Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Unified Approach to benzo[*c*]phenanthridines via Cascade Dual Annulation/Formylation of 2-Alkynyl/alkenylbenzonitriles

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X-Ray Crystallographic Studies

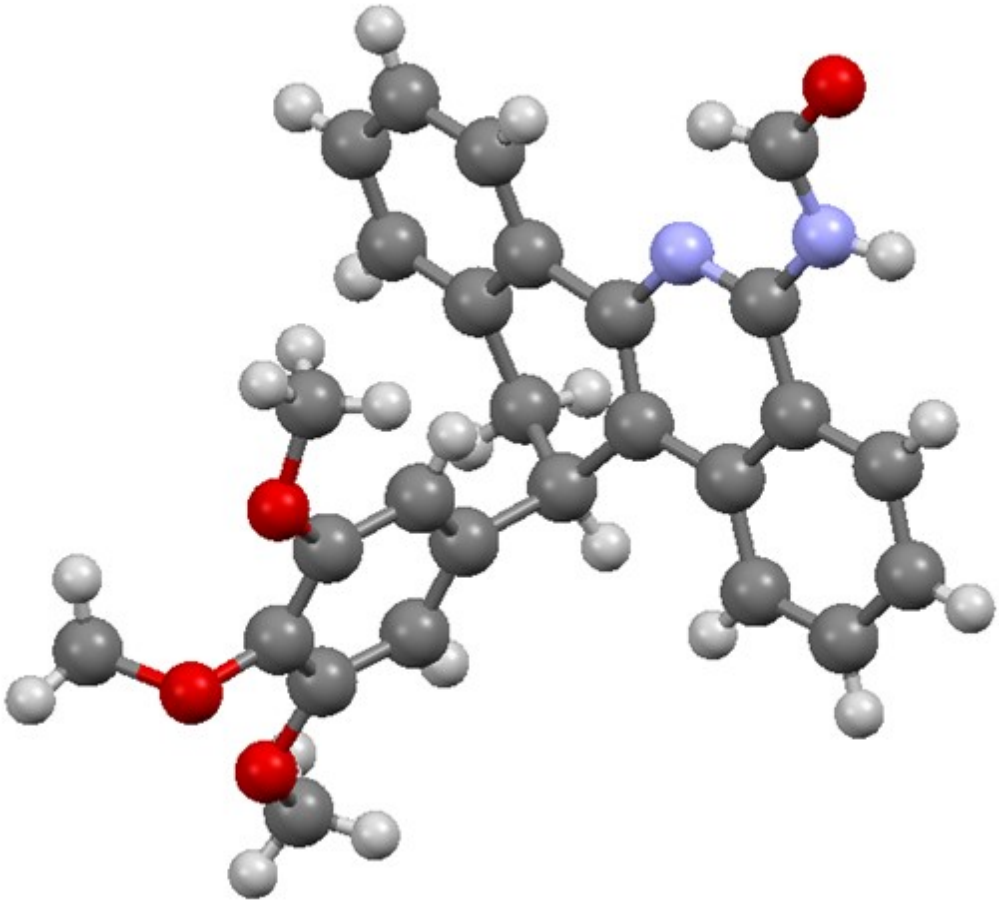


Figure I. Crystal structure of compound **10b.** CCDC No. 2067325

General Experimental Procedure

General Method. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and 19F NMR (376 MHz) spectra were recorded in $CDCl_3$/DMSO-d_6. Chemical shifts for protons and carbons are reported in ppm from tetramethylsilane and are referenced to the carbon resonance of the solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet), coupling constants in Hertz and integration. High-resolution mass spectra were recorded on electrospray mass spectrometer (ESI-TOF). Crystal structure analysis was accomplished on single needles X-ray diffractometer. TLC analysis was performed on commercially prepared 60 F_{254} silica gel plates and visualized by UV irradiation. All purchased chemicals were used as received. All melting points are uncorrected.

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. HPLC grade ACN, THF, DMF, DMSO, MeOH, DMPU, 1,4-dioxane, hexanes, ethyl acetate,

and CH_2Cl_2 were purchased from Merck Chemical Co. Palladium(II) chloride, PPh_3, alkynes, 2-bromobenzonitrile, 2-chloronicotinonitrile, 3-methylthiophene-2-carbonitrile and 2-methylbenzonitrile derivatives were purchased from Aldrich Chemical Co., Inc.

General procedure for the preparation of *o*–alkynylbenzonitriles (1)

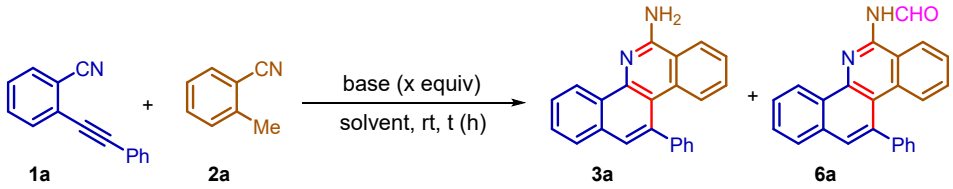
To probe the viability of the designed tandem strategy, 2–alkynylbenzonitriles **1a-m** was readily prepared by standard Sonogashira cross–coupling[1] reaction of commercially available 2–halobenzonitriles with terminal alkynes. This coupling procedure has readily accommodated a large variety of functional groups and provided the coupling products in good to excellent yields. The structure and purity of starting materials were confirmed by comparison of their physical and spectral data (^{1}H NMR and ^{13}C NMR).[1,2]

Standardization of reaction conditions

To determine the optimal reaction condition, we chose 2-(phenylethynyl)benzonitrile **1a** and 2-methylbenzonitrile **2a** as a model substrate. Having successful results with KOH-DMSO system,[11] we envisioned that reaction of **1a** with **2a** using 1.0 equiv of KOH in DMSO could yield the desired product, however, there was no reaction (Table 1, entry 1). The use of K^{t}BuO instead of KOH was also not successful to proceed with the reaction (entry 2). Switching the solvent from DMSO to DMF gives the only trace of product 11-phenylbenzo[*c*]phenanthridin-6-amine **3a** (entry 3). Increasing loading of K^{t}BuO to 3.0 equiv able to give only 10% yield of **3a** only (entry 4-5). Further increasing the loading of K^{t}BuO to 6.0 equiv also not led to complete consumption of starting material **1a** and enhance the yield of **3a** only up to 16% yield along with a trace of product *N*-(11-phenylbenzo[*c*]phenanthridin-6-yl)formamide **6a** (entry 6). Running the reactions in other solvents such as DMA, DCE and toluene was completely unfavorable for this reaction and led to no reaction (entry 7-9). Surprisingly, conducting the reaction in THF resulted in the formation of 3-(*o*-tolyl)isoquinolin-1-amine 12 in 85% yield by self-condensation of **2a** with complete recovery of **1a** (entry 10 and Scheme 5). To our delight conducting the reaction in *N,N*′-Dimethylpropyleneurea (DMPU) affords the desired product **3a** in 88% yield only in 5 min. (entry 11). Increasing the loading of K^{t}BuO to 4.0 equiv does not have much effect on yield (entry 12) while decreasing the loading of K^{t}BuO to 1.0 equiv decreases the yield of 3a with the recovery of **1a** (entry 13-14). After having an optimal reaction condition for product **3a** (entry 11) and intrigued by the formation of **6a** in the case of DMF (entry 6), we desire to optimize for product **6a** which is expected to form *via* in-situ formylation of product **3a**. We

anticipated that the addition of DMF as a co-solvent with DMPU could enhance the yield of **6a**; however, increasing the ratio of DMF alone did not have much effect on yield (entry 15-17). Interestingly, increasing the loading of K^{t}BuO to 6.0 equiv furnished the desired product **6a** selectively in 82% yield (entry 18). Further, increasing or decreasing the loading of K^{t}BuO has a deleterious effect on the yield of **6a** (entry 19-20).

Table S1. Optimization of reaction conditions

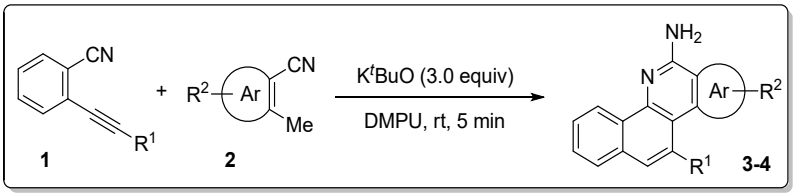


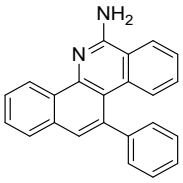
Entry	solvent	base (equiv)	t (h/min)	yield (%)[b] **3a/6a**
1	DMSO	KOH (1.0)	24 h	NR
2	DMSO	K^{t}BuO (1.0)	24 h	NR
3	DMF	K^{t}BuO (1.0)	24 h	trace
4	DMF	K^{t}BuO (2.0)	24 h	trace
5	DMF	K^{t}BuO (3.0)	24 h	10/00[c]
6	DMF	K^{t}BuO (6.0)	24 h	16/trace[c]
7	DMA	K^{t}BuO (3.0)	24 h	NR
8	DCE	K^{t}BuO (3.0)	24 h	NR
9	toluene	K^{t}BuO (3.0)	24 h	NR
10	THF	K^{t}BuO (3.0)	24 h	00
11	**DMPU**	**K^{t}BuO (3.0)**	**5 min**	**88/00**
12	DMPU	K^{t}BuO (4.0)	5 min	86/00
13	DMPU	K^{t}BuO (2.0)	5 min	56/00[c,d]
14	DMPU	K^{t}BuO (1.0)	5 min	24/00[c,d]
15	DMPU/DMF (1:1)	K^{t}BuO (3.0)	24 h	82/trace
16	DMPU/DMF (1:2)	K^{t}BuO (3.0)	24 h	80/12
17	DMPU/DMF (1:4)	K^{t}BuO (3.0)	24 h	78/18
18	**DMPU/DMF (1:4)**	**K^{t}BuO (6.0)**	**16 h**	**00/82**
19	DMPU/DMF (1:4)	K^{t}BuO (7.0)	16 h	00/79
20	DMPU/DMF (1:4)	K^{t}BuO (5.0)	16 h	12/78

[a]Reactions were performed using 0.5 mmol of **1a**, 1.0 equiv of **2a** and base in 2.0 mL of solvent at rt. [b]Isolated yield. [c]Incomplete consumption of starting material. [d]results were same even after 24 h.

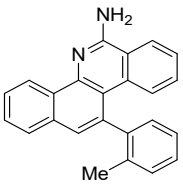
General procedure for the synthesis of functionalized 11-aryl/alkylbenzo[*c*]phenanthridin-6-amine (3a-m) and 4-arylbenzo[*h*]thieno[3,2-c]quinolin-11-amine (4a-d)

In an oven-dried 10 mL round bottom flask, a solution of 2-alkynylbenzonitrile **1** (0.5 mmol), 2-methylbenzonitrile **2a/2b** (1.0 equiv) and K^{t}BuO (3.0 equiv) in 2 mL of DMPU was stirred at rt for 5 minutes. Progression of the reaction was monitored by TLC analysis; after complete consumption of starting material, the reaction was diluted with ethyl acetate (50 mL) and water (50 mL). The layers were separated, and the organic layer was washed with aqueous saturated brine solution and dried over Na_2SO_4. Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel (100−200) (hexane:ethyl acetate; 85/15). The structure and purity of products were confirmed by comparison of their physical and spectral data (^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS).



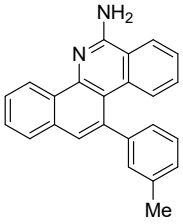


11-Phenylbenzo[*c*]phenanthridin-6-amine (3a). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3a** as white solid (140.8 mg, 88%): mp 165–166 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.67-7.74 (m, 4H), 7.50-7.54 (m, 5H), 7.43 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 5.51 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 144.9, 142.7, 137.6, 134.7, 132.8, 130.3, 129.1, 128.9, 128.8, 128.1, 127.5, 127.4, 127.2, 126.8, 126.1, 125.0, 122.9, 118.9, 116.3; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{23}H_{17}N_2$ 321.1386, found 321.1371.

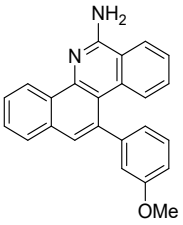


11-(*o*-Tolyl)benzo[*c*]phenanthridin-6-amine (3b). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3b** as white solid

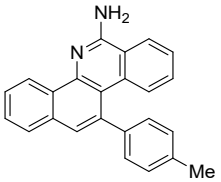
(145.3 mg, 87%): mp 168–169 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 7.5 Hz, 1H), 7.71-7.64 (m, 3H), 7.55 (s, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.45-7.40 (m, 3H), 7.37-7.31 (m, 2H), 5.43 (s, 2H), 2.0 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 144.5, 142.2, 136.9, 136.2, 135.2, 132.9, 130.4, 129.7, 129.4, 127.6, 127.4, 127.1, 126.6, 126.3, 126.2, 126.1, 125.9, 125.1, 123.0, 118.6, 116.6, 20.1; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{24}H_{19}N_2$ 335.1543, found 335.1530.



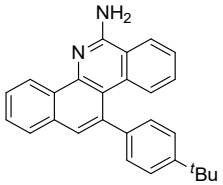
11-(*m*-Tolyl)benzo[*c*]phenanthridin-6-amine (3c). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3c** as white solid (143.6 mg, 86%): mp 170–171 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.87-7.90 (m, 2H), 7.77 (dd, J = 5.4, 3.1 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.63-7.69 (m, 1H), 7.61 (s, 1H), 7.48-7.52 (m, 1H), 7.32-7.40 (m, 2H), 7.29 (d, J = 7.3 Hz, 2H), 5.45 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 144.8, 138.5, 137.6, 134.8, 134.3, 132.7, 129.6, 128.74, 128.72, 128.1, 127.8, 127.4, 127.2, 126.7, 126.2, 126.0, 125.9, 124.9, 123.6, 122.8, 118.9, 116.3, 21.6; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{24}H_{19}N_2$ 335.1543, found 335.1530.



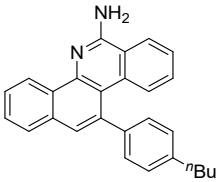
11-(3-Methoxyphenyl)benzo[*c*]phenanthridin-6-amine (3d). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3d** as white solid (157.5 mg, 90%): mp 177–178 °C: ^{1}H NMR (400 MHz $CDCl_3$) δ 9.27 (d, J = 7.8 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 7.3 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.68-7.63 (m, 3H), 7.49 (t, J = 7.5 Hz, 1H), 7.41 (t, J = 8.1 Hz, 1H), 7.34 (t, J = 7.9 Hz, 1H), 7.09-7.01 (m, 3H), 5.46 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 154.5, 146.2, 142.5, 137.3, 134.7, 132.7, 130.3, 129.9, 128.8, 128.1, 127.5, 127.3, 126.6, 126.1, 126.0, 124.9, 122.8, 121.7, 118.9, 116.2, 114.4, 112.9, 55.4; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{24}H_{19}N_2O$ 351.1492, found 351.1488.



11-(*p*-Tolyl)benzo[*c*]phenanthridin-6-amine (3e). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3e** as pale yellow needles (141.9 mg, 85%): mp 169-170 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.82-7.85 (m, 2H), 7.70-7.72 (m, 2H), 7.59-7.65 (m, 1H), 7.57 (s, 1H), 7.45 (t, J = 7.3 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.26-7.31 (m, 2H), 5.49 (s, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 141.9, 137.5, 136.7, 134.9, 134.3, 132.8, 129.4, 128.9, 128.7, 128.1, 127.4, 127.2, 126.8, 126.0, 125.9, 124.9, 123.6, 122.8, 118.9, 116.4, 21.3; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{24}H_{19}N_2$ 335.1543, found 335.1530.

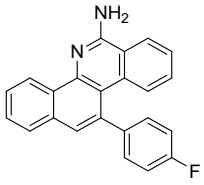


11-(4-(*tert*-Butyl)phenyl)benzo[*c*]phenanthridin-6-amine (3f). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3f** as pale yellow needles (161.7 mg, 86%): mp 165-166 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, J = 7.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.87-7.90 (m, 1H), 7.62-7.71 (m, 4H), 7.50 (dd, J = 16.4, 7.9 Hz, 3H), 7.43 (d, J = 8.3 Hz, 2H), 7.28-7.32 (m, 1H), 5.43 (s, 2H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 150.1, 141.8, 137.4, 134.8, 134.3, 132.8, 130.2, 128.6, 128.1, 127.4, 127.2, 126.7, 126.0, 125.8, 125.7, 124.9, 123.6, 122.7, 118.9, 116.5, 34.7, 31.5; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{27}H_{25}N_2$ 377.2012, found 377.1992.

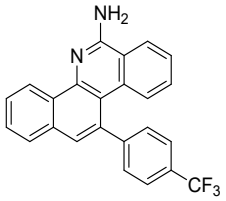


11-(4-Butylphenyl)benzo[*c*]phenanthridin-6-amine (3g). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3g** as pale yellow needles (167.3 mg, 89%): mp 163-164 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.89 (q, J = 2.8 Hz, 2H), 7.78 (q, J = 2.8 Hz, 1H), 7.62-7.70 (m, 3H), 7.49 (t, J = 7.4 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.47 (s, 2H), 2.76 (t, J = 7.8 Hz, 2H), 1.70-1.78 (m, 2H), 1.47 (td, J = 14.7, 7.3 Hz, 2H), 1.02 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 142.0, 141.8, 137.5, 134.8, 134.3, 132.8, 128.93, 128.88, 128.7, 128.1, 127.4, 127.2, 126.7, 126.0, 125.9, 124.9, 123.6, 122.8,

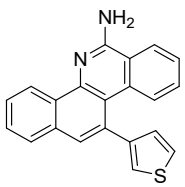
118.9, 116.4, 35.4, 33.7, 22.4, 14.0; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{27}H_{25}N_2$ 377.2012, found 377.1992.



11-(4-Fluorophenyl)benzo[*c*]phenanthridin-6-amine (3h). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3h** as pale yellow needles (142.0 mg, 84%): mp 113-114 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 6.5 Hz, 1H), 7.67 (dd, J = 15.4, 6.9 Hz, 3H), 7.59 (s, 1H), 7.44-7.52 (m, 3H), 7.35 (t, J = 8.3 Hz, 1H), 7.20 (t, J = 8.8 Hz, 2H), 5.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, J = 255.8 Hz, 1C), 154.3, 142.5, 140.8 (d, J = 3.6 Hz, 1C), 136.4, 134.5, 134.2, 132.6, 130.6 (d, J = 8.0 Hz, 1C), 130.2, 128.8, 127.8, 127.5, 127.2, 126.9, 126.1, 124.9, 123.7, 122.9, 118.9, 116.1, 115.8 (d, J = 21.1 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.3 (s); HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{23}H_{16}FN_2$ 339.1292, found 339.1288.

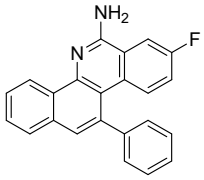


11-(4-(Trifluoromethyl)phenyl)benzo[*c*]phenanthridin-6-amine (3i). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3i** as off-white solid (157.1 mg, 81%): mp 158-159 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 7.3 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.70-7.66 (m, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 9.0 Hz, 2H), 7.52 (t, J = 7.1 Hz, 1H), 7.35 (t, J = 8.3 Hz, 1H), 5.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 148.5, 142.7, 135.9, 134.3, 134.3, 132.6, 130.4, 129.4, 129.0, 127.8, 127.7, 127.4, 127.1, 126.4, 126.2, 125.8 (q, J = 3.4 Hz, 1C), 125.0, 123.7, 123.0, 119.0, 115.7; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{24}H_{16}F_3N_2$ 389.1260, found 389.1245.

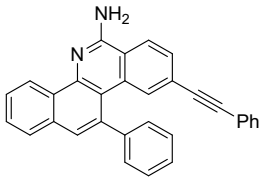


11-(Thiophen-3-yl)benzo[*c*]phenanthridin-6-amine (3j). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3j** as white solid

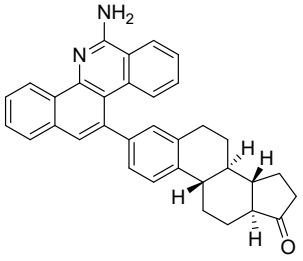
(141.8 mg, 87%): mp 178–179 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, J = 7.7 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.82-7.87 (m, 2H), 7.71-7.75 (m, 2H), 7.62 (dd, J = 14.9, 7.2 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.38 (d, J = 20.2 Hz, 2H), 7.03 (d, J = 3.7 Hz, 1H), 5.50 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 145.2, 142.3, 134.8, 132.7, 132.0, 130.3, 129.4, 129.2, 127.54, 127.49, 127.3, 126.8, 126.3, 126.1, 124.8, 123.8, 123.0, 121.7, 118.9, 116.7; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{21}H_{15}N_2S$ 327.0950, found 327.0935.



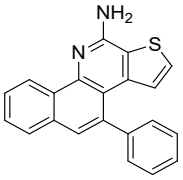
8-Fluoro-11-phenylbenzo[*c*]phenanthridin-6-amine (3k). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3k** as white solid (131.8 mg, 78%): mp 148–149 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (dd, J = 11.3, 2.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.84 (dd, J = 8.8, 5.8 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.59 (s, 1H), 7.52-7.49 (m, 6H), 7.39 (td, J = 8.5, 2.8 Hz, 1H), 7.29-7.33 (m, 1H), 5.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (d, J = 244.7 Hz, 1C), 154.5, 144.6, 141.8, 136.7, 134.6, 131.5 (d, J = 8.7 Hz, 1C), 129.5 (d, J = 9.4 Hz, 1C), 129.1, 128.9, 128.1, 127.2, 126.3 (d, J = 16.0 Hz, 1C), 122.9, 119.1, 117.1 (d, J = 25.5 Hz, 1C), 116.7, 109.2 (d, J = 23.3 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –114.0 (s);HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{23}H_{16}FN_2$ 339.1292, found 339.1288.



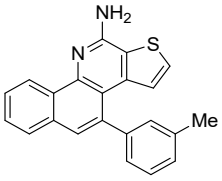
8-Fluoro-11-phenylbenzo[*c*]phenanthridin-6-amine (3l). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3l** as white solid (128.1 mg, 61%): mp 172–173 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (d, J = 8.8 Hz, 1H), 8.03 (s, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.62-7.59 (m, 3H), 7.54 (s, 1H), 7.45 (d, J = 11.3 Hz, 6H), 7.36 (d, J = 7.0 Hz, 3H), 7.27 (d, J = 7.8 Hz, 1H), 5.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 144.6, 142.4, 138.3, 134.6, 132.4, 131.7, 130.7, 129.7, 129.0, 128.95, 128.86, 128.6, 128.4, 128.3, 128.1, 127.3, 126.29, 126.27, 125.1, 123.4, 122.8, 122.0, 119.0, 116.9, 90.2, 90.1; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{31}H_{21}N_2$ 421.1699, found 421.1692.



(8S,9S,13S,14S)-3-(6-Aminobenzo[*c*]phenanthridin-11-yl)-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (3m). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3m** as white solid (103.0 mg, 43%): mp 182–183 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.81-7.89 (m, 2H), 7.61-7.68 (m, 3H), 7.51 (t, J = 7.1 Hz, 2H), 7.35-7.40 (m, 2H), 7.24 (d, J = 9.3 Hz, 1H), 5.57 (s, 2H), 2.98 (s, 2H), 2.51-2.60 (m, 3H), 2.03-2.25 (m, 5H), 1.54-1.71 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 221.1, 154.7, 142.2, 138.7, 137.4, 137.2, 137.1, 135.0, 134.9, 132.9, 129.3, 129.0, 128.2, 127.5, 127.3, 127.1, 126.6, 126.2, 126.1, 125.7, 124.9, 122.9, 118.9, 116.3, 50.9, 48.0, 44.4, 38.3, 36.0, 31.9, 29.4, 26.7, 25.5, 21.7; HRMS (ESI-TOF) $[M]^+$ Calcd for $C_{34}H_{30}N_2O$ 482.2353, found 482.2352.

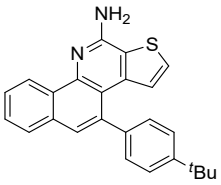


4-Phenylbenzo[*h*]thieno[2,3-*c*]quinolin-11-amine (4a). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **4a** as white solid (150.0 mg, 92%): mp 176–177 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 6.4 Hz, 3H), 7.50 – 7.37 (m, 7H), 7.29 – 7.22 (m, 1H), 5.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 144.8, 141.3, 138.7, 137.1, 136.9, 134.9, 129.25, 129.20, 128.9, 128.3, 127.9, 127.1, 125.9, 124.5, 123.1, 122.3, 119.2, 115.1; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{21}H_{15}N_2S$ 327.0950, found 327.0935.

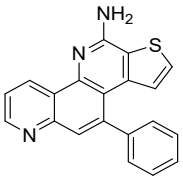


4-(*m*-Tolyl)benzo[*h*]thieno[2,3-*c*]quinolin-11-amine (4b). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **4b** as white solid (153.0 mg, 90%): mp 179–180 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.57 (d, J = 4.8 Hz, 2H), 7.40-7.46 (m, 2H), 7.34 (t, J = 7.5 Hz, 1H), 7.20-7.30 (m, 4H), 5.49 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1,

144.9, 138.8, 138.7, 137.2, 135.0, 129.9, 129.3, 128.8, 128.4, 128.0, 127.9, 126.3, 126.0, 124.5, 123.1, 122.3, 119.1, 115.1, 21.6; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{22}H_{17}N_2S$ 341.1107, found 341.1125.



4-(4-(*tert*-Butyl)phenyl)benzo[*h*]thieno[2,3-*c*]quinolin-11-amine (4c). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **4c** as white solid (168.1 mg, 88%): mp 179–180 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 1H), 7.60 (s, 1H), 7.57 (d, J = 5.5 Hz, 1H), 7.43-7.48 (m, 3H), 7.40 (d, J = 8.9 Hz, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.25 (s, 2H), 5.57 (s, 2H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 150.1, 144.9, 141.7, 138.9, 137.2, 129.3, 128.8, 128.3, 128.0, 126.0, 125.6, 124.5, 123.2, 122.5, 34.7, 31.6; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{25}H_{23}N_2S$ 383.1576, found 383.1558.

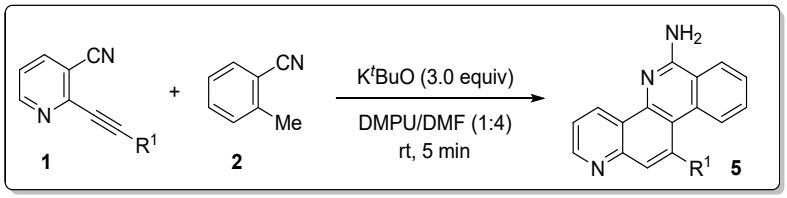


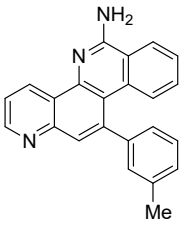
10-Phenylthieno[2,3-*c*][1,7]phenanthrolin-6-amine (4d). The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **4d** as white solid (119.3 mg, 73%): mp 192–193 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, J = 4.3, 1.6 Hz, 1H), 8.12 (dd, J = 8.2, 1.6 Hz, 1H), 7.64 (s, 1H), 7.62 (d, J = 5.4 Hz, 1H), 7.44 (d, J = 5.4 Hz, 2H), 7.37-7.38 (m, 4H), 7.31 (q, J = 4.2 Hz, 1H), 5.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 145.9, 140.1, 138.1, 132.7, 131.9, 130.8, 129.4, 129.0, 129.0, 128.9, 127.6, 125.8, 124.8, 123.1, 120.7, 113.6, 108.2; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{20}H_{14}N_3S$ 328.0903, found 328.0919.

General procedure for the synthesis of 11-aryl/alkylbenzo[*c*]phenanthrolin-6-amine (5a-d)

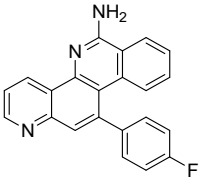
In an oven-dried 10 mL round bottom flask, a solution of 2-(arylethynyl)nicotinonitrile **1** (0.5 mmol), 2-methylbenzonitrile **2** (1.0 equiv) and K^{t}BuO (3.0 equiv) in 2 mL of DMF/DMPU (4:1) was stirred at rt for 5 minutes. Progression of the reaction was monitored by TLC analysis; after complete consumption of starting material, the reaction was diluted with ethyl acetate (50 mL) and water (50 mL). The layers were separated, and the organic layer was washed with aqueous

saturated brine solution and dried over Na_2SO_4. Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel (100−200) (hexane:ethyl acetate; 70/30). The structure and purity of products were confirmed by comparison of their physical and spectral data (^{1}H NMR, ^{13}C NMR, and HRMS). The structure and purity of products were confirmed by comparison of their physical and spectral data (^{1}H NMR, ^{13}C NMR, and HRMS).



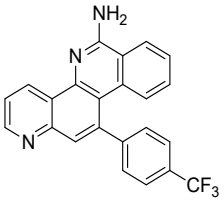


11-(*m*-Tolyl)benzo[*c*][1,7]phenanthrolin-6-amine (5a). The crude product was purified by column chromatography (hexane/EtOAc = 70/30) to afford **5a** as white solid (117.2 mg, 70%): mp 193–194 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, J = 8.3 Hz, 1H), 9.01 (d, J = 4.3 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.49-7.58 (m, 2H), 7.31-7.40 (m, 5H), 5.59 (s, 2H), 2.4l4 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 151.0, 147.9, 143.8, 141.6, 139.4, 138.7, 134.4, 133.5, 129.5, 129.1, 128.8, 128.20, 128.17, 127.2, 126.6, 126.0, 123.0, 120.9, 118.9, 116.5, 114.0, 21.6; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{23}H_{18}N_3$ 336.1495, found 336.1508.

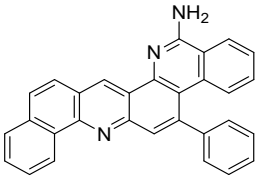


11-(4-Fluorophenyl)benzo[*c*][1,7]phenanthrolin-6-amine (5b). The crude product was purified by column chromatography (hexane/EtOAc = 70/30) to afford **5b** as white solid (115.3 mg, 68%): mp 190– 191 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (d, J = 8.5 Hz, 1H), 9.01 (s, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.84 (s, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.55 (dd, J = 14.3, 8.3 Hz, 2H), 7.44-7.48 (m, 2H), 7.37 (t, J = 7.8 Hz, 1H), 7.20 (t, J = 8.4 Hz, 2H), 5.62 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J = 246.6 Hz, 1C), 155.0, 151.1, 147.8, 140.2, 140.0 (d, J = 3.6 Hz, 1C), 134.3, 133.5, 130.5 (d, J = 7.9 Hz, 1C), 129.2, 127.8, 127.4, 126.7, 123.0, 121.1, 119.0, 116.3, 116.0 (d, J = 21.5 Hz); ^{19}F NMR (376 MHz,

$CDCl_3$) δ –114.6 (s); HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{22}H_{15}FN_3$ 340.1245, found 340.1231.



11-(4-(Trifluoromethyl)phenyl)benzo[*c*][1,7]phenanthrolin-6-amine (5c). The crude product was purified by column chromatography (hexane/EtOAc = 70/30) to afford **5c** as white solid (126.4 mg, 65%): mp 199–200 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (d, J = 8.3 Hz, 1H), 9.02 (s, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.85 (s, 1H), 7.77 (d, J = 7.8 Hz, 2H), 7.64 (d, J = 7.8 Hz, 2H), 7.55-7.60 (m, 3H), 7.37 (t, J = 7.6 Hz, 1H), 5.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 151.3, 147.9, 147.7, 142.5, 139.6, 134.0, 133.5, 129.8, (q, J = 3.7 Hz, 2C), 129.30, 129.26, 127.8, 127.6, 126.7, 126.1, 125.7 (q, J = 37.8 Hz, 1C), 122.2 (q, J = 178.0 Hz, CF_3), 119.0, 115.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.2 (s, CF_3); HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{23}H_{15}F_3N_3$ 390.1213, found 390.1201.

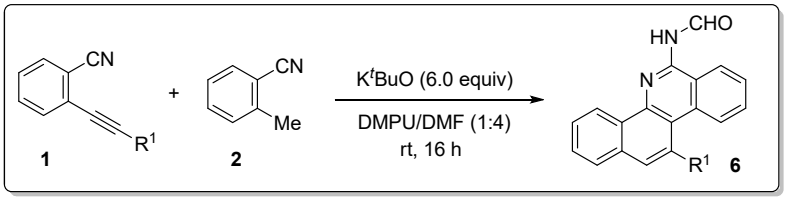


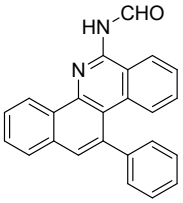
5-Phenylbenzo[*c*]naphtho[1,2-*j*][1,7]phenanthrolin-16-amine (5d). The crude product was purified by column chromatography (hexane/EtOAc = 70/30) to afford **5d** as white solid (126.3 mg, 60%): mp 204–205 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, J = 8.5 Hz, 1H), 8.07 (s, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.63-7.66 (m, 4H), 7.58 (s, 1H), 7.50 (s, 5H), 7.40 (d, J = 7.3 Hz, 3H), 5.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 144.6, 138.3, 134.7, 132.4, 131.9, 130.7, 129.1, 129.0, 128.8, 128.5, 128.4, 128.2, 127.5, 126.5, 125.2, 123.5, 123.0, 122.1, 119.1, 117.0; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{30}H_{20}N_3$ 422.1652, found 422.1650.

General procedure for the synthesis of *N*-(11-aryl/alkylbenzo[*c*]phenanthridin-6-yl)formamide (6a-i)

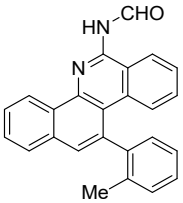
In an oven-dried 10 mL round bottom flask, a solution of 2-alkynylbenzonitrile **1** (0.5 mmol), 2-methylbenzonitrile **2** (1.0 equiv) and K^{t}BuO (6.0 equiv) in 2 mL of DMF/DMPU (4:1) was stirred at rt for 16 h. Progression of the reaction was monitored by TLC analysis; After 5 min starting material was completely consumed and a new spot formed which corresponds to the aminated

compounds 3, further stirring the reaction mixture started the formylation of amino group to yield the product 4. Therefore, the reaction was stirred for 16 h and the progression was monitored by TLC analysis; after complete consumption of starting material, the reaction was diluted with ethyl acetate (50 mL) and water (50 mL). The layers were separated, and the organic layer was washed with aqueous saturated brine solution and dried over Na_2SO_4. Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel (100−200) (hexane:ethyl acetate; 80/20). The structure and purity of products were confirmed by comparison of their physical and spectral data (^{1}H NMR, ^{13}C NMR, and HRMS).



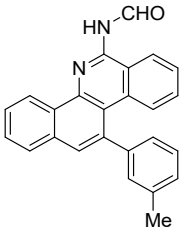


***N*-(11-phenylbenzo[*c*]phenanthridin-6-yl)formamide (6a).** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **6a** as white solid (142.7 mg, 82%): mp 205–206 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.46 (d, J = 9.0 Hz, 1H), 9.98 (d, J = 9.0 Hz, 1H), 9.20 (d, J = 9.3 Hz, 1H), 8.58 (d, J = 8.3 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 7.84 (s, 1H), 7.74-7.77 (m, 2H), 7.62-7.67 (m, 2H), 7.52-7.57 (m, 3H), 7.42-7.50 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.6, 148.8, 144.1, 140.8, 137.2, 134.8, 132.7, 130.5, 130.0, 129.6, 129.1, 128.5, 128.0, 127.5, 127.2, 125.2, 124.8, 119.5, 118.3; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{24}H_{17}N_2O$ 349.1335, found 349.1341.

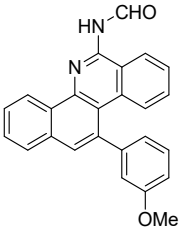


***N*-(11-(*o*-tolyl)benzo[*c*]phenanthridin-6-yl)formamide (6b).** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **6b** as white solid (153.8 mg, 85%): mp 211–212 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.44 (d, J = 7.8 Hz, 1H), 9.96 (d, J = 7.0 Hz, 1H), 9.23 (d, J = 7.5 Hz, 1H), 8.59 (d, J = 8.3 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.71-7.77 (m, 3H), 7.65 (t, J = 7.5 Hz, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.44 (dt, J = 19.1, 6.9 Hz, 5H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.7, 148.5,

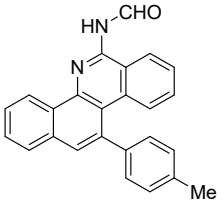
143.8, 140.5, 136.5, 135.7, 135.1, 132.8, 130.9, 130.6, 129.5, 128.7, 128.5, 128.4, 127.8, 127.6, 127.3, 127.2, 125.3, 124.9, 119.1, 118.5, 20.1; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{25}H_{19}N_2O$ 363.1492, found 363.1491.



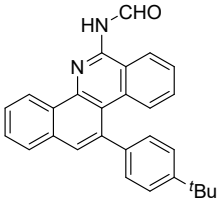
***N*-(11-(*m*-tolyl)benzo[*c*]phenanthridin-6-yl)formamide (6c).** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **6c** as white solid (141.2 mg, 78%): mp 213–214 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.44 (s, 1H), 9.96 (s, 1H), 9.16 (d, J = 6.6 Hz, 1H), 8.56 (d, J = 8.2 Hz, 1H), 8.03 (d, J = 6.3 Hz, 1H), 7.79 (s, 1H), 7.73 (p, J = 6.8 Hz, 2H), 7.64 (dd, J = 12.3, 8.2 Hz, 2H), 7.47 – 7.37 (m, 2H), 7.32 (s, 2H), 7.20 (d, J = 7.4 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.7, 148.6, 144.1, 140.7, 138.8, 137.3, 134.6, 132.6, 130.4, 130.0, 129.5, 129.4, 129.0, 128.6, 128.4, 127.9, 127.4, 127.3, 127.2, 126.3, 125.1, 124.7, 119.4, 118.2, 21.5 HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{25}H_{19}N_2O$ 363.1492, found 363.1491.



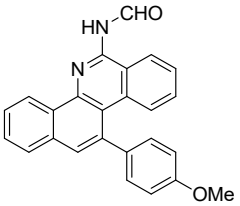
***N*-(11-(3-methoxyphenyl)benzo[*c*]phenanthridin-6-yl)formamide (6d).** The crude product was purified by column chromatography (hexane/EtOAc = 70/30) to afford **6d** as white solid (162.5 mg, 86%): mp 218–219 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.43 (d, J = 9.0 Hz, 1H), 9.95 (d, J = 8.8 Hz, 1H), 9.15 (d, J = 8.8 Hz, 1H), 8.55 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.81 (s, 1H), 7.60-7.74 (m, 4H), 7.40-7.46 (m, 2H), 7.06 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 7.3 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.5, 160.2, 148.6, 145.5, 140.7, 137.0, 134.6, 132.7, 130.6, 130.5, 130.0, 128.9, 128.4, 127.9, 127.4, 127.3, 127.2, 125.1, 124.7, 121.5, 119.4, 118.1, 114.6, 113.6, 55.7; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{25}H_{19}N_2O_2$ 379.1441, found 379.1423.



***N*-(11-(*p*-tolyl)benzo[*c*]phenanthridin-6-yl)formamide (6e).** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **6e** as white solid (152.0 mg, 84%): mp 209–210 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.44 (d, J = 8.5 Hz, 1H), 9.97 (d, J = 7.8 Hz, 1H), 9.19 (d, J = 8.0 Hz, 1H), 8.57 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.80 (s, 1H), 7.71-7.74 (m, 3H), 7.64 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.36 (s, 4H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.7, 148.8, 141.2, 140.8, 137.2, 137.1, 134.8, 132.8, 130.4, 130.2, 130.1, 129.1, 129.0, 128.5, 127.9, 127.5, 127.3, 127.2, 125.2, 124.8, 119.4, 118.4, 21.4; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{25}H_{19}N_2O$ 363.1492, found 363.1491.

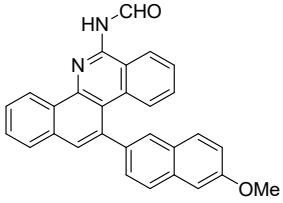


***N*-(11-(4-(*tert*-butyl)phenyl)benzo[*c*]phenanthridin-6-yl)formamide (6f).** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **6f** as white solid (167.7 mg, 83%): mp 211–212 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.47 (d, J = 8.9 Hz, 1H), 9.98 (d, J = 8.8 Hz, 1H), 9.19 (d, J = 8.9 Hz, 1H), 8.57 (d, J = 8.4 Hz, 1H), 8.08 – 7.97 (m, 1H), 7.84 (s, 1H), 7.77 – 7.69 (m, 2H), 7.67 – 7.60 (m, 2H), 7.55 (d, J = 8.1 Hz, 2H), 7.40 (t, J = 10.3 Hz, 3H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.7, 150.5, 148.7, 141.2, 140.8, 137.1, 134.7, 132.7, 130.4, 130.0, 129.1, 128.8, 128.5, 128.0, 127.5, 127.3, 127.2, 126.3, 125.1, 124.7, 119.4, 118.3, 34.9, 31.7; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{28}H_{25}N_2O$ 405.1961, found 405.1979.

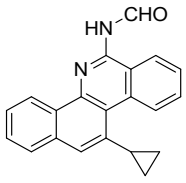


***N*-(11-(4-methoxyphenyl)benzo[*c*]phenanthridin-6-yl)formamide (6g).** The crude product was purified by column chromatography (hexane/EtOAc = 70/30) to afford **6g** as white solid (166.3 mg, 88%): mp 221–222 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.37 (d, J = 8.2 Hz, 1H), 9.89 (d, J = 6.7 Hz, 1H), 9.09-9.07 (m, 1H), 8.48 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 4.9 Hz, 1H), 7.68-7.61 (m, 4H), 7.56 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.7 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz,

DMSO-d_6) δ 164.7, 159.2, 148.6, 140.8, 136.9, 136.4, 134.8, 132.7, 130.4, 130.3, 130.0, 129.1, 128.4, 127.9, 127.4, 127.2, 127.1, 125.1, 124.7, 119.4, 118.4, 115.0, 55.7; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{25}H_{19}N_2O_2$ 379.1441, found 379.1423.



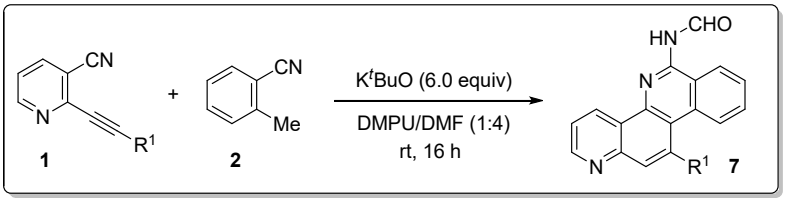
***N*-(11-(6-methoxynaphthalen-2-yl)benzo[*c*]phenanthridin-6-yl)formamide (6h).** The crude product was purified by column chromatography (hexane/EtOAc = 70/30) to afford **6h** as white solid (173.3 mg, 81%): mp 224–225 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.05 (s, 1H), 10.06 (s, 1H), 9.22 (d, J = 7.3 Hz, 1H), 8.57 (d, J = 5.8 Hz, 1H), 8.06 (d, J = 12.1 Hz, 2H), 7.83-7.90 (m, 3H), 7.74 (s, 2H), 7.62 (s, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.39-7.41 (m, 2H), 7.32 (d, J = 8.2 Hz, 1H), 7.21 (dd, J = 8.9, 2.2 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.8, 158.1, 148.9, 140.9, 139.3, 137.2, 134.9, 134.6, 134.0, 132.8, 130.5, 130.1, 129.7, 129.5, 128.6, 128.5, 128.1, 127.8, 127.6, 127.3, 126.9, 125.2, 124.8, 119.7, 118.2, 106.4, 55.7; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{29}H_{21}N_2O_2$ 429.1598, found 429.1582.

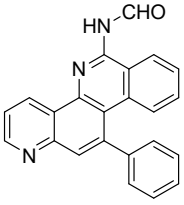


***N*-(11-cyclopropylbenzo[*c*]phenanthridin-6-yl)formamide (6i).** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **6i** as white solid (115.4 mg, 74%): mp 195–196 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.40 (d, J = 8.8 Hz, 1H), 9.90 (d, J = 8.5 Hz, 1H), 9.69 (d, J = 8.5 Hz, 1H), 9.13-9.11 (m, 1H), 8.64 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 17.0 Hz, 3H), 7.83 (t, J = 7.5 Hz, 1H), 7.67 (t, J = 3.0 Hz, 2H), 2.76 (d, J = 4.8 Hz, 1H), 1.30 (d, J = 6.8 Hz, 2H), 0.95 (d, J = 4.5 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.7, 148.2, 140.5, 137.3, 135.4, 132.8, 131.0, 130.2, 128.1, 127.9, 127.5, 127.4, 126.8, 126.7, 125.2, 124.7, 120.6, 119.4, 20.1, 10.3; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{21}H_{17}N_2O$ 313.1335, found 313.1354.

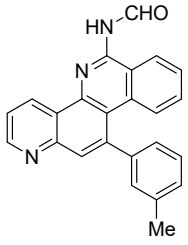
General procedure for the synthesis of *N*-(11-arylbenzo[*c*][1,7]phenanthrolin-6-yl)formamide (7a-d)

In an oven-dried 10 mL round bottom flask, a solution of 2-(arylethynyl)nicotinonitrile**1** (0.5 mmol), 2-methylbenzonitrile **2** (1.0 equiv) and K^{t}BuO (6.0 equiv) in 2 mL of DMF/DMPU (4:1) was stirred at rt for 16 h. Progression of the reaction was monitored by TLC analysis; After 5 min starting material was completely consumed and a new spot formed which corresponds to the aminated compounds **5**, further stirring the reaction mixture started the formylation of amino group to yield the product **7**. Therefore, the reaction was stirred for 16 h and the progression was monitored by TLC analysis; after complete consumption of starting material, the reaction was diluted with ethyl acetate (50 mL) and water (50 mL). The layers were separated, and the organic layer was washed with aqueous saturated brine solution and dried over Na_2SO_4. Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel (100−200) (hexane:ethyl acetate; 60/40). The structure and purity of products were confirmed by comparison of their physical and spectral data (^{1}H NMR, ^{13}C NMR, and HRMS).

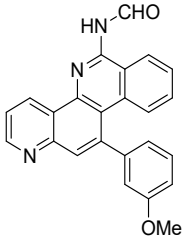




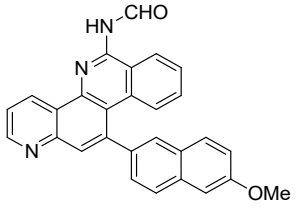
***N*-(11-phenylbenzo[*c*][1,7]phenanthrolin-6-yl)formamide (7a).** The crude product was purified by column chromatography (hexane/EtOAc = 60/40) to afford **7a** as off-white solid (108.2 mg, 62%): mp 220–221 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.41 (d, J = 8.0 Hz, 1H), 8.96 (d, J = 2.8 Hz, 1H), 8.40 (d, J = 8.3 Hz, 1H), 7.64 (q, J = 4.2 Hz, 1H), 7.43-7.56 (m, 10H), 7.31 (t, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.8, 151.5, 148.0, 144.3, 143.5, 141.5, 134.1, 133.2, 131.0, 129.6, 129.3, 128.9, 128.1, 127.1, 126.9, 125.6, 125.1, 125.0, 121.4, 119.5, 114.7; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{23}H_{16}N_3O$ 350.1288, found 350.1289.



***N*-(11-(*m*-tolyl)benzo[*c*][1,7]phenanthrolin-6-yl)formamide (7b).** The crude product was purified by column chromatography (hexane/EtOAc = 60/40) to afford **7b** as white solid (116.1 mg, 64%): mp 223–224 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.49 (d, J = 8.9 Hz, 1H), 9.98 (d, J = 8.7 Hz, 1H), 9.48 (d, J = 8.3 Hz, 1H), 9.03 (d, J = 5.2 Hz, 1H), 8.58 (d, J = 8.3 Hz, 1H), 7.79 (s, 1H), 7.71 (dd, J = 8.3, 4.3 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 8.6 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.35 (d, J = 9.8 Hz, 2H), 7.24 (d, J = 7.5 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.8, 152.2, 149.4, 147.7, 143.5, 141.0, 140.6, 139.0, 134.4, 133.5, 130.3, 129.5, 129.4, 129.0, 127.9, 127.3, 126.1, 125.6, 124.8, 122.5, 119.4, 118.2, 21.5; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{24}H_{18}N_3O$ 364.1444, found 364.1429.



***N*-(11-(3-methoxyphenyl)benzo[*c*][1,7]phenanthrolin-6-yl)formamide (7c).** The crude product was purified by column chromatography (hexane/EtOAc = 60/40) to afford **7c** as white solid (123.2 mg, 65%): mp 229–230 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.41 (d, J = 8.3 Hz, 1H), 8.96 (d, J = 4.0 Hz, 1H), 8.40 (d, J = 8.3 Hz, 1H), 7.63 (q, J = 4.2 Hz, 1H), 7.58 (s, 1H), 7.54 (dd, J = 15.0, 8.0 Hz, 2H), 7.41-7.45 (m, 3H), 7.36 (t, J = 7.8 Hz, 1H), 7.06 (d, J = 7.3 Hz, 2H), 7.00 (d, J = 7.8 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.2, 156.7, 151.5, 148.0, 145.6, 143.4, 141.2, 134.0, 133.2, 130.5, 129.3, 127.3, 126.9, 125.4, 125.0, 121.4, 119.4, 114.7, 114.3, 113.6, 55.6; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{24}H_{18}N_3O_2$ 380.1394, found 380.1410.

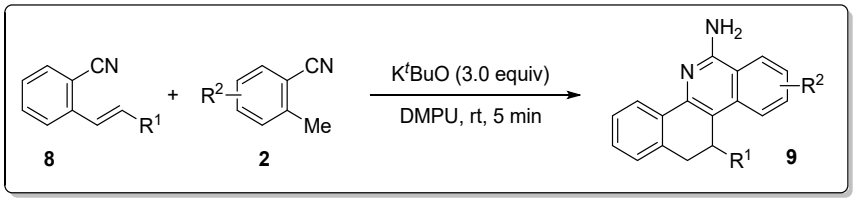


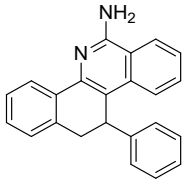
***N*-(11-(6-methoxynaphthalen-2-yl)benzo[*c*][1,7]phenanthrolin-6-yl)formamide (7d).** The crude product was purified by column chromatography (hexane/EtOAc = 60/40) to afford **7d** as white solid (124.4 mg, 58%): mp 235–236 °C: ^{1}H

NMR (400 MHz, DMSO-d_6) δ 9.47 (d, J = 8.3 Hz, 1H), 9.01 (s, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.10 (s, 1H), 7.93 (dd, J = 12.5, 8.8 Hz, 2H), 7.68-7.72 (m, 3H), 7.53 (dd, J = 13.1, 7.9 Hz, 3H), 7.43 (d, J = 11.0 Hz, 2H), 7.27 (t, J = 8.9 Hz, 2H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.3, 156.8, 151.2, 141.8, 139.2, 134.1, 134.0, 133.7, 130.2, 129.6, 129.3, 128.2, 127.9, 127.2, 127.1, 126.8, 125.0, 121.5, 119.6, 119.4, 115.0, 106.5, 55.8; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{28}H_{20}N_3O_2$ 430.1550, found 430.1569.

General procedure for the synthesis of 11-aryl-8-fluoro-11,12-dihydrobenzo[*c*] phenanthridin-6-amine (9a-d)

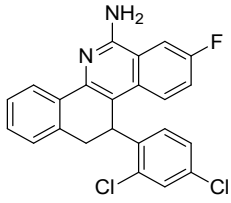
In an oven-dried 10 mL round bottom flask, a solution of 2-alkenylbenzonitrile **8** (0.5 mmol), 2-methylbenzonitrile **2** (1.0 equiv) and K^{t}BuO (3.0 equiv) in 2 mL of DMPU was stirred at rt for 5 minutes. Progression of the reaction was monitored by TLC analysis; after complete consumption of starting material, the reaction was diluted with ethyl acetate (50 mL) and water (50 mL). The layers were separated, and the organic layer was washed with aqueous saturated brine solution and dried over Na_2SO_4. Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel (100−200) (hexane:ethyl acetate; 90/10). The structure and purity of products were confirmed by comparison of their physical and spectral data (^{1}H NMR, ^{13}C NMR, and HRMS).



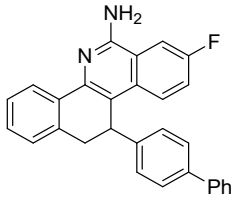


11-Phenyl-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9a). The crude product was purified by column chromatography (hexane/EtOAc = 90/10) to afford **9a** as white solid (138.5 mg, 86%): mp 132–133 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 7.7 Hz, 1H), 7.79 (dd, J = 8.3, 2.4 Hz, 2H), 7.50-7.54 (m, 1H), 7.33-7.40 (m, 2H), 7.19 (t, J = 7.4 Hz, 1H), 7.04-7.12 (m, 6H), 5.29 (s, 2H), 4.78 (d, J = 7.0 Hz, 1H), 3.63 (dd, J = 15.3, 7.3 Hz, 1H), 3.14 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 144.3, 143.4, 136.5,

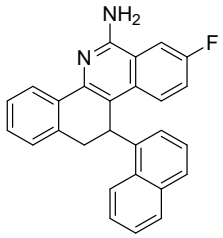
135.4, 134.7, 130.5, 128.4, 127.7, 127.1, 126.4, 125.4, 124.7, 123.8, 123.3, 118.1, 117.9, 38.9, 37.1; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{23}H_{19}N_2$ 323.1543, found 323.1522.



11-(2,4-Dichlorophenyl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9b). The crude product was purified by column chromatography (hexane/EtOAc = 90/10) to afford **9b** as white solid (165.6 mg, 81%): mp 134–135 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 10.2, 2.7 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.58 (q, J = 8.3 Hz, 2H), 7.44-7.46 (m, 1H), 7.41 (d, J = 2.2 Hz, 1H), 6.95-6.99 (m, 1H), 6.88 (td, J = 8.3, 2.7 Hz, 1H), 6.73 (dd, J = 8.4, 2.1 Hz, 1H), 6.38 (d, J = 8.4 Hz, 1H), 5.33 (s, 2H), 5.19 (d, J = 6.9 Hz, 1H), 3.46 (dd, J = 15.5, 7.4 Hz, 1H), 3.08 (d, J = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 260.1 Hz, 1C), 156.1, 143.7, 138.3, 137.0 (d, J = 7.7 Hz, 1C), 136.0, 133.4, 132.7, 131.0, 130.3, 129.8 (d, J = 7.7 Hz, 1C), 129.5, 127.2, 126.2, 123.4 (d, J = 11.6 Hz, 1C), 118.1, 117.4, 115.1 (d, J = 21.2 Hz, 1C), 111.8 (d, J = 24.1 Hz, 1C), 34.8, 33.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.3 (s); HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{23}H_{16}Cl_2FN_2$ 409.0669, found 409.0664.



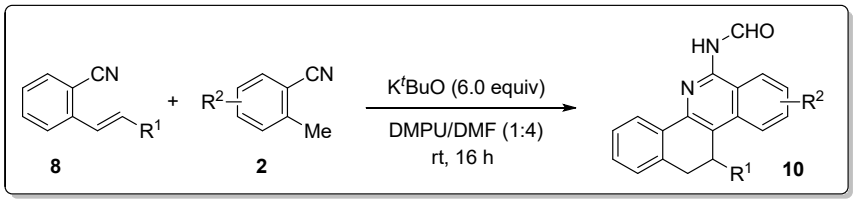
11-([1,1'-biphenyl]-4-yl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9c). The crude product was purified by column chromatography (hexane/EtOAc = 90/10) to afford **9c** as white solid (162.2 mg, 78%): mp 144–145 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 10.2 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.58 (t, J = 7.4 Hz, 1H), 7.43-7.47 (m, 3H), 7.31-7.36 (m, 4H), 7.24-7.27 (m, 1H), 7.03-7.06 (m, 2H), 7.00 (d, J = 7.8 Hz, 1H), 6.88 (td, J = 8.3, 2.7 Hz, 1H), 5.80 (s, 2H), 4.79 (d, J = 6.9 Hz, 1H), 3.55 (dd, J = 15.3, 7.1 Hz, 1H), 3.15 (d, J = 15.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 242.7 Hz, 1C), 155.4, 141.7, 140.7, 139.3, 136.1, 131.1, 129.9 (d, J = 2.2 Hz, 1C), 129.6 (d, J = 7.3 Hz, 1C), 128.6, 128.0, 127.1, 127.0, 127.0, 126.2, 123.9, 123.7, 118.2 (d, J = 32.7 Hz, 1C), 115.0 (d, J = 21.8 Hz, 1C), 111.5 (d, J = 24.0 Hz, 1C), 38.5, 36.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.5 (s); HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{29}H_{22}FN_2$ 417.1762, found 417.1758.

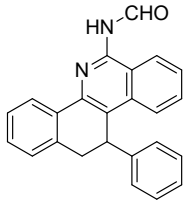


8-Fluoro-11-(naphthalen-1-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9d). The crude product was purified by column chromatography (hexane/EtOAc = 90/10) to afford **9d** as white solid (144.3 mg, 74%): mp 142–143 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 10.2 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.71-7.75 (m, 1H), 7.60 (d, J = 7.8 Hz, 2H), 7.53-7.57 (m, 1H), 7.33-7.39 (m, 2H), 6.98 (t, J = 7.7 Hz, 1H), 6.81 (d, J = 7.0 Hz, 2H), 6.63 (d, J = 6.6 Hz, 1H), 5.62 (d, J = 7.6 Hz, 1H), 5.51 (s, 2H), 3.65 (q, J = 7.5 Hz, 1H), 3.26 (d, J = 21.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 241.9 Hz, 1C), 155.7, 143.7, 137.4, 136.7 (d, J = 8.0 Hz, 1C), 136.2, 134.3, 130.8, 130.7, 130.3, 129.7 (d, J = 8.0 Hz, 1C), 129.5, 127.1, 126.4, 125.9, 125.6, 125.5, 125.4, 123.8, 123.3, 122.8, 118.3 (d, J = 17.4 Hz, 1C), 114.7 (d, J = 21.8 Hz, 1C), 111.7 (d, J = 23.2 Hz, 1C), 34.8, 34.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.7 (s); HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{27}H_{20}FN_2$ 391.1605, found 391.1595.

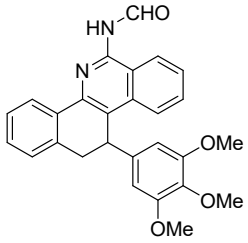
General procedure for the synthesis of *N*-(11-aryl-11,12-dihydrobenzo[*c*] phenanthridin-6-yl)formamide (10a-g)

In an oven-dried 10 mL round bottom flask, a solution of 2-alkenylbenzonitrile **8** (0.5 mmol), 2-methylbenzonitrile **2a** (1.0 equiv) and K^{t}BuO (6.0 equiv) in 2 mL of DMF/DMPU (4:1) was stirred at rt for 16 h. Progression of the reaction was monitored by TLC analysis; After 5 min starting material was completely consumed and a new spot formed which corresponds to the aminated compounds **9**, further stirring the reaction mixture started the formylation of amino group to yield the product **10**. Therefore, the reaction was stirred for 16 h and the progression was monitored by TLC analysis; after complete consumption of starting material, the reaction was diluted with ethyl acetate (50 mL) and water (50 mL). The layers were separated, and the organic layer was washed with aqueous saturated brine solution and dried over Na_2SO_4. Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel (100−200) (hexane:ethyl acetate; 85/15). The structure and purity of products were confirmed by comparison of their physical and spectral data (^{1}H NMR, ^{13}C NMR, and HRMS).

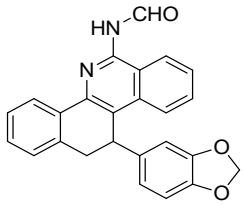




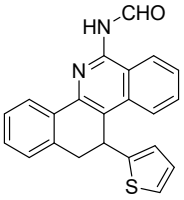
***N*-(11-Phenyl-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10a).** The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **10a** as white solid (133.0 mg, 76%): mp 184–185 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (d, J = 8.0 Hz, 1H), 10.04 (d, J = 8.2 Hz, 1H), 8.40 (d, J = 7.7 Hz, 1H), 8.29 (d, J = 8.2 Hz, 1H), 7.85-7.90 (m, 2H), 7.72 (dd, J = 5.5, 3.0 Hz, 1H), 7.56-7.63 (m, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.07-7.12 (m, 2H), 7.02 (d, J = 6.5 Hz, 2H), 4.89 (d, J = 7.0 Hz, 1H), 3.65 (dd, J = 15.5, 7.3 Hz, 1H), 3.19 (d, J = 15.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 147.6, 143.9, 142.8, 136.8, 134.6, 134.3, 131.0, 129.0, 128.6, 127.6, 127.4, 127.0, 126.5, 124.9, 123.9, 123.7, 118.4, 39.0, 36.6; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{24}H_{19}N_2O$ 351.1492, found 351.1476.



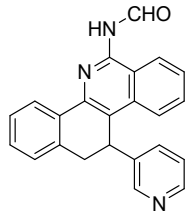
***N*-(11-(3,4,5-trimethoxyphenyl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10b).** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **10b** as white solid (202.4 mg, 92%): mp 190–191 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (d, J = 9.5 Hz, 1H), 10.04 (d, J = 9.5 Hz, 1H), 8.31-8.37 (m, 2H), 7.95 (d, J = 8.5 Hz, 1H), 7.64-7.68 (m, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.24 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 7.3 Hz, 1H), 6.24 (s, 2H), 4.78 (d, J = 6.7 Hz, 1H), 3.71 (s, 3H), 3.56 (s, 7H), 3.14 (d, J = 15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 153.1, 147.8, 143.7, 138.5, 136.7, 136.6, 134.8, 134.7, 131.2, 129.0, 128.7, 127.3, 127.1, 124.8, 123.8, 123.6, 123.2, 118.4, 104.5, 60.8, 56.1, 39.1, 36.8; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{27}H_{25}N_2O_4$ 441.1809, found 441.1791.



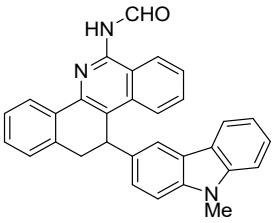
***N*-(11-(Benzo[*d*][1,3]dioxol-5-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10c).** The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **10c** as white solid (163.5 mg, 83%): mp 183–184 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.25 (d, J = 9.1 Hz, 1H), 9.74 (d, J = 6.3 Hz, 1H), 8.43 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 7.0 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.68 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.20 (td, J = 7.4, 1.1 Hz, 1H), 7.11 (d, J = 7.4 Hz, 1H), 6.56 (d, J = 8.1 Hz, 2H), 6.32 (dd, J = 8.0, 1.6 Hz, 1H), 5.80 (d, J = 5.8 Hz, 2H), 4.91 (d, J = 6.9 Hz, 1H), 3.46 (dd, J = 15.7, 7.1 Hz, 1H), 3.08 (d, J = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.6, 149.1, 147.6, 146.2, 143.3, 137.3, 136.5, 135.1, 134.7, 131.8, 129.3, 128.9, 127.5, 127.3, 125.2, 124.8, 124.1, 123.4, 123.3, 120.8, 108.5, 108.3, 101.3, 37.4, 36.5; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{25}H_{19}N_2O_3$ 395.1390, found 395.1375.



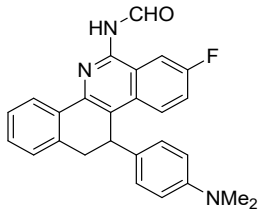
***N*-(11-(thiophen-2-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10d).** The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **10d** as white solid (138.8 mg, 78%): mp 178–179 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.23 (d, J = 8.9 Hz, 1H), 9.72 (s, 1H), 8.44 (d, J = 8.2 Hz, 1H), 8.28 (d, J = 7.6 Hz, 1H), 8.12 (d, J = 8.5 Hz, 1H), 7.73-7.76 (m, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.21-7.34 (m, 3H), 7.04 (d, J = 4.8 Hz, 1H), 6.67-6.69 (m, 1H), 6.64 (s, 1H), 5.29 (d, J = 5.8 Hz, 1H), 3.48 (dd, J = 15.7, 6.3 Hz, 1H), 3.23 (d, J = 15.7 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.5, 149.0, 146.9, 142.6, 136.2, 135.3, 134.4, 131.7, 129.5, 129.1, 127.6, 127.4, 126.8, 125.3, 125.2, 124.7, 124.5, 124.1, 123.7, 118.6, 36.3, 33.5; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{22}H_{17}N_2OS$ 357.1056, found 357.1090.



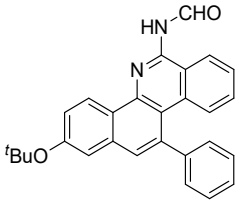
***N*-(11-(pyridin-3-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10e).** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **10e** as white solid (119.3 mg, 68%): mp 202–203 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.27 (d, J = 8.7 Hz, 1H), 9.74 (s, 1H), 8.40-8.45 (m, 2H), 8.28 (d, J = 7.6 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.66-7.70 (m, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.26-7.37 (m, 2H), 7.11-7.20 (m, 2H), 7.01-7.04 (m, 1H), 6.55 (d, J = 7.8 Hz, 1H), 5.03 (d, J = 6.0 Hz, 1H), 3.39-3.53 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.6, 162.2, 149.7, 149.1, 143.6, 137.2, 136.9, 135.2, 134.5, 131.9, 129.3, 128.7, 127.5, 127.3, 125.3, 124.8, 124.0, 122.3, 122.2, 121.8, 118.5, 55.6, 34.6; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{23}H_{18}N_3O$ 352.1444, found 352.1459.



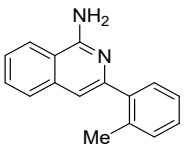
***N*-(11-(9-methyl-9*H*-carbazol-3-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10f).** The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **10f** as white solid (158.5 mg, 70%): mp 196–197 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.27 (d, J = 9.1 Hz, 1H), 9.80 (d, J = 8.7 Hz, 1H), 8.44 (d, J = 8.4 Hz, 1H), 8.37 (d, J = 7.6 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.81 (s, 1H), 7.60-7.65 (m, 1H), 7.50-7.55 (m, 1H), 7.42 (d, J = 8.1 Hz, 1H), 7.33 (dd, J = 12.6, 7.1 Hz, 2H), 7.14-7.20 (m, 2H), 7.03-7.07 (m, 2H), 6.91 (d, J = 8.7 Hz, 1H), 5.16 (d, J = 6.9 Hz, 1H), 3.65 (s, 3H), 3.59 (dd, J = 15.7, 6.9 Hz, 1H), 3.20 (d, J = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.5, 149.0, 143.3, 141.3, 139.9, 136.6, 135.4, 135.0, 134.0, 131.7, 129.3, 128.9, 127.6, 127.2, 126.1, 125.6, 125.2, 124.7, 124.2, 123.8, 122.6, 122.2, 120.5, 119.2, 119.0, 109.6, 109.4, 38.0, 37.3, 29.3; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{31}H_{24}N_3O$ 454.1914, found 454.1900.



***N*-(11-(4-(dimethylamino)phenyl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10g).** The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **10g** as white solid (154.1 mg, 75%): mp 192–193 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.28 (d, J = 9.0 Hz, 1H), 9.79 (s, 1H), 8.48 (d, J = 8.3 Hz, 1H), 8.09 (d, J = 10.3 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.15-7.18 (m, 1H), 7.05 (t, J = 8.4 Hz, 1H), 6.76 (d, J = 8.5 Hz, 2H), 6.44 (d, J = 8.5 Hz, 2H), 4.90 (d, J = 6.8 Hz, 1H), 3.42 (dd, J = 15.6, 6.9 Hz, 1H), 3.11 (d, J = 15.5 Hz, 1H), 2.71 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.6, 162.2 (d, J = 230.3 Hz, 1C), 149.6, 149.1 142.1, 137.0 (d, J = 8.0 Hz, 1C), 136.4, 131.7, 131.3 (d, J = 2.8 Hz, 1C), 130.6 (d, J = 7.3 Hz, 1C), 130.5, 128.2, 127.5, 124.7, 124.3, 119.0, 115.6 (d, J = 32.7 Hz, 1C), 112.8, 111.5 (d, J = 23.2 Hz, 1C), 36.9, 35.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.7 (s); HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{26}H_{23}FN_3O$ 412.1820, found 412.1797.



