Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Palladium-Catalyzed Sequential Acylation/Annulation of Indoles with Acyl Chlorides Using Primary Amine as the Directing Group

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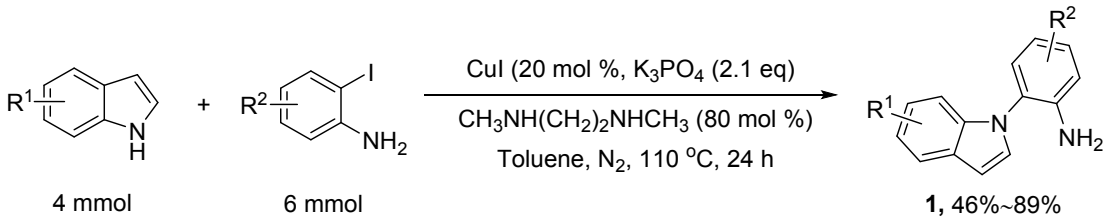
A. Instrumentation and Chemicals

All purchased reagents and solvents were used without further purification unless otherwise noted. Analytical thin layer chromatography was performed by using commercially prepared 100-400 mesh silica gel plates (GF_{254}) and visualization was effected at 254 nm. All the acyl chlorides were prepared according to known procedures. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using $CDCl_3$ as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument.

B. Experimental Procedure

1. General Procedure for Synthesis of Indoles [1]

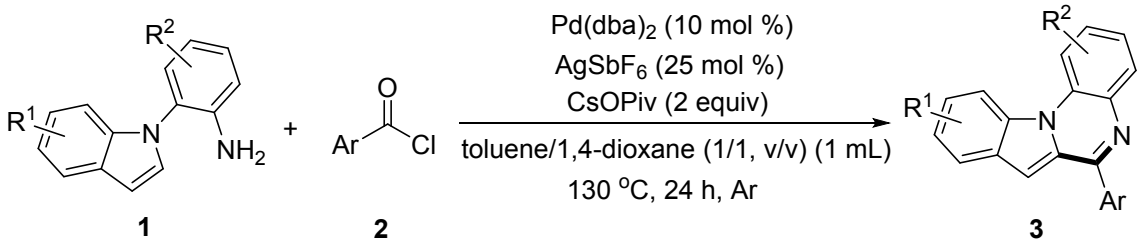


4 mmol 6 mmol **1,** 46%~89%

To a resealable Schlenk tube or alternatively, a screw-cap pressure tube, were added indole (4.0 mmol, 1.0 equiv), CuI (20 mol %), aromatic iodide (6.0 mmol, 1.5 equiv), *N,N′*-dimethylethylenediamine (80 mol %), K_3PO_4 (8.4 mmol, 2.1 equiv), toluene (6.0 mL) and a stir bar. The reaction vessel was fitted with a rubber septum, and was

evacuated and back-filled with nitrogen. The reaction tube was sealed and immersed in a preheated oil bath at 110 °C for 24 h and the solution was stirred with the aid of a magnetic stirrer. After attaining ambient temperature, the reaction mixture was diluted with ethyl acetate and filtered through a plug of silica gel. The filtrate was concentrated and the resulting residue was purified by column chromatography (silica gel, petroleum ether /EtOAc) to give the desired substrates.

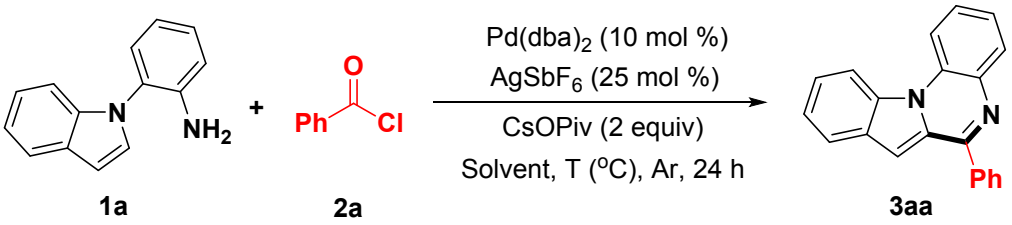
2. General Procedure for Synthesis of **3**



1 **2** **3**

2-(1*H*-indol-1-yl)anilines **1** (0.1 mmol), acyl chloride **2** (0.2 mmol), $Pd(dba)_2$ (10 mol %), $AgSbF_6$ (25 mol %), CsOPiv (0.2 mmol) and anhydrous toluene/1,4-dioxane = 1:1 (1 mL) were sealed in a Schlenk tube under Ar atmosphere. The mixture was then stirred at 130 °C (oil bath temperature) for 24 h. After the condensation was completed (monitored by TLC), the resulting mixture was cooled to room temperature and extracted with ethyl acetate, dried over anhydrous $MgSO_4$, filtered and evaporated in vacuo. The desired products **3** were obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.

C. Optimization of Reaction Conditions[a]

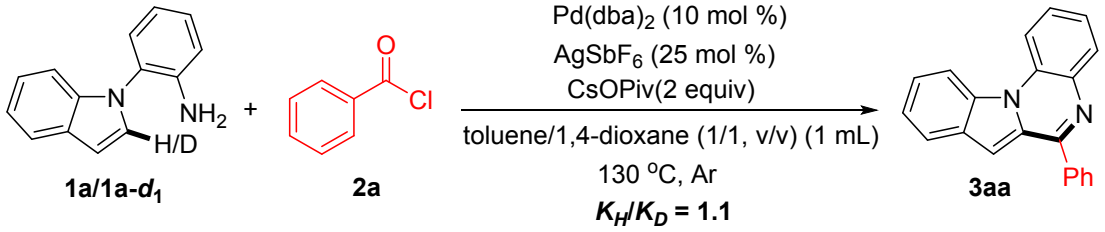


1a **2a** **3aa**

Entry	Catalyst	Additive	Base	Solvent	Yield[b] (%)
1	$Pd(dba)_2$	$AgSbF_6$	CsOPiv	DMSO	7
2	$Pd(dba)_2$	$AgSbF_6$	CsOPiv	THF	n.d.
3	$Pd(dba)_2$	$AgSbF_6$	CsOPiv	EtOH	n.d.
4	$Pd(dba)_2$	$AgSbF_6$	CsOPiv	Toluene	23
5	$Pd(dba)_2$	$AgSbF_6$	CsOPiv	1,4-dioxane	41
6	$Pd(dba)_2$	$AgSbF_6$	CsOPiv	toluene:1,4-dioxane = 3:1	49
7	$Pd(dba)_2$	$AgSbF_6$	CsOPiv	toluene:1,4-dioxane = 2:1	53
8	$Pd(dba)_2$	$AgSbF_6$	CsOPiv	toluene:1,4-dioxane = 1:1	76
9	$Pd(dba)_2$	$AgSbF_6$	CsOPiv	toluene:1,4-dioxane = 1:2	62
10	$Pd(dba)_2$	$AgSbF_6$	CsOPiv	toluene:1,4-dioxane = 1:3	55
11[c]	$Pd(dba)_2$	$AgSbF_6$	CsOPiv	toluene:1,4-dioxane = 1:1	68
12[d]	$Pd(dba)_2$	$AgSbF_6$	CsOPiv	toluene:1,4-dioxane = 1:1	71

[a]Reaction Conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $Pd(dba)_2$ (10 mol %), $AgSbF_6$ (25 mol %), CsOPiv (0.2 mmol) and solvent (1.0 mL) were sealed in a 25 mL Schlenk tube at 130 °C for 24 h under Ar; [b]Isolated yields; n.d. = not detected; [c]120 °C; [d]140 °C.

D. Mechanism Study



2-(1*H*-indol-1-yl)aniline **1a** (0.05 mmol) or 2-(1*H*-indol-1-yl-2-*d*)aniline **1a-*d*$_1$** (0.05 mmol) were added to two separate dried 25 mL resealable Schlenk tube equipped with a magnetic stir bar along with benzoyl chloride (**2a**) (0.1 mmol), $Pd(dba)_2$ (10 mol %), $AgSbF_6$ (25 mol %), CsOPiv (0.1 mmol) and anhydrous toluene/1,4-dioxane = 1:1 (1 mL). Each of the reaction was stirred at 130 °C under Ar atmosphere for a selected period of time. Then, the resulting mixture was cooled to room temperature and extracted with ethyl acetate, dried over anhydrous $MgSO_4$, filtered and evaporated in vacuo. The desired products **3aa** was obtained in the corresponding yields after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.

Time	1 h	2 h	3 h	4 h
1a/3aa	**0.15**	**0.21**	**0.29**	**0.38**
1a-*d*$_1$/3aa	**0.09**	**0.17**	**0.21**	**0.27**

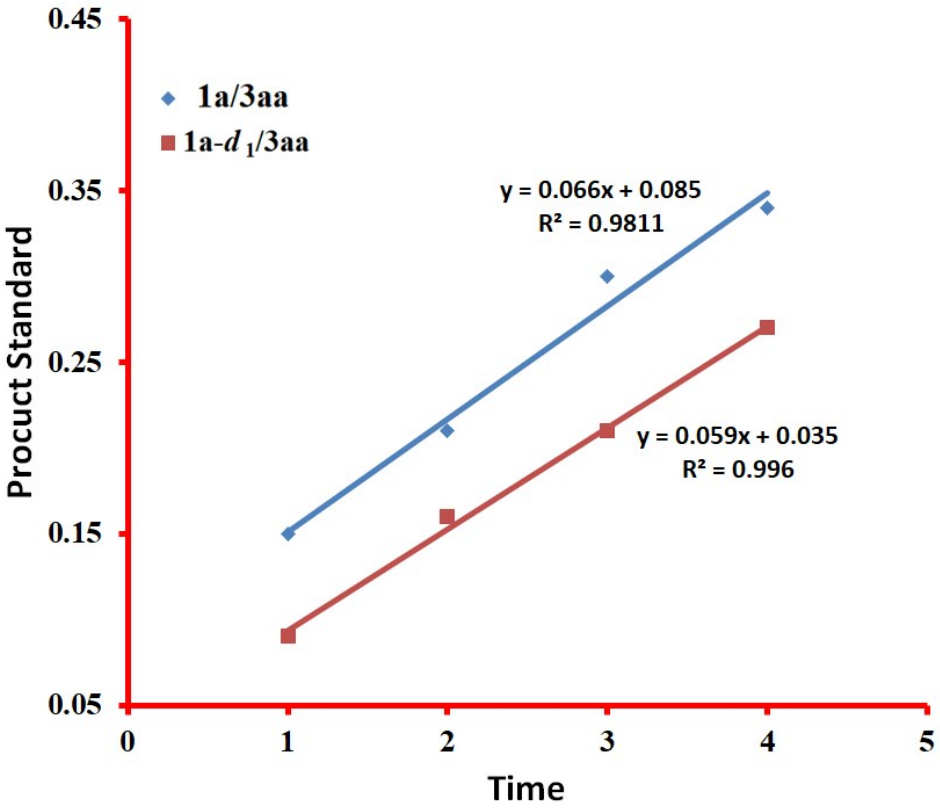


Fig S1 Kinetic isotope effect study

E. Proposed Mechanism

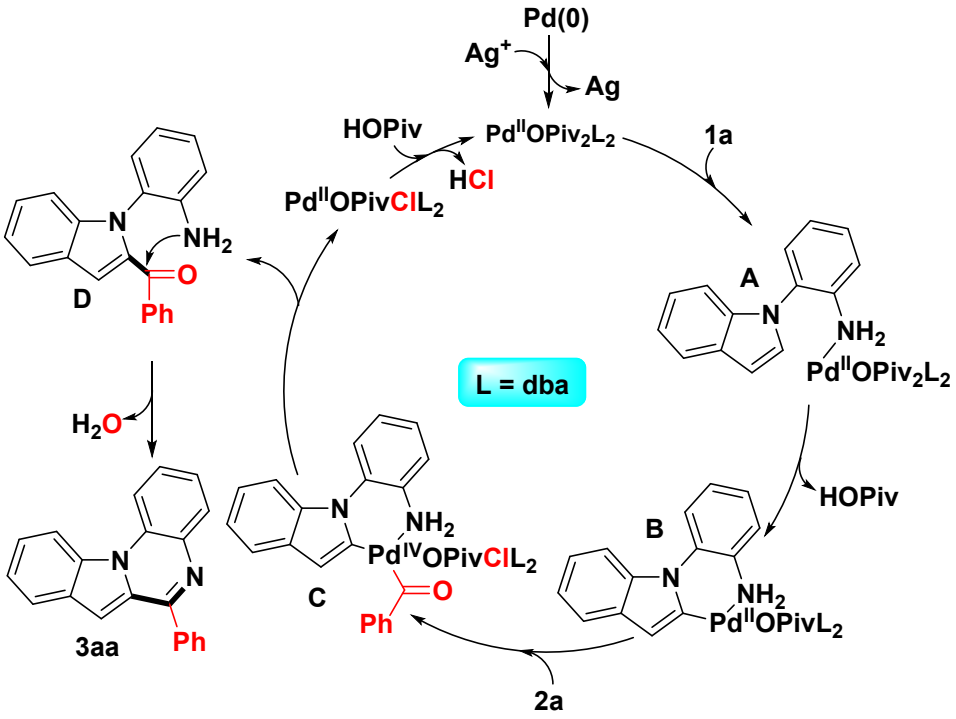
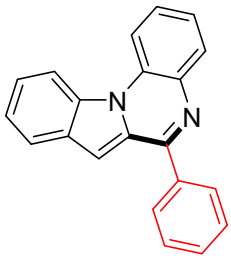
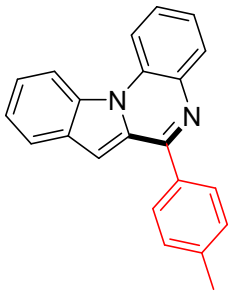


Fig S2 Proposed mechanism

F. Characterization Data of Products 3aa-3va and 3ab-3as[2]

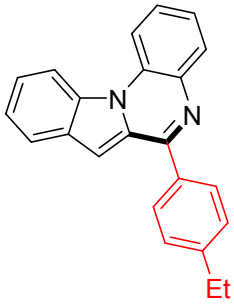


6-phenylindolo[1,2-*a*]quinoxaline, Compound **3aa** was obtained in 76% yield (22. 3 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 171-172 °C; R_f = 0.6 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (dd, J = 11.9, 8.9 Hz, 2H), 8.12 (d, J = 7.9 Hz, 1H), 8.09-8.01 (m, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.65-7.55 (m, 5H), 7.46 (dd, J = 13.7, 6.9 Hz, 2H), 7.26 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2, 138.3, 136.3, 133.1, 130.6, 130.2, 130.0, 129.2, 129.1, 128.7, 128.7, 128.3, 124.4, 124.2, 122.8, 122.7, 114.7, 114.6, 102.5; HRMS (ESI) m/z: calcd for $C_{21}H_{15}N_2$ $[M+H]^+$, 295.1230; found 295.1231.

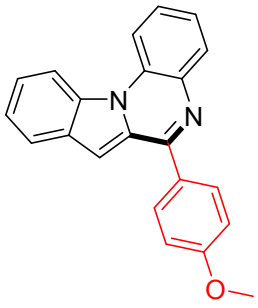


6-(*p*-tolyl)indolo[1,2-*a*]quinoxaline, Compound **3ba** was obtained in 80% yield (24. 5 mg) according to the general procedure (0.1 mmol); Yellow oil; R_f = 0.6 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (t, J = 8.9 Hz, 2H), 8.14 (d, J = 7.7 Hz, 1H), 8.01-7.93 (m, 3H), 7.61 (m, J = 20.1, 7.9 Hz, 2H), 7.50-7.40 (m, 4H), 7.29 (d, J = 5.8 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 140.3, 136.1, 135.2, 133.2, 130.35, 130.2, 129.4, 129.3, 129.2, 128.6, 128.3, 124.4,

124.2, 122.8, 122.9, 114.7, 114.6, 102.8, 21.5; HRMS (ESI) m/z: calcd for $C_{22}H_{17}N_2$ $[M+H]^+$, 309.1386; found 309.1391.

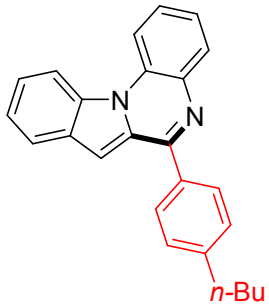


6-(4-ethylphenyl)indolo[1,2-*a*]quinoxaline, Compound **3ca** was obtained in 75% yield (24.2 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 93-94 °C; R_f = 0.6 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (t, J = 8.4 Hz, 2H), 8.06 (dd, J = 7.9, 1.3 Hz, 1H), 7.93 (dd, J = 13.2, 8.0 Hz, 3H), 7.61-7.50 (m, 2H), 7.42 (dd, J = 13.7, 7.6 Hz, 4H), 7.26 (s, 1H), 2.77 (q, J = 7.6 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 146.5, 136.4, 135.7, 133.1, 130.5, 130.2, 129.2, 129.2, 128.7, 128.2, 128.1, 124.3, 124.1, 122.8, 122.6, 114.6, 114.6, 102.5, 29.0, 15.6; HRMS (ESI) m/z: calcd for $C_{23}H_{19}N_2$ $[M+H]^+$, 323.1543; found 323.1548.

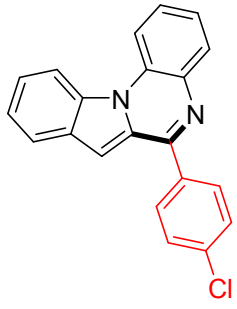


6-(4-methoxyphenyl)indolo[1,2-*a*]quinoxaline, Compound **3da** was obtained in 69% yield (22.3 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 166-167 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (400 MHz,

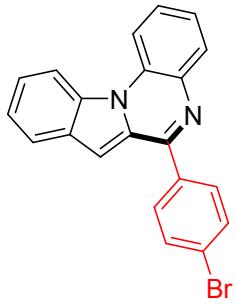
$CDCl_3$) δ 8.52 (t, J = 8.1 Hz, 2H), 8.11-7.92 (m, 4H), 7.65-7.53 (m, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.29 (s, 2H), 7.10 (d, J = 8.7 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 155.7, 136.9, 133.2, 130.3, 130.2, 130.1, 129.3, 129.1, 128.2, 128.1, 127.7, 124.5, 124.3, 122.8, 122.7, 114.7, 114.6, 114.1, 55.5; HRMS (ESI) m/z: calcd for $C_{22}H_{17}N_2O$ $[M+H]^+$, 325.1335; found 325,1339.



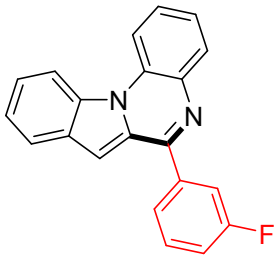
6-(4-butylphenyl)indolo[1,2-*a*]quinoxaline, Compound **3ea** was obtained in 79% yield (27.6 mg) according to the general procedure (0.1 mmol); Yellow oil; R_f = 0.6 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (t, J = 8.5 Hz, 2H), 8.07 (dd, J = 7.9, 1.4 Hz, 1H), 7.94 (dd, J = 7.3, 5.3 Hz, 3H), 7.63-7.53 (m, 2H), 7.47-7.36 (m, 4H), 7.27 (s, 1H), 2.78-2.70 (m, 2H), 1.67 (d, J = 7.6 Hz, 2H), 1.43 (m, J = 14.9, 7.4 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 145.3, 136.3, 135.6, 133.1, 130.4, 130.2, 129.3, 129.2, 128.8, 128.6, 128.2, 124.3, 124.2, 122.8, 122.6, 114.6, 114.6, 102.7, 35.7, 33.6, 22.4, 14.0; HRMS (ESI) m/z: calcd for $C_{25}H_{23}N_2$ $[M+H]^+$, 351.1856; found 351.1861.



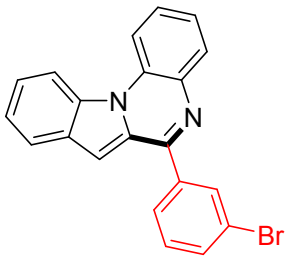
6-(4-chlorophenyl)indolo[1,2-*a*]quinoxaline, Compound **3fa** was obtained in 72% yield (23.2 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 239-240 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, J = 11.8, 8.9 Hz, 2H), 8.18 (d, J = 9.1 Hz, 1H), 8.01 (dd, J = 19.6, 8.0 Hz, 3H), 7.71-7.57 (m, 4H), 7.50 (t, J = 7.4 Hz, 2H), 7.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 136.4, 133.3, 130.3, 130.2, 130.1, 129.3, 129.0, 128.8, 128.7, 124.9, 124.5, 123.0, 123.0, 114.8, 114.7, 103.0; HRMS (ESI) m/z: calcd for $C_{21}H_{14}ClN_2$ $[M+H]^+$, 329.0840; found 329.0838.



6-(4-bromophenyl)indolo[1,2-*a*]quinoxaline, Compound **3ga** was obtained in 67% yield (25.0 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 243-244 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (t, J = 9.4 Hz, 2H), 8.13 (d, J = 7.9 Hz, 1H), 7.96 (dd, J = 7.7, 6.1 Hz, 3H), 7.75 (d, J = 8.3 Hz, 2H), 7.63 (m, J = 23.7, 7.6 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 136.8, 135.9, 133.2, 131.9, 130.4, 130.3, 130.2, 129.2, 128.7, 128.7, 124.7, 124.7, 124.6, 124.4, 122.9, 114.7, 114.6, 102.6; HRMS (ESI) m/z: calcd for $C_{21}H_{14}BrN_2$ $[M+H]^+$, 373.0335; found 373.0331.

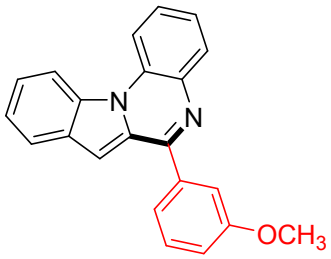


6-(3-fluorophenyl)indolo[1,2-*a*]quinoxaline, Compound **3ha** was obtained in 77% yield (24.1 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 165-166 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57-8.49 (m, 2H), 8.11 (d, J = 7.9 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 9.5 Hz, 1H), 7.66 (t, J = 7.8 Hz, 1H), 7.58 (q, J = 8.4 Hz, 2H), 7.48 (t, J = 7.2 Hz, 2H), 7.30 (dd, J = 12.3, 6.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, J = 245.0 Hz), 154.8 (d, J = 3.0 Hz), 140.2 (d, J = 8.0 Hz), 136.0, 133.1, 130.6, 130.4, 130.3 (d, J = 2.0 Hz), 129.2, 128.7, 124.6, 124.4 (d, J = 3.0 Hz), 124.3, 122.9, 122.8, 117.0 (d, J = 21.0 Hz), 115.8 (d, J = 23.0 Hz), 114.7 (d, J = 11.0 Hz), 102.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.3 (q, J = 11.3 Hz, 1F); HRMS (ESI) m/z: calcd for $C_{21}H_{14}FN_2$ $[M+H]^+$, 313.1134; found 313.1138.

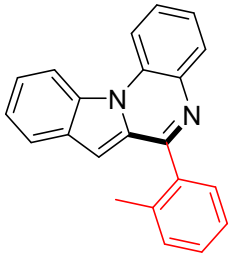


6-(3-bromophenyl)indolo[1,2-*a*]quinoxaline, Compound **3ia** was obtained in 70% yield (25.7 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 189-190 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (dd, J = 13.8, 8.5 Hz, 2H), 8.20 (t, J = 1.6 Hz, 1H), 8.09 (dd, J = 7.9,

1.3 Hz, 1H), 7.98 (t, J = 8.2 Hz, 2H), 7.72 (dd, J = 8.0, 0.8 Hz, 1H), 7.68-7.64 (m, 1H), 7.60 (t, J = 7.3 Hz, 1H), 7.50-7.45 (m, 3H), 7.24 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 140.2, 136.1, 133.1, 133.0, 131.6, 130.7, 130.2, 129.2, 128.8, 128.7, 127.3, 124.6, 124.3, 122.9, 122.9, 114.7, 114.6, 102.3; HRMS (ESI) m/z: calcd for $C_{21}H_{14}BrN_2$ $[M+H]^+$, 373.0335; found 373.0338.

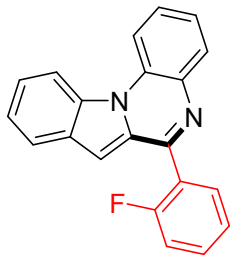


6-(3-methoxyphenyl)indolo[1,2-*a*]quinoxaline, Compound **3ja** was obtained in 68% yield (22.3 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 120-121 ^{o}C; R_f = 0.6 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57-8.50 (m, 2H), 8.12 (dd, J = 7.9, 1.4 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.66-7.63 (m, 2H), 7.58 (m, J = 8.5, 4.9, 1.5 Hz, 2H), 7.53-7.45 (m, 3H), 7.30 (s, 1H), 7.17-7.12 (m, 1H), 3.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 156.1, 139.6, 136.3, 133.1, 130.6, 130.3, 129.7, 129.2, 129.1, 128.4, 124.4, 124.2, 122.9, 122.7, 121.1, 116.0, 114.7, 114.6, 113.9, 102.6, 55.5; HRMS (ESI) m/z: calcd for $C_{22}H_{17}N_2O$ $[M+H]^+$, 325.1335; found 325.1339.

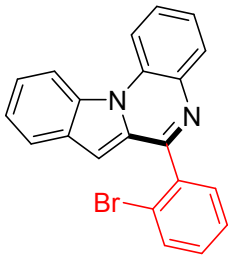


6-(*o*-tolyl)indolo[1,2-*a*]quinoxaline, Compound **3ka** was obtained in 76% yield (23.5

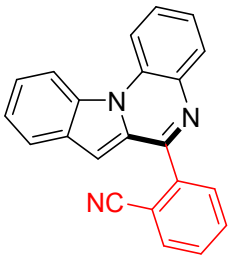
mg) according to the general procedure (0.1 mmol); Yellow solid; mp 133-134 °C; R_f = 0.6 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, J = 17.2, 8.5 Hz, 2H), 8.08 (dd, J = 7.9, 1.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.71-7.64 (m, 1H), 7.56 (dd, J = 17.3, 8.2 Hz, 2H), 7.42 (ddd, J = 23.3, 14.2, 7.5 Hz, 5H), 6.82 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 137.3, 136.5, 136.0, 133.2, 130.9, 130.5, 130.4, 129.9, 129.3, 129.2, 128.8, 128.5, 125.8, 124.5, 124.2, 122.9, 122.7, 114.7, 114.6, 102.6, 19.7; HRMS (ESI) m/z: calcd for $C_{22}H_{17}N_2$ $[M+H]^+$, 309.1386; found 309.1390.



6-(2-fluorophenyl)indolo[1,2-*a*]quinoxaline, Compound **3la** was obtained in 66% yield (20.6 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 177-178 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58-8.49 (m, 2H), 8.11 (dd, J = 7.9, 1.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.78 (m, J = 7.4, 1.8 Hz, 1H), 7.70-7.66 (m, 1H), 7.58 (ddd, J = 9.2, 7.6, 4.8 Hz, 2H), 7.50-7.43 (m, 2H), 7.38 (m, J = 7.5, 1.0 Hz, 1H), 7.35-7.29 (m, 1H), 7.02 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3 (d, J = 199.0 Hz), 152.6, 136.0, 133.0, 131.4 (d, J = 6.0 Hz), 131.1, 130.7, 130.4, 129.4, 129.2, 128.8, 126.1, 126.0, 124.5 (d, J = 3.0 Hz), 124.4, 124.2, 122.9, 122.7, 116.4 (d, J = 17.0 Hz), 114.7 (d, J = 16.0 Hz), 102.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.8 (s, 1F); HRMS (ESI) m/z: calcd for $C_{21}H_{14}FN_2$ $[M+H]^+$, 313.1136; found 313.1140.

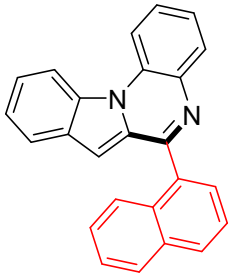


6-(2-bromophenyl)indolo[1,2-*a*]quinoxaline, Compound **3ma** was obtained in 62% yield (23.1 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 170-171 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, J = 20.1, 8.5 Hz, 2H), 8.12 (d, J = 7.9 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.62-7.54 (m, 2H), 7.52-7.38 (m, 4H), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 138.6, 135.8, 133.4, 133.2, 130.7, 130.7, 130.6, 130.5, 129.2, 128.9, 127.6, 124.6, 124.3, 123.0, 122.8, 122.3, 114.8, 114.6, 102.5; HRMS (ESI) m/z: calcd for $C_{21}H_{14}BrN_2$ $[M+H]^+$, 373.0335; found 373.0339.

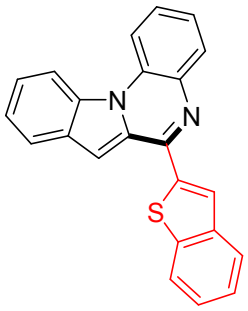


2-(Indolo[1,2-*a*]quinoxalin-6-yl)benzonitrile, Compound **3na** was obtained in 30% yield (9.6 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 232.9-233.9 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 10/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (dd, J = 19.2, 8.6 Hz, 2H), 8.16 (d, J = 7.8 Hz, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.96 (dd, J = 7.9, 3.3 Hz, 2H), 7.82 (t, J = 7.7 Hz, 1H), 7.74-7.67 (m, 2H), 7.63 (t, J = 7.8 Hz, 1H), 7.55-7.47 (m, 2H), 7.03 (s, 1H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 152.9, 140.9, 135.7, 134.3, 133.3, 132.6, 130.9, 130.44, 129.9, 129.8, 129.4, 129.1, 128.7, 124.9, 124.5, 123.0, 122.9, 117.53 114.8, 114.7, 112.6, 102.2; HRMS (ESI) m/z: calcd for $C_{22}H_{13}N_3$ $[M+H]^+$, 320.1182; found 320.1184.

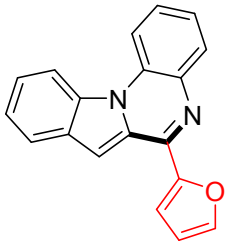


6-(naphthalen-1-yl)indolo[1,2-*a*]quinoxaline, Compound **3oa** was obtained in 71% yield (24.5 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 182-183 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 8.4 Hz, 1H), 8.52 (d, J = 8.7 Hz, 1H), 8.13 (d, J = 7.9 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.95 (d, J = 8.6 Hz, 2H), 7.82 (dd, J = 11.5, 7.6 Hz, 2H), 7.72-7.61 (m, 2H), 7.59-7.46 (m, 3H), 7.40 (t, J = 7.5 Hz, 2H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 136.1, 135.2, 134.0, 133.1, 131.5, 130.7, 130.5, 130.5, 129.9, 129.2, 128.7, 128.4, 127.0, 126.6, 126.3, 125.7, 125.3, 124.6, 124.3, 122.9, 122.8, 114.8, 114.6, 103.0; HRMS (ESI) m/z: calcd for $C_{25}H_{17}N_2$ $[M+H]^+$, 345.1386; found 345.1388.

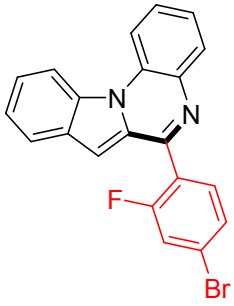


6-(benzo[*b*]thiophen-2-yl)indolo[1,2-*a*]quinoxaline, Compound **3pa** was obtained in 57% yield (19.9 mg) according to the general procedure (0.1 mmol); Yellow solid;

mp 203-204 °C; R_f = 0.7 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, J = 8.2, 6.1 Hz, 2H), 8.26 (s, 1H), 8.07 (dd, J = 7.9, 1.3 Hz, 1H), 8.00-7.91 (m, 3H), 7.64-7.53 (m, 3H), 7.48-7.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 142.3, 140.7, 140.0, 135.6, 132.9, 130.4, 130.0, 129.3, 128.7, 127.7, 125.8, 125.5, 124.7, 124.6, 124.5, 124.3, 122.9, 122.8, 122.4, 114.6, 101.6; HRMS (ESI) m/z: calcd for $C_{23}H_{15}N_2S$ $[M+H]^+$, 351.0950; found 351.0945.

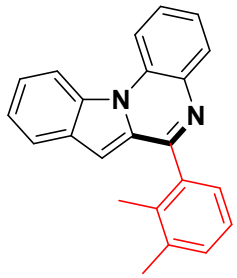


6-(furan-2-yl)indolo[1,2-*a*]quinoxaline, Compound **3ra** was obtained in 63% yield (17.9 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 170-171 °C; R_f = 0.7 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (t, J = 9.5 Hz, 2H), 8.07 (dd, J = 7.9, 1.4 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 0.7 Hz, 2H), 7.63-7.55 (m, 2H), 7.52-7.43 (m, 3H), 6.71 (dd, J = 3.5, 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 145.0, 144.7, 135.8, 132.8, 130.3, 130.1, 129.5, 128.2, 126.8, 124.5, 124.2, 122.9, 122.7, 114.6, 114.6, 113.3, 112.1, 102.1; HRMS (ESI) m/z: calcd for $C_{19}H_{13}N_2O$ $[M+H]^+$, 285.1022; found 285.1020.



