SUPPORTING INFORMATION

Base-Controlled Chemoselectivity Reaction of Vinylanilines with Isothiocyanates for Synthesis of Quinolino-2-thione and 2-Aminoquinoline derivatives

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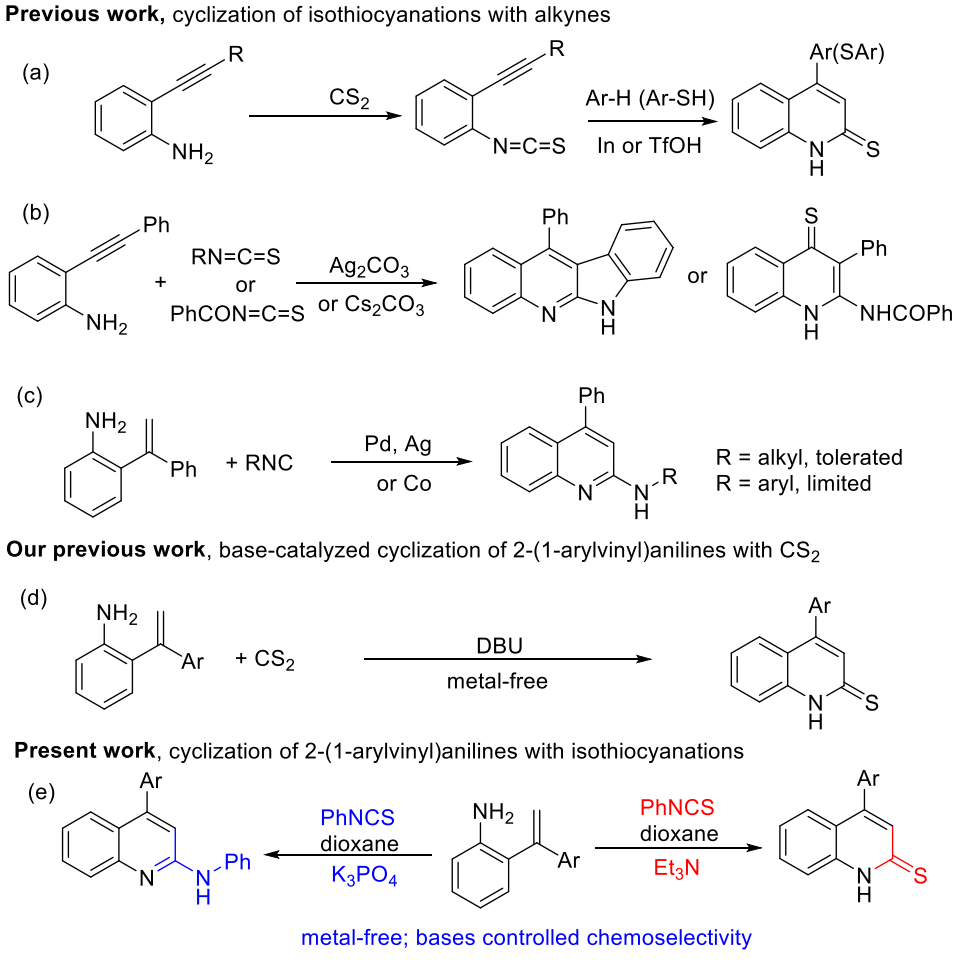
Experimental

1.1. General information

^{1}H NMR and ^{13}C NMR data analyses were performed with a Varian Mercury plus-400 and Agilent 600 MHz DD2 instruments unless otherwise specified. $CDCl_3$ and DMSO-d_6 as solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectrum as 0.00 ppm. The data of ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. Chemical shift for ^{13}C NMR spectra were recorded in ppm from TMS using the central peak of $CDCl_3$ (77.0 ppm) as the internal standard. ^{19}F NMR spectra were recorded on a Varian Mercury 400 plus instrument. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Melting points were measured with an XT-4 apparatus. High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltonics APEX II 47e and Orbitrap Elite mass spectrometer. Column chromatography was generally performed on silica gel (200-300 mesh) and TLC analyses were conducted on silica gel GF254 plates. All reagents were directly used from purchased without any further purification unless otherwise specified.

1.2 Scheme S-1. Roads to quinoline derivatives from arylisothiocyanates and alkynes/alkenes.

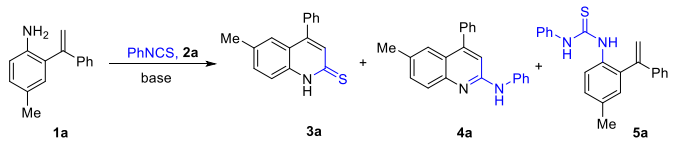


Scheme S-1. Roads to quinoline derivatives from arylisothiocyanates and alkynes/alkenes.

1.3 Optimization of thio-lactamization of 2-(1-arylvinyl)anilines with CS_2

We first explored the solvent effects in the cyclization thio-lactamization of 2-(1-arylvinyl)aniline (**1a**) with phenyl isothiocyante (**2a**) employing catalytical amount of Et_3N as base-catalyst (Supporting Informations, Table S-1, entries 1-6). The desired product **3a** was obtained with excellent selective in 94% and 93% yield in DSMO and dioxane, respectively (entries 1 and 2). The use of THF and DMF lowered selectivity, along with forming aminoquinoline (**4a**) and trance amount of thiourea (**5a**). Surprisingly, the regioselectivity and conversion were terribly deduced when MeCN and EtOH were employed as solvents, without offering the product **3a** (entries 5 and 6). In addition, selective production of **3a** was also obtained in the case of using other bases such as DBU and *t*-BuONa; nevertheless, formation of **4a** and slightly low yield was observed (entries 7 and 8). The use of Cs_2CO_3 as base resulted in a clear drop in yield (entry 9). In contrast, use of excess amounts of bases favoured the formation of **4a** (entries 11-14 vs entries 1-9). We found that the chemoselectivity was completely reversed when 2 equivalents of K_3PO_4 were employed as base in dioxane for 12 h, solely offering the product **4a** in 84% yield with excellent chemo-selectivity (entry 13). Evaluation of alternative solvents or bases gave a visible effect, and both of lower selectivity and lower yield were observed (entries 14-18). The reaction stopped completely when it was carried out in EtOH solvent (entry 18).

Table S-1. Optimization of thio-lactamization of 2-(1-arylvinyl)anilines with CS_2[a]



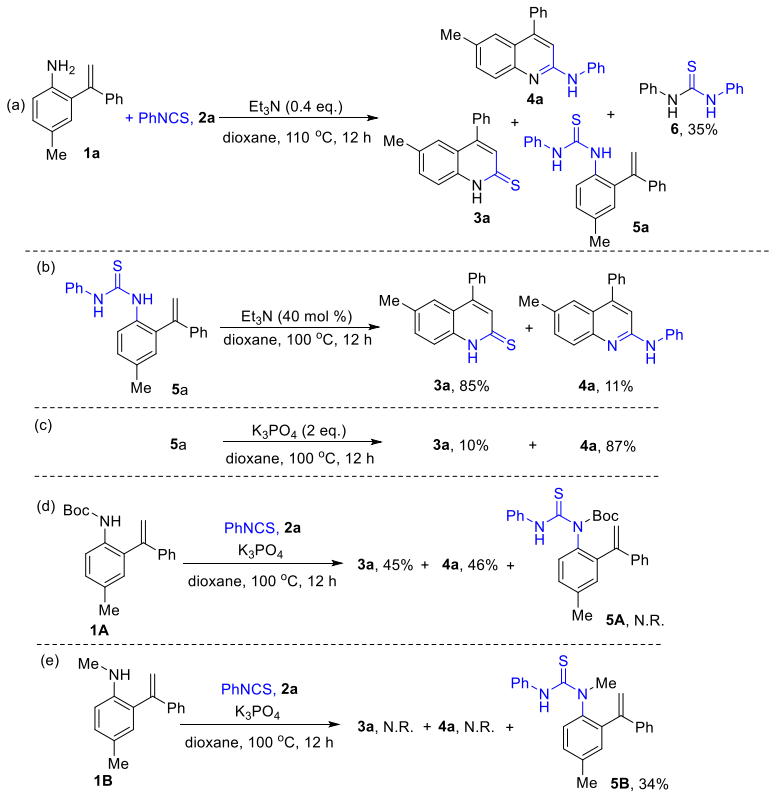
entry	Catalyst (eq.)/ pKa (in water)	Solvent	Solvent pKa	Temp. (°C)	**3a**/Yield (%)[b]	**4a**/Yield (%)[b]	**5a**/Yield (%)[b]
1	NEt_3 (0.4)/11	DMSO	35	140	94	trace	trace
2	NEt_3 (0.4)/11	dioxane	10 (18% H_2O)	110	93	trace	trace
3	NEt_3 (0.4)/11	THF	-	65	84	9	trace
4	NEt_3 (0.4)/11	DMF	30	140	77	16	trace
5	NEt_3 (0.4)/11	CH_3CN	25	80	ND	17	11
6	NEt_3 (0.4)/11	EtOH	16	80	ND	ND	ND
7	DBU (0.4)/12	DMF	30	140	88	5	trace
8	*t*-BuONa (0.4)/20	DMF	30	100	65	12	6
9	Cs_2CO_3 (0.4)/12	DMF	30	140	ND	10	trace
10	K_3PO_4 (0.4)/13	dioxane	10 (18% H_2O)	100	45	35	10
11	NEt_3 (2.0)/11	dioxane	10 (18% H_2O)	100	53	18	15
12	Cs_2CO_3 (2)/12	dioxane	10 (18% H_2O)	100	11	48	8
13	K_3PO_4 (2.0)/13	dioxane	10 (18% H_2O)	100	trace	84	trace
14	*t*-BuONa (2.0)/20	dioxane	10 (18% H_2O)	100	trace	62	trace

15	K_3PO_4 (2.0)/13	THF	-	100	30	53	12
16	K_3PO_4 (2.5)/13	CH_3CN	25	100	15	56	12
17	K_3PO_4 (2.5)/13	toluene	41	100	36	55	10
18	K_3PO_4 (2.0)/13	EtOH	16	100	N.R.	N.R.	N.R.

[a] Performed with **1a** (0.5 mmol) and phenyl isothiocyante **2a** (0.9 mmol), in solvent (3.0 mL), 12 h. [b] Yield of isolated products.

1.4 Controlled experiments

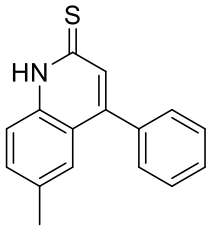
To test whether the products are formed from thiourea product via addition of vinylaniline into isothiocyante, the addition product **5a** was synthesized and tested under the optimized conditions. As expected, quinolino-2-thione (**3a**) formed in 85% yield by losing one molecular phenylamine catalyzed by Et_3N (Scheme S-2b), meanwhile, in the presence of K_3PO_4, desulfurization is more favorable to give **4a** in 87% yield (Scheme S-2c). The fact that formation of desired product was observed suggests that the reaction through cyclization of phenylamino-1,2-dihydroquinoline-2-thiol or 2-vinylphenylcarbodiimide derived from thiourea is more likely. When N-(*t*-butyloxycarbonyl) substituted vinylaniline derivatives **1A** was used as substrate reacting with **2a** in the presence of 2 equivalents of K_3PO_4, the deprotected product **3a** and **4a** was obtained (Scheme S-2d). No reaction occurred when N-methyl protected 2-(1-arylvinyl)aniline (**1B**) was used, while addition reaction proceeded to afford a thiourea **5B** in 34% yield (Scheme S-2e).



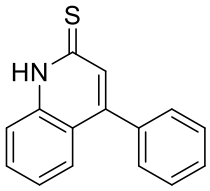
Scheme S-2. Controlled experiments

1.5 General procedure for the synthesis of 2-(1-aryvinyl)aniline 1. Starting materials **1** was prepared according to the reported procedures.[1] 1.0 g of montmorillonites K10 was added to a solution of phenylacetylene (1.0 g, 10.0 mmol) and *para*-toltfidine (1.1 g, 10.0 mmol) in the xylene (10.0 mL). The mixture was heated at the 140 °C under stirring for 5 hours. After cooling to room temperature, filtration, washing with diethyl ether and distillation of the solvents. The volatiles were removed in vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether 1:5) to give the corresponding products.

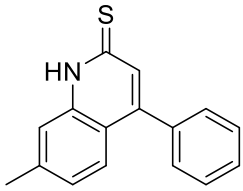
1.6 General procedure for the synthesis of 4-phenylquinoline-2(1H)-thione 3. Under an atmosphere of air, 2-(1-phenylvinyl) aniline **1a** (0.5 mmol, 0.104 g), PhNCS **2a** (1.2 eq. 0.6 mmol, 0.081 g), Et_3N (40 mol%, 0.040 g) were added to a tube. Dixoane (3.0 mL) was added by dropper and the mixture was stirred for 12 h at 110 °C and the reaction was monitored by TLC analysis. Then, 2.0 mL ammonium chloride were added to the mixture to quench the reaction and extracted with ethyl acetate (3×25 mL). The combined organic layers were washed with aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and the volatiles were removed in vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether 1:5) to give the corresponding products. All of the products **3b-u** were synthesized according to above described procedure.



6-Methyl-4-phenylquinoline-2(1H)-thione (3a). Yellow solid (93%, 0.117 g): mp 215-217 °C. IR (KBr) 3435, 1713, 1649, 1362, 1035, 1007, 825 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ: 13.68 (s, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.54 - 7.51 (m, 3H), 7.48-7.46 (m, 3H), 7.25 (s, 1H), 7.08 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 184.48, 150.91, 143.17, 141.21, 138.83, 137.89, 136.13, 134.21, 134.00, 130.40, 130.38, 126.40, 121.82, 26.01. HRMS (ESI^+) m/z: Calcd for $C_{16}H_{14}NS$ 252.0841 $[M+H]^+$, Found 252.0843.

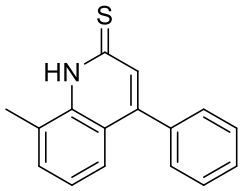


4-Phenylquinoline-2(1H)-thione (3b). Yellow solid (87%, 0.103 g): mp 187-188 °C. IR (KBr) 3055, 1745, 1651, 1116, 1045, 823 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.75 (s, 1H), 7.63 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.49 (dd, *J* = 4.8, 1.8 Hz, 3H), 7.40 - 7.38 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 158.93, 149.16, 146.84, 136.76, 132.34, 131.04, 130.32, 129.33, 128.96, 128.80, 125.98, 124.82, 118.21.HRMS (ESI^+) m/z: Calcd for $C_{l5}H_{12}NS$ 238.0685 $[M+H]^+$, Found 238.0684.

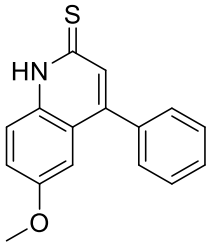


7-Methyl-4-phenylquinoline-2(1H)-thione (3c). Yellow solid (85%, 0.106 g): mp 252-254 °C. ^1H NMR (600 MHz, DMSO-d_6) δ: 13.52 (s, 1H), 7.52 (d, *J* = 7.2 Hz, 3H), 7.46 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.39 (d, *J* = 9.0

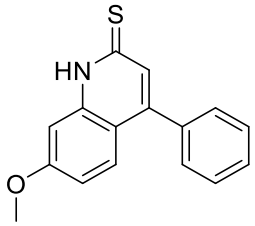
Hz, 1H), 7.21 (d, *J* = 2.4 Hz, 1H), 6.97 (s, 1H), 6.93 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 180.55, 161.93, 146.59, 141.96, 136.58, 129.48, 129.23, 129.19, 128.72, 127.98, 116.05, 114.28, 99.23, 56.05. HRMS (ESI$^+$) m/z: Calcd for $C_{16}H_{14}NS$ 252.0841 $[M+H]^+$, Found 252.0842.



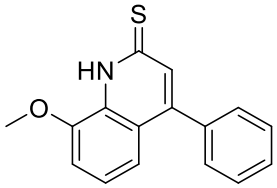
8-Methyl-4-phenylquinoline-2(1H)-thione (3d). Yellow solid (84%, 0.105 g): mp 185-187 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 13.01 (s, 1H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.53 - 7.47 (m, 6H), 7.27 - 7.23 (m, 1H), 7.03 (d, *J* = 3.0 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 177.34, 156.63, 147.48, 136.37, 131.39, 129.25, 129.16, 128.81, 128.80, 128.64, 121.15, 117.94, 107.50, 55.59. HRMS (ESI$^+$) m/z: Calcd for $C_{16}H_{14}NS$ 252.0841 $[M+H]^+$, Found 252.0844.



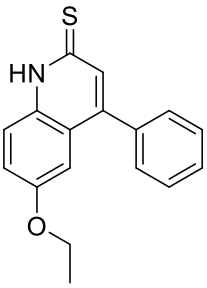
6-Methoxy-4-phenylquinoline-2(1H)-thione (3e). Yellow solid (90%, 0.120 g): mp 181-182 °C. IR (KBr) 1725, 1676, 1296, 1035, 1028, 822 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.75 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 4.0 Hz, 5H), 7.36 (dd, *J* = 12, 4.0 Hz, 1H), 7.15 (s, 1H), 6.92 (d, *J* = 2.8 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 178.38, 156.09, 145.83, 136.42, 135.23, 131.70, 129.57, 129.32, 129.18, 122.54, 121.16, 118.72, 107.34, 55.76. HRMS (ESI$^+$) m/z: Calcd for $C_{16}H_{14}NOS$ 268.0791 $[M+H]^+$, Found 268.0793.



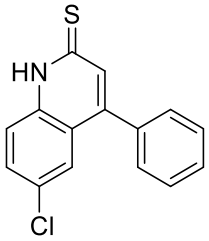
7-Methoxy-4-phenylquinoline-2(1H)-thione (3f). Yellow solid (85%, 0.113 g): mp 256-258 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.10 (s, 1H), 7.57 - 7.50 (m, 5H), 7.30 - 7.28 (m, 2H), 7.19 (s, 1H), 7.08 (dd, *J* = 7.2, 2.4 Hz, 1H), 4.00 (s, 3H).^{13}C NMR (150 MHz, DMSO-d_6) δ: 180.20, 146.42, 146.32, 136.37, 132.00, 130.39, 129.57, 129.25, 129.21, 124.84, 122.30, 118.00, 112.00, 56.89. HRMS (ESI$^+$) m/z: Calcd for $C_{16}H_{14}NOS$ 268.0791 $[M+H]^+$, Found 268.0790.



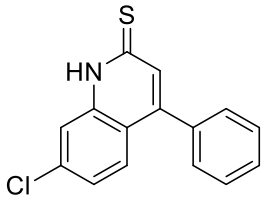
8-Methoxy-4-phenylquinoline-2(1H)-thione (3g). Yellow solid (83%, 0.110 g): mp 216-218 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.96 (s, 1H), 7.51 - 7.44 (m, 6H), 7.20 (d, *J* = 6.8 Hz, 2H), 7.04 (dd, *J* = 6.8, 2.4 Hz, 1H), 4.04 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 180.04, 147.14, 136.29, 131.97, 130.00, 129.10, 128.90, 128.65, 123.99, 118.45, 110.17, 56.21. HRMS (ESI$^+$) m/z: Calcd for $C_{16}H_{14}NOS$ 268.0791 $[M+H]^+$, Found 268.0794.



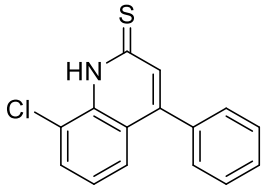
6-Ethoxy-4-phenylquinoline-2(1H)-thione (3h). Yellow solid (78%, 0.109 g): mp 159-162 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.68 (s, 1H), 7.65 (d, J = 6.0 Hz, 1H), 7.54 - 7.49 (m, 5H), 7.31 (dd, J = 6.0, 6.0 Hz, 1H), 7.10 (s, 1H), 6.85 (d, J = 3.0 Hz, 1H), 3.89 (q, J = 6.6 Hz, 2H), 1.25 (t, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 178.35, 155.37, 145.84, 136.43, 135.13, 131.63, 129.56, 129.32, 129.16, 122.58, 121.41, 118.69, 108.03, 63.87, 14.87. HRMS (ESI$^+$) m/z: Calcd for $C_{17}H_{16}NOS$ 282.0947 $[M+H]^+$, Found 282.0943.



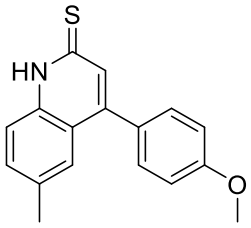
6-Chloro-4-phenylquinoline-2(1H)-thione (3i). Yellow solid (79%, 0.107 g): mp 213-215 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 4.0 Hz, 1H), 7.76 (s, 1H), 7.63 (dd, J = 8.0, 4.0 Hz, 1H), 7.50 - 7.48 (m, 3H), 7.39 (dd, J = 8.0, 4.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 158.94, 149.14, 146.86, 136.77, 132.33, 131.03, 130.33, 129.33, 128.96, 128.80, 125.98, 124.81, 118.21. HRMS (ESI$^+$) m/z: Calcd for $C_{15}H_{11}ClNS$ 272.0295 $[M+H]^+$, Found 272.0292.



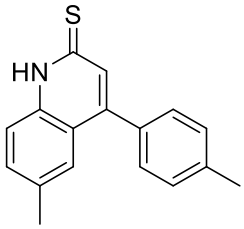
7-Chloro-4-phenylquinoline-2(1H)-thione (3j). Yellow solid (86%, 0.116 g): mp 243-245 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.96 (s, 1H), 7.73 (dd, J = 8.4, 1.2 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.45 - 7.43 (m, 3H), 7.35 - 7.32 (m, 3H), 7.05 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 180.19, 144.95, 142.11, 139.35, 135.18, 131.92, 131.44, 128.57, 128.54, 128.33, 127.49, 119.10, 116.76. HRMS (ESI$^+$) m/z: Calcd for $C_{15}H_{11}ClNS$ 272.0295 $[M+H]^+$, Found 272.0297.



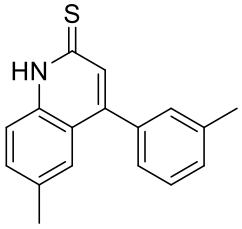
8-Chloro-4-phenylquinoline-2(1H)-thione (3k). Yellow solid (77%, 0.104 g): mp 187-188 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.73 (s, 1H), 7.68 (d, J = 2.4 Hz, 1H), 7.54 - 7.51 (m, 3H), 7.48 - 7.45 (m, 3H), 7.30 (dd,J = 1.8, J = 8.4 Hz, 1H), 7.10 (d, J = 1.2 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 186.36, 150.52, 145.49, 140.98, 140.64, 136.39, 134.43, 134.03 (d, J = 8.6 Hz), 133.16, 129.56, 125.25, 120.93.HRMS (ESI$^+$) m/z: Calcd for $C_{l5}H_{11}ClNS$ 272.0295 $[M+H]^+$, Found 272.0297.



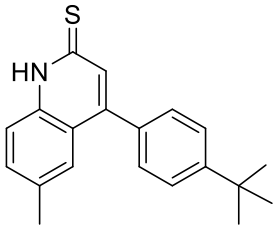
4-(4-Methoxyphenyl)-6-methylquinoline-2(1H)-thione (3l). Yellow solid (78%, 0.127 g): mp 192-194 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.91 (d, *J* = 9.0 Hz, 1H), 7.52 - 7.46 (m, 8H), 7.14 (s, 1H), 2.72 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 179.69, 146.16, 143.90, 138.44, 134.00, 133.76, 133.07, 131.27, 129.17 (d, *J* = 10.1 Hz), 125.69, 121.66, 117.07, 35.34, 21.27. HRMS (ESI^+) m/z: Calcd for $C_{17}H_{16}NOS$ 282.0947 $[M+H]^+$, Found 282.0950.



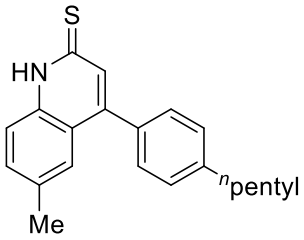
6-Methyl-4-(p-tolyl)quinoline-2(1H)-thione (3m). Yellow solid (85%, 0.112 g): mp 194-196 °C. IR (KBr) 2924, 1722, 1646, 1367, 1120, 833 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 8.4 Hz, 1H), 7.72 (s, 1H), 7.60 (d, *J* = 1.6 Hz, 1H), 7.51 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.31 - 7.27 (m, 4H), 2.42 (d, *J* = 1.6 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 157.74, 149.39, 147.03, 138.47, 136.21, 134.74, 132.22, 129.39, 129.25, 128.42, 125.23, 124.80, 117.36, 21.74, 21.28. HRMS (ESI^+) m/z: Calcd for $C_{17}H_{16}NS$ 266.0998 $[M+H]^+$, Found 266.1000.



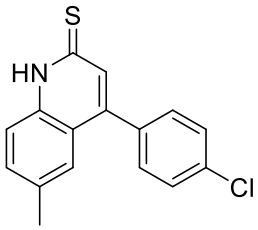
6-Methyl-4-(m-tolyl)quinoline-2(1H)-thione (3n). Yellow solid (88%, 0.116 g): mp 242-244 °C. IR (KBr) 3207, 3004, 1691, 1593, 1535, 1495, 1315, 1028, , 823 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 12.99 (s, 1H), 7.62 (d, *J* = 9.0Hz, 1H), 7.41 (dd, *J* = 18.0, 10.8Hz, 4H), 7.32 (d, *J* = 7.2Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 2.45 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 178.62, 148.02, 138.54, 137.77, 136.36, 134.67, 132.83, 131.00, 129.78, 129.56, 128.49, 126.10 (d, *J* = 2.7 Hz), 122.49, 116.41, 21.40. HRMS (ESI^+) m/z: Calcd for $C_{17}H_{16}NS$ 266.0998 $[M+H]^+$, Found 266.0996.



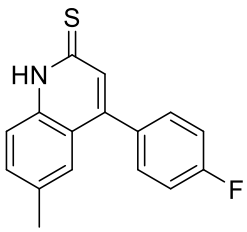
4-(4-(*Tert*-butyl)phenyl)-6-methylquinoline-2(1H)-thione (3o). Yellow solid (85%, 0.130 g): mp 253-255 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 13.34 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.48 (s, 1H), 7.46 (s, 1H), 7.11 (t, *J* = 8.4 Hz, 3H), 2.37 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 178.34, 152.30, 147.91, 137.91, 134.62, 133.43, 132.78, 130.97, 128.80, 126.11, 125.66, 122.47, 116.54, 34.81, 31.31, 21.35. HRMS (ESI^+) m/z: Calcd for $C_{20}H_{22}NS$ 322.1624 $[M+H]^+$, Found 322.1626.



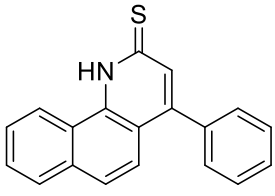
6-Methyl-4-(4-pentylphenyl)quinoline-2(1H)-thione (3p). Yellow solid (89%, 0.143 g): mp 215-217 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 13.0 (s, 1H), 7.64 - 7.61 (m, 1H), 7.45 (d, *J* = 10.2 Hz, 2H), 7.40 (m, 3H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.78 - 2.61 (m, 1H), 2.36 (s, 2H), 1.79 - 1.65 (m, 1H), 1.38 (dd, *J* = 7.4, 3.6 Hz, 2H), 0.97 - 0.86 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 178.55, 147.97, 144.19, 137.80, 134.62, 133.63, 132.78, 130.97, 128.93, 128.72, 126.15, 122.48, 116.42, 35.77, 31.58, 31.01, 22.54, 21.33, 14.03. HRMS (ESI^+) m/z: Calcd for $C_{21}H_{24}NS$ 322.1624 $[M+H]^+$, Found 322.1627.



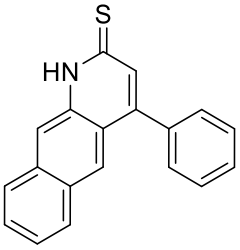
4-(4-Chlorophenyl)-6-methylquinoline-2(1H)-thione (3q). Yellow solid (88%, 0.125 g): mp 240-243 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 13.16 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.46 - 7.32 (m, 4H), 7.35 (s, 1H), 7.22 (t, *J* = 8.4 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 178.55, 164.03, 162.37, 146.76, 137.81, 134.90, 133.00, 132.33 (d, *J* = 3.4 Hz), 131.18, 130.79 (d, *J* = 8.4 Hz), 125.78, 122.37, 116.52, 115.97, 115.82, 21.35. HRMS (ESI^+) m/z: Calcd for $C_{16}H_{13}ClNS$ 286.0452 $[M+H]^+$, Found286.0455.



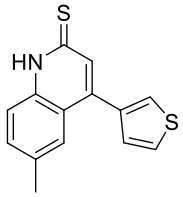
4-(4-Fluorophenyl)-6-methylquinoline-2(1H)-thione (3r). Yellow solid (78%, 0.104 g): mp 230-233 °C. **¹**H NMR (600 MHz, $CDCl_3$) δ 11.86 (s, 1H), 7.51-7.34 (m, 8H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 179.73, 144.93, 135.27, 134.28 (d, *J* = 66.0 Hz), 133.23, 131.46, 131.17, 129.30, 125.49, 121.48, 117.08, 21.23. ^{19}F NMR (CDCl3, 376.5 MHz) δ -112.22 - (-)112.27 (m). HRMS (ESI^+) m/z: Calcd for $C_{16}H_{13}FNS$ 270.0747 $[M+H]^+$, Found 270.0745.



4-Phenylbenzo[h]quinoline-2(1H)-thione (3s). Yellow solid (90%, 0.129 g): mp 180-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.24 (d, *J* = 12.0 Hz, 1H), 7.90 (s, 1H), 7.84 (d, *J* = 11.6 Hz, 1H), 7.17 - 7.56 (m, 5H), 7.44 (s, 5H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 157.37, 149.56, 146.89, 137.96, 133.59, 130.90, 129.58, 128.53, 128.48, 128.42, 127.40, 127.16, 127.02, 125.21, 122.73 (d, *J* = 30.0 Hz), 118.73. HRMS (ESI^+) m/z: Calcd for $C_{19}H_{14}NS$ 288.0841 $[M+H]^+$, Found288.0843.

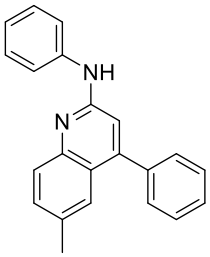


4-Phenylbenzo[g]quinoline-2(1H)-thione (3t). Yellow solid (80%, 0.115 g): mp 244-246 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 14.07 (s, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 9.2 Hz, 1H), 7.58 - 7.57 (m, 3H), 7.47 - 7.40 (m, 3H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 178.13, 147.36, 141.06 (d, *J* = 1.5 Hz), 134.19, 134.00, 131.23, 129.70 (d, *J* = 3.0 Hz), 129.11 (d, *J* = 11.0 Hz), 127.99, 127.07, 126.11, 125.85, 117.32, 116.64. HRMS (ESI$^+$) m/z: Calcd for $C_{19}H_{14}NS$ 288.0841 $[M+H]^+$, Found 288.0843.



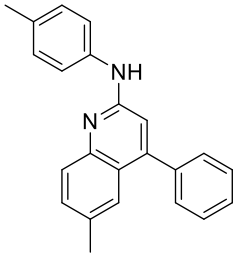
6-Methyl-4-(thiophen-3-yl)quinoline-2(1H)-thione (3u). Yellow solid (73%, 0.094 g): mp 333-335 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.91 (s, 1H), 7.93 (d, *J* = 6.0 Hz, 1H), 7.79 (s, 1H), 7.73 (s, 1H),7.54 (d, *J* = 6.0 Hz, 1H), 7.52 (d, *J* = 0.6 Hz, 1H), 7.45 - 7.42 (m, 2H), 7.23 (dd, *J* = 1.2, 1.2 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 157.81, 147.11, 144.00, 138.10, 136.44, 132.33, 128.78, 128.53, 126.21, 125.21, 125.16, 124.57, 117.19, 21.78. HRMS (ESI$^+$) m/z: Calcd for $C_{14}H_{12}NS_2$ 258.0406 $[M+H]^+$, Found 258.0408.

1.7 General procedure for the synthesis of 2-aminoquinoline 4. Under an atmosphere of air, 2-(1-phenylvinyl) aniline **1a** (0.5 mmol, 0.104 g), PhNCS (1.8 eq. 0.9 mmol, 0.121 g), K_3PO_4 (2 eq, 0.212 g) were added to a tube. Dixoane (3.0 mL) was added by dropper and the mixture was stirred for 12 h at 100 °C and the reaction was monitored by TLC analysis. Then, 2.0 mL ammonium chloride were added to the mixture to quench the reaction and extracted with ethyl acetate (3×25 mL). The combined organic layers were washed with aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and the volatiles were removed in vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether 1:5) to give the corresponding products. All of the products **4b-4A** were synthesized according to above described procedure.

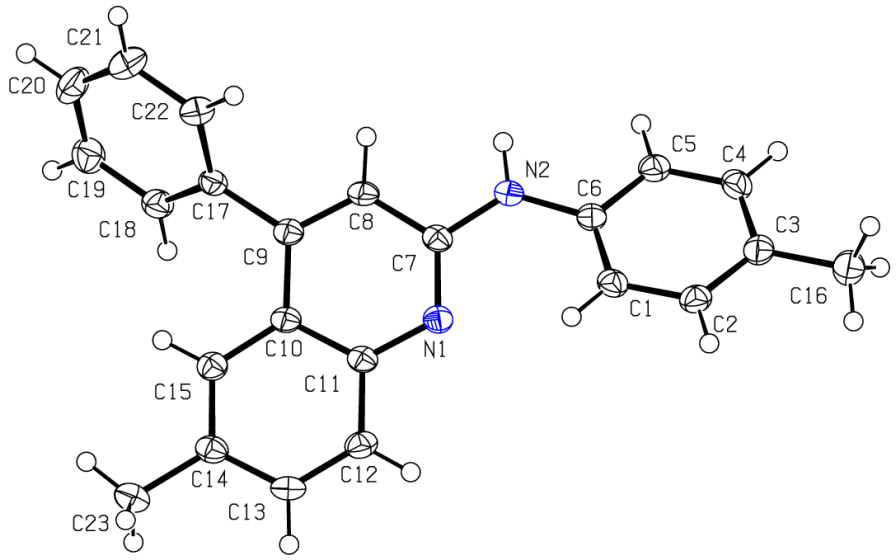


6-Methyl-N,4-diphenylquinolin-2-amine (4a). Oil (84 %, 0.130 g). IR (KBr) 3408, 3018, 2943, 1739, 1618, 1362, 1216, 1093 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.91 (dd, J = 2.4, 2.4 Hz, 1H), 7.68 - 7.65 (m, 2H), 7.57 (s, 1H), 7.56 - 7.45 (m, 7H), 7.42 - 7.38 (m, 2H), 7.13 - 7.10 (m, 1H), 6.95 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.75, 149.64, 146.74, 140.67, 138.57, 132.73, 131.77, 129.44, 129.28, 128.54, 128.28, 127.06, 124.86,

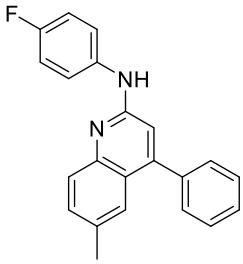
123.11, 122.81, 120.42, 21.55. HRMS (ESI+) m/z: Calcd for $C_{22}H_{19}N_2$ 311.1543 $[M+H]^+$, Found: 311.1551.



Methyl-4-phenyl-N-(p-tolyl)quinolin-2-amine (4b). Solid (80 %, 0.1296 g): mp 153-155 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.72 (d, J = 8.4 Hz, 1H), 7.50 - 7.38 (m, 9H), 7.14 (d, J = 7.2 Hz, 2H), 6.87 (s, 1H), 6.85 (s, 1H), 2.38 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.91, 149.61, 146.62, 138.53, 137.64, 132.82, 132.48, 131.67, 129.80, 129.32, 128.41, 128.15, 126.69, 124.75, 122.91, 121.15, 111.21, 21.44, 20.84. HRMS (ESI+) m/z: Calcd for $C_{23}H_{21}N_2$ 325.1699 $[M+H]^+$, Found: 325.1703.

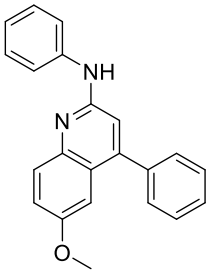


The crystal structure of compound **4b** (CCDC 1823828).

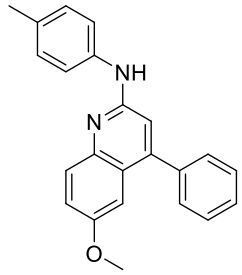


N-(4-Fluorophenyl)-6-methyl-4-phenylquinolin-2-amine (4c). Oil (75 %, 0.123 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, J = 8.0 Hz, 1H), 7.56 - 7.41 (m, 10H), 7.07 - 7.02 (m, 2H), 6.78 (d, J =2.0 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 153.48, 149.89, 138.33, 132.80, 131.80, 129.26, 128.46, 128.25, 126.67, 124.76, 122.93, 122.50, 122.44, 115.91, 115.76, 111.28, 21.42. HRMS (ESI+) m/z: Calcd for $C_{22}H_{18}FN_2$ 329.1449 $[M+H]^+$,

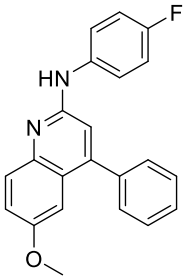
Found: 329.1453.



