, 1H; Ar-*H*), 7.50-7.27 (m, 7H; 7(Ar-*H*)), 7.19 (d, *J* = 5.0 Hz, 3H; 3(Ar-*H*)), 5.33 (s, 1H;

C=CH*H*), 5.20 (s, 1H; C=CH*H*), 2.53 (s, 3H; Ar-C$H_3$), 1.67 (s, 3H; $CH_2$=CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.0, 139.8, 139.4, 137.2, 136.9, 136.1, 134.9, 134.6, 131.9, 130.6, 129.1, 129.1, 129.0, 128.2, 123.6, 122.2, 121.1, 97.3, 85.2, 20.2, 19.2.

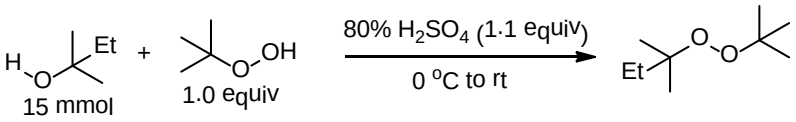
***N*,2-diphenyl-*N*-((2-(phenylethynyl)phenyl)sulfonyl)acrylamide (1ae)**[2]




According to general procedure A with 2-phenylacryloyl chloride, **1ae** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1, v:v) as an eluent and obtained in 41% yield (382 mg, yellow solid, three steps). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.0 Hz, 1H; Ar-*H*), 7.75 (d, *J* = 7.6 Hz, 1H; Ar-*H*), 7.66 (t, *J* = 7.5 Hz, 1H; Ar-*H* ), 7.59 (t, *J* = 7.7 Hz, 1H; Ar-*H*), 7.34 (t, *J* = 7.0 Hz, 1H; Ar-*H*), 7.30-7.19 (m, 4H; 4(Ar-*H*)), 7.16 (q, *J* = 7.3 Hz, 3H; 3(Ar-*H*)), 7.08 (d, *J* = 7.8 Hz, 2H; 2(Ar-*H*)), 7.03 (d, *J* = 7.4 Hz, 1H; Ar-*H* ), 6.98-6.86 (m, 4H; 4(Ar-*H*)), 5.59 (s, 1H; C=CH*H*), 5.44 (s, 1H; C=CH*H*); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 169.9, 145.3, 139.4, 135.5, 134.9, 134.6, 133.3, 133.3, 132.0, 131.3, 129.0, 128.7, 128.4, 128.3, 128.2, 128.1, 128.0, 126.2, 122.4, 122.3, 121.3, 97.6, 86.4.

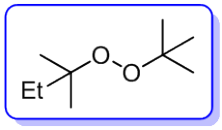
**3.2** Synthesis of alkylated reagents:

**3.2.1** General procedure B1[4]:



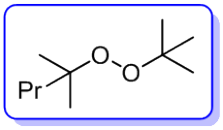

To a aqueous solution of 80% $H_2SO_4$ (21 g, 1.1 equiv) was added *tert*-amyl alcohol (15 mmol) dropwise below 10 °C, then the solution was kept at 0 °C for 15 min, added dropwise by *tert*-butyl hydroperoxide (1.5 g, 1.0 equiv, 70% in water), and stirred for 2 hours to complete the reaction. The oil layer was separated from the reaction mixture, washed with 10% aqueous NaOH, dried with anhydrous $Na_2SO_4$ and distilled at reduced pressure to give *tert*-butyl *tert*-amyl peroxide in 77% yield (1.85 g, colorless oil).

***tert*-Butyl *tert*-amyl peroxide**[4]



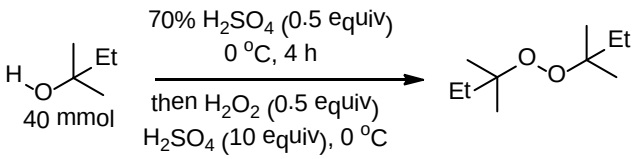

$^1$H NMR (400 MHz, $CDCl_3$) δ 1.56 (q, *J* = 7.5 Hz, 2H; C$H_2$CH$_3$), 1.23 (s, 9H; C(C$H_3$)$_3$), 1.18 (s, 6H; C(C$H_3$)$_2$CH$_2$CH$_3$), 0.89 (t, *J* = 7.6 Hz, 3H; CH$_2$C$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 80.3, 78.0, 32.0, 26.6, 24.0, 8.4.

***tert*-Butyl 1,1-dimethylbutyl peroxide**[4]



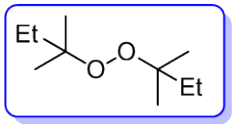
According to general procedure B1 with 2-methyl-2-pentanol, *tert*-butyl 1,1-dimethylbutyl peroxide was obtained in 59% yield (1.54 g, colorless oil). $^1$H NMR (400 MHz, $CDCl_3$) δ 1.53-1.45 (m, 2H; $CH_2CH_2CH_3$), 1.42-1.31 (m, 2H; $CH_2CH_2CH_3$), 1.21 (s, 9H; $C(CH_3)_3$), 1.18 (s, 6H; $C(CH_3)_2Pr$), 0.91 (t, $J$ = 7.3 Hz, 3H; $CH_2CH_2CH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 80.1, 78.0, 41.9, 26.6, 24.5, 17.3, 14.6.

**3.2.2** General procedure B2[5]:



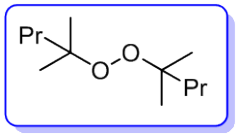

A 10 mL two necked bottle was equipped with a rubber septum and magnetic stir bar and charged with *tert*-amyl alcohol (40 mmol) and concentrated sulfuric acid (3.0 g, 0.5 equiv) at 0 °C. The mixture was stirred vigorously for 4 hours at 0 °C. Then hydrogen peroxide (30%, 3.0 g, 0.5 equiv) and concentrated sulfuric acid (8.5 g, 10 equiv) were to the reaction mixture *dropwise* at 0 °C. When the reaction system became into two layers, the organic layer was then seperated, washed with water, dried over anhydrous $Na_2SO_4$, and distilled under reduced pressure to give di-*tert*-amyl peroxide in 43% yield (1.23 g, colorless oil).

**di-*tert*-Amyl peroxide**[5]



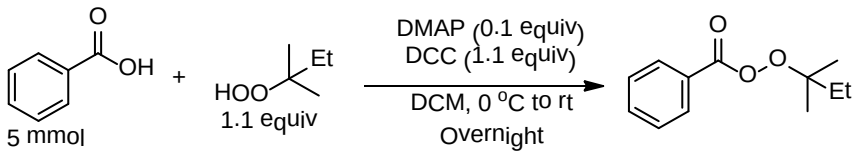
$^1$H NMR (400 MHz, $CDCl_3$) δ 1.57 (q, $J$ = 6.8 Hz, 4H; $2(CH_2CH_3)$), 1.18 (s, 12H; $2(C(CH_3)_2)$), 0.90 (t, $J$ = 6.8 Hz, 6H; $2(CH_2CH_3)$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 80.2, 31.9, 24.1, 8.3.

**di-*iso*-Hexyl peroxide**[5]

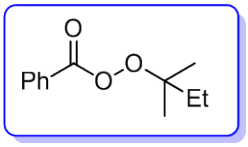


According to general procedure B2 with 2-methyl-2-pentanol (25 mmol), di-*iso*-hexyl peroxide was obtained in 28% yield (470 mg, colorless oil). $^1$H NMR (400 MHz, $CDCl_3$) δ 1.51 (t, $J$ = 7.8 Hz, 4H; $2(CH_2CH_2CH_3)$), 1.41-1.30 (m, 4H; $2(CH_2CH_2CH_3)$), 1.19 (s, 12H; $2(C(CH_3)_2)$, 0.93 (t, $J$ = 7.2 Hz, 6H; $2(CH_2CH_2CH_3)$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 80.1, 41.9, 24.6, 17.3, 14.7.

**3.3** Synthesis of *tert*-amyl peroxybenzoate[6]:

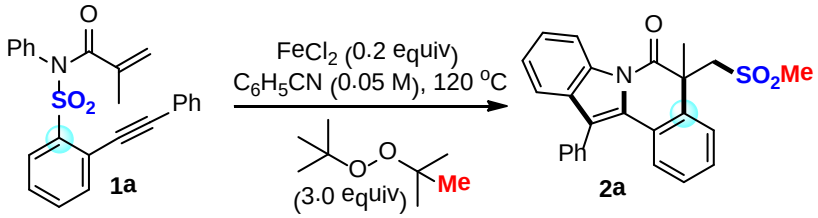


A solution of phenyl carboxylic acid (5 mmol) and DMAP (0.5 mmol, 0.1 equiv) in $CH_2Cl_2$ (4 mL) was cooled to 0 $^oC$ and *tert*-amyl hydroperoxide (5.5 mmol, 1.1 equiv, 30% in water) was added *dropwise*. The reaction mixture was stirred for 10 min. DCC (5.5 mmol, 1.1 equiv) was added to the reaction mixture. The resulting mixture was stirred at 0 $^oC$ for 30 min, then warmed to room temperature and stirred overnight. The reaction solution was then filtered. The filtrate was concentrated in vacuo and purified by flash column chromatography (petroleum ether and ethyl acetate, 20:1, v:v) to afford the ***tert*-amyl peroxybenzoate**[6] in 78% yield (811 mg, colorless oil).



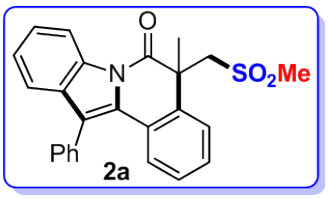

$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H, 2(Ar-*H*)), 7.60 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.47 (t, *J* = 7.7 Hz, 2H, 2(Ar-*H*)), 1.76 (q, *J* = 7.5 Hz, 2H, $CH_2CH_3$), 1.38 (s, 6H, $C(CH_3)_2$), 1.01 (t, *J* = 7.5 Hz, 3H, $CH_2CH_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 164.3, 133.3, 129.0, 128.6, 127.8, 86.2, 31.6, 23.8, 8.3.

**4.** Synthesis of **2a**-**2ae**: general procedure C



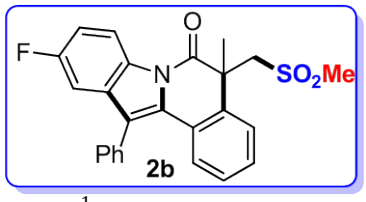

A 10 mL sealed tube was equipped with a rubber septum and magnetic stirring bar, and charged with **1a** (0.2 mmol), $FeCl_2$ (0.04 mmol, 0.2 equiv). The tube was evacuated and backfilled with argon for 3 times, DTBP (0.6 mmol, 3.0 equiv) and $C_6H_5CN$ (4.0 mL) were added under argon. The mixture was then sealed and heated 120 $^oC$ overnight. After completion (detected by TLC), the mixture was cooled to room temperature and purified directly by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as eluent. **2a** was obtained in 82% yield (67 mg, white solid).

**5-Methyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2a)**




$^1H$ NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.61-7.45 (m, 8H; 8(Ar-*H*)), 7.37-7.32 (m 3H; 3(Ar-*H*)), 7.10 (t, *J* = 7.7 Hz, 1H; Ar-*H*), 4.48 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 3.93 (d, *J* = 14.7 Hz, 1H; CH*H*SO$_2$), 2.73 (s, 3H; SO$_2$C*H*$_3$), 1.78 (s, 3H; CC*H*$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 170.9, 135.4, 134.3, 133.9, 132.4, 130.2, 129.3, 129.1, 128.5, 128.2, 127.6, 126.2, 126.1, 125.9, 125.3, 124.8, 121.3, 119.7, 116.7, 62.9, 47.1, 44.1, 31.1; HRMS (ESI) exact mass calculated for $C_{25}H_{22}NO_3S^+$ [M+H$^+$]: 416.1315, found: 416.1321; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1695, 1450, 1392, 1365, 1308, 1126, 753, 703; m.p. 105-107 $^oC$.

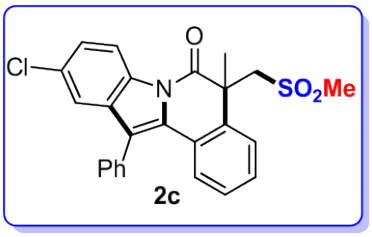
**10-Fluoro-5-methyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2b)**




According to general procedure C with **1b**, **2b** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 71% yield (62 mg, white solid). $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 9.0, 4.6 Hz, 1H; Ar-*H*), 7.61-7.47 (m, 8H; 8(Ar-*H*)), 7.36 (s, 1H; Ar-*H*), 7.18-7.05 (m, 2H; 2(Ar-*H*)), 6.97 (dd, *J* = 8.7, 2.5 Hz, 1H; Ar-*H*), 4.47 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 3.94 (d, *J* = 14.7 Hz, 1H; CH*H*SO$_2$), 2.71 (s, 3H; SO$_2$C*H*$_3$), 1.77 (s, 3H; CC*H*$_3$); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 170.8, 160.6 (d, *J* = 242.0 Hz), 135.5, 133.8 (d, *J* = 9.9 Hz), 133.4, 130.6 (d, *J* = 1.2

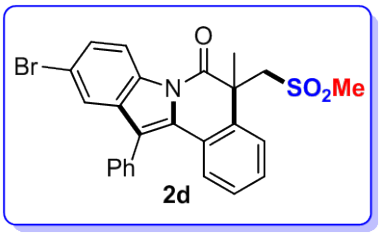
Hz), 130.5, 130.1, 129.4, 128.7, 128.5, 127.7, 126.1, 126.0, 125.0, 120.8 (d, *J* = 4.3 Hz), 117.9 (d, *J* = 9.0 Hz), 113.8, 113.5, 105.4 (d, *J* = 24.5 Hz), 63.0, 46.9, 44.1, 31.1; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -(117.31-117.37) (m); HRMS (ESI) exact mass calculated for $C_{25}H_{21}FNO_3S^+$ [M+H$^+$]: 434.1220, found: 434.1212; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1694, 1446, 1366, 1304, 1168, 1124, 734, 701; m.p. 105-107 $^oC$.

**10-Chloro-5-methyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinoli n-6(5*H*)-one (2c)**



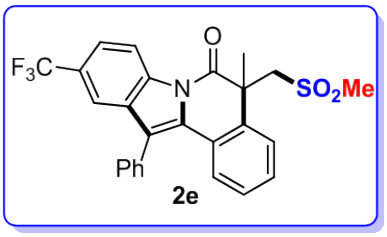

According to general procedure C with **1c**, **2c** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 76% yield (69 mg, white solid). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.7 Hz, 1H; Ar-*H*), 7.62-7.44 (m, 7H; 7(Ar-*H*)), 7.40-7.34 (m 2H; 2(Ar-*H*)), 7.27 (d, *J* = 2.1 Hz, 1H; Ar-*H*), 7.14-7.08 (m, 1H; Ar-*H*), 4.45 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 3.93 (d, *J* = 14.8 Hz, 1H; CH*H*SO$_2$), 2.69 (s, 3H; SO$_2$C*H*$_3$), 1.77 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 135.5, 133.8, 133.2, 132.6, 130.6, 130.3, 130.1, 129.5, 128.8, 128.5, 127.7, 126.1, 126.1, 126.1, 124.9, 120.3, 119.2, 117.7, 63.0, 46.9, 44.1, 31.0; HRMS (ESI) exact mass calculated for $C_{25}H_{21}ClNO_3S^+$ [M+H$^+$]: 450.0925, found: 450.0934; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1699, 1446, 1392, 1365, 1309, 1127, 763, 713; m.p. 92-94 $^oC$.

**10-Bromo-5-methyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinoli n-6(5*H*)-one (2d)**



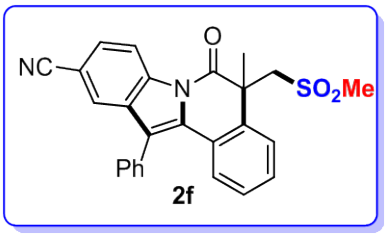

According to general procedure C with **1d**, **2d** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 89% yield (88 mg, white solid). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.7 Hz, 1H; Ar-*H*), 7.66-7.42 (m, 9H; 9(Ar-*H*)), 7.36 (t, *J* = 7.6 Hz, 1H; Ar-*H*), 7.11 (t, *J* = 7.7 Hz, 1H; Ar-*H*), 4.45 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 3.94 (d, *J* = 14.8 Hz, 1H; CH*H*SO$_2$), 2.69 (s, 3H; SO$_2$C*H*$_3$), 1.77 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.0, 135.5, 134.2, 133.2, 133.0, 130.2, 130.1, 129.5, 128.9, 128.8, 128.5, 127.7, 126.2, 126.1, 124.9, 122.3, 120.2, 118.3, 118.1, 63.0, 47.0, 44.1, 31.0; HRMS (ESI) exact mass calculated for $C_{25}H_{21}BrNO_3S^+$ [M+H$^+$]: 494.0420, found: 494.0407; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1698, 1444, 1390, 1364, 1308, 1266, 1127, 706; m.p. 128-130 $^oC$.

**5-Methyl-5-((methylsulfonyl)methyl)-12-phenyl-10-(trifluoromethyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (2e)**



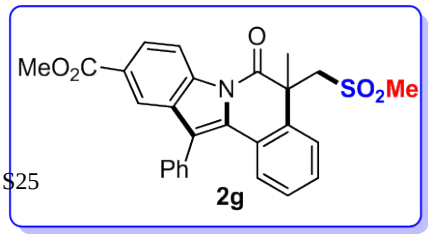

According to general procedure C with **1e**, **2e** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 66% yield (64 mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.6 Hz, 1H; Ar-*H*), 7.69 (dd, *J* = 8.7, 1.8 Hz, 1H; Ar-*H*), 7.65-7.46 (m, 8H; 8(Ar-*H*)), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H; Ar-*H*), 7.16-7.09 (m, 1H; Ar-*H*), 4.47 (d, *J* = 14.7 Hz, 1H; CH*H*$SO_2$), 3.96 (d, *J* = 14.7 Hz, 1H; C*H*H$SO_2$), 2.71 (s, 3H; $SO_2CH_3$), 1.79 (s, 3H; $CCH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.3, 135.8, 135.4, 133.0, 132.3, 130.7, 130.1, 129.6, 129.0, 128.7, 127.8, 127.1 (q, *J* = 32.2 Hz), 126.2, 126.2, 124.8, 124.5 (q. *J* = 273.1), 122.8 (q, *J* = 3.5 Hz), 120.8, 117.0, 116.9 (q, *J* = 4.1 Hz), 63.1, 47.1, 44.1, 31.0; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.27 (s); HRMS (ESI) exact mass calculated for $C_{26}H_{21}F_3NO_3S^+$ [M+H$^+$]: 484.1189, found: 484.1194; IR (neat): $\nu_{max}$ ($cm^{-1}$) = 1702, 1392, 1308, 1273, 1119, 1058, 737, 703; m.p. 111-112 $^{o}$C.

**5-Methyl-5-((methylsulfonyl)methyl)-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-*a*]isoquinoline-10-carbonitrile (2f)**




According to general procedure C with **1f**, **2f** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 76% yield (68 mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.5 Hz, 1H; Ar-*H*), 7.68 (dd, *J* = 8.5, 1.6 Hz, 1H; Ar-*H*), 7.64-7.48 (m, 8H; 8(Ar-*H*)), 7.40 (td, *J* = 7.6, 1.3 Hz, 1H; Ar-*H*), 7.14 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H; Ar-*H*), 4.45 (d, *J* = 14.7 Hz, 1H; CH*H*$SO_2$), 3.97 (d, *J* = 14.8 Hz, 1H; CH*H*$SO_2$), 2.69 (s, 3H; $SO_2CH_3$), 1.79 (s, 3H; $CCH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.4, 136.1, 135.5, 132.6, 132.5, 131.2, 130.0, 129.6, 129.3, 129.1, 128.8, 127.9, 126.3, 126.3, 124.5, 124.3, 120.2, 119.4, 117.5, 108.2, 63.1, 47.1, 44.1, 31.0; HRMS (ESI) exact mass calculated for $C_{26}H_{21}N_2O_3S^+$ [M+H$^+$]: 441.1267, found: 441.1271; IR (neat): $\nu_{max}$ ($cm^{-1}$) = 1705, 1460, 1391, 1362, 1307, 1128, 732, 702; m.p. 134-136 $^{o}$C.

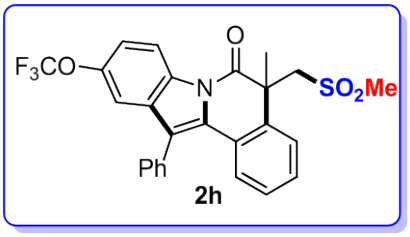
**5-Methyl-5-((methylsulfonyl)methyl)-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-*a*]isoquinoline-10-carboxylate (2g)**




According to general procedure C with **1g**, **2g** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to

3:1, v:v) as an eluent and obtained in 70% yield (67 mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.6 Hz, 1H; Ar-*H*), 8.14 (dd, *J* = 8.6, 1.7 Hz, 1H; Ar-*H*), 8.02 (d, *J* = 1.7 Hz, 1H; Ar-*H*), 7.65-7.45 (m, 7H; 7(Ar-*H*)), 7.37 (dd, *J* = 7.5, 1.3 Hz, 1H; Ar-*H*), 7.16-7.05 (m, 1H; Ar-*H*), 4.46 (d, *J* = 14.8 Hz, 1H; C*H*HSO$_2$), 3.95 (m, 4H; CH*H*SO$_2$ and Ar-CO$_2$CC*H*$_3$), 2.70 (s, 3H; SO$_2$C*H*$_3$), 1.78 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.2, 167.2, 136.9, 135.4, 133.2, 132.3, 130.3, 130.2, 129.5, 128.8, 128.5, 127.7, 127.4, 126.7, 126.1, 124.9, 121.6, 121.2, 116.4, 63.0, 52.1, 47.1, 44.1, 31.0; HRMS (ESI) exact mass calculated for $C_{27}H_{24}NO_5S^+$ [M+H$^+$]: 474.1370, found: 474.2078; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1705, 1391, 1300, 1256, 1225, 1127, 757, 705; m.p. 128-130 $^{o}$C.

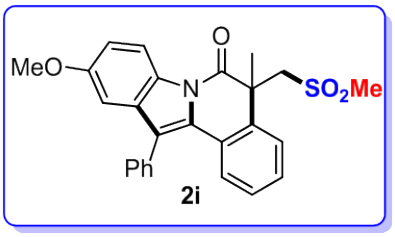
**5-Methyl-5-((methylsulfonyl)methyl)-12-phenyl-10-(trifluoromethoxy)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (2h)**



**2h**

According to general procedure C with **1h**, **2h** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 78% yield (78 mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.9 Hz, 1H; Ar-*H*), 7.76-7.42 (m, 7H; 7(Ar-*H*)), 7.38 (t, *J* = 7.6 Hz, 1H; Ar-*H*), 7.30 (dd, *J* = 9.5, 2.6 Hz, 1H; Ar-*H*), 7.18-7.06 (m, 2H; Ar-*H* ), 4.47 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 3.95 (d, *J* = 14.7 Hz, 1H; CH*H*SO$_2$), 2.71 (s, 3H; SO$_2$C*H*$_3$), 1.78 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.0, 146.5 (q, *J* = 2.0 Hz), 135.5, 133.5, 133.1, 132.5, 130.8, 130.1, 129.5, 128.9, 128.6, 127.7, 126.1, 126.1, 124.9, 120.6 (q, J = 257.7 Hz), 119.2, 117.7, 112.1, 63.0, 46.9, 44.1, 31.0; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -57.91 (s); HRMS (ESI) exact mass calculated for $C_{26}H_{21}F_3NO_4S^+$ [M+H$^+$]: 500.1138, found: 500.1143; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1699, 1448, 1248, 1216, 1162, 1126, 738, 703; m.p. 101-103 $^{o}$C.

**10-Methoxy-5-methyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2i)**

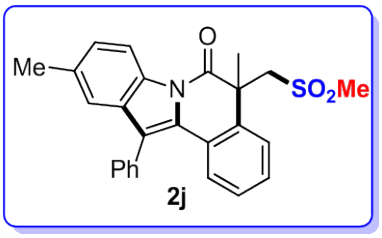


**2i**

According to general procedure C with **1i**, **2i** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 84% yield (75 mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.9 Hz, 1H; Ar-*H*), 7.69-7.50 (m, 5H; 5(Ar-*H*)), 7.46 (dt, *J* = 8.1, 1.5 Hz, 2H; Ar-*H*), 7.36-7.30 (m, 1H; Ar-*H*), 7.15-6.99 (m, 2H; Ar-*H*), 6.75 (d, *J* = 2.5 Hz, 1H;

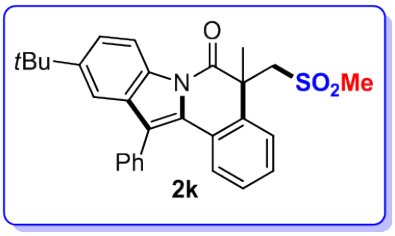
Ar-*H* ), 4.46 (d, *J* = 14.7 Hz, 1H; CH*H*$SO_2$), 3.91 (d, *J* = 14.7 Hz, 1H; C*H*H$SO_2$), 3.81 (s, 3H; Ar-OC$H_3$), 2.70 (s, 3H; $SO_2$C$H_3$), 1.76 (s, 3H; CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.5, 135.5, 133.9, 133.5, 130.2, 129.7, 129.4, 128.9, 128.4, 128.3, 127.5, 126.1, 125.8, 125.3, 121.1, 117.5, 114.4, 102.4, 62.9, 55.8, 46.8, 44.0, 31.1; HRMS (ESI) exact mass calculated for $C_{26}H_{24}NO_4S^+$ [M+H$^+$]: 446.1420, found: 446.1414; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1689, 1441, 1397, 1306, 1265, 1126, 732, 701; m.p. 134-136 $^o$C.

**5,10-Dimethyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2j)**




According to general procedure C with **1j**, **2j** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 61% yield (52 mg, white solid). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.4 Hz, 1H; Ar-*H*), 7.64-7.41 (m, 7H; 7(Ar-*H*)), 7.37-7.30 (m, 1H; Ar-*H*), 7.30-7.22 (m, 1H; Ar-*H*), 7.14-7.01 (m, 2H; 2(Ar-*H*)), 4.47 (d, *J* = 14.7 Hz, 1H; C*H*H$SO_2$), 3.92 (d, *J* = 14.8 Hz, 1H; CH*H*$SO_2$), 2.72 (s, 3H; $SO_2$C$H_3$), 2.43 (s, 3H; Ar-C$H_3$), 1.77 (s, 3H; CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.6, 135.4, 134.6, 134.0, 132.6, 132.5, 130.2, 129.3, 129.1, 128.3, 128.2, 127.5, 127.4, 126.0, 125.9, 125.4, 121.1, 119.5, 116.3, 62.9, 47.0, 44.1, 31.1, 21.5; HRMS (ESI) exact mass calculated for $C_{26}H_{24}NO_3S^+$ [M+H$^+$]: 430.1471, found: 430.1464; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1693, 1453, 1394, 1366, 1308, 1128, 736, 702; m.p. 119-121 $^o$C.

**10-(*tert*-butyl)-5-methyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2k)**

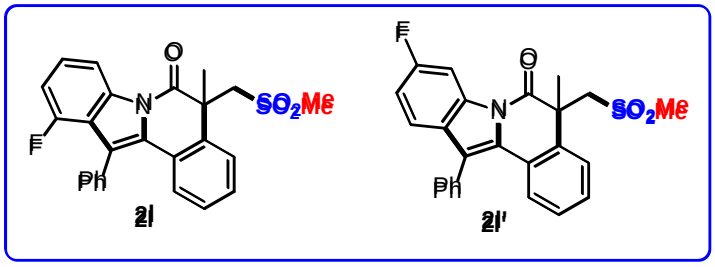



According to general procedure C with **1k**, **2k** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 72% yield (66 mg, white solid). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.7 Hz, 1H; Ar-*H*), 7.70-7.52 (m, 6H; 6(Ar-*H*)), 7.50 (ddd, *J* = 7.9, 4.8, 1.2 Hz, 2H; 2(Ar-*H*)), 7.40-7.30 (m, 2H; 2(Ar-*H*)), 7.10 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H; Ar-*H*), 4.48 (d, *J* = 14.7 Hz, 1H; C*H*H$SO_2$), 3.97 (d, *J* = 14.8 Hz, 1H; CH*H*$SO_2$), 2.70 (s, 3H; $SO_2$C$H_3$), 1.77 (s, 3H; CC$H_3$), 1.39 (s, 9H; Ar-(C$H_3$)$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.7, 148.2, 135.4, 134.0, 132.4, 132.2, 130.3, 129.4, 129.2, 128.3, 128.3, 127.5, 126.3, 125.8, 125.4, 124.1, 121.5, 116.2, 115.7, 63.0, 46.9, 44.1, 34.9, 31.7, 31.1; HRMS (ESI) exact mass calculated for $C_{29}H_{30}NO_3S^+$ [M+H$^+$]: 472.1267, found:

472.1271; IR (neat): $\nu_{max}$ ($cm^{-1}$) = 1696, 1459, 1395, 1366, 1310, 1130, 761, 712; m.p. 132-134 $^{o}$C.

**9-Fluoro-5-methyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2l)**

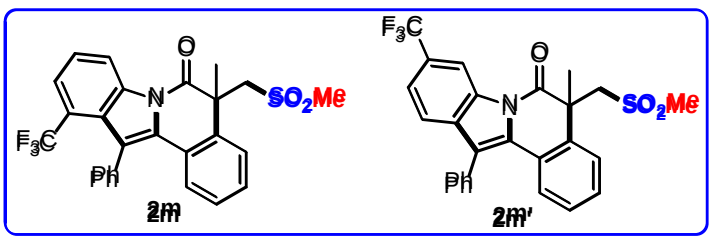
**11-Fluoro-5-methyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2l')**




According to general procedure C with **1l**, **2l** (**2l'**) was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 78% total yield (67 mg, white solid, **2l** and **2l'** in a ratio of 4 to 1 determined by crude NMR). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.3 Hz, 1H; Ar-*H*) (8.42 (dd, *J* = 10.0, 2.4 Hz, 1H; Ar-*H*)), 7.71-7.44 (m, 6H; 6(Ar-*H*)), 7.40-7.19 (m, 3H; 3(Ar-*H* )), 7.17-6.93 (m, 2H; 2(Ar-*H* )), 4.46 (d, *J* = 14.8 Hz, 1H; C*H*HSO$_2$), 4.20-3.84 (m, 1H; C*H*HSO$_2$), 2.69 (s, 3H; SO$_2$C*H*$_3$) (2.70 (s, 3H; SO$_2$C*H*$_3$)), 1.77 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.1 (171.1), 156.3 (d, *J* = 251.4 Hz) (161.9 (d, *J* = 242.8 Hz)), 136.19 (d, *J* = 8.1 Hz) (128.7 (d, *J* = 1.7 Hz)), 135.1 (135.4), 134.4 (d, *J* = 1.7 Hz) (126.7 (d, *J* = 7.5 Hz)), 134.3, 133.5, 130.1 (129.4), 128.9, 128.7, 128.5, 128.4, 128.3, 127.7, 126.2, 126.1 (d, *J* = 6.2 Hz), 125.6, 125.0 (125.2), 121.0-120.1 (m), 118.8 (d, *J* = 3.0 Hz), 113.2-112.7 (m), 111.0 (110.8), 104.4 (104.1), 63.1, 47.1 (47.0), 44.1, 31.0; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -120.93 (dd, *J* = 10.6, 5.2 Hz) (-114.91 (td, *J* = 9.5, 5.2 Hz)); HRMS (ESI) exact mass calculated for $C_{25}H_{21}FNO_3S^+$ [M+H$^+$]: 434.1221, found: 434.1216; IR (neat): $\nu_{max}$ ($cm^{-1}$) = 1699, 1436, 1390, 1366, 1307, 1125, 737, 702; m.p. 146-147 $^{o}$C.

**5-Methyl-5-((methylsulfonyl)methyl)-12-phenyl-9-(trifluoromethyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (2m)**

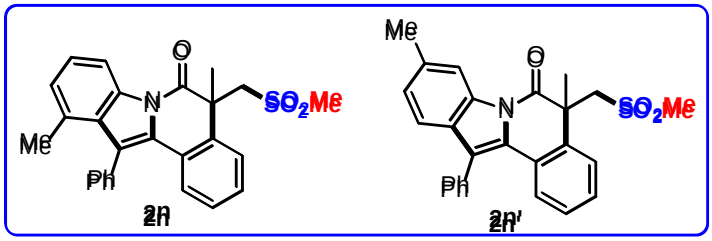
**5-Methyl-5-((methylsulfonyl)methyl)-12-phenyl-11-(trifluoromethyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (2m')**




According to general procedure C with **1m**, **2m (2m')** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 84% total yield

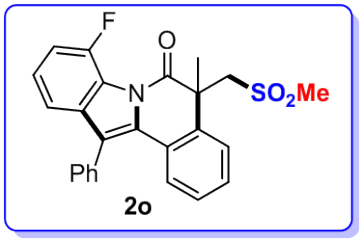
(84 mg, white solid, **2m** and **2m'** in a ratio of 2 to 1 determined by crude NMR). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 8.4 Hz, 1H; Ar-*H*) (9.00 (s, 1H; Ar-*H*)), 7.77-7.31 (m, 7H; 7(Ar-*H*)), 7.20-6.85 (m, 2H; 2(Ar-*H*)), 4.51-4.44 (m, 1H; C*H*$HSO_2$), 40.0-3.93 (m, 1H; CH*H*$SO_2$) (2.74 (s, 3H; $SO_2CH_3$)), 2.65 (s, 3H; $SO_2CH_3$) (1.79 (s, 3H; $CCH_3$)), 1.77 (s, 3H; $CCH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.3 (171.3), 135.7, 135.6, 134.3 (q, *J* = 1.8 Hz) (135.6, 134.9 (q, *J* = 1.1 Hz)), 133.1 (133.5), 131.9, 131.5, 131.4 (131.4), 130.1 (130.80), 129.5 (129.2), 128.9, 128.8, 128.8 (128.6), 128.5, 128.1 (q, *J* = 1.2 Hz), 127.0 (q, *J* = 52.5 Hz), 127.8 (127.8), 126.6 (126.3), 126.2, 125.0, 124.8 (124.7), 123.1 (q, *J* = 6.5 Hz), 121.6 (q, *J* = 3.7 Hz) (114.22 (q, *J* = 4.5 Hz)), 120.5, 120.5, 120.4, 119.9, 63.2 (62.9), 47.0 (47.1), 44.0 (44.2), 31.2 (31.1); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -56.25 (s) (-60.94 (s)); HRMS (ESI) exact mass calculated for $C_{26}H_{21}F_3NO_3S^+$ [M+$H^+$]: 484.1189, found: 484.1195; IR (neat): $\nu_{max}$ ($cm^{-1}$) = 1704, 1428, 1366, 1324, 1165, 1126, 758, 703; m.p. 116-118 $^{o}$C.

**5,9-Dimethyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2n)**
**5,11-Dimethyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2n')**



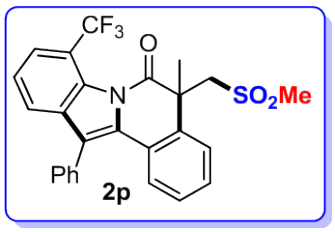

According to general procedure C with **1n**, **2n (2n')** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 71% total yield (62 mg, white solid, **2n** and **2n'** in a ratio of 3 to 1 determined by crude NMR). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.3 Hz, 1H; Ar-*H*) (8.52 (s, 1H; Ar-*H*)), 7.58-7.51 (m, 5H; 5(Ar-*H*)), 7.46 (t, *J* = 8.1 Hz, 2H; 2(Ar-*H*)), 7.32 (dt, *J* = 9.5, 7.1 Hz, 2H; 2(Ar-*H*), 7.21-6.95 (m, 3H; 3(Ar-*H*)), 4.47 (d, *J* = 14.8 Hz, 1H; C*H*$HSO_2$), 3.92 (dd, *J* = 14.8, 5.9 Hz, 1H; CH*H*$SO_2$), 2.70 (d, *J* = 3.8 Hz, 3H; $SO_2CH_3$) (2.56 (s, 3H; $SO_2CH_3$)), 1.97 (s, 3H; Ar-$CH_3$), (1.77 (s, 3H; $CCH_3$)), 1.75 (s, 3H; $CCH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9 (170.9), 136.4 (136.5), 135.2 (135.1), 134.5 (134.7), 134.0, 131.6 (130.8), 130.2 (130.2), 129.6, 129.3 (129.2), 129.2 (129.1), 128.4 (128.3), 128.2-128.1 (m), 127.6, 127.0, 126.2, 126.1 (126.0), 125.9, 125.7 (125.5), 122.1 (121.4), 119.3, 116.9 (114.6), 63.0 (62.9), 47.0, 44.1, 31.2 (31.1), 22.0 (19.9); HRMS(ESI) exact mass calculated for $C_{26}H_{24}NO_3S^+$ [M+$H^+$]: 430.1471, found: 430.1464; IR (neat): $\nu_{max}$ ($cm^{-1}$) = 1695, 1422, 1364, 1308, 1126, 758, 737, 702; m.p. 132-134 $^{o}$C.

**8-Fluoro-5-methyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2o)**



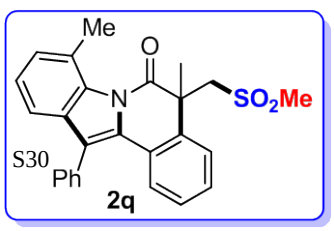

According to general procedure C with **1o**, **2o** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 60% yield (52 mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.62-7.46 (m, 6H; 6(Ar-*H*)), 7.43 (dd, *J* = 8.1, 1.2 Hz, 1H; Ar-*H*), 7.36 (td, *J* = 7.7, 1.3 Hz, 1H; Ar-*H*), 7.30-7.22 (m, 1H; Ar-*H*), 7.19-7.13 (m, 1H; Ar-*H*), 7.11-7.05 (m, 2H; 2(Ar-*H*)), 4.49 (d, *J* = 14.7 Hz, 1H; CH*H*$SO_2$), 3.94 (d, *J* = 14.7 Hz, 1H; C*H*H$SO_2$), 2.77 (s, 3H; $SO_2CH_3$), 1.82 (s, 3H; $CCH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 169.7, 150.5 (d, *J* = 255.2 Hz), 136.6 (d, *J* = 3.7 Hz), 136.0, 133.5, 131.6, 130.2, 129.4, 128.9, 128.4, 127.6, 126.1 (d, *J* = 4.9 Hz), 125.8 (d, *J* = 7.2 Hz), 125.3, 121.3 (d, *J* = 1.6 Hz), 121.1 (d, *J* = 11.4 Hz), 115.7, 115.6, 113.6, 113.3, 63.1, 47.7, 45.4-43.5 (m), 30.8; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -(106.77-111.67) (m); HRMS (ESI) exact mass calculated for $C_{25}H_{21}FNO_3S^+$ [M+H$^+$]: 434.1221, found: 434.1226; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1717, 1432, 1307, 1125, 966, 761, 733, 701; m.p. 109-111 $^{o}$C.

**5-Methyl-5-((methylsulfonyl)methyl)-12-phenyl-8-(trifluoromethyl)indolo[2,1-*a*]isoquinolin- (5*H*)-one (2p)**




According to general procedure C with **1p**, **2p** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 62% yield (60 mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 1H; Ar-*H*), 7.60-7.51 (m, 6H; 6(Ar-*H*)), 7.49-7.35 (m, 4H; 4(Ar-*H*)), 7.16-7.07 (m, 1H; Ar-*H*), 4.49 (d, *J* = 14.6 Hz, 1H; C*H*H$SO_2$), 3.84 (d, *J* = 14.6 Hz, 1H; CH*H*$SO_2$), 2.71 (s, 3H; $SO_2CH_3$), 1.87 (s, 3H; $CCH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.6, 136.1, 135.4, 133.6, 132.9, 130.7, 130.2 (q, *J* = 11.4), 129.4, 128.9, 128.5, 127.6, 124.9-124.4 (m), 126.4 (q, *J* = 5.8), 126.2, 123.6, 120.5, 63.0, 47.5, 44.3, 29.8; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -58.25 (s); HRMS (ESI) exact mass calculated for $C_{26}H_{21}F_3NO_3S^+$ [M+H$^+$]: 484.1189, found: 484.1194; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1729, 1425, 1309, 1170, 1125, 1107, 763, 704; m.p. 103-105 $^{o}$C.

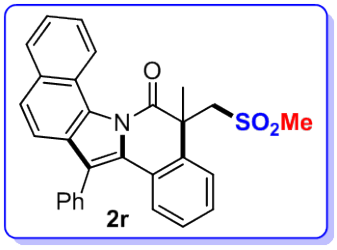
**5,8-Dimethyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2q)**




According to general procedure C with **1q**, **2q** was purified by flash column chromatography on silica gel using

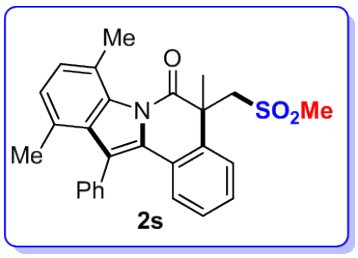
petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 71% yield (61mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.54 (q, *J* = 6.7 Hz, 5H; 5(Ar-*H*)), 7.45 (d, *J* = 7.9 Hz, 1H; Ar-*H* ), 7.40-7.24 (m, 4H; 4(Ar-*H*)), 7.21-7.14 (m, 1H; Ar-*H*), 7.08 (t, *J* = 7.8 Hz, 1H; Ar-*H*), 4.43 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 3.86 (d, *J* = 14.7 Hz, 1H; CH*H*SO$_2$), 2.69 (s, 6H; SO$_2$C*H*$_3$ and Ar-C*H*$_3$), 1.84 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.8, 135.7, 134.7, 134.1, 133.9, 131.4, 130.3, 129.3, 129.1, 128.3, 128.1, 127.5, 127.2, 126.5, 126.1, 126.0, 125.2, 121.7, 117.4, 63.3, 47.6, 44.1, 30.7, 22.3; HRMS (ESI) exact mass calculated for $C_{26}H_{24}NO_3S^+$ [M+H$^+$]: 430.1471, found: 430.1463; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1713, 1449, 1345, 1309, 1262, 1120, 762, 699; m.p. 135-136 °C.

**5-Methyl-5-((methylsulfonyl)methyl)-14-phenylbenzo[6,7]indolo[2,1-*a*]isoquinoli n-6(5*H*)-one (2r)**




According to general procedure C with **1r**, **2r** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 51% yield (47 mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.6 Hz, 1H; Ar-*H*), 7.94 (d, *J* = 8.1 Hz, 1H; Ar-*H*), 7.78 (d, *J* = 8.5 Hz, 1H; Ar-*H*), 7.67-7.46 (m, 8H; 8(Ar-*H*)), 7.41 (d, *J* = 8.7 Hz, 2H; 2(Ar-*H*)), 7.34 (s, 1H; Ar-*H*), 7.10 (t, *J* = 7.7 Hz, 1H; Ar-*H*), 4.50 (d, *J* = 14.6 Hz, 1H; CH*H*SO$_2$), 3.93 (d, *J* = 14.6 Hz, 1H; C*H*HSO$_2$), 2.68 (s, 3H; SO$_2$C*H*$_3$), 1.94 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.0, 135.2, 133.8, 133.1, 131.7, 131.4, 130.9, 130.4, 129.4, 128.8, 128.2, 128.1, 127.6, 127.4, 126.5, 125.9, 125.9, 125.4, 125.0, 123.8, 122.3, 118.2, 63.4, 47.7, 44.1, 30.5; HRMS (ESI) exact mass calculated for $C_{29}H_{24}NO_3S^+$ [M+H$^+$]: 466.1471, found: 466.1478; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1708, 1400, 1307, 1258, 1126, 816, 736, 701; m.p. 119-121 °C.

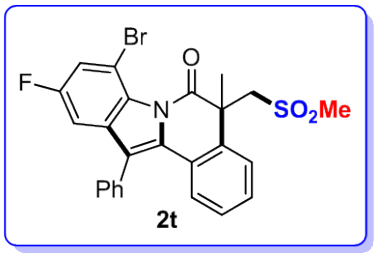
**5,8,11-Trimethyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6 (5*H*)-one (2s)**




According to general procedure C with **1s**, **2s** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 72% yield (64 mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 16.8 Hz, 5H; 5(Ar-*H*)), 7.42 (d, *J* = 8.0 Hz, 1H; Ar-*H*), 7.33-7.24 (m, 1H; Ar-*H*), 7.11 (d, *J* = 7.5 Hz, 1H; Ar-*H*), 7.06 (d, *J* = 8.0 Hz, 1H; Ar-*H*), 6.99 (t, *J* = 6.2 Hz, 2H; 2(Ar-*H*)), 4.42 (d, *J* = 14.7 Hz, 1H; CH*H*SO$_2$), 3.83 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 2.65 (s, 3H;

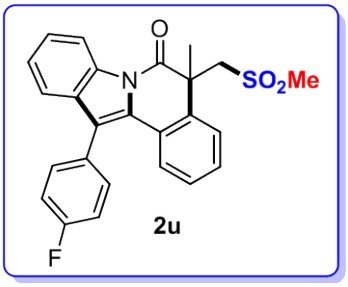
$SO_2CH_3$), 2.59 (s, 3H; Ar-C$H_3$), 1.93 (s, 3H; Ar-C$H_3$), 1.84 (s, 3H; CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.7, 136.3, 135.7, 134.9, 131.6, 131.2, 130.8, 130.5, 129.3, 129.0, 128.9, 128.6, 128.1, 128.0, 127.5, 127.5, 126.8, 126.0, 125. 9, 124.7, 122.5, 63.3, 47.6, 44.1, 30.6, 21.8, 19.6; HRMS (ESI) exact mass calculated for $C_{27}H_{26}NO_3S^+$ [M+H$^+$]: 444.1628, found: 444.1634; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1710, 1450, 1396, 1341, 1310, 1126, 760, 703; m.p. 135-136 $^o$C.

**8-Bromo-10-fluoro-5-methyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2t)**




According to general procedure C with **1t**, **2t** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 70% yield (72 mg, white solid). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.63-7.42 (m, 6H; 6(Ar-*H*)), 7.41-7.33 (m, 3H; 3(Ar-*H*)), 7.09 (t, *J* = 7.6 Hz, 1H; Ar-*H*), 7.00 (dd, *J* = 8.1, 2.4 Hz, 1H; Ar-*H*), 4.47 (d, *J* = 14.6 Hz, 1H; C*H*HSO$_2$), 3.85 (d, *J* = 14.6 Hz, 1H; CH*H*SO$_2$), 2.74 (s, 3H; $SO_2CH_3$), 1.88 (s, 3H; CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 169.9, 160.3 (d, *J* = 246.1 Hz), 137.3 (d, *J* = 9.9 Hz), 136.4, 135.0, 132.6, 131.3, 130.2, 129.5, 129.1, 128.7, 127.6, 126.3, 126.2, 126.0, 120.3 (d, *J* = 4.3 Hz), 118.5 (d, *J* = 27.8 Hz), 109.9 (d, *J* = 10.9 Hz), 105.1 (d, *J* = 24.1 Hz), 63.1, 47.9, 44.4, 29.9; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -116.31 (t, *J* = 8.4 Hz); HRMS (ESI) exact mass calculated for $C_{25}H_{20}BrFNO_3S^+$ [M+H$^+$]: 512.0925, found: 512.0932; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1725, 1462, 1413, 1308, 1169, 1124, 1103, 763; m.p. 141-143 $^o$C.

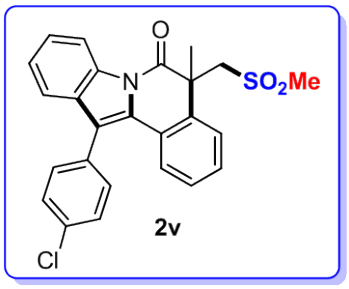
**12-(4-Fluorophenyl)-5-methyl-5-((methylsulfonyl)methyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (2u)**




According to general procedure C with **1u**, **2u** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 81% yield (71 mg, white solid). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.59-7.41 (m, 5H; 5(Ar-*H*)), 7.40-7.25 (m, 5H; 5(Ar-*H*)), 7.13 (td, *J* = 7.7, 7.2, 1.2 Hz, 1H; Ar-*H*), 4.48 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 3.93 (d, *J* = 14.8 Hz, 1H; CH*H*SO$_2$), 2.73 (s, 3H; $SO_2CH_3$), 1.77 (s, 3H; CC$H_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 162.7 (d, *J* = 247.6 Hz), 135.5, 134.3, 132.3, 132.0 (d, *J* = 8.0 Hz), 129.8 (d, *J* = 3.5 Hz), 129.3, 128.6, 127.6, 126.2 (d, *J* = 9.9 Hz), 125.8, 125.2, 124.9, 120.1, 119.4, 116.7, 116.6, 116.3, 62.9, 47.1, 44.1, 31.1; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -(113.27-113.35) (m); HRMS (ESI)

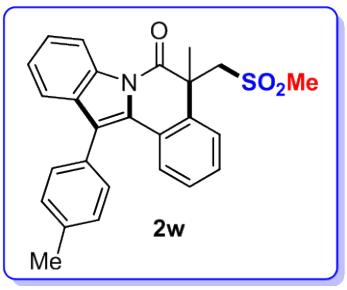
exact mass calculated for $C_{25}H_{21}FNO_3S^+$ [M+H$^+$]: 434.1221, found: 434.1226; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1694, 1511, 1451, 1391, 1308, 1125, 751, 734; m.p. 115-117 $^oC$.

**12-(4-Chlorophenyl)-5-methyl-5-((methylsulfonyl)methyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (2v)**



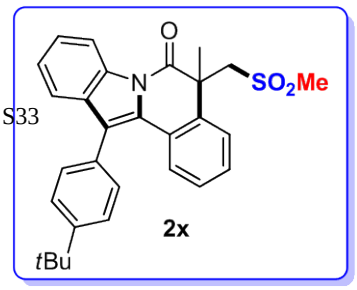

According to general procedure C with **1v**, **2v** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 79% yield (71 mg, white solid). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.58 (d, *J* = 8.1 Hz, 2H; 2(Ar-*H*)), 7.54-7.42 (m, 5H; 5(Ar-*H*)), 7.41-7.24 (m, 3H; 3(Ar-*H*)), 7.15 (t, *J* = 7.7 Hz, 1H; Ar-*H*)), 4.48 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 3.94 (d, *J* = 14.7 Hz, 1H; CH*H*SO$_2$), 2.72 (s, 3H; SO$_2$C*H*$_3$), 1.76 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 135.5, 134.3, 134.2, 132.4, 132.1, 131.7, 129.7, 129.3, 128.7, 127.7, 126.3, 126.2, 125.8, 125.0, 124.9, 119.8, 119.4, 116.8, 62.9, 47.1, 44.1, 31.1; HRMS (ESI) exact mass calculated for $C_{25}H_{21}ClNO_3S^+$ [M+H$^+$]: 450.0925, found: 450.0932; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1697, 1452, 1391, 1309, 1126, 1083, 967, 756; m.p. 80-81 $^oC$.

**5-Methyl-5-((methylsulfonyl)methyl)-12-(p-tolyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (2w)**




According to general procedure C with **1w**, **2w** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 79% yield (68 mg, white solid). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.58 (d, *J* = 8.1 Hz, 1H; Ar-*H*), 7.52-7.25 (m, 9H; 9(Ar-*H*)), 7.12 (t, *J* = 7.7 Hz, 1H; Ar-*H*), 4.48 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 3.93 (d, *J* = 14.8 Hz, 1H; CH*H*SO$_2$), 2.72 (s, 3H; SO$_2$C*H*$_3$), 2.53 (s, 3H; Ar-C*H*$_3$), 1.77 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 138.0, 135.3, 134.3, 132.6, 130.7, 130.0 (d, *J* = 1.7 Hz), 128.9, 128.4, 127.5, 126.1, 126.0, 126.0, 125.4, 124.8, 121.3, 119.7, 116.6, 62.9, 47.1, 44.1, 31.1, 21.5; HRMS (ESI) exact mass calculated for $C_{26}H_{24}NO_3S^+$ [M+H$^+$]: 430.1471, found: 430.1462; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1693, 1448, 1390, 1364, 1305, 1125, 751, 733; m.p. 132-133 $^oC$.

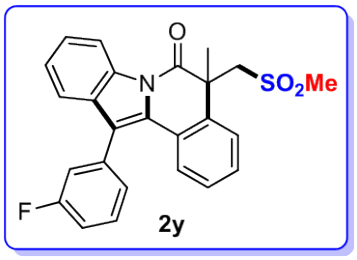
**12-(4-(*tert*-Butyl)phenyl)-5-methyl-5-((methylsulfonyl)methyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (2x)**




According to general procedure C with **1x**, **2x** was purified by flash column chromatography on silica gel

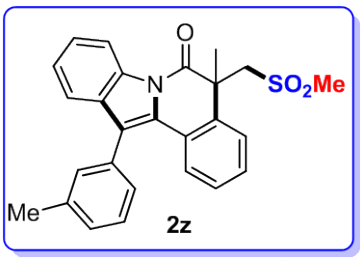
using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 86% yield (81 mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.58 (dd, *J* = 8.2, 4.5 Hz, 3H; 3(Ar-*H*)), 7.52-7.40 (m, 4H; 4(Ar-*H*)), 7.39-7.29 (m, 3H; 3(Ar-*H*)), 7.12 (t, *J* = 7.7 Hz, 1H; Ar-*H*), 4.47 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 3.93 (d, *J* = 14.7 Hz, 1H; CH*H*SO$_2$), 2.71 (s, 3H; SO$_2$C*H*$_3$), 1.77 (s, 3H; CC*H*$_3$), 1.47 (s, 9H; Ar-C(C*H*$_3$)$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 151.2, 135.3, 134.3, 132.6, 130.6, 129.8, 128.9, 128.3, 127.6, 126.1, 126.1, 126.0, 126.0, 125.5, 124.7, 121.4, 119.8, 116.6, 62.9, 47.1, 44.1, 34.8, 31.5, 31.1; HRMS (ESI) exact mass calculated for $C_{29}H_{30}NO_3S^+$ [M+H$^+$]: 472.1941, found: 472.1934; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1697, 1452, 1392, 1365, 1310, 1265, 1127, 753; m.p. 153-155 $^{o}$C.

**12-(3-Fluorophenyl)-5-methyl-5-((methylsulfonyl)methyl)indolo[2,1-*a*]isoquinoli n-6(5*H*)-one (2y)**




According to general procedure C with **1y**, **2y** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 74% yield (64 mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.57 (td, *J* = 7.9, 6.0 Hz, 1H; Ar-*H*), 7.51-7.41 (m, 3H; 3(Ar-*H*)), 7.41-7.21 (m, 6H; 6(Ar-*H*)), 7.18-7.07 (m, 1H; Ar-*H*), 4.47 (d, *J* = 14.8 Hz, 1H; C*H*HSO$_2$), 3.94 (d, *J* = 14.8 Hz, 1H; CH*H*SO$_2$), 2.72 (s, 3H; SO$_2$C*H*$_3$), 1.77 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.0, 163.4 (d, *J* = 247.6 Hz), 136.2 (d, *J* = 8.1 Hz), 135.6, 134.3, 132. 0, 131.0 (d, *J* = 8.5 Hz), 129.3, 128.7, 127.7, 126.3, 126.2 (d, *J* = 1.9 Hz), 126.1 (d, *J* = 2.9 Hz), 125.9, 125.0, 119.8 (d, *J* = 2.2 Hz), 119.4, 117.2 (d, *J* = 21.6 Hz), 116.7, 115.3 (d, *J* = 20.9 Hz), 62.9, 47.1, 44.1, 31.1; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -111.75 (s); HRMS (ESI) exact mass calculated for $C_{25}H_{21}FNO_3S^+$ [M+H$^+$]: 434.1221, found: 434.1227; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1698, 1614, 1450, 1389, 1365, 1309, 1128, 754; m.p. 73-75 $^{o}$C.

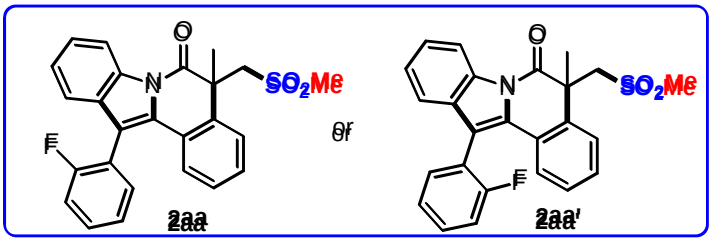
**5-Methyl-5-((methylsulfonyl)methyl)-12-(m-tolyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (2z)**




According to general procedure C with **1z**, **2z** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 79% yield (68 mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.54 (d, *J* = 8.1 Hz, 1H; Ar-*H*), 7.51-7.42 (m, 3H; 3(Ar-*H*)), 7.40-7.28 (m, 6H; 6(Ar-*H*)), 7.11 (t, *J* = 7.7 Hz, 1H; Ar-*H*), 4.48 (d, *J* = 14.8 Hz, 1H; C*H*HSO$_2$),

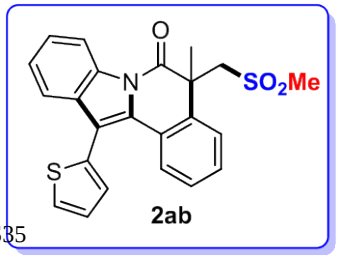
3.94 (d, *J* = 14.8 Hz, 1H; CH*H*$SO_2$), 2.72 (s, 3H; $SO_2CH_3$), 2.48 (s, 3H; Ar-$CH_3$), 1.77 (s, 3H; $CCH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 139.0, 135.3, 134.3, 133.8, 132.5, 130.7, 129.2, 129.0, 128.9, 128.4, 127.6, 126.1, 126.0, 126.0, 125.4, 124.8, 121.5, 119.7, 116.6, 62.9, 47.1, 44.1, 31.1, 21.5; HRMS (ESI) exact mass calculated for $C_{26}H_{24}NO_3S^+$ [M+H$^+$]: 430.1471, found: 430.1479; IR (neat): $\nu_{max}$ ($cm^{-1}$) = 1693, 1447, 1389, 1306, 1124, 751, 732, 704; m.p. 101-103 $^oC$.

**12-(2-Fluorophenyl)-5-methyl-5-((methylsulfonyl)methyl)indolo[2,1-*a*]isoquinoli n-6(5*H*)-one (2aa)**




According to general procedure C with **1aa**, **2aa** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 69% yield (60 mg, white solid, **2aa** (major): **2aa'** (minor) = 1.7:1 as determined by crude NMR). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.67-7.44 (m, 6H; 6(Ar-*H*)), 7.43-7.24 (m, 6H; 6(Ar-*H*)), 7.23-7.08 (m, 1H; Ar-*H*), 4.49 (d, *J* = 14.7 Hz, 1H; C*H*$HSO_2$) (4.39 (d, *J* = 14.8 Hz, 1H; C*H*$HSO_2$)), 3.95 (d, *J* = 14.8 Hz, 1H; CH*H*$SO_2$) (3.88 (d, *J* = 14.8 Hz, 1H; CH*H*$SO_2$)), 2.74 (s, 3H; $SO_2CH_3$) (2.65 (s, 3H; $SO_2CH_3$), 1.80 (s, 3H; $CCH_3$) (1.77 (s, 3H; $CCH_3$)); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.0 (170.7), 160.5 (d, *J* = 249.8), 160.3 (d, *J* = 248.9), 135.5 (135.5), 134.4, 132.6 (d, *J* = 2.8 Hz) (132.3 (d, *J* = 2.9 Hz)), 131.8 (131.6, 130.5 (d, *J* = 7.8 Hz)), 130.9 (d, *J* = 8.0 Hz), 130.4 (130.2), 128.8 (d, *J* = 90.9Hz) (128.3 (d, *J* = 88.4 Hz)), 126.3 (d, *J* = 7.3 Hz), 126.2 (126.0), 125.3 (d, *J* = 2.2 Hz), 125.3, 125.0 (d, *J* = 3.7 Hz), 124.9 (125.6), 124.9, 121.5 (d, *J* = 16.3, 8.5 Hz) (121.4(d, *J* = 16. 3)), 119.3 (119.6), 116.8 (116.8), 116.7 (116.6), 116.5, 116.3, 113.8 (114.4), 62.8 (63.2), 47.2 (47.1), 44.2 (43.8), 31.2 (30.4); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -(112.50-112.52) (m) (-(111.12-111.18) (m)); HRMS (ESI) exact mass calculated for $C_{25}H_{21}FNO_3S^+$ [M+H$^+$]: 434.1221, found: 434.1208; IR (neat): $\nu_{max}$ ($cm^{-1}$) = 1697, 1447, 1390, 1365, 1308, 1125, 752, 735; m.p. 122-124 $^oC$.

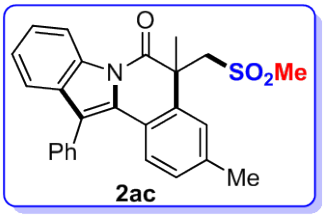
**5-Methyl-5-((methylsulfonyl)methyl)-12-(thiophen-2-yl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (2ab)**




According to general procedure C with **1ab**, **2ab** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 74% yield (62 mg, white solid).

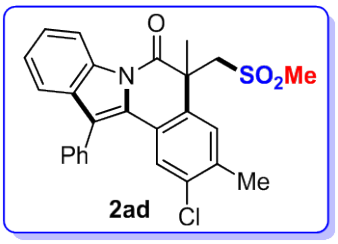
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.68 (d, *J* = 8.1 Hz, 1H; Ar-*H*), 7.59 (dd, *J* = 5.1, 1.3 Hz, 1H; Ar-*H*), 7.50-7.42 (m, 3H; 3(Ar-*H*)), 7.41-7.33 (m, 2H; 2(Ar-*H*)), 7.32-7.27 (m, 1H; Ar-*H*), 7.25 (dd, *J* = 3.5, 1.3 Hz, 1H; Ar-*H*), 7.19 (t, *J* = 7.7 Hz, 1H; Ar-*H*), 4.47 (d, *J* = 14.8 Hz, 1H; C*H*HSO$_2$), 3.94 (d, *J* = 14.8 Hz, 1H; CH*H*SO$_2$), 2.71 (s, 3H; SO$_2$C*H*$_3$), 1.76 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 135.6, 134.1, 134.0, 132.8, 130.9, 128.8, 128.6, 128.1, 127.8, 127.4, 126.3, 126.2, 126.0, 125.0, 124.9, 119.6, 116.6, 113.5, 62.9, 47.1, 44.1, 31.1; HRMS (ESI) exact mass calculated for $C_{23}H_{20}NO_3S_2^+$ [M+H$^+$]: 422.0879, found: 422.0869; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1698, 1451, 1383, 1364, 1308, 1130, 757, 703; m.p. 130-133 °C.

**2,5-Dimethyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2ac)**




According to general procedure C with **1ac**, **2ac** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 66% yield (57 mg, white solid). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.66-7.49 (m, 5H; 5(Ar-*H*)), 7.48-7.39 (m, 2H; 2(Ar-*H*)), 7.33 (d, *J* = 5.7 Hz, 2H; 2(Ar-*H*)), 7.30-7.25 (m, 1H; Ar-*H*), 6.93 (d, *J* = 8.3 Hz, 1H; Ar-*H*), 4.46 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 3.96 (s, 1H; CH*H*SO$_2$), 2.71 (s, 3H; SO$_2$C*H*$_3$), 2.39 (s, 3H; Ar-C*H*$_3$), 1.77 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.0, 138.6, 135.4, 134.3, 134.0, 132.5, 130.3, 129.3, 129.3, 128.6, 128.2, 126.6, 125.9, 125.9, 124.8, 122.6, 120.4, 119.5, 116.6, 63.0, 47.0, 44.1, 31.1, 21.6; HRMS (ESI) exact mass calculated for $C_{26}H_{24}NO_3S^+$ [M+H$^+$]: 430.1471, found: 430.1478; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1694, 1452, 1387, 1364, 1306, 1129, 749, 702; m.p. 125-127 °C.

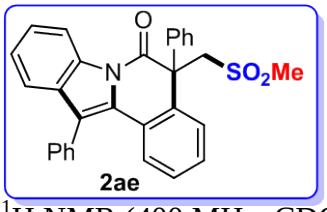
**3-Chloro-2,5-dimethyl-5-((methylsulfonyl)methyl)-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2ad)**




According to general procedure C with **1ad**, **2ad** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 66% yield (61 mg, white solid). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.78-7.49 (m, 5H; 5(Ar-*H*)), 7.47-7.42 (m, 3H; 3(Ar-*H*)), 7.39-7.31 (m, 2H; 2(Ar-*H*)), 7.29 (d, *J* = 3.2 Hz, 1H; Ar-*H*), 4.49 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 3.91 (d, *J* = 14.7 Hz, 1H; C*H*HSO$_2$), 2.84 (s, 3H; SO$_2$C*H*$_3$), 2.40 (s, 3H; Ar-C*H*$_3$), 1.73 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.7, 136.5, 134.3, 134.0, 133.9, 133.2, 132.2, 130.1, 129.4, 128.5, 128.2, 128.0, 126.3, 126.0, 124.9, 124.3, 121.4,

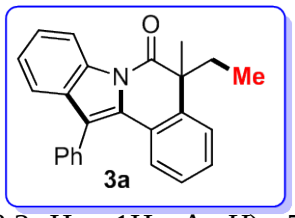
119.8, 116.6, 62.5, 47.0, 44.4, 31.3, 20.3; HRMS (ESI) exact mass calculated for $C_{26}H_{23}ClNO_3S^+$ [M+H$^+$]: 464.1082, found: 464.1088; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1696, 1449, 1383, 1367, 1309, 1132, 748, 703; m.p. 147-149 $^oC$.

**5-((Methylsulfonyl)methyl)-5,12-diphenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (2ae)**



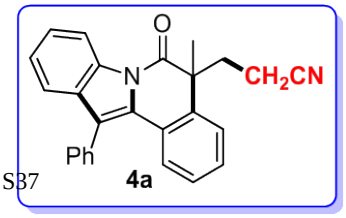

According to general procedure C with **1ae**, **2ae** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 50 % yield (48 mg, white solid). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.55 (m, 6H; 6(Ar-*H*)), 7.45-7.21 (m, 10H; 10(Ar-*H*)), 7.18 (d, *J* = 7.6 Hz, 1H; Ar-*H*), 5.06 (d, *J* = 14.6 Hz, 1H; C*H*HSO$_2$), 4.27 (d, *J* = 14.5 Hz, 1H; CH*H*SO$_2$), 2.90 (s, 3H; SO$_2$C*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 169.0, 141.0, 134.6, 134.4, 133.7, 132.3, 130.2, 129.3, 129.2, 128.4, 128.3, 128.3, 128.3, 128.3, 127.9, 126.7, 126.2, 126.0, 124.8, 119.7, 116.5, 62.2, 55.2, 44.7; HRMS (ESI) exact mass calculated for $C_{30}H_{24}NO_3S^+$ [M+H$^+$]: 478.1471, found: 478.1458; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1693, 1449, 1389, 1365, 1308, 1129, 735, 701; m.p. 140-142 $^oC$.

