Supporting Information

Indoles oxidative ring-opening/cyclization cascade with the 1,2-diaminoarenes: direct synthesis of 2-aryl-3-(2-aminoaryl)quinoxalines

Jianwei Yan[a,*], Linxia Zheng[a], Jiangfei Wang[a], Xiaomin Liu[a], Youhong Hu[b]

[a] *School of Pharmacy, Xinxiang Medical University, Xinxiang, Henan 453003, P. R. China*

[b] *State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 201203, China*

E-mail: jwyansimm@163.com

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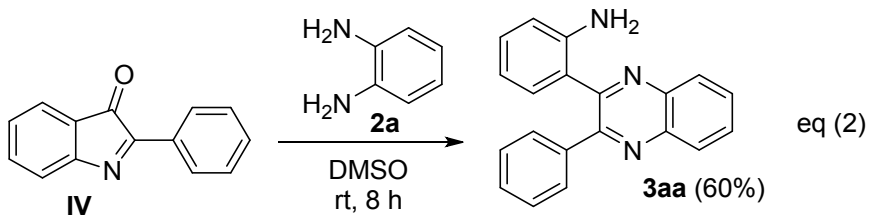
1. Experiment procedures.

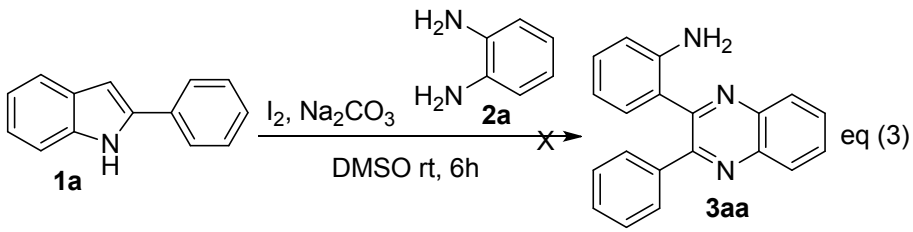
All ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were measured in $CDCl_3$ using a Bruker ASCEND 400 spectrometer. Chemical shifts are expressed in ppm and *J* values are given in Hz. High resolution mass spectra were recorded on bruker micrOTOF-QIII MS (ESI). Single crystal of **3af'** was cultured from methanol by slow evaporation at room temperature, and its structure was determined on a Bruker D8 diffractometer. Column chromatography was performed with 200-300 mesh silica gel using flash column techniques. Melting points (uncorrected) were determined on a yalixien X-4 melting point apparatus. All the solvents and reagents were used directly as obtained commercially unless otherwise noted.

Representative procedure for the synthesis of 3aa. NIS (45 mg, 0.2 mmol) was added to a solution of 2-phenyl indole (**1a**) (38.6 mg, 0.2 mmol) in DMSO (2.0 mL) under an air atmosphere. The mixture was stirred at room temperature for 2 hours (complete consumption of 2-phenyl indole and 3-iodo-2-phenyl indole indicated by TLC), benzene-1,2-diamine (21.6 mg, 0.2 mmol) was added into the solution, the reaction for another 5 hours at ambient condition. The reaction mixture was poured into 30 ml saturated aqueous NaCl solutions, and extracted with ethyl acetate (2×30ml). After drying over sodium sulphate and concentration in vacuo, the combined organic phase gave a residue that was subjected to flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1 as an eluent) to afford **3aa** as a yellow solid (49.3 mg, 83%). For reactions that require heating, oil baths were used.

2. Reaction control and optimization.

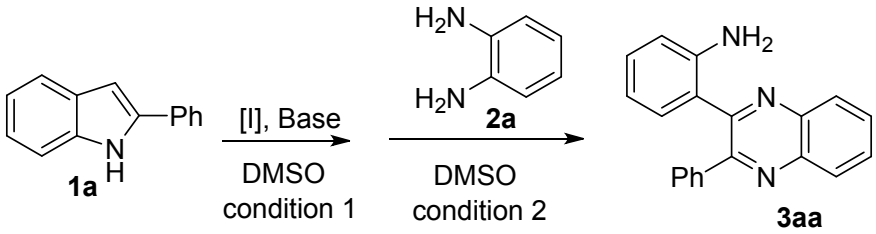


eq (2)



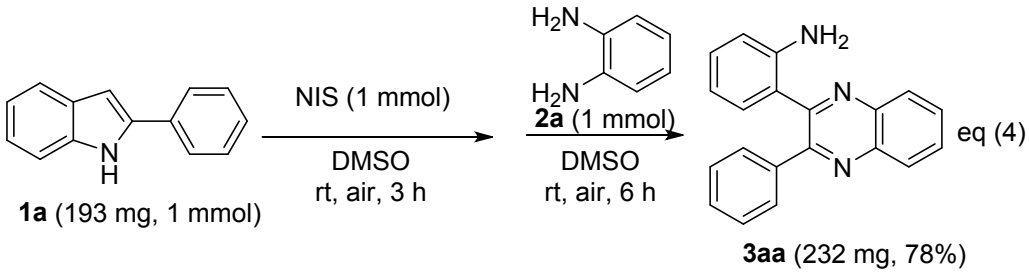
eq (3)

Table 1. Optimization of the indole oxidative ring-opening reaction with 1,2-diaminobenzene.[a]



Entry	Reagent	Base	Condition 1	Condition 2	Yield[b]
1	I_2	Na_2CO_3	rt, 3 h	rt, 6 h	50%
2	I_2	K_2CO_3	rt, 2 h	rt, 6 h	31%
3	I_2	$NaHCO_3$	50 ºC, 4 h	50 ºC, 12 h	39%
4	NIS	Na_2CO_3	rt, 2 h	rt, 6 h	28%
5	NIS	--	rt, 2 h	rt, 5 h	83%
6	NIS	--	rt, 2 h	50 ºC, 6 h	69%
7	NIS	--	rt, 2 h	80 ºC, 6 h	71%
8	NIS	--	rt, 2 h	120 ºC, 5 h	69%
9[c]	NIS	--	rt, 1 h	rt, 6 h	77%
10[d]	NIS	--	rt, 6 h	rt, 6 h	80%
11	NBS	--	50 ºC, 6 h	80 ºC, 12 h	NP[e]
12	DIH	--	rt, 2 h	rt, 6 h	52%

[a] Reaction conditions: open to air, a mixture of 2-phenyl indole **1a** (38.6 mg, 0.2 mmol) and halogenated reagent (0.2 mmol) in DMSO (2.0 mL) were stirred under corresponding condition 1, then o-phenylenediamine 2a (21.6 mg, 0.2 mmol) was added and following transformation was completed under condition 2. [b] Isolated yields. [c] Under O_2 (1 atm). [d] Under N_2. [e] No product.

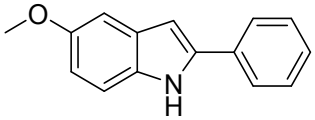


3. The synthesis and characterization data of 1b-1v.

The starting material **1b-d**, **1f**, **1g**, **1i**, **1j**, **1k, 1l-n** and **1q** were prepared according to the method reported in the literature 1; compounds **1e**, **1h**, **1o**, **1p** and **1r-v** were prepared according to the procedure reported in the literature 2.

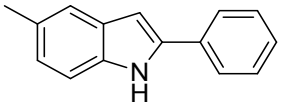
1) S.-D. Yang, C.-L. Sun, Z. Fang, B.-J. Li, Y.-Z. Li, Z.-J. Shi, Palladium-Catalyzed Direct Arylation of (Hetero)Arenes with Aryl Boronic Acids, *Angew. Chem. Int. Ed.*, 2008, **47** (8), 1473-1476.

2) A. Arcadi, G. Bianchi, F.J.C. Marinelli, Gold (III)-Catalyzed Annulation of 2-Alkynylanilines: A Mild and Efficient Synthesis of Indoles and 3-Haloindoles, 2004, 610-618.



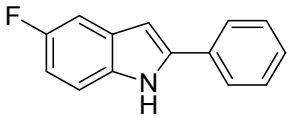
5-methoxy-2-phenyl-1H-indole (1b)

As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.66 – 7.61 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.26 (m, 2H), 7.09 (d, *J* = 2.3 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.76 (d, *J* = 1.7 Hz, 1H), 3.86 (s, 3H).



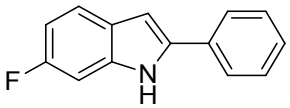
5-methyl-2-phenyl-1H-indole (1c)

As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.68 – 7.62 (m, 2H), 7.47 – 7.39 (m, 3H), 7.34 – 7.26 (m, 2H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 0.9 Hz, 1H), 2.45 (s, 3H).



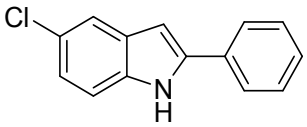
5-fluoro-2-phenyl-1H-indole (1d)

As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.67 – 7.62 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.25 (m, 3H), 6.93 (td, *J* = 8.7, 2.1 Hz, 1H), 6.78 (d, *J* = 1.6 Hz, 1H).



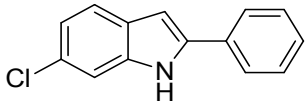
6-fluoro-2-phenyl-1H-indole (1e)

As a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.55 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.00 (dd, *J* = 9.5, 2.2 Hz, 1H), 6.85 – 6.78 (m, 1H), 6.71 (s, 1H).



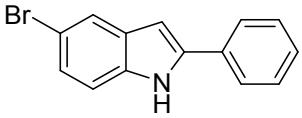
5-chloro-2-phenyl-1H-indole (1f)

As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.58 (d, *J* = 1.8 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.13 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.75 (d, *J* = 1.7 Hz, 1H).



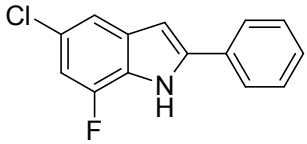
6-chloro-2-phenyl-1H-indole (1g)

As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.41 – 7.29 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.79 (s, 1H).



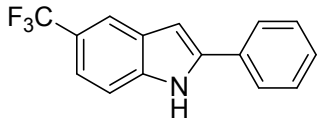
5-bromo-2-phenyl-1H-indole (1h)

As a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.67 (s, 1H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.21 – 7.15 (m, 2H), 6.68 (d, *J* = 1.9 Hz, 1H).



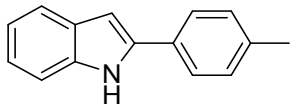
5-chloro-7-fluoro-2-phenyl-1H-indole (1i)

As a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.23 (m, 2H), 6.84 (d, *J* = 10.5 Hz, 1H), 6.70 – 6.65 (m, 1H).



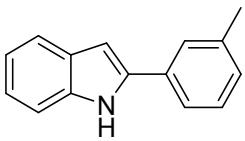
2-phenyl-5-(trifluoromethyl)-1H-indole (1j)

As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.92 (s, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.45 (m, 3H), 7.42 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 1.5 Hz, 1H).



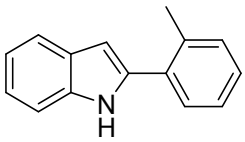
2-(p-tolyl)-1H-indole (1k)

As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.22 – 7.16 (m, 1H), 7.15 – 7.09 (m, 1H), 6.79 (s, 1H), 2.40 (s, 3H).



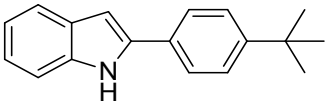
2-(m-tolyl)-1H-indole (1l)

As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.56 – 7.43 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.07 (m, 3H), 6.82 (s, 1H), 2.42 (s, 3H).



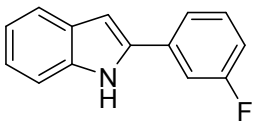
2-(o-tolyl)-1H-indole (1m)

As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.66 (t, *J* = 7.1 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.25 (m, 3H), 7.25 – 7.18 (m, 1H), 7.18 – 7.11 (m, 1H), 6.65 – 6.57 (m, 1H), 2.51 (s, 1.4 H), 2.50 (s, 1.6 H).



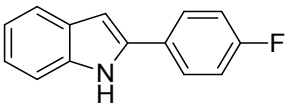
2-(4-(tert-butyl) phenyl)-1H-indole (1n)

As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.65 – 7.56 (m, 3H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 1.3 Hz, 1H), 1.36 (s, 9H).



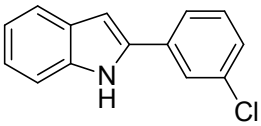
2-(3-fluorophenyl)-1H-indole (1o)

As a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.30 – 7.25 (m, 1H), 7.17 – 7.11 (m, 1H), 7.09 – 7.03 (m, 1H), 6.98 – 6.91 (m, 1H), 6.77 (d, *J* = 1.4 Hz, 1H).



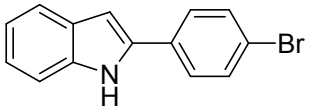
2-(4-fluorophenyl)-1H-indole (1p)

As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.58 – 7.47 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.15 – 7.09 (m, 1H), 7.09 – 7.00 (m, 3H), 6.68 (d, *J* = 1.4 Hz, 1H).



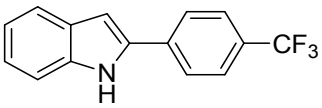
2-(3-chlorophenyl)-1H-indole (1q)

As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.66 – 7.61 (m, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 1.6 Hz, 1H).



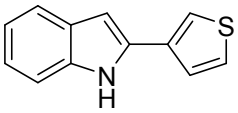
2-(4-bromophenyl)-1H-indole (1r)

As a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.16 – 7.11 (m, 1H), 7.09 – 7.02 (m, 1H), 6.74 (s, 1H).



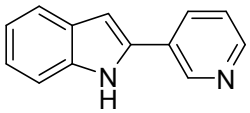
2-(4-(trifluoromethyl) phenyl)-1H-indole (1s)

As a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 1.4 Hz, 1H).



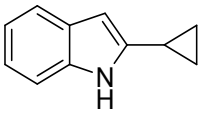
2-(thiophen-3-yl)-1H-indole (1t)

As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.40 (s, 3H), 7.37 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.14 – 7.09 (m, 1H), 6.70 (dd, *J* = 2.1, 0.8 Hz, 1H).



2-(pyridin-3-yl)-1H-indole (1u)

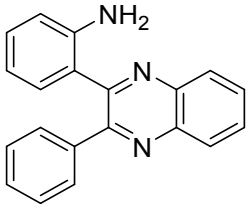
As a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 1.8 Hz, 1H), 8.70 (s, 1H), 8.49 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.93 – 7.86 (m, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.37 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.31 (dd, *J* = 7.5, 4.8 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.10 – 7.05 (m, 1H), 6.83 (d, *J* = 1.4 Hz, 1H).



2-cyclopropyl-1H-indole (1v)

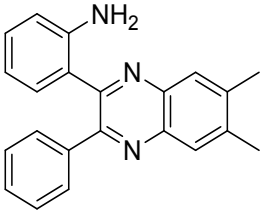
As a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.14 – 7.08 (m, 1H), 7.08 – 7.02 (m, 1H), 6.15 (s, 1H), 2.09 – 1.83 (m, 1H), 1.07 – 0.89 (m, 2H), 0.85 – 0.68 (m, 2H).

4. The characterization data of 3aa-3ap.



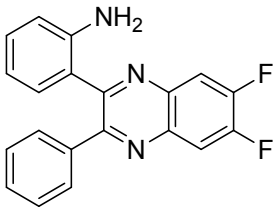
2-(3-phenylquinoxalin-2-yl) aniline (3aa)

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3aa** as a light yellow solid (49.3 mg, 83%); m.p.151-152 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.15 (m, 1H), 8.15 – 8.06 (m, 1H), 7.84 – 7.72 (m, 2H), 7.65 – 7.52 (m, 2H), 7.42 – 7.29 (m, 3H), 7.20 – 7.08 (m, 1H), 6.91 – 6.78 (m, 2H), 6.55 (t, *J* = 7.5 Hz, 1H), 4.62 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.3, 151.9, 144.3, 140.0, 139.4, 137.9, 130.7, 129.0, 128.9, 128.9, 128.5, 128.2, 127.8, 127.6, 127.2, 122.1, 117.0, 115.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{16}N_3$ 298.1339; Found 298.1341.



2-(6,7-dimethyl-3-phenylquinoxalin-2-yl) aniline (3ab)

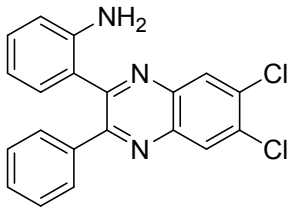
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3ab** as a yellow solid (53.3 mg, 82%); m.p.169-171 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.85 (s, 1H), 7.58 – 7.51 (m, 2H), 7.34 – 7.27 (m, 3H), 7.10 (td, *J* = 8.1, 1.5 Hz, 1H), 6.84 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.54 (td, *J* = 7.6, 1.0 Hz, 1H), 4.57 (s, 2H), 2.52 (s, 3H), 2.51 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.3, 151.9, 145.3, 140.6, 140.6, 140.1, 139.5, 139.2, 131.8, 129.7, 129.6, 128.6, 128.3, 128.2, 127.7, 123.6, 118.0, 116.9, 20.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}N_3$ 326.1652; Found 326.1650.



2-(6,7-difluoro-3-phenylquinoxalin-2-yl) aniline (3ac)

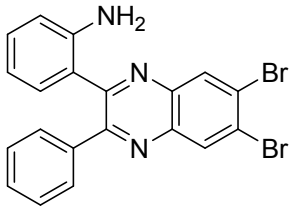
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3ac** as a yellow solid (40 mg, 60%); m. p. 127-129 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 1H), 7.86 – 7.80 (m, 1H), 7.59 – 7.52 (m, 2H), 7.40 – 7.29 (m, 3H), 7.17 – 7.10 (m, 1H), 6.86 – 6.77 (m, 2H), 6.55

(t, J = 7.5 Hz, 1H), 4.57 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.5 (d, J = 2.4 Hz), 151.5 (dd, J =258.2, 18.0 Hz), 152.2 (d, J = 2.5 Hz), 151.4 (dd, J = 258.2, 17.8 Hz), 144.2, 137.3, 137.3 (dd, J = 9.6, 2.0 Hz), 136.6 (dd, J = 8.9, 3.2 Hz), 130.7, 129.2, 128.5, 128.1, 127.3, 121.6, 117.1, 116.0, 113.9 (dd, J = 15.5, 3.6 Hz), 113.2 (dd, J = 12.0, 7.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.8 (d, J = 21.0 Hz), δ -129.8 (d, J = 21.0 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{14}F_2N_3$ 334.1150; Found 334.1155.



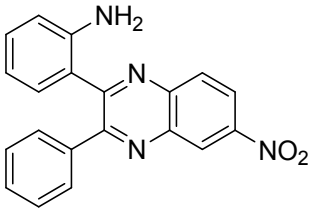
2-(6,7-dichloro-3-phenylquinoxalin-2-yl) aniline (3ad)

Silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) gave **3ad** as a yellow solid (58.6 mg, 80%); m. p. 174-176 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.20 (s, 1H), 7.56 (dd, J = 7.9, 1.5 Hz, 2H), 7.40 – 7.29 (m, 3H), 7.17 – 7.10 (m, 1H), 6.87 – 6.78 (m, 2H), 6.54 (t, J = 7.5 Hz, 1H), 4.66 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.3, 154.2, 145.5, 139.7, 139.1, 138.3, 134.4, 131.8, 130.4, 129.9, 129.5, 129.4, 129.2, 128.4, 122.3, 118.1, 117.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{14}Cl_2N_3$ 366.0559; Found 366.0557.



2-(6,7-dibromo-3-phenylquinoxalin-2-yl) aniline (3ae)

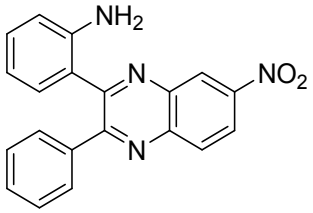
Silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) gave **3ae** as a yellow solid (79.2 mg, 87%); m. p. 216-218 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.39 (s, 1H), 7.55 (d, J = 6.7 Hz, 2H), 7.41 – 7.29 (m, 3H), 7.13 (t, J = 7.3 Hz, 1H), 6.81 (t, J = 7.8 Hz, 2H), 6.53 (t, J = 7.5 Hz, 1H), 4.68 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.4, 154.3, 145.5, 140.2, 139.5, 138.4, 133.3, 132.6, 131.8, 130.5, 129.5, 129.4, 128.4, 126.5, 126.4, 122.3, 118.0, 117.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{14}Br_2N_3$ 453.9549; Found 453.9546.



2-(6-nitro-3-phenylquinoxalin-2-yl) aniline (3af)

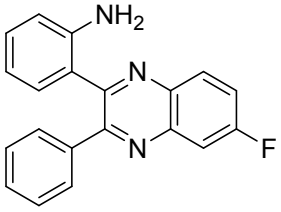
Silica gel column chromatography (petroleum ether/ethyl acetate = 2:1) gave **3af** as a yellow solid (11.0 mg, 16%); m. p. 242-244 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, J = 2.4 Hz, 1H), 8.53 (dd, J = 9.1, 2.5 Hz, 1H), 8.21 (d, J = 9.1 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.44 – 7.34 (m, 3H), 7.20 –

7.14 (m, 1H), 6.88 (dd, J = 7.8, 1.1 Hz, 1H), 6.86 – 6.81 (m, 1H), 6.55 (t, J = 7.5 Hz, 1H), 4.83 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.5, 156.2, 147.8, 145.8, 142.7, 139.7, 138.1, 133.0, 130.9, 130.1, 129.7, 129.6, 128.5, 125.6, 123.4, 121.8, 118.1, 117.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}N_4O_2$ 343.1190; Found 343.1191.



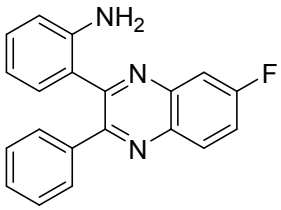
2-(7-nitro-3-phenylquinoxalin-2-yl) aniline (3af')

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3af'** as a yellow solid (51.3 mg, 75%); m. p. 153-155 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 2.4 Hz, 1H), 8.53 (dd, J = 9.2, 2.5 Hz, 1H), 8.29 (d, J = 9.2 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.44 – 7.32 (m, 3H), 7.20 – 7.09 (m, 1H), 6.90 – 6.77 (m, 2H), 6.55 (t, J = 7.3 Hz, 1H), 4.81 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.2, 155.5, 147.8, 145.8, 143.3, 139.0, 138.1, 131.9, 130.8, 130.8, 129.8, 129.7, 128.5, 125.0, 123.3, 121.73, 118.0, 117.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}N_4O_2$ 343.1190; Found 343.1194.



2-(7-fluoro-3-phenylquinoxalin-2-yl) aniline (3ag)

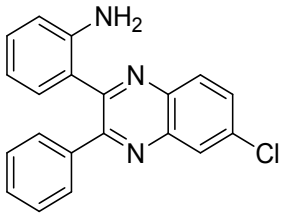
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3ag** as a yellow solid (12.0 mg, 19%); m. p. 152-154 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, J = 9.2, 5.7 Hz, 1H), 7.73 (dd, J = 9.1, 2.7 Hz, 1H), 7.61 – 7.49 (m, 3H), 7.38 – 7.29 (m, 3H), 7.16 – 7.09 (m, 1H), 6.84 (d, J = 7.7 Hz, 1H), 6.81 (d, J = 8.1 Hz, 1H), 6.55 (t, J = 7.5 Hz, 1H), 4.60 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.9 (d, J = 252.0 Hz), 153.8, 153.7 (d, J = 3.1 Hz), 145.4, 141.1(d, J = 13.2 Hz), 138.7, 138.2, 131.8, 131.3 (d, J = 10.1 Hz), 130.2, 129.5, 128.9, 128.3, 122.7, 120.3 (d, J = 26.0 Hz), 118.1, 117.0, 112.1 (d, J = 21.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}FN_3$ 316.1245; Found 316.1244.



2-(6-fluoro-3-phenylquinoxalin-2-yl) aniline (3ag')

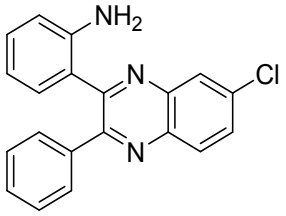
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3ag'** as a yellow solid (37.2 mg, 59%); m. p. 137-139 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 9.2, 5.7 Hz, 1H),

7.80 (dd, J = 9.2, 2.7 Hz, 1H), 7.63 – 7.51 (m, 3H), 7.40 – 7.29 (m, 3H), 7.17 – 7.09 (m, 1H), 6.84 (dd, J = 7.7, 1.0 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 6.55 (t, J = 7.4 Hz, 1H), 4.57 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.9 (d, J = 251.8 Hz), 155.1, 152.3 (d, J = 3.1 Hz), 145.3, 141.8 (d, J = 13.2 Hz), 138.6, 137.6, 131.8, 130.7 (d, J = 10.1 Hz), 130.1, 129.6, 129.2, 128.3, 123.0, 120.4 (d, J = 26.1 Hz), 118.1, 117.0, 112.8 (d, J = 21.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}FN_3$ 316.1245, Found 316.1244.



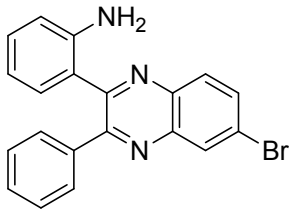
2-(6-chloro-3-phenylquinoxalin-2-yl) aniline (3ah)

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3ah** as a yellow solid (18.6 mg, 28%); m. p. 178-180 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 2.2 Hz, 1H), 7.96 (d, J = 8.9 Hz, 1H), 7.63 (dd, J = 8.9, 2.2 Hz, 1H), 7.49 (dd, J = 7.6, 1.5 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.08 – 7.02 (m, 1H), 6.80 – 6.75 (m, 1H), 6.73 (d, J = 8.1 Hz, 1H), 6.47 (t, J = 7.5 Hz, 1H), 4.54 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.1, 152.1, 144.3, 140.3, 137.8, 137.5, 134.7, 130.7, 129.9, 129.1, 128.8, 128.5, 128.1, 127.3, 127.1, 121.7, 117.0, 116.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}ClN_3$ 332.0949; Found 332.0949.



2-(7-chloro-3-phenylquinoxalin-2-yl) aniline (3ah')

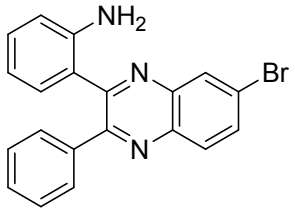
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3ah'** as a yellow solid (31.9 mg, 48%); m. p. 177-179 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 6.4 Hz, 1H), 8.01 (s, 1H), 7.63 (dd, J = 9.0, 2.2 Hz, 1H), 7.49 (dd, J = 7.6, 1.8 Hz, 2H), 7.32 – 7.21 (m, 3H), 7.10 – 7.01 (m, 1H), 6.76 (dd, J = 7.8, 1.2 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.47 (dd, J = 11.0, 4.0 Hz, 1H), 4.59 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.4, 152.9, 144.4, 139.6, 138.6, 137.6, 134.6, 130.8, 129.9, 129.4, 129.2, 128.5, 128.0, 127.3, 126.4, 121.5, 117.0, 116.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}ClN_3$ 332.0949; Found 332.0948.



2-(7-bromo-3-phenylquinoxalin-2-yl) aniline (3ai)

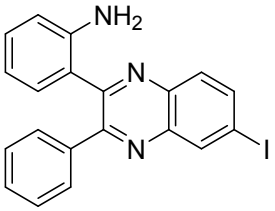
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3ai** as a yellow solid

(23.3 mg, 31%); m. p. 182-184 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 1.9 Hz, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.83 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.38 – 7.30 (m, 3H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.55 (t, *J* = 7.5 Hz, 1H), 4.62 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.1, 153.3, 145.3, 141.6, 139.1, 138.5, 133.5, 131.8, 131.6, 130.2, 129.9, 129.6, 129.2, 128.3, 123.9, 122.8, 118.1, 117.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}BrN_3$ 376.0444; Found 376.0442.



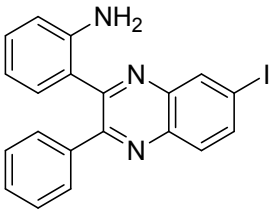
2-(6-bromo-3-phenylquinoxalin-2-yl) aniline (3ai')

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3ai'** as a yellow solid (32.3 mg, 43%); m. p. 195-197 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 2.1 Hz, 1H), 8.03 (d, *J* = 8.9 Hz, 1H), 7.84 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.56 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.39 – 7.29 (m, 3H), 7.16 – 7.09 (m, 1H), 6.89 – 6.76 (m, 2H), 6.54 (t, *J* = 7.4 Hz, 1H), 4.67 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.6, 153.9, 145.5, 140.9, 139.8, 138.7, 133.5, 131.8, 130.9, 130.6, 130.3, 129.5, 129.1, 128.3, 123.9, 122.6, 118.0, 117.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}BrN_3$ 376.0444; Found 376.0446.



2-(6-iodo-3-phenylquinoxalin-2-yl) aniline (3aj)

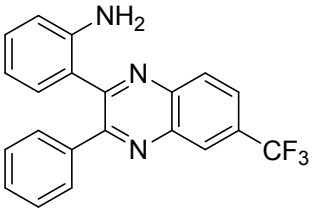
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3aj** as a yellow solid (27.9 mg, 33%); m. p. 212-213 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.56 (d, *J* = 6.7 Hz, 2H), 7.42 – 7.27 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.54 (t, *J* = 7.4 Hz, 1H), 4.63 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.9, 153.5, 145.4, 141.8, 139.5, 138.8, 138.6, 138.3, 131.8, 130.2, 129.9, 129.6, 129.2, 128.3, 122.8, 118.1, 117.1, 95.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}IN_3$ 424.0305; Found 424.0292.



2-(7-iodo-3-phenylquinoxalin-2-yl) aniline (3aj')

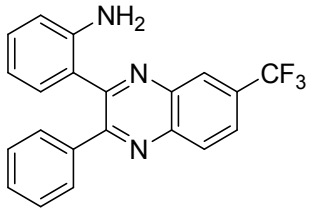
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3aj'** as a yellow solid

(40.6 mg, 48%); m. p. 167-168 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 1.8 Hz, 1H), 8.01 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.56 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.39 – 7.28 (m, 3H), 7.16 – 7.08 (m, 1H), 6.82 (t, *J* = 7.9 Hz, 2H), 6.54 (t, *J* = 7.2 Hz, 1H), 4.60 (br s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.8, 153.7, 145.5, 141.1, 140.2, 138.8, 138.7, 137.7, 131.9, 130.5, 130.3, 129.5, 129.1, 128.3, 122.6, 118.0, 117.1, 95.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}IN_3$ 424.0305; Found 424.0305.



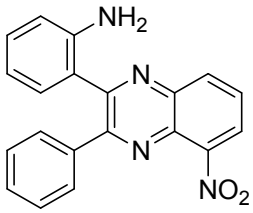
2-(3-phenyl-7-(trifluoromethyl) quinoxalin-2-yl) aniline (3ak)

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3ak** as a yellow solid (21.2 mg, 29%); m. p. 215-217 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.82 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.51 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.30 – 7.23 (m, 3H), 7.08 – 7.03 (m, 1H), 6.78 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.52 – 6.45 (m, 1H), 4.96 (br s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.6, 153.9, 143.8, 140.3, 138.9, 137.3, 130.8, 130.5 (q, *J* = 33.0 Hz), 129.4, 128.79, 128.5, 128.3, 127.3, 126.2 (q, *J* = 4.3 Hz), 124.5 (q, *J* = 3.1 Hz), 122.7 (q, *J* = 272.7 Hz), 121.7, 117.4, 116.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{15}F_3N_3$ 366.1213; Found 366.1210.



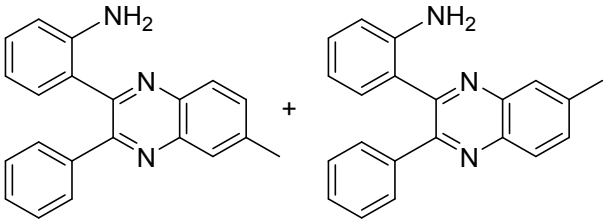
2-(3-phenyl-6-(trifluoromethyl) quinoxalin-2-yl) aniline (3ak')

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3ak'** as a yellow solid (35.8 mg, 49%); m. p. 149-151 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 7.85 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.32 – 7.22 (m, 3H), 7.08 – 7.03 (m, 1H), 6.76 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.49 – 6.43 (m, 1H), 4.62 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.2, 153.5, 144.5, 141.0, 138.2, 137.4, 130.6, 130.5 (q, *J* = 32.9 Hz), 129.4, 129.4, 128.5, 128.4, 127.3, 125.6 (q, *J* = 4.3 Hz), 124.5 (q, *J* = 2.9 Hz), 122.7 (q, *J* = 272.5 Hz), 121.2, 117.0, 116.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{15}F_3N_3$ 366.1213; Found 366.1211.



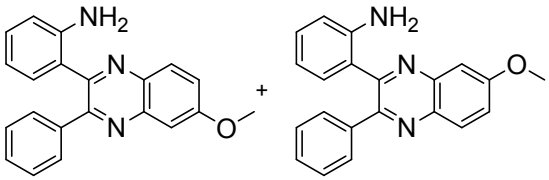
2-(5-nitro-3-phenylquinoxalin-2-yl) aniline (3al')

Silica gel column chromatography (petroleum ether/ethyl acetate = 2:1) gave **3al'** as a yellow solid (44.5 mg, 65%); m. p. 193-195 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.56 (d, *J* = 6.7 Hz, 2H), 7.42 – 7.22 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.54 (t, *J* = 7.4 Hz, 1H), 4.63 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.6, 154.5, 147.0, 145.5, 139.9, 137.7, 133.1, 133.0, 131.9, 130.8, 130.0, 129.9, 128.4, 128.1, 124.5, 121.9, 118.2, 117.3. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{15}N_4O_2$ 343.1190; Found 343.1191.



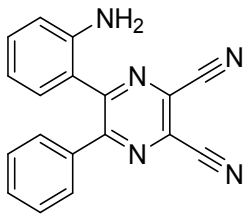
2-(7-methyl-3-phenylquinoxalin-2-yl) aniline (3am) + 2-(6-methyl-3-phenylquinoxalin-2-yl) aniline (3am')

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3am+3am'** as a yellow solid (39.2 mg, 35%+28%); m. p. 156-160 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 0.45 H), 7.90 (d, *J* = 8.5 Hz, 0.55 H), 7.85 (s, 0.55 H), 7.79 (s, 0.45 H), 7.55 – 7.38 (m, 3H), 7.21 – 7.18 (m, 3H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.48(t, *J* = 7.5 Hz, 1H), 4.64 (br s, 2 H), 2.51 (s, 1.65 H), 2.50 (s, 1.35 H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.1, 152.3, 151.6, 150.8, 143.9, 143.7, 140.1, 139.5, 139.5, 139.4, 138.5, 138.0, 137.8, 131.3, 131.2, 130.8, 130.7, 128.7, 128.5, 128.5, 128.5, 127.7, 127.7, 127.6, 127.1, 127.1, 126.5, 122.6, 122.5, 117.3, 117.2, 116.1, 116.1, 20.9. HRMS (ESI) m/z: (M + H)$^+$ Calcd for $C_{21}H_{18}N_3$ 312.1495; Found 312.1494.



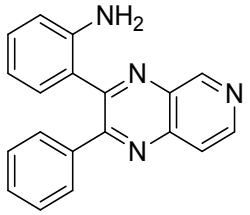
2-(7-methoxy-3-phenylquinoxalin-2-yl) aniline + 2-(6-methoxy-3-phenylquinoxalin-2-yl) aniline (3an + 3an')

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3an+3an'** as a yellow solid (37.9 mg, 39+19%); m. p. 102-104 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 9.1 Hz, 0.33H), 7.98 (d, *J* = 9.1 Hz, 0.67H), 7.59 – 7.51 (m, 2H), 7.48 – 7.38 (m, 2H), 7.35 – 7.28 (m, 3H), 7.14 – 7.06 (m, 1H), 6.89 – 6.81 (m, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.59 – 6.51 (m, 1H), 4.54 (s, 2H), 3.98 (s, 2H), 3.97 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.1, 160.9, 154.2, 152.8, 151.7, 150.3, 145.2, 145.2, 142.7, 142.1, 139.1, 139.0, 137.3, 136.6, 131.8, 131.7, 130.3, 129.9, 129.7, 129.7, 129.5, 129.5, 128.8, 128.6, 128.2, 128.2, 123.5, 123.5, 123.4, 118.1, 116.9, 106.6, 106.1, 55.9, 55.9. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{21}H_{18}N_3O$ 328.1444; Found 328.1444.



5-(2-aminophenyl)-6-phenylpyrazine-2,3-dicarbonitrile (3ao)

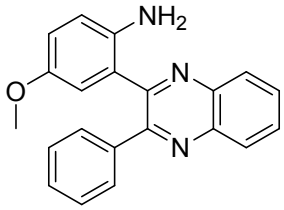
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **3ao** as a yellow solid (30.9 mg, 52%); m. p. 220-222 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.45 (t, *J* = 7.5 Hz, 1H), 4.76 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.0, 154.5, 145.3, 134.5, 131.4, 130.7, 130.2, 128.5, 128.1, 127.8, 127.3, 117.6, 117.2, 116.9, 112.1, 112.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{12}N_5$ 298.1087; Found 298.1085.



2-(2-phenylpyrido [3,4- b] pyrazine -3-yl) aniline (3ap)

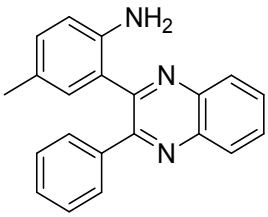
Silica gel column chromatography (methylene chloride/methanol = 25:1) gave **3ap** as a yellow solid (22.1mg, 37%); m. p. 200-202 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 8.74 (d, *J* = 5.8 Hz, 1H), 7.84 (d, *J* = 5.8 Hz, 1H), 7.52 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.35 – 7.23 (m, 3H), 7.11 – 7.04 (m, 1H), 6.79 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.47 (t, *J* = 7.5 Hz, 1H), 4.71 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.9, 156.2, 154.4, 147.4, 145.7, 142.7, 138.3, 136.1, 131.9, 130.8, 129.5, 129.5, 128.4, 122.0, 120.8, 118.0, 117.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}N_4$ 299.1291; Found 299.1293.

5. The characterization data of 4ba-4va.



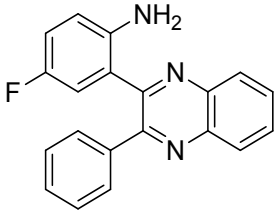
4-methoxy-2-(3-phenylquinoxalin-2-yl) aniline (4ba)

Silica gel column chromatography (petroleum ether/ethyl acetate = 2:1) gave **4ba** as a yellow solid (48.4 mg, 74%); m. p. 174-176 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.08 (m, 1H), 8.08 – 7.99 (m, 1H), 7.78 – 7.64 (m, 2H), 7.51 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.34 – 7.22 (m, 3H), 6.67 (d, *J* = 1.4 Hz, 2H), 6.36 (s, 1H), 4.30 (s, 2H), 3.31 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.2, 151.8, 151.0, 140.0, 139.4, 138.2, 138.0, 129.0, 129.0, 128.5, 128.2, 127.8, 127.6, 127.3, 122.6, 117.5, 116.6, 115.0, 54.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}N_3O$ 328.1444; Found 328.1443.



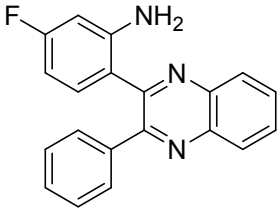
4-methyl-2-(3-phenylquinoxalin-2-yl) aniline (4ca)

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4ca** as a yellow solid (50.4 mg, 81%); m. p. 152-154 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.15 (m, 1H), 8.14 – 8.08 (m, 1H), 7.80 – 7.73 (m, 2H), 7.63 – 7.55 (m, 2H), 7.37 – 7.30 (m, 3H), 6.94 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.75 – 6.66 (m, 2H), 4.36 (s, 2H), 2.02 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.3, 153.1, 142.7, 141.1, 140.6, 138.9, 132.0, 130.7, 130.0, 129.9, 129.5, 129.3, 128.9, 128.7, 128.2, 127.4, 123.5, 117.1, 20.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}N_3$ 312.1495; Found 312.1491.