***N*-(2-(*tert*-butoxy)-11-phenylbenzo[*c*]phenanthridin-6-yl)formamide (11).** The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **11** as white solid (155.4 mg, 74%): mp 192–193 °C: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.35 (d, J = 8.9 Hz, 1H), 9.90 (s, 1H), 9.11 (d, J = 8.9 Hz, 1H), 8.42 (d, J = 8.9 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.65-7.67 (m, 3H), 7.42-7.50 (m, 5H), 7.30 (s, 1H), 7.18 (d, J = 9.1 Hz, 1H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.7, 157.0, 148.5, 144.4, 141.2, 137.2, 136.4, 132.6, 130.6, 129.8, 129.3, 129.1, 128.5, 128.0, 127.8, 127.2, 126.3, 125.2, 124.4, 118.7, 117.9, 115.1, 79.7, 28.9; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{28}H_{25}N_2O_2$ 421.1911, found 421.1899.



3-(*o*-Tolyl)isoquinolin-1-amine (12). The crude product was purified by column chromatography (hexane/EtOAc = 90/10) to afford **12** as white solid (99.4 mg, 85%): mp 122–123 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.7 Hz, 1H), 7.68 (d, J = 7.8 Hz,

1H), 7.58 (t, J = 7.6 Hz, 1H), 7.40-7.45 (m, 2H), 7.24-7.26 (m, 3H), 7.07 (s, 1H), 5.48 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 151.9, 140.9, 137.9, 135.5, 130.6, 130.3, 129.7, 127.9, 127.3, 126.0, 125.8, 122.8, 116.6, 112.0, 20.0; HRMS (ESI-TOF) $[M+H]^+$ Calcd for $C_{16}H_{15}N_2$ 235.1230, found 235.1251.

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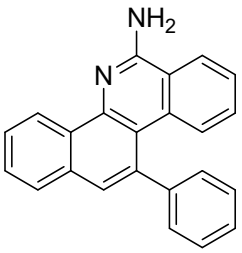
1. (a) Verma, S.; Mishra, P. K.; Kumar, M.; Sur S.; Verma, A. K. *J. Org. Chem.* **2018**, *83*, 6650; (b) Verma, S.; Kumar, M.; Verma, A. K. *Org. Lett.* **2020***, 22,* 130.

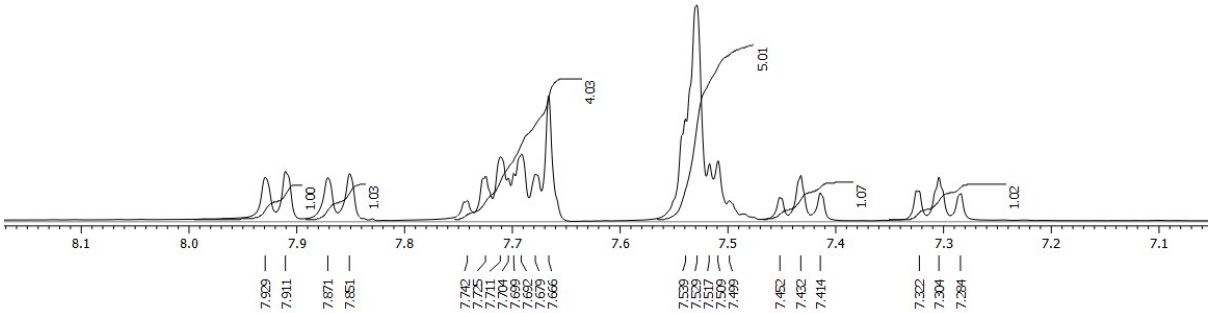
2. (a) He, Y.; Zhang, X.; Fan, X. *Chem. Commun.*, **2014**, *50*, 5641; (b) Zhu, X.-T.; Zhao, Q.; Liu, F.; Wang, A.-F.; Cai, P.-J.; Hao, W.-J.; Tu, S.-J.; Jiang, B. *Chem. Commun.* **2017**, *53*, 6828; (c) Madhubabu, M. V.; Shankar, R.; More, S. S.; Rao, M. V. B.; Kumar, U. K. S.; Raghunadh, A. *RSC Adv.* **2016**, *6*, 36599.

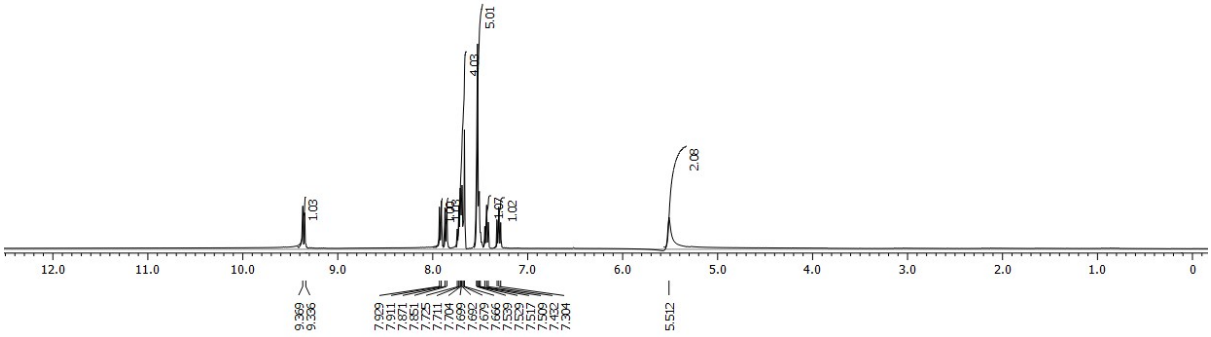
Copies of ^{1}H, ^{13}C, ^{19}F NMR and HRMS

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

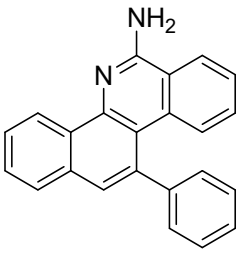


11-Phenylbenzo[*c*]phenanthridin-6-amine (3a)

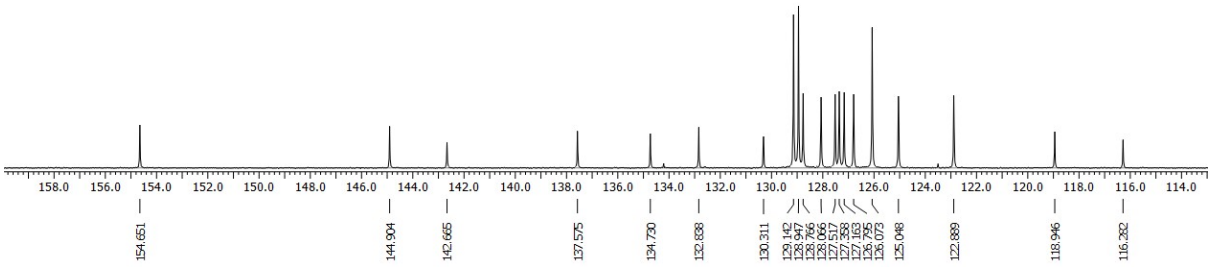


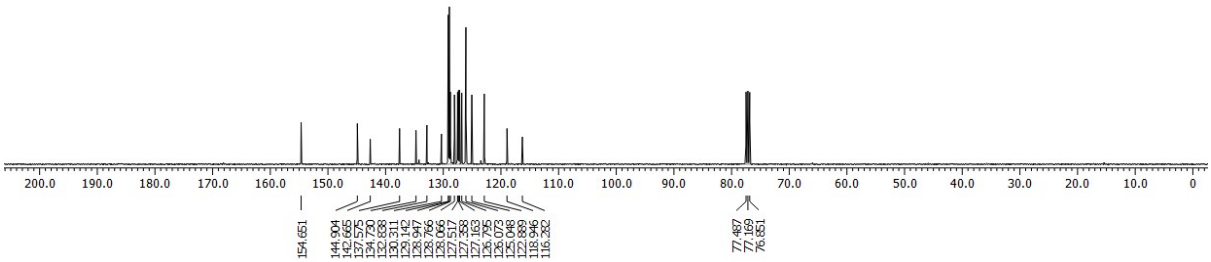


^{13}C NMR (100 MHz, $CDCl_3$)

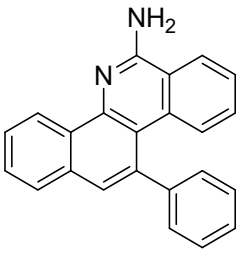


11-Phenylbenzo[*c*]phenanthridin-6-amine (3a)

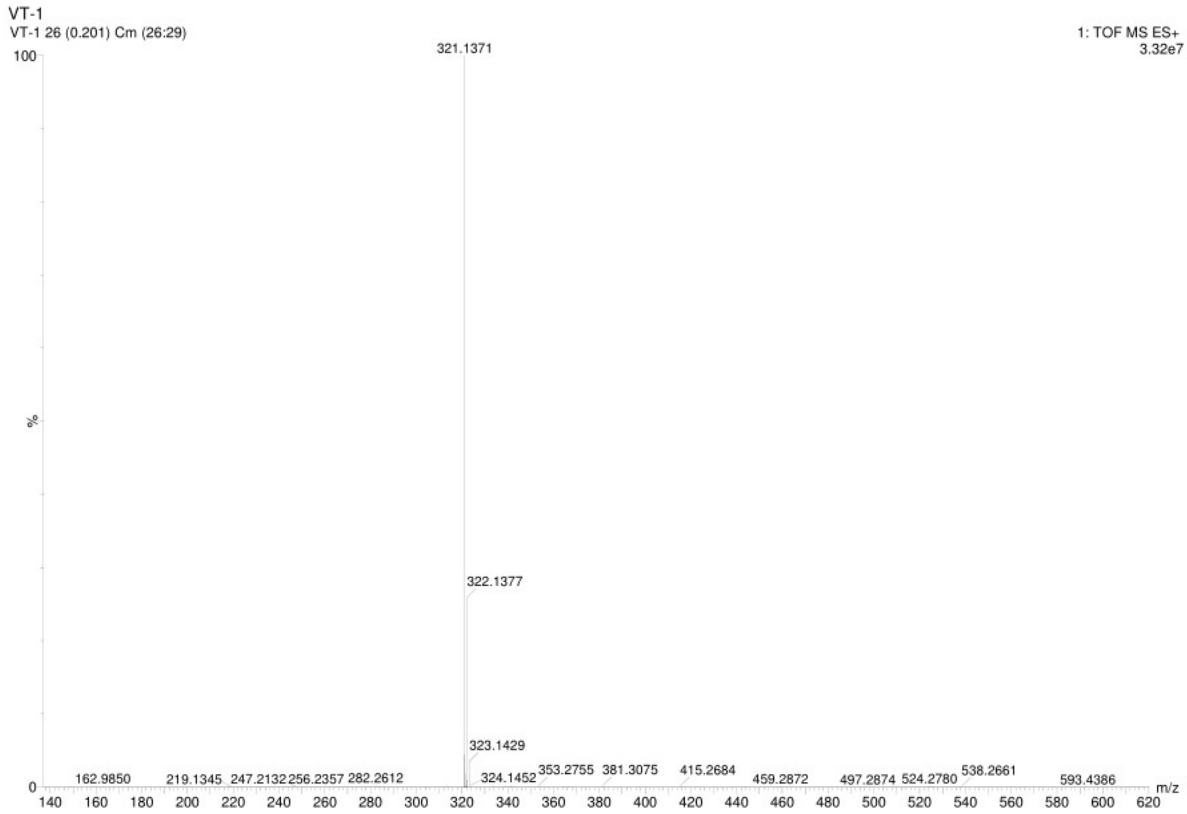




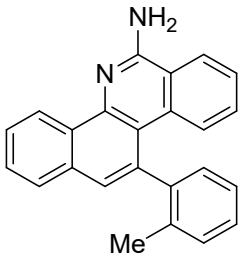
HRMS



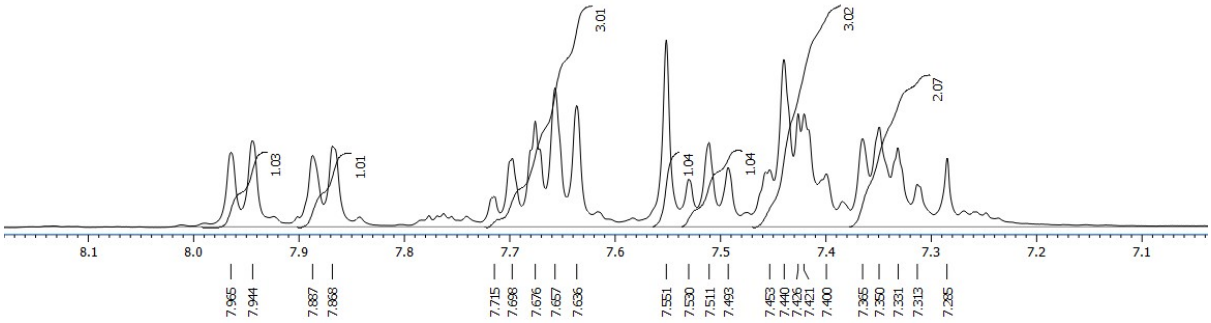
11-Phenylbenzo[*c*]phenanthridin-6-amine (3a)

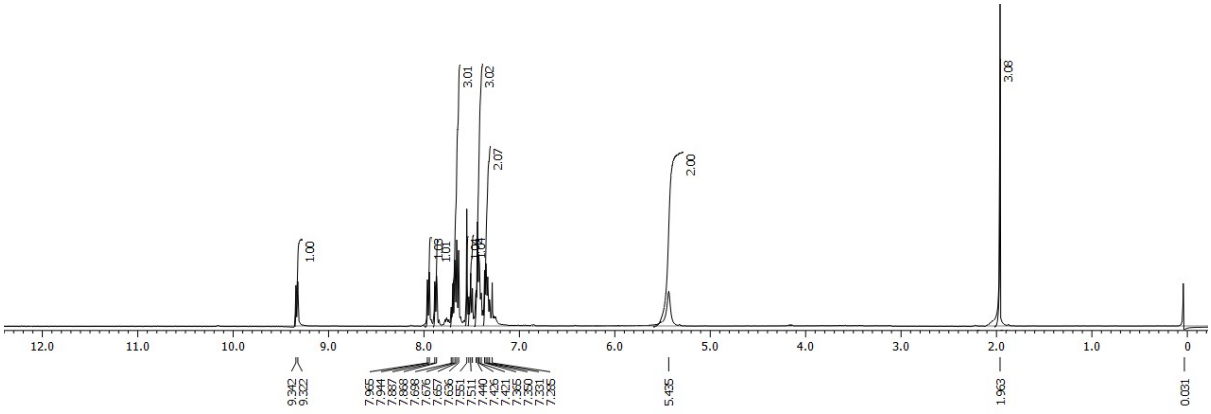


^{1}H NMR (400 MHz, $CDCl_3$)

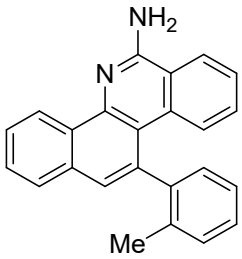


11-(*o*-Tolyl)benzo[*c*]phenanthridin-6-amine (3b)

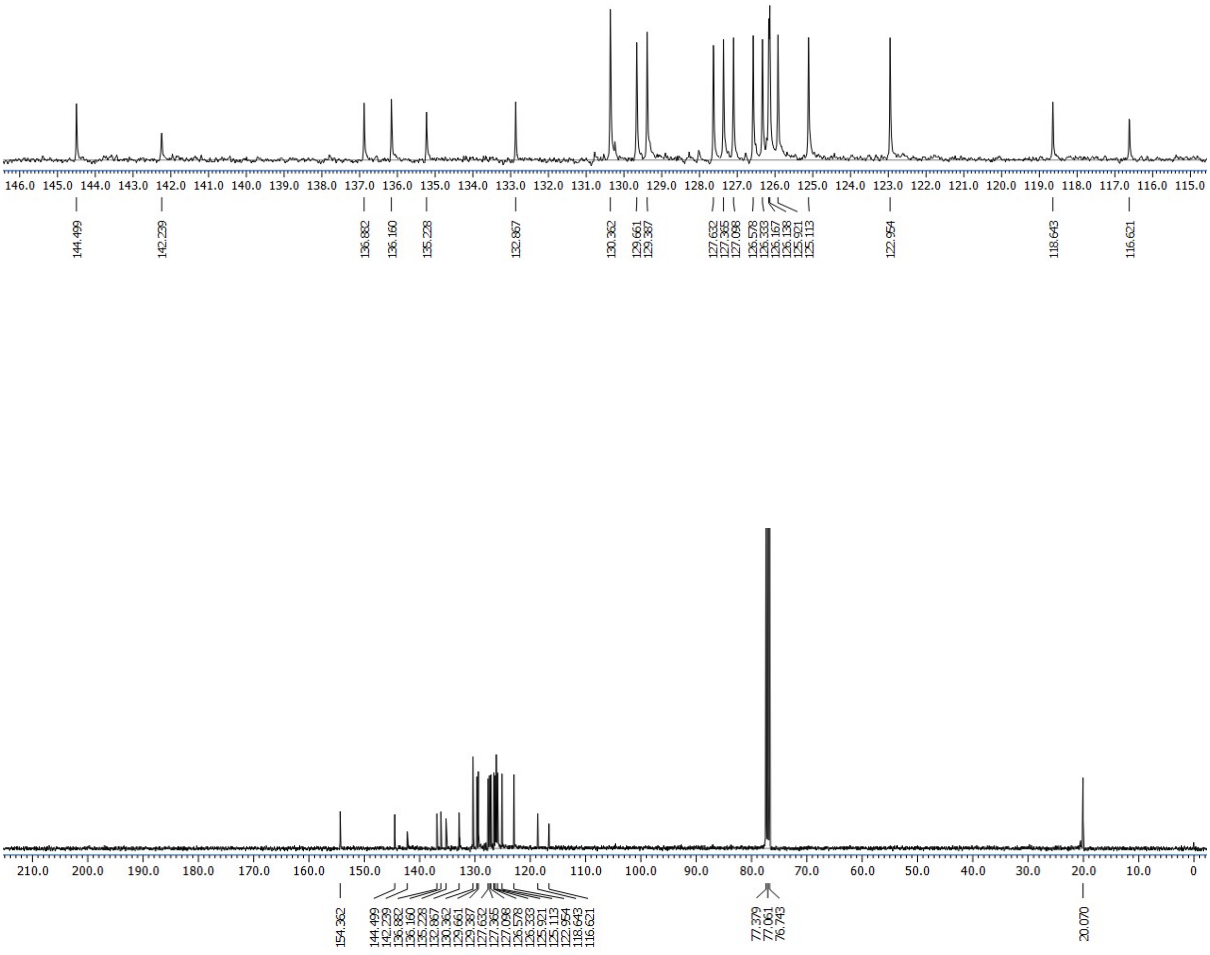




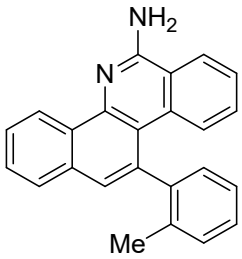
^{13}C NMR (100 MHz, $CDCl_3$)



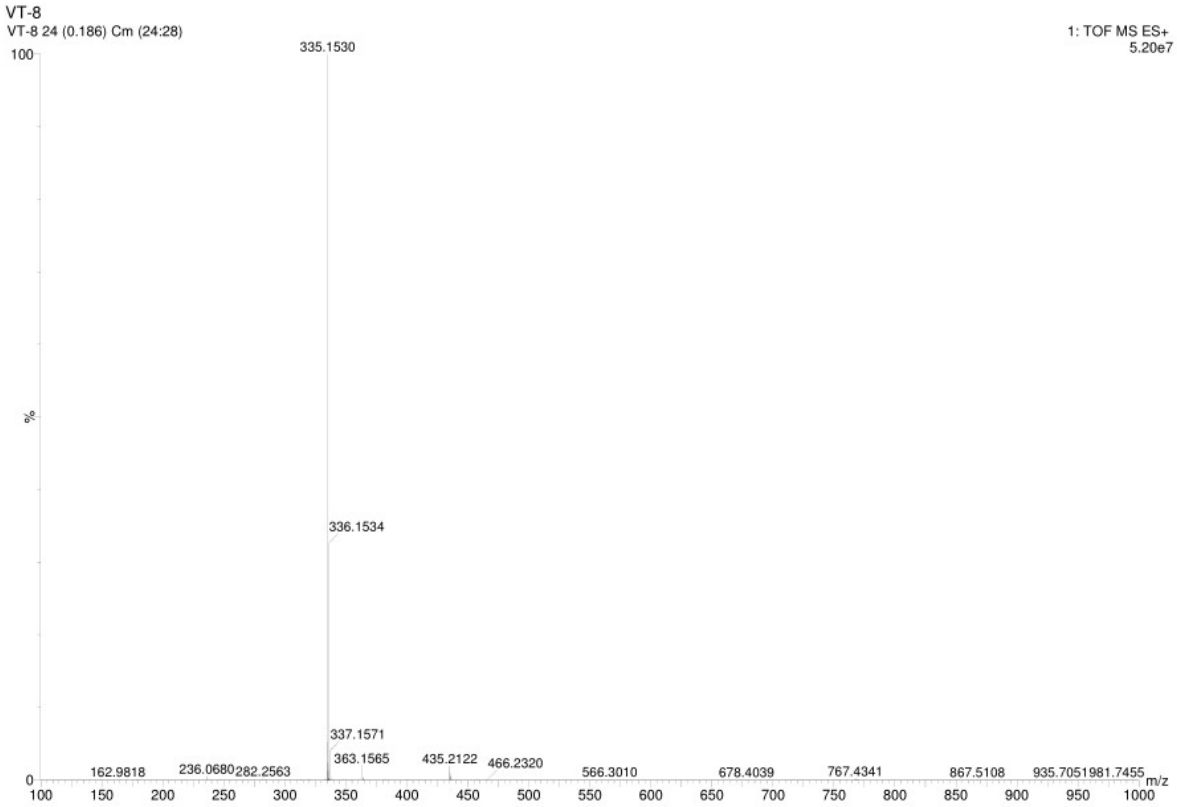
11-(*o*-Tolyl)benzo[*c*]phenanthridin-6-amine (3b)



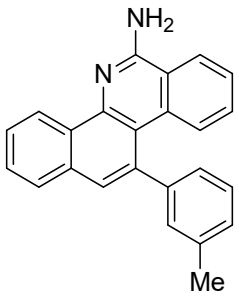
HRMS



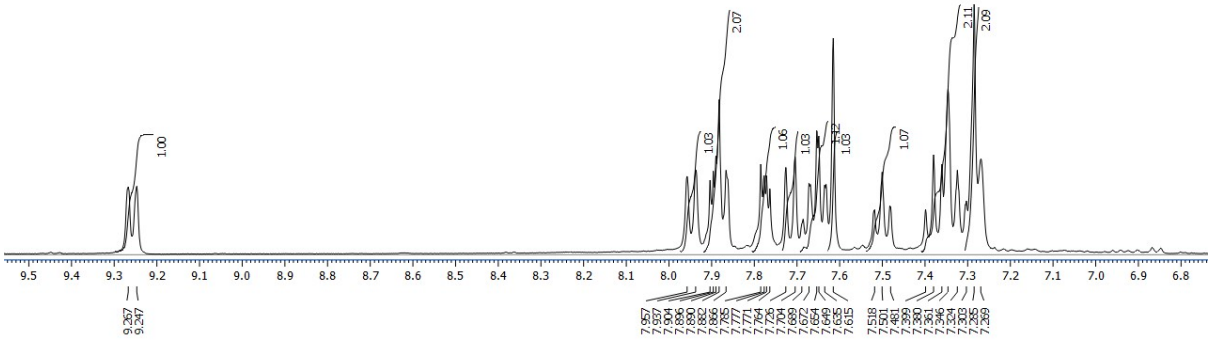
11-(*o*-Tolyl)benzo[*c*]phenanthridin-6-amine (3b)

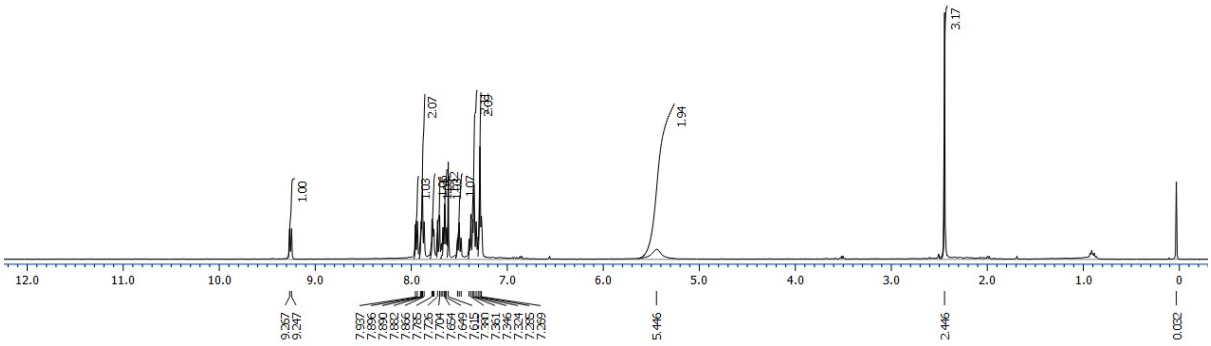


^{1}H NMR (400 MHz, $CDCl_3$)

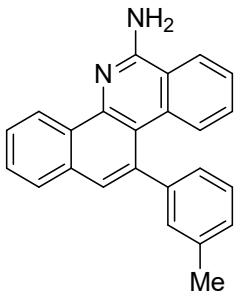


11-(*m*-Tolyl)benzo[*c*]phenanthridin-6-amine (3c)

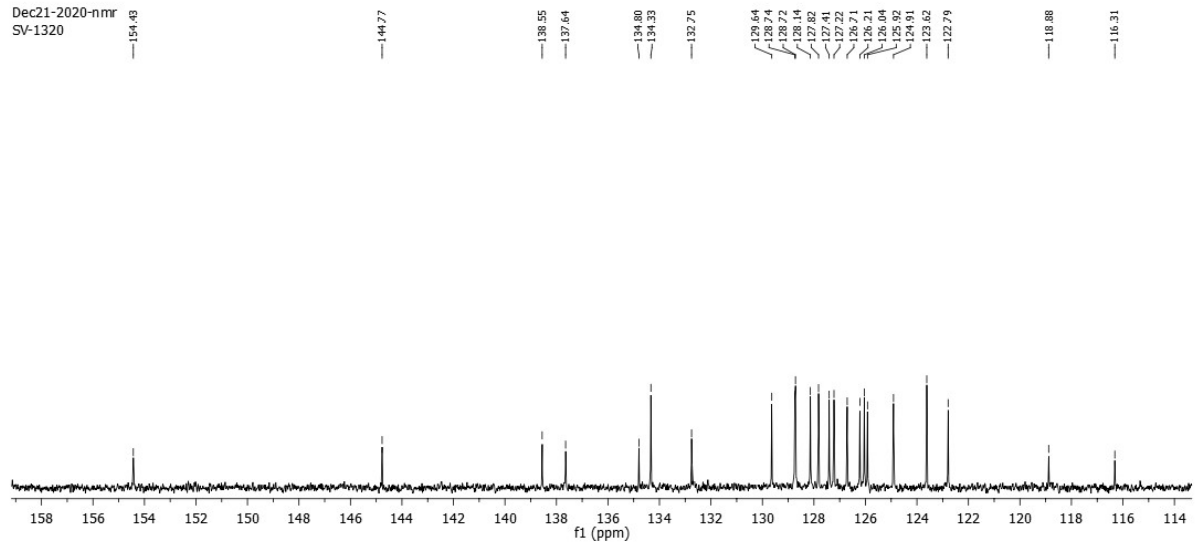


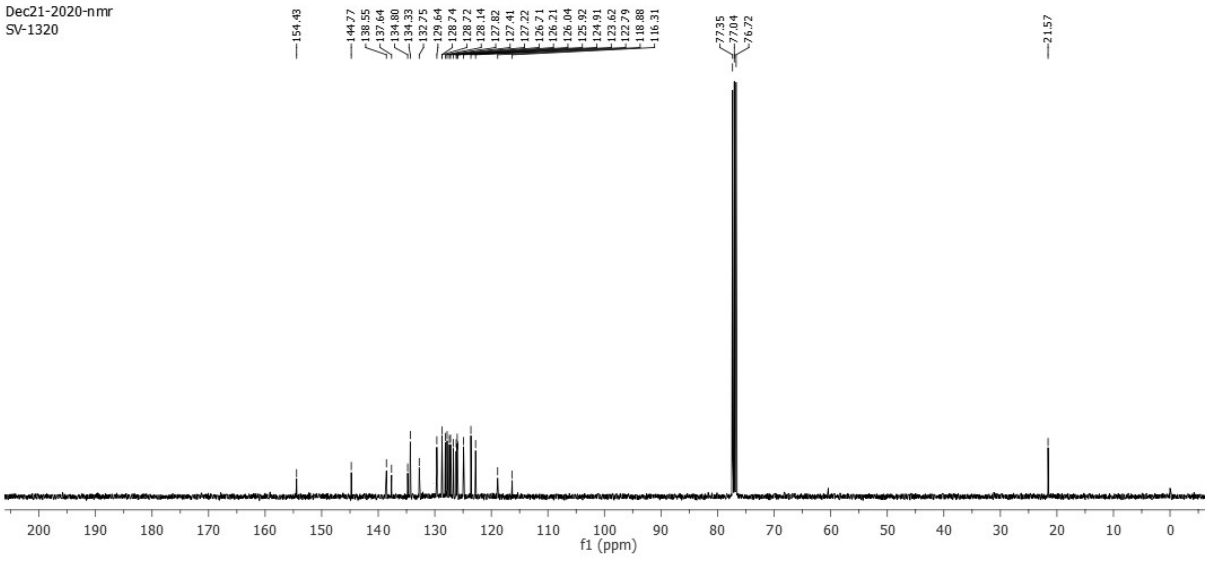


^{13}C NMR (100 MHz, $CDCl_3$)



11-(*m*-Tolyl)benzo[*c*]phenanthridin-6-amine (3c)





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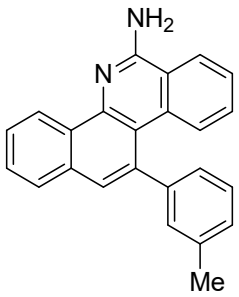
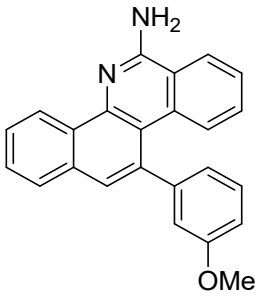
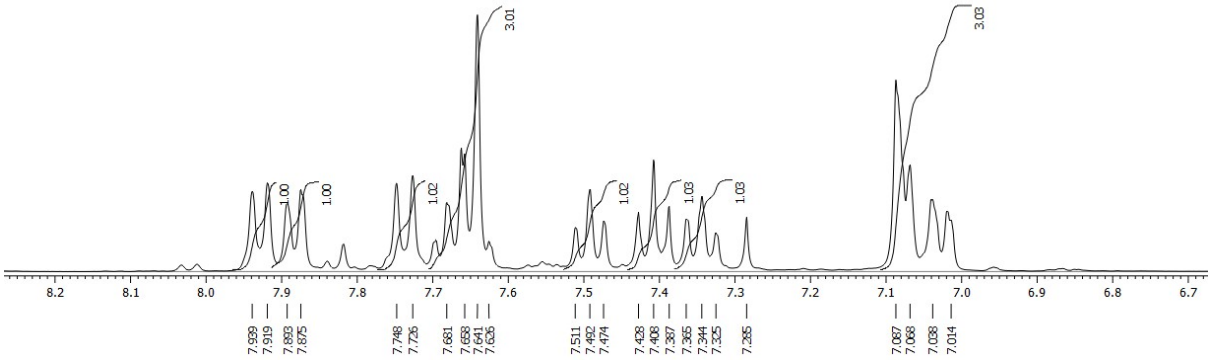


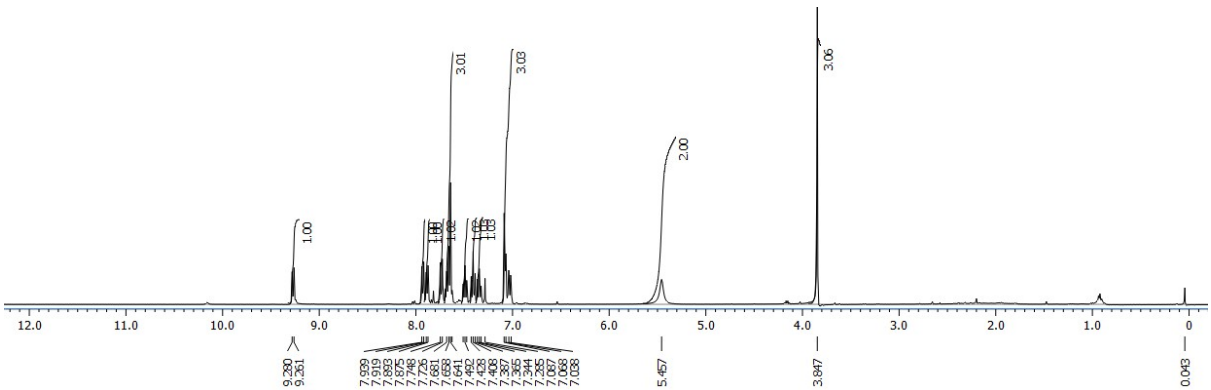
11-(*m*-Tolyl)benzo[*c*]phenanthridin-6-amine (3c)

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

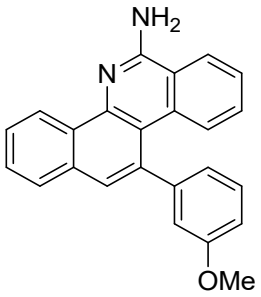


11-(3-Methoxyphenyl)benzo[*c*]phenanthridin-6-amine (3d)

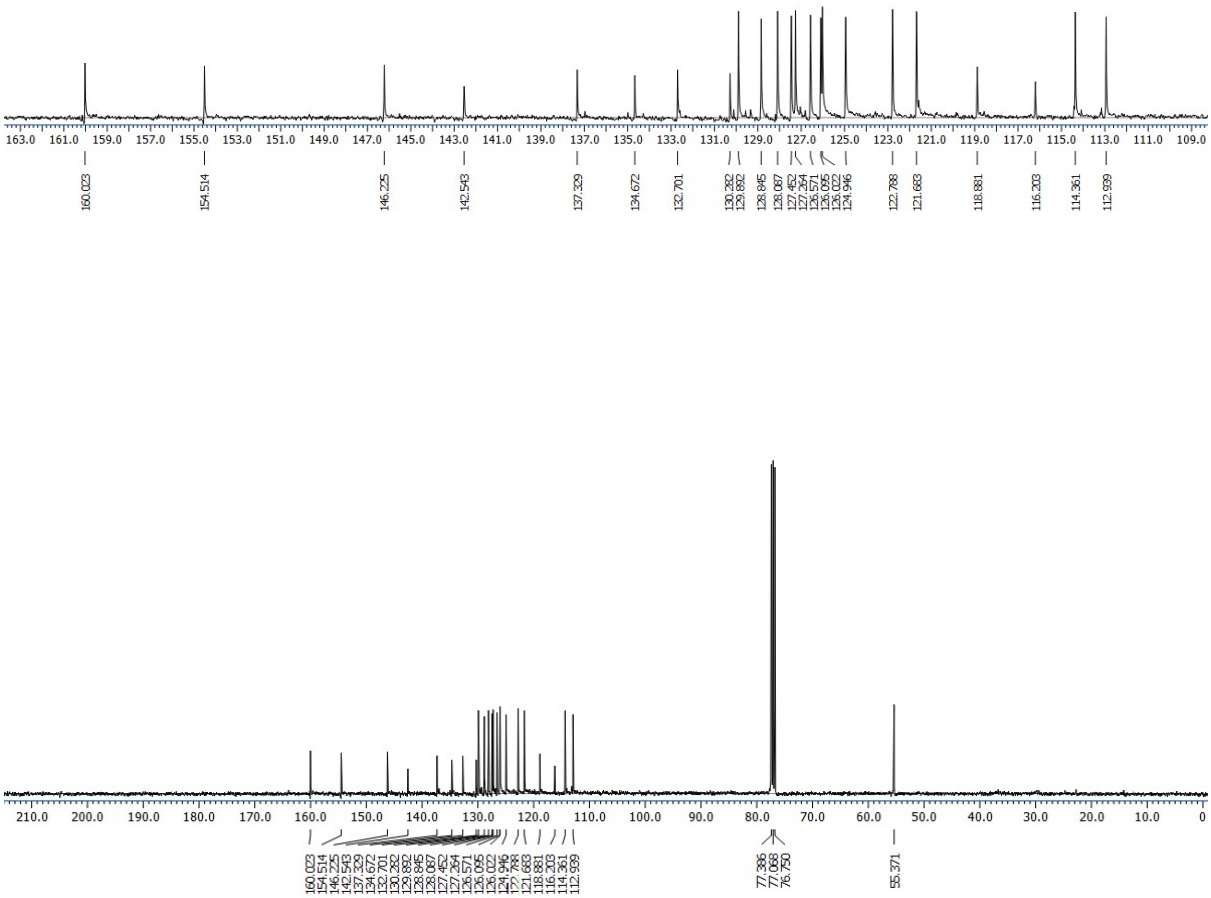




^{13}C NMR (100 MHz, $CDCl_3$)



11-(3-Methoxyphenyl)benzo[*c*]phenanthridin-6-amine (3d)



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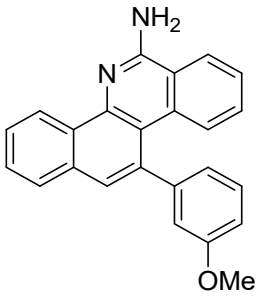
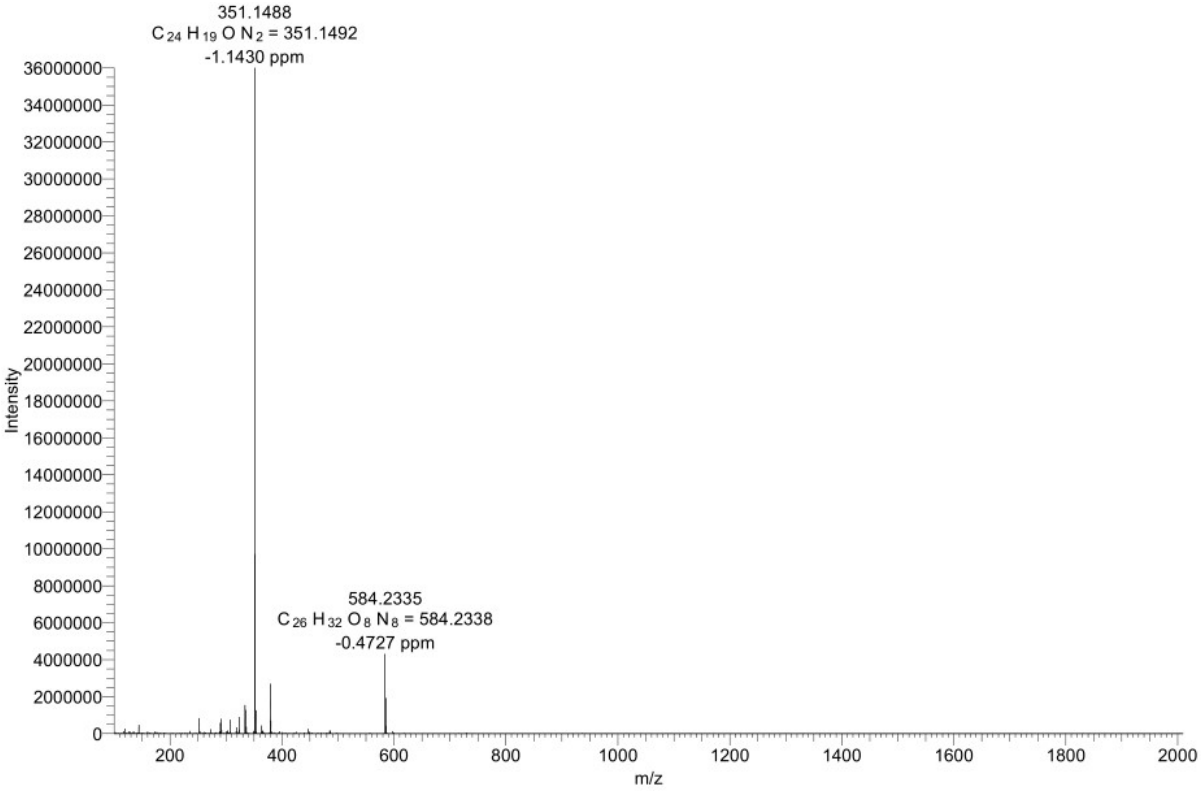
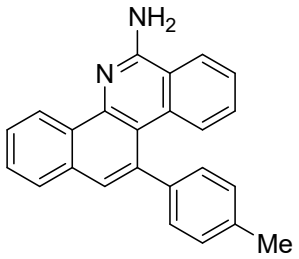


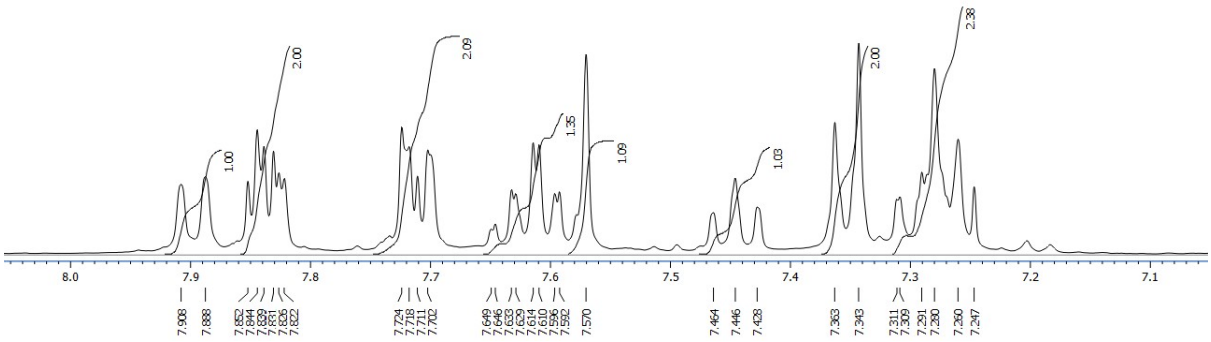
11-(3-Methoxyphenyl)benzo[*c*]phenanthridin-6-amine (3d)

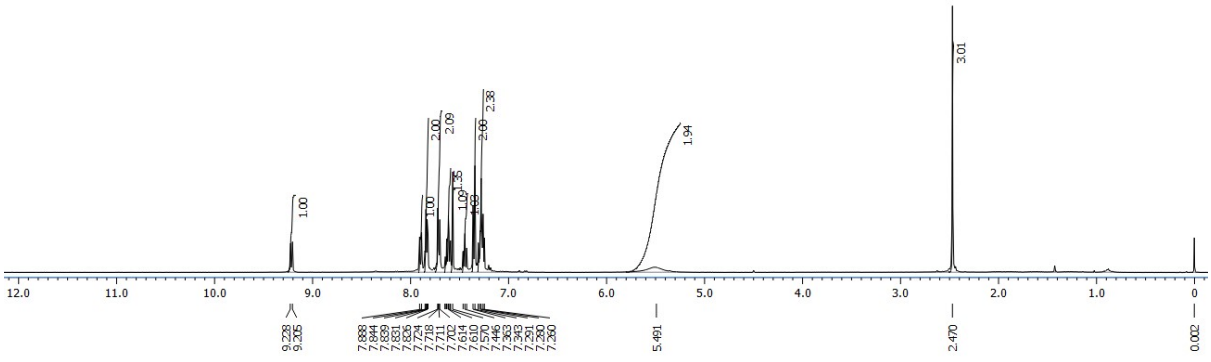


^{1}H NMR (400 MHz, $CDCl_3$)

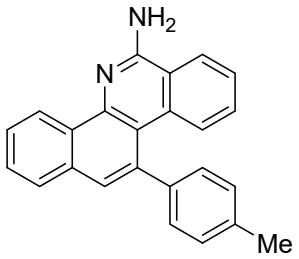


11-(*p*-Tolyl)benzo[*c*]phenanthridin-6-amine (3e)

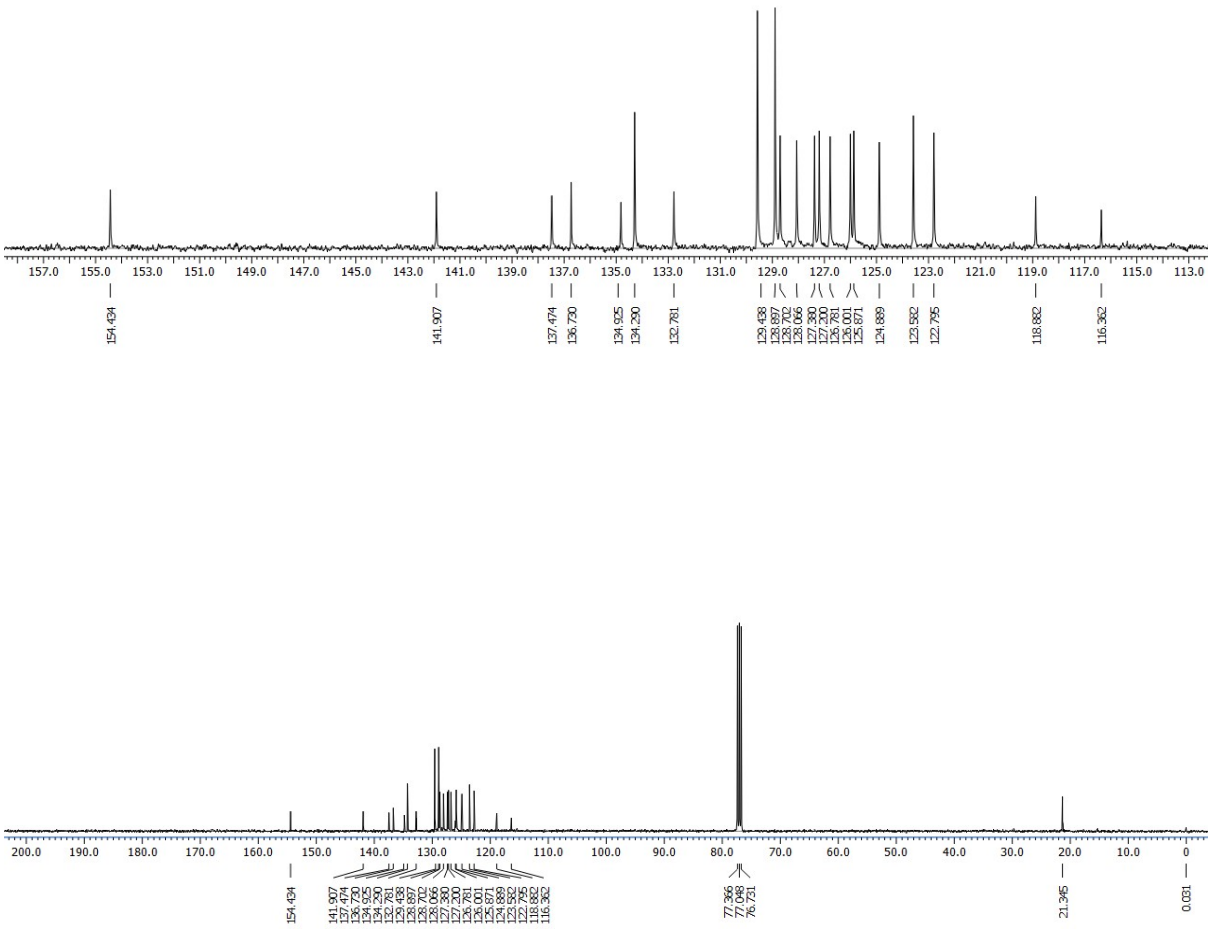




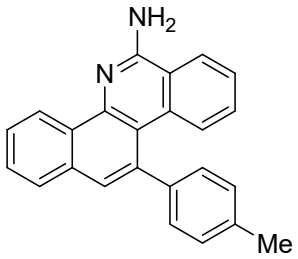
^{13}C NMR (100 MHz, $CDCl_3$)



11-(*p*-Tolyl)benzo[*c*]phenanthridin-6-amine (3e)

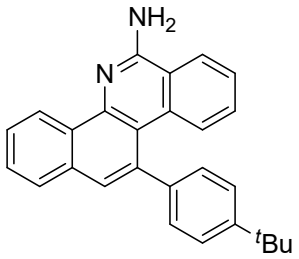


HRMS

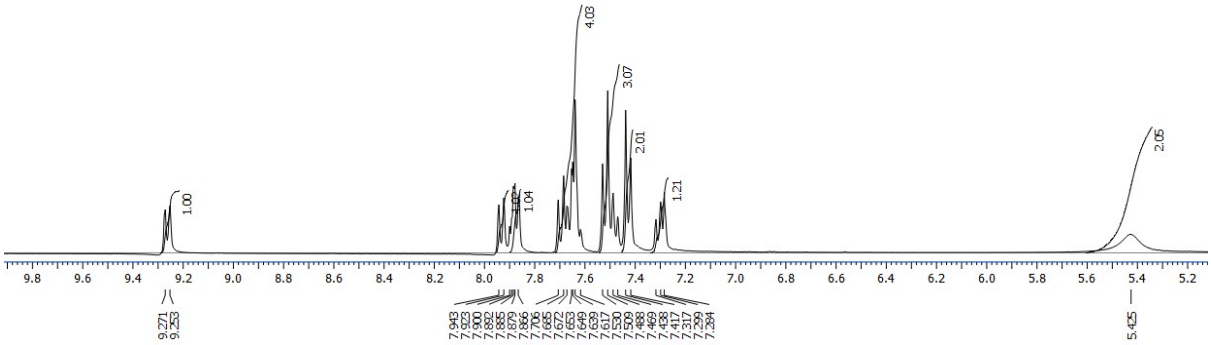


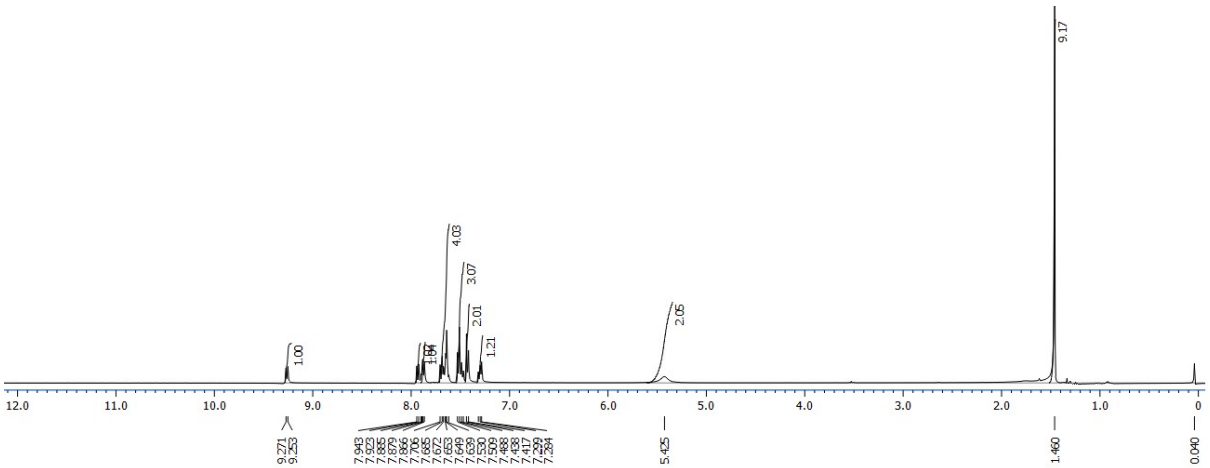
11-(*p*-Tolyl)benzo[*c*]phenanthridin-6-amine (3e)

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

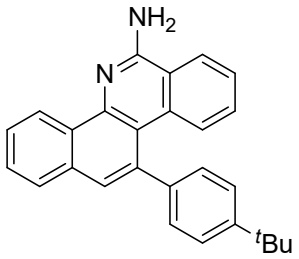


11-(4-(*tert*-Butyl)phenyl)benzo[*c*]phenanthridin-6-amine (3f)

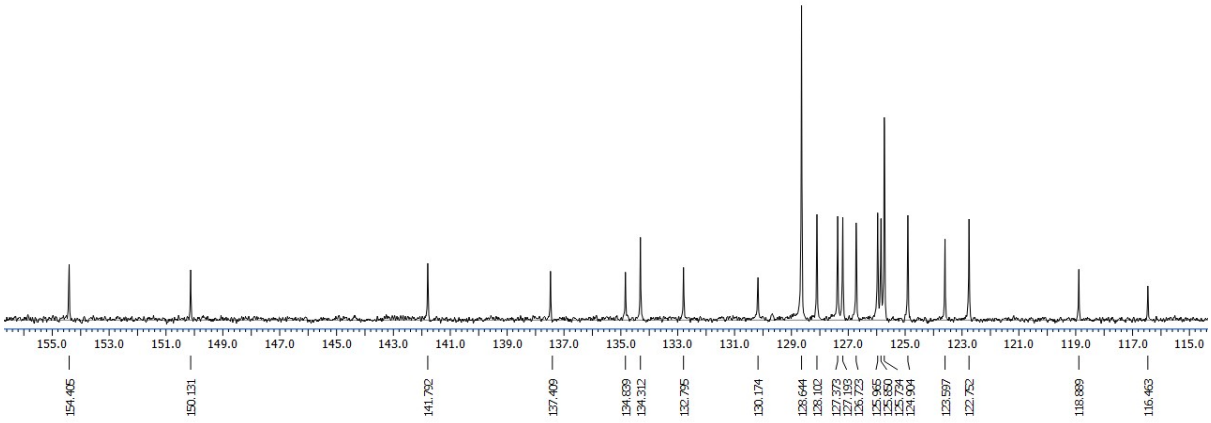


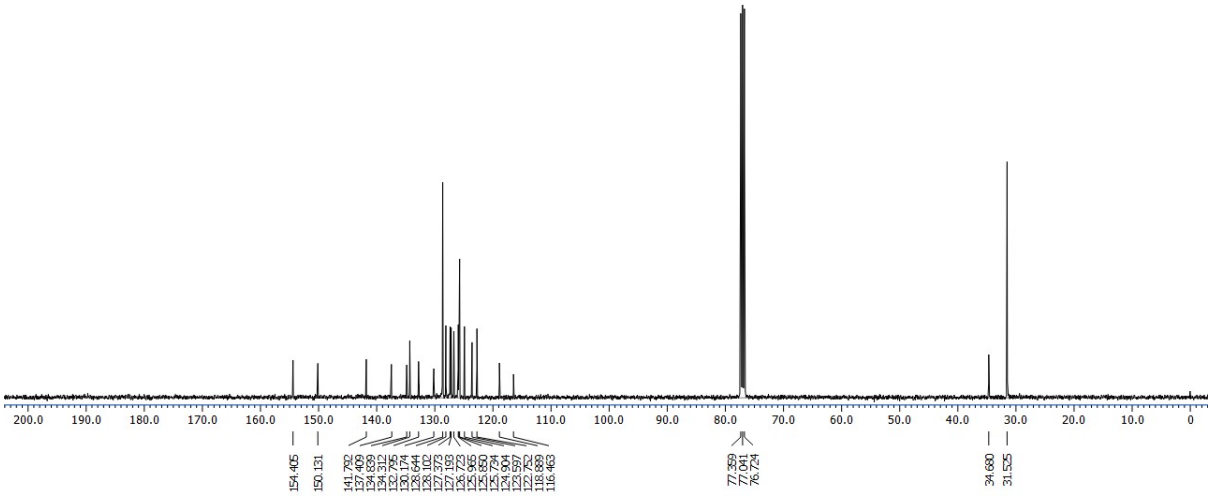


^{13}C NMR (100 MHz, $CDCl_3$)

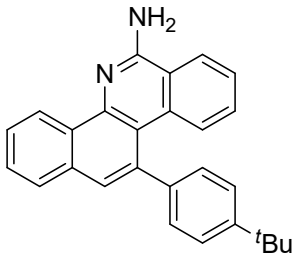


11-(4-(*tert*-Butyl)phenyl)benzo[*c*]phenanthridin-6-amine (3f)

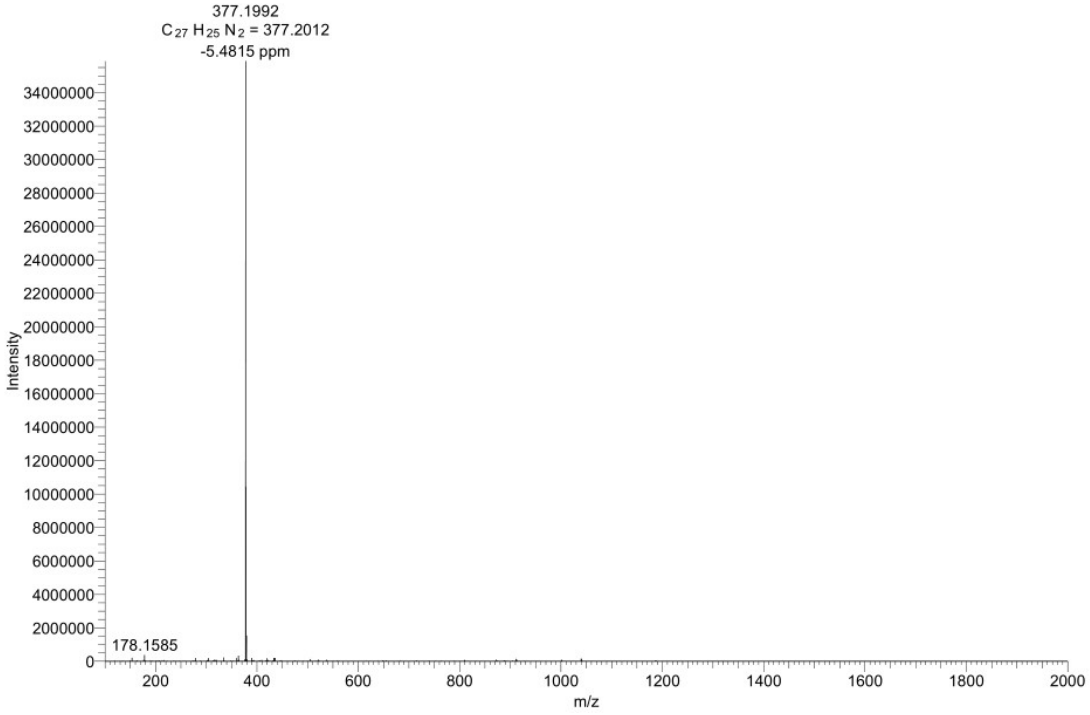




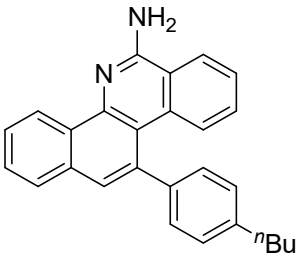
HRMS



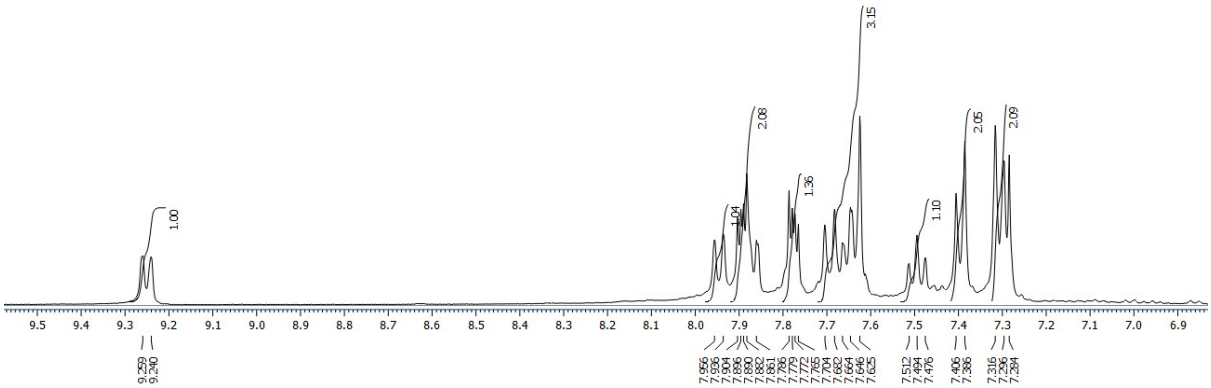
11-(4-(*tert*-Butyl)phenyl)benzo[*c*]phenanthridin-6-amine (3f)

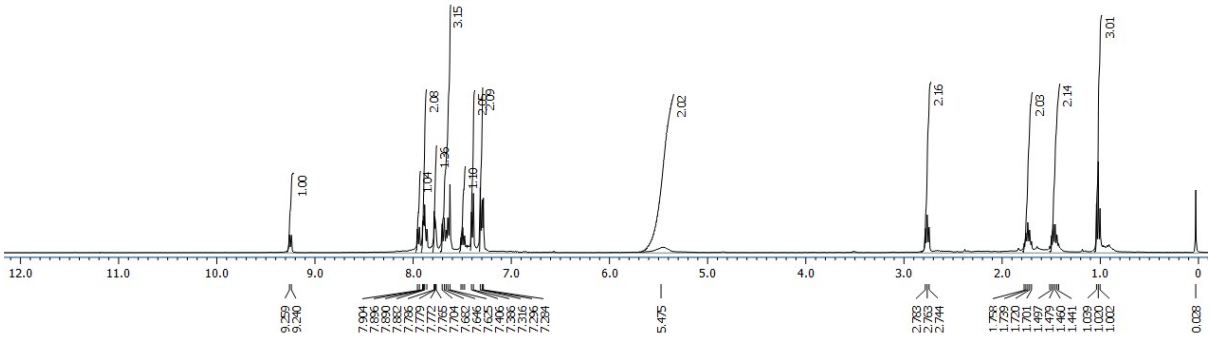


^{1}H NMR (400 MHz, $CDCl_3$)

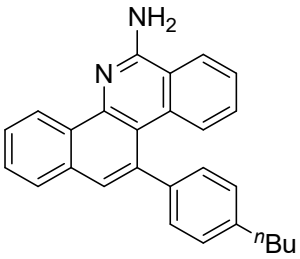


11-(4-Butylphenyl)benzo[*c*]phenanthridin-6-amine (3g)

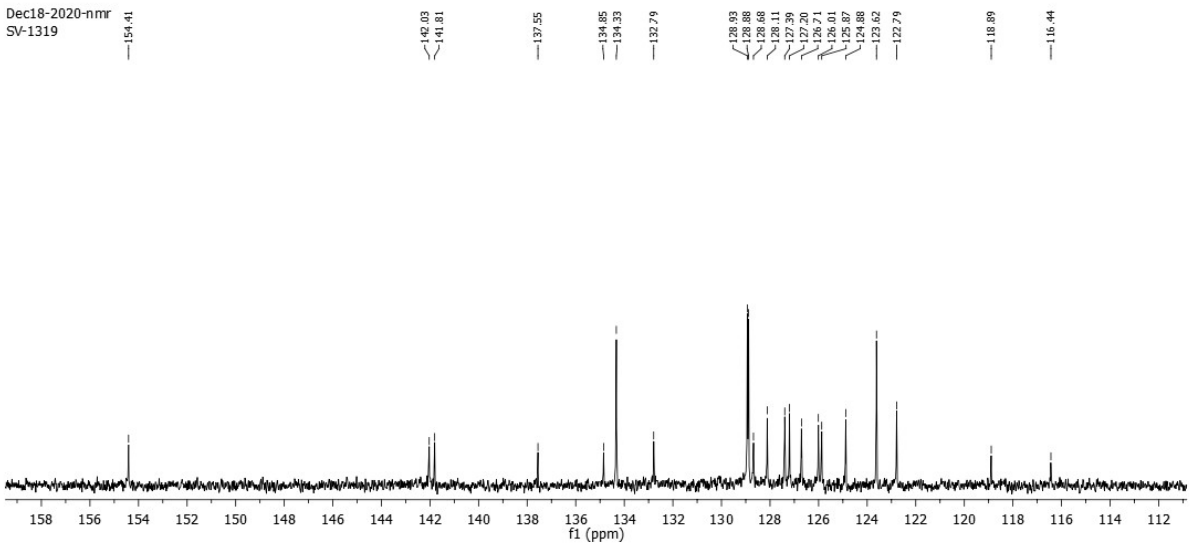


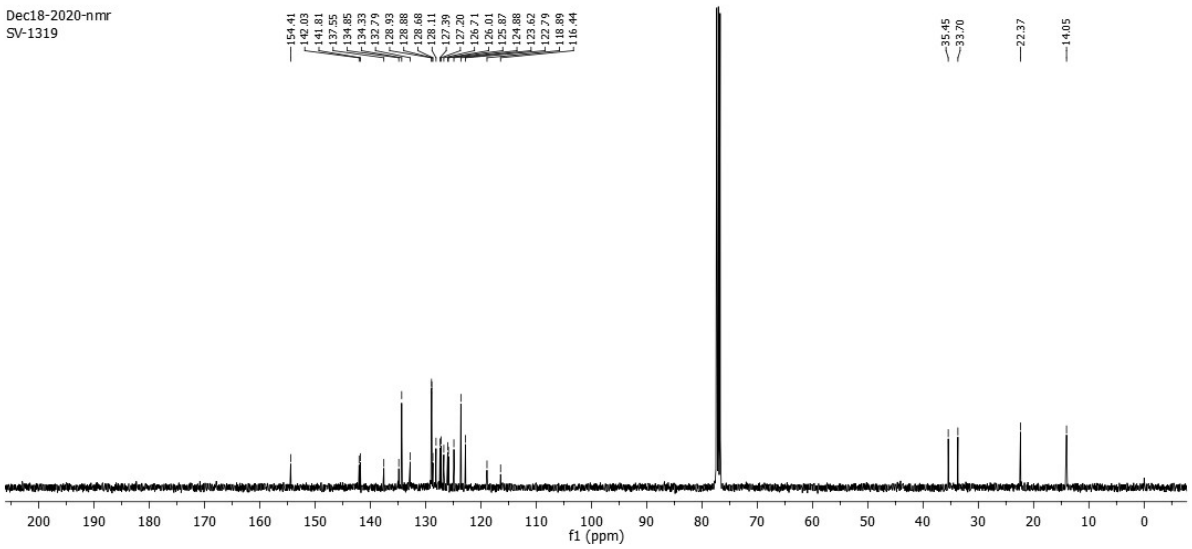


^{13}C NMR (100 MHz, $CDCl_3$)



11-(4-Butylphenyl)benzo[*c*]phenanthridin-6-amine (3g)





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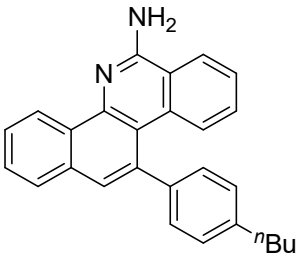
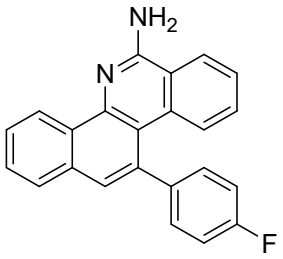
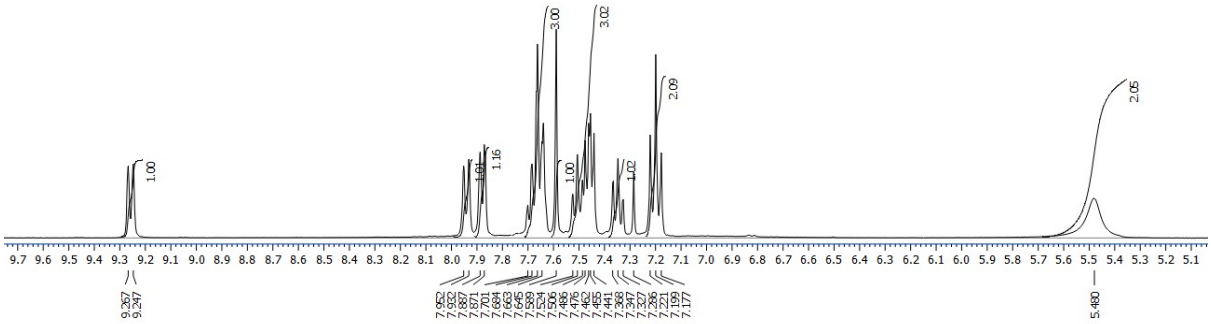