**5-Ethyl-5-methyl-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (3a)**




According to general procedure C with **1a**, **3a** was purified by flash column chromatography on silica gel using petroleum ether as an eluent and obtained in 25% yield (17 mg, white solid). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.61-7.52 (m, 5H; 5(Ar-*H*)), 7.50-7.37 (m, 3H; 3(Ar-*H*)), 7.37-7.21 (m, 3H; 3(Ar-*H*)), 7.06 (t, *J* = 7.7 Hz, 1H; Ar-*H*), 2.42 (dt, *J* = 14.8, 7.3 Hz, 1H; C*H*HCH$_3$), 2.02 (dq, *J* = 14.7, 7.5 Hz, 1H; CH*H*CH$_3$), 1.78 (s, 3H; CC*H*$_3$), 0.73 (t, *J* = 7.4 Hz, 3H; CHHC*H*$_3$ ); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.4, 139.0, 134.2, 134.2, 132.2, 130.3, 129.8, 129.3, 128.4, 128.0, 126.5, 126.2, 125.8, 125.8, 125.3, 124.5, 119.9, 119.4, 116.6, 49.3, 36.4, 27.4, 9.6; HRMS (ESI) exact mass calculated for $C_{25}H_{22}NO$ [M+H$^+$]: 352.1696, found: 352.1693; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1695, 1450, 1388, 1358, 1333, 1264, 739, 701; m.p. 42-43 $^oC$.

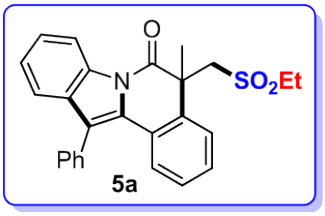
**3-(5-Methyl-6-oxo-12-phenyl-5,6-dihydroindolo[2,1-*a*]isoquinolin-5-yl)propanenitrile (4a)**




According to general procedure C with **1a** using $CH_3CN$ as the solvent, **4a** was purified by flash column chromatography on silica gel using petroleum ether and

ethyl acetate (20:1, v:v) as an eluent and obtained in 21% yield (16 mg, white solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.3 Hz, 1H; Ar-*H*), 7.62-7.51 (m, 5H; 5(Ar-*H*)), 7.48-7.40 (m, 3H; 3(Ar-*H*)), 7.39-7.32 (m, 3H; 3(Ar-*H*)), 7.10 (t, *J* = 7.8 Hz, 1H; Ar-*H*), 2.89 (dq, *J* = 16.2, 5.5 Hz, 1H; C*H*HCH$_2$CN), 2.39 (dq, *J* = 13.3, 4.7 Hz, 1H; CH*H*CH$_2$CN), 2.23 (ddd, *J* = 16.7, 10.8, 5.4 Hz, 1H; C*H*HCN), 2.13-1.99 (m, 1H; CH*H*CN), 1.78 (s, 3H; CC*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.6, 136.4, 134.1, 133.7, 132.3, 130.1, 129.4, 129.3, 129.0, 128.9, 128.3, 127.5, 126.3, 125.8, 125.7, 124.9, 121.1, 119.7, 118.7, 116.6, 48.1, 36.7, 29.2, 13.6; HRMS (ESI) exact mass calculated for $C_{26}H_{21}N_2O$ [M+H$^+$]: 377.1648, found: 377.1642; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1693, 1450, 1389, 1362, 1333, 751, 736, 703; m.p. 48-50 °C.

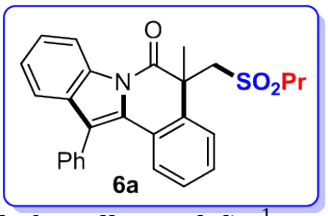
**5-((Ethylsulfonyl)methyl)-5-methyl-12-phenylindolo[2,1-*a*]isoquinolin-6(5*H*)-one (5a)**



**5a**

According to general procedure C with di-*tert*-amyl peroxide, **5a** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 70% yield (60 mg, light yellow solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.3 Hz, 1H; Ar-*H*), 7.60-7.42 (m, 8H; 8(Ar-*H*)), 7.38-7.23 (m, 3H; 3(Ar-*H*)), 7.09 (t, *J* = 7.8 Hz, 1H; Ar-*H*), 4.45 (d, *J* = 14.5 Hz, 1H; C*H*HSO$_2$), 3.87 (d, *J* = 14.6 Hz, 1H; CH*H*SO$_2$), 2.92-2.80 (m, 2H; SO$_2$C*H*$_2$CH$_3$), 1.77 (s, 3H; CC*H*$_3$), 1.34 (t, *J* = 7.5 Hz, 3H; SO$_2$CH$_2$C*H*$_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.1, 135.6, 134.4, 134.0, 132.5, 130.2, 129.3, 129.2, 128.3, 128.2, 127.5, 126.0, 125.9, 125.2, 124.8, 121.2, 119.7, 116.7, 60.1, 50.5, 47.0, 31.2, 6.4; HRMS (ESI) exact mass calculated for $C_{26}H_{24}NO_3S$ [M+H$^+$]: 430.1471, found: 430.1469; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1694, 1448, 1391, 1364, 1310, 1123, 751, 703; m.p. 113-114 °C.

**5-Methyl-12-phenyl-5-((propylsulfonyl)methyl)indolo[2,1-*a*]isoquinolin-6(5*H*)-one (6a)**

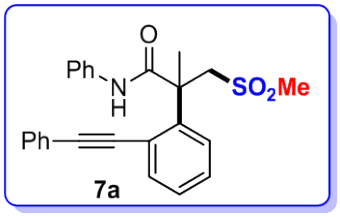


**6a**

According to general procedure C with di-*iso*-hexyl peroxide, **6a** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 45% yield (40 mg, light yellow solid). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.2 Hz, 1H; Ar-*H*), 7.61-7.43 (m, 8H; 8(Ar-*H*)), 7.38-7.27 (m, 3H; 3(Ar-*H*)), 7.10 (t, *J* = 7.8 Hz, 1H; Ar-*H*), 4.43 (d, *J* = 14.5 Hz, 1H; C*H*HSO$_2$), 3.86 (d, *J* = 14.6 Hz, 1H; CH*H*SO$_2$), 2.78 (dt, *J* = 12.6, 7.8 Hz, 2H; SO$_2$C*H*$_2$CH$_2$CH$_3$), 1.93-1.70 (m, 5H; SO$_2$CH$_2$C*H*$_2$CH$_3$ and

CC*H*$_3$), 1.01 (t, *J* = 7.4 Hz, 3H; $SO_2CH_2CH_2CH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.0, 135.6, 134.4, 134.0, 132.5, 130.2, 129.3, 129.2, 128.3, 128.2, 127.5, 126.1, 126.0, 125.9, 125.2, 124.7, 121.1, 119.6, 116.7, 60.7, 57.7, 47.0, 31.1, 15.6, 13.0; HRMS (ESI) exact mass calculated for $C_{27}H_{26}NO_3S$ [M+H$^+$]: 444.1628, found: 444.1622; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1646, 1452, 1364, 1124, 907, 849, 731, 703; m.p. 102-104 $^o$C.

**2-Methyl-3-(methylsulfonyl)-N-phenyl-2-(2-(phenylethynyl)phenyl)butanamide (7a)**

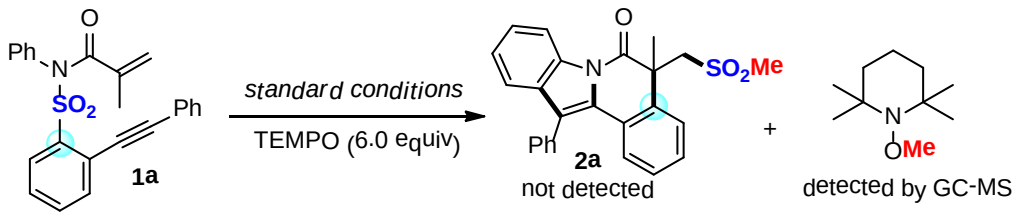



According to general procedure C using $CF_3SO_3H$ as the catalyst, **7a** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v:v) as an eluent and obtained in 68% yield (57 mg, light yellow solid). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.0, 1.3 Hz, 1H; Ar-*H*), 7.70 (dd, *J* = 7.5, 1.5 Hz, 1H; Ar-*H*), 7.60-7.45 (m, 4H; 4(Ar-*H*)), 7.39-7.31 (m, 5H; 5(Ar-*H*)), 7.24 (t, *J* = 7.9 Hz, 2H; 2(Ar-*H*)), 7.10-7.02 (m, 1H; Ar-*H*), 6.84 (s, 1H; N*H*), 4.62 (d, *J* = 15.5 Hz, 1H; C*H*$HSO_2$), 4.04-3.92 (m, 1H; CH*H*$SO_2$), 2.25 (s, 3H; CC*H*$_3$), 2.19 (s, 3H; $SO_2CH_3$); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.1, 139.2, 137.4, 134.3, 131.6, 129.4, 129.2, 129.1, 129.1, 128.9, 128.4, 124.8, 123.8 , 122.0, 120.7, 97.4, 86.5, 59.6, 50.3, 42.5, 24.3; HRMS (ESI) exact mass calculated for $C_{25}H_{24}NO_3S$ [M+H$^+$]: 418.1471, found: 418.1468; IR (neat): $\nu_{max}$ (cm$^{-1}$) = 1686, 1522, 1493, 1439, 1308, 1265, 733, 691; m.p. 92-94 $^o$C.

## 5. Mechanistic Study:

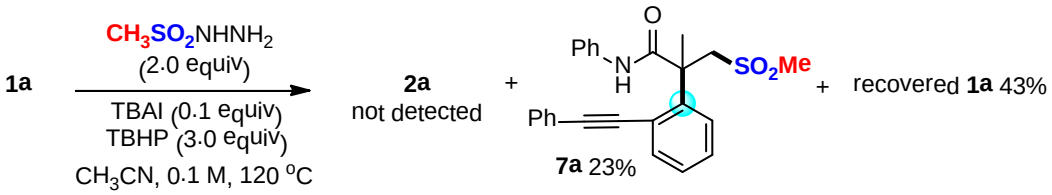
**5.1** Control experiments:

**a)**



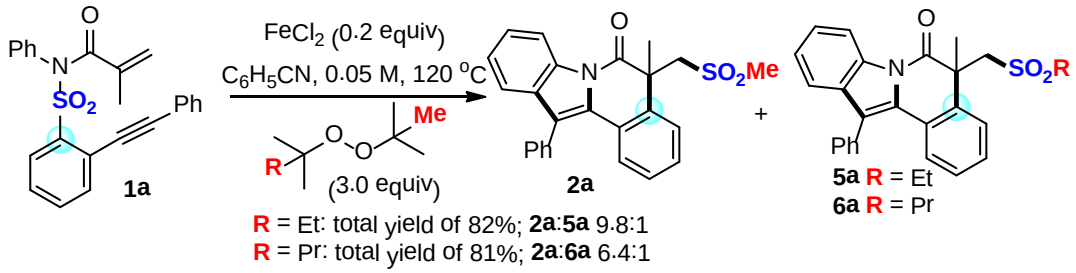

A 10 mL sealed tube was equipped with a rubber septum and magnetic stirring bar and charged with **1a** (0.2 mmol), $FeCl_2$ (0.04 mmol, 0.2 equiv). The flask was evacuated and backfilled with argon for 3 times. DTBP (0.6 mmol, 3.0 equiv), TEMPO (1.2 mmol, 6.0 equiv) and $C_6H_5CN$ (4.0 mL) were added subsequently under argon. The mixture was then sealed and heated at 120 $^oC$ overnight. The reaction mixture was cooled to room temperature, filtered by Celite. The crude reaction mixture analysis by GC-MS showed that trace amount of TEMPO-Me was formed and **2a** was not detected.

**b)**




A 10 mL sealed tube was equipped with a rubber septum and magnetic stirring bar. The tube was evacuated and backfilled with argon for 3 times, charged with **1a** (0.2 mmol), $CH_3SO_2NHNH_2$ (0.4 mmol, 2.0 equiv), TBAI (0.04 mmol, 0.2 equiv), TBHP (0.6 mmol, 3.0 equiv) and $CH_3CN$ (2.0 mL). The mixture was then sealed and heated at 120 $^oC$ for 6 hours. After completion (detected by TLC), the reaction mixture was cooled to room temperature, purified directly by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 3:1) as an eluent. **7a** was obtained in 23% yield (19 mg) with 43% **1a** recovered (35 mg).

**5.2** Alkyl competition experiments:

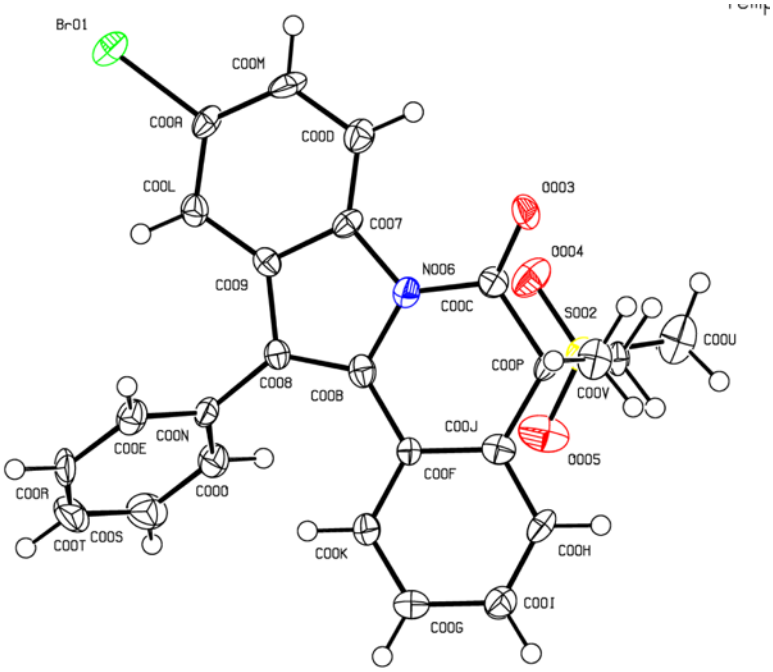



Under standard conditions (**1a** (0.2 mmol), $FeCl_2$ (0.04 mmol, 0.2 equiv), oxidant (0.6 mmol, 3.0 equiv), $C_6H_5CN$ (4 mL), 120 $^oC$), different oxdiants were used.

## 6. X-Ray data for 2d and 7a:

The CCDC number for **2d** (CCDC 1564426) and **7a** (CCDC 1564681) contains the supplementary crystallographic data for this paper. These data can be charge from Cambridge Data Centre *via* www.ccdc.ac.uk/data-request/cif.

### **6.1** X-Ray data for **2d**



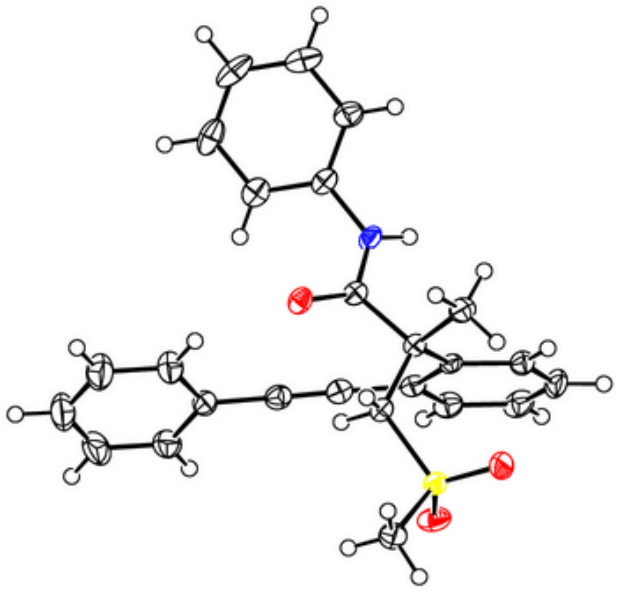

Thermal ellipsoids are set at 50% probability.

Crystal data and structure refinement for **2d** (CCDC 1564426**)**

| | |
|---|---|
| Empirical formula | $C_{25}H_{20}BrNO_3S$ |
| Formula weight | 494.39 |
| Temperature/K | 293 |
| Crystal system | monoclinic |
| Space group | $P_{21}/c$ |
| a/Å | 9.2360(13) |
| b/Å | 23.305(2) |
| c/Å | 10.0010(14) |
| α/° | 90 |
| β/° | 100.675(14) |

| | |
|---|---|
| γ/° | 90 |
| Volume/Å$_3$ | 2115.4 (5) |
| Z | 4 |
| $\rho_{calc}$mg/cm$^3$ | 1.552 |
| $\mu$/mm$^{-1}$ | 2.070 |
| F(000) | 1008.0 |
| 2θ range for data collection/ | 4.512 to 62.376 |
| Index ranges | -13<=h<=13; -29<=k<=29; -14<=14 |
| Reflections collected | 19182 |
| Independent reflections | 5684 [$R_{int}$ = 0.1058] |
| Data/restraints/parameters | 5684/0/282 |
| Goodness-of-fit on $F^2$ | 1.039 |
| Final R indices [I >= 2 σ (I)] | $R^1$ = 0.0686, $wR^2$ = 0.1592 |
| R indices (all data) | $R^1$= 0.1658, $wR^2$=0.2064 |
| Largest diff. peak/hole / eÅ$^{-3}$ | 149.3/ -0.705 |

**6.2** X-Ray data for **7a**



Thermal ellipsoids are set at 50% probability.

Crystal data and structure refinement for **7a** (CCDC1564681**)**

| | |
|---|---|
| Empirical formula | $C_{25}H_{23}NO_3S$ |
| Formula weight | 417.14 |
| Temperature/K | 293 |
| Crystal system | Monoclinic |
| Space group | $P_{21}/c$ |
| a/Å | 24.6971(12) |
| b/Å | 72.4777(5) |
| c/Å | 15.4813(8) |
| α /° | 90 |
| β /° | 94.716(5) |
| γ /° | 90 |
| Volume/$Å_3$ | 4754.7 (4) |
| Z | 4 |
| $\rho_{calc}$mg/cm$^3$ | 1.290 |
| $\mu$/mm$^{-1}$ | 0.170 |
| F(000) | 1952.0 |
| 2 θ range for data collection/ | 3.31 to 62.036 |
| Index ranges | -33<=h<=34; -12<=k<=18; -21<=21 |
| Reflections collected | 42173 |
| Independent reflections | 12474 [$R_{int}$ = 0.0468] |
| Data/restraints/parameters | 12474/0/601 |
| Goodness-of-fit on $F^2$ | 1.028 |
| Final R indices [I >= 2 σ (I)] | $R^1$ = 0.0506, $wR^2$ = 0.1356 |

| | |
|---|---|
| R indices (all data) | $R^1$= 0.0860, $wR^2$=0.1567 |
| Largest diff. peak/hole / e$Å^{-3}$ | 0.389 / -0.511 |

## 7. References

[1] (a) W. Kong, M. Casimiro, N. Fuentes, E. Merino, C. Nevado, *Angew. Chem. Int. Ed.,* 2013, **52**, 13086; (b) R. Anana, P. N. P. Rao, Q.-H. Chen, E. E. Knaus, *Bioorg. Med. Chem*., 2006, **14**, 5259; (c) H. Murase, K. Senda, M.; Hata, T. Senoo, H. Urabe, *Chem. Eur. J*., 2014, **20**, 317.

[2] N. Fuentes, W. Kong, L. Fernández-Sánchez, E. Merino, C. Nevado, *J. Am. Chem. Soc*., 2015, **137**, 964.

[3] H. Huang. Y. Li, *J. Org. Chem*., 2017, **8**, 4449.

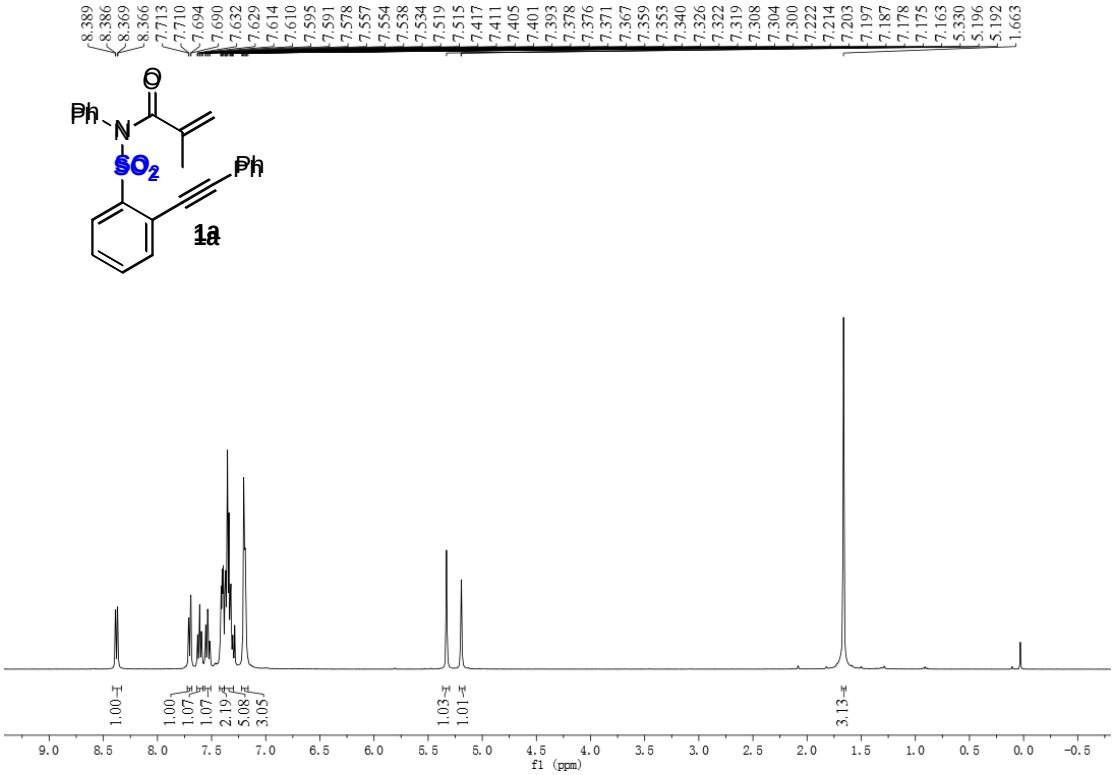
[4] N. A. Milas, D. M. Surgenor, *J. Am. Chem. Soc*., 1946, **68**, 643.

[5] M. Kazuo, H.Yoshiki, *Bull. Chemi. Soc. Jpn*. 1991, **64**, 259.

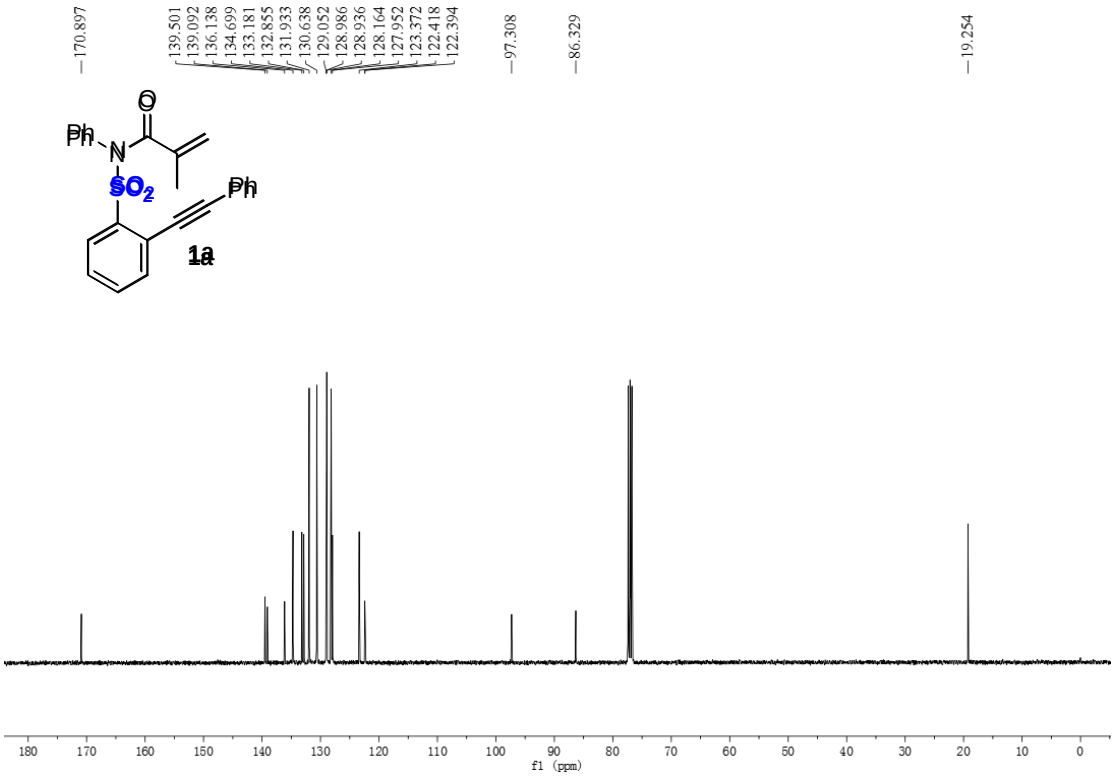
[6] N. Zhu, J. Zhao, H. Bao, *Chem. Sci*., 2017, **8**, 2081.

## 8. Spectra Data

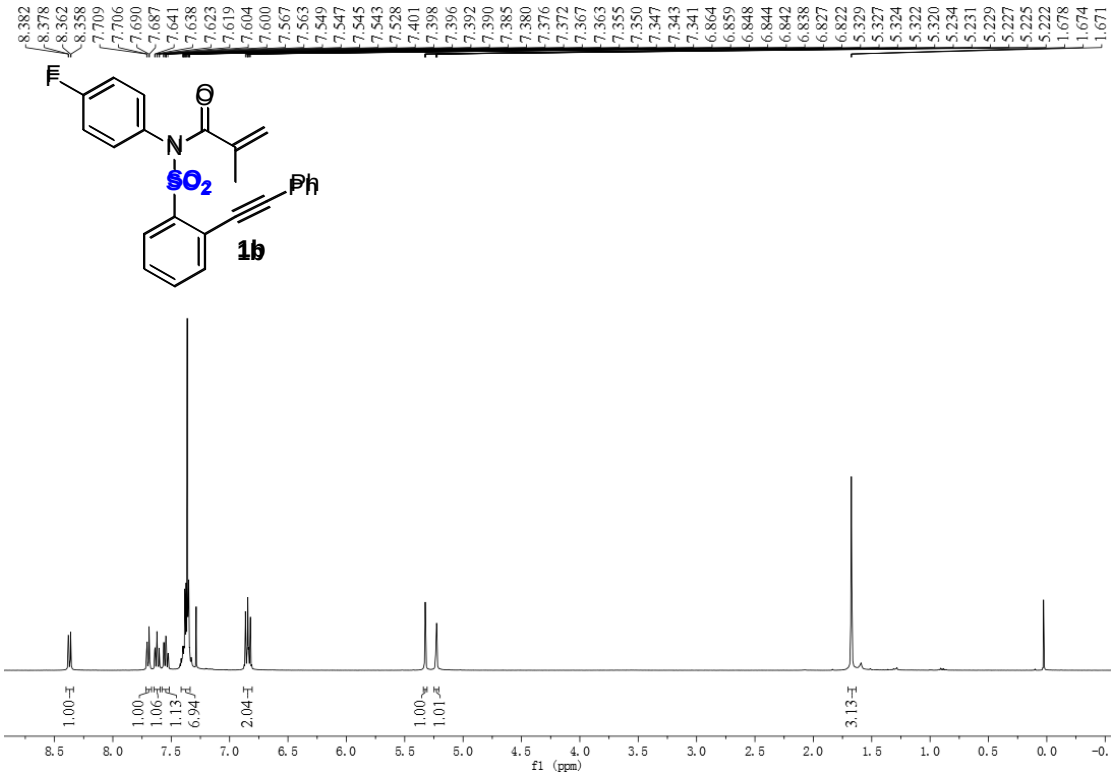
$^{1}$H NMR for **1a** (400 MHz, $CDCl_3$)



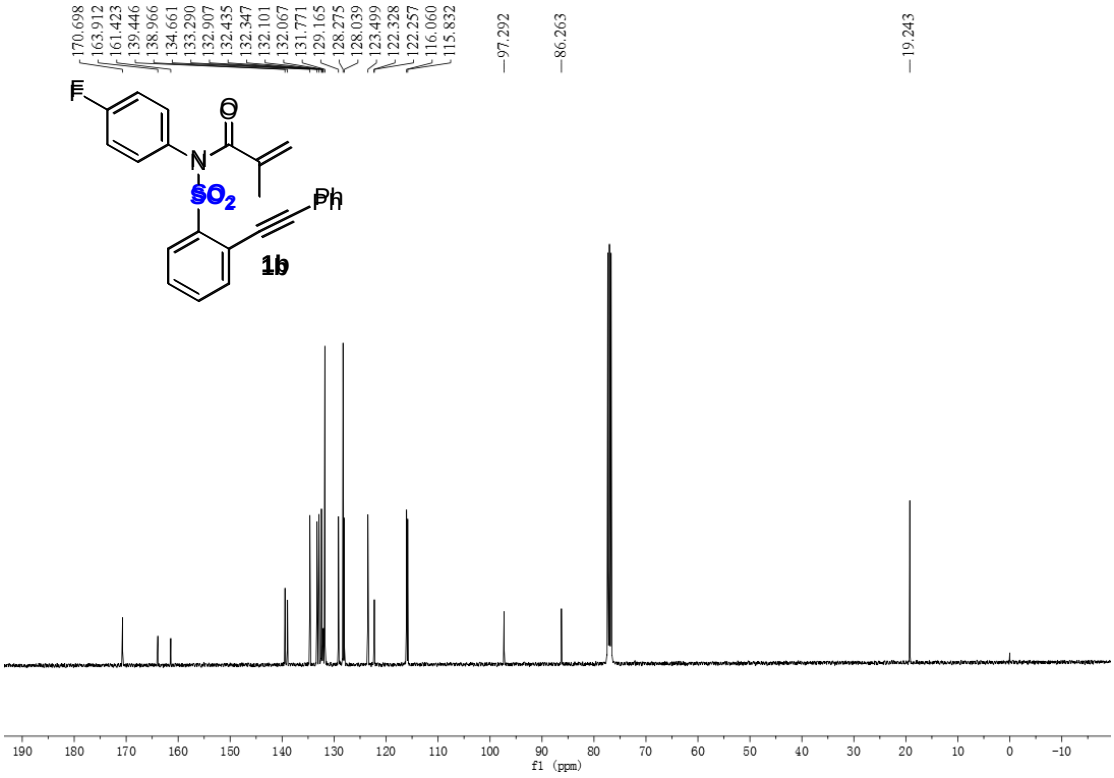

$^{13}$C NMR for **1a** (101 MHz, $CDCl_3$)



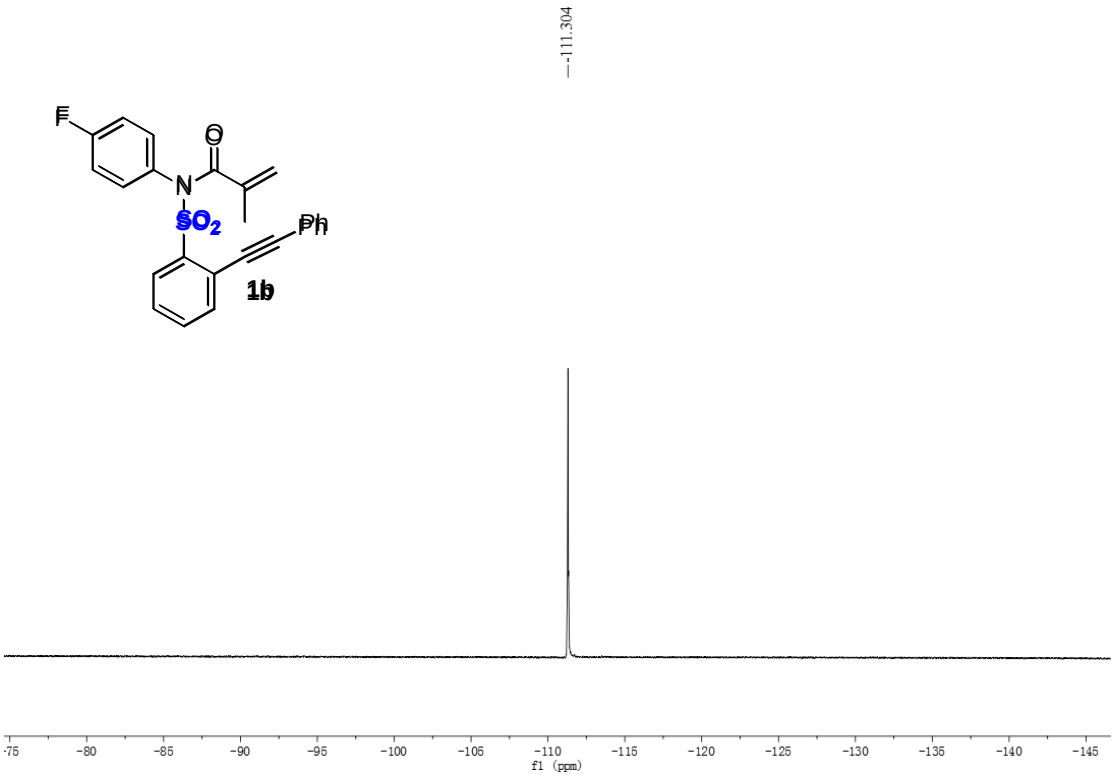
$^{1}$H NMR for **1b** (400 MHz, $CDCl_3$)



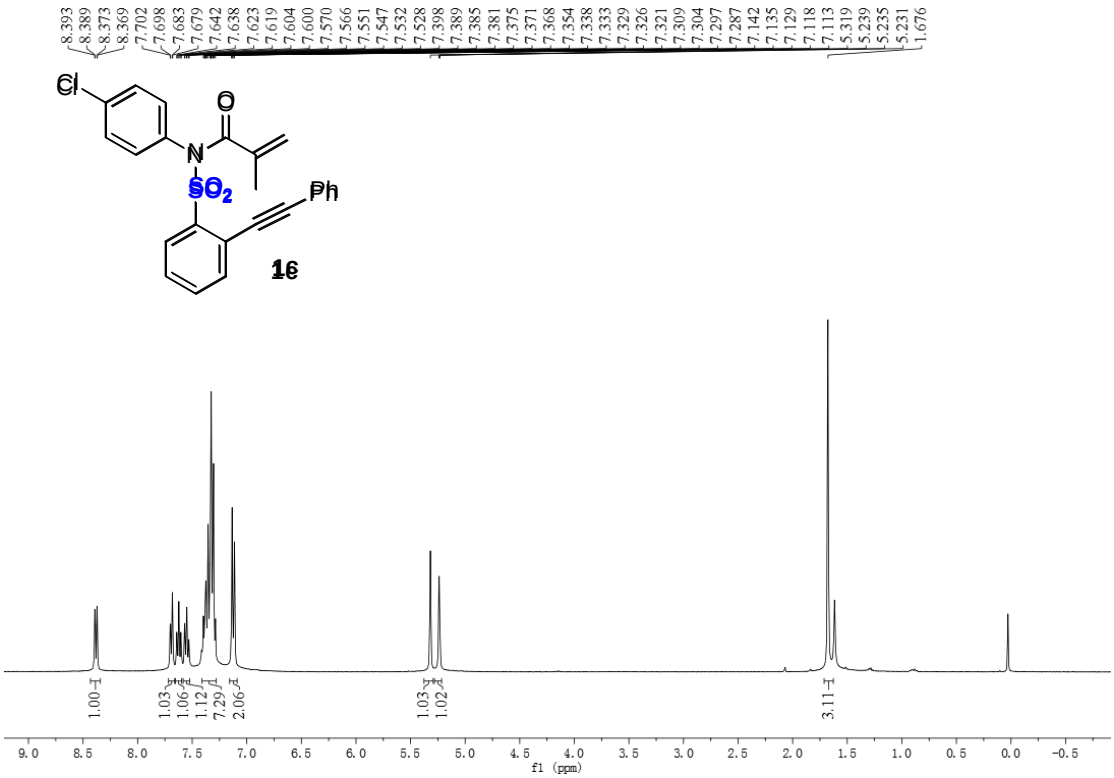

$^{13}$C NMR for **1b** (101 MHz, $CDCl_3$)



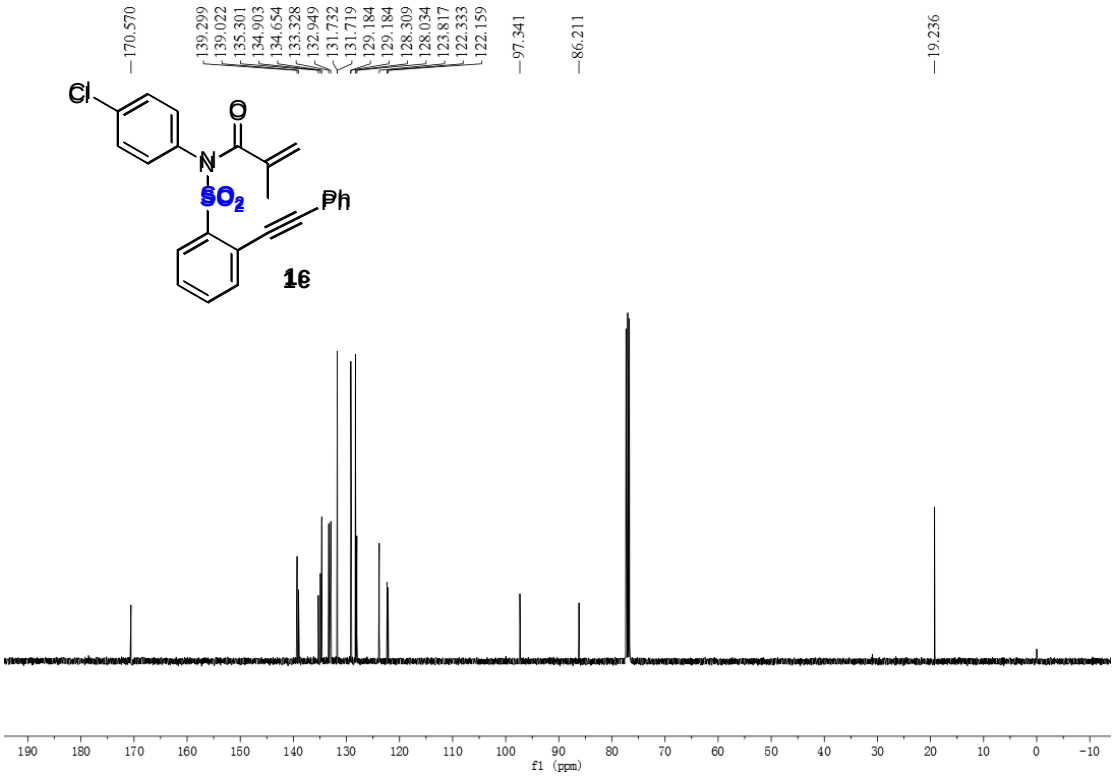
$^{19}$F NMR for **1b** (376 MHz, $CDCl_3$)



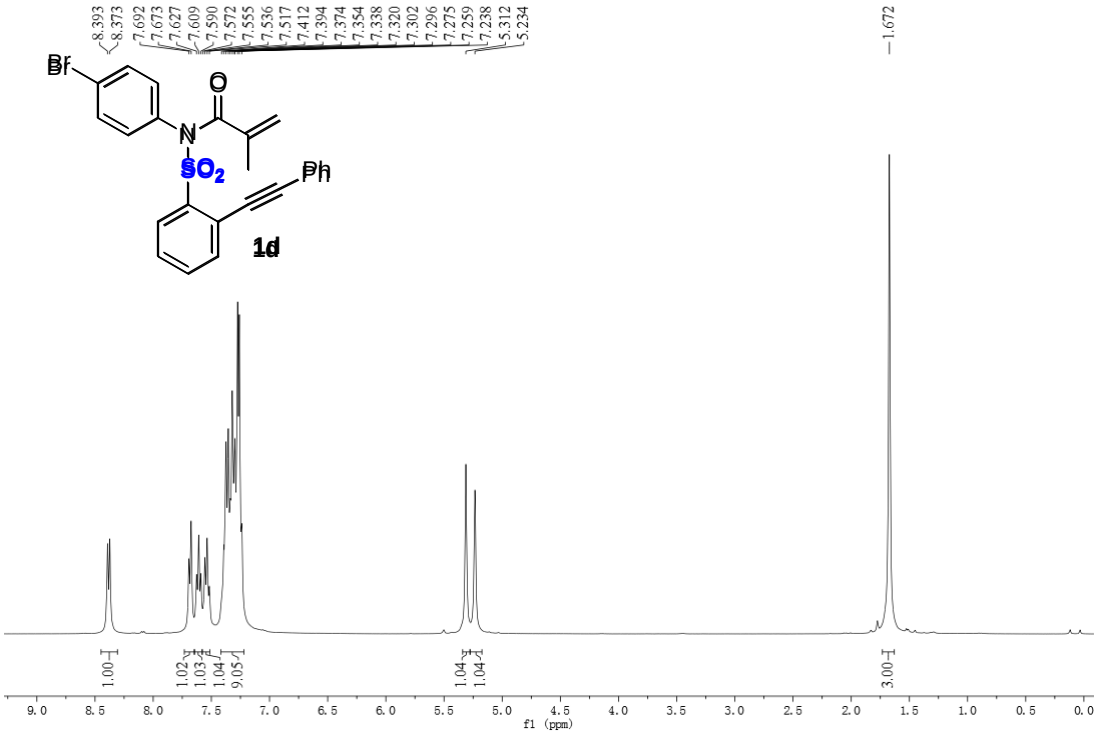

$^{1}$H NMR for **1c** (400 MHz, $CDCl_3$)



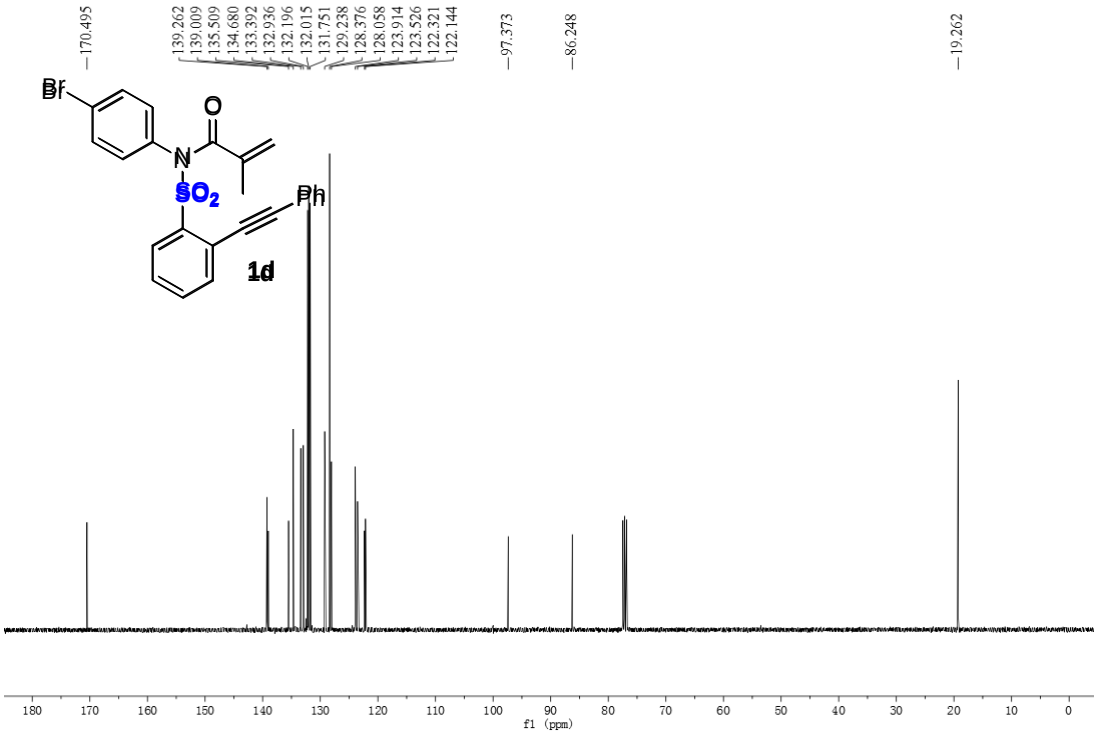
$^{13}$C NMR for **1c** (101 MHz, $CDCl_3$)




$^{1}$H NMR for **1d** (400 MHz, $CDCl_3$)



$^{13}$C NMR for **1d** (101 MHz, $CDCl_3$)

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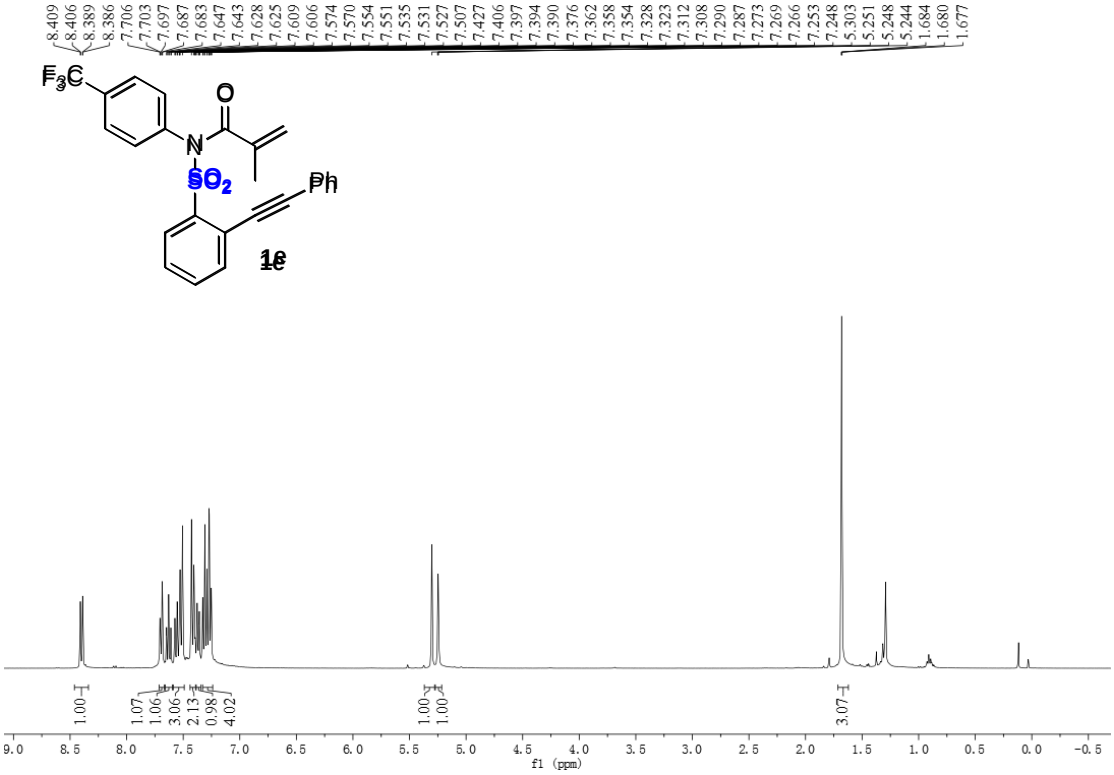
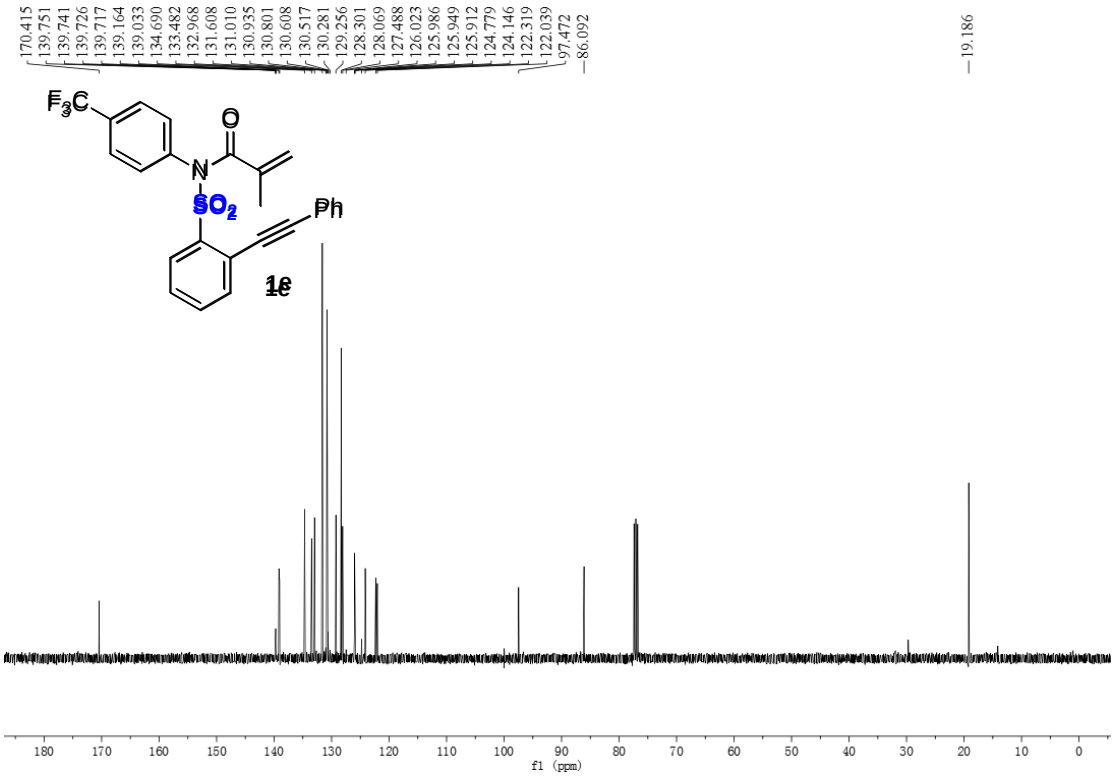
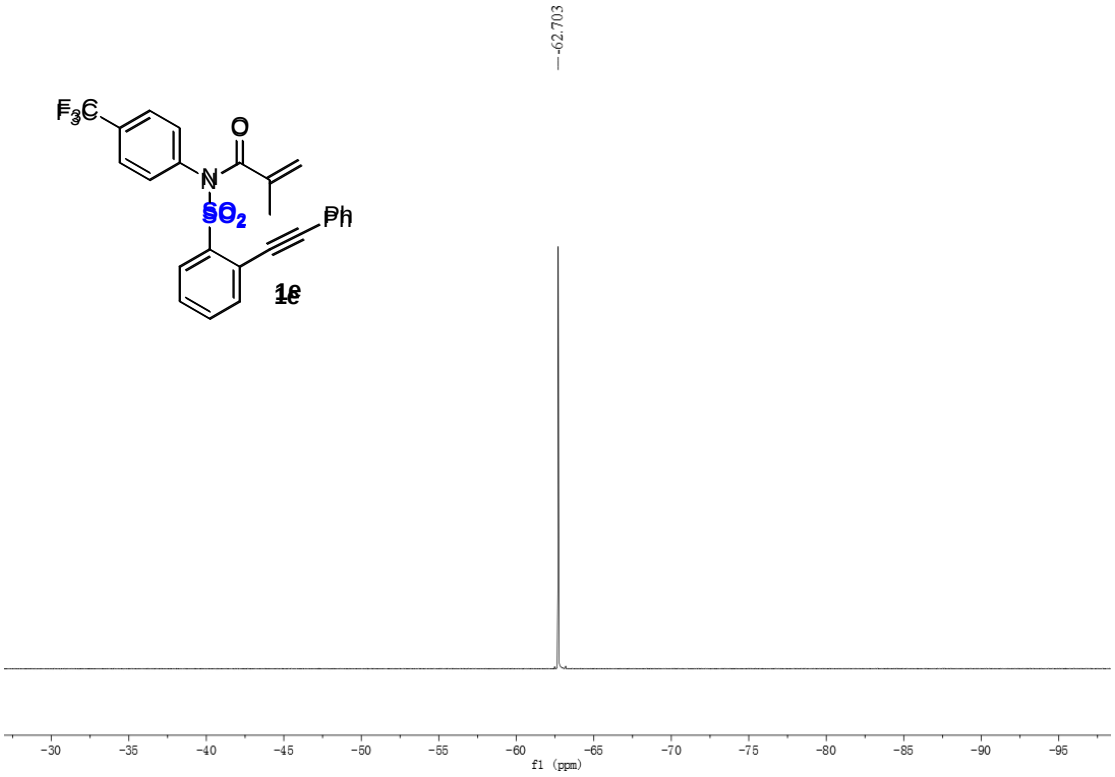


$^{13}$C NMR for **1e** (101 MHz, $CDCl_3$)




$^{19}$F NMR for **1e** (376 MHz, $CDCl_3$)



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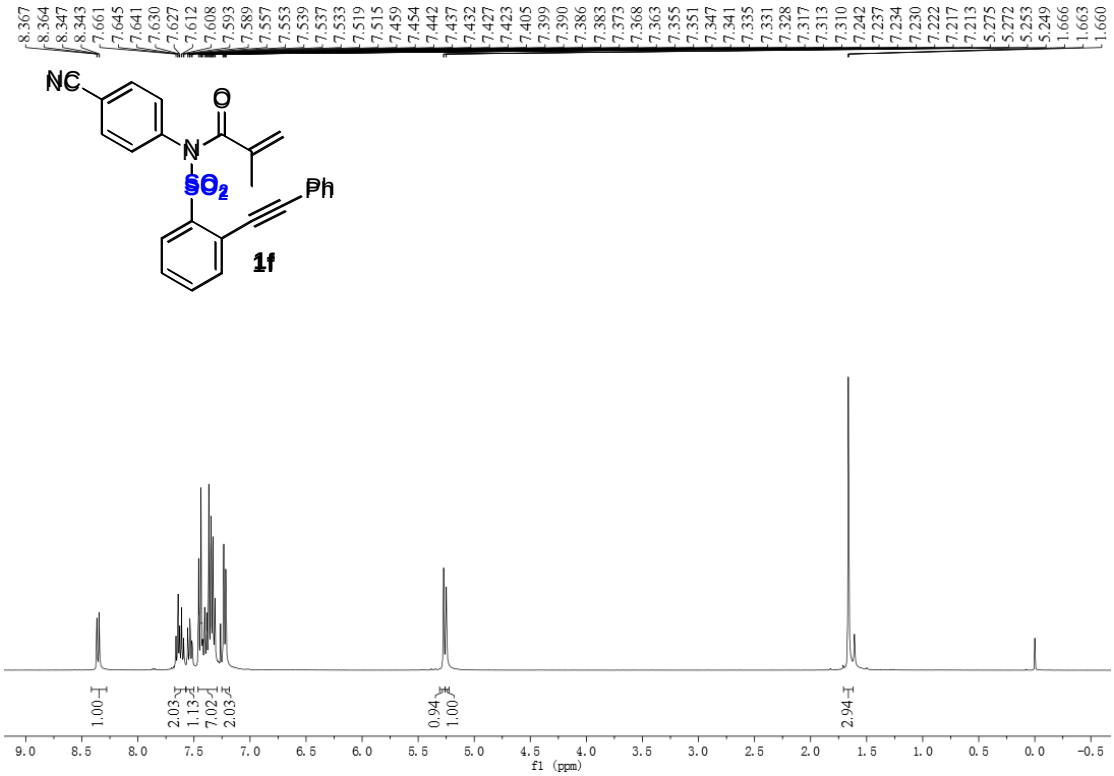
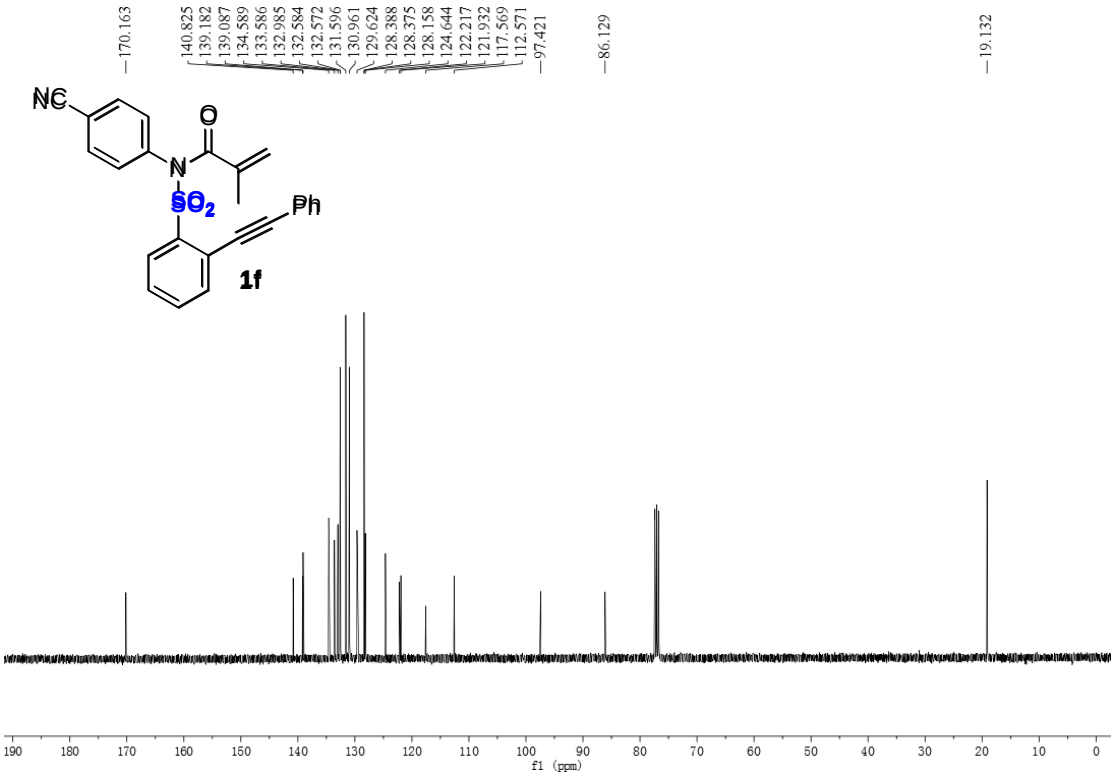
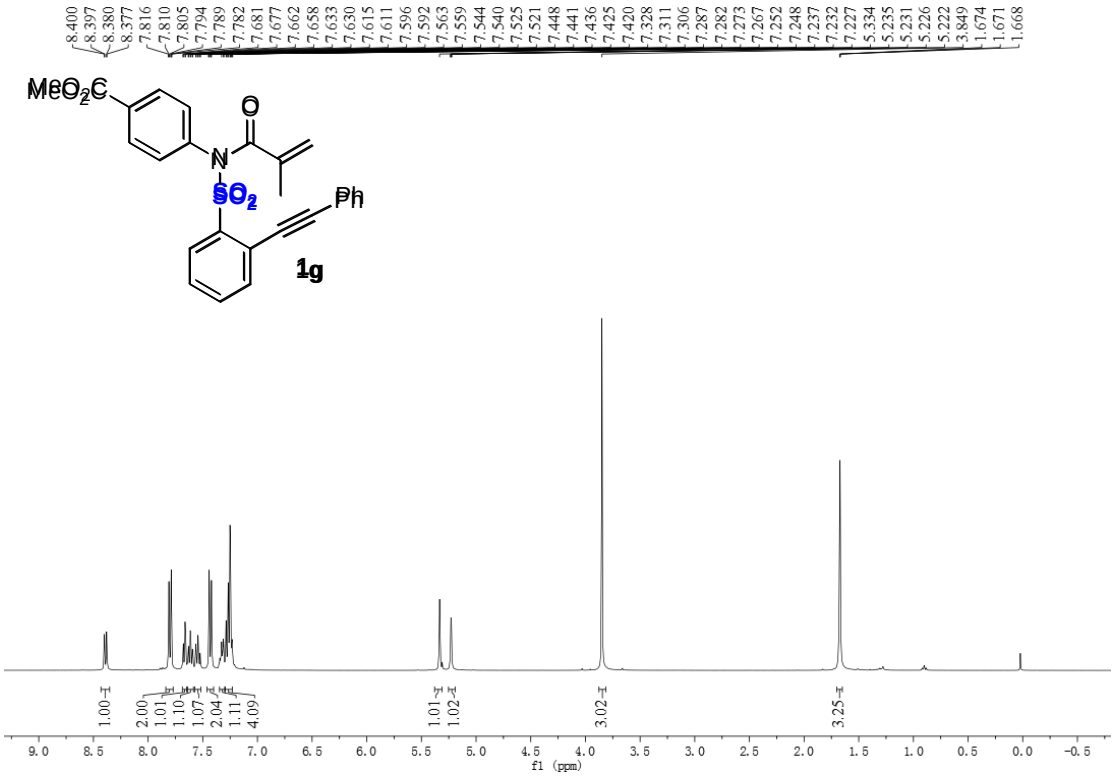


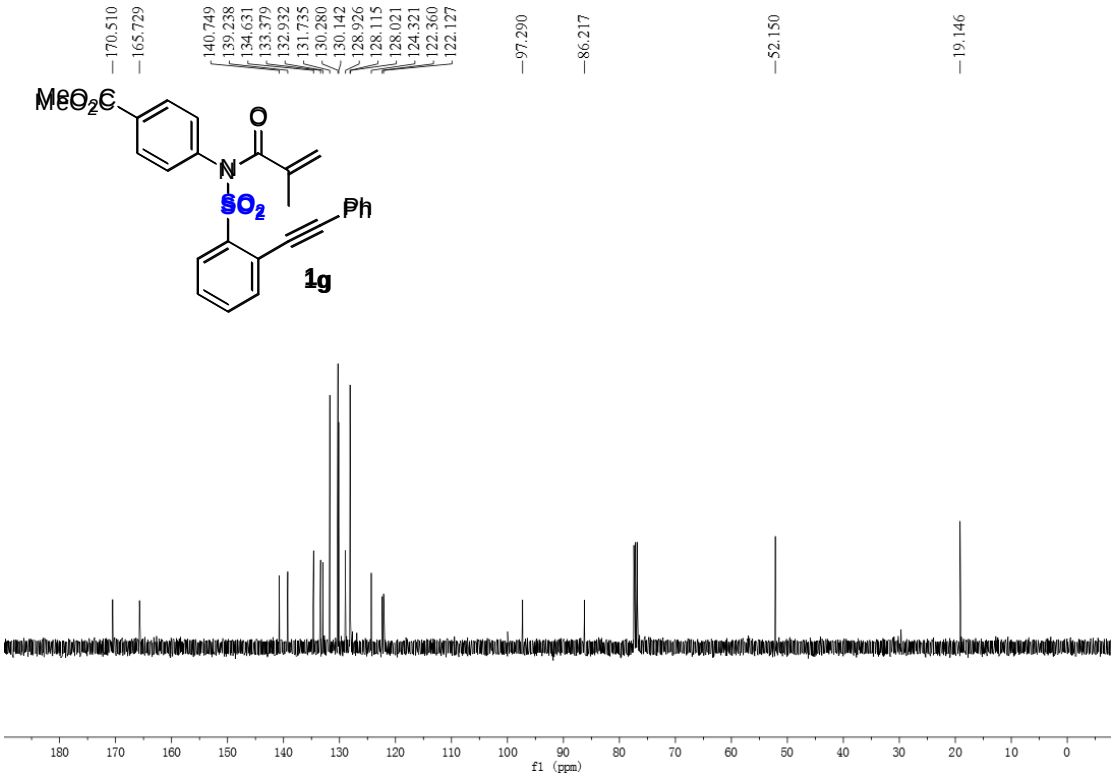

$^{13}$C NMR for **1f** (101 MHz, $CDCl_3$)



$^{1}$H NMR for **1g** (400 MHz, $CDCl_3$)




$^{13}$C NMR for **1g** (101 MHz, $CDCl_3$)



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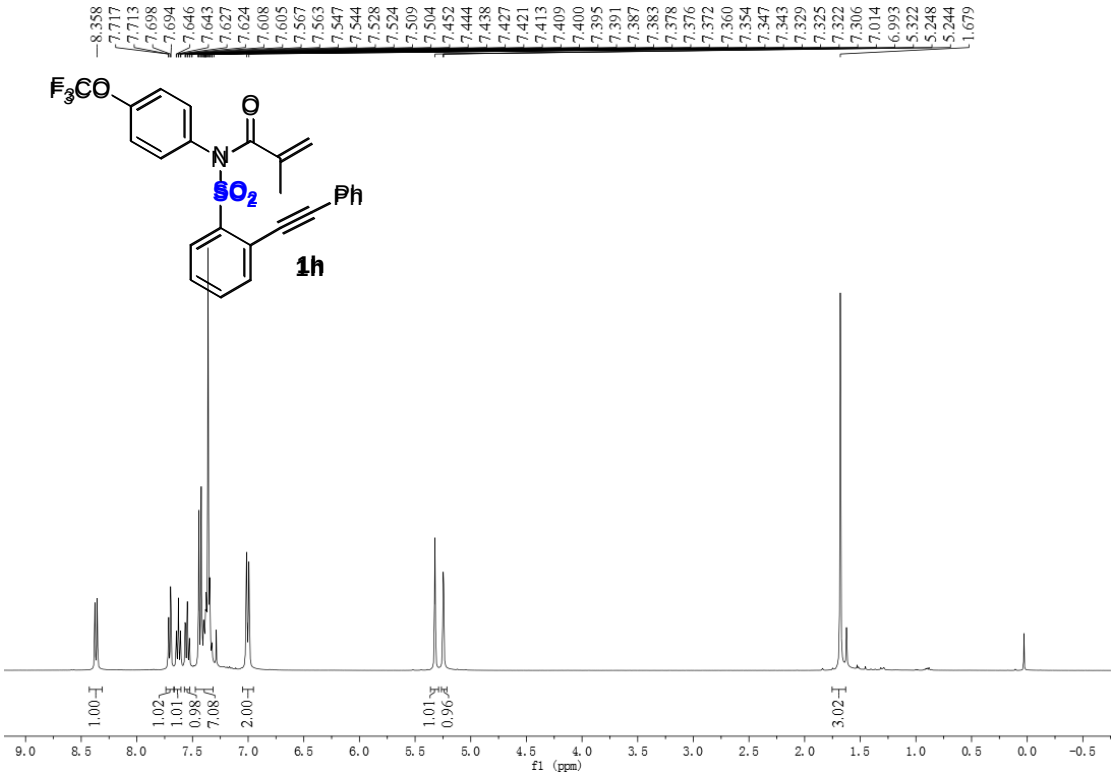
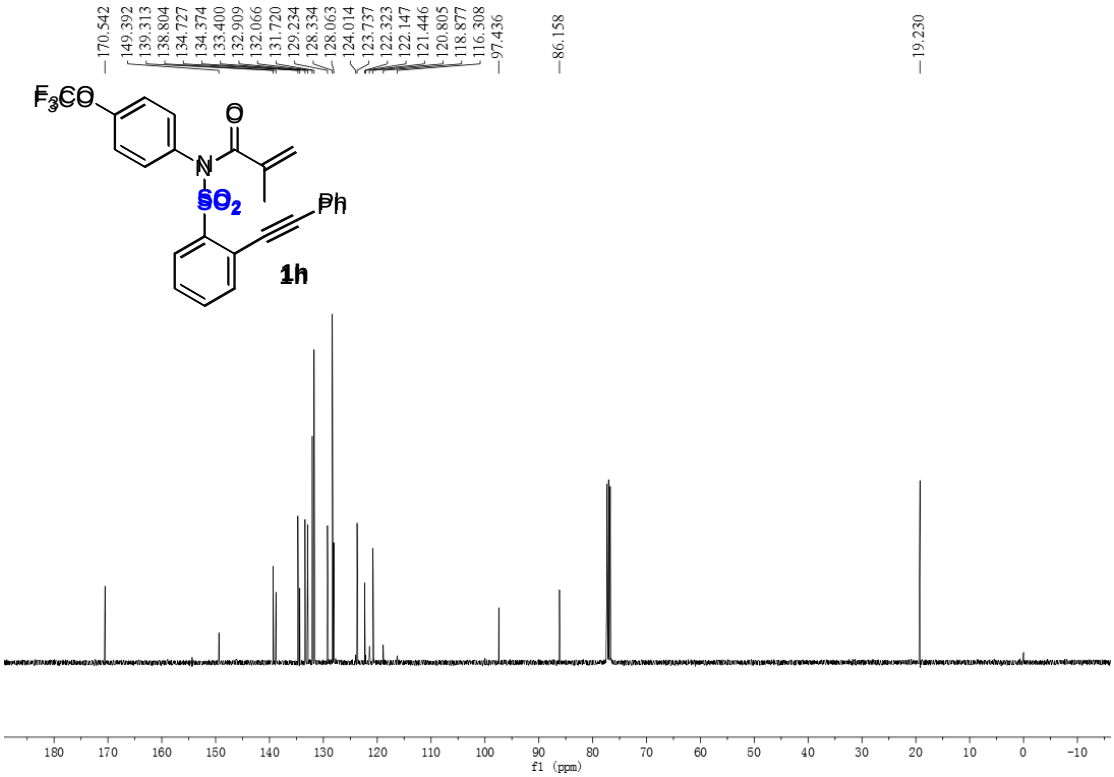
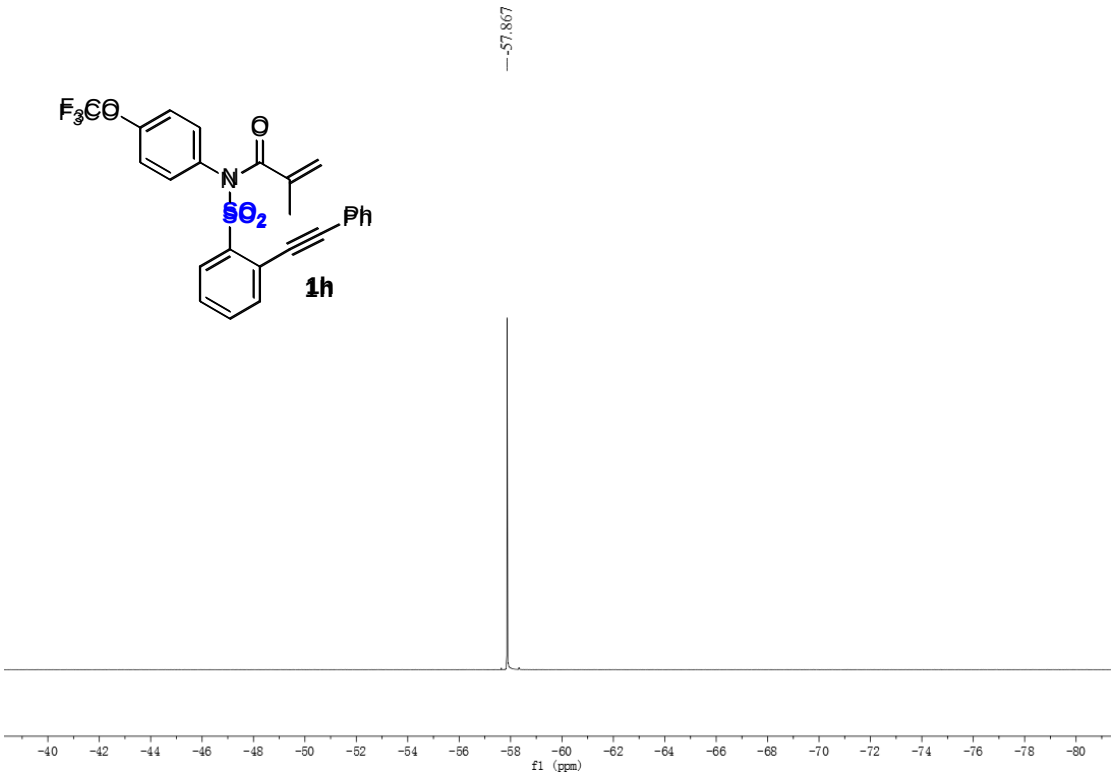