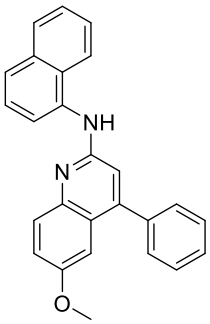
6-Methoxy-N,4-diphenylquinolin-2-amine (4d). Oil (88 %, 0.143 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.78 (d, J = 9.0 Hz, 1H), 7.54 (d, J = 7.8 Hz, 2H), 7.50 (dd, J = 0.6, 6.6 Hz, 4H), 7.34 (t, J = 9.6 Hz, 2H), 7.29 (d, J = 3.0 Hz, 1H), 7.27 (d, J = 3.0 Hz, 1H), 7.07 - 7.03 (m, 2H), 6.93 (s, 1H), 6.80 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 155.63, 152.73, 149.03, 145.18, 143.87, 140.80, 138.55, 129.40, 129.25, 128.63, 128.33, 123.59, 122.51, 120.92, 119.96, 112.29, 105.25, 55.48. HRMS (ESI+) m/z: Calcd for $C_{22}H_{19}N_2O$ 327.1492 $[M+H]^+$, Found: 327.1486.



6-Methoxy-4-phenyl-N-(p-tolyl)quinolin-2-amine (4e). Oil (82 %, 0.139 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.78 (d, J = 9.6 Hz, 1H), 7.51 – 7.44 (m, 5H), 7.42 - 7.39 (m, 2H), 7.28 (dd, J = 3.0, 3.0 Hz, 1H), 7.15 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 2.4 Hz, 1H), 6.90 (s, 2H), 3.75 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 155.45, 153.14, 149.04, 143.92, 138.57, 137.91, 132.51, 129.78, 129.18, 128.53, 128.40, 128.22, 123.44, 120.86, 120.83, 111.67, 105.20, 55.44, 20.83. HRMS (ESI+) m/z: Calcd for $C_{23}H_{21}N_2O$ 341.1648 $[M+H]^+$, Found: 341.1641.

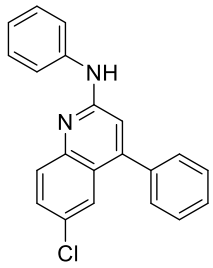


N-(4-Fluorophenyl)-6-methoxy-4-phenylquinolin-2-amine (4f). Oil (78 %, 0.134 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.78 (d, J = 9.0 Hz, 1H), 7.54 - 7.47 (m, 7H), 7.28 (dd, J = 3.0, 3.0 Hz, 1H), 7.07 (d, J = 3.0 Hz, 1H), 7.03 (t, J = 17.4 Hz, 2H), 6.91 (s, 1H), 6.79 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 159.47, 157.87, 155.59, 152.80, 149.22, 143.65, 138.39, 129.13, 128.58, 128.44, 128.32, 122.07, 120.94, 115.84, 115.69, 111.83, 105.22, 55.44. HRMS (ESI+) m/z: Calcd for $C_{22}H_{18}FN_2O$ 345.1398 $[M+H]^+$, Found: 345.1401.

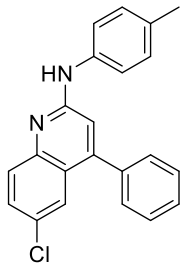


6-Methoxy-N-(naphthalen-1-yl)-4-phenylquinolin-2-amine (4g). Solid (73 %, 0.137 g): mp 161-163 °C. IR (KBr) 3406, 3020, 2923, 1740, 1606, 1513, 1368, 1217, 1118 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.14

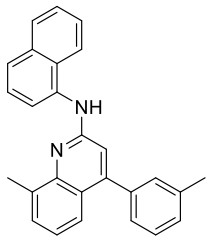
(d, J = 7.2 Hz, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 9.6 Hz, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.53 - 7.41 (m, 8H), 7.30 (dd, J = 3.0, 2.4 Hz, 1H), 7.08 (d, J = 3.0 Hz, 1H), 6.86 (s, 1H), 4.16 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 155.54, 154.42, 149.26, 144.02, 138.52, 135.97, 134.67, 129.16, 128.49, 128.21, 126.30, 126.19, 125.93, 125.14, 124.83, 123.61, 122.10, 121.12, 120.12, 111.17, 109.66, 105.24, 55.47. HRMS (ESI+) m/z: Calcd for $C_{26}H_{21}N_2O$ 377.1648 $[M+H]^+$, Found: 377.1641.



6-Chloro-N,4-diphenylquinolin-2-amine (4h). Oil (70 %, 0.115 g). IR (KBr) 3433, 3006, 2925, 1739, 1618, 1366, 1218, 1114 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.78 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 1.8 Hz, 1H), 7.58 (dd, J = 1.2, 1.2 Hz, 2H), 7.53 - 7.48 (m, 4H), 7.45 - 7.43 (m, 2H), 7.38 - 7.35 (m, 2H), 7.20 (s, 1H), 7.12 - 7.09 (m, 1H), 6.91 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 154.22, 149.42, 146.74, 139.92, 137.56, 130.32, 129.30, 129.21, 128.70, 128.61, 128.58, 128.55, 124.64, 123.82, 123.35, 120.69, 112.43. HRMS (ESI+) m/z: Calcd for $C_{21}H_{16}ClN_2$ 311,0997 $[M+H]^+$, Found: 311.1012.

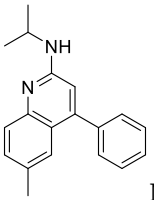


6-Chloro-4-phenyl-N-(p-tolyl)quinolin-2-amine (4i). Solid (75 %, 0.129 g): mp 152-154 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.74 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 2.4 Hz, 1H), 7.52 - 7.47 (m, 4H), 7.44 - 7.40 (m, 4H), 7.17 (d, J = 8.4 Hz, 2H), 6.89 (s, 1H), 6.79 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 154.48, 149.43, 137.62, 137.03, 133.42, 130.30, 129.86, 129.17, 128.64, 128.54, 128.38, 128.35, 124.62, 123.72, 121.43, 111.92, 20.85. HRMS (ESI+) m/z: Calcd for $C_{22}H_{18}ClN_2$ 345.1153 $[M+H]^+$, Found: 345.1148.

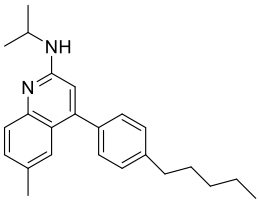


8-Methyl-N-(naphthalen-1-yl)-4-(m-tolyl)quinolin-2-amine (4j). Oil (78 %, 0.145 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.03 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 7.2 Hz, 1H), 7.79 (d, J = 1.8 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.43 - 7.38 (m, 4H), 7.25 (t, J = 15.0 Hz, 1H), 7.15 (d, J = 7.8 Hz, 3H), 7.09 (t, J = 15.6 Hz, 1H), 6.80 (d, J = 3.0 Hz, 1H), 2.77 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 154.47, 150.75, 147.47, 138.83, 138.07, 135.93, 134.78, 134.67, 130.12, 130.04, 128.90, 128.66, 128.58, 128.30, 126.59, 126.23, 126.09, 126.06, 124.76, 123.99, 123.18, 122.64, 121.94, 119.56, 110.88, 21.53, 18.68. HRMS (ESI+) m/z: Calcd for $C_{27}H_{23}N_2$ 375.1856 $[M+H]^+$,

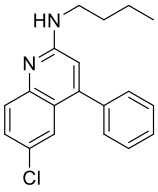
Found: 375.1860.



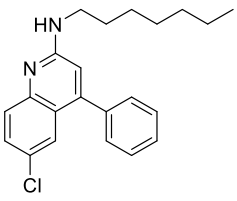
N-isopropyl-6-methyl-4-phenylquinolin-2-amine (4k). Oil (72 %, 0.099 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.63 (d, J = 9.0 Hz, 1H), 7.52 - 7.45 (m, 4H), 7.36 (d, J = 9.6 Hz, 2H), 6.53 (s, 1H), 4.69 (s, 1H), 4.22 - 4.15 (m, 1H), 2.35 (s, 3H), 1.29 (d, J = 6.0 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 155.55, 149.22, 146.89, 138.82, 131.39, 131.30, 129.28, 128.36, 128.01, 126.11, 124.74, 122.10, 110.96, 42.96, 23.25, 21.31. HRMS (ESI+) m/z: Calcd for $C_{19}H_{21}N_2$ 277.1699 $[M+H]^{+}$, Found: 277.1703.



N-isopropyl-6-methyl-4-(4-pentylphenyl)quinolin-2-amine (4l). Oil (65 %, 0.112 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.62 (d, J = 8.4 Hz, 1H), 7.41 (s, 1H), 7.39 - 7.33 (m, 3H), 7.31 (d, J = 7.8 Hz, 2H), 6.53 (s, 1H), 4.69 (s, 1H), 4.18-4.13 (m, 1H), 2.72 - 2.68 (m, 2H), 2.36 (s, 3H), 1.73-1.68 (m, 2H), 1.40 - 1.38 (m, 4H), 1.29 (d, J = 6.6 Hz, 6H), 0.96 - 0.91 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 142.97, 136.00, 131.37, 129.36, 129.17, 128.66, 128.51, 128.39, 124.85, 115.74, 110.82, 43.01, 35.75, 31.62, 31.13, 29.68, 23.25, 22.56, 21.31, 14.04. HRMS (ESI+) m/z: Calcd for $C_{24}H_{31}N_2$ 347.2482 $[M+H]^{+}$, Found: 347.2486.

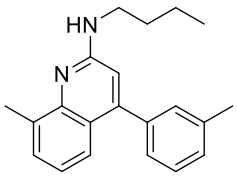


N-butyl-6-chloro-4-phenylquinolin-2-amine (4m). Oil (72 %, 0.111 g). IR (KBr) 3448, 2921, 1739, 1647, 1367, 1217, 1051 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.65 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 2.4 Hz, 1H), 7.52 - 7.42 (m, 6H), 6.56 (s, 1H), 4.78 (s, 1H), 3.49 (q, J = 6.6 Hz, 2H), 1.68 - 1.63 (m, 2H), 1.49-1.43 (m, 2H), 0.97 (t, J = 15.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 156.75, 148.81, 147.25, 137.91, 129.95, 129.15, 128.59, 128.39, 127.96, 127.11, 124.59, 123.08, 111.77, 41.51, 31.86, 20.20, 13.87. HRMS (ESI+) m/z: Calcd for $C_{19}H_{20}ClN_2$ 311.1310 $[M+H]^{+}$, Found: 311.1312.

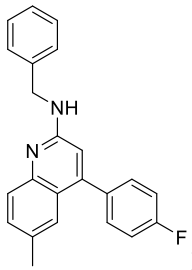


6-Chloro-N-heptyl-4-phenylquinolin-2-amine (4n). Oil (65 %, 0.114 g). IR (KBr) 3395, 2920, 2843, 1739, 1709, 1645, 1366, 1220, 1055 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.65 (d, J = 9.0 Hz, 1H), 7.56 (d, J = 2.4 Hz, 1H), 7.52 - 7.45 (m, 4H), 7.44 - 7.42 (m, 2H), 6.56 (s, 1H), 4.77 (s, 1H), 3.49 - 3.45 (m, 2H), 1.69 - 1.64 (m, 2H), 1.45 - 1.39 (m, 2H), 1.38 - 1.27 (m, 6H), 0.89 (t, J =13.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 156.74, 148.81, 147.26, 137.92, 129.95, 129.15, 128.58, 128.39, 127.96, 127.11, 124.58, 123.07, 111.74, 41.82, 31.77, 29.75, 29.05,

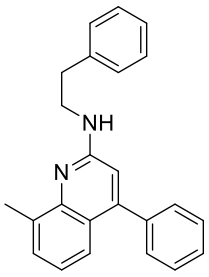
27.01, 22.60, 14.06. HRMS (ESI+) m/z: Calcd for $C_{22}H_{26}ClN_2$ 353.1779 $[M+H]^+$, Found: 353.1783.



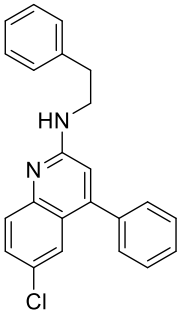
N-butyl-8-methyl-4-(m-tolyl)quinolin-2-amine (4o). Oil (62 %, 0.094 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.50 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.38 (t, J = 15.0 Hz, 1H), 7.30 - 7.26 (m, 3H), 7.06 (t, J = 21.0, 1H), 6.54 (s, 1H), 4.71 (s, 1H), 3.55 (q, J = 8.0 Hz, 2H), 2.73 (s, 3H), 2.45 (s, 3H), 1.73 - 1.68 (m, 2H), 1.52 - 1.46(m, 2H), 1.01 (t, J = 14.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 155.68, 149.89, 147.46, 139.09, 137.95, 134.24, 130.02, 129.51, 128.65, 128.17, 126.47, 123.71, 122.07, 121.21, 110.77, 41.49, 31.87, 21.48, 20.33, 18.32, 13.96. HRMS (ESI+) m/z: Calcd for $C_{21}H_{25}N_2$ 305.2012 $[M+H]^+$, Found: 305.2016.



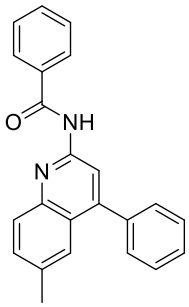
N-benzyl-4-(4-fluorophenyl)-6-methylquinolin-2-amine (4p). Oil (61 %, 0.104 g).^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, J = 13.2 Hz, 1H), 7.43 - 7.37 (m, 6H), 7.34 (d, J = 6.6 Hz, 3H), 7.21 - 7.12 (m, 2H), 6.52 (d, J = 1.8 Hz, 1H), 5.03 (s, 1H), 4.74 (d, J = 7.8 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 163.50, 155.71, 139.35, 134.50, 131.81, 131.56, 130.94, 130.88, 128.62, 127.77, 127.29, 126.40, 124.53, 122.35, 115.49, 115.34, 111.27, 45.91, 21.35. HRMS (ESI+) m/z: Calcd for $C_{23}H_{20}FN_2$ 343.1605 $[M+H]^+$, Found: 343.1610



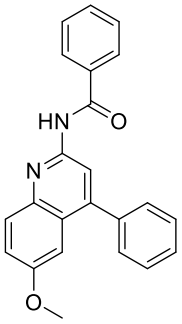
8-Methyl-N-phenethyl-4-phenylquinolin-2-amine (4q). Oil (65 %, 0.110 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.52 - 7.45 (m, 6H), 7.36 (t, J = 15.6 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.28 - 7.26 (m, 1H), 7.09 (t, J = 15.0 Hz, 2H), 6.51 (s, 1H), 4.75 (s, 1H), 3.85 (q, J = 6.6 Hz, 2H), 3.07 (t, J = 14.4 Hz, 2H), 2.78 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 155.17, 149.71, 147.41, 139.81, 139.00, 134.48, 129.59, 129.36, 128.93, 128.57, 128.31, 127.97, 126.29, 123.64, 122.10, 121.49, 111.42, 43.08, 35.70, 18.42. HRMS (ESI+) m/z: Calcd for $C_{24}H_{23}N_2$ 338.1856 $[M+H]^+$, Found: 339.1852.



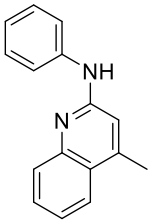
6-Chloro-N-phenethyl-4-phenylquinolin-2-amine (4r). Oil (68 %, 0.121 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.69 (d, J = 9.0 Hz, 1H), 7.57 (d, J = 2.4 Hz, 1H), 7.52 - 7.45 (m, 4H), 7.43 - 7.40 (m, 2H), 7.33 - 7.31 (m, 2H), 7.28 - 7.22 (m, 3H), 6.51 (s, 1H), 4.91 (s, 1H), 3.80 (q, J = 6.6 Hz, 2H), 3.00 (t, J = 14.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 156.35, 148.87, 147.05, 139.20, 137.77, 130.01, 129.14, 128.84, 128.63, 128.59, 128.44, 128.00, 127.35, 126.46, 124.61, 123.13, 112.15, 42.80, 35.75. HRMS (ESI+) m/z: Calcd for $C_{23}H_{20}ClN_2$ 359.1310 $[M+H]^+$, Found: 359.1314.



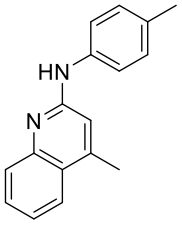
N-(6-methyl-4-phenylquinolin-2-yl)benzamide (4s). Solid (75 %, 0.126 g): mp 140-142 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ: 1H 9.13 (s, 1H), 8.54 (s, 1H), 7.98 (d, J = 7.2 Hz, 2H), 7.77 (d, J = 9.0 Hz, 1H), 7.62 (s, 1H), 7.57 - 7.43 (m, 9H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.69, 151.19, 150.80, 146.18, 138.91, 135.75, 134.87, 132.94, 132.73, 130.26, 129.44, 129.17, 129.07, 128.08, 128.0, 125.70 , 125.47, 115.34, 22.36. HRMS (ESI+) m/z: Calcd for $C_{23}H_{19}N_2O$ 334.1492 $[M+H]^+$, Found: 334.1499



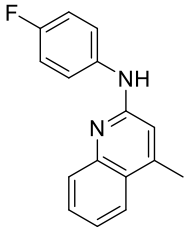
N-(6-methoxy-4-phenylquinolin-2-yl)benzamide (4t). Solid (78 %, 0.138 g): mp 174-176 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.80 (s, 1H), 8.53 (s, 1H), 7.99 - 7.96 (m, 2H), 7.81 (d, J = 9.0 Hz, 1H), 7.60 - 7.56 (m, 3H), 7.55 - 7.48 (m, 5H), 7.35 (dd, J = 3.0, 3.0 Hz, 1H), 7.19 (d, J = 4.2 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 165.78, 157.04, 149.83, 148.91, 142.91, 138.33, 134.27, 132.26, 129.38, 129.15, 128.82, 128.58, 128.42, 127.24, 125.87, 122.09, 114.79, 104.34, 55.45. HRMS (ESI+) m/z: Calcd for $C_{23}H_{19}N_2O_2$ 355.1441 $[M+H]^+$, Found: 355.1445



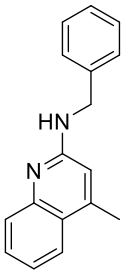
Methyl-N-phenylquinolin-2-amine (4u). Oil (65 %, 0.076 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.82 - 7.78 (m, 2H), 7.60 - 7.54 (m, 3H), 7.38 - 7.27 (m, 4H), 7.20 (s, 1H), 7.10 - 7.07 (m,1H), 6.84 (d, J = 1.2 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 154.13, 145.82, 140.24, 129.55, 129.35, 129.21, 127.01, 124.44, 123.58, 122.99, 122.92, 120.55, 111.73, 18.92. HRMS (ESI+) m/z: Calcd for $C_{16}H_{15}N_2$ 235.1230 $[M+H]^+$, Found: 235.1234.



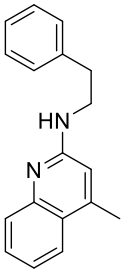
4-Methyl-N-(p-tolyl)quinolin-2-amine (4v). Oil (73 %, 0.095 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.81-7.77 (m, 2H), 7.57 (m, 1H), 7.42 - 7.39 (m, 2H), 7.32-7.29 (m, 1H), 7.18 (d, J = 6.0 Hz, 2H), 6.98 (s, 1H), 6.80 (s, 1H), 2.56 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 154.77, 147.78, 145.57, 137.65, 132.85, 129.77, 129.44, 127.04, 124.42, 123.59, 122.64, 121.35, 111.45, 20.88, 18.90. HRMS (ESI+) m/z: Calcd for $C_{17}H_{17}N_2$ 249.1386 $[M+H]^+$, Found: 249.1390.



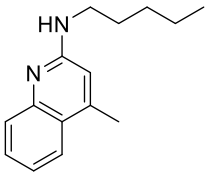
N-(4-fluorophenyl)-4-methylquinolin-2-amine (4w). Oil (80 %, 0.1 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.80 (dd, J = 1.8, 1.2Hz, 1H), 7.76 (d, J =0.8 Hz, 1H), 7.58-7.55 (m, 1H), 7.53 - 7.51 (m, 2H), 7.32-7.30 (m , 1H), 7.06 - 7.02 (m, 2H), 6.71 (s, 1H), 2.56 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 159.72, 158.12, 154.27, 147.22, 145.97, 136.22, 129.61, 126.89, 123.60, 122.94, 122.69, 115.85, 111.54, 18.90. HRMS (ESI+) m/z: Calcd for $C_{16}H_{14}FN_2$ 253.1136 $[M+H]^+$, Found: 253.1140.



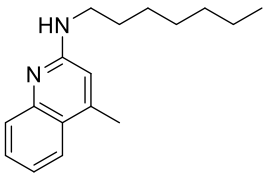
N-benzyl-4-methylquinolin-2-amine (4x). Oil (46 %, 0.057 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.77 (dd, J= 1.8, 1.2 Hz, 1H), 7.73 (dd, J= 1.2, 1.2 Hz, 1H), 7.54 (m, 1H), 7.41 (d, J= 7.8 Hz, 2H), 7.34 - 7.30 (m, 2H), 7.30 - 7.23 (m, 2H), 6.48 (s, 1H), 5.01 (s, 1H), 4.72 (d, J= 5.4 Hz, 2H), 2.54 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 156.58, 147.97, 145.10, 139.52, 129.30, 128.61, 127.75, 127.24, 126.69, 123.95, 123.57, 121.92, 111.42, 45.74, 18.82. HRMS (ESI+) m/z: Calcd for $C_{17}H_{17}N_2$ 249.1386 $[M+H]^+$, Found: 249.1390.



4-Methyl-N-phenethylquinolin-2-amine (4y). Oil (49 %, 0.064 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ:7.76 (dd, J = 1.2, 1.8 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.55 - 7.52 (m, 1H), 7.34 - 7.32 (m, 2H), 7.29 - 7.23 (m, 4H), 6.43 (s, 1H), 4.75 (s, 1H), 3.78 (q, J = 6.6 Hz, 2H), 2.99 (t, J = 13.8 Hz, 2H), 2.54 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 156.59, 148.03, 144.91, 139.44, 129.26, 128.88, 128.59, 126.63, 126.38, 123.81, 123.57, 121.81, 111.57, 42.76, 35.84, 18.79. HRMS (ESI+) m/z: Calcd for $C_{18}H_{19}N_2$ 263.1543 $[M+H]^+$, Found: 263.1540.



4-Methyl-N-pentylquinolin-2-amine (4z). Oil (53 %, 0.057 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.74 (d, J= 6.0 Hz, 1H), 7.66 (d, J= 6.0 Hz, 1H), 7.51 (t, J= 12.0 Hz, 1H), 7.23 - 7.19 (m, 1H), 6.49 (s, 1H), 4.71 (s, 1H), 3.45 (q, J= 1.8 Hz, 2H), 2.55 (s, 3H), 1.66 - 1.61 (m,2H), 1.48 - 1.42 (m, 2H), 0.97 (t, J= 1.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ:156.96, 148.03, 144.97, 129.25, 126.39, 123.67, 123.54, 121.61, 111.01, 41.49, 31.94, 20.20, 18.85, 13.88. HRMS (ESI+) m/z: Calcd for $C_{14}H_{19}N_2$ 215.1543 $[M+H]^+$, Found: 215.1548.



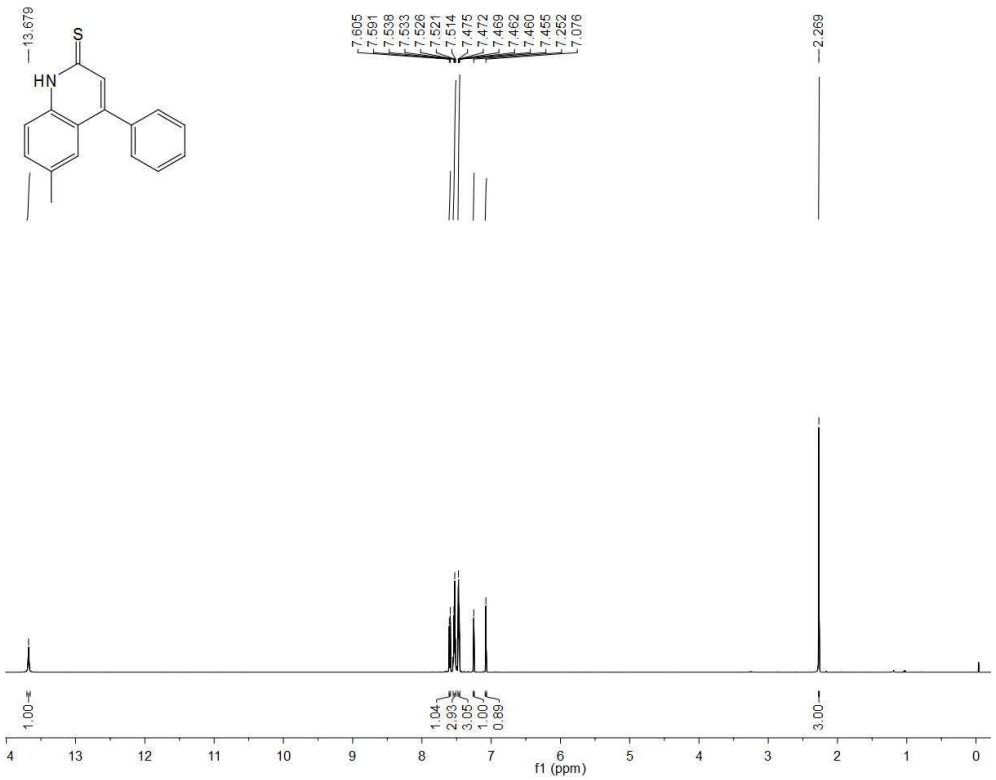
Heptyl-4-methylquinolin-2-amine (4A). Oil (48 %, 0.061 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.74 (dd, J = 1.8, 1.2 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.52 - 7.50 (m, 1H), 7.22 - 7.20 (m, 1H), 6.48 (s, 1H), 4.70 (s, 1H), 3.44 (td, J = 7.8, 6.6 Hz, 2H), 2.55 (s, 3H), 1.67 - 1.62 (m, 2H), 1.44 - 1.38 (m, 2H), 1.37 - 1.27 (m, 6H), 0.89 (t, J=13.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 156.98, 148.10, 144.90, 129.22, 126.45, 123.69, 123.53, 121.59, 111.05, 41.79, 31.80, 29.83, 29.08, 27.03, 22.61, 18.83, 14.07. HRMS (ESI+) m/z: Calcd for $C_{17}H_{25}N_2$ 257.2012 $[M+H]^+$, Found: 257.2016.

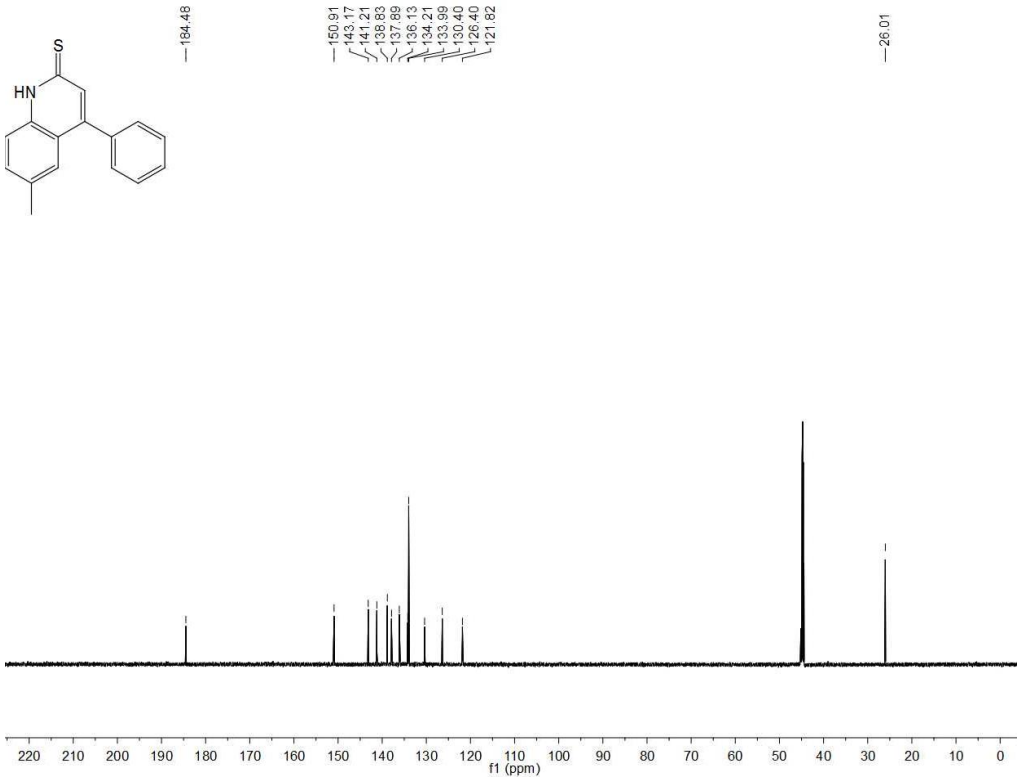
1.8 References

1. (a) Mameda, N.; Peraka, S.; Kodumuri, S.; Chevella, D.; Marri, M. R.; Nama, N. *RSC Adv.* **2015**, *5*, 78374. (b) Arienti, A. Bigi, F.; Maggi, R.; Marzi, E.; Moggi, P.; Rastelli, M.; Sartori, G.; Tarantola, F. *Tetrahedron* **1997**, *53*, 3795.

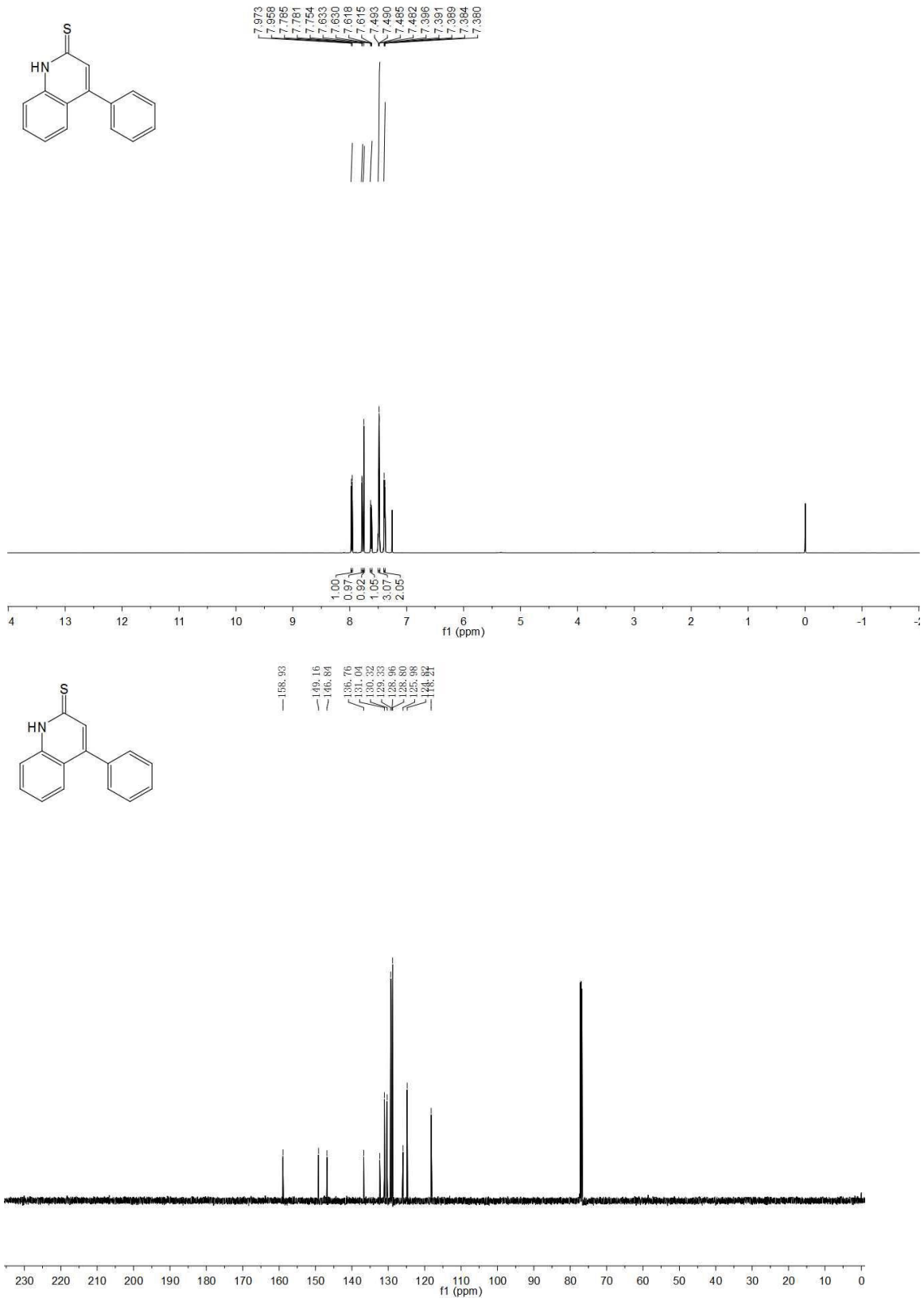
1.9 Copies of ^{1}H and ^{13}C Spectra for products

^{1}H and ^{13}C Spectra of compound 3a ($CDCl_3$,600 MHz)

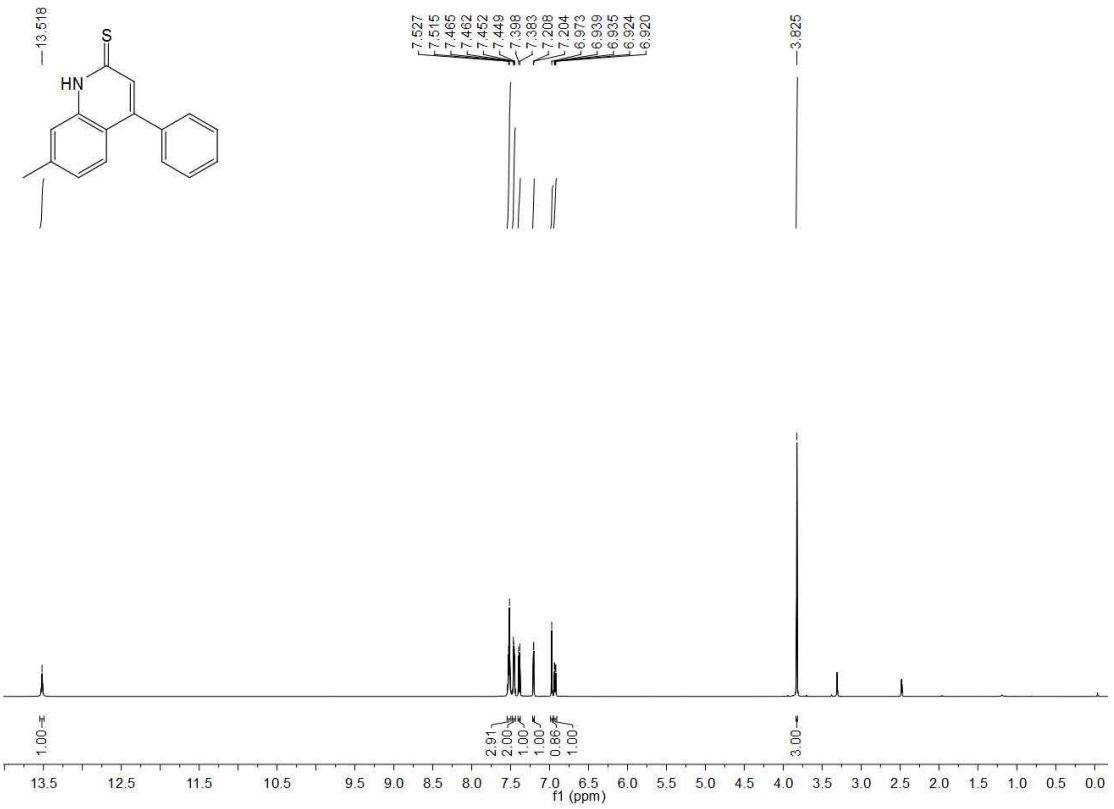


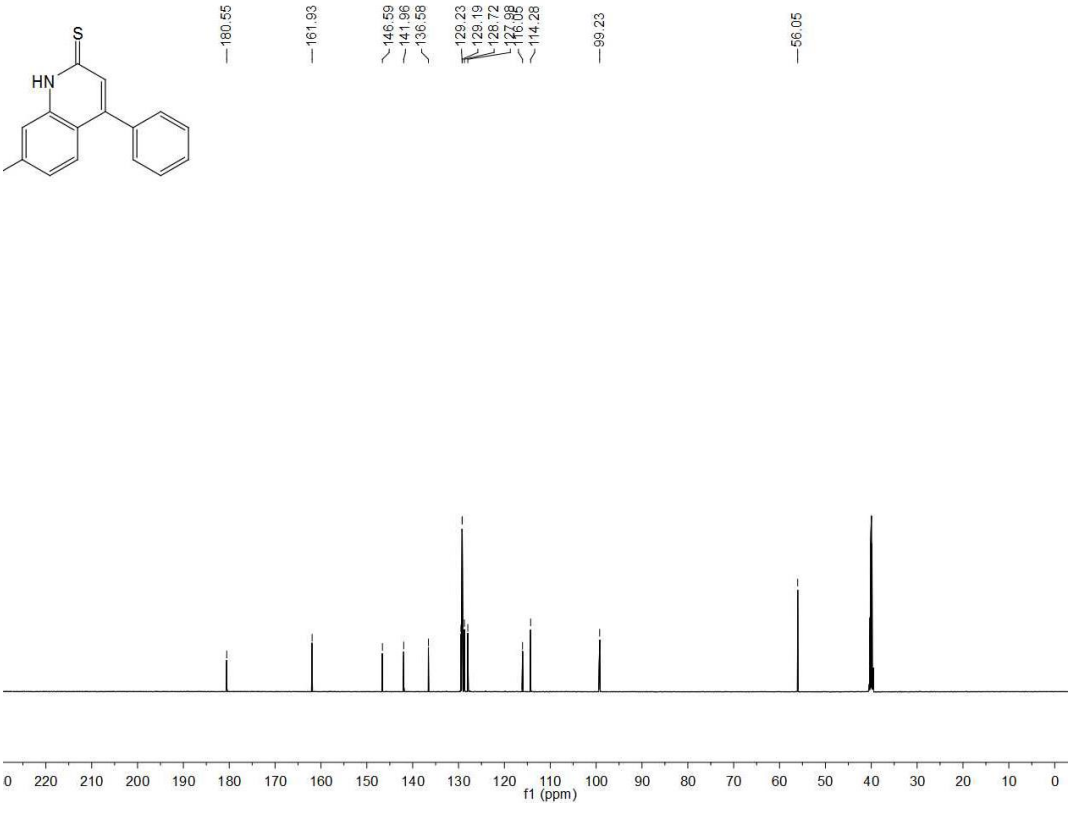


^{1}H and ^{13}C Spectra of compound 3b ($CDCl_3$,600 MHz)



