Supplementary Information

Synthesis of Poly-Substituted Phenanthridines via Ligand-Free Copper-Catalyzed Annulation

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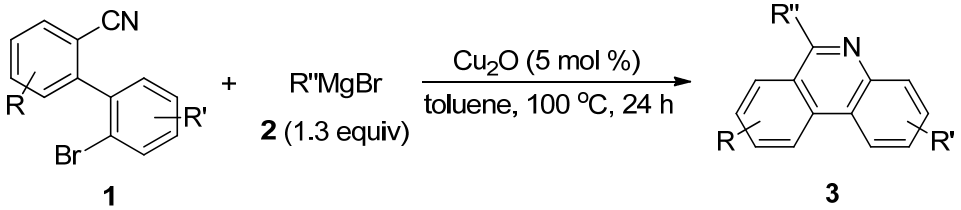
Table of Contents

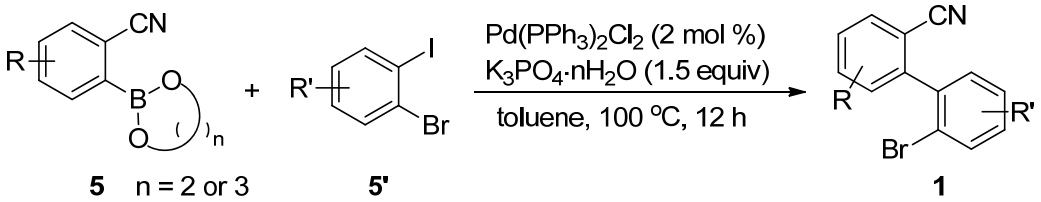
General information: All reagents were purchased from Sigma-Aldrich, Fisher-Acros, TCI, or Alfa-Aesar, and were used without further purification unless otherwise noted. THF and Et_2O were distilled from sodium, and CH_3CN was distilled from CaH_2. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique. Flash column chromatography was performed using silica gel (230-400 mesh). Analytical thin layer chromatography (TLC) was performed on 60 F_{254} (0.25 mm) plates and visualization was accomplished with UV light (254 and 354 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on Bruck 300 or Bruck 600 spectrometer with Me_4Si or solvent resonance as the internal standard (^{1}H NMR, Me_4Si at 0 ppm, $CHCl_3$ at 7.26 ppm, DMSO at 2.49 ppm; ^{13}C NMR, Me_4Si at 0 ppm, $CDCl_3$ at 77.0 ppm, d_6-DMSO at 39.7 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. IR spectral data were recorded on a Brucker TENSOR 37 spectrometer. Melting points (mp) were determined using a SRS OptiMelt MPA100. GC-MS data were obtained from the HP 5890 Series II GC/ HP 5972 GC MASS Spectrometer System. High Resolution Mass spectral data were obtained from the MAT-95XL HRMS by using EI method.

General procedure for the copper-catalyzed cyclization:



(Reactions were conducted in glove box.) To a screw-capped vial (10-mL) were added Cu_2O (0.02 mmol, 2.8 mg, 5 mol %) and substrate **1** (0.4 mmol, 1.0 equiv) in toluene (2 mL). The vial was kept stirring for a while. Grignard reagent **2** (3 M in Et_2O for alkyl Grignard and 0.5 M in THF for aryl Grignard, 0.52 mmol, 1.3 equiv) was then injected into the reaction mixture, sealed with cap and allowed to stir at 100 °C for 24 h. The crude reaction mixture was diluted with CH_2Cl_2, filtered through a thin Celite pad, and concentrated *in vacuo*. The residue was isolated through a column chromatography by using hexane and ethyl acetate as eluent to give the pure product. Products **3** were obtained according to this procedure. The known structures were characterized by the HRMS, ^{1}H NMR and ^{13}C NMR spectra of reported literatures. Spectral data, melting point, HRMS data and the copies of ^{1}H NMR and ^{13}C NMR spectra for all compounds are listed below.

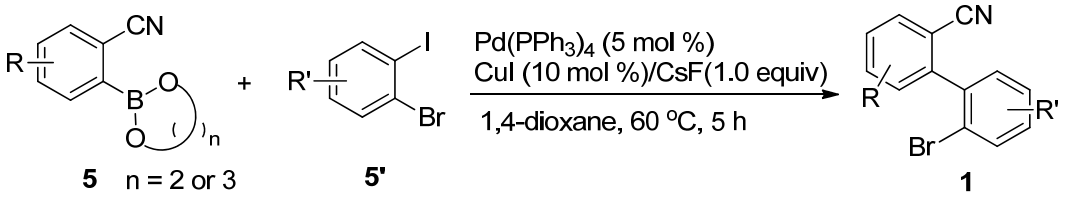
General procedure A for the synthesis of substrate (1):[1]



5 n = 2 or 3 **5'** **1**

To a Schlenk tube (50-mL) were added $Pd(PPh_3)_2Cl_2$ (70.1 mg, 0.1 mmol, 2 mol %), $K_3PO_4 \cdot nH_2O$ (1727 mg, 7.5 mmol) and substrate **5** (5 mmol). The mixture was closed by a septum, purged by nitrogen gas for several times then the dry toluene (20 mL) was added into the mixture and allowed to stir for a while; *o*-bromoiodoarene **5'** (7.5 mmol) was then slowly injected into the mixture by a syringe. The septum was removed and the Schlenk tube was sealed with cap; again quickly purged by nitrogen gas for several times and move to oil bath and allowed to stir at 100 °C for 12 h. The crude reaction mixture was diluted with CH_2Cl_2, filtered through a thin Celite pad to remove salt and concentrated *in vacuo*. The residue was isolated through flash column chromatography by using hexane and ethyl acetate as eluent to give compound **1**. Compounds **1a, 1b**, **1A**–**1H and 1K**–**1P** were obtained according to this procedure.

General procedure B for the synthesis of substrate (1):[2]

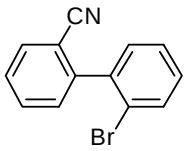


5 n = 2 or 3 **5'** **1**

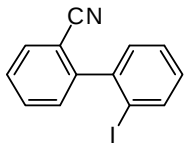
To a Schlenk tube (25-mL) were added $Pd(PPh_3)_4$ (114.4 mg, 0.1 mmol, 5 mol %), CsF (619.6 mg, 4 mmol, 2.0 equiv), CuI (38 mg, 0.2 mmol, 10 mol %) and substrate **5** (2 mmol). The mixture was closed by a septum, purged by nitrogen gas for several times then the dry 1,4-dioxane (8 mL) was added into the mixture and allowed to stir for a while; *o*-bromoiodoarene **5'** (2.4 mmol) was then slowly injected into the mixture by a syringe. The septum was removed and the Schlenk tube was sealed with cap; again quickly purged by nitrogen gas for several times and move to oil bath and allowed to stir at 60 °C for 6 h. The crude reaction mixture was diluted with CH_2Cl_2, filtered through a thin Celite pad to remove salt and concentrated *in vacuo*. The residue was isolated through flash column chromatography by using hexane and ethyl acetate as eluent to give compound **1**. Compounds **1I**, **1J, 1Q and 1R** were obtained according to this procedure.

General procedures for the Syntheses of the compounds **5**, please see our previous reports for the detail.[3, 4]

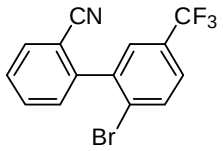
Spectral Data for all substrates:



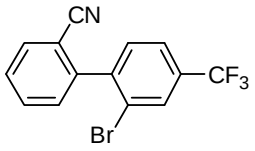
2'-Bromo-[1,1'-biphenyl]-2-carbonitrile (1a): White solid (1.097 g, 85%), mp: 66–67 °C; IR (KBr): 3064, 2230, 1601, 811, 763, 658, 619 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.72 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.66 (td, *J* = 7.8, 1.2 Hz, 1H), 7.50 (td, *J* = 7.8, 1.2 Hz, 1H), 7.44–7.41 (m, 2H), 7.35–7.30 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.7, 139.0, 133.1, 132.8, 132.3, 130.9, 130.7, 130.3, 128.2, 127.5, 122.8, 117.7, 112.9; HRMS: $C_{13}H_8BrN$ calculated 256.9840, found 256.9837; Registry Number: [54245-41-9].



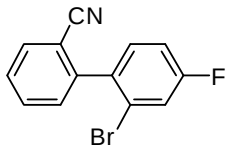
2'-Iodo-[1,1'-biphenyl]-2-carbonitrile (1b): White solid (666 mg, 43%), mp: 71–73 °C; IR (KBr): 3055, 2229, 1602, 1560, 1460, 1424, 1025, 994, 753, 650, 625 cm^{-1}**;** ^1H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 147.7, 143.1, 139.4, 132.7, 132.3, 130.7, 130.2, 129.8, 128.3, 128.3, 117.6, 112.8, 98.3; HRMS: $C_{13}H_8IN$ calculated 304.9702, found 304.9701; Registry Number: [36271-73-5].



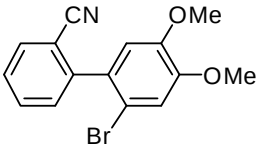
2'-Bromo-5'-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile (1A): White solid (668 mg, 41%), mp: 122–123 °C; IR (KBr): 3070, 2229, 1333, 1136, 1086, 766, 533 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.79 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.70 (td, *J* = 7.8, 1.2 Hz, 1H), 7.60 (d, *J* = 1.8 Hz, 1H), 7.58–7.54 (m, 2H), 7.43 (dd, *J* = 7.8, 0.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.2, 139.9, 133.8, 132.9, 132.6, 130.4, 130.1 (q, *J* = 33.0 Hz), 128.9, 127.6 (q, *J* = 3.0 Hz), 127.0, 126.9 (q, *J* = 3.0 Hz), 123.5 (q, *J* = 271.5 Hz), 117.2, 112.9; HRMS: $C_{14}H_7BrF_3N$ calculated 324.9714, found 324.9711; New compound.



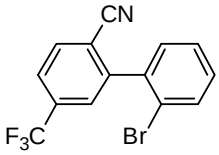
2'-Bromo-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile (1B): White solid (880 mg, 54%), mp: 92–93 °C; IR (KBr): 3065, 2232, 1396, 1086, 772, 669 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 8.4 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.3, 142.6, 132.9, 132.7, 132.4 (q, *J* = 33.0 Hz), 131.4, 130.3, 130.1 (q, *J* = 3.0 Hz), 128.9, 124.4 (q, *J* = 3.0 Hz), 123.3, 122.9 (q, *J* = 271.5 Hz), 117.3, 112.6; HRMS: $C_{14}H_7BrF_3N$ calculated 324.9714, found 324.9711; New compound.



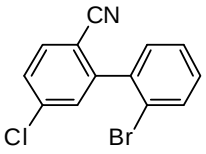
2'-Bromo-4'-fluoro-[1,1'-biphenyl]-2-carbonitrile (1C): White solid (884 mg, 64%), mp: 84–85 ^{o}C; IR (KBr): 3065, 2226, 1602, 1474, 1199, 766, 536 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.66 (td, *J* = 7.8, 1.2 Hz, 1H), 7.51 (td, *J* = 7.8, 1.2 Hz, 1H), 7.47 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.41 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.33 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.15 (td, *J* = 8.4, 2.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.4 (d, *J* = 252.0 Hz), 143.8, 135.2, 132.9, 132.4, 132.0 (d, *J* = 9.0 Hz), 130.9, 128.5, 123.3 (d, *J* = 10.5 Hz), 120.5 (d, *J* = 24.0 Hz), 117.6, 114.9 (d, *J* = 21.0 Hz), 113.2; HRMS: $C_{13}H_7BrFN$ calculated 274.9746, found 274.9743; New compound.



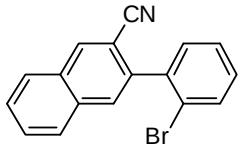
2'-Bromo-4',5'-dimethoxy-[1,1'-biphenyl]-2-carbonitrile (1D): White solid (827 mg, 52%), mp: 98–99 ^{o}C; IR (KBr): 3004, 2837, 2226, 1485, 1216, 1016, 766, 558 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.15 (s, 1H), 6.82 (s, 1H), 3.93 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 149.9, 148.4, 144.7, 132.8, 132.3, 131.1, 131.0, 128.1, 117.9, 115.8, 113.6, 113.3, 113.1, 56.2, 56.2; HRMS: $C_{15}H_{12}BrNO_2$ calculated 317.0051, found 317.0050; New compound.



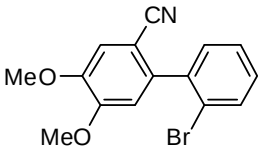
2'-Bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile (1E): White solid (717 mg, 44%), mp: 60–61 ^{o}C; IR (KBr): 2240, 1655, 1635, 1472, 1413, 1327, 1294, 1177, 1133, 1072, 841, 761, 664, 633, 569 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.77 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.72 (s, 1H), 7.46 (td, *J* = 7.8, 1.2 Hz, 1H), 7.38–7.34 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.6, 137.6, 134.2 (q, *J* = 33 Hz), 133.4, 133.4, 130.9, 130.8, 127.8 (2C), 125.1 (q, *J* = 4.5 Hz), 123.0 (q, *J* = 271.5 Hz), 122.6, 116.6, 116.5; HRMS: $C_{14}H_7BrF_3N$ calculated 324.9714, found 324.9713; New compound.



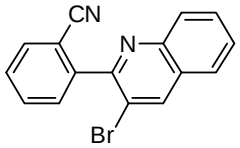
2'-Bromo-5-chloro-[1,1'-biphenyl]-2-carbonitrile (1F): White solid (702 mg, 48%), mp: 97–98 ^{o}C, IR (KBr): 3070, 2923, 2235, 1594, 1460, 1091, 1008, 833, 755, 730, 664 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.44 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.2, 138.9, 137.8, 133.9, 133.3, 131.1, 130.8, 130.7, 128.7, 127.6, 122.6, 116.9, 111.5; HRMS: $C_{13}H_7BrClN$ calculated 290.9450, found 290.9445; New compound.



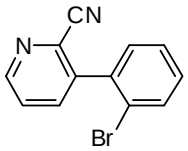
3-(2-Bromophenyl)-2-naphthonitrile (1G): White solid (324 mg, 21%), mp: 118–120 °C, IR (KBr): 2226, 1649, 1627, 1477, 1419, 1022, 744, 486 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.86 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.68 (td, *J* = 7.8, 1.2 Hz, 1H), 7.64 (td, *J* = 7.8, 0.6 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.41 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.34 (td, *J* = 8.4, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.2, 138.9, 134.9, 134.3, 133.1, 131.6, 131.3, 130.2, 129.9, 129.4, 128.2, 128.2, 127.8, 127.5, 123.5, 118.0, 110.8; HRMS: $C_{17}H_{10}BrN$ calculated 306.9997, found 306.9996; New compound.



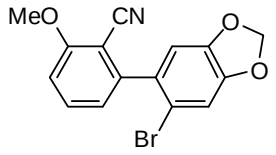
2'-Bromo-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile (1H): Yellow solid (487 mg, 31%), mp: 123–125 °C; IR (KBr): 3061, 2936, 2224, 1269, 1019, 766, 547 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.15 (s, 1H), 6.87 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.0, 148.6, 139.1, 138.9, 133.1, 131.2, 130.1, 127.5, 123.1, 118.1, 114.1, 113.4, 104.2, 56.2, 56.2; HRMS: $C_{15}H_{12}BrNO_2$ calculated 317.0051, found 317.0049; New compound.



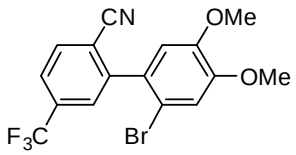
2-(3-Bromoquinolin-2-yl)benzonitrile (1I): White solid (556 mg, 90%), mp: 117–118 °C; IR (KBr): 3056, 2951, 2226, 1941, 1830, 1580, 1483, 1455, 1438, 1402, 1361, 1127, 1069, 905, 764, 730, 692, 594, 542 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.53 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.82–7.76 (m, 3H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 155.1, 146.3, 143.5, 139.9, 133.0, 132.3, 130.5, 130.2, 129.6, 129.0, 128.7, 128.2, 126.6, 117.6, 116.5, 112.7; HRMS: $C_{16}H_9BrN_2$ calculated 307.9949, found 307.9941; New compound.



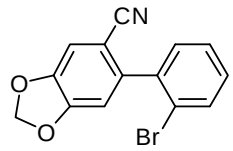
3-(2-Bromophenyl)picolinonitrile (1J): White solid (383 mg, 74%), mp: 96–97; IR (KBr): 2993, 2240, 1771, 1755, 1377, 1241, 1050 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.74 (d, *J* = 4.2 Hz, 1H), 7.81 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.74 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.59 (dd, .*J* = 7.8, 4.8 Hz, 1H), 7.46 (td, *J* = 8.4, 1.2 Hz, 1H), 7.37–7.34 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.0, 141.5, 138.5, 136.2, 133.5, 133.3, 131.0, 130.9. 127.8, 126.0, 122.8, 116.1; HRMS: $C_{12}H_7BrN_2$ calculated 257.9793, found 257.9790; New compound.



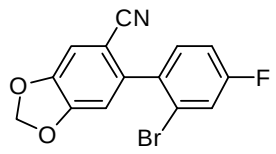
2-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)-6-methoxybenzonitrile (1K): Yellow solid (980 mg, 59%), mp: 109–110 ^{o}C; IR (KBr): 3017, 2912, 2224, 1586, 1233, 1033, 797, 555 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (t, *J* = 7.8 Hz, 1H), 7.12 (s, 1H), 6.98 (d, *J* = 9.0 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.77 (s, 1H), 6.04 (d, *J* = 9.6 Hz, 2H), 3.98 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.6, 148.8, 147.4, 146.5, 133.4, 132.0, 122.8, 115.1, 113.7, 113.0, 110.5, 110.3, 103.0, 102.1, 56.2; HRMS: $C_{15}H_{10}BrNO_3$ calculated 330.9844, found 330.9837; New compound.



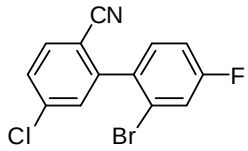
2'-Bromo-4',5'-dimethoxy-5-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile (1L): White solid (502 mg, 26%), mp: 175–177 ^{o}C; IR (KBr): 3009, 2934, 2232, 1519, 1413, 1335, 1172, 1136, 1025, 786, 539 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.72 (s, 1H), 7.17 (s, 1H), 6.82 (s, 1H), 3.94 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.4, 148.6, 145.6, 134.1 (q, *J* = 33.0 Hz), 133.4, 129.4, 128.1 (q, *J* = 3.0 Hz), 124.9 (q, *J* = 3.0 Hz), 123.0 (q, *J* = 271.5 Hz), 116.8, 116.7, 115.8, 113.3, 113.0, 56.3, 56.2; HRMS: $C_{16}H_{11}BrF_3NO_2$ calculated 384.9925, found 384.9923; New compound.



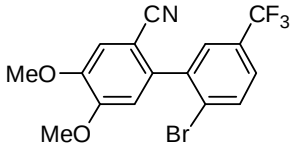
6-(2-Bromophenyl)benzo[*d*][1,3]dioxole-5-carbonitrile (1M): White solid (1.01 g, 67%), mp: 137–138 ^{o}C; IR (KBr): 2915, 2224, 1626, 1471, 1377, 1252, 1044, 761, 547 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.38 (td, *J* = 7.8, 1.2 Hz, 1H), 7.31 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.27 (td, *J* = 7.8, 1.8 Hz, 1H), 7.10 (s, 1H), 6.82 (s, 1H), 6.08 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.9, 147.3, 140.9, 138.6, 132.9, 130.9, 130.1, 127.3, 122.9, 117.6, 111.2, 110.8, 105.1, 102.5; HRMS: $C_{14}H_8NO_2Br$ calculated 300.9738, found 300.9735; New compound.