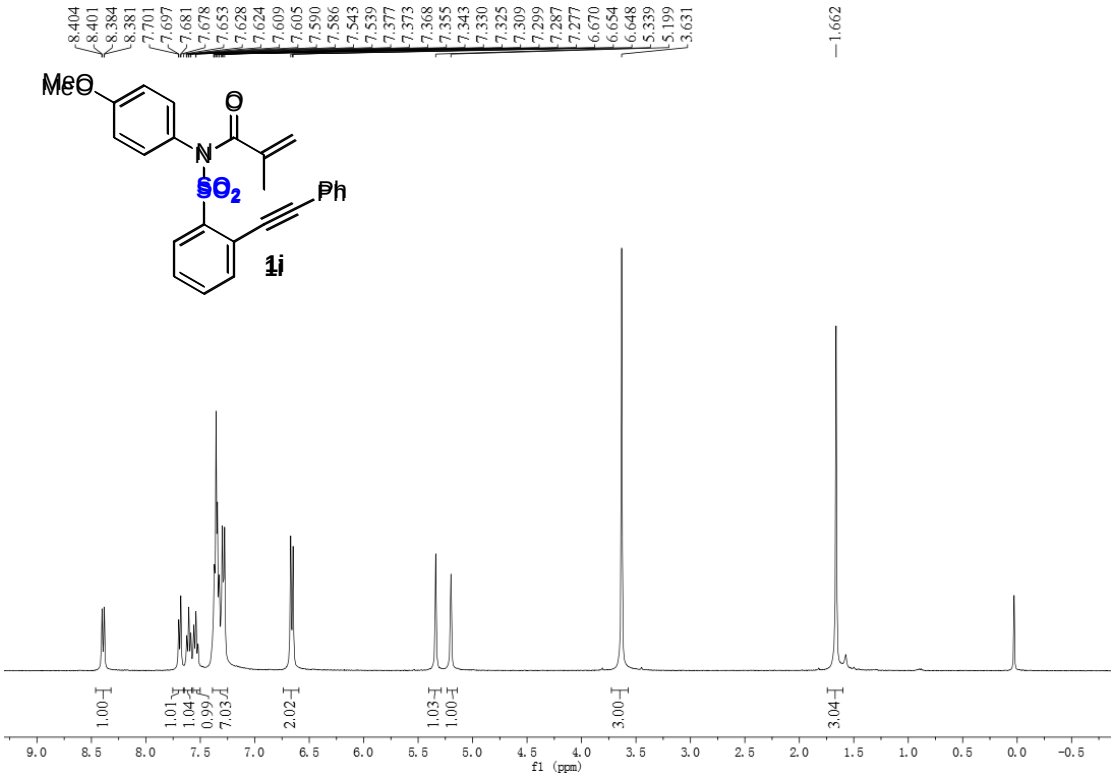

$^{13}$C NMR for **1h** (101 MHz, $CDCl_3$)



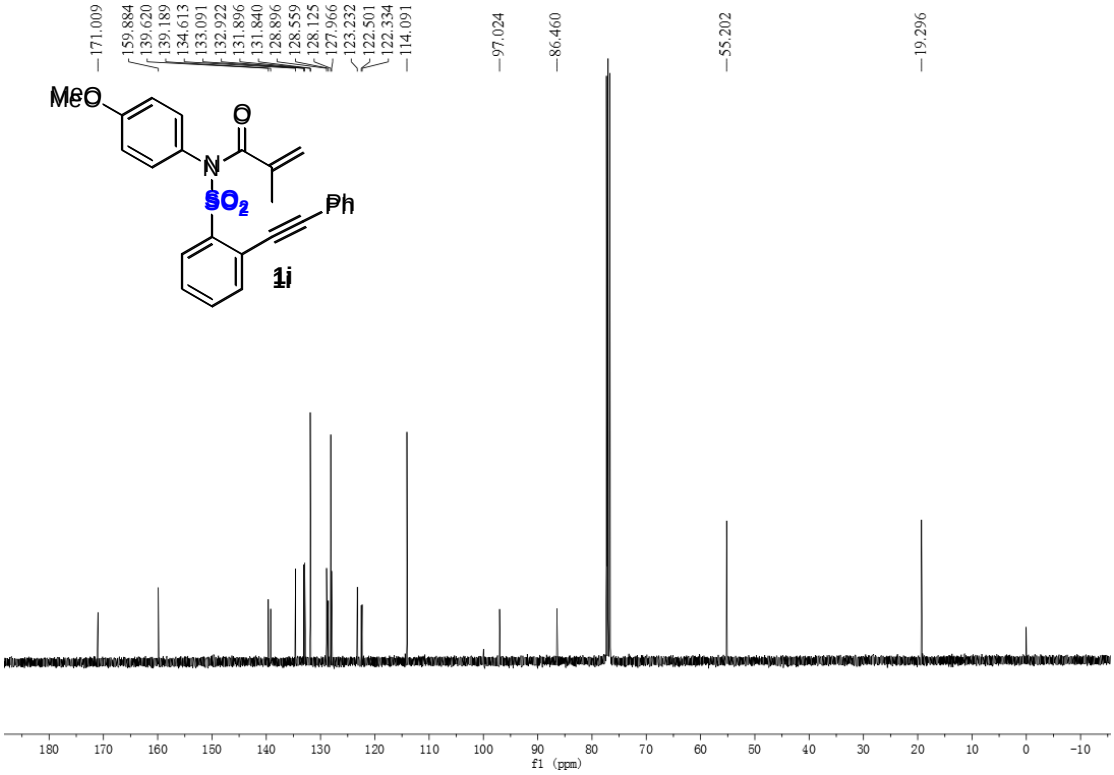
$^{19}$F NMR for **1h** (376 MHz, $CDCl_3$)



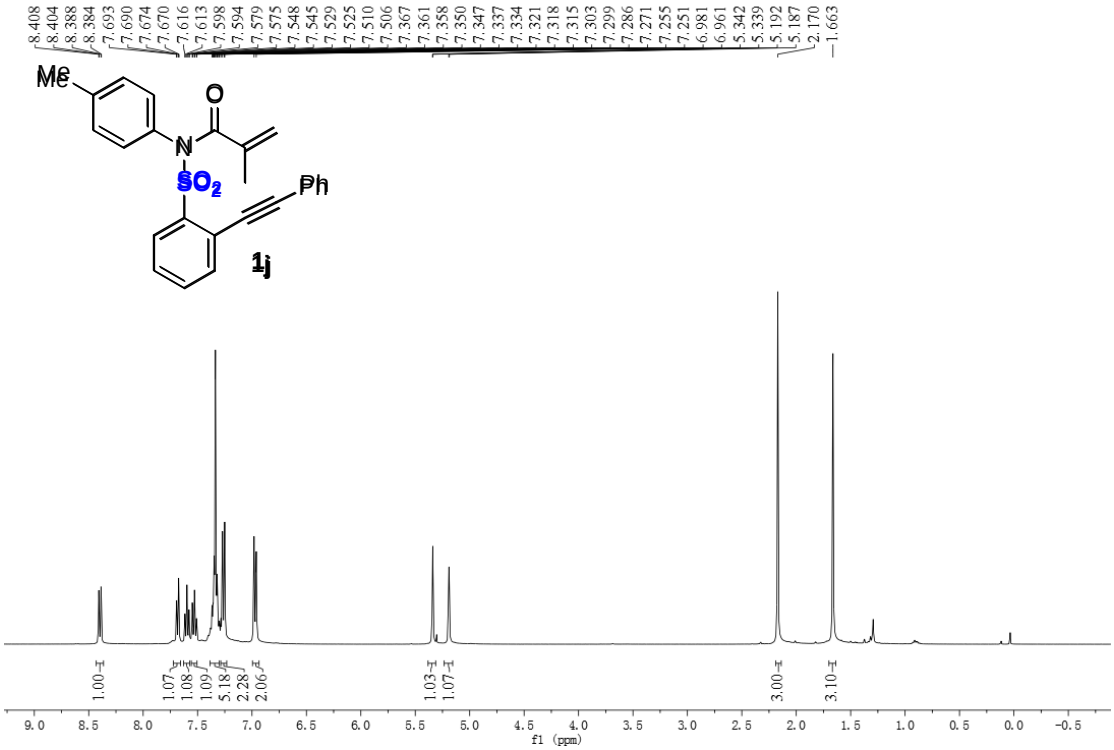

$^{1}$H NMR for **1i** (400 MHz, $CDCl_3$)



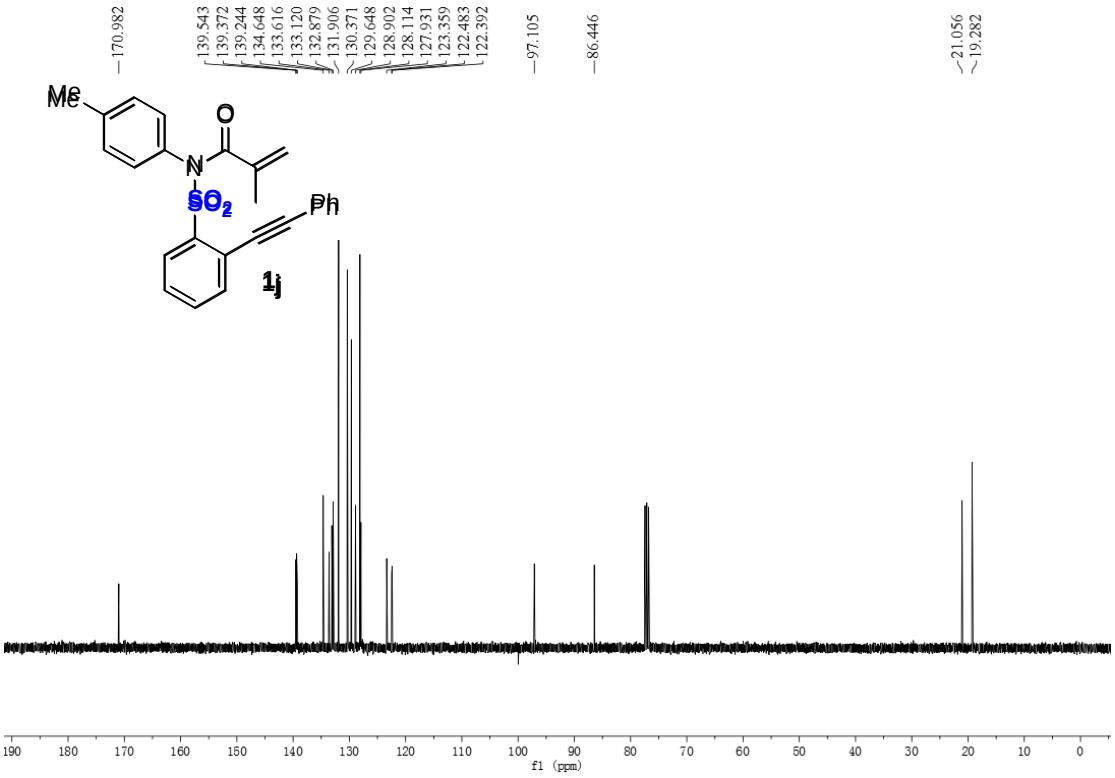
$^{13}$C NMR for **1i** (101 MHz, $CDCl_3$)



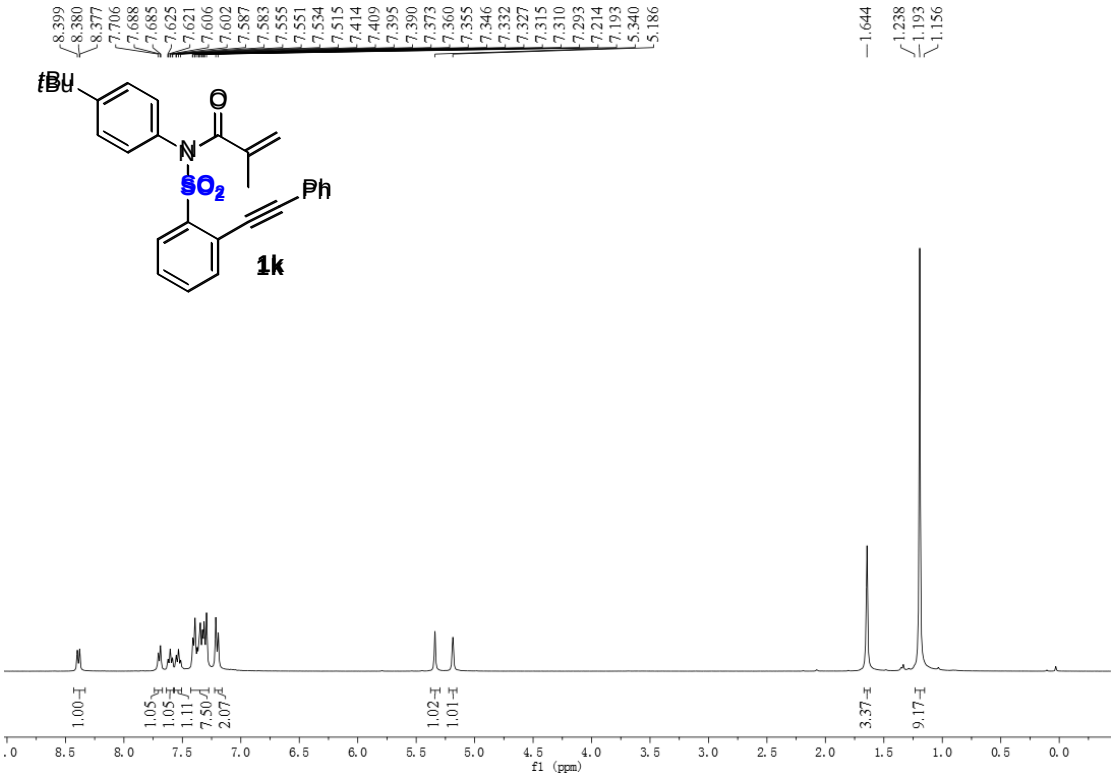

$^{1}$H NMR for **1j** (400 MHz, $CDCl_3$)



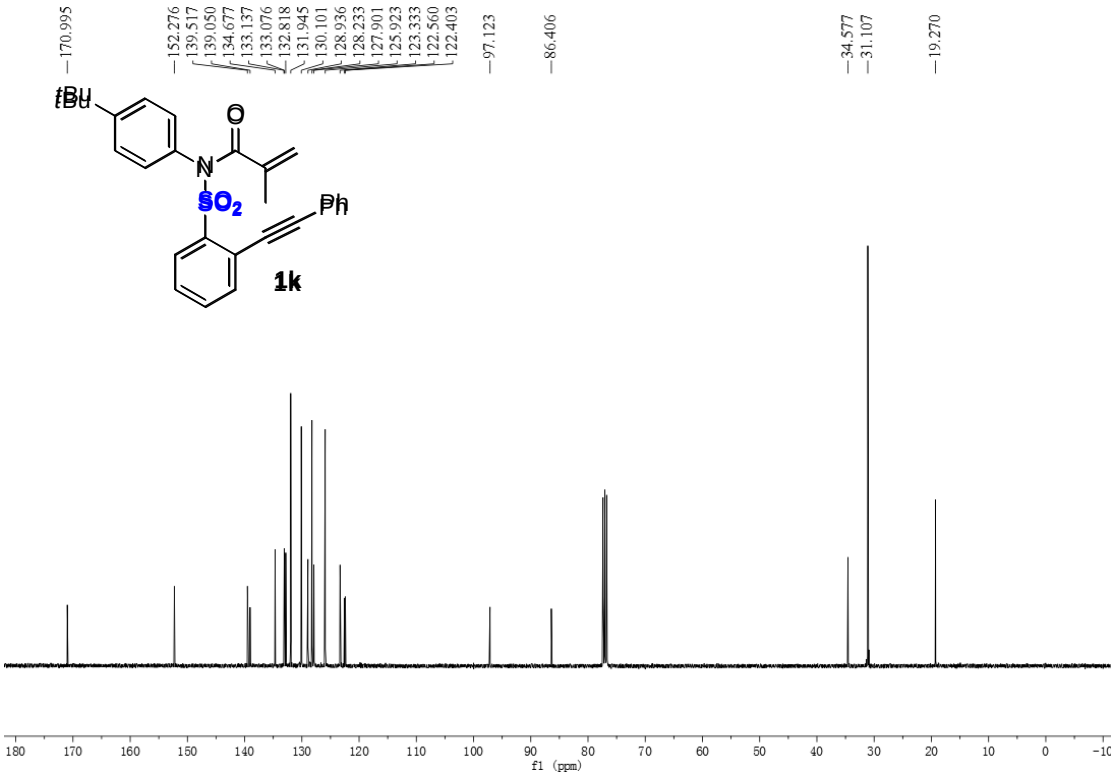
$^{13}$C NMR for **1j** (101 MHz, $CDCl_3$)



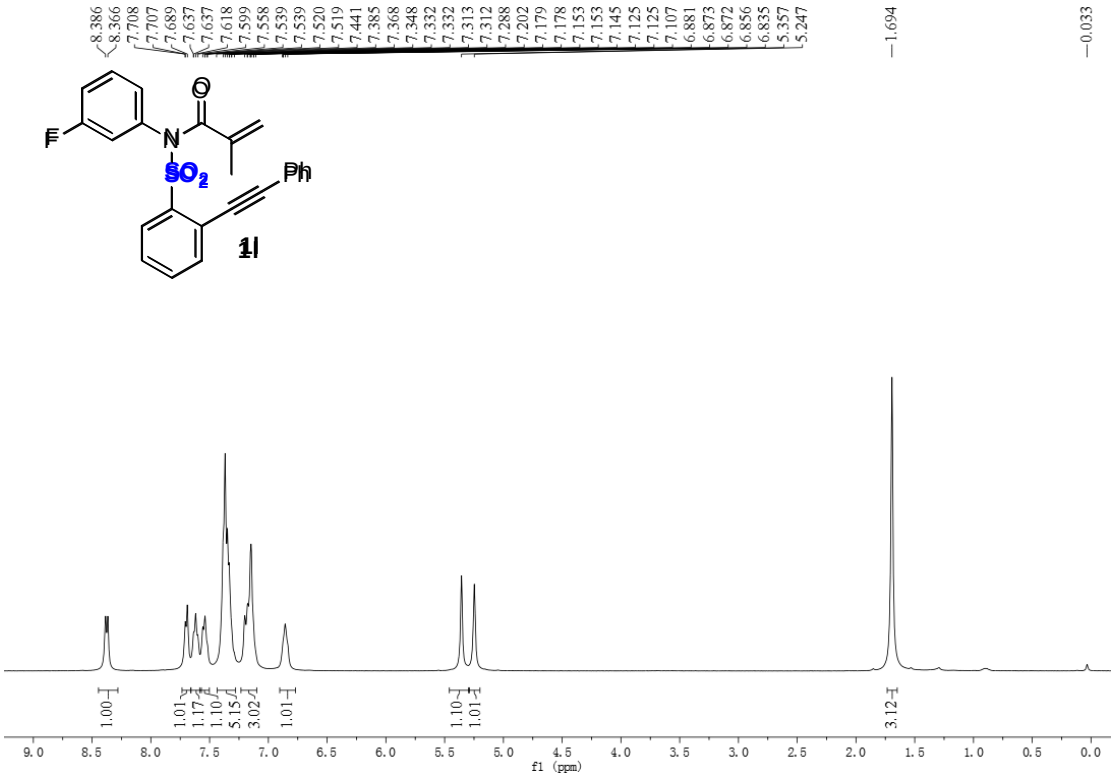

$^{1}$H NMR for **1k** (400 MHz, $CDCl_3$)



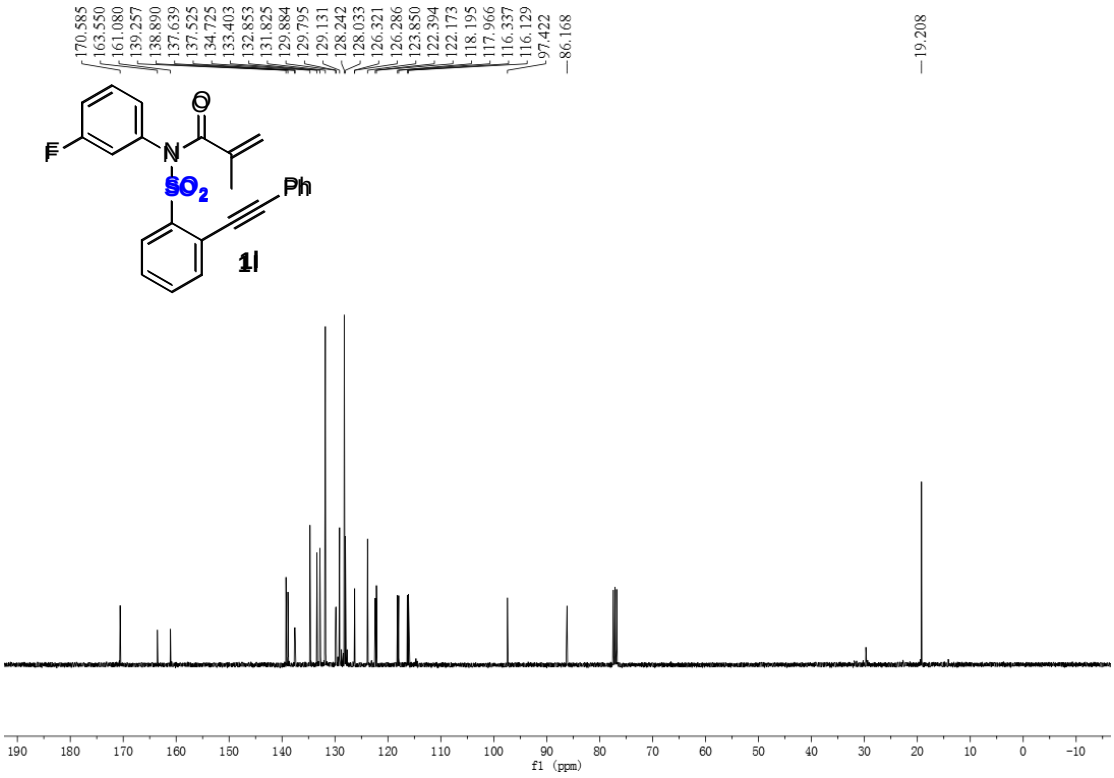
$^{13}$C NMR for **1k** (101 MHz, $CDCl_3$)



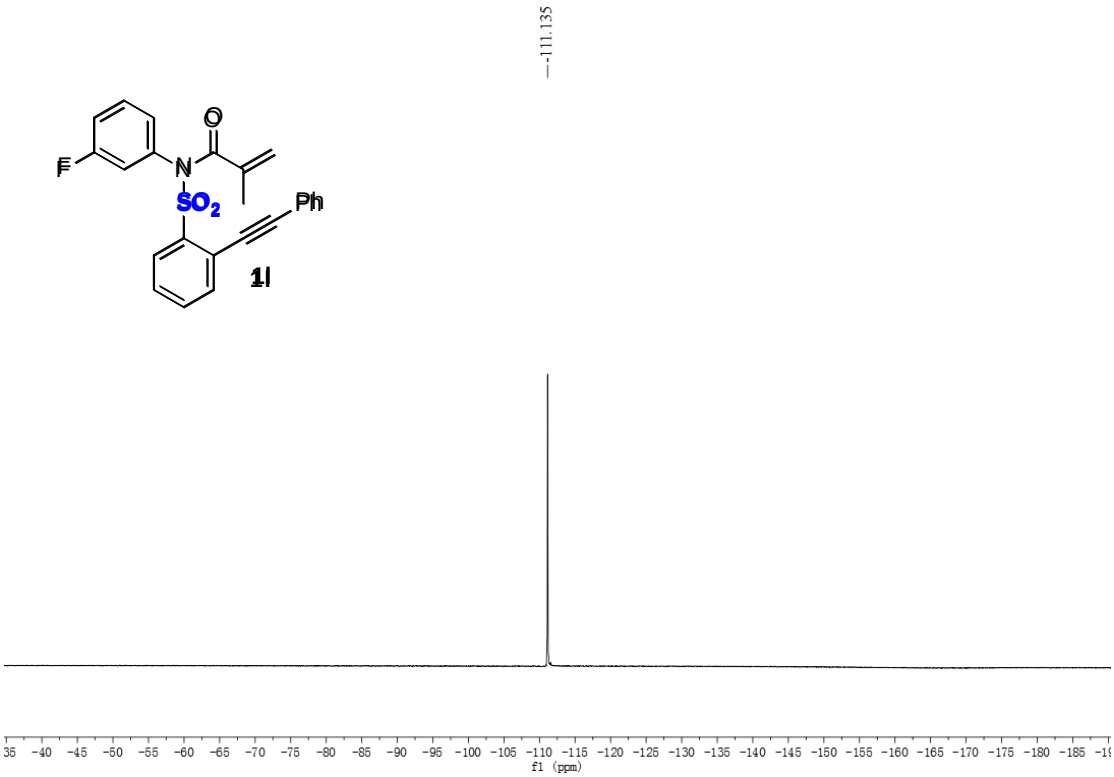

$^{1}$H NMR for **1l** (400 MHz, $CDCl_3$)



$^{13}$C NMR for **1l** (101 MHz, $CDCl_3$)




$^{19}$F NMR for **1l** (376 MHz, $CDCl_3$)



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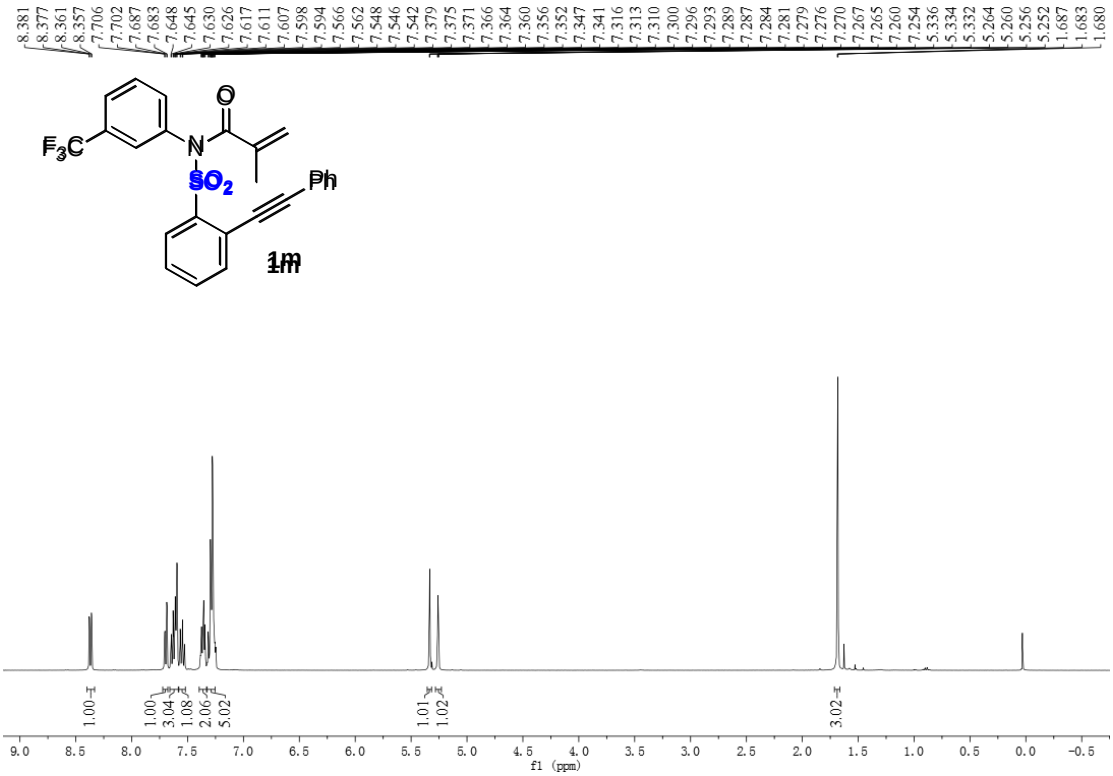
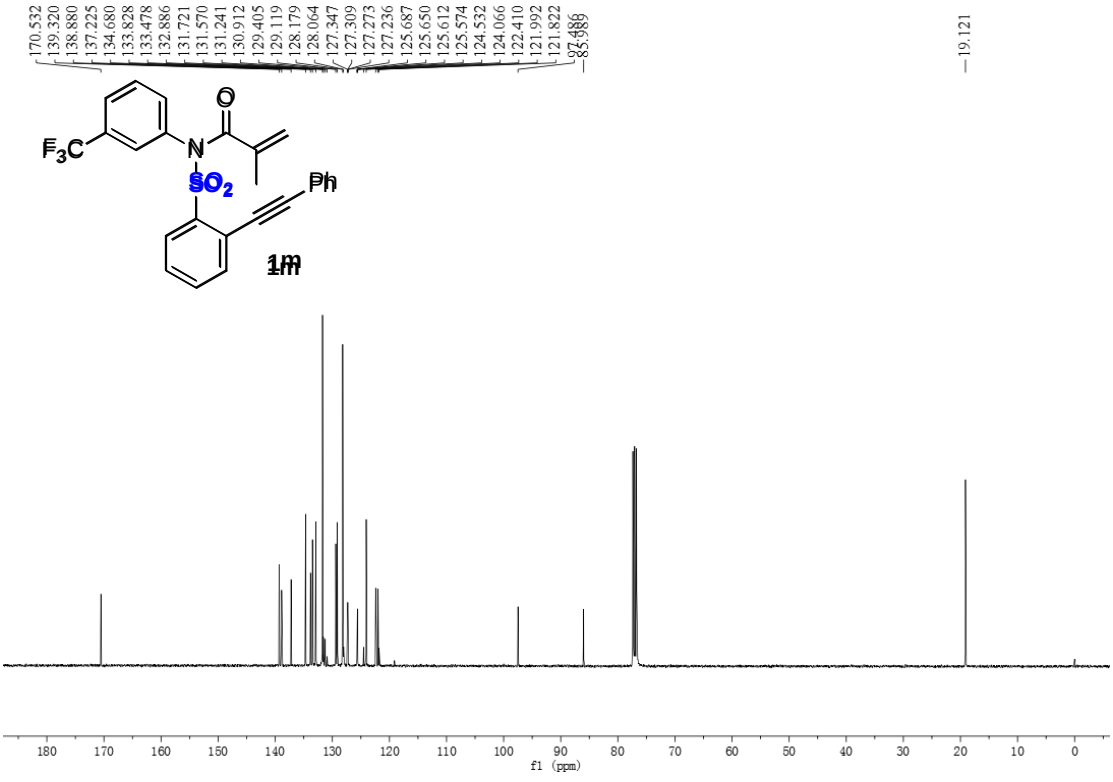
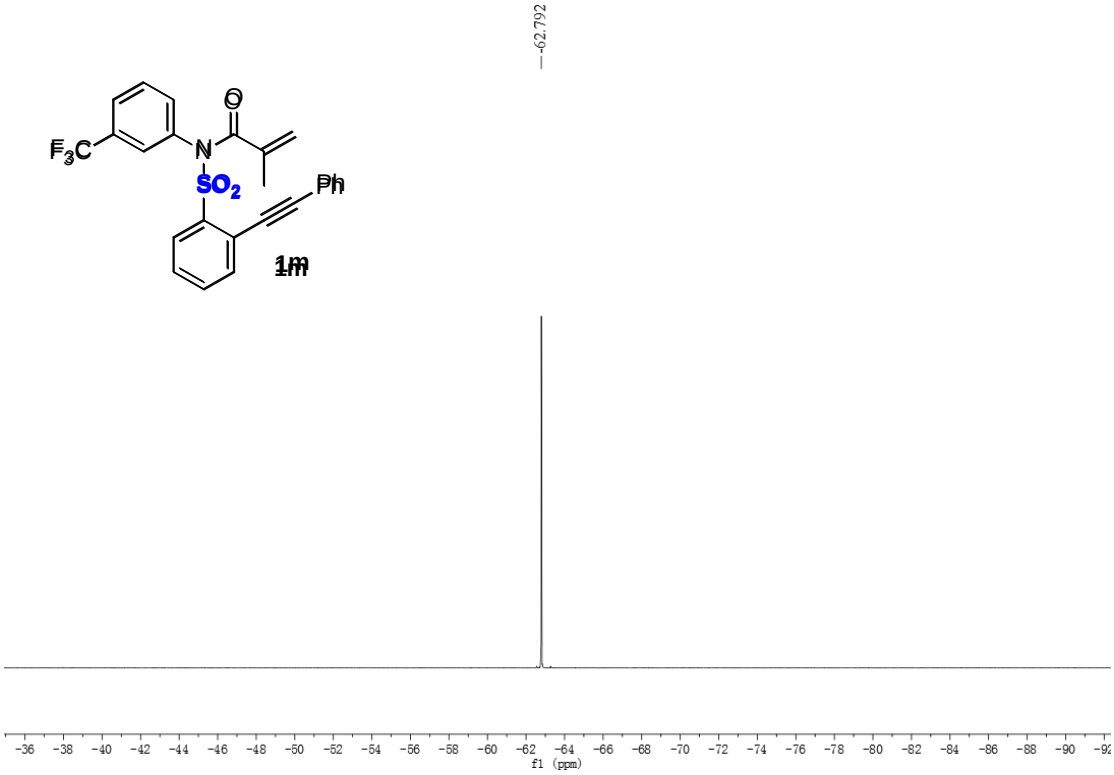


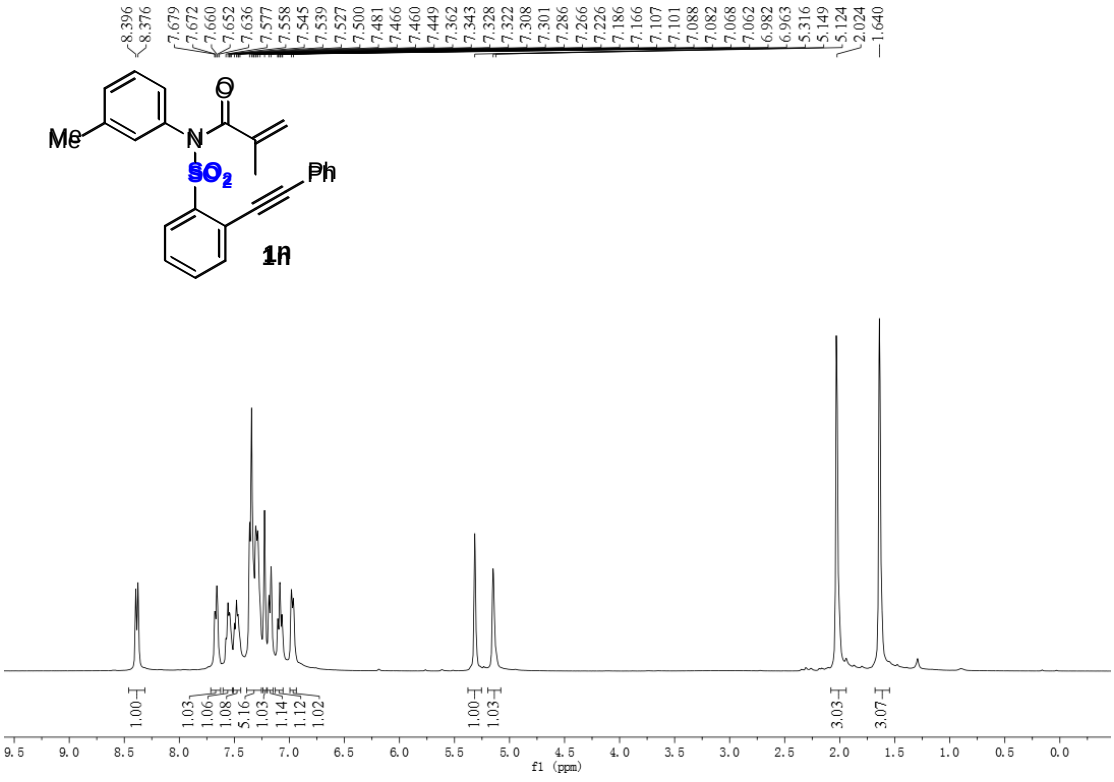

$^{13}$C NMR for **1m** (101 MHz, $CDCl_3$)



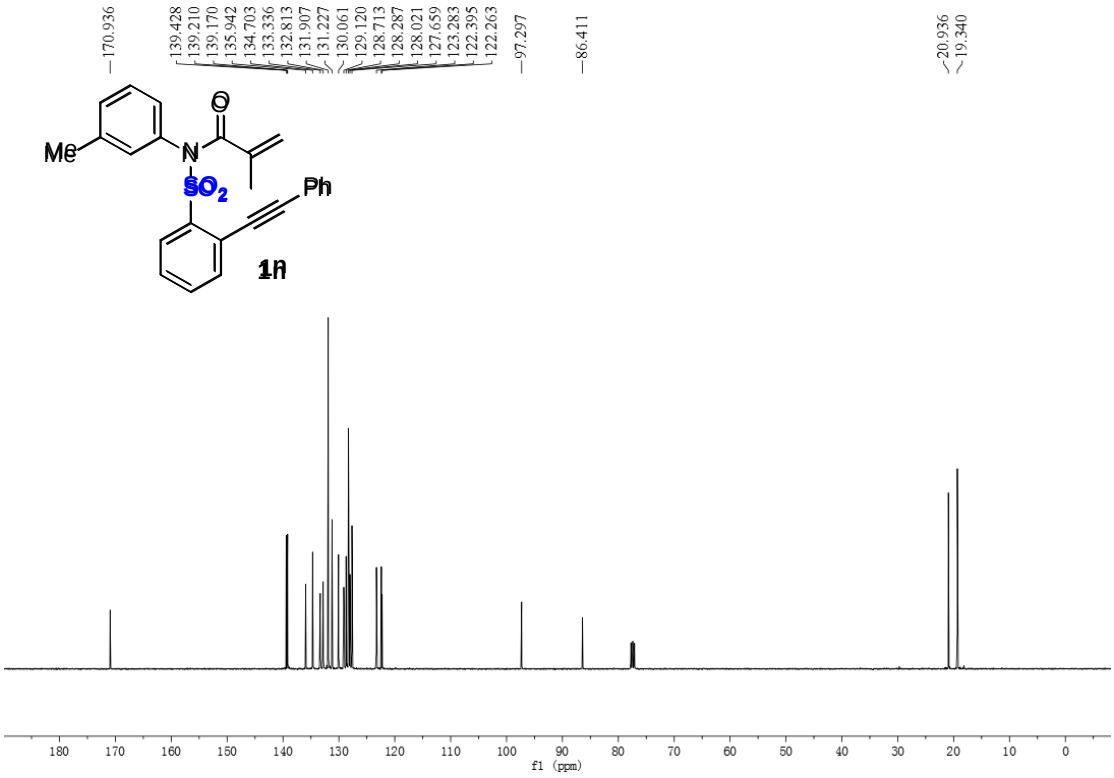
$^{19}$F NMR for **1m** (376 MHz, $CDCl_3$)




$^{1}$H NMR for **1n** (400 MHz, $CDCl_3$)



$^{13}C$ NMR for **1n** (101 MHz, $CDCl_3$)

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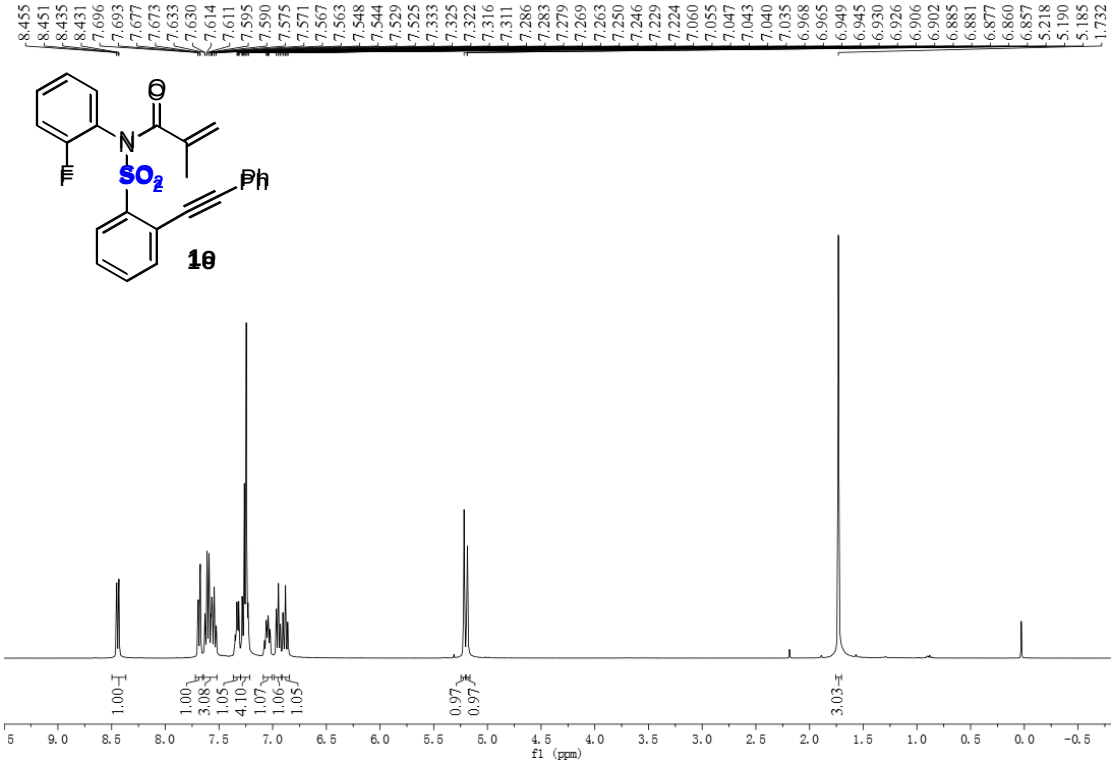

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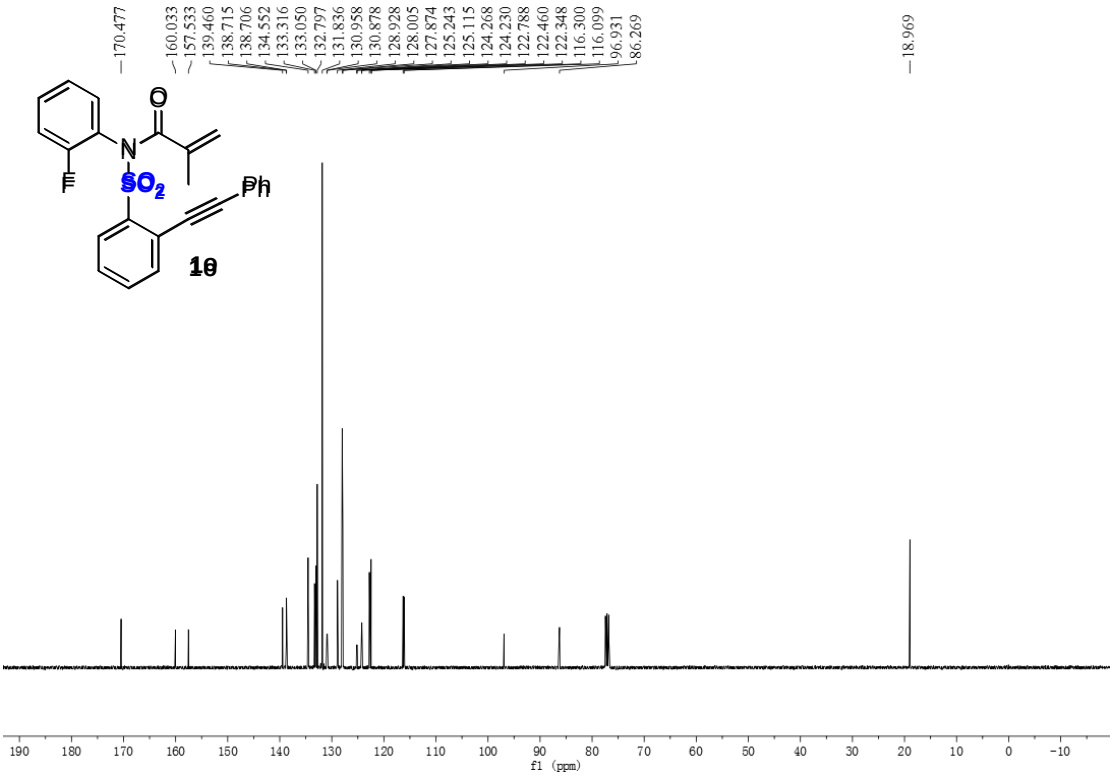


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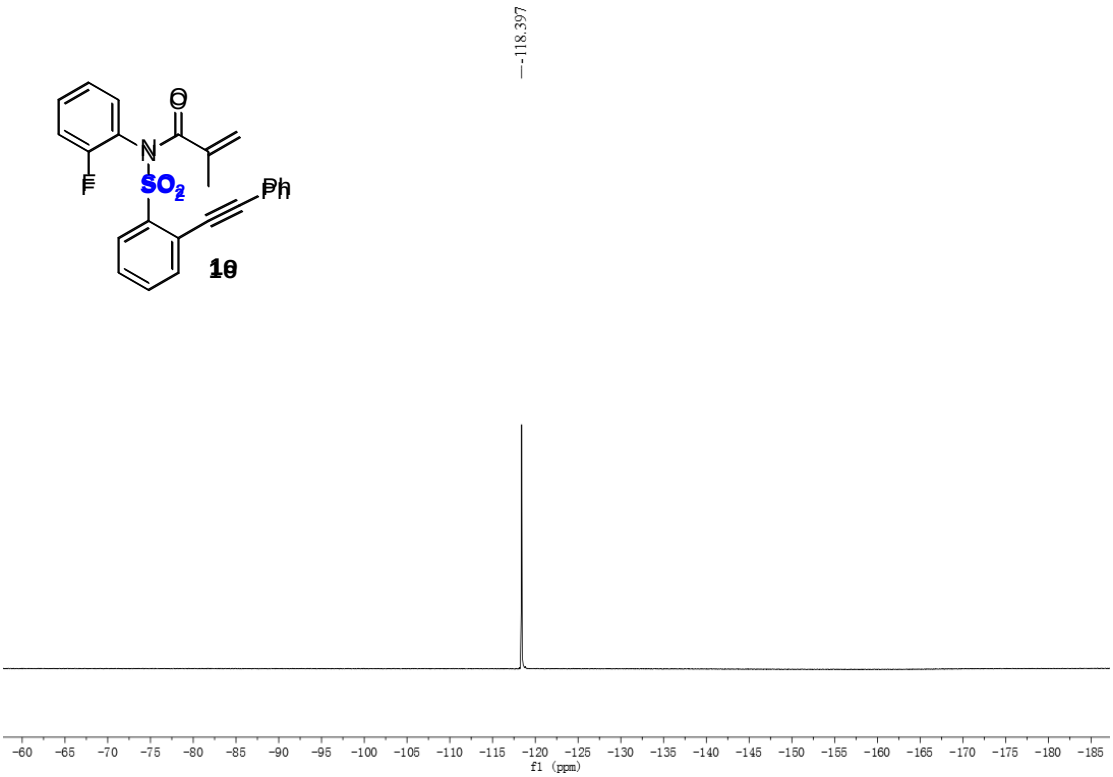

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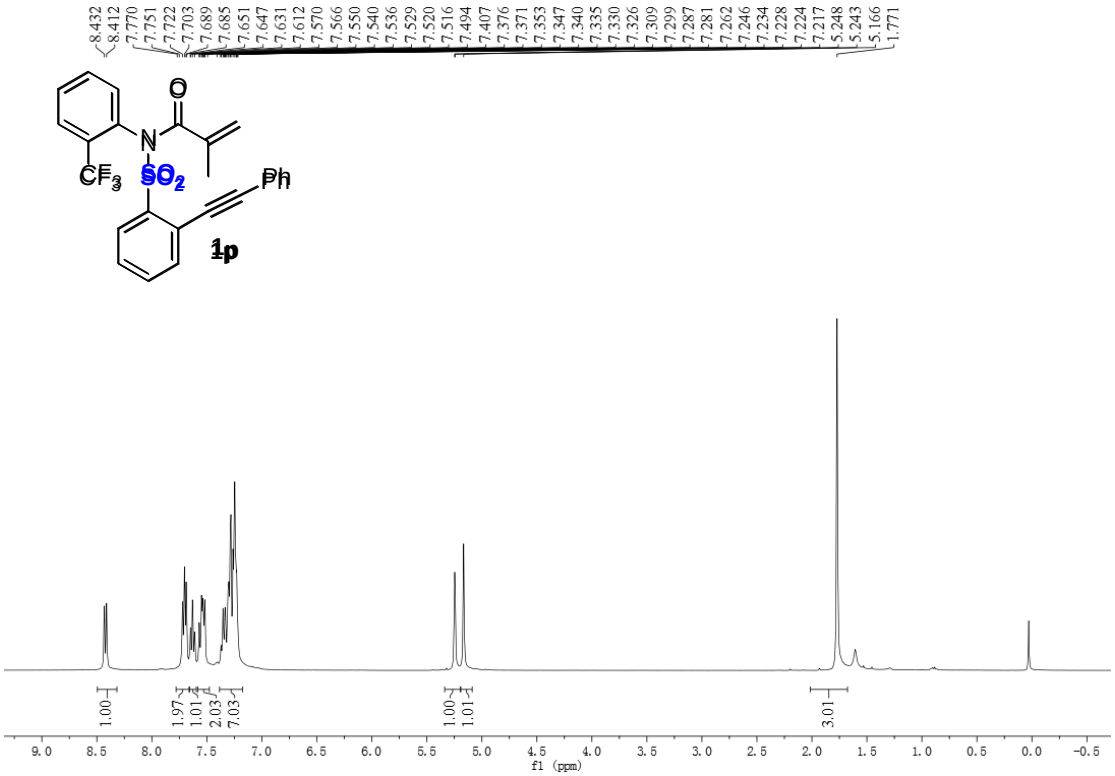


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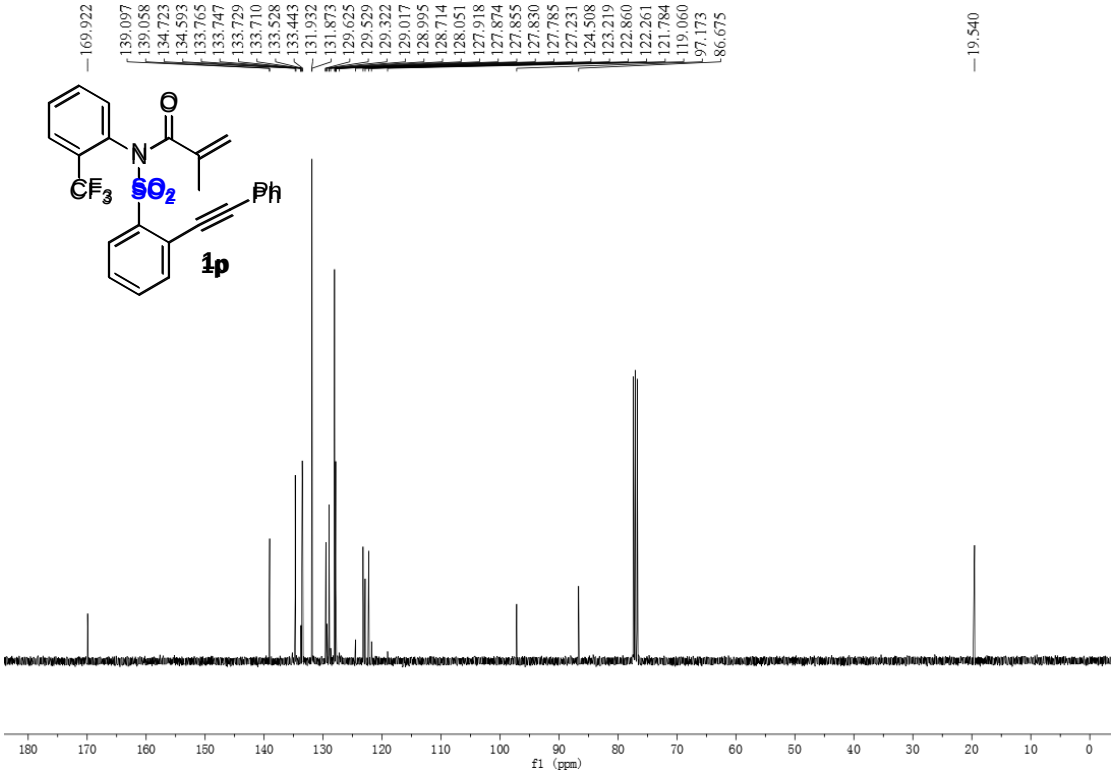
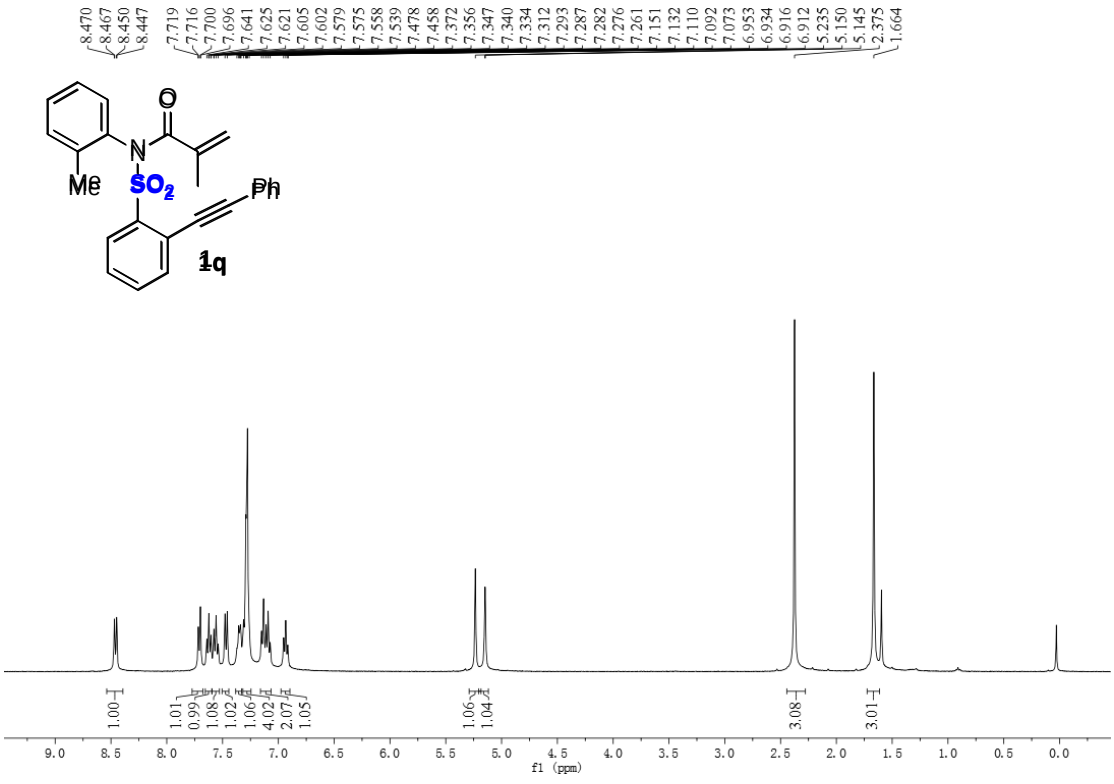


$^{19}$F NMR for **1p** (376 MHz, $CDCl_3$)


$^{1}$H NMR for **1q** (400 MHz, $CDCl_3$)



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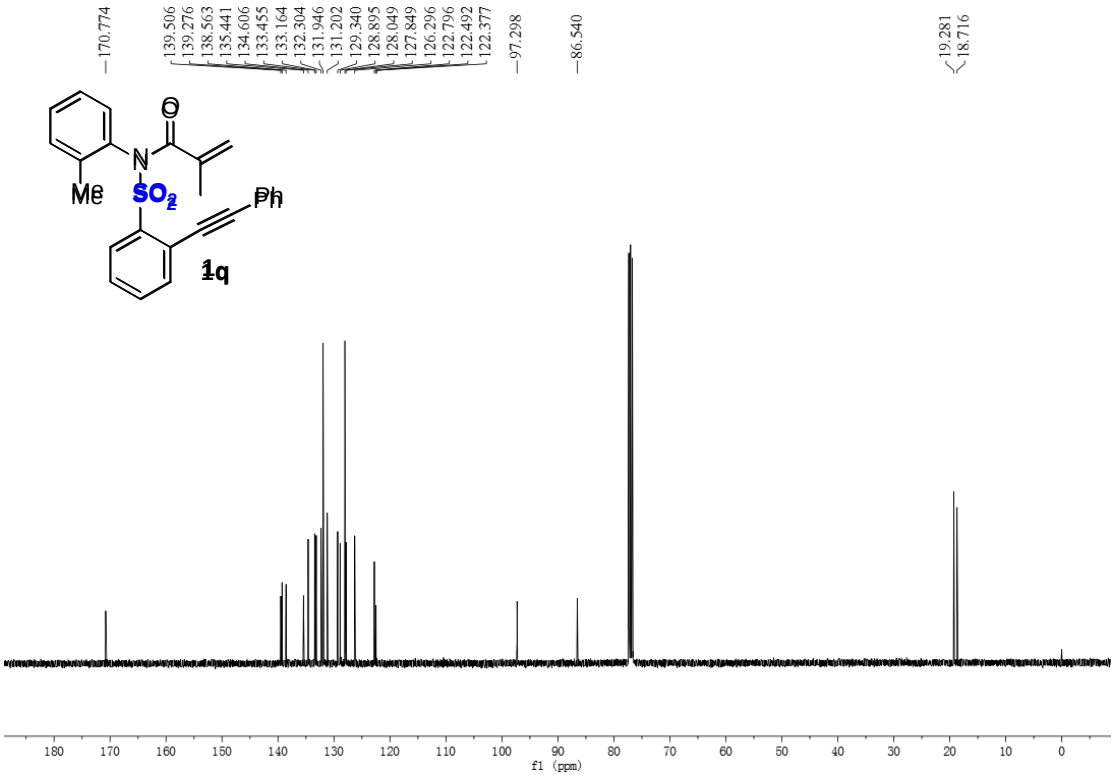
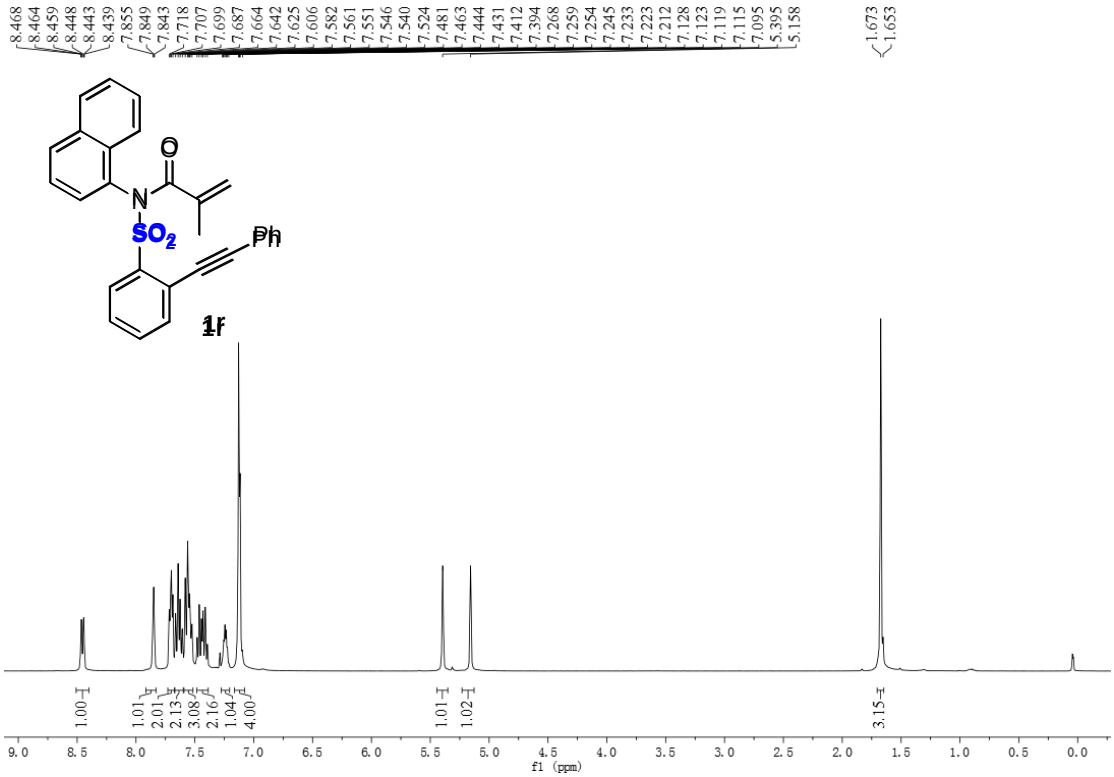



$^{1}$H NMR for **1r** (400 MHz, $CDCl_3$)



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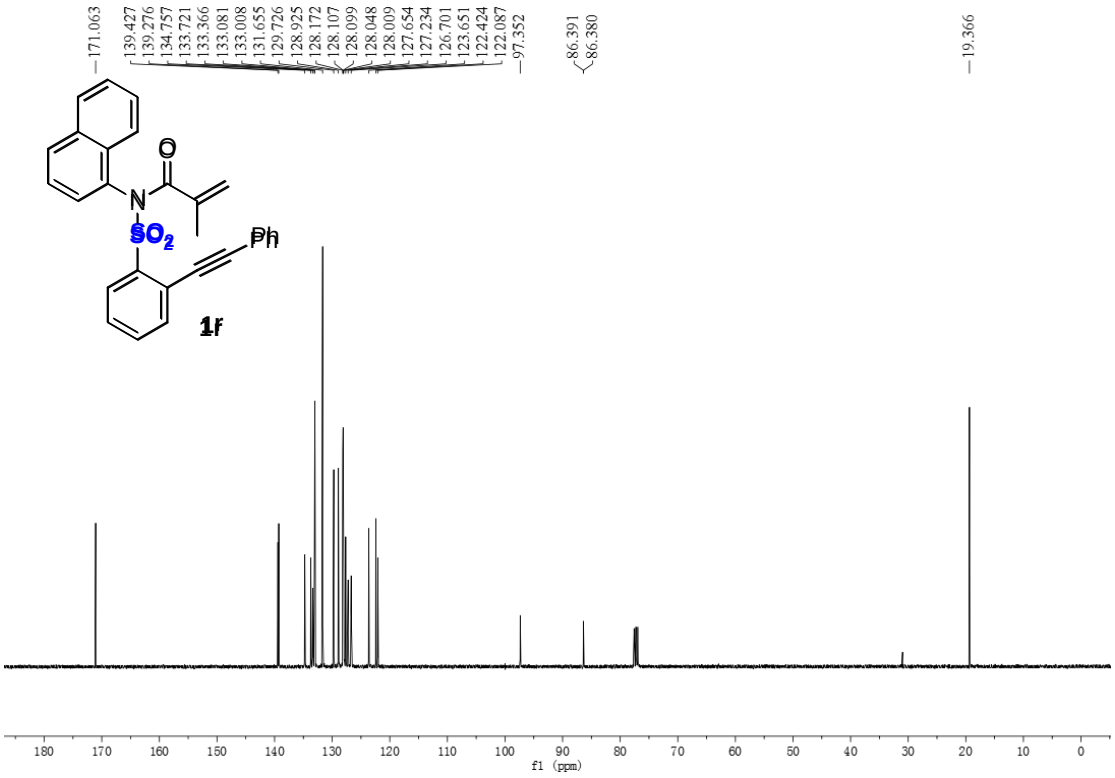
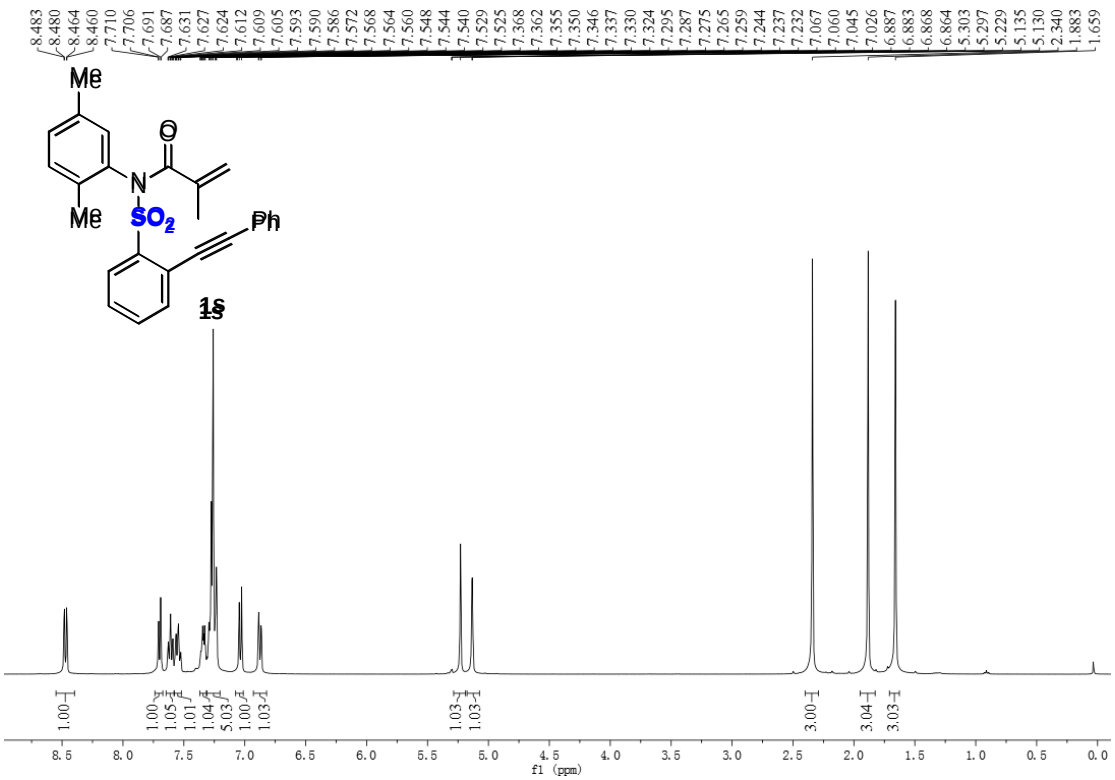