4-fluoro-2-(3-phenylquinoxalin-2-yl) aniline (4da)

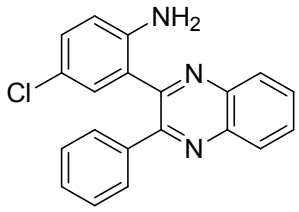
Silica gel column chromatography (petroleum ether/ethyl acetate = 2:1) gave **4da** as a yellow solid (50.5 mg, 80%); m. p. 132-134 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.16 (m, 1H), 8.15 – 8.08 (m, 1H), 7.83 – 7.76 (m, 2H), 7.58 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.39 – 7.32 (m, 3H), 6.87 (td, *J* = 8.4, 2.9 Hz, 1H), 6.74 (dd, *J* = 8.8, 4.7 Hz, 1H), 6.61 (dd, *J* = 9.2, 2.9 Hz, 1H), 4.41 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.6 (d, *J* = 236.5 Hz), 154.0, 151.7 (d, *J* = 2.1 Hz), 141.5 (d, *J* = 2.0 Hz), 141.5, 141.2, 140.4, 138.4, 130.4, 130.2, 129.4, 129.3, 129.2, 128.7, 128.4, 124.2 (d, *J* = 7.1 Hz), 118.0 (d, *J* = 7.6 Hz), 117.6 (d, *J* = 23.6 Hz), 116.9 (d, *J* = 22.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}FN_3$ 316.1245; Found 316.1243.



5-fluoro-2-(3-phenylquinoxalin-2-yl) aniline (4ea)

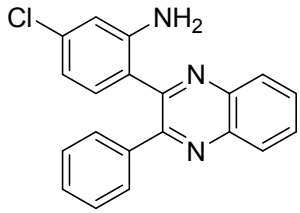
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4ea** as a yellow solid (43.5 mg, 69%); m. p. 119-121 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.71-7.63 (m, 2H), 7.51 – 7.47 (m, 2H), 7.31 – 7.25 (m, 3H), 6.73 (dd, *J* = 8.6, 6.3 Hz, 1H), 6.50 (dd, *J* = 10.4, 2.4 Hz, 1H), 6.21 (td, *J* = 8.4, 2.4 Hz, 1H), 4.91 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 247.5 Hz), 153.2, 150.7, 144.8 (d, *J* = 9.4 Hz), 139.9, 139.2, 137.7, 132.6 (d, *J* = 10.2 Hz), 129.1, 129.1, 128.5, 128.2, 127.9, 127.5, 127.4, 118.8, 105.0 (d, *J* = 22.3 Hz), 103.2 (d, *J* = 23.8

Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}FN_3$ 316.1245; Found 316.1243.



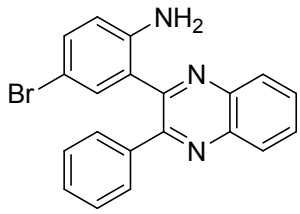
4-chloro-2-(3-phenylquinoxalin-2-yl) aniline (4fa)

Silica gel column chromatography (petroleum ether/ethyl acetate = 2:1) gave **4fa** as a yellow solid (47.8 mg, 72%); m. p. 156-158 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 1H), 8.06 – 7.98 (m, 1H), 7.75 – 7.68 (m, 2H), 7.50 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.00 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.63 (d, *J* = 8.6 Hz, 1H), 4.45 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.1, 151.5, 143.9, 141.3, 140.4, 138.4, 131.2, 130.4, 130.2, 129.8, 129.4, 129.4, 129.2, 128.7, 128.5, 124.5, 122.7, 118.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}ClN_3$ 332.0949; Found 332.0948.



5-chloro-2-(3-phenylquinoxalin-2-yl) aniline (4ga)

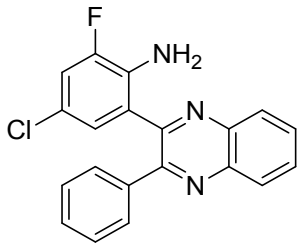
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4ga** as a yellow solid (47.8 mg, 72%); m. p. 142-144 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 1H), 8.05 – 7.96 (m, 1H), 7.73 – 7.67 (m, 2H), 7.49 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.31 – 7.24 (m, 3H), 6.73 (d, *J* = 1.9 Hz, 1H), 6.68 (d, *J* = 8.3 Hz, 1H), 6.42 (dd, *J* = 8.3, 1.9 Hz, 1H), 4.74 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.2, 152.0, 146.7, 141.1, 140.3, 138.7, 135.5, 133.1, 130.2, 130.2, 129.5, 129.3, 129.0, 128.6, 128.5, 121.3, 118.0, 116.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}ClN_3$ 332.0949; Found 332.0946.



4-bromo-2-(3-phenylquinoxalin-2-yl) aniline (4ha)

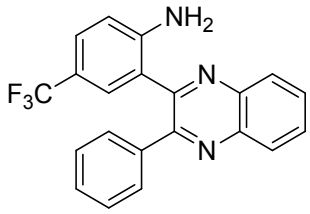
Silica gel column chromatography (petroleum ether/ethyl acetate = 2:1) gave **4ha** as a yellow solid (54.2 mg, 72%); m. p. 165-167 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.3 Hz, 1H), 8.06 – 7.98 (m, 1H), 7.77 – 7.62 (m, 2H), 7.54 – 7.42 (m, 2H), 7.35 – 7.23 (m, 3H), 7.12 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.92 (d, *J* = 1.6 Hz, 1H), 6.59 (d, *J* = 8.6 Hz, 1H), 4.36 (br s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.0, 151.3, 143.9, 141.2, 140.4, 138.4, 134.1, 132.7, 130.5, 130.25, 129.5, 129.3,

129.2, 128.7, 128.5, 125.1, 118.7, 109.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}BrN_3$ 376.0444; Found 376.0443.



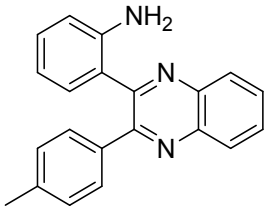
4-chloro-2-fluoro-6-(3-phenylquinoxalin-2-yl) aniline (4ia)

Silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) gave **4ia** as a yellow solid (58.8 mg, 84%); m. p. 125-127 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 1H), 8.07 – 8.02 (m, 1H), 7.78 – 7.72 (m, 2H), 7.52 – 7.47 (m, 2H), 7.35 – 7.28 (m, 3H), 6.93 (dd, *J* = 10.5, 2.3 Hz, 1H), 6.60 (dd, *J* = 2.1, 1.6 Hz, 1H), 4.35 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.8, 151.8 (d, *J* = 242.6 Hz), 150.6, 150.5, 141.1, 140.3, 138.0, 133.2 (d, *J* = 13.8 Hz), 130.8, 130.5, 129.4, 129.3, 128.7, 128.6, 126.7 (d, *J* = 3.4 Hz), 125.5 (d, *J* = 4.2 Hz), 121.4 (d, *J* = 10.5 Hz), 116.1 (d, *J* = 22.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{14}ClFN_3$ 350.0855; Found 350.0852.



2-(3-phenylquinoxalin-2-yl)-4- (trifluoromethyl) aniline (4ja)

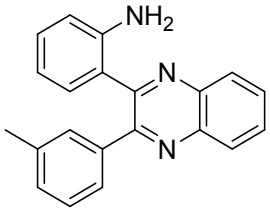
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4ja** as a yellow solid (38 mg, 52%); m. p. 161-162 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.16 (m, 1H), 8.14 – 8.08 (m, 1H), 7.85 – 7.77 (m, 2H), 7.56 – 7.48 (m, 2H), 7.40 – 7.31 (m, 4H), 7.10 (d, *J* = 1.4 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 5.07 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.3, 151.6, 148.4, 141.2, 140.2, 138.4, 130.5, 130.3, 129.7 (q, *J* =3.9 Hz), 129.4, 129.2, 128.6, 128.5, 126.8 (q, *J* = 3.6 Hz), 124.3 (q, *J* =270.6 Hz), 121.7, 119.5 (q, *J* =24.8 Hz), 116.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.8. HRMS (ESI) m/z: $(M + H)^+$ Calcd for $C_{21}H_{15}F_3N_3$ 366.1213; Found 366.1211.



2-(3-(p- tolyl) quinoxalin-2-yl) aniline (4ka)

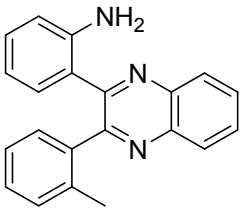
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4ka** as a yellow solid (48.0 mg, 77%); m. p. 136-137 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 6.8 Hz, 1H), 8.09 (d, *J* = 7.0 Hz, 1H), 7.83 – 7.66 (m, 2H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.20 – 7.04 (d, 3H), 6.89 (d, *J* = 7.4

Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 6.58 (t, J = 7.2 Hz, 1H), 4.58 (s, 2H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.3, 152.9, 145.3, 141.1, 140.3, 138.9, 136.0, 131.7, 130.0, 129.9, 129.8, 129.5, 129.3, 129.0, 128.7, 123.5, 118.1, 117.0, 21.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}N_3$ 312.1495; Found 312.1496.



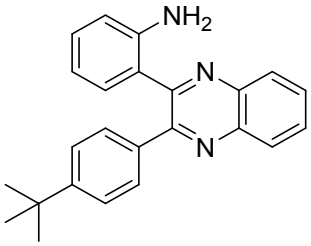
2-(3-(m-tolyl) quinoxalin-2-yl) aniline (4la)

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4la** as a yellow solid (36.8 mg, 59%); m. p. 94-96 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.07 (m, 1H), 8.06 – 7.99 (m, 1H), 7.73 – 7.65 (m, 2H), 7.41 (s, 1H), 7.21 – 7.17 (m, 1H), 7.12 – 7.02 (m, 3H), 6.79 (dd, J = 7.7, 1.3 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.48 (t, J = 7.5 Hz, 1H), 4.53 (s, 2H), 2.25 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.4, 151.9, 143.7, 140.0, 139.3, 137.7, 137.0, 130.7, 129.1, 128.9, 128.9, 128.8, 128.6, 128.2, 127.6, 126.9, 125.8, 122.5, 117.3, 116.1, 20.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}N_3$ 312.1495; Found 312.1496.



2-(3-(o-tolyl) quinoxalin-2-yl) aniline (4ma)

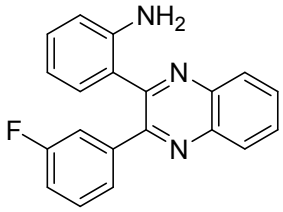
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4ma** as a yellow solid (29.9 mg, 48%); m. p. 116-118 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.15 (m, 1H), 8.14 – 8.07 (m, 1H), 7.84 – 7.74 (m, 2H), 7.41 – 7.34 (m, 1H), 7.30 – 7.19 (m, 2H), 7.15 (d, J = 7.5 Hz, 1H), 7.09 – 7.02 (m, 1H), 6.80 – 6.70 (m, 2H), 6.41 (t, J = 7.6 Hz, 1H), 4.93 (s, 2H), 2.08 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.6, 153.7, 145.9, 140.6, 140.3, 138.9, 136.1, 131.4, 130.5, 130.1, 130.1, 130.0, 129.9, 129.3, 128.7, 128.6, 125.9, 122.0, 117.4, 116.9, 19.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}N_3$ 312.1495; Found 312.1495.



2-(3-(4-(tert-butyl) phenyl) quinoxalin-2-yl) aniline (4na)

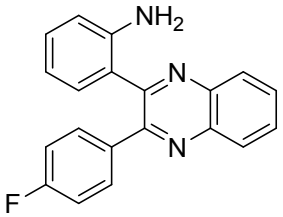
Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave 4na as a yellow solid (50.2 mg, 71%); m. p. 121-123 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.13 (m, 1H), 8.13 – 8.05

(m, 1H), 7.82 – 7.70 (m, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.18 – 7.10 (m, 1H), 6.90 (dd, J = 7.7, 1.2 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.57 (t, J = 7.5 Hz, 1H), 4.63 (s, 2H), 1.30 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.2, 151.9, 151.0, 144.3, 140.1, 139.2, 134.9, 130.8, 128.9, 128.7, 128.2, 128.2, 127.6, 124.2, 122.3, 117.0, 115.9, 33.6, 30.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}N_3$ 354.1965; Found 354.1964.



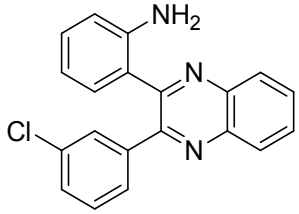
2-(3-(3-fluorophenyl) quinoxalin-2-yl) aniline(4oa)

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4oa** as a yellow solid (47.3 mg, 75%); m. p. 158-160 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.15 (m, 1H), 8.14 – 8.08 (m, 1H), 7.83 – 7.76 (m, 2H), 7.40 – 7.34 (m, 1H), 7.30 – 7.23 (m, 2H), 7.14 (td, J = 8.1, 1.5 Hz, 1H), 7.07 – 6.99 (m, 1H), 6.89 – 6.78 (m, 2H), 6.58 (td, J = 7.6, 1.0 Hz, 1H), 4.62 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.6 (d, J = 246.0 Hz), 161.4, 152.9 (d, J = 2.4 Hz), 152.8, 145.4, 141.1 (d, J = 7.6 Hz), 140.9, 140.6, 131.7, 130.4, 130.2, 129.7 (d, J = 8.1 Hz), 129.3, 128.7, 125.4 (d, J = 3.0 Hz), 122.7, 118.2, 117.1, 116.5 (d, J = 23.0 Hz), 115.9 (d, J = 21.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}FN_3$ 316.1245; Found 316.1249.



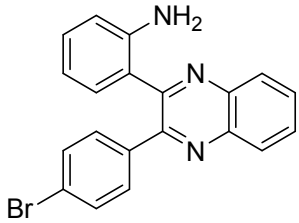
2-(3-(4-fluorophenyl) quinoxalin-2-yl) aniline (4pa)

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4pa** as a yellow solid (42.9 mg, 68%); m. p. 152-154 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.14 (m, 1H), 8.14 – 8.07 (m, 1H), 7.82 – 7.75 (m, 2H), 7.62 – 7.54 (m, 2H), 7.18 – 7.12 (m, 1H), 7.02 (t, J = 8.7 Hz, 2H), 6.83 (t, J = 7.3 Hz, 2H), 6.58 (t, J = 7.5 Hz, 1H), 4.60 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.2 (d, J = 249.2 Hz), 153.2, 152.8, 145.3, 141.0, 140.5, 135.0 (d, J = 3.3 Hz), 131.6, 131.5 (d, J = 8.6 Hz), 130.2, 130.1, 130.1, 129.2, 128.7, 123.0, 118.2, 117.0, 115.4 (d, J = 21.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}FN_3$ 316.1245; Found 316.1246.



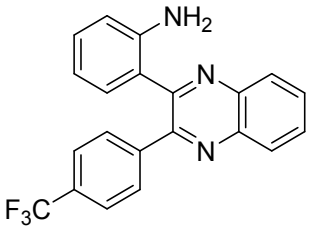
2-(3-(3-chlorophenyl) quinoxalin-2-yl) aniline (4qa)

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4qa** as a yellow solid (55.8 mg, 84%); m. p. 159-161 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.15 (m, 1H), 8.14 – 8.07 (m, 1H), 7.83 – 7.76 (m, 2H), 7.71 (s, 1H), 7.37 – 7.28 (m, 2H), 7.20 (t, *J* = 7.9 Hz, 1H), 7.17 – 7.11 (m, 1H), 6.87 – 6.78 (m, 2H), 6.58 (t, *J* = 7.5 Hz, 1H), 4.63 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.8, 145.4, 141.0, 140.7, 140.6, 134.3, 131.7, 130.4, 130.3, 129.6, 129.3, 129.0, 128.7, 127.9, 122.6, 118.2, 117.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}ClN_3$ 332.0949; Found 332.0949.



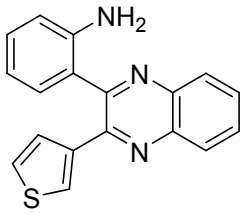
2-(3-(4-bromophenyl) quinoxalin-2-yl) aniline (4ra)

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4ra** as a yellow solid (51.1 mg, 68%); m. p. 88-89 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.72 – 7.65 (m, 2H), 7.42 – 7.35 (m, 4H), 7.07 (td, *J* = 8.1, 1.5 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.77 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.56 (td, *J* = 7.7, 0.9 Hz, 1H), 5.18 (br. s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.0, 152.4, 144.0, 141.0, 140.4, 137.8, 131.7, 131.5, 131.3, 130.3, 130.2, 129.2, 128.8, 123.9, 123.6, 123.6, 119.1, 117.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}B_rN_3$ 376.0449; Found 376.0440.



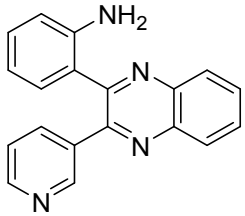
2-(3-(4-(trifluoromethyl) phenyl) quinoxalin-2-yl) aniline (4sa)

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4sa** as a yellow solid (46.8 mg, 64%); m. p. 129-131 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 1H), 8.07 – 8.00 (m, 1H), 7.75 – 7.70 (m, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.11 – 7.03 (m, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.72 (dd, *J* = 7.7, 1.0 Hz, 1H), 6.48 (t, *J* = 7.4 Hz, 1H), 4.59 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.7, 144.4, 141.5, 139.9, 139.6, 130.7, 129.6 (q, *J* = 32.5 Hz), 129.5, 129.3, 128.9, 128.3, 127.7, 124.1 (q, *J* = 3.8 Hz), 123.0 (q, *J* = 272.2 Hz), 121.4, 117.2, 116.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{15}F_3N_3$ 366.1213; Found 366.1211.



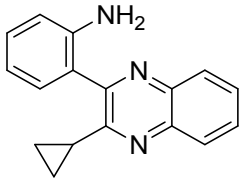
2-(3-(thiophen-3-yl) quinoxalin-2-yl) aniline (4ta)

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4ta** as a yellow solid (43.1 mg, 71%); m. p. 130-132 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.10 (m, 1H), 8.10 – 8.04 (m, 1H), 7.78 – 7.70 (m, 2H), 7.49 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.37 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.05 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.72 (td, *J* = 7.5, 1.0 Hz, 1H), 4.09 (br s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.4, 149.2, 145.0, 141.2, 140.4, 139.9, 131.1, 130.3, 130.1, 129.8, 129.1, 128.7, 128.6, 127.5, 125.2, 123.8, 118.5, 116.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{14}N_3S$ 304.0903; Found 304.0905.



2-(3-(pyridin-3-yl) quinoxalin-2-yl) aniline(4ua)

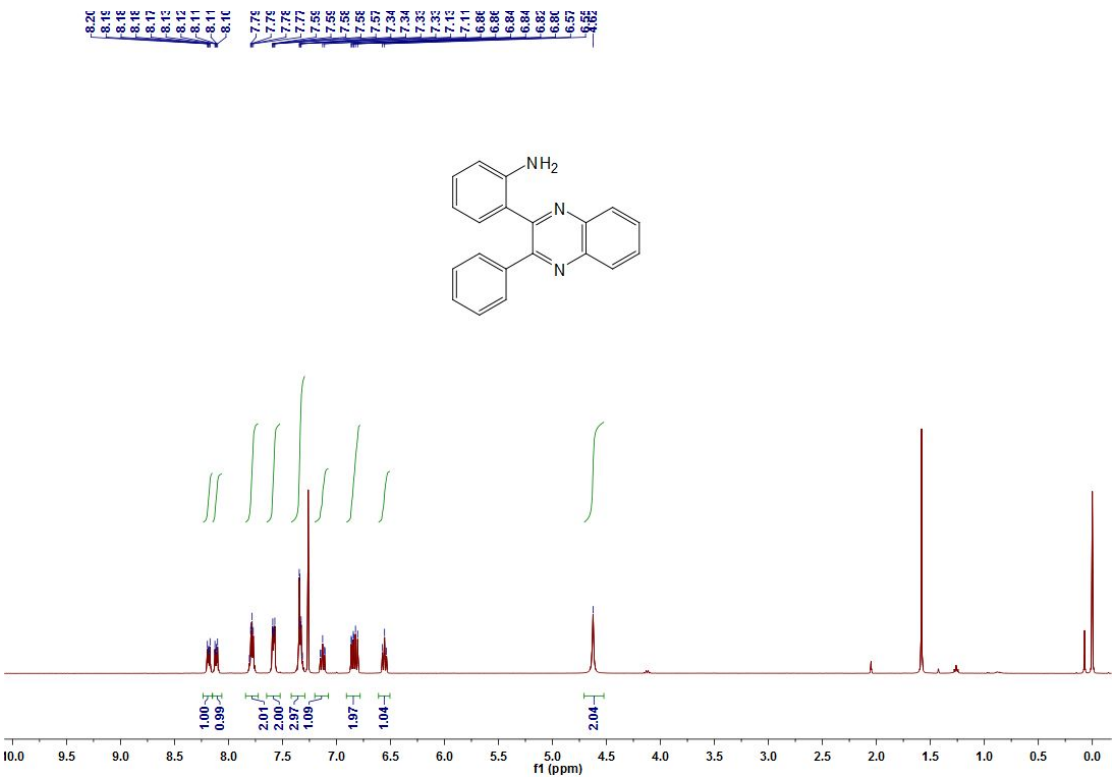
Silica gel column chromatography (methylene chloride/methanol = 25:1) gave **4ua** as a yellow solid (50.7 mg, 85%); m. p. 145-147 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.57 (d, *J* = 4.0 Hz, 1H), 8.23 – 8.15 (m, 1H), 8.15– 8.07 (m, 1H), 7.88 – 7.74 (m, 3H), 7.23 (dd, *J* = 7.6, 5.0 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.82 (dd, *J* = 7.7, 2.1 Hz, 2H), 6.58 (t, *J* = 7.5 Hz, 1H), 4.31 (br s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.8, 151.4, 150.4, 149.6, 145.4, 141.1, 140.7, 136.9, 134.8, 131.6, 130.6, 130.4, 130.4, 129.3, 128.8, 122.9, 122.4, 118.3, 117.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}N_4$ 299.1291; Found 299.1295.



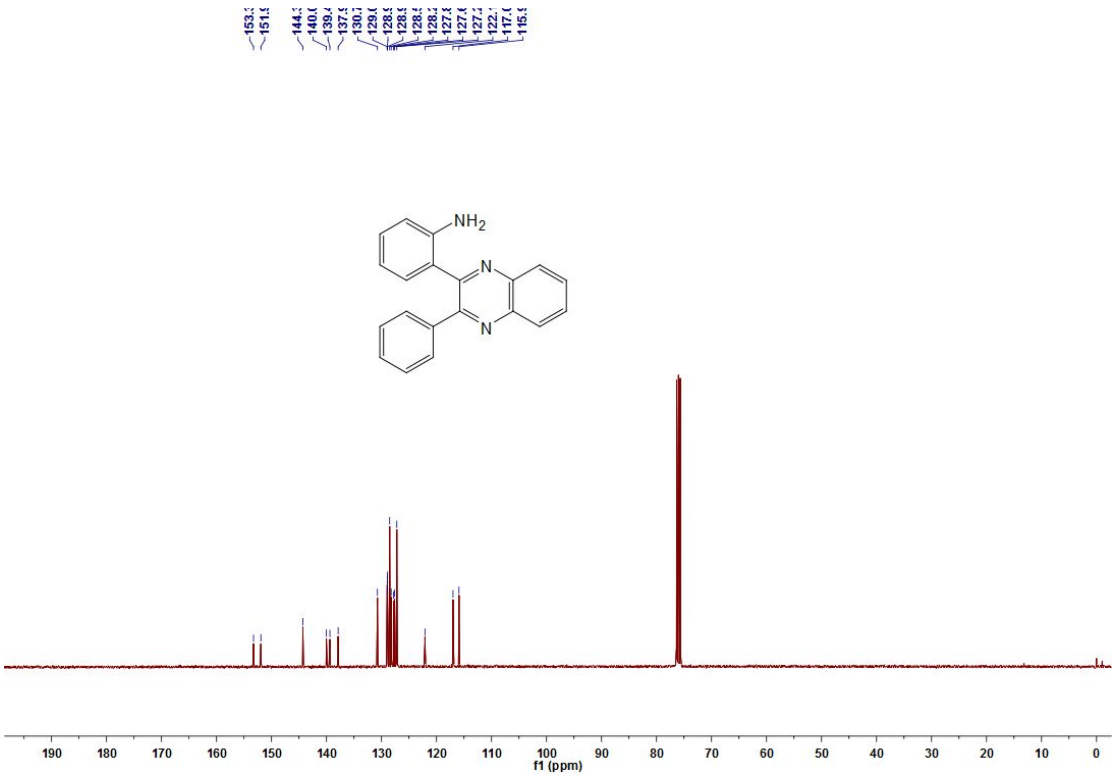
2-(3-cyclopropylquinoxalin-2-yl) aniline (4va)

Silica gel column chromatography (petroleum ether/ethyl acetate = 5:1) gave **4va** as a yellow solid (33.5 mg, 64%); m. p. 82-83 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.95 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.66 – 7.61 (m, 1H), 7.43 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.25 (td, *J* = 7.6, 1.5 Hz, 1H), 6.91 – 6.83 (m, 2H), 4.34 (br s, 2H), 2.34 – 2.26 (m, 1H), 1.38 – 1.32 (m, 2H), 1.08 – 1.01 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.9, 153.4, 145.4, 141.4, 139.8, 130.9, 130.1, 129.6, 128.7, 128.5, 128.4, 122.9, 118.2, 116.9, 15.2, 12.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}N_3$ 262.1339; Found 262.1342.

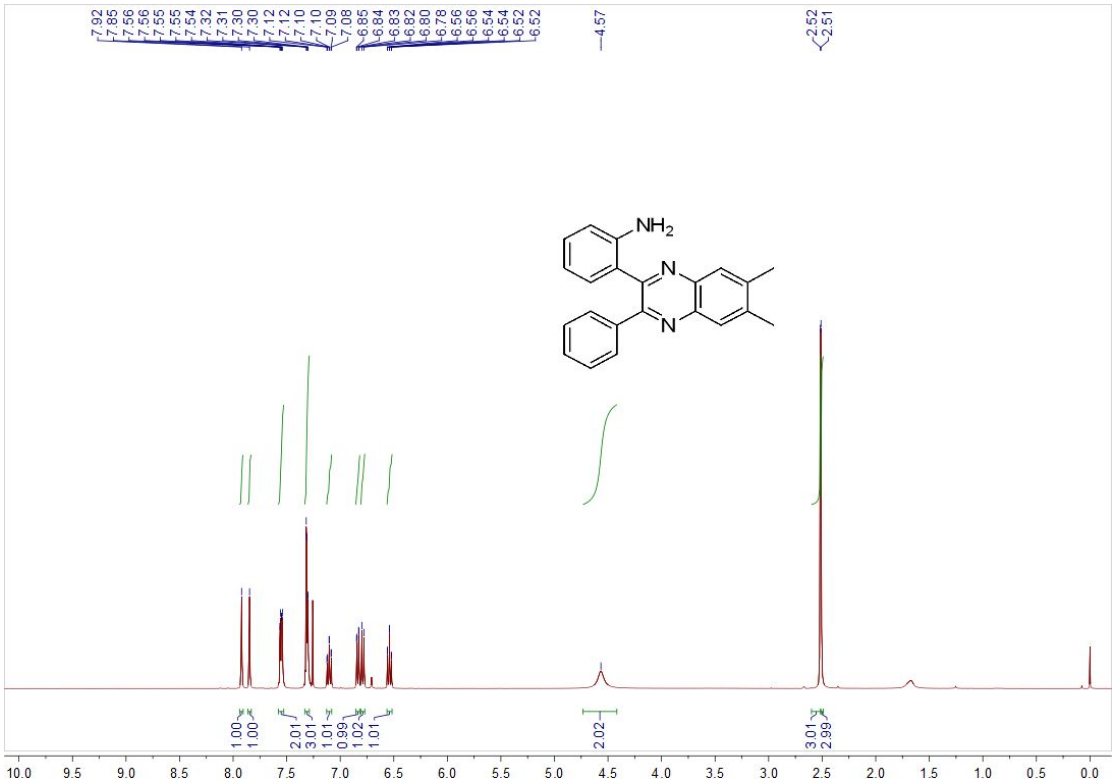
6. ^{1}H, ^{13}C and ^{19}F NMR spectra of 3aa-3ap.



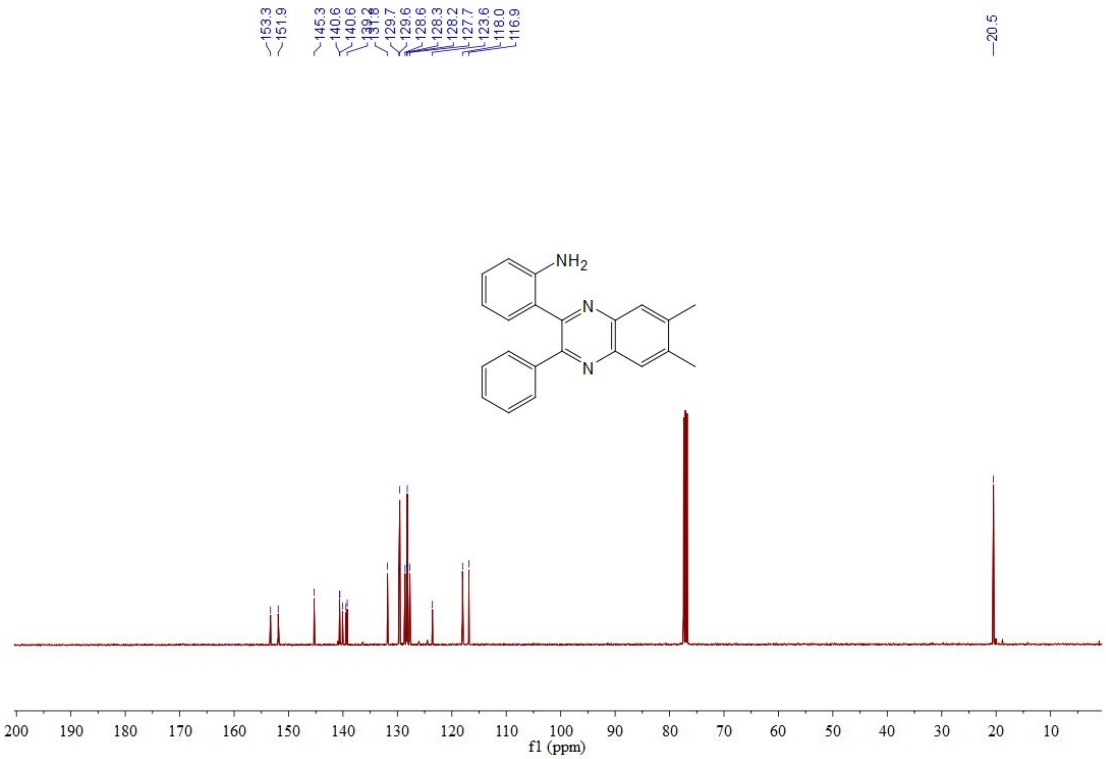
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aa**



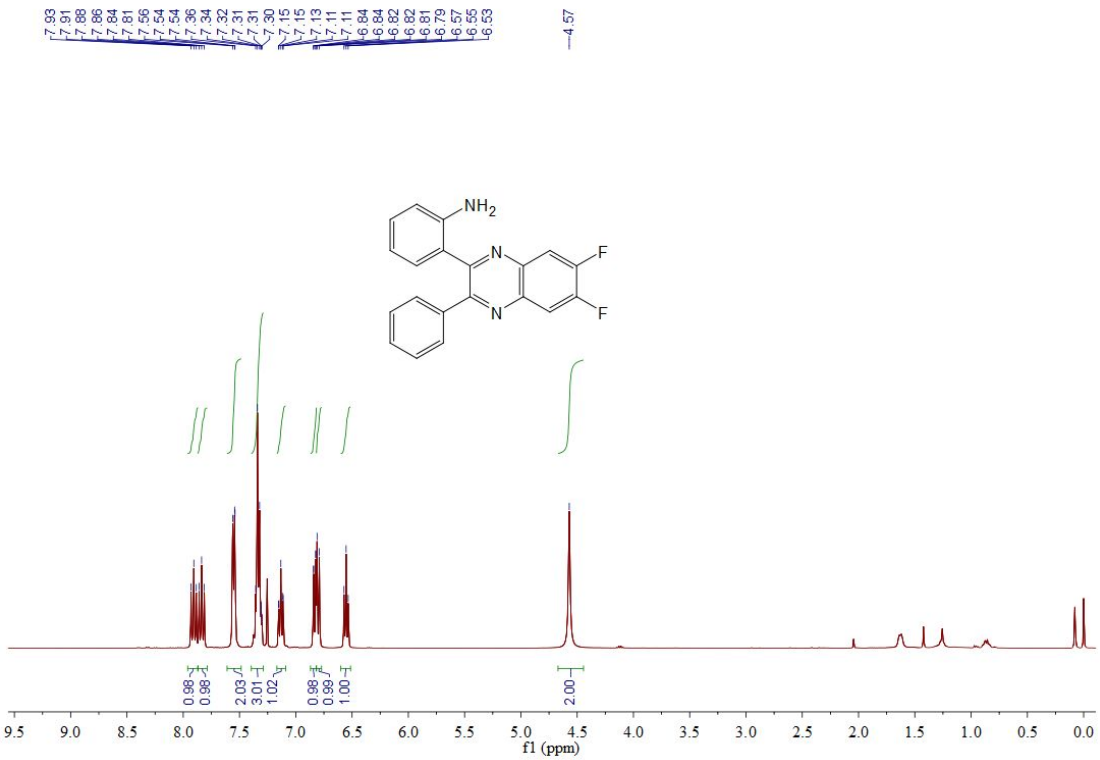
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3aa**



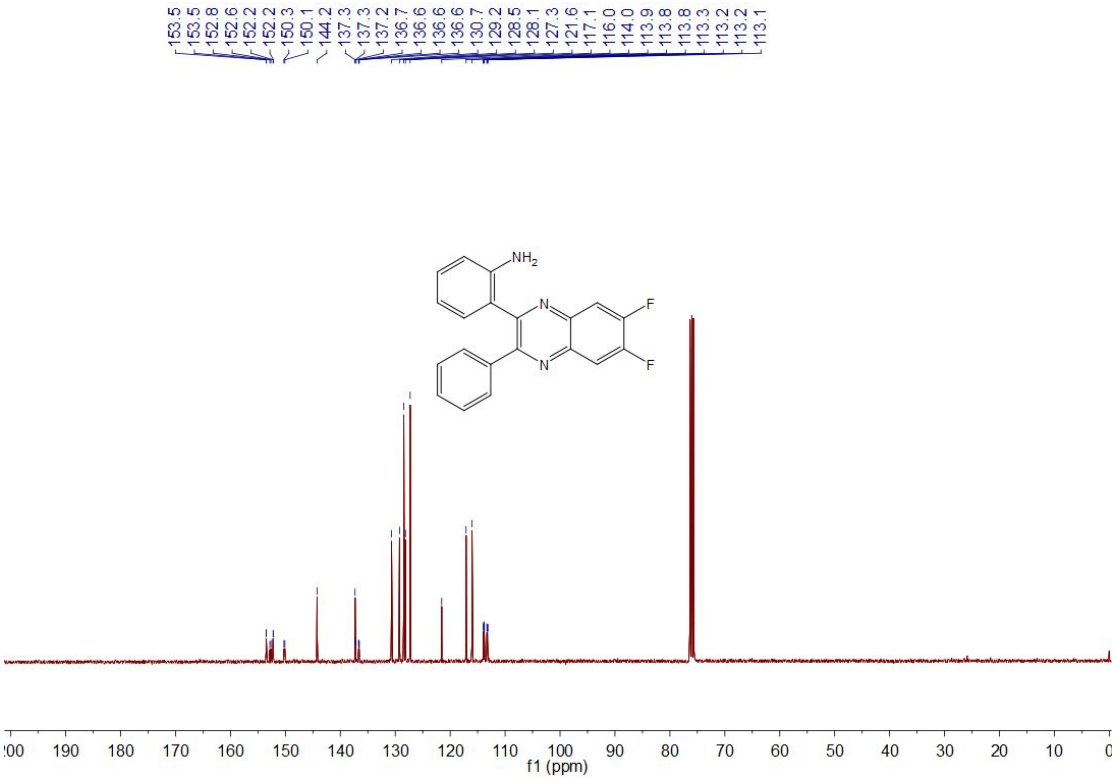
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ab**



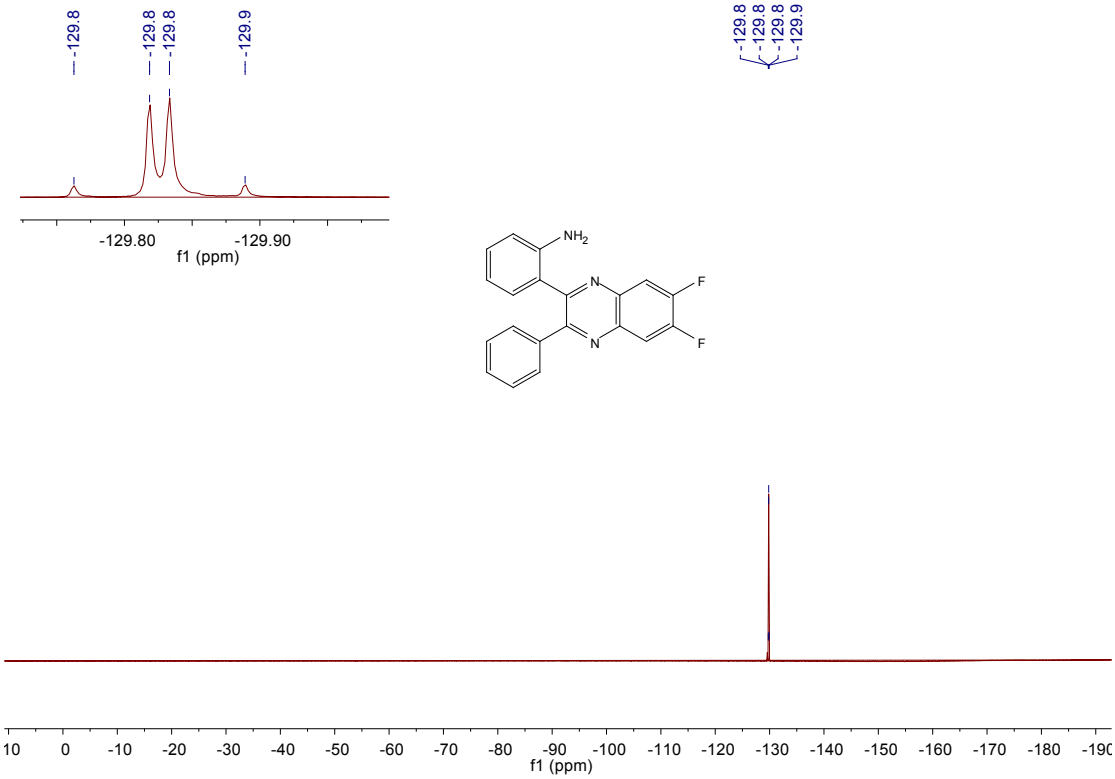
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3ab**



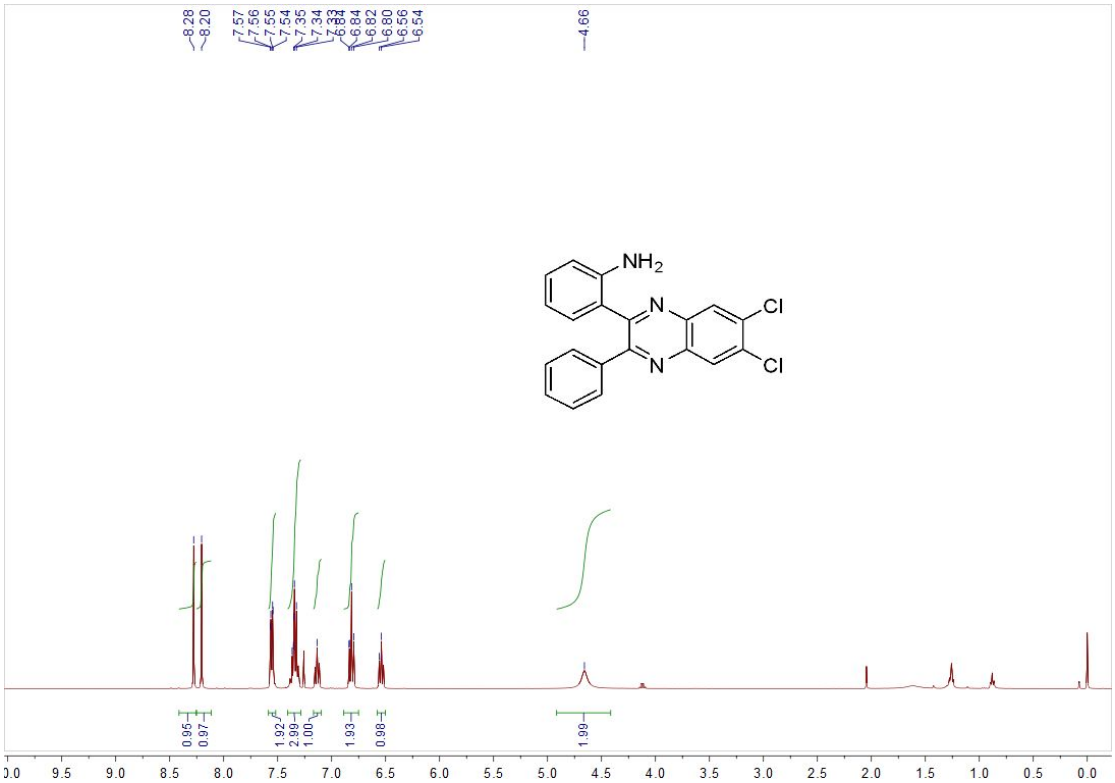
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ac**



