Supporting Information

Palladium-catalyzed dual C–H activation for the synthesis of indolo[1,2-*f*]phenanthridines

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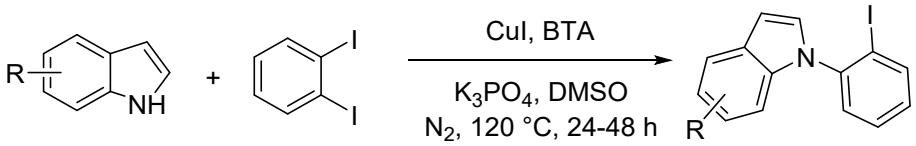
1) General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) at room temperature, unless otherwise noted. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR, δ = 77.00 for ^{13}C-NMR) or DMSO-d_6 (δ = 2.50 for ^{1}H-NMR, δ = 39.60 for ^{13}C-NMR) as an internal reference. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HPLC/Q-TOF-MS analysis was performed with an Agilent 1290 LC systemcoupled with a 6530Q-TOF/MS accurate-mass spectrometer (Agilent Technologies, USA). The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. Reactions were monitored by thin-layer chromatography Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Unless otherwise noted, all starting materials were commercially available and were used without further purification.

2) Synthesis of starting materials

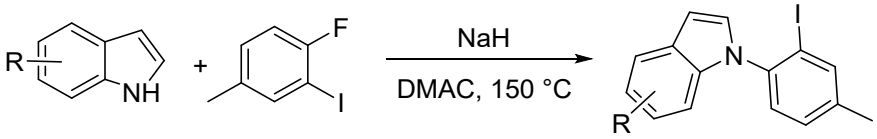
a) General procedure for the Synthesis of 1a-1m, 1q-1u.[1]



CuI (0.5 mmol, 95.00 mg) and benzotriazole (1.0 mmol, 0.12 g) ligand were added to a 50 mL round bottom flask containing the 1,2-diiodobenzene (5.0 mmol, 1.65 g), indole (5.5 mmol, 0.64 g), and K_3PO_4 (10.0 mmol, 2.12 g) in 20.0 mL of DMSO. The flask was sealed with a cap containing a PTFE septum. The mixture was heated at 120 °C until the 1,2-diiodobenzene were consumed, as determined by TLC. The reaction mixture was cooled to room temperature, diluted with dichloromethane and water, filtered on diatomite, and extracted with dichloromethane (10 mL*3). The separated aqueous phase was combined and extracted with dichloromethane (5 mL*3).

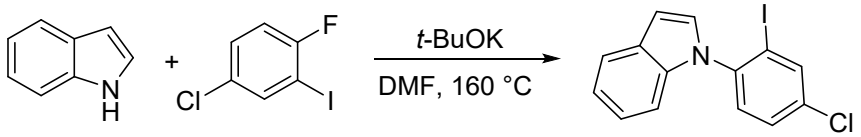
The organic phase was combined and washed with saline (10 mL*3) and dried with Na_2SO_4. The solvent was removed in vacuo and the crude residue was purified by column chromatography on silica gel using a mixture of n-hexane and dichloromethane (60: 1, *V/V*) as eluent.

b) General procedure for the Synthesis of 1n, 1p.[1]



In a dried Schlenk tube, indole (5.0 mmol) and sodium hydride (10.0 mmol) were added at room temperature. Then a solution of 1-fluoro-2-iodo-4-methylbenzene (10.0 mmol) dissolved in 20 mL DMAC was introduced into the reaction mixture by a syringe. The resulting mixture was continually stirred at 150 °C in oil bath for 12 hours and indole was almost completely consumed determined by TLC analysis. The mixture was filtered through diatomaceous earth, saturated NH_4Cl was added to the mixture and extracted with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the crude residue was purified by column chromatography on silica gel using a mixture of n-hexane and dichloromethane (60: 1, *V/V*) as eluent.

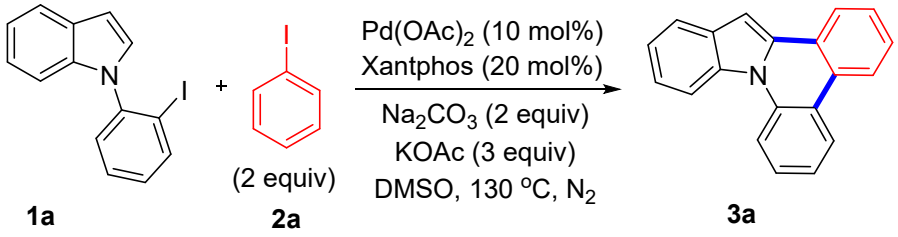
c) Procedure for the Synthesis of 1o.[1]



In a sealed tube, indoles (3.0 mmol), 4-chloro-1-fluoro-2-iodobenzene (3.3 mmol), *t*-BuOK (4.5mmol, 504.9 mg) and DMF (10.0 mL) were stirred at 160 °C (oil bath) under N_2. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. After removal of the EA, the residue was purified by chromatography on silica gel to afford **1o**.

3) Typical Experimental Procedures

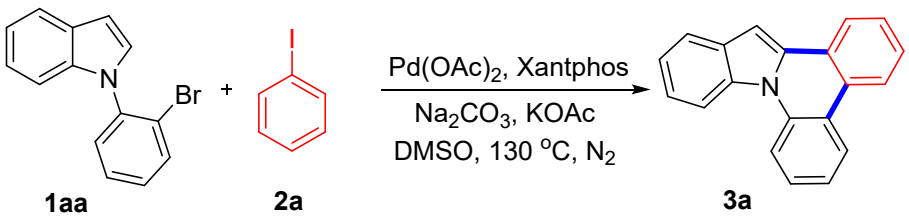
(a) Synthesis of indolo[1,2-*f*]phenanthridine **(3a)** from 1-(2-iodophenyl)-1*H*-indole and iodobenzene



Scheme 7

The stirred mixture of 1-(2-iodophenyl)-1*H*-indole (53.4 mg, 0.2 mmol, 1.0 equiv), iodobenzene (81.6 mg, 0.4 mmol 2.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%), Na_2CO_3 (42.4 mg, 0.4 mmol, 2.0 equiv), and KOAc (58.8 mg, 0.6 mmol, 3.0 equiv) in DMSO (2 mL), place in a preheated oil bath at 130 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was washed by saturated NH_4Cl solution and then evaporated under reduced pressure, the crude product was purified by column chromatography to provide the desired product **3a** (42 mg, 78%).

(b) Synthesis of indolo[1,2-*f*]phenanthridine **(3a)** from 1-(2-bromophenyl)-1*H*-indole and iodobenzene

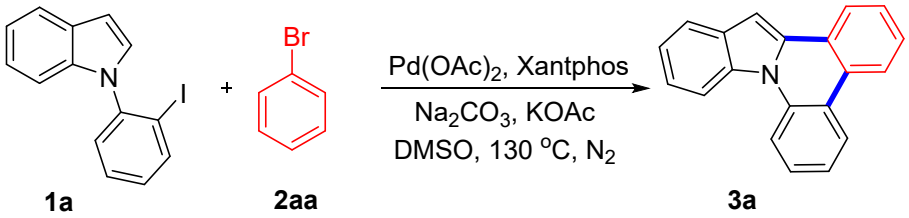


Scheme 8

The stirred mixture of 1-(2-bromophenyl)-1*H*-indole (54.0 mg, 0.2 mmol, 1.0 equiv), iodobenzene (81.6 mg, 0.4 mmol 2.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%), Na_2CO_3 (42.4 mg, 0.4 mmol,

2.0 equiv), and KOAc (58.8 mg, 0.6 mmol, 3.0 equiv) in DMSO (2 mL), place in a preheated oil bath at 130 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was washed by saturated NH_4Cl solution and then evaporated under reduced pressure, the crude product was purified by column chromatography to provide the desired product **3a** (30 mg, 56%).

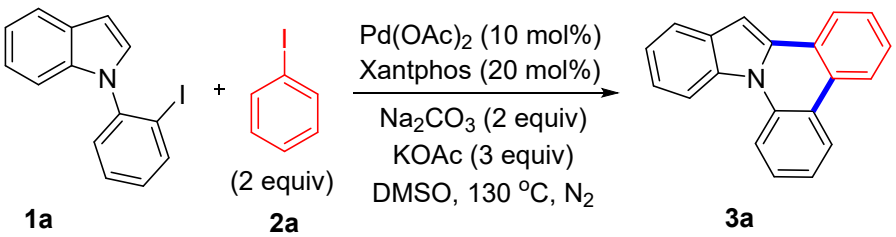
(c) Synthesis of indolo[1,2-*f*]phenanthridine **(3a)** from 1-(2-iodophenyl)-1*H*-indole and bromobenzene



Scheme 9

The stirred mixture of 1-(2-iodophenyl)-1*H*-indole (53.4 mg, 0.2 mmol, 1.0 equiv), bromobenzene (62.4 mg, 0.4 mmol 2.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), Xantphos (23.1 mg, 0.04 mmol, 20 mol%), Na_2CO_3 (42.4 mg, 0.4 mmol, 2.0 equiv), and KOAc (58.8 mg, 0.6 mmol, 3.0 equiv) in DMSO (2 mL), place in a preheated oil bath at 130 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was washed by saturated NH_4Cl solution and then evaporated under reduced pressure, the crude product was purified by column chromatography to provide the desired product **3a** (25 mg, 47%).

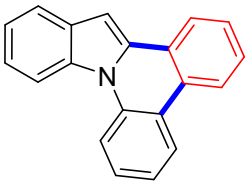
4) Larger-Scale Experiment



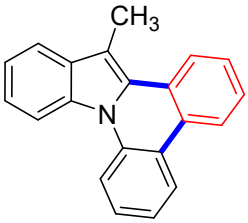
Scheme 10

The stirred mixture of 1-(2-iodophenyl)-1*H*-indole (1335 mg, 5.0 mmol, 1.0 equiv), iodobenzene (2040 mg, 10.0 mmol 2.0 equiv), $Pd(OAc)_2$ (112.5 mg, 0.5 mmol, 10 mol%), Xantphos (577.5 mg, 1.0 mmol, 20 mol%), Na_2CO_3 (1060 mg, 10.0 mmol, 2.0 equiv), and KOAc (1470 mg, 15.0 mmol, 3.0 equiv) in DMSO (50 mL), place in a preheated oil bath at 130 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was washed by saturated NH_4Cl solution and then evaporated under reduced pressure, the crude product was purified by column chromatography to provide the desired product **3a**.

5) Characterization Data

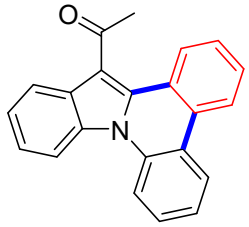


indolo[1,2-*f*]phenanthridine (3a): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a white solid, isolated yield 78% (42 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, J = 8.26 Hz, 1H), 8.37 (d, J = 7.39 Hz, 1H), 8.26 (d, J = 7.82 Hz, 1H), 8.16 (d, J = 4.34 Hz, 1H), 8.09 (d, J = 4.34 Hz, 1H), 7.86 (d, J = 6.52 Hz, 1H), 7.55 (t, J = 7.39 Hz, 1H), 7.47-7.39 (m, 4H), 7.31 (t, J = 7.39 Hz, 1H), 7.23 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.9, 135.1, 133.8, 130.3, 128.6, 128.0, 127.7, 126.7, 126.0, 124.0, 123.9, 122.9, 122.3, 122.0, 121.9, 121.7, 121.0, 116.2, 114.2, 96.1. The spectral data were in accordance with the literature.[2]

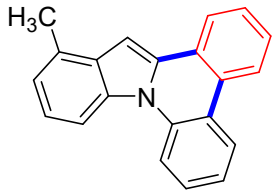


14-methylindolo[1,2-*f*]phenanthridine (3b): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale green

solid, m.p. 131-132 °C, isolated yield 84% (47 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, J = 8.44, 0.79 Hz, 1H), 8.37-8.32 (m, 2H), 8.28 (dd, J = 9.49, 1.41 Hz, 1H), 8.26-8.24 (m, 1H), 7.86-7.84 (m, 1H), 7.56-7.50 (m, 2H), 7.47 (td, J = 8.08, 1.58 Hz, 1H), 7.44-7.36 (m, 2H), 7.31 (td, J = 8.05, 1.09 Hz, 1H), 2.82 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.1, 132.6, 131.4, 130.2, 128.7, 128.1, 127.9, 127.7, 126.9, 125.2, 123.9, 122.8, 122.4, 122.3, 122.1, 121.2, 118.8, 116.3, 114.0, 107.0, 12.0. The spectral data were in accordance with the literature.[2]

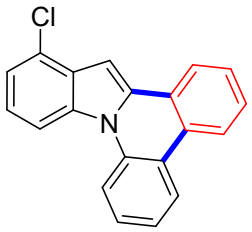


1-(indolo[1,2-*f*]phenanthridin-14-yl)ethan-1-one (3c): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a pale green solid, m.p. 109-111 °C, isolated yield 73% (45 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 8.54 Hz, 1H), 8.43-8.38 (m, 2H), 8.36-8.34 (m, 1H), 8.24 (dd, J = 7.97, 0.95 Hz, 1H), 8.16-8.12 (m, 1H), 7.67-7.61 (m, 2H), 7.55 (td, J = 8.16, 1.33 Hz, 1H), 7.49-7.43 (m, 3H), 2.78 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.4, 135.8, 134.7, 133.1, 129.3, 129.2, 128.8, 128.7, 128.4, 128.0, 124.8, 124.2, 123.4, 123.3, 122.7, 122.5, 120.8, 114.4, 114.2, 32.1. The spectral data were in accordance with the literature.[2]

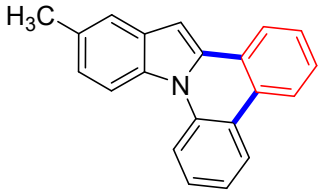


13-methylindolo[1,2-*f*]phenanthridine (3d): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale green solid, m.p. 192-193 °C, isolated yield 88% (49 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55-8.53 (m, 1H), 8.31 (dd, J = 8.03, 1.24 Hz, 1H), 8.24-8.20 (m, 2H), 8.17-8.15 (m, 1H), 7.60-7.55 (m, 1H), 7.52-7.46 (m, 2H), 7.37-7.29 (m, 2H), 7.17 (d, J = 7.12 Hz, 1H), 2.72 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.0, 134.7, 133.6, 130.2,

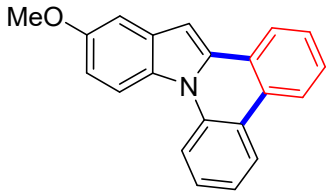
130.1, 128.7, 128.1, 127.6, 126.8, 126.2, 124.1, 123.9, 123.0, 122.4, 122.1, 122.1, 121.9, 116.4, 111.9, 94.6, 19.0. The spectral data were in accordance with the literature.[2]



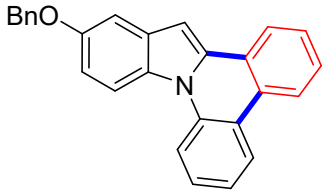
13-chloroindolo[1,2-*f*]phenanthridine (3e): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale green solid, isolated yield 68% (41 mg), m.p. 173-174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 8.37 Hz, 1H), 8.34-8.32 (m, 1H), 8.26 (d, J = 8.37 Hz, 1H), 8.22 (dd, J = 6.14, 3.35 Hz, 1H), 8.20-8.15 (m, 1H), 7.60-7.56 (m, 1H), 7.54-7.50 (m, 1H), 7.40-7.35 (m, 3H), 7.28 (t, J = 8.37 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.8, 135.6, 134.4, 129.1, 128.8, 128.4, 128.3, 126.9, 126.1, 125.7, 124.4, 124.1, 123.6, 122.4, 122.3, 121.5, 116.4, 112.7, 94.6. HRMS (ESI) m/z $(M+H)^+$ calcd for $C_{20}H_{13}ClN^+$ 302.0731, found 302.0733.