$^{1}$H NMR for **1s** (400 MHz, $CDCl_3$)



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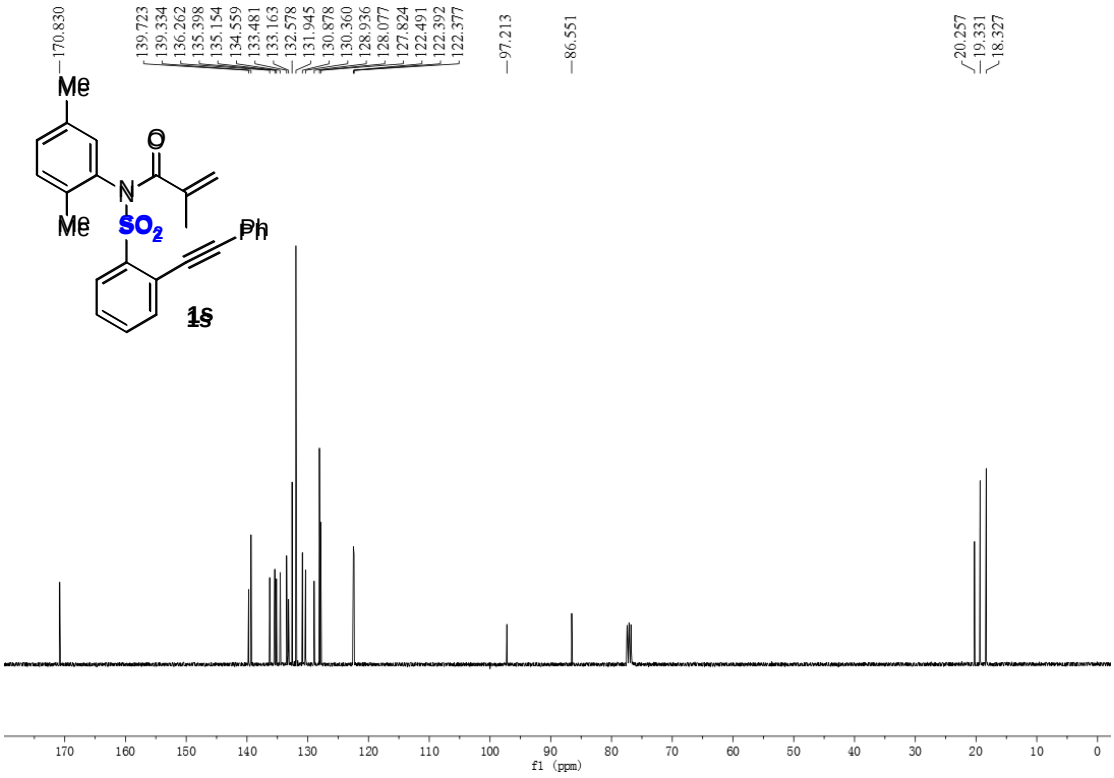


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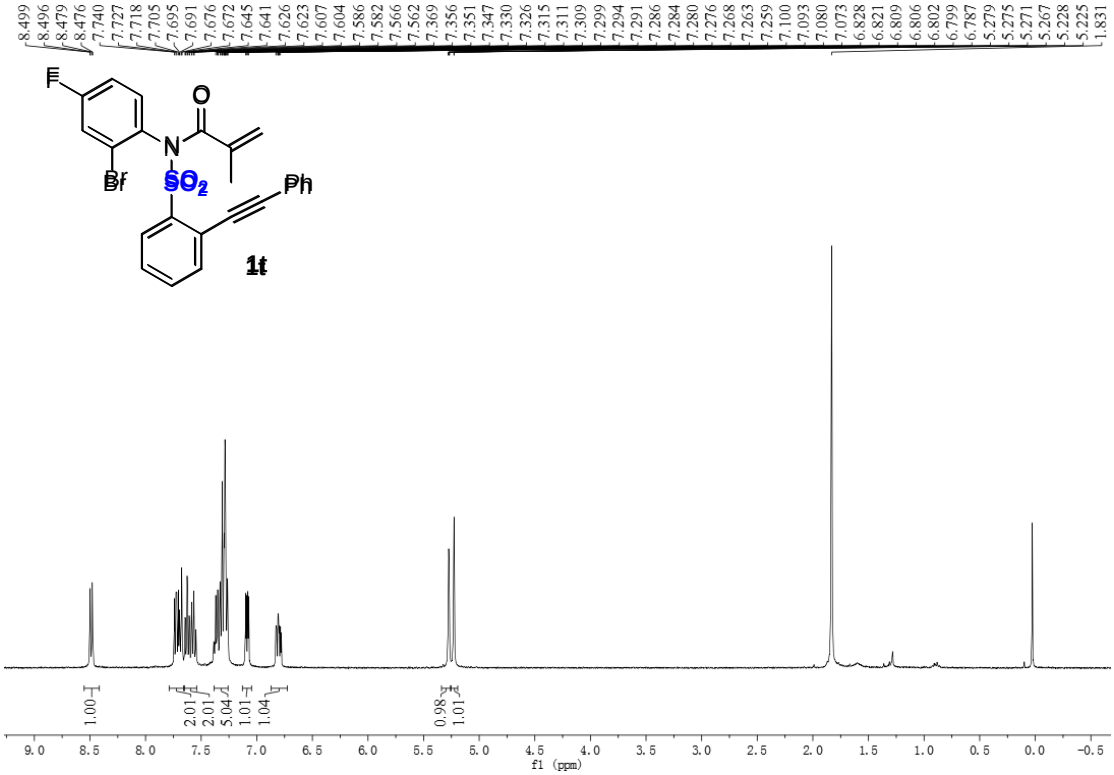
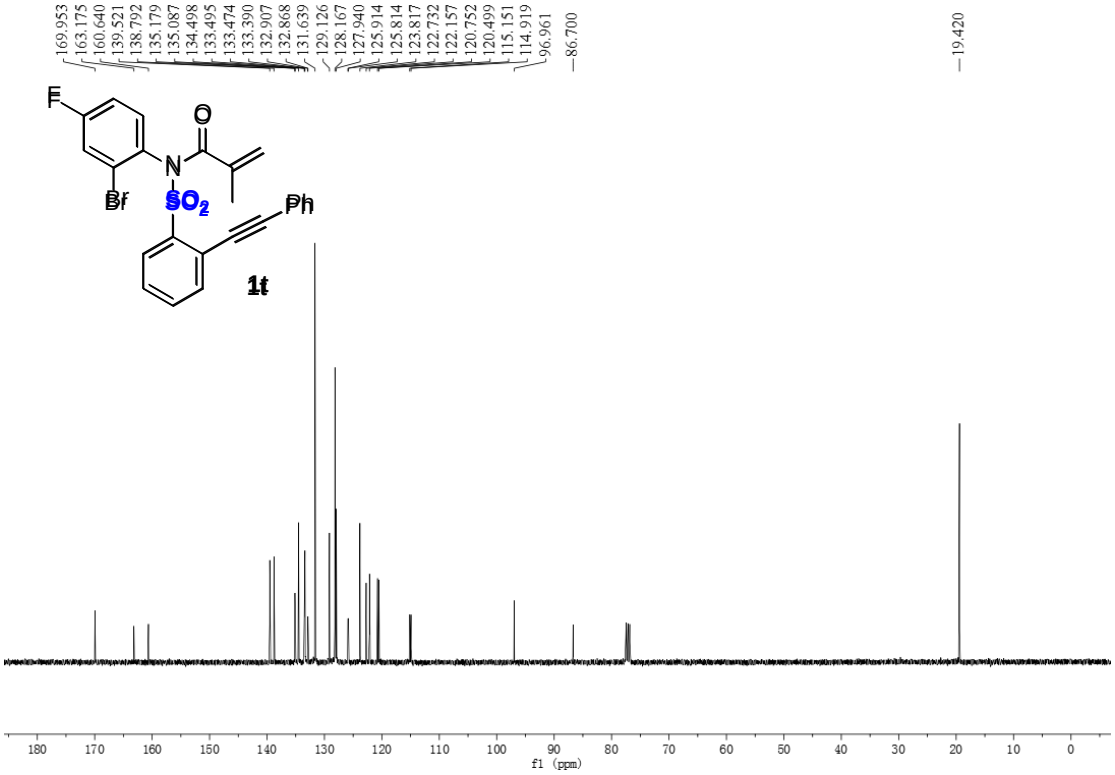
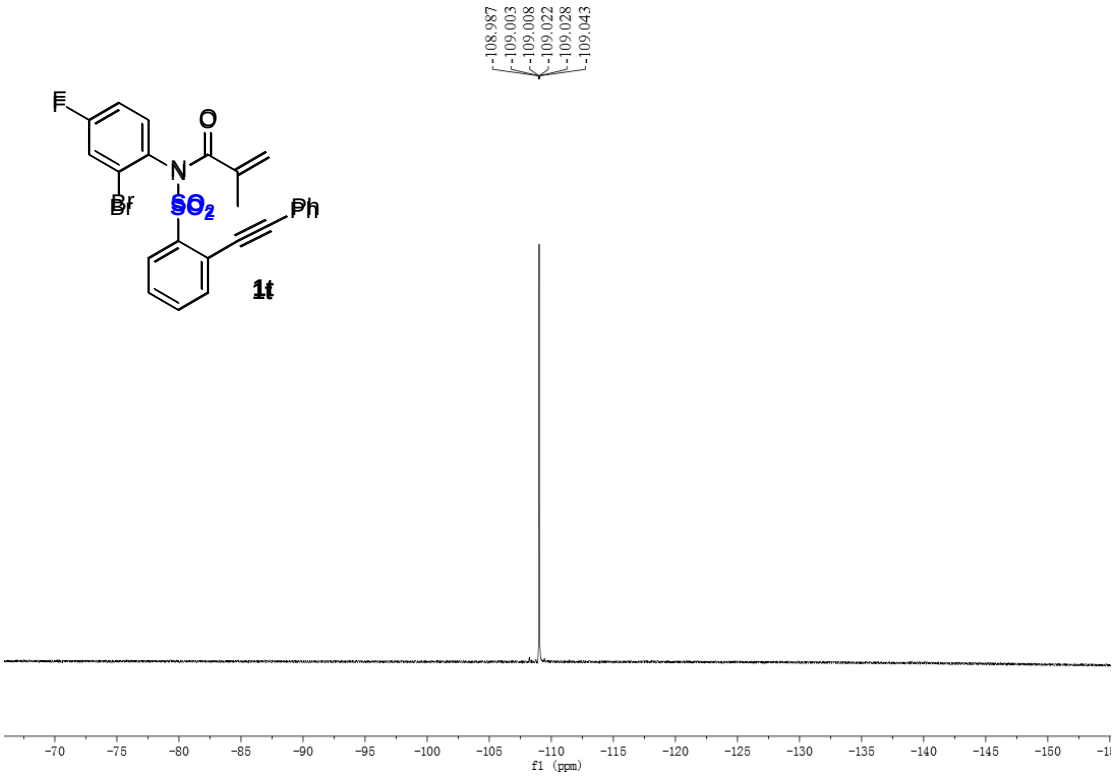


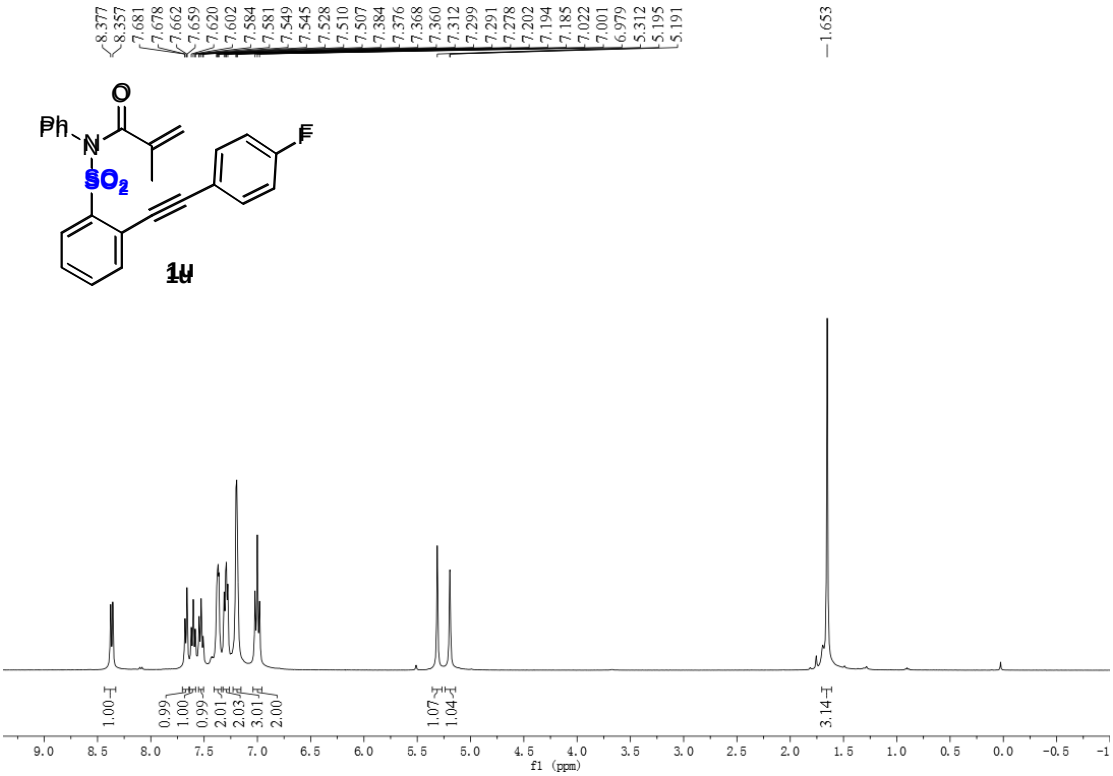
$^{13}$C NMR for **1t** (101 MHz, $CDCl_3$)




$^{19}$F NMR for **1t** (376 MHz, $CDCl_3$)



$^{1}$H NMR for **1u** (400 MHz, $CDCl_3$)

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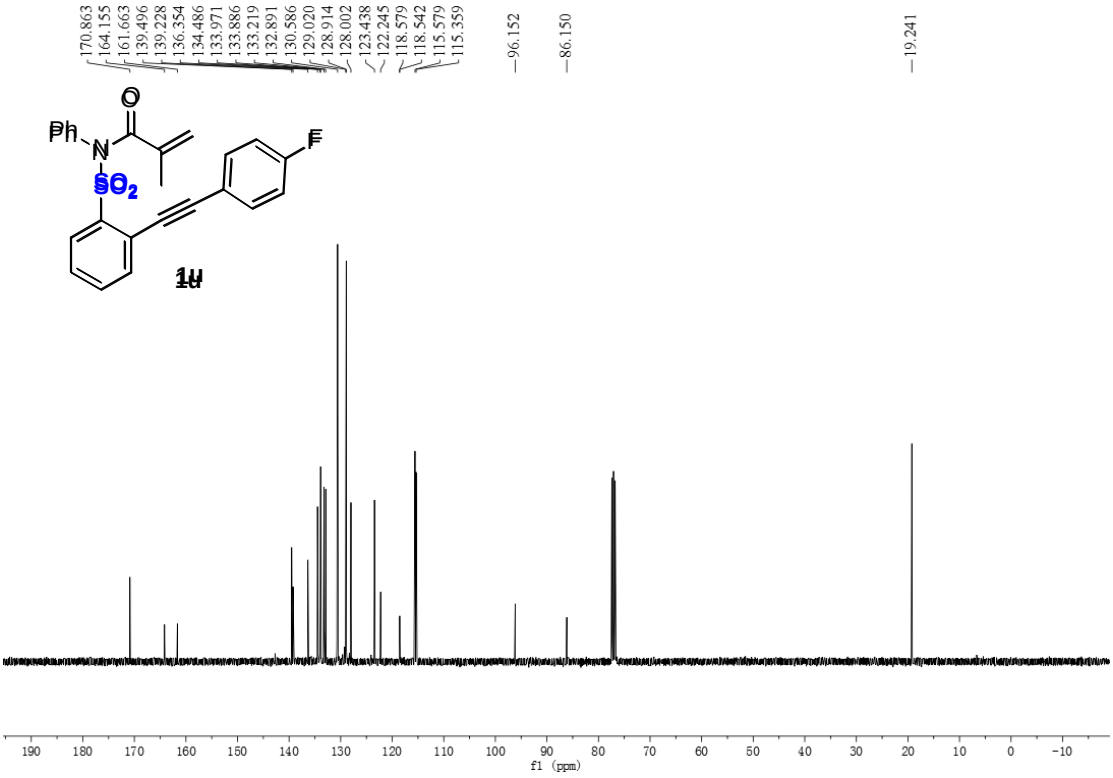

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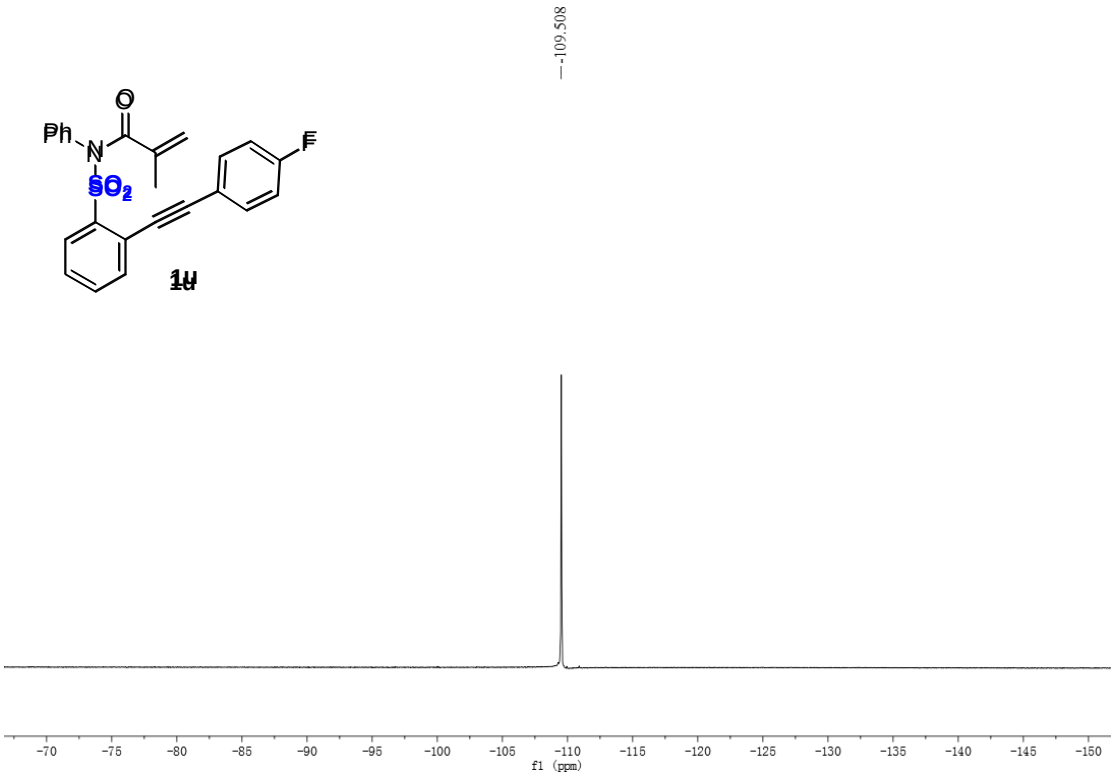
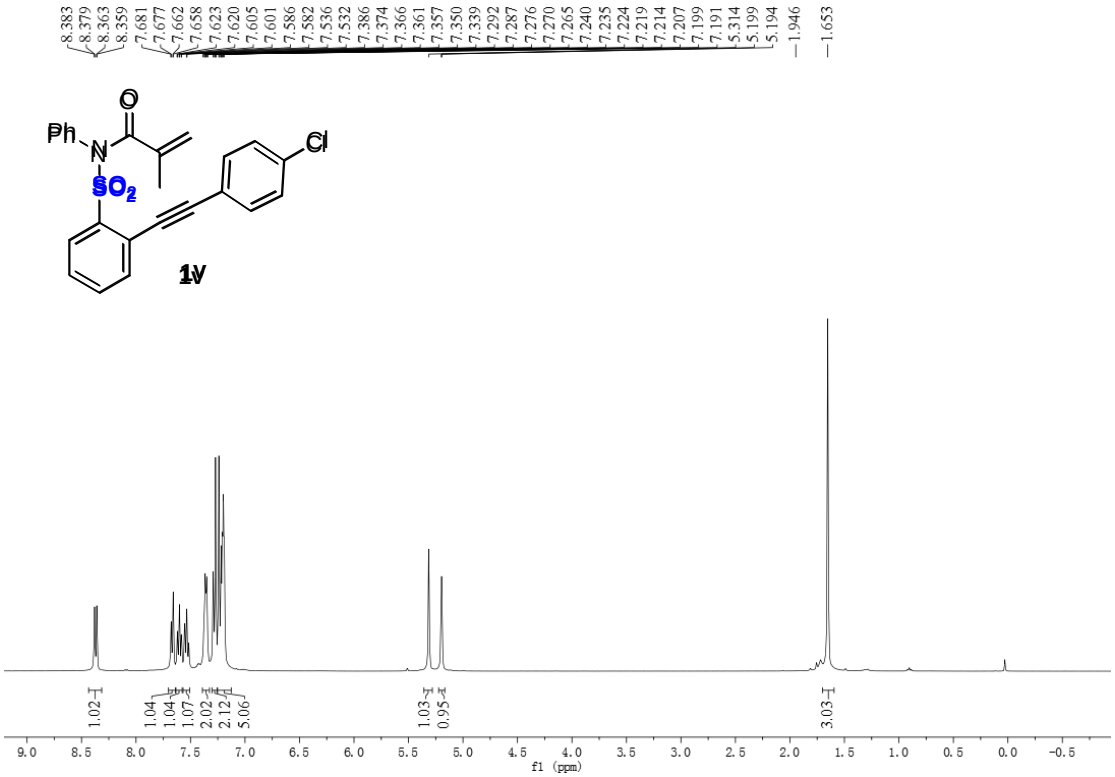
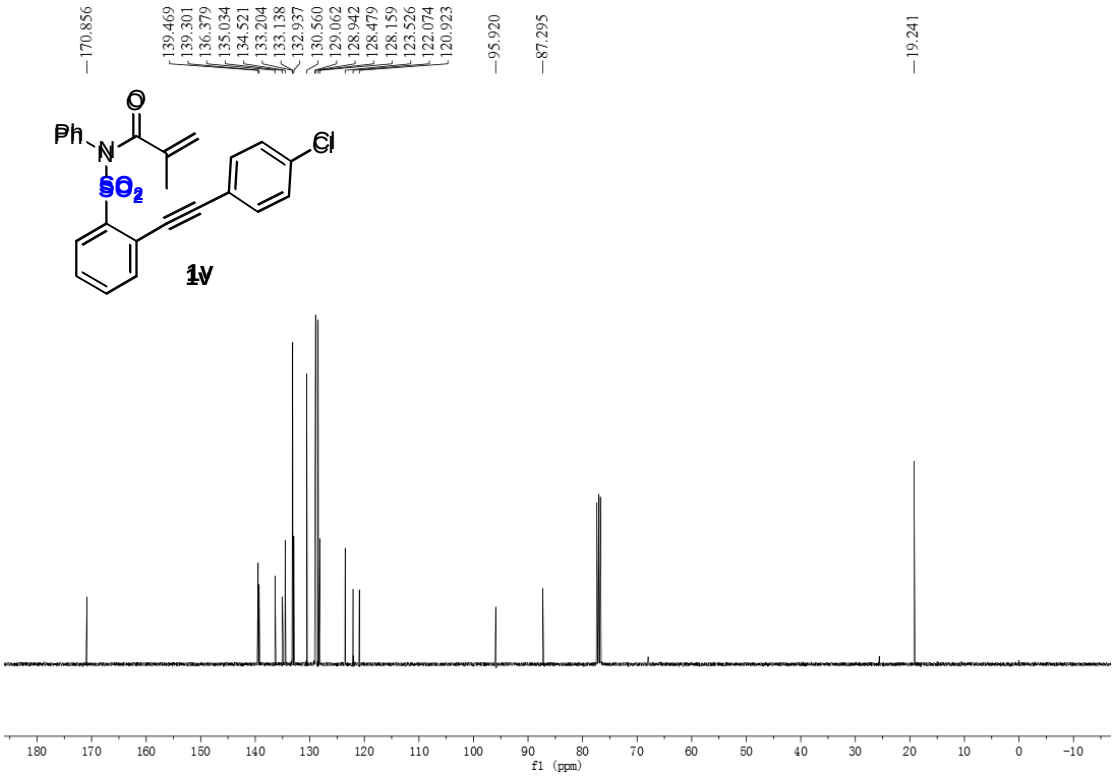


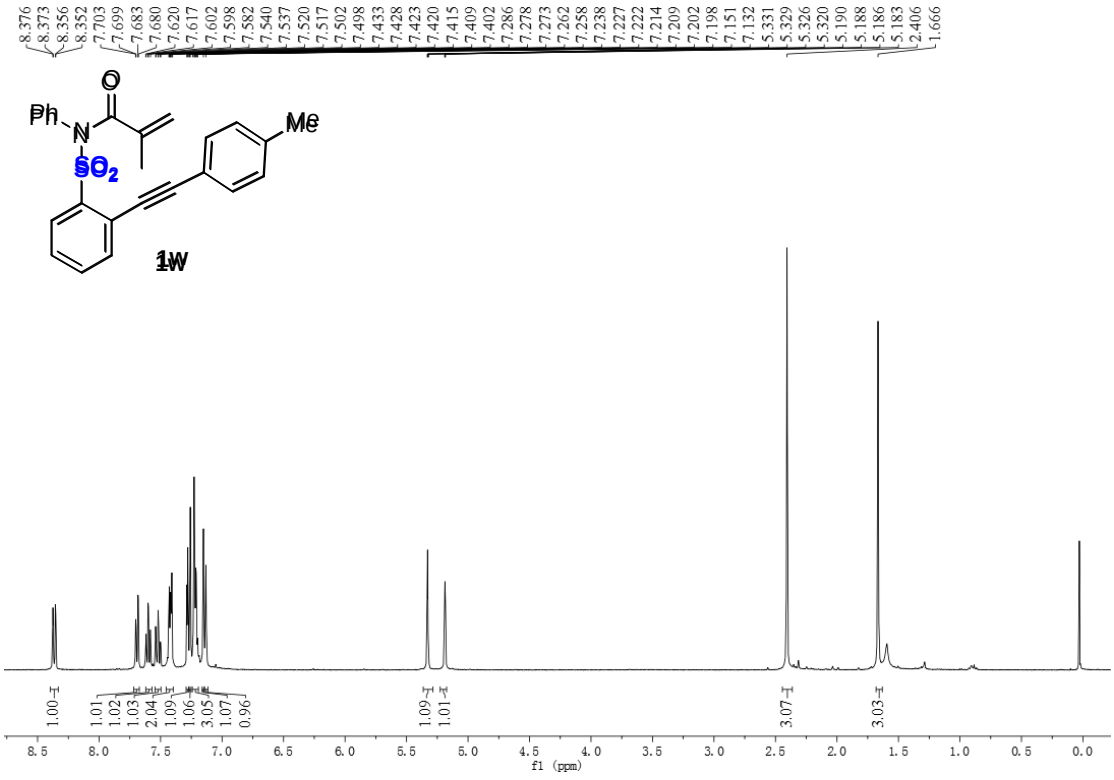

$^{1}$H NMR for **1v** (400 MHz, $CDCl_3$)



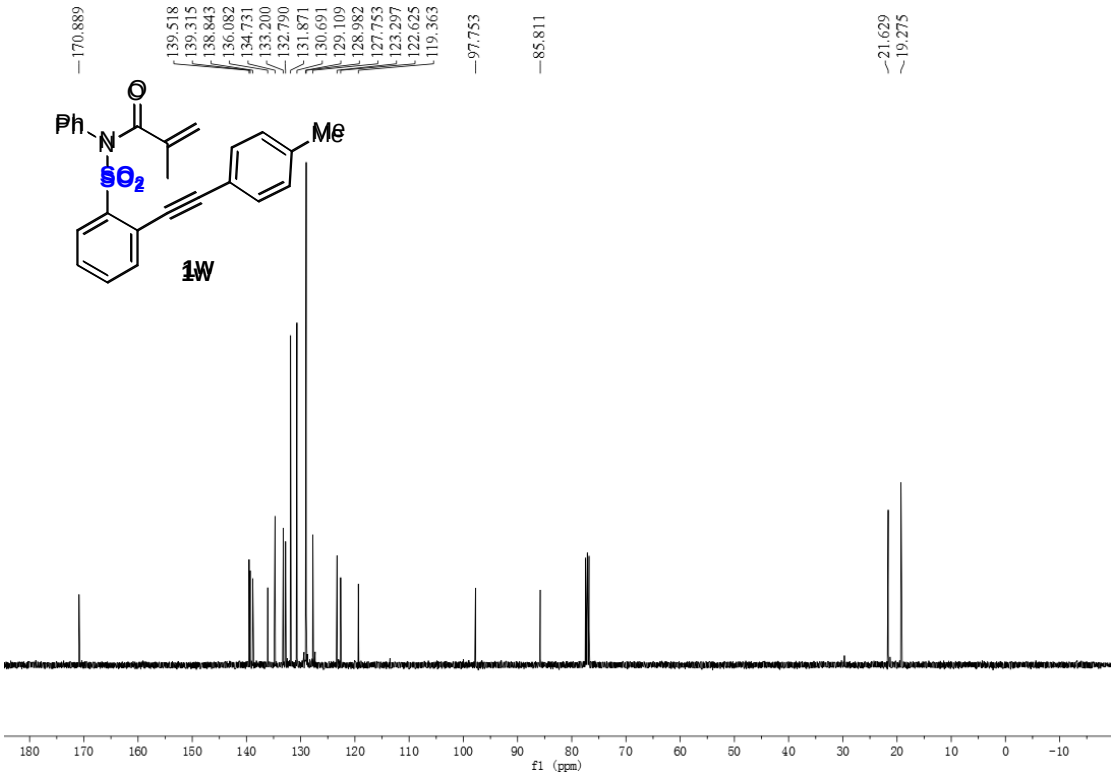
$^{13}$C NMR for **1v** (101 MHz, $CDCl_3$)



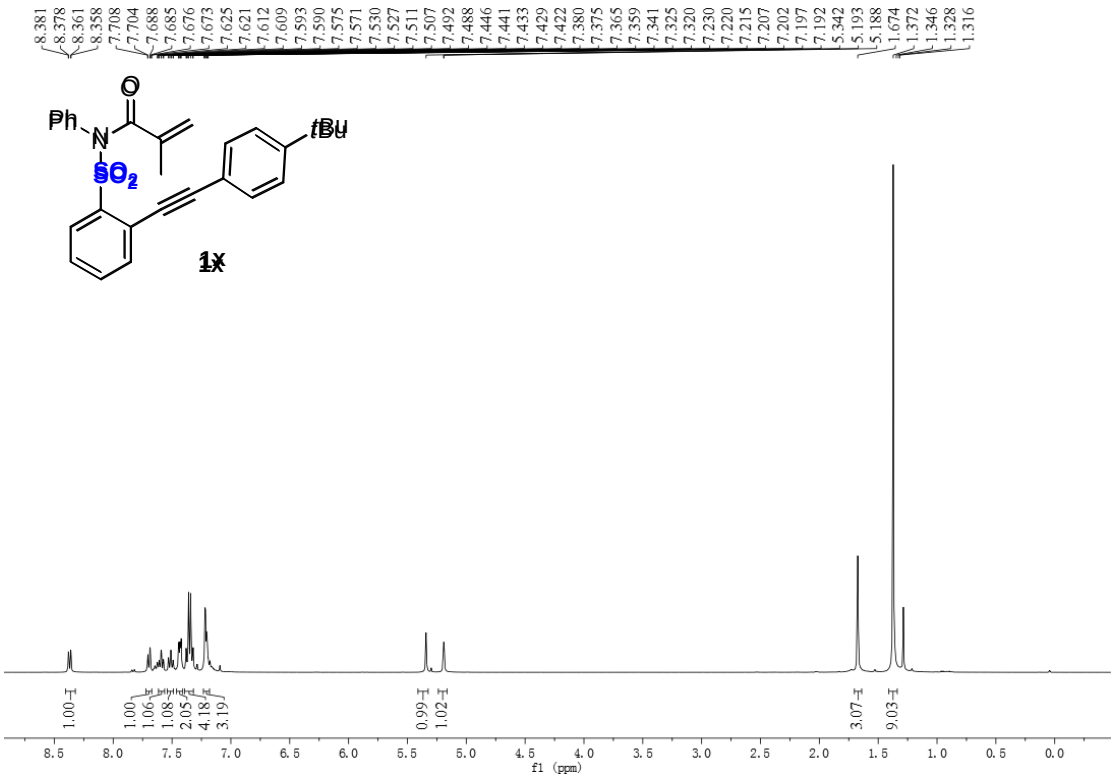

$^{1}$H NMR for **1w** (400 MHz, $CDCl_3$)



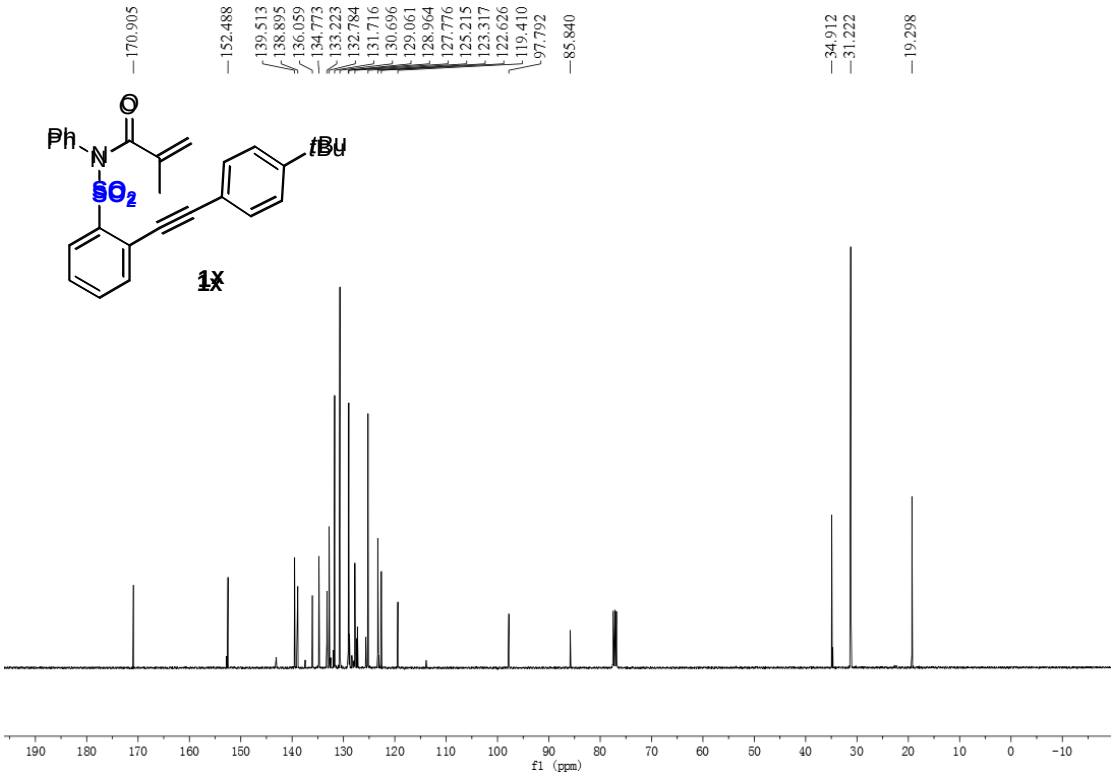
$^{13}$C NMR for **1w** (101 MHz, $CDCl_3$)



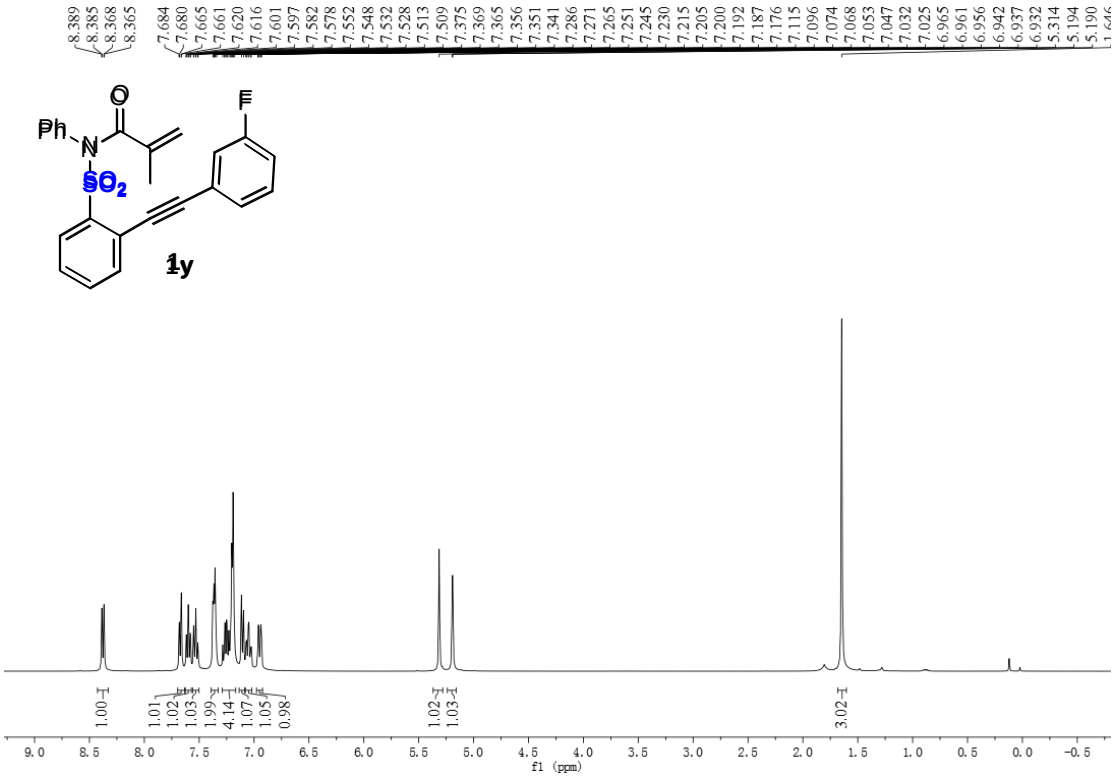

$^{1}$H NMR for **1x** (400 MHz, $CDCl_3$)



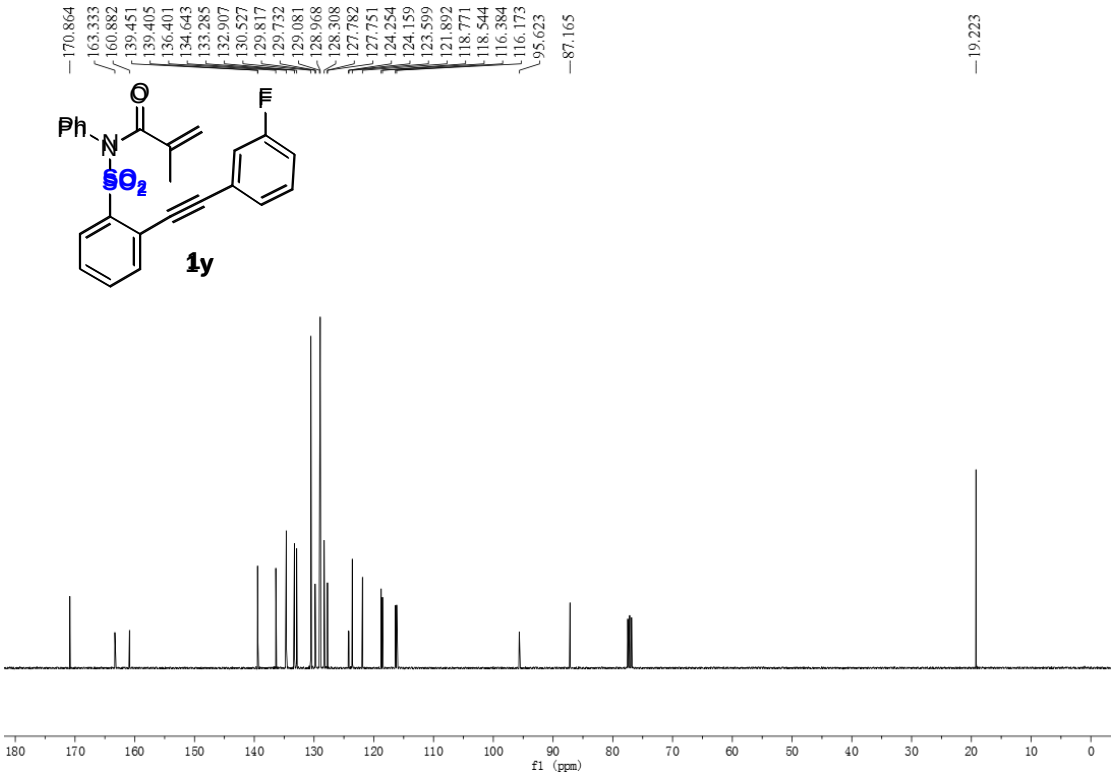
$^{13}$C NMR for **1x** (101 MHz, $CDCl_3$)



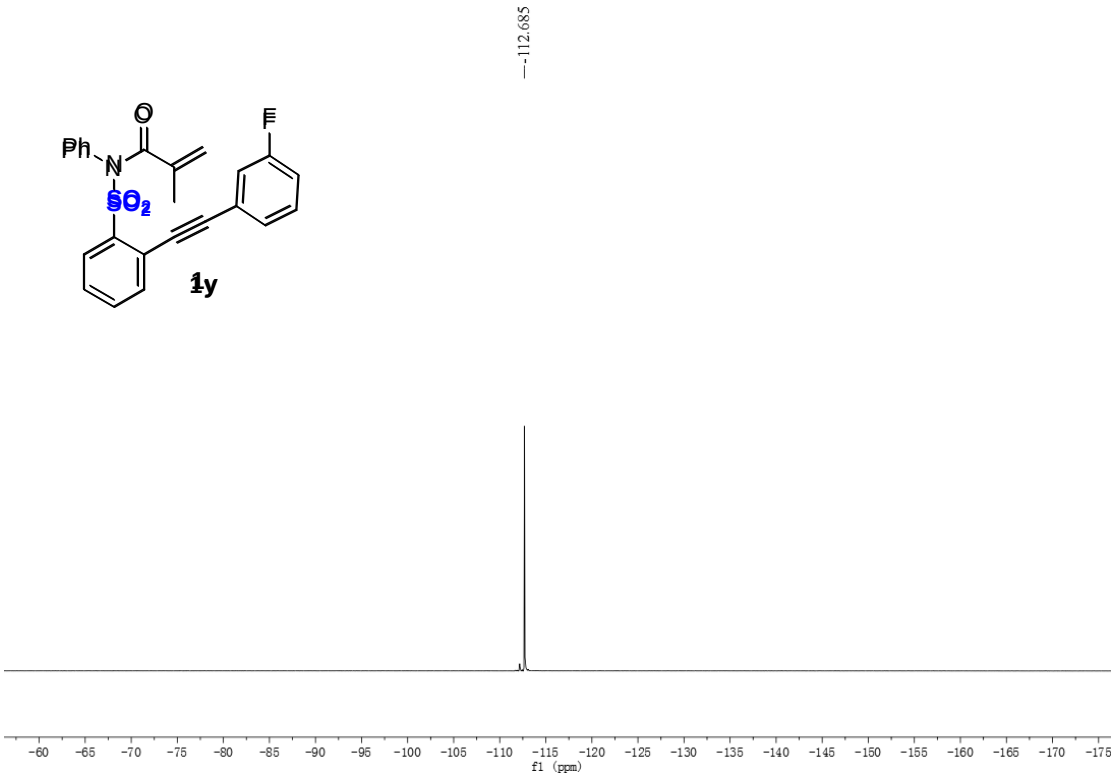

$^{1}$H NMR for **1**y (400 MHz, $CDCl_3$)



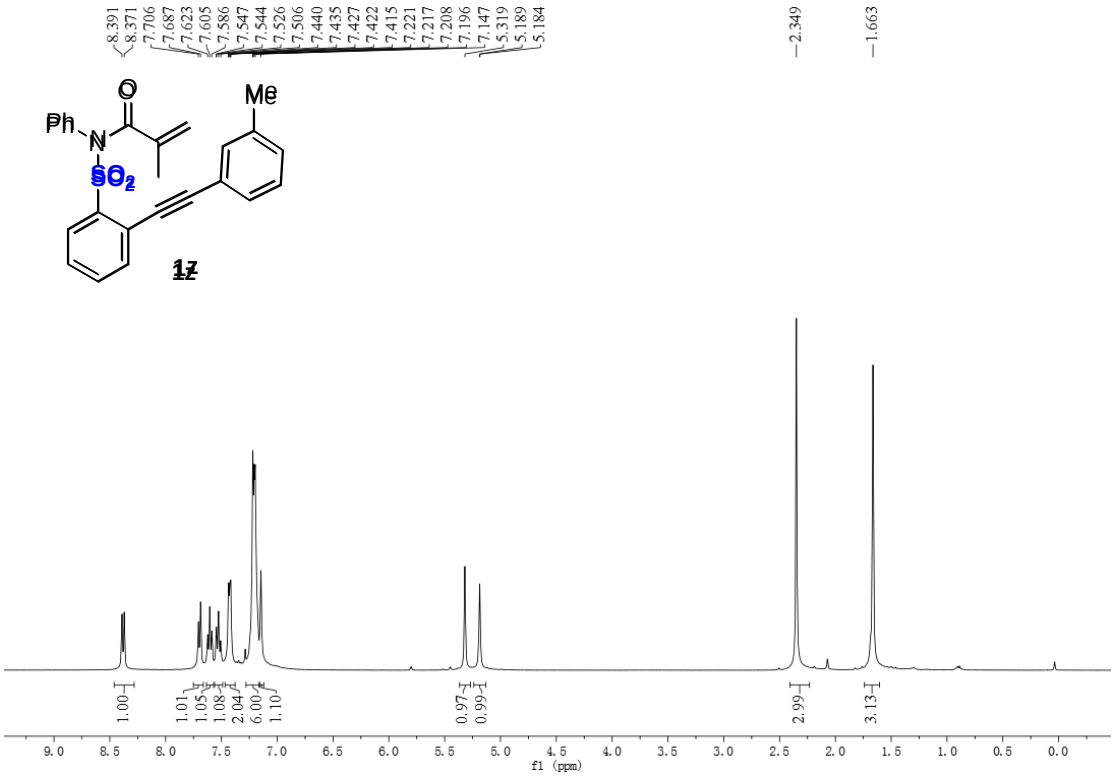
$^{13}$C NMR for **1y** (101 MHz, $CDCl_3$)



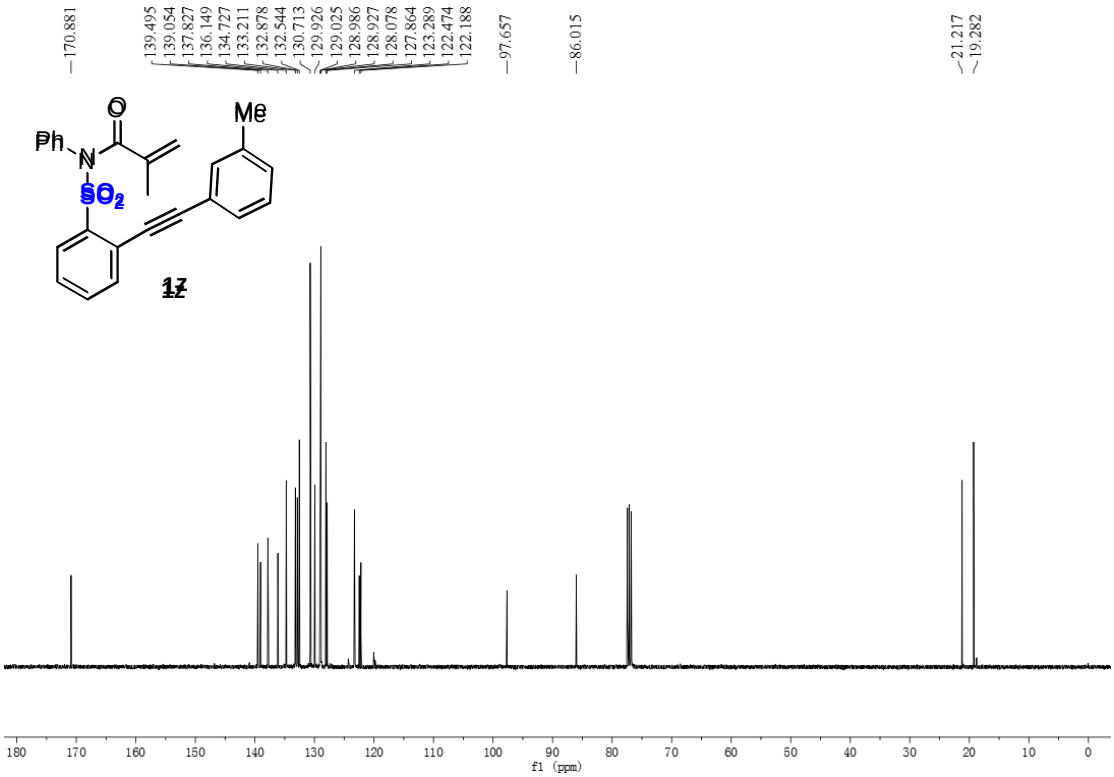

$^{19}$F NMR for **1y** (376 MHz, $CDCl_3$)



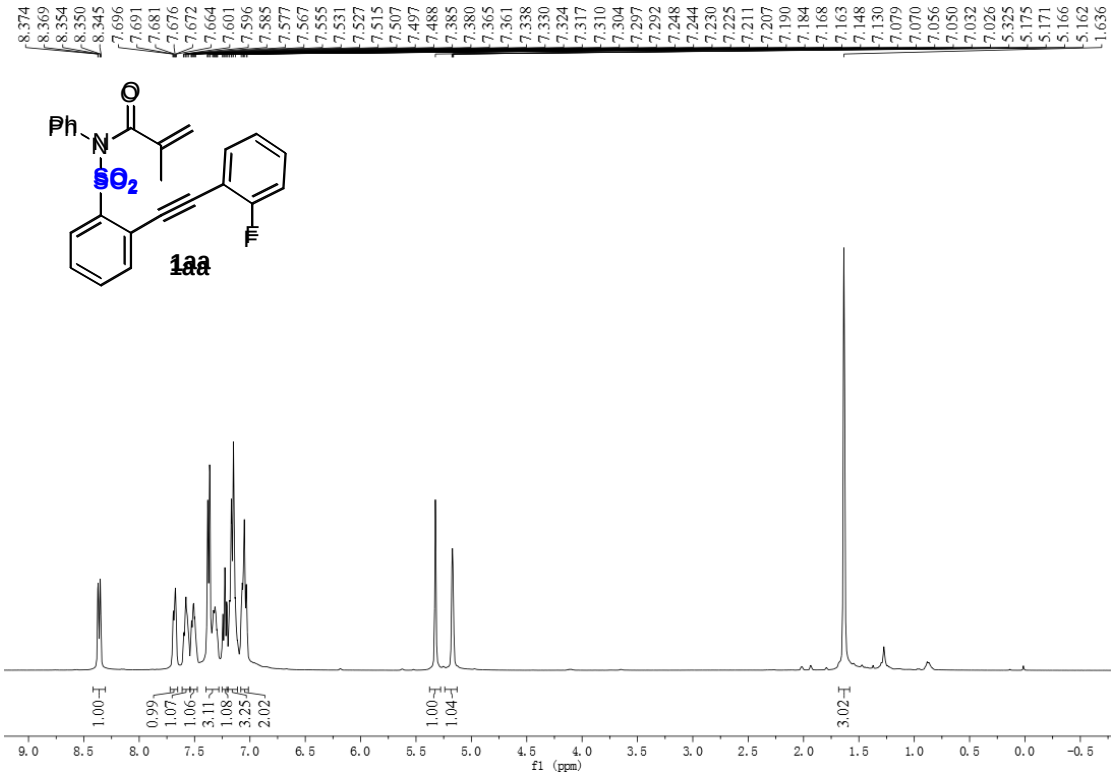
$^{1}$H NMR for **1z** (400 MHz, $CDCl_3$)



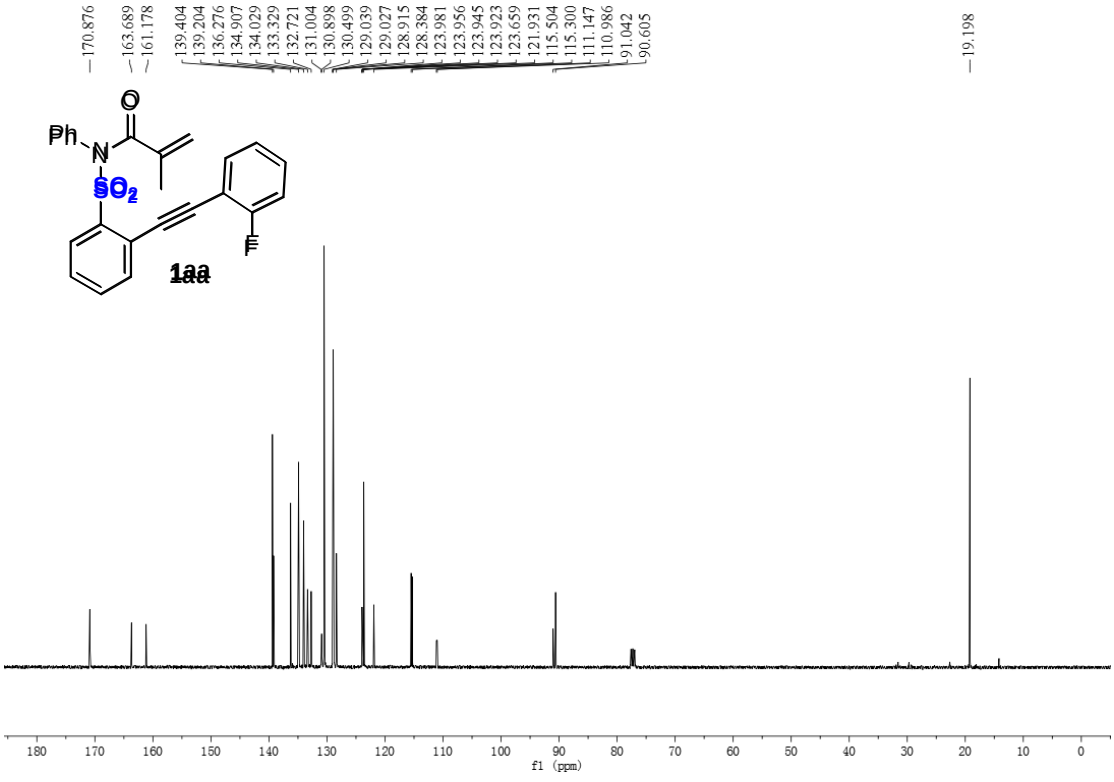

$^{13}$C NMR for **1z** (101 MHz, $CDCl_3$)



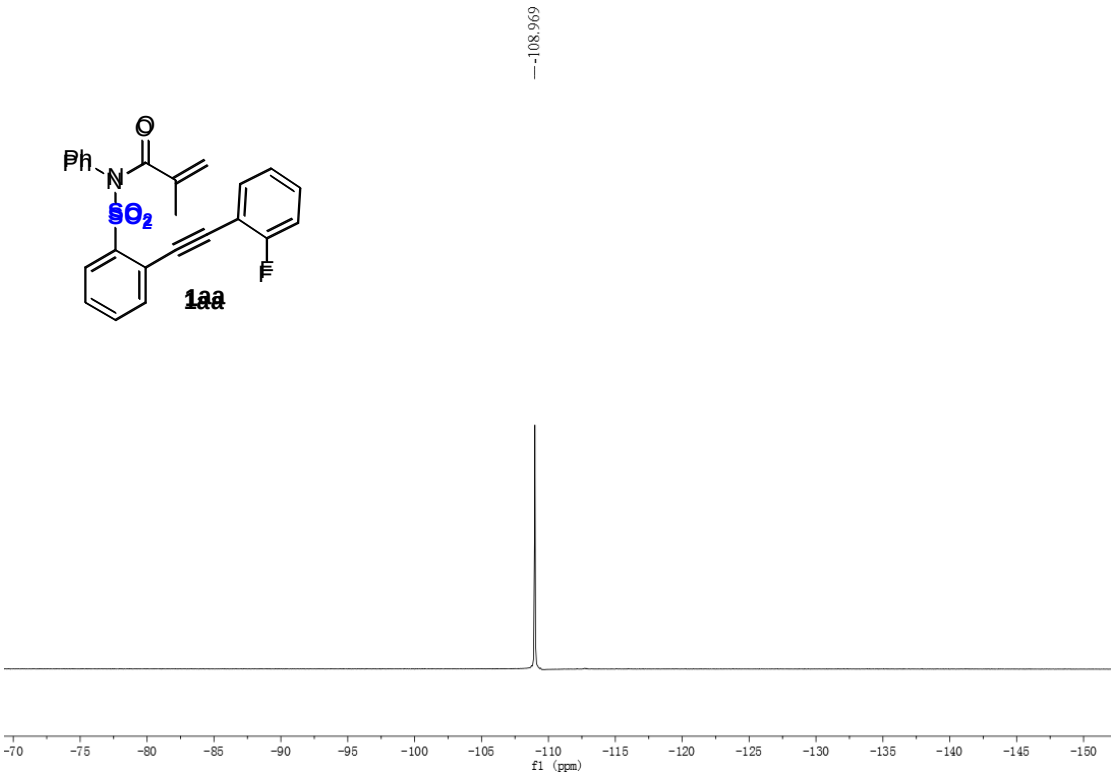
$^{1}$H NMR for **1aa** (400 MHz, $CDCl_3$)



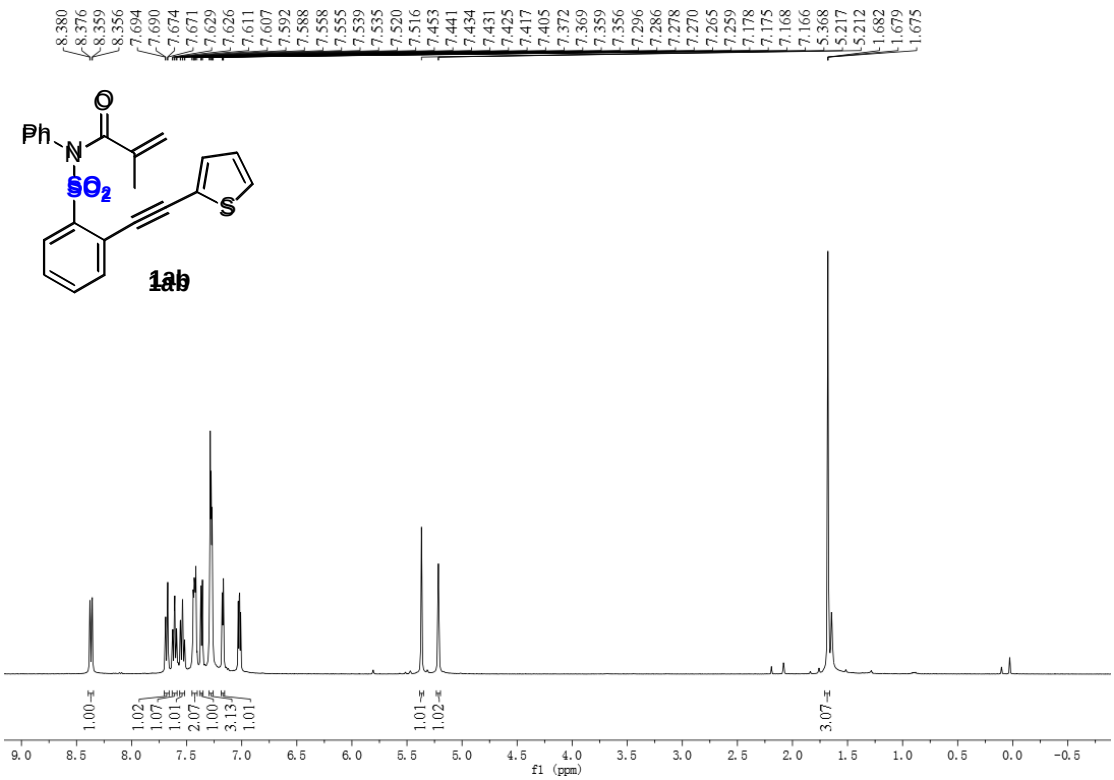

$^{13}$C NMR for **1aa**(101 MHz, $CDCl_3$)



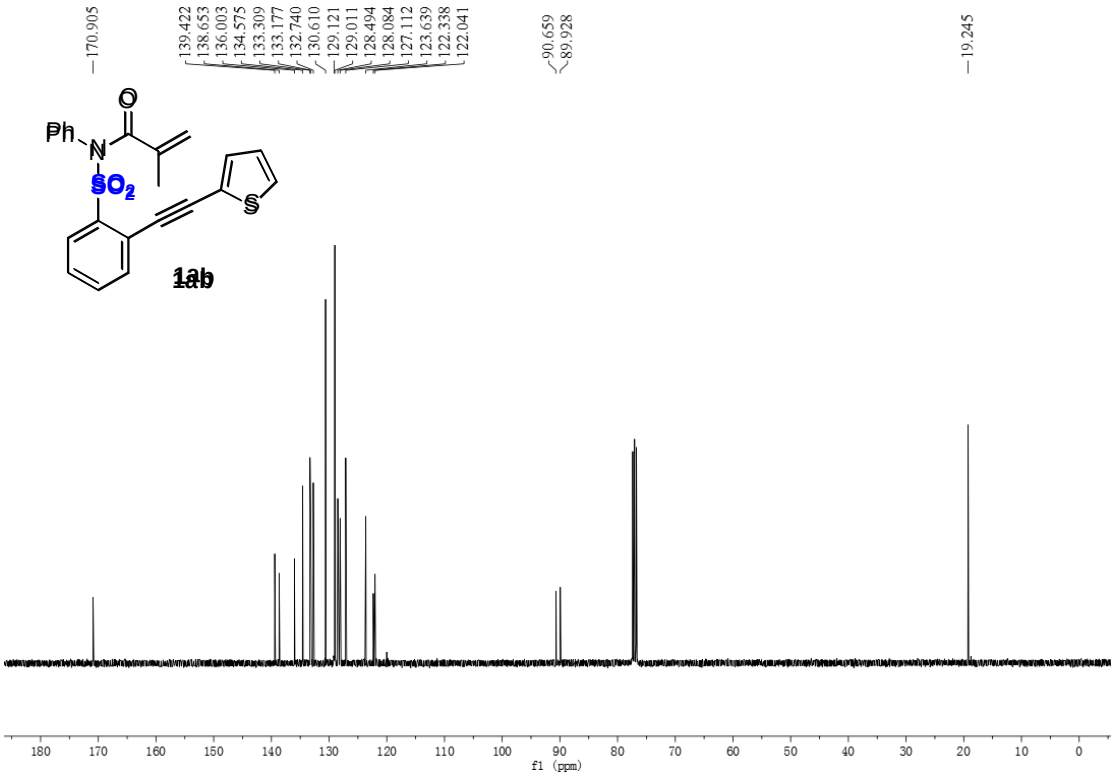
$^{19}$F NMR for **1aa** (376 MHz, $CDCl_3$)



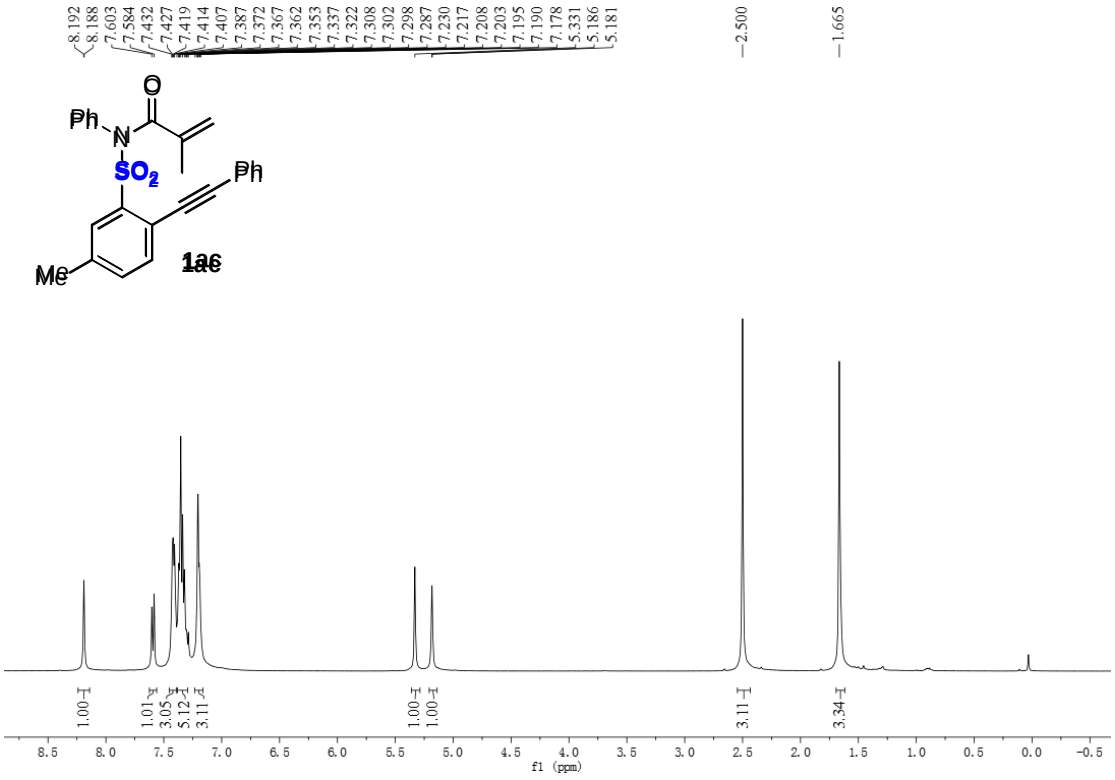

$^{1}$H NMR for **1ab** (400 MHz, $CDCl_3$)