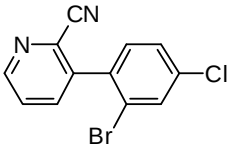
6-(2-Bromo-4-fluorophenyl)benzo[*d*][1,3]dioxole-5-carbonitrile (1N): White solid (928 mg, 58%), mp: 136–138 ^{o}C; IR (KBr): 3084, 2920, 2226, 1602, 1505, 1480, 1238, 1041, 933, 869, 822, 733 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 (dd, *J* = 8.4, 3.0 Hz, 1H), 7.30 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.12 (td, *J* = 7.8, 2.4 Hz, 1H), 7.11 (s, 1H), 6.81 (s, 1H), 6.13 (d, *J* = 1.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.4 (d, *J* = 252.0 Hz), 151.1, 147.6, 140.2, 134.9 (d, *J* = 3.0 Hz), 132.1 (d, *J* = 7.5 Hz), 123.5 (d, *J* = 10.5 Hz), 120.5 (d, *J* = 24.0 Hz), 117.6, 114.8 (d, *J* = 22.5 Hz), 111.5, 111.1, 105.7, 102.6; HRMS: $C_{14}H_7BrFNO_2$ calculated 318.9644, found 318.9640; New compound.



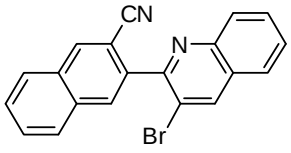
2'-Bromo-5-chloro-4'-fluoro-[1,1'-biphenyl]-2-carbonitrile (1O): White solid (834 mg, 54%), mp: 167–168 °C; IR (KBr): 2235, 1652, 1586, 1468, 1394, 1379, 1255, 1095, 879, 824, 622 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.42 (s, 1H), 7.31 (td, *J* = 7.8, 1.2 Hz, 1H), 7.16 (td, *J* = 7.8, 0.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.7 (d, *J* = 253.5 Hz), 145.3, 139.0, 134.0 (d, *J* = 3.0 Hz), 133.9, 131.8 (d, *J* = 9.0 Hz), 131.2, 128.9, 123.1 (d, *J* = 9.0 Hz), 120.7 (d, *J* = 24.0 Hz), 116.8, 115.1 (d, *J* = 21 Hz), 111.7; HRMS: $C_{13}H_6BrClFN$ calculated 308.9356, found 308.9354; New compound.



2'-Bromo-4,5-dimethoxy-5'-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile (1P): White solid (700 mg, 36%), mp: 188–189 °C; IR (KBr): 3006, 2942, 2224, 1519, 1466, 1410, 1352, 1333, 1274, 1230, 1166, 1124, 1086, 1044, 966, 864, 741, 644, 625, 539 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H), 7.55 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.17 (s, 1H), 6.83 (s, 1H), 3.96 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.3, 149.1, 139.9, 137.6, 133.8, 130.1 (q, *J* = 33 Hz), 127.9, 127.4, 126.8, 123.5 (q, *J* = 271.5 Hz), 117.7, 114.2, 113.0, 104.3, 56.3 (2C); HRMS: $C_{16}H_{11}BrF_3NO_2$ calculated 384.9925, found 384.9917; New compound.

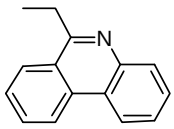


3-(2-Bromo-4-chlorophenyl)picolinonitrile (1Q): White solid (290 mg, 50%), mp: 93–95 °C; IR (KBr): 3059, 2954, 2235, 1571, 1546, 1474, 1441, 1369, 1247, 1122, 1097, 1066, 1047, 872, 808, 775, 697, 669, 542 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.76 (d, *J* = 4.8 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.77 (s, 1H), 7.60 (dd, *J* = 8.4, 4.8 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.3, 140.5, 138.5, 136.4, 134.7, 133.5, 133.1, 131.6, 128.2, 126.1, 123.4, 115.9; HRMS: $C_{12}H_6BrClN_2$ calculated 291.9403, found 291.9409; New compound.

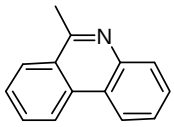


3-(3-Bromoquinolin-2-yl)-2-naphthonitrile (1R): White solid (632 mg, 88%), mp: 192–193 °C; IR (KBr): 3054, 2226, 1766, 1580, 1485, 1397, 1272, 1119, 953, 889, 786, cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.40 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.13 (s, 1H), 7.98 (d, *J* = 7.8, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.80 (td, *J* = 8.4, 1.2 Hz, 1H), 7.72–7.64 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 155.4, 146.4, 139.9, 137.8, 135.2, 134.2, 132.0, 130.5, 130.1, 129.7, 129.5, 128.8, 128.5, 128.3, 128.2 (2C), 126.7, 117.9, 117.2, 110.2; HRMS: $C_{20}H_{11}BrN_2$ calculated 358.0106, found 358.0112; New compound.

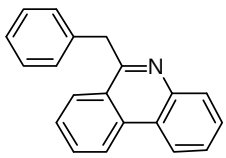
Spectral Data for all products:



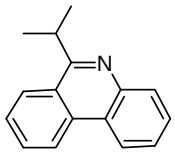
6-Ethylphenanthridine (3a): Yellow oil (72 mg, 86%); IR (KBr): 3073, 2926, 1688, 1583, 1455, 1374, 1361, 1022, 869 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.65 (d, *J* = 8.4 Hz, 1H), 8.54 (dd, *J* = 7.8, 0.6 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.13 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.83 (td, *J* = 7.8, 1.2 Hz, 1H), 7.73–7.68 (m, 2H), 7.62 (td, *J* = 7.8, 1.2 Hz, 1H), 3.42 (q, *J* = 7.8 Hz, 2H), 1.52 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.2, 143.8, 132.9, 130.3, 129.6, 128.6, 127.2, 126.3, 126.2, 125.0, 123.7, 122.5, 121.9, 29.4, 13.6; HRMS: $C_{15}H_{13}N$ calculated 207.1048, found 207.1041; Registry Number: [13362-58-8].



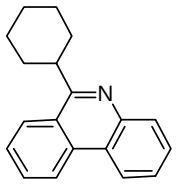
6-Methylphenanthridine (3b): Yellow oil (69 mg, 89%); IR (KBr): 3070, 2956, 2923, 1616, 1585, 1485, 1374, 1355, 1316, 864, 755, 725 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.63 (d, *J* = 8.4, 1H), 8.54 (dd, *J* = 8.4, 0.6 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.85 (td, *J* = 8.4, 0.6 Hz, 1H), 7.72 (dd, *J* = 7.2, 0.6 Hz, 1H), 7.69 (dd, *J* = 7.2, 0.6 Hz, 1H), 7.62 (td, *J* = 7.8, 0.6 Hz, 1H), 3.05 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.9, 143.7, 132.6, 130.5, 129.4, 128.6, 127.3, 126.5, 126.3,. 125.9, 123.8, 122.3, 121.9, 23.4; HRMS: $C_{14}H_{11}N$ calculated 193.0891, found 193.0895; Registry Number: [3955-65-5].



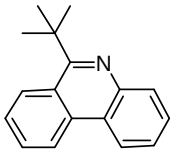
6-Benzylphenanthridine (3c): Yellow solid (74 mg, 69%), mp: 103–104 °C IR (KBr): 2932, 1610, 1585, 1527, 1488, 1455, 1316, 953 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.62 (d, *J* = 7.8 Hz, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 8.4 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 4.80 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.1, 143.7, 139.1, 133.2, 130.3, 129.8, 128.6, 128.5 (2C), 128.5 (2C), 127.3, 127.0, 126.6, 126.3, 125.3, 123.9, 122.3, 121.9, 43.0; HRMS: $C_{20}H_{15}N$ calculated 269.1204, found 269.1203; Registry Number: [16573-51-6].



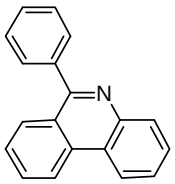
6-Isopropylphenanthridine (3d): Colorless oil (41 mg, 46%); IR (KBr): 3070, 2965, 2929, 1716, 1610, 1574, 1491, 1458, 1383, 1299, 1188, 1083, 914, 764, 725 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.66 (d, *J* = 7.8 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 4.01 (m, 1H), 1.54 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8, 143.8, 133.0, 129.9, 129.9, 128.4, 127.1, 126.2, 125.7, 124.7, 123.4, 122.6, 121.8, 31.5, 21.9 (2C); HRMS: $C_{16}H_{15}N$ calculated 221.1204, found 221.1207; Registry Number: [16573-52-7].



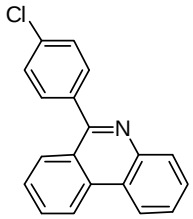
6-Cyclohexylphenanthridine (3e): Colorless oil (43 mg, 41%); IR (KBr): 2926, 1677, 1652, 1546, 1277, 1261, 764 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.66 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 7.8 Hz, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.81 (td, *J* = 7.8, 0.6 Hz, 1H), 7.71 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.68 (d, *J* = 6.6 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 3.62 (m, 1H), 2.09–2.07 (m, 2H), 1.98–1.84 (m, 5H), 1.61–1.42 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.3, 143.9, 133.0, 129.9, 129.9, 128.4, 127.0, 126.1, 125.6, 124.8, 123.3, 122.6, 121.8, 42.0, 32.3 (2C), 26.9 (2C), 26.3; HRMS: $C_{19}H_{19}N$ calculated 261.1517, found 261.1518; Registry Number: [16573-53-8].



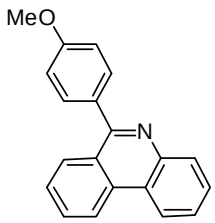
6-(*tert*-Butyl)phenanthridine (3f): Yellow oil (31 mg, 33%); IR (KBr): 3073, 2962, 2932, 1569, 1527, 1463, 1399, 1369, 767 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.69 (d, *J* = 8.4 Hz, 1H), 8.63 (d, *J* = 9.0 Hz, 1H), 8.53 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 1.73 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.6, 143.0, 134.0, 130.3,129.2, 128.3, 128.2, 126.4, 125.9, 124.3, 123.4, 123.0, 121.6, 40.2, 31.2 (3C); HRMS: $C_{17}H_{17}N$ calculated 235.1361, found 235.1360; Registry Number: [400820-16-8].



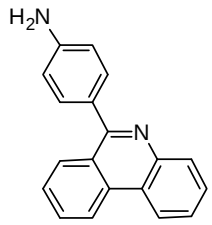
6-Phenylphenanthridine (3g): White solid (98 mg, 96%), mp: 98–99 ^oC; IR (KBr): 3029, 2923, 2848, 1613, 1577, 1560, 1527, 1458, 1358, 1136, 961, 769, 728, 697, 672, 617 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.72 (d, *J* = 8.4 Hz, 1H), 8.63 (d, *J* = 8.4 Hz, 1H), 8.25 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.87 (td, *J* = 7.8, 1.2 Hz, 1H), 7.78–7.74 (m, 3H), 7.70 (td, *J* = 7.8, 1.2 Hz, 1H), 7.62 (td, *J* = 7.8, 0.6 Hz, 1H), 7.58–7.52 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.3, 143.8, 139.8, 133.5, 130.5, 130.4, 129.7 (2C), 128.9, 128.8, 128.7, 128.4 (2C), 127.1, 126.9, 125.3, 123.7, 122.2, 121.9; HRMS: $C_{19}H_{13}N$ calculated 255.1048, found 255.1041; Registry Number: [2720-93-6].



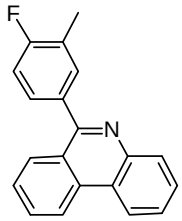
6-(4-Chlorophenyl)phenanthridine (3h): White solid (86 mg, 74%), mp: 153–154 ^oC; IR (KBr): 3048, 2923, 1610, 1558, 1519, 1485, 1460, 1355, 1108, 830, 750 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.71 (d, *J* = 7.8 Hz, 1H), 8.62 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.87 (t, *J* = 7.8 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.70 (m, *J* = 8.4 Hz, 3H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.0, 143.7, 138.2, 134.9, 133.5, 131.1 (2C), 130.7, 130.3, 129.0, 128.7 (2C), 128.5, 127.3, 127.1, 125.0, 123.8, 122.3, 122.0; HRMS: $C_{19}H_{12}ClN$ calculated 289.0658, found 289.0653; Registry Number: [98351-80-5].



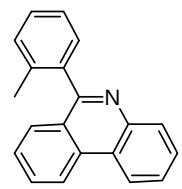
6-(4-Methoxyphenyl)phenanthridine (3i): White solid (87 mg, 76%), mp: 146–147 °C; IR (KBr): 2995, 2954, 1610, 1583, 1558, 1485, 1455, 1358, 1330, 1280, 1255, 1169, 961, 839, 761, 733 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.69 (d, *J* = 8.4 Hz, 1H), 8.61 (d, *J* = 7.8 Hz, 1H), 8.24 (d, *J* = 7.8 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.85 (t, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.9, 160.1, 143.9, 133.5, 132.3, 131.2 (2C), 130.4, 130.3, 128.9, 128.8, 127.0, 126.7, 125.4, 123.6, 122.2, 121.9, 113.9 (2C), 55.4; HRMS: $C_{20}H_{15}NO$ calculated 285.1154, found 285.1156; Registry Number: [98351-86-1].



6-(4-Aminophenyl)phenanthridine (3j): Yellow solid (89 mg, 82%), mp: 193–194 °C; IR (KBr): 3029, 2934, 1616, 1560, 1485, 1458, 1327, 1183, 969, 839, 769, 672, 542 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.68 (dd, *J* = 8.4, 0.6 Hz, 1H), 8.59 (dd, *J* = 7.8, 0.6 Hz, 1H), 8.23 (dd, *J* = 3.6, 0.6 Hz, 1H), 8.22 (dd, *J* = 3, 0.6 Hz. 1H), 7.84 (td, *J* = 7.8, 1.2 Hz, 1H), 7.73 (td, *J* = 7.8, 1.2 Hz, 1H), 7.65 (td, *J* = 7.8, 1.2 Hz, 1H), 7.63–7.59 (m, 3H), 6.86 (dd, *J* = 6.6, 1.8 Hz, 2H), 3.87 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.2, 147.1, 144.0, 133.5, 131.2 (2C), 130.3, 130.2, 130.0, 129.1, 128.7, 126.9, 126.5, 125.4, 123.5, 122.1, 121.9, 114.8 (2C); HRMS: $C_{19}H_{14}N_2$ calculated 270.1157, found 270.1144; Registry Number: [452070-80-3].

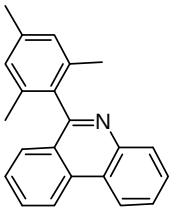


6-(4-Fluoro-3-methylphenyl)phenanthridine (3k): White solid (94 mg, 82%), mp: 97–99 °C; IR (KBr): 3076, 2929, 1613, 1596, 1571, 1508, 1483, 1460, 1402, 1333, 1249, 1222, 764, 728 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.70 (d, *J* = 7.8 Hz, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.86 (t, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 8.4 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.8 (d, *J* = 244.5 Hz), 160.4, 143.7, 135.6, 133.5, 132.9 (d, *J* = 6.0 Hz), 130.6, 130.3, 128.9, 128.8, 128.7, 127.2, 127.0, 125.2, 125.2 (d, *J* = 21.0 Hz), 123.7, 122.2, 121.9, 114.9 (d, *J* = 22.5 Hz), 14.6; HRMS: $C_{20}H_{14}FN$ calculated 287.1110, found 287.1107; New compound.

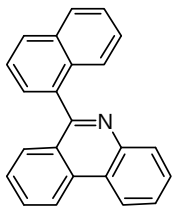


6-(*o*-Tolyl)phenanthridine (3l): Yellow oil (100 mg, 93%); IR (KBr): 2959, 1616, 1571, 1458, 1363, 1330, 1299, 1141, 733, 686, 617 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.71 (d, *J* = 8.4 Hz, 1H), 8.65 (d, *J* = 7.8 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.85 (td, *J* = .7.8, 1.2 Hz, 1H),

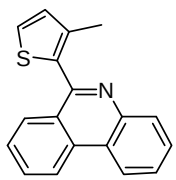
7.78 (td, *J* = 8.4, 1.2 Hz, 1H), 7.73–7.70 (m, 2H), 7.58 (td, *J* = 8.4, 0.6 Hz, 1H), 7.44–7.41 (m, 2H), 7.38–7.37 (m, 2H), 2.12 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.9, 143.8, 139.2, 136.4, 133.0, 130.6, 130.3, 130.3, 129.3, 128.8, 128.6, 128.5, 127.3, 126.9, 125.8 (2C), 123.8, 122.1, 122.0, 19.8; HRMS: $C_{20}H_{15}N$ calculated 269.1204, found 269.1193; Registry Number: [32317-26-3].



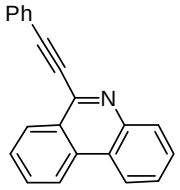
6-Mesitylphenanthridine (3m): White solid (100 mg, 84%), mp: 156–157 ^{o}C; IR (KBr): 2979, 2915, 2854, 1613, 1583, 1569, 1483, 1455, 1430, 1377, 1352, 1316, 1297, 1261, 1169, 1119, 1041, 964, 936, 866, 758, 733 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.70 (d, *J* = 7.8 Hz, 1H), 8.65 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.84 (t, *J* = 7.8 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.03 (s, 2H), 2.40 (s, 3H), 1.95 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.2, 144.2, 137.8, 136.2 (2C), 135.6, 132.9, 130.7, 130.3, 128.6, 128.4 (2C), 127.9, 127.5, 126.8, 125.9, 123.7, 122.2, 122.0, 21.2, 19.7 (2C); HRMS: $C_{22}H_{19}N$ calculated 297.1517, found 297.1519; Registry Number: [32317-27-4].



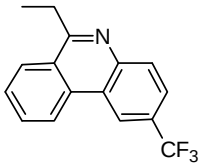
6-(Naphthalen-1-yl)phenanthridine (3n): White solid (101 mg, 83%), mp: 68–69 ^{o}C; IR (KBr): 3009, 1610, 1566, 1524, 1508, 1480, 1441, 1349, 1327, 1294, 1041, 1019, 767 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.73 (d, *J* = 8.4 Hz, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.84–7.81 (m, 2H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.71–7.66 (m, 3H), 7.50 (t, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.0, 143.8, 137.1, 133.6, 132.9, 132.2, 130.7, 130.4, 129.0, 128.8 (2C), 128.2, 127.3, 127.2, 127.1, 126.5, 126.3, 126.0, 125.9, 125.3, 123.9, 122.0 (2C); HRMS: $C_{23}H_{15}N$ calculated 305.1204, found 305.1195; Registry Number: [42028-08-1].



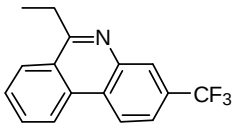
6-(3-Methylthiophen-2-yl)phenanthridine (3o): Yellow solid (86 mg, 78%), mp: 120–121 ^{o}C; IR (KBr): 3070, 2920, 1608, 1583, 1522, 1485, 1460, 1433, 1352, 1313, 1216, 1166, 1136, 1036, 1011, 833, 758, 725, 705, 619, 567 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.84 (td, *J* = 7.8, 1.2 Hz, 1H), 7.76 (td, *J* = 7.8, 1.2 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.64 (t, 8.4 Hz, 1H), 7.44 (d, *J* = 5.4 Hz, 1H), 7.05 (d, *J* = 4.8 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 155.2, 143.8, 137.1, 134.7, 133.1, 130.7, 130.3, 130.0, 128.8, 128.7, 127.3, 127.2, 126.0, 125.6, 123.8, 122.1, 121.9, 15.0; HRMS: $C_{18}H_{13}NS$ calculated 275.0769, found 275.0761; New compound.



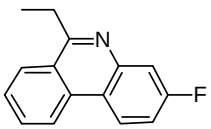
6-(Phenylethynyl)phenanthridine (3p): Yellow solid (30 mg, 27%), mp: 42–44 °C; IR (KBr): 2204, 1724, 1563, 1369, 683, 661 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.68 (d, *J* = 7.8 Hz, 1H), 8.66 (d, *J* = 8.4 Hz, 1H), 8.59 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.91 (t, *J* = 7.8 Hz, 1H), 7.79–7.75 (m, 4H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.45–7.44 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.0, 144.2, 132.6, 132.4 (2C), 131.1, 130.2, 129.4, 129.0, 128.5 (2C), 128.2, 127.8, 127.7, 126.8, 123.9, 122.1 (2C), 122.1, 93.7, 87.1; HRMS: $C_{21}H_{13}N$ calculated 279.1048, found 279.1050; New compound.