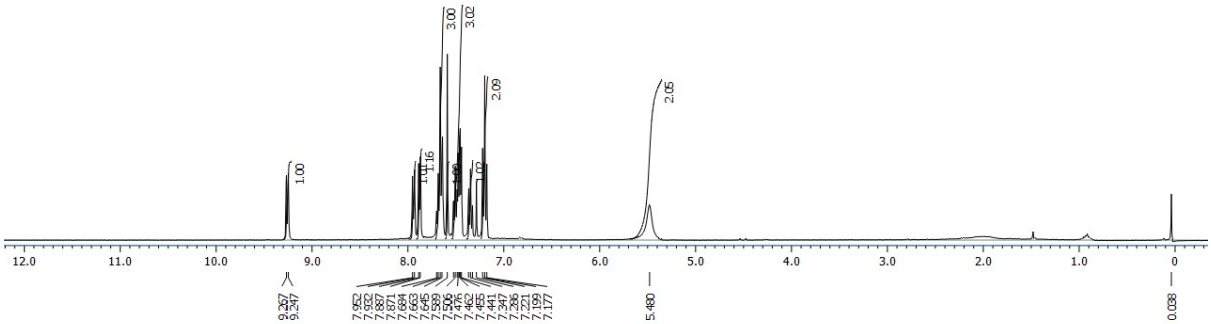
11-(4-Butylphenyl)benzo[*c*]phenanthridin-6-amine (3g)

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

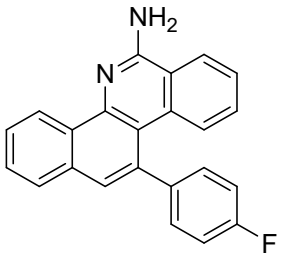


11-(4-Fluorophenyl)benzo[*c*]phenanthridin-6-amine (3h)

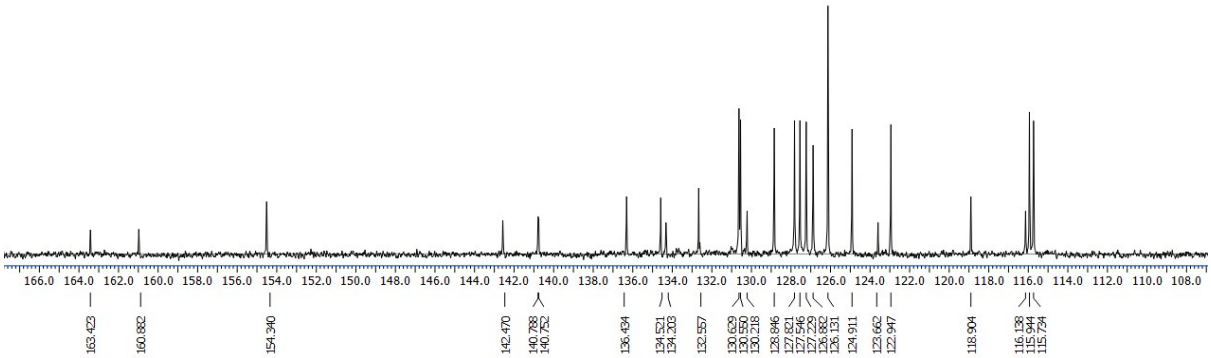


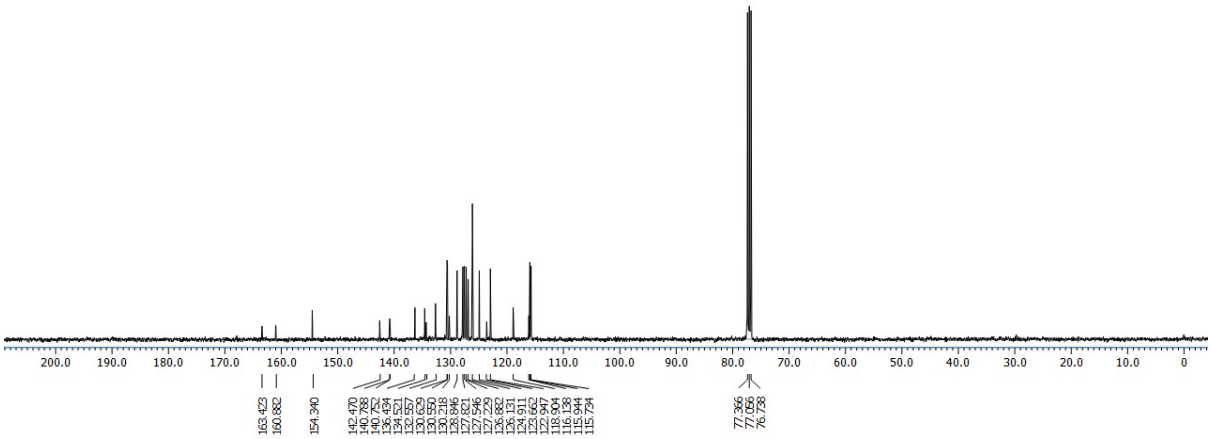


^{13}C NMR (100 MHz, $CDCl_3$)

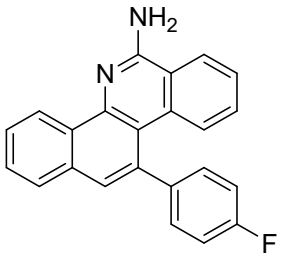


11-(4-Fluorophenyl)benzo[*c*]phenanthridin-6-amine (3h)

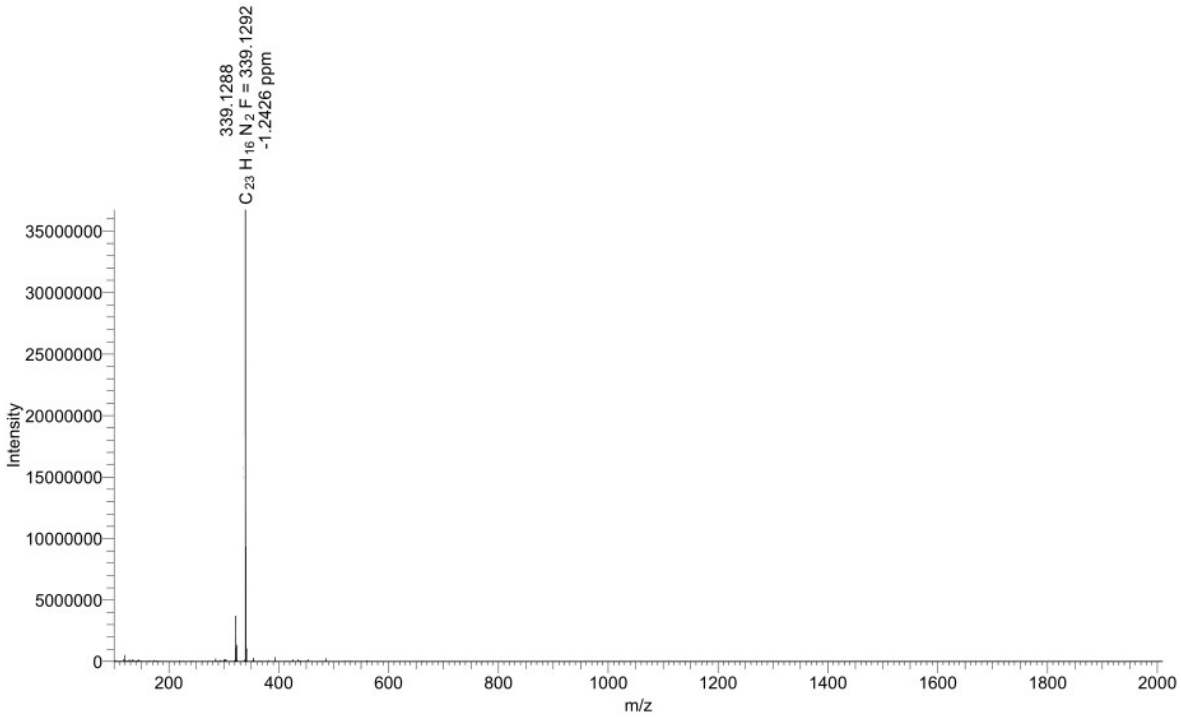




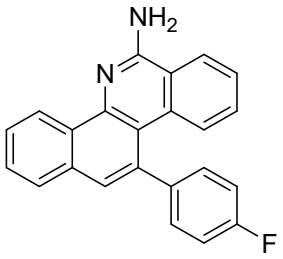
HRMS



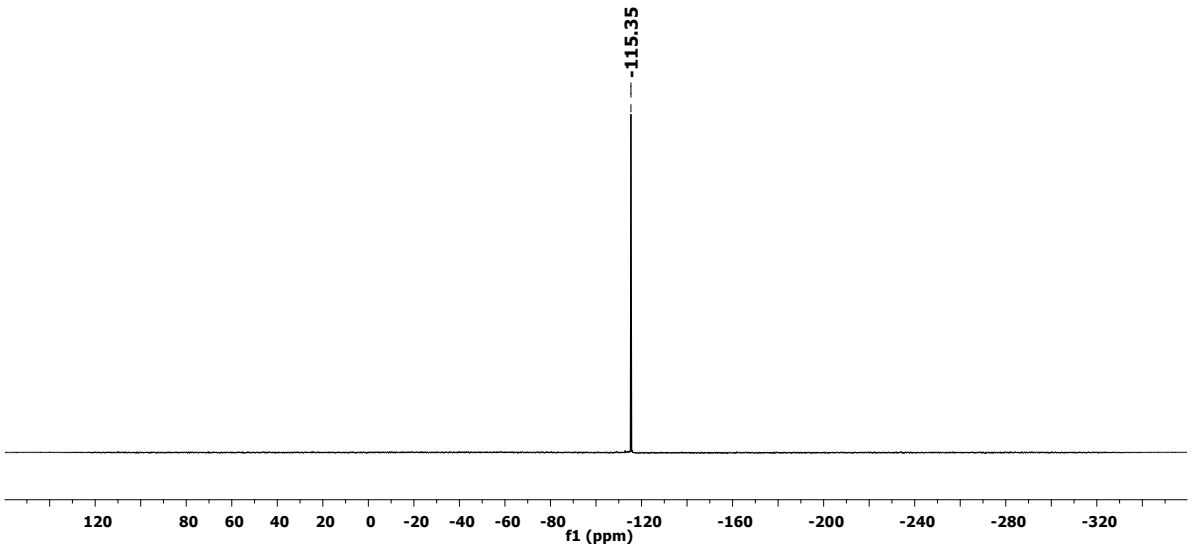
11-(4-Fluorophenyl)benzo[*c*]phenanthridin-6-amine (3h)



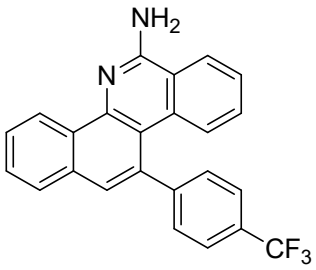
^{19}F NMR (376 MHz, $CDCl_3$)



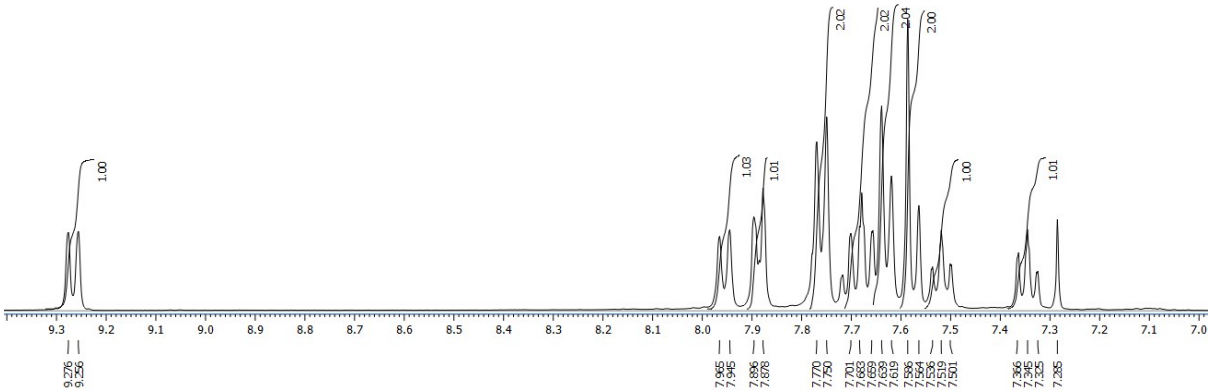
11-(4-Fluorophenyl)benzo[*c*]phenanthridin-6-amine (3h)

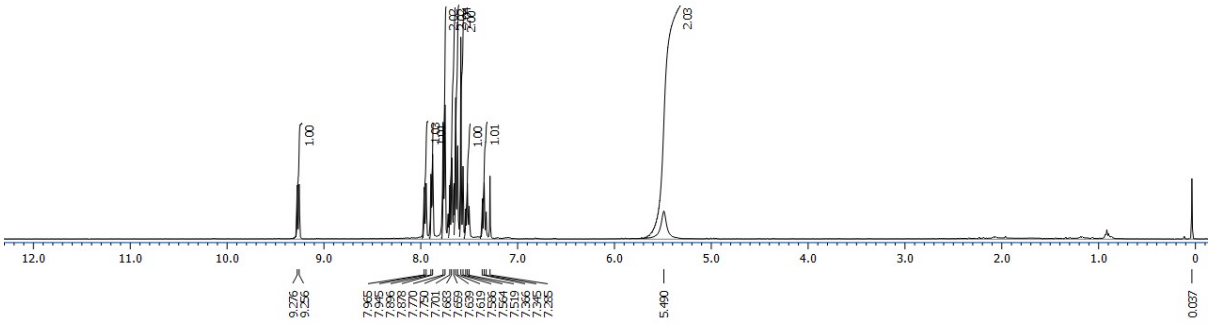


^{1}H NMR (400 MHz, $CDCl_3$)

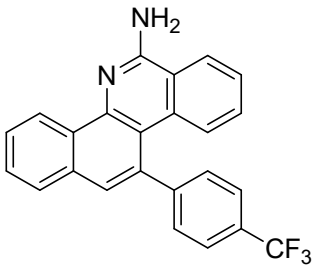


11-(4-(Trifluoromethyl)phenyl)benzo[*c*]phenanthridin-6-amine (3i)

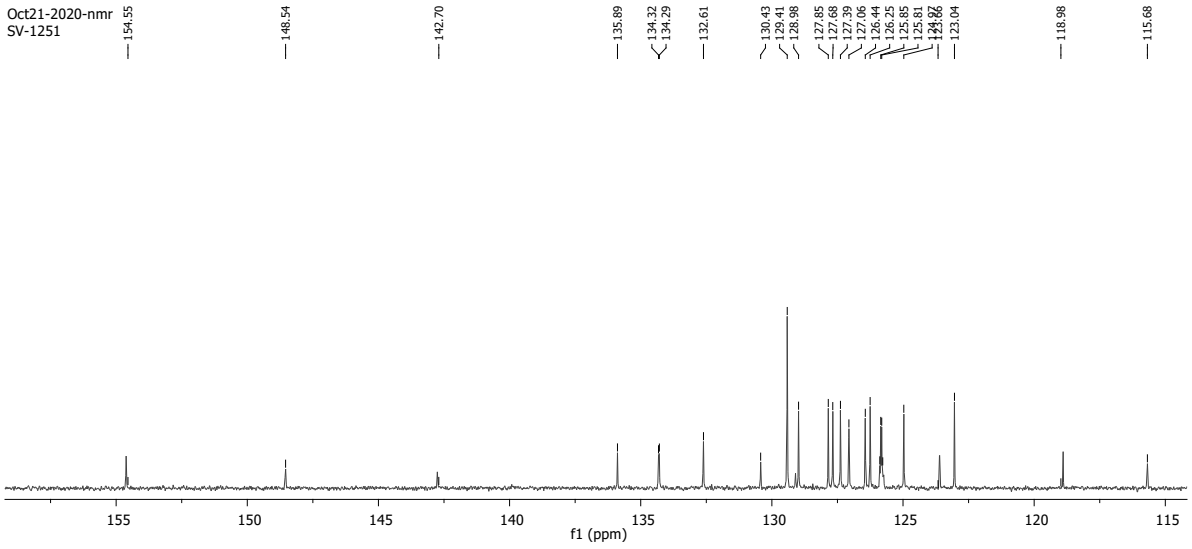


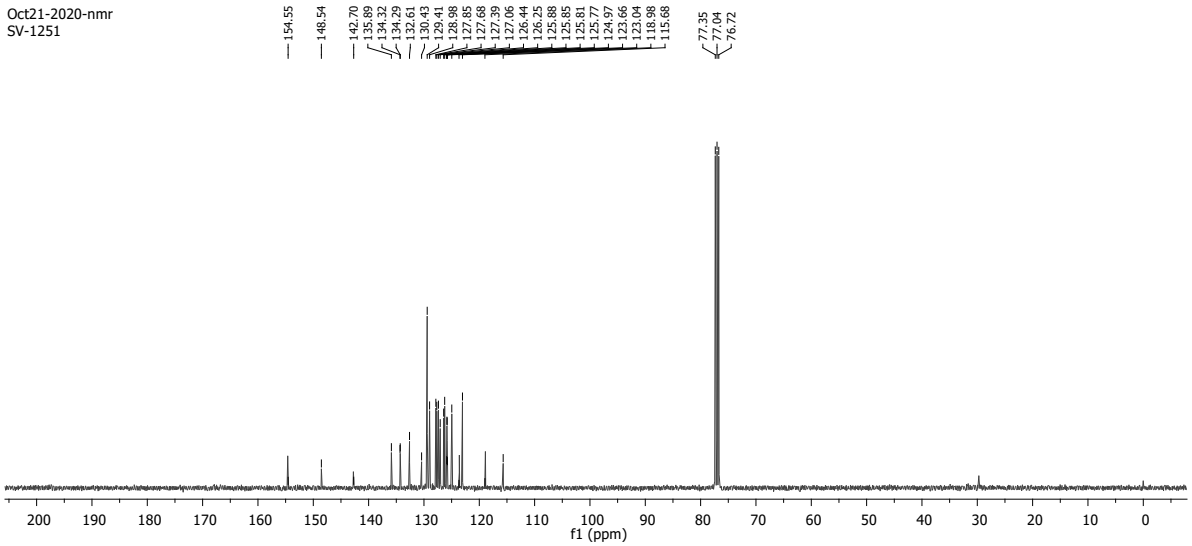


^{13}C NMR (100 MHz, $CDCl_3$)

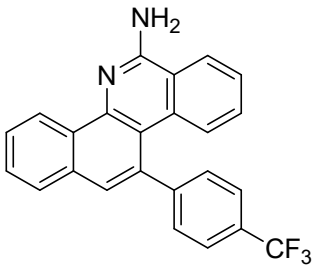


11-(4-(Trifluoromethyl)phenyl)benzo[*c*]phenanthridin-6-amine (3i)

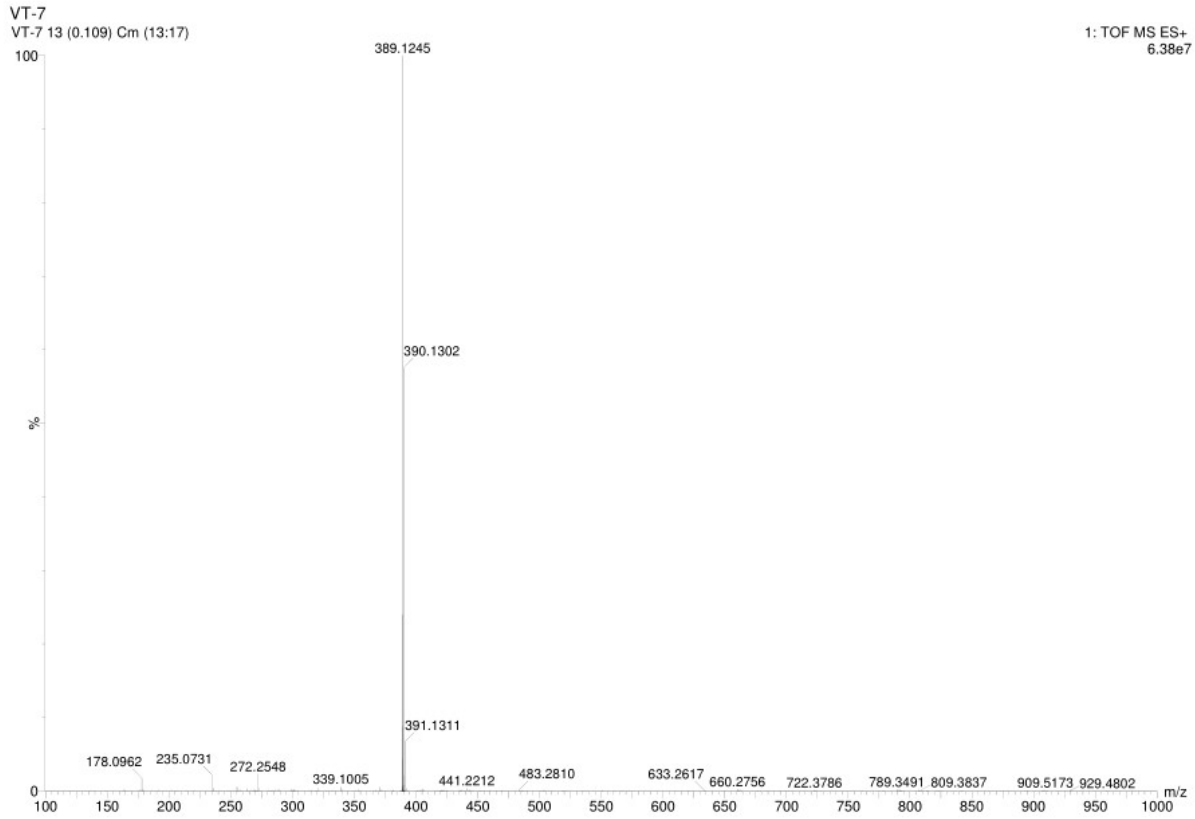




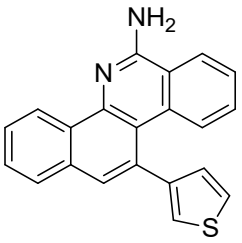
HRMS



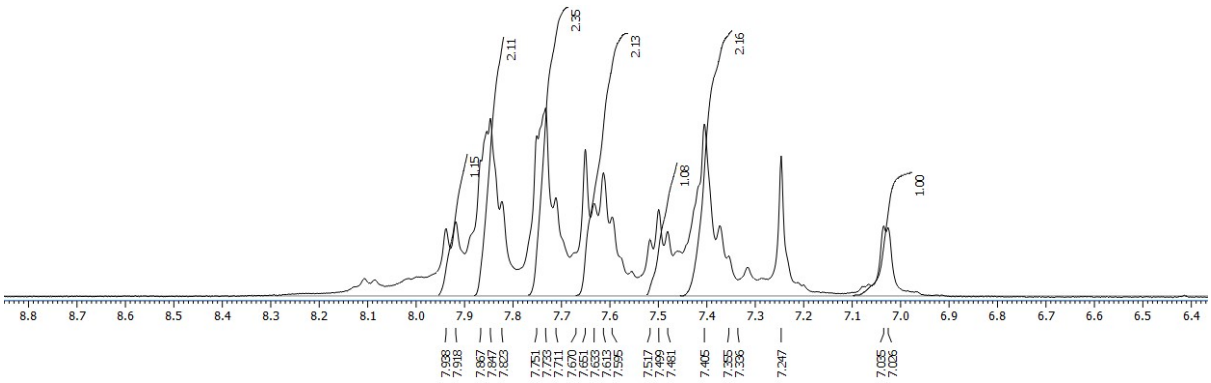
11-(4-(Trifluoromethyl)phenyl)benzo[*c*]phenanthridin-6-amine (3i)

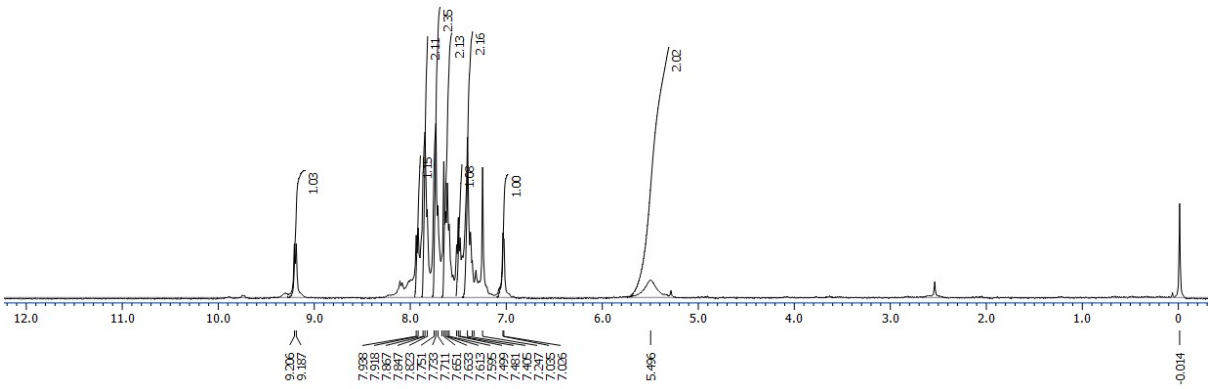


^{1}H NMR (400 MHz, $CDCl_3$)

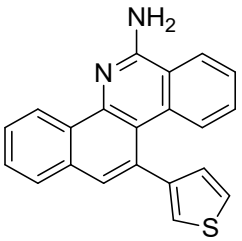


11-(Thiophen-3-yl)benzo[*c*]phenanthridin-6-amine (3j)

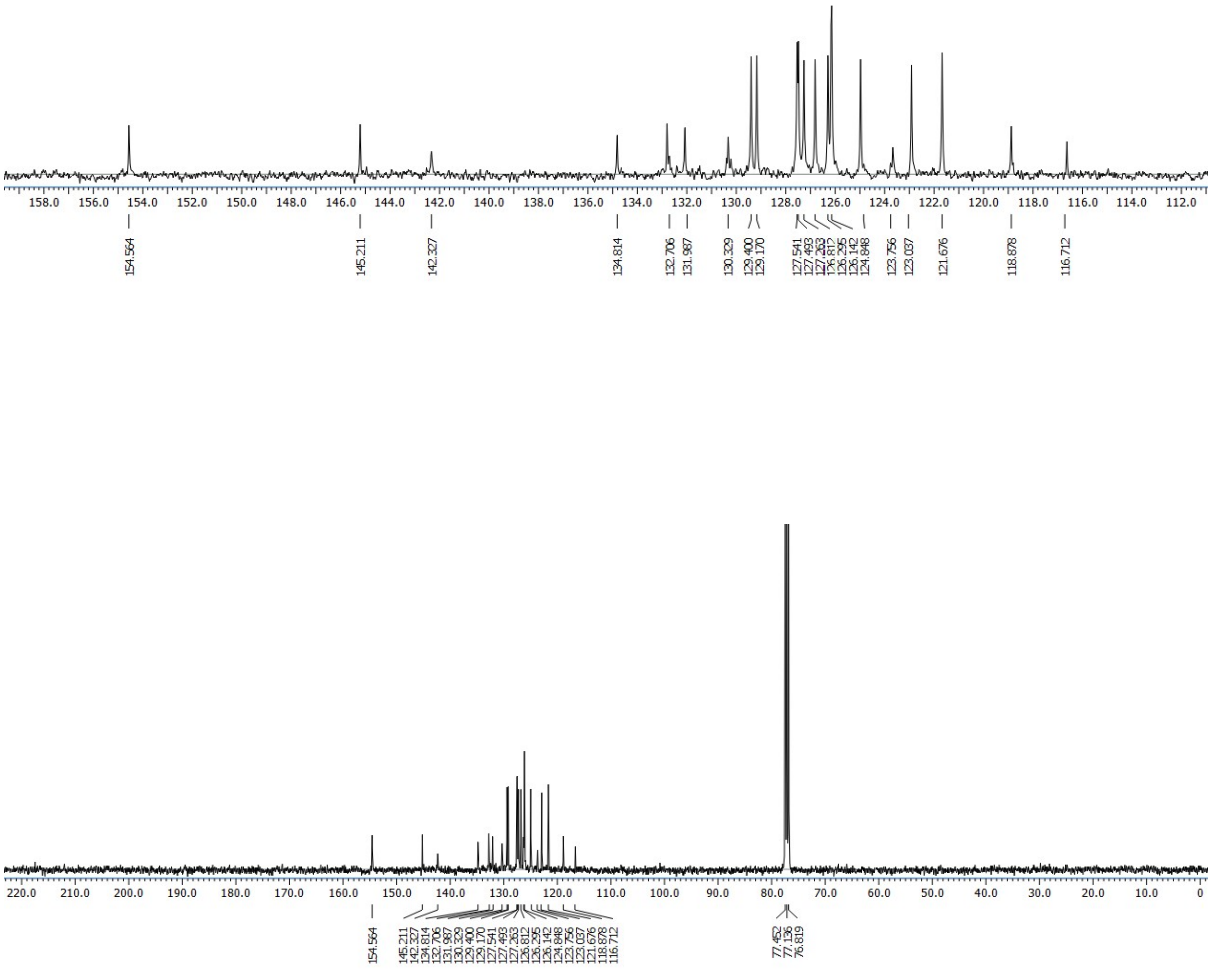




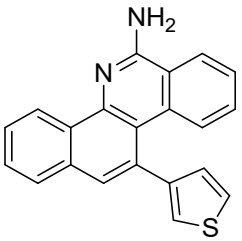
^{13}C NMR (100 MHz, $CDCl_3$)



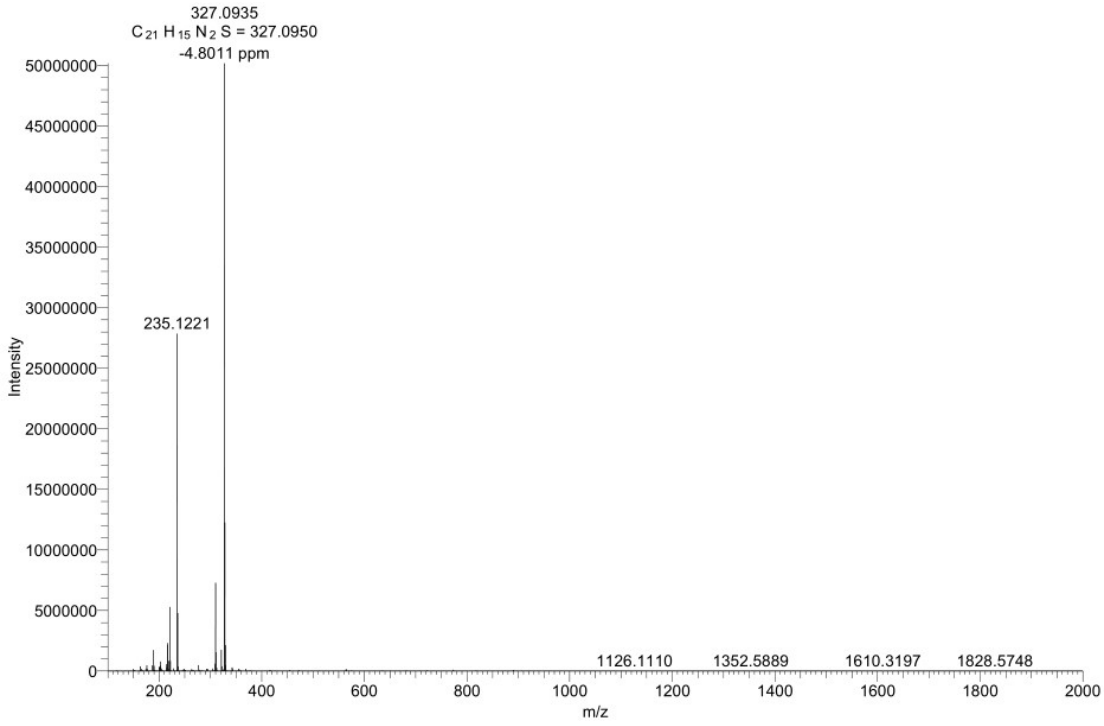
11-(Thiophen-3-yl)benzo[*c*]phenanthridin-6-amine (3j)



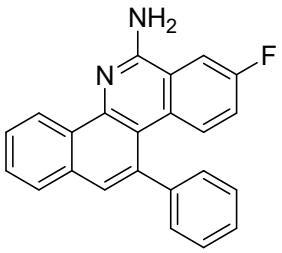
HRMS



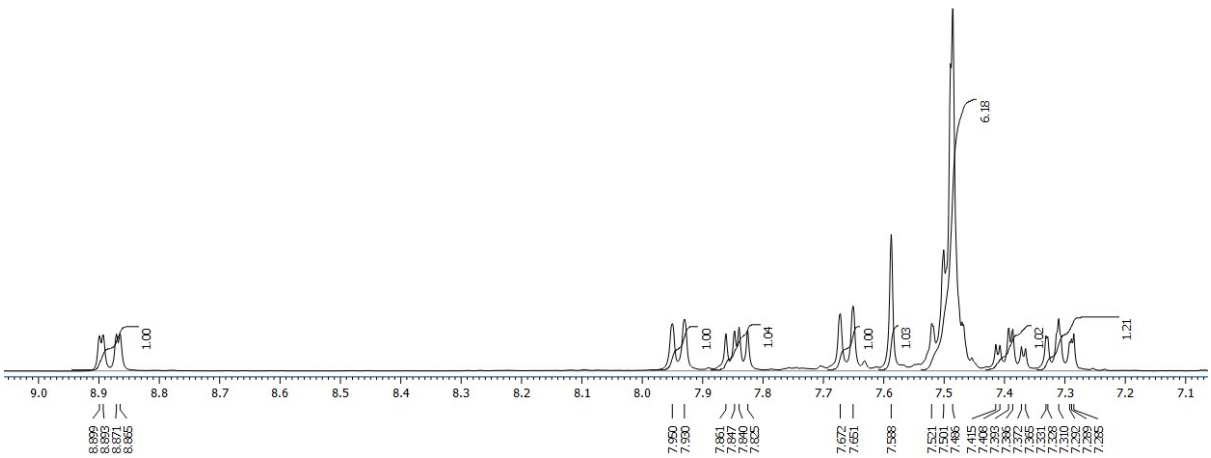
11-(Thiophen-3-yl)benzo[*c*]phenanthridin-6-amine (3j)

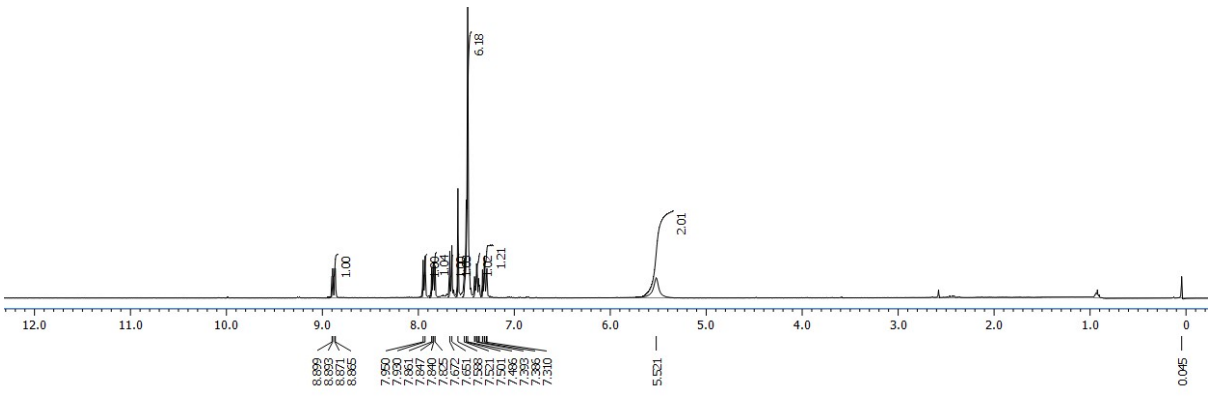


^{1}H NMR (400 MHz, $CDCl_3$)

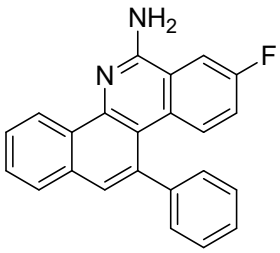


8-Fluoro-11-phenylbenzo[*c*]phenanthridin-6-amine (3k)

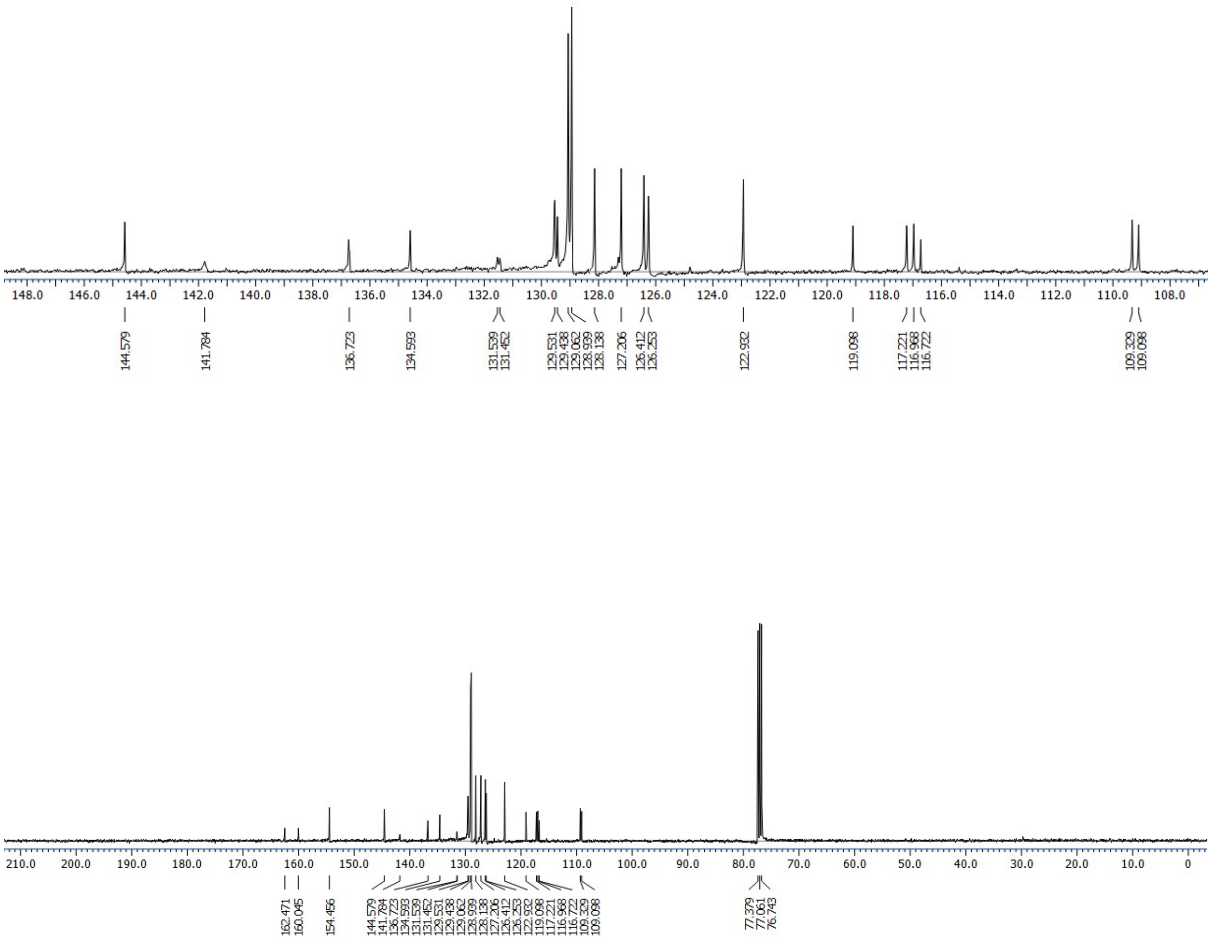




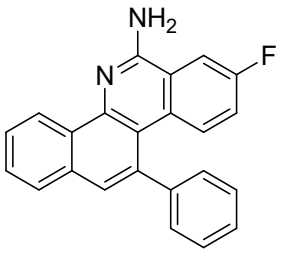
^{13}C NMR (100 MHz, $CDCl_3$)



8-Fluoro-11-phenylbenzo[*c*]phenanthridin-6-amine (3k)

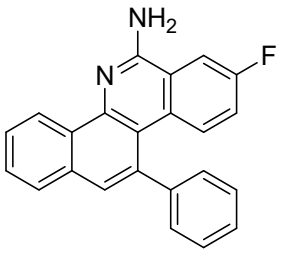


HRMS

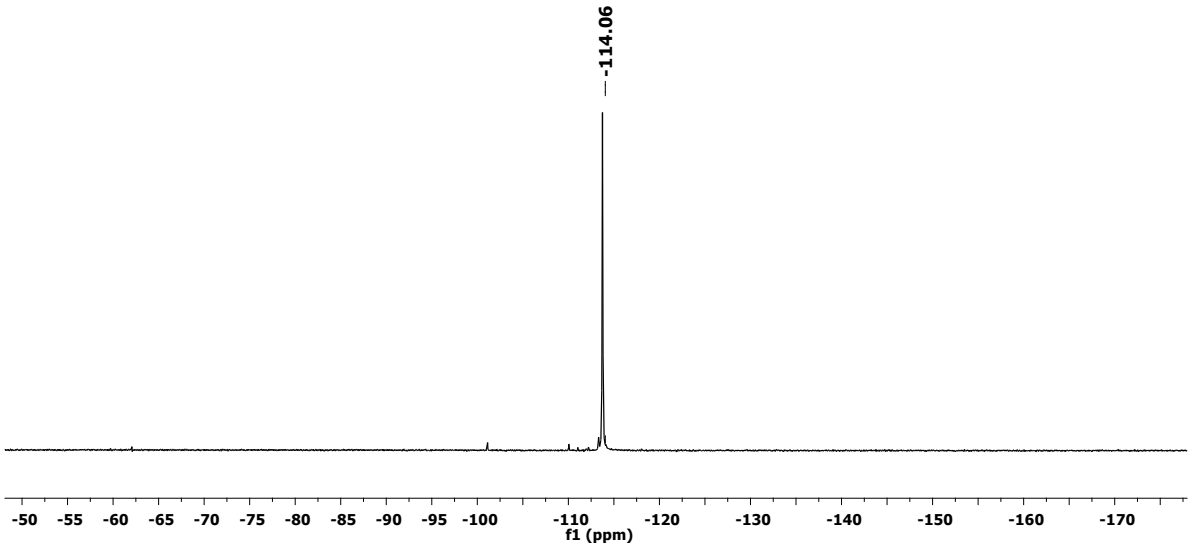


8-Fluoro-11-phenylbenzo[*c*]phenanthridin-6-amine (3k)

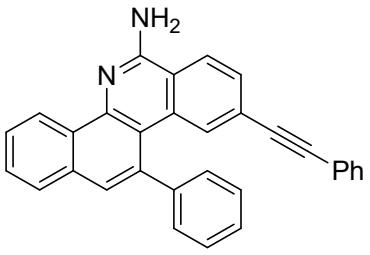
^{19}F NMR (376 MHz, $CDCl_3$)



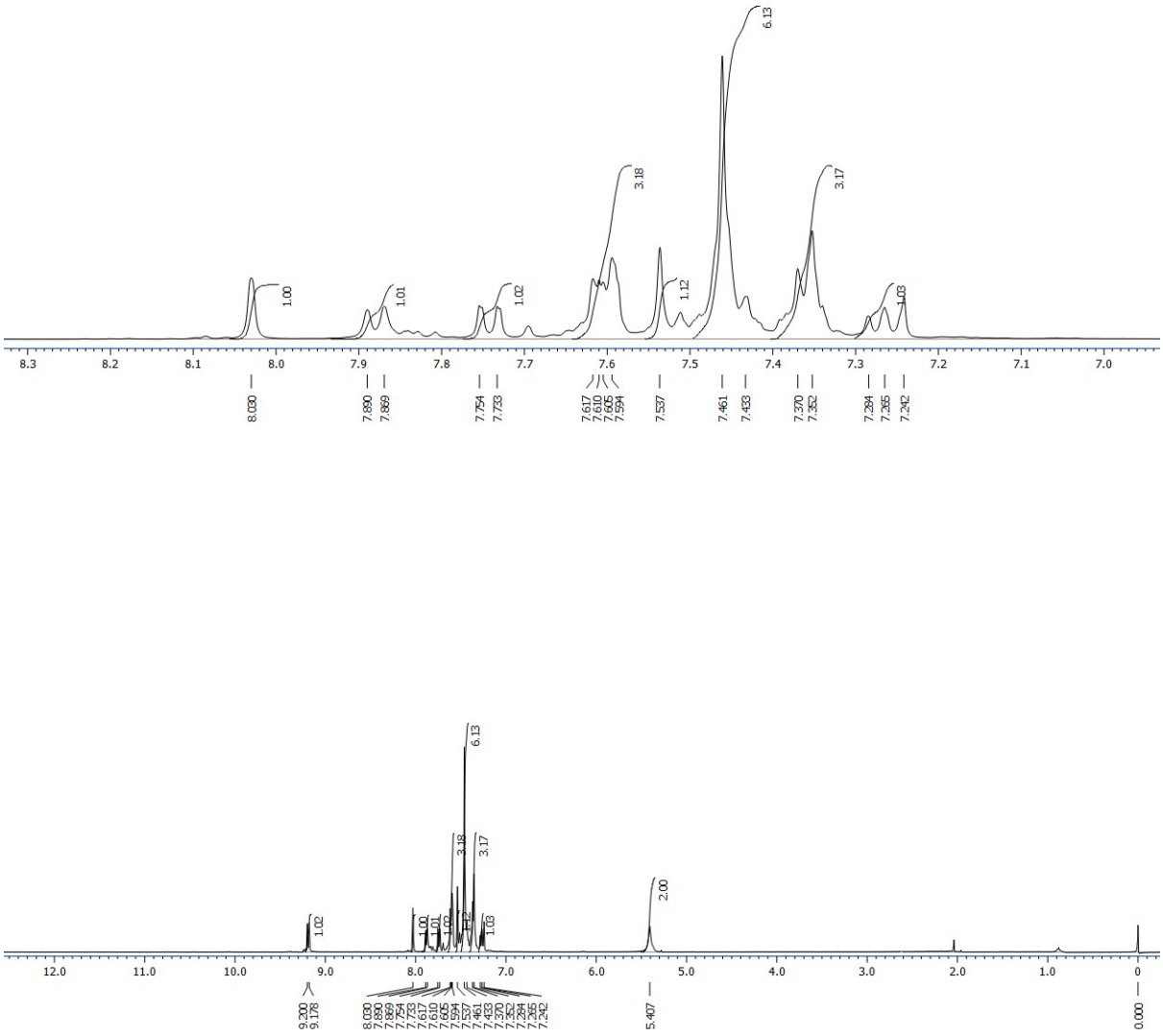
8-Fluoro-11-phenylbenzo[*c*]phenanthridin-6-amine (3k)



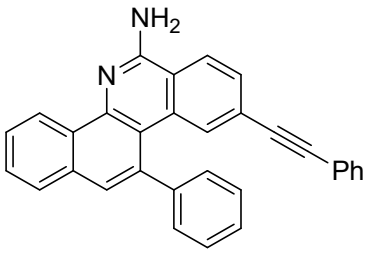
^{1}H NMR (400 MHz, $CDCl_3$)



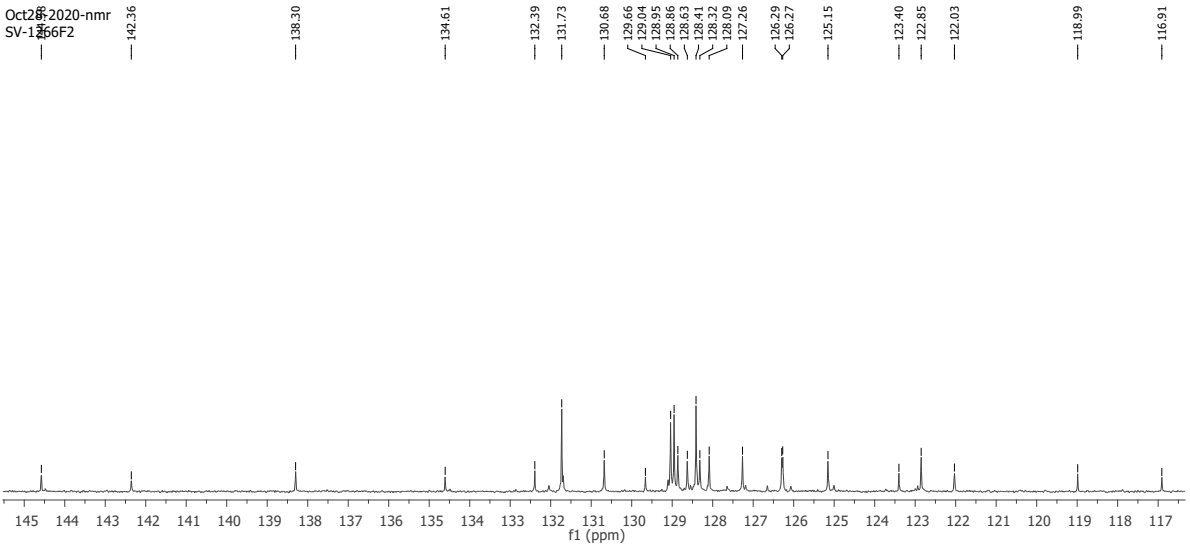
11-Phenyl-9-(phenylethynyl)benzo[*c*]phenanthridin-6-amine (3l)

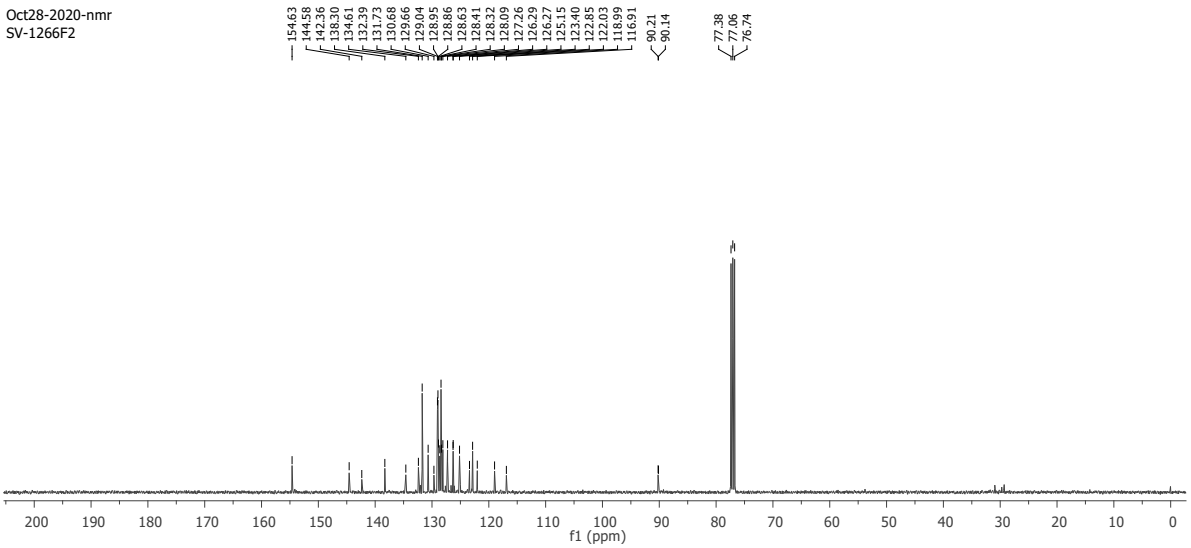


^{13}C NMR (100 MHz, $CDCl_3$)

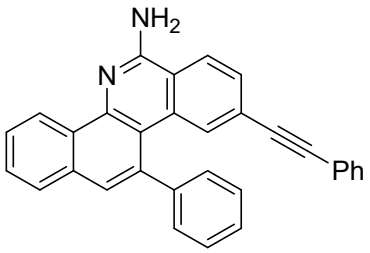


11-Phenyl-9-(phenylethynyl)benzo[*c*]phenanthridin-6-amine (3l)

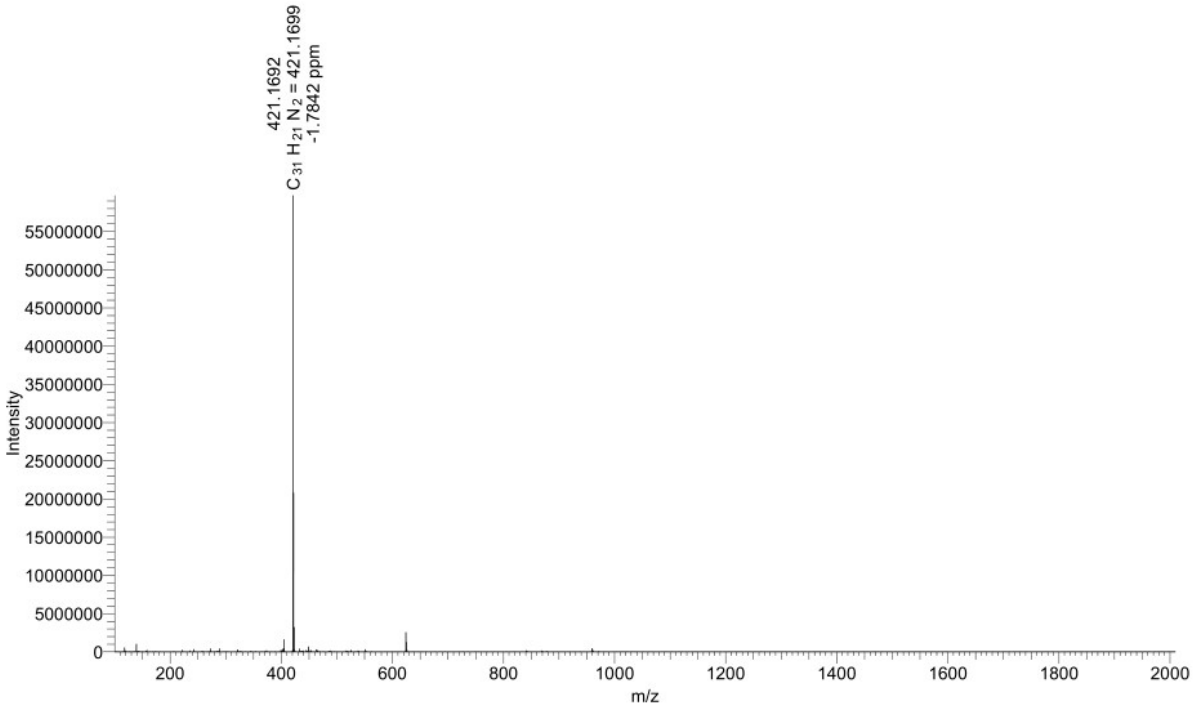




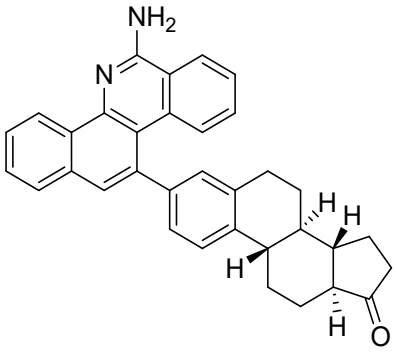
HRMS



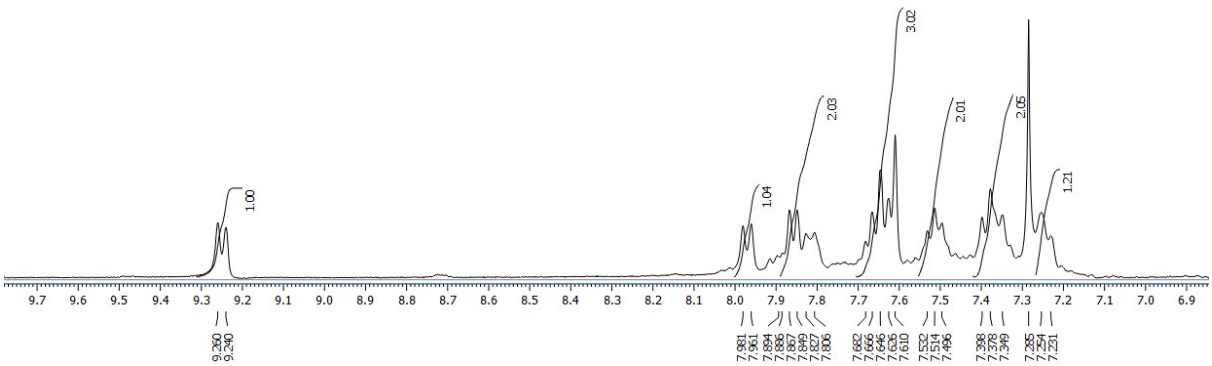
11-Phenyl-9-(phenylethynyl)benzo[*c*]phenanthridin-6-amine (3l)

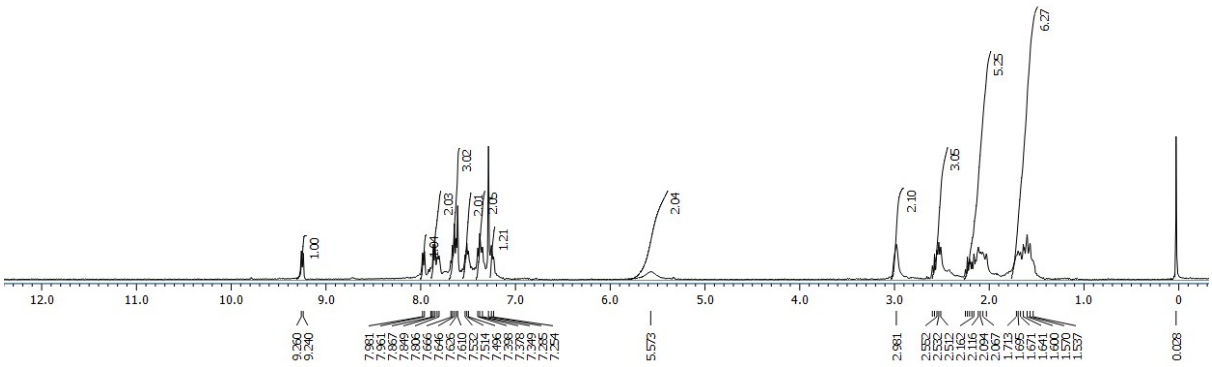


^{1}H NMR (400 MHz, $CDCl_3$)

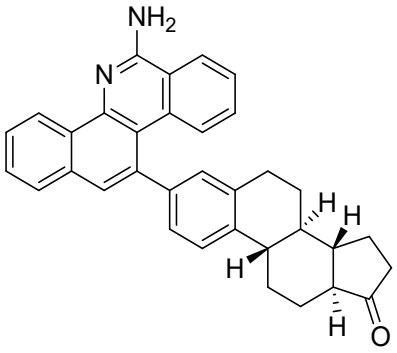


(8S,9S,13S,14S)-3-(6-aminobenzo[*c*]phenanthridin-11-yl)-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (3m)

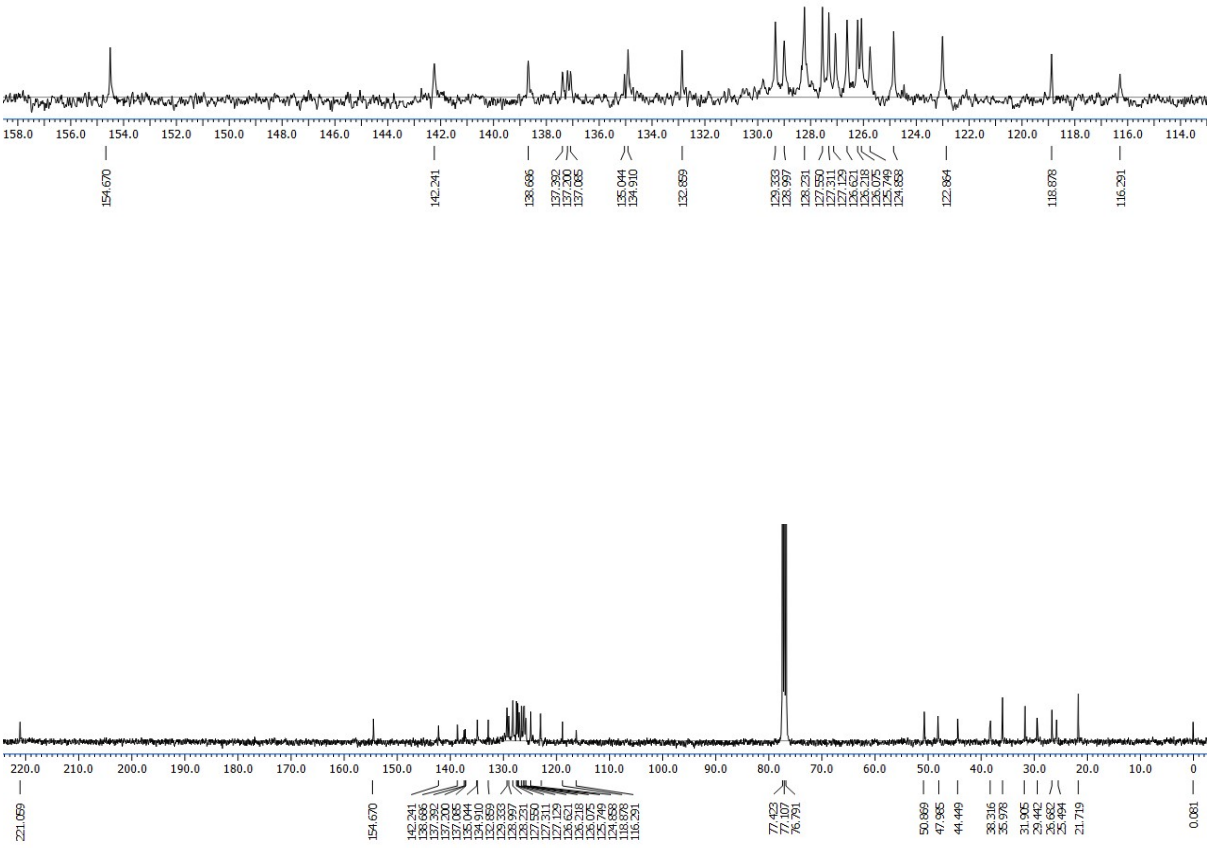




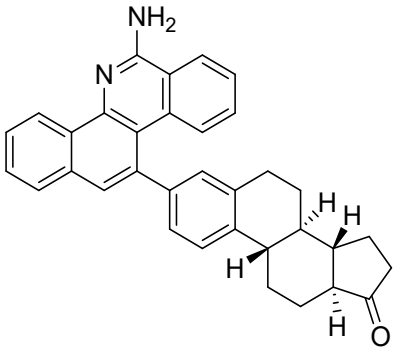
^{13}C NMR (100 MHz, $CDCl_3$)



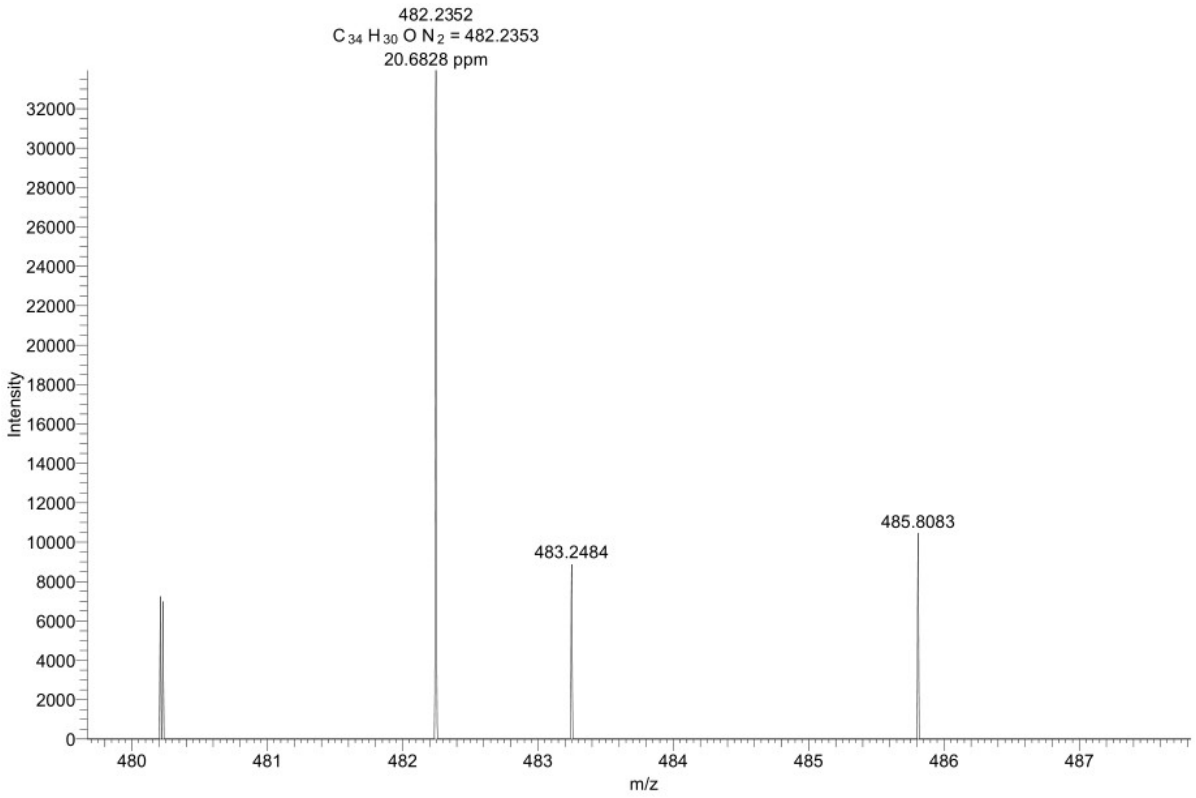
(8S,9S,13S,14S)-3-(6-aminobenzo[*c*]phenanthridin-11-yl)-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (3m)



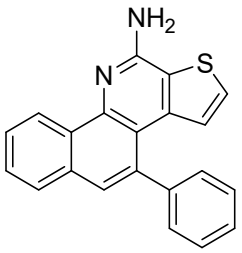
HRMS



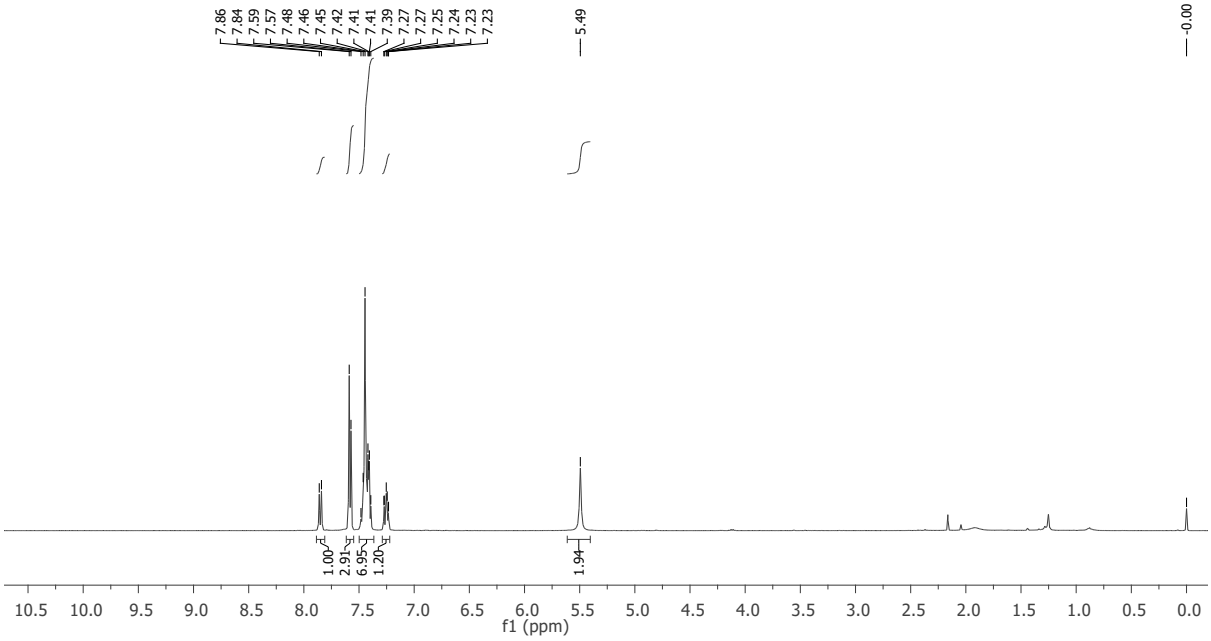
(8S,9S,13S,14S)-3-(6-aminobenzo[*c*]phenanthridin-11-yl)-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (3m)