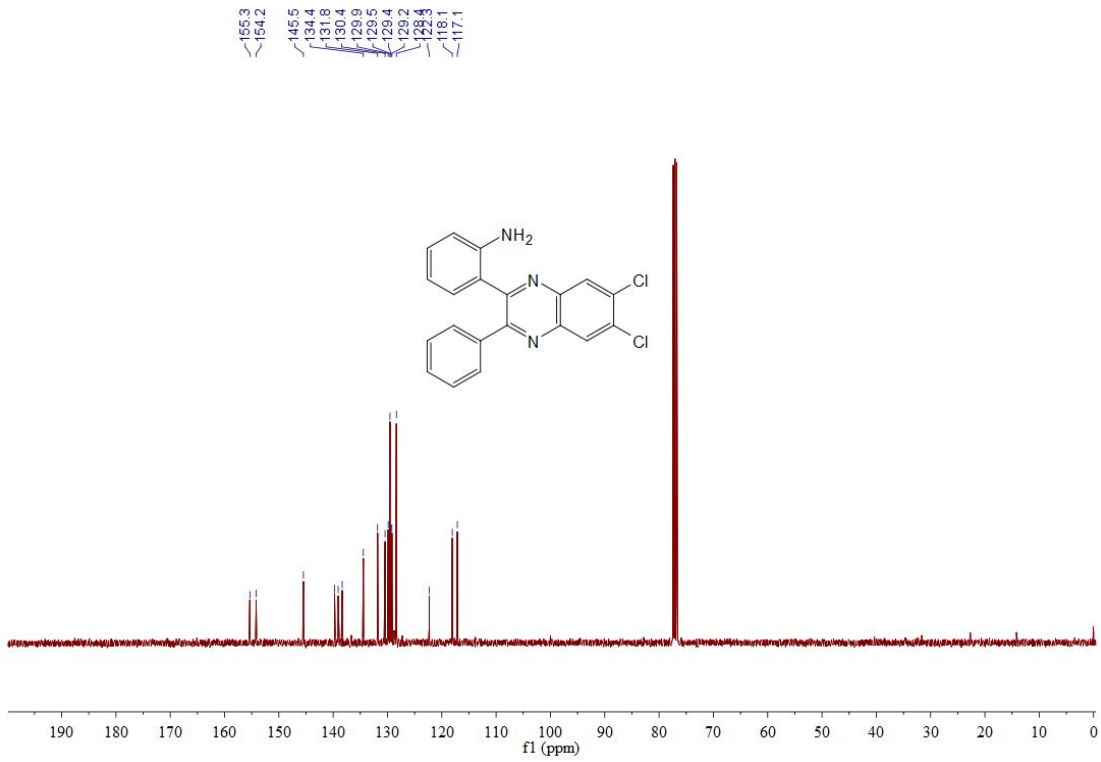
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3ac**



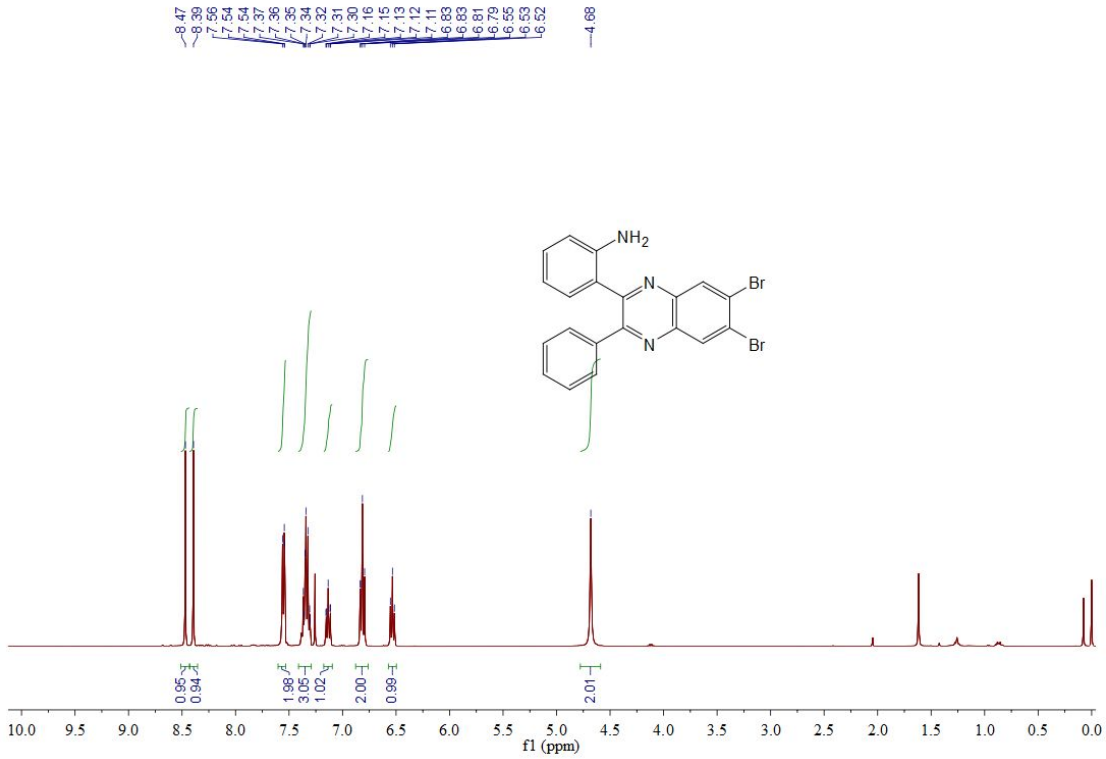
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ac**



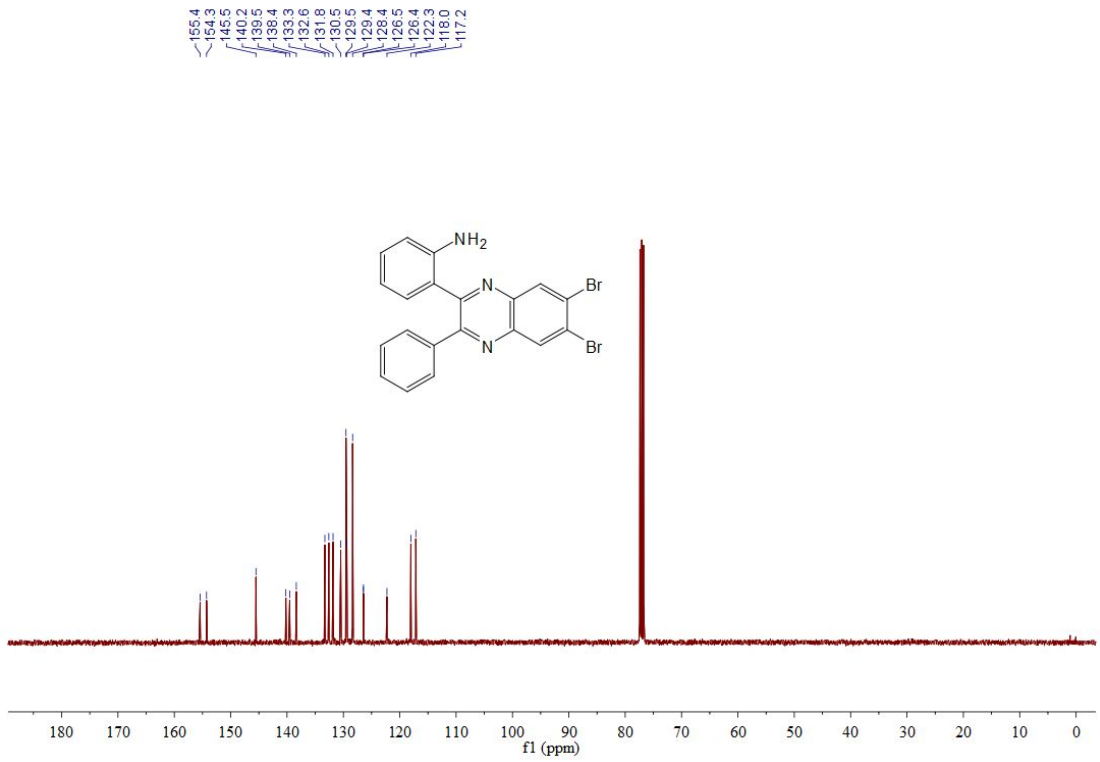
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ad**



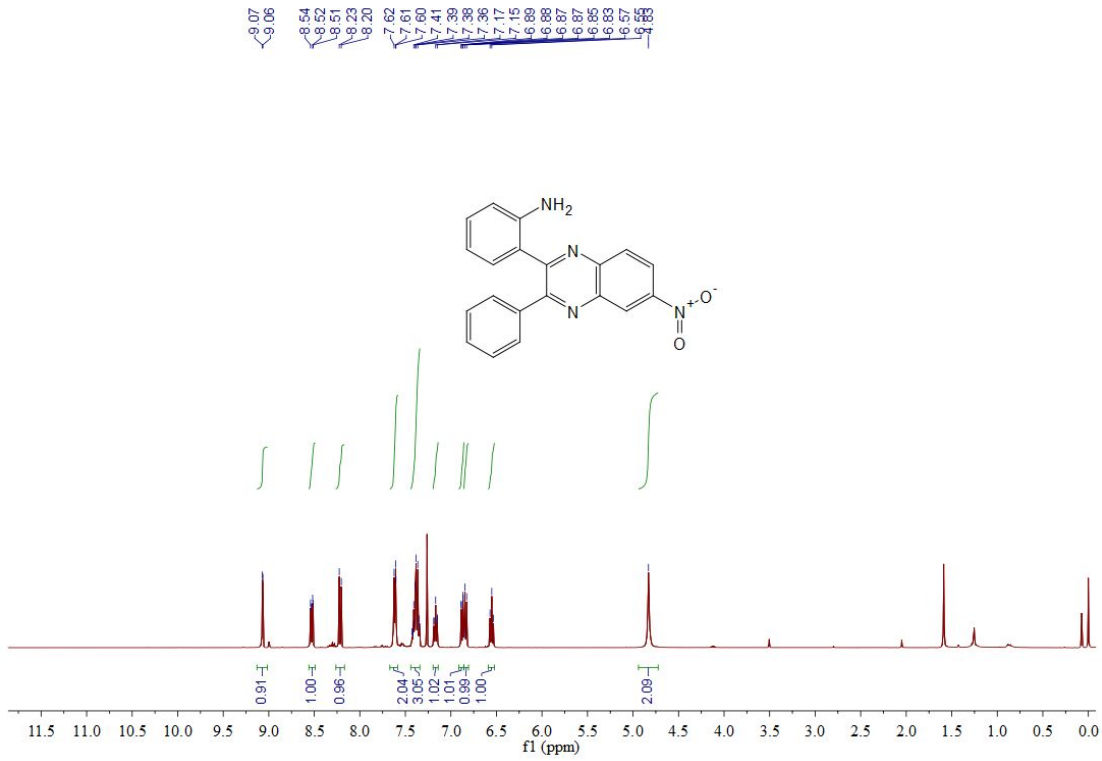
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ad**



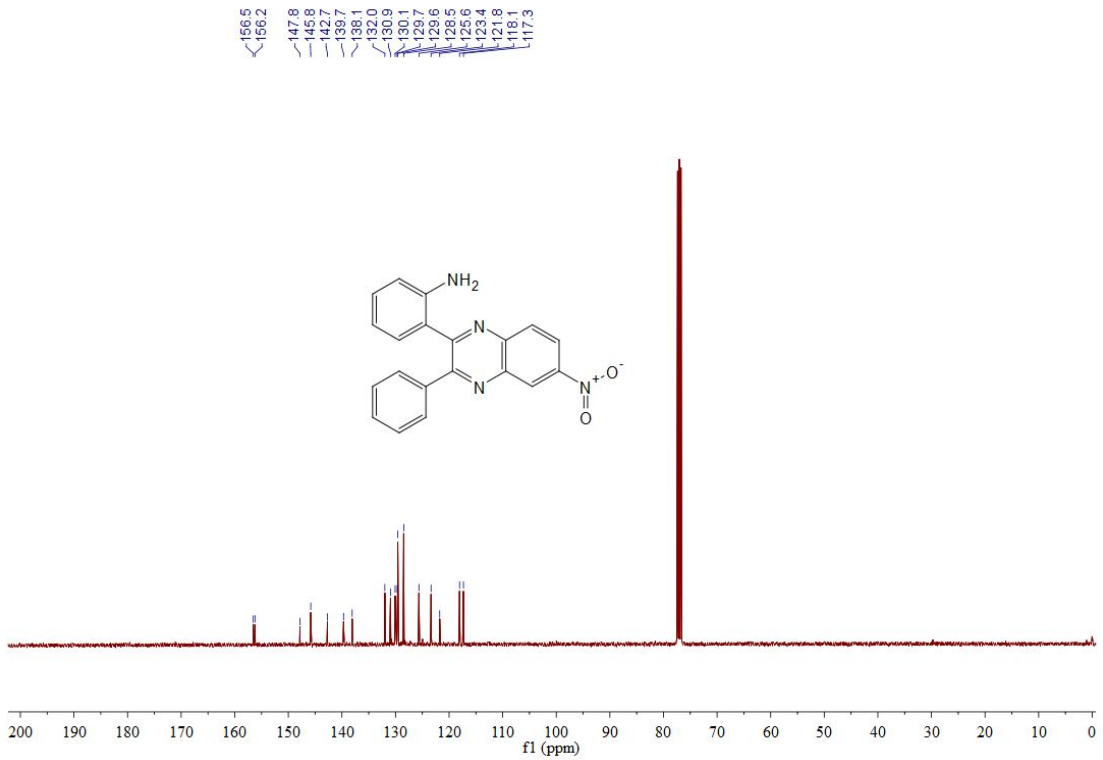
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ae**



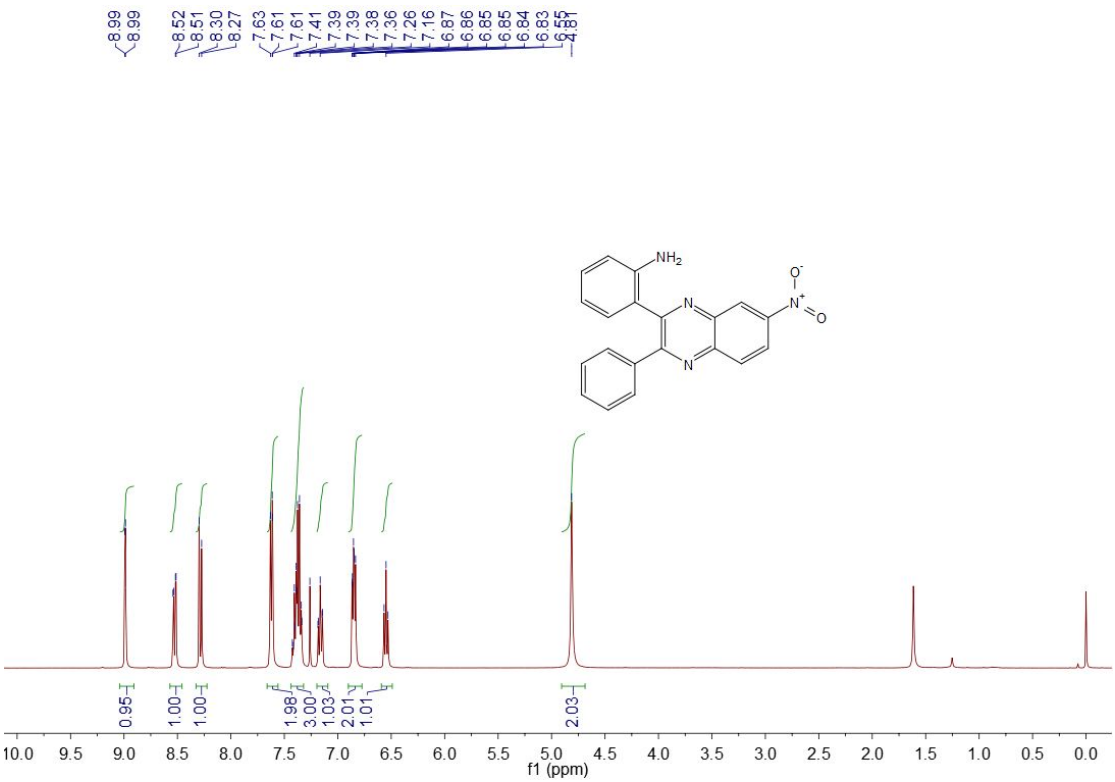
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ae**



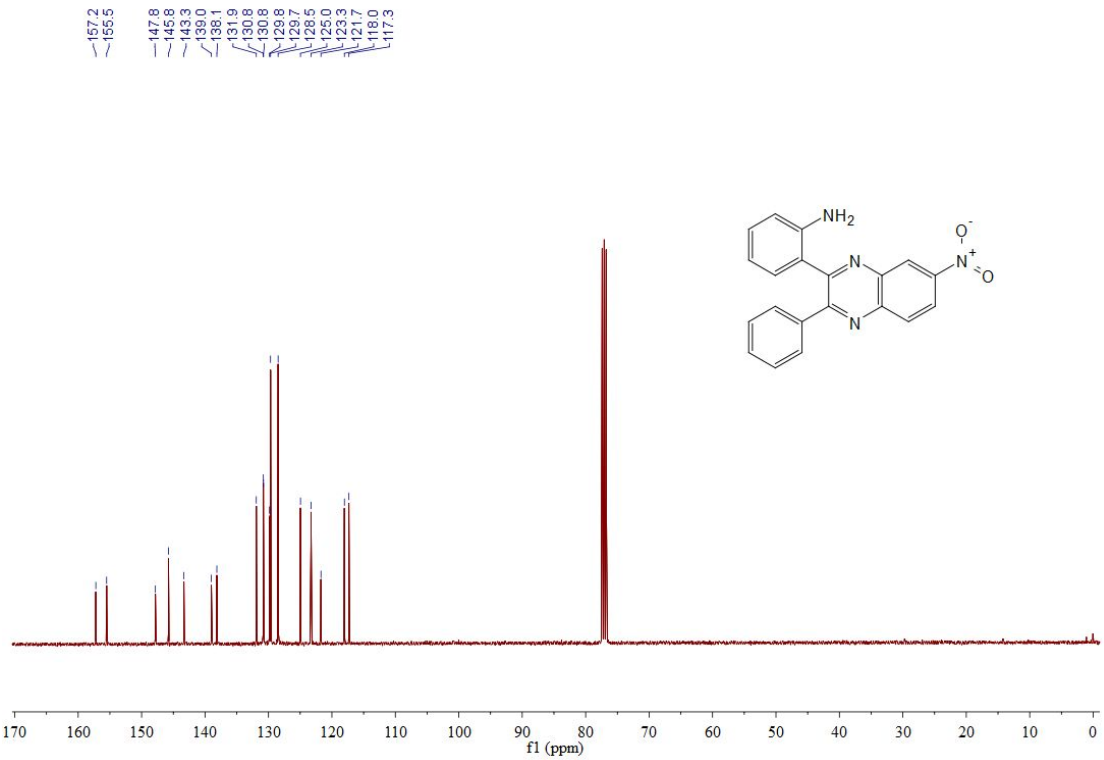
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3af**



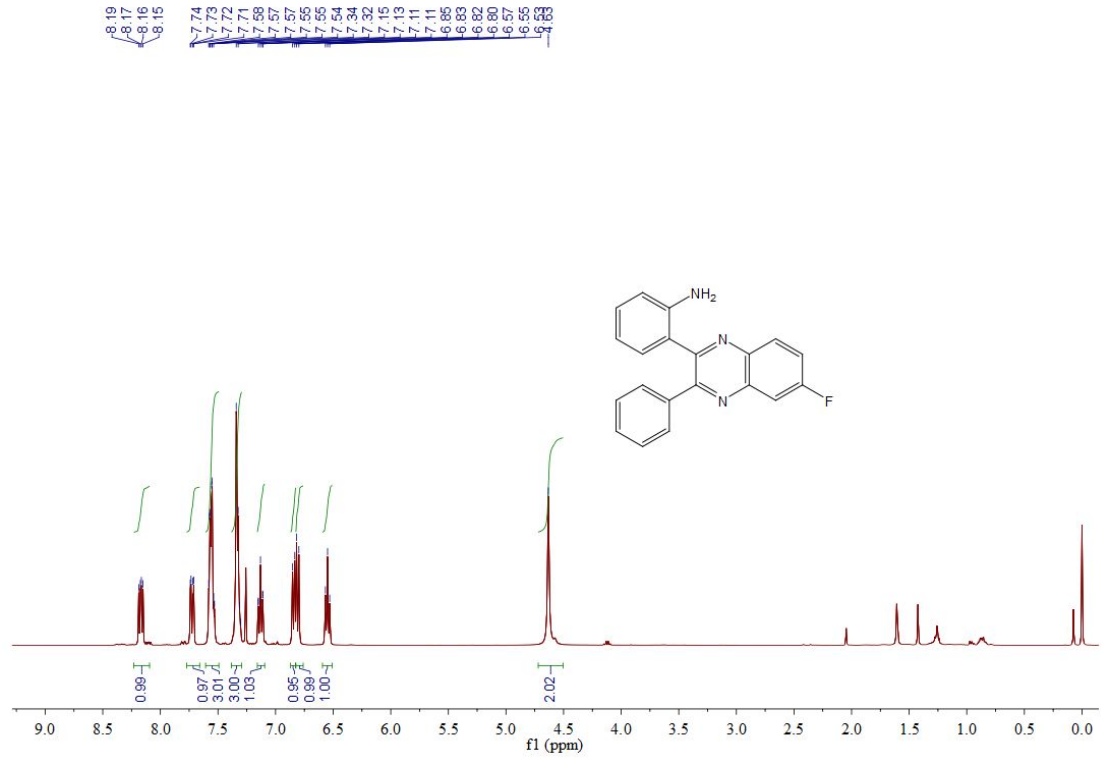
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3af**



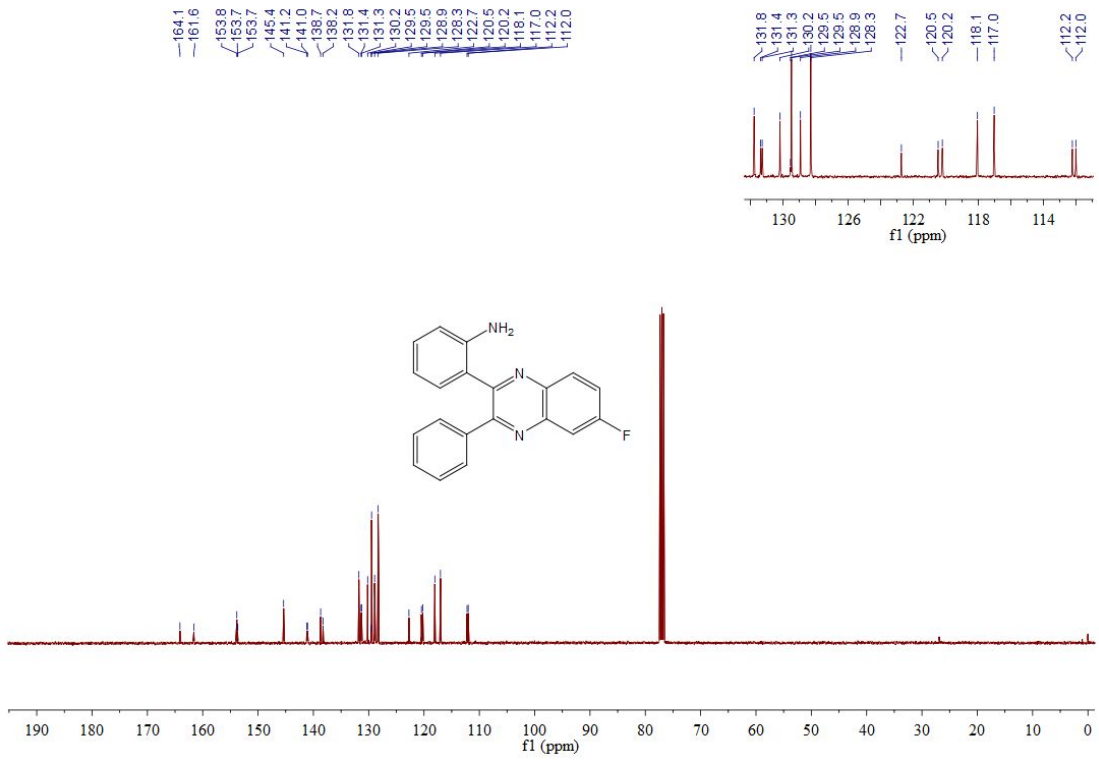
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3af'**



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3af'**

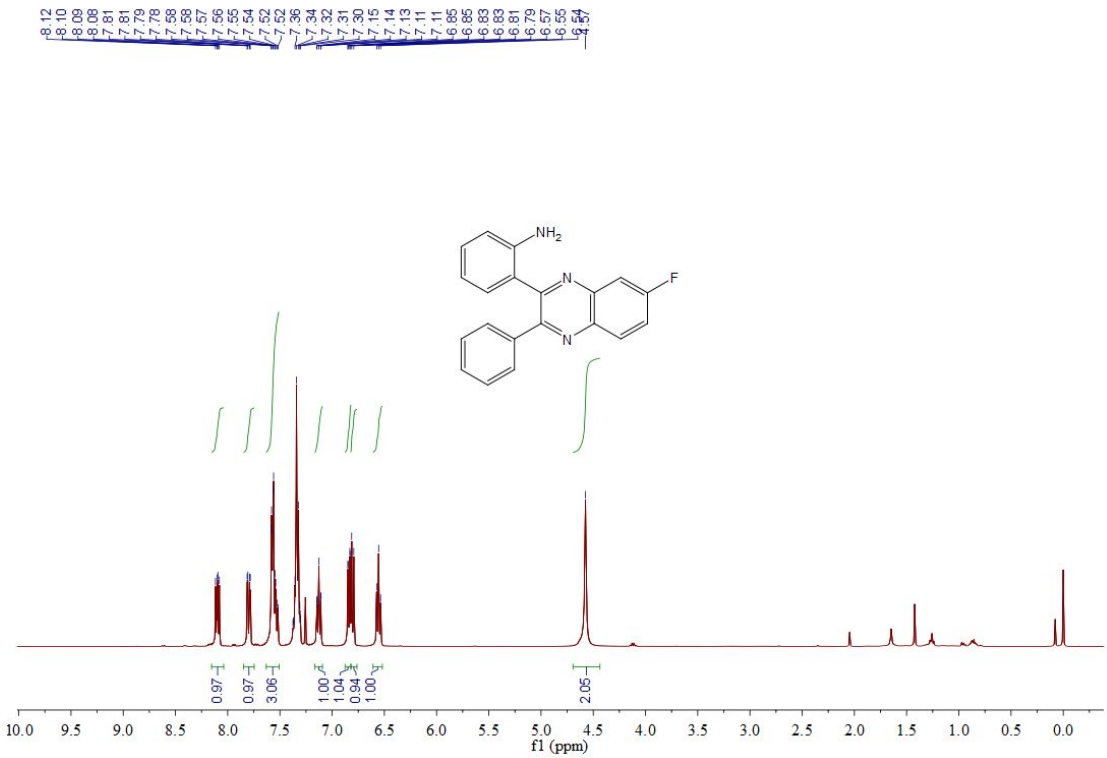


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ag**

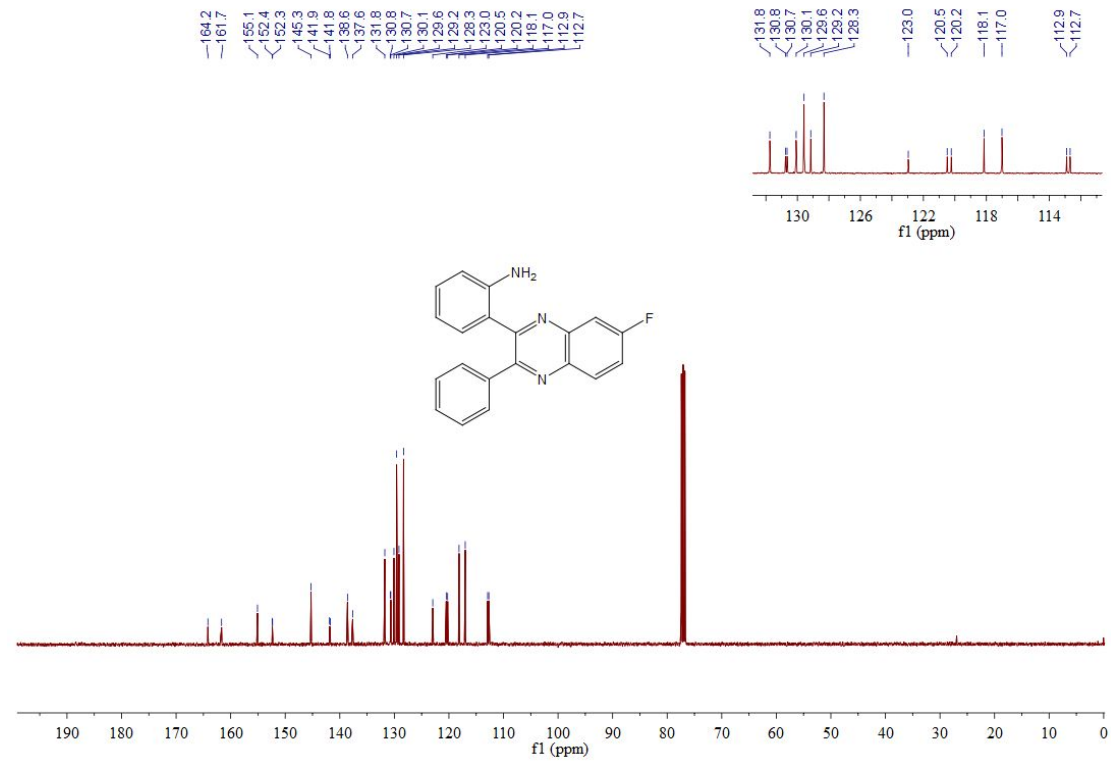


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ag**

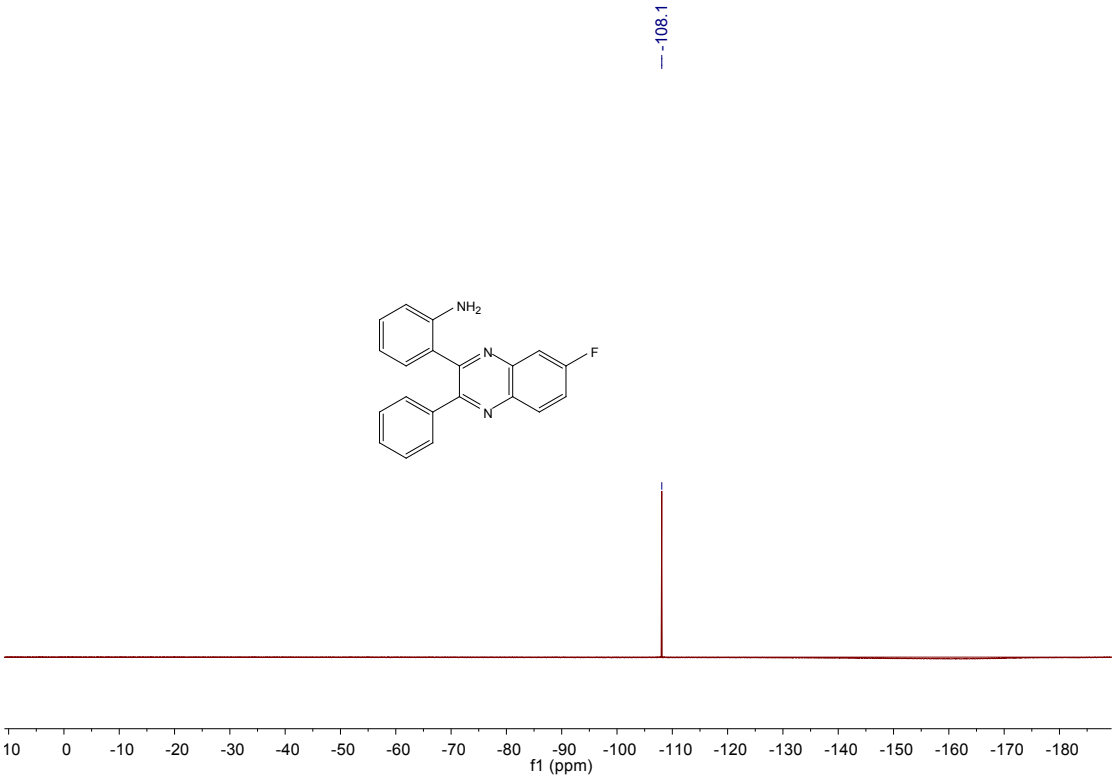
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ag**



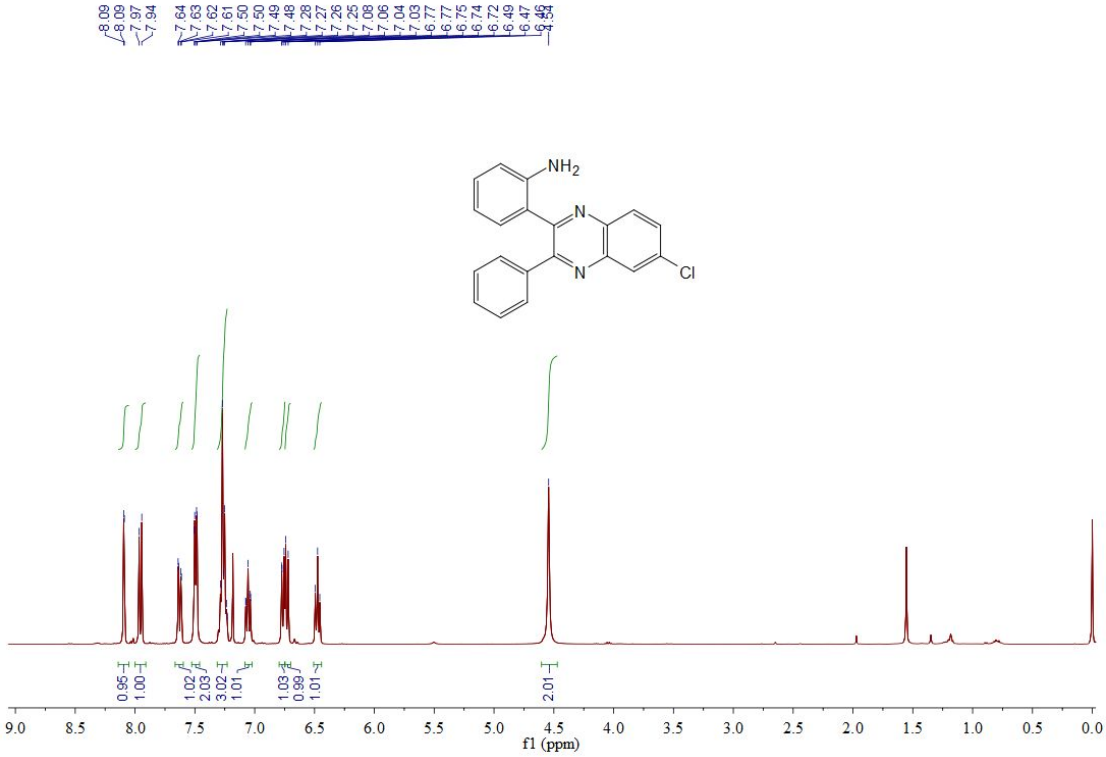
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ag'**



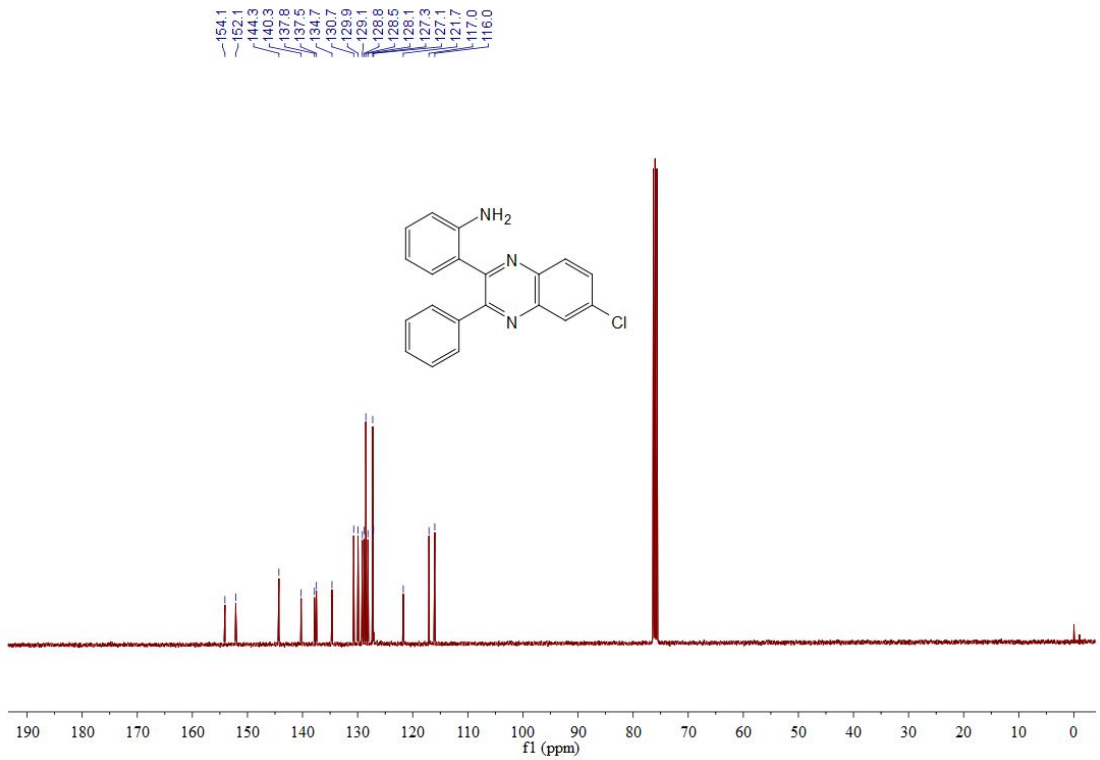
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3ag'**



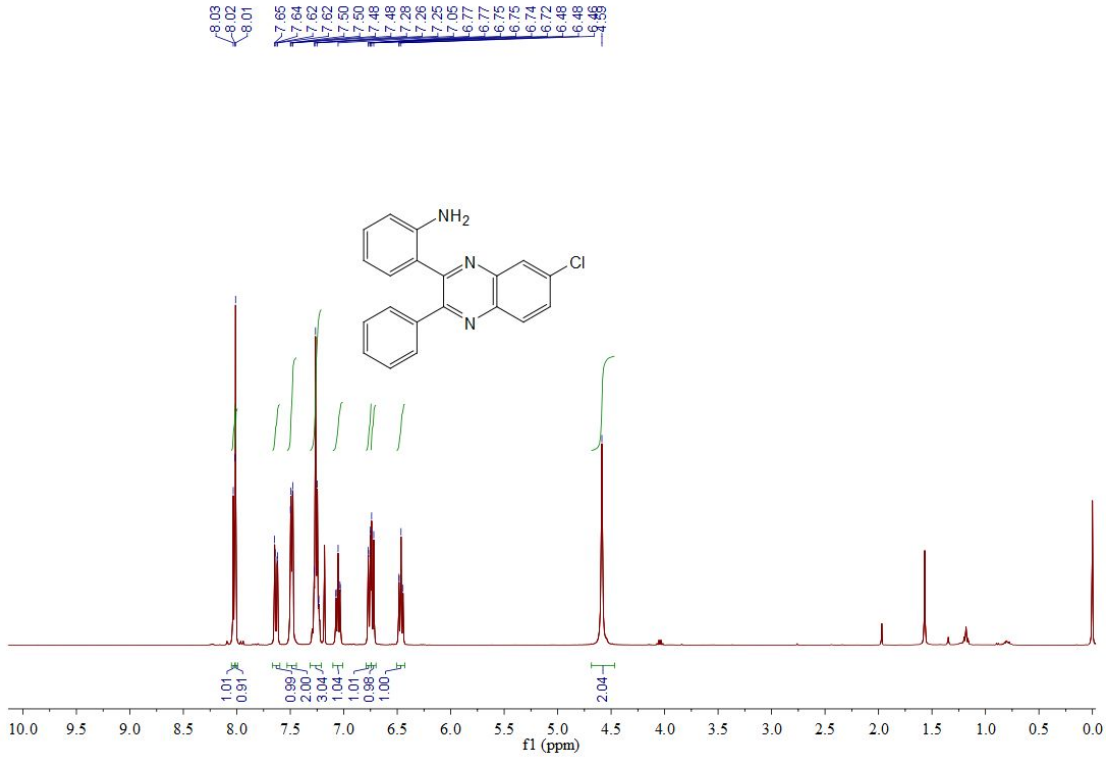
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ag'**