^{1}H and ^{13}C Spectra of compound 3c ($CDCl_3$,600 MHz)





^{1}H and ^{13}C Spectra of compound 3d ($CDCl_3$,600 MHz)

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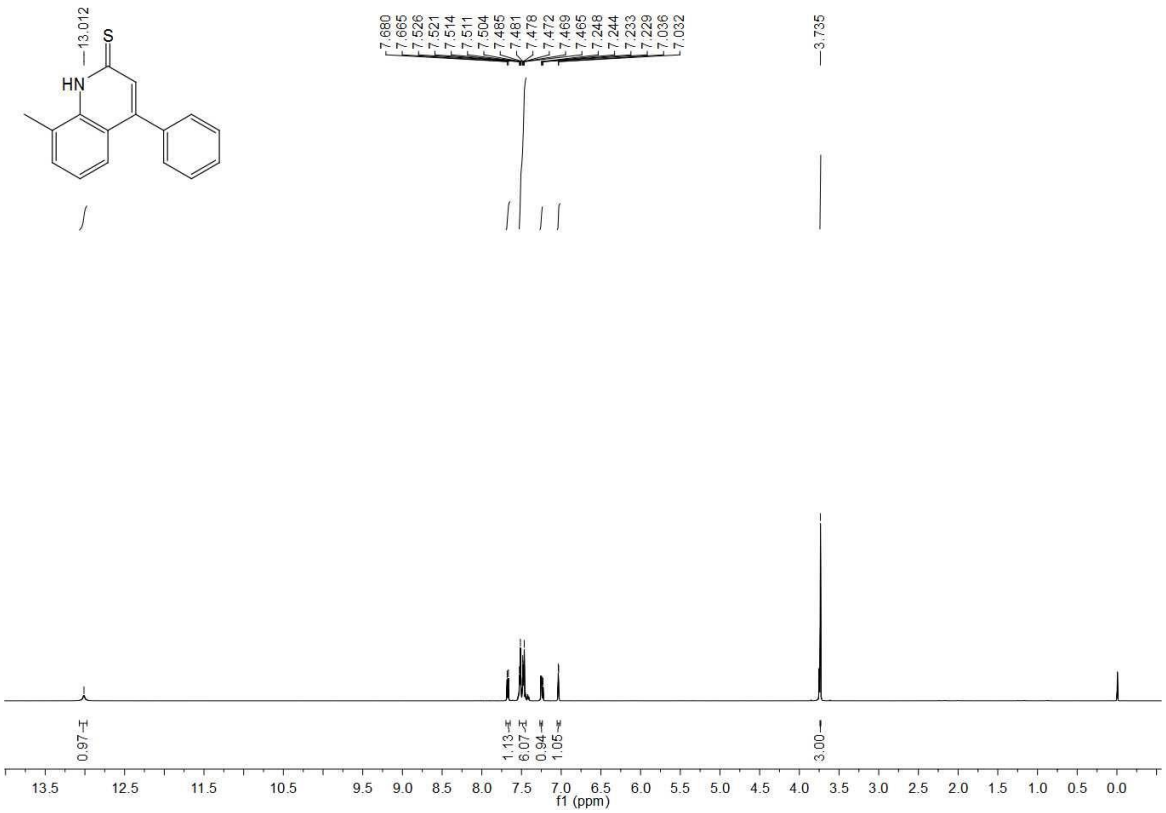
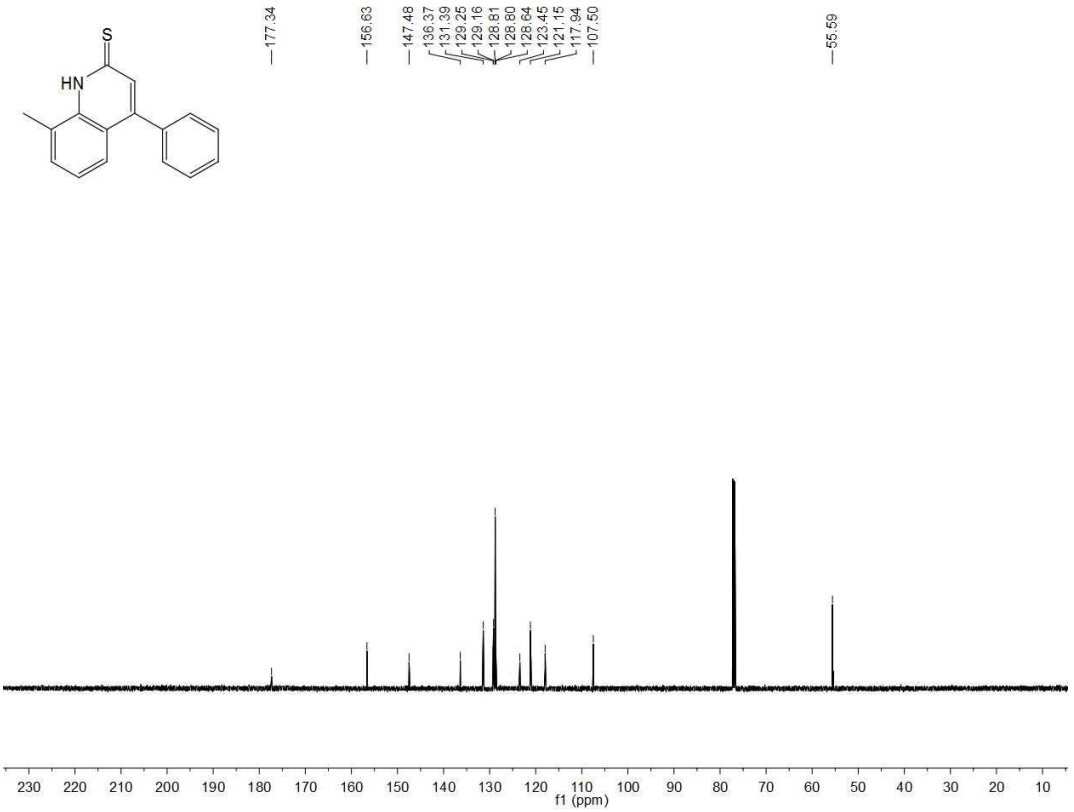
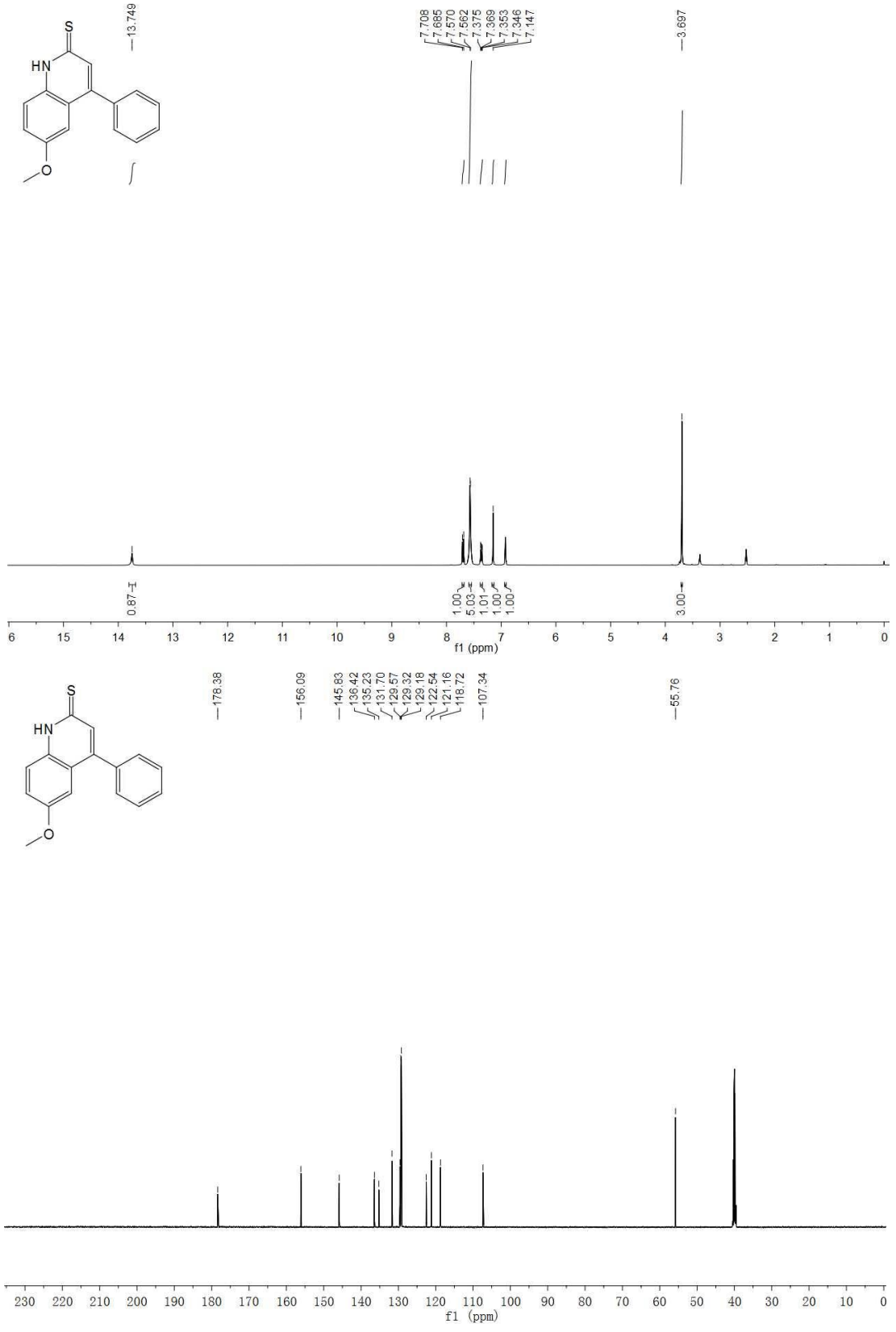
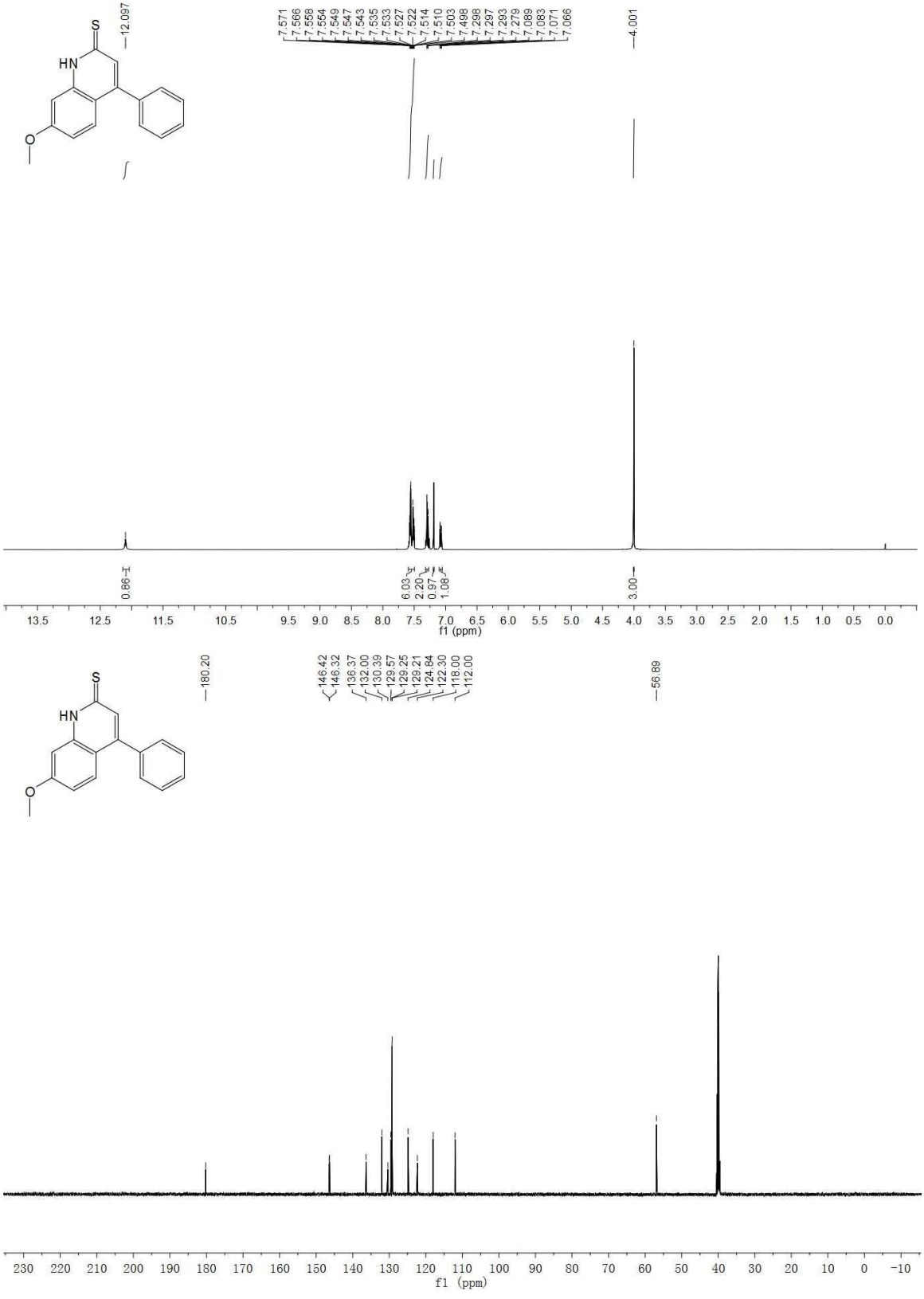




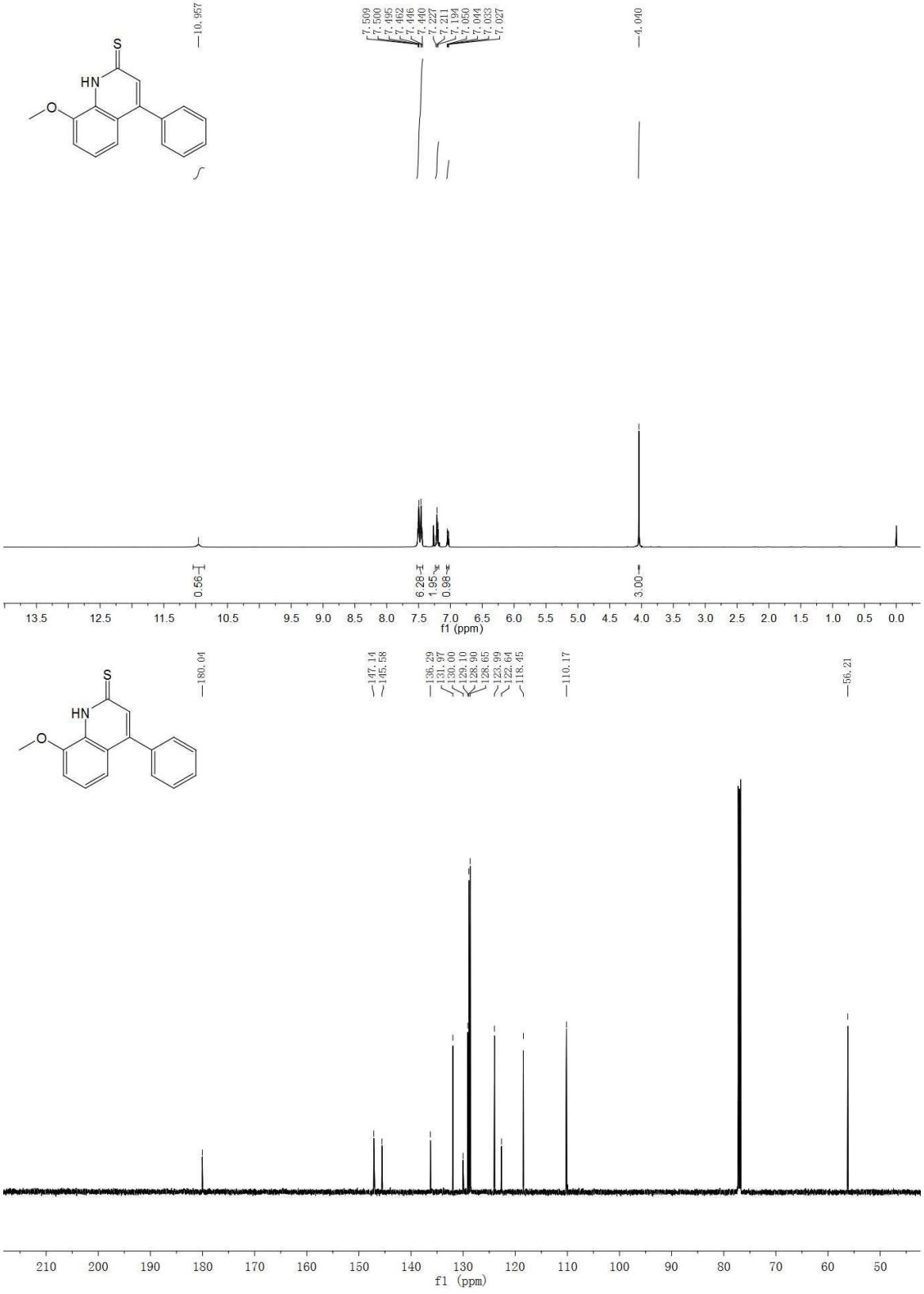
^{1}H and ^{13}C Spectra of compound 3e ($CDCl_3$,600 MHz)



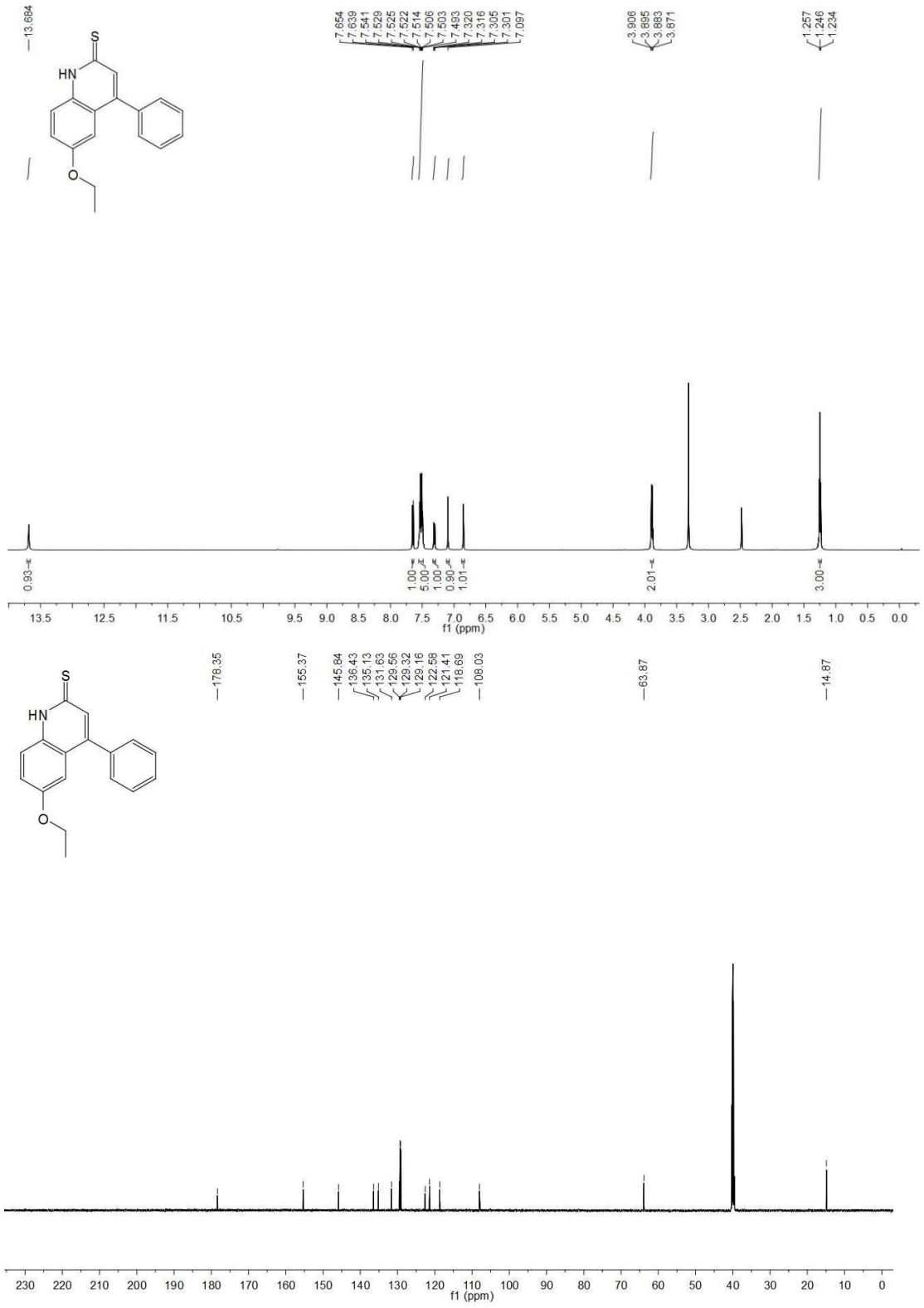
^{1}H and ^{13}C Spectra of compound 3f ($CDCl_3$,600 MHz)



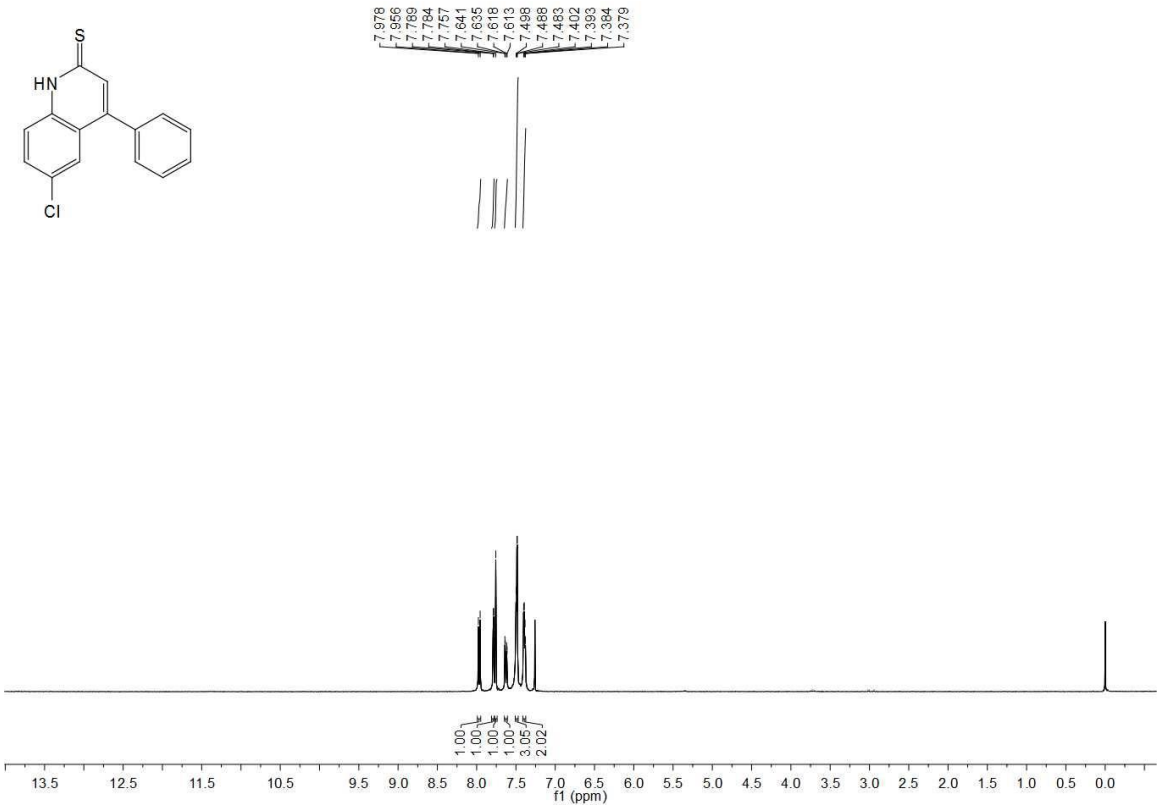
^{1}H and ^{13}C Spectra of compound 3g ($CDCl_3$,600 MHz)

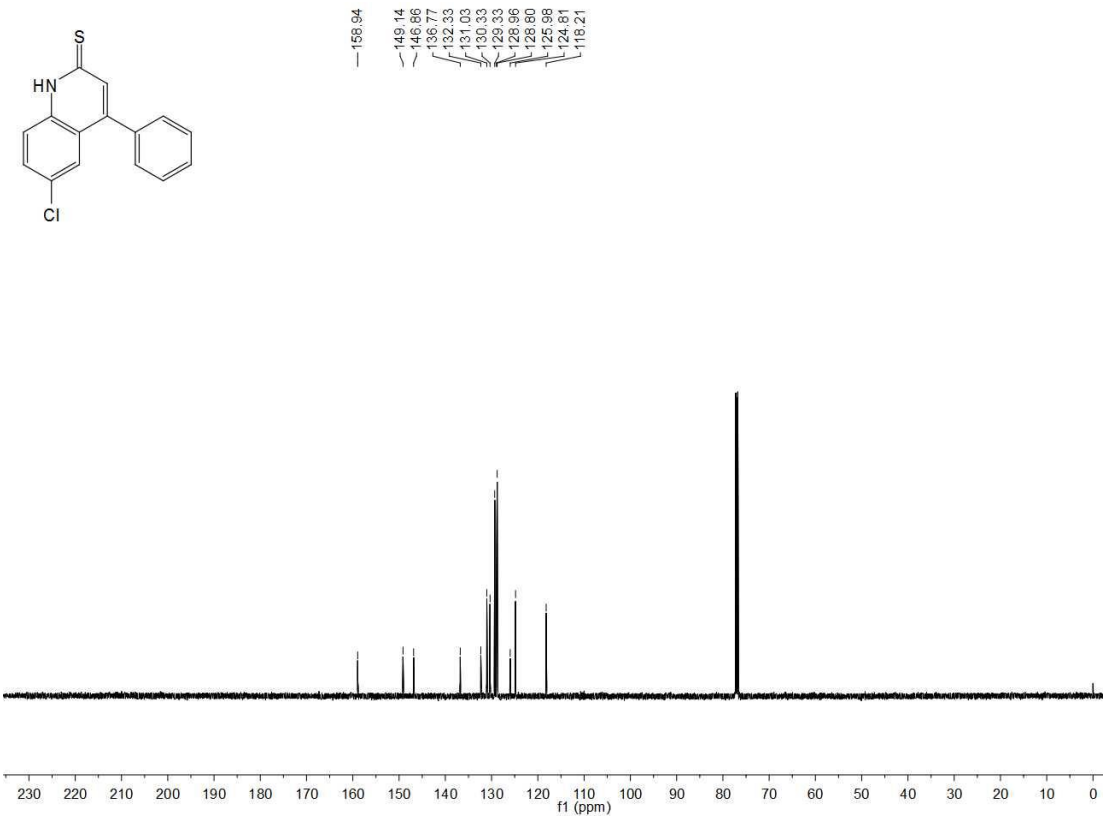


^{1}H and ^{13}C Spectra of compound 3h ($CDCl_3$,600 MHz)

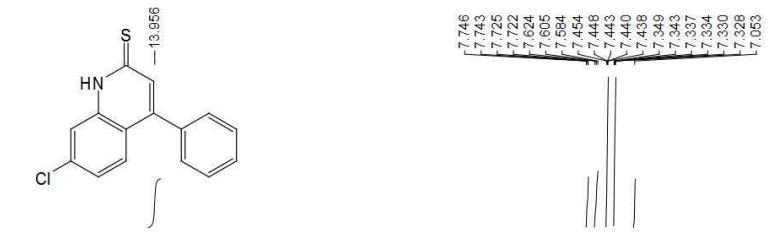


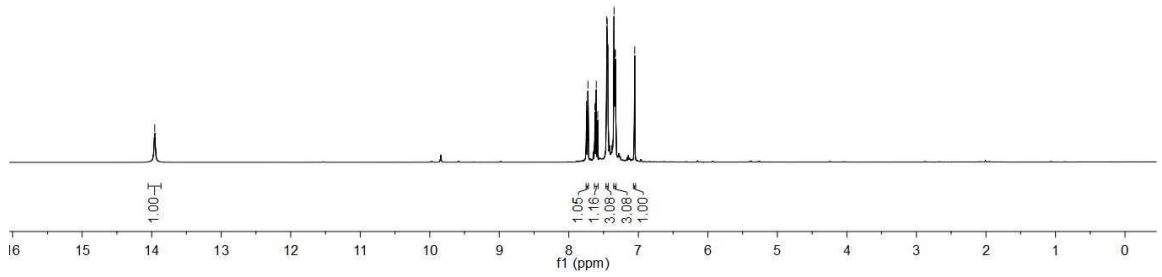
^{1}H and ^{13}C Spectra of compound 3i ($CDCl_3$,600 MHz)

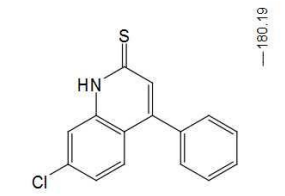


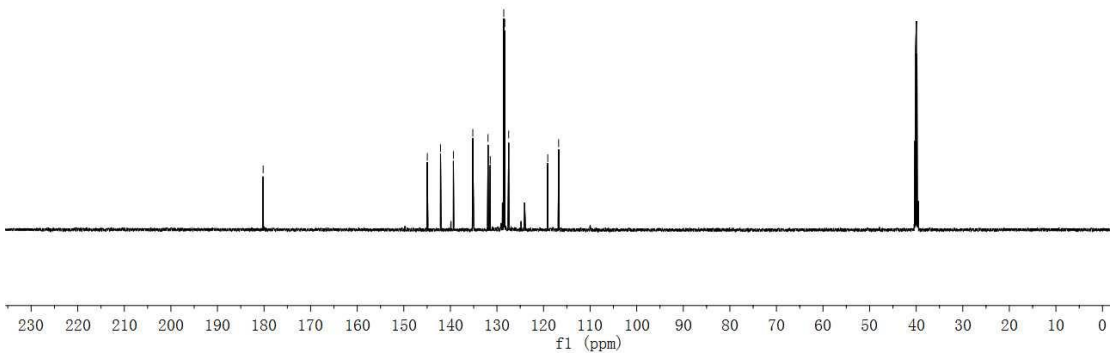


^{1}H and ^{13}C Spectra of compound 3j ($CDCl_3$,600 MHz)

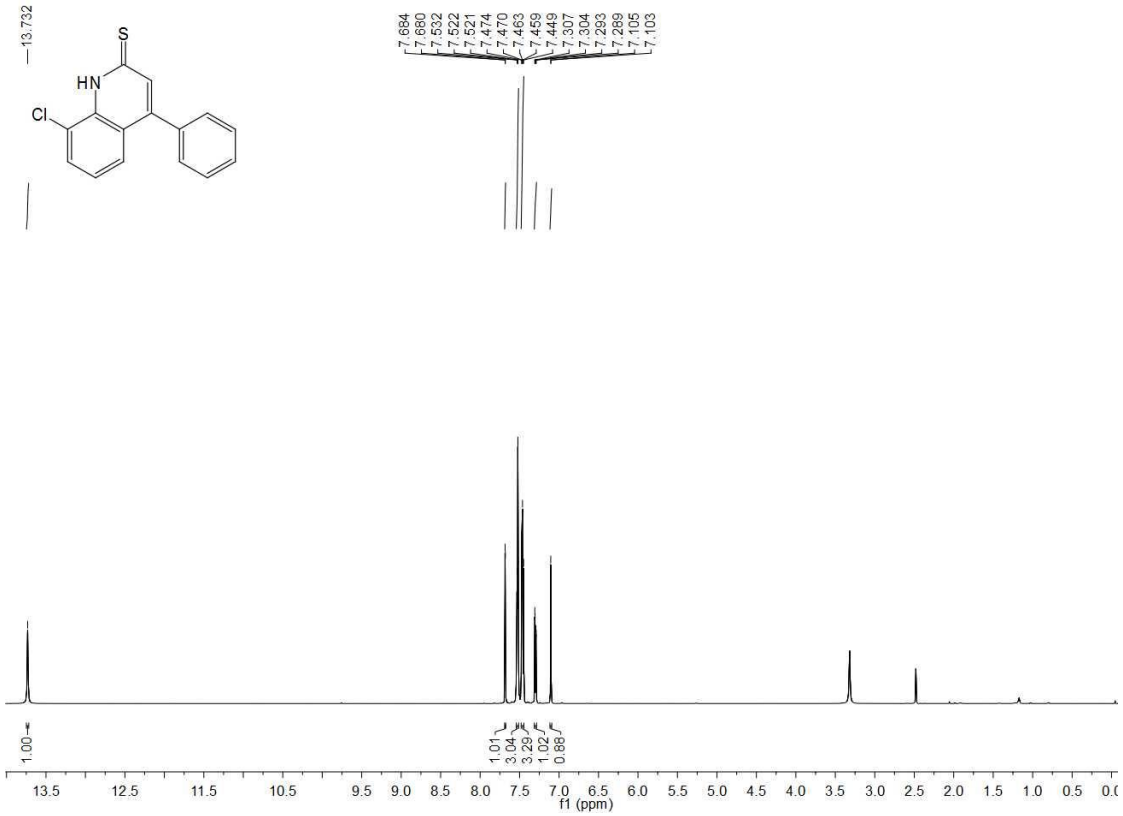


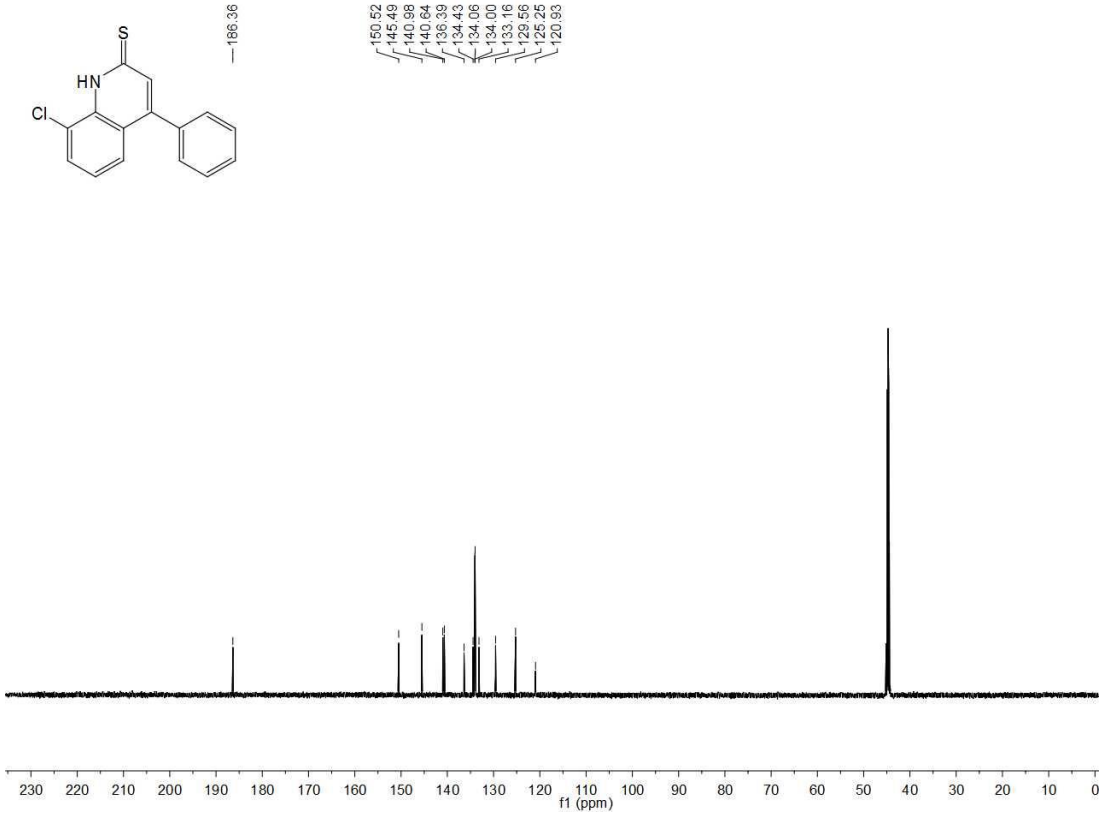




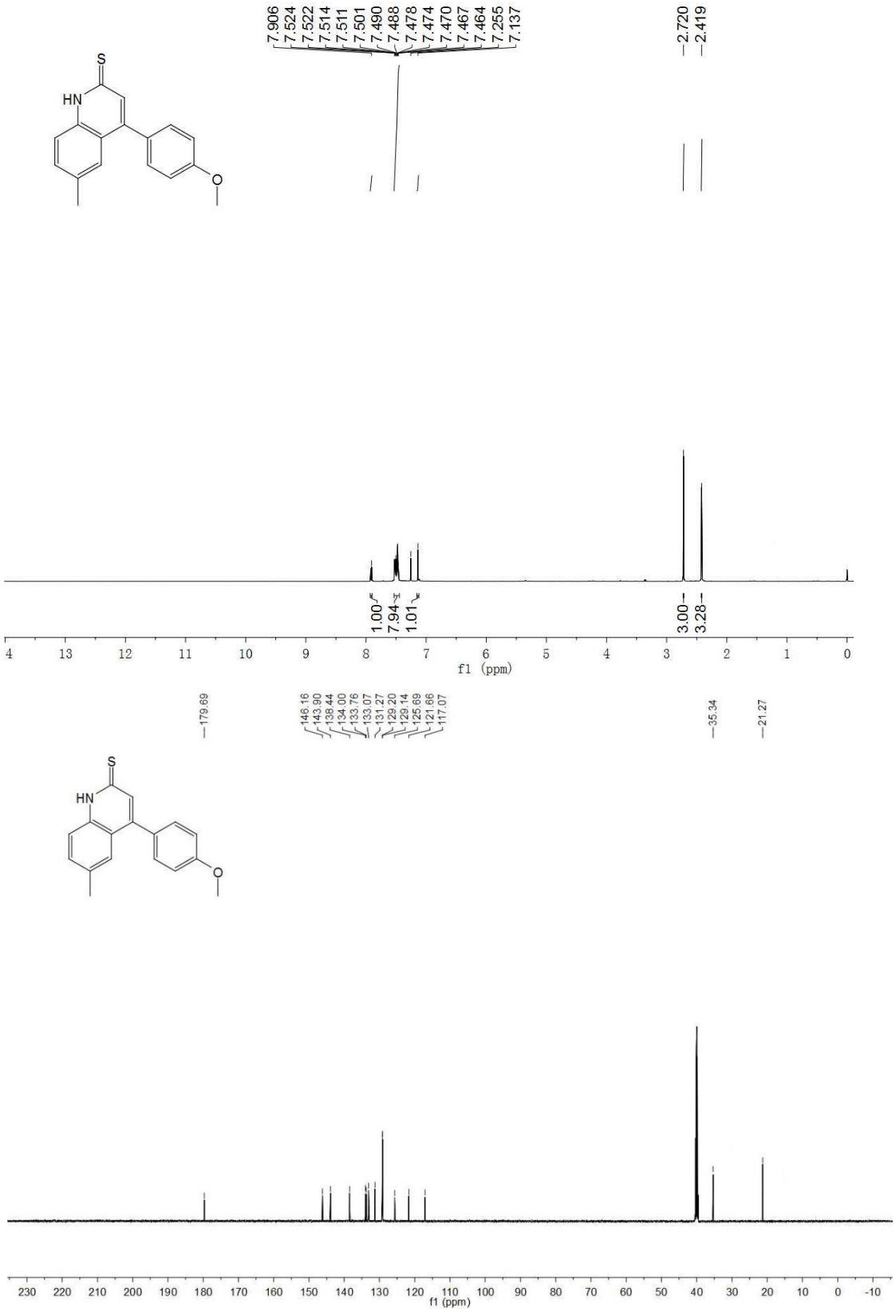


^{1}H and ^{13}C Spectra of compound 3k ($CDCl_3$,600 MHz)