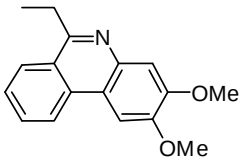
6-Ethyl-2-(trifluoromethyl)phenanthridine (3A): White solid (79 mg, 72%), mp: 48–49 °C; IR (KBr): 2929, 2873, 1633, 1591, 1458, 1435, 1358, 1324, 1291, 1227, 1125, 1075, 969, 769 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.66 (d, *J* = 7.8 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 9.0 Hz, 1H), 7.90 (t, *J* = 7.8, 0.6 Hz, 2H), 7.77 (t, *J* = 7.8, 0.6 Hz, 1H), 3.44 (q, *J* = 7.8 Hz, 2H), 1.53 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.6, 145.3, 132.5, 130.9, 130.5, 128.2, 128.0 (q, *J* = 31.5 Hz), 126.4, 125.4, 124.5 (q, *J* = 3.0 Hz), 124.4 (q, *J* = 273 Hz), 123.3, 122.5, 119.8 (q, *J* = 4.5 Hz), 29.4, 13.2; HRMS: $C_{16}H_{12}F_3N$ calculated 275.0922, found 275.0911; New compound.



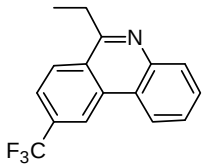
6-Ethyl-3-(trifluoromethyl)phenanthridine (3B): Yellow solid (79 mg, 72%), mp: 50–52 °C; IR (KBr): 2932, 2854, 1721, 1591, 1535, 1469, 1336, 1269, 1122, 1069, 825, 755, 722 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.67 (d, *J* = 8.4, Hz, 1H), 8.64 (d, *J* = 9.0 Hz, 1H), 8.43 (s, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.90 (td, *J* = 7.8, 1.2 Hz, 1H), 7.81 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.78 (td, *J* = 8.4, 0.6 Hz, 1H), 3.43 (q, *J* = 7.8 Hz, 2H), 1.53 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.7, 143.2, 132.1, 130.8, 130.4 (q, *J* = 31.5 Hz), 128.4, 127.2, 126.4, 126.0, 125.7, 124.2 (q, *J* = 270.0 Hz), 122.9, 122.9, 122.1, 29.2, 13.1; HRMS: $C_{16}H_{12}F_3N$ calculated 275.0922, found 275.0921; New compound.



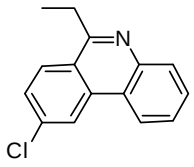
6-Ethyl-3-fluorophenanthridine (3C): White solid (71 mg, 79%), mp: 70–71 °C; IR (KBr): 2879, 1619, 1580, 1488, 1455, 1152, 964, 878 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.53 (d, *J* = 8.4 Hz, 1H), 8.48 (dd, *J* = 9.0, 6.0 Hz, 1H), 8.24 (d, *J* = 7.8 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.77 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.35 (td, *J* = 8.4, 2.4 Hz, 1H), 3.39 (q, *J* = 7.8 Hz, 2H), 1.50 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.6, 162.6 (d, *J* = 246 Hz), 145.1 (d, *J* = 12 Hz), 132.7, 130.6, 127.0, 126.3, 124.6, 123.8 (d, *J* = 9.0 Hz), 122.3, 120.3, 115.2 (d, *J* = 24 Hz), 114.1 (d, *J* = 21 Hz), 29.3, 13.3; HRMS: $C_{15}H_{12}FN$ calculated 225.0954, found 225.0943; New compound.



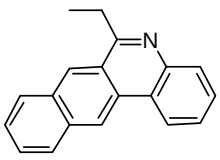
6-Ethyl-2,3-dimethoxyphenanthridine (3D): Yellow solid (41 mg, 38%), mp: 117–119 °C; IR (KBr): 2965, 2934, 1646, 1502, 1458, 1438, 1261, 1219, 1205, 1158, 1041, 850, 750 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.50 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 1H), 7.80 (t, *J* = 7.2 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.56 (s, 1H), 4.12 (s, 3H), 4.07 (s, 3H), 3.39 (q, *J* = 7.8 Hz, 2H), 1.50 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.3, 150.9, 149.0, 139.9, 132.6, 129.9, 126.4, 126.1, 124.2, 122.0, 117.7, 109.8, 101.8, 56.1 (2C), 29.3, 13.8; HRMS: $C_{17}H_{17}NO_2$ calculated 267.1259, found 267.1254; New compound.



6-Ethyl-9-(trifluoromethyl)phenanthridine (3E): White solid (79 mg, 72%), mp: 76–78 °C; IR (KBr): 2973, 2934, 1596, 1583, 1494, 1430, 1355, 1316, 1269, 1177, 1122, 1072, 1016, 894, 831, 761 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.77 (td, *J* = 7.8, 1.2 Hz, 1H), 7.67 (td, *J* = 7.8, 1.2 Hz, 1H), 3.42 (q, *J* = 7.8 Hz, 2H), 1.52 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.5, 144.1, 132.7, 131.7 (q, *J* = 33 Hz), 129.9, 129.5, 127.1, 126.9, 126.5, 124.0 (q, *J* = 270 Hz), 123.2 (q, *J* = 3.0 Hz), 123.0, 121.9, 120.1 (q, *J* = 3.0 Hz), 29.3, 13.2; HRMS: $C_{16}H_{12}F_3N$ calculated 275.0922, found 275.0927; New compound.

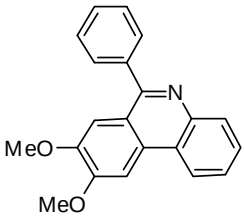


9-Chloro-6-ethylphenanthridine (3F): White solid (73 mg, 76%), mp: 192–194 °C; IR (KBr): 2926, 2854, 1641, 1605, 1513, 1494, 1455, 1413, 1380, 1361, 1222, 872, 764 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 9.09 (d, *J* = 7.8 Hz, 1H), 8.73 (s, 1H), 8.57 (d, *J* = 7.8 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 7.94 (t, *J* = 7.8 Hz, 1H), 7.91–7.90 (m, 2H), 3.98 (q, *J* = 7.8 Hz, 2H), 1.64 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.5, 143.6, 136.1, 134.0, 132.1, 130.6, 130.2, 130.1, 123.3, 123.2, 123.1, 122.5, 121.3, 25.0, 15.2; HRMS: $C_{15}H_{12}ClN$ calculated 241.0658, found 241.0663; New compound.

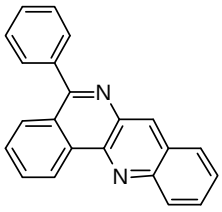


6-Ethylbenzo[*j*]phenanthridine (3G): White solid (83 mg, 81%), mp: 58–60 °C; IR (KBr): 2970, 2882, 2848, 1649, 1602, 1563, 1546, 1496, 1472, 1374, 1349, 1286, 1183, 1030, 941, 886, 750 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 9.10 (s, 1H), 8.79 (s, 1H), 8.68 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.67–7.60 (m, 3H), 3.52 (q, *J* = 7.8 Hz, 2H), 1.59 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.2, 143.0, 133.8, 131.9, 129.6 (2C), 128.9, 128.6, 128.1, 127.6, 126.5, 126.3 (2C), 123.8, 123.6, 122.1, 121.2, 29.5, 13.4; HRMS:

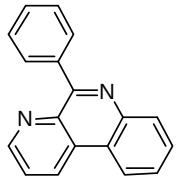
$C_{19}H_{15}N$ calculated 257.1204, found 257.1199; New compound.



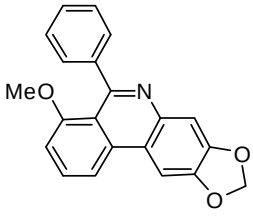
8,9-Dimethoxy-6-phenylphenanthridine (3H): White solid (74 mg, 59%), mp: 133–135 °C; IR (KBr): 3059, 2962, 2937, 2862, 2837, 1616, 1585, 1558, 1494, 1466, 1422, 1266, 1213, 1177, 1136, 1105, 1033, 855, 758 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.46 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.96 (s, 1H), 7.75 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.69 (td, *J* = 7.8, 0.6 Hz, 1H), 7.63 (t, *J* = 8.4 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.43 (s, 1H), 4.15 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.6, 152.4, 149.3, 143.5, 140.1, 130.3, 129.5 (2C), 129.2, 128.6, 128.5 (2C), 127.9, 126.4, 123.4, 121.4, 120.4, 108.3, 102.1, 56.1, 55.9; HRMS: $C_{21}H_{17}NO_2$ calculated 315.1259, found 315.1265; New compound.



5-Phenyldibenzo[*b*,*h*][1,5]naphthyridine (3I): Yellow solid (83 mg, 68%), mp: 198–199 °C; IR (KBr): 1621, 1588, 1555, 1485, 1444, 1383, 919, 855, 769, 667, 611 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 9.54 (d, *J* = 7.8 Hz, 1H), 9.00 (s, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.10 (dd, *J* = 7.8, 4.2 Hz, 2H), 7.97 (t, *J* = 10.2 Hz, 1H), 7.86 (t, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.65–7.56 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.7, 147.8, 142.6, 139.2, 136.2, 136.1, 134.0, 133.7, 131.2, 130.2, 129.6 (2C), 129.5, 129.1, 128.7, 128.6, 128.5 (2C), 128.4, 127.5, 126.4, 124.7; HRMS: $C_{22}H_{14}N_2$ calculated 306.1157, found 306.1160; Registry Number: [1195521-66-4].

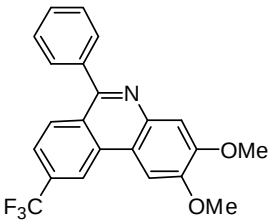


5-Phenylbenzo[*f*][1,7]naphthyridine (3J): Yellow solid (85 mg, 83%), mp: 133–135 °C; IR (KBr): 2920, 2857, 1677, 1558, 1474, 1455, 1152, 1027, 997, 767 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 9.08 (dd, *J* = 4.2, 0.6 Hz, 1H), 8.98 (d, *J* = 8.4 Hz, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 7.2 Hz, 2H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.76 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.7, 150.1, 143.8, 141.0, 138.8, 131.0 (2C), 130.6, 130.4, 129.5, 129.1, 128.8, 128.0 (2C), 127.3, 124.7, 123.2, 121.9; HRMS: $C_{18}H_{12}N_2$ calculated 256.1000, found 256.0998; New compound.

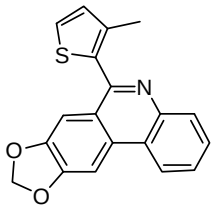


4-Methoxy-5-phenyl-[1,3]dioxolo[4,5-*b*]phenanthridine (3K): Yellow solid (75 mg, 57%), mp: 144–146 °C; IR (KBr): 2918, 1616, 1566, 1466, 1261, 1213, 1191, 1094, 1044, 941 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.87 (s,

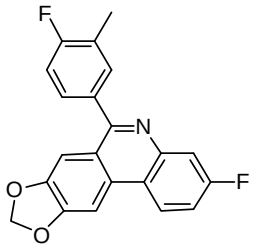
1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.55 (s, 1H), 7.48–7.47 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.14 (s, 2H), 3.54 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.9, 157.1, 149.5, 148.0, 145.1, 141.0, 135.6, 131.0, 127.9 (2C), 127.2 (2C), 126.9, 119.1, 115.9, 114.3, 107.6, 107.4, 101.7, 99.6, 55.3; HRMS: $C_{21}H_{15}NO_3$ calculated 329.1052, found 329.1054; New compound.



2,3-Dimethoxy-6-phenyl-9-(trifluoromethyl)phenanthridine (3L): White solid (94 mg, 61%), mp: 197–199 °C; IR (KBr): 2932, 2845, 1613, 1508, 1469, 1438, 1336, 1286, 1252, 1211, 1127, 1069, 958 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.87 (s, 1H), 7.73–7.69 (m, 4H), 7.60–7.53 (m, 3H), 4.19 (s, 3H), 4.07 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.7, 151.8, 150.1, 140.5, 139.3, 132.6, 131.6 (q, *J* = 33 Hz), 129.9, 129.7 (2C), 128.8, 128.6 (2C), 125.7, 124.1 (q, *J* = 271.5 Hz), 121.8, 119.3, 117.6, 110.5, 101.4, 56.4, 56.2; HRMS: $C_{22}H_{16}F_3NO_2$ calculated 383.1133, found 383.1129; New compound.

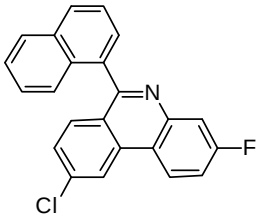


6-(3-Methylthiophen-2-yl)-[1,3]dioxolo[4,5-*j*]phenanthridine (3M): Yellow solid (95 mg, 74%), mp: 192–193 °C; IR (KBr): 2926, 2854, 1463, 1247, 1030, 944, 753, 669 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.41 (d, *J* = 7.8 Hz, 1H), 8.20 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.98 (s, 1H), 7.70 (td, *J* = 7.8, 0.6 Hz, 1H), 7.64 (td, *J* = 7.8, 1.2 Hz, 1H), 7.41 (d, *J* = 5.4 Hz, 1H), 7.31 (s, 1H), 7.01 (d, *J* = 4.8 Hz, 1H), 6.15 (s, 2H), 2.14 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.8, 151.1, 148.3, 143.6, 136.8, 135.0, 131.0, 130.4, 129.9, 128.2, 126.9, 125.5, 124.0, 123.0, 121.8, 105.8, 101.9, 100.0, 14.9; HRMS: $C_{19}H_{13}NO_2S$ calculated 319.0667, found 319.0660; New compound.

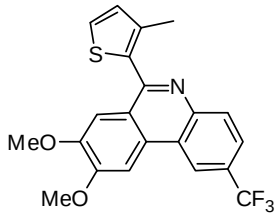


3-Fluoro-6-(4-fluoro-3-methylphenyl)-[1,3]dioxolo[4,5-*j*]phenanthridine (3N): White solid (94 mg, 67%), mp: 192–193 °C; IR (KBr): 3081, 2962, 1710, 1596, 1577, 1508, 1483, 1449, 1369, 1263, 1238, 1208, 1119, 1033, 866, 825, 744, 631, 531 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.36 (dd, *J* = 9.0, 5.4 Hz, 1H), 7.90 (s, 1H), 7.81 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.52 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.44 (td, *J* = 7.8, 2.4 Hz, 1H), 7.38 (td, *J* = 8.4, 2.4 Hz, 1H), 7.36 (s, 1H), 7.17 (t, *J* = 9.0 Hz, 1H), 6.14 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 162.4 (d, *J* = 246.0 Hz), 161.7 (d, *J* = 246.0 Hz), 160.3, 151.3, 147.8, 144.7 (d, *J* = 10.5 Hz), 135.6 (d, *J* = 3.0 Hz), 132.6 (d, *J* = 4.5 Hz), 131.2, 128.5 (d, *J* = 7.5 Hz), 125.3 (d, *J* = 18.0 Hz), 123.7 (d, *J* = 9.0 Hz), 121.4, 120.6, 115.9 (d, *J* = 24.0 Hz), 115.0 (d, *J* = 22.5 Hz), 114.4 (d, *J* = 21.0 Hz), 105.9, 102.0, 100.0, 14.6 (d, *J* = 1.5

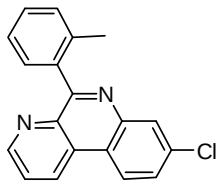
Hz); HRMS: $C_{21}H_{13}F_2NO_2$ calculated 349.0914, found 349.0919; New compound.



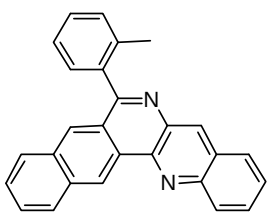
9-Chloro-3-fluoro-6-(naphthalen-1-yl)phenanthridine (3O): White solid (109 mg, 76%), mp: 90–92 ^{o}C; IR (KBr): 3059, 2959, 2918, 2851, 1608, 1574, 1480, 1447, 1408, 1355, 1294, 1191, 1089, 1019, 972, 936, 872, 839, 778, 672, 622, 578 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.62 (d, *J* = 1.8 Hz, 1H), 8.58 (dd, *J* = 9.0, 6.0 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.92 (dd, *J* = 9.6, 3.0 Hz, 1H), 7.67–7.62 (m, 2H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.53–7.49 (m, 2H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.33 (td, *J* = 7.8, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.2 (d, *J* = 247.5 Hz), 161.9, 145.6 (d, *J* = 10.5 Hz), 137.8, 136.4, 134.1, 133.7, 132.0, 130.9, 129.3, 128.4, 127.8, 127.4, 126.6, 126.2, 125.7, 125.3, 124.4, 124.1 (d, *J* = 9.0 Hz), 121.6, 119.7, 116.6 (d, *J* = 24.0 Hz), 115.1 (d, *J* = 19.5 Hz); HRMS: $C_{23}H_{13}ClFN$ calculated 357.0721, found 357.0728; New compound.



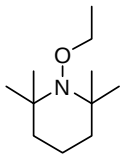
8,9-Dimethoxy-6-(3-methylthiophen-2-yl)-3-(trifluoromethyl)phenanthridine (3P): Yellow solid (77 mg, 48%), mp: 205–207 ^{o}C; IR (KBr): 3009, 2968, 2929, 2848, 1713, 1596, 1524, 1466, 1427, 1319, 1263, 1213, 1172, 1125, 1030, 853, 767, 750 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.72 (s, 1H), 8.32 (s, 1H), 7.95 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 4.8 Hz, 1H), 7.45 (s, 1H), 7.06 (d, *J* = 4.8 Hz, 1H), 4.21 (s, 3H), 3.94 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 155.7, 153.4, 150.4, 138.8, 137.5, 131.2, 130.3 (2C), 129.1, 126.3, 124.4 (q, *J* = 271.5 Hz), 124.0, 123.1, 121.8, 119.4 (q, *J* = 3.0 Hz), 108.4, 102.0 (2C), 56.5, 56.1, 15.3; HRMS: $C_{21}H_{16}F_3NO_2S$ calculated 403.0854, found 403.0846; New compound.



8-Chloro-5-(*o*-tolyl)benzo[*f*][1,7]naphthyridine (3Q): White solid (82 mg, 67%), mp: 140–142 ^{o}C; IR (KBr): 3065, 1608, 1560, 1463, 1349, 1222, 908, 789, 719 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.04 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.92 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 1.8 Hz, 1H), 7.76 (dd, *J* = 7.8, 4.2 Hz, 1H), 7.71 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.47 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.43 (td, *J* = 7.8, 1.2 Hz, 1H), 7.38–7.36 (m, 2H), 2.15 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.3, 150.8, 144.3, 141.3, 138.8, 136.6, 135.3, 130.2, 130.2, 129.8, 129.5, 128.9, 128.1, 128.0, 125.6, 125.2, 123.3, 121.8, 20.2; HRMS: $C_{19}H_{13}ClN_2$ calculated 304.0767, found 304.0759; New compound.



7-(*o*-Tolyl)benzo[*b*]naphtho[2,3-*h*][1,5]naphthyridine (3R): Yellow solid (101 mg, 68%), mp: 213–215 ^{o}C; IR (KBr): 2968, 2884, 1630, 1466, 1277, 1258, 767, 747 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.0 (s, 1H), 8.94 (s, 1H), 8.48 (s, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.19 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.89 (t, *J* = 7.8 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.54–7.50 (m, 2H), 7.46–7.43 (m, 2H), 2.24 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.7, 143.4, 138.6, 136.5, 135.8, 134.4, 133.3, 130.7, 130.4, 129.8, 129.4, 129.2 (2C), 129.1 (2C), 129.0, 128.7, 128.4 (2C), 128.3, 127.3, 126.6, 126.2, 126.0 (2C), 124.6, 19.8; HRMS: $C_{27}H_{18}N_2$ calculated 370.1470, found 370.1466; New compound.



1-Ethoxy-2,2,6,6-tetramethylpiperidine (4a): Red oil, easy to evaporate and decompose; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.10 (q, *J* = 6.4 Hz, 2H), 1.77–1.66 (m, 6H), 1.47–1.22 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 72.0, 59.3, 39.4, 32.8, 31.9, 19.9, 17.0, 13.4; GC-MS (EI) for $C_{10}H_{10}NO$: 185; Registry Number: [34672-83-8]

References

(1) Urawa, Y.; Naka, H.; Miyazawa, M.; Souda, S.; Ogura, K. *J. Organomet. Chem.* **2002**, *653*, 269.

