# Photo-Induced Aerobic Cross-Coupling of Quinoxazolines and Electron-Rich Thiophenes

Wei Huang,[a] Tong Wang,[a] Shu-Ying Chen,[a] Quan Zhou,*[a] and Lei Wang[a,b]

[a] School of Pharmaceutical Sciences, Advanced Research Institute and Department of Chemistry, Taizhou University, Taizhou, Zhejiang 318000, P. R. China, E-mail: qzhou@tzc.edu.cn

[b] College of Material Chemistry and Chemical Engineering, Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou, 311121, Zhejiang, P. R. China

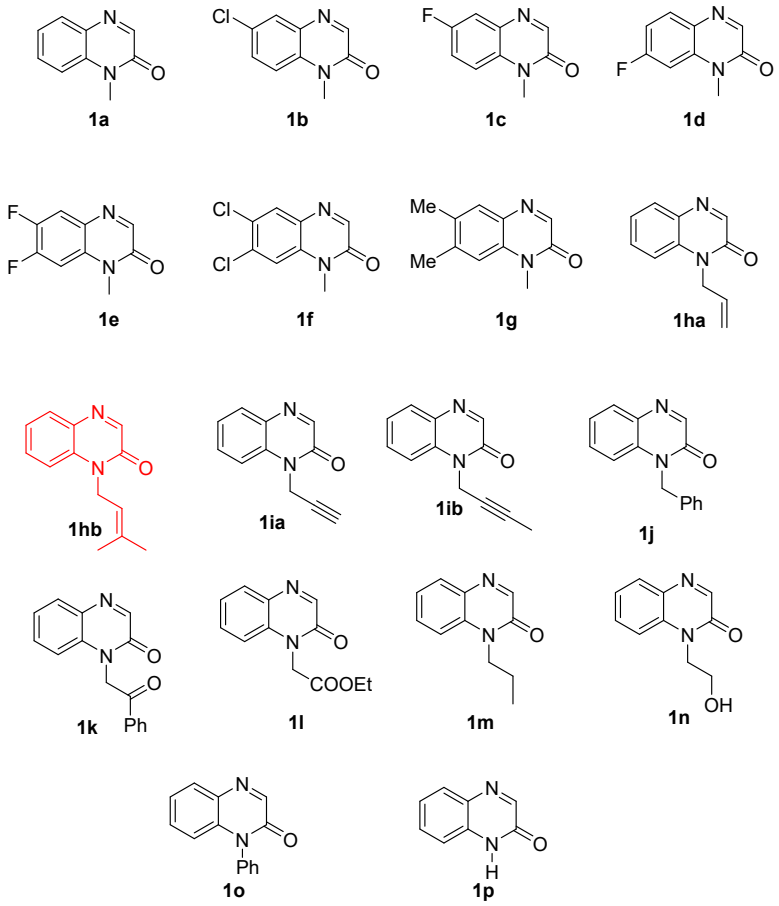
## *Table of Contents*

# 1. General considerations

Unless otherwise noted, chemicals and materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to the general methods. All $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Products were purified by flash chromatography on 200–300 mesh silica gels, $SiO_2$. Stern-Volmer quenching data was collected on Cary Eclipse EL05083125 (Varian, California, America).

# 2. Substrate synthesis

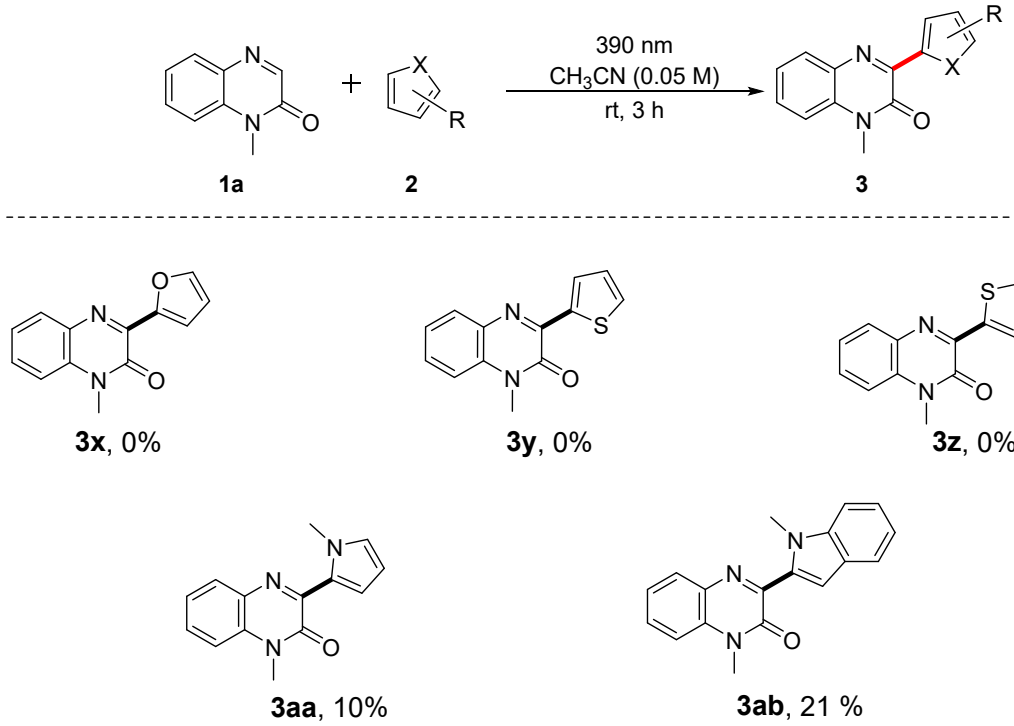
Substrate **1a–1g**[1], **1ha**[1], **1hb**[2], **1ia**[1], **1ib**[3], **1j**[1], **1k**[1], **1l**[1], **1m**[1], **1n**[1], **1o**[1] were showed in Scheme S1 and synthesized according to the corresponding literature. Substrate **1p** was purchased and used directly.




**Scheme S1** Substrates of quinoxalin-2(1*H*)-ones used in this paper

## 3. Scope of thiophene derivative

The following Scheme S2 list the scope of other thiophenyl analogues




**Scheme S2** Scope of thiophene derivative

## 4. Redox property study of thiophenes

To address thiophenes' oxidative potential, we made an investigation of redox property of a plethora of thiophenes. The results were shown in Figure S1 and Table S1. Cyclic voltammetry (CV) experiments were carried out with a Chenhua CHI760E electrochemical workstation using a typical three-electrode cell with a round glassy carbon (GC, Ø = 3 mm) working electrode, a Ag/AgCl (KCl, 3M) reference electrode, a Pt wire (Ø = 0.5 mm) counter electrode and $^{n}Bu_4NPF_6$ (0.1 M) was used as the supporting electrolyte. Reference electrode was calibrated with ferrocene (Fc) before and after electrochemical measurements [$E_{1/2}$ ($Fc^{\bullet+}/Fc^{0}$) = 0.490 V *vs* Ag/AgCl]. The conversion constant of 690 mV was taken for $Fc^{+}$/Fc against NHE. The conversion constant of 245 mV was taken for SCE against NHE.

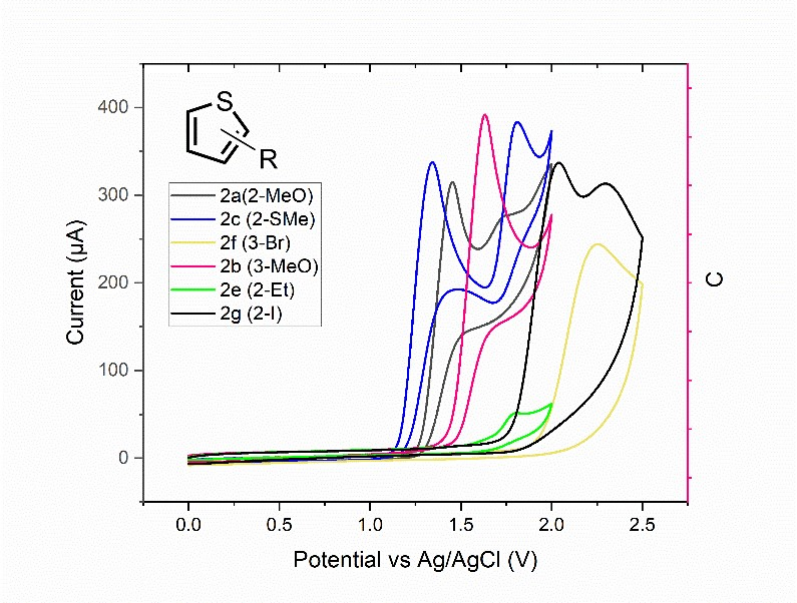
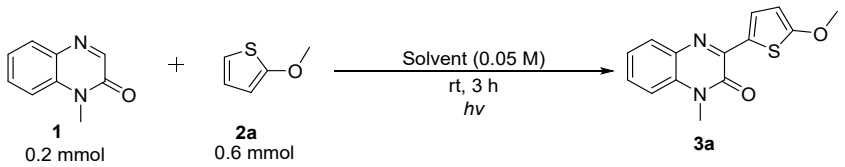



Figure S1. Redox property of thiophenes derivative

**Table S1**: Redox values of thiophenes*

| Compound | $E_{p/2}$ | Compound | $E_{p/2}$ |
|---|---|---|---|
| **2a** | +1.32 | **2b** | +1.50 |
| **2c** | +1.20 | **2e** | +1.69 |
| **2f** | +2.03 | **2g** | +1.85 |
| *Potential have been converted from Ag/AgCl to SCE | | | |

## 5. Representative procedure for the model reaction

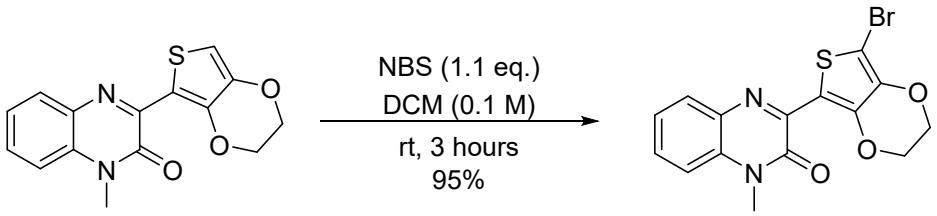



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with *N*-methylquinoxalin-2(1*H*)-one (**1a**, 0.20 mmol), 2-methoxythiophene (**2a**, 0.60 mmol), acetonitrile (4.0 mL). The reaction vessel was exposed to LED irradiation at room temperature in air with stirring for 3 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further

purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give the desired product **3a**.

## 6. Transformations of obtained products

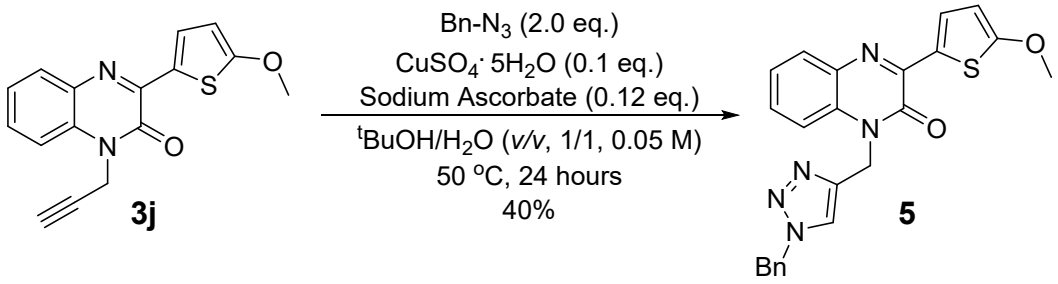
### 5.1 Electrophilic bromination of **3s**




**3s** **4**

A 25 mL oven-dried reaction flask equipped with a magnetic stirrer bar was charged with **3s** (30 mg, 0.10 mmol), dichloromethane (DCM, 3.0 mL). the reaction solution was cooled in ice-water bath, NBS (20 mg, 0.11 mmol, 1.1 eq.) was dissolved in DCM and added dropwise into the reaction vessel, then the reaction was stirred at room temperature for 3 hours. After finished, the reaction was directly concentrated under reduced pressure, the residue was applied on silica gel chromatography (DCM/MeOH = 30:1), which afforded the targeted compound 3-(7-bromo-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-1-methylquinoxalin-2(1*H*)-one (**4**, 36 mg, 95%); yellow solid; m.p. 271–273 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.04 (d, J = 8.2 Hz, 1H), 7.76 (t, J = 7.9 Hz, 1H), 7.64–7.51 (m, 2H), 4.75 (dd, J = 5.4, 2.8 Hz, 2H), 4.60 – 4.39 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 153.3, 151.7, 141.1, 140.4, 131.9, 130.4, 127.1, 122.3, 121.4, 121.0, 115.2, 106.5, 67.9, 64.5, 31.3; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{15}H_{12}BrN_2O_3S^+$, 378.9747 (100.0%), Found 378.9746 (100.0%).

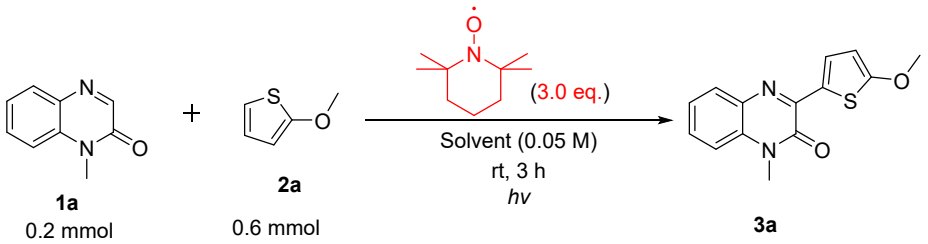
5.2 Click reaction of **3j**




A 25 mL oven-dried reaction flask equipped with a magnetic stirrer bar was charged with **3j** (60 mg, 0.2 mmol), $BnN_3$ (53.2 mg, 0.4 mmol, 2.0 eq.), $CuSO_4 \bullet 5H_2O$ (5 mg, 0.02 mmol, 0.1 eq.), Sodium Ascorbate (4.7mg, 0.024 mmol, 0.12 eq.), $^t$BuOH (2 mL), $H_2O$ (2 mL), the resulting mixture was stirred at 50 ℃ for 24 hours. After finished, the reaction solution was concentrated under reduced pressure to remove $^t$BuOH and water. The residual was applied on silica gel (PE/EA = 20/1~1/1) and forged 1-((1-benzyl-1*H*-1,2,3-triazol-5-yl)methyl)-3-(5-methoxythiophen-2-yl)quinoxalin-2(1*H*)-one (**5**, 34 mg; 40%); yellow solid; m.p. 145–147 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.22 (d, $J$ = 4.3 Hz, 1H), 7.85 (d, $J$ = 8.4 Hz, 1H), 7.78 (d, $J$ = 8.0 Hz, 1H), 7.60 (s, 1H), 7.48 (t, $J$ = 7.8 Hz, 1H), 7.33 (dt, $J$ = 5.5, 2.6 Hz, 4H), 7.23 (dd, $J$ = 6.8, 2.9 Hz, 2H), 6.31 (d, $J$ = 4.3 Hz, 1H), 5.58 (s, 2H), 5.45 (s, 2H), 3.99 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 172.3, 153.6, 147.7, 142.9, 134.2, 133.5, 132.0, 131.2, 129.2, 129.1, 128.8, 128.3, 128.1, 125.6, 124.2, 123.4, 114.6, 105.9, 60.1, 54.3, 38.2; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{23}H_{20}N_5O_2S^+$, 430.1332 (100.0%), Found 430.1335 (100%).

# 7. Mechanism investigation

## 7.1 Radical trapping experiment




A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with *N*-methylquinoxalin-2(1*H*)-one (**1a**, 0.20 mmol), 2-methoxythiophene (**2a**, 0.60 mmol), 2,2,6,6-tetramethyl-1-piperdinyloxy (TEMPO, 93.6 mg, 3.0 eq.), acetonitrile (4.0 mL). The reaction vessel was exposed to LED irradiation at room temperature in air with stirring for 3 h. After completion of the reaction, the mixture solution was analyzed by HR-MS. no desired product **3a** was detected. Meanwhile, an adduct radical intermediate with TEMPO was formed during the reaction, and was detected by HRMS analysis (Figure S2).

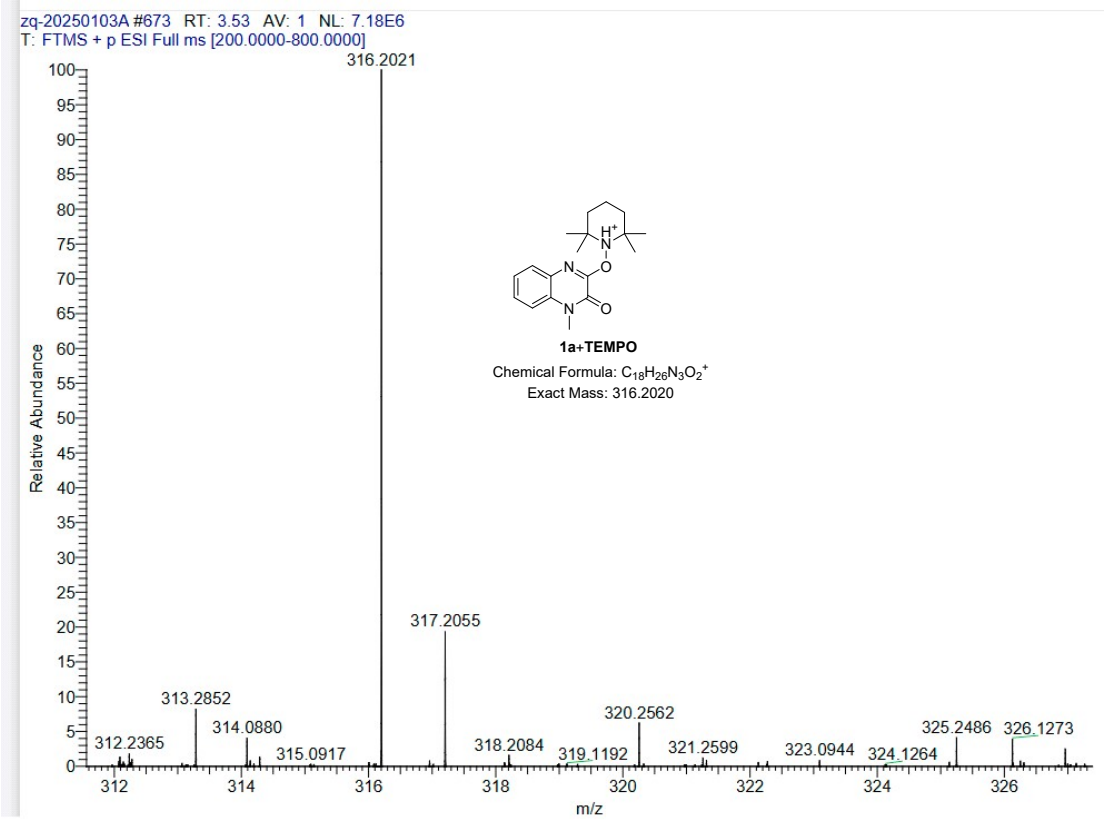



Figure S2 *in-situ* detected intermediate **1a**+TEMPO

## 7.2 Stern-Volmer quenching experiment

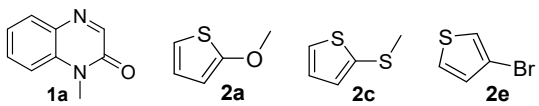
Rates of quenching ($k_{SV}$) were determined using Stern–Volmer kinetics[4] (eq. 1).

$$\frac{I_0}{I} = 1 + k_{SV}[Quencher] \quad \text{(eq. 1)}$$

Where $\boldsymbol{I_0}$ is the luminescence intensity without the quencher, $\boldsymbol{I}$ is the intensity with the quencher, the test conditions for quenching reaction (Table S2):

**Table S2.** Photosensitizer and quenchers' solution preparation

| Compound | *Mr* | *m*/mg | *n*/mmol | *V*/mL | *C* (mol·L$^{-1}$) in ACN* |
|---|---|---|---|---|---|
| **1a** | 160 | 12 | 4 | 20 | $3.75*10^{-3}$ |
| **2a** | 114 | 342 | 2 | 2 | 1.5 |
| **2c** | 130 | 486 | 2 | 2 | 1.5 |
| **2e** | 163 | 389 | 2 | 2 | 1.5 |

| | |
|---|---|
|   | *acetonitrile (ACN) as testing solvent |

For each quencher's fluorescent quenching experiment, five or six datum points was collected *under $N_2$ and photo protection*. Excited wavelength: 420 nm; Fluorescent intensity data was collected at maximum emission peak (490 nm). Quenching experiment when 2a, 2c, 2e as quencher were layered in the following pictures (Figure S3, **2a**; Figure S4, **2c**; Figure S5, **2e**).