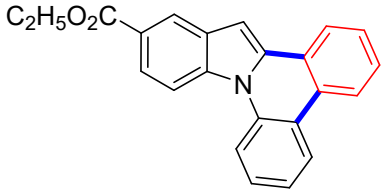
12-methylindolo[1,2-*f*]phenanthridine (3f): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale green solid, m.p. 184-185 °C, isolated yield 86% (48 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.30 Hz, 1H), 8.30 (dd, J = 7.99, 0.93 Hz, 1H), 8.24 (d, J = 8.74 Hz, 1H), 8.22-8.19 (m, 1H), 8.13-8.09 (m, 1H), 7.61 (s, 1H), 7.59-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.35-7.31 (m, 1H), 7.21 (dd, J = 8.64, 1.34 Hz, 1H), 7.17 (s, 1H), 2.55 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.0, 135.2, 132.2, 131.1, 130.6, 128.7, 128.1, 127.6, 126.8, 126.2, 124.1, 123.9, 123.6, 122.8, 122.3, 121.9, 120.7, 116.1, 113.9, 95.7, 21.4. The spectral data were in accordance with the literature.[2]



12-methoxyindolo[1,2-*f*]phenanthridine (3g): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a pale green solid, isolated yield 90% (53 mg), mp: 173-174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.34 Hz, 1H), 8.32 (d, J = 7.82 Hz, 1H), 8.25 (d, J = 9.12 Hz, 1H), 8.24-8.21 (m, 1H), 8.12-8.10 (m, 1H), 7.59-7.55 (m, 1H), 7.51-7.46 (m, 2H), 7.34 (t, J = 7.69 Hz, 1H), 7.25 (d, J = 2.48 Hz, 1H), 7.18 (s, 1H), 7.02 (dd, J = 9.12, 2.48 Hz, 1H), 3.94 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.1, 135.8, 135.8, 131.3, 129.0, 128.7, 128.1, 127.7, 126.7, 126.0, 124.1, 124.0, 122.8, 122.4, 121.8, 115.9, 115.0, 111.9, 102.1, 95.8, 55.6. The spectral data were in accordance with the literature.[2]

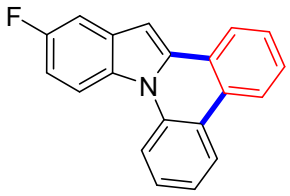


12-(benzyloxy)indolo[1,2-*f*]phenanthridine (3h): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=5:1) as a brown solid, isolated yield 87% (65 mg), mp: 175-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 8.26 Hz, 1H), 8.30 (d, J = 7.77 Hz, 1H), 8.25 (d, J = 9.06 Hz, 1H), 8.23-8.20 (m, 1H), 8.10-8.08 (m, 1H), 7.58-7.55 (m, 2H), 7.53 (s, 1H), 7.48 (t, J = 4.21 Hz, 2H), 7.43 (t, J = 7.12 Hz, 2H), 7.38-7.32 (m, 3H), 7.16 (s, 1H), 7.10 (dd, J = 9.06, 2.27 Hz, 1H), 5.19 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.3, 137.4, 135.8, 135.8, 131.3, 129.2, 128.7, 128.6, 128.1, 127.9, 127.7, 127.6, 126.7, 125.9, 124.1, 124.0, 122.8, 122.4, 121.8, 115.9, 115.0, 112.5, 103.6, 95.9, 70.5. The spectral data were in accordance with the literature.[2]

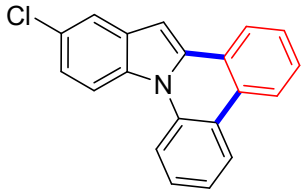


ethyl indolo[1,2-*f*]phenanthridine-12-carboxylate (3i): Purification by column

chromatography on silica gel (petroleum ether: ethyl acetate=5:1) as a brown solid, isolated yield 72% (49 mg), mp: 158-160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 1.63 Hz, 1H), 8.45 (d, J = 8.42 Hz, 1H), 8.32 (d, J = 8.99 Hz, 1H), 8.28 (dd, J = 8.23, 1.15 Hz, 1H), 8.20-8.16 (m, 1H), 8.09-8.06 (m, 1H), 8.03 (dd, J = 8.99, 1.91 Hz, 1H), 7.56 (td, J = 7.27, 1.34 Hz, 1H), 7.51-7.46 (m, 2H), 7.38-7.34 (m, 1H), 7.26 (s, 1H), 4.46 (q, J = 7.27 Hz, 2H), 1.47 (t, J = 7.08 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.2, 136.4, 135.9, 135.4, 129.8, 128.8, 128.3, 128.2, 126.8, 125.7, 124.2, 124.1, 123.8, 123.7, 123.4, 122.9, 122.4, 122.3, 116.5, 113.6, 97.1, 60.8, 14.5. HRMS (ESI) m/z $(M+H)^+$ calcd for $C_{23}H_{18}NO_2^+$ 340.1332, found 340.1335.

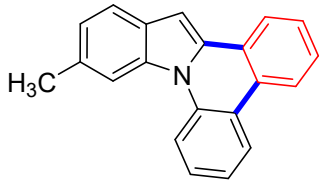


12-fluoroindolo[1,2-*f*]phenanthridine (3j): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=5:1) as a pale green solid, isolated yield 64% (36 mg), mp: 146-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 8.21 Hz, 1H), 8.35 (dd, J = 8.11, 1.15 Hz, 1H), 8.30 (dd, J = 9.26, 4.30 Hz, 1H), 8.28-8.24 (m, 1H), 8.15-8.11 (m, 1H), 7.60 (td, J = 7.35, 1.34 Hz, 1H), 7.55-7.50 (m, 2H), 7.45 (dd, J = 8.97, 2.58 Hz, 1H), 7.40-7.36 (m, 1H), 7.22 (s, 1H), 7.11 (td, J = 8.97, 2.58 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.8, 157.4, 136.8, 135.6, 131.2 (d, J = 10.28 Hz), 130.5, 128.9, 128.3, 128.2, 126.9, 125.7, 124.2 (d, J = 12.84 Hz), 123.3, 122.5, 122.0, 116.0, 115.0 (d, J = 7.71 Hz), 110.1 (d, J = 25.69 Hz), 105.6 (d, J = 23.12 Hz), 96.0 (d, J = 4.65 Hz). The spectral data were in accordance with the literature.[2]

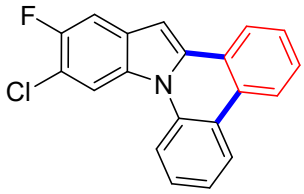


12-chloroindolo[1,2-*f*]phenanthridine (3k): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale green solid, isolated yield 70% (42 mg), mp: 173-174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.58

Hz, 1H), 8.31 (d, J = 7.80 Hz, 1H), 8.25-8.21 (m, 2H), 8.10-8.07 (m, 1H), 7.74 (d, J = 1.98 Hz, 1H), 7.57 (t, J = 7.49 Hz, 1H), 7.53-7.48 (m, 2H), 7.36 (t, J = 7.49 Hz, 1H), 7.29 (dd, J = 9.04 Hz, 1.98 Hz, 1H), 7.14 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 139.4, 136.4, 135.5, 132.1, 131.4, 128.8, 128.3, 128.2, 127.3, 126.9, 125.6, 124.2, 124.1, 123.4, 122.4, 122.0, 116.1, 115.1, 95.5. The spectral data were in accordance with the literature.[2]

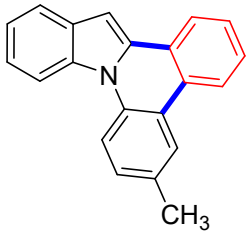


11-methylindolo[1,2-*f*]phenanthridine (3l): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale green solid, isolated yield 85% (48 mg), mp: 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 8.66 Hz, 1H), 8.28 (d, J = 7.94 Hz, 1H), 8.19-8.17 (m, 2H), 8.11-8.07 (m, 1H), 7.73 (d, J = 8.30 Hz, 1H), 7.59-7.55 (m, 1H), 7.49-7.43 (m, 2H), 7.33 (t, J = 7.94 Hz, 1H), 7.22-7.20 (m, 2H), 2.65 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 136.0, 134.7, 134.3, 131.8, 128.6, 128.1, 128.1, 127.5, 126.6, 126.3, 123.9, 123.9, 123.4, 122.8, 122.3, 122.1, 120.6, 116.3, 114.2, 96.0, 22.4. The spectral data were in accordance with the literature.[2]

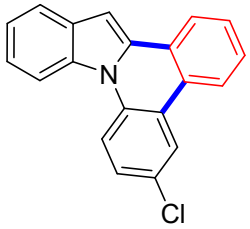


11-chloro-12-fluoroindolo[1,2-*f*]phenanthridine (3m): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale green solid, isolated yield 71% (45 mg), mp: 193-195 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32-8.28 (m, 3H), 8.23-8.18 (m, 1H), 8.06-8.02 (m, 1H), 7.60-7.56 (m, 1H), 7.54-7.49 (m, 2H), 7.46 (d, J = 9.19 Hz, 1H), 7.39-7.35 (m, 1H), 7.10 (d, J = 0.29 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 155.0, 152.6, 137.1, 135.2, 130.0, 129.6 (d, J = 8.42 Hz), 129.0, 128.4 (d, J = 2.97 Hz), 126.9, 125.4, 124.2 (d, J = 5.94 Hz), 123.6, 122.5, 122.1, 115.8, 115.5 115.2, 115.0, 106.4 (d, J = 22.58 Hz), 95.9 (d, J = 4.16 Hz).

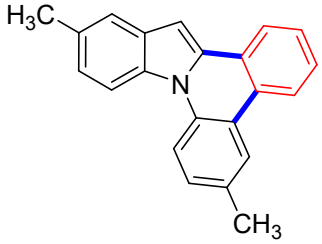
HRMS (ESI) m/z $(M+H)^+$ calcd for $C_{20}H_{12}ClFN^+$ 320.0637, found 320.0640.



6-methylindolo[1,2-*f*]phenanthridine (3n): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale green solid, isolated yield 79% (44 mg), mp: 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36-8.32 (m, 2H), 8.18-8.14 (m, 1H), 8.11-8.07 (m, 1H), 8.03 (s, 1H), 7.86-7.84 (m, 1H), 7.48-7.43 (m, 2H), 7.42-7.35 (m, 2H), 7.31 (dd, J = 8.41, 1.40 Hz, 1H), 7.23 (s, 1H), 2.47 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.1, 133.8, 133.7, 132.2, 130.2, 129.4, 127.9, 127.6, 126.8, 126.1, 124.1, 124.0, 122.3, 121.8, 121.8, 121.5, 120.9, 116.0, 114.1, 95.8, 21.0. The spectral data were in accordance with the literature.[3]

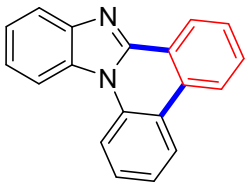


6-chloroindolo[1,2-*f*]phenanthridine (3o): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale green solid, isolated yield 66% (40 mg), mp: 173-175 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 9.13 Hz, 1H), 8.30 (d, J = 8.30 Hz, 1H), 8.26 (d, J = 2.49 Hz, 1H), 8.17-8.13 (m, 2H), 7.86-7.84 (m, 1H), 7.56-7.48 (m, 3H), 7.42-7.36 (m, 2H), 7.27 (d, J = 0.51 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 134.9, 134.5, 133.8, 130.3, 130.1, 128.9, 128.5, 128.0, 126.4, 125.8, 124.3, 124.2, 123.9, 122.6, 122.4, 122.1, 121.3, 117.5, 114.0, 96.7. HRMS (ESI) m/z $(M+H)^+$ calcd for $C_{20}H_{13}ClN^+$ 302.0731, found 302.0734.

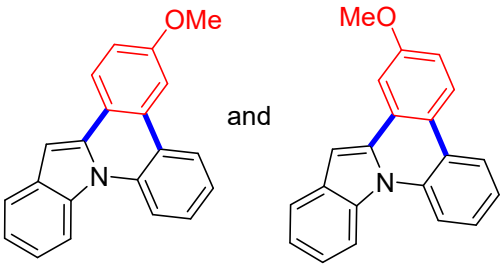


6,12-dimethylindolo[1,2-*f*]phenanthridine (3p): Purification by column

chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale green solid, isolated yield 80% (47 mg), mp: 199-201 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.54 Hz, 1H), 8.24-8.22 (m, 2H), 8.14-8.11 (M, 2H), 7.61 (s, 1H), 7.50-7.46 (m, 2H), 7.37 (dd, J = 8.54, 1.39 Hz, 1H), 7.21-7.17 (m, 2H), 2.55 (s, 3H), 2.51 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.2, 133.9, 132.2, 132.1, 131.0, 130.5, 129.6, 128.0, 127.6, 126.8, 126.3, 124.2, 124.1, 123.5, 122.3, 121.8, 120.6, 116.0, 113.8, 95.4, 21.4, 21.1. HRMS (ESI) m/z calcd for $C_{22}H_{18}N^+$ $(M+H)^+$ 296.1434, found 296.1437.

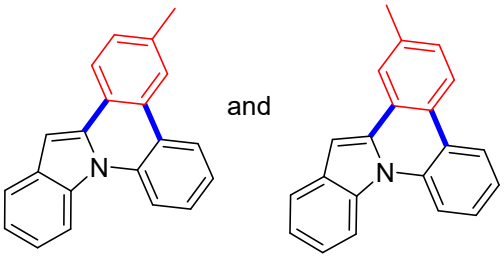


benzo[4,5]imidazo[1,2-*f*]phenanthridine (3q): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a white solid, isolated yield 62% (33 mg), mp: 144-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79-8.76 (m, 1H), 8.37-8.35 (m, 1H), 8.27 (dd, J = 8.14, 1.02 Hz, 1H), 8.21-8.19 (m, 2H), 8.02-8.00 (m, 1H), 7.64-7.57 (m, 2H), 7.55-7.51 (m, 1H), 7.48 (td, J = 7.93, 0.86 Hz, 1H), 7.43-7.39 (m, 1H), 7.36-7.32 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.3, 144.4, 134.2, 131.7, 130.2, 129.3, 128.9, 128.4, 125.9, 124.2, 124.0, 123.9, 123.2, 122.8, 122.1, 121.4, 120.2, 115.7, 113.8. The spectral data were in accordance with the literature.[2]

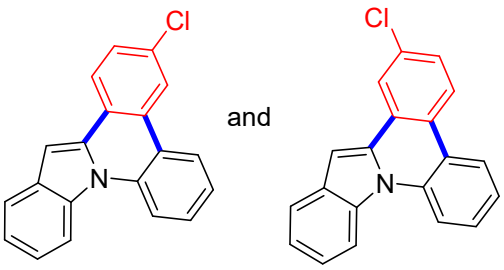


3-methoxyindolo[1,2-*f*]phenanthridine and 2-methoxyindolo[1,2-*f*]phenanthridine (3r: 3r' = 4: 1): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a pale green solid, isolated yield 67% (40 mg), mp: 143-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, J = 8.31 Hz, 1.25H), 8.28-8.23 (m, 1.25H), 8.06-8.02 (m, 1.25H), 7.92 (d, J = 9.02 Hz, 0.25H), 8.83 (d, J =

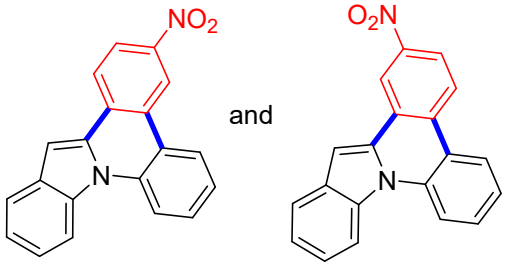
8.78 Hz, 1H), 7.77-7.70 (m, 1.25H), 7.46-7.41 (m, 2H), 7.40-7.38 (m, 0.25H), 7.35-7.32 (m, 0.25H), 7.32-7.26 (m, 2.5H), 7.21-7.17 (m, 1.25H), 7.07 (s, 0.25H), 6.95 (s, 1H), 6.93-6.89 (m, 1.25H), 3.81 (s, 0.75H), 3.81 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.3, 159.3, 136.1, 135.3, 135.0, 134.9, 133.9, 133.6, 130.6, 130.2, 128.7, 128.1, 127.4, 127.1, 125.6, 124.0, 123.8, 123.2, 122.9, 122.7, 122.0, 121.9, 121.7, 121.6, 121.3, 120.9, 120.6, 120.2, 119.6, 116.2, 116.1, 116.0, 115.9, 114.2, 114.1, 106.2, 105.5, 96.1, 94.5, 55.3, 55.3. The spectral data were in accordance with the literature.[2]



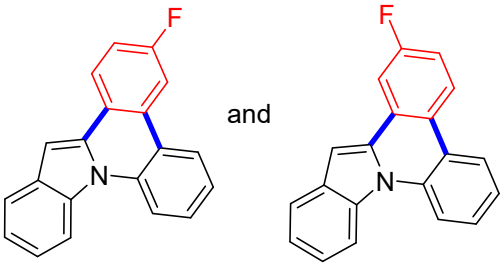
3-methylindolo[1,2-*f*]phenanthridine and 2-methylindolo[1,2-*f*]phenanthridine (3s: 3s' = 5: 3): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale green solid, isolated yield 76% (43 mg), mp: 113-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, J = 8.43 Hz, 1.6H), 8.25-8.22 (m, 1.6H), 8.13 (dd, J = 8.00, 1.14 Hz, 0.6H), 8.10 (dd, J = 8.00, 1.14 Hz, 1H), 7.91 (d, J = 8.29 Hz, 1H), 7.84-7.82 (m, 1H), 7.75 (s, 1H), 7.73-7.69 (m, 1.6H), 7.43-7.38 (m, 1.6H), 7.29-7.22 (m, 3.2H), 7.20-7.16 (m, 1.6H), 7.14-7.09 (m, 3.4H), 2.36 (s, 1.8H), 2.34 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 138.0, 137.5, 136.0, 135.6, 135.4, 135.3, 133.9, 133.7, 130.4, 130.3, 129.54, 129.1, 128.5, 128.1, 126.7, 125.9, 124.3, 124.1, 124.0, 123.8, 123.6, 123.6, 122.9, 122.8, 122.4, 122.3, 122.2, 122.0, 121.8, 121.7, 121.6, 120.9, 120.8, 116.2, 116.2, 114.2, 114.1, 95.9, 95.4, 21.8, 21.4. The spectral data were in accordance with the literature.[2]



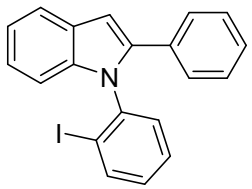
3-chloroindolo[1,2-*f*]phenanthridine and 2-chloroindolo[1,2-*f*]phenanthridine (3t: 3t' = 5: 2): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale green solid, isolated yield 54% (33 mg), mp: 126-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 8.43 Hz, 1.4H), 8.38 (d, J = 8.43 Hz, 1.4H), 8.27-8.23 (m, 1.4H), 8.18 (d, J = 1.98 Hz, 0.4H), 8.15 (d, J = 8.68 Hz, 1H), 8.09 (d, J = 2.23 Hz, 1H), 8.05 (d, J = 8.43 Hz, 0.4H), 7.86-7.83 (m, 1.4H), 7.64-7.58 (m, 1.4H), 7.46-7.44 (m, 1H), 7.42-7.40 (m, 1.4H), 7.39-7.38 (m, 1H), 7.37 (s, 1.4H), 7.35 (s, 0.4H), 7.26 (s, 1.4H), 7.24 (s, 0.4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.2, 135.9, 134.4, 134.1, 134.0, 133.9, 133.8, 130.3, 130.1, 129.5, 129.1, 128.4, 128.4, 128.0, 127.6, 125.6, 125.3, 124.6, 124.2, 124.1, 124.0, 123.7, 123.3, 122.6, 122.4, 122.4, 122.0, 121.4, 121.3, 121.2, 121.0, 116.4, 114.2, 114.2, 97.1, 96.6. HRMS (ESI) m/z calcd for $C_{20}H_{13}ClN^+$ $(M+H)^+$ 302.0731, found 302.0734.



