Supporting Information

Visible-Light-Mediated Synthesis of 2-Sulfenylated Pyrrolo[1,2-α]quinoxalines via Isocyanide/Disulfide Radical Cascades

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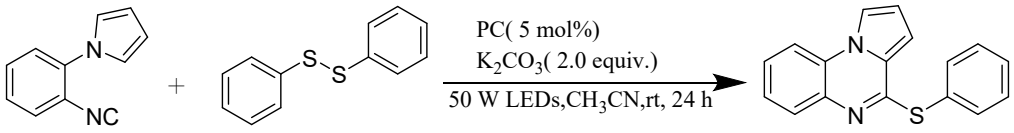
I. General Experimental Information

All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. Reagents were purchased from Accela, Acros, Aladdin, Adamas, Energy Chemical or TCI. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Purifications of reaction products were carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd silica gel (400-630 mesh). ^{1}H NMR、^{13}C NMR and ^{19}F NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature on a Bruker Avance III 400 MHz or 500 MHz for ^{1}H NMR and 100 MHz or 126 MHz for ^{13}C NMR and 471 MHz for ^{19}F NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), doublet of doublet (dd), quartet (q). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass)

II. Optimization of Reaction Conditions

Table S1. Catalyst screening for the cross-coupling reaction of 1-(2-isocyanophenyl)-1H-pyrrole 1a with 1,2-Diphenyldisulfane 2a

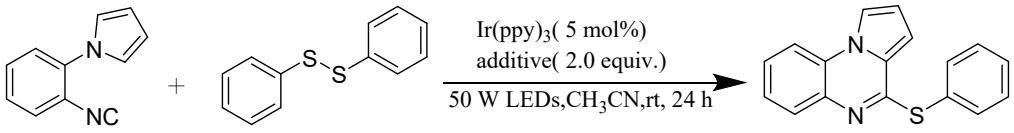


1a **2a** **3a**

entry	catalyst	yield **3a**(%)[b]
1	$Ir(ppy)_3$	41
2	$Ru(bpy)_3$	0
3	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	37
4	Eosin Y	0
5	4CzIPN	0
6	Mes-Acr^+-Me ClO_4^-	0

[a]All the reactions were carried out employing 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (0.10 mmol), 1,2-Diphenyldisulfane **2a** (0.10 mmol), K_2CO_3 (0.20 mmol) with catalysts (5 mol %) in CH_3CN (2 mL) at rt for 24 h under 50 W blue LEDs and Air in an open tube, followed by flash chromatography on SiO_2. [b]Isolated yield.

Table S2. Additive screening for the reaction of 1-(2-isocyanophenyl)-1H-pyrrole 1a with 1,2-Diphenyldisulfane 2a

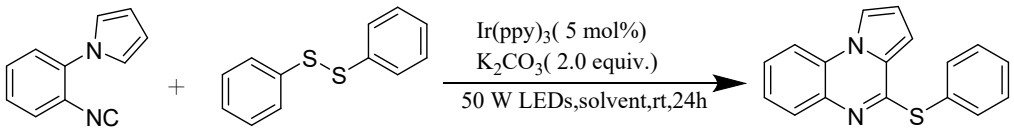


1a **2a** **3a**

entry	additive	yield **3a** (%)[b]
1	K_2CO_3	41
2	Na_2CO_3	33
3	Cs_2O_3	29
4	K_3PO_4	21
5	Na_2HPO_4	17
6	CH_3COOK	0
7	Et_3N	0
8	DIPEA	0

[a]All the reactions were carried out employing 1-(2-isocyanophenyl)-1H-pyrrole **1a** (0.10 mmol), 1,2-Diphenyldisulfane **2a** (0.10 mmol), additive (0.20 mmol) with $Ir(ppy)_3$ (5 mol %) in CH_3CN (2 mL) at rt for 24 h under 50 W blue LEDs and Air in an open tube, followed by flash chromatography on SiO_2. [b]Isolated yield.

Table S3. Various solvents screening for the reaction of 1-(2-isocyanophenyl)-1H-pyrrole 1a with 1,2-Diphenyldisulfane 2a

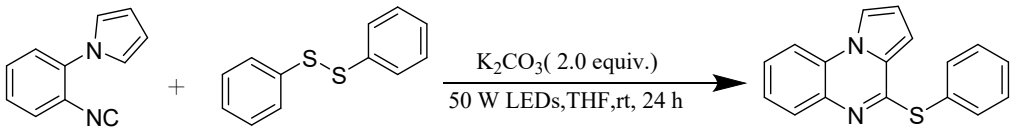


1a **2a** **3a**

entry	solvent	yield **3a** (%)[b]
1	CH_3CN	47
2	THF	64
3	Toluene	50
4	DCE	49
5	DMF	0
6	MeOH	0
7	1,4-dioxane	0

[a]All the reactions were carried out employing 1-(2-isocyanophenyl)-1H-pyrrole **1a** (0.10 mmol), 1,2-Diphenyldisulfane **2a** (0.10 mmol), K_2CO_3 (0.20 mmol) with $Ir(ppy)_3$ (5 mol %) in solvent (2 mL) at rt for 24 h under 50 W blue LEDs and Air in an open tube, followed by flash chromatography on SiO_2. [b]Isolated yield.

Table S4. photocatalyst screening for the reaction of 1-(2-isocyanophenyl)-1H-pyrrole 1a with 1,2-Diphenyldisulfane 2a

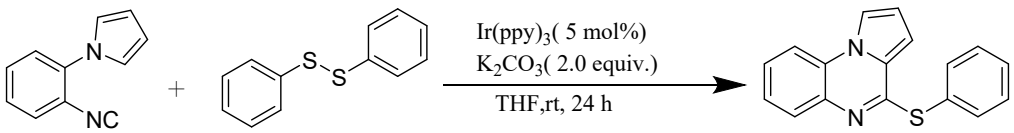


1a **2a** **3a**

entry	conditions	yield **3a**(%)[b]
1	no photocatalyst	0

[a]All the reactions were carried out employing 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (0.10 mmol), 1,2-Diphenyldisulfane **2a** (0.10 mmol), K_2CO_3 (0.20 mmol) in THF (2 mL) at rt for 24 h under 50 W blue LEDs and Air in an open tube, no product was formed.

Table S5. Lighting screening for the reaction of 1-(2-isocyanophenyl)-1H-pyrrole 1a with 1,2-Diphenyldisulfane 2a



1a **2a** **3a**

entry	conditions	yield **3a**(%)[b]
1	no light	0

[a]All the reactions were carried out employing 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (0.10 mmol), 1,2-Diphenyldisulfane **2a** (0.10 mmol), K_2CO_3 (0.20 mmol) with $Ir(ppy)_3$ (5 mol %) in THF (2 mL) at rt for 24 h under Air in an open tube, no product was formed.

III. **Study on the Gram-scale Reaction**

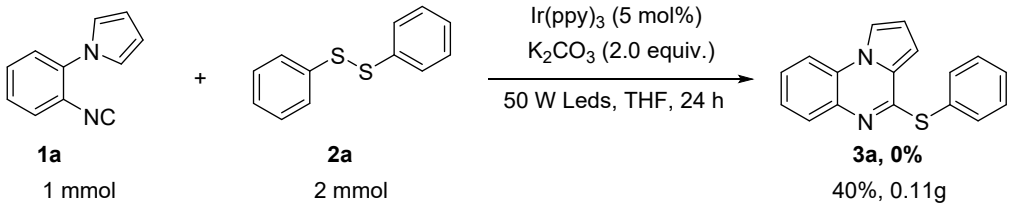


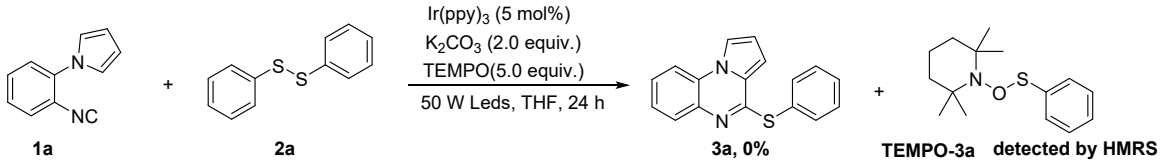
Figure S1. Gram-scale reaction

An oven-dried sealed tube charged 1-(2-isocyanophenyl)-1H-pyrrole **1a** (1 mmol), diphenyl sulfides **2a** (2 mmol), K_2CO_3 (2 mmol), $Ir(ppy)_3$ (5 mol %) and THF (10 mL) was added under 50 W blue LEDs and Air atmosphere. The reaction mixture was then allowed to stir at rt for 48 h. After the reaction mixture was cooled down and filtrated, the corresponding filtrate was further concentrated under reduced pressure, followed by flash chromatography on silica gel using ethyl acetate/petroleum ether (1 : 250) as eluent to afford the desired products.

VI. Control Experiments for the Mechanism Studies

a) TEMPO was added to the reaction of 1-(2-isocyanophenyl)-1H-pyrrole 1a with 1,2-Diphenyldisulfane 2a

The reactions were carried out employing 1-(2-isocyanophenyl)-1H-pyrrole **1a** (0.10 mmol), 1,2-Diphenyldisulfane **2a** (0.10 mmol), K_2CO_3 (0.20 mmol), TEMPO (5.0 equiv.) with $Ir(ppy)_3$ (5 mol %) in THF (2 mL) at rt for 24 h under 50 W blue LEDs and Air in an open tube, no product was formed.Moreover, the intermediates 2,2,6,6-tetramethyl-1-((phenylthio)oxy)piperidine in the reaction mixture were detected by HRMS.



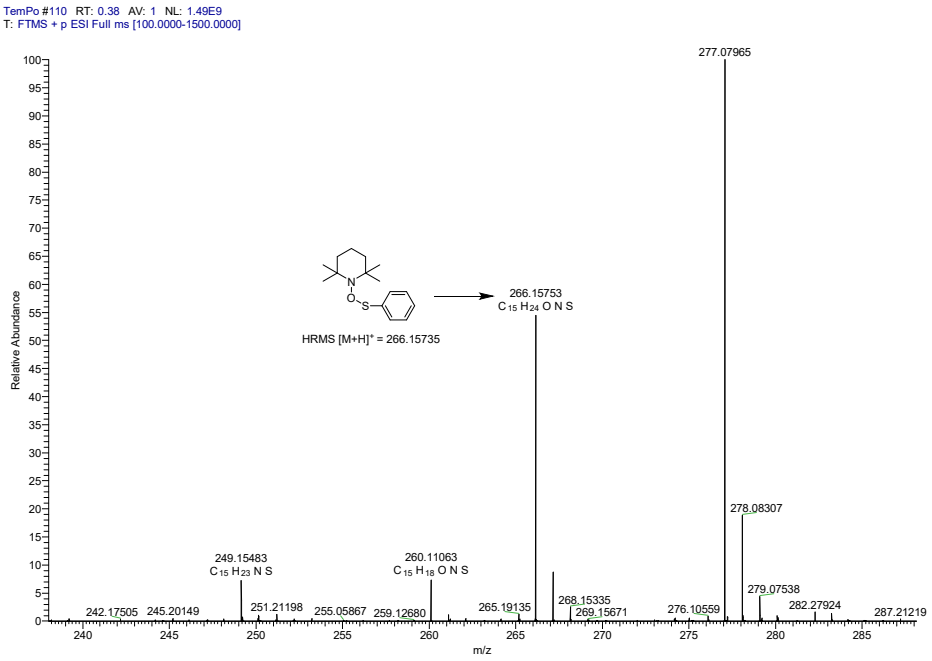
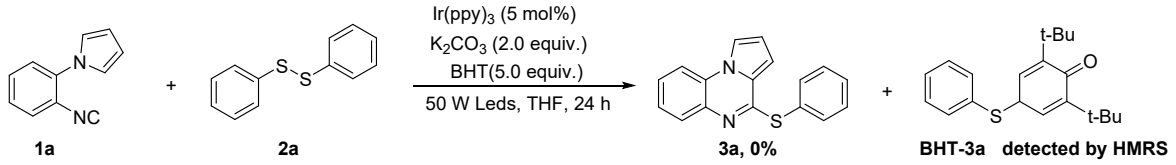


Figure S2. HRMS spectra of reaction mixture in radical trapping experiment

b) BHT was added to the reaction of 1-(2-isocyanophenyl)-1H-pyrrole 1a with 1,2-Diphenyldisulfane 2a

The reactions were carried out employing 1-(2-isocyanophenyl)-1H-pyrrole **1a** (0.10 mmol), 1,2-Diphenyldisulfane **2a** (0.10 mmol), K_2CO_3 (0.20 mmol), BHT (5.0 equiv.) with $Ir(ppy)_3$ (5 mol %) in THF (2 mL) at rt for 24 h under 50 W blue LEDs and Air in an open tube, no product was formed.Moreover, the intermediates (2,6-di-*tert*-butylphenoxy)(phenyl)sulfane in the reaction mixture were detected by HRMS.



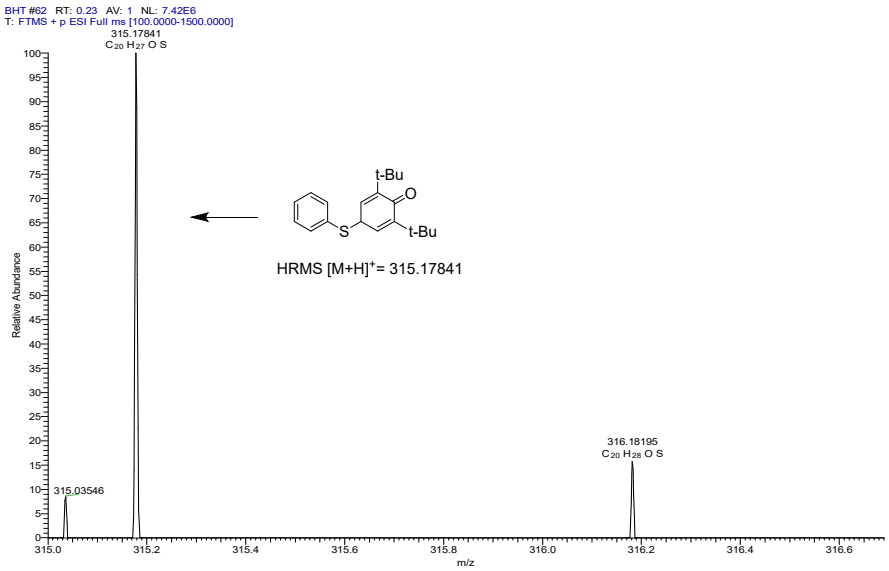


Figure S3. HRMS spectra of reaction mixture in radical trapping experiment

c) 4-ethylbenzenethiol 6a reacted with 1-(2-isocyanophenyl)-1H- pyrrole 1a

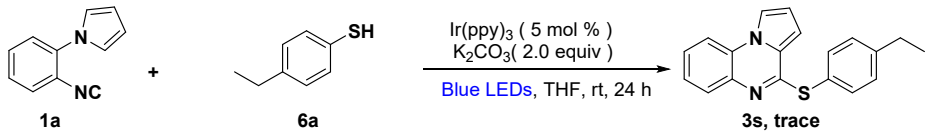
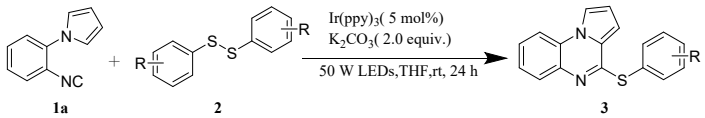


Figure S4. 4-Ethylbenzenethiol 6a reacted with 1-(2-isocyanophenyl)-1H- pyrrole 1a

The reactions were carried out employing 1-(2-isocyanophenyl)-1H-pyrrole **1a** (0.10 mmol), 4-ethylben zenethiol **6a** (0.10 mmol), K_2CO_3 (0.20 mmol) with $Ir(ppy)_3$ (5 mol %) in THF (2 mL) at rt for 24 h under 50 W blue LEDs and Air in an open tube, no product is produced.

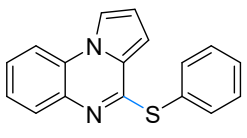
V. Detail Characterization for the Compounds 3



An oven-dried sealed tube charged 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (0.10 mmol), diphenyl sulfides **2**

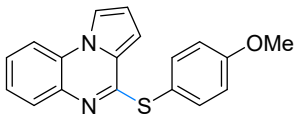
(0.10 mmol), K_2CO_3 (0.20 mmol), $Ir(ppy)_3$ (5 mol %) and THF (2 mL) was added under 50 W blue LEDs and Air atmosphere. The reaction mixture was then allowed to stir at rt for 24 h. After the reaction mixture was cooled down and filtrated, the corresponding filtrate was further concentrated under reduced pressure, followed by flash chromatography on silica gel using ethyl acetate/petroleum ether (1 : 250) as eluent to afford the desired products.

IV. Analysis Data for All the Products



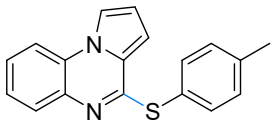
3a

4-(Phenylthio)pyrrolo[1,2-a]quinoxaline (3a): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-Diphenyldisulfane **2a** (21.80 mg, 0.10 mmol) and was purified by column chromatography (250:1 petroleum ether: ethyl acetate) to give a white solid; 17 mg, 64% yield; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ: 7.91 (dd, 1H), 7.81 (d, *J* = 1.0 Hz, 1H), 7.74 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.72 – 7.70 (m, 2H), 7.47 – 7.43 (m, 4H), 7.37 (t, 1H), 6.95 (dd, *J* = 4.0, 1.2 Hz, 1H), 6.85 (dd, *J* = 3.9, 2.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 153.6, 135.8, 134.8, 129.3, 129.2, 129.0, 128.7, 126.9, 126.8, 125.1, 124.5, 114.5, 113.6, 113.6, 106.5. **HRMS (ESI)** m/z calcd for $C_{17}H_{13}N_2S^+$ $[M+H]^+$: 277.07939, found 277.07910.