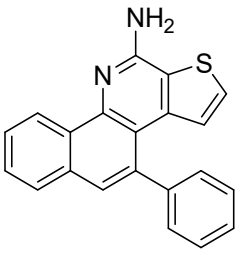
^{1}H NMR (400 MHz, $CDCl_3$)



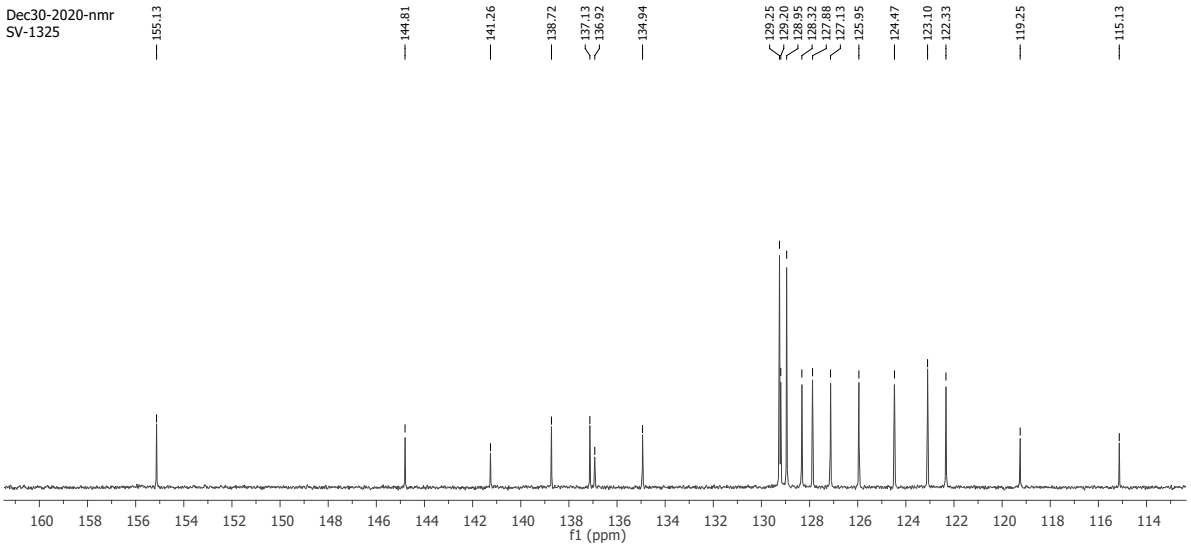
4-Phenylbenzo[*h*]thieno[2,3-*c*]quinolin-11-amine (4a)

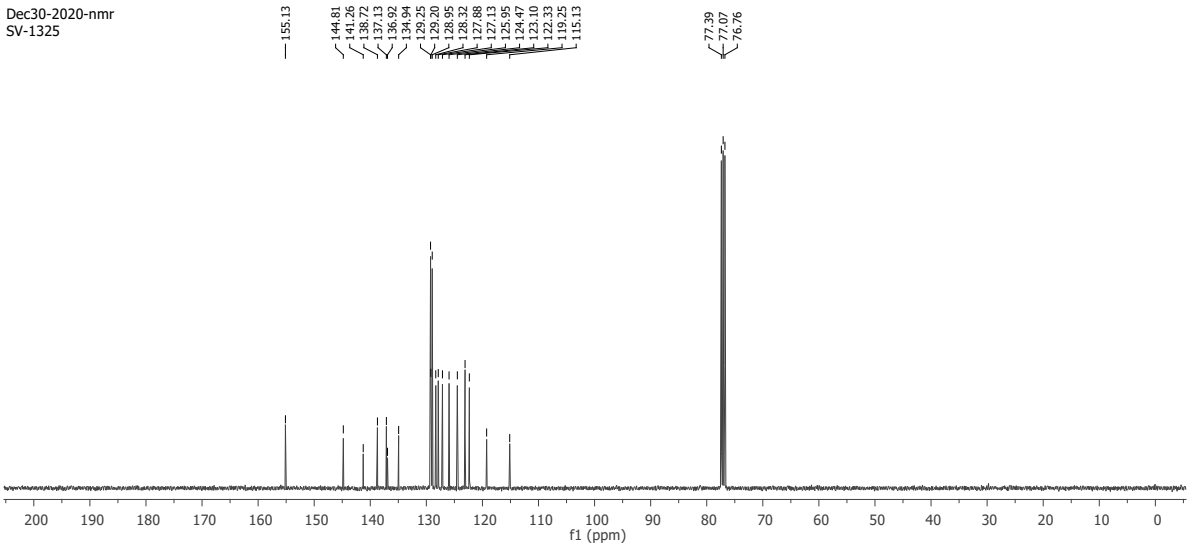


^{13}C NMR (100 MHz, $CDCl_3$)

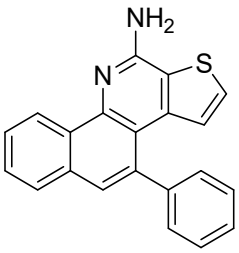


4-Phenylbenzo[*h*]thieno[2,3-*c*]quinolin-11-amine (4a)



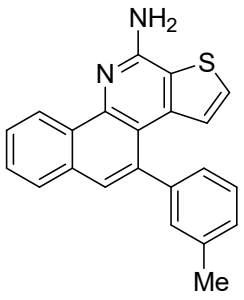


HRMS

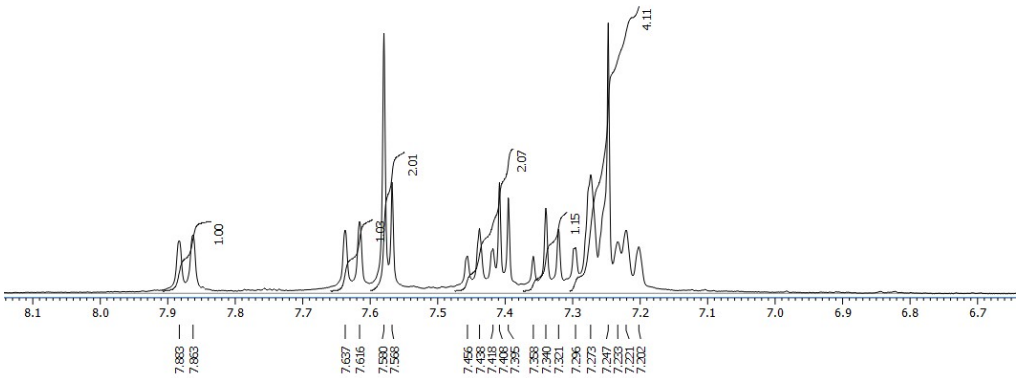


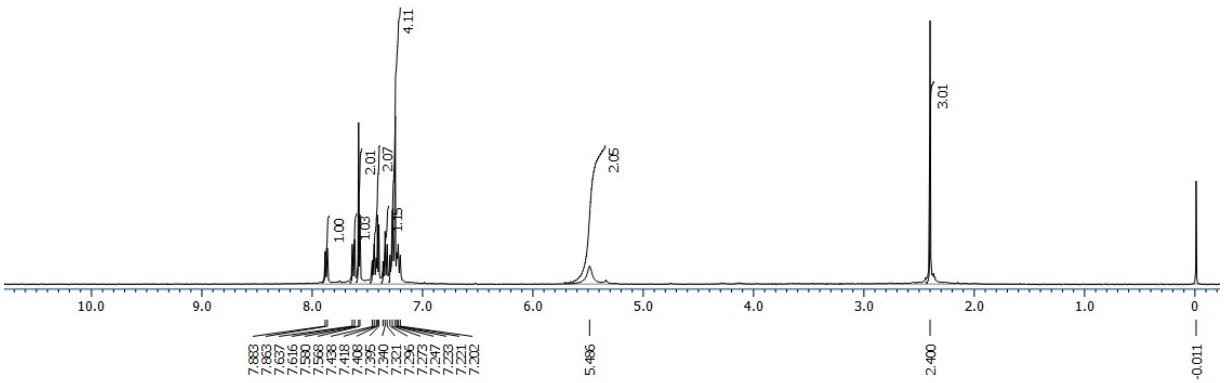
4-Phenylbenzo[*h*]thieno[2,3-*c*]quinolin-11-amine (4a)

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

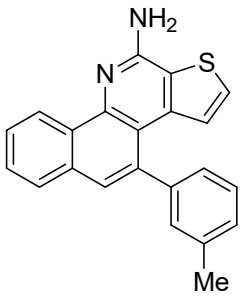


4-(*m*-Tolyl)benzo[*h*]thieno[2,3-*c*]quinolin-11-amine (4b)

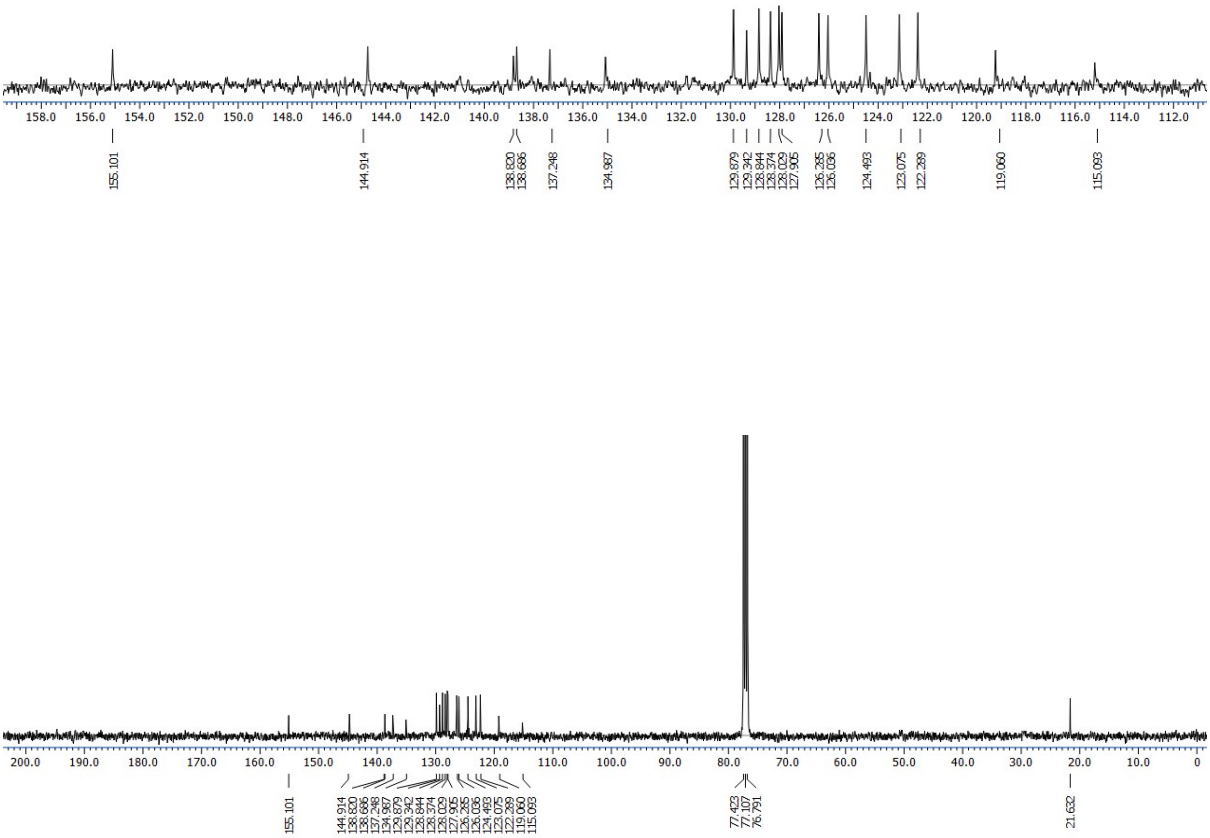




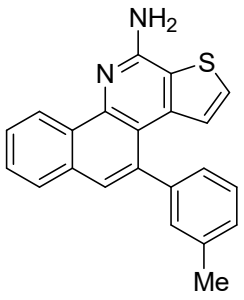
^{13}C NMR (100 MHz, $CDCl_3$)



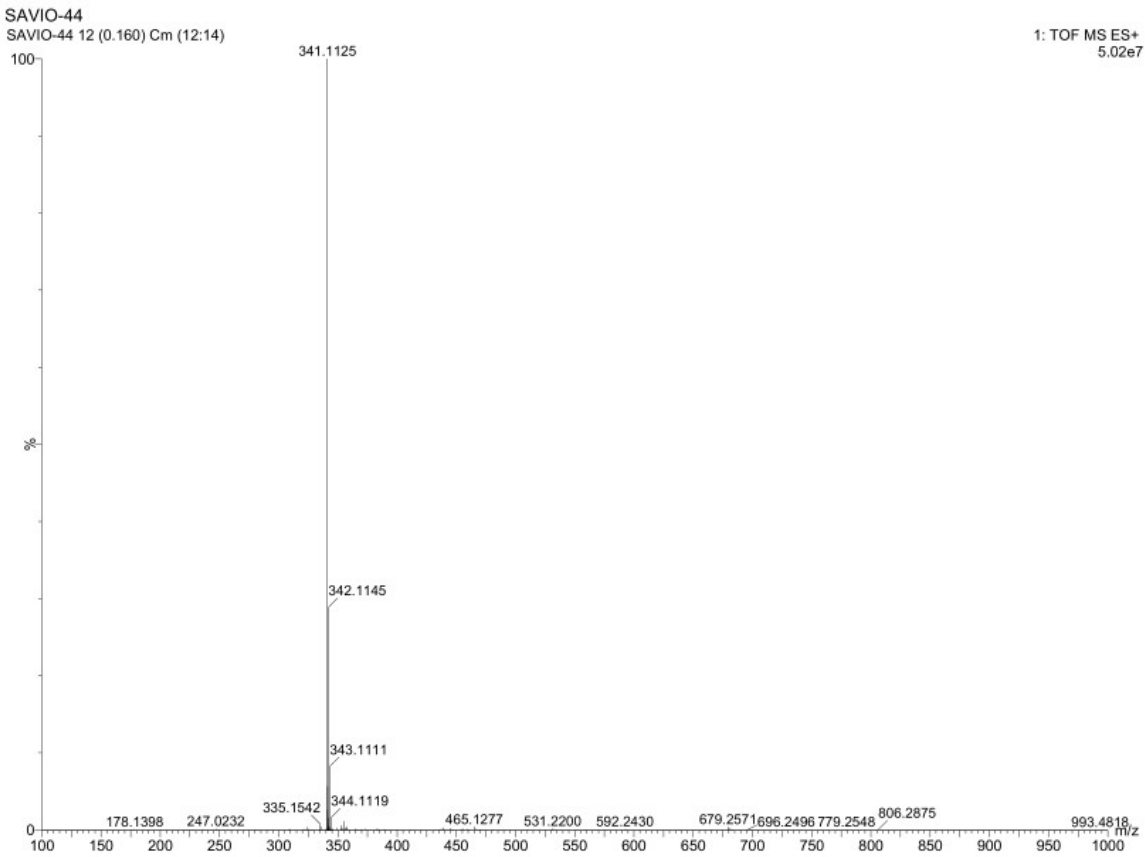
4-(*m*-Tolyl)benzo[*h*]thieno[2,3-*c*]quinolin-11-amine (4b)



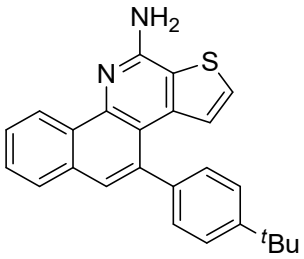
HRMS



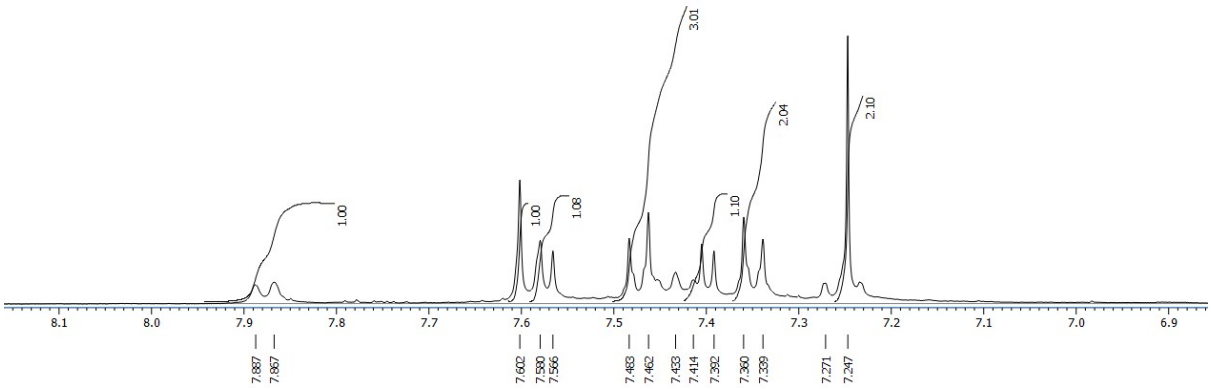
4-(*m*-Tolyl)benzo[*h*]thieno[2,3-*c*]quinolin-11-amine (4b)

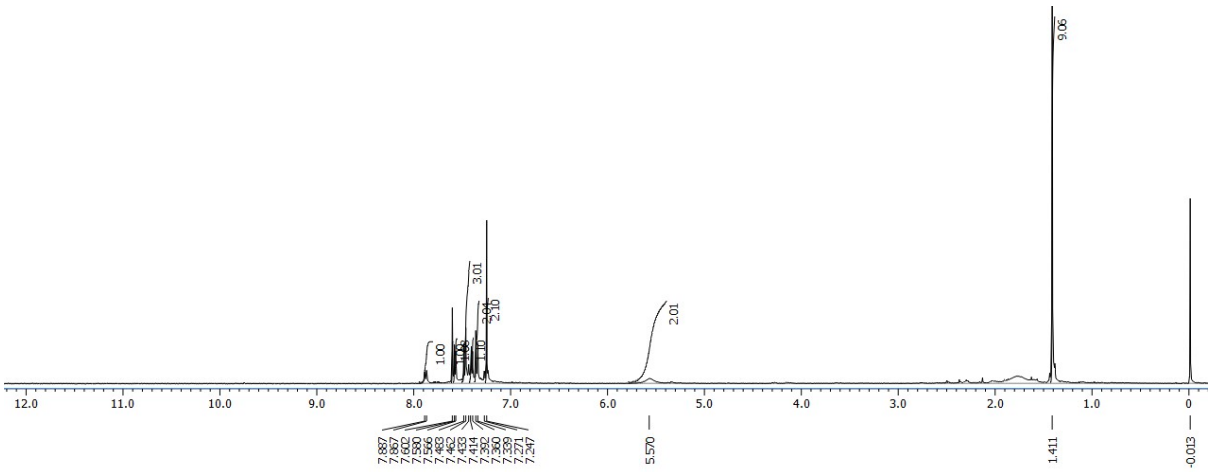


^{1}H NMR (400 MHz, $CDCl_3$)

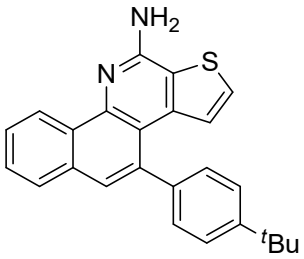


4-(4-(*tert*-Butyl)phenyl)benzo[*h*]thieno[2,3-*c*]quinolin-11-amine (4c)

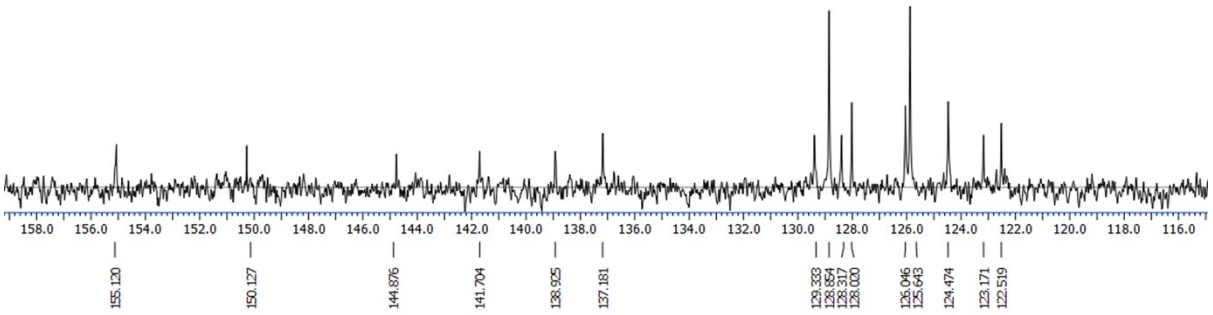


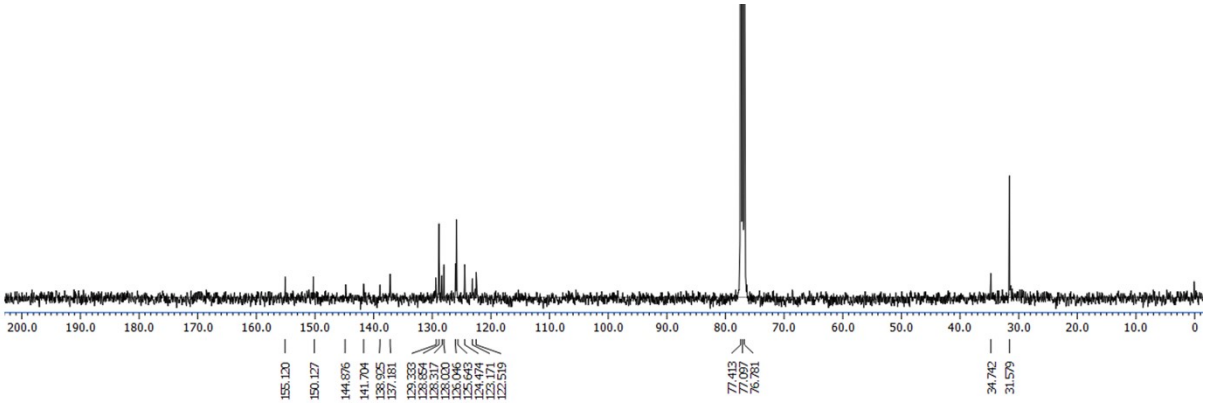


^{13}C NMR (100 MHz, $CDCl_3$)

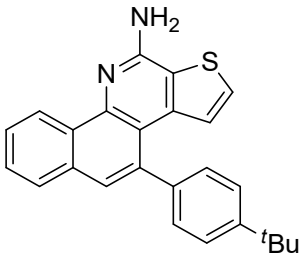


4-(4-(*tert*-Butyl)phenyl)benzo[*h*]thieno[2,3-*c*]quinolin-11-amine (4c)

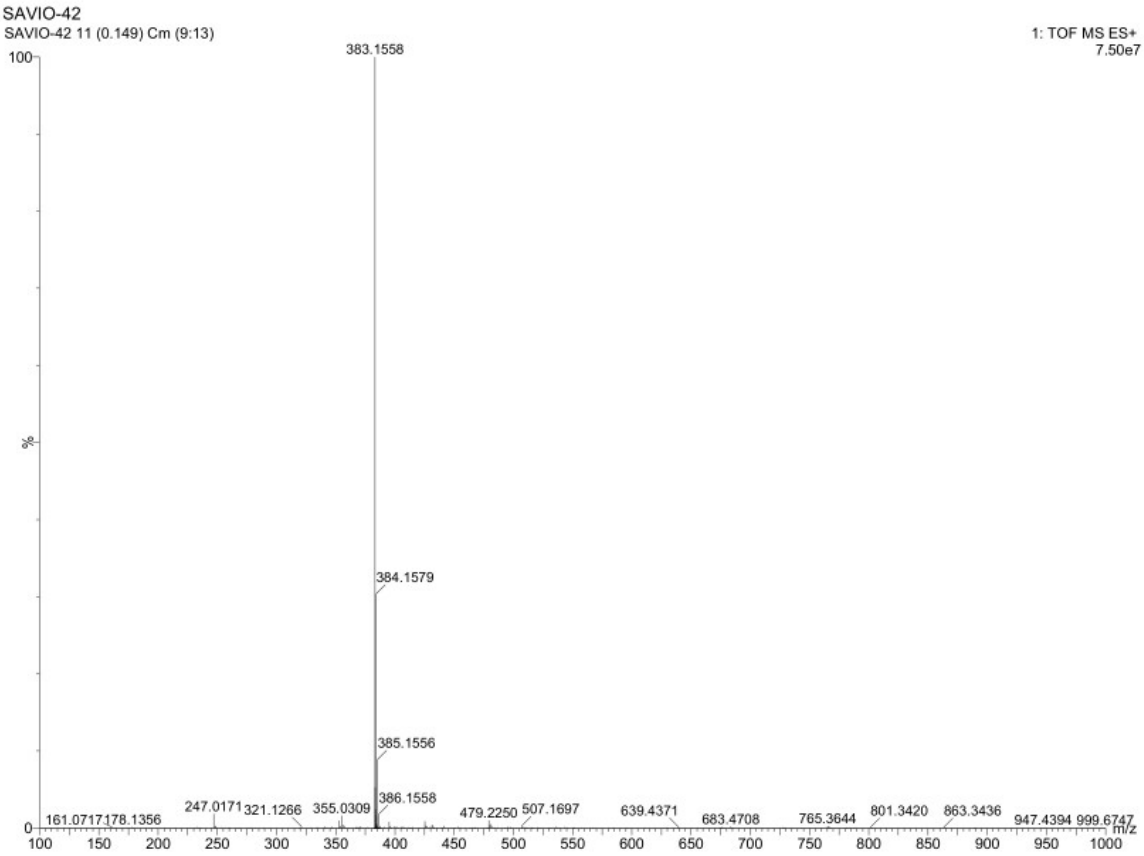




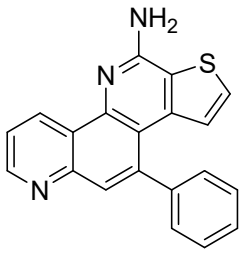
HRMS



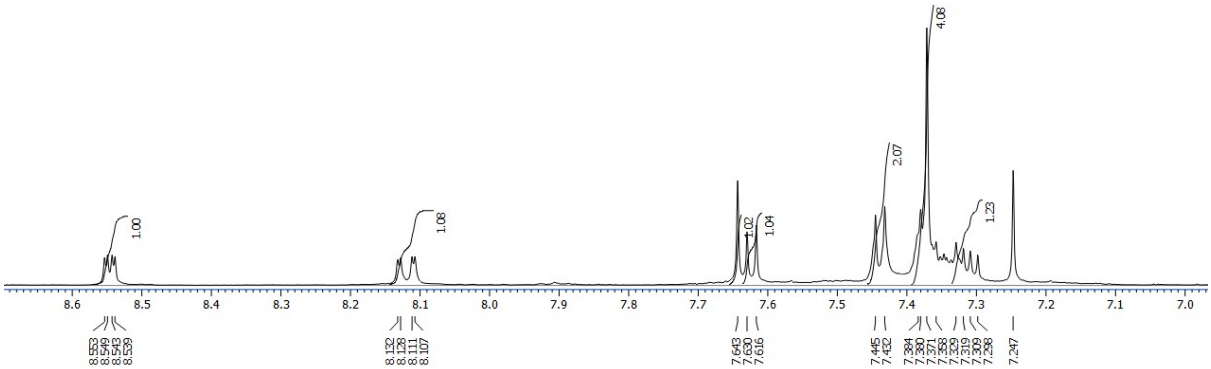
4-(4-(*tert*-Butyl)phenyl)benzo[*h*]thieno[2,3-*c*]quinolin-11-amine (4c)

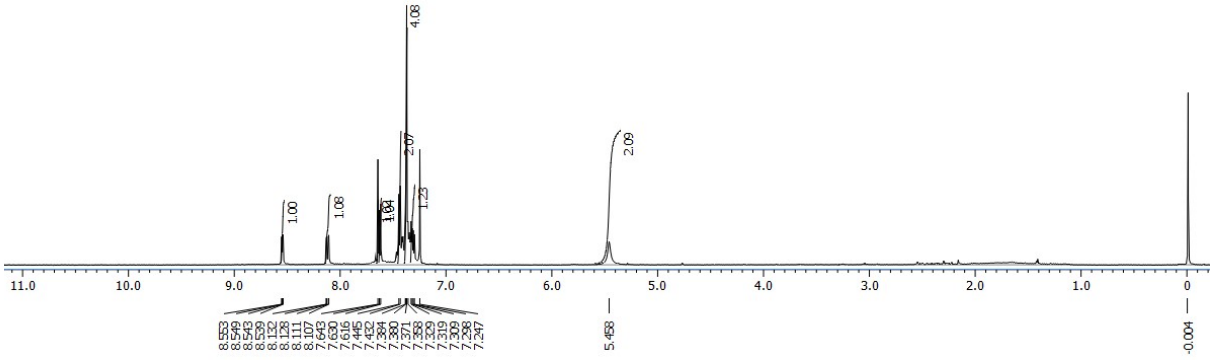


^{1}H NMR (400 MHz, $CDCl_3$)

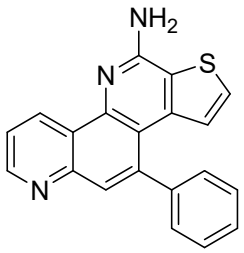


10-Phenylthieno[2,3-*c*][1,7]phenanthrolin-6-amine (4d)

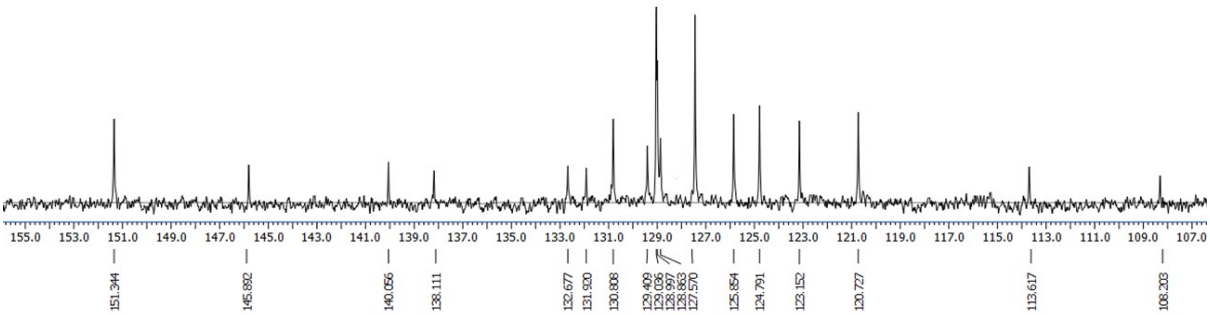


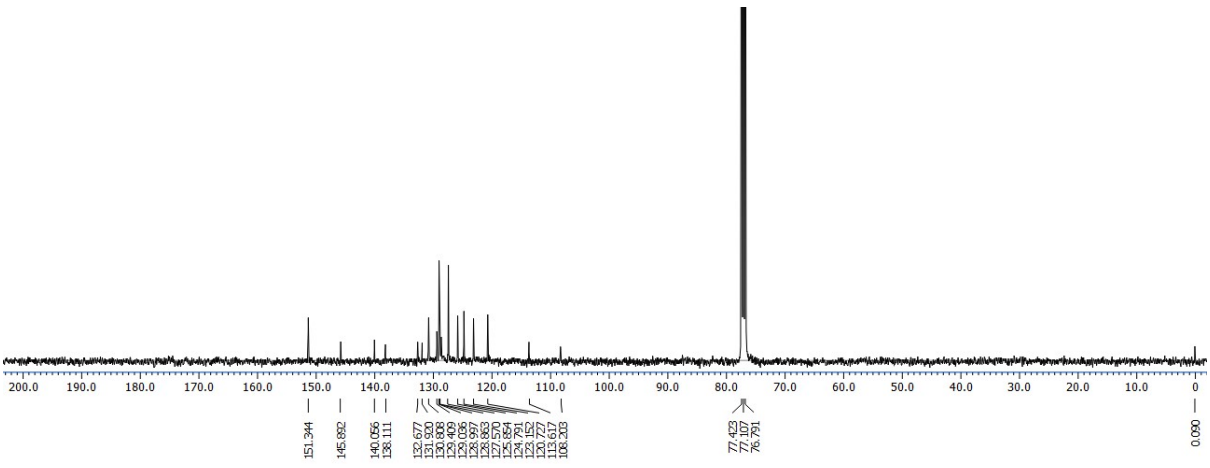


^{13}C NMR (100 MHz, $CDCl_3$)



10-Phenylthieno[2,3-*c*][1,7]phenanthrolin-6-amine (4d)





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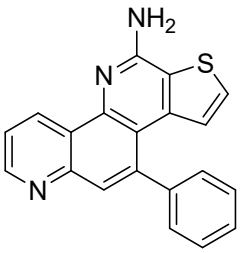
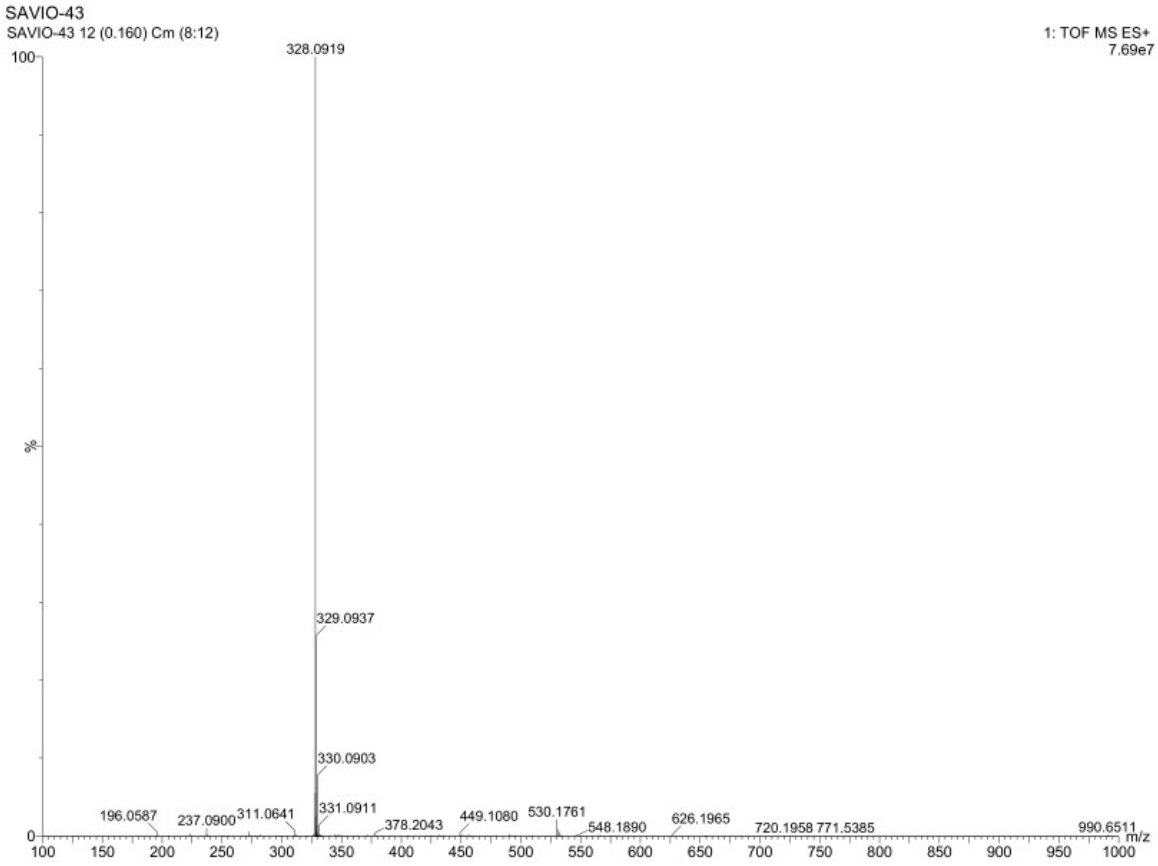
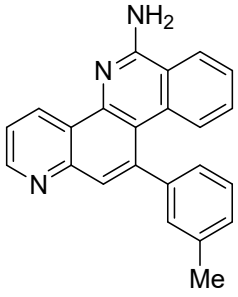


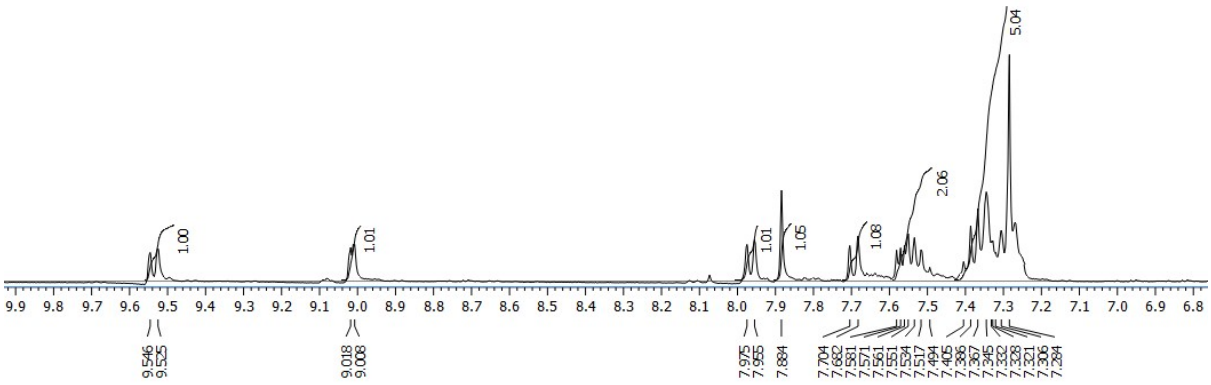
10-Phenylthieno[2,3-*c*][1,7]phenanthrolin-6-amine (4d)

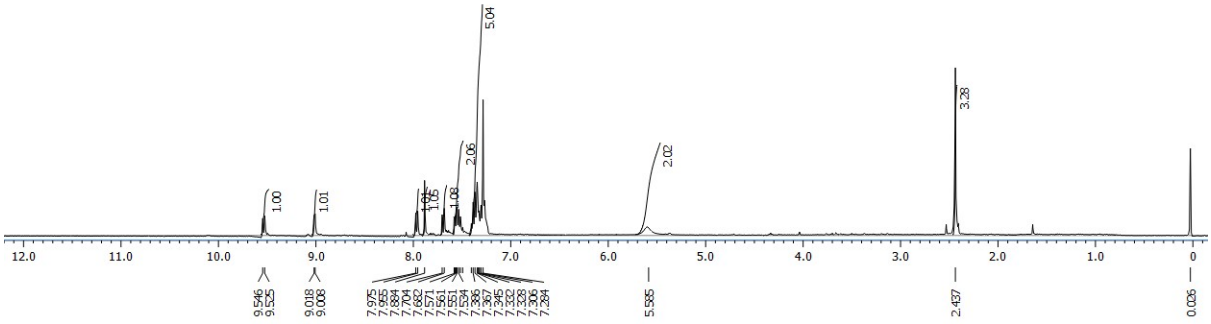


^{1}H NMR (400 MHz, $CDCl_3$)

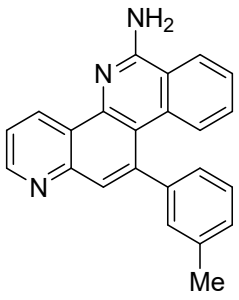


11-(*m*-Tolyl)benzo[*c*][1,7]phenanthrolin-6-amine (5a)

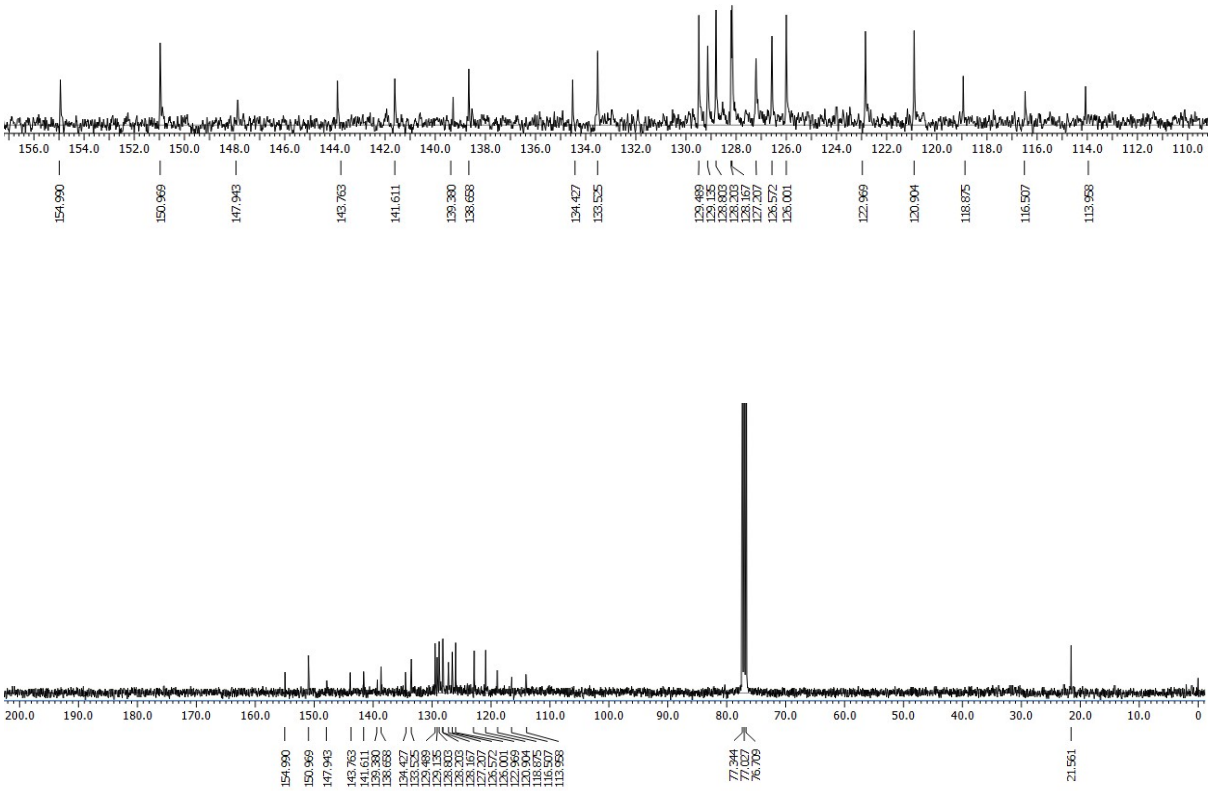




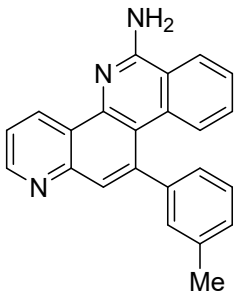
^{13}C NMR (100 MHz, $CDCl_3$)



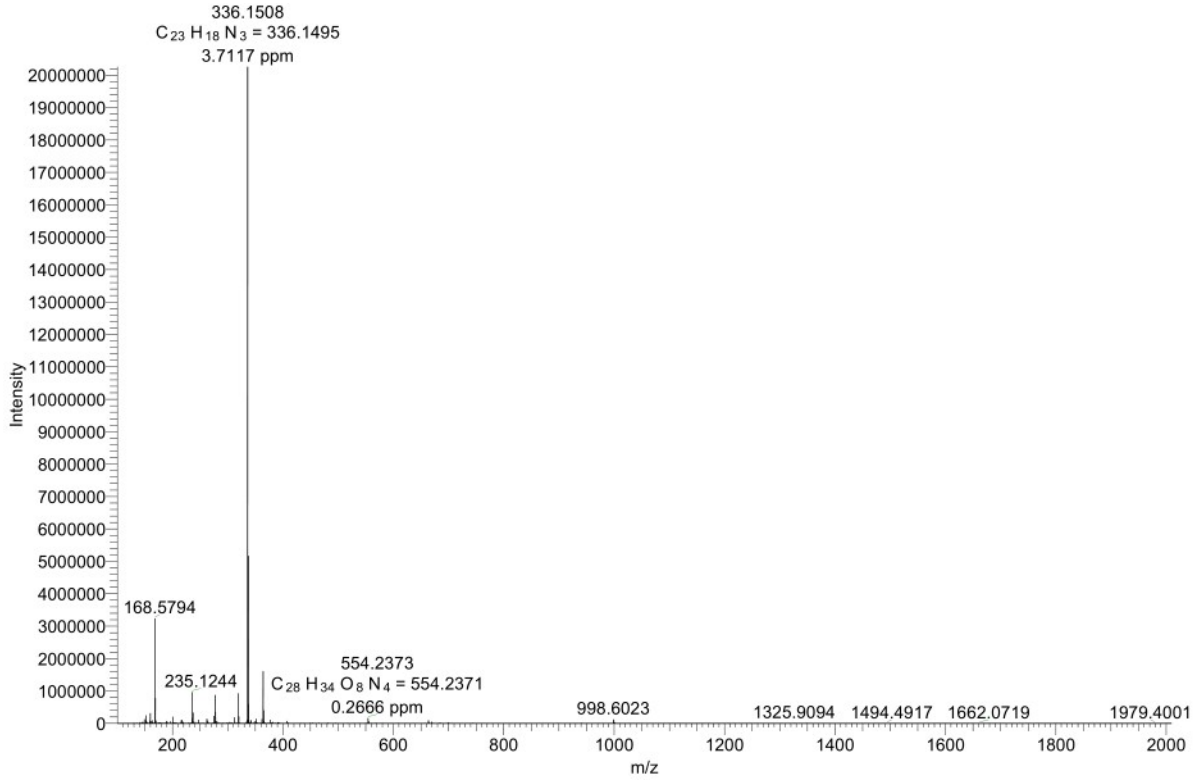
11-(*m*-Tolyl)benzo[*c*][1,7]phenanthrolin-6-amine (5a)



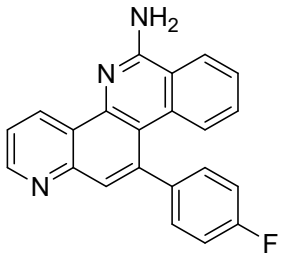
HRMS



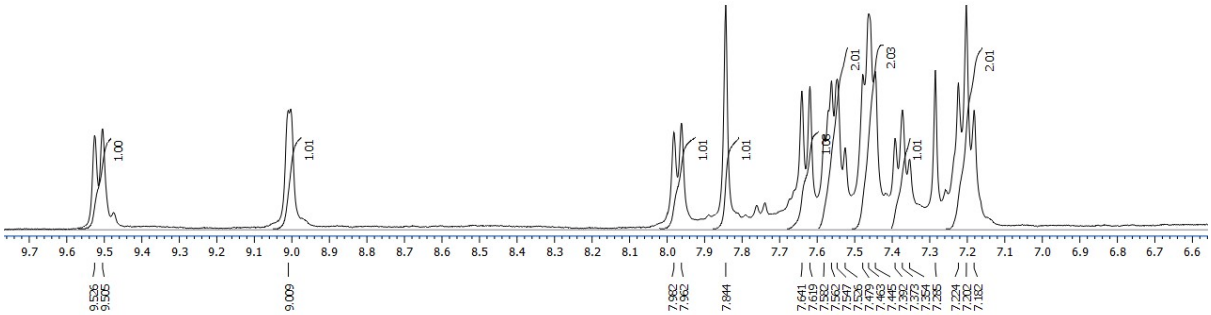
11-(*m*-Tolyl)benzo[*c*][1,7]phenanthrolin-6-amine (5a)

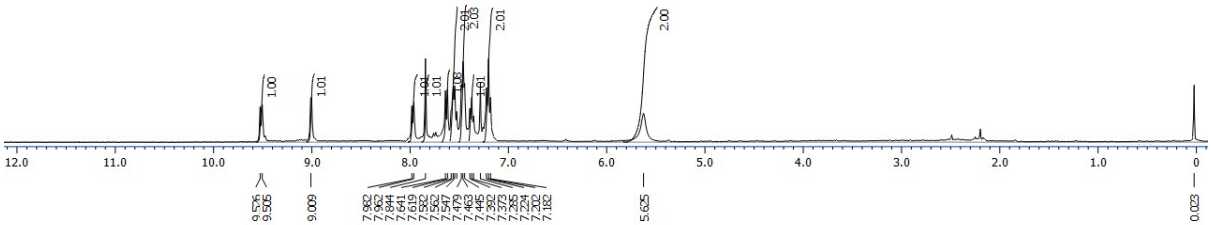


^{1}H NMR (400 MHz, $CDCl_3$)

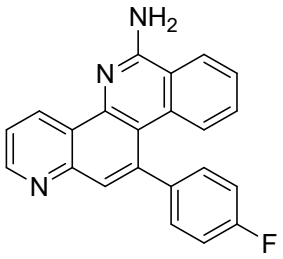


11-(4-Fluorophenyl)benzo[*c*][1,7]phenanthrolin-6-amine (5b)

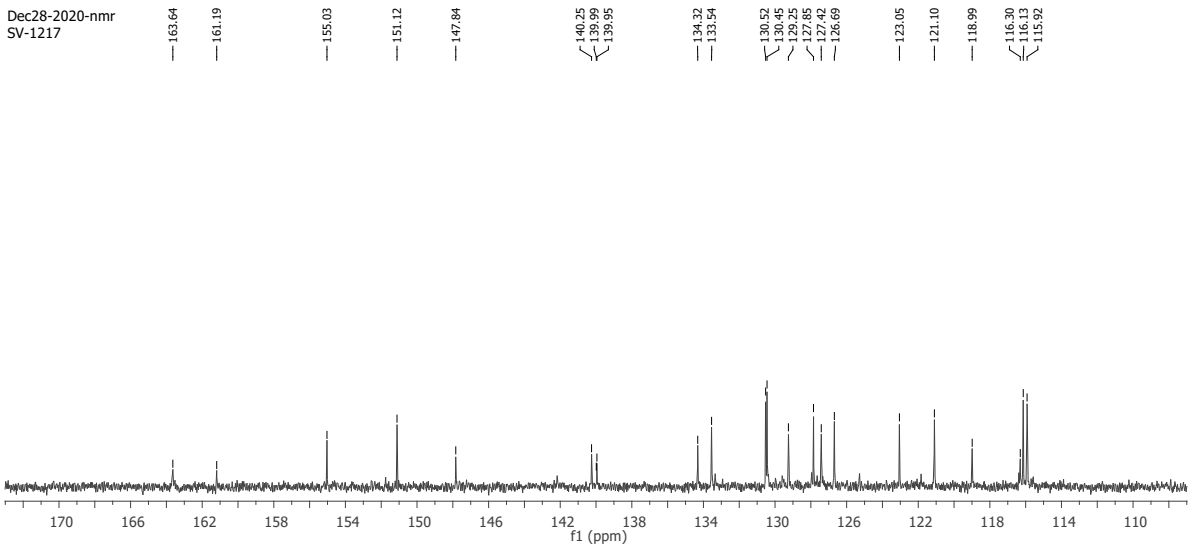


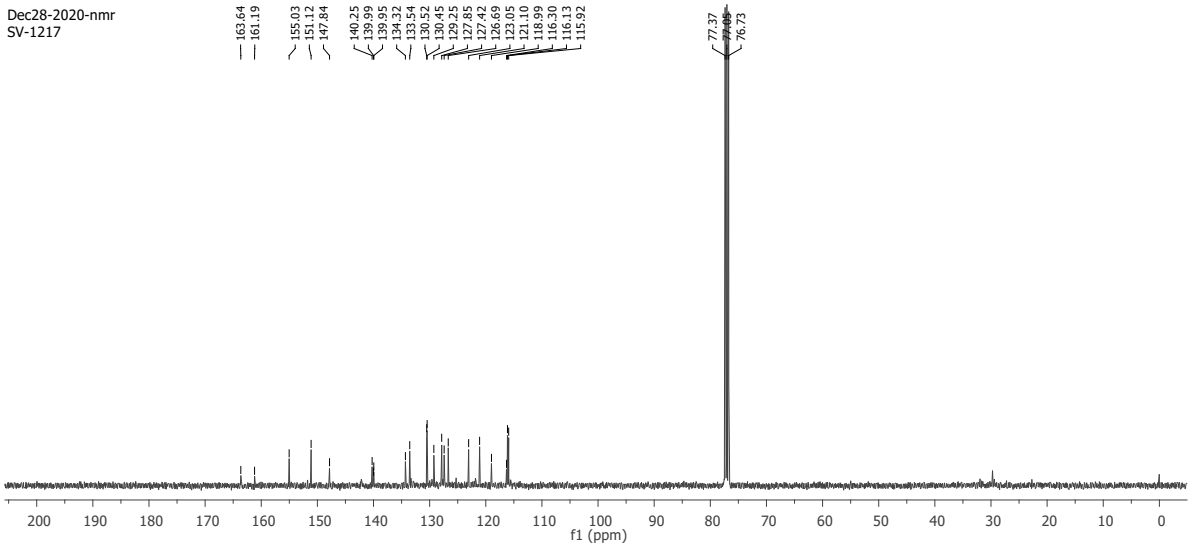


^{13}C NMR (100 MHz, $CDCl_3$)

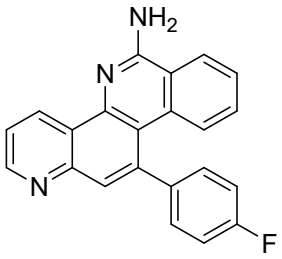


11-(4-Fluorophenyl)benzo[*c*][1,7]phenanthrolin-6-amine (5b)

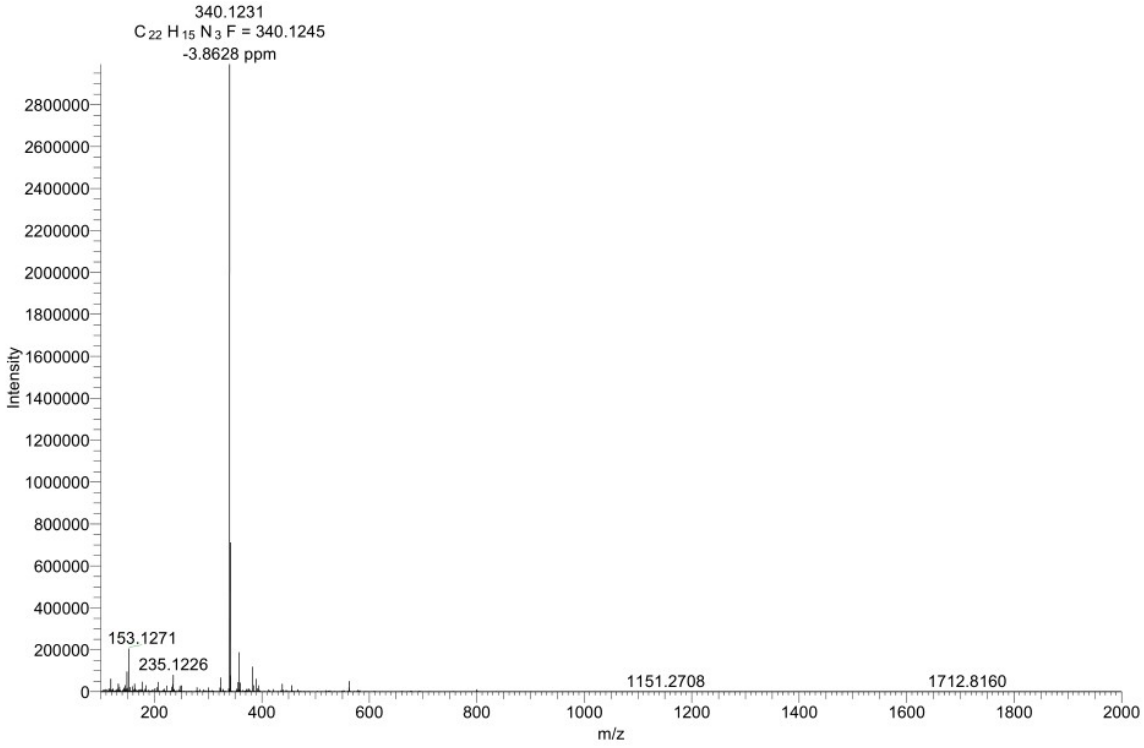




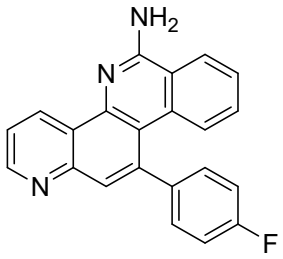
HRMS



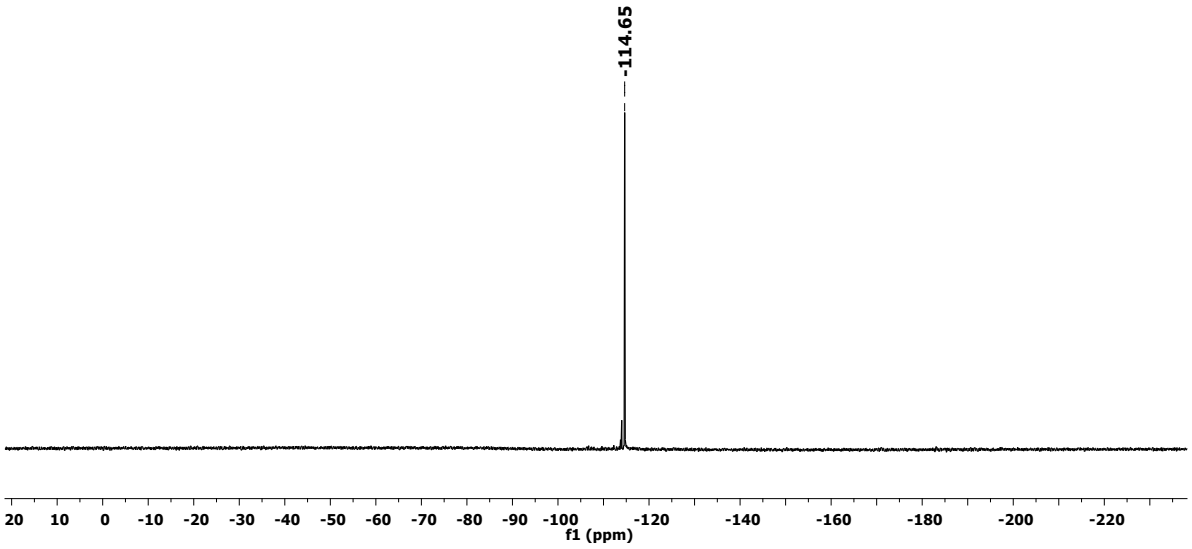
11-(4-Fluorophenyl)benzo[*c*][1,7]phenanthrolin-6-amine (5b)



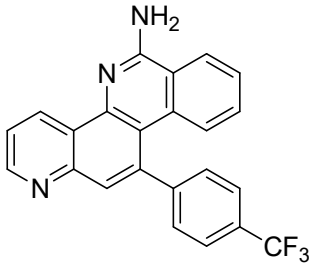
^{19}F NMR (376 MHz, $CDCl_3$)



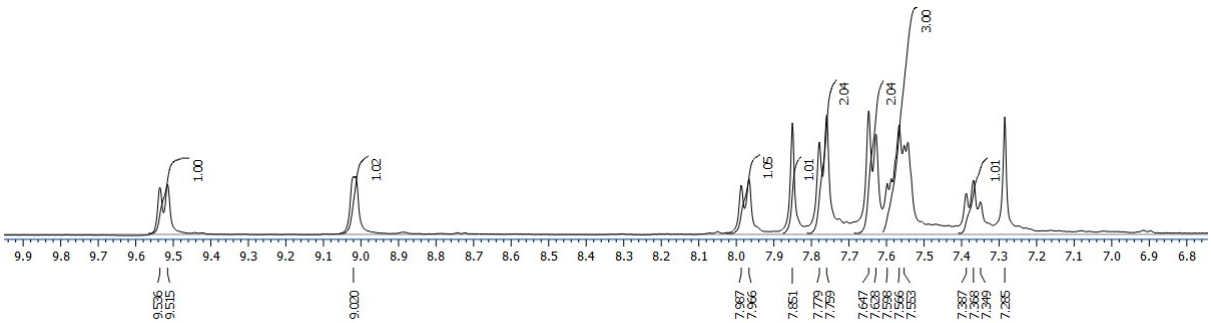
11-(4-Fluorophenyl)benzo[*c*][1,7]phenanthrolin-6-amine (5b)

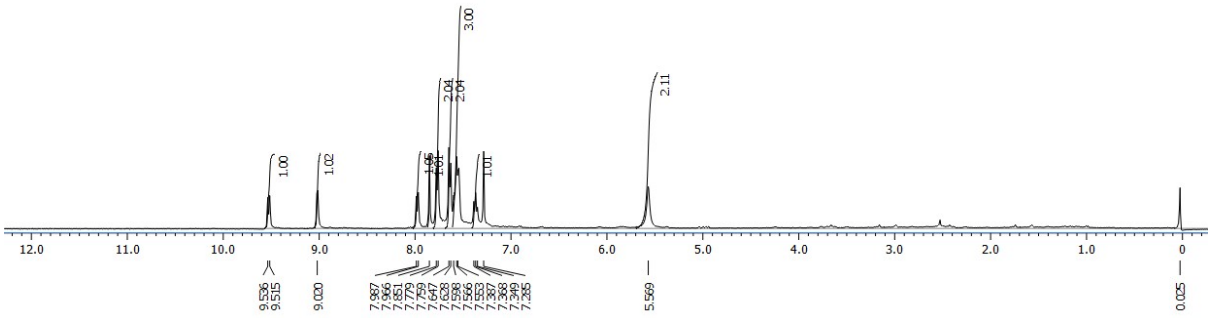


^{1}H NMR (400 MHz, $CDCl_3$)

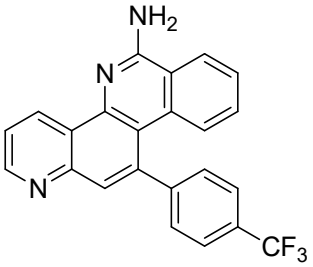


11-(4-(Trifluoromethyl)phenyl)benzo[*c*][1,7]phenanthrolin-6-amine (5c)

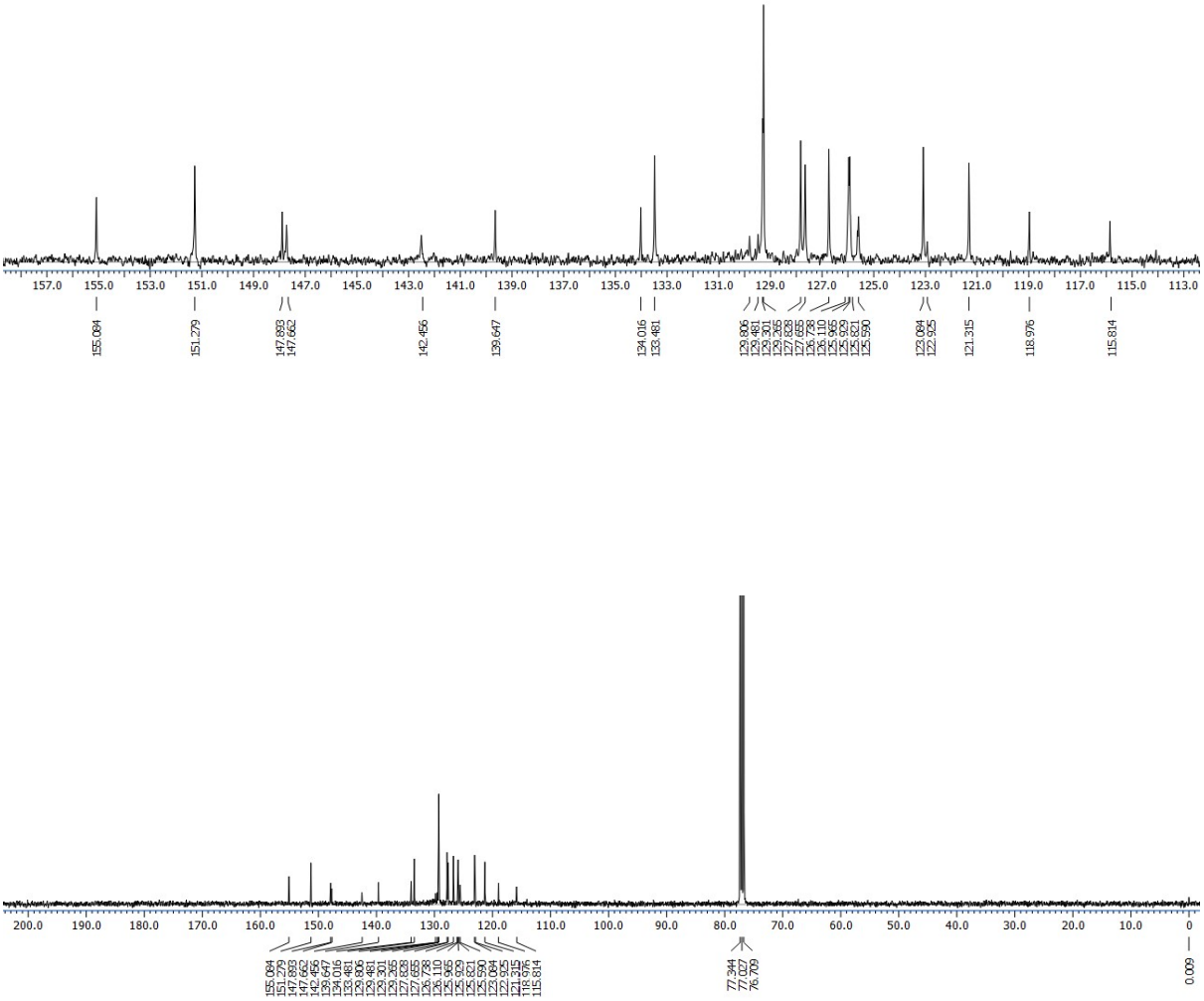




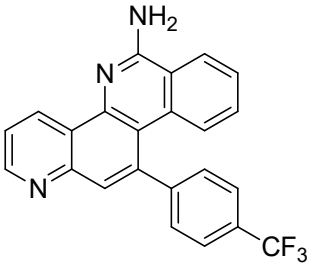
^{13}C NMR (100 MHz, $CDCl_3$)