3-nitroindolo[1,2-*f*]phenanthridine and 2-nitroindolo[1,2-*f*]phenanthridine (3u: 3u' = 2: 1): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a pale yellow solid, isolated yield 39% (24 mg), mp: 154-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, J = 2.01 Hz, 0.5H), 8.73 (s, 1H), 8.44 (d, J = 8.22 Hz, 1.5H), 8.30 (t, J = 8.59 Hz, 1.5H), 8.23-8.21 (m, 0.5H), 8.17 (td, J = 8.04, 1.10 Hz, 1.5H), 8.12 (d, J = 2.01 Hz, 2H), 8.01 (d, J = 8.77 Hz, 0.5H), 7.86-7.82 (m, 1.5H), 7.66-7.59 (m, 1.5H), 7.49-7.39 (m, 3H), 7.38-7.33 (m, 1.5H), 7.29 (s, 0.5H), 7.23 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.0, 146.6, 136.7, 136.0, 134.3, 133.8, 133.1, 132.9, 131.7, 130.9, 130.8, 130.1, 129.9, 127.2, 126.6, 125.0, 124.6, 124.3, 123.7, 123.6, 123.4, 123.4, 123.2, 122.4, 122.4, 121.8, 121.6, 121.5, 120.4, 120.2, 119.3, 118.2, 116.4, 116.3, 114.3, 114.2, 99.7, 98.2. HRMS (ESI) m/z calcd for $C_{20}H_{13}N_2O_2^+$ $(M+H)^+$ 313.0972, found 313.0975.

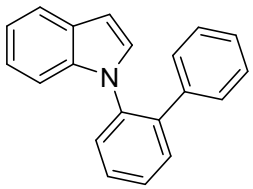


3-fluoroindolo[1,2-*f*]phenanthridine and 2-fluoroindolo[1,2-*f*]phenanthridine (3v: 3v' = 100: 33): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a pale yellow solid, isolated yield 65% (37 mg), mp: 144-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 8.36 Hz, 1.33H), 8.30-8.26 (m, 1.33H), 8.09 (dd, J = 8.06 Hz, 1.19 Hz, 0.33H), 8.05-8.02 (m, 1.33H), 7.94 (dd, J = 8.86, 5.77 Hz, 1H), 7.81-7.77 (m, 1.33H), 7.70 (dd, J = 10.75 Hz, 2.59 Hz, 1H), 7.62 (dd, J = 9.56 Hz, 2.69 Hz, 0.33H), 7.54-7.47 (m, 1.33H), 7.41-7.33 (m, 2.66H), 7.29-7.24 (m, 1.33H), 7.13-7.09 (m, 1.33H), 7.09-7.05 (m, 1.33H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.6, 161.2 (d, J = 2.92 Hz), 136.0, 135.3, 134.4, 134.0 (d, J = 3.82 Hz), 133.9, 133.6, 130.3, 130.0, 129.2, 128.7 (d, J = 8.11 Hz), 128.4, 127.7 (d, J = 9.07 Hz), 126.1 (d, J = 8.59 Hz), 124.6 (d, J = 9.07 Hz), 124.0, 123.6, 123.0, 122.9, 122.4 (d, J = 2.80 Hz), 121.9, 121.8 (d, J = 2.03 Hz), 121.3, 121.2, 121.1 (d, J = 2.92 Hz), 120.9, 116.2, 116.1, 115.9, 115.6, 115.4, 114.2, 114.1, 109.6, 109.4, 108.4, 108.2, 97.0, 95.8 (d, J = 1.9 Hz). HRMS (ESI) m/z calcd for $C_{20}H_{13}FN^+$ $(M+H)^+$ 286.1027, found 286.1030.



1-(2-iodophenyl)-2-phenyl-1*H*-indole (4): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale yellow solid, isolated yield 70% (55 mg), mp: 163-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.99 Hz, 1.02 Hz, 1H), 7.82-7.80 (m, 1H), 7.47 (td, J = 7.70 Hz, 1.02 Hz, 1H), 7.41 (dd, J = 7.99 Hz, 1.89 Hz, 2H), 7.36-7.32 (m, 4H), 7.31-7.27 (m, 2H), 7.20 (td, J = 7.84 Hz, 1.45 Hz, 1H), 7.06-7.03 (m, 1H), 6.94 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.5, 140.8, 140.0, 138.5, 132.3, 130.8, 129.8, 129.2, 128.7, 128.2, 127.4, 122.3,

120.8, 120.5, 111.1, 103.4, 99.9. HRMS (ESI) m/z $(M+H)^+$ calcd for $C_{20}H_{15}IN^+$ 396.0244, found 396.0247.



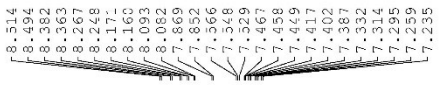
1-([1,1'-biphenyl]-2-yl)-1*H*-indole (5): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale yellow solid, isolated yield 55% (30 mg), mp: 186-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.61 (m, 2H), 7.57-7.51 (m, 3H), 7.32-7.30 (m, 1H), 7.20-7.13 (m, 5H), 7.07-7.04 (m, 2H), 6.86 (d, J = 3.14 Hz, 1H), 6.50 (d, J = 3.27 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.9, 138.5, 136.8, 136.7, 131.5, 129.1, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.3, 121.9, 120.7, 119.9, 110.5, 102.7. HRMS (ESI) m/z $(M+H)^+$ calcd for $C_{20}H_{16}N^+$ 270.1277, found 270.1280.

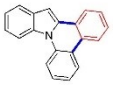
6) References

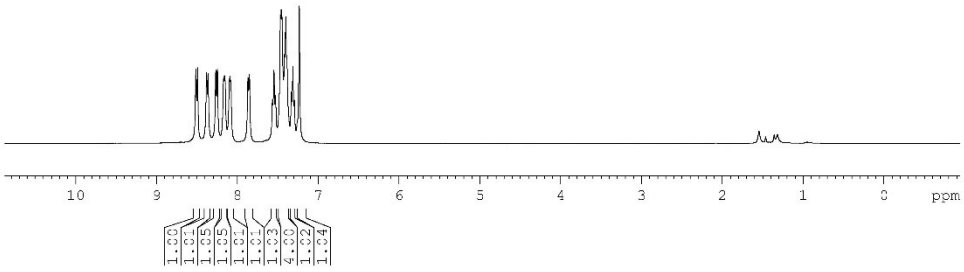
1. Wang, Z.; Yuan, Y.; Jin, S.; Wang, Y.; Gu, Y.; Wang, C.; Li, Y., Copper-catalyzed synthesis of benzo[4,5]thiazolo[3,2-a]indoles from elemental sulfur and 1-(2-iodophenyl)-1*H*-indoles. New J. Chem. 2023, 47, 1055-1058.
2. Liu, X.; Ban, Y.-L.; Liu, Y.; Zhuang, M.; Zhou, Y. Palladium-catalyzed C–H bond activation and decarboxylation for the assembly of indolo[1,2-*f*] phenanthridine. *Org. Biomol. Chem*., **2024**, *22*, 9188-9191.
3. Ngo, T. N.; Ehlers, P.; Dang, T. T. Villingera, A.; Langer, P. Synthesis of indolo[1,2-*f*]phenanthridines by Pd-catalyzed domino C–N coupling/hydroamination/C–H arylation reactions. *Org. Biomol. Chem*., **2015**, *13*, 3321-3330.

7) Scanned ^{1}H NMR and ^{13}C NMR Spectra of All Compounds.

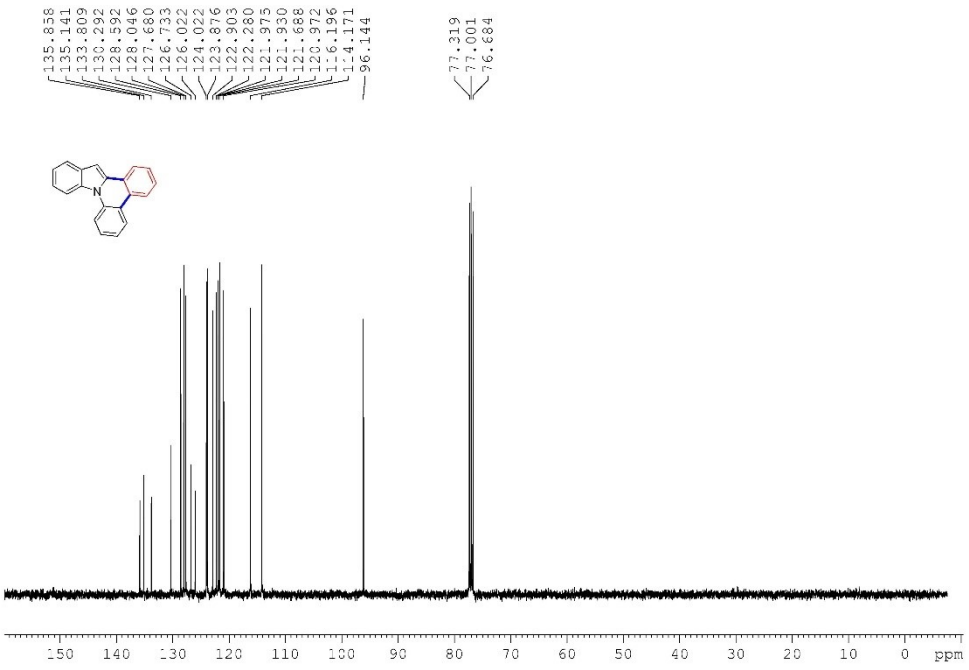
indolo[1,2-*f*]phenanthridine (3a):
^{1}H NMR (400 MHz, $CDCl_3$)



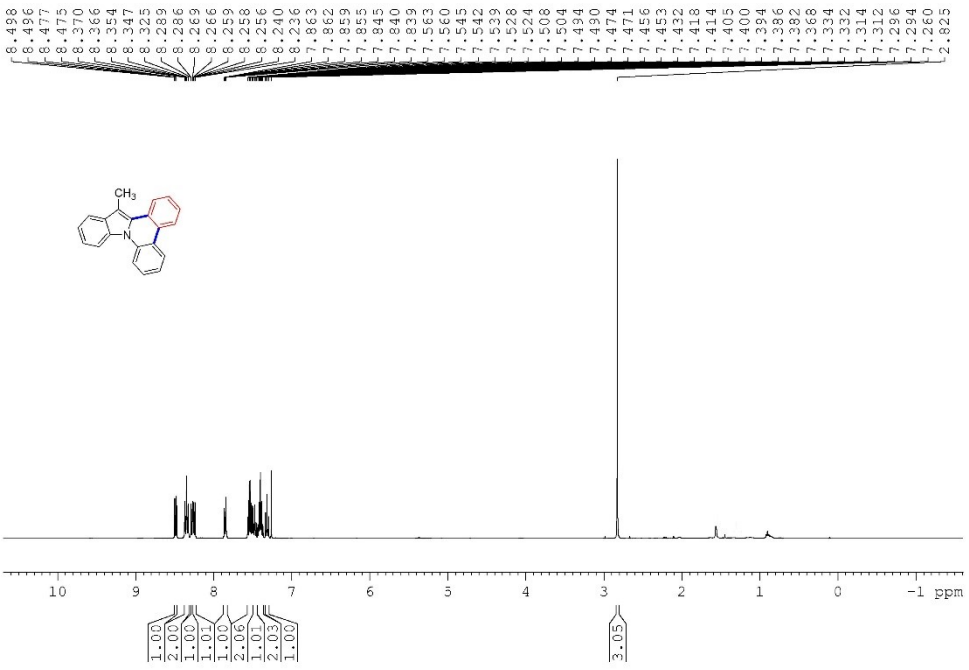




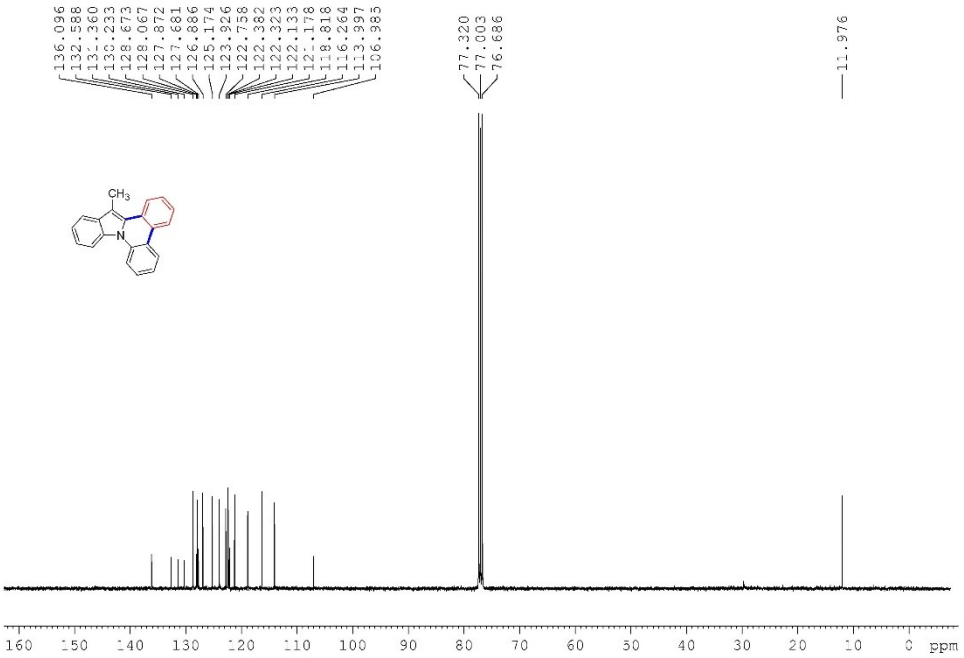
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



14-methylindolo[1,2-*f*]phenanthridine (3b):
^{1}H NMR (400 MHz, $CDCl_3$)

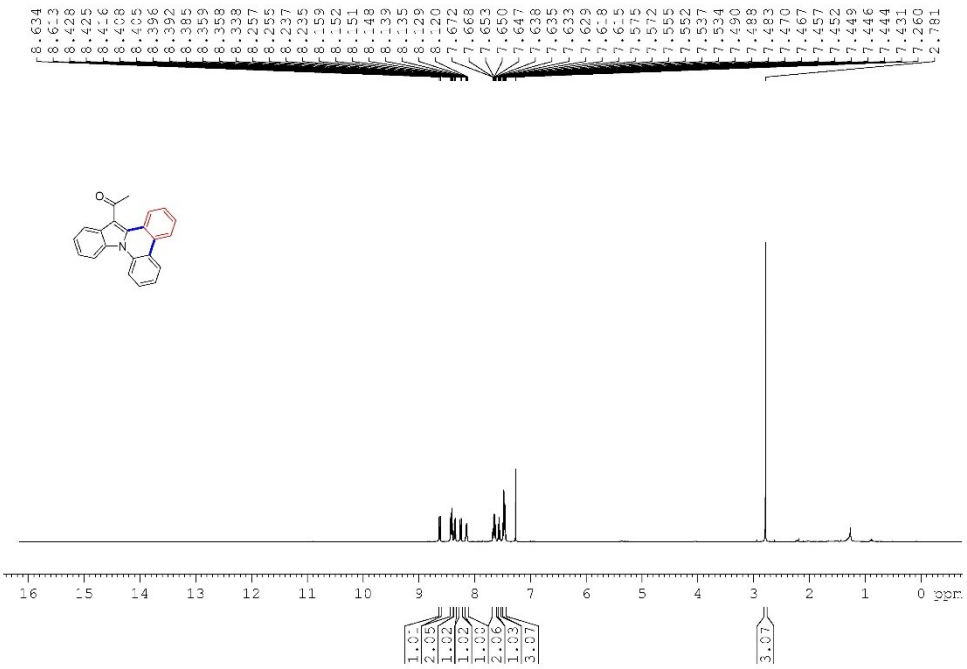


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

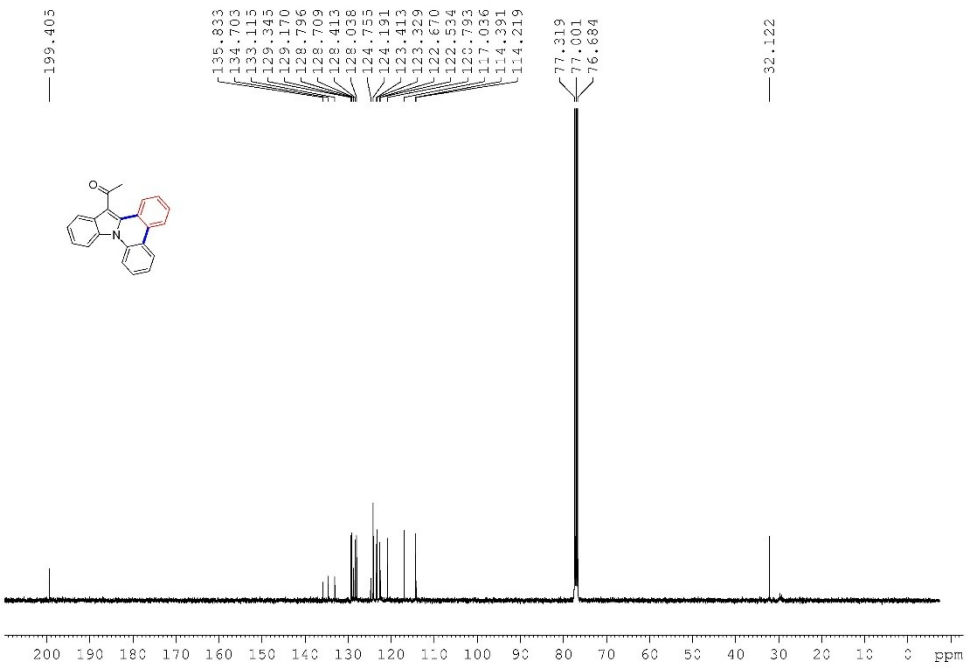


1-(indolo[1,2-*f*]phenanthridin-14-yl)ethan-1-one (3c):