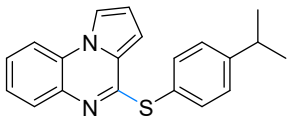
3b

4-((Methoxyphenyl)thio)pyrrolo[1,2-a]quinoxaline (3b): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-bis(4-methoxyphenyl)disulfane **2b** (27.80 mg, 0.10 mmol) and was purified by column chromatography (250:1 petroleum ether: ethyl acetate) to give a pale yellow oil; 20 mg, 67% yield; **^{1}H NMR** (500 MHz, Chloroform-d) δ: 7.89 (dd, *J* = 2.7, 1.2 Hz, 1H), 7.79 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.71 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.45–7.40 (m, 1H), 7.37–7.32 (m, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.94 (dd, *J* = 4.0, 1.2 Hz, 1H), 6.84 (dd, *J* = 3.9, 2.8 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 160.4, 154.5; 137.0, 135.9, 129.3, 126.9, 126.6, 125.0, 124.3, 119.2, 114.7, 114.3, 113.5, 113.5, 106.1, 55.4. **HRMS (ESI)** m/z calcd for $C_{18}H_{15}ON_2S^+$ $[M+H]^+$: 307.08996, found 307.08957.



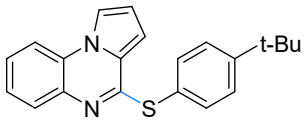
3c

4-(P-tolylthio)pyrrolo[1,2-a]quinoxaline (3c): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-diptolyldisulfane **2c** (24.60 mg, 0.10 mmol) and was purified by column chromatography (250:1 petroleum ether: ethyl acetate) to give a pale yellow oil; 16 mg, 53% yield; **^{1}H NMR** (500 MHz, Chloroform-d) δ: 7.90 (d, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.1 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 3.9 Hz, 1H), 6.84 (t, 1H), 2.45 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.1, 139.0, 135.8, 135.0, 129.8, 129.3, 126.9, 126.7, 125.4, 125.0, 124.4, 114.4, 113.5, 106.4, 21.4. **HRMS (ESI)** m/z calcd for $C_{18}H_{15}N_2S^+$ $[M+H]^+$: 291.09504, found 291.09451.



3d

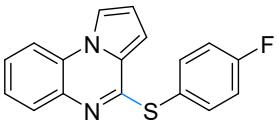
4-((4-Isopropylphenyl)thio)pyrrolo[1,2-a]quinoxaline (3d): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-bis(4-isopropylphenyl)disulfane **2d** (30.20 mg, 0.10 mmol) and was purified by column chromatography (250:1 petroleum ether: ethyl acetate) to give a pale yellow oil; 30 mg, 93% yield; ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.91–7.88 (m, 1H), 7.77 (dd, *J* = 15.4, 8.1 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.39–7.32 (m, 3H), 6.97 (d, *J* = 4.0 Hz, 1H), 6.87–6.82 (m, 1H), 3.06 - 2.97 (m, 1H), 1.35 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 154.0, 149.8, 135.9, 134.9, 129.3, 127.2, 126.9, 126.7, 125.7, 125.0, 124.4, 114.4, 113.5, 106.3, 34.0, 24.0. **HRMS (ESI)** m/z calcd for $C_{20}H_{19}N_2S^+$ $[M+H]^+$: 319.12634, found 319.12592.



3e

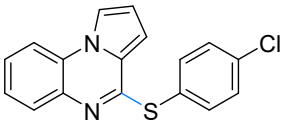
4-((4-(Tert-butyl)phenyl)thio)pyrrolo[1,2-a]quinoxaline (3e): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-bis(4-(tert-butyl)phenyl)disulfane **2e** (33.01 mg, 0.10 mmol) and was purified by

column chromatography (250:1 petroleum ether: ethyl acetate) to give a pale yellow oil; 24 mg, 71% yield; **^{1}H NMR** (500 MHz, Chloroform-d) δ: 7.89 (dd, *J* = 2.5, 1.1 Hz, 1H), 7.81–7.74 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.46-7.41 (m, 1H), 7.39-7.33 (m, 1H), 6.97 (dd, *J* = 4.0, 1.1 Hz, 1H), 6.88–6.83 (m, 1H), 1.42 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 154.0, 152.0, 135.9, 134.6, 129.3, 126.9, 126.7, 126.1, 125.5, 125.0, 124.5, 114.4, 113.6, 106.3, 34.8, 31.3. **HRMS (ESI)** m/z calcd for $C_{21}H_{21}N_2S^+$ $[M+H]^+$: 333.14199, found 333.14154.



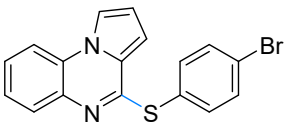
3f

4-((4-Fluorophenyl)thio)pyrrolo[1,2-a]quinoxaline (3f): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-bis(4-fluorophenyl)disulfane **2f** (25.40 mg, 0.10 mmol) and was purified by column chromatography (250:1 petroleum ether: ethyl acetate) to give a pale yellow oil; 24 mg, 82% yield; **^{1}H NMR** (500 MHz, Chloroform-d) δ: 7.90 (dd, *J* = 2.7, 1.2 Hz, 1H), 7.78 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.72–7.67 (m, 3H), 7.46–7.40 (m, 1H), 7.38–7.32 (m, 1H), 7.17 (t, *J* = 8.7 Hz, 1H), 6.97 (dd, *J* = 4.0, 1.2 Hz, 1H), 6.86 (dd, *J* = 3.9, 2.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 164.3, 162.4, 153.5, 137.3(d, C-F, $^3J_{C\text{-}F}$ = 35 Hz), 137.3, 135.7, 129.2, 126.9, 126.8, 125.1, 124.2, 123.9, 123.9(d, C-F, $^2J_{C\text{-}F}$ = 15 Hz), 121.4, 116.3, 116.1, 114.6 , 113.6, 113.6 (d, C-F, $^1J_{C\text{-}F}$ = 10 Hz), 110.6, 106.1； **^{19}F NMR** (471 MHz, $CDCl_3$) δ: -110.0, -111.6, -112.1, -114.8. **HRMS (ESI)** m/z calcd for $C_{17}H_{12}N_2FS^+$ $[M+H]^+$: 295.06997, found 295.06964.



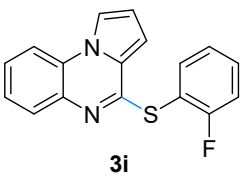
3g

4-((4-Chlorophenyl)thio)pyrrolo[1,2-a]quinoxaline (3g): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-bis(4-chlorophenyl)disulfane **2g** (28.60 mg, 0.10 mmol) and was purified by column chromatography (250:1 petroleum ether: ethyl acetate) to give a white solid; 29 mg, 93% yield; **^{1}H NMR** (500 MHz, Chloroform-d) δ: 7.91 (t, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.73 (d, 1H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.47–7.41 (m, 3H), 7.37 (t, 1H), 6.96 (d, *J* = 4.0 Hz, 1H), 6.86 (t, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 154.0, 136.1, 135.7, 135., 129.3, 129.2, 127.5, 127.0, 126.9, 125.2, 124.3, 114.7, 113.7, 113.6, 106.3; **HRMS (ESI)** m/z calcd for $C_{17}H_{12}N_2ClS^+$ $[M+H]^+$: 311.04042, found 311.03989.



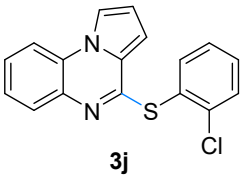
3h

4-((4-Bromophenyl)thio)pyrrolo[1,2-a]quinoxaline (3h): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-bis(4-bromophenyl)disulfane **2h** (37.38 mg, 0.10 mmol) and was purified by column chromat ography (250:1 petroleum ether: ethyl acetate) to give a white solid; 26 mg, 72% yield; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ: 7.89 (dd, *J* = 2.5, 1.0 Hz, 1H), 7.80 – 7.77 (m, 1H), 7.69 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.56 – 7.51 (m, 4H), 7.45 – 7.41 (m, 1H), 7.37 – 7.32 (m, 1H), 6.92 (dd, *J* = 4.0, 1.0 Hz, 1H), 6.84 – 6.82 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 152.8, 136.3, 135.7, 132.1, 129.3, 128.2, 127.0, 126.9, 125.2, 124.3, 123.2, 114.6, 113.7, 113.6, 106.3. **HRMS (ESI)** m/z calcd for $C_{17}H_{12}N_2BrS^+$ $[M+H]^+$: 354.98990, found 354.98935.



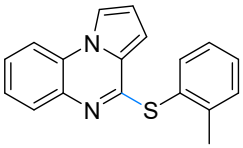
3i

4-((2-Fluorophenyl)thio)pyrrolo[1,2-a]quinoxaline (3i): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-bis(2-fluorophenyl)disulfane **2i** (25.40 mg, 0.10 mmol) and was purified by column chromato graphy (250:1 petroleum ether: ethyl acetate) to give a white solid; 21 mg, 70 % yield; **^{1}H NMR** (500 MHz, Chloroform-d) δ: 7.88 (dd, *J* = 2.6, 1.2 Hz, 1H), 7.76 (dd, 1H), 7.68 (td, *J* = 7.3, 1.6 Hz, 1H), 7.63 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.46 (m, *J* = 9.3, 5.1, 1.7 Hz, 1H), 7.42–7.38 (m, 1H), 7.33–7.29 (m, 1H), 7.25–7.18 (m, 2H), 6.96 (dd, *J* = 4.0, 1.1 Hz, 1H), 6.86–6.79 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 164.0, 162.0, 152.2, 137.2, 135.8, 131.5, 131.5 (d, C-F, $^1J_{C\text{-}F}$ = 35 Hz), 129.3, 126.9, 126.8, 125.1, 124.5, 124.5(d, C-F, $^2J_{C\text{-}F}$ = 15 Hz), 124.2, 116.1, 116.0, 114.5, 113.6(d, C-F, $^3J_{C\text{-}F}$ = 35 Hz), 113.6, 105.4， 106.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ: -105.3. **HRMS (ESI)** m/z calcd for $C_{17}H_{12}N_2FS^+$ $[M+H]^+$: 295.06997, found 295.06949.



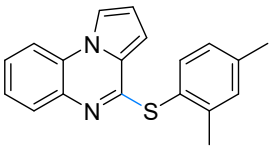
3j

4-((2-Chlorophenyl)thio)pyrrolo[1,2-a]quinoxaline (3j): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2 -bis-(2-chlorophenyl)disulfane **2j** (28.60 mg, 0.10 mmol) and was purified by column chromatography (250:1 petroleum ether: ethyl acetate) to give a white solid; 18 mg, 58 % yield; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ: 7.90 (dd, *J* = 2.7, 1.3 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.71 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.57 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.44 (td, *J* = 8.2, 7.7, 1.5 Hz, 1H), 7.41 – 7.31 (m, 3H), 6.99 (dd, *J* = 4.0, 1.3 Hz, 1H), 6.89 – 6.85 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 152.2, 138.6, 136.8, 135.8, 130.2, 130.1, 129.4, 128.8, 127.1, 127.0, 126.9, 125.1, 124.5, 114.6, 113.7, 113.6, 106.4. **HRMS (ESI)** m/z calcd for $C_{17}H_{12}N_2ClS^+$ $[M+H]^+$: 311.04042, found 311.03989.



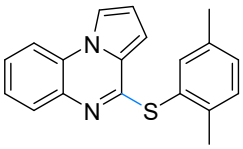
3k

4-(o-tolylthio)pyrrolo[1,2-a]quinoxaline (3k): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-di-o-tolyldisulfane **2k** (24.60 mg, 0.10 mmol) and was purified by column chromatography (250:1 petroleum ether: ethyl acetate) to give a pale yellow oil; 19 mg, 64 % yield; ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.82 (dd, *J* = 2.6, 1.2 Hz, 1H), 7.73–7.67 (m, 2H), 7.49–7.45 (m, 2H), 7.38–7.34 (m, 1H), 7.32–7.26 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 6.89 (dd, *J* = 4.0, 1.2 Hz, 1H), 6.77 (dd, *J* = 3.9, 2.8 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 153.8, 138.8, 135.9, 135.2, 131.9, 129.6, 129.4, 128.9, 128.8, 126.9, 126.8, 125.1, 124.6, 114.5, 113.6, 113.6, 106.5, 21.4. **HRMS (ESI)** m/z calcd for $C_{18}H_{15}N_2S^+$ $[M+H]^+$: 291.09504, found 291.09451.



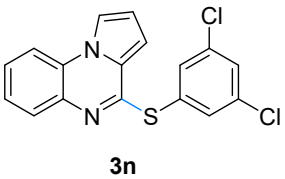
3l

4-((2,4-Dimethylphenyl)thio)pyrrolo[1,2-a]quinoxaline (3l): The title compound was prepared from N-(2-(1H-pyrrol-1-yl)phenyl)methanimine **1a** (17 mg, 0.10 mmol) and 1,2-bis(2,4-dimethylphenyl)disulfane **2l** (27.40 mg, 0.10 mmol) and was purified by column chromatography (250:1 petroleum ether: ethyl acetate) to give a pale yellow oil; 19 mg, 64 % yield; **^{1}H NMR** (500 MHz, Chloroform-d) δ: 7.88 (dd, *J* = 2.6, 1.1 Hz, 1H), 7.77 (dd, 1H), 7.72 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.43–7.39 (m, 1H), 7.36–7.32 (m, 1H), 7.24 (s, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.97 (dd, *J* = 4.0, 1.1 Hz, 1H), 6.87–6.84 (m, 1H), 2.47 (d, *J* = 19.7 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 153.9, 143.1, 139.8, 136.5, 136.0, 129.2, 127.4, 126.8, 126.5, 125.0, 124.5, 124.4, 114.3, 113.6, 113.5, 106.1, 21.4, 21.1. **HRMS (ESI)** m/z calcd for $C_{19}H_{17}N_2S^+$ $[M+H]^+$: 305.11069, found 305.11008.



3m

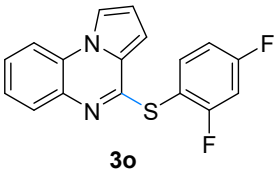
4-((2,5-Dimethylphenyl)thio)pyrrolo[1,2-a]quinoxaline (3m): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-bis(2,5-dimethylphenyl)disulfane **2m** (27.40 mg, 0.10 mmol) and was purified by columnchrom atography (250:1 petroleum ether: ethyl acetate) to give a pale yellow oil; 24 mg, 77 % yield; **^{1}H NMR** (500 MHz, Chloroform-d) δ: 7.83 (dd, *J* = 2.7, 1.2 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.65 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.49 (s, 1H), 7.38–7.34 (m, 1H), 7.30–7.26 (m, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 6.89 (dd, *J* = 4.0, 1.2 Hz, 1H), 6.81–6.76 (m, 1H), 2.35 (d, *J* = 26.0 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 153.7, 140.0, 136.8, 136.0, 135.9, 130.5, 130.4, 129.3, 127.6, 126.8, 126.5, 125.0, 124.4, 114.3, 113.5, 113.5, 106.1, 20.9, 20.6. **HRMS (ESI)** m/z calcd for $C_{19}H_{17}N_2S^+$ $[M+H]^+$: 305.11069, found 305.11020.



3n

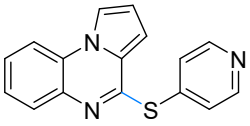
4-((3,5-Dichlorophenyl)thio)pyrrolo[1,2-a]quinoxaline (3n): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-bis(3,5-dichlorophenyl)disulfane **2n** (35.39 mg, 0.10 mmol) and was purified by column chromatography (250:1 petroleum ether: ethyl acetate) to give a white solid; 28 mg, 80 % yield; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ:7.88 (dd, *J* = 2.6, 1.1 Hz, 1H), 7.78 – 7.75 (m, 1H), 7.57 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.36 – 7.32

(m, 1H), 7.31 – 7.27 (m, 1H), 6.95 (dd, J = 4.0, 1.1 Hz, 1H), 6.83 (dd, J = 3.9, 2.8 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ:151.3, 142.2, 135.8, 131.0, 129.3, 128.6, 127.8, 126.9, 126.7, 125.0, 124.0, 114.5, 113.6, 105.8. **HRMS (ESI)** m/z calcd for $C_{17}H_{11}N_2Cl_2S^+$ $[M+H]^+$: 345.00145, found 345.00082.



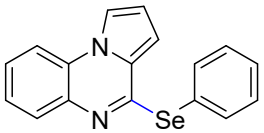
3o

4-((2,4-Difluorophenyl)thio)pyrrolo[1,2-a]quinoxaline (3o): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-bis(2,4-difluorophenyl)disulfane **2o** (29.00 mg, 0.10 mmol) and was purified by column chromatography (250:1 petroleum ether: ethyl acetate) to give a pale yellow oil; 25 mg, 79 % yield. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ: 7.90 – 7.87 (m, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.67 (dt, J = 24.7, 7.7 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.05 – 6.99 (m, 3H), 6.89 – 6.84 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 165.3(d, C-F, $^1J_{C\text{-}F}$ = 50 Hz), 165.2, 164.6(d, C-F, $^2J_{C\text{-}F}$ = 50 Hz), 164.5, 163.3(d, C-F, $^3J_{C\text{-}F}$ = 50 Hz), 163.2, 162.6(d, C-F, $^4J_{C\text{-}F}$ = 50 Hz), 162.5, 151.9, 138.6(d, C-F, $^5J_{C\text{-}F}$ = 5 Hz), 138.6, 138.5,(d, C-F, $^6J_{C\text{-}F}$ = 5 Hz) 138.5, 135.7, 129.2, 126.6, 126.8, 125.1, 124.0, 114.6, 113.6(d, C-F, $^7J_{C\text{-}F}$ = 35 Hz), 113.6, 112.1(d, C-F, $^8J_{C\text{-}F}$ = 15 Hz), 112.0, 111.9, 111.9, 111.4(d, C-F, $^9J_{C\text{-}F}$ = 15 Hz), 111.4, 111.3(d, C-F, $^{10}J_{C\text{-}F}$ = 15 Hz), 111.2, 106.0, 104.9, 104.7(t, C-F, $^1J_{C\text{-}F}$ = 105 Hz), 104.5, 87.1, 67.3, 32.6, 29.7, 24.6; **^{19}F NMR** (471 MHz, $CDCl_3$) δ: -100.14, -100.16, -103.84, -103.86, -106.80, -106.82, -109.82. **HRMS (ESI)** m/z calcd for $C_{17}H_{11}N_2F_2S^+$ $[M+H]^+$: 313.06055, found 313.06003.