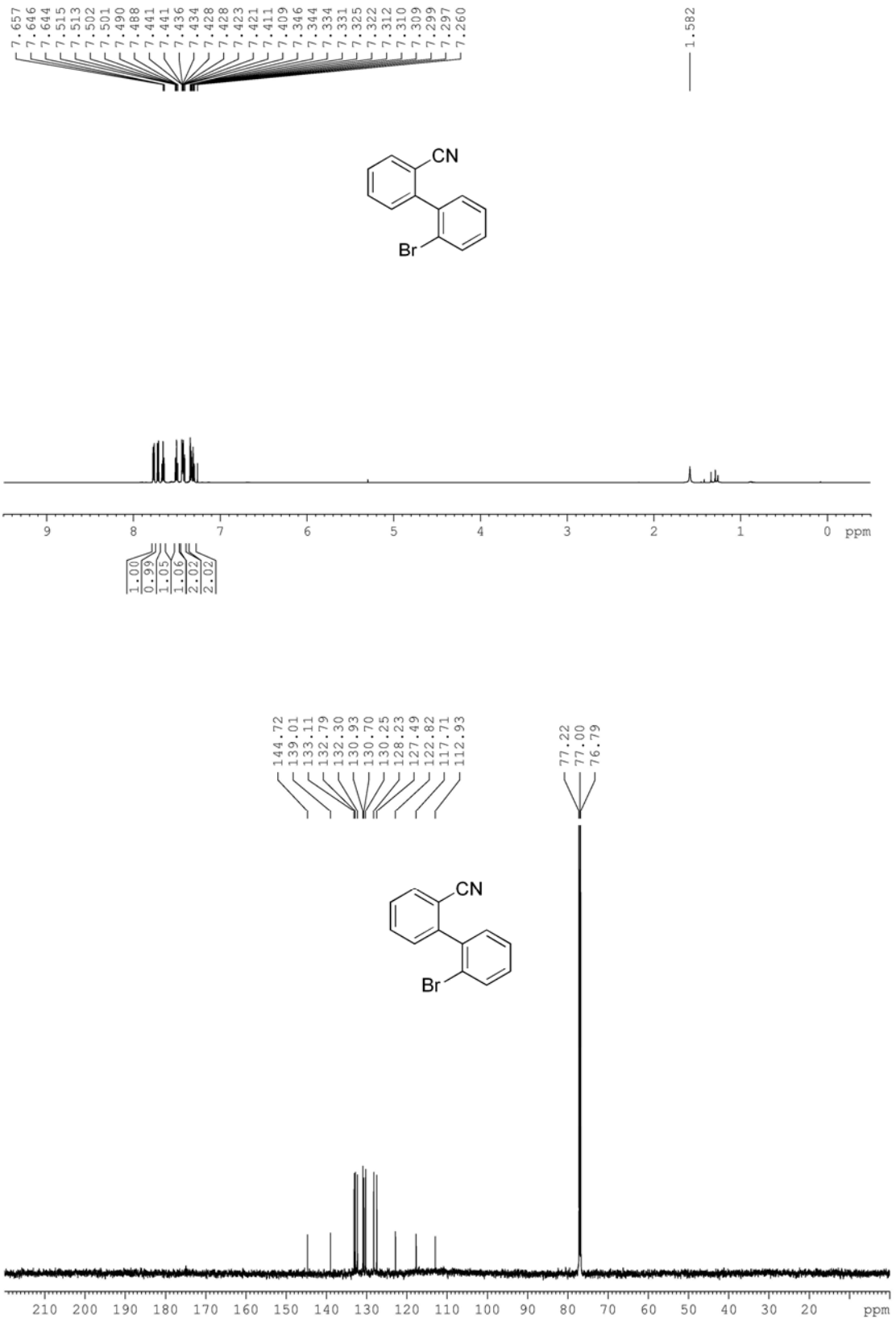
(2) Hansen, H. M.; Lysén, M.; Begtrup, M.; Kristensen, J. L. *Tetrahedron* **2005**, *61*, 9955.

(3) Wan, J.-C.; Huang, J.-M.; Jhan, Y.-H.; Hsieh, J.C. *Org. Lett.* **2013,** *15*, 2742.

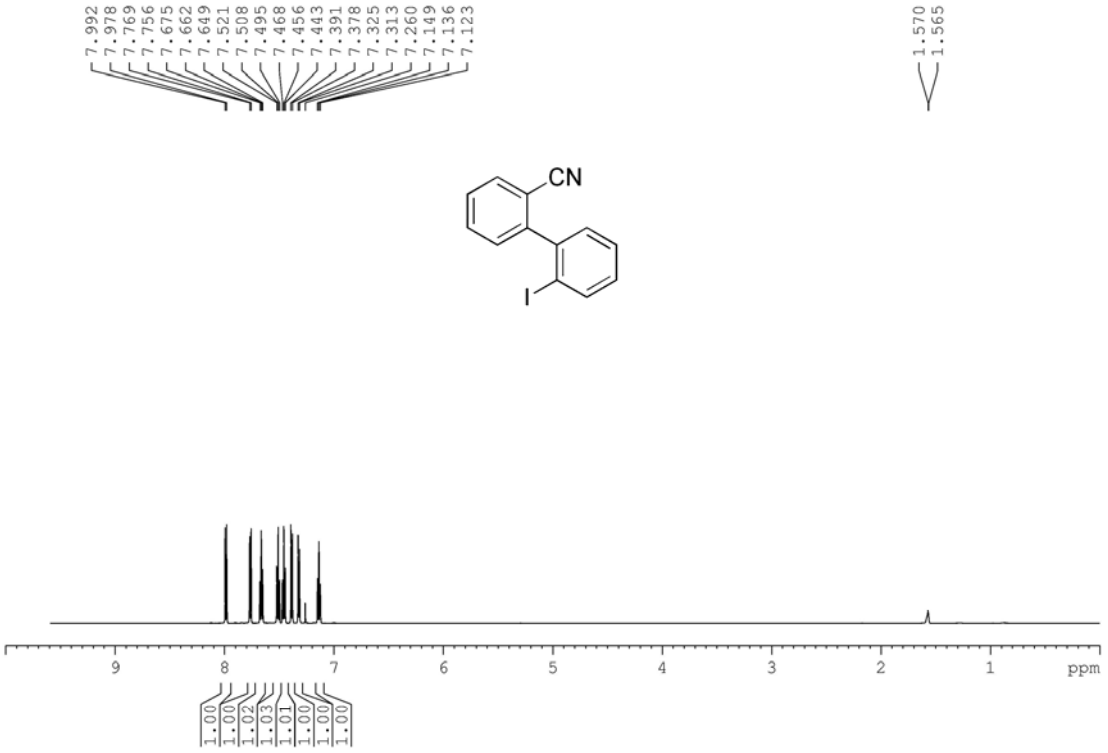
(4) Chen, Y.-F.; Wu, Y.-S.; Jhan, Y.-H.; Hsieh, J.-C. *Org. Chem. Front.* **2014**, *1*, 253.

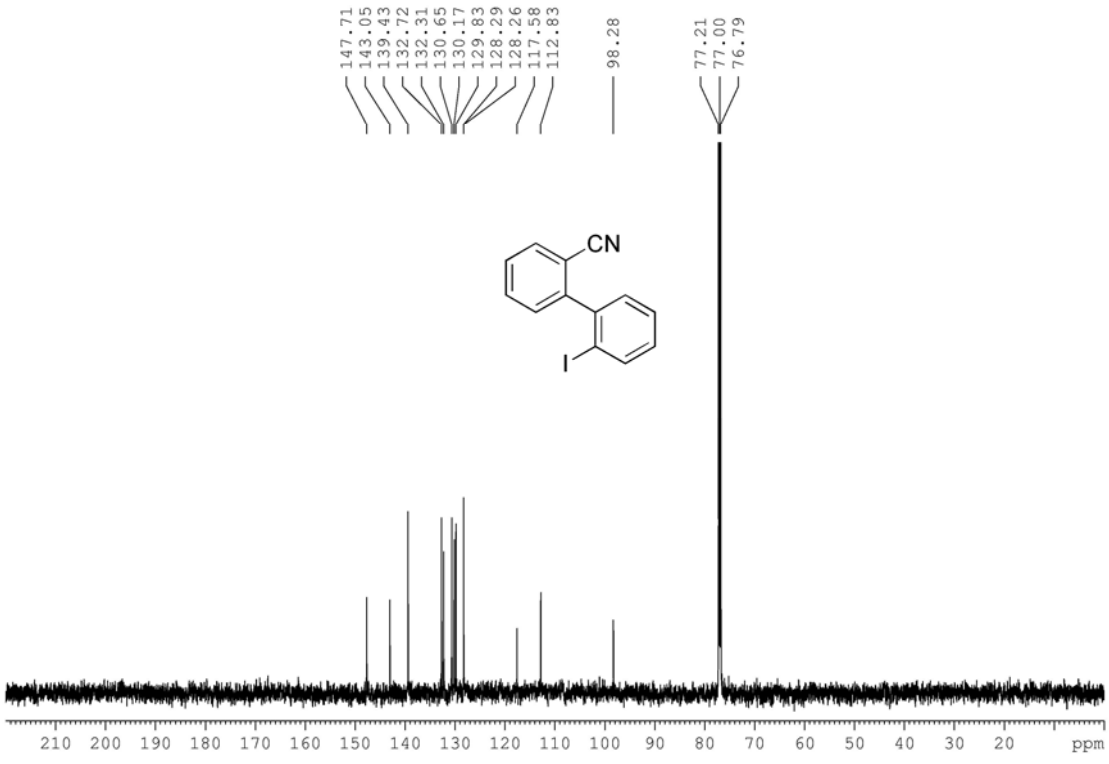
^{1}H and ^{13}C NMR Spectra for Substartes (600 MHz, $CDCl_3$)

2'-Bromo-[1,1'-biphenyl]-2-carbonitrile (1a)

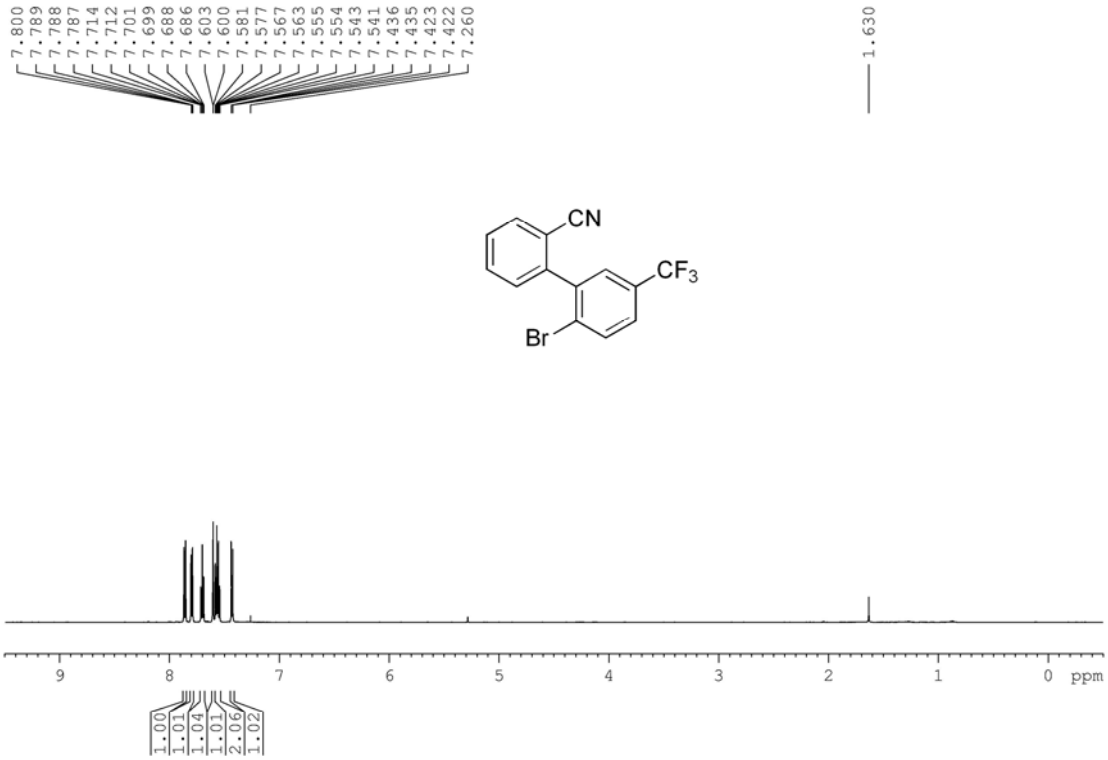


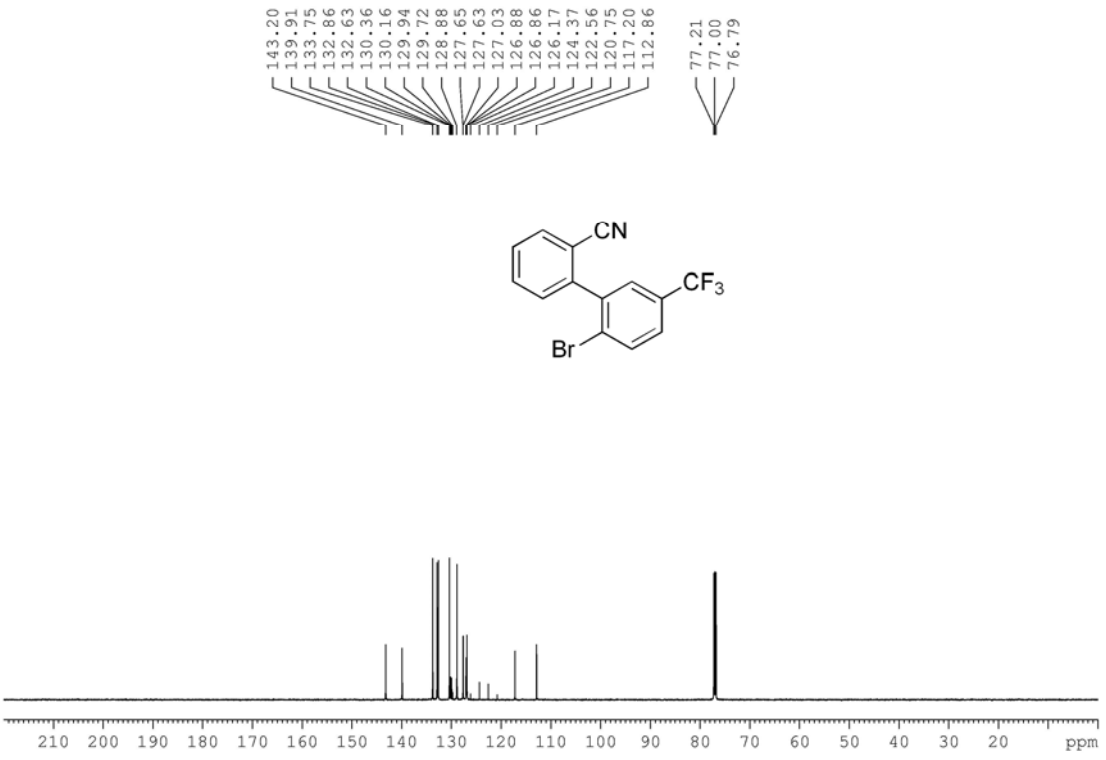
2'-Iodo-[1,1'-biphenyl]-2-carbonitrile (1b)



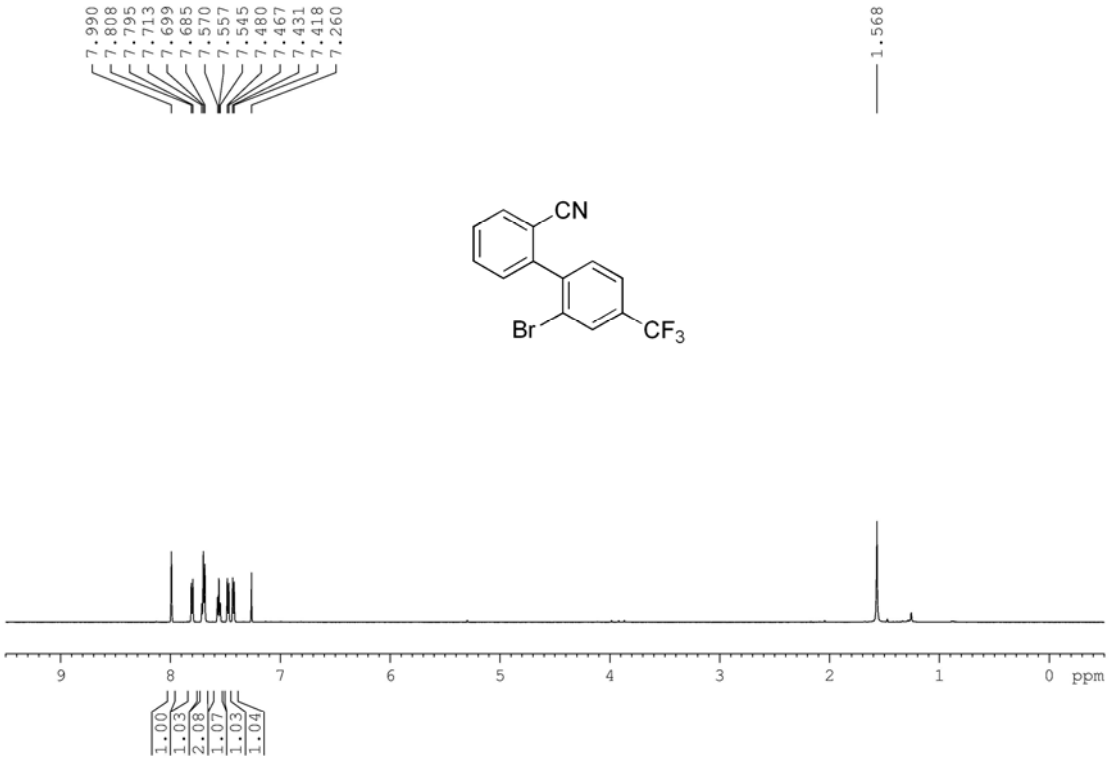


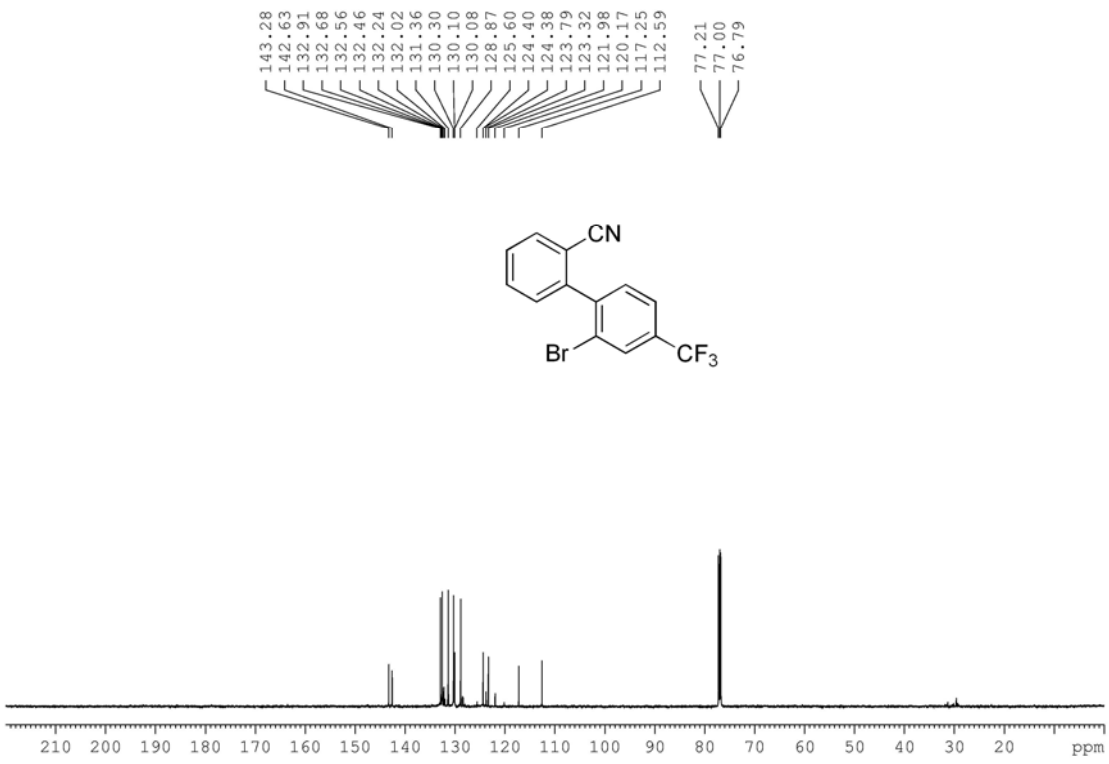
2'-Bromo-5'-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile (1A)