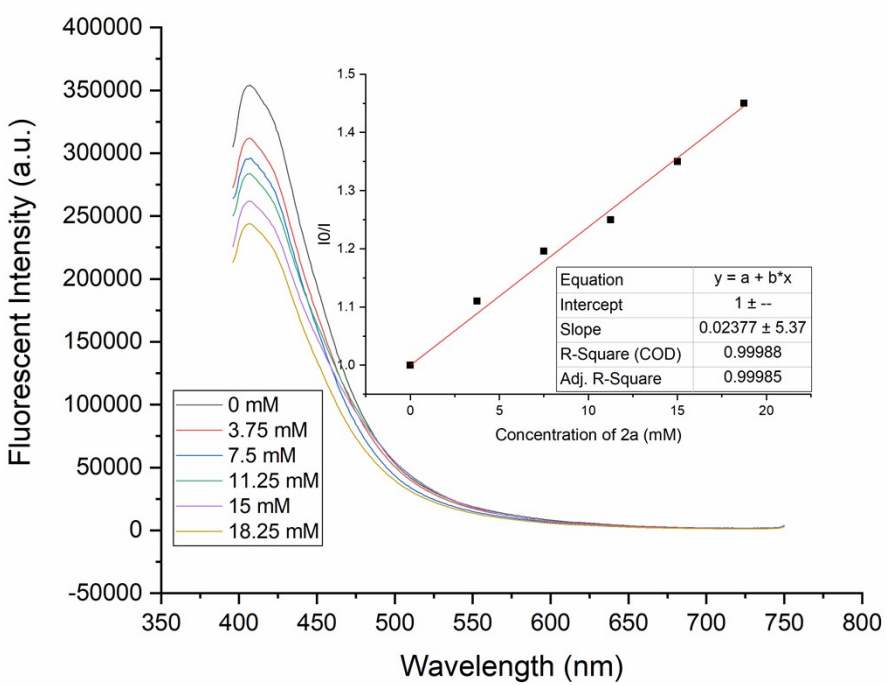



Figure S3 (**2a** as quencher)

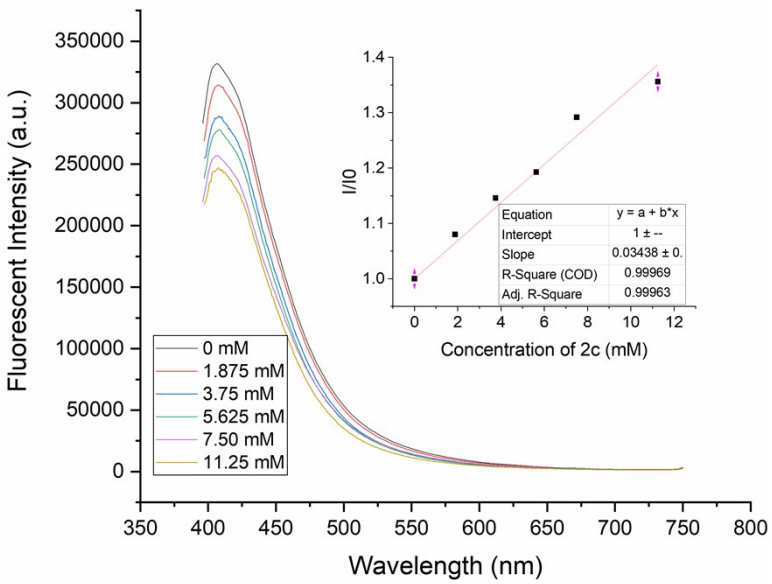



Figure S4 (**2c** as quencher)

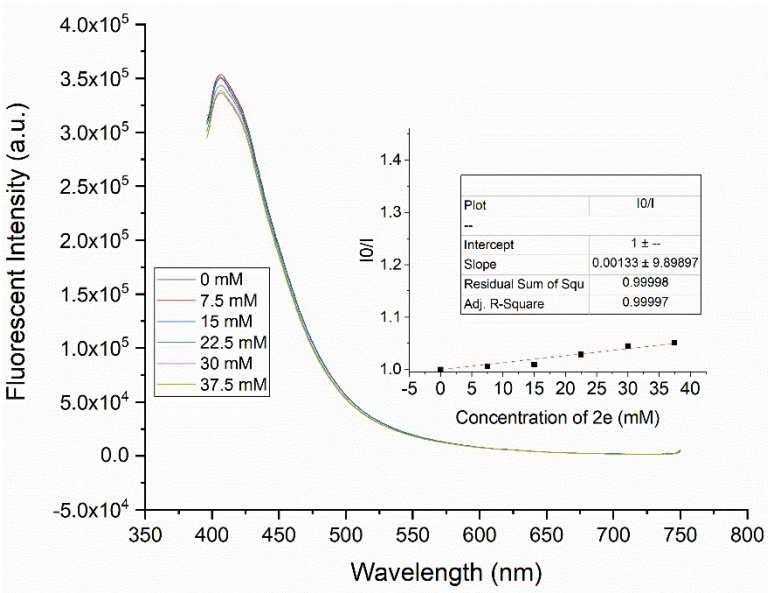
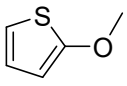
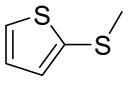
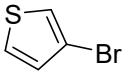


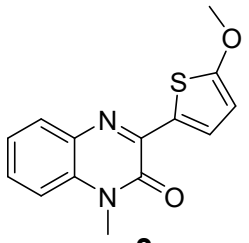

Figure S5 (**2e** as quencher)

**Table S3** Quencher **2a**/**2c**/**2e** Stern-Volmer constant ($K_{SV}$)

| |  **2a** |  **2c** |  **2e** |
|---|---|---|---|
| $K_{SV}$ ($\mu M^{-1}$) | 22.3 | 34.1 | 1.3 |

# 8. Characterization data for all products

**3-(5-Methoxythiophen-2-yl)-1-methylquinoxalin-2(1*H*)-one (3a)**



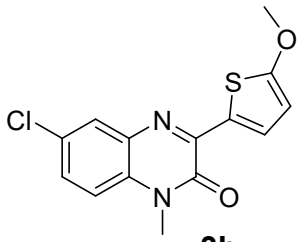
**3a**

Purified by petroleum ether: ethyl acetate = 10:1.

46 mg; 85% (0.2 mmol scale); yellow solid. m.p. 146–148 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.24 (d, $J$ = 4.3 Hz, 1H), 7.80 (dd, $J$ = 8.0, 1.2 Hz, 1H), 7.48–7.42 (m, 1H), 7.35–7.30 (m, 1H), 7.27 (dd, $J$ = 5.5, 4.8 Hz, 1H), 6.31 (d, $J$ = 4.3 Hz, 1H), 3.98 (s, 3H), 3.75 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 172.4, 153.9, 148.1, 133.5, 132.3, 132.2, 129.4, 128.9, 125.9, 124.0, 113.6, 106.0, 60.2, 29.3; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{14}H_{13}N_2O_2S^+$, 273.0692 (100.0%), Found 273.0689 (100%).

**6-Chloro-3-(5-methoxythiophen-2-yl)-1-methylquinoxalin-2(*1H*)-one (3b)**



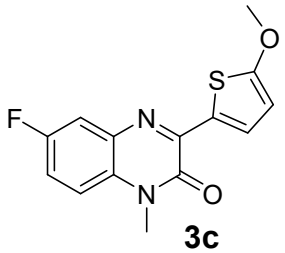
**3b**

Purified by petroleum ether: ethyl acetate = 10:1.

51 mg; 83% (0.2 mmol scale); yellow solid; m.p. 183–185 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.23 (d, $J$ = 4.3 Hz, 1H), 7.75 (d, $J$ = 2.3 Hz, 1H), 7.37 (dd, $J$ = 8.9, 2.3 Hz, 1H), 7.17 (d, $J$ = 8.9 Hz, 1H), 6.30 (d, $J$ = 4.3 Hz, 1H), 3.98 (s, 3H), 3.70 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 173.1, 153.5, 148.9, 134.1, 133.0, 130.9, 129.3, 128.6, 128.4, 125.5, 114.7, 106.2, 60.2, 29.4; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{14}H_{12}ClN_2O_2S^+$, 307.0303 (100.0%), Found 307.0297 (100%).

**6-Fluoro-3-(5-methoxythiophen-2-yl)-1-methylquinoxalin-2(*1H*)-one (3c)**



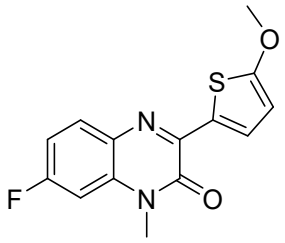
**3c**

Purified by petroleum ether: ethyl acetate = 10:1.

40 mg; 68% (0.2 mmol scale); yellow solid; m.p. 176–177 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.26 (d, $J$ = 4.3 Hz, 1H), 7.48 (dd, $J$ = 9.0, 2.2 Hz, 1H), 7.24 – 7.13 (m, 2H), 6.32 (d, $J$ = 4.3 Hz, 1H), 4.00 (s, 3H), 3.74 (s, 3H); **$^{19}$F NMR** (376 MHz, $CDCl_3$) $\delta$ –118.99 (td, $J$ = 8.4, 5.0 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 173.2, 159.1 (d, $J$ = 243.4 Hz), 153.6, 149.1, 134.2 (d, $J$ = 11.6 Hz), 132.99, 128.9 (d, $J$ = 1.8 Hz), 125.5, 116.4 (d, $J$ = 24.2 Hz), 114.6 (d, $J$ = 9.3 Hz), 114.5 (d, $J$ = 22.5 Hz), 106.2, 60.3, 29.5; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{14}H_{12}FN_2O_2S^+$, 291.0598 (100.0%), Found 291.0589 (100%).

**7-Fluoro-3-(5-methoxythiophen-2-yl)-1-methylquinoxalin-2(1*H*)-one (3d)**



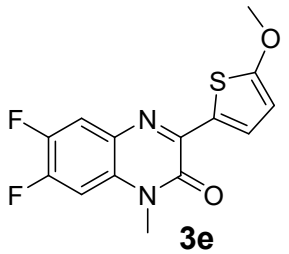
**3d**

Purified by petroleum ether: ethyl acetate = 10:1.

40 mg; 69% (0.2 mmol scale); yellow solid. m.p. 169–171 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.19 (d, $J$ = 4.3 Hz, 1H), 7.75 (dd, $J$ = 8.9, 6.0 Hz, 1H), 7.06–6.98 (m, 1H), 6.95 (dd, $J$ = 10.0, 2.6 Hz, 1H), 6.29 (d, $J$ = 4.3 Hz, 1H), 3.98 (s, 3H), 3.69 (s, 3H); **$^{19}$F NMR** (376 MHz, $CDCl_3$) $\delta$ –109.06 (td, $J$ = 8.9, 5.8 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 172.2, 162.5 (d, $J$ = 249.4 Hz), 153.6, 146.9 (d, $J$ = 3.3 Hz), 133.4 (d, $J$ = 11.5 Hz), 132.0, 130.9 (d, $J$ = 10.2 Hz), 130.0 (d, $J$ = 2.2 Hz), 125.6, 111.7 (d, $J$ = 23.4 Hz), 105.8, 100.5 (d, $J$ = 27.9 Hz), 60.1, 29.4; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{14}H_{12}FN_2O_2S^+$, 291.0598 (100.0%), Found 291.0598 (100%).

**6,7-Difluoro-3-(5-methoxythiophen-2-yl)-1-methylquinoxalin-2(1*H*)-one (3e)**



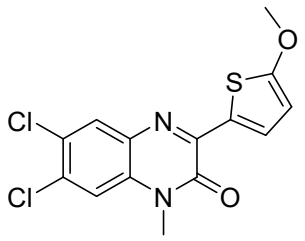
**3e**

Purified by petroleum ether: ethyl acetate = 10:1.

36 mg; 59% (0.2 mmol scale); yellow solid. m.p. 198–201 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.27 (d, $J$ = 4.3 Hz, 1H), 7.63 (dd, $J$ = 10.4, 8.3 Hz, 1H), 7.29 (s, 1H), 7.11 (dd, $J$ = 11.3, 7.1 Hz, 1H), 6.34 (d, $J$ = 4.3 Hz, 1H), 4.02 (s, 3H), 3.73 (s, 3H); $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ −132.86 (ddd, $J$ = 21.8, 11.3, 8.3 Hz), −142.00 (ddd, $J$ = 22.2, 10.3, 7.0 Hz); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 153.8, 150.8 (dd, $J$ = 255.8, 14.4 Hz), 147.9 (dd, $J$ = 252.2, 14.1 Hz), 143.2, 140.3, 127.5 (d, $J$ = 8.8 Hz), 122.9 (d, $J$ = 7.1 Hz), 117.2, 113.6 (m), 112.5, 111.1 (d, $J$ = 21 Hz), 103.8 (d, $J$ = 24 Hz), 61.8, 31.1; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{14}H_{11}F_2N_2O_2S^+$, 309.0504 (100.0%), Found 309.0494 (100%).

**6,7-Dichloro-3-(5-methoxythiophen-2-yl)-1-methylquinoxalin-2(1*H*)-one (3f)**



**3f**

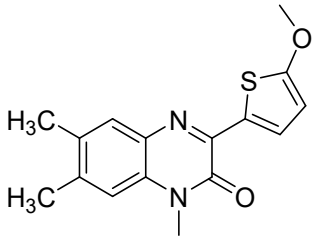
Purified by petroleum ether: ethyl acetate = 10:1.

58 mg; 85% (0.2 mmol scale); yellow solid; m.p. 175–178 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.25 (d, $J$ = 4.4 Hz, 1H), 7.87 (s, 1H), 7.35 (s, 1H), 6.31 (d, $J$ = 4.4 Hz, 1H), 3.99 (s, 3H), 3.70 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.5, 153.4, 148.9, 133.5, 132.7, 132.4, 131.6, 129.8, 127.8, 125.4, 115.1, 106.4, 60.3, 29.6;

**HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{14}H_{11}Cl_2N_2O_2S^+$, 340.9913 (100.0%), Found 340.9910 (100%).

**3-(5-Methoxythiophen-2-yl)-1,6,7-trimethylquinoxalin-2(1*H*)-one**



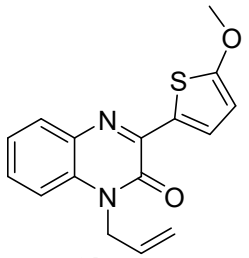
**3g**

Purified by petroleum ether: ethyl acetate = 10:1.

35 mg; 58% (0.2 mmol scale); yellow solid; m.p. 171–173 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.19 (d, $J$ = 4.3 Hz, 1H), 7.55 (s, 1H), 7.02 (s, 1H), 6.29 (d, $J$ = 4.3 Hz, 1H), 3.98 (s, 3H), 3.71 (s, 3H), 2.40–2.35 (m, 3H), 2.33 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.8, 153.9, 147.0, 138.8, 132.9, 131.8, 131.3, 130.3, 129.4, 126.3, 114.2, 105.7, 60.2, 29.2, 20.7, 19.3; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{16}H_{17}N_2O_2S^+$, 301.1005 (100.0%), Found 301.1001 (100%).

**1-Allyl-3-(5-methoxythiophen-2-yl)quinoxalin-2(1*H*)-one (3h)**



**3h**

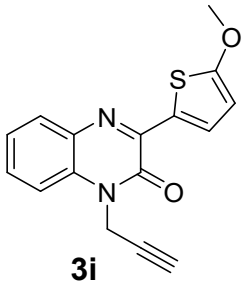
Purified by petroleum ether: ethyl acetate = 10:1.

45 mg; 75% (0.2 mmol scale); yellow solid. m.p. 84–87 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.25 (d, $J$ = 4.3 Hz, 1H), 7.80 (dd, $J$ = 8.0, 1.1 Hz, 1H), 7.41 (t, $J$ = 8.4 Hz, 1H), 7.30 (t, $J$ = 7.4 Hz, 1H), 7.24 (d, $J$ = 8.4 Hz, 1H), 6.30 (d, $J$ = 4.3 Hz, 1H), 5.96 (ddd, $J$ = 22.2, 10.2, 5.0 Hz, 1H), 5.26 (d, $J$ = 10.4 Hz, 1H), 5.17 (d, $J$ = 17.3 Hz, 1H), 4.95 (d, $J$ = 5.0 Hz, 2H), 3.98 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$)

δ 172.4, 153.4, 148.0, 133.6, 132.2, 131.4, 130.7, 129.4, 128.8, 125.9, 124.0, 118.1, 114.2, 105.9, 60.2, 44.7; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{16}H_{15}N_2O_2S^+$, 299.0849 (100.0%), Found 299.0840 (100%).

**3-(5-Methoxythiophen-2-yl)-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (3i)**



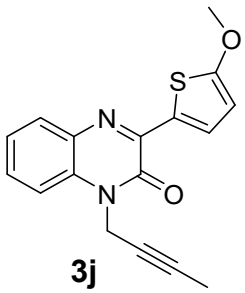
**3i**

Purified by petroleum ether: ethyl acetate = 10:1.

46 mg; 78% (0.2 mmol scale); yellow solid. m.p. 191–193 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 4.3 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.31 (d, *J* = 4.3 Hz, 1H), 5.11 (d, *J* = 2.2 Hz, 2H), 3.99 (s, 3H), 2.29 (s, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.6, 153.0, 147.9, 133.7, 132.7, 130.8, 129.5, 129.0, 125.9, 124.4, 114.1, 106.1, 73.3, 60.3, 31.7; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{16}H_{13}N_2O_2S^+$, 297.0692 (100.0%), Found 297.0688 (100%).

**1-(But-2-yn-1-yl)-3-(5-methoxythiophen-2-yl)quinoxalin-2(1*H*)-one (3j)**



**3j**

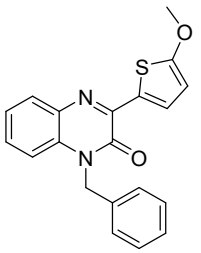
Purified by petroleum ether: ethyl acetate = 10:1.

47 mg; 75% (0.2 mmol scale); yellow solid. m.p. 200–202 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 4.4 Hz, 1H), 7.81 (d, *J* = 2.3 Hz, 1H), 7.44 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.38 (d, *J* = 8.9 Hz, 1H), 6.32 (d, *J* = 4.3 Hz, 1H), 5.02 (q, *J*

= 2.4 Hz, 2H), 4.00 (s, 3H), 1.78 (t, *J* = 2.4 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.1, 152.6, 148.8, 134.2, 133.3, 129.5, 129.4, 128.6, 128.4, 125.6, 115.4, 106.2, 81.4, 71.9, 60.2, 32.3, 3.4; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{17}H_{15}N_2O_2S^+$, 311.0849 (100.0%), Found 311.0848 (100%).

**1-Benzyl-3-(5-methoxythiophen-2-yl)quinoxalin-2(1*H*)-one** (**3k**)



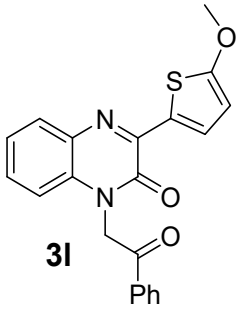
**3k**

Purified by petroleum ether: ethyl acetate = 10:1.

56 mg; 81% (0.2 mmol scale); yellow solid. m.p. 144–146 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 8.30 (d, *J* = 4.3 Hz, 1H), 7.82 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.40 – 7.12 (m, 9H), 6.32 (d, *J* = 4.3 Hz, 1H), 5.56 (s, 2H), 3.99 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) *δ* 172.5, 154.0, 148.2, 135.4, 133.7, 132.5, 131.7, 129.4, 129.1, 128.9, 127.8, 126.9, 126.1, 124.1, 114.4, 106.1, 60.2, 46.1; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{20}H_{17}N_2O_2S^+$, 349.1005 (100.0%), Found 349.0994 (100%).

**3-(5-Methoxythiophen-2-yl)-1-(2-oxo-2-phenylethyl)quinoxalin-2(1*H*)-one (3l)**



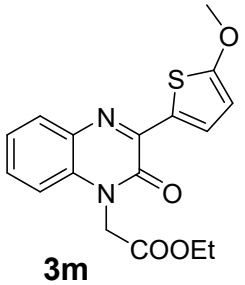
**3l**

Purified by petroleum ether: ethyl acetate = 8:1.

62 mg; 83% (0.2 mmol scale); yellow solid. m.p. 209–210 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 4.3 Hz, 1H), 8.13 – 8.05 (m, 2H), 7.85 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.34 (dtd, *J* = 8.1, 7.4, 1.2 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.31 (d, *J* = 4.3 Hz, 1H), 5.80 (s, 2H), 3.99 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 191.2, 172.5, 153.7, 147.9, 134.7, 134.5, 133.7, 132.4, 131.8, 129.7, 129.2, 129.0, 128.3, 126.0, 124.2, 113.5, 106.1, 60.3, 48.7; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{21}H_{17}N_2O_3S^+$, 377.0954 (100.0%), Found 377.0948 (100%).

**Ethyl 2-(3-(5-methoxythiophen-2-yl)-2-oxoquinoxalin-1(2*H*)-yl)acetate (3m)**



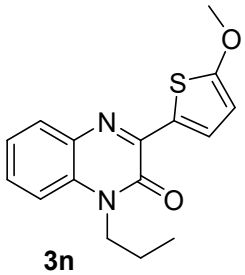

**3m**

Purified by petroleum ether: ethyl acetate = 3:1.

63 mg; 92% (0.2 mmol scale); yellow solid. m.p. 158–160 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 4.3 Hz, 1H), 7.82 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.45 – 7.36 (m, 1H), 7.32 (dd, *J* = 11.6, 4.3 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.30 (d, *J* = 4.3 Hz, 1H), 5.08 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 1.26 (t, *J* = 7.4 Hz, 5H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.5, 167.3, 153.5, 147.9, 133.5, 132.6, 131.5, 129.6, 129.0, 125.9, 124.3, 113.1, 106.1, 62.2, 60.2, 43.8, 14.2; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{17}H_{17}N_2O_4S^+$, 345.0904 (100.0%), Found 345.0899 (100%).

**3-(5-Methoxythiophen-2-yl)-1-propylquinoxalin-2(1H)-one (3n)**



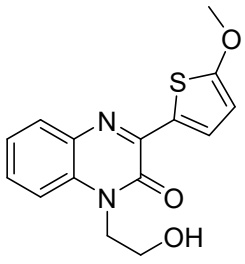
**3n**

Purified by petroleum ether: ethyl acetate = 10:1.

45 mg; 76% (0.2 mmol scale); yellow solid. m.p. 101–103 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 4.3 Hz, 1H), 7.80 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.33 – 7.24 (m, 2H), 6.31 (d, *J* = 4.3 Hz, 1H), 4.28 – 4.21 (m, 2H), 3.98 (s, 3H), 1.81 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.4, 153.6, 148.0, 133.7, 132.0, 131.4, 129.6, 128.8, 125.8, 123.8, 113.6, 105.9, 60.2, 44.1, 20.8, 11.5; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{16}H_{17}N_2O_2S^+$, 301.1005 (100.0%), Found 301.1001 (100%).

**1-(2-Hydroxyethyl)-3-(5-methoxythiophen-2-yl)quinoxalin-2(1*H*)-one (3o)**



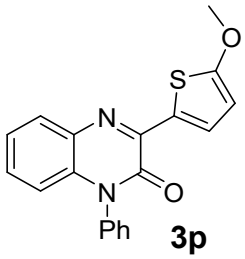
**3o**

Purified by petroleum ether: ethyl acetate = 5:1.

37 mg; 61% (0.2 mmol scale); yellow solid. m.p. 150–153 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.29 – 8.16 (m, 1H), 7.91 – 7.77 (m, 1H), 6.31 (d, *J* = 4.3 Hz, 1H), 4.59 – 4.49 (m, 2H), 4.15 – 4.04 (m, 2H), 3.99 (s, 3H), 2.54 – 2.37 (m, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.5, 154.8, 147.9, 133.8, 132.3, 131.7, 129.6, 129.0, 125.7, 124.2, 113.8, 106.0, 60.8, 60.2, 45.2; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{15}H_{15}N_2O_3S^+$, 303.0798 (100.0%), Found 303.0790 (100%).