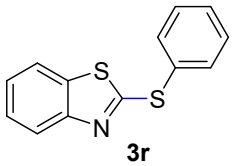
3p

4-(Pyridin-4-ylthio)pyrrolo[1,2-a]quinoxaline (3p): The title compound was prepared from 1-(2-isocyanophenyl)-1*H*-pyrrole **1a** (17 mg, 0.10 mmol) and 1,2-di(pyr idin-4-yl)disulfane **2p** (22 mg, 0.10 mmol) and was purified by column chromatography (250:1 petroleum ether: ethyl acetate) to give a white solid; 19 mg, 67 % yield; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ: 8.55 (d, J = 5.3 Hz, 2H), 7.96 (dd, J = 2.7, 1.2 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.57 – 7.49 (m, 3H), 7.45 – 7.40 (m, 1H), 6.97 (dd, J = 4.0, 1.2 Hz, 1H), 6.87 (dd, J = 4.0, 2.8 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 150.1, 149.5, 142.6, 135.5, 129.6, 127.9, 127.1, 126.1, 125.5, 125.0, 115.2, 114.1, 113.8, 107.1. **HRMS (ESI)** m/z calcd for $C_{16}H_{12}N_3S^+$ $[M+H]^+$: 278.07464, found 278.07425.



3q

4-(phenylselanyl)pyrrolo[1,2-a]quinoxaline (3r): The title compound was prepared from 2-isocyano-1,1'-biphenyl **1a** (17 mg, 0.10 mmol) and 1,2-diphenyldisefane **2q** (31.20 mg) and was purified by column chromatography (500:1 petroleum ether: ethyl acetate) to give a pale yellow solid; 8 mg, 27 % yield; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ :7.86 (dd, J = 2.7, 1.3 Hz, 1H), 7.77 – 7.73 (m, 4H), 7.42 (td, J = 8.5, 7.9, 1.5 Hz, 1H), 7.38 – 7.32 (m, 4H), 6.82 (dd, J = 4.0, 1.3 Hz, 1H), 6.78 (dd, J = 4.0, 2.7 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ: 151.58, 136.0, 135.5, 129.6, 129.2, 128.4, 127.2, 127.2, 127.1, 126.2, 125.1, 114.5, 113.6, 107.7. **HRMS (ESI)** m/z calcd for $C_{17}H_{23}NSe^+$ $[M+H]^+$: 319.02980, found 319.10059.

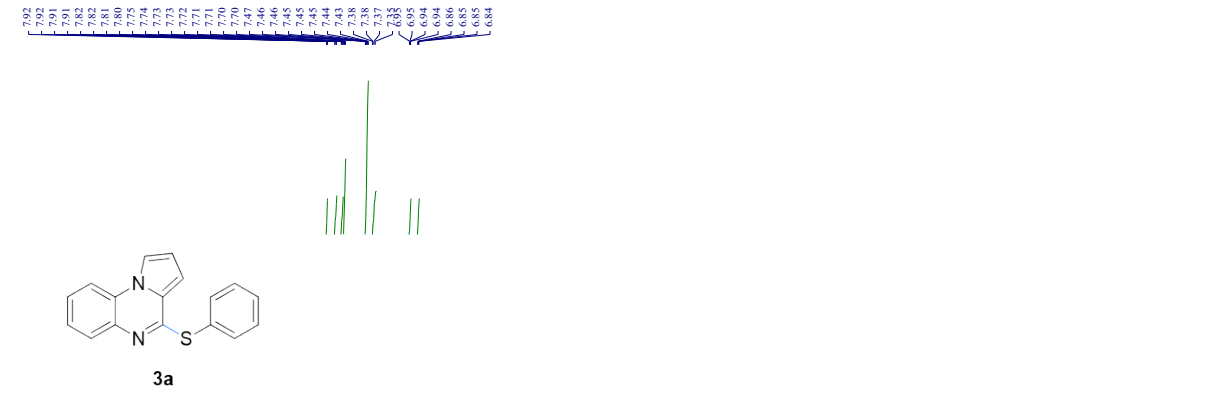


3r

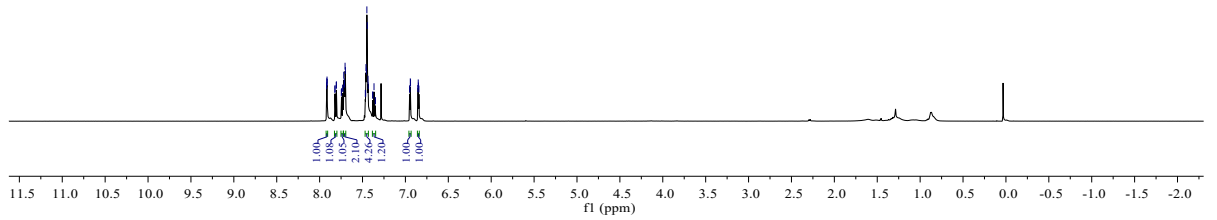
2-(phenylthio)benzo[d]thiazole (3t): The title compound was prepared from (2-isocyanophenyl)(methyl)sulfane **5a** (14.90 mg, 0.10 mmol) and 1,2-Dipheny ldisulfane **2a** (21.80 mg) and was purified by column chromatography (50:1 petroleum ether: ethyl acetate) to give a pale yellow oil; 18 mg, 73 % yield; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ :7.91 (dt, J = 8.2, 0.8 Hz, 1H), 7.75 – 7.71 (m, 2H), 7.65 – 7.61 (m, 1H), 7.52 – 7.44 (m, 3H), 7.40 (ddd, J = 8.4, 7.3, 1.2 Hz, 1H), 7.25 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.6, 154.0, 135.6, 135.4, 130.5, 130.0, 126.2, 124.4, 122.0, 120.9. **HRMS (ESI)** m/z calcd for $C_{13}H_{10}NS_2^+$ $[M+H]^+$: 244.02491, found 244.02405.

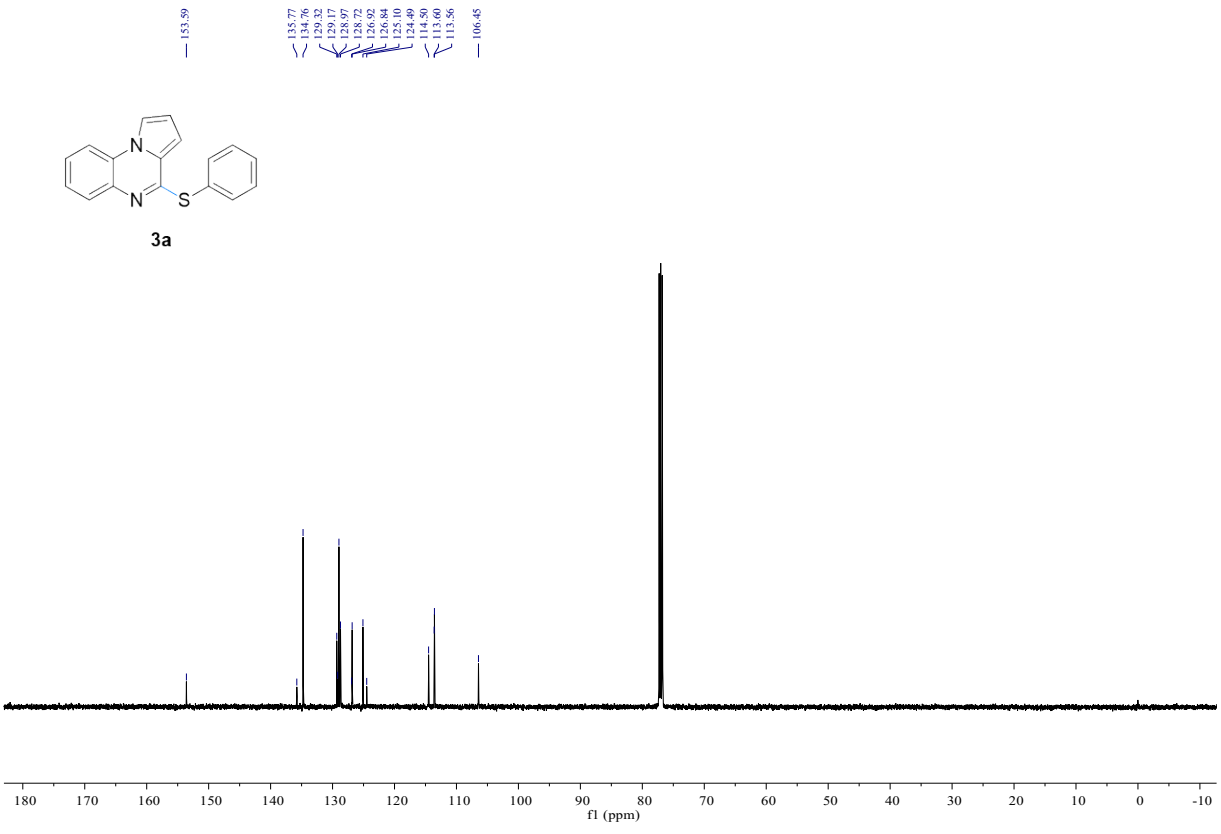
IX. ^{1}H NMR, and ^{13}C NMR and ^{19}F NMR Spectrum of All Products.

The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3a** (using $CDCl_3$ as solvent)



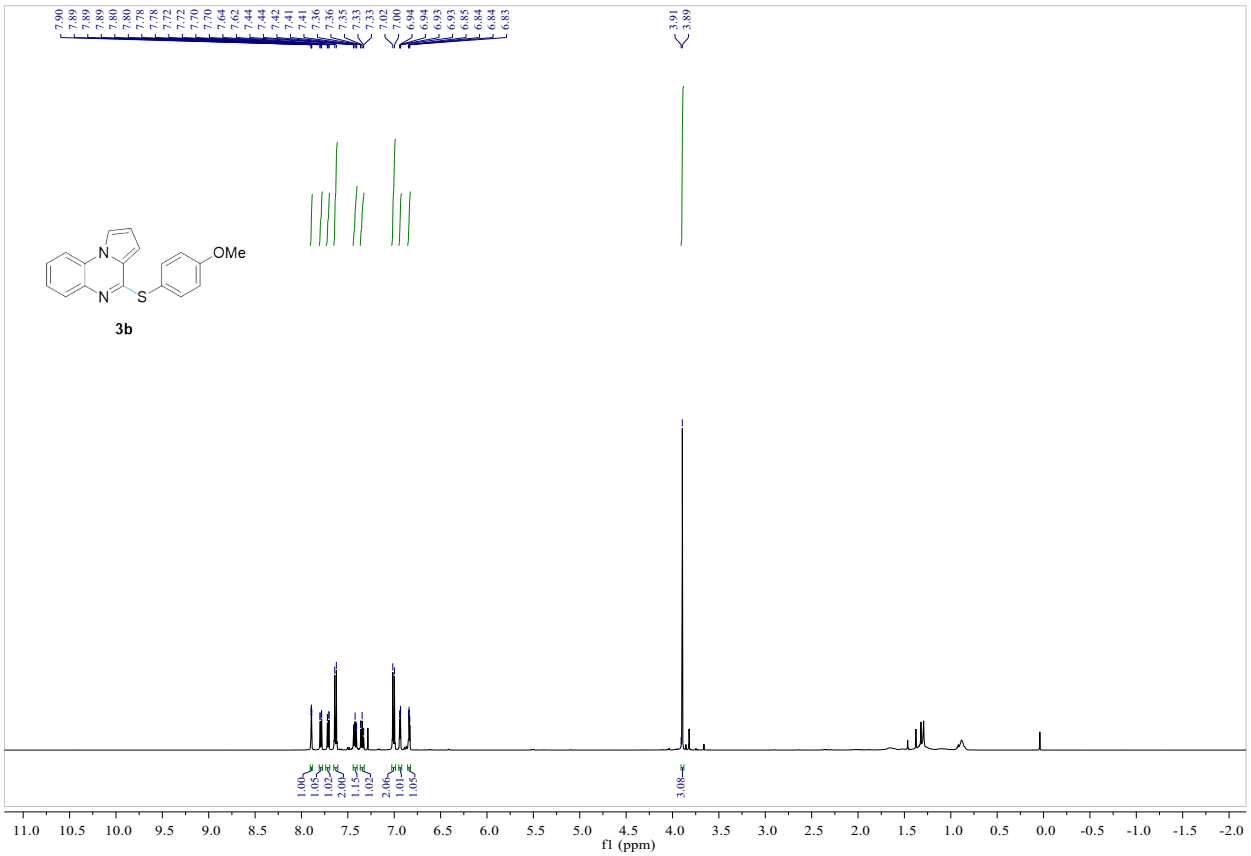
3a

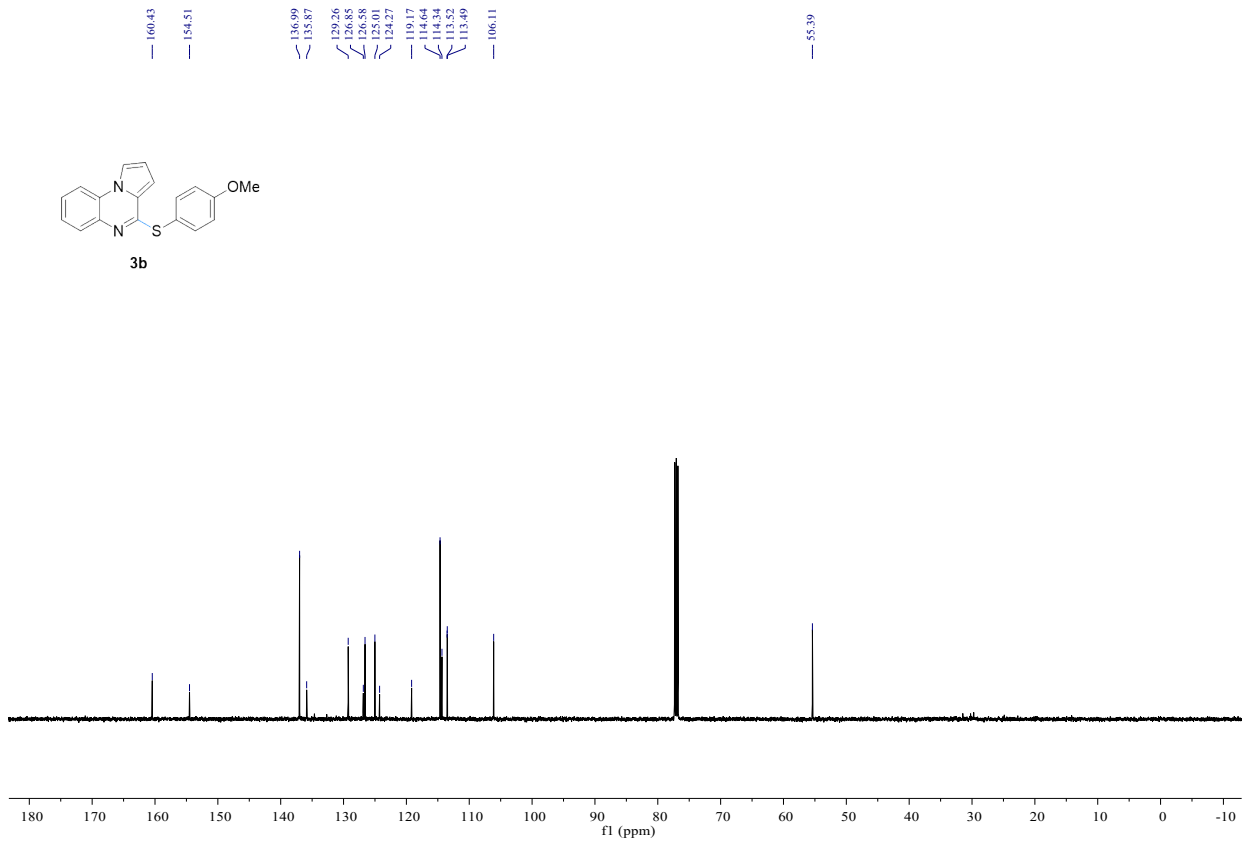




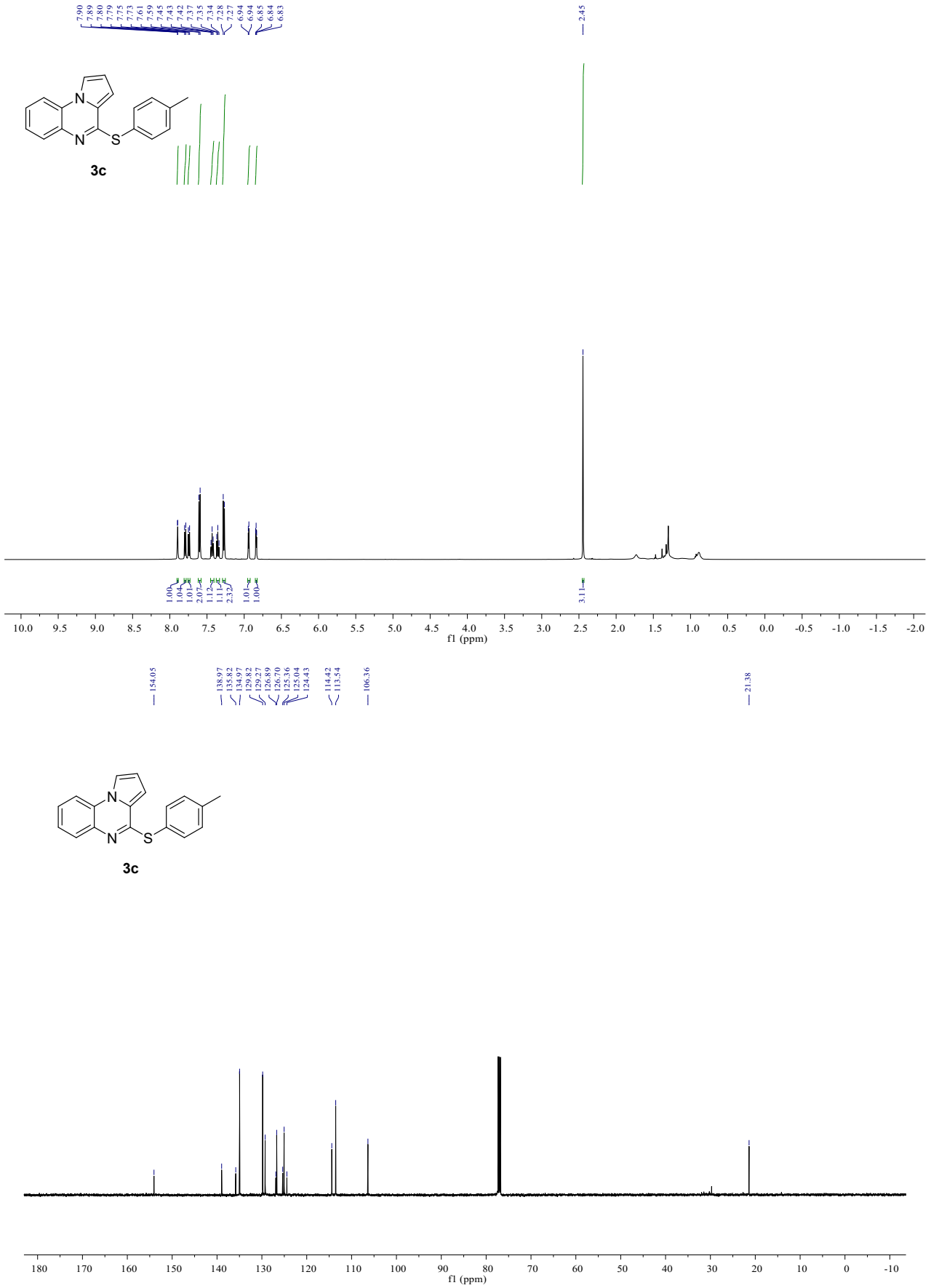
3a

The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3b** (using $CDCl_3$ as solvent)

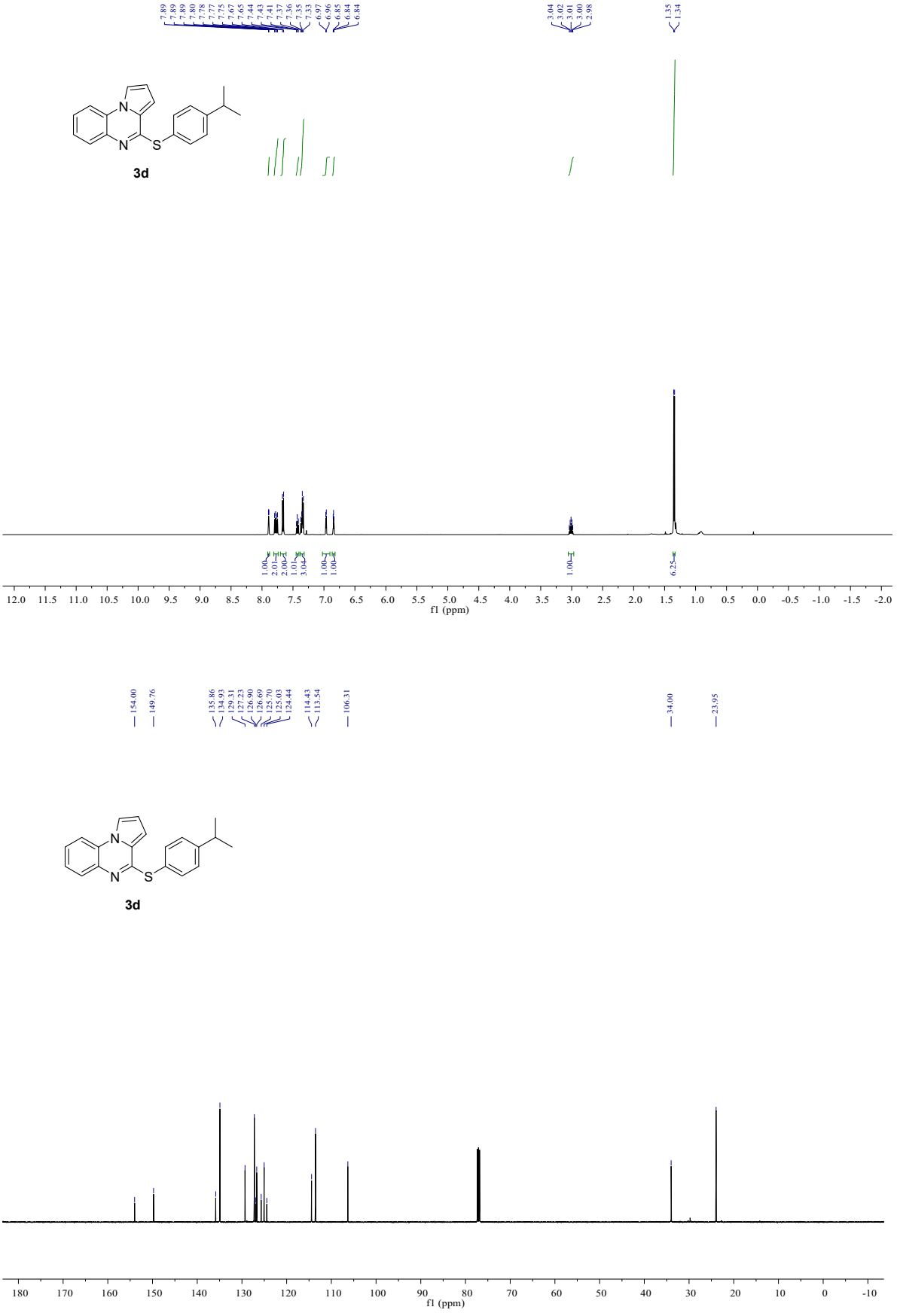




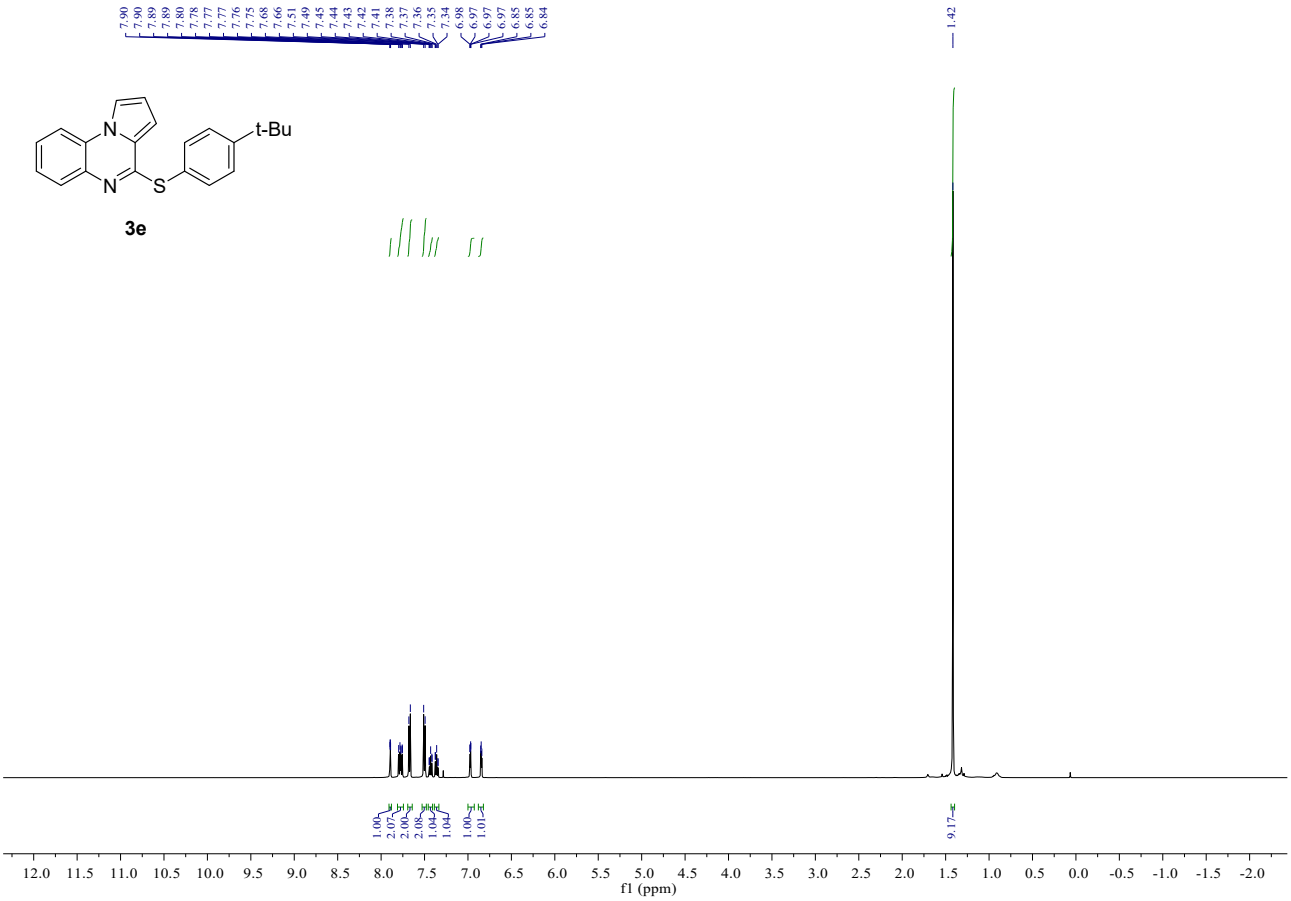
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3c** (using $CDCl_3$ as solvent)

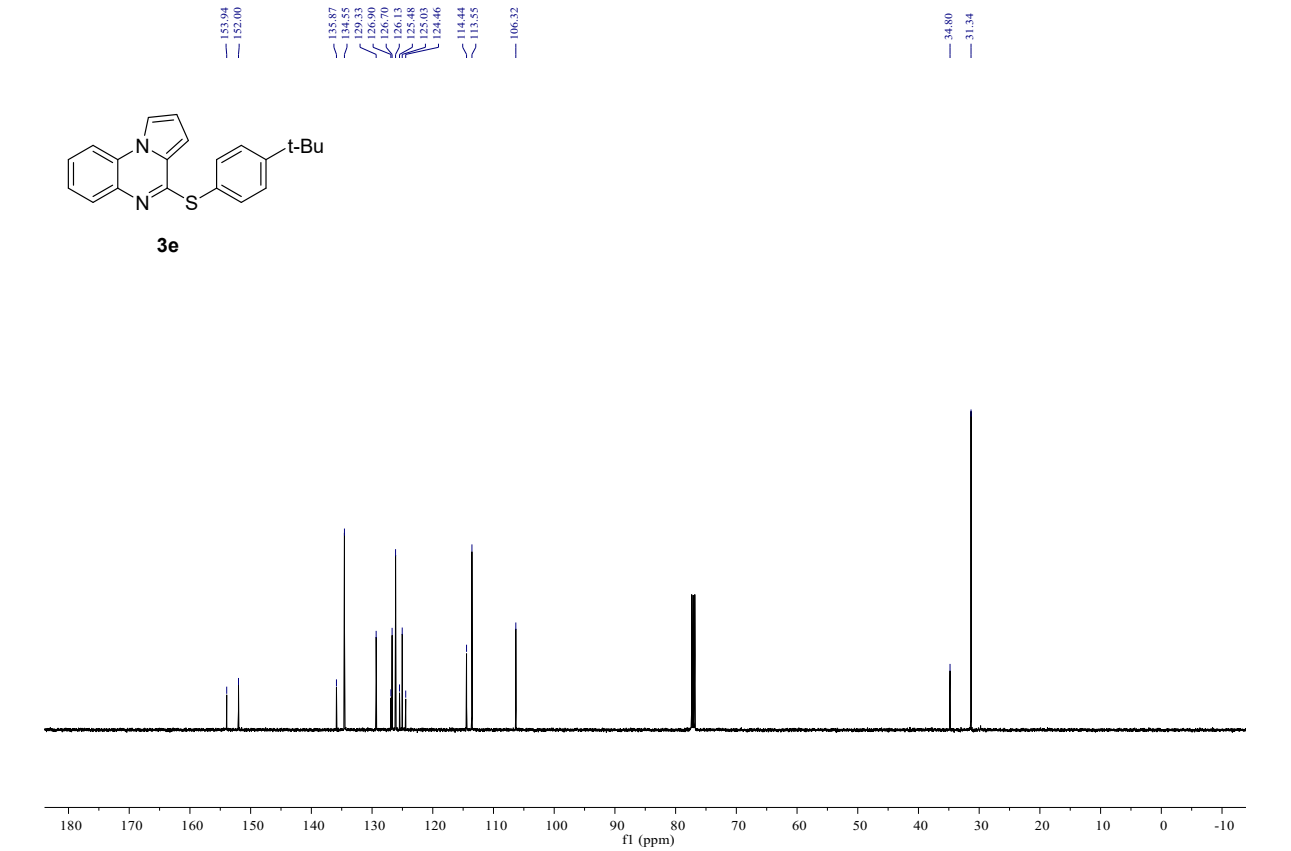


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3d** (using $CDCl_3$ as solvent)

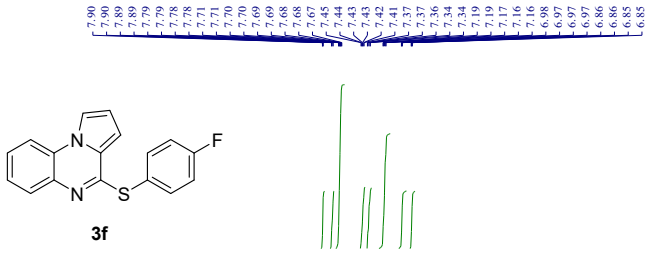


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3e** (using $CDCl_3$ as solvent)

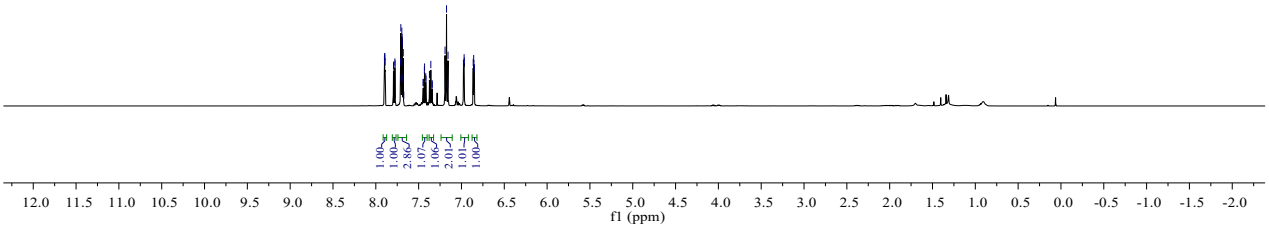


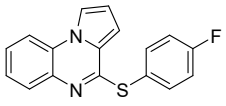


The ^{1}H NMR (400 MHz) 、^{13}C NMR (101 MHz) and ^{19}F NMR(471 MHz) for **3f** (using $CDCl_3$ as solvent)

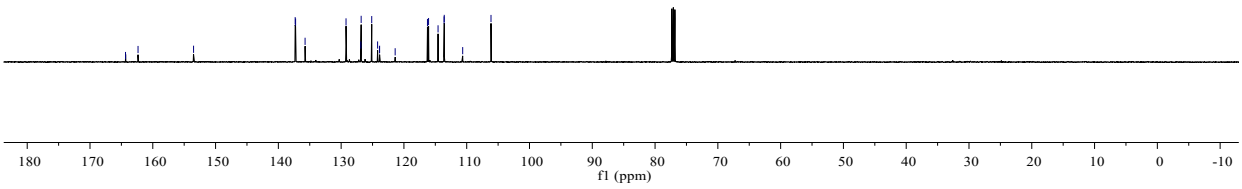


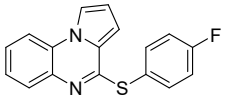
3f



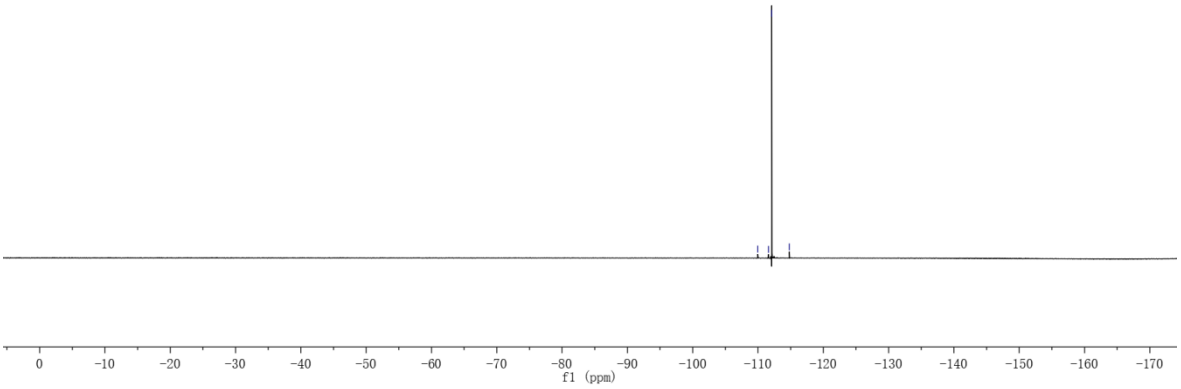


3f

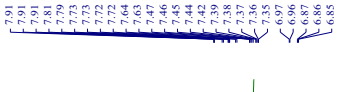


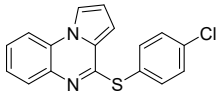


3f

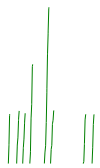


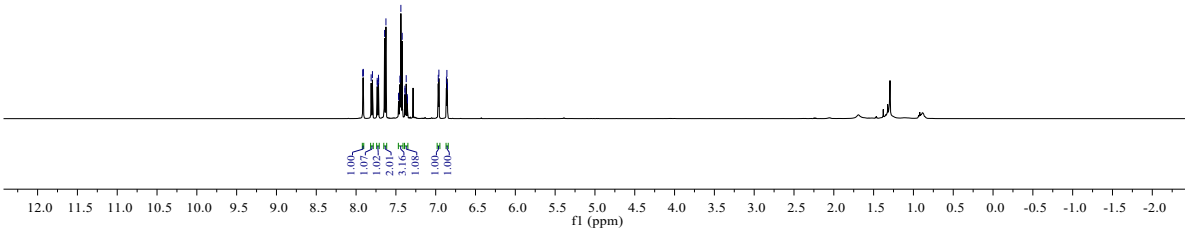
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3g** (using $CDCl_3$ as solvent)

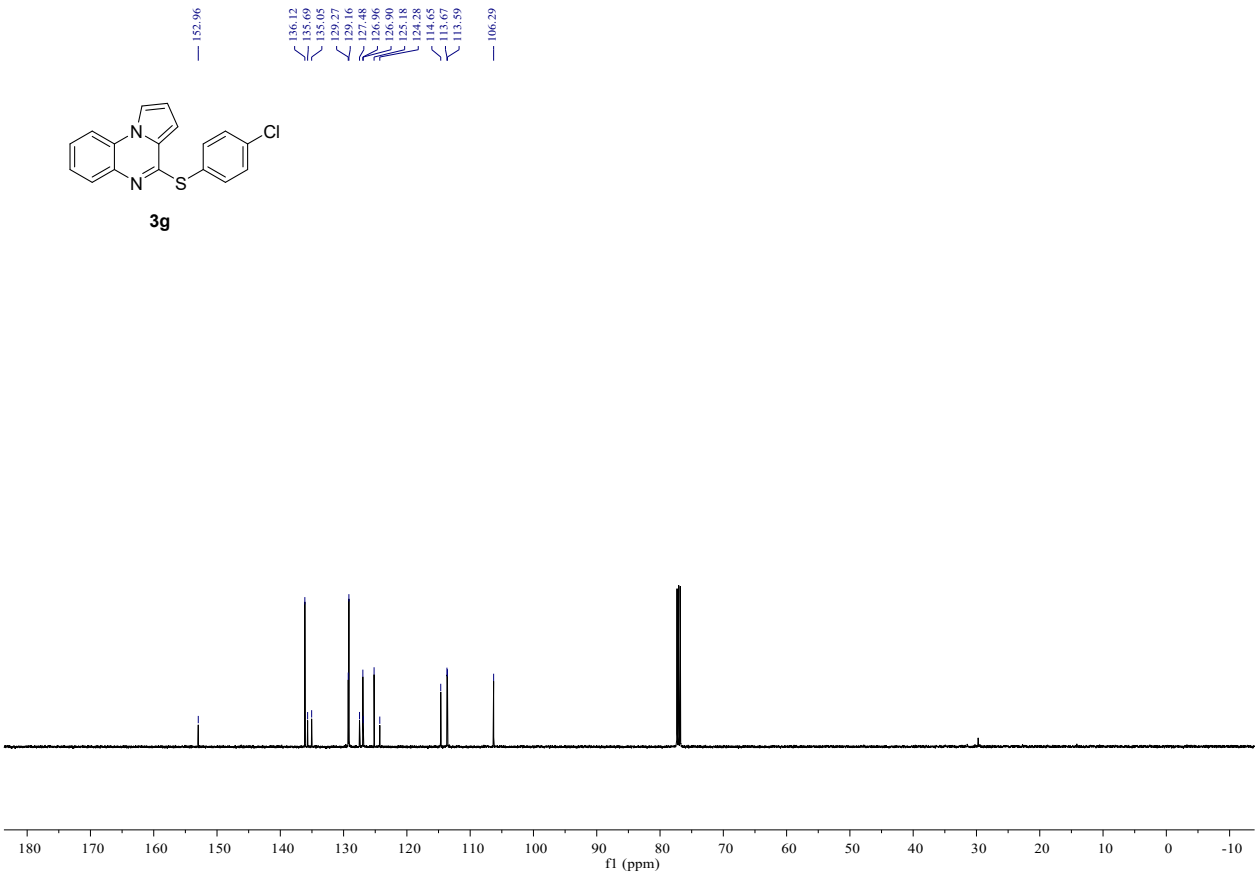




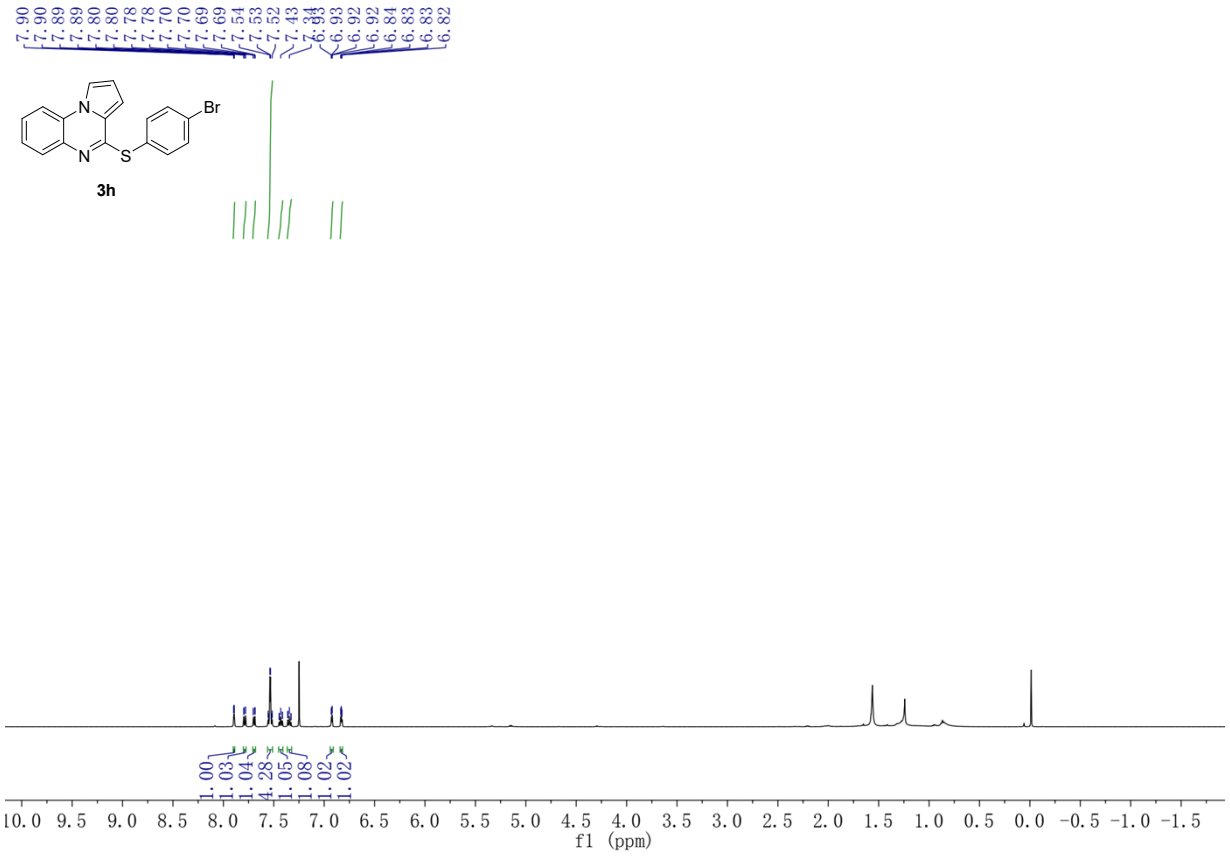
3g

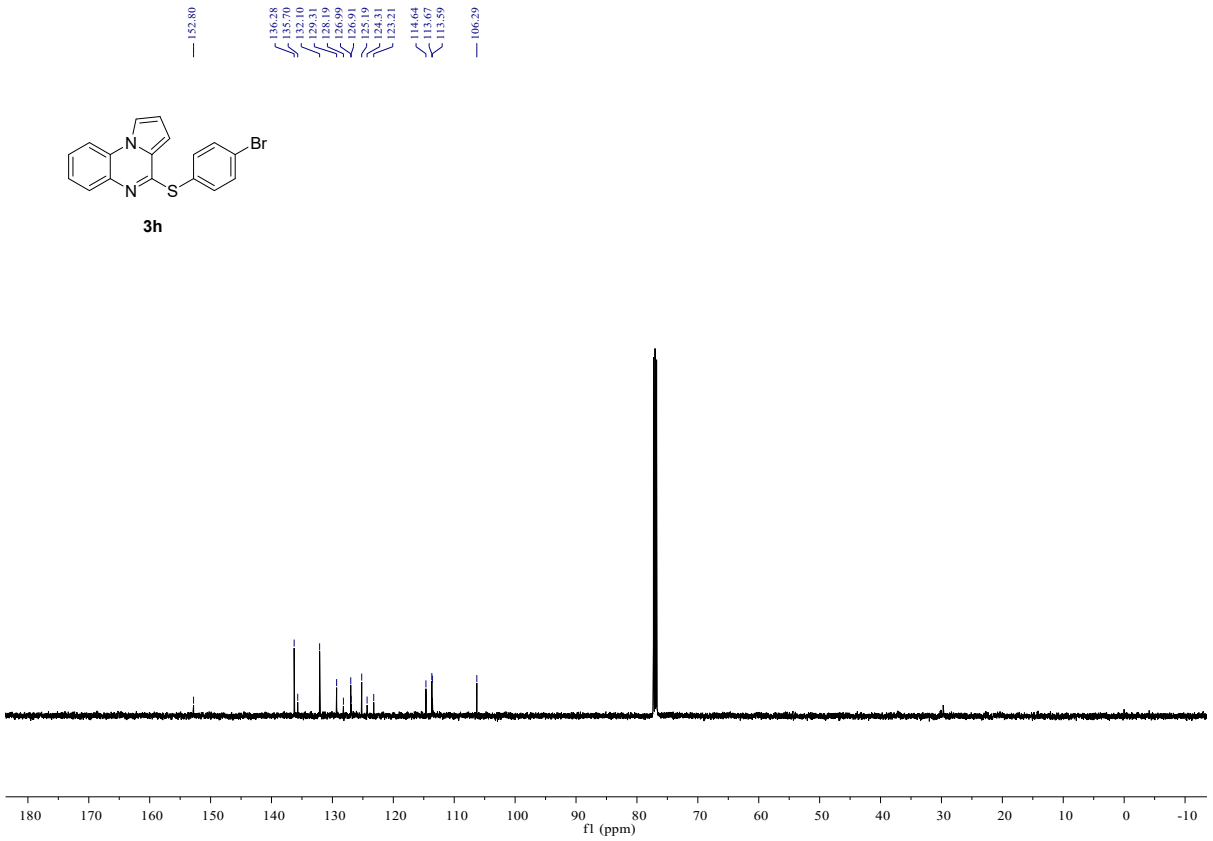




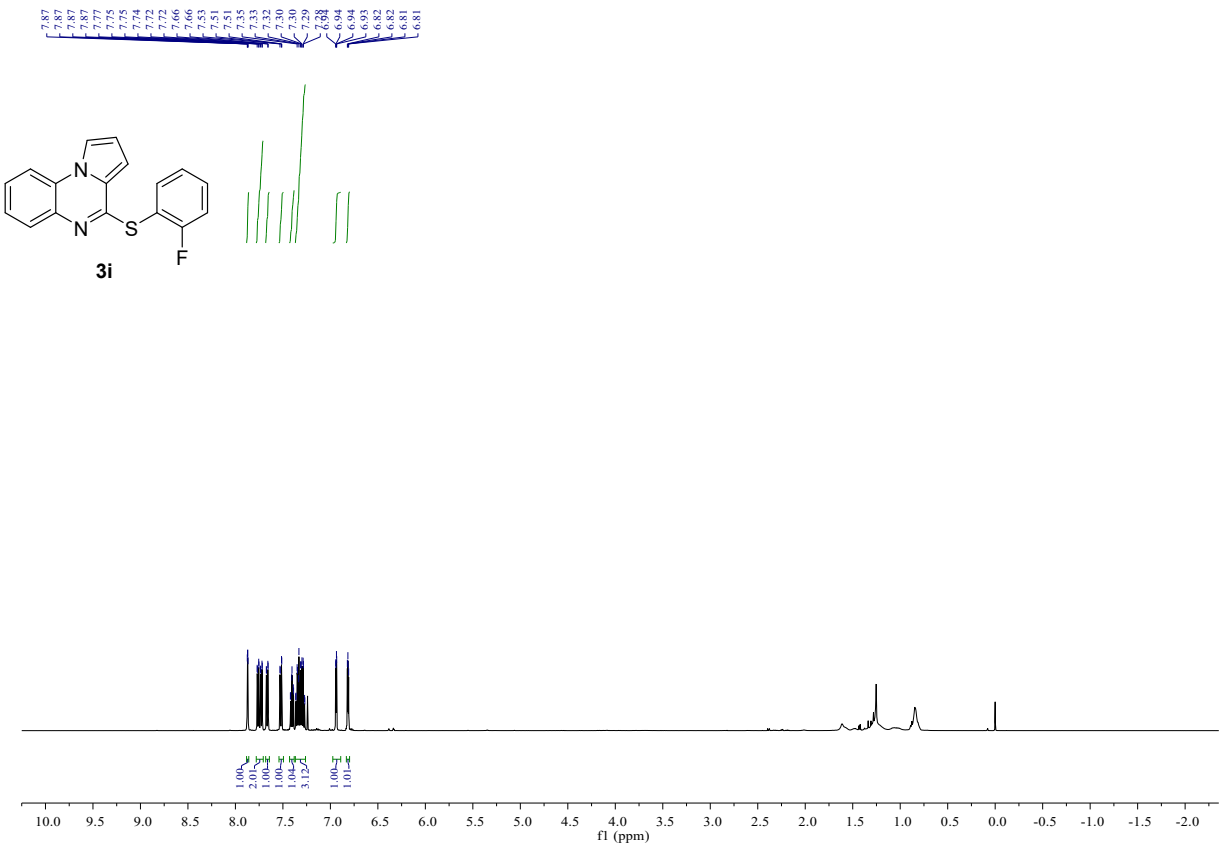


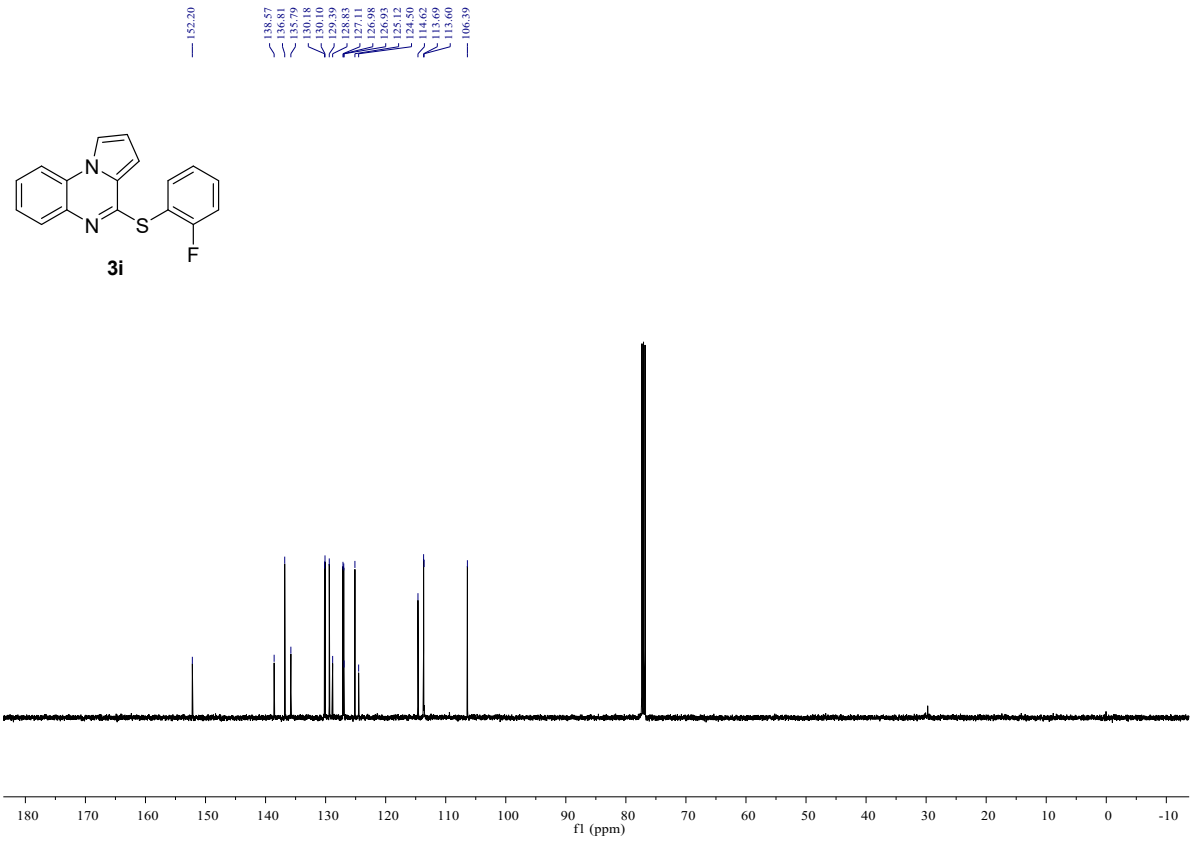
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3h** (using $CDCl_3$ as solvent)