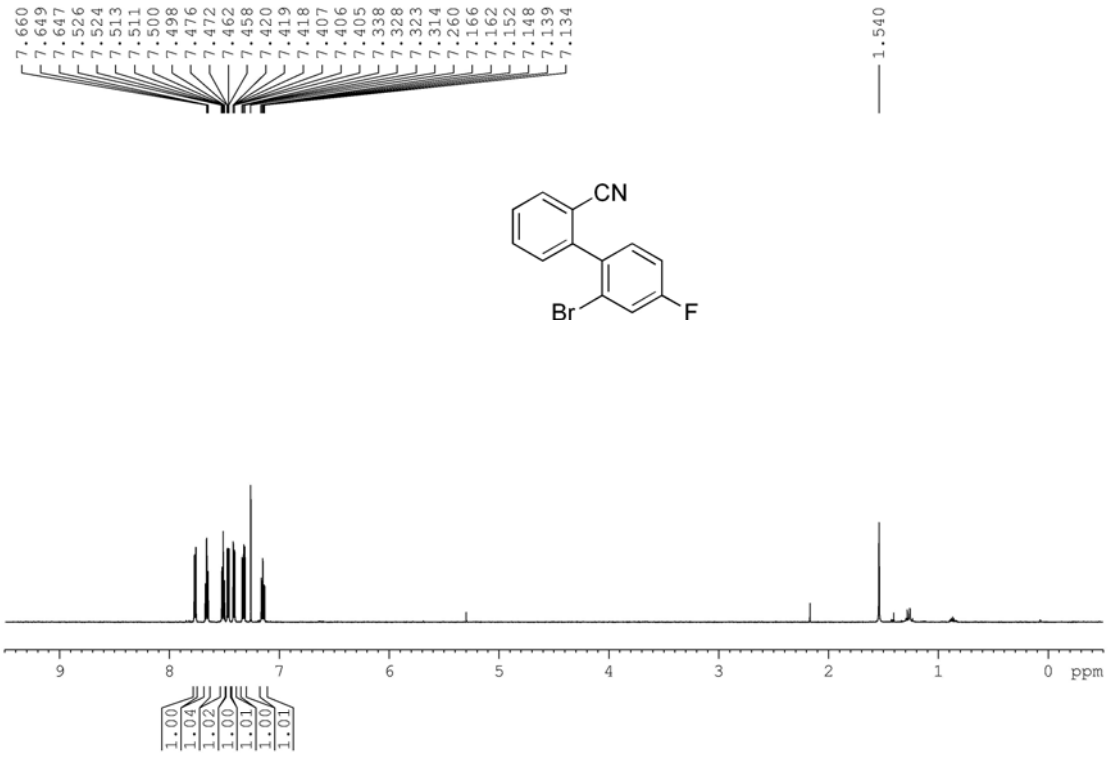


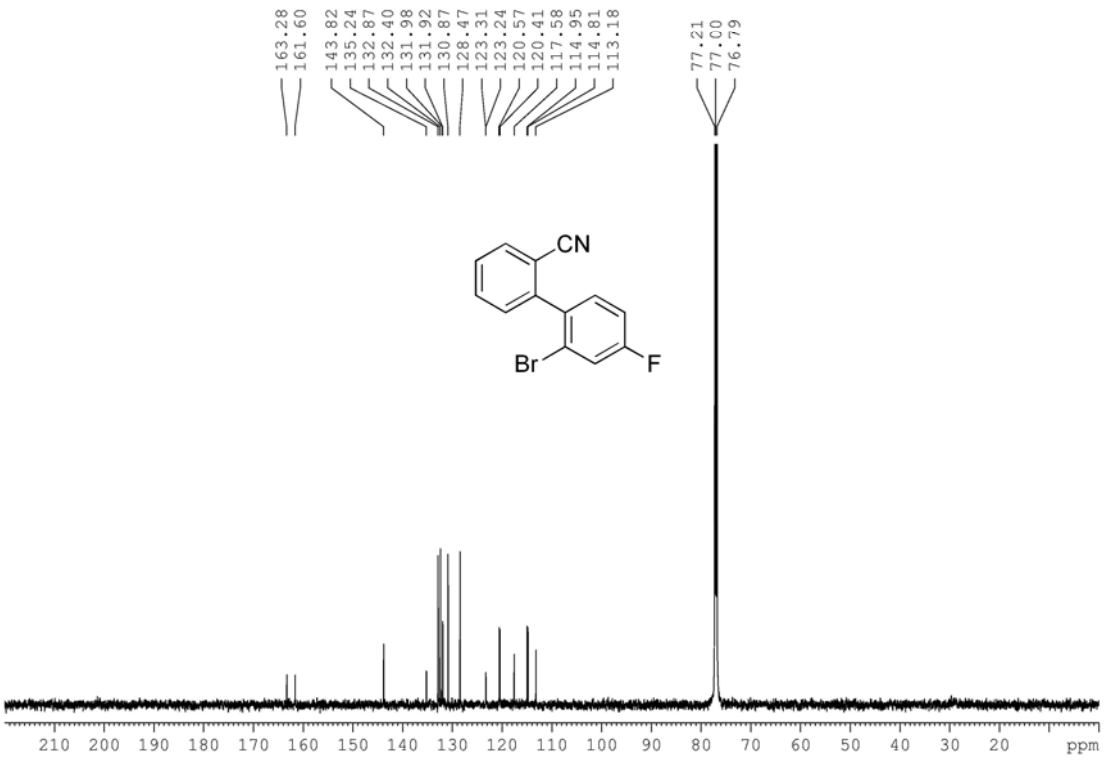
2'-Bromo-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrilele (1B)



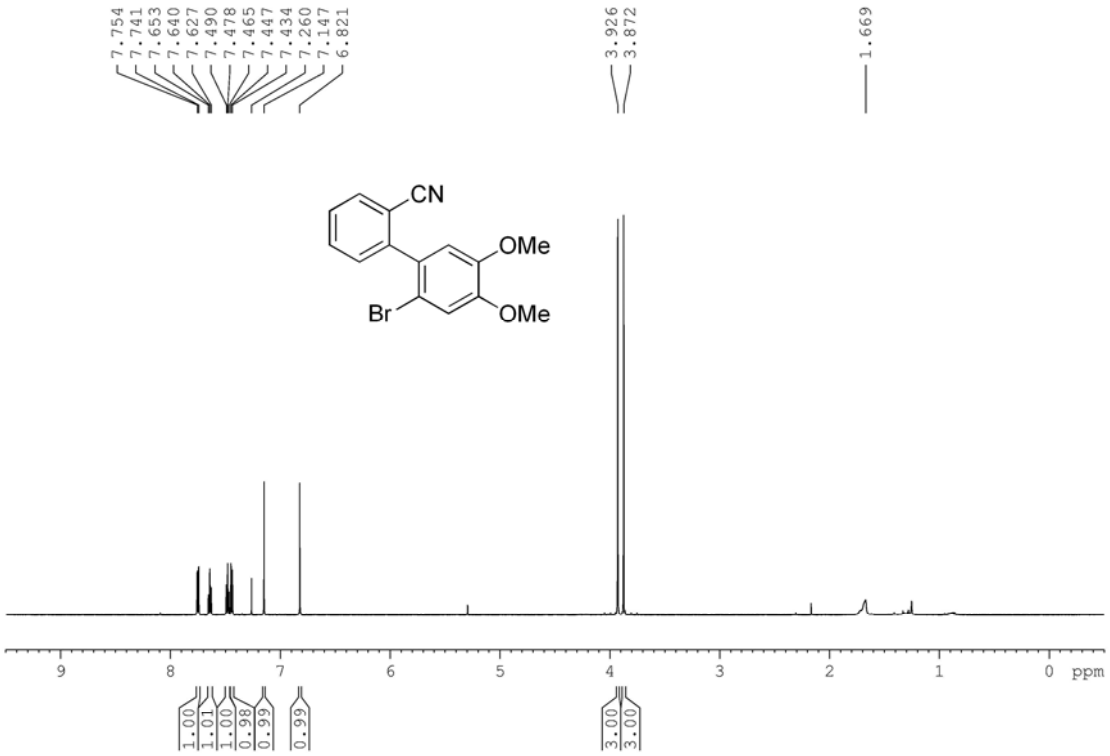


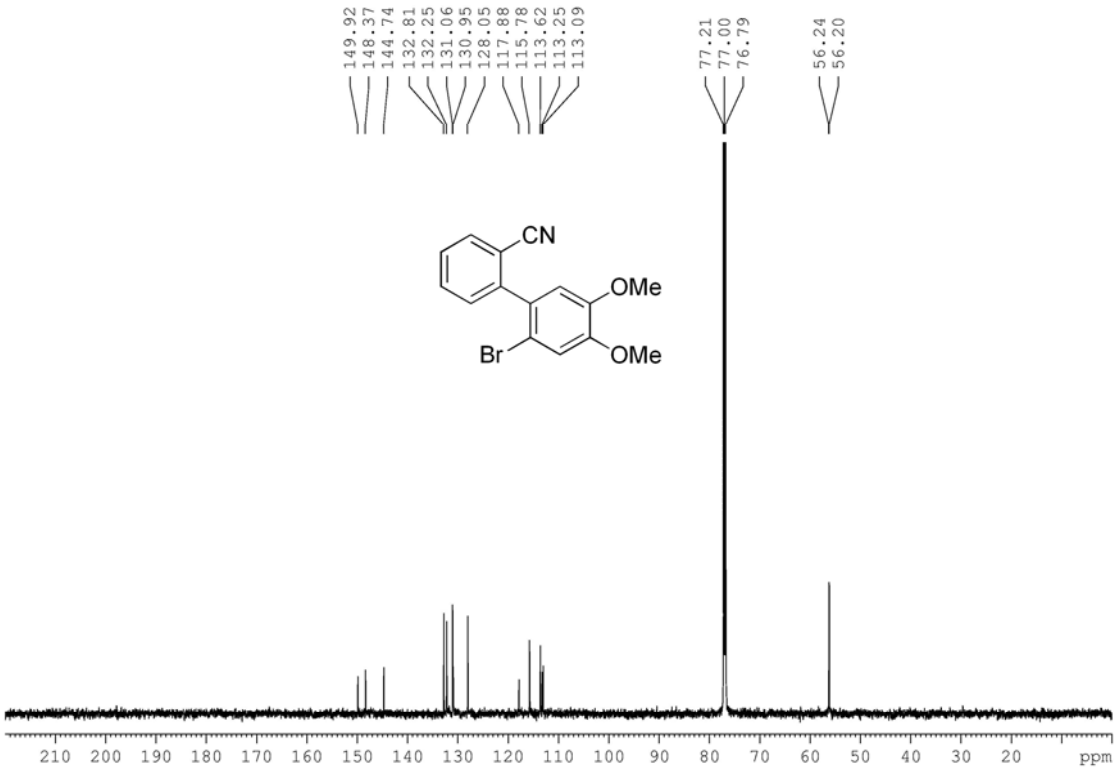
2'-Bromo-4'-fluoro-[1,1'-biphenyl]-2-carbonitrile (1C)



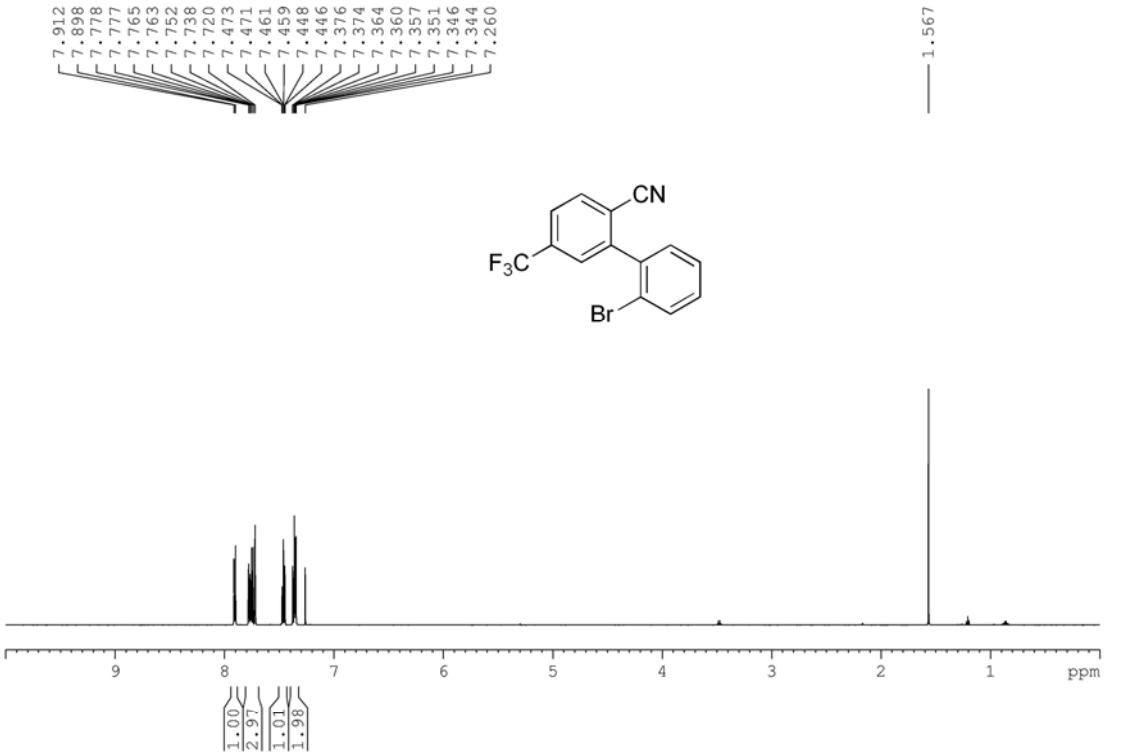


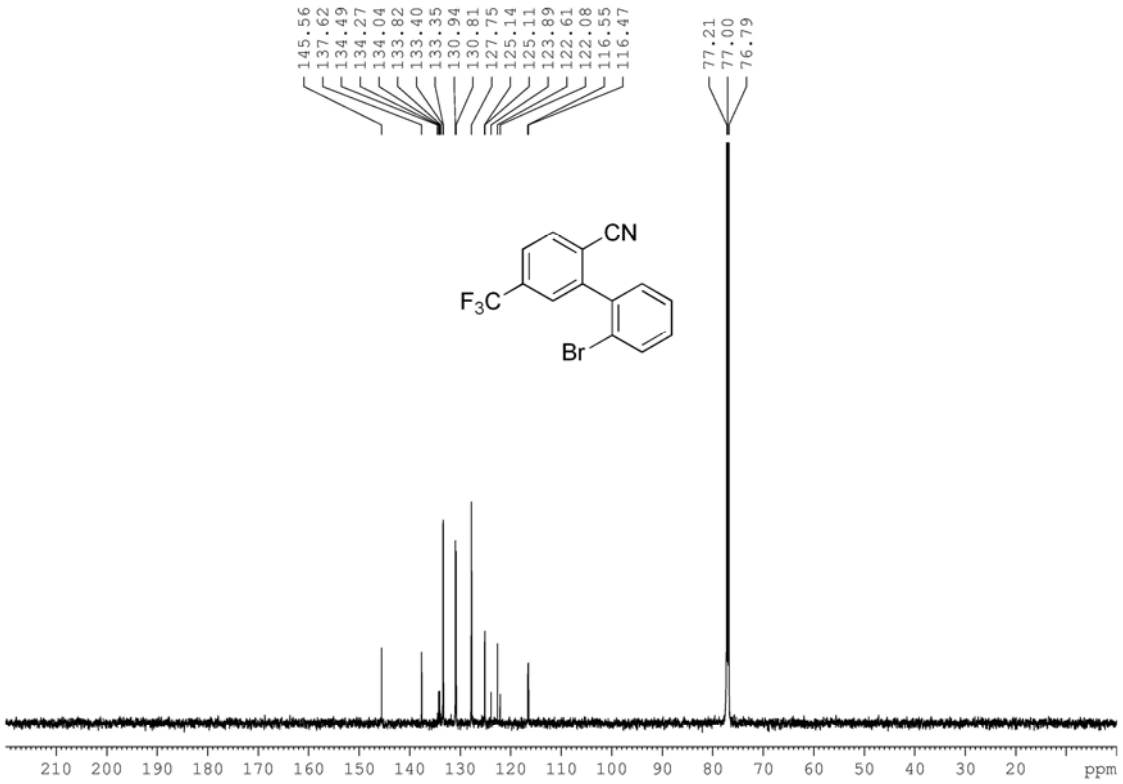
2'-Bromo-4',5'-dimethoxy-[1,1'-biphenyl]-2-carbonitrile (1D)



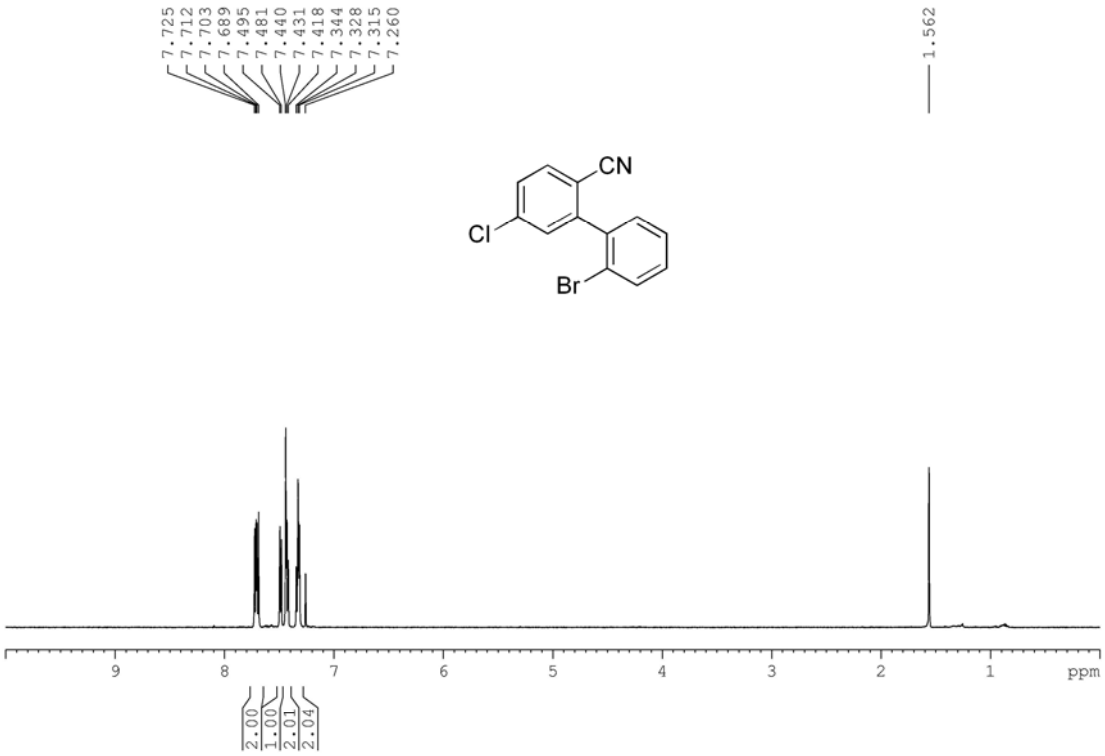


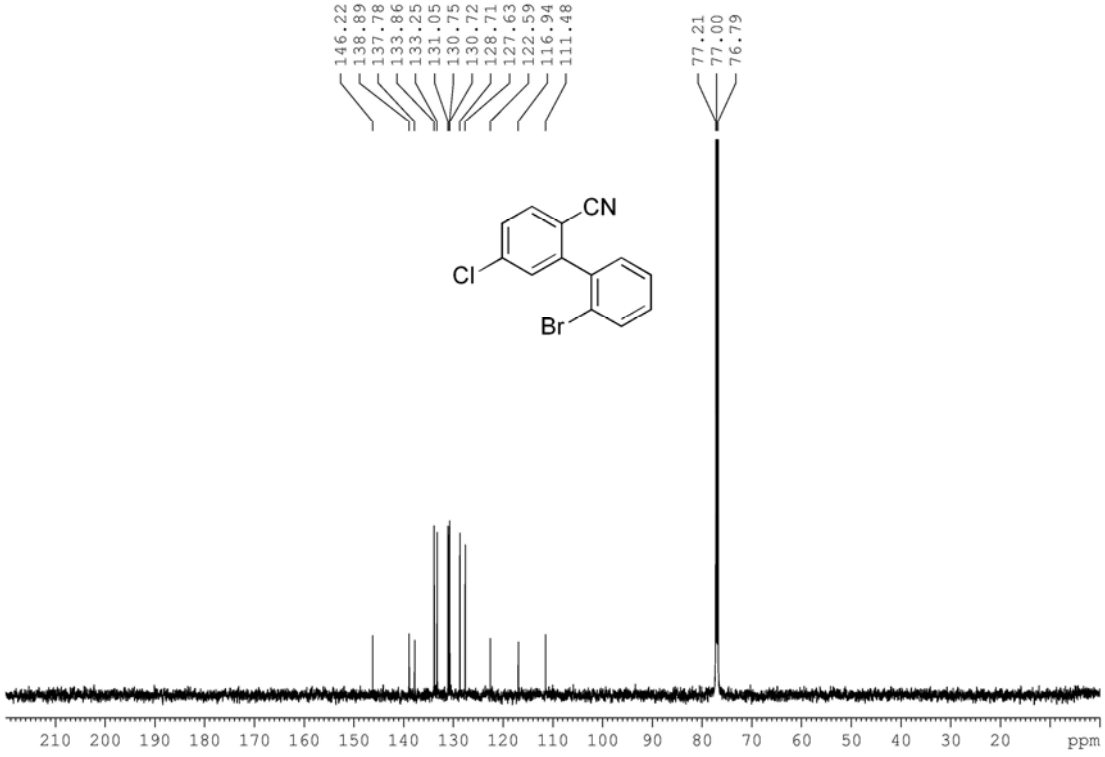
2'-Bromo-5-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile (1E)