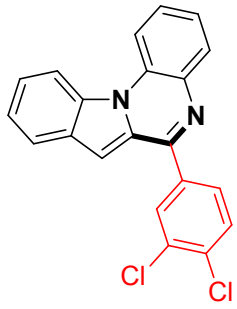
6-(4-bromo-2-fluorophenyl)indolo[1,2-*a*]quinoxaline, Compound **3ta** was obtained

in 68% yield (26.7 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 206-207 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 8.3 Hz, 1H), 8.51 (d, J = 8.7 Hz, 1H), 8.08 (dd, J = 7.9, 1.2 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.71-7.65 (m, 1H), 7.58 (m, J = 7.6, 5.9 Hz, 2H), 7.54-7.42 (m, 3H), 7.25-7.20 (m, 1H), 6.79 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2 (d, J = 252.0 Hz), 155.3, 135.8, 134.9 (d, J = 3.0 Hz), 133.2, 131.8 (d, J = 9.0 Hz), 130.7, 130.5, 129.2, 129.1, 129.0, 124.5 (d, J = 32.0 Hz), 122.9 (d, J = 6.0 Hz), 122.8, 120.8 (d, J = 24.0 Hz), 115.1, 114.8, 114.7, 102.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.7 (d, 1F); HRMS (ESI) m/z: calcd for $C_{21}H_{13}BrFN_2$ $[M+H]^+$, 391.0241; found 391.0242.

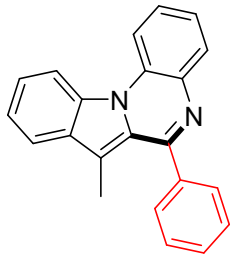


6-(2,3-Dimethylphenyl)indolo[1,2-*a*]quinoxaline, Compound **3ua** was obtained in 72% yield (23.2 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 182.3-183.3 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (dd, J = 21.6, 8.4 Hz, 2H), 8.12 (dd, J = 7.9, 1.1 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.69 (s, 1H), 7.60 (s, 1H), 7.53-7.45 (m, 2H), 7.41 (d, J = 7.4 Hz, 1H), 7.36 (d, J = 7.2 Hz, 1H), 7.30 (d, J = 7.5 Hz, 1H), 6.84 (s, 1H), 2.43 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 137.8, 137.5, 136.2, 134.9, 133.1, 130.7, 130.6, 130.4, 130.2, 129.2, 128.4, 126.6, 125.6, 124.4, 124.2, 122.9, 122.7,

114.7, 114.7, 102.6, 20.4, 16.7; HRMS (ESI) m/z: calcd for $C_{23}H_{18}N_2$ $[M+H]^+$, 323.1543; found 323.1547.

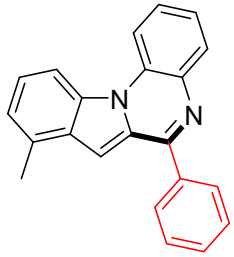


6-(3,4-Dichlorophenyl)indolo[1,2-a]quinoxaline, Compound **3va** was obtained in 64% yield (23.2 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 202.7-203.7 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, J = 13.9, 8.5 Hz, 2H), 8.18 (d, J = 2.0 Hz, 1H), 8.08 (dd, J = 7.9, 1.3 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.92 (dd, J = 8.3, 2.0 Hz, 1H), 7.71-7.65 (m, 2H), 7.64-7.58 (m, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.24 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 138.0, 136.0, 134.2, 133.1, 133.1, 130.6, 130.6, 130.2, 129.1, 128.9, 128.5, 127.8, 124.7, 124.4, 122.9, 122.9, 114.7, 114.6, 102.1; HRMS (ESI) m/z: calcd for $C_{21}H_{12}Cl_2N_2$ $[M+H]^+$, 363.0451; found 363.0448.

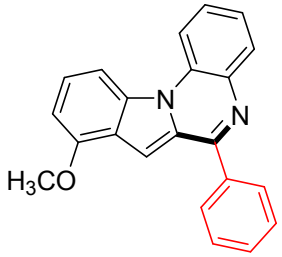


7-methyl-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3ab** was obtained in 82% yield (25.3 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 168-169 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (dd, J = 8.4, 5.4 Hz, 2H), 8.04 (dd, J = 7.9, 1.5 Hz, 1H), 7.91 (d, J =

8.1 Hz, 1H), 7.66 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.61-7.56 (m, 5H), 7.44 (ddd, *J* = 15.2, 11.7, 4.4 Hz, 2H), 2.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7, 139.7, 135.8, 132.0, 130.6, 130.3, 130.2, 129.3, 128.6, 128.5, 128.3, 125.8, 124.7, 123.8, 122.0, 120.8, 114.4, 110.9, 11.1; HRMS (ESI) m/z: calcd for $C_{22}H_{17}N_2$ $[M+H]^+$, 309.1386; found 309.1381.

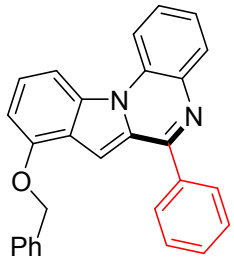


8-methyl-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3ac** was obtained in 84% yield (25.9 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 169-170 ^{o}C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.3 Hz, 1H), 8.30 (d, *J* = 8.7 Hz, 1H), 8.10 (ddd, *J* = 9.4, 7.3, 1.3 Hz, 3H), 7.67-7.59 (m, 4H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 3.4 Hz, 2H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 156.2, 138.4, 136.4, 132.9, 132.3, 130.5, 130.2, 130.0, 129.3, 128.7, 128.7, 128.3, 124.6, 124.2, 122.6, 114.7, 112.1, 100.9, 19.1; HRMS (ESI) m/z: calcd for $C_{22}H_{17}N_2$ $[M+H]^+$, 309.1386; found 309.1388.

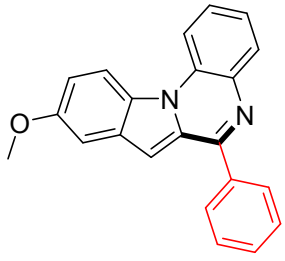


8-methoxy-6-phenylindolo[1,2-a]quinoxaline, Compound **3ad** was obtained in 72% yield (23.3 mg) according to the general procedure (0.1 mmol); Yellow solid; mp

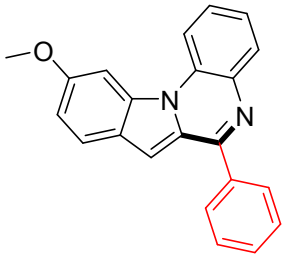
166-167 °C; R_f = 0.6 (petroleum ether/ethyl acetate = 6/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 8.2 Hz, 1H), 8.13-8.00 (m, 4H), 7.65-7.55 (m, 4H), 7.47 (m, J = 12.5, 7.8 Hz, 2H), 7.38 (s, 1H), 6.81 (d, J = 7.8 Hz, 1H), 4.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.38, 154.47, 138.24, 136.50, 134.17, 130.34, 130.16, 129.96, 128.68, 128.66, 128.11, 125.44, 124.27, 120.89, 114.76, 107.47, 101.39, 99.96, 55.47; HRMS (ESI) m/z: calcd for $C_{22}H_{17}N_2O$ $[M+H]^+$, 325.1335; found 325.1339.



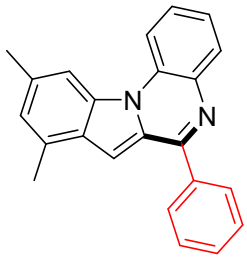
8-(benzyloxy)-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3ae** was obtained in 76% yield (30. 3 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 181-182 °C; R_f = 0.4 (petroleum ether/ethyl acetate = 10/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, J = 8.4 Hz, 1H), 8.12-8.04 (m, 4H), 7.63-7.58 (m, 4H), 7.56-7.52 (m, 2H), 7.49-7.42 (m, 5H), 7.38 (dd, J = 8.6, 6.0 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 5.30 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 153.6, 138.3, 136.9, 136.5, 134.3, 130.4, 130.2, 129.9, 128.7, 128.7, 128.6, 128.1, 128.1, 127.6, 125.4, 124.3, 121.2, 114.8, 107.7, 102.9, 100.1, 70.2; HRMS (ESI) m/z: calcd for $C_{28}H_{21}N_2O$ $[M+H]^+$, 401.1648; found 401.1654.



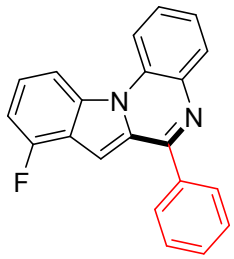
9-methoxy-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3af** was obtained in 71% yield (23.0 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 177-178 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 9.3 Hz, 1H), 8.07 (d, J = 7.9 Hz, 1H), 8.03-7.98 (m, 2H), 7.60-7.53 (m, 4H), 7.41 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 2.8 Hz, 1H), 7.20-7.12 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 155.7, 138.3, 136.1, 130.5, 130.3, 130.0, 129.6, 128.7, 128.7, 128.4, 128.3, 124.0, 115.7, 115.5, 114.3, 102.3, 102.0, 55.6; HRMS (ESI) m/z: calcd for $C_{22}H_{17}N_2O$ $[M+H]^+$, 325.1335; found 325.1339.



10-methoxy-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3ag** was obtained in 67% yield (21.7 mg) according to the general procedure (0.1 mmol); Yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.3 Hz, 1H), 8.06 (d, J = 7.9 Hz, 1H), 8.00 (dd, J = 6.5, 3.1 Hz, 2H), 7.88 (s, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.63-7.53 (m, 4H), 7.43 (t, J = 7.6 Hz, 1H), 7.17 (s, 1H), 7.13 (dd, J = 8.8, 1.8 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 156.3, 138.3, 136.4, 133.8, 130.3, 130.2, 130.0, 128.7, 128.6, 127.9, 124.1, 123.8, 123.4, 114.3, 113.4, 102.9, 97.6, 55.9; HRMS (ESI) m/z: calcd for $C_{22}H_{17}N_2O$ $[M+H]^+$, 325.1335; found 325.1340.

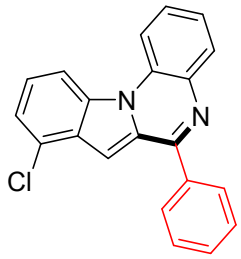


8,10-dimethyl-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3ah** was obtained in 80% yield (25.8 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 176-177 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 8.7 Hz, 1H), 8.22 (s, 1H), 8.10 (dd, J = 7.5, 1.9 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.61-7.52 (m, 4H), 7.44 (t, J = 7.5 Hz, 1H), 7.27 (s, 1H), 7.16 (s, 1H), 2.80 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 138.8, 138.5, 138.0, 133.1, 132.7, 130.0, 129.8, 129.4, 129.1, 128.9, 128.5, 126.8, 123.8, 122.6, 122.5, 114.9, 112.9, 101.3, 22.2, 18.5; HRMS (ESI) m/z: calcd for $C_{23}H_{19}N_2$ $[M+H]^+$, 323.1543; found 323.1546.

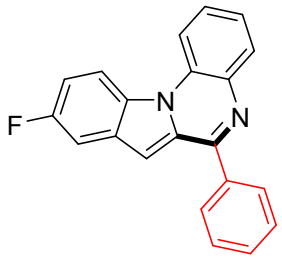


8-fluoro-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3ai** was obtained in 70% yield (21.8 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 190-191 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (dd, J = 8.3, 0.7 Hz, 1H), 8.24 (d, J = 8.7 Hz, 1H), 8.10 (dd, J = 7.9, 1.4 Hz, 1H), 8.08-8.00 (m, 2H), 7.68-7.58 (m, 4H), 7.53-7.43 (m, 2H), 7.34 (d, J = 0.5 Hz, 1H), 7.11 (dd, J = 9.5, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1 (d, J =

200.0 Hz), 156.2, 137.9, 136.4, 135.0 (d, J = 8.0 Hz), 130.6, 130.2, 129.3 (d, J = 25.0 Hz), 128.8, 128.6, 128.5, 124.8, 124.7, 124.6, 119.1 (d, J = 19.0 Hz), 114.7, 110.7 (d, J = 3.0 Hz), 106.9 (d, J = 15.0 Hz), 98.2; HRMS (ESI) m/z: calcd for $C_{21}H_{14}FN_2$ $[M+H]^+$, 313.1136; found 313.1140.

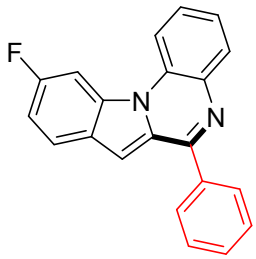


8-chloro-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3aj** was obtained in 78% yield (25.6 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 174-175 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.3 Hz, 1H), 8.41-8.34 (m, 1H), 8.12 (dd, J = 7.9, 0.8 Hz, 1H), 8.06 (dd, J = 6.5, 3.0 Hz, 2H), 7.68-7.60 (m, 4H), 7.53-7.45 (m, 3H), 7.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 137.8, 136.3, 133.5, 130.7, 130.26, 129.8, 129.3, 128.8, 128.7, 128.6, 128.1, 128.0, 124.8, 124.6, 122.3, 114.7, 113.1, 100.9; HRMS (ESI) m/z: calcd for $C_{21}H_{14}ClN_2$ $[M+H]^+$, 329.0840; found 329.0842.

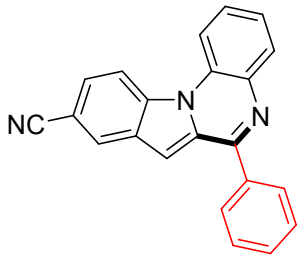


9-fluoro-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3ak** was obtained in 67% yield (20.9 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 191-192 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz,

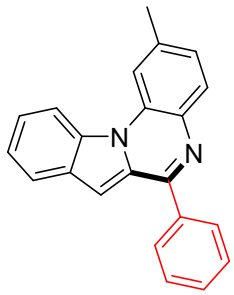
$CDCl_3$) δ 8.44-8.38 (m, 2H), 8.10 (dd, J = 7.9, 1.5 Hz, 1H), 8.07-7.99 (m, 2H), 7.65-7.58 (m, 4H), 7.52 (dd, J = 8.8, 2.6 Hz, 1H), 7.50-7.44 (m, 1H), 7.31-7.26 (m, 1H), 7.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8 (d, J = 191.0 Hz), 155.8, 138.1, 136.2, 130.8, 130.4, 130.1, 130.0 (d, J = 8.0 Hz), 129.8 (d, J = 5.0 Hz), 128.7, 128.6, 128.5, 124.4, 115.7 (d, J = 7.0 Hz), 114.2, 113.2 (d, J = 21.0 Hz), 106.7 (d, J = 19.0 Hz), 102.1 (d, J = 5.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.4 (m, 1F); HRMS (ESI) m/z: calcd for $C_{21}H_{14}FN_2$ $[M+H]^+$, 313.1136; found 313.1141.



10-fluoro-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3al** was obtained in 65% yield (20.5 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 205-206 ^{o}C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.3 Hz, 1H), 8.07 (dd, J = 17.3, 9.3 Hz, 2H), 7.98 (dd, J = 6.4, 2.6 Hz, 2H), 7.81 (dd, J = 8.8, 5.8 Hz, 1H), 7.61-7.53 (m, 4H), 7.42 (t, J = 7.6 Hz, 1H), 7.23-.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (d, J = 241.0 Hz), 156.2, 138.0, 136.2, 132.5 (d, J = 12.0 Hz), 130.6, 130.1, 129.8, 129.7, 128.7 (d, J = 10.0 Hz), 128.4, 125.7, 124.5, 123.7 (d, J = 10.0 Hz), 114.3, 112.2 (d, J = 25.0 Hz), 102.6, 101.1, 100.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.1 (d, 1F); HRMS (EI) m/z: calcd for $C_{21}H_{14}FN_2$ $[M+H]^+$, 313.1136; found 313.1140.

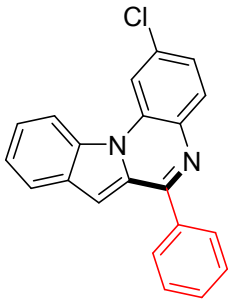


6-phenylindolo[1,2-*a*]quinoxaline-9-carbonitrile, Compound **3am** was obtained in 45% yield (14.4 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 276-277 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 10/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 9.0 Hz, 1H), 8.48 (d, J = 8.2 Hz, 1H), 8.29 (s, 1H), 8.16 (d, J = 8.1 Hz, 1H), 8.03-7.98 (m, 2H), 7.76 (dd, J = 9.0, 1.4 Hz, 1H), 7.72-7.65 (m, 1H), 7.63-7.58 (m, 3H), 7.54 (t, J = 7.6 Hz, 1H), 7.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 137.3, 136.2, 134.0, 130.9, 130.7, 130.6, 129.4, 129.0, 128.9, 128.7, 128.6, 128.4, 126.2, 125.5, 119.5, 115.6, 114.8, 106.2, 103.1; HRMS (ESI) m/z: calcd for $C_{22}H_{14}N_3$ $[M+H]^+$, 320.1182; found 320.1180.

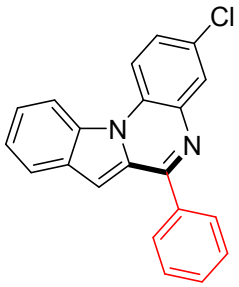


2-methyl-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3an** was obtained in 85% yield (26.2 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 166-167 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, J = 8.7 Hz, 1H), 8.34 (s, 1H), 8.04 (dd, J = 7.4, 1.7 Hz, 2H), 7.99 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.63-7.55 (m, 4H), 7.46 (t, J = 7.5 Hz, 1H), 7.30-7.27 (m, 1H), 7.24 (s, 1H), 2.66 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.2,

138.8, 138.4, 134.3, 133.0, 130.3, 130.1, 129.9, 129.3, 128.6, 125.3, 124.1, 122.7, 122.6, 115.0, 114.7, 102.1, 22.3; HRMS (ESI) m/z: calcd for $C_{22}H_{17}N_2$ $[M+H]^+$, 309.1386; found 309.1390.

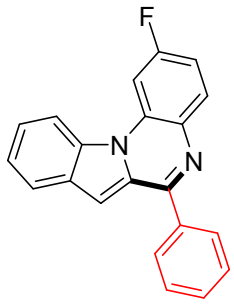


2-chloro-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3ao** was obtained in 76% yield (24.9 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 188-189 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (dd, J = 8.7, 4.5 Hz, 2H), 8.07 (d, J = 2.3 Hz, 1H), 8.03 (dd, J = 6.3, 2.7 Hz, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.58 (ddd, J = 11.1, 7.6, 2.8 Hz, 5H), 7.47 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 2.7 Hz, 1H); ^{13}C NMR (125 MHz, CDCl3) δ 157.3, 157.3, 137.9, 137.4, 133.0, 130.3, 129.9, 129.2, 129.1, 128.8, 128.76, 128.7, 128.6, 128.0, 124.8, 123.0, 122.9, 115.6, 114.3, 103.2; HRMS (ESI) m/z: calcd for $C_{21}H_{14}ClN_2$ $[M+H]^+$, 329.0840; found 329.0841.

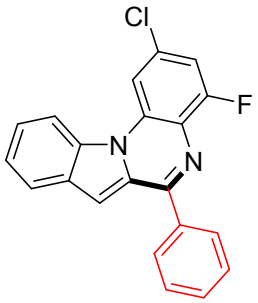


3-chloro-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3ap** was obtained in 73% yield (23.9 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 192-193 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (500 MHz,

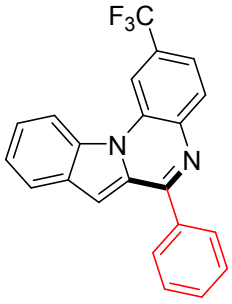
$CDCl_3$) δ 8.32 (d, J = 8.9 Hz, 2H), 8.05-8.00 (m, 3H), 7.90 (d, J = 8.0 Hz, 1H), 7.63-7.59 (m, 3H), 7.55-7.49 (m, 2H), 7.43 (t, J = 7.5 Hz, 1H), 7.23 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 137.9, 137.3, 132.9, 130.3, 129.8, 129.1, 129.0, 128.7, 128.7, 128.7, 127.9, 124.7, 123.0, 122.9, 115.5, 114.3, 103.2; HRMS (ESI) m/z: calcd for $C_{21}H_{14}ClN_2$ $[M+H]^+$, 329.0840; found 329.0845.



2-fluoro-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3aq** was obtained in 69% yield (21.5 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 204-205 ^{o}C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.7 Hz, 1H), 8.17 (dd, J = 10.4, 2.5 Hz, 1H), 8.05 (dd, J = 8.7, 6.4 Hz, 1H), 7.99 (dd, J = 6.5, 2.9 Hz, 2H), 7.91 (d, J = 8.0 Hz, 1H), 7.56 (dd, J = 7.2, 5.2 Hz, 4H), 7.44 (t, J = 7.5 Hz, 1H), 7.24 (s, 1H), 7.15 (m, J = 8.6, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, J = 246.0 Hz), 155.3 (d, J = 3.0 Hz), 137.9, 133.0, 132.8 (d, J = 2.0 Hz), 131.9 (d, J = 10.0 Hz), 130.7, 130.8, 130.1, 129.4, 128.8, 128.7, 128.6, 124.7, 123.0 (d, J = 16.0 Hz), 114.2, 111.5 (d, J = 23.0 Hz), 103.0, 102.0 (d, J = 19.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.59 (s, 1F); HRMS (ESI) m/z: calcd for $C_{21}H_{14}FN_2$ $[M+H]^+$, 313.1136; found 313.1139.



2-chloro-4-fluoro-6-phenylindolo[1,2-*a*]quinoxaline, Compound **3ar** was obtained in 56% yield (19.4 mg) according to the general procedure (0.1 mmol); Yellow solid; mp 213-214 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, J = 20.0, 8.5 Hz, 2H), 8.08 (dd, J = 7.9, 1.2 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.71-7.65 (m, 1H), 7.58 (m, J = 7.6, 5.9 Hz, 2H), 7.55-7.42 (m, 3H), 7.25-7.19 (m, 1H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7 (d, J = 256.0 Hz), 156.3 (d, J = 1.0 Hz), 137.7, 133.5 (d, J = 12.0 Hz), 133.0, 131.6 (d, J = 4.0 Hz), 130.4, 128.8, 128.8, 128.7, 125.3, 124.9 (d, J = 12.0 Hz), 123.4, 123.1, 114.3 111.9, 111.7, 110.7 (d, J = 4.0 Hz), 104.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.04 (d, 1F); HRMS (ESI) m/z: calcd for $C_{21}H_{13}ClFN_2$ $[M+H]^+$, 347.0746; found 347.0742.



6-phenyl-2-(trifluoromethyl)indolo[1,2-*a*]quinoxaline, Compound **3as** was obtained in 38% yield (13.8 mg) according to the general procedure (0.1 mmol);Yellow solid; mp 215-216 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 20/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.45 (d, J = 8.7 Hz, 1H), 8.23 (d, J =

8.5 Hz, 1H), 8.05 (dd, J = 6.5, 2.8 Hz, 2H), 7.97 (d, J = 8.0 Hz, 1H), 7.72-7.59 (m, 5H), 7.50 (t, J = 7.5 Hz, 1H), 7.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 147.0, 145.1, 143.7, 133.3, 130.8, 130.8, 130.6, 130.0, 129.6, 129.4, 128.8, 128.7, 125.7, 125.4, 123.6, 123.3 (d, J = 9.0 Hz), 120.9 (q, J = 4.0 Hz), 114.3, 111.9 (q, J = 4.0 Hz), 104.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.9 (s, 3F); HRMS (ESI) m/z: calcd for $C_{22}H_{14}F_3N_2$ $[M+H]^+$, 363.1104; found 363.1105.

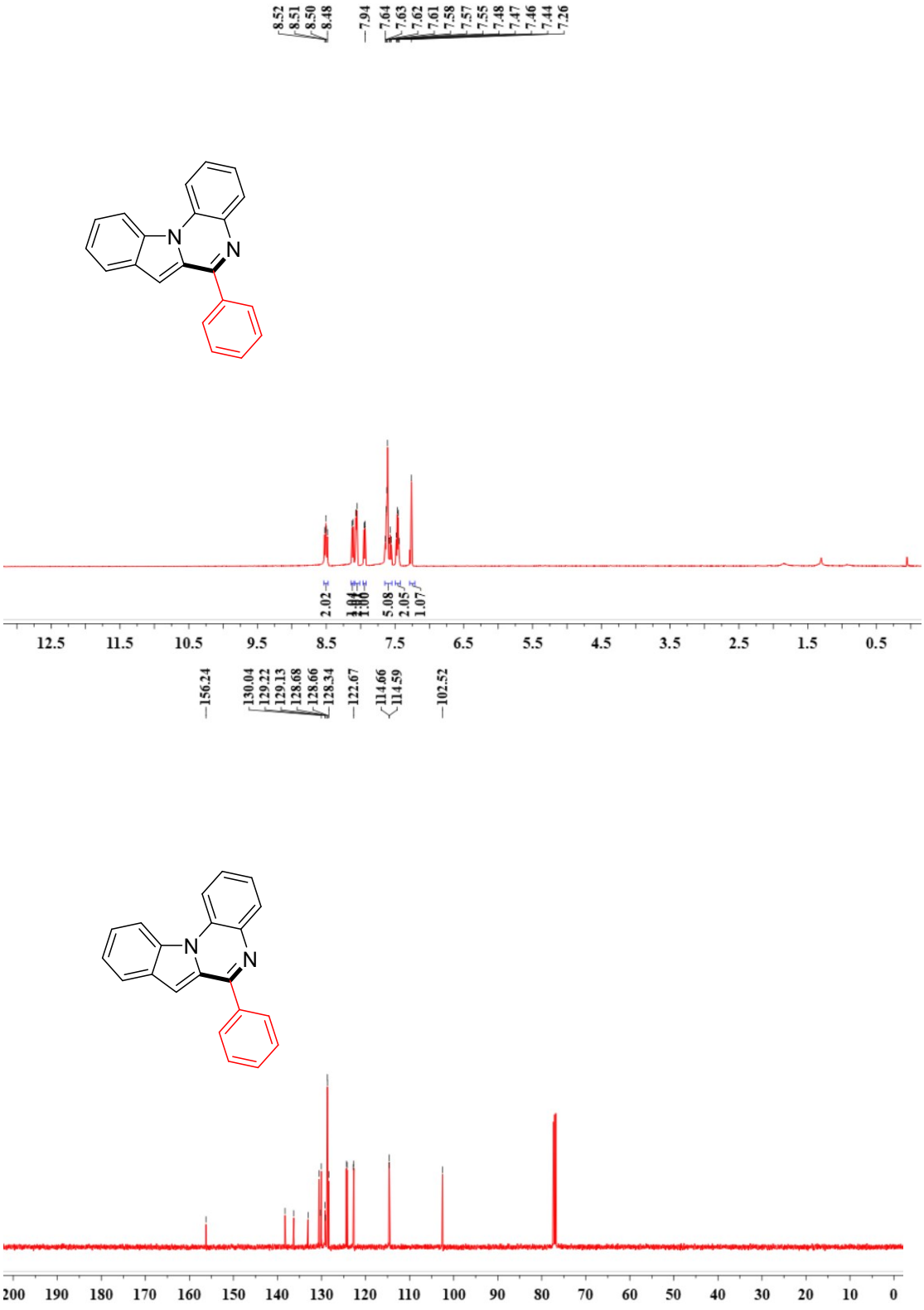
G.References

[1] (a) Patil, N. T.; Kavthe, R. D.; Shinde, V. S.; Sridhar, B. *J. Org. Chem*., **2010**, *75*, 3371; (b) Wu, W.; Fang, S.; Jiang, G.; Li, M.; Jiang, H. *Org. Chem. Front.*, **2019**, *6*, 2200.

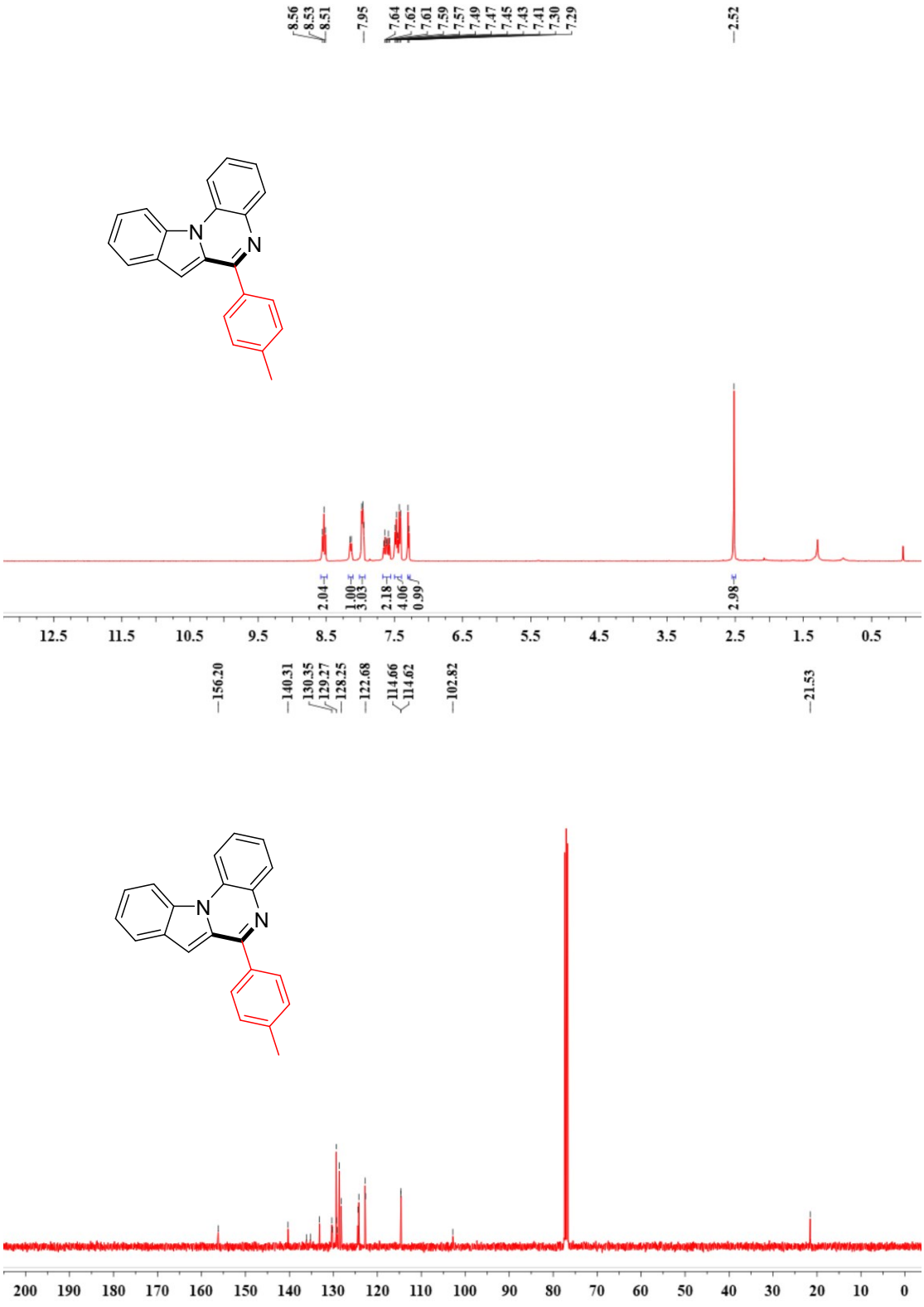
[2] (a) Rubio-Preas, R.; Pedrosa, M. R.; Fernández-Rodríguez, M. A.; Arnáiz, F. J.; Sanz, R. *Org. Lett.*, **2017**, *19*, 5470-5473; (b) Ramamohan, M.; Sridhar, R.; Raghavendrarao, K.; Paradesi, N.; Chandrasekhar, K. B.; Jayaprakash, S. *Synlett*., **2015**, *26*, 1096-1100; (c)Huo, H.-R.; Tang, X.-Y.; Gong, Y.-F. *Synthesis.*, **2018**, *50*, 2727-2740.