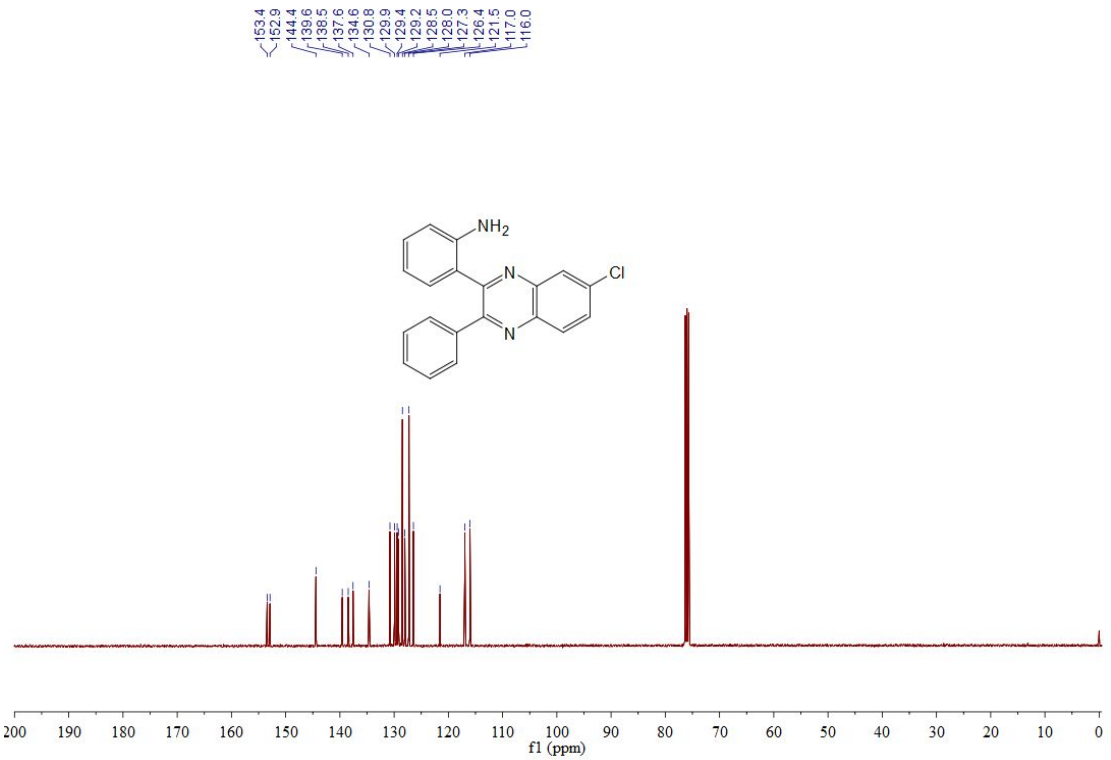
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ah**



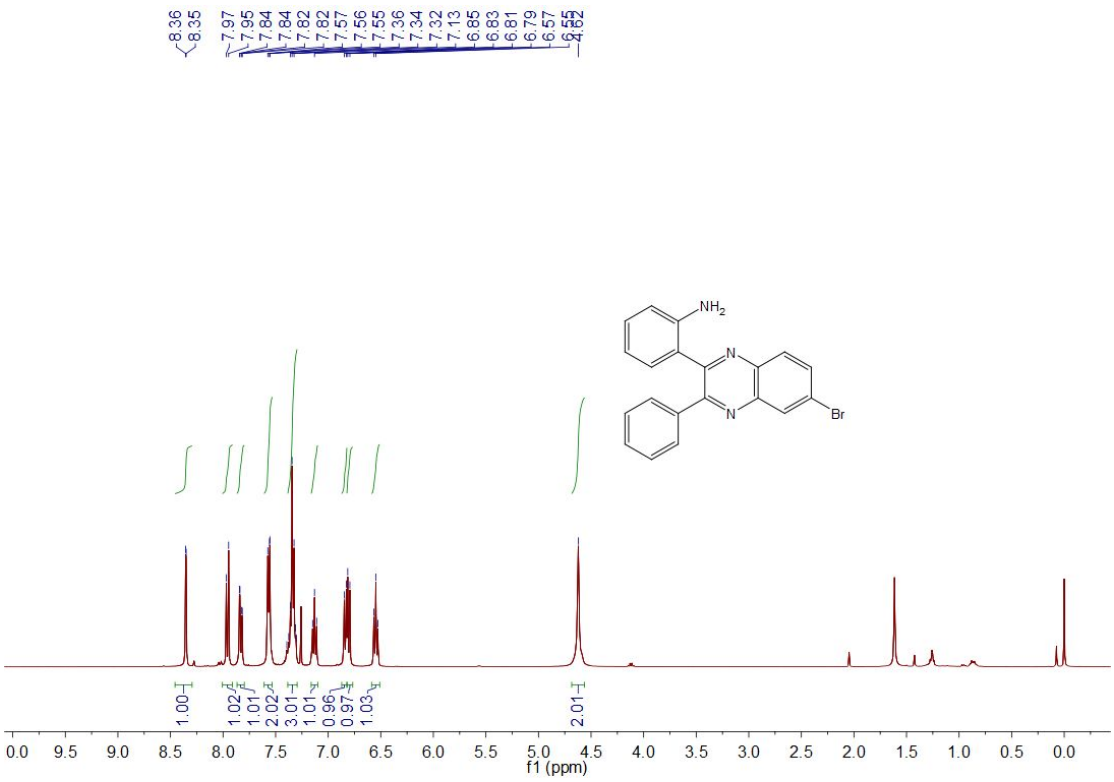
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ah**



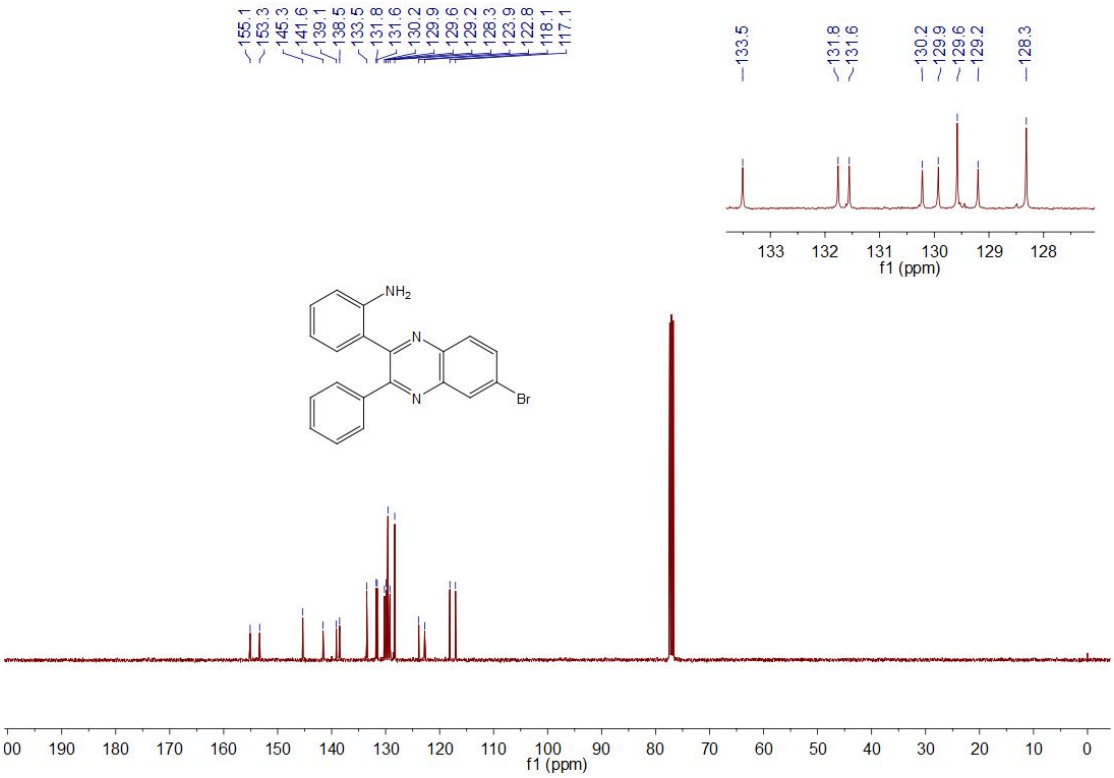
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ah'**



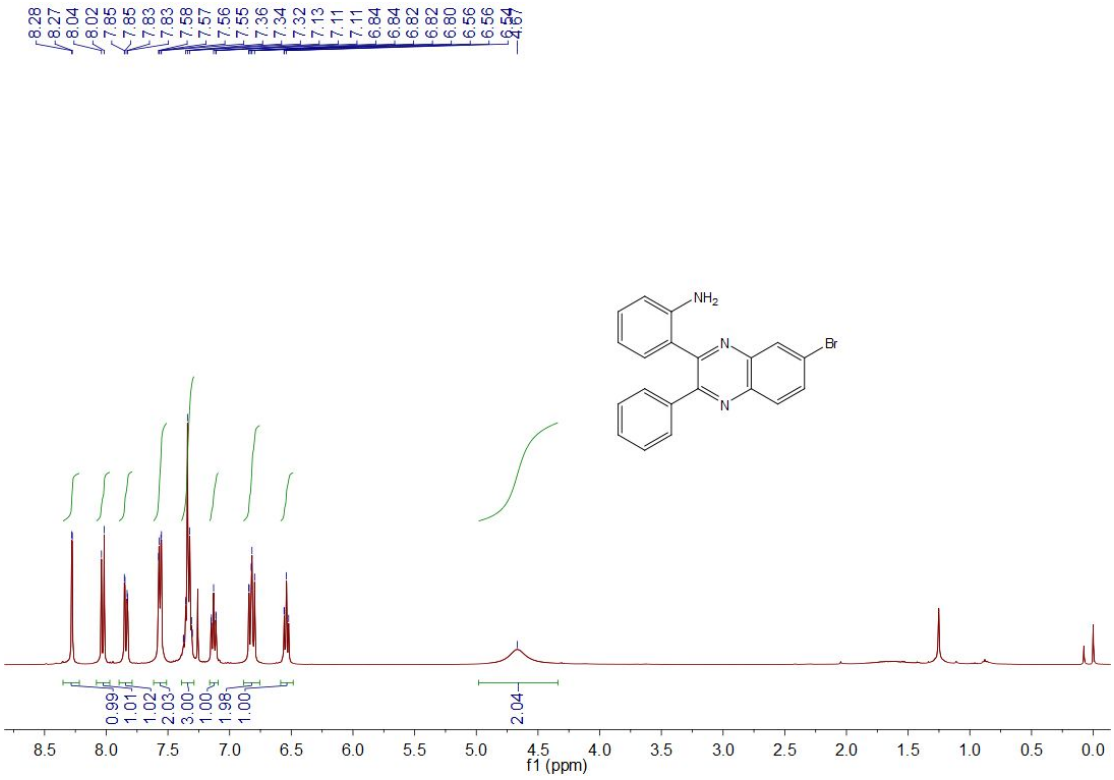
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ah'**



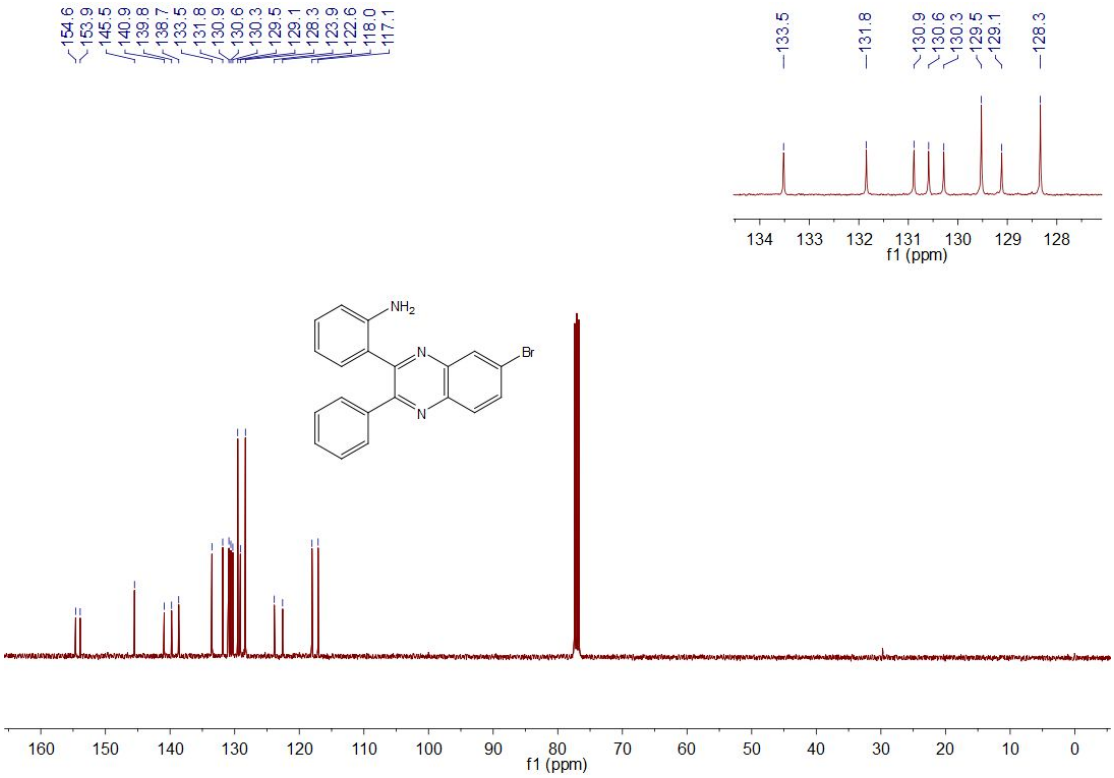
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ai**



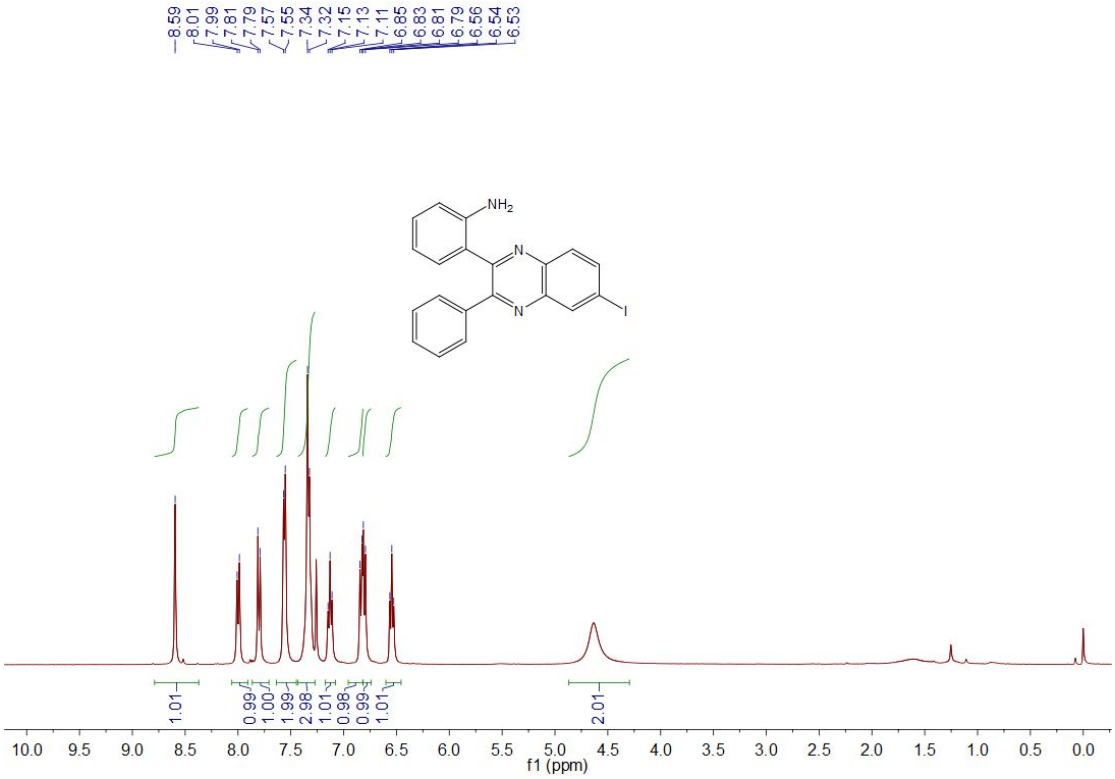
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ai**



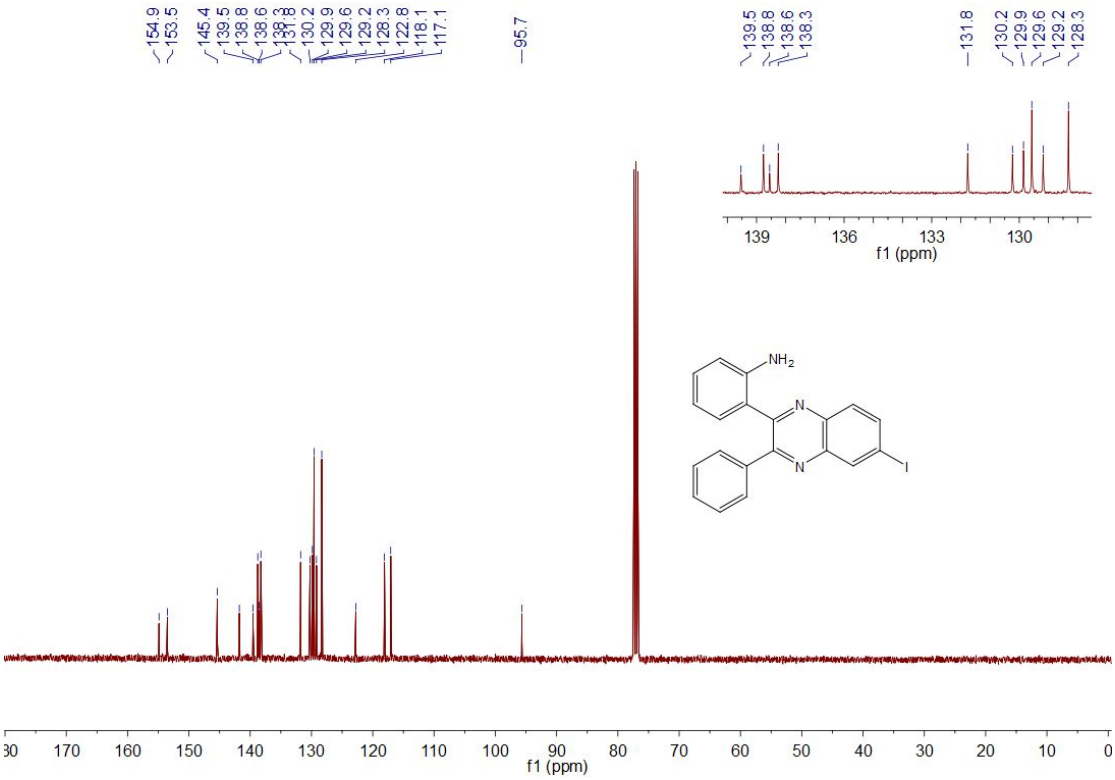
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ai'**



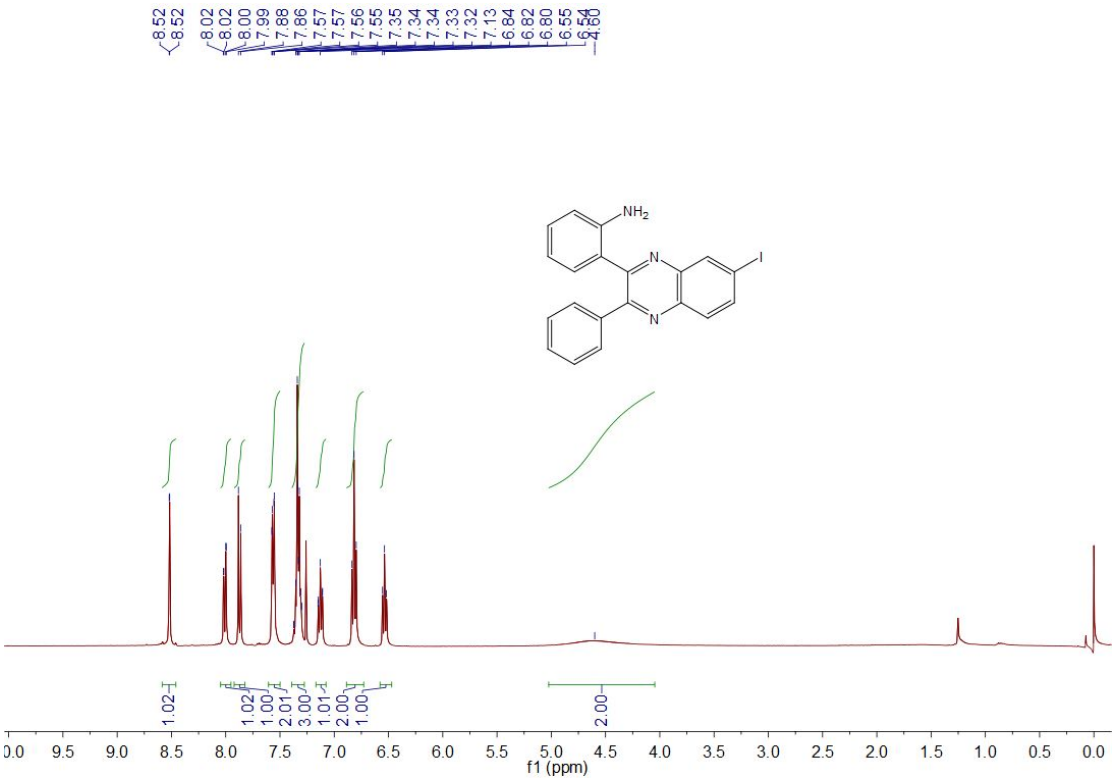
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ai'**



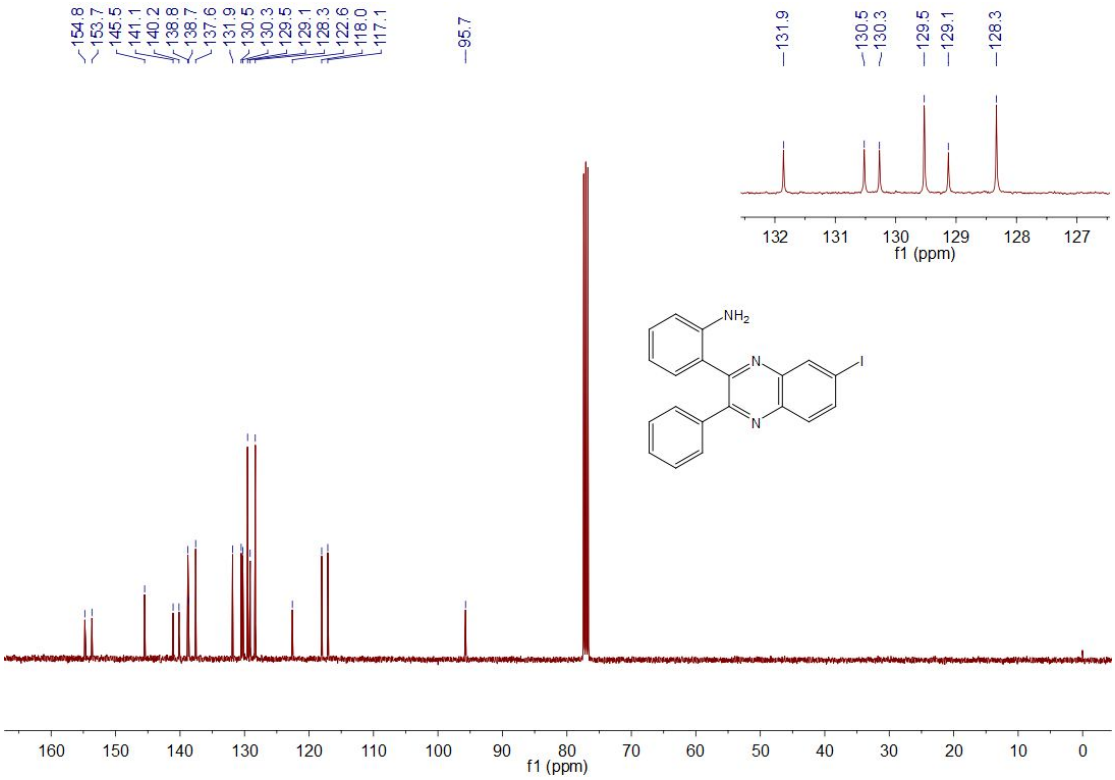
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aj**



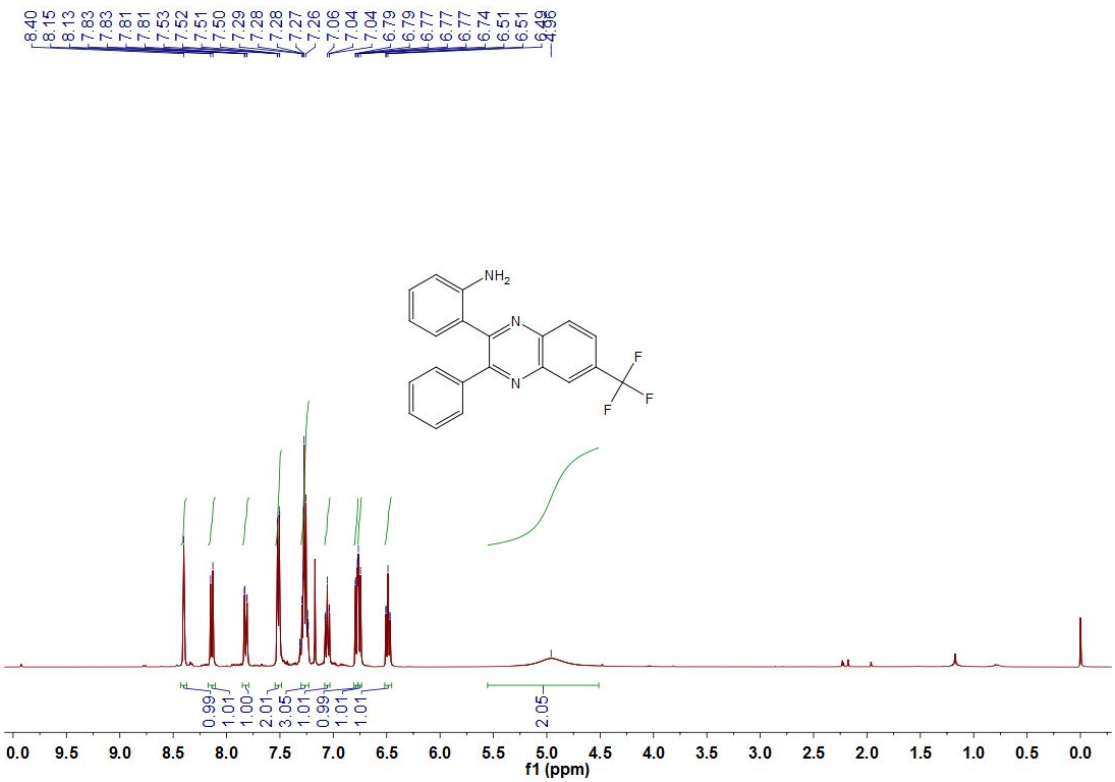
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3aj**



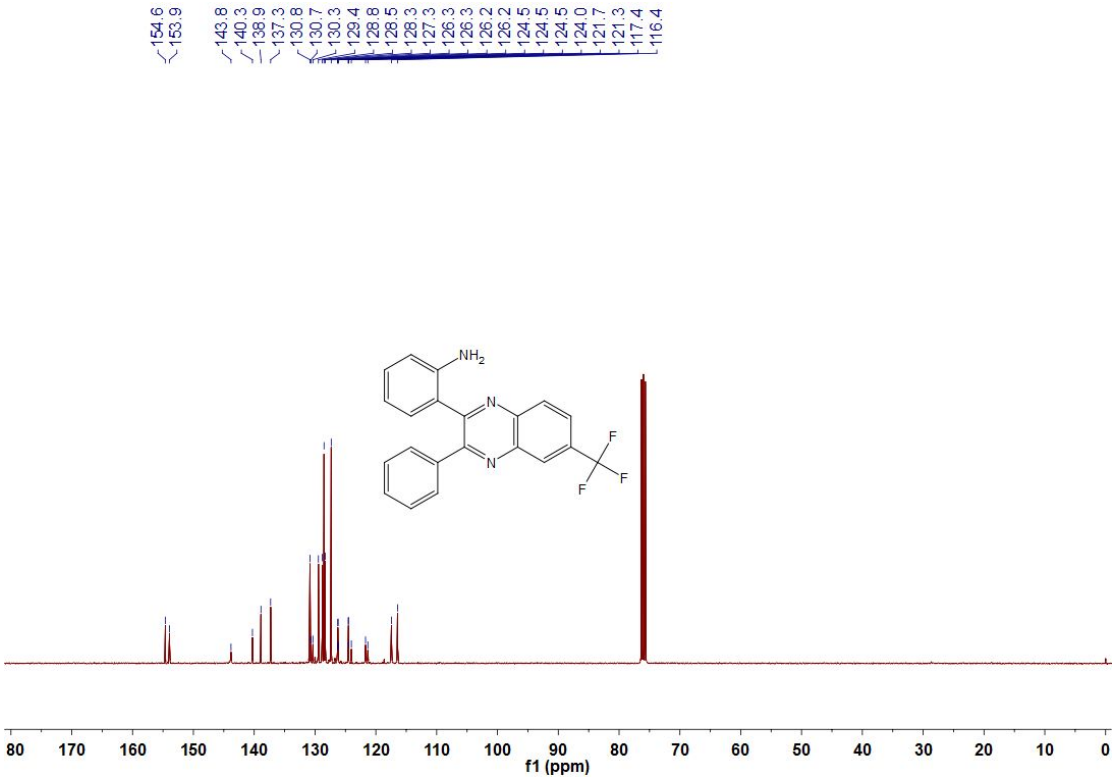
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aj'**



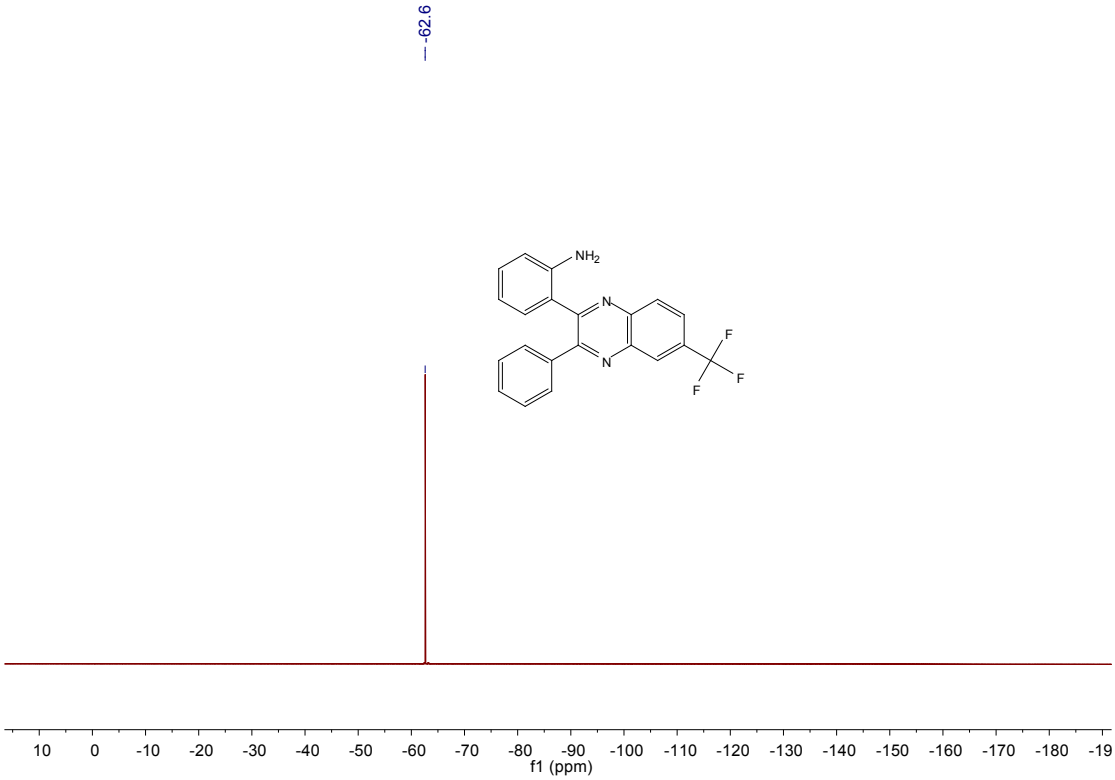
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3aj'**



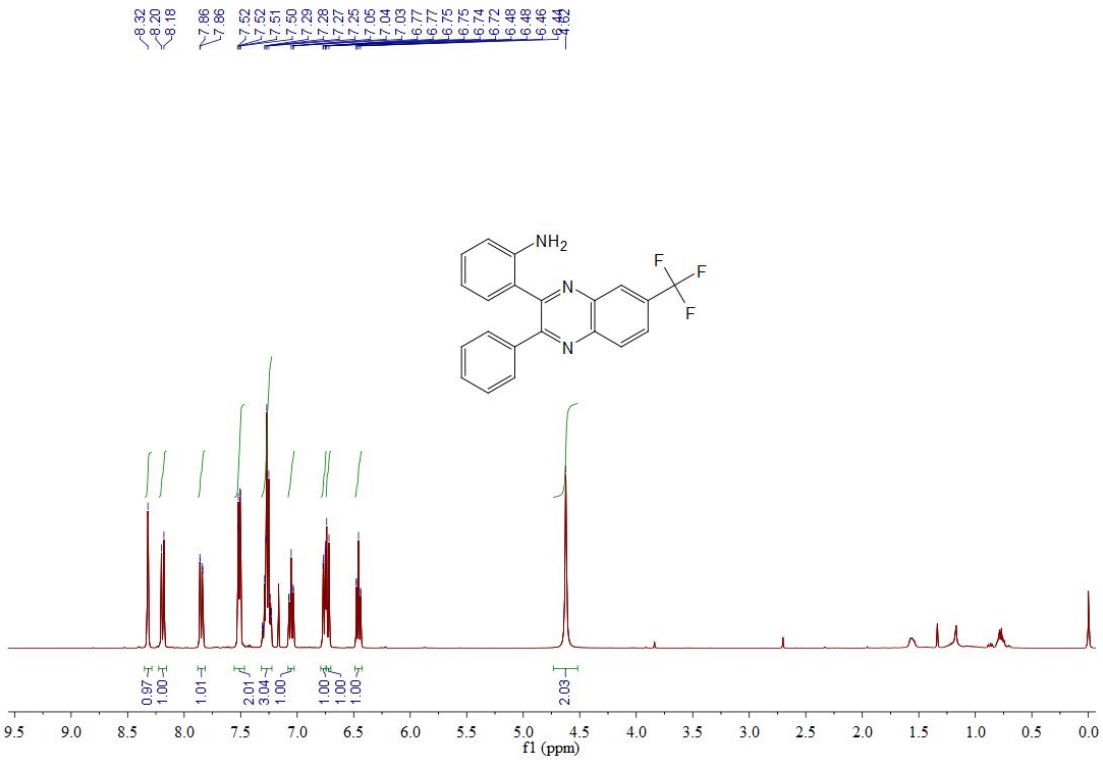
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ak**



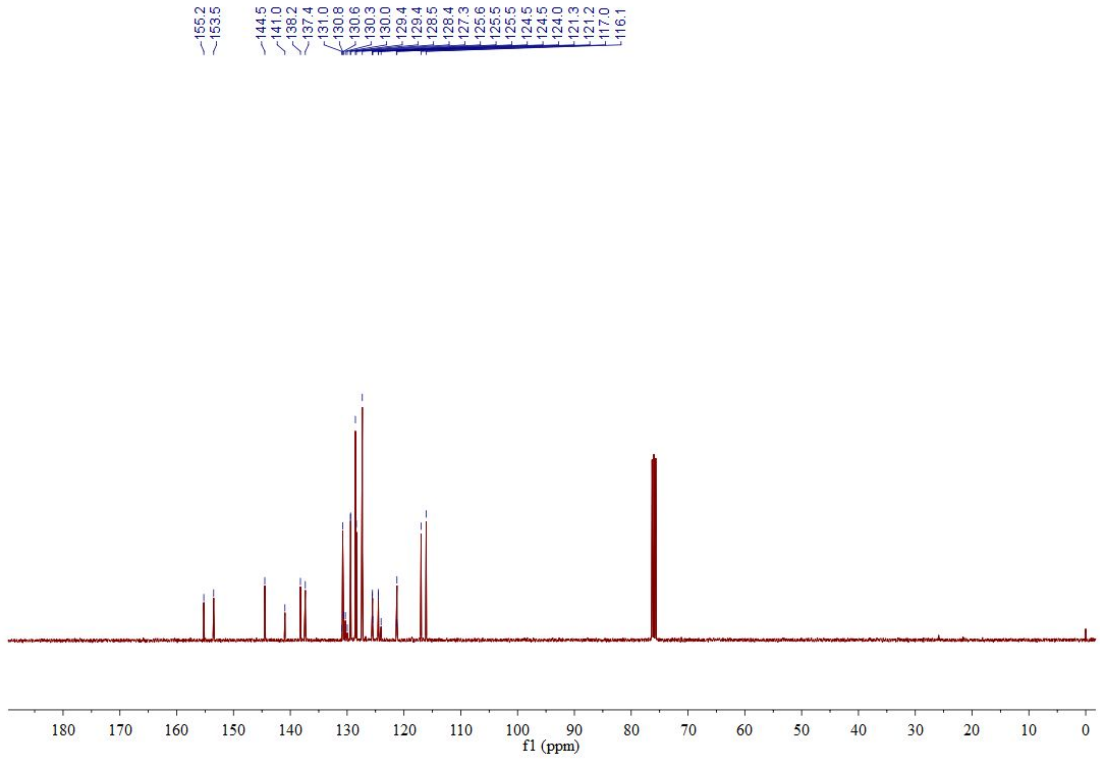
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ak**



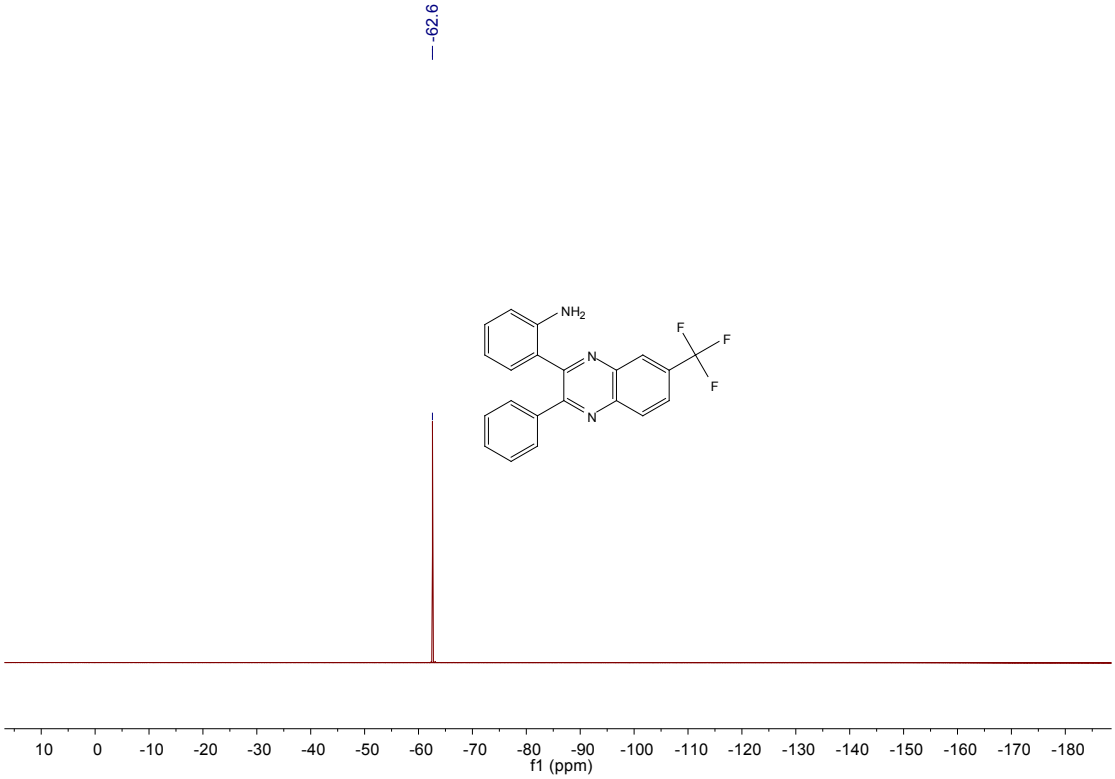
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ak**