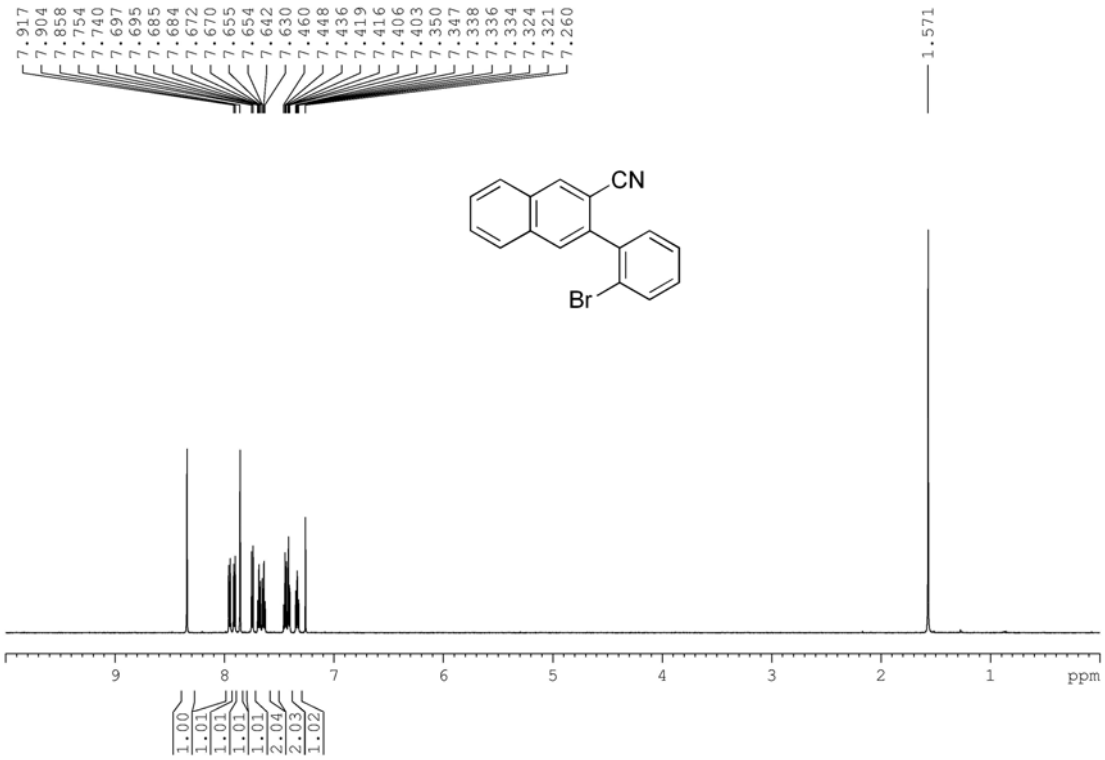


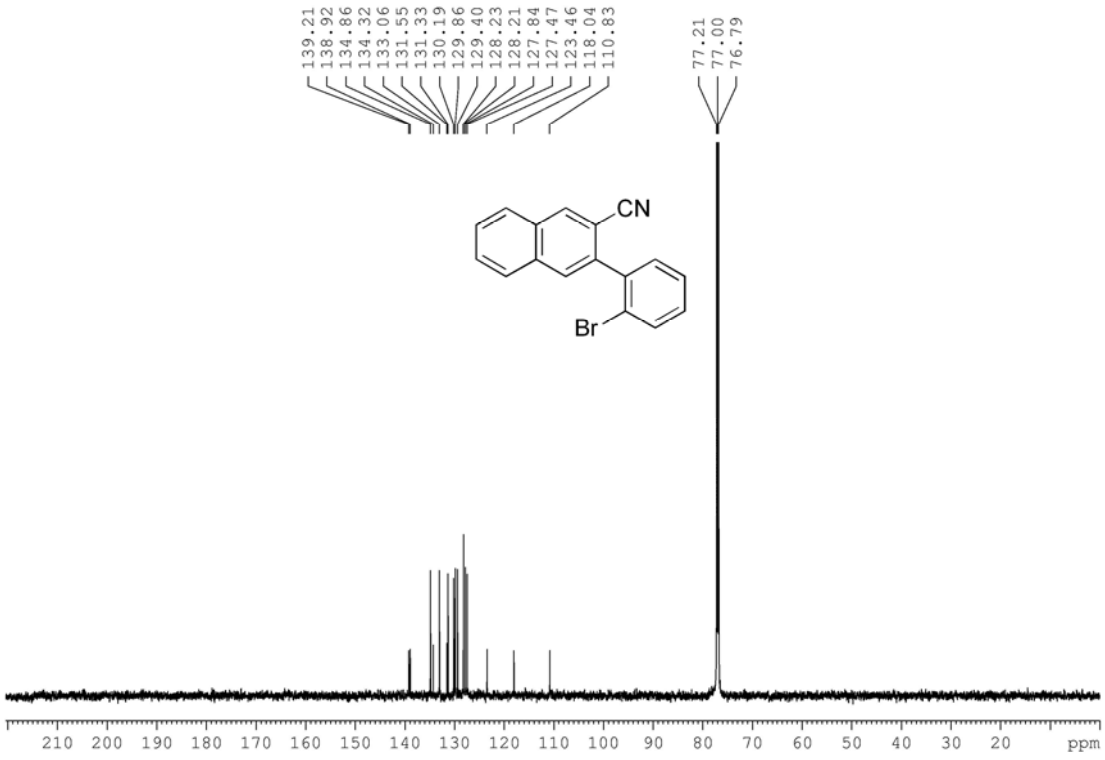
2'-Bromo-5-chloro-[1,1'-biphenyl]-2-carbonitrile (1F)



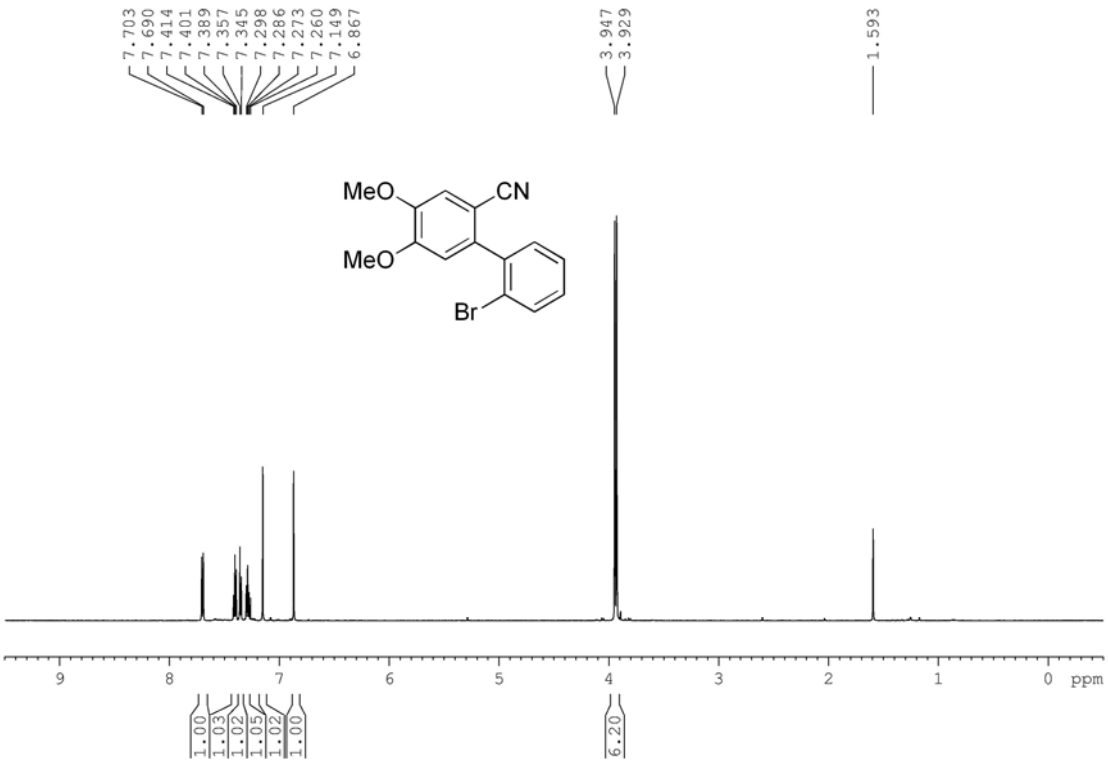


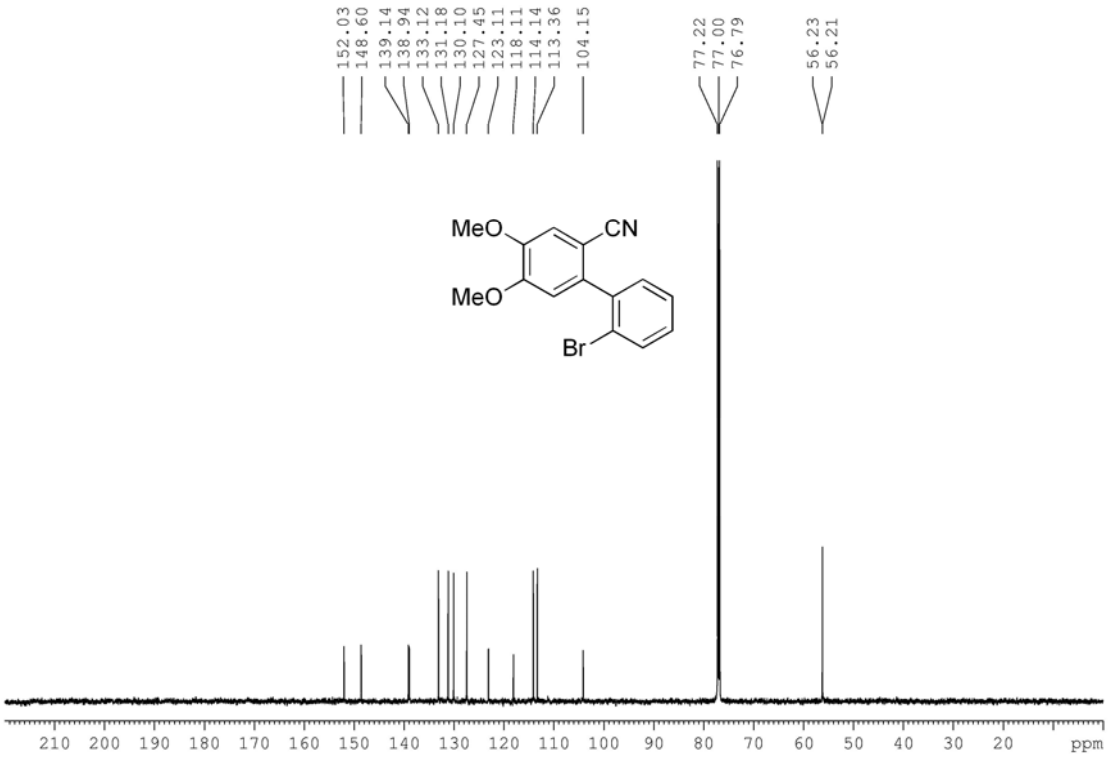
3-(2-Bromophenyl)-2-naphthonitrile (1G)



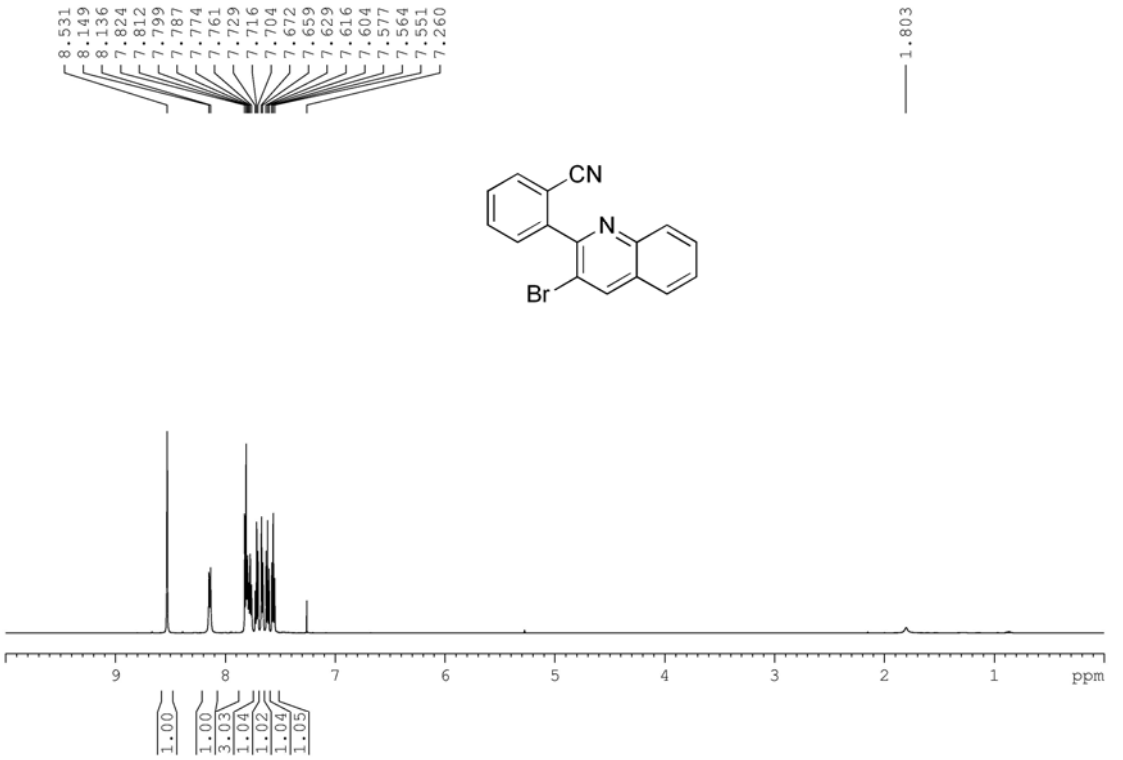


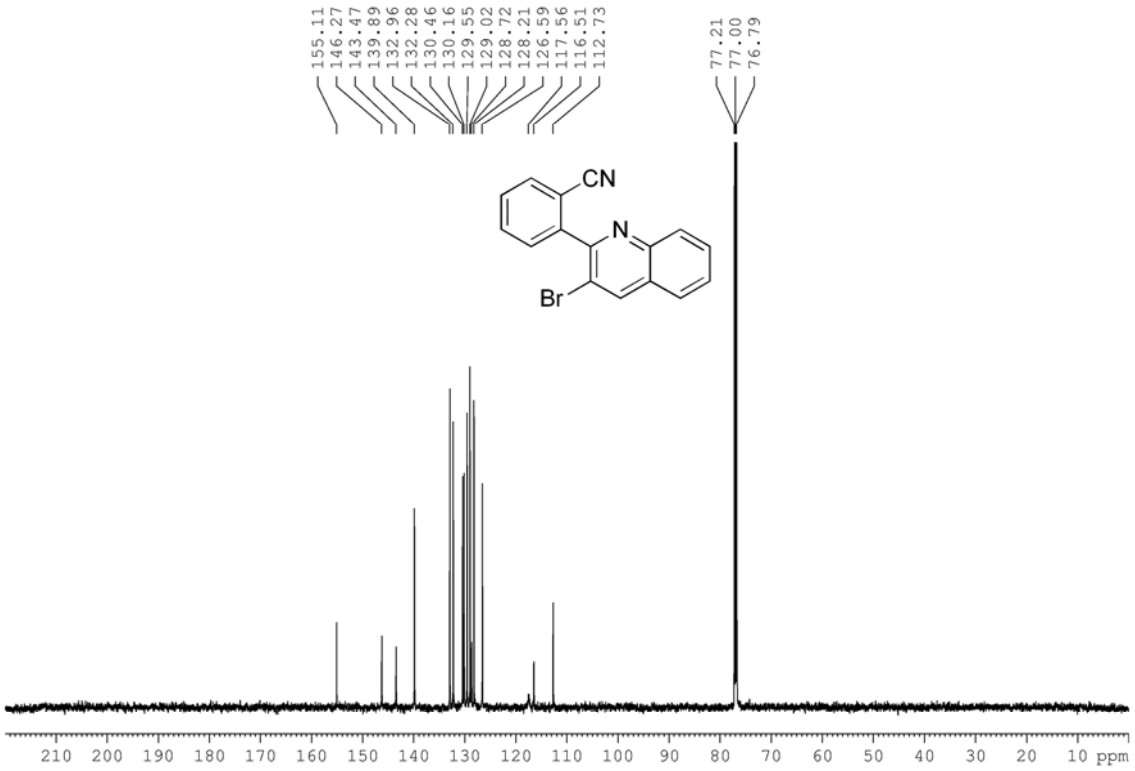
2'-Bromo-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile (1H)