H. Copies of ^{1}H and ^{13}C NMR spectra

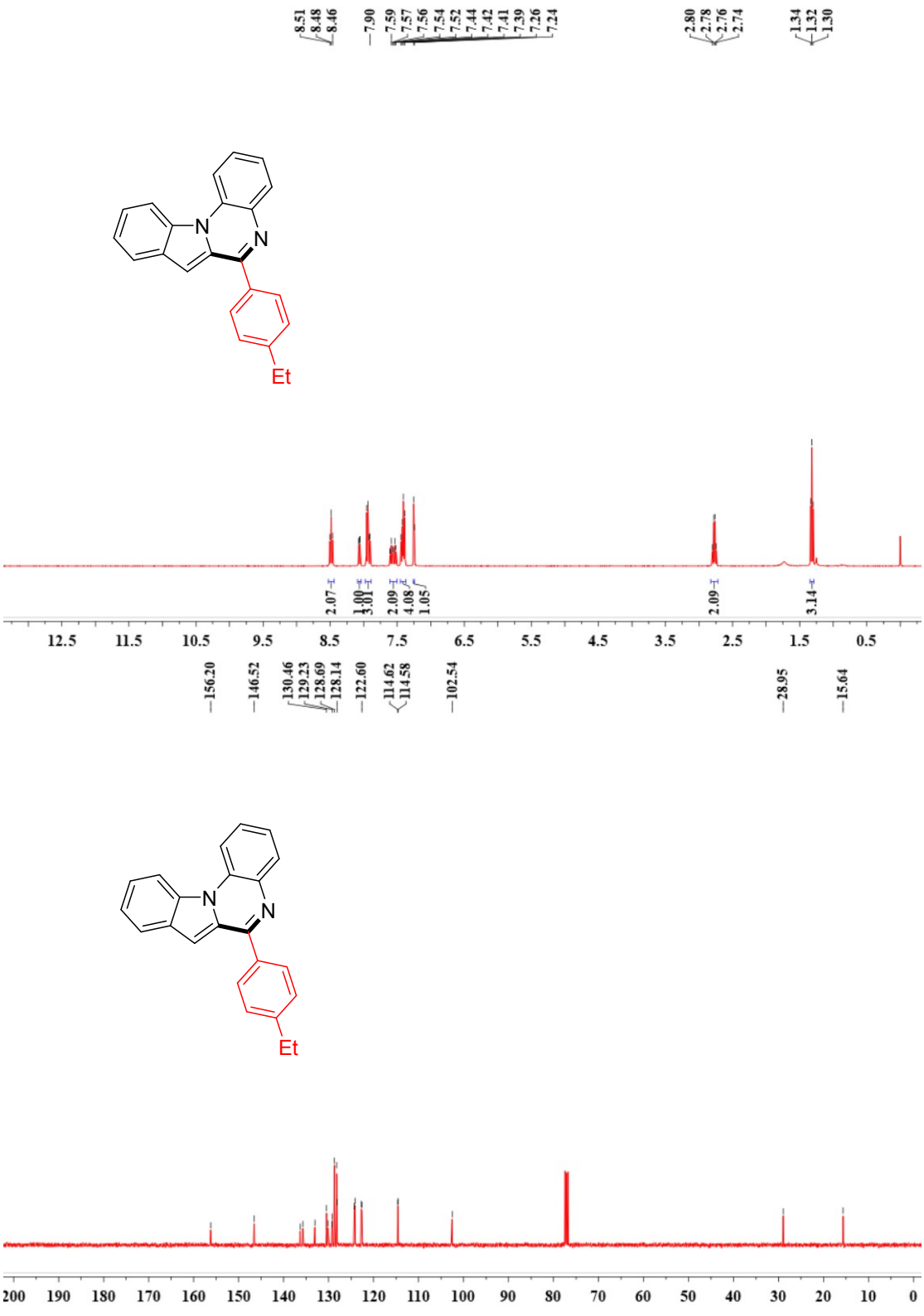
6-phenylindolo[1,2-*a*]quinoxaline (3aa)



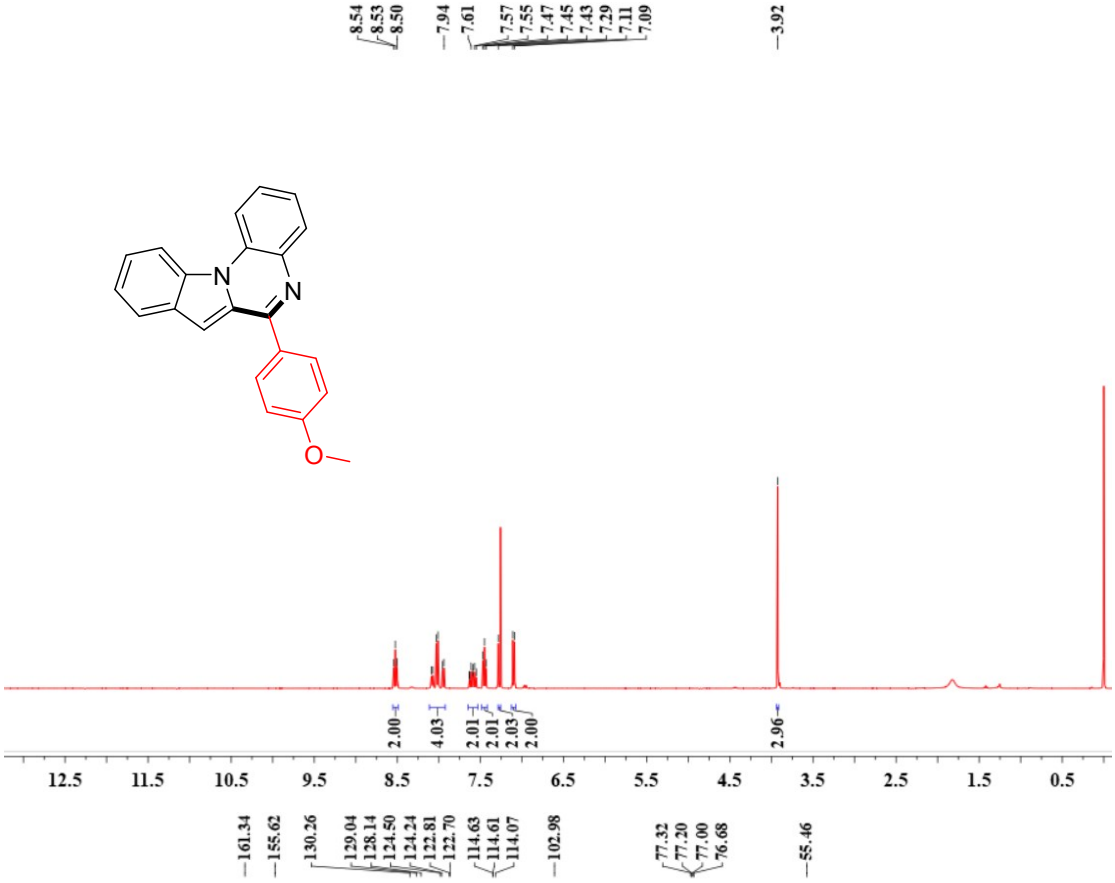
6-(*p*-tolyl)indolo[1,2-*a*]quinoxaline (3ba)

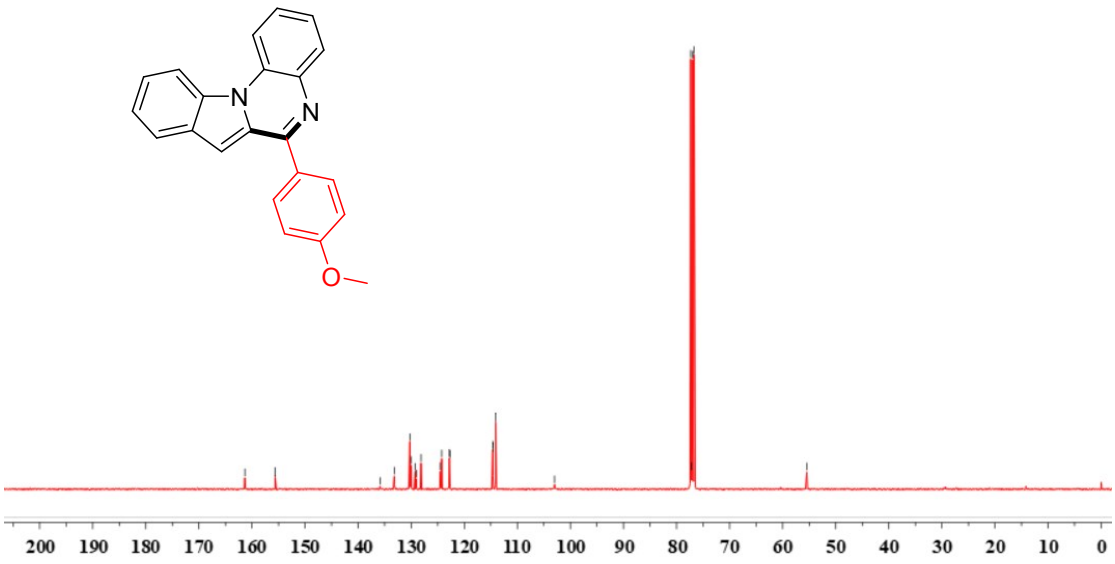


6-(4-ethylphenyl)indolo[1,2-*a*]quinoxaline (3ca)

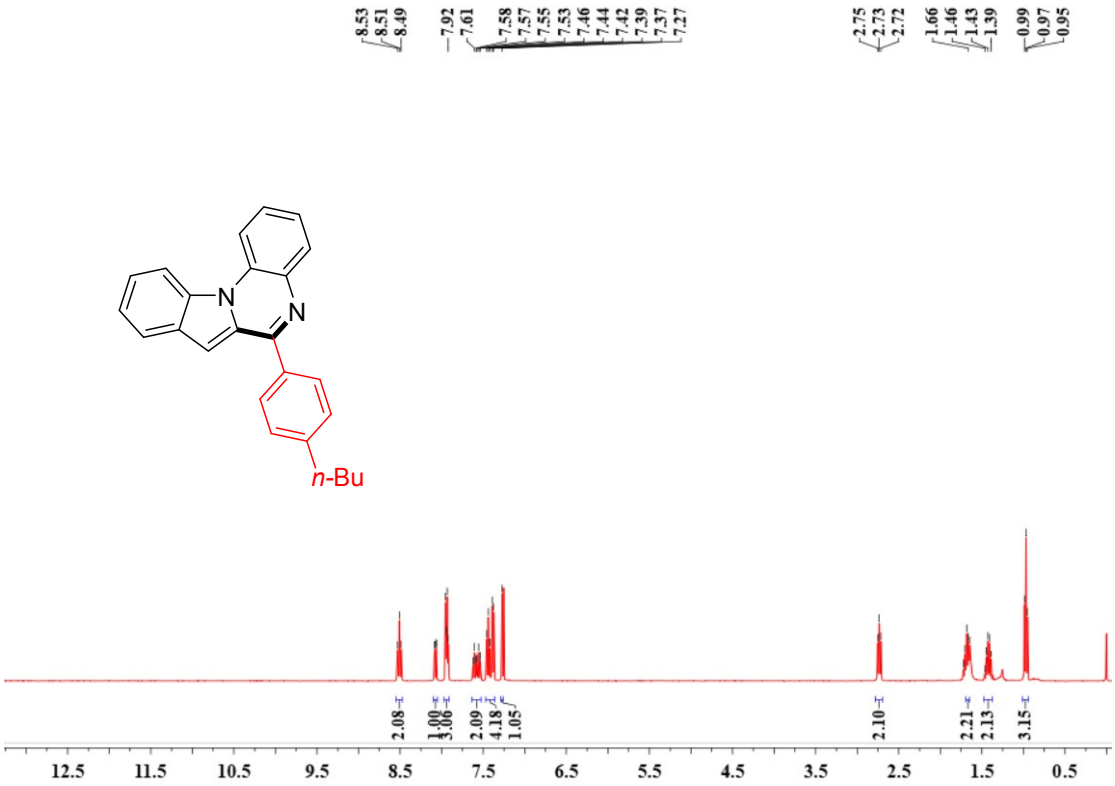


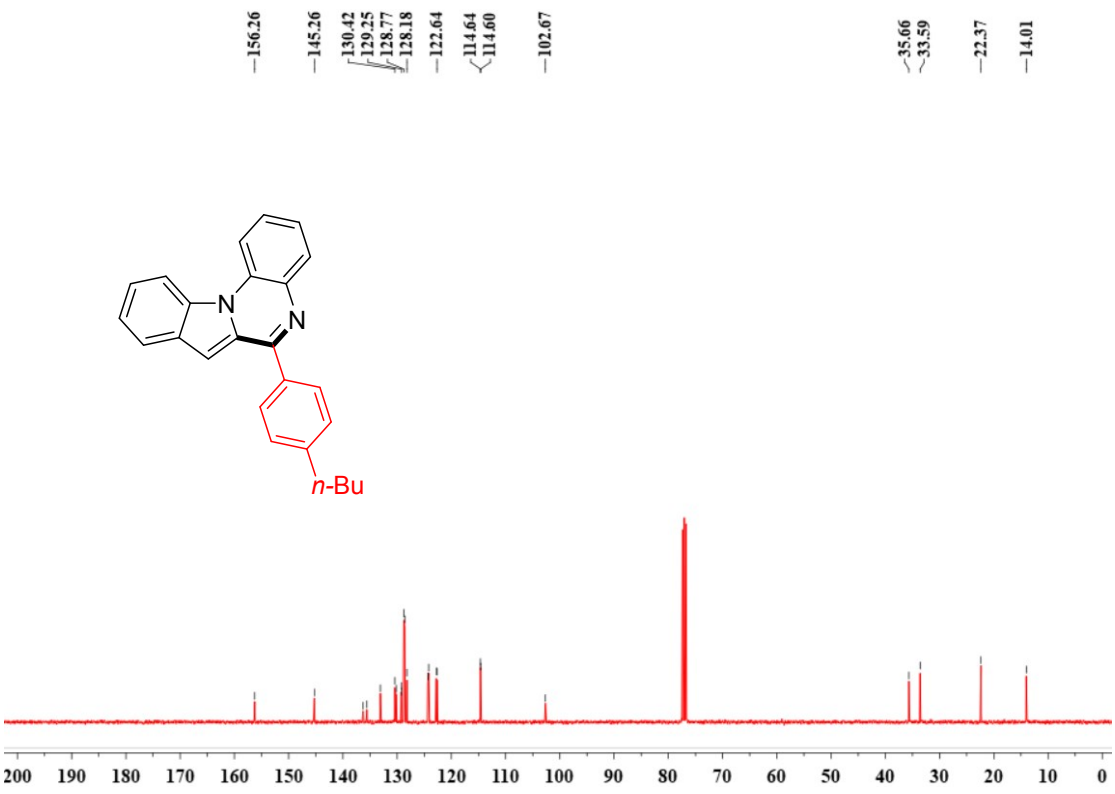
6-(4-methoxyphenyl)indolo[1,2-*a*]quinoxaline (3da)



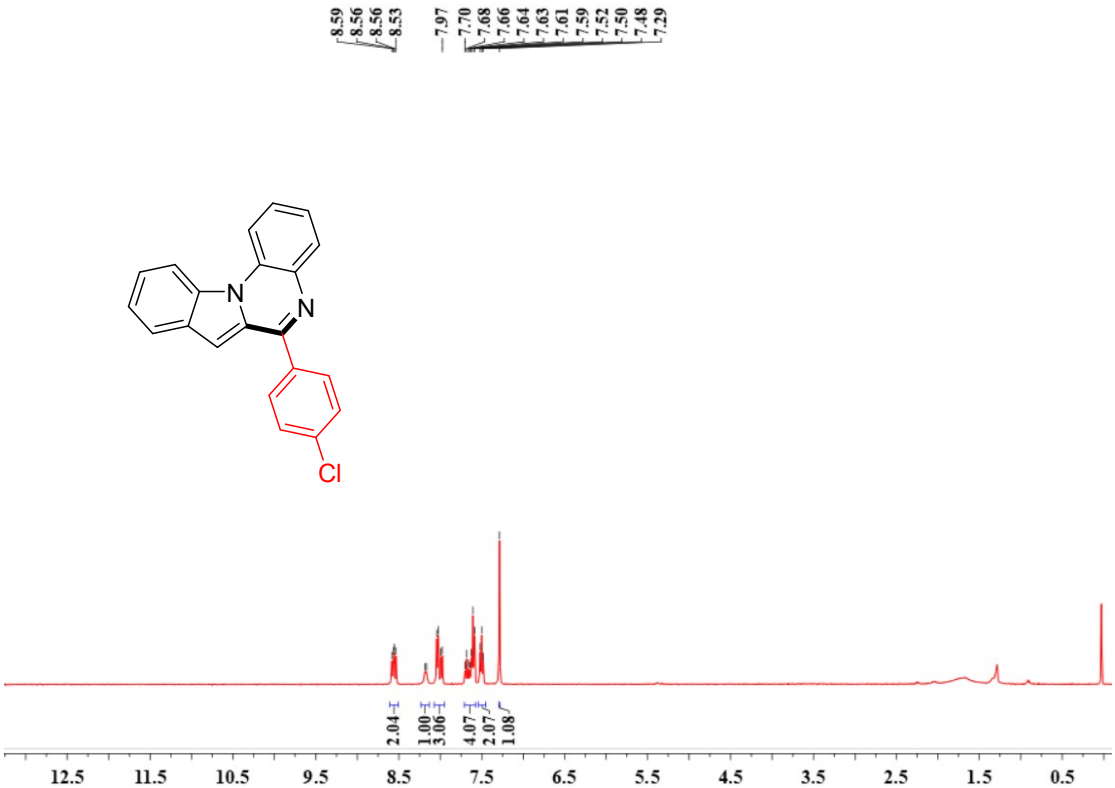


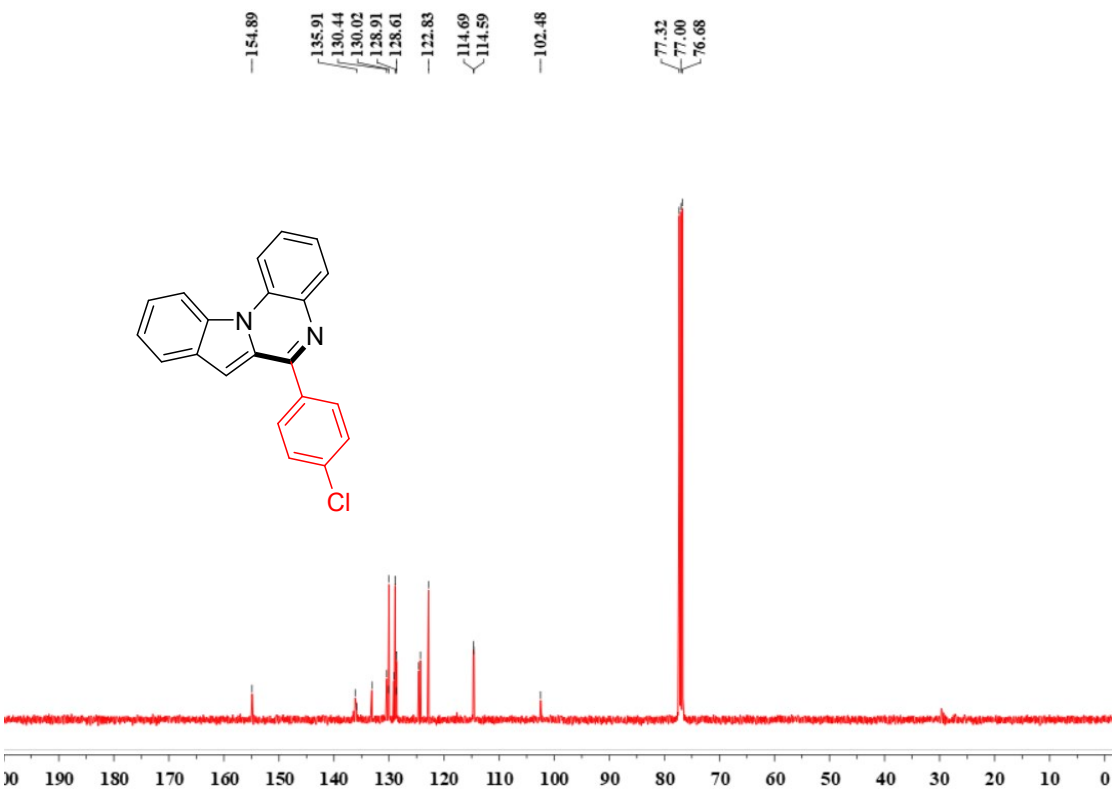
6-(4-butylphenyl)indolo[1,2-*a*]quinoxaline (3ea)



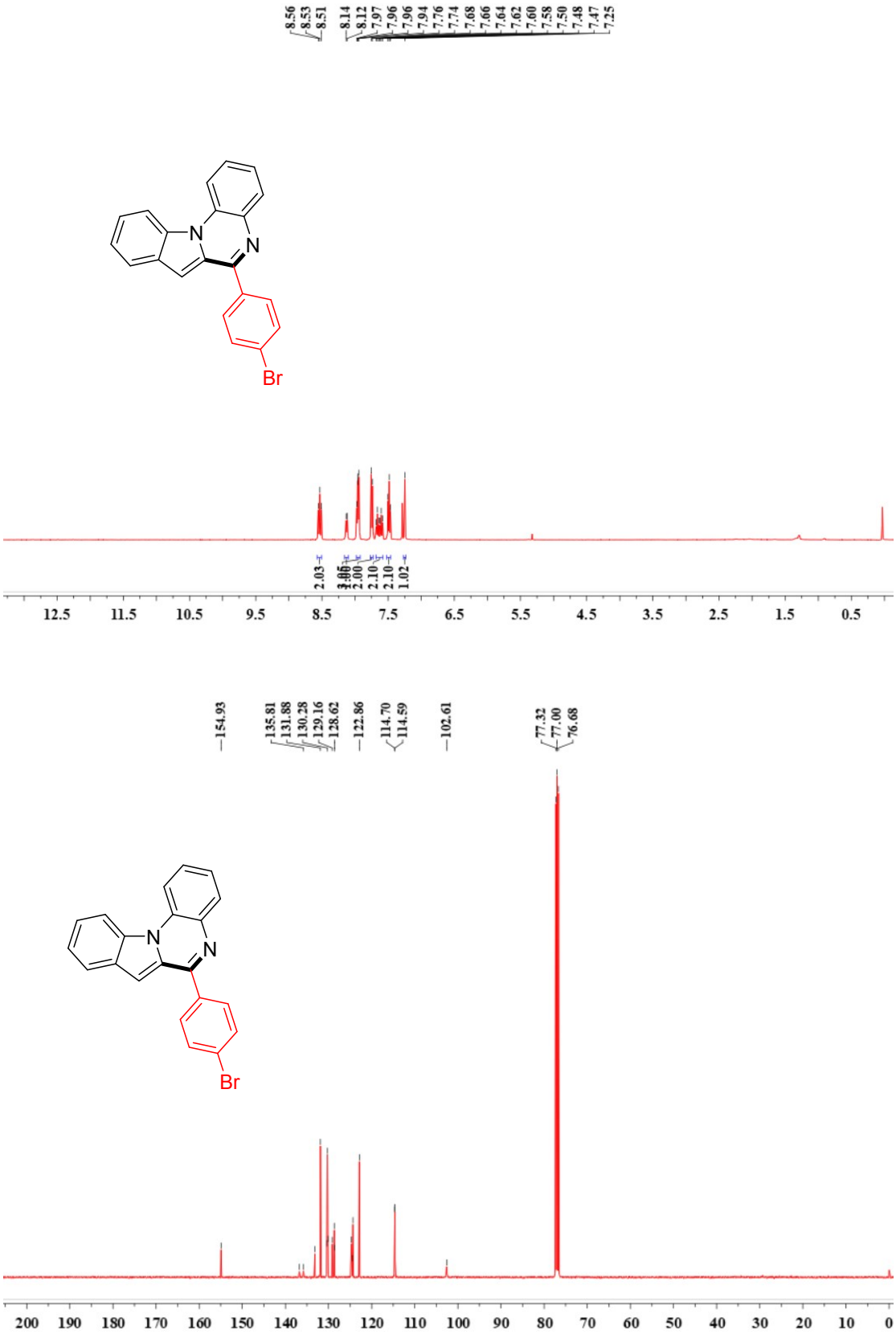


6-(4-chlorophenyl)indolo[1,2-*a*]quinoxaline (3fa)

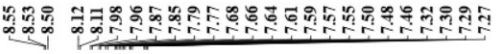


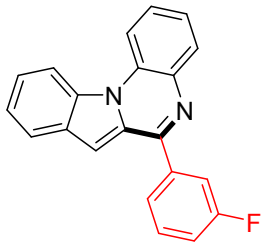


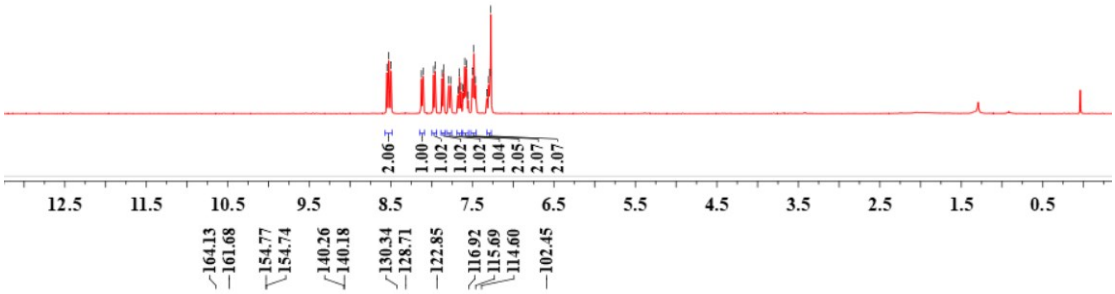
6-(4-bromophenyl)indolo[1,2-*a*]quinoxaline (3ga)

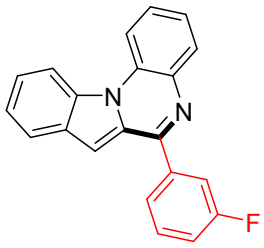


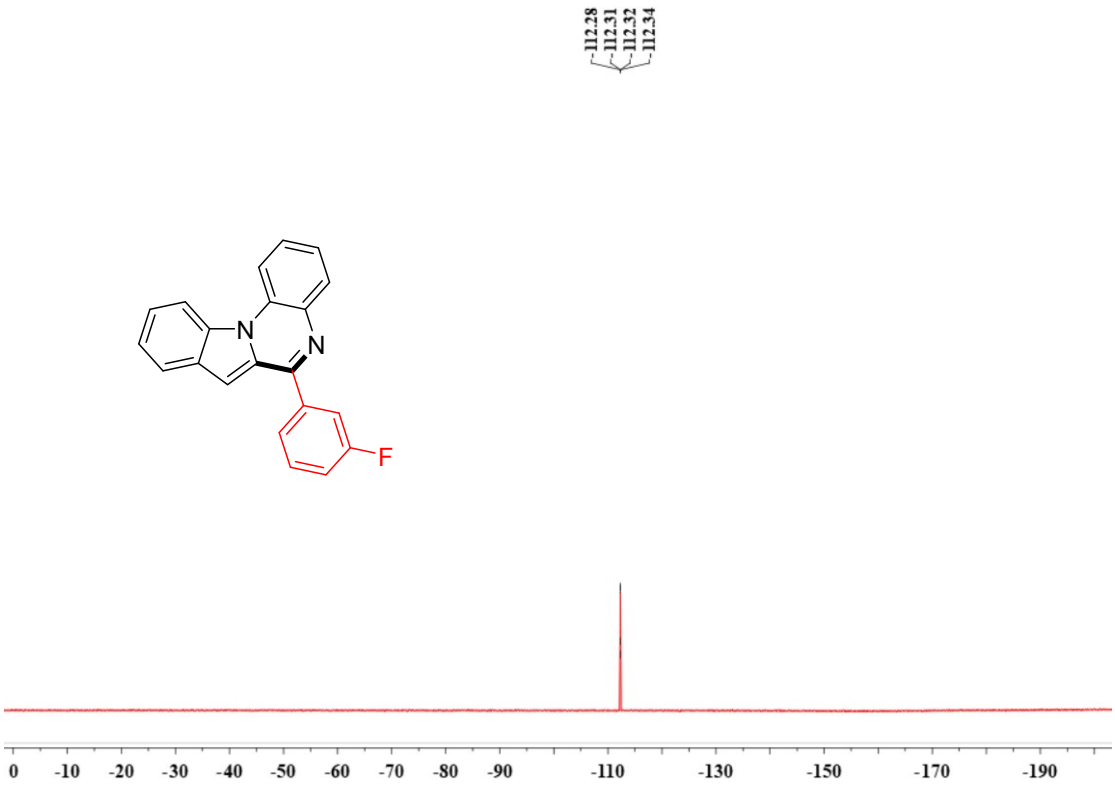
6-(3-fluorophenyl)indolo[1,2-*a*]quinoxaline (3ha)



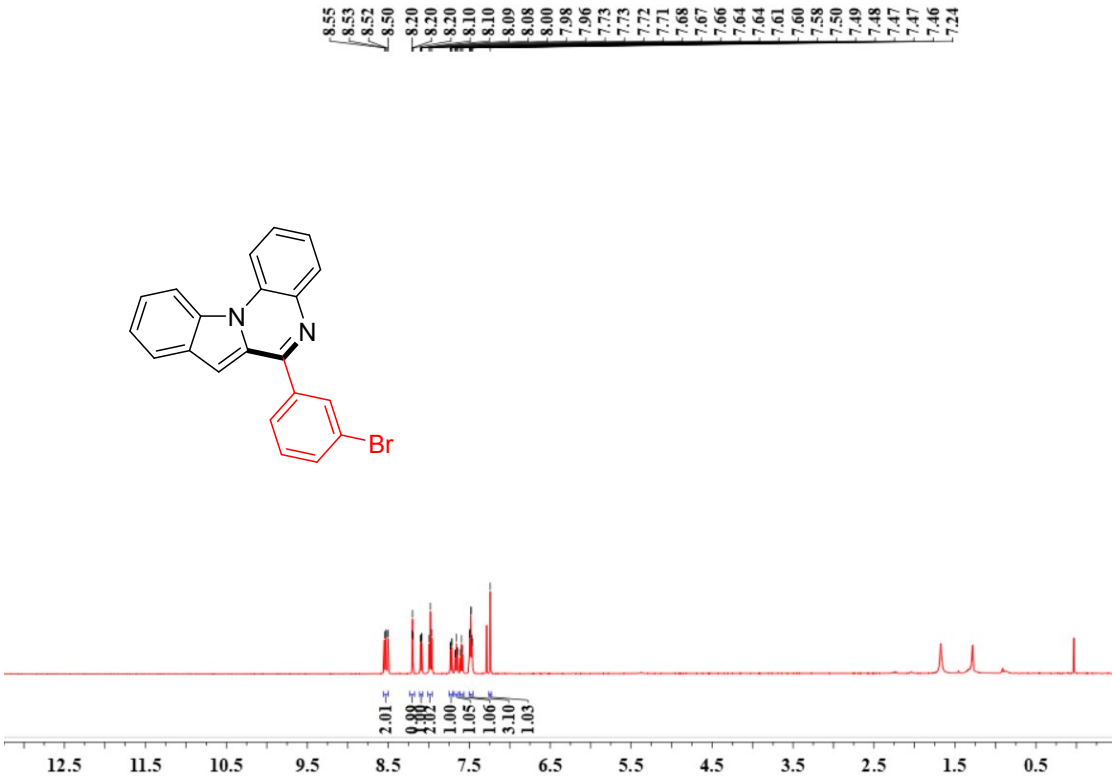


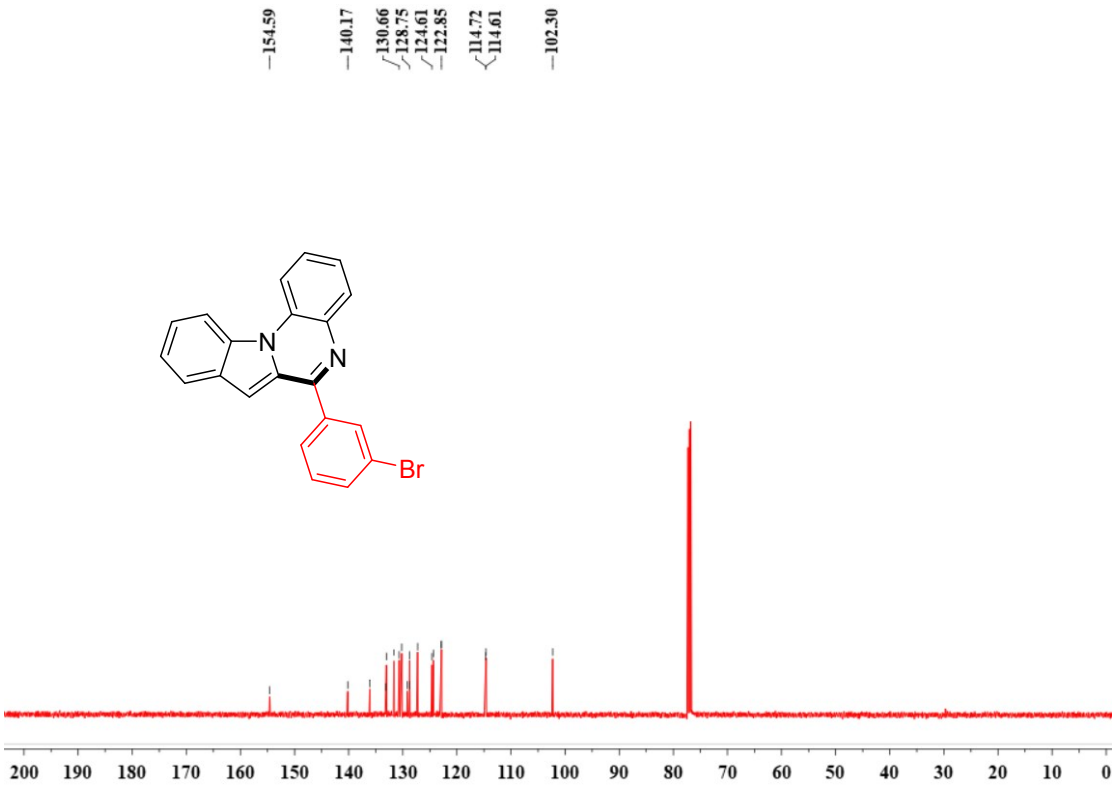




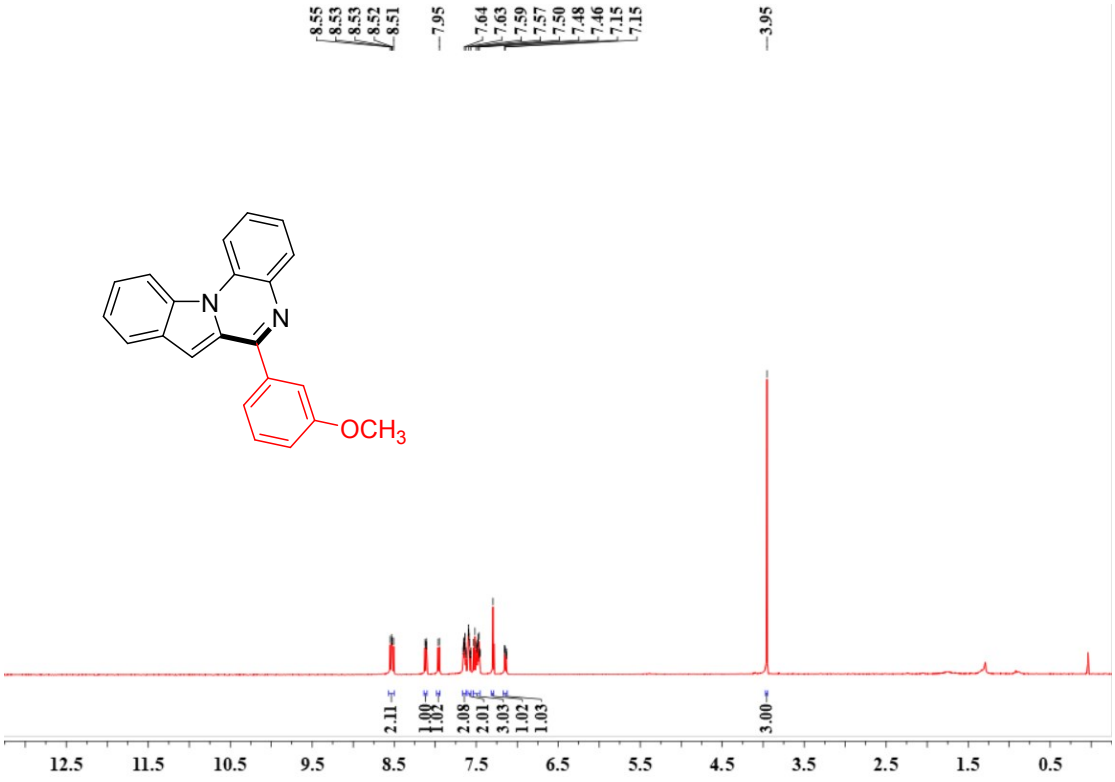


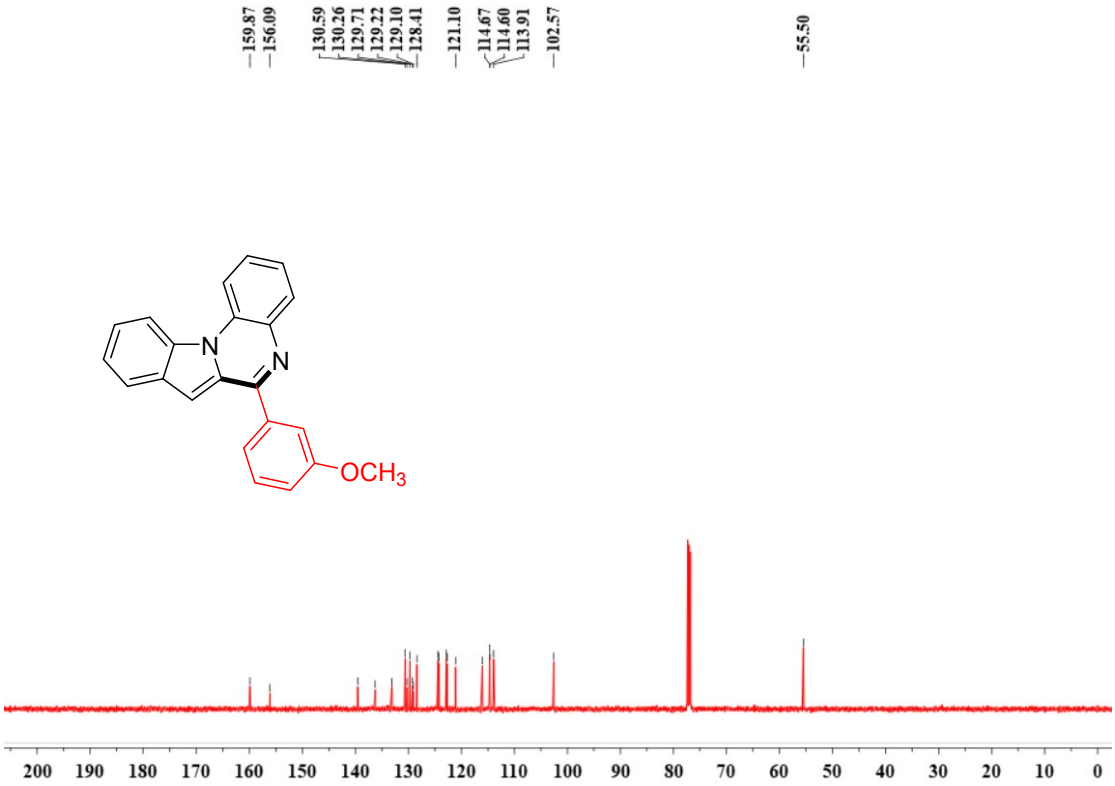
6-(3-bromophenyl)indolo[1,2-*a*]quinoxaline (3ia)