**3-(5-Methoxythiophen-2-yl)-1-phenylquinoxalin-2(1*H*)-one (3p)**



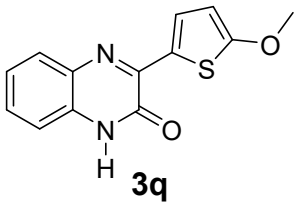
**3p**

Purified by petroleum ether: ethyl acetate = 10:1.

45 mg; 68% (0.2 mmol scale); yellow solid. m.p. 189–191 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.26 (t, *J* = 5.6 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.64 (dd, *J* = 10.2, 4.8 Hz, 2H), 7.57 (dd, *J* = 6.0, 3.9 Hz, 1H), 7.33 – 7.21 (m, 3H), 6.64 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.30 (d, *J* = 4.3 Hz, 1H), 3.98 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.5, 153.8, 148.6, 136.1, 133.4, 133.2, 132.6, 130.4, 129.6, 128.9, 128.5, 128.4, 126.0, 124.2, 115.5, 106.1, 60.2; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{19}H_{15}N_2O_2S^+$, 335.0849(100.0%), Found 335.0842 (100%).

**3-(5-Methoxythiophen-2-yl)quinoxalin-2(1*H*)-one (3q)**



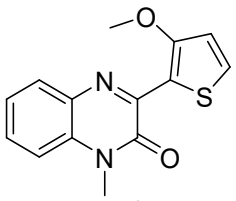
**3q**

Purified by dichloromethane: methanol = 30:1.

40 mg; 78% (0.3 mmol scale); yellow solid; m.p. 208–210 °C.

**$^1$H NMR** (400 MHz, DMSO) δ 12.60 (s, 1H), 8.18 (d, *J* = 4.3 Hz, 1H), 7.69 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.45 (ddd, *J* = 8.3, 7.1, 1.4 Hz, 1H), 7.36 – 7.22 (m, 2H), 6.45 (d, *J* = 4.3 Hz, 1H), 3.96 (s, 3H); **$^{13}$C NMR** (101 MHz, DMSO) δ 171.7, 154.0, 148.9, 132.5, 132.3, 131.4, 129.4, 128.0, 125.9, 124.1, 115.7, 106.2, 60.7; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{13}H_{11}N_2O_2S^+$, 259.0536 (100.0%), Found 259.0532 (100%).

**3-(3-Methoxythiophen-2-yl)-1-methylquinoxalin-2(1*H*)-one (3r)**



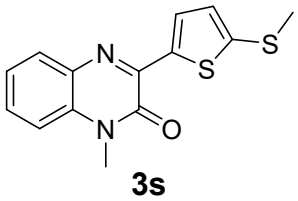
**3r**

Purified by petroleum ether: ethyl acetate = 10:1.

26 mg; 49% (0.2 mmol scale); yellow solid; m.p. 136–138 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.48 (d, *J* = 5.8 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 5.6 Hz, 1H), 4.05 (s, 3H), 3.77 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.1, 154.2, 149.4, 133.6, 131.9, 130.7, 130.0, 129.3, 124.0, 115.5, 113.7, 113.5, 59.3, 29.6; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{14}H_{13}N_2O_2S^+$, 273.0692 (100.0%), Found 273.0689 (100%).

**1-Methyl-3-(5-(methylthio)thiophen-2-yl)quinoxalin-2(1*H*)-one (3s)**



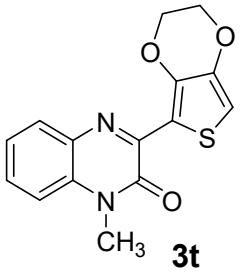
**3s**

Purified by petroleum ether: ethyl acetate = 10:1.

41 mg; 72% (0.2 mmol scale); yellow solid; m.p. 139–141 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 4.0 Hz, 1H), 7.86 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.36 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 1H), 7.32 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.03 (d, *J* = 4.0 Hz, 1H), 3.78 (s, 3H), 2.63 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.7, 147.6, 145.9, 138.9, 133.3, 132.5, 132.2, 129.8, 129.6, 128.1, 124.1, 113.6, 29.3, 20.1; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{14}H_{13}N_2OS_2^+$, 289.0464 (100.0%), Found 289.0464 (100%).

**3-(7-Methoxy-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-1-methylquinoxalin-2(1*H*)-one (3t)**



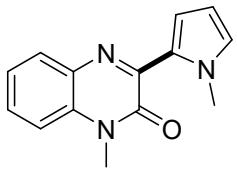
**3t**

Purified by petroleum ether: ethyl acetate = 10:1.

38 mg; 63% (0.2 mmol scale); yellow solid; m.p. 255–258 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.54–7.46 (m, 1H), 7.41–7.33 (m, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 6.68 (s, 1H), 4.54–4.42 (m, 2H), 4.37–4.27 (m, 2H), 3.78 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.9, 148.4, 144.4, 141.5, 133.4, 131.6, 129.8, 129.3, 123.9, 113.4, 112.1, 107.5, 65.3, 64.0, 29.4; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{15}H_{13}N_2O_3S^+$, 301.0641 (100.0%), Found 301.0632 (100%).

**1-Methyl-3-(1-methyl-1*H*-pyrrol-2-yl)quinoxalin-2(1*H*)-one (3aa)**



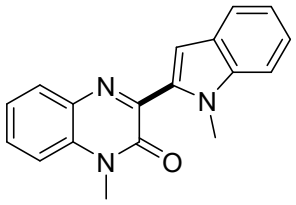
**3aa**

Purified by petroleum ether: ethyl acetate = 10:1.

5 mg; 10% (0.2 mmol scale); yellow solid; m.p. 150–152 °C.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.68 (dd, *J* = 4.0, 1.8 Hz, 1H), 7.47 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.35 – 7.27 (m, 2H), 6.86 (t, *J* = 2.2 Hz, 1H), 6.24 (dd, *J* = 4.0, 2.6 Hz, 1H), 4.10 (s, 3H), 3.75 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 154.1, 147.3, 132.9, 132.2, 129.9, 129.3, 128.8, 127.9, 123.6, 119.5, 113.6, 108.2, 77.5, 77.2, 76.8, 38.6, 29.4; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{14}H_{14}N_3O^+$, 240.1131 (100.0%), Found 240.1127 (100%).

**1-Methyl-3-(1-methyl-1*H*-indol-2-yl)quinoxalin-2(1*H*)-one (3ab)**



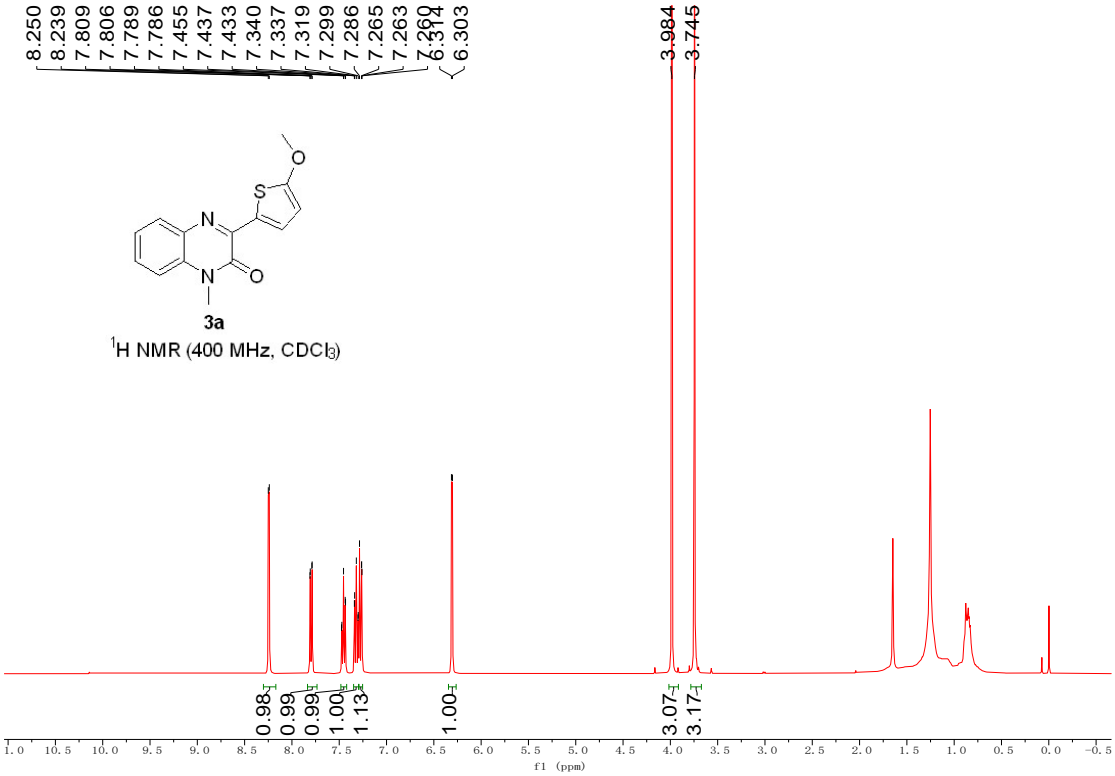
**3ab**

Purified by petroleum ether: ethyl acetate = 10:1.

12 mg; 21% (0.2 mmol scale); yellow solid; m.p. 241–243 °C.

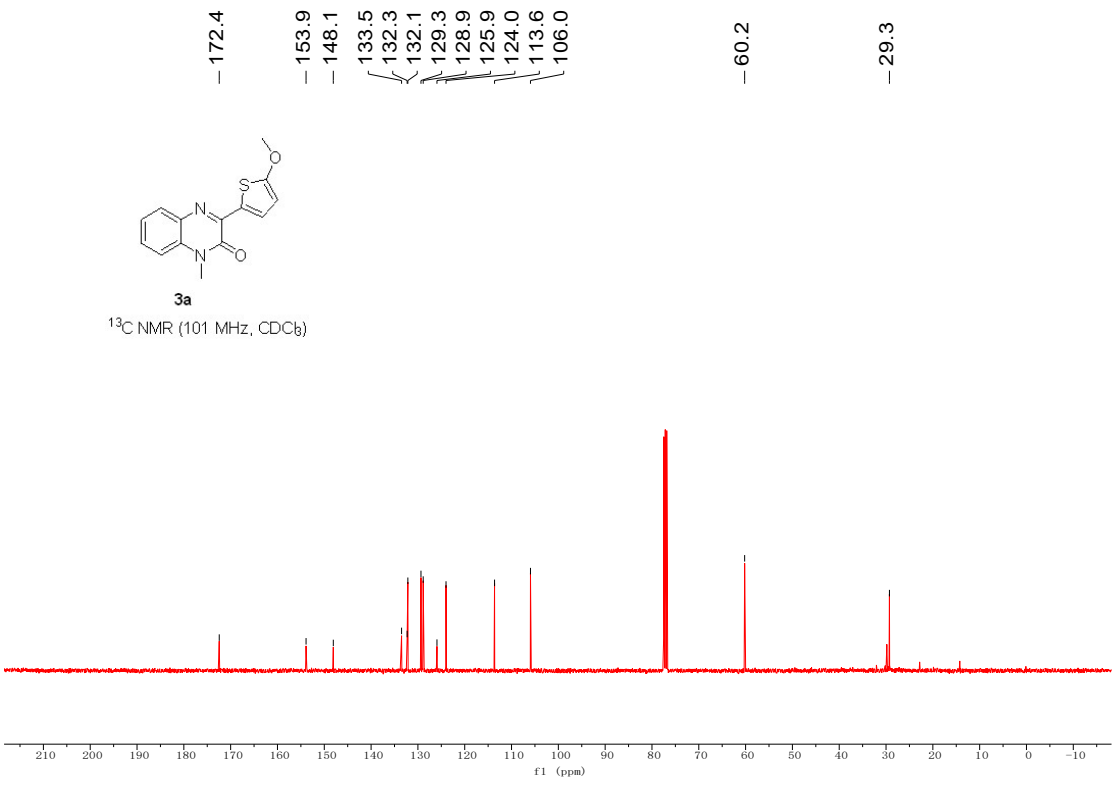
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.03 (dd, *J* = 7.0, 2.2 Hz, 1H), 8.84 (s, 1H), 7.98 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.36 (dq, *J* = 7.2, 3.6 Hz, 4H), 7.30 – 7.27 (m, 1H), 3.87 (s, 3H), 3.77 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 154.6, 150.8, 137.1, 136.7, 133.9, 131.6, 129.3, 128.1, 127.5, 123.7, 123.6, 122.9, 121.6, 113.4, 111.4, 109.4, 33.4, 29.2; **HR-MS** (ESI): Calculated $[M + H]^+$ for $C_{18}H_{16}N_3O^+$, 290.1288 (100.0%), Found 290.1285 (100%).

# 9. Copies of NMR spectra



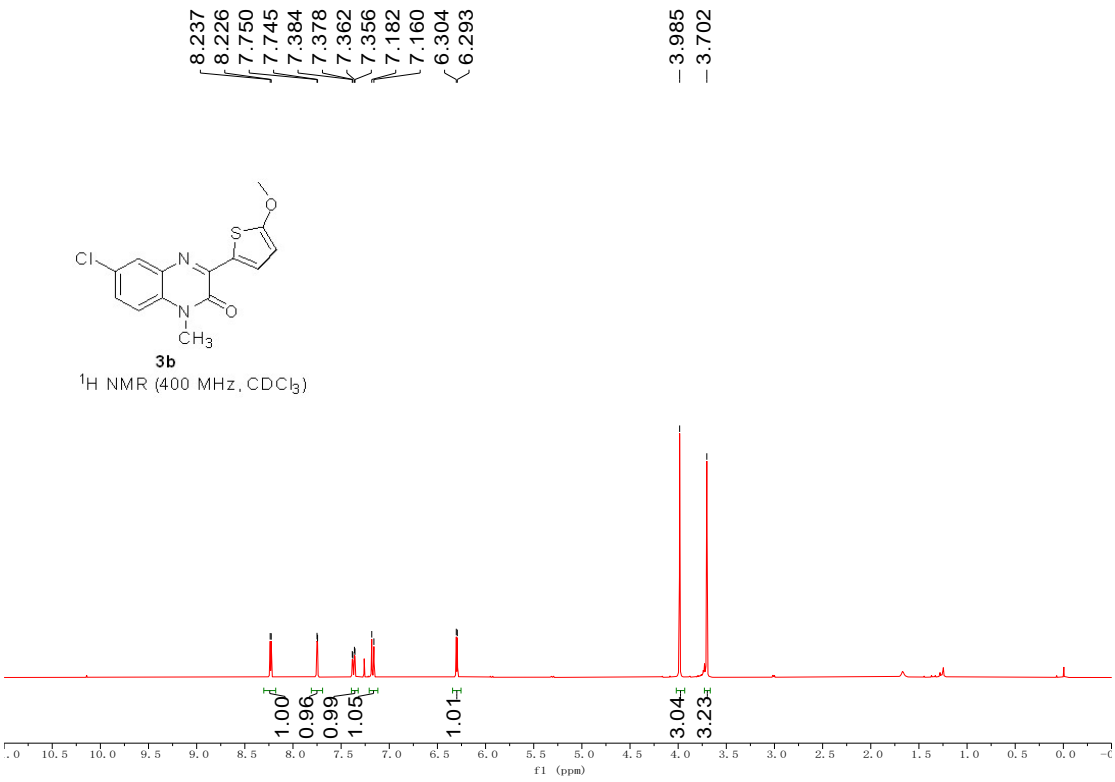

**3a**

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



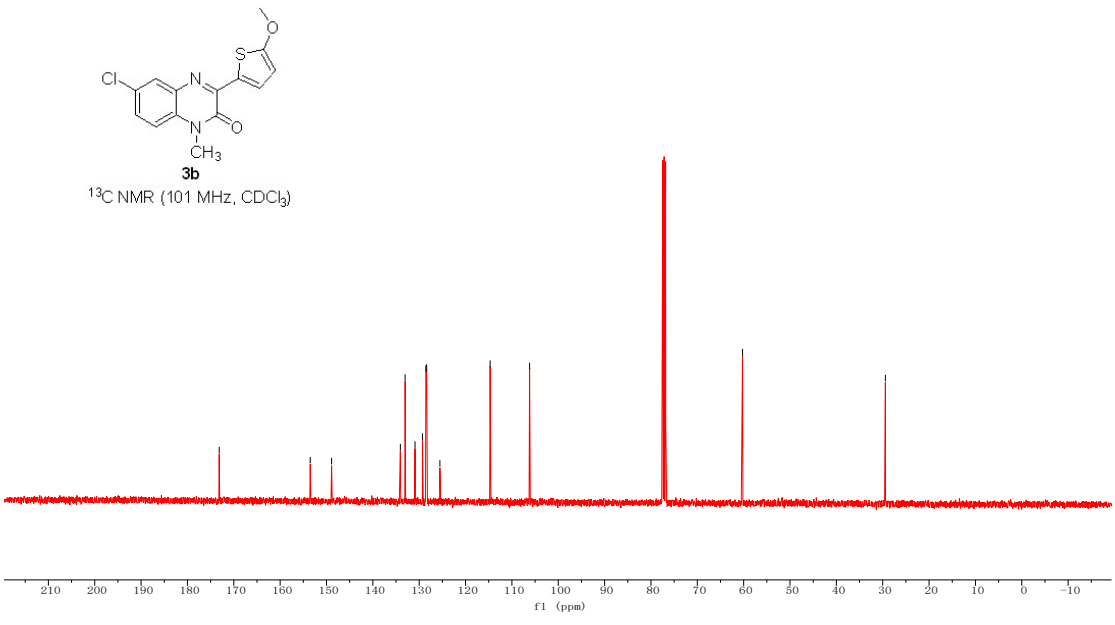

**3a**

$^{13}$C NMR (101 MHz, $CDCl_3$)



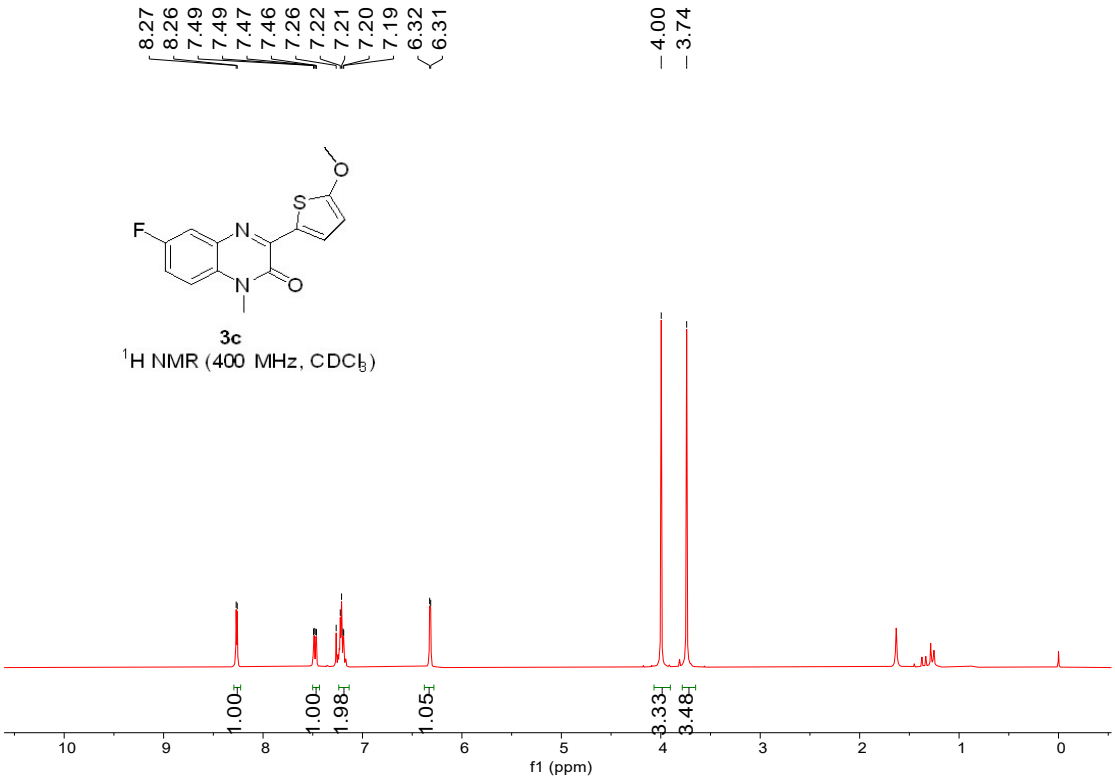

**3b**

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



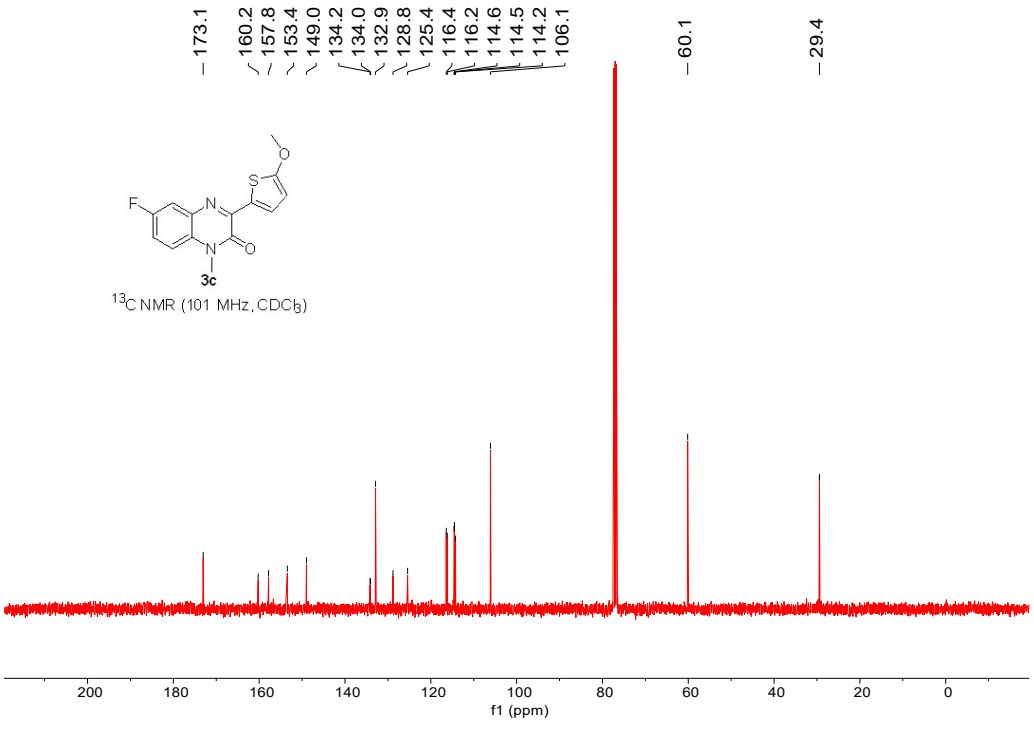

**3b**

$^{13}$C NMR (101 MHz, $CDCl_3$)




**3c**

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

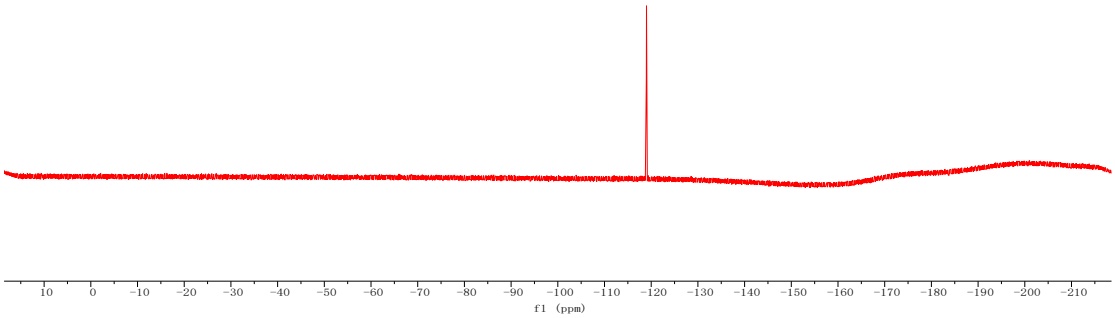



**3c**

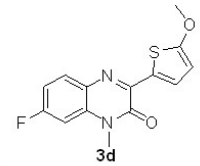
$^{13}$C NMR (101 MHz, $CDCl_3$)


**3c**

$^{19}$F NMR (376 MHz, $CDCl_3$)

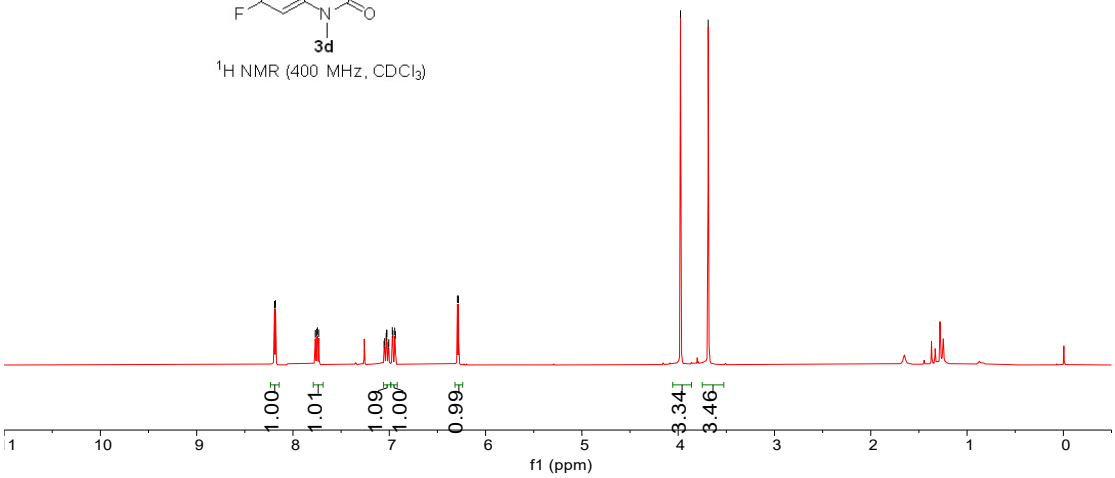




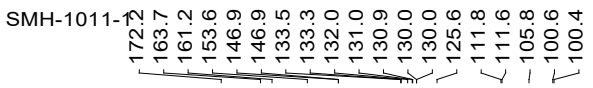


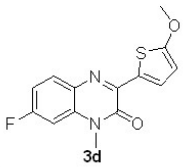

**3d**

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



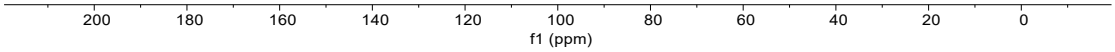
SMH-1011-1



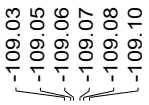



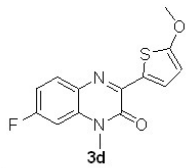

**3d**

$^{13}$C NMR (101 MHz, $CDCl_3$)



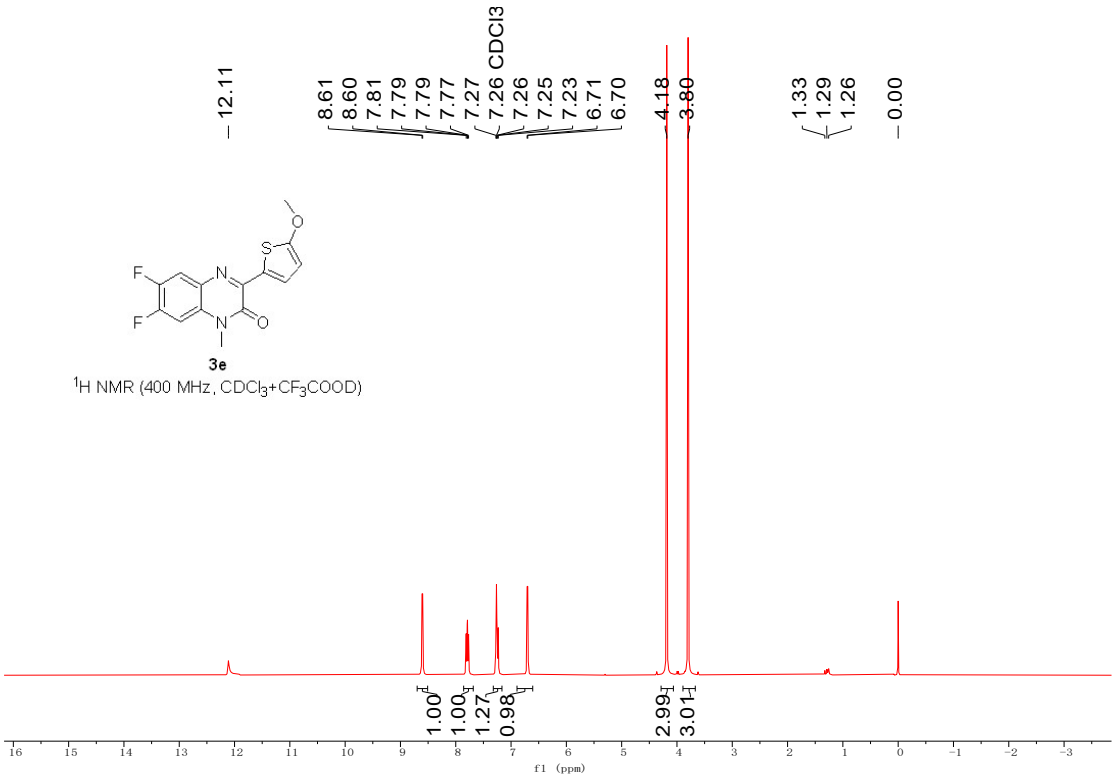

zq-7F.1.fid




**3d**

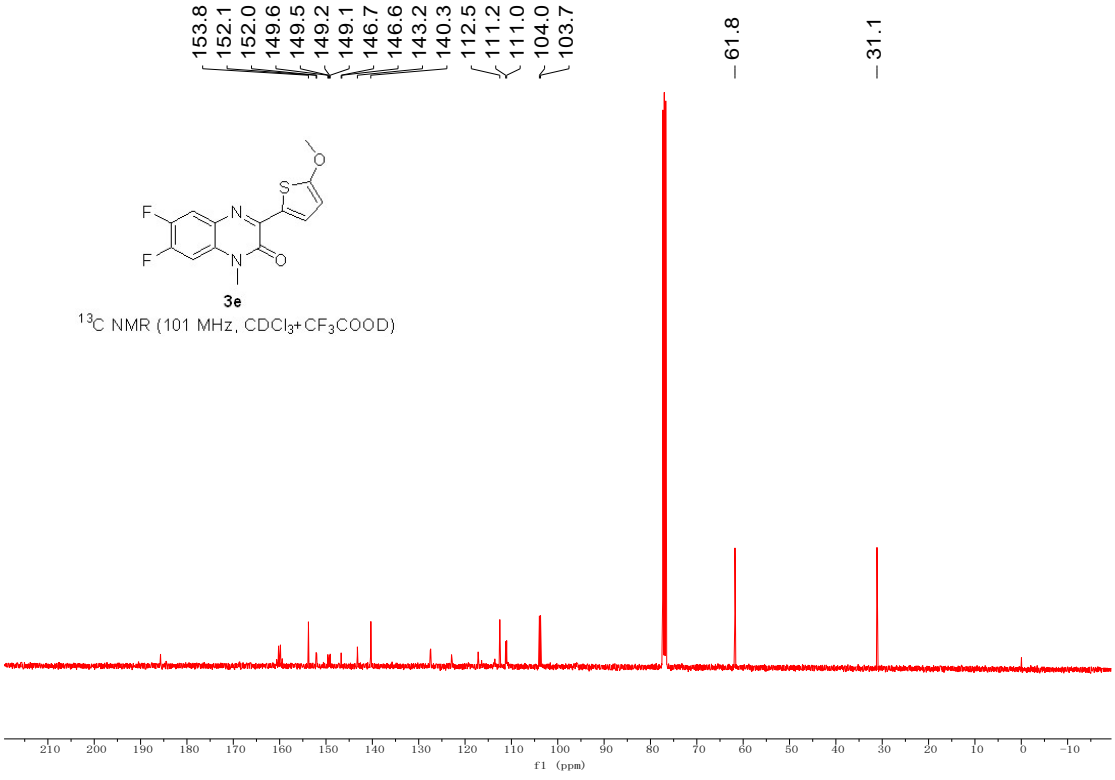
$^{19}$F NMR (376 MHz, $CDCl_3$)






**3e**

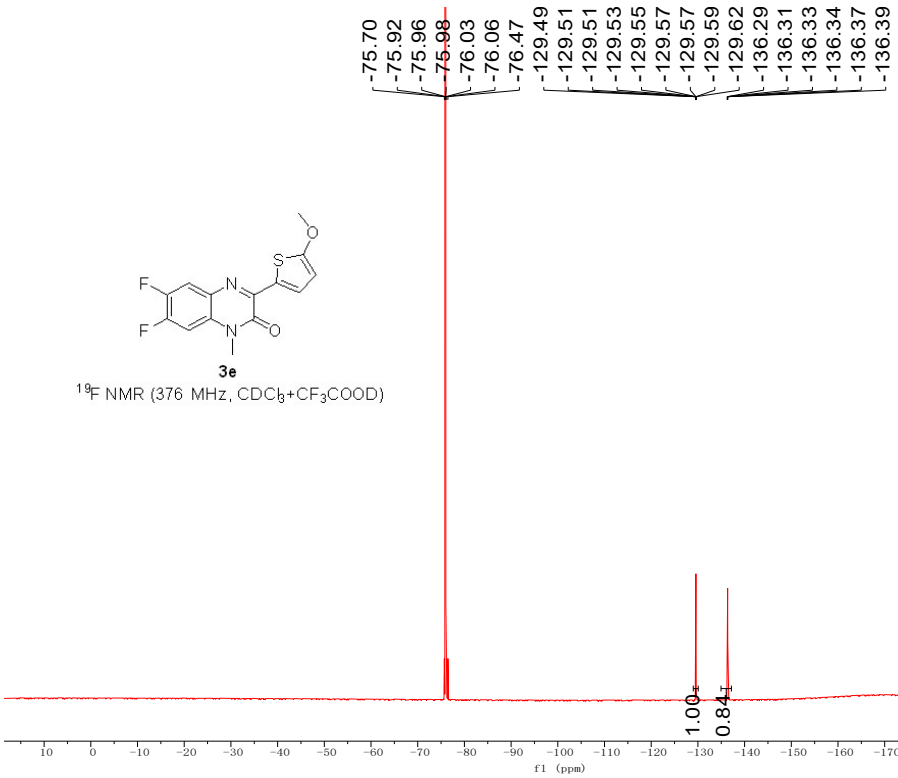
$^{1}$H NMR (400 MHz, $CDCl_3$+$CF_3COOD$)






**3e**

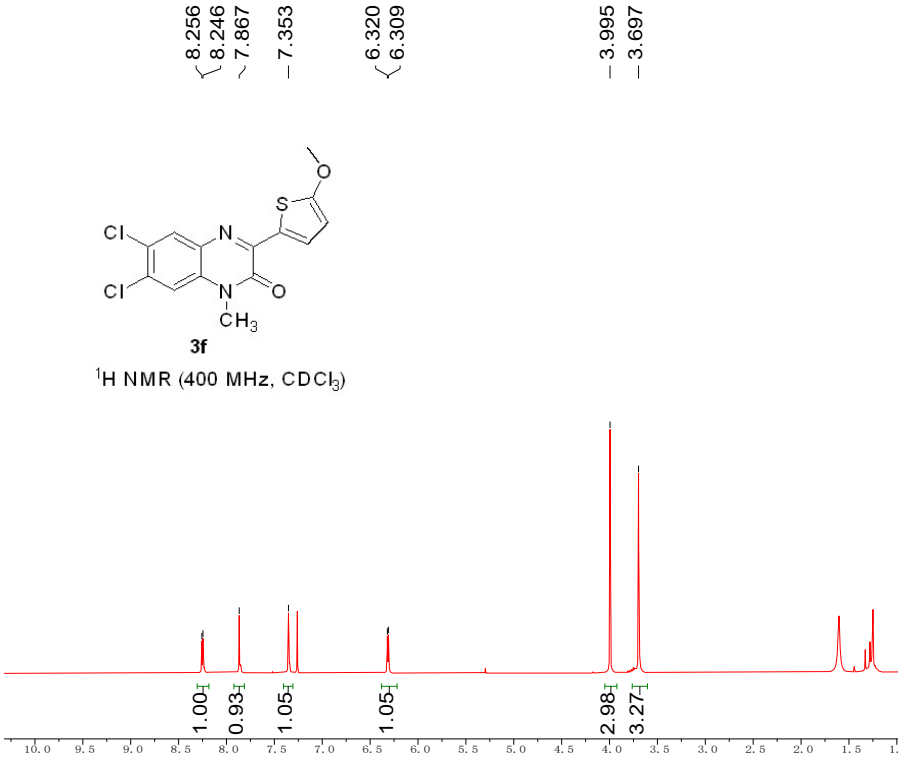
$^{13}$C NMR (101 MHz, $CDCl_3$+$CF_3COOD$)






**3e**

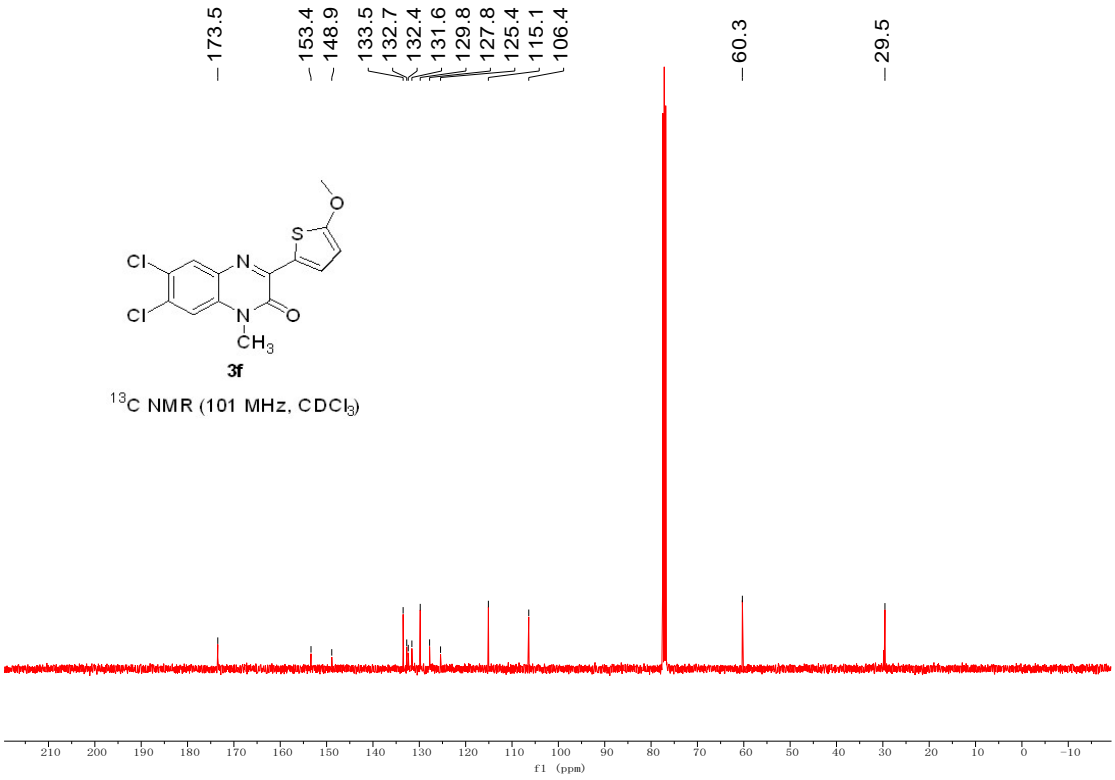
$^{19}$F NMR (376 MHz, $CDCl_3$+$CF_3COOD$)





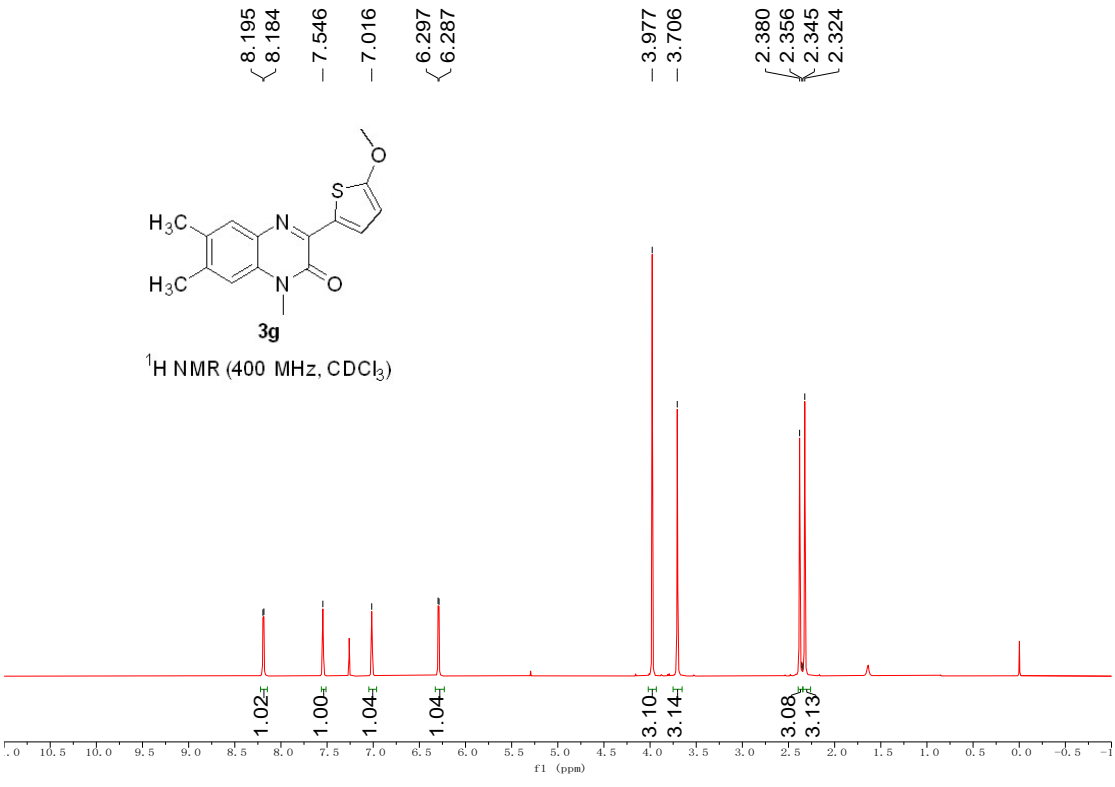

**3f**

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



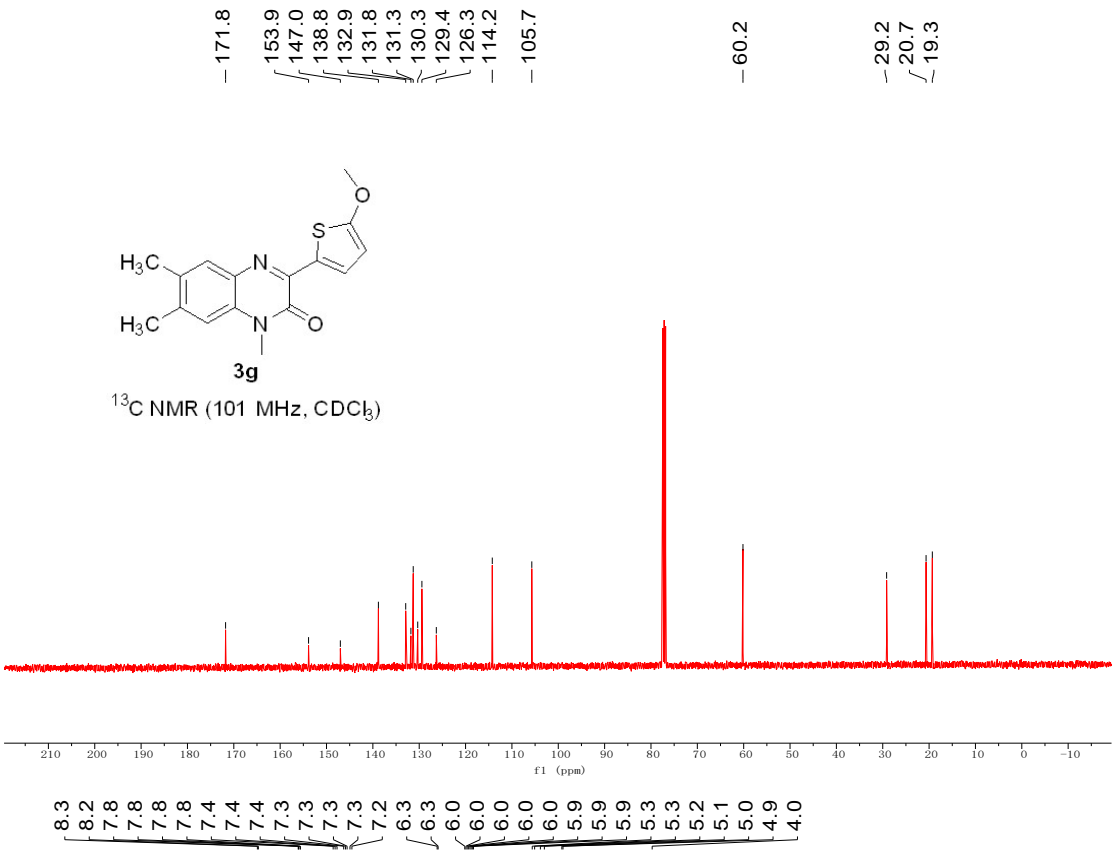

**3f**

$^{13}$C NMR (101 MHz, $CDCl_3$)



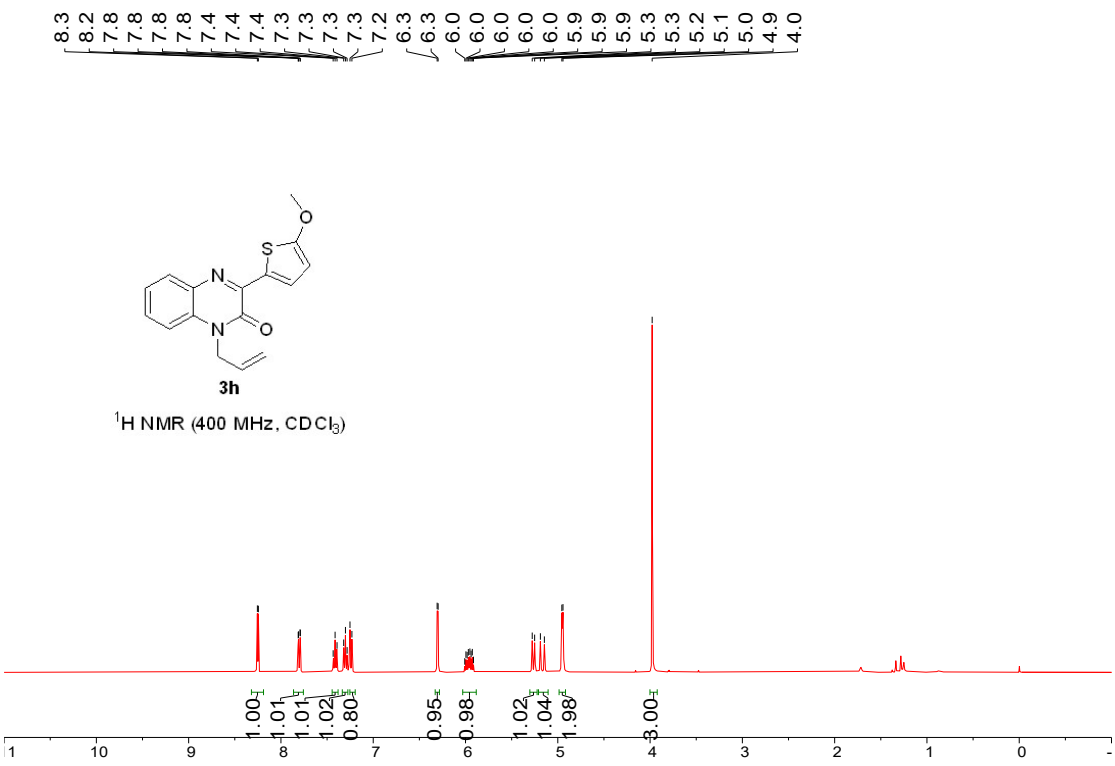

**3g**

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



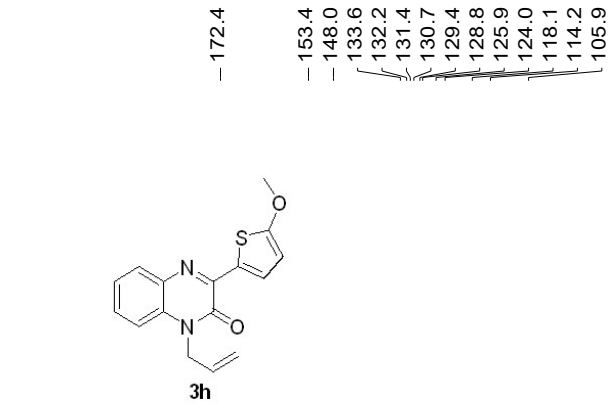

**3g**

$^{13}$C NMR (101 MHz, $CDCl_3$)



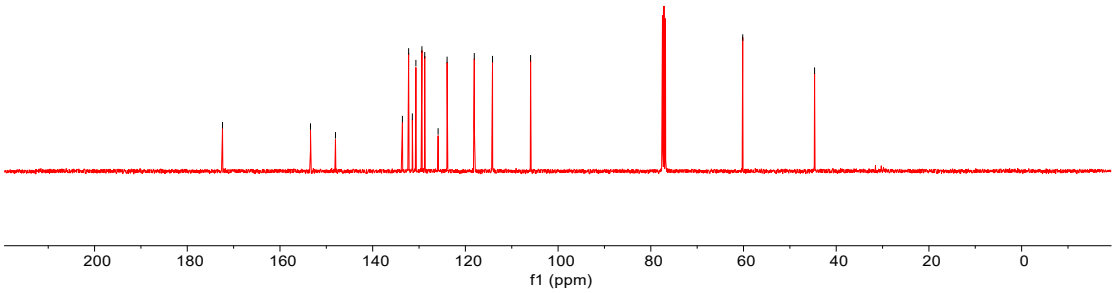

**3h**

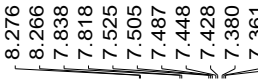
$^{1}$H NMR (400 MHz, $CDCl_3$)

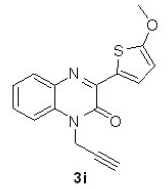



**3h**

$^{13}$C NMR (101 MHz, $CDCl_3$)

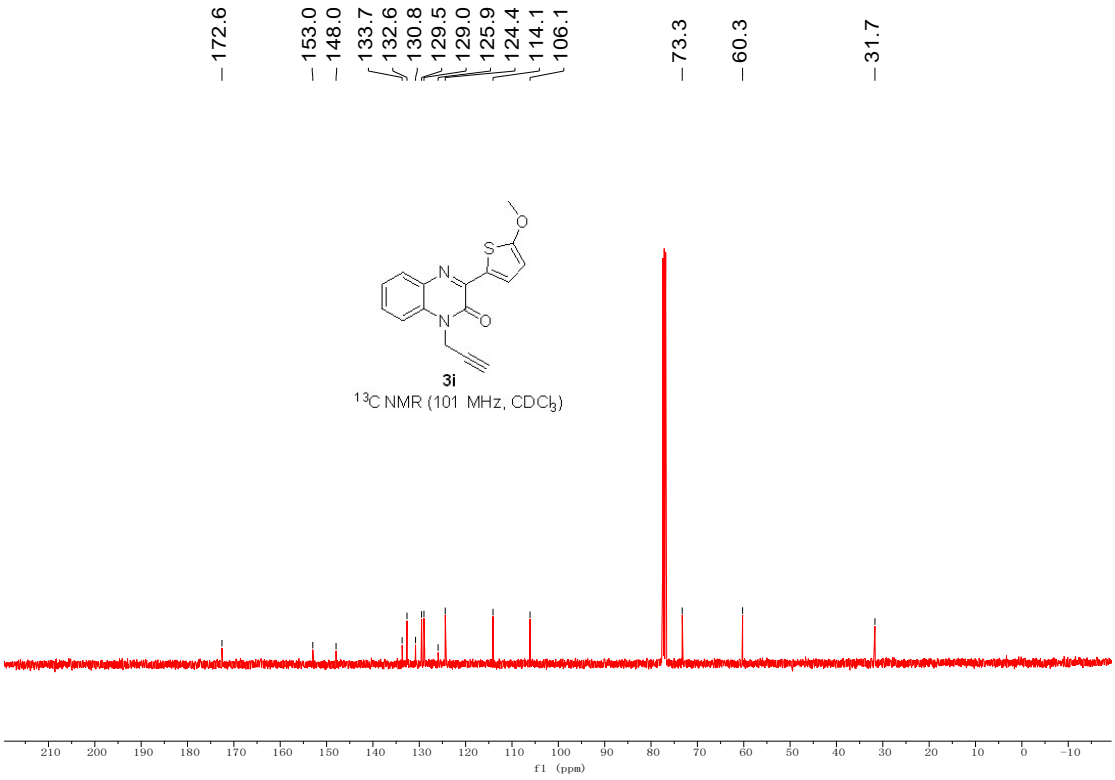


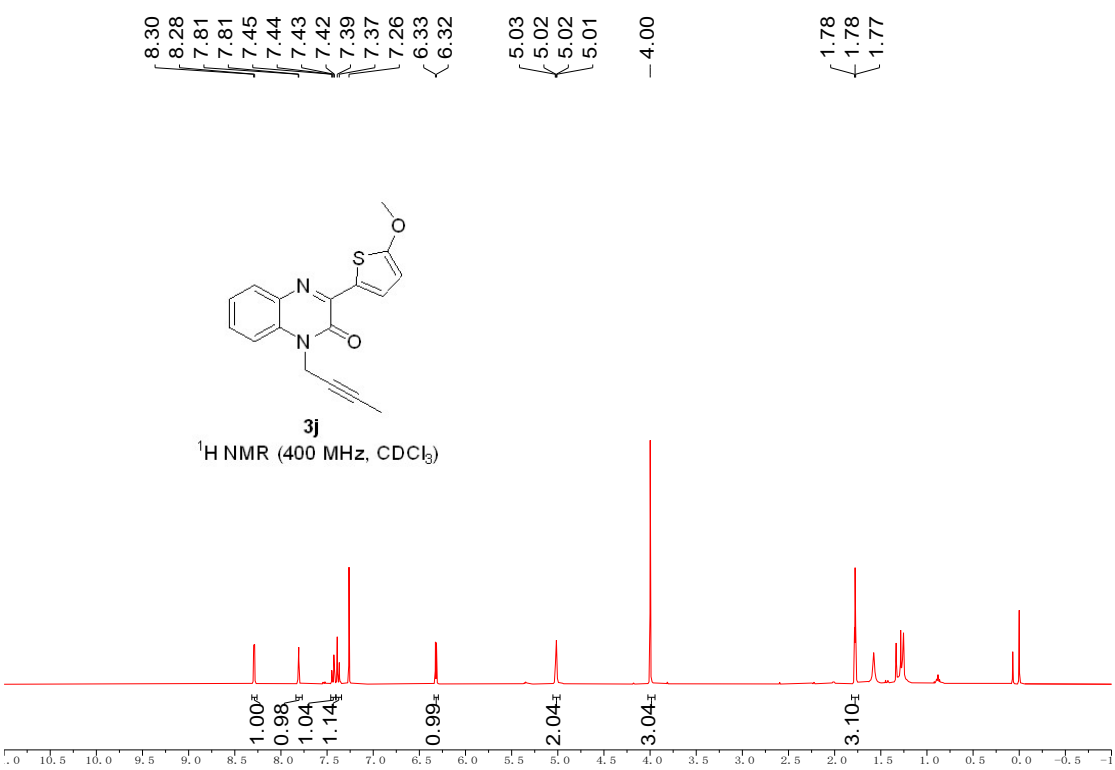

**3i**

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



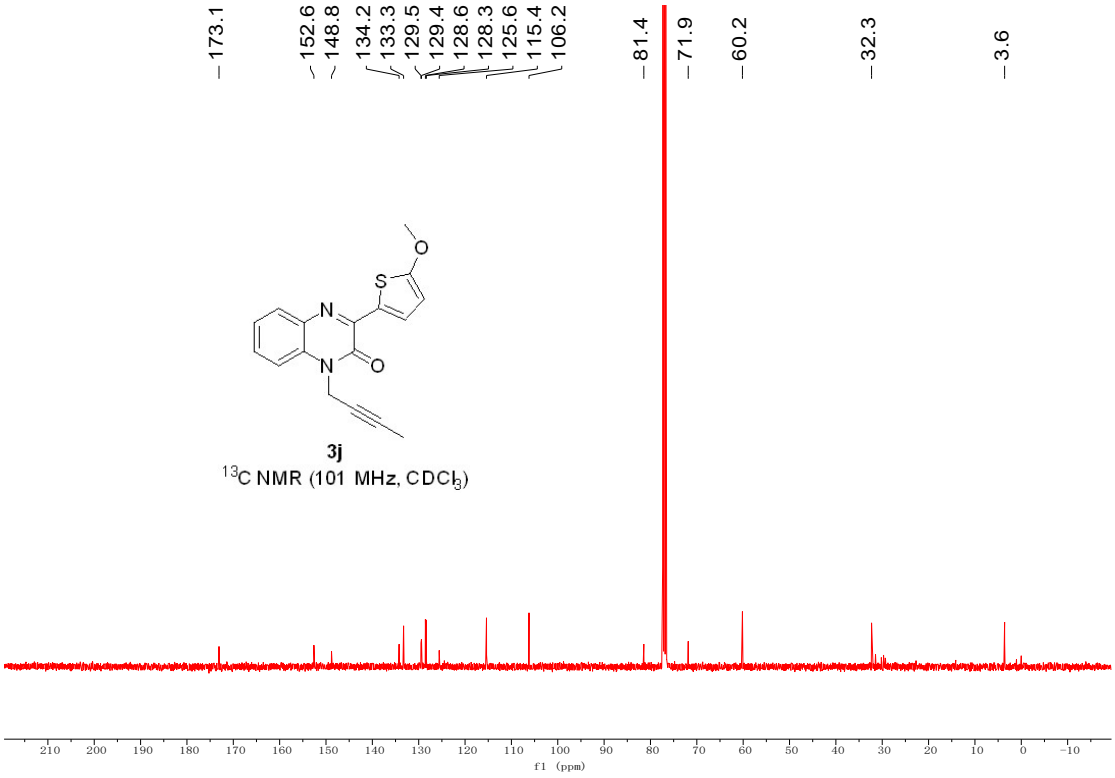

**3i**

$^{13}$C NMR (101 MHz, $CDCl_3$)



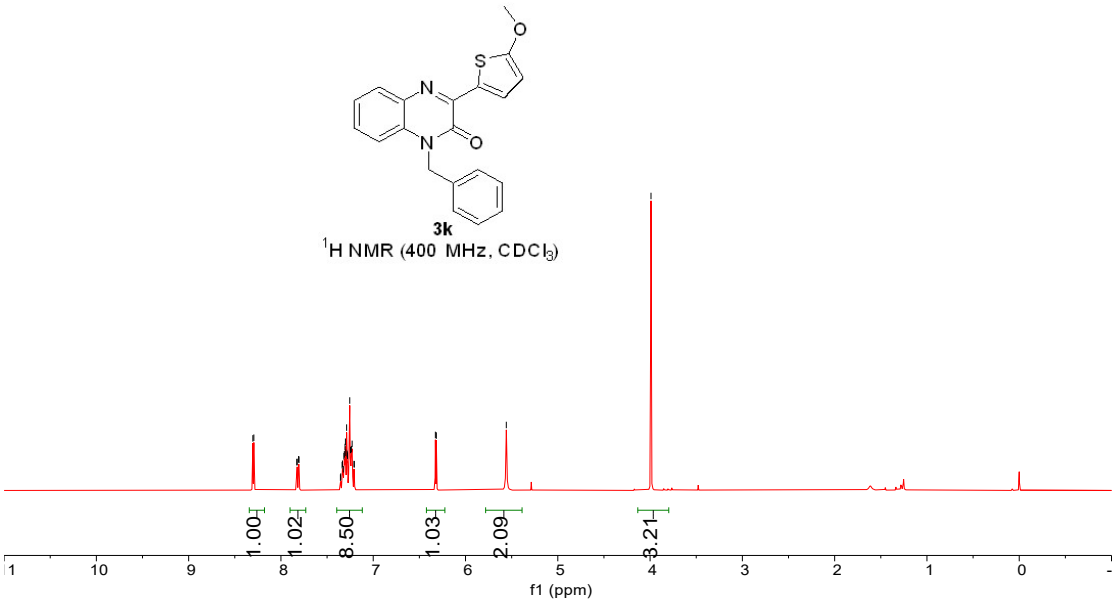

**3j**

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




**3j**

$^{13}$C NMR (101 MHz, $CDCl_3$)

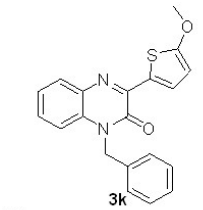




**3k**

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

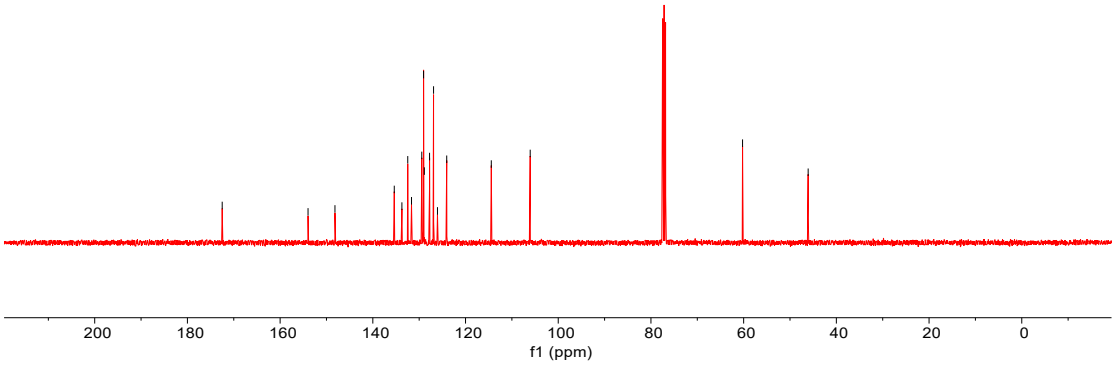
SMH1010-4

172.5
154.0
148.2
135.4
133.7
132.5
131.7
129.4
129.1
128.9
127.8
126.9
126.1
124.1
114.4
106.0
60.2
46.1

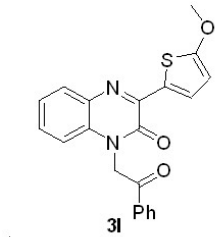


3k

$^{13}$C NMR (101 MHz, $CDCl_3$)

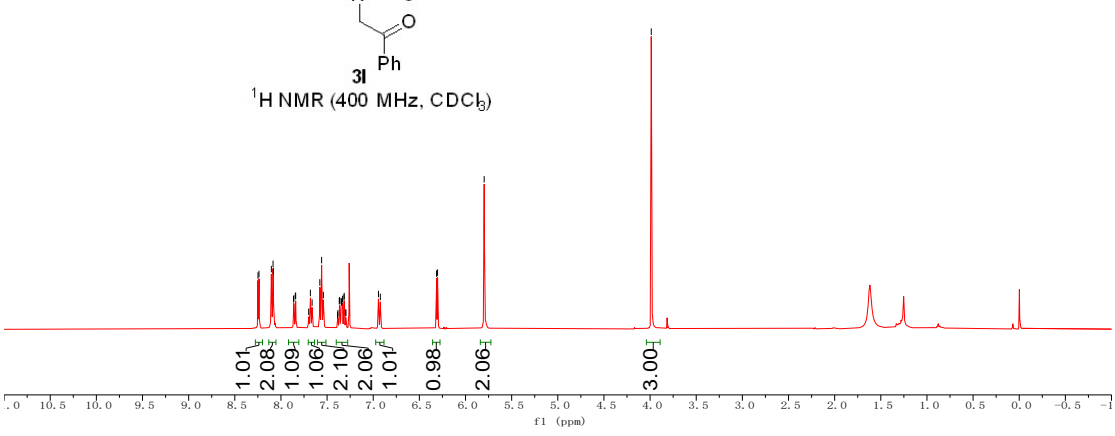


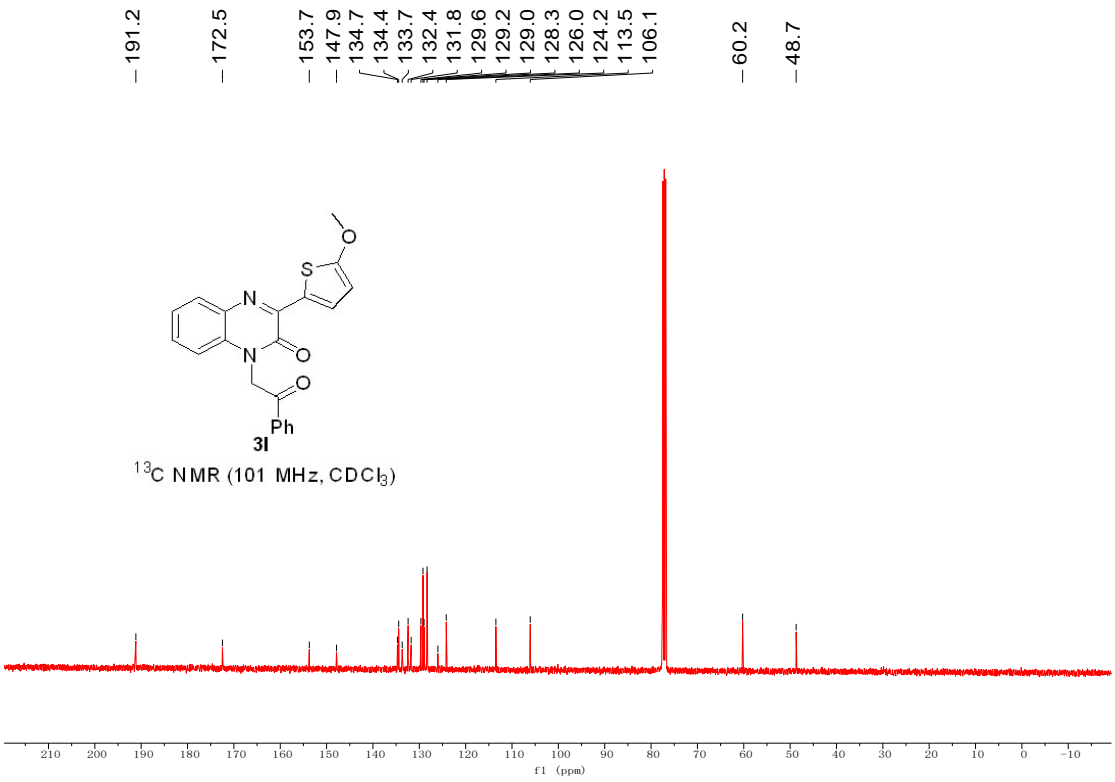

8.249
8.238
8.104
8.086
8.083
7.864
7.860
7.844
7.840
7.699
7.681
7.662
7.579
7.559
7.540
7.387
7.383
7.368
7.365
7.349
7.344
7.337
7.333
7.317
7.315
7.299
7.296
6.943
6.923
6.314
6.303
5.798
3.987

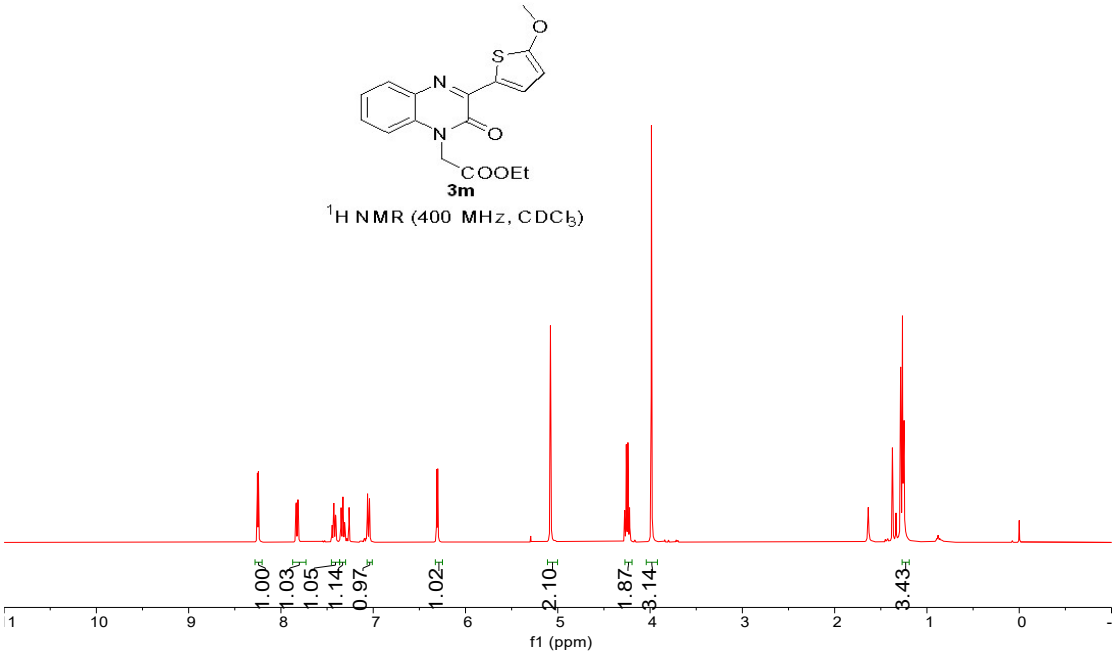


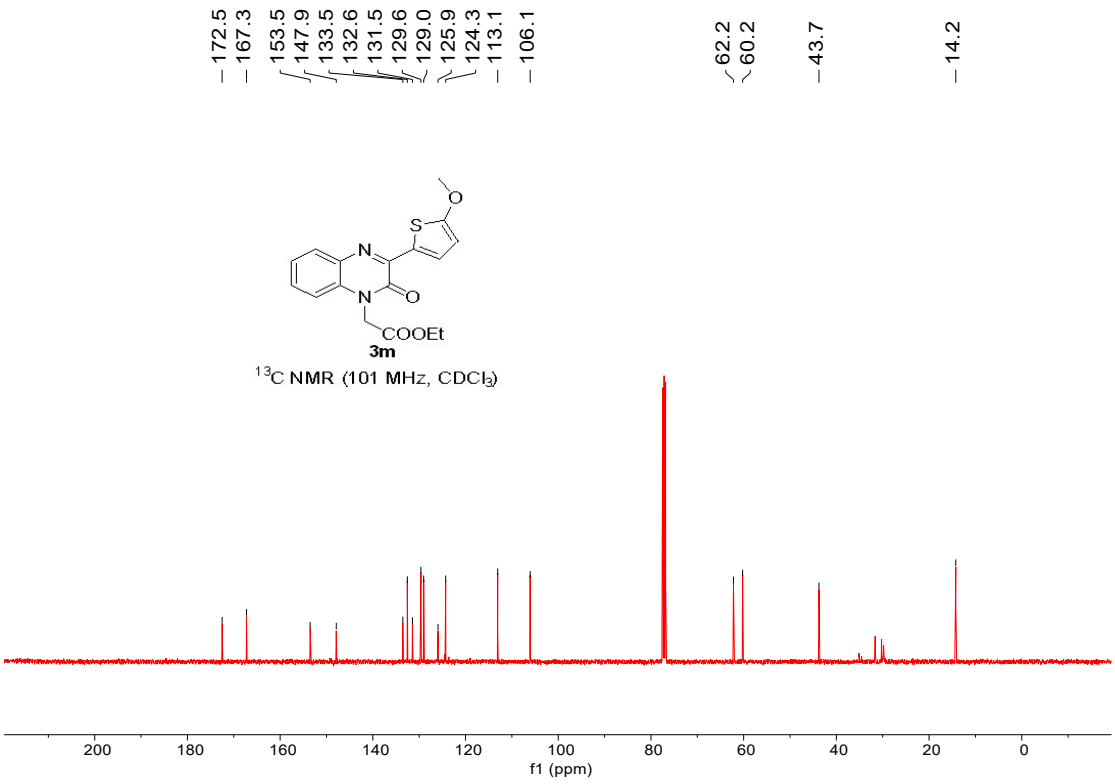
3l

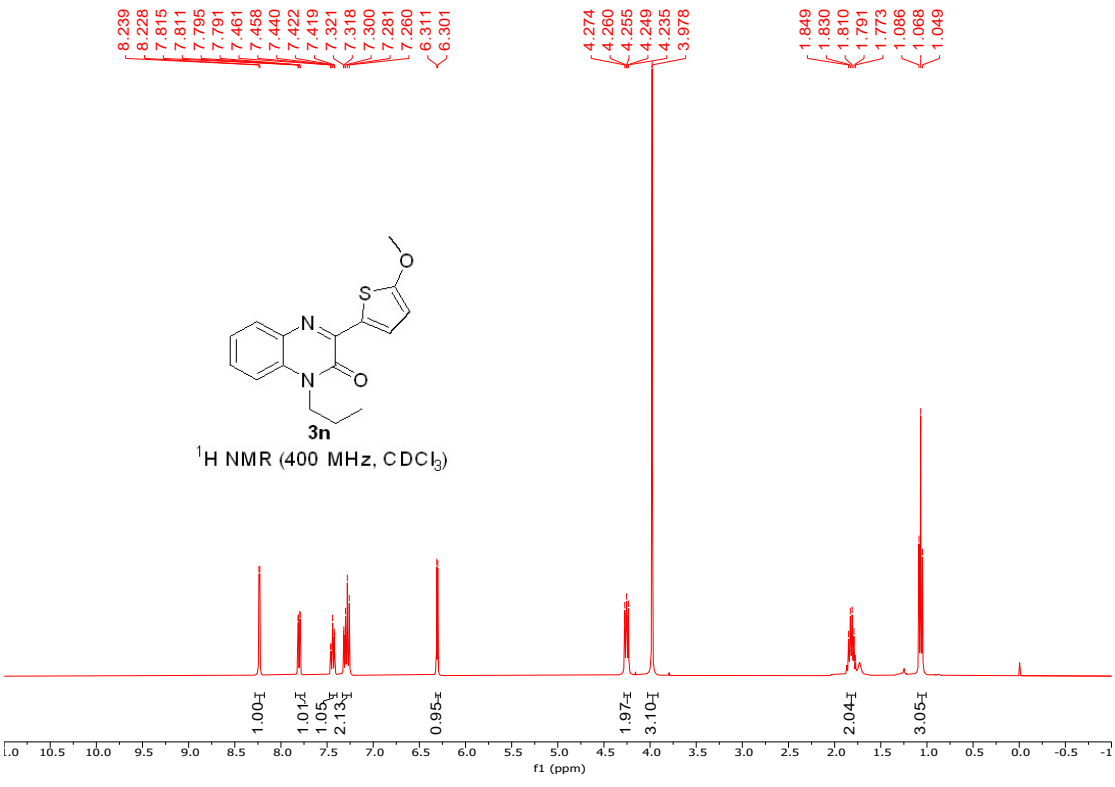
$^{1}$H NMR (400 MHz, $CDCl_3$)

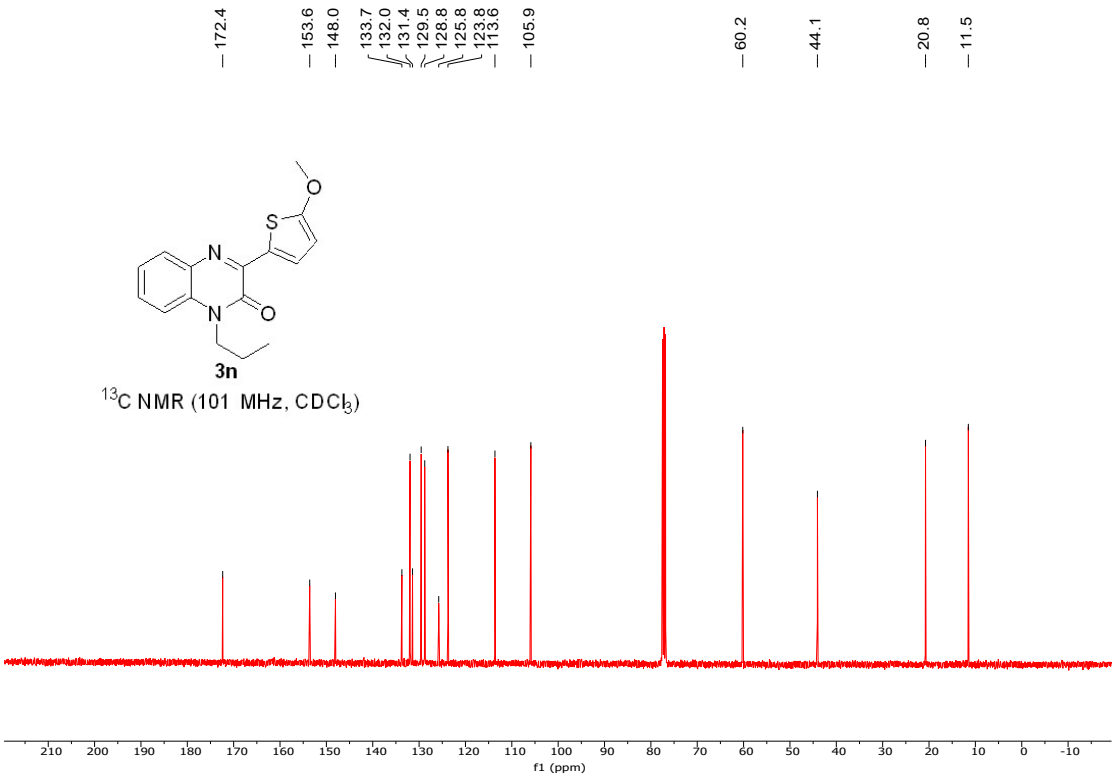


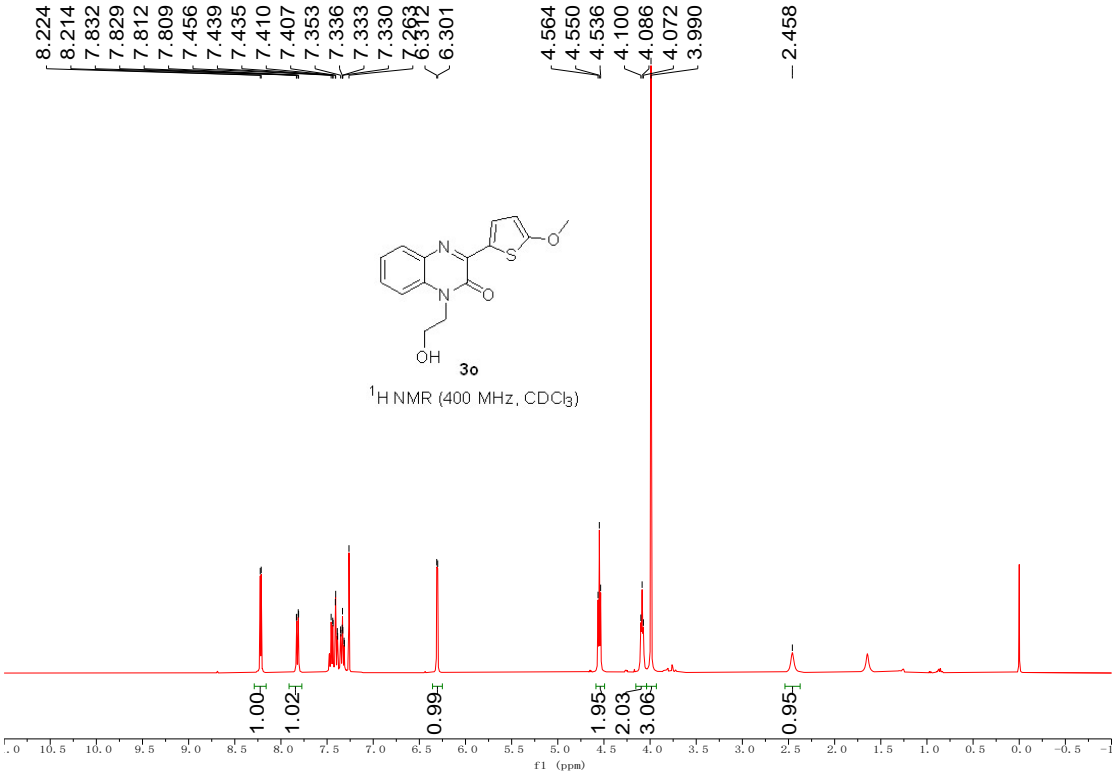

191.2
172.5
153.7
147.9
134.4
134.7
133.7
132.4
131.8
129.6
129.2
129.0
128.3
126.0
124.2
113.5
106.1
60.2
48.7
O
S
N
N
O
O
Ph
3l
13C NMR (101 MHz, CDCl3)
f1 (ppm)

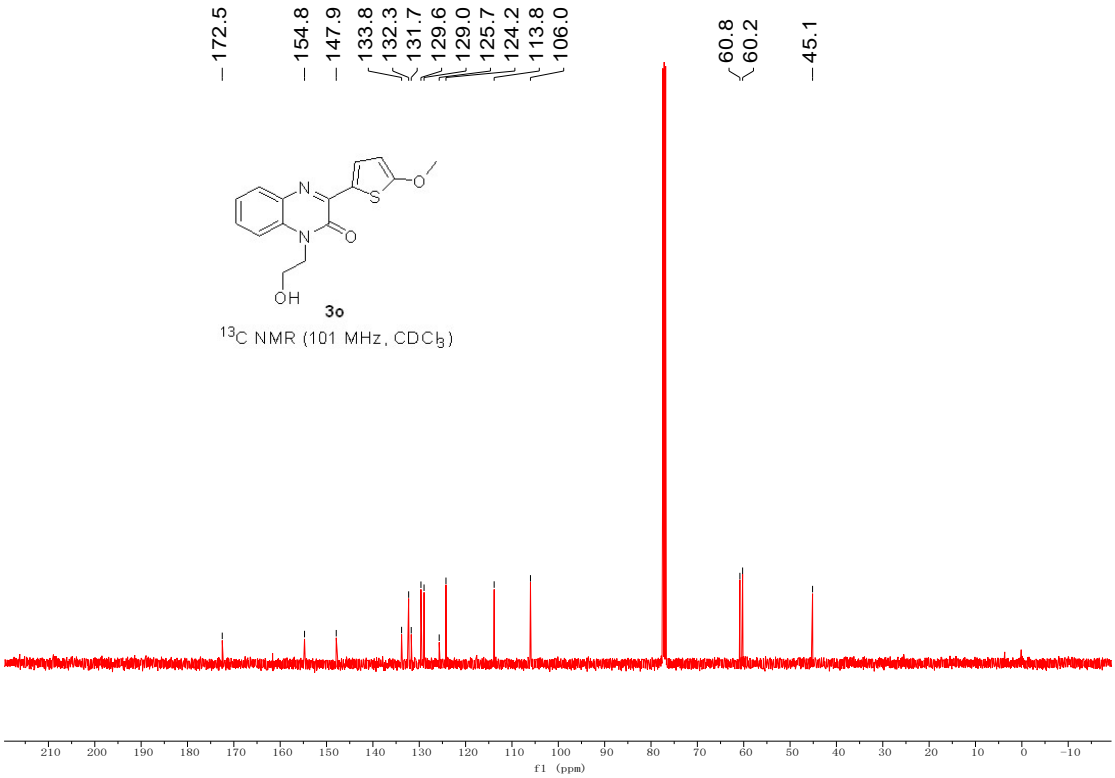

O
S
N
N
O
COOEt
3m
1H NMR (400 MHz, CDCl3)
1.00
1.03
1.05
1.14
0.97
1.02
2.10
1.87
3.14
3.43
f1 (ppm)


172.5
167.3
153.5
147.9
133.5
132.6
131.5
129.6
129.0
125.9
124.3
113.1
106.1
62.2
60.2
43.7
14.2
O
S
N
N
O
COOEt
3m
$^{13}$C NMR (101 MHz, CDCl$_3$)
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


8.239
8.228
7.815
7.811
7.795
7.791
7.461
7.458
7.440
7.422
7.419
7.321
7.318
7.300
7.281
7.260
6.311
6.301
4.274
4.260
4.255
4.249
4.235
3.978
1.849
1.830
1.810
1.791
1.773
1.086
1.068
1.049
O
S
N
N
O
3n
$^{1}$H NMR (400 MHz, CDCl$_3$)
1.00
1.01
1.05
2.13
0.95
1.97
3.10
2.04
3.05
f1 (ppm)

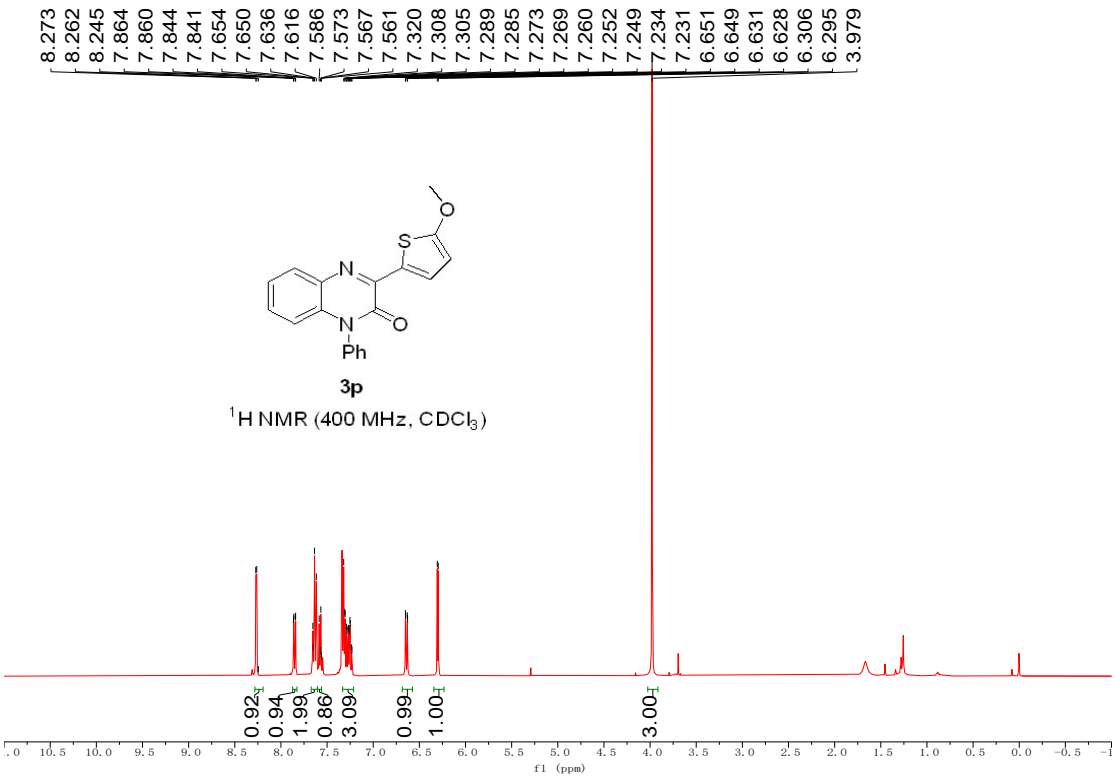

172.4
153.6
148.0
133.7
132.0
131.4
129.5
128.8
125.8
123.8
113.6
105.9
60.2
44.1
20.8
11.5
O
S
N
N
O
3n
13C NMR (101 MHz, CDCl3)
f1 (ppm)


8.224
8.214
7.832
7.829
7.812
7.809
7.456
7.439
7.435
7.410
7.407
7.353
7.336
7.333
7.330
6.312
6.301
4.564
4.550
4.536
4.100
4.086
4.072
3.990
2.458
N
S
O
N
O
OH
3o
1H NMR (400 MHz, CDCl3)
1.00
1.02
0.99
1.95
2.03
3.06
0.95
f1 (ppm)



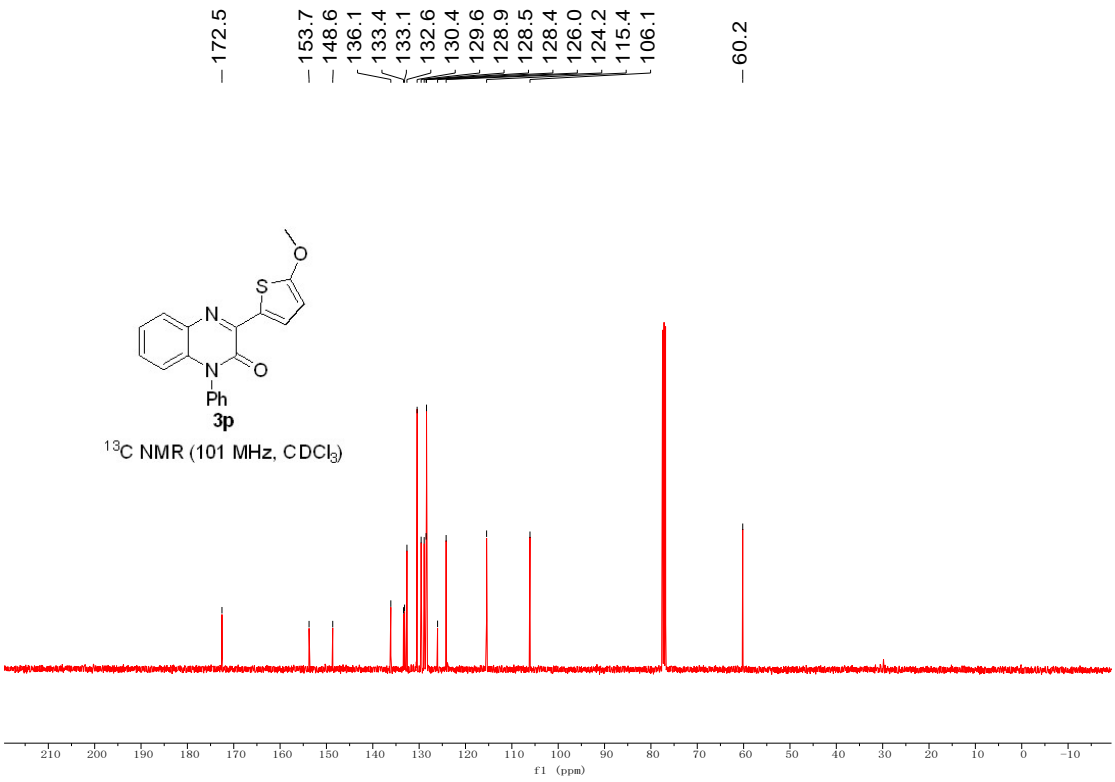

**3o**

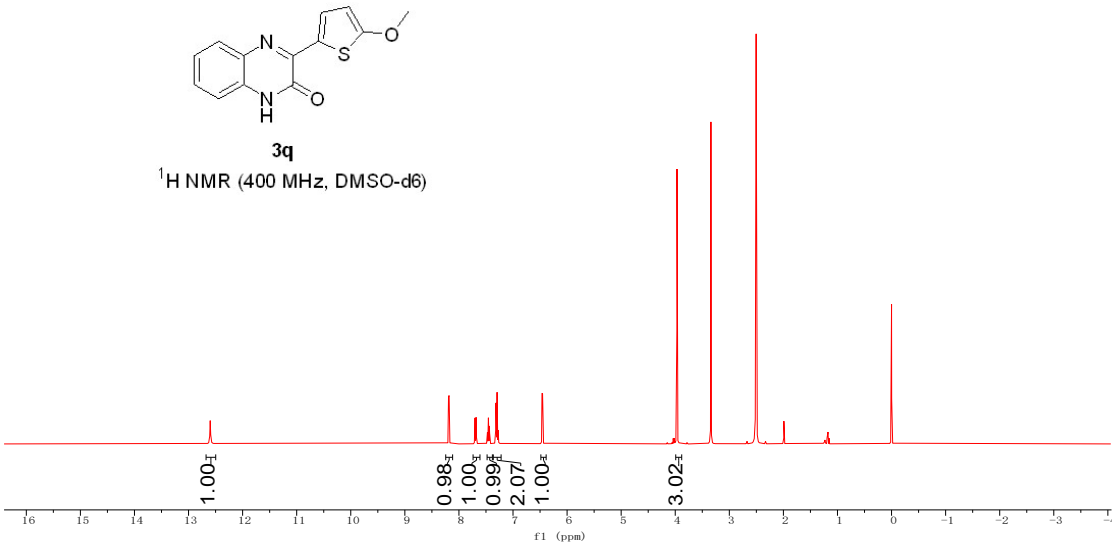
$^{13}$C NMR (101 MHz, $CDCl_3$)

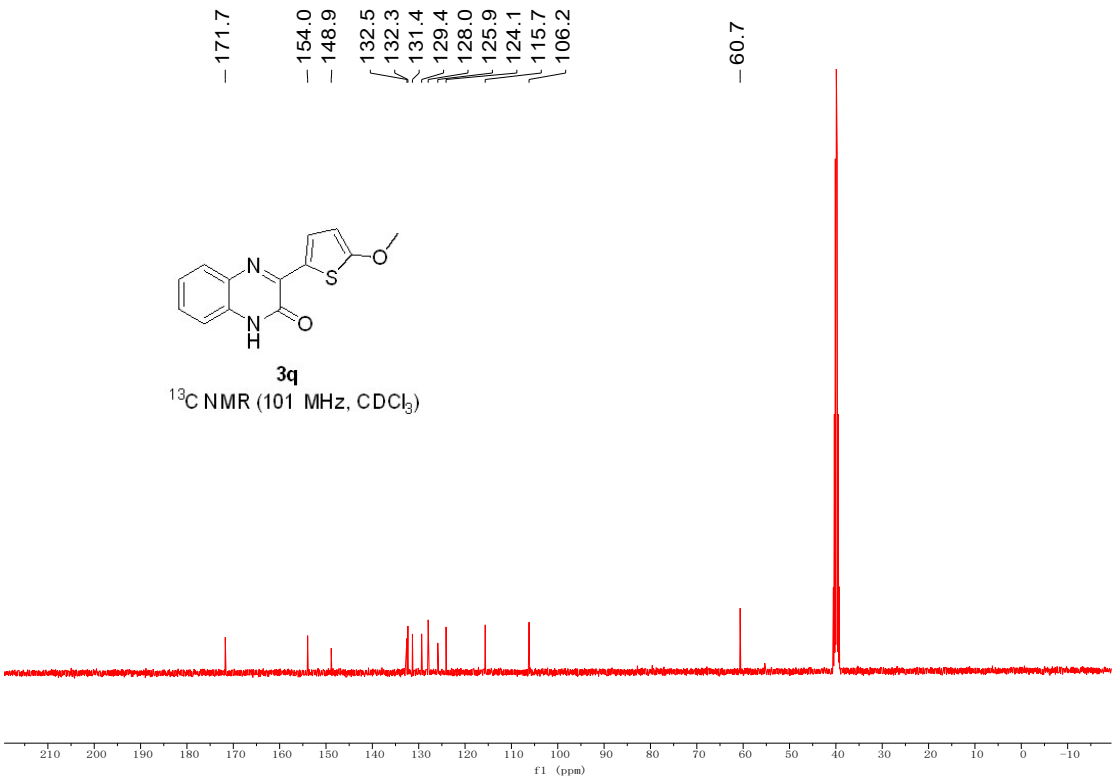



**3p**

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

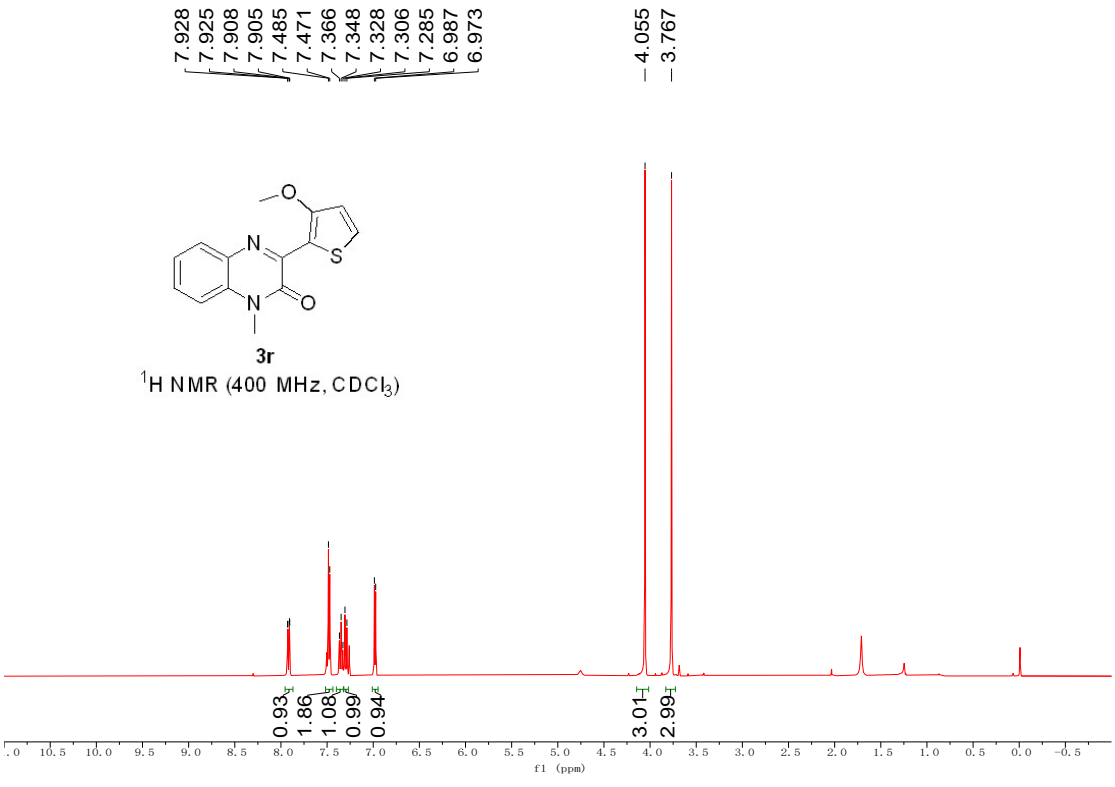

172.5
153.7
148.6
136.1
133.4
133.1
132.6
130.4
129.6
128.9
128.5
128.4
126.0
124.2
115.4
106.1
60.2
O
S
N
N
O
Ph
3p
13C NMR (101 MHz, CDCl3)
f1 (ppm)


N
S
O
N
H
O
3q
1H NMR (400 MHz, DMSO-d6)
1.00
0.98
1.00
0.99
2.07
1.00
3.02
f1 (ppm)



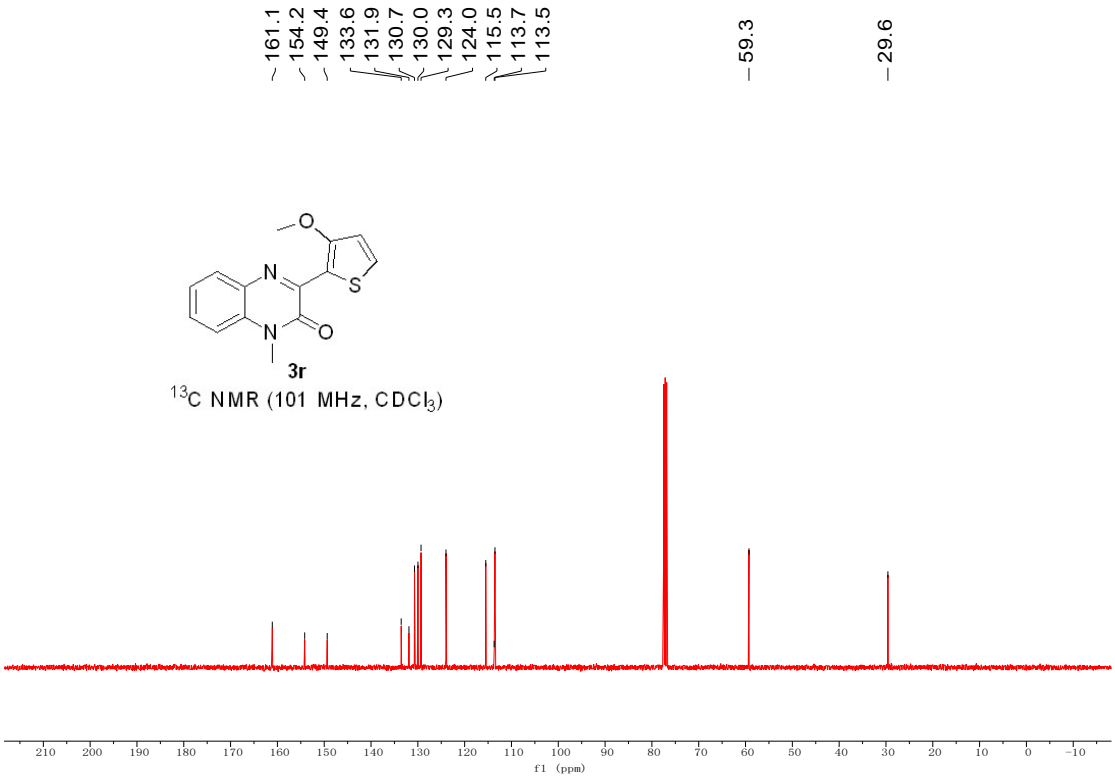

**3q**

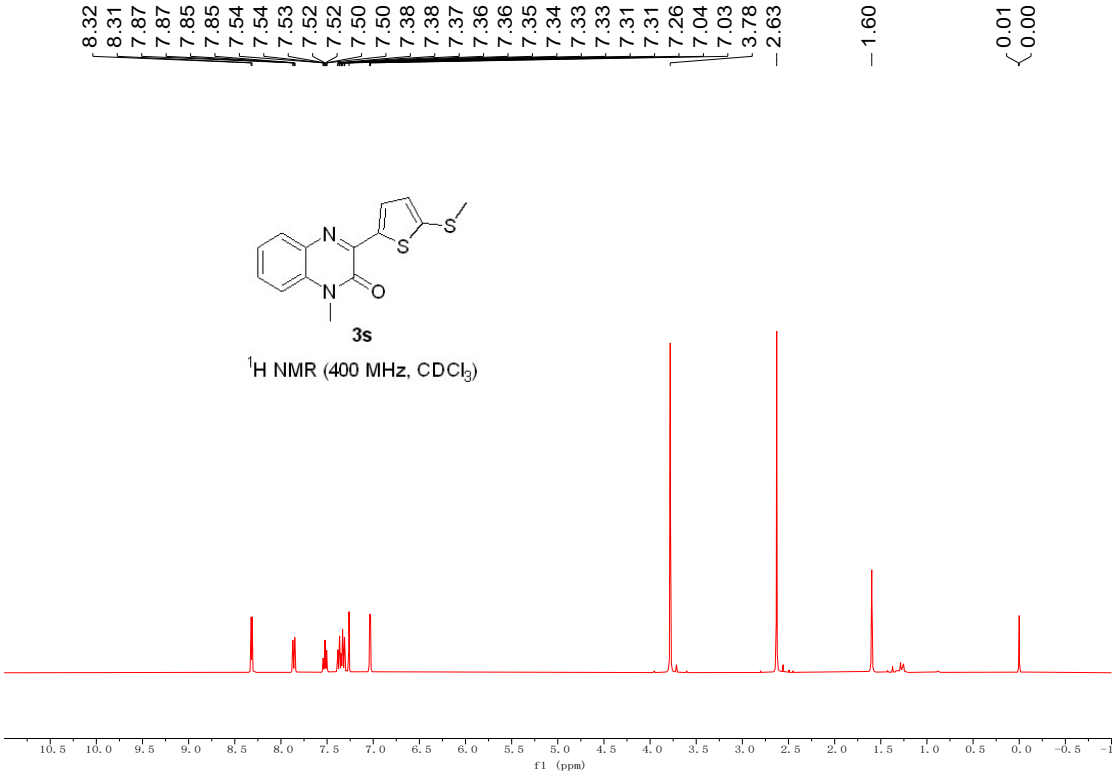
$^{13}$C NMR (101 MHz, $CDCl_3$)

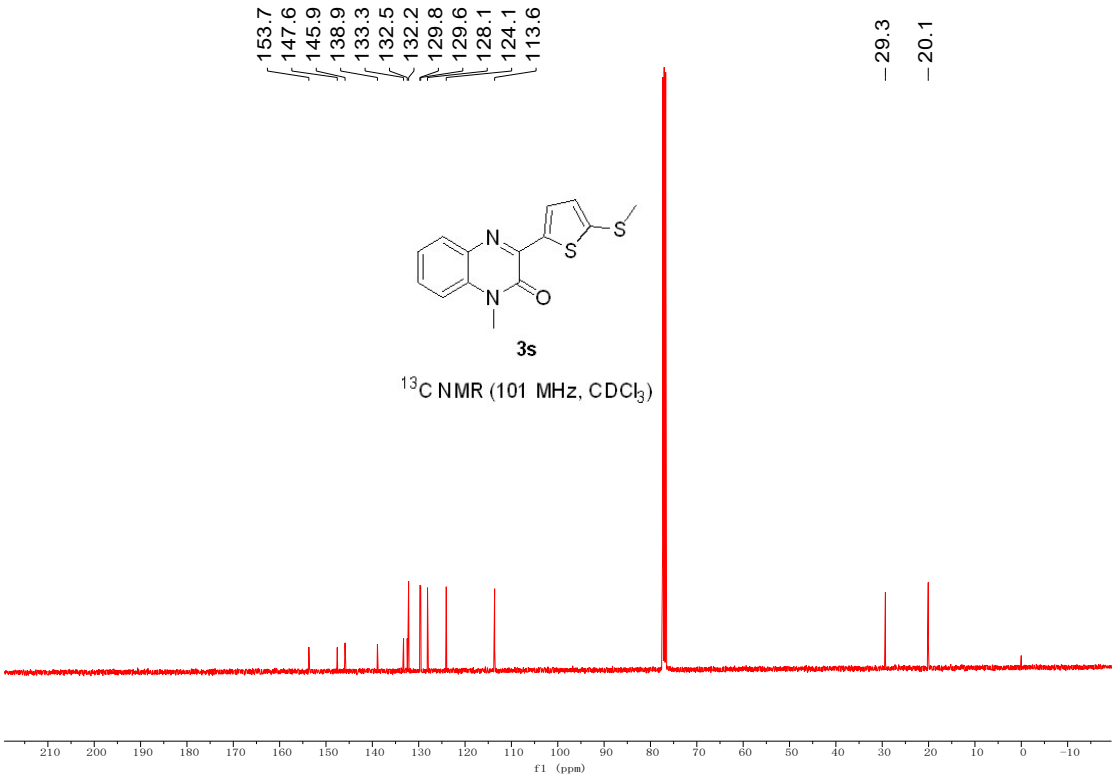



**3r**

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

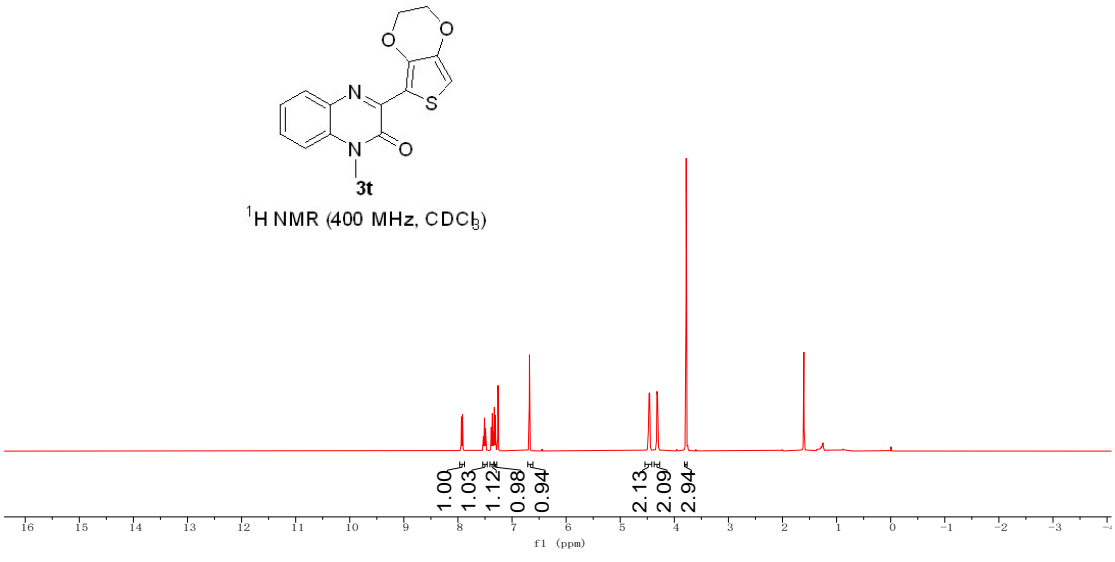

161.1
154.2
149.4
133.6
131.9
130.7
130.0
129.3
124.0
115.5
113.7
113.5
59.3
29.6
O
N
S
N
O
3r
13C NMR (101 MHz, CDCl3)
f1 (ppm)


8.32
8.31
7.87
7.87
7.85
7.85
7.54
7.54
7.53
7.52
7.52
7.50
7.50
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.31
7.31
7.26
7.04
7.03
3.78
2.63
1.60
0.01
0.00
N
S
S
N
O
3s
1H NMR (400 MHz, CDCl3)
f1 (ppm)



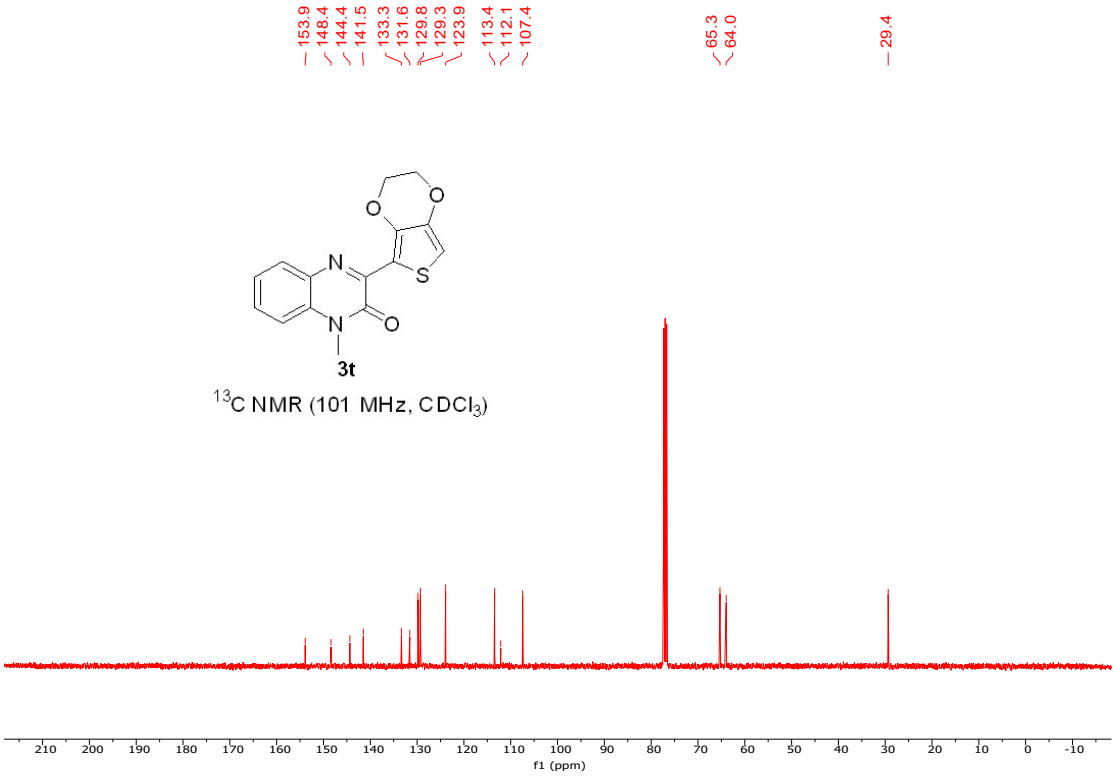

**3s**

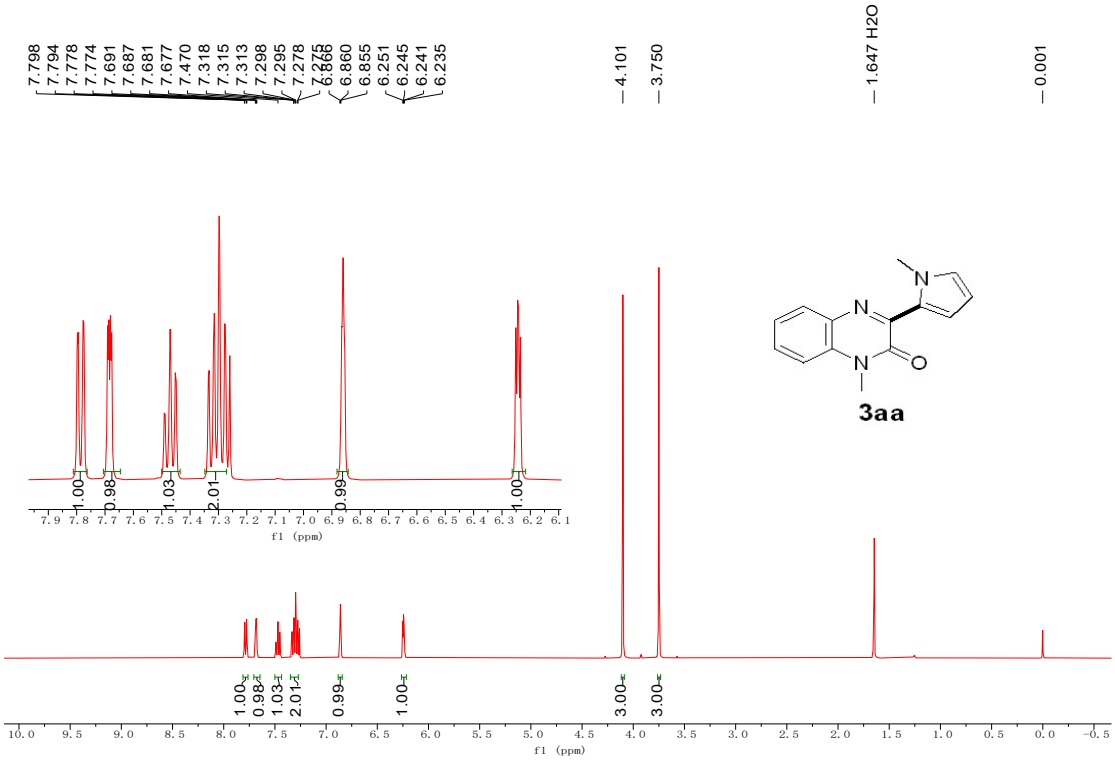
$^{13}$C NMR (101 MHz, $CDCl_3$)

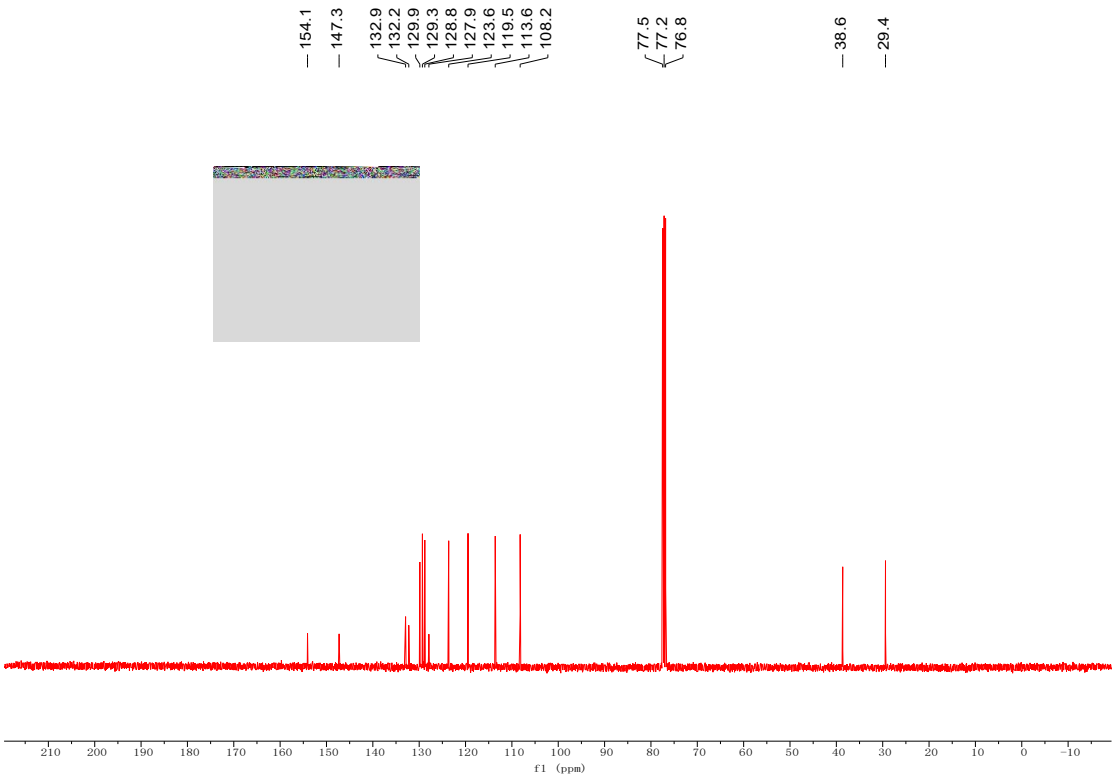


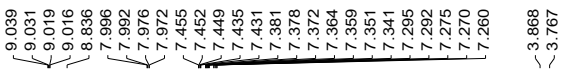

**3t**

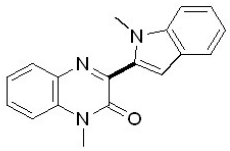
$^{1}$H NMR (400 MHz, $CDCl_3$)


153.9
148.4
144.4
141.5
133.3
131.6
129.8
129.3
123.9
113.4
112.1
107.4
65.3
64.0
29.4
3t
13C NMR (101 MHz, CDCl3)
f1 (ppm)


7.798
7.794
7.778
7.774
7.691
7.687
7.681
7.677
7.470
7.318
7.315
7.313
7.298
7.295
7.278
6.860
6.855
6.251
6.245
6.241
6.235
4.101
3.750
1.647 H2O
0.001
3aa
f1 (ppm)

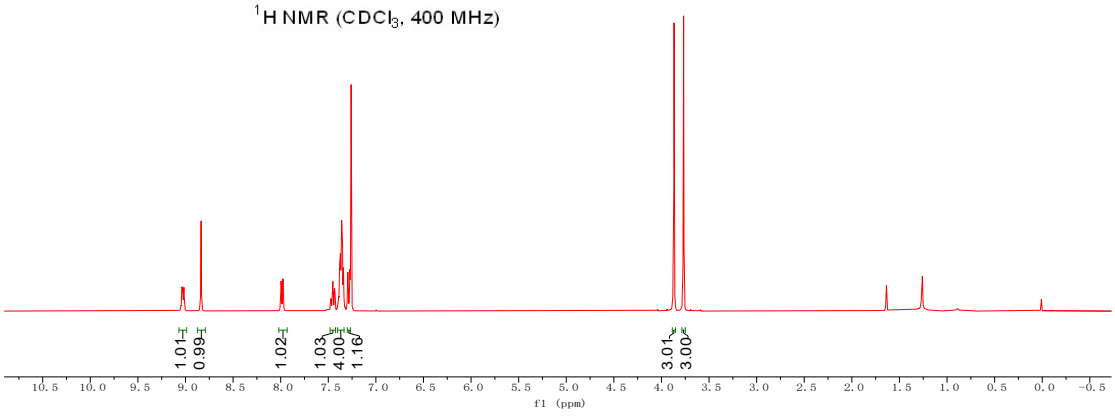


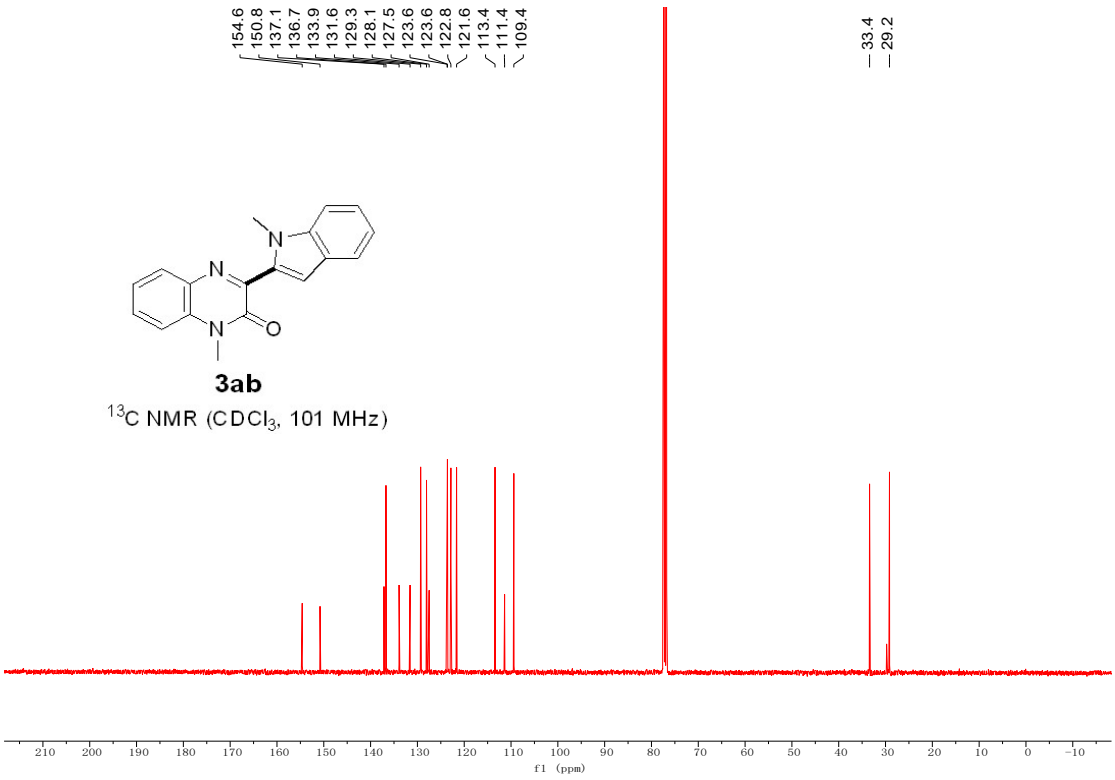



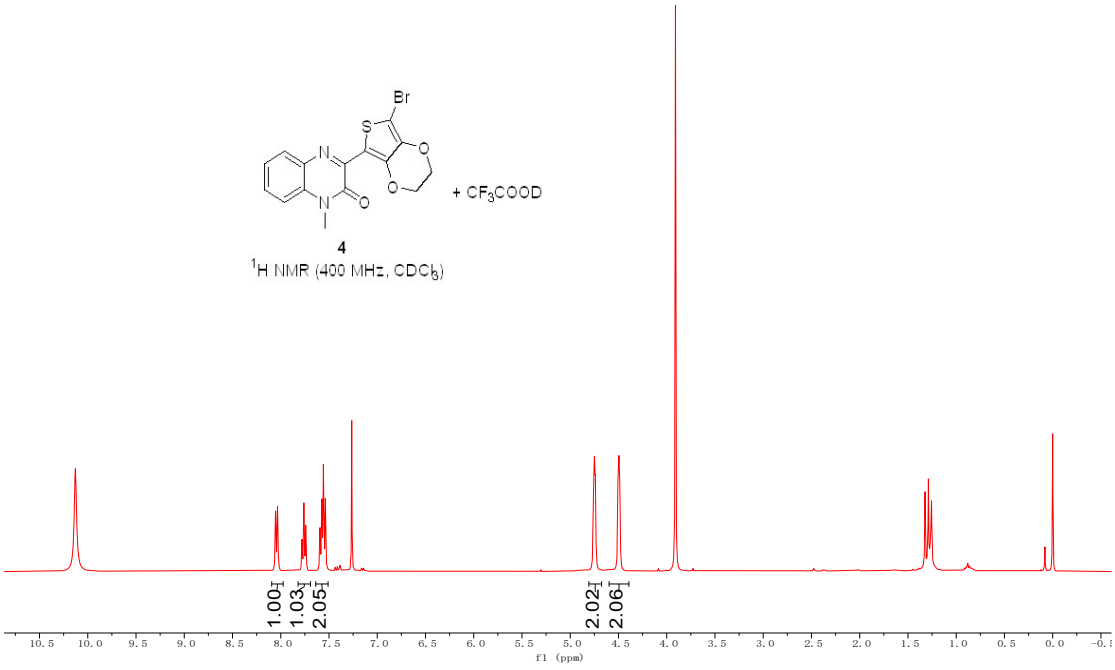



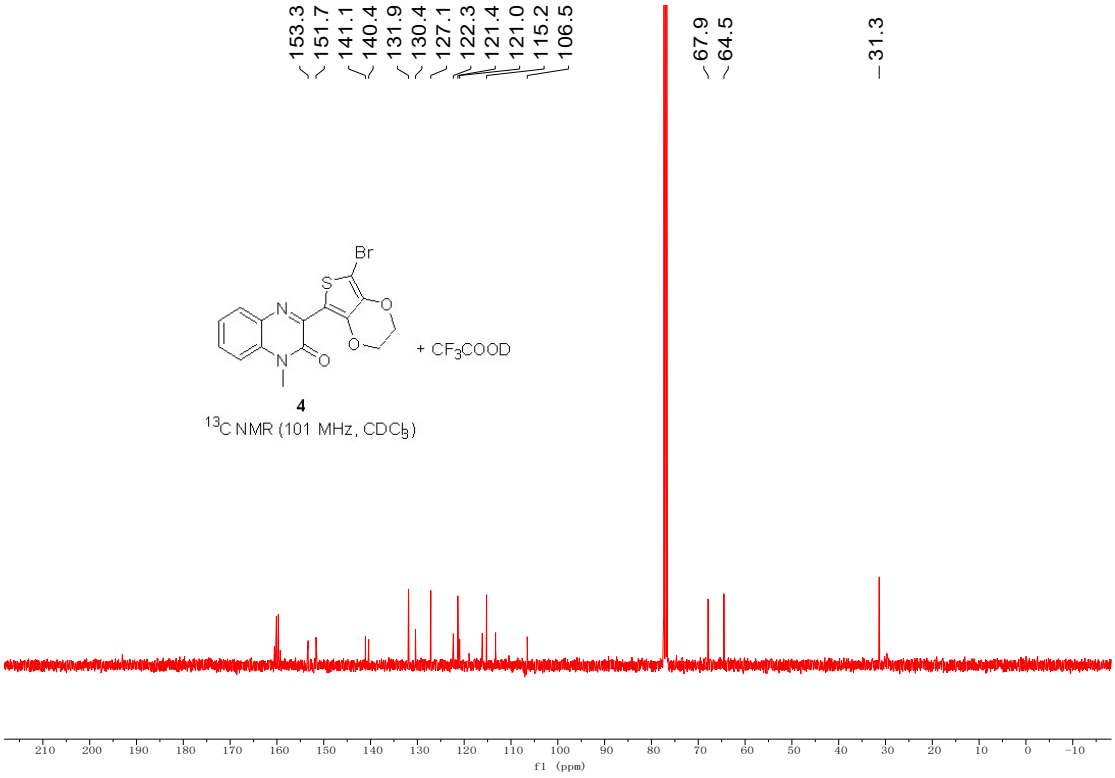
**3ab**

$^1$H NMR ($CDCl_3$, 400 MHz)



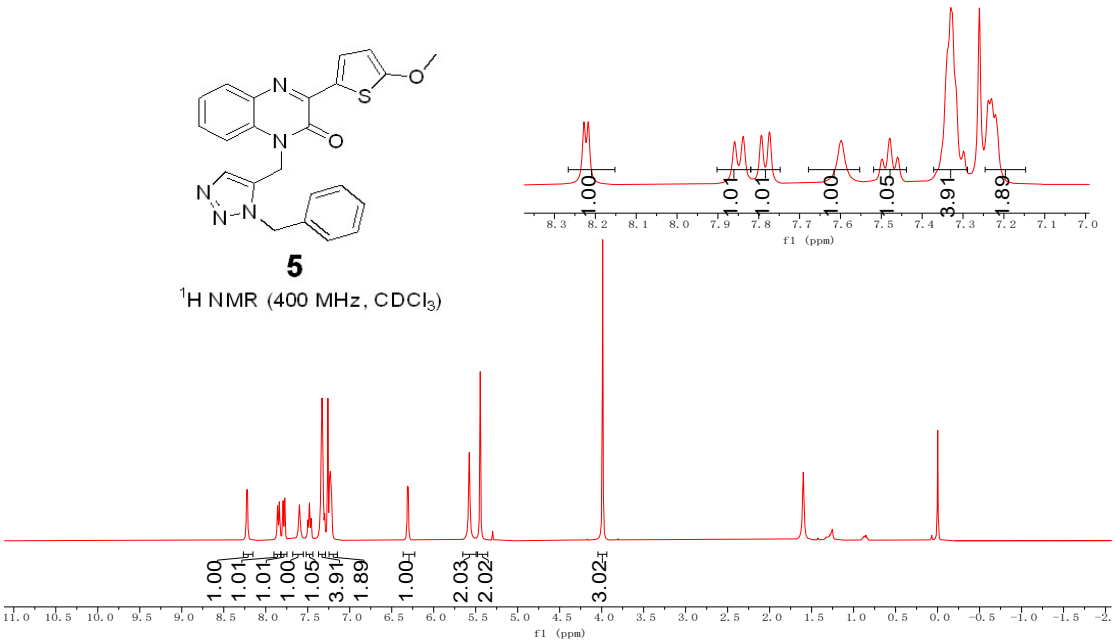

154.6
150.8
137.1
136.7
133.9
131.6
129.3
128.1
127.5
123.6
123.6
122.8
121.6
113.4
111.4
109.4
33.4
29.2
N
N
O
N
3ab
13C NMR (CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Br
S
N
O
O
O
N
O
+ CF3COOD
4
1H NMR (400 MHz, CDCl3)
1.00
1.03
2.05
2.02
2.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



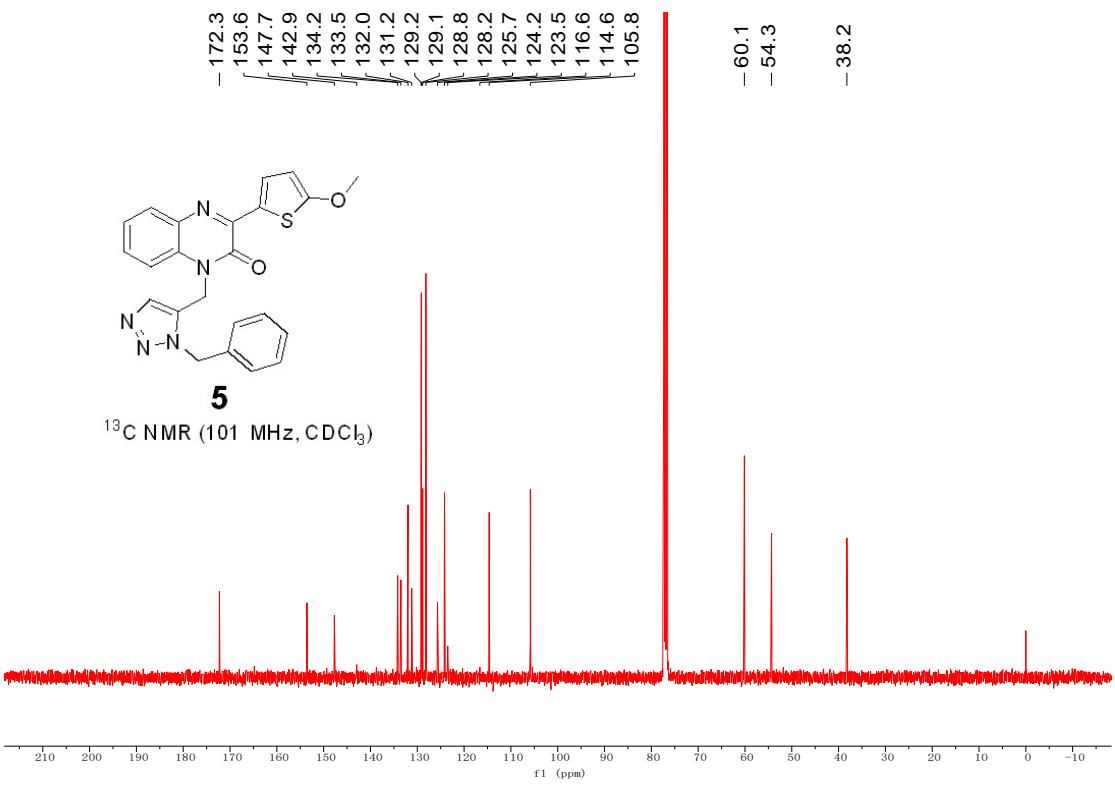

**4**

$^{13}$C NMR (101 MHz, $CDCl_3$)




**5**

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




# 10. Reference


1. M. Shen, L. Li, Q. Zhou, J. Wang and L. Wang, *Chin. J. Org. Chem.*, 2023, **43**, 697-704.
2. P. Dai, Y. Li, Y. Chen, J. Jiao, Q. Wang, C. Li, Y. Gu, Y. Zhang, Q. Xia and W.-H. Zhang, *Org. Lett.*, 2022, **24**, 1357-1361.
3. L. Liu, J. Liu, S. Li, M. Yang, X. Zhao and K. Lu, *Org. Biomol. Chem.*, 2025, **23**, 629-637.
4. S. Mukherjee, B. Maji, A. Tlahuext-Aca and F. Glorius, *J. Am. Chem. Soc.*, 2016, **138**, 16200-16203.