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

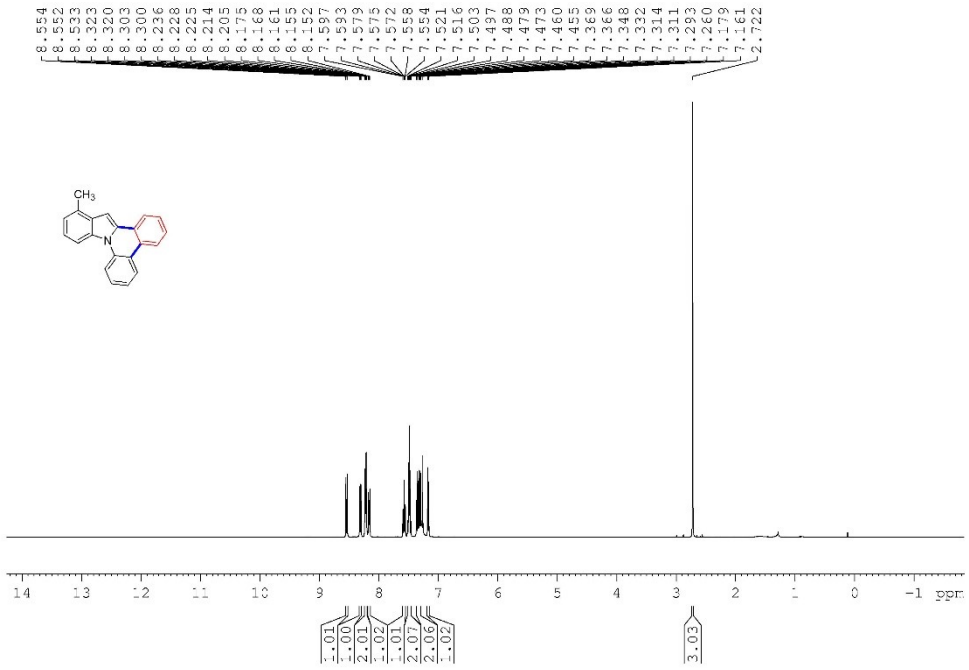


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

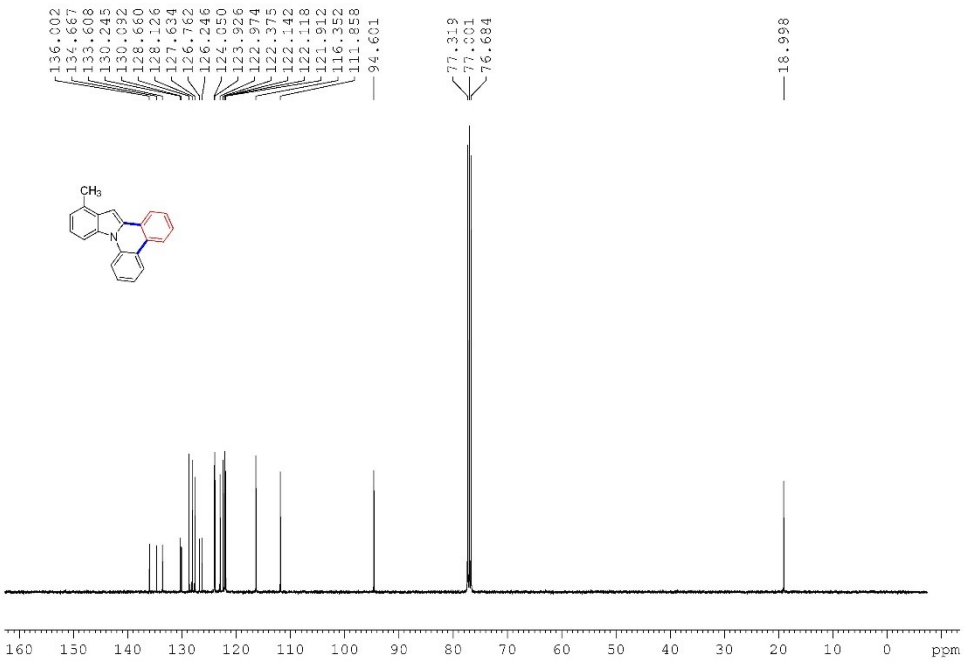


13-methylindolo[1,2-*f*]phenanthridine (3d):

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

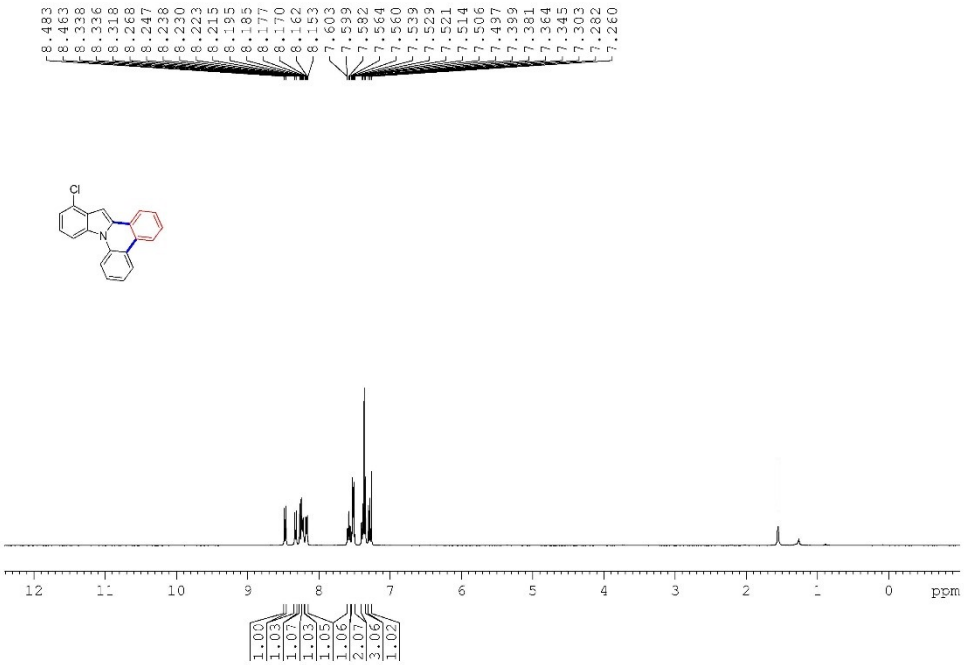


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

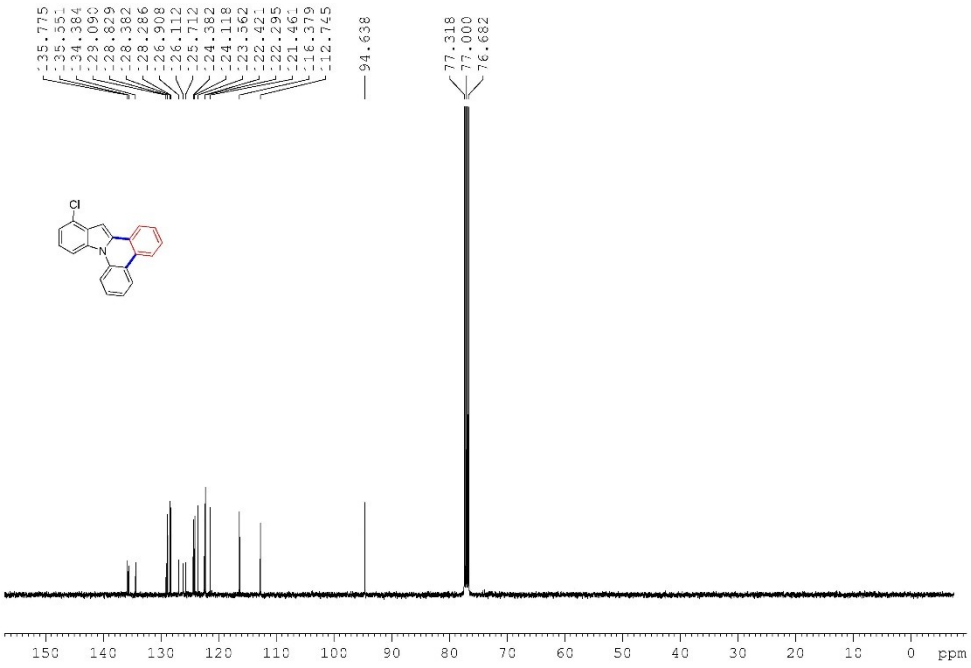


13-chloroindolo[1,2-*f*]phenanthridine (3e):

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

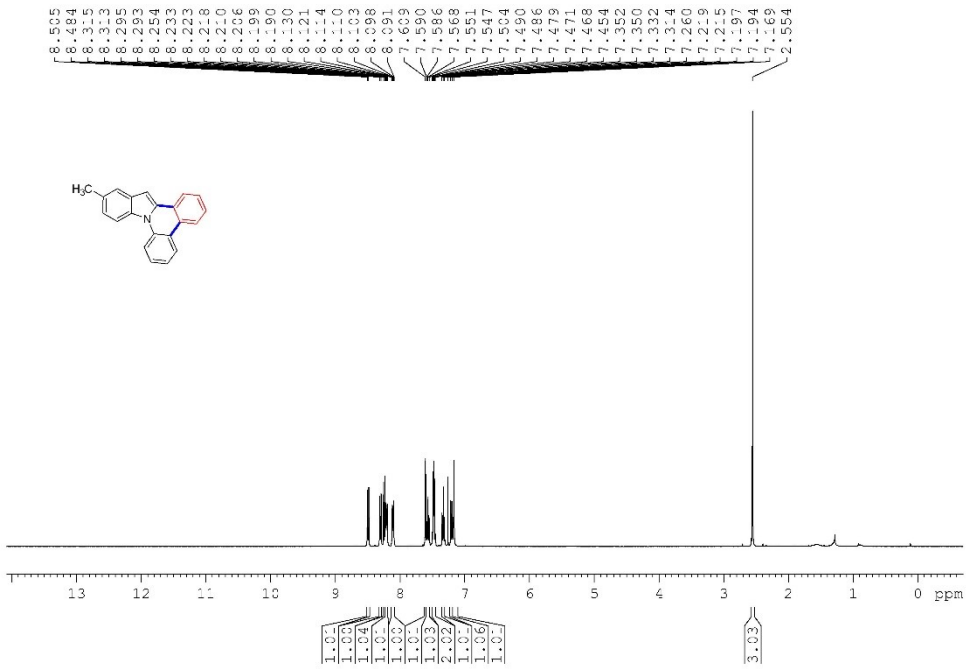


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

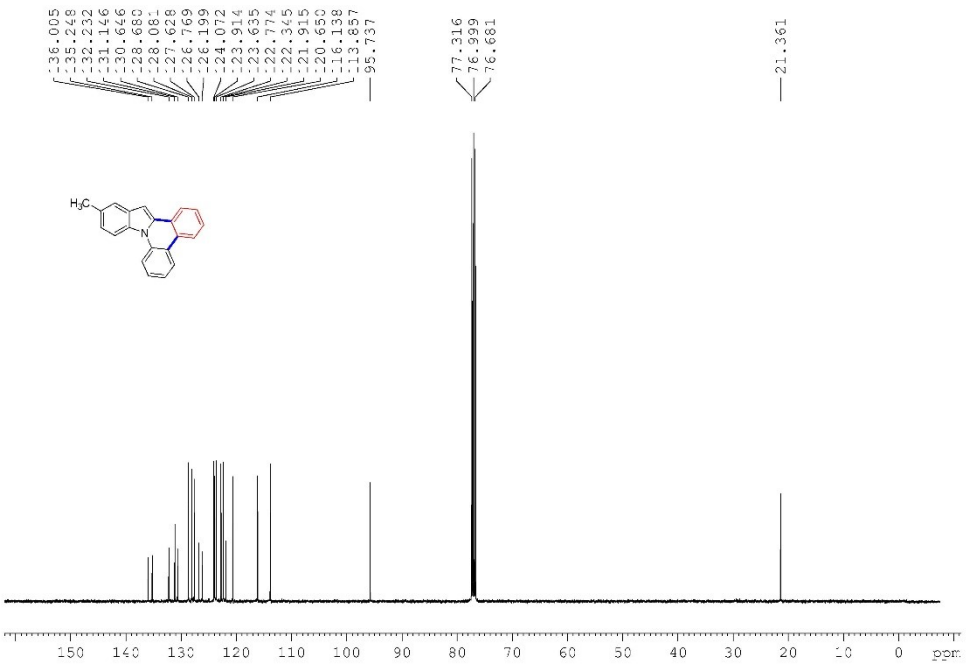


12-methylindolo[1,2-*f*]phenanthridine (3f):

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

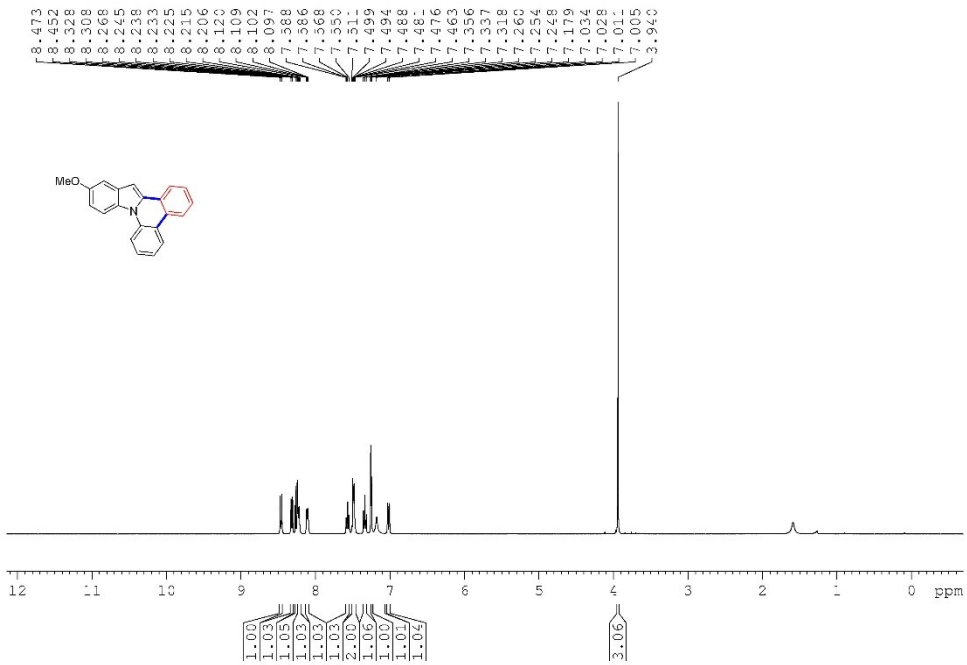


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

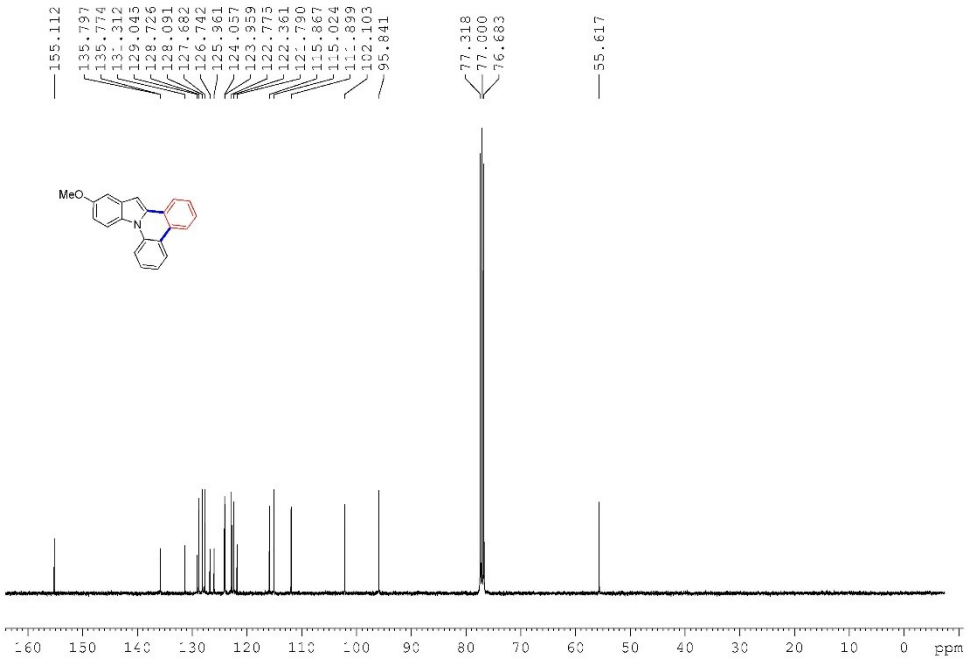


12-methoxyindolo[1,2-*f*]phenanthridine (3g):

