Supporting Information

Copper-Catalyzed Synthesis of Quinazolines via Cascade Cyclization/ Hydrodehalogenation

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1. General methods

All solvents were purchased and without further purified and dried. Cuprous Iodide was purchased from Steam Chem Co., Ltd. Cesium carbonate was purchased from J&K. Chem Co., Ltd. Commercial materials were obtained from Adamas-beta, TCI shanghai, Alfa Aesar and Bidepharmatech.

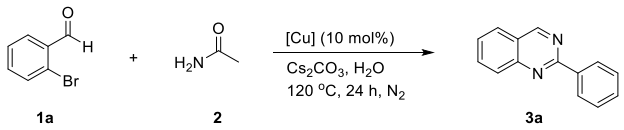
Reactions were monitored by thin-layer chromatography (TLC). TLC was performed using commercially precoated silica gel plates produced from Yantai Xinnuo Silica Gel development Co., Ltd, and visualized by UV light 254 nm or potassium permanganate solution. Organic solutions were concentrated under reduced pressure on XY-2000 rotary evaporator. Flash column chromatography was performed on Silica Gel (200-300 mesh) purchased from Yantai Xinnuo Silica Gel development Co., Ltd.

^{1}H and ^{13}C NMR spectra were recorded on Bruker instruments (400 MHz and 101 MHz, manual and auto simpler respectively) and internally referenced to tetramethylsilane (TMS) signal or residual protic solvent signals. ^{19}F NMR spectra were recorded on a Bruker instrument (376 MHz) referenced relative to $CFCl_3$. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Melting points were determined on a SGWX-4B melting point apparatus. High resolution mass spectrum (HRMS) was performed on a Bruker mior OTOF-QII instrument.

2. Optimization of reaction conditions

To a 10 mL Schlenk tube equipped with a teflon septum and a magnetic stir bar was charged with the catalyst (10 mol%), base (1.0 mmol) and a selected solvent (1.0 mL). Then 2-bromobenzaldehyde (**1a**, 1.0 mmol) and acetamide (**2**, 0.5 mmol) were added. After stirring at 120 ℃ for 24 h under N_2, the reaction was cooled to room temperature and the organic layer was extracted with ethyl acetate (2.0 mL) three times. The combined organic layer was dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give the desired quinazolines **3**.

Table S1. Optimization of Reaction Conditions



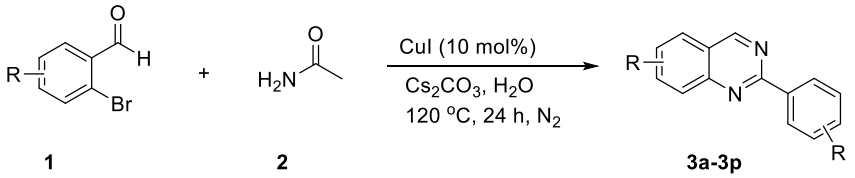
1a 2 3a

entry [a]	catalyst	base	solvent	Yield (%)
1	CuI	NaOH	H_2O	56
2	CuI	NaOH	toluene	trace
3	CuI	NaOH	DMSO	0
4	CuI	NaOH	MeCN	11
5	CuI	NaOH	NMP	0
6	CuI	NaOH	THF	5
7	CuI	NaOH	dioxane	9
8	CuCl	NaOH	H_2O	45
9	CuBr	NaOH	H_2O	14
10	CuCN	NaOH	H_2O	31
11	CuOAc	NaOH	H_2O	49
12	$Cu(OAc)_2$	NaOH	H_2O	0
13	$Cu(OTf)_2$	NaOH	H_2O	0
14	CuO	NaOH	H_2O	0
15	CuI	Cs_2CO_3	H_2O	80
16	CuI	K_2CO_3	H_2O	58
17	CuI	Et_3N	H_2O	0
18	CuI	DABCO	H_2O	0
19	-	Cs_2CO_3	H_2O	0
20[b]	CuI	Cs_2CO_3	H_2O	48
21[c]	CuI	Cs_2CO_3	H_2O	67
22[d]	CuI	Cs_2CO_3	H_2O	78
23[e]	CuI	Cs_2CO_3	H_2O	54
21[f]	CuI	Cs_2CO_3	H_2O	62

[a]Reaction conditions: 1a (1.0 mmol), 2 (0.5 mmol), base (1.0 mmol) and [Cu] (10 mol%) in solvent (1.0 mL) at 120 ℃ for 24 h. Isolated yield. [b]CuI (5 mol%). [c]110 ℃. [d]130 ℃.[e]Under Air. [f]NH_4OAc instead of **2a**.

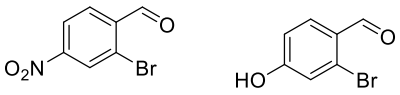
3. General procedure for Cu(I)-catalyzed synthesis of quinazolines

3.1 General Procedure A

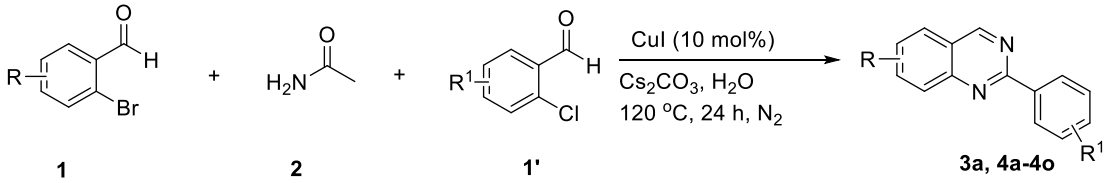


A Schlenk tube (10 mL) equipped with a teflon septum and a magnetic stir bar was charged with CuI (0.025 mmol, 10 mol%), Cs_2CO_3 (1.0 mmol) or NaOH (1.0 mmol). Then 2-bromoaryl aldehyde (1.0 mmol) or 2-iodoaryl aldehyde (1.0 mmol) and acetamide (0.5 mmol) were mixed in 1.0 mL of H_2O. After stirring at 120 ℃ for 24 h under N_2, the reaction was cooled to room temperature and the organic layer was extracted with ethyl acetate (2.0 mL) three times. The combined organic layer was dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give the desired quinazolines **3a-3p**.

Unsuccessful substrates



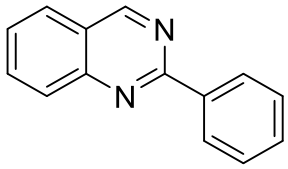
3.2 General Procedure B



A Schlenk tube (10 mL) equipped with a teflon septum and a magnetic stir bar was charged with CuI (0.025 mmol, 10 mol%) and Cs_2CO_3 (1.0 mmol). Then 2-bromoaryl aldehyde (**1**, 0.3 mmol), acetamide (**2**, 0.5 mmol) and 2-chloraryl aldehyde (**1'**, 0.5 mmol) were mixed in 1.0 mL of H_2O. After stirring at 120 ℃ for 24 h under N_2, the reaction was cooled to room temperature and the organic layer was extracted with ethyl acetate (2.0 mL) three times. The combined organic layer was dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give the desired quinazolines **3a** and **4a-4o**.

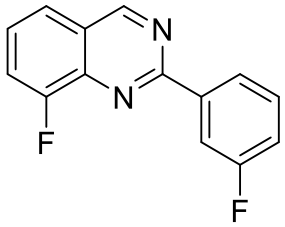
4. Characterization data of quinazolines

2-phenylquinazoline (3a)



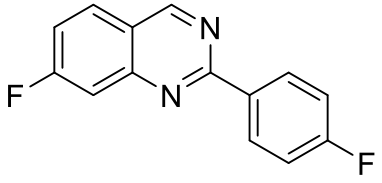
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 80% yield (41.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.63 – 8.61 (m, 2H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.89 (t, *J* = 8.6 Hz, 2H), 7.60 (t, *J* = 8.6 Hz, 1H), 7.56 – 7.50 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 160.5, 150.8, 138.1, 134.1, 130.6, 128.7, 128.6, 127.3, 127.2, 123.6. Analytical data matched well with that reported in literature.[1]

8-fluoro-2-(3-fluorophenyl)quinazoline (3b)



The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 54% yield (32.6 mg). mp. 116-117 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, *J* = 1.6 Hz, 1H), 8.46 (dt, *J* = 1.3, 1.3 Hz, 1H), 8.38 – 8.35 (m, 1H), 7.76 – 7.74 (m, 1H), 7.64 – 7.55 (m, 2H), 7.53 – 7.48 (m, 1H), 7.24 – 7.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (d, *J* = 246.4 Hz), 160.4, 157.4 (d, *J* = 8.1 Hz), 141.1 (d, *J* = 8.1 Hz), 139.9, 130.1 (d, *J* = 8.1 Hz), 127.4 (d, *J* = 21.2 Hz), 125.0, 124.4 (d, *J* = 3.0 Hz), 122.8 (d, *J* = 5.1 Hz), 118.3 (d, *J* = 18.2 Hz), 117.9 (d, *J* = 21.2 Hz), 115.6 (d, *J* = 23.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.1, -125.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_9N_2F_2$ 243.0734; found 243.0742.

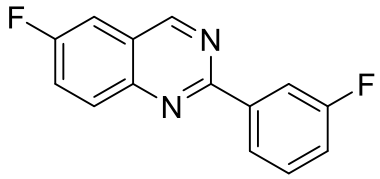
7-fluoro-2-(4-fluorophenyl)quinazoline (3c)



The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 58% yield (35.1 mg). mp. 160-161 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ

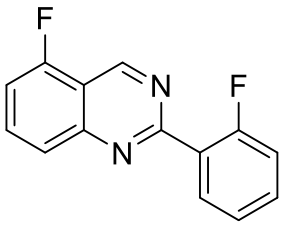
9.40 (d, *J* = 0.9, 1H), 8.64 – 8.60 (m, 2H), 7.96 – 7.92 (m, 1H), 7.67 (dd, *J* = 9.8, 2.4 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.21 (t, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1 (d, *J* = 257.5 Hz), 164.9 (d, *J* = 252.5 Hz), 160.9, 160.0, 154.6, 146.0, 137.6, 133.8, 130.8 (d, *J* = 11.1 Hz), 129.7 (d, *J* = 18.2 Hz), 120.8, 118.0 (d, *J* = 26.3 Hz), 115.6 (d, *J* = 22.2 Hz), 112.4 (d, *J* = 21.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.3, -109.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_8N_2F_2Na$ 265.0553; found 265.0554.

8-chloro-2-(3-chlorophenyl)quinazoline (3d)



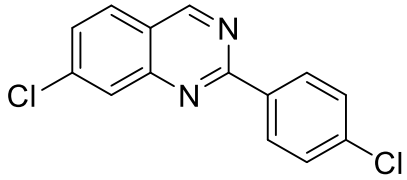
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 61% yield (36.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.39 (d, *J* = 7.8 Hz, 1H), 8.32 – 8.29 (m, 1H), 8.10 (dd, *J* = 9.2, 5.0 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.55 (dd, *J* = 7.6, 2.7 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.22 – 7.18 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (d, *J* = 245.4 Hz), 160.6 (d, *J* = 253.5 Hz), 159.9 (d, *J* = 5.1 Hz), 147.8, 140.1, 131.5 (d, *J* = 9.1 Hz), 130.1 (d, *J* = 8.1 Hz), 124.8 (d, *J* = 26.3 Hz), 124.2, 124.1 (d, *J* = 3.0 Hz), 117.6 (d, *J* = 21.2 Hz), 115.3 (d, *J* = 23.2 Hz), 110.2 (d, *J* = 21.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.0, -113.0. Analytical data matched well with that reported in literature.[2]

5-fluoro-2-(2-fluorophenyl)quinazoline (3e)



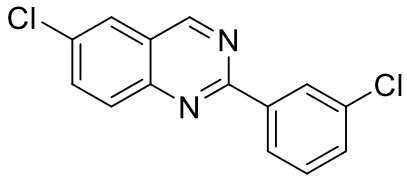
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 60% yield (36.3 mg). mp. 82-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.20 – 8.16 (m, 1H), 7.95 – 7.87 (m, 2H), 7.51 – 7.49 (m, 1H), 7.34 – 7.30 (m, 2H), 7.28 – 7.22 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, *J* = 256.5 Hz), 158.1 (d, *J* = 260.6 Hz), 154.9 (d, *J* = 4.0 Hz), 151.3, 134.4 (d, *J* = 9.1 Hz), 132.2 (d, *J* = 2.0 Hz), 132.0 (d, *J* = 9.1 Hz) 126.6, 124.7 (d, *J* = 4.0 Hz), 124.3 (d, *J* = 4.0 Hz), 117.0 (d, *J* = 22.2 Hz), 111.6 (d, *J* = 19.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.6, -122.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_8N_2F_2Na$ 265.0553; found 265.0557.

7-chloro-2-(4-chlorophenyl)quinazoline (3f)



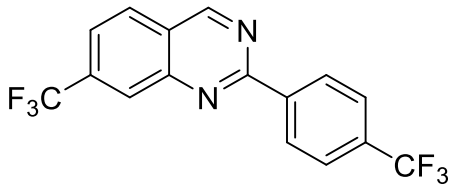
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 50% yield (34.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.57 – 8.55 (m, 2H), 8.08 (d, *J* = 2.1 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.58 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.52 – 7.49 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 160.2, 151.2, 140.6, 137.3, 136.1, 130.0, 128.9, 128.7, 128.4, 127.7, 122.0. Analytical data matched well with that reported in literature.[3]

6-chloro-2-(3-chlorophenyl)quinazoline (3g)



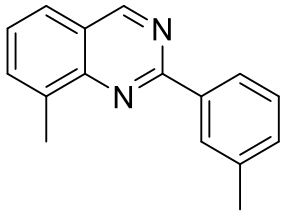
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow oil in 47% yield (32.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 8.61 (d, *J* = 2.2 Hz, 1H), 8.51 – 8.48 (m, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.93 (d, *J* = 2.3 Hz, 1H), 7.85 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.49 – 7.46 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 159.6, 149.2, 139.4, 135.3, 134.9, 133.3, 130.8, 130.4, 129.9, 128.7, 126.7, 125.9, 124.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_9N_2Cl_2$ 275.0143; found 275.0149.

7-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)quinazoline (3h)



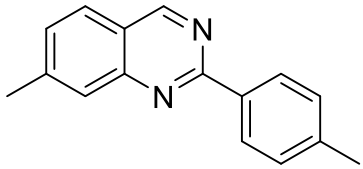
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 67% yield (57.3 mg). mp. 147-148 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.76 (d, *J* = 8.4 Hz, 2H), 8.43 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.82 (dd, *J* = 13.3, 8.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 150.1, 140.5, 136.0, 135.7, 132.9, 132.5, 129.0, 128.5, 126.8 (q, *J* = 1.0 Hz, 1H), 125.7 (q, *J* = 0.9 Hz, 1H), 124.8, 124.7, 123.6 (q, *J* = 0.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8, -63.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_9N_2F_6$ 343.0670; found 343.0672.

8-methyl-2-(m-tolyl)quinazoline (3i)



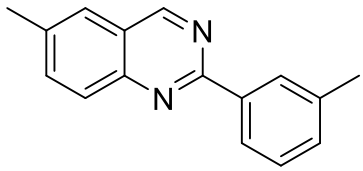
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 77% yield (45.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.40 – 8.38 (m, 2H), 7.68 – 7.65 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 2.79 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 160.1, 149.8, 138.2, 137.2, 133.9, 131.3, 129.1, 128.5, 126.9, 125.7, 124.8, 123.5, 21.6, 17.0. Analytical data matched well with that reported in literature.[4]

7-methyl-2-(p-tolyl)quinazoline (3j)



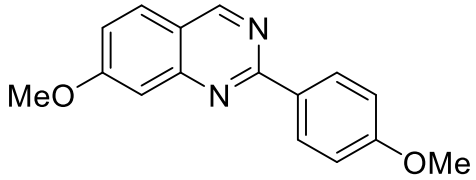
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 80% yield (46.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.42 (d, *J* = 8.2 Hz, 2H), 7.77 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 2.52 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 159.8, 151.1, 145.1, 140.7, 135.5, 129.4, 129.3, 128.5, 127.5, 126.8, 121.8 22.4, 21.5. Analytical data matched well with that reported in literature.[5]

6-methyl-2-(m-tolyl)quinazoline (3k)



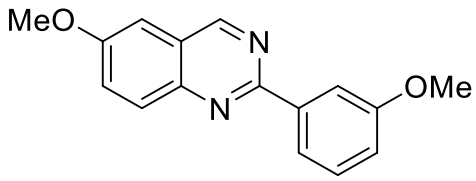
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 82% yield (48.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.33 – 8.30 (m, 2H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.66 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.61 (s, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.3 Hz, 1H), 2.50 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 159.8, 149.4, 138.3, 138.1, 137.4, 136.4, 131.2, 129.0, 128.6, 128.3, 125.8, 125.6, 123.6, 21.7, 21.6. Analytical data matched well with that reported in literature.[6]

7-methoxy-2-(4-methoxyphenyl)quinazoline (3l)



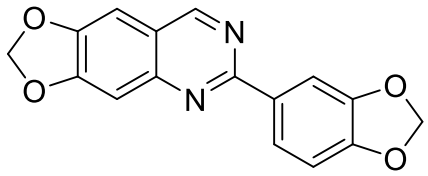
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 83% yield (55.2 mg). mp. 84-85 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.54 (d, *J* = 9.0 Hz, 2H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.18 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.99 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 161.8, 161.4, 158.9, 153.2, 130.9, 130.1, 128.4, 120.2, 118.9, 113.9, 106.0, 55.8, 55.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}N_2O_2Na$ 289.0953; found 289.0957.

6-methoxy-2-(3-methoxyphenyl)quinazoline (3m)



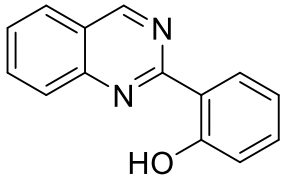
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 85% yield (56.5 mg). mp. 108-109 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, *J* = 0.7 Hz, 1H), 8.19 – 8.13 (m, 2H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.55 (dd, J = 9.3, 2.8 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 2.7 Hz, 1H), 7.06 – 7.03 (m, 1H), 3.96 (d, *J* = 7.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 159.2, 158.8, 158.3, 147.0, 139.7, 130.2, 129.6, 127.2, 124.6, 120.8, 116.9, 112.7, 103.9, 55.8, 55.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}N_2O_2Na$ 289.0953; found 289.0961.

6-(benzo[d][1,3]dioxol-5-yl)-[1,3]dioxolo[4,5-g]quinazoline (3n)



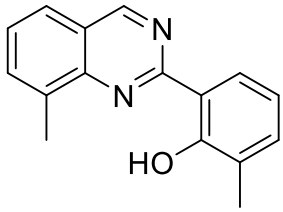
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 78% yield (57.3 mg). mp.168-169 ^{o}C.^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.14 (dd, *J* = 8.2, 1.7 Hz, 1H), 8.04 (d, *J* = 1.7 Hz, 1H), 7.30 (s, 1H), 7.10 (s, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.15 (s, 2H), 6.04 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 157.4, 154.1, 150.3, 149.5, 148.1, 132.7, 122.9, 120.5, 108.4, 108.3, 104.9, 102.2, 101.9, 101.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{11}N_2O_4$ 295.0719; found 295.0724.

2-(quinazolin-2-yl)phenol (3o)



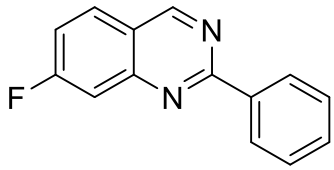
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 64% yield (35.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.68 (s, 1H), 9.42 (s, 1H), 8.59 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.96 – 7.87 (m, 3H), 7.60 – 7.56 (m, 1H), 7.38 – 7.33 (m, 1H), 7.01 (d, *J* = 8.2, 1H), 6.96 – 6.91 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 160.6, 135.0, 133.3, 129.7, 127.6, 127.5, 127.1, 123.1, 119.1, 117.9. Analytical data matched well with that reported in literature.[7]

2-methyl-6-(8-methylquinazolin-2-yl)phenol (3p)



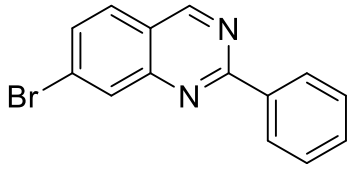
The title compound was prepared according to the general procedure A and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 69% yield (43.1 mg). mp. 96-97 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.25 (s, 1H), 9.45 – 9.43 (m, 1H), 8.54 (d, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 6.2 Hz, 2H), 7.54 – 7.50 (m, 1H), 7.31 (d, *J* = 7.0 Hz, 1H), 6.94 – 6.89 (m, 1H), 2.80 (d, *J* = 4.9 Hz, 3H), 2.38 (d, *J* = 4.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 159.4, 134.9, 134.1, 127.3, 127.1, 126.5, 125.2, 122.9, 118.4, 17.4, 16.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O$ 251.1184; found 251.1192.

7-fluoro-2-phenylquinazoline (4a)



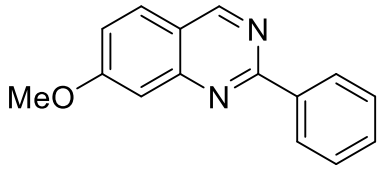
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 48% yield (26.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.62 – 8.60 (m, 2H), 7.94 (dd, *J* = 8.9, 5.9 Hz, 1H), 7.70 (dd, *J* = 9.9, 2.7 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.40 – 7.35 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 (d, *J* = 256.5 Hz), 161.9, 160.0, 152.5 (d, *J* = 14.1 Hz), 137.7, 131.0, 129.8 (d, *J* = 11.1 Hz), 128.7, 120.9, 118.0 (d, *J* = 25.3 Hz), 112.5 (d, *J* = 20.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.5. Analytical data matched well with that reported in literature.[2]

7-bromo-2-phenylquinazoline (4b)



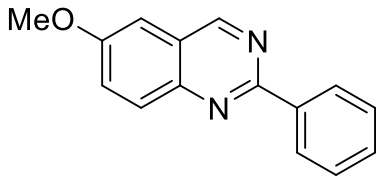
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 41% yield (29.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.61 – 8.59 (m, 2H), 8.28 (t, *J* = 1.0 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.69 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.54 – 7.52 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 160.3, 151.4, 137.6, 131.2, 131.0, 131.0, 128.9, 128.7, 128.3, 122.2. Analytical data matched well with that reported in literature.[8]

7-methoxy-2-phenylquinazoline (4c)



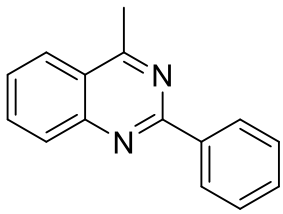
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 62% yield (36.6 mg). mp. 167-168 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 – 9.27 (m, 1H), 8.59 – 8.57 (m, 2H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.56 – 7.50 (m, 3H), 7.36 (d, *J* = 2.6 Hz, 1H), 7.22 (dd, J = 8.8, 2.4 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 161.6, 159.0, 153.2, 138.2, 130.5, 128.6, 128.5, 128.4, 120.8, 119.2, 106.2, 55.8. Analytical data matched well with that reported in literature.[9]

6-methoxy-2-phenylquinazoline (4d)



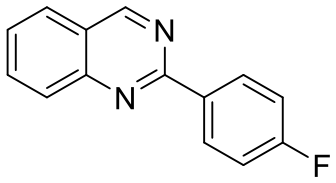
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 68% yield (40.1 mg). mp. 152-153 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.58 – 8.56 (m, 2H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.57 – 7.48 (m, 4H), 7.15 (d, *J* = 2.8 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 158.9, 158.3, 147.0, 138.2, 130.2, 130.2, 128.6, 128.2, 127.2, 124.5, 103.9, 55.8. Analytical data matched well with that reported in literature.[7]

4-methyl-2-phenylquinazoline (4e)



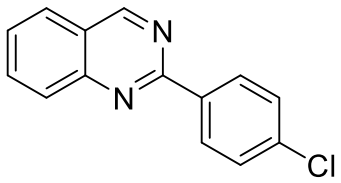
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 64% yield (35.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.2 Hz, 2H), 8.10 – 8.06 (m, 2H), 7.88 – 7.84 (m, 1H), 7.60 – 7.49 (m, 4H), 3.02 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 160.2, 150.4, 138.3, 133.5, 130.4, 129.3, 128.6, 128.6, 126.9, 125.0, 123.0, 22.1. Analytical data matched well with that reported in literature.[10]

2-(4-fluorophenyl)quinazoline (4f)



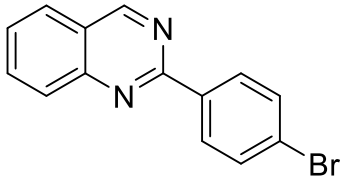
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 46% yield (25.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.63 – 8.60 (m, 2H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.89 (t, *J* = 7.5 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.22 – 7.18 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7 (d, *J* = 250.5 Hz), 160.5, 160.1, 150.7, 134.2, 130.7 (d, *J* = 9.1 Hz), 128.6, 127.3 (d, *J* = 13.1 Hz), 123.5, 115.6 (d, *J* = 21.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.5. Analytical data matched well with that reported in literature.[3]

2-(4-chlorophenyl)quinazoline (4g)



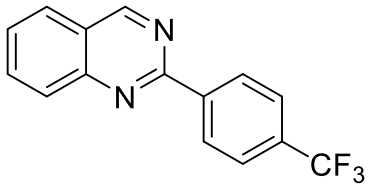
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a white solid in 55% yield (33.0 mg). mp. 124-125 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.58 – 8.55 (m, 2H), 8.10 – 8.04 (m, 1H), 7.92 – 7.88 (m, 2H), 7.63 – 7.59 (m, 1H), 7.51 – 7.47 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 160.0, 150.7, 136.8, 136.5, 134.3, 129.9, 128.8, 128.6, 127.5, 127.2, 123.6. Analytical data matched well with that reported in literature.[1]

2-(4-bromophenyl)quinazoline (4h)



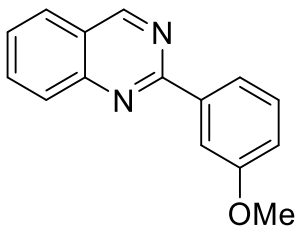
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 44% yield (31.4 mg). mp. 124-125 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.51 – 8.48 (m, 2H), 8.09 – 8.06 (d, *J* = 8.1 Hz, 1H), 7.92 – 7.89 (m, 2H), 7.67 – 7.60 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 160.1, 150.7, 137.0, 134.3, 131.8, 130.2, 128.6, 127.5, 127.2, 125.4, 123.7. Analytical data matched well with that reported in literature.[1]

2-(4-(trifluoromethyl)phenyl)quinazoline (4i)



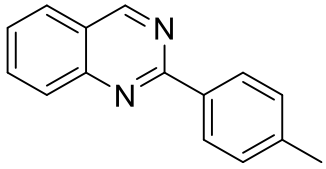
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 53% yield (36.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.74 (d, *J* = 8.4 Hz, 2H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.94 (t, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 159.6, 150.7, 141.3, 134.4, 128.8, 128.8, 127.9, 127.2, 125.5 (q, *J* = 3.7 Hz), 123.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. Analytical data matched well with that reported in literature.[7]

2-(3-methoxyphenyl)quinazoline (4j)



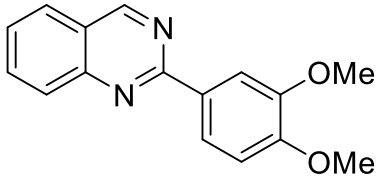
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 58% yield (34.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 8.10 (s, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.81 (t, *J* = 8.5 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 6.99 – 6.97 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 160.5, 160.0, 150.7, 139.5, 134.1, 129.7, 128.7, 127.3, 127.1, 123.7, 121.2, 117.3, 113.0, 55.5. Analytical data matched well with that reported in literature.[1]

2-(p-tolyl)quinazoline (4k)



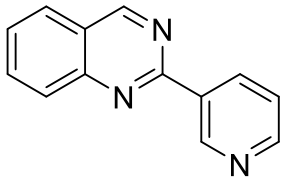
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a pale yellow solid in 57% yield (31.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.51 (d, *J* = 8.3 Hz, 2H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.60 – 7.57 (m, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 160.5, 150.8, 140.9, 135.3, 134.1, 129.4, 128.6, 128.5, 127.1, 127.1, 123.5, 21.5. Analytical data matched well with that reported in literature.[1]

2-(3,4-dimethoxyphenyl)quinazoline (4l)



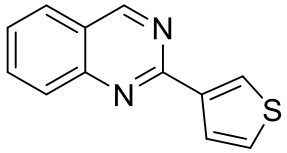
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 74% yield (49.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (d, *J* = 0.9 Hz, 1H), 8.26 (dd, *J* = 8.5, 2.1 Hz, 1H), 8.20 (d, *J* = 2.0 Hz, 1H), 8.06 – 8.03 (m, 1H), 7.89 – 7.85 (m, 2H), 7.58 – 7.54 (m, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 4.06 (s, 3H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 160.4, 151.4, 150.8, 149.0, 134.1, 130.9, 128.4, 127.2, 126.9, 123.3, 122.0, 111.1, 110.8, 56.0, 56.0. Analytical data matched well with that reported in literature.[11]

2-(pyridin-3-yl)quinazoline (4m)



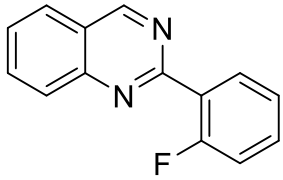
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5/1) to afford a yellow solid in 40% yield (20.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 9.48 (d, *J* = 6.1 Hz, 1H), 8.88 – 8.86 (m, 1H), 8.74 (d, *J* = 4.9 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.45 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 159.2, 151.2, 150.7, 150.3, 135.8, 134.5, 133.6, 128.7, 127.8, 127.2, 123.8, 123.5. Analytical data matched well with that reported in literature.[12]

2-(thiophen-3-yl)quinazoline (4n)



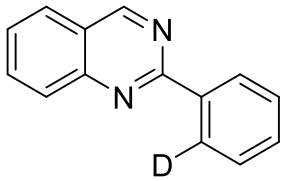
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 28% yield (14.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.43 (dd, *J* = 3.1, 1.2 Hz, 1H), 8.06 – 8.01 (m, 2H), 7.89 – 7.84 (m, 2H), 7.58 – 7.54 (m, 1H), 7.41 (q, *J* = 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 158.3, 150.7, 142.1, 134.2, 128.4, 128.3, 127.7, 127.2, 127.0, 126.1, 123.4. Analytical data matched well with that reported in literature.[13]

2-(2-fluorophenyl)quinazoline (4o)



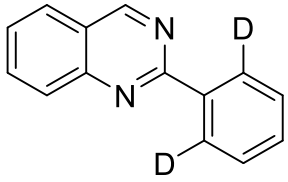
The title compound was prepared according to the general procedure B and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford a yellow solid in 51% yield (28.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 8.18 – 8.11 (m, 2H), 7.99 – 7.92 (m, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.27 – 7.24 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, *J* = 255.5 Hz), 160.5, 159.8 (d, *J* = 7.1 Hz), 150.6, 134.4, 132.2 (d, *J* = 2.0 Hz), 131.7 (d, *J* = 8.1 Hz), 128.7, 127.9, 127.1, 124.3 (d, *J* = 4.0 Hz), 123.3, 116.9 (d, *J* = 22.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.1. Analytical data matched well with that reported in literature.[14]

2-(phenyl-2-*d*)quinazoline (3a-d_1)



Yellow solid, 78% yield (40.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.62 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.51 (m, 3H).

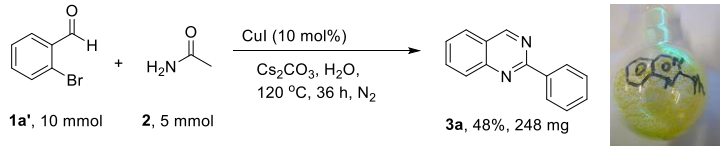
2-(phenyl-2,6-d_2)quinazoline (3a-d_2)



Yellow solid, 90% yield (46.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.92 (dd, *J* = 12.1, 8.1 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.56 – 7.52 (m, 3H).