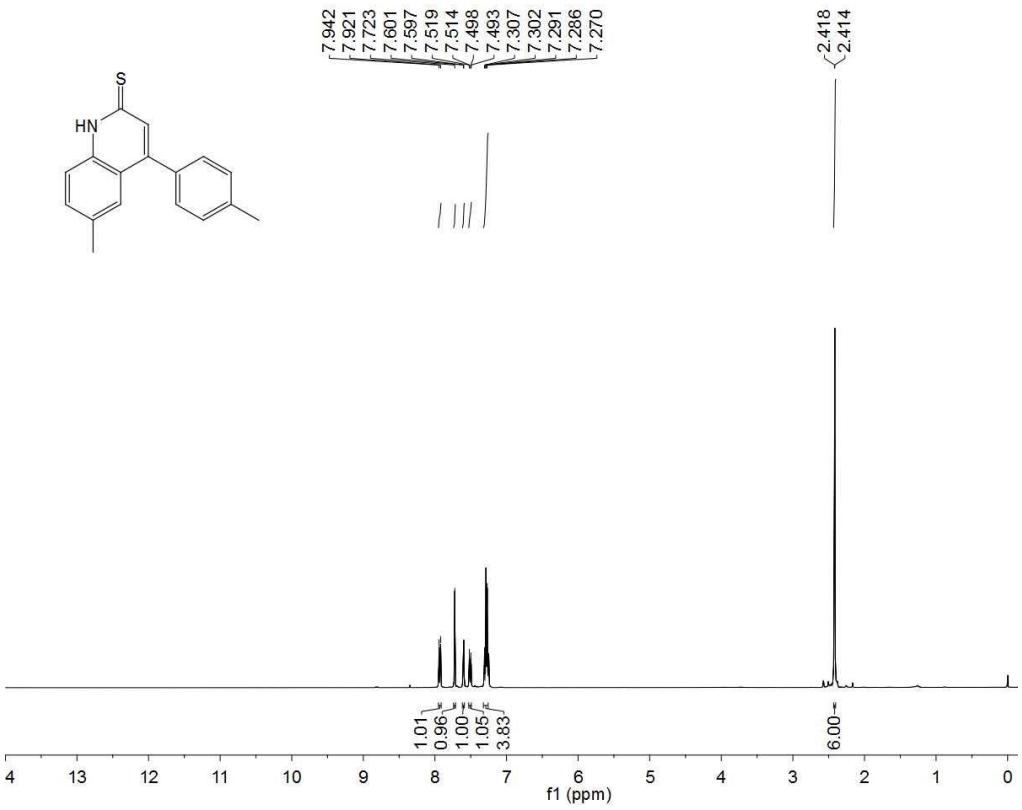


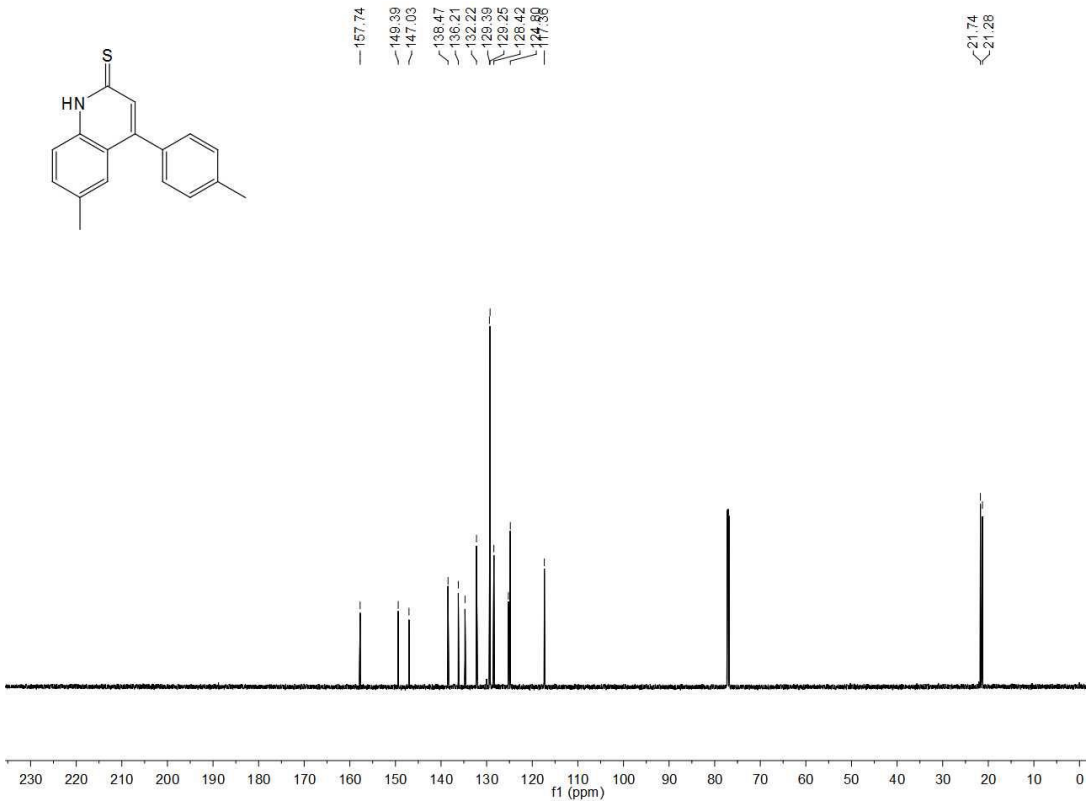


^{1}H and ^{13}C Spectra of compound 3l ($CDCl_3$,600 MHz)

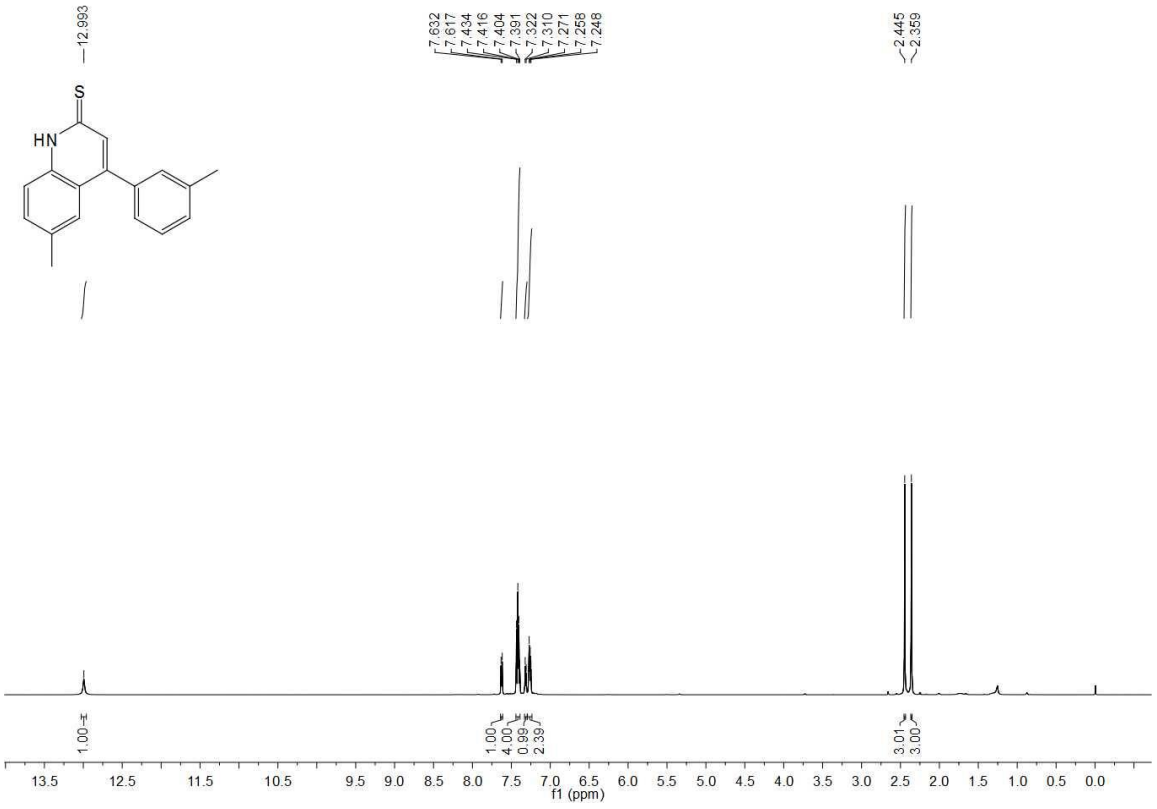


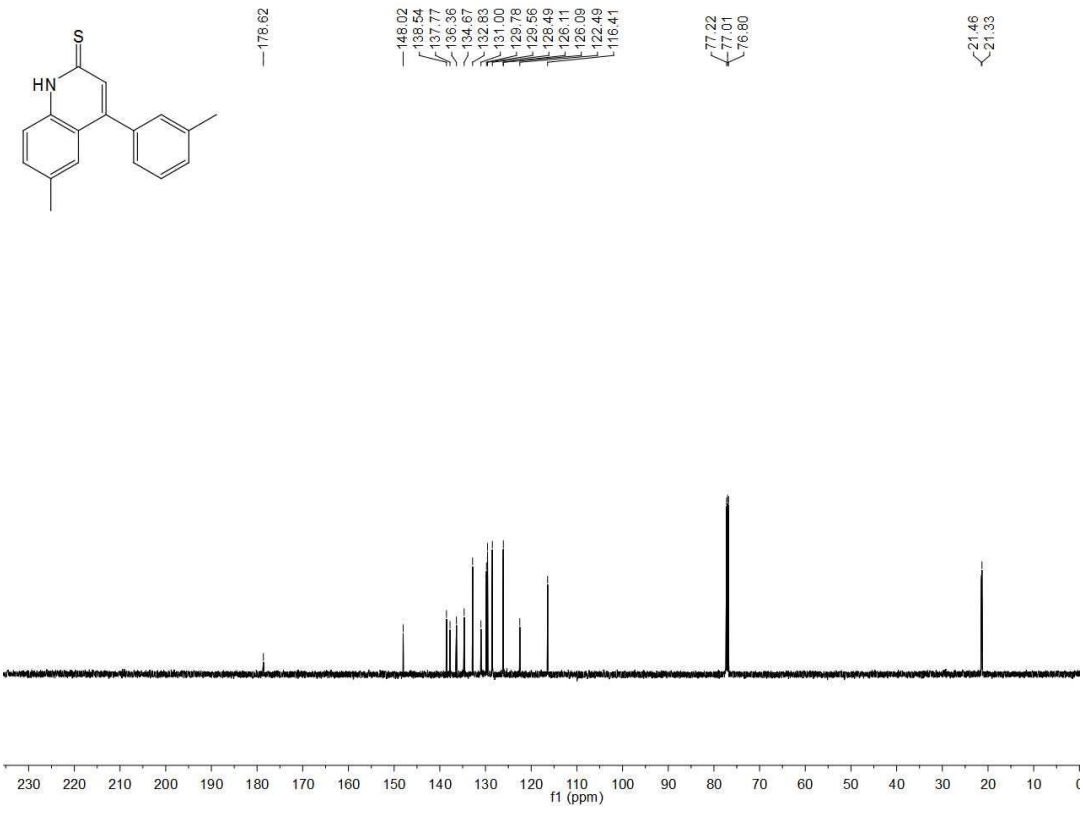
^{1}H and ^{13}C Spectra of compound 3m ($CDCl_3$,600 MHz)



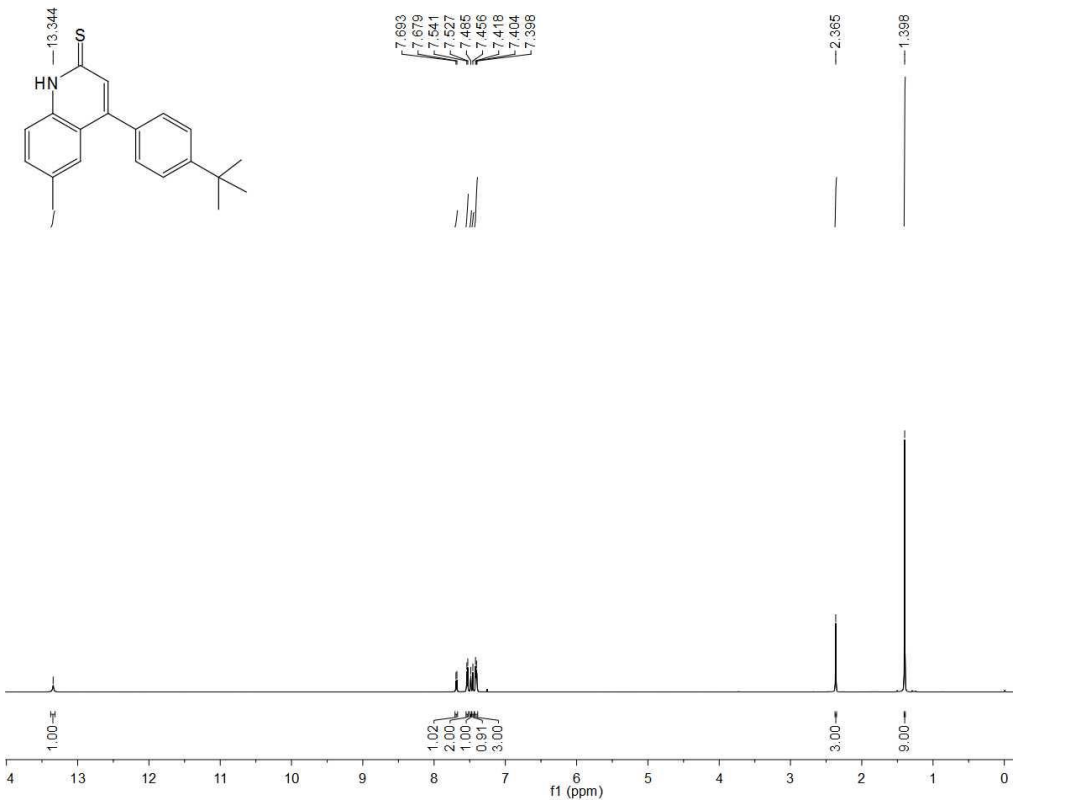


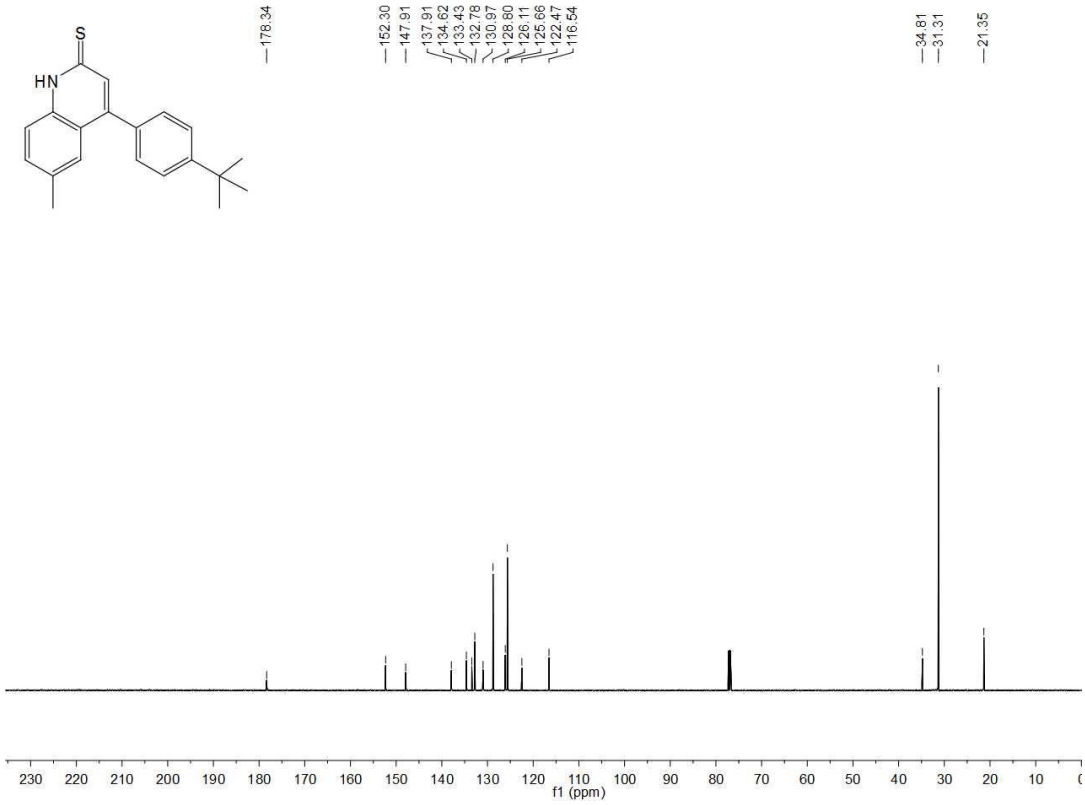
^{1}H and ^{13}C Spectra of compound 3n ($CDCl_3$,600 MHz)



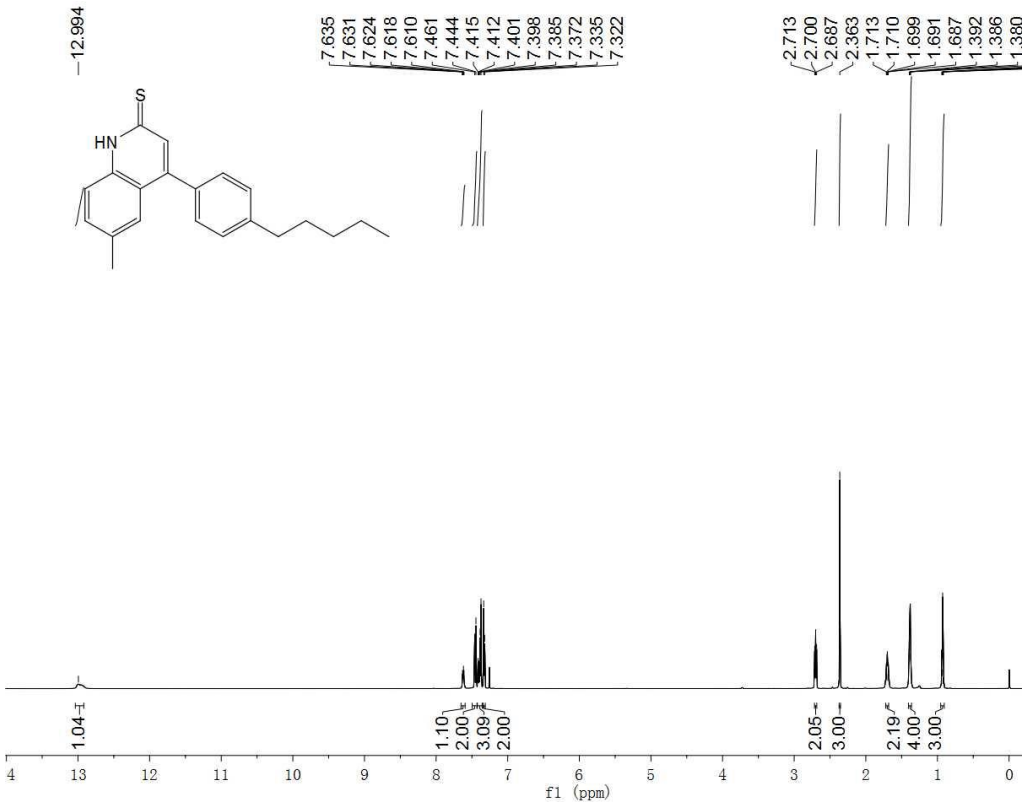


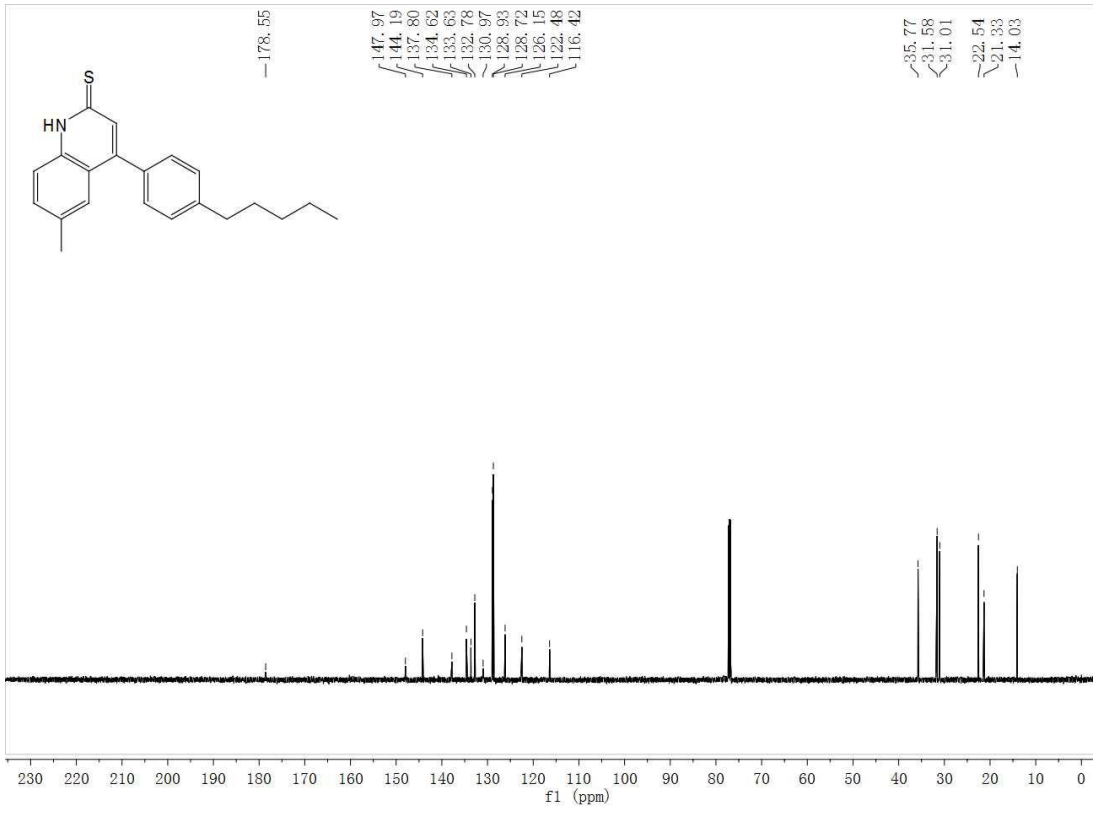
^{1}H and ^{13}C Spectra of compound 3o ($CDCl_3$,600 MHz)



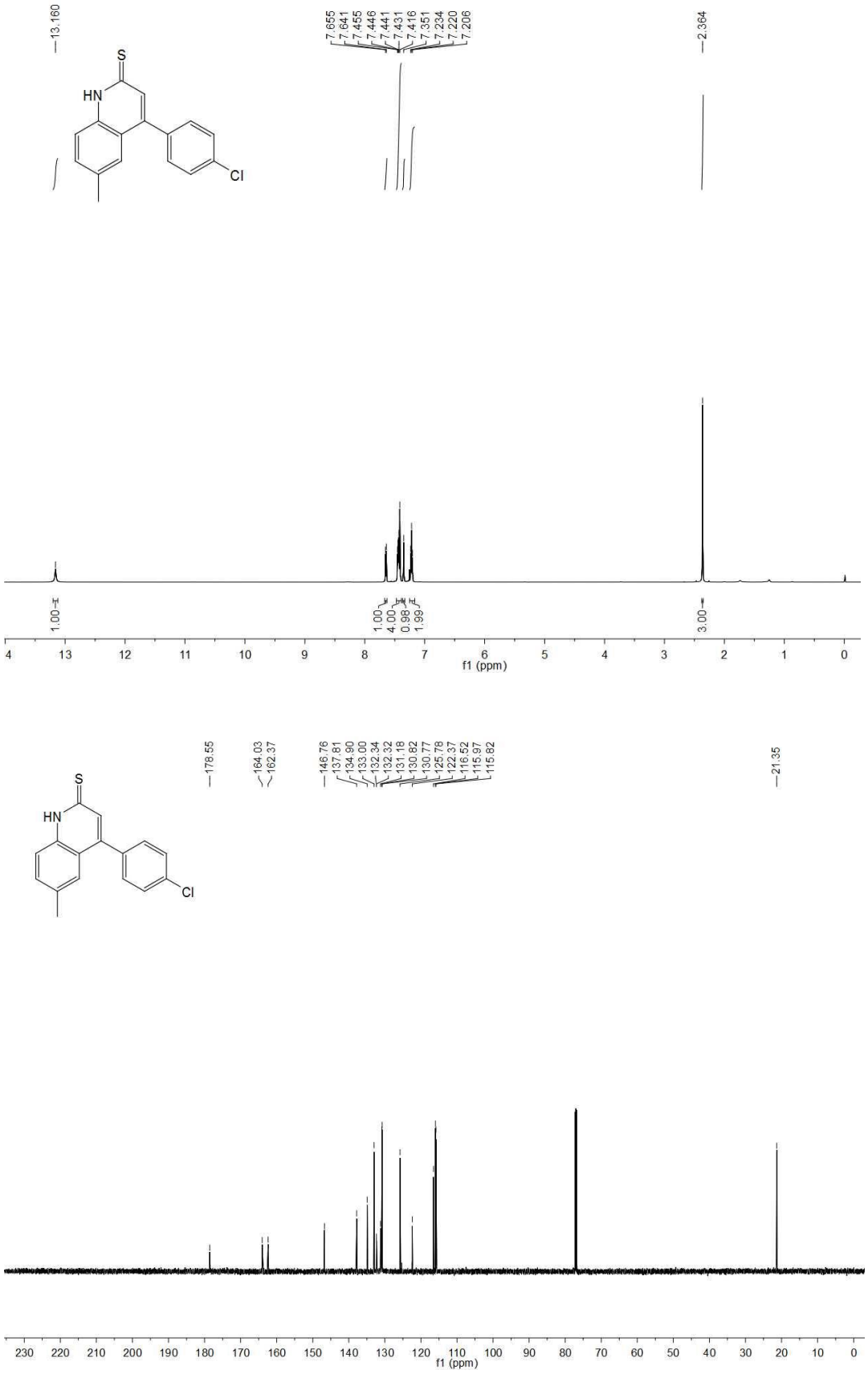


^{1}H and ^{13}C Spectra of compound 3p ($CDCl_3$,600 MHz)

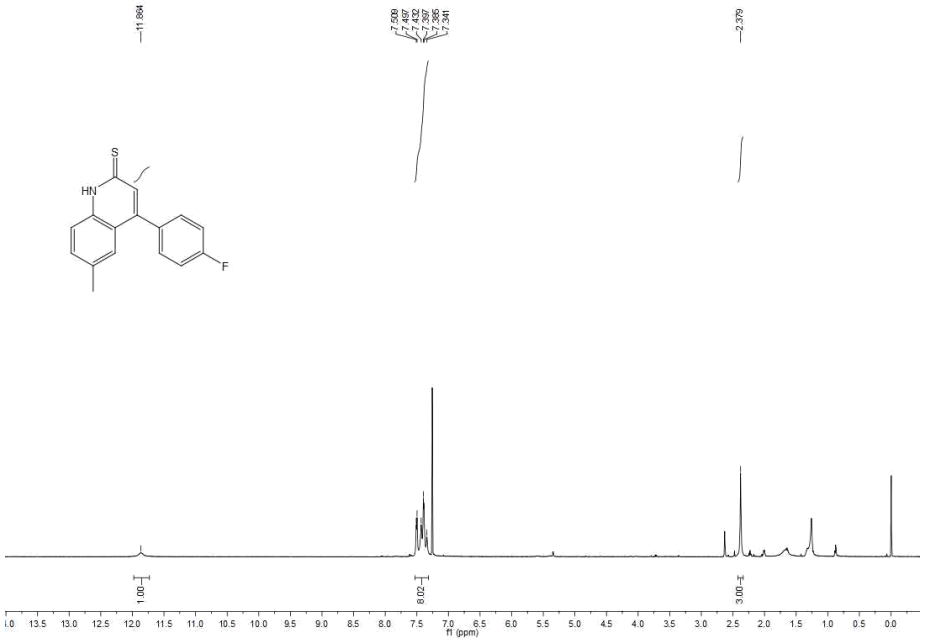


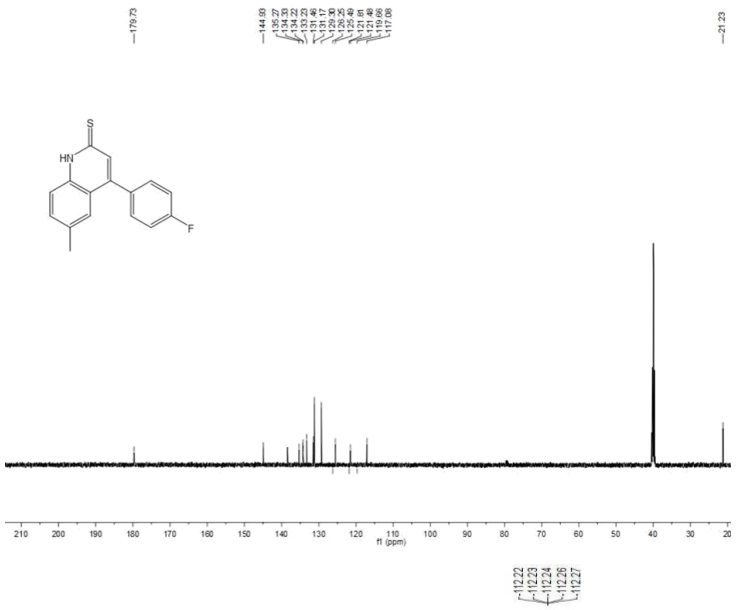


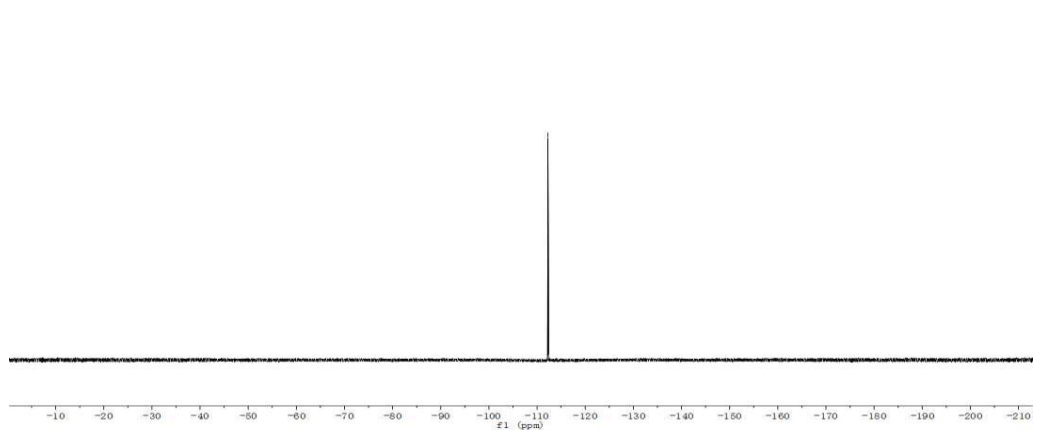
^{1}H and ^{13}C Spectra of compound 3q ($CDCl_3$,600 MHz)



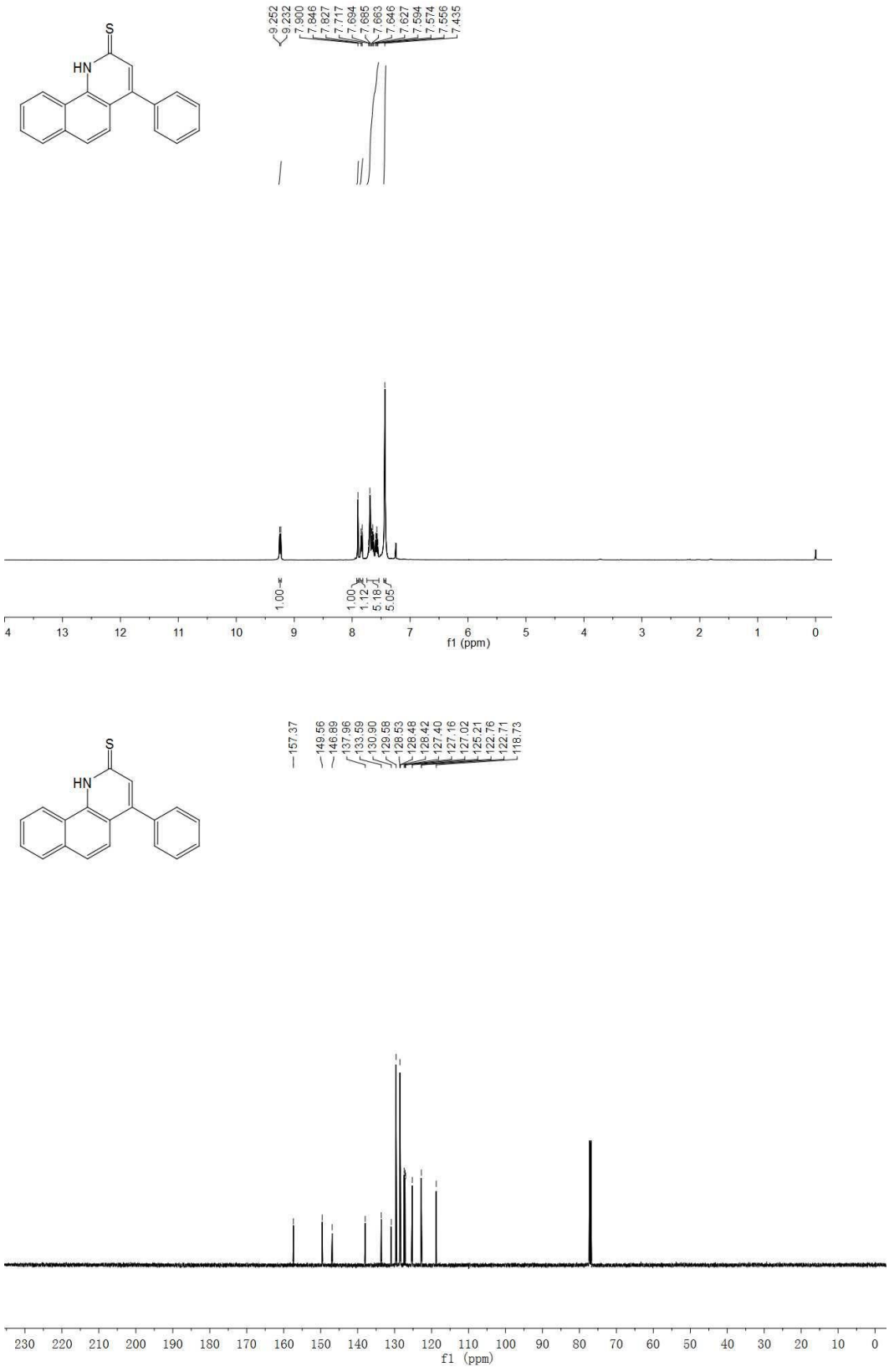
^{1}H (F) and ^{13}C Spectra of compound 3r ($CDCl_3$,600 MHz)