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

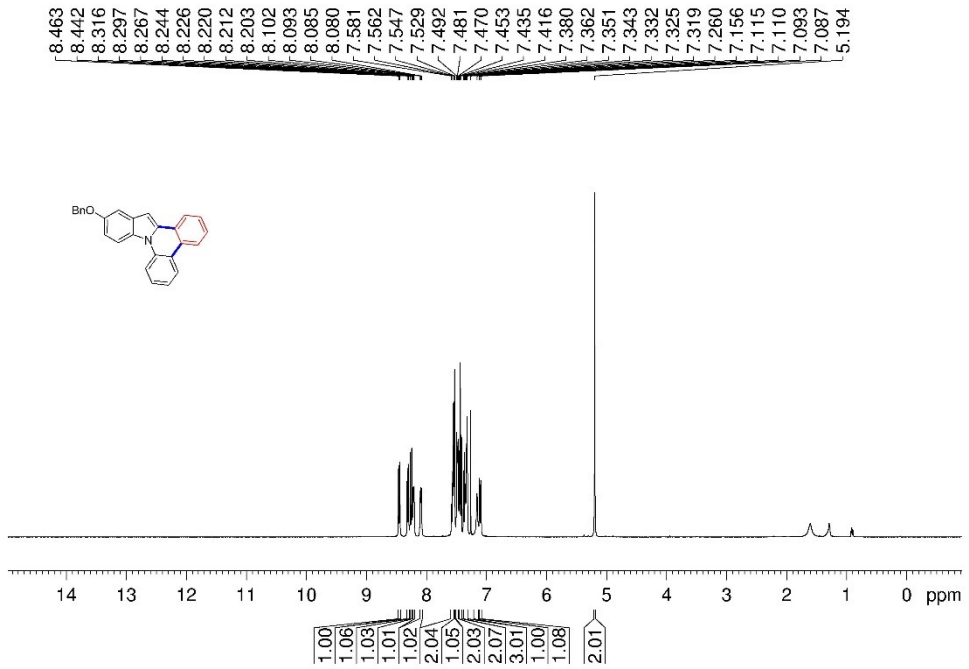


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

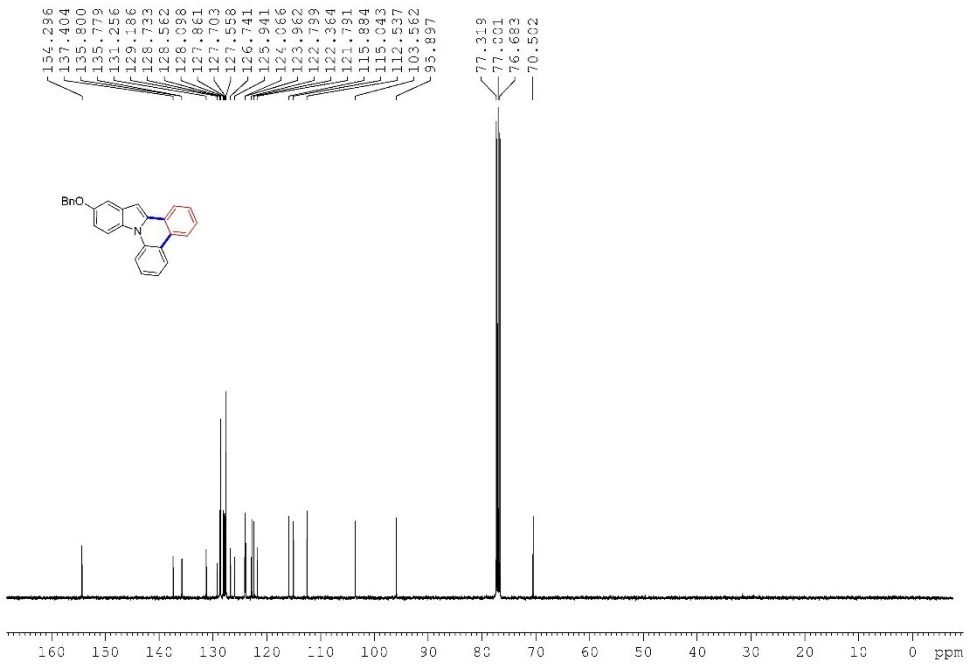


12-(benzyloxy)indolo[1,2-*f*]phenanthridine (3h):

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

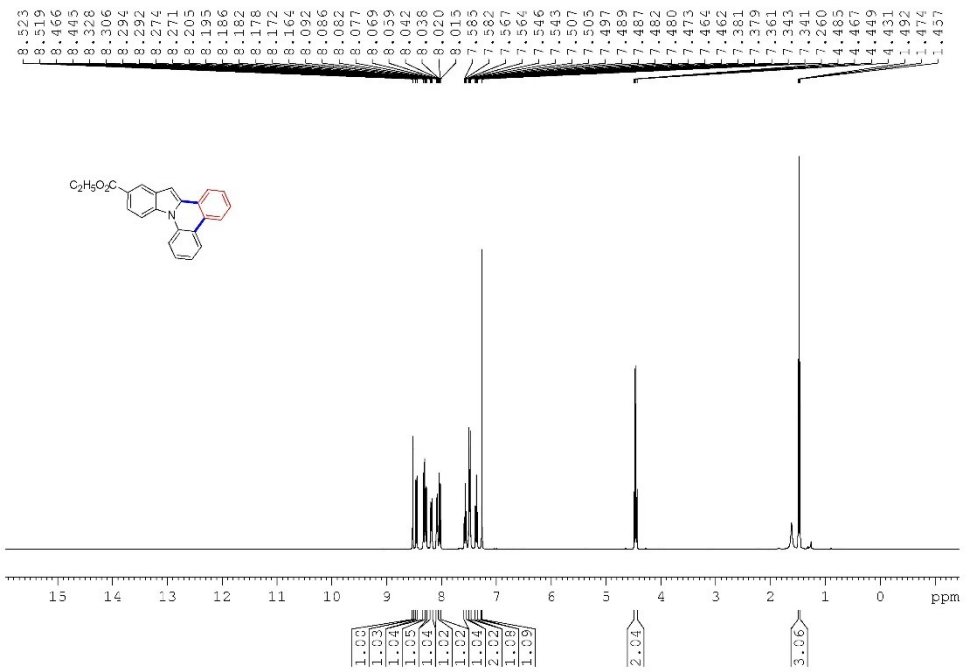


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

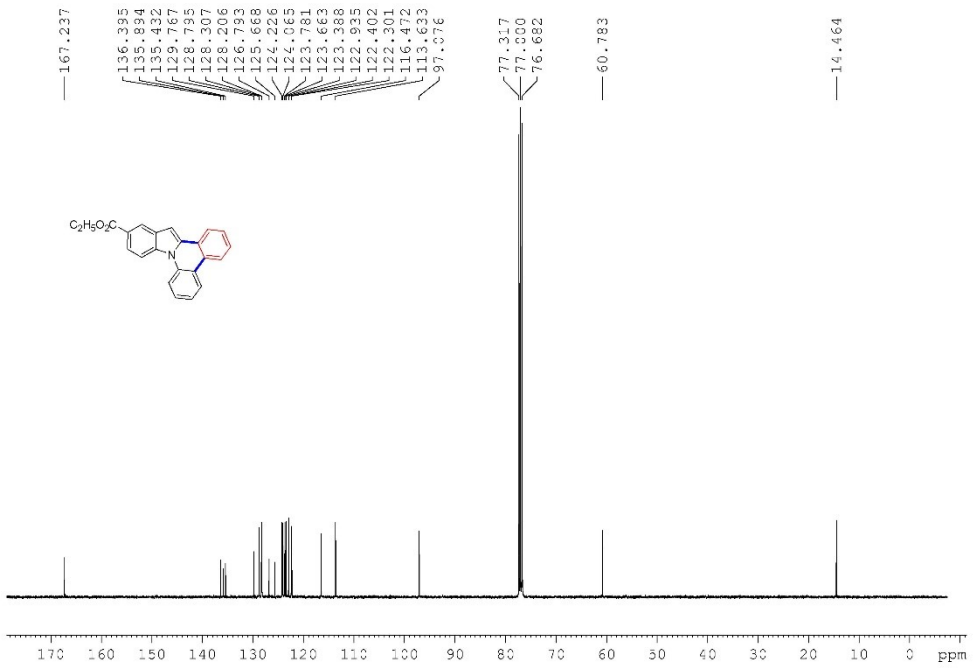


ethyl indolo[1,2-*f*]phenanthridine-12-carboxylate (3i):

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

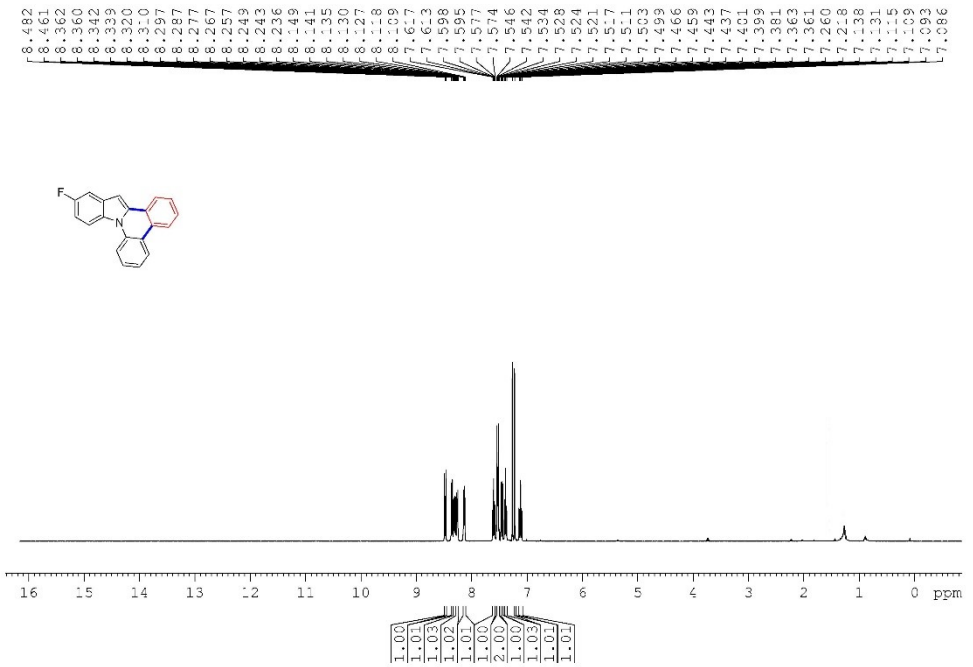


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

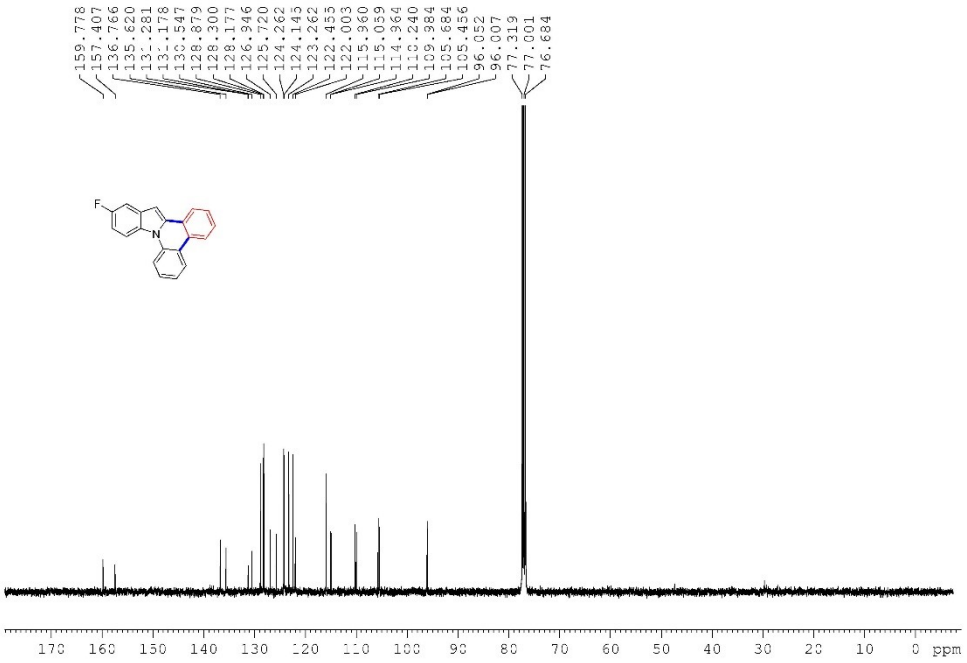


12-fluoroindolo[1,2-*f*]phenanthridine (3j):

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

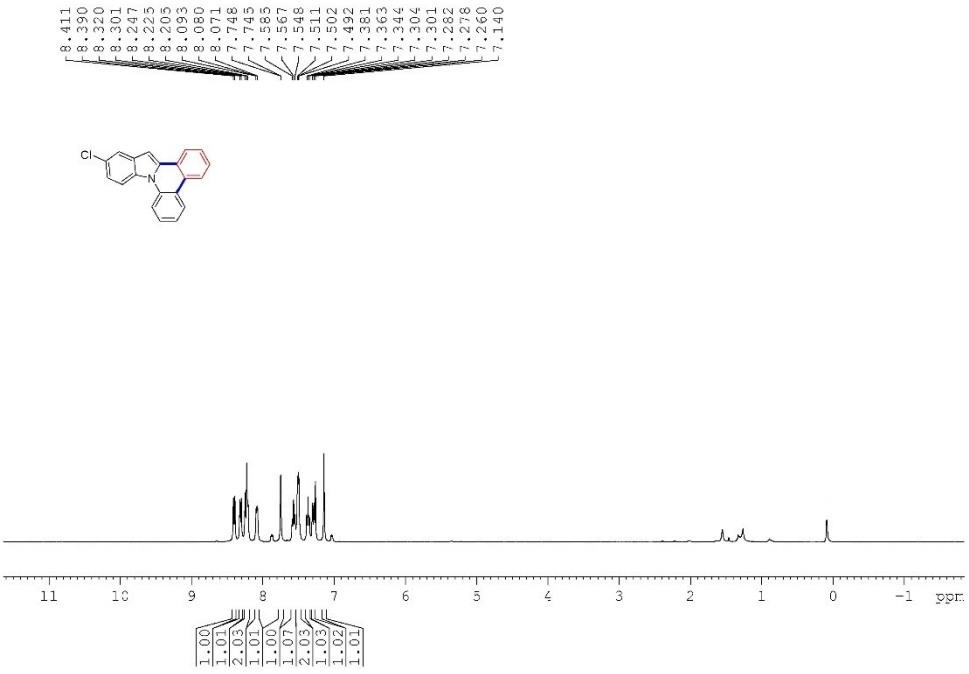


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

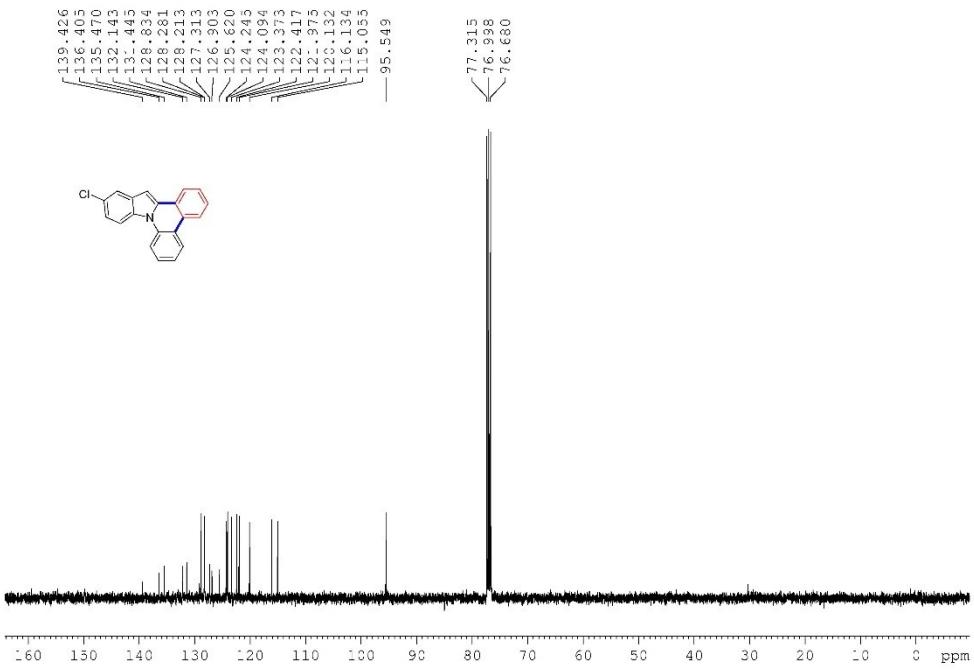


12-chloroindolo[1,2-*f*]phenanthridine (3k):