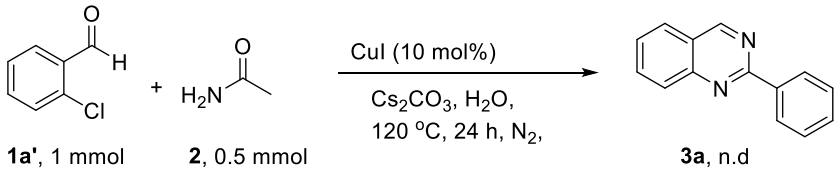
5. Mechanistic studies

Scheme S1. 2.5 mmol-scale experiment



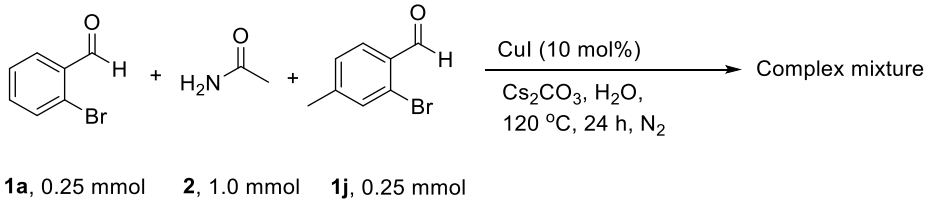
To a 10 mL Schlenk tube equipped with a teflon septum and a magnetic stir bar was charged with CuI (0.25 mmol, 10 mol%), Cs_2CO_3 (10.0 mmol) and 10 mL of H_2O. Then 2-bromobenzaldehyde (**1a**, 10 mmol) and acetamide (**2**, 5.0 mmol) were added to above mixture. After stirring at 120 ℃ for 36 h, the reaction was cooled to room temperature. The organic layer was extracted with ethyl acetate (10 mL) three times. The combined organic layer was dried over Na_2SO_4, and concentrated in vacuo. The desired product **3a** was obtained in 48% yield.

Scheme S2. Investigations of the effect of 2-chlorobenzaldehyde



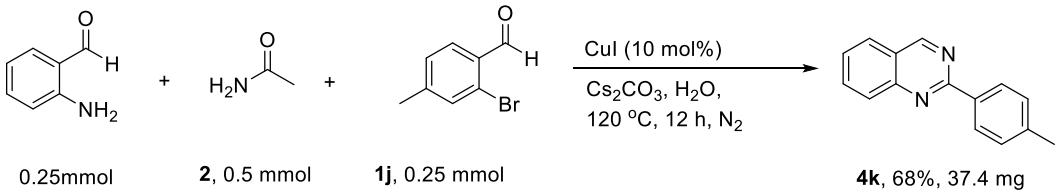
To a 10 mL Schlenk tube equipped with a teflon septum and a magnetic stir bar was charged with CuI (0.025 mmol, 10 mol%), Cs_2CO_3 (1.0 mmol) and 1.0 mL of H_2O. Then 2-chlorobenzaldehyde (**1a'**, 1.0 mmol) and acetamide (**2**, 0.5 mmol) were added to above mixture. After stirring at 120 ℃ for 24 h under N_2, the reaction was cooled to room temperature. The organic layer was extracted with ethyl acetate (2.0 mL) three times. The combined organic layer was dried over Na_2SO_4, and concentrated in vacuo. The desired product **3a** was not observed.

Scheme S3. Investigations of the effect of two different 2-bromobenzaldehydes



To a 10 mL Schlenk tube equipped with a teflon septum and a magnetic stir bar was charged with CuI (0.025 mmol, 10 mol%), Cs_2CO_3 (1.0 mmol) and 1.0 mL of H_2O. Then 2-bromobenzaldehyde (**1a**, 0.25 mmol), acetamide (**2**, 1.0 mmol), and 2-bromo-4-methylbenzaldehyde (**2**, 0.25 mmol) were added to above mixture. After stirring at 120 ℃ for 24 h under N_2, the reaction was cooled to room temperature. The organic layer was extracted with ethyl acetate (2.0 mL) three times. The combined organic layer was dried over Na_2SO_4, and concentrated in vacuo, a complex mixture was obtained.

Scheme S4. Investigations of the role of 2-aminobenzaldehyde

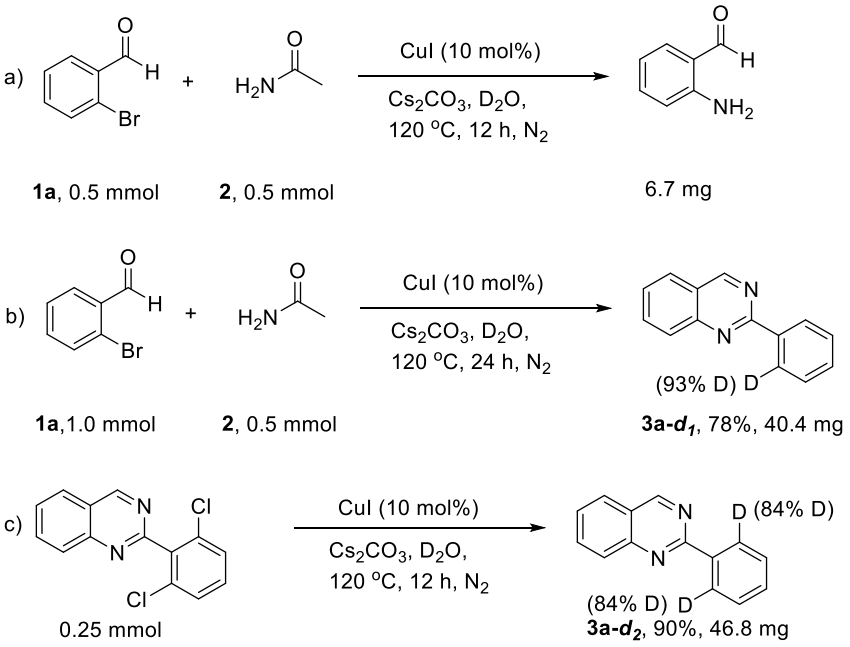


0.25mmol **2**, 0.5 mmol **1j**, 0.25 mmol **4k**, 68%, 37.4 mg

To a 10 mL Schlenk tube equipped with a teflon septum and a magnetic stir bar was charged with CuI (0.025 mmol, 10 mol%), Cs_2CO_3 (0.5 mmol) and 1.0 mL of H_2O. Then 2-aminobenzaldehyde (**1a**, 0.25 mmol), acetamide (**2**, 0.5 mmol), and 2-bromo-4-methylbenzaldehyde (**1j**, 0.25 mmol) were added to above mixture. After stirring at 120 ℃ for 12 h under N_2, the reaction was cooled to room temperature. The organic layer was extracted with ethyl acetate (2.0 mL) three times. The combined organic layer was dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give quinazoline **4k** in 68% yield (37.4 mg).

These results illustrated that the 2-aminobenzaldehyde may be served as an intermediate for this reaction.

Scheme S5. Deuterium labeling experiments



a) To a 10 mL Schlenk tube equipped with a teflon septum and a magnetic stir bar was charged with CuI (0.025 mmol, 10 mol%), Cs_2CO_3 (0.5 mmol) and 1.0 mL of D_2O. Then 2-bromobenzaldehyde (**1a**, 0.5 mmol) and acetamide (**2**, 0.5 mmol) were added to above mixture. After stirring at 120 ℃ for 12 h under N_2, the reaction was cooled to room temperature. The organic layer was extracted with ethyl acetate (2.0 mL) three times. The combined organic layer was dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel. The desired 2-aminobenzaldehyde was successfully obtained (6.7 mg).

b) To a 10 mL Schlenk tube equipped with a teflon septum and a magnetic stir bar was charged with CuI (0.025 mmol, 10 mol%), Cs_2CO_3 (1.0 mmol) and 1.0 mL of D_2O. Then

2-bromobenzaldehyde (**1a**, 1.0 mmol) and acetamide (**2**, 0.5 mmol) were added to above mixture. After stirring at 120 ℃ for 24 h under N_2, the reaction was cooled to room temperature. The organic layer was extracted with ethyl acetate (2.0 mL) three times. The combined organic layer was dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel. The desired quinazoline **3a-*d*$_1$** was obtained in 78% yield (40.4 mg).

c) To a 10 mL Schlenk tube equipped with a teflon septum and a magnetic stir bar was charged with CuI (0.025 mmol, 10 mol%), Cs_2CO_3 (0.5 mmol) and 1.0 mL of D_2O. Then 2-(2,6-dichlorophenyl)quinazoline (0.25 mmol) was added to above mixture. After stirring at 120 ℃ for 12 h, the reaction was cooled to room temperature. The organic layer was extracted with ethyl acetate (2.0 mL) three times. The combined organic layer was dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give quinazoline **3a-*d*$_2$** in 90% yield (46.8 mg).

The above results illustrated that the reaction proceeded via hydrodehalogenation and H_2O was used as hydrogen source.

6. References

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7. NMR Spectra of the described compounds

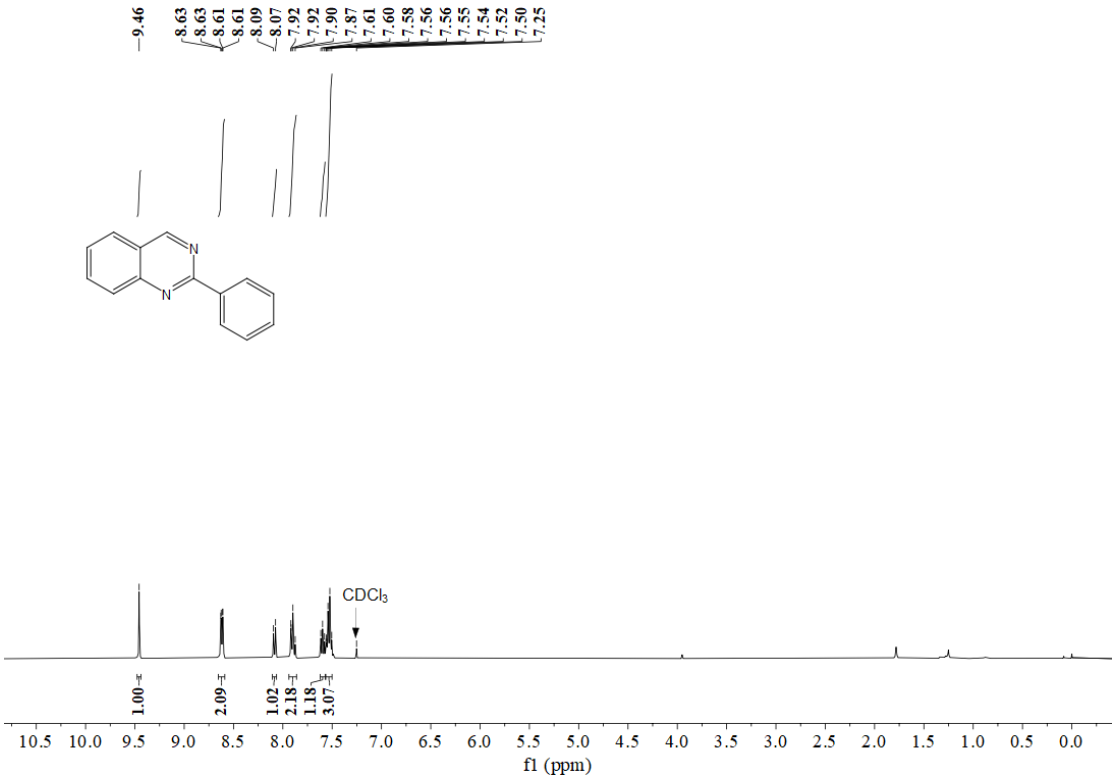


Figure S1. ^{1}H NMR Spectrum of **3a**

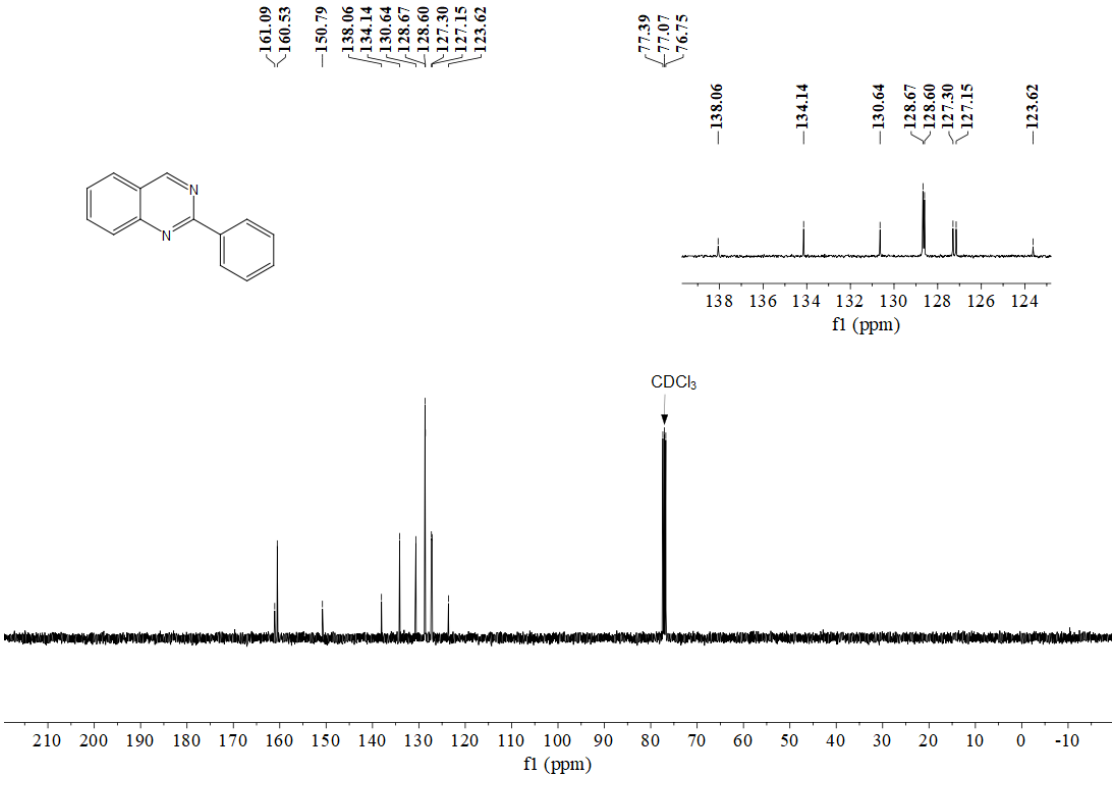


Figure S2. ^{13}C NMR Spectrum of **3a**

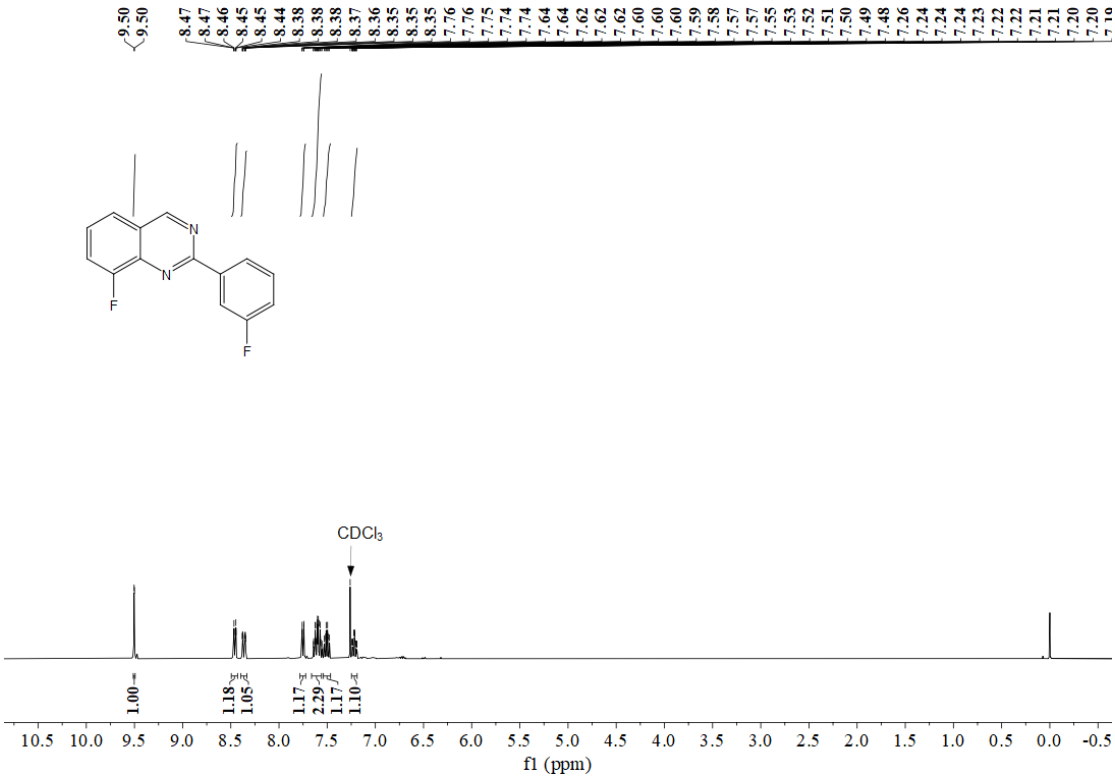


Figure S3. ^{1}H NMR Spectrum of **3b**

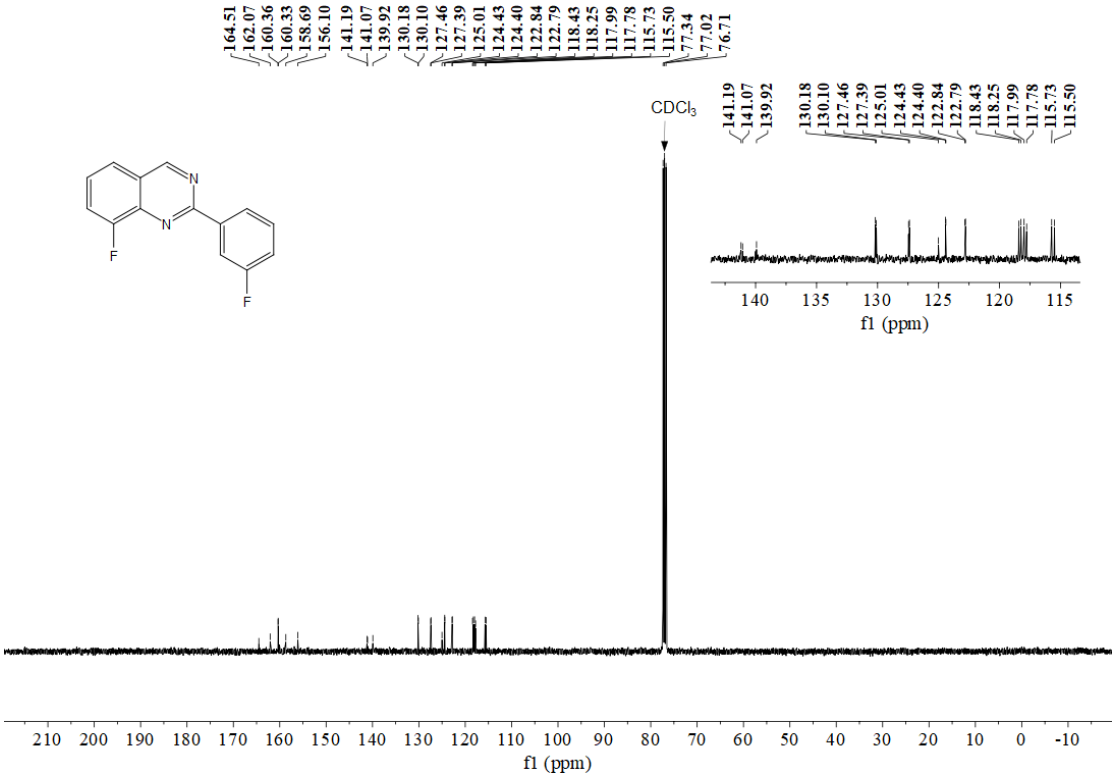


Figure S4. ^{13}C NMR Spectrum of **3b**

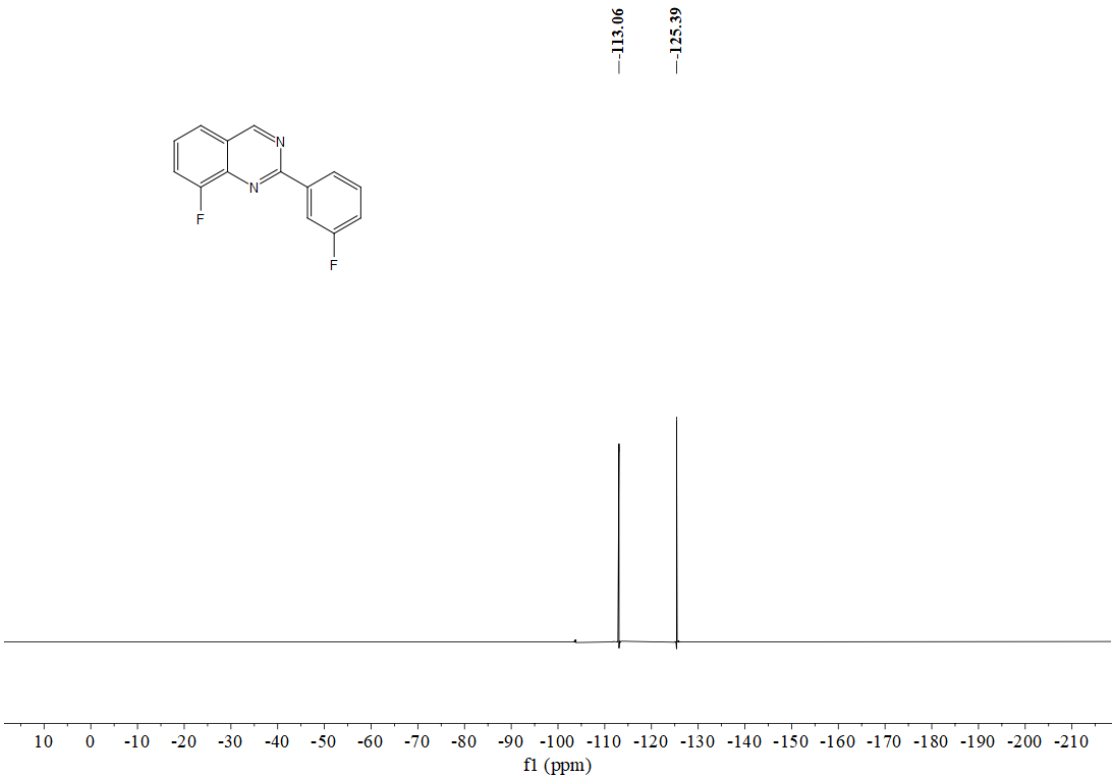


Figure S5. ^{19}F NMR Spectrum of **3b**

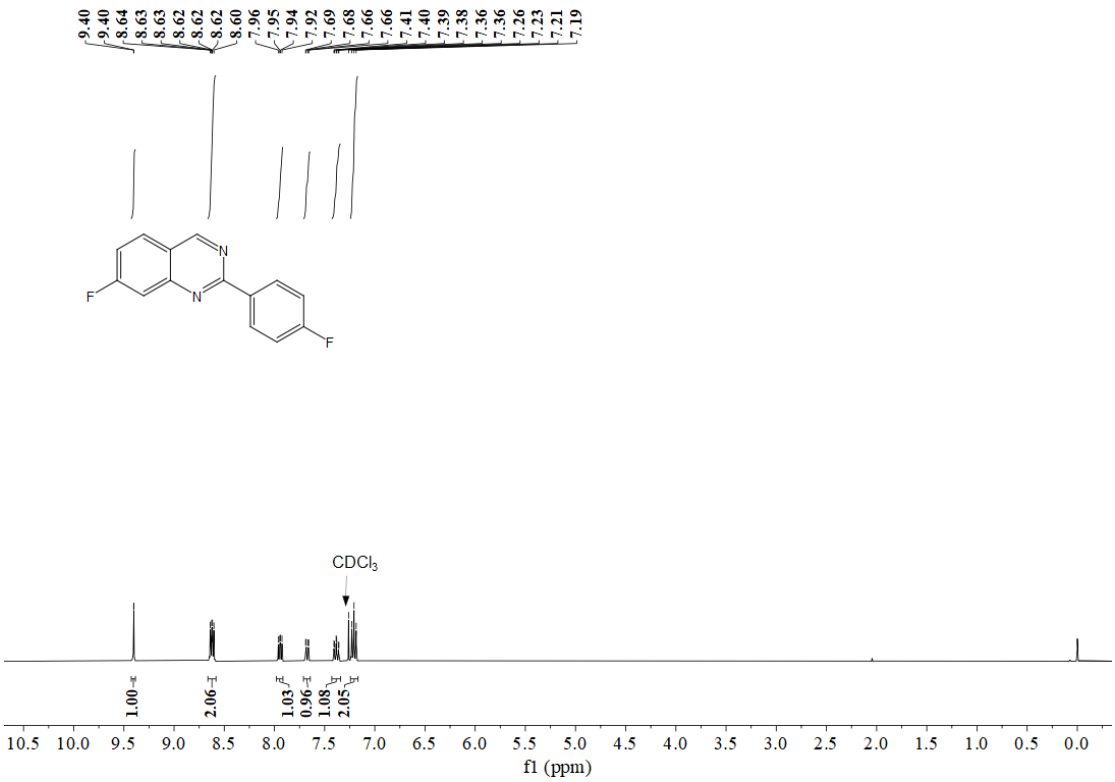


Figure S6. ^{1}H NMR Spectrum of **3c**

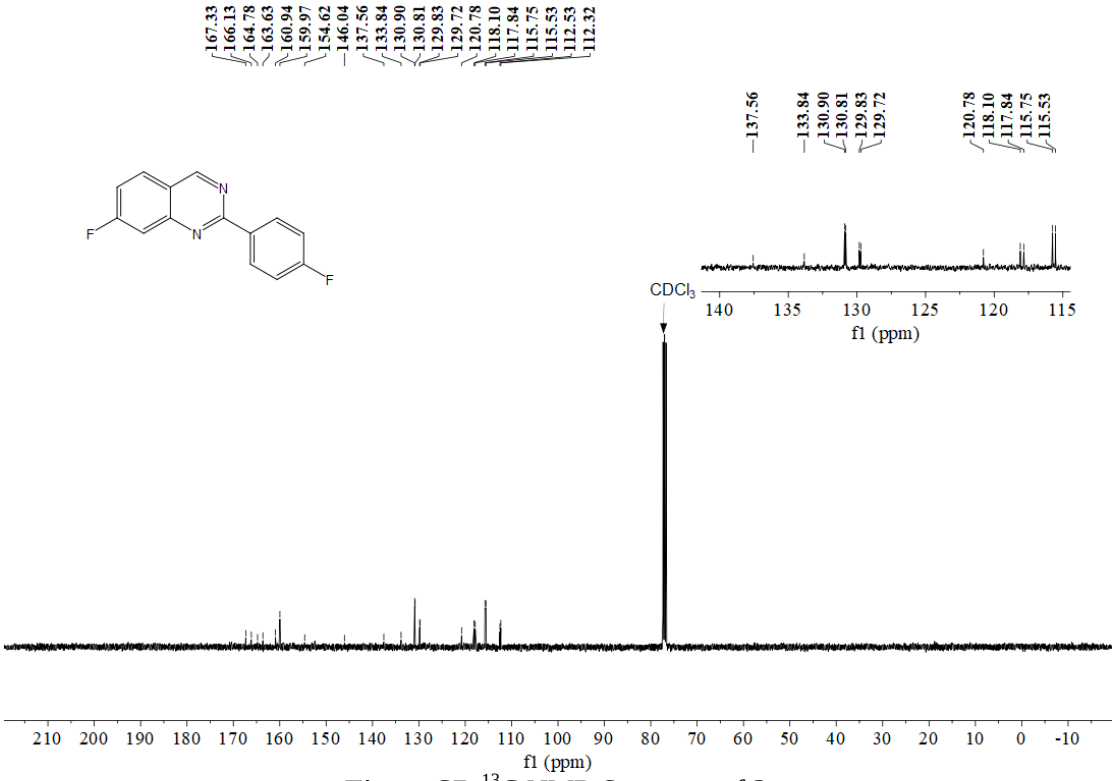


Figure S7. ^{13}C NMR Spectrum of **3c**

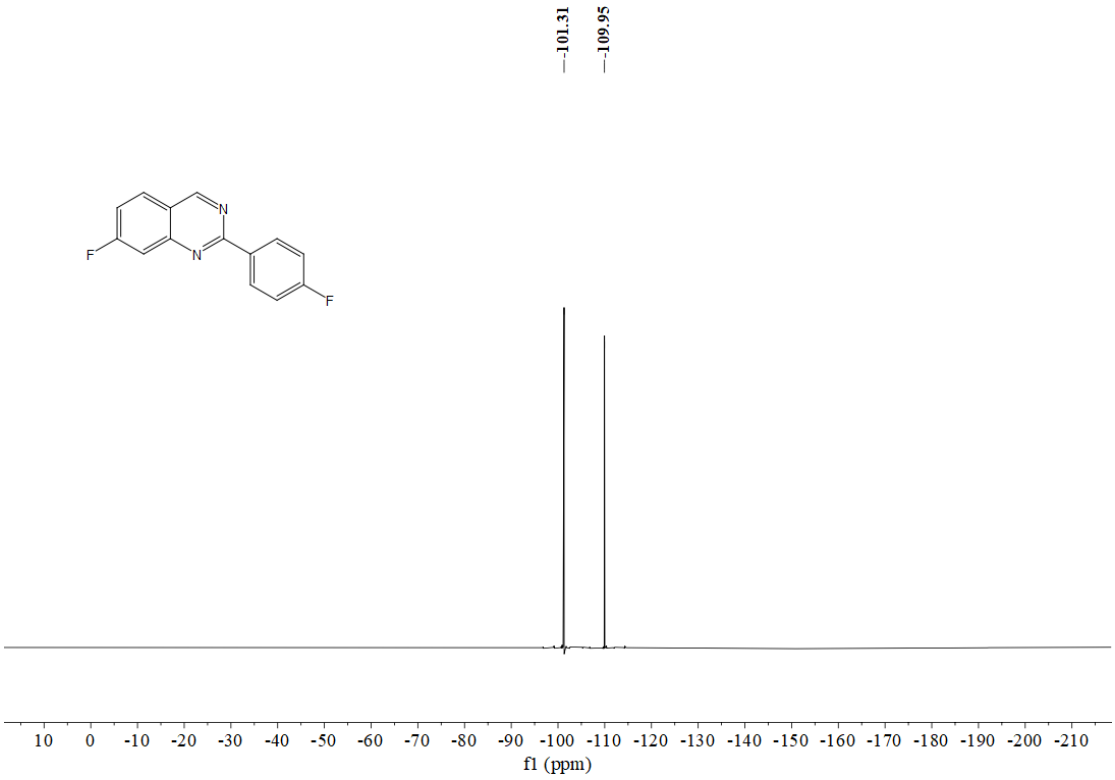


Figure S8. ^{19}F NMR Spectrum of **3c**

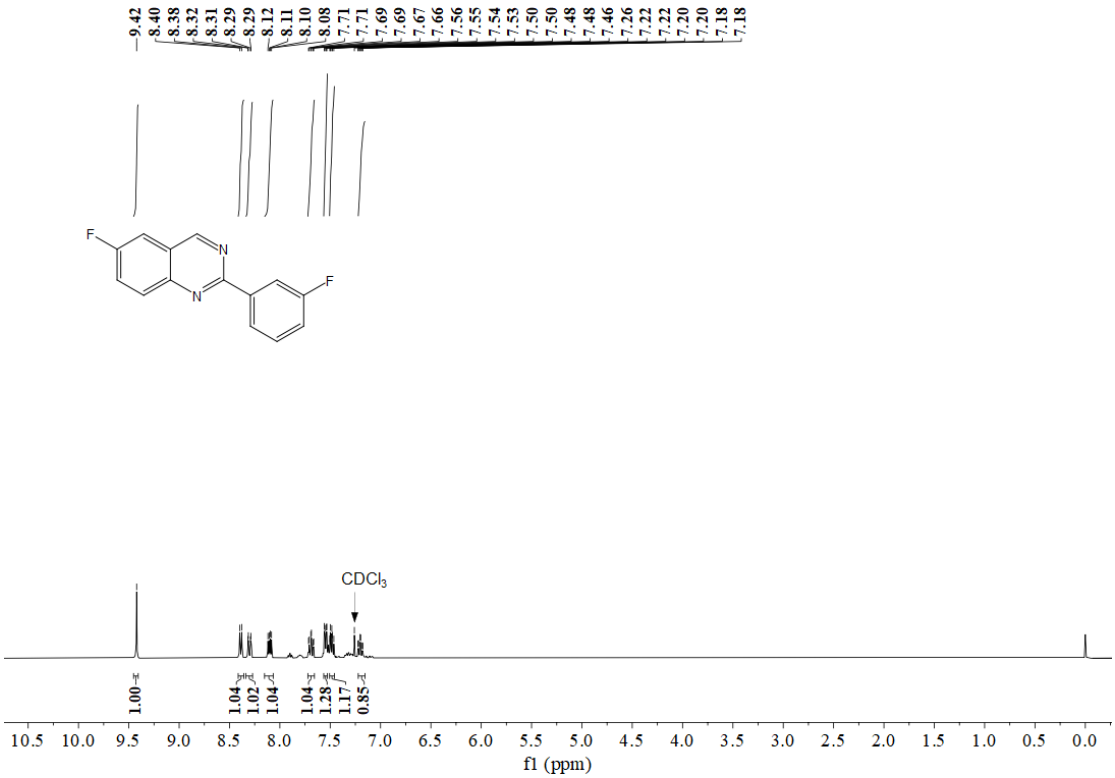


Figure S9. ^{1}H NMR Spectrum of **3d**

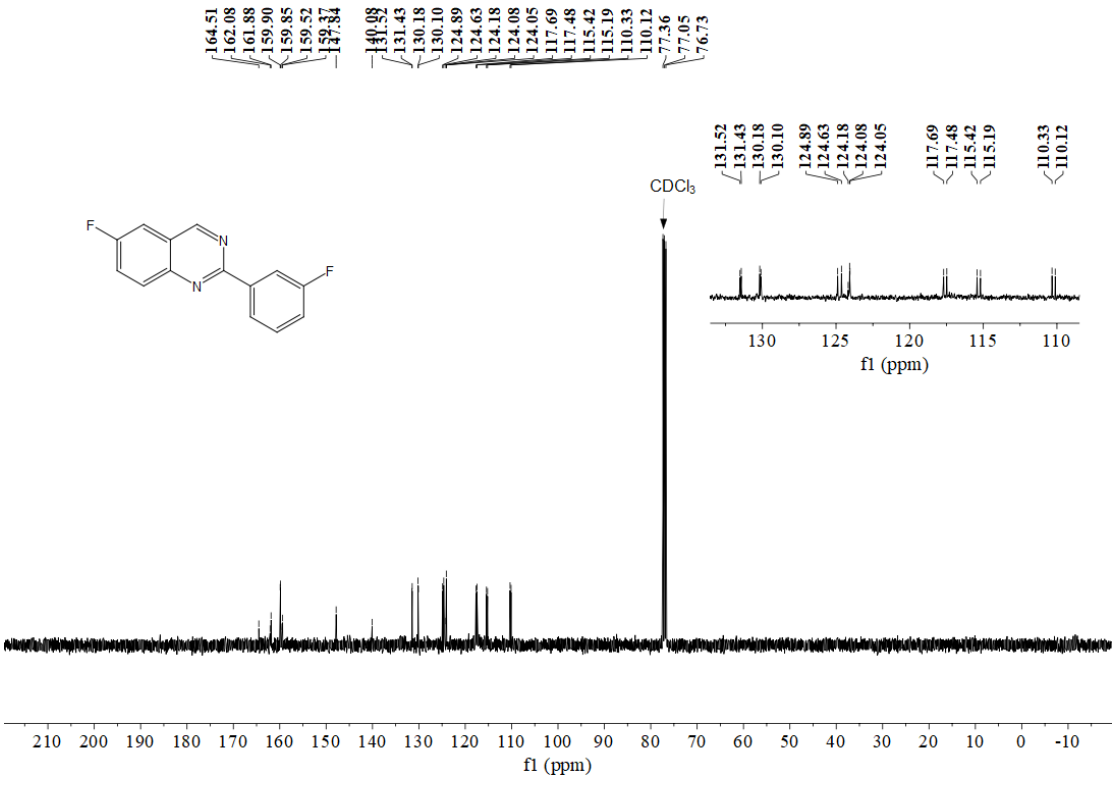


Figure S10. ^{13}C NMR Spectrum of **3d**

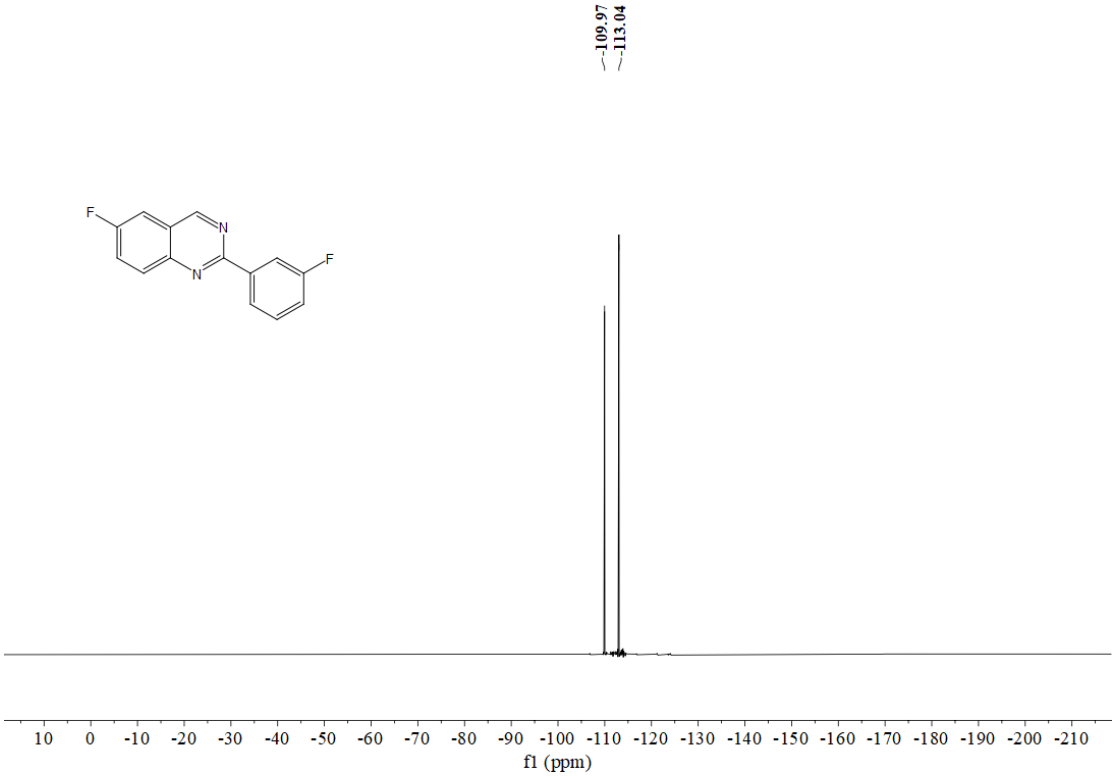


Figure S11. ^{19}F NMR Spectrum of **3d**

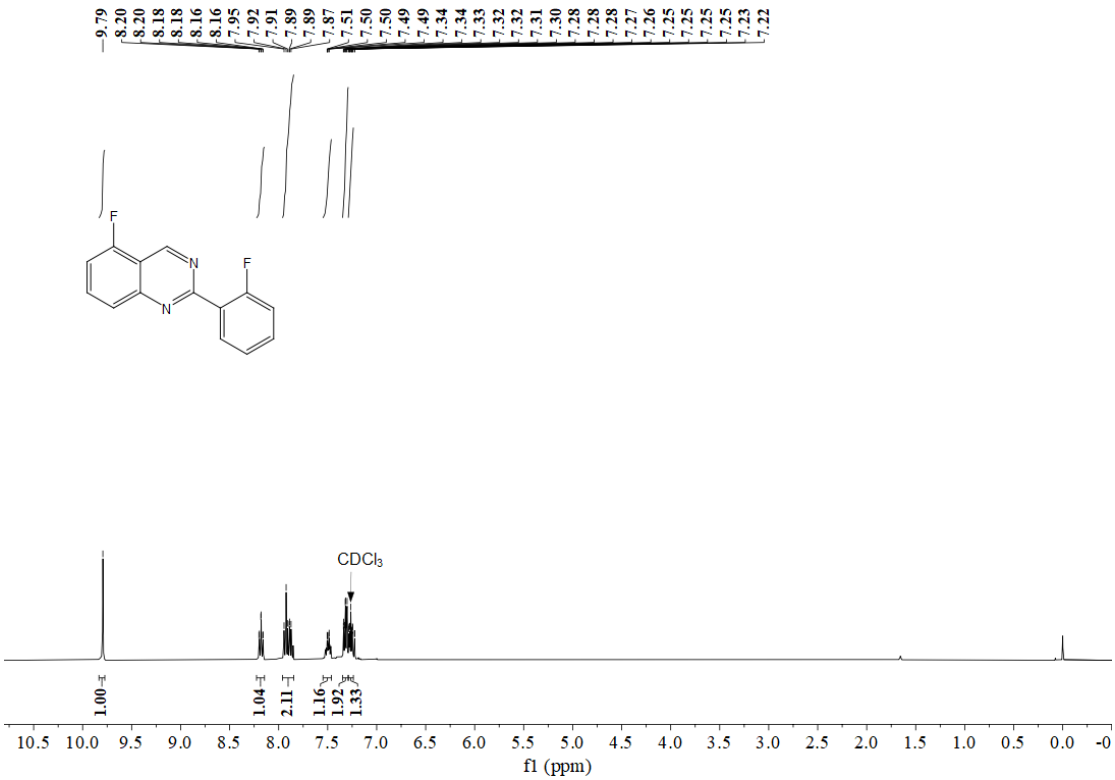


Figure S12. ^{1}H NMR Spectrum of **3e**

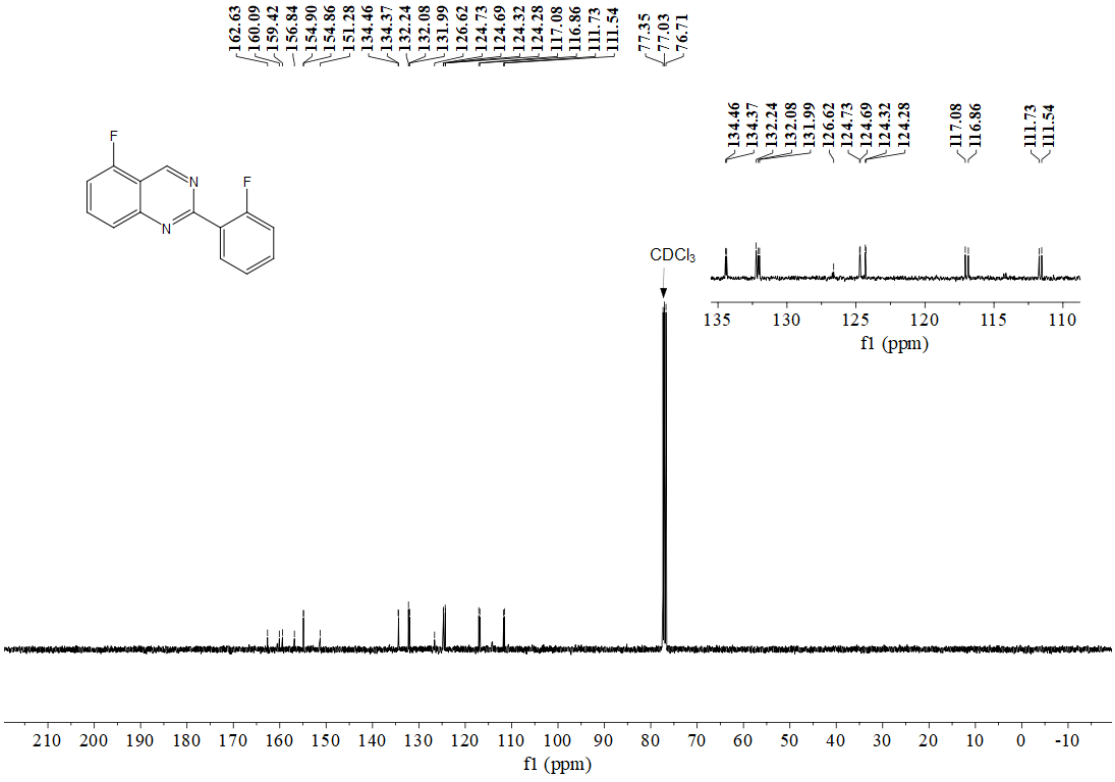


Figure S13. ^{13}C NMR Spectrum of **3e**

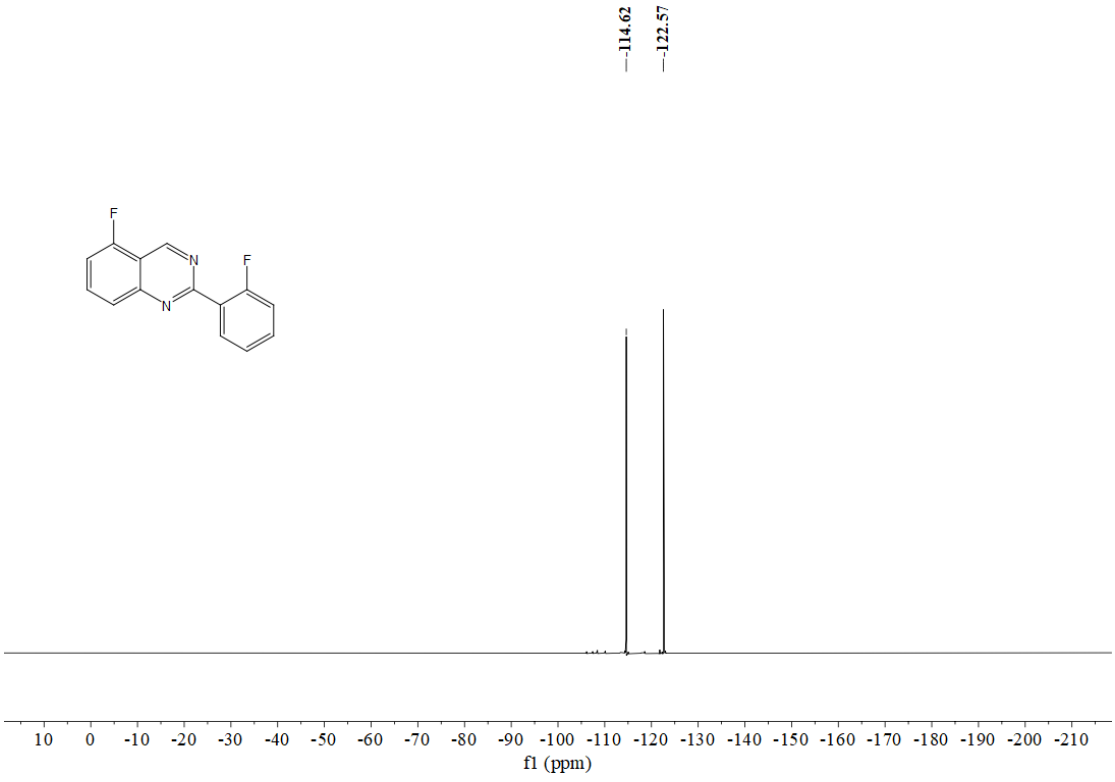


Figure S14. ^{19}F NMR Spectrum of **3e**

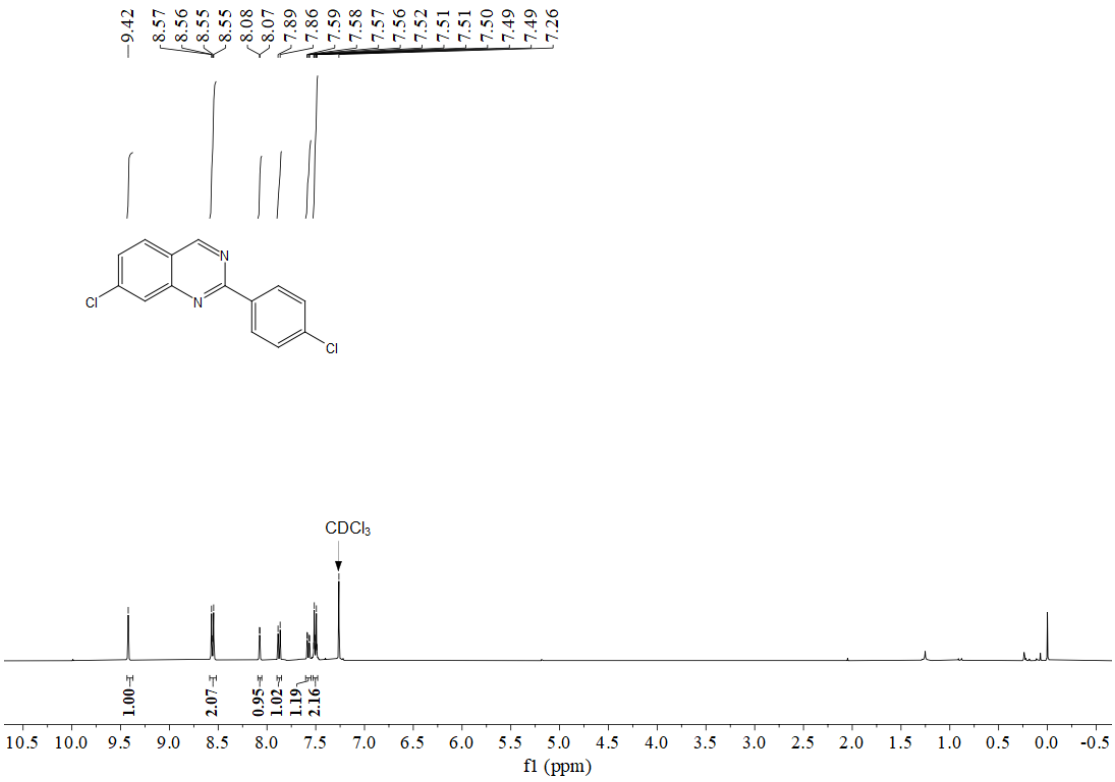


Figure S15. ^{1}H NMR Spectrum of **3f**

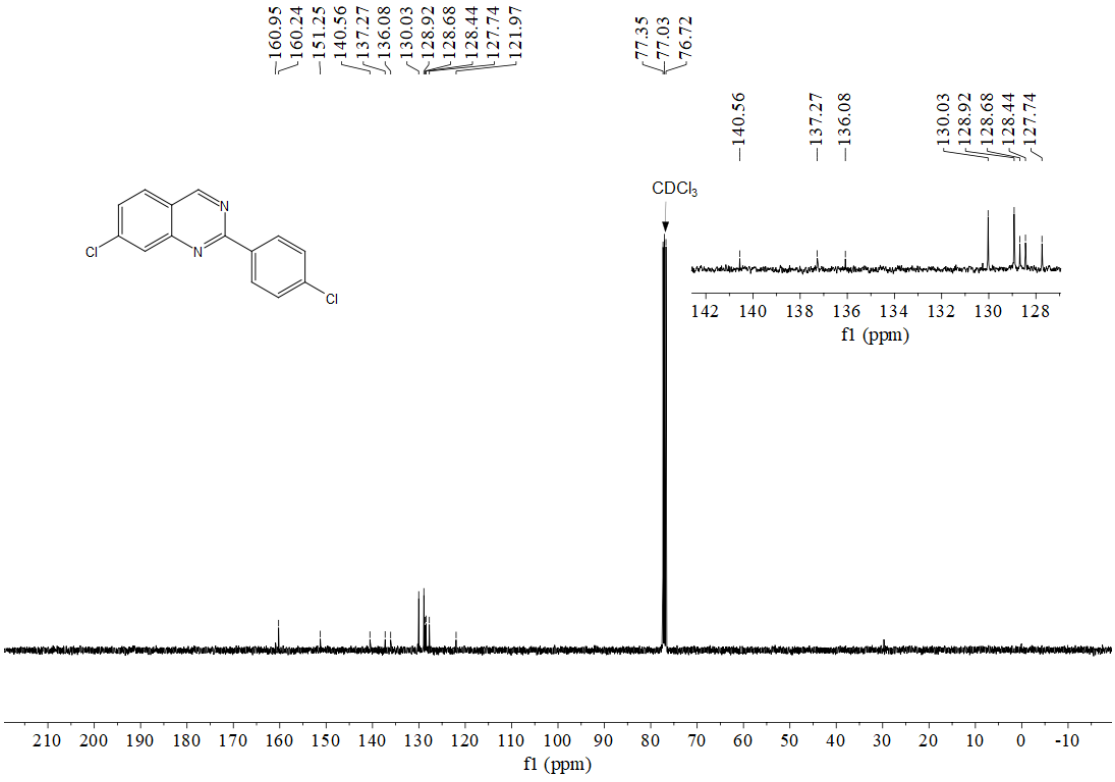


Figure S16. ^{13}C NMR Spectrum of **3f**

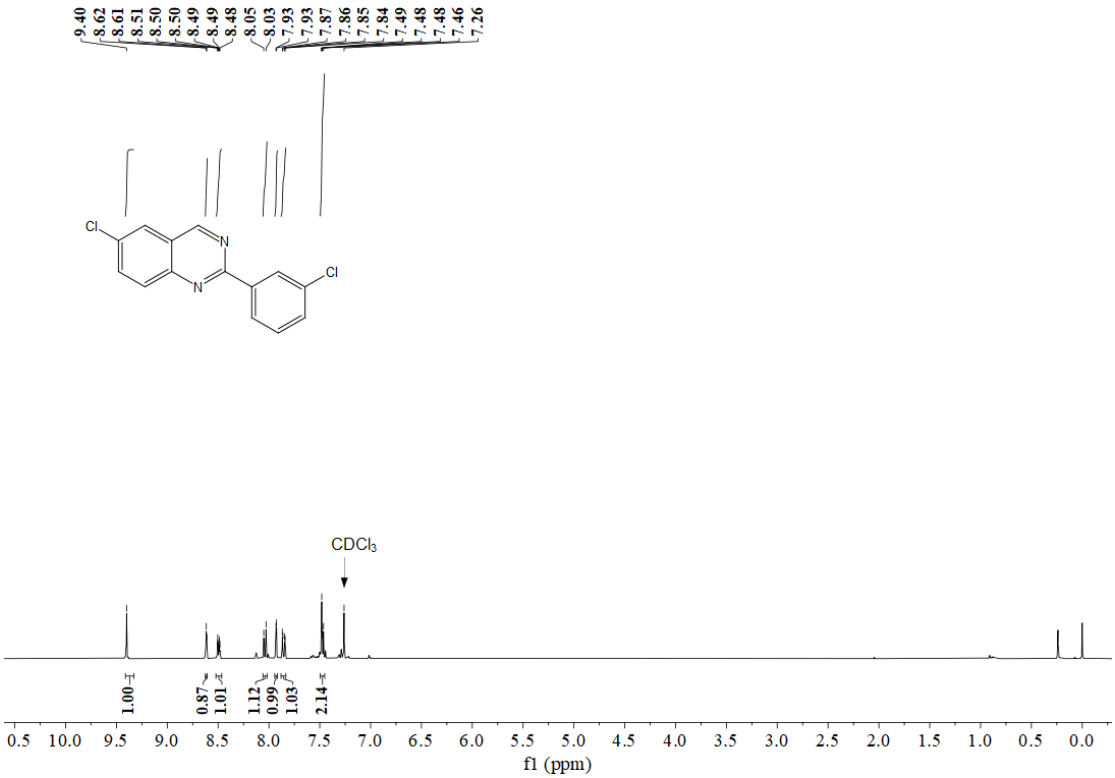


Figure S17. ^{1}H NMR Spectrum of **3g**

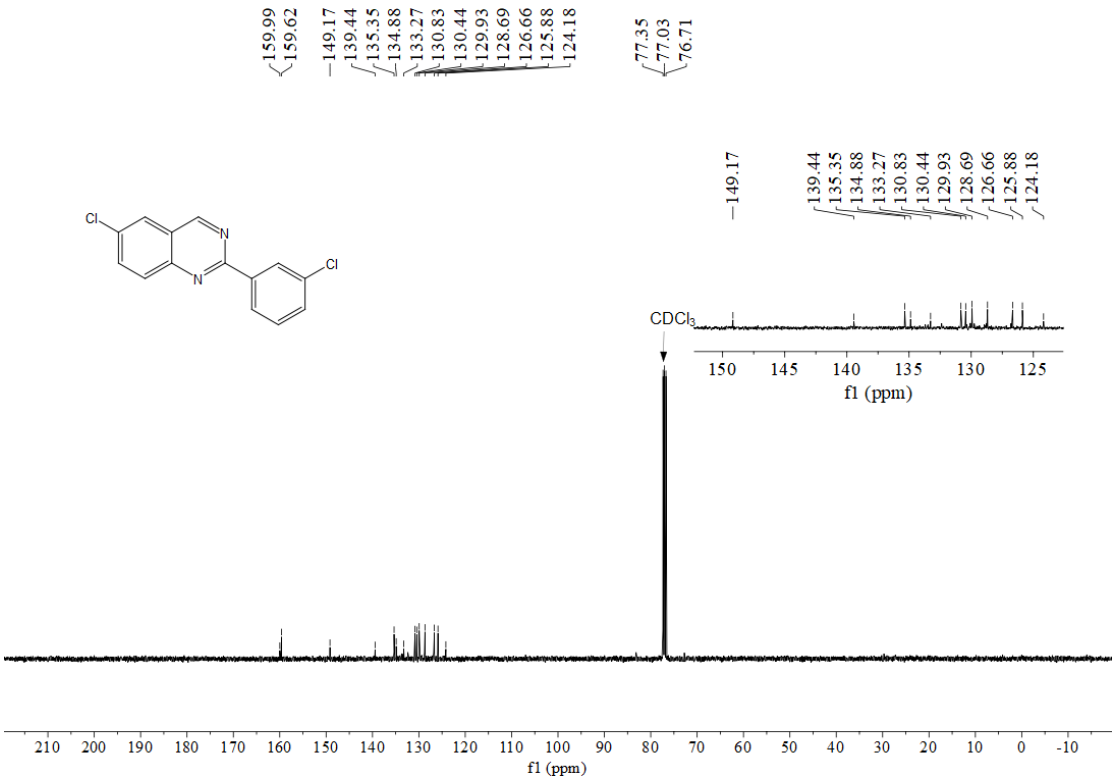


Figure S18. ^{13}C NMR Spectrum of **3g**

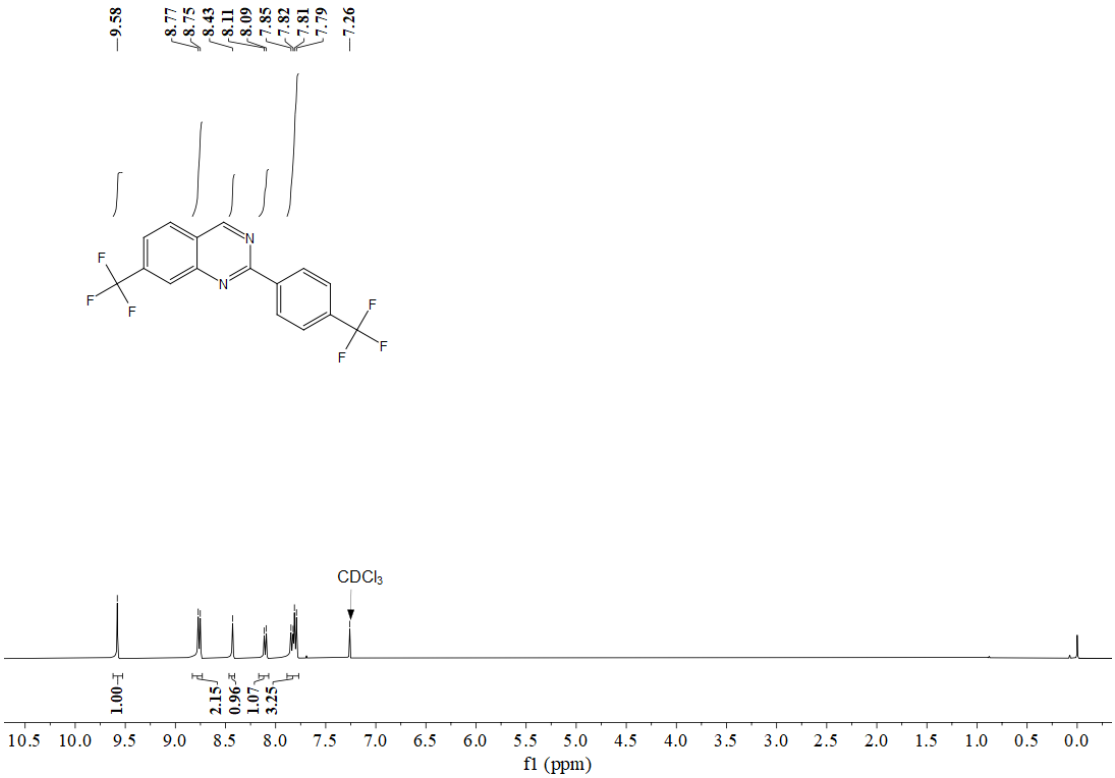


Figure S19. ^{1}H NMR Spectrum of **3h**

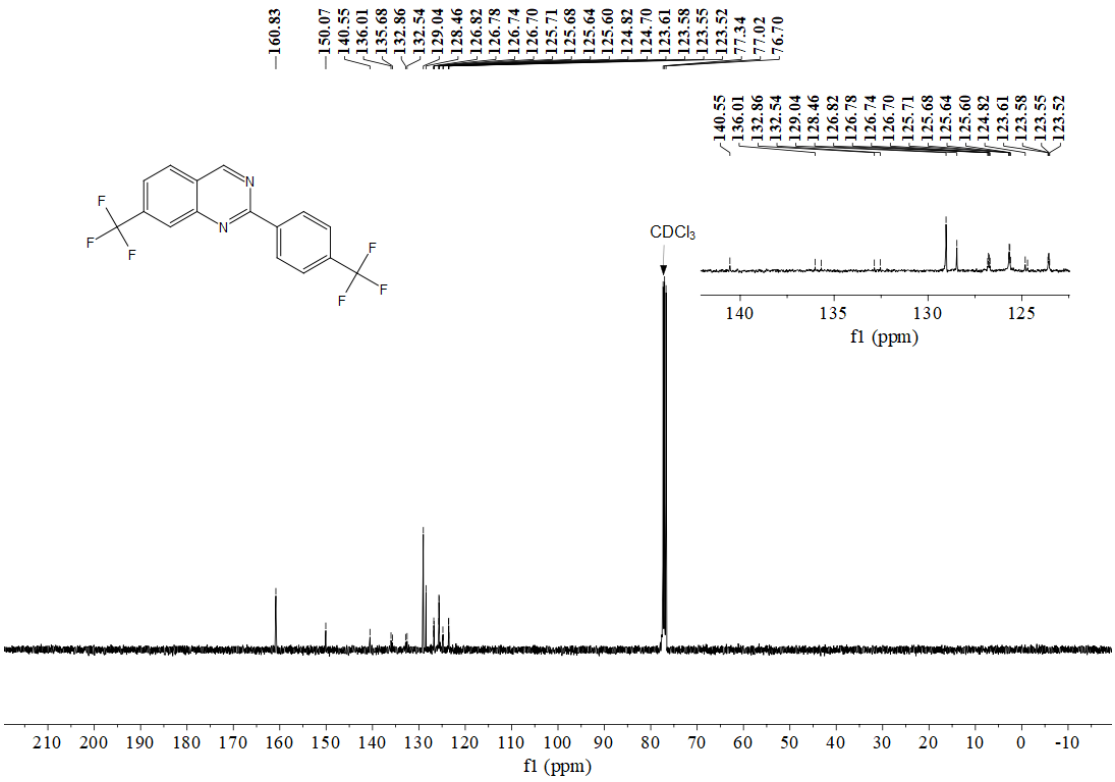


Figure S20. ^{13}C NMR Spectrum of **3h**

Figure S21. ^{19}F NMR Spectrum of **3h**

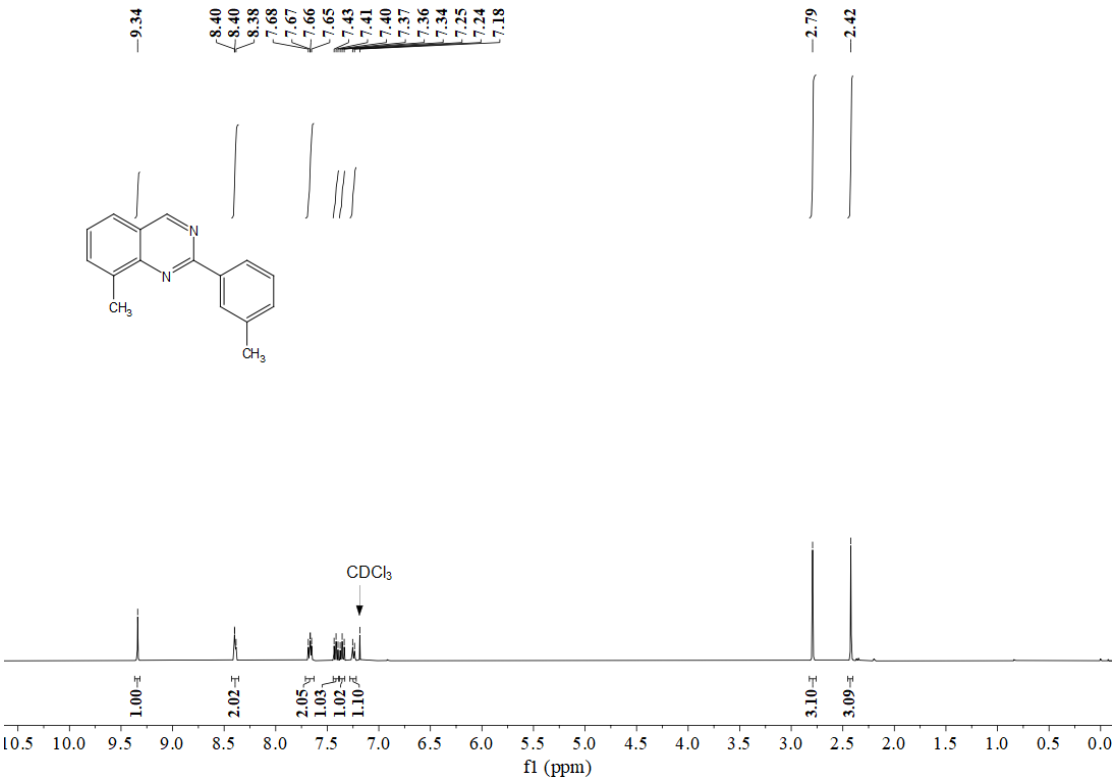


Figure S22. ^{1}H NMR Spectrum of **3i**

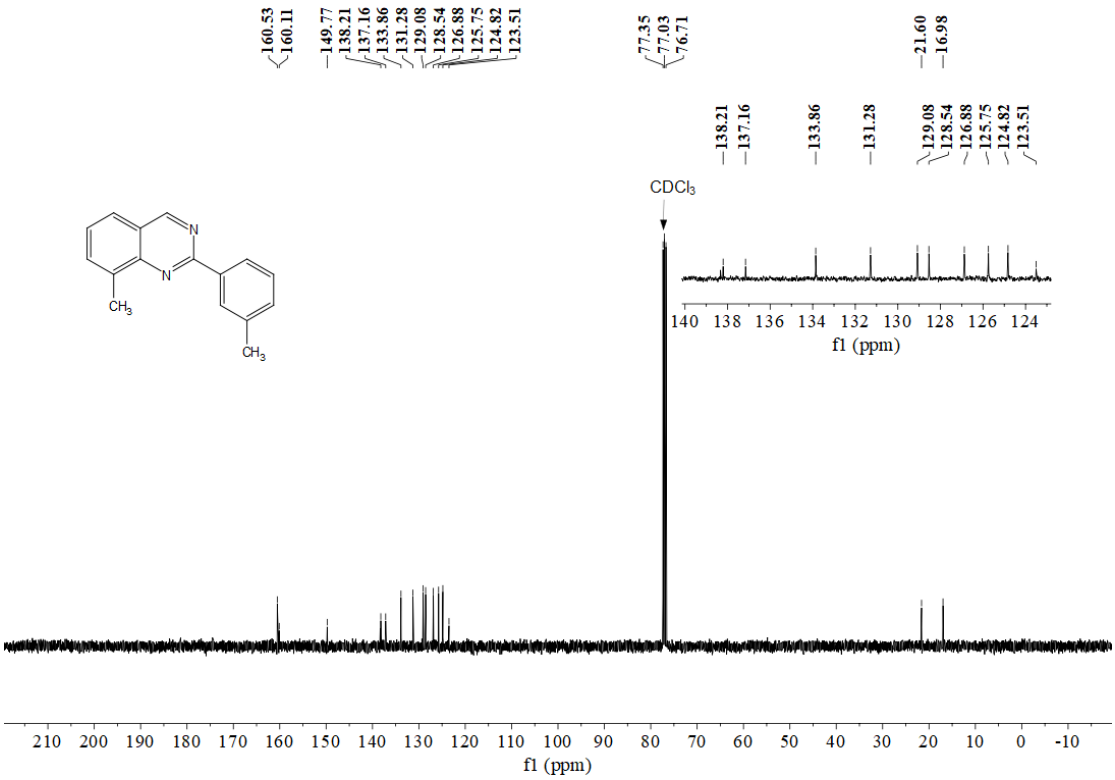


Figure S23. ^{13}C NMR Spectrum of **3i**

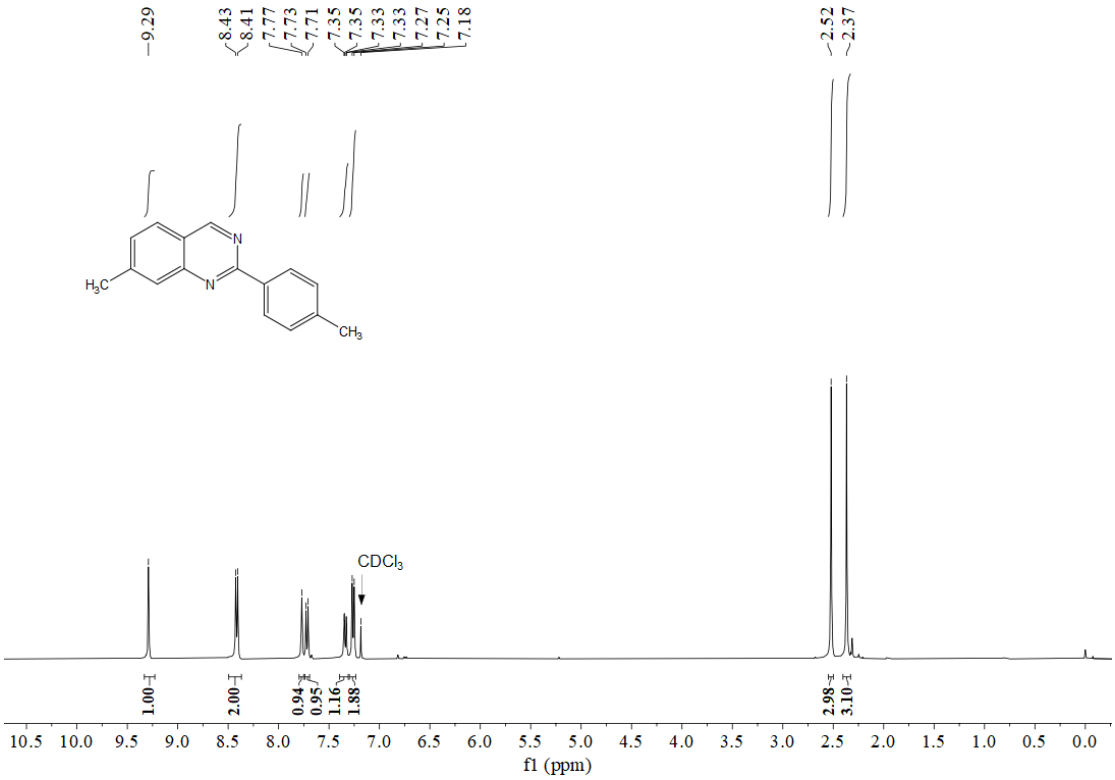


Figure S24. ^{1}H NMR Spectrum of **3j**

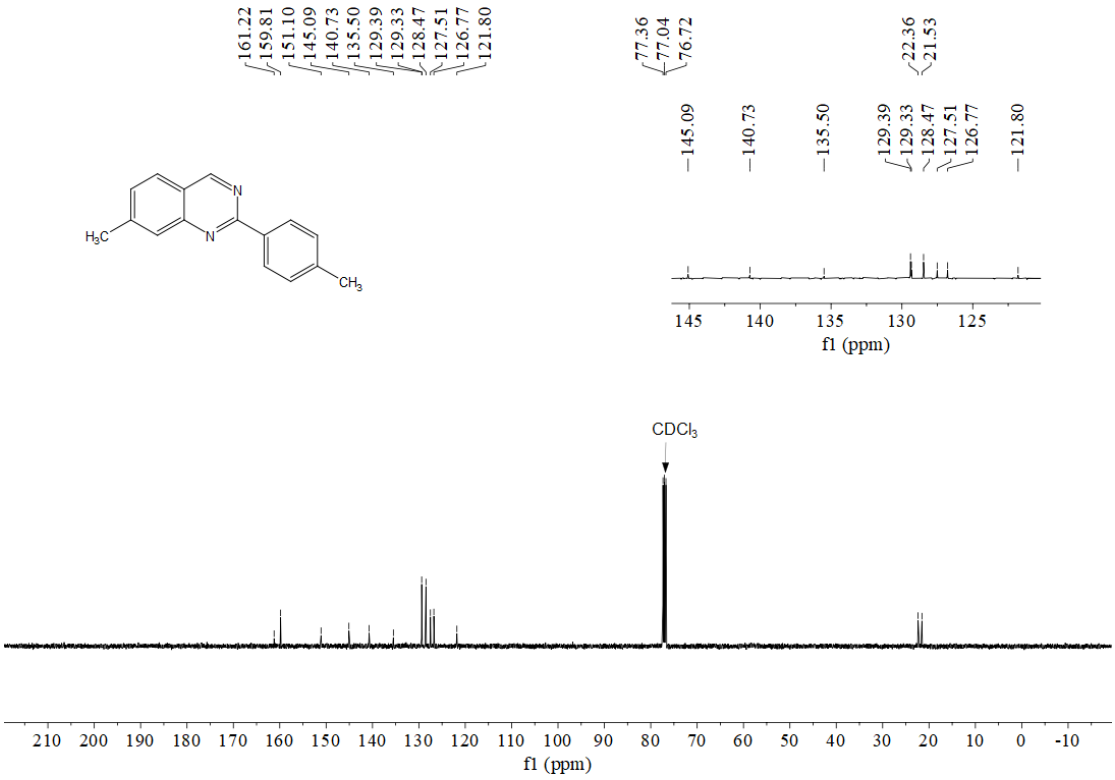


Figure S25. ^{13}C NMR Spectrum of **3j**

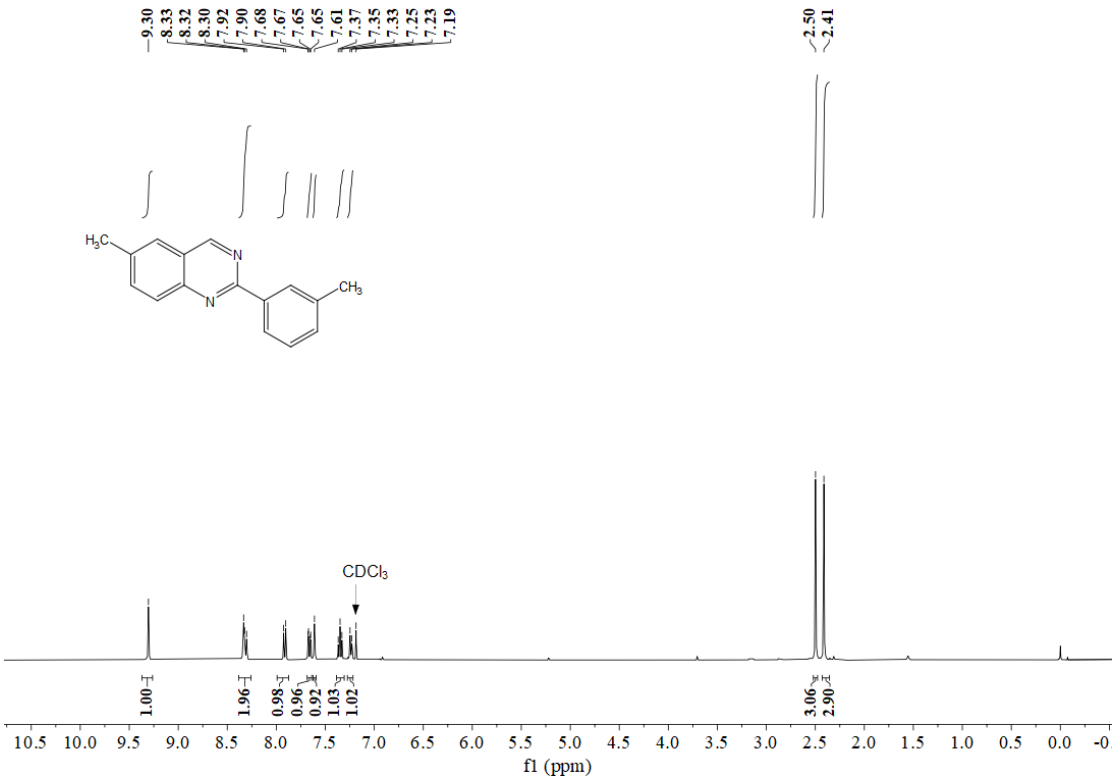


Figure S26. ^{1}H NMR Spectrum of **3k**

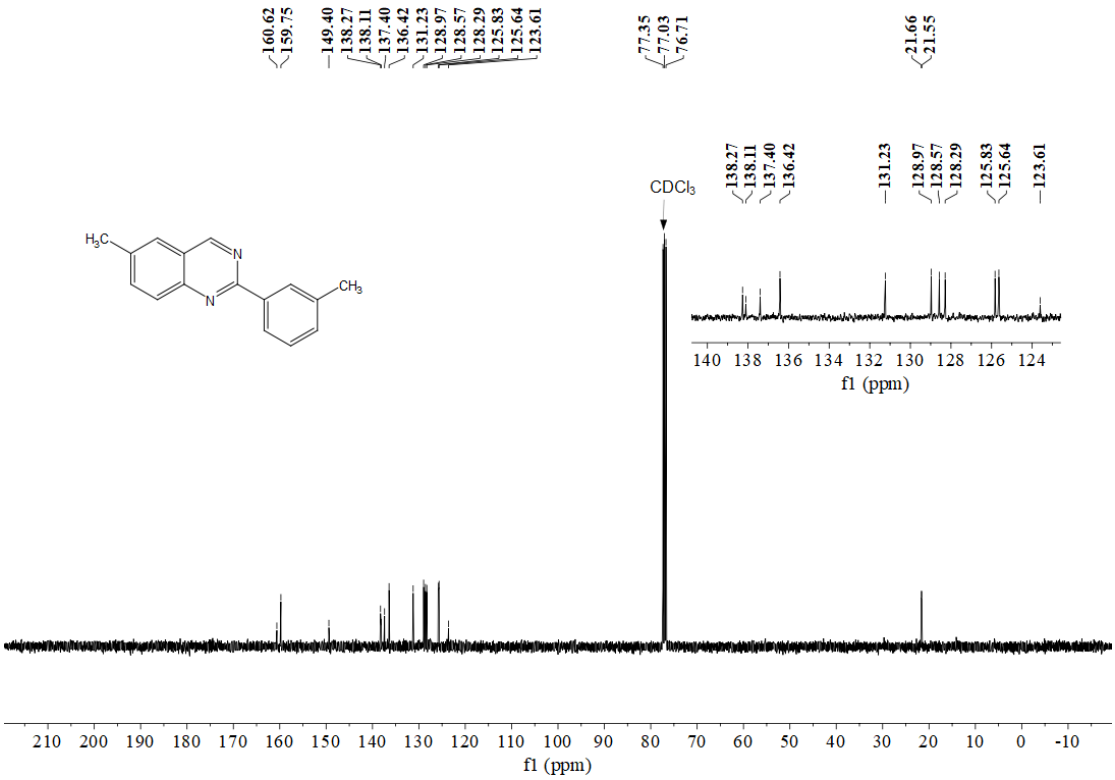


Figure S27. ^{13}C NMR Spectrum of **3k**

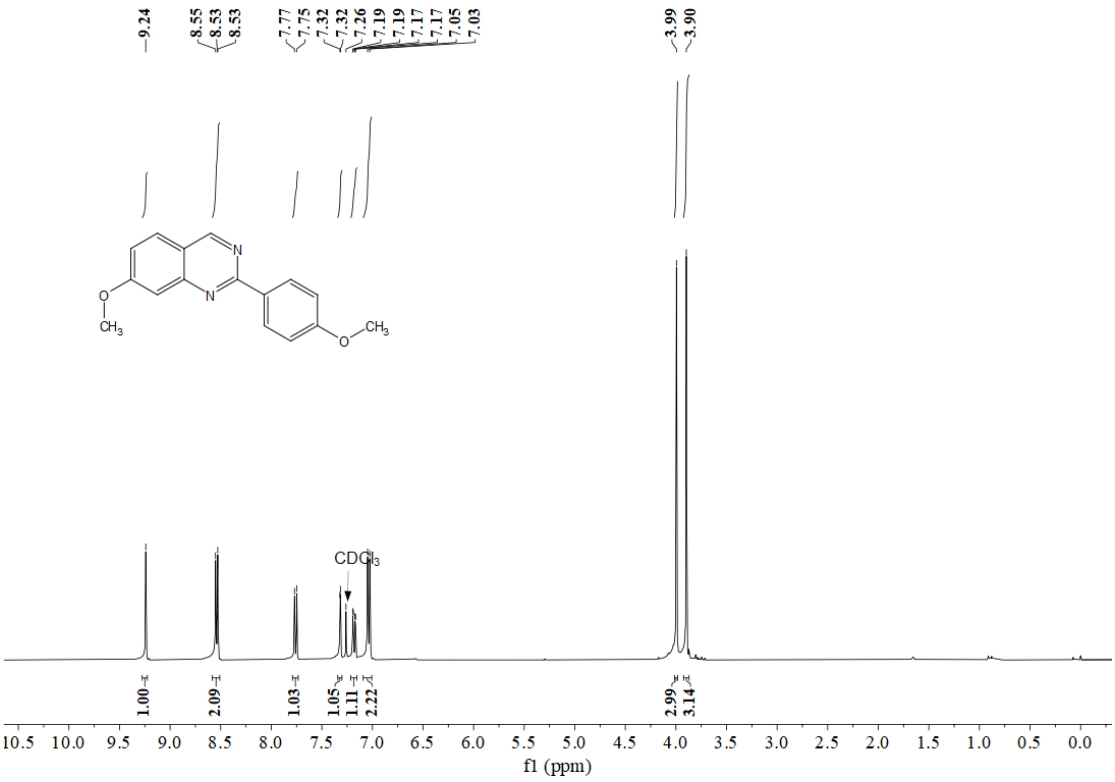


Figure S28. ^{1}H NMR Spectrum of **3l**

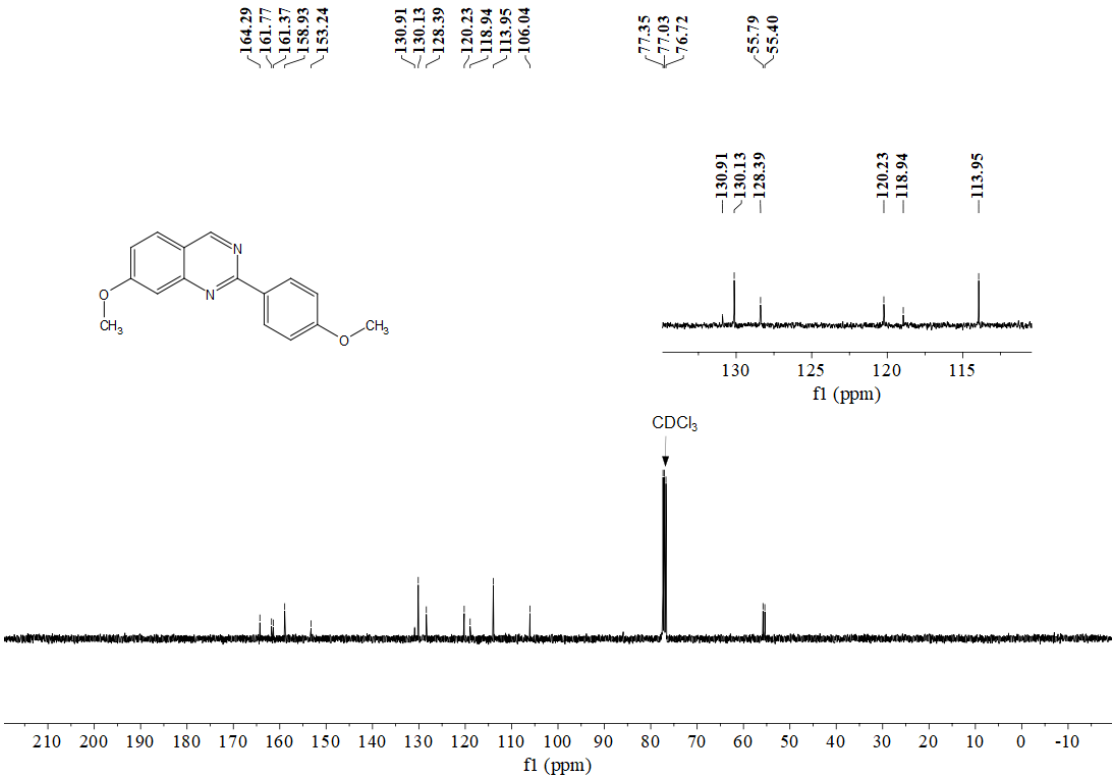


Figure S29. ^{13}C NMR Spectrum of **3l**

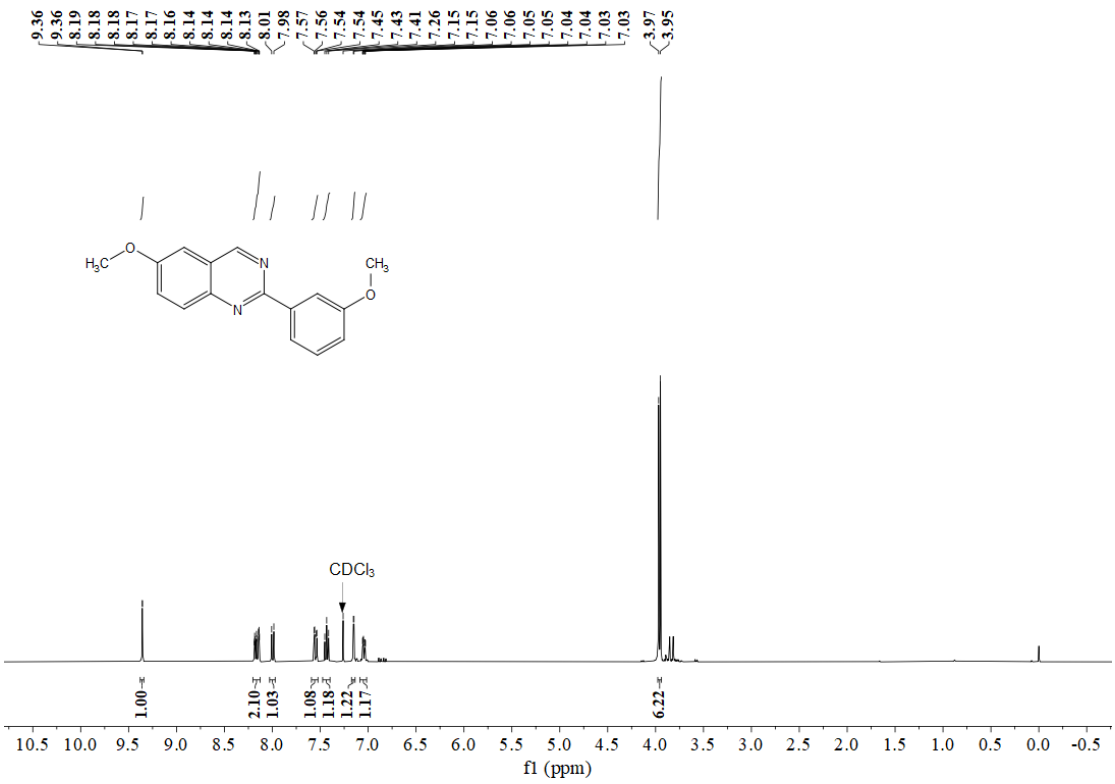


Figure S30. ^{1}H NMR Spectrum of **3m**

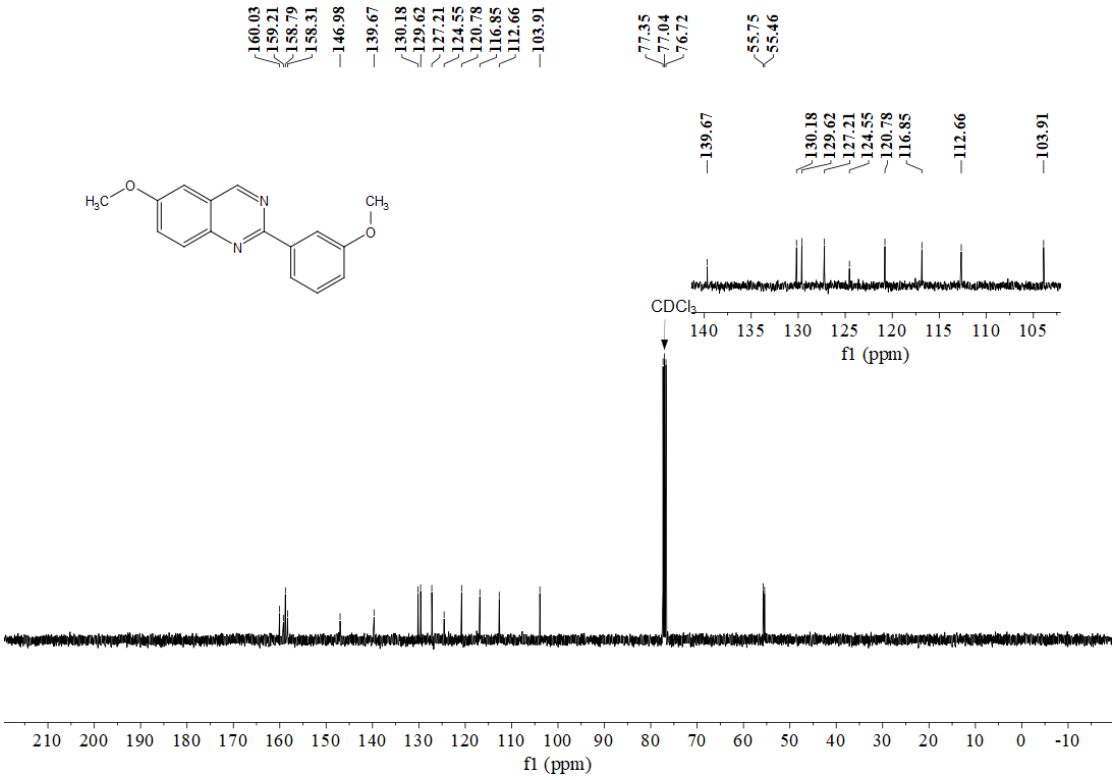


Figure S31. ^{13}C NMR Spectrum of **3m**

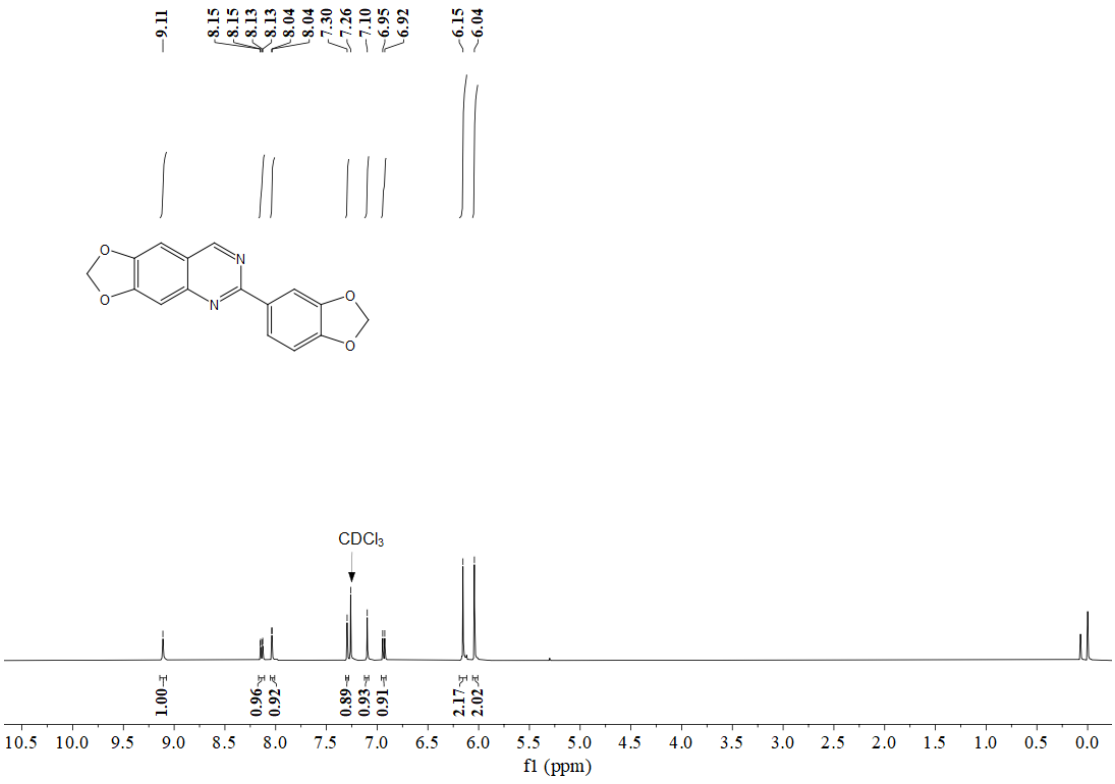


Figure S32. ^{1}H NMR Spectrum of **3n**

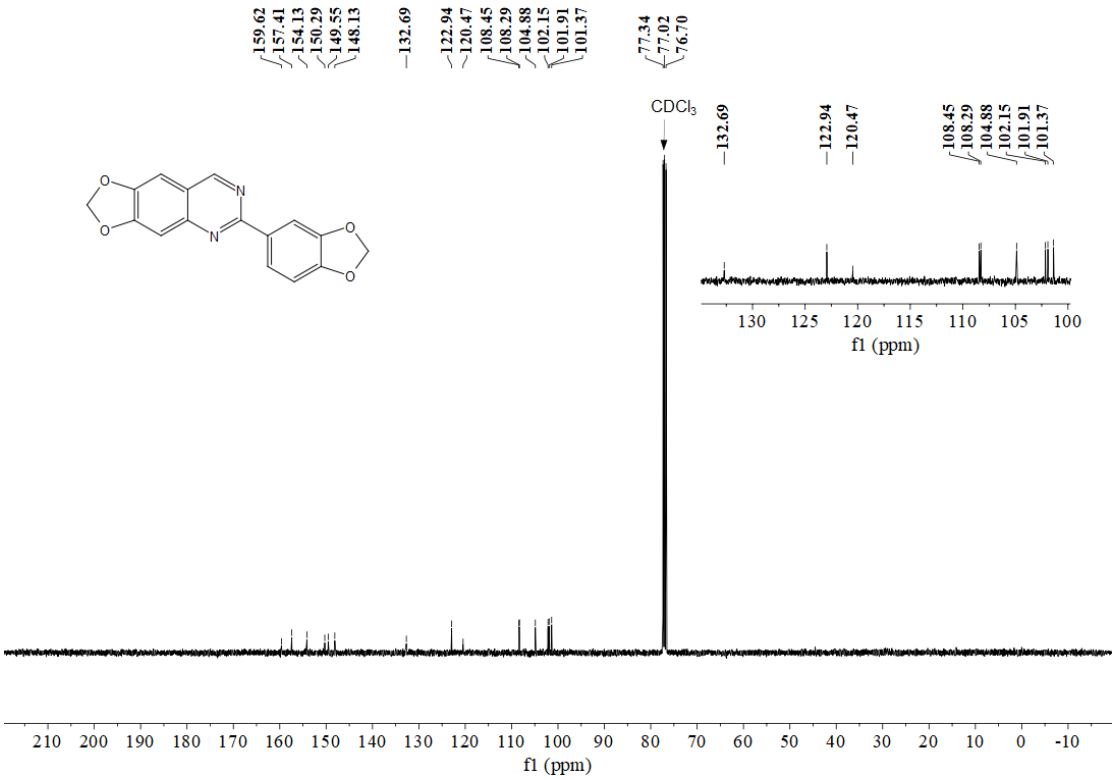


Figure S33. ^{13}C NMR Spectrum of **3n**

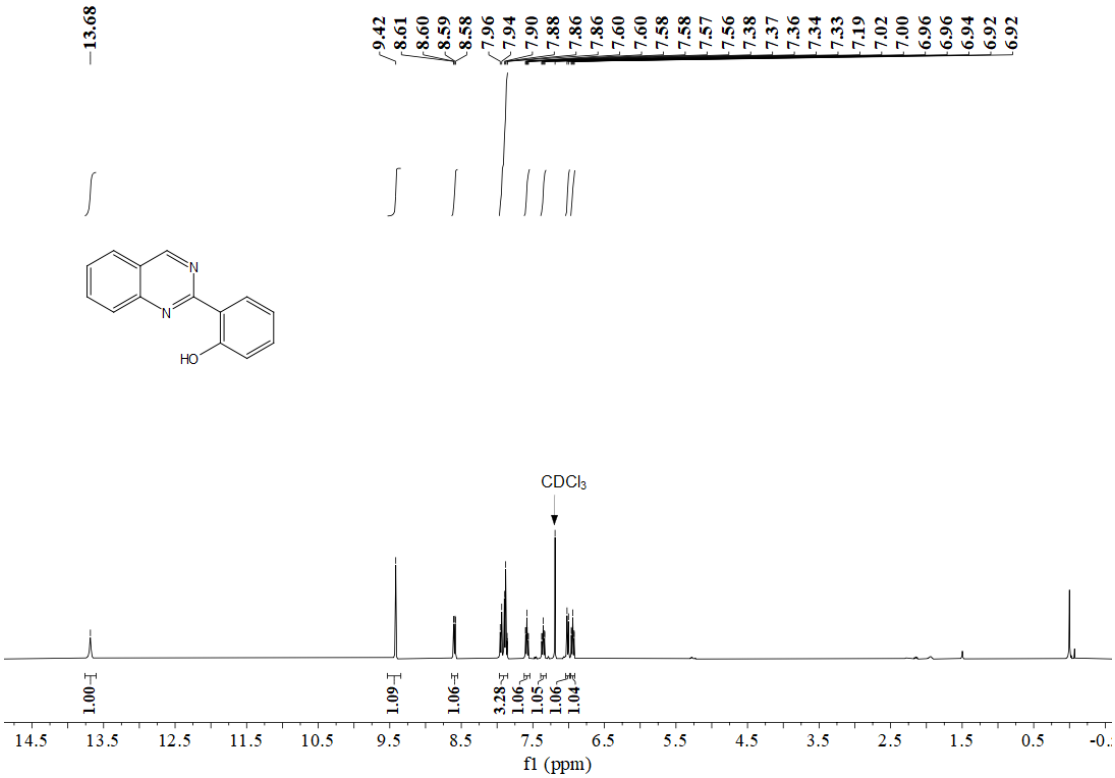


Figure S34. ^{1}H NMR Spectrum of **3o**

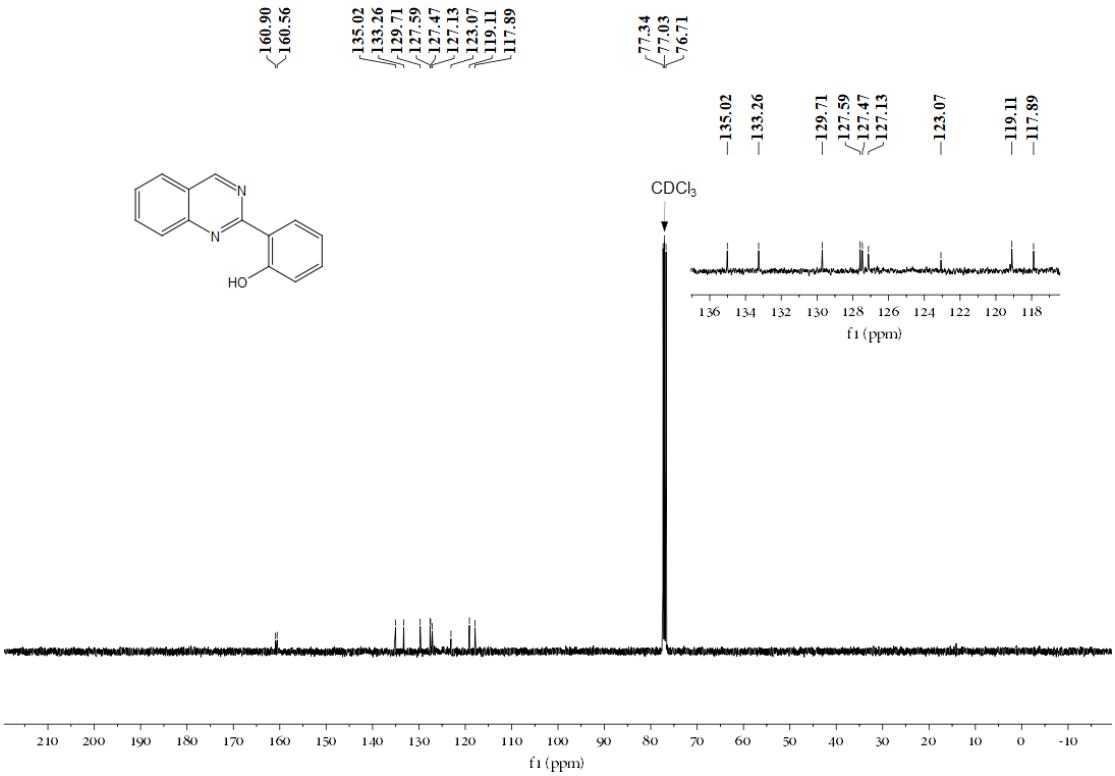


Figure S35. ^{13}C NMR Spectrum of **3o**

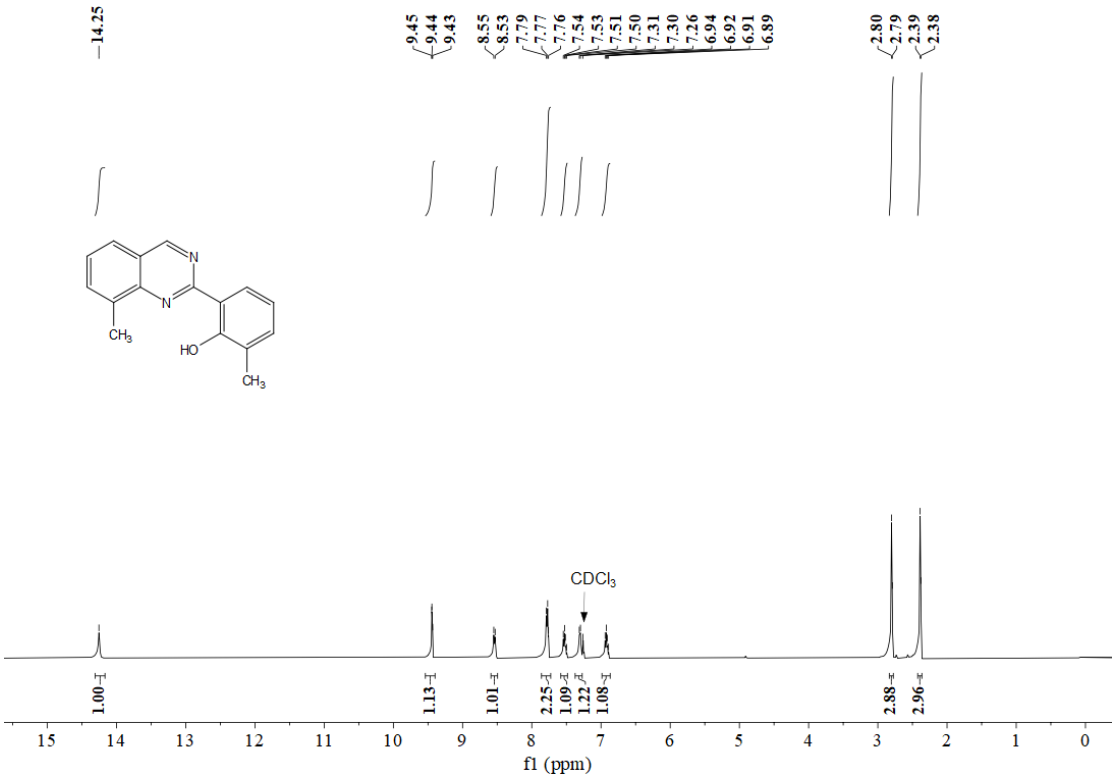


Figure S36. ^{1}H NMR Spectrum of **3p**

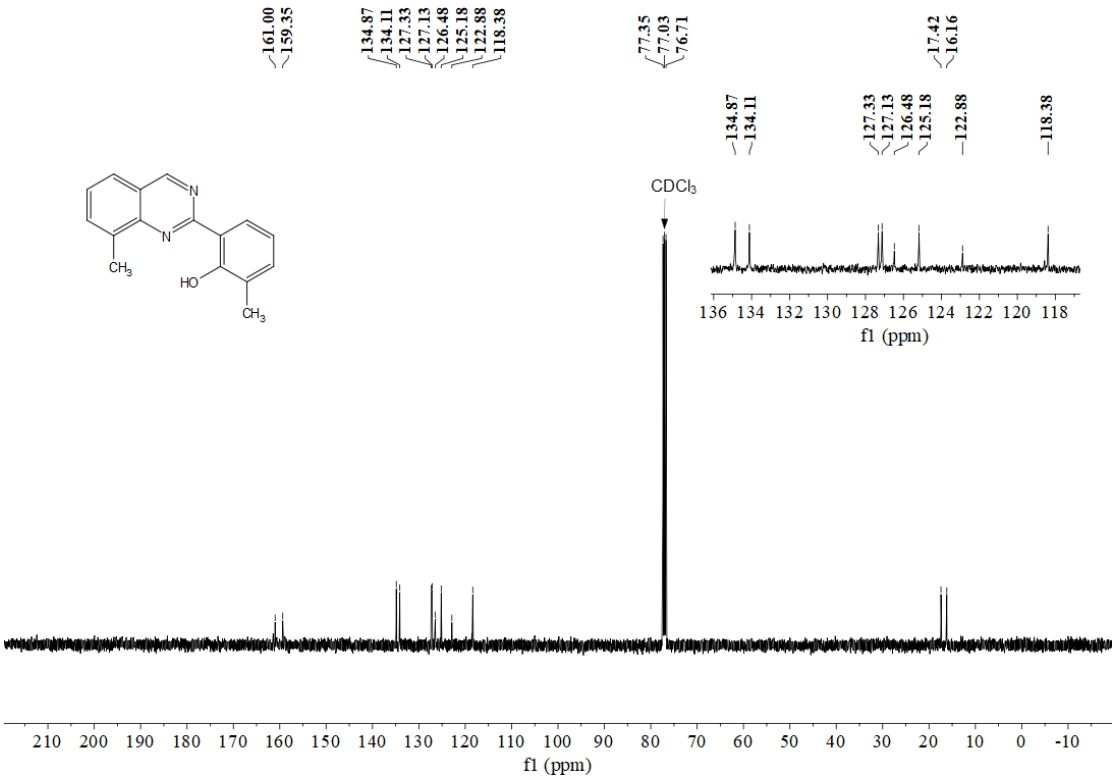


Figure S37. ^{13}C NMR Spectrum of **3p**

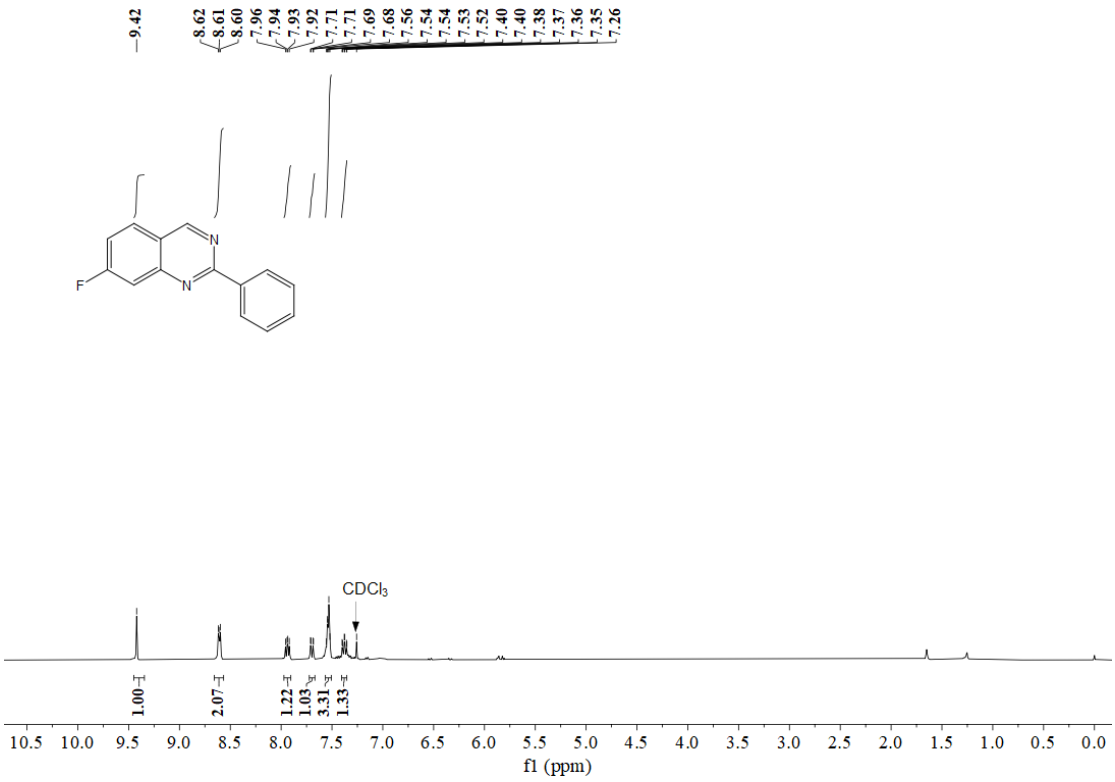


Figure S38. ^{1}H NMR Spectrum of **4a**

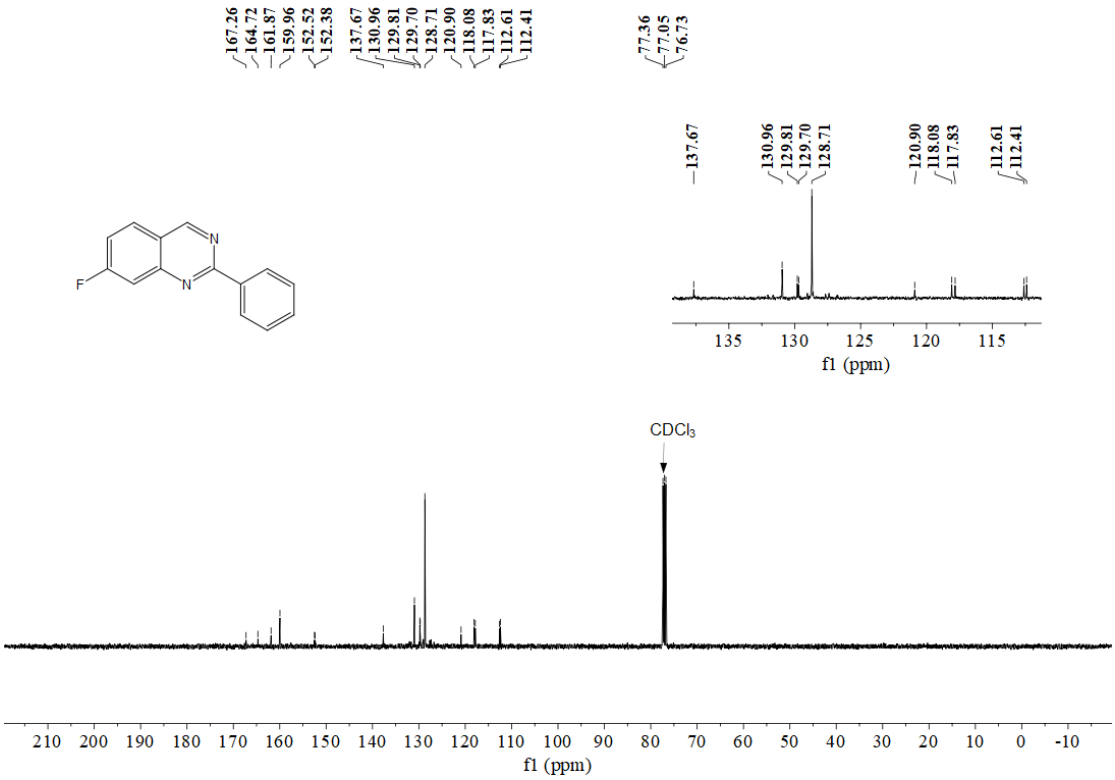


Figure S39. ^{13}C NMR Spectrum of **4a**

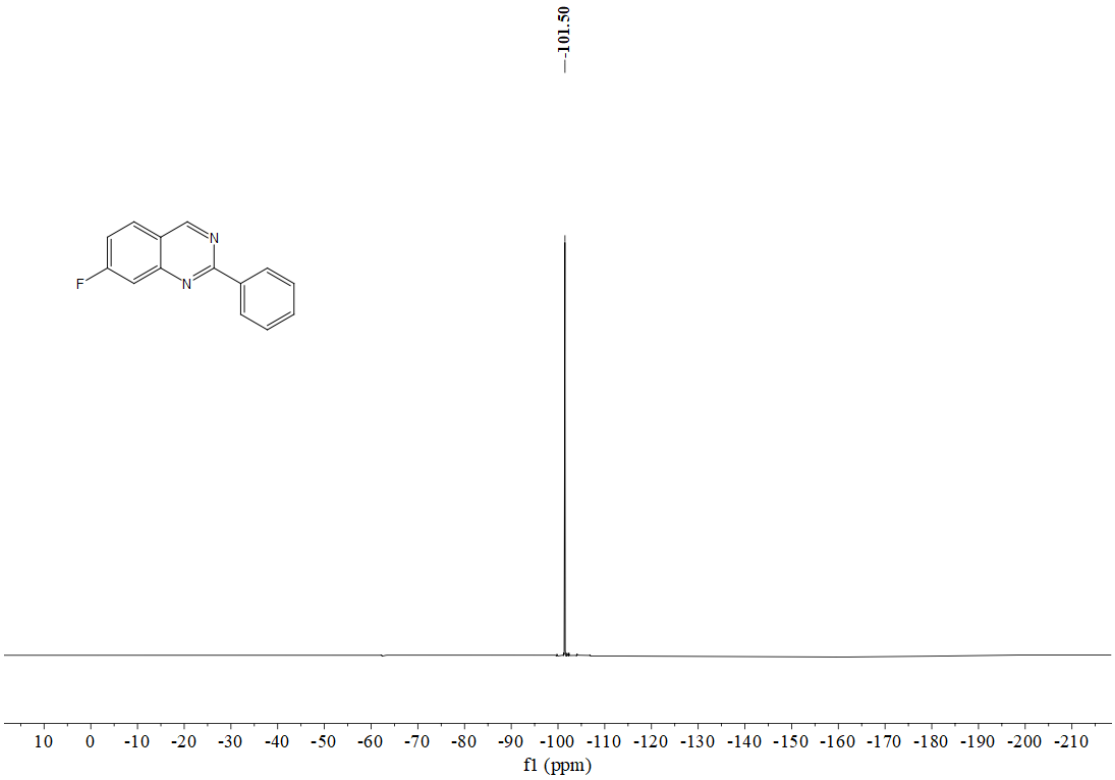


Figure S40. ^{19}F NMR Spectrum of **4a**

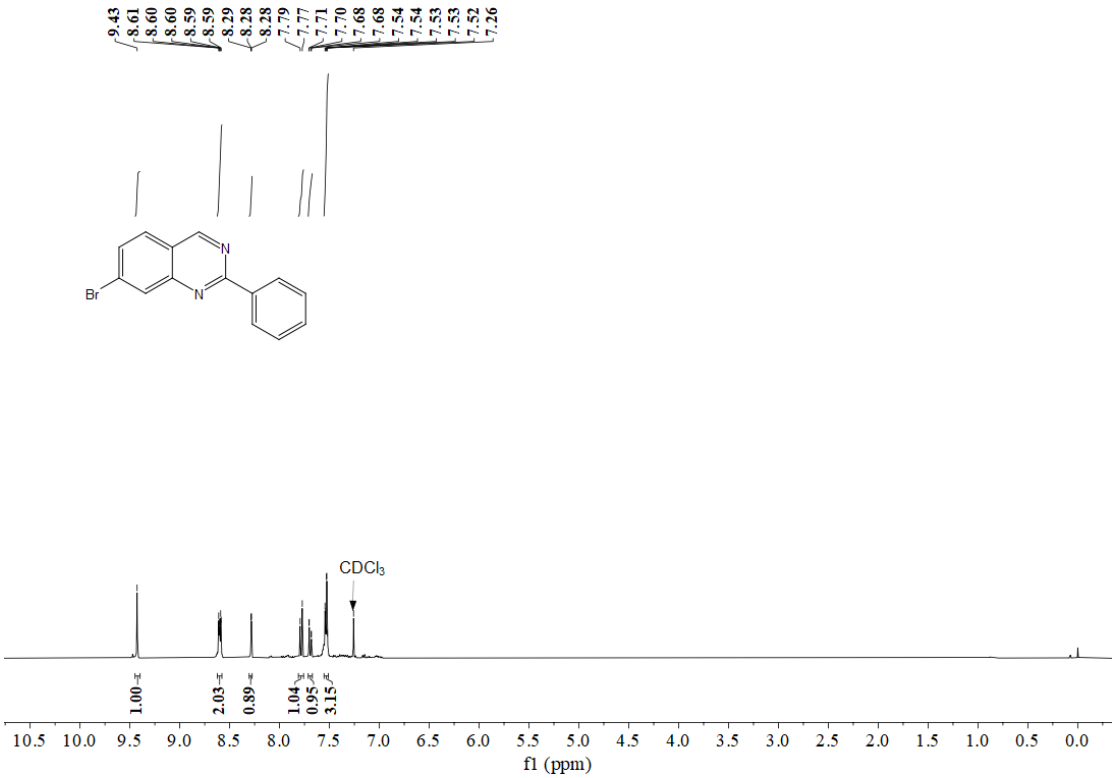


Figure S41. ^{1}H NMR Spectrum of **4b**

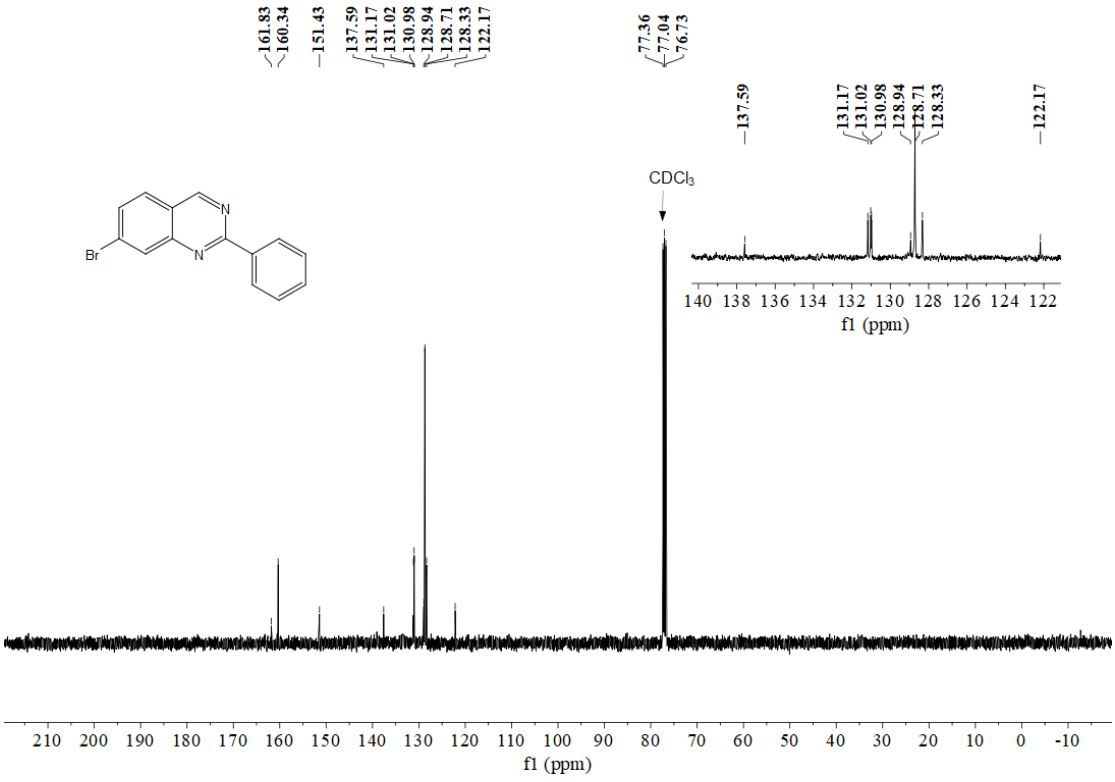


Figure S42. ^{13}C NMR Spectrum of **4b**

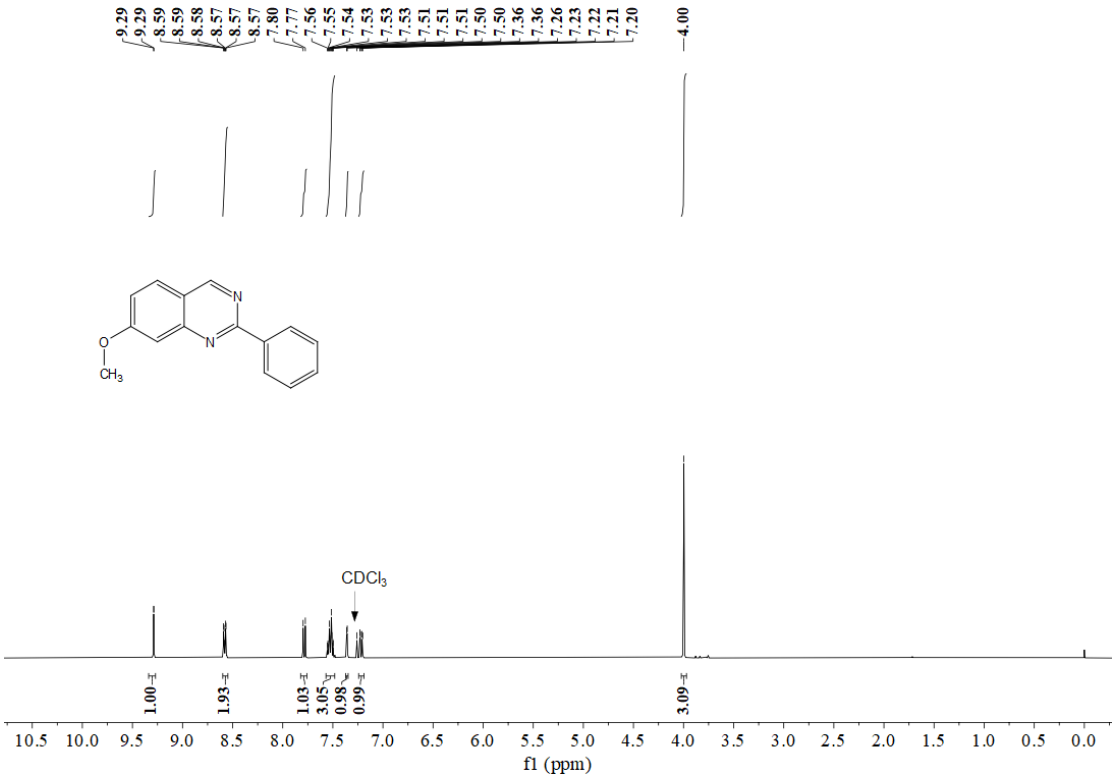


Figure S43. ^{1}H NMR Spectrum of **4c**

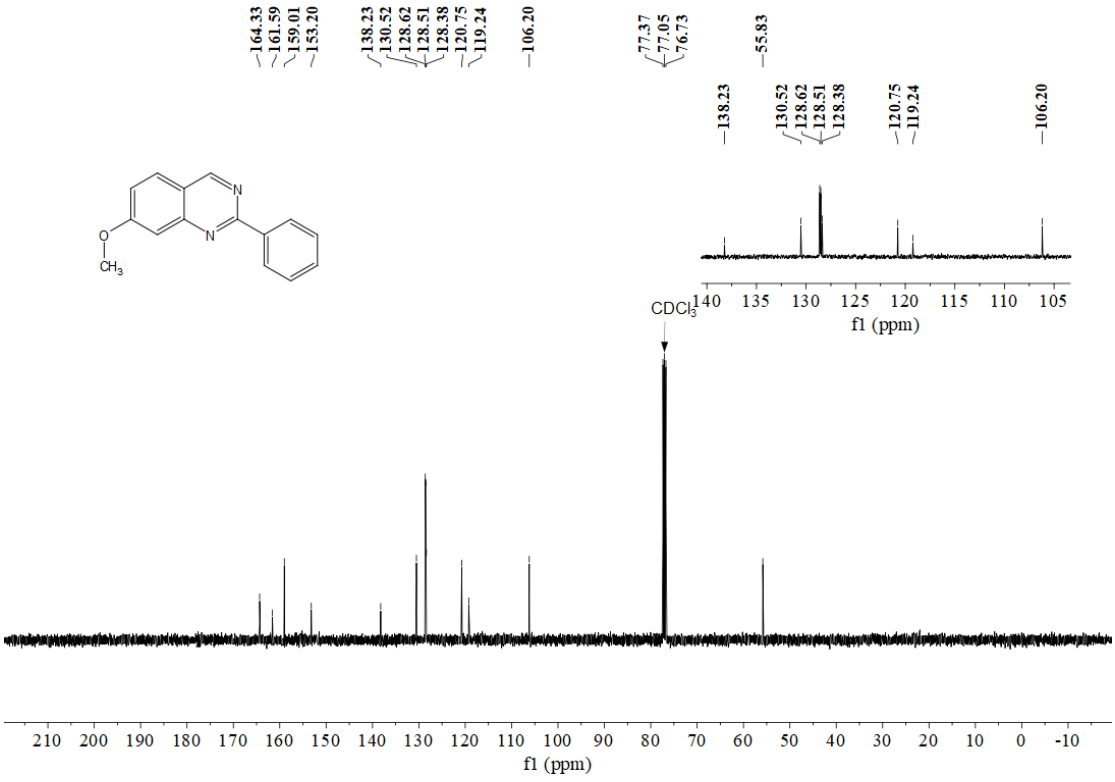


Figure S44. ^{13}C NMR Spectrum of **4c**

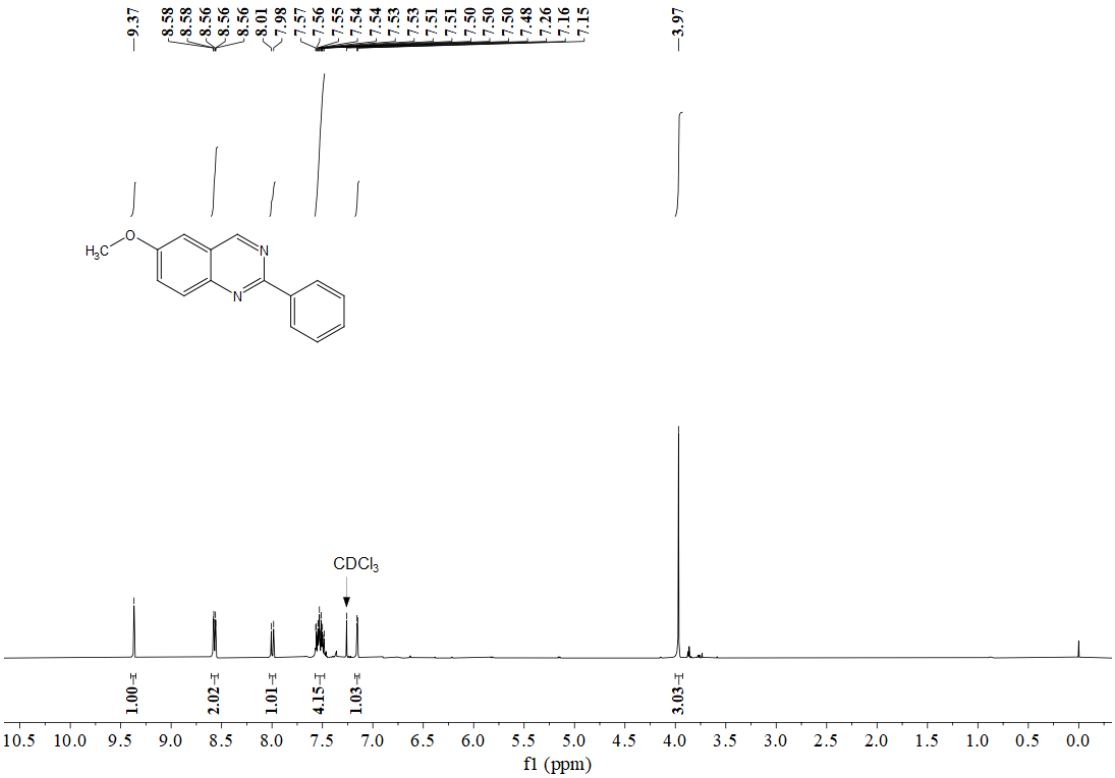


Figure S45. ^{1}H NMR Spectrum of **4d**

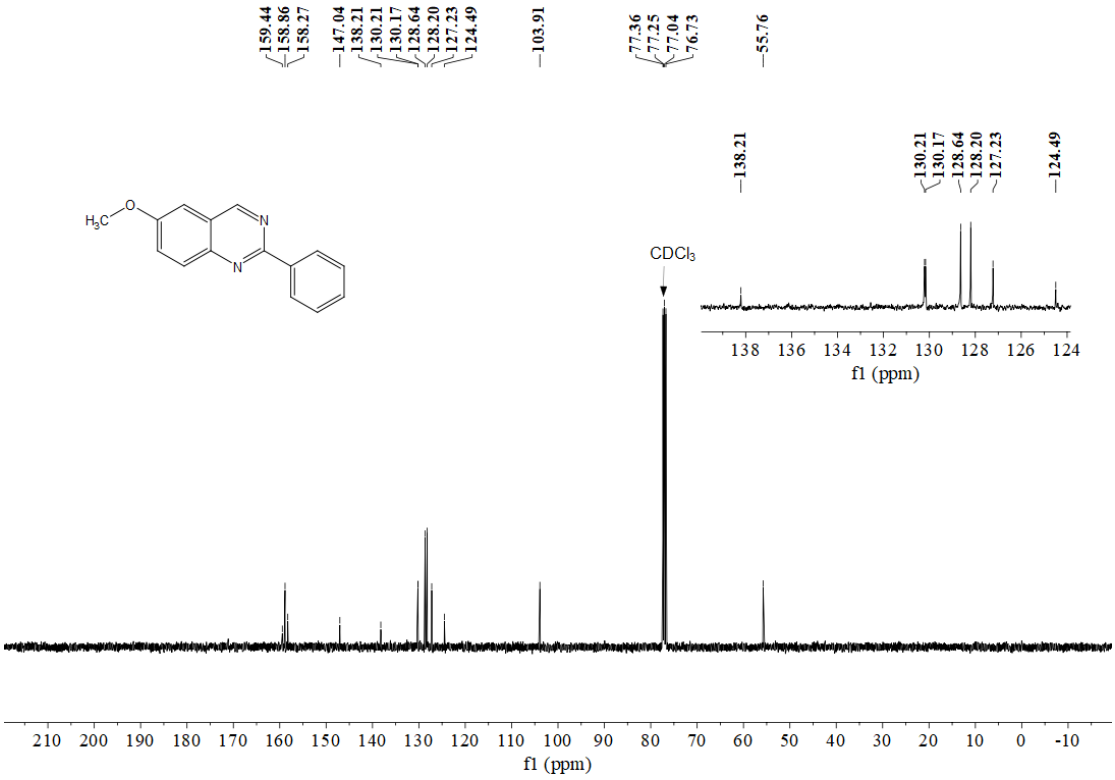


Figure S46. ^{13}C NMR Spectrum of **4d**

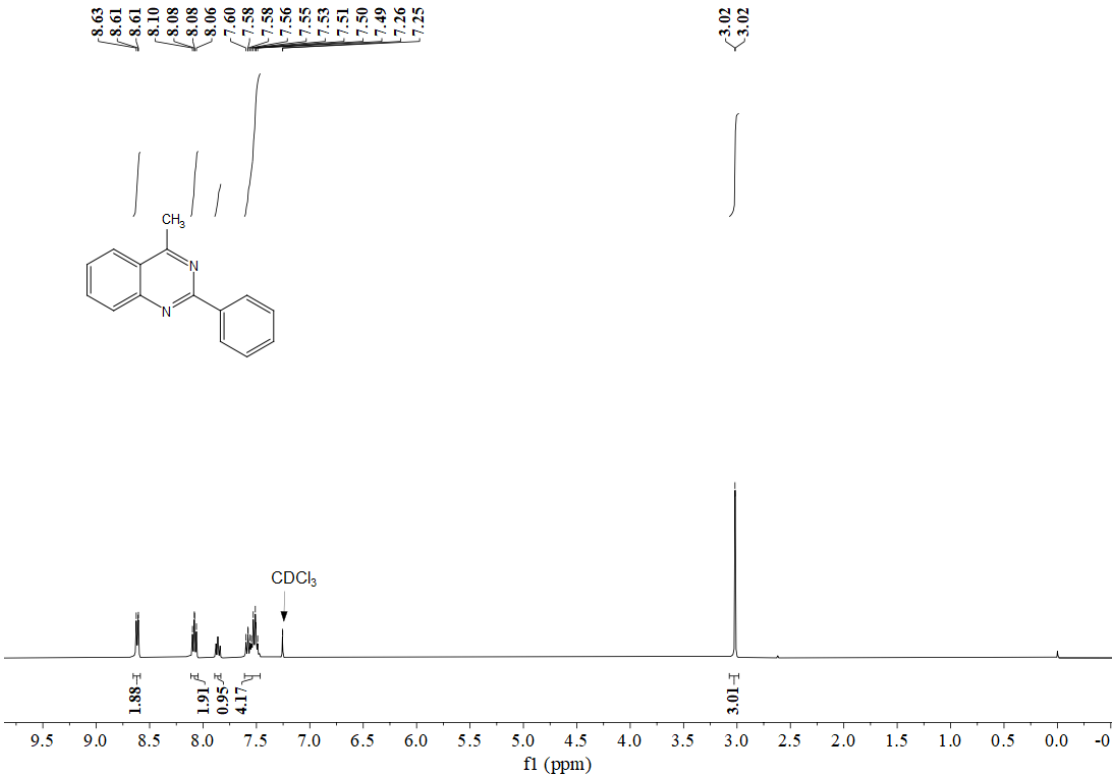


Figure S47. ^{1}H NMR Spectrum of **4e**

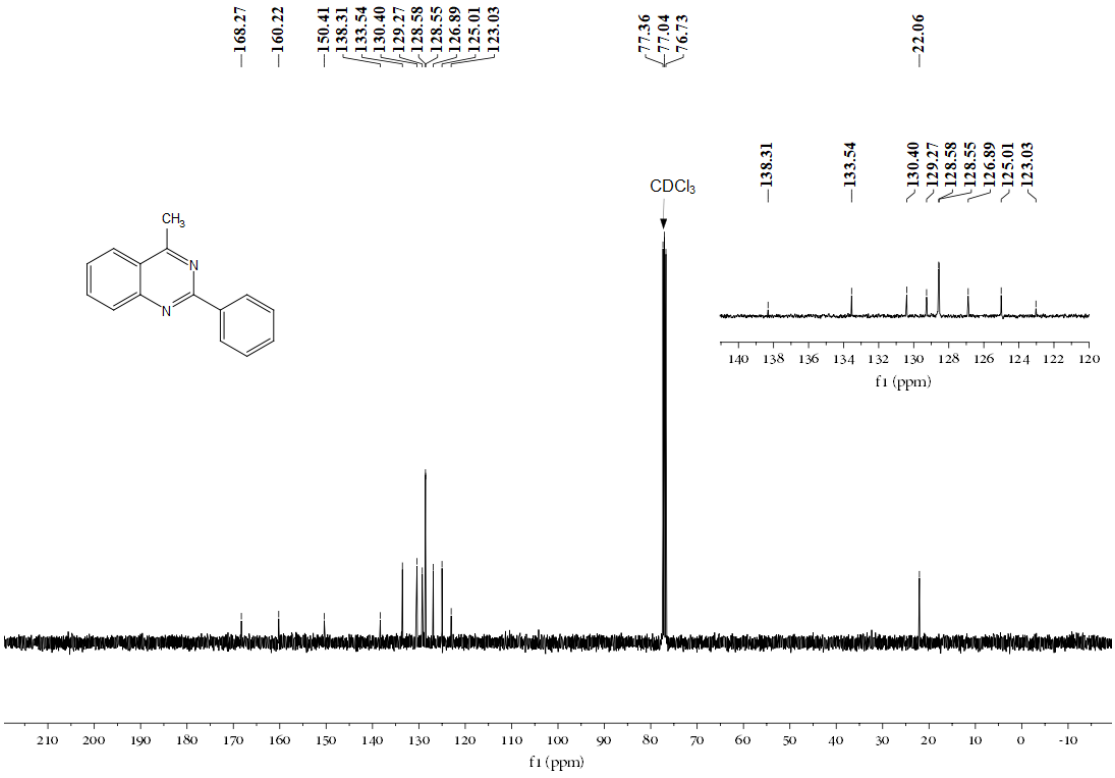


Figure S48. ^{13}C NMR Spectrum of **4e**

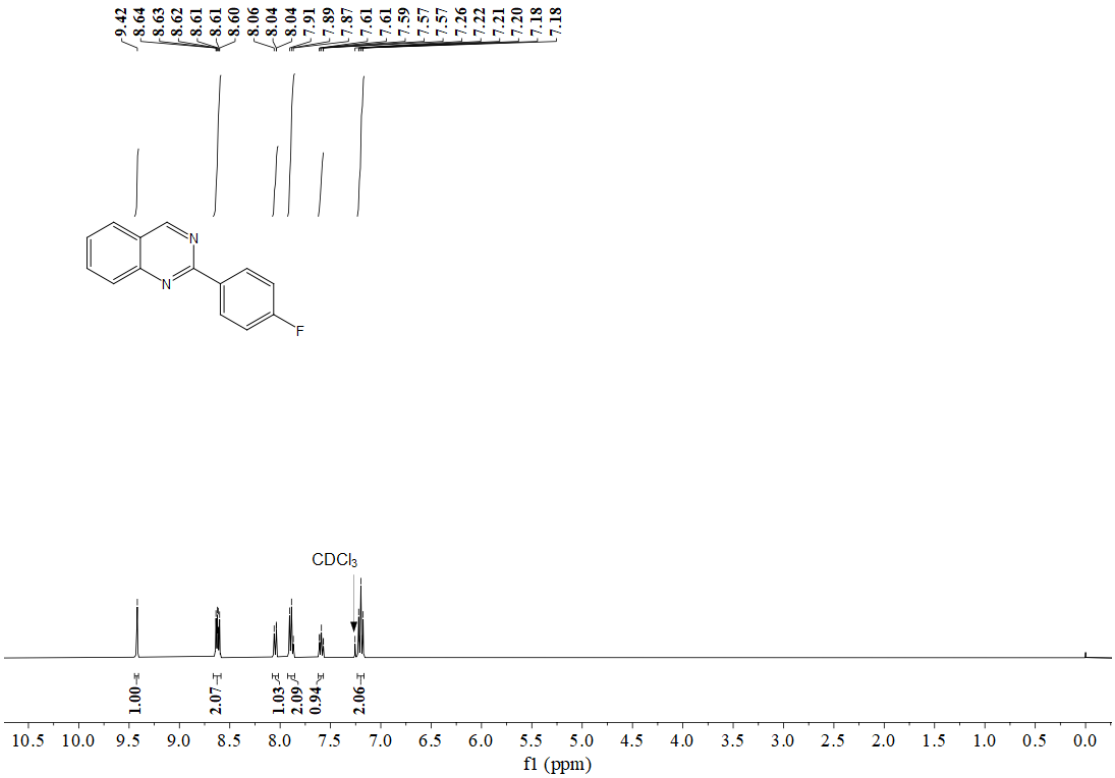


Figure S49. ^{1}H NMR Spectrum of **4f**

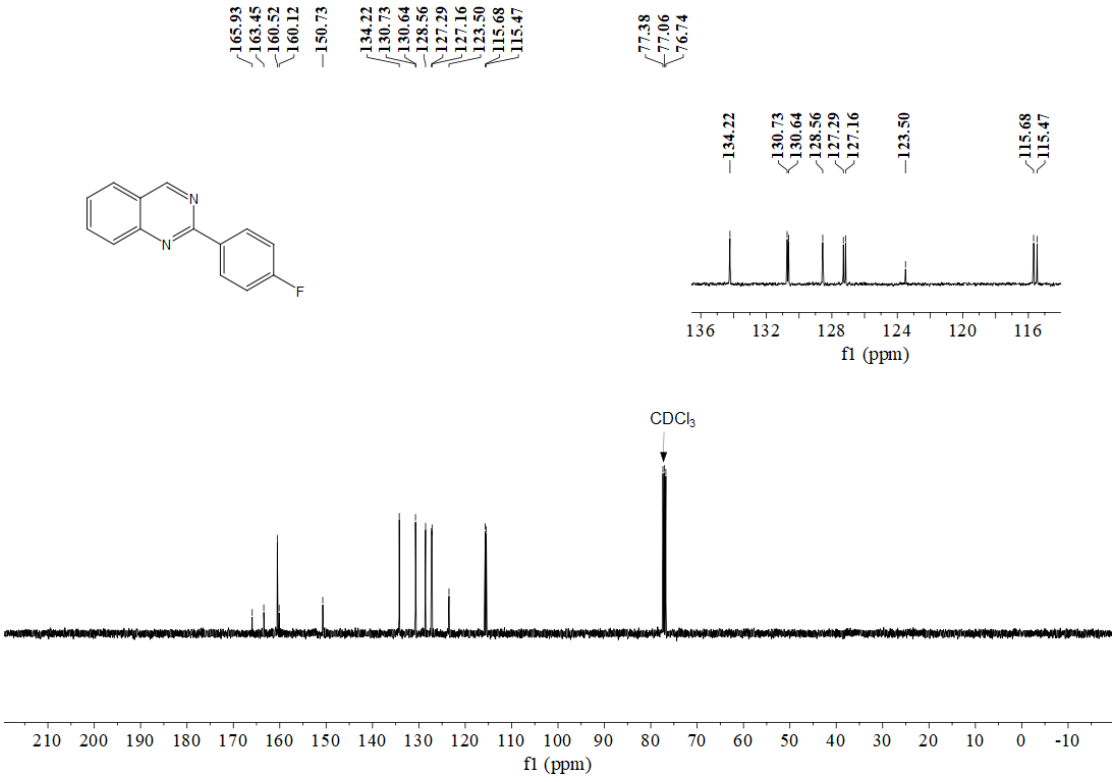


Figure S50. ^{13}C NMR Spectrum of **4f**

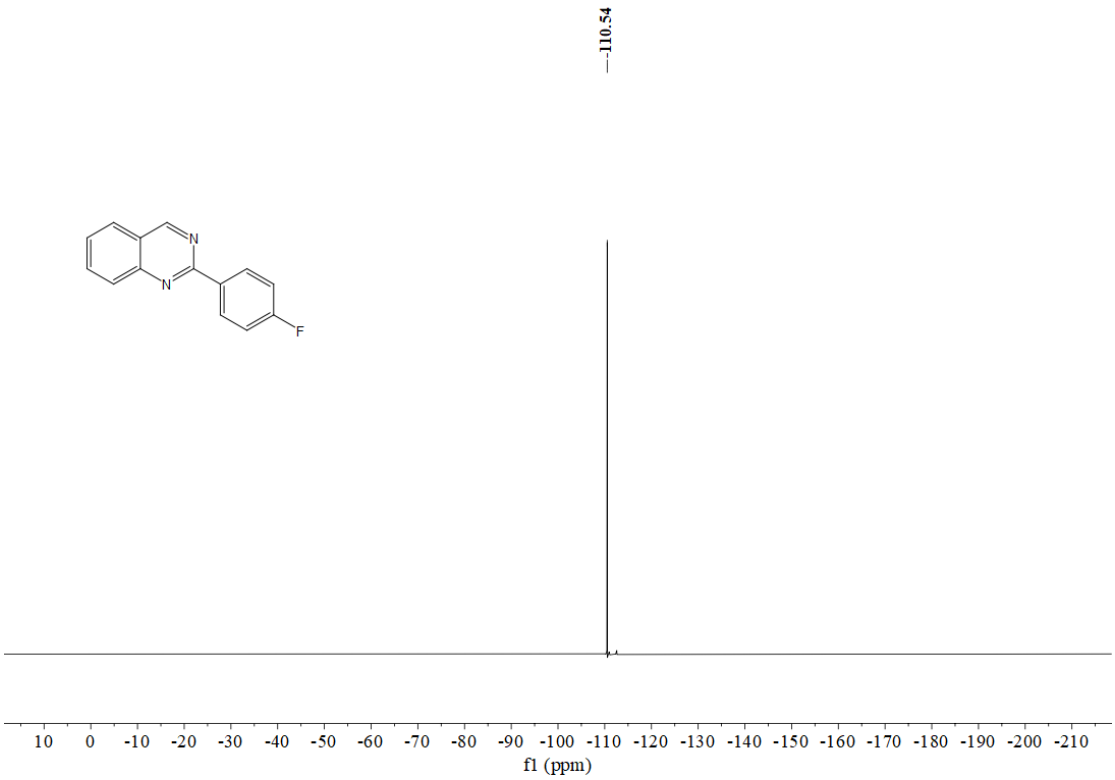


Figure S51. ^{19}F NMR Spectrum of **4f**

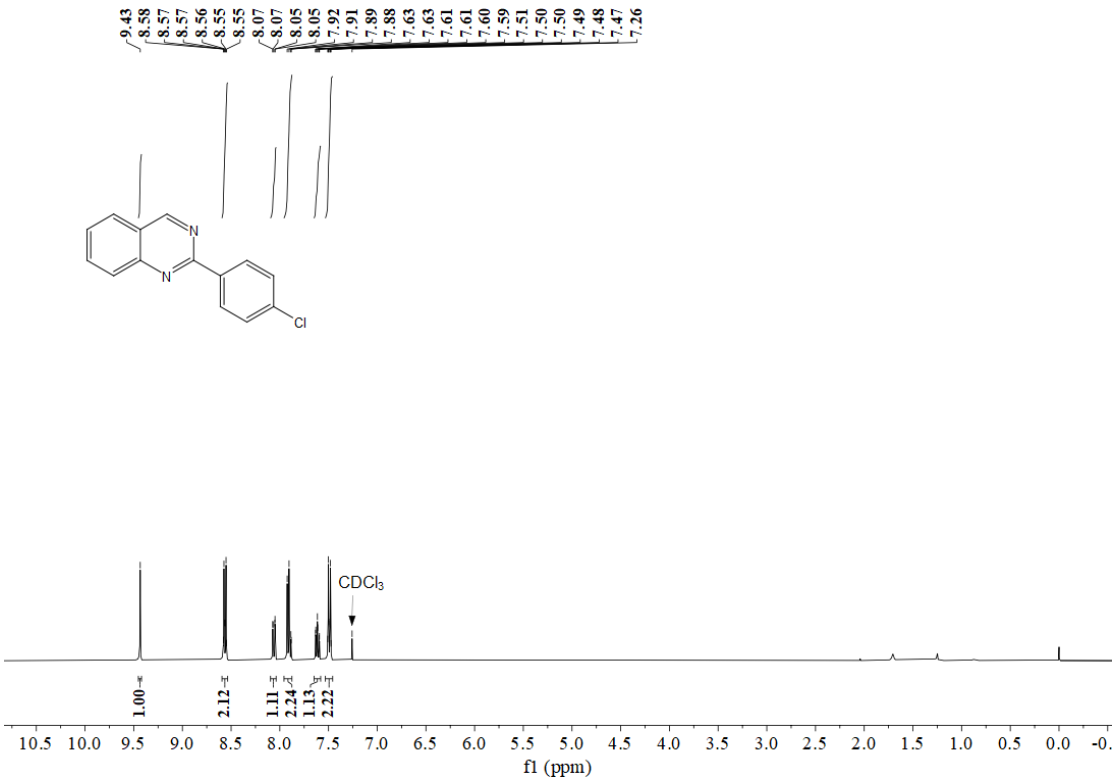


Figure S52. ^{1}H NMR Spectrum of **4g**

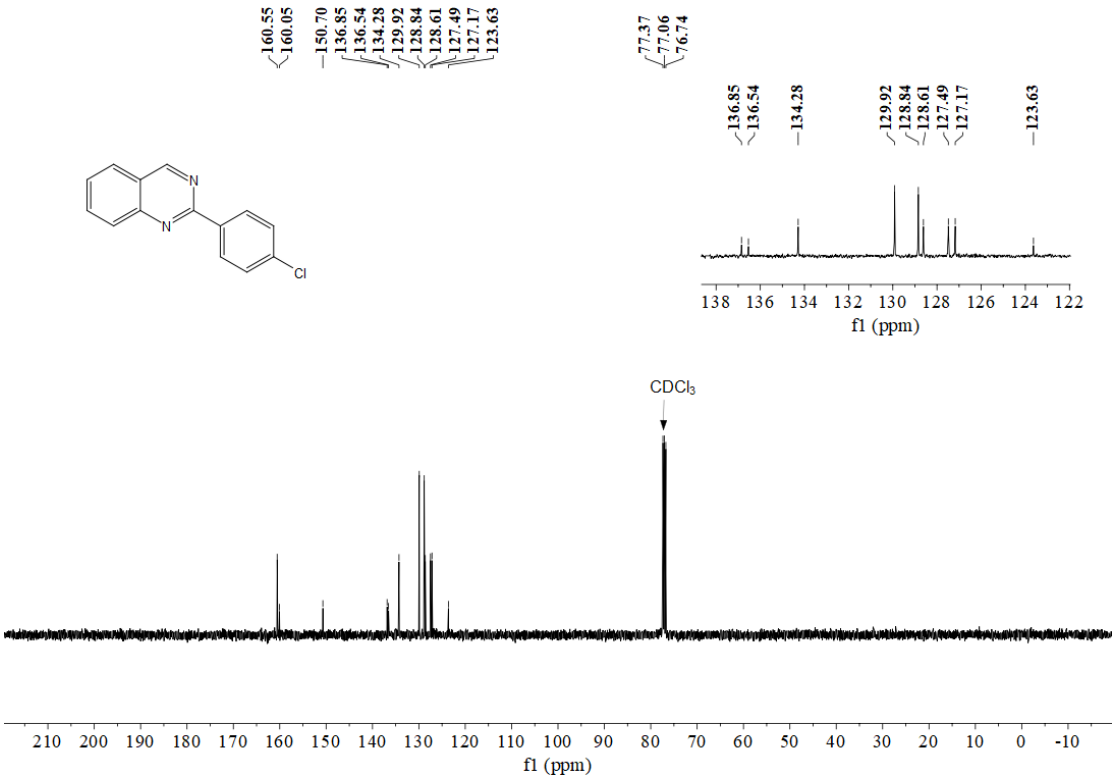


Figure S53. ^{13}C NMR Spectrum of **4g**

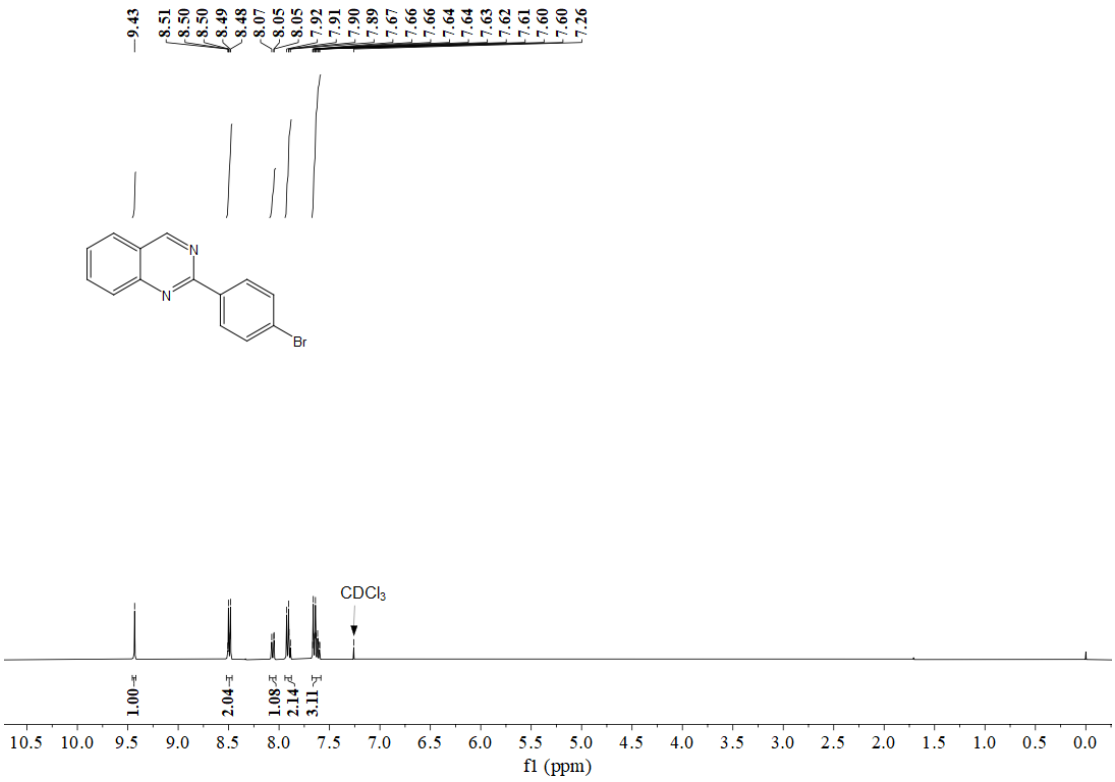


Figure S54. ^{1}H NMR Spectrum of **4h**

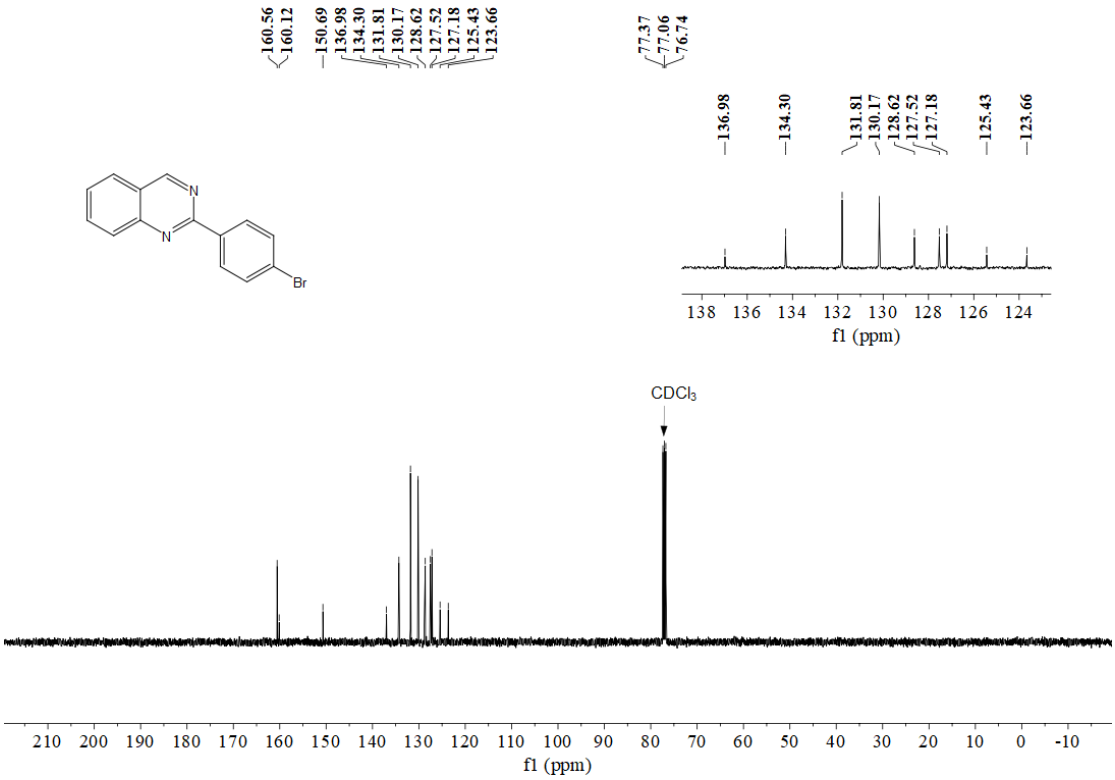


Figure S55. ^{13}C NMR Spectrum of **4h**

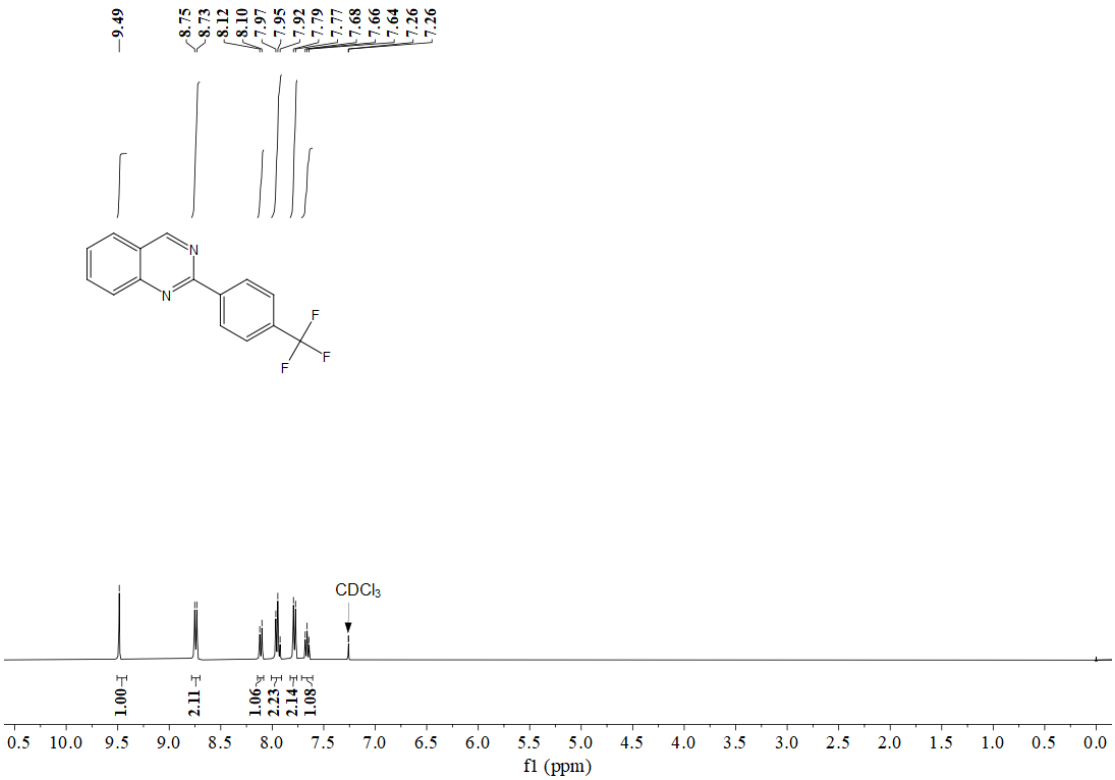


Figure S56. ^{1}H NMR Spectrum of **4i**

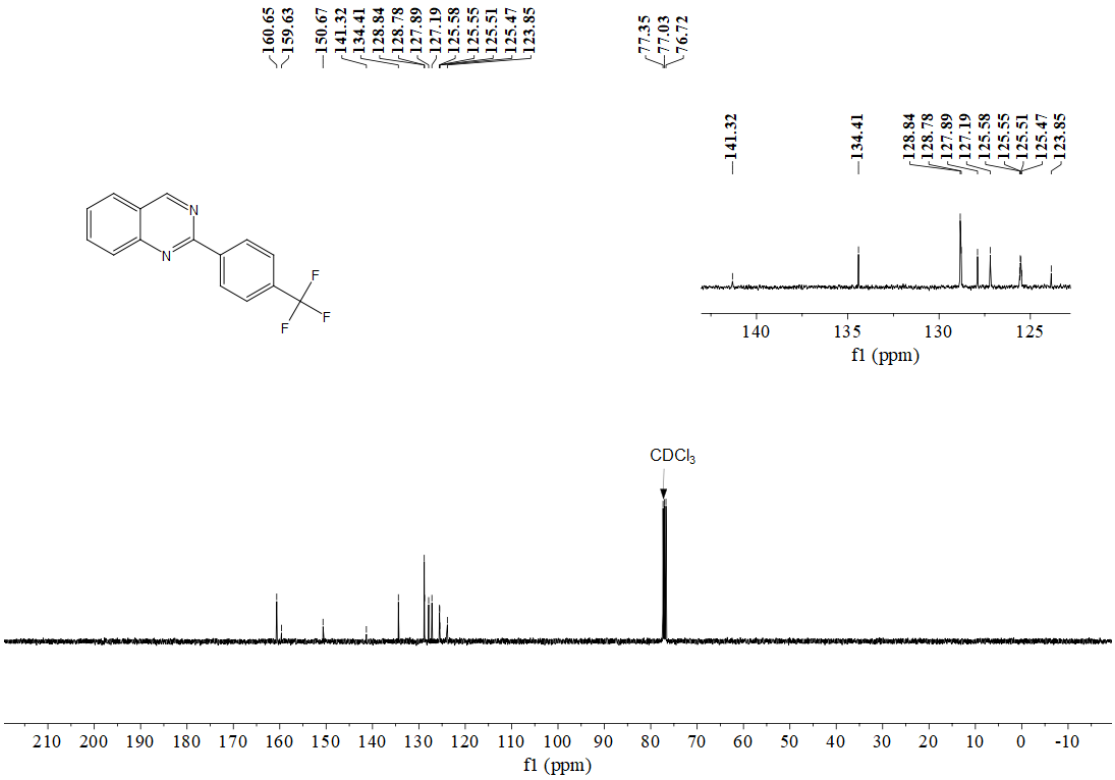


Figure S57. ^{13}C NMR Spectrum of **4i**

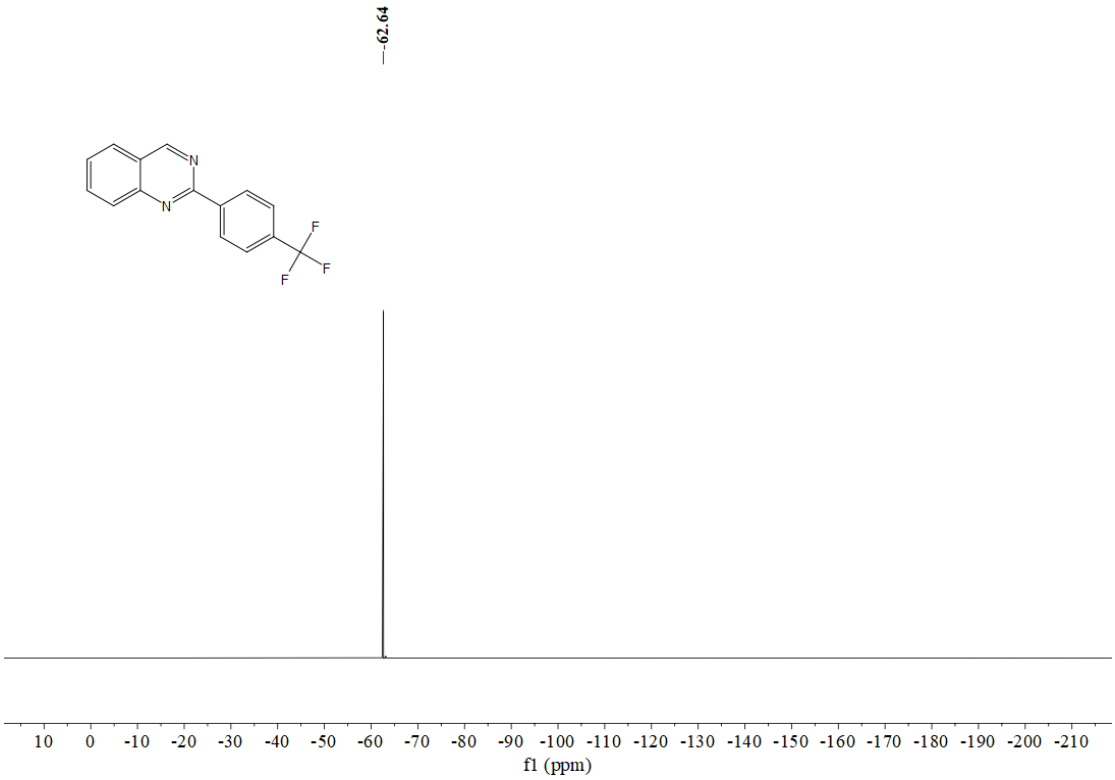


Figure S58. ^{19}F NMR Spectrum of **4i**

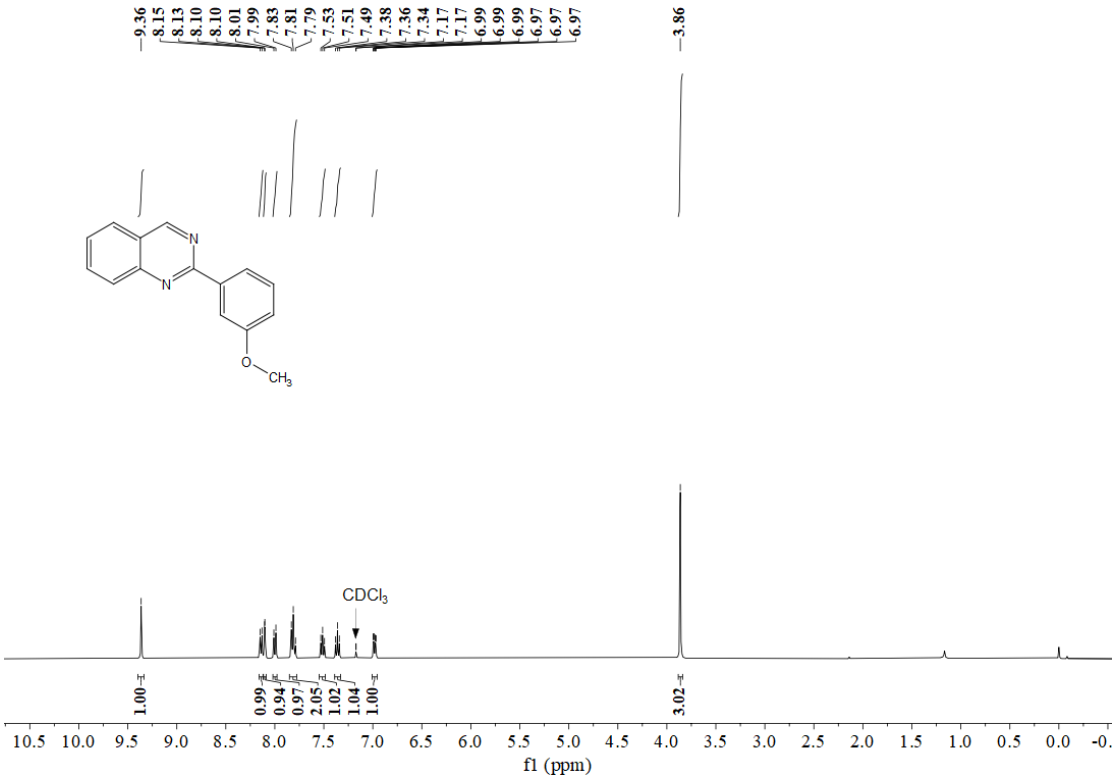


Figure S59. ^{1}H NMR Spectrum of **4j**

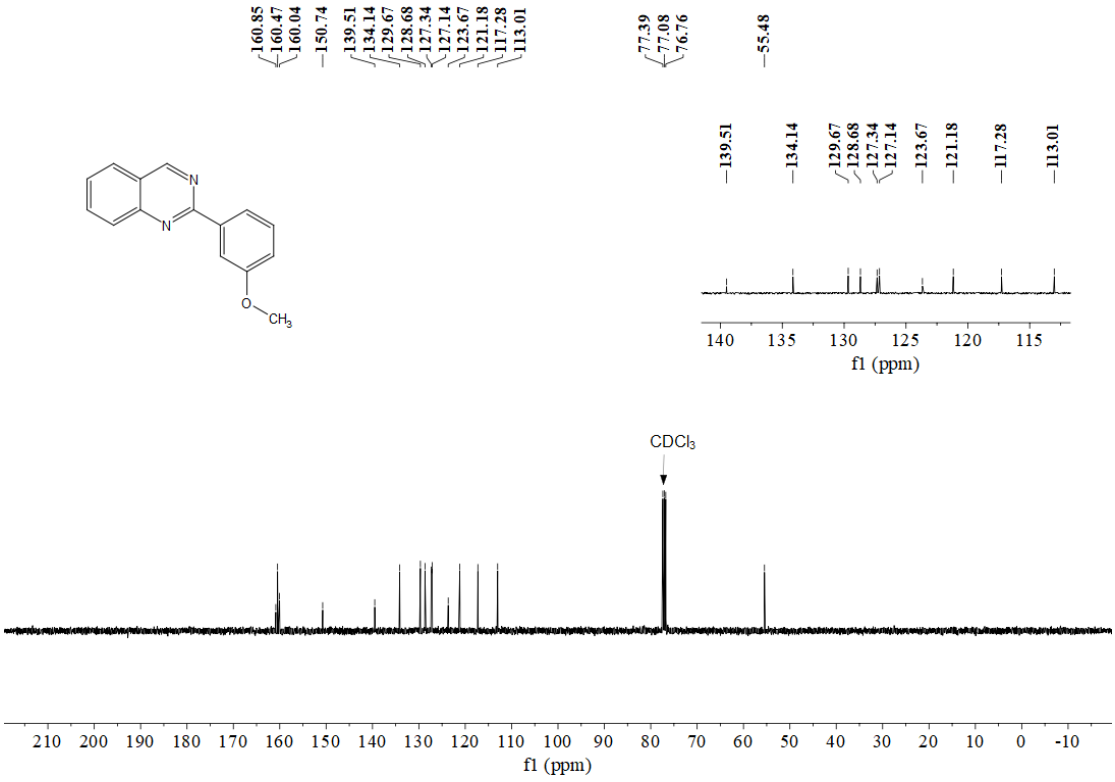


Figure S60. ^{13}C NMR Spectrum of **4j**

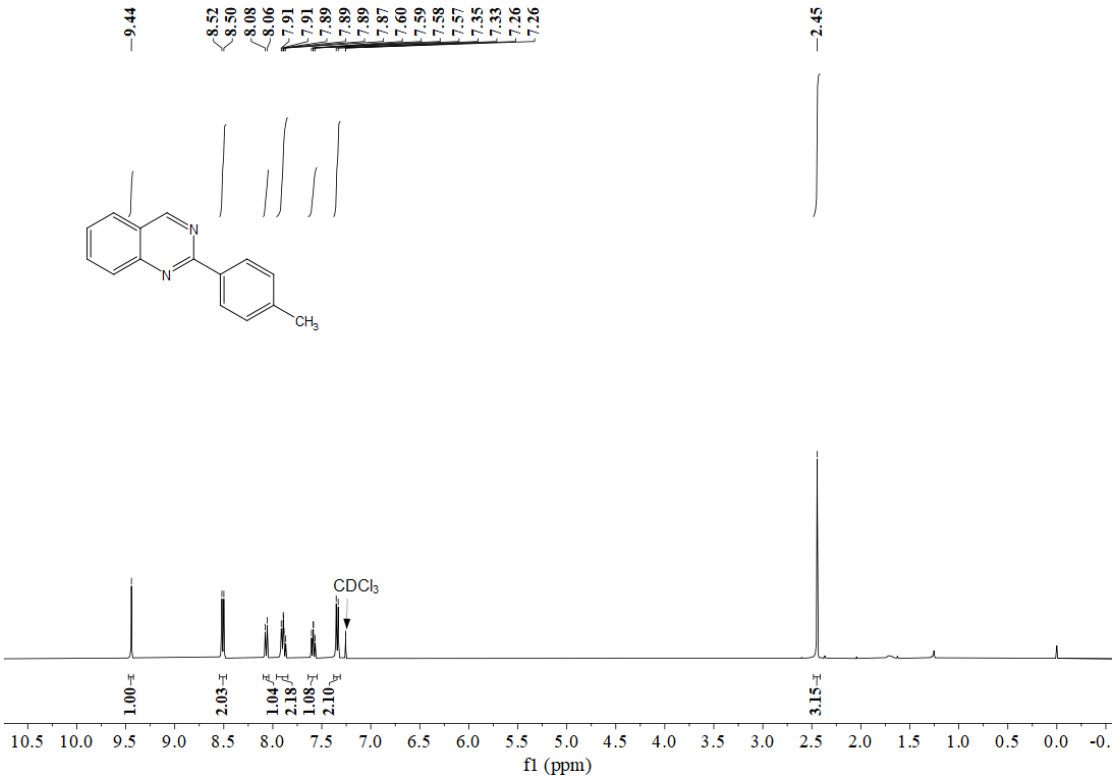


Figure S61. ^{1}H NMR Spectrum of **4k**

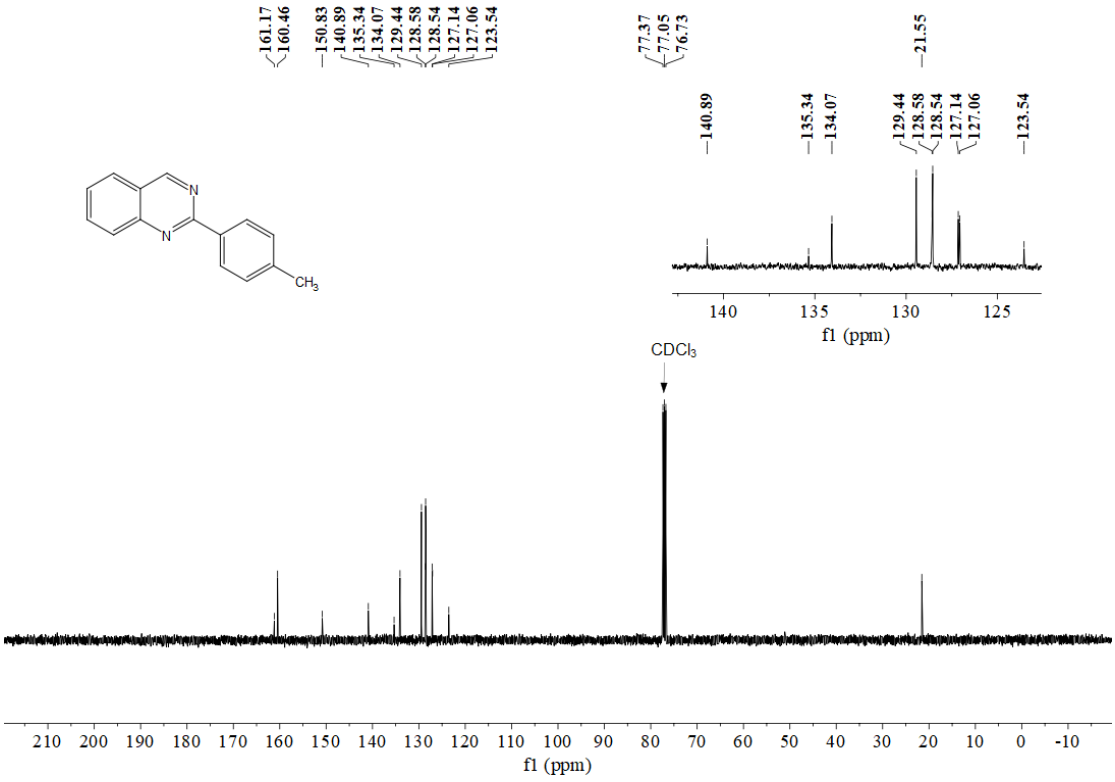


Figure S62. ^{13}C NMR Spectrum of **4k**

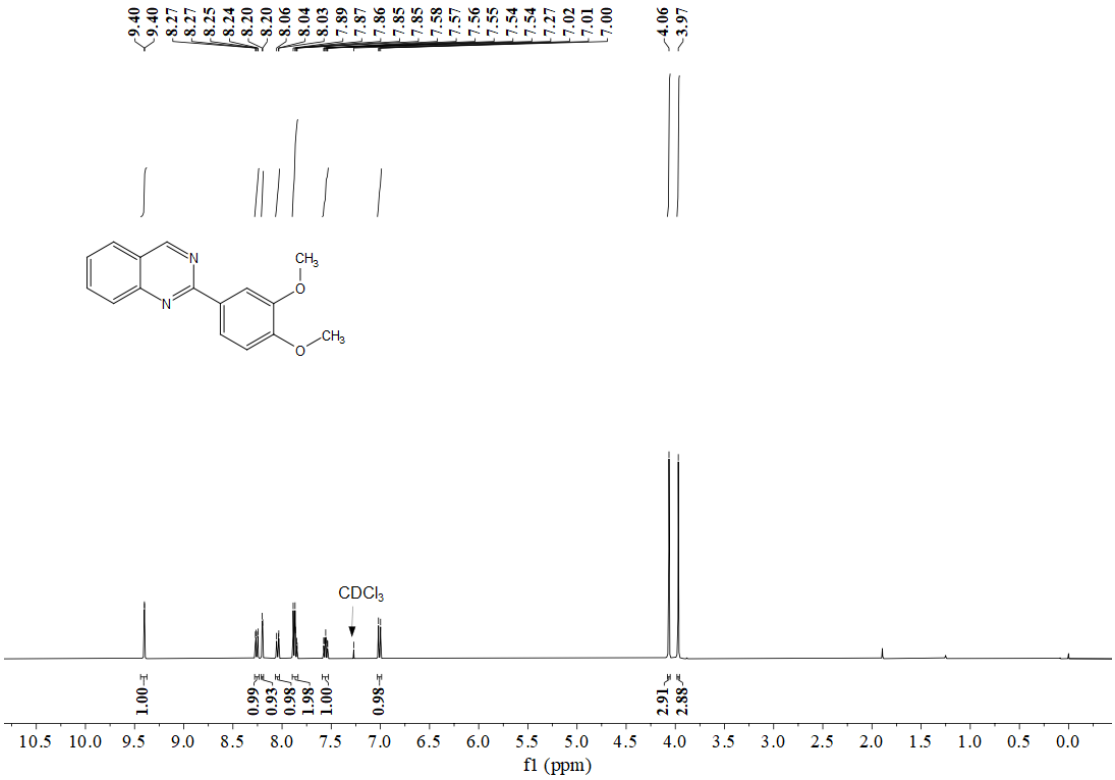


Figure S63. [1]HNMR Spectrum of **4l**

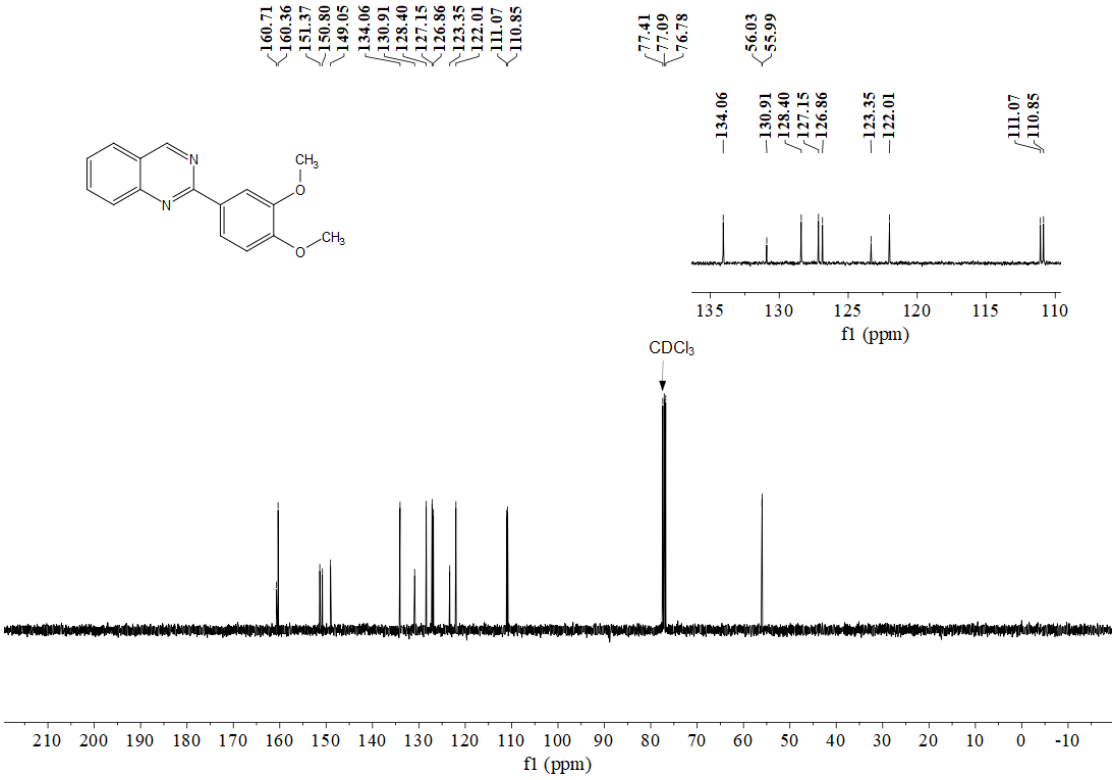


Figure S64. [13]C NMR Spectrum of **4l**

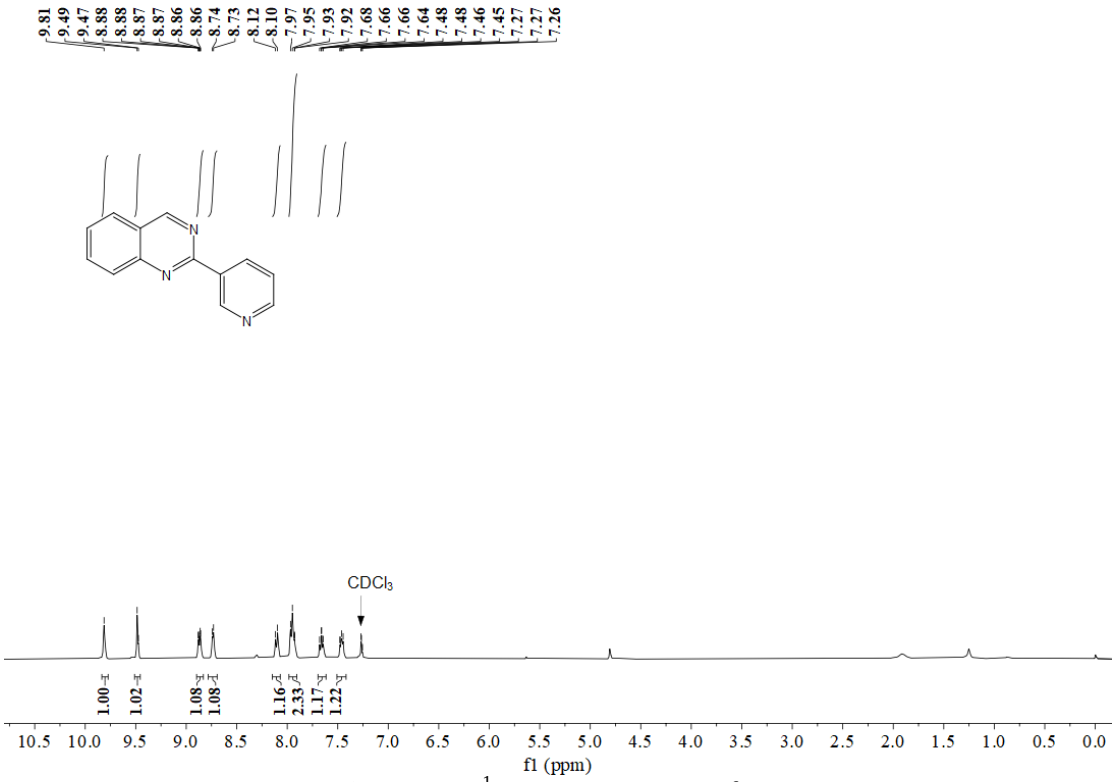


Figure S65. ^{1}H NMR Spectrum of **4m**

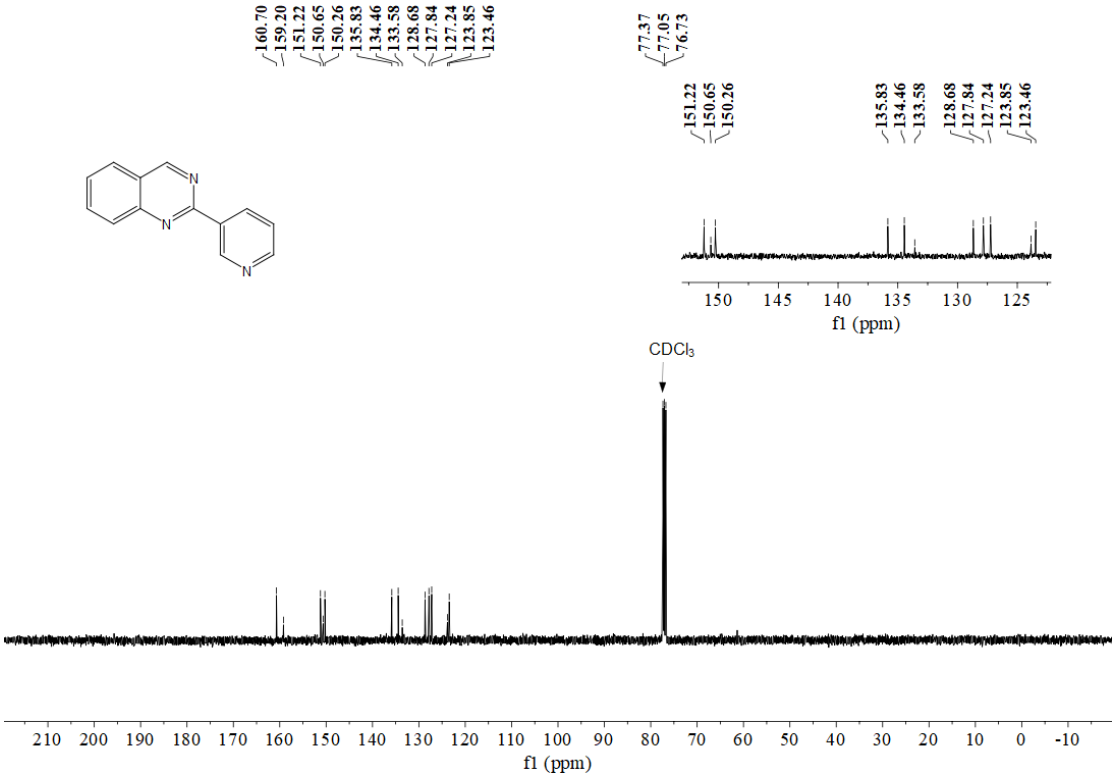


Figure S66. ^{13}C NMR Spectrum of **4m**

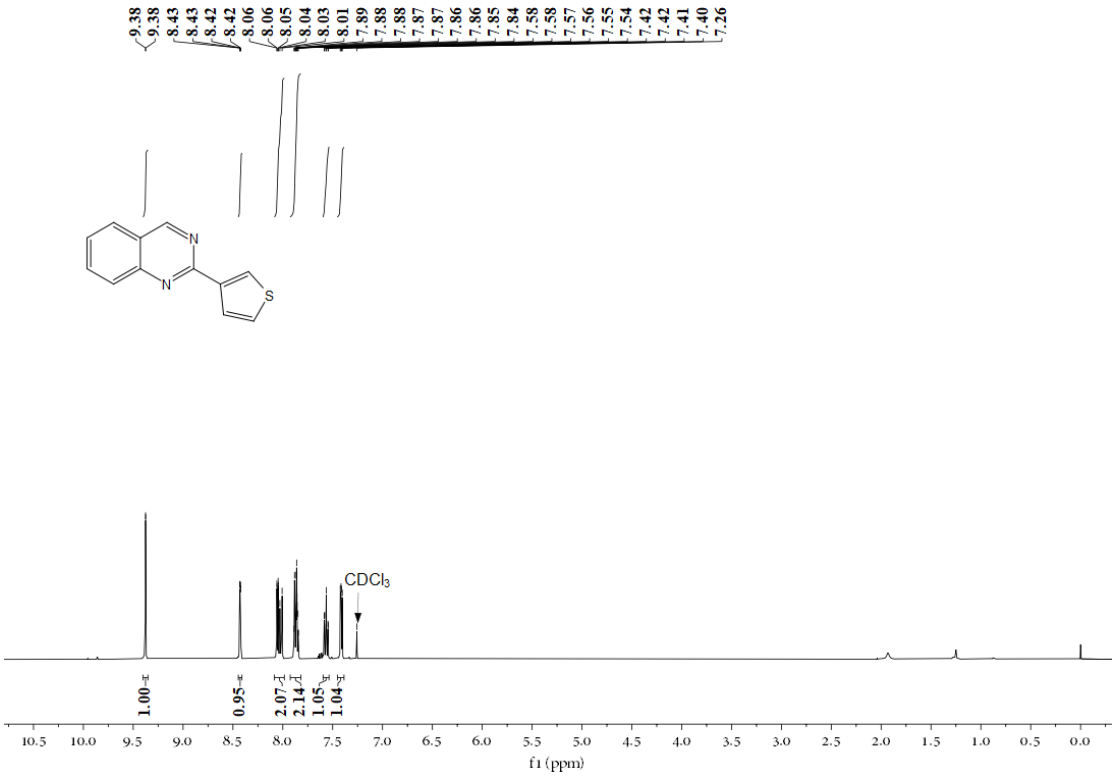


Figure S67. ^{1}HNMR Spectrum of **4n**

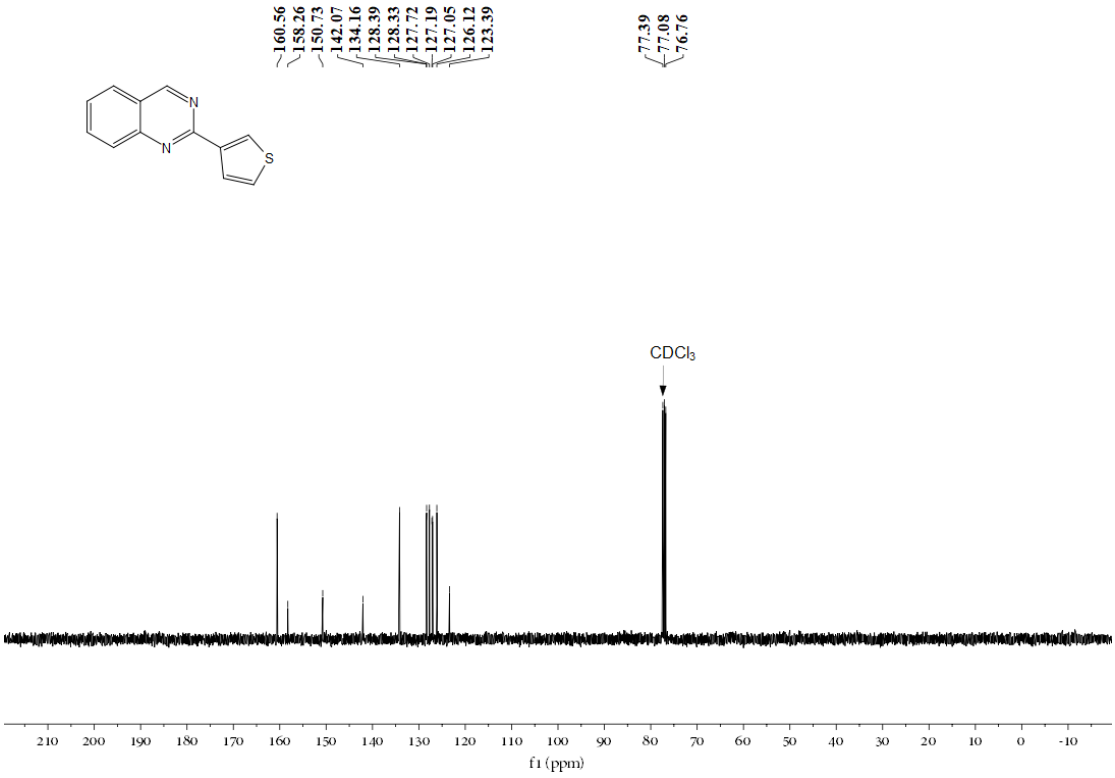


Figure S68. ^{13}C NMR Spectrum of **4n**

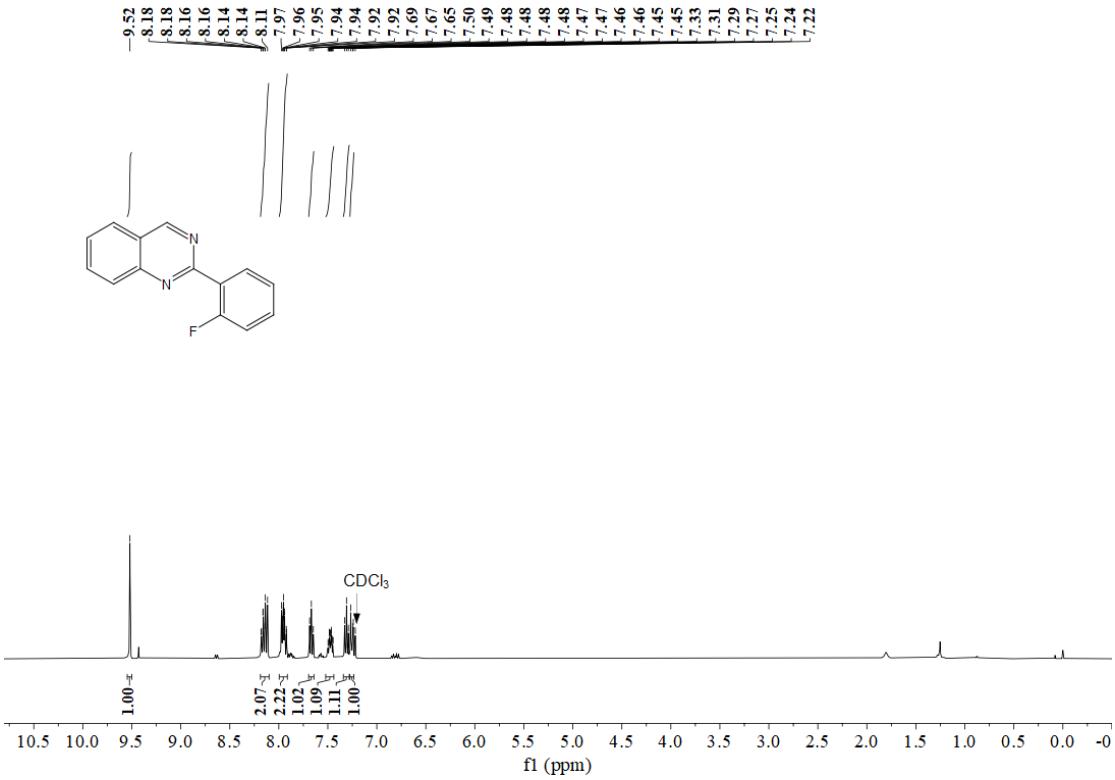


Figure S69. [1]HNMR Spectrum of **4o**

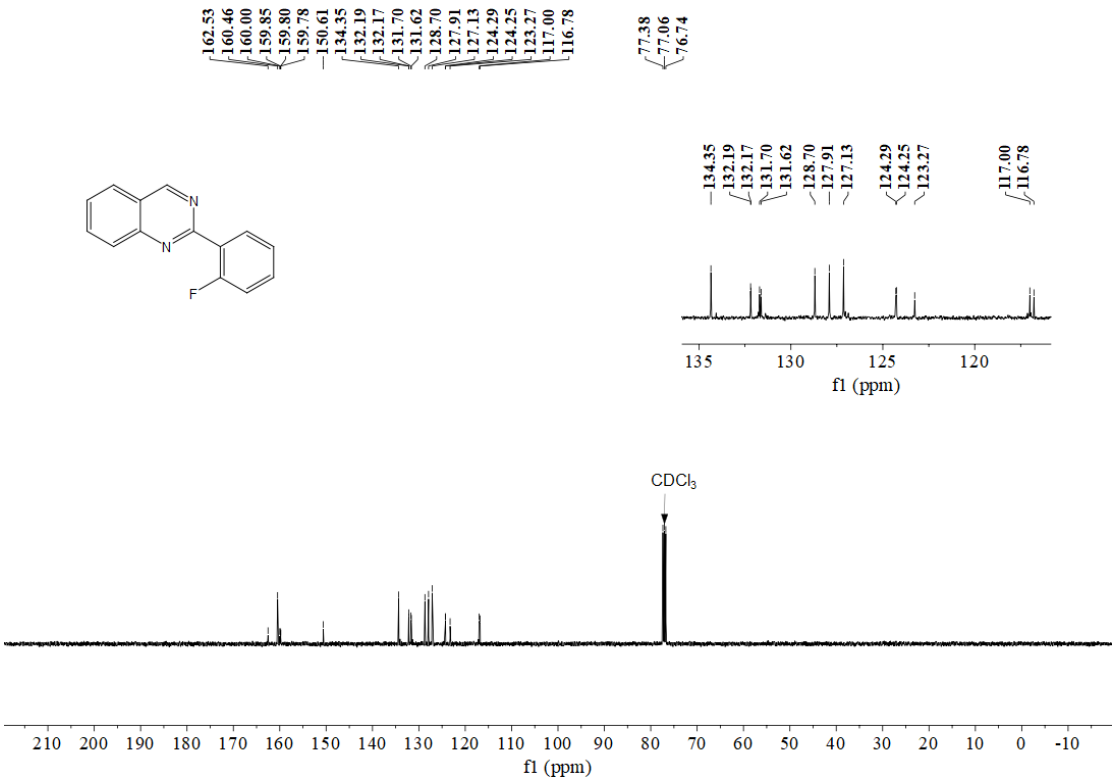


Figure S70. [13]C NMR Spectrum of **4o**

Figure S71. ^{19}F NMR Spectrum of **4o**

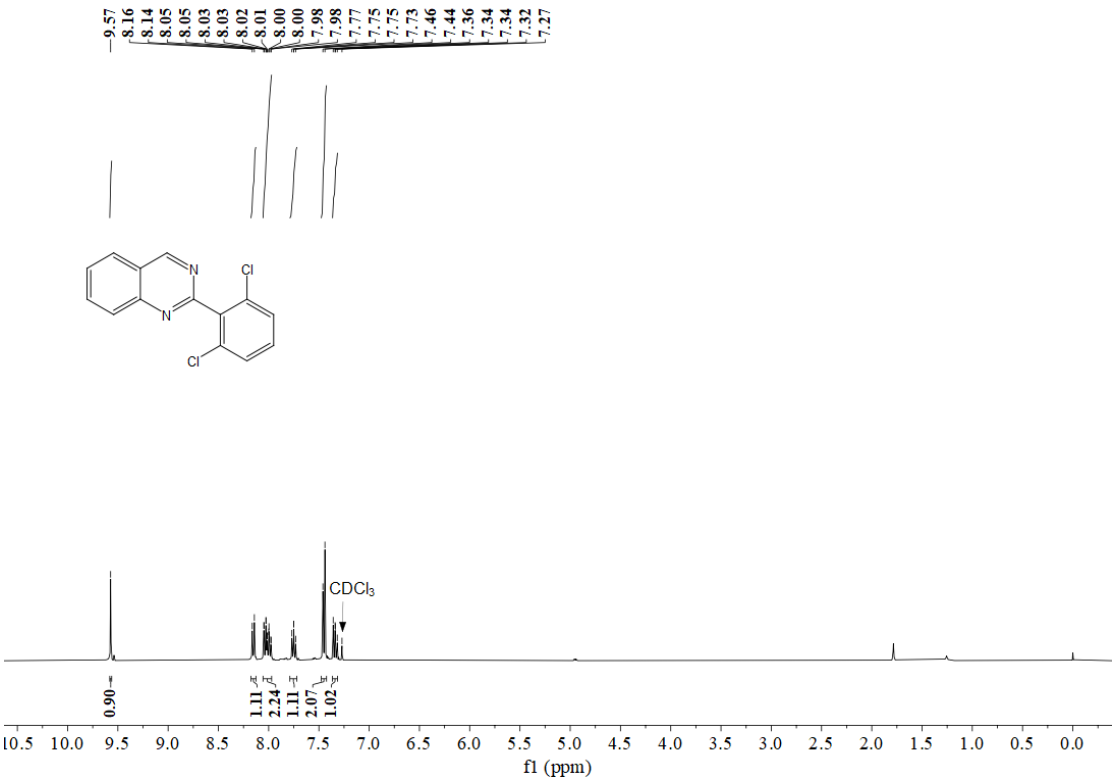


Figure S72. ^{1}H NMR Spectrum of **2-(2,6-dichlorophenyl)quinazoline**

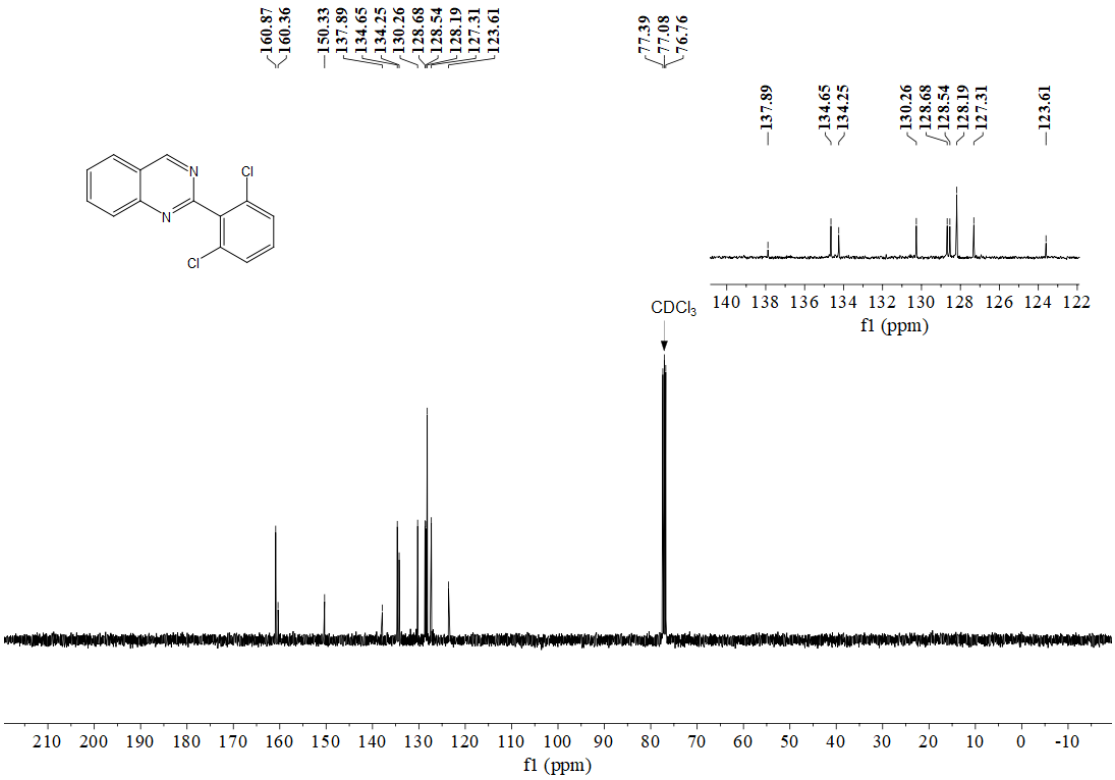


Figure S73. ^{13}C NMR Spectrum of **2-(2,6-dichlorophenyl)quinazoline**

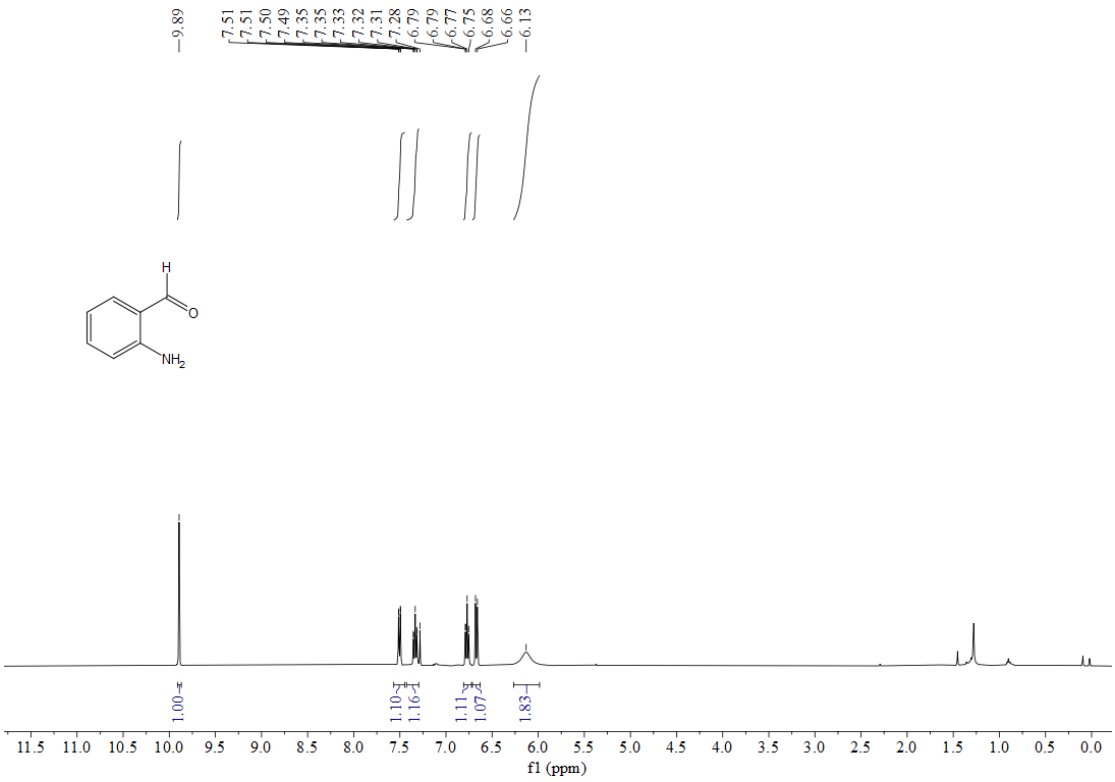


Figure S74. ^{1}H NMR Spectrum of **2-aminobenzaldehyde**

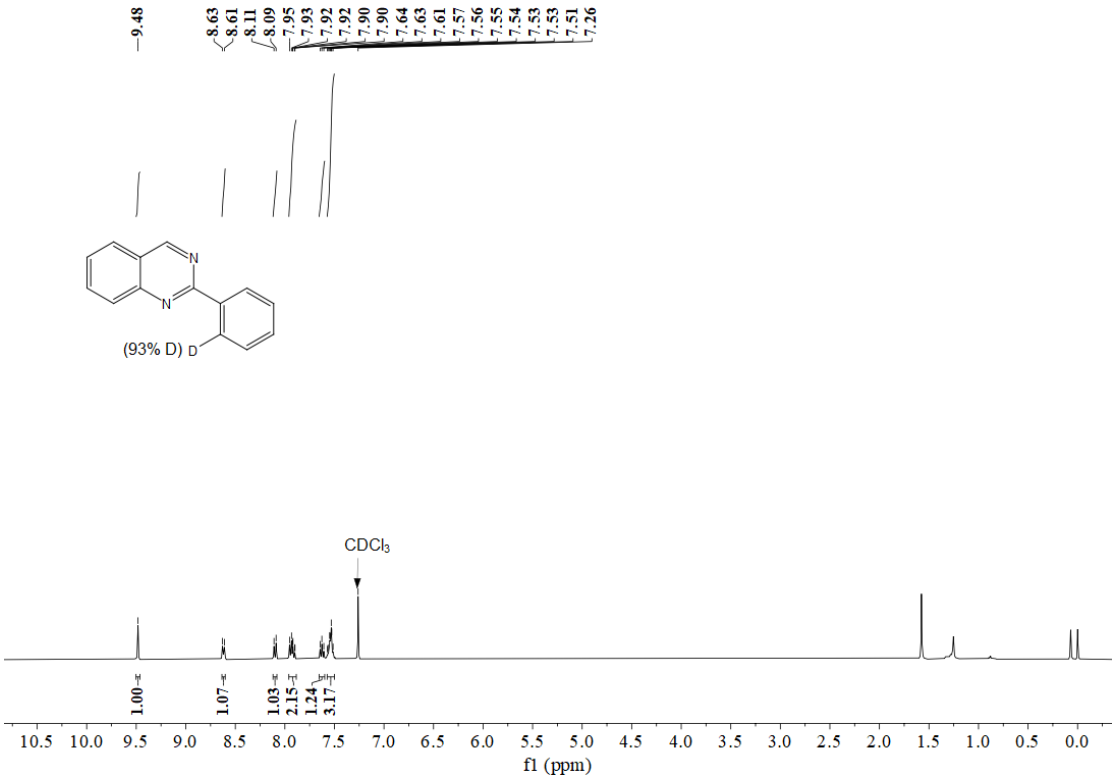


Figure S75. ^{1}H NMR Spectrum of **3a-*d*$_1$**

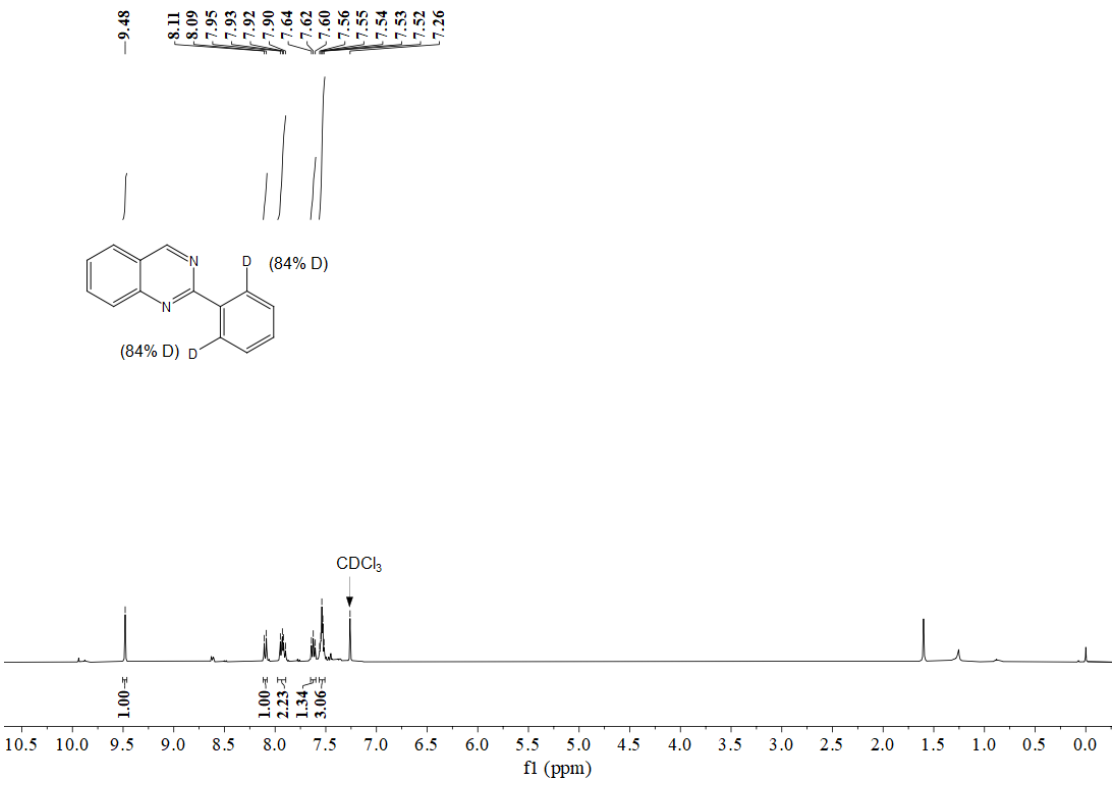


Figure S76. ^{1}H NMR Spectrum of **3a-*d*$_2$**

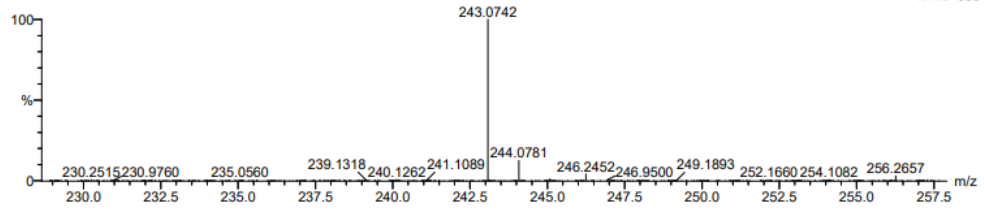
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
324 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 14-14 H: 0-100 N: 0-50 O: 0-50 F: 1-3

10
221123-6-2-1 5 (0.051)

1: TOF MS ES+
4.41e+005



Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
243.0742	243.0734	0.8	3.3	10.5	431.3	n/a	n/a	C14 H9 N2 F2

Figure S77. ^{1}H NMR Spectrum of **3b**

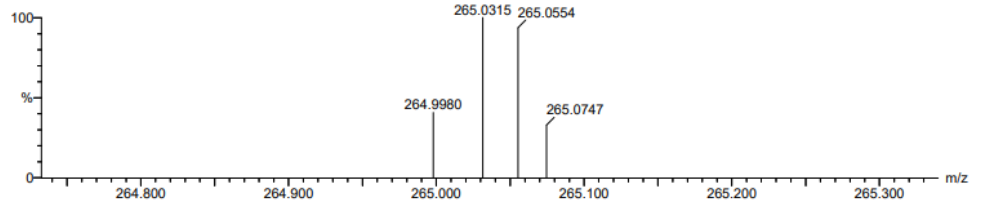
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
107 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 14-14 H: 0-100 N: 0-50 O: 0-50 F: 2-2 Na: 1-1

10
221123-6-2-2 48 (0.285)

1: TOF MS ES+
5.90e+001



Minimum:				-1.5				
Maximum:		5.0	20.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
265.0554	265.0553	0.1	0.4	10.5	20.8	n/a	n/a	C14 H8 N2 F2 Na

Figure S78. ^{1}H NMR Spectrum of **3d**

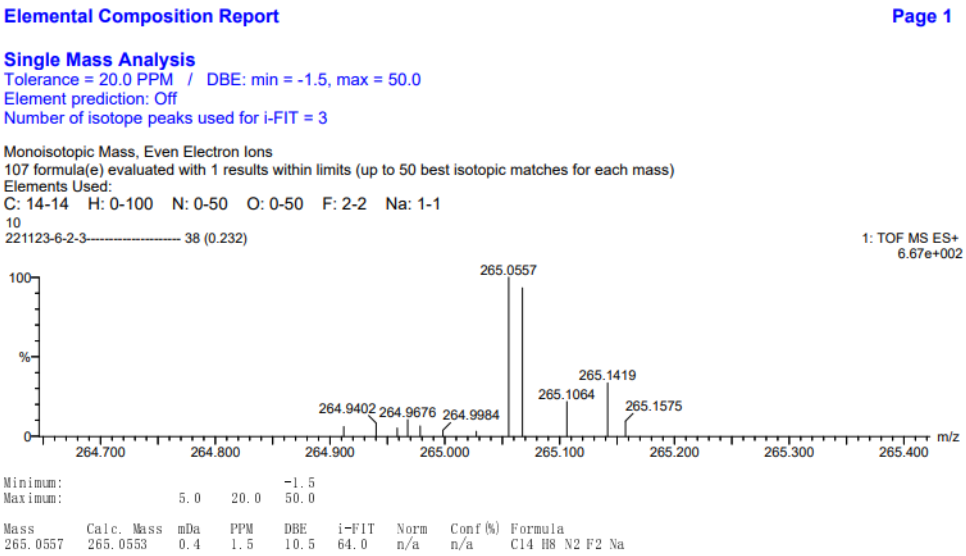


Figure S79. ^{1}H NMR Spectrum of **3e**

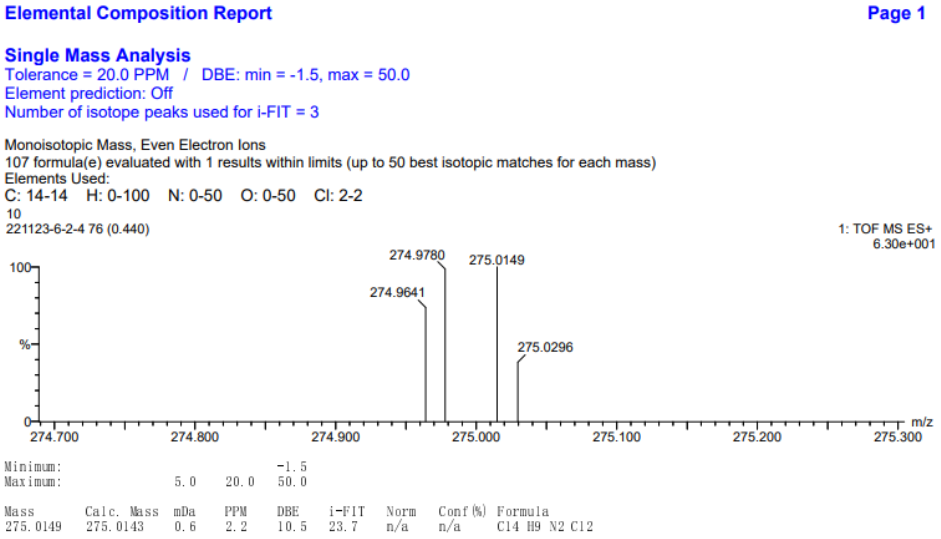


Figure S80. ^{1}H NMR Spectrum of **3g**

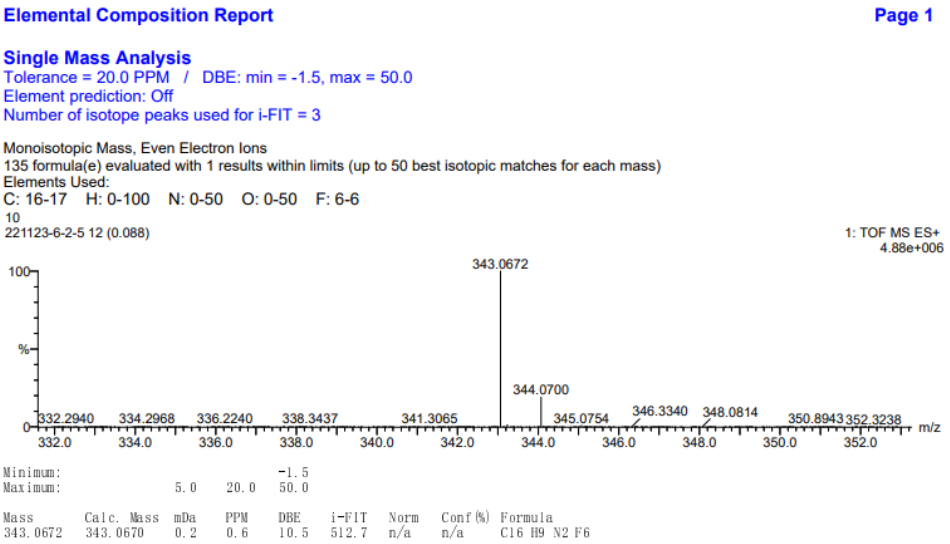


Figure S81. ^{1}H NMR Spectrum of **3h**

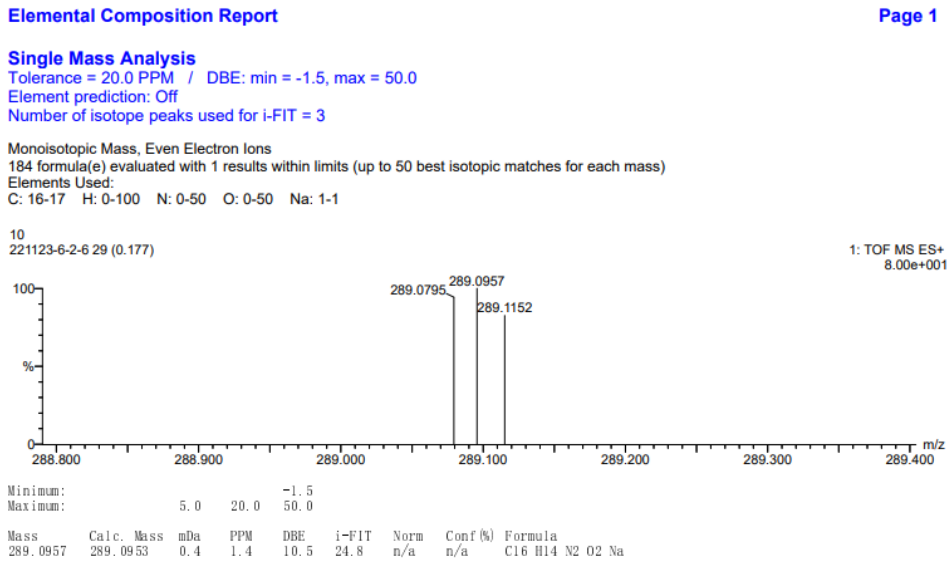


Figure S82. ^{1}H NMR Spectrum of **3l**

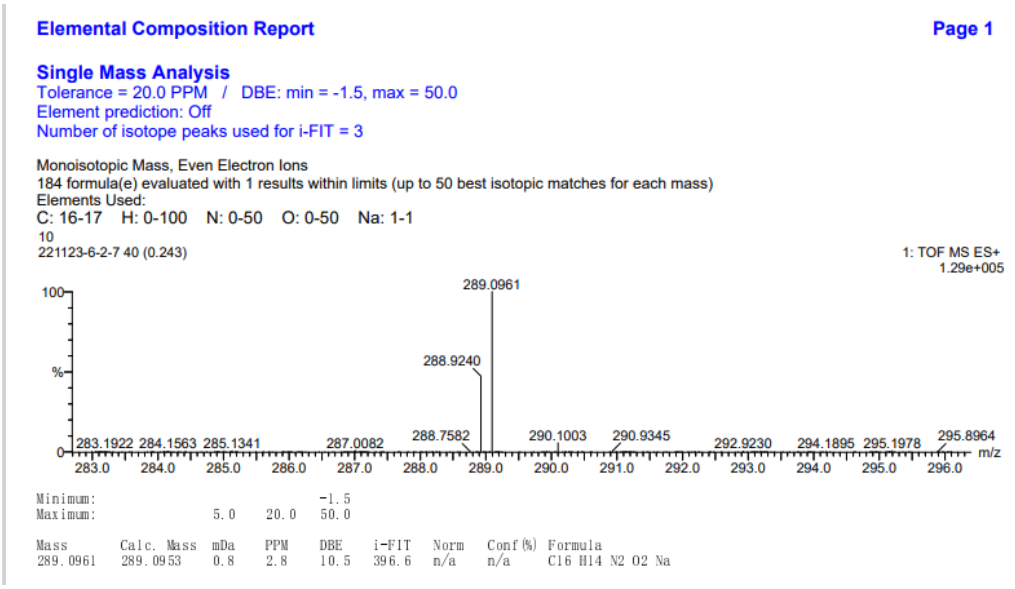


Figure S83. ^{1}H NMR Spectrum of **3m**

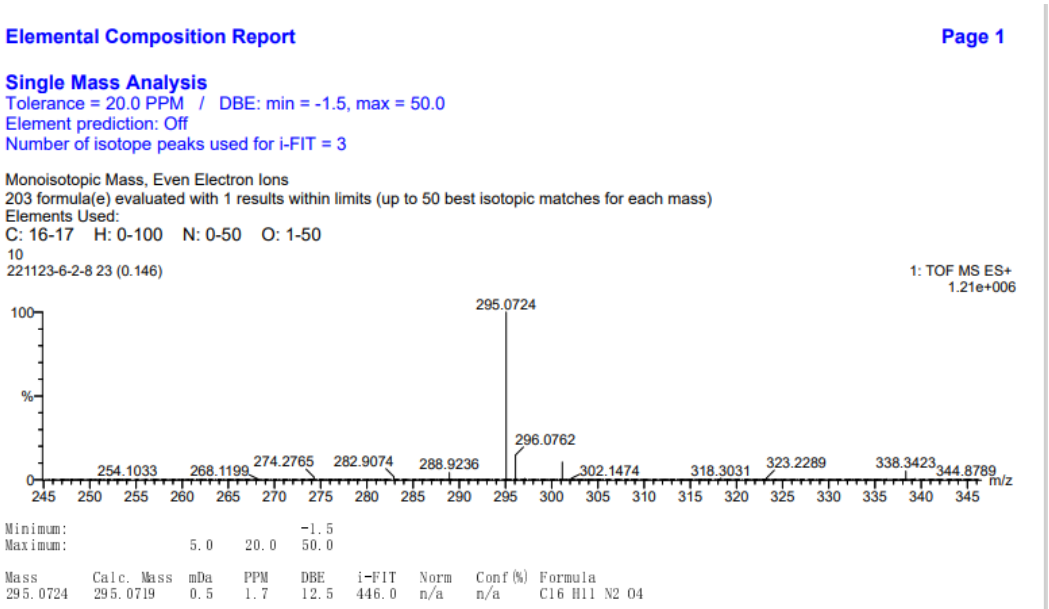


Figure S84. ^{1}H NMR Spectrum of **3n**

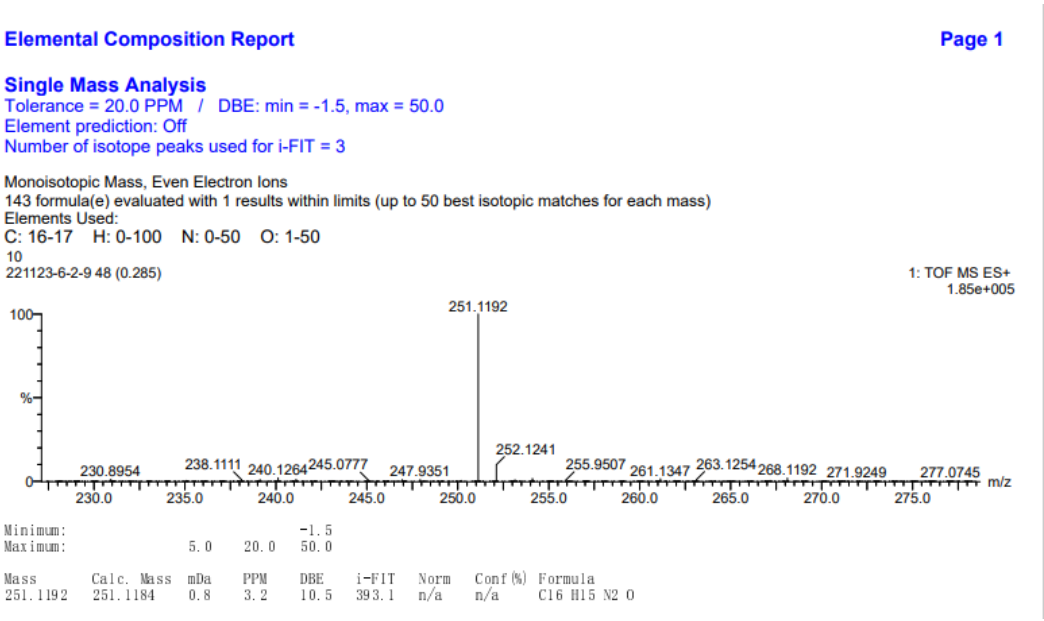


Figure S85. ^{1}H NMR Spectrum of **3p**