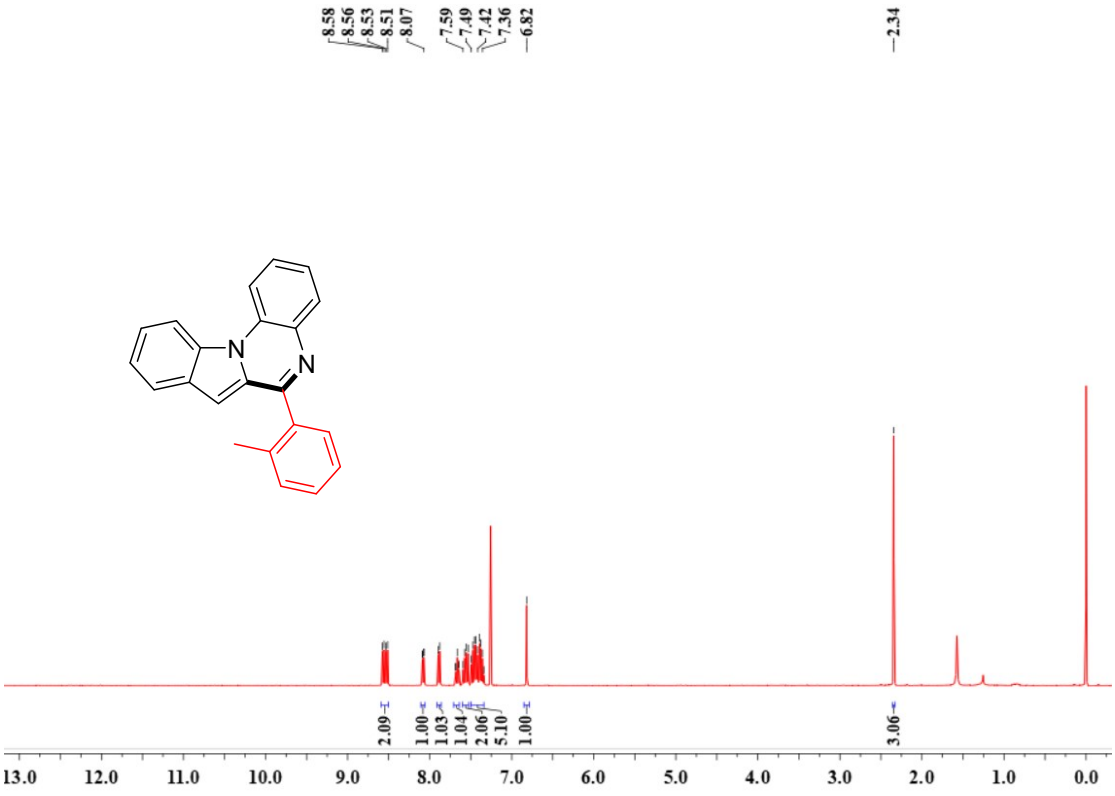


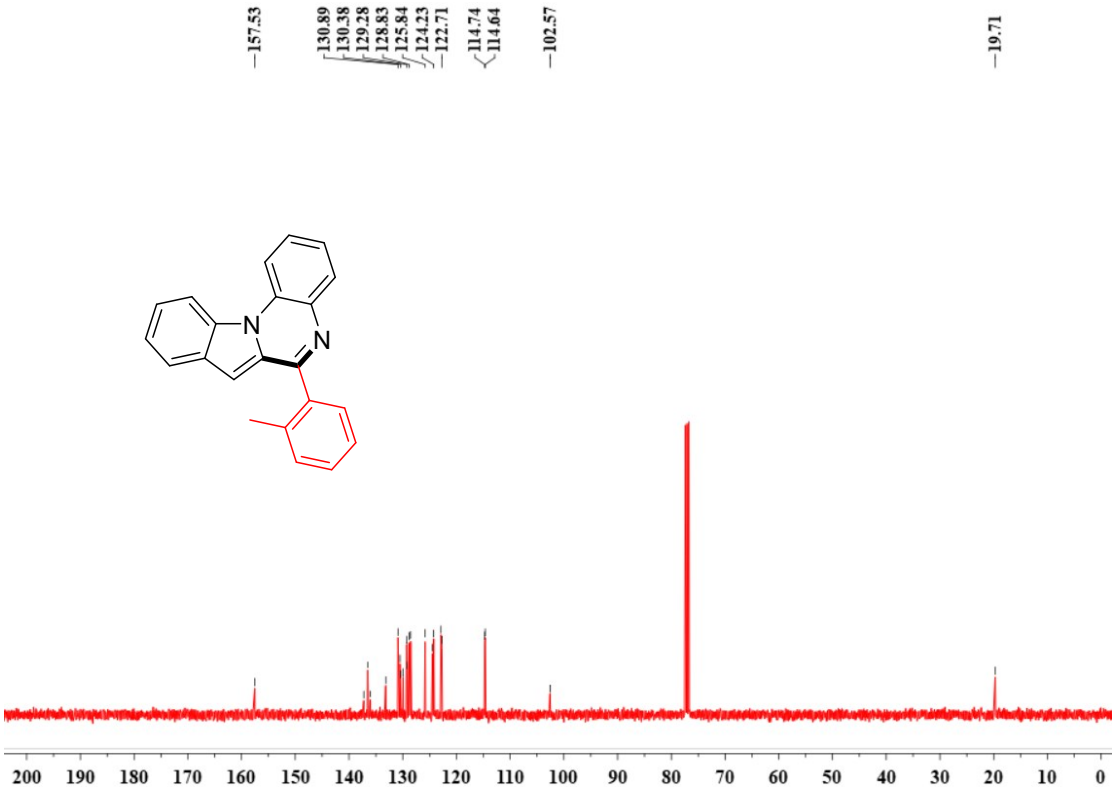
6-(3-methoxyphenyl)indolo[1,2-*a*]quinoxaline (3ja)



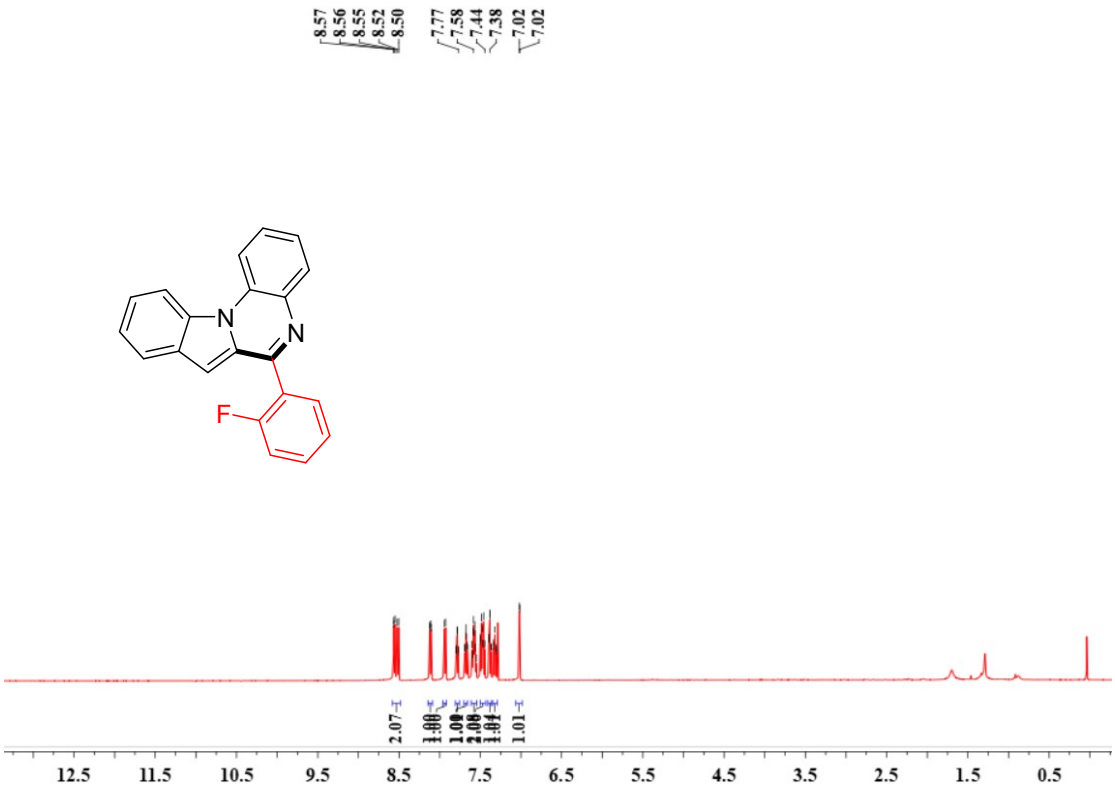


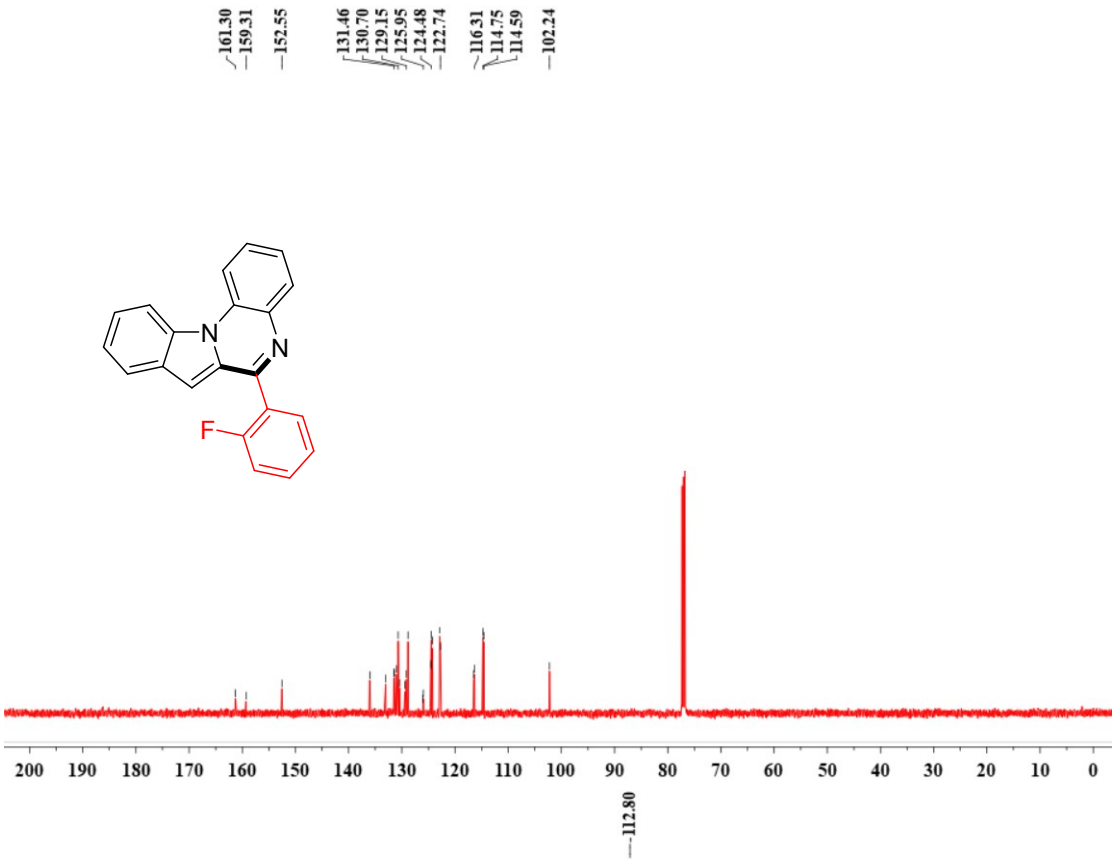
6-(*o*-tolyl)indolo[1,2-*a*]quinoxaline (3ka)





6-(2-fluorophenyl)indolo[1,2-*a*]quinoxaline (3la)

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F
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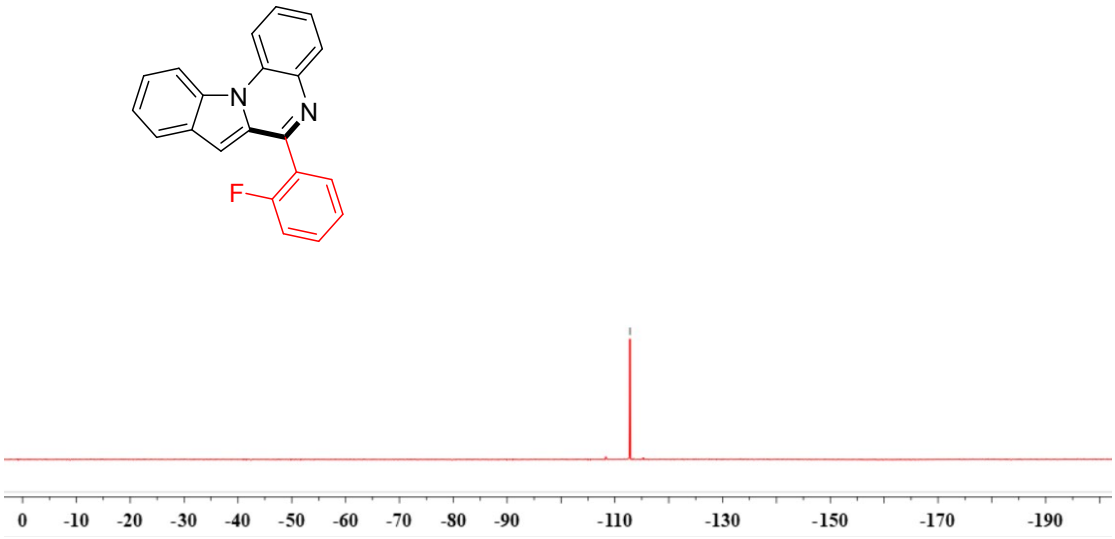
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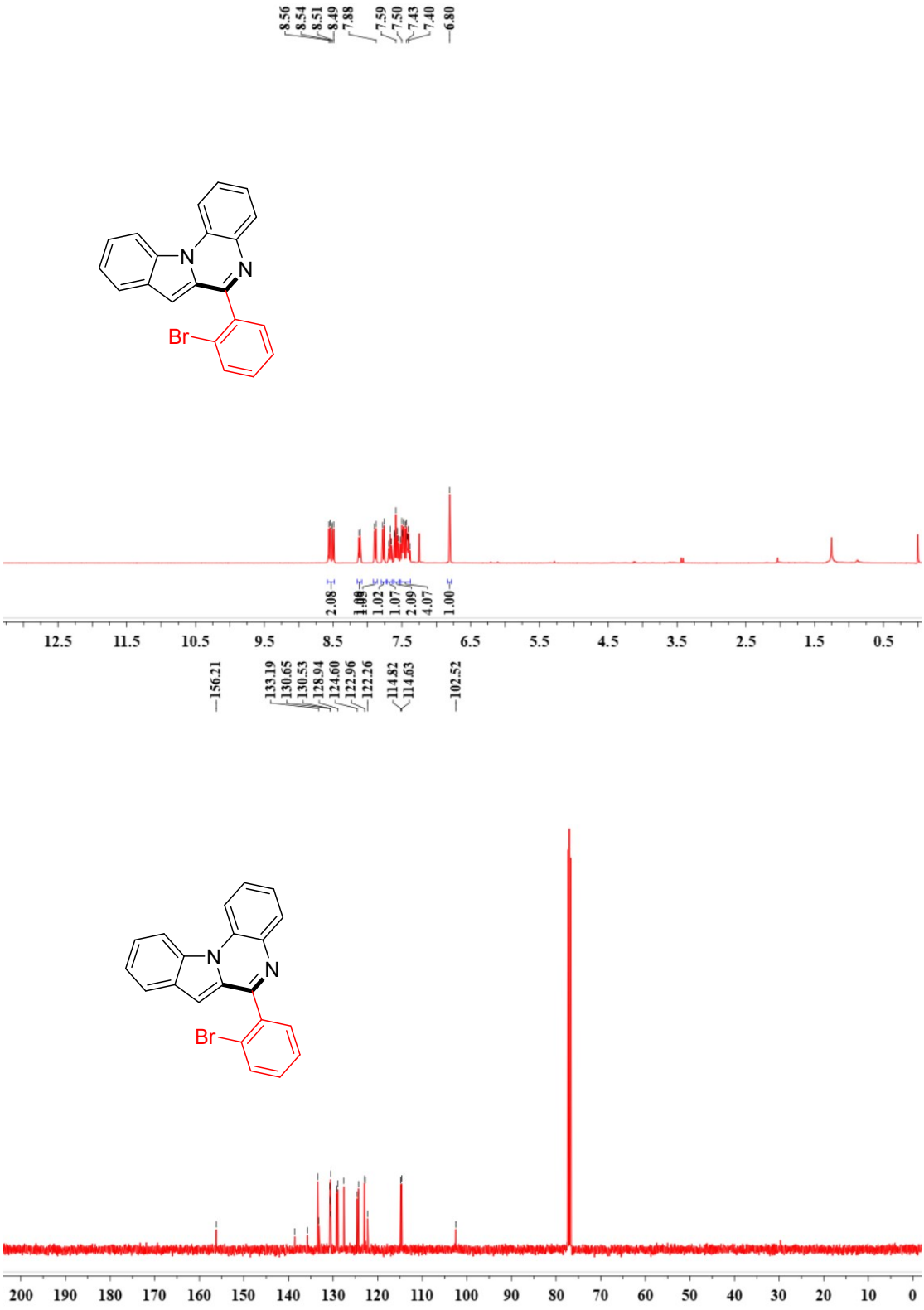
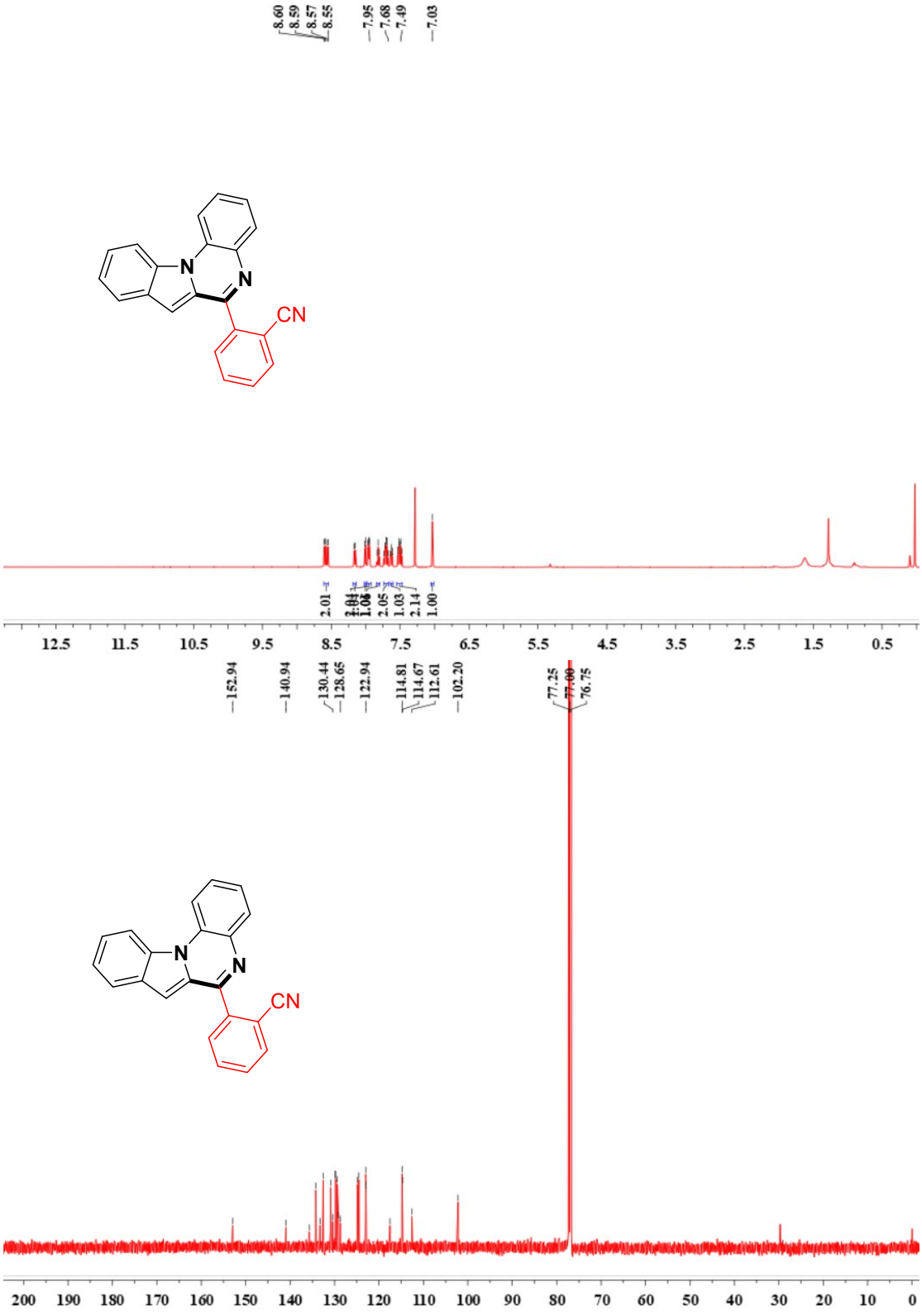
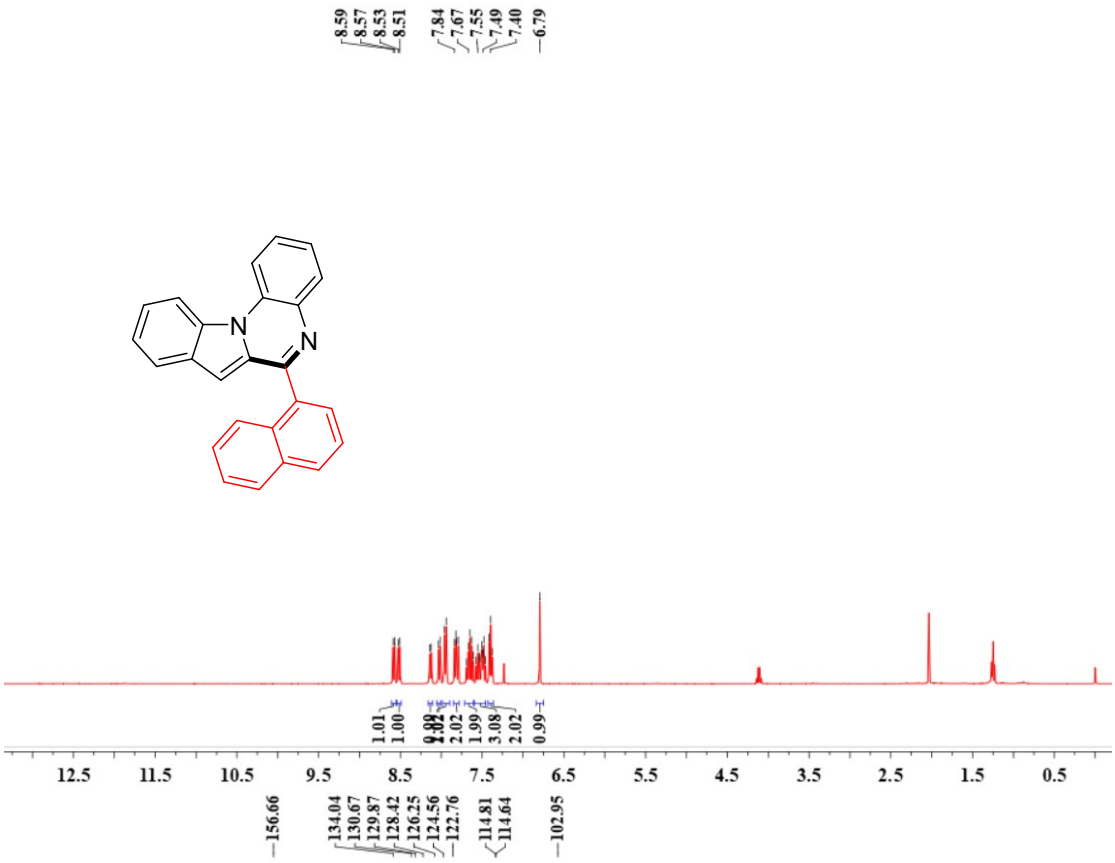
6-(2-bromophenyl)indolo[1,2-*a*]quinoxaline (3ma)

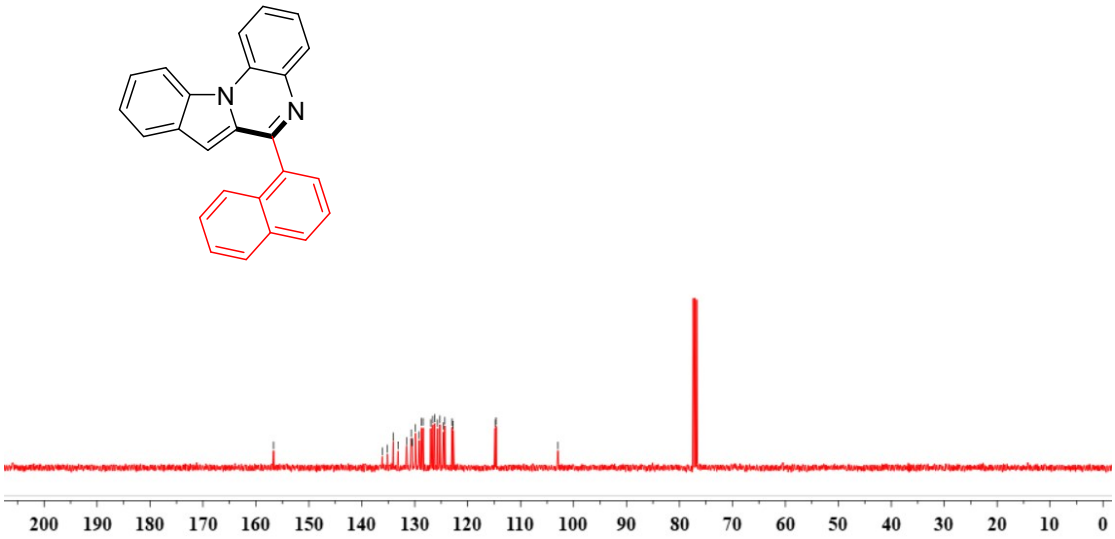


2-(Indolo[1,2-*a*]quinoxalin-6-yl)benzonitrile (3na)

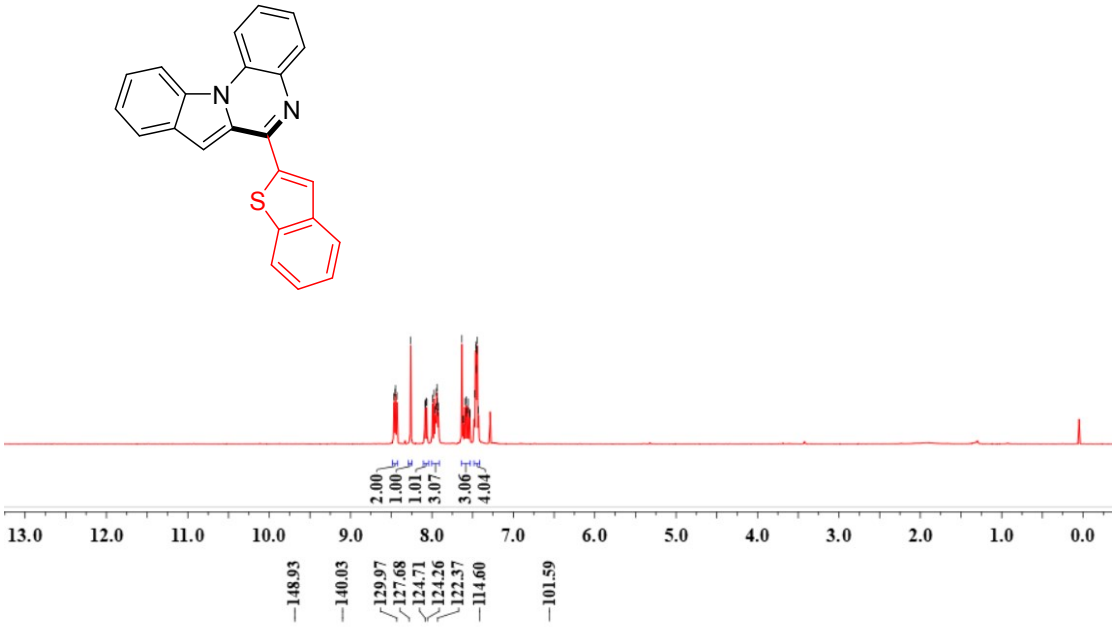


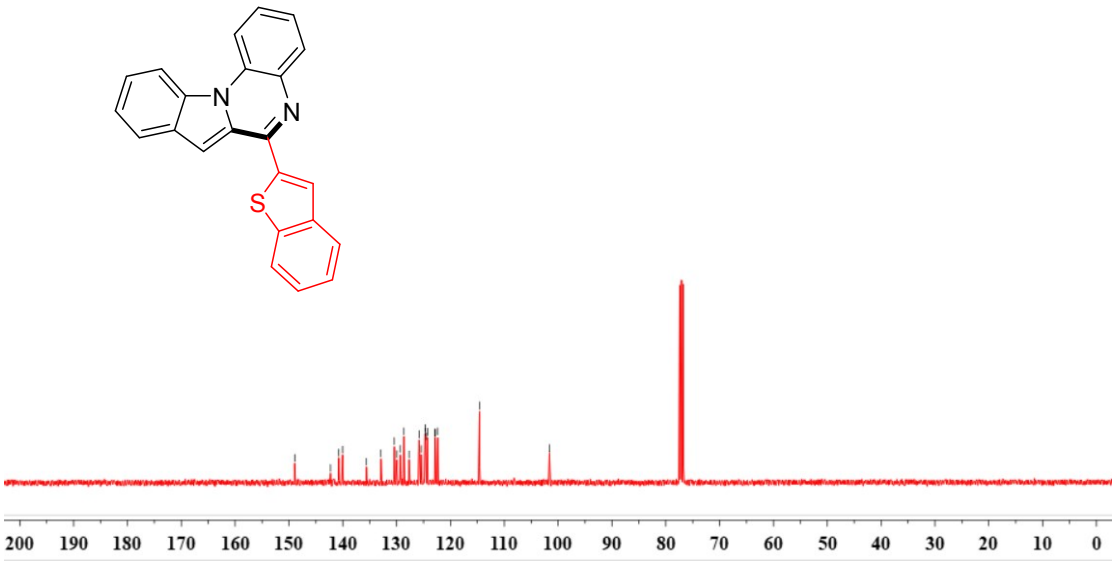
6-(naphthalen-1-yl)indolo[1,2-*a*]quinoxaline (3oa)