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

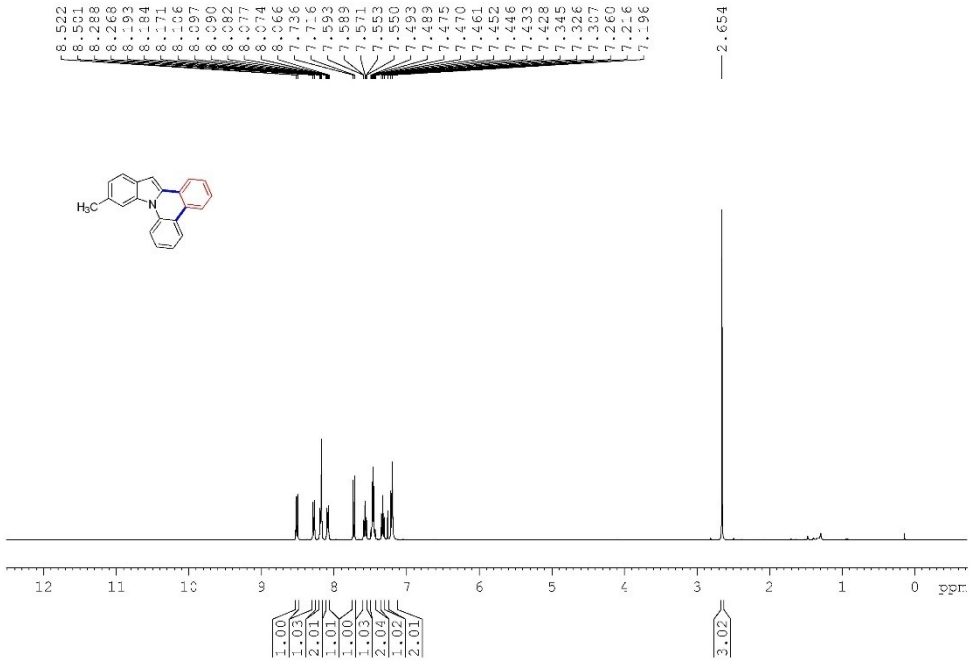


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

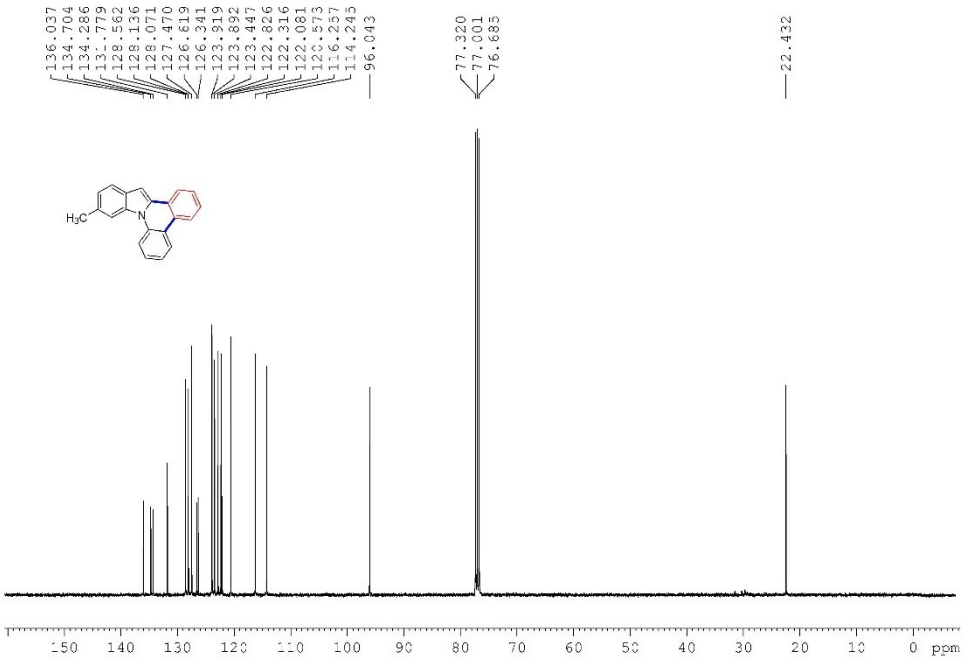


11-methylindolo[1,2-*f*]phenanthridine (3l):

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

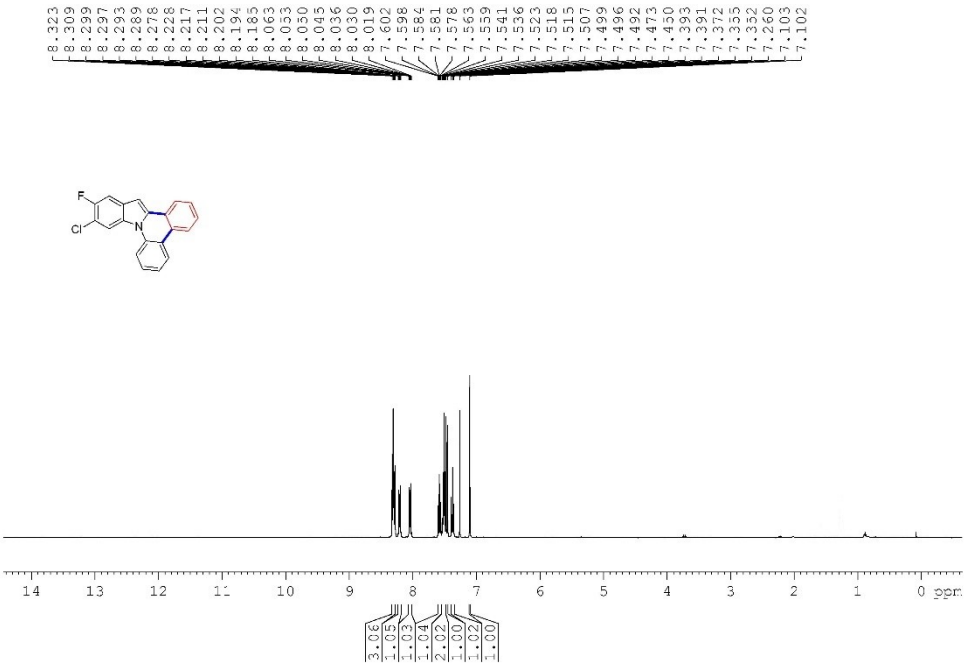


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

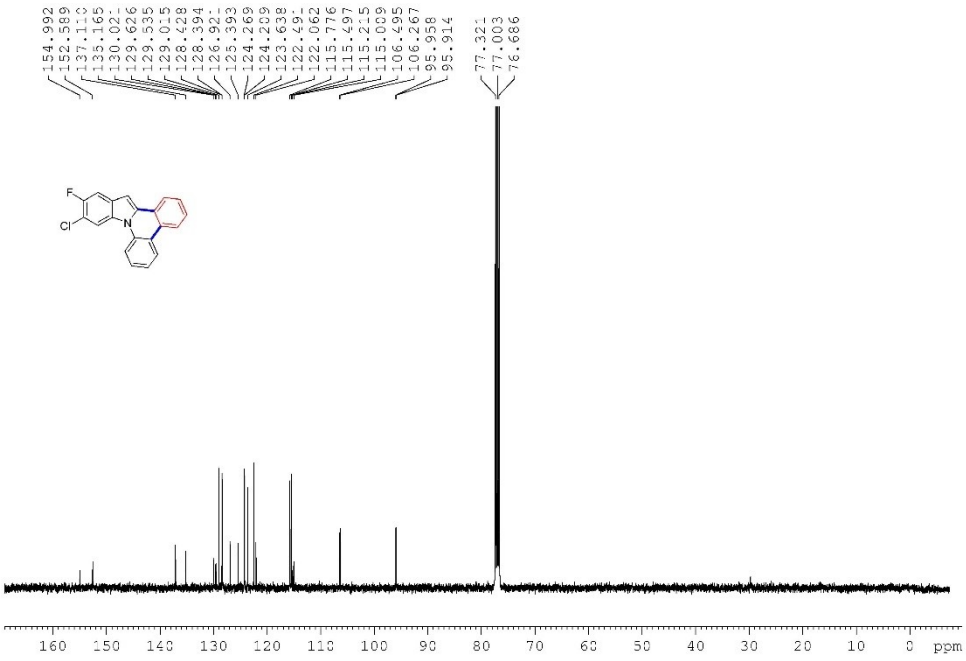


11-chloro-12-fluoroindolo[1,2-*f*]phenanthridine (3m):

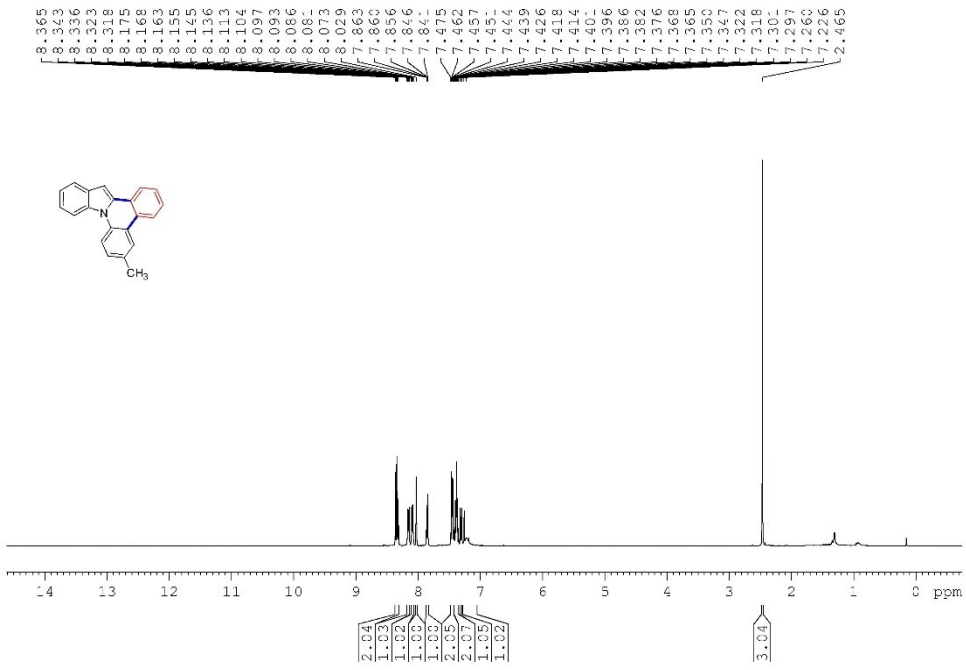
^{1}H NMR (400 MHz, $CDCl_3$)



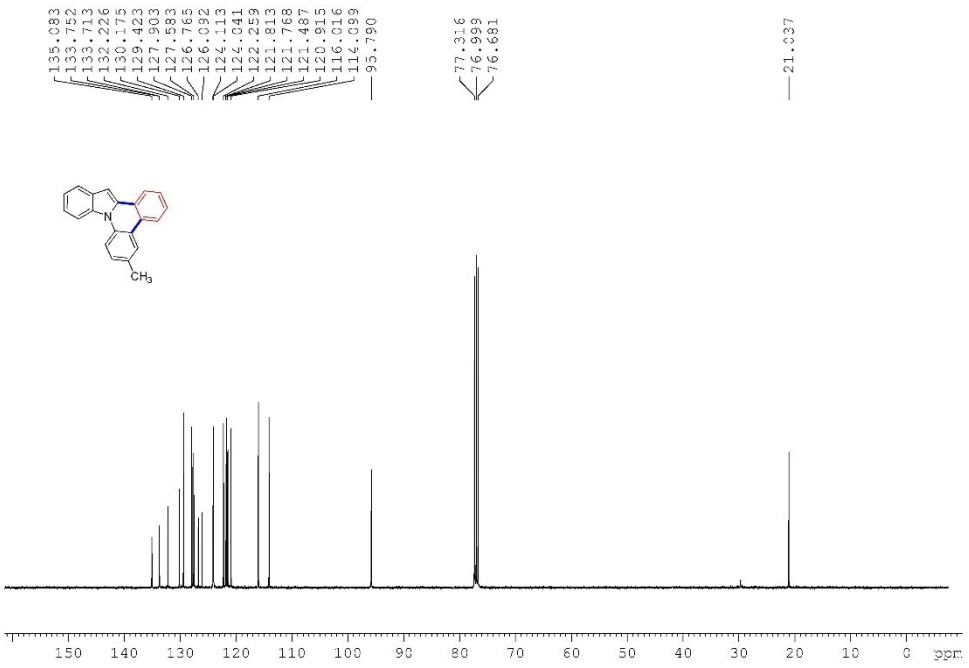
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



6-methylindolo[1,2-*f*]phenanthridine (3n):
^{1}H NMR (400 MHz, $CDCl_3$)

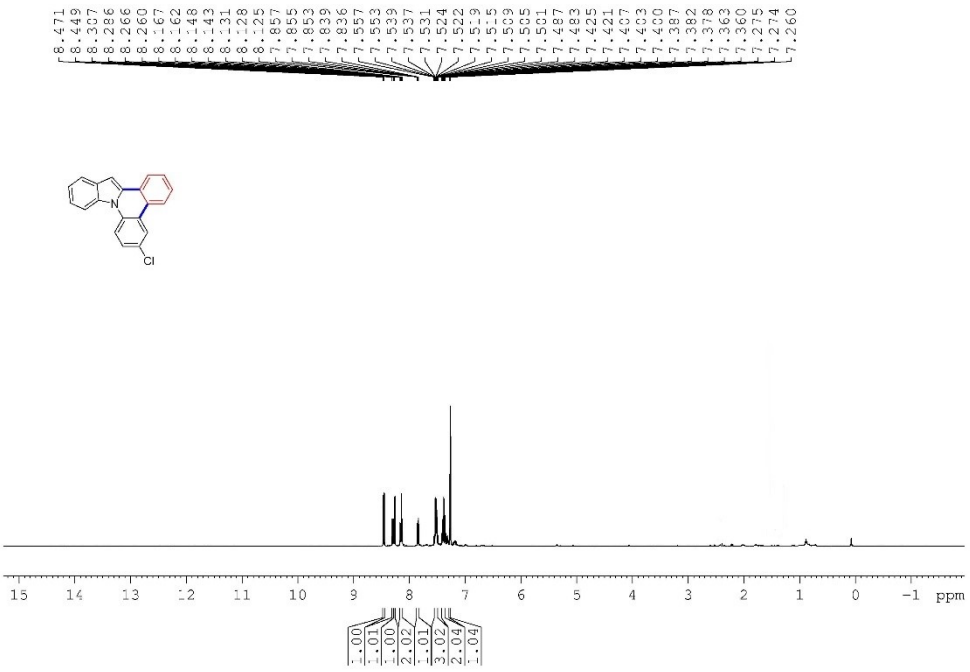


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

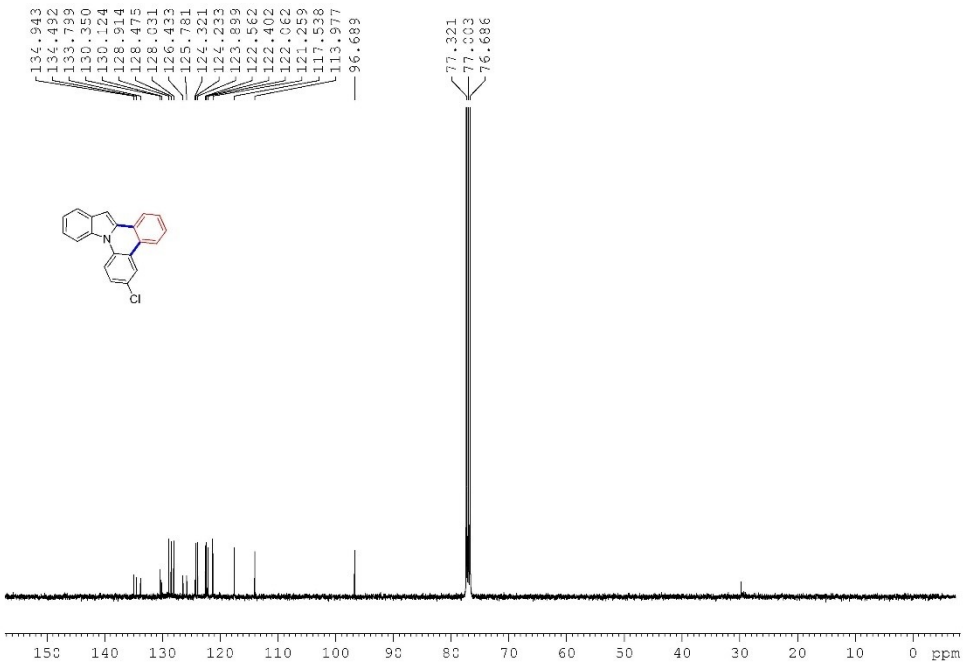


6-chloroindolo[1,2-*f*]phenanthridine (3o):

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

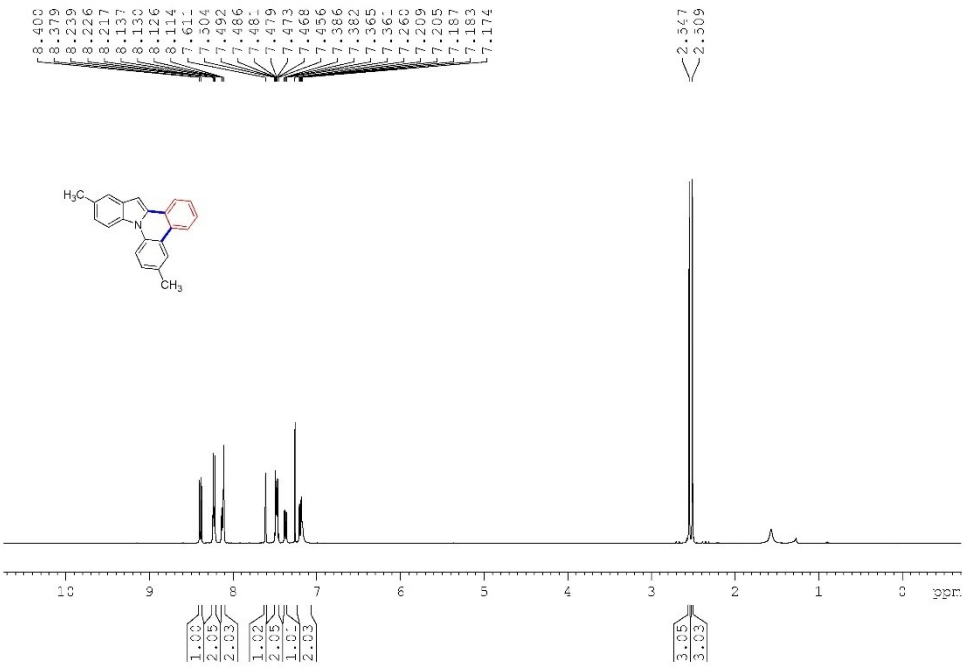


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

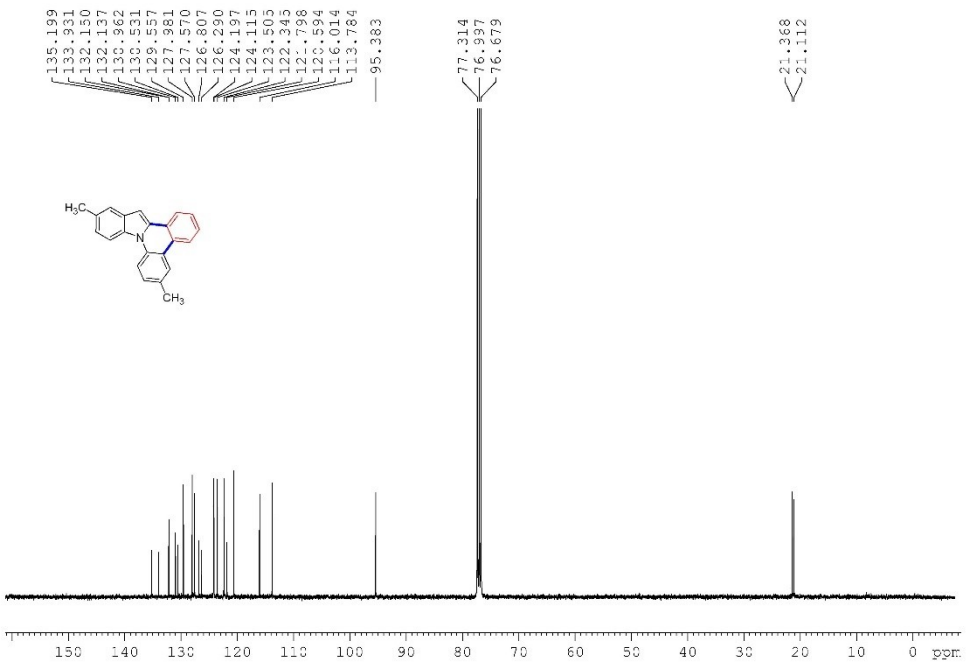


6,12-dimethylindolo[1,2-*f*]phenanthridine (3p):

