Supporting information for

Synthesis of Cationic [4], [5], and [6]Azahelicenes with Extended π-Conjugated Systems.

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1. General

All commercially available reagents were purchased from available sources (Fluorochem, Sigma Aldrich, Alfa Aesar, Acros Organics, PENTA and Strem Chemicals) and were used without further purification. Solvents were purified and dried by distillation as follows: dichloromethane from calcium hydride, tetrahydrofuran from sodium/benzophenone, or by molecular sieves: *N*,*N*-dimethylformamide. Ethyl acetate, hexane and dichloromethane used for column chromatography were distilled.

The reactions were monitored by using thin layer chromatography (TLC) which was performed on SiliCycle silica gel 60 F_{254} coated aluminium plates. Compounds were visualised by UV lamp (254 nm). Column chromatography was performed on SiliCycle silica gel 60 (0,040–0,063 mm).

NMR spectra were recorded on Bruker Avance III HD 400 spectrometer (400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C) or on Bruker Avance III HD 600 spectrometer (600.17 MHz for ^{1}H, 150.04 for ^{13}C). NMR spectra were recorded in $CDCl_3$ at 25 °C. Chemical shifts are given in δ scale listed in ppm, and were referenced to a residual $CDCl_3$ signal (^{1}H, δ = 7.26 ppm; ^{13}C, δ = 77.16 ppm) or to a residual $(CD_3)_2CO$ signal (^{1}H, δ = 2.05 ppm; ^{13}C, δ = 29.84, 206.26 ppm). Coupling constants *J* are given in Hz, and multiplicity is defined as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, or the combination of above-mentioned. NMR spectra were processed by MestReNova program.

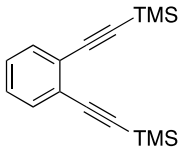
Infrared spectra were recorded using two methods. First method is measurement by Thermo Nicolet AVATAR 370 FT-IR spectrometer using KBr tablets of the compounds via DRIFT method and IR spectra are reported in wave numbers (cm^{-1}). Second method is measurement by Vertex 70v FT-IR spectrometer using powder of the compounds and IR spectra are reported in wave numbers (cm^{-1}). Mass spectra were recorded on compact™ ESI QTOF Mass Spectrometer (Bruker Daltonics). Absorption UV/VIS spectra were recorded on SPECORD 50 PLUS. Emission spectra were recorded on Hamamatsu Quantaurus-QY Plus UV-NIR absolute quantum yield spectrometer C13534 (λ_{exc} = 330 nm).

2. Synthesis of starting material

2.1. Synthesis of biphenylene

1,2-Bis((trimethylsilyl)ethynyl)benzene.

1,2-Dibromobenzene (40 mmol, 9.4 g) was dissolved in diisopropylamine (80 mL). The solution was bubbled with argon in a round bottom pressure flask. To a stirred solution, trimethylsilylacetylene (240 mmol, 36 mL), CuI (4 mmol, 0.76 g) and $Pd(PPh_3)_4$ (2 mmol, 2.3 g) were added. The reaction mixture was heated at 100 °C for 24 h. After that, the reaction was left stirring at 25 °C overnight. Then the reaction mixture was filtered through a pad of Celite and washed with DCM (200 mL). Volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (hexane → 20/1, hexane/EtOAc) provided 10.5 g (97%) of the title compound as a yellow oil.

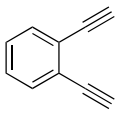


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 5.8, 3.4 Hz, 2H), 7.24 (dd, *J* = 5.8, 3.3 Hz, 2H), 0.28 (s, 18H).

The recorded spectral data agreed with the published data.[1]

1,2-Diethynylbenzene.

1,2-Bis((trimethylsilyl)ethynyl)benzene (38.8 mmol, 10.5 g) was dissolved in 1:1 mixture of methanol and chloroform (40 mL), and K_2CO_3 (155 mmol, 22.1 g) was added to a stirred solution. The reaction mixture was left at 25 °C for 3 h. Then volatiles were removed under reduced pressure and the residue was dissolved in DCM (20 mL) and HCl (10%) was added until the pH of the mixture was in the acidic region. The reaction mixture was then extracted by DCM (3×50 mL), the combined organic layers were dried over anhydrous Na_2SO_4, volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (hexane → 20/1, hexane/EtOAc) provided 4.41 g (90%) of the title compound as a slightly red liquid.

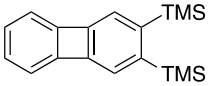


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 5.7, 3.4 Hz, 2H), 7.30 (dd, *J* = 5.8, 3.4 Hz, 2H), 3.36 (s, 2H).

The recorded spectral data agreed with the published data.[1]

2,3-Bis(trimethylsilyl)biphenylene.

1,2-Bis(trimethylsilyl)acetylene (BTSA, 232 mmol, 50.0 mL) was heated in a three-neck flask under argon atmosphere to 140 °C. Then a solution of 1,2-diethynylbenzene (12.2 mmol, 1.54 g) and $CpCo(CO)_2$ (1.22 mmol, 0.162 mL) in BTSA 116



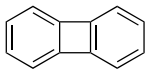
mmol, 25 mL) was added to into it in portions of 2.5 mL every 10 minutes. During the course of the reaction, the flask was irradiated with a lamp (300 W), which was placed as close to the centre of the flask as possible. After 2 h, the reaction was left to cool down to 25 °C and remaining BTSA was evaporated under reduced pressure. Column chromatography of the residue on silica gel (hexane) provided 2.89 g (80%) of the title compound as a yellow oil. The reaction was repeated twice and the title compound was isolated in 77% and 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 2H), 6.79–6.73 (m, 2H), 6.72–6.67 (m, 2H), 0.38 (s, 18H).

The recorded spectral data agreed with the published data.[2]

Biphenylene (1).

2,3-Bis(trimethylsilyl)biphenylene (9.70 mmol, 2.88 g) was dissolved in DCM (20 mL) and to



a stirring solution was added trifluoroacetic acid (194 mmol, 14.8 mL) in one portion. The reaction mixture was left stirring at 25 °C for 2 h. Then small amount of water (5 mL) was added. The reaction mixture was extracted with DCM (3×20 mL), the combined organic layers were dried over anhydrous Na_2SO_4, volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (hexane) provided 1.33 g (90%) of the title compound as a colorless solid. The reaction was repeated twice and the product **1** was isolated with 79% and 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76–6.70 (m, 4H), 6.65–6.60 (m, 4H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 128.4, 117.5.

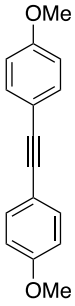
The recorded spectral data agreed with the published data.[3]

2.2. Synthesis of substituted diphenylalkynes

General procedure.

$PdCl_2(PPh_3)_2$ (0.42 mmol, 295 mg), CuI (0.70 mmol, 133 mg) and an aryl iodide (7.00 mmol) were dissolved in dry benzene (35 mL) in a round bottom pressure flask. DBU (42.0 mmol, 6.27 mL) is then added by syringe. While stirring, the reaction mixture was bubbled with argon. After that, ice-chilled trimethylsilylethylene (3.50 mmol, 0.48 mL) was added followed immediately by distilled water (0.05 mL). The reaction mixture was left stirring at 25 °C or 60 °C for 18 h. Then the reaction mixture was partitioned between diethyl ether (50 mL) and distilled water (50 mL). The organic layer was washed with HCl (10%, 3×75 mL), saturated aqueous solution of NaCl (75 mL), dried over anhydrous Na_2SO_4 and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel provided the respective products.

1,2-Bis(4-methoxyphenyl)ethyne (6b).



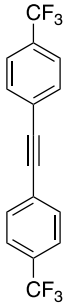
1-Iodo-4-methoxybenzene (7.00 mmol, 1.64 g) was used, the reaction was carried out at 60 °C. Column chromatography of the residue on silica gel (hexane/EtOAc, 40/1 → 20/1) provided 0.53 g (63%) of the title compound as a yellow powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.8 Hz, 4H), 6.87 (d, *J* = 8.9 Hz, 4H), 3.83 (s, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 133.0, 115.9, 114.1, 88.1, 55.4.

The recorded spectral data agreed with the published data.[4]

1,2-Bis(4-(trifluoromethyl)phenyl)ethyne (6c).



1-Iodo-4-(trifluoromethyl)benzene (7.00 mmol, 1.00 mL) was used, the reaction carried out at 25 °C. Column chromatography of the residue on silica gel (hexane → 70/1, hexane/EtOAc) provided 0.99 g (90%) of the title compound as a colorless powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.61 (m, 8H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.1, 130.7 (q, *J* = 32.7 Hz), 126.5, 125.6 (q, *J* = 3.9 Hz), 124.0 (q, *J* = 271.3 Hz), 90.3.

The recorded spectral data agreedwith the published data.[5]

2.3. Synthesis of phenanthren-4-ylboronic acid

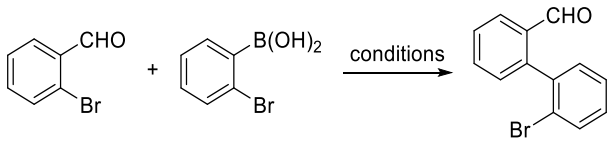
Optimization of reaction conditions for preparation of 2'-bromo-[1,1'-biphenyl]-2-carbaldehyde.

Suzuki-Miyaura cross-coupling of 2-bromobenzaldehyde with 2-bromophenylboronic acid to form 2'-bromo-[1,1'-biphenyl]-2-carbaldehyde.

Initially, the reaction was carried out using published conditions: $Pd(PPh_3)_4$ (10 mol%), Et_3N (3 eq.) in DMF at 90 °C for 8 or 12 h under argon atmosphere (Table S1, Entries 1 and 2). Only traces of 2'-bromo-[1,1'-biphenyl]-2-carbaldehyde were observed by respective TLC analyses. The starting material, 2-bromobenzaldehyde, was almost fully recovered in each case. Then, the reaction was carried out using other published conditions: $Pd(OAc)_2$ (10 mol%), PPh_3 (25 mol%), NaOAc (1.5 eq.) in DMF at 80 °C for 3 h (Entry 3).[6] Once again only traces of 2'-bromo-[1,1'-biphenyl]-2-carbaldehyde were detected by TLC analyses and the starting material, 2-bromobenzaldehyde, was recovered in almost quantitative amount.

Finally, were used classical conditions for Suzuki-Miyaura cross-coupling ($Pd(PPh_3)_4$ (2.5 mol%), K_2CO_3 (5 eq.) in THF/H_2O (5/1)) at 90 °C for 24 h under argon atmosphere (Entry 4).[7] After 24 hours, the starting material was fully consumed and 2'-bromo-[1,1'-biphenyl]-2-carbaldehyde was furnished in 75% isolated yield.

Table S1. Suzuki-Miyaura cross-coupling of 2-bromobenzaldehyde with 2-bromophenylboronic acid under various conditions.

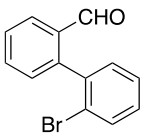


Entry	Catalyst (mol%)	Base (eq.)	Solvent	*T* (°C)	*t* (h)	Yield (%)[a]
1	$Pd(PPh_3)_4$ (10)	Et_3N (3)	DMF	90	8	0[b]
2	$Pd(PPh_3)_4$ (10)	Et_3N (3)	DMF	90	12	0[b]
3	$Pd(OAc)_2$ (10)	NaOAc (1.5)	DMF	80	6	0[b]
4	$Pd(PPh_3)_4$ (2.5)	K_2CO_3 (5 eq.)	THF/H_2O (5/1)	90	24	75

[a]Isolated yields.

[b]Traces of the product.

2'-Bromo-[1,1'-biphenyl]-2-carbaldehyde.



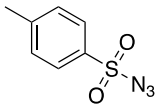
A representative procedure: 2-bromobenzaldehyde (1.71 mmol, 0.20 mL), 2-bromophenylboronic acid (2.05 mmol, 412 mg), $Pd(PPh_3)_4$ (44.0 μmol, 51 mg) and K_2CO_3 (8.00 mmol, 1.11 g) were dissolved in THF (5 mL) and distilled water (1 mL). Stirred reaction mixture was bubbled with argon and heated at 90 °C for 24 h. After cooling down to 25 °C volatiles were removed under reduced pressure. The residue was dissolved in EtOAc (10 mL) and partitioned between EtOAc (20 mL) and distilled water (20 mL). The aqueous phase was extracted with EtOAc (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (40:1 → 20/1 hexane/EtOAc,) provided 333 mg (75%) of the title compound as a yellow oil. The reaction was done once more in 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.04 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.71–7.64 (m, 2H), 7.58–7.53 (m, 1H), 7.44–7.39 (m, 1H), 7.35–7.29 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 144.6, 139.0, 133.82, 133.78, 132.9, 131.7, 131.0, 130.0, 128.7, 127.53, 127.50, 123.98.

The recorded spectral data agreed with the published data.[8]

Ohira-Bestmann reagent.

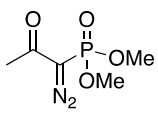


TsCl (42.0 mmol, 8.00 g) and NaN_3 (42.0 mmol, 2.73 g) were dissolved in acetone (120 mL) and distiller water (120 mL). The reaction mixture was left stirring at 0 °C for 2 h. After that, acetone was removed under reduced pressure and the reaction mixture was extracted with diethyl ether (3×50 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Volatiles were removed under reduced pressure yielding 7.87 g (95%) of depicted tosyl azide as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 2.47 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 135.5, 130.4, 127.6, 21.8.

The recorded spectral data agreed with the published data.[9]



NaH (60% dispersion in mineral oil, 7.90 mmol, 316 mg) was dissolved in dry THF (19.2 mL) and the solution was cooled down to 0 °C. To a stirring reaction mixture, a solution of dimethyl-(2-oxopropyl)phosphonate (7.2 mmol, 1 mL) in dry THF (19.2 mL) was added dropwise. After stirring at 0 °C for 1 h, tosyl azide (7.9 mmol, 1.56 g) was added. The resulting mixture was left stirring at 0 °C for 30 min. Then the

reaction mixture was passed through a short column of silica gel (EtOAc) to give 1.34 g (97%) of Ohira-Bestman reagent as an orange oil. The reaction was done once more in 97% yield.

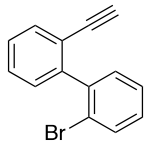
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 3.79 (s, 3H), 2.22 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 189.9, 53.7, 53.6, 27.2.

The recorded spectral data agreed with the published data.[10]

2-Bromo-2'-ethynyl-1,1'-biphenyl).

2'-Bromo-[1,1'-biphenyl]-2-carbaldehyde (0.36 mmol, 94 mg), Ohira-Bestmann reagent (1.84 mmol, 354 mg) and K_2CO_3 (0.74 mmol, 102 mg) were suspended in dry MeOH (3 mL). The reaction mixture was left stirring at 25 °C for 48 h. Volatiles were removed under reduced pressure. The residue was dissolved in DCM (10 mL) and partitioned between DCM (20 mL) and the saturated aqueous solution of NaCl (20 mL). The aqueous phase was extracted with DCM (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (hexane) provided 68 mg (73%) of the title compound as a pale-yellow oil. The reaction was repeated multiple times with isolated yields in the range of 48–73%.



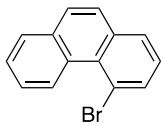
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.62 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.45–7.32 (m, 4H), 7.30–7.22 (m, 2H), 2.95 (s, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 141.5, 133.0, 132.7, 131.4, 129.9, 129.3, 128.6, 127.8, 127.1, 123.5, 121.8, 82.3, 80.5.

The recorded spectral data agreed with the published data.[11]

4-Bromophenanthrene.

2-Bromo-2'-ethynyl-1,1'-biphenyl (0.95 mmol, 245 mg) was dissolved in DCE (5 mL) and the solution was bubbled with argon. $PtCl_2$ (76.0 μmol, 20 mg) was added, and the reaction was heated at 100 °C for 24 h. After cooling down to 25 °C, the reaction mixture was filtered through a pad of Celite and washed with DCM (200 mL). Volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (hexane) provided 158 mg (65%) of the title compound as a pale-yellow oil. The reaction was repeated twice in 51% and 64% isolated yields.



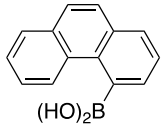
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08–10.04 (m, 1H), 8.00 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.93–7.87 (m, 1H), 7.85 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.70–7.62 (m, 3H), 7.38 (t, *J* = 7.7 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 134.8, 133.5, 129.9, 129.0, 128.73, 128.65, 128.4, 127.3, 127.2, 126.9, 126.7, 125.5, 119.7.

The recorded spectral data agreed with the published data.[11]

Phenanthren-4-ylboronic acid (5c).

4-Bromophenanthrene (0.95 mmol, 244 mg) was dissolved in dry THF (4 mL) under argon atmosphere. The solution was cooled down to –78 °C (dry ice/acetone bath). Then, 1.7 M solution of *t*-BuLi in pentane (1 mmol, 0.6 mL) was added dropwise and the reaction mixture was left stirring for 45 min. Formation of white precipitate was observed. After that, $B(OMe)_3$ (1 mmol, 0.11 mL) was added. The resulting clear solution was left stirring at –78 °C for 1 h. The reaction mixture was then allowed to warm to 25 °C and stirring was continued for 3 h. Then, 10% solution of HCl (2 mL) was added. The reaction mixture was extracted with EtOAc (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and volatiles were removed under reduced pressure. The residue was suspended in hexane (30 mL) and filtered to give 200 mg (95%) of the title compound as a colorless powder. The phenanthren-4-ylboronic acid (**5c**) was used in the next step without further purification.



M.p. 119-124 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79–8.74 (m, 1H), 7.98–7.94 (m, 1H), 7.91 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.80 (s, 2H), 7.74–7.70 (m, 1H), 7.65–7.49 (m, 5H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7, 133.1, 132.3, 131.6, 129.7, 129.4, 128.5, 128.15, 128.14, 127.6, 127.1, 126.7, 126.6, 126.4;

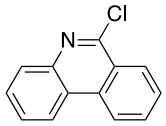
IR (KBr) ν_{max} 3284, 1336, 1292, 1020, 829, 806, 789, 739, 721, 673, 650, 636, 538, 472 cm^{-1};

HRMS (ESI) *m*/*z* calculated for $C_{16}H_{15}BNaO_2$ $[M+Na]^+$ 273,1057, found 273.1057.

2.4. Synthesis of 6-chlorophenanthridine

6-Chlorophenanthridine (2).

Phenanthridin-6(5*H*)-one (15.4 mmol, 3.01 g) was dissolved in $POCl_3$ (154 mmol, 14.3 mL) and anhydrous *N*,*N*-dimethylaniline (7.89 mmol, 1 mL) was added. The reaction mixture was heated under reflux for 3 h while stirring. After cooling down to 25 °C, the reaction mixture was poured over ice and extracted by DCM (4×30 mL). The combined organic layers were washed with saturated aqueous solution of Na_2CO_3 (2×30 mL), dried over anhydrous Na_2SO_4, and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (hexane/EtOAC, 40/1 → 20/1) provided 3.02 g (92%) of the title compound as a colorless powder.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.3 Hz, 1H), 8.53 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.49 (dd, *J* = 8.3, 0.8 Hz, 1H), 8.10 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.91 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.80–7.72 (m, 2H), 7.69 (ddd, *J* = 8.2, 7.2, 1.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 143.5, 134.7, 131.9, 129.52, 129.50, 128.4, 127.9, 127.6, 125.1, 124.2, 122.44, 122.37.

The recorded spectral data agreed with the published data.[12]

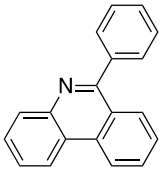
2.5. Synthesis of 6-substituted phenanthridines

2.5.1. Synthesis of 6-substituted phenanthridines via C–C cleavage reactions process

General procedure C–C bond cleavage. Biphenylene (**1**) (1.00 mmol, 152 mg), nitrile **3** (10.0 mmol), [$Rh(COD)_2BF_4$] (0.1 mmol, 41 mg) and dppe (0.10 mmol, 40 mg) were dissolved in dry THF (5 mL). The reaction mixture in a microwave vial was bubbled with argon and heated in a microwave reactor at 180 °C for 2 h. Then volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (hexane/EtOAc, 40:1 → 10/1) provided the respective products.

6-Phenylphenanthridine (4a).

According to the general procedure. Benzonitrile (**3a**) (4 ml) was used. Column chromatography of the residue on silica gel (10/1 hexane/EtOAc) provided 239 mg (88%) of the title compound as a slightly yellow powder.



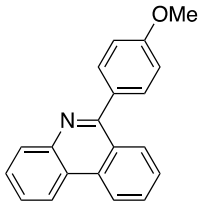
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.4 Hz, 1H), 8.63 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.25 (dd, *J* = 8.1, 1.0 Hz, 1H), 8.11 (app d, *J* = 8.3 Hz, 1H), 7.87 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.79–7.72 (m, 3H), 7.70 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.62 (ddd, *J* = 8.3, 7.1, 1.1 Hz, 1H) 7.60–7.50 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 143.9, 139.9, 133.6, 130.7, 130.5, 129.9, 129.1, 129.0, 128.9, 128.6, 127.3, 127.1, 125.4, 123.9, 122.4, 122.1.

The recorded values agree with the previously reported data.[13]

6-(4-Methoxyphenyl)phenanthridine (4b).

According to the general procedure. 4-methoxybenzonitril (**3b**) (10 mmol, 1.17 g) was used. Column chromatography of the residue on silica gel (10/1 hexane/EtOAc) provided 127 mg (47%) of the title compound as a slightly yellow powder.



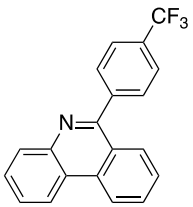
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.3 Hz, 1H), 8.61 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.24 (dd, *J* = 8.2, 0.9 Hz, 1H), 8.17 (app d, *J* = 8.3 Hz, 1H), 7.85 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.78–7.59 (m, 5H), 7.10 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 160.3, 144.0, 133.7, 132.4, 131.3, 130.5, 130.4, 129.1, 128.9, 127.2, 126.6, 125.5, 123.8, 122.3, 122.1, 113.9, 55.6.

The recorded values agree with the previously reported data.[14]

6-(4-Trifluoromethylphenyl)phenanthridine (4c).

According to the general procedure. 4-(Trifluoromethyl)benzonitril **(3c**) (10 mmol, 1.71 g) was used. Column chromatography of the residue on silica gel (10/1 hexane/EtOAc) provided 274 mg (85%) of the title compound as a slightly yellow powder.



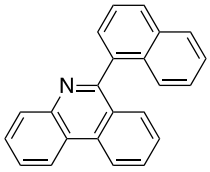
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (app d, *J* = 8.3 Hz, 1H), 8.65 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.03 (dd, *J* = 8.3, 0.6 Hz, 1H), 7.93 – 7.82 (m, 5H), 7.79 (ddd, *J* = 8.0, 6.6, 1.5 Hz, 1H), 7.73 (ddd, *J* = 8.0, 7.0, 1.4 Hz, 1H), 7.65 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.9, 143.8, 143.5 (q, *J* = 1.2 Hz), 133.7, 130.99, 130.97 (q, *J* = 32.6 Hz), 130.6, 130.3, 129.2, 128.5, 127.5, 125.6 (q, *J* = 3.7 Hz), 125.0, 124.3 (q, *J* = 272.2 Hz), 124.0, 122.6, 122.2.

The recorded values agree with the previously reported data.[15]

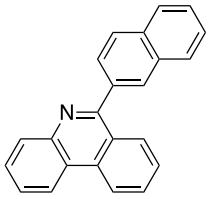
6-(Naphthalen-1-yl)phenanthridine (4d).

According to the general procedure. 1-Naphthonitrile (**3d**) (10 mmol, 1.53 g) was used. The reaction was carried out at 180 °C. Column chromatography of the residue on silica gel provided 9 mg (3%) of the title compound as a colorless powder. For spectra characteristics, see its preparation by using cross-coupling reaction.



6-(Naphthalen-2-yl)phenanthridine (4e).

According to the general procedure. 2-Naphthonitrile (**3e**) (10.0 mmol, 1.53 g) was used. The reaction was carried out at 200 °C. Column chromatography of the residue on silica gel provided 189 mg (62%) of the title compound as a slightly yellow powder.



M.p. 146-147 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.3 Hz, 1H), 8.66 (d, *J* = 8.1 Hz, 1H), 8.34 (br s, 1H), 8.25 (s, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 8.00–7.94 (m, 2H), 7.92–7.85 (m, 2H), 7.80 (t, *J* = 7.4 Hz, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.61–7.55 (m, 2H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.3, 143.7, 136.9, 133.8, 133.6, 133.3, 131.0, 130.3, 129.6, 129.3, 129.2, 128.7, 128.3, 128.0, 127.50, 127.45, 127.3, 126.8, 126.6, 125.5, 124.0, 122.4, 122.2;

IR (KBr) ν_{max} 850, 822, 814, 758, 741, 723, 714, 681, 478, 428 cm^{-1};

HRMS (ESI) *m*/*z* calculated for $C_{23}H_{16}N$ $[M+H]^+$ 306.1277, found 306.1281.

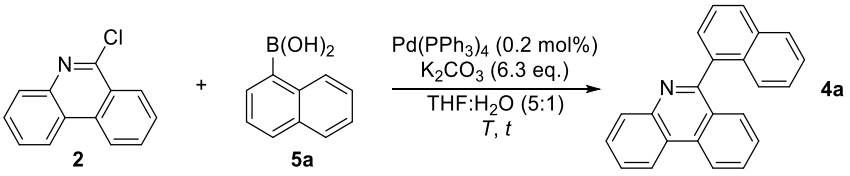
2.5.2. Synthesis of 6-substituted phenanthridines via Suzuki-Miyaura cross-coupling

Optimization of Suzuki-Miyaura cross-coupling of 4 with arylboronic acids.

The Suzuki-Miyaura cross-coupling of 6-chlorophenanthridine (**2**) with various boronic acids was reported previously to proceed under the following reaction conditions: $Pd(PPh_3)_4$ (0.2 mol%) as a catalyst and K_2CO_3 (6.3 eq.) as a base in a mixture of THF:H_2O (5:1) under reflux.[16] Therefore, coupling of 6-chlorophenanthridine (**2**) with naphthalen-1-ylboronic acid (**5a**) was examined under the same conditions (Table S2).

Carrying out the reaction at 80 °C for 24 h furnished **4a** in 23% isolated yield in (Entry 1). TLC analyses of the reaction mixture confirmed that the starting material did not fully react, and the unreacted 6-chlorophenanthridine (**2**) was successfully recovered. A reaction was also performed under reflux and the reaction mixture was monitored using TLC analyses (Entry 2). The starting material was not detected after 6 hours and the formation of only one product was observed. 6-(Naphth-1-yl)phenanthridine (**4a**) was isolated in 85% yield. Scale up of the reaction to 2 mmol (Entry 3) led to a lower yield of **4a**, which was isolated in 50% yield. Again, a TLC analysis of the reaction mixture showed the presence of **4a** and the unreacted starting material only.

Table S2. Screening of the Suzuki-Miyaura cross-coupling reaction conditions.



Entry	Scale (mmol)	Temperature	Reaction time *t*	Yield (%)[a]
1[b]	0.6	80 °C	24 h	23
2	0.6	reflux	6 h	85
3	2	reflux	6 h	50

[a]Isolated yields.

[b]Reaction performed in a sealed vial.

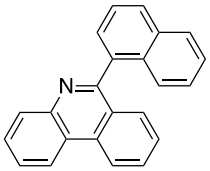
General procedure for Suzuki-Miyaura cross-coupling.

6-Chlorophenanthridine (**2**) (0.63 mmol, 135 mg), arylboronic acid **5** (0.63 mmol), $Pd(PPh_3)_4$ (1.26 μmol, 1.5 mg) were dissolved in THF (10 mL). Then a solution of K_2CO_3 (2M, 2 mL) was added and while stirring the reaction mixture was bubbled with argon. The reaction was kept under reflux for 6 or 8 h. After cooling down to 25 °C volatiles were removed under reduced pressure. The residue was dissolved in DCM (10 mL) and partitioned between DCM

(20 mL) and distilled water (20 mL). The aqueous phase was extracted with DCM (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (hexane/EtOAc, 40:1 → 10/1) provided the respective products.

6-(Naphthalen-1-yl)phenanthridine (4d).