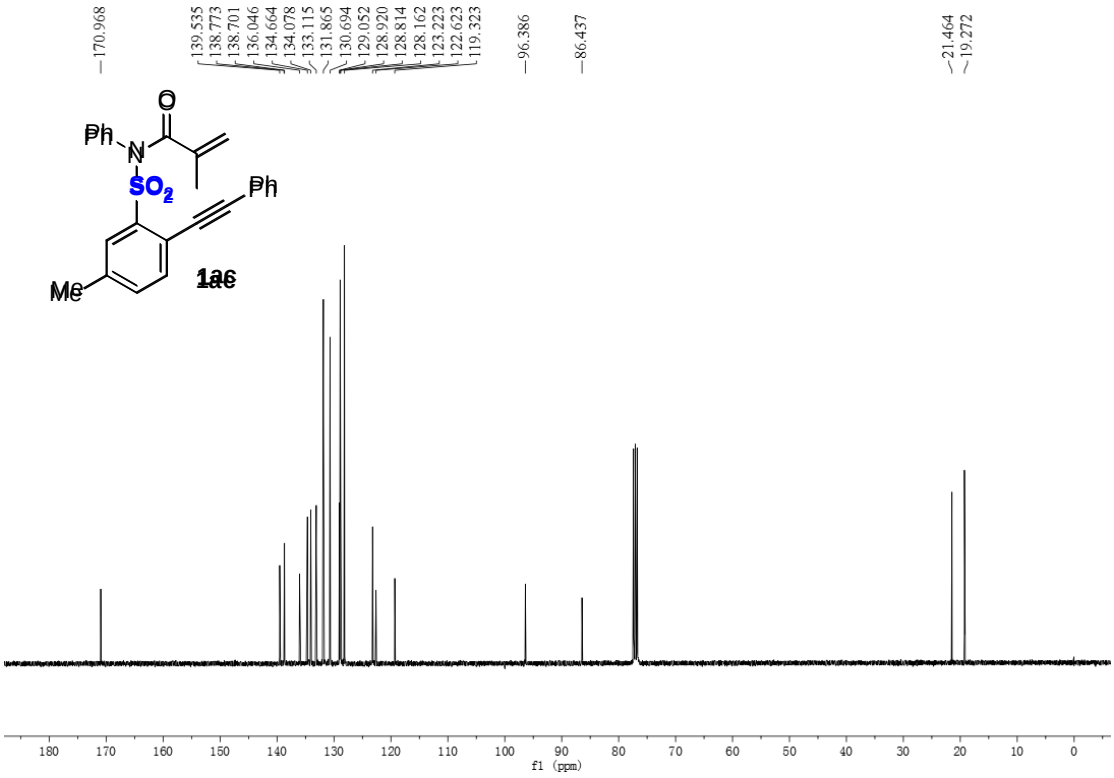
$^{13}$C NMR for **1ab** (101 MHz, $CDCl_3$)



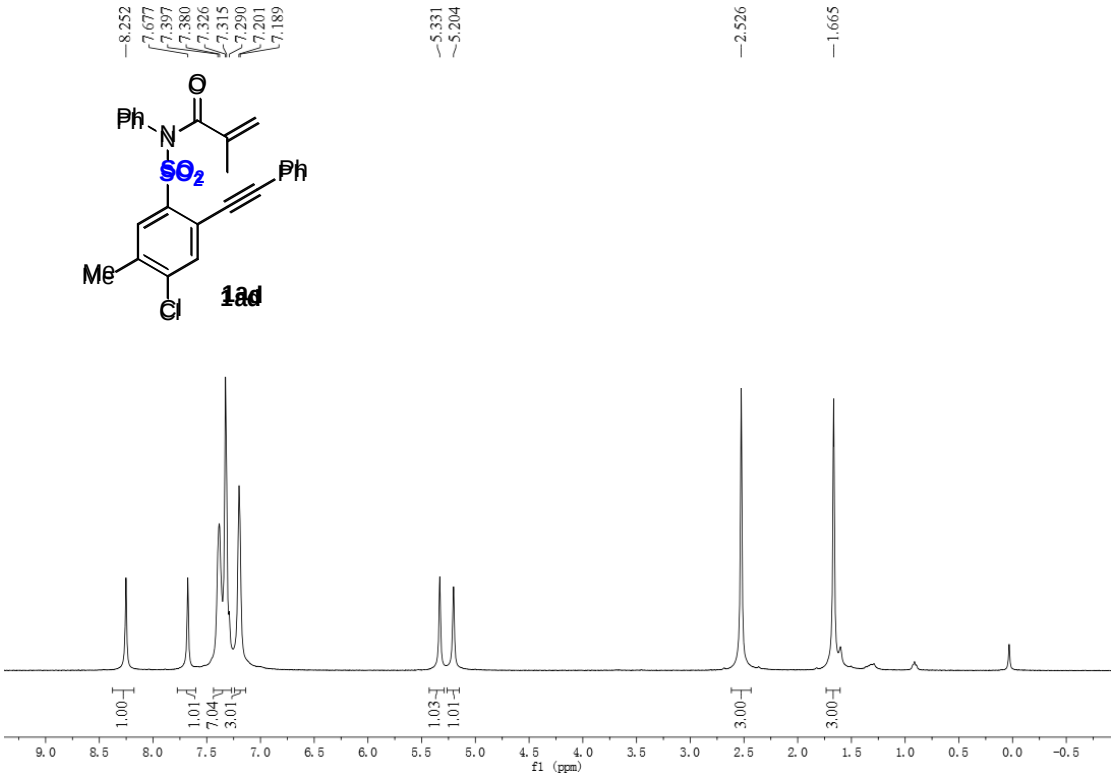

$^{1}$H NMR for **1ac** (400 MHz, $CDCl_3$)



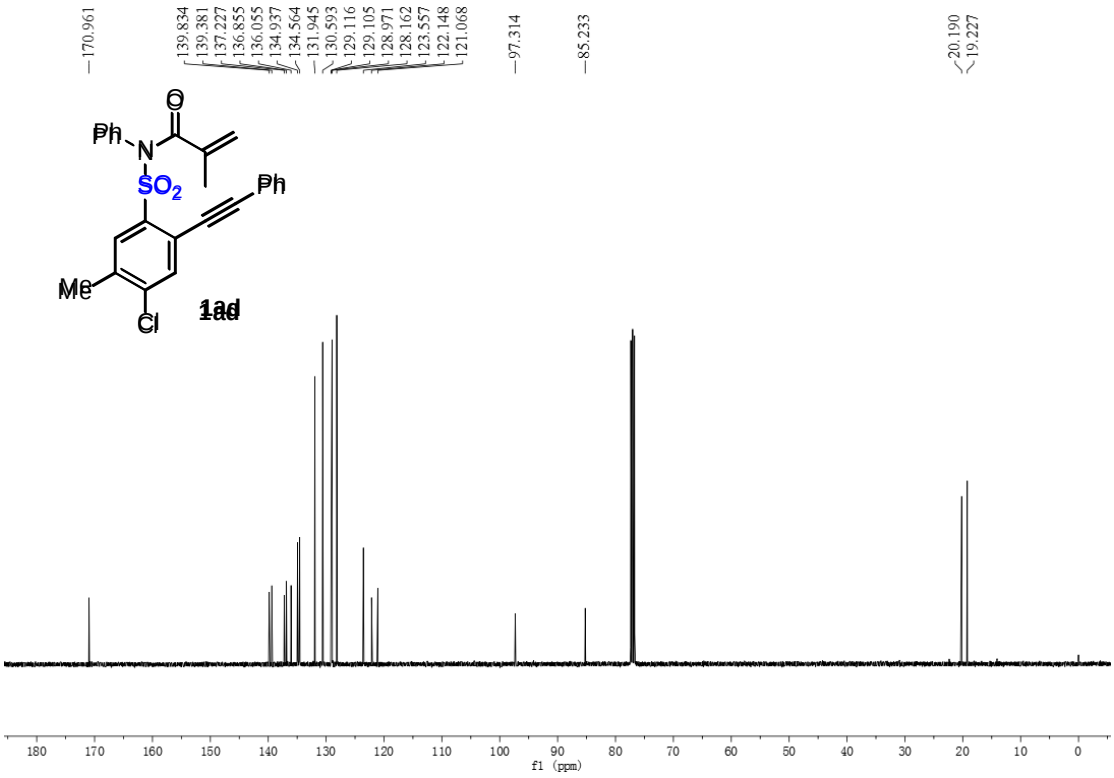
$^{13}$C NMR for **1ac** (101 MHz, $CDCl_3$)



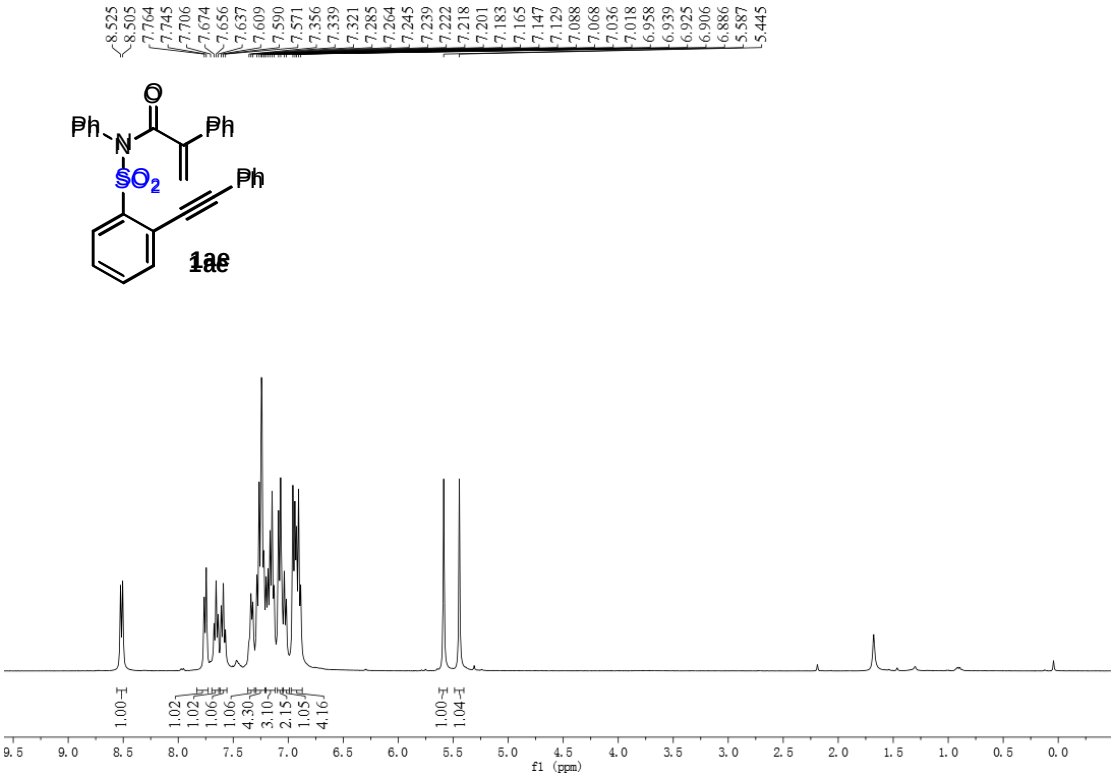

$^{1}$H NMR for **1ad** (400 MHz, $CDCl_3$)



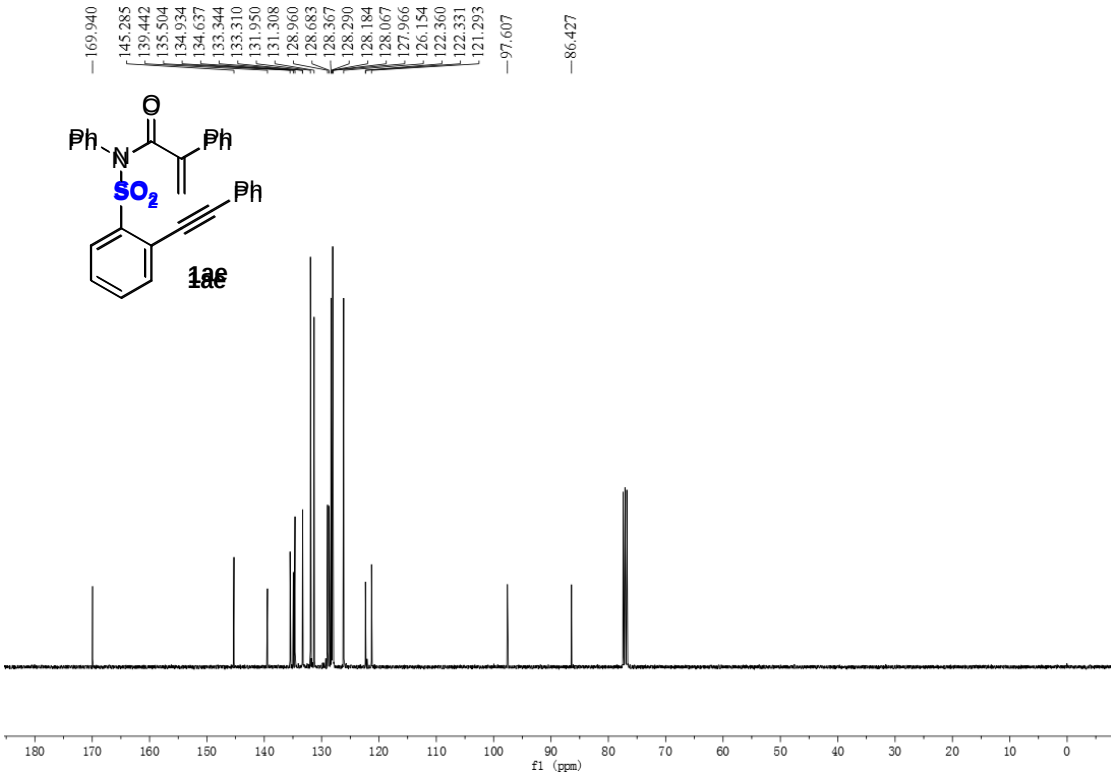
$^{13}$C NMR for **1ad** (101 MHz, $CDCl_3$)



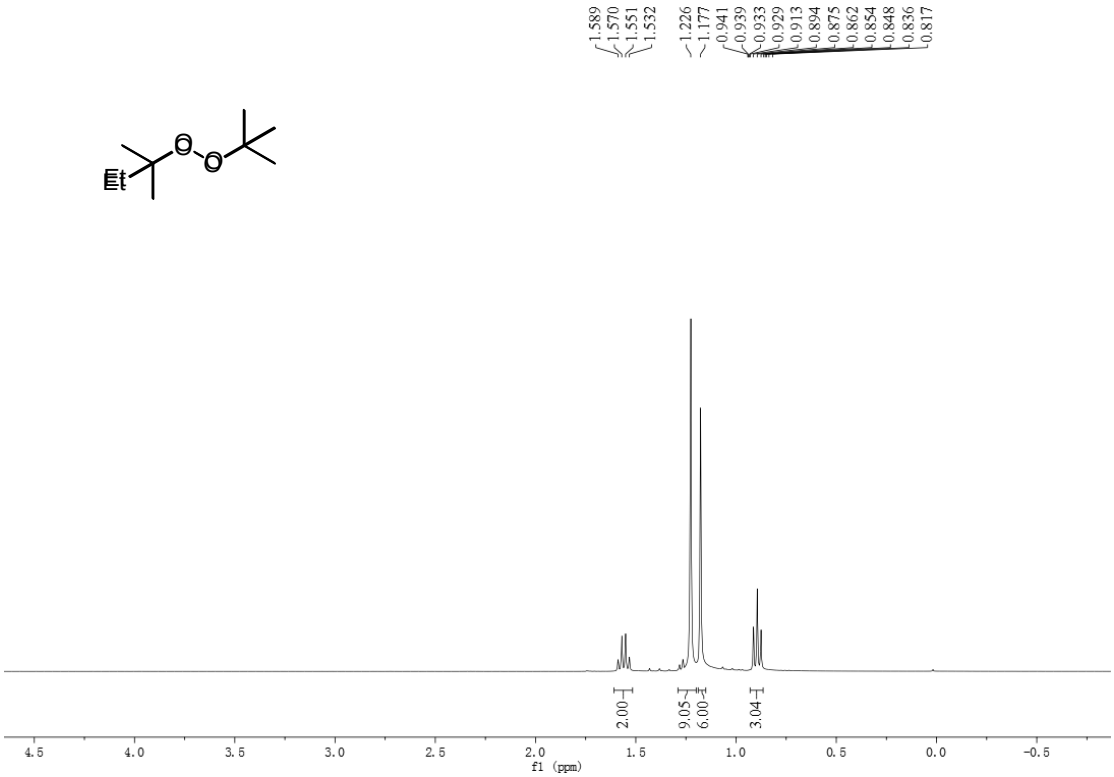

$^{1}$H NMR for **1ae** (400 MHz, $CDCl_3$)



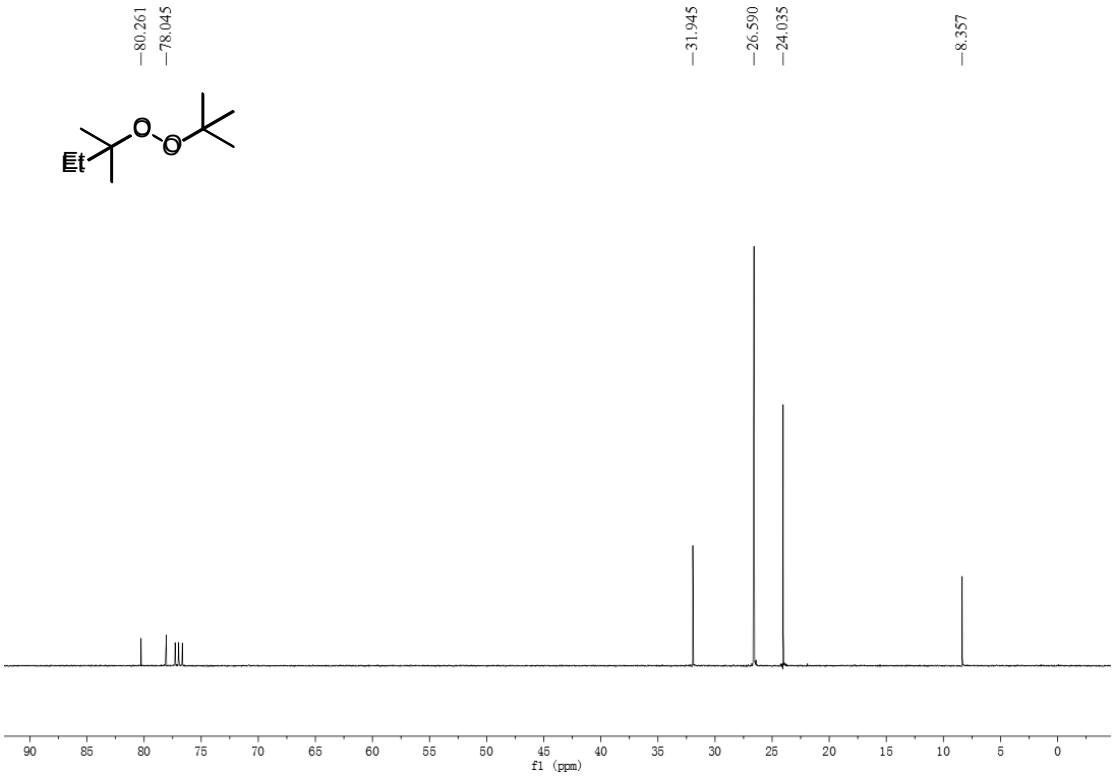
$^{13}$C NMR for **1ae** (101 MHz, $CDCl_3$)



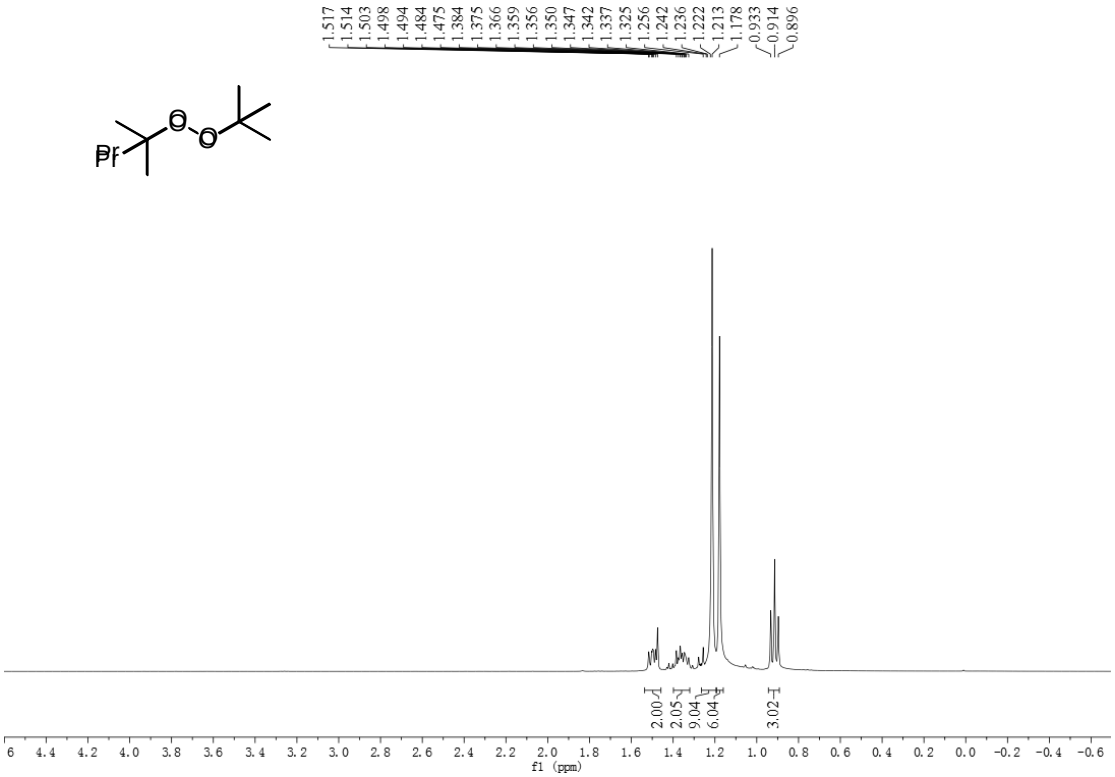

$^{1}$H NMR for ***tert*-butyl *tert*-pentyl peroxide** (400 MHz, $CDCl_3$)



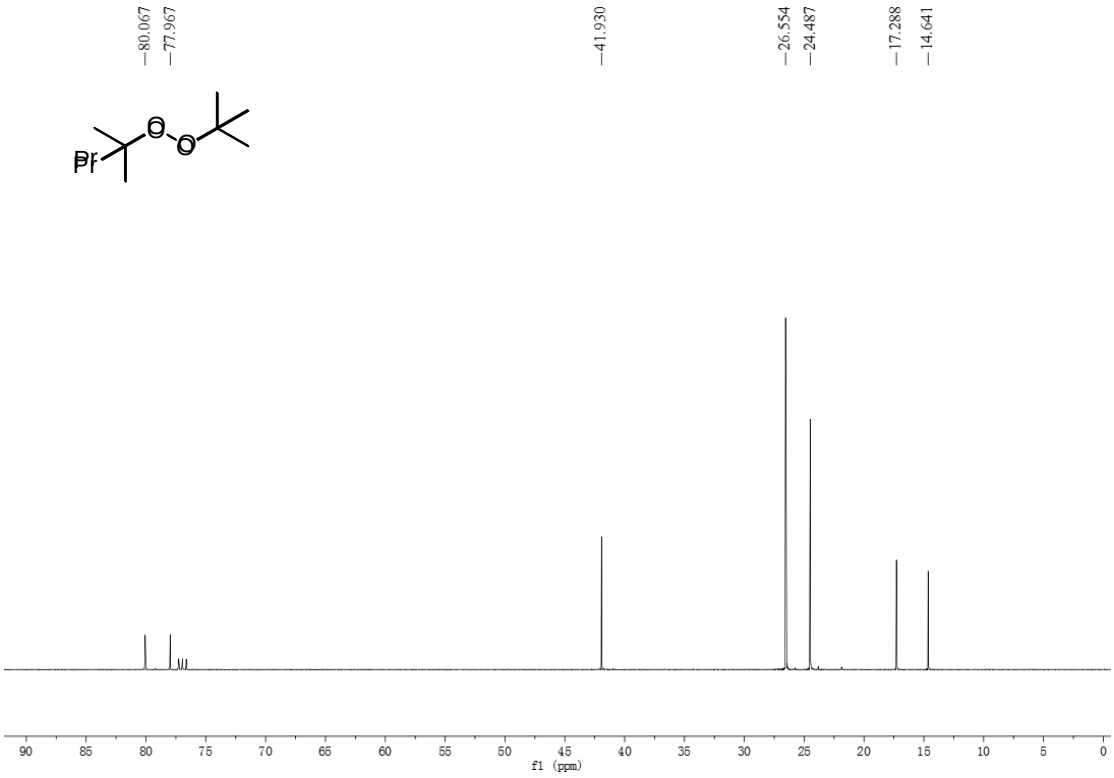
$^{13}$C NMR for ***tert*-butyl *tert*-pentyl peroxide** (101 MHz, $CDCl_3$)



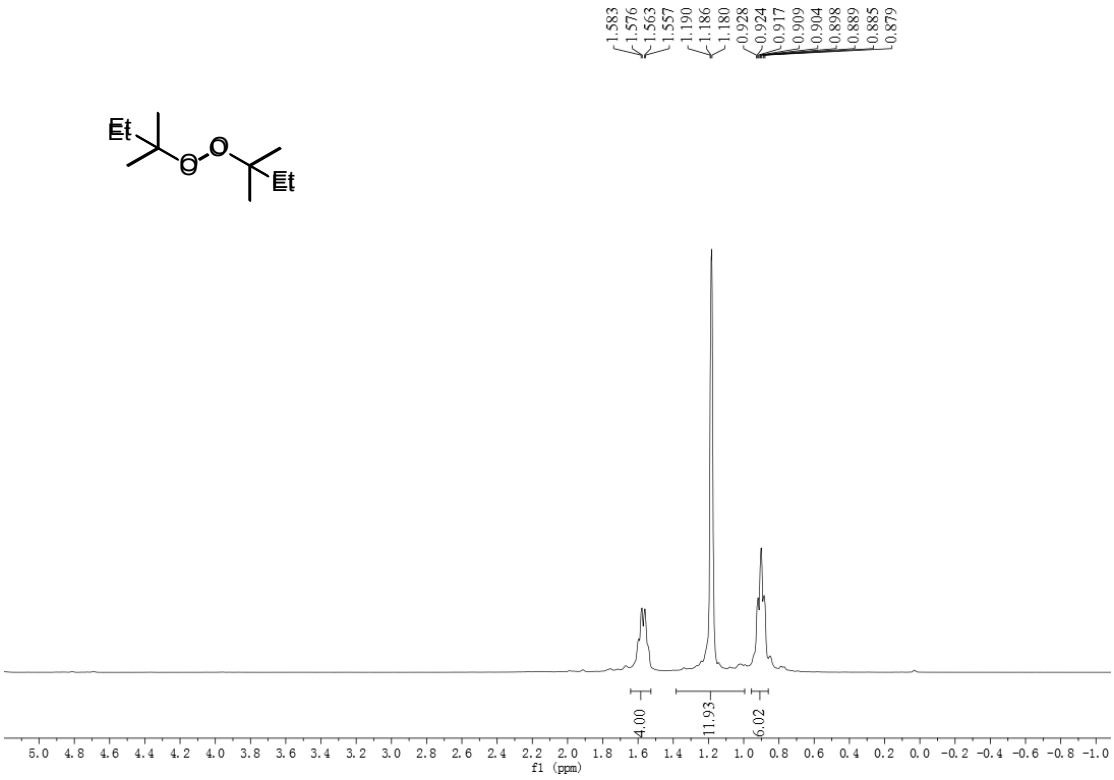

$^{1}$H NMR for ***tert*-butyl 1,1-dimethylbutyl peroxide** (400 MHz, $CDCl_3$)



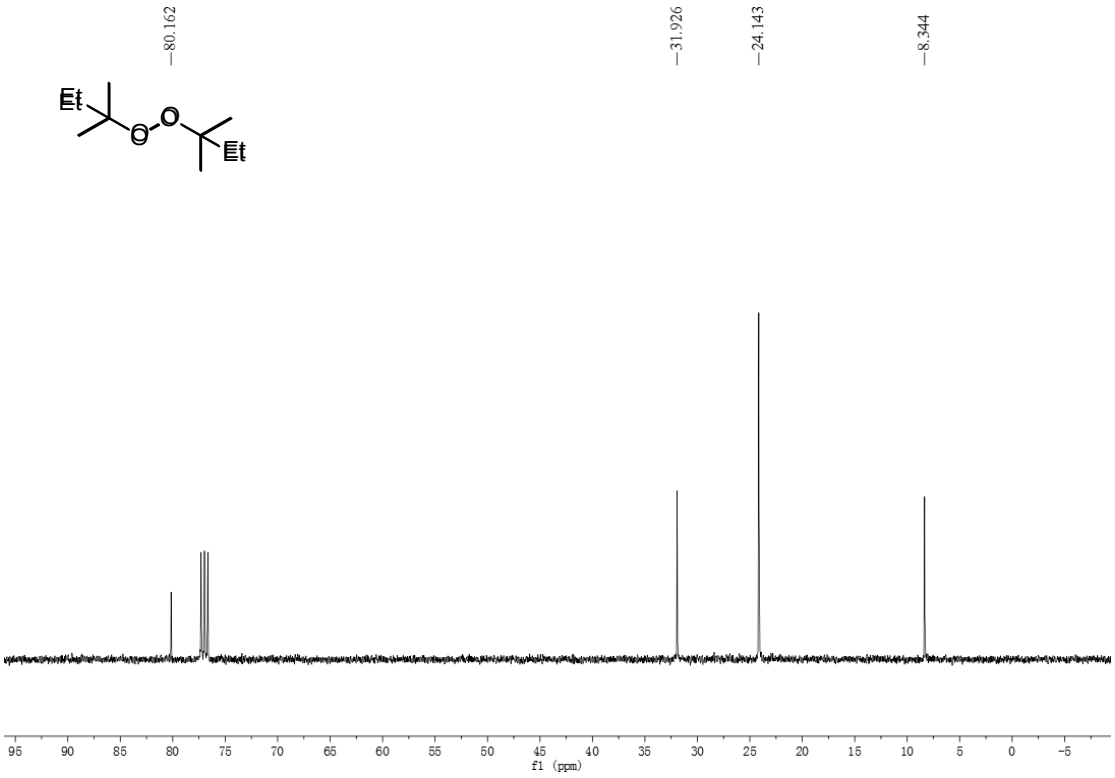
$^{13}$C NMR for ***tert*-butyl 1,1-dimethylbutyl peroxide** (101 MHz, $CDCl_3$)



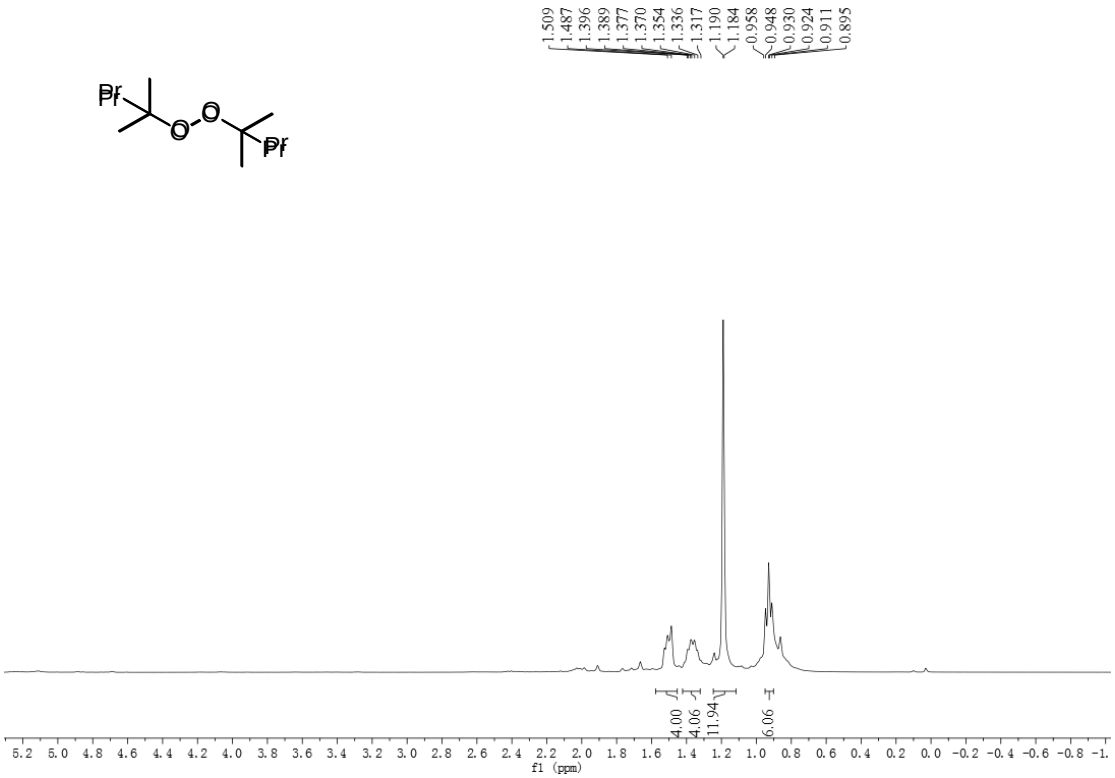

$^{1}$H NMR for **di-*tert*-amyl peroxide** (400 MHz, $CDCl_3$)



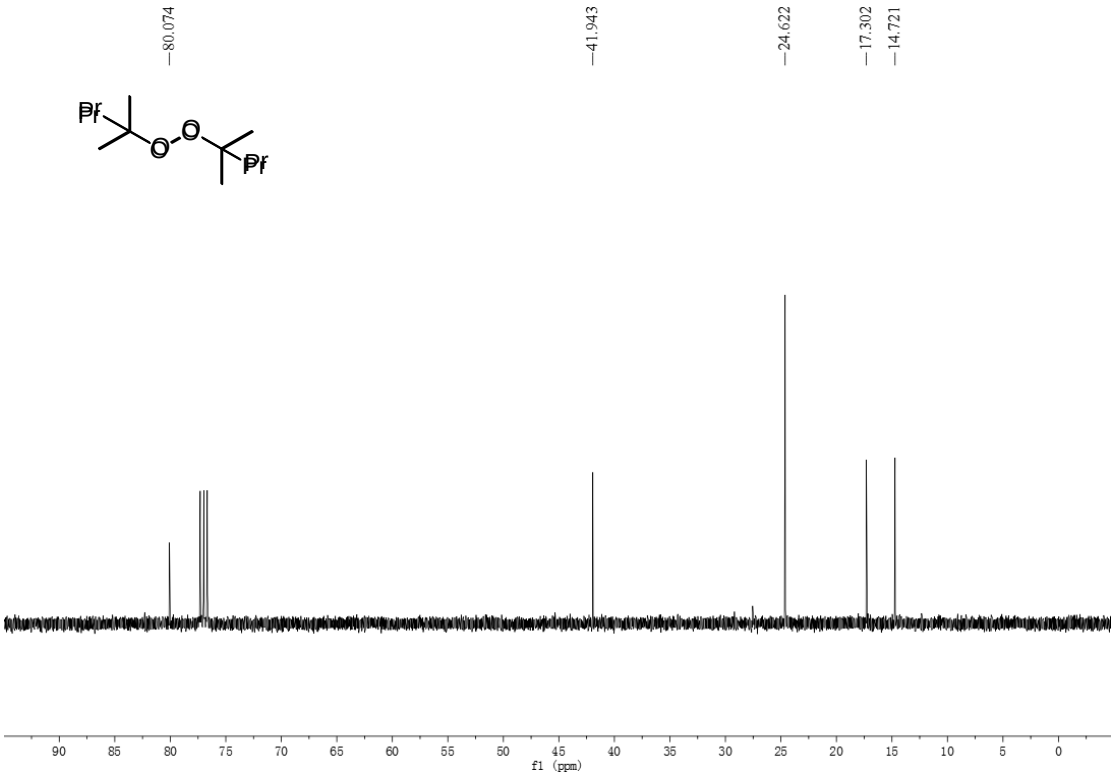
$^{13}$C NMR for **di-*tert*-amyl peroxide** (101 MHz, $CDCl_3$)



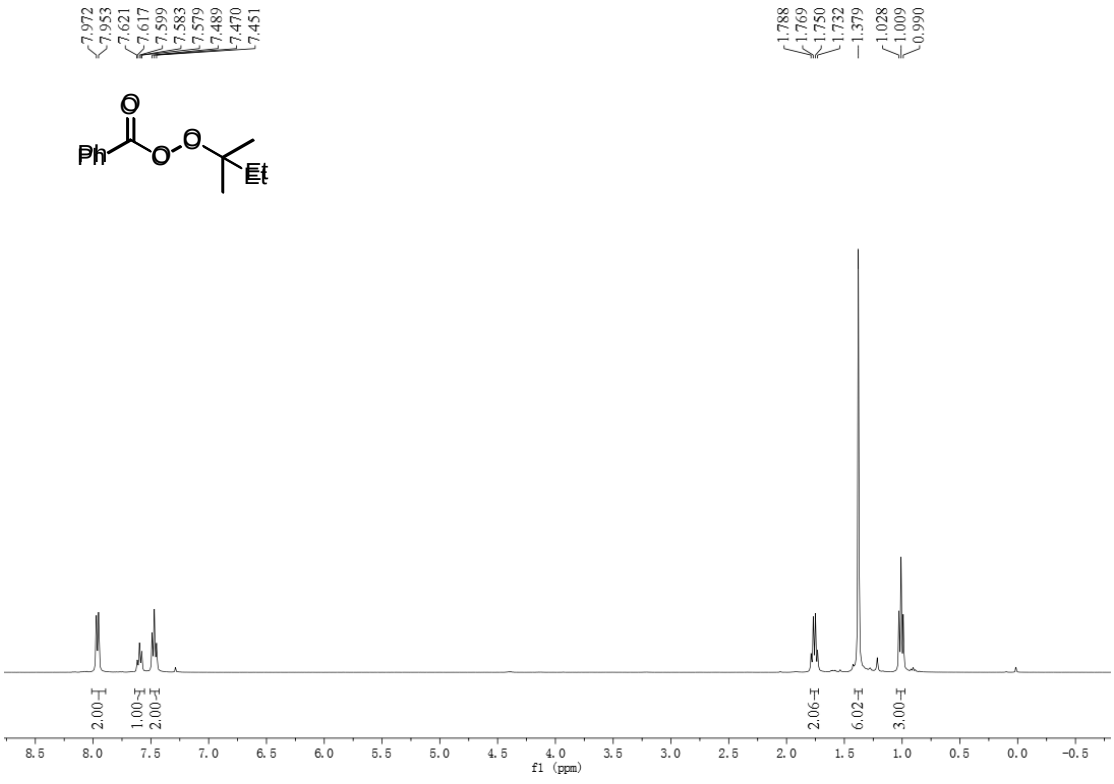

$^{1}$H NMR for **di-*iso*-hexyl peroxide** (400 MHz, $CDCl_3$)



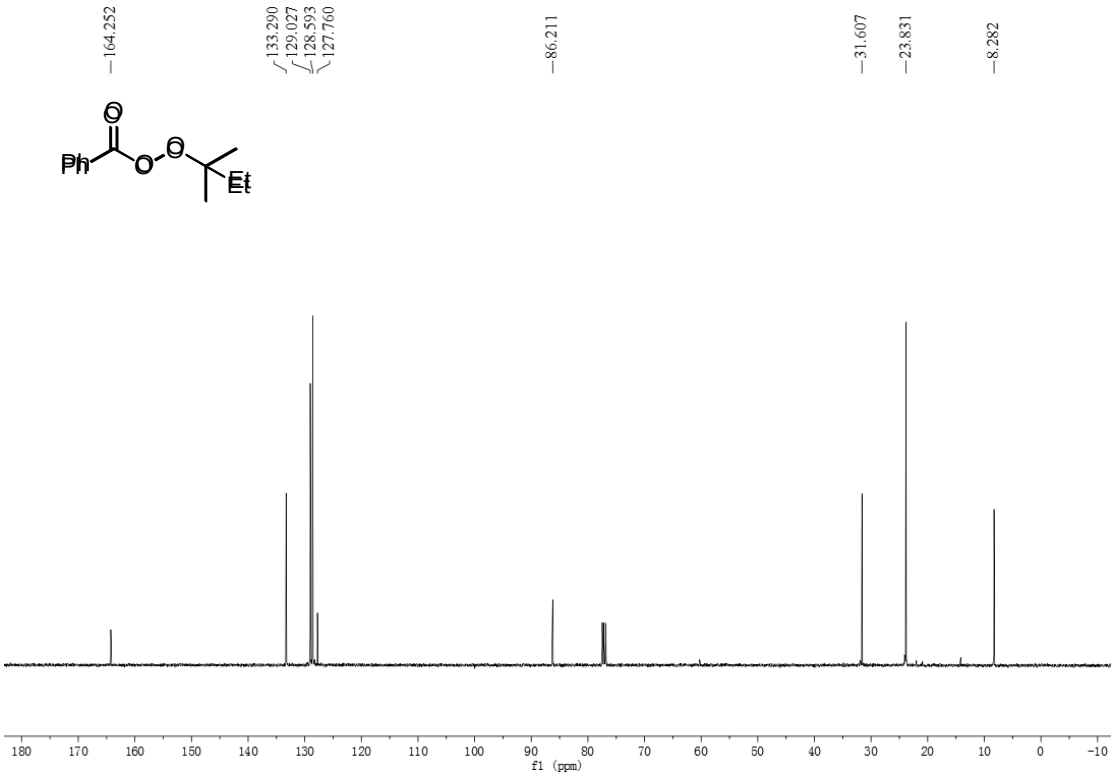
$^{13}$CNMR for **di-*iso*-hexyl peroxide** (101 MHz, $CDCl_3$)



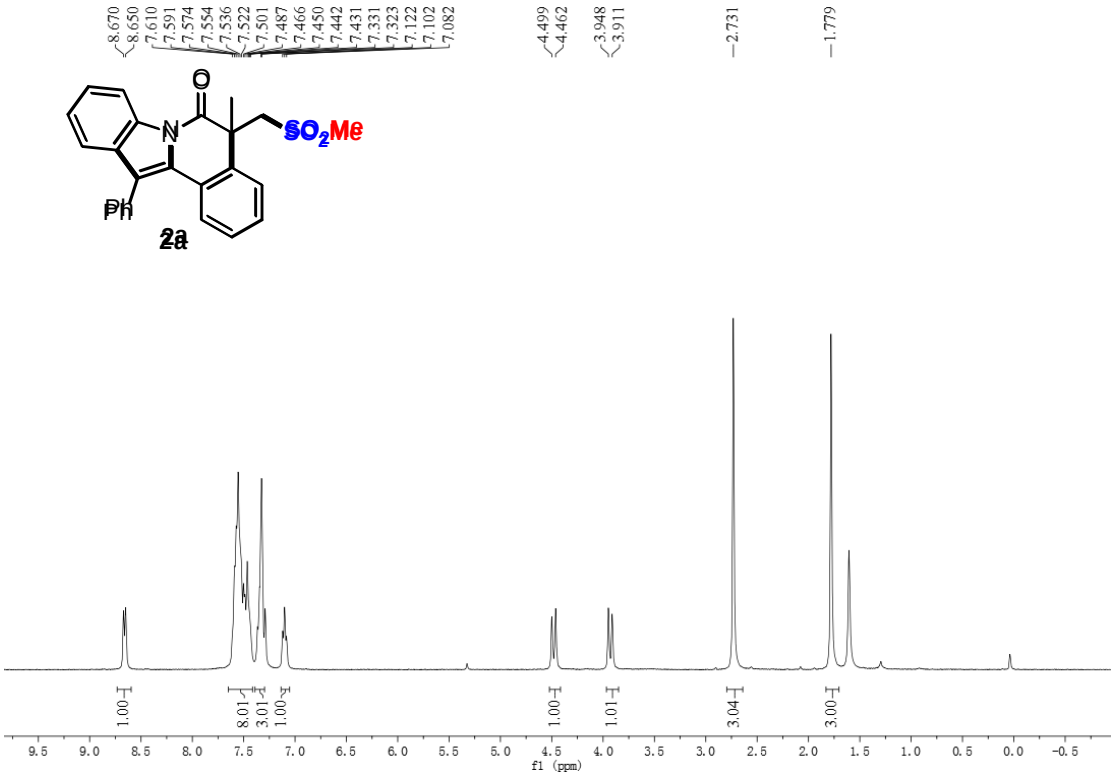

$^{1}$H NMR for ***tert*-Amyl peroxybenzzoate** (400 MHz, $CDCl_3$)



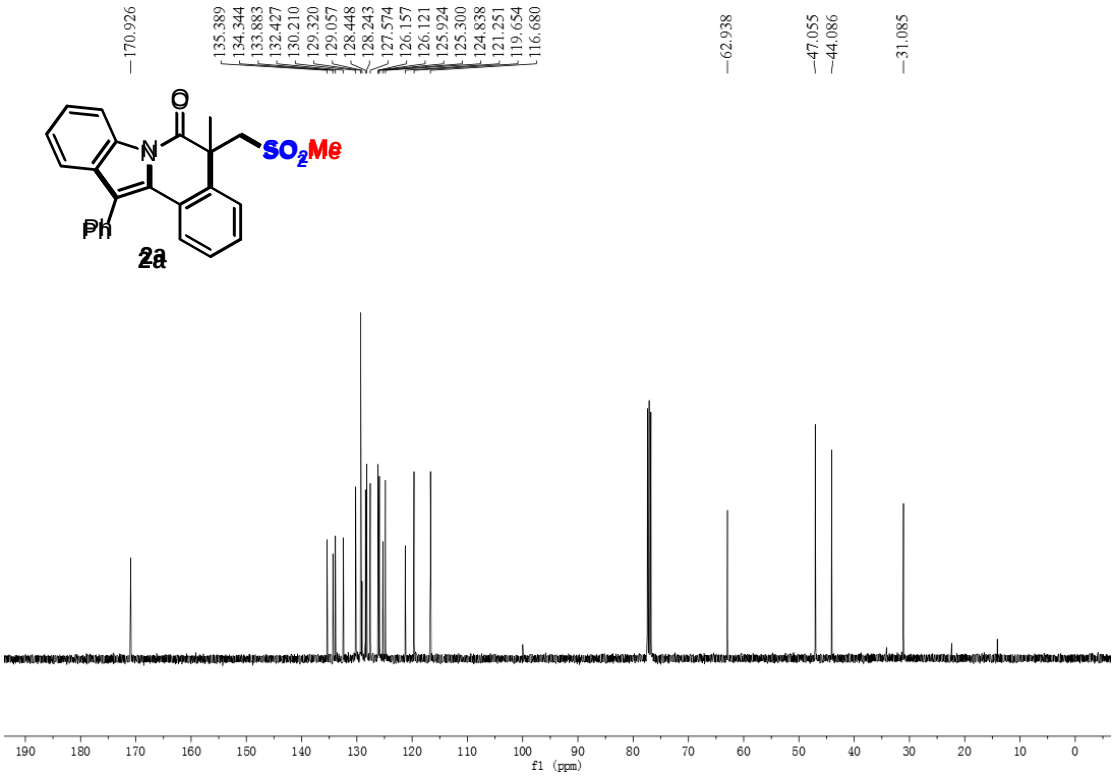
$^{13}$C NMR for ***tert*-Amyl peroxybenzzoate** (101 MHz, $CDCl_3$)



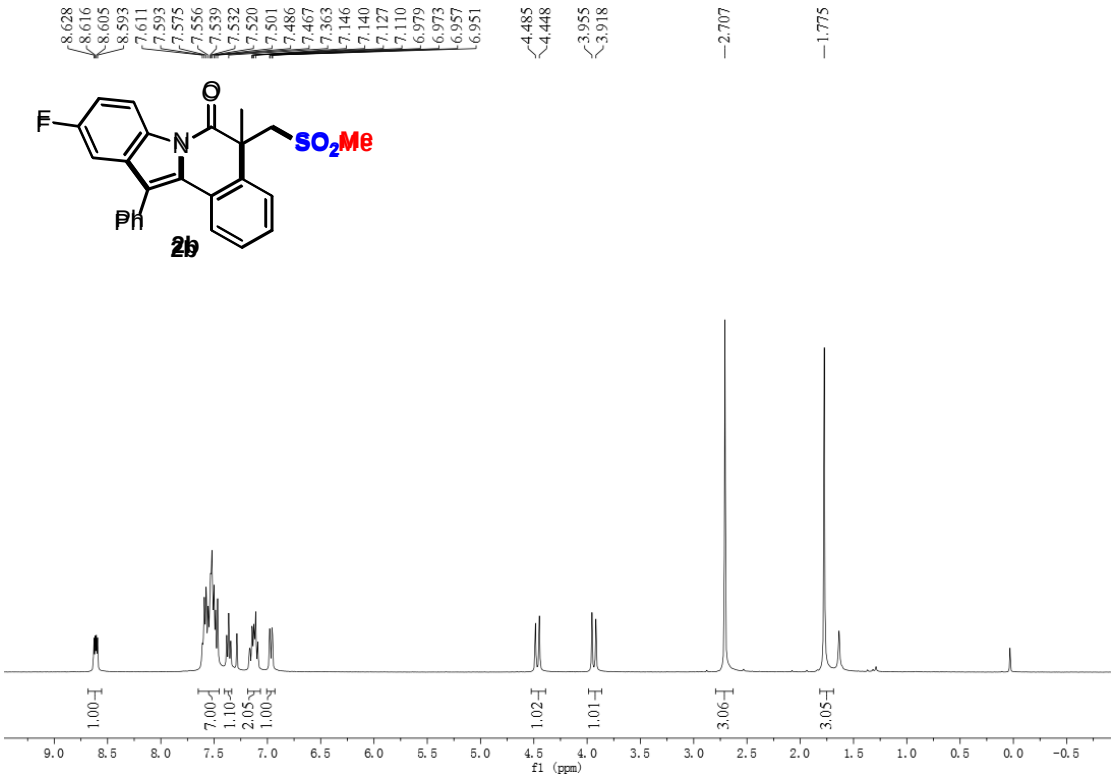

$^{1}$H NMR for **2a** (400 MHz, $CDCl_3$)



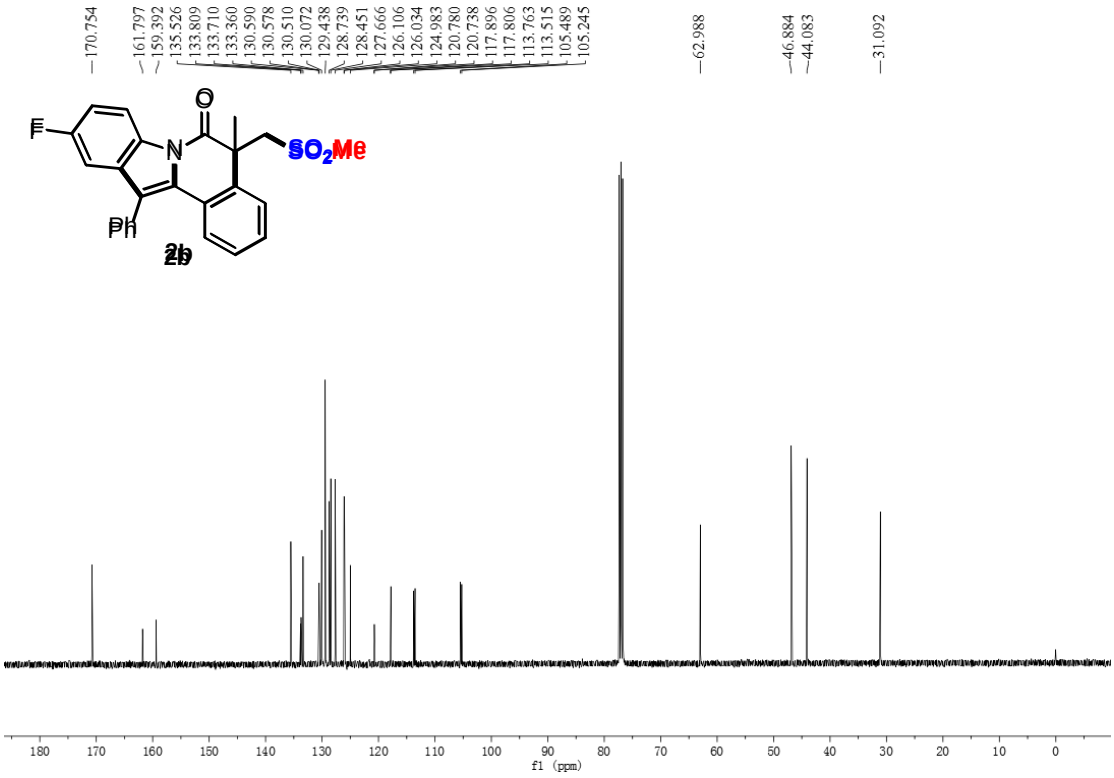
$^{13}$C NMR for **2a** (101 MHz, $CDCl_3$)



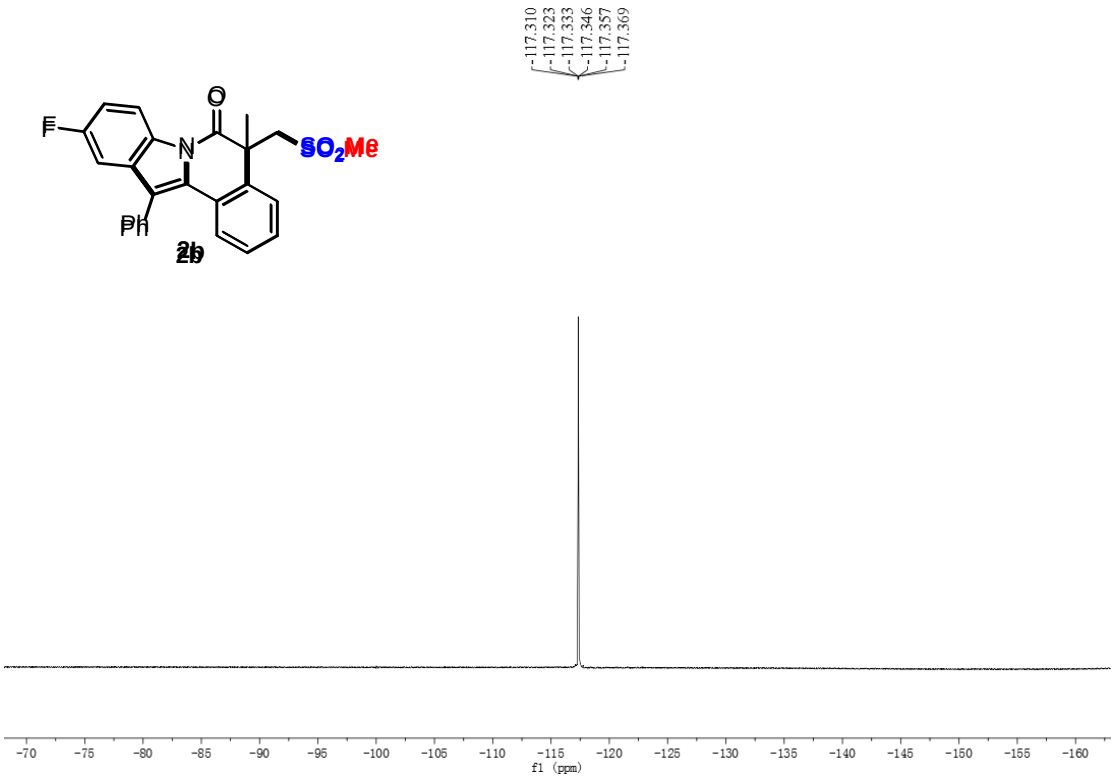

$^{1}$H NMR for **2b** (400 MHz, $CDCl_3$)



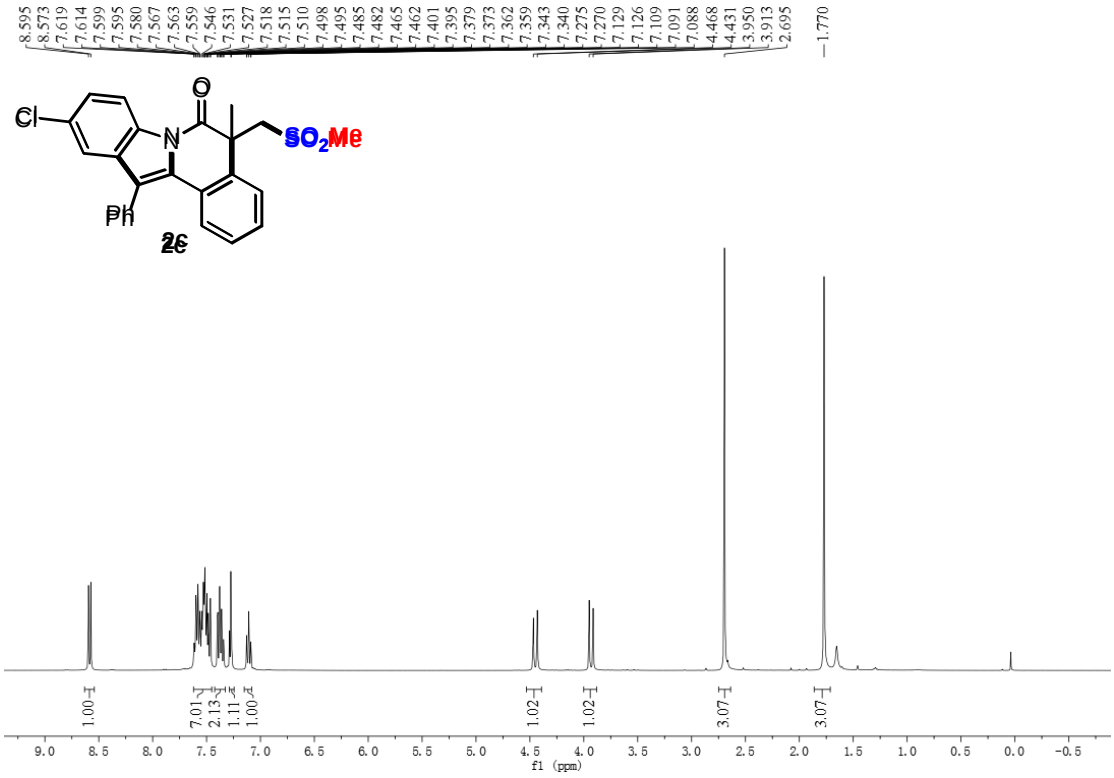
$^{13}$C NMR for **2b** (101 MHz, $CDCl_3$)



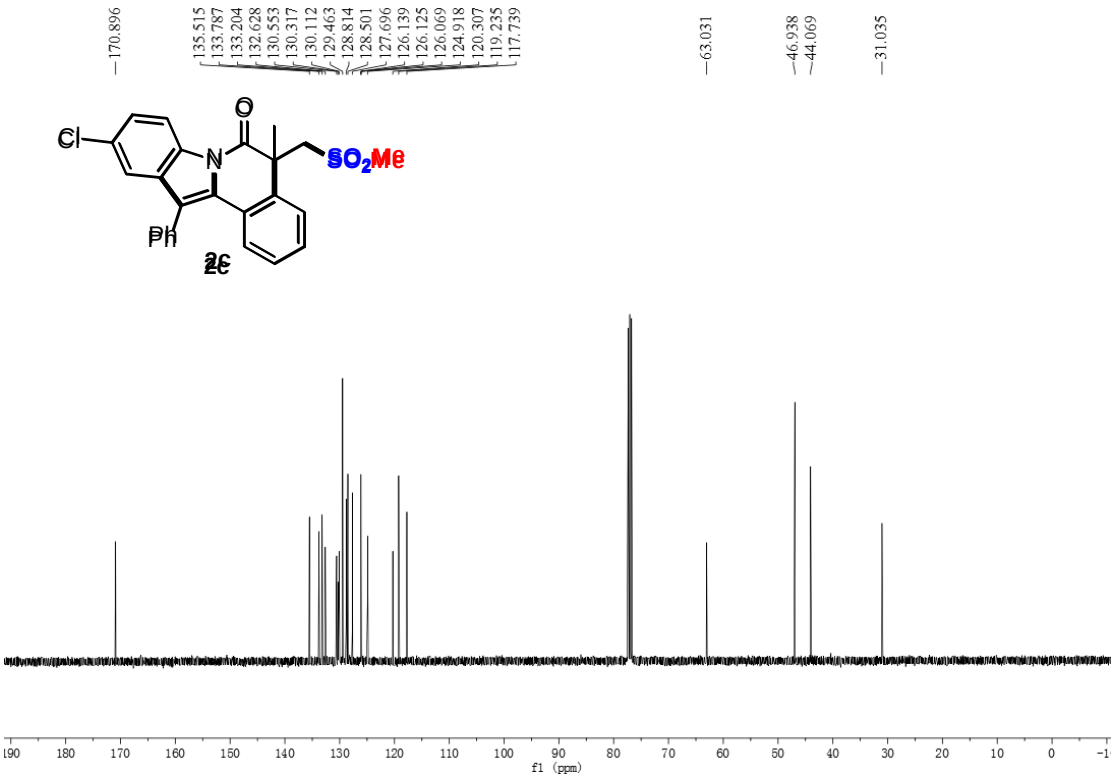

$^{19}$F NMR for **2b** (376 MHz, $CDCl_3$)



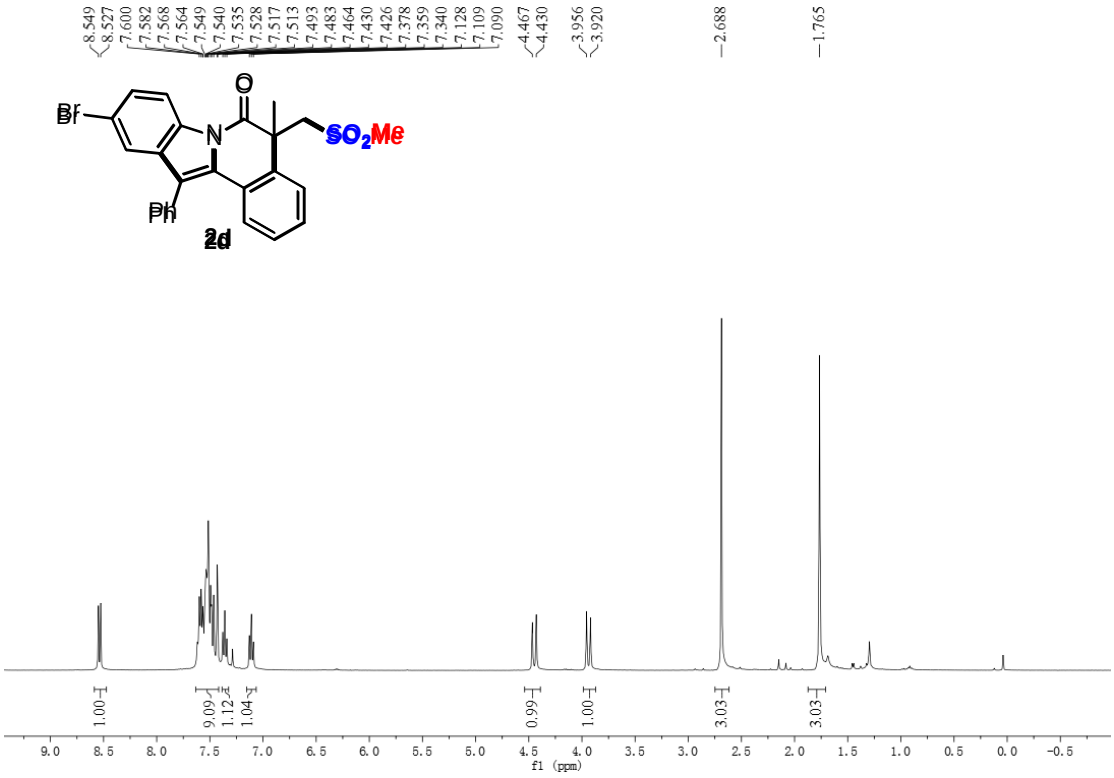
$^{1}$H NMR for **2c** (400 MHz, $CDCl_3$)



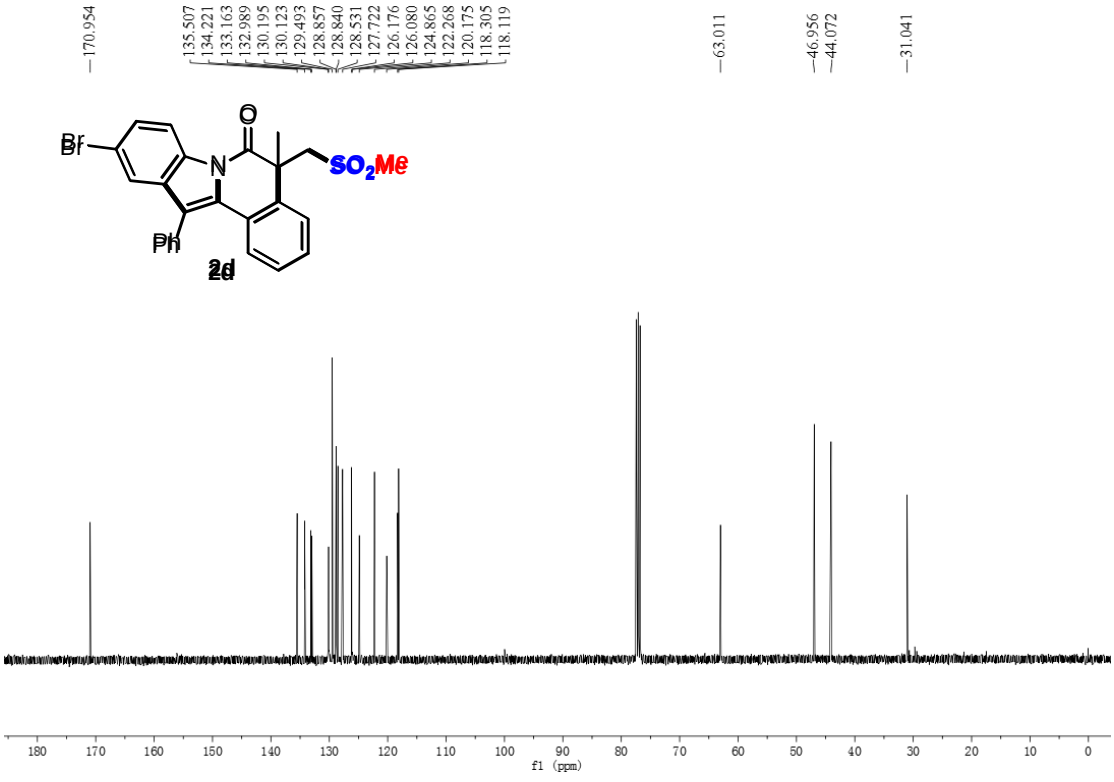

$^{13}$C NMR for **2c** (101 MHz, $CDCl_3$)