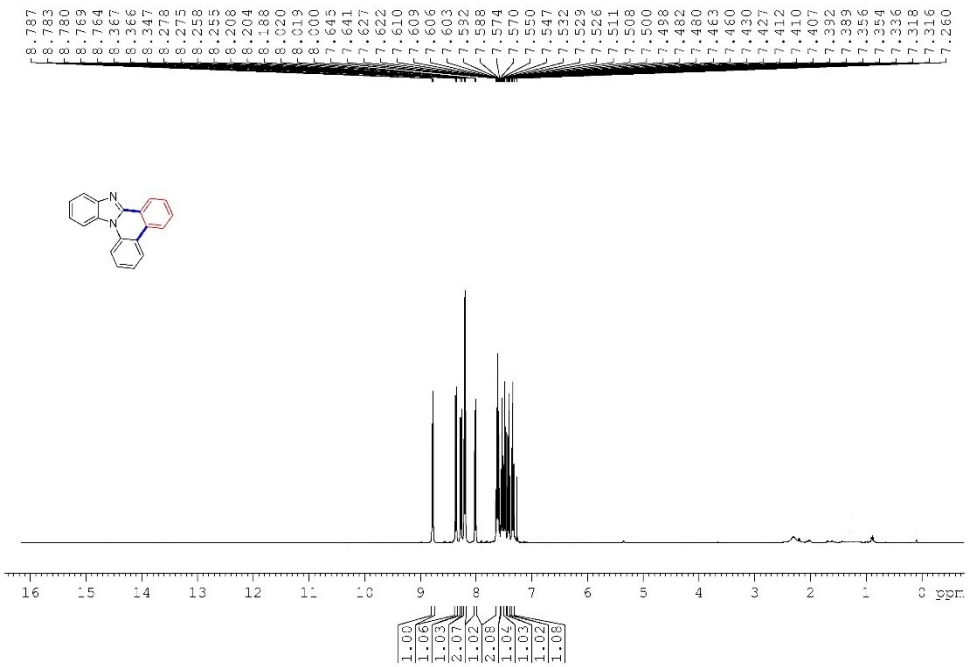
^{1}H NMR (400 MHz, $CDCl_3$)



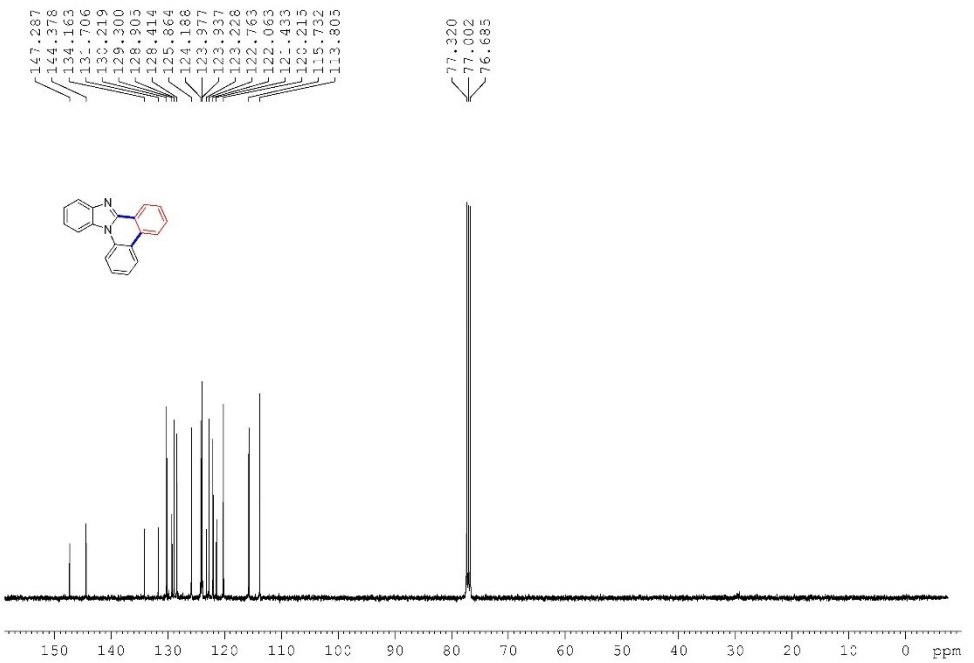
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



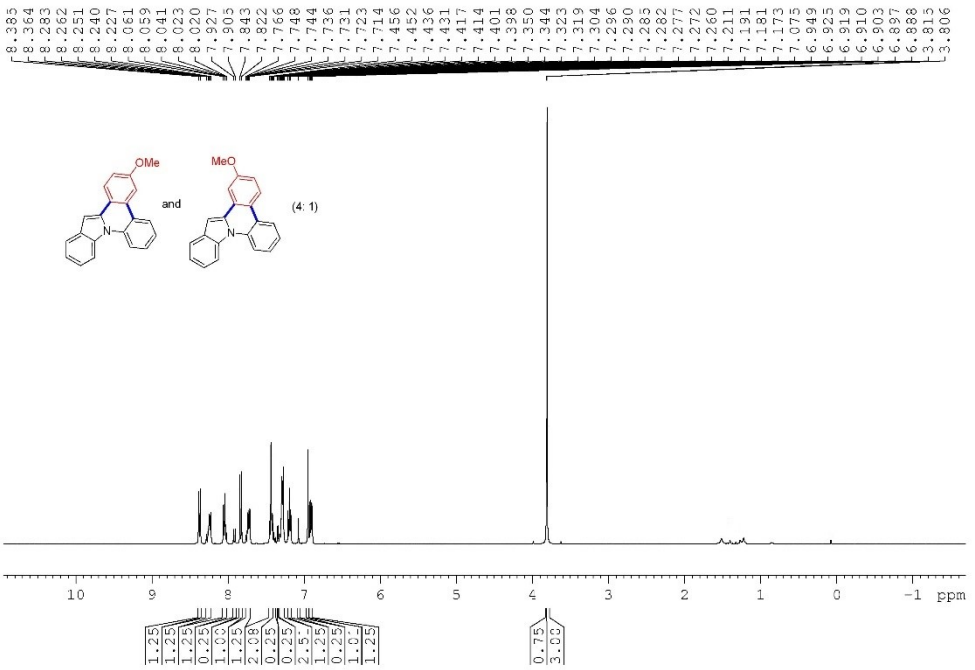
benzo[4,5]imidazo[1,2-*f*]phenanthridine (3q):
^{1}H NMR (400 MHz, $CDCl_3$)



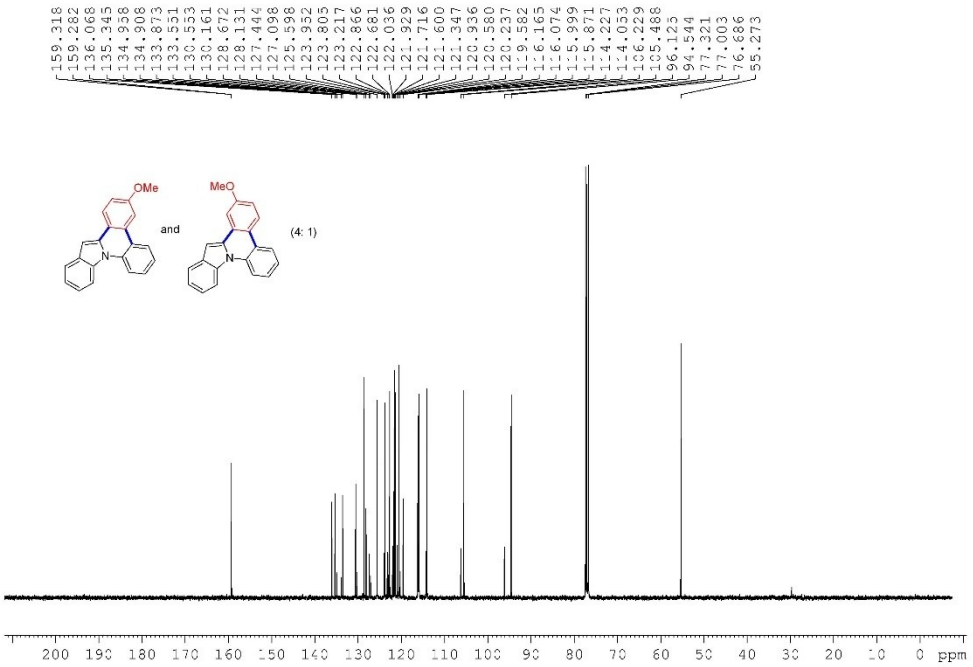
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



3-methoxyindolo[1,2-*f*]phenanthridine and 2-methoxyindolo[1,2-*f*]phenanthridine (3r: 3r' = 4: 1):
^{1}H NMR (400 MHz, $CDCl_3$)

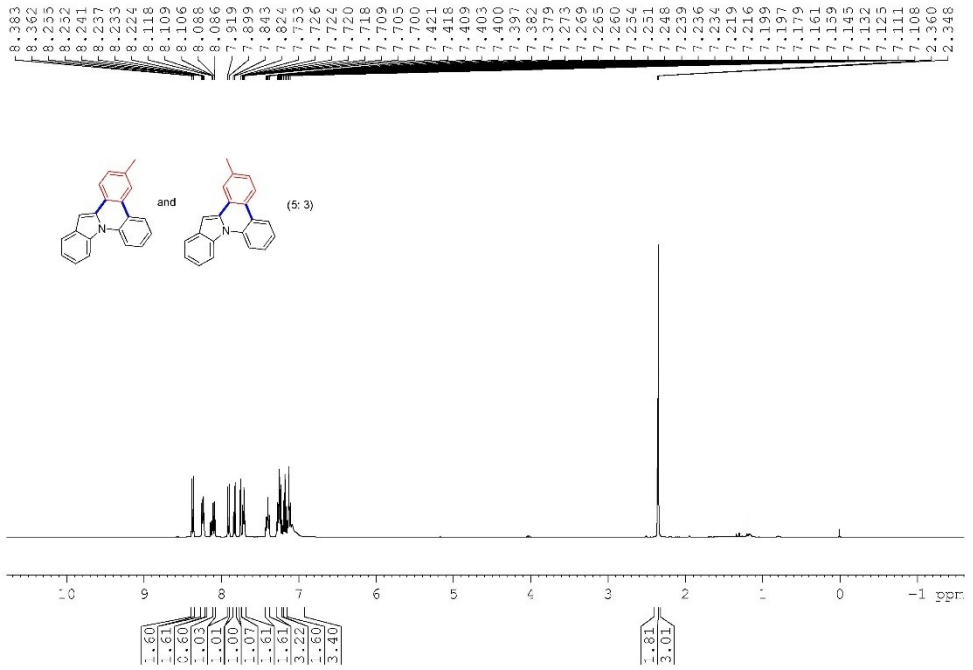


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

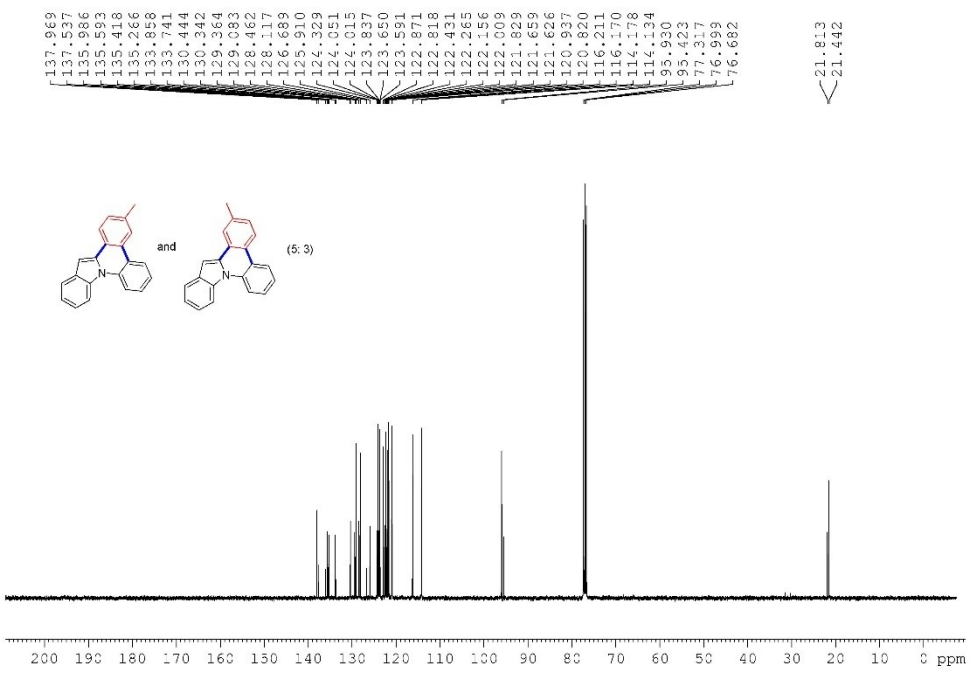


3-methylindolo[1,2-*f*]phenanthridine and 2-methylindolo[1,2-*f*]phenanthridine (3s: 3s' = 5: 3):

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

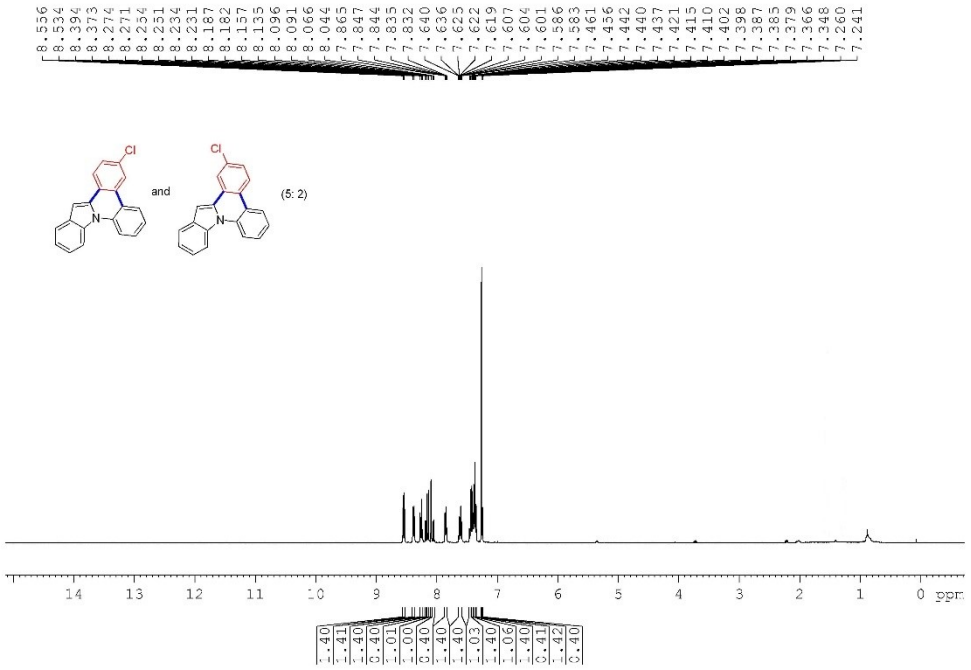


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

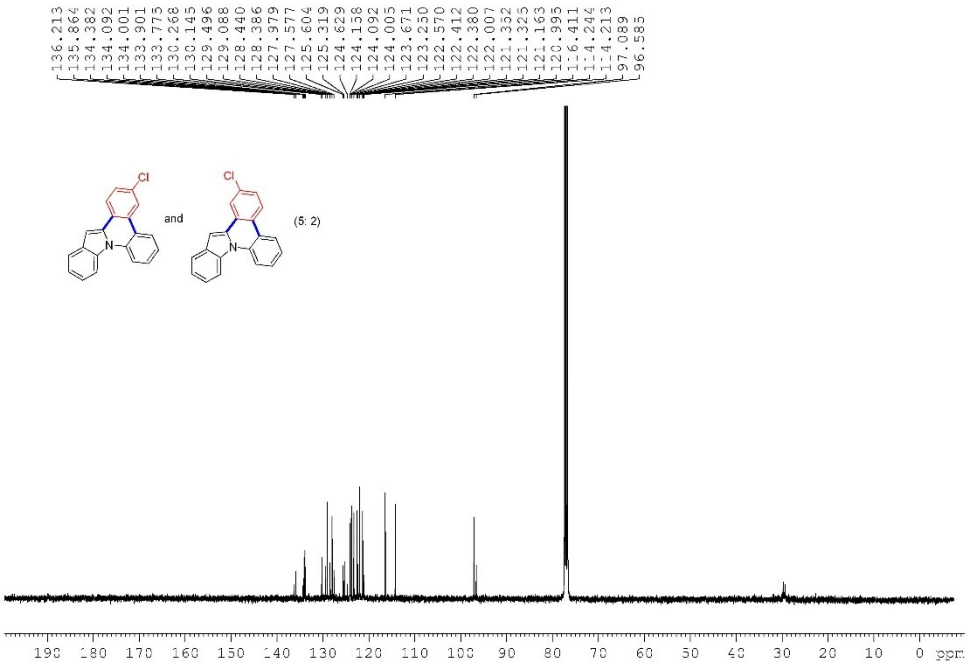


3-chloroindolo[1,2-*f*]phenanthridine and 2-chloroindolo[1,2-*f*]phenanthridine (3t: 3t' = 5: 2):