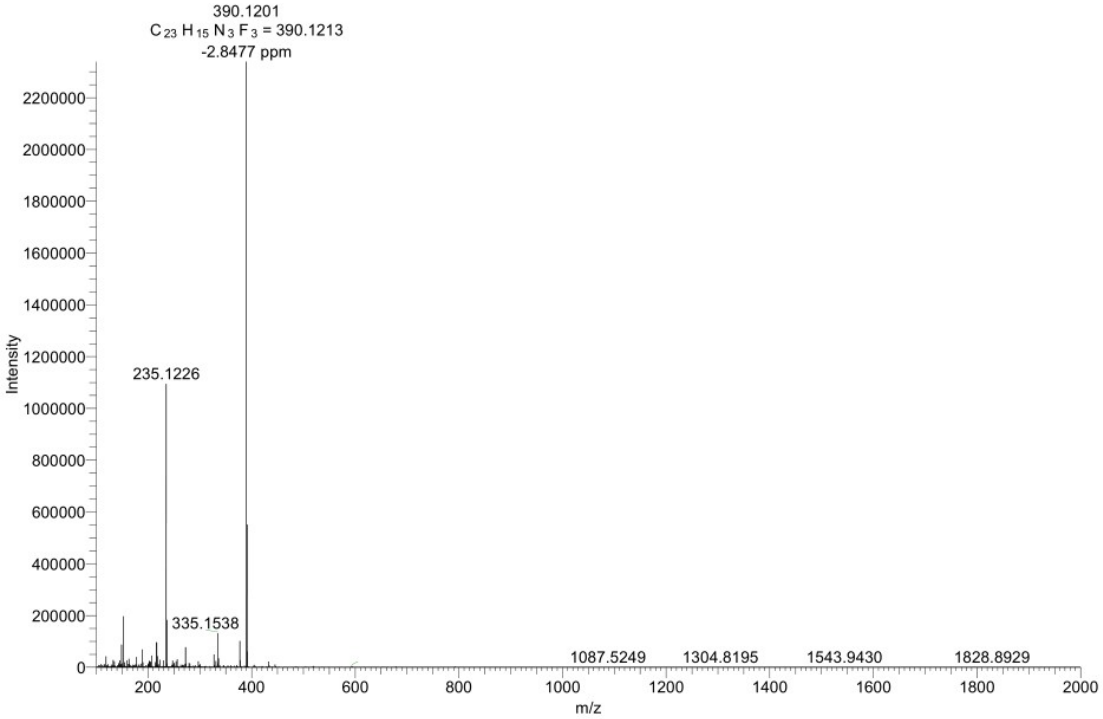
11-(4-(Trifluoromethyl)phenyl)benzo[*c*][1,7]phenanthrolin-6-amine (5c)



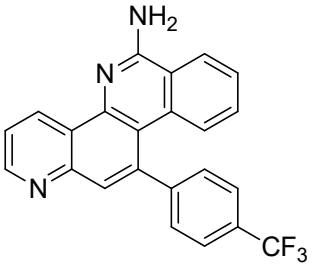
HRMS



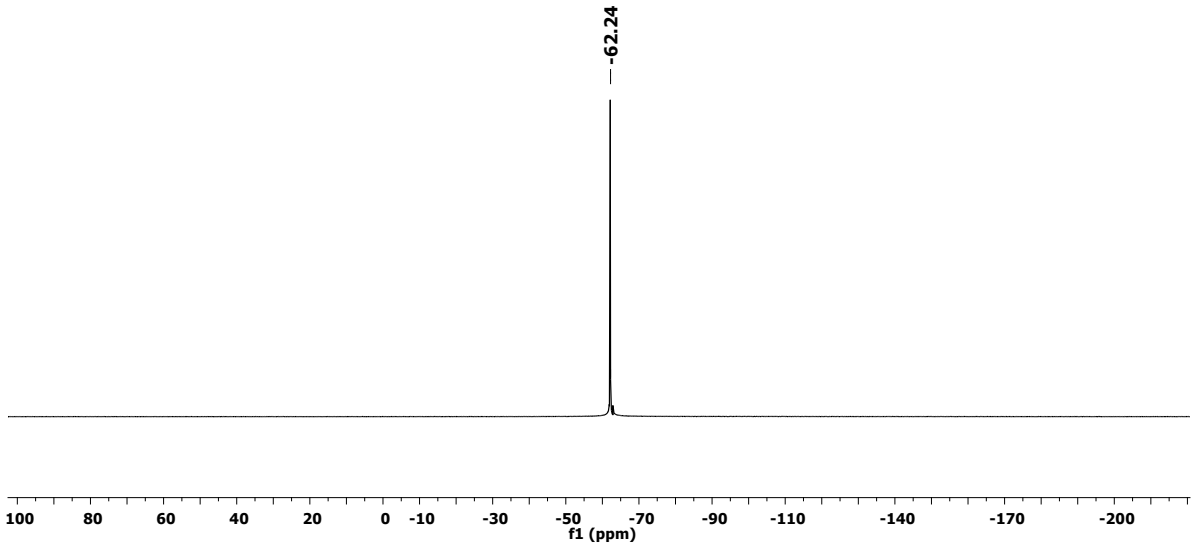
11-(4-(Trifluoromethyl)phenyl)benzo[*c*][1,7]phenanthrolin-6-amine (5c)



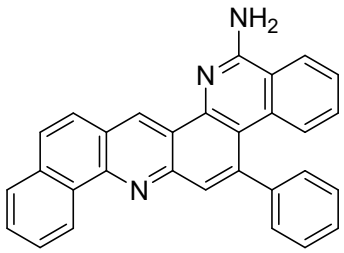
^{19}F NMR (376 MHz, $CDCl_3$)



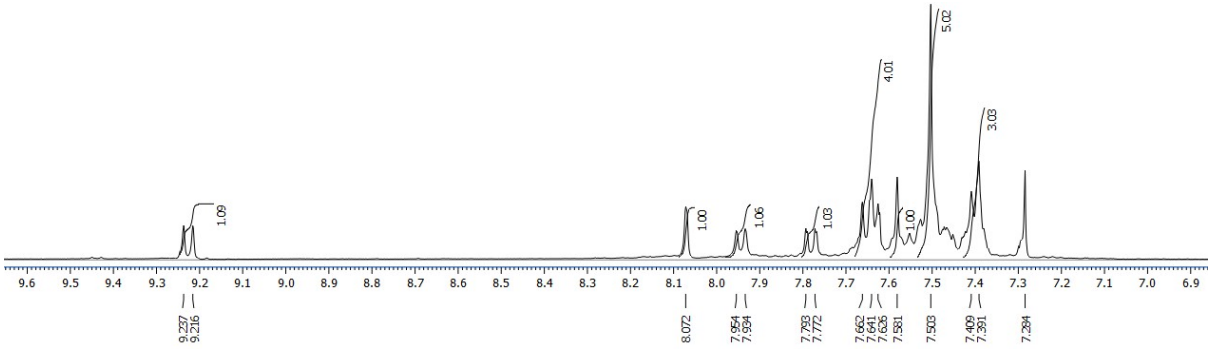
11-(4-(Trifluoromethyl)phenyl)benzo[*c*][1,7]phenanthrolin-6-amine (5c)

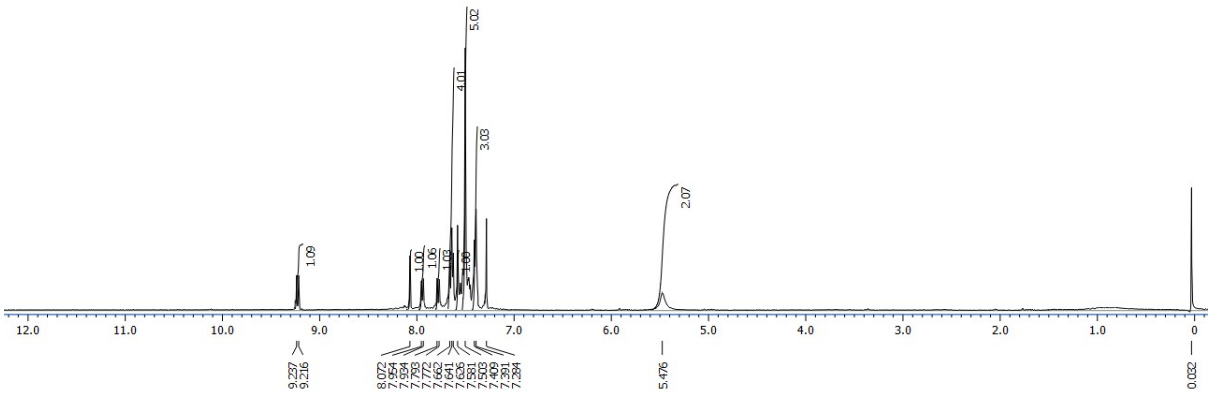


^{1}H NMR (400 MHz, $CDCl_3$)

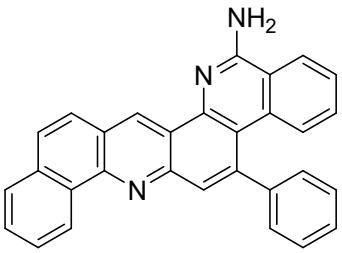


5-Phenylbenzo[*c*]naphtho[1,2-*j*][1,7]phenanthrolin-16-amine (5d)

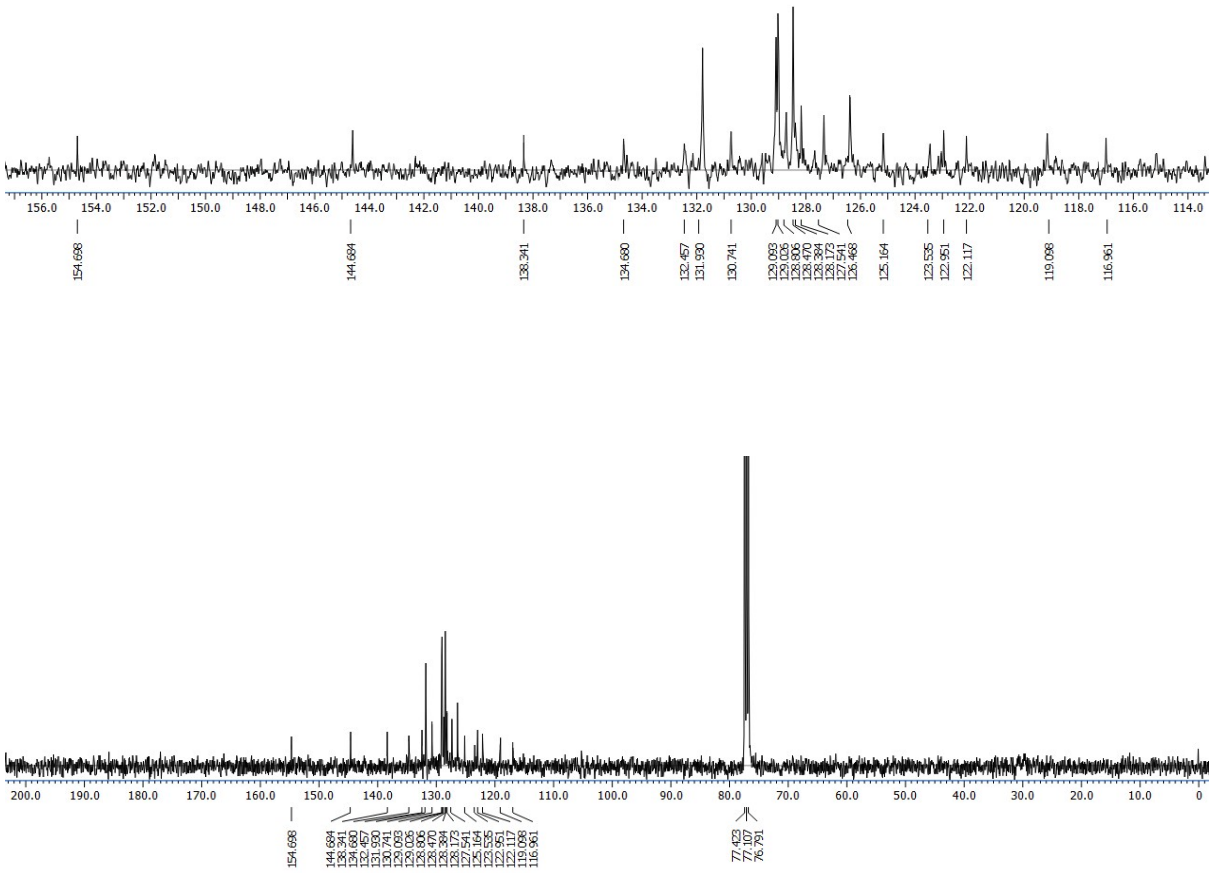




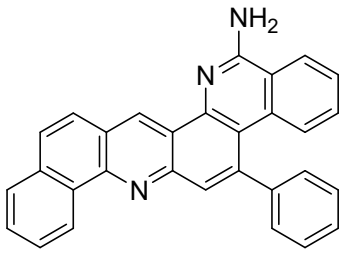
^{13}C NMR (100 MHz, $CDCl_3$)



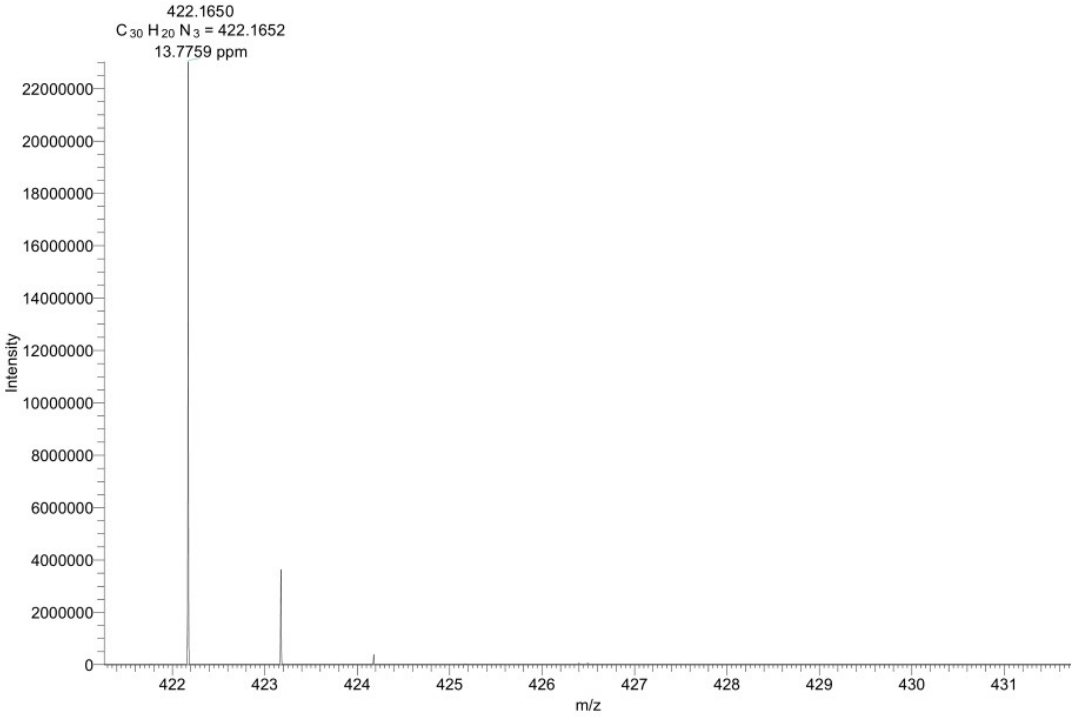
5-Phenylbenzo[*c*]naphtho[1,2-*j*][1,7]phenanthrolin-16-amine (5d)



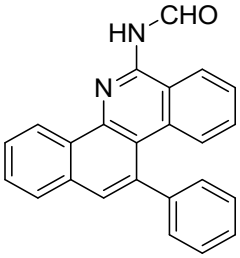
HRMS



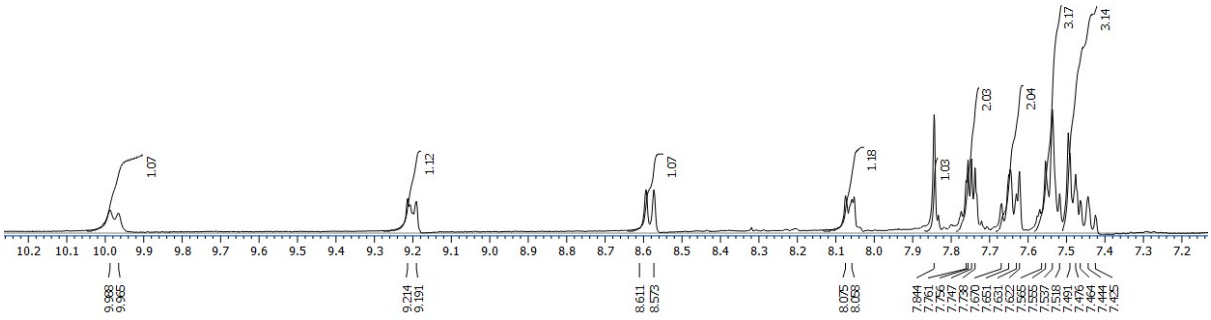
5-Phenylbenzo[*c*]naphtho[1,2-*j*][1,7]phenanthrolin-16-amine (5d)

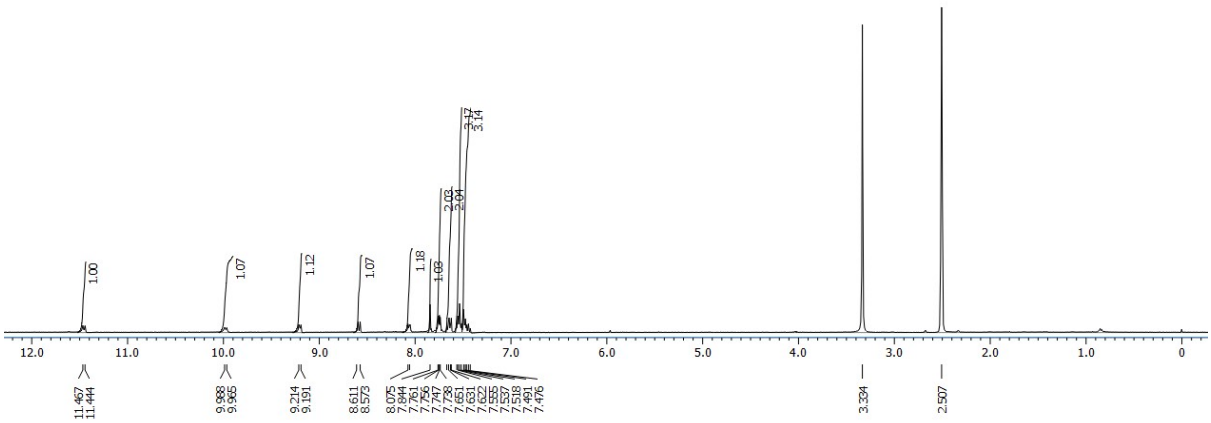


^{1}H NMR (400 MHz, $CDCl_3$)

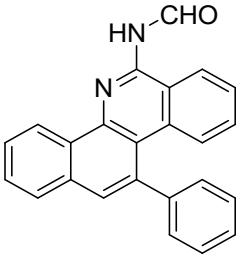


***N*-(11-phenylbenzo[*c*]phenanthridin-6-yl)formamide (6a)**

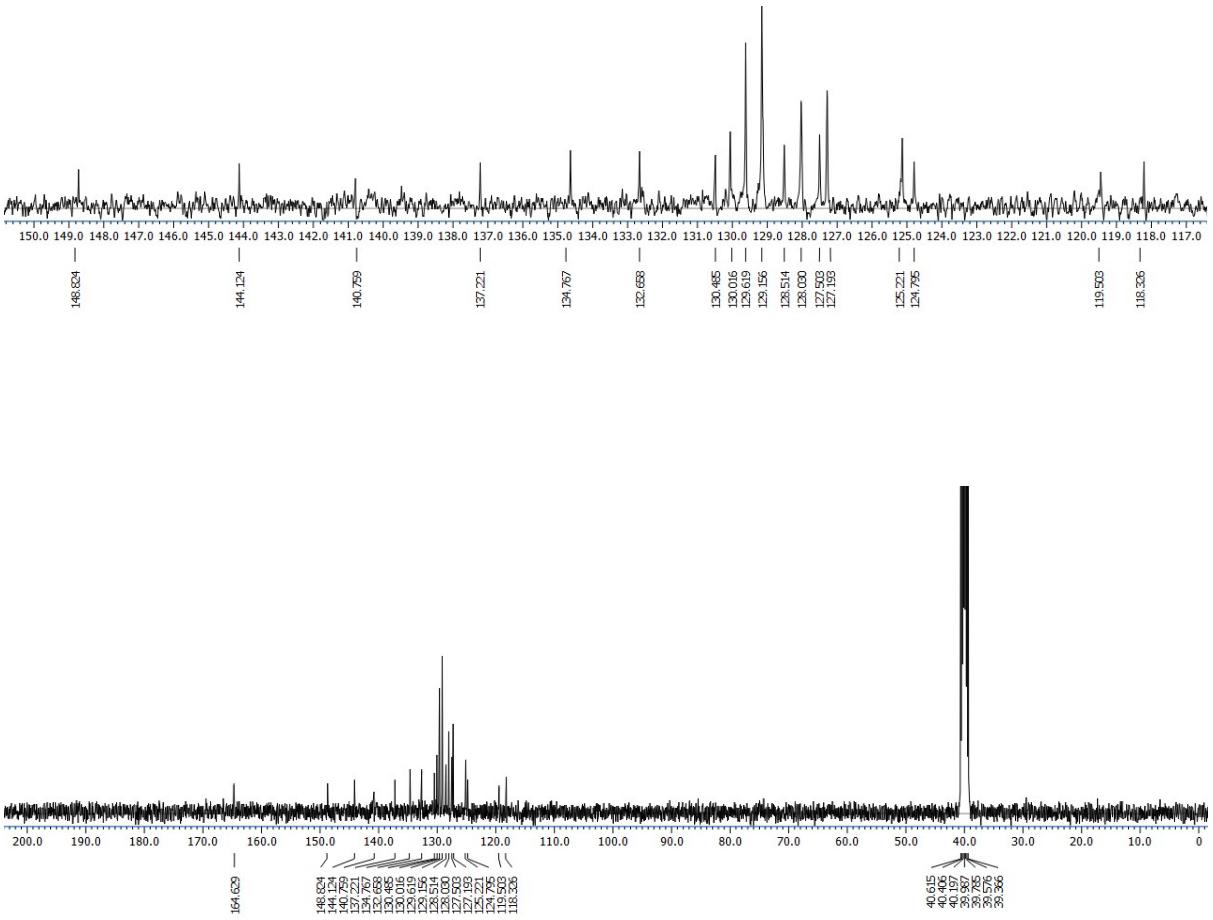




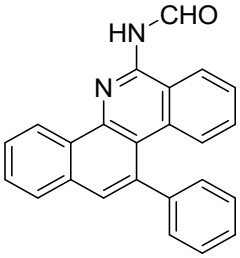
^{13}C NMR (100 MHz, $CDCl_3$)



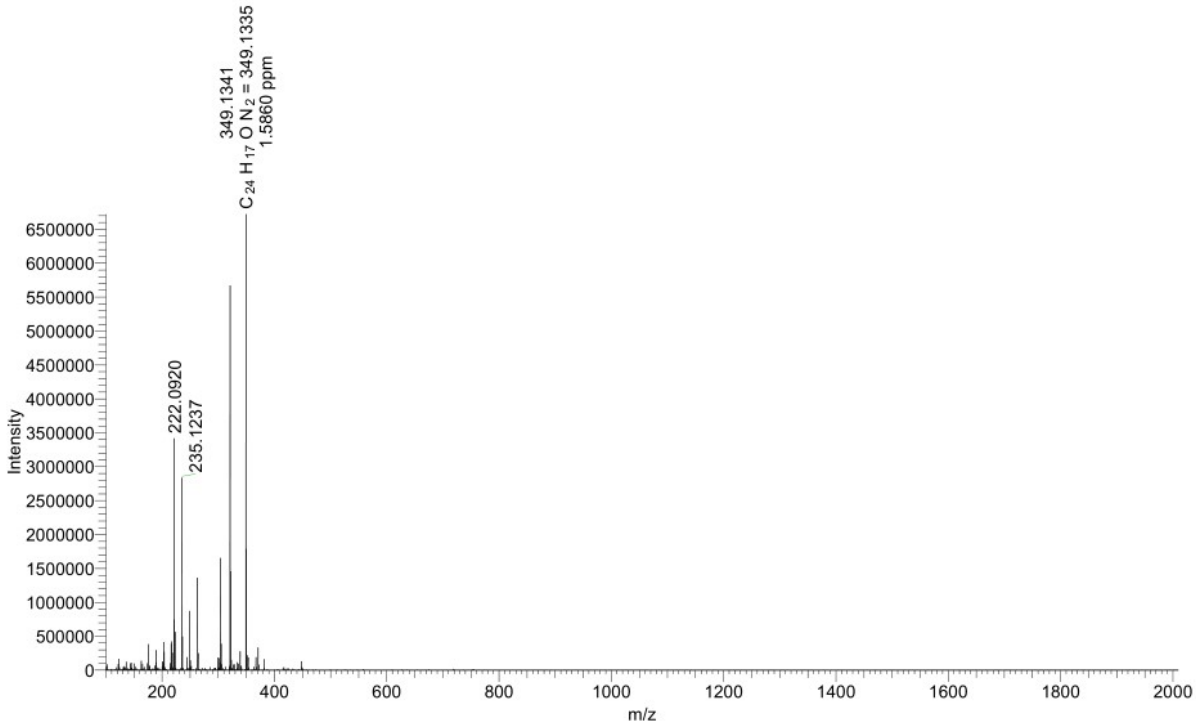
***N*-(11-phenylbenzo[*c*]phenanthridin-6-yl)formamide (6a)**



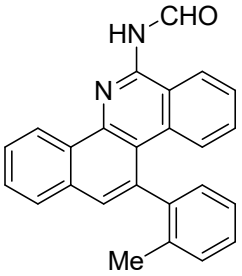
HRMS



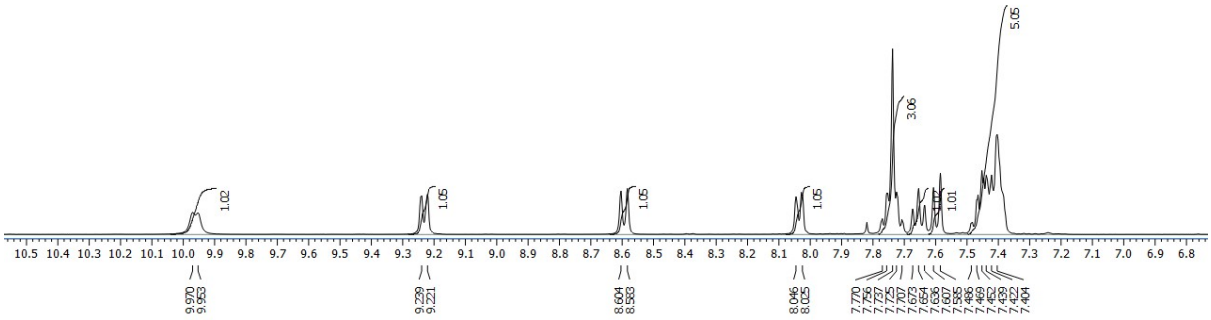
***N*-(11-phenylbenzo[*c*]phenanthridin-6-yl)formamide (6a)**

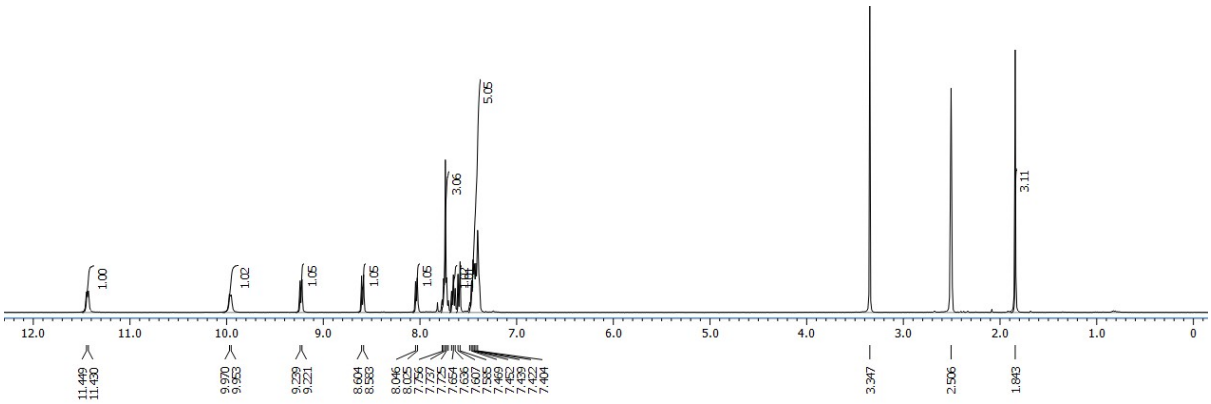


^{1}H NMR (400 MHz, $CDCl_3$)

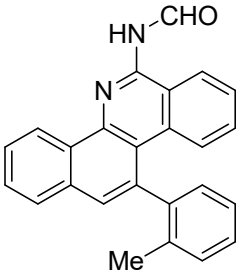


***N*-(11-(*o*-tolyl)benzo[*c*]phenanthridin-6-yl)formamide (6b)**

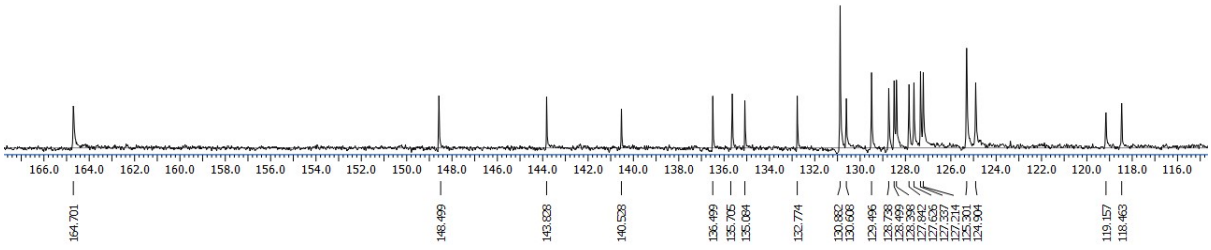


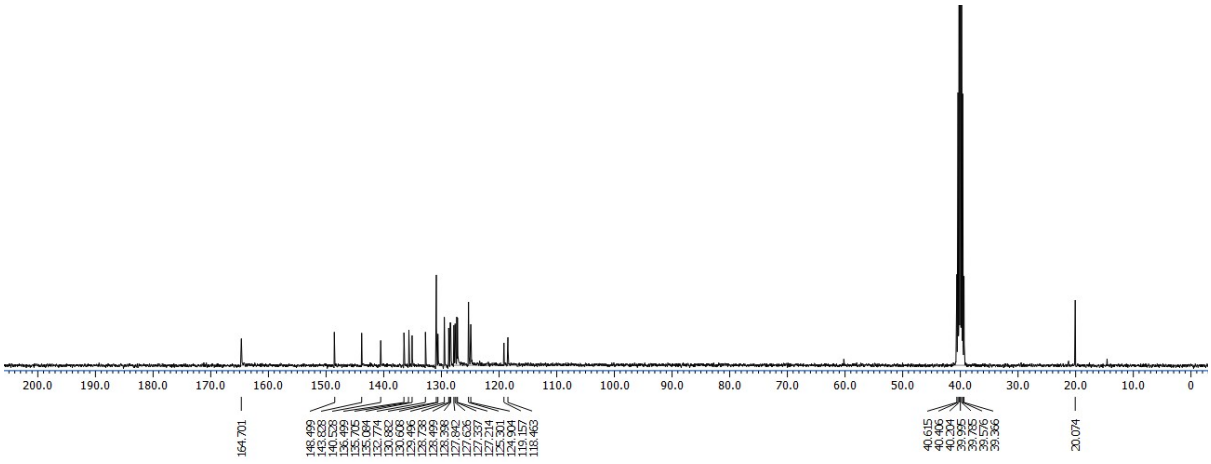


^{13}C NMR (100 MHz, $CDCl_3$)

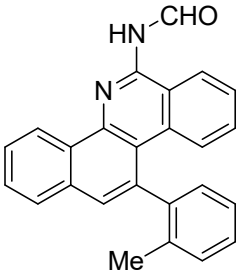


***N*-(11-(*o*-tolyl)benzo[*c*]phenanthridin-6-yl)formamide (6b)**

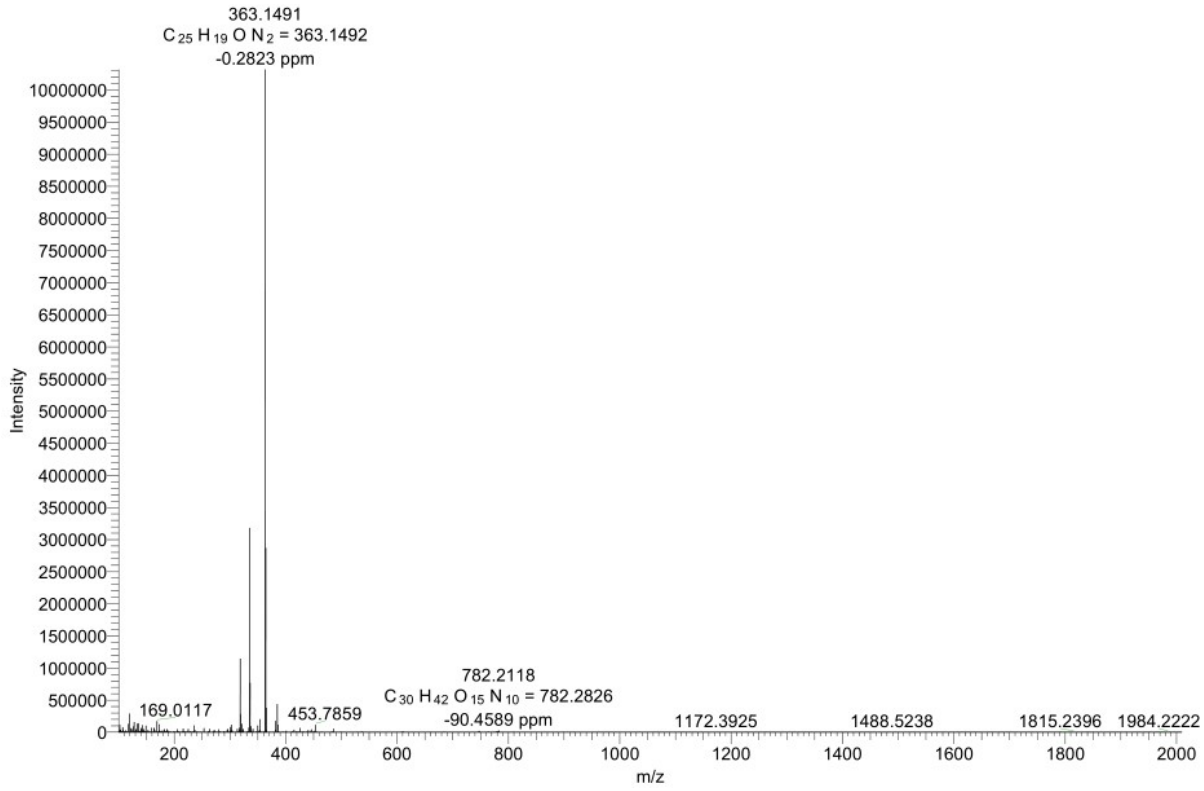




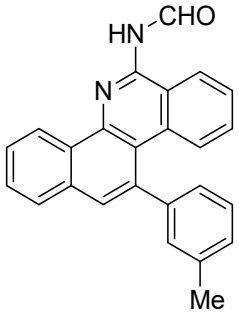
HRMS



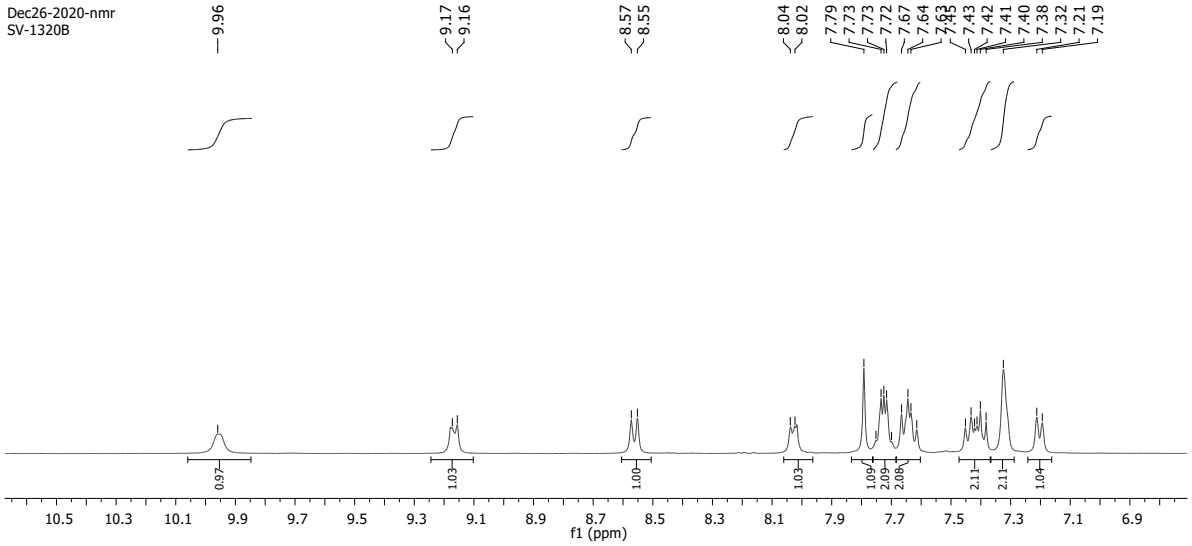
***N*-(11-(*o*-tolyl)benzo[*c*]phenanthridin-6-yl)formamide (6b)**

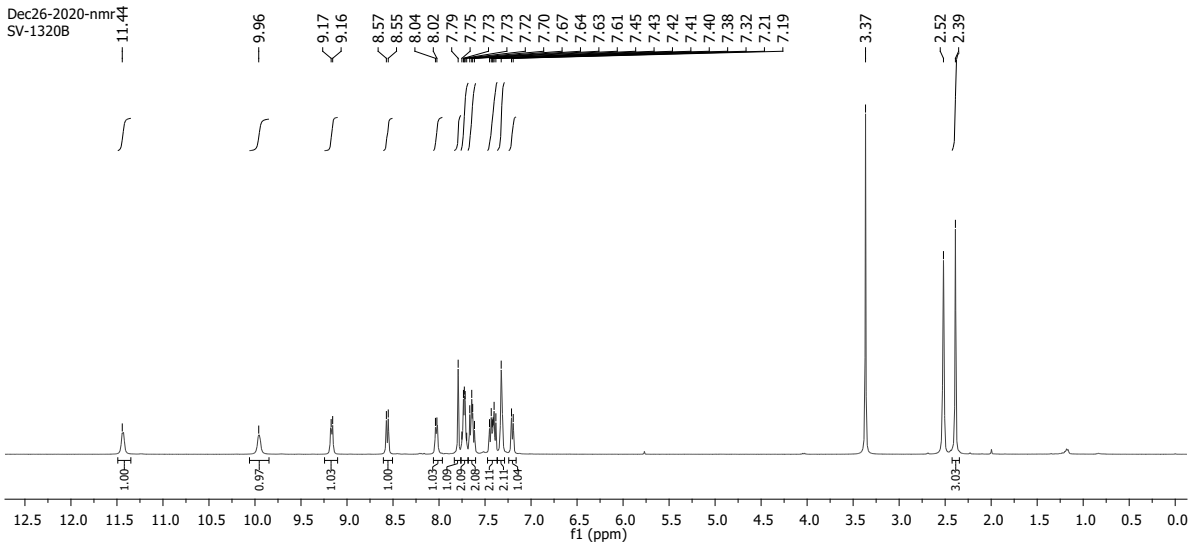


^{1}H NMR (400 MHz, $CDCl_3$)

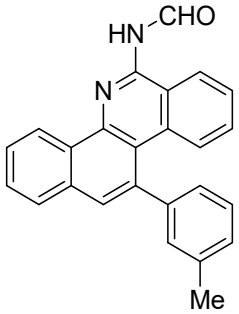


***N*-(11-(*m*-tolyl)benzo[*c*]phenanthridin-6-yl)formamide (6c)**

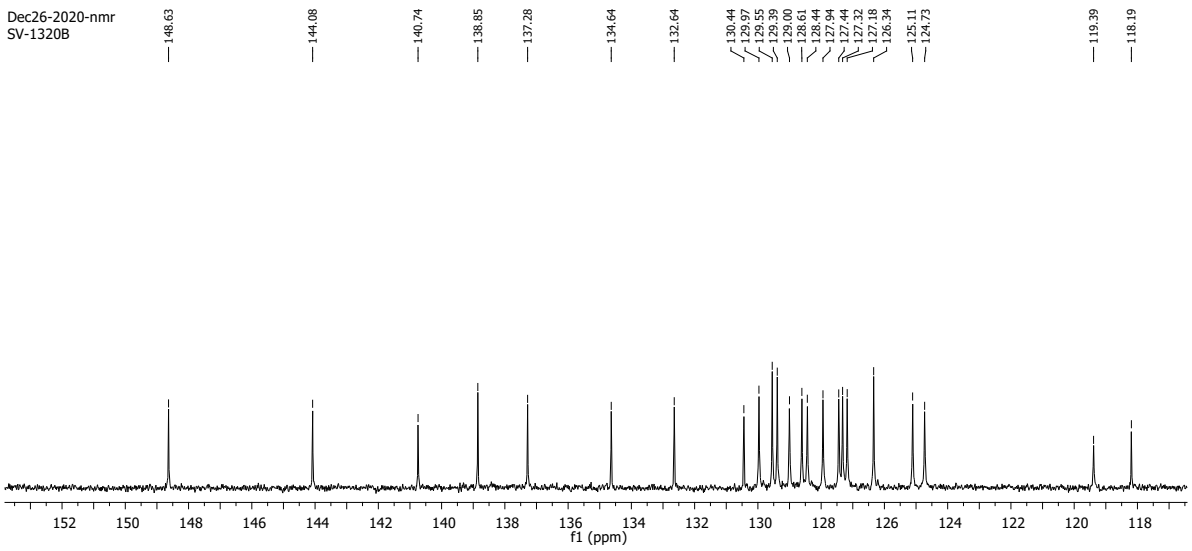


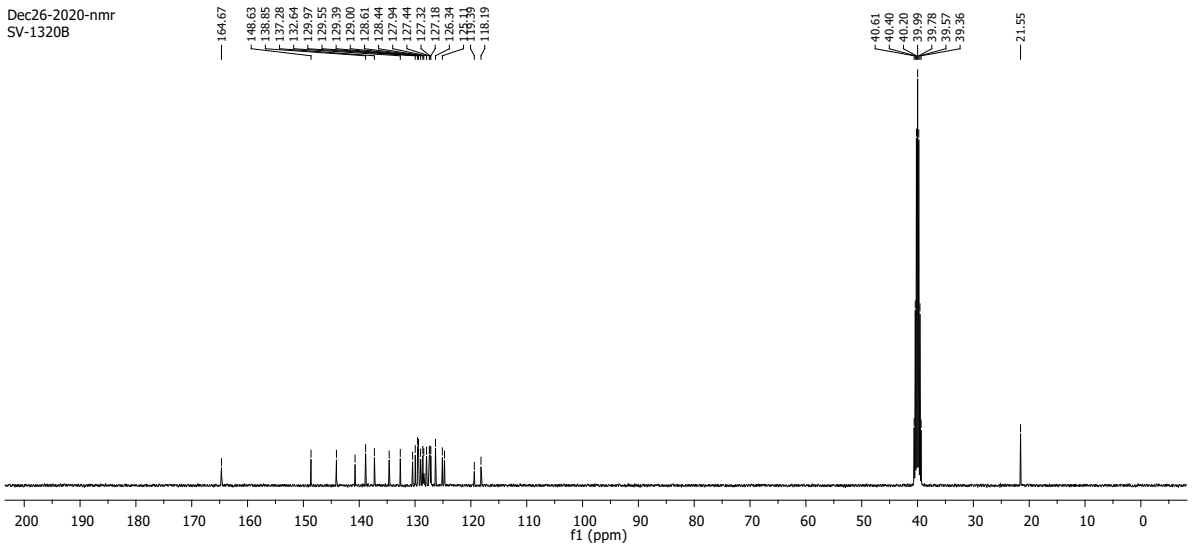


^{13}C NMR (100 MHz, $CDCl_3$)

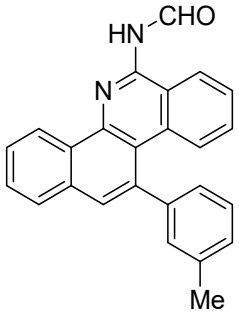


***N*-(11-(*m*-tolyl)benzo[*c*]phenanthridin-6-yl)formamide (6c)**



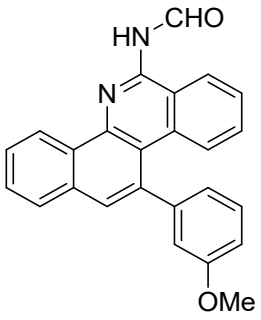


HRMS

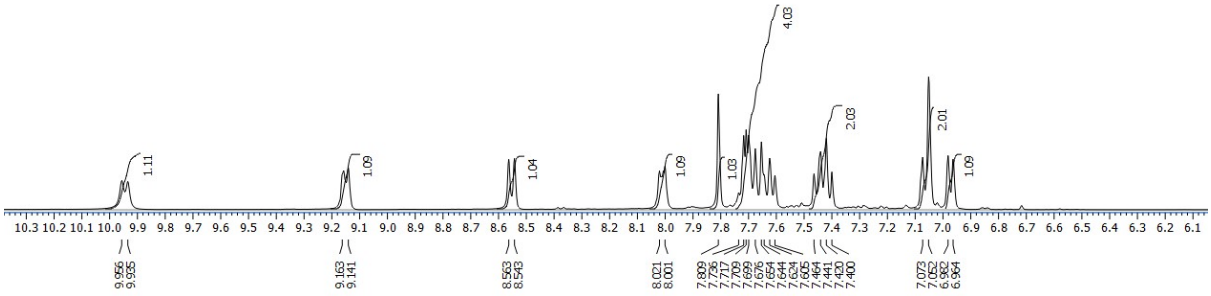


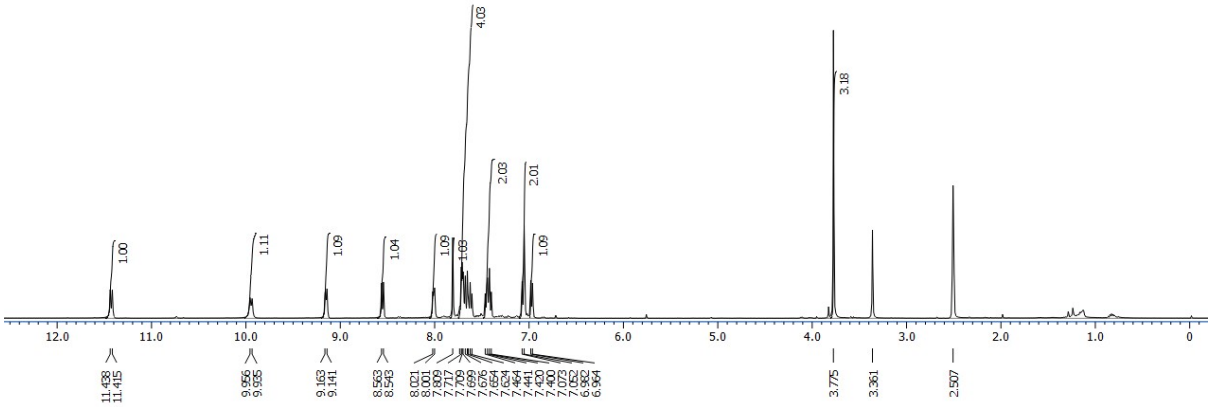
***N*-(11-(*m*-tolyl)benzo[*c*]phenanthridin-6-yl)formamide (6c)**

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

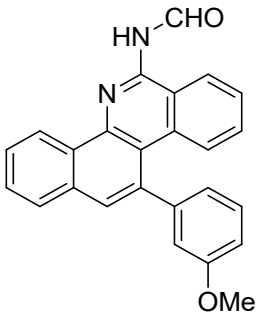


***N*-(11-(3-methoxyphenyl)benzo[*c*]phenanthridin-6-yl)formamide (6d)**

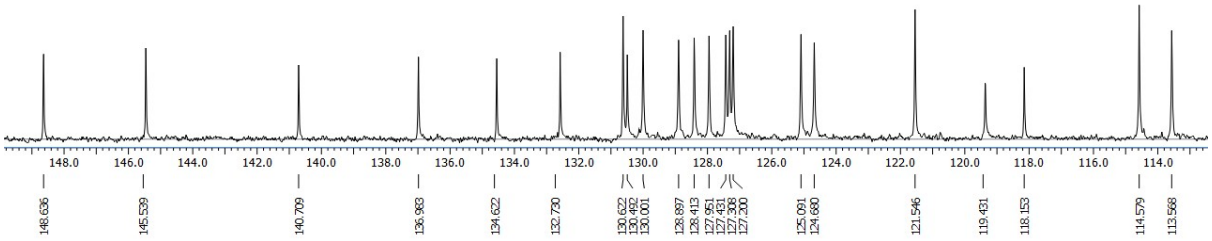


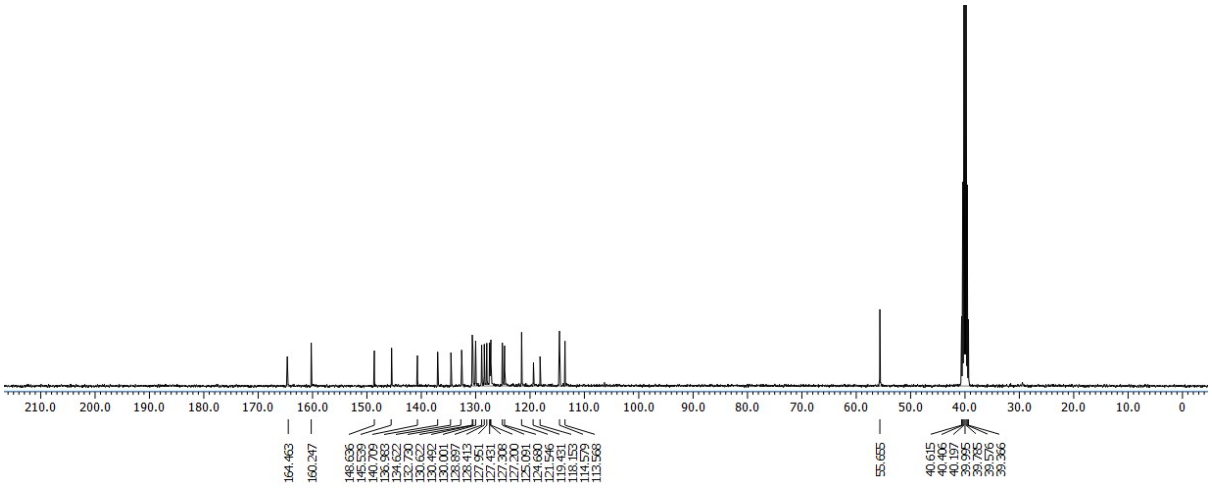


^{13}C NMR (100 MHz, $CDCl_3$)

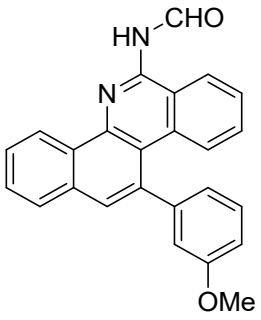


***N*-(11-(3-methoxyphenyl)benzo[*c*]phenanthridin-6-yl)formamide (6d)**

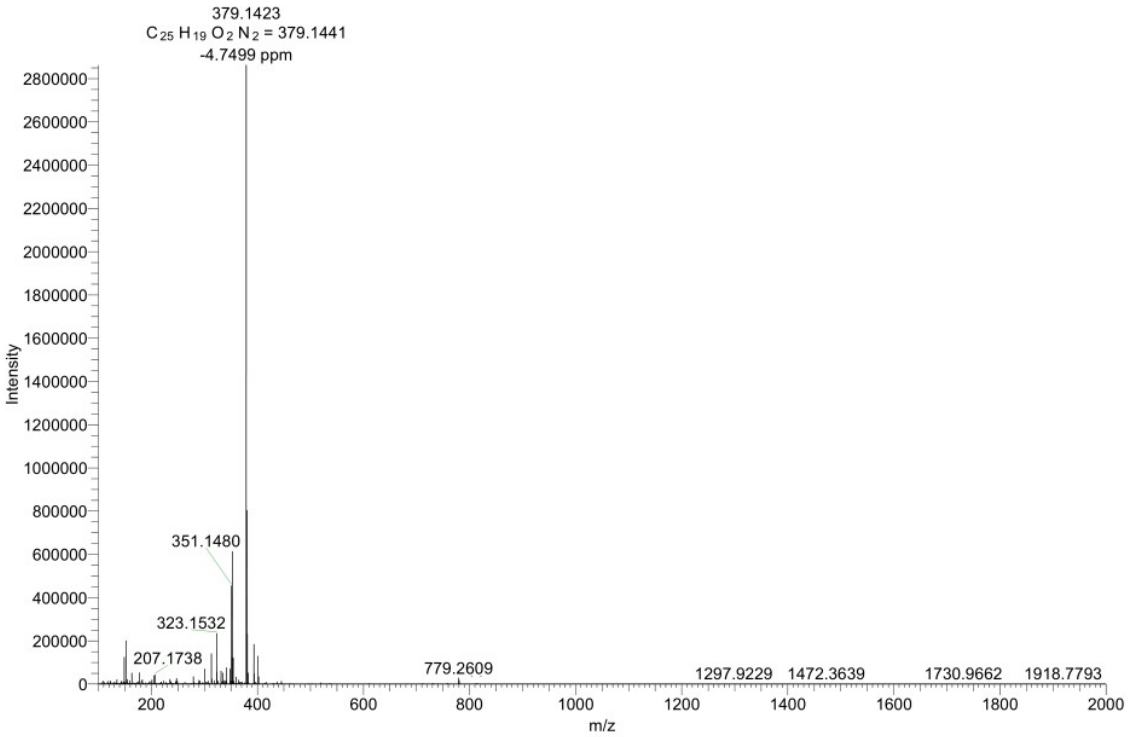




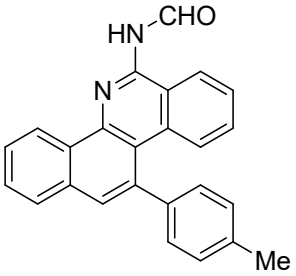
HRMS



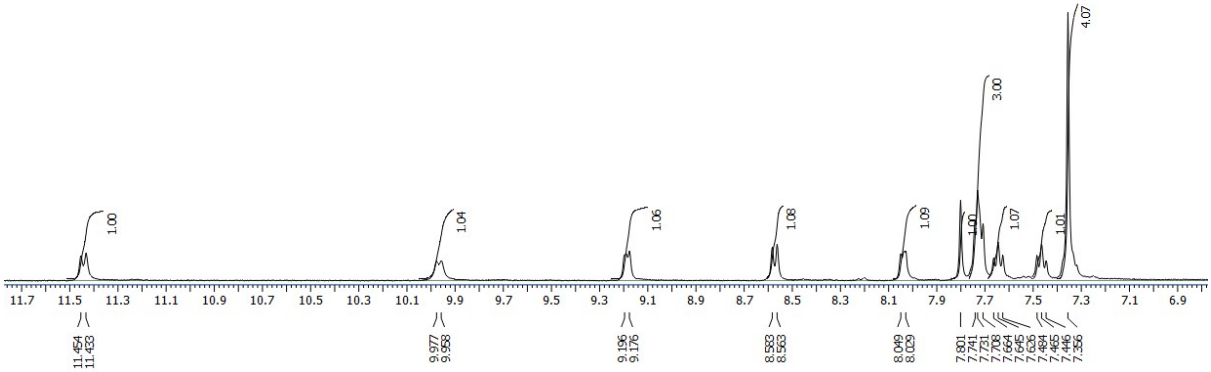
***N*-(11-(3-methoxyphenyl)benzo[*c*]phenanthridin-6-yl)formamide (6d)**

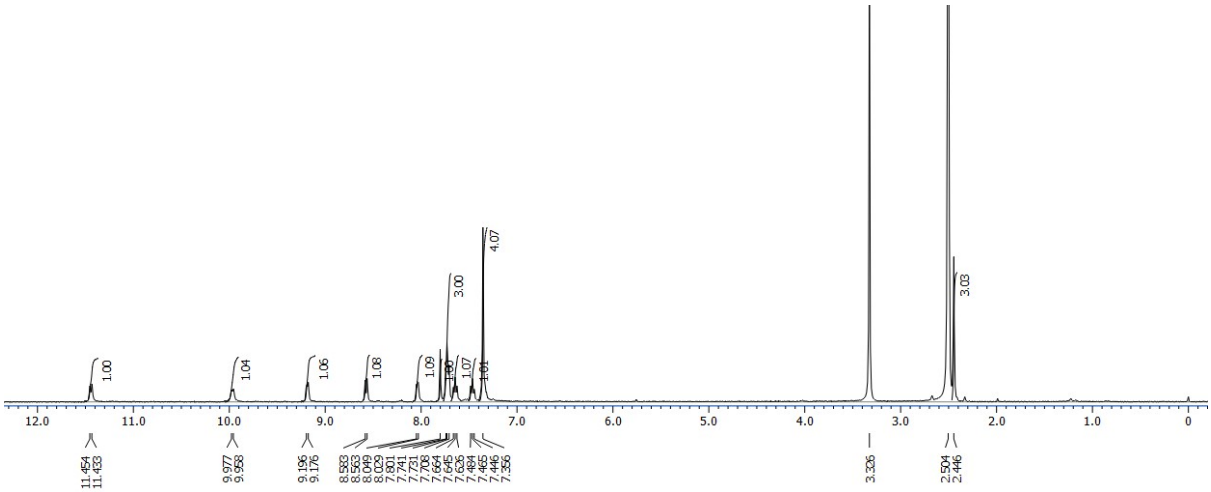


^{1}H NMR (400 MHz, $CDCl_3$)

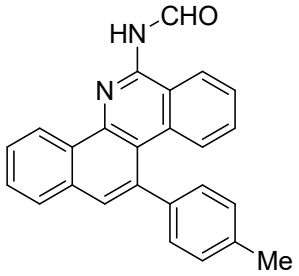


***N*-(11-(*p*-tolyl)benzo[*c*]phenanthridin-6-yl)formamide (6e)**

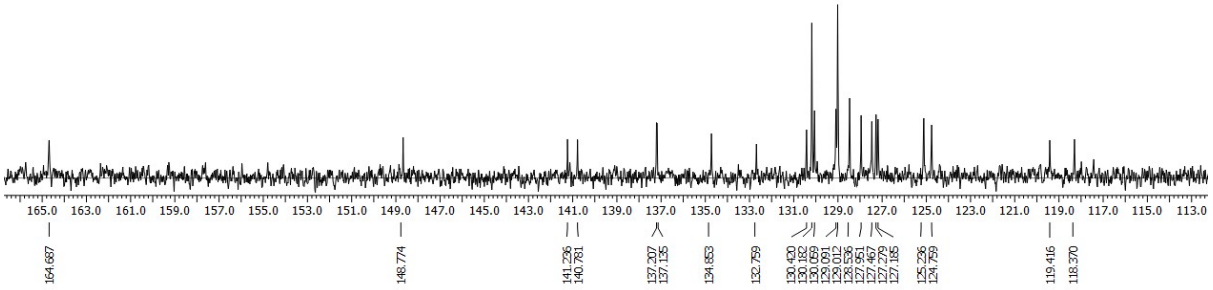


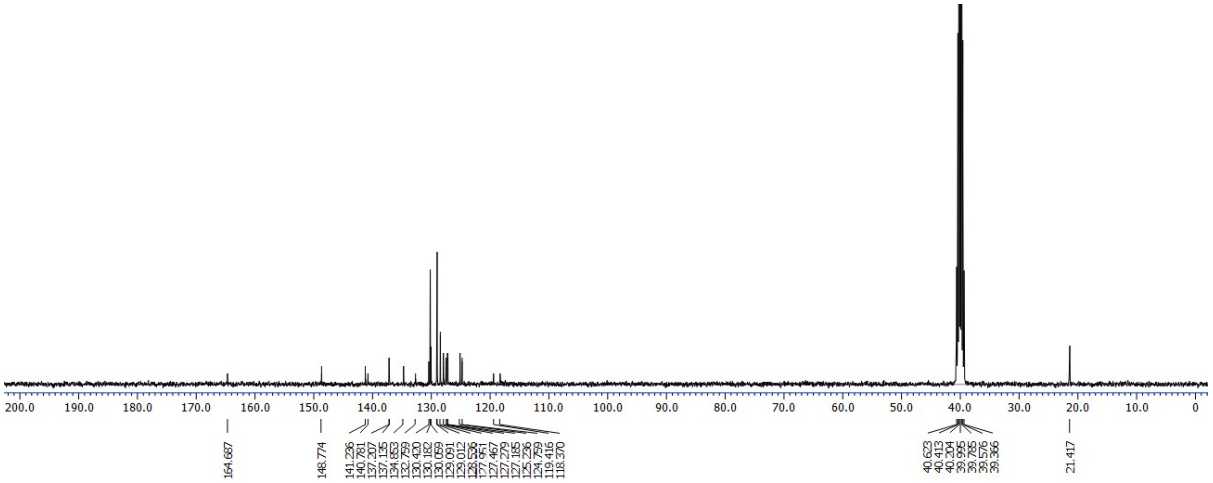


^{13}C NMR (100 MHz, $CDCl_3$)

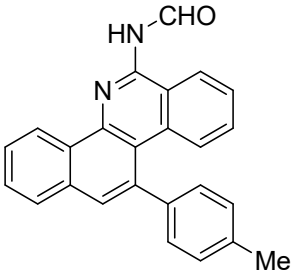


***N*-(11-(*p*-tolyl)benzo[*c*]phenanthridin-6-yl)formamide (6e)**



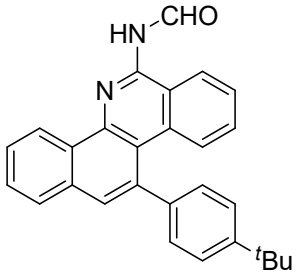


HRMS

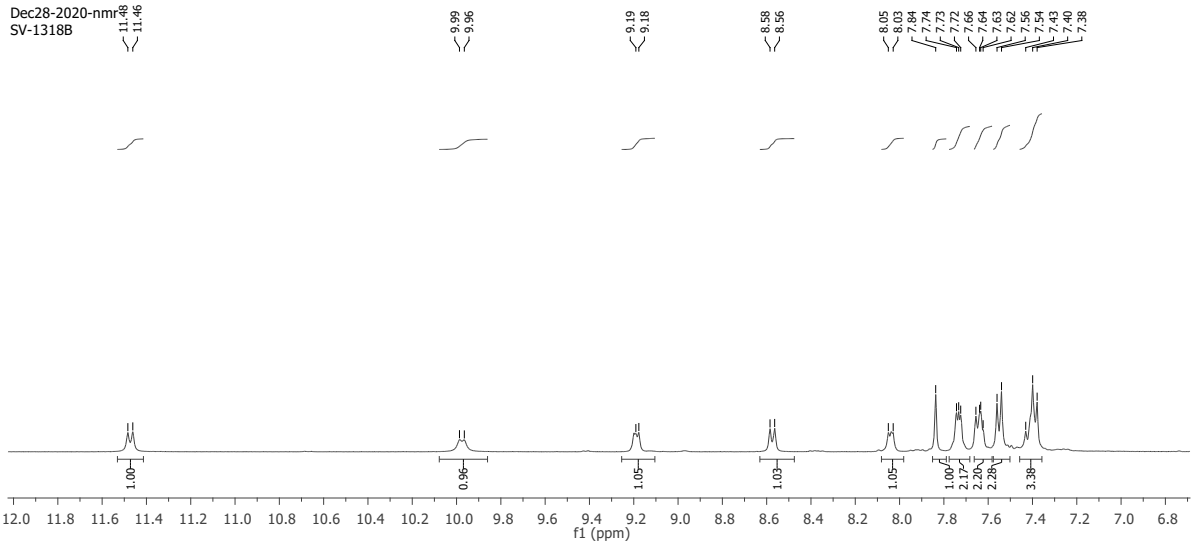


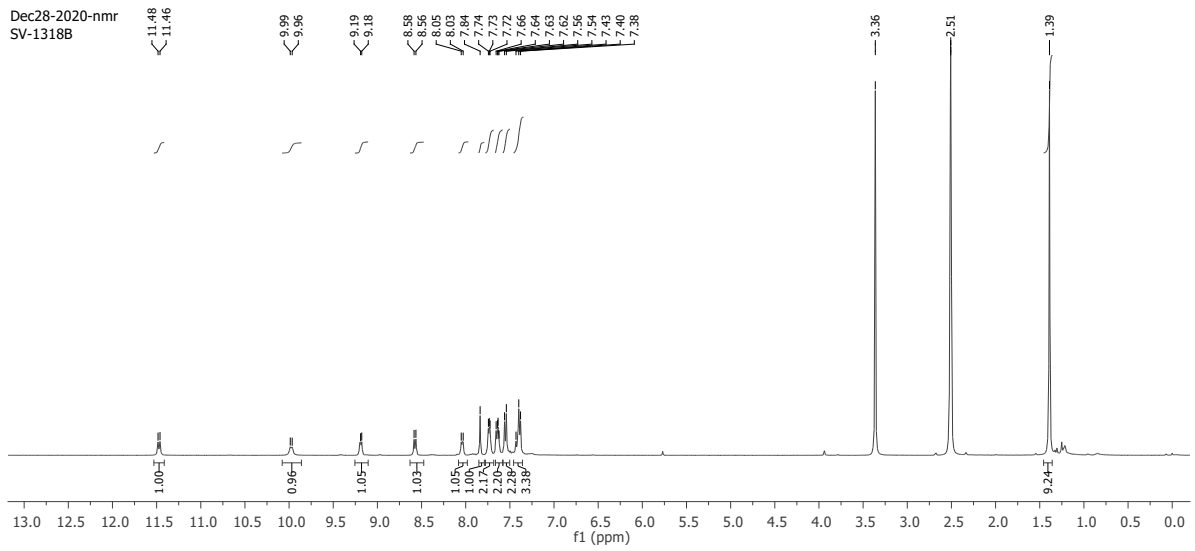
***N*-(11-(*p*-tolyl)benzo[*c*]phenanthridin-6-yl)formamide (6e)**

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

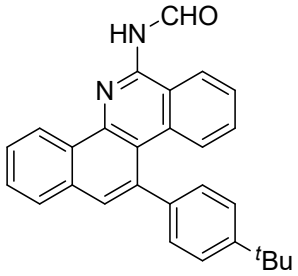


N-(11-(4-(*tert*-butyl)phenyl)benzo[*c*]phenanthridin-6-yl)formamide (6f)