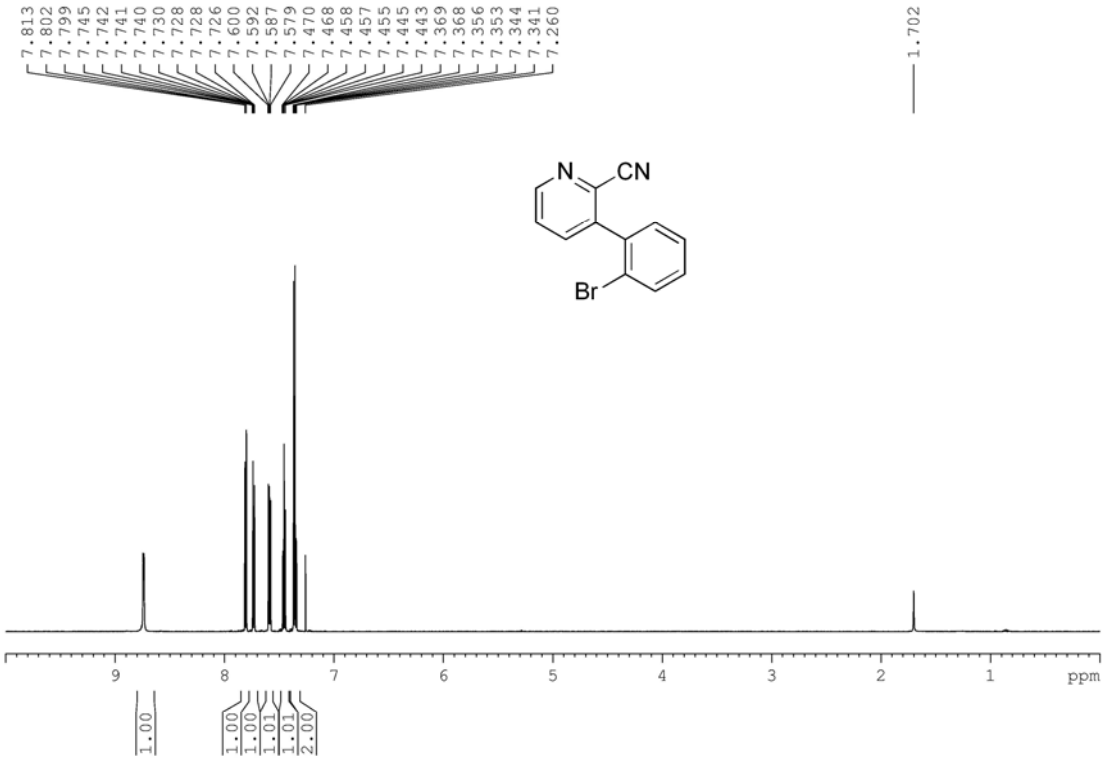


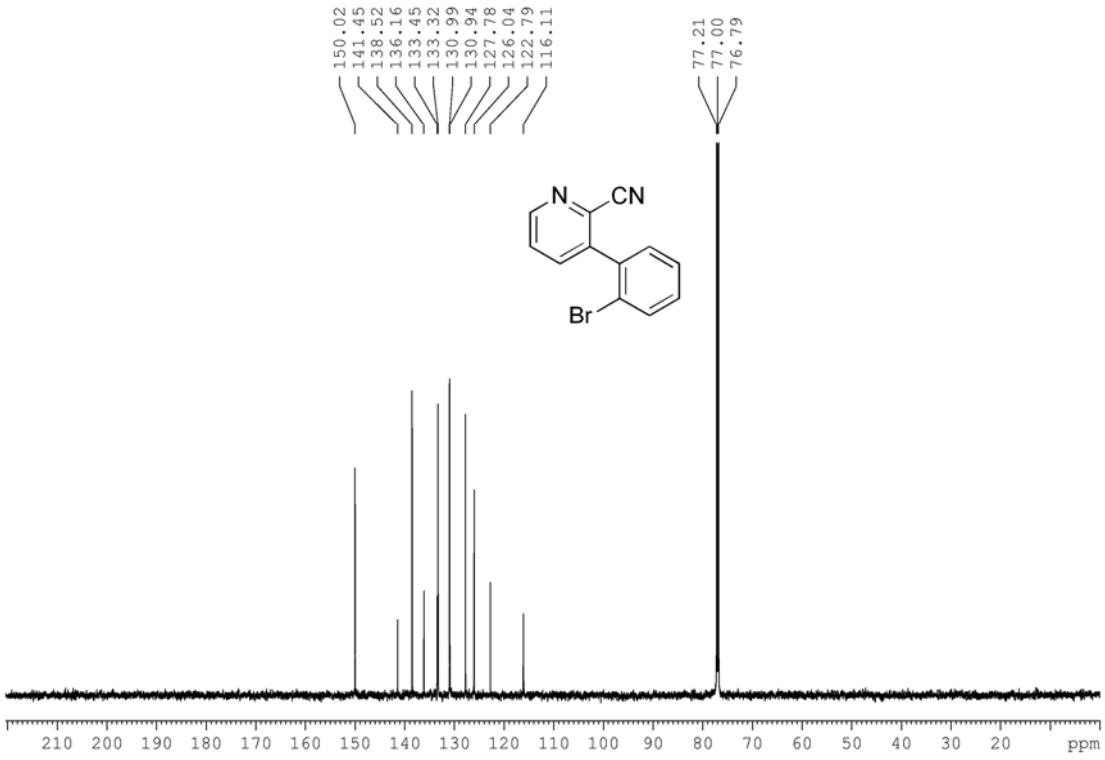
2-(3-Bromoquinolin-2-yl)benzonitrile (1I)



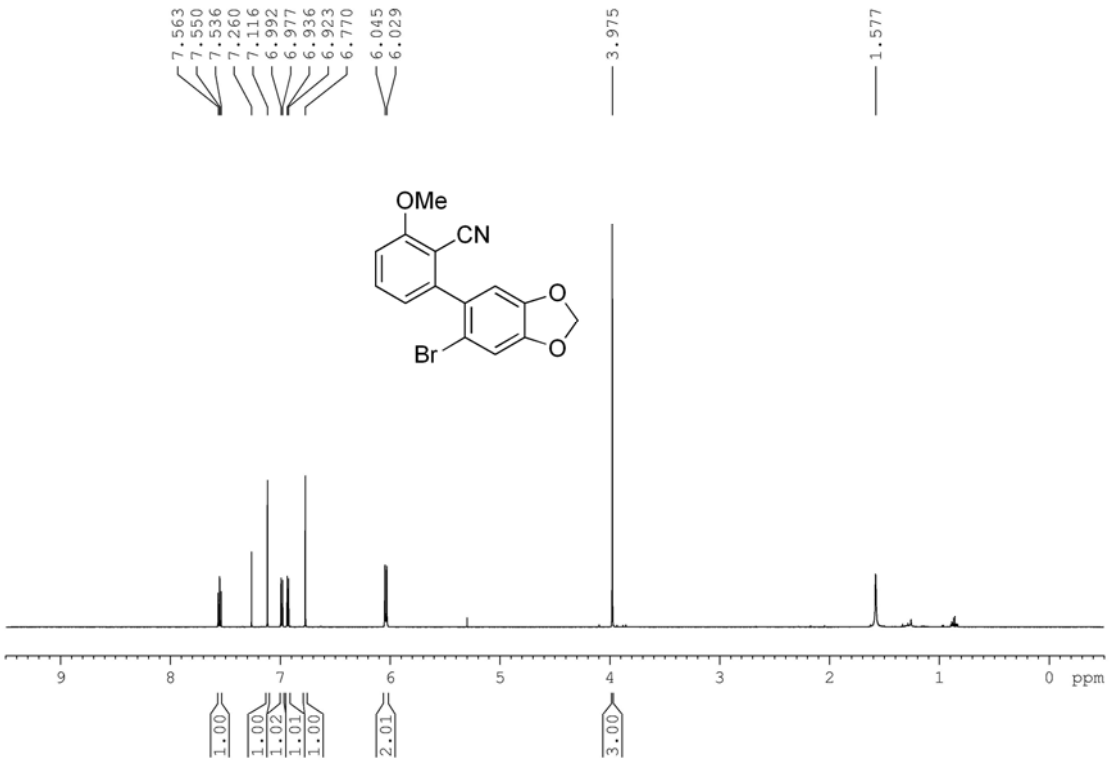


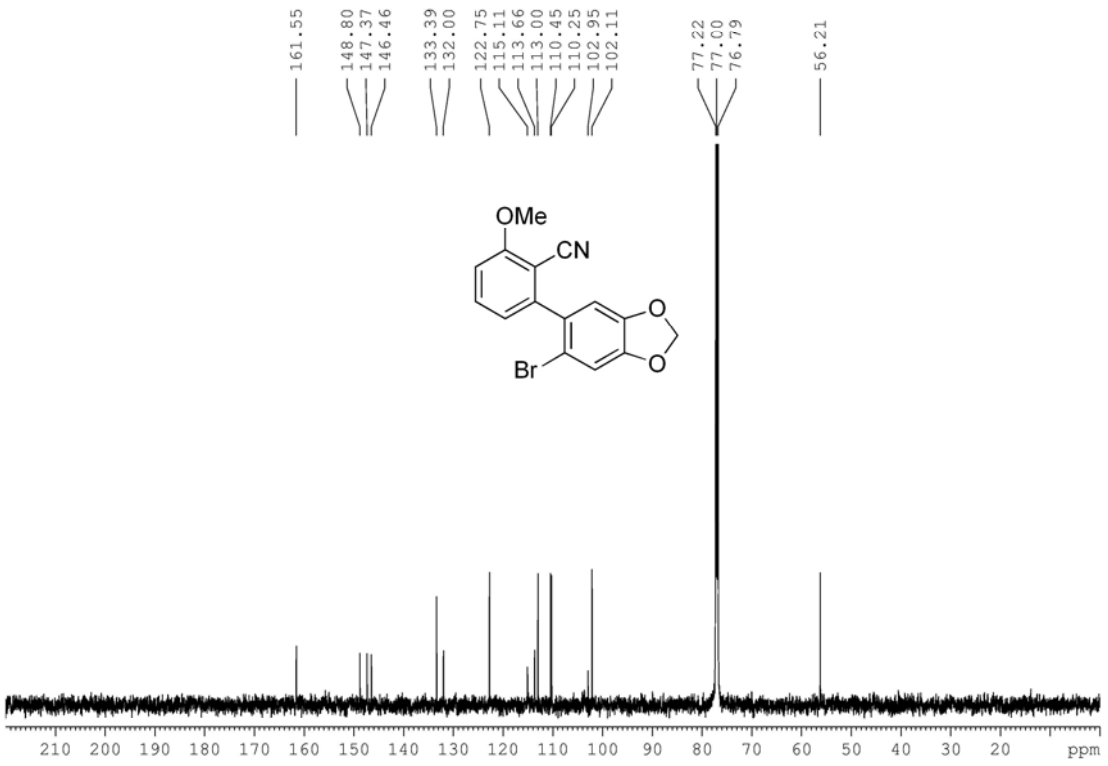
3-(2-Bromophenyl)picolinonitrile (1J)



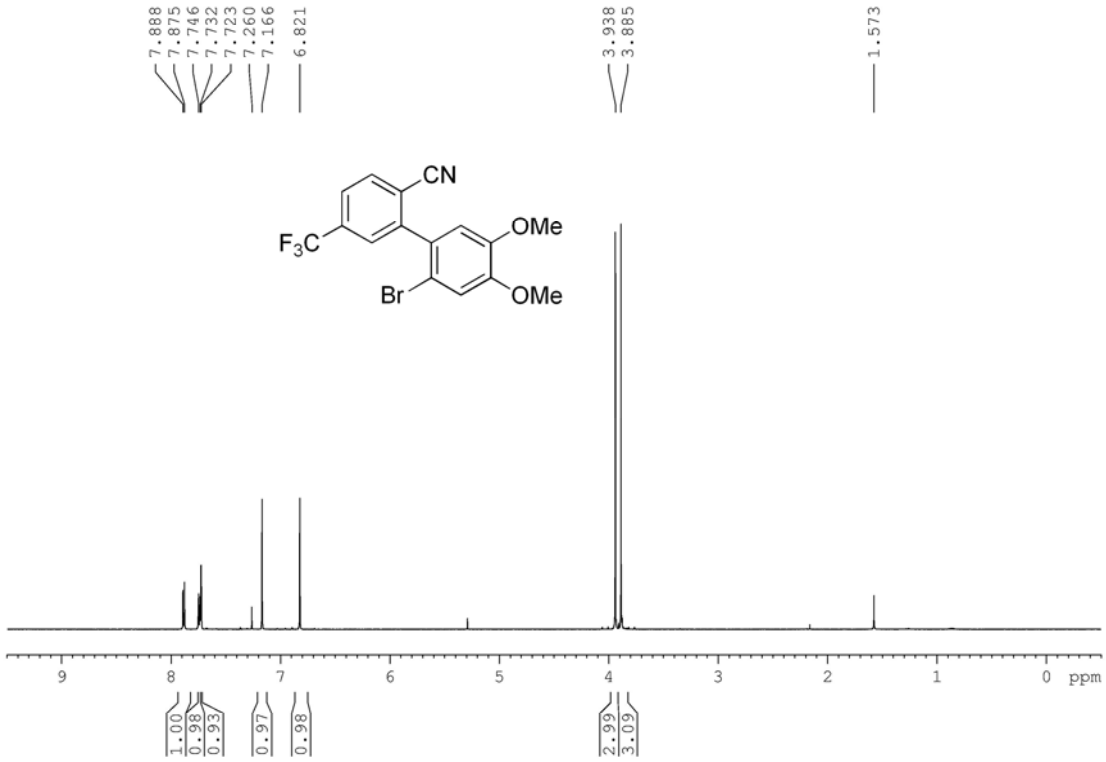


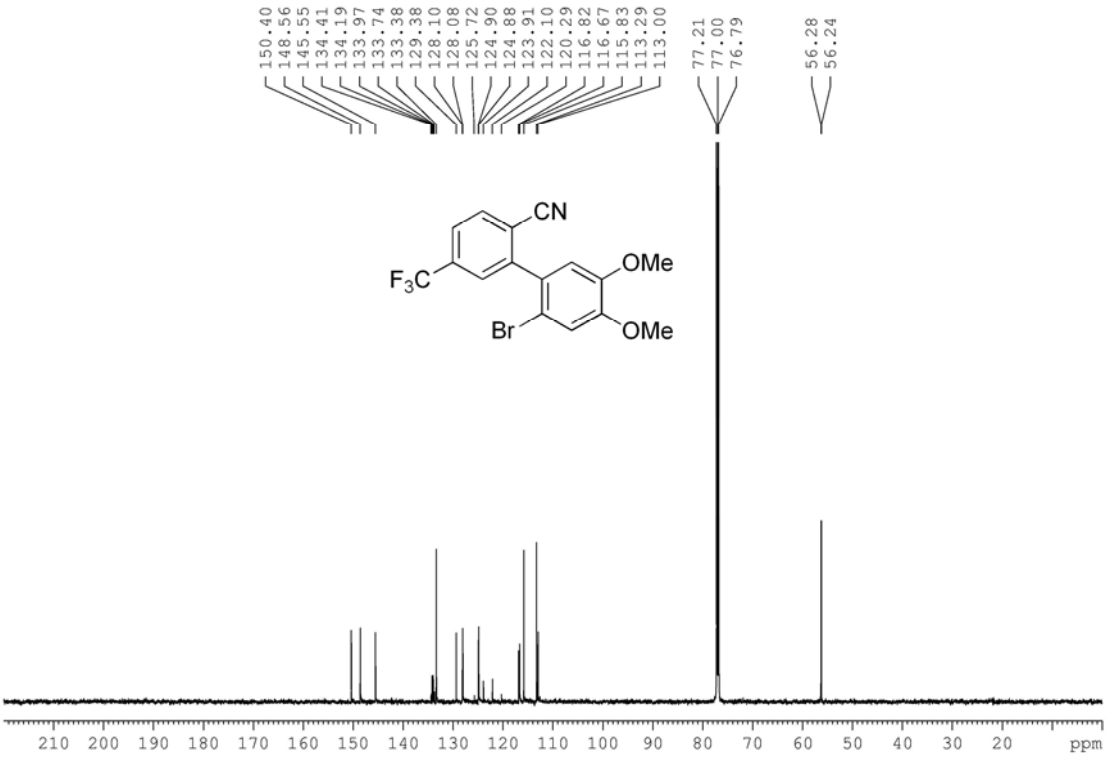
2-(6-Bromobenzo[*d*][1,3]dioxol-5-yl)-6-methoxybenzonitrile (1K)



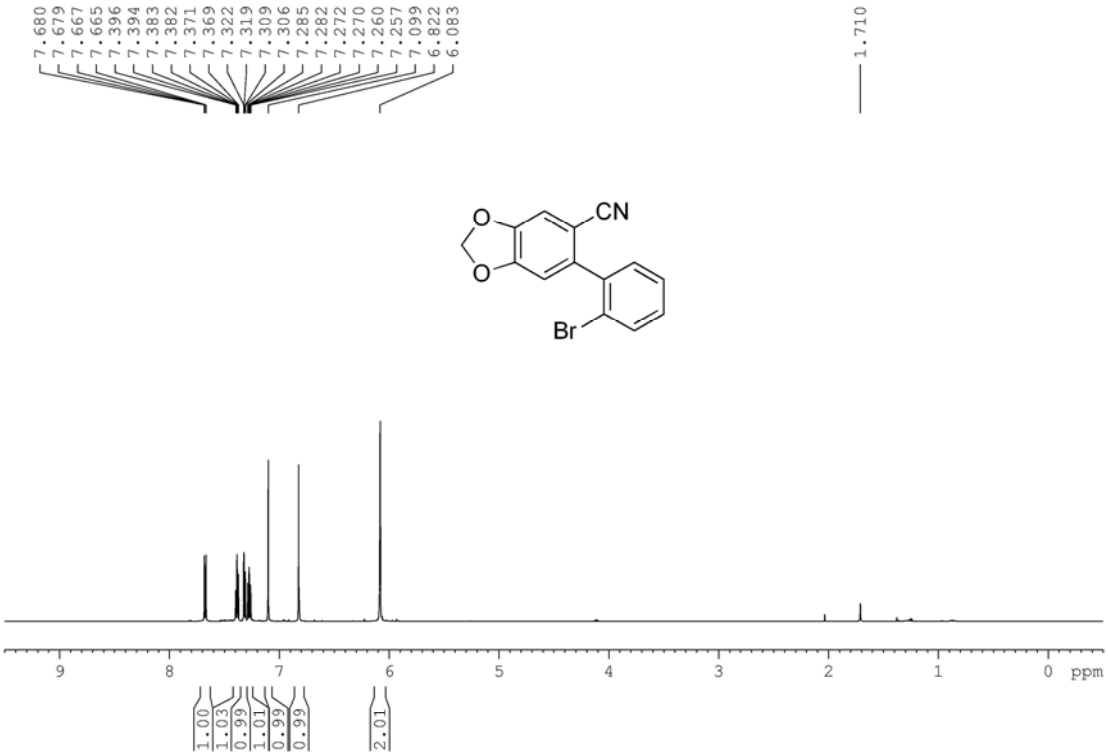


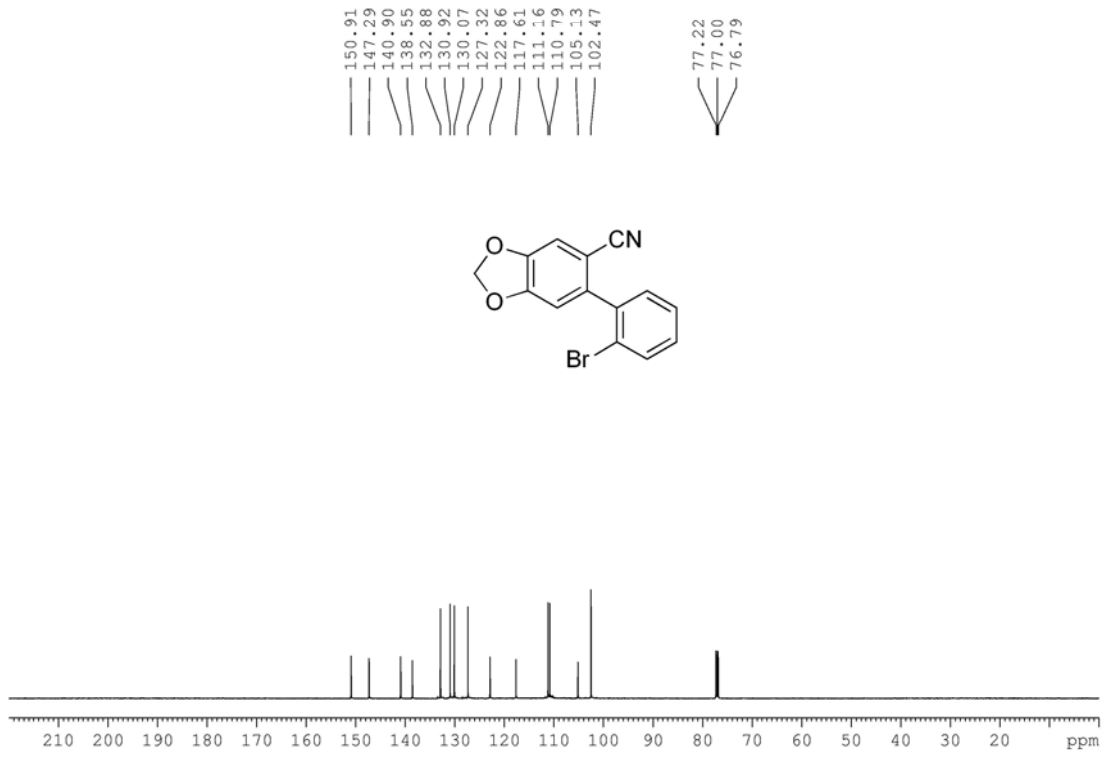
2'-Bromo-4',5'-dimethoxy-5-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile (1L)