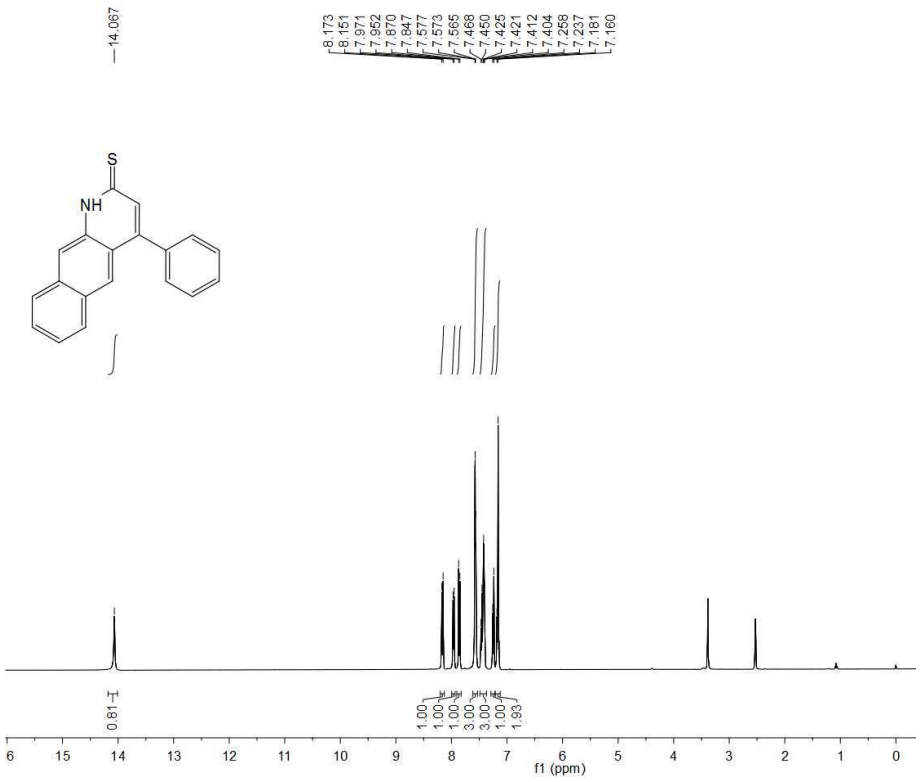


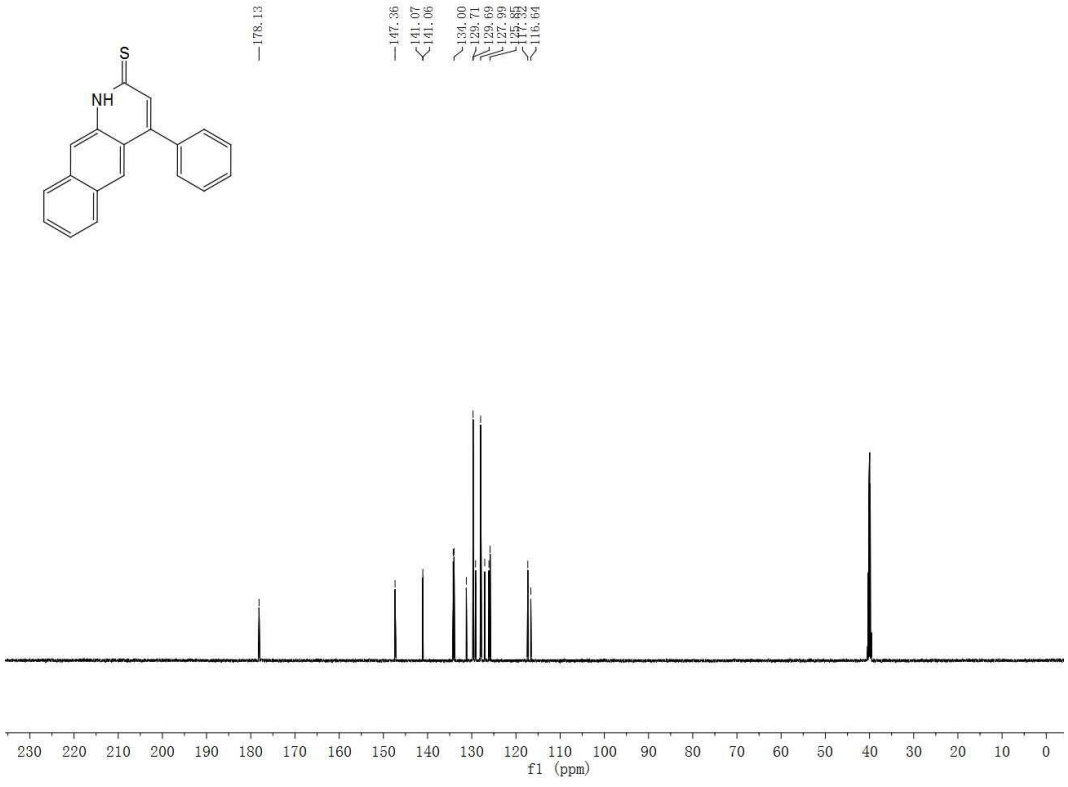


^{1}H and ^{13}C Spectra of compound 3s ($CDCl_3$,600 MHz)

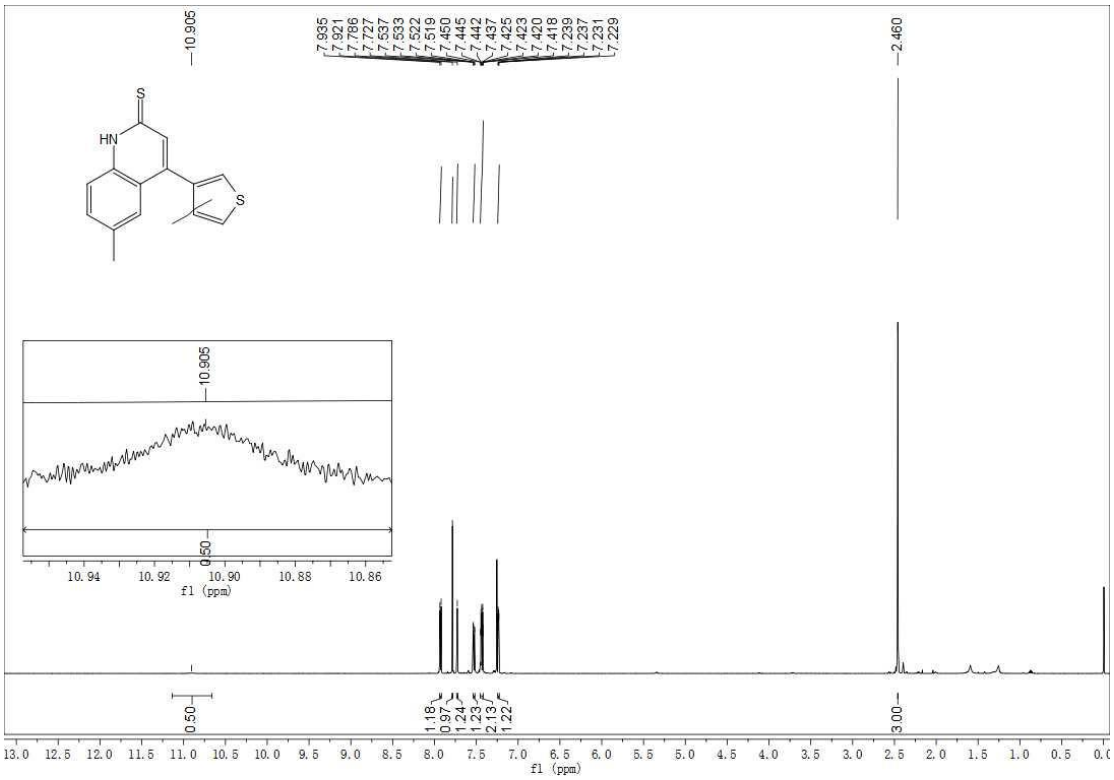


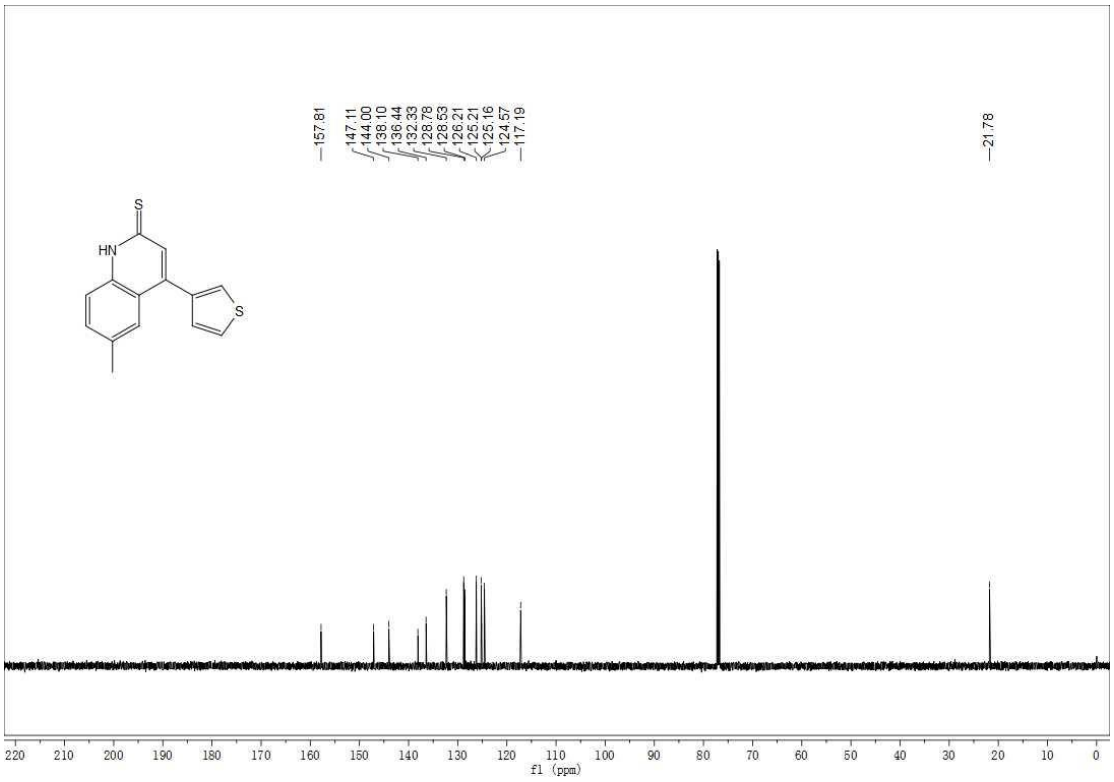
^{1}H and ^{13}C Spectra of compound 3t ($CDCl_3$,600 MHz)



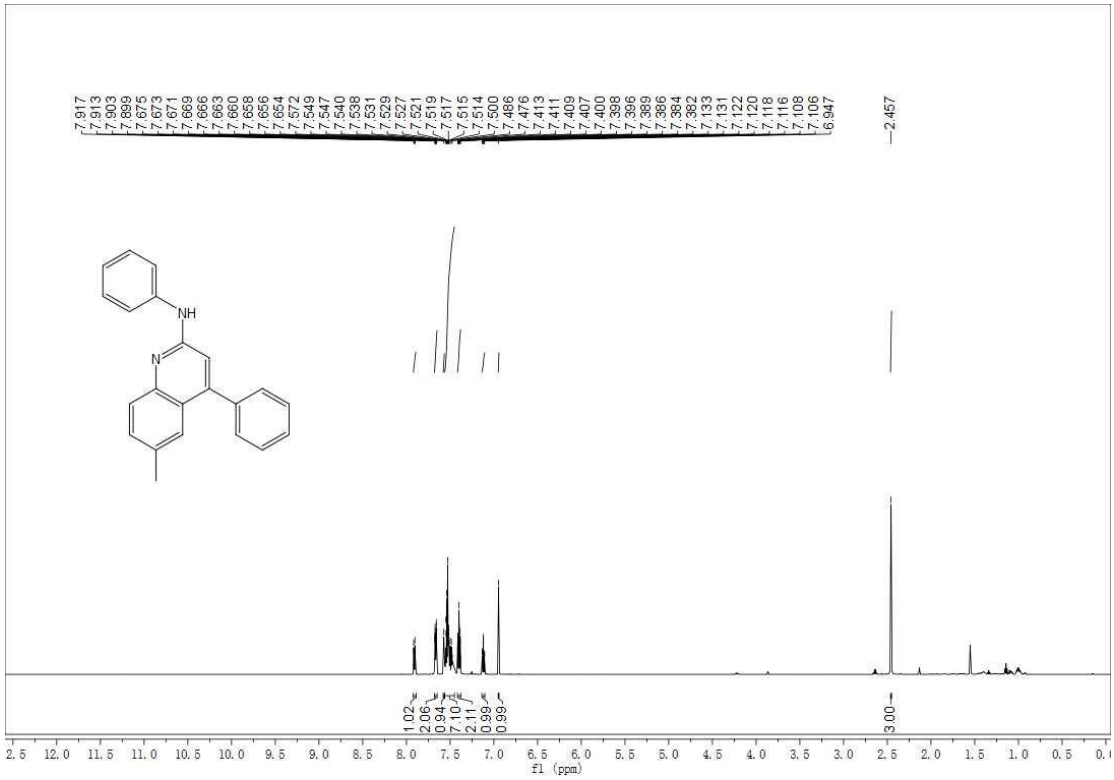


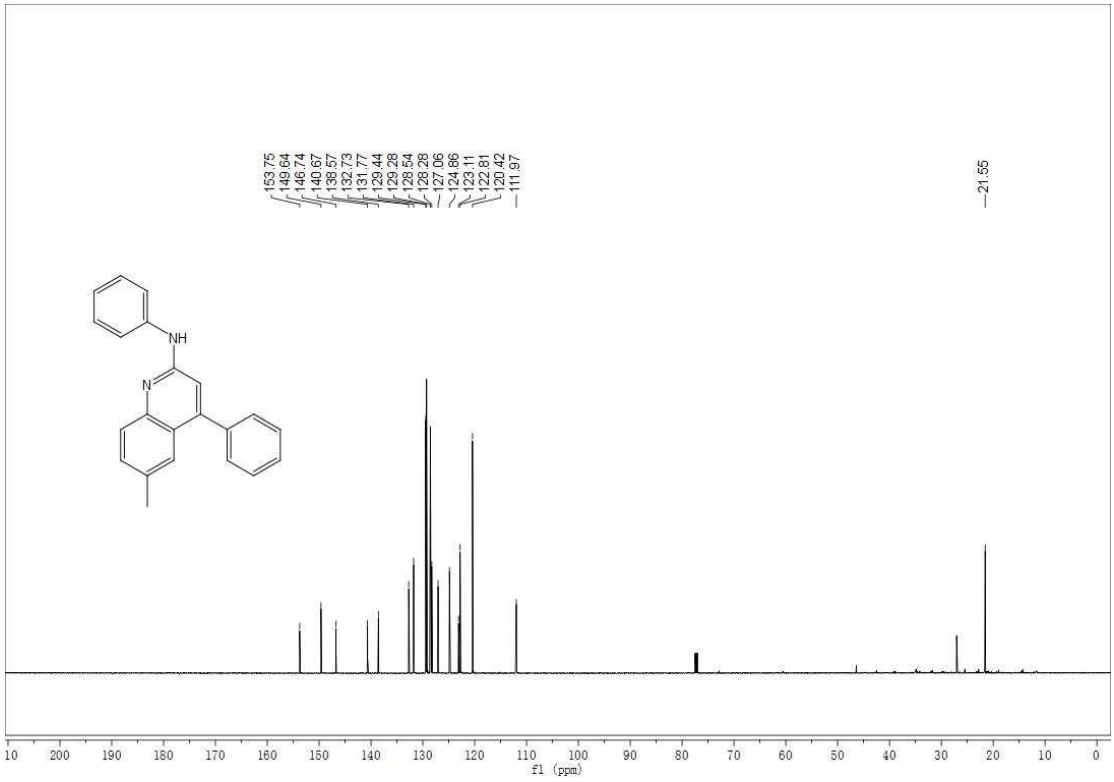
^{1}H and ^{13}C Spectra of compound 3u ($CDCl_3$,600 MHz)



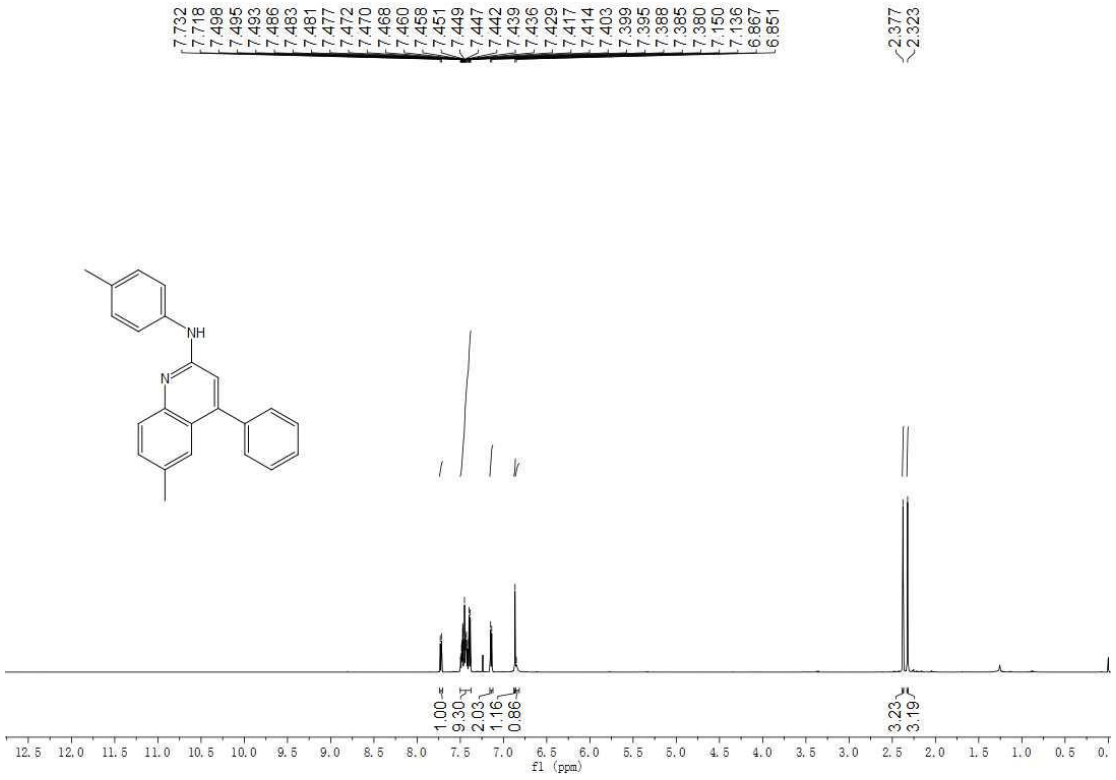


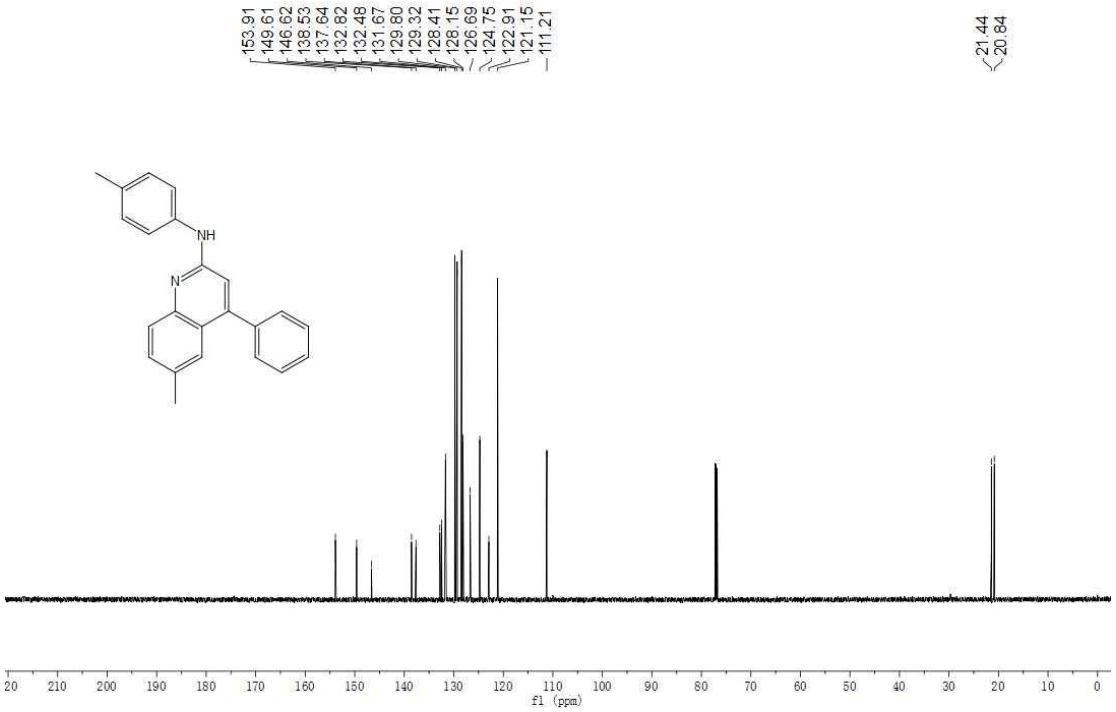
^{1}H and ^{13}C Spectra of compound 4a ($CDCl_3$,600 MHz)



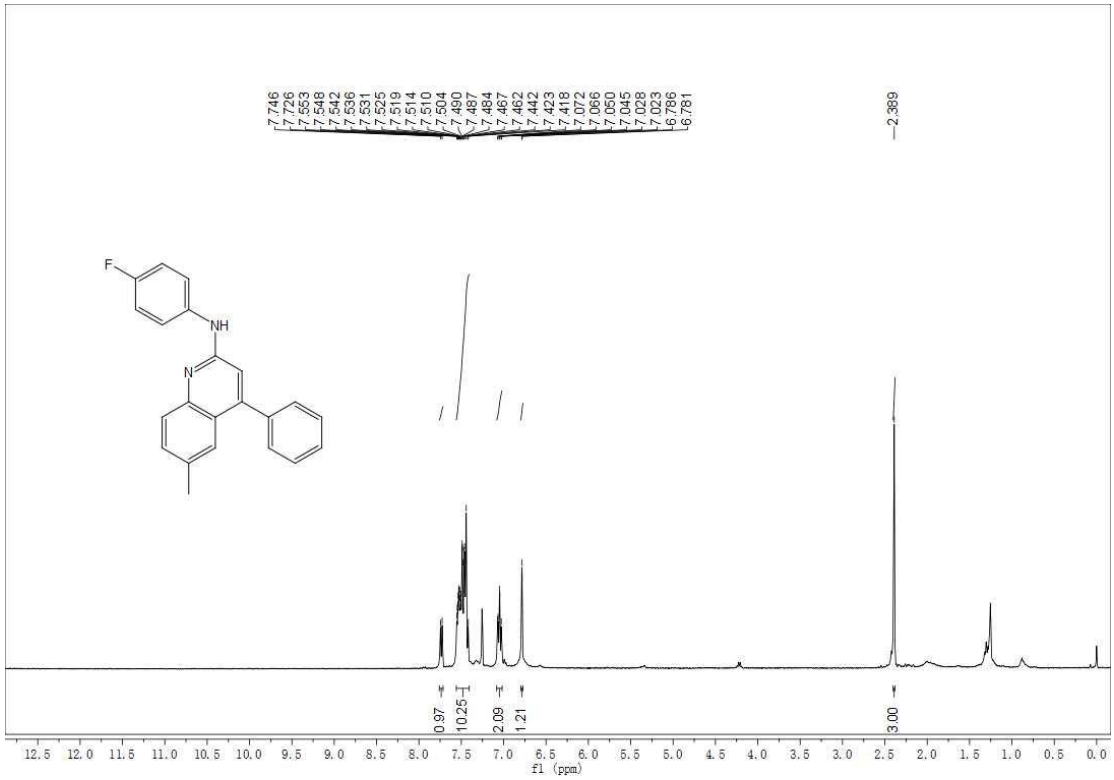


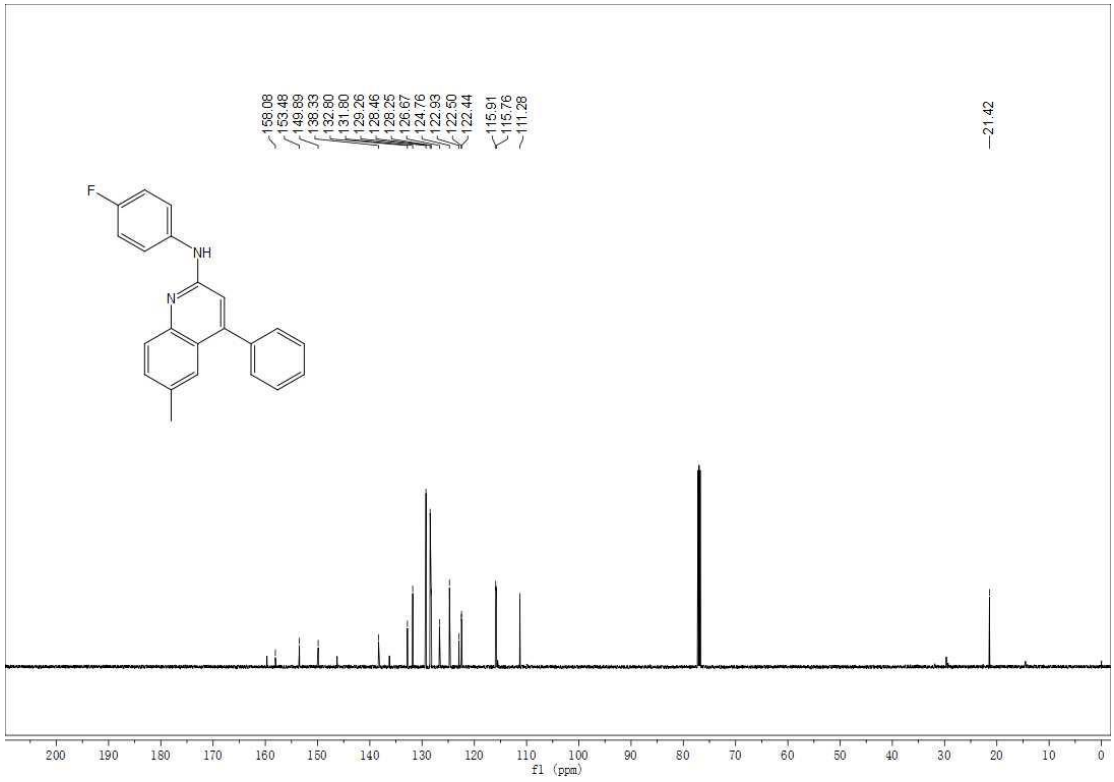
^{1}H and ^{13}C Spectra of compound 4b ($CDCl_3$,600 MHz)



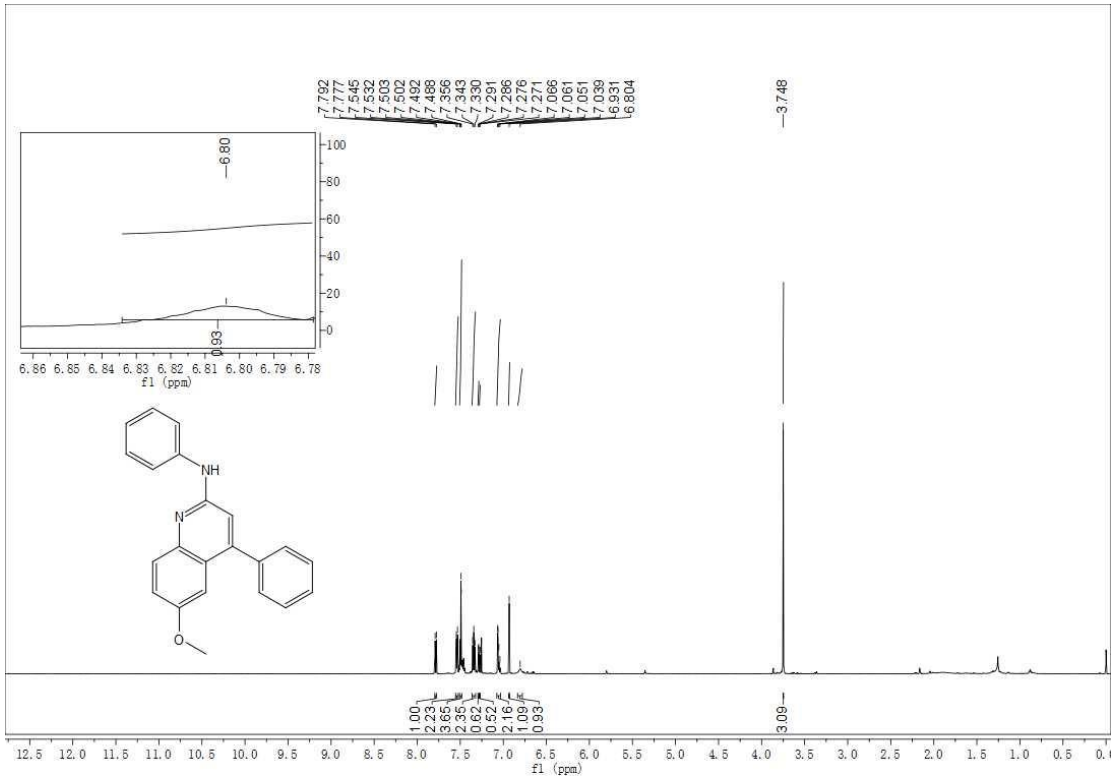


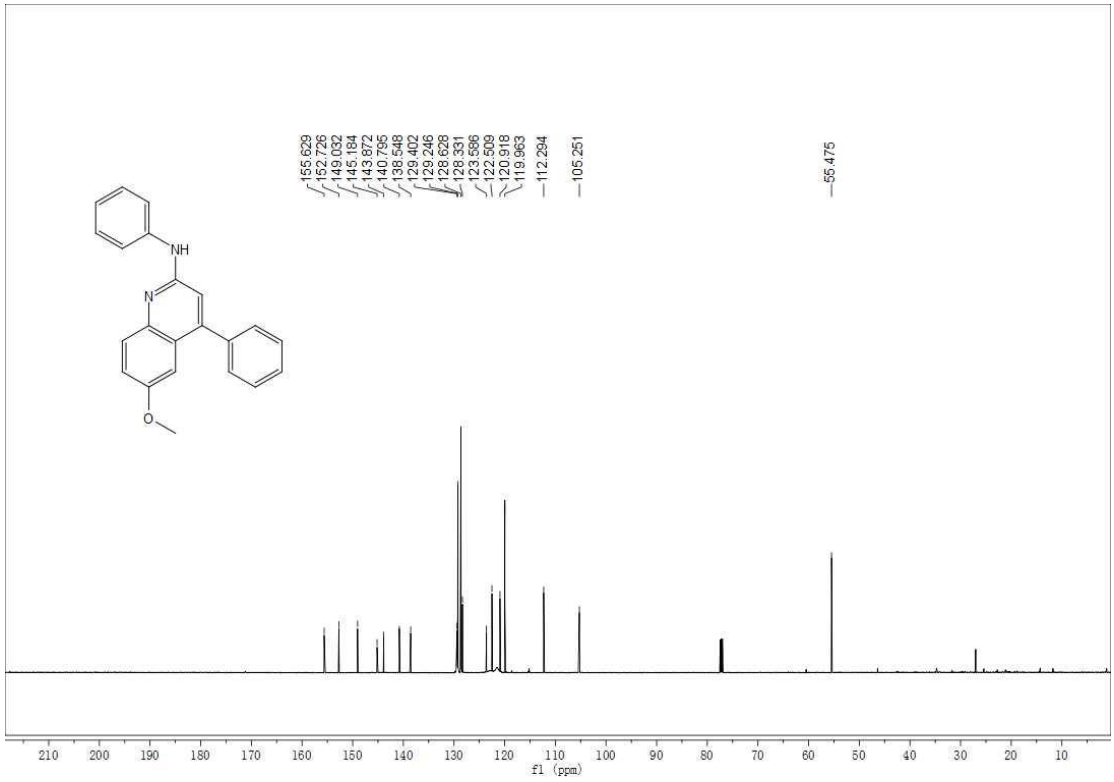
^{1}H and ^{13}C Spectra of compound 4c ($CDCl_3$,400 MHz)



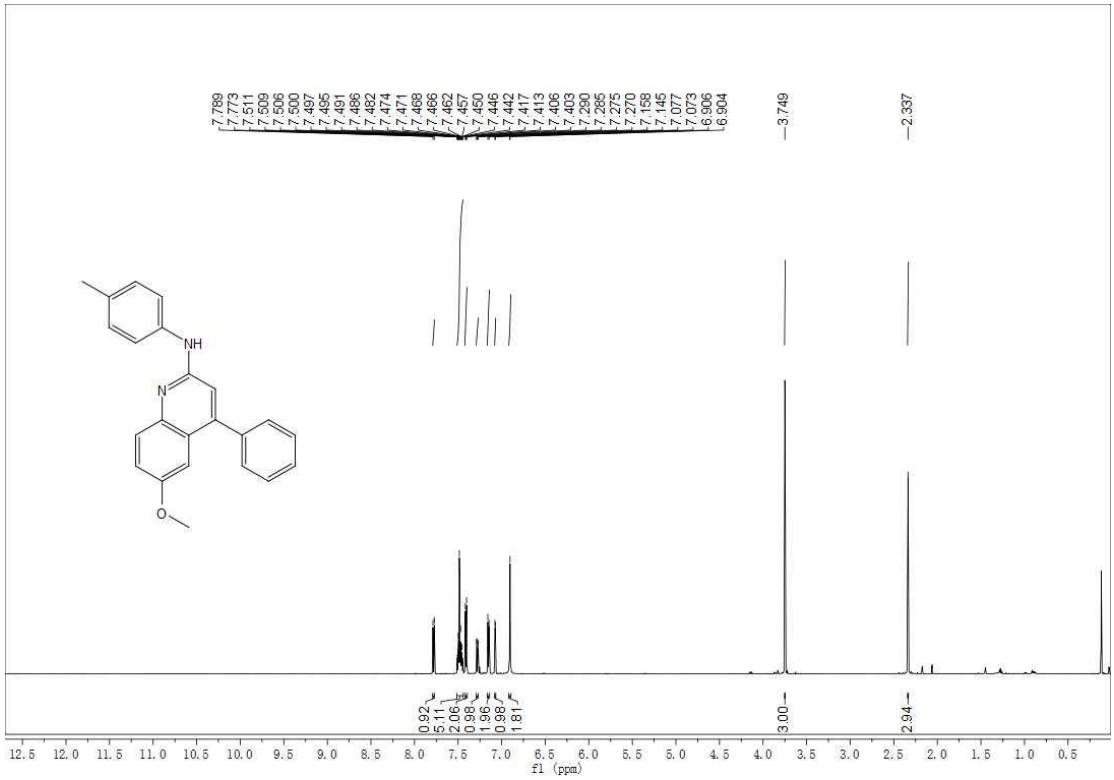


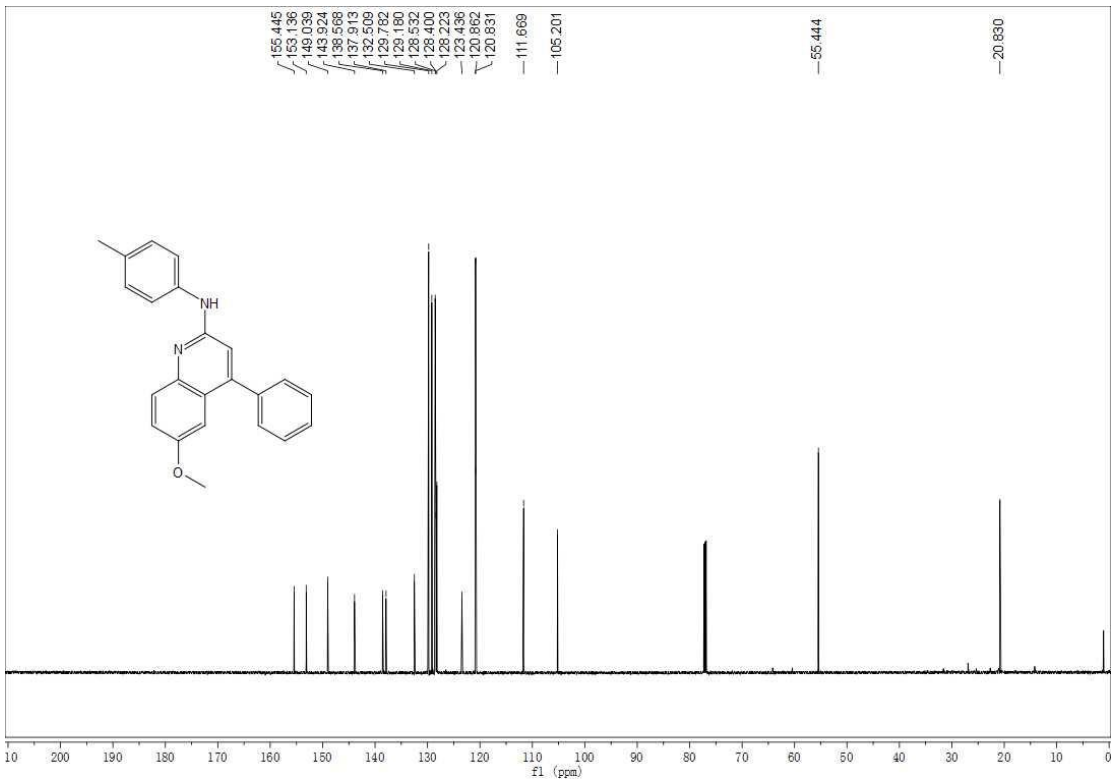
^{1}H and ^{13}C Spectra of compound 4d ($CDCl_3$,600 MHz)