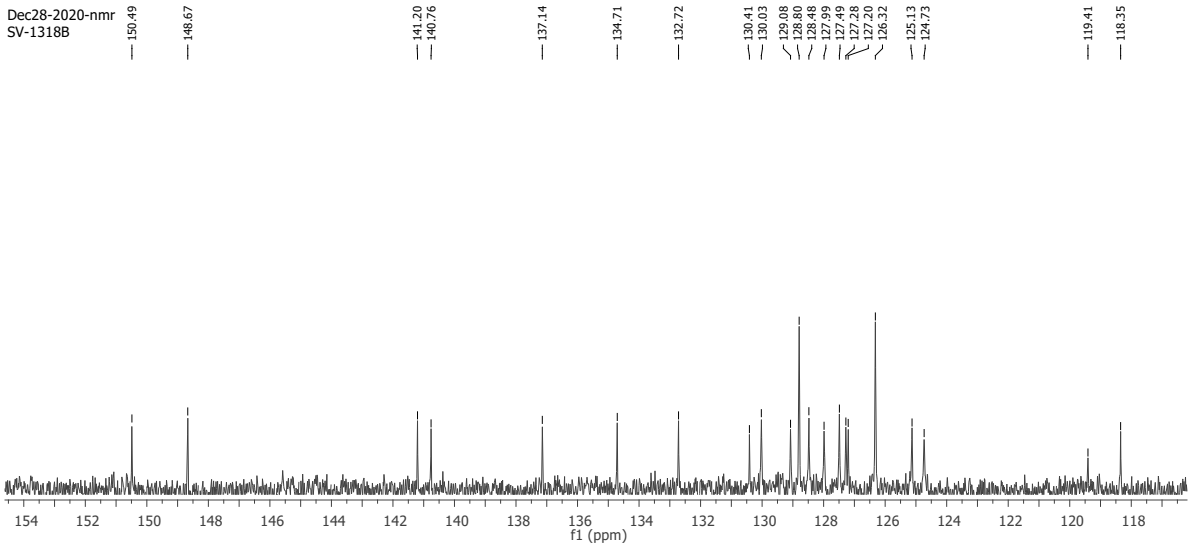


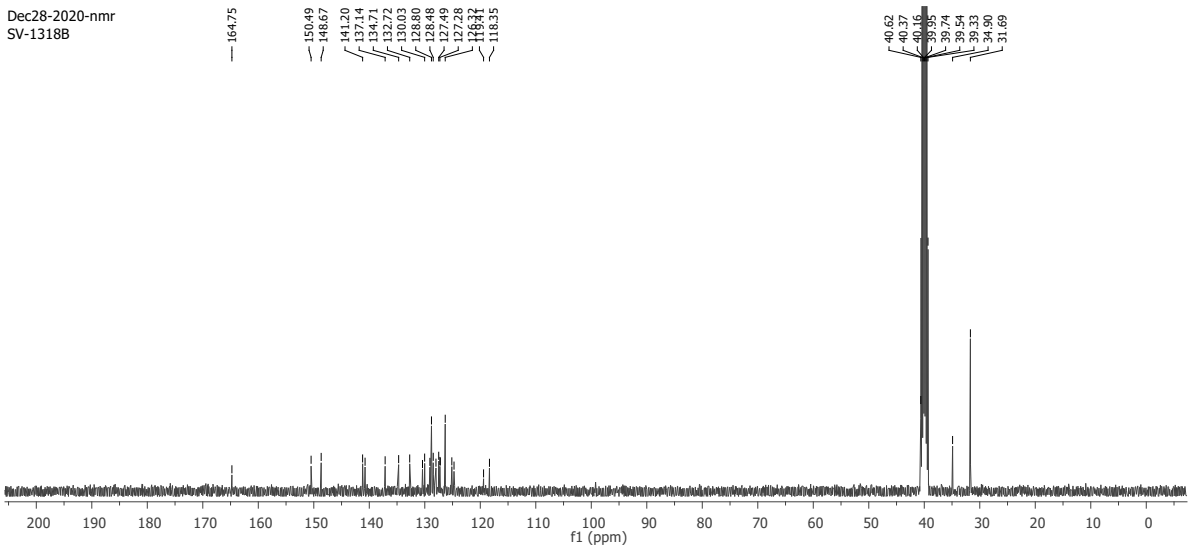


^{13}C NMR (100 MHz, $CDCl_3$)

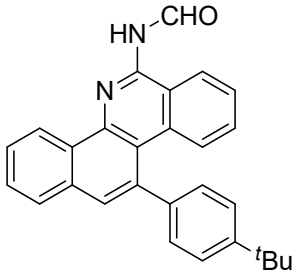


N-(11-(4-(*tert*-butyl)phenyl)benzo[*c*]phenanthridin-6-yl)formamide (6f)

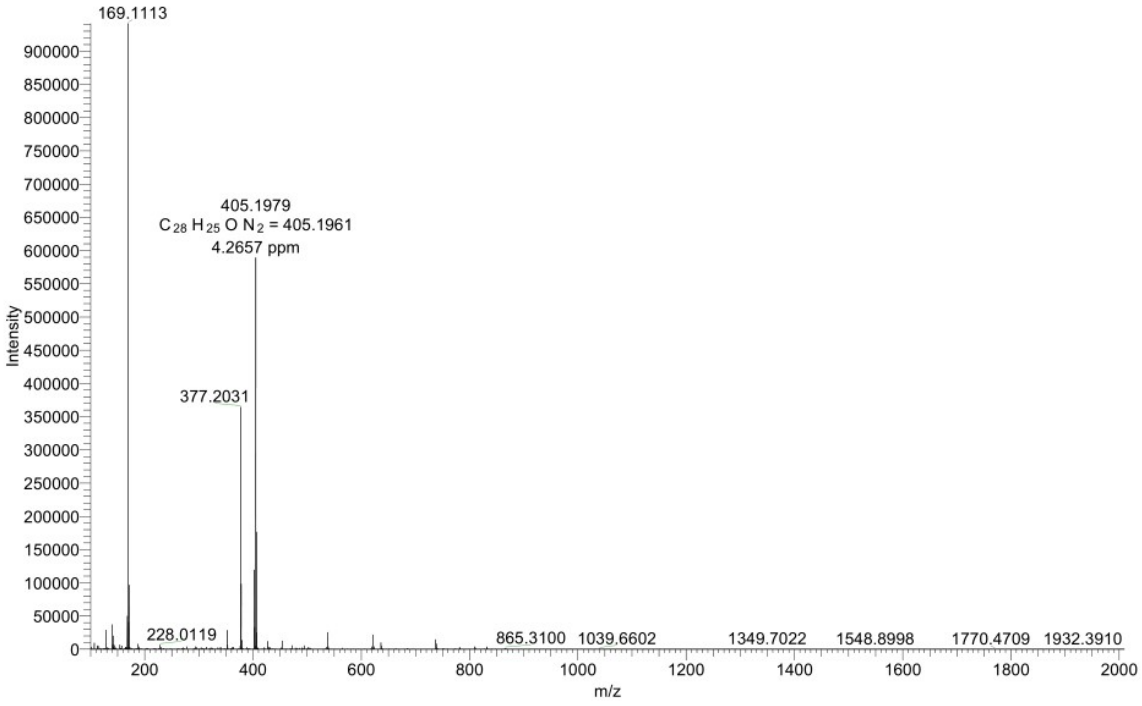




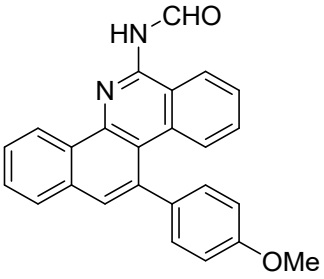
HRMS



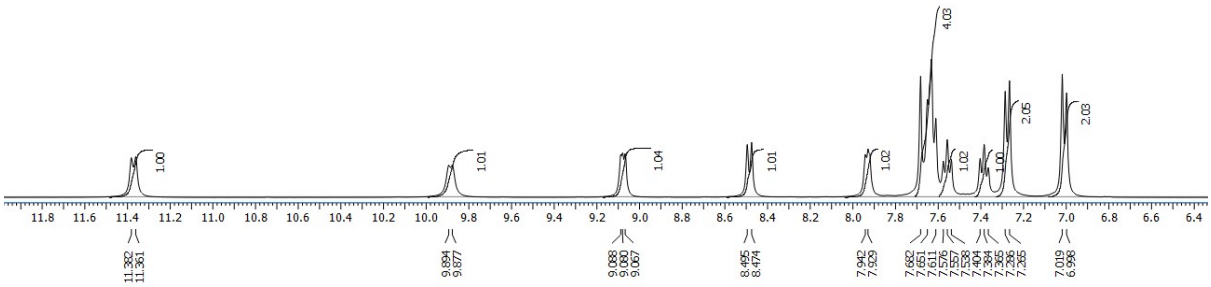
N-(11-(4-(*tert*-butyl)phenyl)benzo[*c*]phenanthridin-6-yl)formamide (6f)

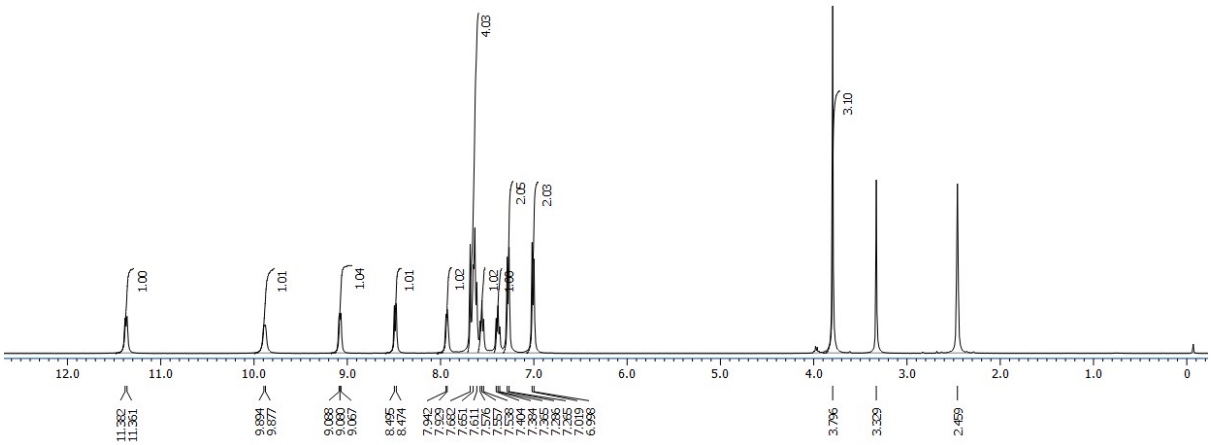


^{1}H NMR (400 MHz, $CDCl_3$)

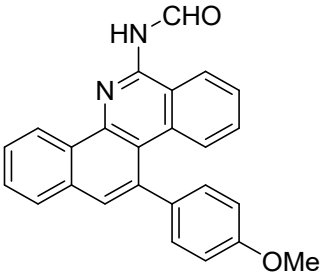


***N*-(11-(4-methoxyphenyl)benzo[*c*]phenanthridin-6-yl)formamide (6g)**

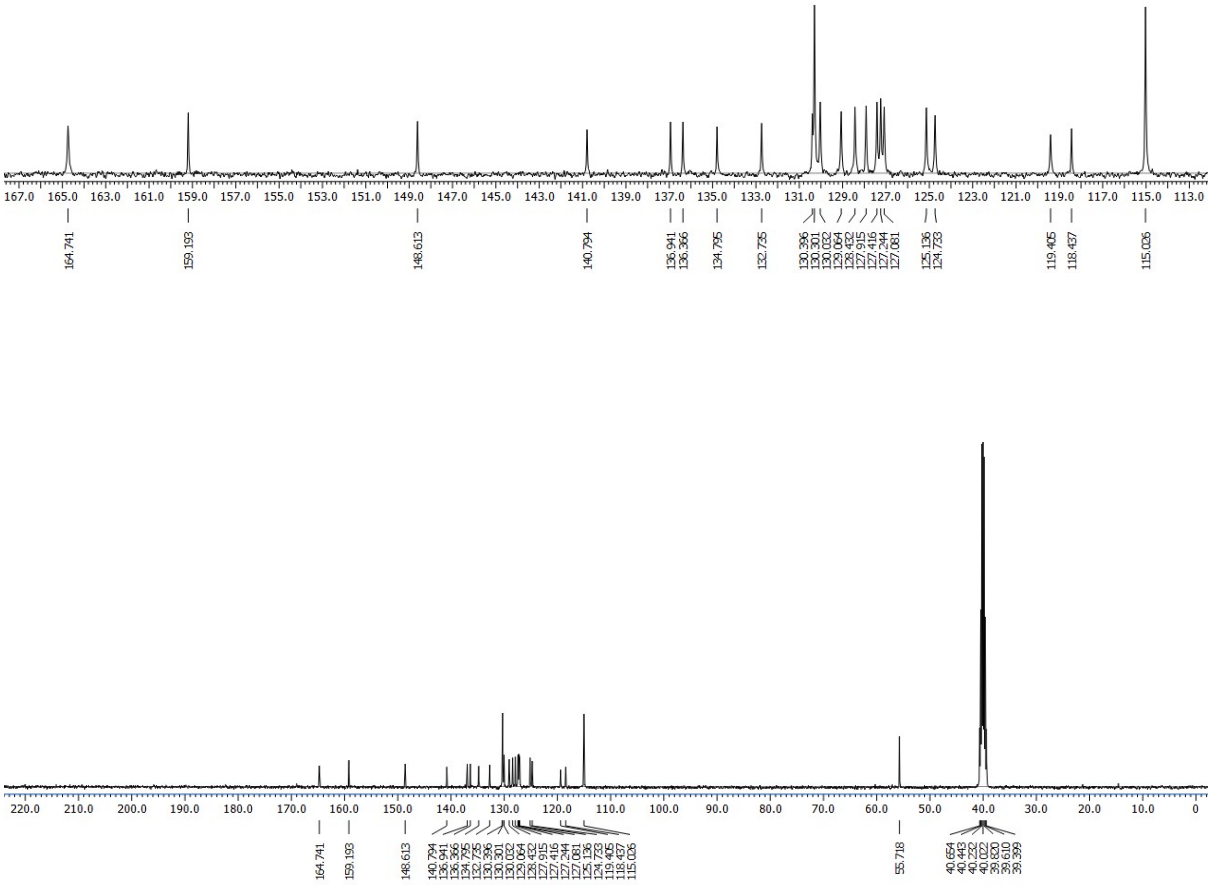




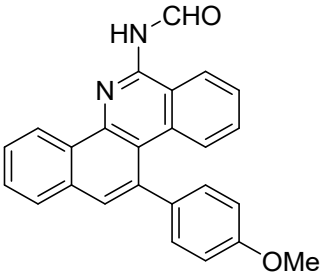
^{13}C NMR (100 MHz, $CDCl_3$)



***N*-(11-(4-methoxyphenyl)benzo[*c*]phenanthridin-6-yl)formamide (6g)**

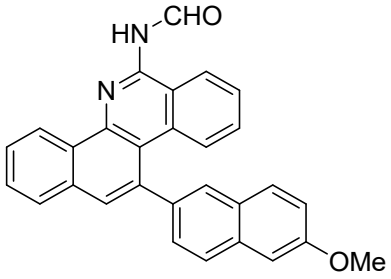


HRMS

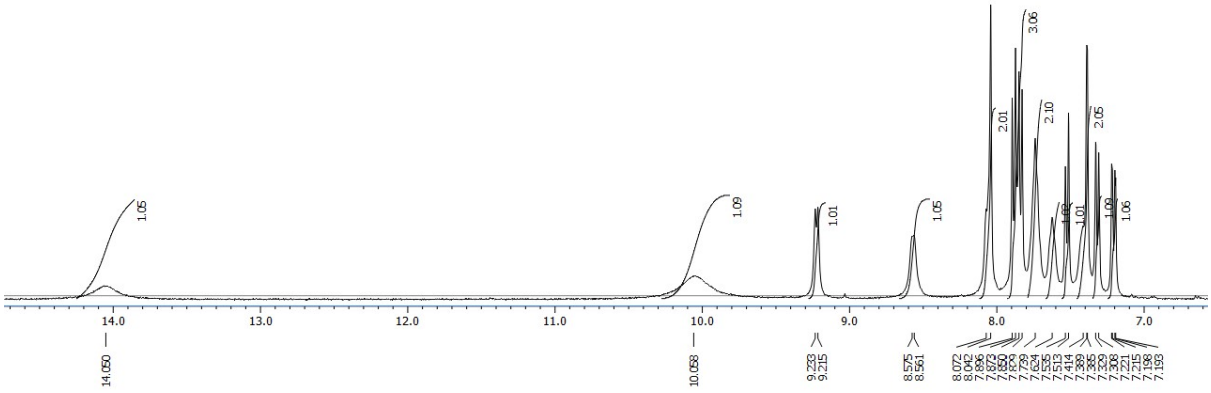


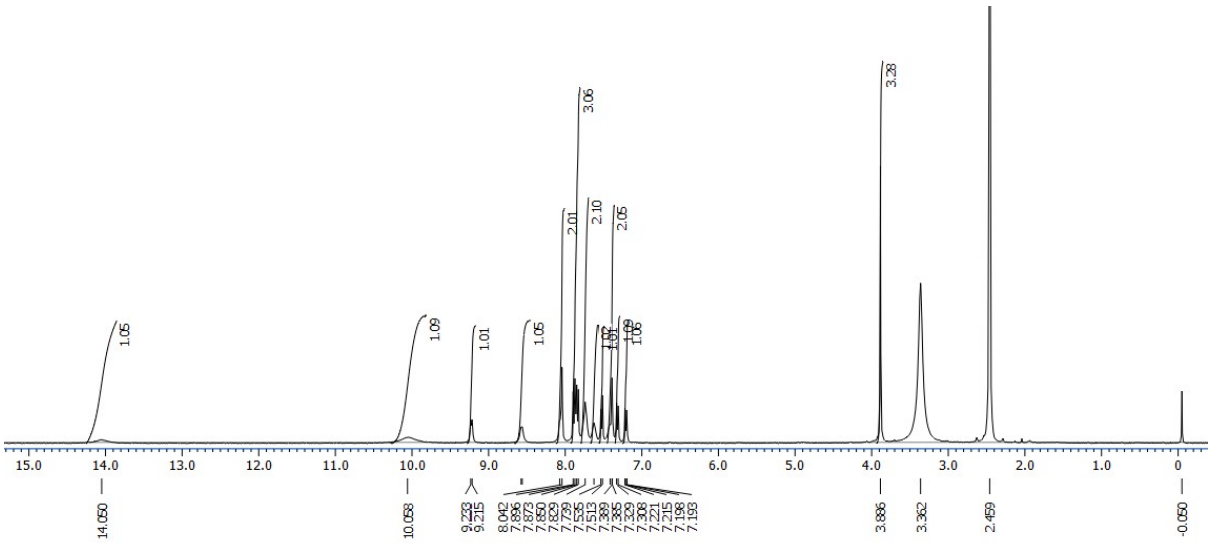
***N*-(11-(4-methoxyphenyl)benzo[*c*]phenanthridin-6-yl)formamide (6g)**

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

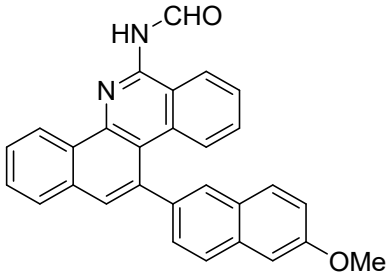


***N*-(11-(6-methoxynaphthalen-2-yl)benzo[*c*]phenanthridin-6-yl)formamide (6h)**

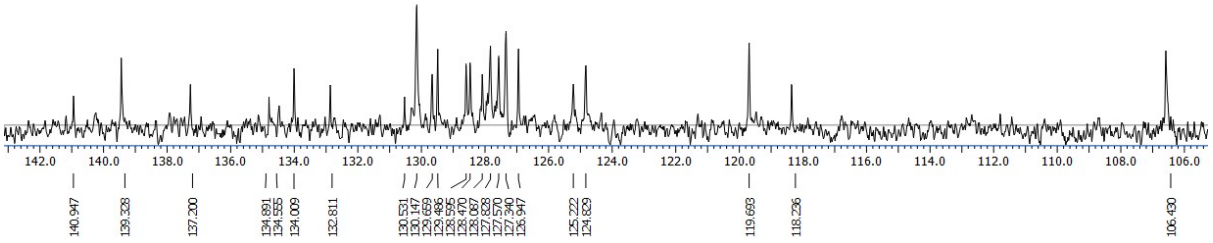


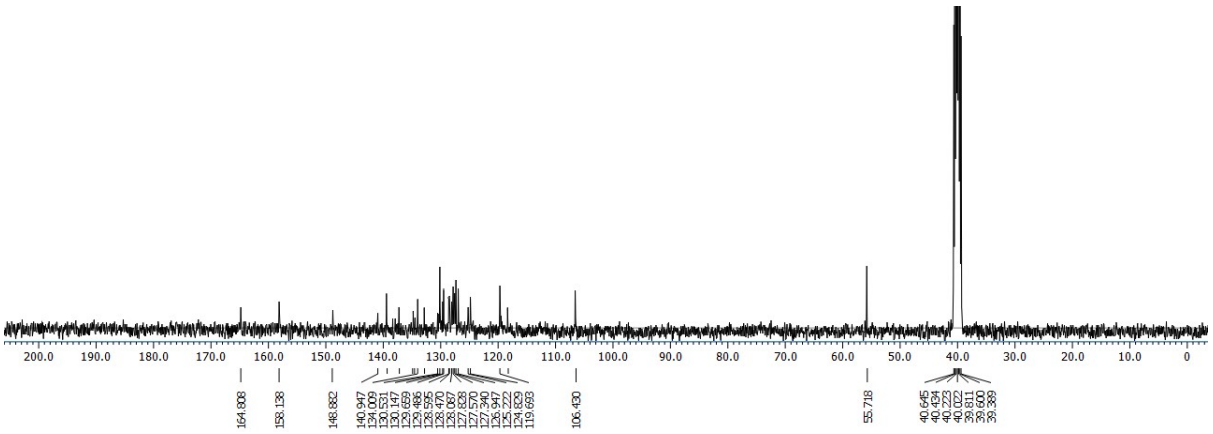


^{13}C NMR (100 MHz, $CDCl_3$)

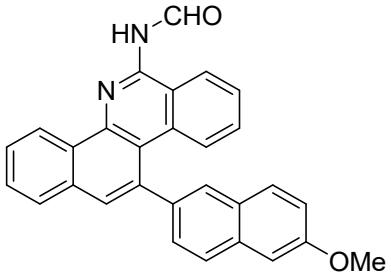


***N*-(11-(6-methoxynaphthalen-2-yl)benzo[*c*]phenanthridin-6-yl)formamide (6h)**

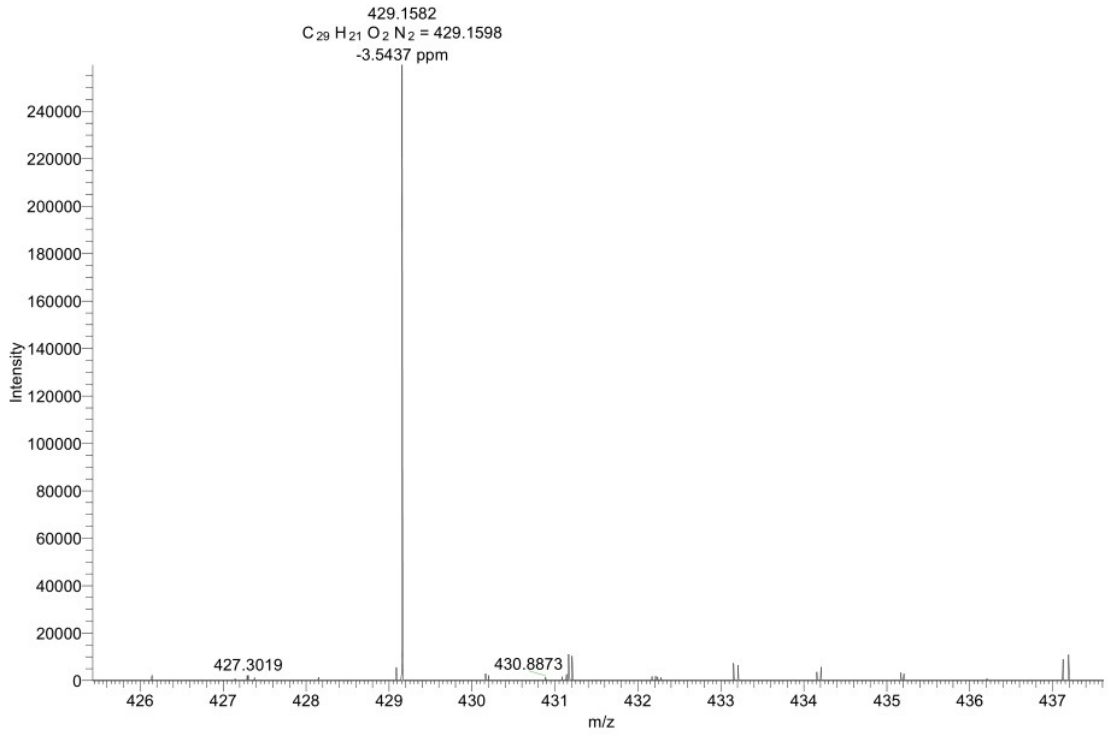




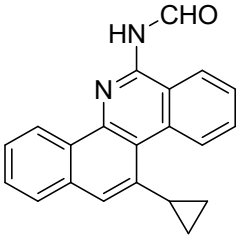
HRMS



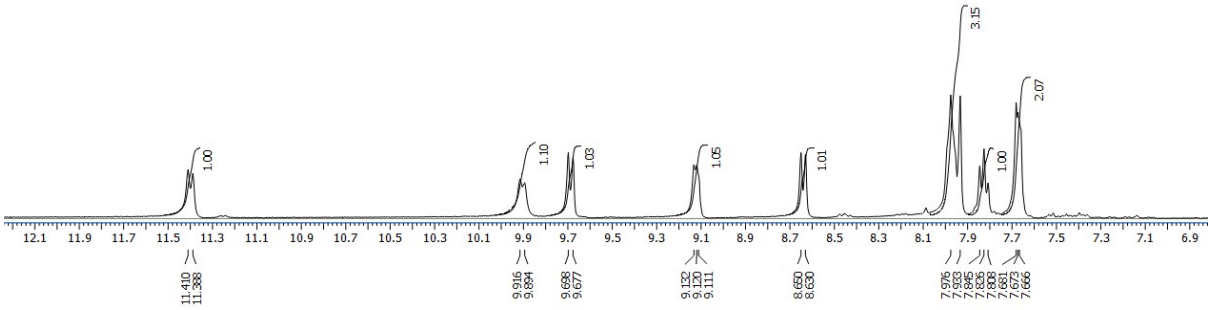
***N*-(11-(6-methoxynaphthalen-2-yl)benzo[*c*]phenanthridin-6-yl)formamide (6h)**

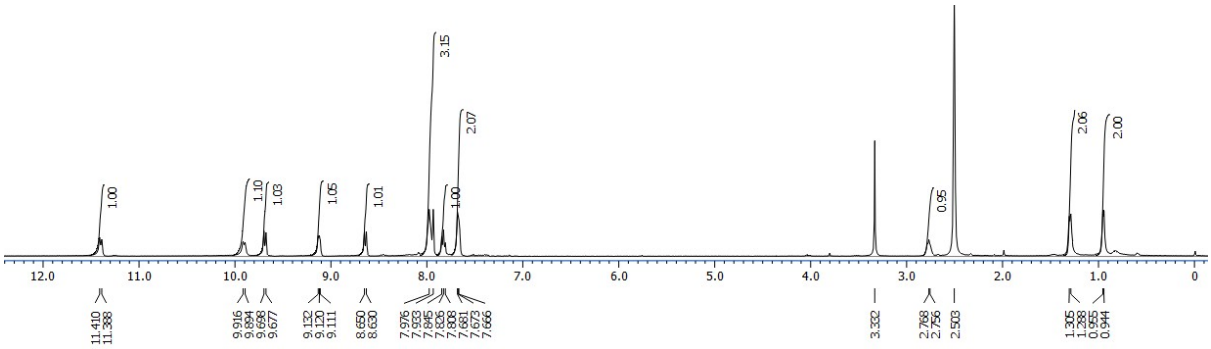


^{1}H NMR (400 MHz, $CDCl_3$)

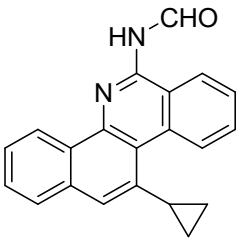


***N*-(11-cyclopropylbenzo[*c*]phenanthridin-6-yl)formamide (6i)**

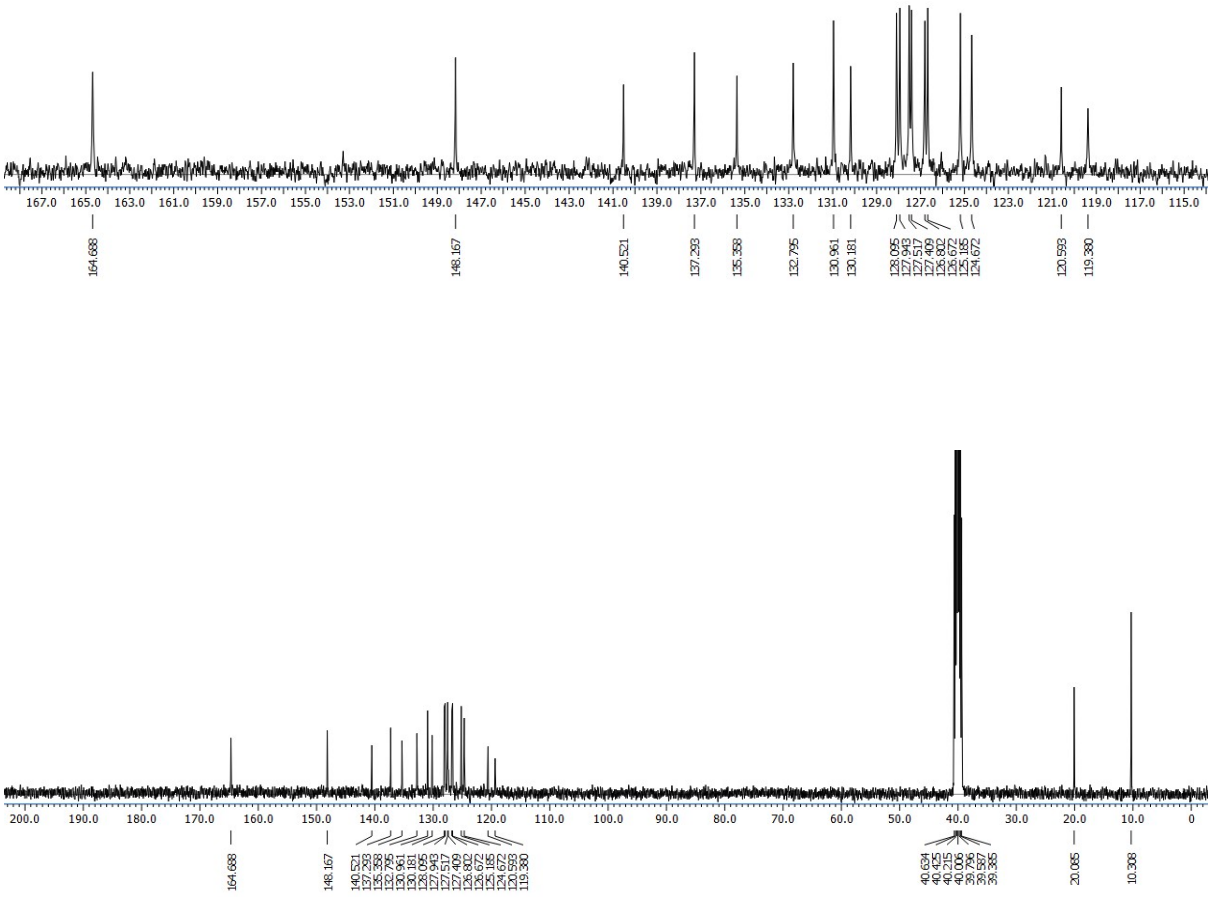




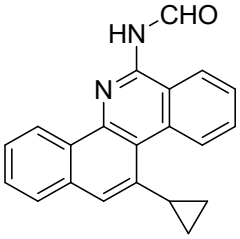
^{13}C NMR (100 MHz, $CDCl_3$)



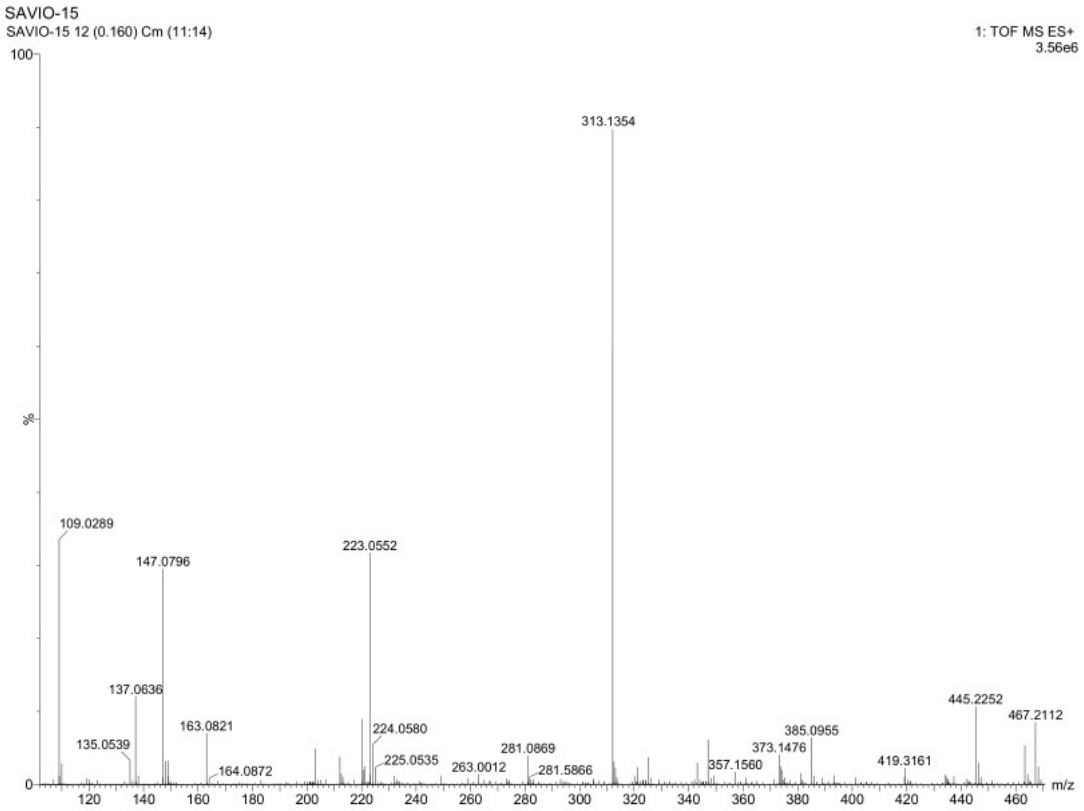
***N*-(11-cyclopropylbenzo[*c*]phenanthridin-6-yl)formamide (6i)**



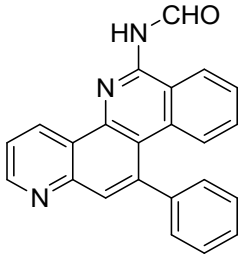
HRMS



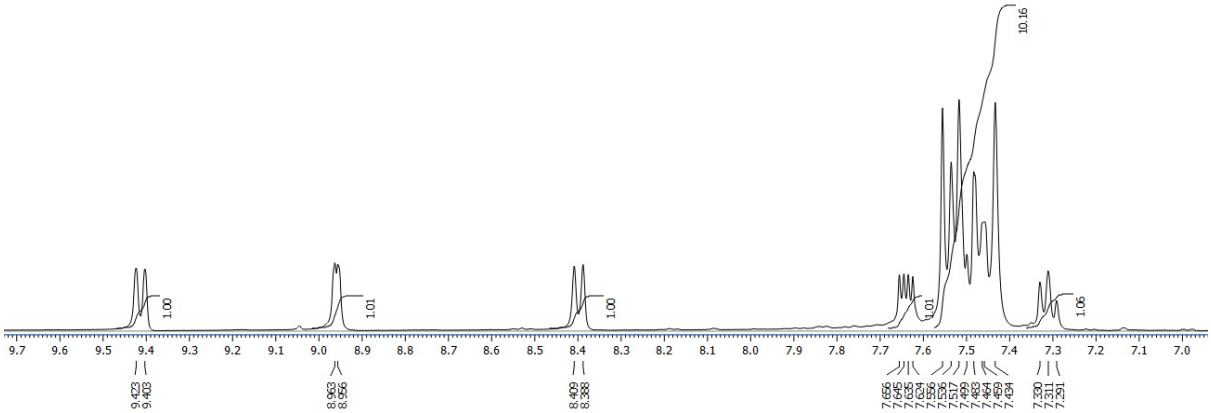
***N*-(11-cyclopropylbenzo[*c*]phenanthridin-6-yl)formamide (6i)**

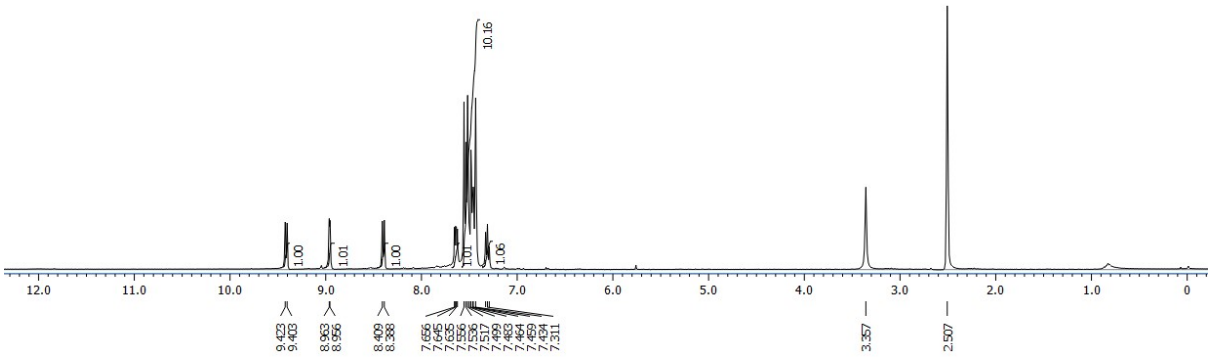


^{1}H NMR (400 MHz, $CDCl_3$)

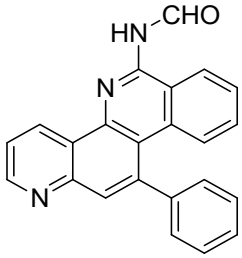


***N*-(11-phenylbenzo[*c*][1,7]phenanthrolin-6-yl)formamide (7a)**

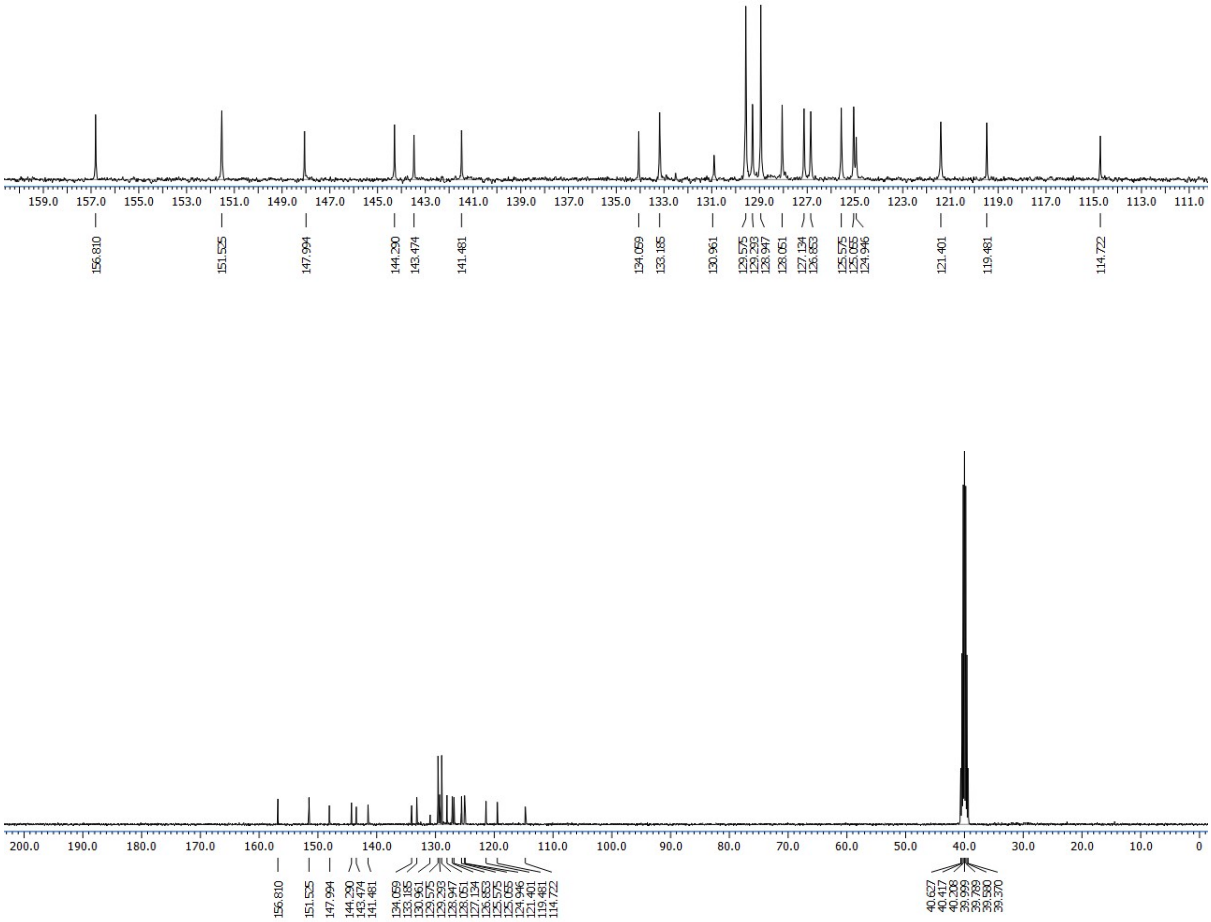




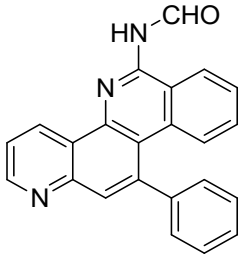
^{13}C NMR (100 MHz, $CDCl_3$)



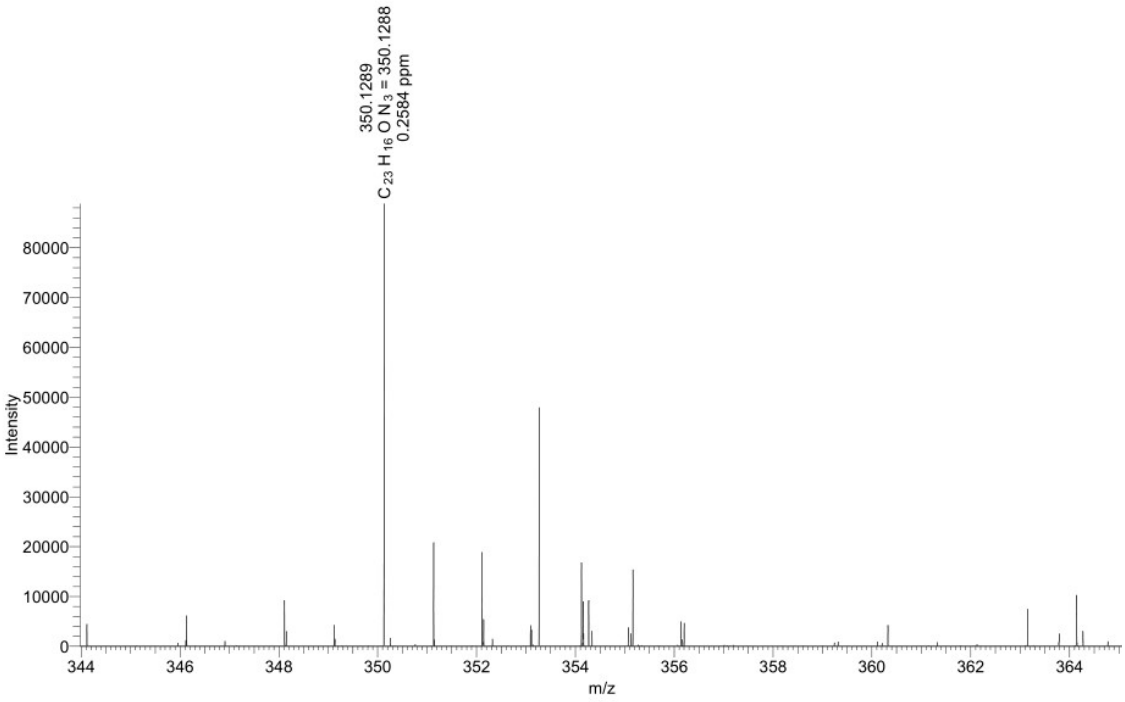
***N*-(11-phenylbenzo[*c*][1,7]phenanthrolin-6-yl)formamide (7a)**



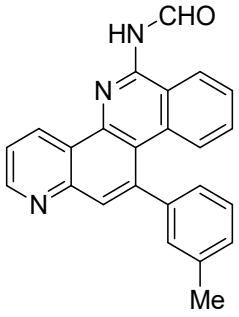
HRMS



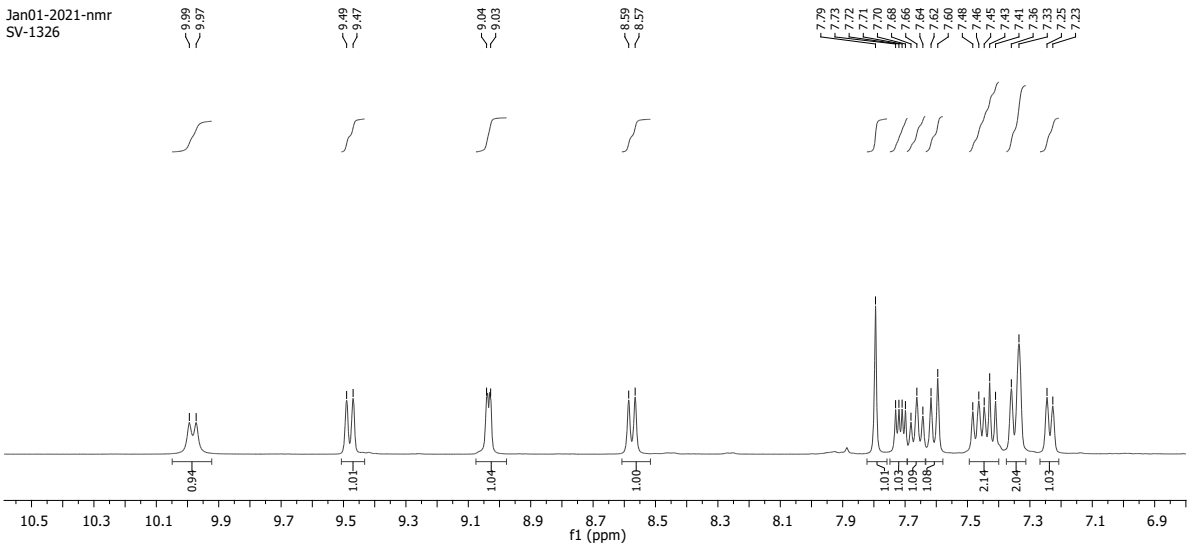
***N*-(11-phenylbenzo[*c*][1,7]phenanthrolin-6-yl)formamide (7a)**

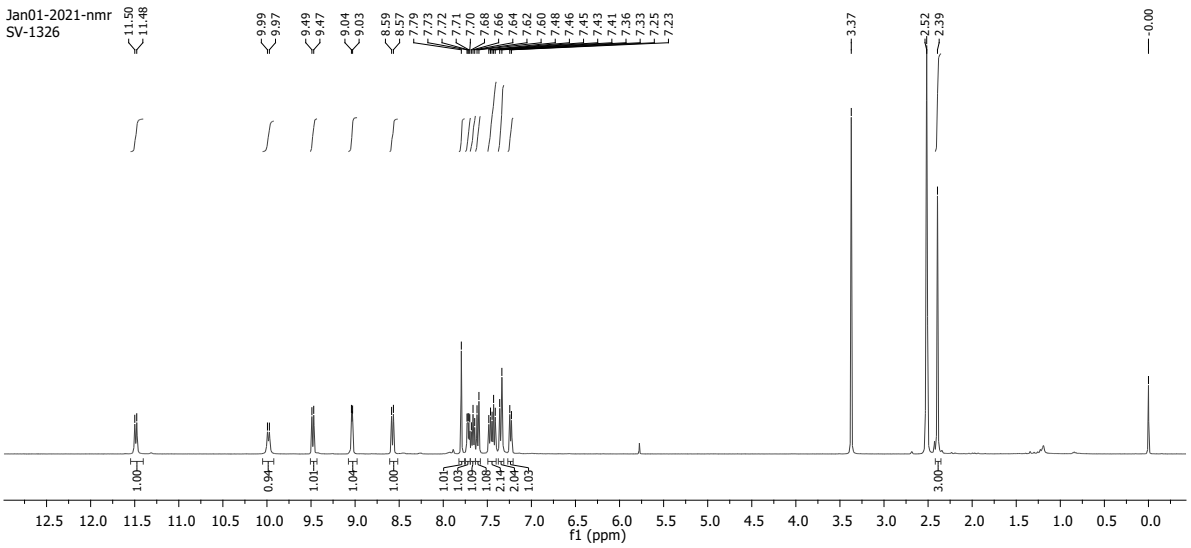


^{1}H NMR (400 MHz, $CDCl_3$)

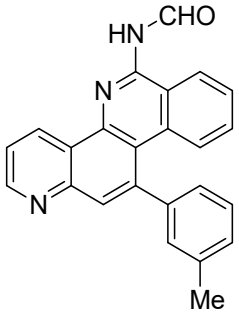


***N*-(11-(*m*-tolyl)benzo[*c*][1,7]phenanthrolin-6-yl)formamide (7b)**

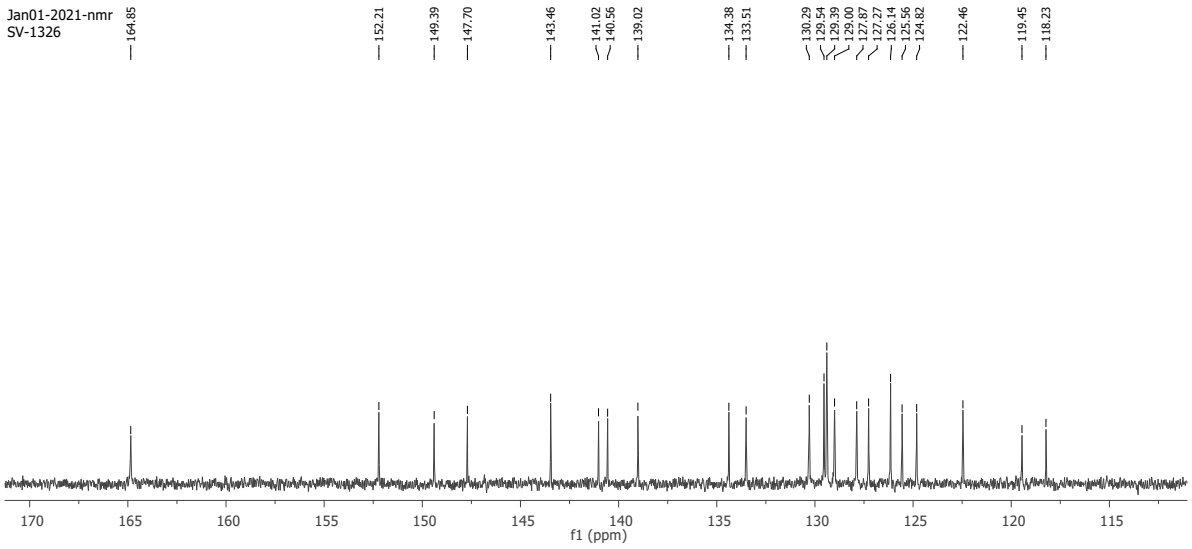


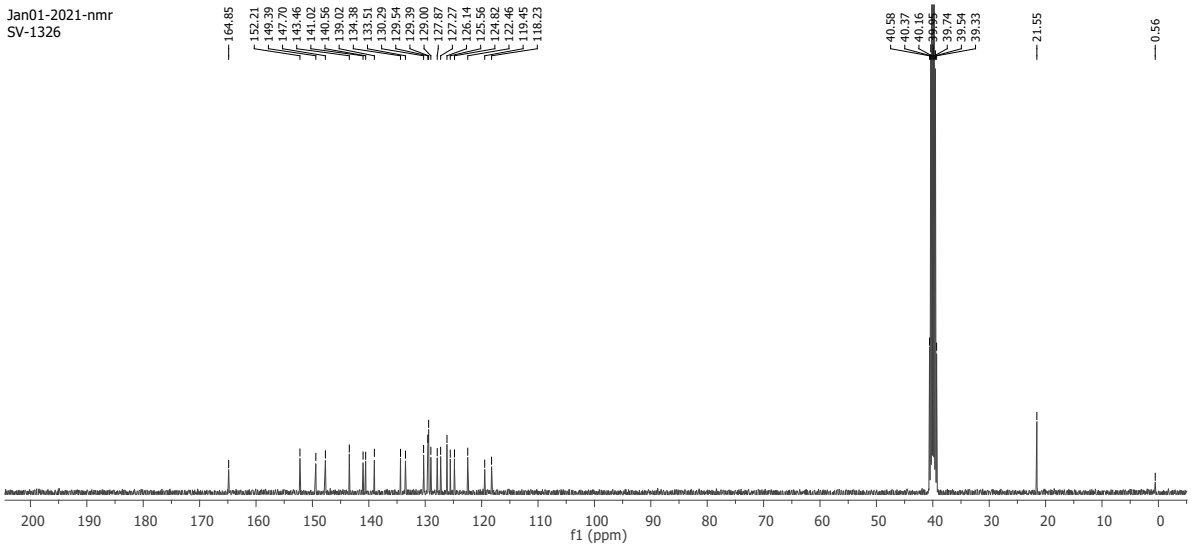


^{13}C NMR (100 MHz, $CDCl_3$)

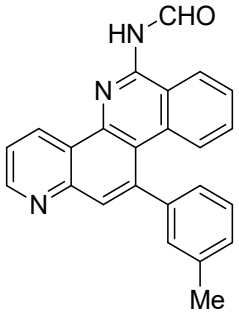


***N*-(11-(*m*-tolyl)benzo[*c*][1,7]phenanthrolin-6-yl)formamide (7b)**

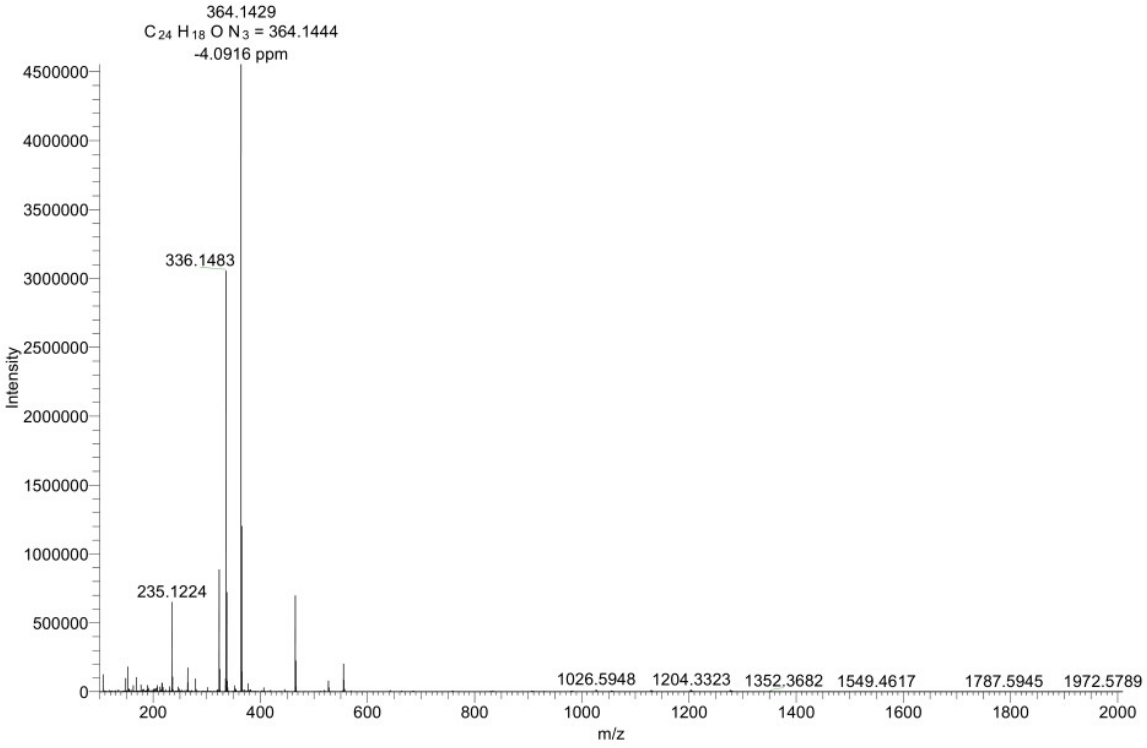




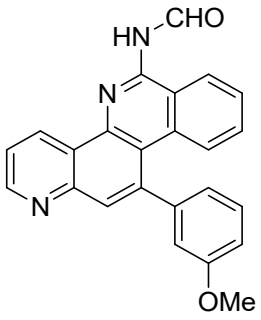
HRMS



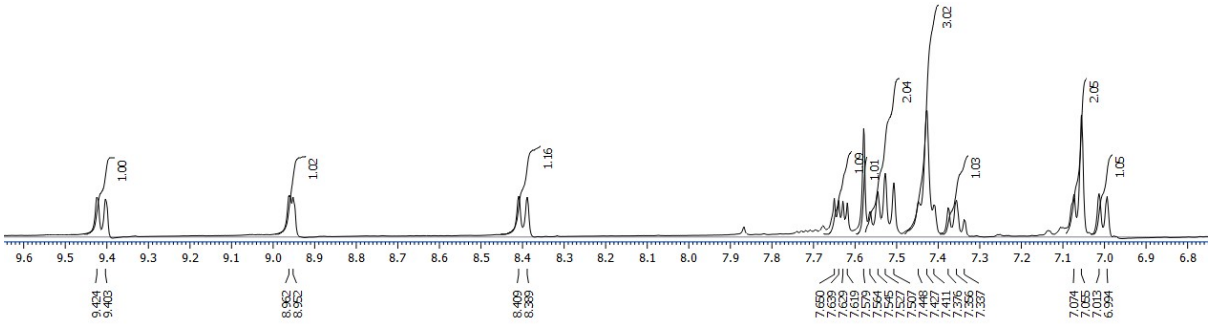
***N*-(11-(*m*-tolyl)benzo[*c*][1,7]phenanthrolin-6-yl)formamide (7b)**

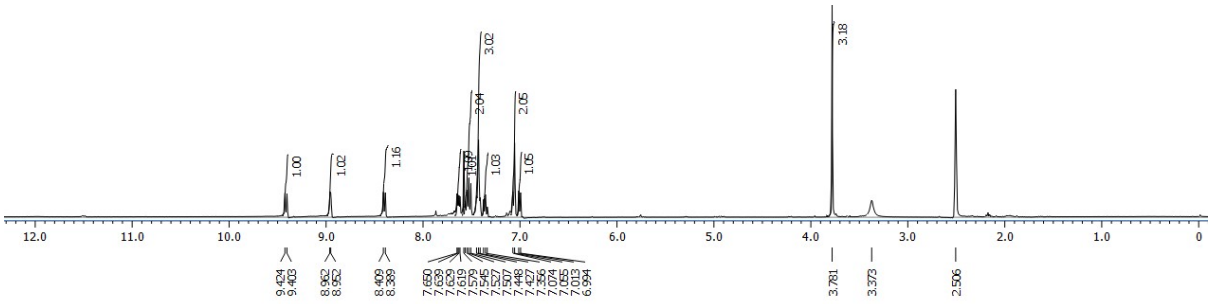


^{1}H NMR (400 MHz, $CDCl_3$)

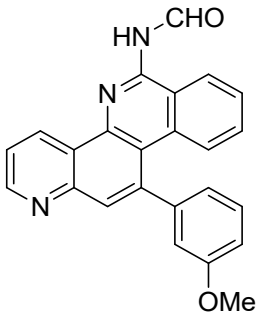


***N*-(11-(3-methoxyphenyl)benzo[*c*][1,7]phenanthrolin-6-yl)formamide (7c)**

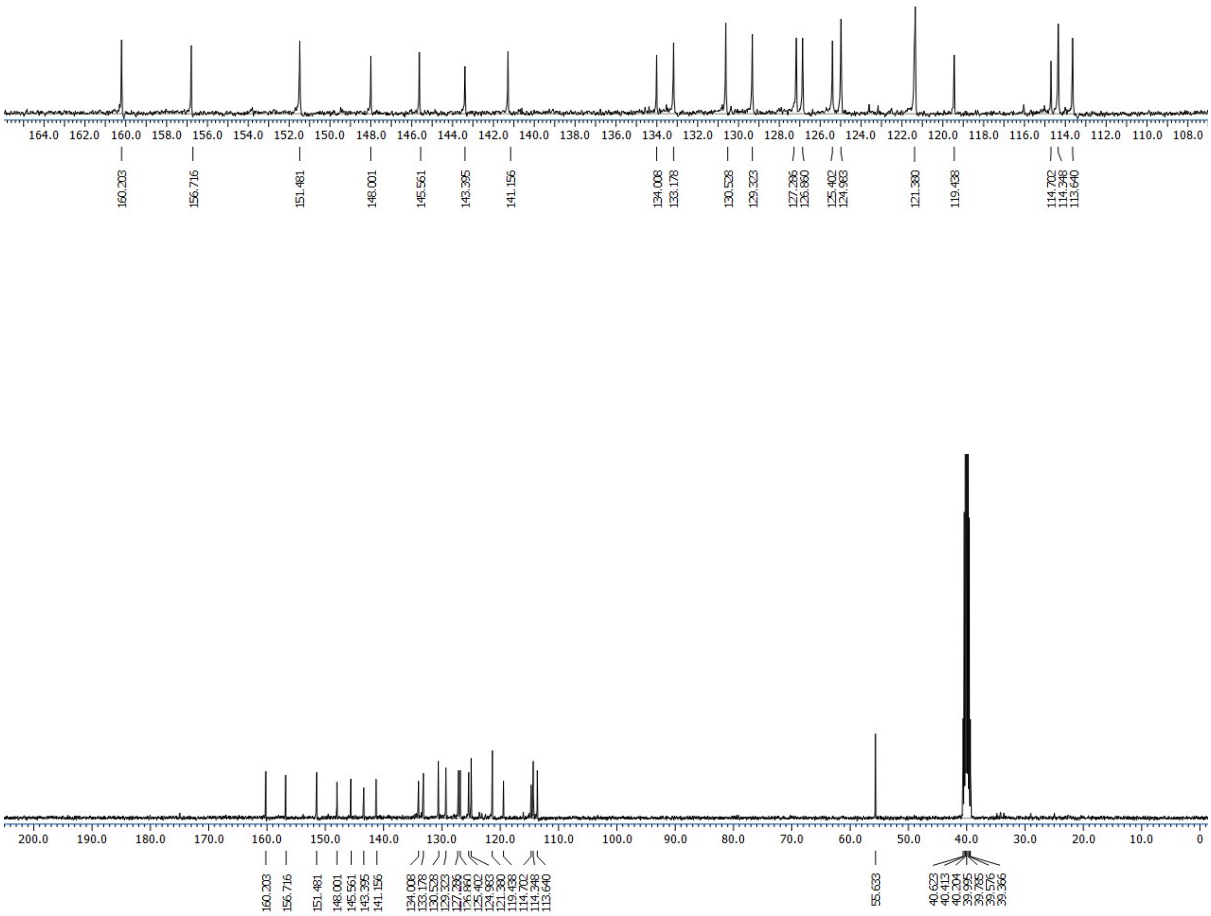




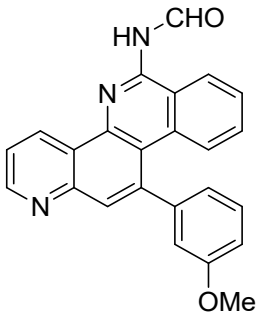
^{13}C NMR (100 MHz, $CDCl_3$)



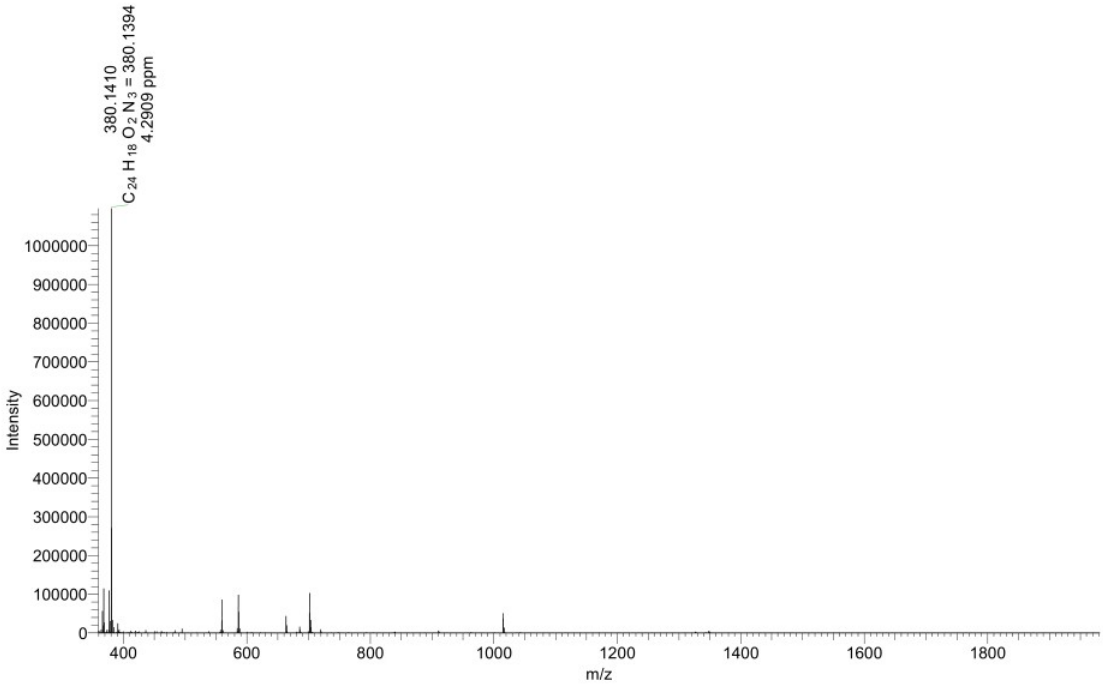
***N*-(11-(3-methoxyphenyl)benzo[*c*][1,7]phenanthrolin-6-yl)formamide (7c)**



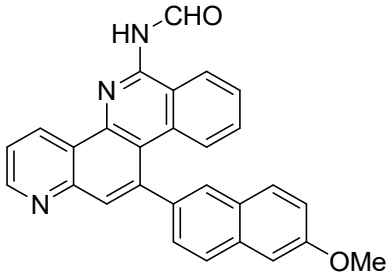
HRMS



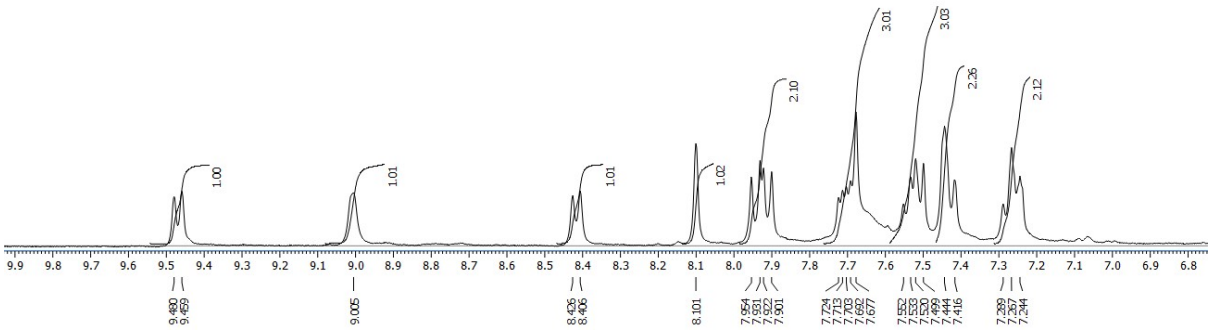
***N*-(11-(3-methoxyphenyl)benzo[*c*][1,7]phenanthrolin-6-yl)formamide (7c)**