General procedure. Naphthalen-1-ylboronic acid (**5a**) (0.63 mmol, 108 mg) was used. The reaction time was 6 h. Column chromatography of the residue on silica gel provided 164 mg (85%) of the title compound as a colorless powder.



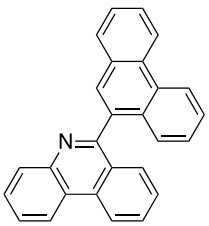
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.4 Hz, 1H), 8.70 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.33 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.04 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.87–7.79 (m, 2H), 7.75 (ddd, *J* = 8.3, 7.1, 1.5 Hz, 1H), 7.71–7.64 (m, 3H), 7.53–7.44 (m, 3H), 7.32 (ddd, *J* = 8.2, 6.7, 1.2 Hz, 1H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 143.9, 137.2, 133.9, 133.3, 132.5, 131.0, 130.5, 129.4, 129.2, 128.5, 127.6, 127.5, 127.4, 126.7, 126.6, 126.20, 126.18, 125.5, 124.2, 122.3, 122.2.

The recorded spectral data agreed with the published data.[17]

6-(Phenanthren-9-yl)phenanthridine (4f).

General procedure. Phenanthren-9-ylboronic acid (**5b**) (0.63 mmol, 140 mg) was used. The reaction time was 8 h. Column chromatography of the residue on silica gel provided 179 mg (80%) of the title compound as a colorless powder.



M.p. 243-244 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86–8.78 (m, 2H), 8.76 (d, *J* = 8.3 Hz, 1H), 8.72 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.35 (d, *J* = 7.8 Hz, 1H), 7.97 (s, 1H), 7.95 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.88–7.72 (m, 5H), 7.70–7.64 (m, 2H), 7.50–7.44 (m, 2H), 7.40 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H);

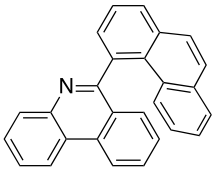
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 143.9, 135.9, 133.2, 131.5, 131.4, 131.1, 130.8, 130.7, 130.5, 129.3, 129.2, 129.1, 128.6, 127.51, 127.45, 127.3, 127.14, 127.08, 126.90, 126.88, 126.7, 124.2, 123.1, 122.8, 122.3, 122.2;

IR (KBr) ν_{max} 1566, 1448, 1356, 760, 748, 726, 615, 548, 503, 434 cm^{-1};

HRMS (ESI) *m*/*z* calculated for $C_{27}H_{18}N$ $[M+H]^+$ 356.1434, found 356.1436.

6-(Phenanthren-4-yl)phenanthridine (4g).

General procedure. Phenanthren-4-ylboronic acid (**5c**) (0.63 mmol, 140 mg) was used. The reaction time was 8 h. Column chromatography of the residue on silica gel provided 76.1 mg (34%) of the title compound as a colorless powder.



M.p. 93-98 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.3 Hz, 2H), 8.33 (d, *J* = 7.8 Hz, 1H), 8.09 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.85–7.72 (m, 6H), 7.68 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.48 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.36–7.29 (m, 3H), 6.83 (ddd, *J* = 8.6, 7.0, 1.5 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 144.1, 137.2, 133.6, 133.4, 133.3, 131.1, 130.61, 130.55, 130.1, 129.9, 129.4, 129.1, 128.70, 128.69, 128.0, 127.7, 127.4, 127.1, 126.21, 126.20, 126.15, 125.9, 124.2, 122.3, 122.2;

IR (KBr) ν_{max} 1294, 829, 760, 741, 725, 710, 683, 613, 496, 440 cm^{-1};

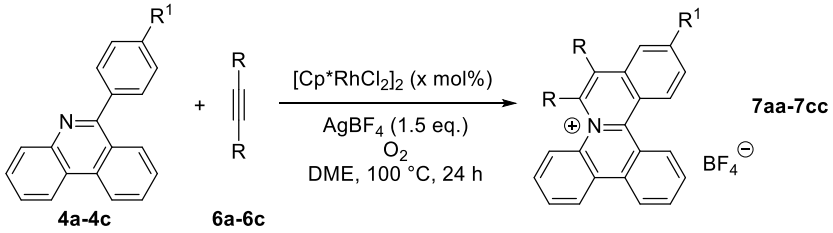
HRMS (ESI) *m*/*z* calculated for $C_{27}H_{18}N$ $[M+H]^+$ 356.1434, found 356.1431.

3. C–H bond activation in phenanthridines

3.1. Synthesis of isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborates

Originally, reaction Entries 1, 5, and 9 were run the first with 1 mol% of $[Cp^*RhCl_2]_2$ (Table S3). Because of unsatisfactory product yields in the first set of reactions, we increased the catalyst's amount to 5 mol% to improve them. Unfortunately, it did not have any effect on the reaction outcomes.

Table S3. Screening of Rh-catalyzed C–H activation/annulation sequence of phenanthridines **4a-4c** with alkynes **6a-6c**.

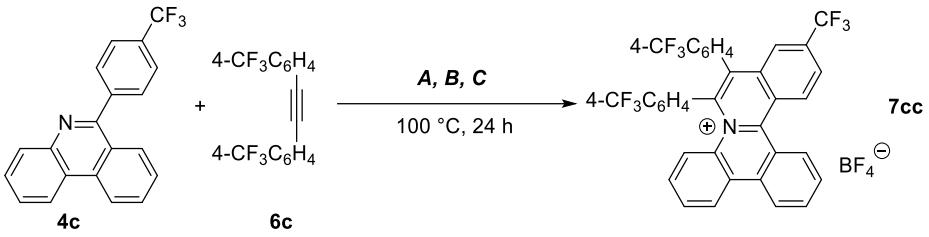


Entry	**4**	R^1	**6**	R	$[Cp^*RhCl_2]_2$ (mol%)	**7**	Yield (%)[a]
1	**4a**	H	**6a**	H	1	**7aa**	32
2	**4a**	H	**6b**	4-$MeOC_6H_4$	5	**7ab**	30
3	**4a**	H	**6c**	4-$CF_3C_6H_4$	5	**7ac**	0
4	**4b**	OMe	**6a**	H	5	**7ba**	29
5	**4b**	OMe	**6b**	4-$MeOC_6H_4$	1	**7bb**	19
6	**4b**	OMe	**6c**	4-$CF_3C_6H_4$	5	**7bc**	18
7	**4c**	CF_3	**6a**	H	5	**7ca**	30
8	**4c**	CF_3	**6b**	4-$MeOC_6H_4$	5	**7cb**	44
9	**4c**	CF_3	**6c**	4-$CF_3C_6H_4$	1	**7cc**	0

[a] Isolated yields.

In order to improve yields of the products that were rather low (see Table S3) different catalytic conditions were tested in the reaction of **6c** with **4c** (Table S4). Those encompassed the previously reported system based on $[Cp^*RhCl_2]_2$ (5 mol%), $Cu(BF_4)_2$ (1.5 eq.), O_2, in DME,[18] our combination of $[Cp^*RhCl_2]_2$ (10 mol%), $NaBF_4$ (1.35 eq.), $Cu(OAc)_2$ (2 eq.), in MeOH because of a previous demonstration that methanol could be a solvent of choice,[19] and finally previously reported system based on $[Cp^*RhCl_2]_2$ (10 mol%), $AgBF_4$ (1 eq.), $Cu(OAc)_2$ (1 eq.), DCE.[20]

Table S4. Screening of various reaction conditions for C–H activation/annulation of **4c** with **6c**.[a]



A: $[Cp^*RhCl_2]_2$ (5 mol%), $Cu(BF_4)_2$ (1.5 eq.), O_2, DME
B: $[Cp^*RhCl_2]_2$ (10 mol%), $NaBF_4$ (1.35 eq.), $Cu(OAc)_2$ (2 eq.), MeOH
C: $[Cp^*RhCl_2]_2$ (10 mol%), $AgBF_4$ (1 eq.), $Cu(OAc)_2$ (1 eq.), DCE

Entry	**6c** (eq.)	Procedure	Yield (%)[b]
1	1	***A***	traces
2	2	***B***	traces
3	3	***C***	70
4	1	***C***	70

[a] Experimental details of each reaction conditions follow this table. [b] Isolated yields.

Procedure A. Phenanthridine **4a-4c** (0.30 mmol), alkyne **6a-6c** (0.30 mmol), $[Cp^*RhCl_2]_2$ (0.03 mmol, 19 mg), and $Cu(BF_4)_2$ (0.45 mmol, 107 mg) were dissolved in DCE (5 mL). Then the reaction flask was filled with oxygen. The reaction mixture was heated at 100 °C for 24 h. After cooling down to 25 °C, the reaction mixture was filtered through a pad of Celite and washed with DCM (200 mL). Volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (DCM, then DCM/MeOH, 100/5) provided the respective products. The products were further purified by precipitation from DCM solutions with cyclohexane.

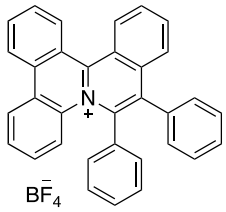
Procedure B. 6-(4-(Trifluoromethyphenyl)phenanthridine (**4c**) (0.1 mmol, 32 mg), 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (**7c**) (0.2 mmol, 62 mg), $[Cp^*RhCl_2]_2$ (0.01 mmol, 6.1 mg), $NaBF_4$ (0.135 mmol, 15 mg), $Cu(OAc)_2 \cdot H_2O$ (0.2 mmol, 40 mg), and MeOH (2 mL).). A reaction mixture was heated at 100 °C for 24 h. After cooling down to 25 °C, the reaction mixture was filtered through a pad of Celite and washed with DCM (200 mL). Volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (DCM, then DCM/MeOH, 100/5) provided the respective products.

Procedure C. Phenanthridine **4a-4c** (0.30 mmol), alkyne **6a-6c** (0.30 mmol), $[Cp^*RhCl_2]_2$ (0.03 mmol, 19 mg), $AgBF_4$ (0.30 mmol, 58 mg) and $Cu(OAc)_2$ (0.33 mmol, 60

mg) were dissolved in DCE (5 mL). A reaction mixture was heated at 100 °C for 24 h. After cooling down to 25 °C, the reaction mixture was filtered through a pad of Celite and washed with DCM (200 mL). Volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (DCM, then DCM/MeOH, 100/5) provided the respective products. The products were further purified by precipitation from DCM solutions with cyclohexane.

6,7-Diphenylisoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7aa).

Procedure C. 6-Phenylphenanthridine (**4a**) (0.3 mmol, 77 mg), 1,2-diphenylethyne (**6a**) (0.3 mmol, 54 mg) were used. Column chromatography of the residue on silica gel provided 137 mg (88%) of the title compound as a yellow solid. Precipitation provided 84 mg (54%) of the title compound as a yellow solid.



M.p. 174–175 °C;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99–8.94 (m, 1H), 8.89 (d, *J* = 7.9 Hz, 1H), 8.76 (d, *J* = 8.0 Hz, 1H), 8.58 (d, *J* = 7.9 Hz, 1H), 8.21 (app t, *J* = 7.6 Hz, 1H), 8.09–8.05 (m, 3H), 7.97–7.93 (m, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.64 (app t, *J* = 7.5 Hz, 1H), 7.44–7.39 (m, 3H), 7.36–7.31 (m, 2H), 7.29 (app t, *J* = 7.9 Hz, 1H), 7.20–7.15 (m, 1H), 7.14–7.09 (m, 4H);

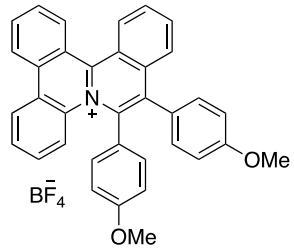
^{13}C NMR (151 MHz, $CDCl_3$) δ 155.9, 141.4, 136.8, 136.7, 136.6, 136.1, 135.8, 134.9, 134.3, 133.4, 132.6, 132.5, 131.5, 131.2, 130.9, 130.8, 129.59, 129.57, 129.1, 128.9, 128.8, 127.4, 126.3, 125.2, 125.0, 124.5, 124.0;

IR (KBr) ν 1608, 1599, 1485, 1442, 1404, 1334, 1153, 1059, 798, 769, 756, 706, 675, 617, 530 cm^{-1};

HR ESI-MS calculated for $C_{33}H_{22}N$ (M^+) 432.17468, found 432.17432.

6,7-Bis(4-methoxyphenyl)isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7ab).

Procedure C. 6-Phenylphenanthridine (**4a**) (0.3 mmol, 77 mg), 1,2-bis(4-methoxyphenyl)ethyne (**6b**) (0.3 mmol, 72 mg) were used. Column chromatography of the residue on silica gel provided 138 mg (80%) of the title compound as an orange solid. Precipitation provided 93 mg (53%) of the title compound as an orange solid.



M. p. 180–181 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (app d, *J* = 8.3 Hz, 1H), 8.84 (d, *J* = 8.2 Hz, 1H), 8.74 (d, *J* = 8.1 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.20 (app t, *J* = 7.7 Hz, 1H), 8.08–8.01 (m, 3H), 7.97 (app d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.64 (app t, *J* = 7.6 Hz, 1H), 7.32 (app t, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.72 (s, 3H);

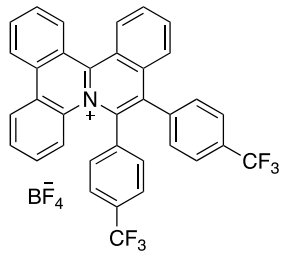
^{13}C NMR (151 MHz, $CDCl_3$) δ 160.2, 159.8, 155.5, 142.0, 137.4, 136.5, 136.4, 135.9, 134.68, 134.66, 133.0, 132.4, 132.3, 132.1, 130.9, 130.8, 129.4, 129.1, 128.4, 127.4, 126.0, 125.5, 125.1, 124.9, 124.5, 124.4, 123.9, 114.43, 114.37, 55.52, 55.45;

IR (KBr) ν 1606, 1514, 1487, 1471, 1462, 1404, 1292, 1254, 1180, 1059, 843, 769, 565, 560, 519 cm^{-1};

HR ESI-MS calculated for $C_{35}H_{26}O_2N$ (M^+) 492.19581, found 492.19567.

6,7-Bis(4-(trifluoromethyl)phenyl)isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7ac).

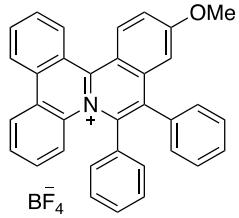
Procedure C. 6-Phenylphenanthridine (**4a**) (0.3 mmol, 77 mg), 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (**6c**) (0.3 mmol, 94 mg) were used. Column chromatography of the residue on silica gel provided 138 mg (70%) of a greenish-yellow solid. Precipitation provided 84 mg (54%) of a yellow solid. Its immediate TLC analysis showed one spot only. However, the isolated solid turned out to be unstable and almost immediately (within a minute after isolation) it started to succumb to degradation into numerous species, which was indicated by TLC analysis (multiple spots were observed). The rather fast degradation did not allow to record ^1H and ^{13}C of reasonable quality to unequivocally confirm the product's structure. On the other hand, the presence of the respective molecular peaks in MS indicates the presence of the desired product.



LC-MS calculated for $C_{35}H_{20}NF_6$ (M^+) 568.15, found 568.36.

9-Methoxy-6,7-diphenylisoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7ba).

Procedure C. 6-(4-Methoxyphenyl)phenanthridine (**4b**) (0.1 mmol, 29 mg), 1,2-diphenylethyne (**6a**) (0.1 mmol, 18 mg) were used. Column chromatography of the residue on silica gel provided 47 mg (85%) of the title compound as a yellow solid.



M.p.: 169–170 °C;

^1H NMR (600 MHz, $CDCl_3$) δ 8.90 (d, *J* = 9.3 Hz, 1H), 8.77 (d, *J* = 8.1 Hz, 1H), 8.67 (d, *J* = 8.2 Hz, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 8.15 (app t, *J* = 7.7 Hz, 1H), 8.04 (app t, *J* = 7.7 Hz, 1H), 7.72–7.67 (m, 2H), 7.57 (app t, *J* = 7.5 Hz, 1H), 7.45–7.39 (m, 3H), 7.33–7.29 (m, 2H), 7.25 (app t, *J* = 8.0 Hz, 1H), 7.20–7.15 (m, 2H), 7.14–7.08 (m, 4H) 3.94 (s, 3H);

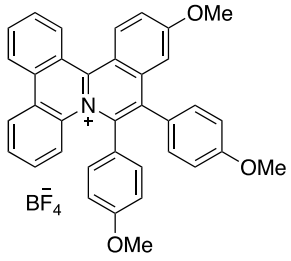
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 154.9, 141.5, 139.8, 135.6, 135.4, 135.1, 134.8, 134.4, 133.6, 132.2, 131.3, 130.8, 130.7, 129.5, 129.03, 129.01, 128.92, 128.90, 128.8, 126.0, 124.7, 124.41, 124.37, 123.8, 122.1, 119.9, 108.2, 56.6;

IR (KBr) ν 1608, 1599, 1487, 1471, 1460, 1406, 1304, 1242, 1059, 860, 756, 729, 700, 530, 451 cm^{-1};

HR ESI-MS calculated for $C_{34}H_{24}ON$ (M^+) 462.18524, found 462.18494.

9-Methoxy-6,7-bis(4-methoxyphenyl)isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7bb).

Procedure C. 6-(4-Methoxyphenyl)phenanthridine (**4b**) (0.3 mmol, 77 mg), 1,2-bis(4-methoxyphenyl)ethyne (**6b**) (0.3 mmol, 72 mg) were used. Column chromatography of the residue on silica gel provided 165 mg (90%) of the title compound as an orange solid. Precipitation provided 129 mg (71%) of the title compound as an orange solid.



M.p.: 184–185 °C;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84 (d, *J* = 9.3 Hz, 1H), 8.71 (d, *J* = 8.1 Hz, 1H), 8.65 (d, *J* = 7.9, 1H), 8.47 (d, *J* = 7.9 Hz, 1H), 8.13 (app t, *J* = 7.6 Hz, 1H), 8.01 (app t, *J* = 7.8 Hz, 1H), 7.68–7.63 (m, 2H), 7.57 (app t, *J* = 7.4 Hz, 1H), 7.28 (ddd, *J* = 8.8, 7.2, 1.4 Hz, 1H), 7.24–7.18 (m, 3H), 7.03–6.96 (m, 4H), 6.64 (app d, *J* = 9.0 Hz, 2H), 3.95 (s, 3H), 3.87 (s, 3H), 3.72 (s, 3H);

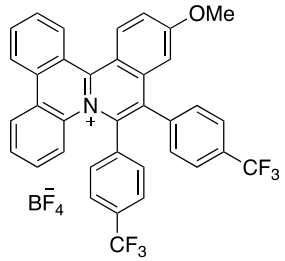
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 160.2, 159.8, 154.5, 142.1, 140.5, 135.4, 135.1, 134.8, 134.7, 134.5, 132.9, 132.1, 131.9, 130.6, 129.1, 128.8, 128.1, 125.7, 125.6, 124.6, 124.5, 124.4, 123.8, 122.1, 119.8, 114.6, 114.3, 107.9, 56.6, 55.5, 55.4;

IR (KBr) ν 1606, 1514, 1487, 1469, 1406, 1300, 1252, 1180, 1061, 1032, 841, 775, 764, 640, 563, 480 cm^{-1};

HR ESI-MS calculated for $C_{36}H_{28}O_3N$ (M^+) 522.20637, found 522.20620.

9-Methoxy-6,7-bis(4-(trifluoromethyl)phenyl)isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7bc).

Procedure C. 6-(4-Methoxyphenyl)phenanthridine (**4b**) (0.3 mmol, 86 mg), 1,2-bis(4-(trifluoromethyl)phenylethyne (**6c**) were used. Column chromatography of the residue on silica gel provided 146 mg (71%) of the title compound as a greenish-yellow solid. Precipitation provided 80 mg (39%) of the title compound as a greenish-yellow solid.



M.p.: > 300 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 (d, *J* = 9.3 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H), 8.64 (d, *J* = 8.1 Hz, 1H), 8.46 (d, *J* = 8.9 Hz, 1H), 8.12 (app t, *J* = 7.5 Hz, 1H), 7.97 (app t, *J* = 7.5 Hz, 1H), 7.71–7.68 (m, 3H), 7.62–7.58 (m, 3H), 7.57 (app t, *J* = 7.5 Hz, 1H), 7.39–7.33 (m, 4H), 7.27 (ddd, *J* = 8.6, 7.5, 0.9 Hz, 1H), 7.06 (d, *J* = 2.4 Hz, 1H), 3.91 (s, 3H);

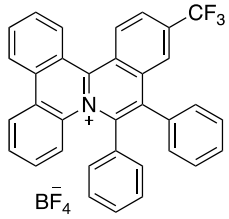
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 155.5, 140.3, 139.5, 138.8, 137.5, 135.5, 135.0, 134.9, 134.6, 134.1, 132.3, 132.0, 131.5, 131.34 (q, *J* = 33.1 Hz), 131.25 (q, *J* = 32.8 Hz), 130.4, 129.3, 129.1, 126.5, 126.0 (q, *J* = 3.7 Hz), 125.7 (q, *J* = 3.6 Hz), 124.8, 124.5, 124.1, 123.9 (q, *J* = 272.8 Hz), 123.7, 123.4 (q, *J* = 272.6 Hz), 122.2, 120.2, 107.8, 56.5;

IR (KBr) ν 1599, 1489, 1460, 1408, 1327, 1244, 1228, 1167, 1128, 1062, 856, 791, 764, 725, 633, 552 cm^{-1};

HR ESI-MS calculated for $C_{36}H_{22}ONF_6$ (M^+) 598.16001, found 598.15973.

6,7-Diphenyl-9-(trifluoromethyl)isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7ca).

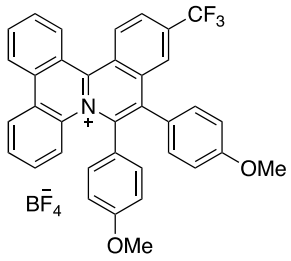
Procedure C. 6-(4-(Trifluoromethylphenyl)phenanthridine (**4c**) (0.3 mmol, 97 mg), 1,2-diphenylethyne (**7a**) (0.3 mmol, 54 mg), $[Cp^*RhCl_2]_2$ (0.03 mmol, 18 mg), $AgBF_4$ (0.3 mmol, 59 mg), $Cu(OAc)_2 \cdot H_2O$ (0.3 mmol, 60 mg). Column chromatography of the residue on silica gel provided 105 mg (60%) of a greenish-yellow solid. Its immediate TLC analysis showed one spot only. However, the isolated solid turned out to be unstable and almost immediately (within a minute after isolation) it started to succumb to degradation into numerous species, which was indicated by TLC analysis (multiple spots were observed). The rather fast degradation did not allow to record ^{1}H and ^{13}C of reasonable quality to unequivocally confirm the product's structure. On the other hand, the presence of the respective molecular peaks in MS indicates the presence of the desired product.



LC-MS calculated for $C_{34}H_{21}NF_3$ (M^+) 500.16, found 500.49.

6,7-Bis(4-methoxyphenyl)-9-(trifluoromethyl)isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7cb).

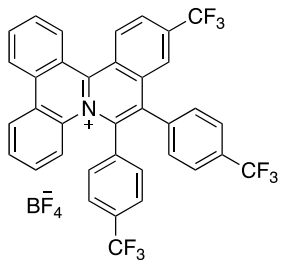
Procedure C. 6-(4-(Trifluoromethylphenyl)phenanthridine (**4c**) (0.3 mmol, 97 mg), 1,2-bis(4-methoxyphenyl)ethyne (**7b**) (0.3 mmol, 72 mg), $[Cp^*RhCl_2]_2$ (0.03 mmol, 18 mg), $AgBF_4$ (0.3 mmol, 59 mg), $Cu(OAc)_2 \cdot H_2O$ (0.3 mmol, 60 mg). Column chromatography of the residue on silica gel provided 125 mg (64%) of an orange solid. Its immediate TLC analysis showed one spot only. However, the isolated solid turned out to be unstable and almost immediately (within a minute after isolation) it started to succumb to degradation into numerous species, which was indicated by TLC analysis (multiple spots were observed). The rather fast degradation did not allow to record ^{1}H and ^{13}C of reasonable quality to



unequivocally confirm the product's structure. On the other hand, the presence of the respective molecular peaks in MS indicates the presence of the desired product.
LC-MS calculated for $C_{36}H_{25}O_2NF_3$ (M^+) 560.18, found 560.26.

9-(Trifluoromethyl)-6,7-bis(4-(trifluoromethyl)phenyl)isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7cc).

Procedure C. 6-(4-(Trifluoromethylphenyl)phenanthridine (**4c**) (0.1 mmol, 32 mg), 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (**7c**) (0.1 mmol, 31 mg), $[Cp^*RhCl_2]_2$ (0.01 mmol, 6.1 mg), $AgBF_4$ (0.1 mmol, 20 mg), $Cu(OAc)_2 \cdot H_2O$ (0.1 mmol, 20 mg). Column chromatography of the residue on silica gel provided 53 mg (70%) of a greenish-yellow solid. Its immediate TLC analysis showed one spot only. However, the isolated solid turned out to be unstable and almost immediately (within a minute after isolation) it started to succumb to degradation into numerous species, which was indicated by TLC analysis (multiple spots were observed). The rather fast degradation did not allow to record ^1H and ^{13}C of reasonable quality to unequivocally confirm the product's structure. On the other hand, the presence of the respective molecular peaks in MS indicates the presence of the desired product.

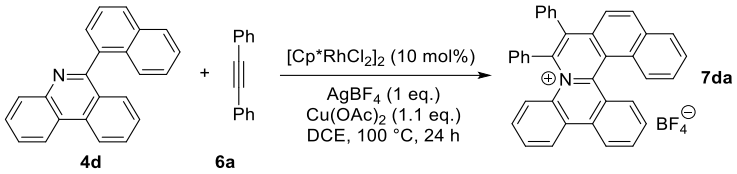


LC-MS calculated for $C_{36}H_{19}NF_9$ (M^+) 636.14, found 636.19.

A comment regarding isolation and characterization of compounds 7ac, 7ca, 7cb, and 7cc. These compounds were not stable. To avoid higher temperature induced decomposition, evaporation of volatiles after column chromatography was carried out at room temperature (20-25 °C). Although, TLC of freshly isolated samples indicated the presence of an individual compounds, repeating analysis of the same sample after 1-5 minutes indicated formation of numerous products. Attempts to isolate any of decomposition products were not successful. Change of the tetrafluoroborate anion for the chloride one did not have any positive effect on behavior of the quinolizinium salts.

3.2. Synthesis of benzo[7,8]isoquinolino[2,1-*f*]phenanthridin-5-ium salts

Table S5. Screening of additives' amounts in the C–H bond activation/annulation reaction of **4d** with **6a**.

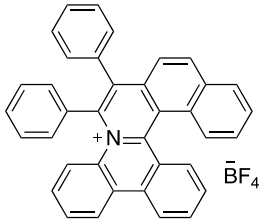


Entry	**3d** (eq.)	$AgBF_4$ (eq.)	$Cu(OAc)_2$ (eq.)	Yield (%)[a]
1	1	1	1	27
2	2	1.35	2	30
3	1	1	2	22
4	1	1	1.1	29[b]
5	1	1	0.2	8

[a]Isolated yields. [b] These reaction conditions are regarded as „Procedure D" and full experimental details are given below.

Procedure D Phenanthridine **4a-4c** (0.30 mmol), alkyne **6a-6c** (0.30 mmol), $[Cp^*RhCl_2]_2$ (0.03 mmol, 19 mg), $AgBF_4$ (0.30 mmol, 58 mg) and $Cu(OAc)_2 \cdot H_2O$ (0.33 mmol, 66 mg) were dissolved in DCE (5 mL). A reaction mixture was heated at 100 °C for 24 h. After cooling down to 25 °C, the reaction mixture was filtered through a pad of Celite and washed with DCM (200 mL). Volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (DCM/MeOH, 100/1 → 20/1) provided the respective products. The products were further purified by precipitation from DCM solutions with cyclohexane.

6,7-Diphenylbenzo[7,8]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7da).



Procedure D. 6-(Naphthalen-1-yl)phenanthridine (**4d**) (0.30 mmol, 92 mg) and diphenylethyne (**6a**) (0.30 mmol, 54 mg) were used. Column chromatography of the residue on silica gel provided 50 mg (29%) of the title compound as a yellow solid. Precipitation provided 23 mg (14%) of the title compound as a yellow powder.

M.p. ~ 300 °C;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 7.5 Hz, 1H), 8.64 (d, *J* = 8.0 Hz, 1H), 8.61 (d, *J* = 7.8 Hz, 1H), 8.52 (d, *J* = 7.2 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.10 (t, *J* = 6.9 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.96 (d, *J* = 6.5 Hz, 1H), 7.85 (d, *J* = 5.4 Hz, 1H), 7.80–7.70 (m, 3H), 7.68

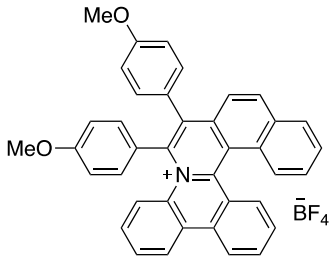
(t, *J* = 6.3 Hz, 1H) 7.63 (t, *J* = 6.7 Hz, 1H), 7.60 (br s, 1H), 7.52 (t, *J* = 7.0 Hz, 1H), 7.43–7.34 (m, 2H), 7.23 (br s, 2H), 7.16 (t, *J* = 7.1 Hz, 1H), 7.09 (br s, 1H), 6.74 (d, *J* = 6.5 Hz, 1H), 6.71 (d, *J* = 7.0 Hz, 1H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 153.4, 145.9, 139.1, 138.6, 136.9, 135.9, 135.1, 134.1, 133.8, 133.7, 133.2, 132.8, 131.2, 130.6, 130.4, 130.32, 130.27, 129.9, 129.73, 129.65, 129.3, 129.1, 129.0, 128.94, 128.88, 128.77, 128.5, 127.7, 127.0, 125.9, 124.5, 124.1, 123.5, 123.0;

IR (KBr) ν_{max} 1078, 1043, 1034, 839, 754, 741, 721, 704, 681, 582, 540, 515, 484, 467, 449 cm^{-1};

HRMS (ESI) *m*/*z* calculated for $C_{37}H_{24}N$ $[M]^+$ 482.1903, found 482.1910.

6,7-Bis(4-methoxyphenyl)benzo[7,8]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7db).



Procedure D. 6-(Naphthalen-1-yl)phenanthridine (**4d**) (0.30 mmol, 92 mg) and 1,2-bis(4-methoxyphenyl)ethyne (**6b**) (0.30 mmol, 72 mg) were used. Column chromatography of the residue on silica gel provided 59 mg (31%) of the title compound as an orange solid. Precipitation provided 20 mg (11%) of the title compound as an orange powder.

M.p. 170-180 °C;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.0 Hz, 1H), 8.55 (d, *J* = 8.6 Hz, 2H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 8.9 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 8.01 (t, *J* = 7.4 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.78–7.72 (m, 2H), 7.68–7.65 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H), 3.74 (s, 3H);

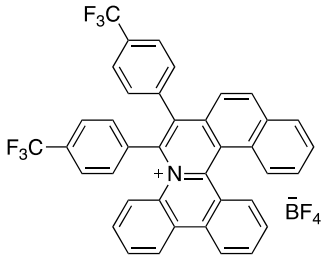
^{13}C NMR (150 MHz, $CDCl_3$) δ 160.6, 159.9, 152.7, 146.4, 139.5, 138.4, 136.6, 135.6, 134.4, 134.2, 133.59, 133.56, 132.54, 132.4, 131.3, 130.4, 130.3, 130.2, 129.5, 129.3, 128.9, 128.8, 128.6, 127.7, 127.6, 126.4, 125.8, 125.7, 124.5, 124.0, 123.2, 123.1, 114.8, 114.6, 114.4, 114.1, 55.53, 55.51;

IR (KBr) ν_{max} 1606, 1514, 1248, 1178, 1051, 1024, 835, 760, 746, 552, 521 cm^{-1};

HRMS (ESI) *m*/*z* calculated for $C_{39}H_{28}NO_2$ $[M]^+$ 542.2115, found 542. 2118.

6,7-Bis(4-(trifluoromethyl)phenyl)benzo[7,8]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7dc).

Procedure D. 6-(Naphthalen-1-yl)phenanthridine (**4d**) (0.30 mmol, 92 mg) and 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (**6c**) (0.30 mmol, 94 mg) were used. Column chromatography of the residue on silica gel provided 45 mg (21%) of the title compound as a yellow-green solid. Precipitation was not successful.



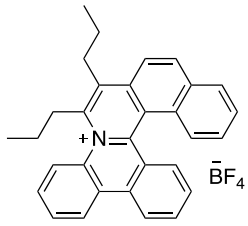
M.p. 170-180 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.5 Hz, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 8.51 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.32–8.25 (m, 2H), 8.04 (d, *J* = 7.7 Hz, 1H), 8.01–7.93 (m, 2H), 7.88 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.74 (ddd, *J* = 7.9, 7.1, 0.8 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.54–7.45 (m, 3H), 7.40 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.32–7.24 (m, 2H (3H, the signal is partially cover by the signal of residual $CHCl_3$), 6.98 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H);

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.0, 144.1, 138.7, 138.4, 138.3 (q, *J* = 1.5 Hz), 137.6 (q, *J* = 1.1 Hz), 135.67, 135.59, 133.69, 133.68, 133.2, 133.0, 131.4 (q, *J* = 34.0 Hz), 131.3, 130.6, 130.5, 130.4, 130.3, 129.7, 129.4, 129.3, 128.99, 128.97, 128.7, 127.7, 127.4, 126.0 (q, *J* = 3.7 Hz), 125.8, 125.7 (q, *J* = 3.7 Hz), 125.5 (q, *J* = 3.5 Hz), 124.7, 124.3, 124.0, 123.60, 123.59, 123.0, 122.6, 122.5;

IR (powder) ν_{max} 1709, 1618, 1607, 1582, 1423, 1408, 1359, 1321, 1112 cm^{-1};

HRMS (ESI) *m*/*z* calculated for $C_{39}H_{22}F_6N$ $[M]^+$ 618.1664, found 618.1660.



6,7-Dipropylbenzo[7,8]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7dd).

Procedure D. 6-(Naphthalen-1-yl)phenanthridine (**4d**) (0.30 mmol, 92 mg) and oct-4-yne (**6d**) (0.30 mmol, 44.0 μL) were used. Column chromatography of the residue on silica gel provided 103 mg (68%) of the title compound as a yellow solid. Precipitation provided 56 mg (37%) of the title compound as a dark yellow powder.

M.p. 123-124 °C;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.0 Hz, 1H), 8.60 (d, *J* = 7.9 Hz, 1H), 8.51 (d, *J* = 8.9 Hz, 1H), 8.47 (d, *J* = 8.5 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.21 (d, *J* = 9.1 Hz, 1H), 8.14 (d, *J* = 8.1 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.01 (t, *J* = 7.5 Hz, 1H), 7.96 (t, *J* = 7.4 Hz, 1H), 7.90 (t, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 3.82–3.74 (m, 1H), 3.61–3.54 (m, 1H), 3.42–3.35 (m, 1H), 3.34–3.27 (m, 1H), 2.06–1.98

(m, 1H), 1.92–1.83 (m, 1H), 1.60–1.53 (m, 1H), 1.53–1.45 (m, 1H) 1.28 (t, J = 7.2 Hz, 3H), 0.74 (t, J = 7.3 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 148.2, 139.1, 138.4, 135.5, 135.4, 133.3, 133.2, 131.5, 130.7, 130.1, 129.83, 129.78, 129.6, 129.5, 129.4, 128.7, 128.5, 128.0, 125.7, 125.5, 125.1, 124.0, 122.4, 120.7, 35.0, 31.4, 24.4, 24.0, 14.8, 13.8;

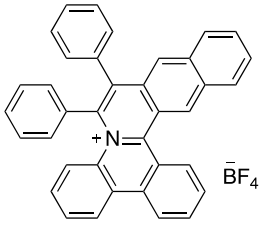
IR (KBr) ν_{max} 1576, 1419, 1406, 1047, 1030, 837, 768, 754, 723, 521 cm^{-1};

HRMS (ESI) m/z calculated for $C_{31}H_{28}N$ $[M]^+$ 414.2216, found 414.2219.

3.3. Synthesis of benzo[6,7]isoquinolino[2,1-*f*]phenanthridin-5-ium salts

6,7-Diphenylbenzo[6,7]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7ea).

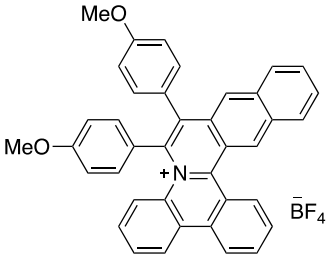
Procedure D. 6-(Naphthalen-2-yl)phenanthridine (**4e**) (0.30 mmol, 92 mg) and diphenylacetylene (**6a**) (0.30 mmol, 54 mg) were used. Column chromatography of the residue on silica gel provided 115 mg (67%) of a dark red solid. Precipitation provided 58 mg (34%) of a dark red solid. Its immediate TLC analysis showed one spot only. However, the isolated solid turned out to be unstable and almost immediately (within a minute after isolation) it started to succumb to degradation into numerous species, which was indicated by TLC analysis (multiple spots were observed). The rather fast degradation did not allow to record ^{1}H and ^{13}C of reasonable quality to unequivocally confirm the product's structure. On the other hand, the presence of the respective molecular peaks in MS indicates the presence of the desired product.



HRMS (ESI) *m*/*z* calculated for $C_{37}H_{24}N$ $[M]^+$ 482.1903, found 482.1904.

6,7-Bis(4-methoxyphenyl)benzo[6,7]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7eb).

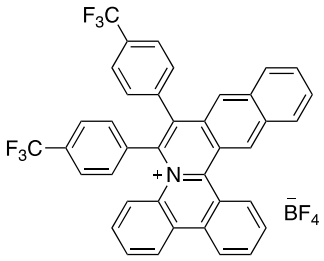
Procedure D. 6-(Naphthalen-2-yl)phenanthridine (**4e**) (0.30 mmol, 92 mg) and 1,2-bis(4-methoxyphenyl)ethyne (**6b**) (0.30 mmol, 72 mg) were used. Column chromatography of the residue on silica gel provided 143 mg (76%) of a dark red solid. Precipitation provided 81 mg (43%) of a dark red solid. Its immediate TLC analysis showed one spot only. However, the isolated solid turned out to be unstable and almost immediately (within a minute after isolation) it started to succumb to degradation into numerous species, which was indicated by TLC analysis (multiple spots were observed). The rather fast degradation did not allow to record ^{1}H and ^{13}C of reasonable quality to unequivocally confirm the product's structure. On the other hand, the presence of the respective molecular peaks in MS indicates the presence of the desired product.



HRMS (ESI) *m*/*z* calculated for $C_{39}H_{28}NO_2$ $[M]^+$ 542.2115, found 542.2114.

6,7-Bis(4-(trifluoromethyl)phenyl)benzo[6,7]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7ec).

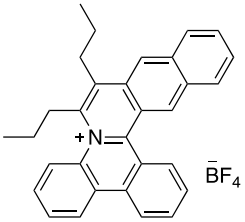
Procedure D. 6-(Naphthalen-2-yl)phenanthridine (**4e**) (0.30 mmol, 92 mg) and 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (**6c**) (0.30 mmol, 94 mg) were used. Column chromatography of the residue on silica gel provided 101 mg (48%) of a dark red solid. Its immediate TLC analysis showed one spot only. However, the isolated solid turned out to be unstable and almost immediately (within a minute after isolation) it started to succumb to degradation into numerous species, which was indicated by TLC analysis (multiple spots were observed). The rather fast degradation did not allow to record ^{1}H and ^{13}C of reasonable quality to unequivocally confirm the product's structure. On the other hand, the presence of the respective molecular peaks in MS indicates the presence of the desired product.



HRMS (ESI) *m*/*z* calculated for $C_{39}H_{22}F_6N$ $[M]^+$ 618.1664, found 618.1662.

6,7-Dipropylbenzo[6,7]isoquinolino[2,1-f]phenanthridin-5-ium tetrafluoroborate (7ed).

Procedure D. 6-(Naphthalen-2-yl)phenanthridine (**4e**) (0.30 mmol, 92 mg) and oct-4-yne (**6d**) (0.30 mmol, 44.0 μL) were used. Column chromatography of the residue on silica gel provided 56 mg (37%) of a red solid. Precipitation provided 56 mg (37%) of a red solid. Its immediate TLC analysis showed one spot only. However, the isolated solid turned out to be unstable and almost immediately (within a minute after isolation) it started to succumb to degradation into numerous species, which was indicated by TLC analysis (multiple spots were observed). The rather fast degradation did not allow to record ^{1}H and ^{13}C of reasonable quality to unequivocally confirm the product's structure. On the other hand, the presence of the respective molecular peaks in MS indicates the presence of the desired product.

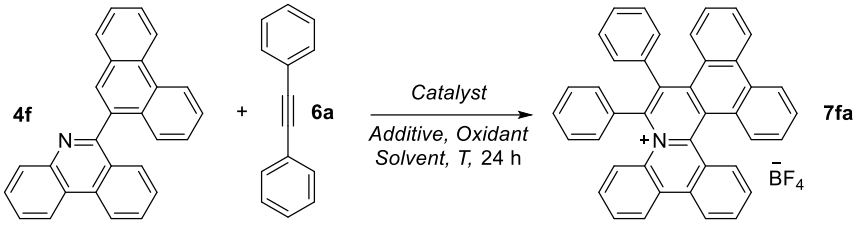


HRMS (ESI) *m*/*z* calculated for $C_{31}H_{28}N$ $[M]^+$ 414.2216, found 414.2217.

3.4. Synthesis of dibenzo[5,6:7,8]isoquinolino[2,1-*f*]phenanthridin-17-ium salts

C–H bond activation in 6-(phenanthren-9-yl)phenanthridine (**4f**) proved to be more challenging than in phenanthridines **4a** and **4b**. A testing reaction of phenanthridine **4f** with diphenylethyne (**6a**) under optimized reaction conditions ($[Cp^*RhCl_2]_2$ (10 mol%) as a catalyst, and $AgBF_4$ (1 eq.), $Cu(OAc)_2$ (1.1 eq.) as additives in DCE at 100 °C for 24 hours) did not proceed as expected (Table S6, Entry 1). According to TLC analyses, some amount of the product was formed, but its separation from the reaction mixture was not successful. Phenanthridine **4f** and diphenylethyne (**6a**) were isolated in almost quantitative amounts. In order to prepare compound **7fa** (18,19-diphenyldibenzo[5,6:7,8]isoquinolino[2,1-f]phenanthridin-17-ium tetrafluoroborate), the reaction was carried out using various reaction conditions to achieve C–H bond activation/annulation sequence.[21] First, as a catalyst was used $[Rh(COD)_2]BF_4$ (20 mol%) with higher loads of additives ($AgBF_4$ (1.35 eq.), $Cu(OAc)_2$ (2 eq.)) (Entry 2). Unfortunately, the outcome of the reaction did not improve. Some product was again formed, but it could not be isolated, and the starting material was recovered in almost quantitative amount. Using $[Cp^*RhCl_2]_2$ (10 mol%) under slightly modified conditions ($NaBF_4$ (1.35 eq.), $Cu(OAc)_2$ (2 eq.) as additives in MeOH at 100 °C for 24 hours) did not work at all (Entry 3). The starting material was fully recovered. The last attempt to synthesize compound **7ca** was done under using milder reaction conditions: $[Cp^*RhCl_2]_2$ (10 mol%), with $NaBF_4$ (5 eq.), $AgBF_4$ (3 eq.) in MeOH at 80 °C for 24 hours (Entry 4). The respective TLC analyses showed that some product was formed, but could not be isolated and phenanthridine **4f** with diphenylethyne (**6a**) were isolated in almost quantitative amounts from the reaction mixture.

Table S6. Screening of conditions for Rh-catalysed C–H activation/annulation sequence in phenanthridine **4f** with diphenylethyne (**6a**).



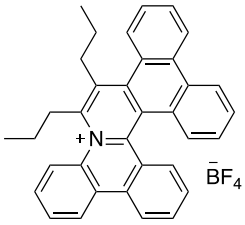
Entry	*Catalyst* (mol%)	*Additive* (eq.)	*T* (°C)	*Oxidant* (eq.)	*Solvent*	Yield (%)[a]
1	$[Cp^*RhCl_2]_2$ (10)	$AgBF_4$ (1)	100	$Cu(OAc)_2$ (1.1)	DCE	0[b]
2	$[Rh(COD)_2]BF_4$ (20)	$AgBF_4$ (1.35)	100	$Cu(OAc)_2$ (2)	DCE	0[b]
3	$[Cp^*RhCl_2]_2$ (10)	$NaBF_4$ (1.35)	100	$Cu(OAc)_2$ (2)	MeOH	0
4	$[Cp^*RhCl_2]_2$ (10)	$NaBF_4$ (5)	80	$AgBF_4$ (3)	MeOH	0[b]

[a] Isolated yields.

[b] Traces of the product.

18,19-Dipropyldibenzo[5,6:7,8]isoquinolino[2,1-f]phenanthridin-17-ium tetrafluoroborate (7fd).

Procedure D. 6-(Phenanthren-9-yl)phenanthridine (**4f**) (0.30 mmol, 107 mg) and oct-4-yne (**6d**) (0.30 mmol, 44.0 μL) were used. Column chromatography of the residue on silica provided 16 mg (10%) of the title compound as a yellow solid. Precipitation provided 13 mg (8%) of the title compound as a yellow powder.



^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84 (d, *J* = 8.4 Hz, 1H), 8.81 (app t, *J* = 9.2 Hz, 2H), 8.77 (d, *J* = 8.3 Hz, 1H), 8.14–8.08 (m, 2H), 8.04–7.99 (m, 2H), 7.88 (ddd, *J* = 8.2, 7.0, 0.9 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.73 (app t, *J* = 7.7 Hz, 2H), 7.53 (app t, *J* = 7.5 Hz, 1H), 7.49 (app t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 2.31–2.20 (m, 2H), 2.12–2.01 (m, 2H), 0.67 (t, *J* = 7.3 Hz, 3H), 0.49–0.40 (m, 2H), 0.09 (t, *J* = 7.3 Hz, 3H), –0.01–(–0.11) (m, 2H);

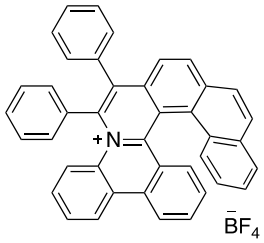
^{13}C NMR: a representative spectrum with good signal to noise ratio could not be obtained due to the insufficient amount of the product.

HRMS (APCI) *m*/*z* calculated for $C_{35}H_{30}N$ $[M]^+$464.2373, found 464.2366.

3.5. Synthesis of naphtho[2',1':7,8]isoquinolino[2,1-f]phenanthridin-5-ium salts

6,7-Diphenylnaphtho[2',1':7,8]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7ga).

Procedure D. 6-(Phenanthren-4-yl)phenanthridine (**4g**) (0.15 mmol, 53 mg), diphenylacetylene (**6a**) (0.15 mmol, 27 mg), $[Cp^*RhCl_2]_2$ (15.0 μmol, 90 mg), $AgBF_4$ (0.15 mmol, 29 mg) and $Cu(OAc)_2$ (0.17 mmol, 31 mg) were dissolved in DCE (5 mL). Stirring reaction mixture was heated at 100 °C for 24 h. After cooling down to 25 °C, the reaction mixture was filtered through a pad of Celite and washed with DCM (200 mL). Volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (DCM/MeOH, 100/1 → 20/1) provided 47 mg (51%) of the title compound as a orange-yellow solid. Precipitation from DCM solution with cyclohexane provided 24 mg (26%) of the title compound as an orange-yellow powder.



M.p. 160-170 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.5 Hz, 1H), 8.46 (d, *J* = 8.1 Hz, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.92–7.87 (m, 2H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.74–7.69 (m, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.37 (dd, *J* = 14.4, 7.3 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.25–7.20 (m, 3H), 7.14 (ddd, *J* = 7.7, 7.7, 0.9 Hz, 1H), 7.11–7.05 (m, 1H), 6.96 (dd, *J* = 15.9, 7.9 Hz, 2H), 6.71 (d, *J* = 7.7 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 145.8, 138.6, 137.8, 136.3, 135.3, 134.38, 134.36, 133.8, 133.7, 133.2, 133.0, 132.6, 132.1, 131.1, 130.6, 129.9, 129.8, 129.7, 129.6, 129.3, 129.12, 129.06, 128.9, 128.72, 128.65, 128.61, 128.55, 128.54, 127.91, 127.87, 127.7, 127.6, 125.74, 125.72, 124.5, 124.1, 123.3, 119.7;

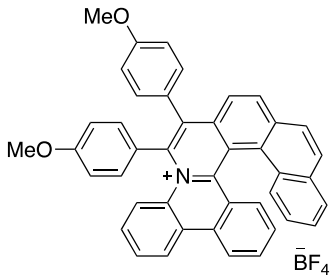
IR (powder) ν_{max} 1603, 1571, 1488, 1478, 1445, 1433, 1400, 1382, 1040 cm^{-1};

HRMS (APCI) *m*/*z* calculated for $C_{41}H_{26}N$ $[M]^+$ 532.2060, found 532.2057.

6,7-Bis(4-methoxyphenyl)naphtho[2',1':7,8]isoquinolino[2,1-f]phenanthridin-5-ium tetrafluoroborate (7gb).

Procedure D. 6-(Phenanthren-4-yl)phenanthridine (**4g**) (0.15 mmol, 53 mg), 1,2-bis(4-methoxyphenyl)ethyne (**6b**) (0.15 mmol, 36 mg), $[Cp^*RhCl_2]_2$ (15 μmol, 9 mg), $AgBF_4$ (0.15 mmol, 29 mg) and $Cu(OAc)_2$ (0.17 mmol, 31 mg) were dissolved in DCE (5 mL). Stirring reaction mixture was heated at 100 °C for 24 h. After cooling down to 25 °C, the reaction

mixture was filtered through a pad of Celite and washed with DCM (200 mL). Volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (DCM/MeOH, 100/1 → 20/1) provided 31.5 mg (31%) of the title compound as a red-orange solid. Precipitation from DCM solution with cyclohexane provided 20 mg (19%) of the title compound as a red-orange powder.



M.p. 150-160 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.2 Hz, 1H), 8.45 (d, *J* = 8.2 Hz, 1H), 8.34 (d, *J* = 9.0 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 9.3 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 1H), 7.16 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.00–6.92 (m, 2H), 6.81 (d, *J* = 7.7 Hz, 1H), 6.72 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.68–6.60 (m, 2H), 6.58 (dd, *J* = 8.5, 1.9 Hz, 1H), 3.86 (s, 3H), 3.76 (s, 3H);

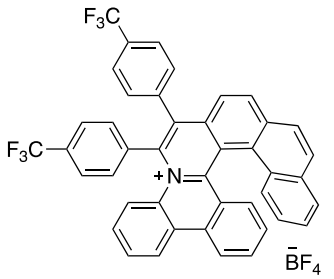
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 159.8, 154.2, 146.2, 139.2, 137.9, 136.2, 134.4, 134.3, 134.0, 133.70, 133.68, 133.2, 132.3, 132.1, 131.3, 130.9, 129.60, 129.55, 129.2, 129.0, 128.72, 128.69, 128.4, 128.3, 128.0, 127.9, 127.7, 127.6, 126.9, 126.3, 125.8, 125.7, 124.6, 124.4, 123.4, 119.5, 114.7, 114.6, 114.4, 114.1, 55.5;

IR (powder) ν_{max} 1608, 1515, 1478, 1401, 1293, 1253, 1180, 1057, 1031 cm^{-1};

HRMS (APCI) *m*/*z* calculated for $C_{43}H_{30}NO_2$ $[M]^+$ 592.2271, found 592.2265.

6,7-Bis(4-(trifluoromethyl)phenyl)naphtho[2',1':7,8]isoquinolino[2,1-f]phenanthridin-5-ium tetrafluoroborate (7gc).

Procedure D. 6-(Phenanthren-4-yl)phenanthridine (**4g**) (56 μmol, 20 mg), 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (**6c**) (56 μmol, 18 mg), $[Cp^*RhCl_2]_2$ (5.6 μmol, 3.5 mg), $AgBF_4$ (56 μmol, 11 mg) and $Cu(OAc)_2$ (62 μmol, 12 mg) were dissolved in DCE (3 mL). Stirring reaction mixture was heated at 100 °C for 24 h. After cooling down to 25 °C, the reaction mixture was filtered through a pad of Celite and washed with DCM (200 mL). Volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (DCM/MeOH, 100/1 → 20/1) provided 8 mg (21%) of the title compound as a yellow-orange solid. Precipitation from DCM solution with cyclohexane provided 7 mg (17%) of the title compound as an orange-yellow powder.



M.p. 250-260 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 8.1, 0.8 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 8.33 (d, *J* = 8.7 Hz, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 9.1 Hz, 1H), 7.89–7.84 (m, 2H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.67–7.60 (m, 3H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 6.4 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H);

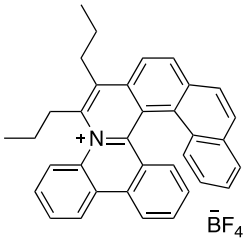
^{13}C NMR (150 MHz, $CDCl_3$) δ 155.3, 143.9, 138.55 (q, *J* = 1 Hz), 138.10 (q, *J* = 1.2 Hz), 138.07, 137.9, 135.1, 134.3, 133.9, 133.7, 133.49, 133.48, 133.2, 132.1, 131.6 (q, *J* = 33.1 Hz), 131.5, 131.1 (q, *J* = 33 Hz), 131.0, 130.99, 130.5, 129.8, 129.73, 129.69, 129.1, 128.9, 128.8, 128.7, 128.5, 128.2, 128.0, 127.9, 127.8, 126.0 (q, *J* = 3.9 Hz), 125.8 (q, *J* = 3.7 Hz), 125.6 (q, *J* = 3.5 Hz), 125.4 (q, *J* = 3.1 Hz), 124.8, 124.4, 124.0, 123.8, 123.0, 122.6, 120.1;

IR (powder) ν_{max} 1618, 1608, 1574, 1403, 1380, 1324, 1166, 1112, 1076, 1064 cm^{-1};

HRMS (APCI) *m*/*z* calculated for $C_{43}H_{24}F_6N$ $[M]^+$ 668.1807, found 668.1800.

6,7-Dipropylnaphtho[2',1':7,8]isoquinolino[2,1-f]phenanthridin-5-ium tetrafluoroborate (7gd).

Procedure D. 6-(Phenanthren-4-yl)phenanthridine (**4g**) (0.11 mmol, 40 mg), oct-4-yne (**6d**) (0.11 mmol, 16 μL), $[Cp^*RhCl_2]_2$ (11.0 μmol, 7 mg), $AgBF_4$ (0.11 mmol, 21 mg) and $Cu(OAc)_2$ (0.12 mmol, 23 mg) were dissolved in DCE (5 mL). Stirring reaction mixture was heated at 100 °C for 24 h. After cooling down to 25 °C, the reaction mixture was filtered through a pad of Celite and washed with DCM (200 mL). Volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (DCM/MeOH, 100/1 → 20/1) provided 12 mg (20%) of the title compound as a yellow-orange solid. Precipitation from DCM solution with cyclohexane provided 11 mg (18%) of the title compound as an orange-yellow powder.



M.p. 100-110 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.58 (d, *J* = 8.9 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.39 (dd, *J* = 8.2, 0.8 Hz, 1H), 8.36 (d, *J* = 8.9 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 8.02–7.95 (m, 2H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.61 (ddd, *J* = 8.2, 7.3, 1.0 Hz, 1H), 7.35 (ddd, *J* = 7.9, 7.1, 0.9 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 7.07 (dd, *J* = 8.4, 0.6 Hz, 1H), 6.93–6.86 (m, 2H), 3.86–3.75 (m, 1H), 3.63–3.53 (m, 1H), 3.48–3.29 (m, 2H), 2.06–1.81 (m, 2H), 1.70–1.58 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.83 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 148.4, 138.3, 137.9, 134.8, 134.3, 133.8, 132.97, 132.95, 132.0, 130.8, 130.4, 129.8, 129.2, 128.8, 128.7, 128.3, 128.2, 128.1, 127.8, 127.4, 125.9, 125.8, 125.6, 125.0, 123.3, 122.0, 118.6, 35.0, 31.6, 24.5, 23.8, 14.9, 14.0;

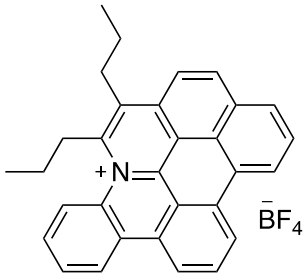
IR (powder) ν_{max} 1605, 1536, 1463, 1431, 1399, 1384, 1254, 1150, 1060 cm^{-1};

HRMS (APCI) *m*/*z* calculated for $C_{35}H_{30}N$ $[M]^+$464.2373, found 464.2367.

4. Scholl reaction

14,15-Dipropylnaphtho[2',1',8':4,5,6]quinolino[1,8,7-fgh]phenanthridin-13-ium tetrafluoroborate (8).

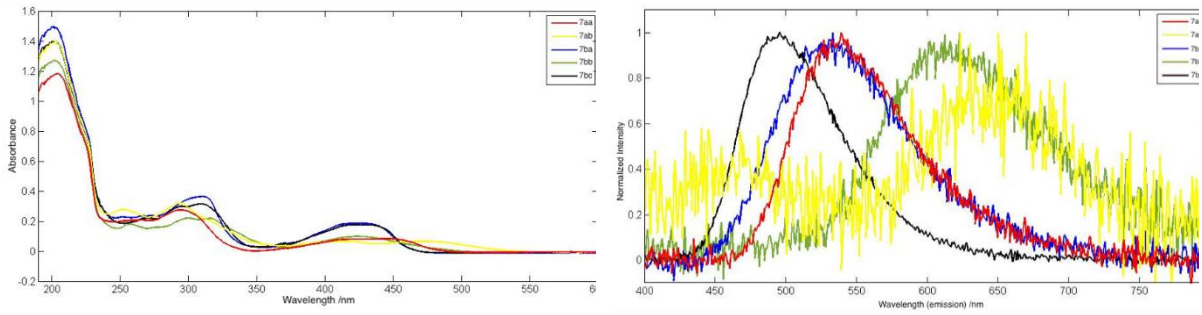
6,7-Dipropylbenzo[7,8]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (**7fd**) (20.0 μmol, 10 mg) and DDQ (0.16 mmol, 36.5 mg) were dissolved in anhydrous DCM (10.5 mL) under argon atmosphere. The resulting stirring solution was cooled down to 0 °C. Trifluoroacetic acid (6.30 mmol, 0.55 mL) was added dropwise and the reaction was left stirring at 0 °C for 30 min. Then, Et_3N (1.2 mL) was added. The reaction mixture was washed with distilled water (3×10 mL) and dried over anhydrous Na_2SO_4. Volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (DCM/MeOH, 100/1 → 20/1) provided 0.71 mg (7%) of a yellow solid. The rather minute amount of the isolated solid did not allow to record ^1H and ^{13}C of reasonable quality to unequivocally confirm the product's structure. On the other hand, the presence of the respective molecular peaks in MS indicates the presence of the desired product.



HRMS (ESI) *m*/*z* calculated for $C_{31}H_{26}N$ $[M]^+$ 412.2060, found 412.2053.

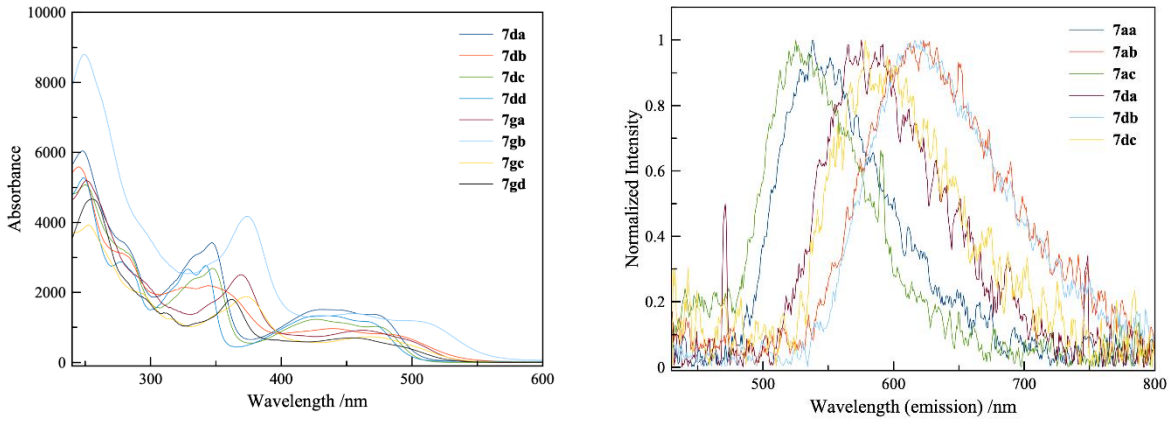
5. Photophysical measurements

The UV/Vis absorption spectra were recorded using Thermo Helios Beta spectrometer as a CH_2Cl_2 solutions (10^{-5} M). Fluorescence emission spectra and emission absolute quantum yields were measured using Hamamatsu Quantaurus-QY Plus UV-NIR absolute PL quantum yield spectrometer C13534 with integrating sphere as a CH_2Cl_2 solutions (10^{-6} M, λ_{exc} = 350 nm)



(**a**) (**b**)

Chart S1. Absorption spectra of compounds **7aa**, **7ab**, and **7ba-7bc** measured in DCM solutions ($c = 10^{-5}$ M) (**1a**). Normalized emission spectra of compounds **7aa**, **7ab**, and **7ba-7bc** (**1b**).



(**a**) (**b**)

Chart S2. Absorption spectra of compounds **7da-7dd** and **7ga-7gd** measured in DCM solutions ($c = 10^{-5}$ M) (**1a**). Normalized emission spectra of compounds **7da-7dc** and **7ga-7gc** (**1b**).

6. Crystallographic data

The diffraction experiments for **sh_67p, sh_68p** and **sh_69p** were performed on Bruker D8 VENTURE Kappa Duo PHOTONIII by IμS micro-focus sealed tube with either MoKα (0.71073) (**sh_68p,sh_69p**) or CuKα (λ= 1.54178) radiation (**sh_67p**) at 150K temperature of the sample The structures were solved by direct methods (XT[22]) and refined by full matrix least squares based on F^2 (SHELXL2018[23]).

The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom), the hydrogen atoms on O were found on difference Fourier map and kept during refinement under the assumption of rigid-body movement with temperature factor $H_{iso}(H) = 1.5\ U_{eq}$(pivot atom).

The real structure of two crystals influenced the precision of results.

1. The sample of **5c** (**sh_67p**) appears to be non-merohedral twin with twin matrix : -1 0 0 ; 0 -1 0; 0.107 0 1 and refined twin ration 0.6:0.4.
2. The four symmetrically independent molecule in unit cell of **4g** (**sh_68p**) are exhibiting large displacement ellipsoids, and therefore producing significant number of weak diffractions resulting in poor precision of results.
3. The symmetry of the molecule of **4f** (**sh_42_p**) enables its two orientation with good overlap of all atoms, where nitrogen is falling into position of carbon of second part of the molecule. This disorder was described by partial occupancy of nitrogen atom.

Table S7. Crystal data, data collection, and refinement parameters for **7da**, **3f**, **3e**, **5c**, **3g**, and **7ga**.

Compound	**7da (sh_43pcr)**	**4f (sh_42_p)**	**4e (sh_55p)**
CCDC	2236123	2236124	2236125
Formula	$C_{37}H_{24}N{\cdot}BF_4$	$C_{27}H_{17}N$	$C_{23}H_{15}N$
M.w.	569.38	355.42	305.36
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$C2/c$	$P2_12_12_1$
a [Å]	10.9809 (3)	14.2839 (7)	4.0016 (1)
b [Å]	16.0022 (5)	10.8710 (6)	17.3408 (5)
c [Å]	16.0342 (4)	12.9148 (10)	21.3147 (6)
α [°]			
β [°]	106.408 (1)	119.080 (2)	
γ [°]			
Z	4	4	4
V[Å^3]	2702.76 (13)	1752.61 (19)	1479.05 (7)
Temperature [K]	120	120	120
Wavelength [Å^3]	0.71073	0.71073	1.54178
D_x [g cm^{-3}]	1.399	1.347	1.371
Crystal size [mm]	0.26×0.24×0.13	0.40×0.20×0.11	0.20×0.07×0.02
Crystal color, shape	Prism, yellow	Prism, colourless	Needle, colourless
μ [mm^{-1}]	0.10	0.08	0.61
T_{min},T_{max}	0.94, 0.99	0.94, 0.99	0.84, 0.99
Measured reflections	41370	57852	16205
Independent diffractions (R_{int}[a])	6200, (0.029)	2028, (0.039)	2872, (0.057)
Observed diffract. [I>2σ(I)]	5420	1875	2525
No. of parameters	388	133	217
R[b]	0.049	0.054	0.036
$wR(F^2)$ for all data	0.127	0.143	0.085
GOF[c]	1.02	1.15	1.05
Residual electron density [e/Å^3]	0.65, −0.48	0.35, −0.20	0.13, -0.19
Disporder in N position	no	yes	no

[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$; [b] $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$; $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$;

[c] $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$

Table S7 cont.

Compound	5c (cu_sh_67p)	4g (mo_sh_68_p)	7ga (mo_sh_69p)
CCDC	2233472	2233473	223374
Formula	$C_{14}H_{11}BO_2$	$8(C_{27}H_{17}N)\cdot 3(CH_2Cl_2)$	$2(C_{41}H_{26}N\cdot BF_4)\cdot CH_2Cl_2$
M.w.	222.04	3098.11	1323.80
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	P-1	$P2_1/n$
a [Å]	5.0472(2)	9.2880 (5)	17.5290 (8)
b [Å]	13.2839(6)	15.0337 (9)	8.0613 (4)
c [Å]	16.0348(7)	29.1305 (19)	22.6605 (11)
α [°]	90	88.378 (2)	90
β [°]	90.967(2)	89.828 (2)	96.985 (2)
γ [°]	90	74.823 (2)	90
Z	4	1	2
V[Å^3]	1074.92(8)	3924.1 (4)	3178.3 (3)
Temperature [K]	150	150	150
Wavelength [Å^3]	1.54178	0.71073	0.71073
D_x [g cm^{-3}]	1.372	1.311	1.383
Crystal size [mm]	0.45×0.10×0.06	0.61×0.18×0.05	0.31×0.24×0.16
Crystal color, shape	Colourless, bar	Colourless, bar	Prism; orange
μ [mm^{-1}]	0.71	0.17	0.18
T_{min},T_{max}	0.830, 0.960	0.770, 0.990	0.820, 0.970
Measured reflections	31537	63562	45632
Independent diffractions (R_{int}[a])	2153 (0.051)	17019, (0.085)	7272, (0.037)
Observed diffract. [I>2σ(I)]	2044	10466	6307
No. of parameters	155	1055	442
R[b]	0.047	0.1184	0.0534
$wR(F^2)$ for all data	0.151	0.304	0.157
GOF[c]	1.11	1.08	1.05
Residual electron density [e/Å^3]	0.25, -0.25	1.00; -1.04	0.44;-1.11
Disporder in N position	no	no	no

[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$; [b] $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$; $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$;

[c] $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$

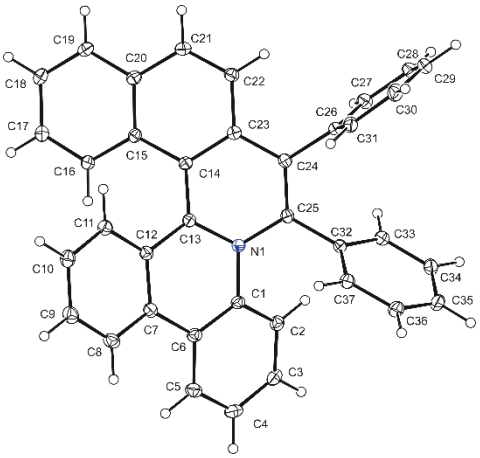


Figure S1. ORTEP drawing of **7da**. Ellipsoids are drawn with 50% probability.

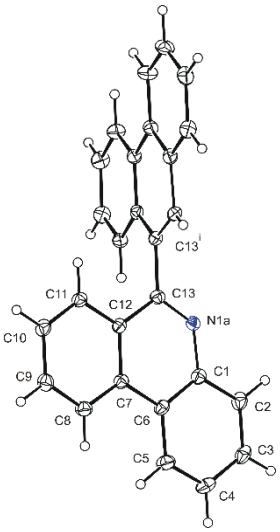


Figure S2. ORTEP drawing of **4f**. Ellipsoids are drawn with 50% probability.

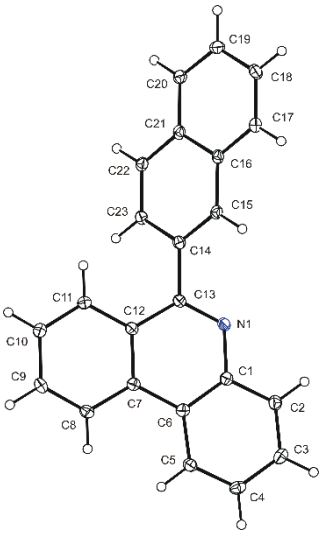


Figure S3. ORTEP drawing of **4e**. Ellipsoids are drawn with 50% probability.

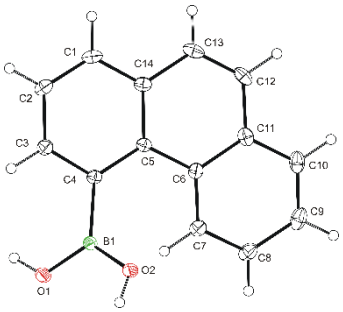


Figure S4. ORTEP drawing of **5c**. Ellipsoids are drawn with 50% probability.

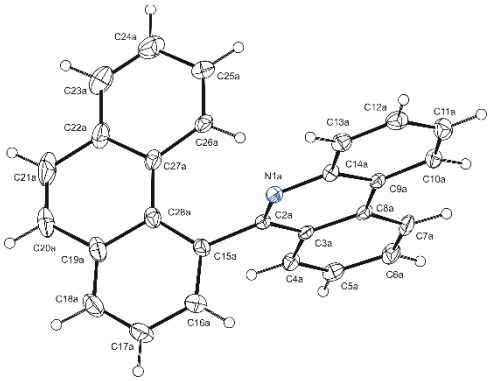


Figure S5. ORTEP drawing of **4g**. Ellipsoids are drawn with 50% probability.

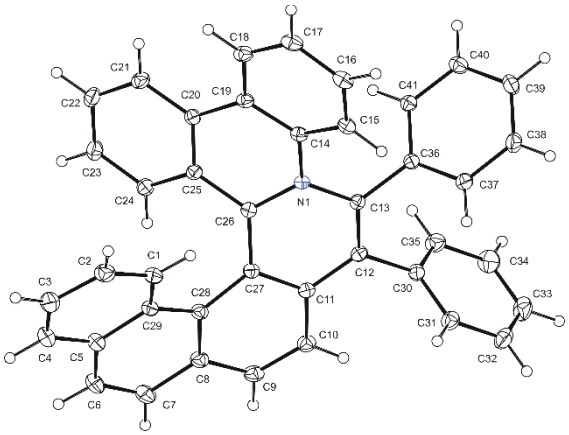
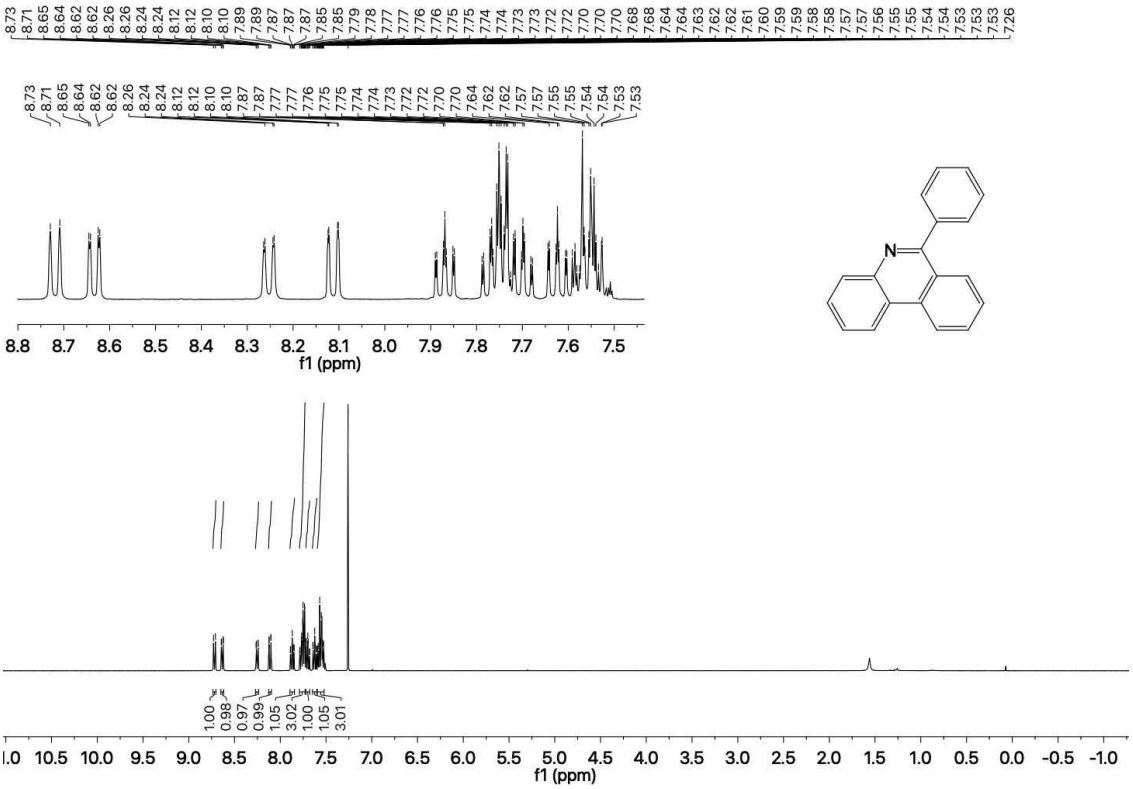


Figure S6. ORTEP drawing of **7ga**. Ellipsoids are drawn with 50% probability.

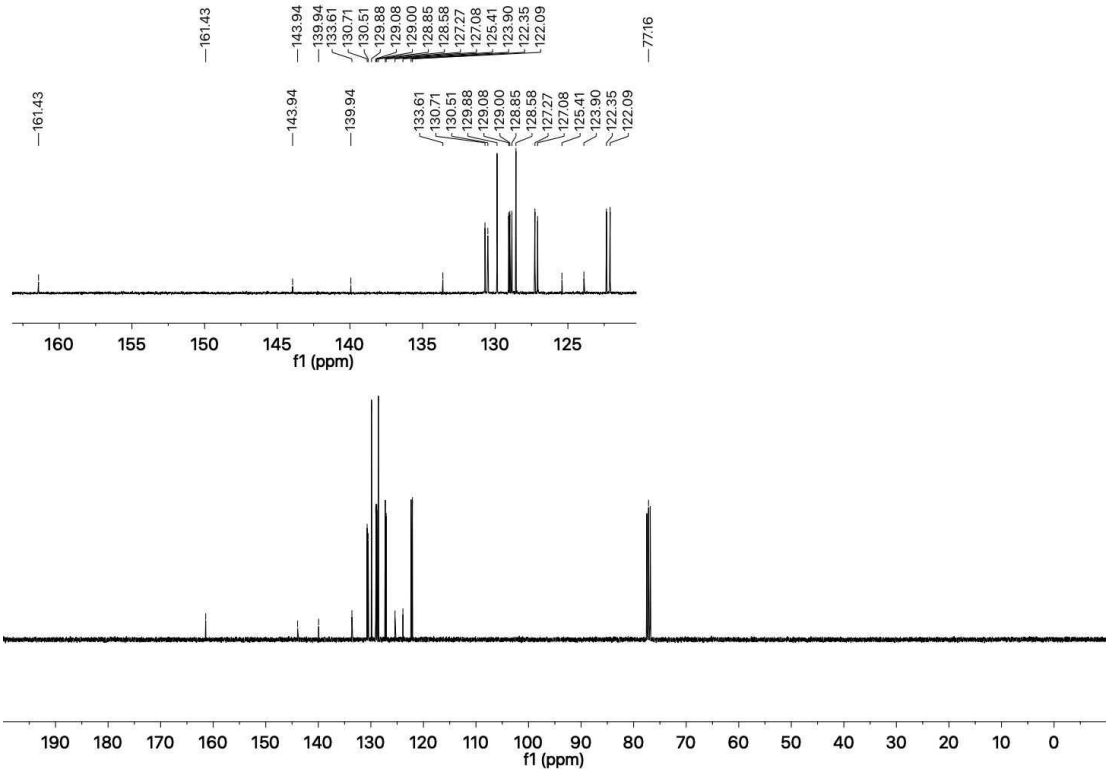
7. Copies of ^{1}H and ^{13}C NMR spectra

6-Phenylphenanthridine (4a).

^{1}H NMR

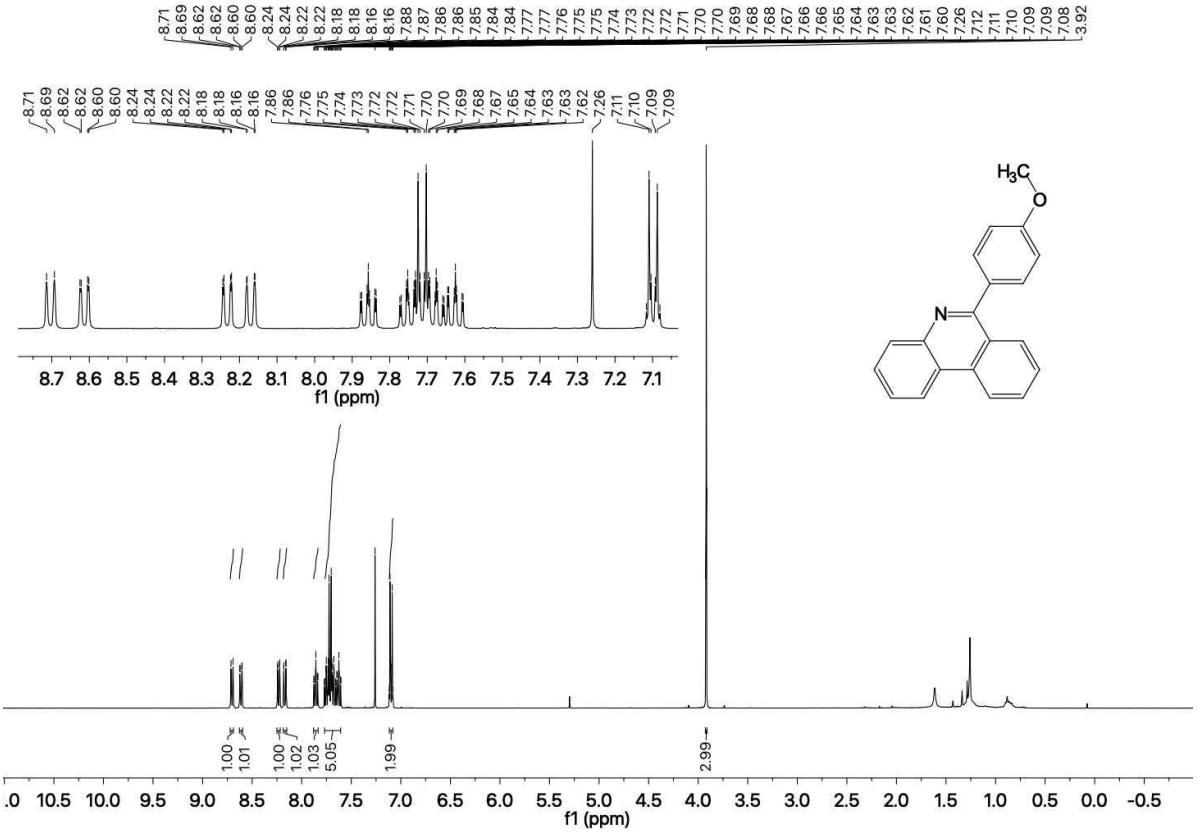


^{13}C NMR

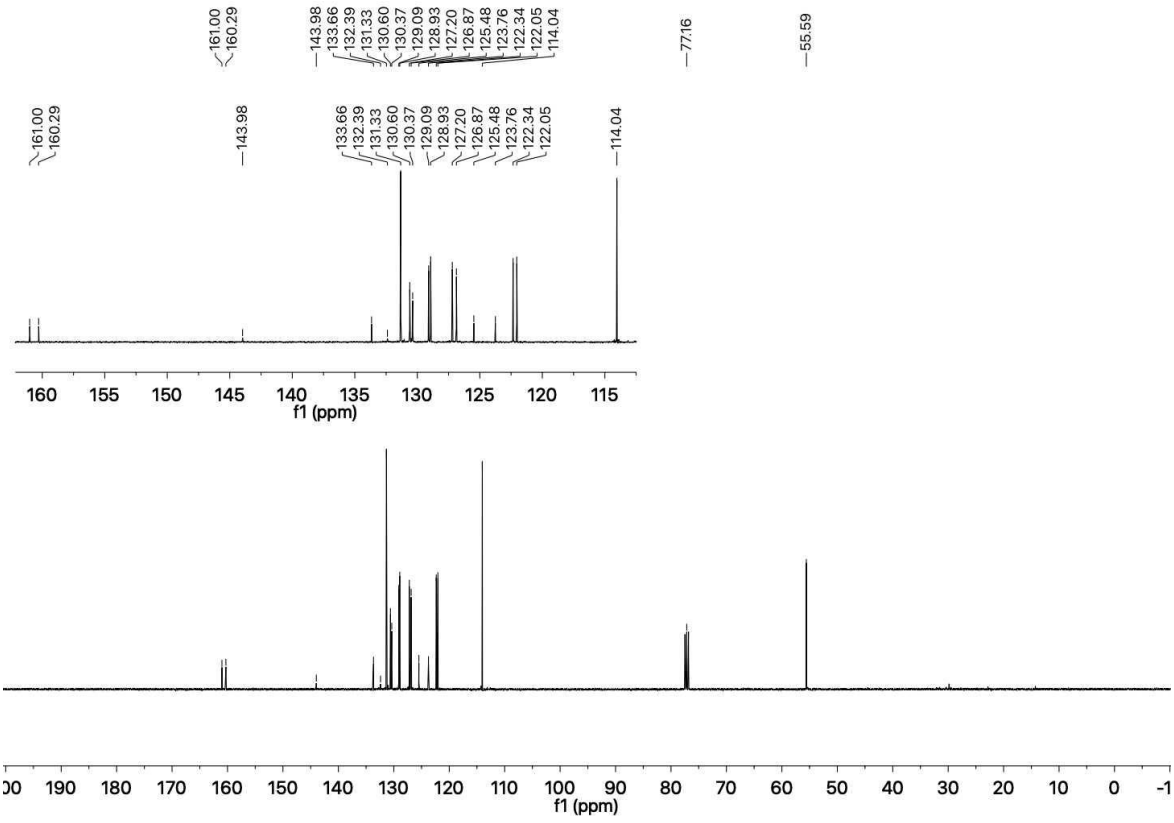


6-(4-Methoxyphenyl)phenanthridine (4b).

^{1}H NMR

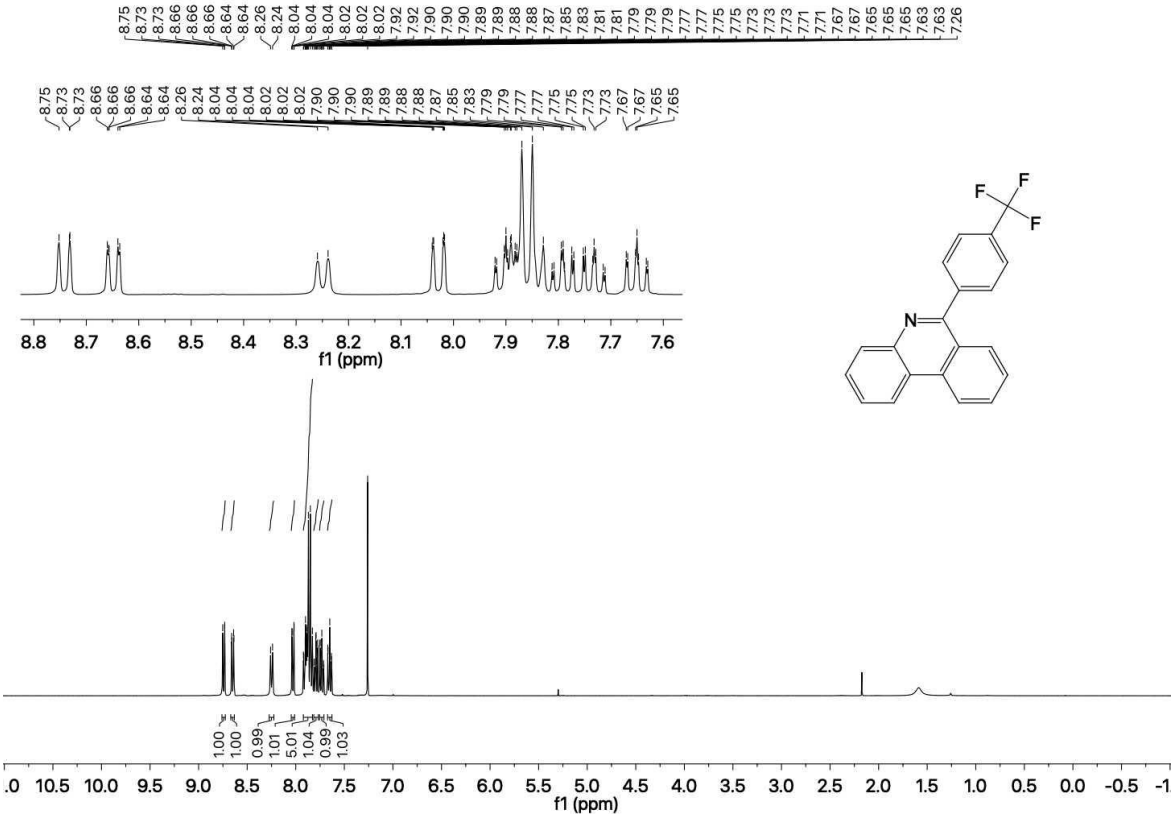


^{13}C NMR

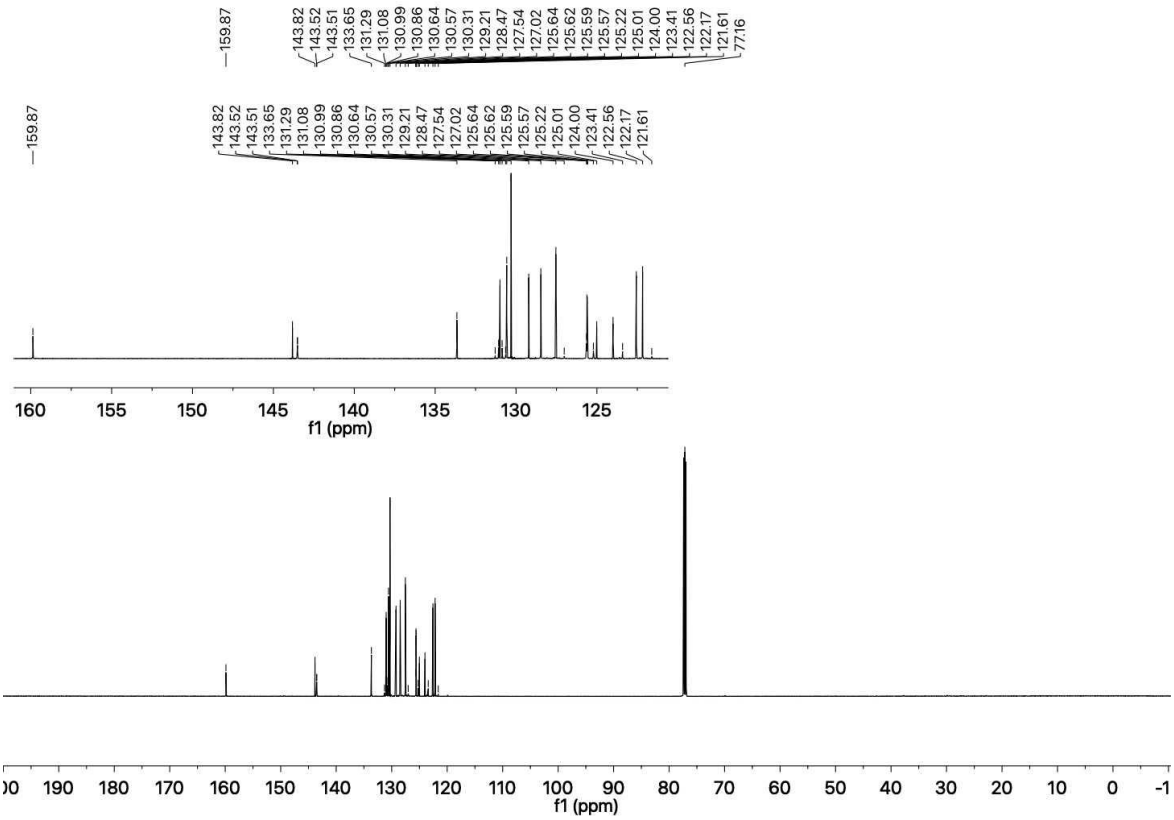


6-(4-Trifluoromethylphenyl)phenanthridine (4c).

^{1}H NMR

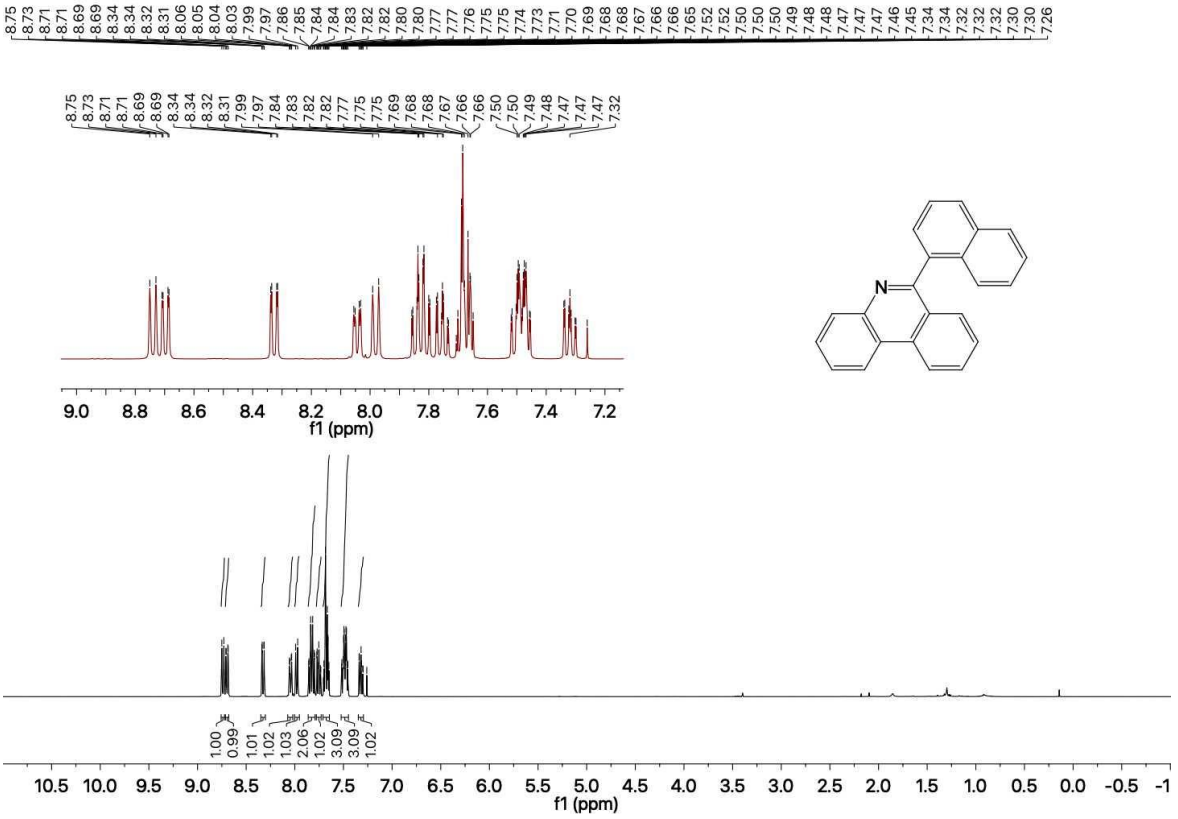


^{13}C NMR

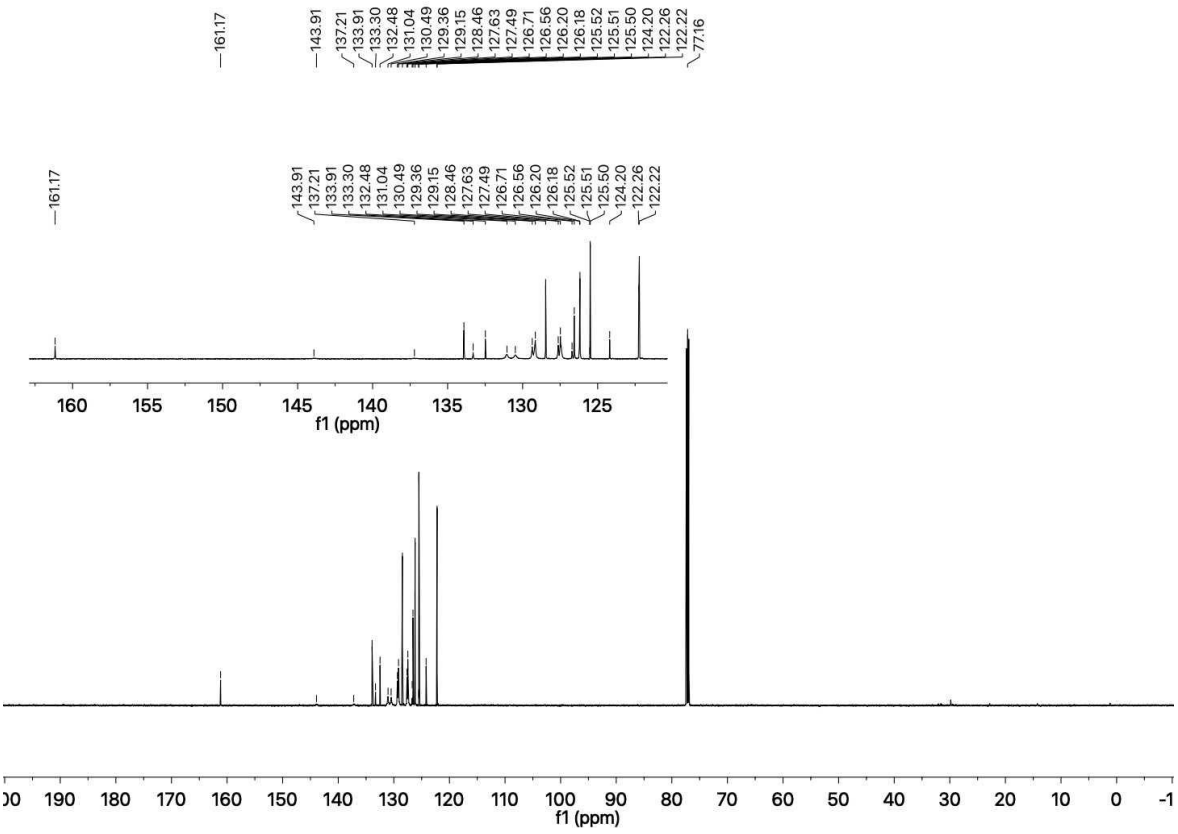


6-(Naphthalen-1-yl)phenanthridine (4d).

^{1}H NMR

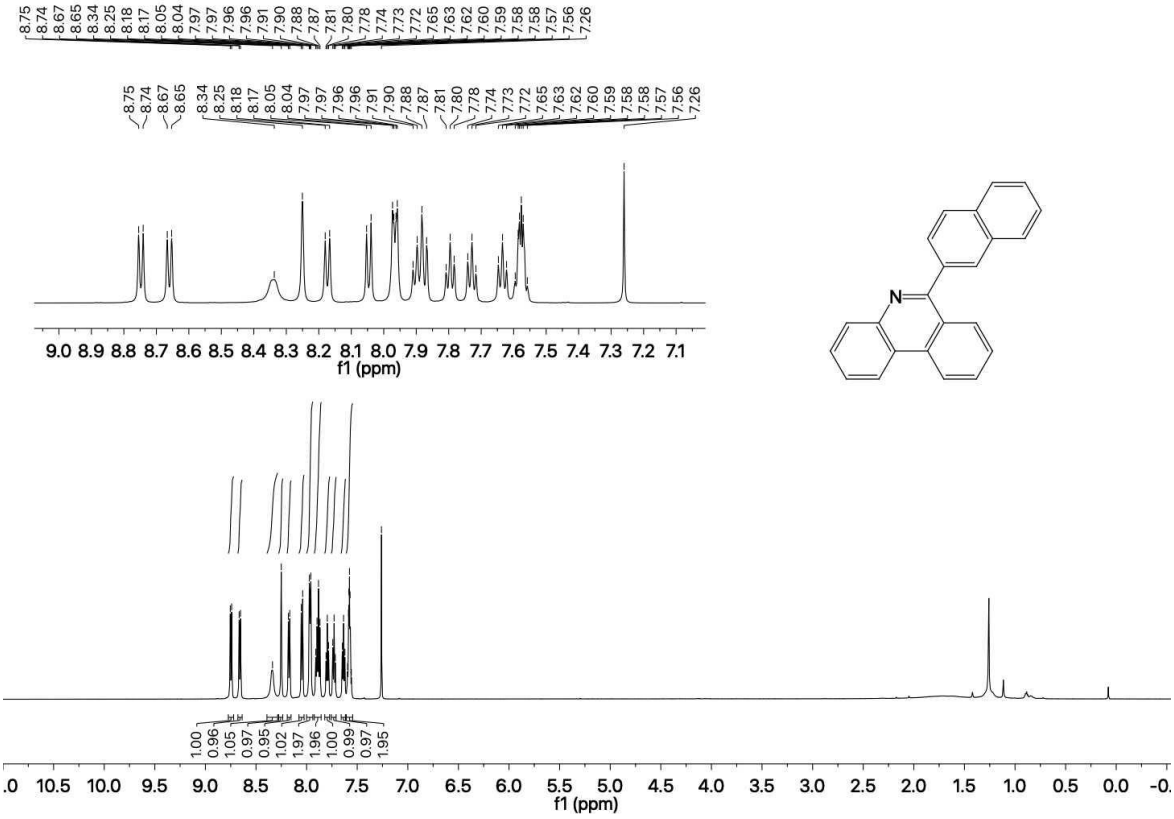


^{13}C NMR

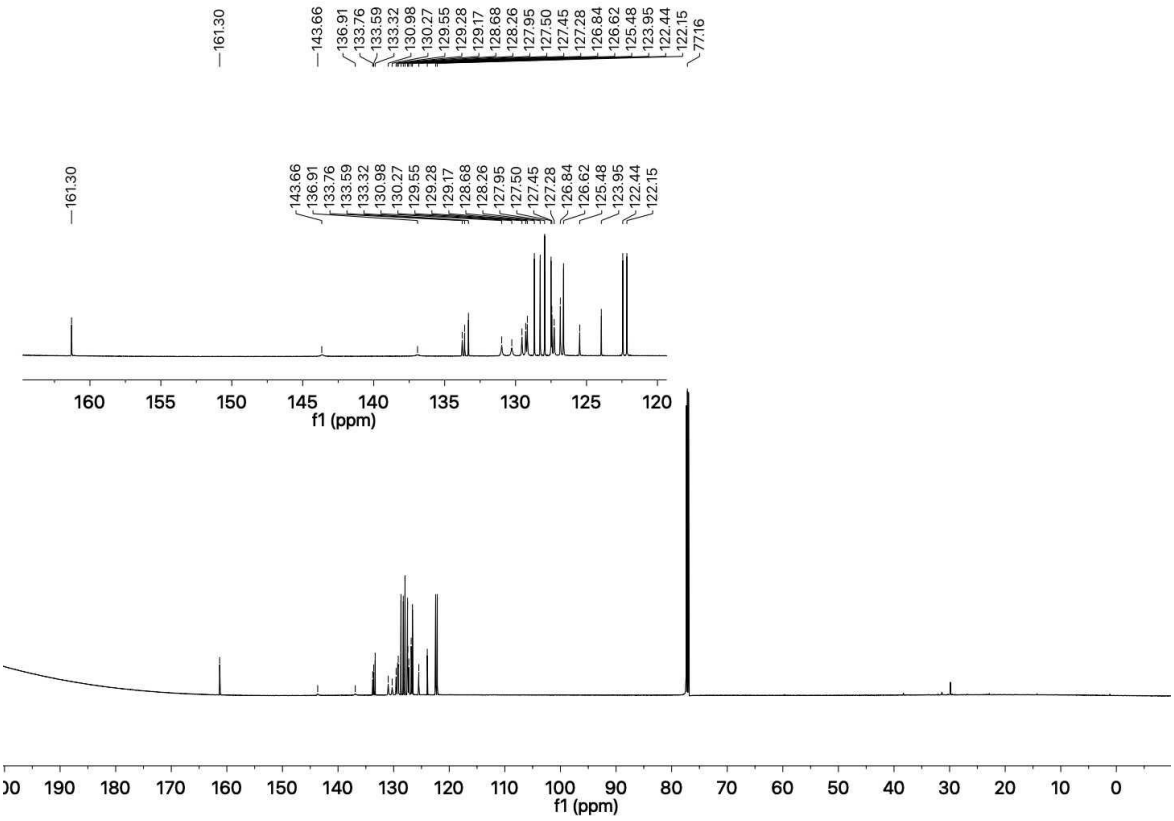


6-(Naphthalen-2-yl)phenanthridine (4e).

^{1}H NMR

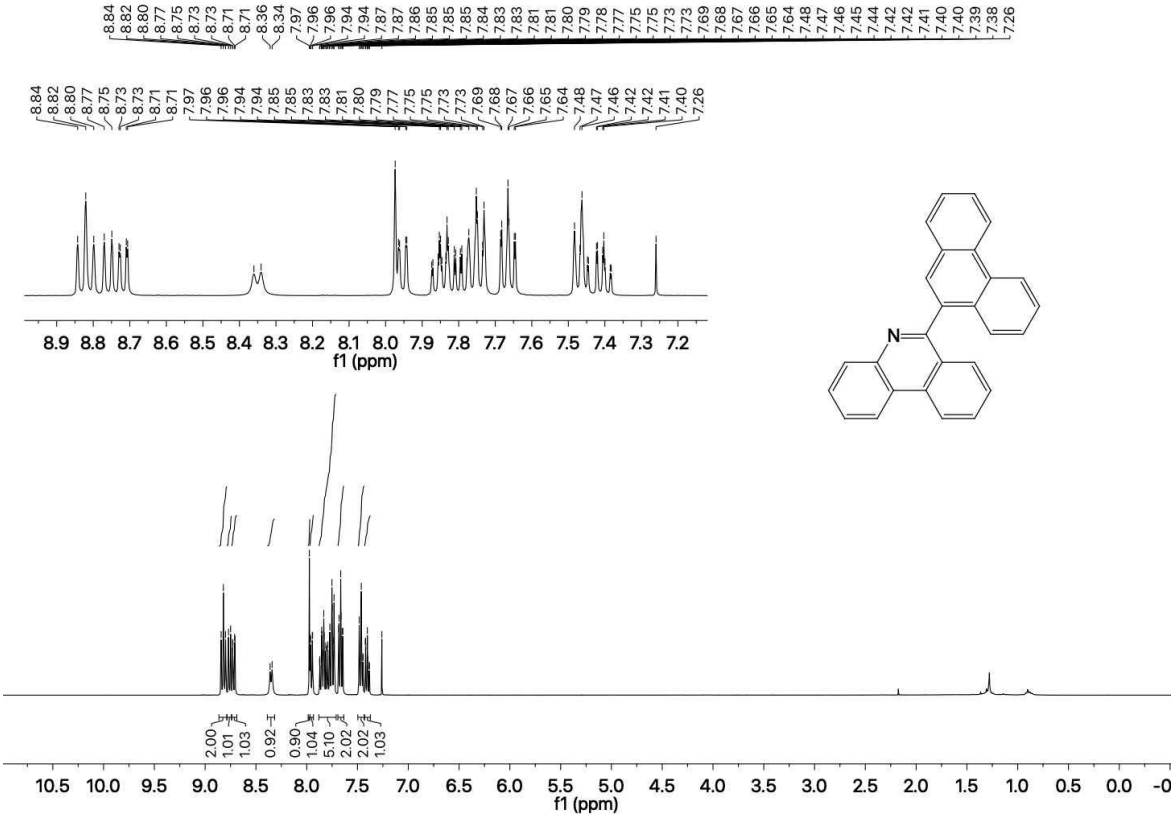


^{13}C NMR

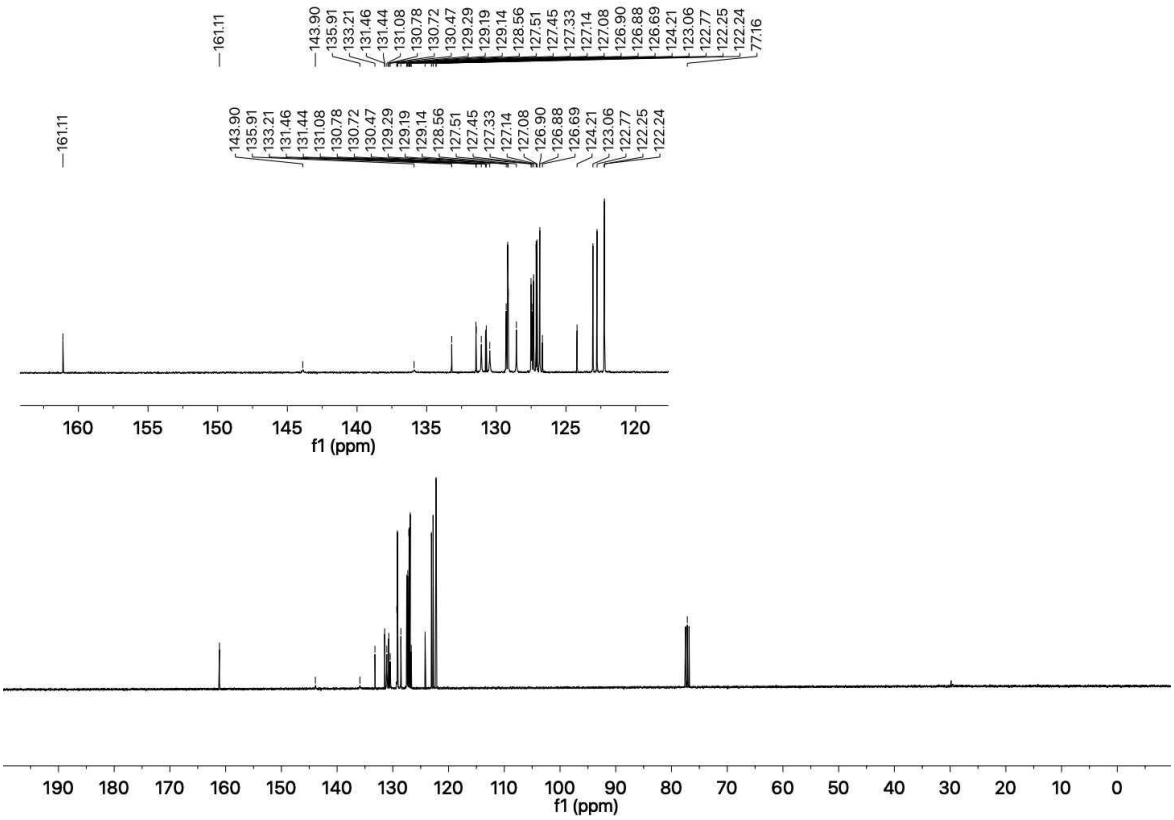


6-(Phenanthren-9-yl)phenanthridine (4f).

^{1}H NMR

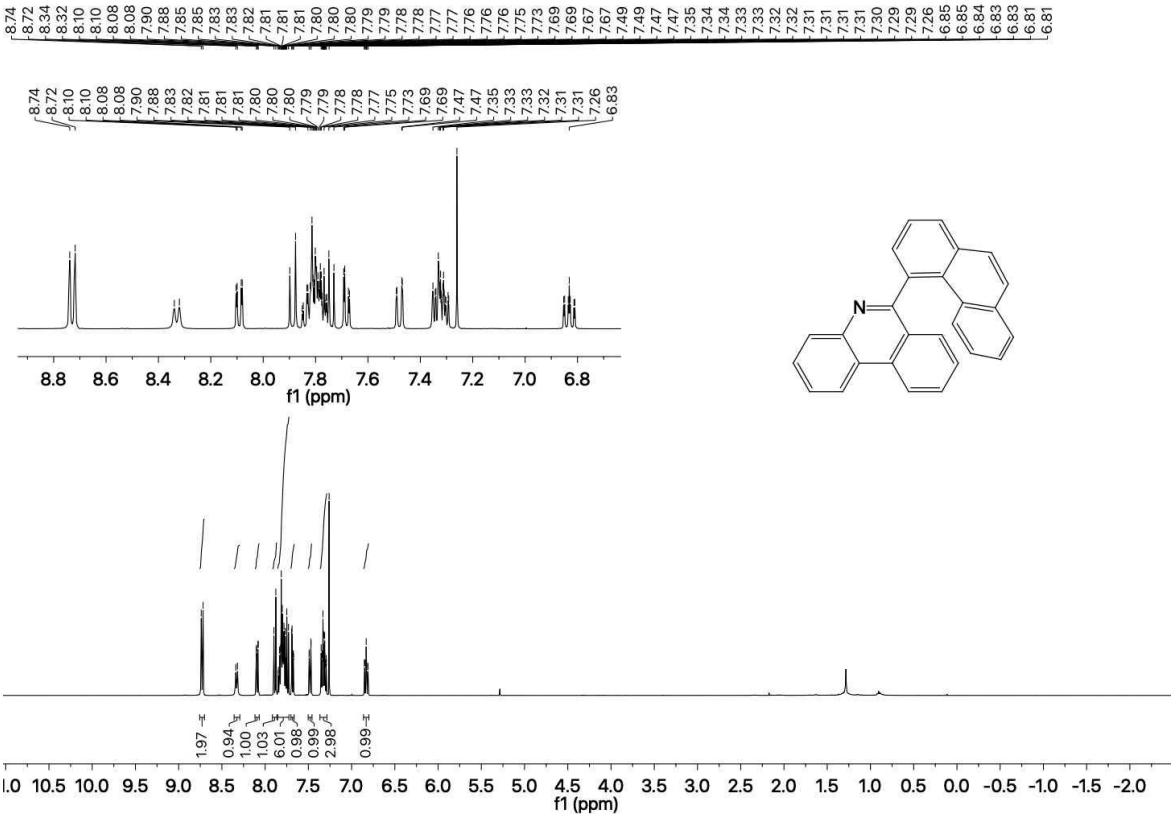


^{13}C NMR

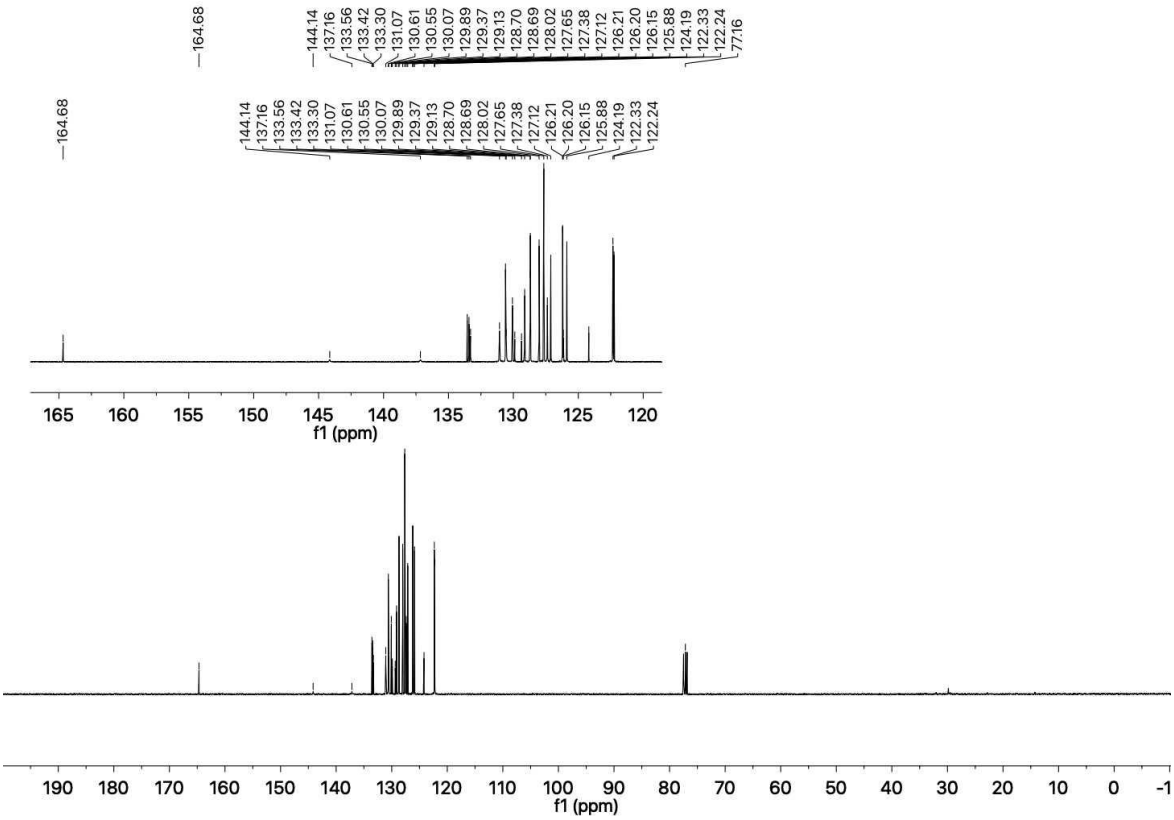


6-(Phenanthren-4-yl)phenanthridine (4g).

^{1}H NMR

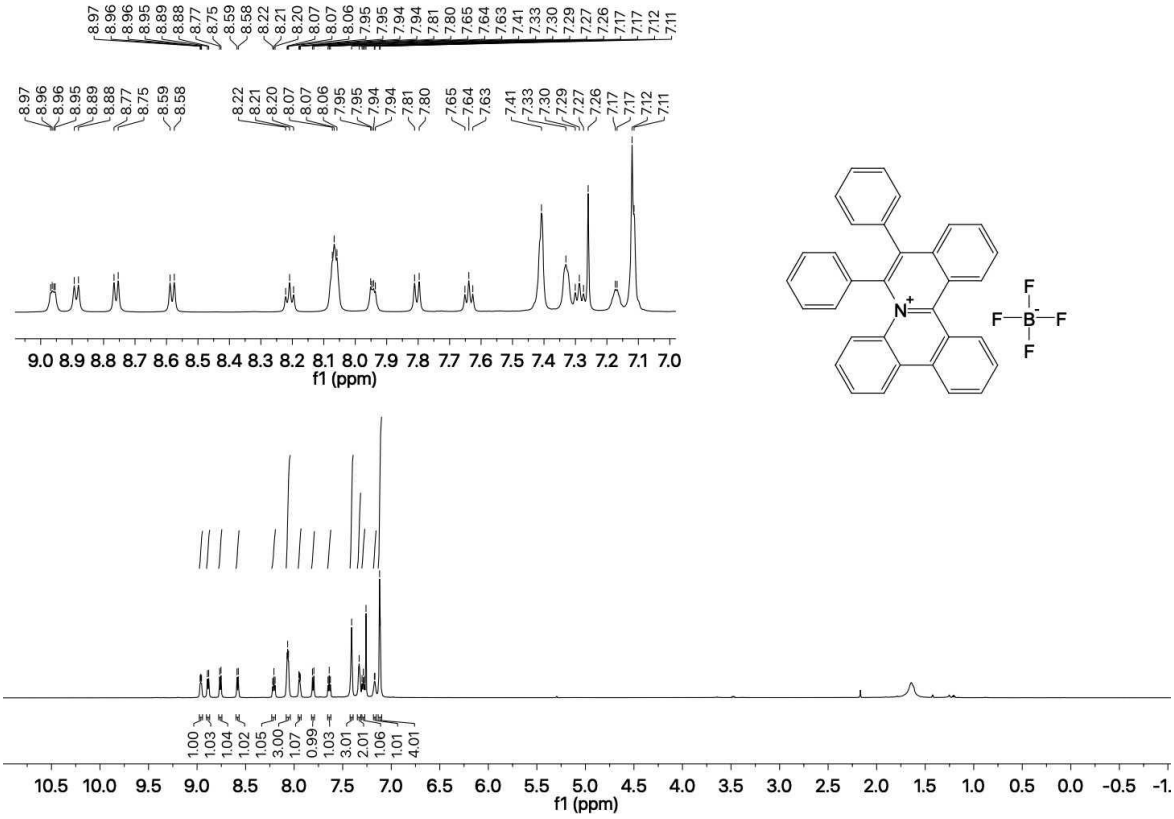


^{13}C NMR

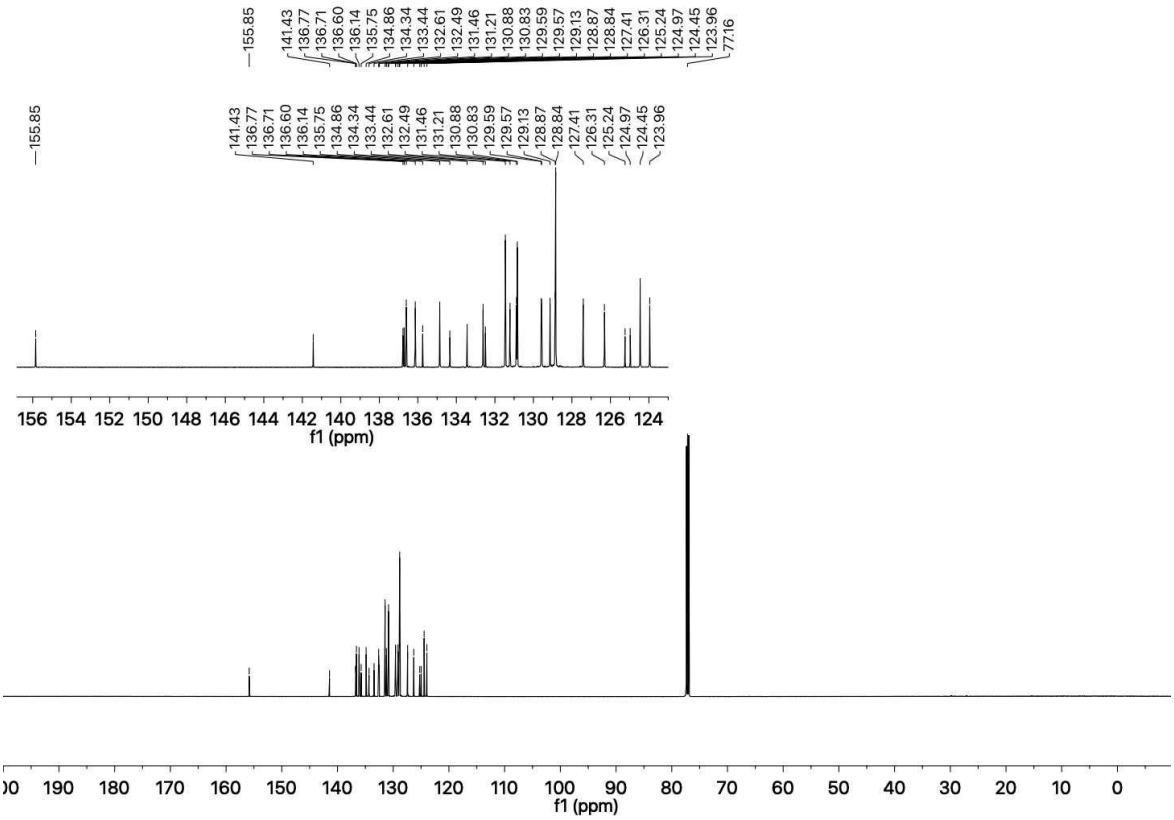


6,7-Diphenylisoquinolíno[2,1-*f*]phenanthridín-5-ium tetrafluoroborate (7aa).

^{1}H NMR

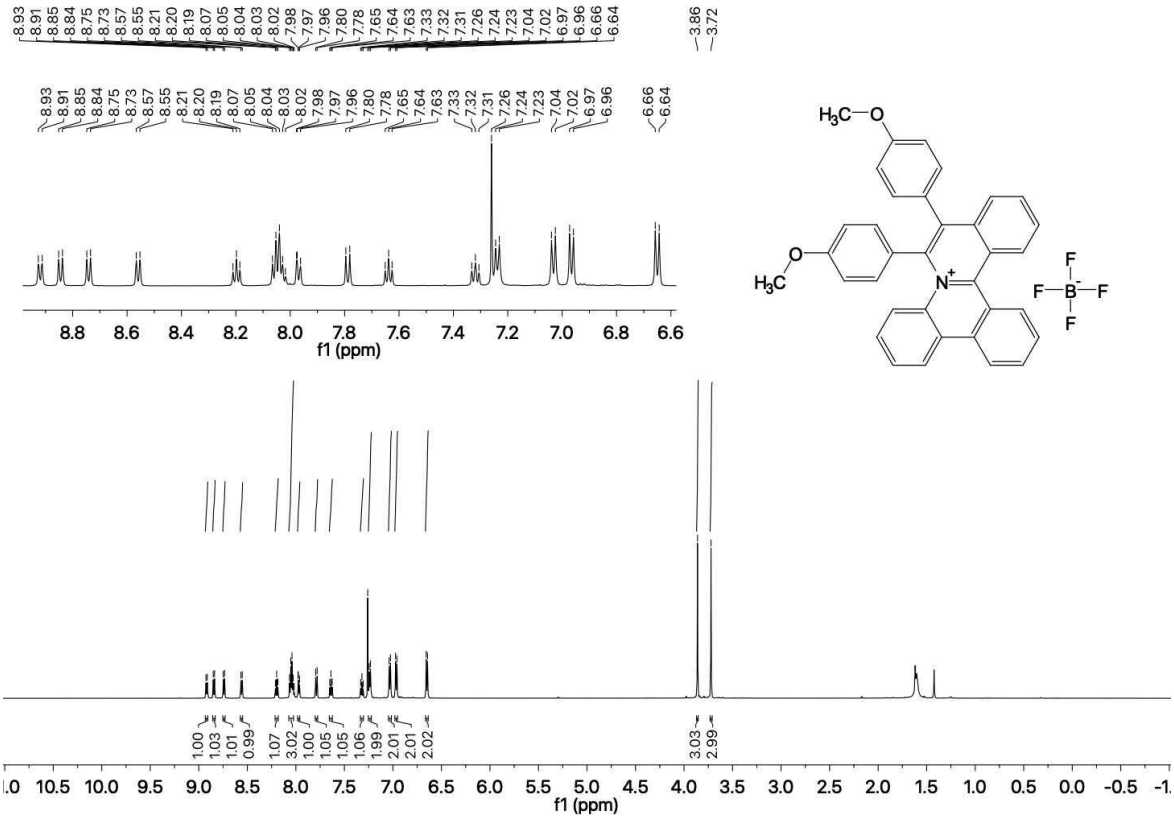


^{13}C NMR

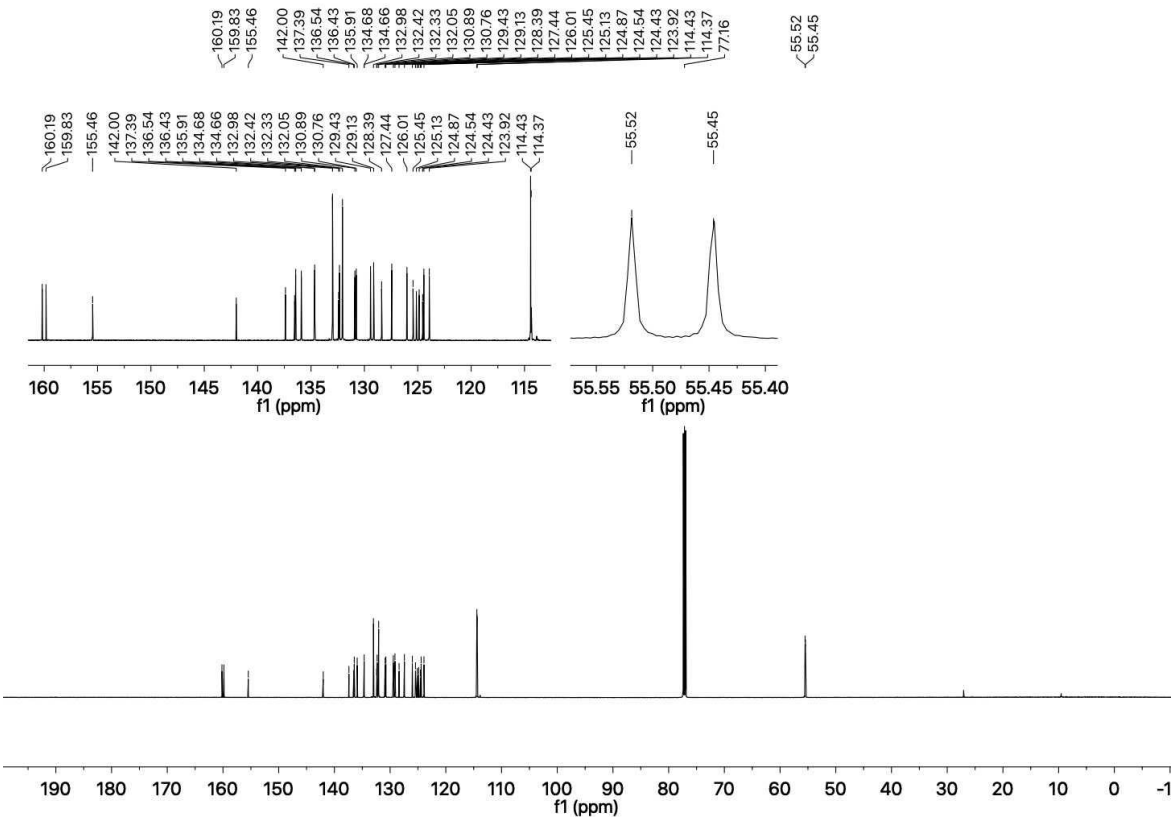


6,7-Bis(4-methoxyphenyl)isoquinolíno[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7ab).

^{1}H NMR

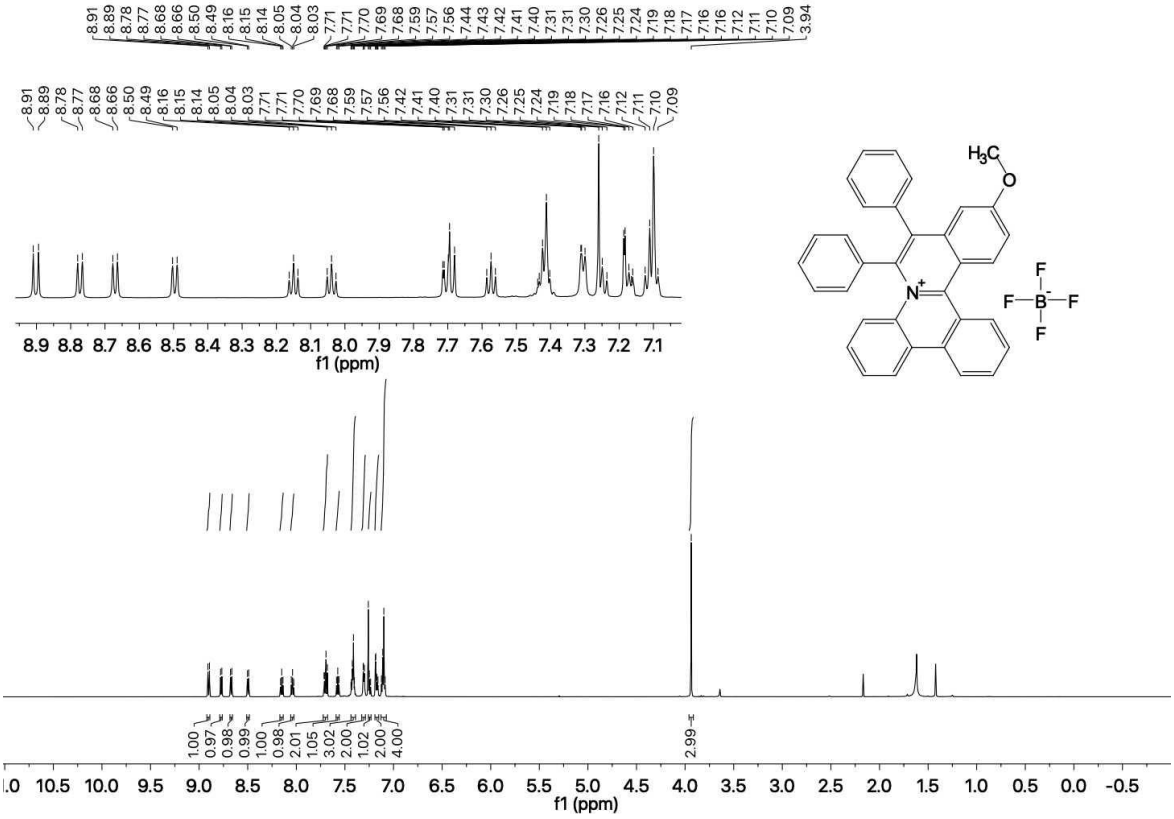


^{13}C NMR

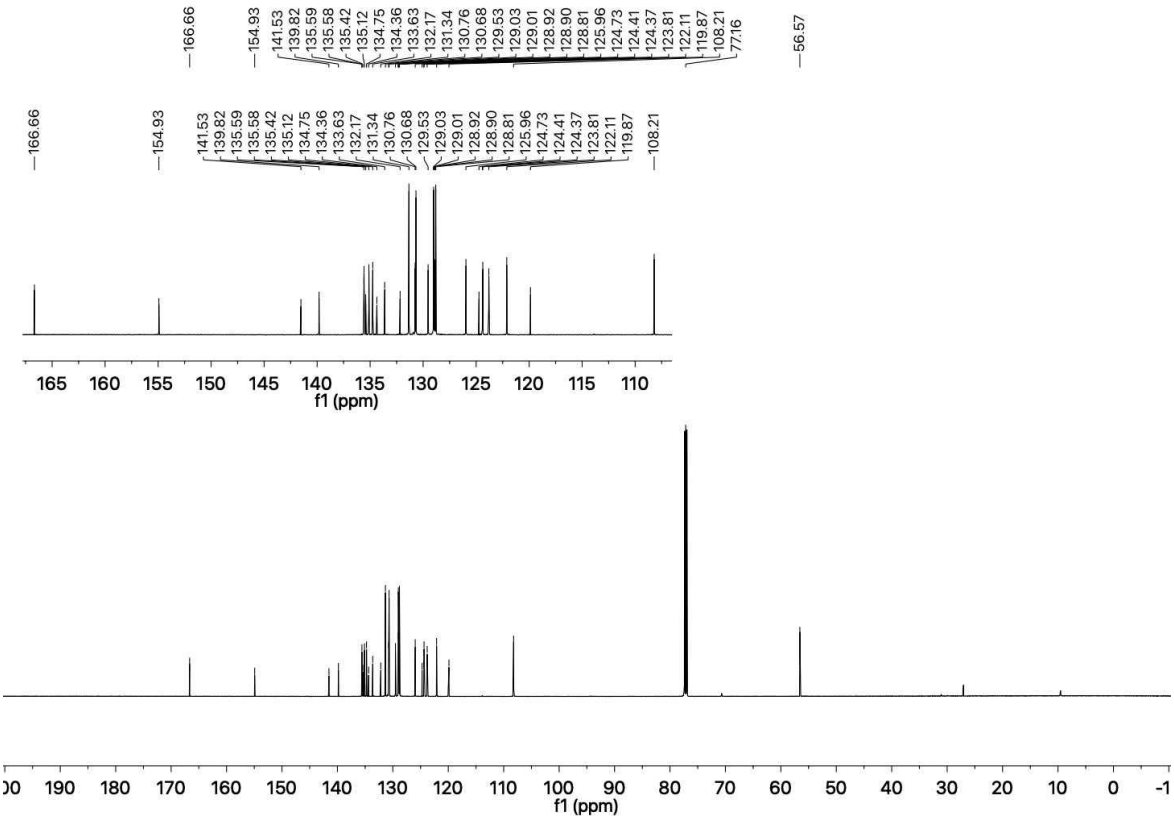


9-Methoxy-6,7-dihenylisoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7ba).

^{1}H NMR

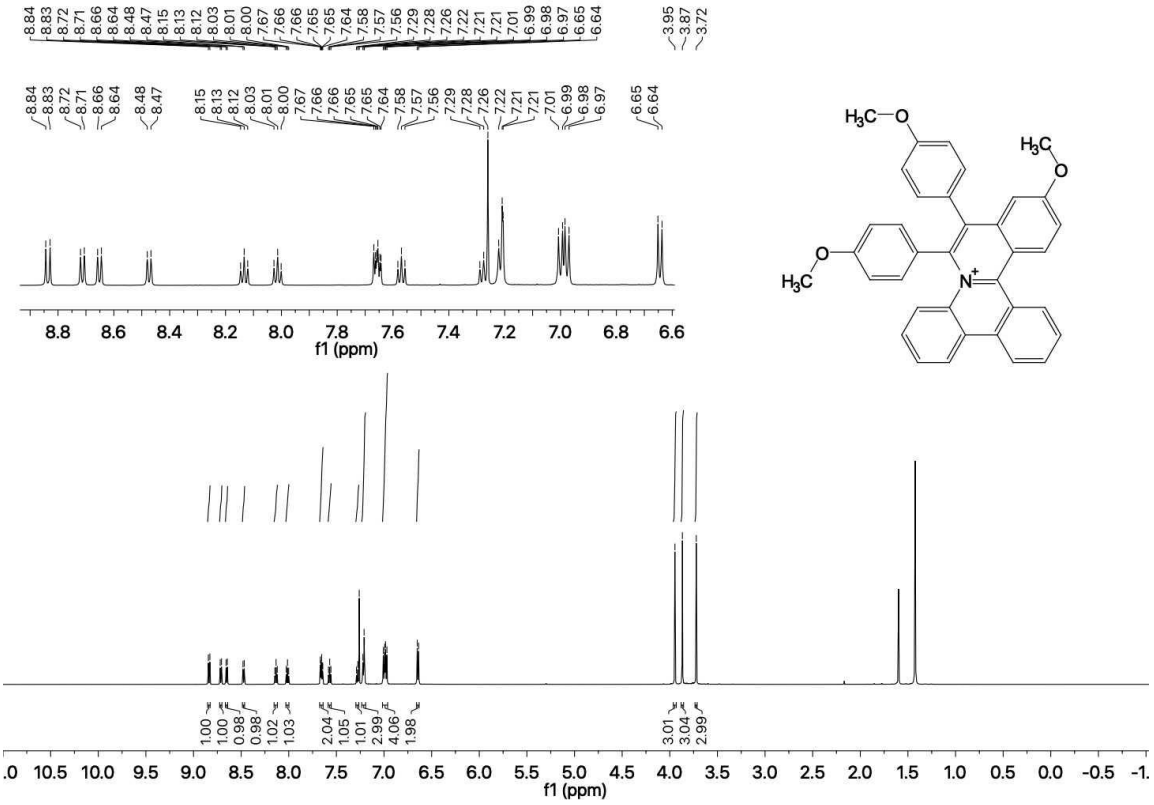


^{13}C NMR

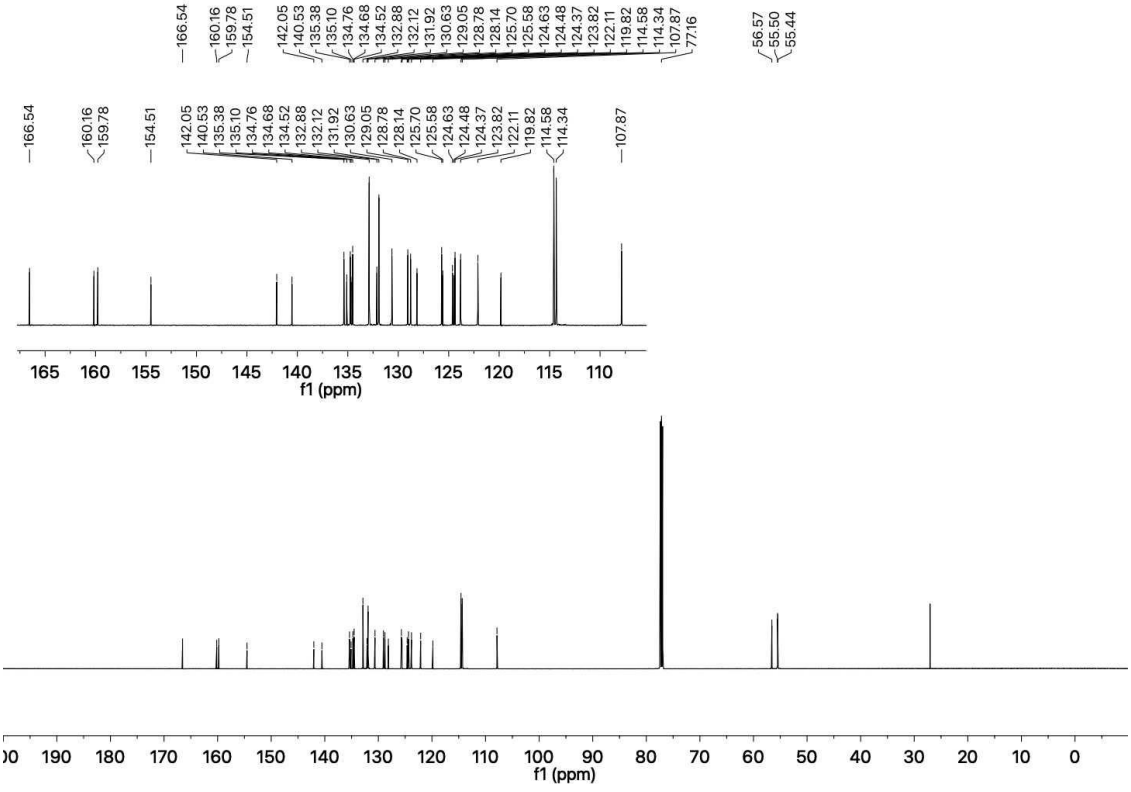


9-Methoxy-6,7-bis(4-methoxyphenyl)isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7bb).

^{1}H NMR

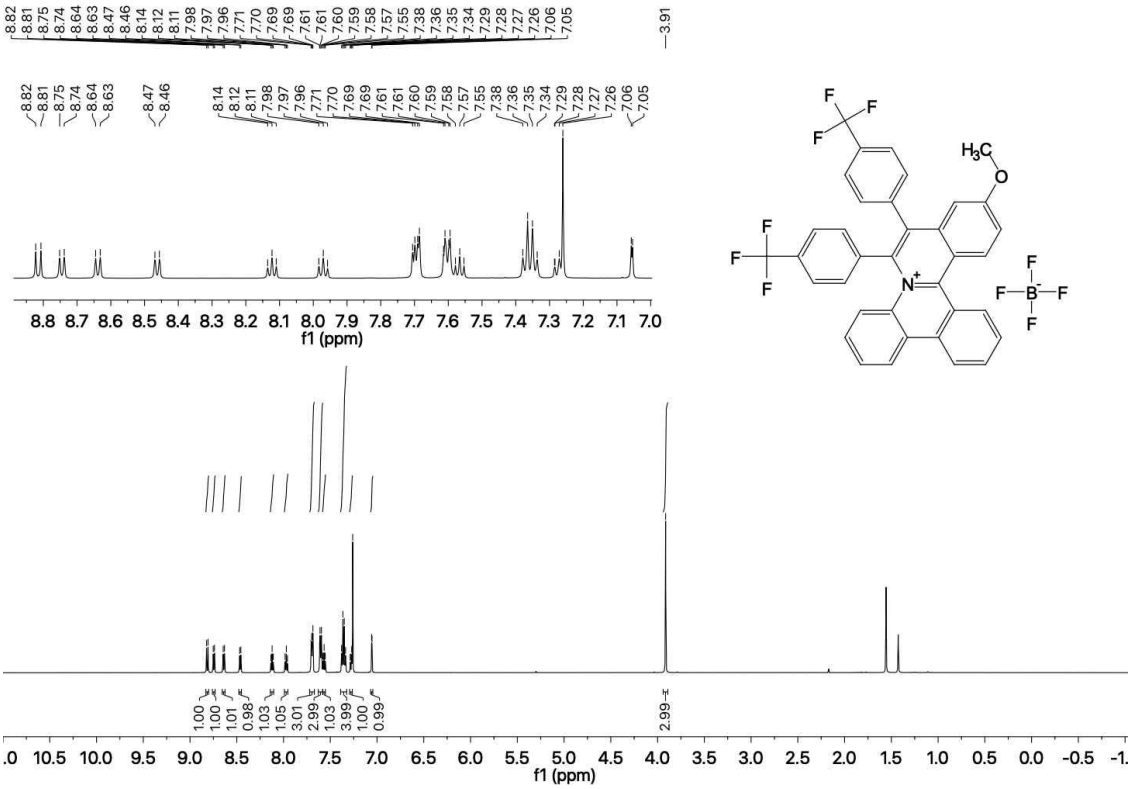


^{13}C NMR

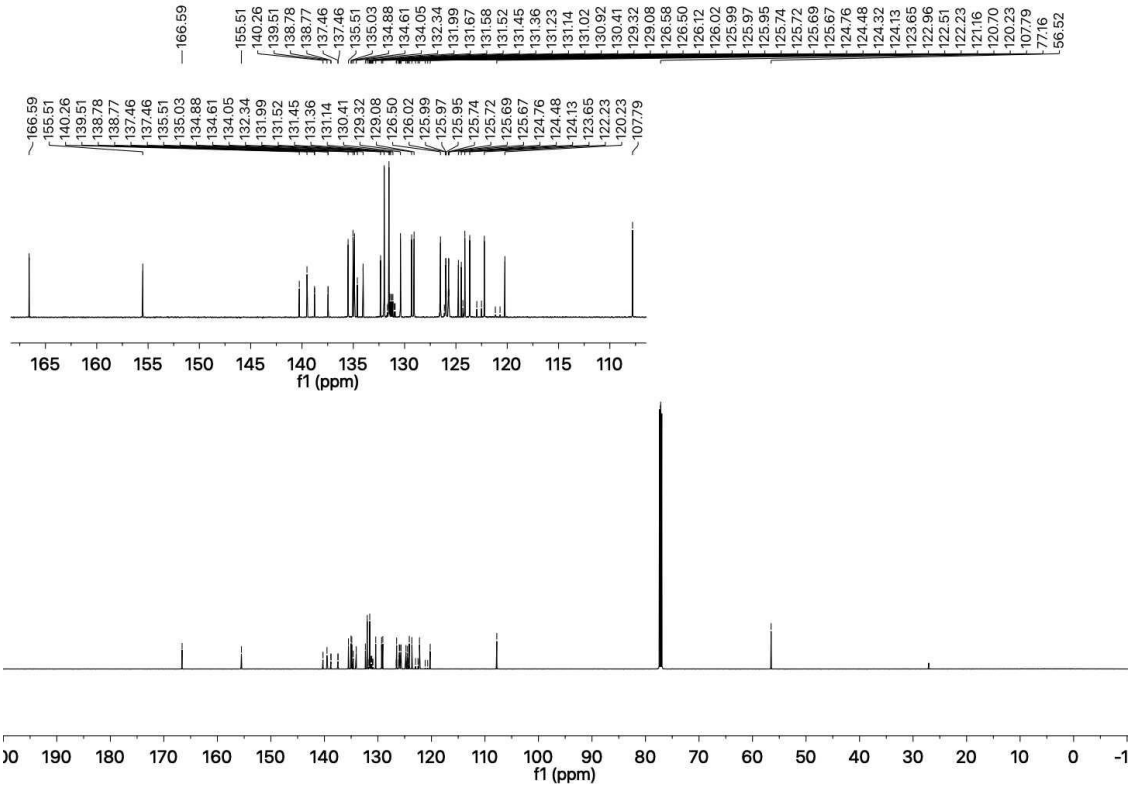


9-Methoxy-6,7-bis(4-(trifluoromethyl)phenyl)isochinolíno[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7bc).

^{1}H NMR

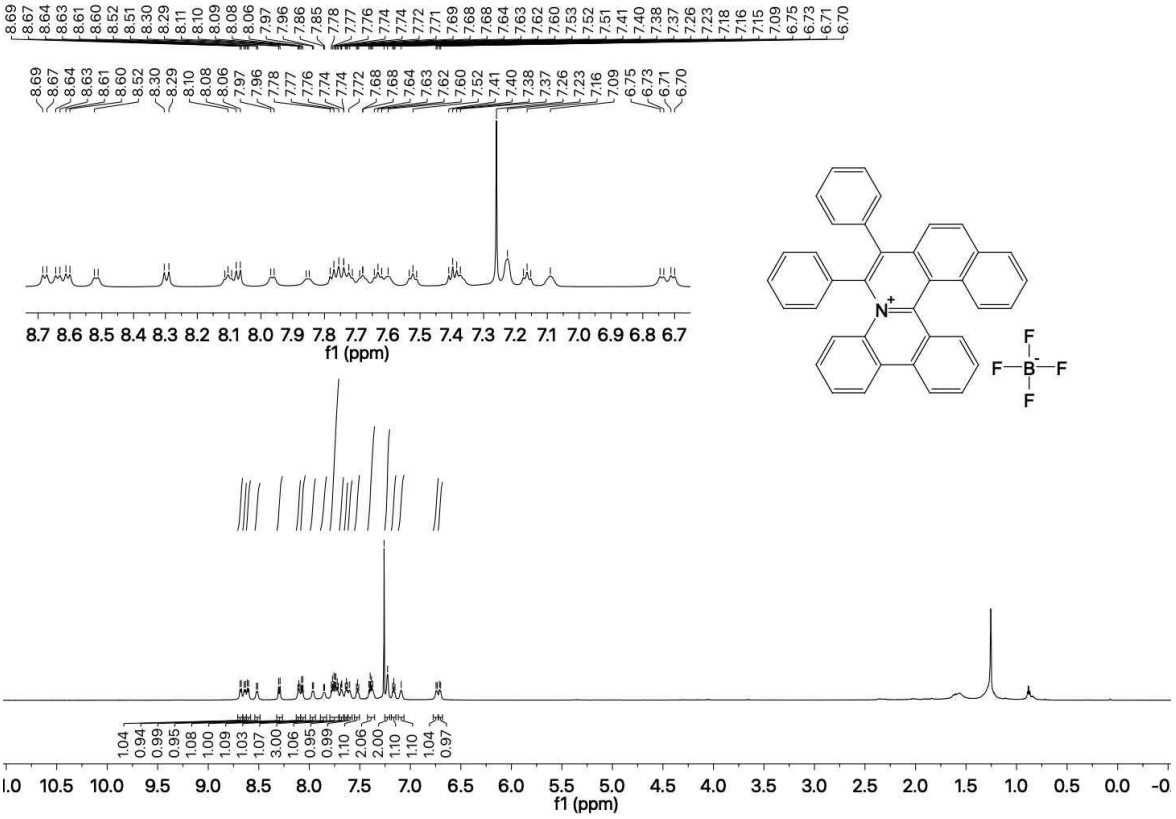


^{13}C NMR

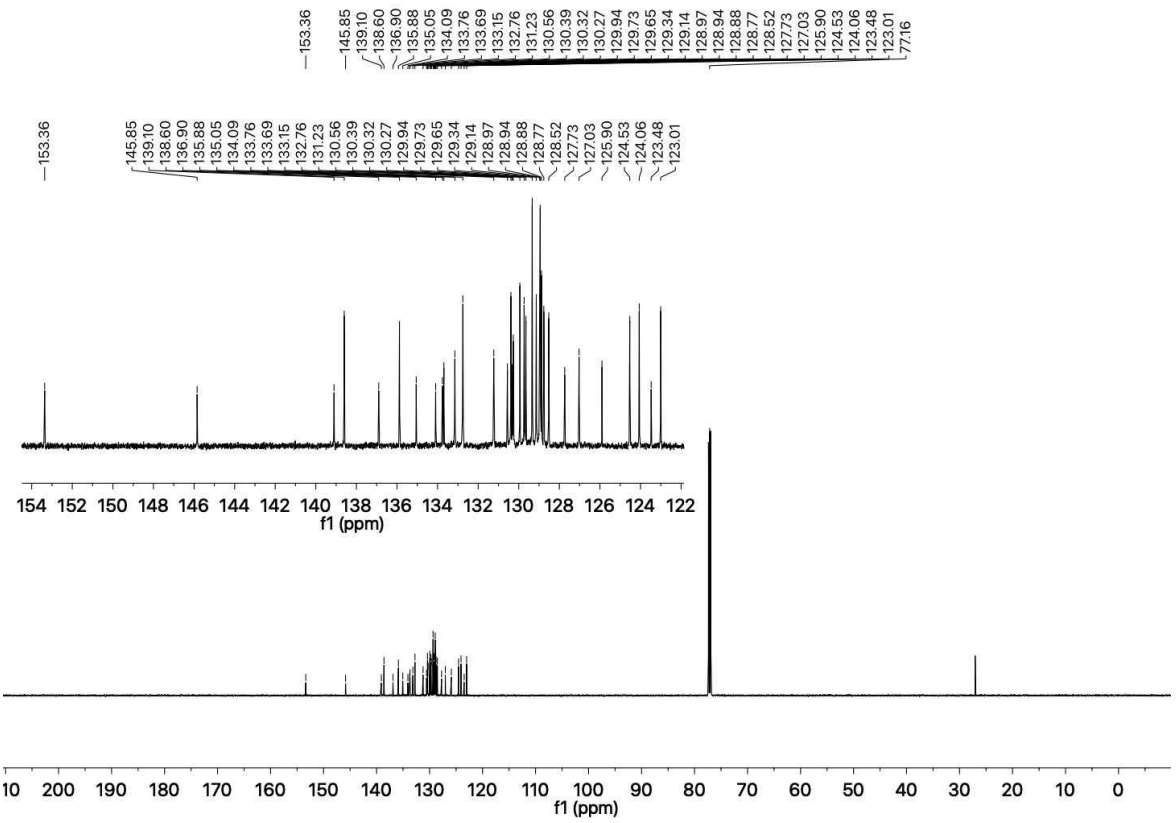


6,7-Diphenylbenzo[7,8]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7da).

^{1}H NMR

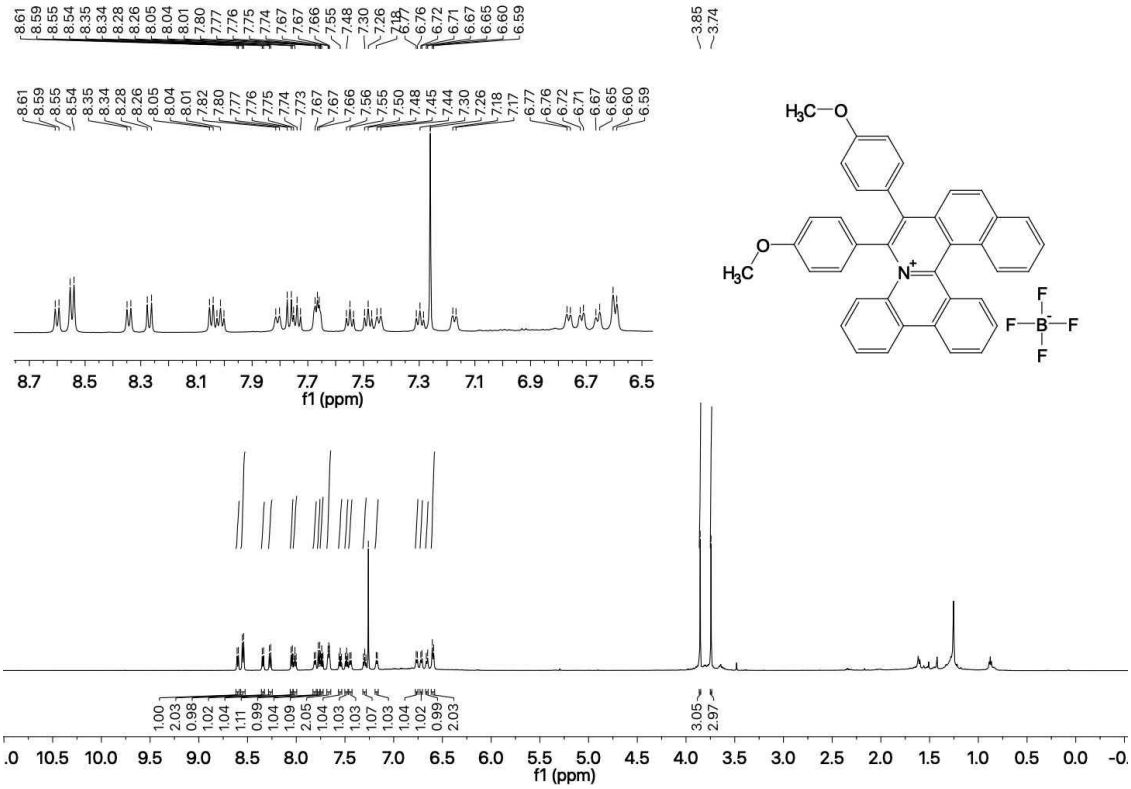


^{13}C NMR

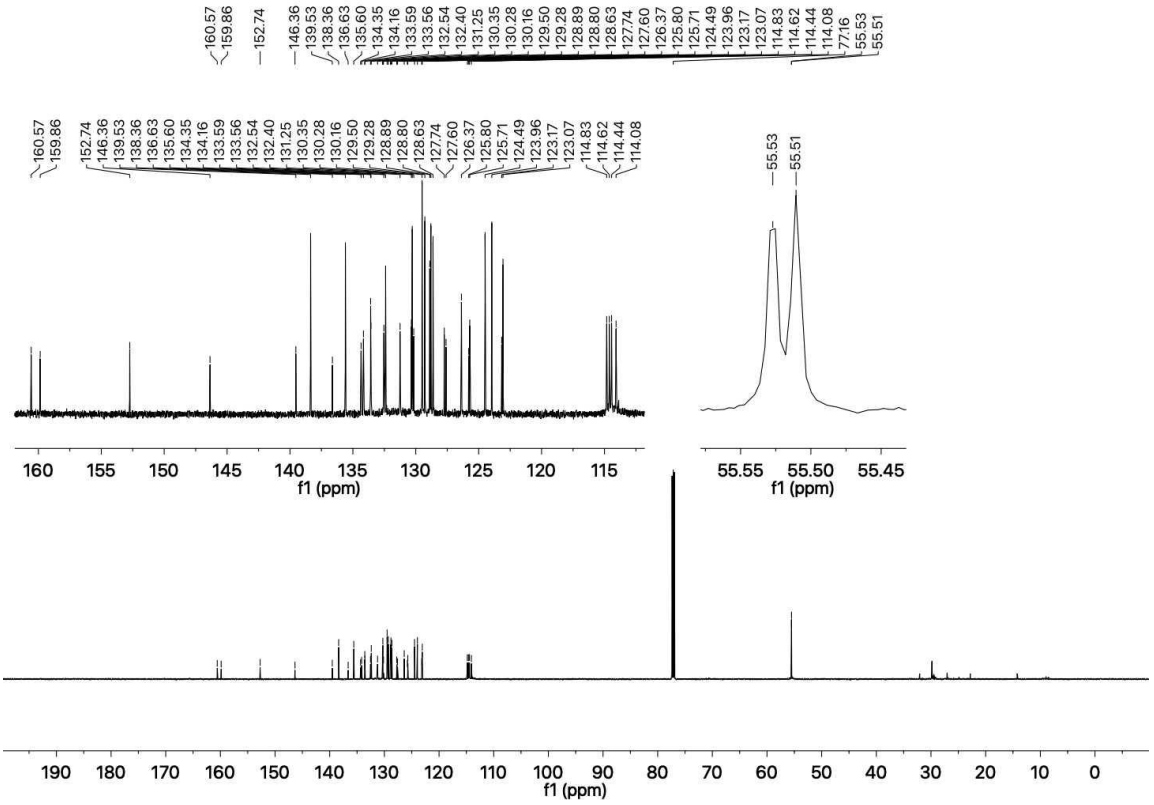


6,7-Bis(4-methoxyphenyl)benzo[7,8]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7db).

^{1}H NMR

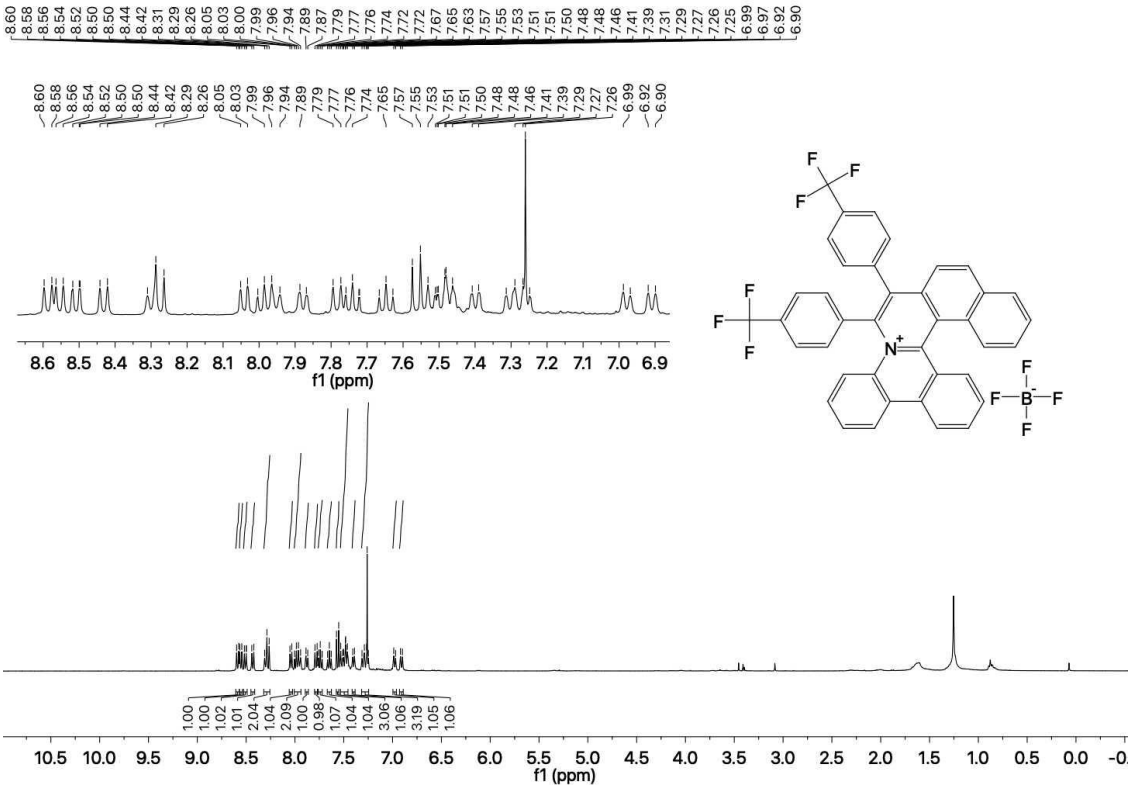


^{13}C NMR

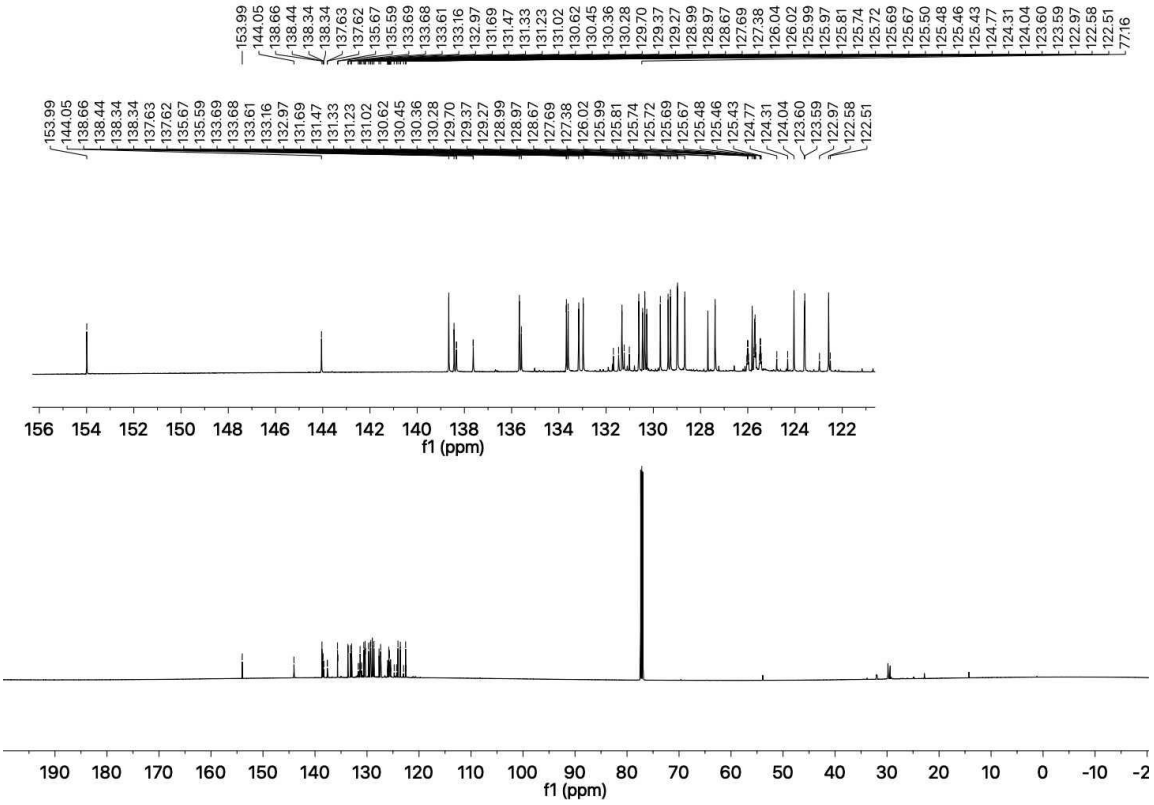


6,7-bis(4-(trifluoromethyl)phenyl)benzo[7,8]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7dc).

^{1}H NMR

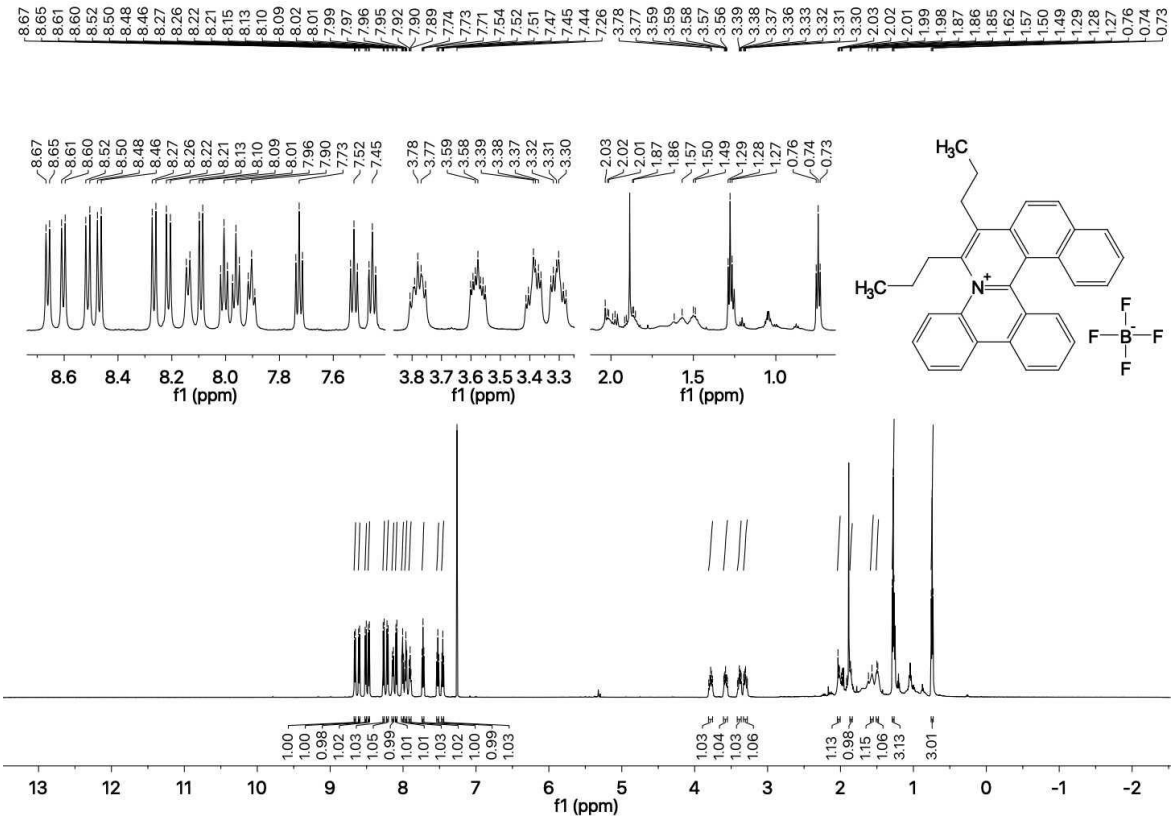


^{13}C NMR

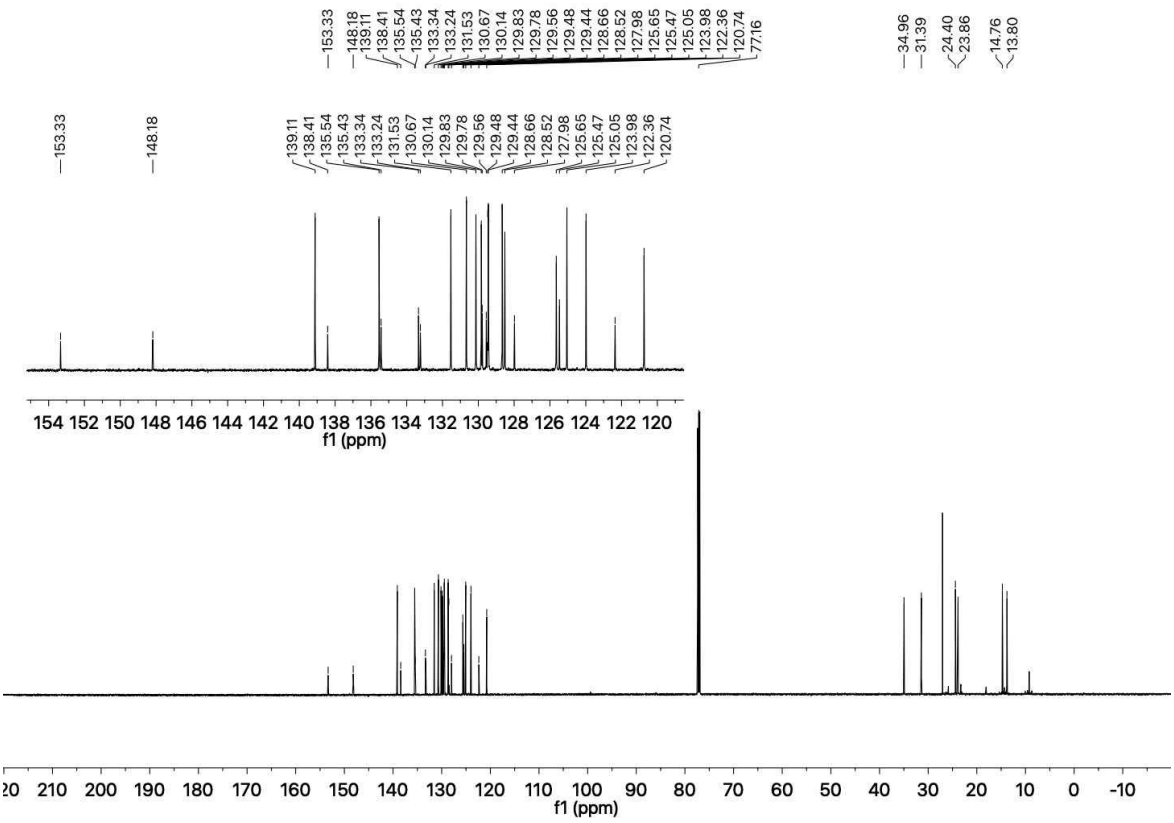


6,7-Dipropylbenzo[7,8]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7dd).

^{1}H NMR

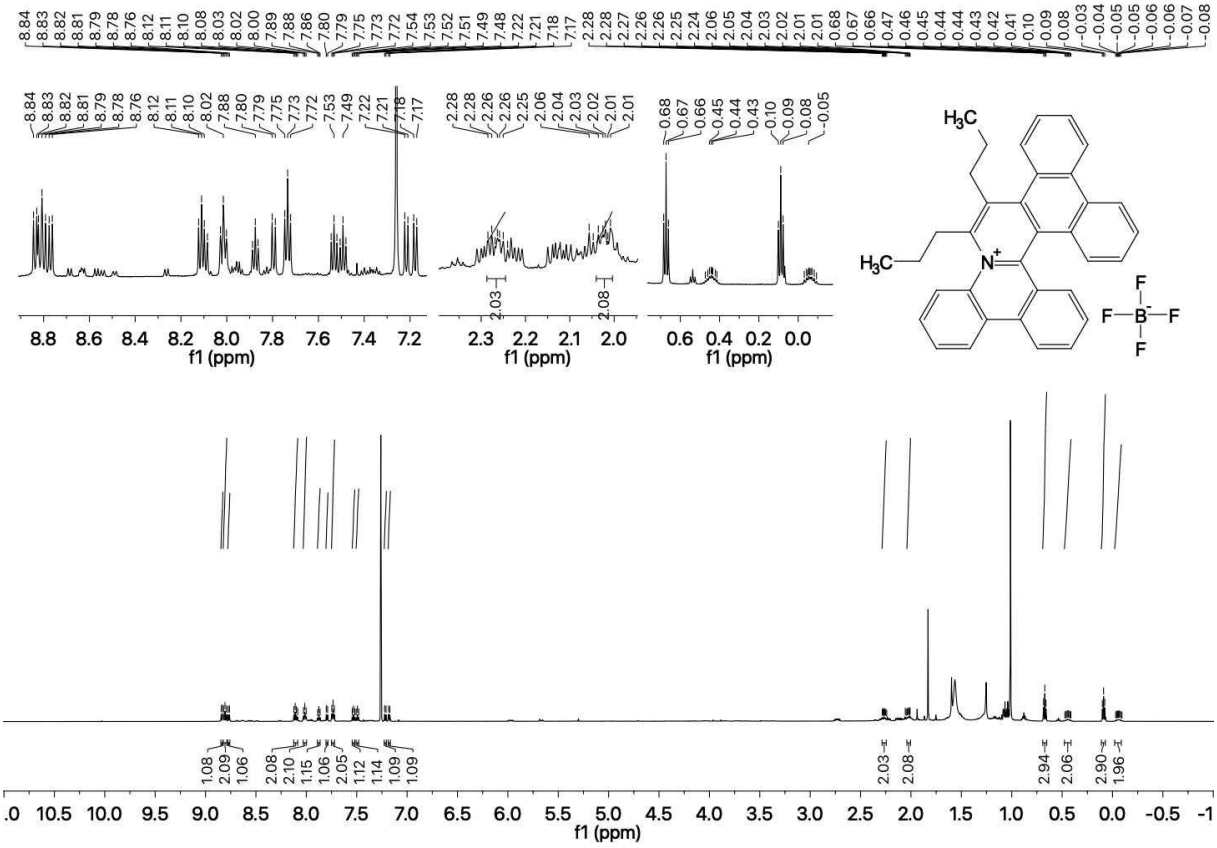


^{13}C NMR



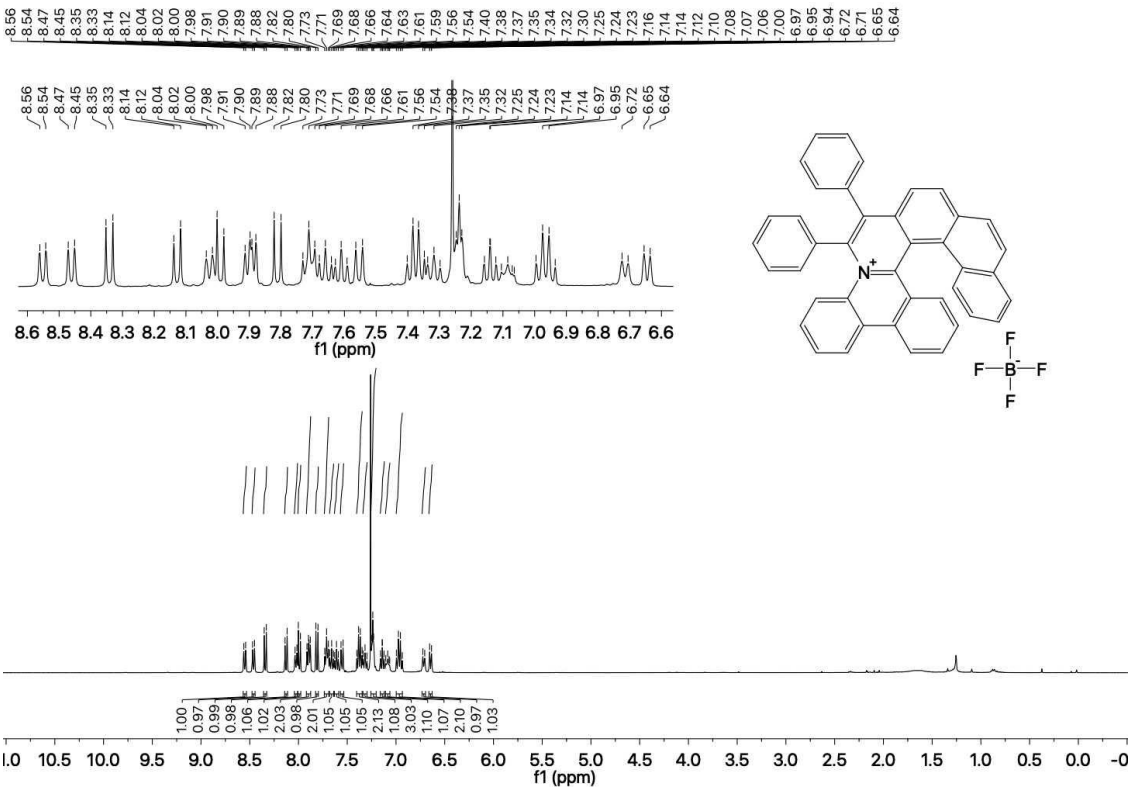
18,19-Dipropyldibenzo[5,6:7,8]isoquinolino[2,1-f]phenanthridin-17-ium tetrafluoroborate (7fd).

^{1}H NMR

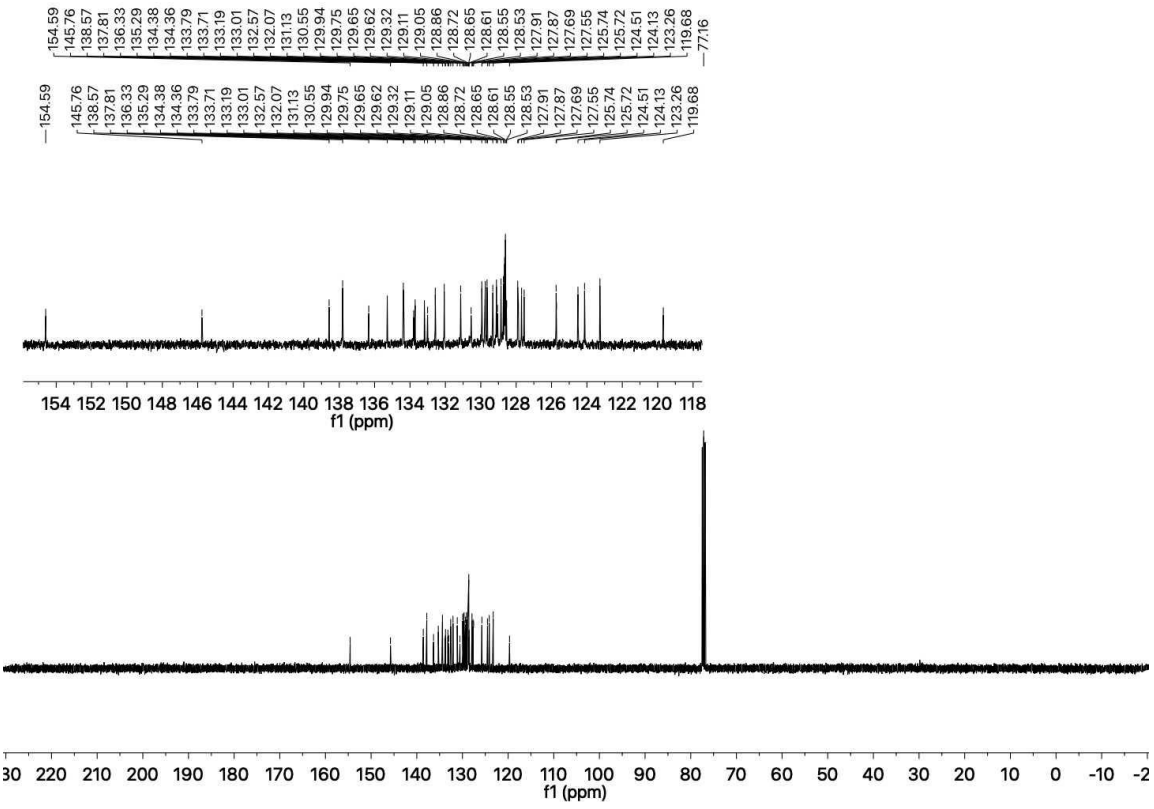


6,7-Diphenylnaphtho[2',1':7,8]isoquinolino[2,1-*f*]phenanthridin-5-ium tetrafluoroborate (7ga).

^{1}H NMR

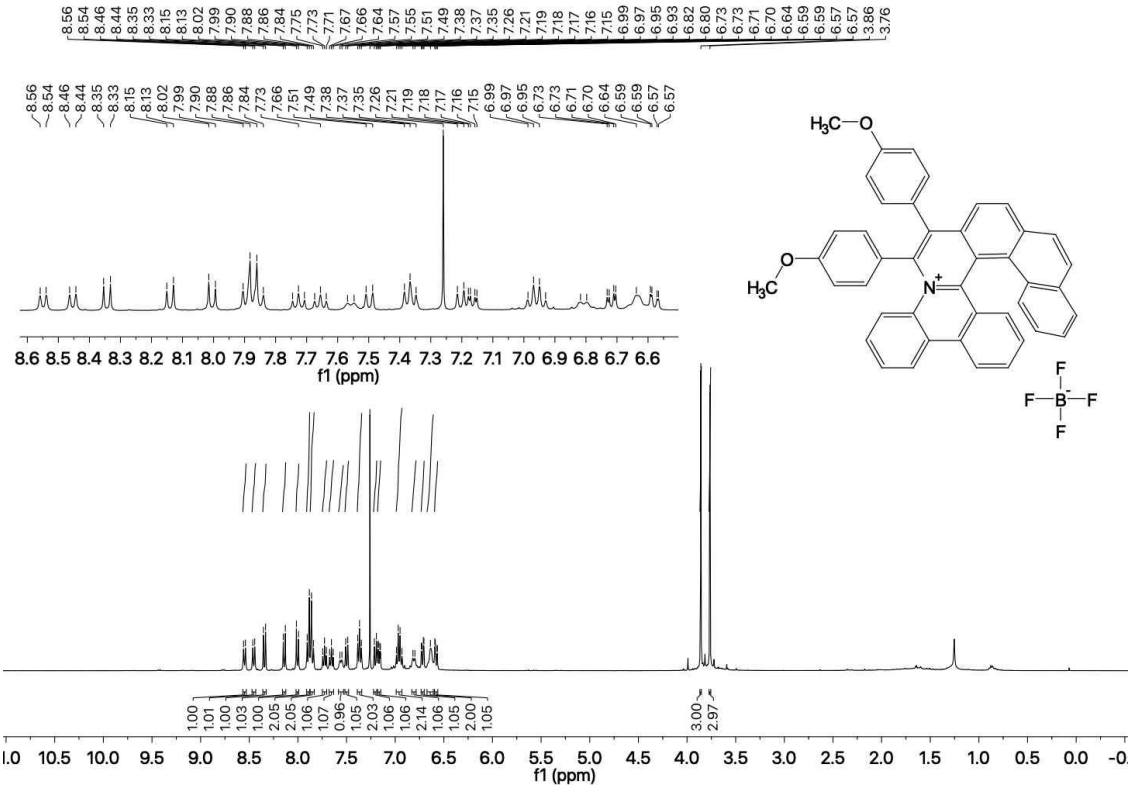


^{13}C NMR

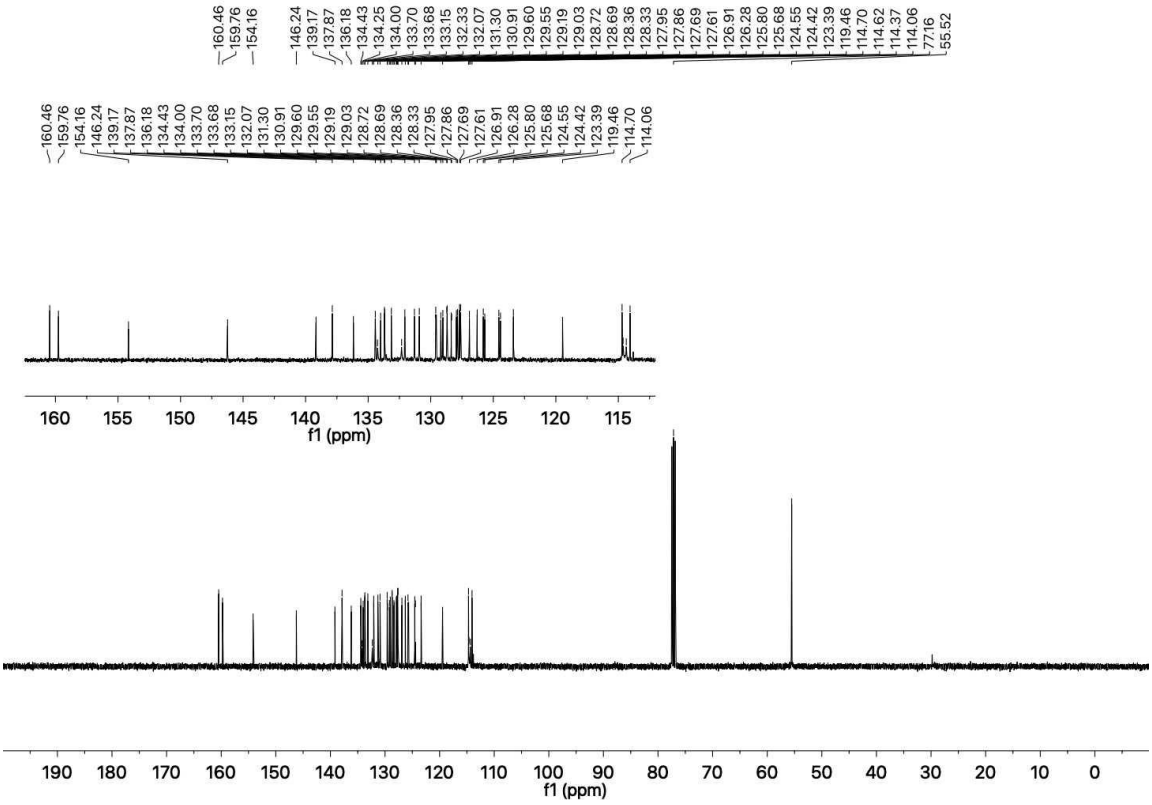


6,7-Bis(4-methoxyphenyl)naphtho[2',1':7,8]isoquinolino[2,1-f]phenanthridin-5-ium tetrafluoroborate (7gb).

^{1}H NMR

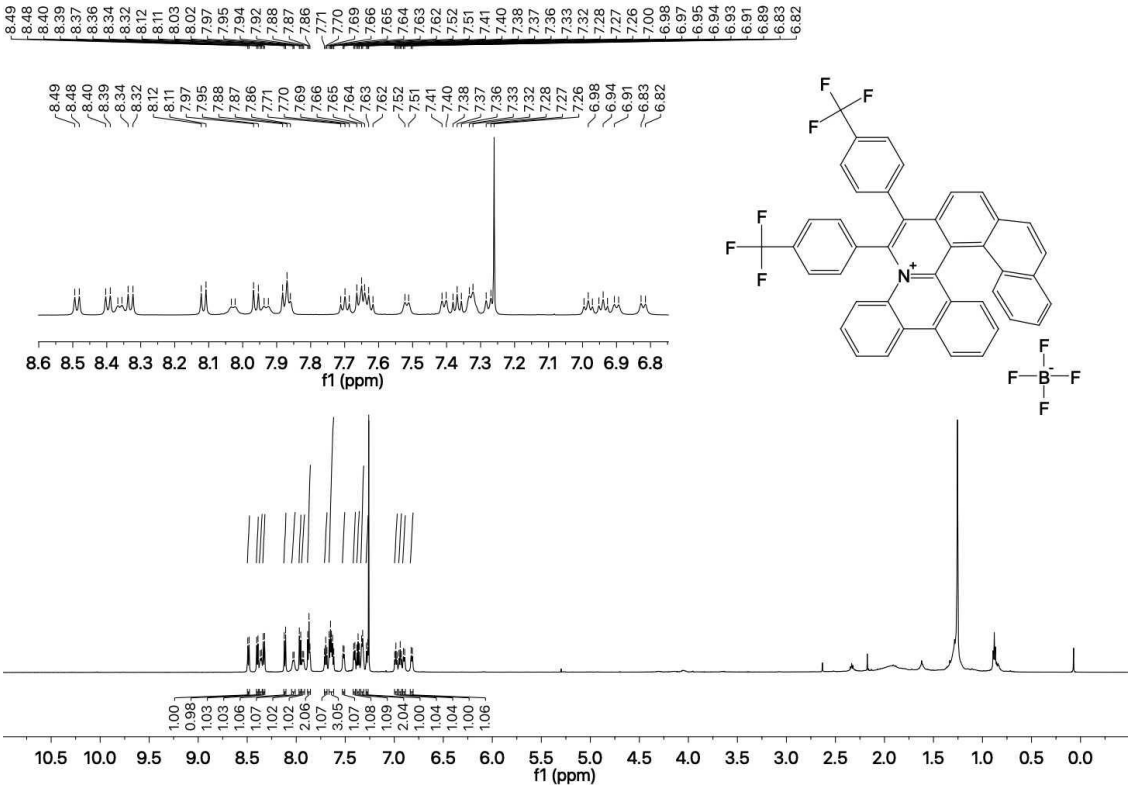


^{13}C NMR

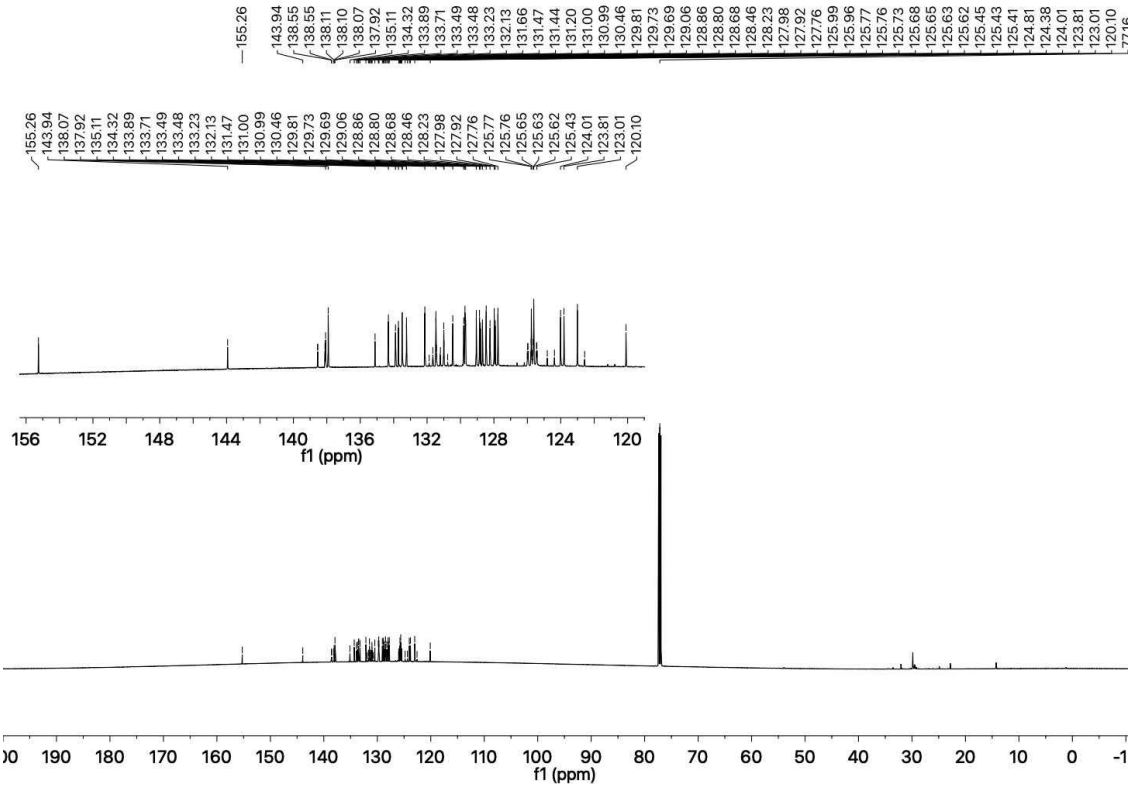


6,7-Bis(4-(trifluoromethyl)phenyl)naphtho[2',1':7,8]isoquinolino[2,1-f]phenanthridin-5-ium tetrafluoroborate (7gc).

^{1}H NMR

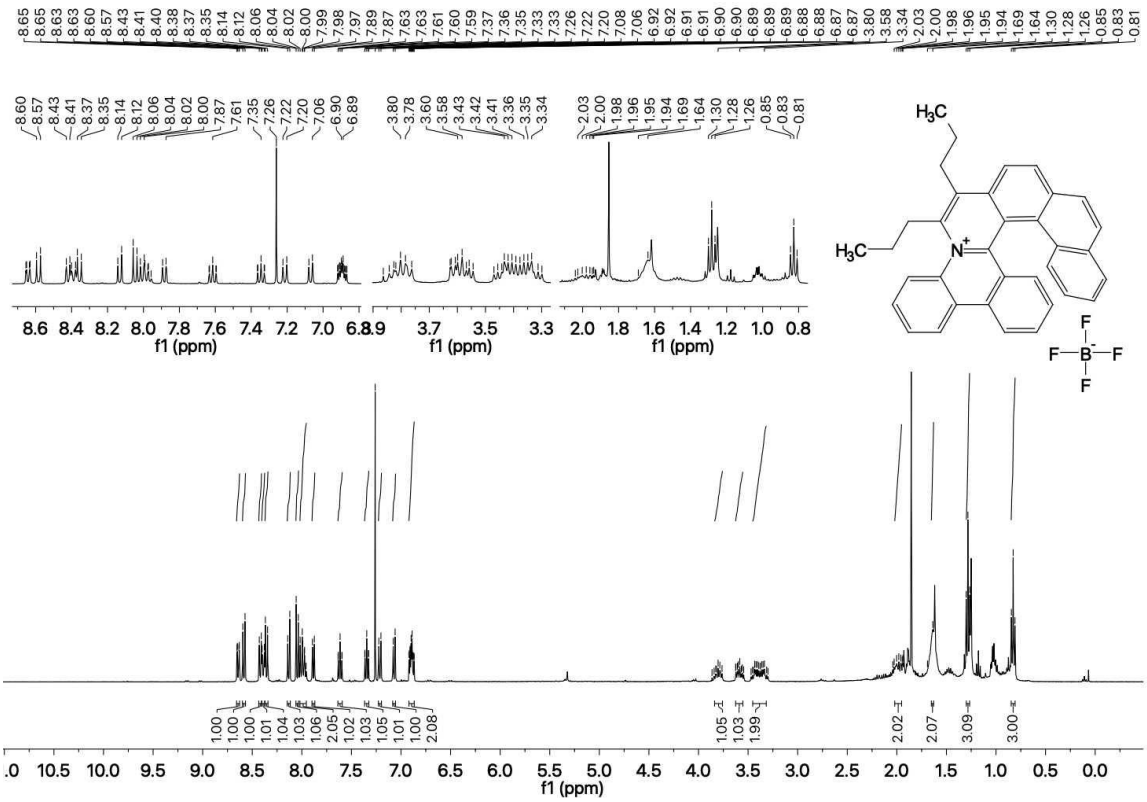


^{13}C NMR

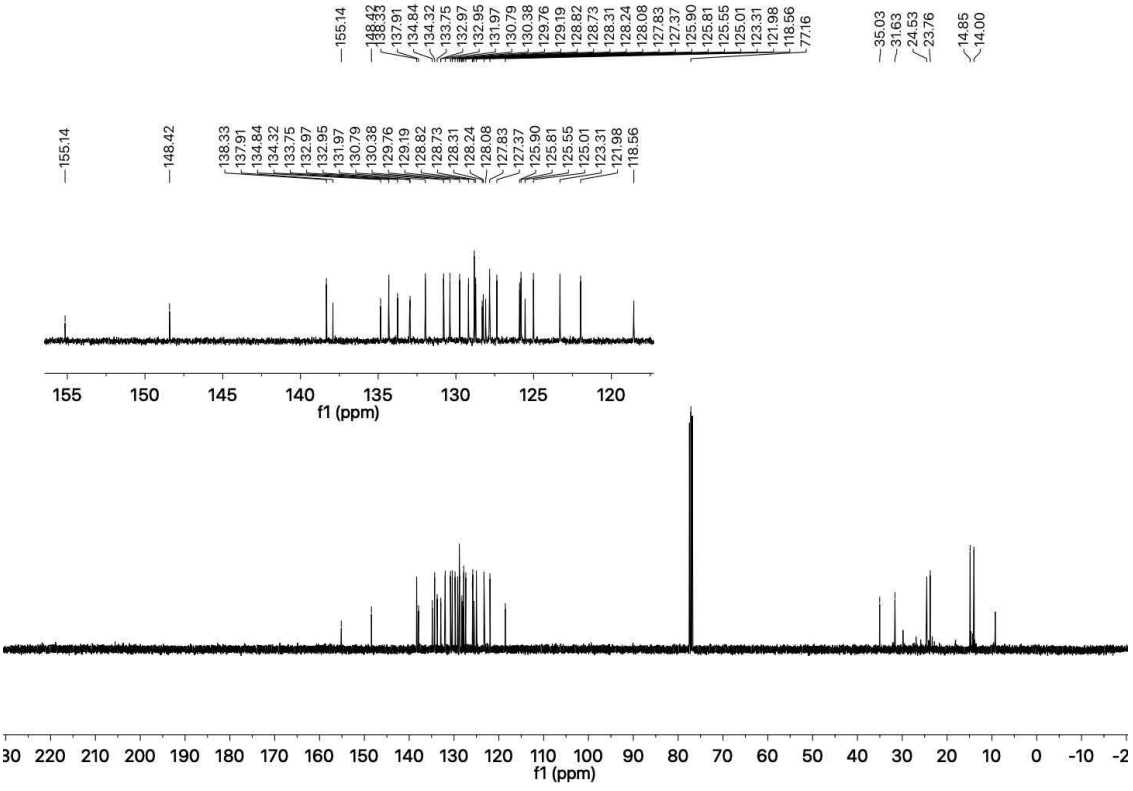


6,7-Dipropylnaphtho[2',1':7,8]isoquinolino[2,1-f]phenanthridin-5-ium tetrafluoroborate (7gd).

^{1}H NMR



^{13}C NMR



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