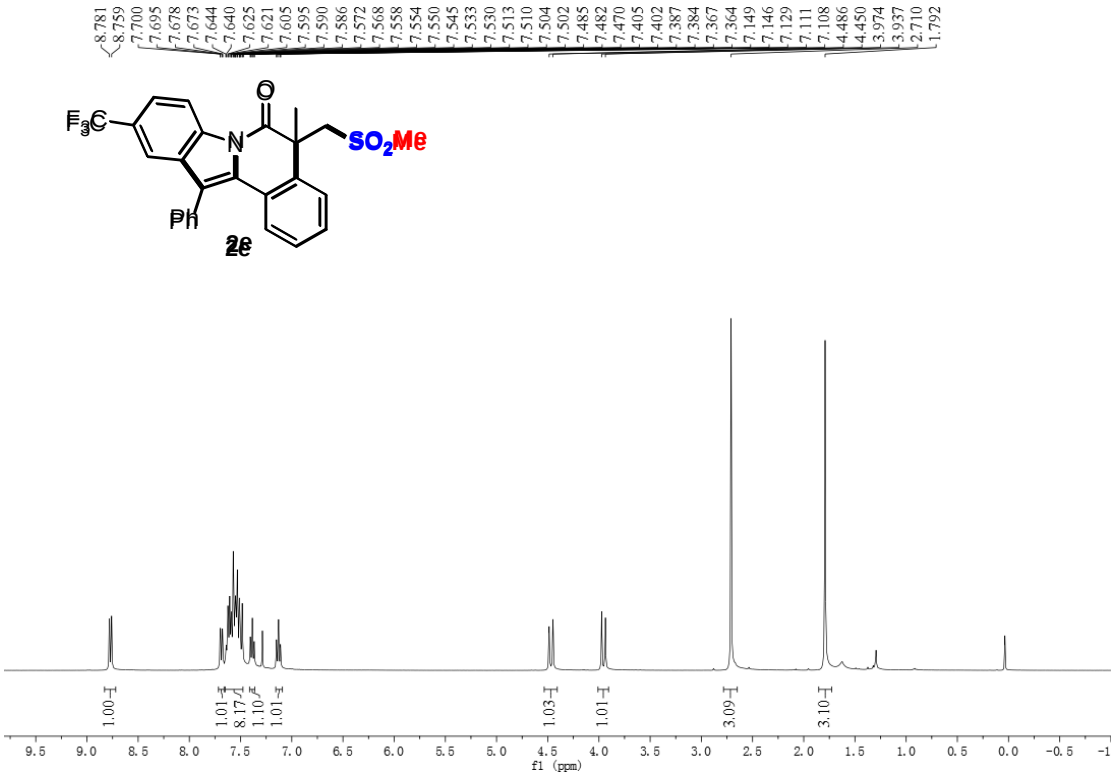
$^{1}$H NMR for **2d** (400 MHz, $CDCl_3$)



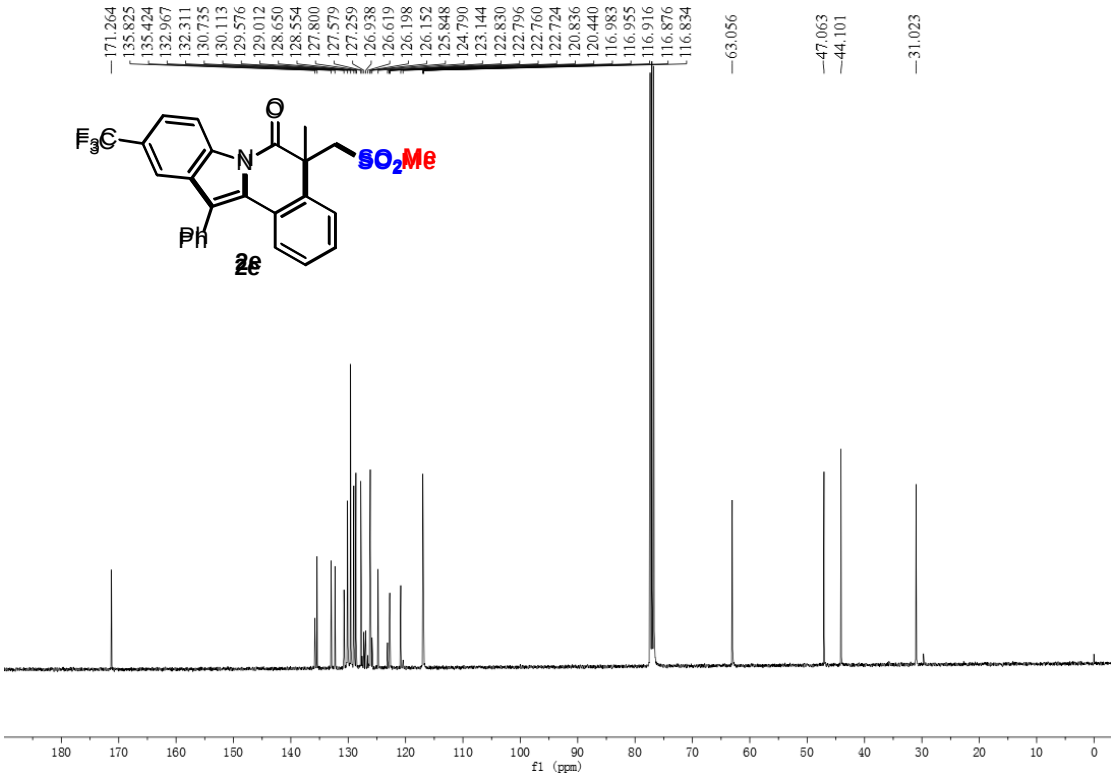

$^{13}$C NMR for **2d**(101 MHz, $CDCl_3$)



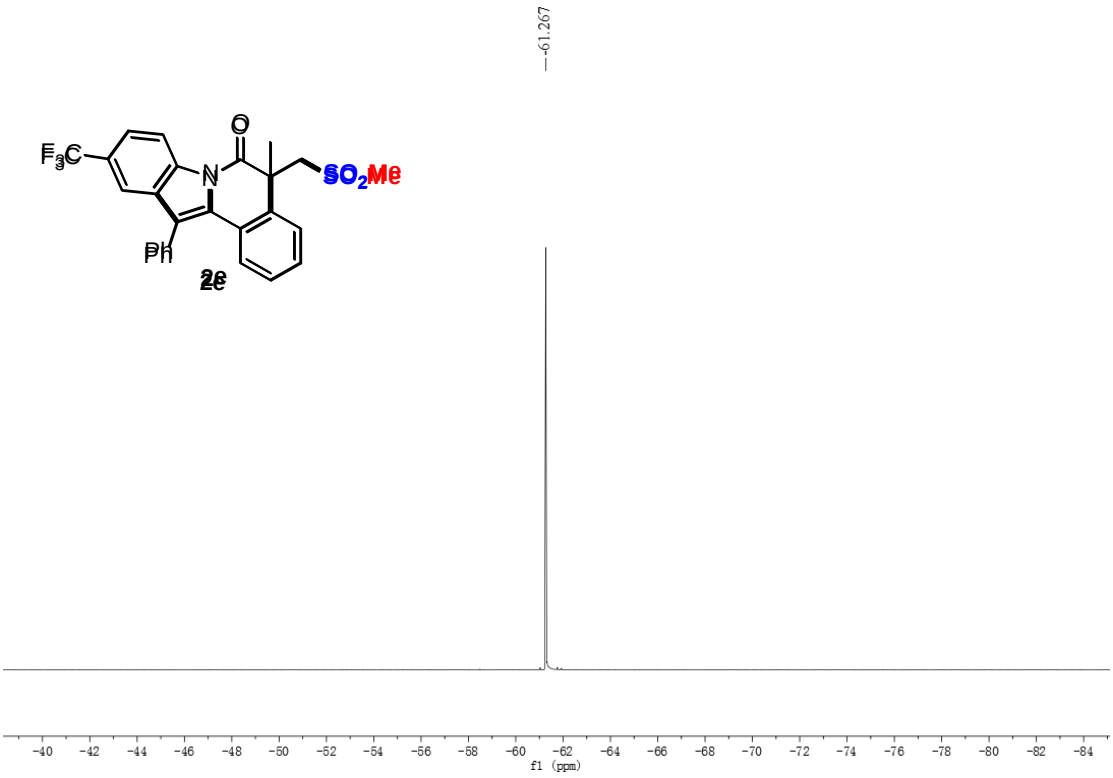
$^{1}$H NMR for **2e** (400 MHz, $CDCl_3$)



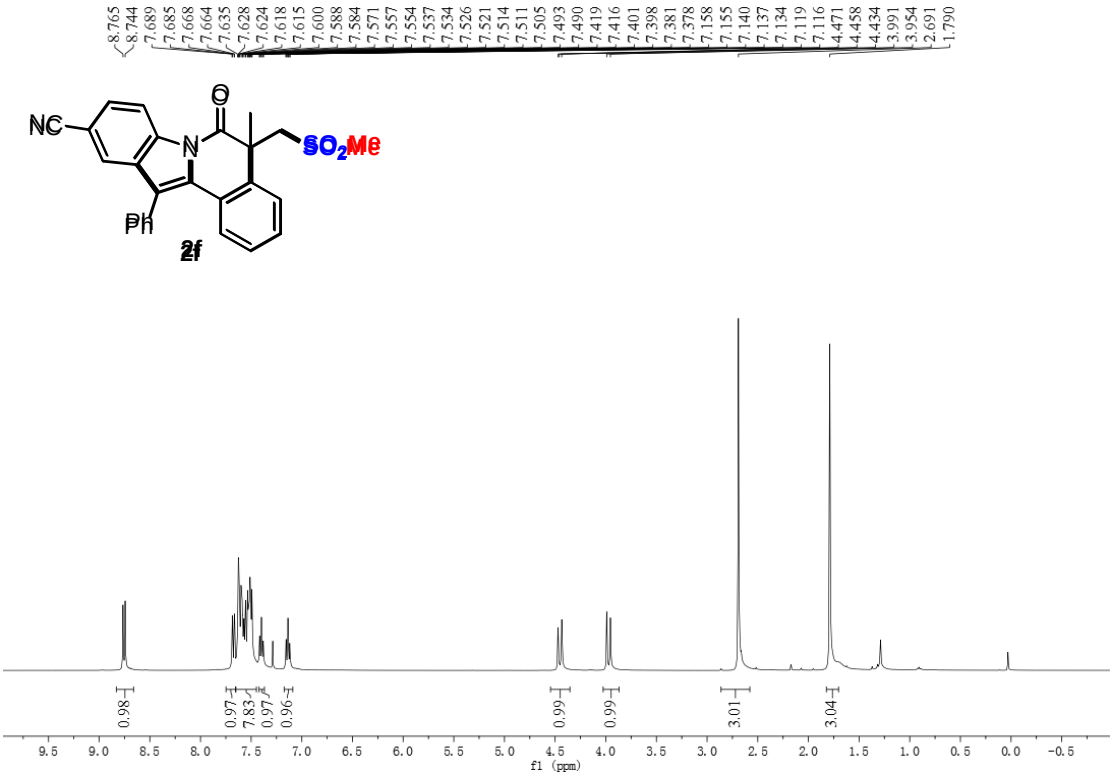

$^{13}$C NMR for **2e** (101 MHz, $CDCl_3$)



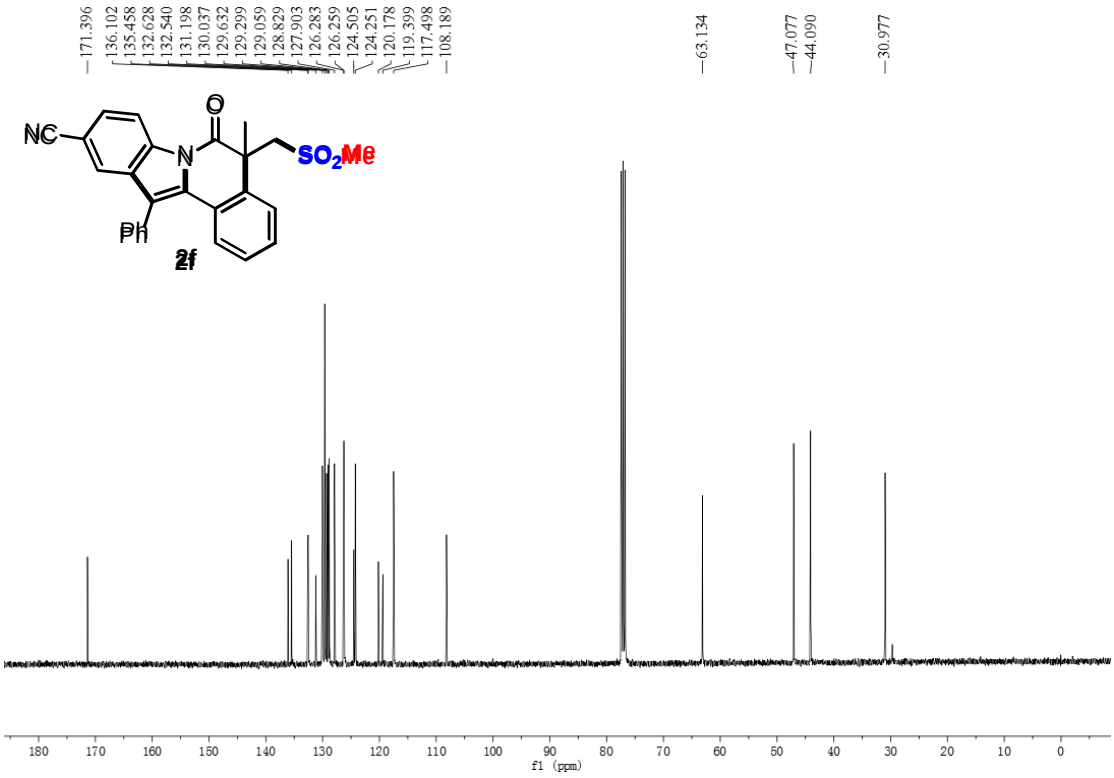
$^{19}$F NMR for **2e** (376 MHz, $CDCl_3$)



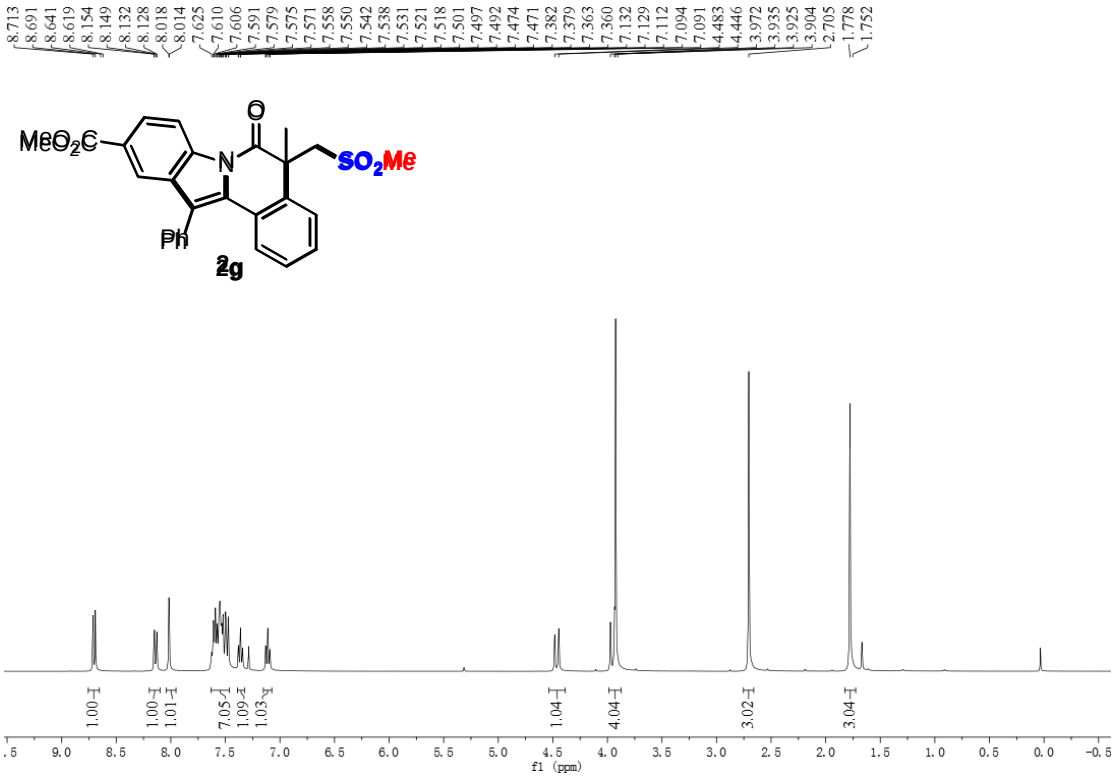

$^{1}$H NMR for **2f** (400 MHz, $CDCl_3$)



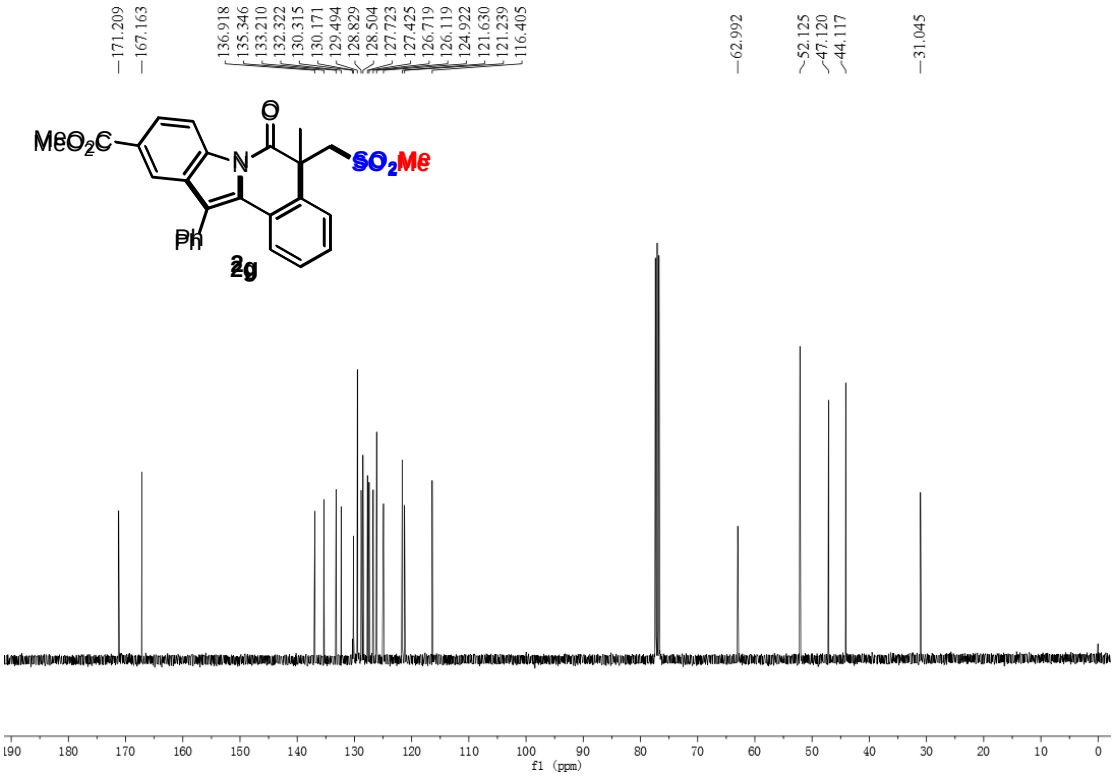
$^{13}$C NMR for **2f** (101 MHz, $CDCl_3$)



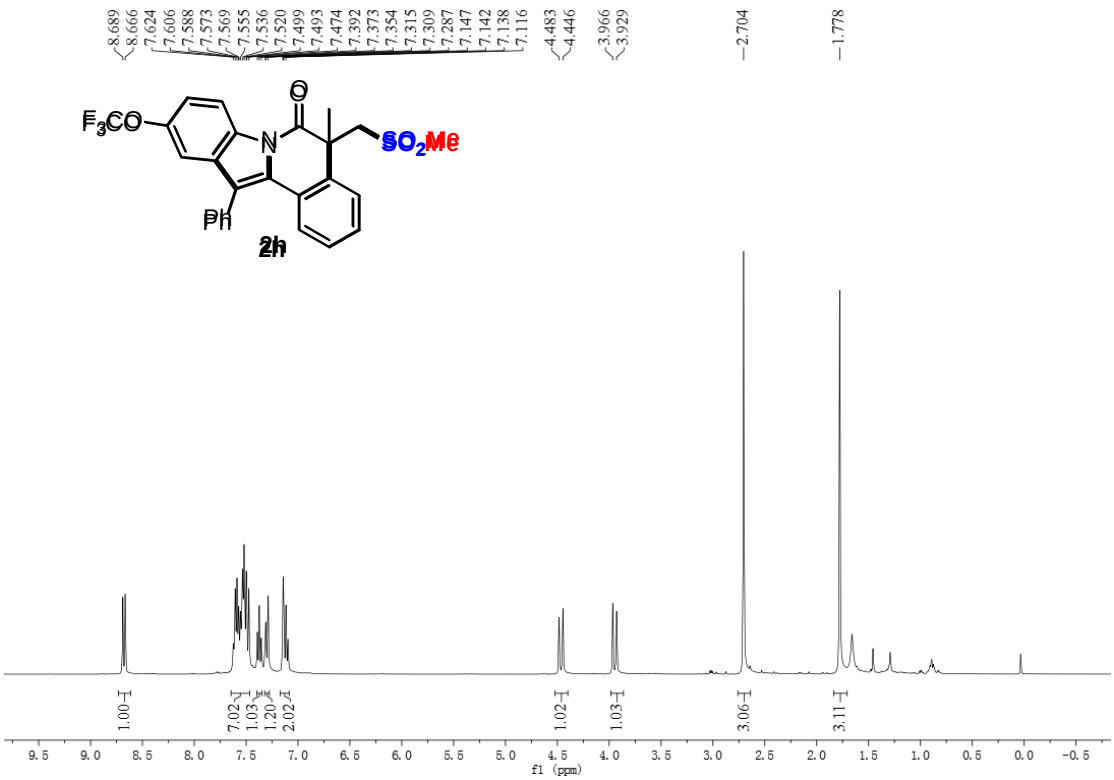

$^{1}$H NMR for **2g** (400 MHz, $CDCl_3$)



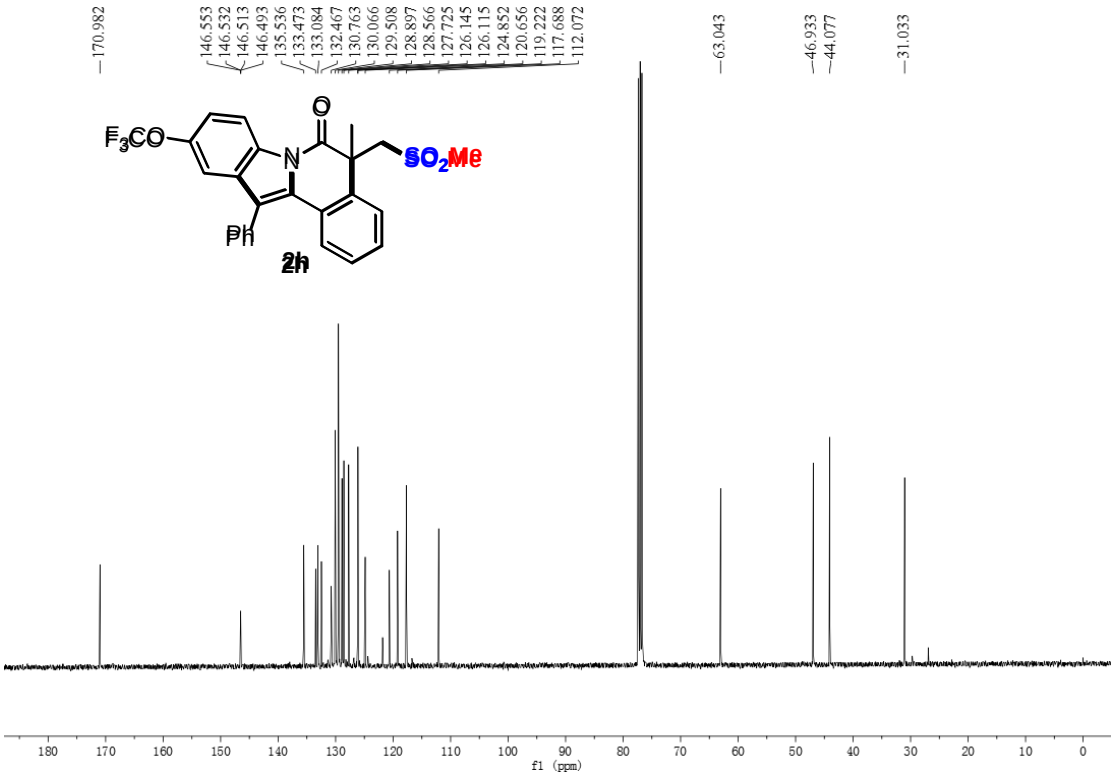
$^{13}$C NMR for **2g** (101 MHz, $CDCl_3$)



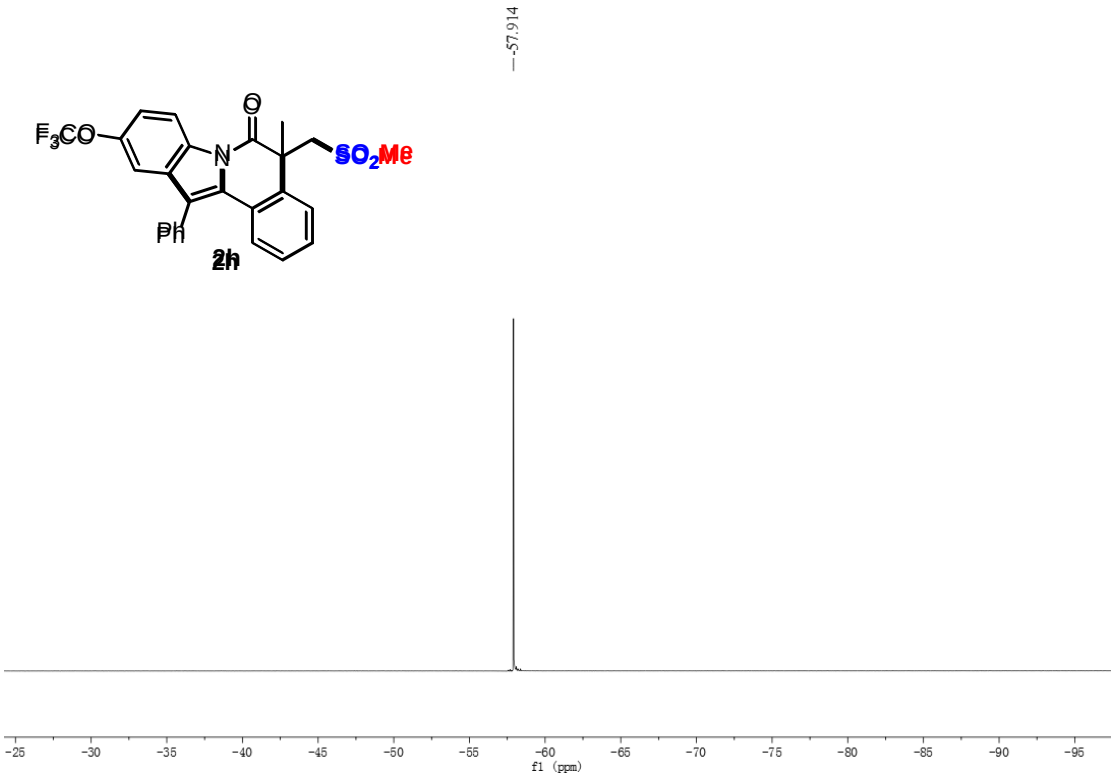

$^{1}$H NMR for **2h** (400 MHz, $CDCl_3$)



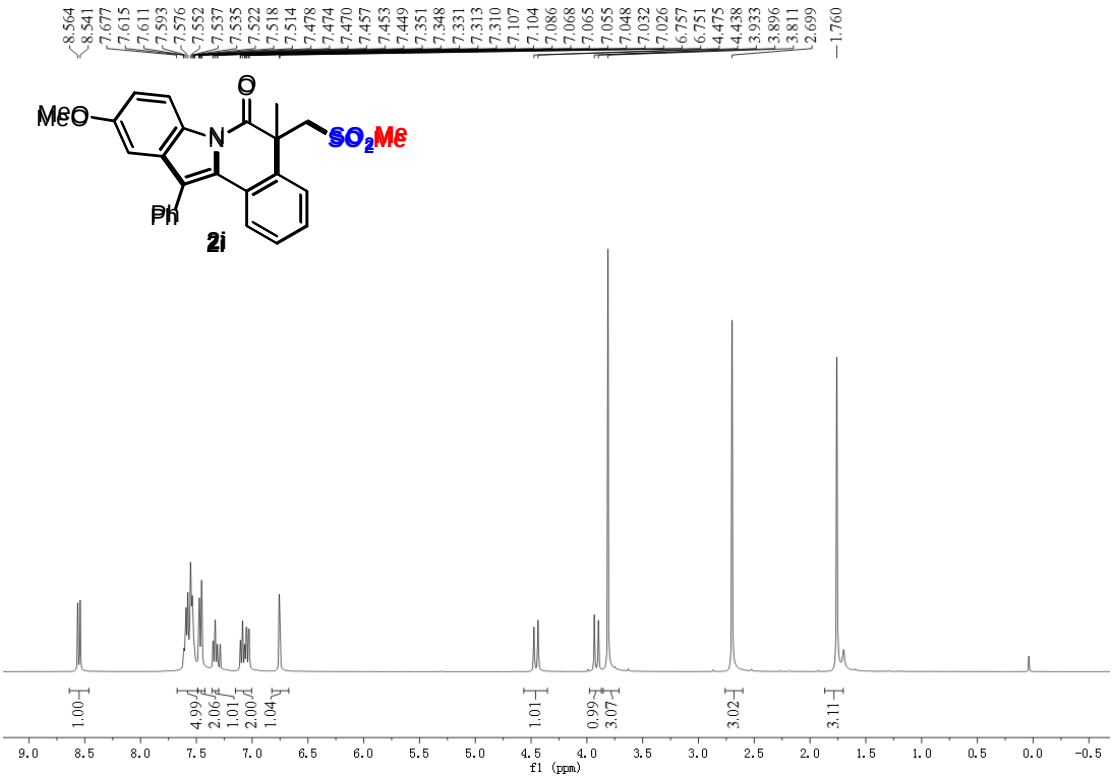
$^{13}$C NMR for **2h** (101 MHz, $CDCl_3$)



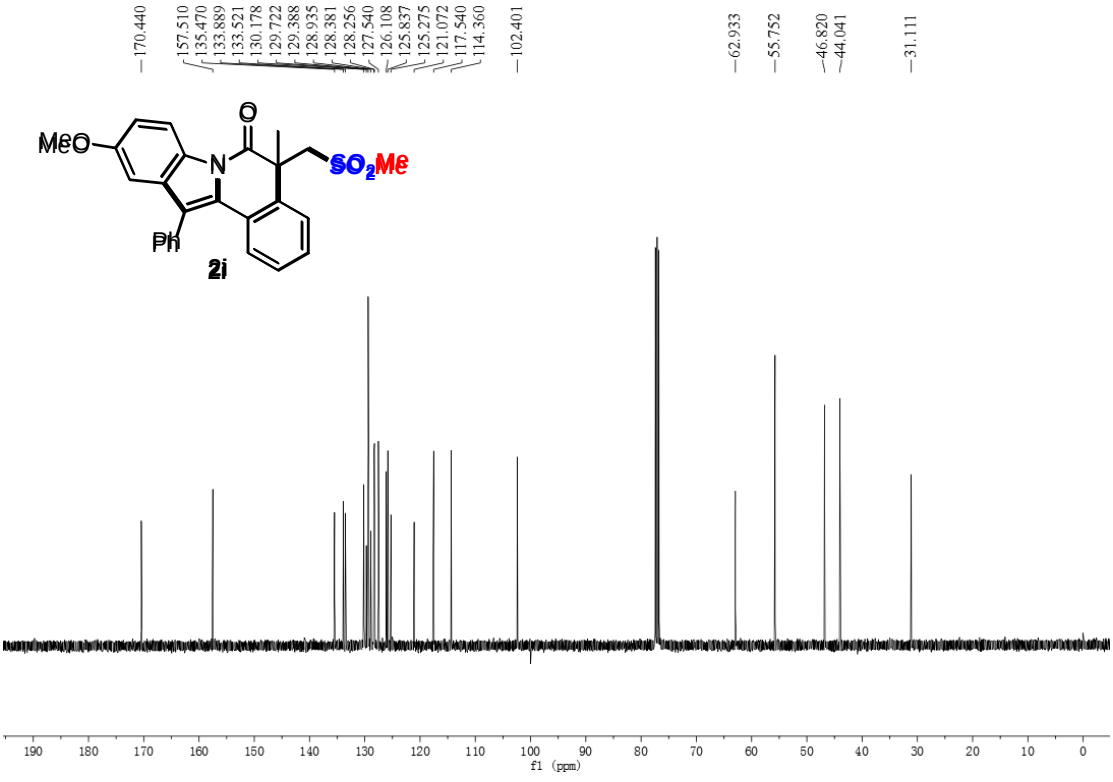

$^{19}$F NMR for **2h** (376 MHz, $CDCl_3$)



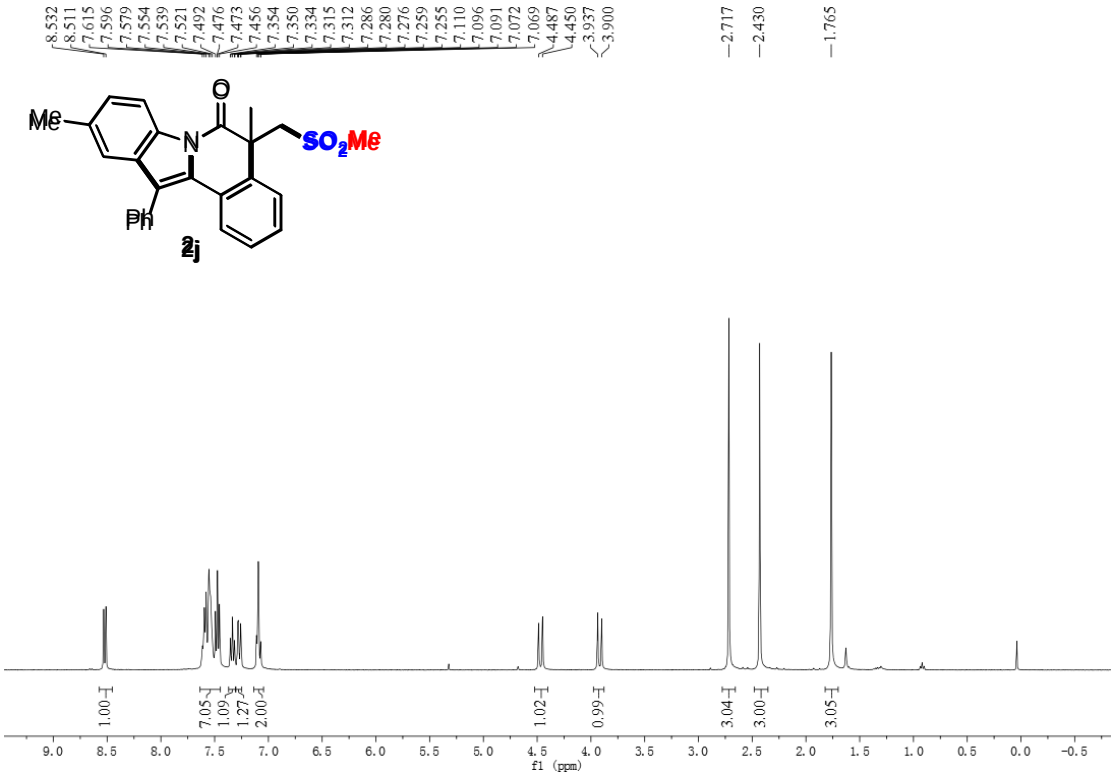
$^{1}$H NMR for **2i** (400 MHz, $CDCl_3$)



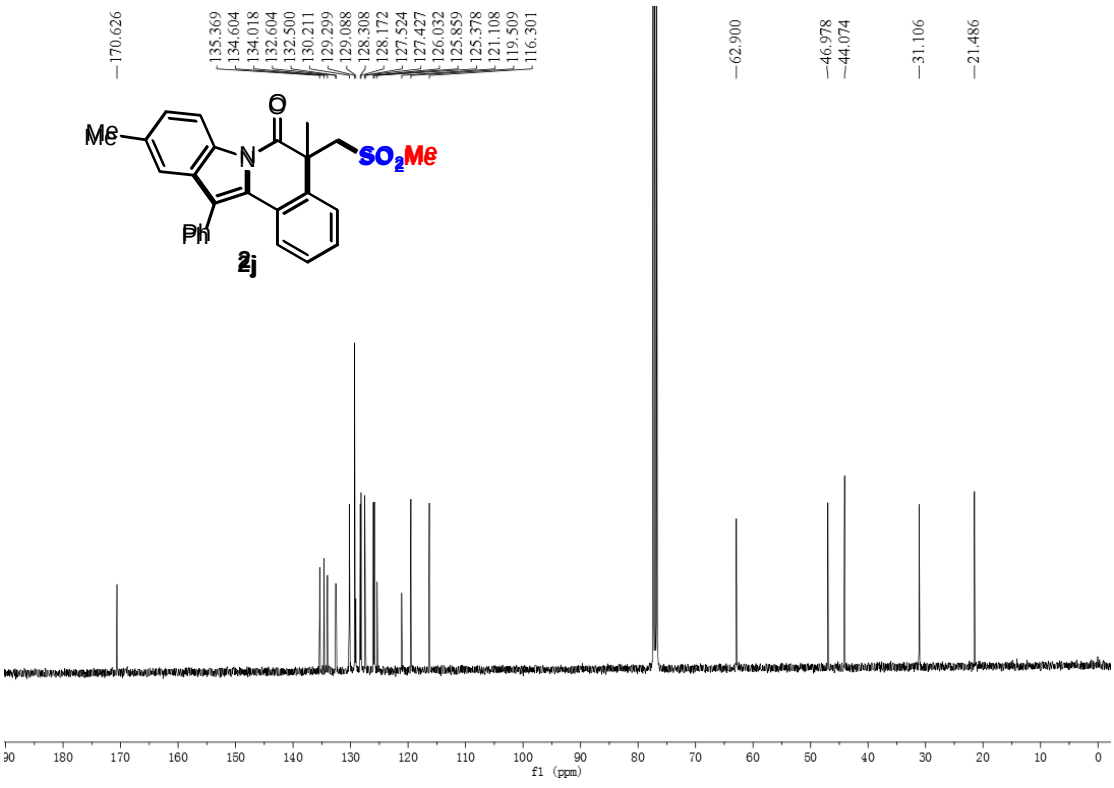

$^{13}$C NMR for **2i** (101 MHz, $CDCl_3$)



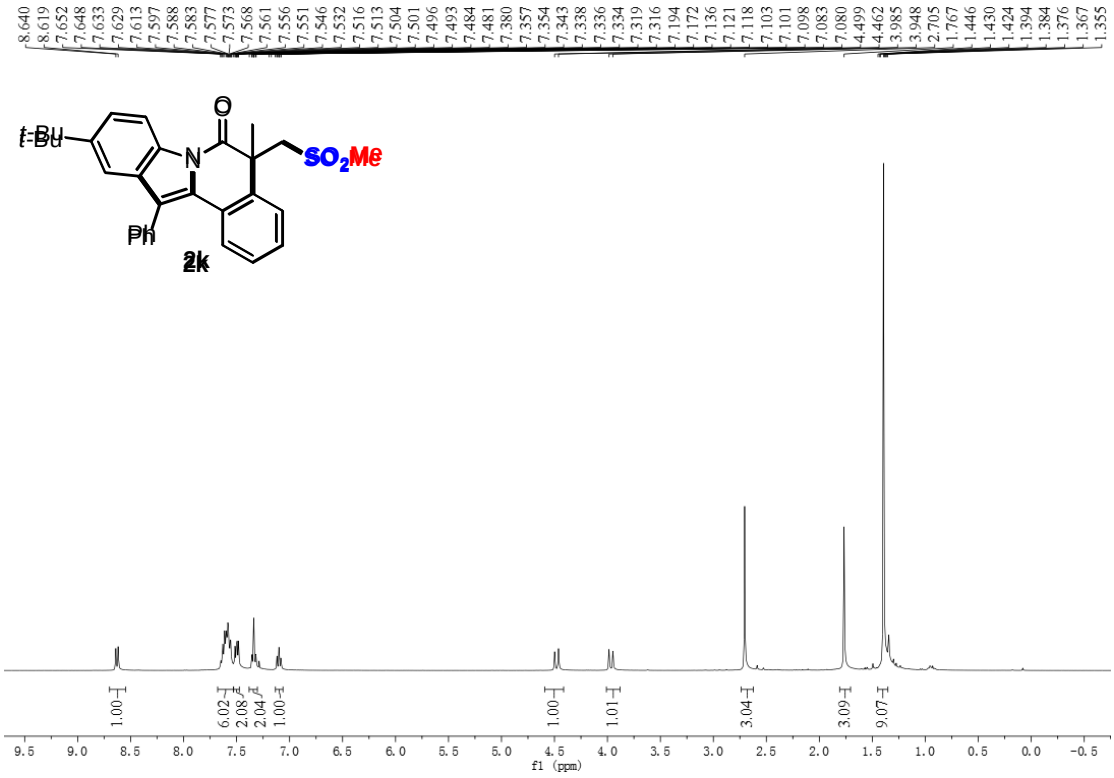
$^{1}$H NMR for **2j** (400 MHz, $CDCl_3$)



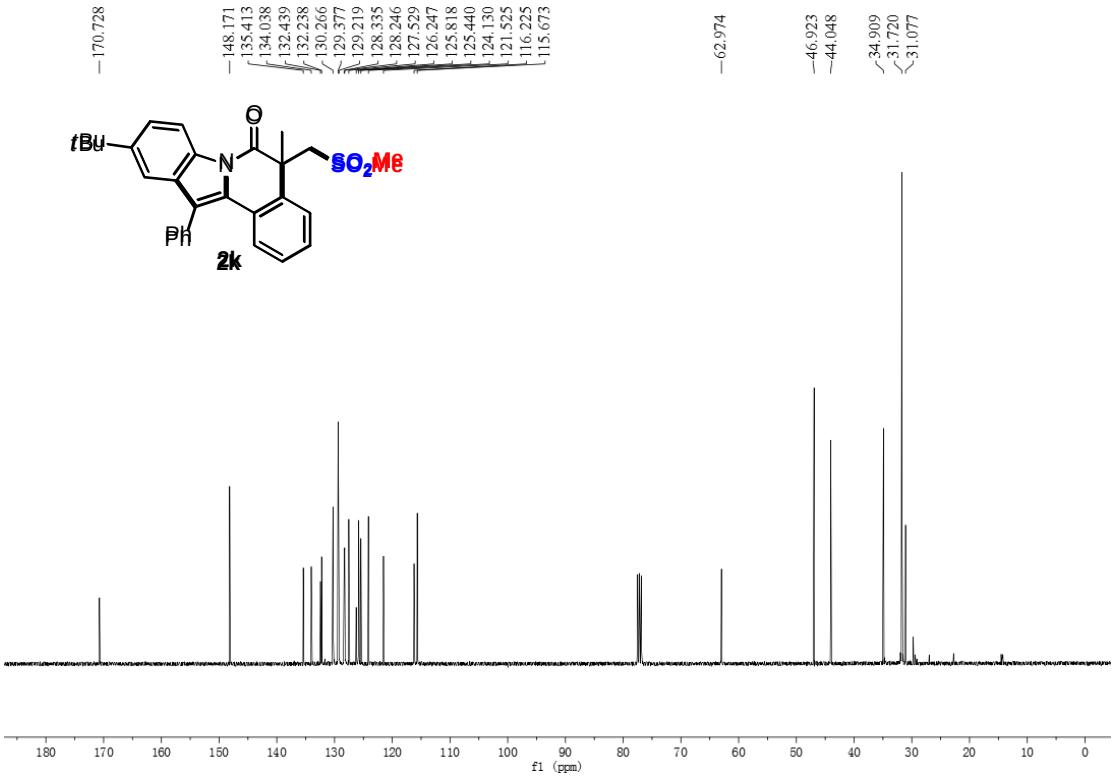

$^{13}$C NMR for **2j** (101 MHz, $CDCl_3$)



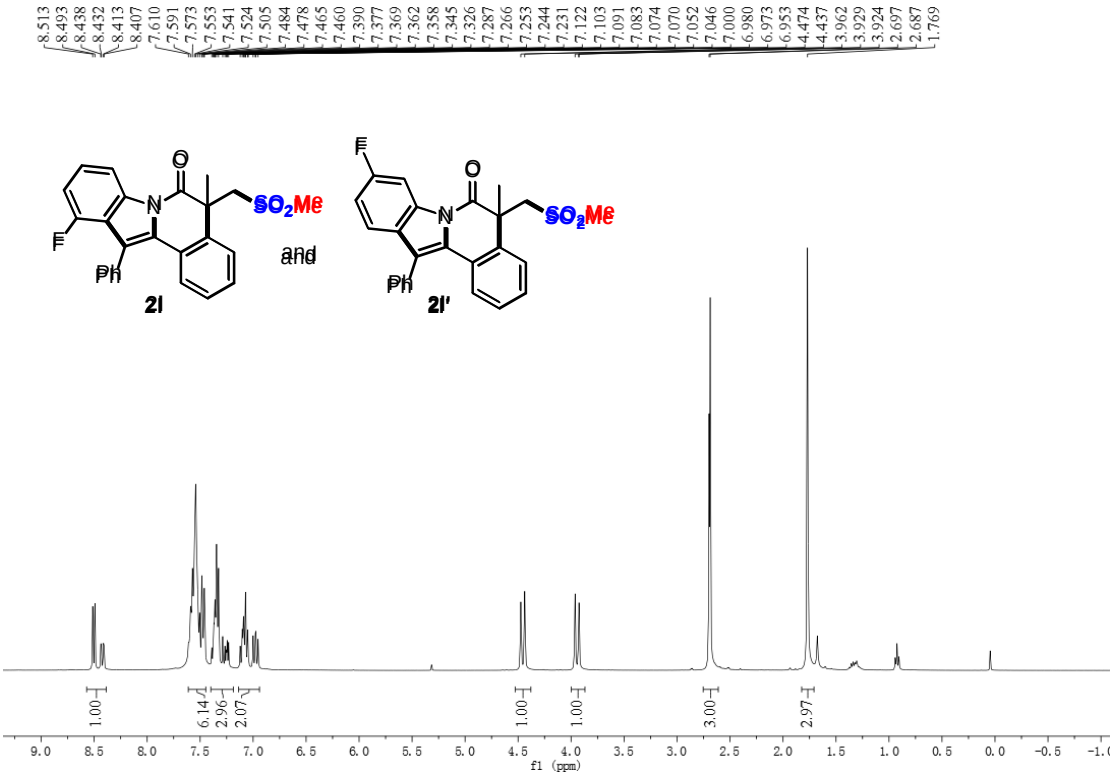
$^{1}$H NMR for **2k** (400 MHz, $CDCl_3$)



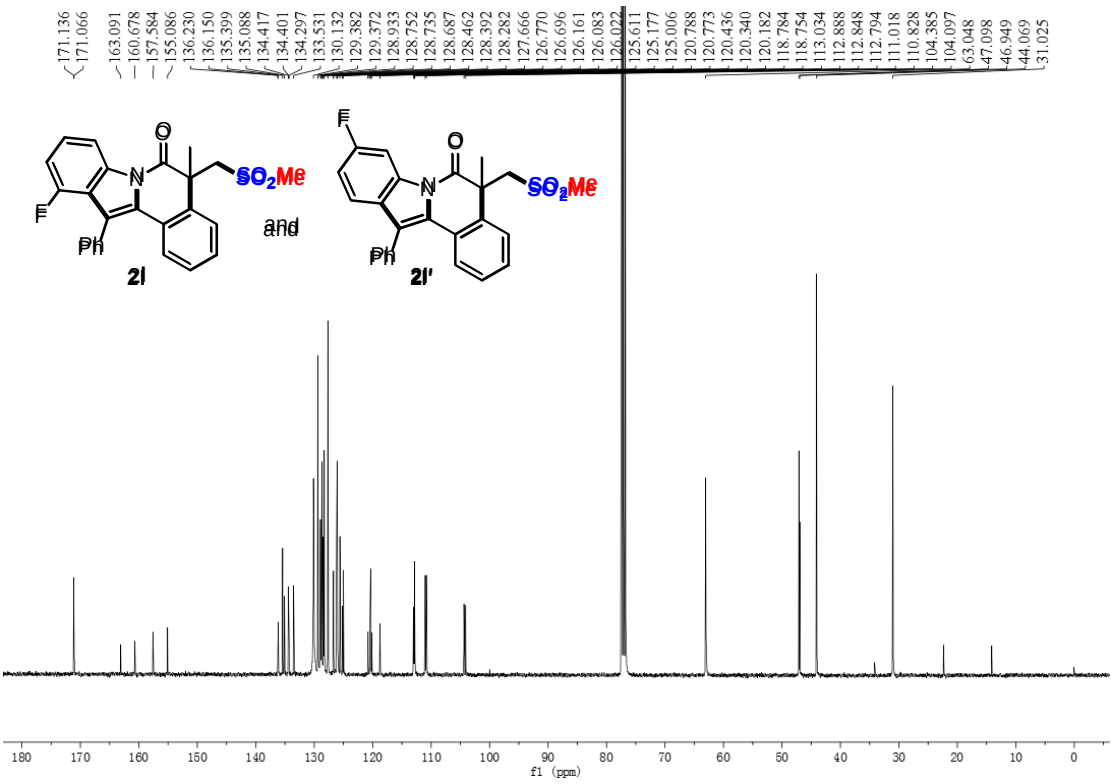

$^{13}$C NMR for **2k** (101 MHz, $CDCl_3$)



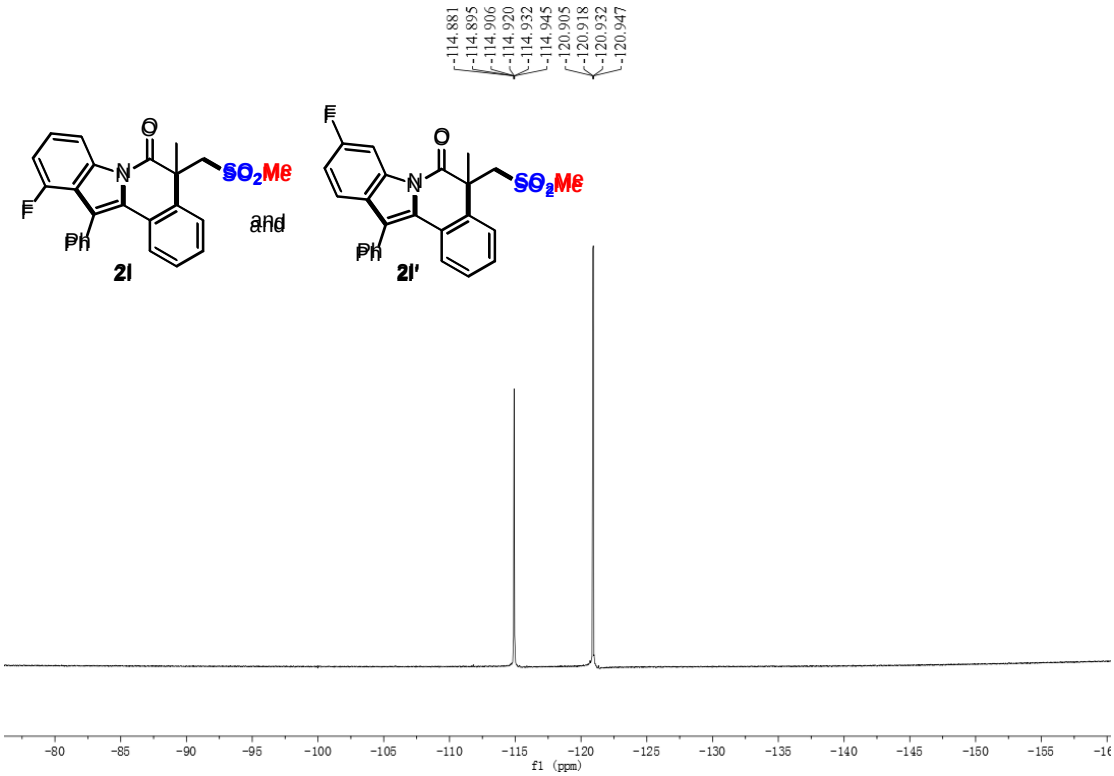
$^{1}$H NMR for **2l** (400 MHz, $CDCl_3$)



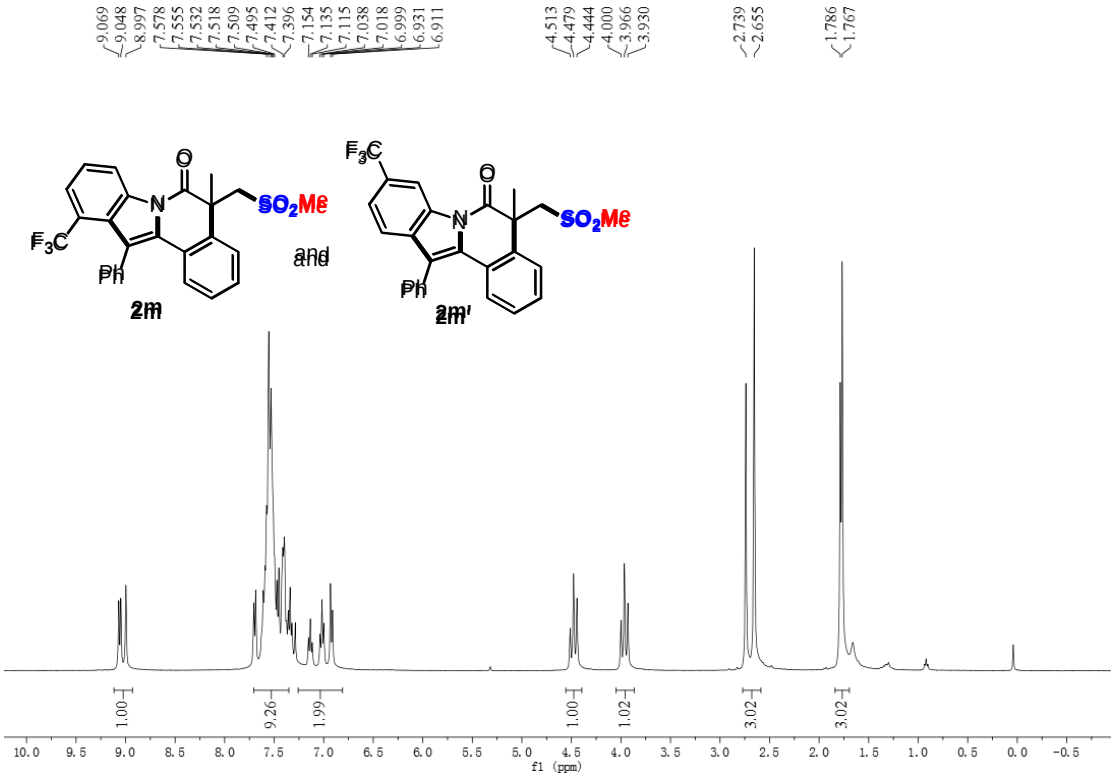

$^{13}$C NMR for **2l** (101 MHz, $CDCl_3$)



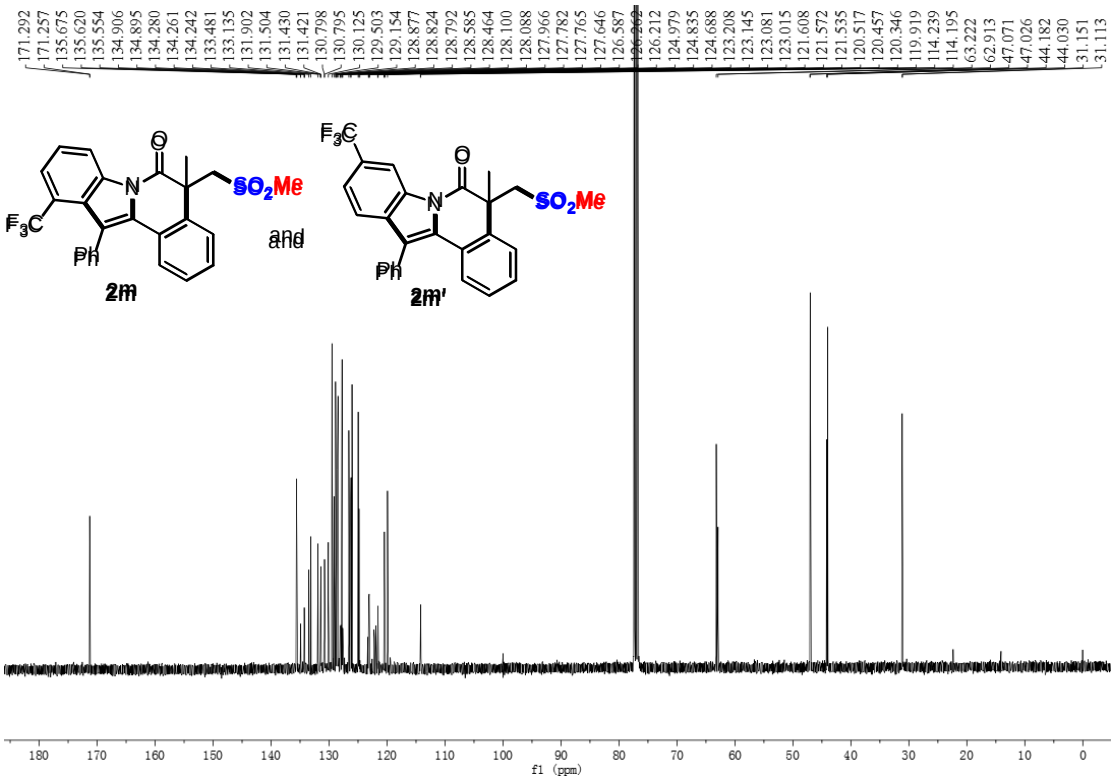
$^{19}$F NMR for **2l** ($CDCl_3$)



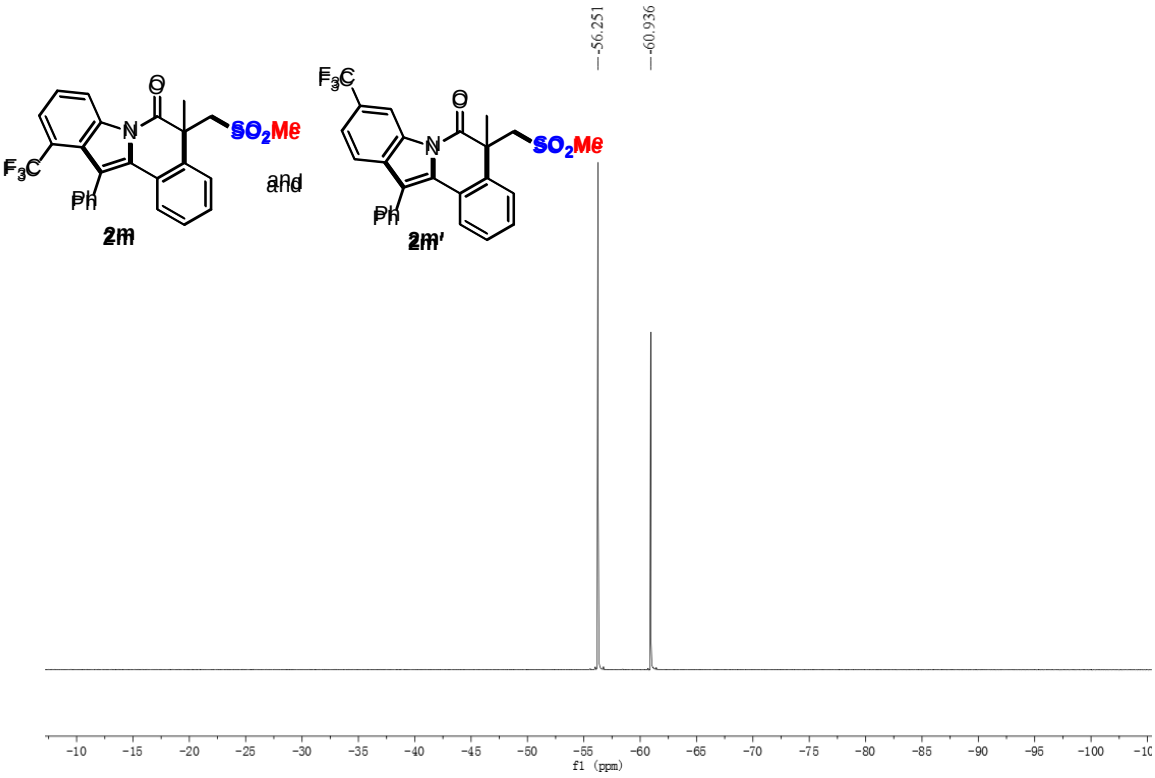

$^{1}$H NMR for **2m** ($CDCl_3$)



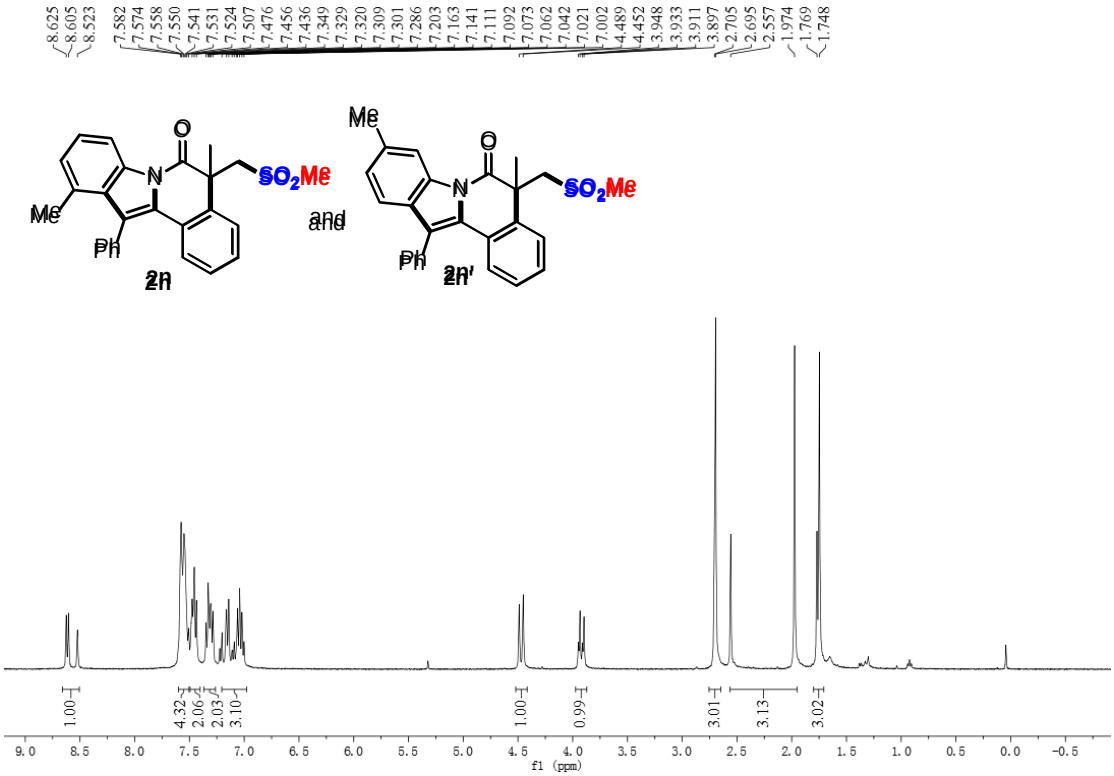
$^{13}C$ NMR for **2m** (101 MHz, $CDCl_3$)



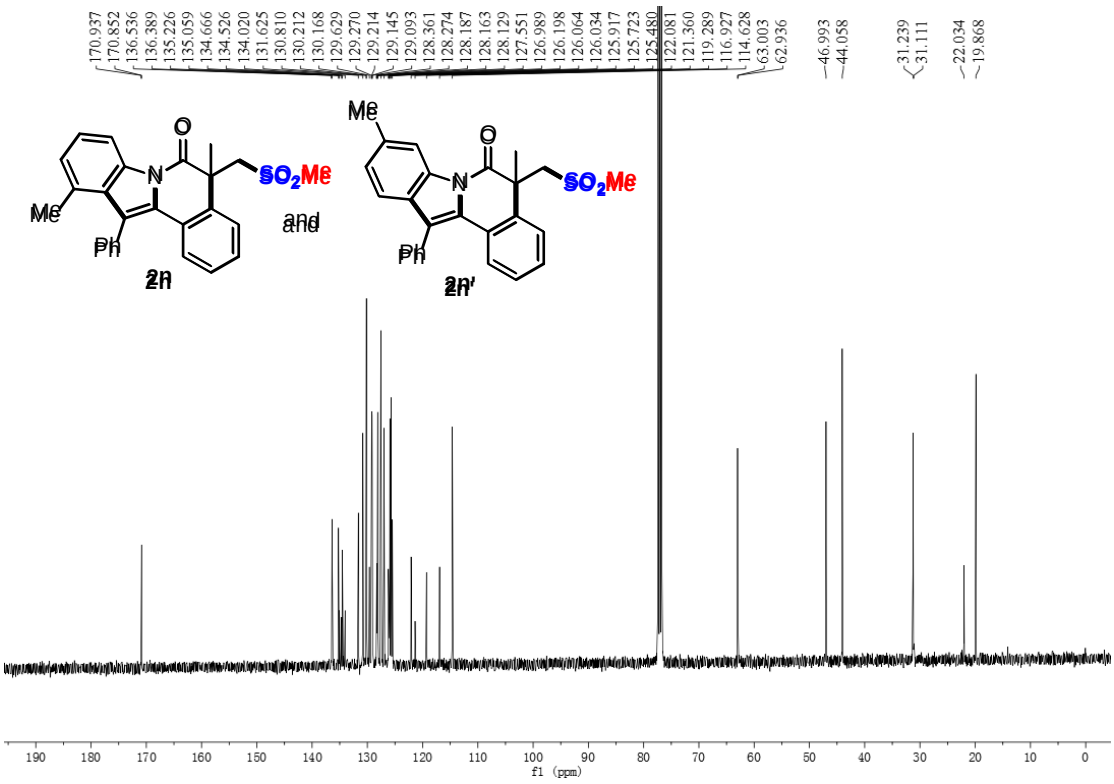

$^{19}F$ NMR for **2m** (376 MHz, $CDCl_3$)