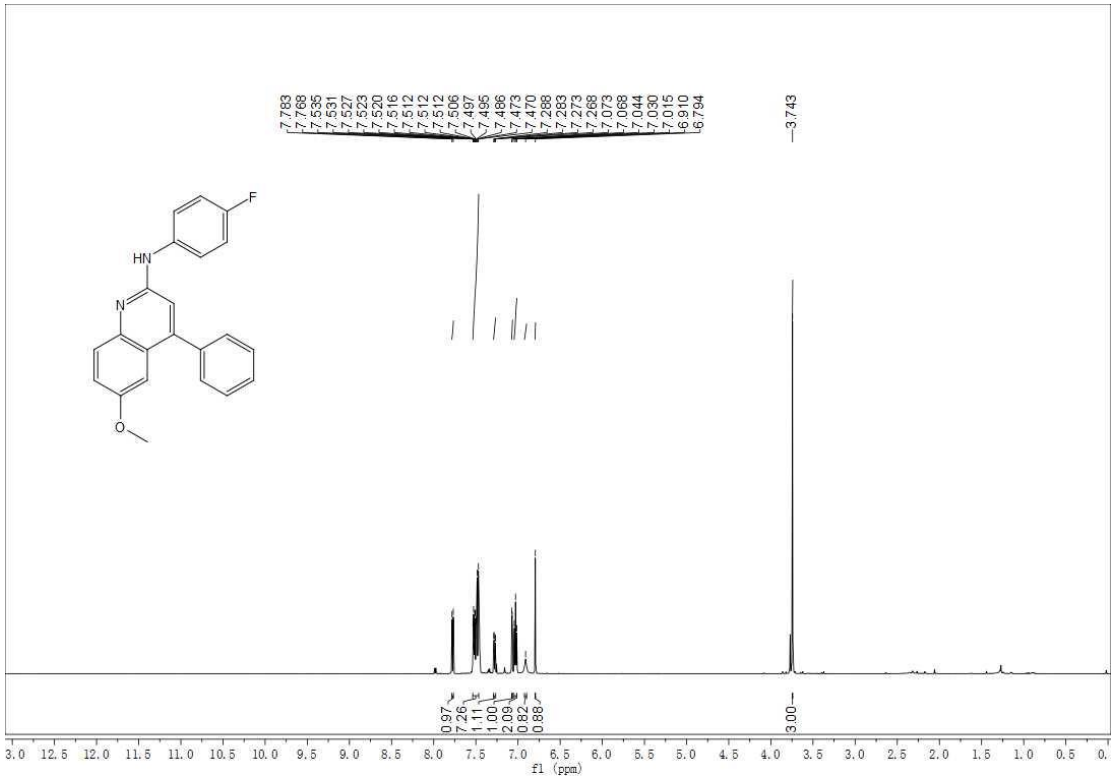


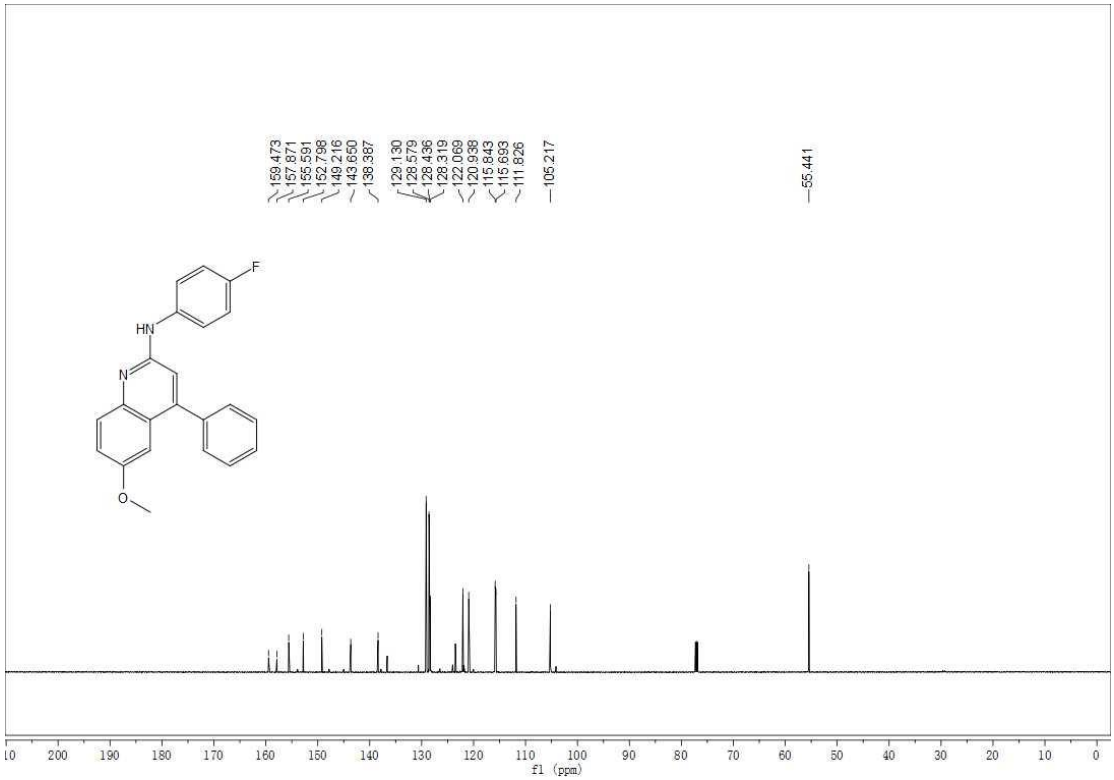
^{1}H and ^{13}C Spectra of compound 4e ($CDCl_3$,600 MHz)



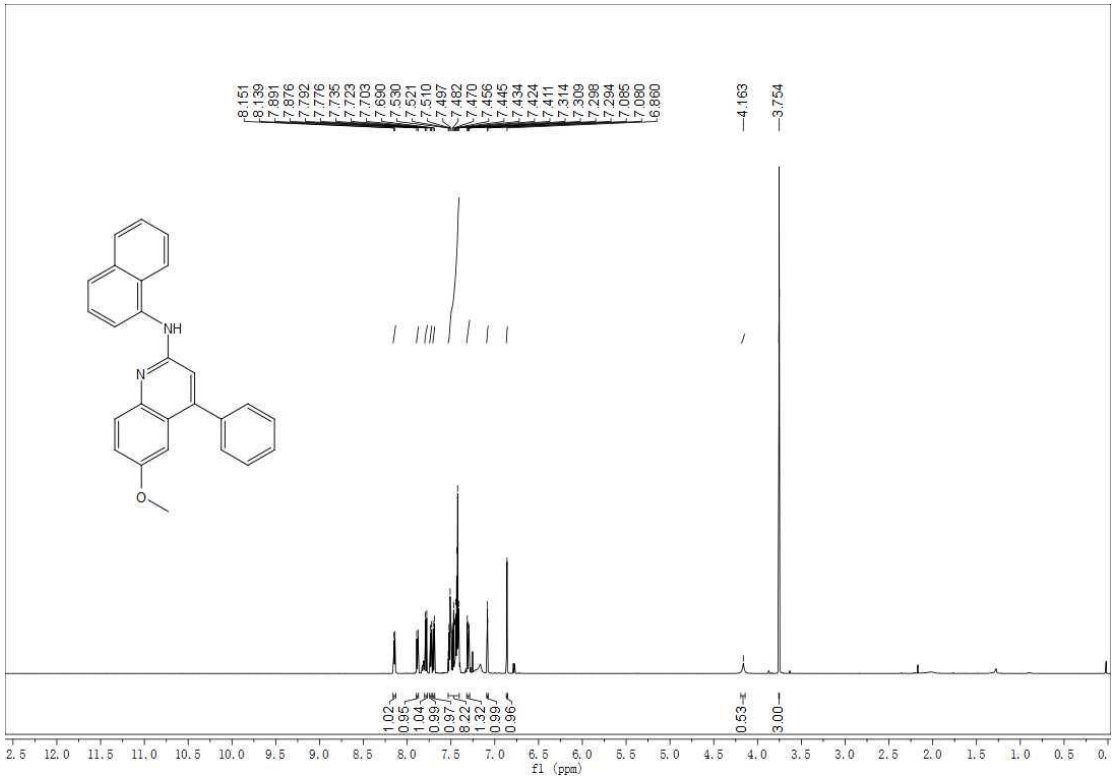


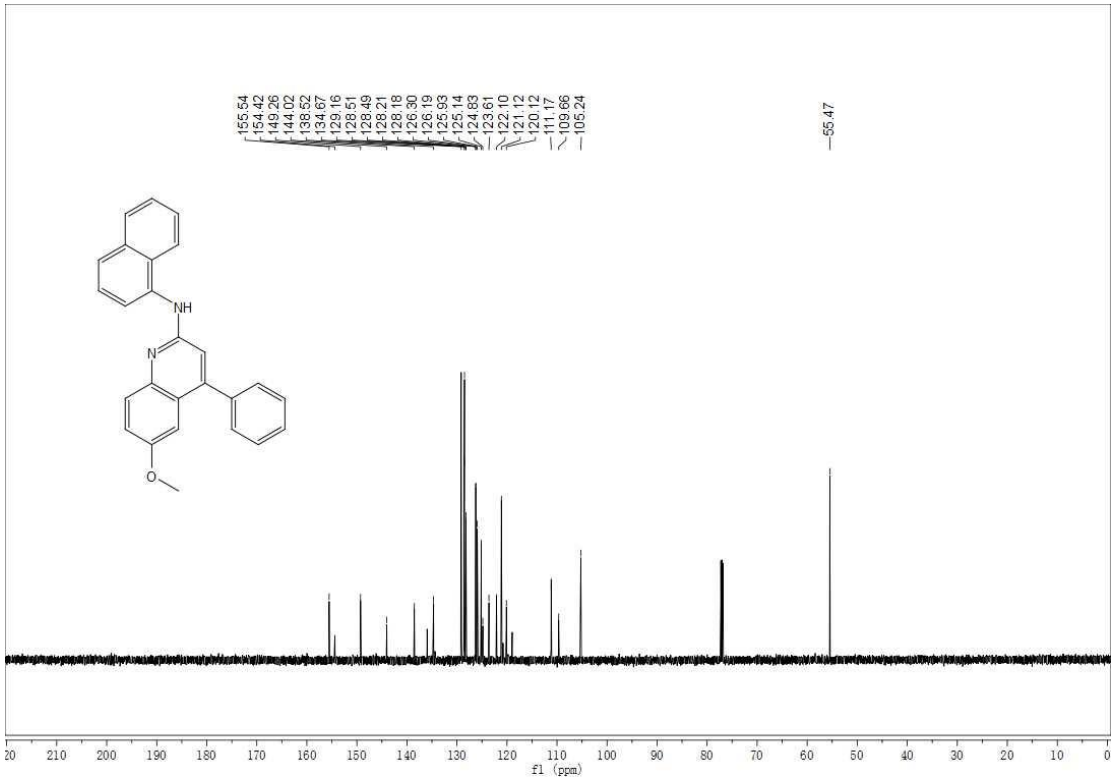
^{1}H and ^{13}C Spectra of compound 4f ($CDCl_3$,600 MHz)



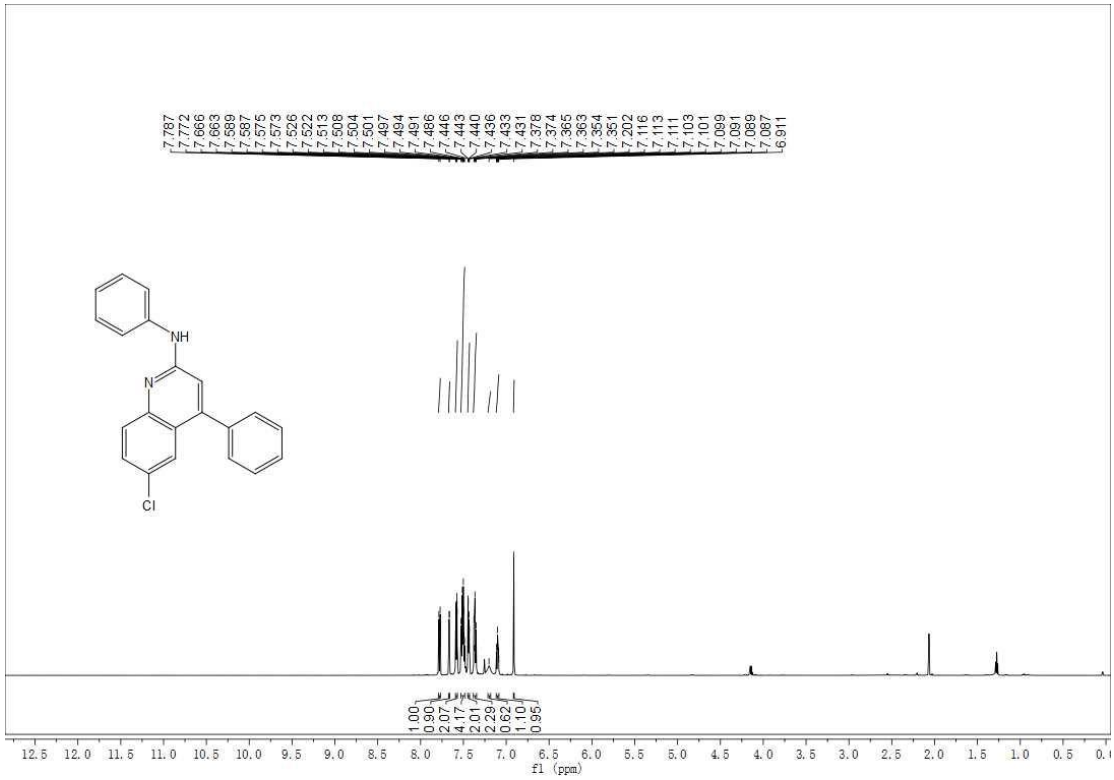


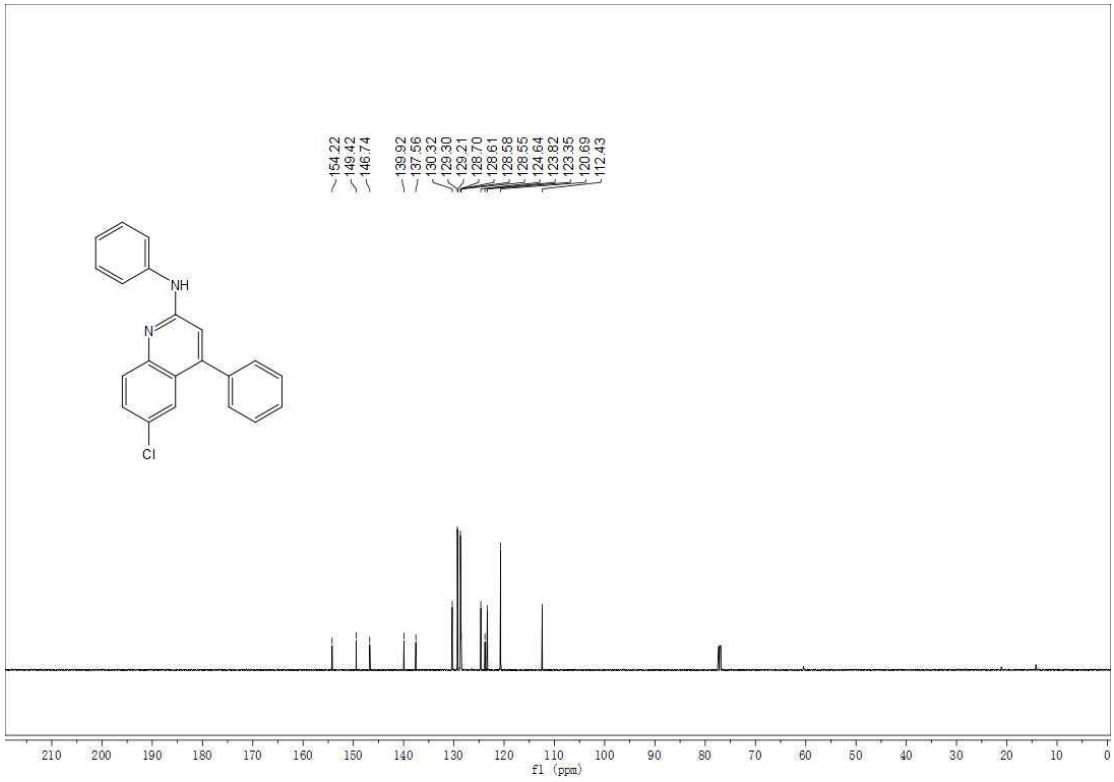
^{1}H and ^{13}C Spectra of compound 4g ($CDCl_3$,600 MHz)



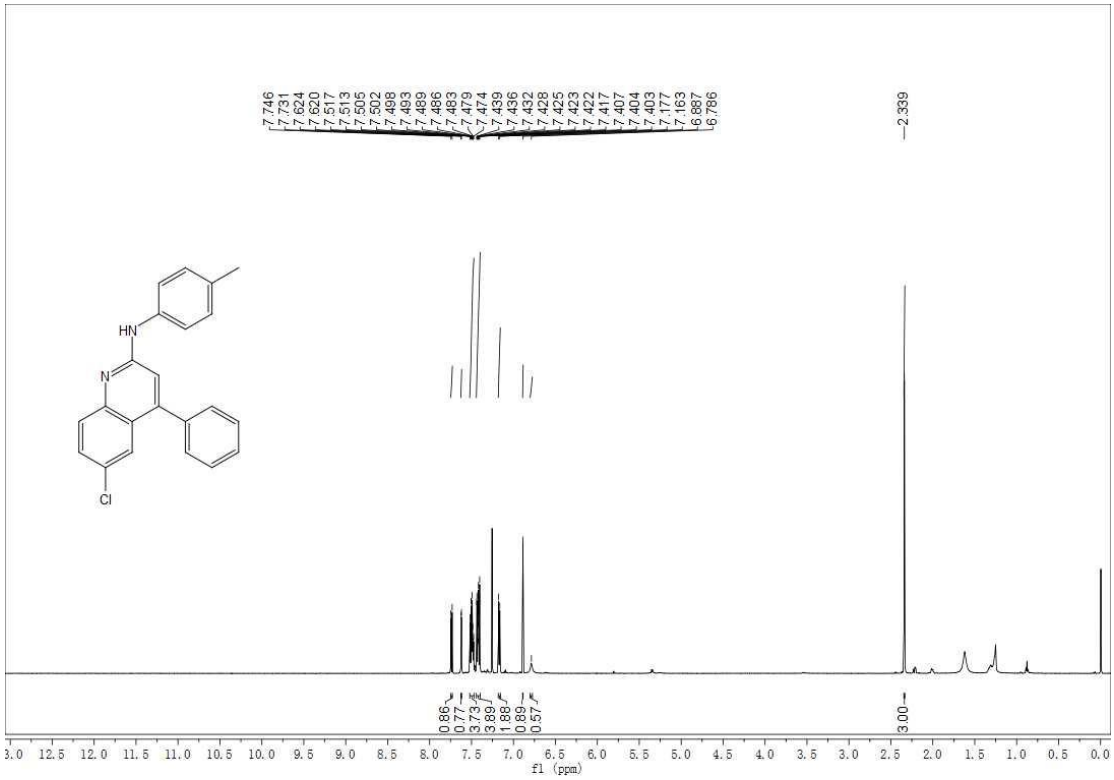


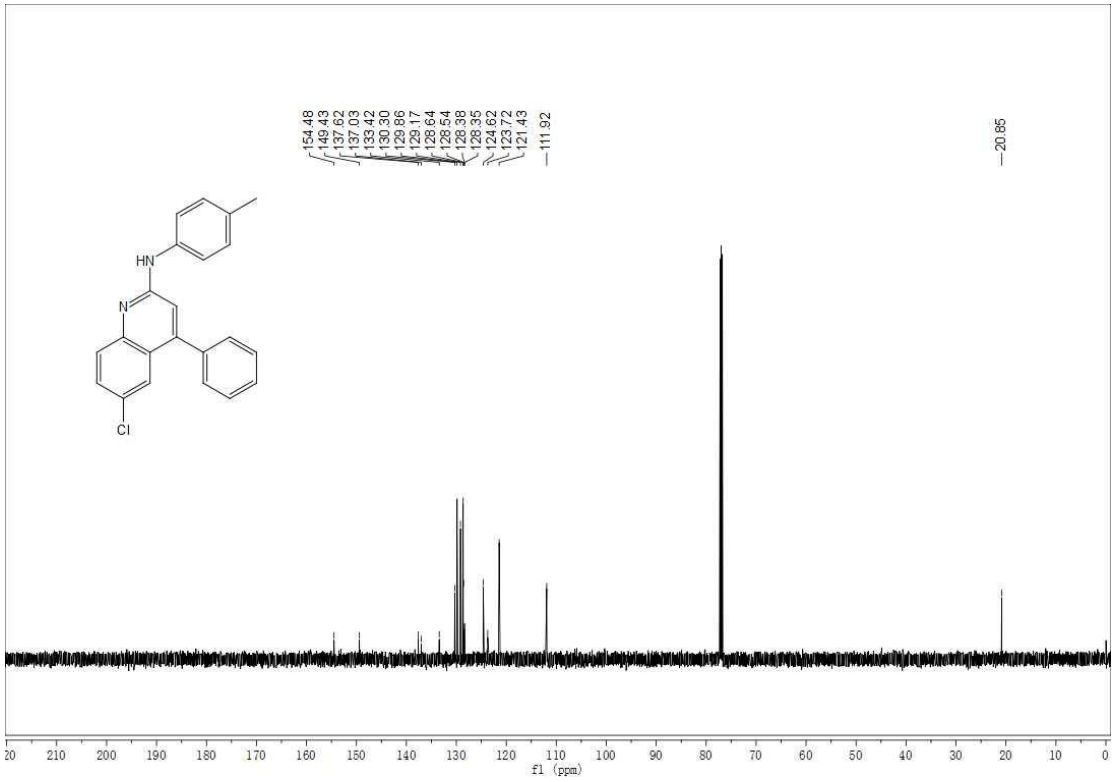
^{1}H and ^{13}C Spectra of compound 4h ($CDCl_3$,600 MHz)



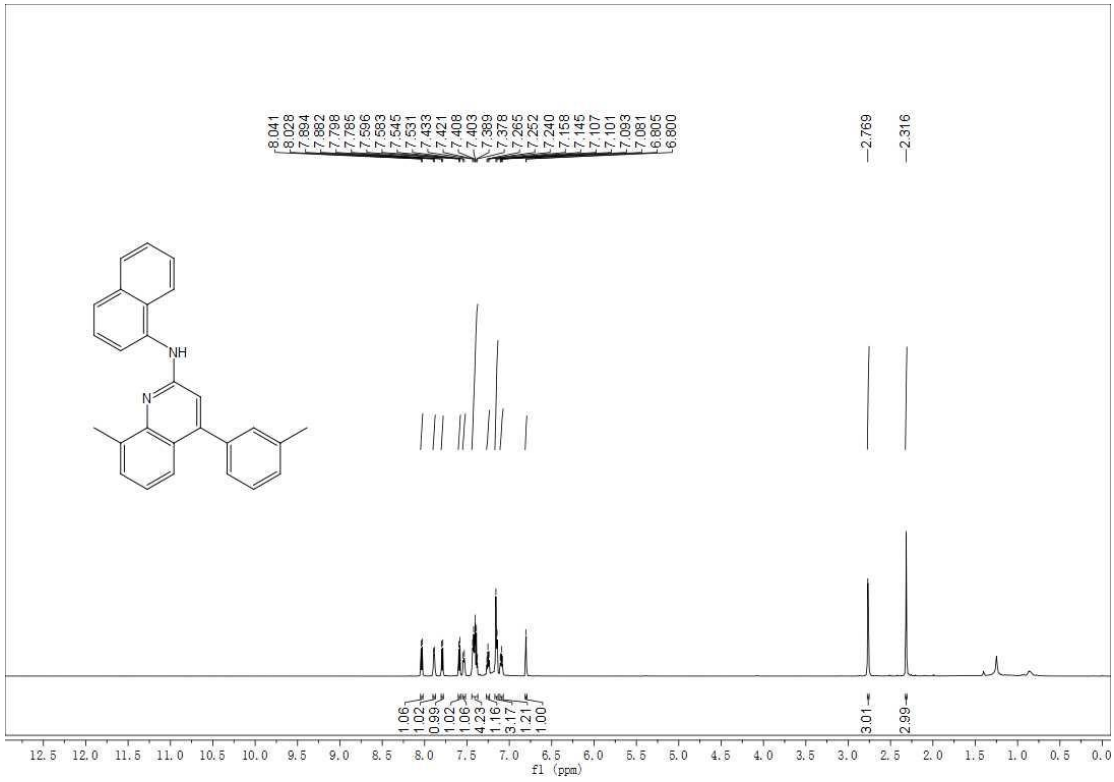


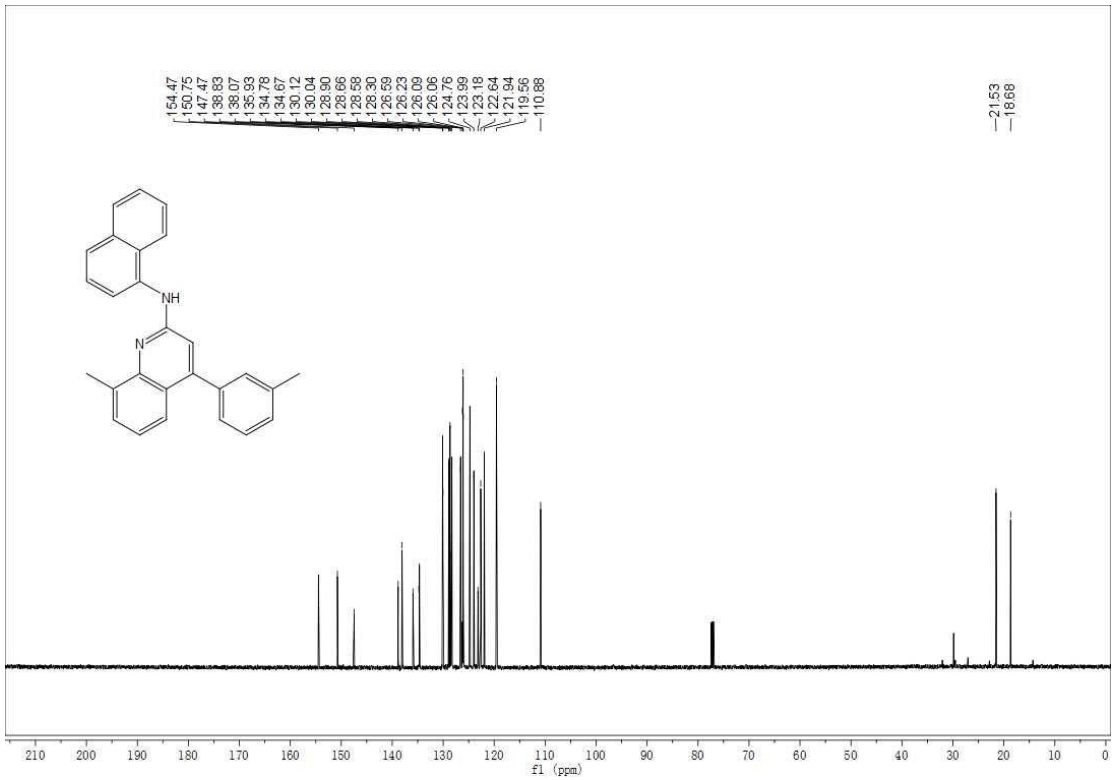
^{1}H and ^{13}C Spectra of compound 4i ($CDCl_3$,600 MHz)



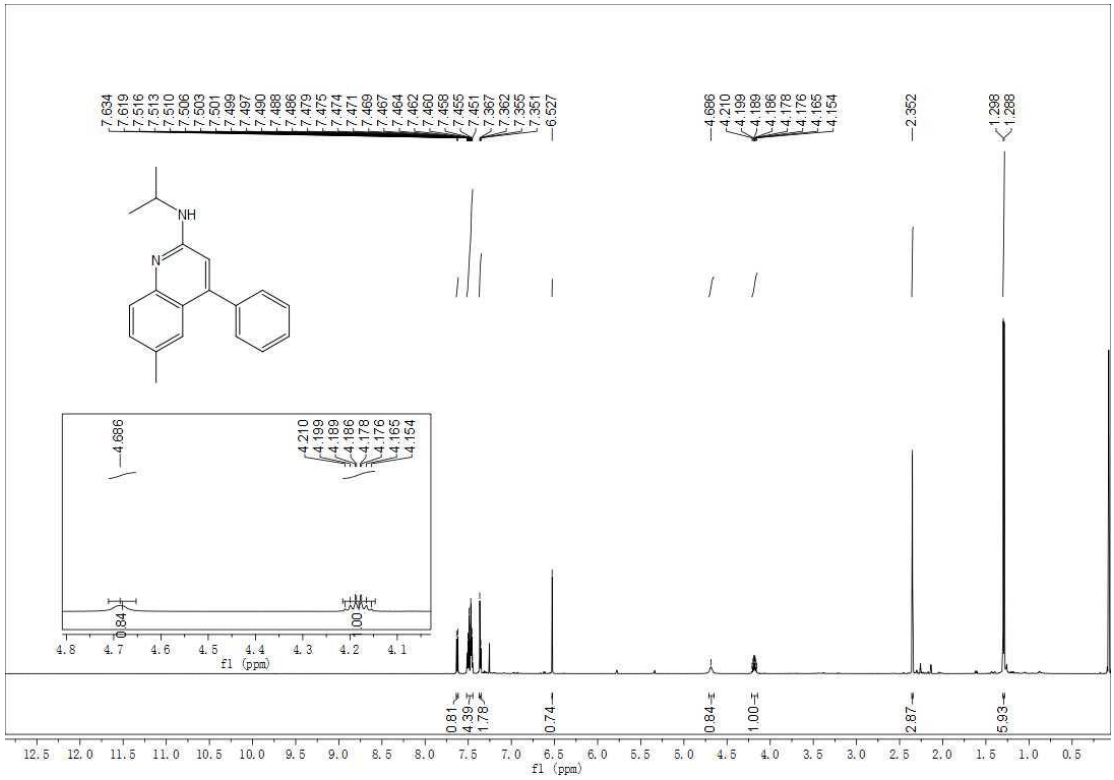


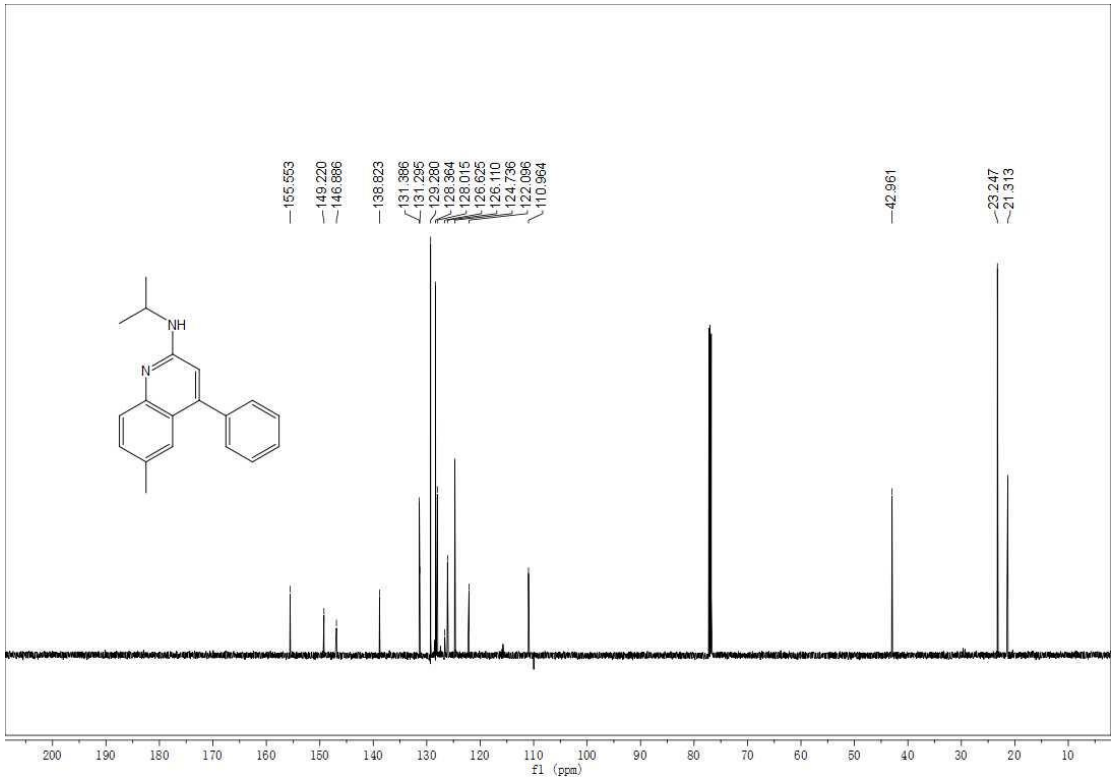
^{1}H and ^{13}C Spectra of compound 4j ($CDCl_3$,600 MHz)



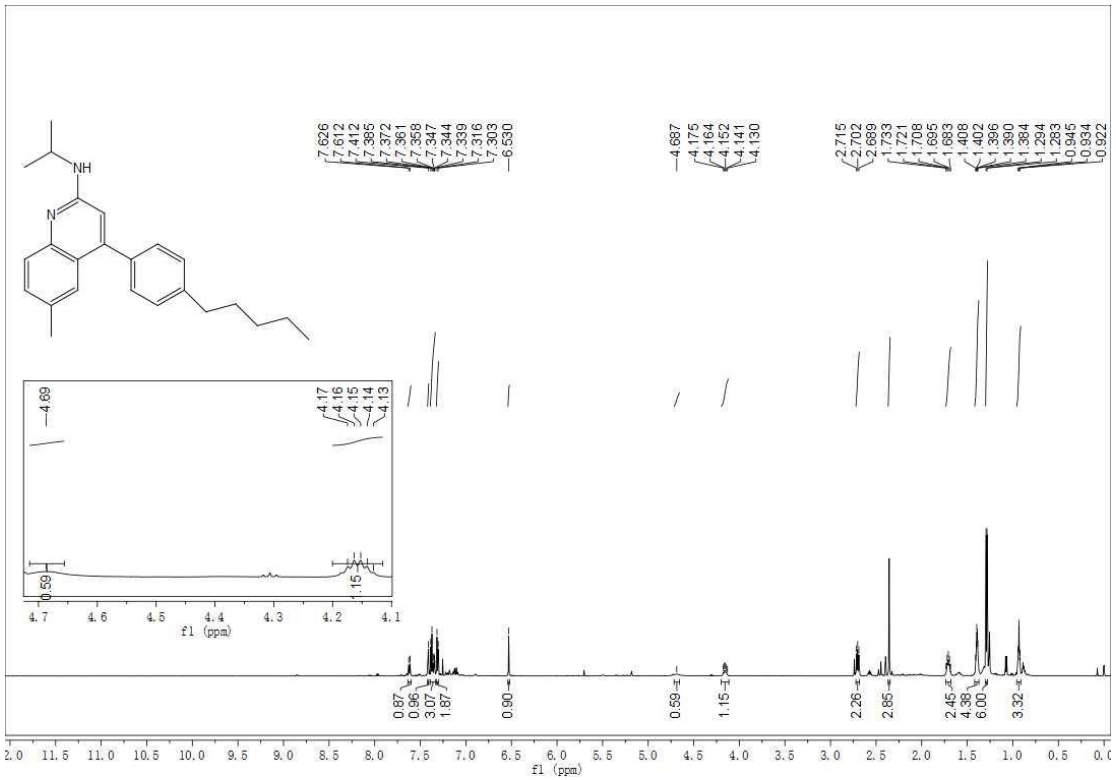


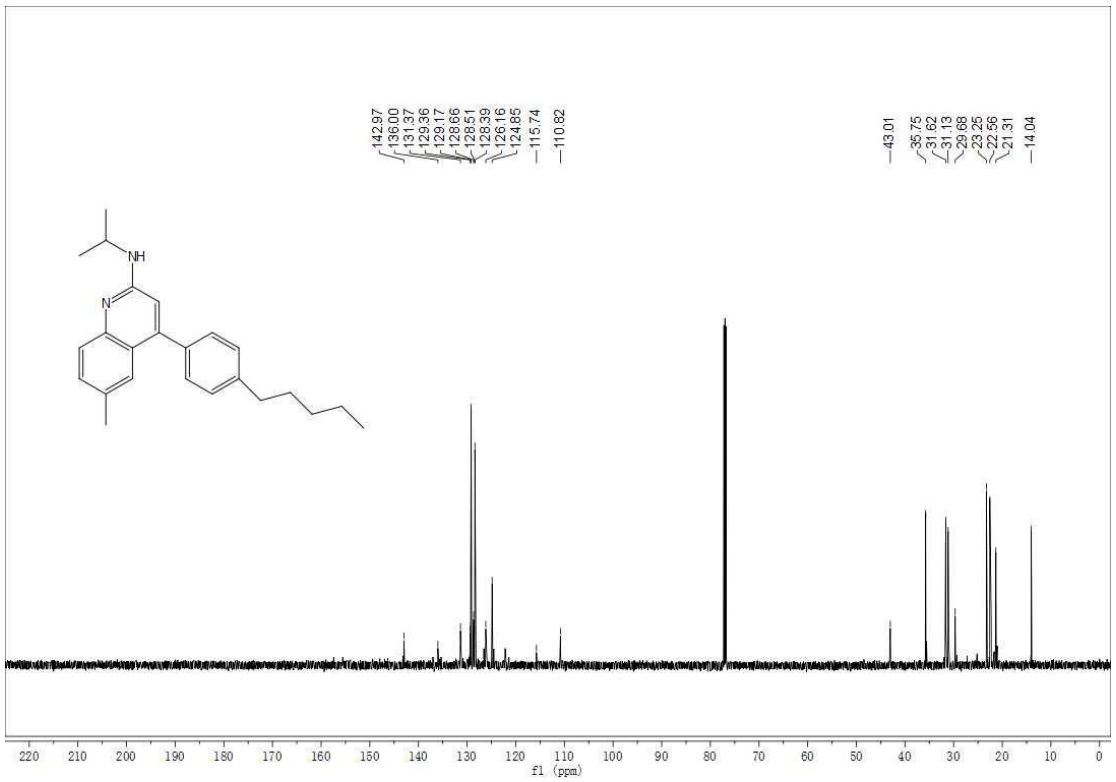
^{1}H and ^{13}C Spectra of compound 4k ($CDCl_3$,600 MHz)



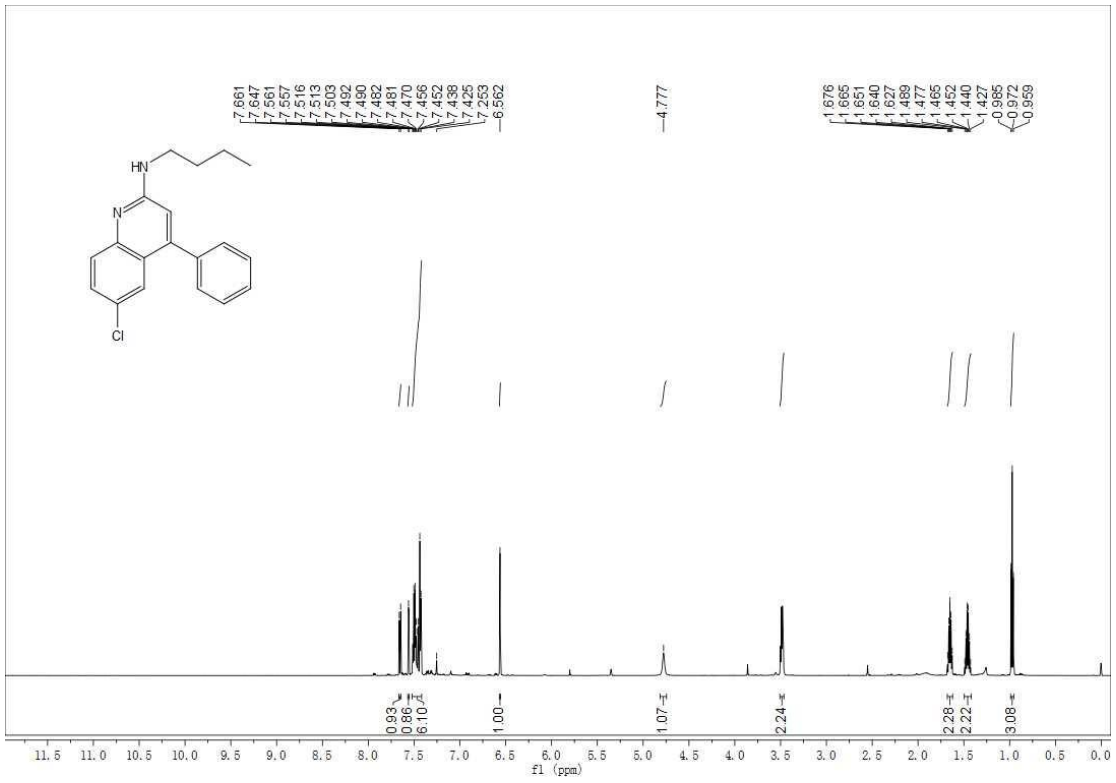


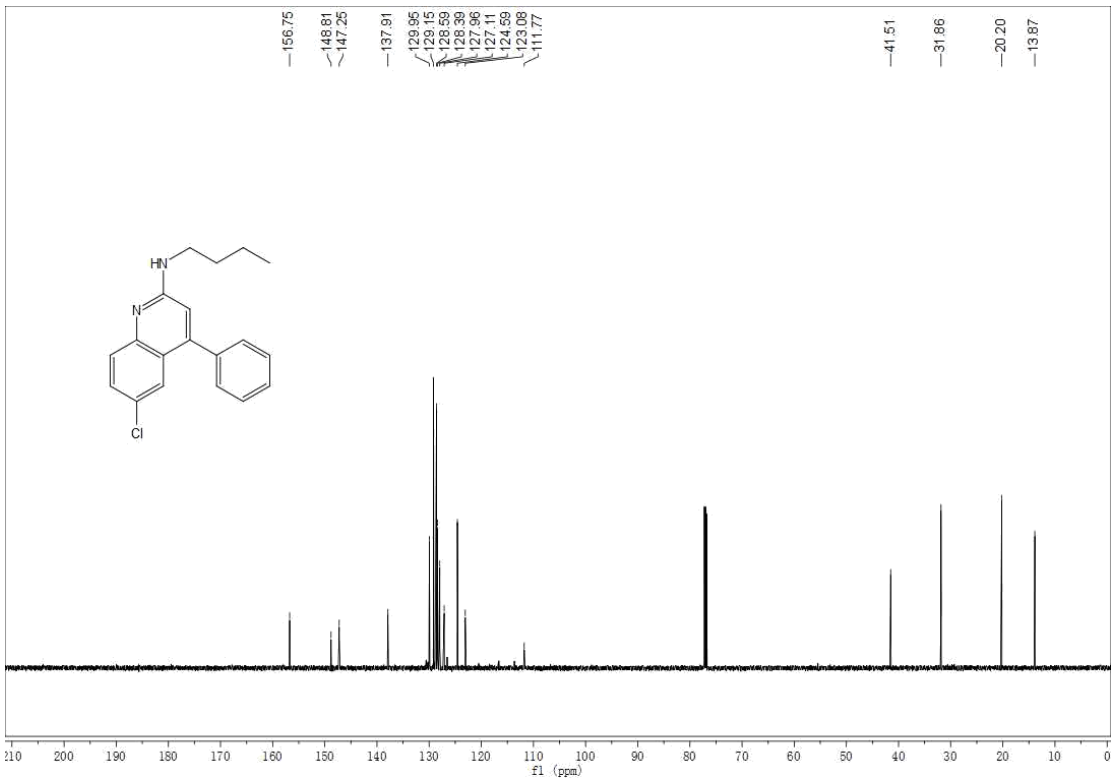
^{1}H and ^{13}C Spectra of compound 4l ($CDCl_3$,600 MHz)



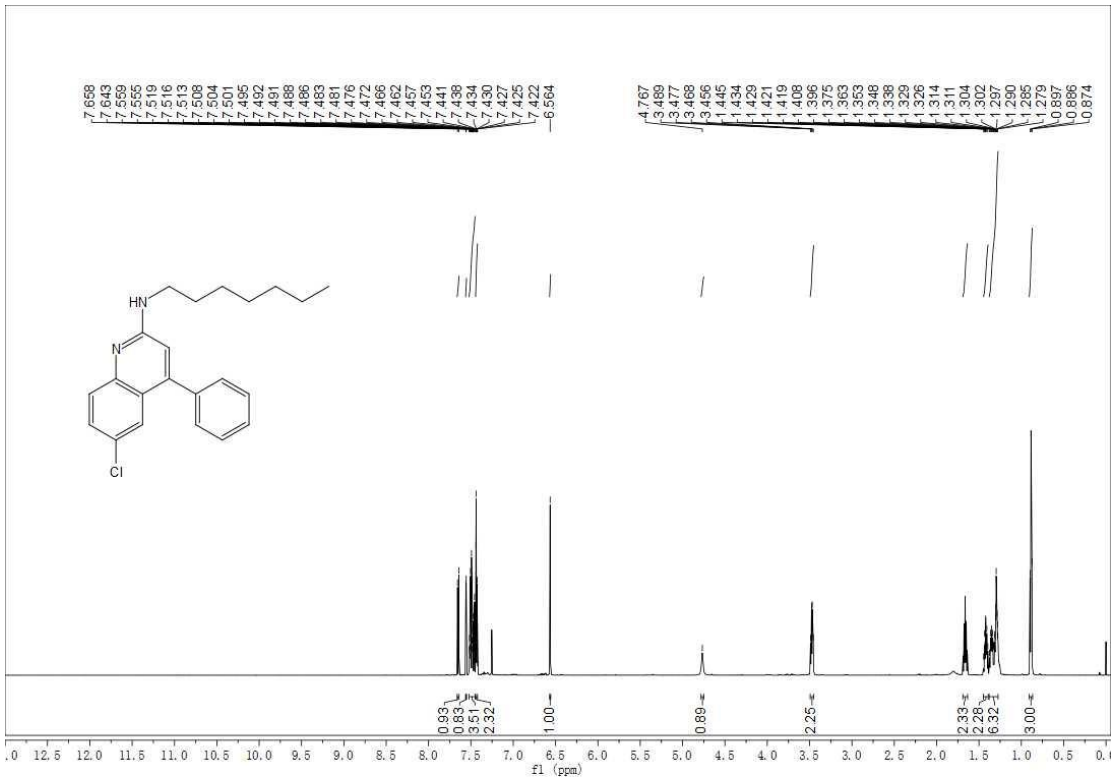


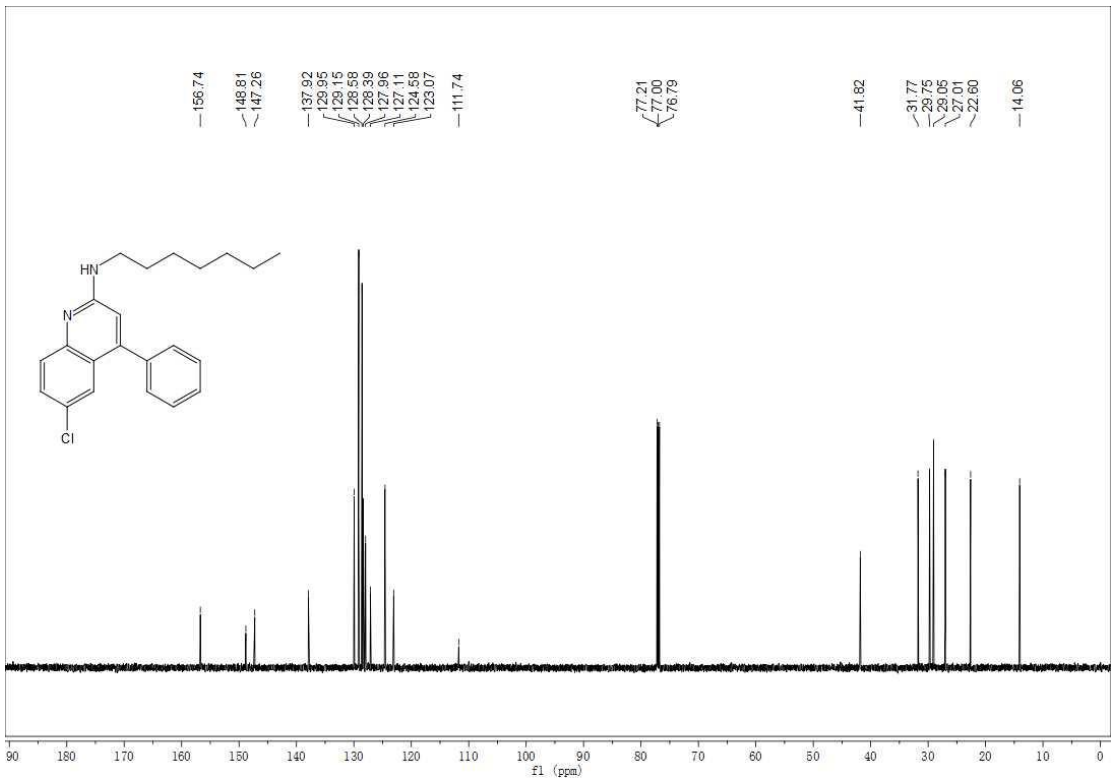
^{1}H and ^{13}C Spectra of compound 4m ($CDCl_3$,600 MHz)



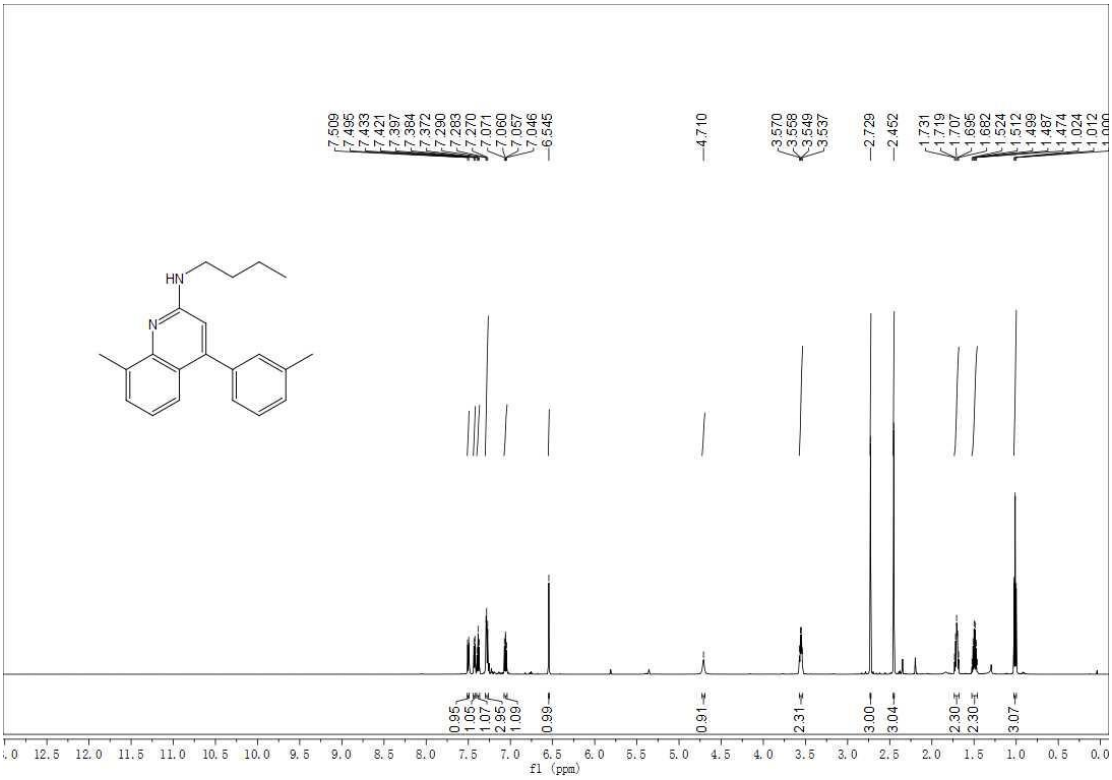


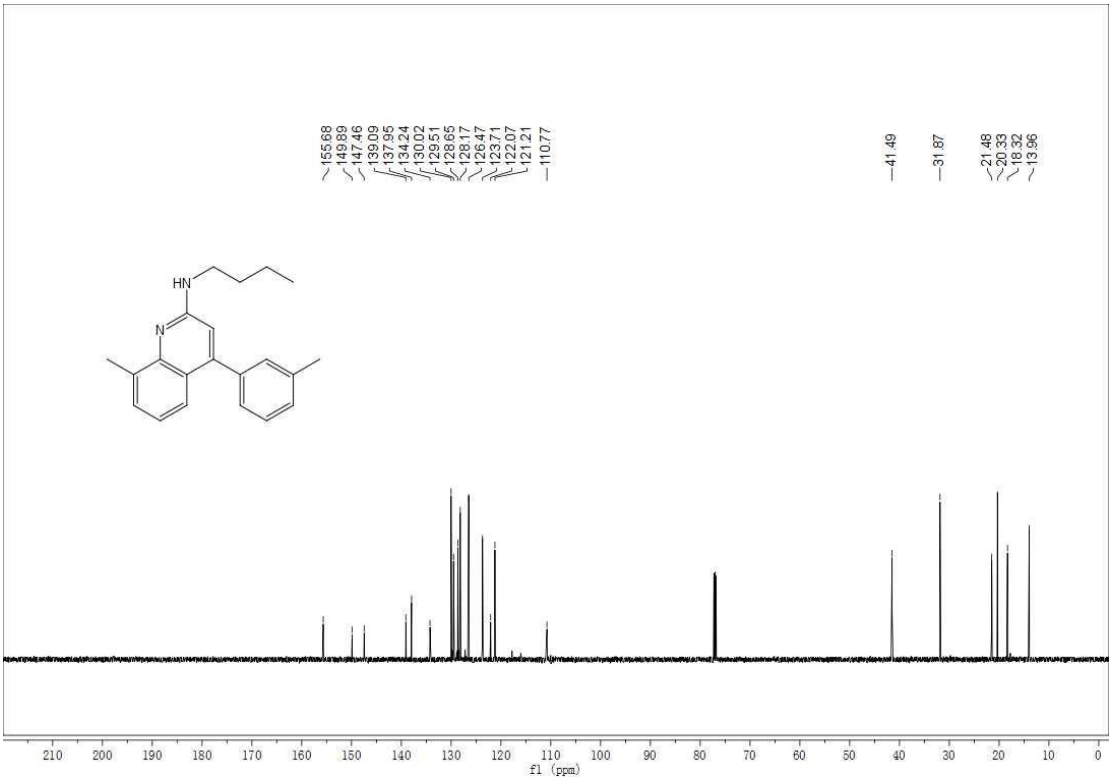
^{1}H and ^{13}C Spectra of compound 4n ($CDCl_3$,600 MHz)



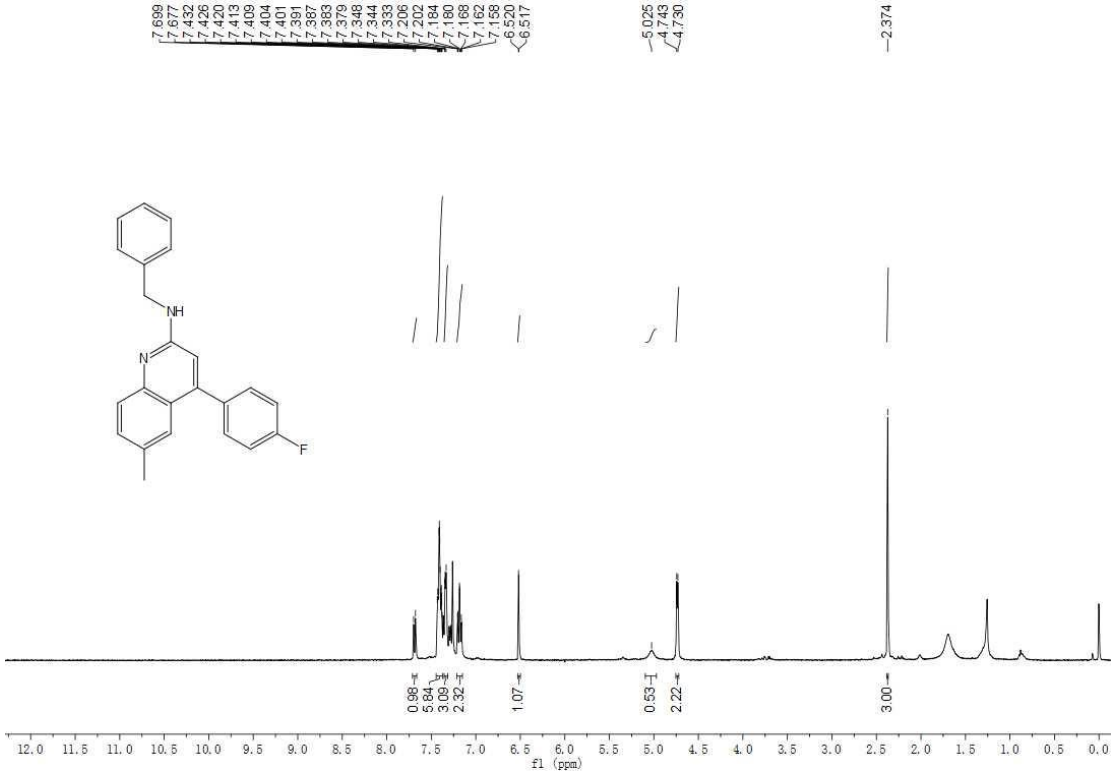


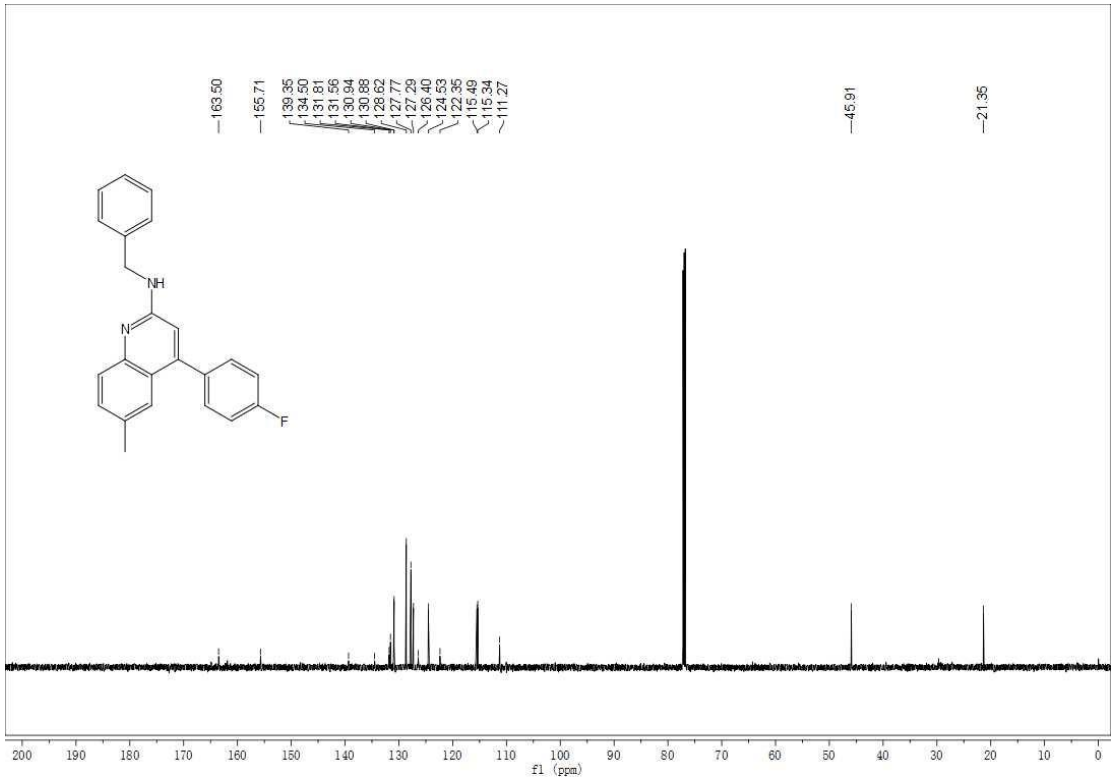
^{1}H and ^{13}C Spectra of compound 4o ($CDCl_3$,600 MHz)



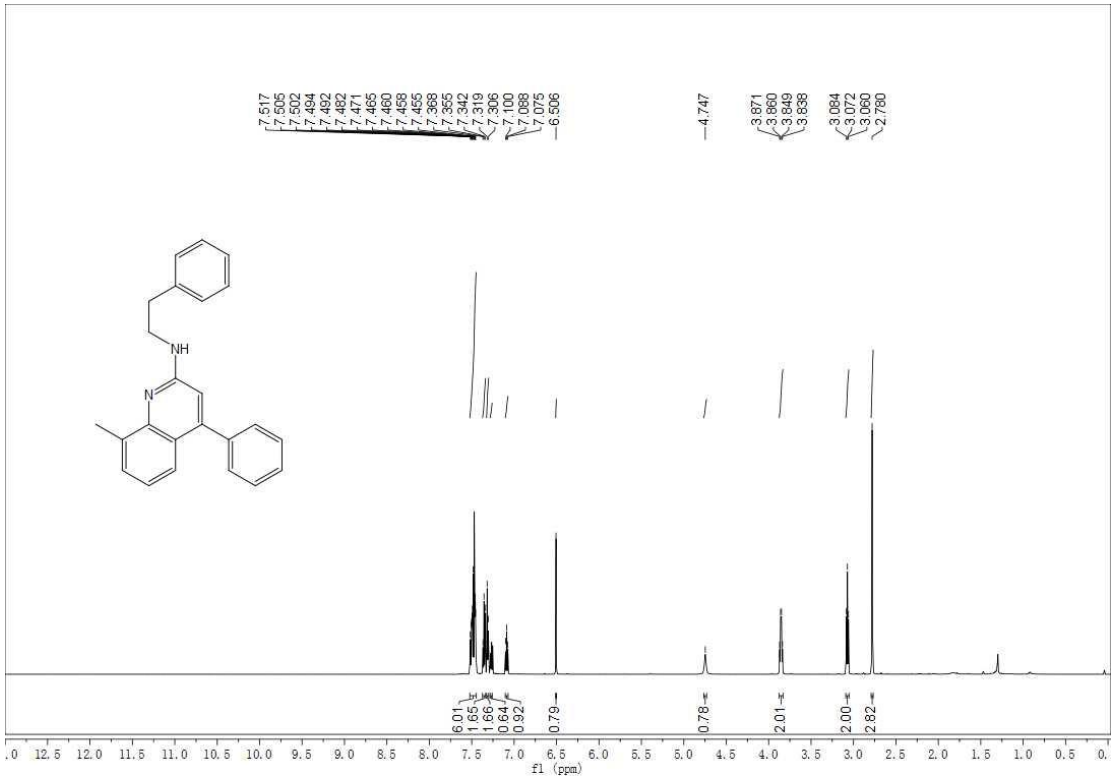


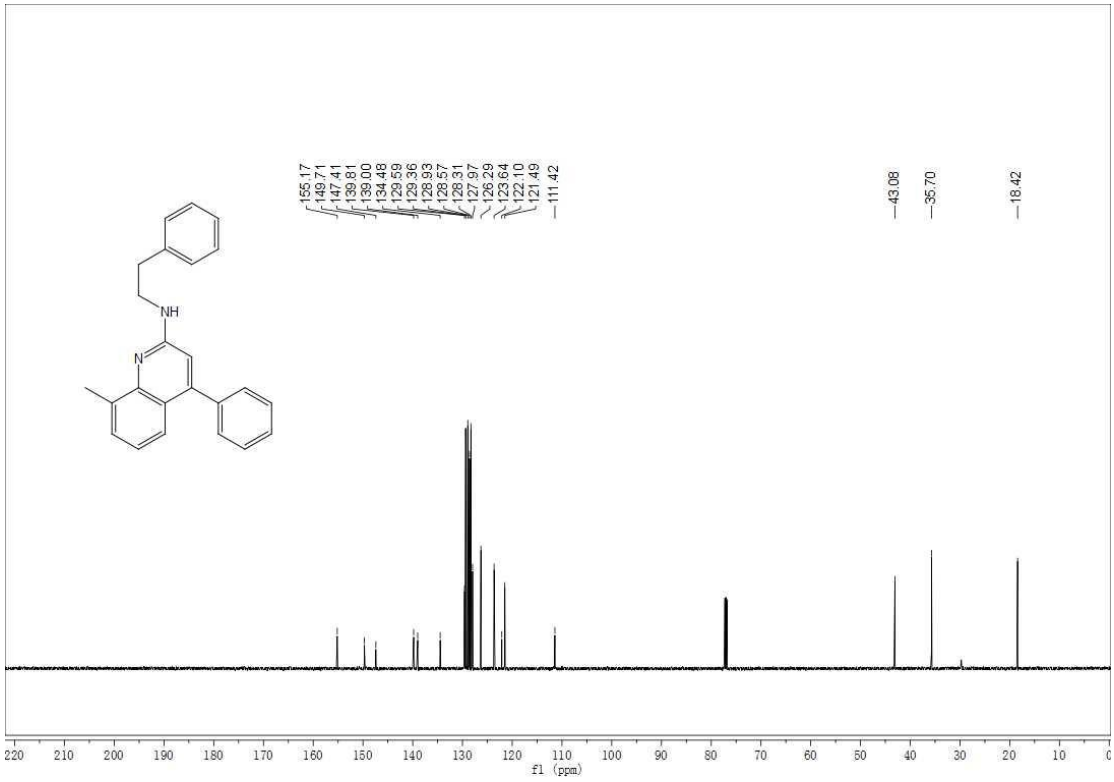
^{1}H and ^{13}C Spectra of compound 4p ($CDCl_3$,400 MHz)



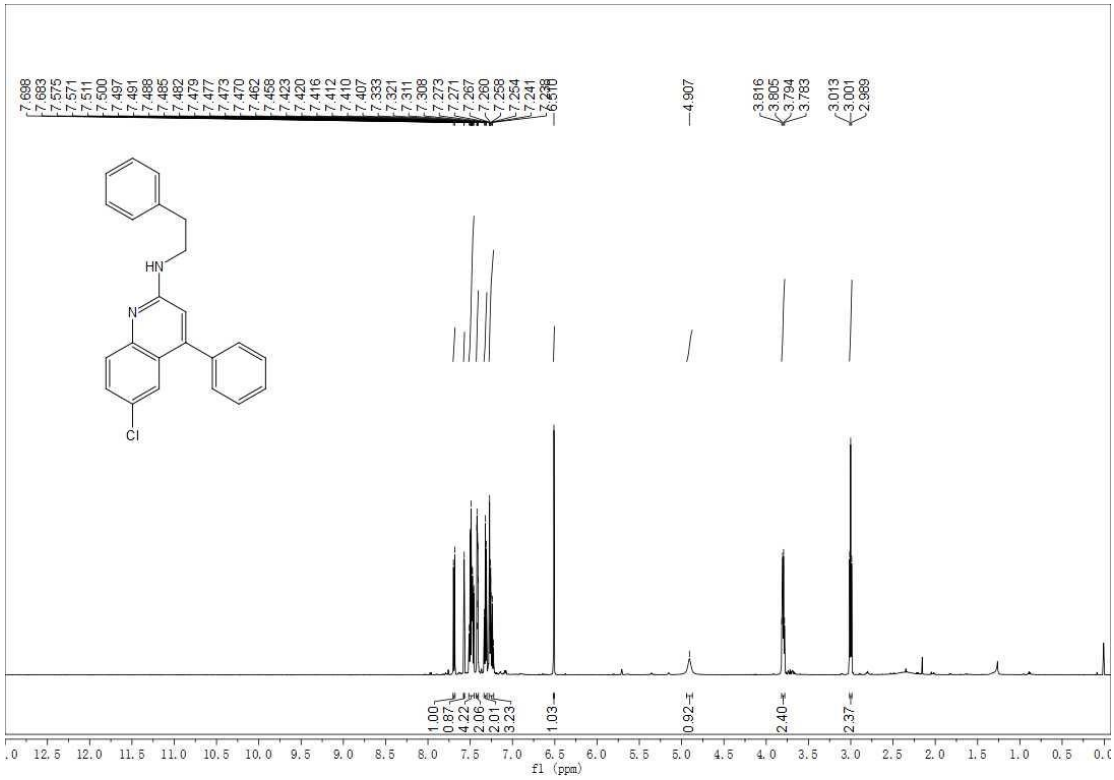


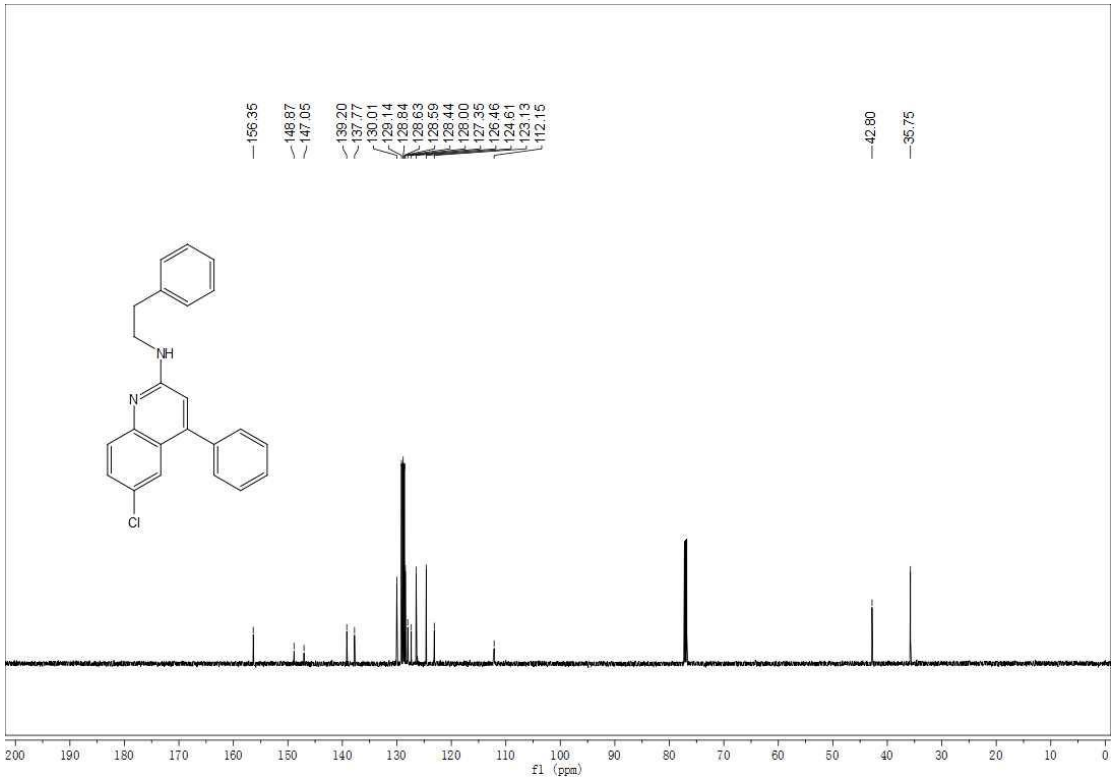
^{1}H and ^{13}C Spectra of compound 4q ($CDCl_3$,600 MHz)



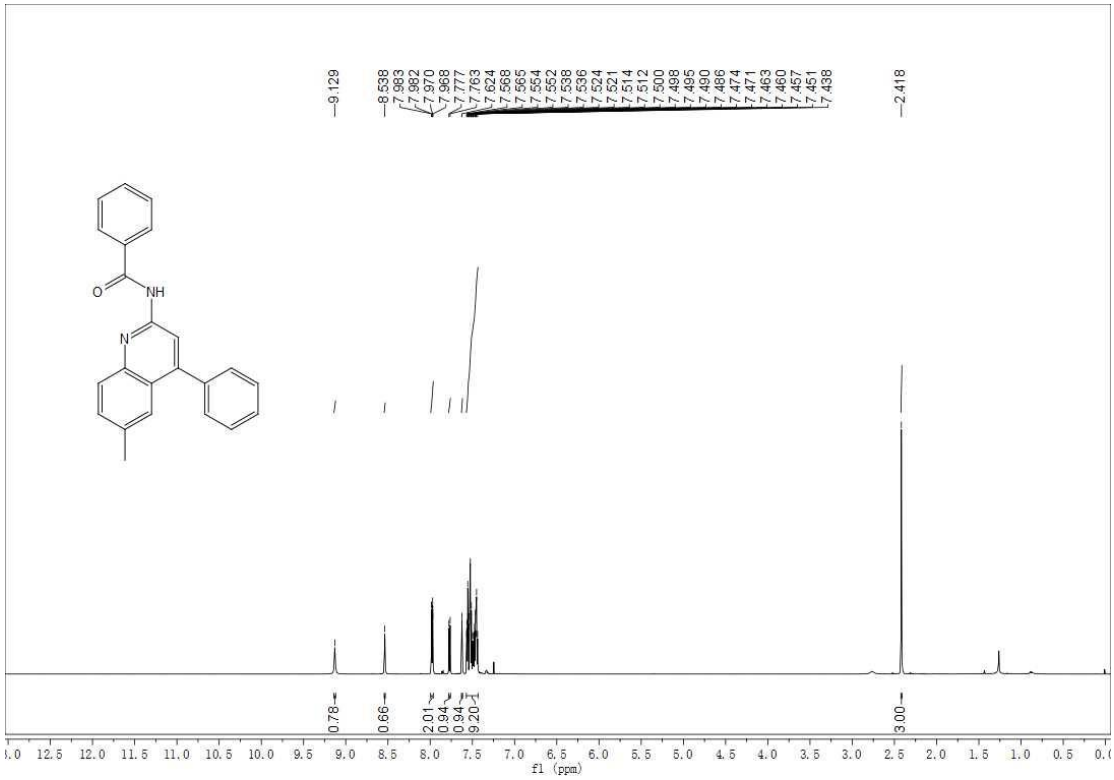


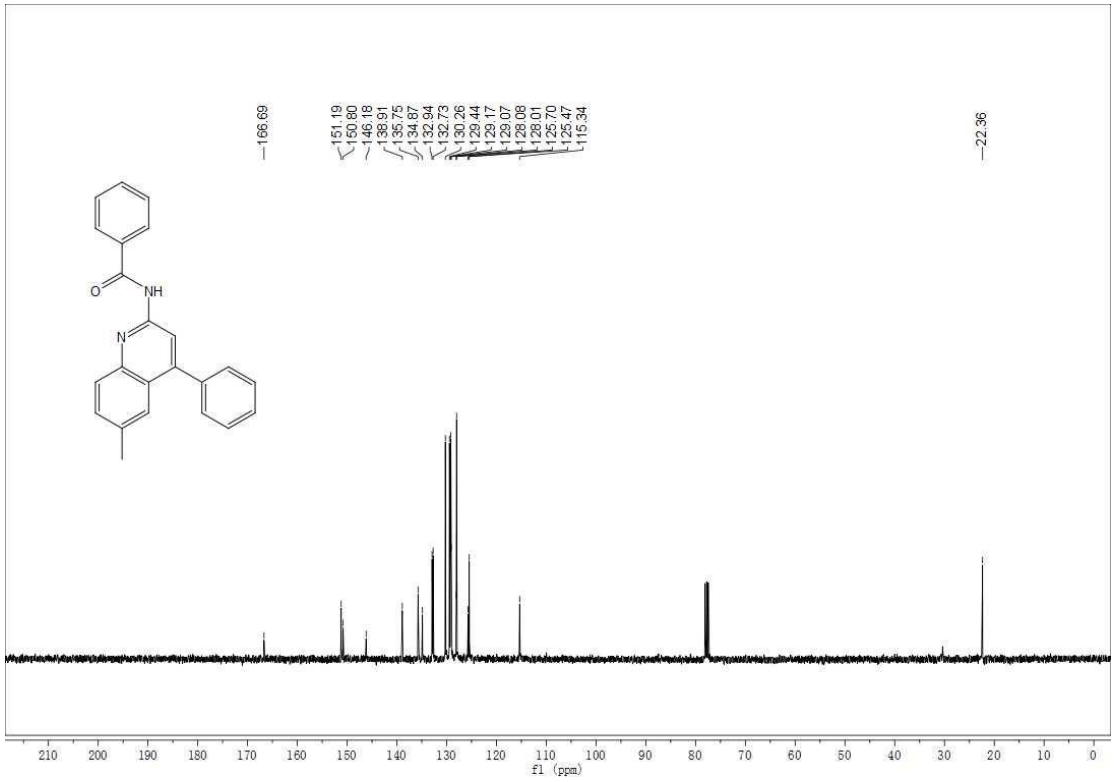
^{1}H and ^{13}C Spectra of compound 4r ($CDCl_3$,600 MHz)



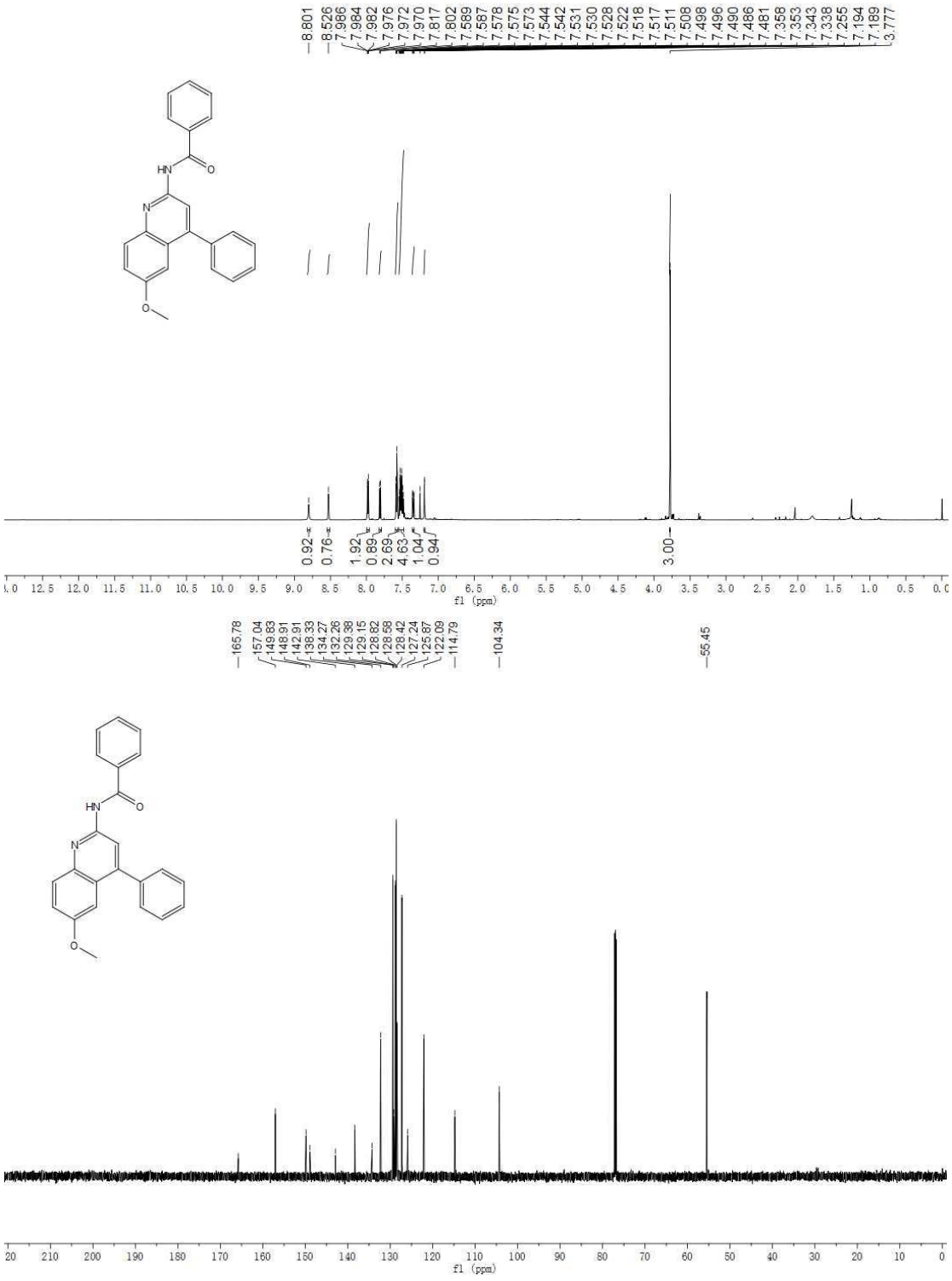


^{1}H and ^{13}C Spectra of compound 4s ($CDCl_3$,600 MHz)

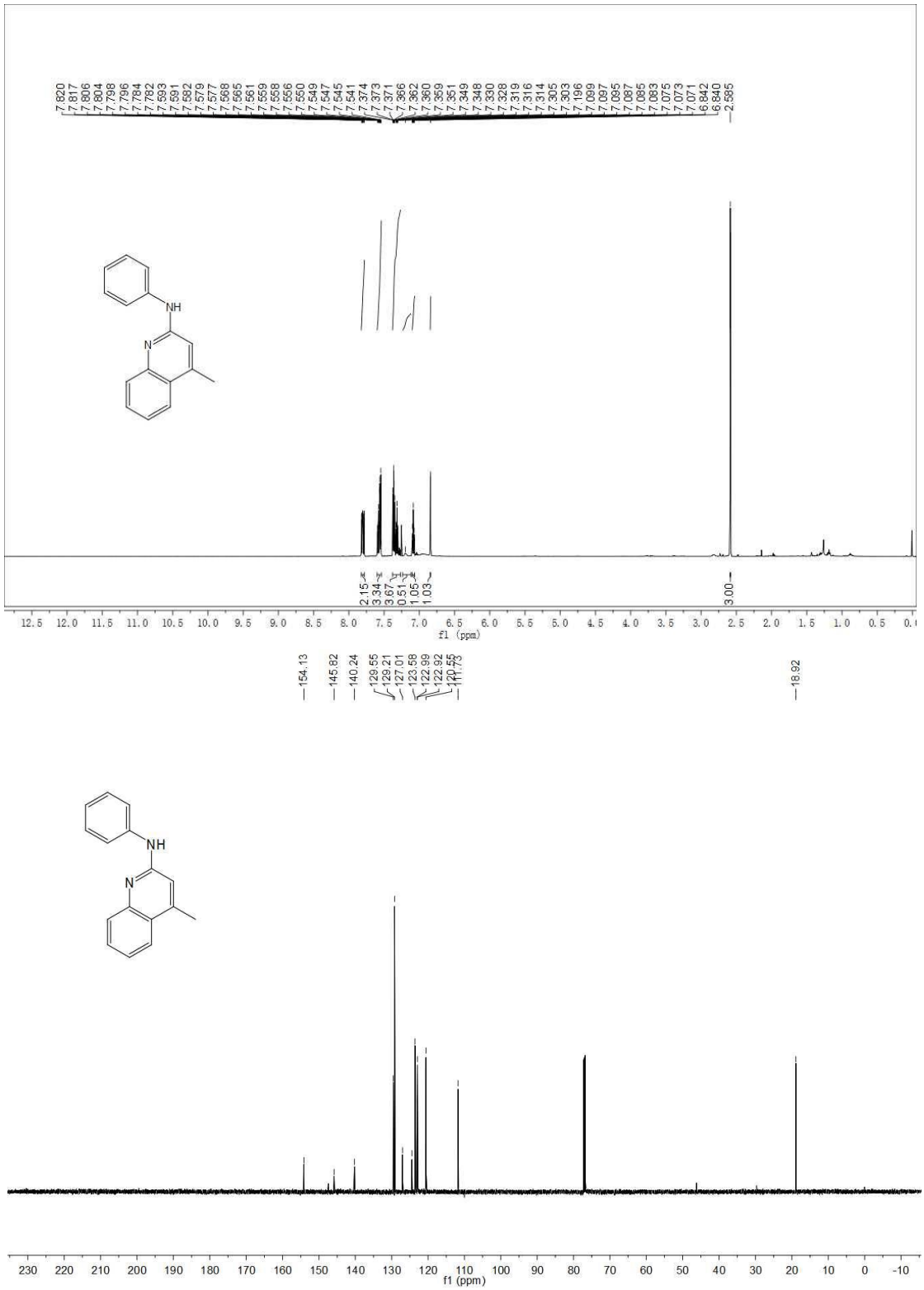




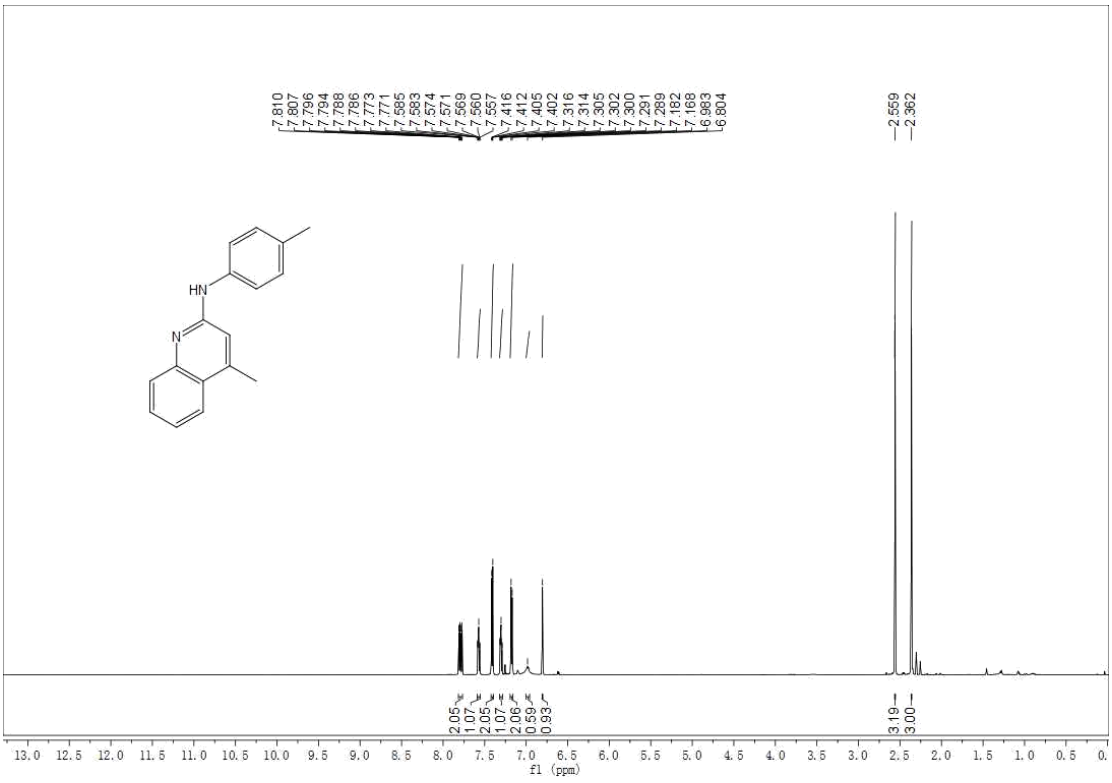
^{1}H and ^{13}C Spectra of compound 4t ($CDCl_3$,600 MHz)

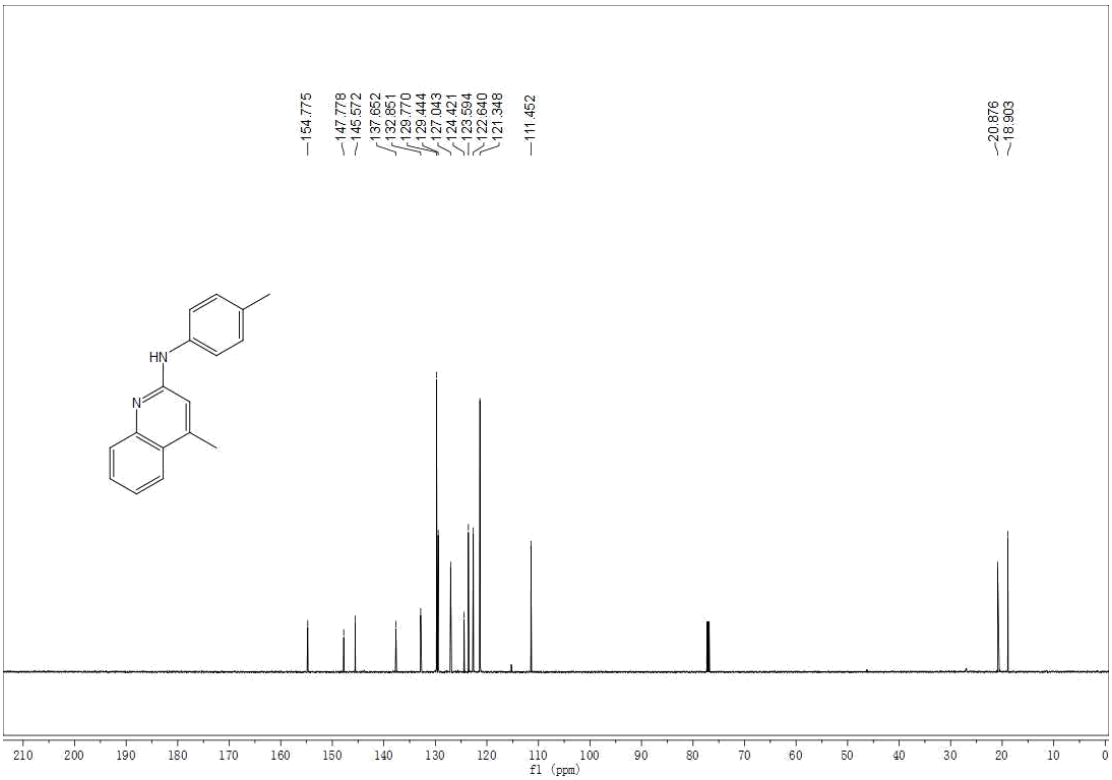


^{1}H and ^{13}C Spectra of compound 4u (CDCl3,600 MHz)

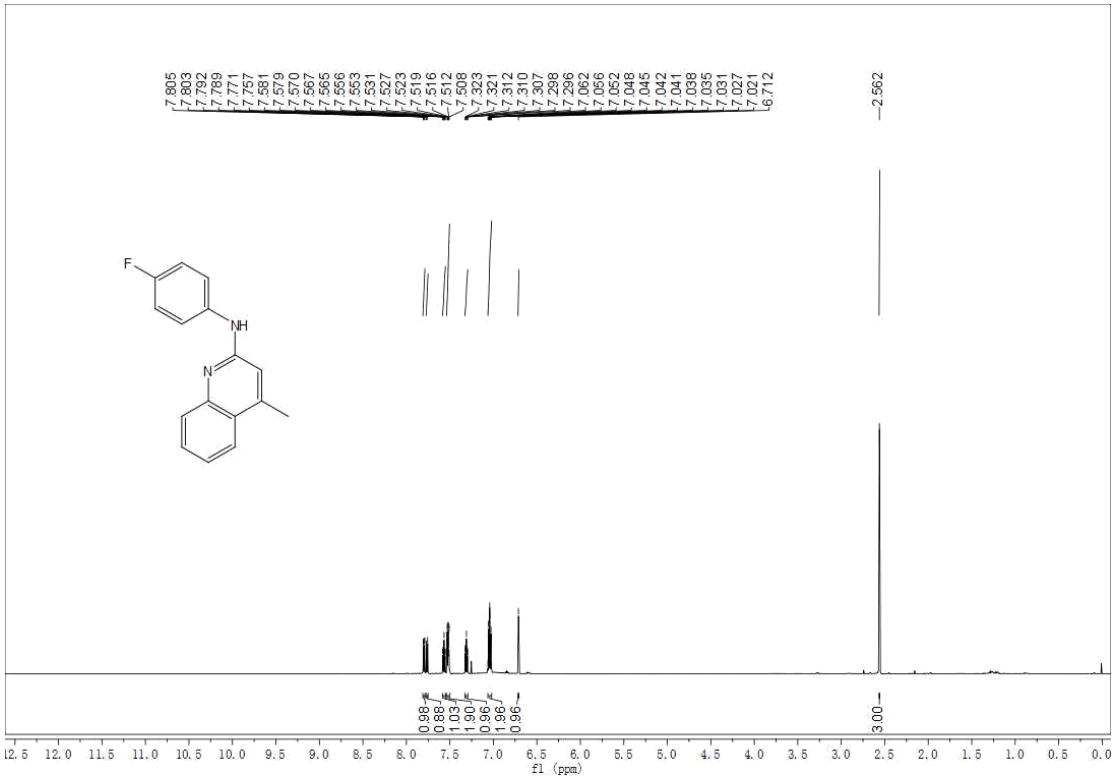


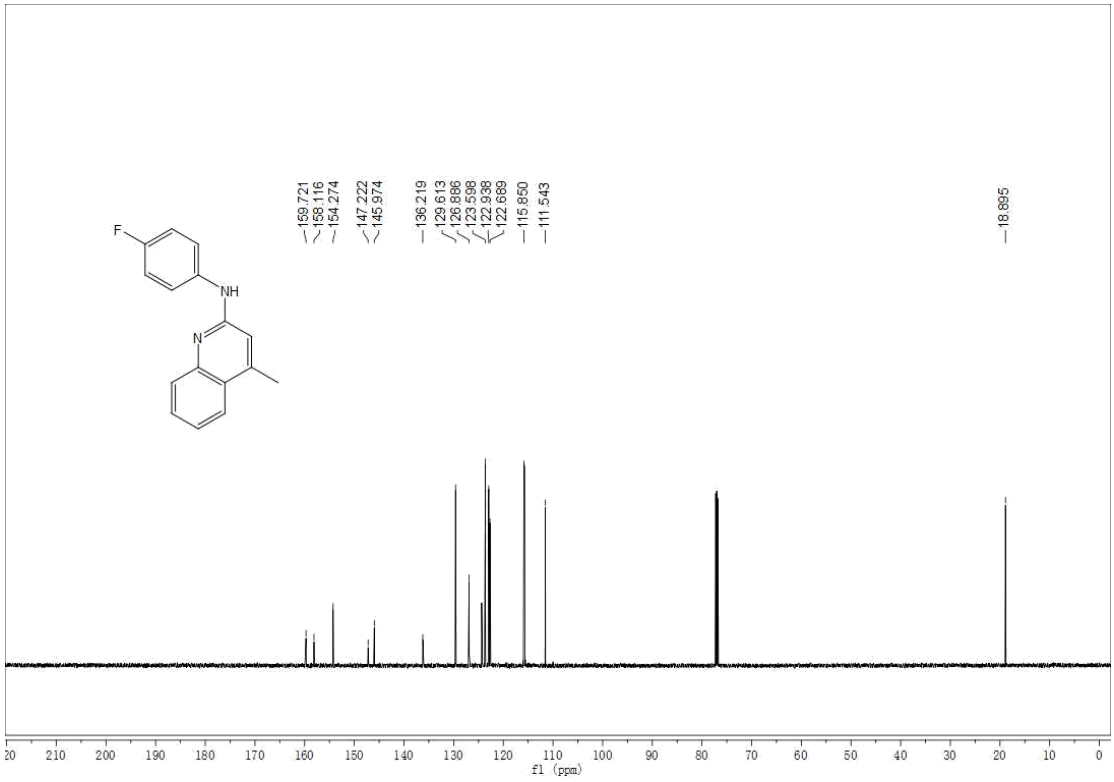
^{1}H and ^{13}C Spectra of compound 4v (CDCl3,600 MHz)



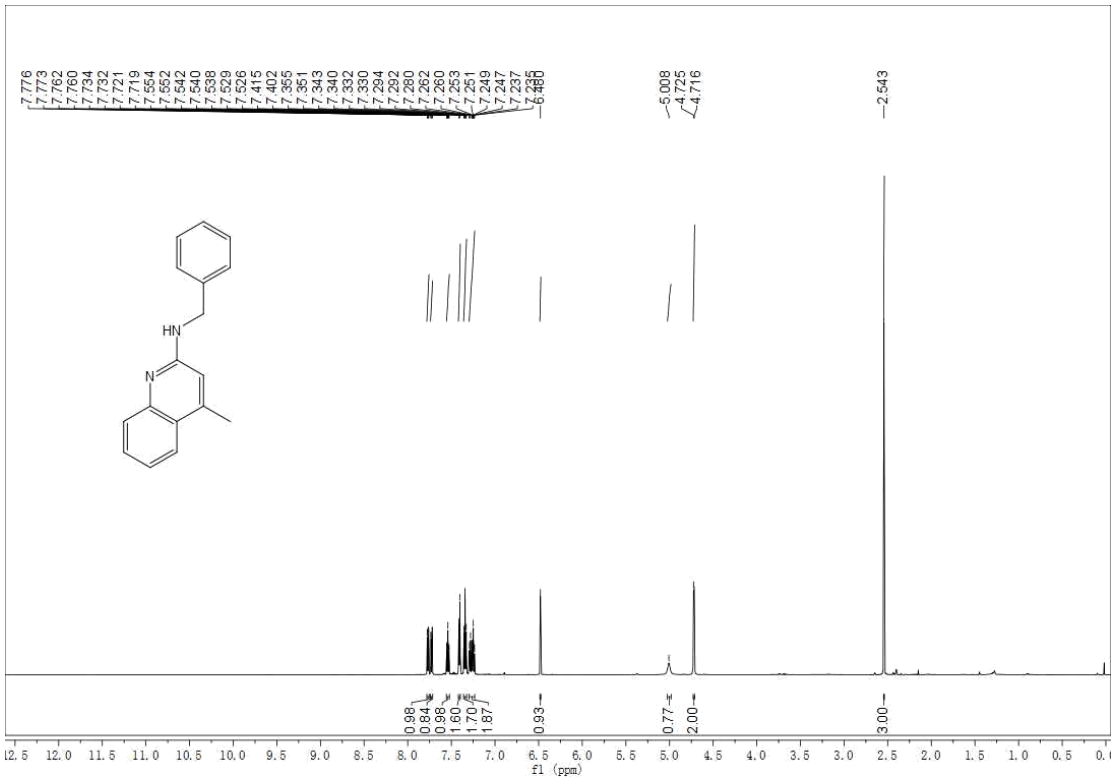


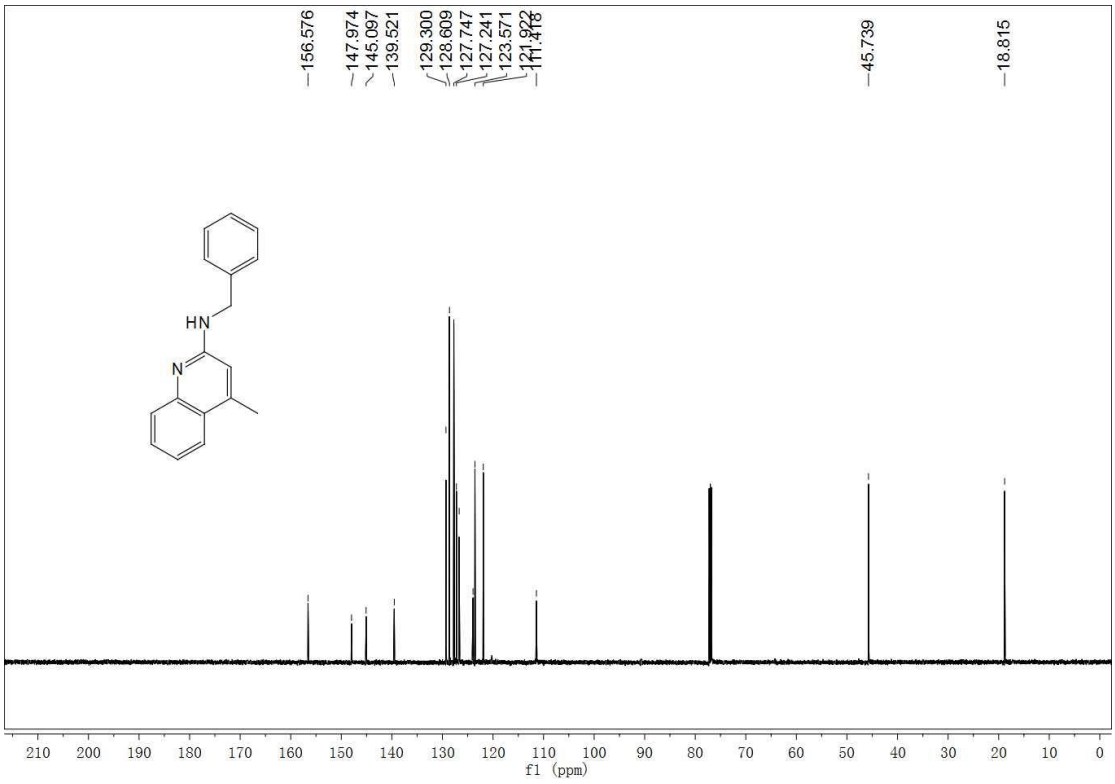
^{1}H and ^{13}C Spectra of compound 4w (CDCl3,600 MHz)



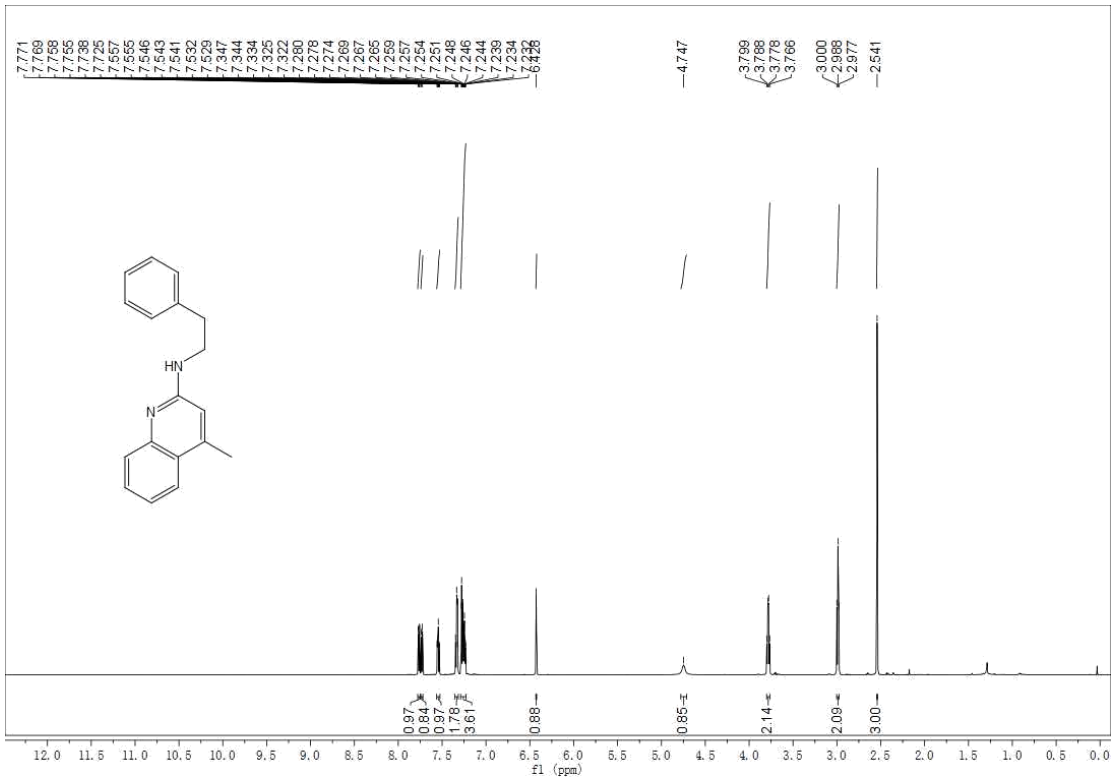


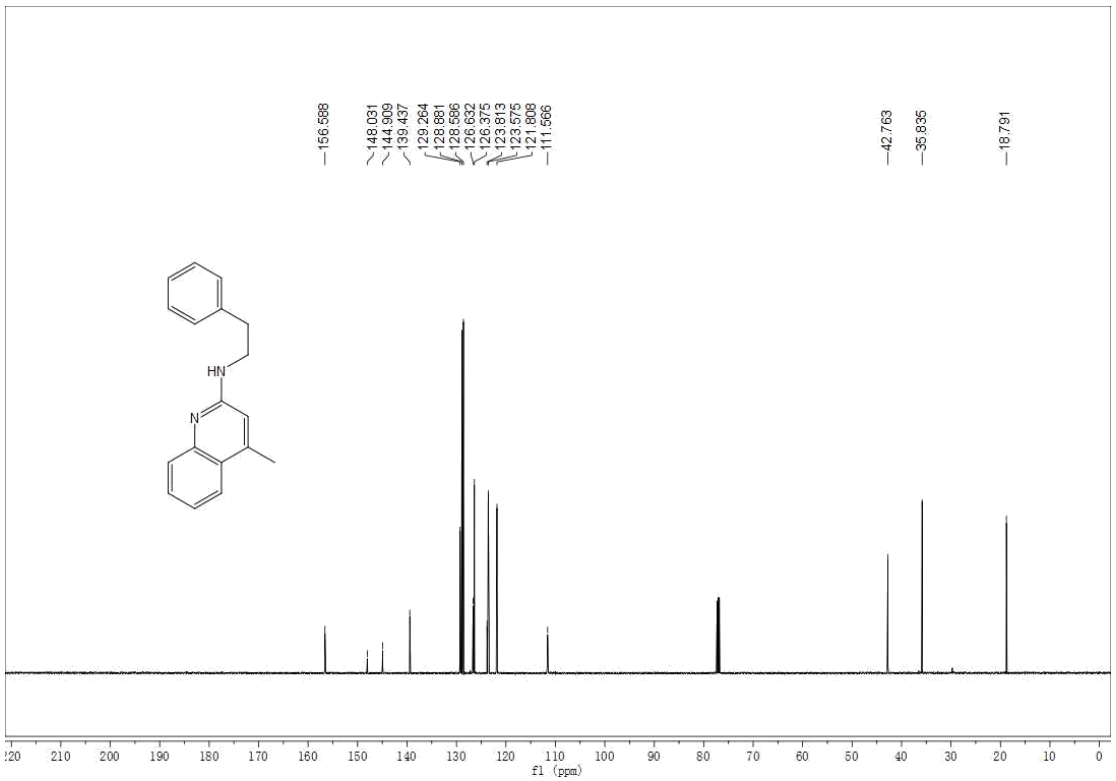
^{1}H and ^{13}C Spectra of compound 4x (CDCl3,600 MHz)



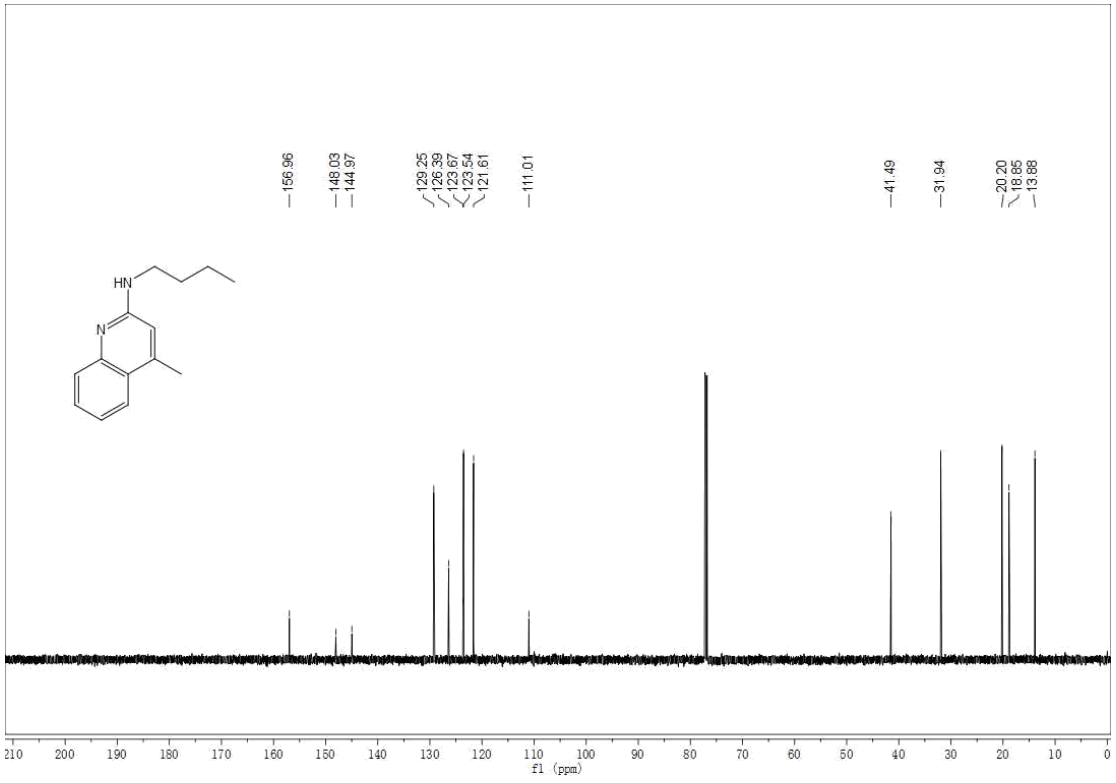


^{1}H and ^{13}C Spectra of compound 4y (CDCl3,600 MHz)





^{1}H and ^{13}C Spectra of compound 4z (CDCl3,600 MHz)



^{1}H and ^{13}C Spectra of compound 4A (CDCl3,600 MHz)