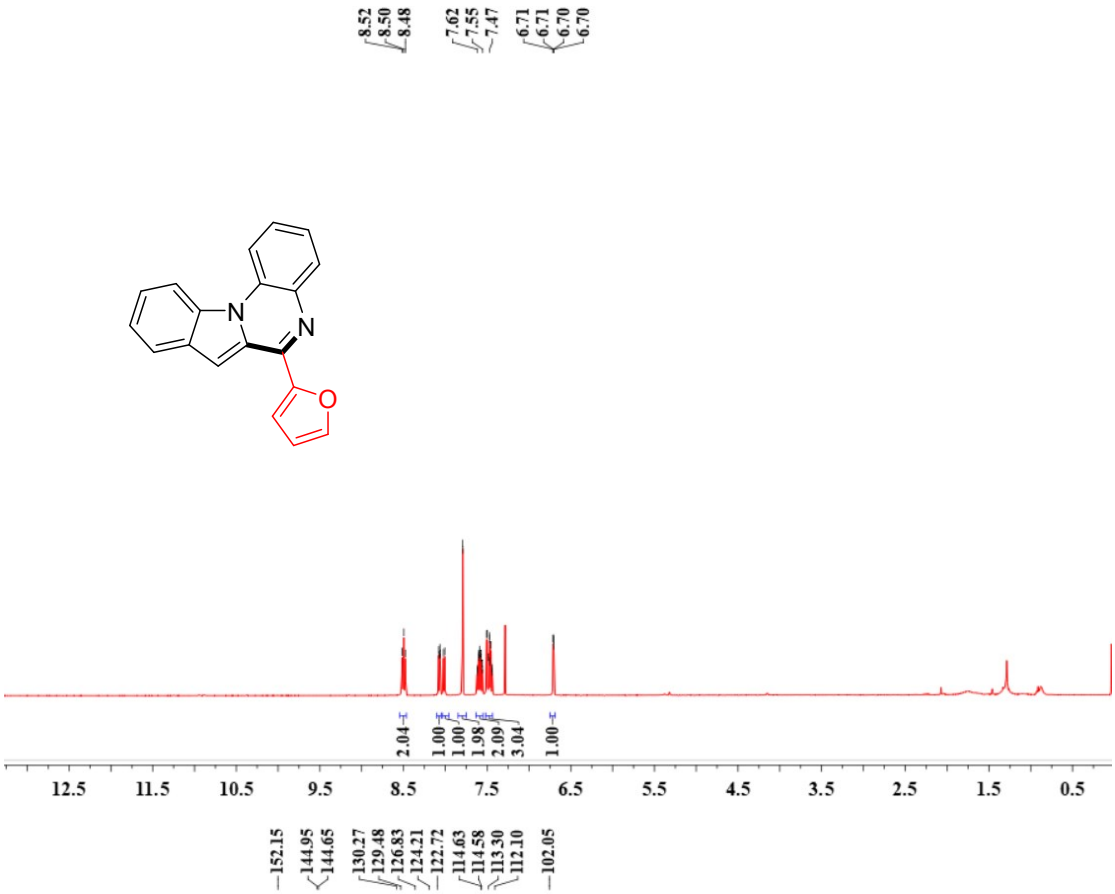


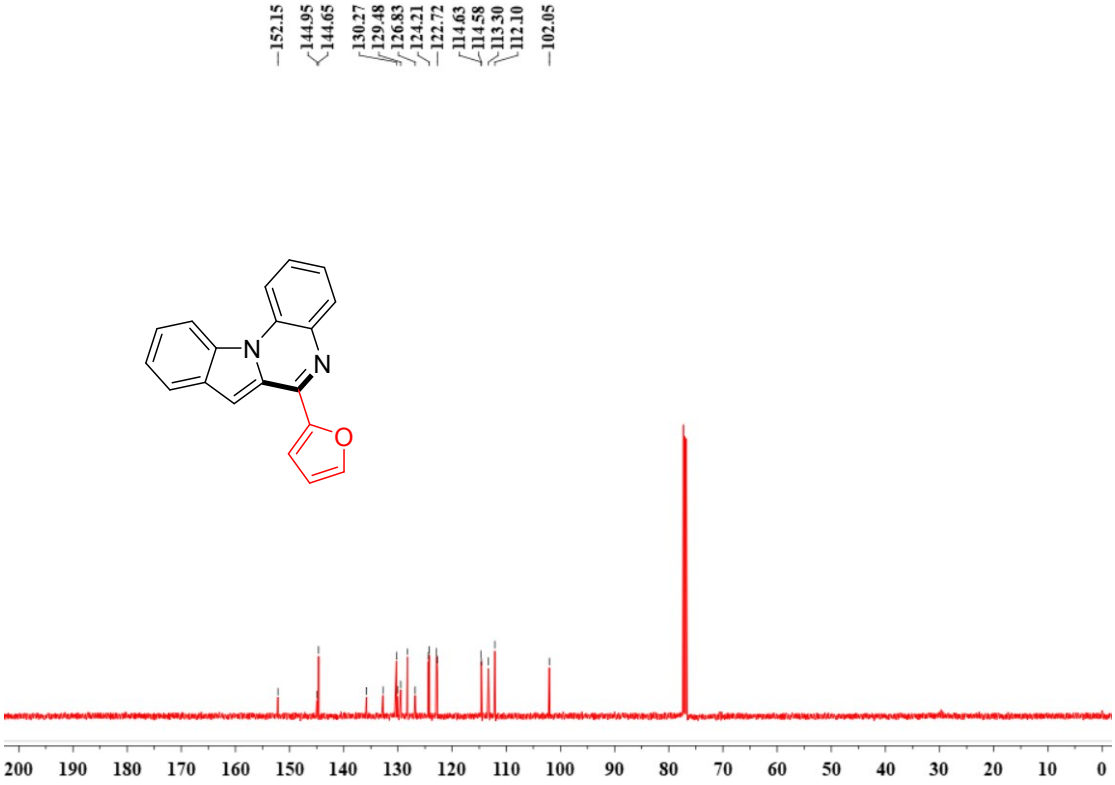
6-(benzo[*b*]thiophen-2-yl)indolo[1,2-*a*]quinoxaline (3pa)



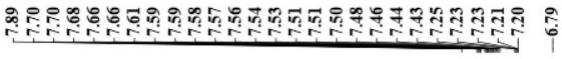


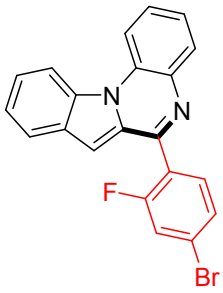
6-(furan-2-yl)indolo[1,2-*a*]quinoxaline (3ra)

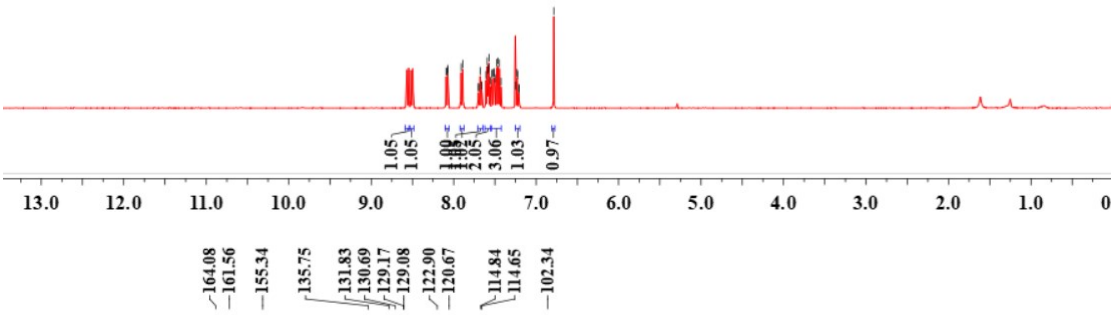


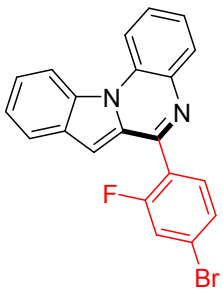


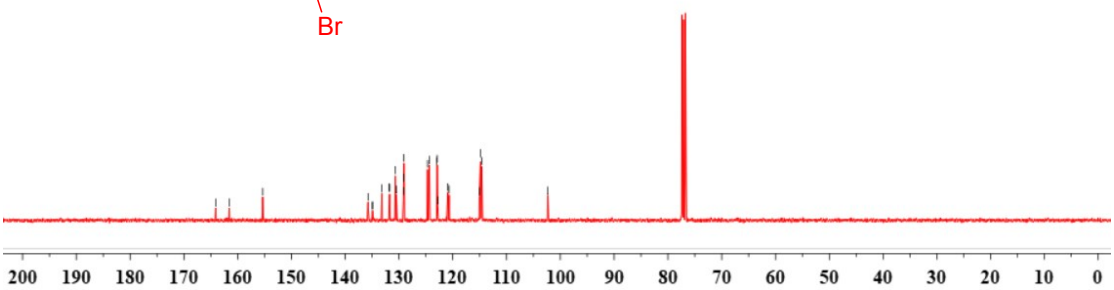
6-(4-bromo-2-fluorophenyl)indolo[1,2-*a*]quinoxaline (3ta)

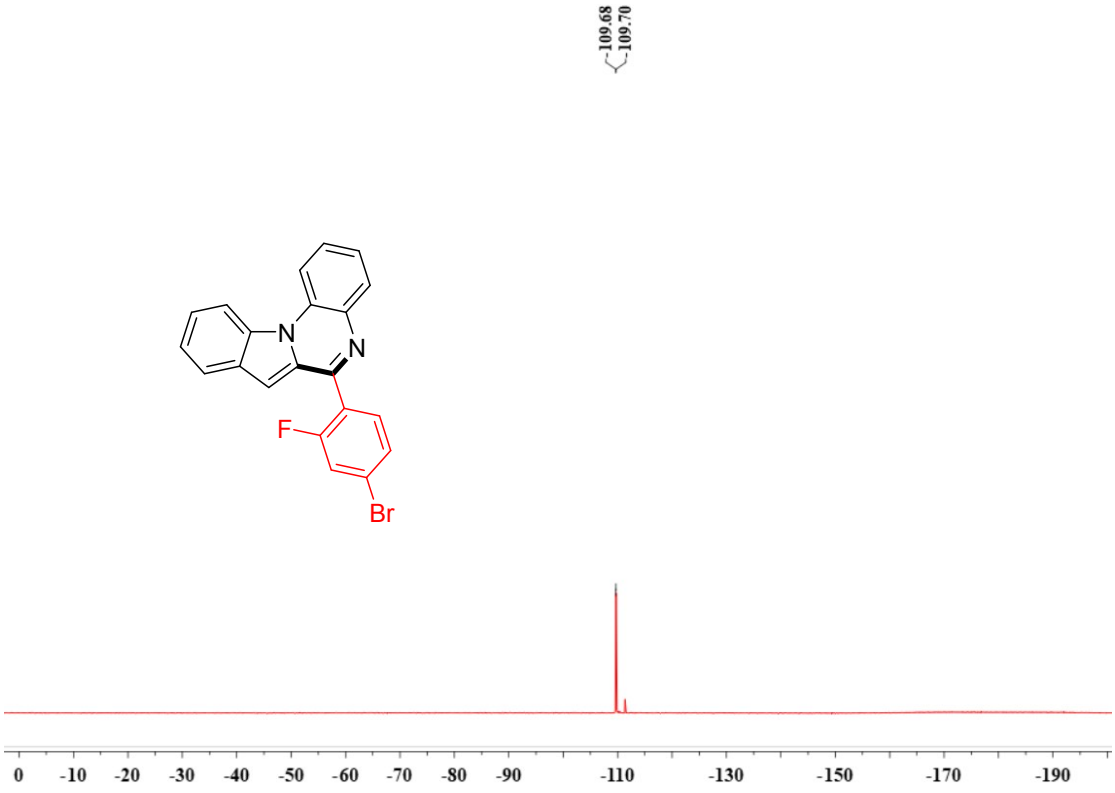




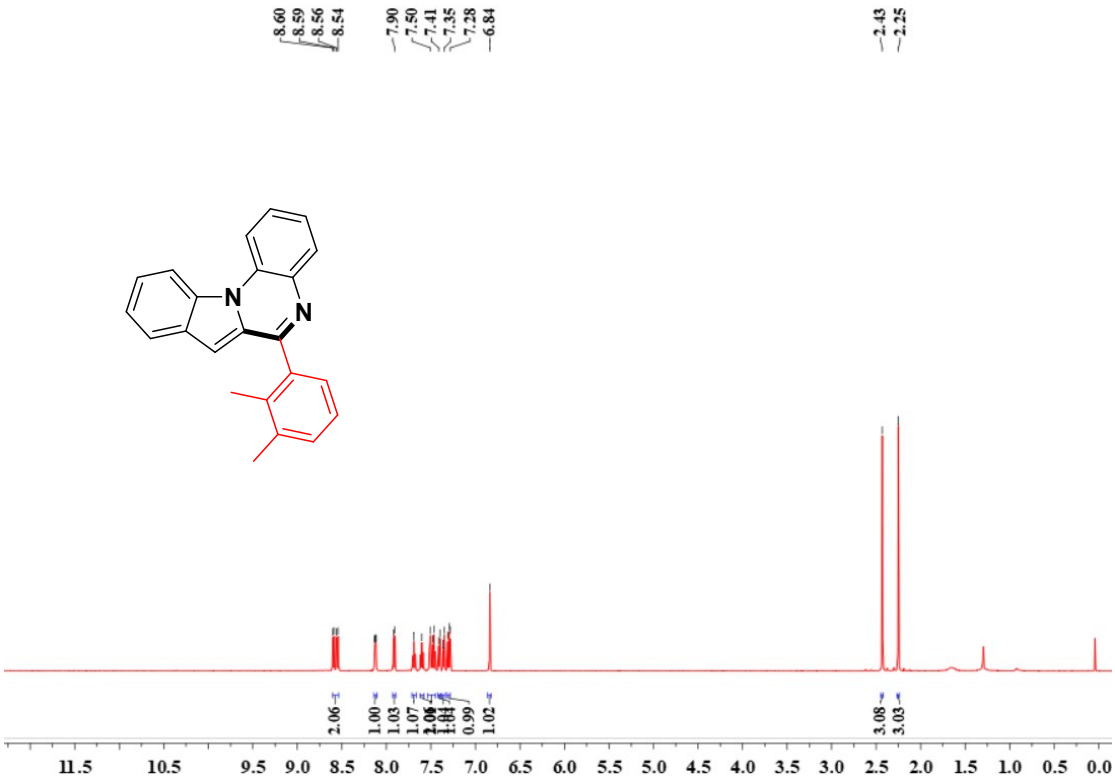


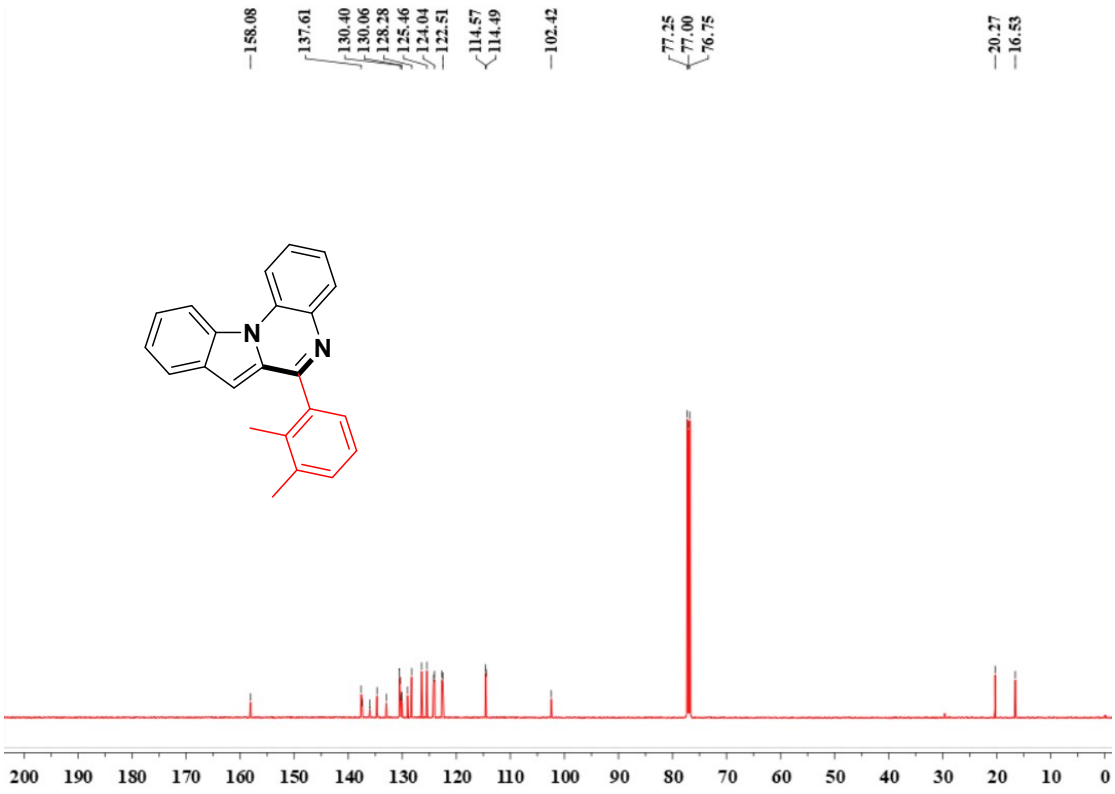




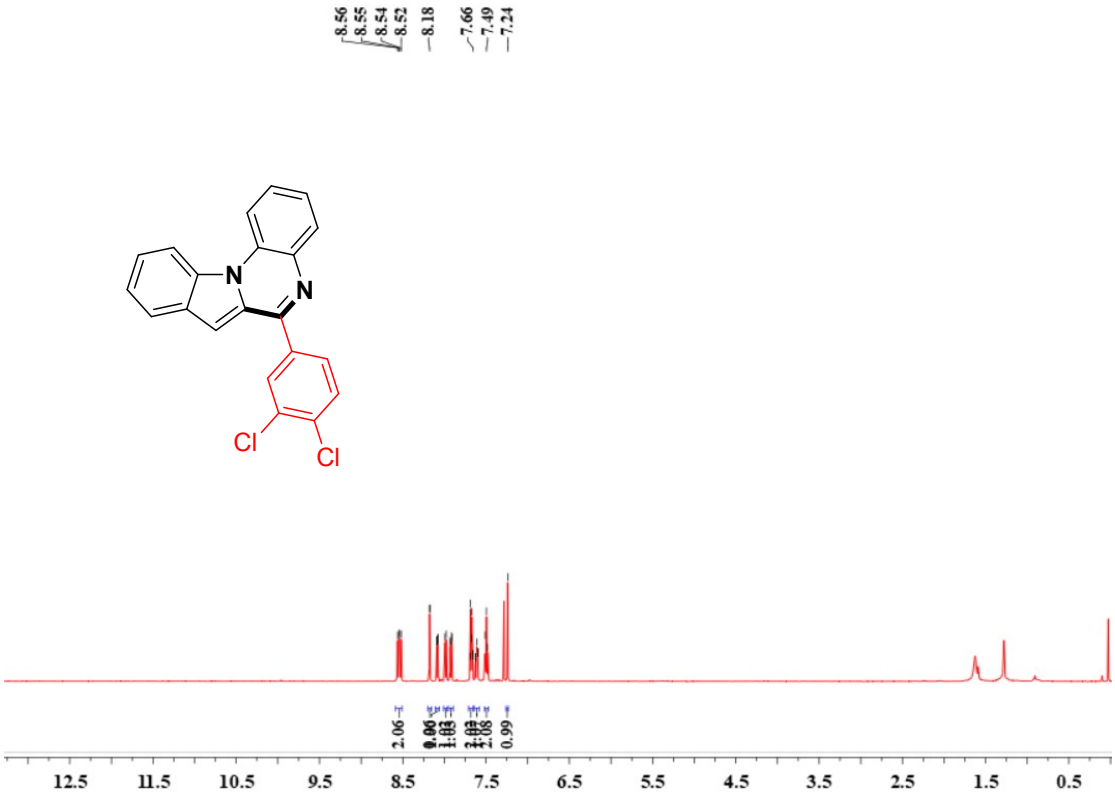


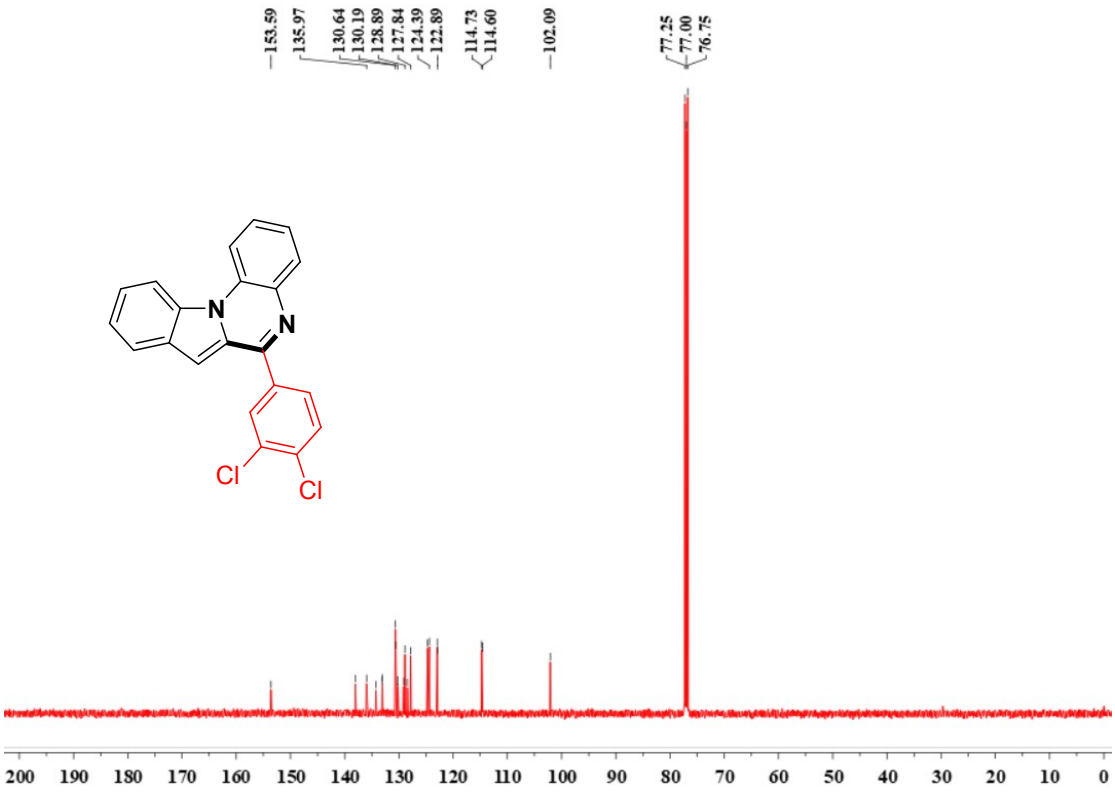
6-(2,3-Dimethylphenyl)indolo[1,2-*a*]quinoxaline (3ua)



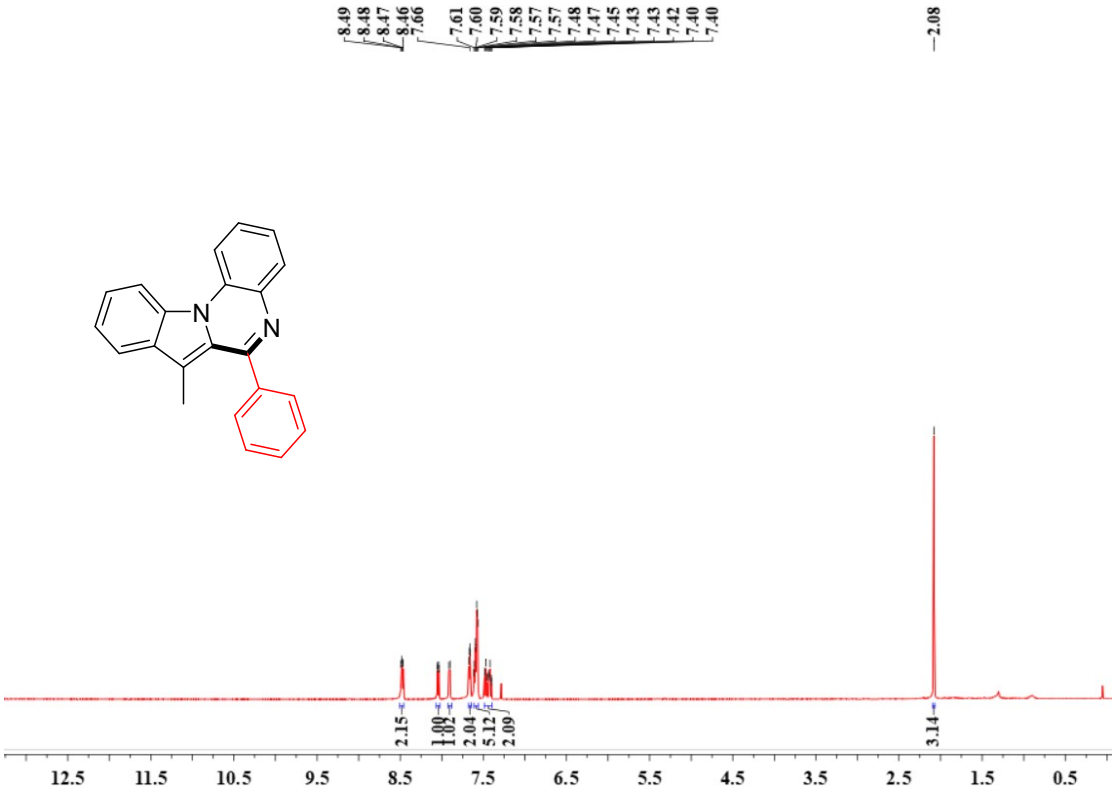


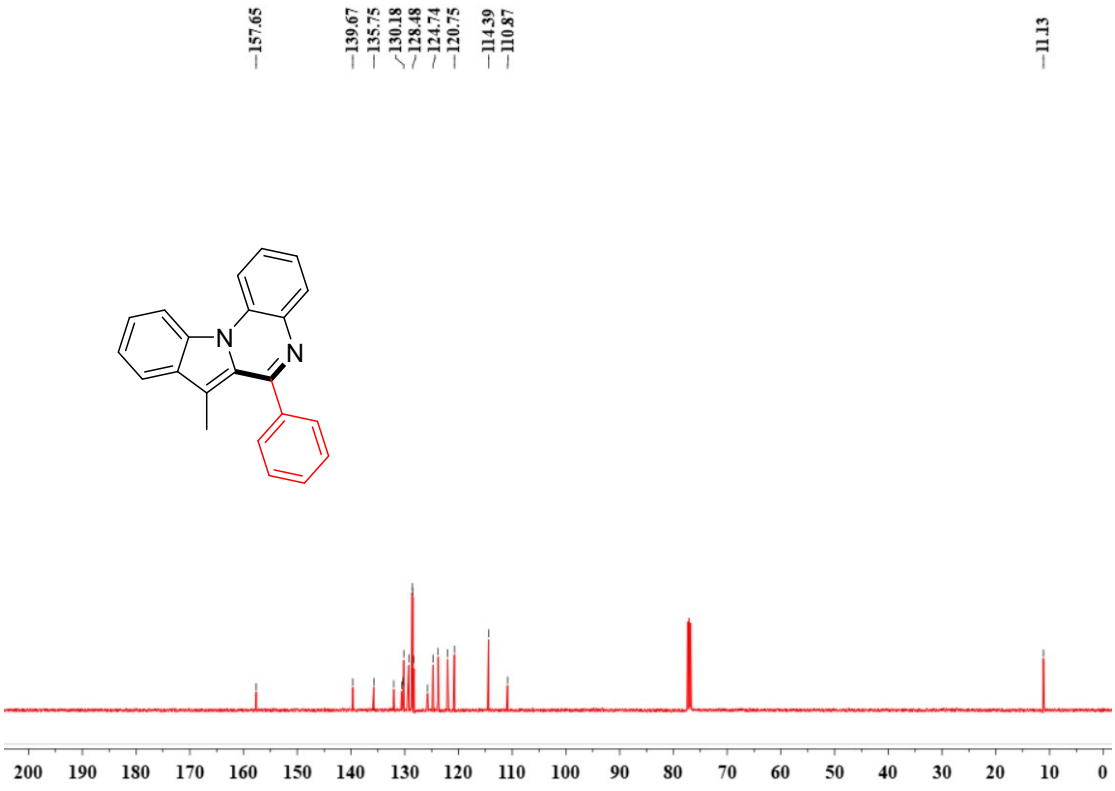
6-(3,4-Dichlorophenyl)indolo[1,2-*a*]quinoxaline (3va)



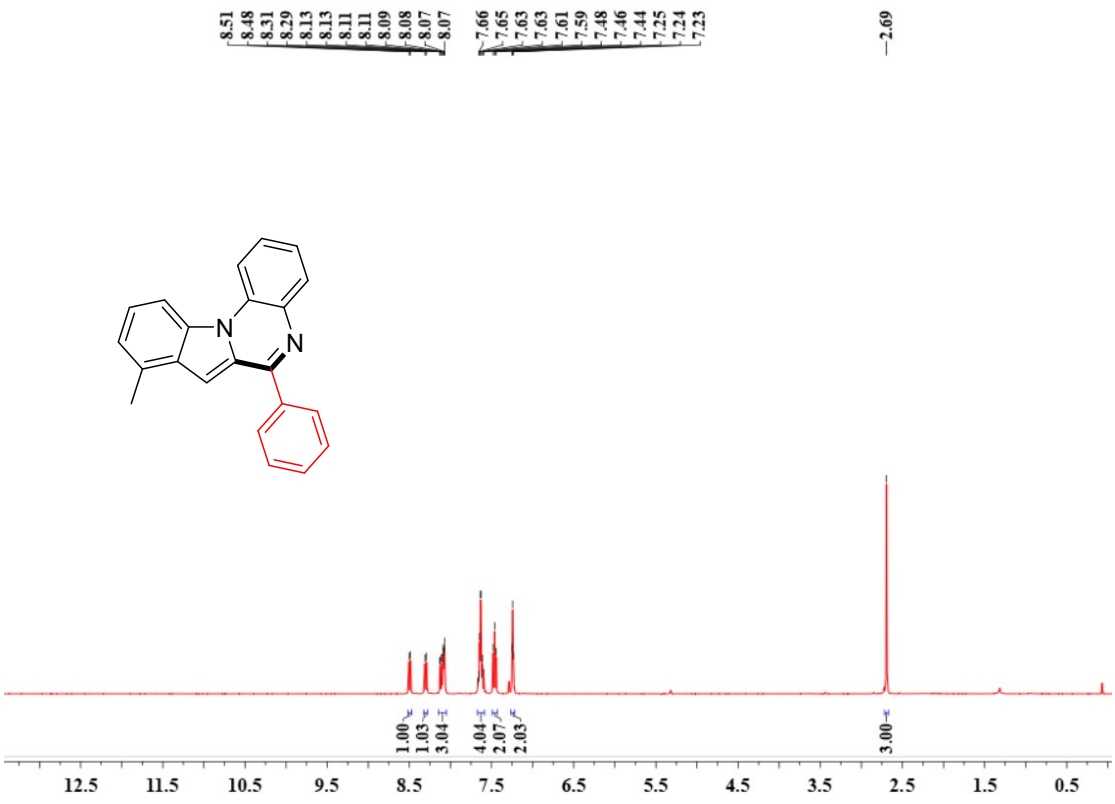


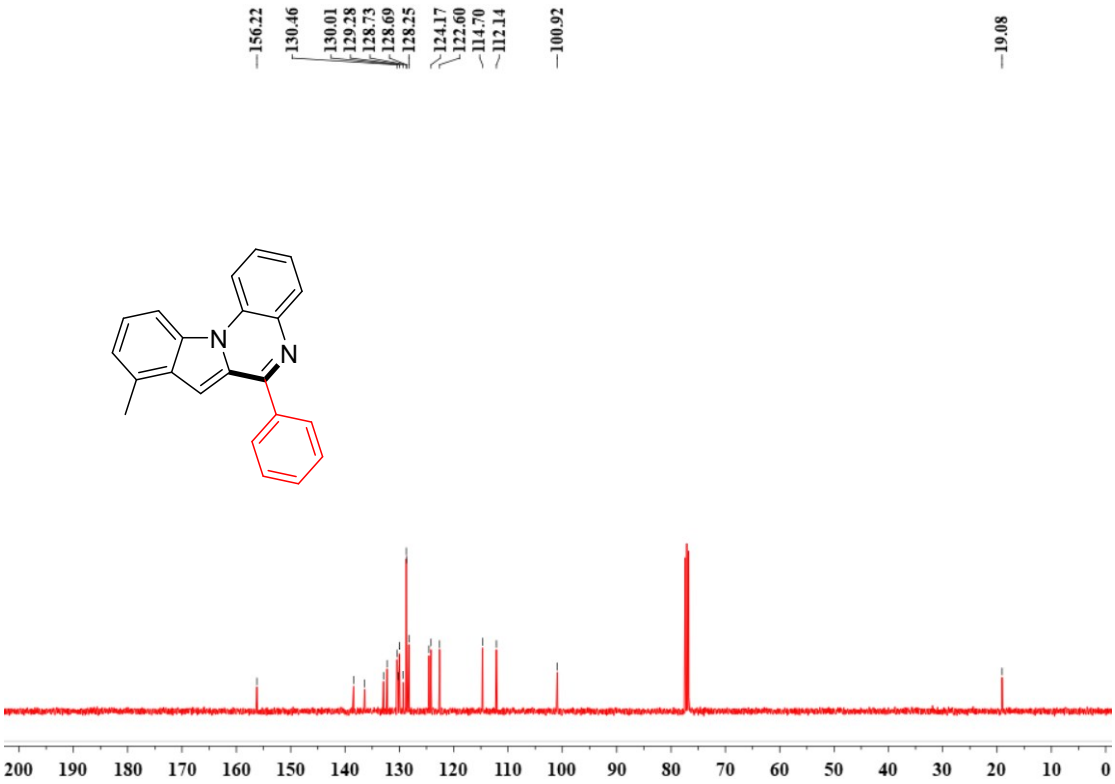
7-methyl-6-phenylindolo[1,2-*a*]quinoxaline (3ab)



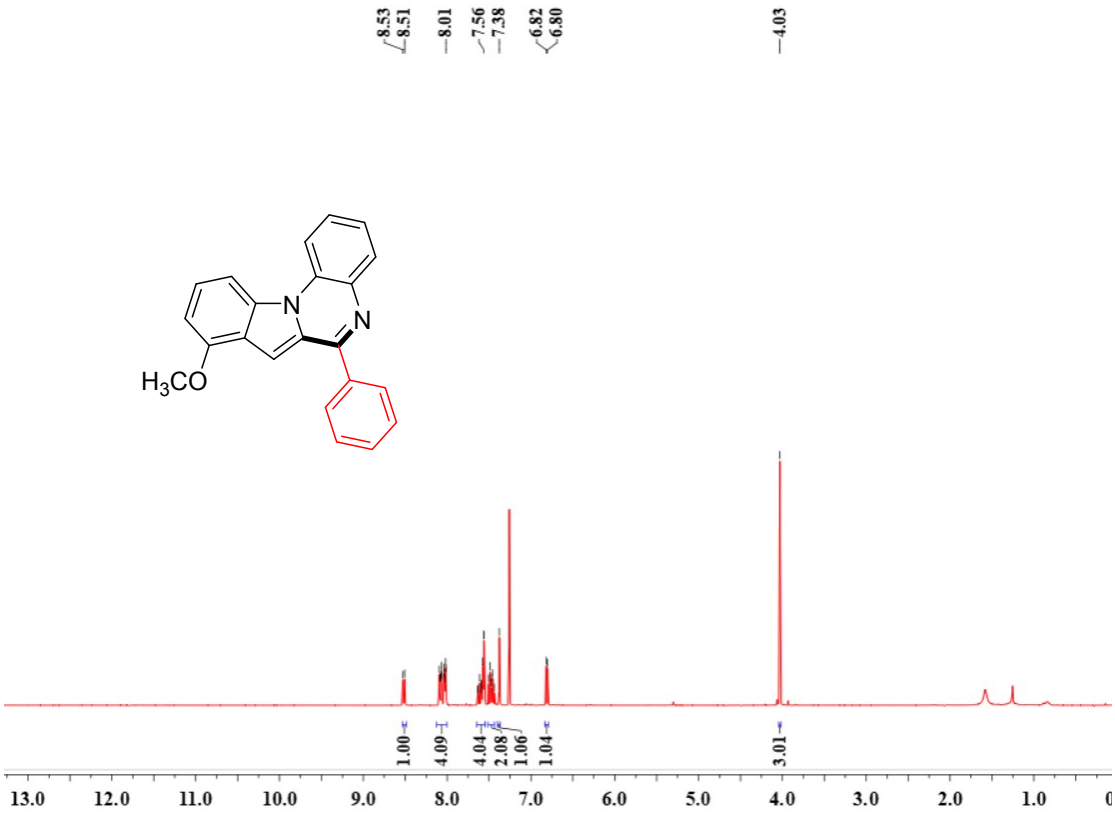


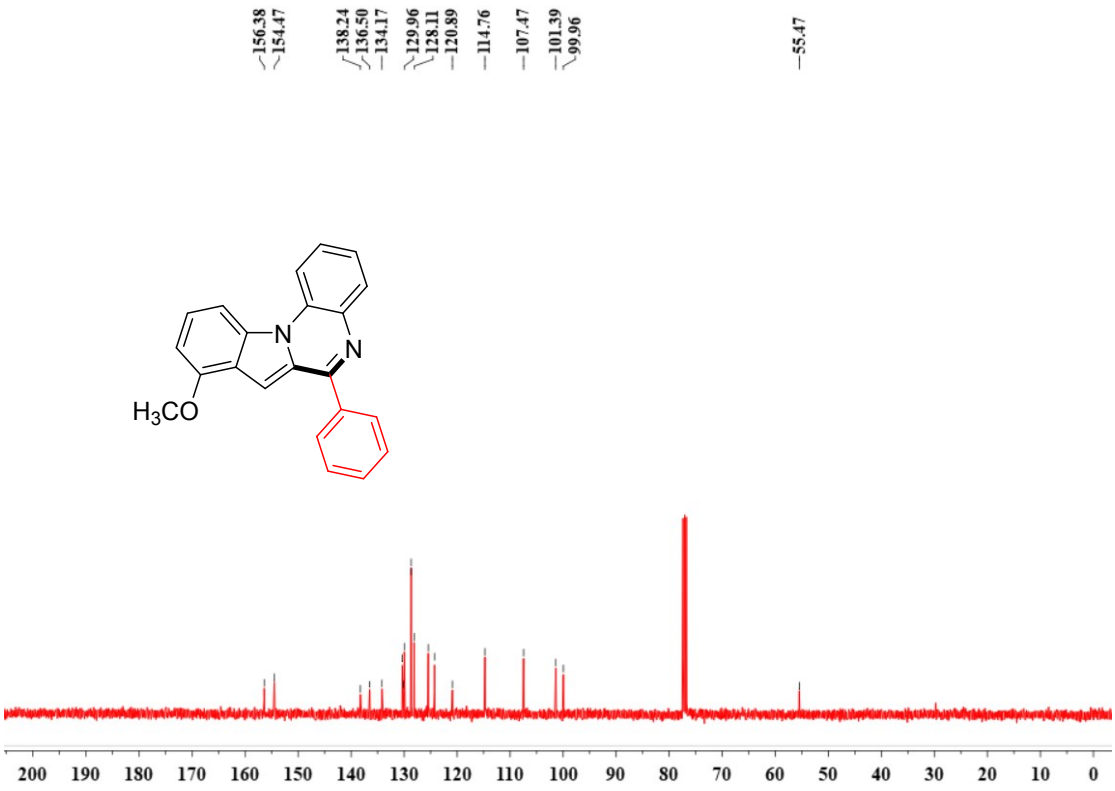
8-methyl-6-phenylindolo[1,2-*a*]quinoxaline (3ac)



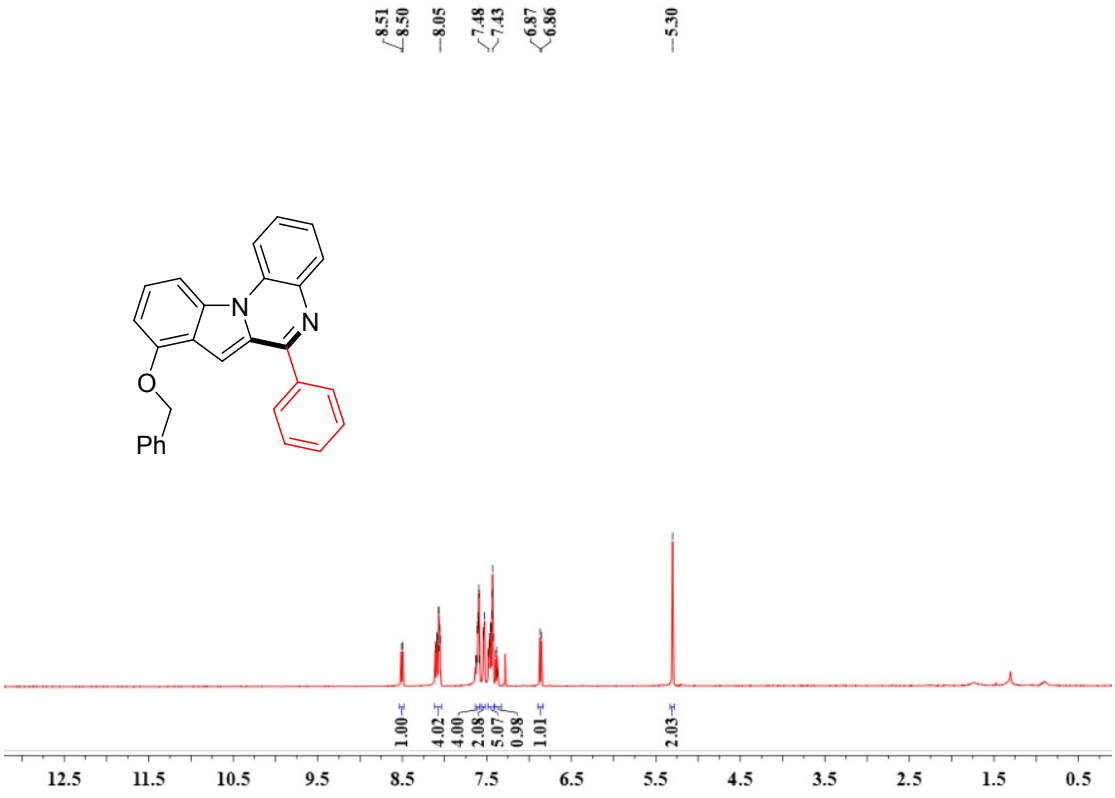


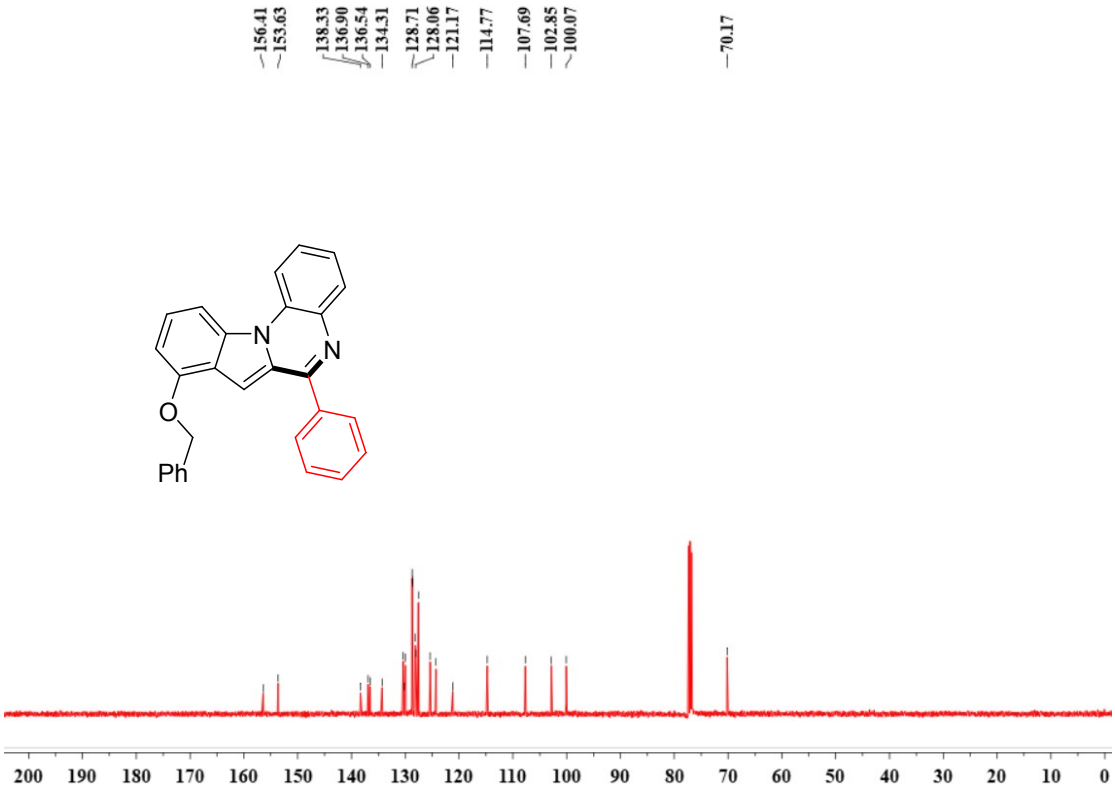
8-methoxy-6-phenylindolo[1,2-*a*]quinoxaline (3ad)



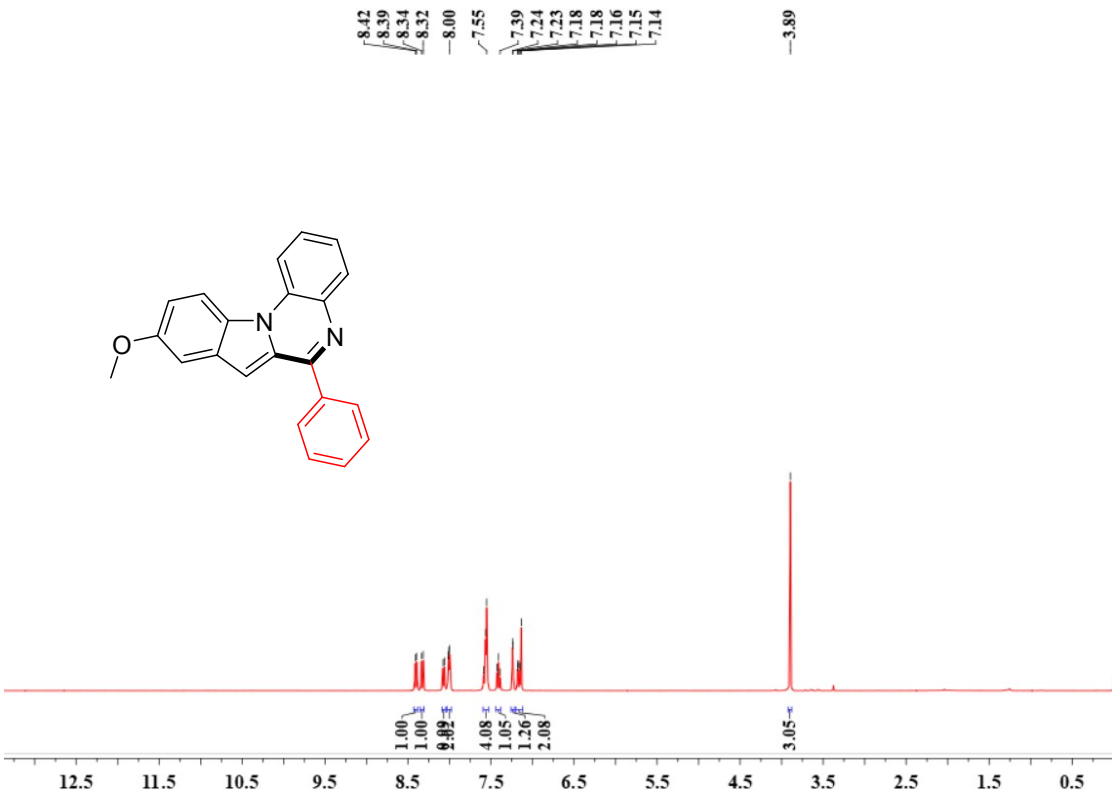


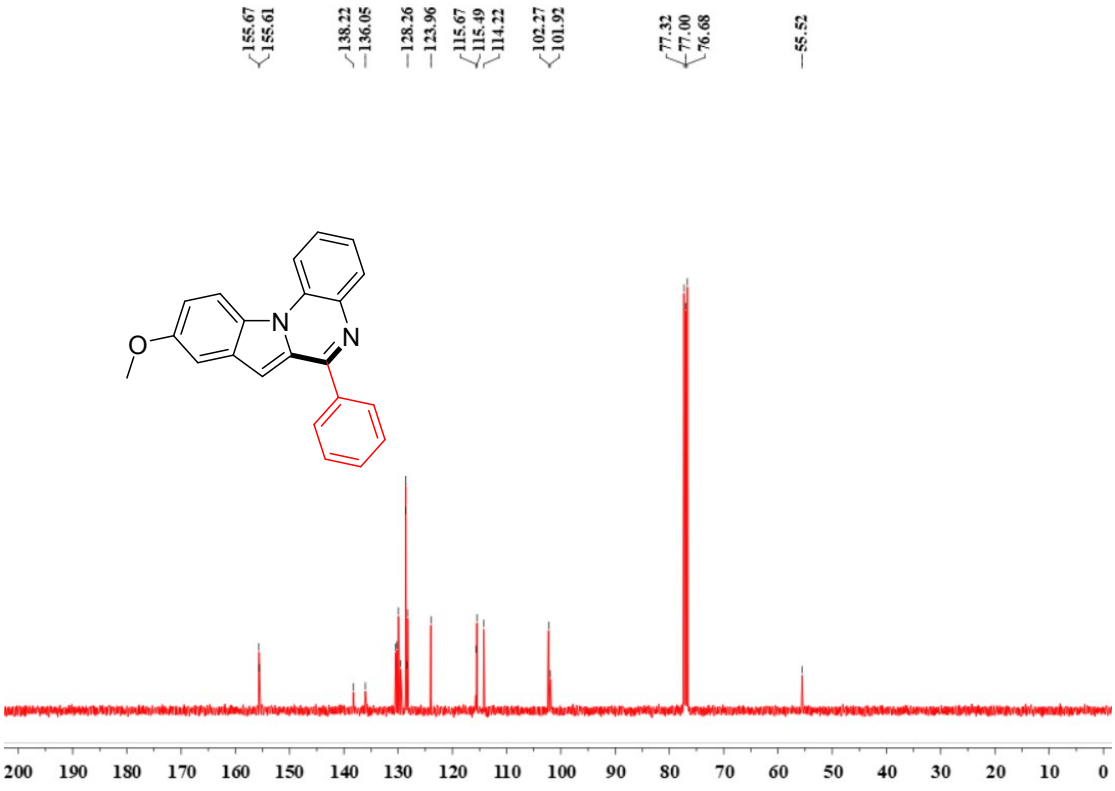
8-(benzyloxy)-6-phenylindolo[1,2-*a*]quinoxaline (3ae)



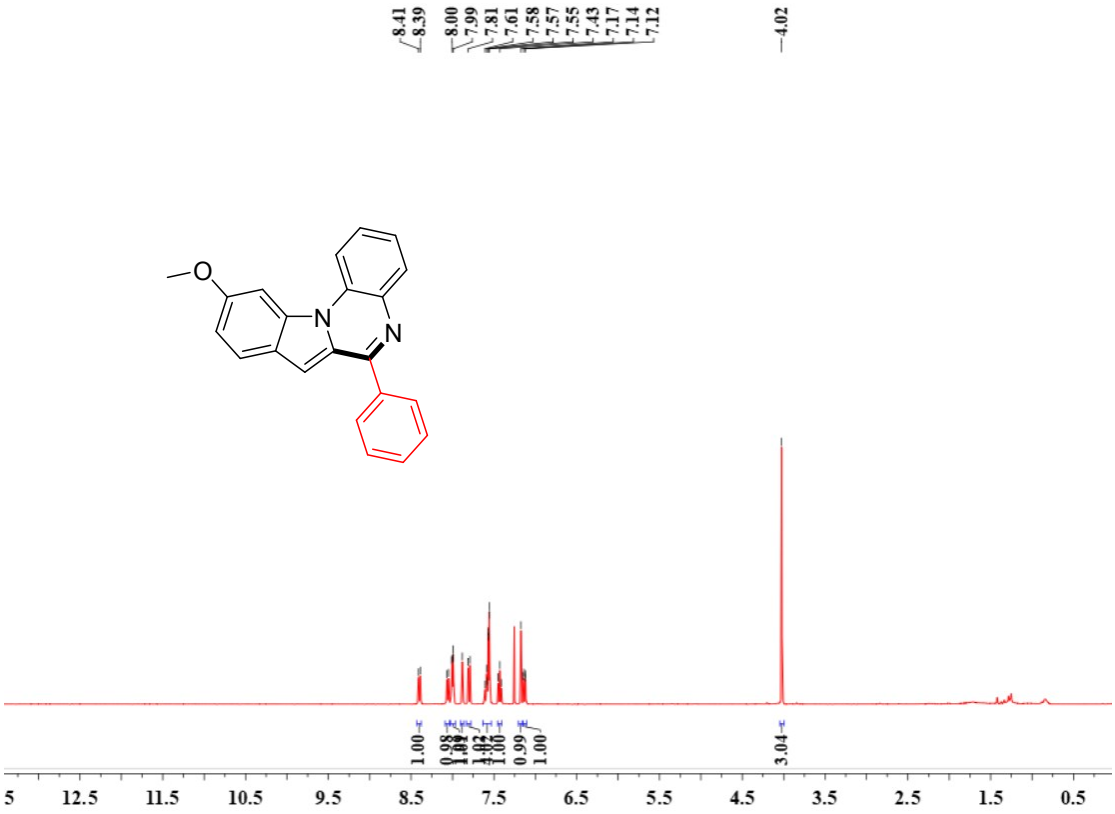


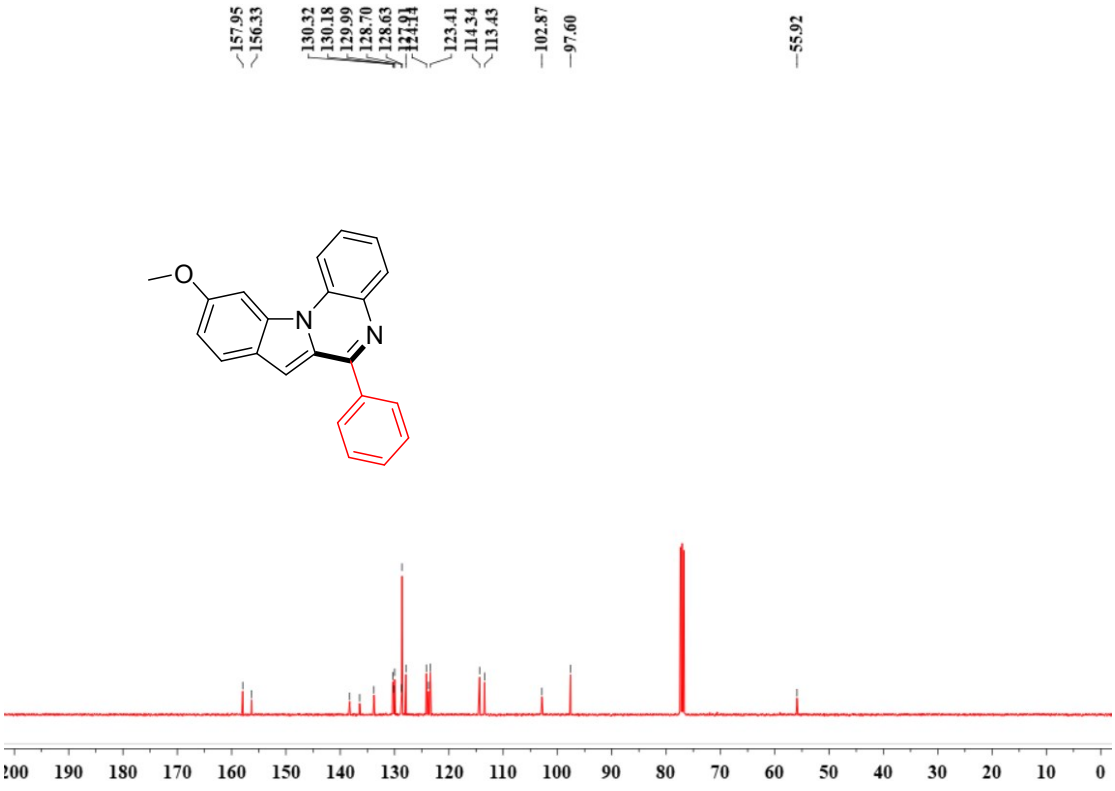
9-methoxy-6-phenylindolo[1,2-*a*]quinoxaline (3af)



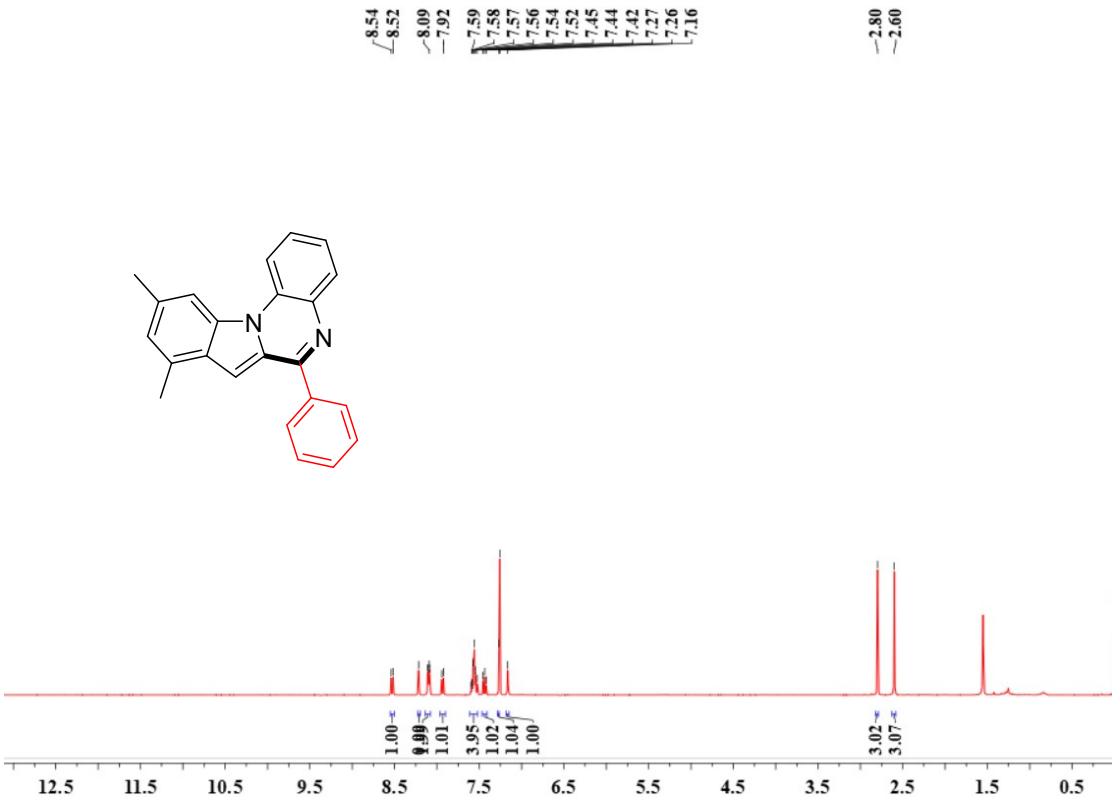


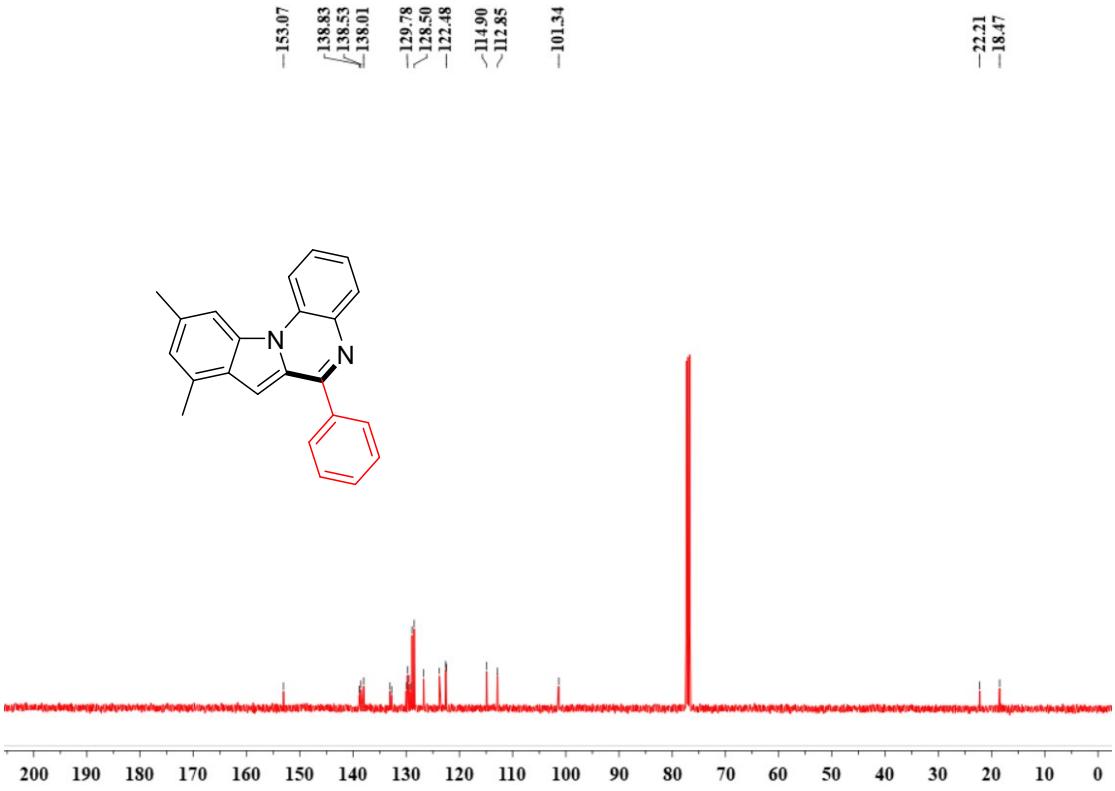
10-methoxy-6-phenylindolo[1,2-*a*]quinoxaline (3ag)



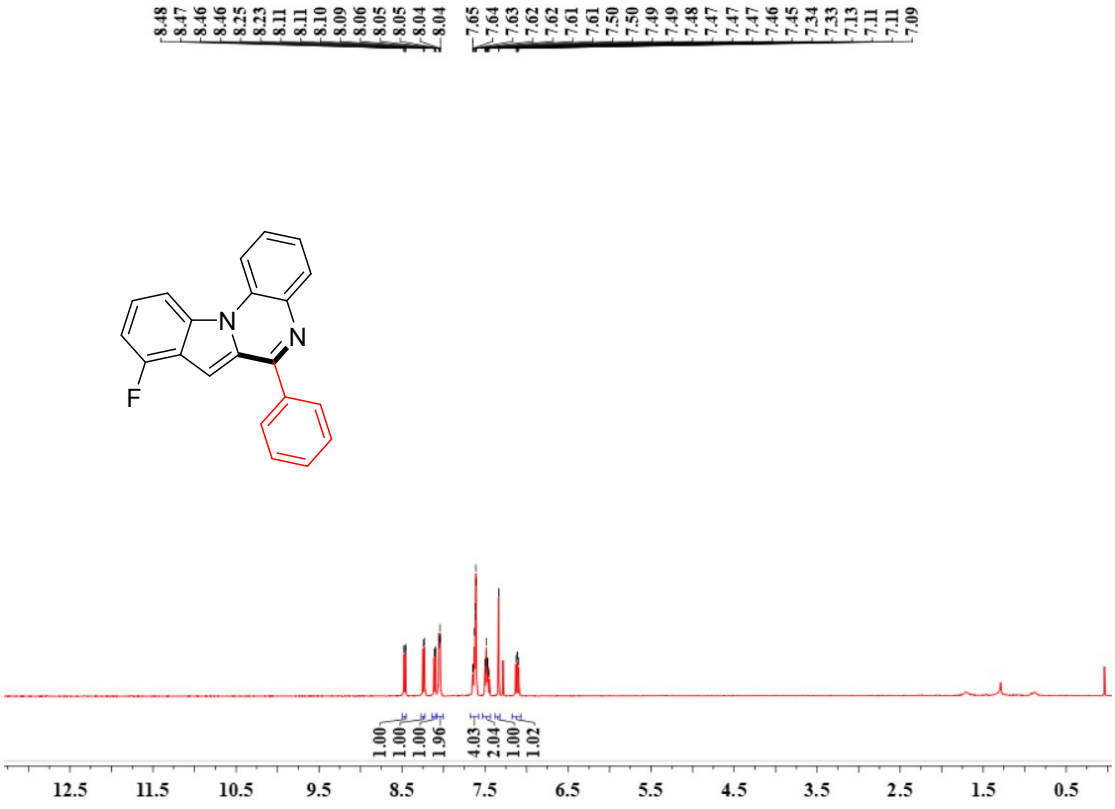


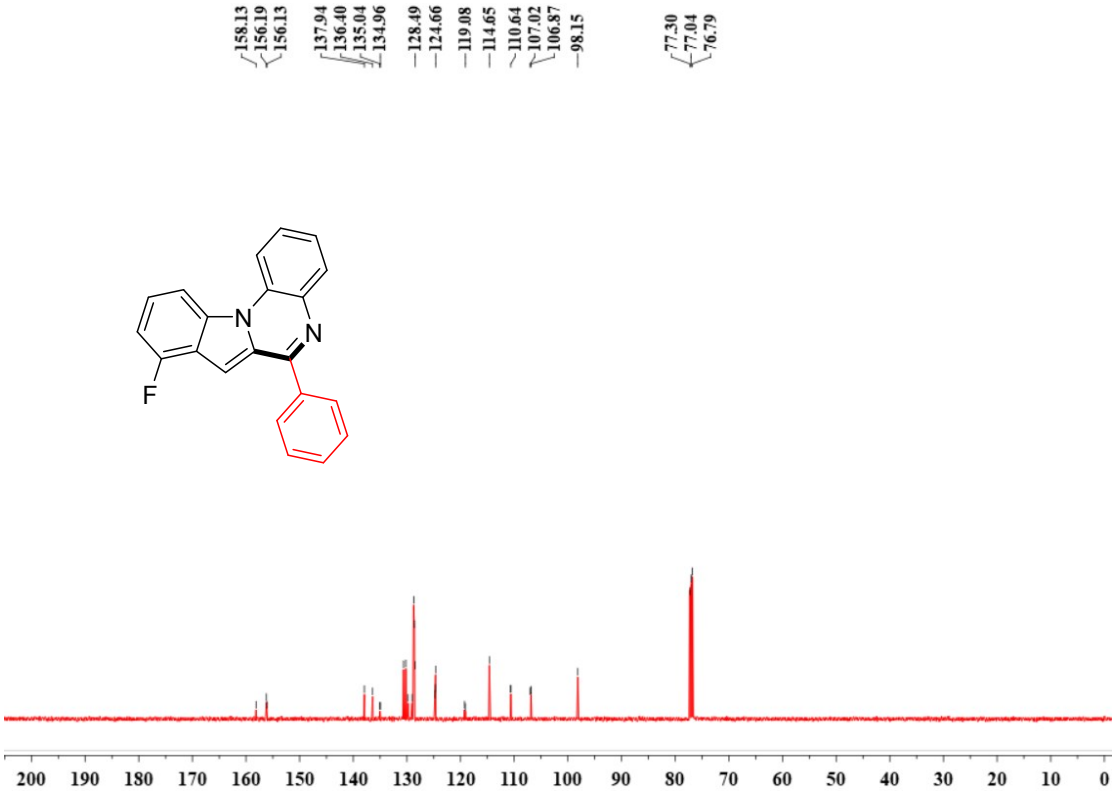
8,10-dimethyl-6-phenylindolo[1,2-*a*]quinoxaline (3ah)



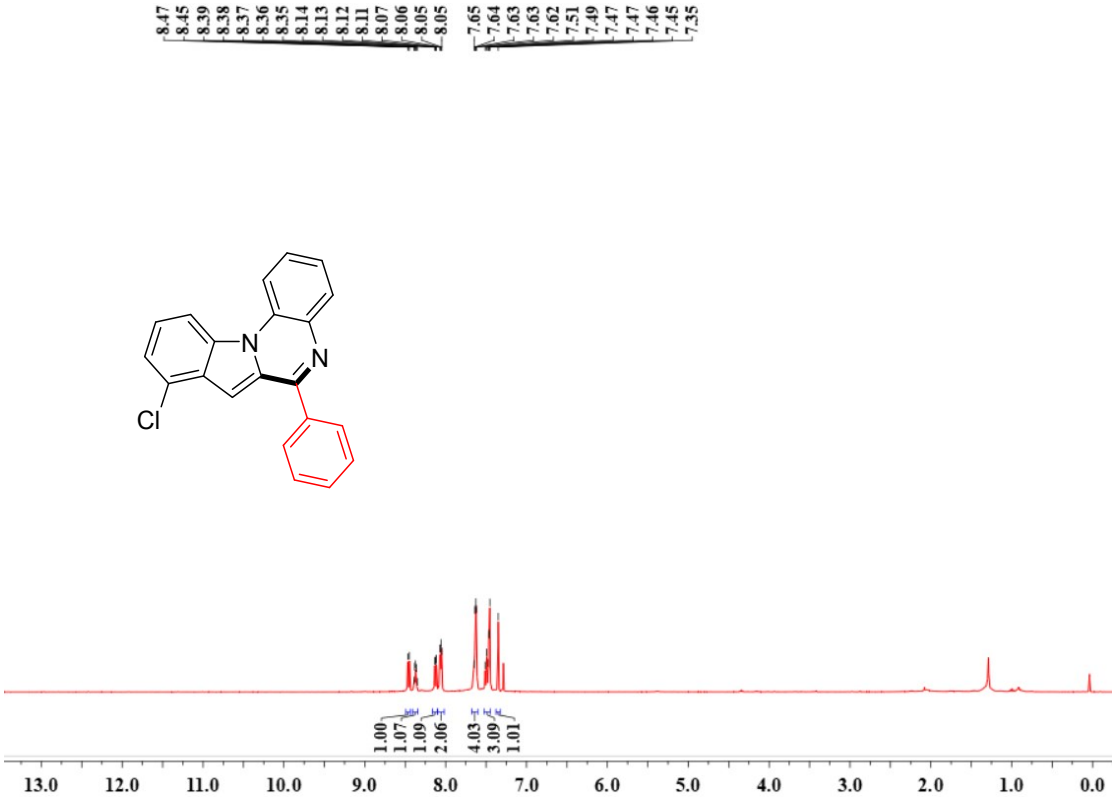


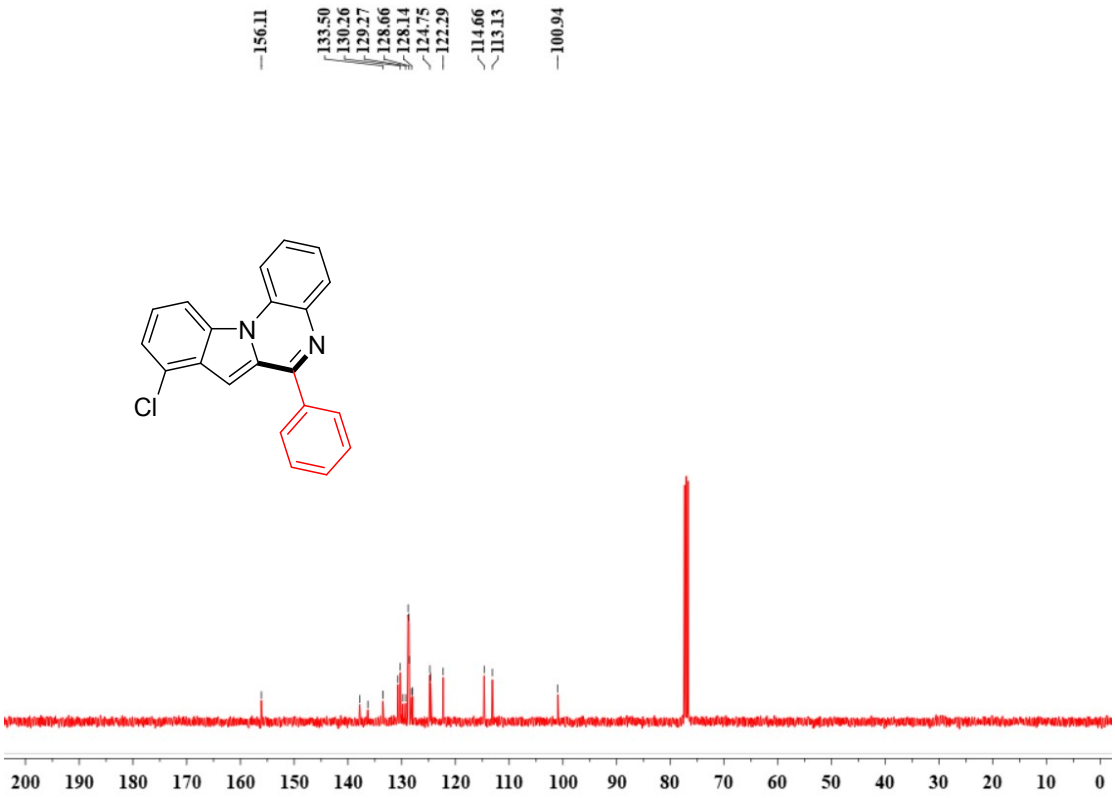
8-fluoro-6-phenylindolo[1,2-*a*]quinoxaline (3ai)



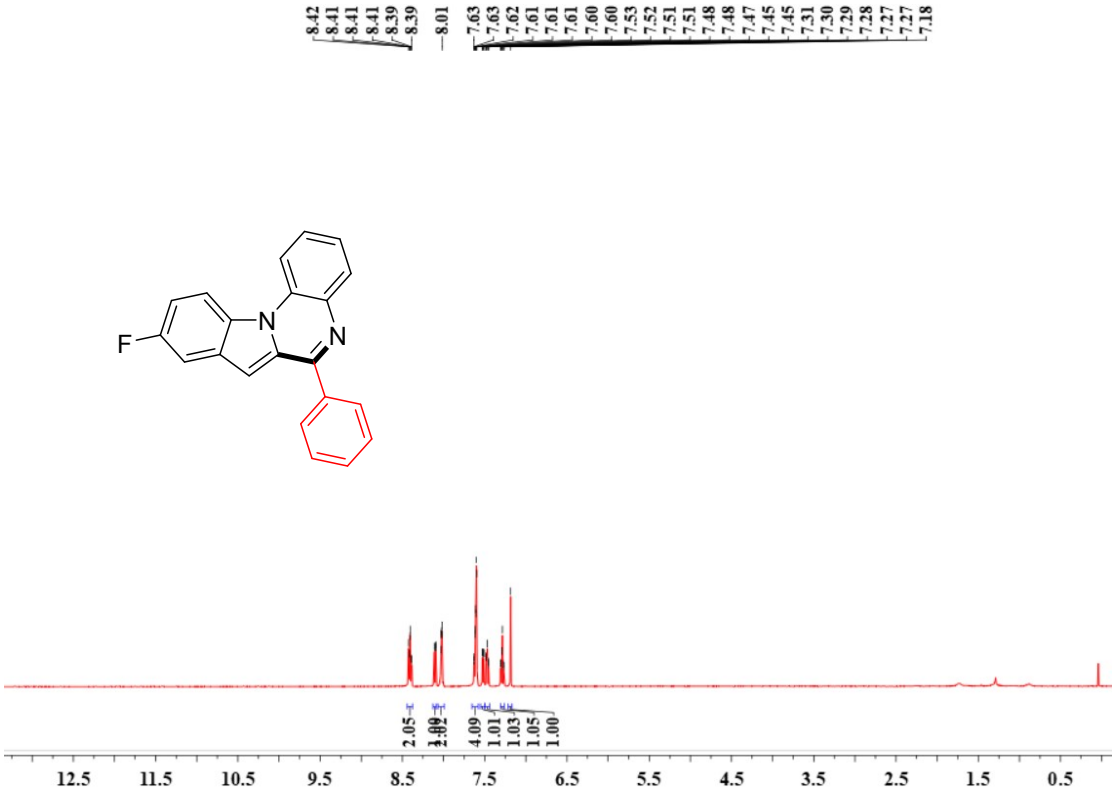


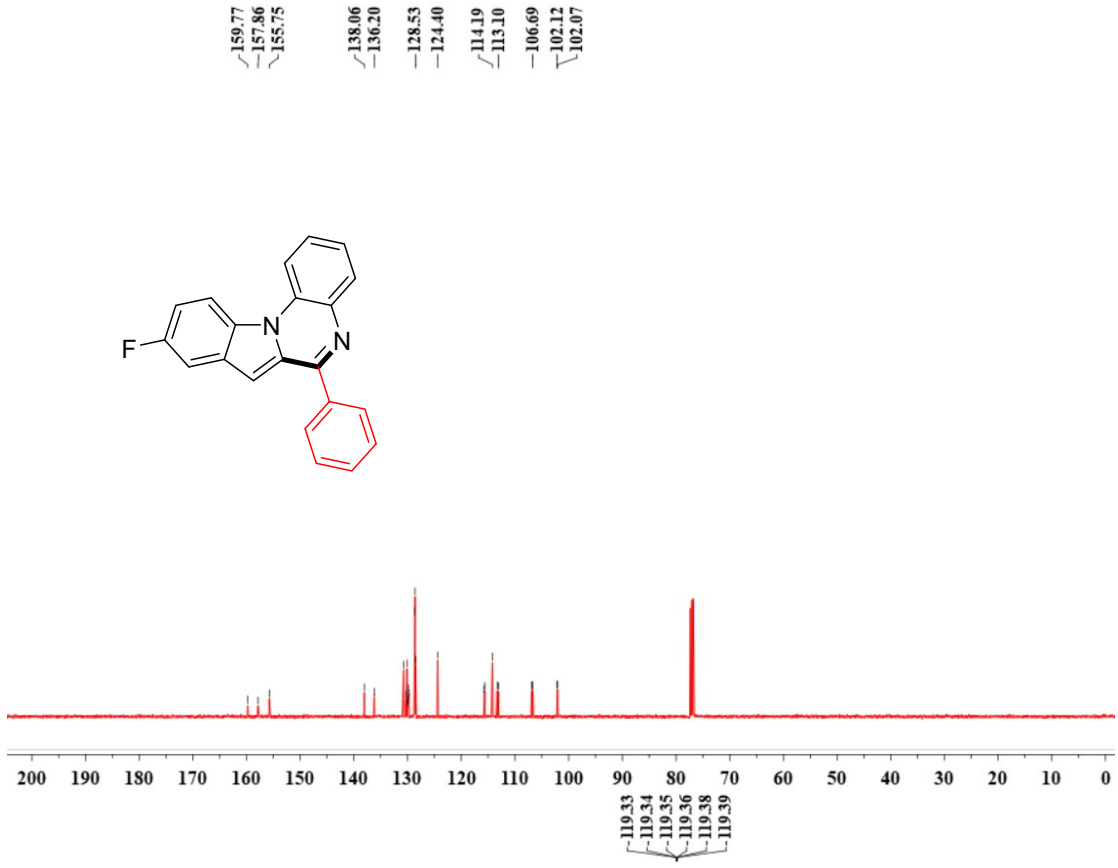
8-chloro-6-phenylindolo[1,2-*a*]quinoxaline (3aj)





9-fluoro-6-phenylindolo[1,2-*a*]quinoxaline (3ak)

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155.75
138.06
136.20
128.53
124.40
114.19
113.10
106.69
102.12
102.07
F
N
N
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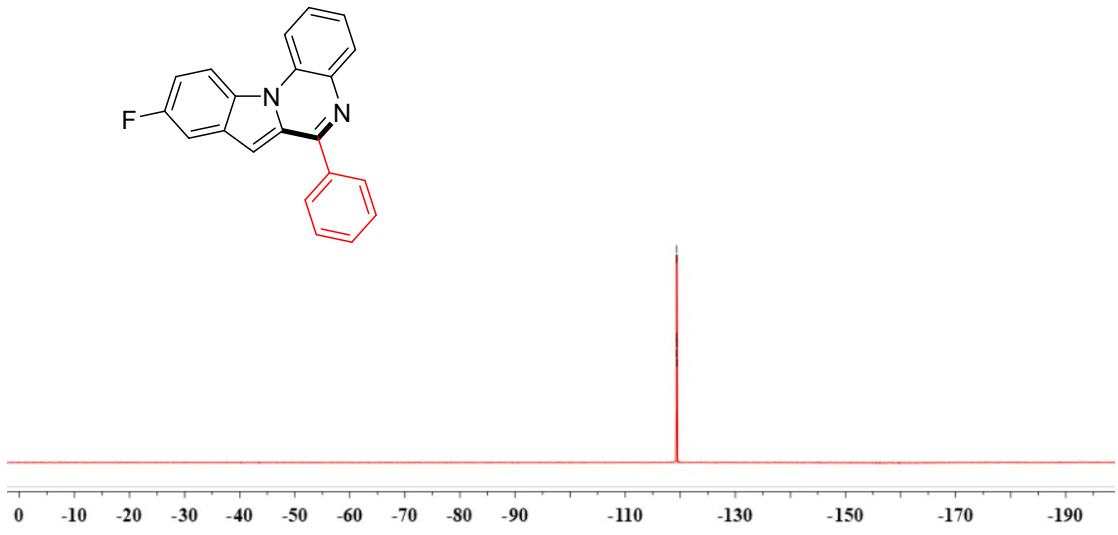
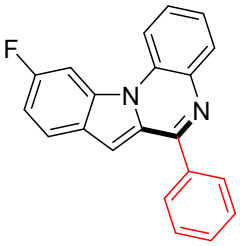
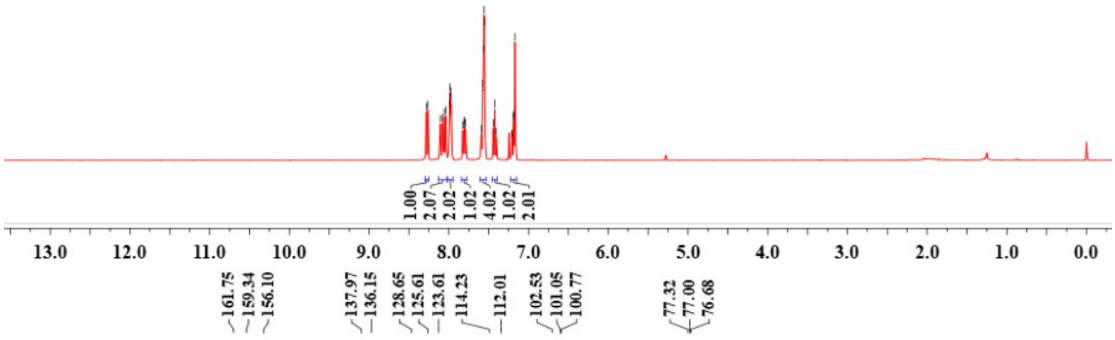
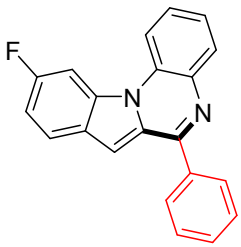
119.33
119.34
119.35
119.36
119.38
119.39

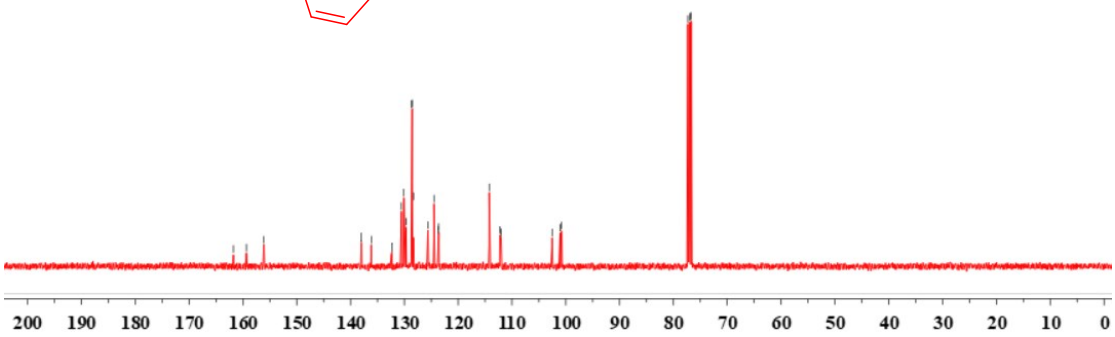

F
N
N
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190

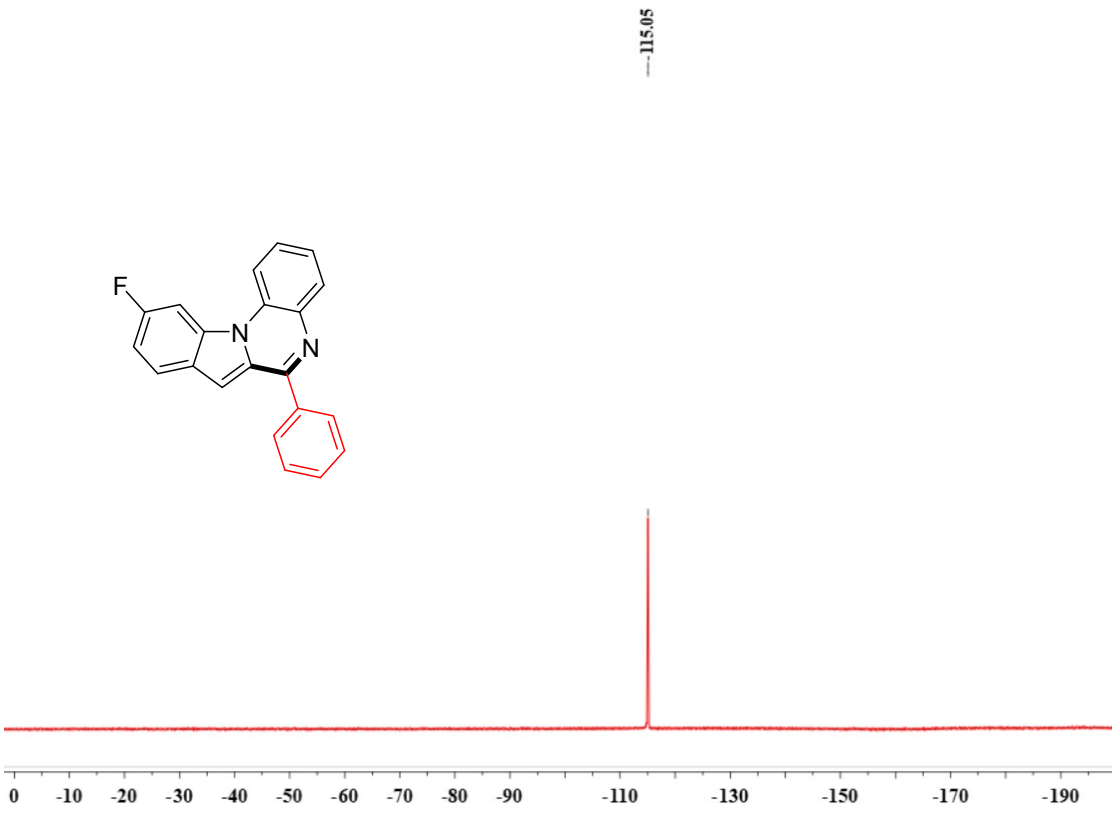
10-fluoro-6-phenylindolo[1,2-*a*]quinoxaline (3al)



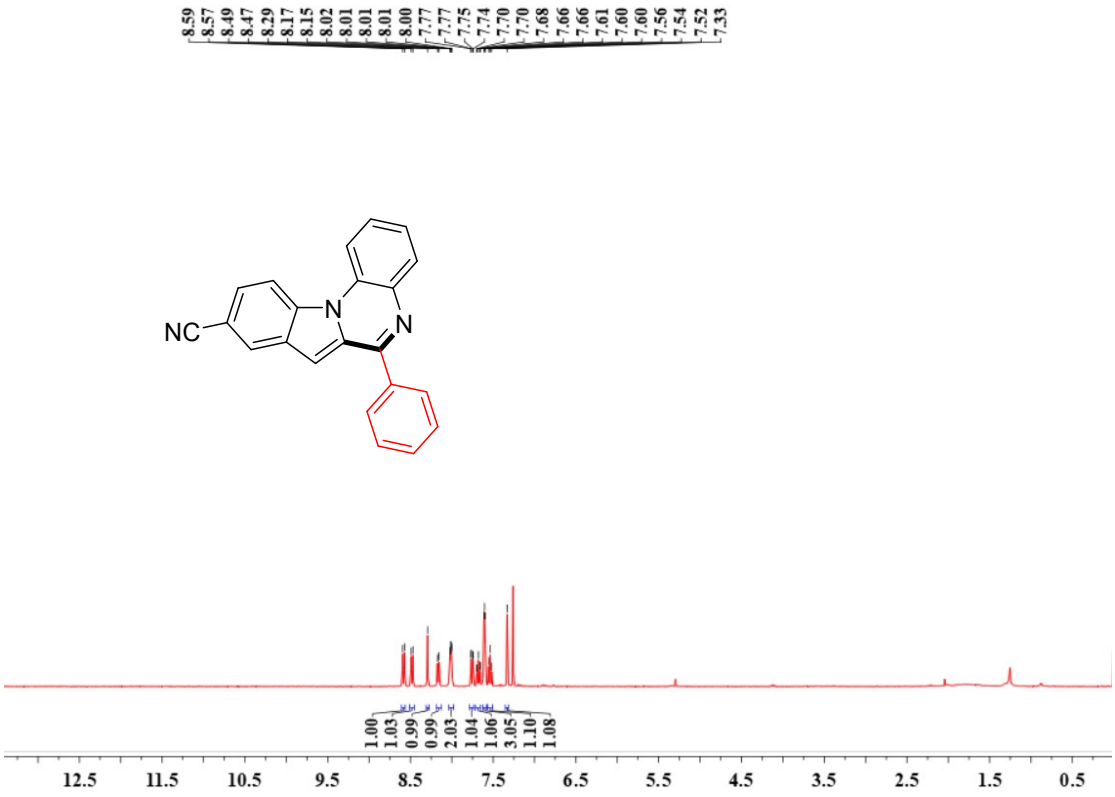


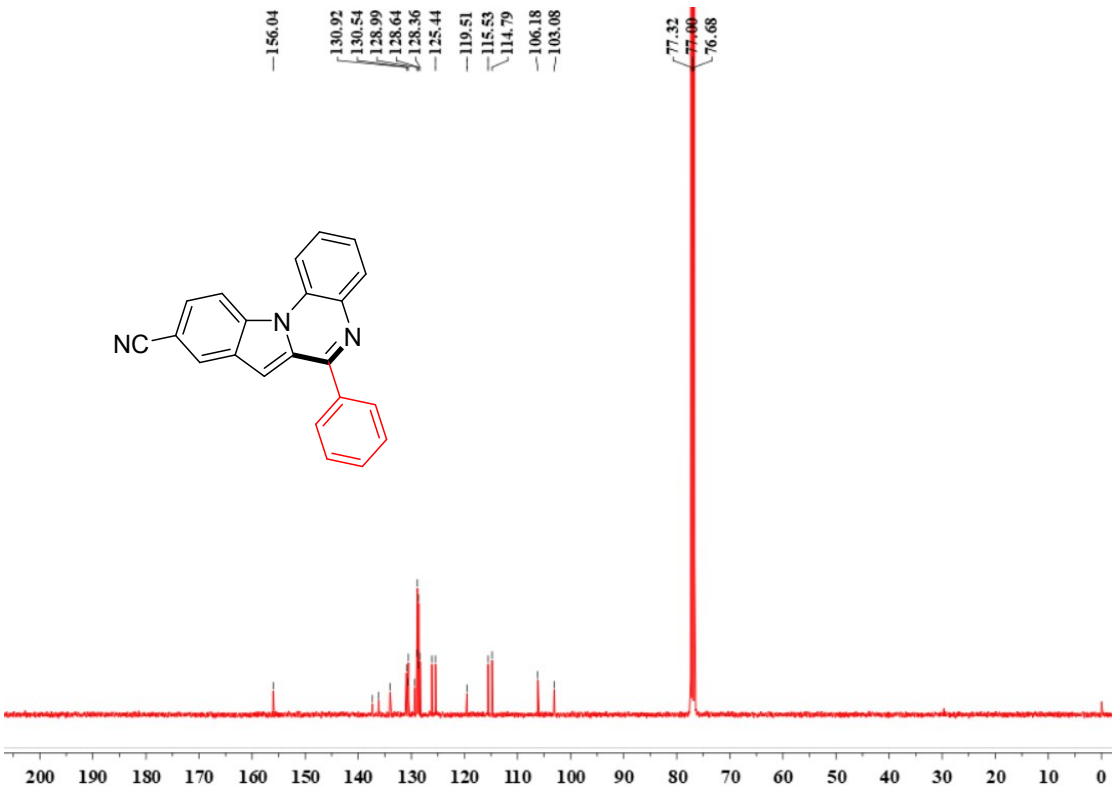




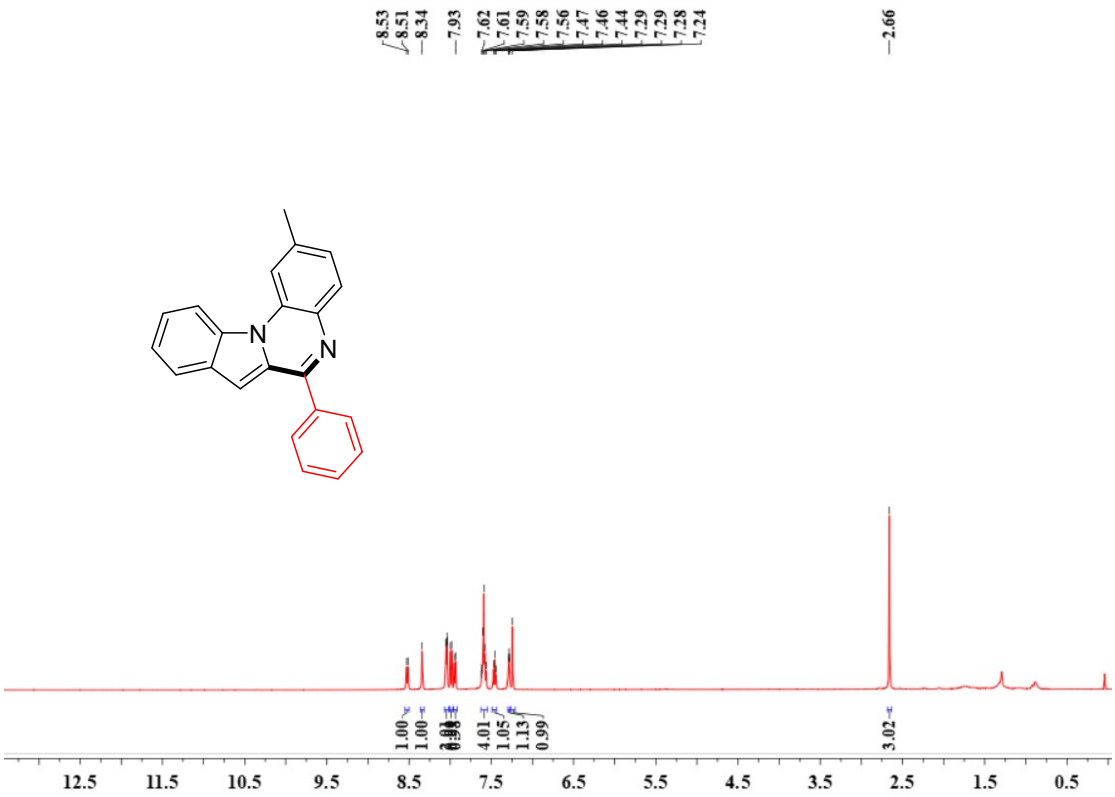


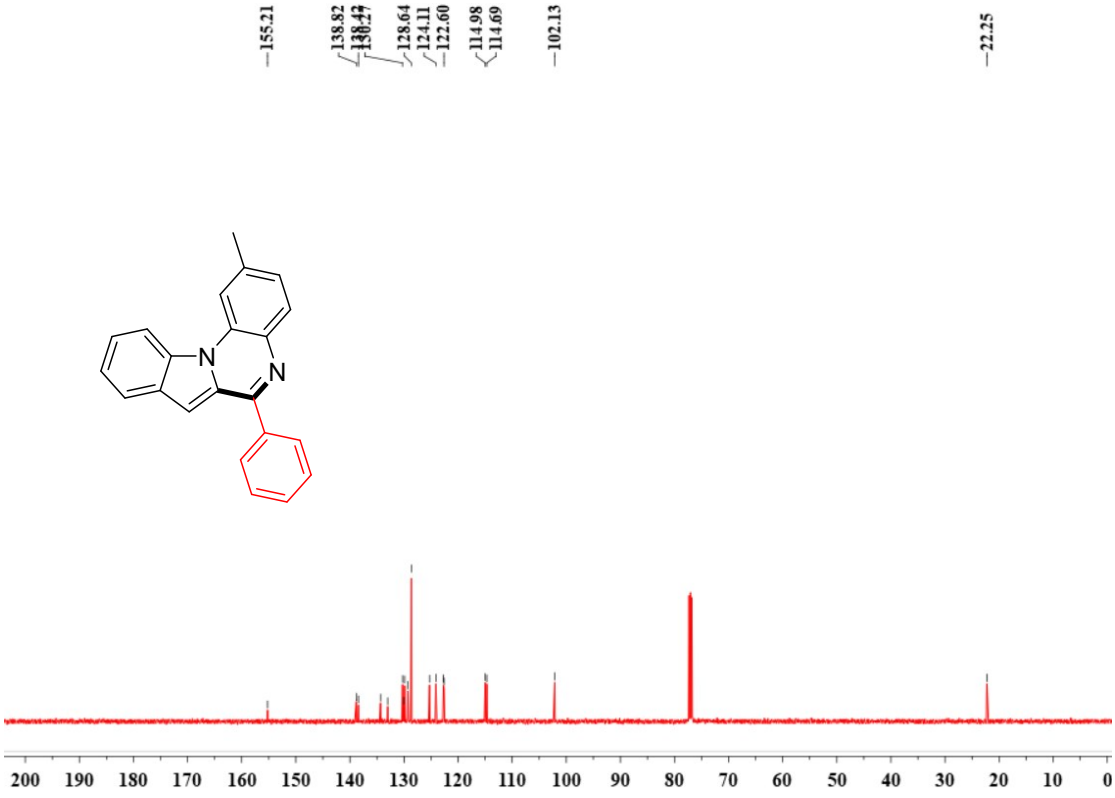
6-phenylindolo[1,2-*a*]quinoxaline-9-carbonitrile (3am)



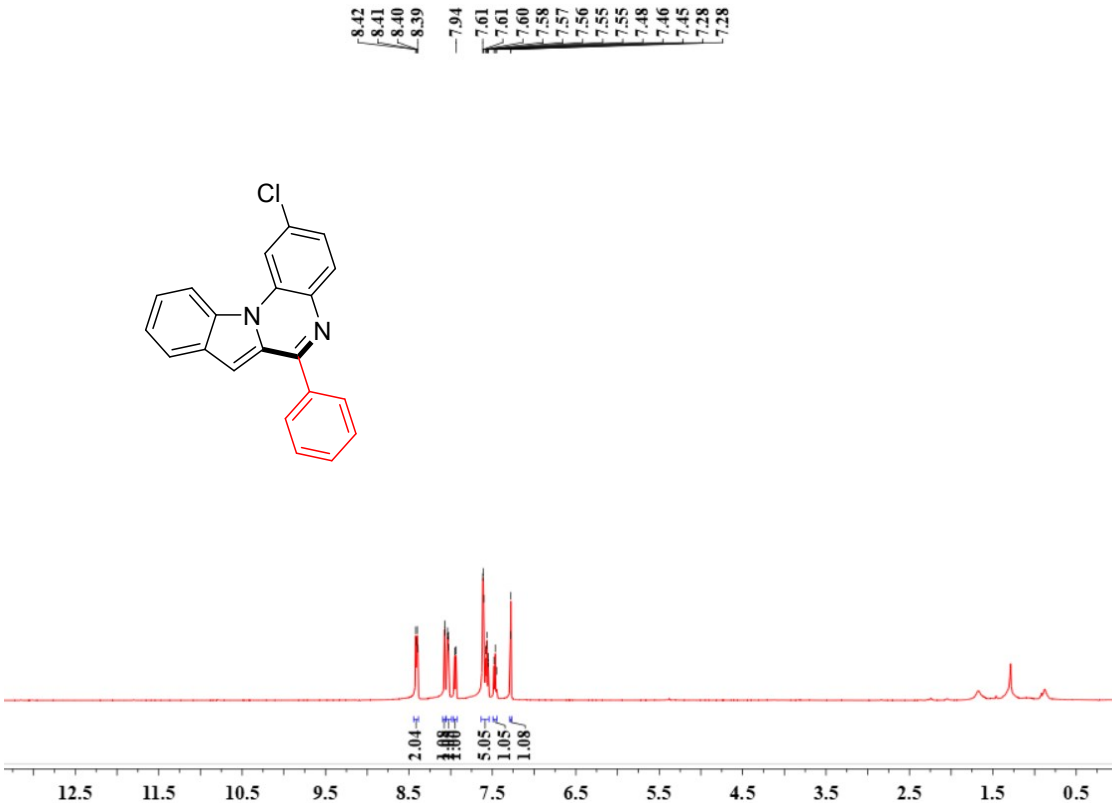


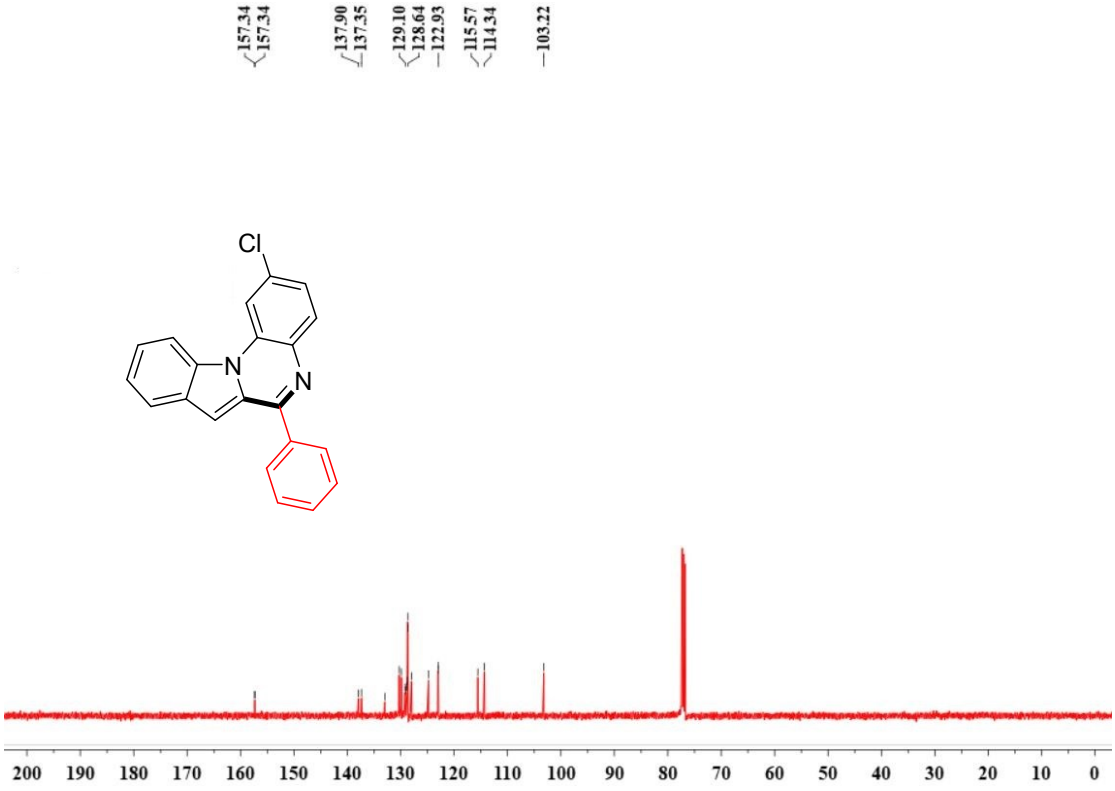
2-methyl-6-phenylindolo[1,2-*a*]quinoxaline (3an)



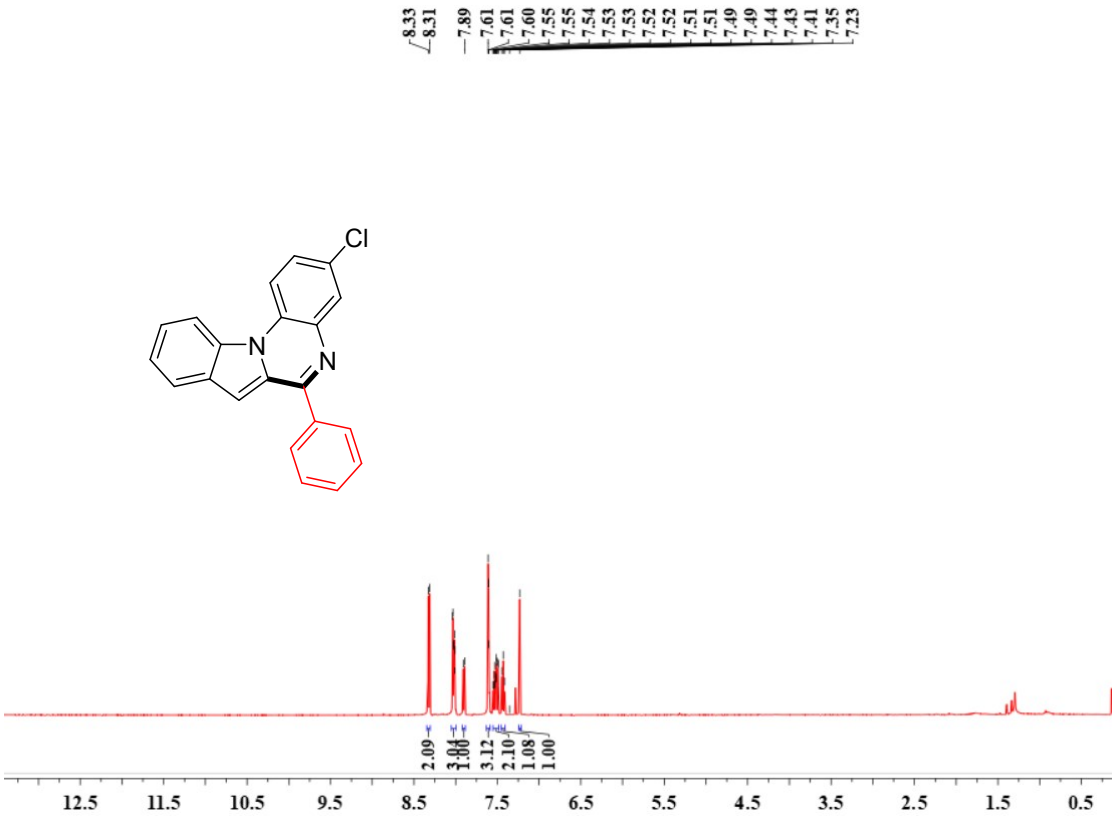


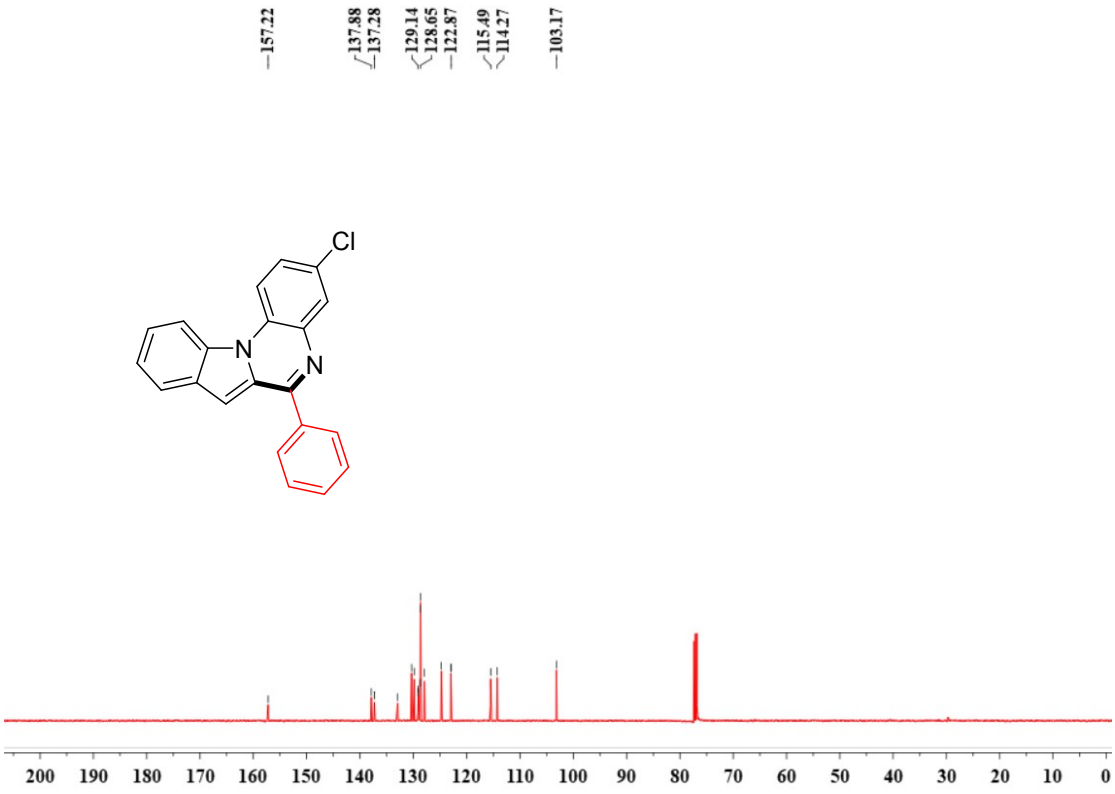
2-chloro-6-phenylindolo[1,2-*a*]quinoxaline (3ao)



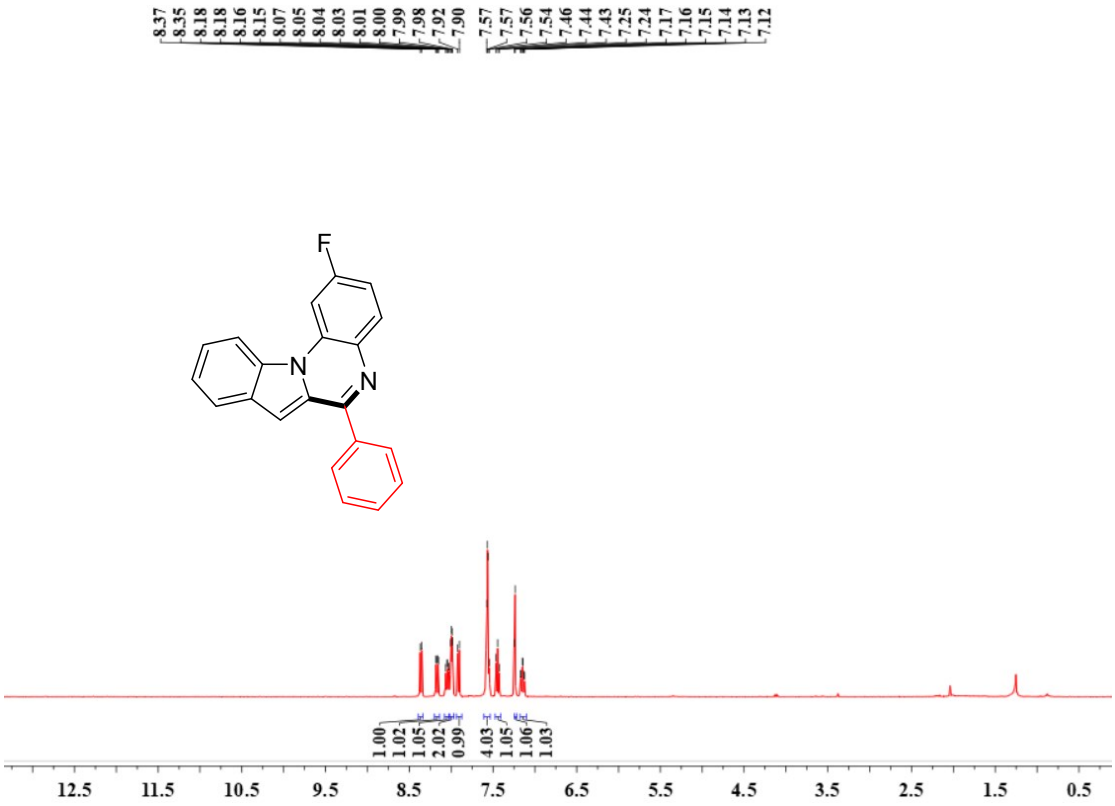


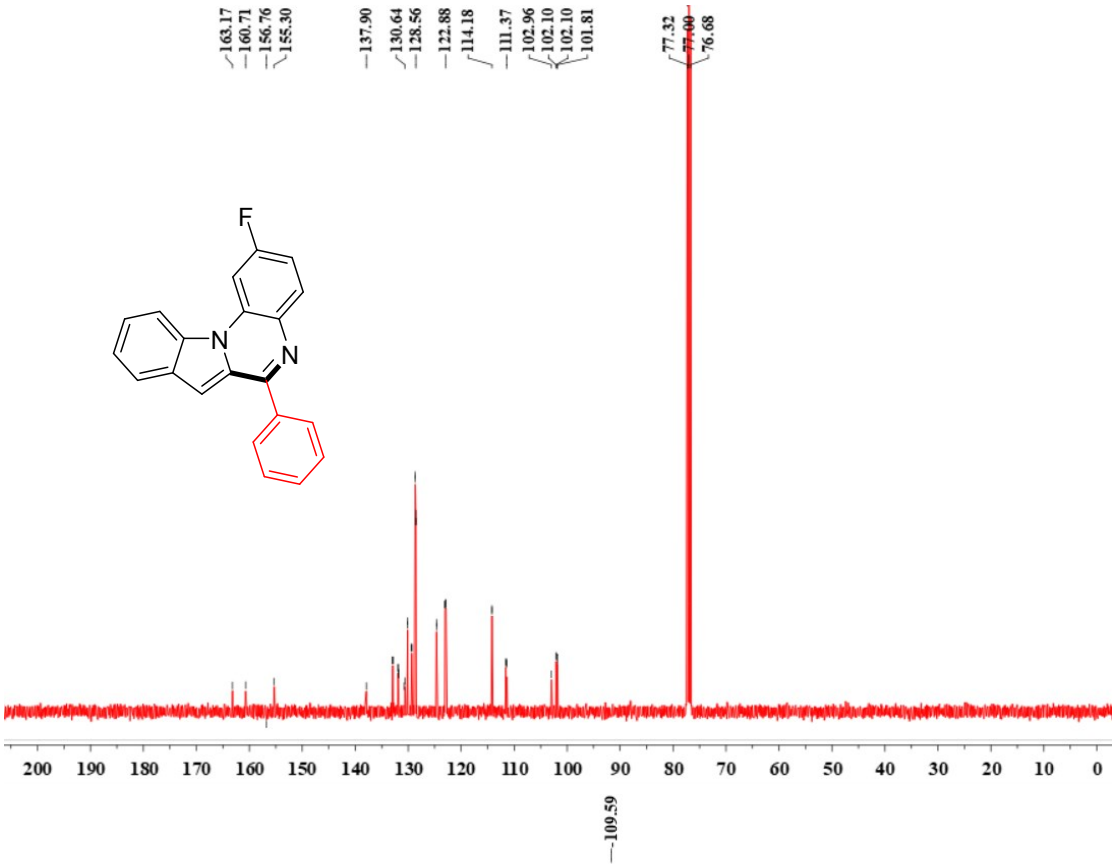
3-chloro-6-phenylindolo[1,2-*a*]quinoxaline (3ap)





2-fluoro-6-phenylindolo[1,2-*a*]quinoxaline (3aq)

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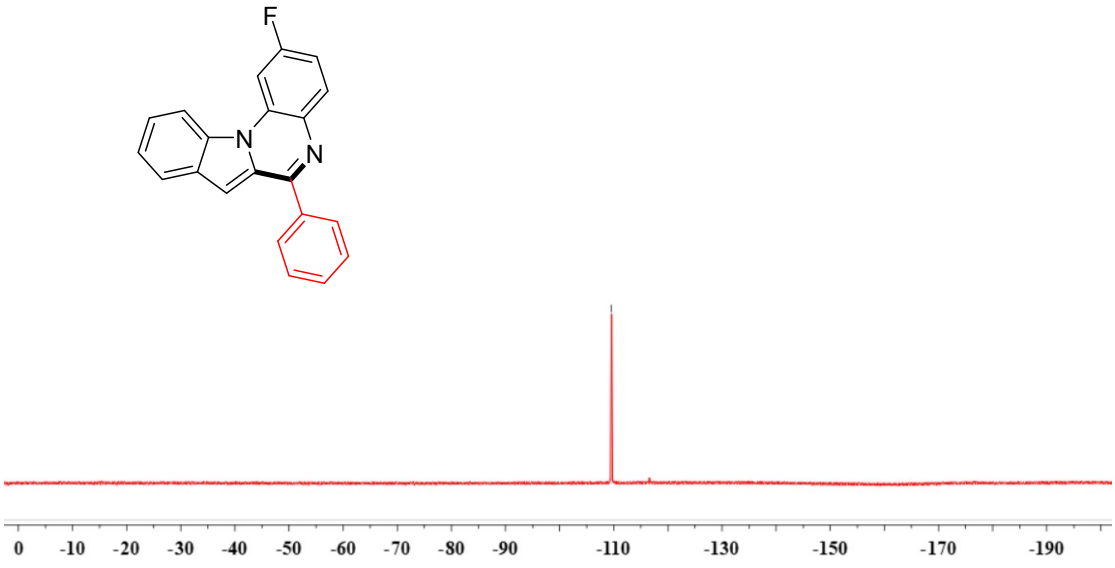
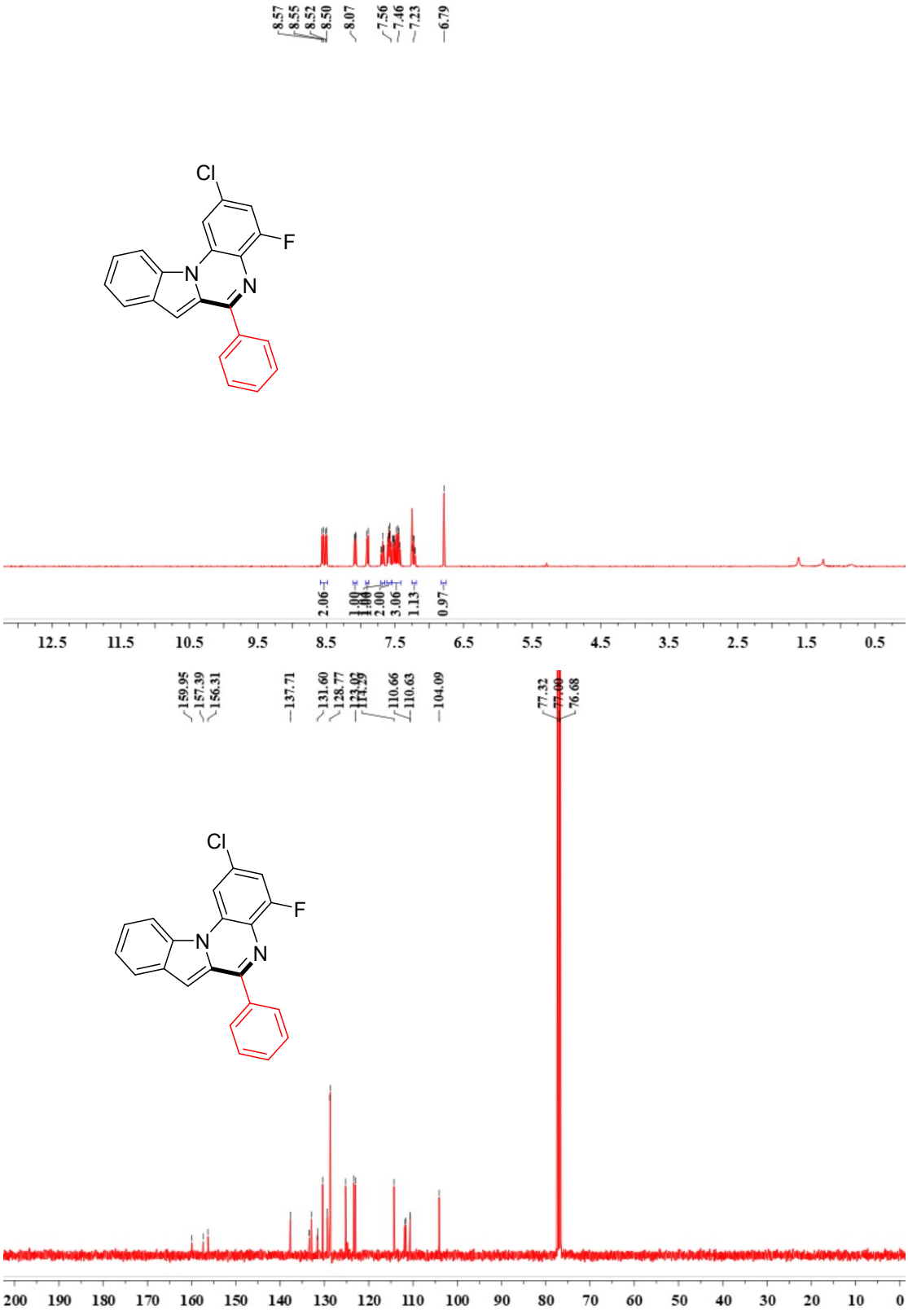
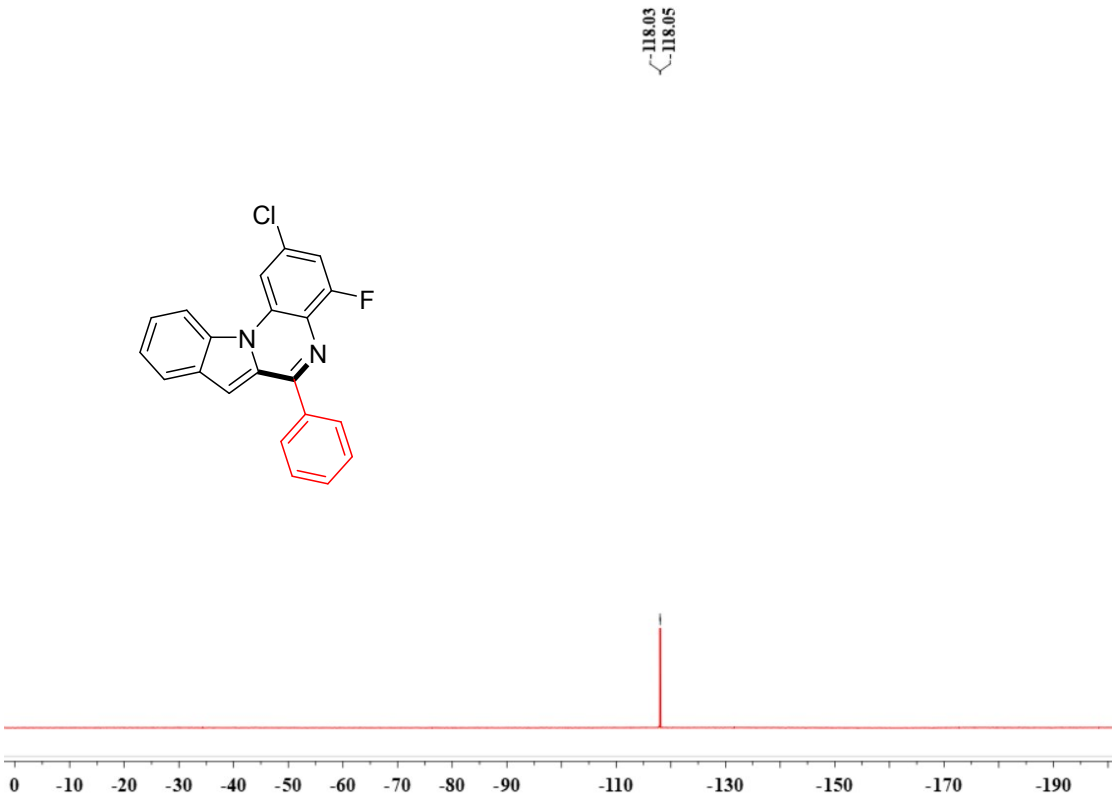
130.64
128.56
122.88
114.18
111.37
102.96
102.10
102.10
101.81
77.32
77.00
76.68
F
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
109.59

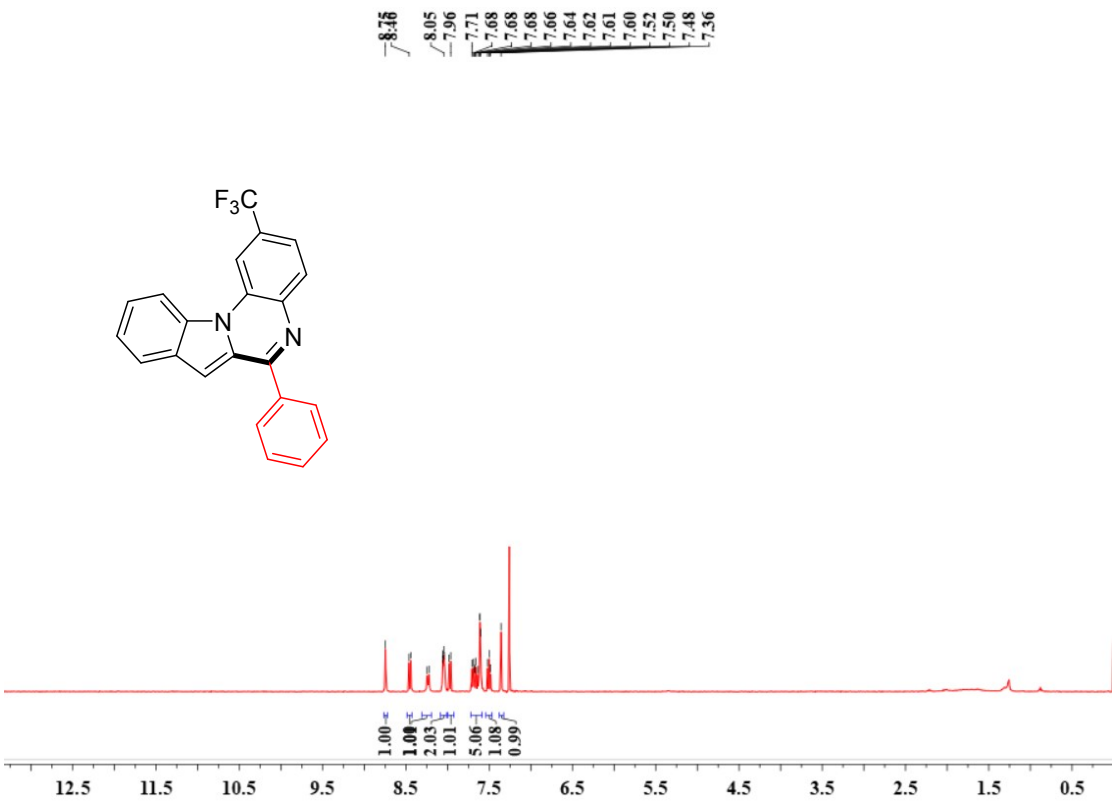

F
N
N
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190

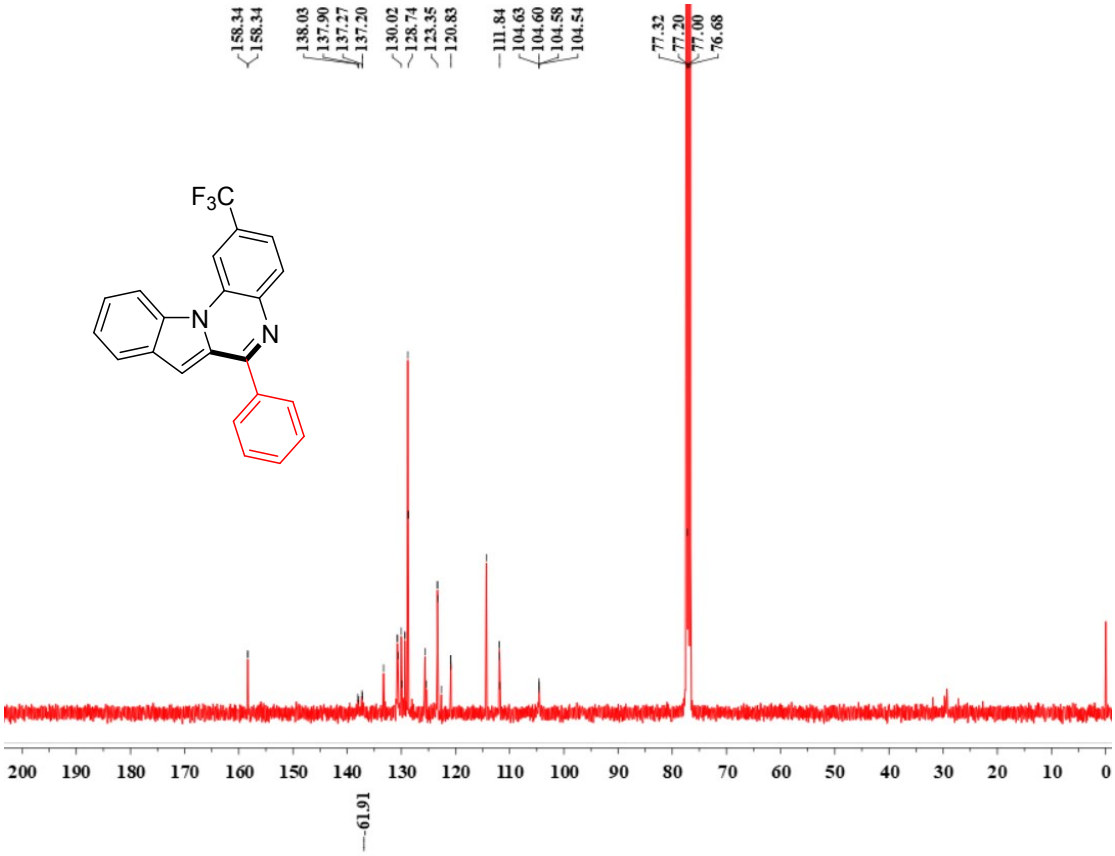
2-chloro-4-fluoro-6-phenylindolo[1,2-*a*]quinoxaline (3ar)





6-phenyl-2-(trifluoromethyl)indolo[1,2-*a*]quinoxaline (3as)

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128.74
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120.83
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104.63
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104.58
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76.68
F3C
N
N
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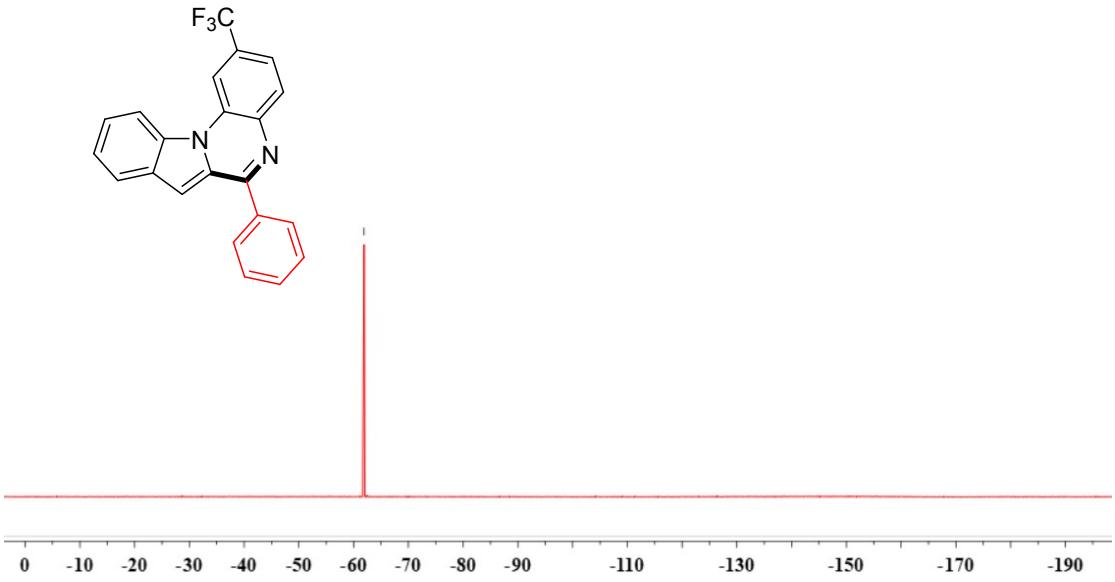
-61.91
F3C
N
N
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190