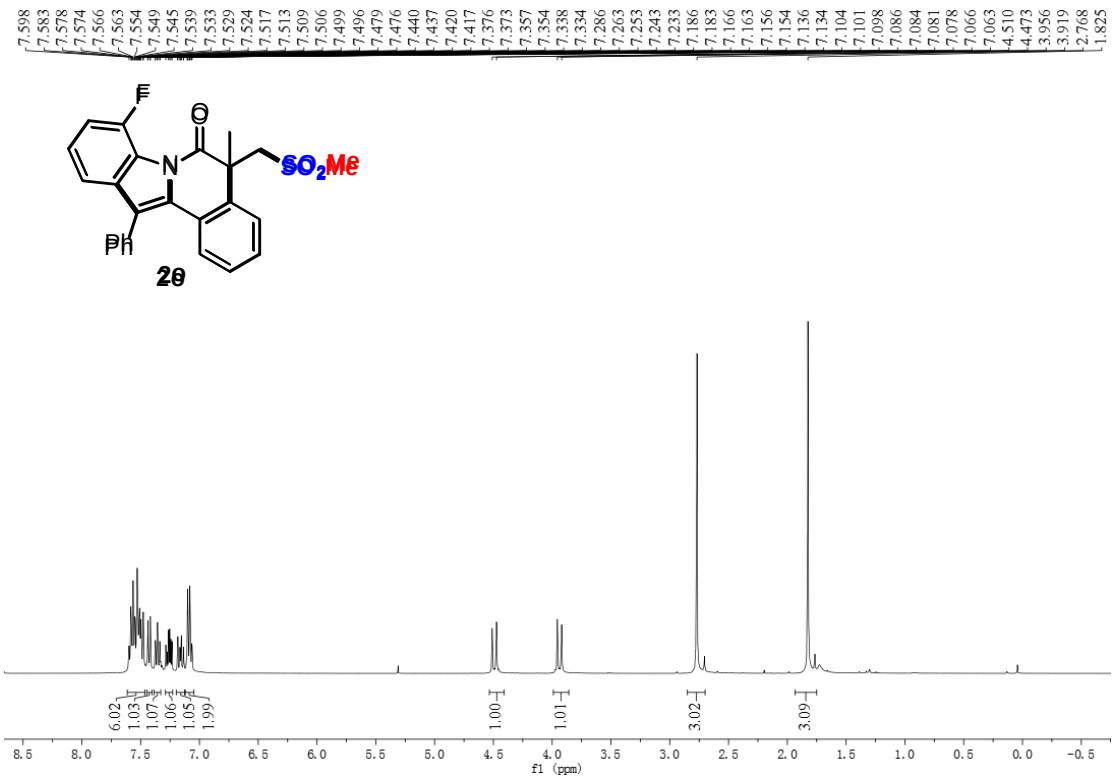
$^{1}$H NMR for **2n** (400 MHz, $CDCl_3$)



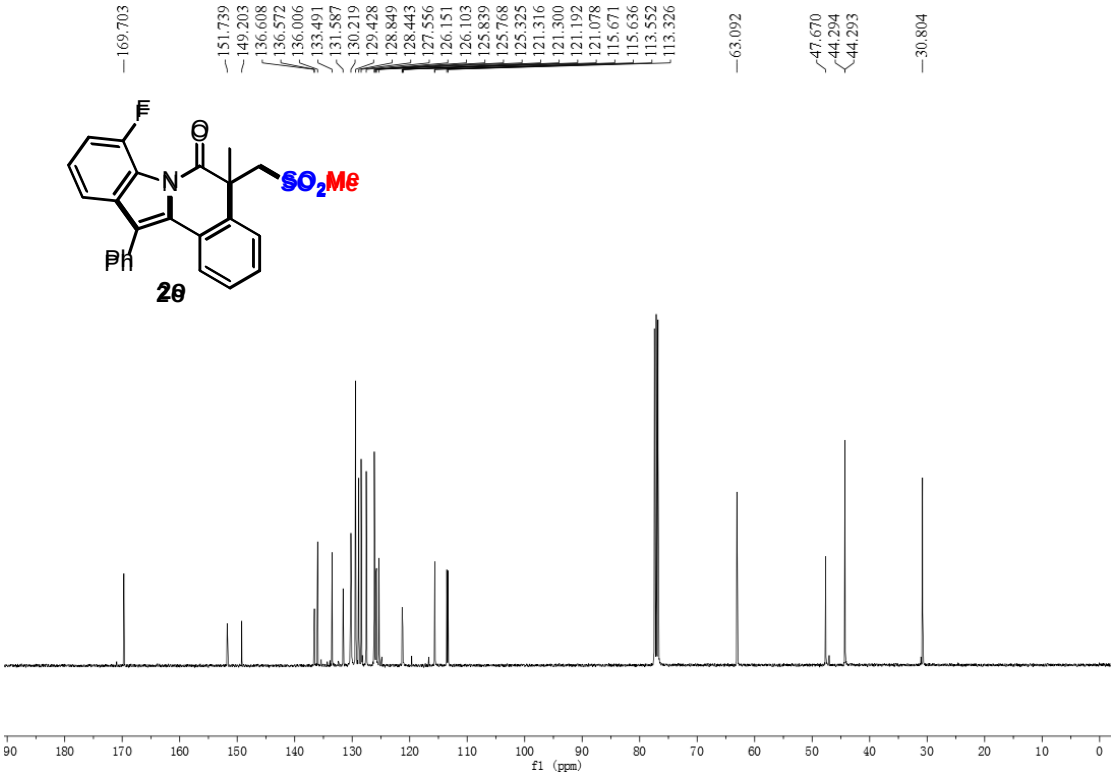

$^{13}$C NMR for **2n** (101 MHz, $CDCl_3$)



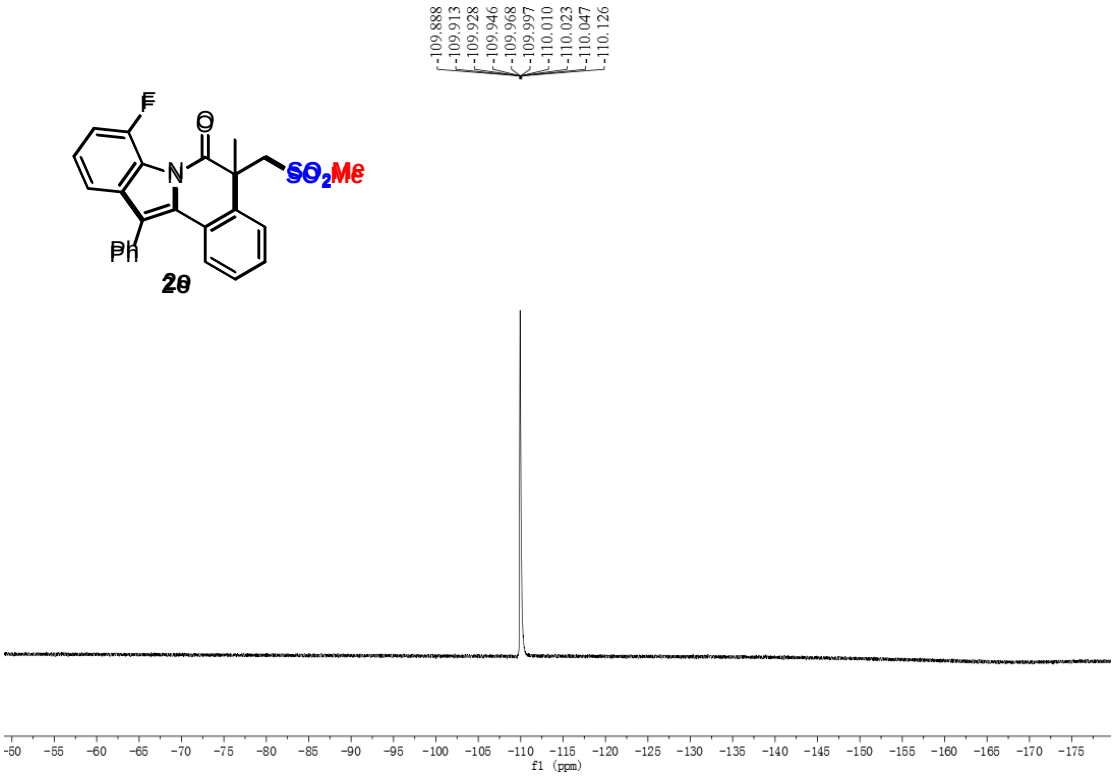
$^{1}$H NMR for **2o** (400 MHz, $CDCl_3$)



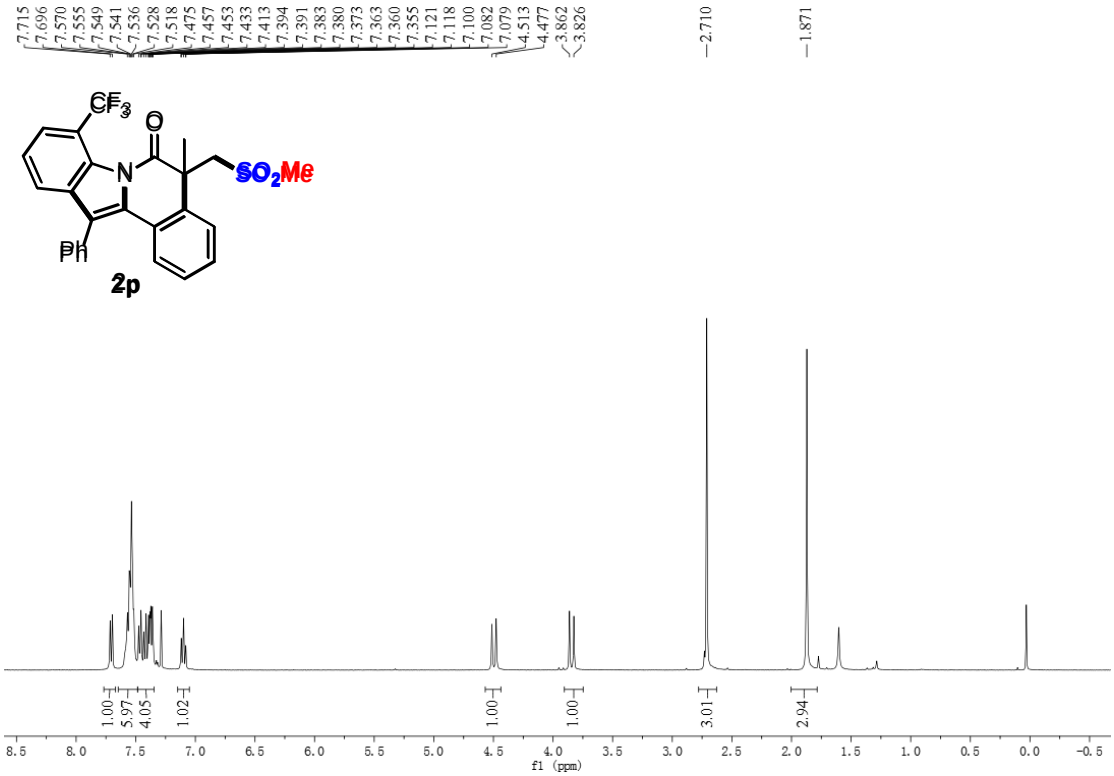

$^{13}$C NMR for **2o** (101 MHz, $CDCl_3$)



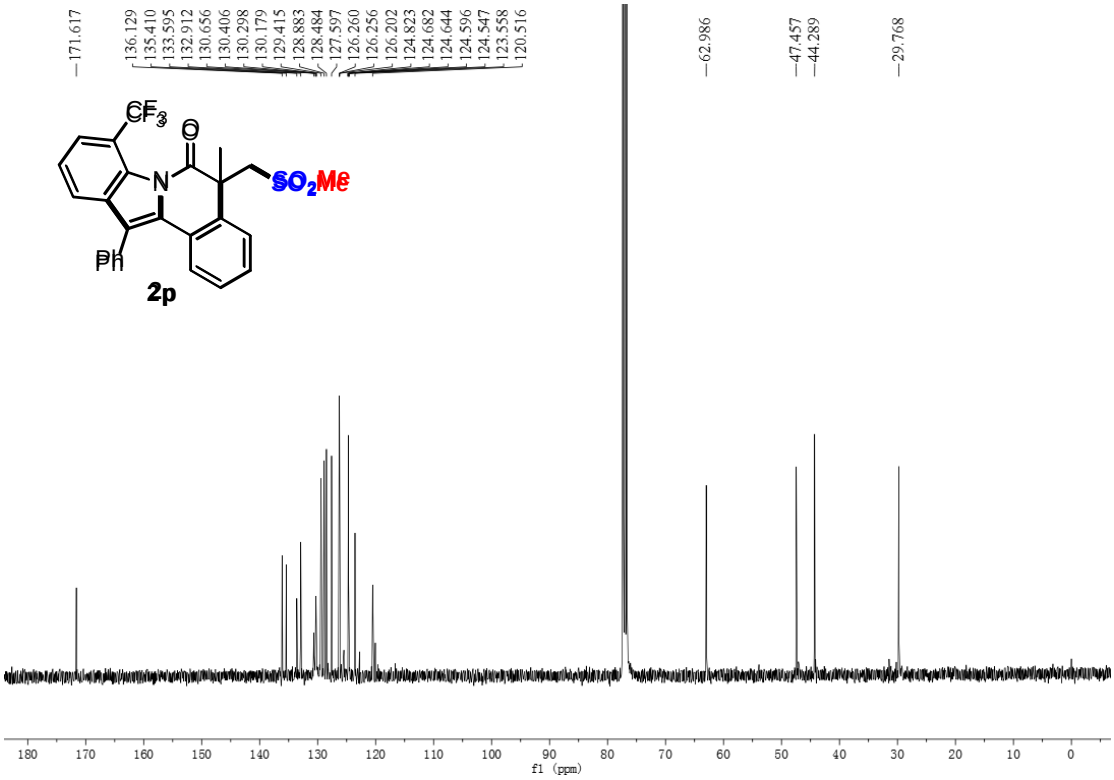
$^{19}$F NMR for **2o** (376 MHz, $CDCl_3$)



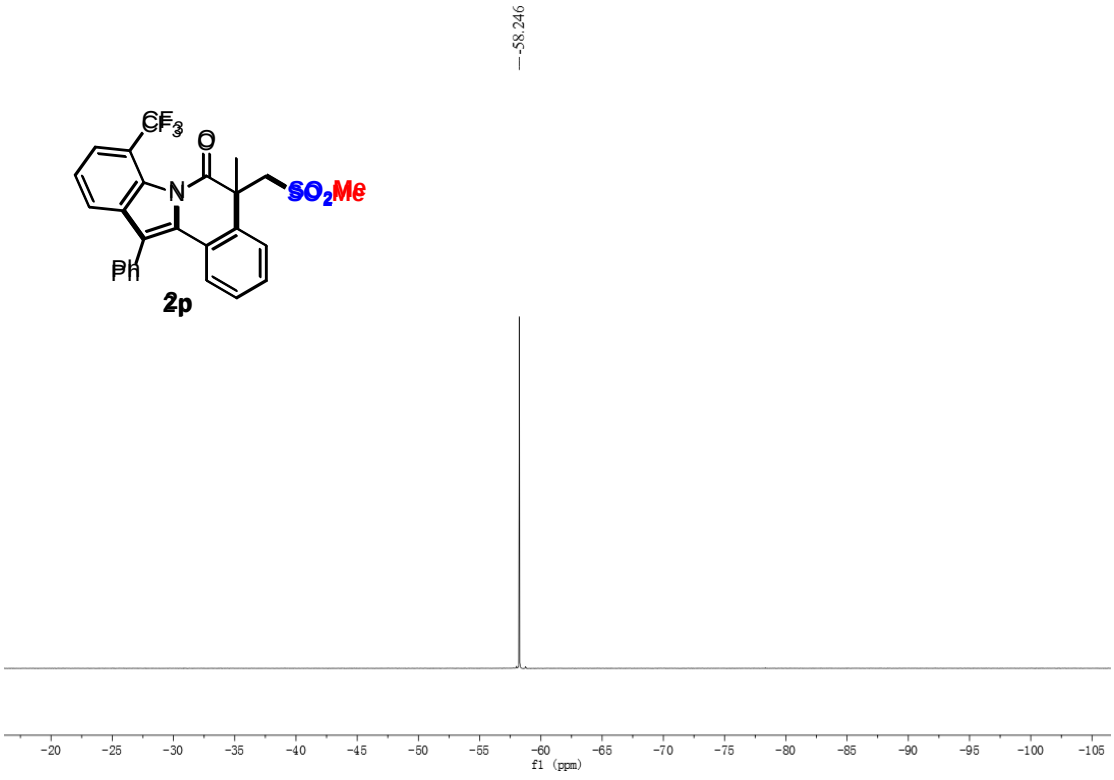

$^{1}$H NMR for **2p** (400 MHz, $CDCl_3$)



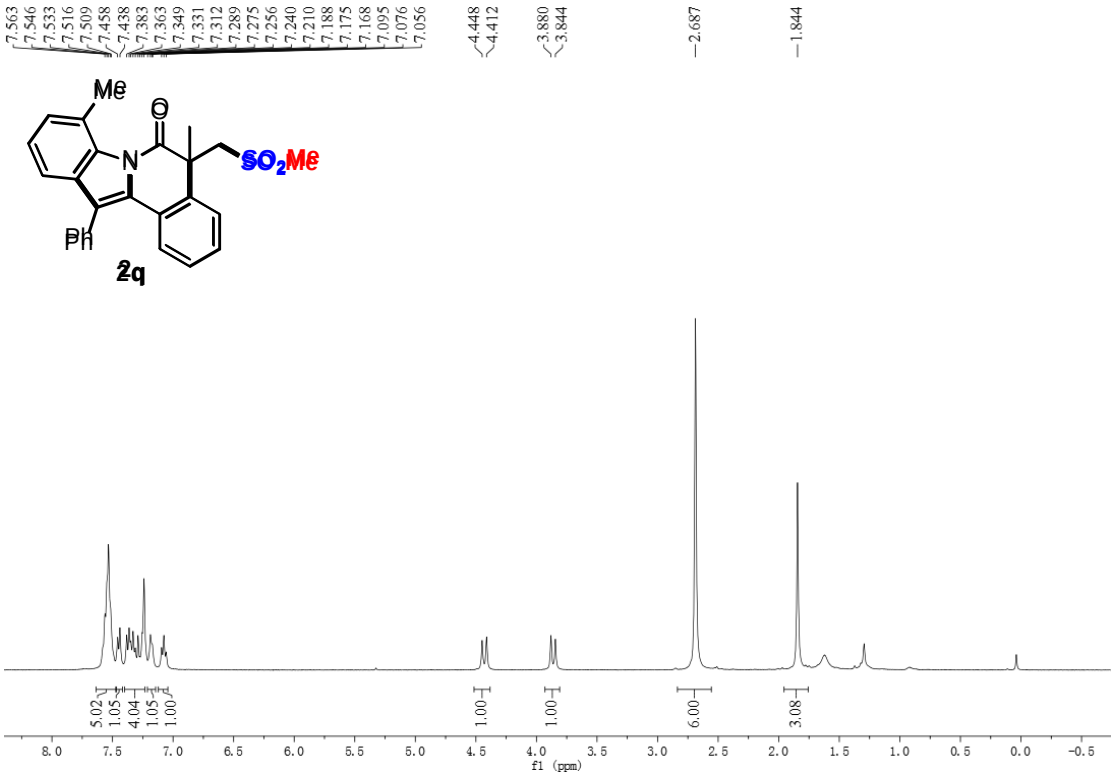
$^{13}$C NMR for **2P** (101 MHz, $CDCl_3$)



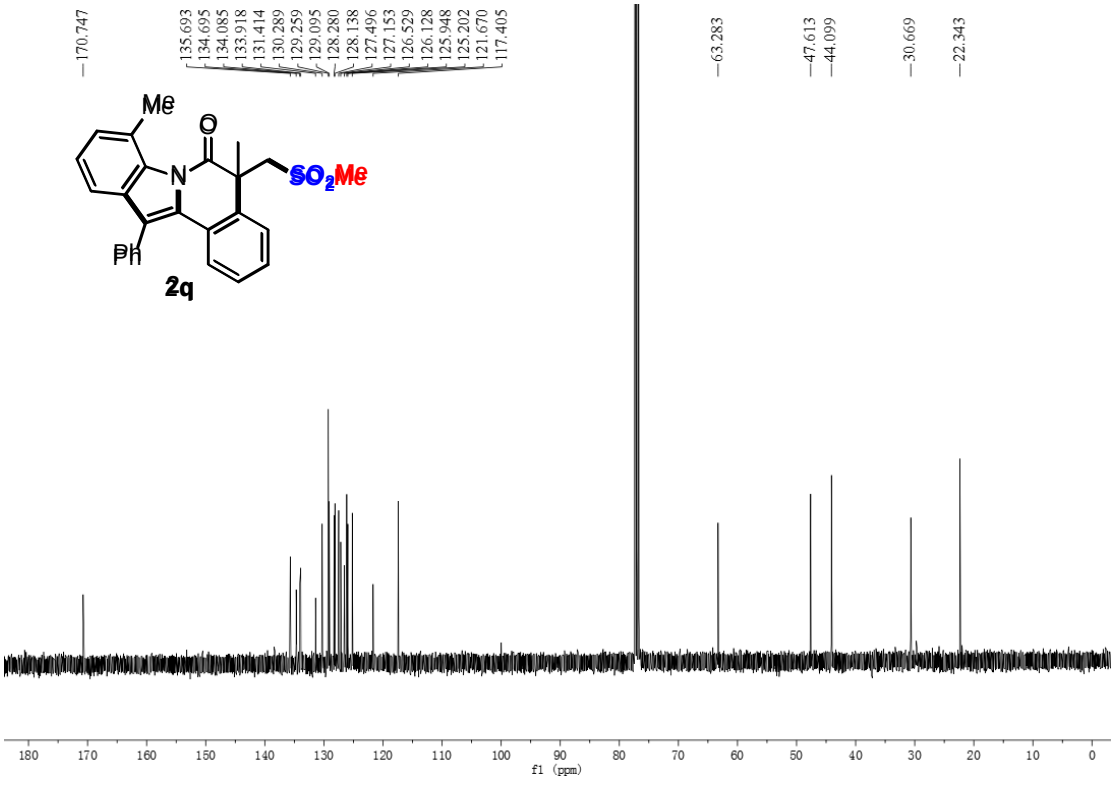

$^{19}$F NMR for **2p** (376 MHz, $CDCl_3$)



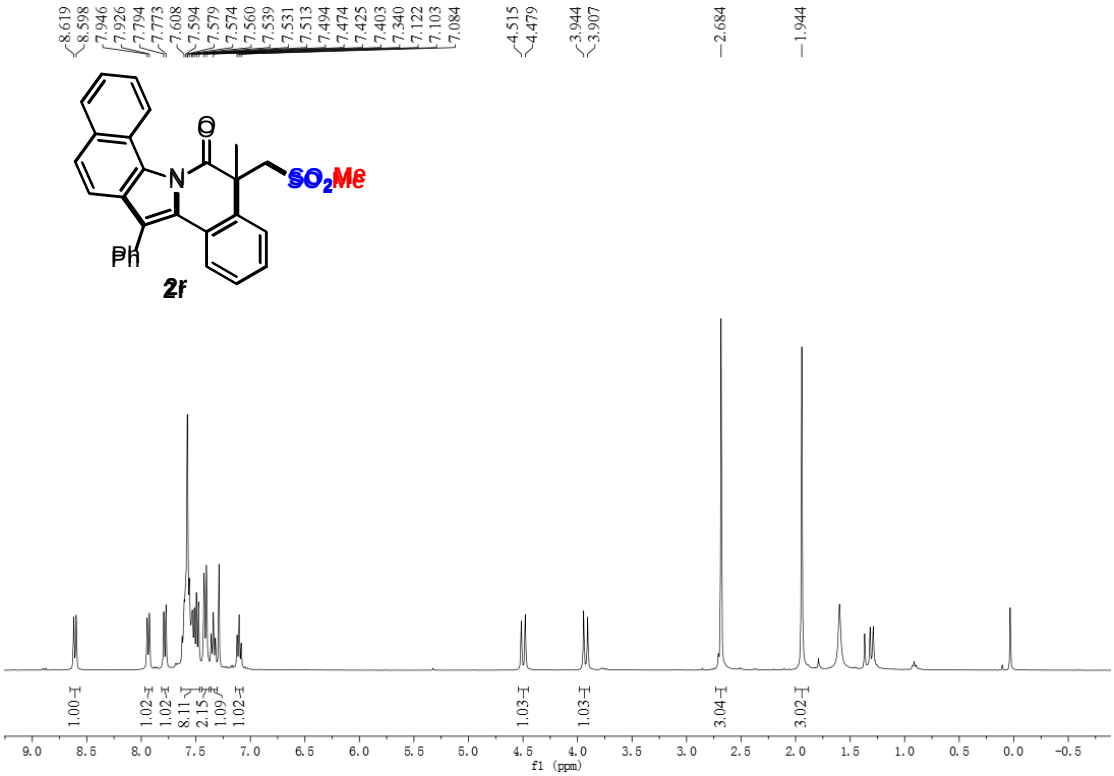
$^{1}$H NMR for **2q** (400 MHz, $CDCl_3$)



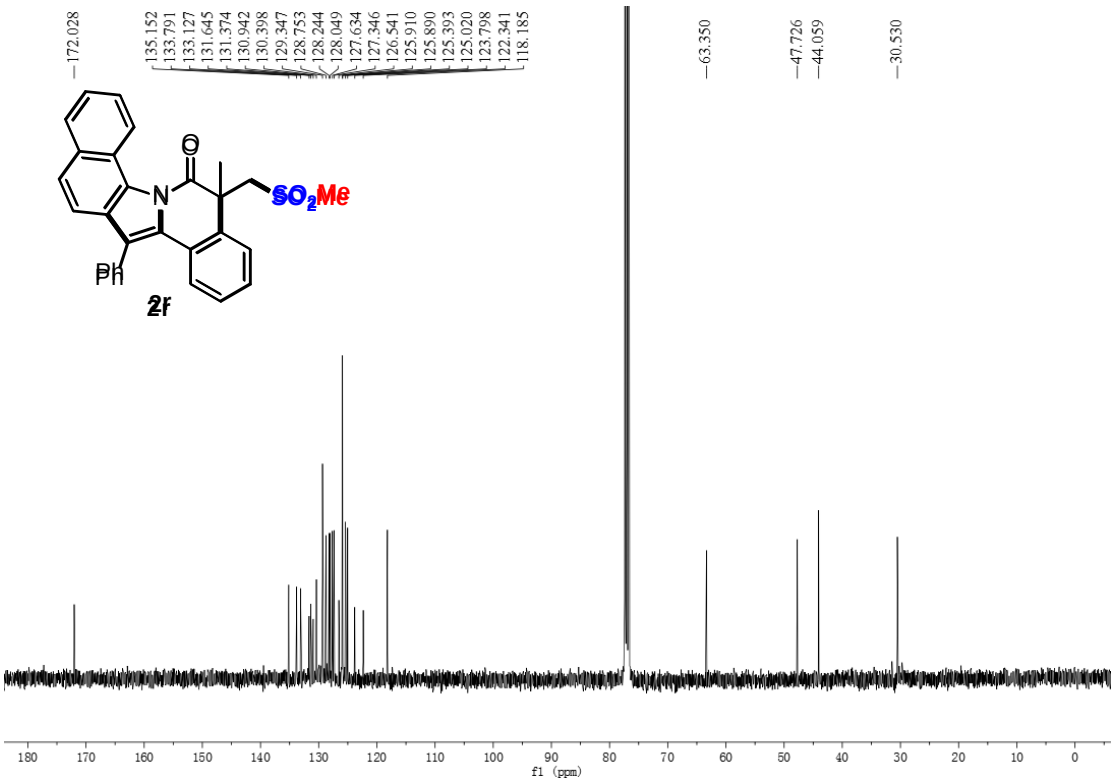

$^{13}$C NMR for **2q** (101 MHz, $CDCl_3$)



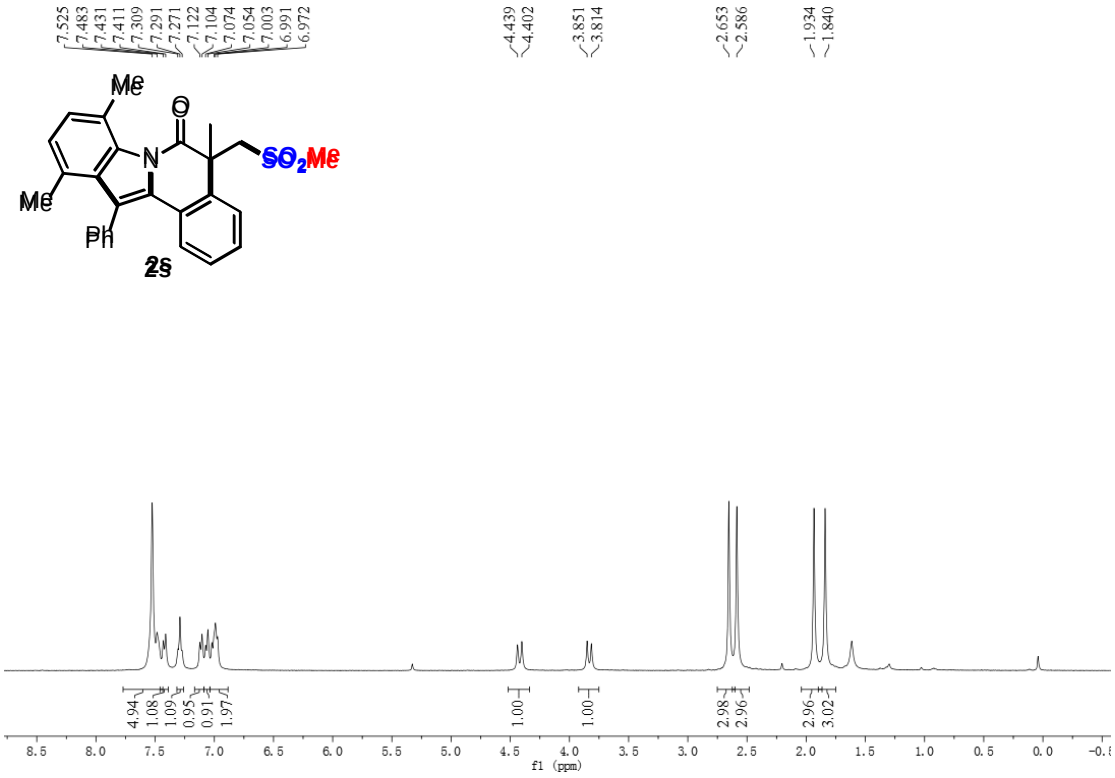
$^{1}$H NMR for **2r** (400 MHz, $CDCl_3$)



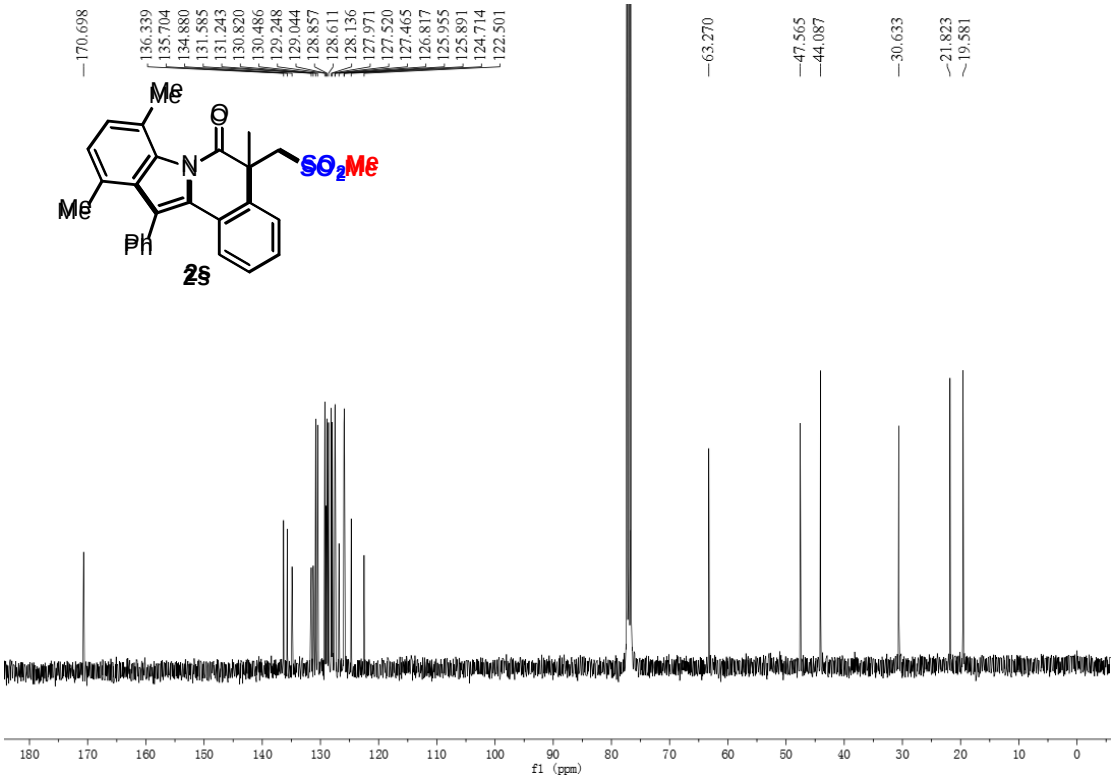

$^{13}$C NMR for **2r** (101 MHz, $CDCl_3$)



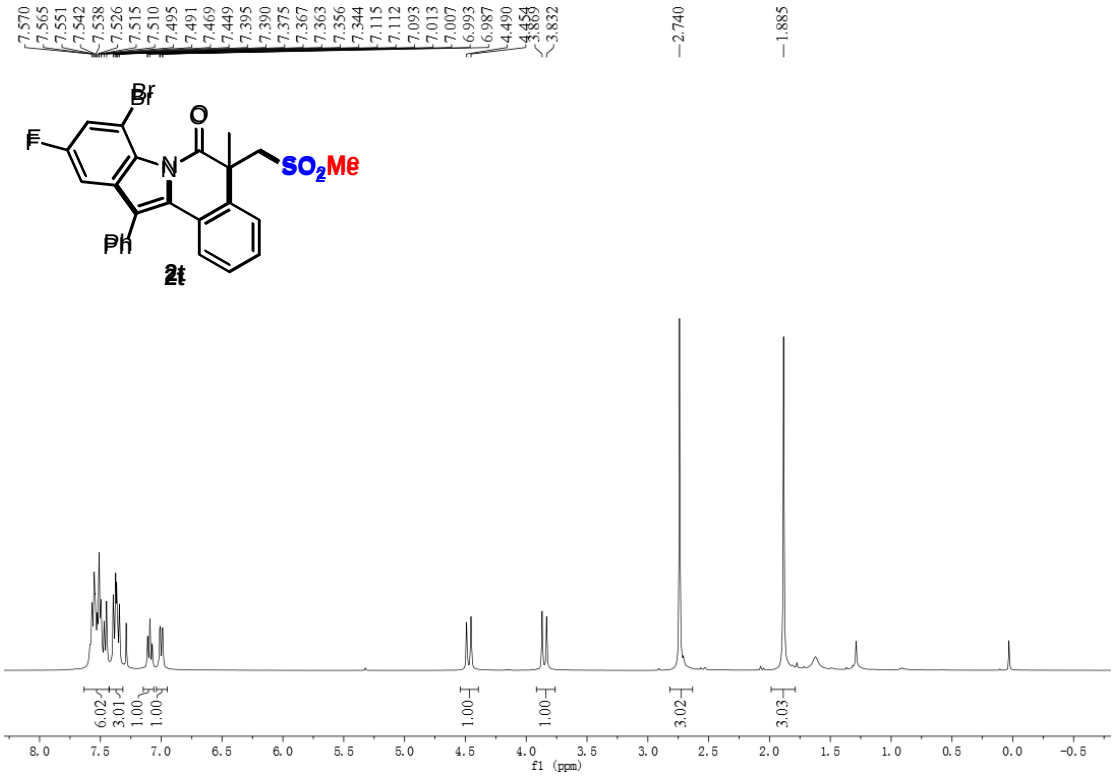
$^{1}$H NMR for **2s** (400 MHz, $CDCl_3$)



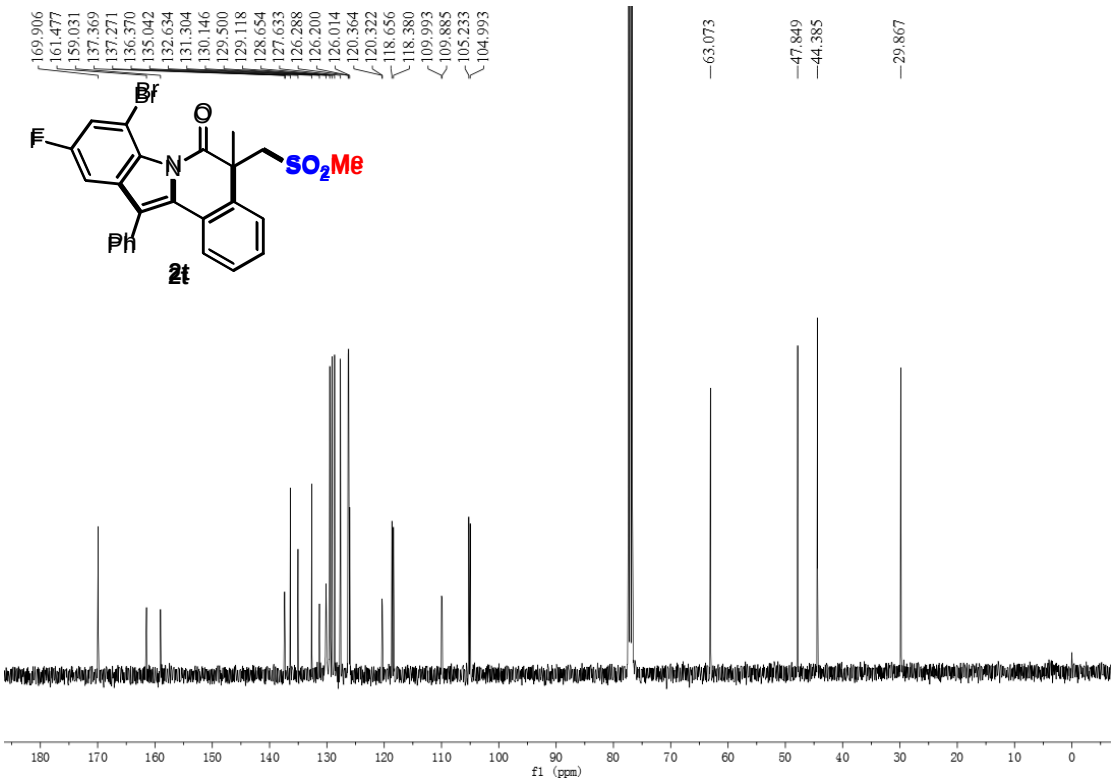

$^{13}$C NMR for **2s** (101 MHz, $CDCl_3$)



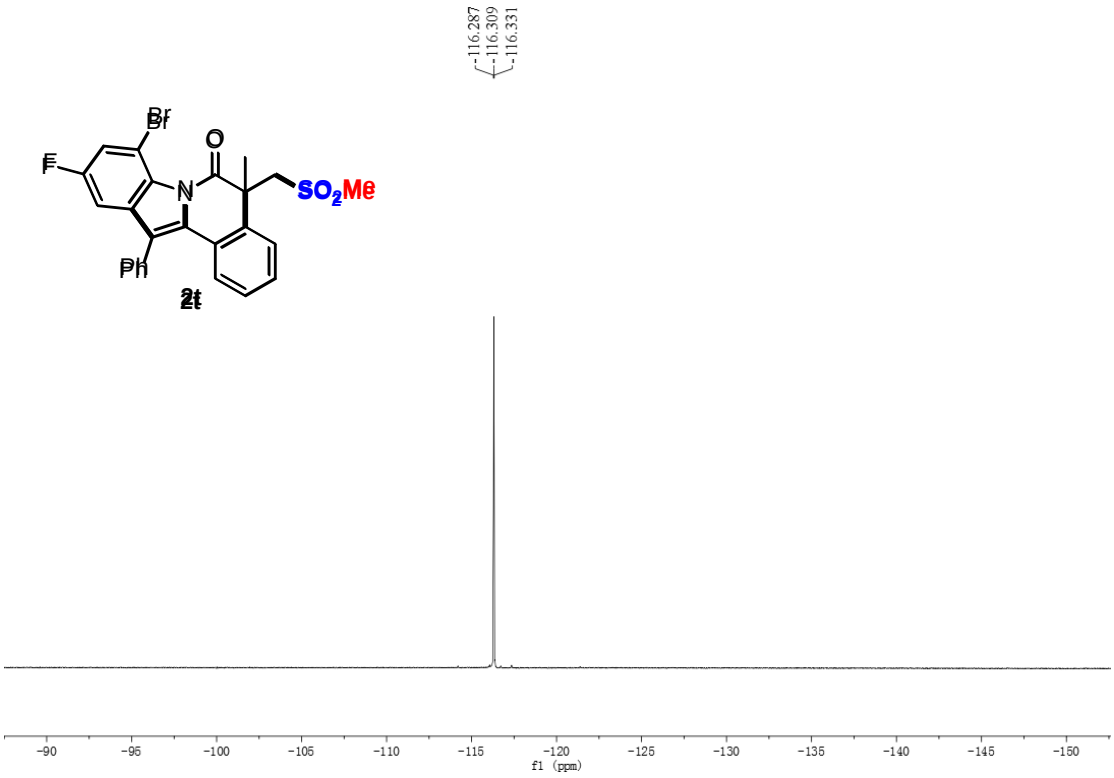
$^{1}$H NMR for **2t** (400 MHz, $CDCl_3$)



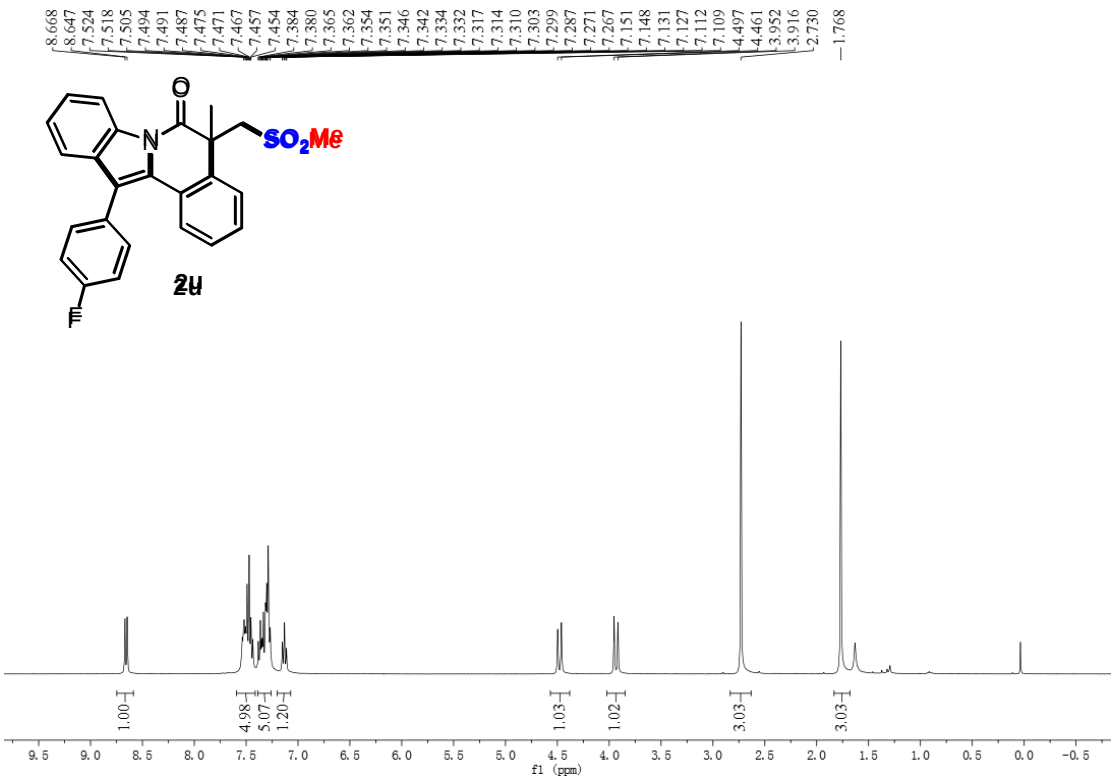

$^{13}$C NMR for **2t** (101 MHz, $CDCl_3$)



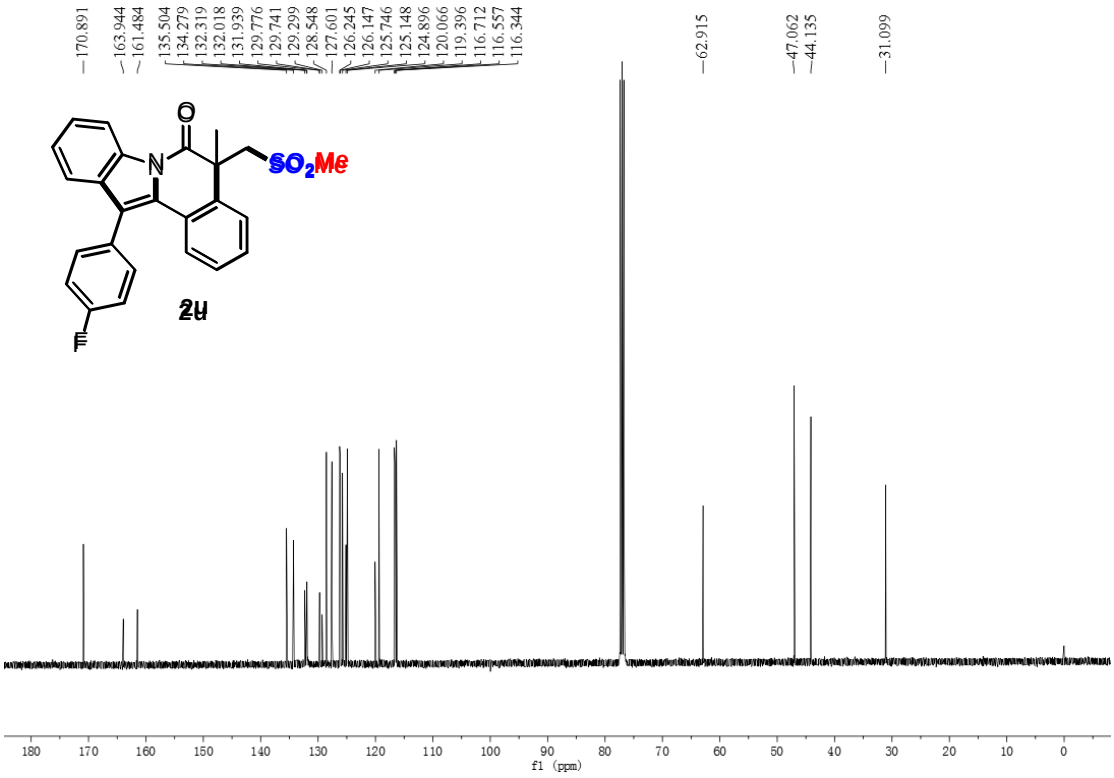
$^{19}$F NMR for **2t** (376 MHz, $CDCl_3$)



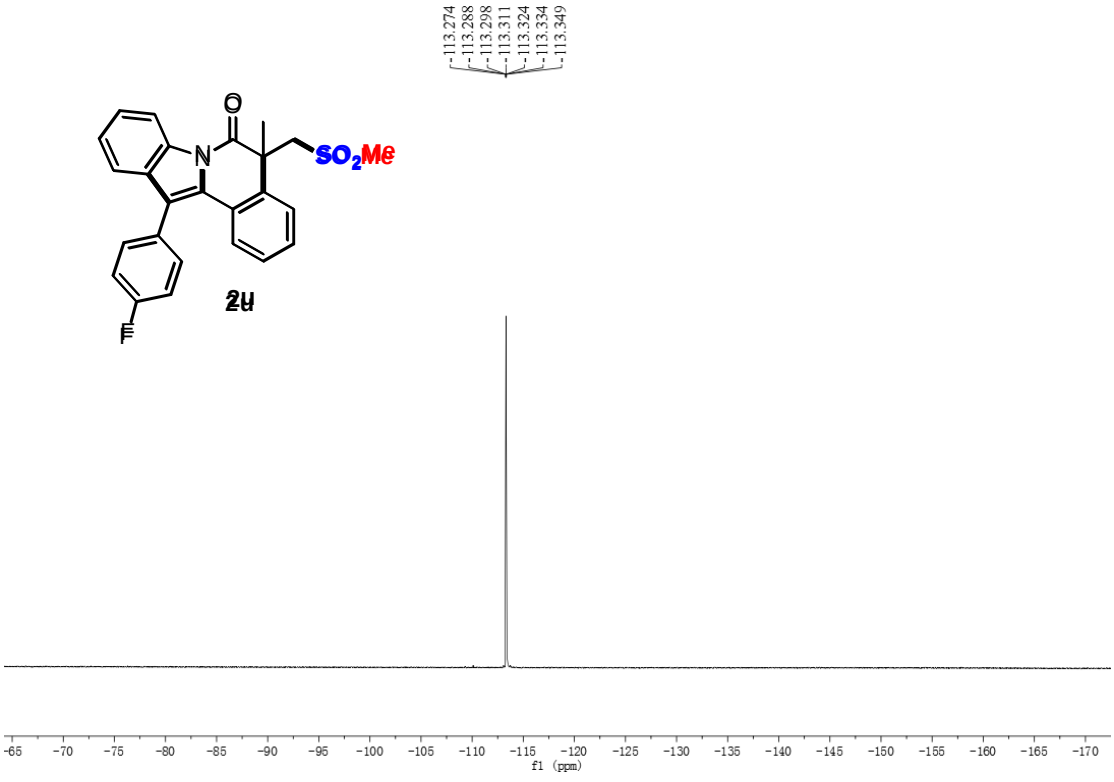

$^{1}$H NMR for **2u** (400 MHz, $CDCl_3$)



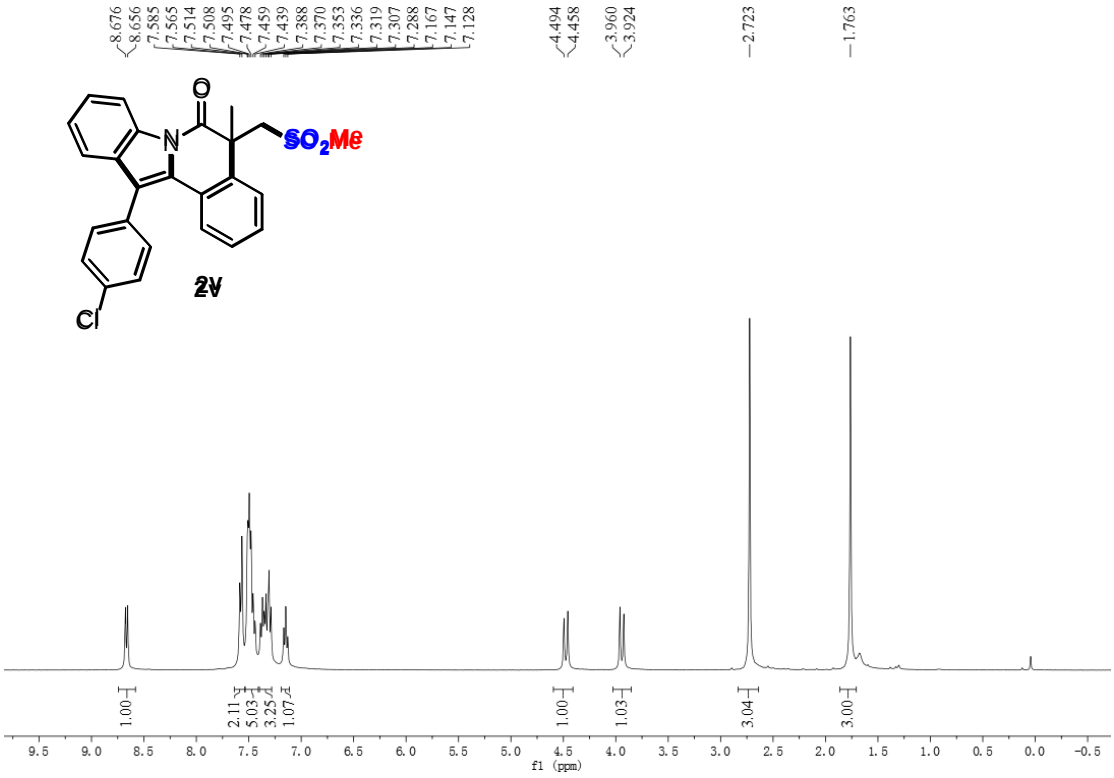
$^{13}$C NMR for **2u** (101 MHz, $CDCl_3$)



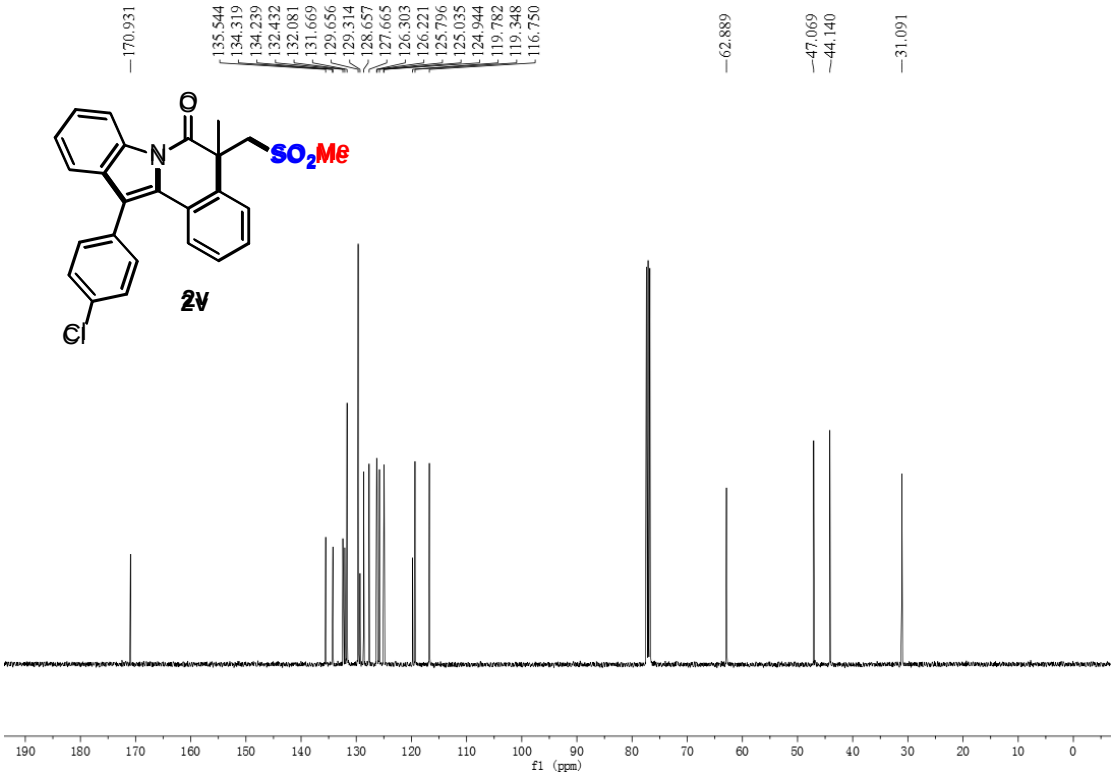

$^{19}$F NMR for **2u** (376 MHz, $CDCl_3$)



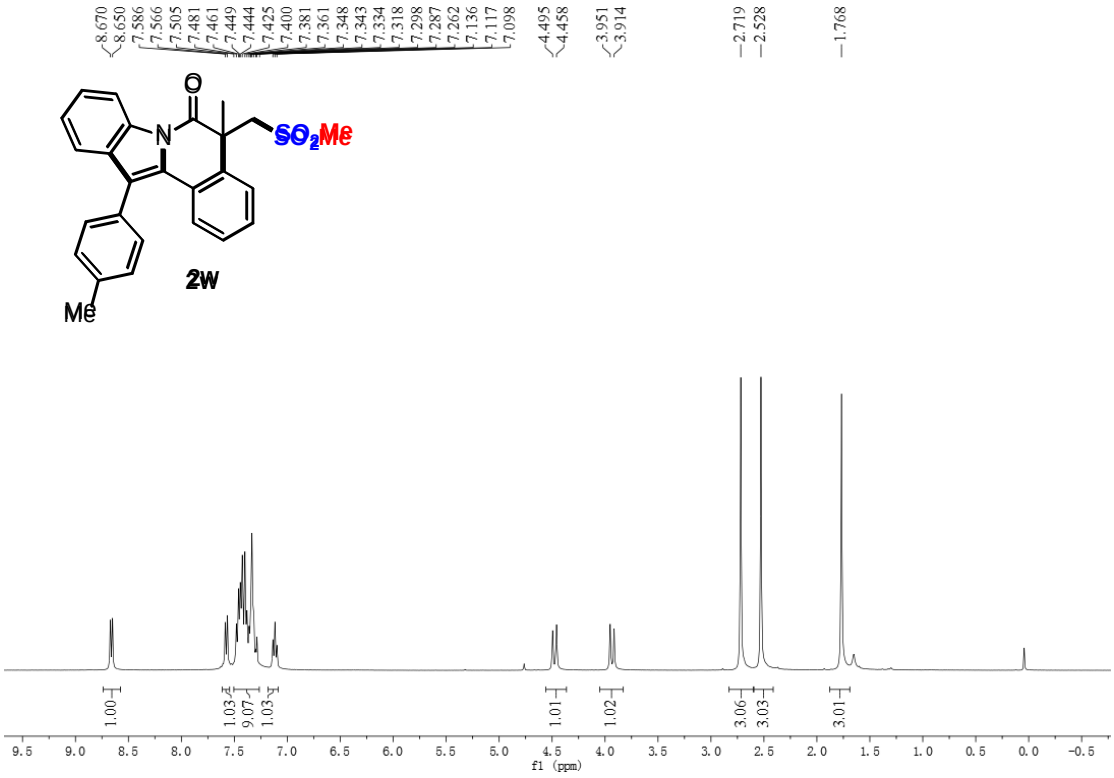
$^{1}$H NMR for **2v** (400 MHz, $CDCl_3$)



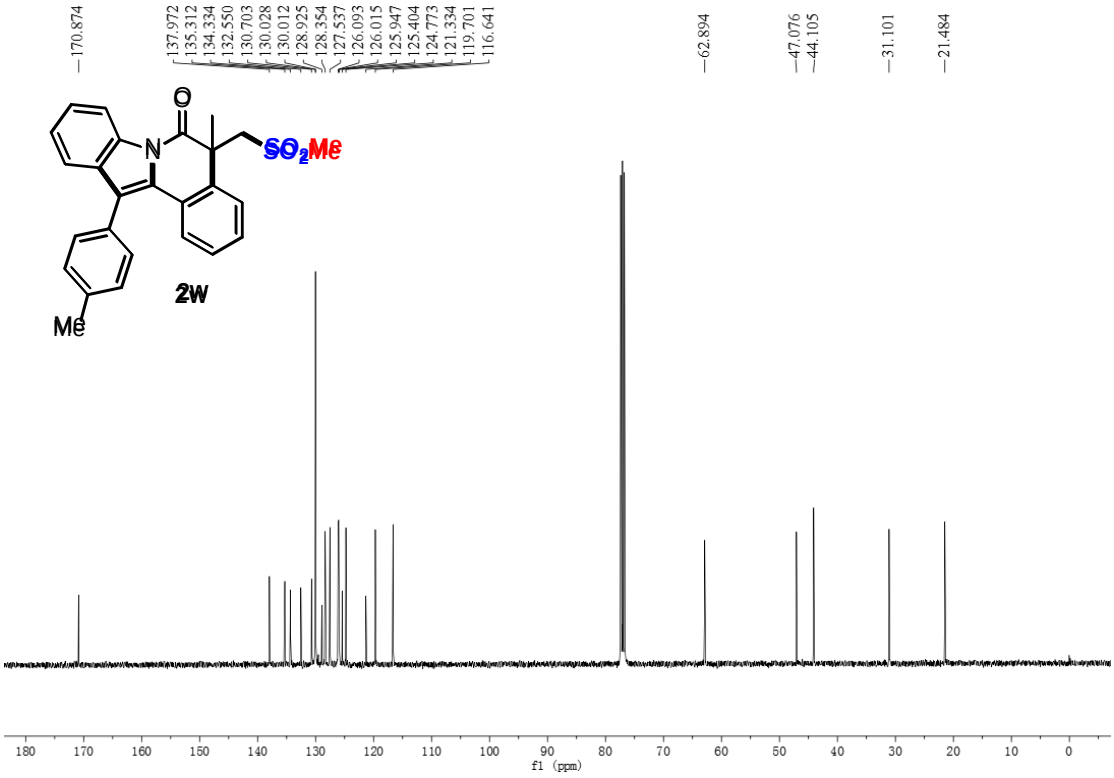

$^{13}$C NMR for **2v** (101 MHz, $CDCl_3$)



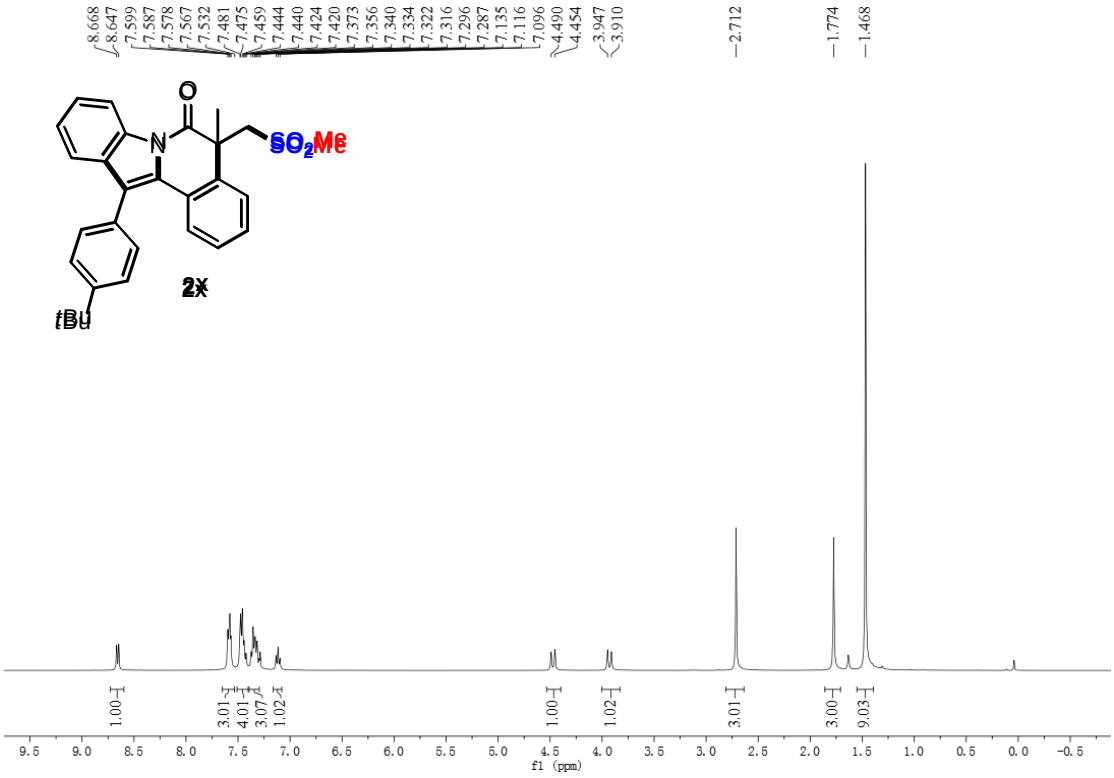
$^{1}$H NMR for **2w** (400 MHz, $CDCl_3$)



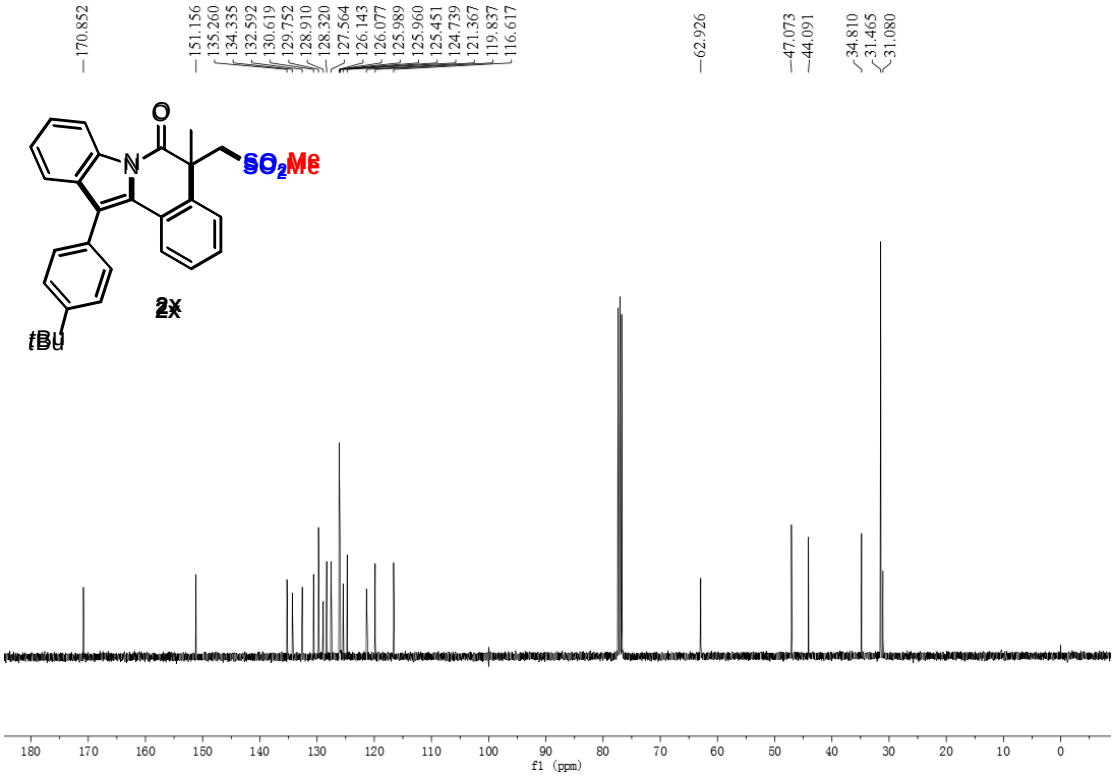

$^{13}$C NMR for **2w** (101 MHz, $CDCl_3$)



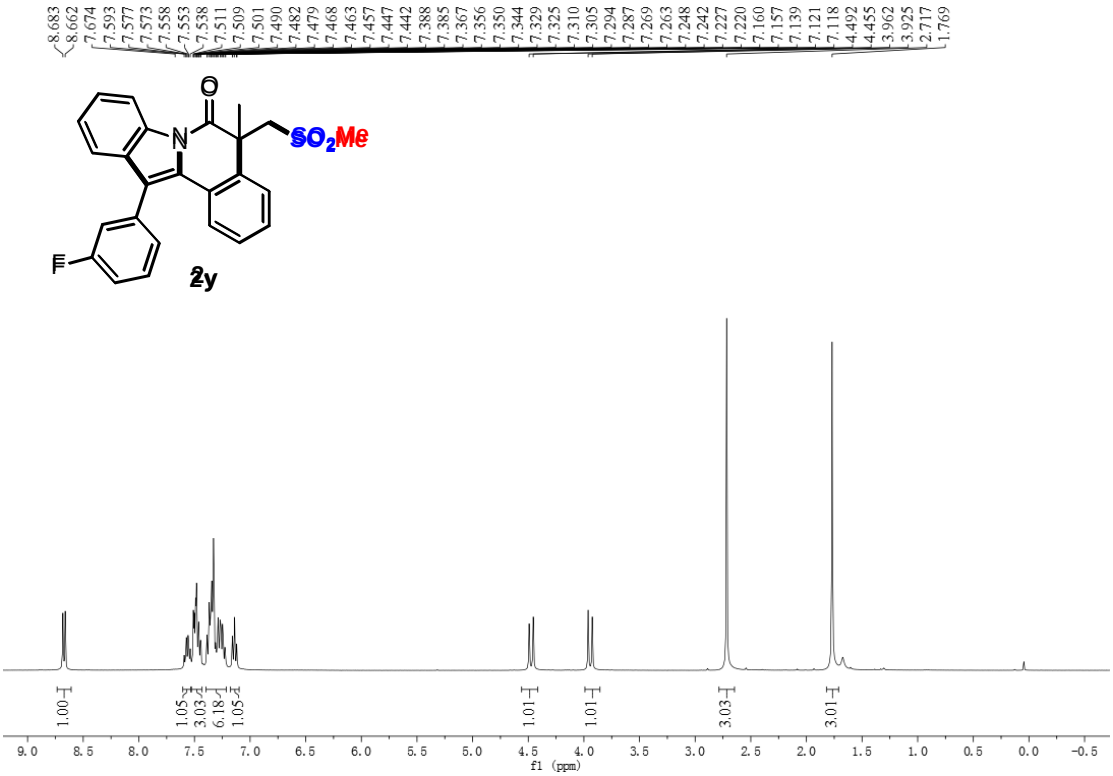
$^{1}$H NMR for **2x** (400 MHz, $CDCl_3$)



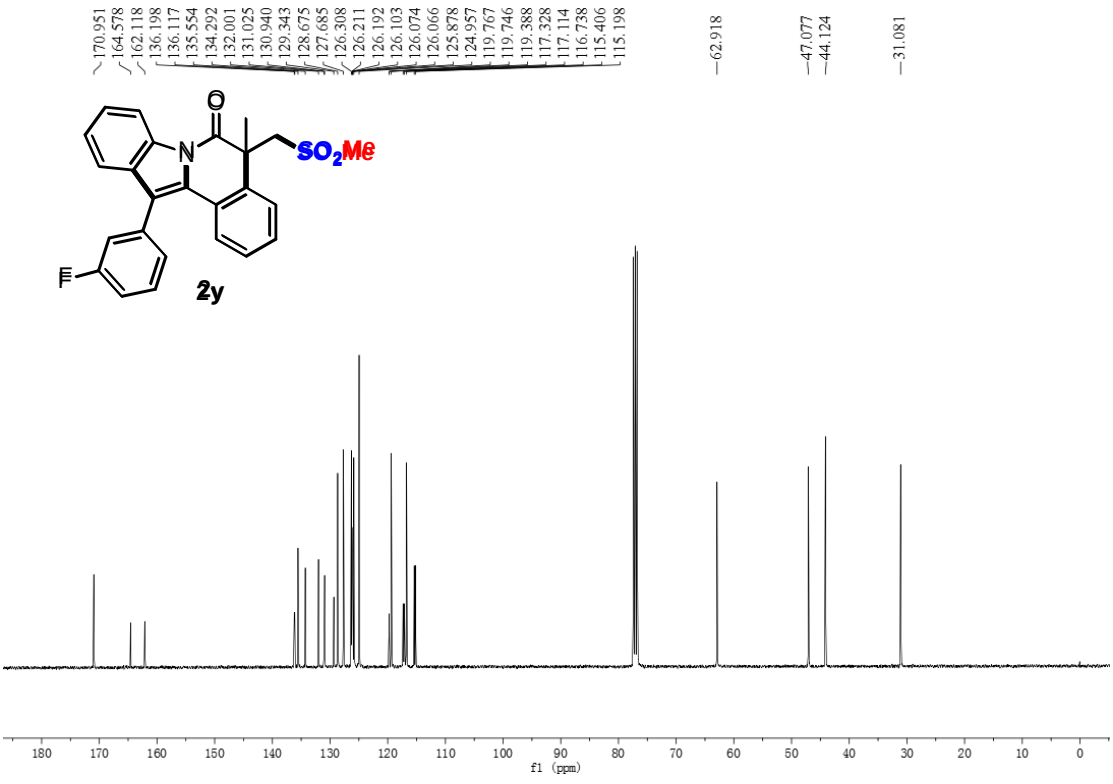

$^{13}$C NMR for **2x** (101 MHz, $CDCl_3$)



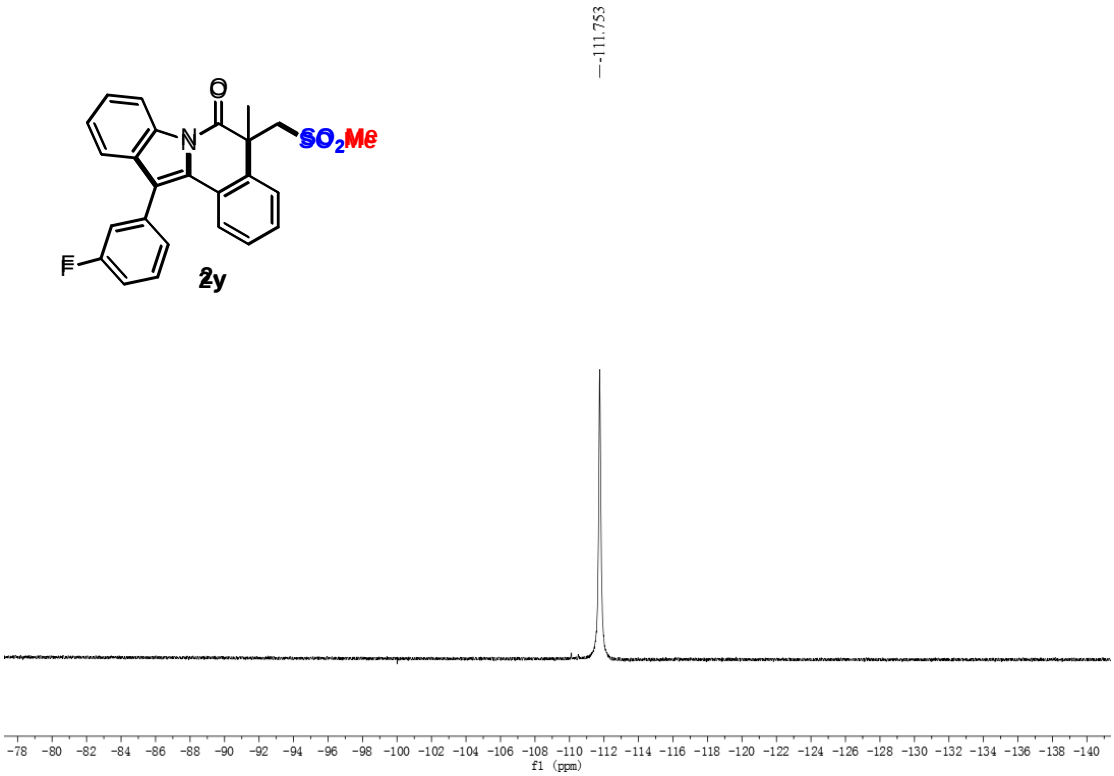
$^{1}$H NMR for **2y** (400 MHz, $CDCl_3$)



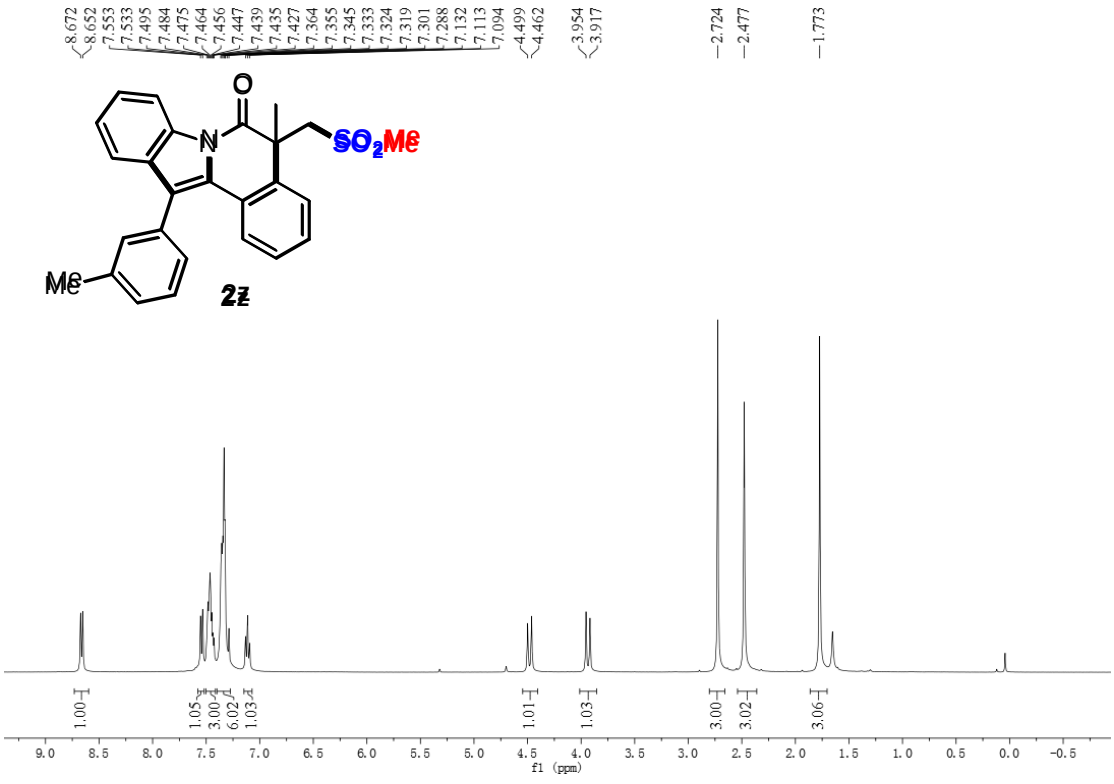

$^{13}$C NMR for **2y** (101 MHz, $CDCl_3$)



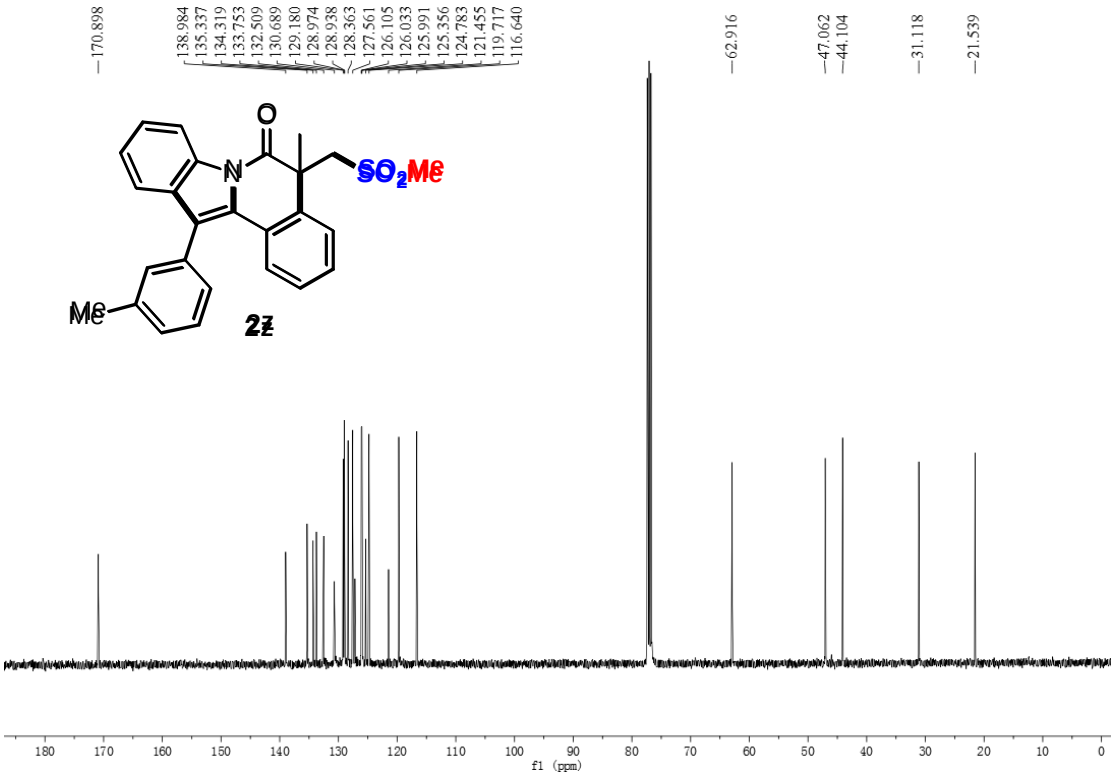
$^{19}$F NMR for **2y** (376 MHz, $CDCl_3$)



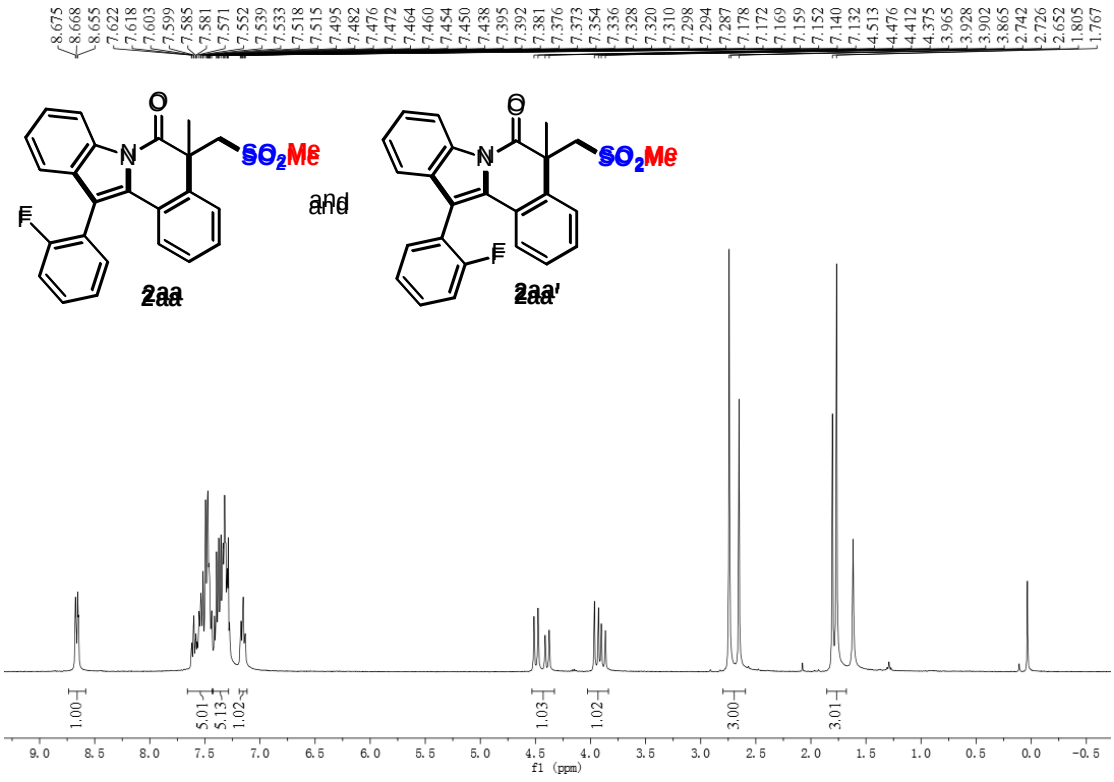

$^{1}$H NMR for **2z** (400 MHz, $CDCl_3$)



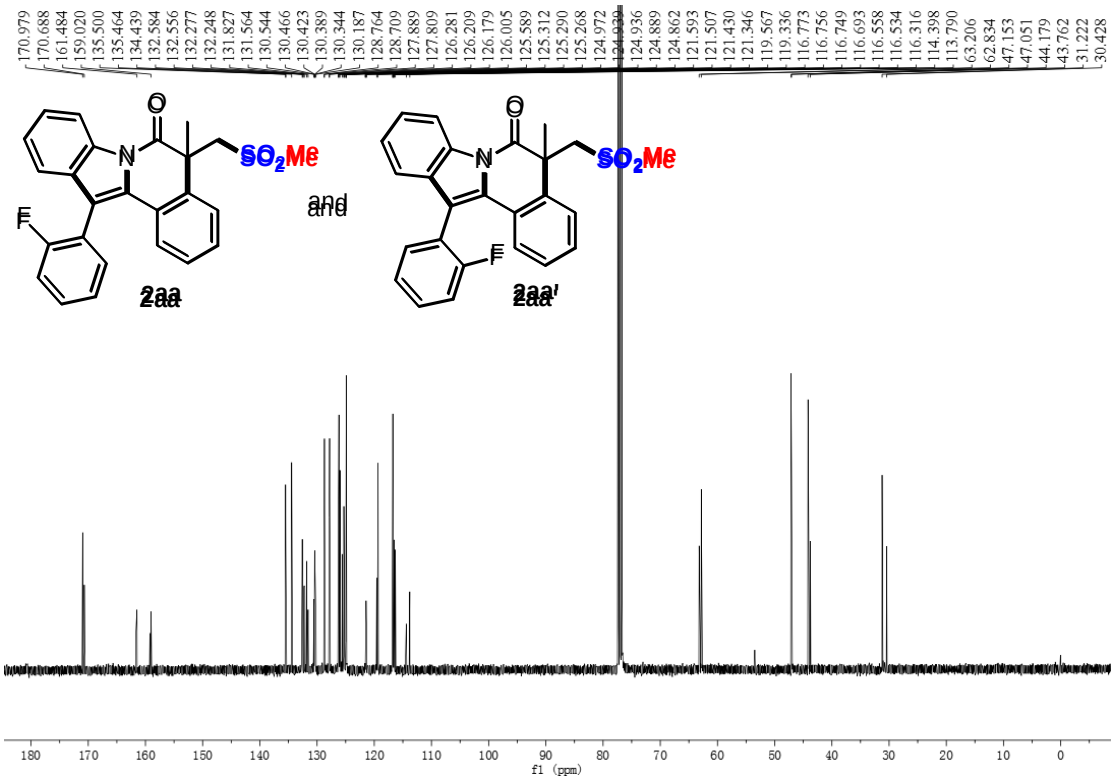
$^{13}$C NMR for **2z** (101 MHz, $CDCl_3$)



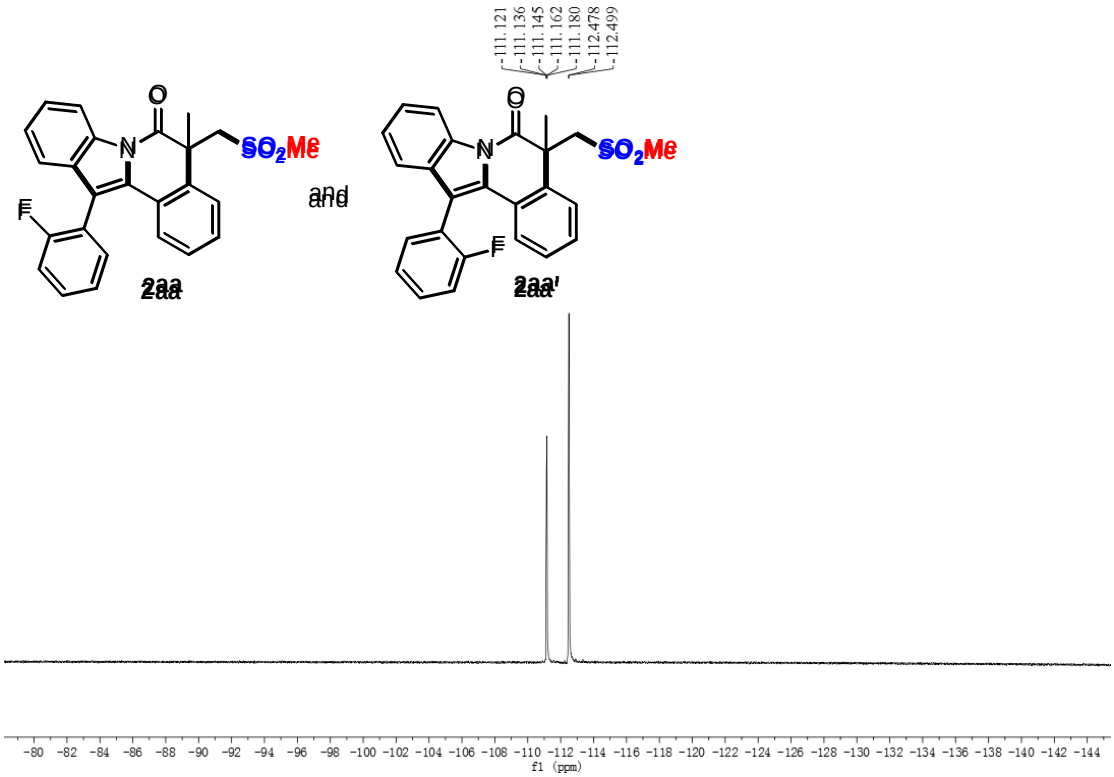

$^{1}$H NMR for **2aa** (400 MHz, $CDCl_3$)



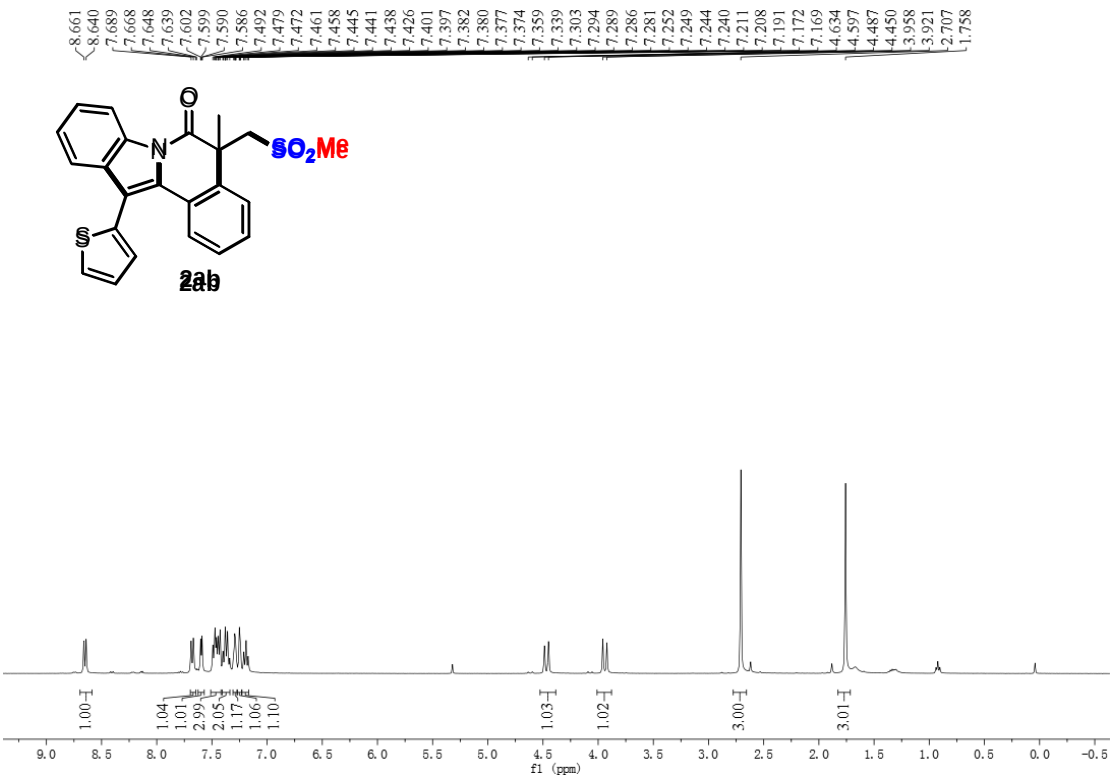
$^{13}C$ NMR for **2aa** (101 MHz, $CDCl_3$)



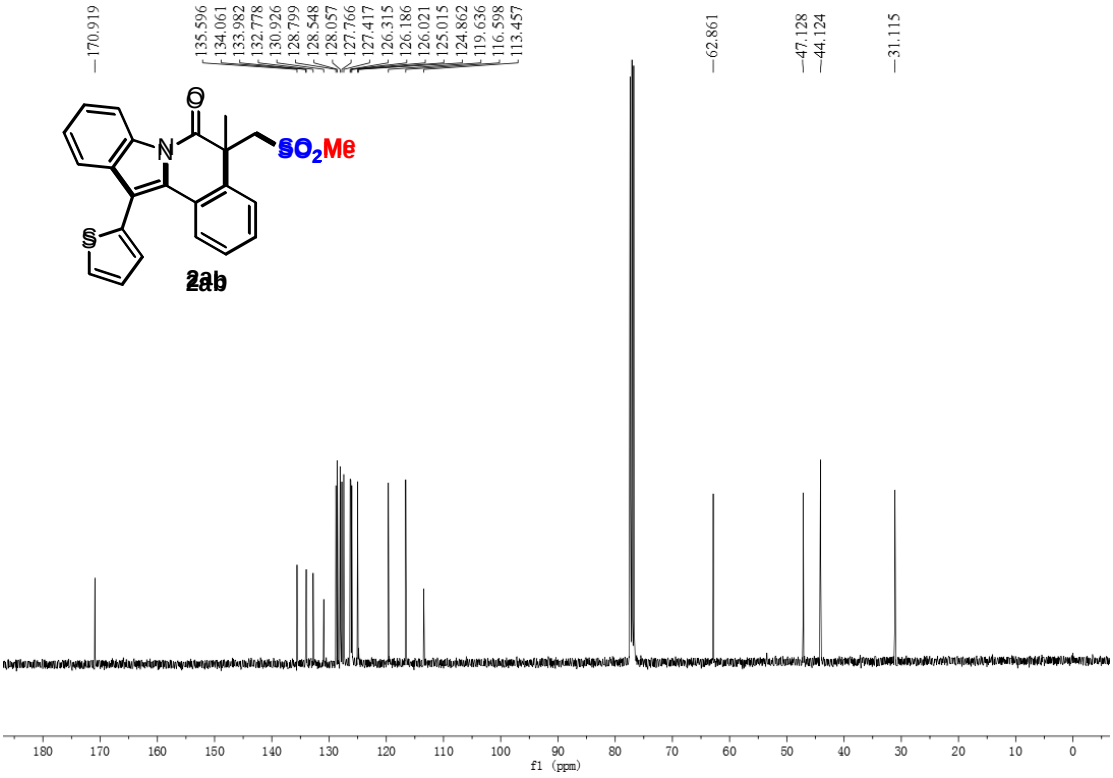

$^{19}F$ NMR for **2aa** (375 MHz, $CDCl_3$)



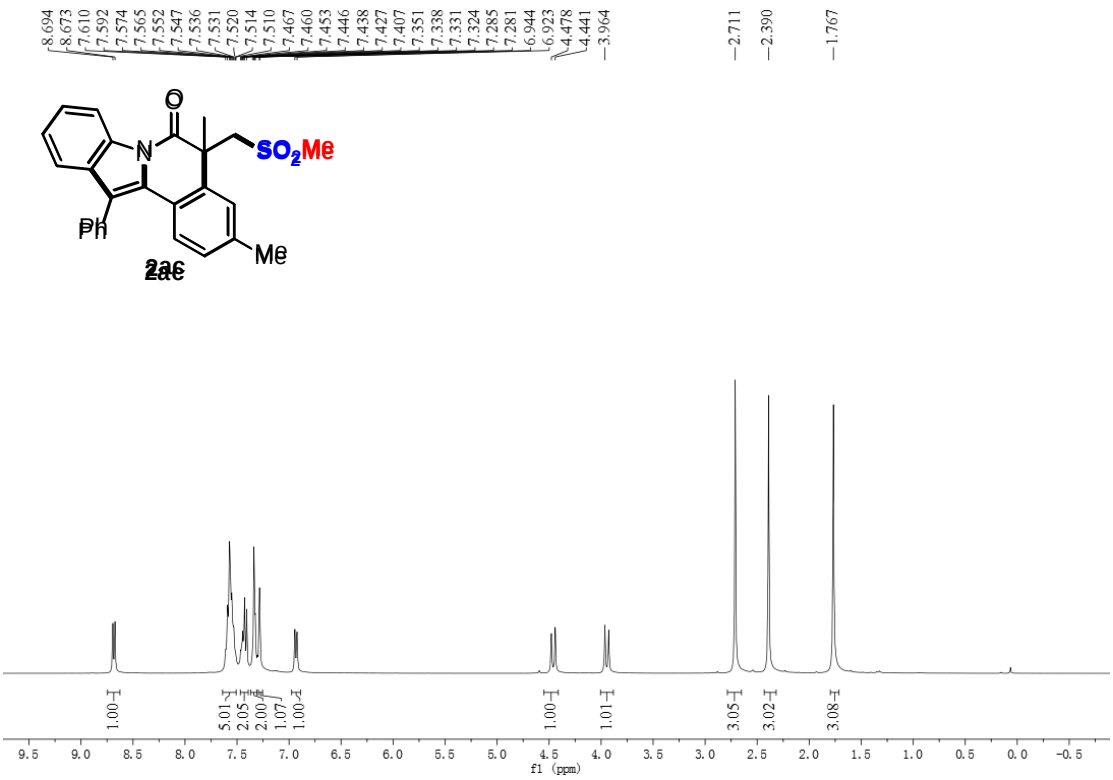
$^{1}$H NMR for **2ab** (400 MHz, $CDCl_3$)



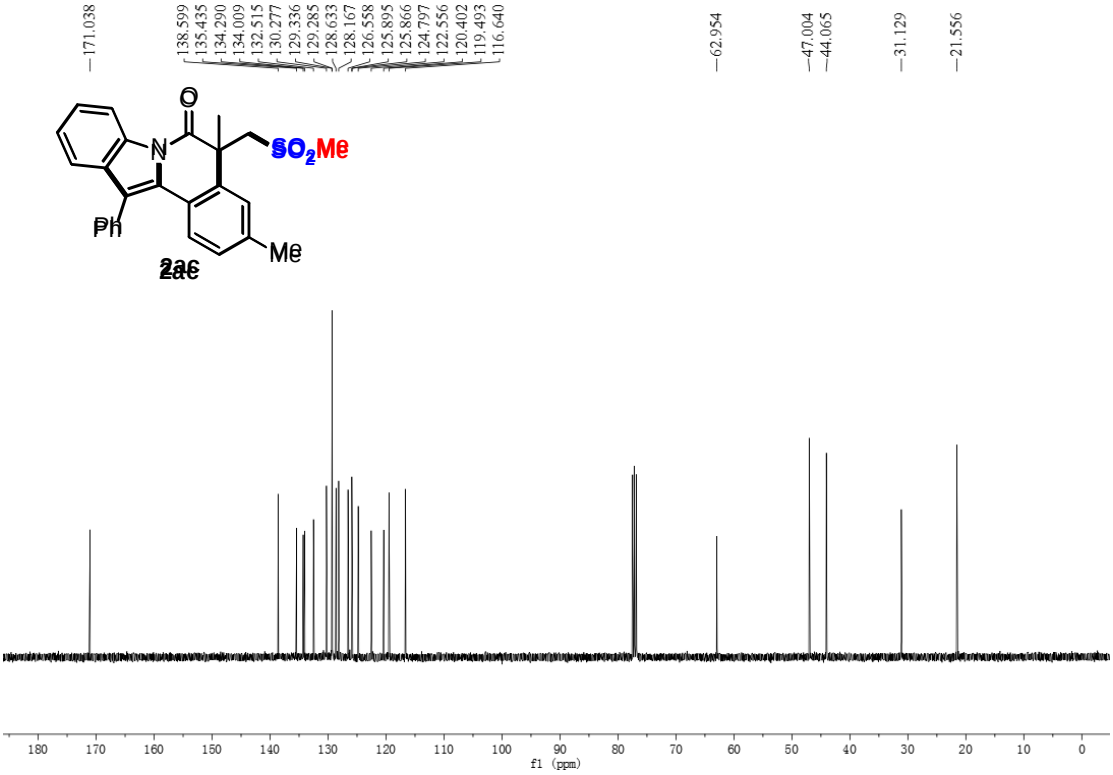

$^{13}$C NMR for **2ab** (101 MHz, $CDCl_3$)



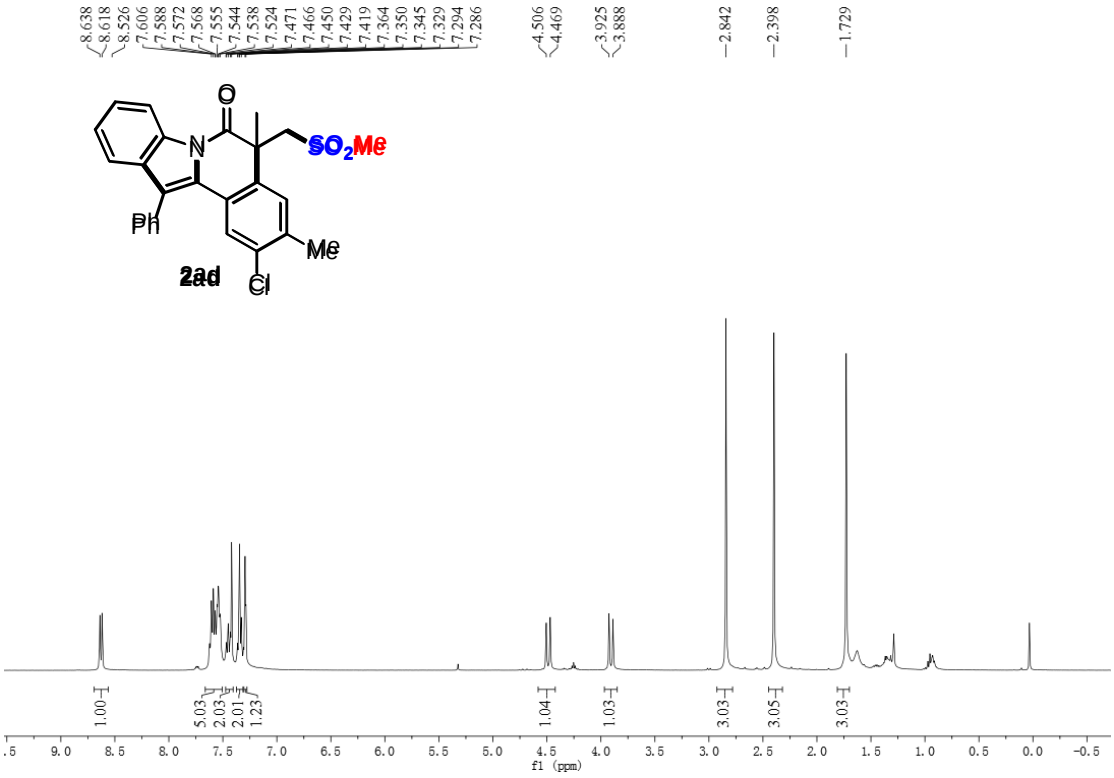
$^{1}$H NMR for **2ac** (400 MHz, $CDCl_3$)



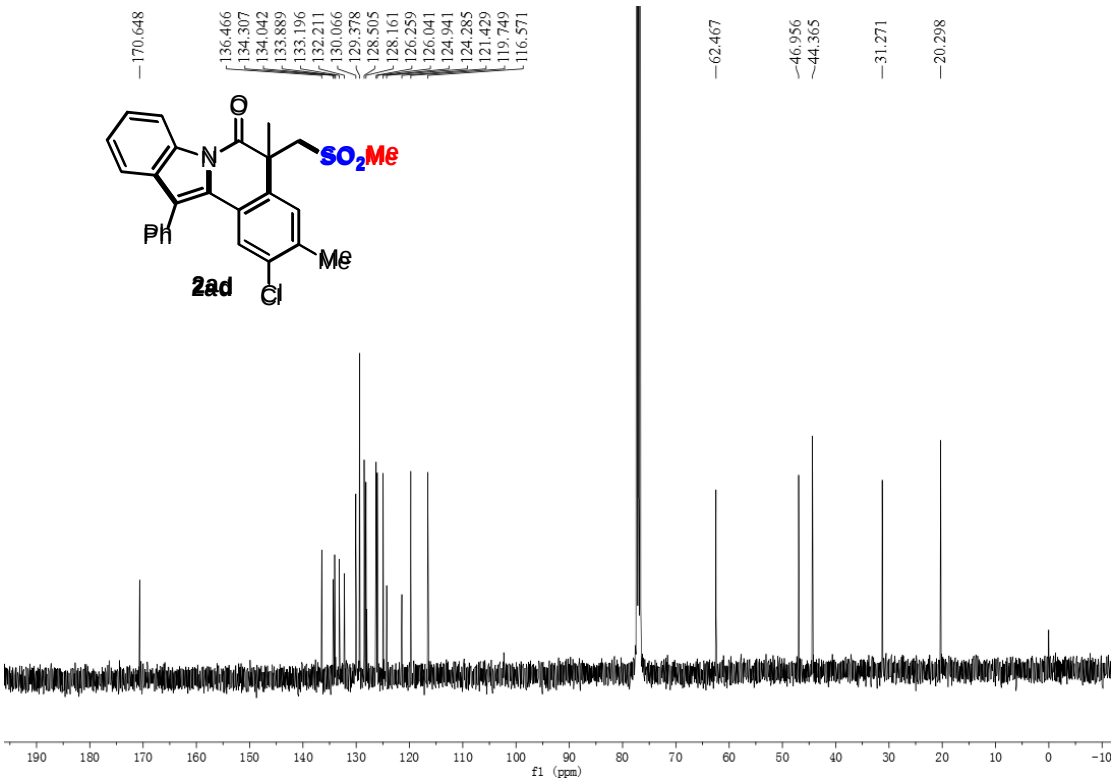

$^{13}$C NMR for **2ac** (101 MHz, $CDCl_3$)



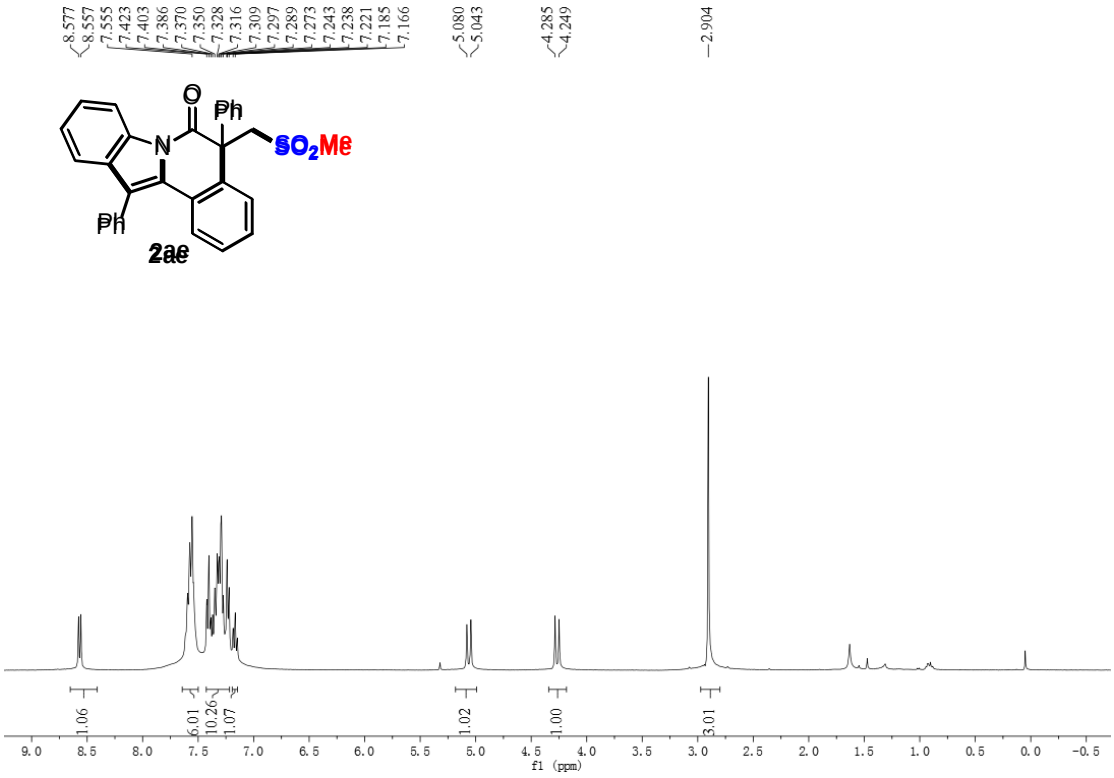
$^{1}$H NMR for **2ad** (400 MHz, $CDCl_3$)



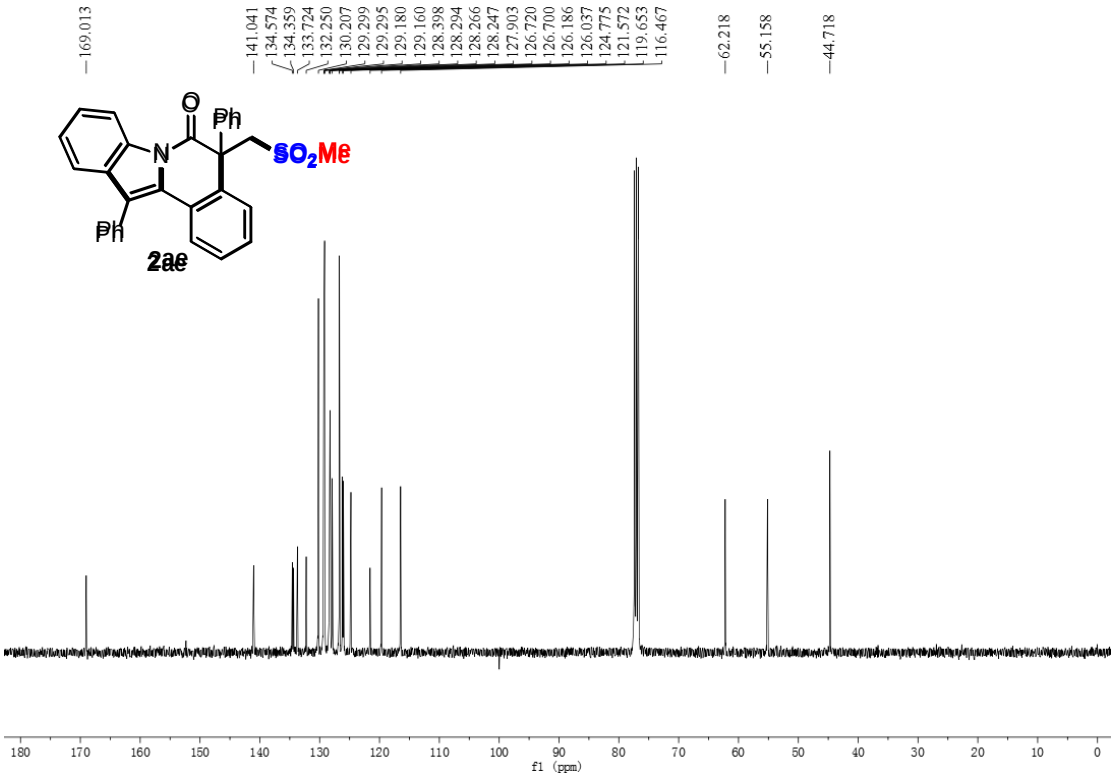

$^{13}$C NMR for **2ad** (101 MHz, $CDCl_3$)



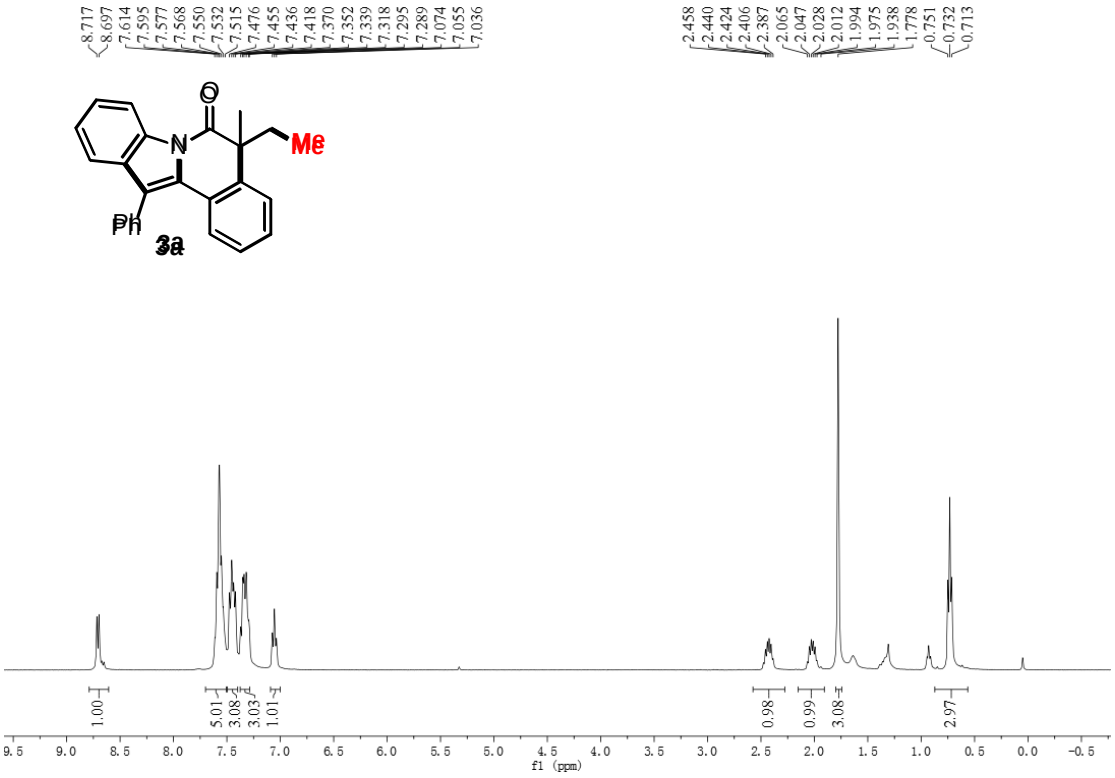
$^{1}$H NMR for **2ae** (400 MHz, $CDCl_3$)



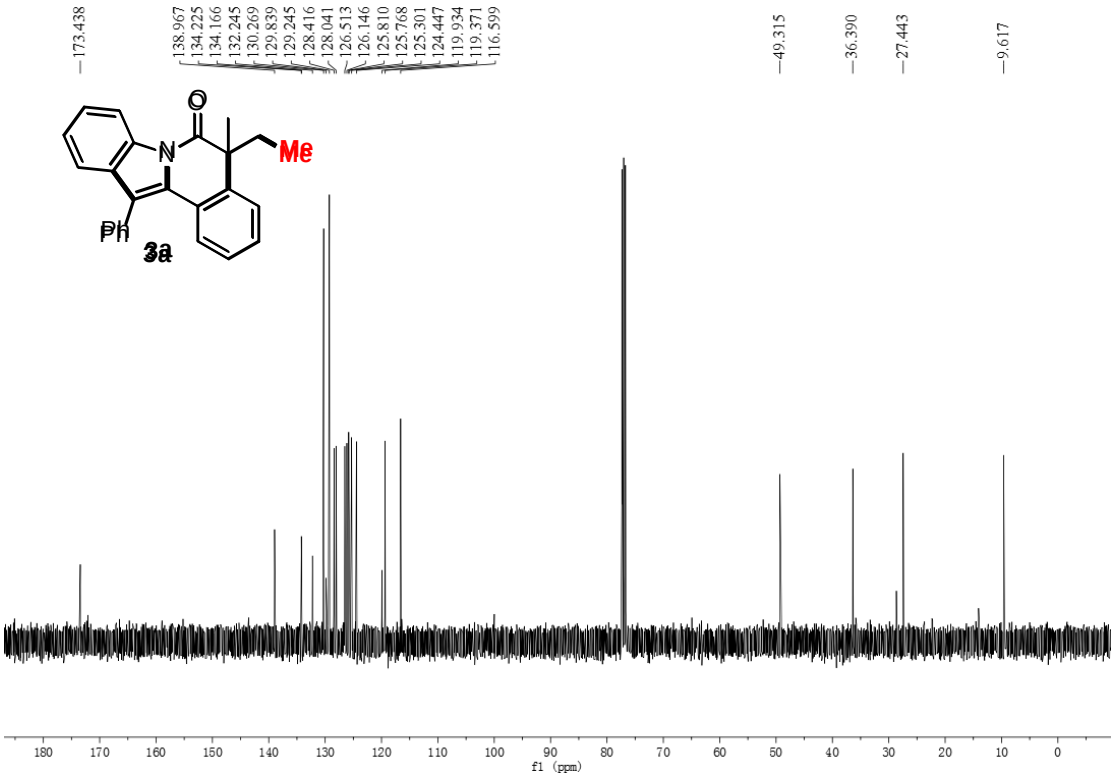

$^{13}$C NMR for **2ae** (101 MHz, $CDCl_3$)



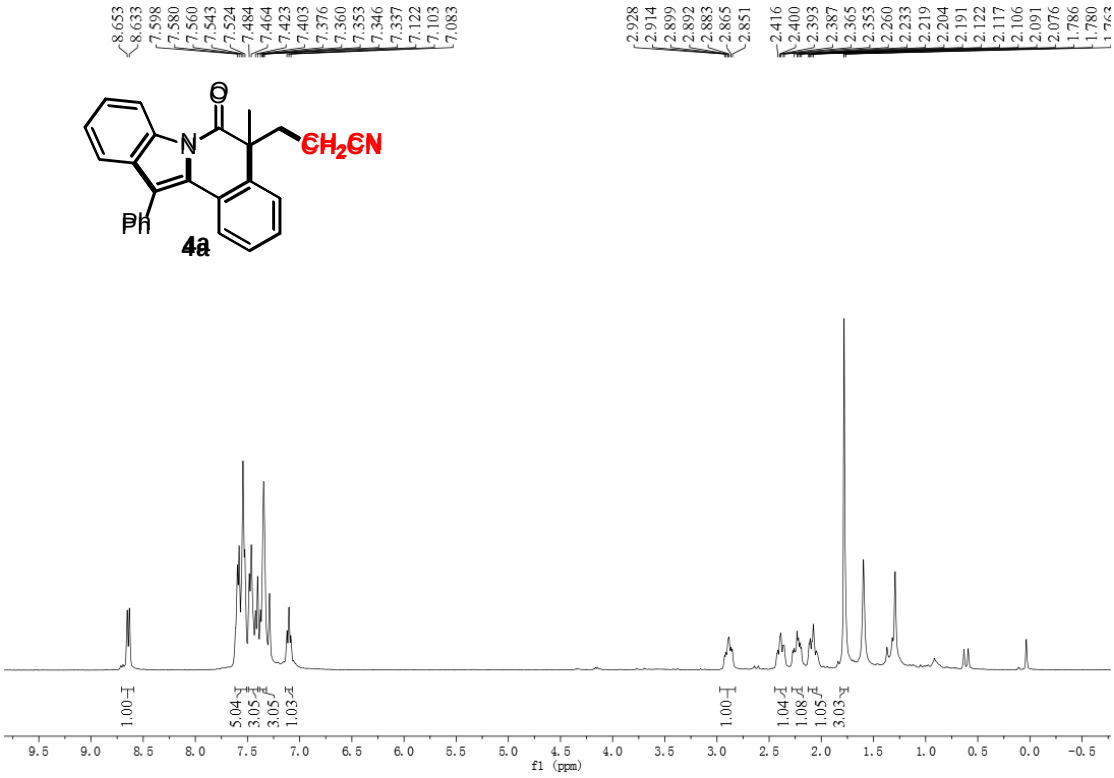
$^{1}$H NMR for **3a** (400 MHz, $CDCl_3$)



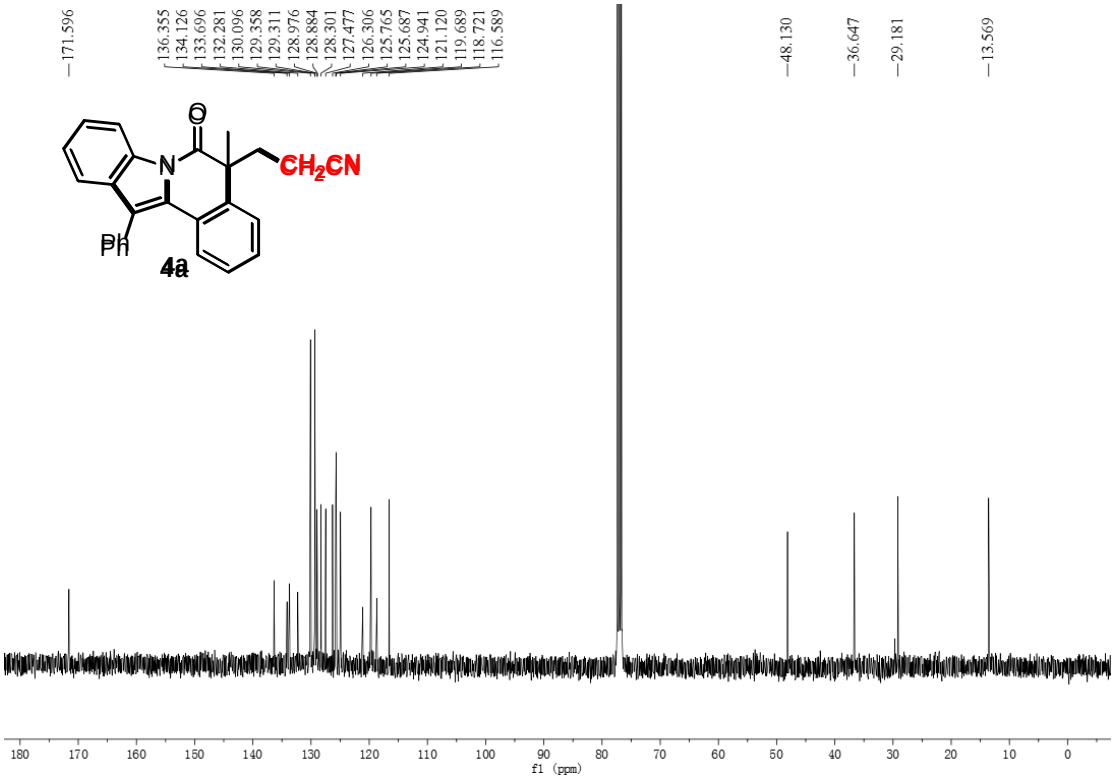

$^{13}$C NMR for **3a** (101 MHz, $CDCl_3$)



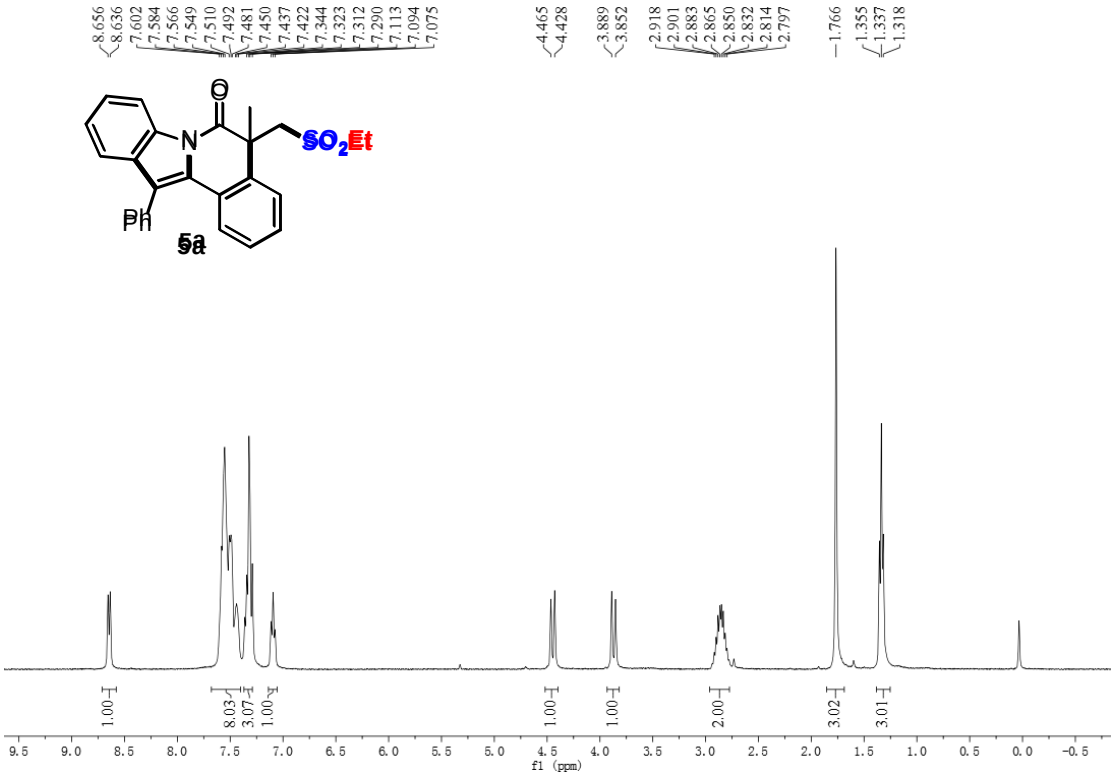
$^{1}$H NMR for **4a** (400 MHz, $CDCl_3$)



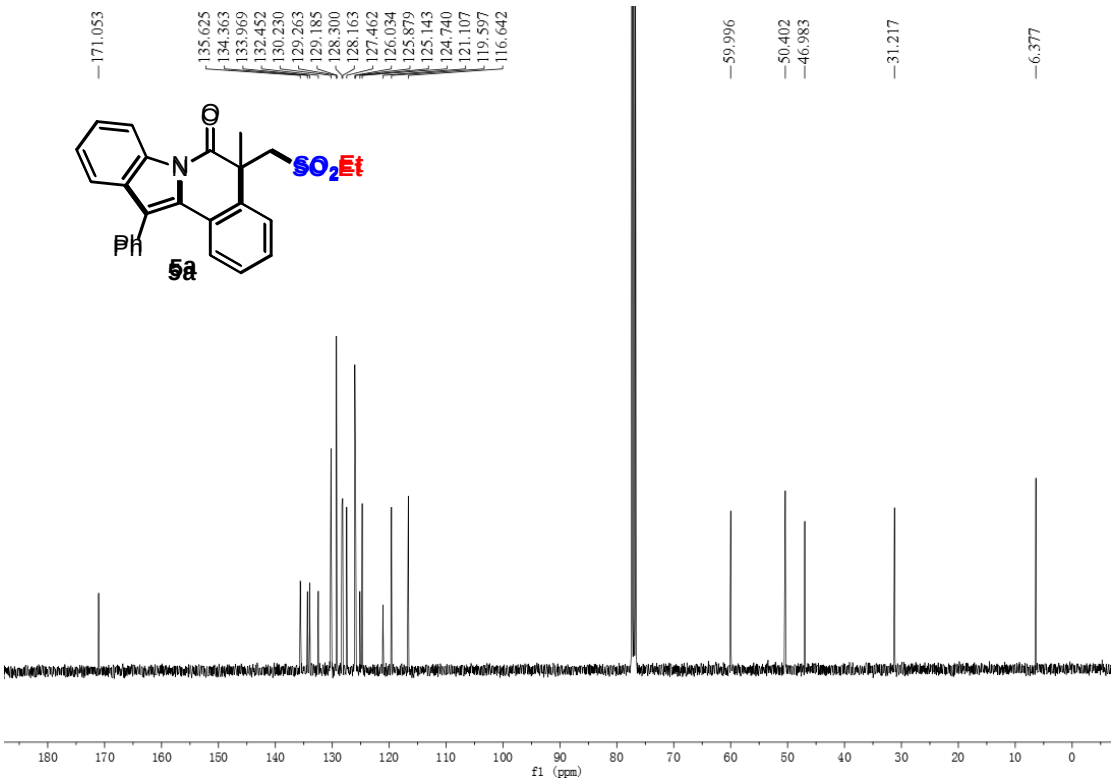

$^{13}$C NMR for **4a** (101 MHz, $CDCl_3$)



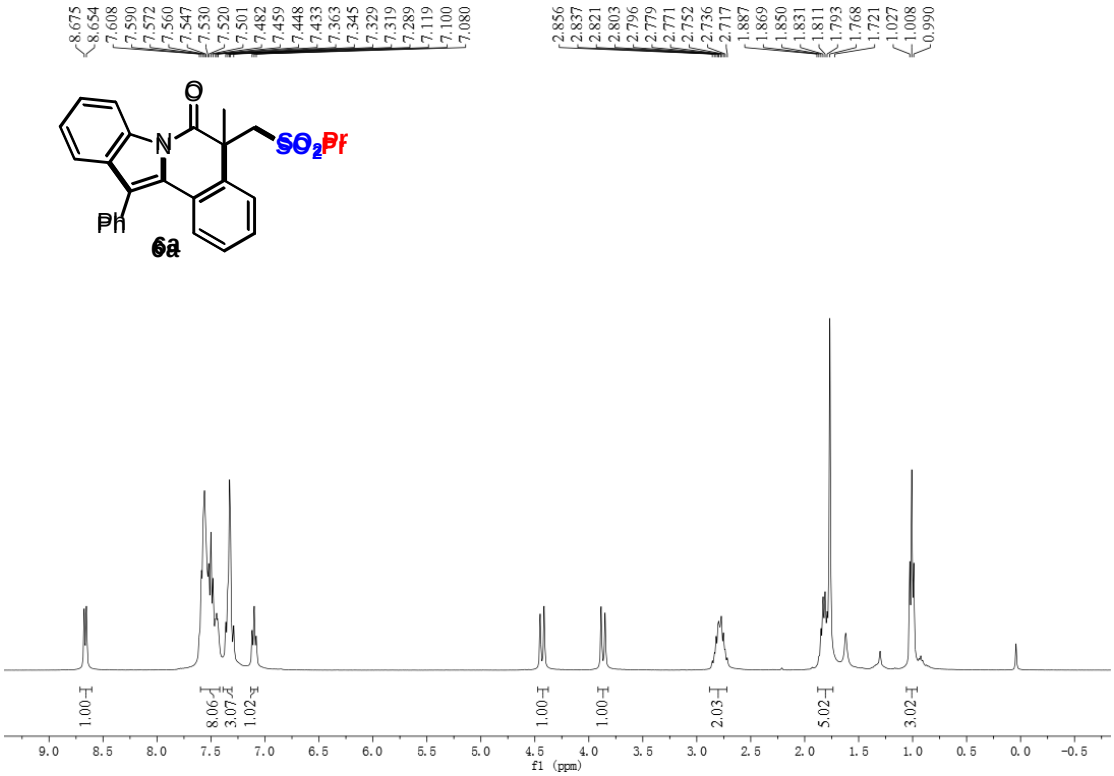
$^{1}$H NMR for **5a** (400 MHz, $CDCl_3$)



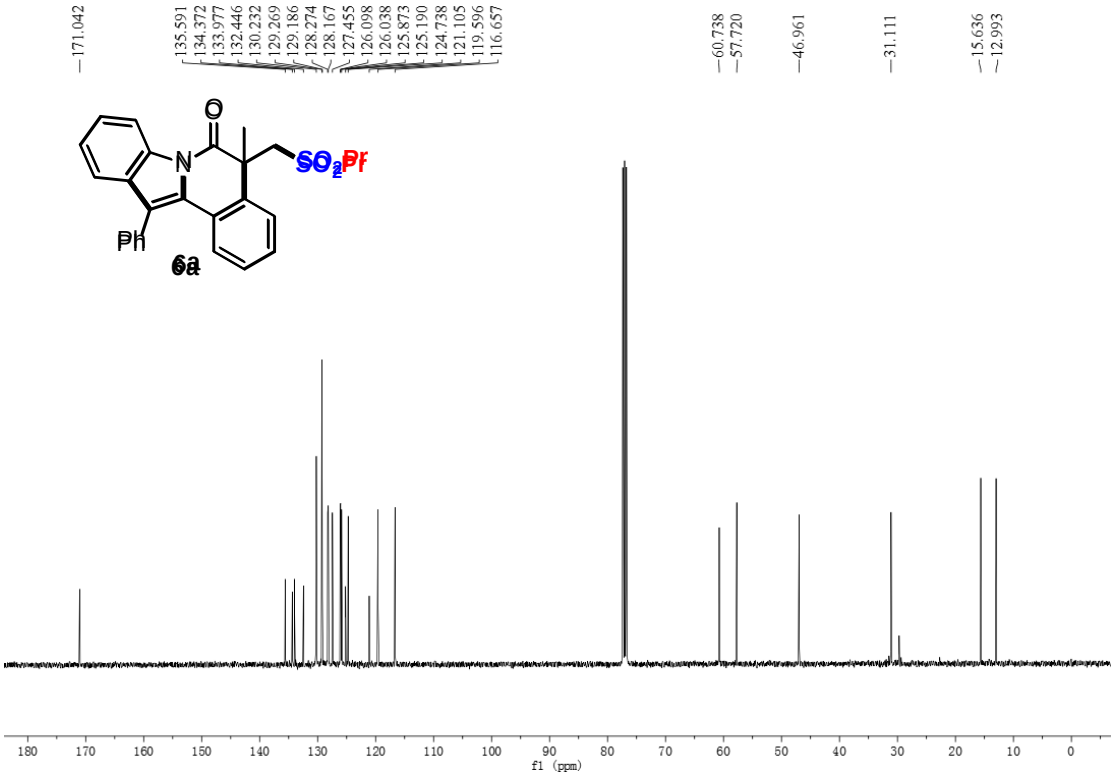

$^{13}$C NMR for **5a** (101 MHz, $CDCl_3$)



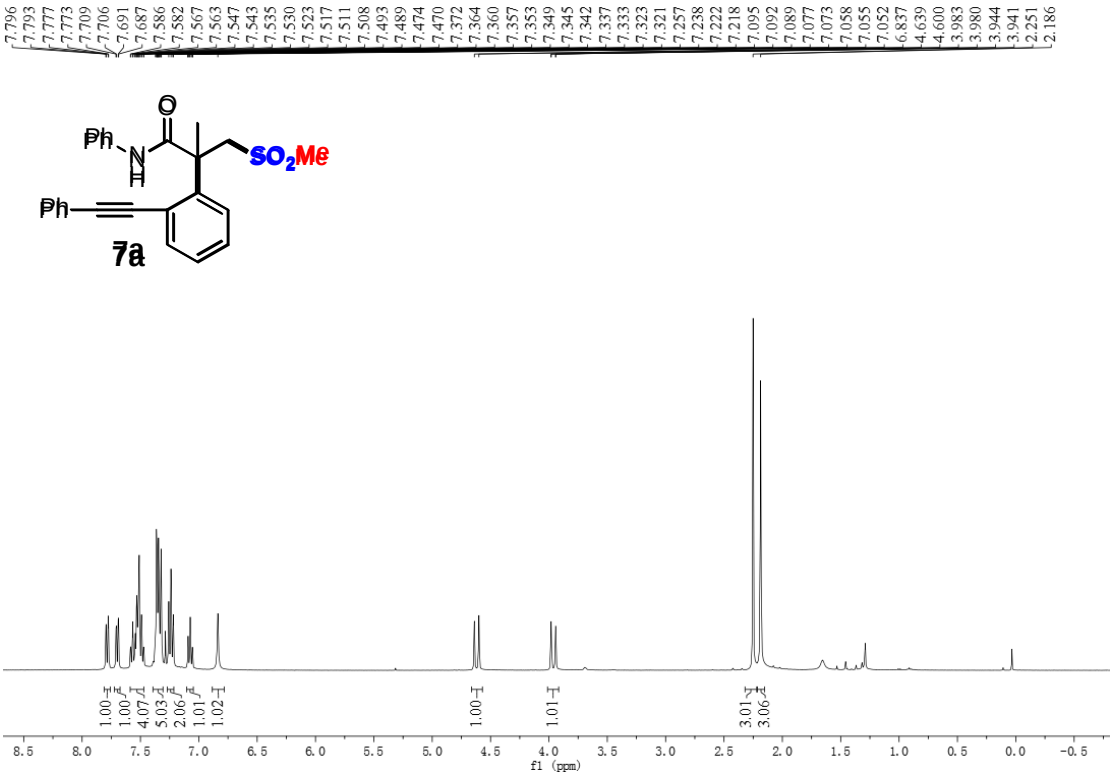
$^{1}$H NMR for **6a** (400 MHz, $CDCl_3$)




$^{13}$C NMR for **6a** (101 MHz, $CDCl_3$)



$^{1}$H NMR for **7a** (400 MHz, $CDCl_3$)




$^{13}$C NMR for **7a** (101 MHz, $CDCl_3$)