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

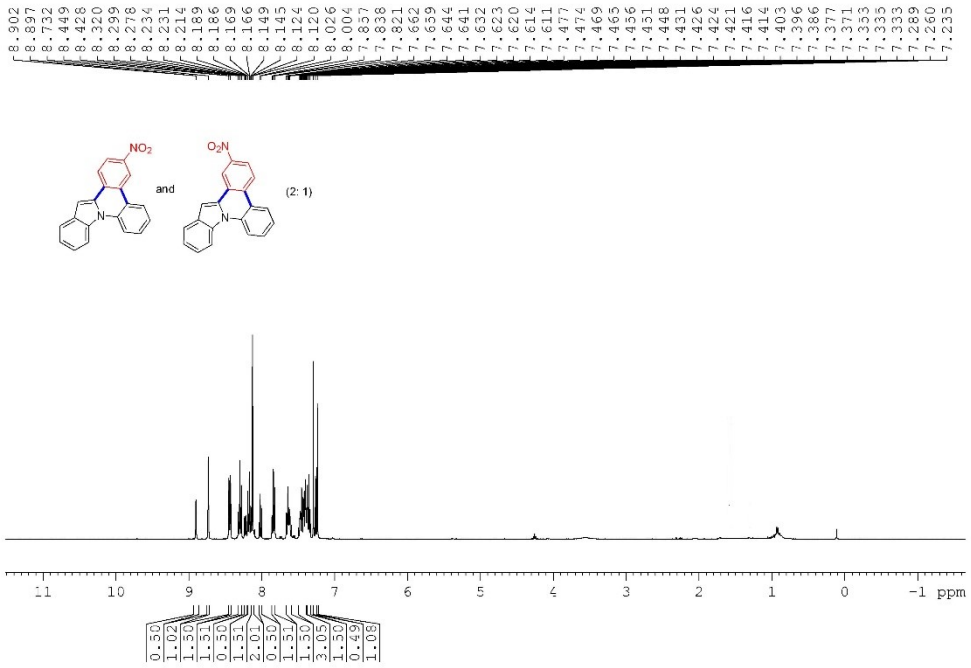


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

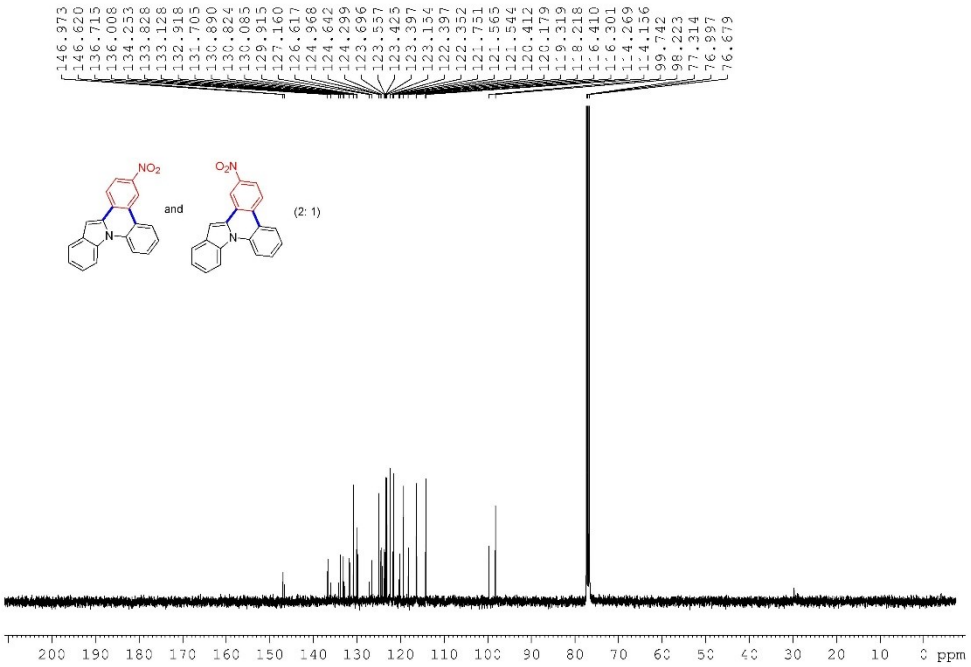


3-nitroindolo[1,2-*f*]phenanthridine and 2-nitroindolo[1,2-*f*]phenanthridine (3u: 3u' = 2: 1):

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

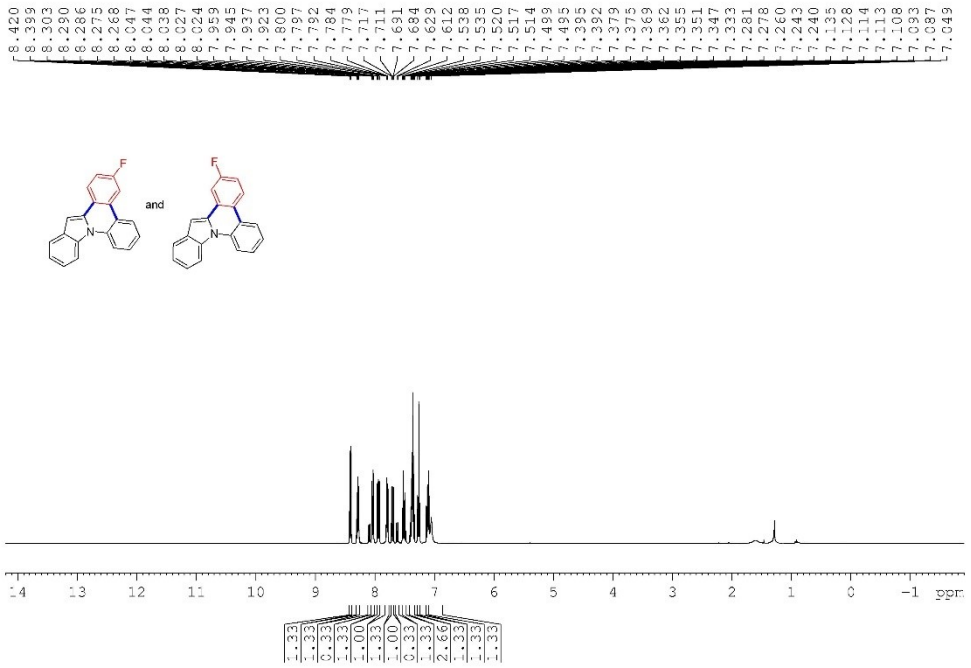


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

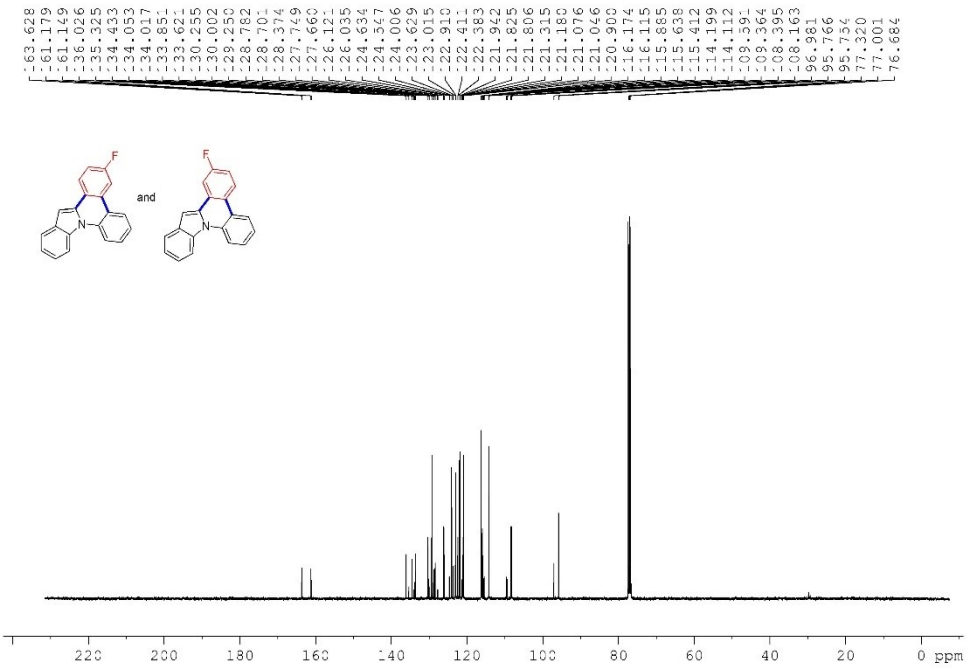


3-fluoroindolo[1,2-*f*]phenanthridine and 2-fluoroindolo[1,2-*f*]phenanthridine (3v: 3v' = 100: 33):

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

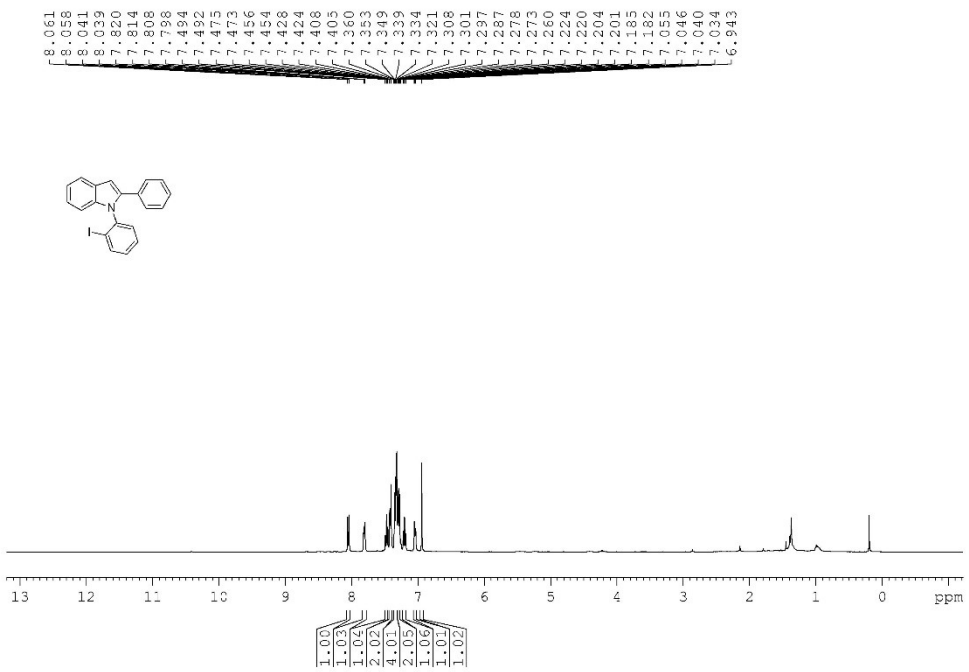


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

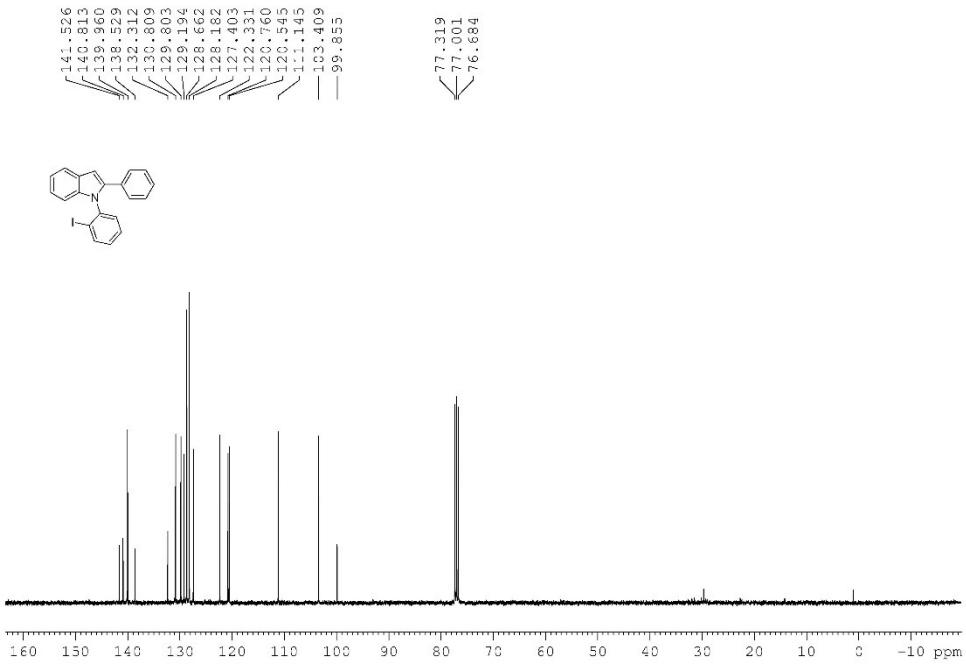


1-(2-iodophenyl)-2-phenyl-1*H*-indole (4):

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

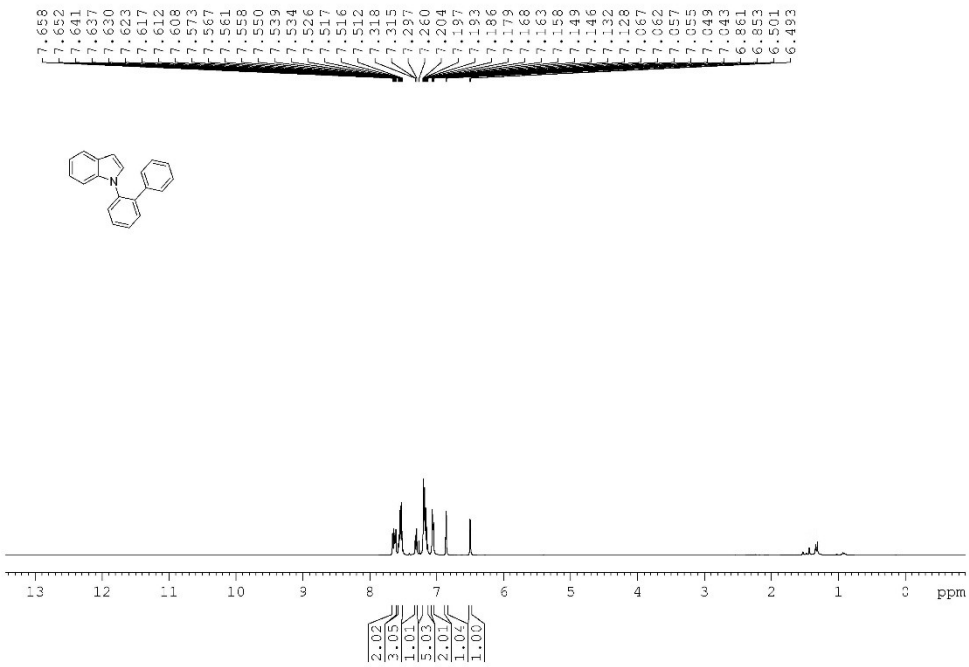


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

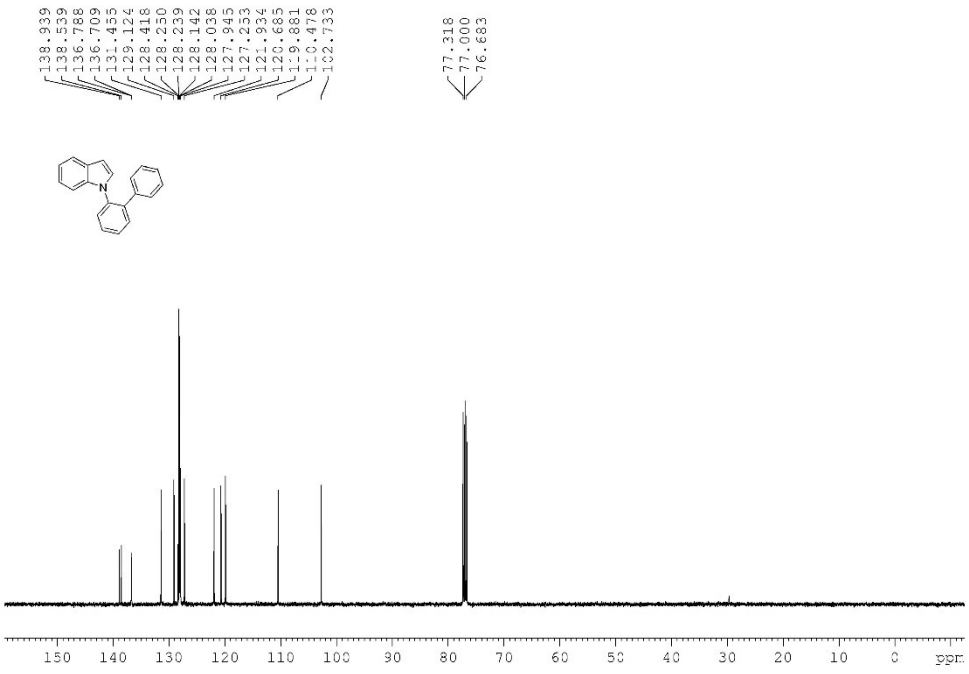


1-([1,1'-biphenyl]-2-yl)-1*H*-indole (5):

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



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)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138.539
136.788
136.709
131.455
129.124
128.418
128.250
128.239
128.142
128.038
127.945
127.253
121.934
120.685
119.881
110.478
102.733
77.318
77.000
76.683
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm