Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Catalyst-Free Aerobic Radical Cascade Reactions of *o*-Vinylphenylisocyanides with Thiols to Access 2-Thio-Substituted Quinolines

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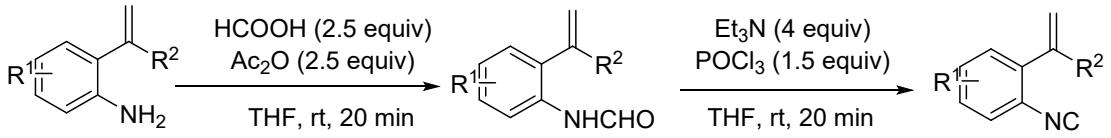
Table of Contents

I. General information

All reagents were commercially available and used without further purification, unless otherwise indicated. Chromatography was carried out on flash silica gel (300−400 mesh). All reactions were monitored by TLC, performed on glass plates with precoated silica gel 60 (F254). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured on a 400 MHz Bruker instrument, with TMS as the internal standard. All chemical shifts are reported in ppm scale. High-resolution mass spectra (HRMS) were acquired using a Bruker microTOF II focusing spectrometer (ESI).

II. Preparation and analytical data of isocyanide 1

o-Vinylphenylisocyanides **1** was prepared according to previous literature report.[1]



1

Typical synthetic procedure for *o*-vinylphenylisocyanides 1 (with **1a** as an example**)**

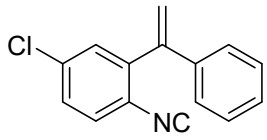
Synthesis of *N*-(2-(3-methylbut-1-en-2-yl)phenyl)formamide:

To a solution of 2-(3-methylbut-1-en-2-yl)aniline (10 mmol, 1.611 g) in THF (15 mL) at 0 °C was added acetic anhydride (25 mmol, 3.3 mL) .The mixture was then stirred at room temperature for 20 minutes. The mixture was quenched with saturated Na_2CO_3 solution and extracted 3 times with DCM. The organic layers were combined, dried over anhydrous Mg_2SO_4 and concentrated under reduced pressure, the solid residue was purified by column chromatography (20% EtOAc/hexane) to give *N*-(2-(3-methylbut-1-en-2-yl)phenyl)formamide (1.798 g, 95 %).

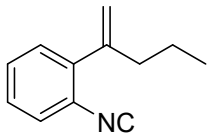
Synthesis of 1-isocyano-2-(3-methylbut-1-en-2-yl)benzene:

N-(2-(3-methylbut-1-en-2-yl)phenyl)formamide (10 mmol, 1.891 g) and Et_3N (5.54 mL) were dissolved in THF (15 mL) under nitrogen atmosphere. $POCl_3$(15 mmol, 1.398 mL) in THF (2 mL) was slowly added to the solution via syringe over 10 min at 0 °C. The reaction mixture was then stirred at room temperature for an additional 20 minutes. After this time, the reaction mixture was diluted with 15 mL of ethyl acetate at 0 °C and slowly quenched with saturated Na_2CO_3 solution while continuing to stir for another 30 minutes. The crude product was then purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give 1-isocyano-2-(3-methylbut-1-en-2-yl)-benzene.

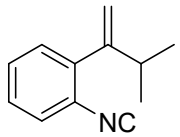
Analytical data of 1 (1f, 1l, 1m,1n)



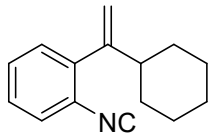
4-chloro-1-isocyano-2-(1-phenylvinyl)benzene (1f). Eluent: PE/EA (50:1)，yellow oil，186.9 mg，78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 - 7.33 (m，6H)，7.27 - 7.247 (m，2H)，5.90 （s，1H），5.42（s，1H）. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1，144.6，140.8，138.7，135.1，130.8，128.7，128.6，128.5，128.3，126.7，123.9, 118.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{15}H_{11}ClN^+$ 240.0575; found 240.0583.



1-isocyano-2-(pent-1-en-2-yl)benzene (1l). Eluent: PE/EA (50:1)，green oil，1.283 mg，75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 - 7.35 (m, 1H), 7.33 (dd, J_1=7.2 Hz, J_2=1.2 Hz, 1H), 7.27 (dd, J = 7.6, 2.0 Hz, 1H), 7.25 - 7.22 (m, 1H), 5.33 (dd, J = 2.8, 1.6 Hz, 1H), 5.10 (t, J = 0.8 Hz, 1H), 2.452 (t, J = 7.6 Hz, 2H), 1.45 - 1.36 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H), **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 145.6, 140.4, 129.2, 129.0, 127.6, 127.2, 124.2, 116.5, 38.4, 20.8, 13.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{12}H_{14}N^+$ 172.1121; found 172.1123.



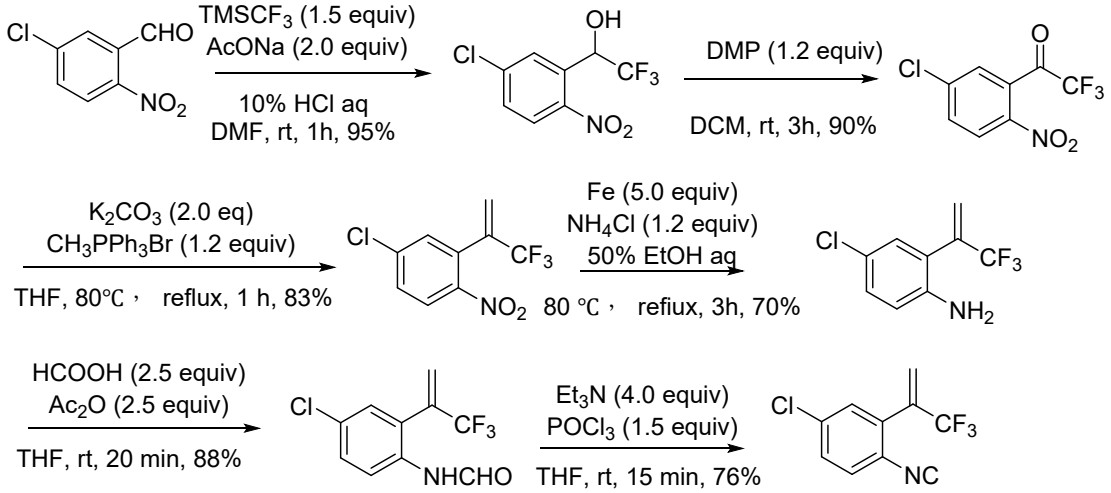
1-isocyano-2-(3-methylbut-1-en-2-yl)benzene (1m). Eluent: PE/EA (50:1)，green oil，1.283 g，75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 （d, J = 7.6 Hz, 1H），7.33 (dd, J = 7.6, 1.6 Hz, 1H), 7.30 - 7.27 (m, 1H), 7.21 (dd, J = 7.6, 1.6 Hz, 1H), 5.32 (s, 1H), 5.02 (s, 1H), 2.71 (septet, J = 7.2 Hz, 1H), 1.10 (d, J = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 151.9, 141.2, 129.5, 128.8, 127.5, 127.0, 124.7, 113.8, 33.8, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{12}H_{14}N^+$ 172.1121; found 172.1123.



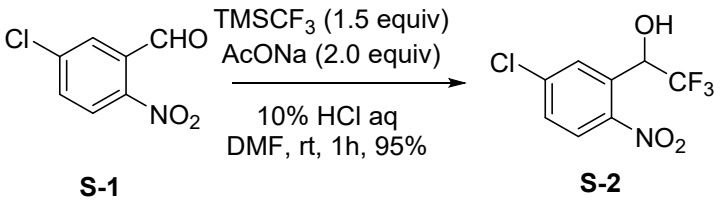
1-(1-cyclohexylvinyl)-2-isocyanobenzene (1n). Eluent: PE/EA (50:1)，green oil，1.691 g，80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8 Hz, 1H), 7.33 (dd, J = 7.6, 1.6 Hz, 1H), 7.29 - 7.25 (m, 1H), 7.20 (dd, J = 7.6, 1.6 Hz, 1H), 5.29 (s, 1H), 5.02 (s, 1H), 2.33 - 2.26 (m, 1H), 1.84 (d, J = 11.6 Hz, 2H), 1.79 - 1.75 (m, 2H), 1.70 - 1.65 (m, 1H), 1.30 - 1.11 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 151.2, 141.3, 129.5, 128. 8, 127.5, 127.0, 124.7, 114.0, 43.8, 31.9, 26.4, 26.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{15}H_{18}N^+$ 212.1434; found 212.1442.

Synthetic procedure for *o*-trifluorovinylphenylisocyanides 1 p

o-Trifluoromethylvinylphenylisocyanides **1p** was prepared according to previous literature report.[2]



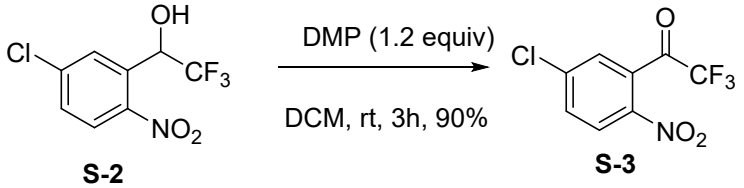
Synthesis of 1-(5-chloro-2-nitrophenyl)-2,2,2-trifluoroethan-1-ol:



S-1 **S-2**

The 5-chloro-2-nitrobenzaldehyde **S-1** (1.85 g, 10 mmol) were placed in a 50 mL two-necked flask. DMF (20 mL) was added, and the mixture was cooled to 0 ℃. $TMSCF_3$ (2.0 M in THF, 15 mmol, 2.21 mL) was added first. After 30 minutes anhydrous sodium acetate (1.64 g, 20 mmol) was added. Then the mixture was stirred for 1 h at room temperature. HCl (10%, 4 mL) was then added, and the resulting mixture was stirred for 30 min. The mixture was extracted with EtOAc (20 mL×3), washed with water (20 ml) and brine (20 mL), dried over Mg_2SO_4, and evaporated in vacuo. The residue was purified by column chromatography (petroleum ether / ethyl acetate = 50 : 1) to afford pure 1-(5-chloro-2-nitrophenyl)-2,2,2-trifluoroethan-1-ol **S-2** (2.42 g, 95%) as a yellow oil.

Synthesis of 1-(5-chloro-2-nitrophenyl)-2,2,2-trifluoroethan-1-one

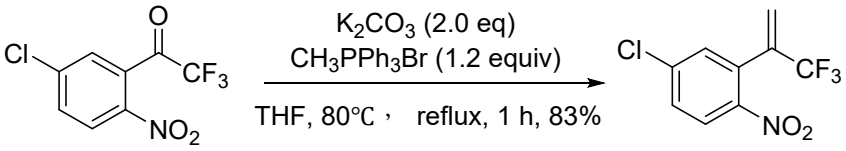


S-2 **S-3**

To a solution of 1-(5-chloro-2-nitrophenyl)-2,2,2-trifluoroethan-1-ol **S-2** (10 mmol) in DCM (15 mL) was added DMP (1.2 equiv.), the resulting mixture was stirred until full conversion of the substrate as indicated by TLC. A solution of NaOH (1 M) was

added and the mixture was extracted with Et_2O (3×20 mL). After concentration in vacuo, the residue was purified by column chromatography over silica gel (petroleum ether / ethyl acetate = 15 : 1, Et_3N 2% was added in the eluent in order to prevent the hydration of the trifluoromethyl ketone) to give the desired trifluoromethyl ketone **S-3** (2.28 g, 90%).

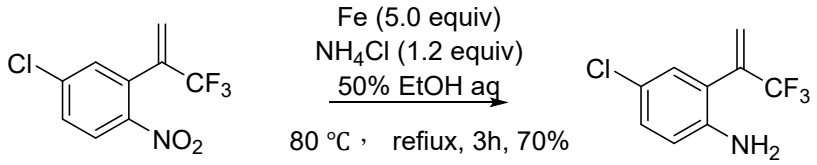
Synthesis of 4-chloro-1-nitro-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene :



S-3 **S-4**

To a solution of methyltriphenylphosphonium bromide (4.28 g, 12 mmol), K_2CO_3 (2.76 g, 20 mmol) in THF (15 mL) was added, then the resulting reaction mixture was stirred at 70 ℃ for 1 h. Afterwards 1-(5-chloro-2-nitrophenyl) -2,2,2-trifluoroethan-1-one **S-3** (10 mmol) in THF (5 mL) was added and the reaction solution was stirred at 70 ℃ for another 1 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (petroleum ether / ethyl acetate = 100 : 1) to give desired product **S-4** as a yellow oil (2.08 g, 83%).

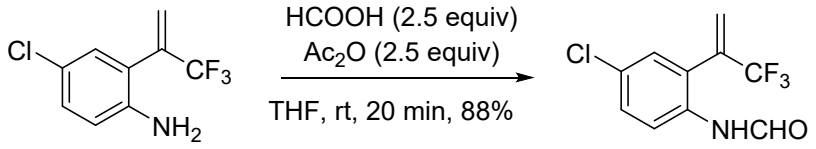
Synthesis of 4-chloro-2-(3,3,3-trifluoroprop-1-en-2-yl)aniline



S-4 **S-5**

Fe powder (2.17 g, 50 mmol) and NH_4Cl (0.64 g, 12 mmol) were placed in a 100-ml two-necked flask equipped with a reflux condenser and a dropping funnel. Aqueous EtOH (50%, 15 mL) was added, and the mixture was heated under reflux for 10 min. A solution of 4-chloro-1-nitro-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene **S-4** (2.51 g, 10 mmol) in EtOH (5 ml) was added dropwise through a dropping funnel, and heating was maintained at 80 ℃ for 3 h. The mixture was cooled to room temperature, filtered, and concentrated in vacuo. The concentrated solution was extracted with EtOAc (20 mL×3), washed with brine (20 mL), dried over Mg_2SO_4, and evaporated in vacuo. The solid residue was purified by column chromatography (petroleum ether / ethyl acetate = 50 : 1) to give 4-chloro-2-(3,3,3-trifluoroprop-1-en-2-yl)aniline **S-5** (1.55 g, 70%).

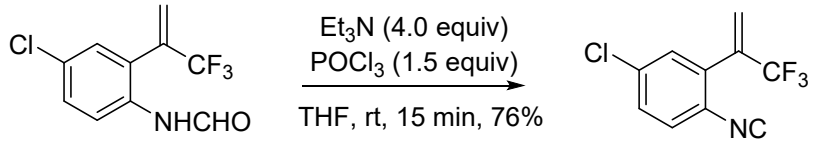
Synthesis of *N*-(4-chloro-2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)formamide



S-5 **S-6**

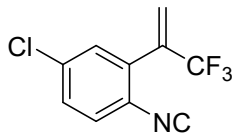
To a solution of 2-(3-methylbut-1-en-2-yl)aniline **S5** (10 mmol, 2.21 g) in THF (15 mL) at 0 °C was added acetic anhydride (25 mmol, 3.3 mL) .The mixture was then stirred at room temperature for 20 minutes. After this time, the mixture was quenched with saturated Na_2CO_3 solution and extracted 3 times with DCM. The organic layers were combined, dried over anhydrous Mg_2SO_4 and concentrated under reduced pressure, the solid residue was purified by column chromatography (petroleum ether / ethyl acetate = 4 : 1) to give *N*-(4-chloro-2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl) formamide **S-6** (2.19 g, 88 %).

Synthesis of 4-chloro-1-isocyano-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene 1p



S-6 **1p**

N-(4-chloro-2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)formamide **S-6** (10 mmol, 2.49 g) and Et_3N (5.54 mL) were dissolved in THF (15 mL) under nitrogen atmosphere. $POCl_3$(15 mmol, 1.398 mL) in THF (2 mL) was slowly added to the solution via syringe over 10 min at 0 °C. The reaction mixture was then stirred at room temperature for an additional 20 minutes. After this time, the reaction mixture was diluted with 15 mL of ethyl acetate at 0 °C and slowly quenched with saturated Na_2CO_3 solution while continuing to stir for another 30 minutes. The crude product was then purified by column chromatography (petroleum ether / ethyl acetate = 10 : 1) to give 4-chloro-1-isocyano-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene **1p** (1.756 g, 76%).



1p

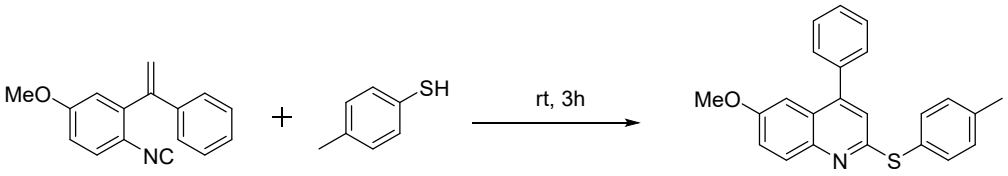
4-chloro-1-isocyano-2-(3, 3, 3-trifluoroprop-1-en-2-yl)benzene (1p). Eluent: PE/EA (40:1)，yellow oil, 1.756 g，76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 1.6 Hz, 2H), 7.40 (s, 1H), 6.35 (d, *J* = 2.0 Hz, 1H), 5.81 (d, *J* = 1.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 135.3, 133.3 (q, *J* = 32.5 Hz), 132.4, 130.2, 130.2, 128.7, 126.2 (q, *J* = 5.1 Hz), 122.1 (q, *J* = 272.0 Hz). **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{10}H_6ClF_3N^+$ 232.0135; found 232.0148.

References

1. Y. Liu, S.-J. Li, X.-L. Chen, L.-L. Fan, X.-Y. Li, S.-S. Zhu, L.-B. Qu and B. Yu, *Adv. Synth. Catal.*, 2020, **362**, 688-694.
2. L. Bao, Y. Liu, J. Peng, Y. Wang, J. Dong and X. Xu, *Org. Lett.* 2022, **24**, 105−109.

III. Optimization of reaction conditions

Table 1. Optimization of reaction solvent [a].

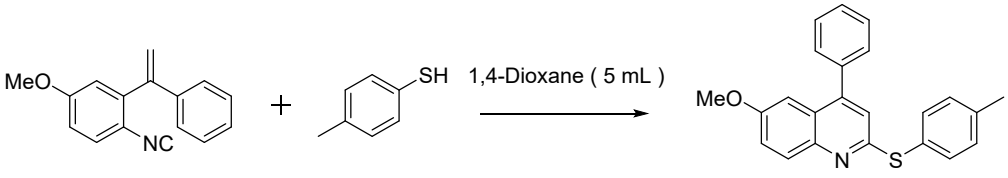


1a **2a** **3a**

Entry	1a : 2a	Solvent(5 mL)	Yield(%)[b]
1[c]	1 : 3	Acetone	8
2	1 : 3	DMSO	0
3	1 : 3	MeOH	0
4[d]	1 : 3	DMF	33
5	1 : 3	DMA	0
6	1 : 3	Toluene	59
7	1 : 3	DCE	0
8	1 : 3	EtOH	0
9	1 : 3	IPA	0
10	1 : 3	DME	0
11	1 : 3	THF	0
12	1 : 3	Ether	6
13	1 : 3	1,4-dioxane	65

a) Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol) and solvent (5 mL) were reacted in a loosely capped vial at room temperature for 3 h. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard. c) 20 h. d) 50℃ and react overnight.

Table 2. Optimization of reaction temperature [a].

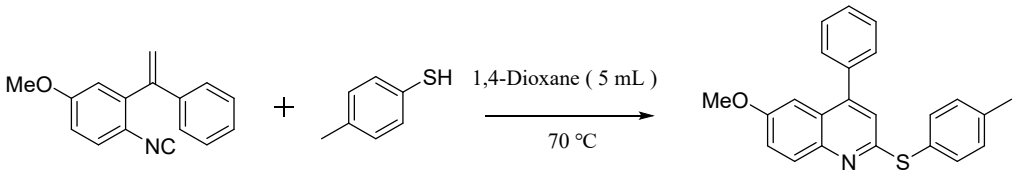


Entry	1a : 2a	Temperature (℃)	Yield (%)[b]

1	1 : 3	30	65
2	1 : 3	50	75
3	1 : 3	60	80
4	1 : 3	70	87
5	1 : 3	80	78
6	1 : 3	90	72

a) Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol) and dioxane (5 mL) were reacted in a loosely capped vial at different temperature for 3 h. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard.

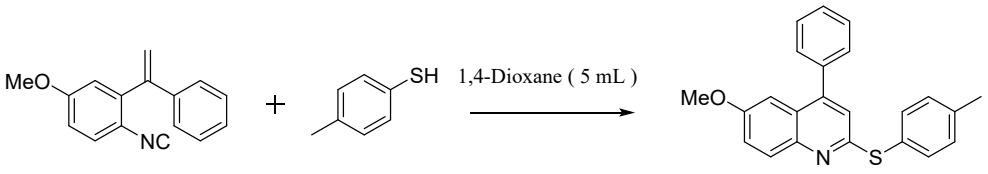
Table 3. Optimization of thiol amount [a].



Entry	**1a** : **2a**	Yield (%)[b]
1	1 : 1.0	73
2	1 : 1.5	76
3	1 : 2.0	78
4	1 : 2.5	80
5	1 : 3.0	87
6	1 : 3.5	87
7	1 : 4.0	84

a) Reaction conditions: **1a** (0.2 mmol), **2a** (x mmol) and dioxane (5 mL) were reacted in a loosely capped vial at 70 °C for 2 h. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard.

Table 4. Optimization of reaction solvent with reduced thiol loading [a].

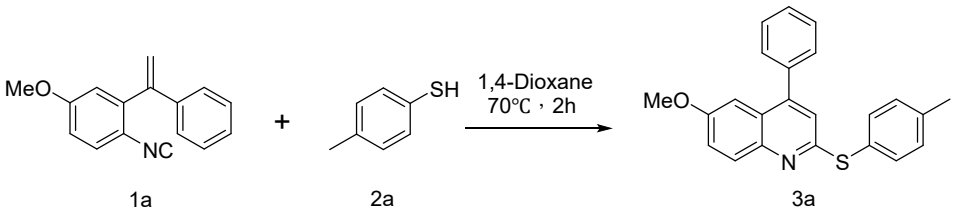


Entry	**1a**:**2a**	Temperature (°C)	Yield (%)[b]
1	1:1.2	30	36
2	1:1.2	50	52
3	1:1.2	60	65
4	1:1.2	70	84
5	1:1.2	80	78
6	1:1.2	90	47

a) Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol) and dioxane (5 mL) were reacted in a loosely capped vial at different temperature for 2 h. b) Determined by ^{1}H

NMR using CH_2Br_2 (0.2 mmol) as internal standard.

Table 5. Optimization of solvent amount [a].



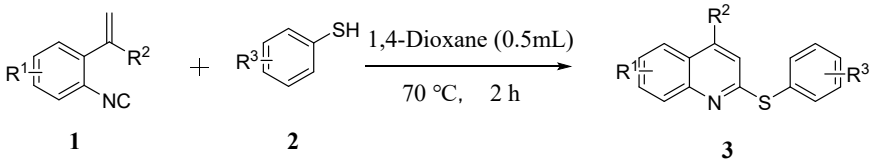
1a 2a 3a

Entry	1a : 2a	Solvent (mL)	Yield(%)[b]
1	1 : 1.2	0.5	87(89)[c]
2	1 : 1.2	1	83
3	1 : 1.2	2	82
4[d]	1 : 1.2	5	80
5	1 : 1.2	10	48

a) Reaction conditions: 1a (0.2 mmol), 2a (0.24 mmol) and 1,4-dioxane (x mL) were reacted at 70 °C for 2 hours. b) Determined by ^{1}H NMR using CH_2Br_2 (0.2 mmol) as internal standard. c) Isolated yield. d) The remaining 16% of the raw material in the reaction 2h.

IV. Preparation and analytical data of quinoline 3

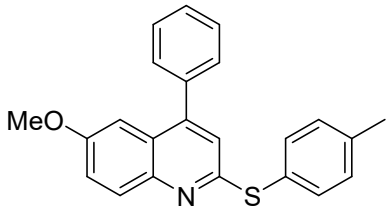
Typical synthetic procedure (with **3a** as an example)



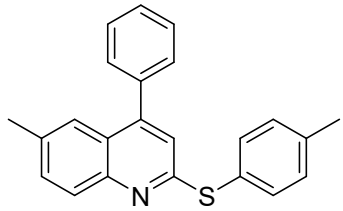
1 **2** **3**

1-isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1** (0.2 mmol, 47 mg) and 4-methylthiophenol **2** (0.24 mmol, 1.2 eq, 30 mg) were dissolved in 0.5 mL 1,4-Dioxane in a 5mL sample vial (the cap of the sample vial was loosened), it was placed in a metal bath and heated at 70 °C for 2 h, until the complete consumption of isocyanide **1** as monitored by TLC. After this time, the mixture was quenched with saturated Na_2CO_3 solution and extracted with DCM (3 × 20mL). The organic layers were combined, dried over anhydrous Mg_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 30 : 1) to give 6-methoxy-4-phenyl-2-(*p*-tolylthio)quinolone **3a** (64 mg, 89 %).

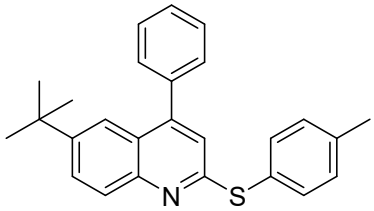
Analytical data of quinoline 3



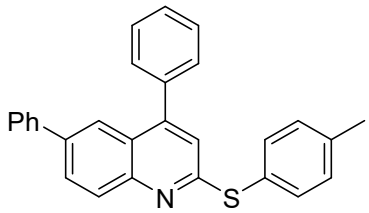
6-methoxy-4-phenyl-2-(p-tolylthio)quinolone (3a). Eluent: PE/EA (30:1)，yellow solid, 64mg，89% yield, m.p.: 146 - 148 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.2 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.48 - 7.44 (m, 3H), 7.40 - 7.38 (m, 2H), 7.33 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.21 (d, *J* = 8 Hz, 2H), 7.06 (d, *J* = 2.8 Hz, 1H), 6.93 (s, 1H), 3.75 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.4, 157.3, 147.7, 144.6, 139.1, 138.0, 134. 8, 130.3, 130.2, 129.2, 128. 6, 128.3, 127.6, 125.5, 121.7, 119.9, 104.2, 55.4, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{20}NOS^+$ 358.1260; found 358.1256.



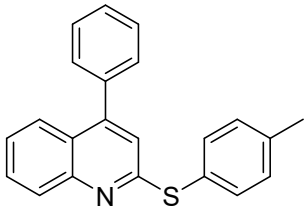
6-methyl-4-phenyl-2-(p-tolylthio)quinolone (3b). Eluent: PE/EA (30:1)，Yellow solid, 66.3 mg，97% yield, m.p.: 125 - 130 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.2 Hz, 1H), 7.55 (d, *J* = 8 Hz, 2H), 7.50 - 7.43 (m, 5H), 7.38 - 7.35 (m, 2H), 7.22 (d, *J* = 8 Hz, 2H), 6.90 (s, 1H), 2.42 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.3, 148.2, 147.1, 139.3, 137.9, 135.6, 135.0, 131.9, 130.4, 129.4, 128.5, 128.5, 128.3, 127.3, 124.6, 124.6, 119.4, 21.7, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{20}NS^+$ 342.1311; found 342.1357.



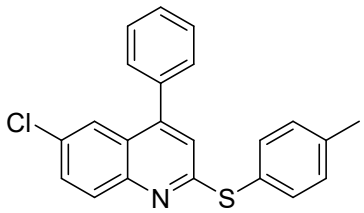
6-(tert-butyl)-4-phenyl-2-(p-tolylthio)quinolone (3c). Eluent: PE/EA (30:1)，Yellow solid, 66.4 mg, 87% yield, m.p.: 127-129 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 1H), 7.76 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.72 (d, *J* = 2 Hz, 1H), 7.54 (d, *J* = 8 Hz, 2H), 7.49 - 7.45 (m, 3H), 7.41 - 7.38 (m, 2H), 7.22 (d, *J* = 8 Hz, 2H), 6.92 (s, 1H), 2.39 (s, 3H), 1.31 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.6, 148.7, 148.5, 147.0, 139.2, 137.9, 134.9, 130.4, 129.4, 128.6, 128.4, 128.3, 128.3, 127.5, 124.1, 120.7, 119.5, 34.9, 31.11, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{26}NS^+$ 384.1780; found 384.1778.



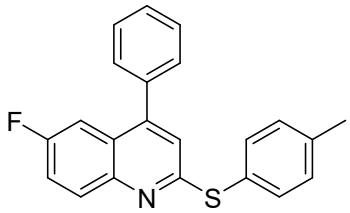
4,6-diphenyl-2-(p-tolylthio)quinolone (3d). Eluent: PE/EA (30:1)，Yellow solid, 71.2 mg，90% yield, m.p.: 153 - 155 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.94 - 7.91 (m, 2H), 7.58 - 7.56 (m, 4H), 7.50 - 7.45 (m, 3H), 7.44 - 7.40 (m, 4H), 7.36 - 7.32 (m, 1H), 7.25 (d, *J* = 7.6 Hz, 2H), 6.96 (s, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.5, 149.0, 148.0, 140.6, 139.5, 138.4, 137.7, 135.1, 130.4, 129.5, 129.4, 129.2, 128.8, 128.6, 128.5, 127.5, 127.3, 127.0, 124.8, 123.6, 119.7, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{28}H_{22}NS^+$ 404.1467; found 404.1446.



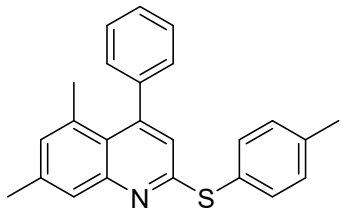
4-phenyl-2-(p-tolylthio)quinolone (3e). Eluent: PE/EA (30:1)，Yellow solid, 53.9 mg，83% yield, m.p.: 121 - 131 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.47 - 7.45 (m, 3H), 7.49 - 7.45 (m, 3H), 7.40 - 7.36 (m, 3H), 7.24 (d, *J* = 7.6 Hz, 2H), 6.93 (s, 1H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.6, 148.8, 148.5, 139.5, 137.7, 135.1, 130.4, 129.8, 129.4, 128.7, 128.5, 128.4, 127.0, 125.7, 124.6, 119.2, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{18}NS^+$ 328.1154; found 328.1179.



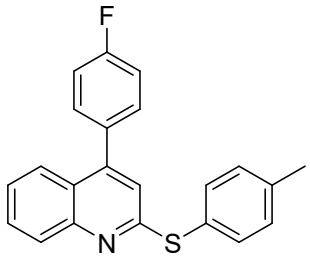
6-chloro-4-phenyl-2-(p-tolylthio)quinolone (3f). Eluent: PE/EA (30:1)，Yellow solid, 54.9 mg，76% yield, m.p.: 128 - 134 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.2 Hz, 1H), 7.58 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.55 (d, *J* = 8 Hz, 2H), 7.50 - 7.46 (m, 3H), 7.36 - 7.34 (m, 2H), 7.24 (d, *J* = 8 Hz, 2H), 6.94 (s, 1H), 2.40 (s, 1H). **^{13} C NMR** (100 MHz, $CDCl_3$) δ 162.1, 148.0, 146.9, 139.7, 137.1, 135.2, 131.4, 130.6, 130.5, 130.3, 129.3, 128.7, 128.7, 126.5, 125.4, 124.6, 119.8, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{17}ClNS^+$ 362.0765; found 362.0790.



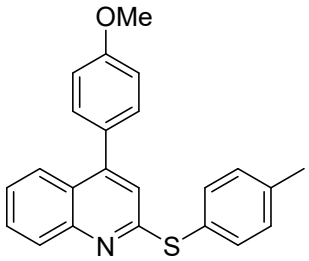
6-fluoro-4-phenyl-2-(p-tolylthio)quinolone (3g). Eluent: PE/EA (30:1)，Yellow solid, 53.1 mg，77% yield, m.p.: 111 - 112 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.68 - 7.64 (m, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.41 - 7.37 (m, 1H), 7.36 - 7.33 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 8.4 Hz, 2H), 6.90 (s, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8 (*J* = 246.4 Hz), 161.5, 148.5, 147.7, 139. 5, 135.1, 133.7 (*J* = 3.3 Hz), 131.1 (*J* = 8.2 Hz), 130.4, 129.9, 128.8, 127.0, 125.8, 125.5, 124.6, 119.3, 115.6 (d, *J* = 21.6 Hz), 21.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{17}FNS^+$ 346.1060; found 346.1065.



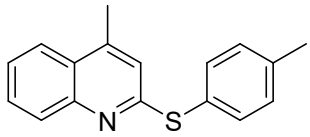
5,7-dimethyl-4-phenyl-2-(p-tolylthio)quinolone (3h). Eluent: PE/EA (30:1)，Yellow solid, 54 mg，76% yield, m.p.: 150 - 152 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.38 - 7.36 (m, 3H), 7.22 - 7.19 (m, 4H), 7.02 (s, 1H), 6.8 (s, 1H), 2.45 (s, 1H), 2.37 (s, 3H), 1.87 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 149.9, 149.1, 142.1, 139.5, 139.1, 135.1, 134.9, 131.4, 130.3, 128.6, 127.8, 127.6, 127.2, 126.8, 122.1, 120.5, 24.1, 21.3, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{24}H_{22}NS^+$ 356.1467; found 356.1494.



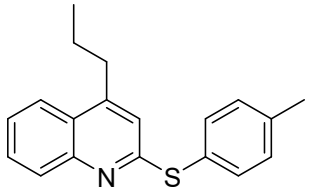
4-(4-fluorophenyl)-2-(p-tolylthio)quinolone (3i). Eluent: PE/EA (30:1)，Yellow solid, 60 mg，87% yield, m.p.: 110 - 115 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.68 - 7.64 (m, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.41 - 7.39 (m, 1H), 7.37 - 7.33 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.19 - 7.13 (m, 2H), 6.90 (s, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 246.9 Hz), 161.6, 148.5, 147.7, 139.5, 135.1, 133.6 (d, *J* = 3.4 Hz), 131.1 (d, *J* = 8.1 Hz) 130.4, 129.9, 128.8, 126.9, 125.5, 124.5, 119.2, 115.5 (d, *J* = 21.4 Hz), 21.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{17}FNS^+$ 346.1060; found 346.1086.



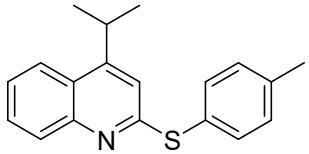
4-(4-methoxyphenyl)-2-(p-tolylthio)quinolone (3j). Eluent: PE/EA (30:1)，Yellow solid, 47 mg，66% yield, m.p.: 93 - 95 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8 .4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.67 - 7.63 (m, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.40 - 7.36 (m, 1H), 7.31 (d, *J* = 8 .4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.91 (s, 1H), 3.87 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.5, 159.8, 148.6, 148.5, 139.4, 135.1, 130.7, 130.4, 130.0, 129.7, 128.7, 127.2, 125.8, 125.6, 124.8, 119.2, 114.0, 55.3, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{20}NOS^+$ 358.1260; found 358.1266.



4-methyl-2-(p-tolylthio)quinolone (3k). Eluent: PE/EA (30:1)，Yellow solid, 42.3 mg，80% yield, m.p.: 125 - 127 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.66 - 7.62 (m, 1H), 7.54 (d, *J* = 8 Hz, 2H), 7.48 - 7.43 (m, 1H), 7.26 (d, *J* = 8 Hz, 2H), 6.81 (s, 1H), 2.53 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.7, 147.8, 144.7, 139.4, 135.2, 130.4, 129.6, 128.9, 127.3, 126.0, 125.4, 123.7, 119.6, 21.4, 18.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{16}NS^+$ 266.0998; found 266.1023.

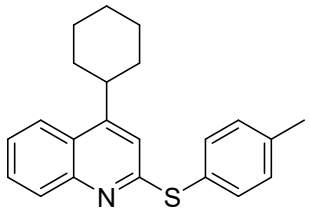


4-propyl-2-(p-tolylthio)quinolone (3l). Eluent: PE/EA (30:1)，Yellow solid, 55.2 mg，95% yield, m.p.: 70 - 71 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.90 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.65 - 7.61 (m, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.46 - 7.42 (m, 1H), 7.25 (d, *J* = 8 Hz, 2H), 6.82 (s, 1H), 2.86 (d, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.70 - 1.62 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.5, 148.7, 148.2, 139.2, 135.0, 130.3, 129.4, 129.1, 127.4, 125.3, 125.3, 123.5, 118.8, 34.1, 23.0, 21.3, 14.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{19}H_{20}NS^+$ 294.1311; found 294.1322.

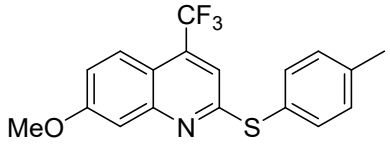


4-isopropyl-2-(p-tolylthio)quinolone (3m). Eluent: PE/EA (30:1)，White solid, 56

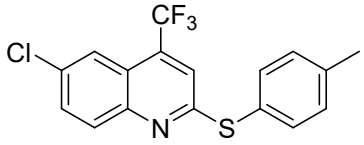
mg，96% yield, m.p.: 131 - 132 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 - 7.93 (m, 2H), 7.63 - 7.59 (m, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.46 - 7.42 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.59 (septet, *J* = 7.2 Hz, 1H), 2.41 (s, 3H), 1.23 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.6, 154.5, 148.3, 139.2, 134.9, 130.2, 129.3, 129.2, 127.4, 125.3, 124.7, 123.0, 115.3, 28.3, 22.6, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{19}H_{20}NS^+$ 294.1311; found 294.1335.



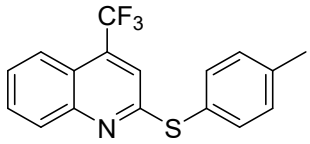
4-cyclohexyl-2-(p-tolylthio)quinolone (3n). Eluent: PE/EA (30:1)，Yellow solid, 64 mg，96% yield, m.p.: 95 - 97 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 - 7.92 (m, 2H), 7.62 - 7.58 (m, 1H), 7.66 - 7.62 (m, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.45 - 7.41 (m, 1H), 7.25 (d, *J* = 7.6 Hz, 2H), 6.93 (s, 1H), 3.21 - 3.14 (m, 1H), 2.42 (s, 3H), 1.90 - 1.76 (m, 5H), 1.50 - 1.42 (m, 2H), 1.33 - 1.22 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.4, 153.5, 148.4, 139.0, 134.8, 130.2, 129.3, 129.2, 127.5, 125.2, 124.7, 122.9, 115.9, 38.9, 33.2, 26.8, 26.1, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{24}NS^+$ 334.1624; found 334.1658.



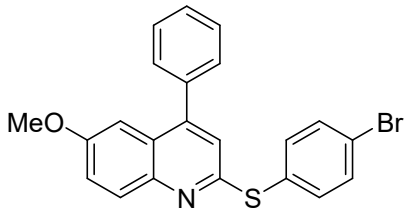
7-methoxy-2-(p-tolylthio)-4-(trifluoromethyl)quinolone (3o). Eluent: PE/EA (30:1)，Yellow solid, 53.9 mg, 78% yield, m.p.: 114 - 116 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 2.8 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.09 (s, 1H), 3.93 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3, 161.4, 150.9, 140.1, 135.3, 134.4 (q, *J* = 31.3Hz), 130.6, 125.9, 124.9 (q, *J* = 2.4 Hz), 123.1 (q, *J* = 273.4 Hz), 120.0, 115.3, 113.8 (q, *J* = 5.6 Hz), 107.4, 55.5, 21.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{18}H_{15}F_3NOS^+$ 350.0821; found 350.0821.



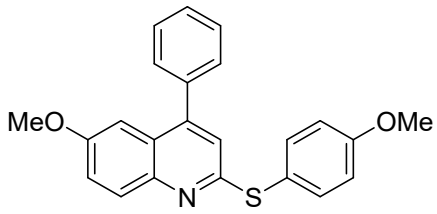
6-chloro-2-(p-tolylthio)-4-(trifluoromethyl)quinolone (3p). Eluent: PE/EA (30:1)，Yellow solid, 45.7 mg，65% yield, m.p.: 98 - 102 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.6 Hz, 1H), 7.92 (d, *J* = 9.2 Hz, 1H), 7.58 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.54 (d, *J* = 8 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.28 (s, 1H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 147.3, 140.4, 135.4, 133.6 (q, *J* = 31.8 Hz), 134.0, 131.6, 130.7, 130.6, 125.3, 123.1 (q, *J* = 2.3 Hz), 122.8 (q, *J* = 273.3 Hz), 117.1 (q, *J* = 5.6 Hz), 21.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{12}ClF_3NOS^+$ 354.0326; found 354.0320.



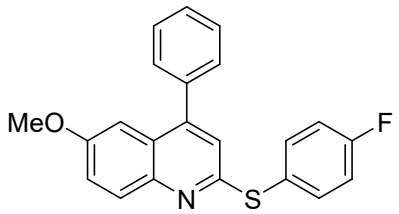
2-(p-tolylthio)-4-(trifluoromethyl)quinolone (3q). Eluent: PE/EA (30:1)，Yellow solid, 54.6 mg，86 % yield, m.p.: 103 - 104 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.56 - 7.52 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.26 (s, 1H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.7, 148.9, 140.1, 135.3, 134.6 (q, *J* = 31.5 Hz), 130.6, 130.6, 129.2, 127.0, 125.8, 123.9, 123.1 (q, *J* = 273.4 Hz), 120.4, 116.3 (q, *J* = 5.4 Hz), 21.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.8. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{17}H_{13}F_3NS^+$ 320.0715; found 320.0721.



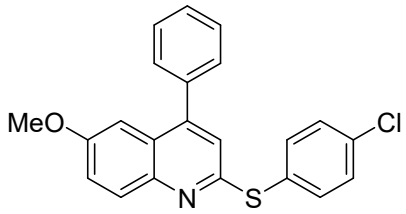
2-((4-bromophenyl)thio)-6-methoxy-4-phenylquinoline (3r). Eluent: PE/EA (30:1)，Yellow solid, 67 mg，80% yield, m.p.: 114 - 116 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.2 Hz, 1H), 7.54 - 7.47 (m, 7H), 7.43 - 7.40 (m, 2H), 7.33 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.09 (d, *J* = 2.8 Hz, 1H), 7.00 (s, 1H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.5, 156.4, 148.0, 144.7, 137.7, 135.7, 132.5, 130.8, 130.3, 129.1, 128.7, 128.5, 125.8, 123.1, 121.9, 120.6, 104.1, 55.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{17}BrNOS^+$ 422.0209; found 422.0244.



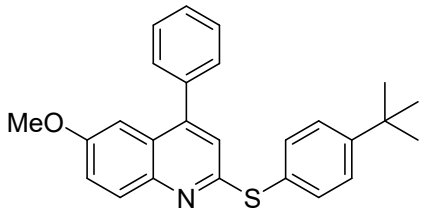
6-methoxy-2-((4-methoxyphenyl)thio)-4-phenylquinoline (3s). Eluent: PE/EA (30:1), Yellow solid, 55.6 mg, 75% yield, m.p.: 120 - 123 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.6 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.49 - 7.43 (m, 3H), 7.40 - 7.36 (m, 2H), 7.32 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.06 (d, *J* = 2.8 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.88 (s, 1H), 3.83 (s, 3H), 3.74 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.5, 159.0, 157.2, 147.6, 144.6, 138.0, 136.9, 130.1, 129.1, 128.5, 128.3, 125.4, 121.6, 121.4, 119.4, 115.1, 104.2, 55.3, 55.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{20}NO_2S^+$ 374.1209; found 374.1218.



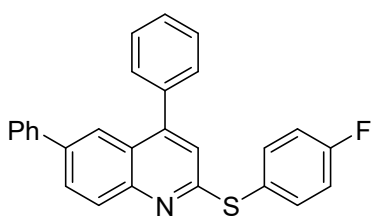
2-((4-fluorophenyl)thio)-6-methoxy-4-phenylquinoline (3t). Eluent: PE/EA (30:1)，White solid, 57.4 mg，80% yield, m.p.: 151 - 153 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.2 Hz, 1H), 7.66 - 7.63 (m, 2H), 7.49 - 7.46 (m, 3H), 7.41 - 7.38 (m, 2H), 7.33 (dd, *J* =9.2, 2.8 Hz, 1H), 7.14 - 7.09 (m, 2H), 7.07 (d, *J* = 2.8 Hz, 1H), 6.92 (s, 1H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3 (d, *J* = 248.1 Hz), 157.5, 157.4, 147.9, 144.6, 137.9, 136.9 (*J* = 8.4 Hz), 130.3, 129.1, 128.7, 128.5, 126.5 (*J* = 3.5 Hz), 125.6, 121.8, 120.0, 116.7 (d, *J* = 21.9 Hz), 104.2, 55.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.8. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{17}FNOS^+$ 362.1009; found 362.1017.



2-((4-chlorophenyl)thio)-6-methoxy-4-phenylquinoline (3u). PE/EA (30:1)，Yellow solid, 60.5 mg，81% yield, m.p.: 94 - 97 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.2 Hz, 1H), 7.59 - 7.56 (m, 2H), 7.51 - 7.46 (m, 3H), 7.42 - 7.40 (m, 2H), 7.39 - 7.36 (m, 2H), 7.33 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.09 (d, *J* = 2.8 Hz, 1H), 6.99 (s, 1H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.5, 156.6, 148.0, 144.7, 137.8, 135.5, 134.9, 130.3, 130.1, 129.6, 129.1, 128.7, 128.5, 125.8, 121.9, 120.5, 104.1, 55.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{17}ClNOS^+$ 378.0714; found 378.0752.

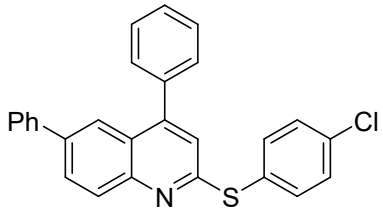


2-((4-(tert-butyl)phenyl)thio)-6-methoxy-4-phenylquinoline (3v). Eluent: PE/EA (30:1)，Yellow solid, 67.9 mg，85% yield, m.p.: 82 - 85 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.2 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.48 - 7.40 (m, 7H), 7.33 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.08 (d, *J* = 2.8 Hz, 1H), 6.98 (s, 1H), 3.76 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.2, 157.3, 152.1, 147.6, 144.6, 138.0, 134.3, 130.3, 129.2, 128.5, 128.3, 127.8, 126.6, 125.5, 121.7, 120.2, 104.1, 55.4, 34.7, 31.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{26}H_{26}NOS^+$ 400.1730; found 400.1735.

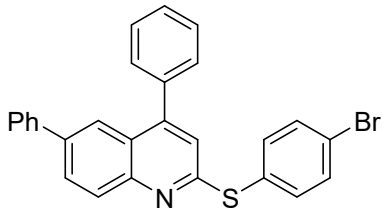


2-((4-fluorophenyl)thio)-4,6-diphenylquinoline (3w). Eluent: PE/EA (30:1)，Yellow solid, 65 mg，80% yield, m.p.: 120 - 122 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.93 (dd, *J* =8.8, 2.0 Hz, 1H), 7.58 -

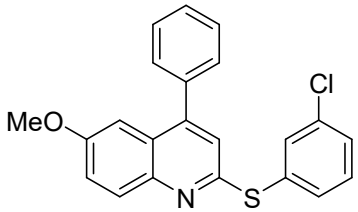
7.56 (m, 2H), 7.53 - 7.47 (m, 3H), 7.45 - 7.41 (m, 4H), 7.37 - 7.32 (m, 1H), 7.17 - 7.13 (m, 2H), 6.97 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3 (d, *J* = 268.5 Hz), 160.5, 149.2, 148.0, 140.5, 138.6, 137.6, 137.3 (d, *J* = 8.5 Hz), 129.5, 129.4, 129.2, 128.9, 128.7, 128.6, 127.5, 127.3, 125.9 (*J* = 3.4 Hz), 124.9, 123.6, 119.7, 116.8 (d, *J* = 21.8 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{27}H_{19}FNS^+$ 408.1217; found 408.1211.



2-((4-chlorophenyl)thio)-4,6-diphenylquinoline (3x). Eluent: PE/EA (30:1), Yellow solid, 71 mg, 84% yield, m.p.: 130 - 131 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 1.6 Hz, 1H), 7.94 (dd, *J* = 8.8, 2 Hz, 1H), 7.65 - 7.61 (m, 2H), 7.59 - 7.56 (m, 2H), 7.52 - 7.49 (m, 3H), 7.47 - 7.41 (m, 6H), 7.37 - 7.33 (m, 1H), 7.05 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 149.2, 148.0, 140.4, 138.7, 137.5, 136.0, 135.3, 129.7, 129.5, 129.3, 129.2, 128.8, 128.7, 128.6, 127.5, 127.3, 125.0, 123.6, 120.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{27}H_{19}ClNS^+$ 424.0921; found 424.0908.

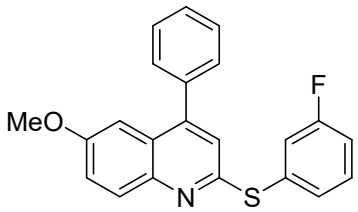


2-((4-bromophenyl)thio)-4,6-diphenylquinoline (3y). Eluent: PE/EA (30:1), Yellow solid, 71 mg, 76% yield, m.p.: 134 - 136 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 1.6 Hz, 1H), 7.94 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.58 - 7.56 (m, 6H), 7.52 - 7.48 (m, 3H), 7.46 - 7.41 (m, 4H), 7.36 - 7.33 (m, 1H), 7.04 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.5, 149.3, 148.0, 140.5, 138.8, 137.5, 136.1, 132.7, 130.1, 129.6, 129.4, 129.2, 128.9, 128.7, 128.6, 127.6, 127.341, 125.0, 123.6, 123.5, 120.2. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for $C_{27}H_{18}BrNNaS^+$ 446.0741; found 446.0769.

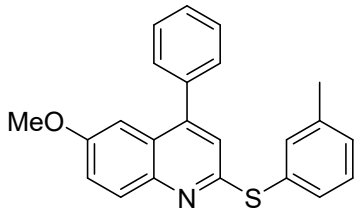


2-((3-chlorophenyl)thio)-6-methoxy-4-phenylquinoline (3z). Eluent: PE/EA (30:1), Yellow solid, 51.9 mg, 69% yield, m.p.: 71 - 72 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.2 Hz, 1H), 7.65 (t, *J* = 1.6 Hz, 1H), 7.52 - 7.47 (m, 4H), 7.44 - 7.42 (m, 2H), 7.36 - 7.30 (m, 3H), 7.11 (d, *J* = 3.2 Hz, 1H), 7.05 (s, 1H), 3.76 (s, 3H).

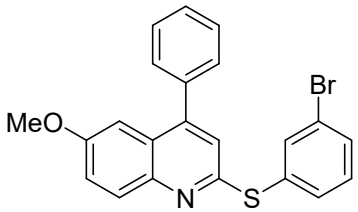
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 155.9, 148.0, 144.7, 137.7, 134.8, 133.8, 133.4, 131.9, 130.4, 130.3, 129.1, 128.7, 128.6, 128.5, 125.9, 121.9, 120.9, 104.1, 55.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{17}ClNOS^+$ 378.0714; found 378.0715.



2-((3-fluorophenyl)thio)-6-methoxy-4-phenylquinoline (3aa). Eluent: PE/EA (30:1)，Yellow solid, 45.9 mg，64% yield, m.p.: 104 - 106 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.2 Hz, 1H), 7.52 - 7.46 (m, 3H), 7.45 - 7.37 (m, 4H), 7.37 - 7.33 (m, 2H), 7.10 (d, *J* = 2.8 Hz, 1H), 7.09 - 7.06 (m, 1H), 7.05 (s, 1H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 247.6 Hz), 157.6, 156.0, 148.1, 144.7, 137.7, 134.1 (d, *J* = 8.0 Hz), 130.6 (d, *J* = 8.4 Hz), 130.4, 129.3 (d, *J* = 3.1 Hz), 129.2, 128.7, 128.5, 125.9, 121.9, 121.0, 120.5 (d, *J* = 22.3 Hz), 115.6 (d, *J* = 20.9 Hz), 104.1, 55.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{17}FNOS^+$ 362.1009; found 362.1020.

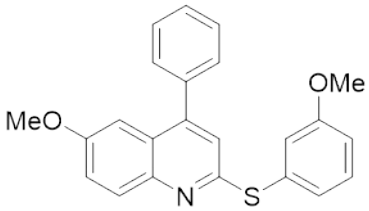


6-methoxy-4-phenyl-2-(m-tolylthio)quinolone (3ab). Eluent: PE/EA (30:1)，Yellow oil, 56.2 mg，79% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.2 Hz, 1H)，7.50 - 7.44 (m, 5H), 7.41 - 7.38 (m, 2H), 7.34 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.078 (d, *J* = 2.8 Hz, 1H), 6.97 (s, 1H), 3.76 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.0, 157.4, 147.7, 144.6, 139.3, 137.9, 135.0, 131.5, 131.2, 130.3, 129.7, 129.3, 129.2, 128.6, 128.4, 125.6, 121.7, 120.4, 104.1, 55.4, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{20}NOS^+$ 358.1260; found 358.1288.

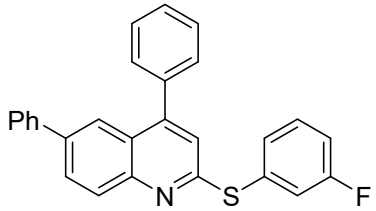


2-((3-bromophenyl)thio)-6-methoxy-4-phenylquinoline (3ac). Eluent: PE/EA (30:1)，Yellow oil, 76.5 mg，91% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.2 Hz, 1H), 7.83 (t, *J* = 2 Hz, 1H), 7.59 - 7.56 (m, 1H), 7.52 - 7.48 (m, 4H), 7.46 - 7.44 (m, 2H), 7.36 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 2.8 Hz, 1H), 7.06 (s, 1H), 3.78 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 155.9, 148.1, 144.7, 137.7, 136.2, 134.1, 132.3, 131.6, 130.6, 130.4, 129.2, 128.7, 128.5, 125.9, 122.9,

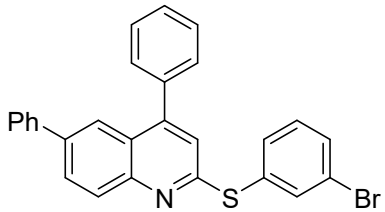
121.9, 121.0, 104.1, 55.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{17}BrNOS^+$ 422.0209; found 422.0268.



6-methoxy-2-((3-methoxyphenyl)thio)-4-phenylquinoline (3ad). Eluent: PE/EA (30:1), Yellow solid, 64.2 mg, 86% yield, m.p.: 78 - 79 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 9.2 Hz, 1H), 7.50 - 7.45 (m, 3H), 7.41 - 7.39 (m, 2H), 7.35 - 7.33 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.24 - 7.21 (m, 2H), 7.09 (d, *J* = 2.8 Hz, 1H), 7.01 (s, 1H), 6.93 - 6.90 (m, 1H), 3.79 (s, 3H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.1, 157.5, 157.4, 147.8, 144.6, 137.9, 132.6, 130.3, 130.2, 129.1, 128.6, 128.4, 126.4, 125.6, 121.8, 120.6, 119.1, 114.9, 104.1, 55.4, 55.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{20}NO_2S^+$ 374.1209; found 374.1170.

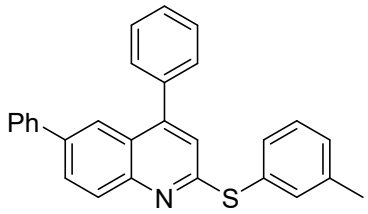


2-((3-fluorophenyl)thio)-4,6-diphenylquinoline (3ae). Eluent: PE/EA (30:1), Yellow solid, 49 mg, 60% yield, m.p.: 112 - 114 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 2.0 Hz, 1H), 7.94 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.59 - 7.56 (m, 2H), 7.53 - 7.39 (m, 10H), 7.37 - 7.33 (m, 1H), 7.14 - 7.09 (m, 1H), 7.06 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 248.8 Hz), 159.3, 149.4, 148.0, 140.5, 138.9, 137.5, 133.2 (*J* = 7.7 Hz), 130.7 (*J* = 7.7 Hz), 130.0 (*J* = 3.0 Hz), 129.6, 129.4, 129.3, 128.8, 128.7, 128.6, 127.6, 127.4, 125.1, 123.6, 121.2 (*J* = 22.2 Hz), 120.5, 116.1 (*J* = 21.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{27}H_{19}FNS^+$ 408.1217; found 408.1211.

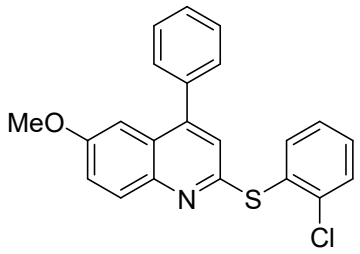


2-((3-bromophenyl)thio)-4,6-diphenylquinoline (3af). Eluent: PE/EA (30:1), Yellow solid, 74.5 mg, 80% yield, m.p.: 124 - 125 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 1.6 Hz, 1H), 7.92 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.84 (d, *J* = 1.6 Hz, 1H), 7.59 - 7.39 (m, 1H), 7.34 - 7.30 (m, 1H), 7.26 (d, *J* = 18.0 Hz, 1H), 7.05 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 149.4, 148.0, 140.5, 138.9, 137.5, 136.8, 133.3, 132.9, 132.0, 131.0, 129.6, 129.4, 129.3, 128.9, 128.7, 128.7, 127.6, 127.4, 125.1, 123.6, 123.0, 120.5. **HRMS (ESI)** m/z: $[M+Na]^+$ calcd for

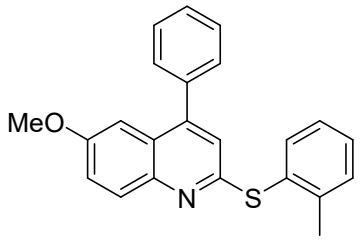
$C_{27}H_{18}BrNNaS^+$ 490.0236; found 490.0216.



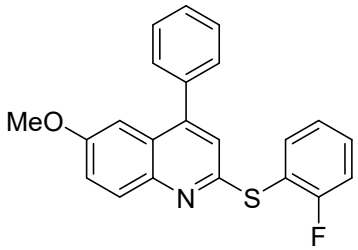
4,6-diphenyl-2-(m-tolylthio)quinolone (3ag). Eluent: PE/EA (30:1)，Yellow solid, 65.1 mg，81% yield, m.p.: 119 - 120 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 1.6 Hz, 1H), 7.94 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.59 - 7.57 (m, 2H), 7.52 - 7.46 (m, 5H), 7.44 - 7.41 (m, 4H), 7.36 - 7.33 (m, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1, 149.0, 148.0, 140.5, 139.5, 138.5, 137.7, 135.4, 131.9, 130.5, 130.0, 129.5, 129.4, 129.2, 128.8, 128.6, 128.5, 127.5, 127.3, 124.8, 123.6, 120.1, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{28}H_{22}NS^+$ 404.1467; found 404.1457.



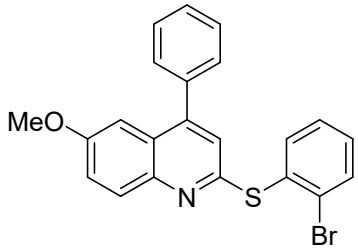
2-((2-chlorophenyl)thio)-6-methoxy-4-phenylquinoline (3ah). Eluent: PE/EA (30:1)，Yellow solid, 30 mg，40% yield, m.p.: 85 - 87 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.2 Hz, 1H), 7.69 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.52 - 7.41 (m, 6H), 7.34 - 7.25 (m, 3H), 7.10 (d, *J* = 2.8 Hz, 1H), 6.96 (s, 1H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.5, 155.6, 147.9, 144.8, 138.1, 137.8, 136.0, 131.0, 130.4, 130.3, 130.1, 129.2, 128.6 128.4, 127.5, 125.8, 121.8, 120.6, 104.1, 55.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{17}ClNOS^+$ 378.0714; found 378.0734.



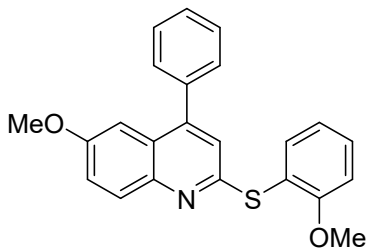
6-methoxy-4-phenyl-2-(o-tolylthio)quinolone (3ai). Eluent: PE/EA (30:1)，Yellow solid, 55.5 mg，78% yield, m.p.: 75 - 77 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.89 (d, *J* = 9.2 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.43 - 7.39 (m, 3H), 7.34 - 7.32 (m, 2H), 7.30 - 7.27 (m, 1H), 7.21 - 7.17 (m, 1H), 7.03 (d, *J* = 9.2 Hz, 1H), 6.76 (s, 1H), 3.70 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 157.2, 147.7, 144.7, 142.4, 137.9, 136.2, 130.9, 130.2, 129.6, 129.1, 128.6, 128.3, 126.9, 125.4, 121.7, 119.4, 104.1, 55.4, 21.0. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{20}NOS^+$ 358.1260; found 358.1310.



2-((2-fluorophenyl)thio)-6-methoxy-4-phenylquinoline (3aj). Eluent: PE/EA (30:1)，White solid, 51.2 mg, 71% yield, m.p.: 100 - 101 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 9.2 Hz, 1H)， 7.69 - 7.65 (m, 1H), 7.32 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.22 - 7.17 (m, 2H), 7.08 (d, *J* = 2.8 Hz, 1H), 6.98 (s, 1H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 247.4 Hz), 157.4, 155.7, 147.9, 144.7, 137.9, 136.8, 131.4 (d, *J* = 7.9 Hz), 130.3, 129.2, 128.6, 128.4, 125.7, 124.9 (d, *J* = 3.9 Hz), 121.7, 119.9, 118.4 (d, *J* = 18.2 Hz), 116.3 (d, *J* = 22.6 Hz), 104.1, 55.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{17}FNOS^+$ 362.1009; found 362.1020.

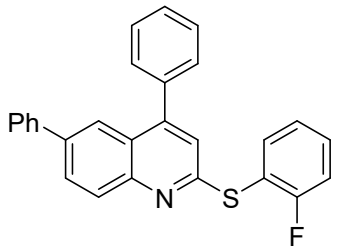


2-((2-bromophenyl)thio)-6-methoxy-4-phenylquinoline (3ak). Eluent: PE/EA (30:1)，Yellow solid, 48.1 mg，58% yield, m.p.: 123 - 124 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.2 Hz, 1H), 7.71 - 7.68 (m, 2H), 7.79 - 7.42 (m, 5H), 7.36 - 7.30 (m, 2H), 7.24 - 7.20 (m, 1H), 7.11 (d, *J* = 2.8 Hz, 1H), 6.97 (s, 1H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 155.6, 147.9, 144.8, 137.8, 135.9, 133.7, 133.3, 130.4, 130.1, 129.2, 128.8, 128.6, 128.4, 128.1, 125.8, 121.8, 120.8, 104.1, 55.4. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{17}BrNOS^+$ 422.0209; found 422.0221.

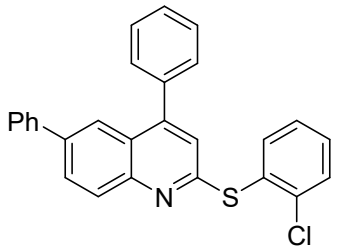


6-methoxy-2-((2-methoxyphenyl)thio)-4-phenylquinoline (3al). Eluent: PE/EA (30:1)，Yellow solid, 65.1 mg，87% yield, m.p.: 85 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8 Hz, 1H), 7.62 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.49 - 7.43 (m, 3H), 7.42 - 7.37 (m, 3H), 7.32 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.06 (d, *J* = 2.8 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 2H), 6.90 (s, 1H), 3.81 (s, 3H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.6, 157.4, 157.2, 147.4, 144.6, 138.1, 136.4, 130.9, 130.2, 129.2, 128.6, 128.3, 125.5, 121.5, 121.3, 120.0, 119.2, 111.5, 104.1, 55.9, 55.4. **HRMS (ESI)** m/z:

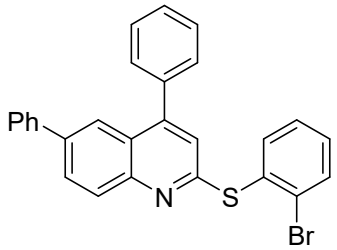
$[M+H]^+$ calcd for $C_{23}H_{20}NO_2S^+$ 374.1209; found 374.1242.



2-((2-fluorophenyl)thio)-4,6-diphenylquinoline (3am). Eluent: PE/EA (30:1), Yellow solid, 68 mg, 84% yield, m.p.: 118 - 120 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 1.6 Hz, 1H), 7.92 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.71 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.58 - 7.56 (m, 2H), 7.50 - 7.40 (m, 8H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.25 - 7.20 (m, 2H), 7.03 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9 (*J* = 247.7 Hz), 158.8, 149.2, 148.0, 140.5, 138.6, 137.6, 137.1, 131.7 (*J* = 8.0 Hz), 129.5, 129.4, 129.2, 128.9, 128.6, 128.6, 127.5, 127.4, 125.0 （*J* = 2.8 Hz）, 124.9, 123.6, 119.6, 117.9 (*J* = 18.1 Hz), 116.4（*J* = 22.6 Hz）. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{27}H_{19}FNS^+$ 408.1217; found 408.1213.

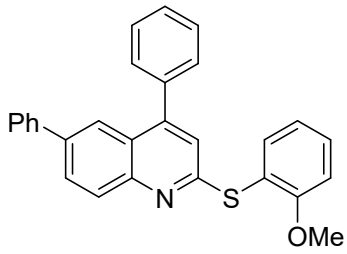


2-((2-chlorophenyl)thio)-4,6-diphenylquinoline (3an). Eluent: PE/EA (30:1), Yellow solid, 48.4 mg, 58% yield, m.p.: 151 - 153 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 1.6 Hz, 1H), 7.94 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.78 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.59 - 7.55 (m, 2H), 7.52 - 7.41 (m, 8H), 7.38 - 7.31 (m, 3H), 6.99 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.8, 149.2, 148.1, 140.5, 138.8, 138.7, 137. 6, 136.8, 130.6, 130.5, 130.2, 129.5, 129.4, 129.3, 128.8, 128.6, 128.6, 127.6, 127.5, 127.4, 125.0, 123.6, 120.1. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{27}H_{19}ClNS^+$ 424.0921; found 424.0958.

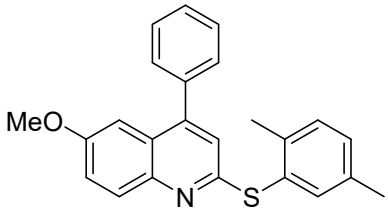


2-((2-bromophenyl)thio)-4,6-diphenylquinoline (3ao). Eluent: PE/EA (30:1), Yellow solid, 60 mg, 65% yield, m.p.: 156 - 157 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 2 Hz, 1H), 7.94 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.79 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59 - 7.56 (m, 2H), 7.10 - 7.44 (m, 5H), 7.43 - 7.39 (m, 2H), 7.37 - 7.32 (m, 2H), 7.30 - 7.26 (m , 1H), 6.98 (s,

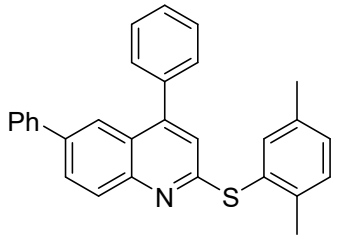
1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.9, 149.2, 148.1, 140.5, 138.8, 137.6, 136.7, 133.8, 132.4, 130.6, 129.7, 129.5, 129.4, 129.3, 128.8, 128.6, 128.6, 128.2, 127.5, 127.3, 125.0, 123.6, 120.2. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{27}H_{19}BrNS^+$ 468.0416; found 468.0397.



2-((2-methoxyphenyl)thio)-4,6-diphenylquinoline (3ap). Eluent: PE/EA (30:1), Yellow solid, 59.6 mg, 72% yield, m.p.: 145 - 147 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.92 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.68 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.49 - 7.40 (m, 8H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.05 - 7.00 (m, 2H), 6.94 (s, 1H), 3.83 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.5, 159.8, 148.6, 148.0, 140.6, 138.3, 137.8, 136.8, 131.3, 129.4, 129.3, 129.2, 128.8, 128.6, 128.4, 127.4, 127.3, 124.8, 123.5, 121.4, 119.6, 118.6, 111.7, 55.9. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{28}H_{22}NOS^+$ 468.0416; found 468.0403.



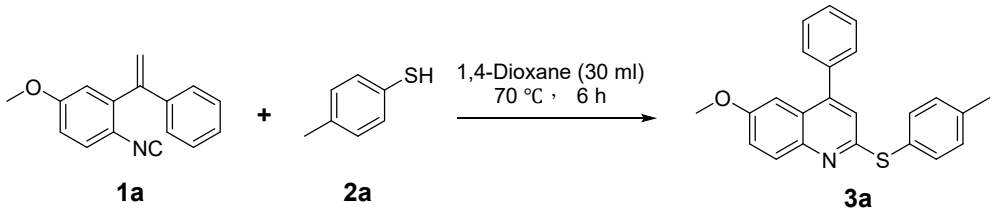
2-((2,5-dimethylphenyl)thio)-6-methoxy-4-phenylquinoline (3aq). Eluent: PE/EA (30:1), Yellow solid, 67.6 mg, 91% yield, m.p.: 122 - 124 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.2 Hz, 1H), 7.50 - 7.44 (m, 4H), 7.39 - 7.37 (m, 2H), 7.33 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.07 (d, *J* = 2.8 Hz, 1H), 6.80 (s, 1H), 3.75 (s, 3H), 2.40 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.0, 157.2, 147.6, 144.7, 139.3, 138.0, 136.7, 136.5, 130.7, 130.5, 130.1, 129.6, 129.1, 128.6, 128.3, 125.3, 121.6, 119.2, 104.1, 55.4, 20.7, 20.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{24}H_{22}NOS^+$ 372.1417; found 372.1420.



2-((2,5-dimethylphenyl)thio)-4,6-diphenylquinoline (3ar). Eluent: PE/EA (30:1), Yellow solid, 65.7 mg, 79% yield, m.p.: 161 - 163 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 1H), 7.94 - 7.90 (m, 2H), 7.57 - 7.55 (m, 2H), 7.52 (s, 1H), 7.49 - 7.39 (m, 7H), 7.35 - 7.31 (m, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.16 (dd, *J* = 7.6, 2.0 Hz, 1H), 6.83 (s, 1H), 2.41 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1,

148.9, 148.1, 140.6, 139.6, 138.4, 137.7, 137.0, 136.7, 130.8, 130.8, 129.4, 129.4, 129.2, 129.1, 128.8, 128.6, 128.5, 127.5, 127.3, 124.7, 123.6, 119.1, 20.7, 20.5. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{29}H_{24}NS^+$ 418.1624; found 418.1616.

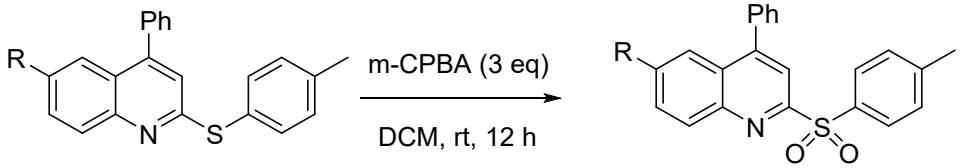
V. Scale-up experiment



In a 100 mL round bottom flask equipped with a condenser was added 1-isocyano-4-methoxy-2-(1-phenylvinyl)benzene (5 mmol, 1.1755 g) **1a**, 4-methylthiophenol **2a** (6 mmol, 1.2 eq, 0.7442 g) and 1,4-dioxane (30 mL). The flask (open to air) was placed in a metal bath and heated at 70 °C for 6 h, until the complete consumption of isocyanide **1a** as monitored by TLC. After this time, the mixture was quenched with saturated Na2CO3 solution and extracted 3 times with DCM. The organic layers were combined, dried over anhydrous Mg_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 30 : 1) to give 6-methoxy-4-phenyl- 2-(*p*-Tolylthio)quinolone **3a** (1.286 g, 72 %).

VI. Synthetic utility of quinoline 3

Synthesis of quinoline sulfones 4

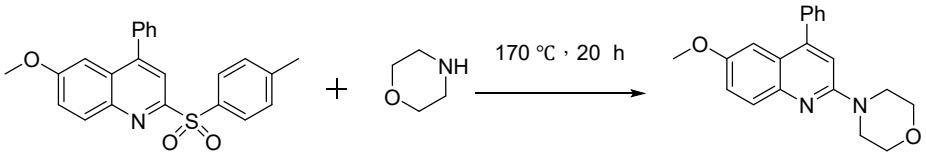


6-methoxy-4-phenyl-2-tosylquinoline (4a): A round bottom flask was charged with the mixture of 6-methoxy-4-phenyl-2-(p-tolylthio)quinoline **3a** (0.2 mmol), mCPBA (0.6 mmol), then stirred in CH_2Cl_2 (1 mL) at room temperature for 12 h. After completion, H_2O (5 mL) was added and the mixture was extracted with CH_2Cl_2 (5 mL x 3), The organic layers were combined, dried over anhydrous Mg_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 15 : 1) to give 6-methoxy-4-phenyl-2-tosylquinoline **4a**. White solid, 66.3 mg, 86 %, yield, m.p. 154-155 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.2 Hz, 1H), 8.08 (s, 1H), 8.03 (d, *J* = 9.2 Hz, 2H), 7.58 - 7.50 (m, 5H), 7.42 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 2.8 Hz, 1H), 3.79 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.9,

155.5, 149.4, 144.6, 144.2, 137.3, 136.6, 132.3, 129.7, 129.3, 129. 0, 129.0, 128.9, 128.8, 123.5, 118.3, 103.3, 55.6, 21.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{23}H_{19}NO_3S^+$ 390.1158; found 390.1165.

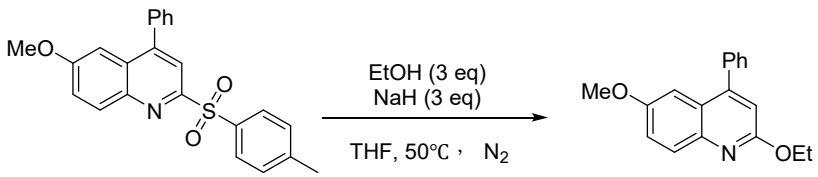
4-phenyl-2-tosylquinoline (4b): A round bottom flask was charged with the mixture of 4-phenyl-2-(p-tolylthio)quinoline **3e** (0.2 mmol), mCPBA (0.6 mmol), then stirred in CH_2Cl_2 (1 mL) at room temperature for 12 h. After completion, then H_2O (5 mL) was added and the mixture was extracted with CH_2Cl_2 (5 mL x 3), The organic layers were combined, dried over anhydrous Mg_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 15 : 1) to give 4-phenyl-2-tosylquinoline **4b**. White solid, 61.4. mg, 87 %, yield, m.p. 127-128 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.15 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 7.2 Hz, 1H), 7.61-7.49 (m, 6H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.9, 151.5, 148.0, 144.8, 136.9, 136.1, 130.7, 130.6, 129.7, 129.5, 129.1, 128.7, 127.3, 125.9, 117.6, 21.6. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{22}H_{17}NO_2S^+$ 360.1053; found 360.1063.

Synthesis of 4-morpholinylquinone 5



4-(6-methoxy-4-phenylquinolin-2-yl)morpholine (5): A Shlenk tube was charged with 6-methoxy-4-phenyl-2-tosylquinoline (0.05 mmol) and stirred in morpholine (0.5 mL) at 170 °C for 20 h. After completion, H_2O (5 mL) was added and the mixture was extracted with CH_2Cl_2 (5 mL x 3). The organic layers were combined, dried over anhydrous Mg_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 20 : 1) to give 4-(6-methoxy-4-phenylquinolin-2-yl)morpholine. White solid, 6.4 mg, 40% yield, m.p. 100-102 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 1H), 7.51-7.46 (m, 5H), 7.26-7.23 (m, 1H), 7.01 (d, *J* = 2.8 Hz, 1H), 6.87 (s, 1H), 3.86 (t, *J* = 4.8 Hz, 4H), 3.73 (s, 3H), 3.67 (m, *J* = 4.8 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.2, 155.3, 149.0, 143.9, 139.0, 129.2, 128.9, 128.5, 128.5, 128.2, 122.7, 120.9, 110.0, 104.9, 66.9, 55.4， 45.9. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{21}H_{22}NO_2^+$ 321.1598; found 321.1629.

Synthesis of 2-ethoxyquinoline 6



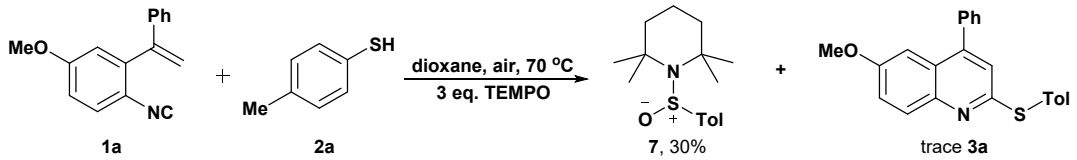
2-ethoxy-6-methoxy-4-phenylquinoline (6): A round bottom flask was charged with the mixture of 6-methoxy-4-phenyl-2-tosylquinoline (0.05 mmol), ethanol (2 eq),

NaH (2 eq), then stirred in THF (1 mL) at 50℃ under nitrogen atmosphere for 24 h.

After completion, then H_2O (5 mL) was added and the mixture was extracted with ethyl acetate (5 mL x 3), The organic layers were combined, dried over anhydrous Mg2SO4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 30 : 1) to give 2-ethoxy-6-methoxy-4-phenylquinoline. White solid, 11 mg, 79 %, yield, m.p. 95-97 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J*=9.2 Hz, 1H), 7.53-7.45 (m, 5H), 7.29 (dd, J_1=9.2 Hz, J_2=2.8 Hz, 1H), 7.12 (d, J=2.8 Hz, 1H), 6.83 (s, 1H), 4.54 (dd, J_1=14 Hz, J_2=7.2 Hz, 2H), 3.76 (s , 3H), 1.46 (t, *J*=7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.6, 156.0, 150.0, 142.6, 138.3, 129.4, 128.9, 128.5, 128.3, 124.4, 120.4, 113.2, 105.2, 61.5, 55.4, 14.7. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{18}H_{18}NO_2^+$ 280.1332; found 280.1320.

VII. Mechanistic investigation

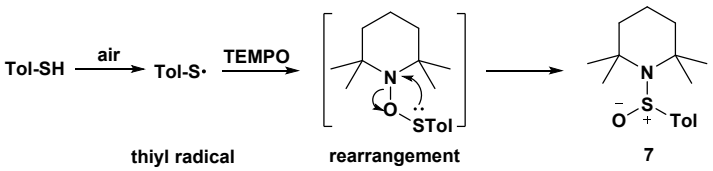
Radical trapping experiment

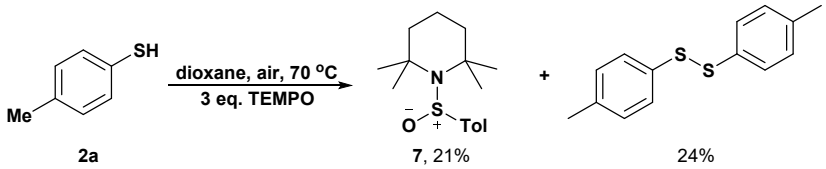


1-Isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1a** (0.2 mmol，47 mg), 4-methylbenzenethiol **2a** (0.24 mmol, 1.2 eq, 30 mg) and TEMPO (0.6 mmol, 3 eq, 94 mg) were dissolved in 1,4-dioxane (0.5 mL). The reaction was stirred at 70 °C un der air atmosphere for 6 h, still a large amount of starting material A remained unreacted. After this time, the mixture was quenched with saturated Na_2CO_3 solution and extracted 3 times with DCM. The organic layers were combined, dried over anhydrous Mg_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 30 : 1) to recover **1** (39 mg, 0.164 mmol) and 2,2,6,6-tetramethyl-1-(*p*-tolylsulfinyl)piperidine **7** (0.073 mmol, 20.4 mg, 30% yield). Only trace amount of desired product **3a** was formed.

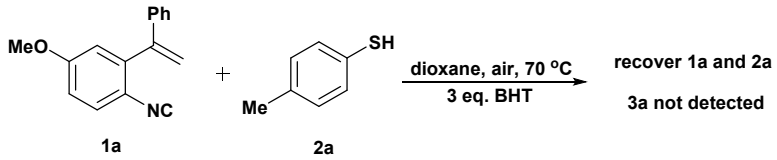
2,2,6,6-tetramethyl-1-(p-tolylsulfinyl)piperidine **7**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 1.65 - 1.49 (m, 5H), 0.91 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.1, 139.4, 129.2, 125.9, 61.1, 58.7, 43.4, 41.3, 35.3, 32.5, 28.7, 27.9, 21.2, 17.3. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{16}H_{26}NOS^+$ 280.1730; found 280.1710.

possible reaction route to form compound 7



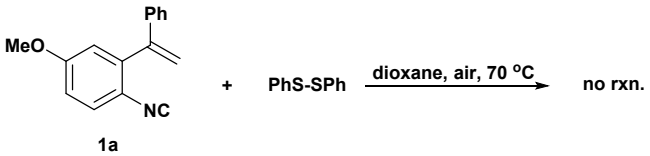


4-methylbenzenethiol **2a** (0.24 mmol) and TEMPO (3 eq) were dissolved in 1,4-dioxane (0.5 mL) and stirred at 70 °C under air atmosphere for 2 h. After this time, the mixture was quenched with saturated Na_2CO_3 solution and extracted 3 times with DCM. The organic layers were combined, dried over anhydrous Mg_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 40 : 1) to form 1,2-di-p-tolyldisulfane (14.3 mg, 0.058 mmol, 24% yield) and obtained the same new product 2,2,6,6-tetramethyl-1-(p-tolylsulfinyl)piperidine **7** (0.051 mmol, 14.2 mg, 21% yield).

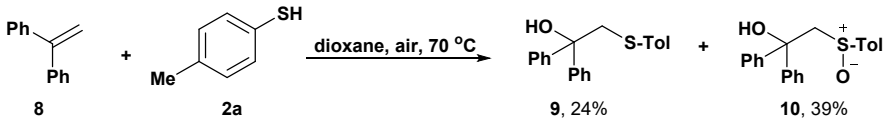


1-Isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1a** (0.2 mmol, 47 mg), 4-methylbenzenethiol **2a** (0.24 mmol, 1.2 eq, 30 mg) and BHT (0.6 mmol, 3 eq, 132.21 mg) were dissolved in 1,4-dioxane (0.5 mL) and the reaction was stirred at 70 °C for 2 h. No desired product **3a** was detected; only a large amount of starting material **1a** and **2a** was recovered.

Control experiment



1-Isocyano-4-methoxy-2-(1-phenylvinyl)benzene **1a** (0.2 mmol, 47 mg) and diphenyldisulfide (0.24 mmol, 1.2 eq, 53 mg) were dissolved in 1,4-dioxane (0.5 mL) and the reaction was stirred at 70 °C for 2 h. No reaction occurred.



Ethene-1,1-diyldibenzene **8** (0.2 mmol, 36 mg) and 4-methylbenzenethiol (1.2 eq, 30 mg) were dissolved in 1,4-dioxane (0.5 mL) and stirred at 70 °C for 2 h. After this time, the mixture was quenched with saturated Na_2CO_3 solution and extracted 3 times with DCM. The organic layers were combined, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 40 : 1) to obtain 1,1-diphenyl-2-(*p*-tolylthio)ethan-1-ol **9** (15.3 mg, 24% yield) and 1,1-diphenyl-2-(*p*-tolylsulfinyl)ethan-1-ol **10** (26.2 mg, 39% yield), which is in accordance with literature report.

VIII. X-ray Crystallographic Data of compound 3a, 3m and 7

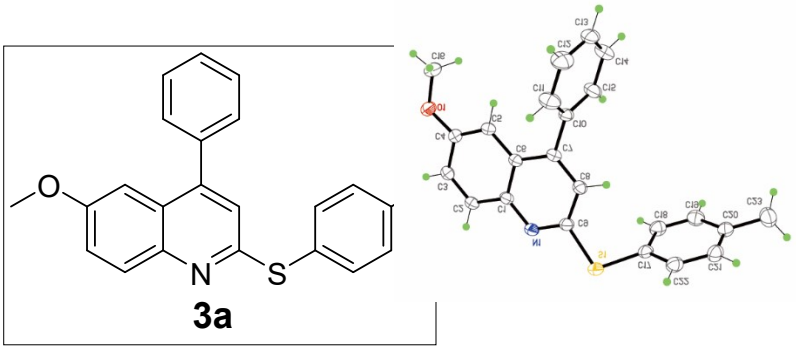
X-ray Crystallographic Data of compound 3a

Sample preparation

30 mg of **3a** was dissolved in CH_2Cl_2 and petroleum ether (500 μL / 3 mL) and the solvent was evaporated slowly at room atmosphere.

Crystal measurement for compound 3a

Suitable single crystals of complex **3a** were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 293K on an Agilent SuperNova CCD-based diffractometer (Cu Kα radiation λ = 1.54184 Å). The raw frame data for the complexes were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT. Corrections for incident and diffracted beam absorption effects were applied using SADABS. None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F2 by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms bonded to carbon and nitrogen were placed in geometrically idealized positions with isotropic displacement parameters set to 1.2Ueq of the attached atom.



3a CCDC 2193502, displacement ellipsoids are drawn at the 30% probability level.

Crystal data and structure refinement for 3a

Empirical formula	$C_{23}H_{19}NOS$
Formula weight	357.45
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.8102(4)
b/Å	17.8902(7)
c/Å	9.7282(4)
α/°	90.00
β/°	96.643(4)
γ/°	90.00
Volume/Å^3	1868.77(13)
Z	4
ρ_{calc}mg/mm^3	1.270
m/mm^{-1}	0.184
F(000)	752.0
Crystal size/mm^3	0.25 × 0.19 × 0.14
2Θ range for data collection	7.02 to 58.36°
Index ranges	$-13 \leq h \leq 14$, $-23 \leq k \leq 13$, $-12 \leq l \leq 11$
Reflections collected	12825
Independent reflections	4362[R(int) = 0.0292]
Data/restraints/parameters	4362/0/237
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0450, wR_2 = 0.1060
Final R indexes [all data]	R_1 = 0.0684, wR_2 = 0.1224
Largest diff. peak/hole / e Å^{-3}	0.20/-0.27

X-ray Crystallographic Data of compound 3m

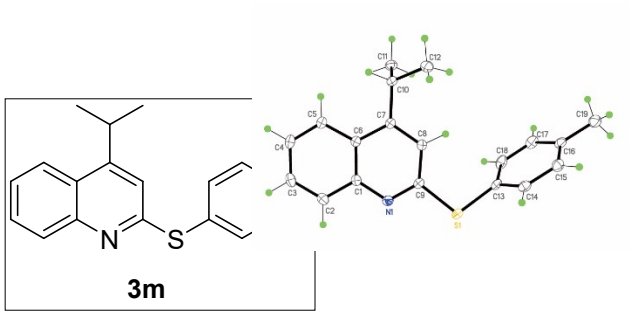
Sample preparation

30 mg of **3m** was dissolved in CH_2Cl_2 and petroleum ether (500 μL / 3 mL) and the solvent was evaporated slowly at room atmosphere.

Crystal measurement for compound 3m

Suitable single crystals of complex **3m** were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 113.15 K on an Agilent SuperNova CCD-based diffractometer (Cu Kα radiation λ = 1.54184 Å). The raw frame data for the complexes were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT. Corrections for incident and diffracted beam absorption effects were applied using SADABS. None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F2 by full-matrix least-squares techniques. Non-hydrogen atoms were

refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms bonded to carbon and nitrogen were placed in geometrically idealized positions with isotropic displacement parameters set to 1.2Ueq of the attached atom.



3m CCDC 2193503, displacement ellipsoids are drawn at the 30% probability level.

Crystal data and structure refinement for 3m

Empirical formula	$C_{19}H_{19}NS$
Formula weight	293.41
Temperature/K	113.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.4233(4)
b/Å	9.6651(5)
c/Å	18.0611(8)
α/°	90.00
β/°	104.894(5)
γ/°	90.00
Volume/Å^3	1589.69(13)
Z	4
ρ_{calc}mg/mm^3	1.226
m/mm^{-1}	0.197
F(000)	624.0
Crystal size/mm^3	0.23 × 0.2 × 0.15
2Θ range for data collection	6.14 to 51.36°
Index ranges	$-11 \le h \le 11$, $-10 \le k \le 11$, $-22 \le l \le 22$
Reflections collected	12903
Independent reflections	3012[R(int) = 0.0471]
Data/restraints/parameters	3012/0/194
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0392, wR_2 = 0.0939
Final R indexes [all data]	R_1 = 0.0474, wR_2 = 0.1021

Largest diff. peak/hole / e Å^{-3}	0.24/-0.25

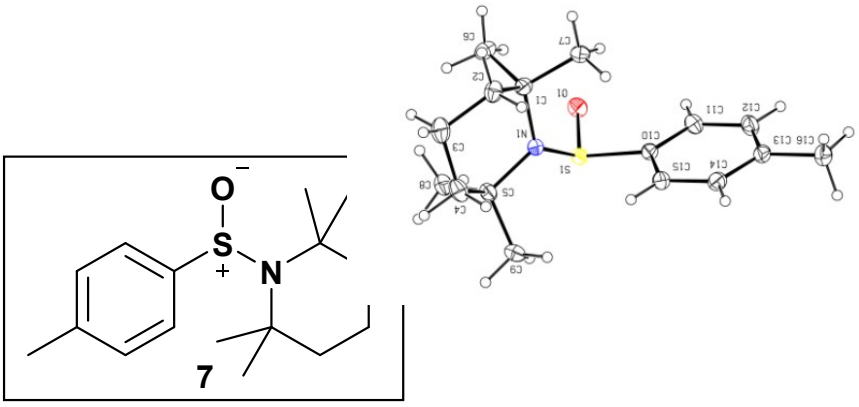
X-ray Crystallographic Data of compound 4a

Sample preparation:

30 mg of **7** was dissolved in CH_2Cl_2 and petroleum ether (500 µL / 3 mL) and the solvent was evaporated slowly at room temperature under air atmosphere.

Crystal measurement for compound 7:

Suitable single crystals of complex **7** were selected and mounted in air onto thin glass fibers.X-ray intensity data were measured at 170 K on an Agilent SuperNova CCD-based diffractometer (Cu Kα radiation λ = 1.54184 Å). The raw frame data for the complexes were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT. Corrections for incident and diffracted beam absorption effects were applied using SADABS. None of the crystals showed evidence of crystal decay during data collection. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F2 by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms bonded to carbon and nitrogen were placed in geometrically idealized positions with isotropic displacement parameters set to 1.2Ueq of the attached atom.



7 CCDC 2193500, displacement ellipsoids are drawn at the 50% probability level.

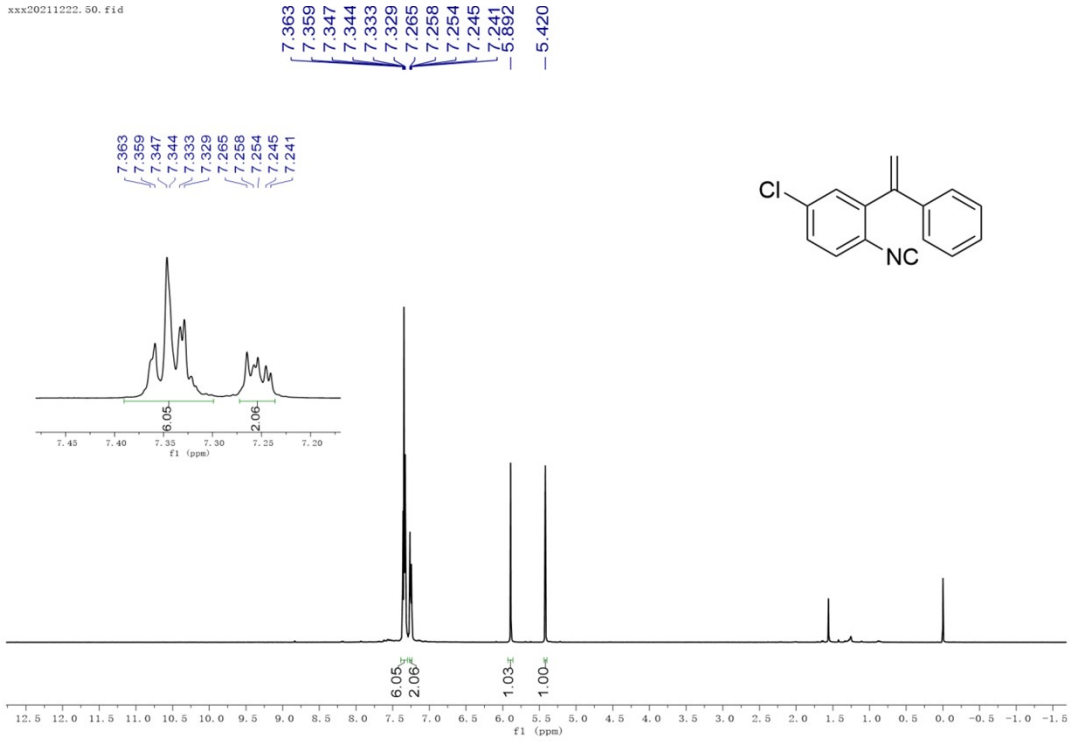
Crystal data and structure refinement for 7

Empirical formula	$C_{16}H_{25}NOS$
Formula weight	279.43
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.3185(8)
b/Å	8.0794(7)

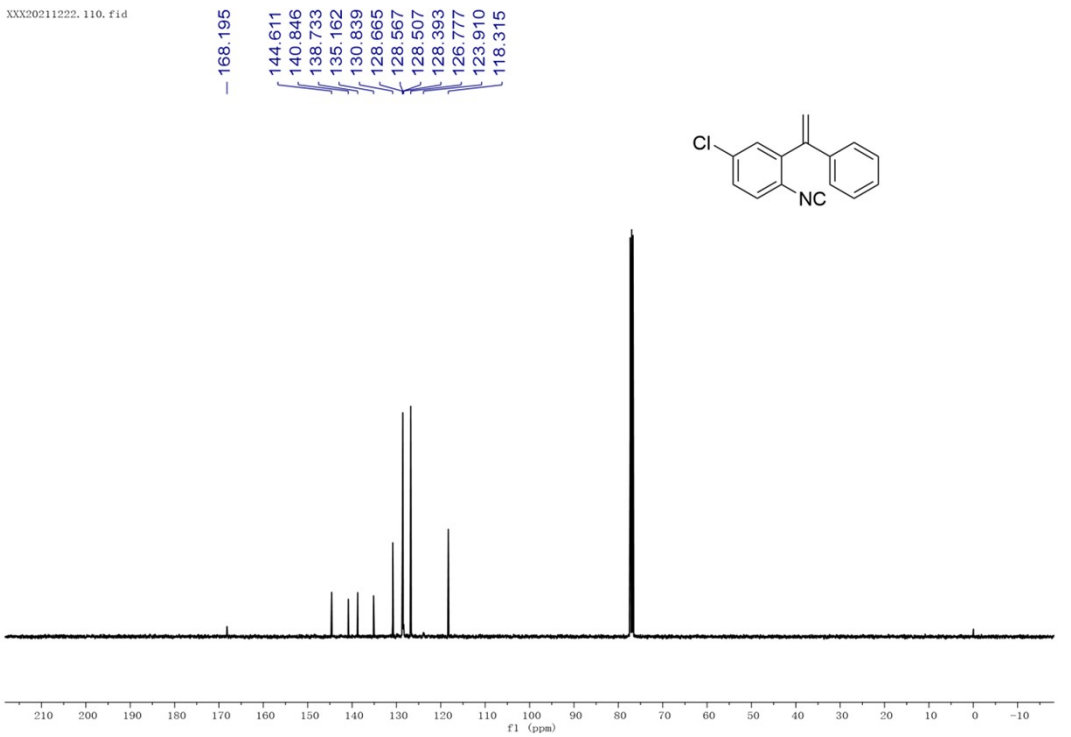
c/Å	20.8639(18)
α/°	90
β/°	90.434(4)
γ/°	90
Volume/Å^3	1570.8(2)
Z	4
ρ_{calc}g/cm^3	1.182
μ/mm^{-1}	1.758
F(000)	608.0
Crystal size/mm^3	0.47 × 0.31 × 0.3
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.476 to 136.65
Index ranges	-9 ≤ h ≤ 11, -9 ≤ k ≤ 9, -25 ≤ l ≤ 25
Reflections collected	9264
Independent reflections	2832 [R_{int} = 0.0473, R_{sigma} = 0.0503]
Data/restraints/parameters	2832/0/177
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0440, wR_2 = 0.1164
Final R indexes [all data]	R_1 = 0.0474, wR_2 = 0.1189
Largest diff. peak/hole / e Å^{-3}	0.38/-0.28

IX. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compounds 1, 3, 4, 5, 6, 7, 9 and 10

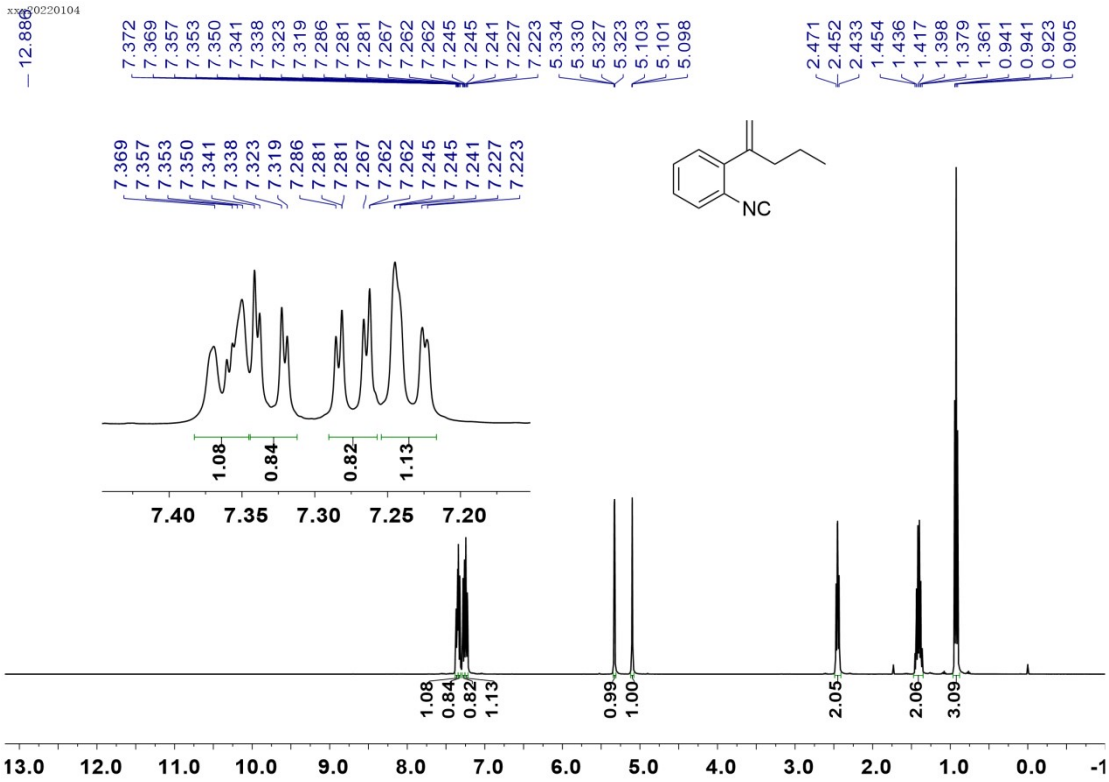
^{1}H NMR (400 MHz, $CDCl_3$) for **1f**



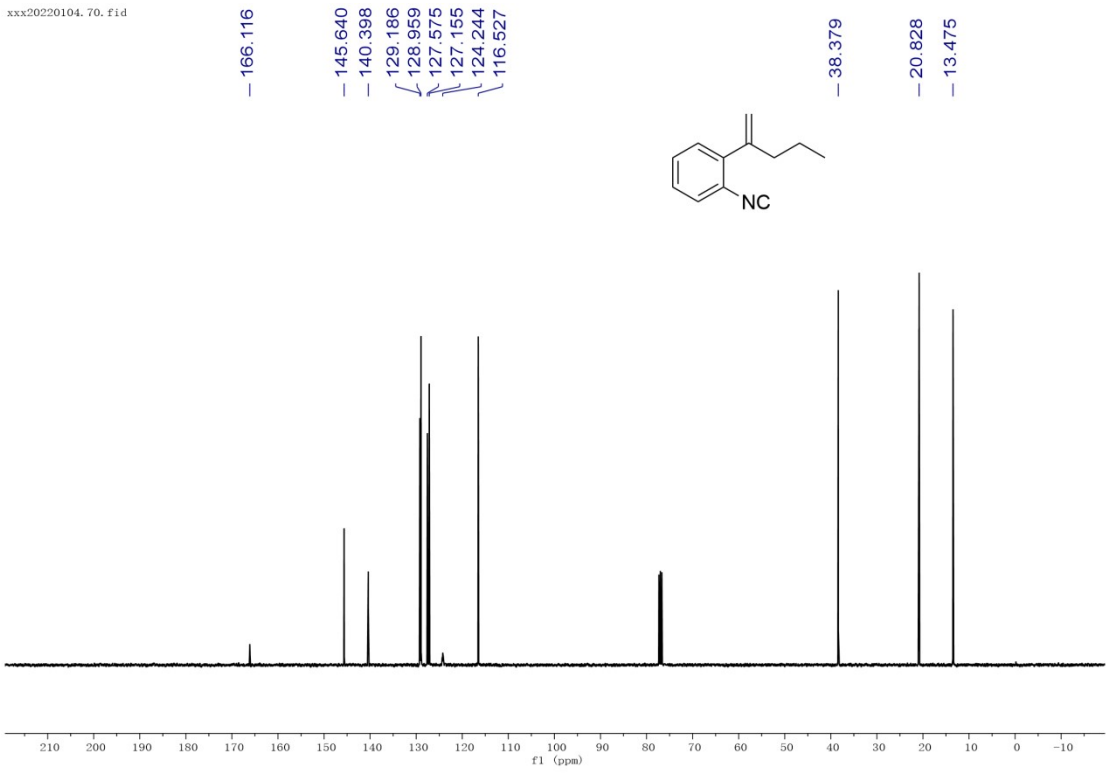
^{13}C NMR (100 MHz, $CDCl_3$) for **1f**



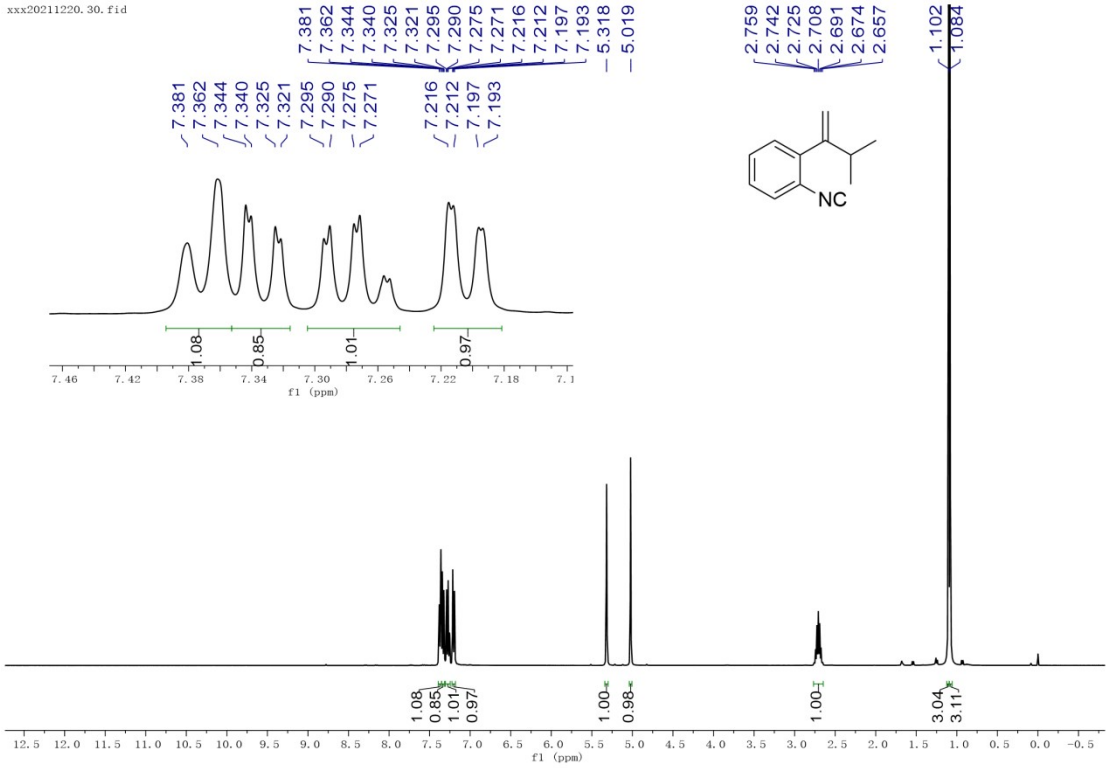
^{1}H NMR (400 MHz, $CDCl_3$) for **1l**



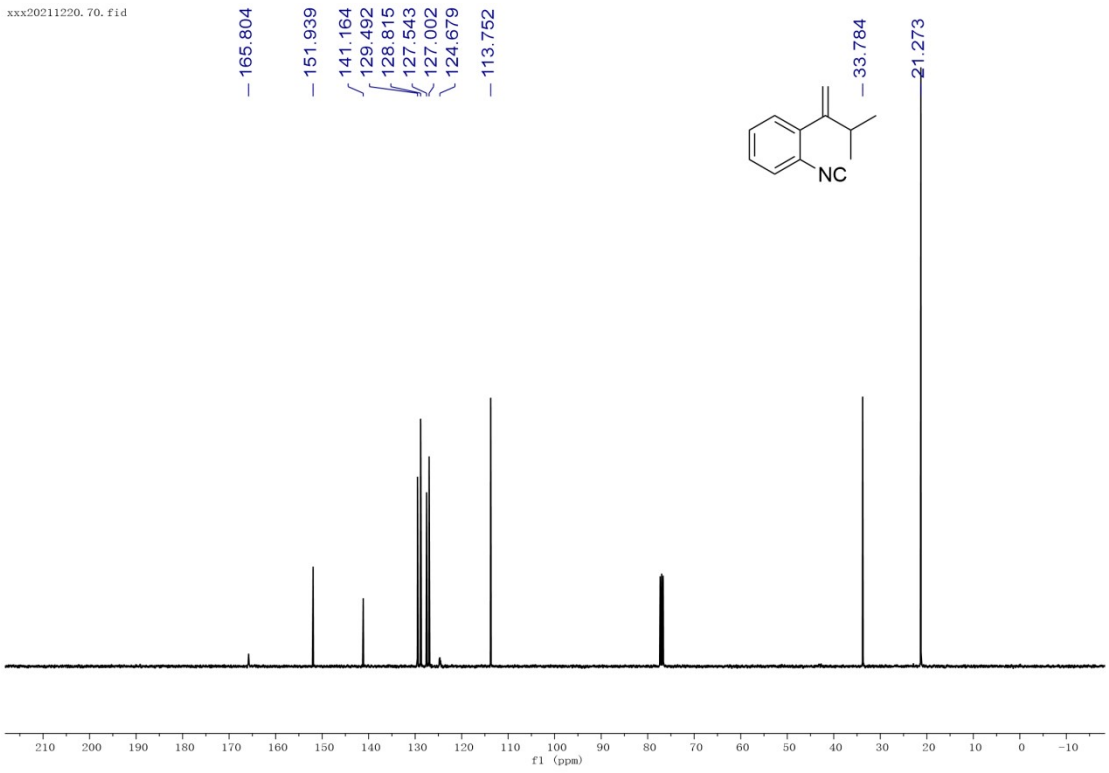
^{13}C NMR (100 MHz, $CDCl_3$) for **1l**



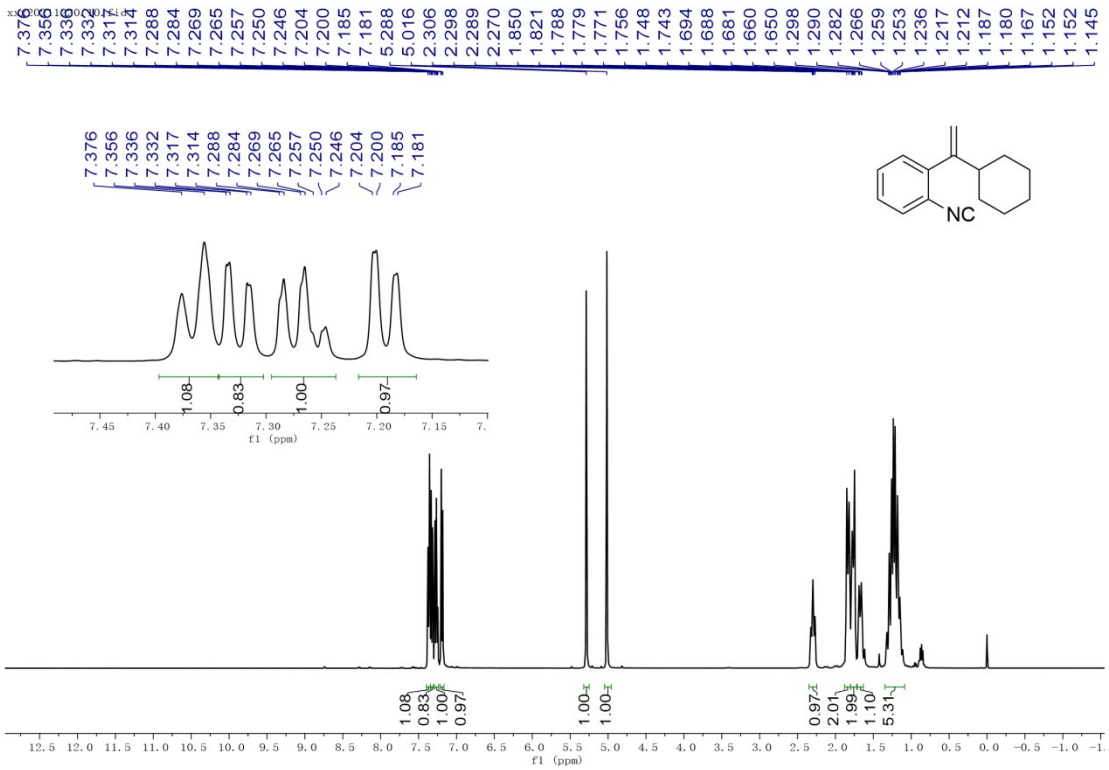
^{1}H NMR (400 MHz, $CDCl_3$) for **1m**



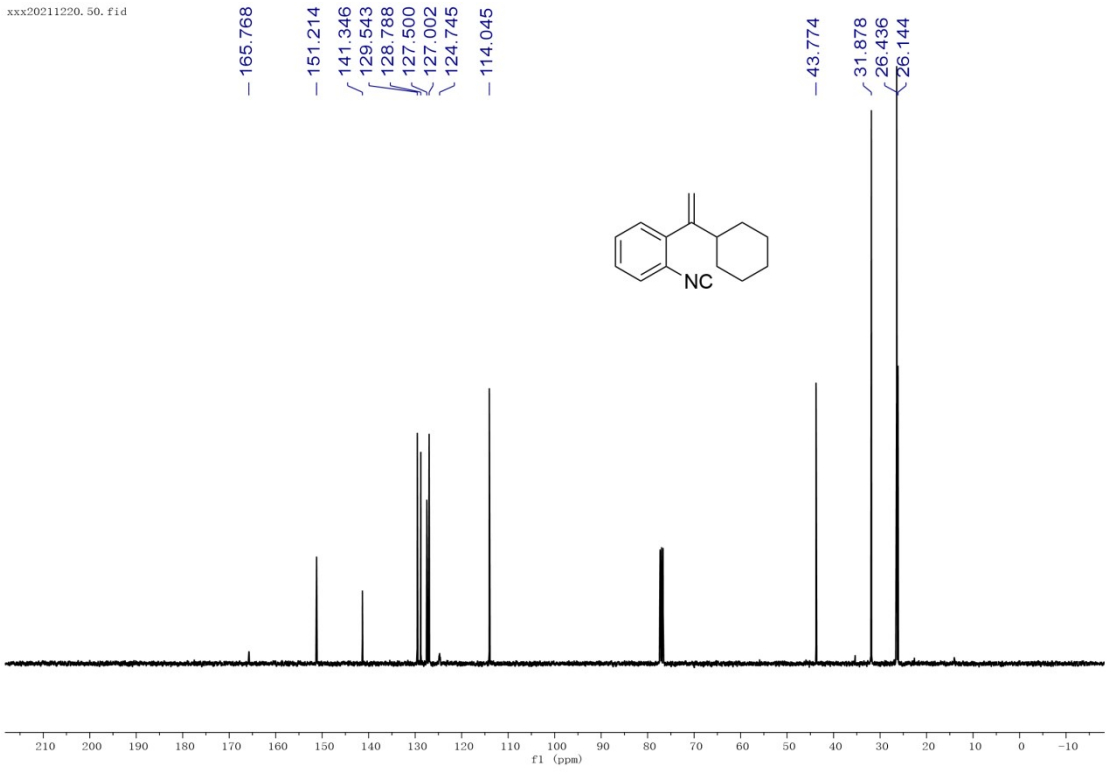
^{13}C NMR (100 MHz, $CDCl_3$) for **1m**



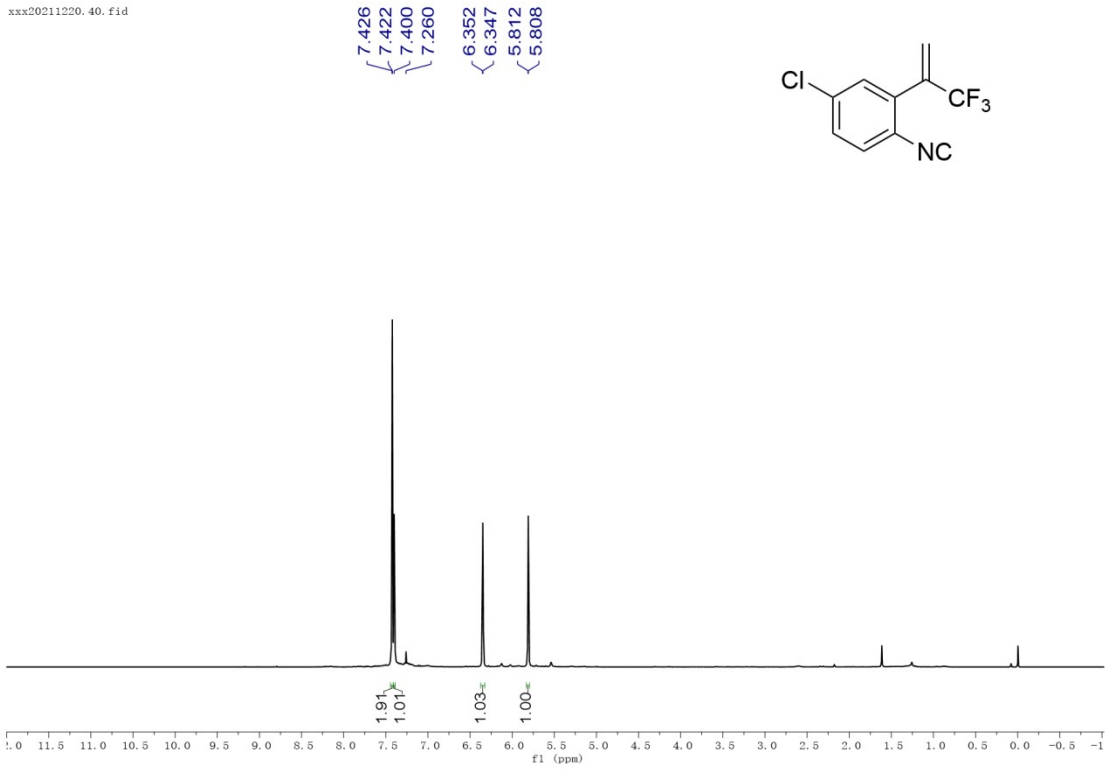
^{1}H NMR (400 MHz, $CDCl_3$) for **1n**



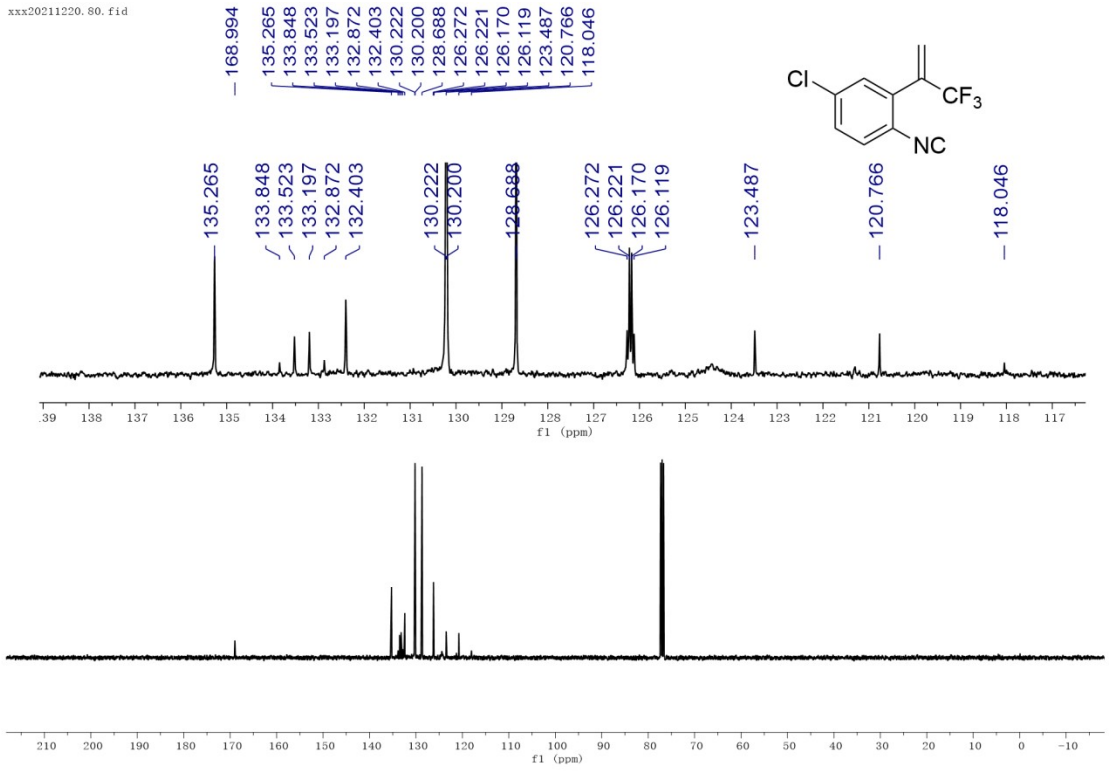
^{13}C NMR (100 MHz, $CDCl_3$) for **1n**



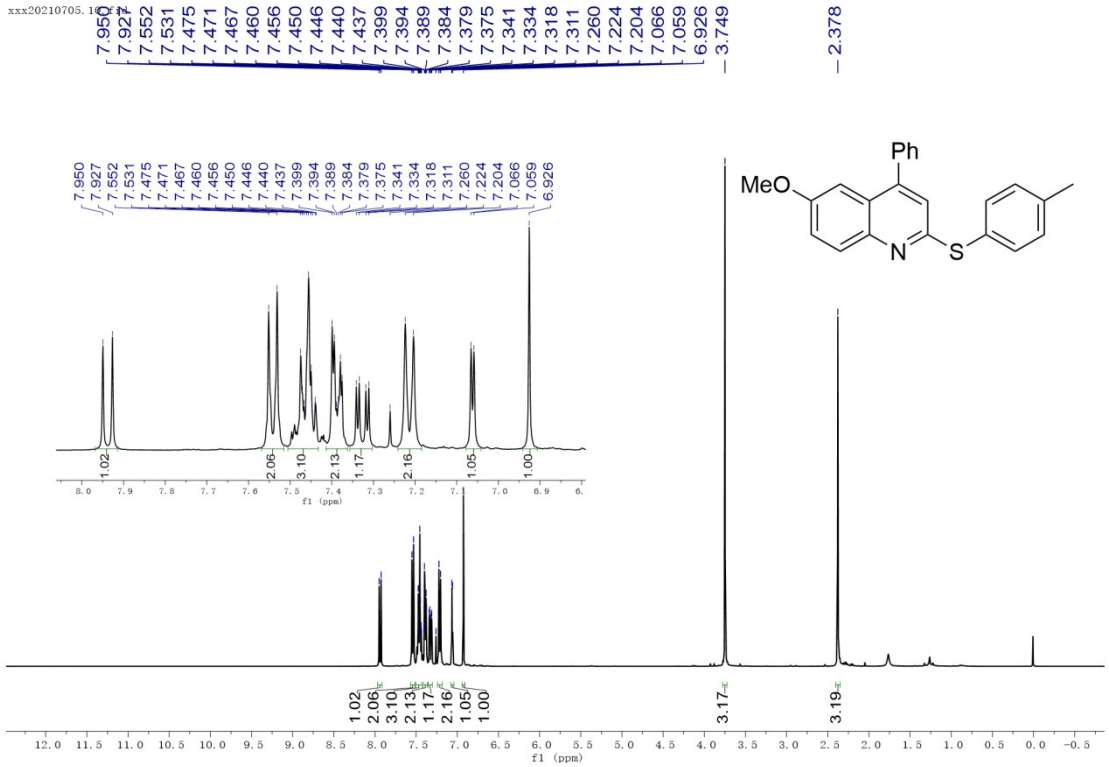
^{1}H NMR (400 MHz, $CDCl_3$) for **1p**



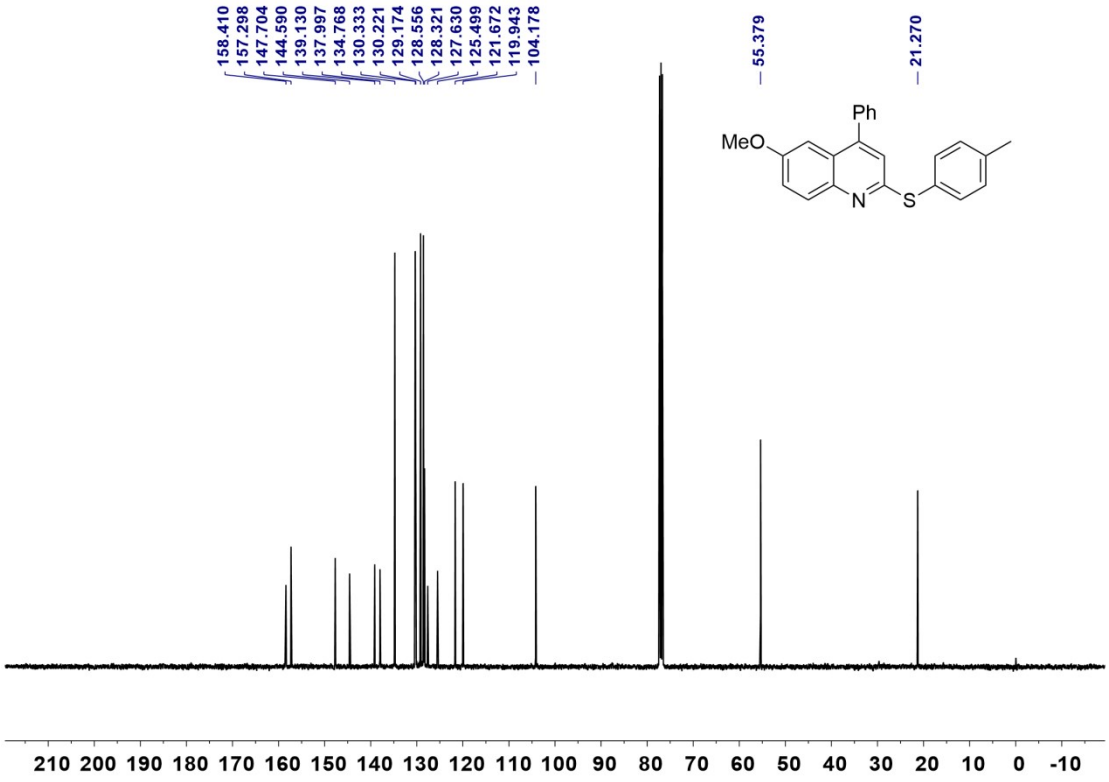
^{13}C NMR (100 MHz, $CDCl_3$) for **1p**



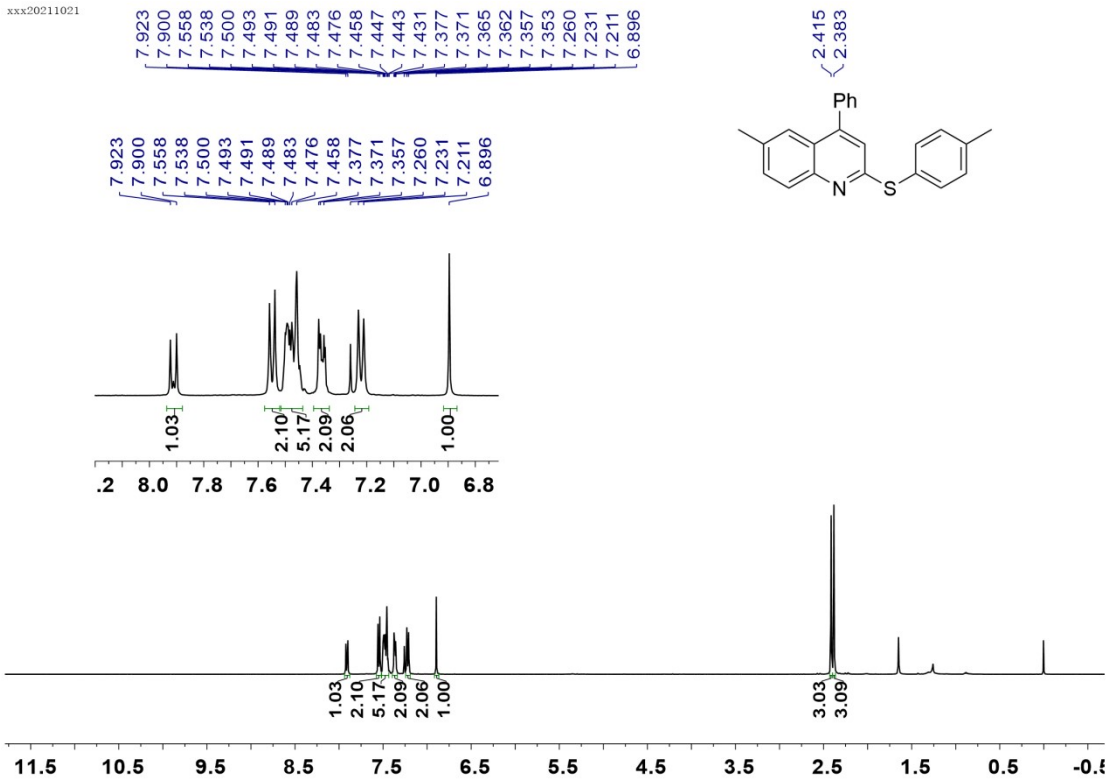
^{1}H NMR (400 MHz, $CDCl_3$) for **3a**



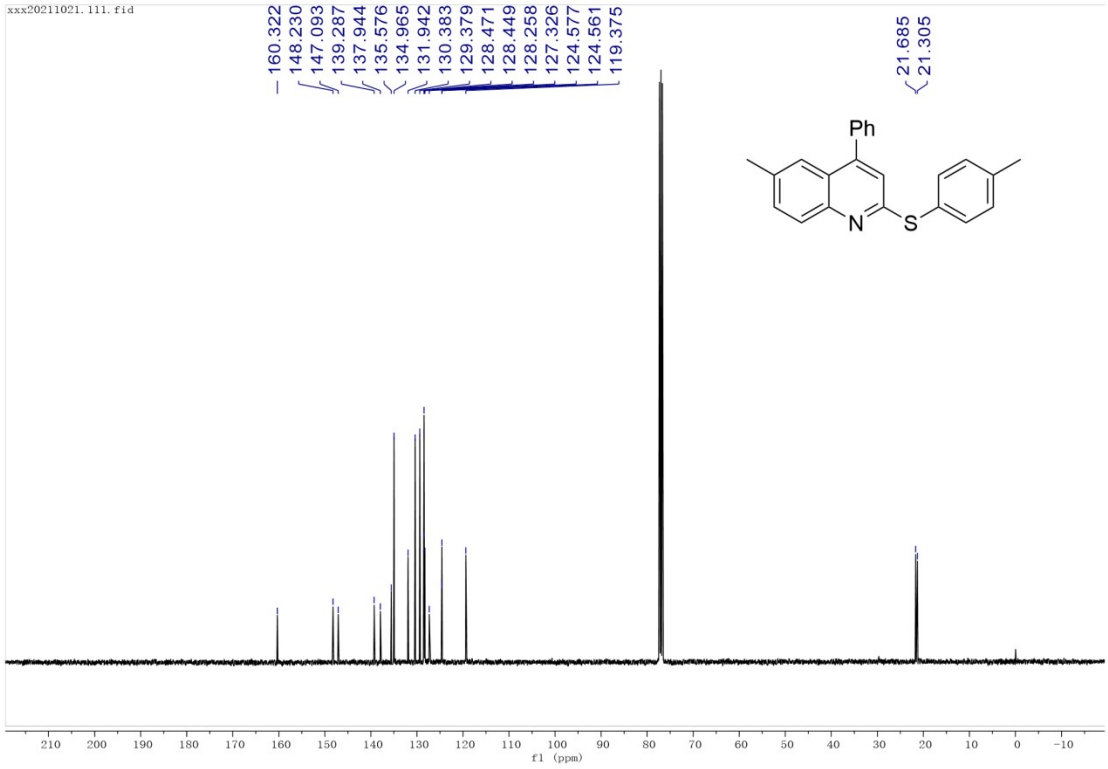
^{13}C NMR (100 MHz, $CDCl_3$) for **3a**



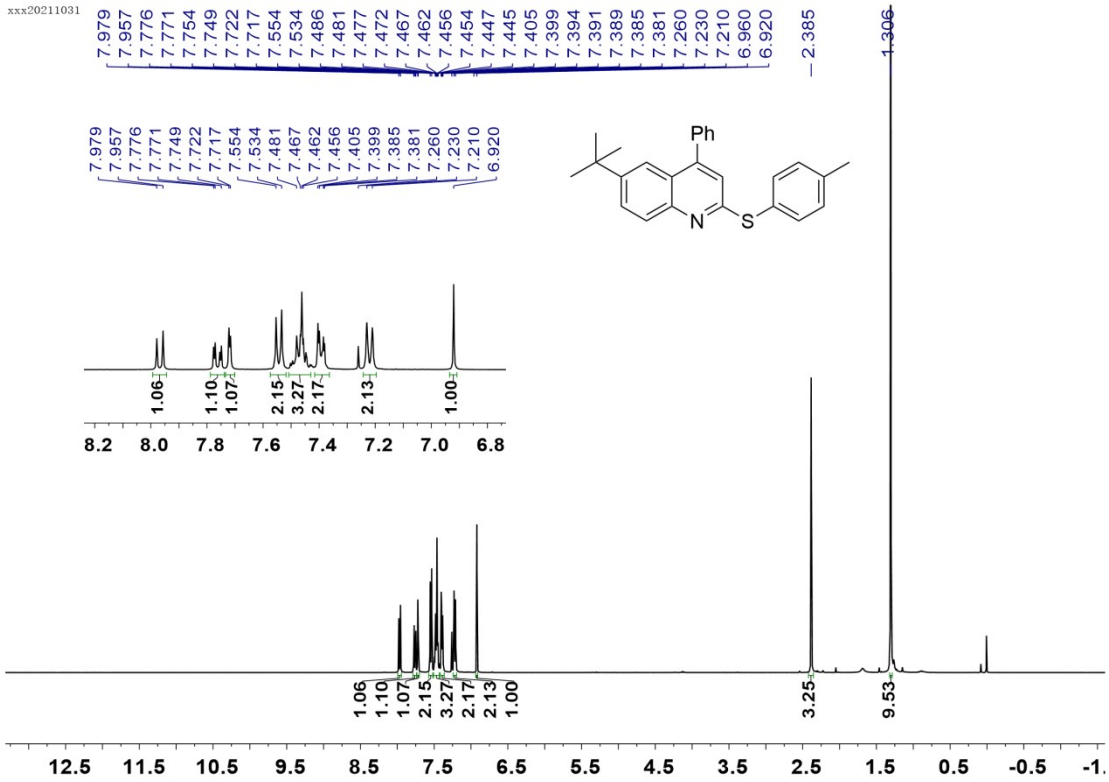
^{1}H NMR (400 MHz, $CDCl_3$) for **3b**



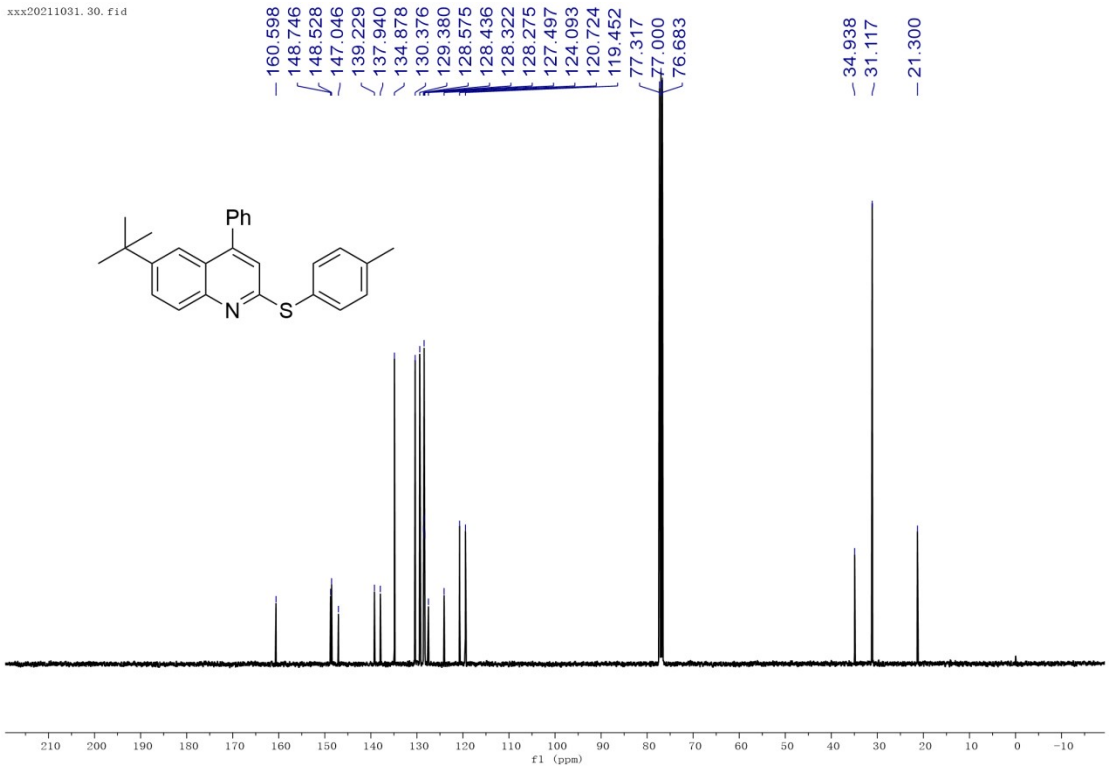
^{13}C NMR (100 MHz, $CDCl_3$) for **3b**



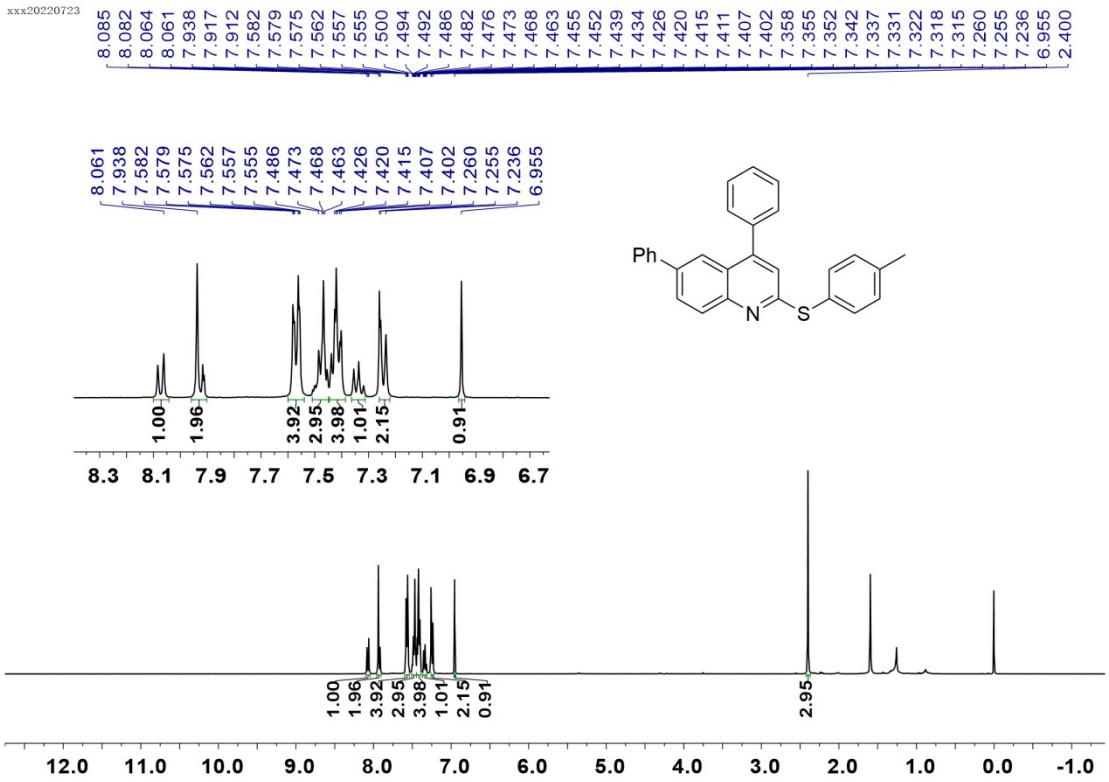
^{1}H NMR (400 MHz, $CDCl_3$) for **3c**



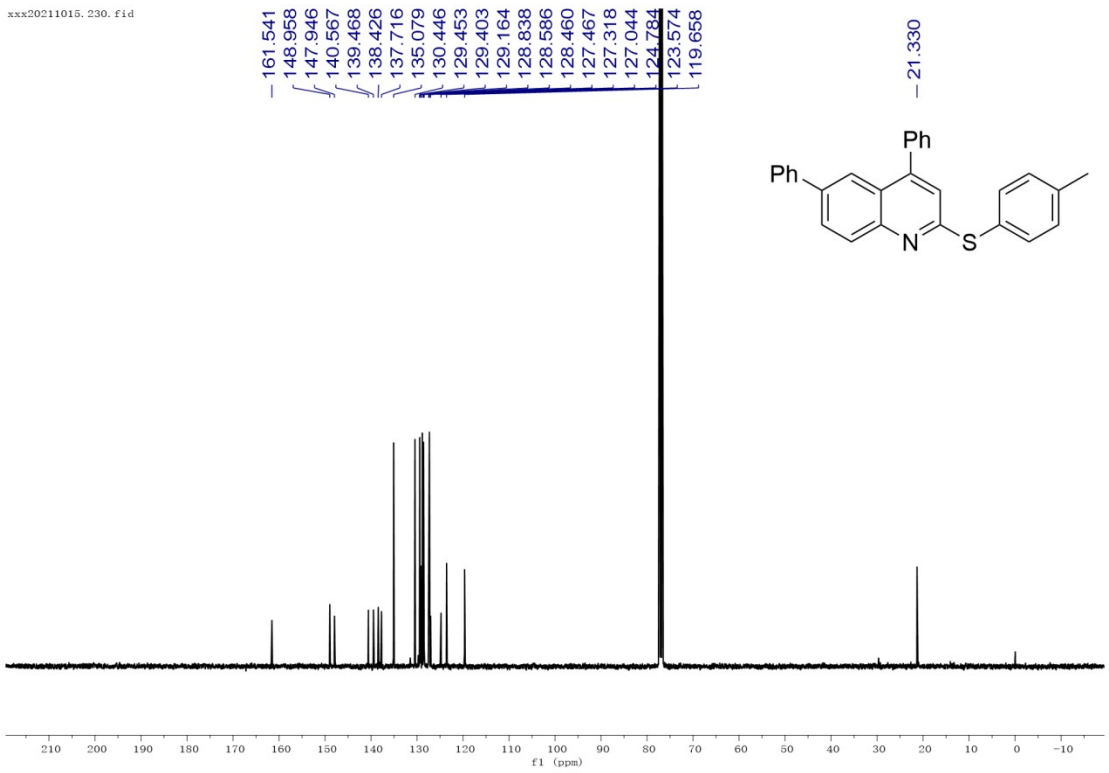
^{13}C NMR (100 MHz, $CDCl_3$) for **3c**



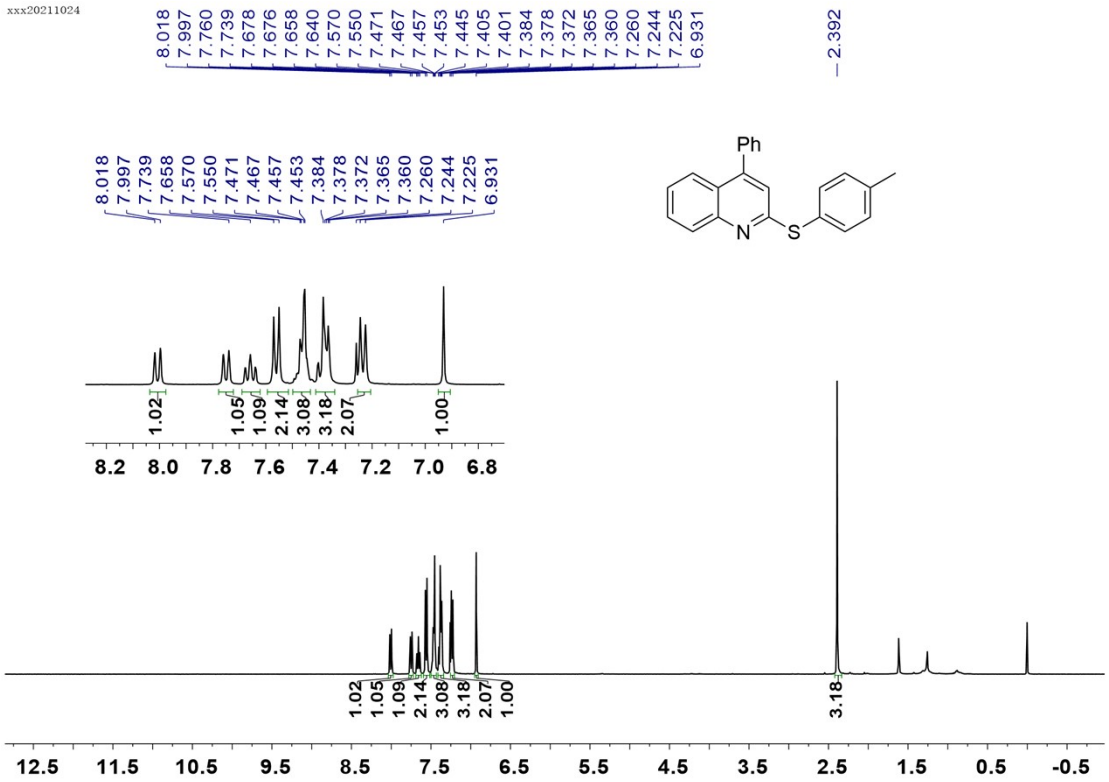
^{1}H NMR (400 MHz, $CDCl_3$) for **3d**



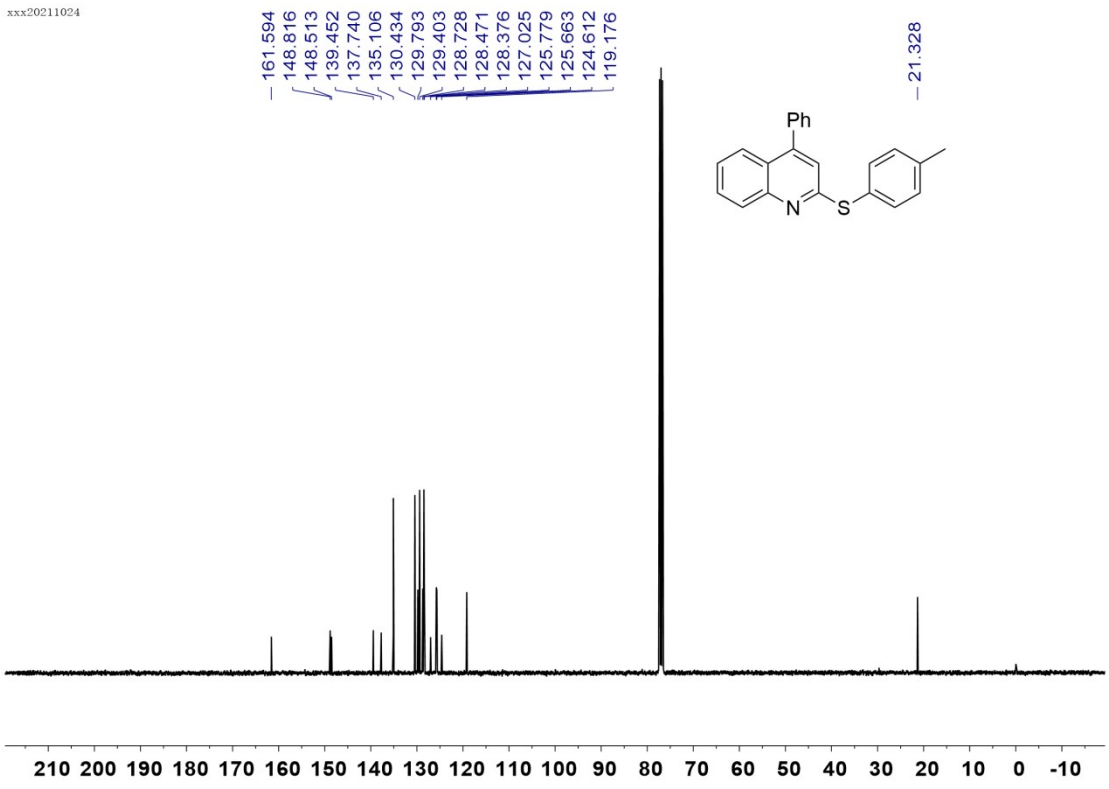
^{13}C NMR (100 MHz, $CDCl_3$) for **3d**



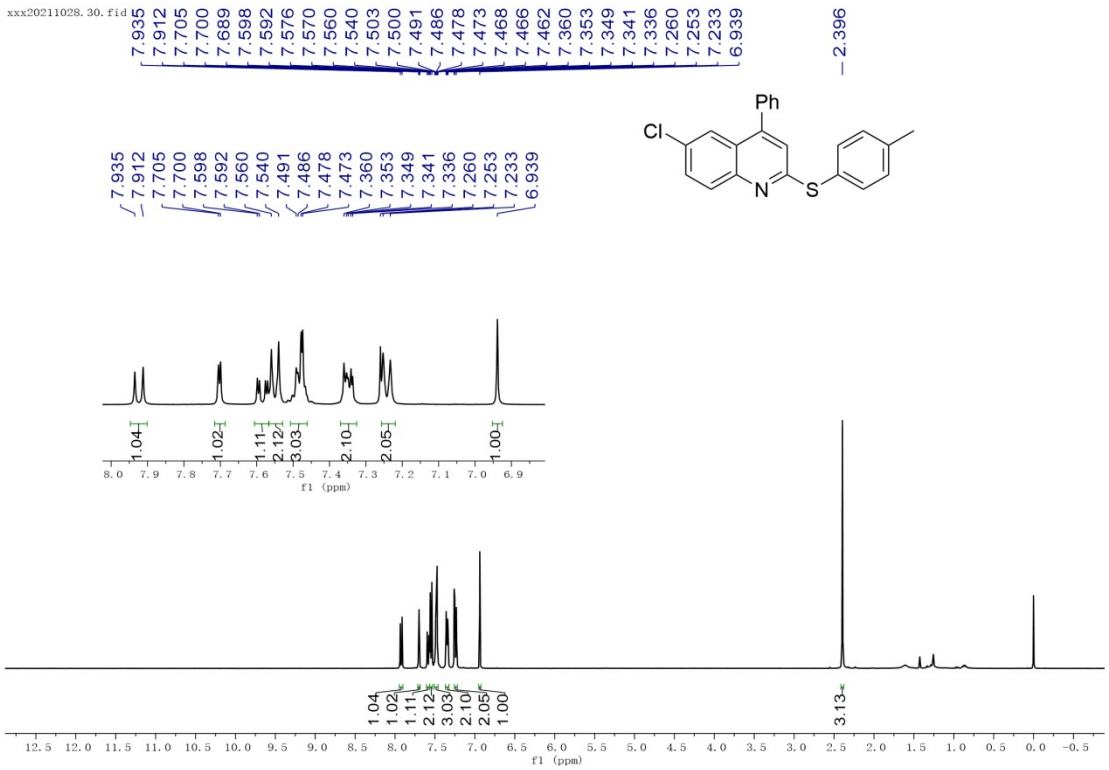
^{1}H NMR (400 MHz, $CDCl_3$) for **3e**



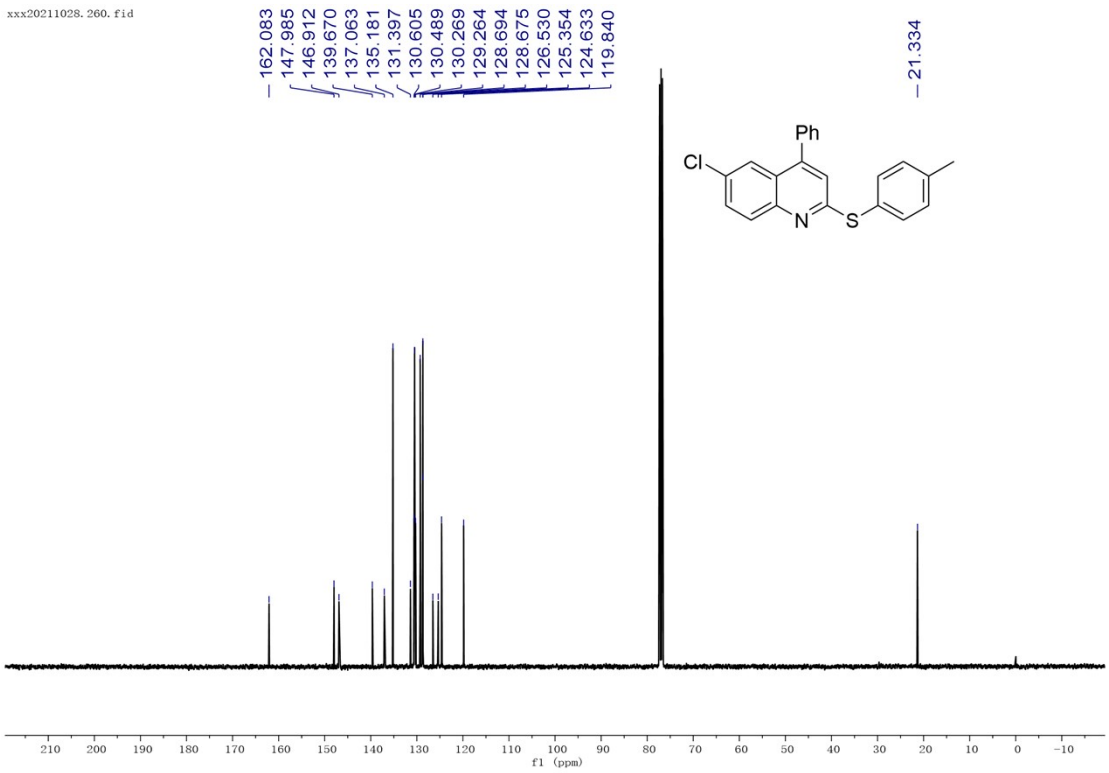
^{13}C NMR (100 MHz, $CDCl_3$) for **3e**



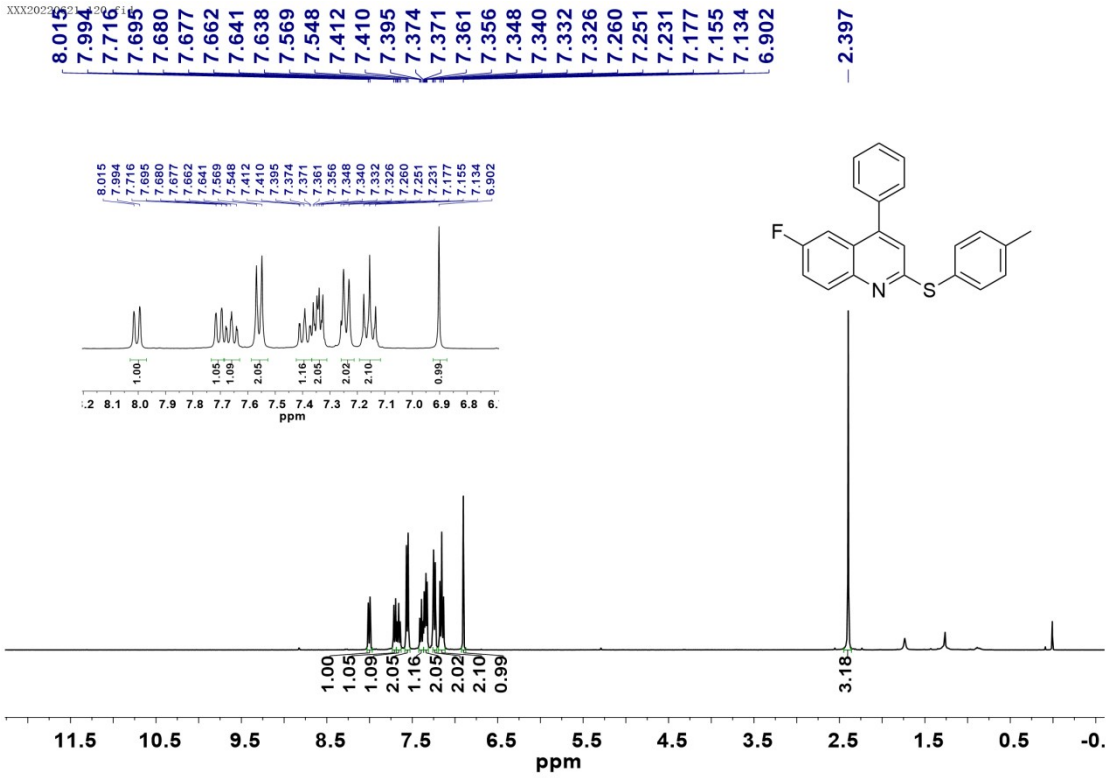
^{1}H NMR (400 MHz, $CDCl_3$) for **3f**



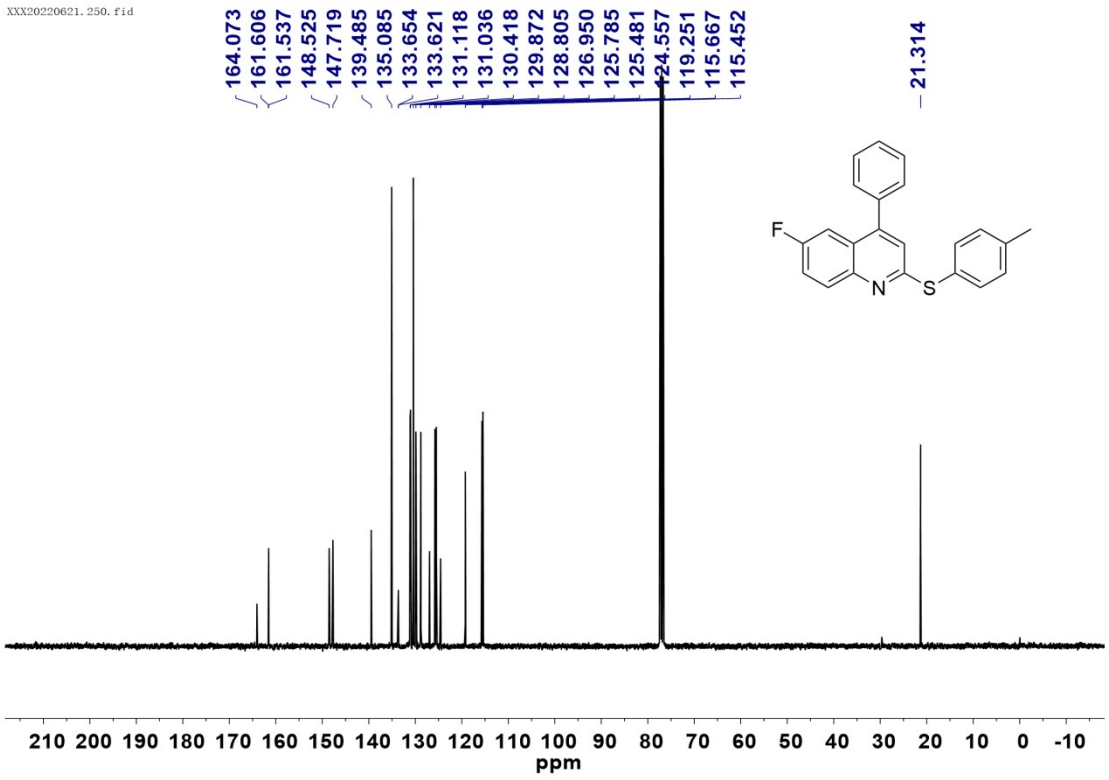
^{13}C NMR (100 MHz, $CDCl_3$) for **3f**



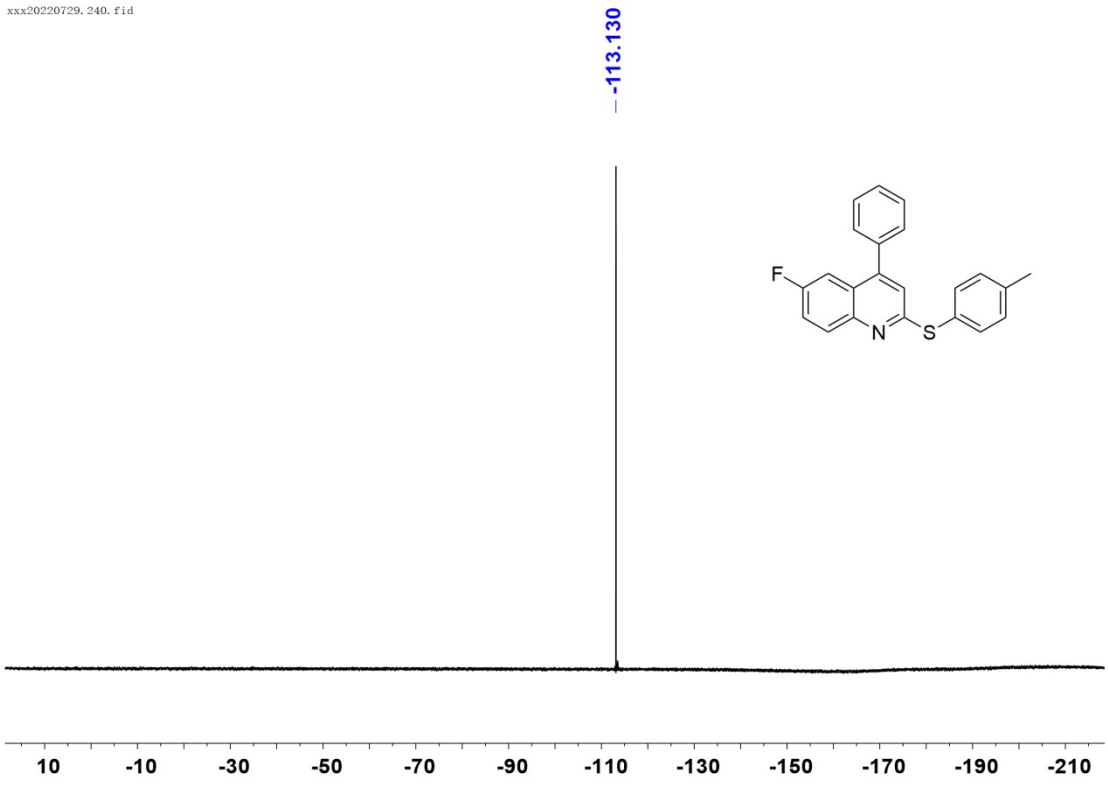
^{1}H NMR (400 MHz, $CDCl_3$) for **3g**



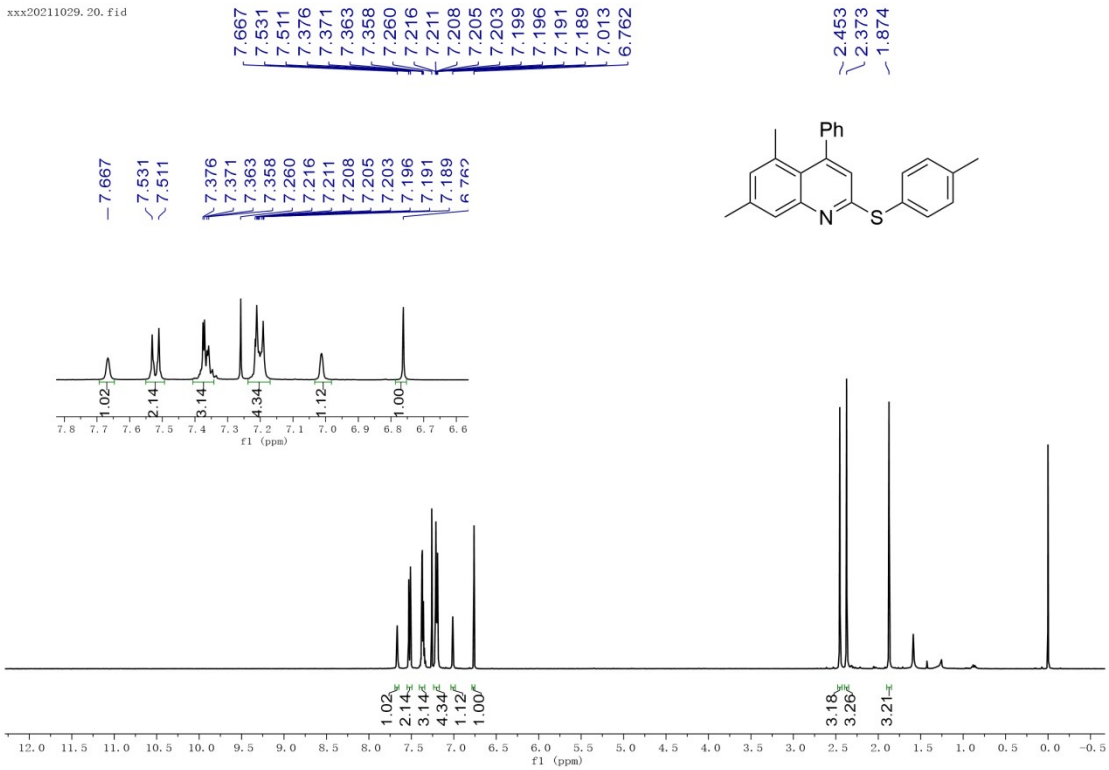
^{13}C NMR (100 MHz, $CDCl_3$) for **3g**



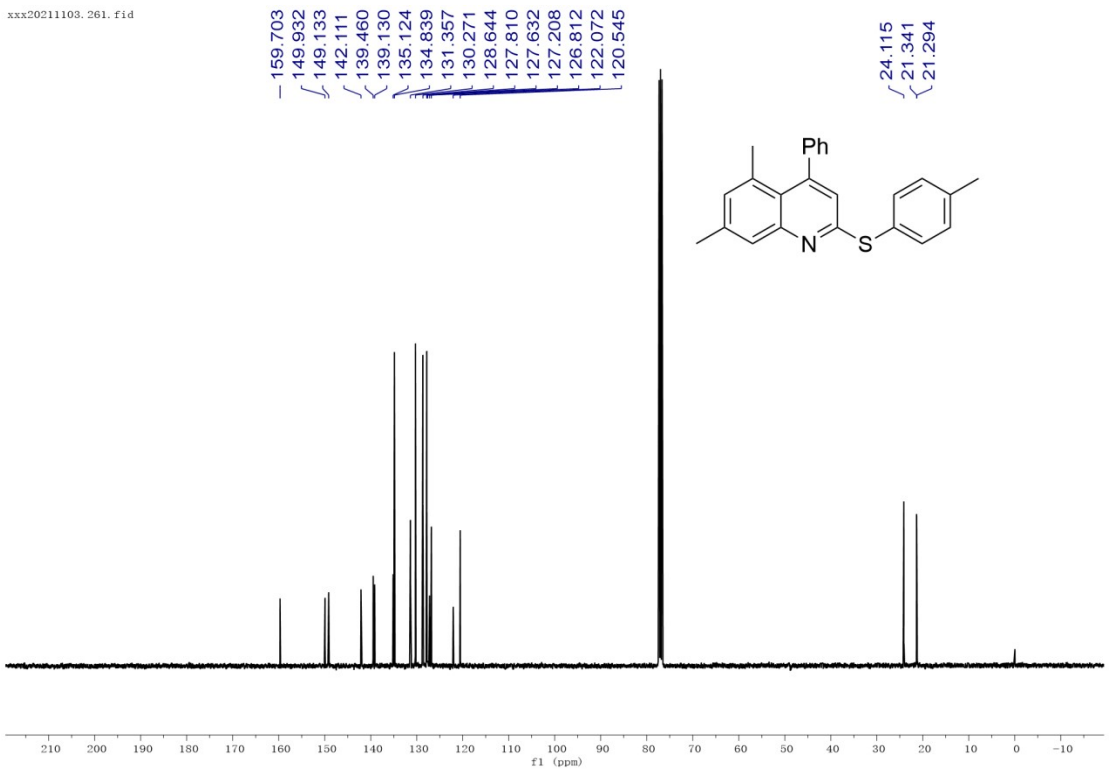
^{19}F NMR (376 MHz, $CDCl_3$) for **3g**



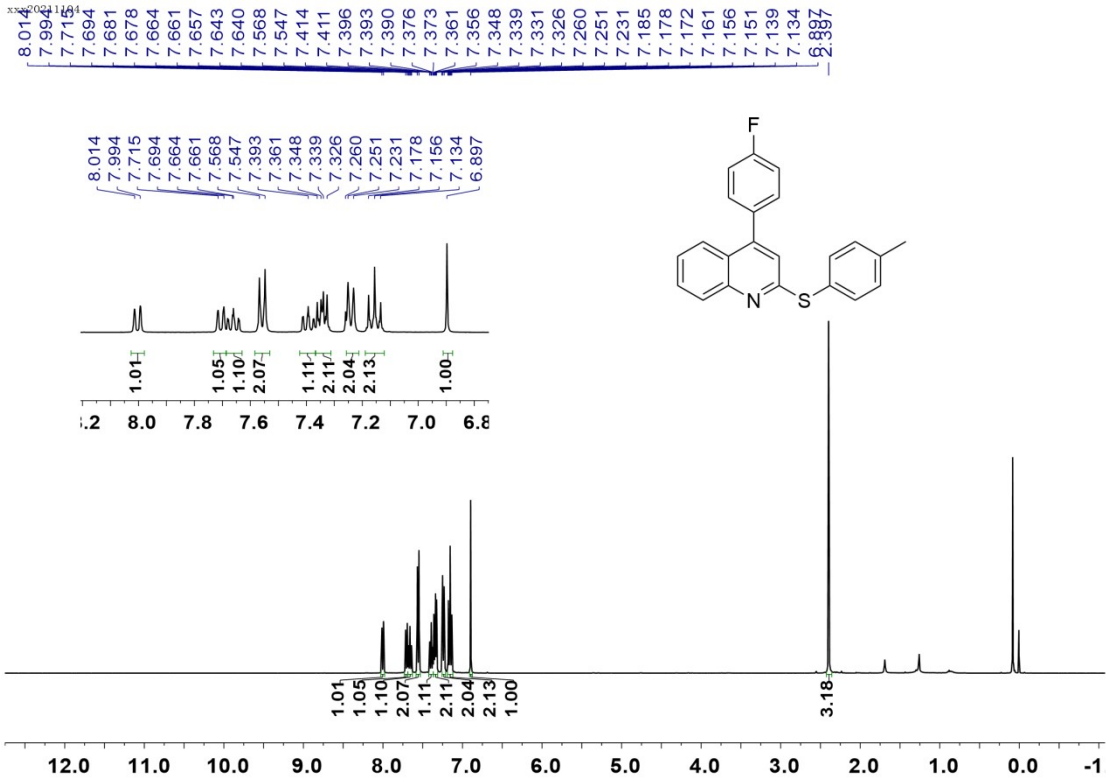
^{1}H NMR (400 MHz, $CDCl_3$) for **3h**



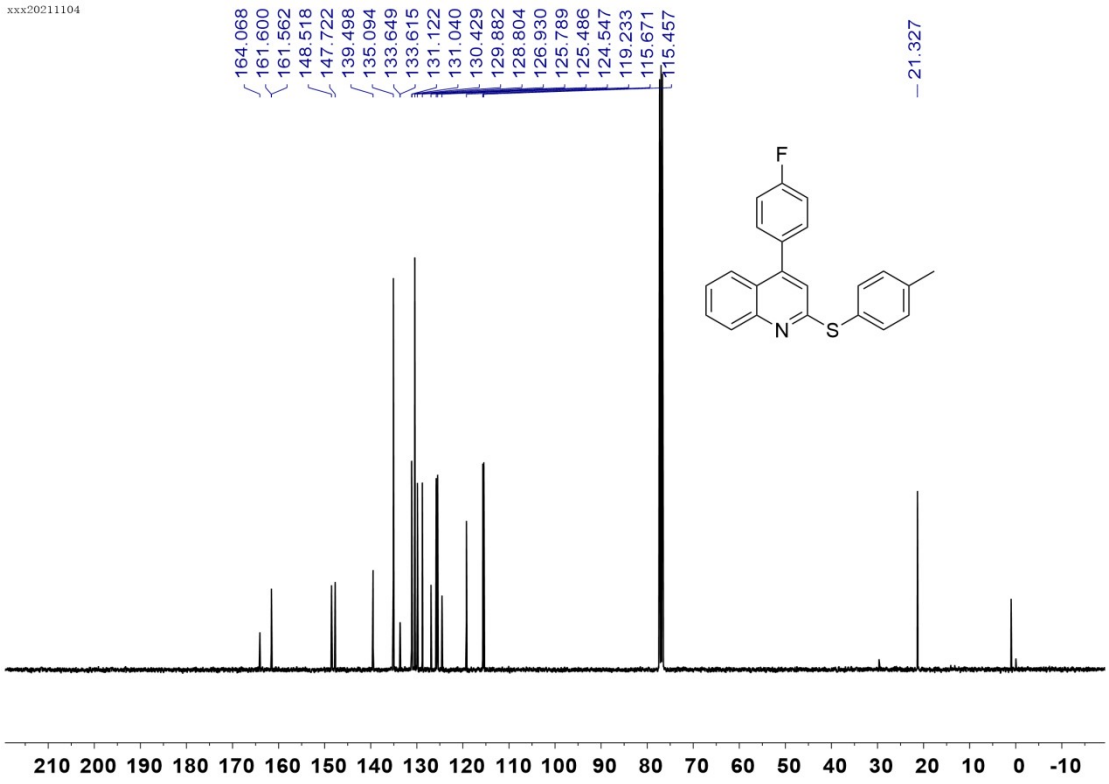
^{13}C NMR (100 MHz, $CDCl_3$) for **3h**



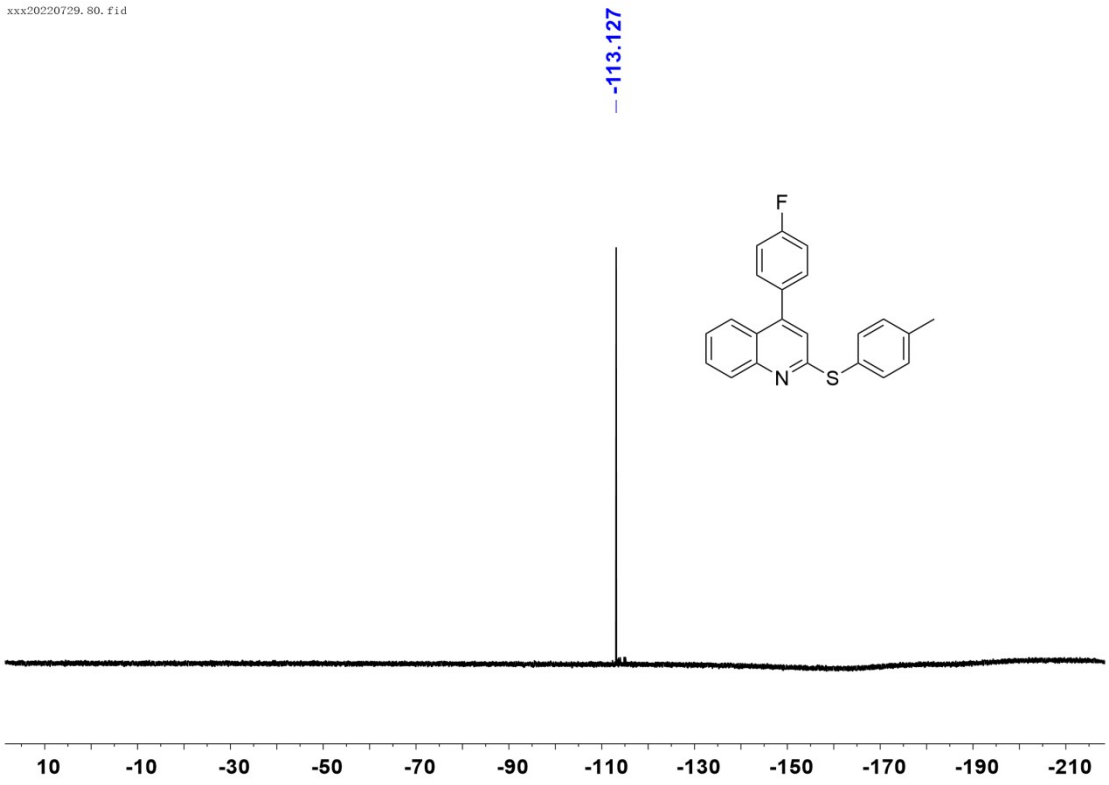
^{1}H NMR (400 MHz, $CDCl_3$) for **3i**



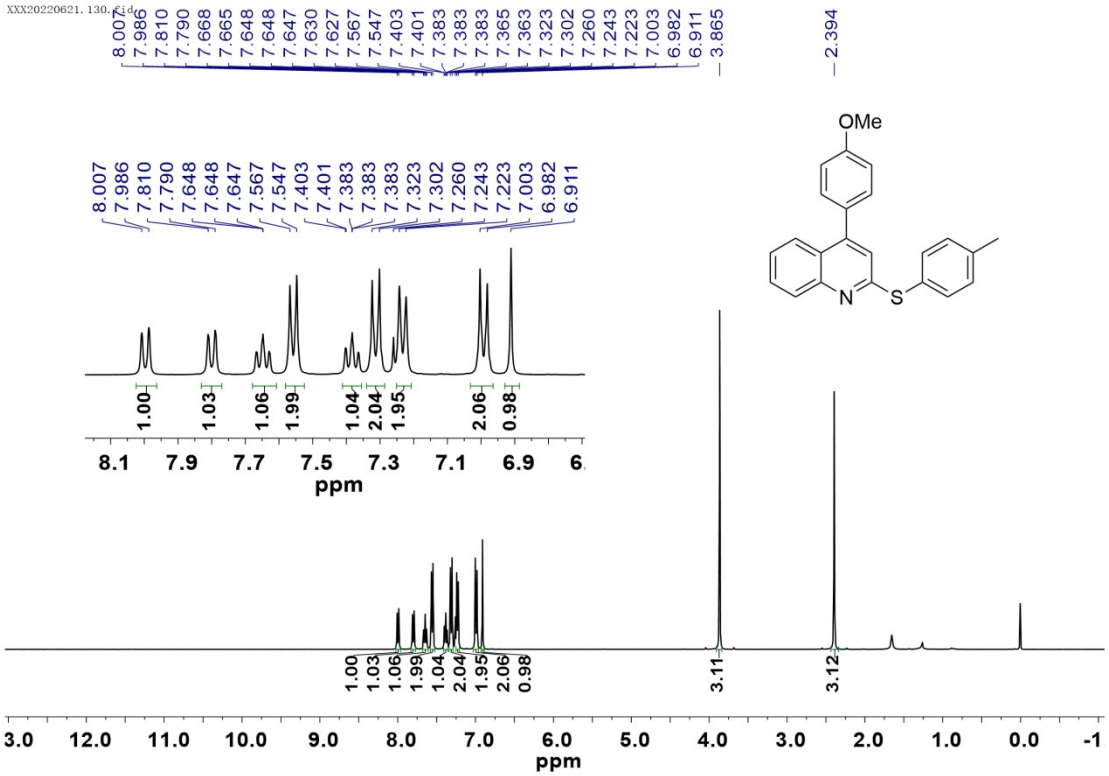
^{13}C NMR (100 MHz, $CDCl_3$) for **3i**



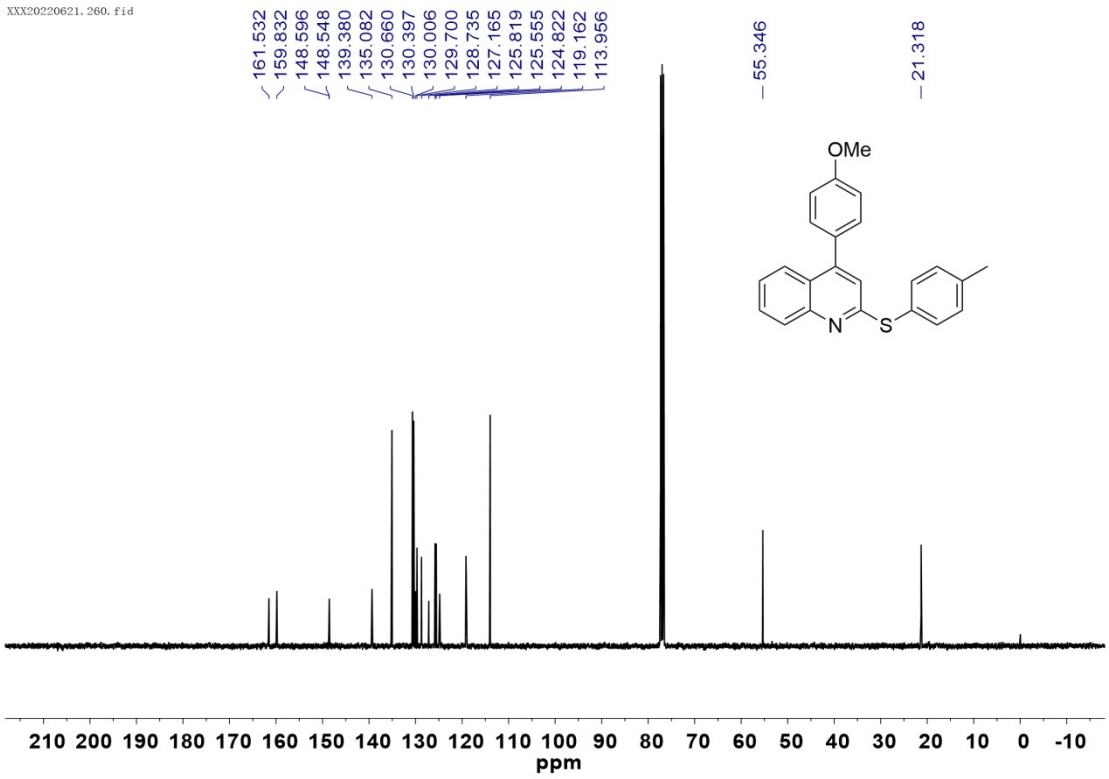
^{19}F NMR (376 MHz, $CDCl_3$) for **3i**



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



^{13}C NMR (100 MHz, $CDCl_3$) for **3j**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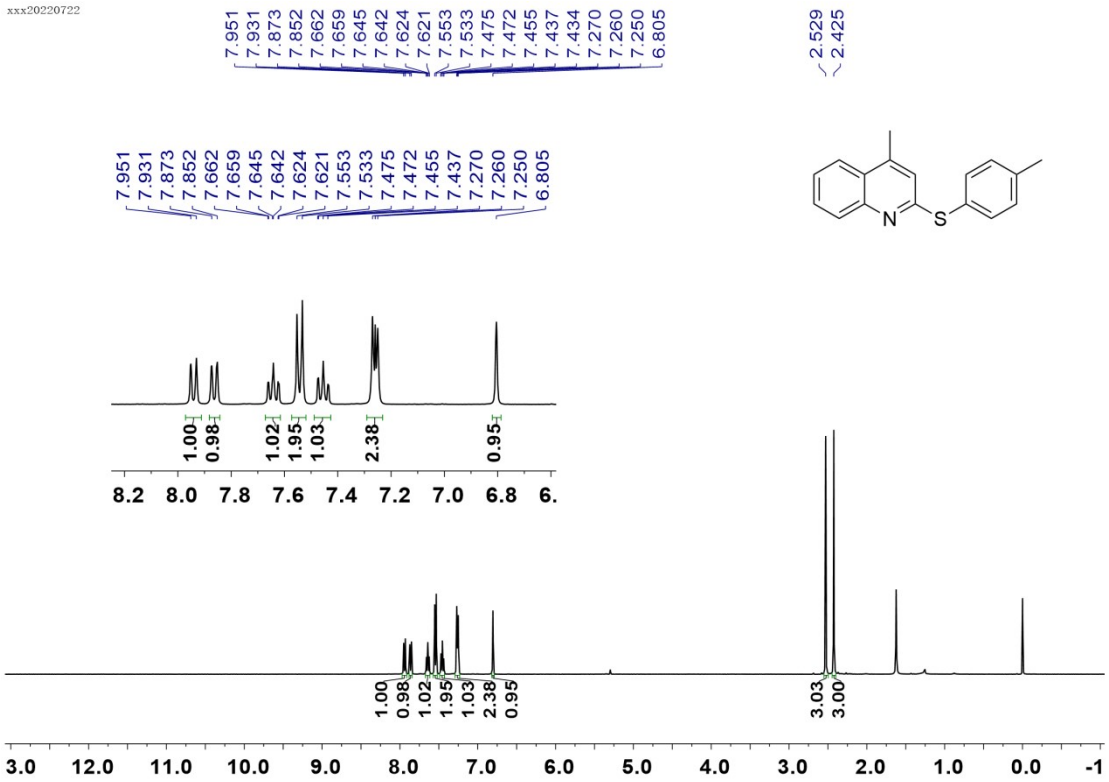
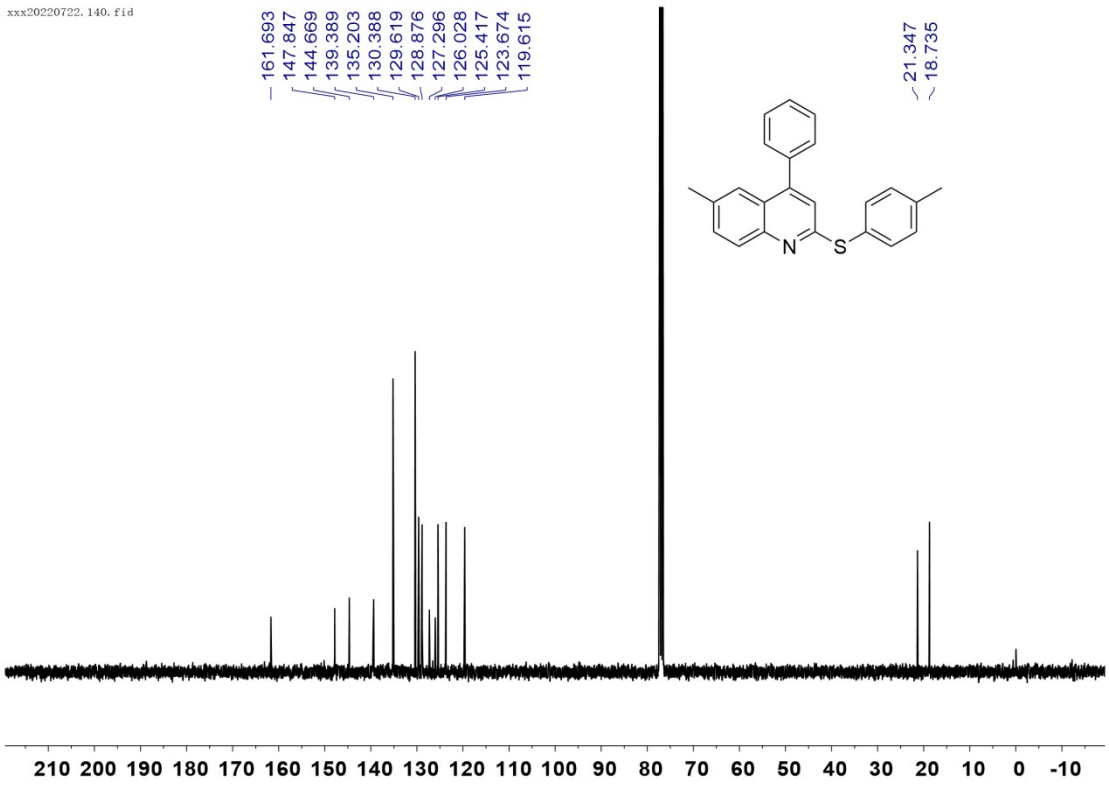
55.346
21.318
OMe
N
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

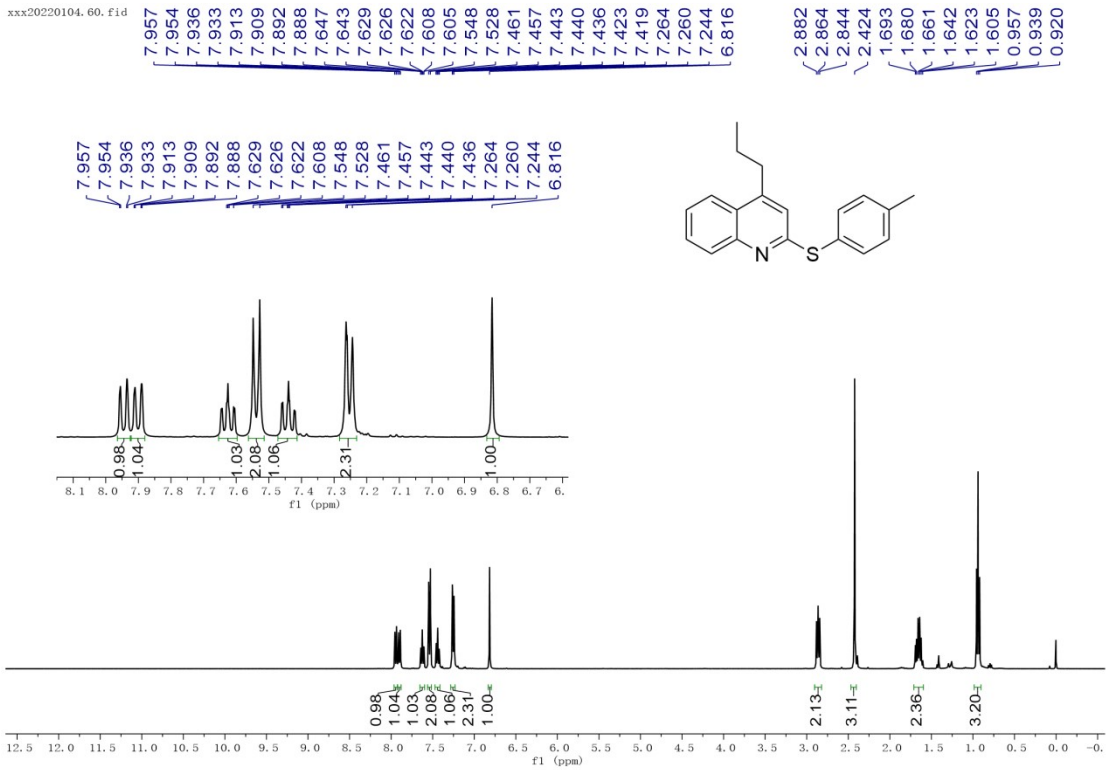
^{1}H NMR (400 MHz, $CDCl_3$) for **3k**



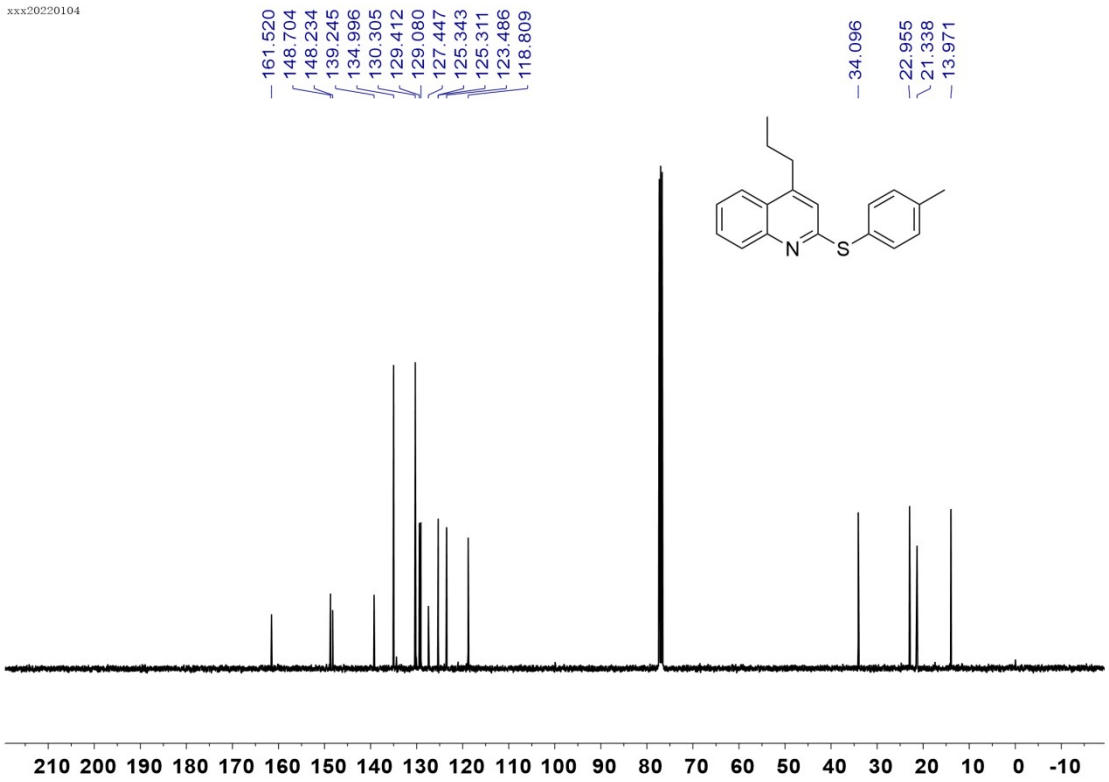
^{13}C NMR (100 MHz, $CDCl_3$) for **3k**



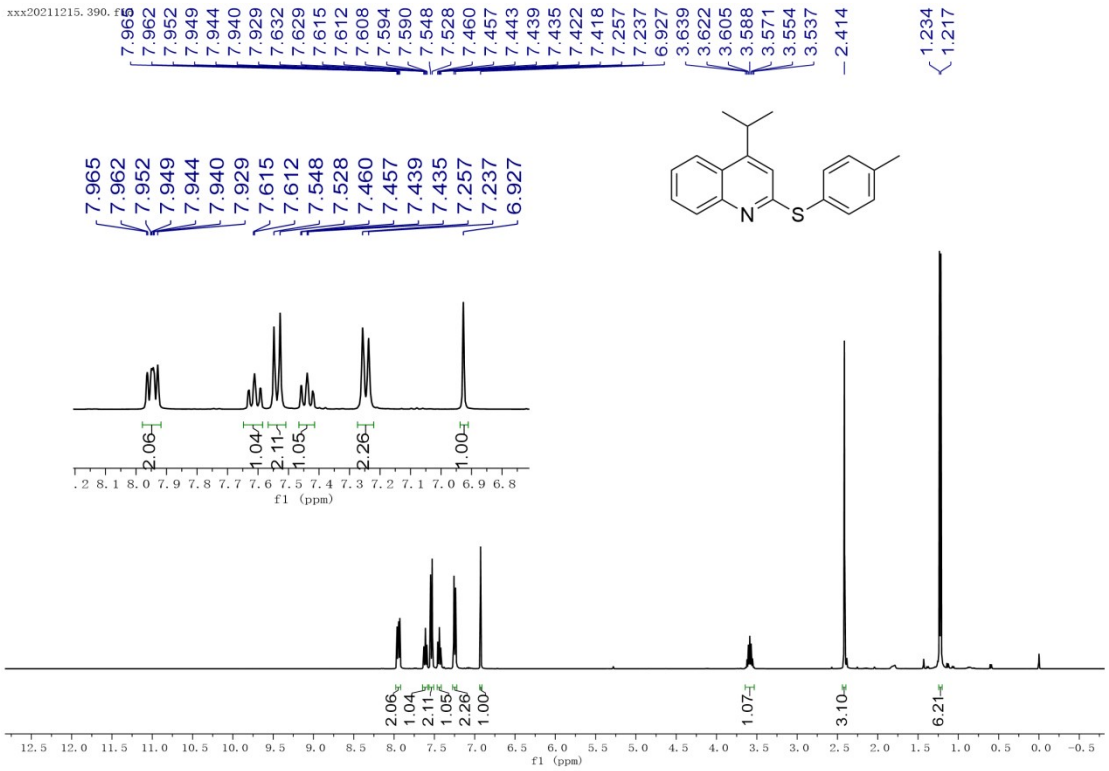
^{1}H NMR (400 MHz, $CDCl_3$) for **3l**



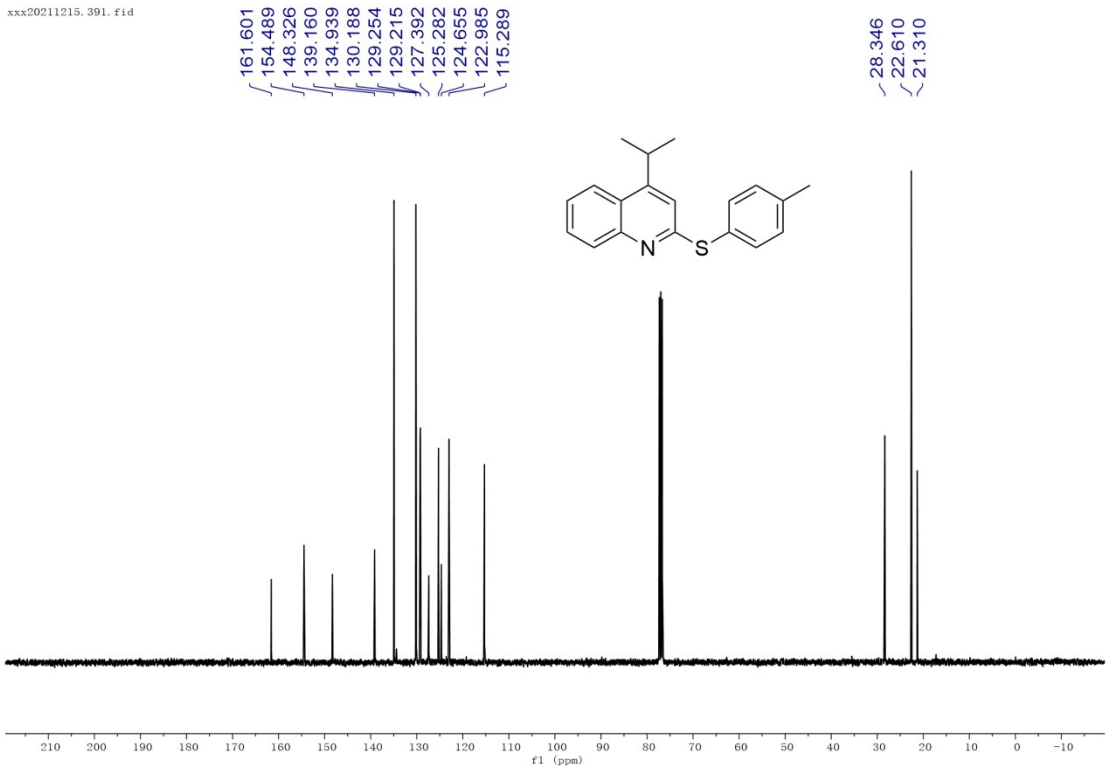
^{13}C NMR (100 MHz, $CDCl_3$) for **3l**



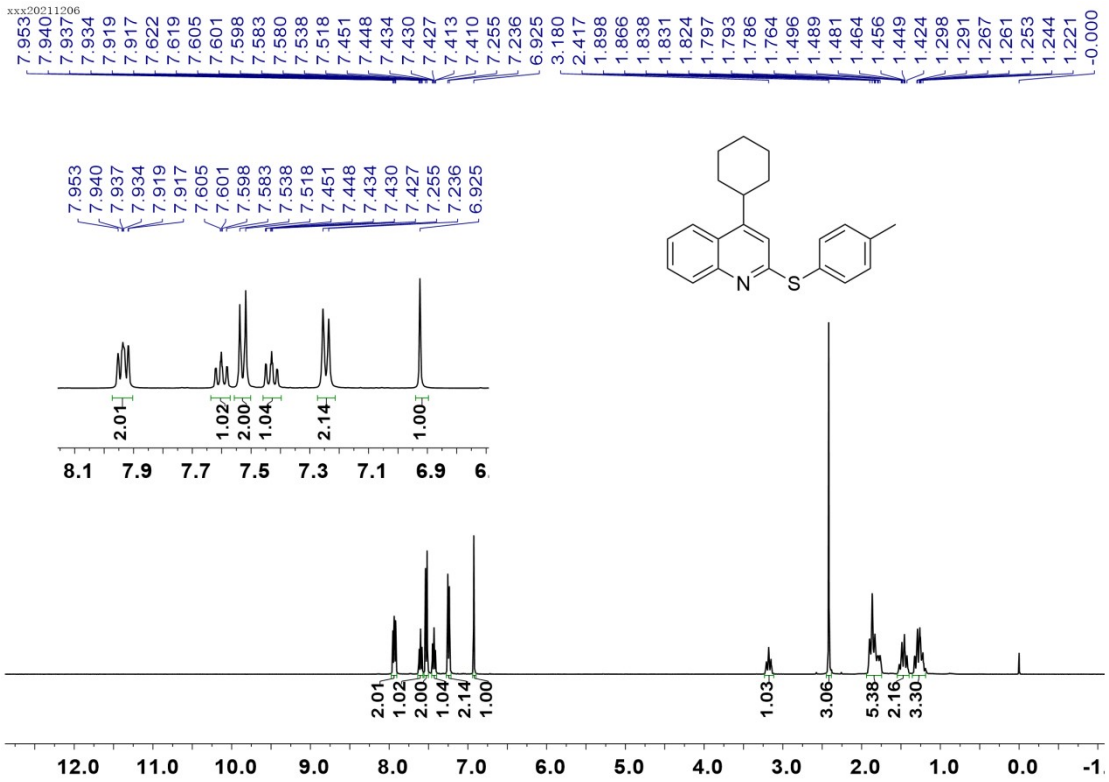
^{1}H NMR (400 MHz, $CDCl_3$) for **3m**



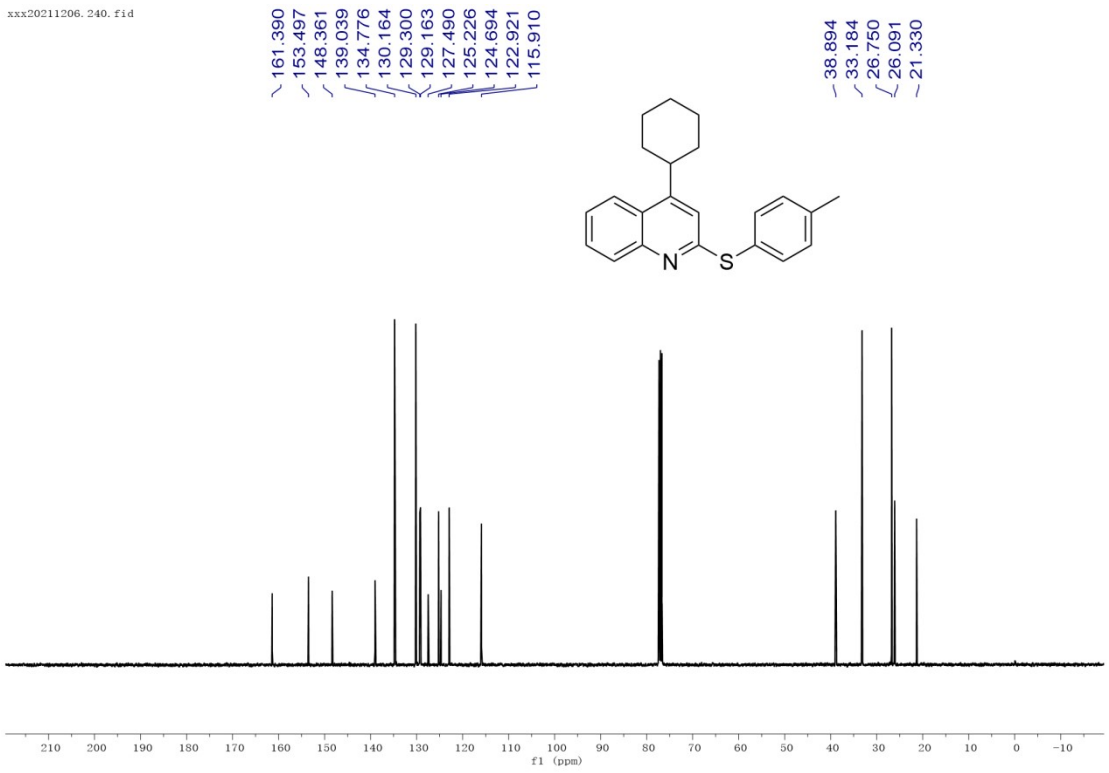
^{13}C NMR (100 MHz, $CDCl_3$) for **3m**



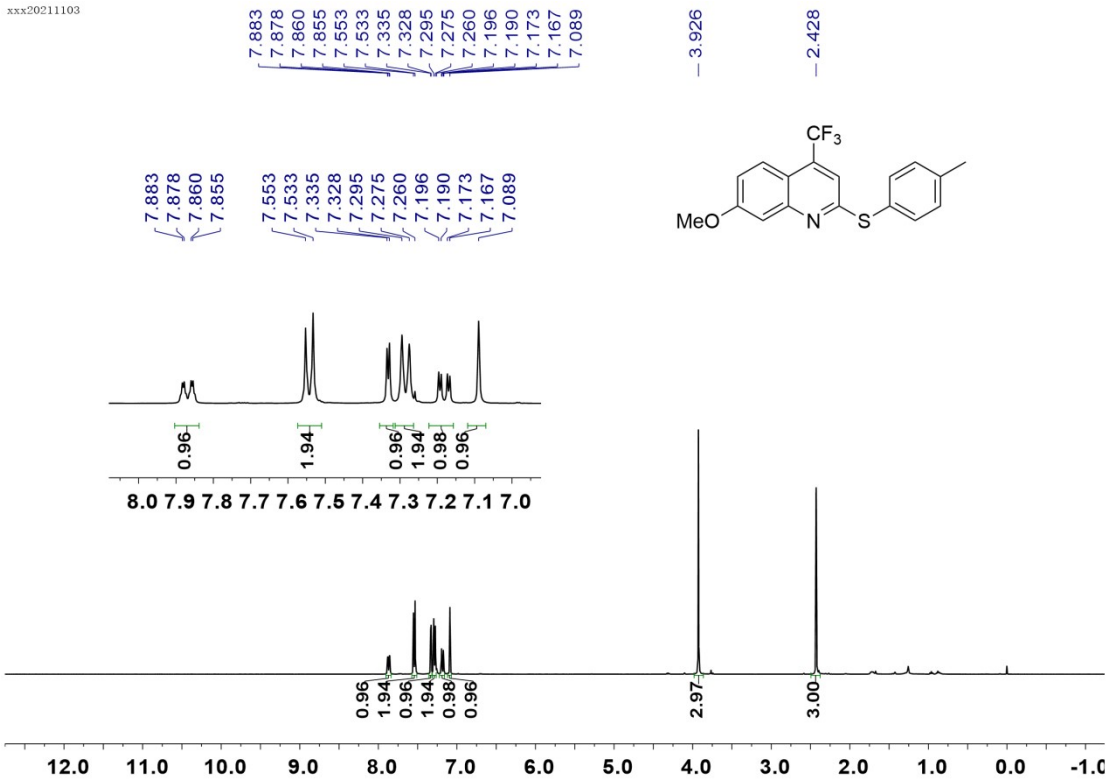
^{1}H NMR (400 MHz, $CDCl_3$) for **3n**



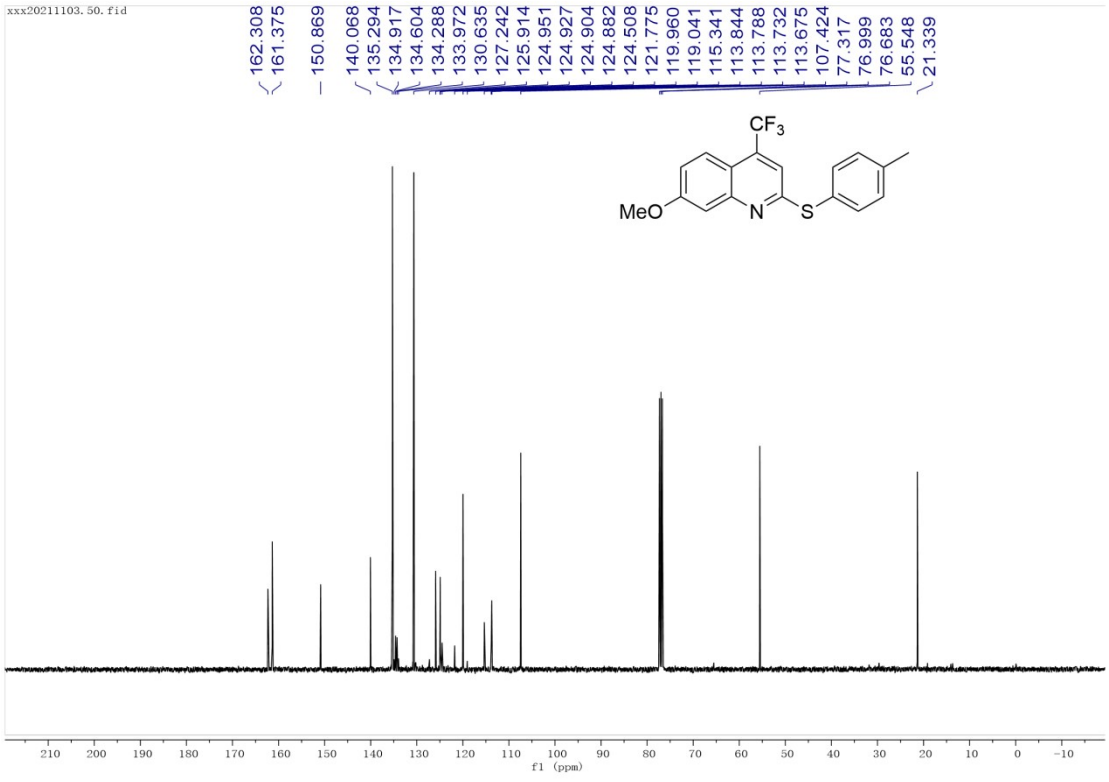
^{13}C NMR (100 MHz, $CDCl_3$) for **3n**



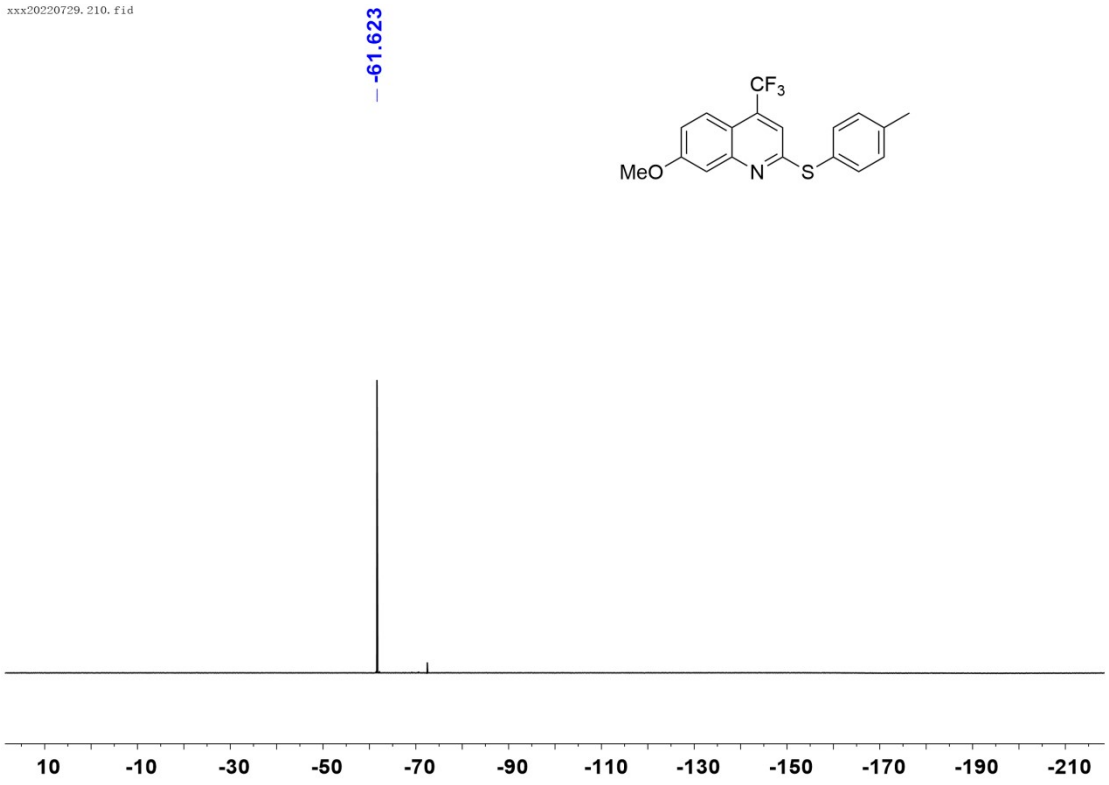
^{1}H NMR (400 MHz, $CDCl_3$) for **3o**



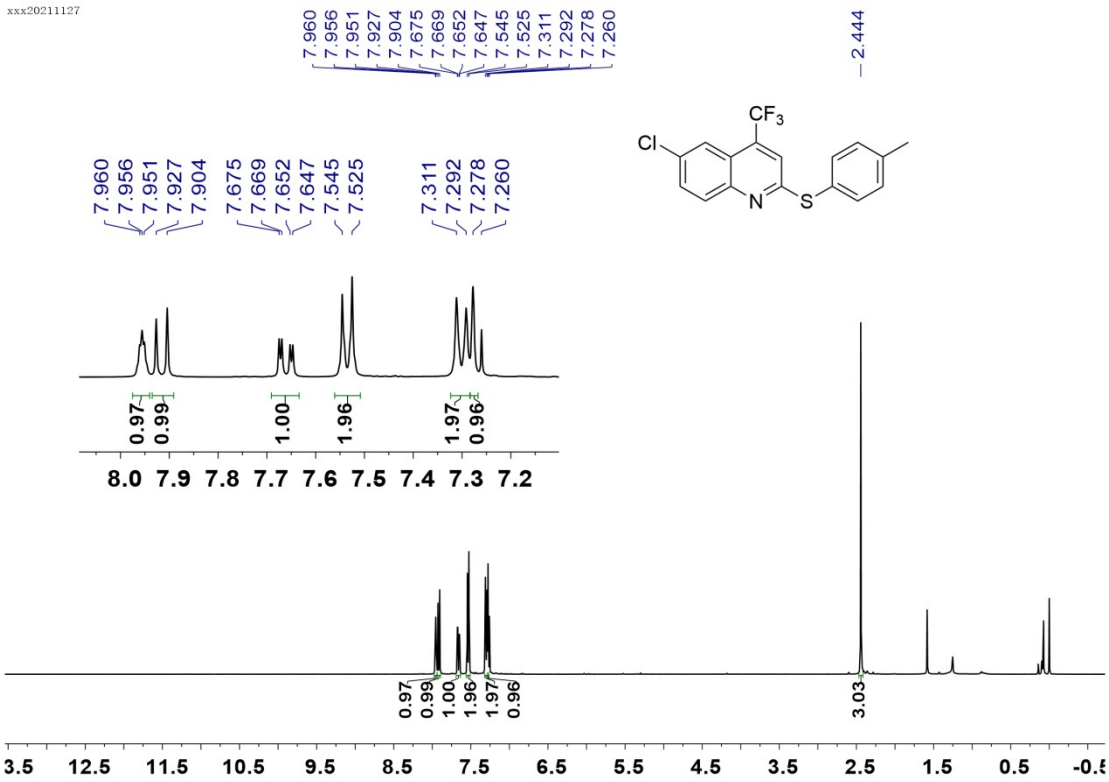
^{13}C NMR (100 MHz, $CDCl_3$) for **3o**



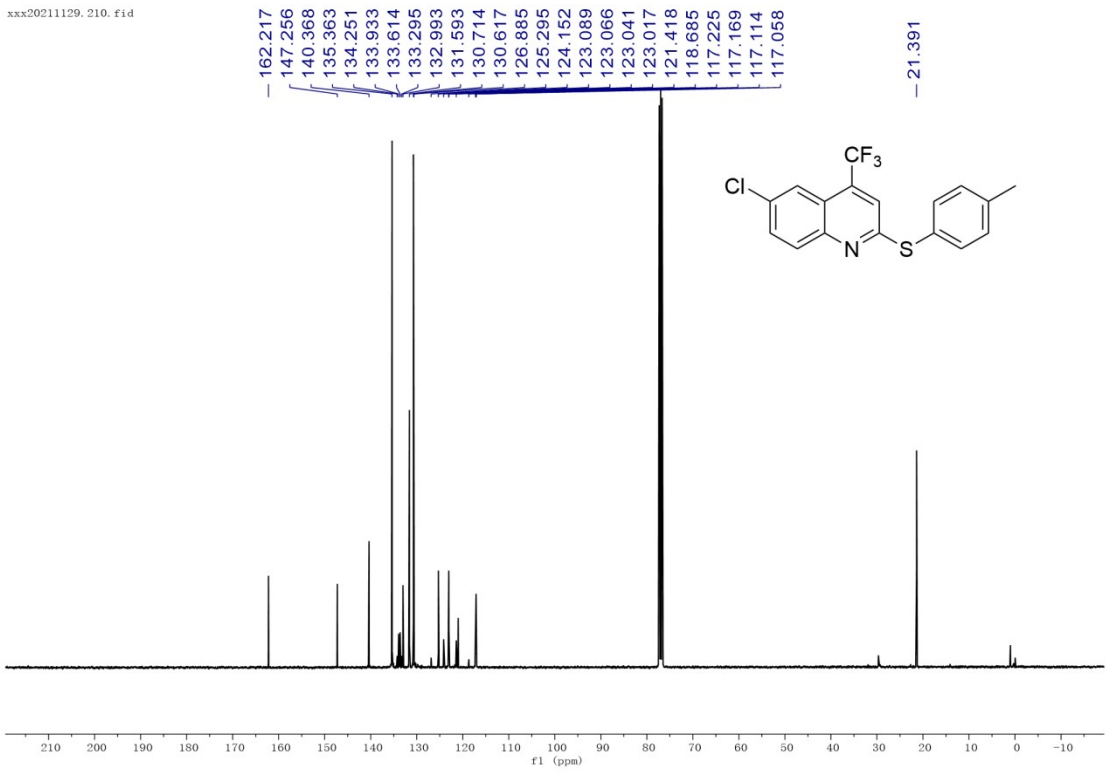
^{19}F NMR (376 MHz, $CDCl_3$) for **3o**



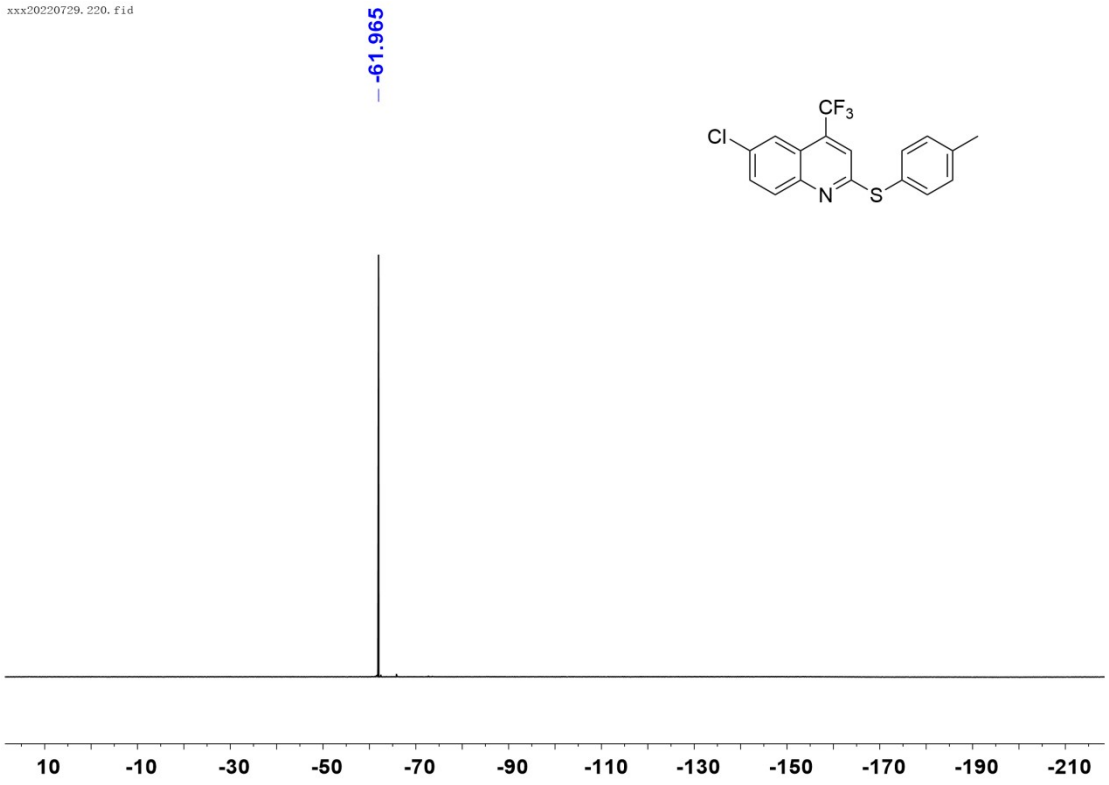
^{1}H NMR (400 MHz, $CDCl_3$) for **3p**



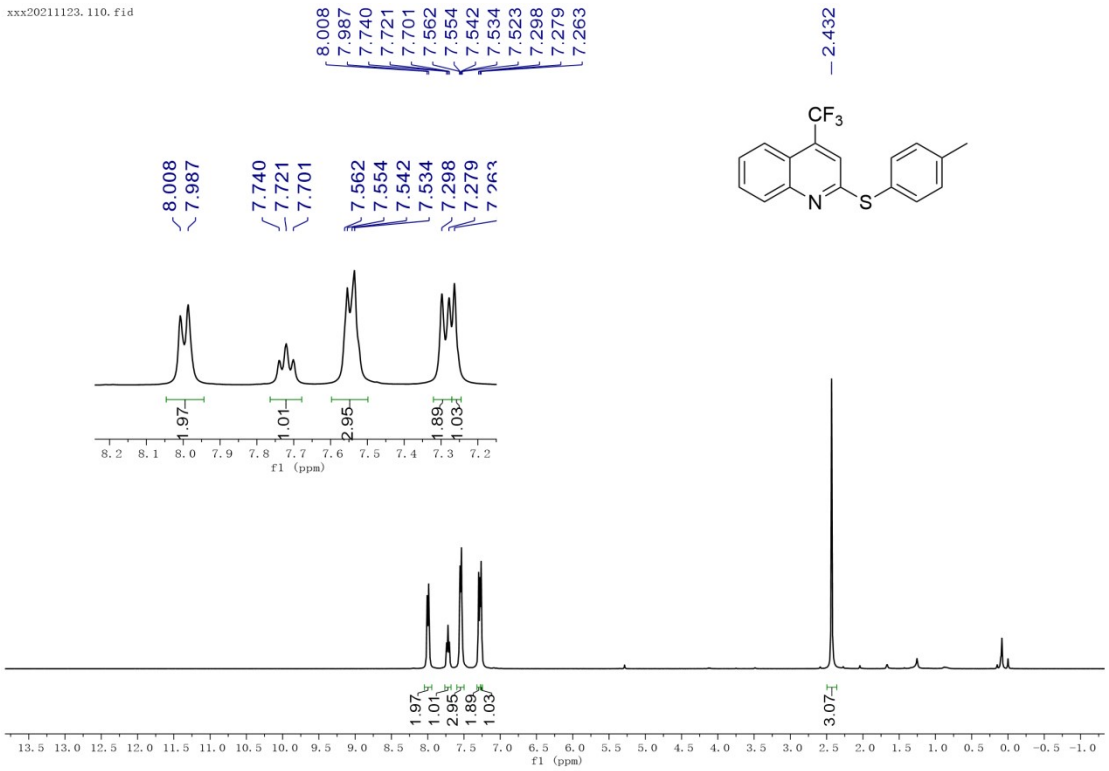
^{13}C NMR (100 MHz, $CDCl_3$) for **3p**



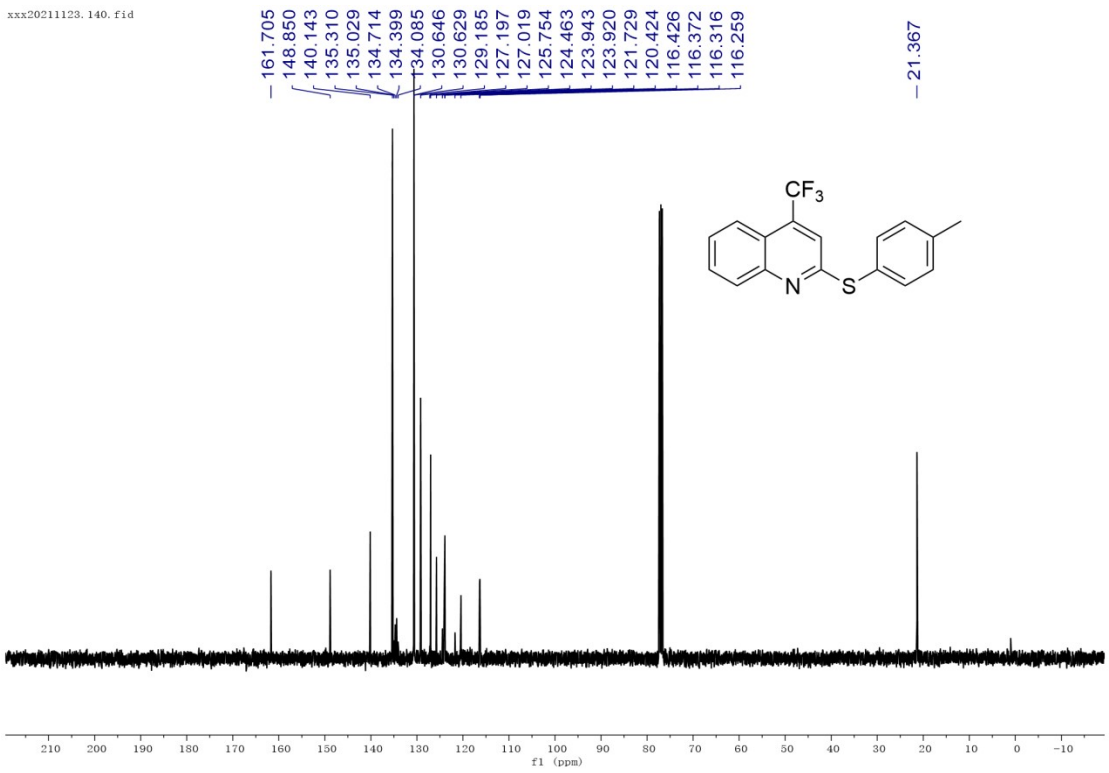
^{19}F NMR (376 MHz, $CDCl_3$) for **3p**



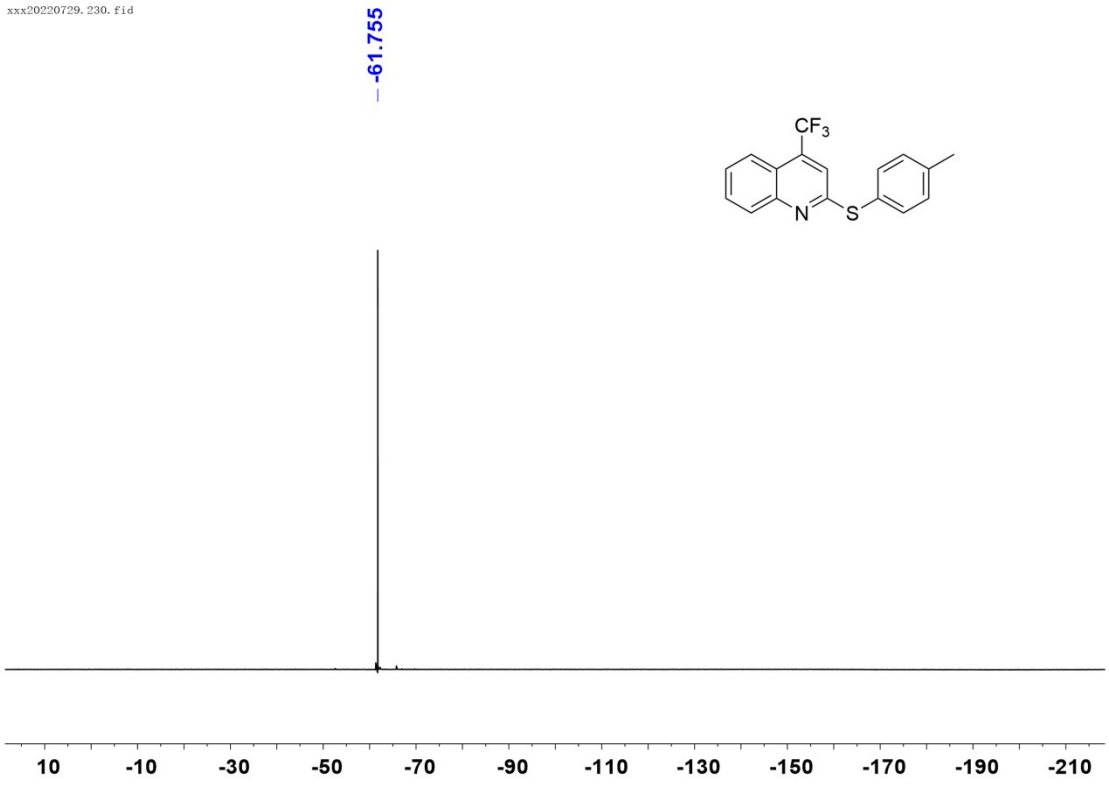
^{1}H NMR (400 MHz, $CDCl_3$) for **3q**



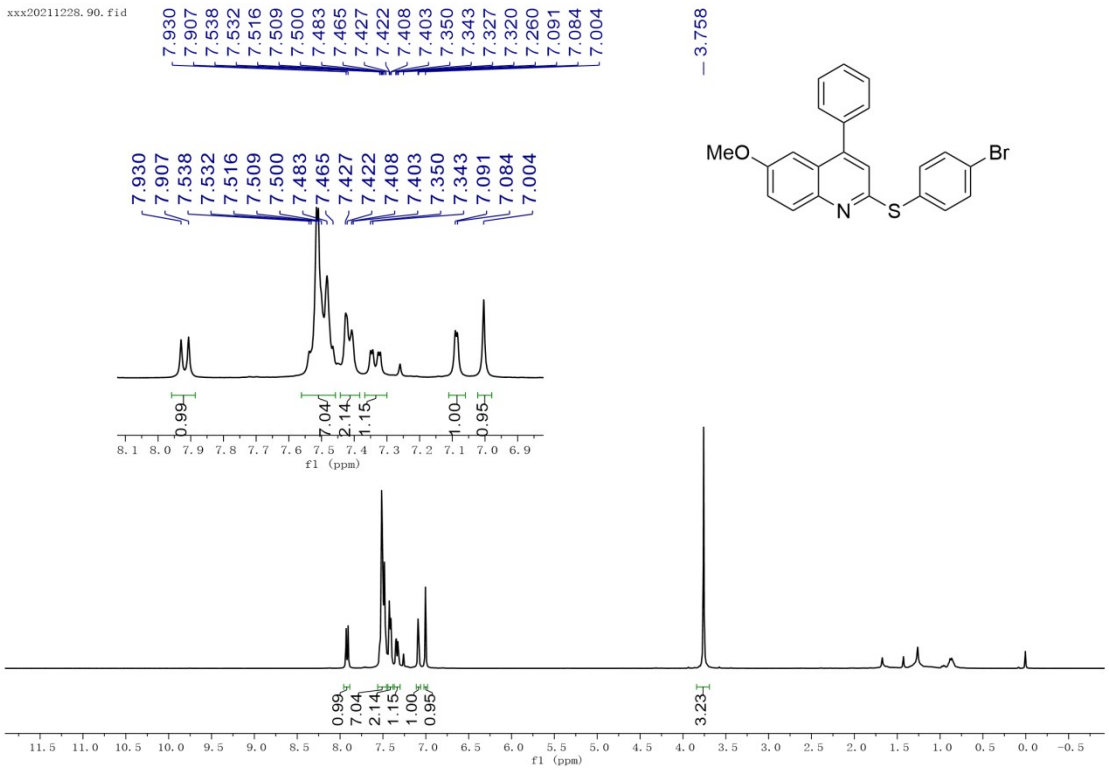
^{13}C NMR (100 MHz, $CDCl_3$) for **3q**



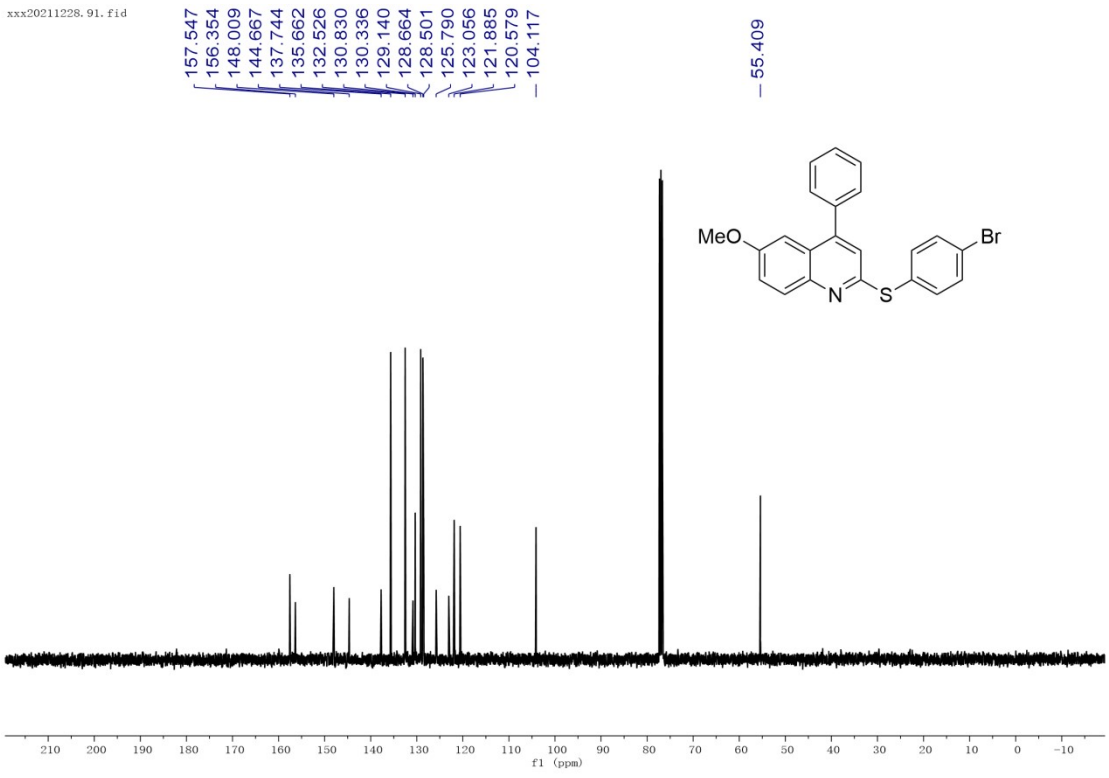
^{19}F NMR (376 MHz, $CDCl_3$) for **3q**



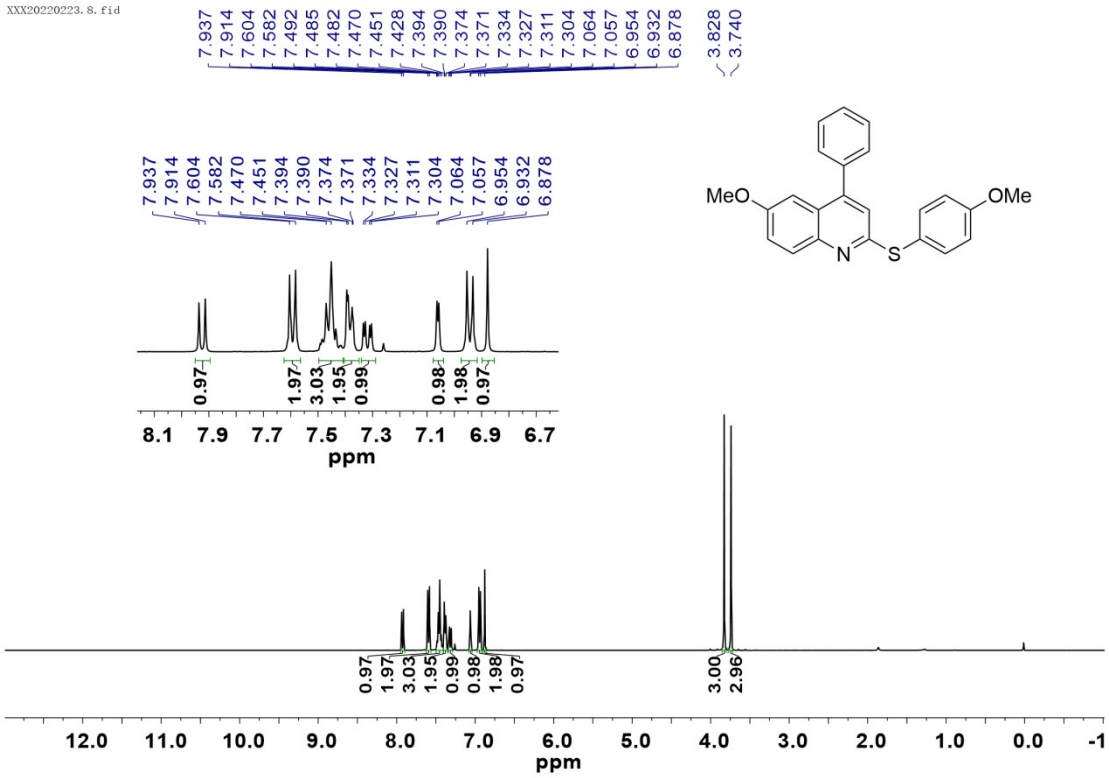
^{1}H NMR (400 MHz, $CDCl_3$) for **3r**



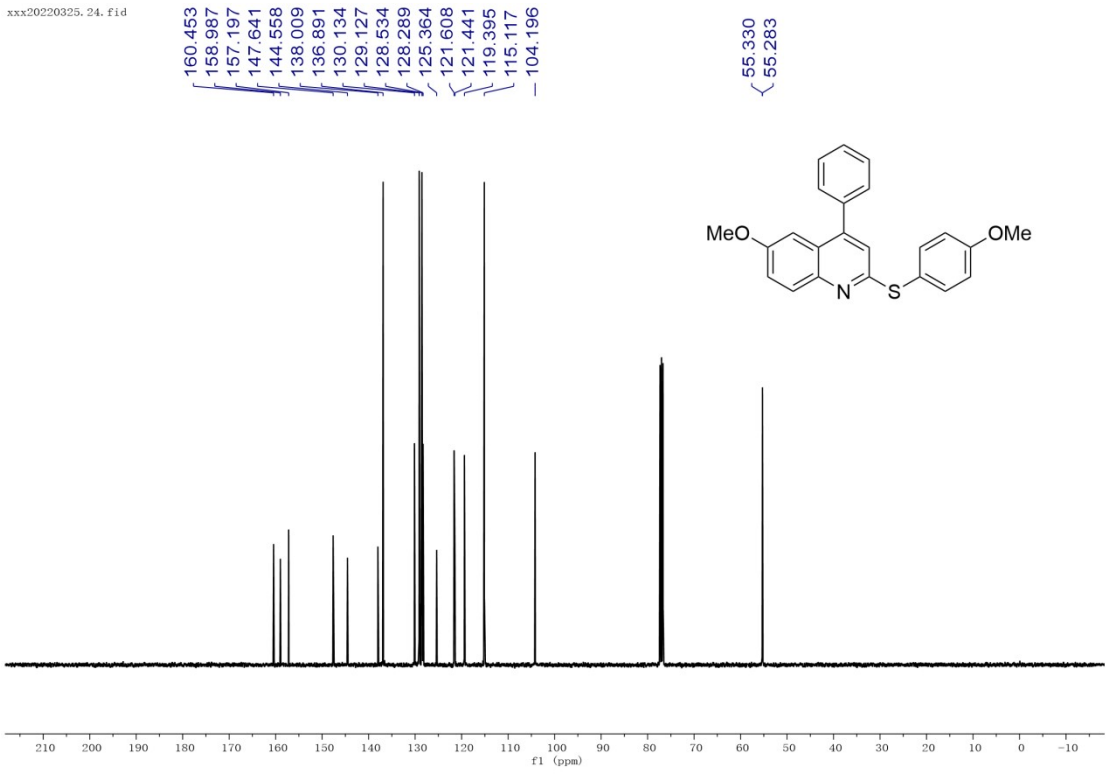
^{13}C NMR (100 MHz, $CDCl_3$) for **3r**



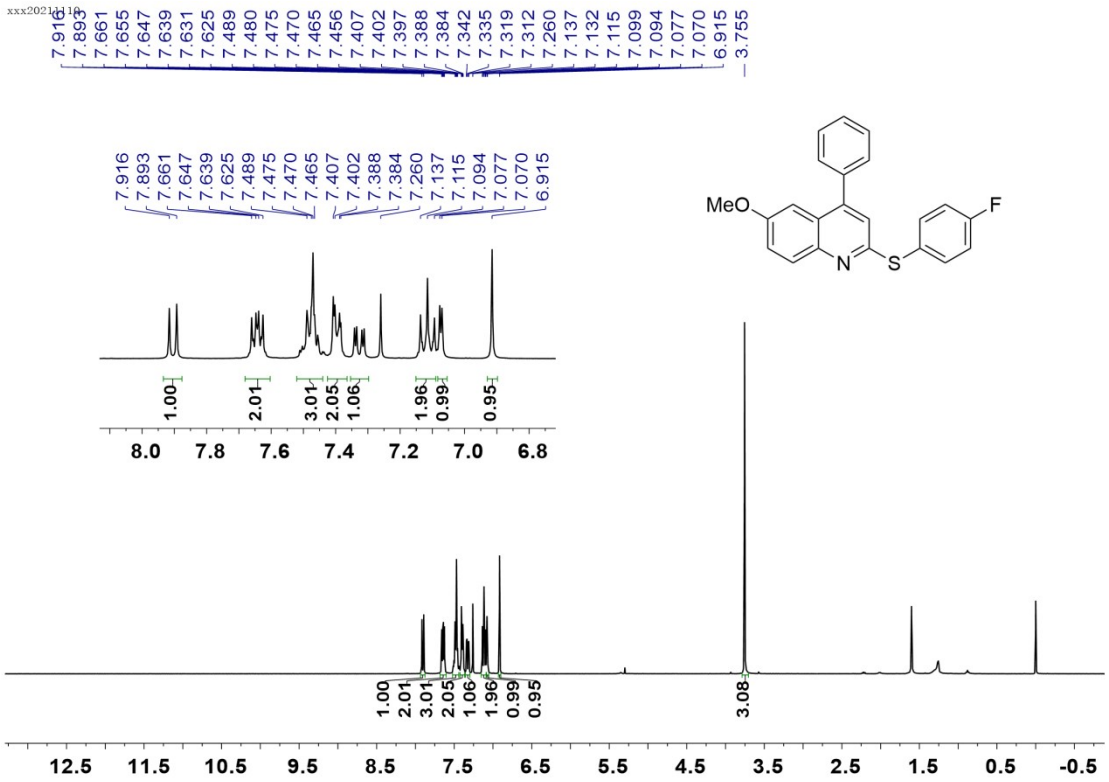
^{1}H NMR (400 MHz, $CDCl_3$) for **3s**



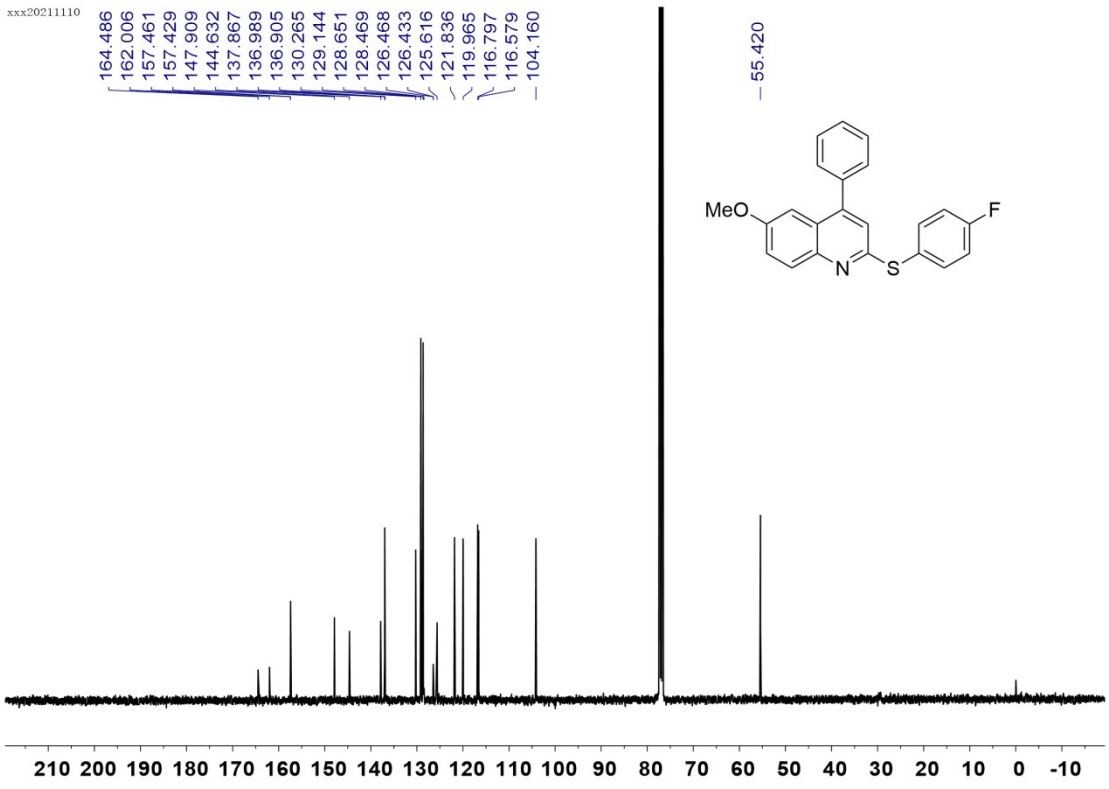
^{13}C NMR (100 MHz, $CDCl_3$) for **3s**



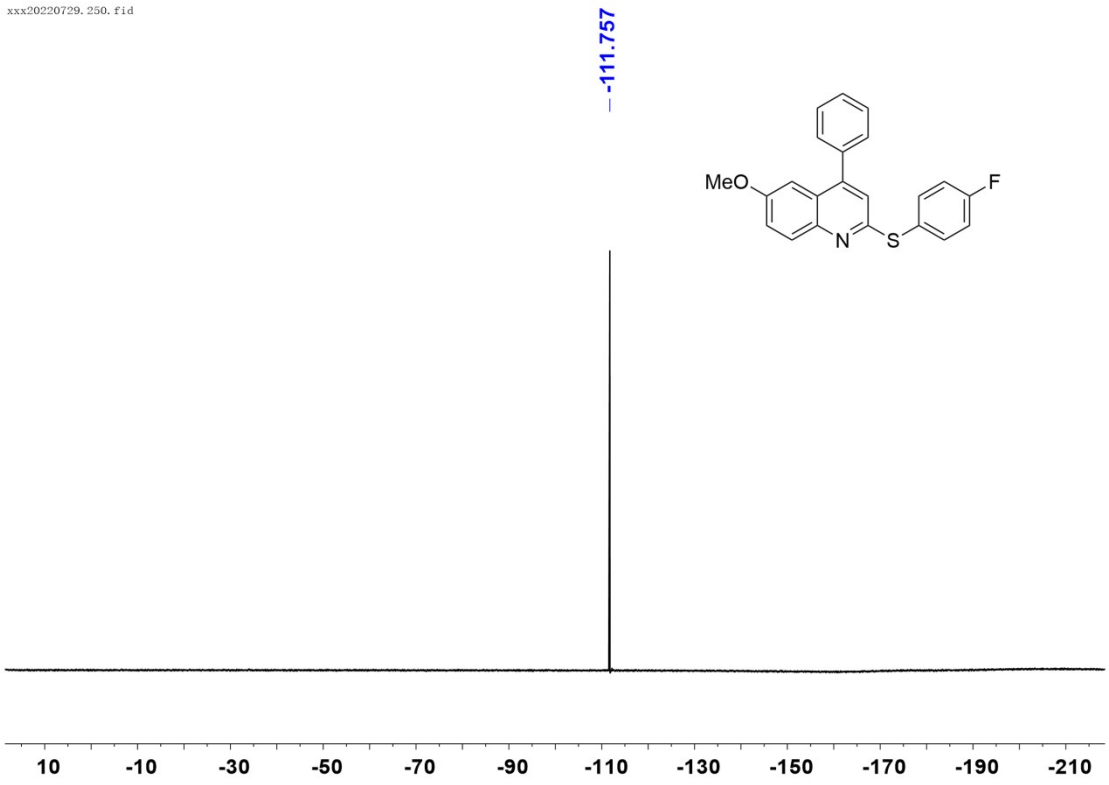
^{1}H NMR (400 MHz, $CDCl_3$) for **3t**



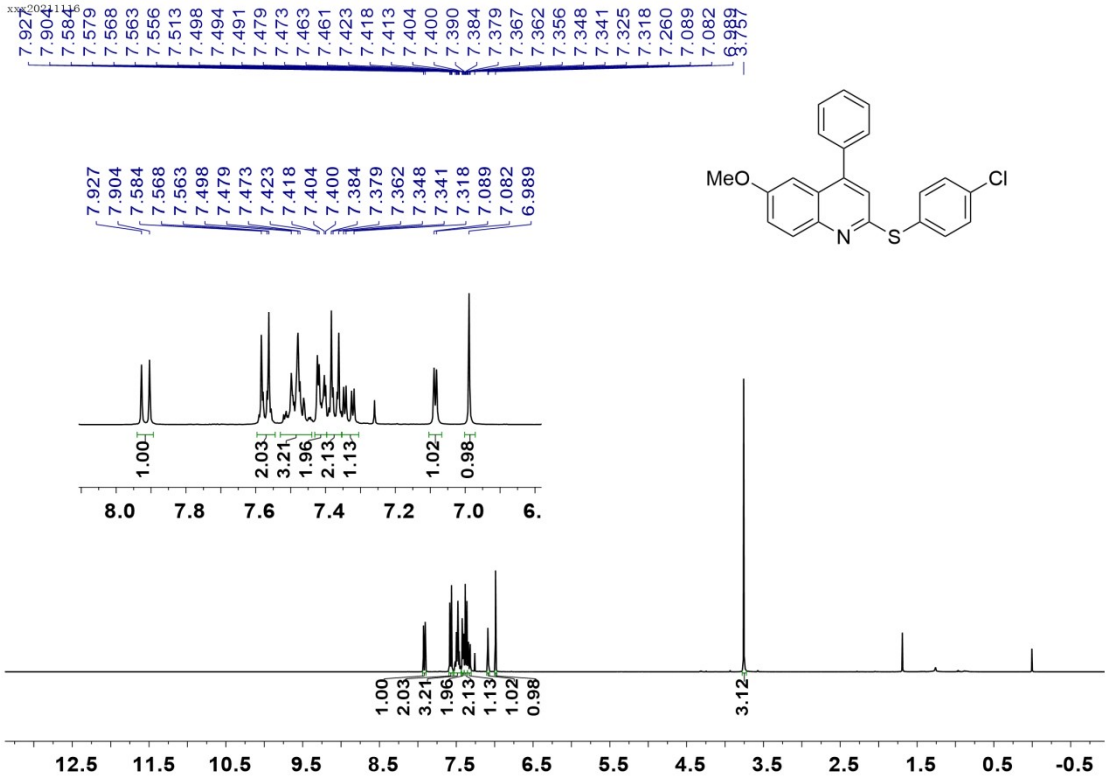
^{13}C NMR (100 MHz, $CDCl_3$) for **3t**



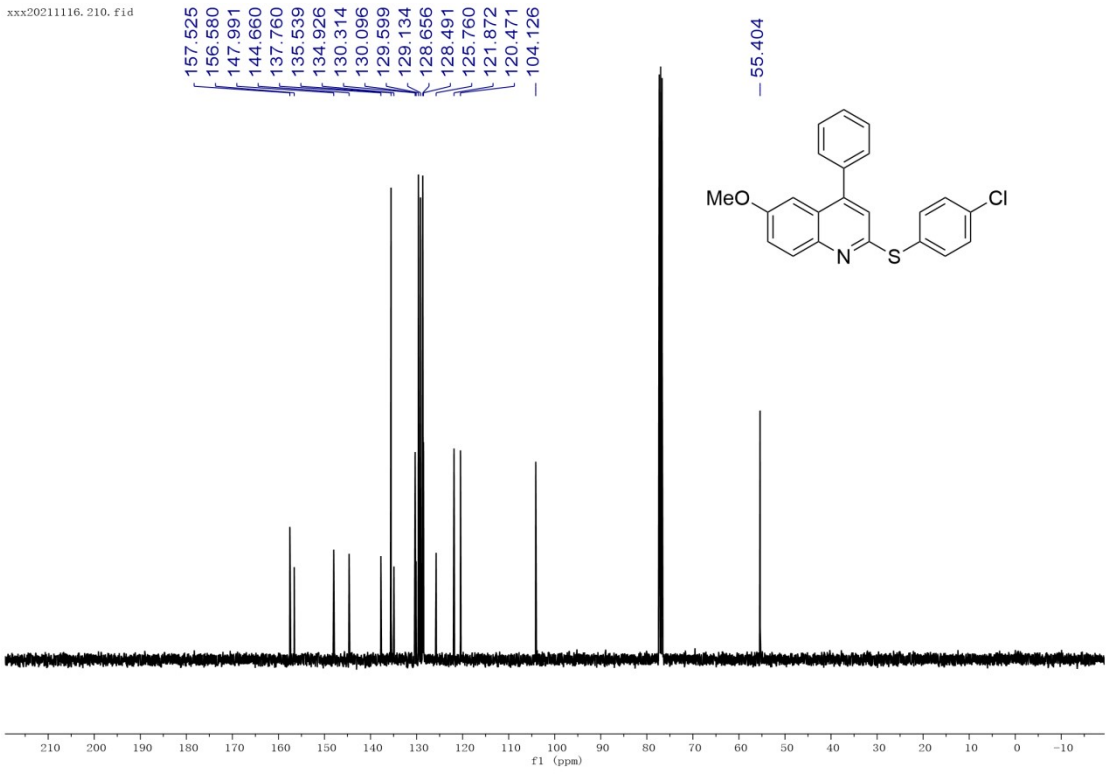
^{19}F NMR (376 MHz, $CDCl_3$) for **3t**



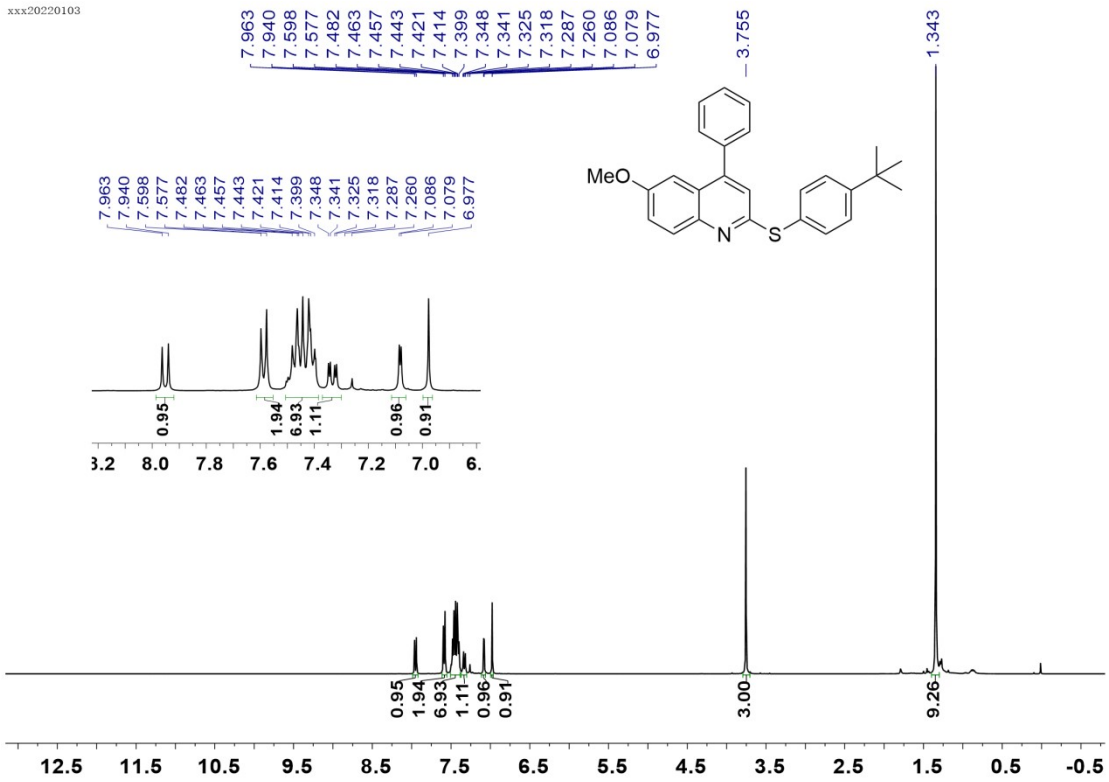
^{1}H NMR (400 MHz, $CDCl_3$) for **3u**



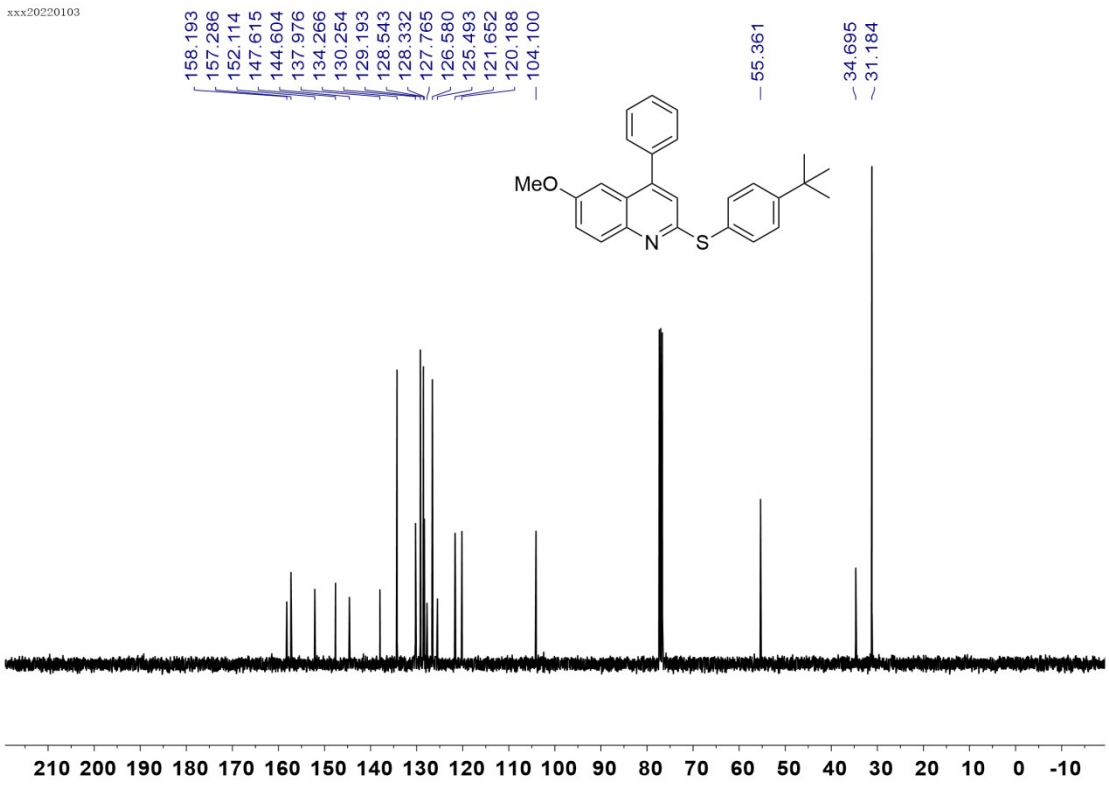
^{13}C NMR (100 MHz, $CDCl_3$) for **3u**



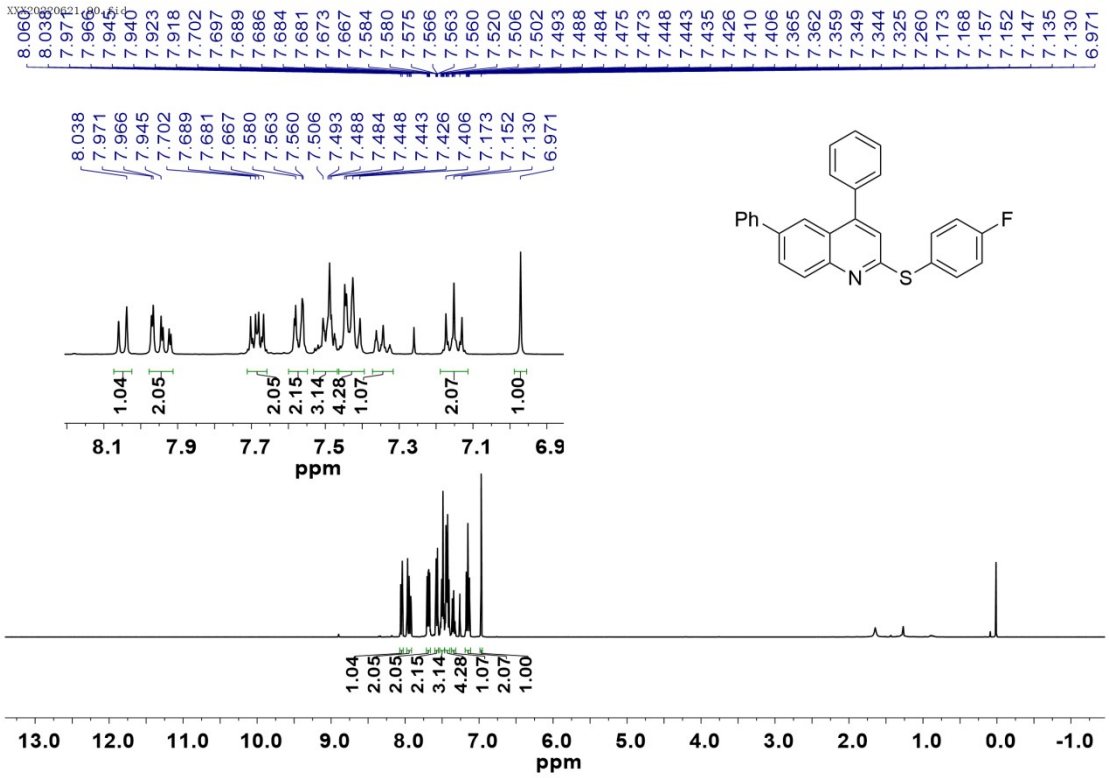
^{1}H NMR (400 MHz, $CDCl_3$) for **3v**



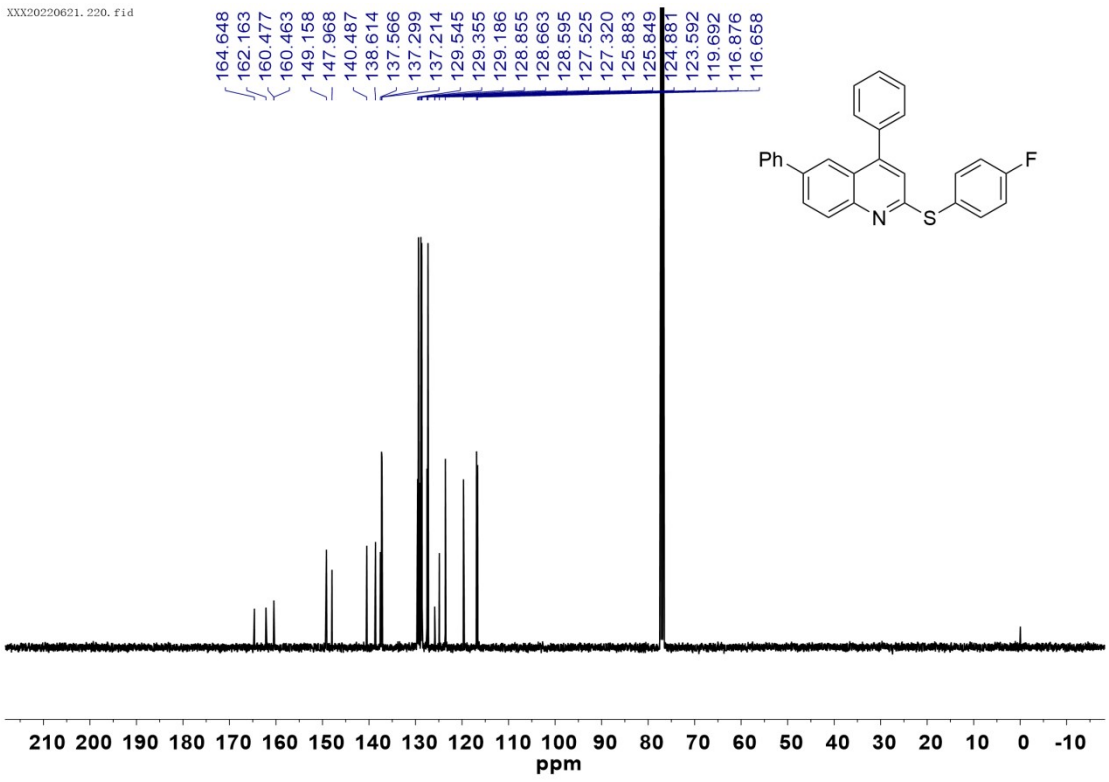
^{13}C NMR (100 MHz, $CDCl_3$) for **3v**



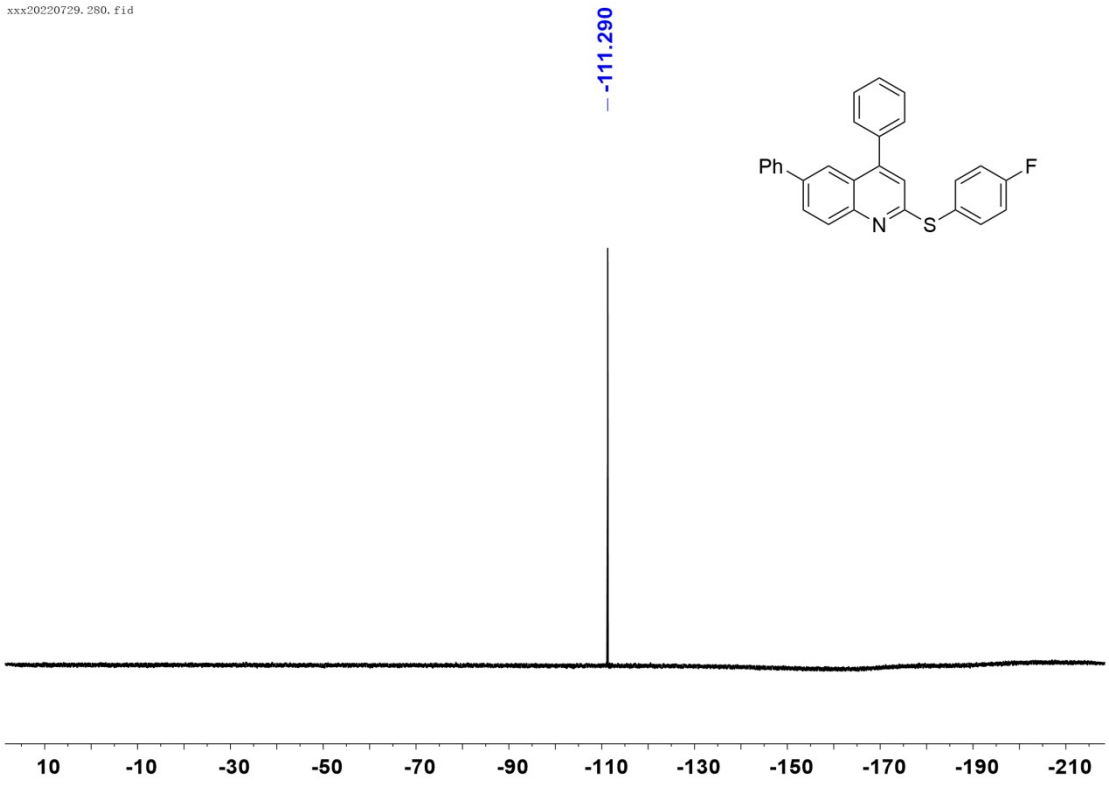
^{1}H NMR (400 MHz, $CDCl_3$) for **3w**



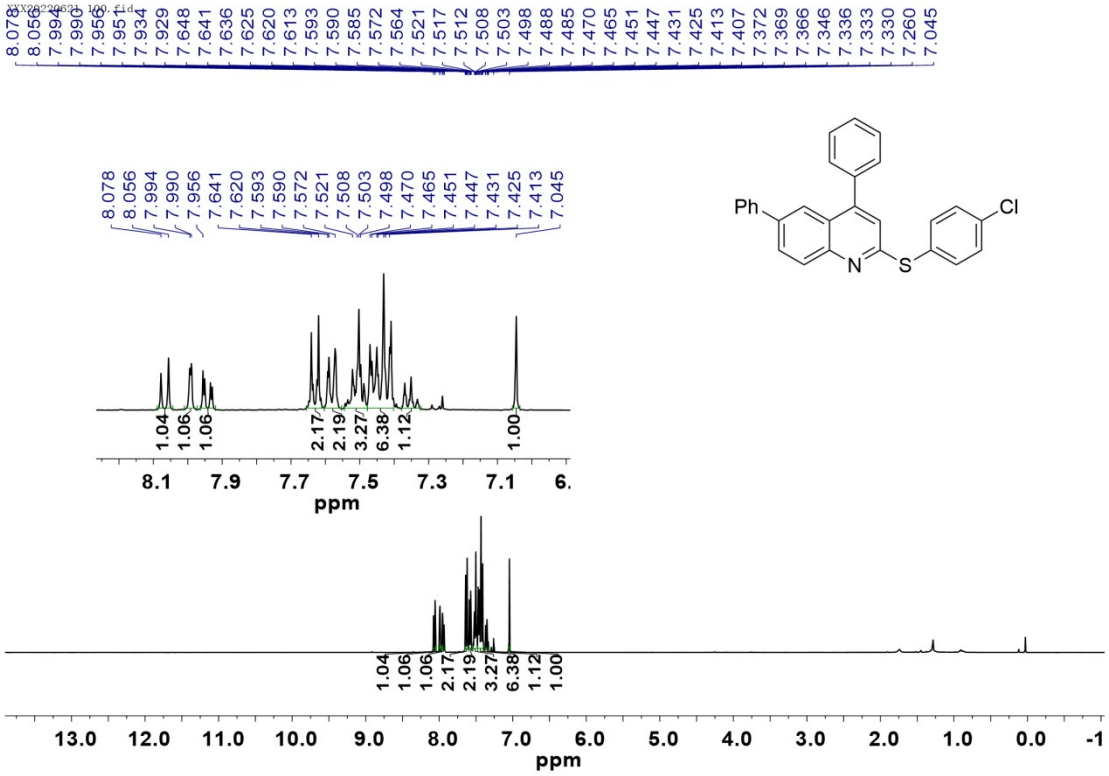
^{13}C NMR (100 MHz, $CDCl_3$) for **3w**



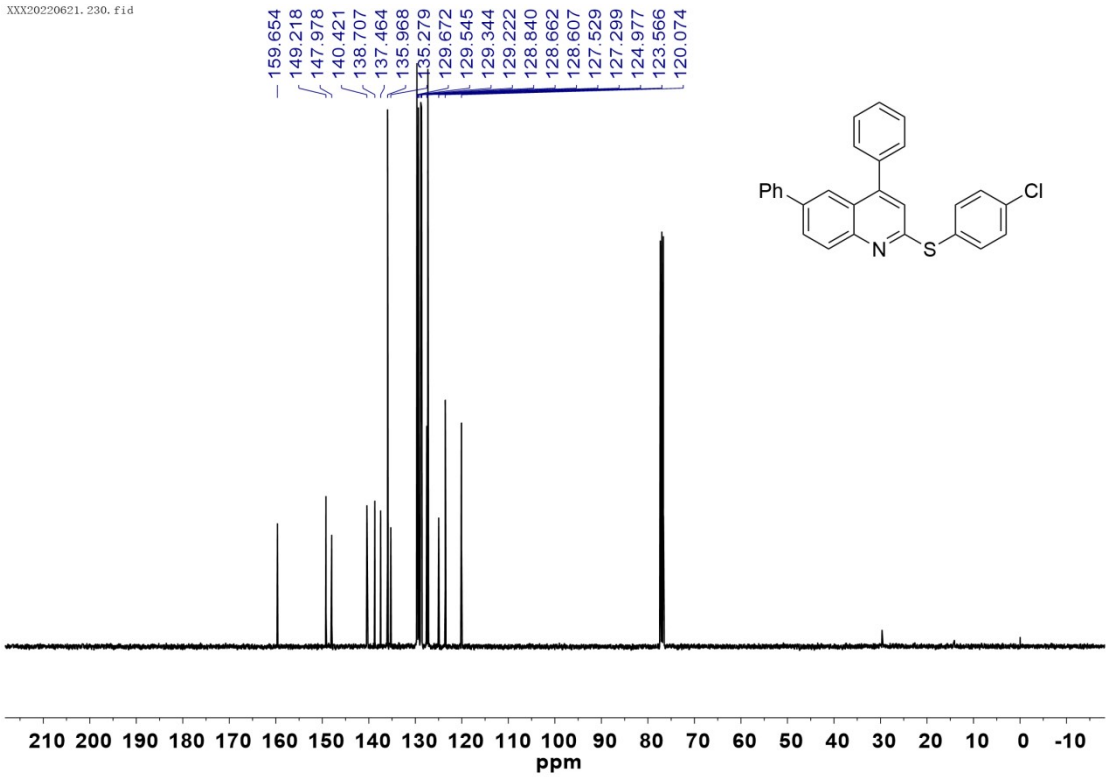
^{19}F NMR (376 MHz, $CDCl_3$) for **3w**



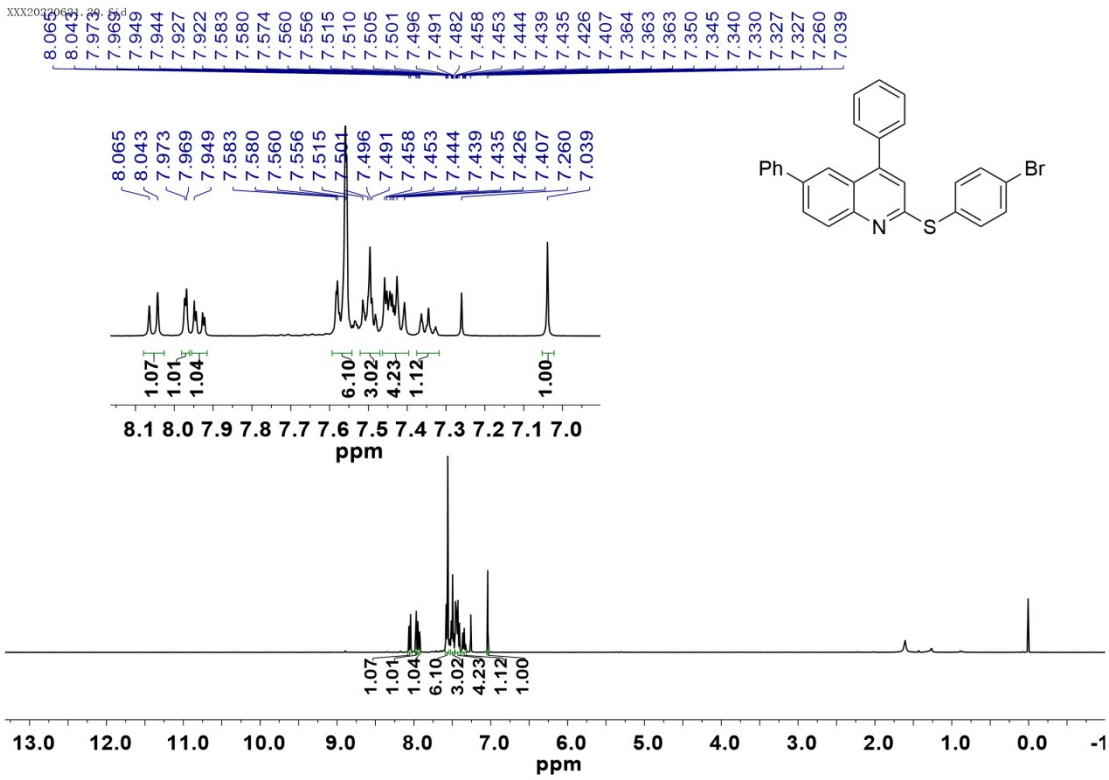
^{1}H NMR (400 MHz, $CDCl_3$) for **3x**



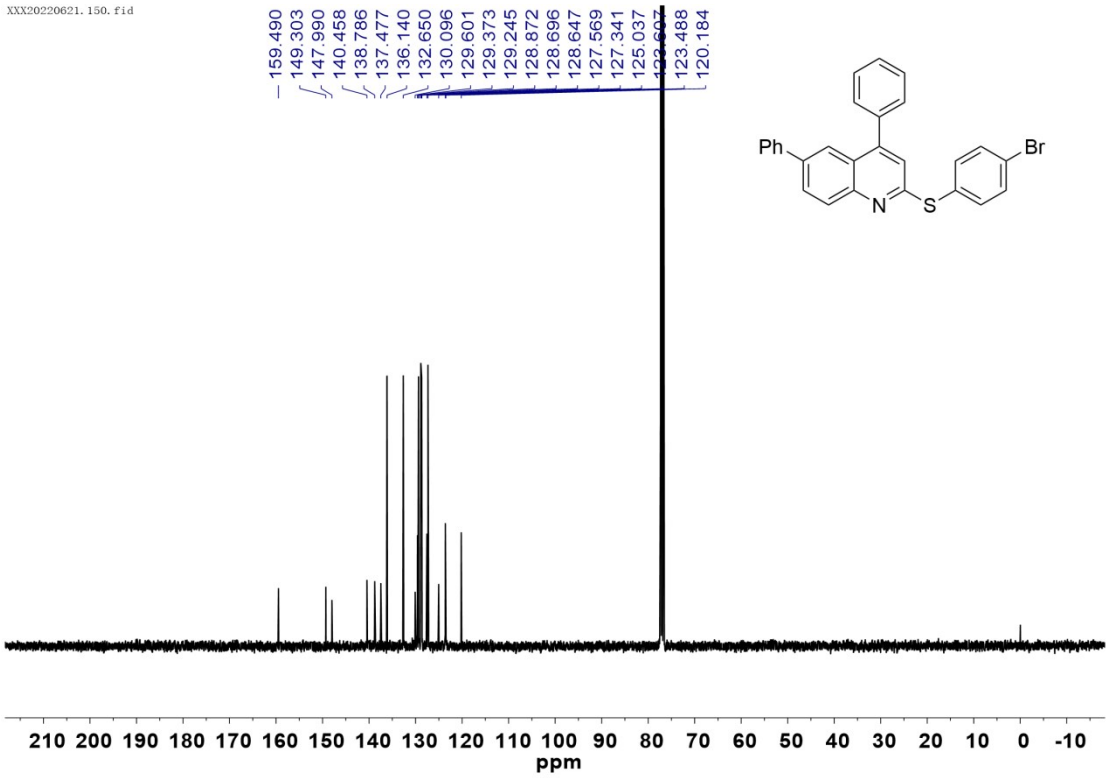
^{13}C NMR (100 MHz, $CDCl_3$) for **3x**



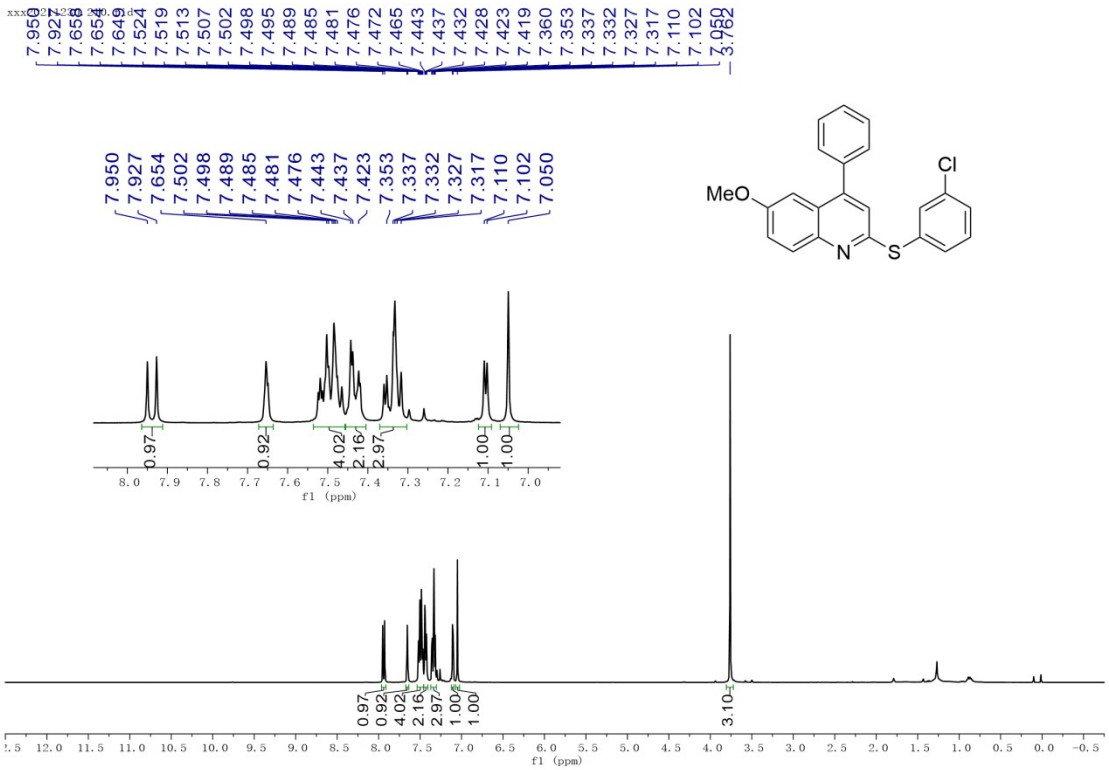
^{1}H NMR (400 MHz, $CDCl_3$) for **3y**



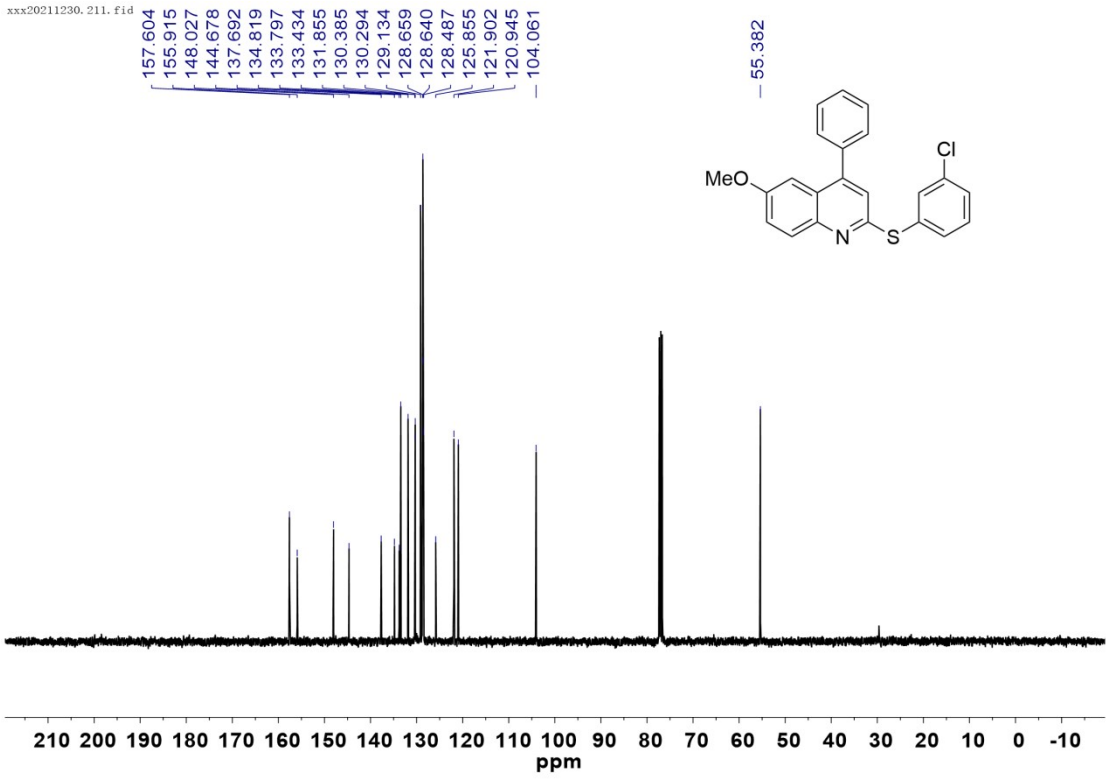
^{13}C NMR (100 MHz, $CDCl_3$) for **3y**



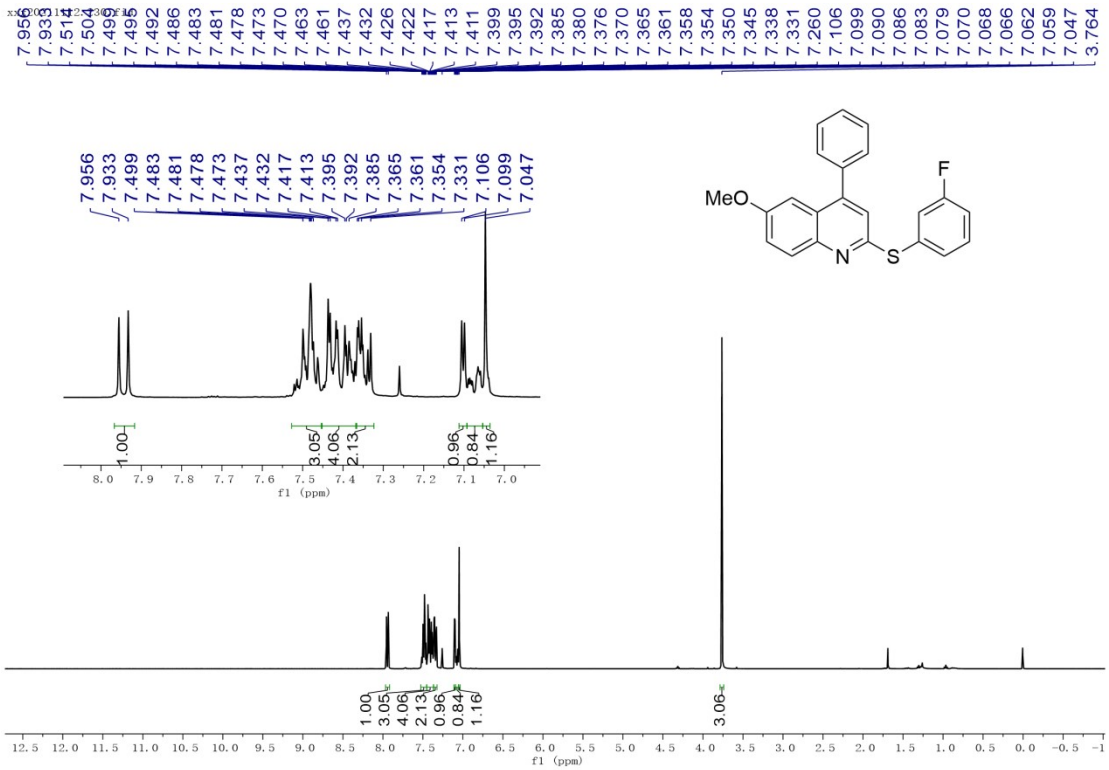
^{1}H NMR (400 MHz, $CDCl_3$) for **3z**



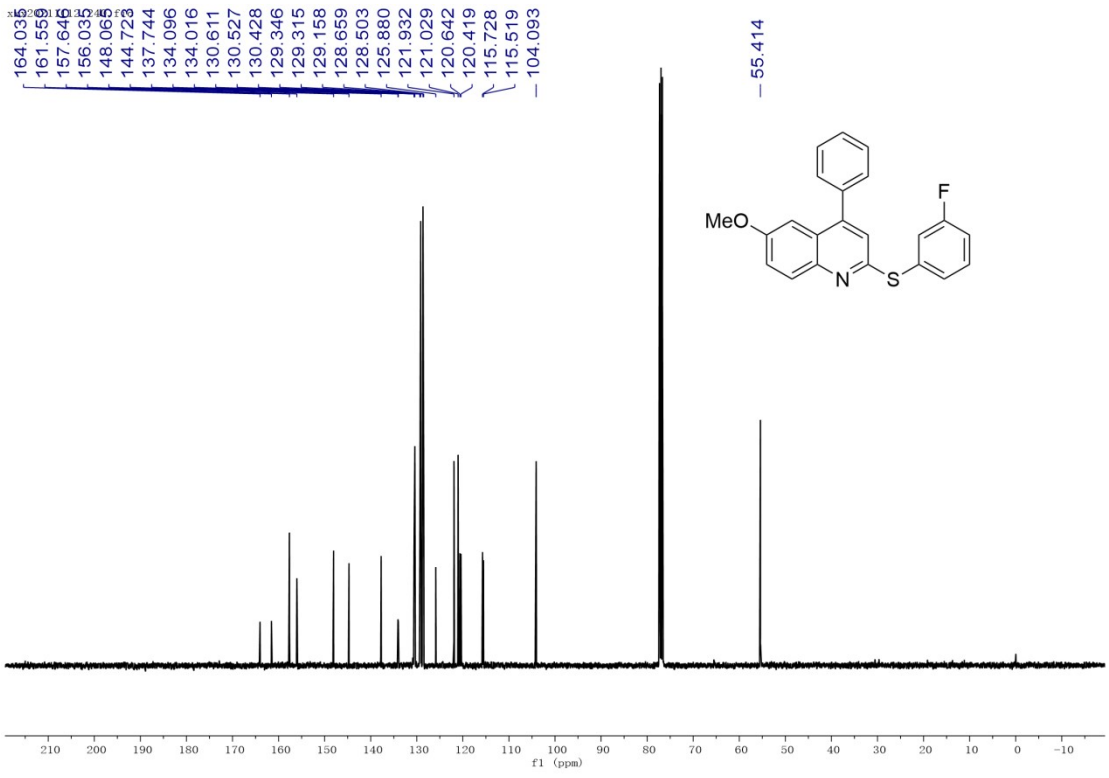
^{13}C NMR (100 MHz, $CDCl_3$) for **3z**



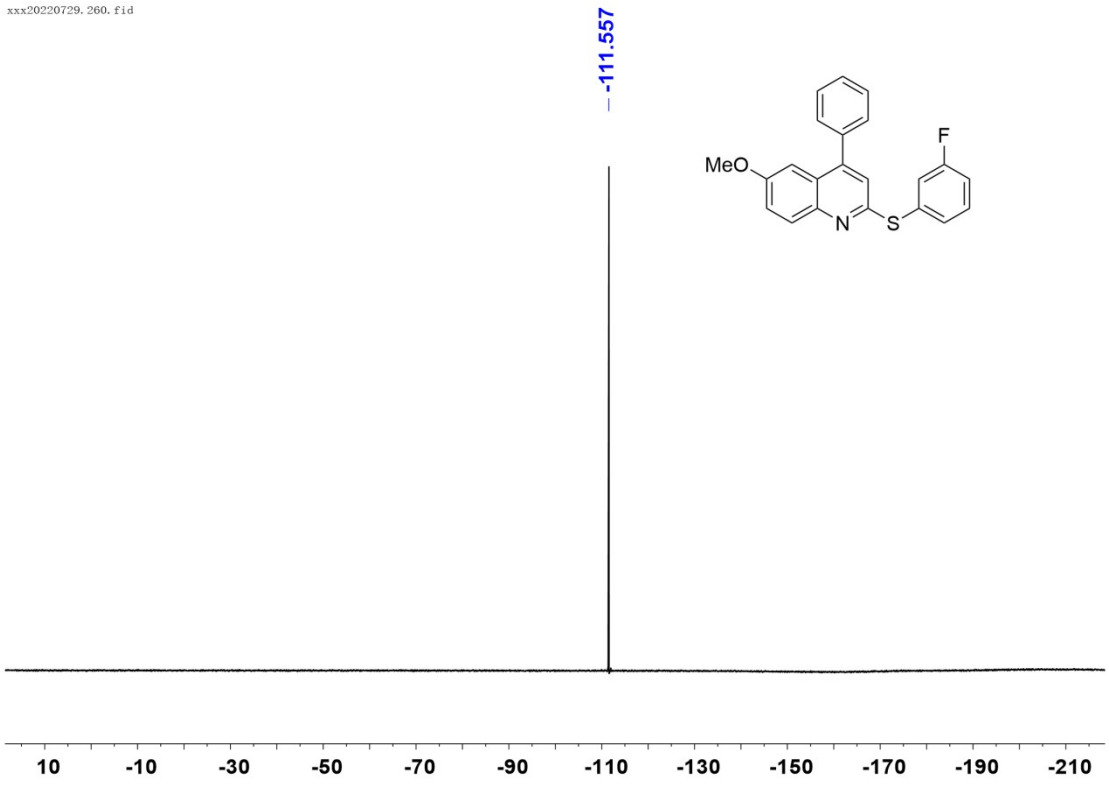
^{1}H NMR (400 MHz, $CDCl_3$) for **3aa**



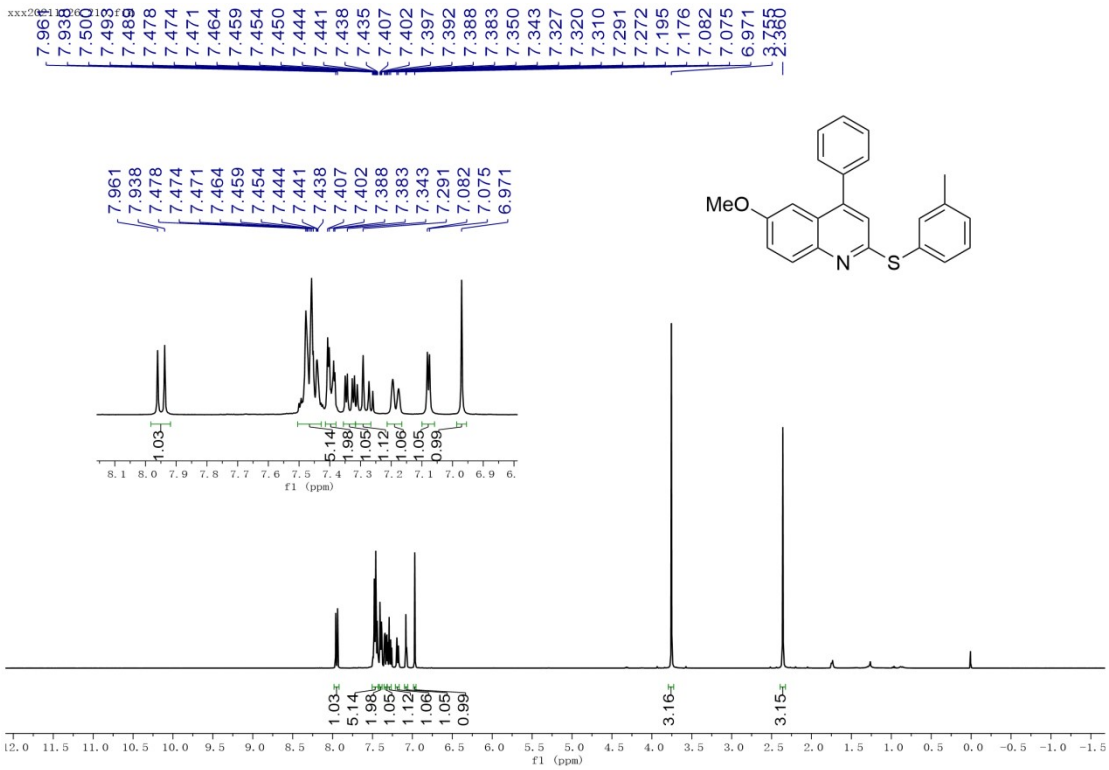
^{13}C NMR (100 MHz, $CDCl_3$) for **3aa**



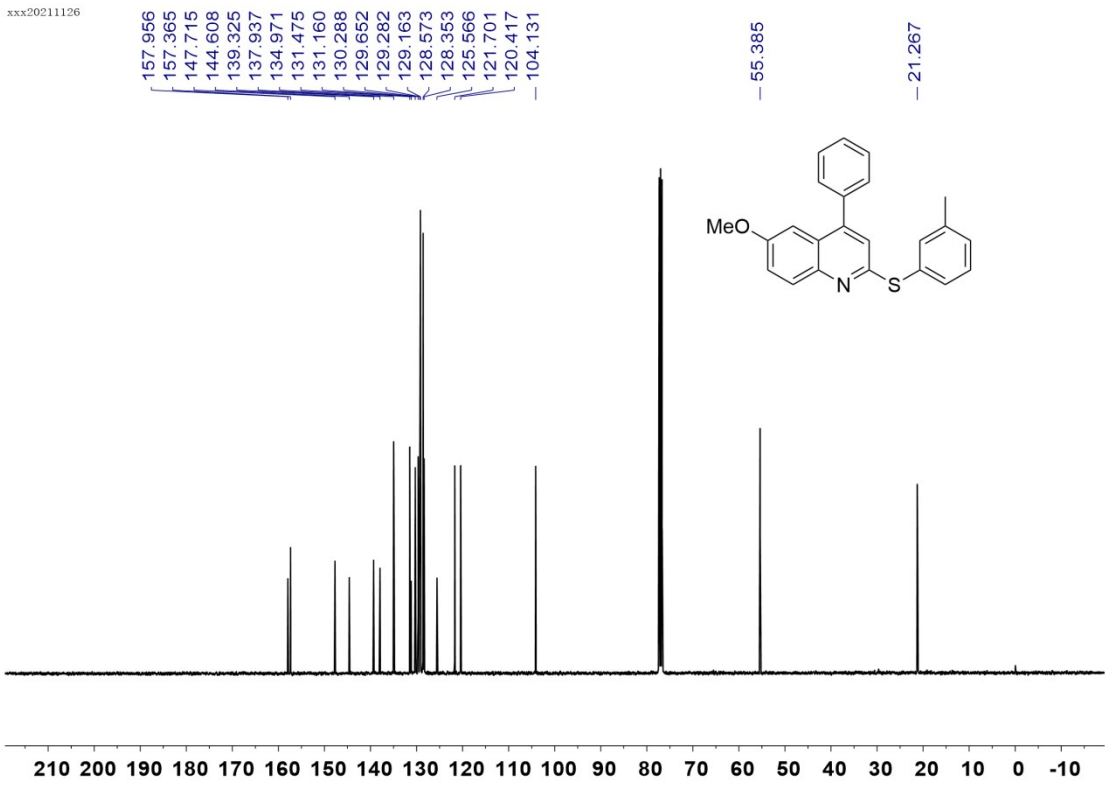
^{19}F NMR (376 MHz, $CDCl_3$) for **3aa**



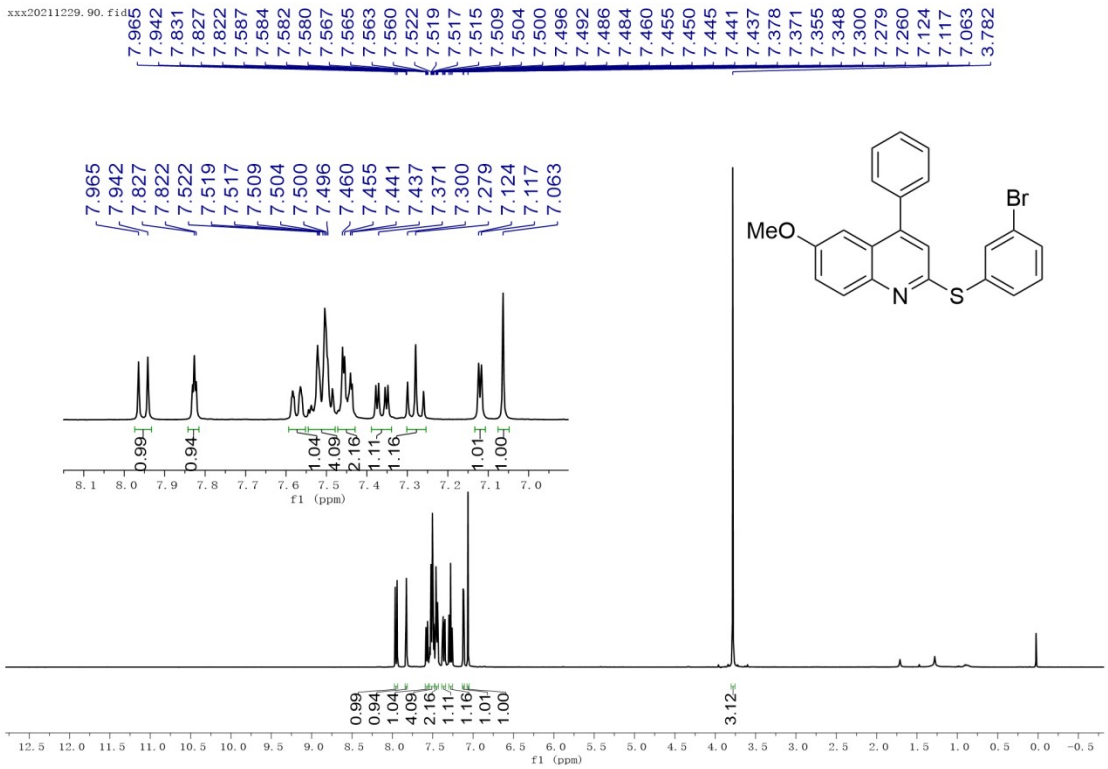
^{1}H NMR (400 MHz, $CDCl_3$) for **3ab**



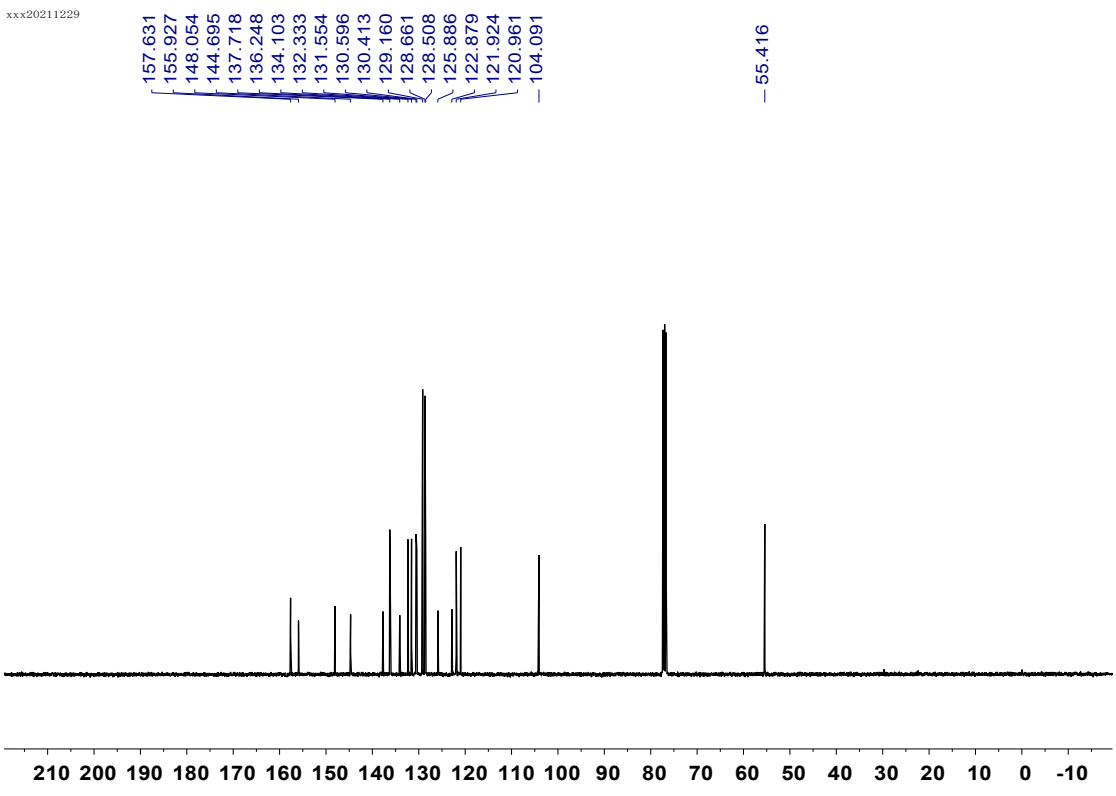
^{13}C NMR (100 MHz, $CDCl_3$) for **3ab**



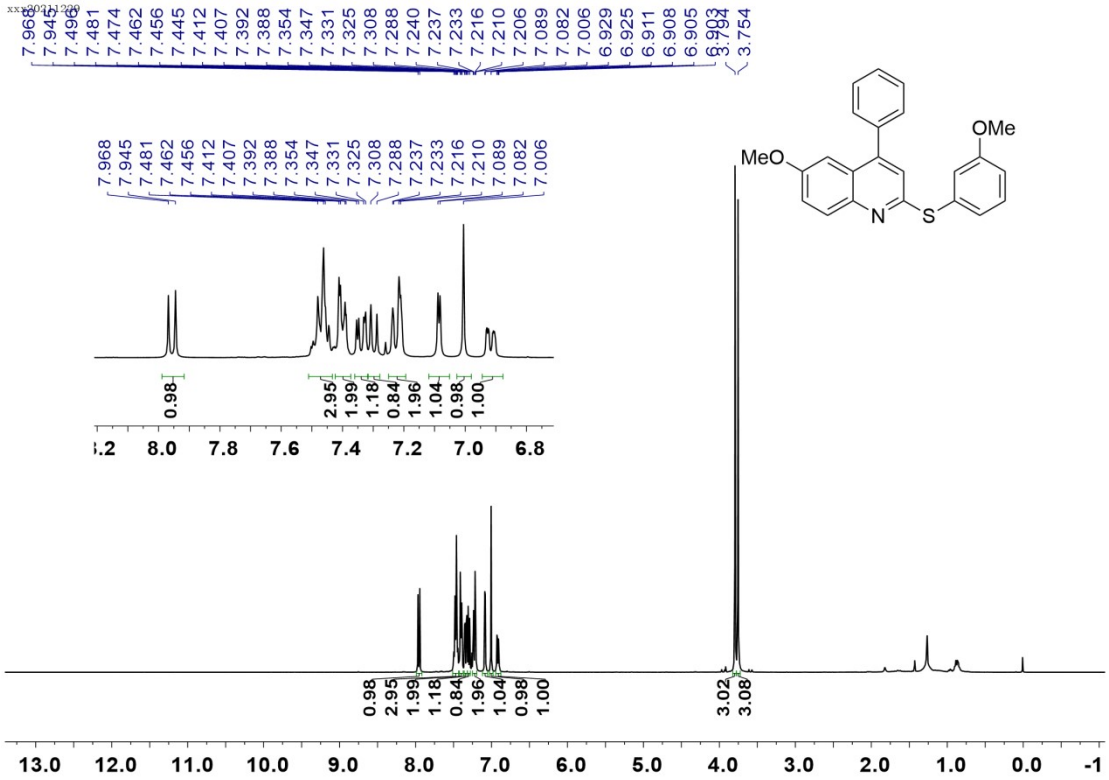
^{1}H NMR (400 MHz, $CDCl_3$) for **3ac**



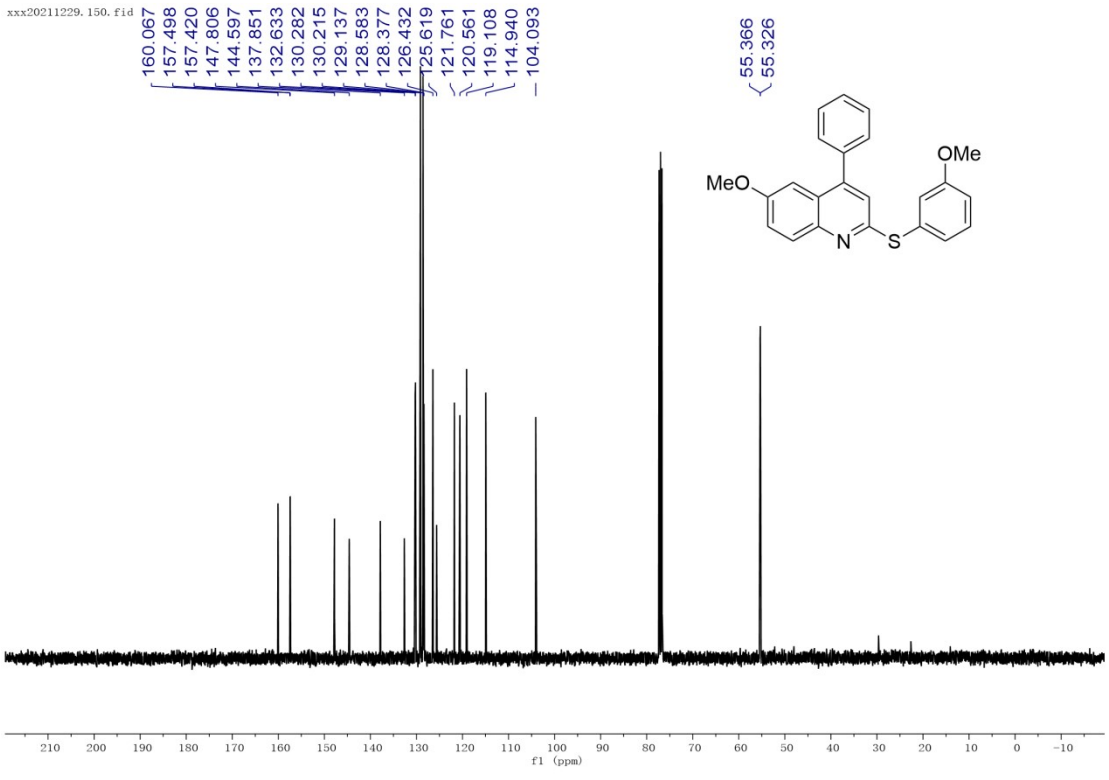
^{13}C NMR (100 MHz, $CDCl_3$) for **3ac**



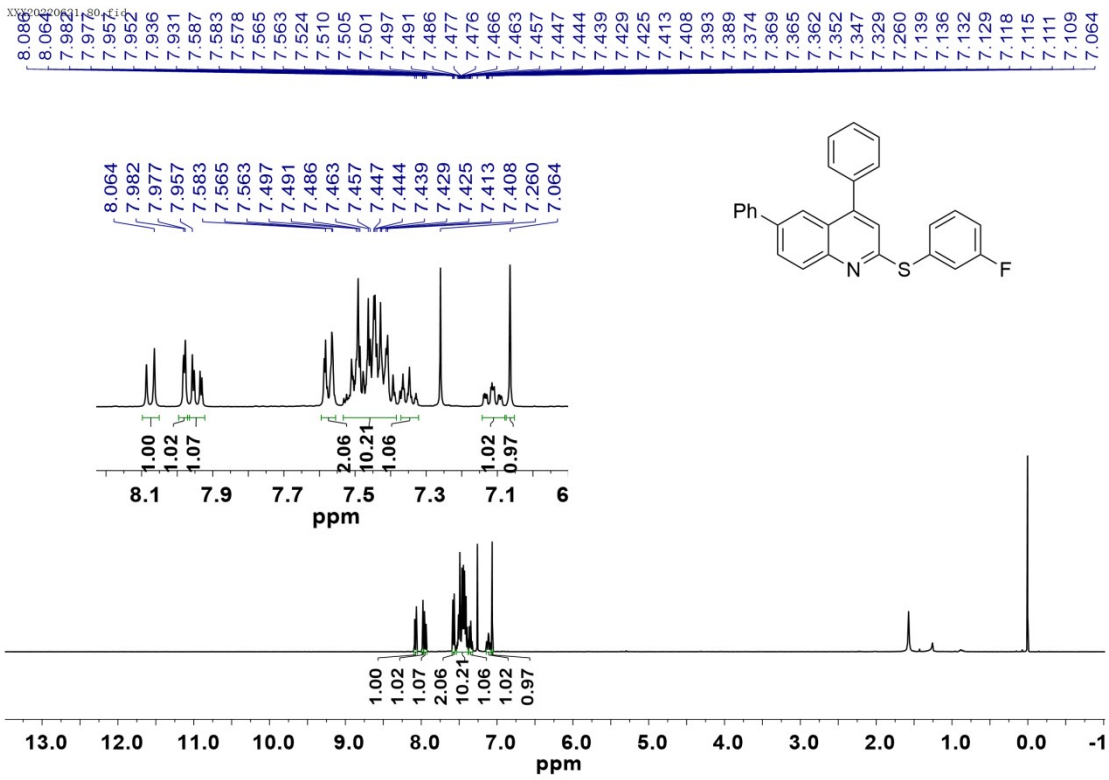
^{1}H NMR (400 MHz, $CDCl_3$) for **3ad**



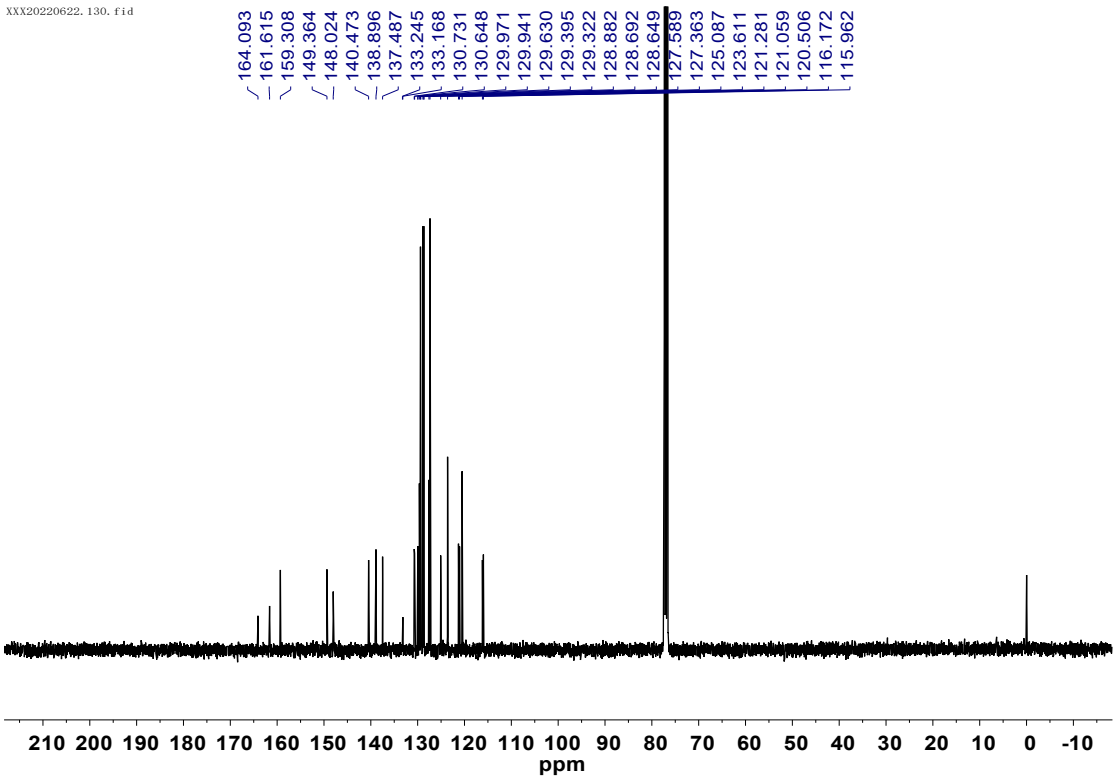
^{13}C NMR (100 MHz, $CDCl_3$) for **3ad**



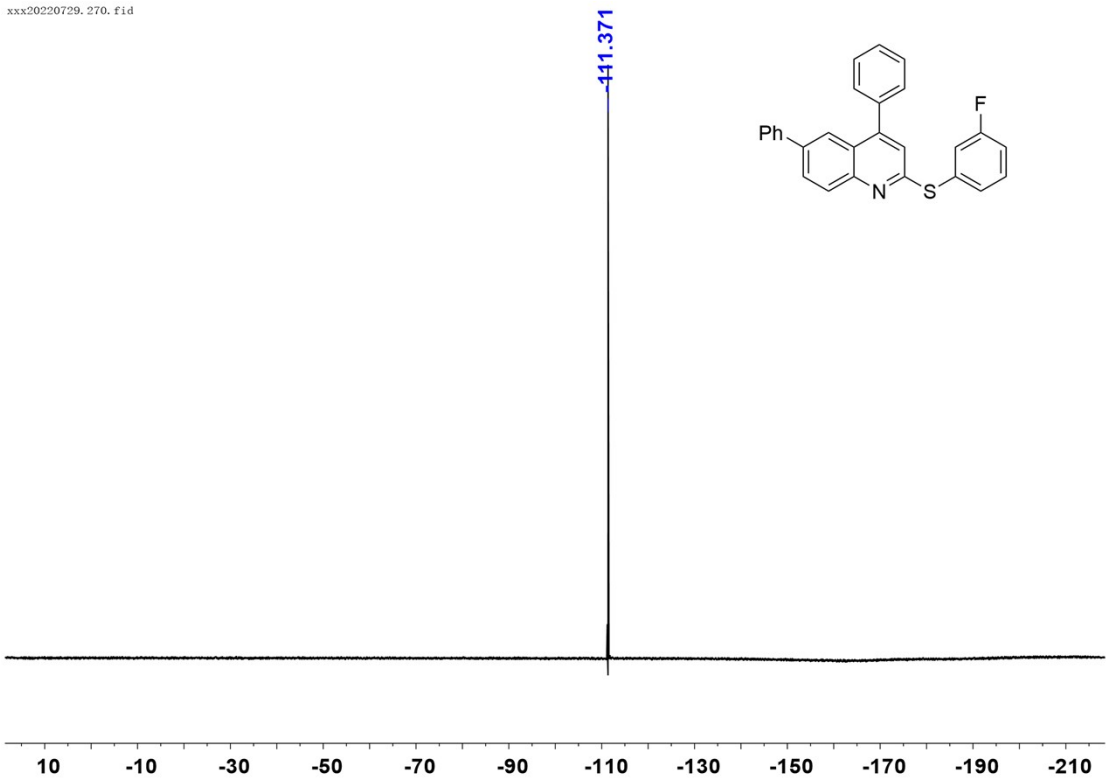
^{1}H NMR (400 MHz, $CDCl_3$) for **3ae**



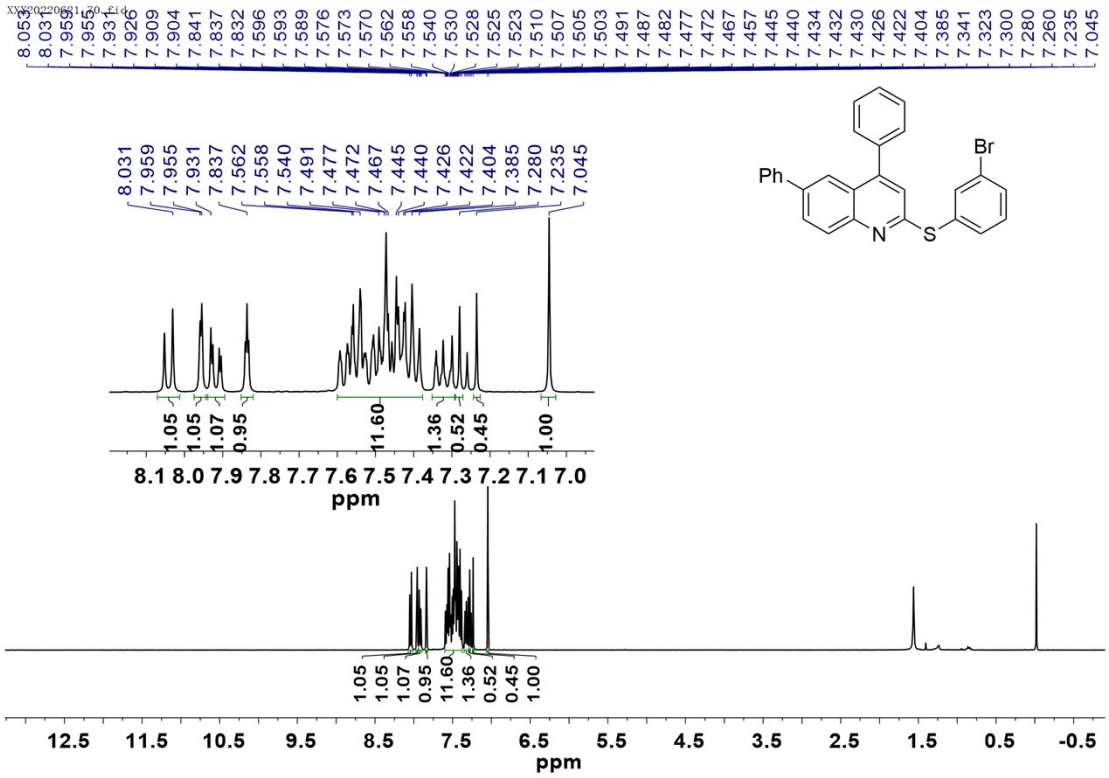
^{13}C NMR (100 MHz, $CDCl_3$) for **3ae**



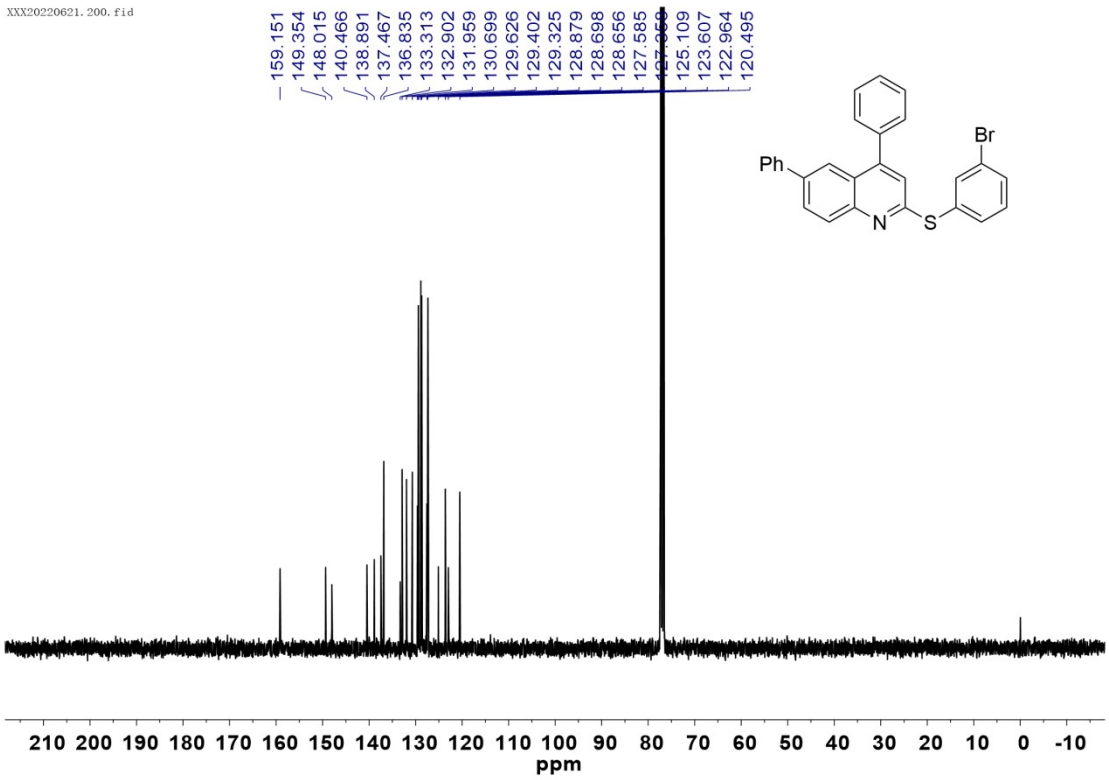
^{19}F NMR (376 MHz, $CDCl_3$) for **3ae**



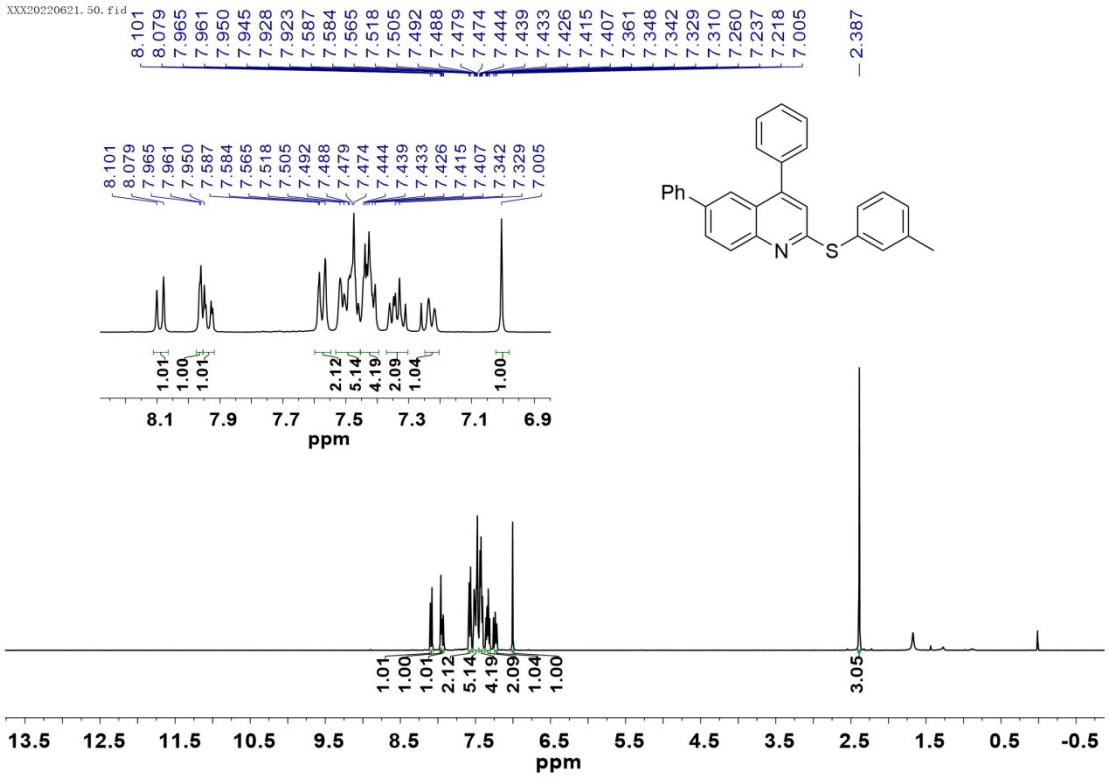
^{1}H NMR (400 MHz, $CDCl_3$) for **3af**



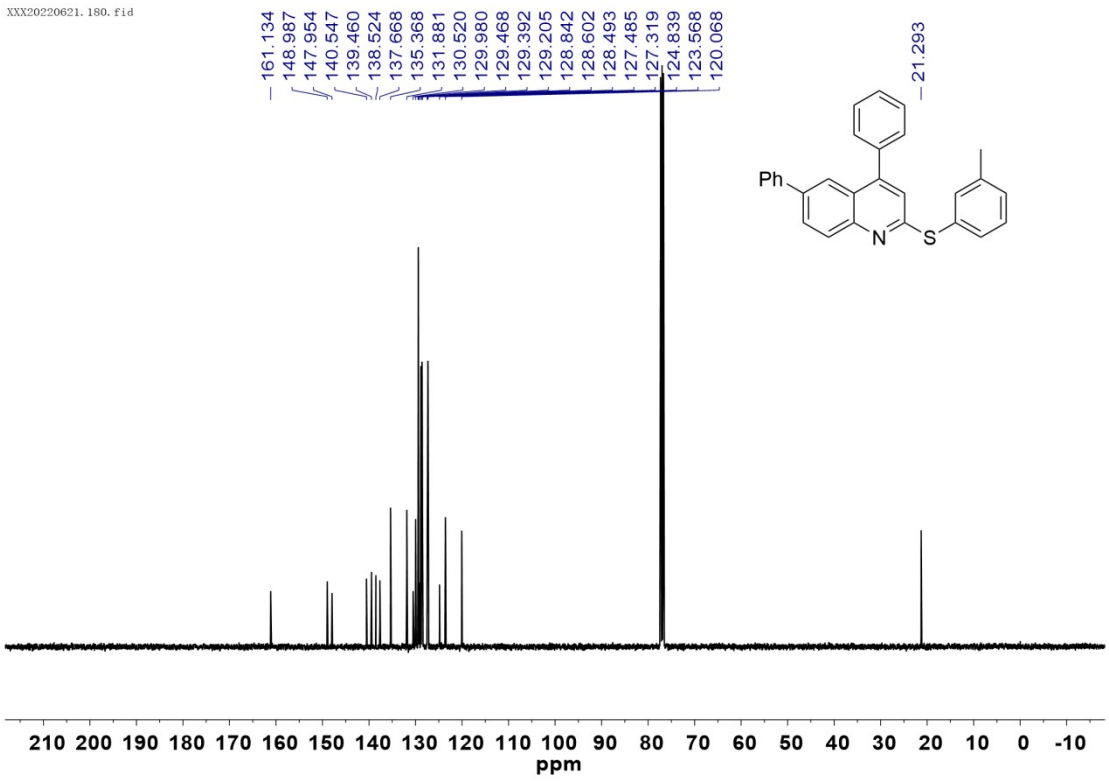
^{13}C NMR (100 MHz, $CDCl_3$) for **3af**



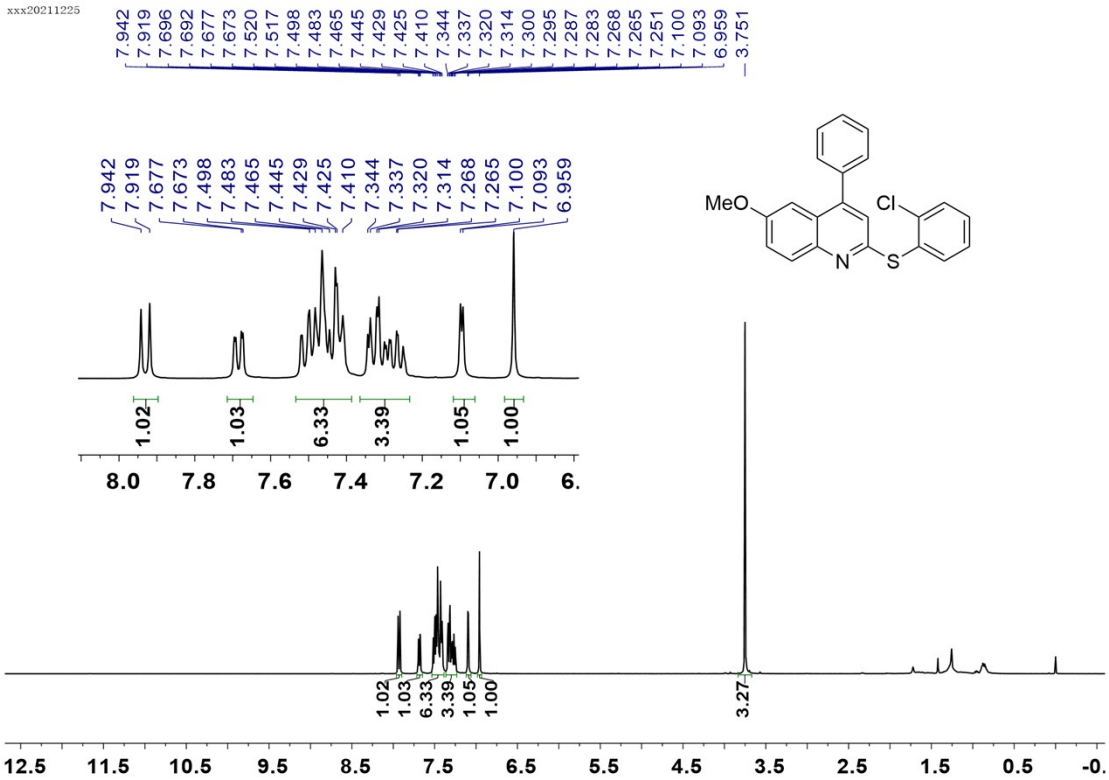
^{1}H NMR (400 MHz, $CDCl_3$) for **3ag**



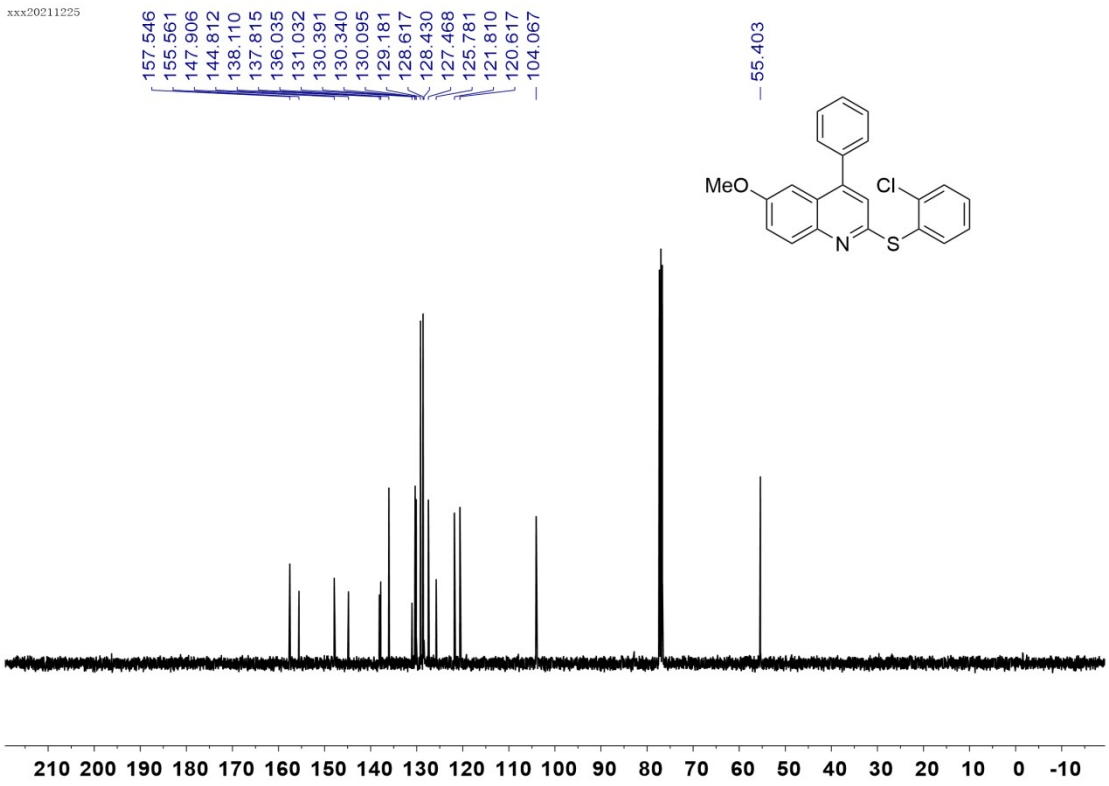
^{13}C NMR (100 MHz, $CDCl_3$) for **3ag**



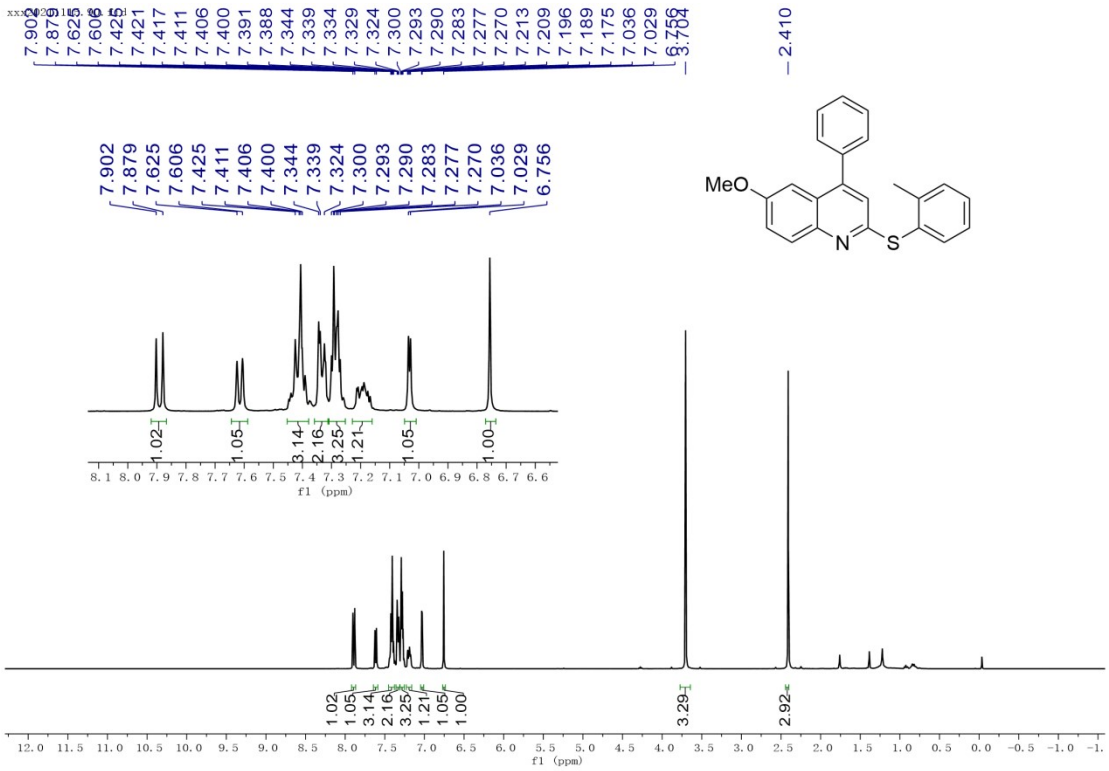
^{1}H NMR (400 MHz, $CDCl_3$) for **3ah**



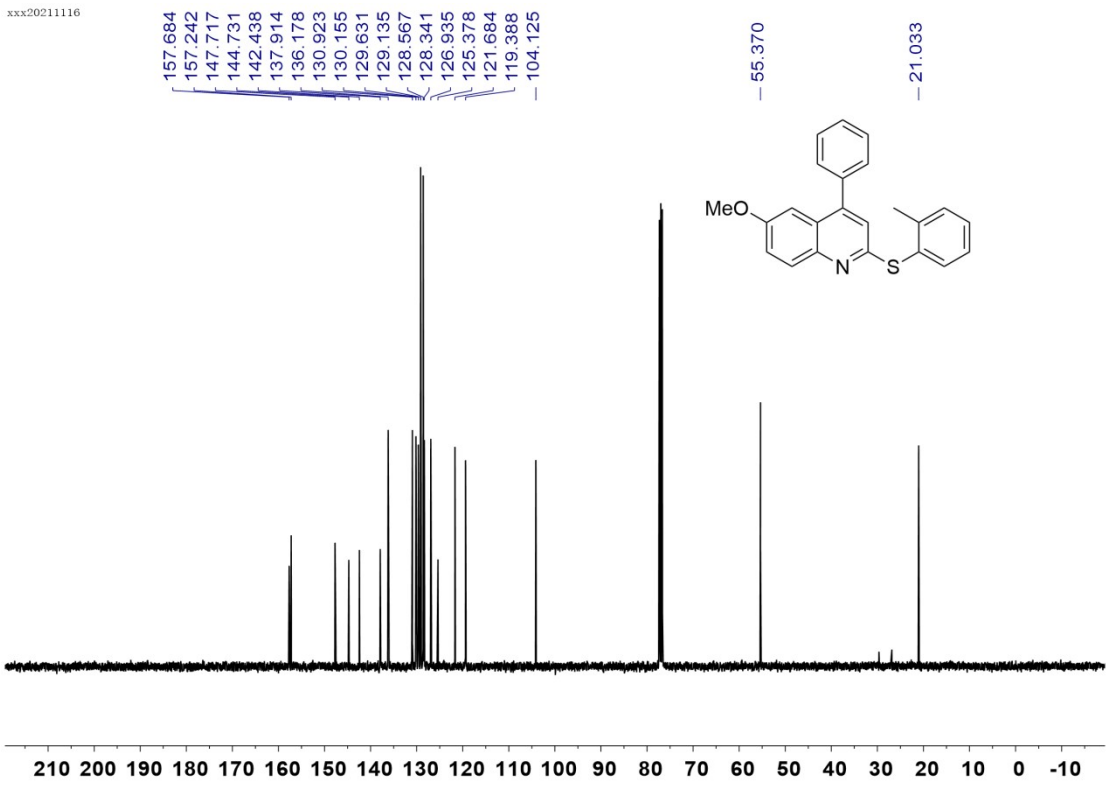
^{13}C NMR (100 MHz, $CDCl_3$) for **3ah**



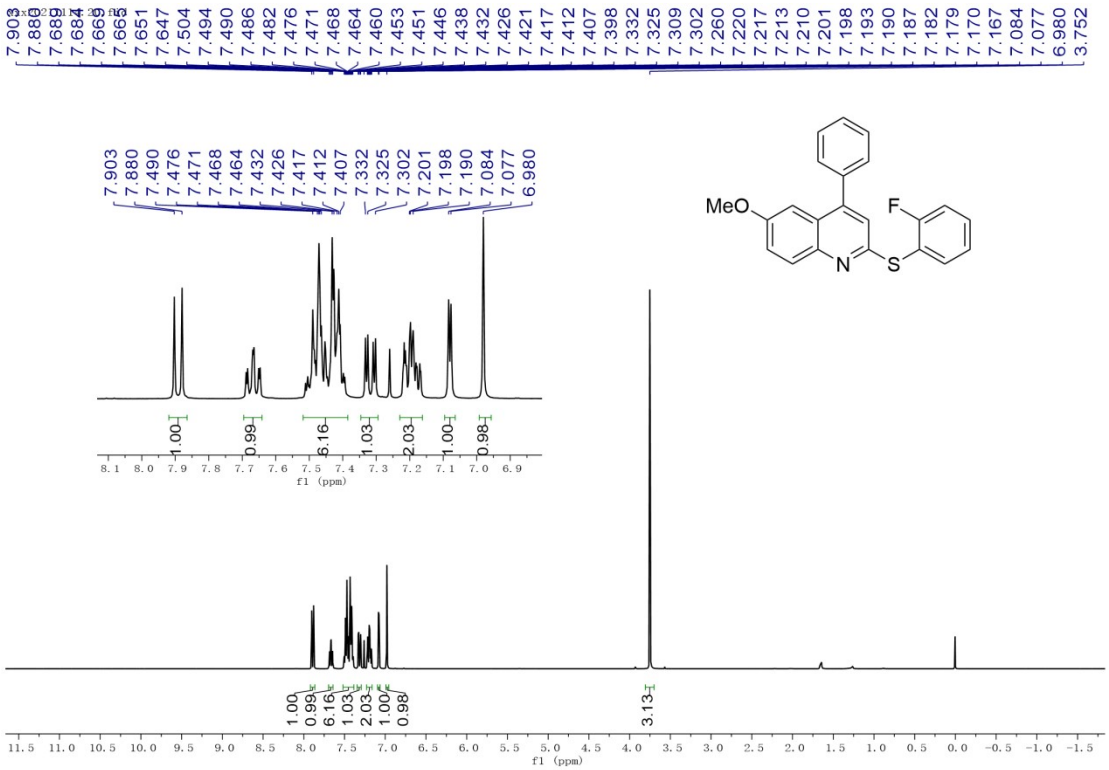
^{1}H NMR (400 MHz, $CDCl_3$) for **3ai**



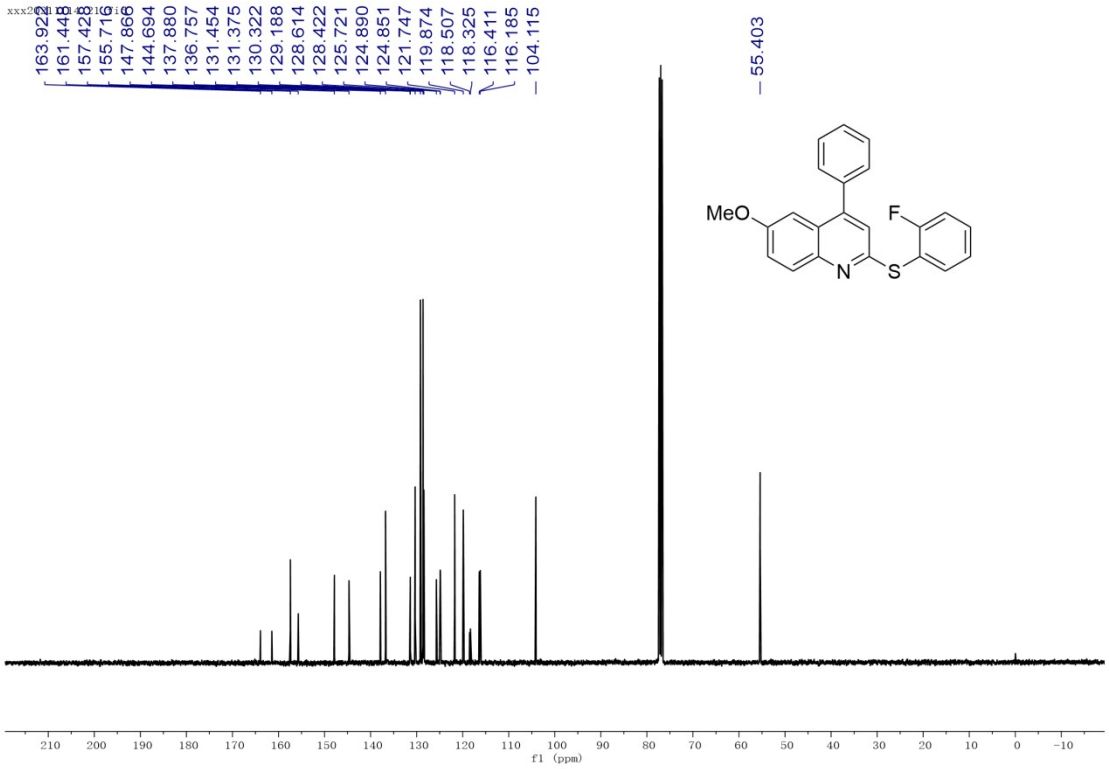
^{13}C NMR (100 MHz, $CDCl_3$) for **3ai**



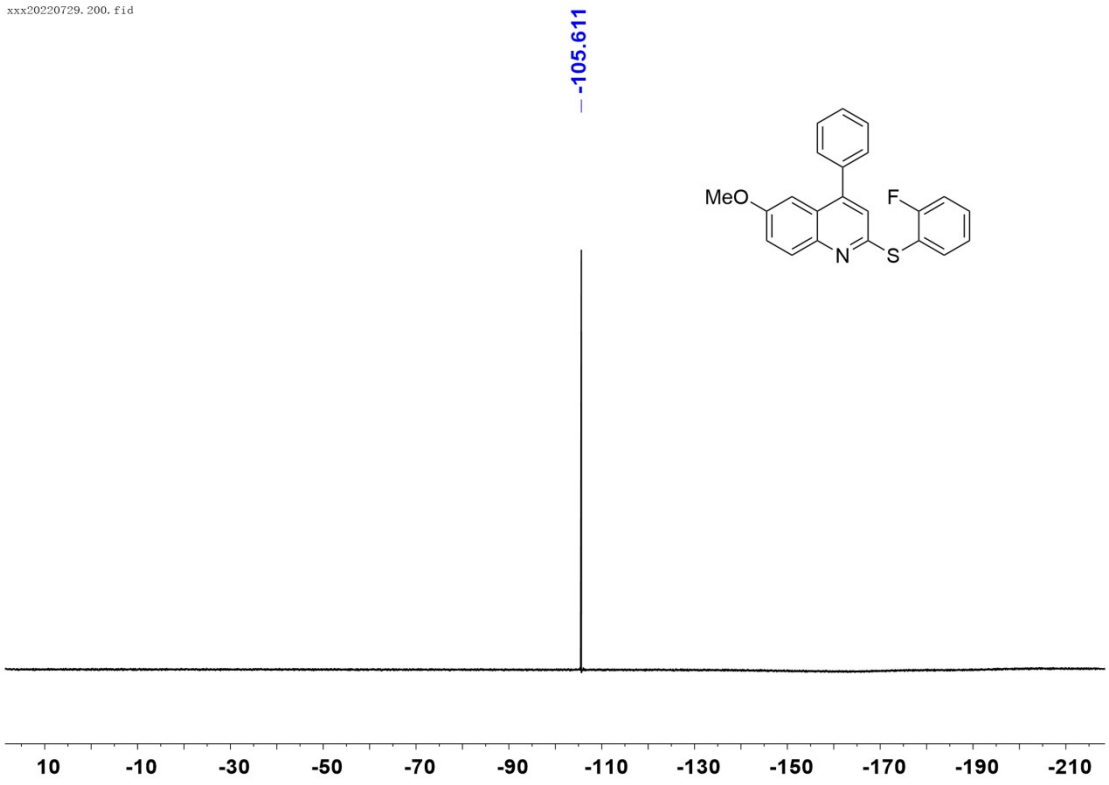
^{1}H NMR (400 MHz, $CDCl_3$) for **3aj**



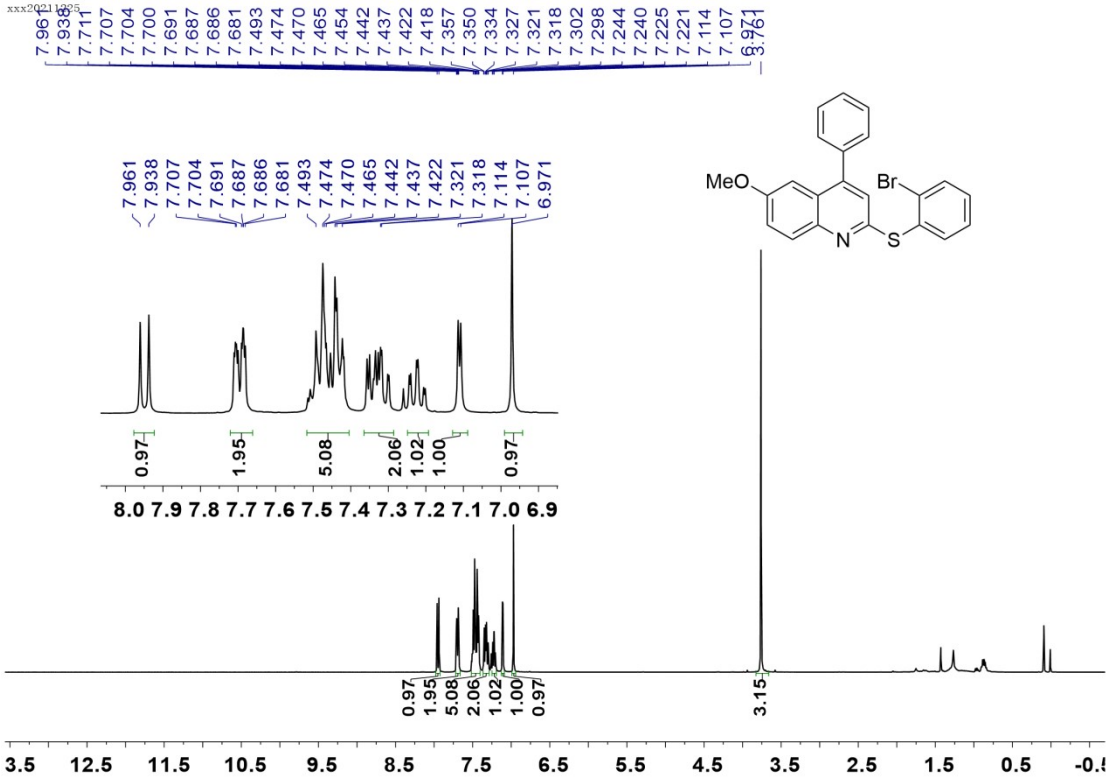
^{13}C NMR (100 MHz, $CDCl_3$) for **3aj**



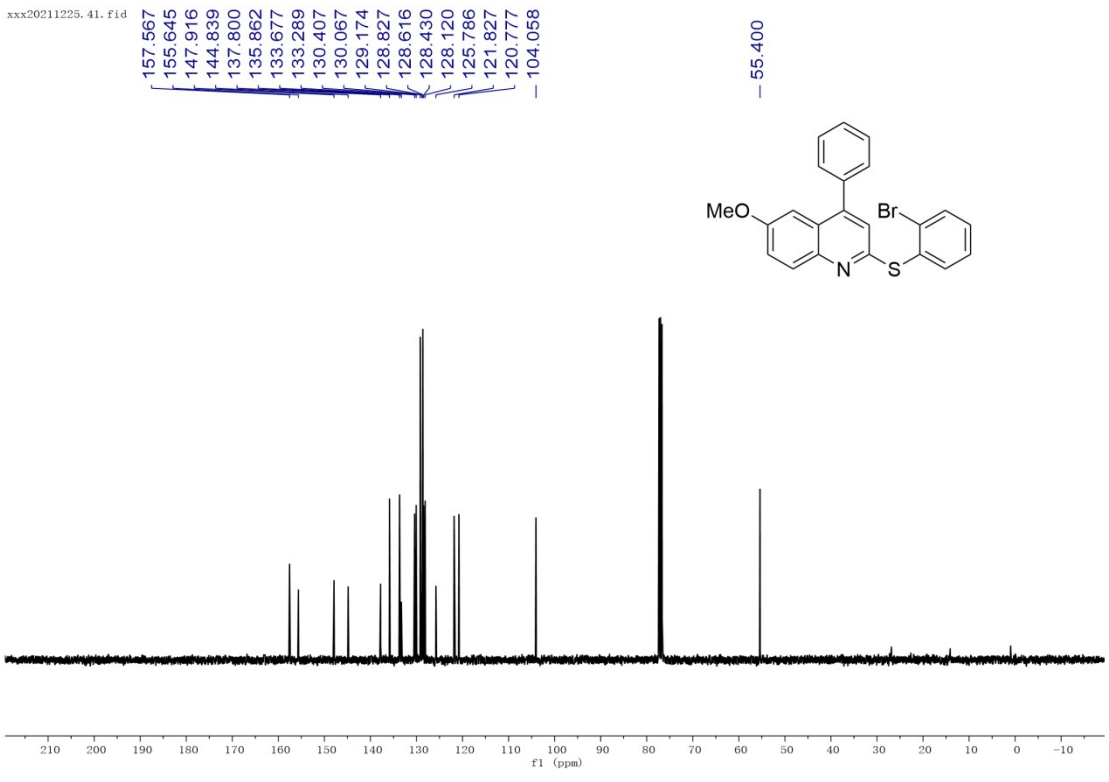
^{19}F NMR (376 MHz, $CDCl_3$) for **3aj**



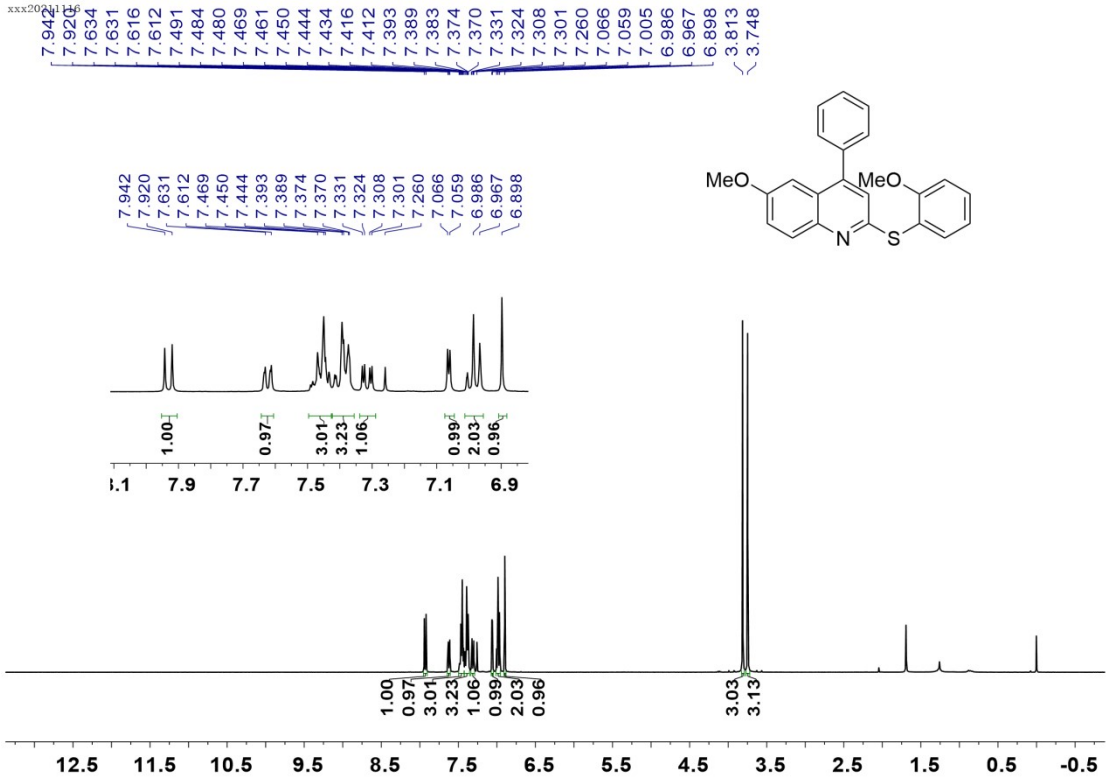
^{1}H NMR (400 MHz, $CDCl_3$) for **3ak**



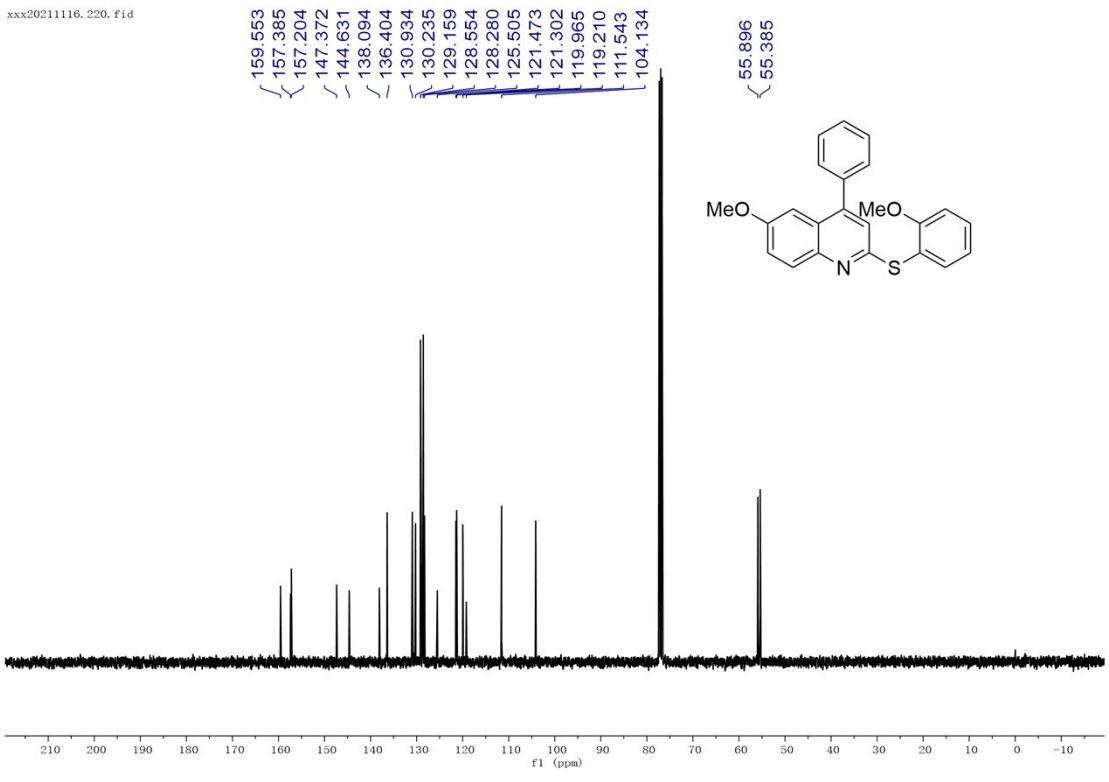
^{13}C NMR (100 MHz, $CDCl_3$) for **3ak**



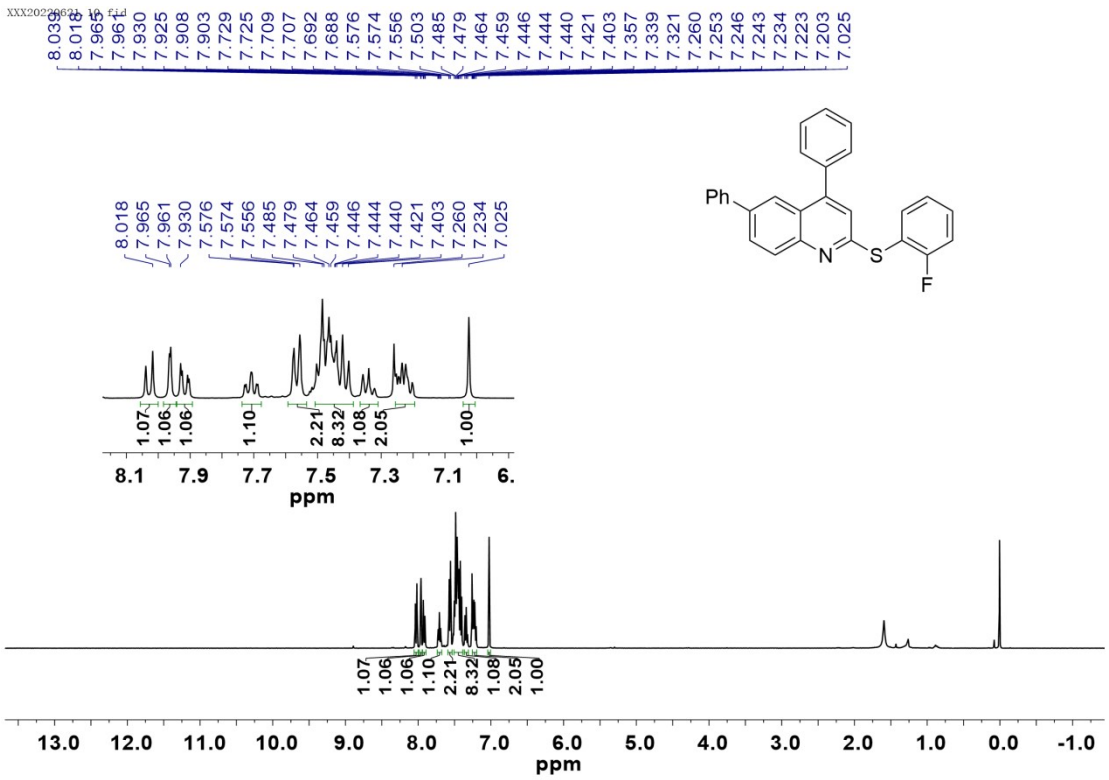
^{1}H NMR (400 MHz, $CDCl_3$) for **3al**



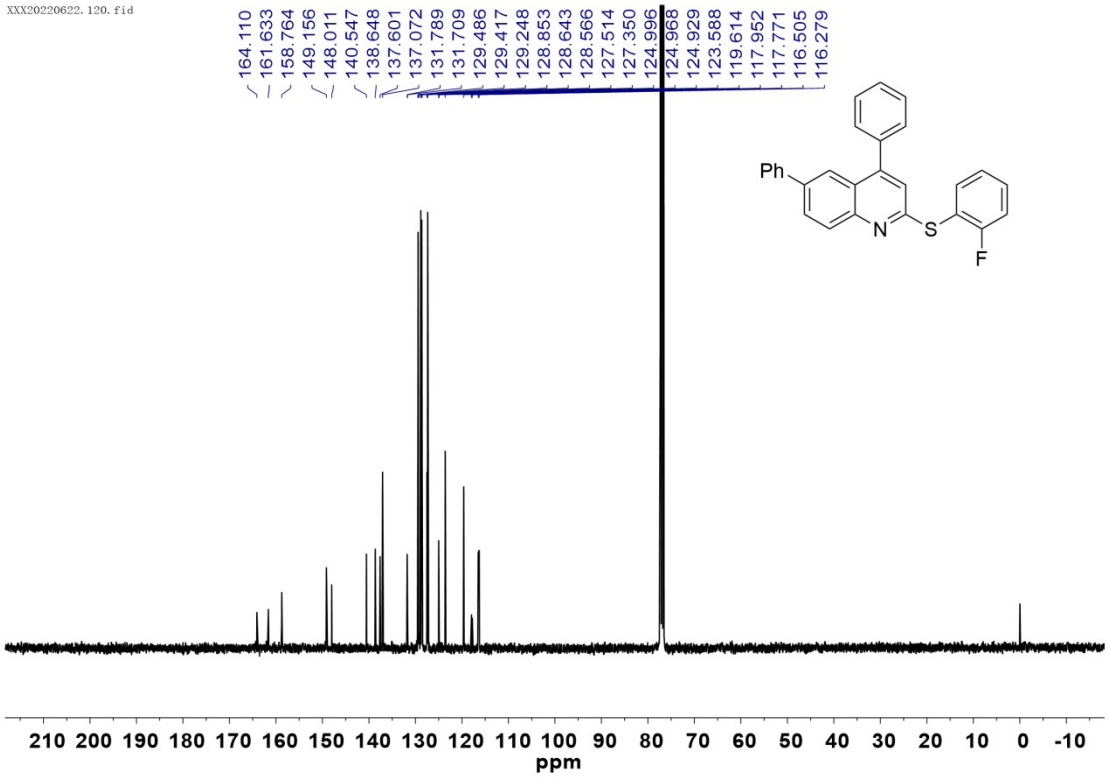
^{13}C NMR (100 MHz, $CDCl_3$) for **3al**



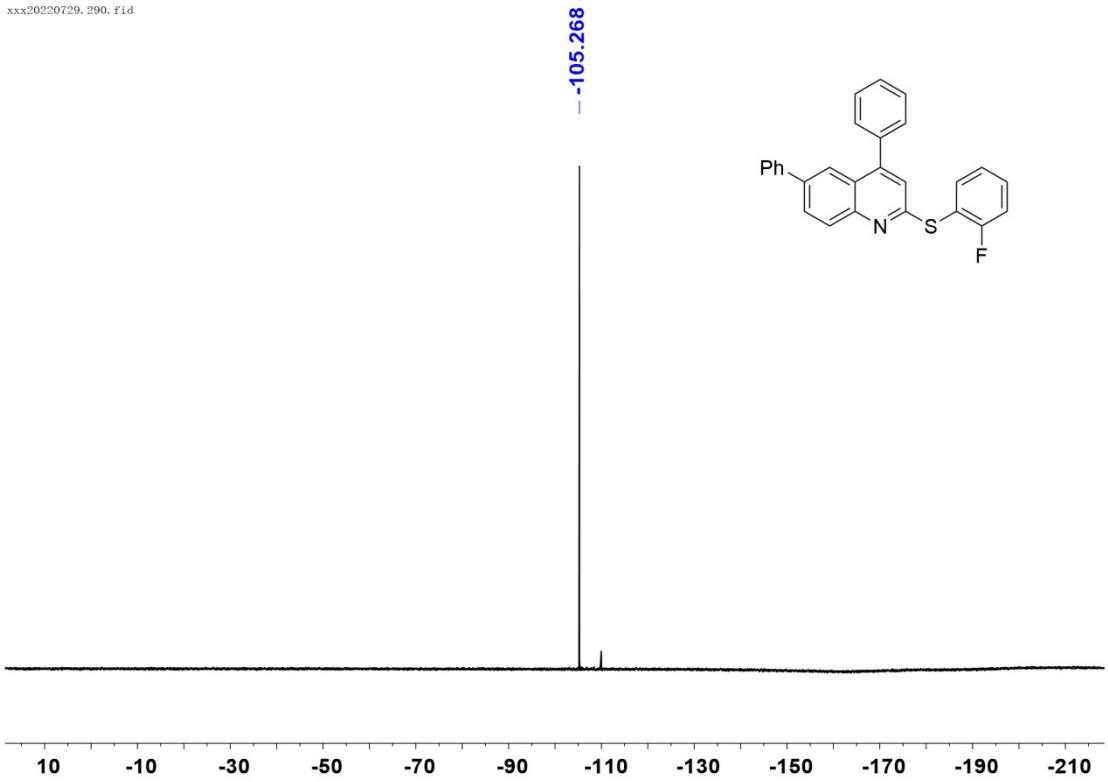
^{1}H NMR (400 MHz, $CDCl_3$) for **3am**



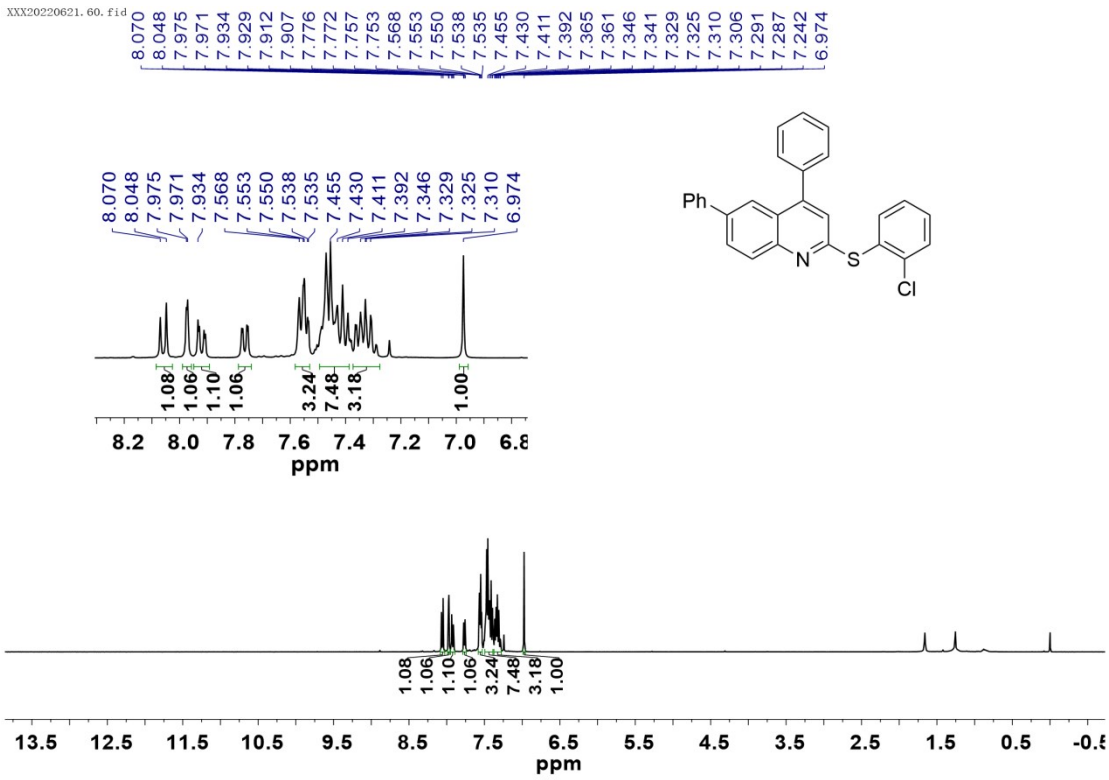
^{13}C NMR (100 MHz, $CDCl_3$) for **3am**



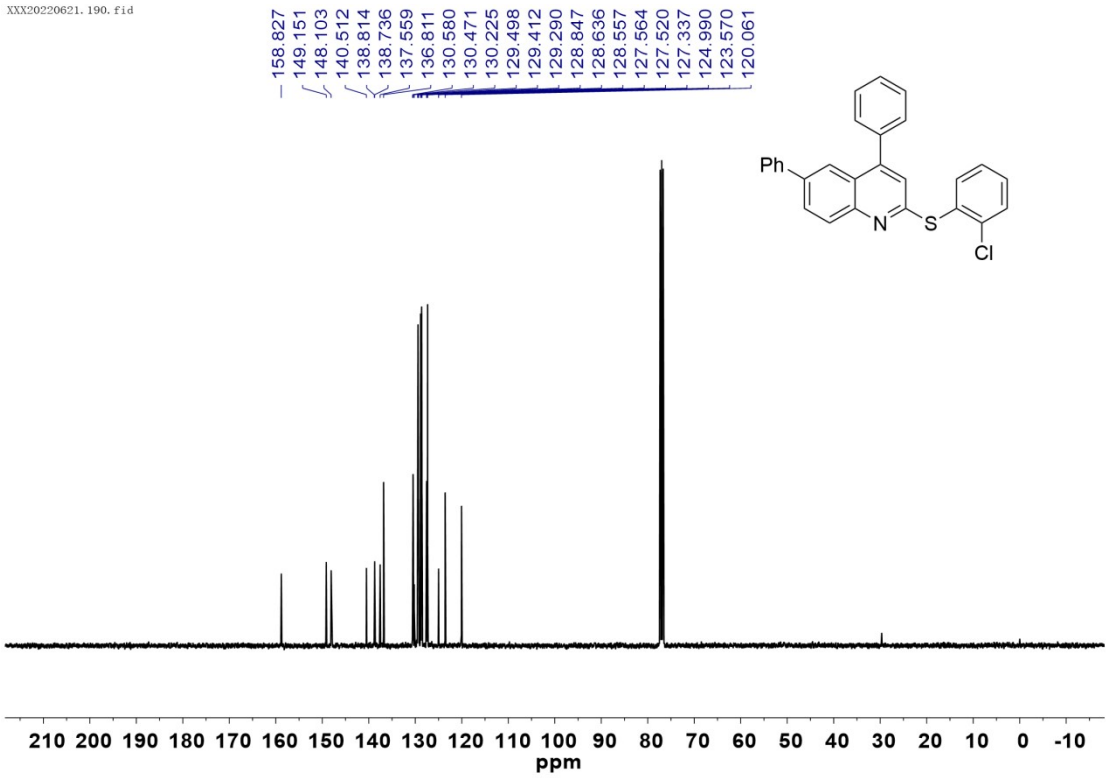
^{19}F NMR (376 MHz, $CDCl_3$) for **3am**



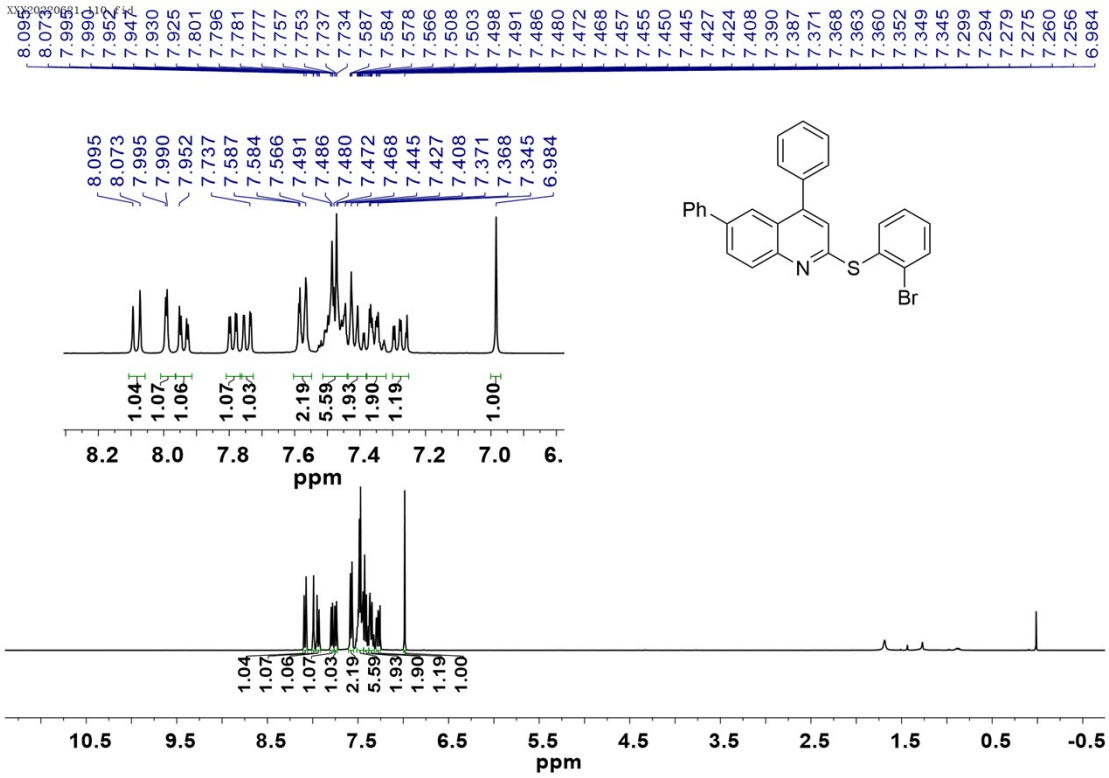
^{1}H NMR (400 MHz, $CDCl_3$) for **3an**



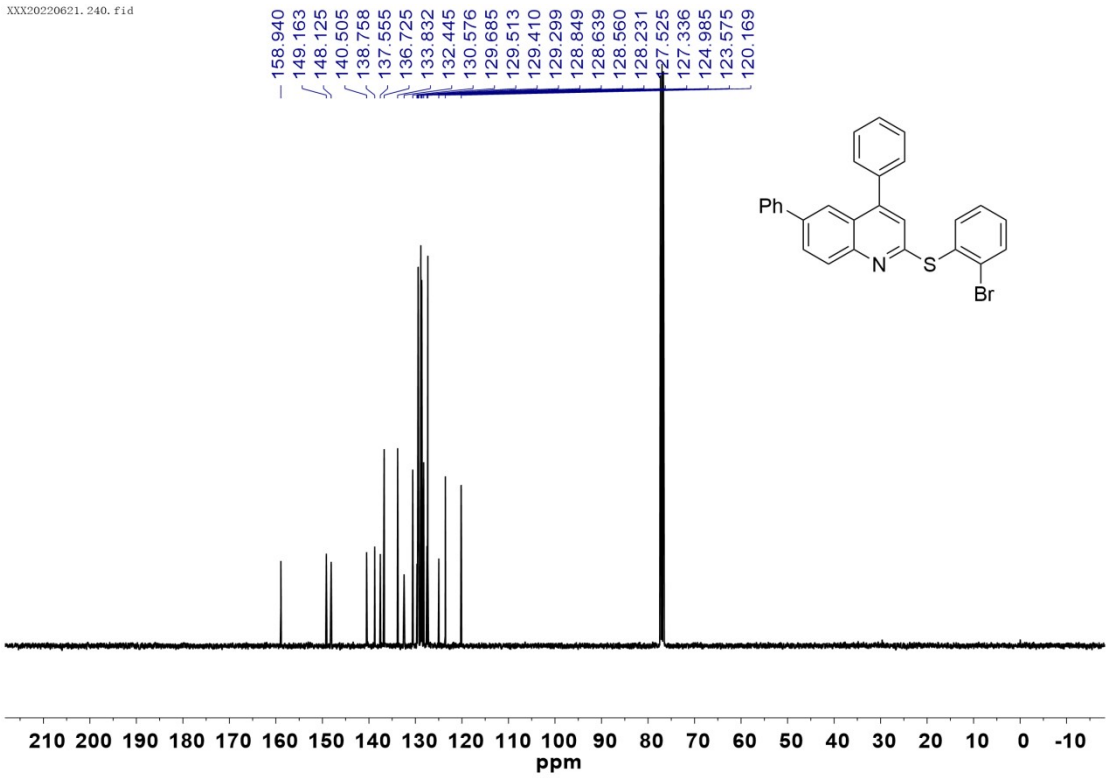
^{13}C NMR (100 MHz, $CDCl_3$) for **3an**



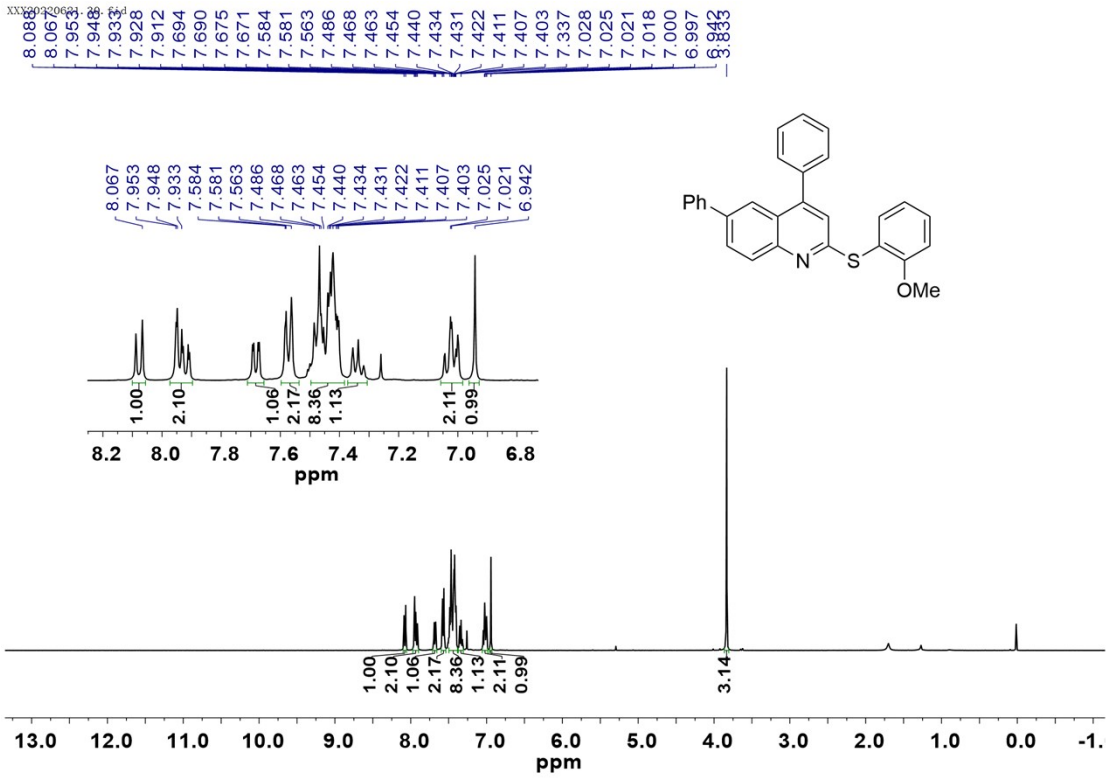
^{1}H NMR (400 MHz, $CDCl_3$) for **3ao**



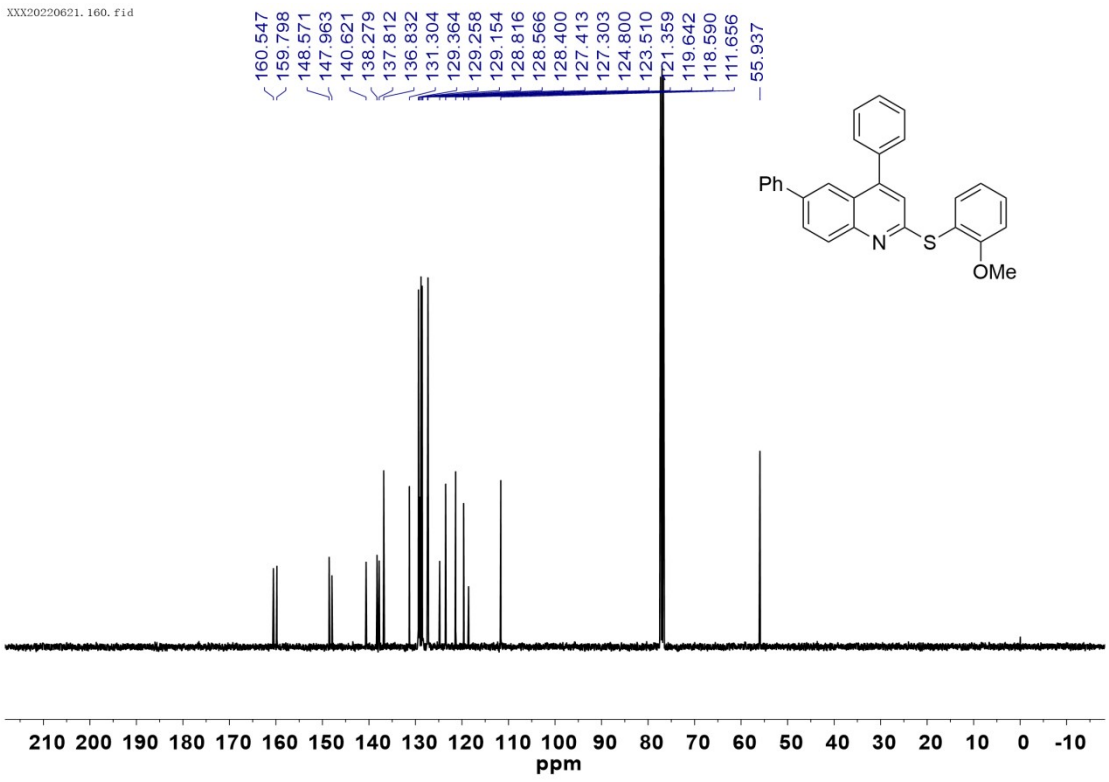
^{13}C NMR (100 MHz, $CDCl_3$) for **3ao**



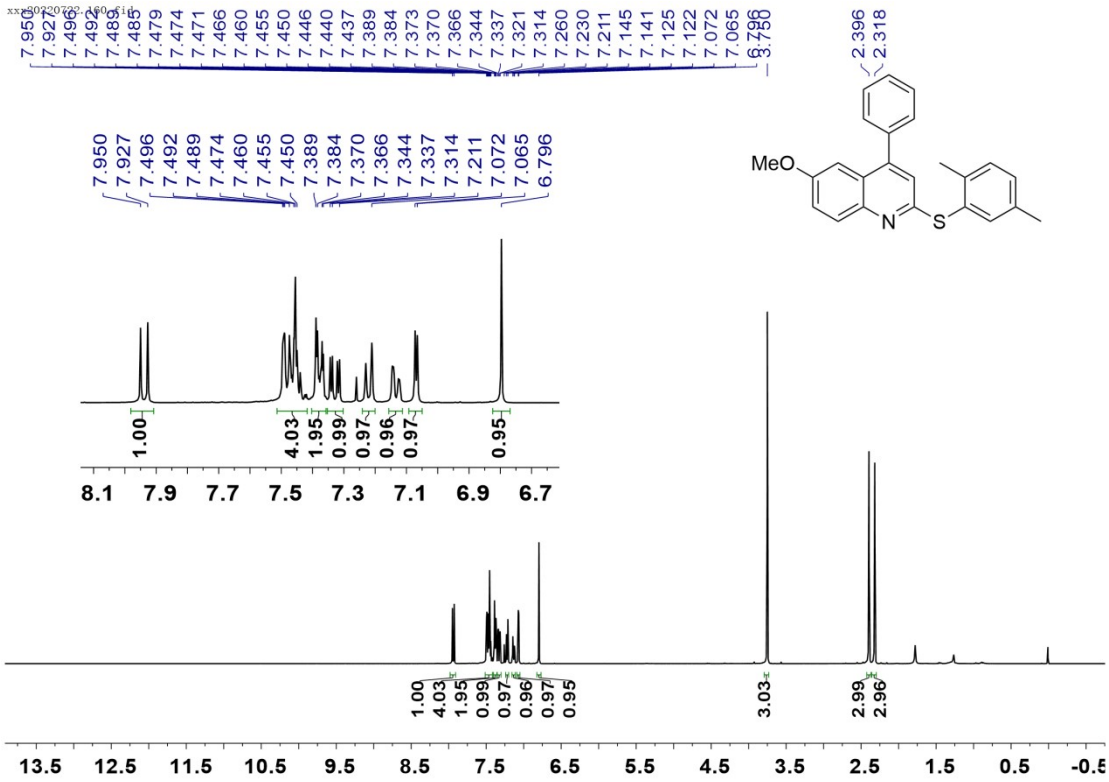
^{1}H NMR (400 MHz, $CDCl_3$) for **3ap**



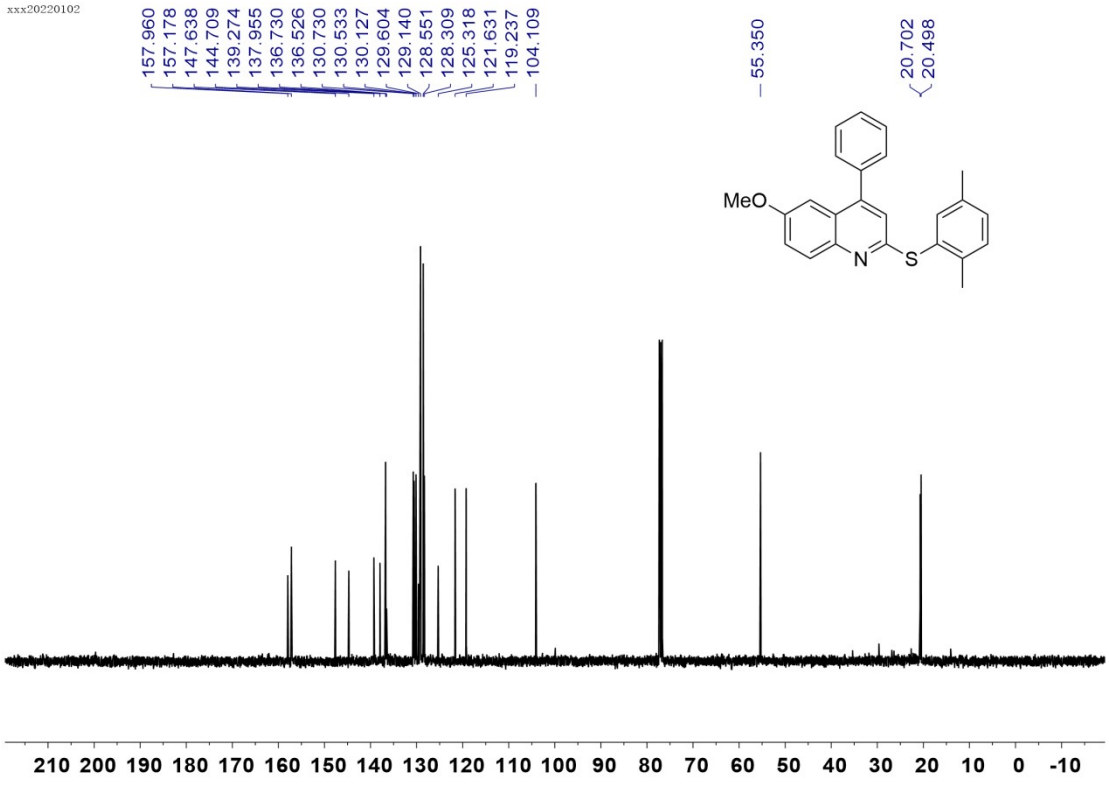
^{13}C NMR (100 MHz, $CDCl_3$) for **3ap**



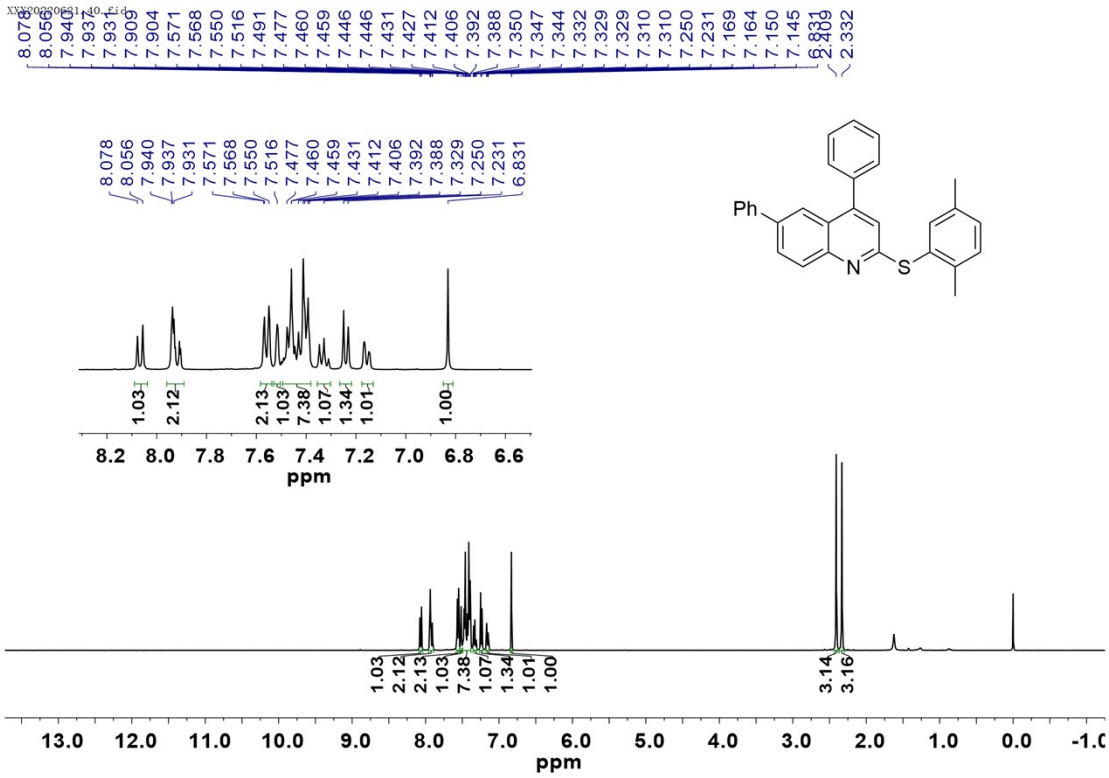
^{1}H NMR (400 MHz, $CDCl_3$) for **3aq**



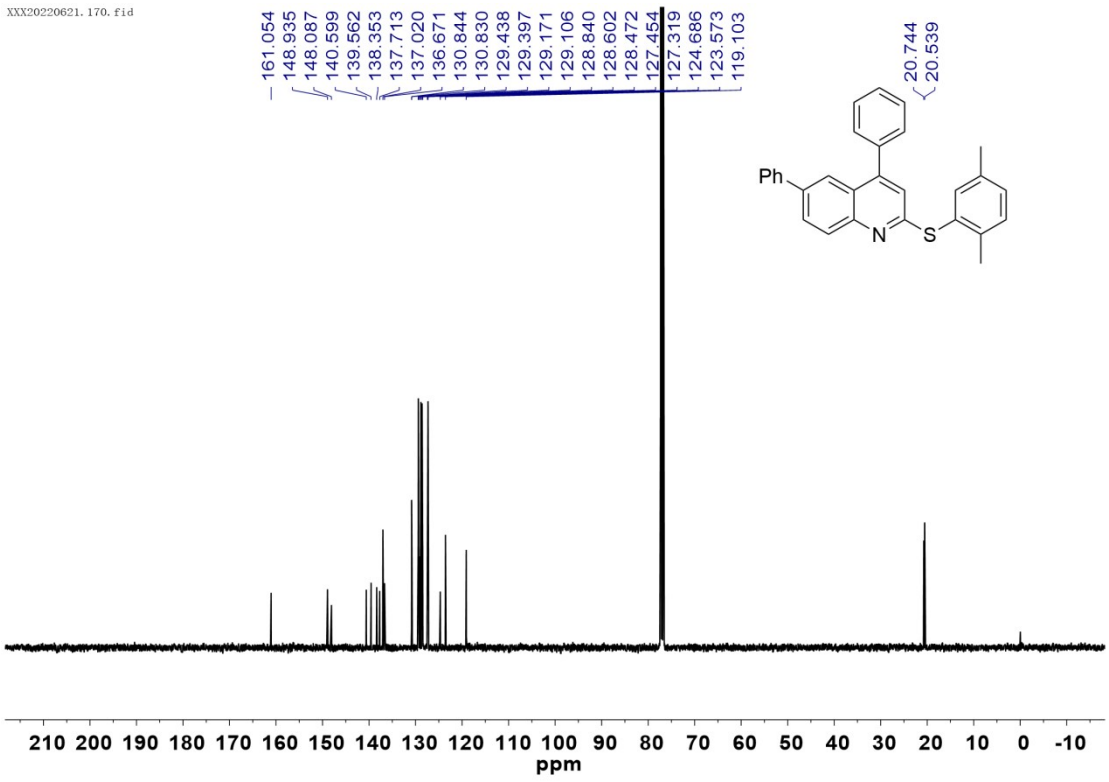
^{13}C NMR (100 MHz, $CDCl_3$) for **3aq**



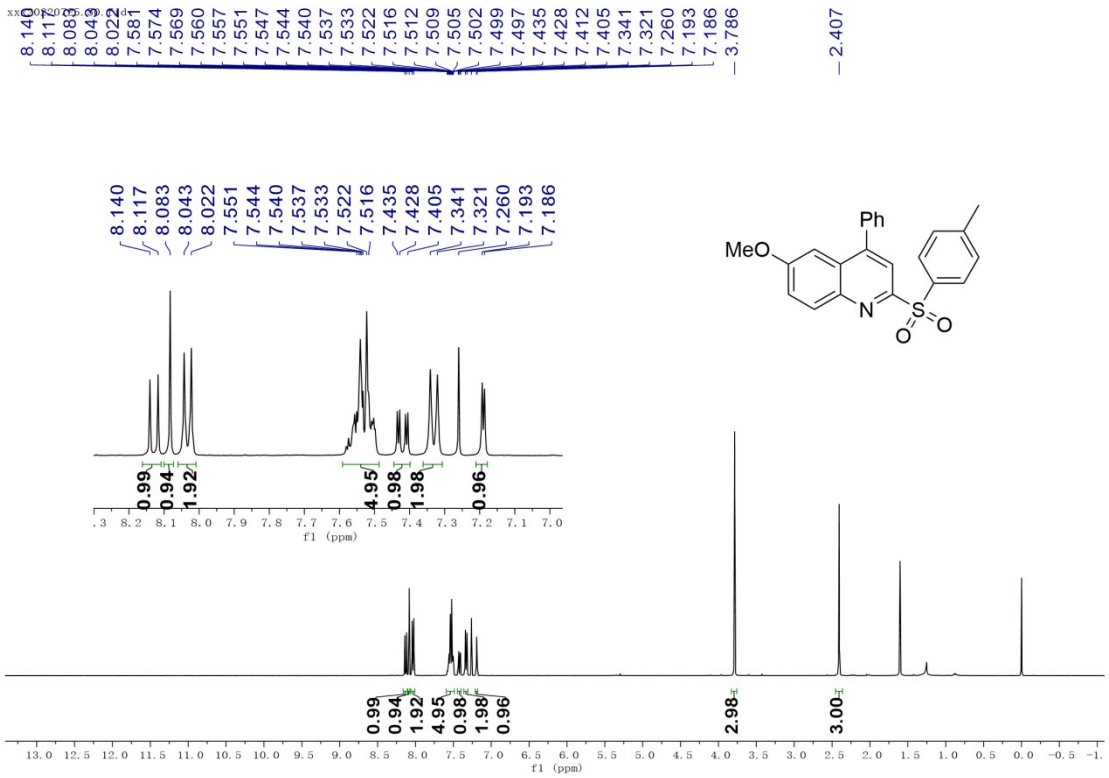
^{1}H NMR (400 MHz, $CDCl_3$) for **3ar**



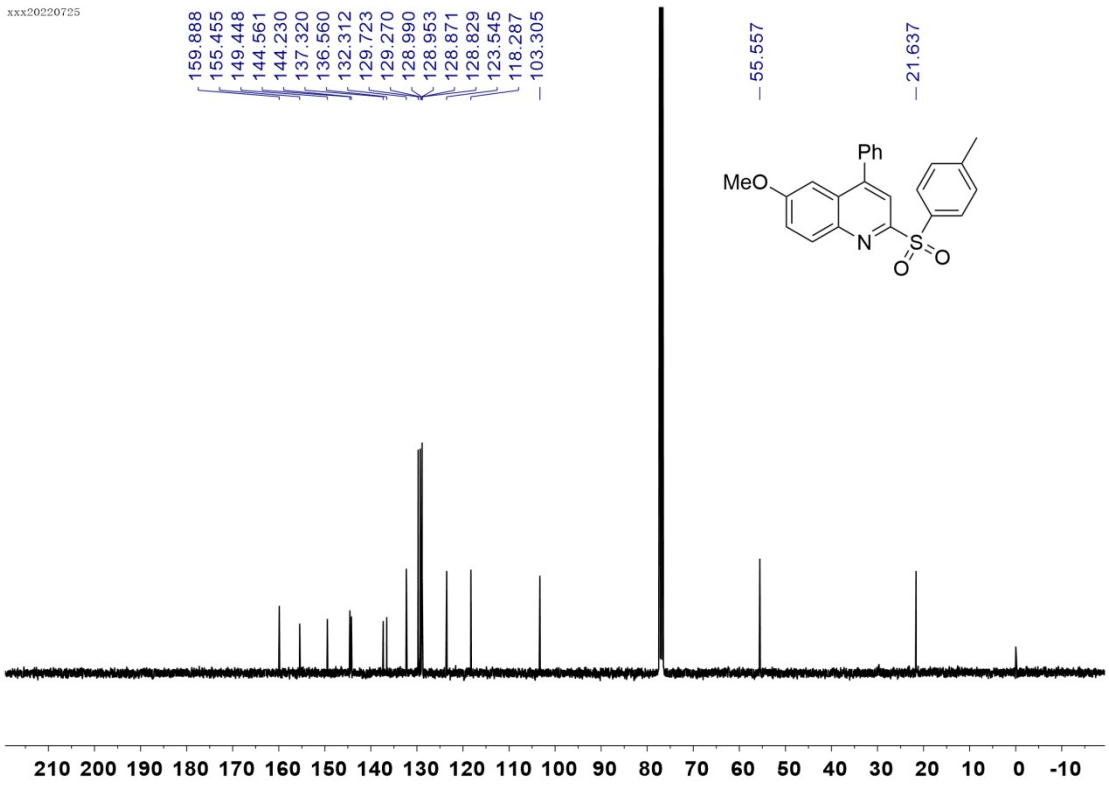
^{13}C NMR (100 MHz, $CDCl_3$) for **3ar**



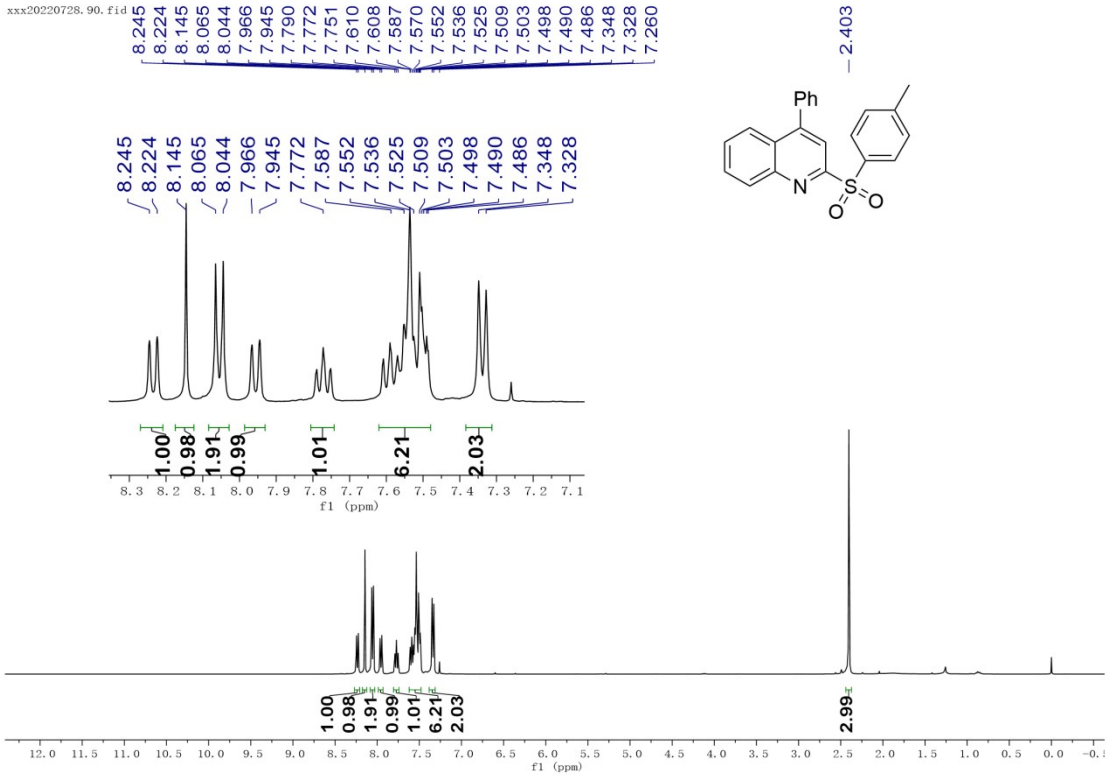
^{1}H NMR (400 MHz, $CDCl_3$) for **4a**



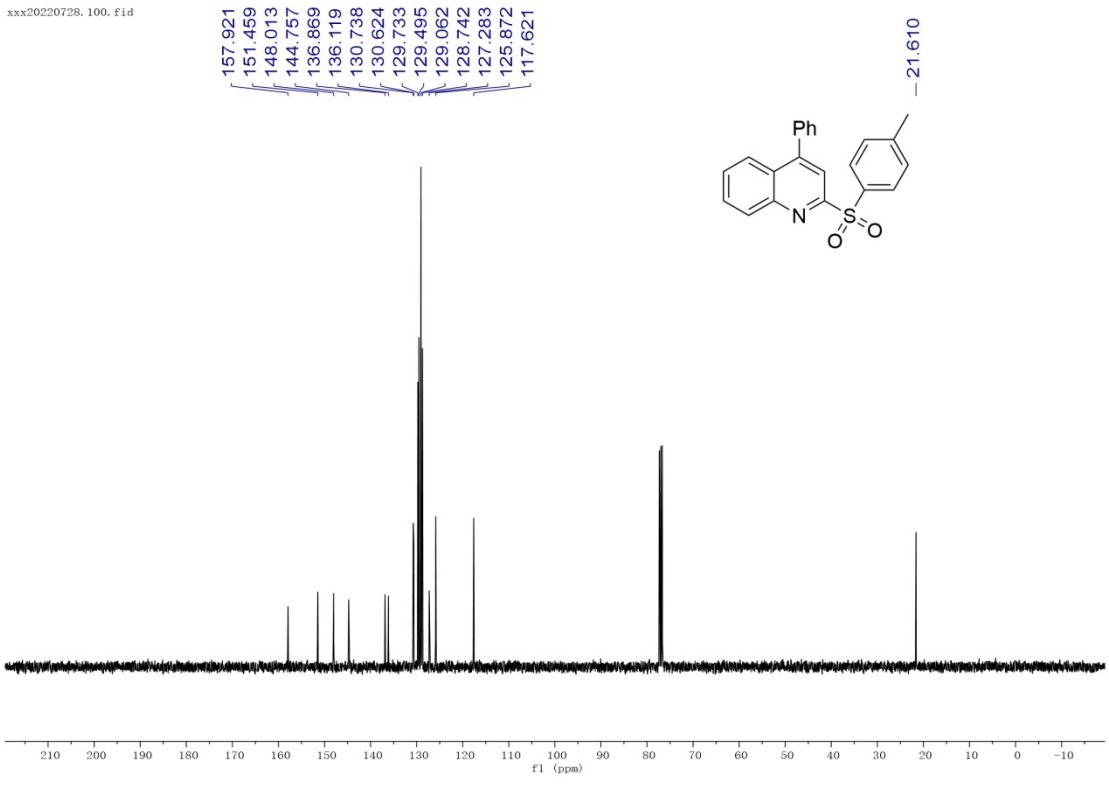
^{13}C NMR (100 MHz, $CDCl_3$) for **4a**



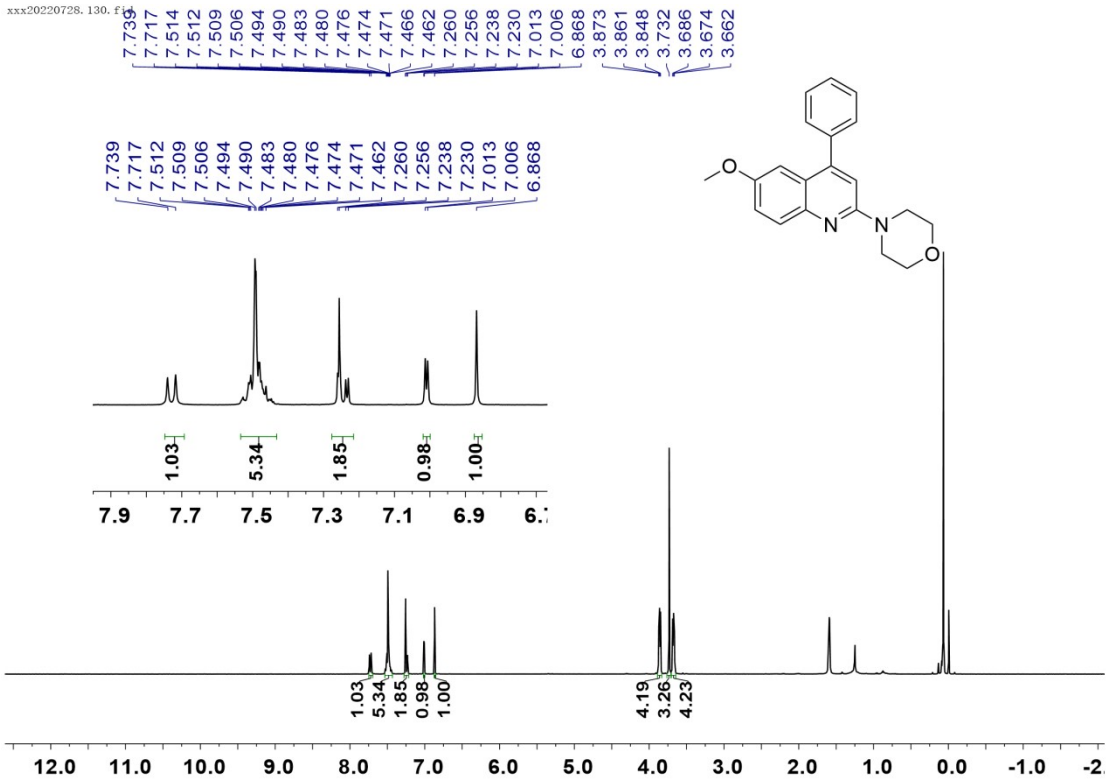
^{1}H NMR (400 MHz, $CDCl_3$) for **4b**



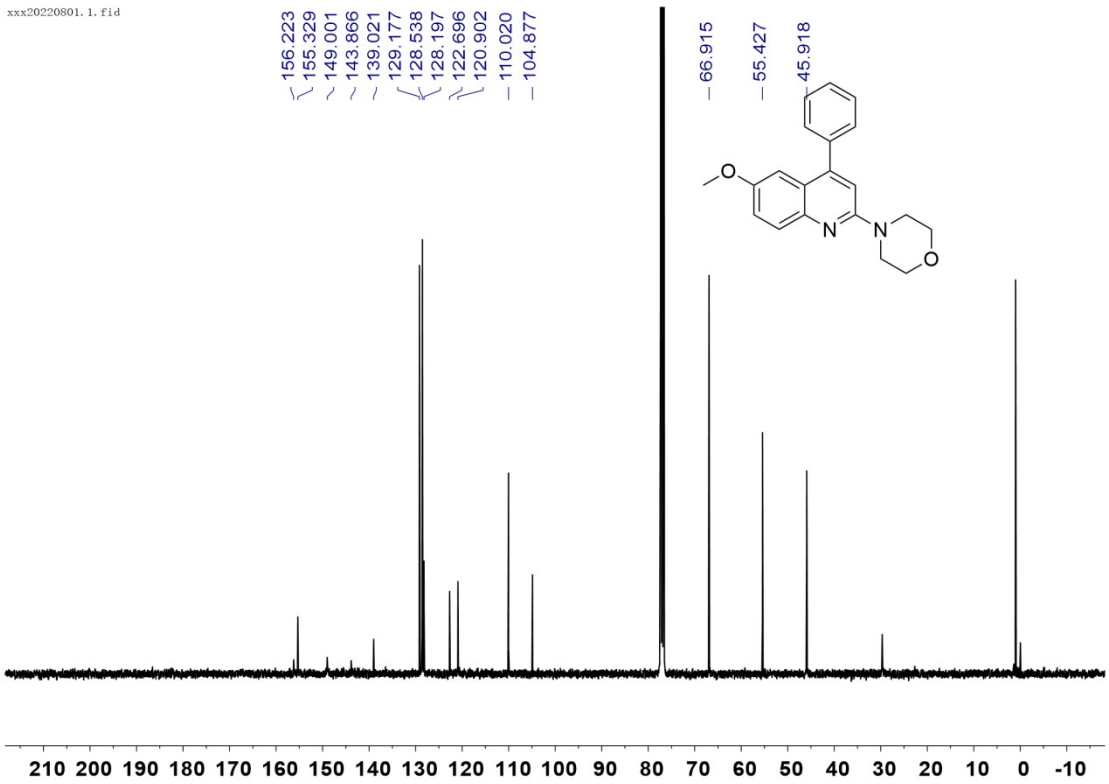
^{13}C NMR (100 MHz, $CDCl_3$) for **4b**



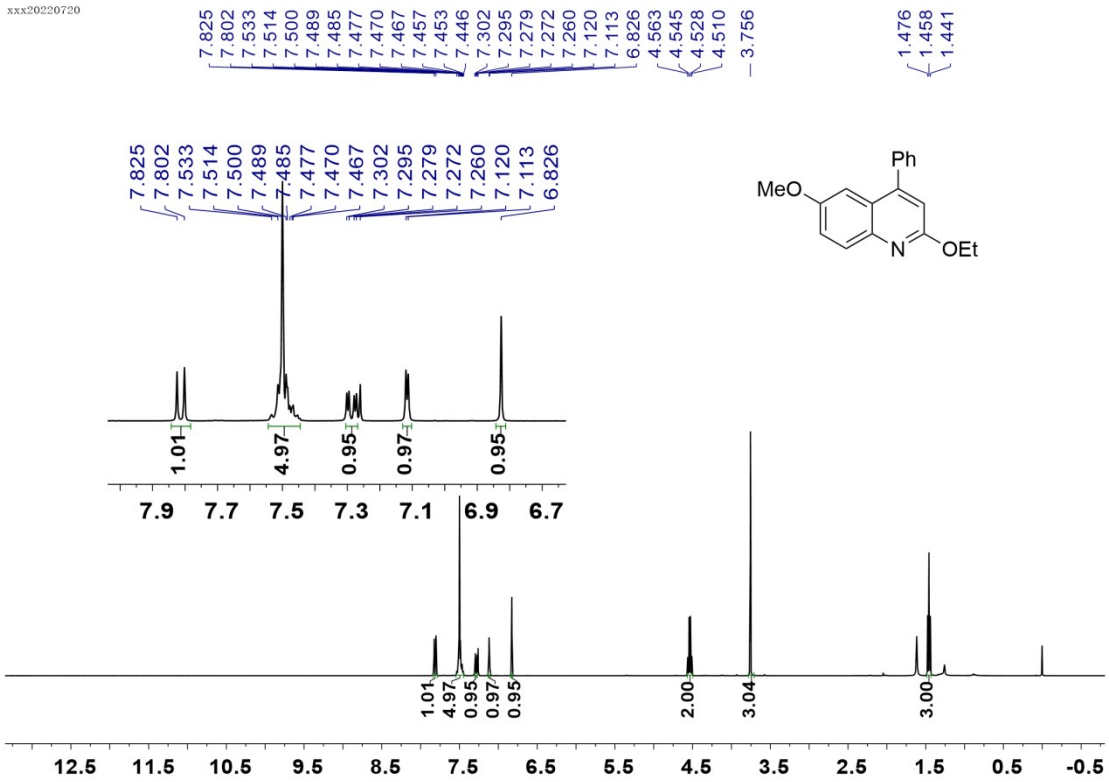
^{1}H NMR (400 MHz, $CDCl_3$) for **5**



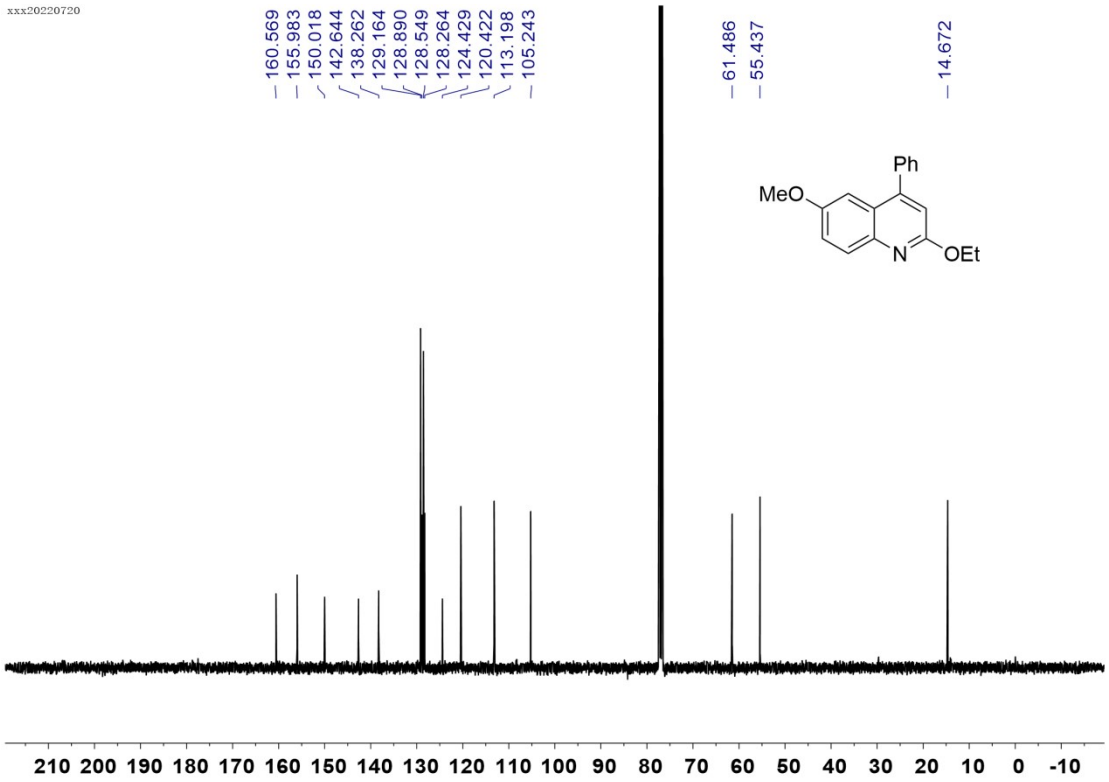
^{13}C NMR (100 MHz, $CDCl_3$) for **5**



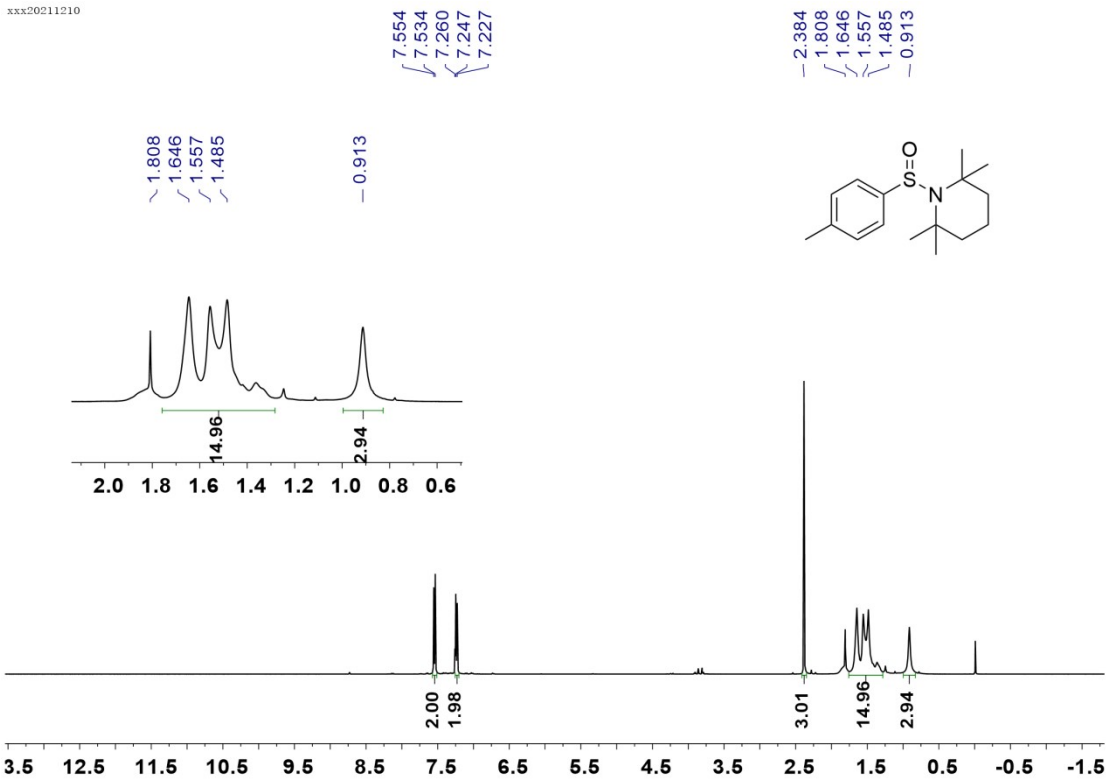
^{1}H NMR (400 MHz, $CDCl_3$) for **6**



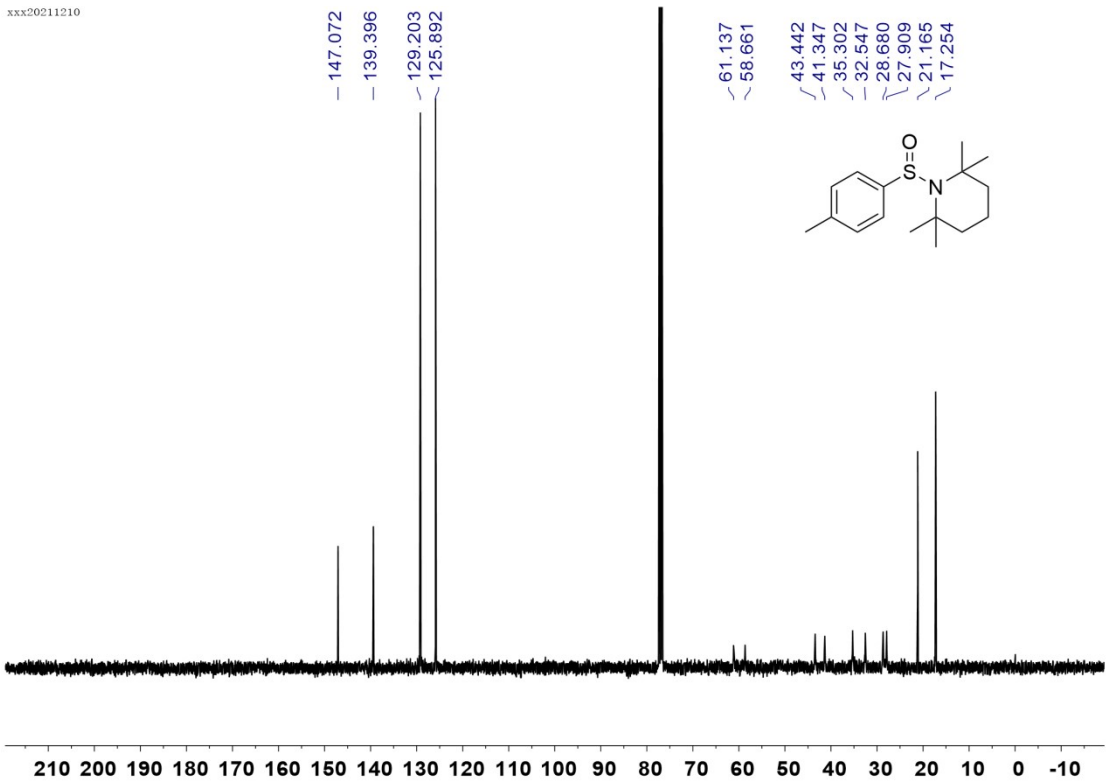
^{13}C NMR (100 MHz, $CDCl_3$) for **6**



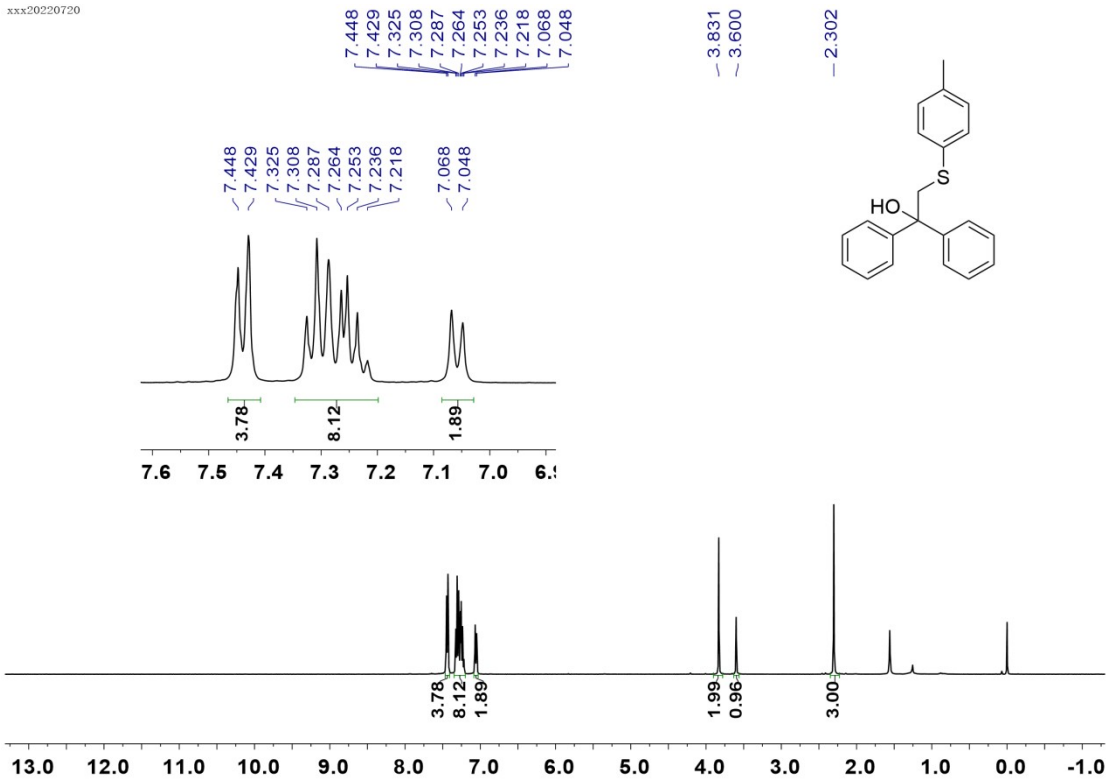
^{1}H NMR (400 MHz, $CDCl_3$) for **7**



^{13}C NMR (100 MHz, $CDCl_3$) for **7**



^{1}H NMR (400 MHz, $CDCl_3$) for **9**



^{1}H NMR (400 MHz, $CDCl_3$) for **10**