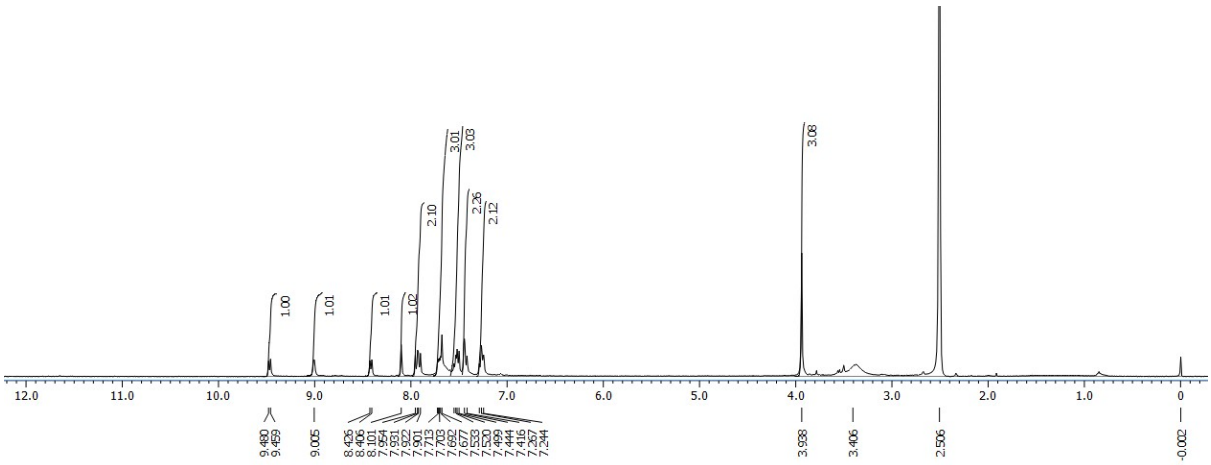


^{1}H NMR (400 MHz, $CDCl_3$)

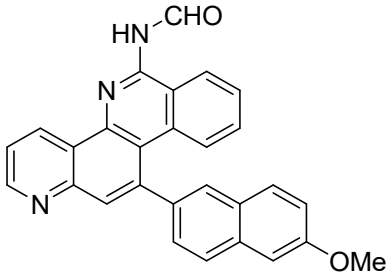


***N*-(11-(6-methoxynaphthalen-2-yl)benzo[*c*][1,7]phenanthrolin-6-yl)formamide (7d)**

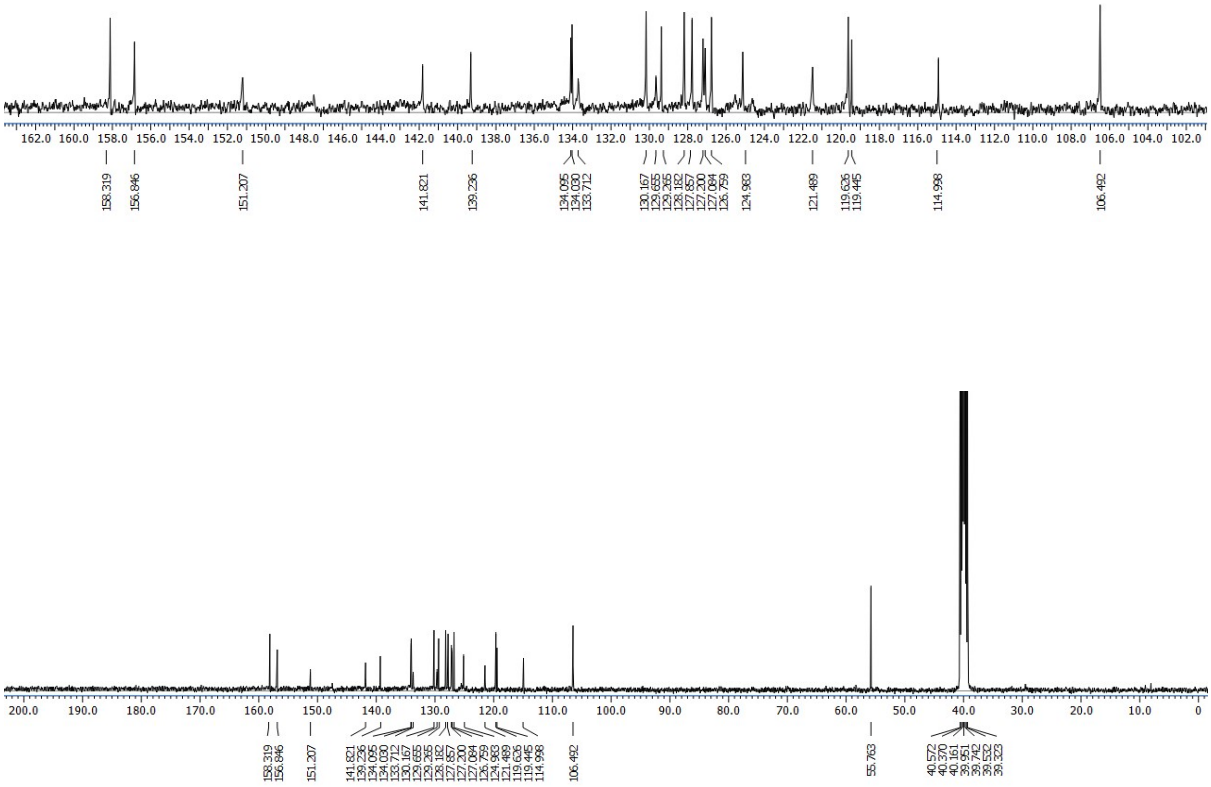




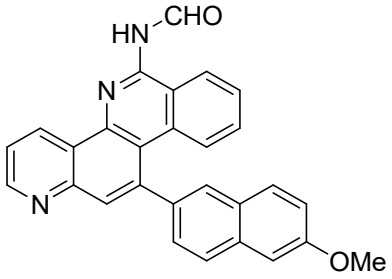
^{13}C NMR (100 MHz, $CDCl_3$)



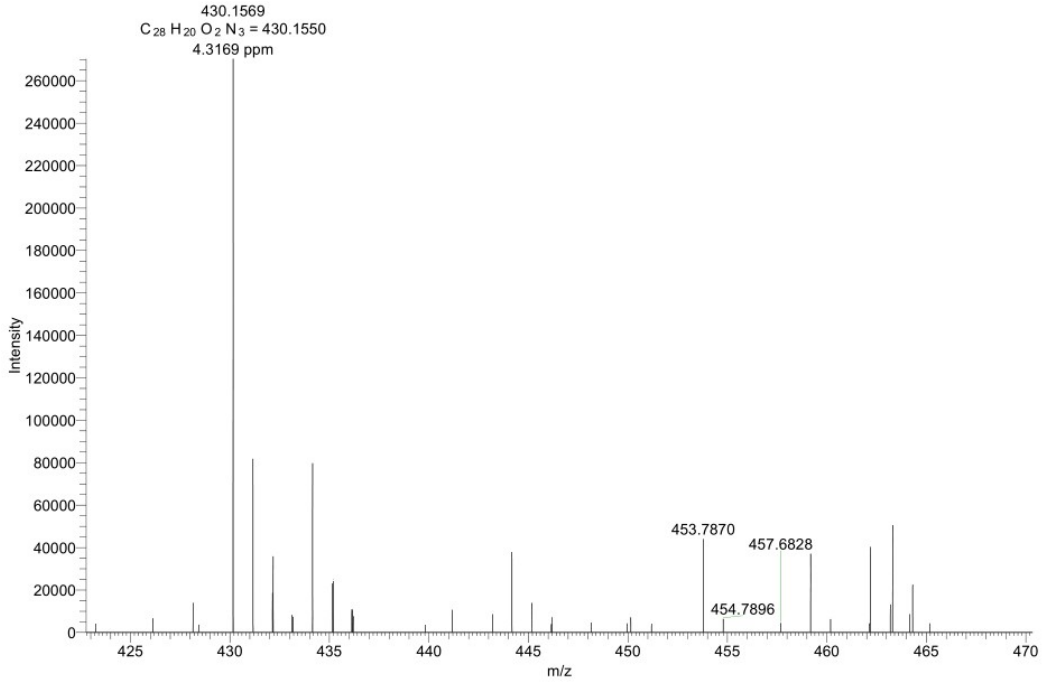
***N*-(11-(6-methoxynaphthalen-2-yl)benzo[*c*][1,7]phenanthrolin-6-yl)formamide (7d)**



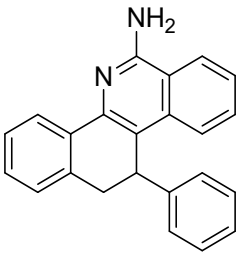
HRMS



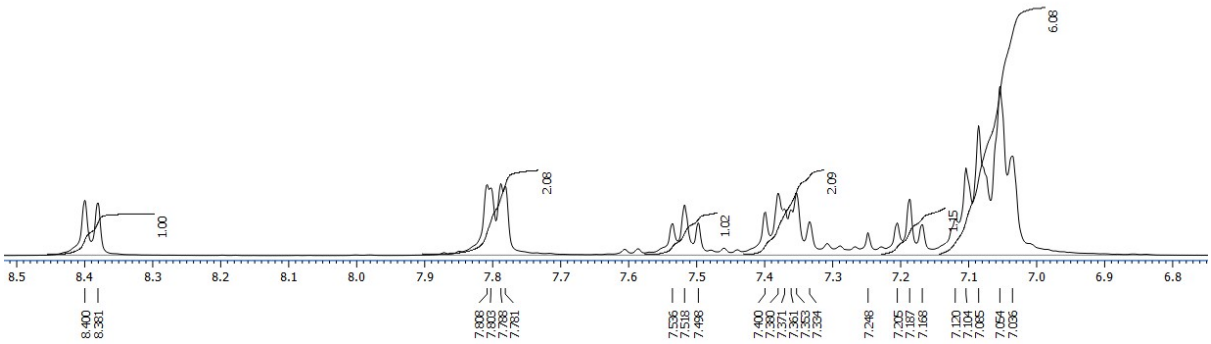
***N*-(11-(6-methoxynaphthalen-2-yl)benzo[*c*][1,7]phenanthrolin-6-yl)formamide (7d)**

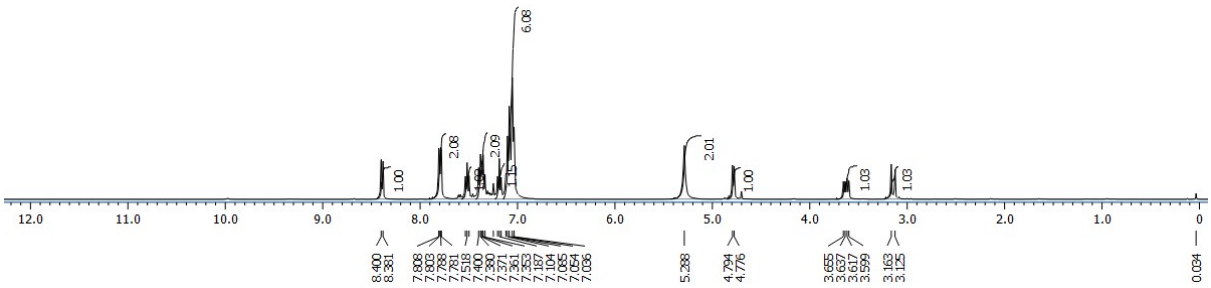


^{1}H NMR (400 MHz, $CDCl_3$)

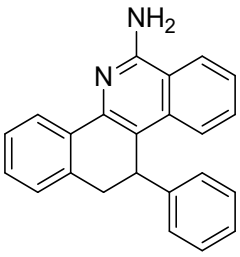


11-Phenyl-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9a)

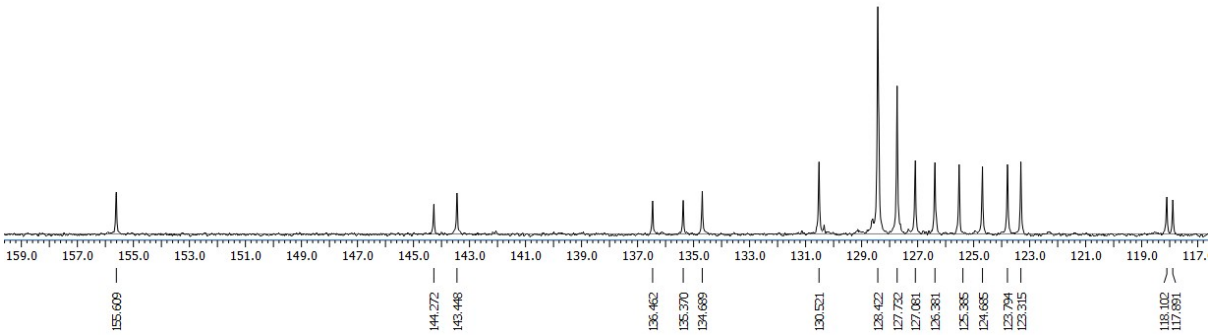


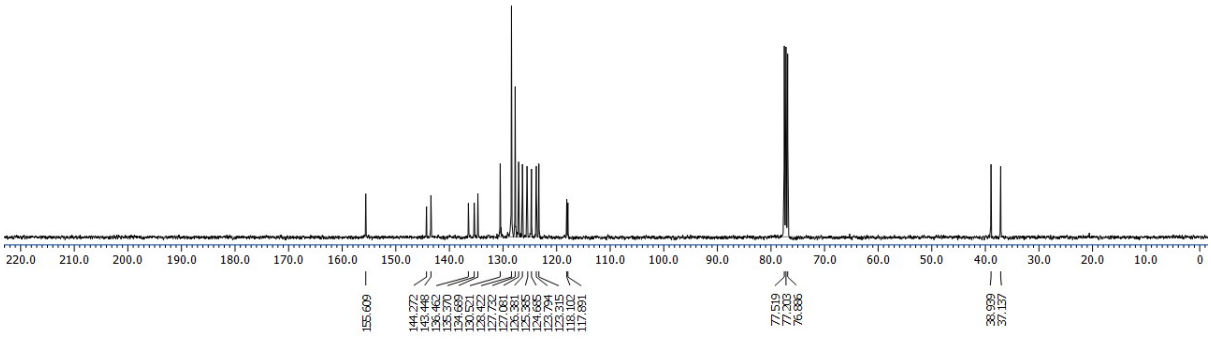


^{13}C NMR (100 MHz, $CDCl_3$)

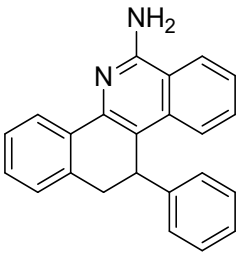


11-Phenyl-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9a)

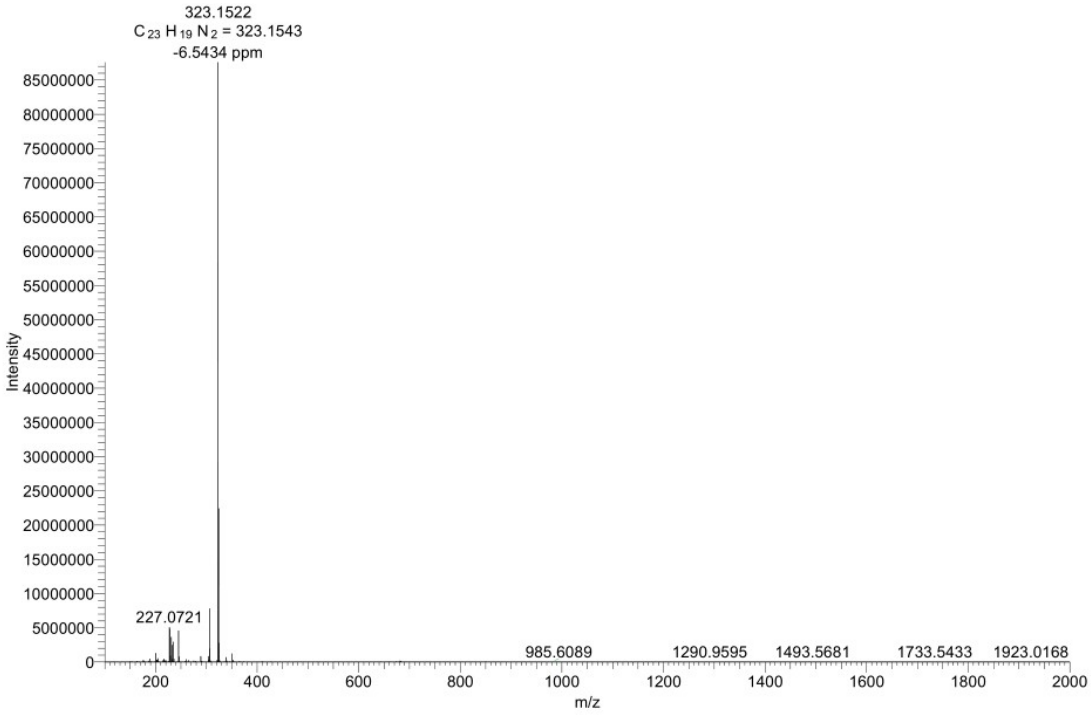




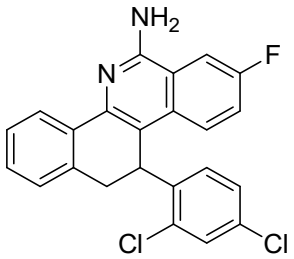
HRMS



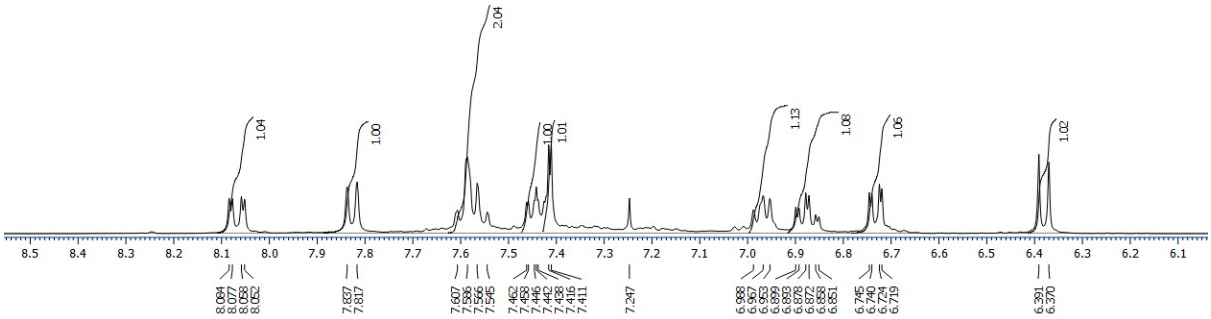
11-Phenyl-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9a)

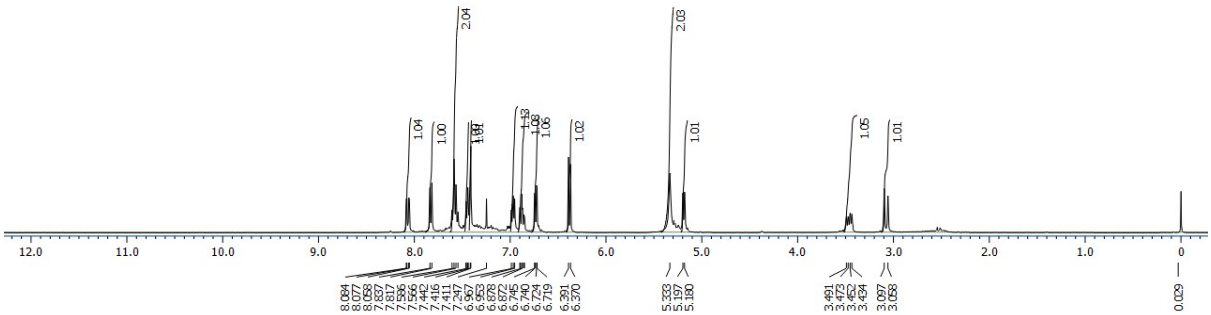


^{1}H NMR (400 MHz, $CDCl_3$)

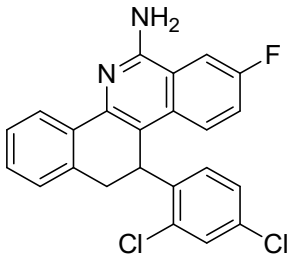


11-(2,4-Dichlorophenyl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9b)

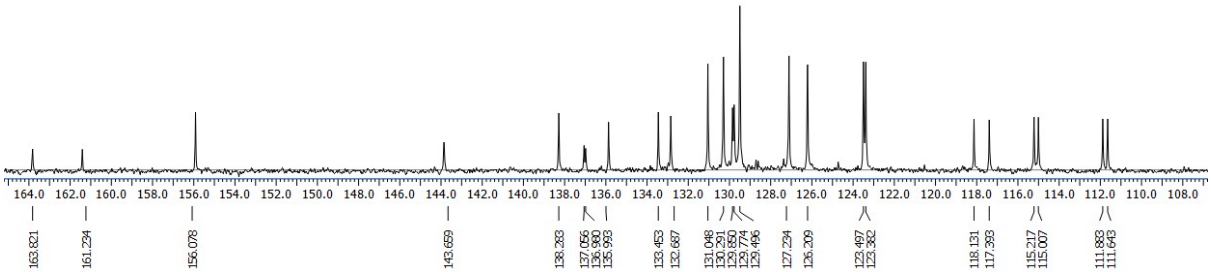


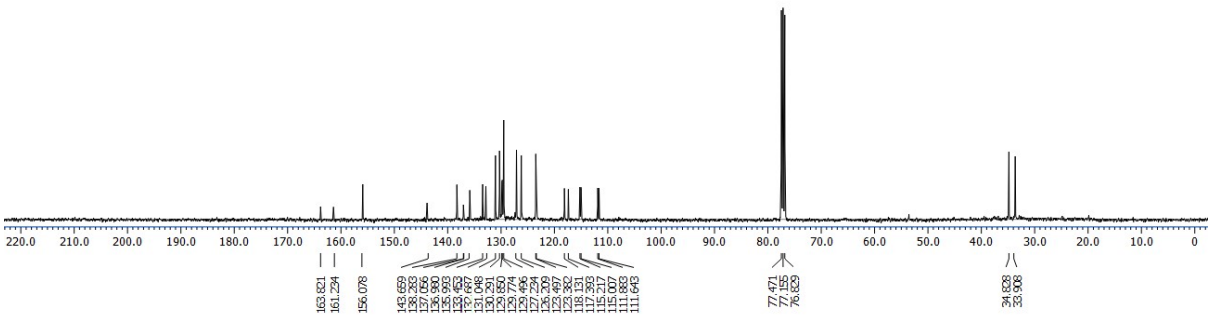


^{13}C NMR (100 MHz, $CDCl_3$)

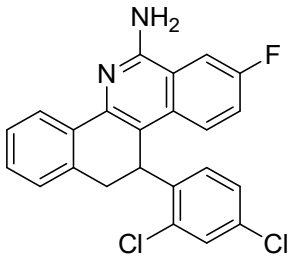


11-(2,4-Dichlorophenyl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9b)

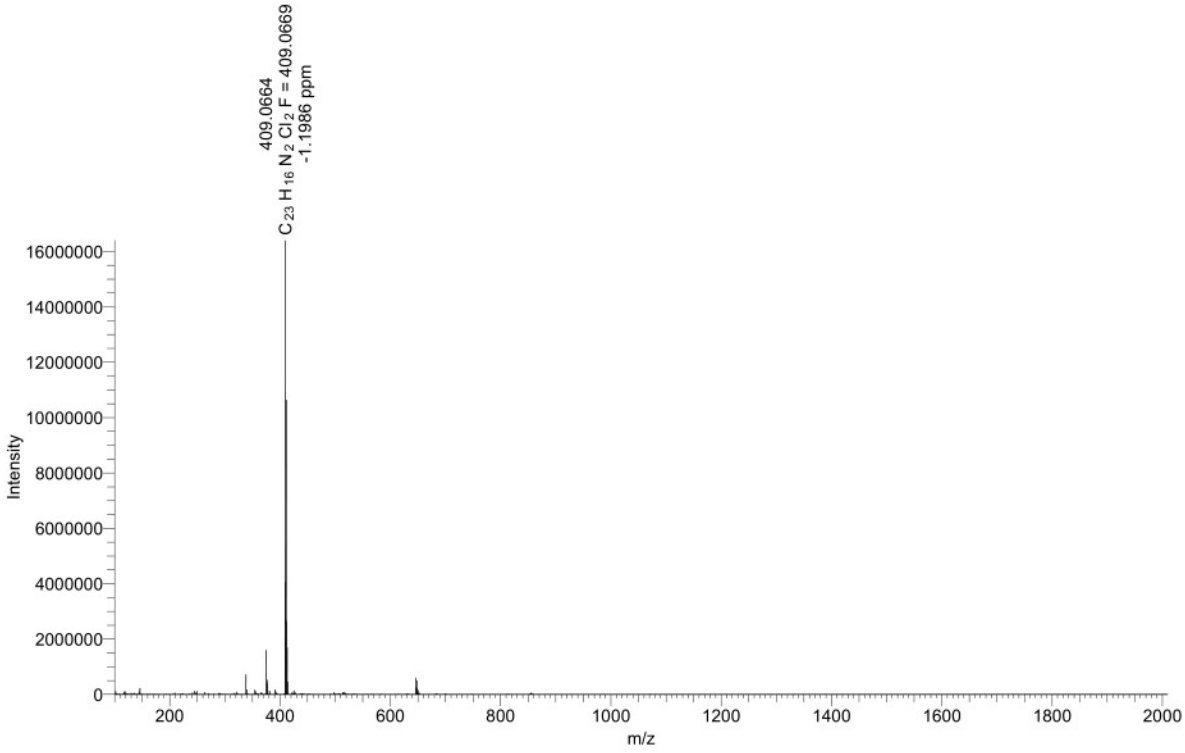




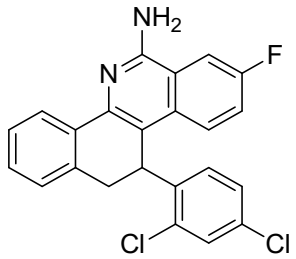
HRMS



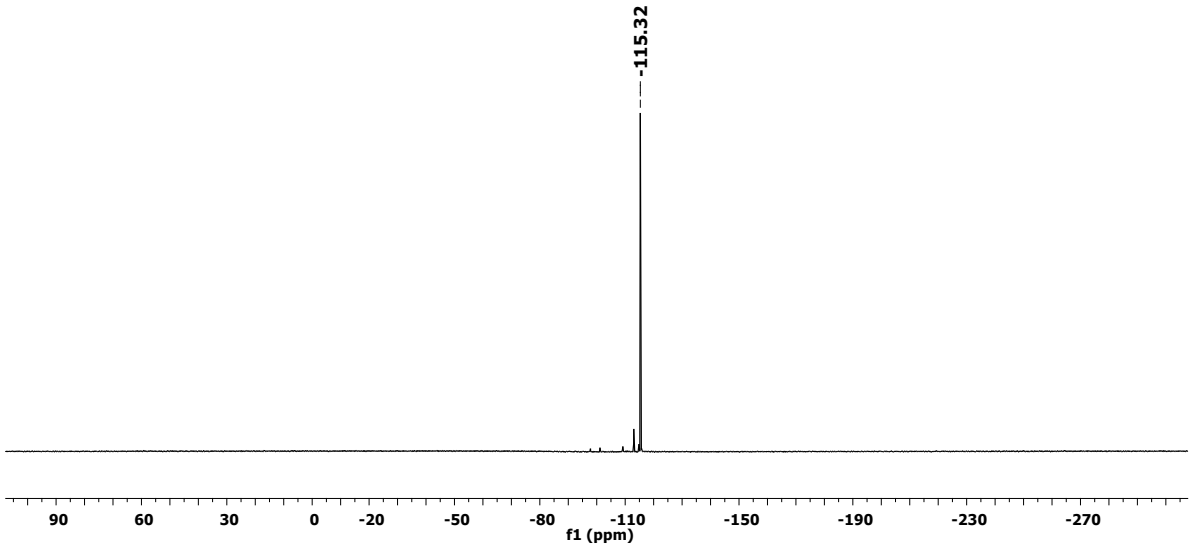
11-(2,4-Dichlorophenyl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9b)



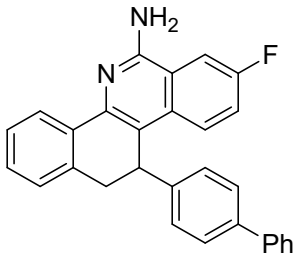
^{19}F NMR (376 MHz, $CDCl_3$)



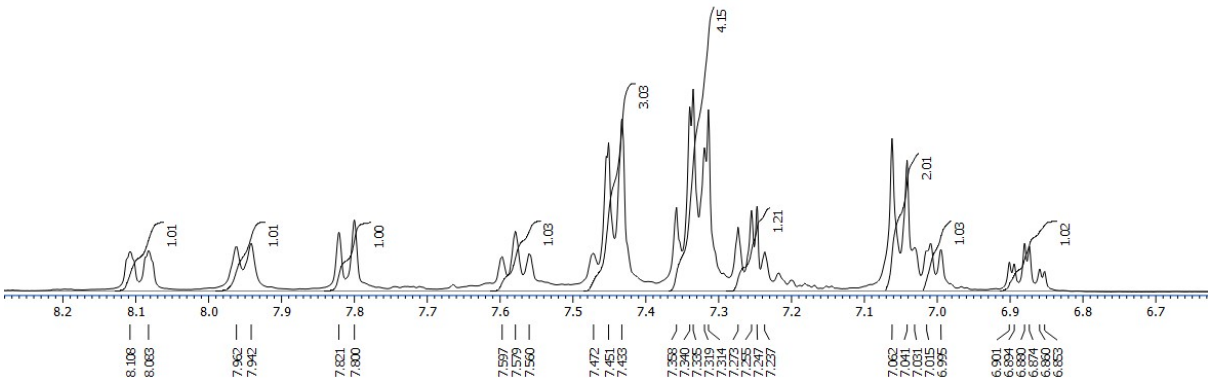
11-(2,4-Dichlorophenyl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9b)

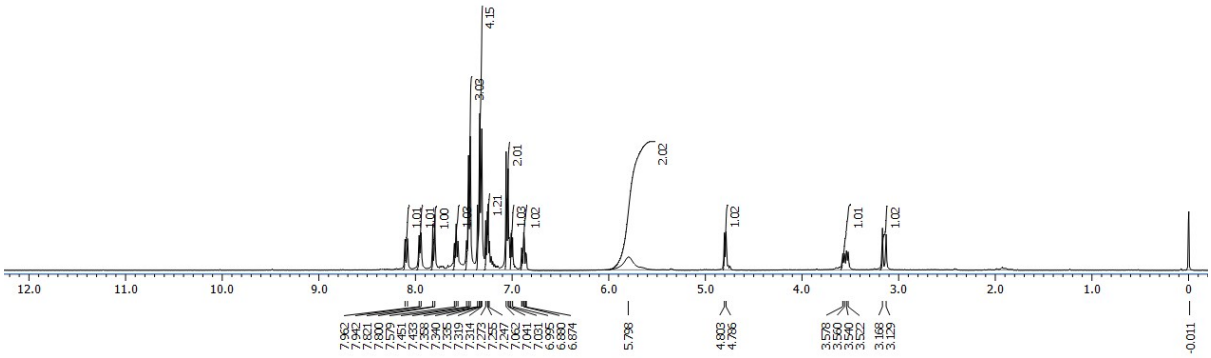


^{1}H NMR (400 MHz, $CDCl_3$)

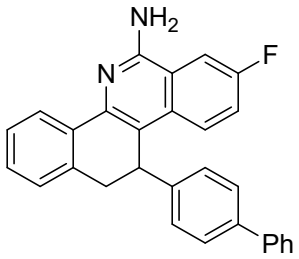


11-([1,1'-Biphenyl]-4-yl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9c)

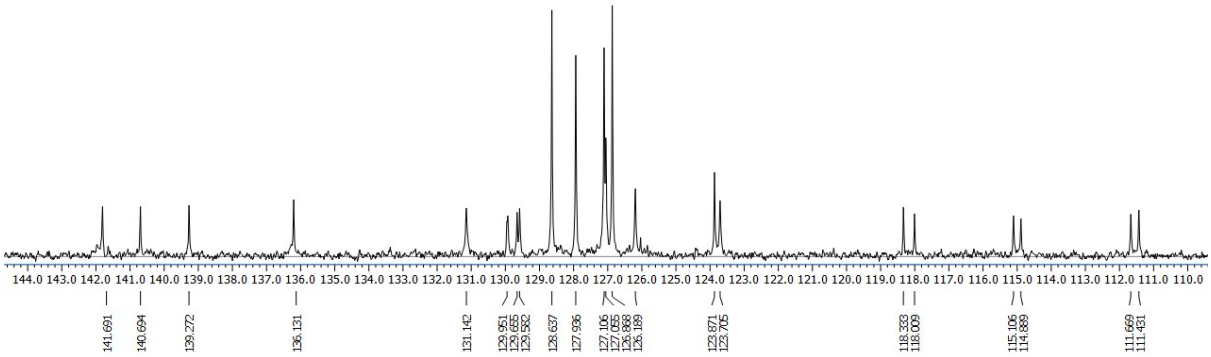


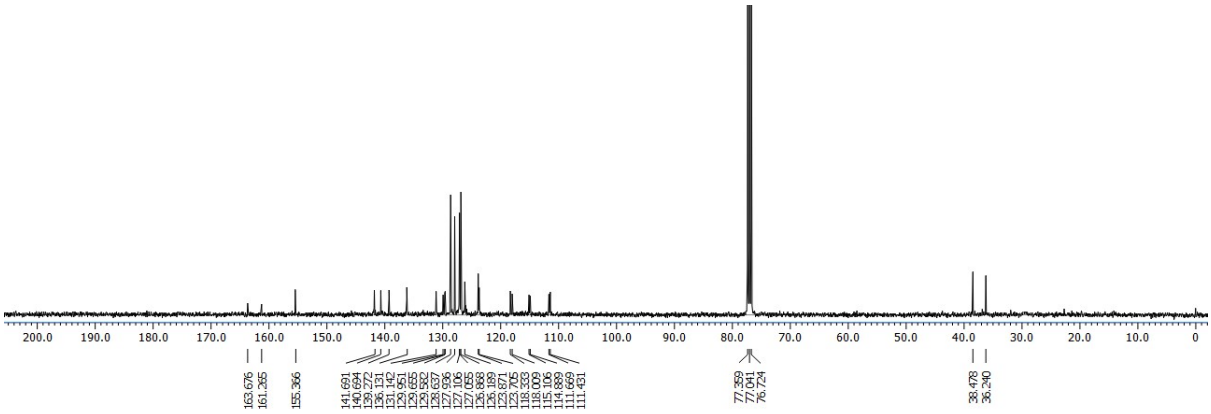


^{13}C NMR (100 MHz, $CDCl_3$)

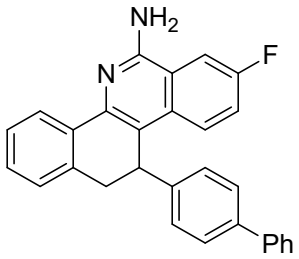


11-([1,1'-Biphenyl]-4-yl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9c)

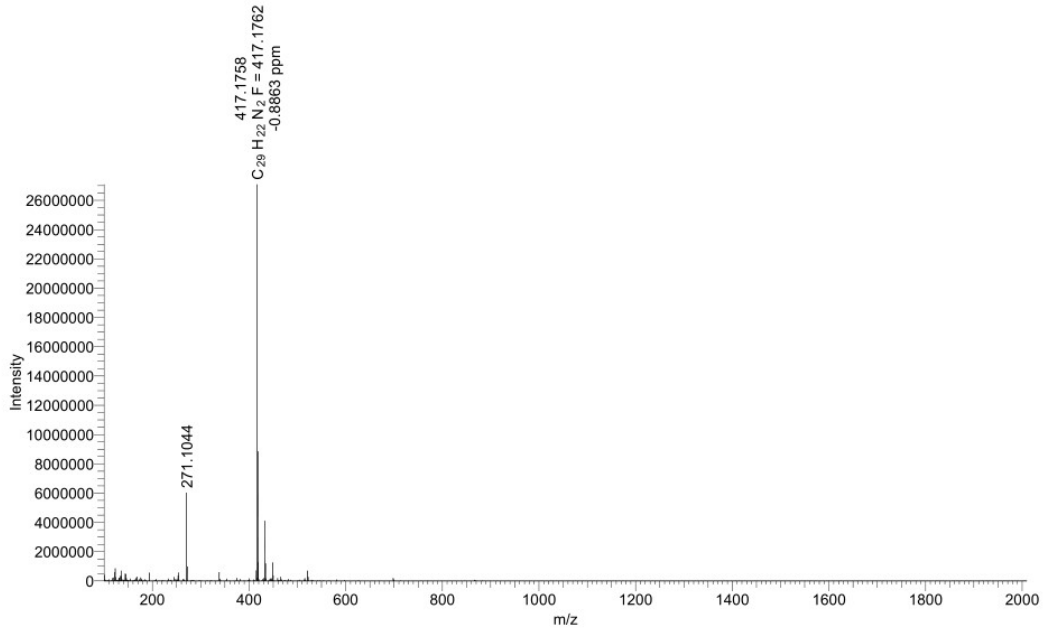




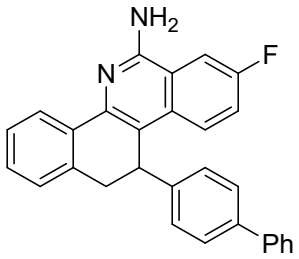
HRMS



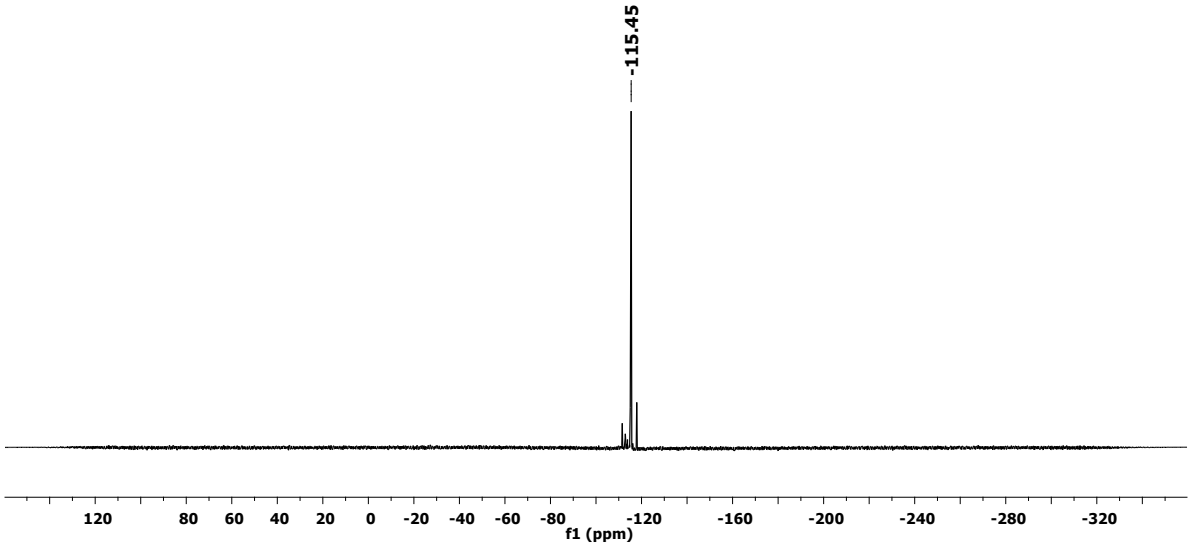
11-([1,1'-Biphenyl]-4-yl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9c)



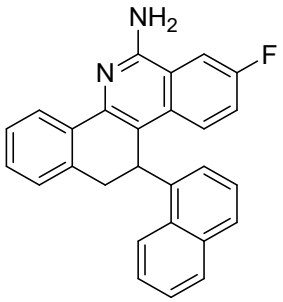
^{19}F NMR (376 MHz, $CDCl_3$)



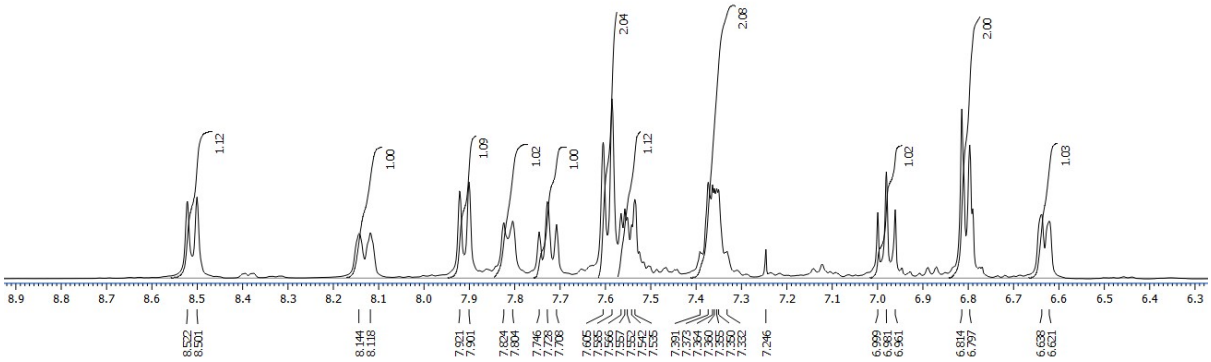
11-([1,1'-Biphenyl]-4-yl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9c)

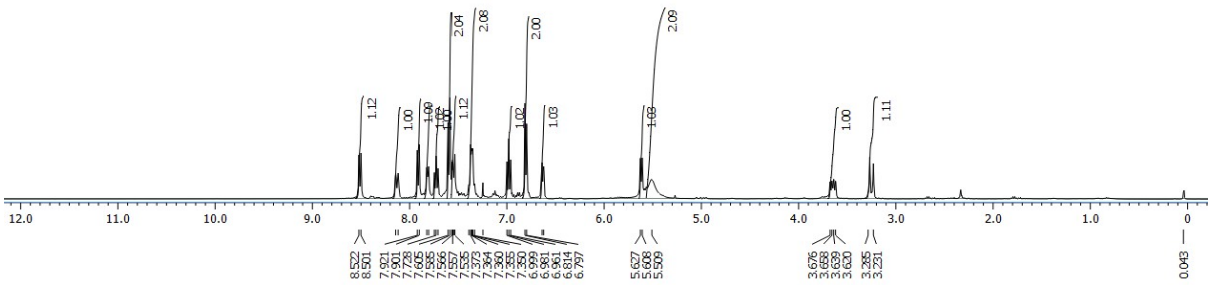


^{1}H NMR (400 MHz, $CDCl_3$)

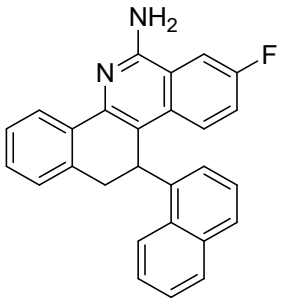


8-Fluoro-11-(naphthalen-1-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9d)

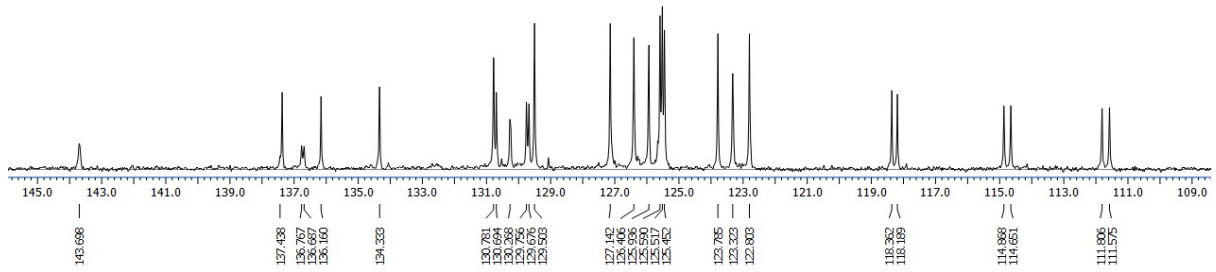


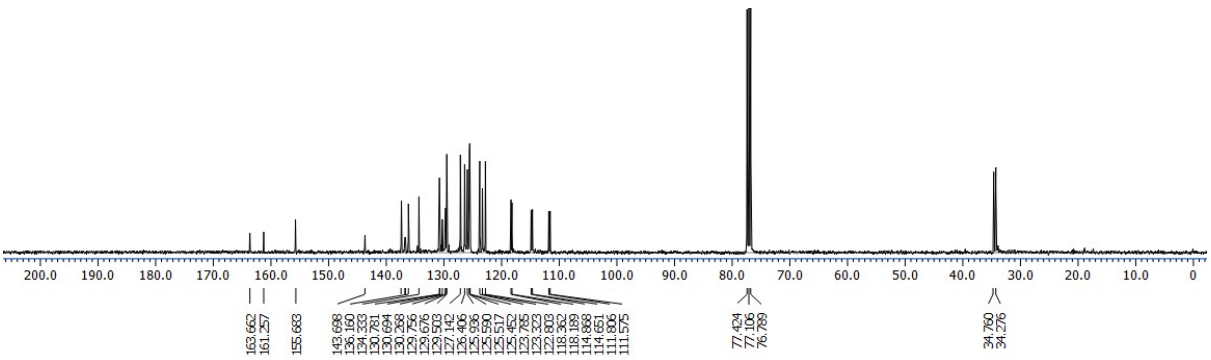


^{13}C NMR (100 MHz, $CDCl_3$)

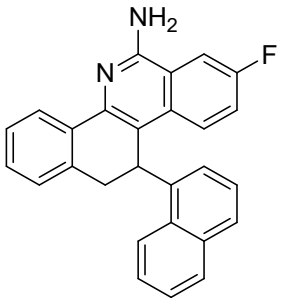


8-Fluoro-11-(naphthalen-1-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9d)

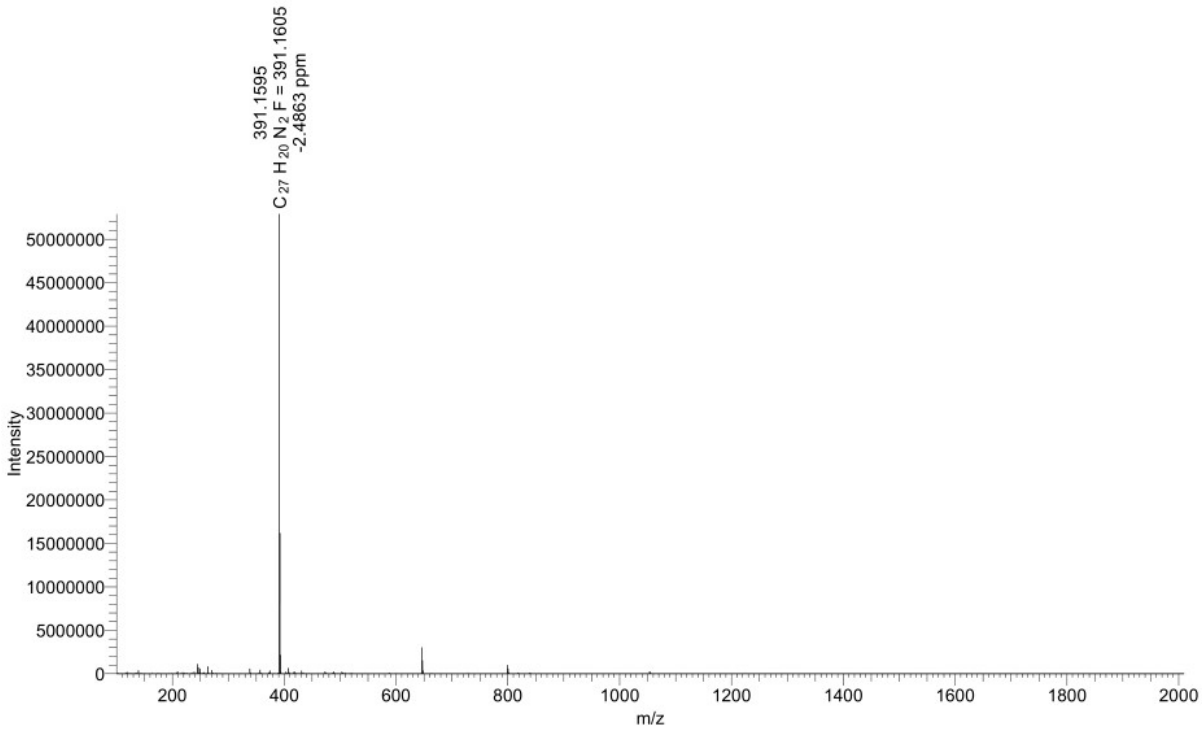




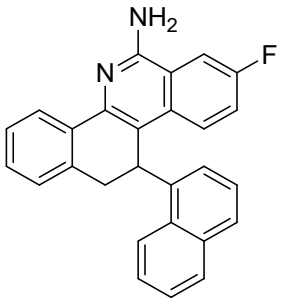
HRMS



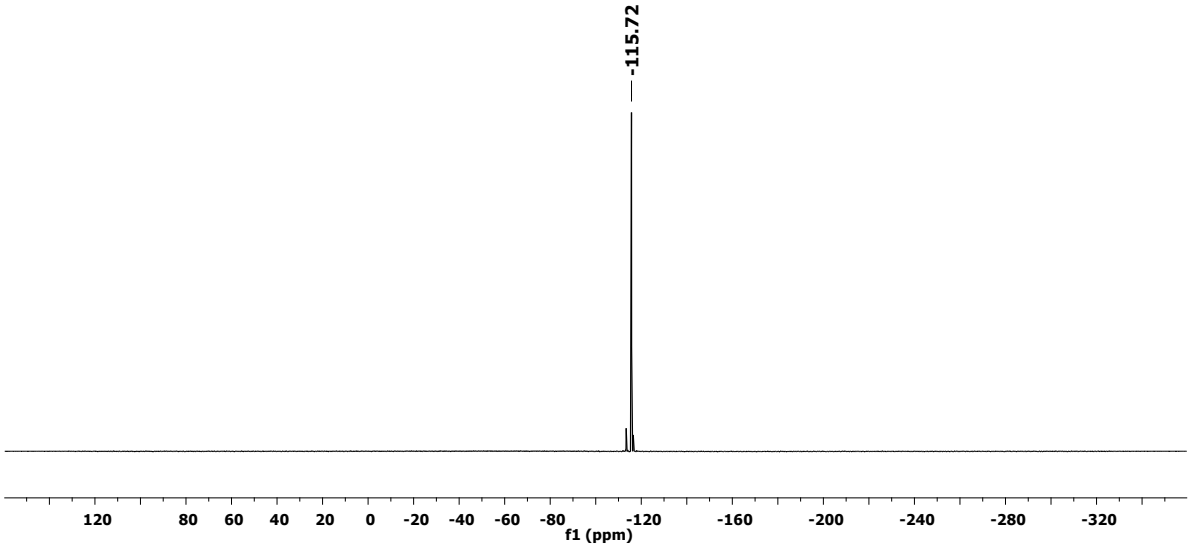
8-Fluoro-11-(naphthalen-1-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9d)



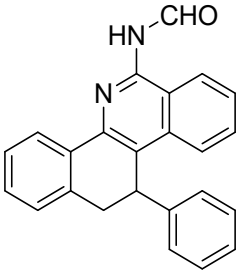
^{19}F NMR (376 MHz, $CDCl_3$)



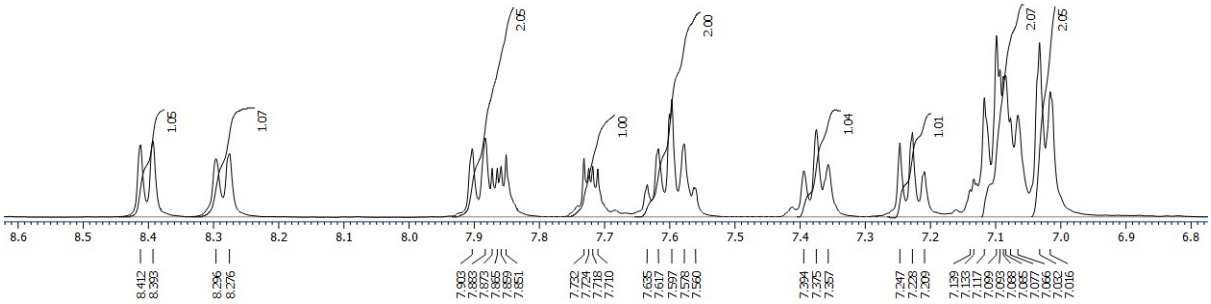
8-Fluoro-11-(naphthalen-1-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-amine (9d)

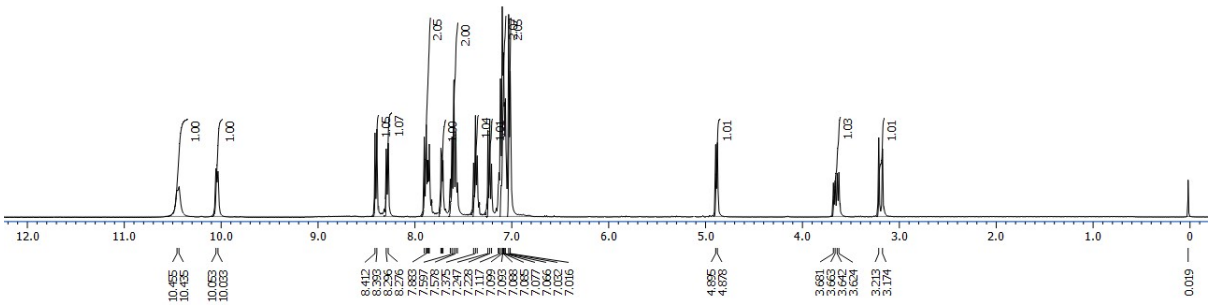


^{1}H NMR (400 MHz, $CDCl_3$)

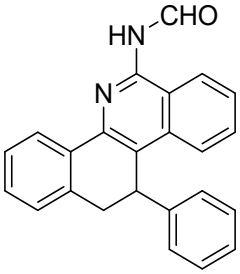


***N*-(11-Phenyl-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10a)**

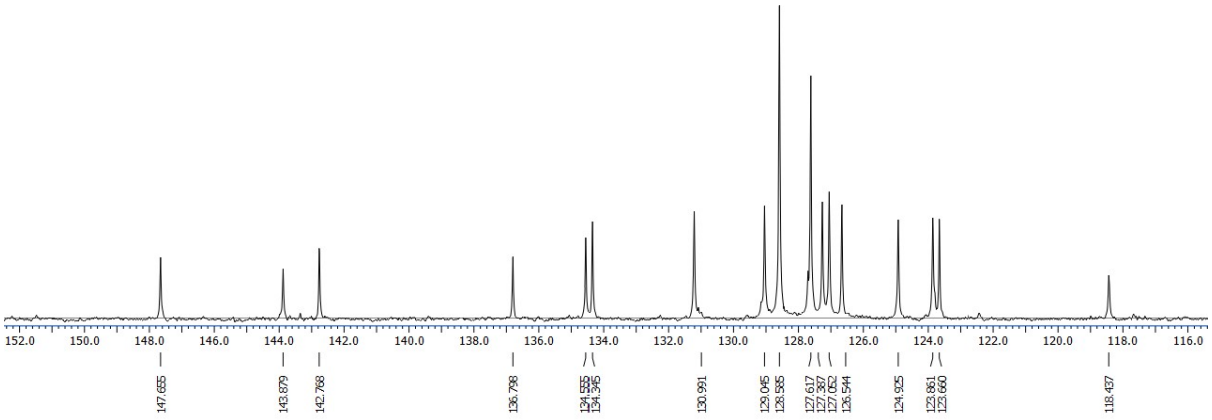


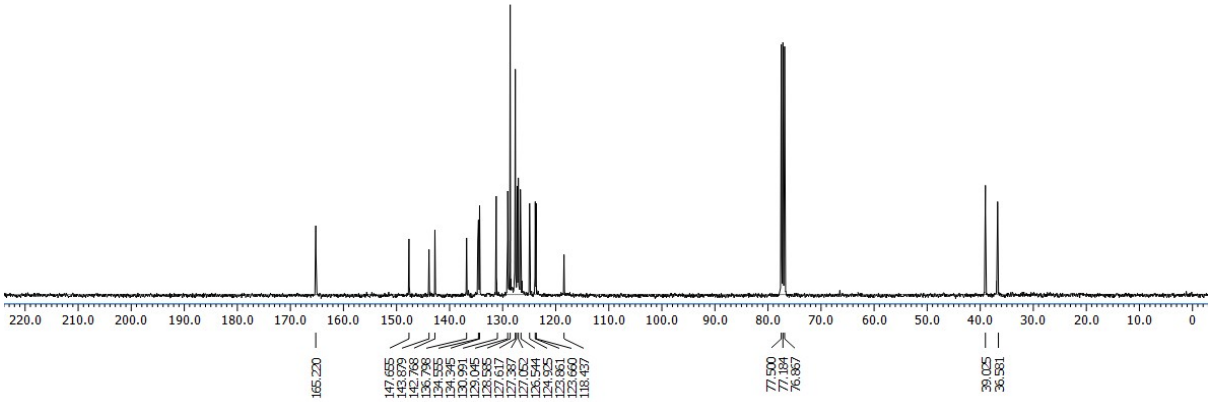


^{13}C NMR (100 MHz, $CDCl_3$)

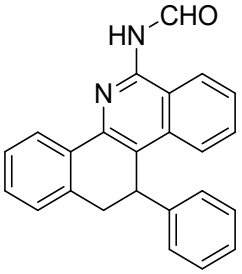


***N*-(11-Phenyl-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10a)**

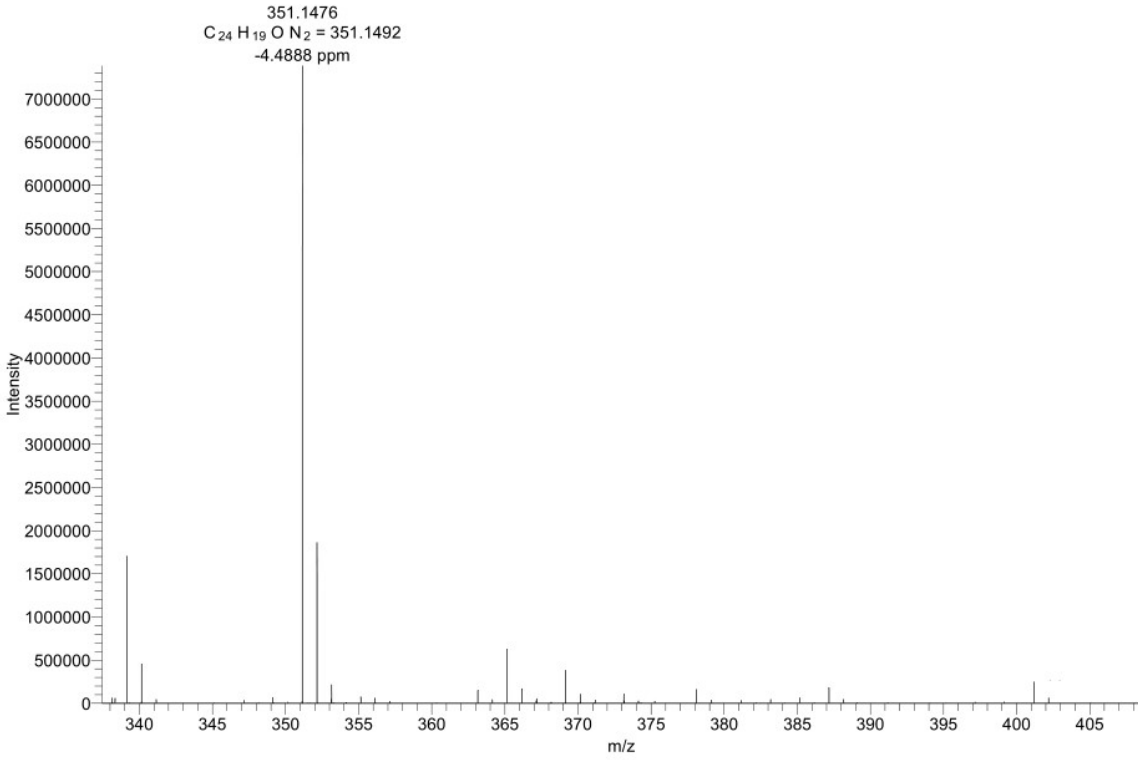




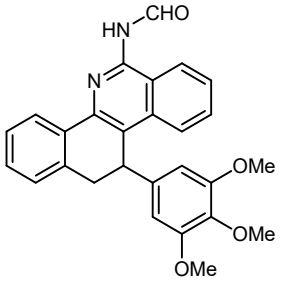
HRMS



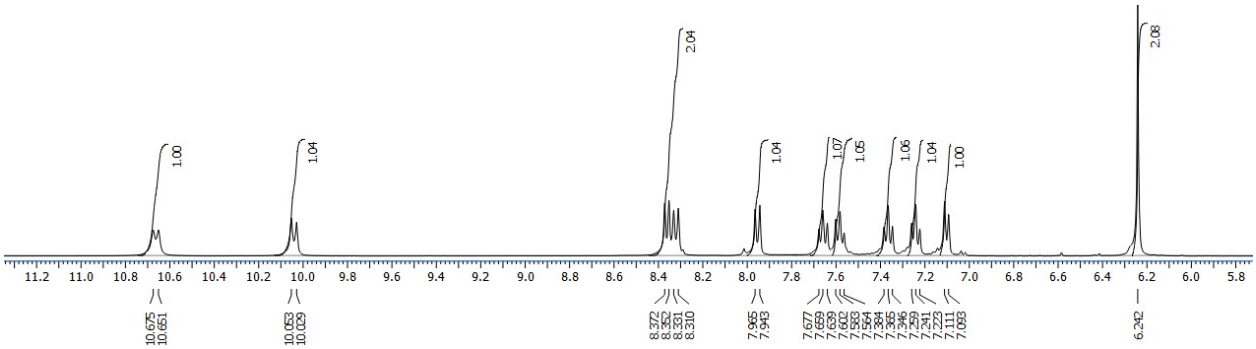
***N*-(11-Phenyl-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10a)**

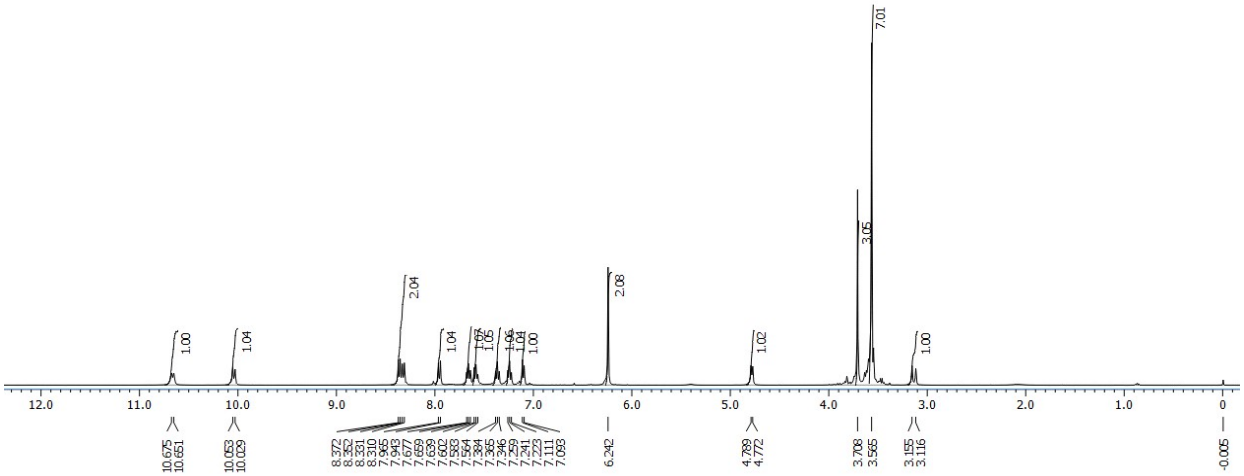


^{1}H NMR (400 MHz, $CDCl_3$)

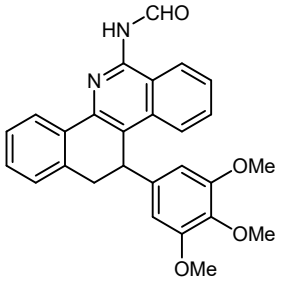


_N_-(11-(3,4,5-Trimethoxyphenyl)-11,12-dihydrobenzo[_c_]phenanthridin-6-yl)formamide (10b)

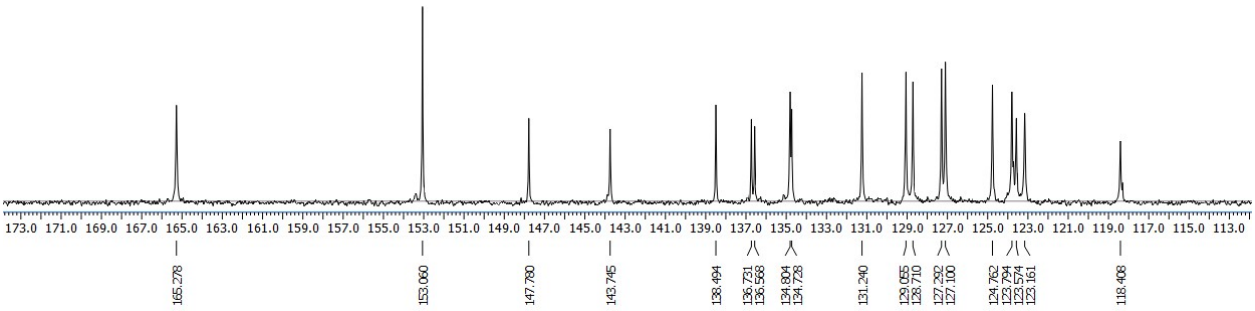


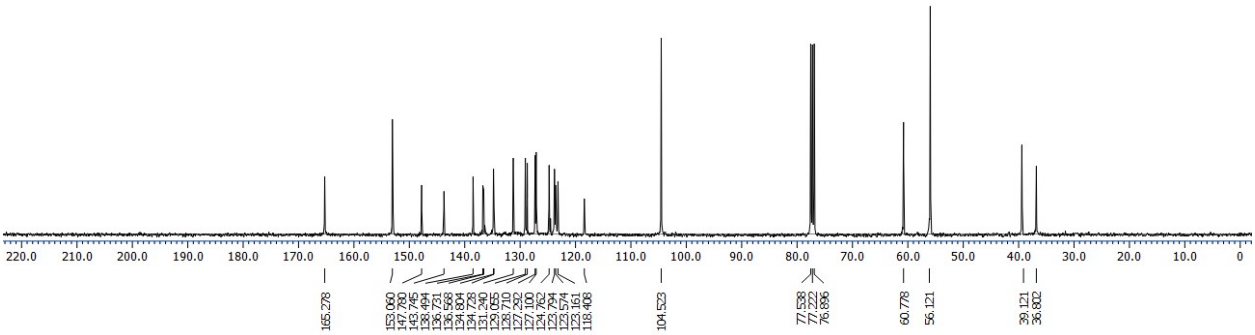


^{13}C NMR (100 MHz, $CDCl_3$)