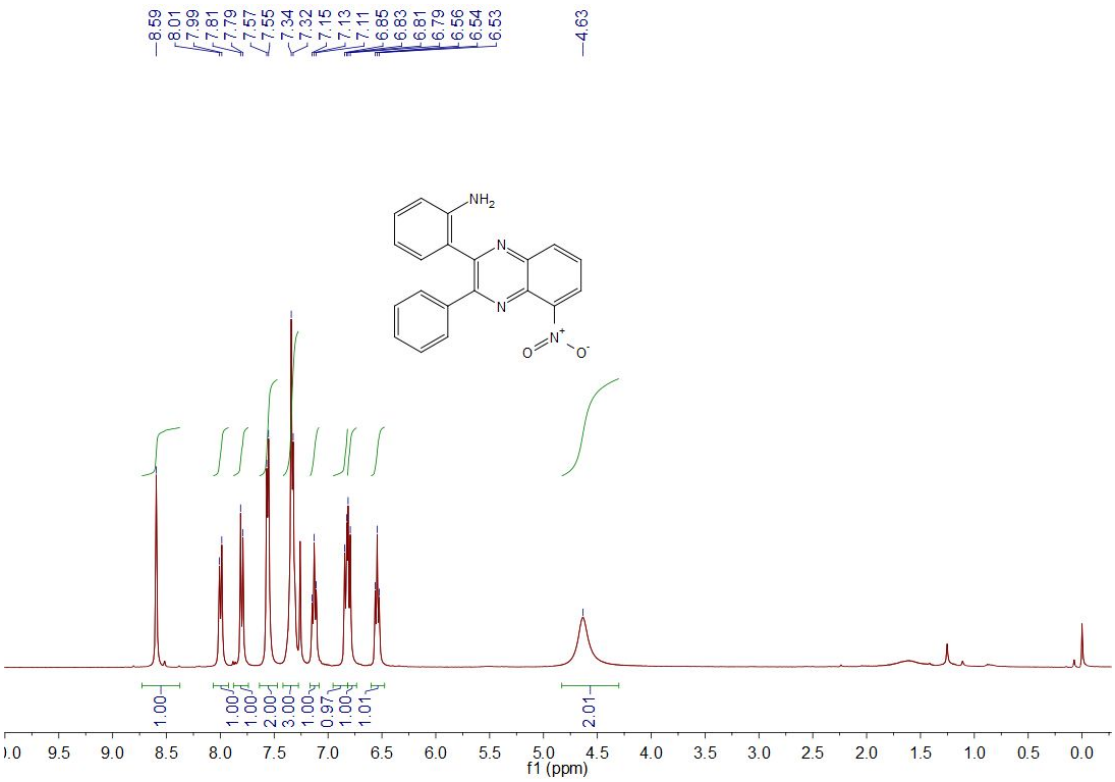
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ak'**



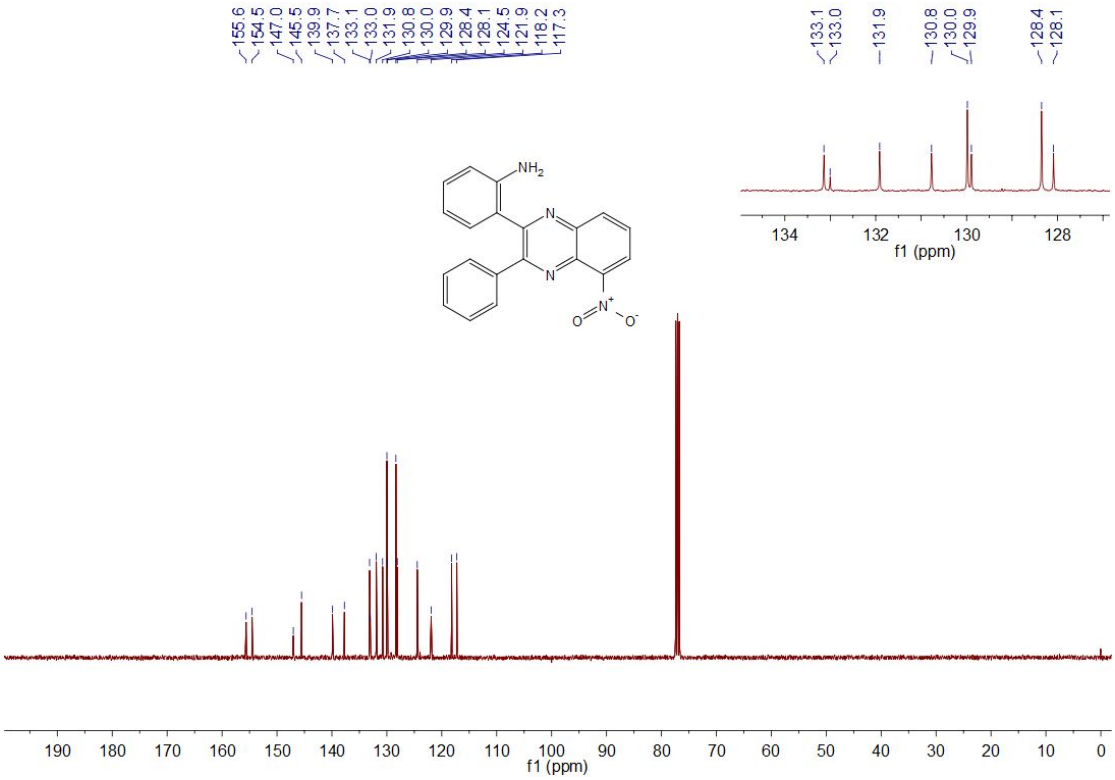
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **3ak'**



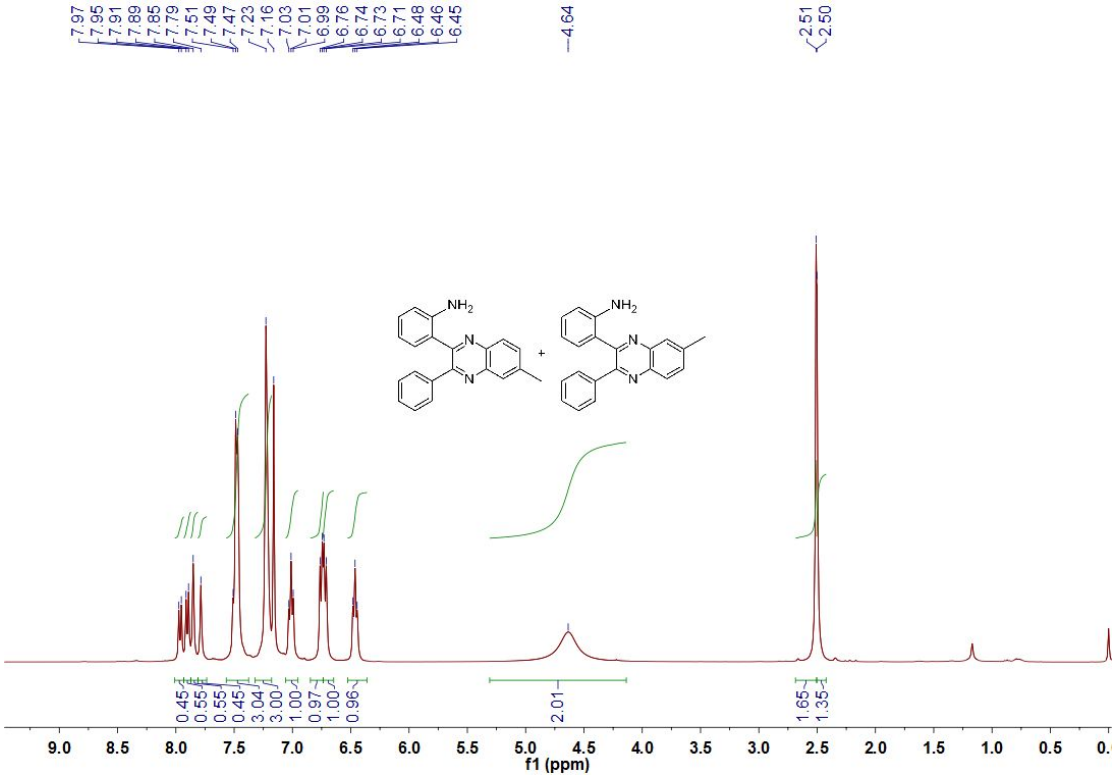
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ak'**



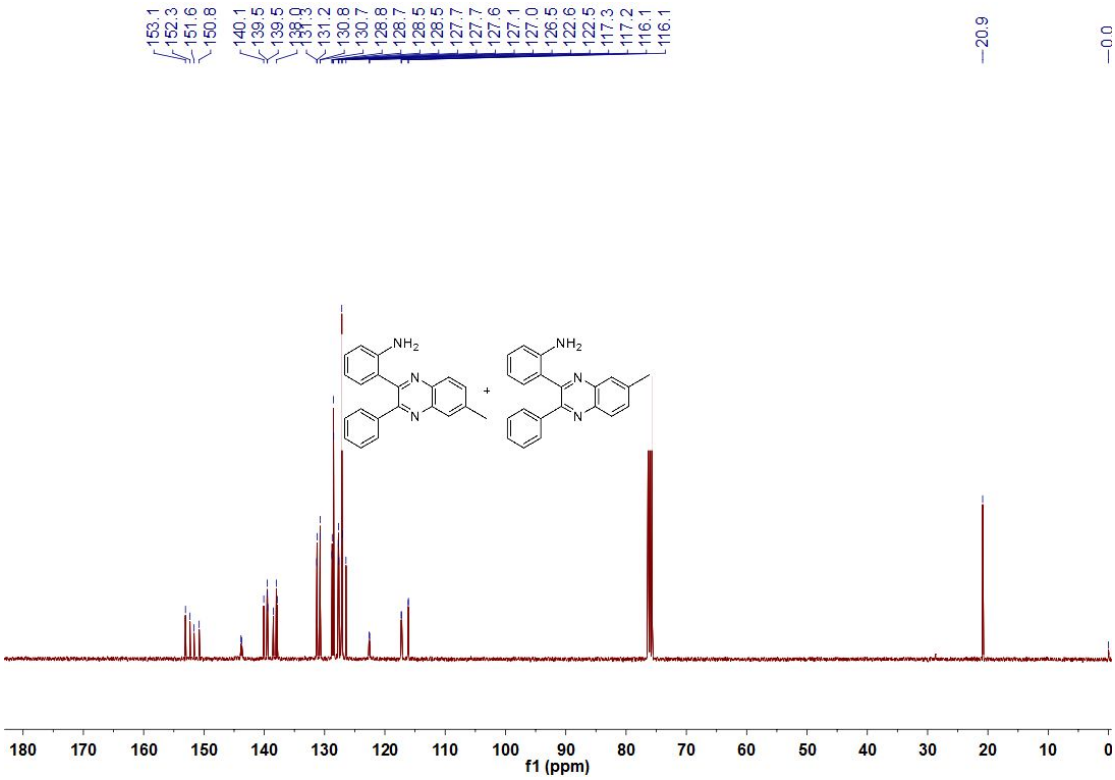
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3al'**



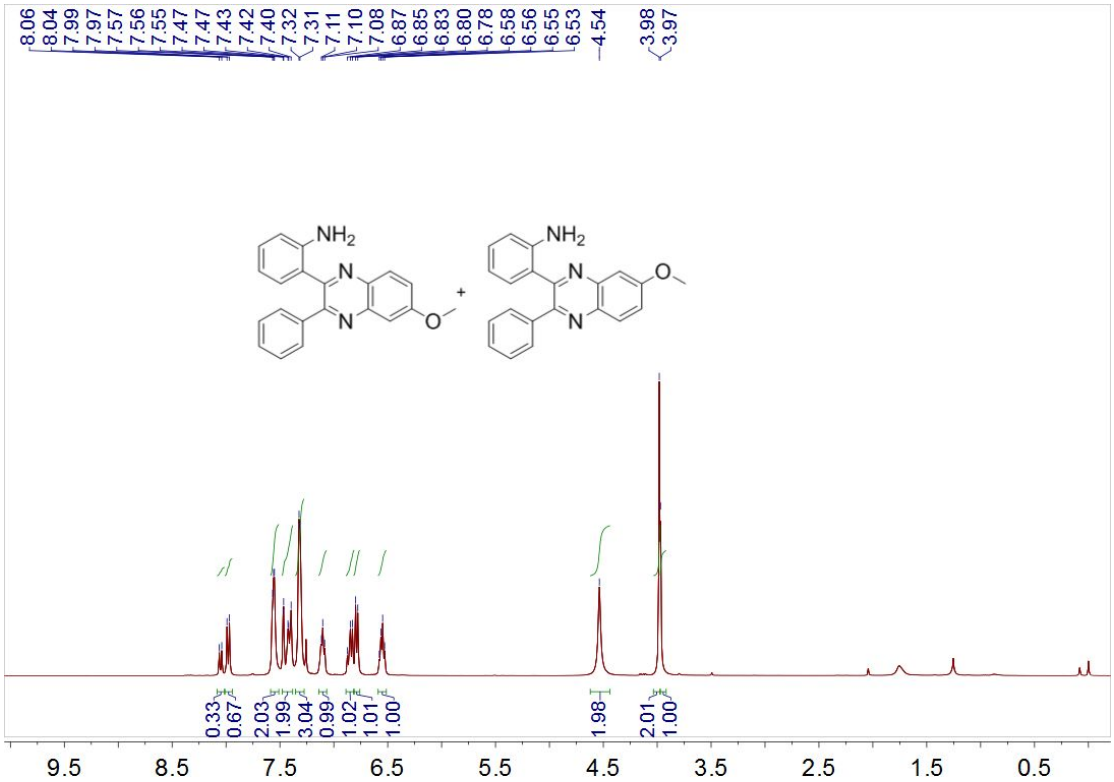
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3al'**



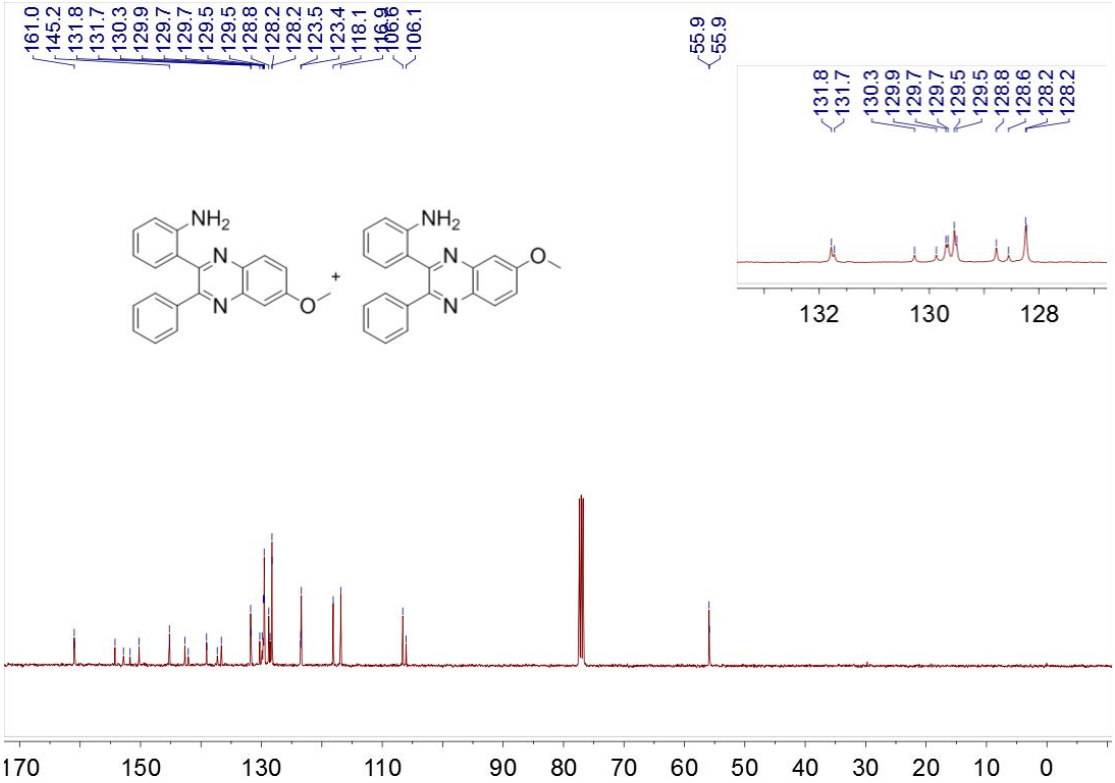
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3am**+**3am'**



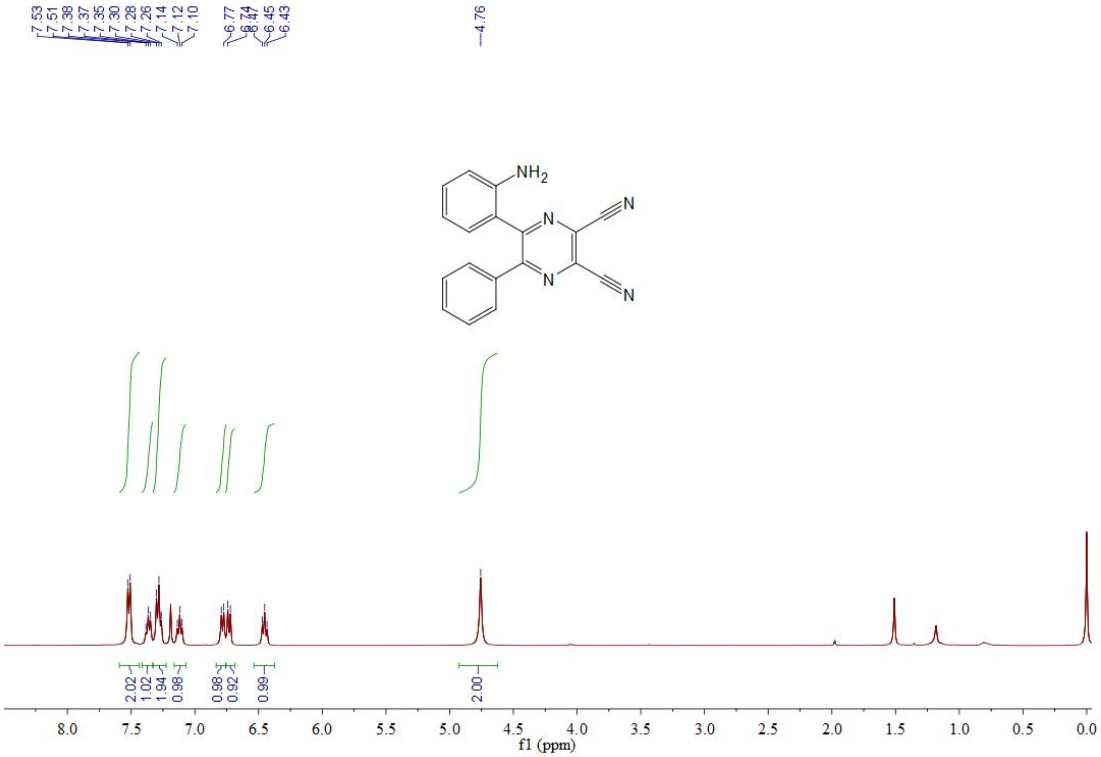
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3am**+**3am'**



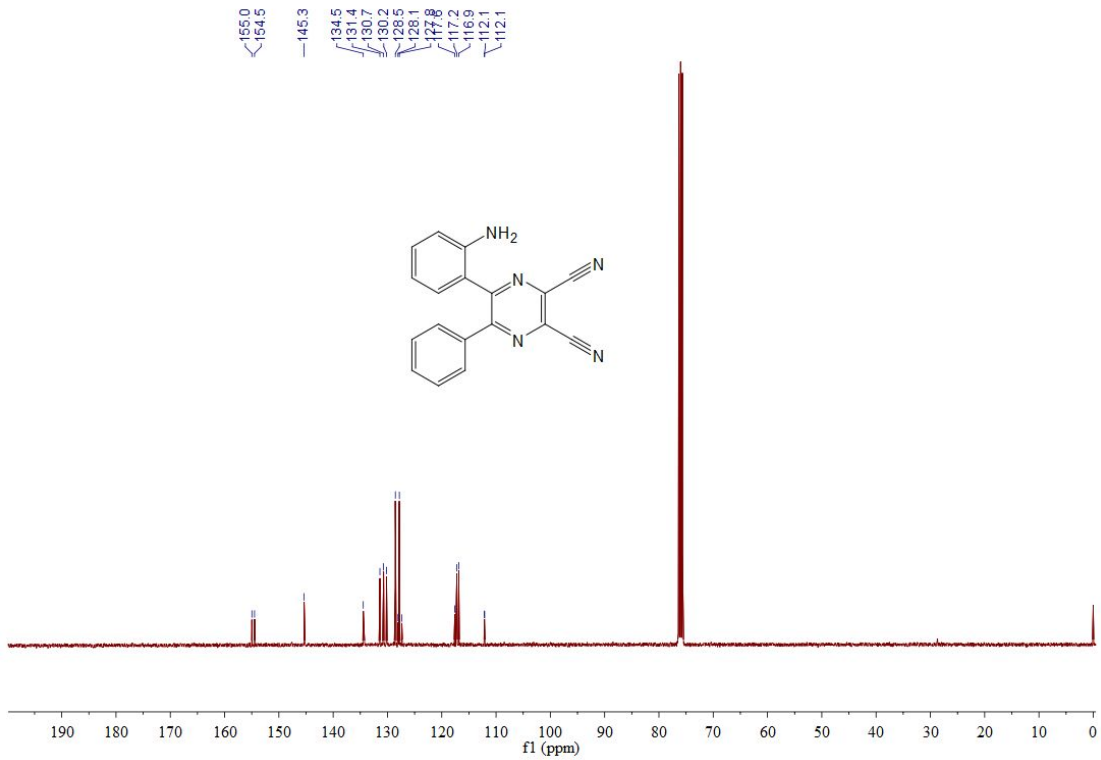
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3an**+**3an'**



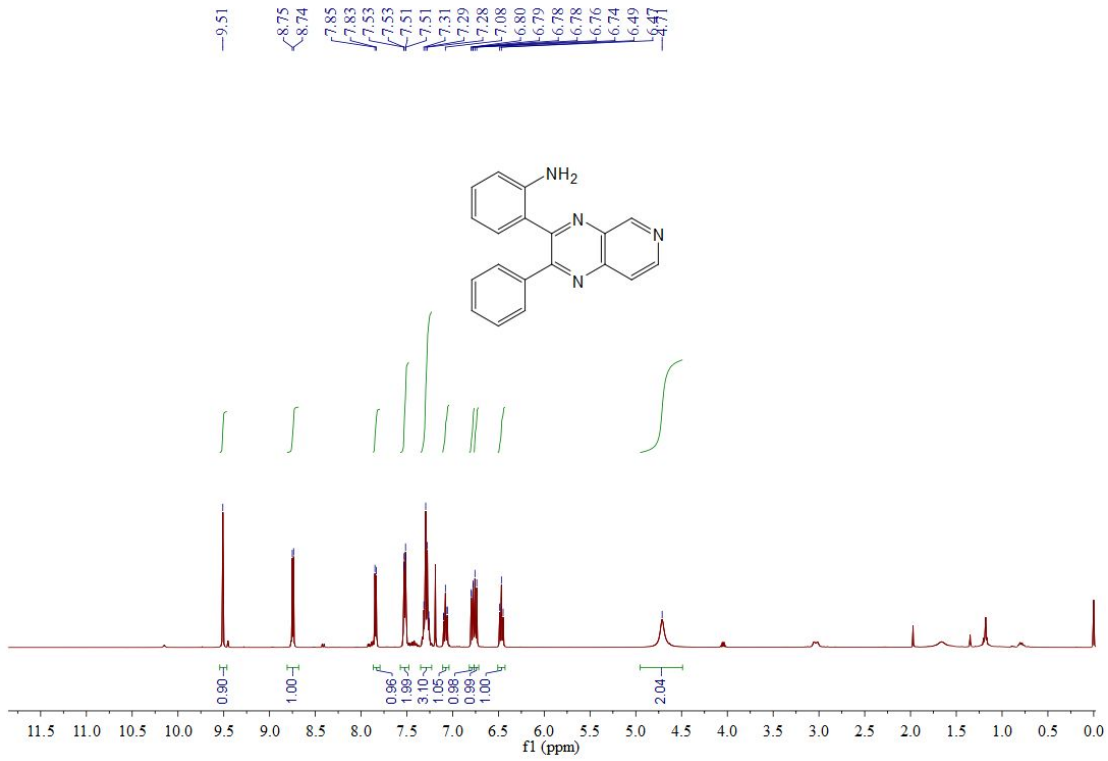
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3an+3an'**



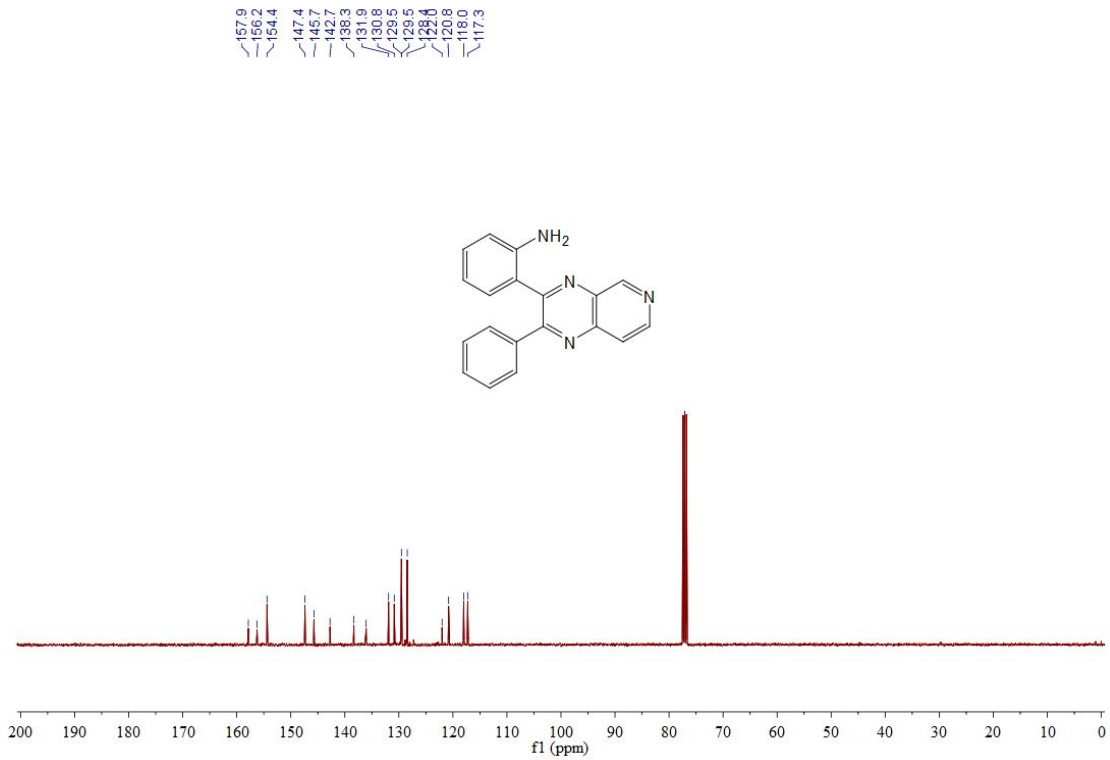
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ao**



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ao**

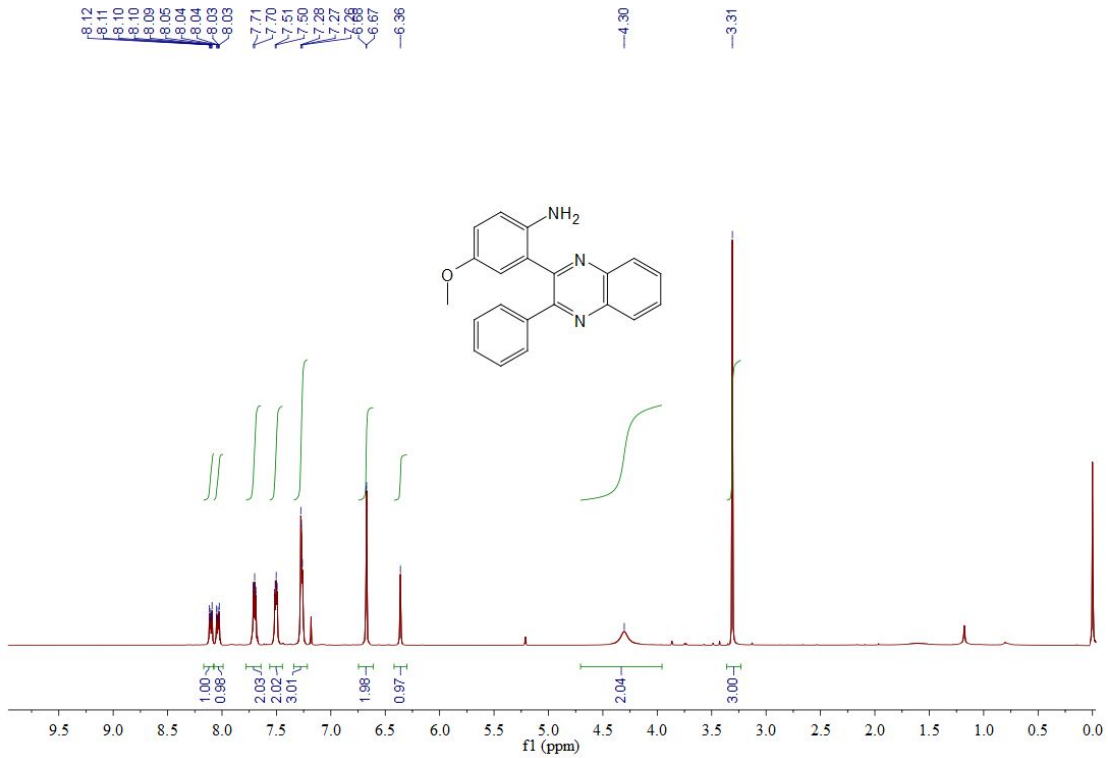


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ap**

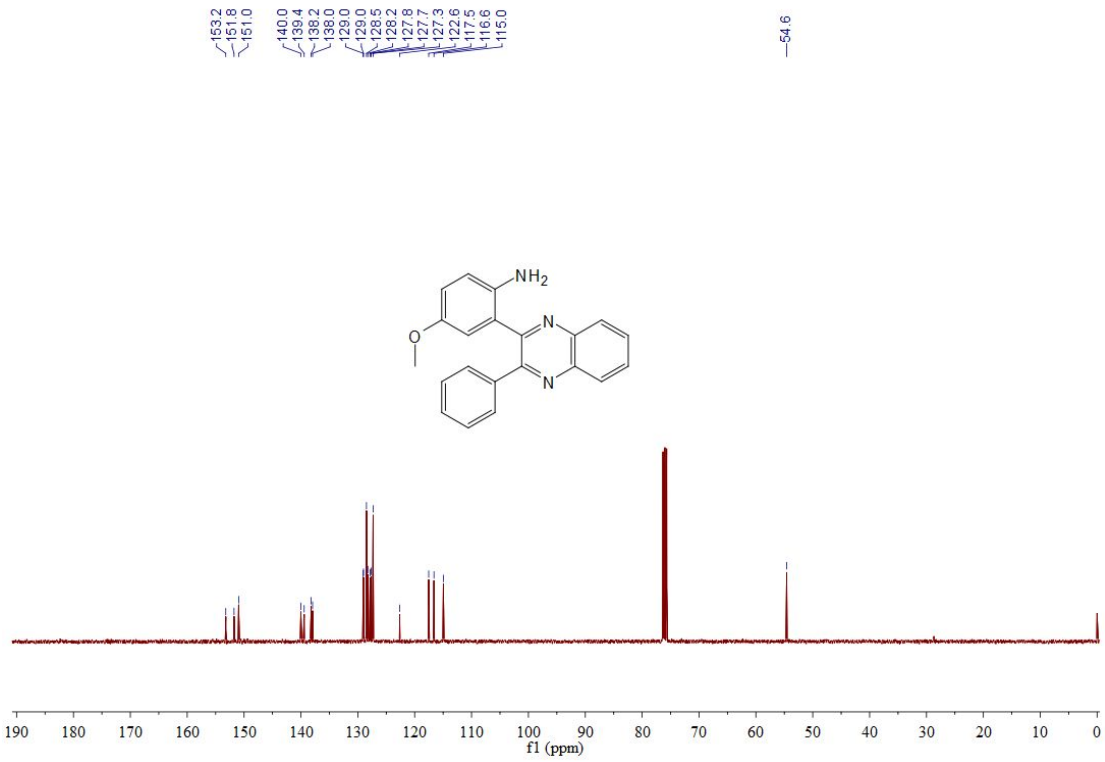


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **3ap**

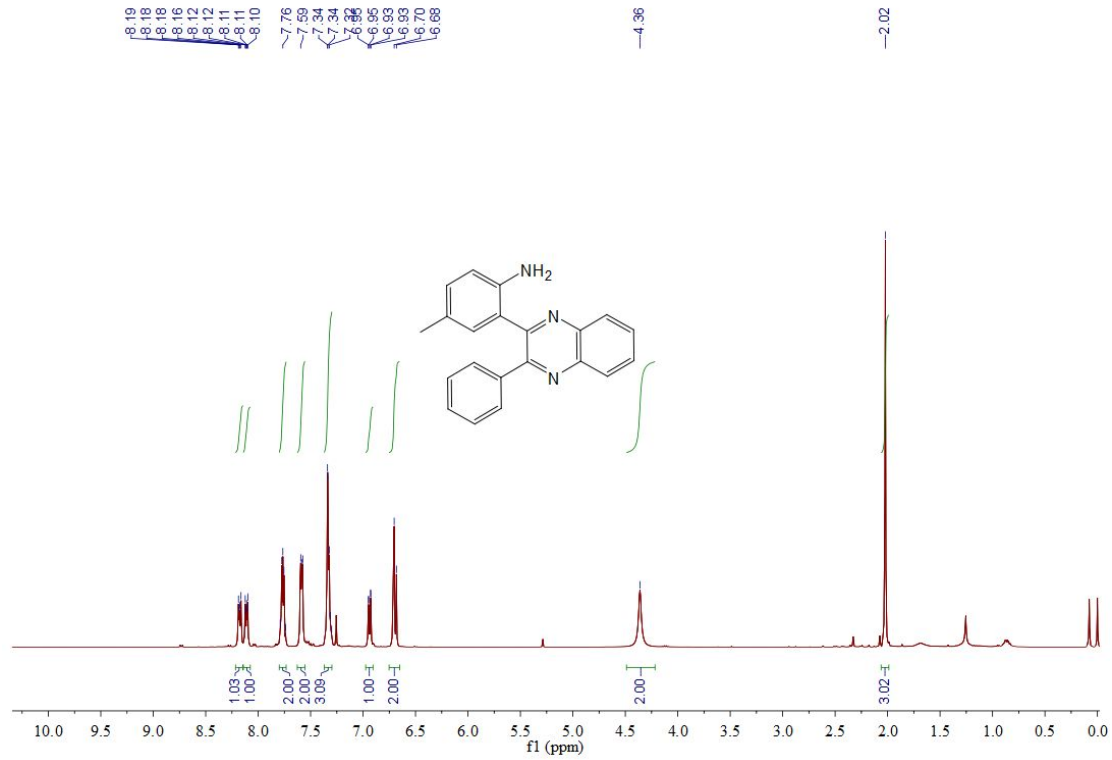
7. ^{1}H, ^{13}C and ^{19}F NMR spectra of 4ba-4va.



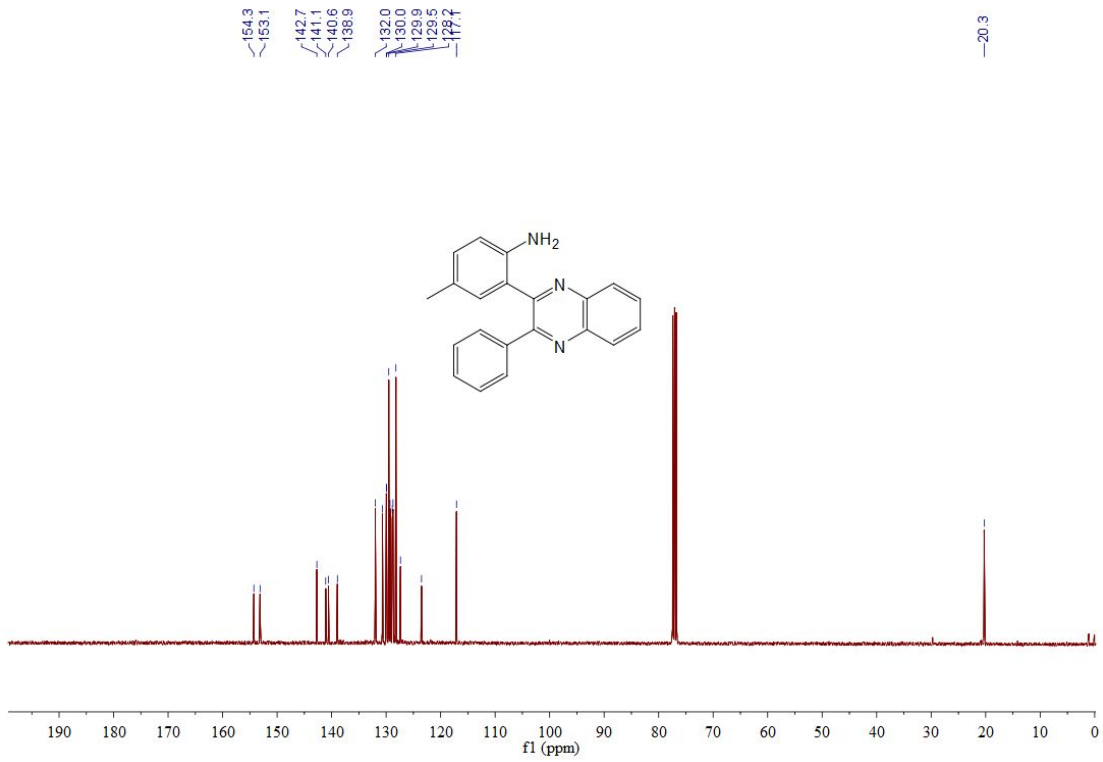
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ba**



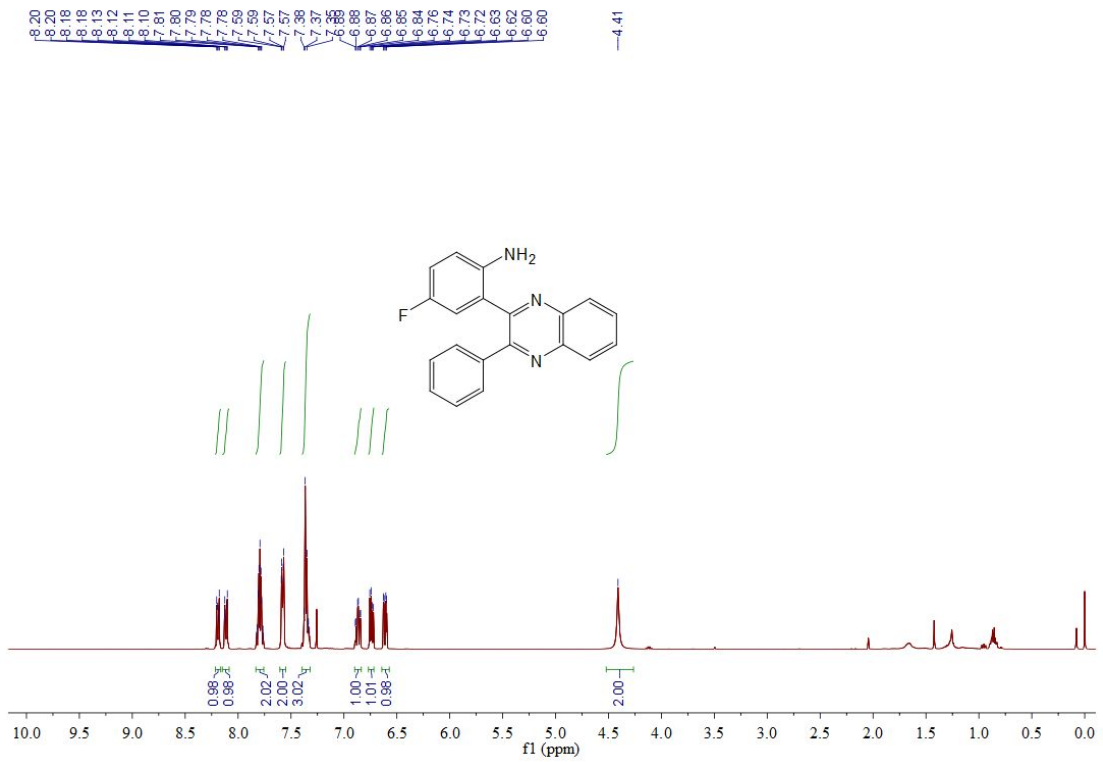
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4ba**



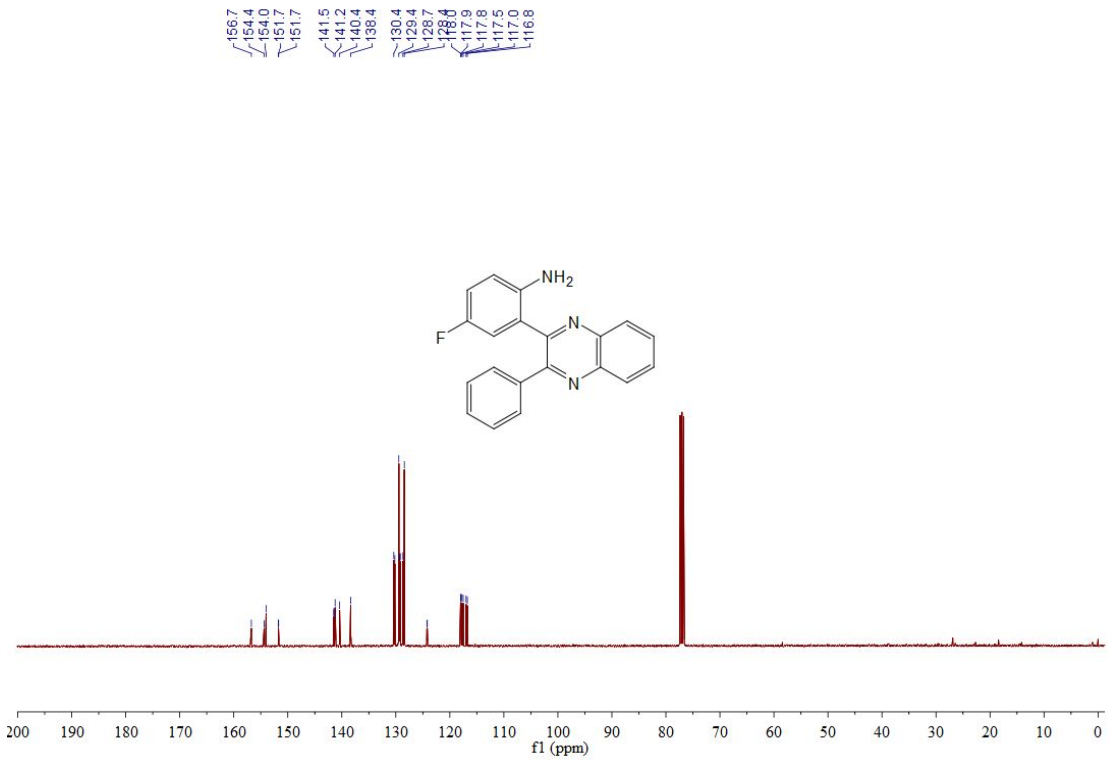
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ca**



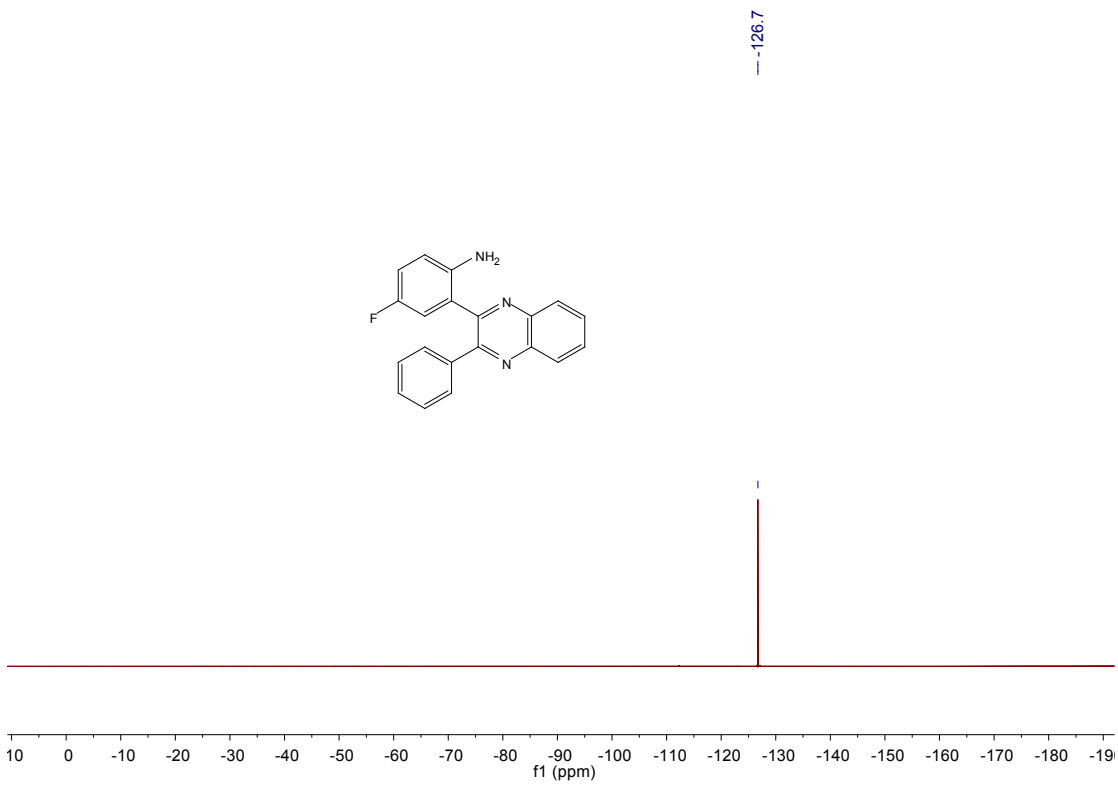
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4ca**



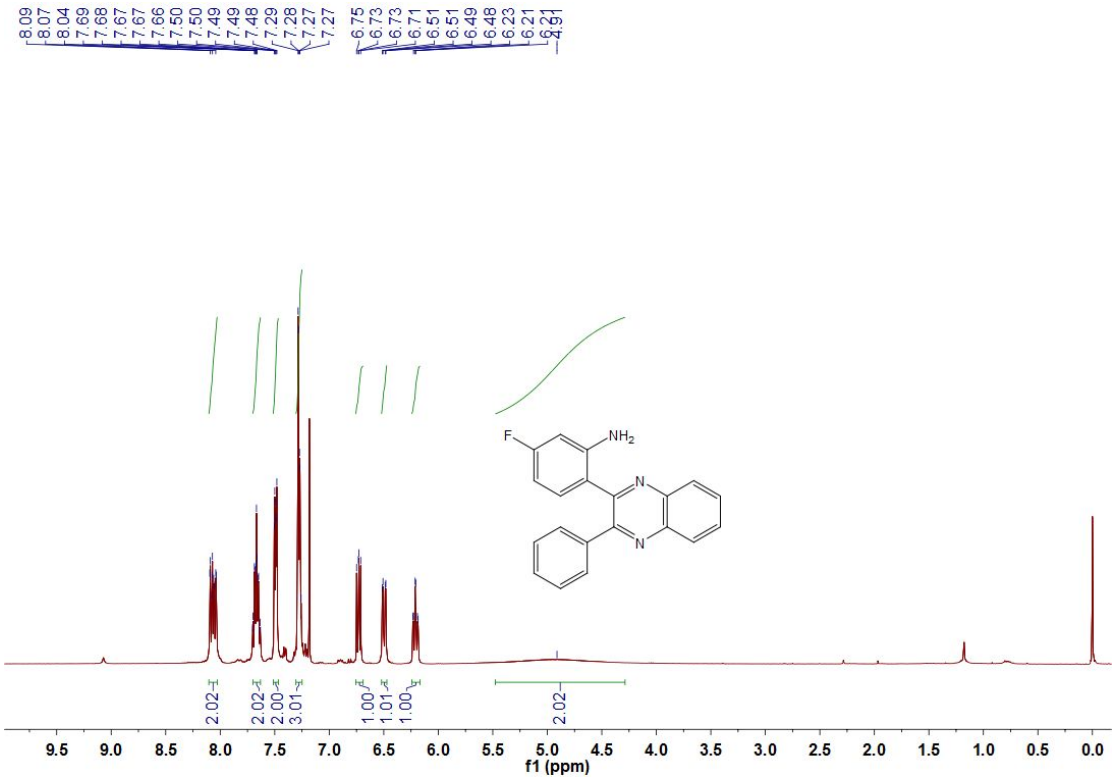
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4da**



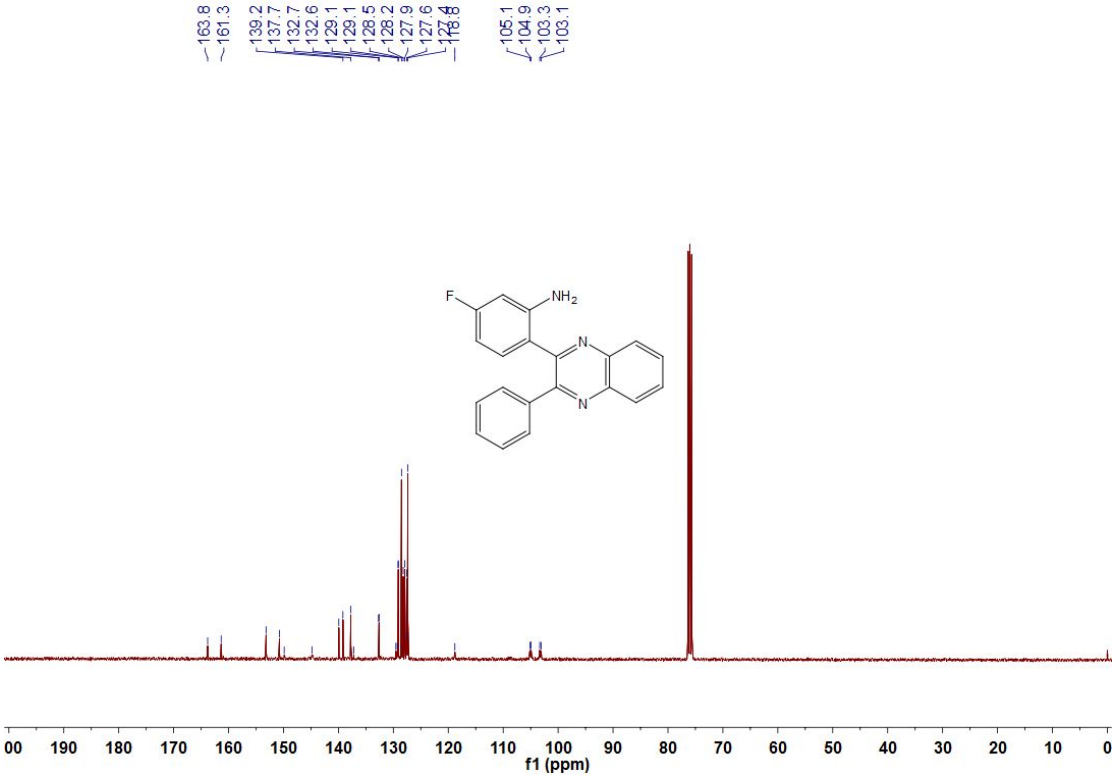
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4da**



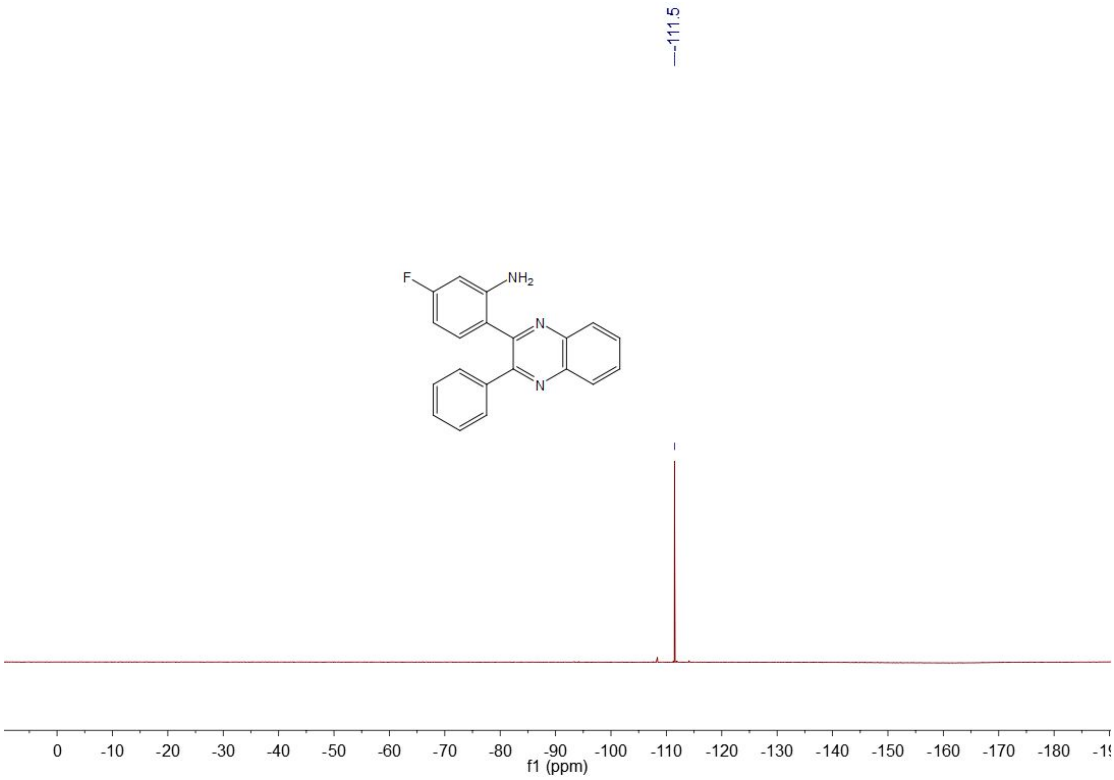
^{19}F NMR spectrum of **4da**



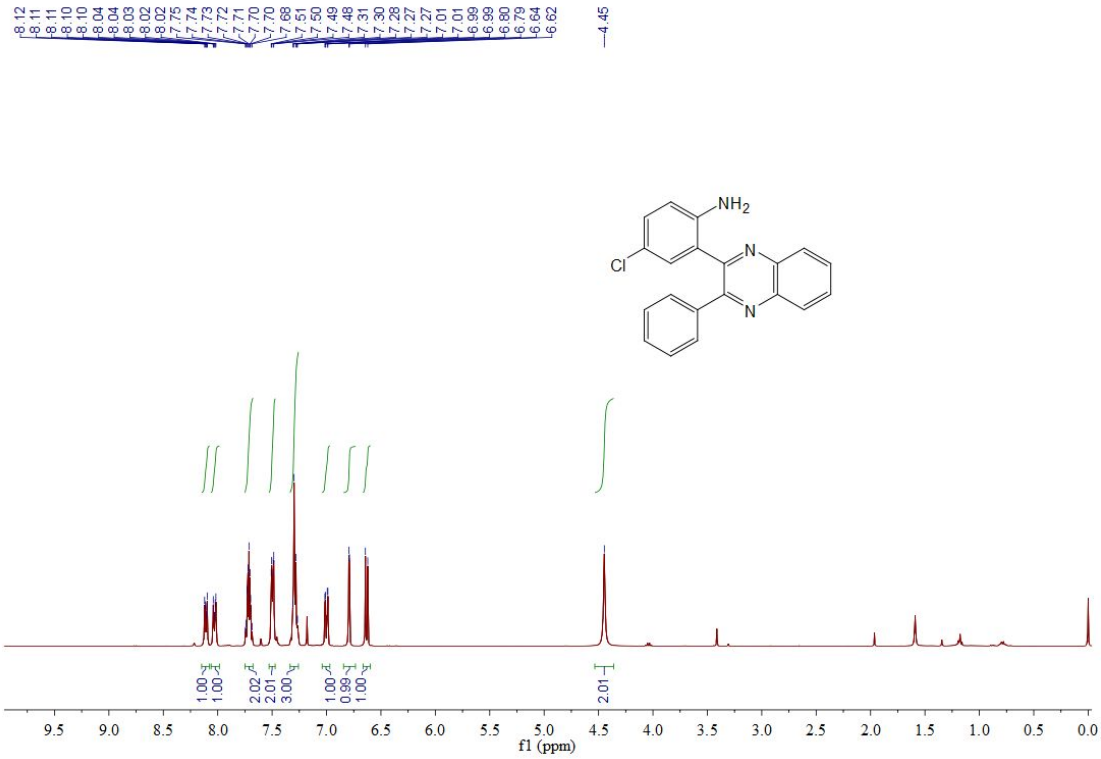
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ea**



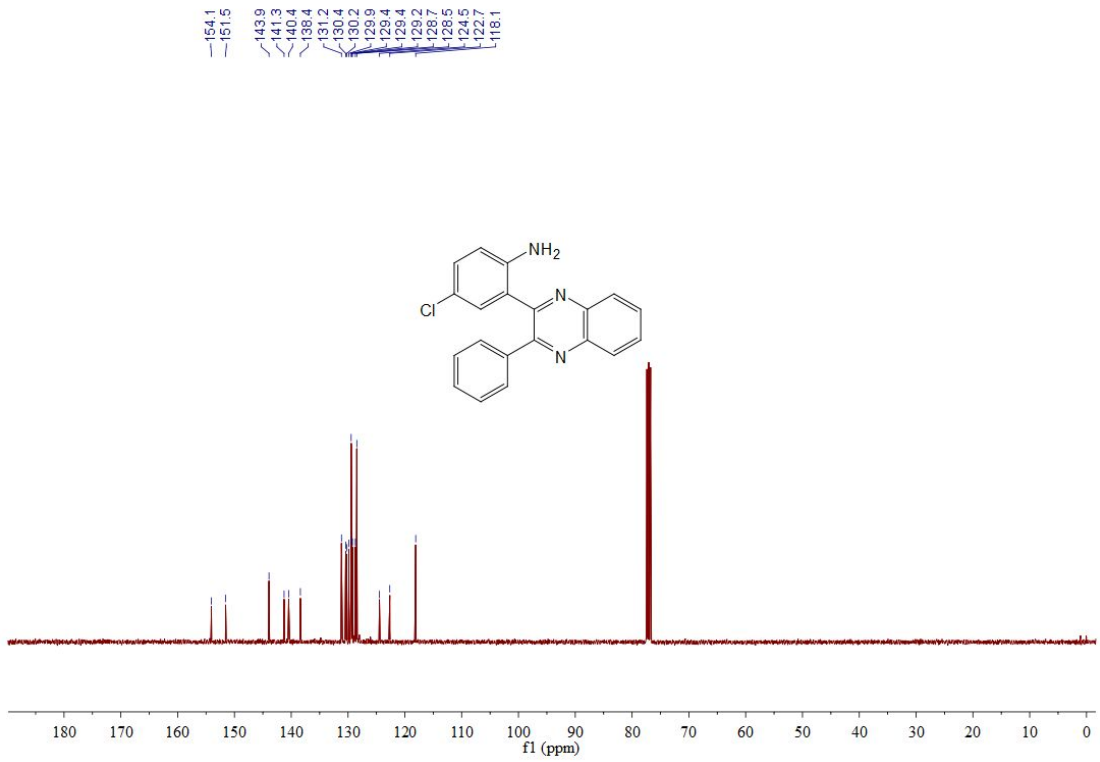
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **4ea**



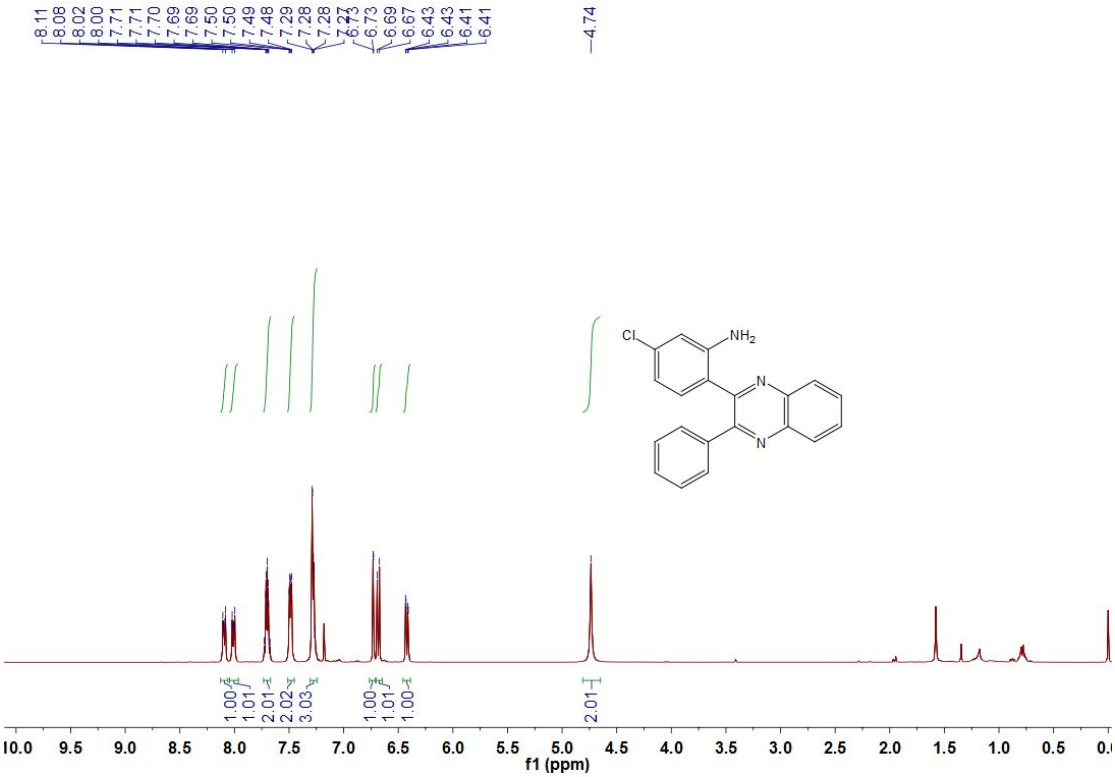
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4ea**



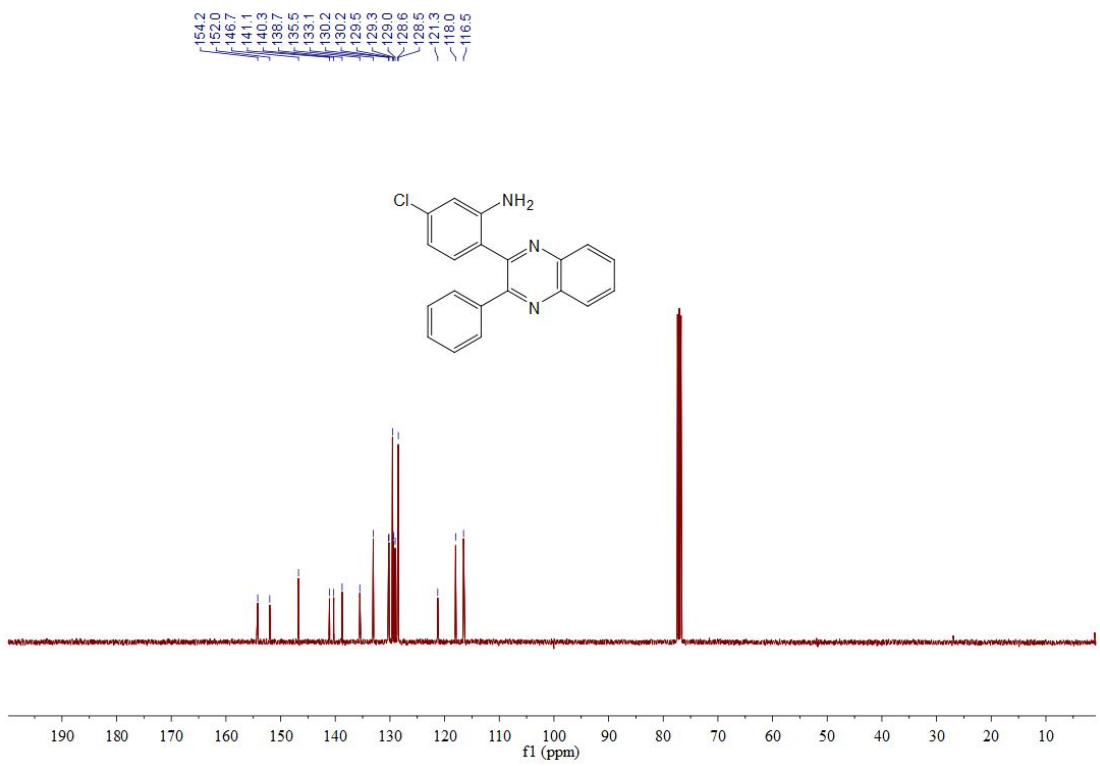
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4fa**



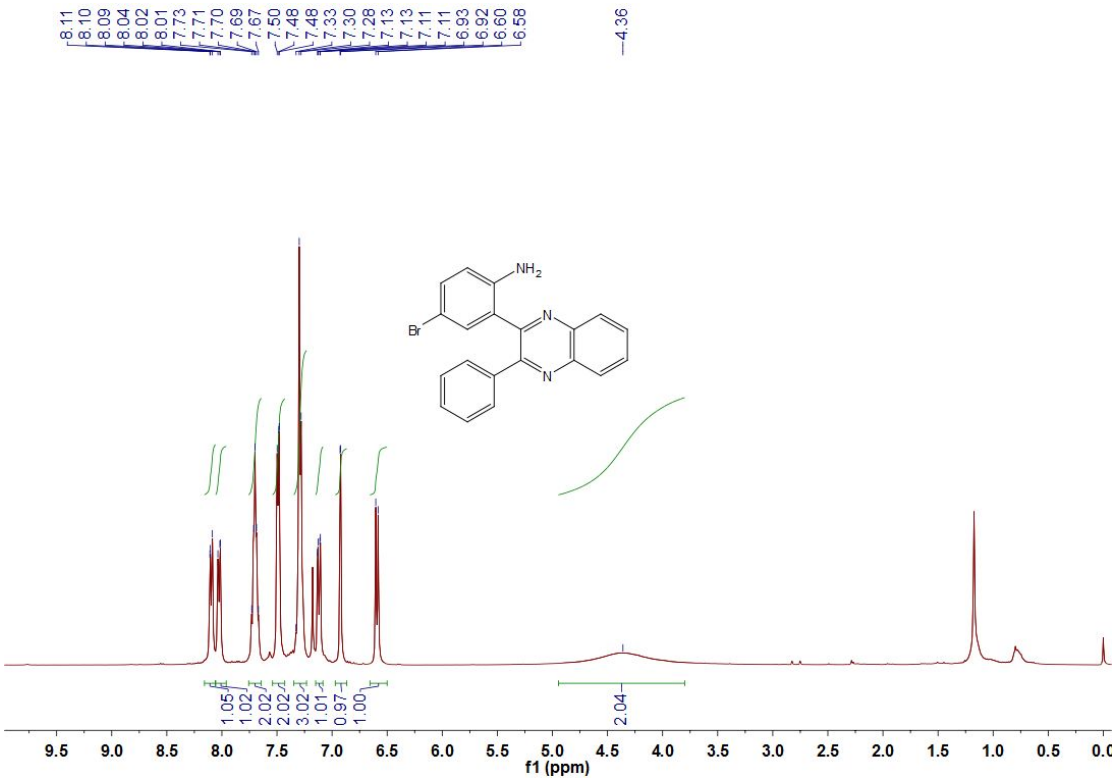
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4fa**



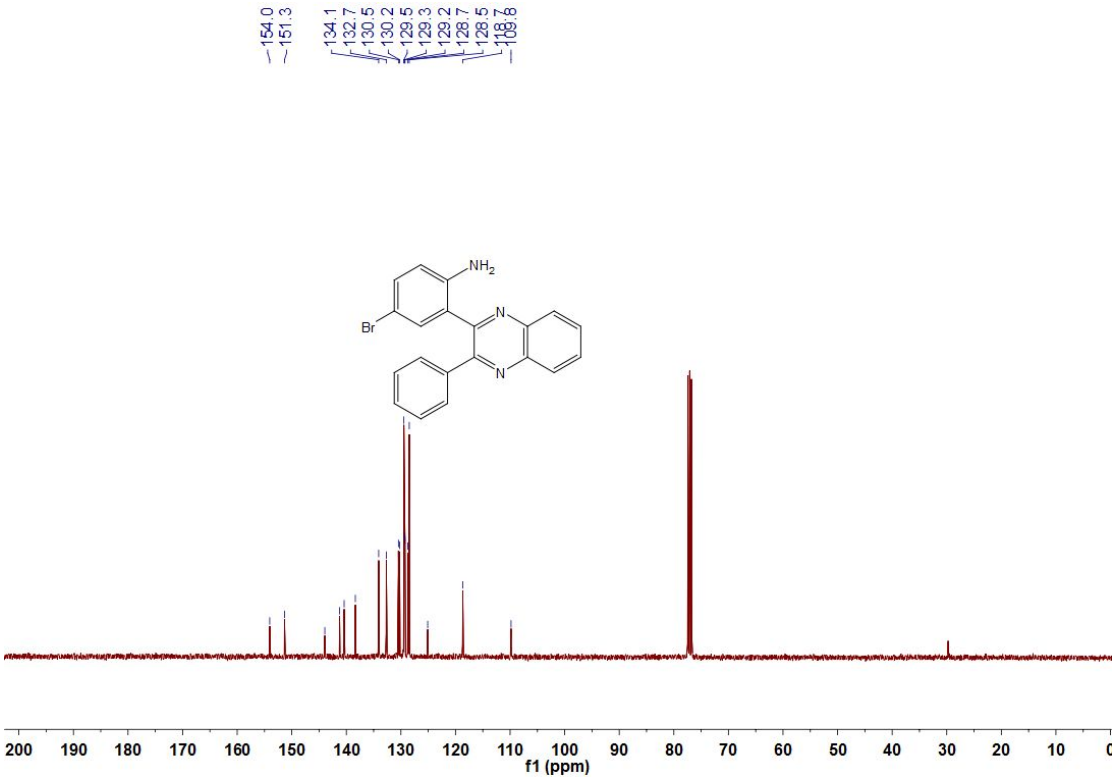
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ga**



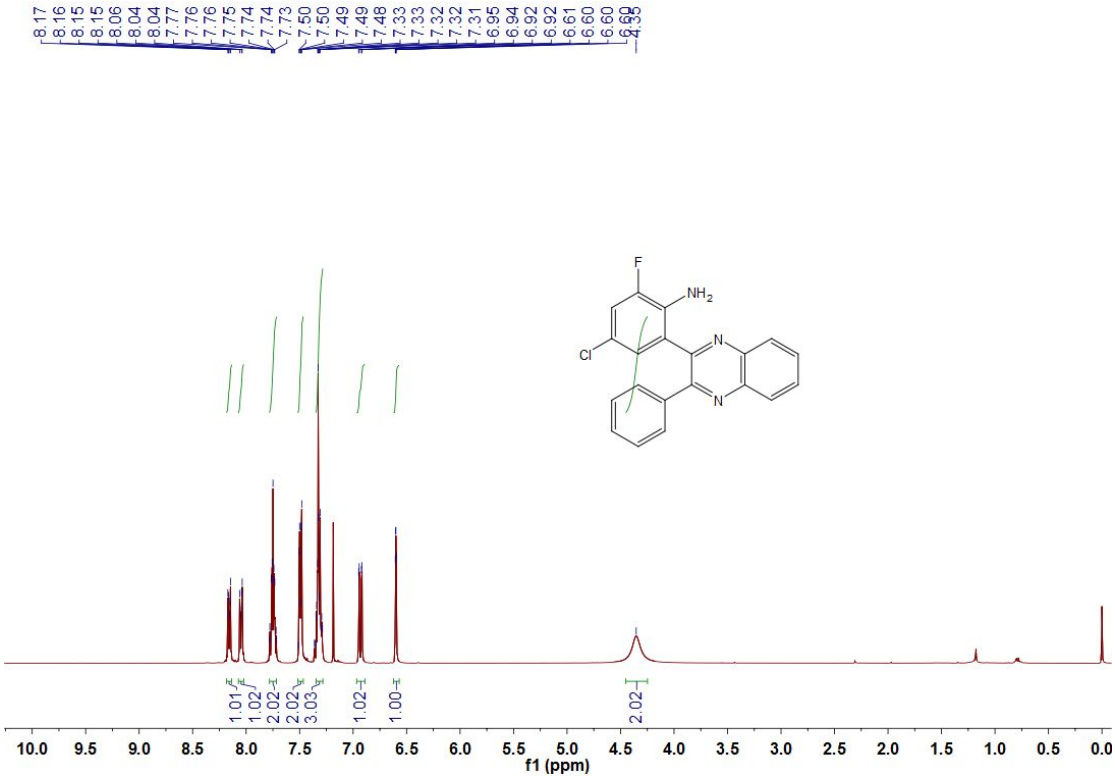
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4ga**



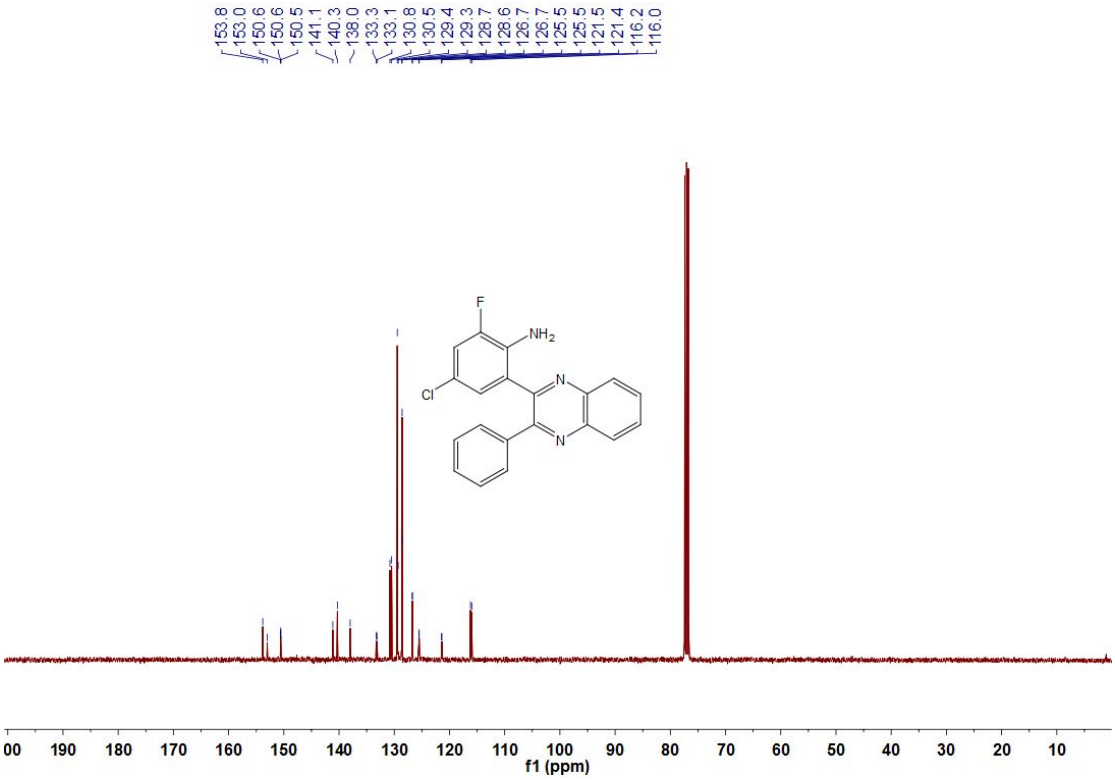
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ha**



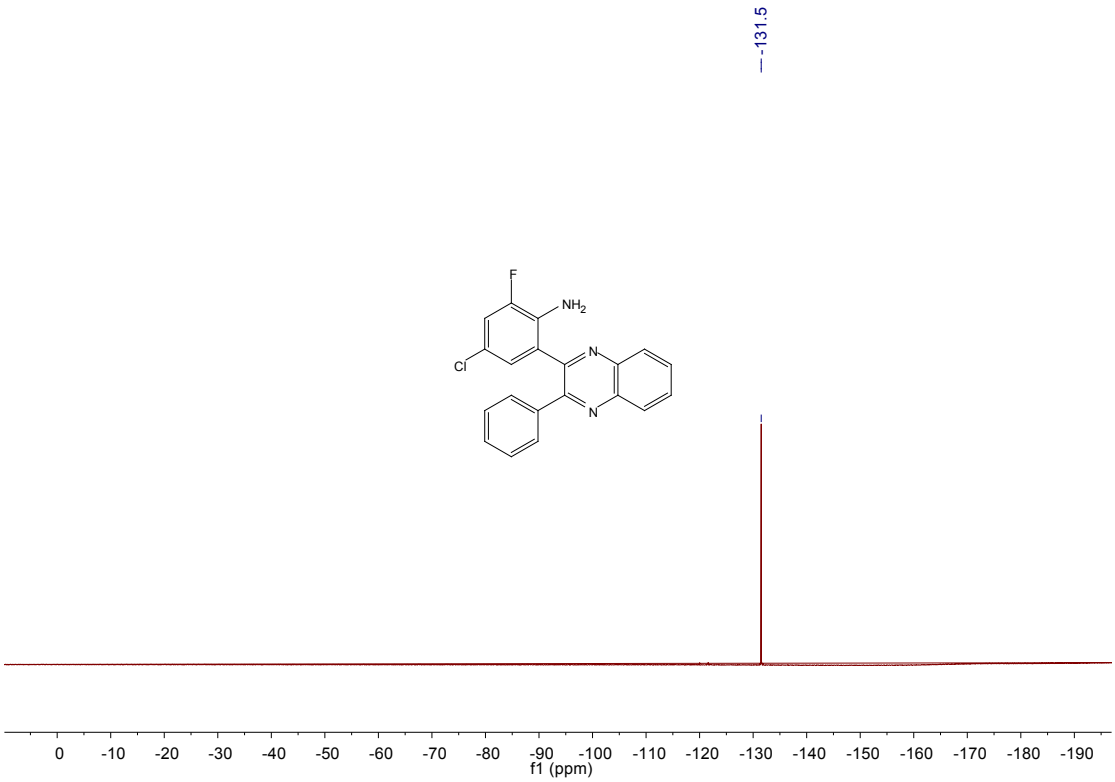
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4ha**



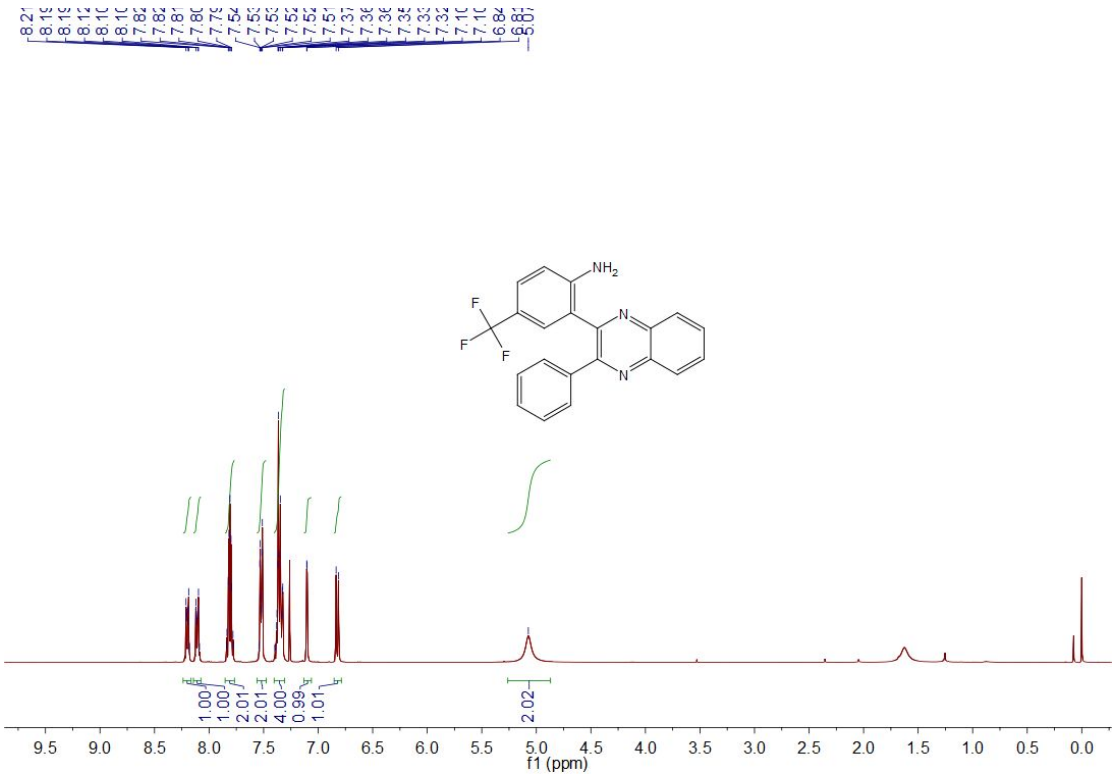
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ia**



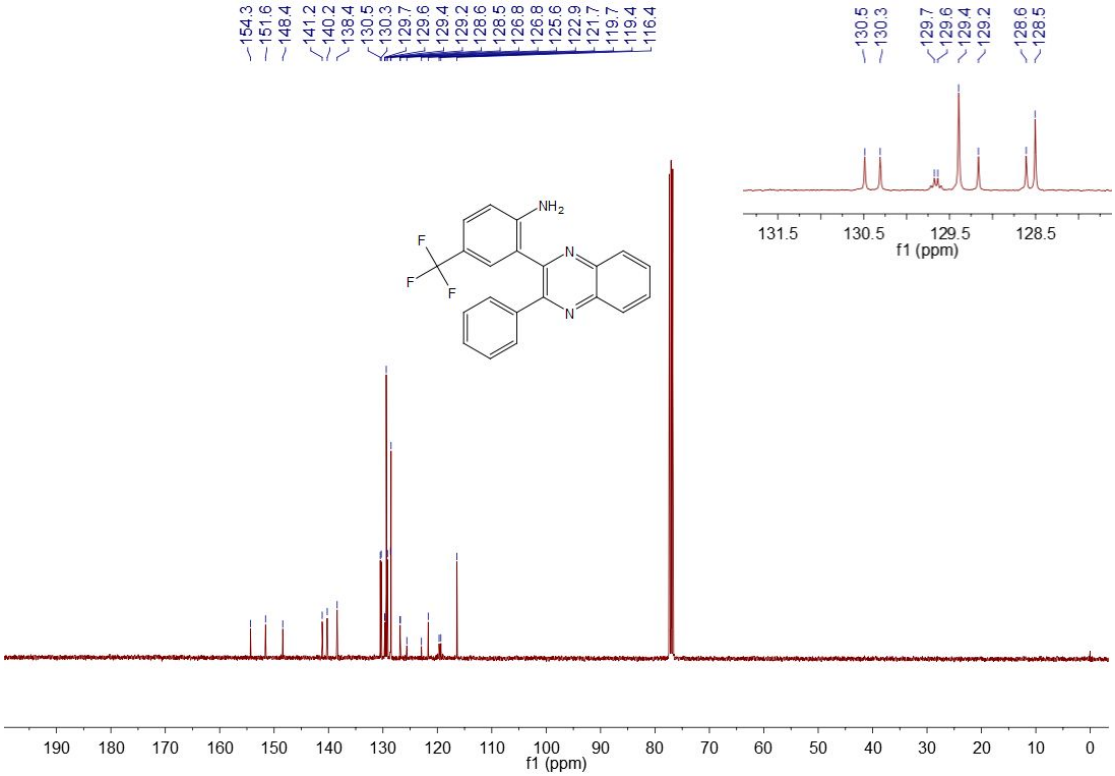
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4ia**



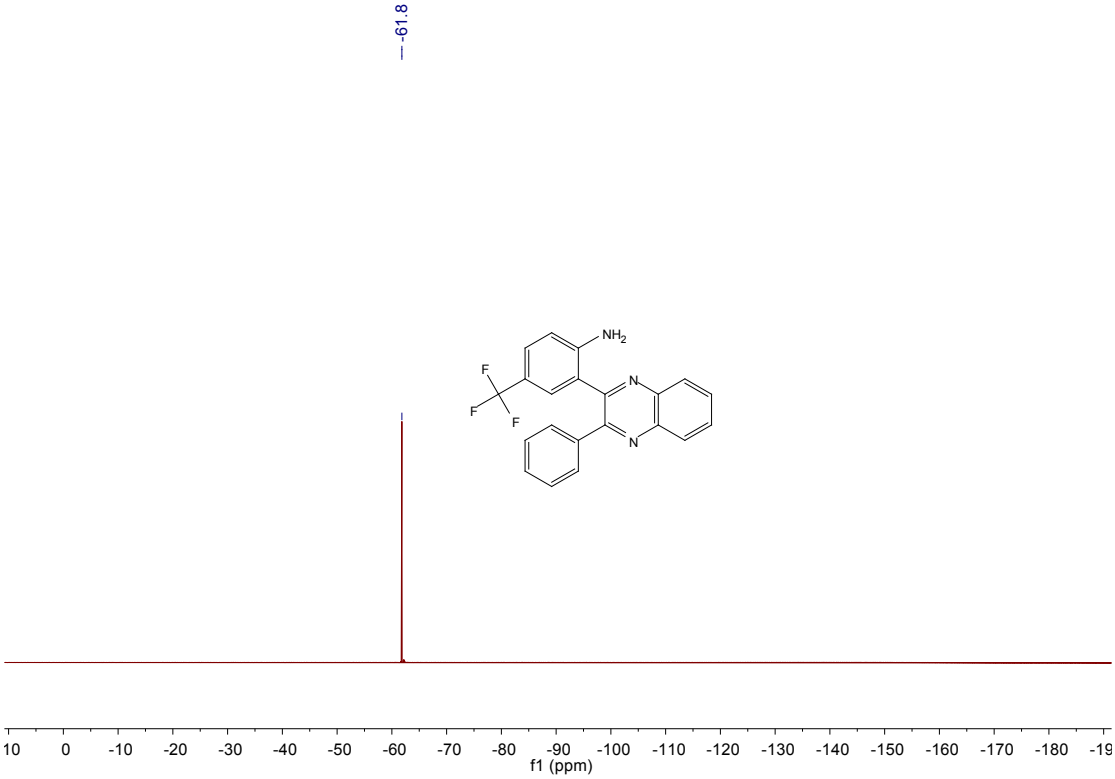
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4ia**



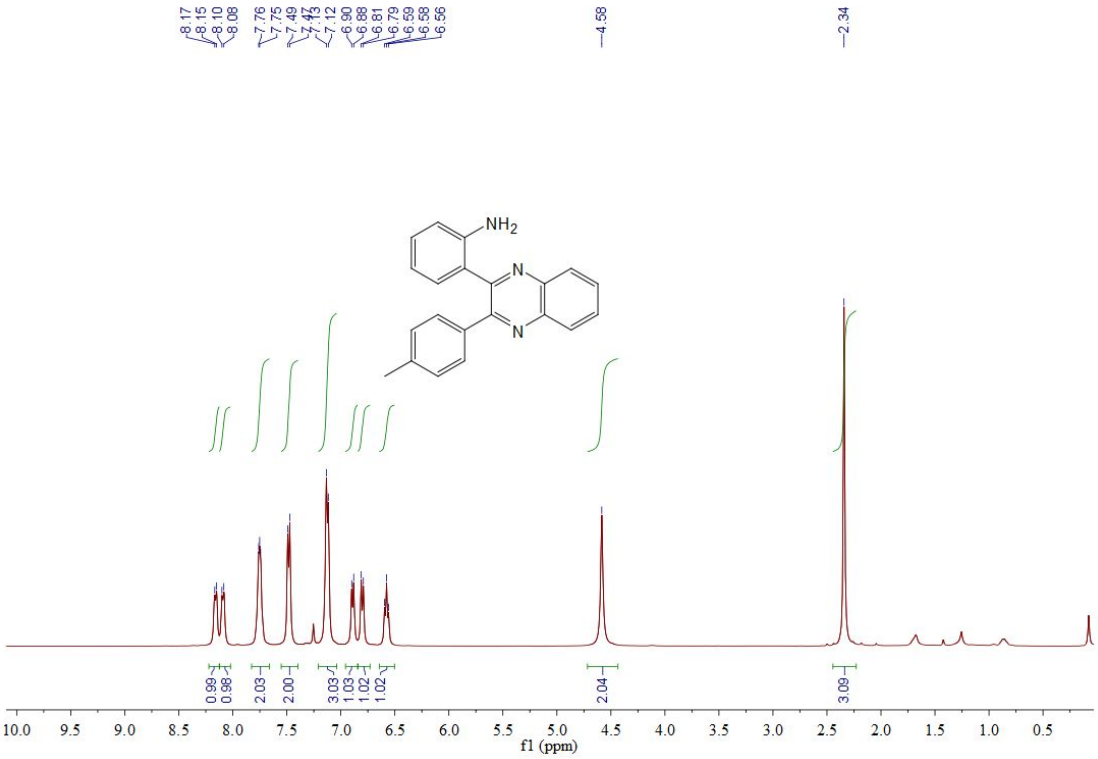
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ja**



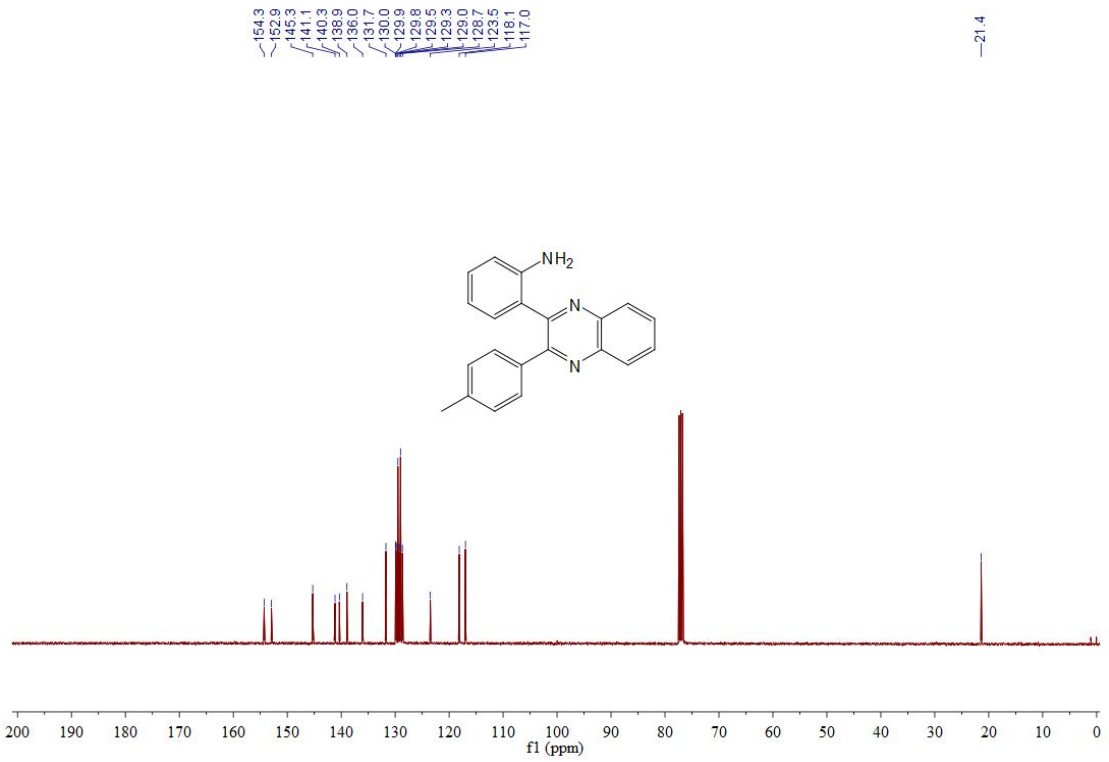
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **4ja**



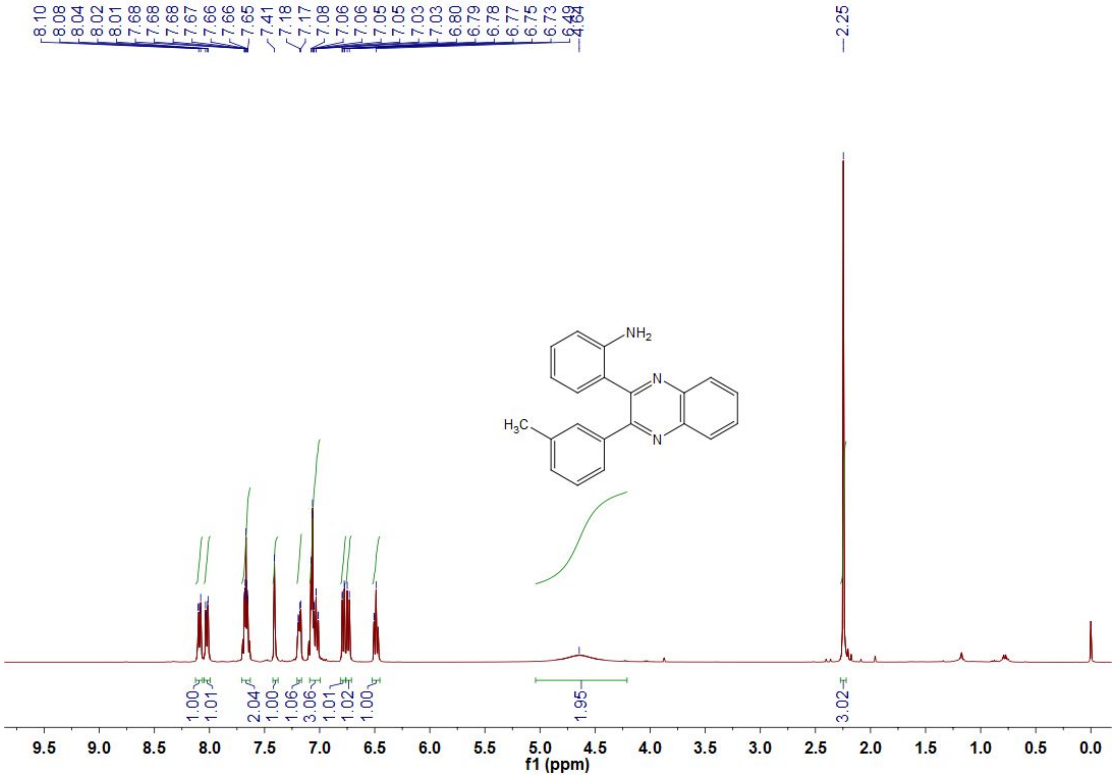
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4ja**



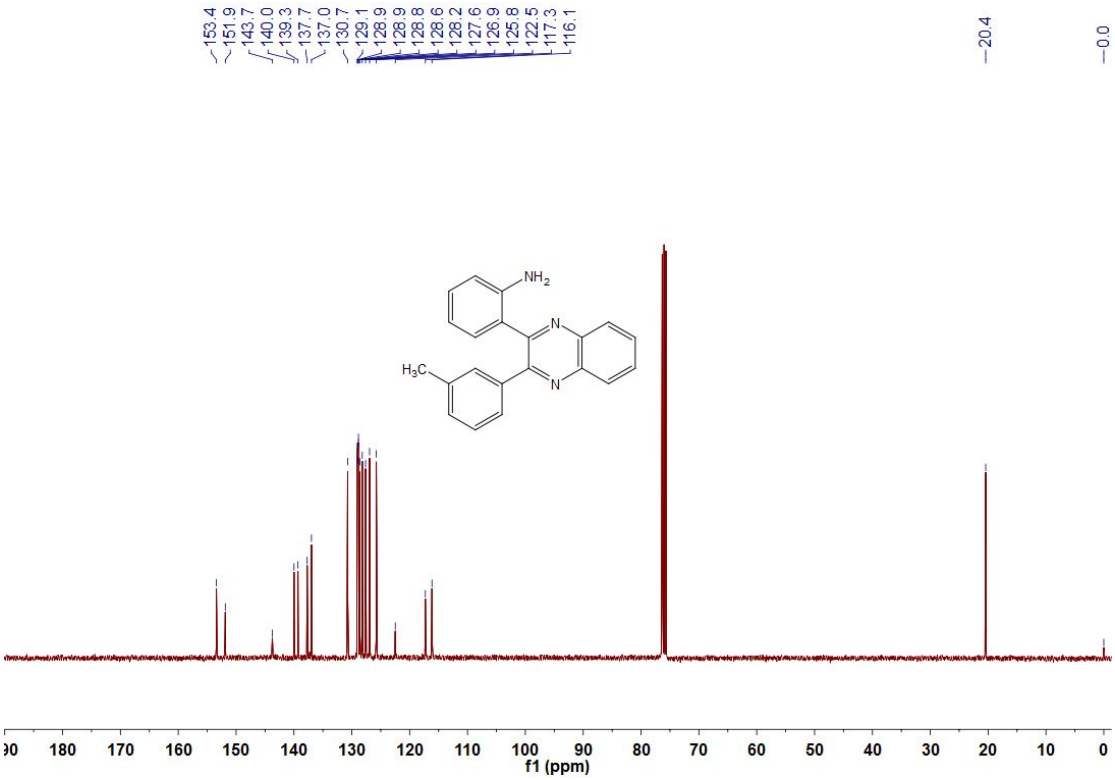
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ka**



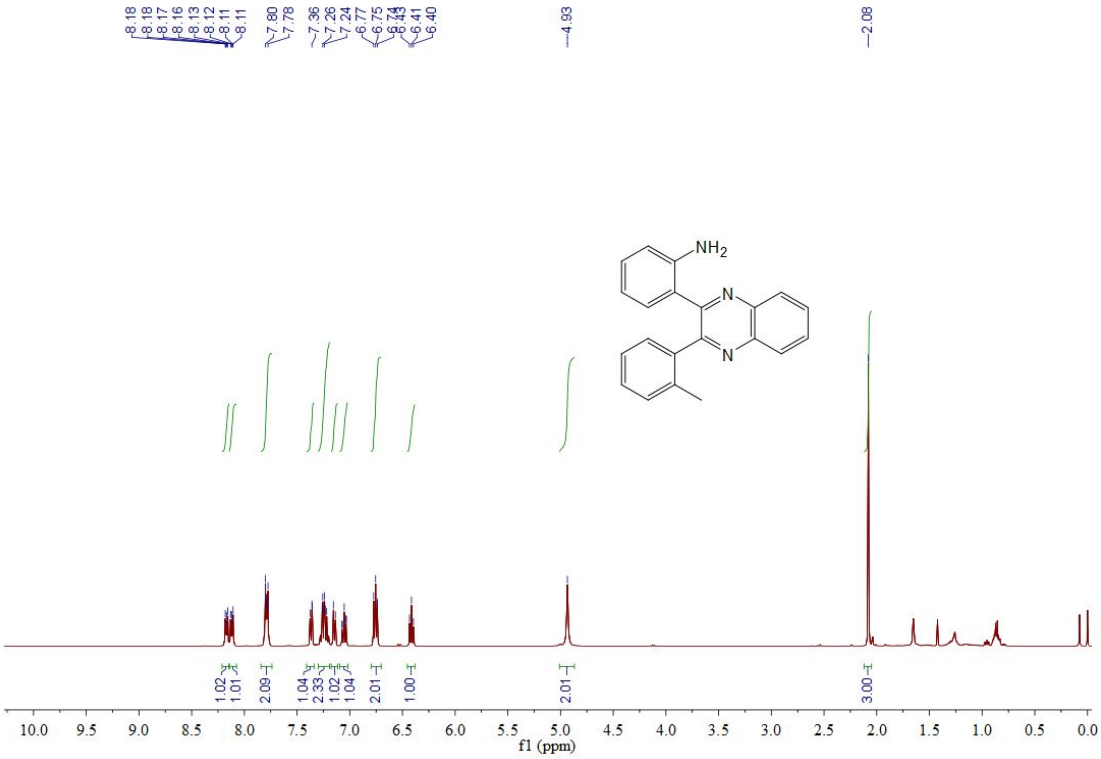
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4ka**



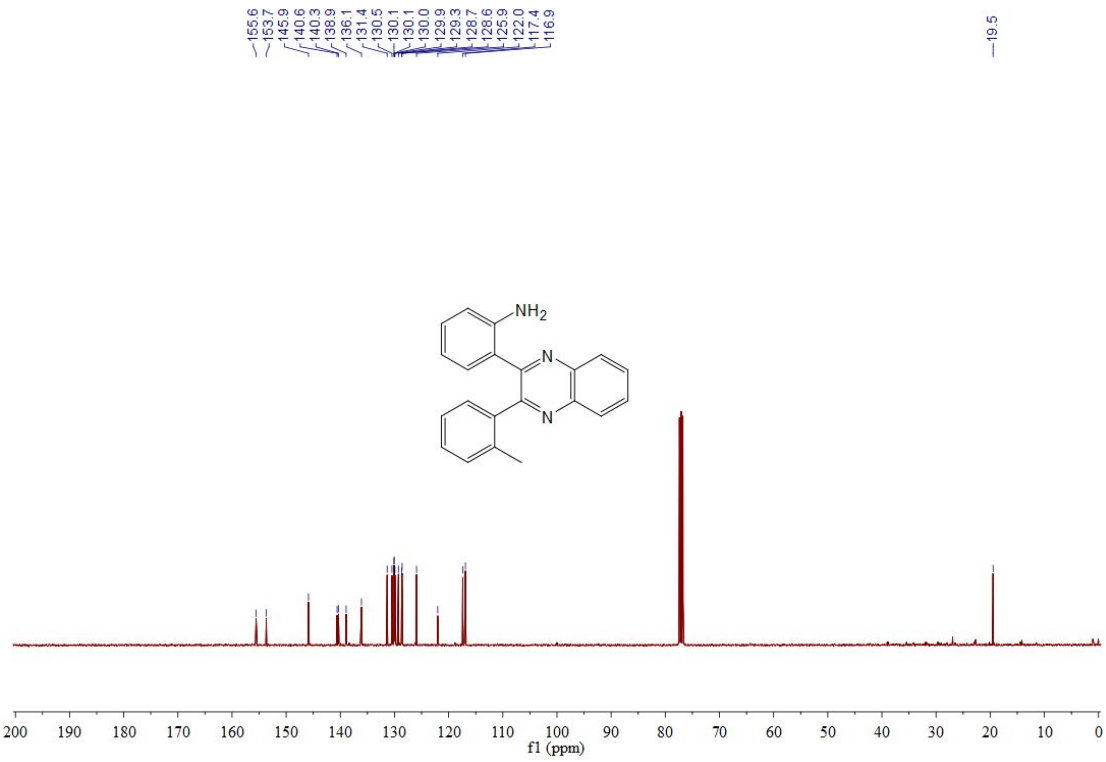
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4la**



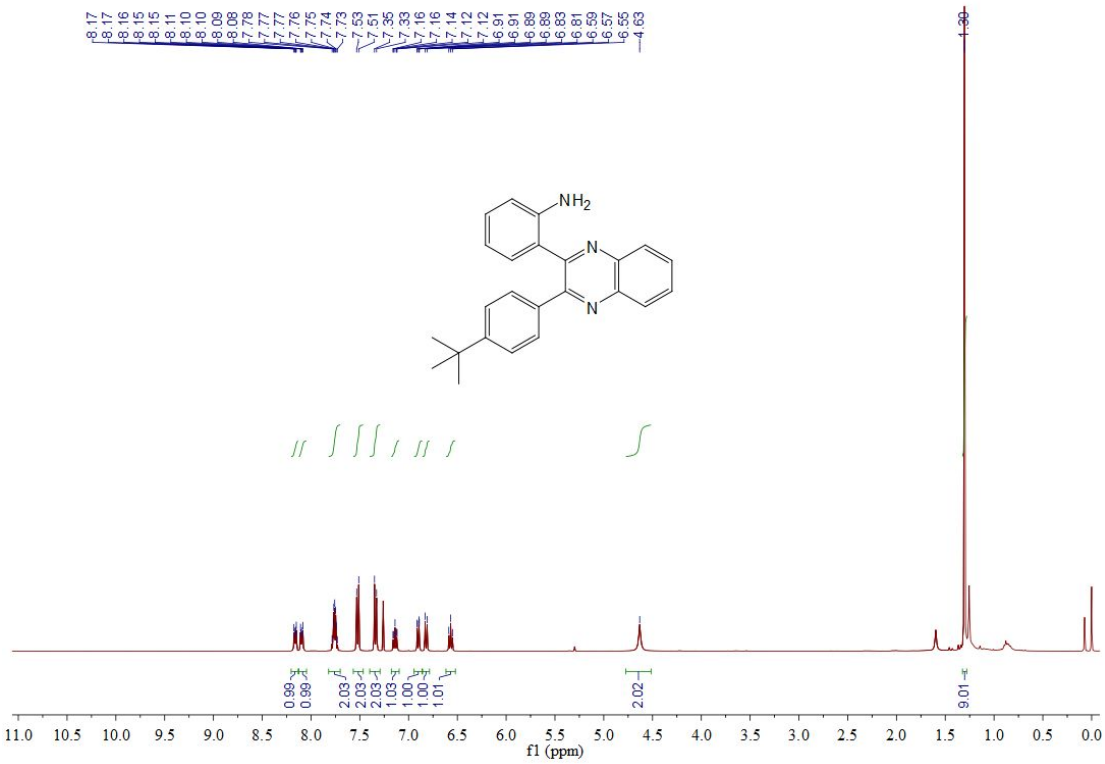
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4la**



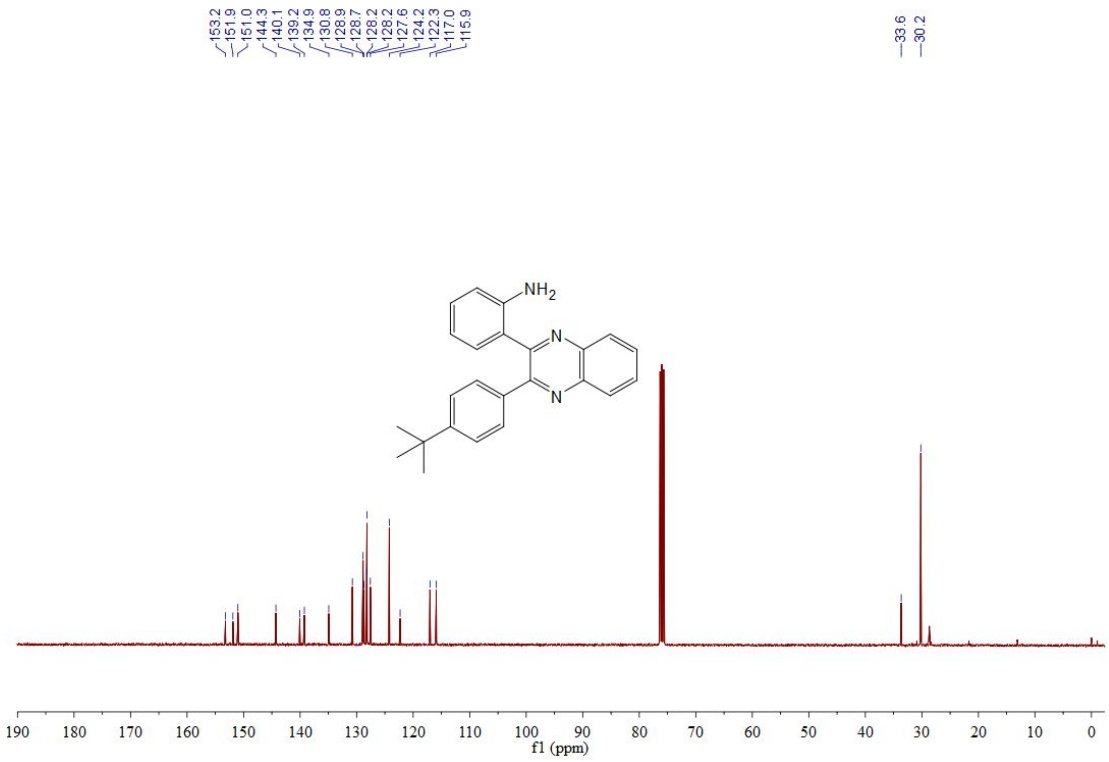
^{1}H NMR (400 MHz, $CDCl_3$)spectrum of **4ma**



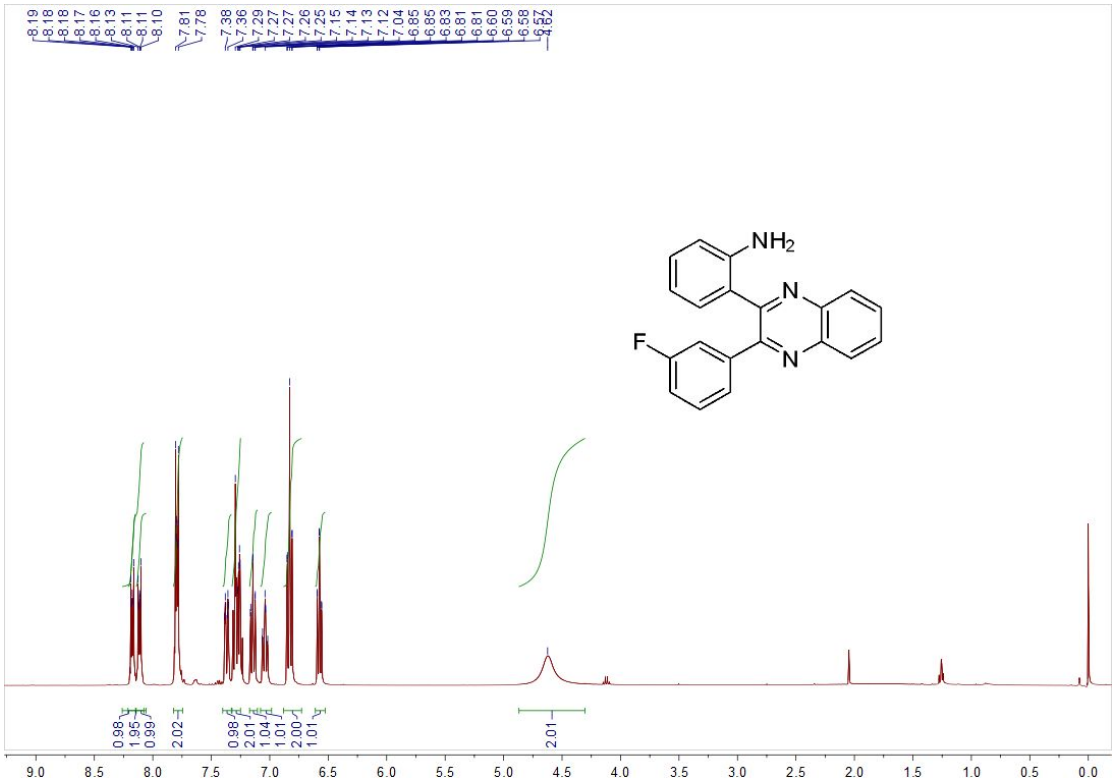
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4ma**



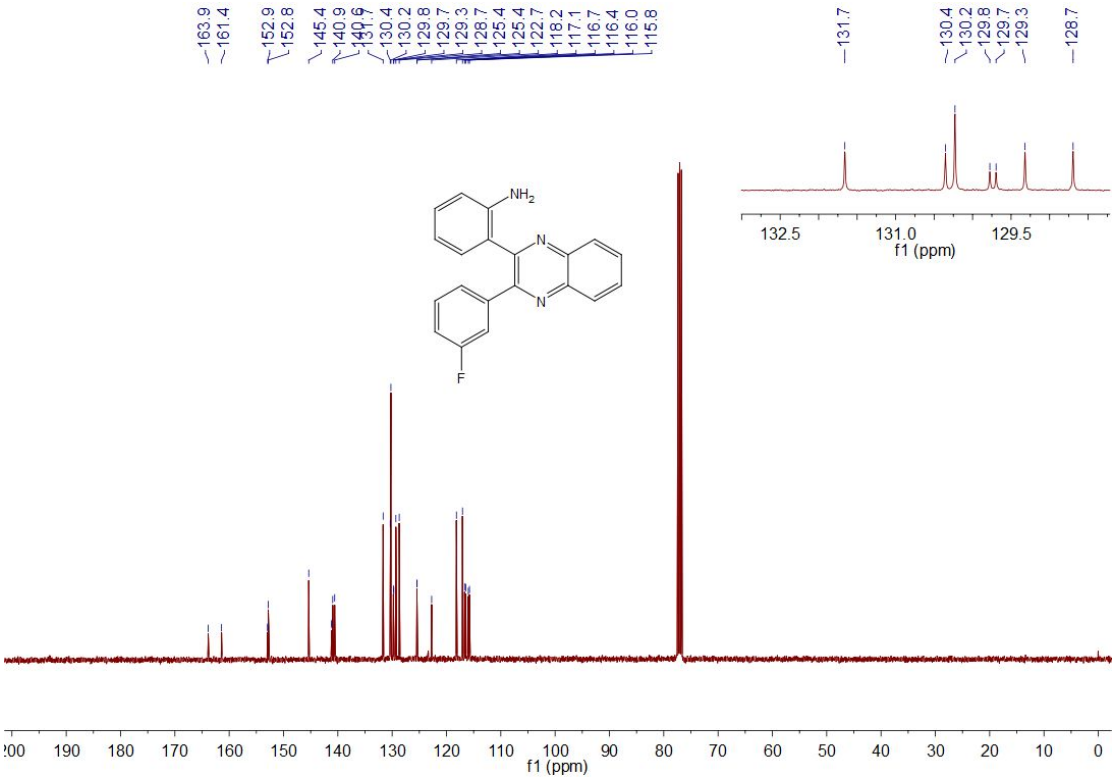
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4na**



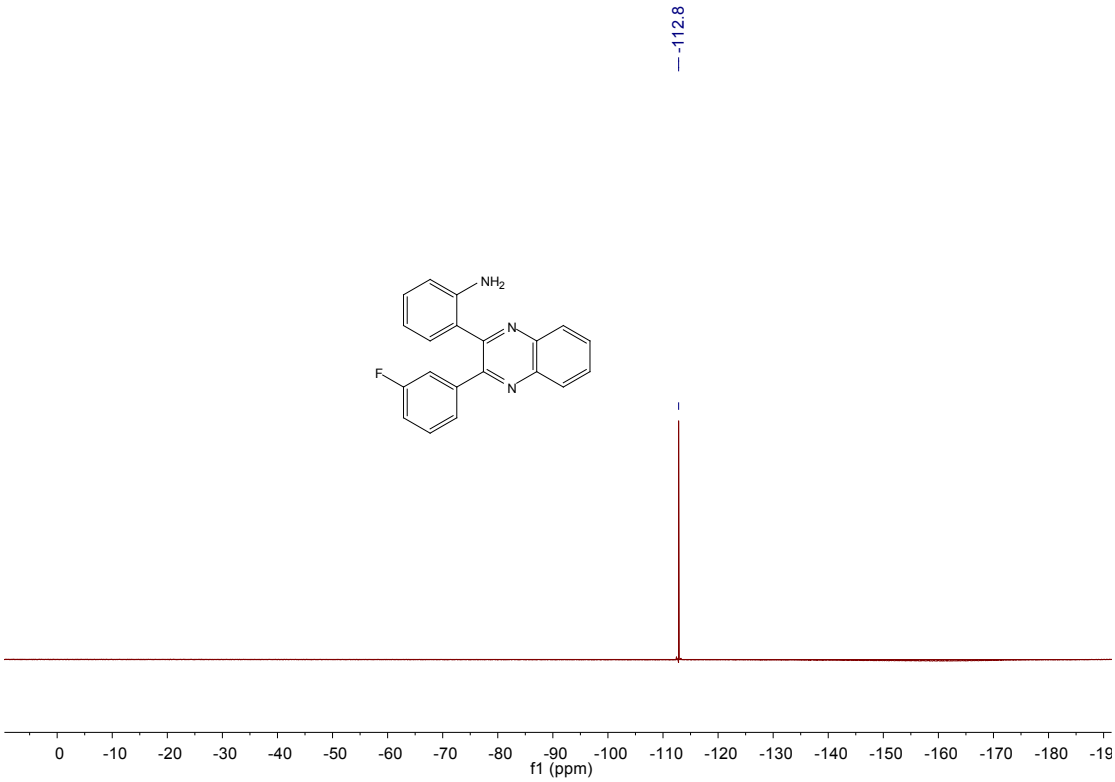
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4na**



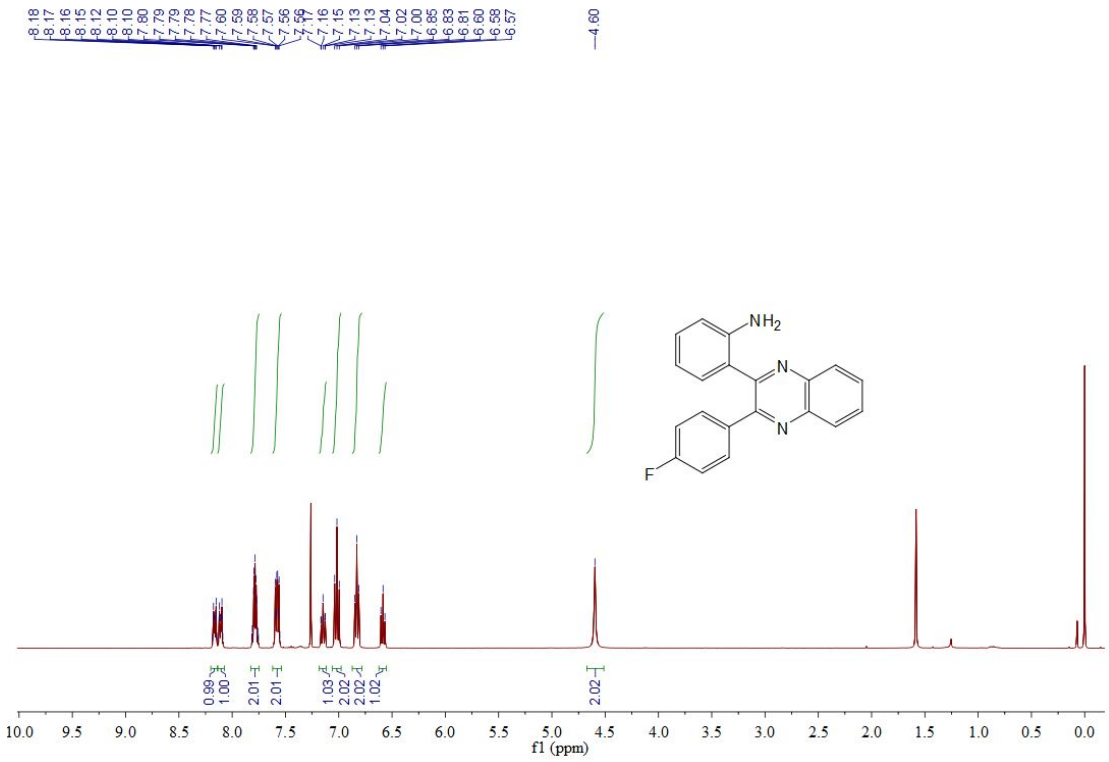
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4oa**



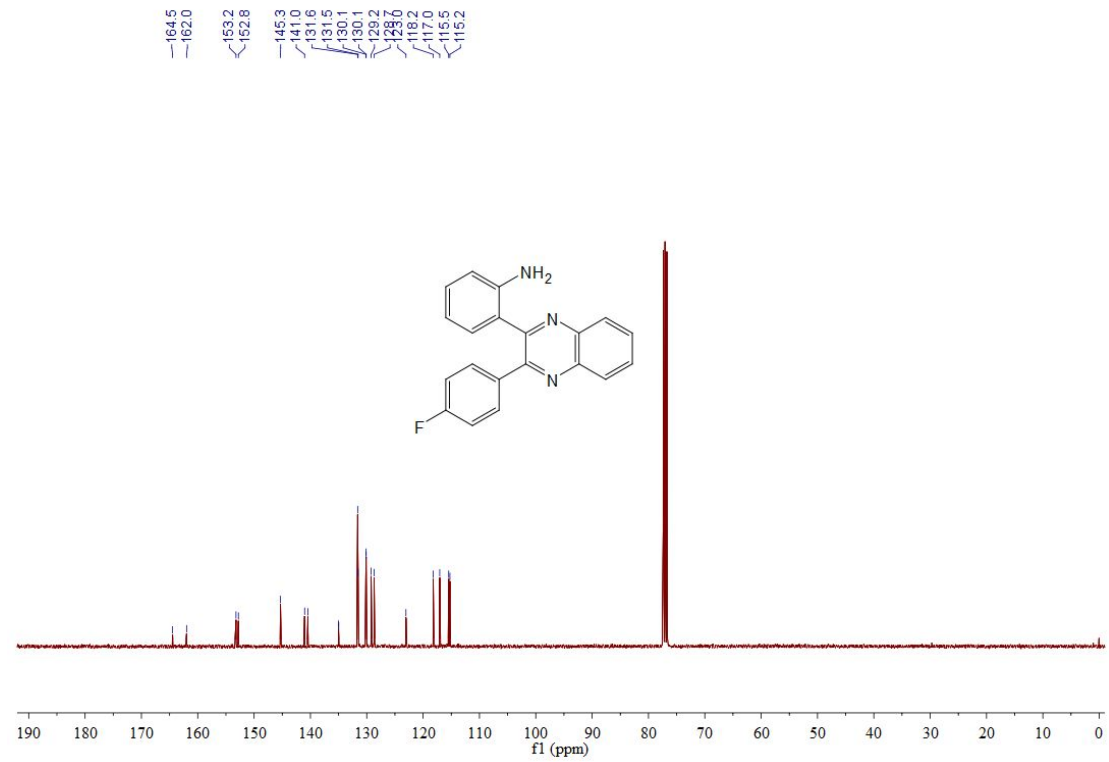
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4oa**



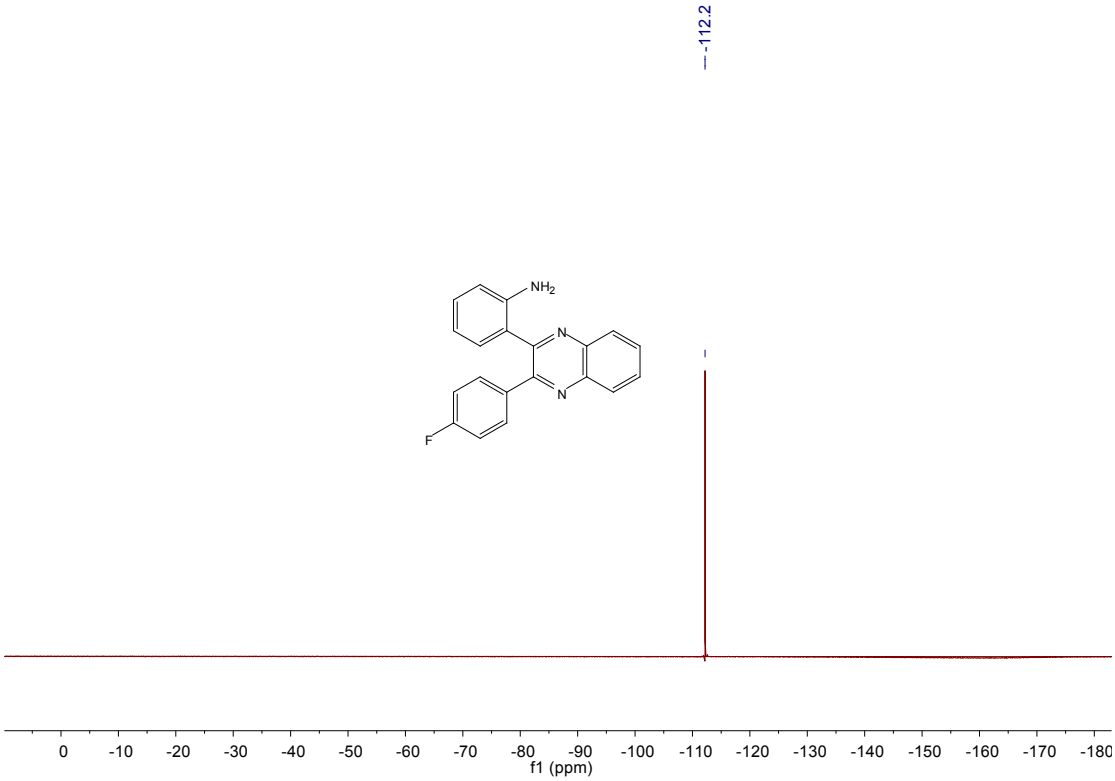
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4oa**



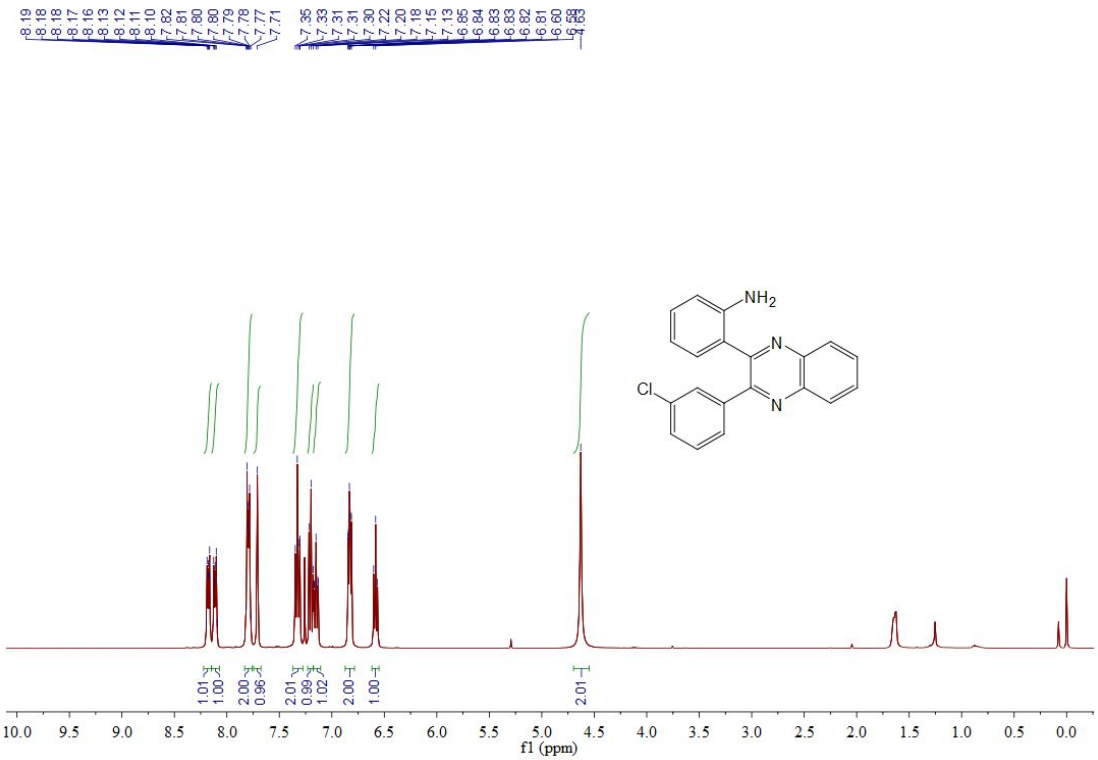
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4pa**



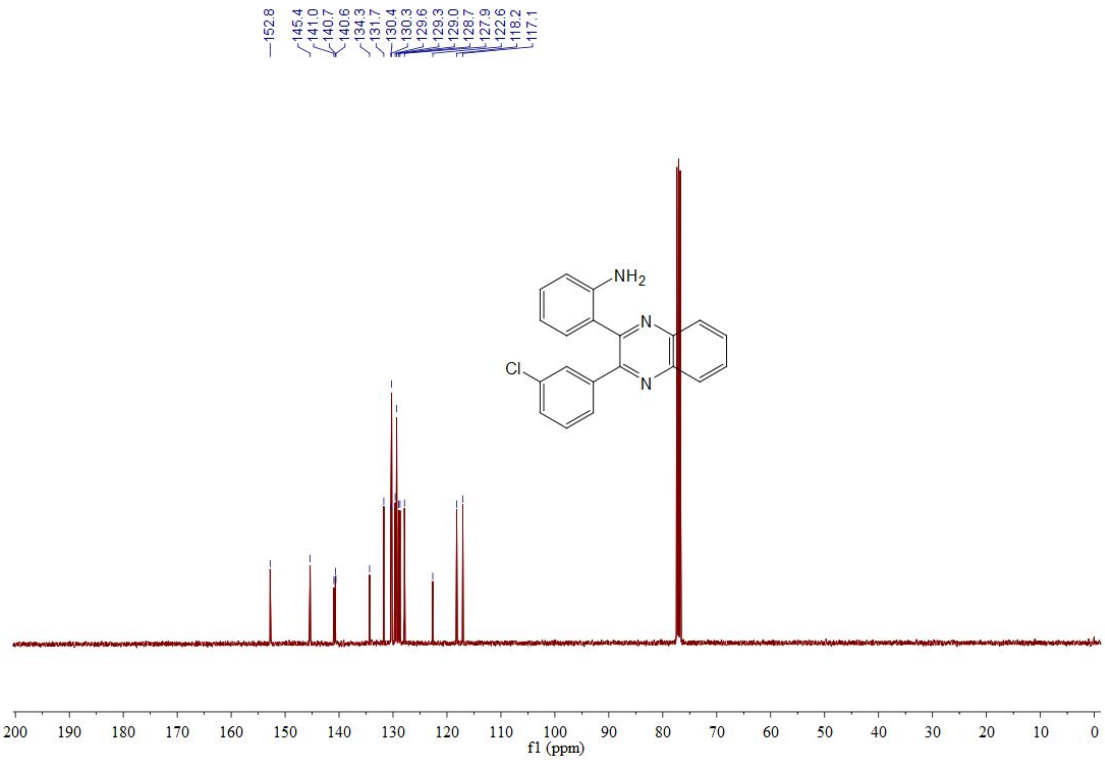
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **4pa**



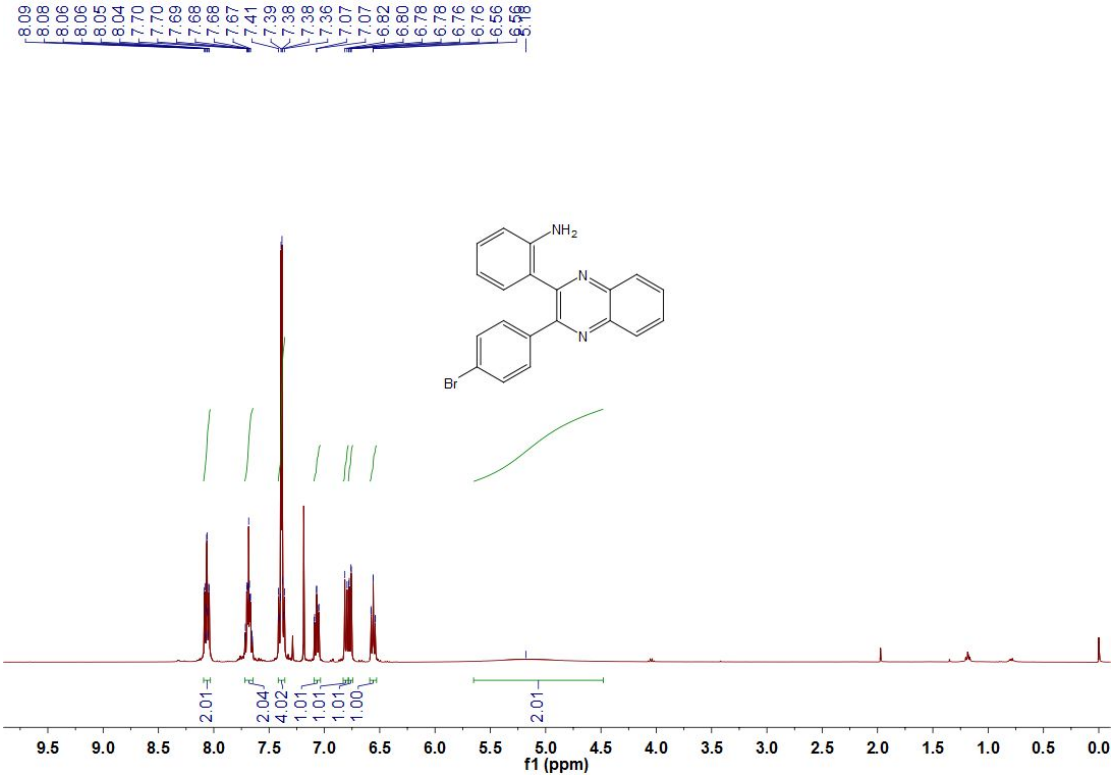
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4pa**



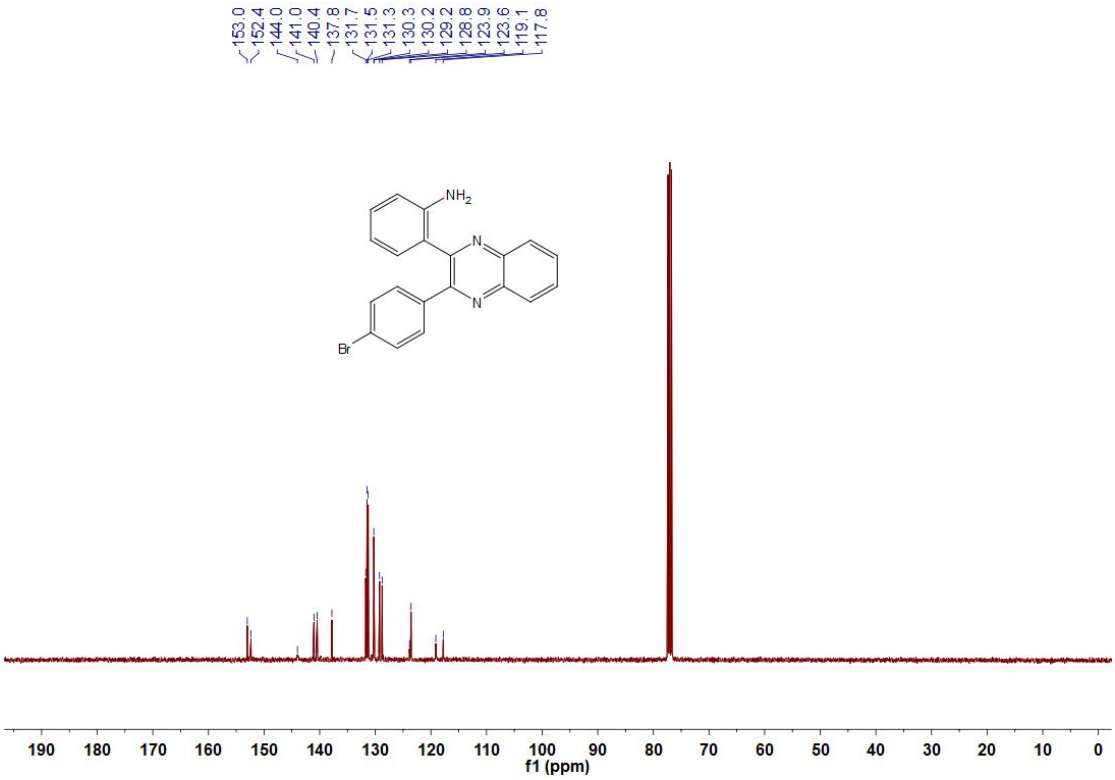
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4qa**



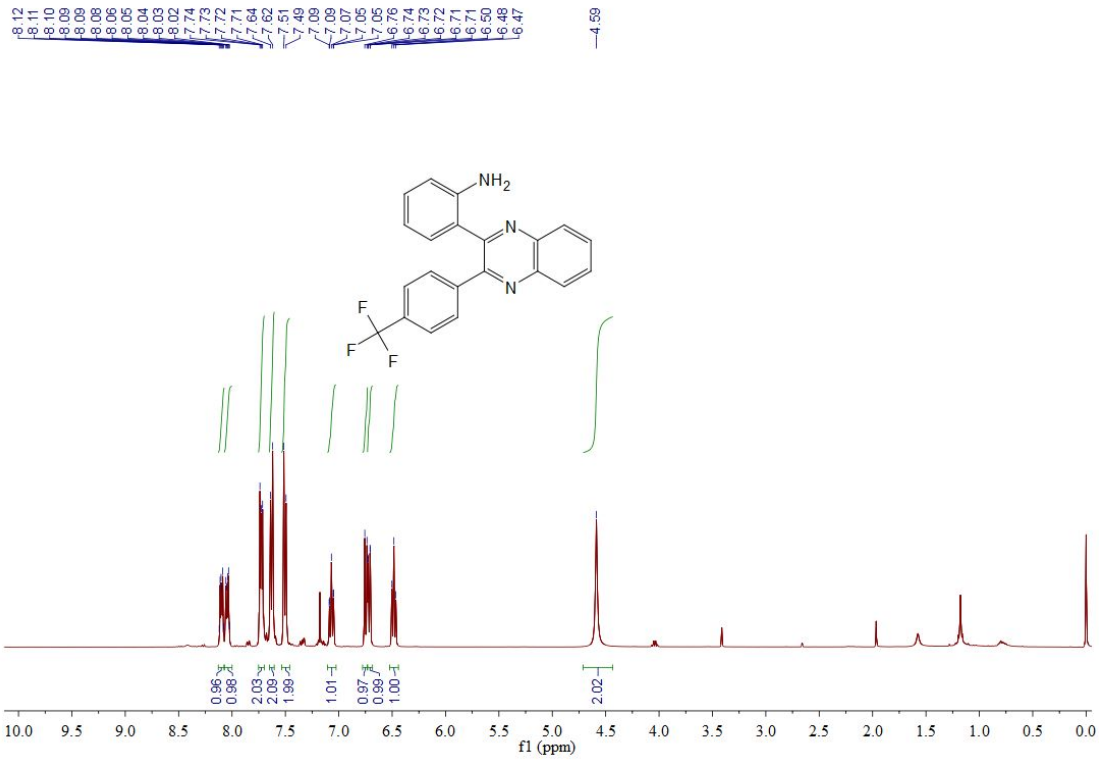
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4qa**



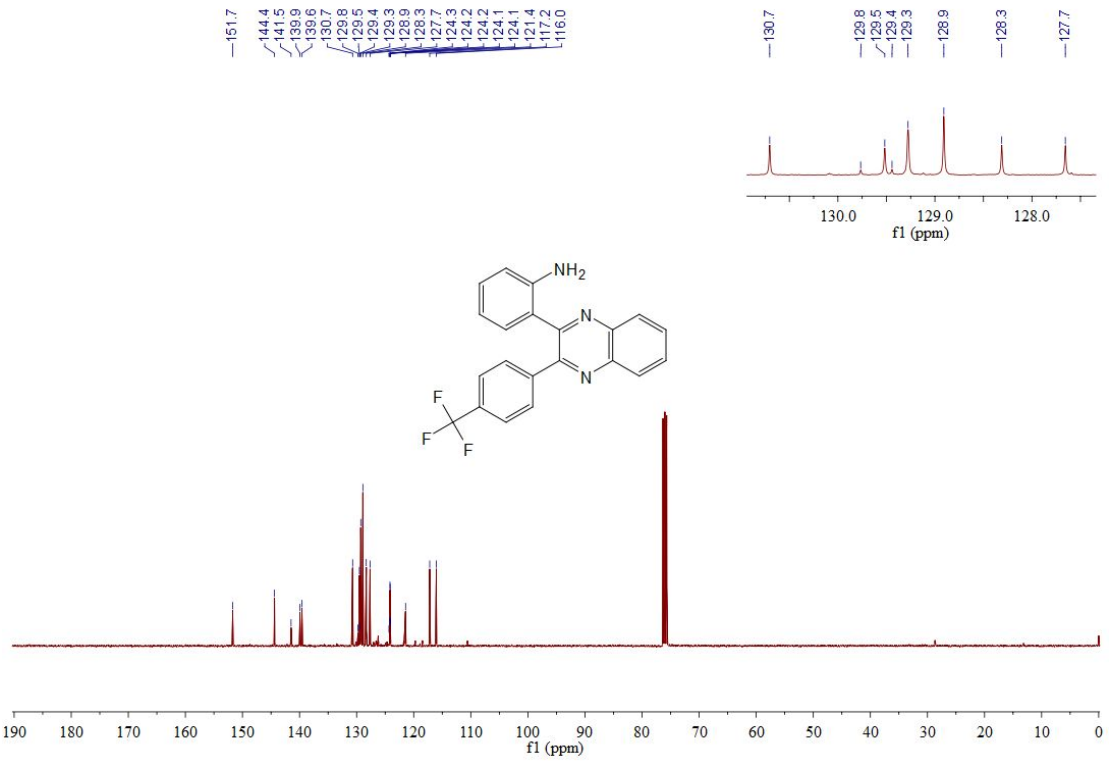
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ra**



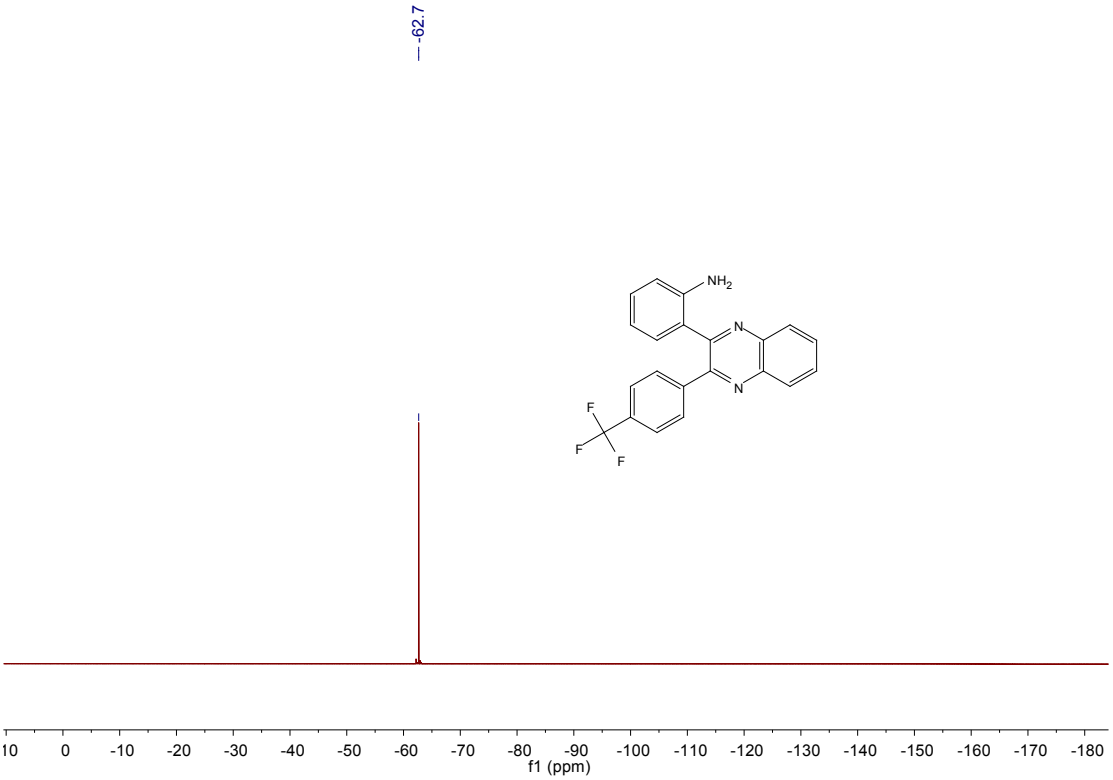
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4ra**



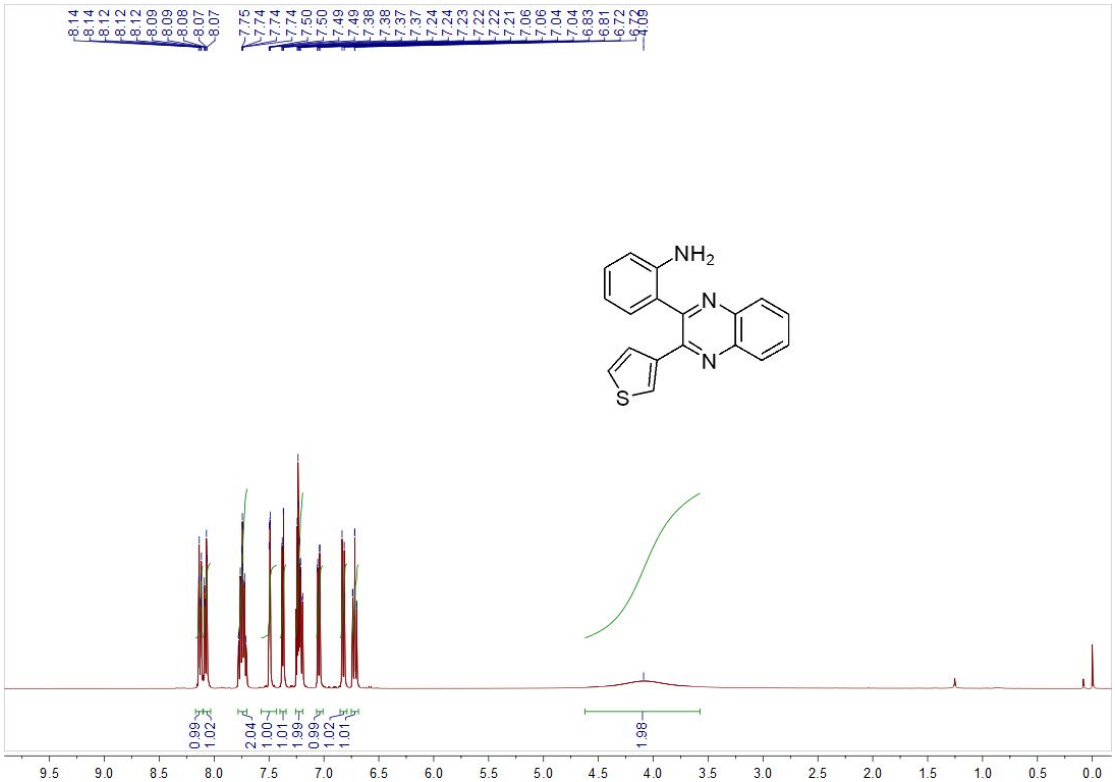
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4sa**



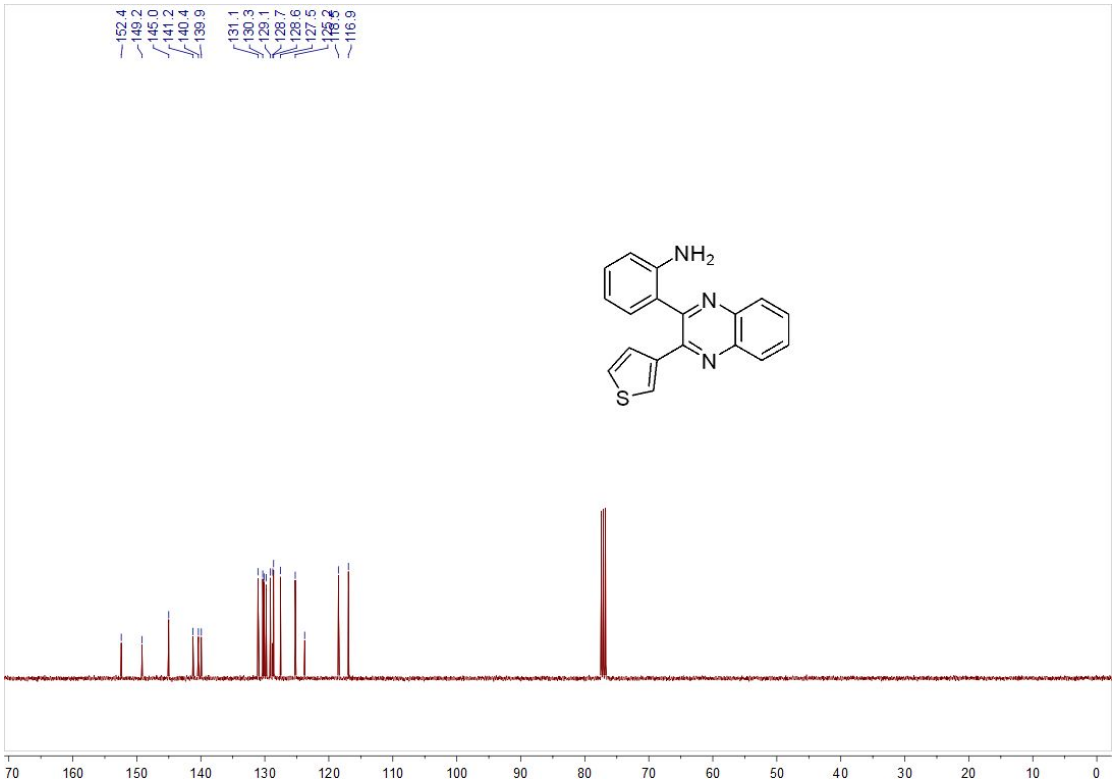
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **4sa**



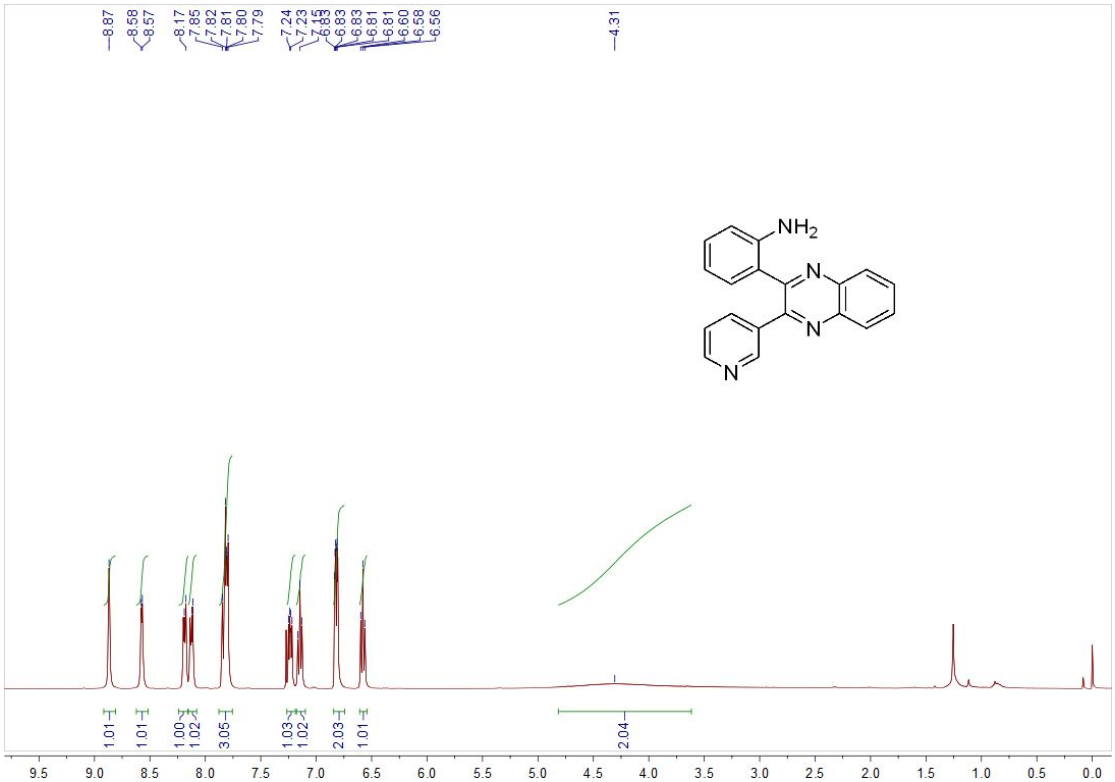
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4sa**



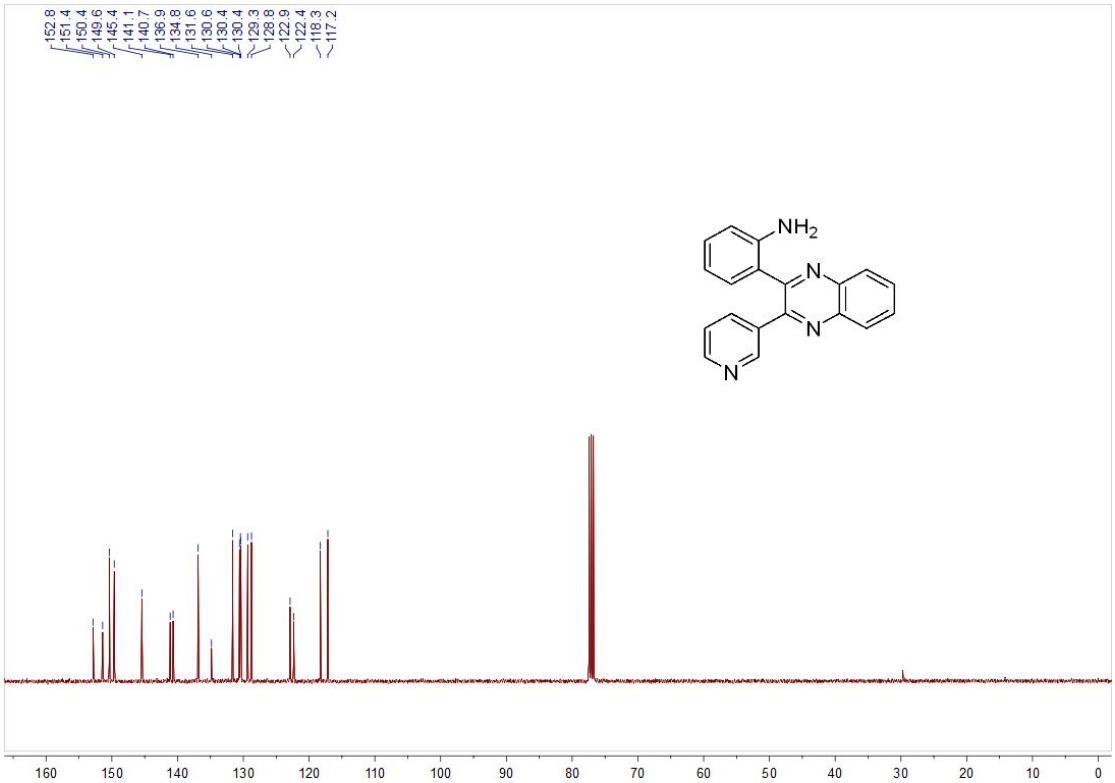
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ta**



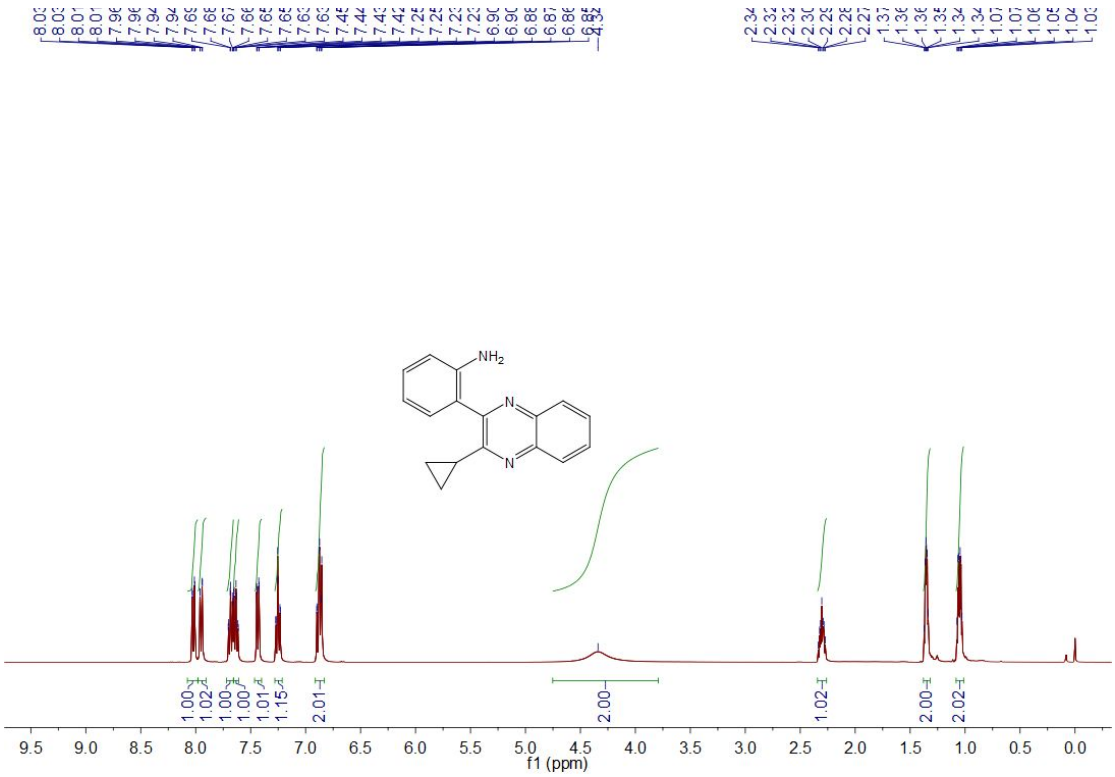
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **4ta**



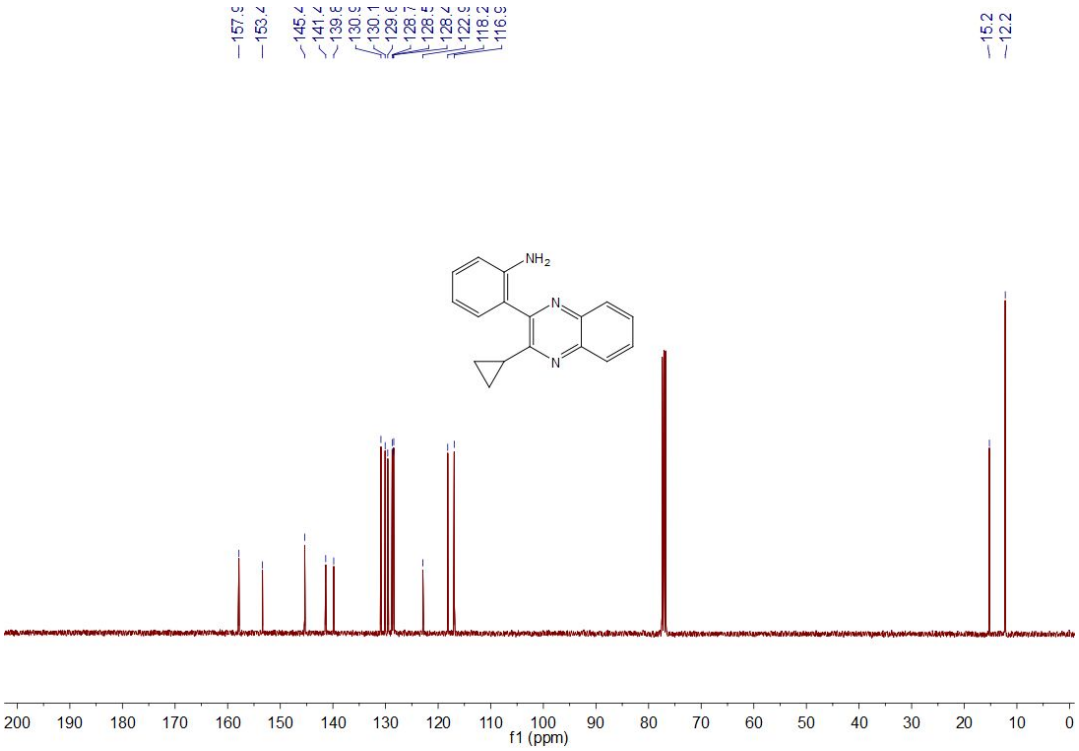
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4ua**



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **4ua**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4va**



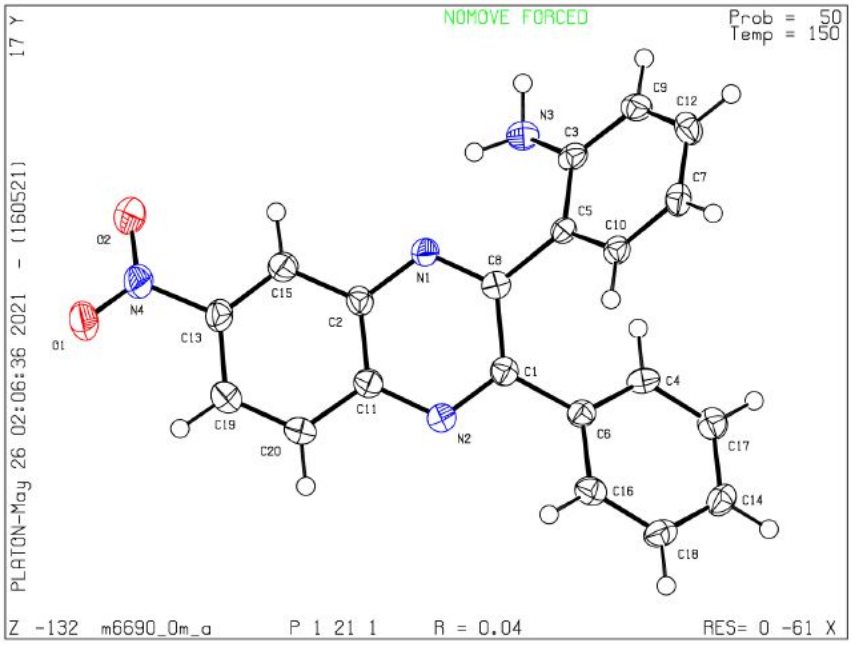
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **4va**

8. X-ray crystal structure of **3af'**.

Datablock: m6690_0m_a

```
Bond precision:  C-C = 0.0040 A          Wavelength=0.71073

Cell:            a=12.6717(6)    b=5.5867(2)         c=12.8577(7)
                 alpha=90        beta=114.975(2)     gamma=90
Temperature:     150 K

                 Calculated                  Reported
Volume           825.12(7)                   825.12(7)
Space group      P 21                        P 1 21 1
Hall group       P 2yb                       P 2yb
Moiety formula   C20 H14 N4 O2               C20 H14 N4 O2
Sum formula      C20 H14 N4 O2               C20 H14 N4 O2
Mr               342.35                      342.35
Dx,g cm-3        1.378                       1.378
Z                2                           2
Mu (mm-1)        0.093                       0.093
F000             356.0                       356.0
F000'            356.14
h,k,lmax         15,6,15                     15,6,15
Nref             3226[ 1788]                 3192
Tmin,Tmax        0.987,0.993                 0.697,0.746
Tmin'            0.984

Correction method= # Reported T Limits: Tmin=0.697 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.79/0.99       Theta(max)= 25.981

R(reflections)= 0.0394( 2683)      wR2(reflections)= 0.0861( 3192)

S = 1.067                  Npar= 236
```

The crystal parameters of **3af'**



ORTEP plot of **3af'** shown with 50% probability ellipsoids