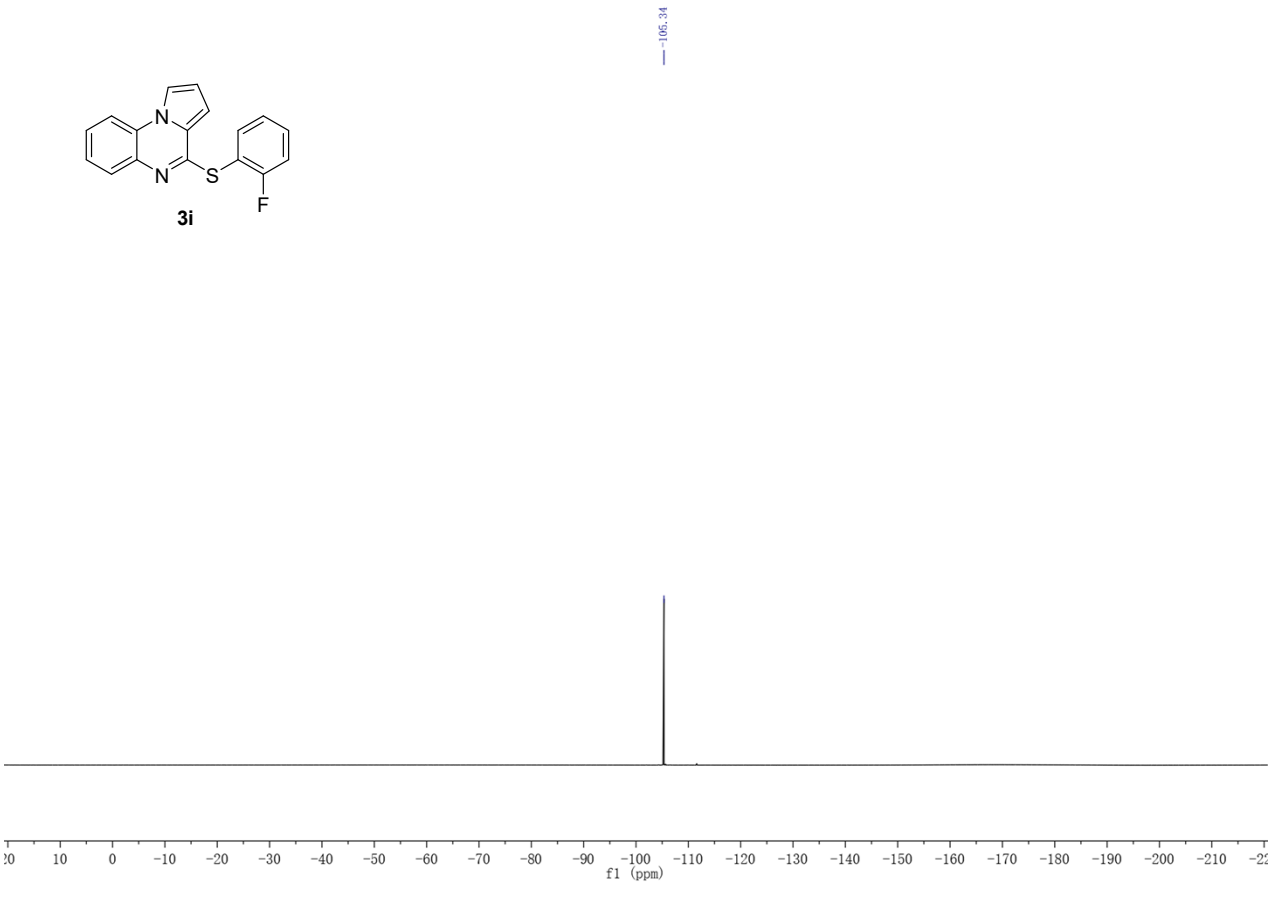




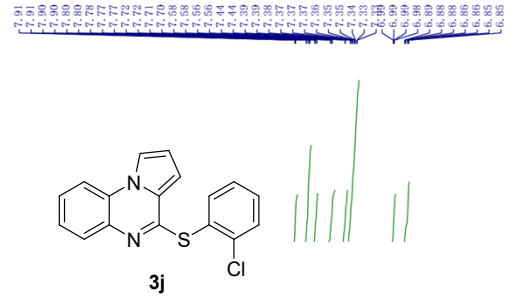
The ^{1}H NMR (400 MHz) 、^{13}C NMR (101 MHz) and ^{19}F NMR(471 MHz) for **3i** (using $CDCl_3$ as solvent)



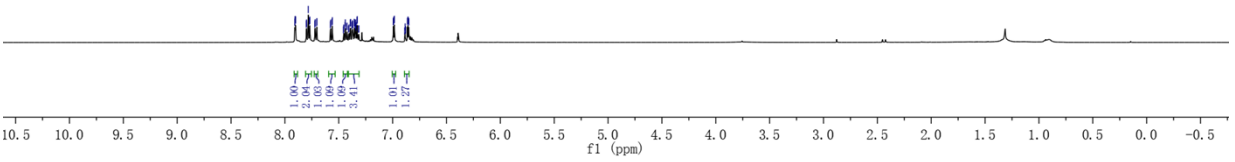

152.20
138.57
136.81
135.79
130.18
130.10
129.39
128.83
127.11
126.98
126.93
125.12
124.50
114.62
113.69
113.60
106.39
N
N
S
F
3i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

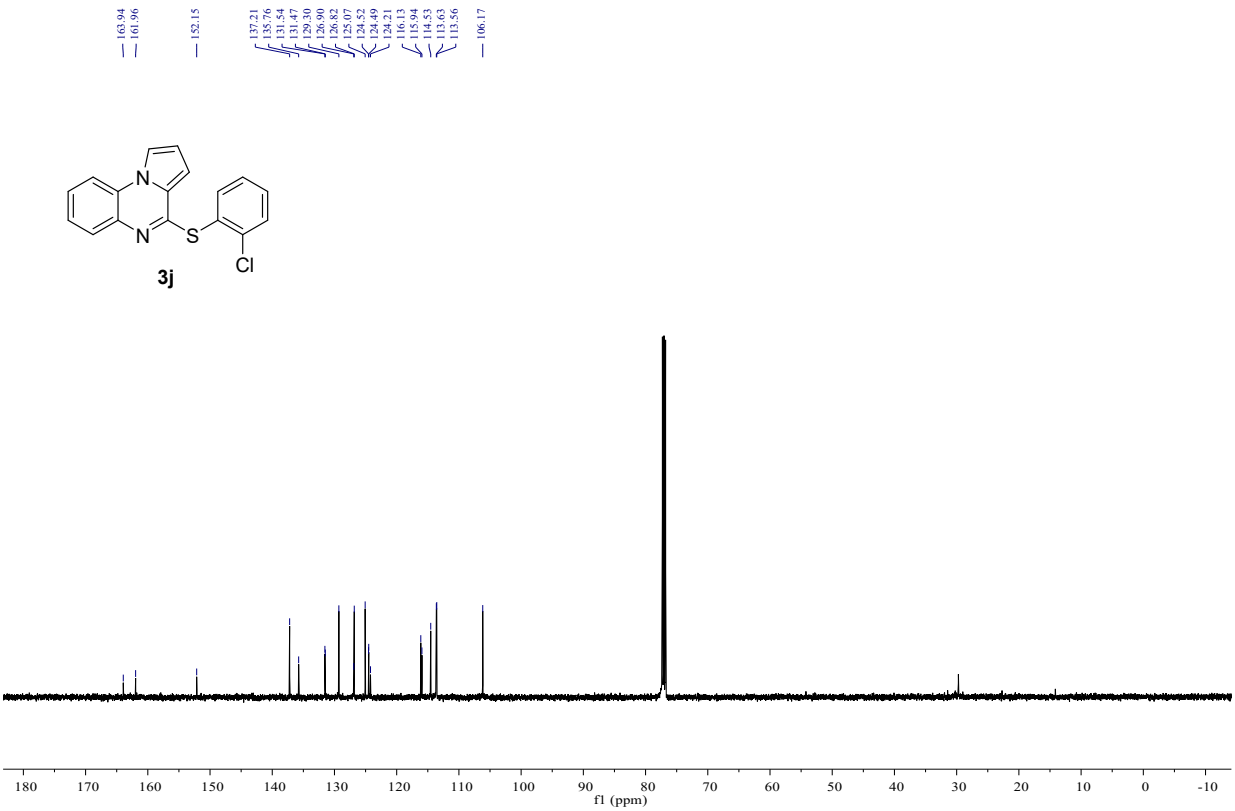

106.34
N
N
S
F
3i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3j** (using $CDCl_3$ as solvent)



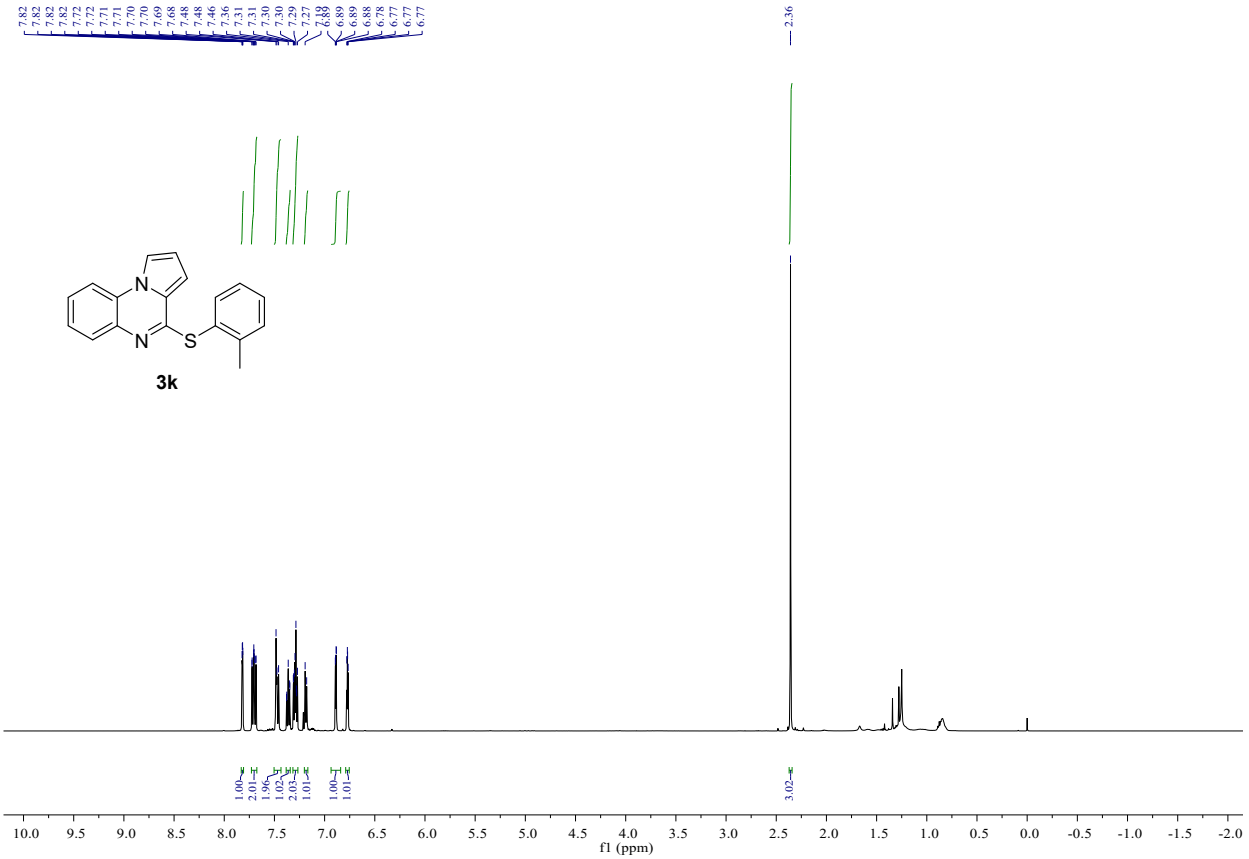
3j

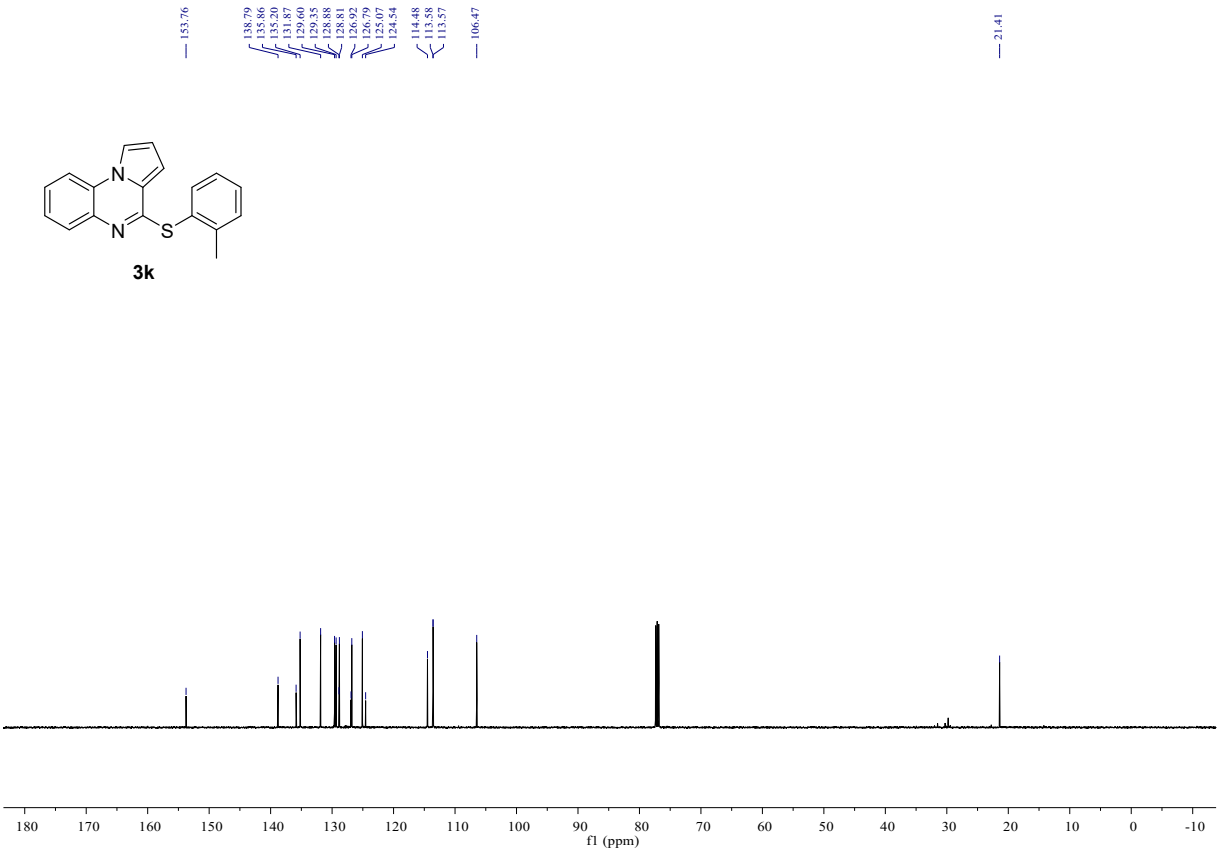




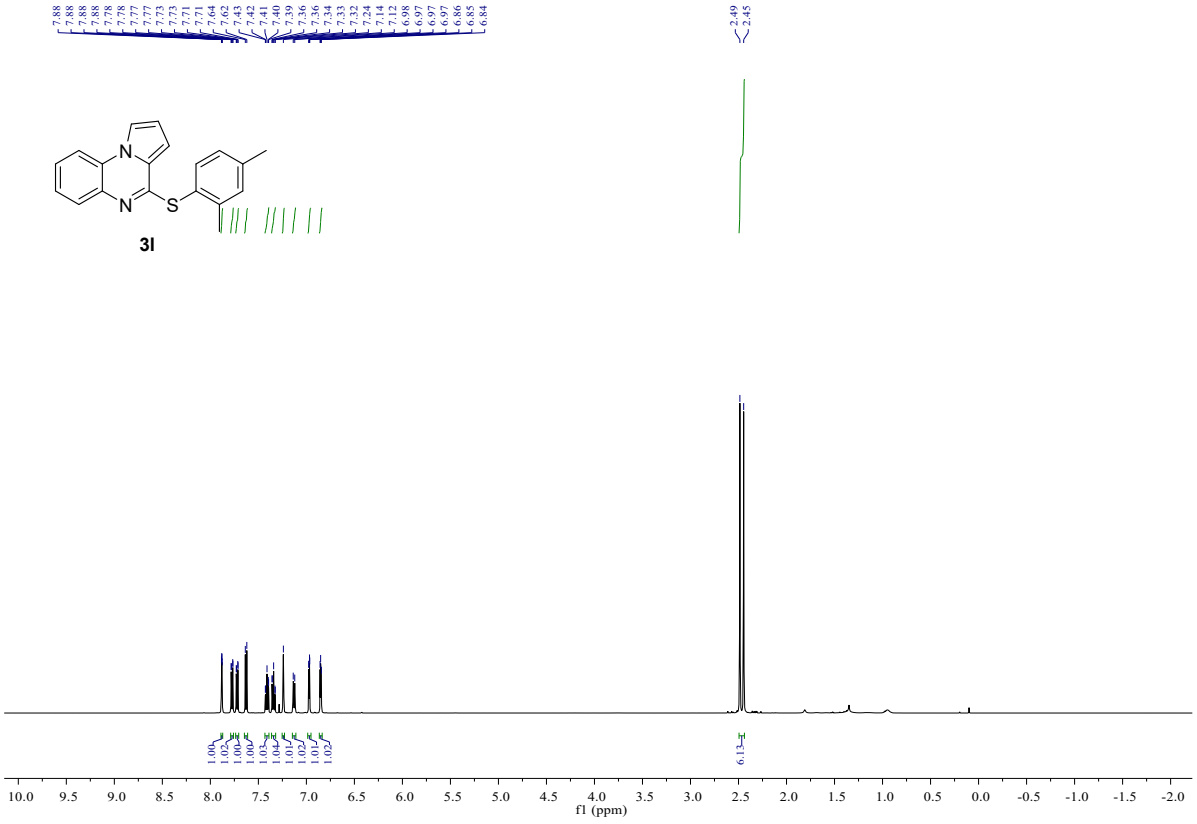
3j

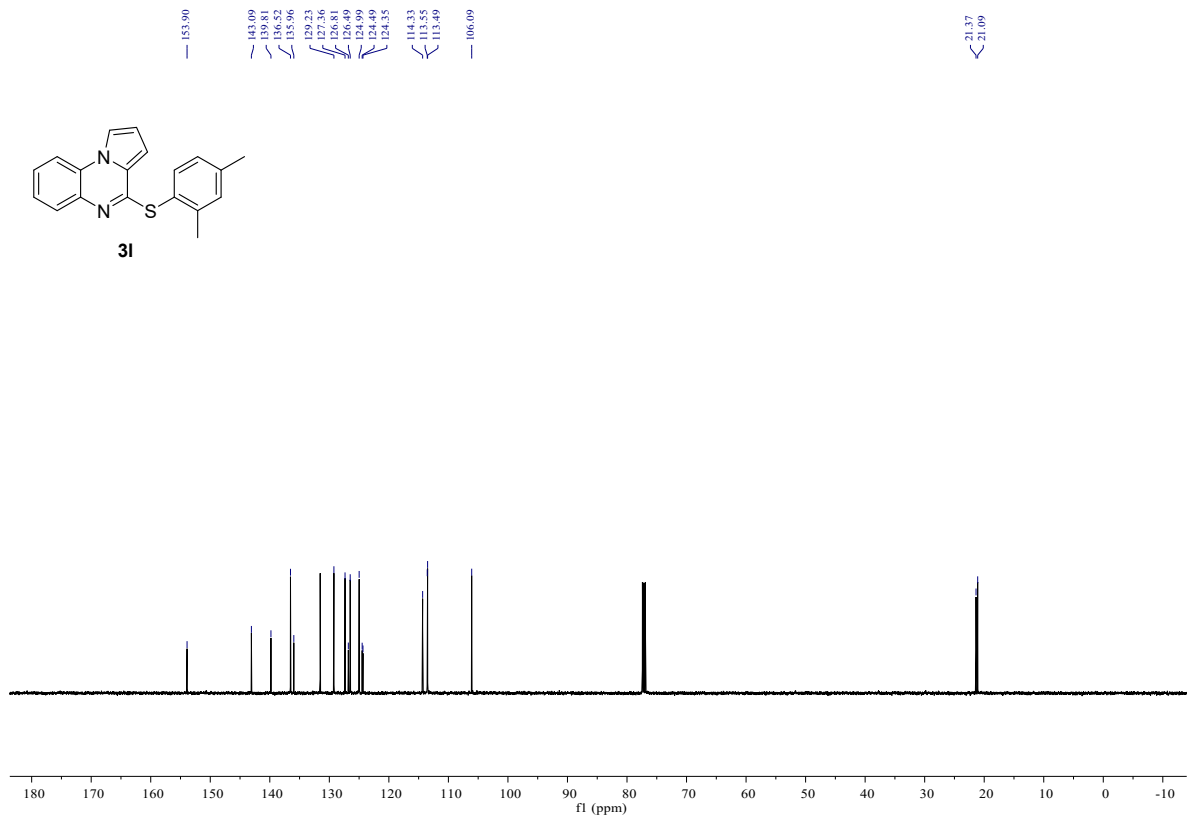
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3k** (using $CDCl_3$ as solvent)



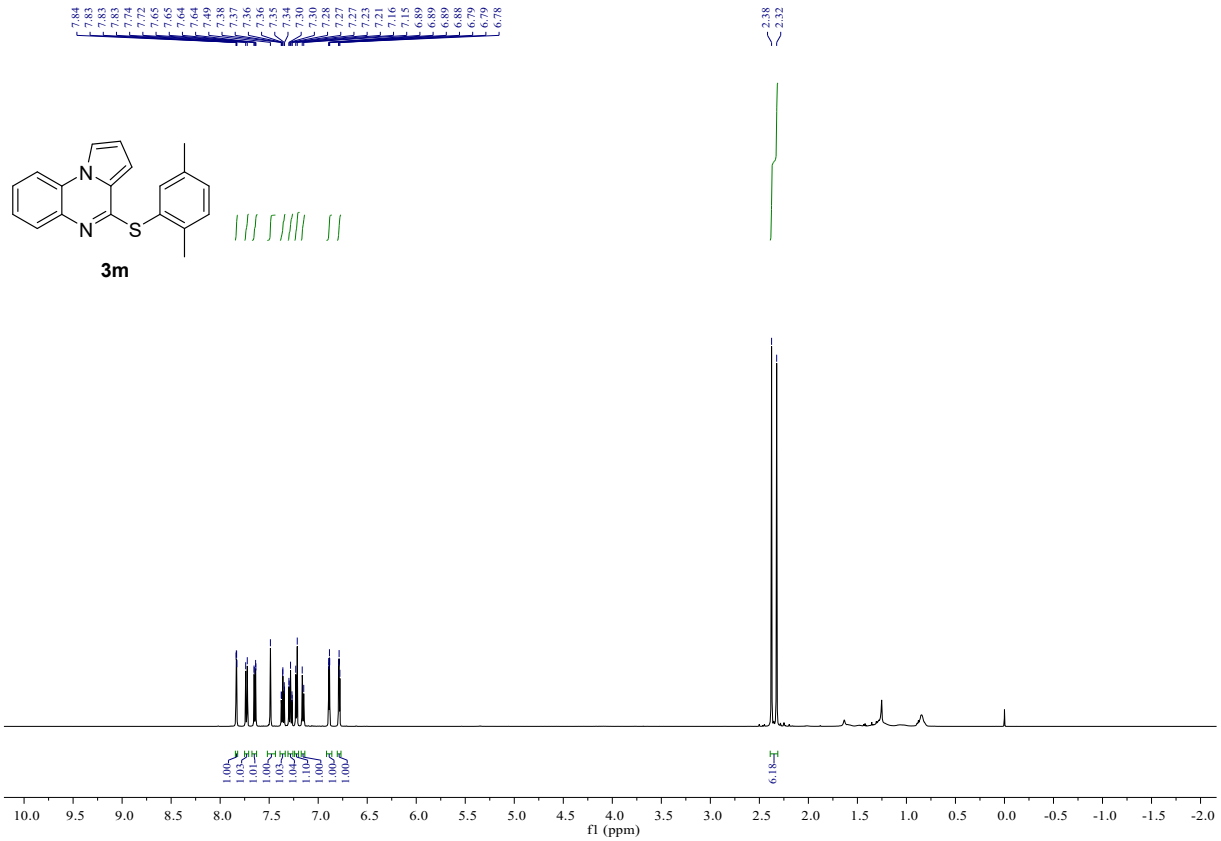


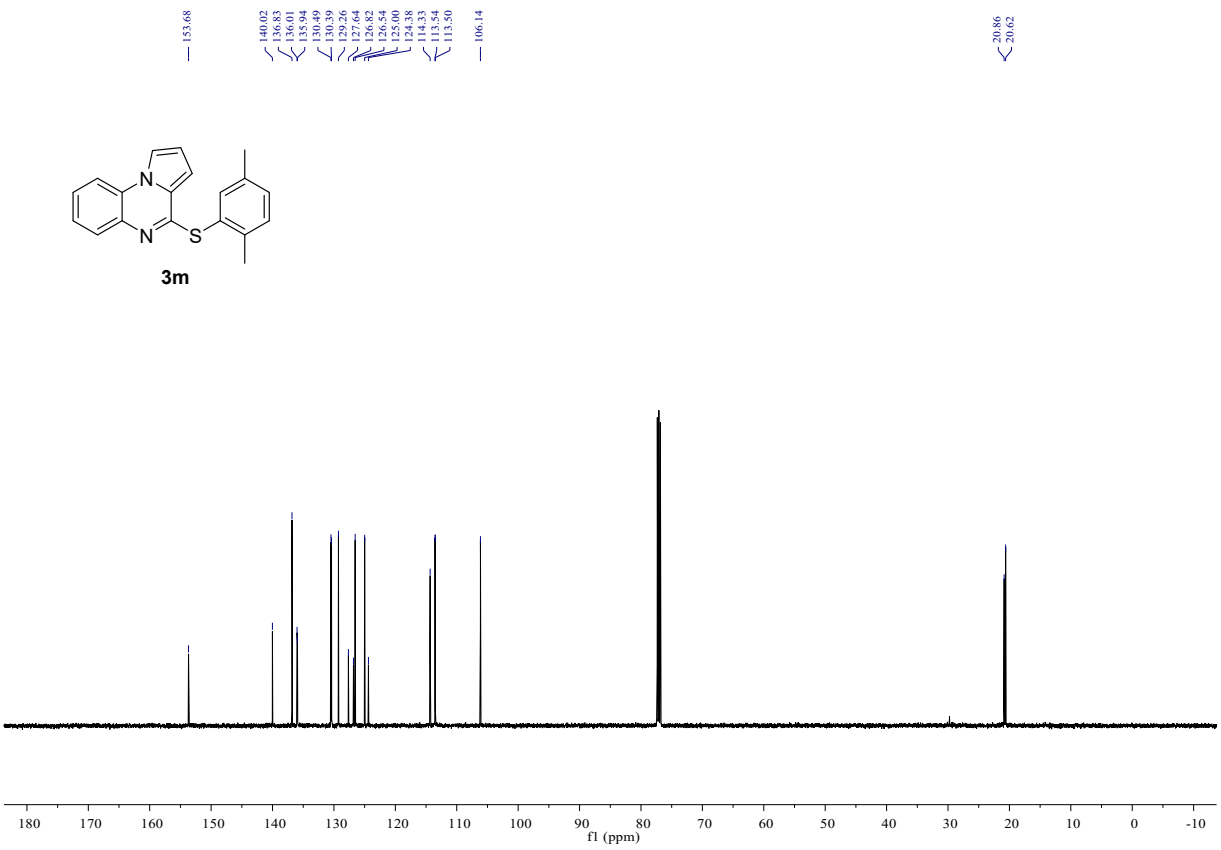
The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3l** (using $CDCl_3$ as solvent)



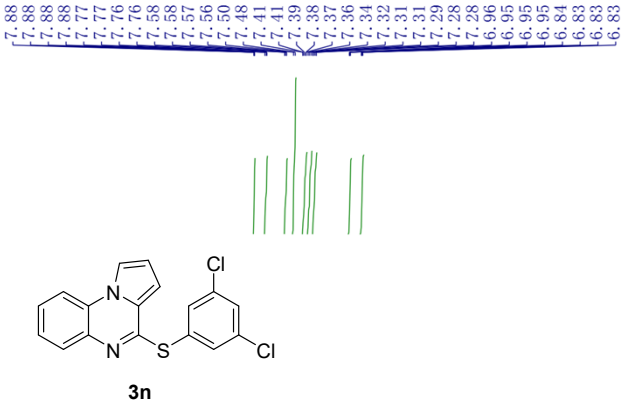


The ^{1}H NMR (400 MHz) and ^{13}C NMR and (101 MHz) for **3m** (using $CDCl_3$ as solvent)

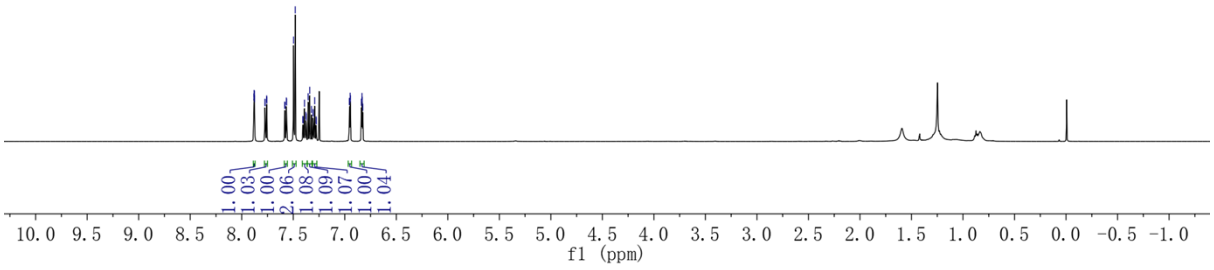


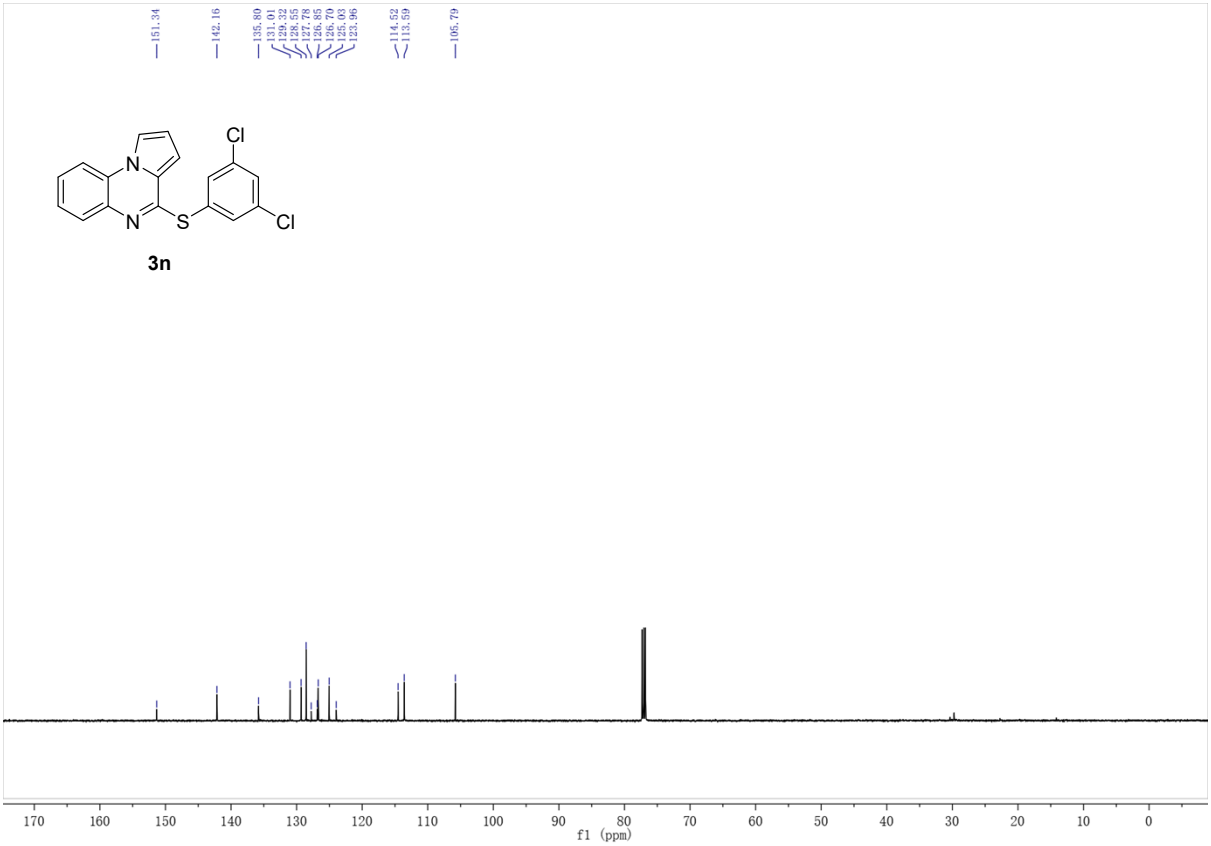


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3n** (using $CDCl_3$ as solvent)



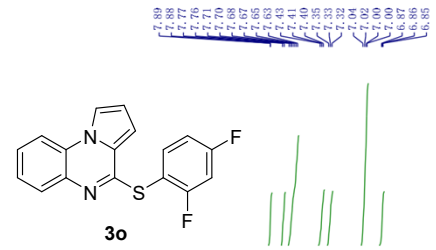
3n

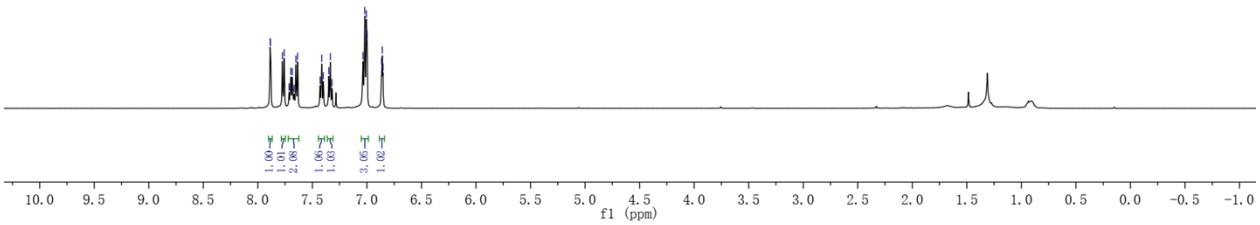


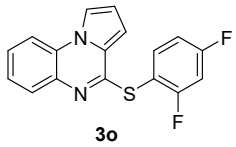


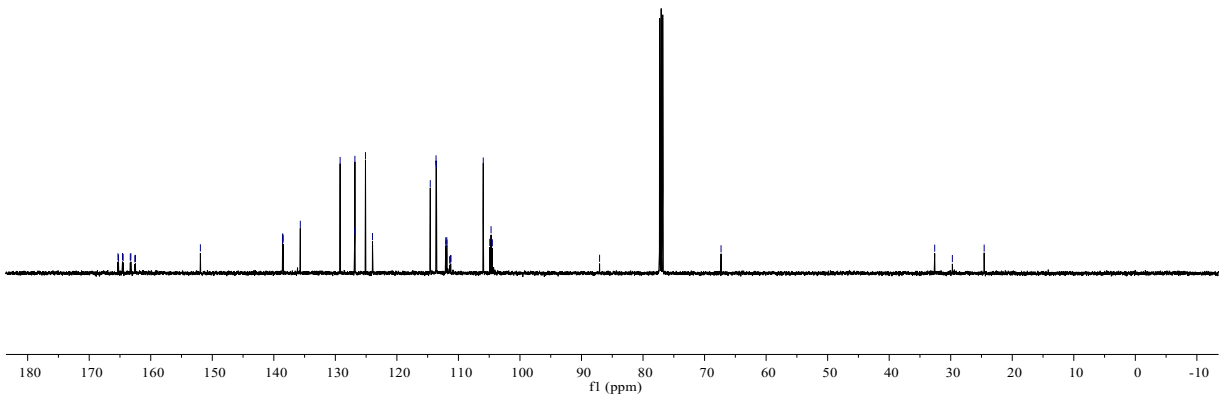
3n

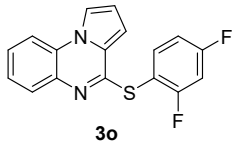
The ^{1}H NMR (400 MHz) 、^{13}C NMR (101 MHz) and ^{19}F NMR(471 MHz) for **3o** (using $CDCl_3$ as solvent)



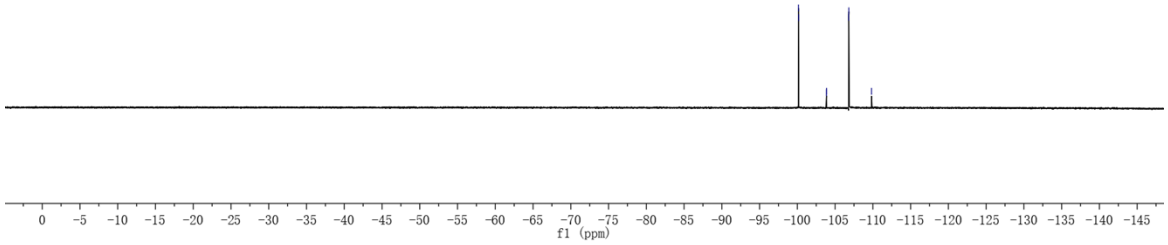




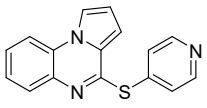




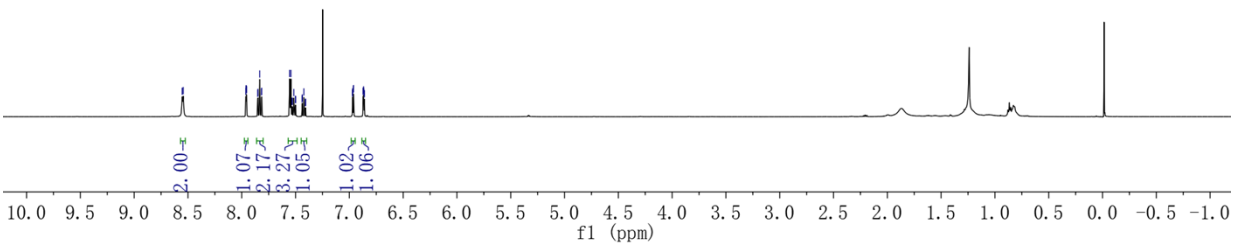
3o

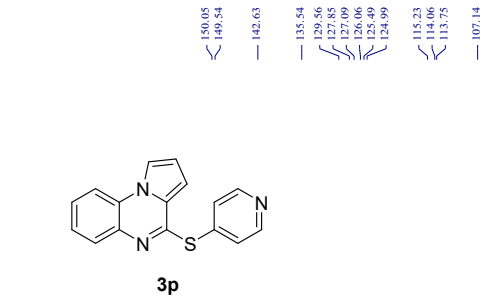


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3p** (using $CDCl_3$ as solvent)

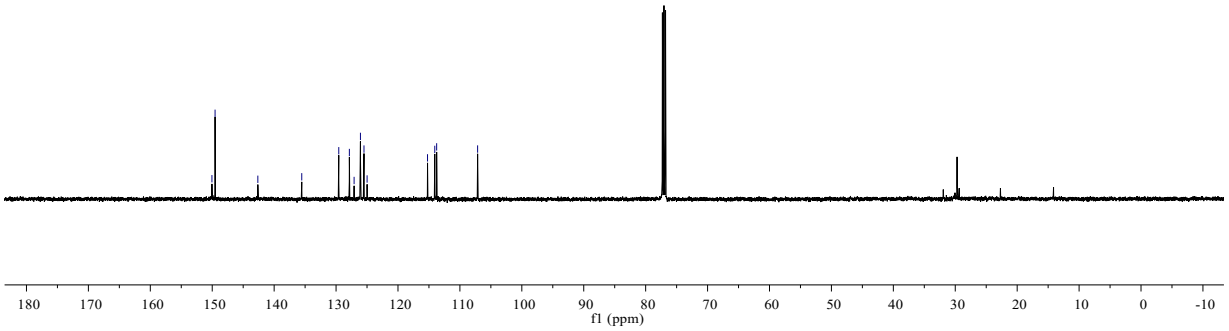


3p

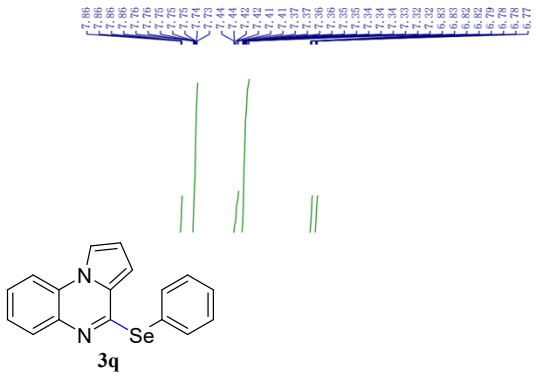




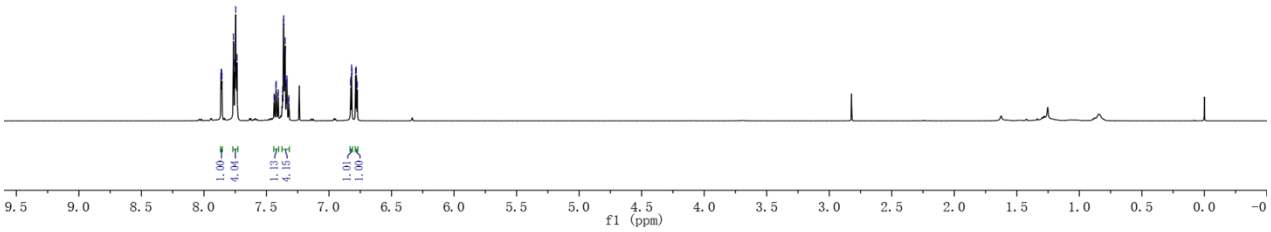
3p

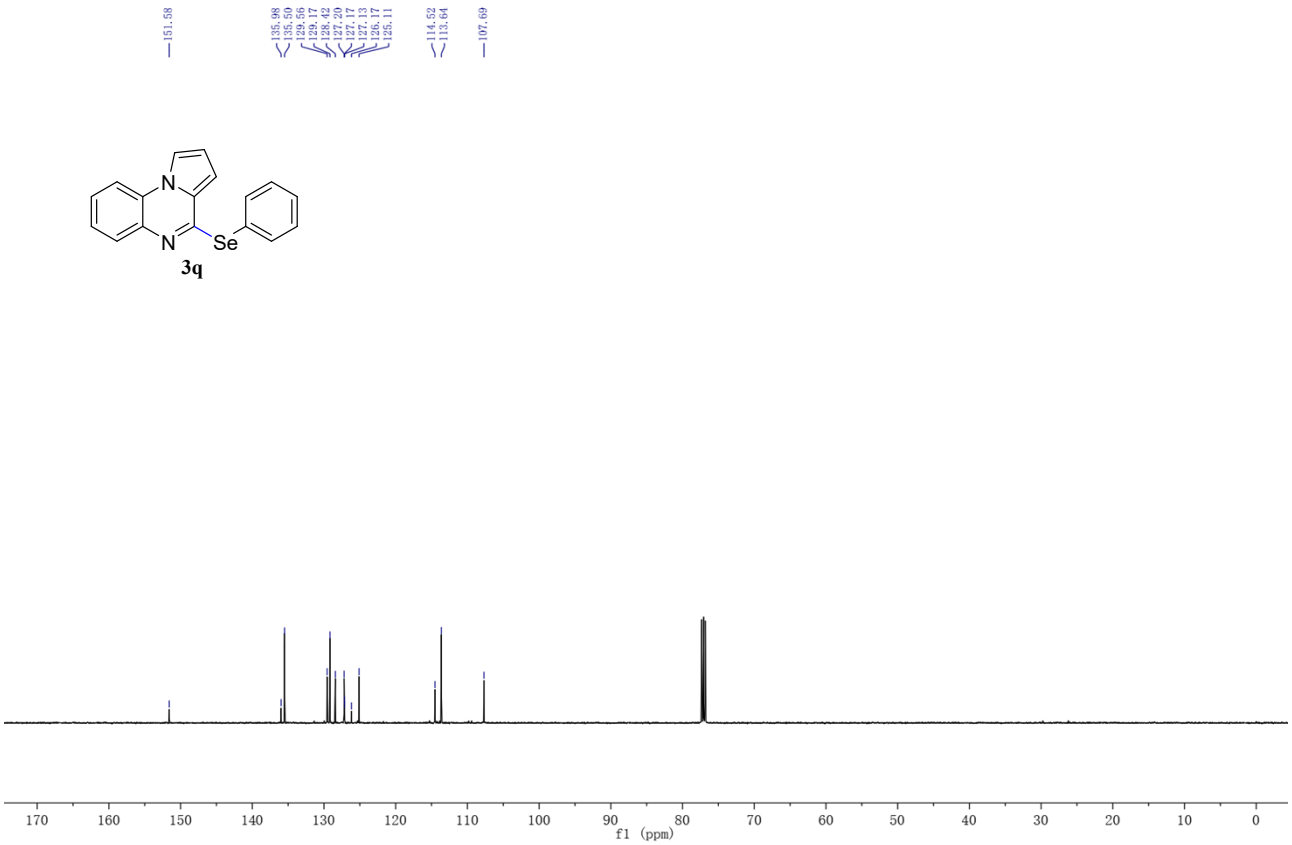


The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3q** (using $CDCl_3$ as solvent)

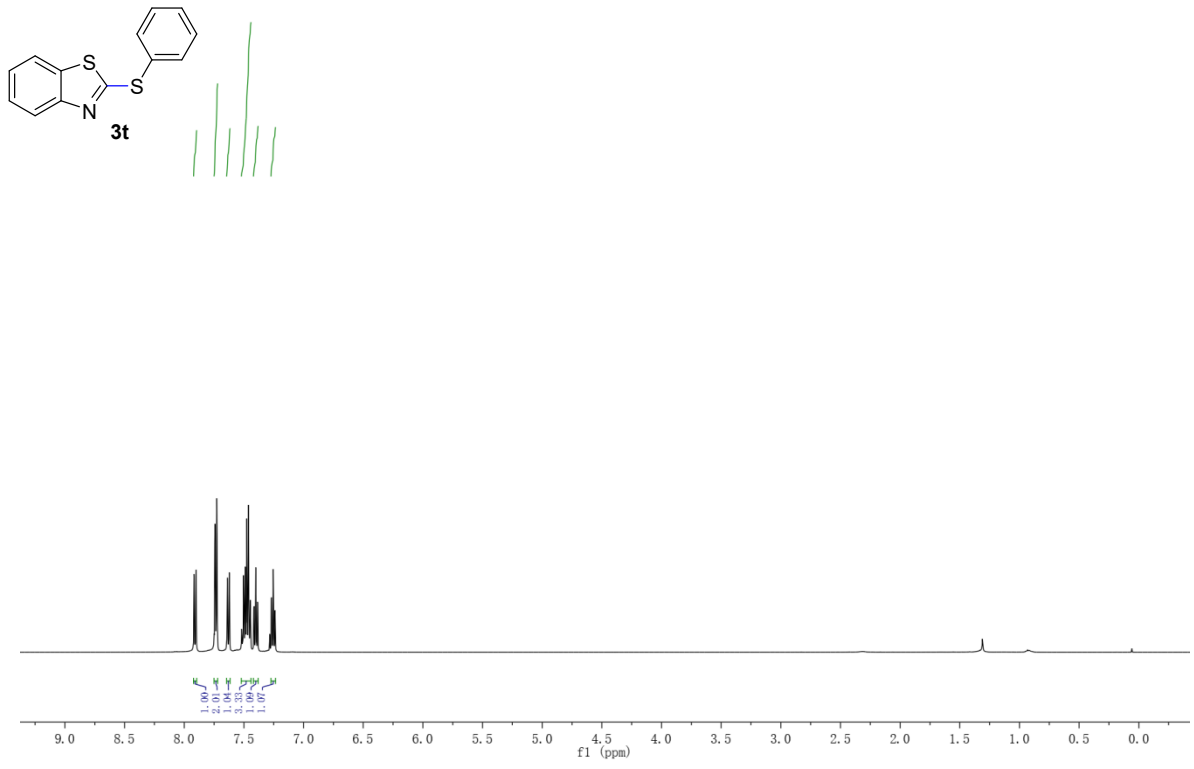


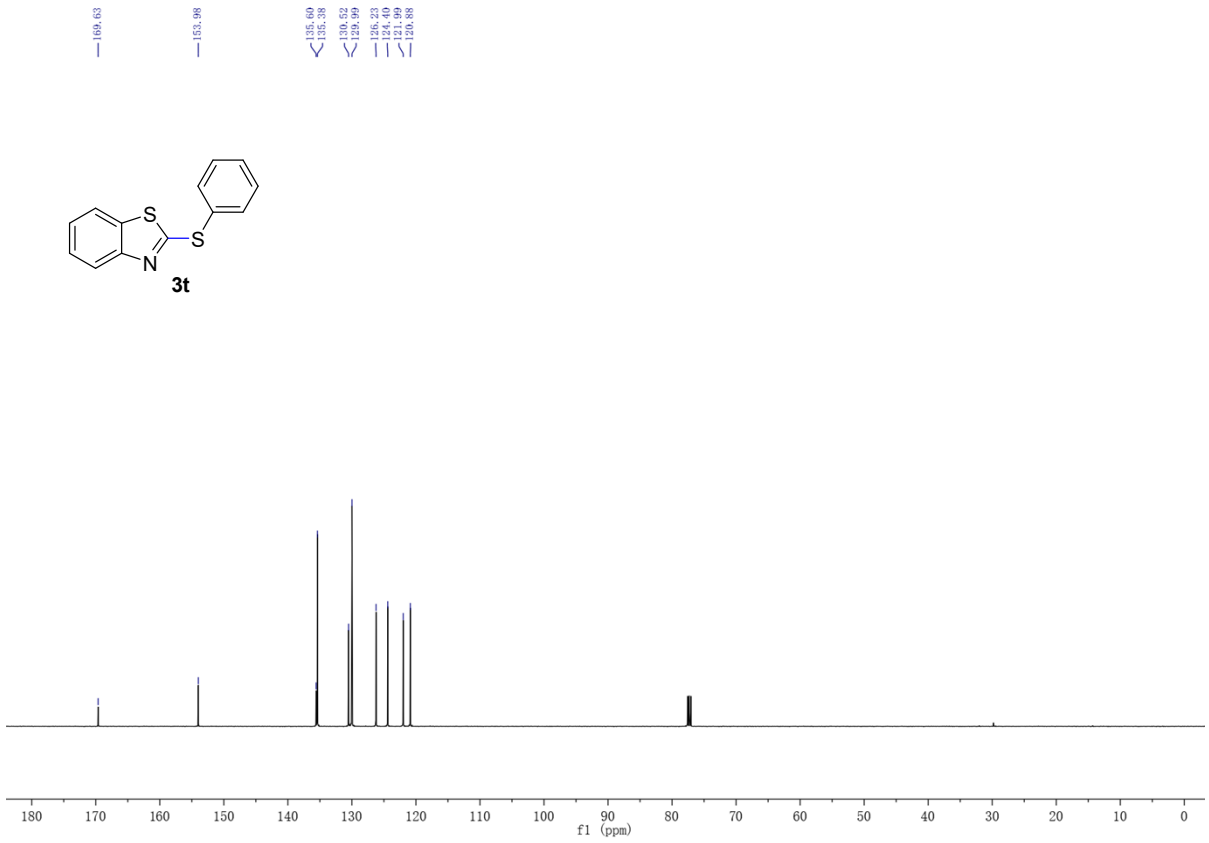
3q





The ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) for **3s** (using $CDCl_3$ as solvent)




169.63
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129.99
126.23
124.40
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120.88
S
S
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170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)