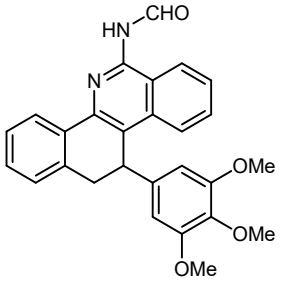


***N*-(11-(3,4,5-trimethoxyphenyl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10b)**

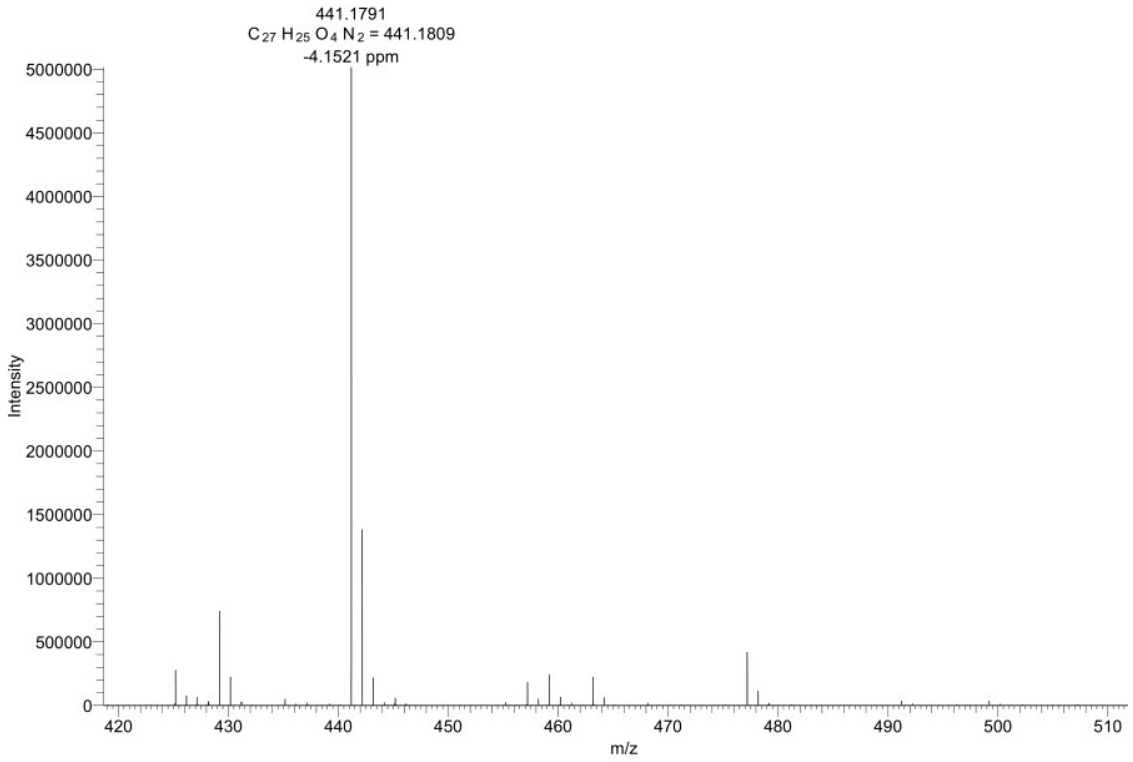




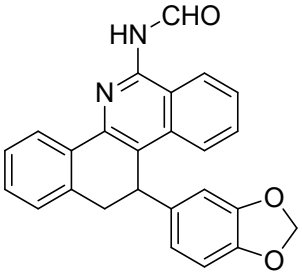
HRMS



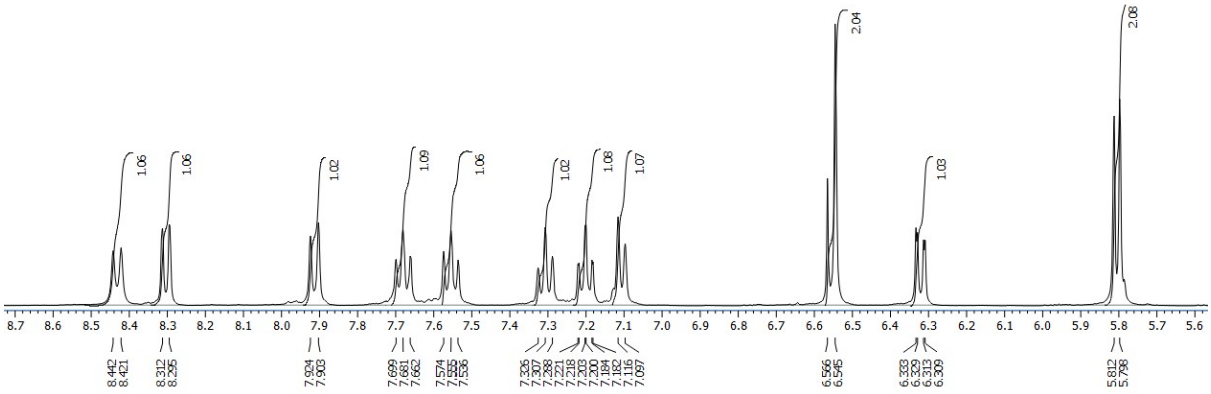
***N*-(11-(3,4,5-trimethoxyphenyl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10b)**

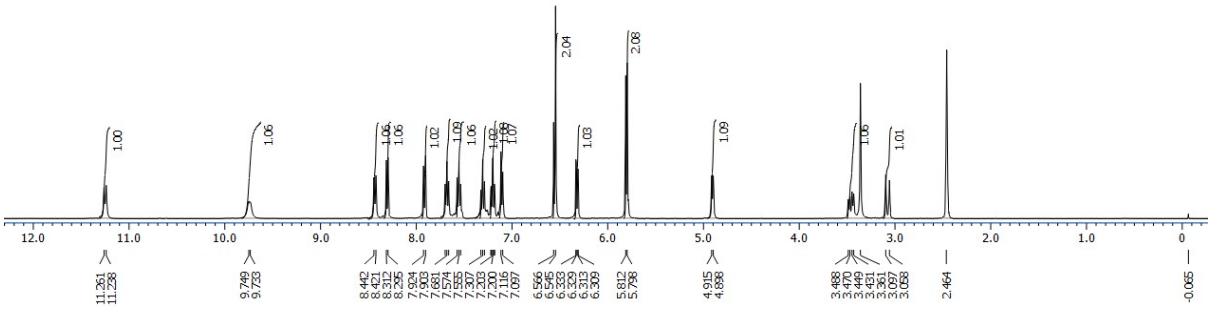


^{1}H NMR (400 MHz, $CDCl_3$)

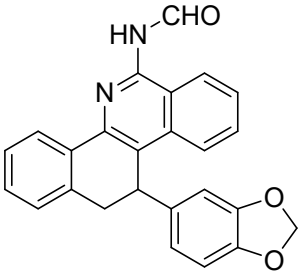


***N*-(11-(Benzo[*d*][1,3]dioxol-5-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10c)**

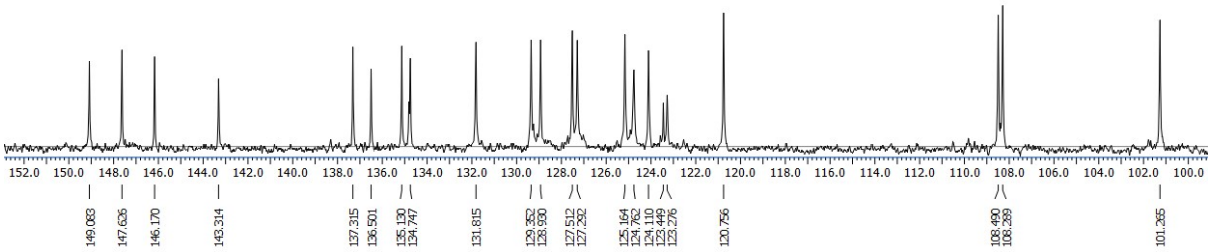


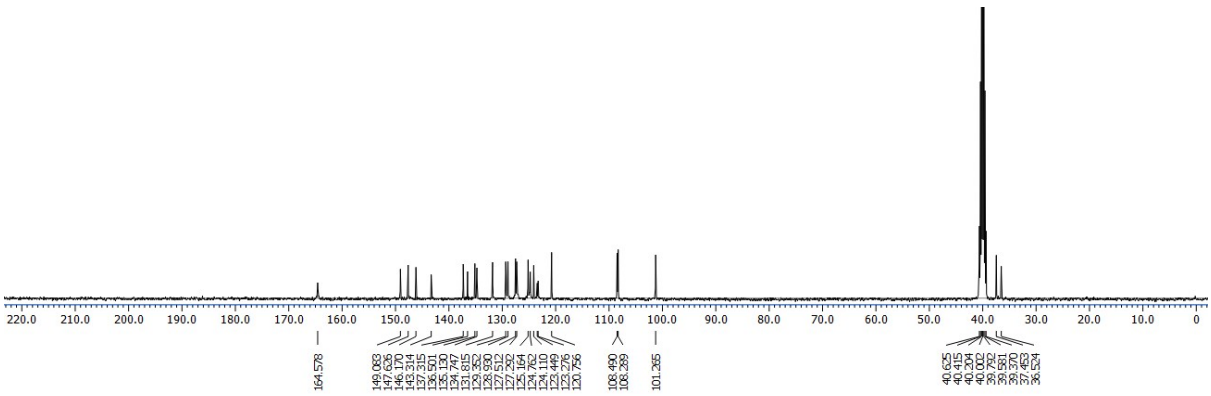


^{13}C NMR (100 MHz, $CDCl_3$)

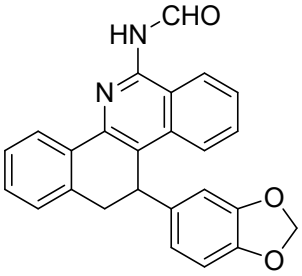


_N_-(11-(Benzo[_d_][1,3]dioxol-5-yl)-11,12-dihydrobenzo[_c_]phenanthridin-6-yl)formamide (10c)

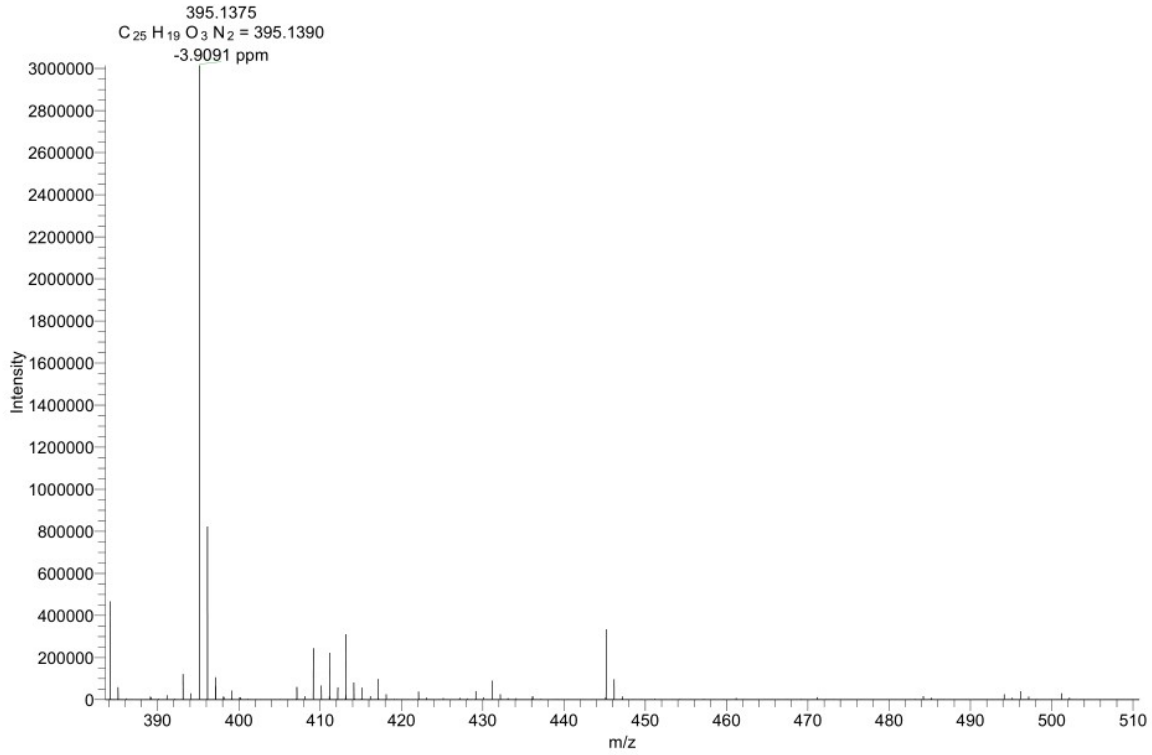




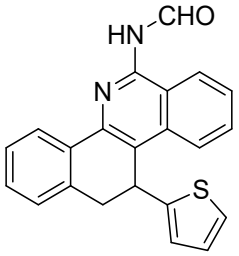
HRMS



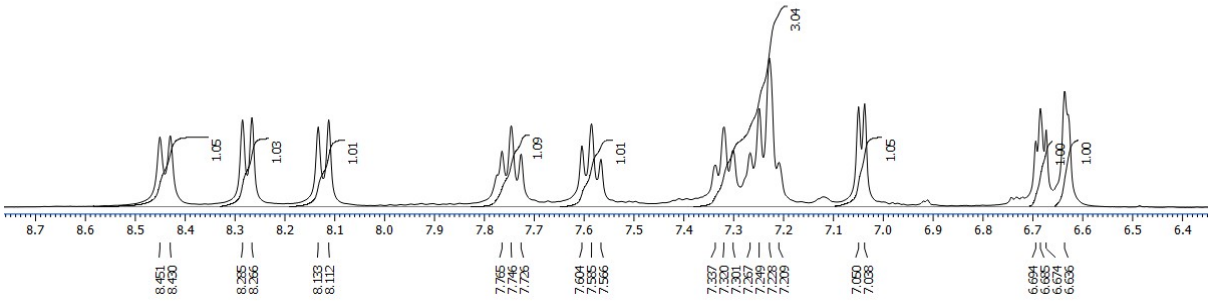
***N*-(11-(Benzo[*d*][1,3]dioxol-5-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10c)**

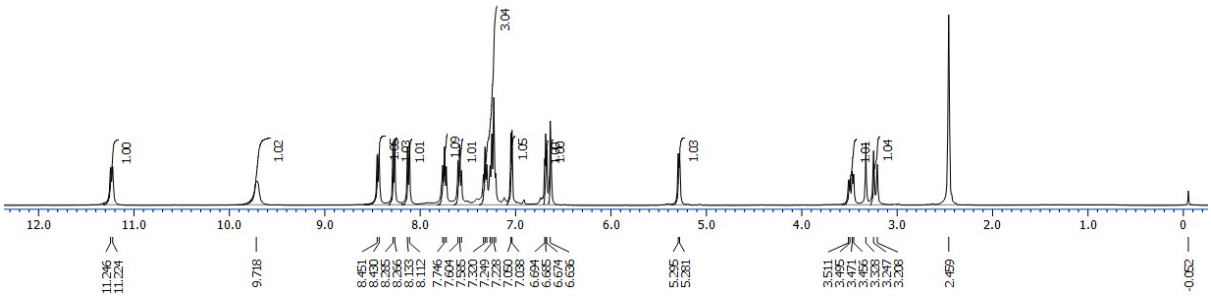


^{1}H NMR (400 MHz, $CDCl_3$)

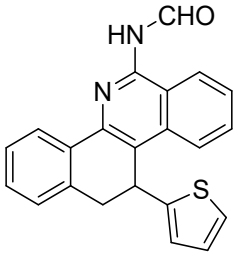


***N*-(11-(Thiophen-2-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10d)**

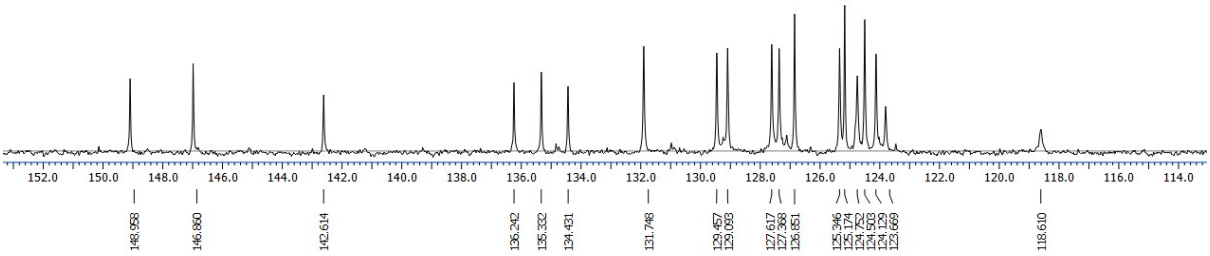


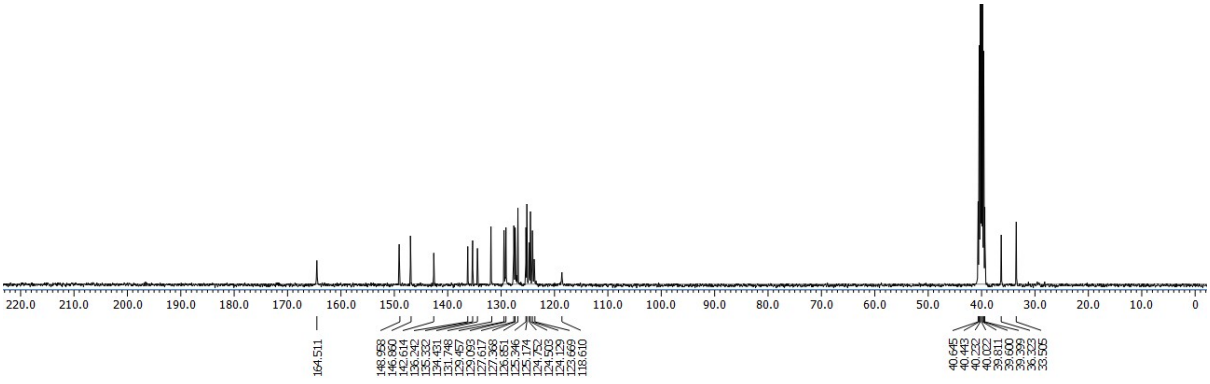


^{13}C NMR (100 MHz, $CDCl_3$)

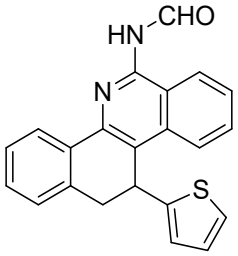


***N*-(11-(Thiophen-2-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10d)**

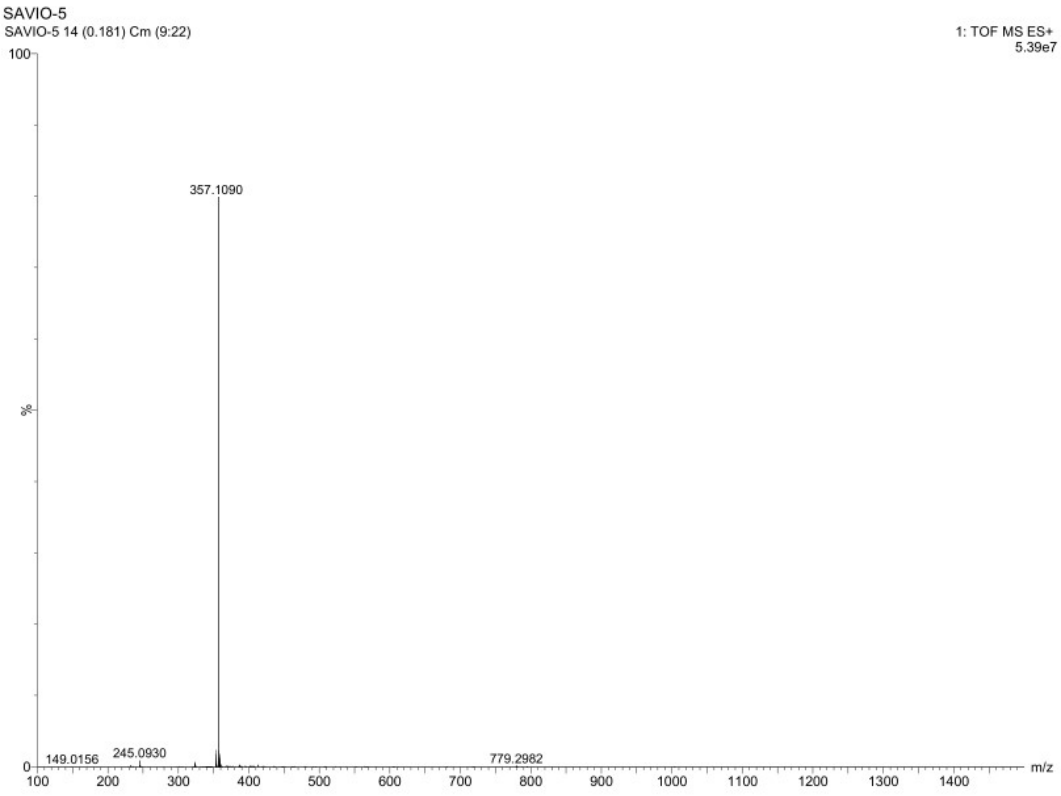




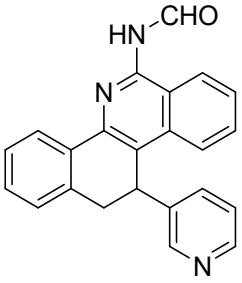
HRMS



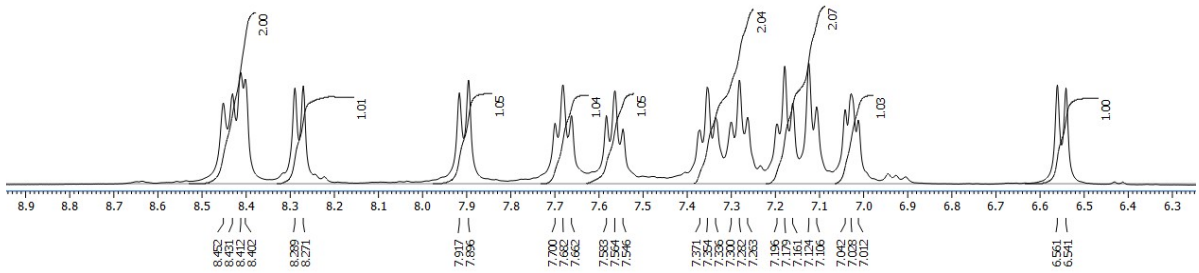
***N*-(11-(Thiophen-2-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10d)**

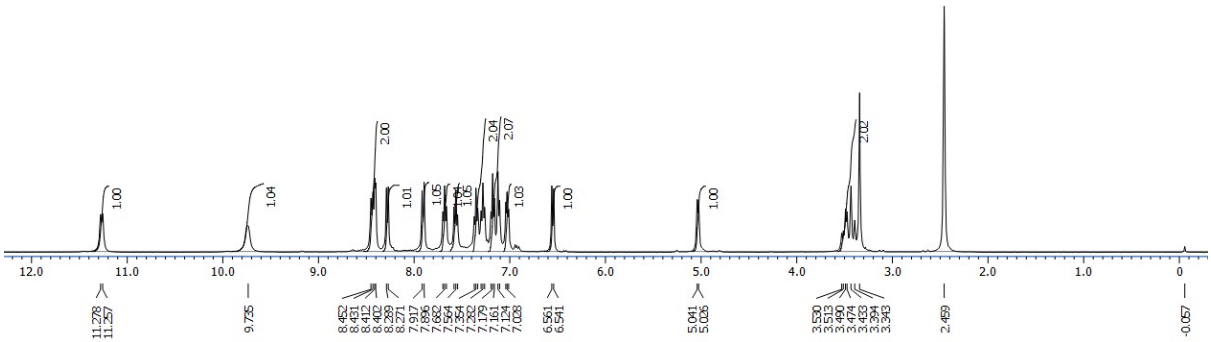


^{1}H NMR (400 MHz, $CDCl_3$)

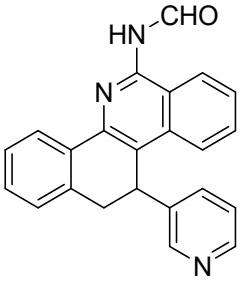


***N*-(11-(pyridin-3-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10e)**

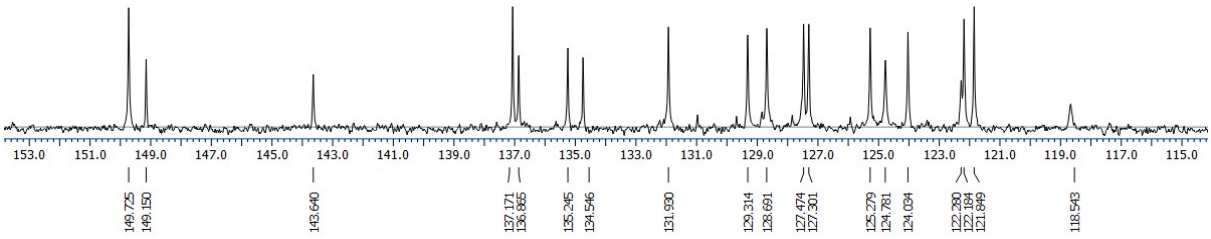


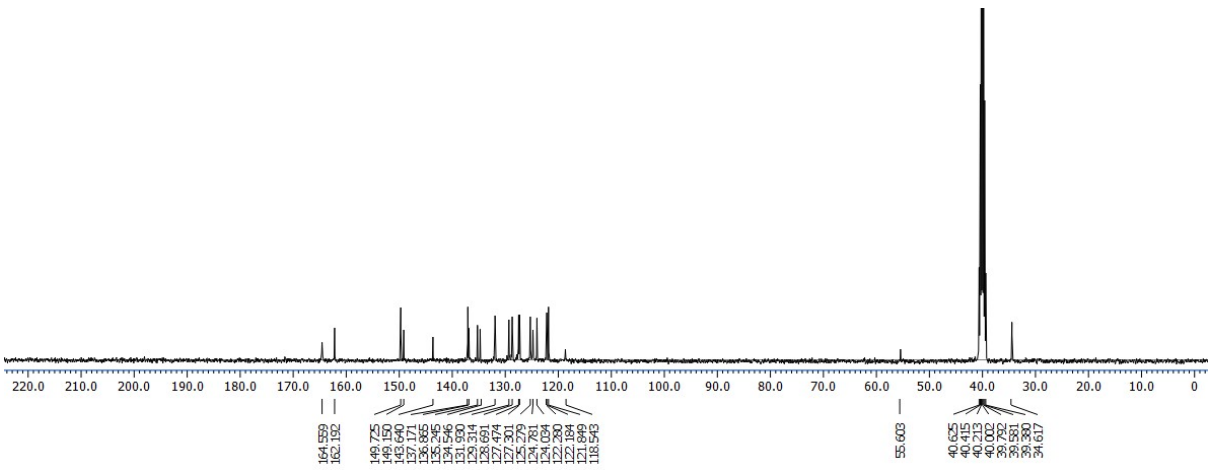


^{13}C NMR (100 MHz, $CDCl_3$)

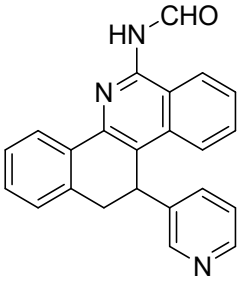


***N*-(11-(pyridin-3-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10e)**

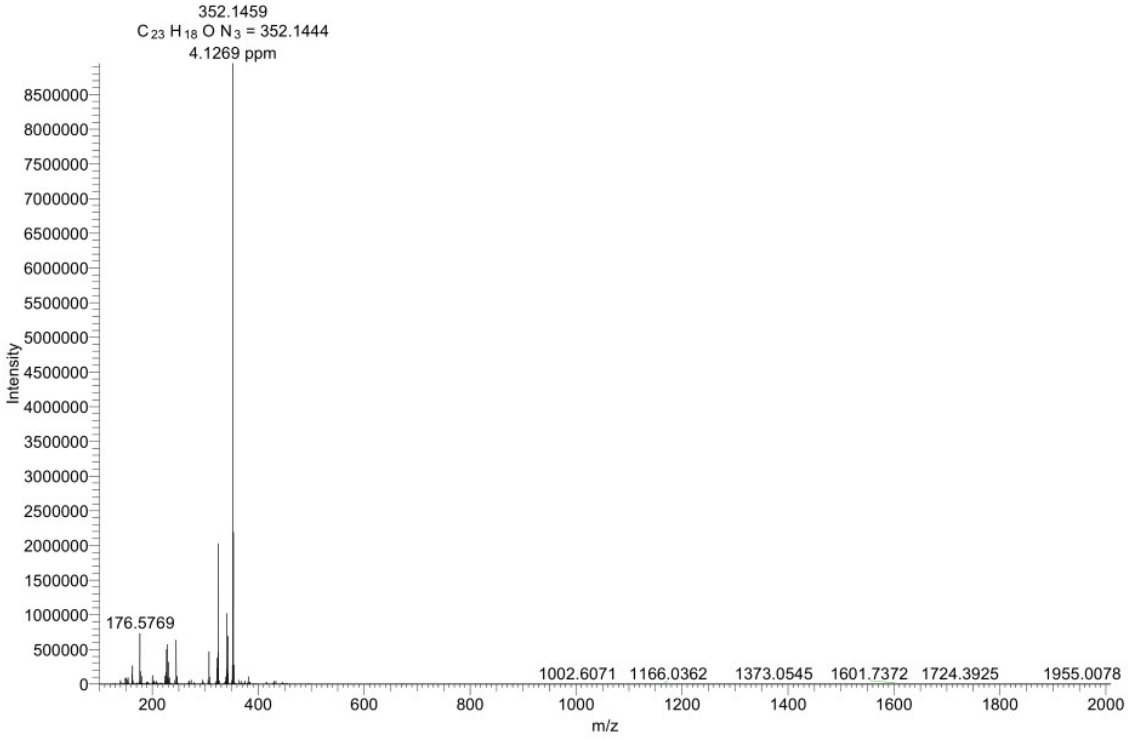




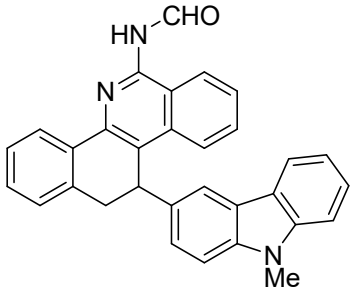
HRMS



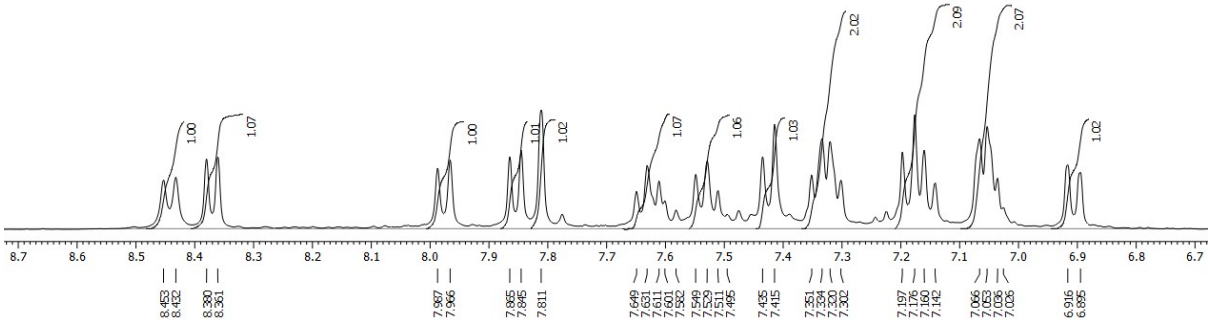
***N*-(11-(pyridin-3-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10e)**

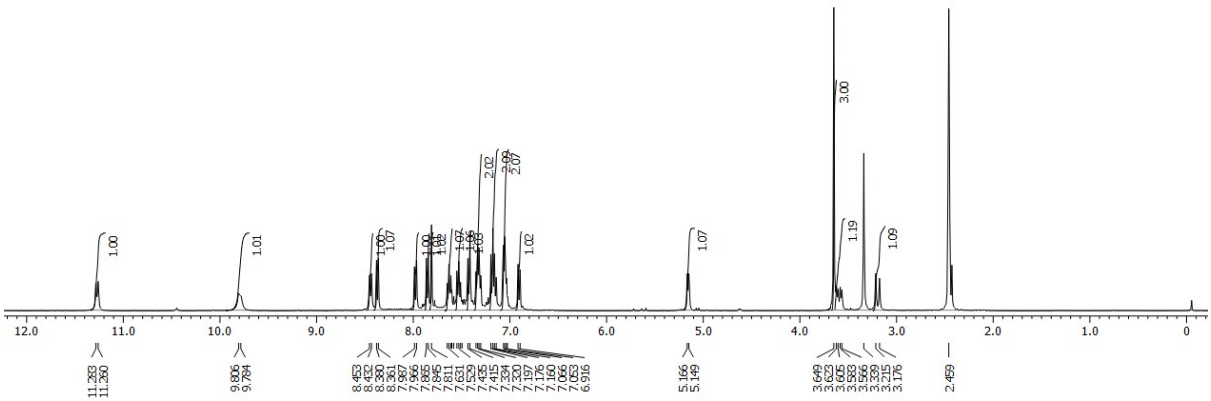


^{1}H NMR (400 MHz, $CDCl_3$)

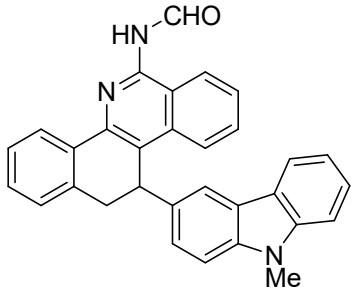


***N*-(11-(9-Methyl-9*H*-carbazol-3-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10f)**

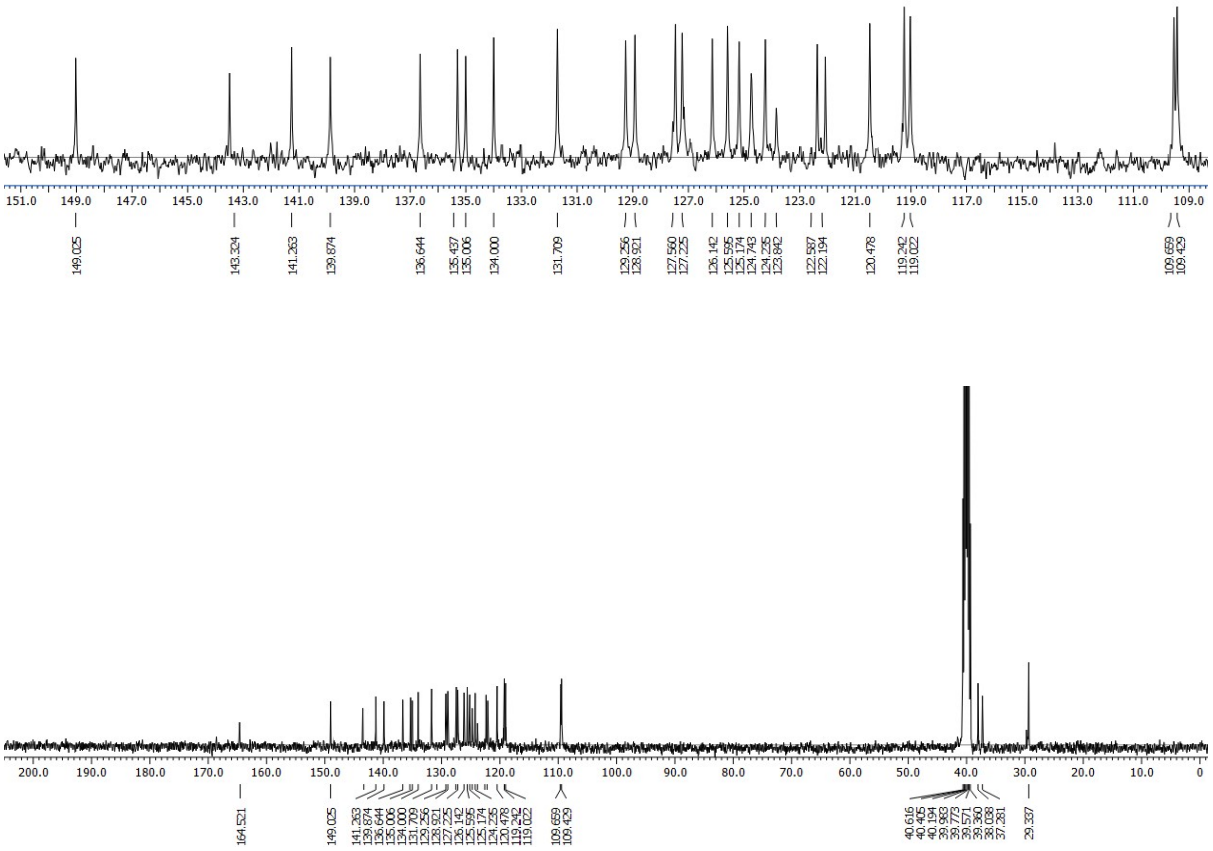




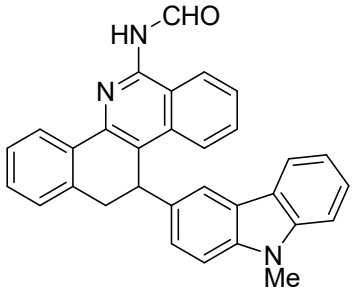
^{13}C NMR (100 MHz, $CDCl_3$)



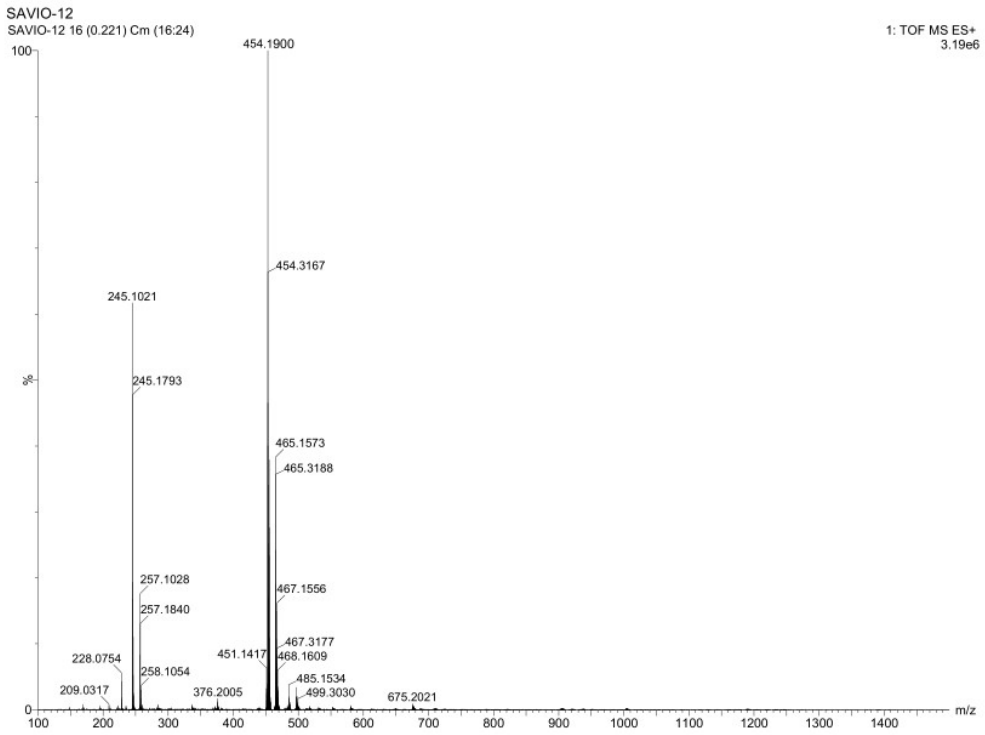
_N_-(11-(9-Methyl-9_H_-carbazol-3-yl)-11,12-dihydrobenzo[_c_]phenanthridin-6-yl)formamide (10f)



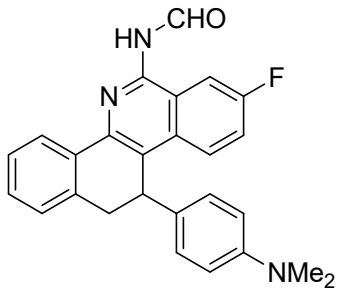
HRMS



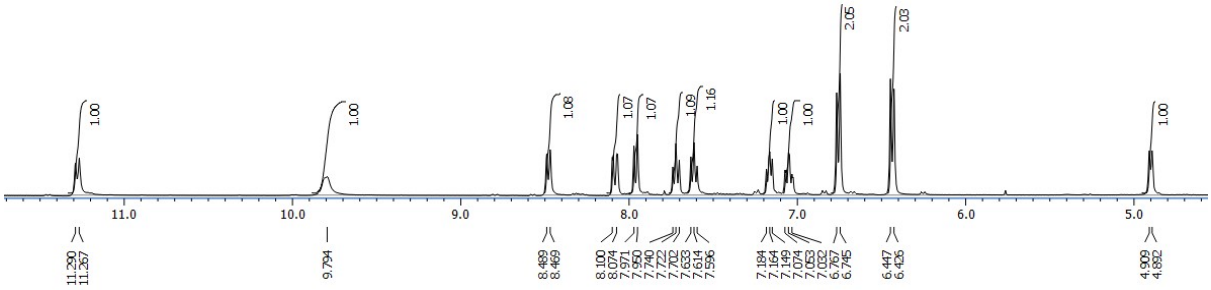
***N*-(11-(9-Methyl-9*H*-carbazol-3-yl)-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10f)**

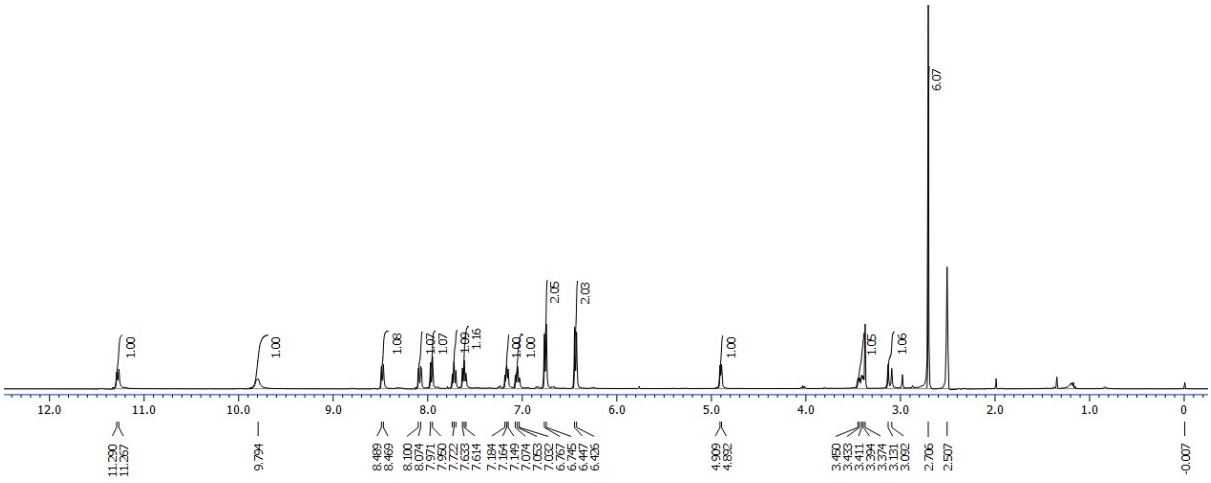


^{1}H NMR (400 MHz, $CDCl_3$)

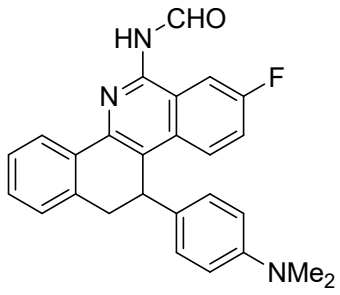


***N*-(11-(4-(dimethylamino)phenyl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10g)**

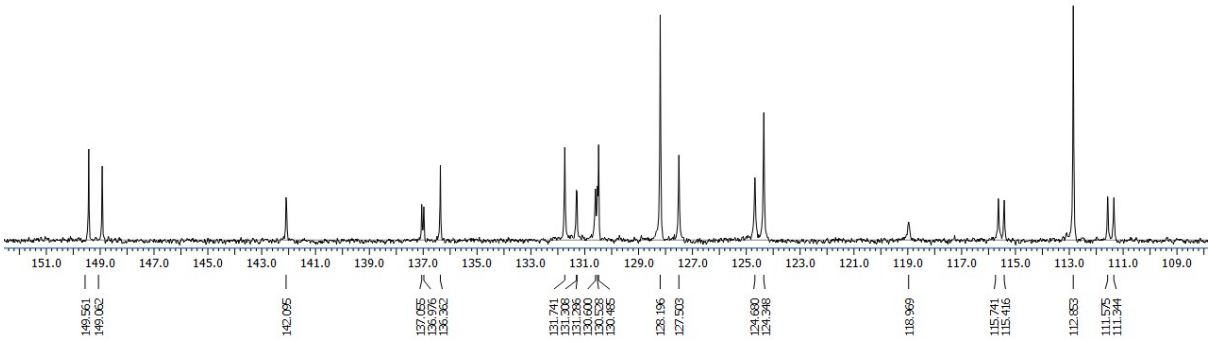


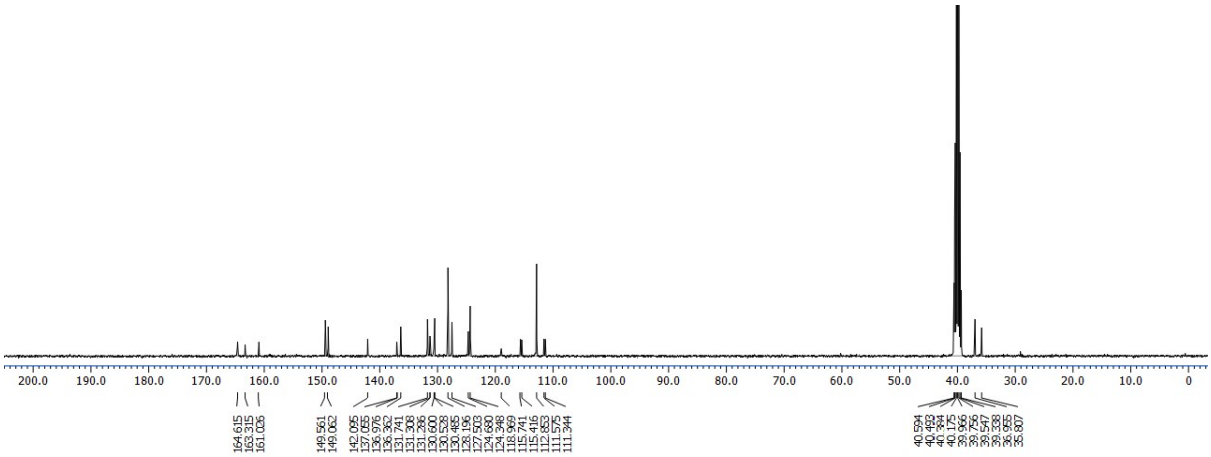


^{13}C NMR (100 MHz, $CDCl_3$)

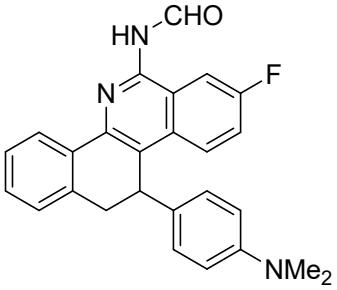


_N_-(11-(4-(dimethylamino)phenyl)-8-fluoro-11,12-dihydrobenzo[_c_]phenanthridin-6-yl)formamide (10g)

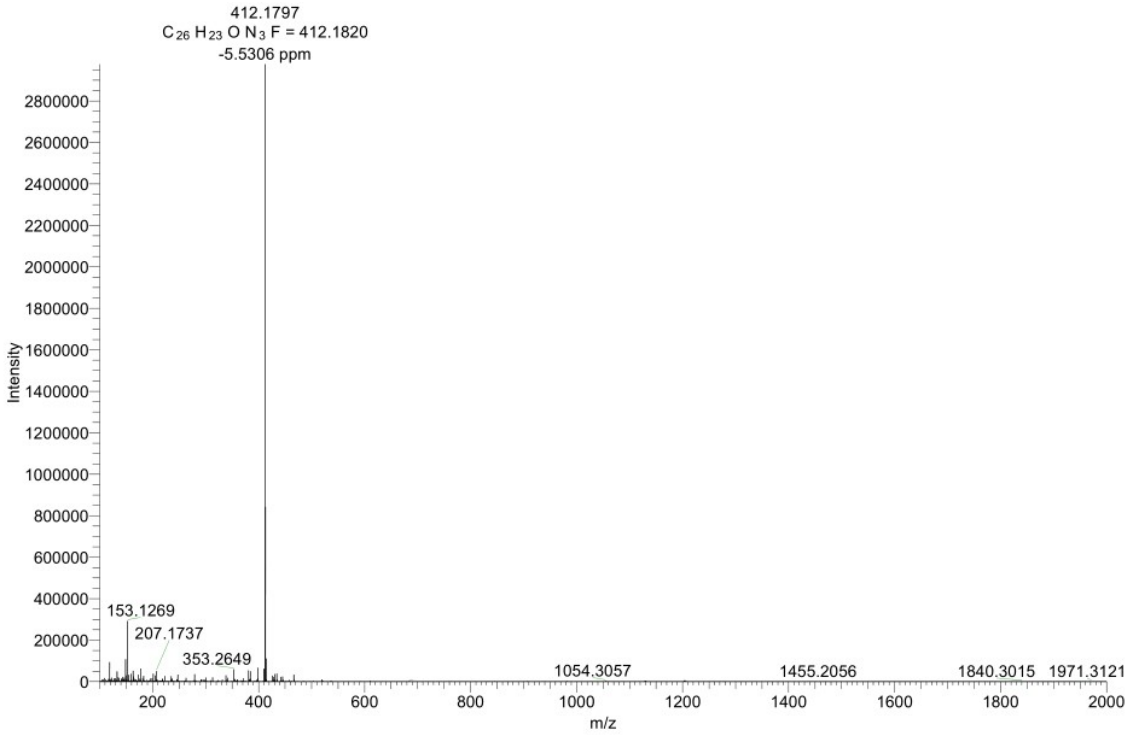




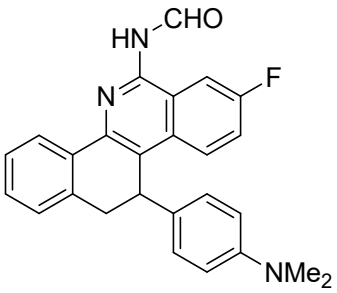
HRMS



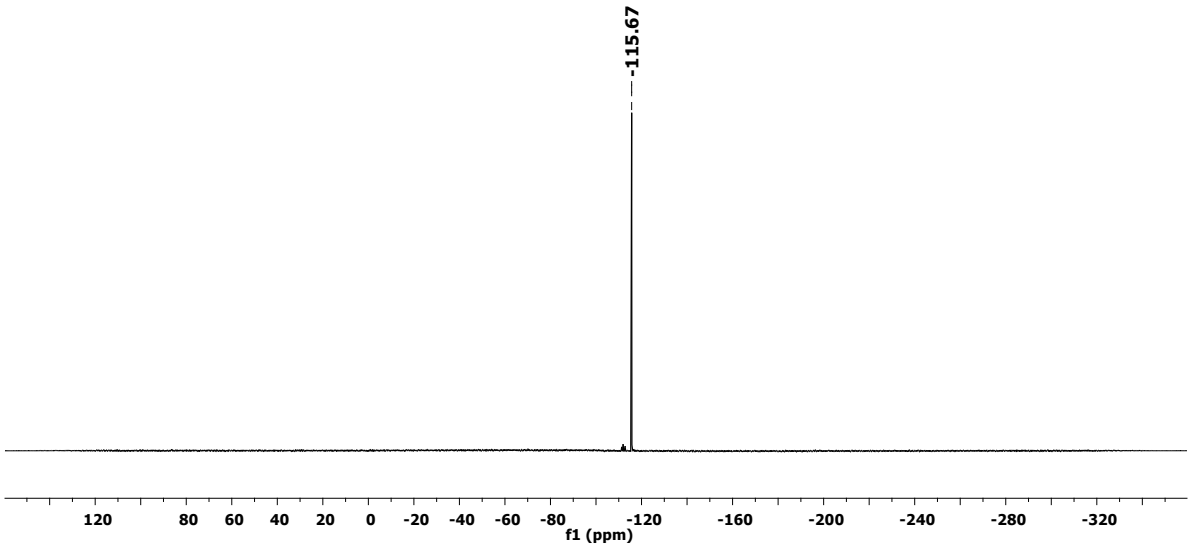
***N*-(11-(4-(dimethylamino)phenyl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10g)**



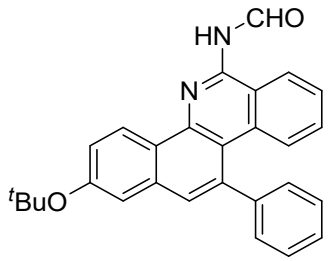
^{19}F NMR (376 MHz, $CDCl_3$)



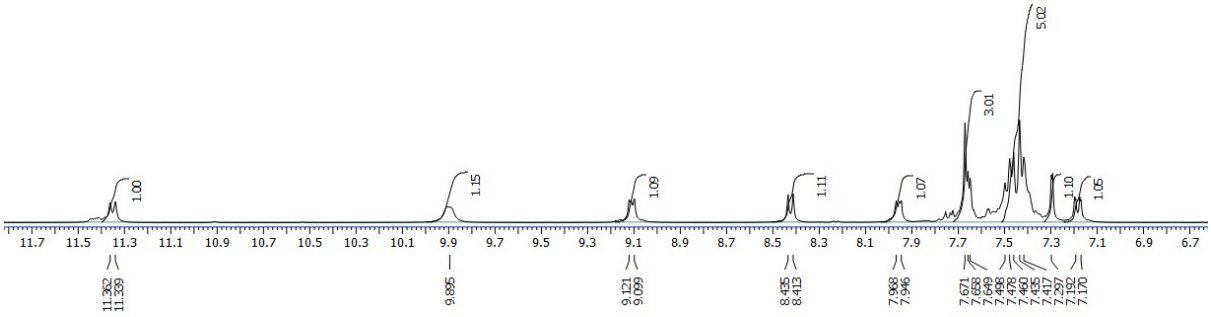
***N*-(11-(4-(dimethylamino)phenyl)-8-fluoro-11,12-dihydrobenzo[*c*]phenanthridin-6-yl)formamide (10g)**

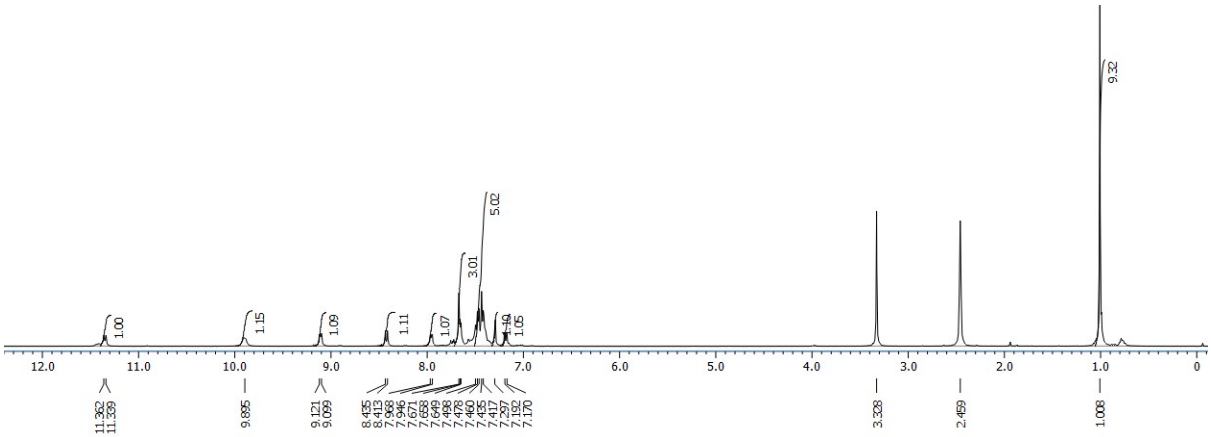


^{1}H NMR (400 MHz, $CDCl_3$)

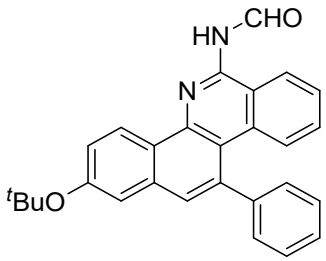


***N*-(2-(*tert*-butoxy)-11-phenylbenzo[*c*]phenanthridin-6-yl)formamide (11)**

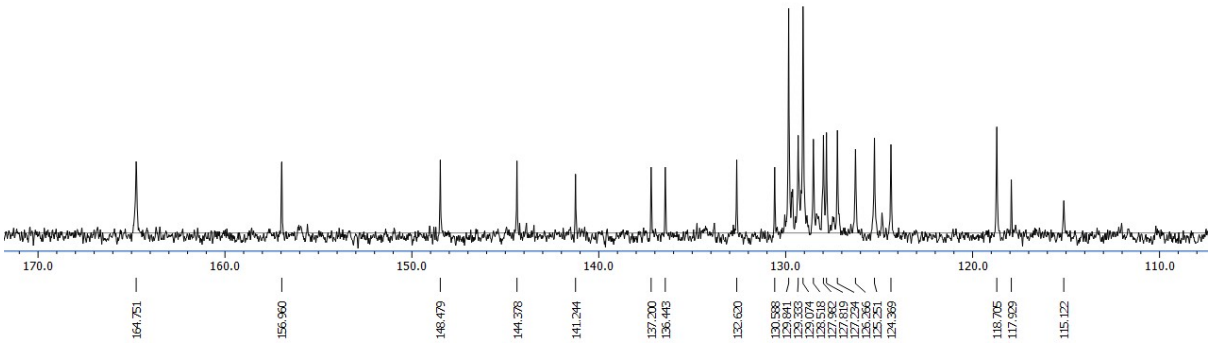


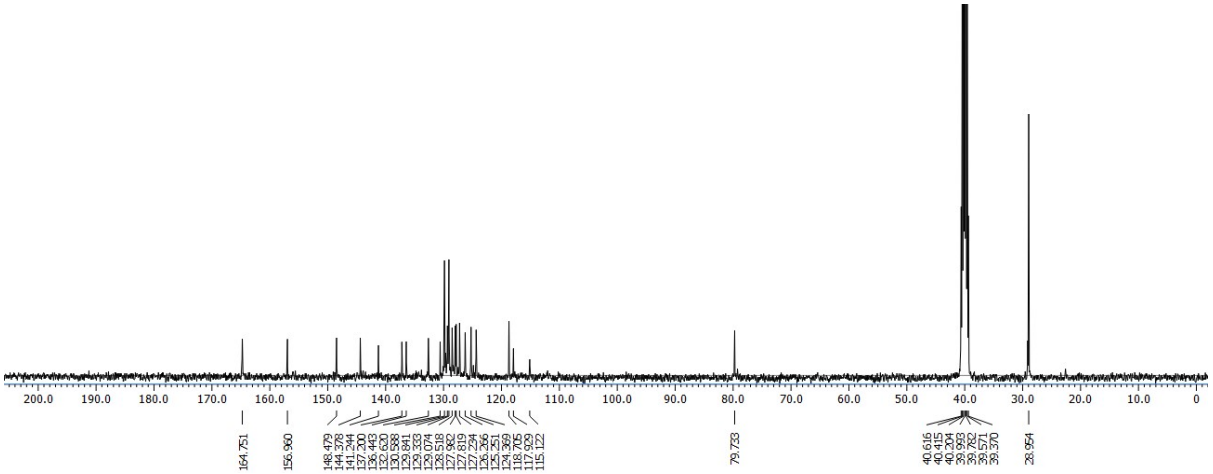


^{13}C NMR (100 MHz, $CDCl_3$)

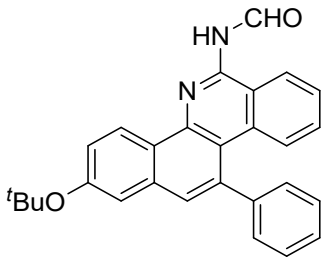


***N*-(2-(*tert*-butoxy)-11-phenylbenzo[*c*]phenanthridin-6-yl)formamide (11)**

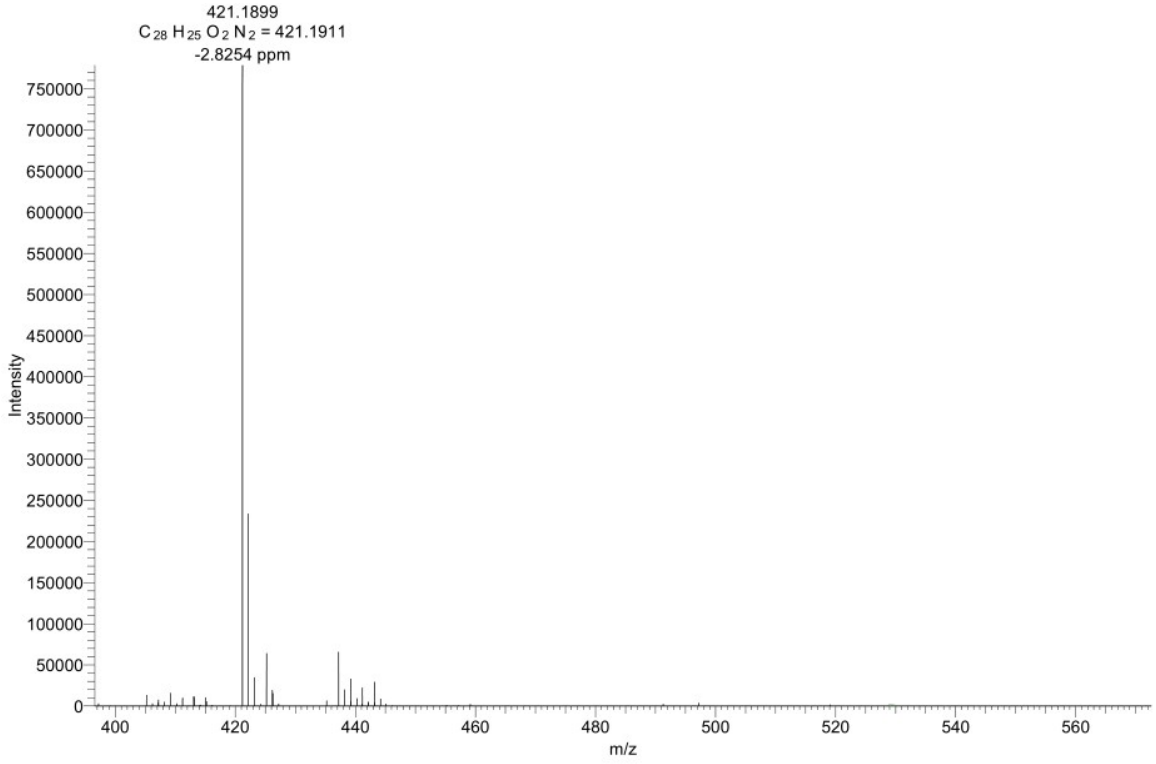




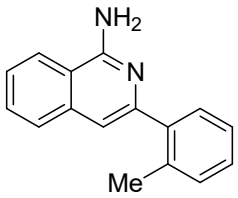
HRMS



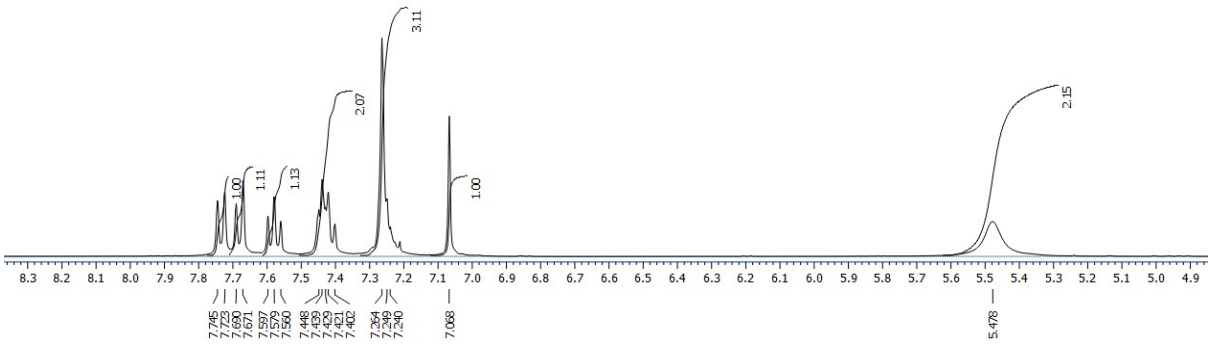
***N*-(2-(*tert*-butoxy)-11-phenylbenzo[*c*]phenanthridin-6-yl)formamide (11)**

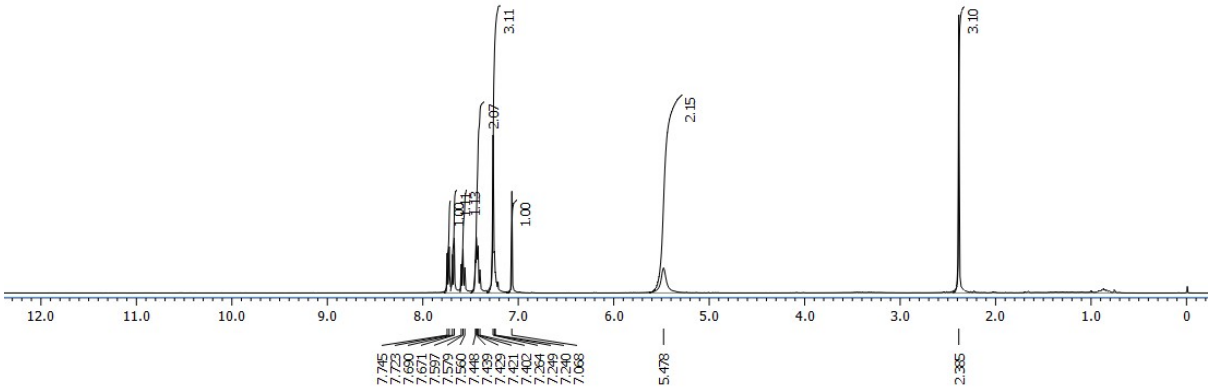


^{1}H NMR (400 MHz, $CDCl_3$)

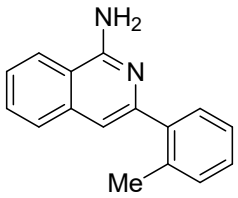


3-(*o*-Tolyl)isoquinolin-1-amine (12)

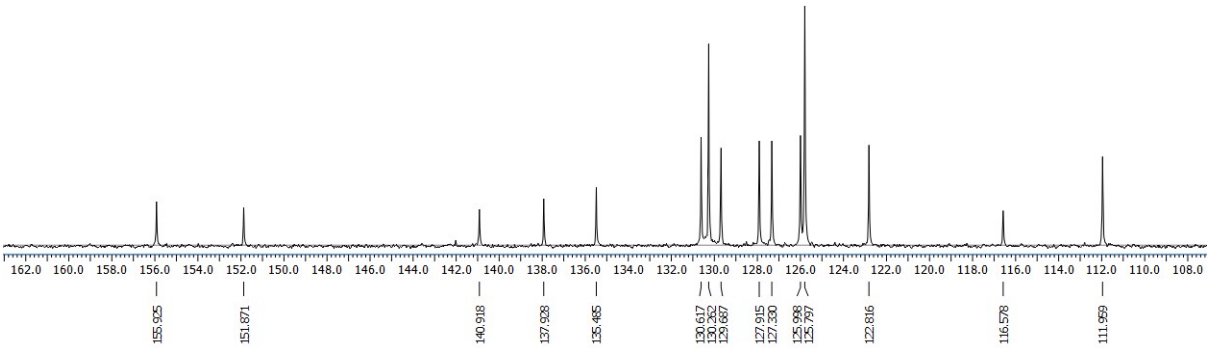


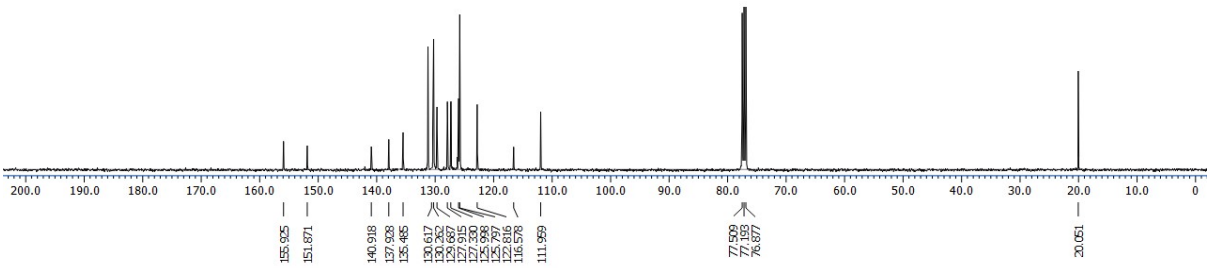


^{13}C NMR (100 MHz, $CDCl_3$)

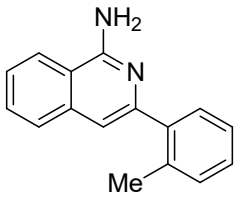


3-(*o*-Tolyl)isoquinolin-1-amine (12)





HRMS



3-(*o*-Tolyl)isoquinolin-1-amine (12)