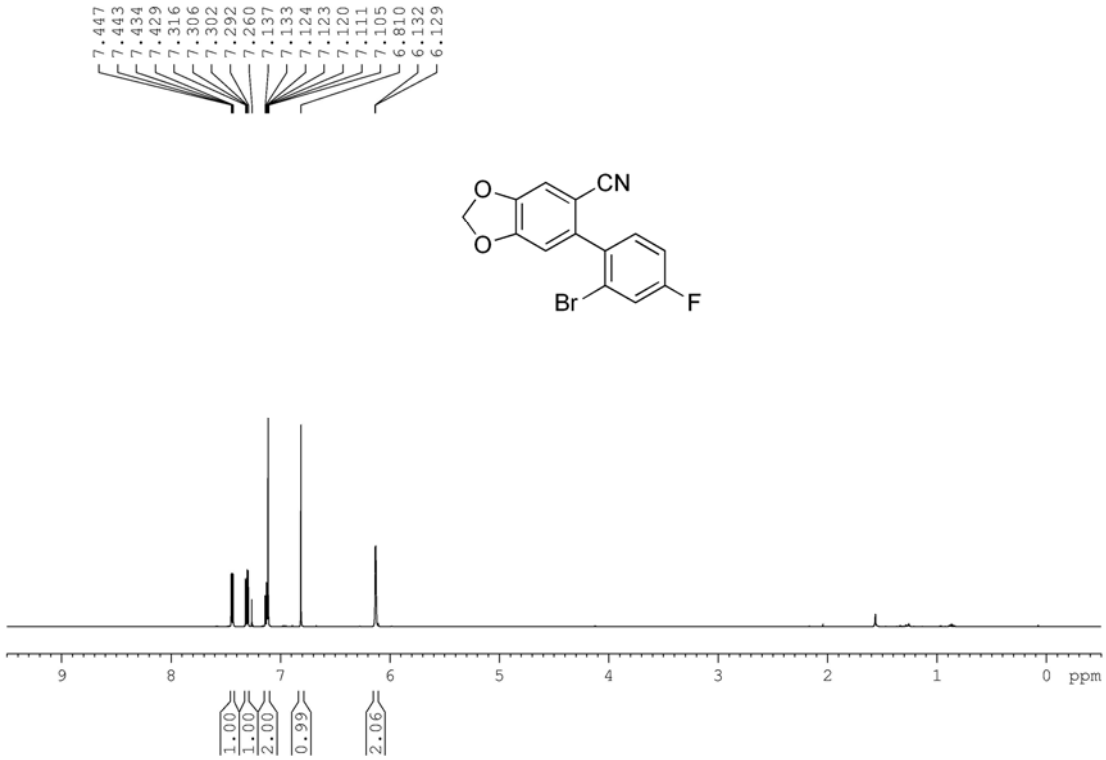


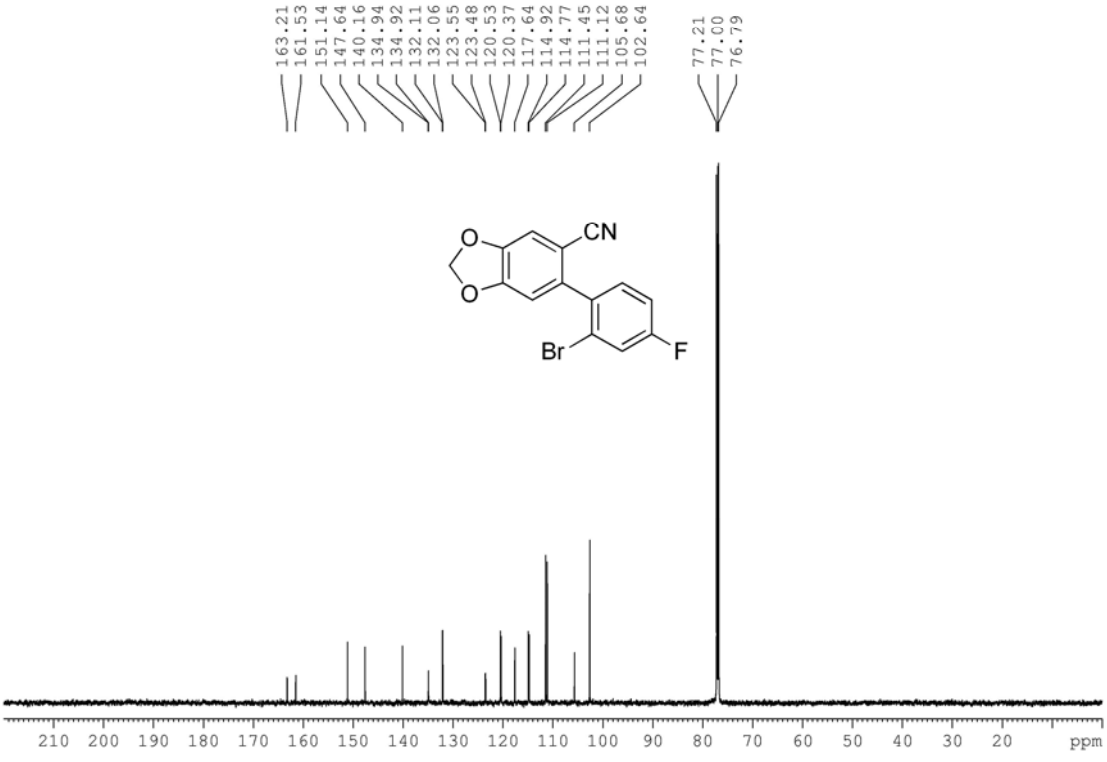
6-(2-Bromophenyl)benzo[*d*][1,3]dioxole-5-carbonitrile (1M)



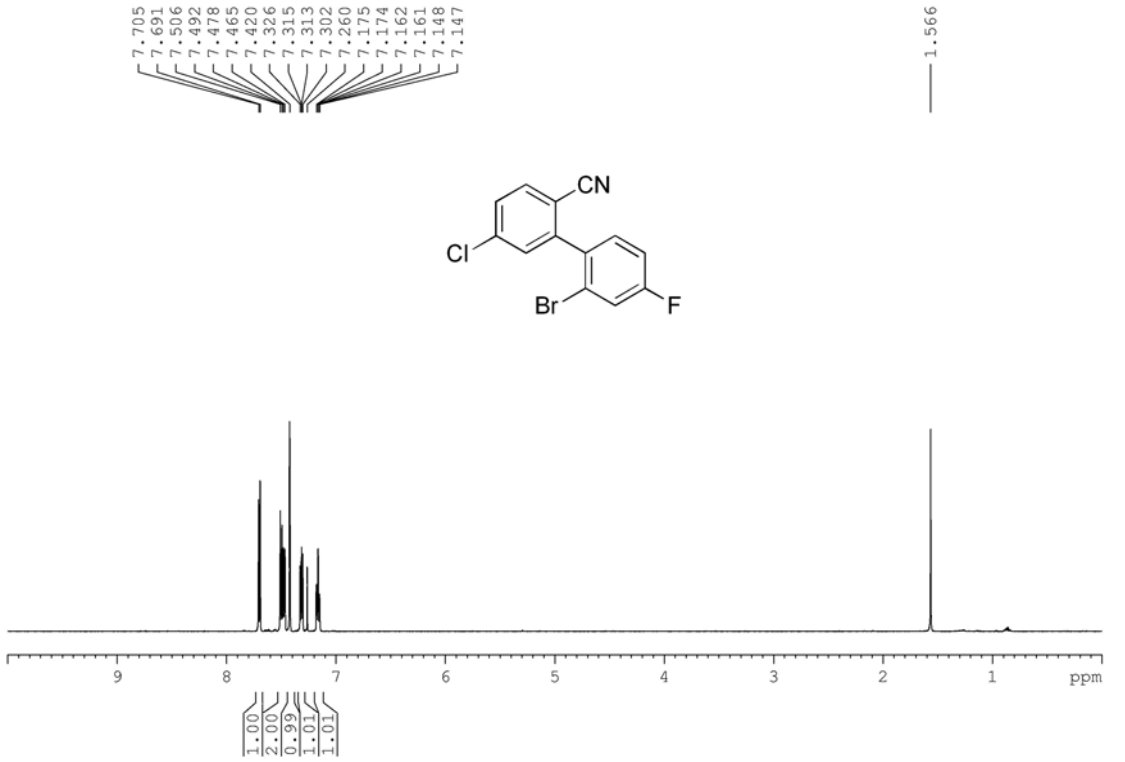


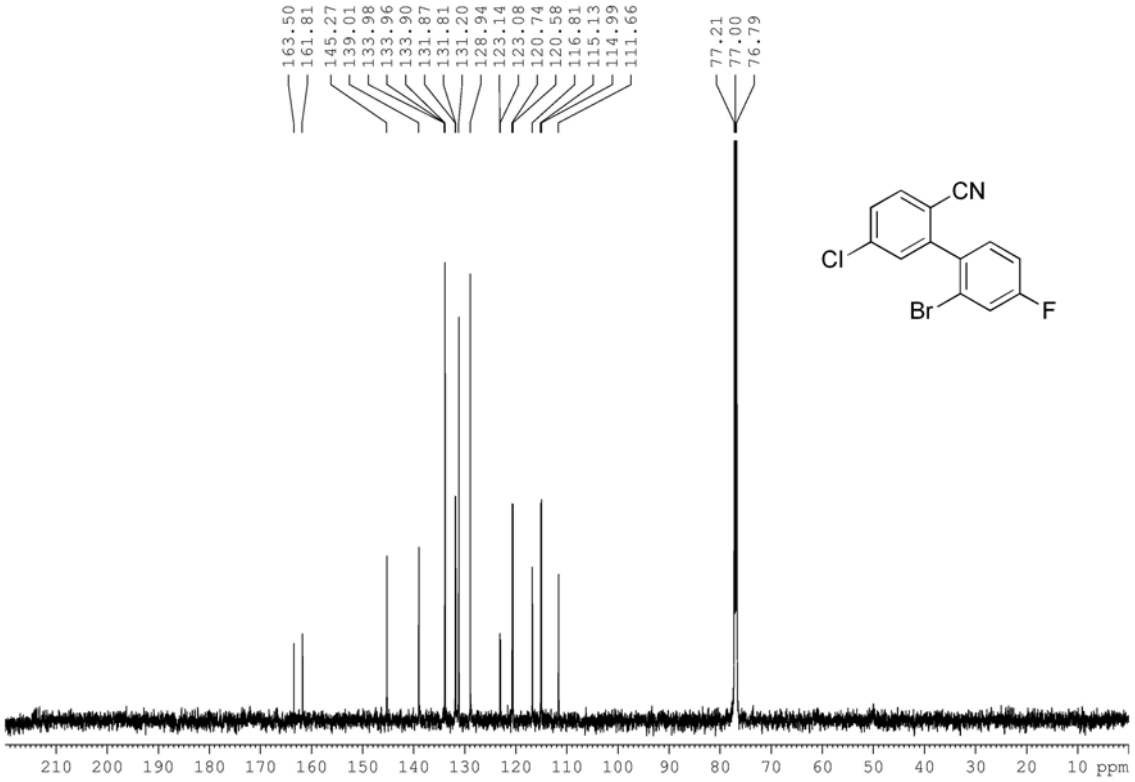
6-(2-Bromo-4-fluorophenyl)benzo[*d*][1,3]dioxole-5-carbonitrile (1N)



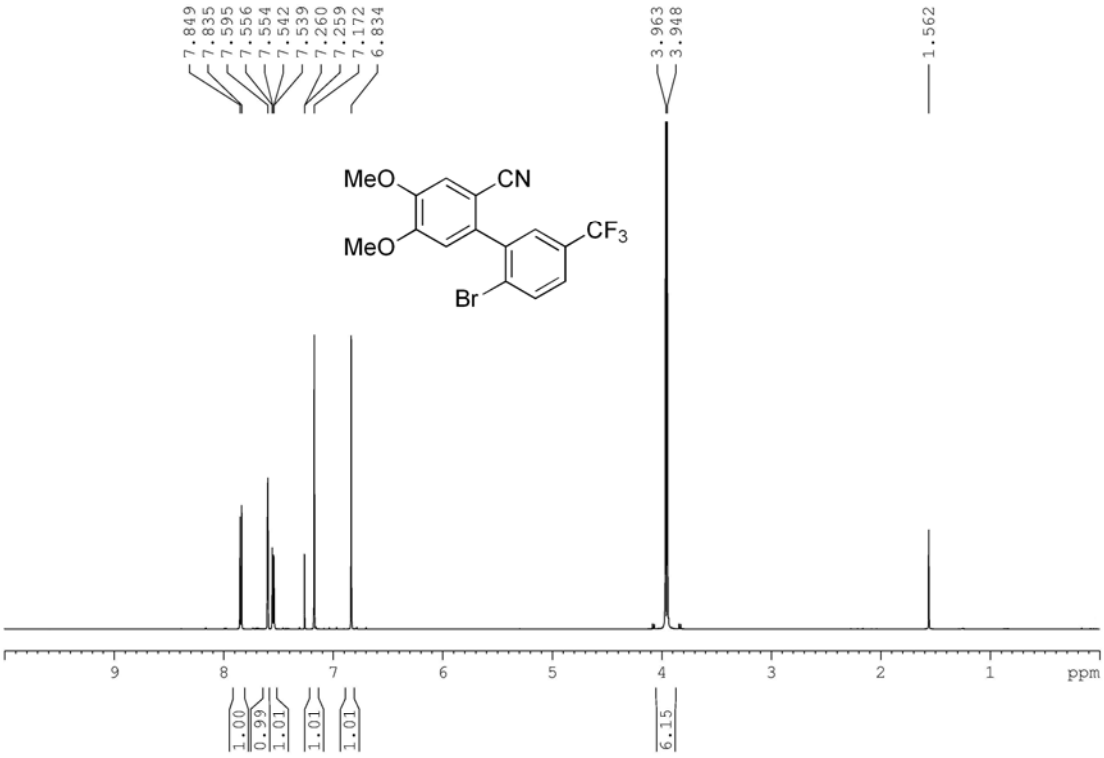


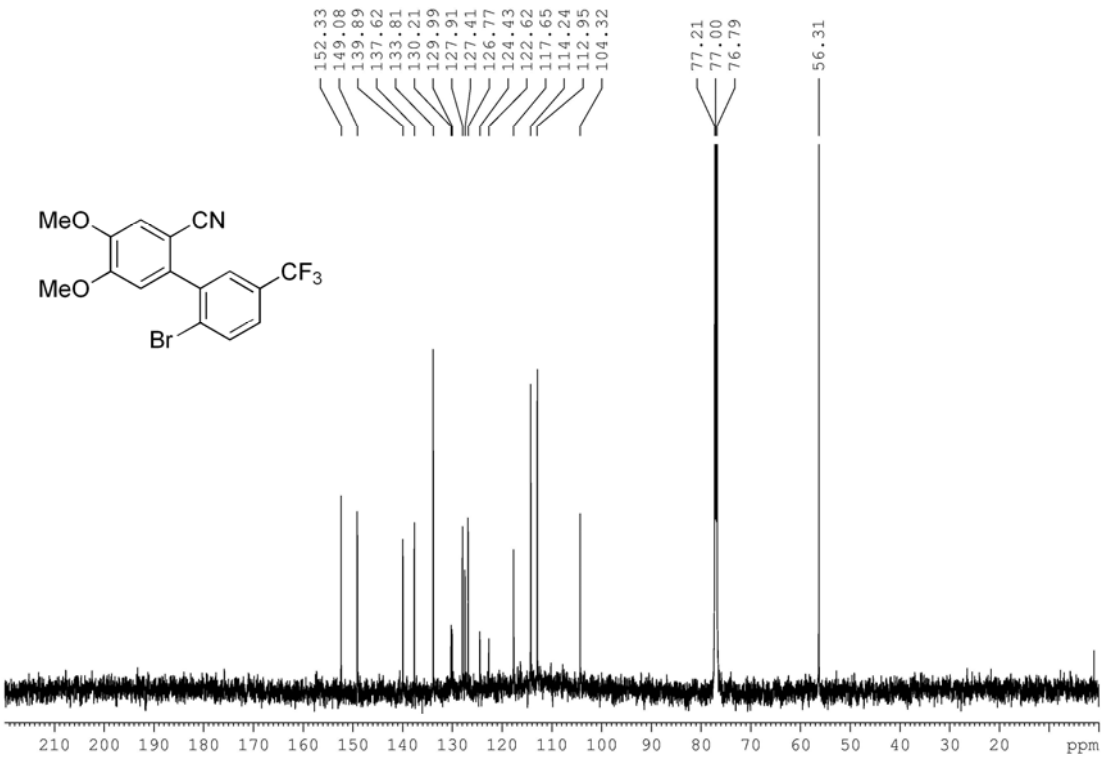
2'-Bromo-5-chloro-4'-fluoro-[1,1'-biphenyl]-2-carbonitrile (1O)



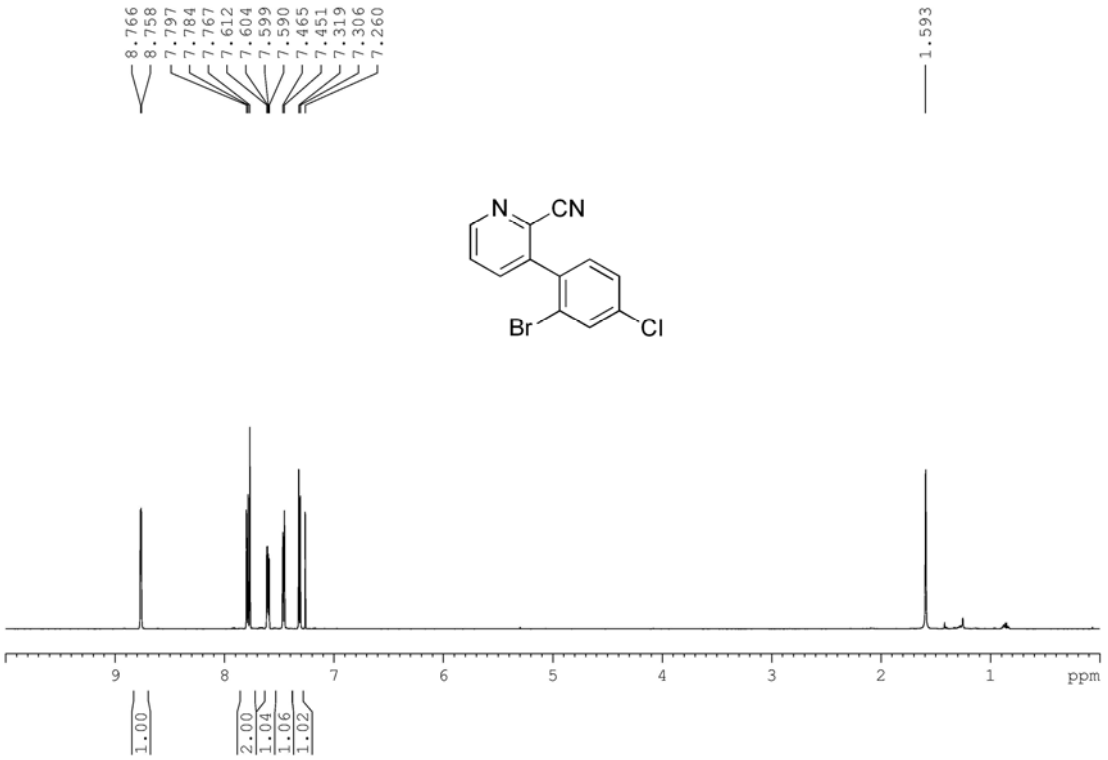


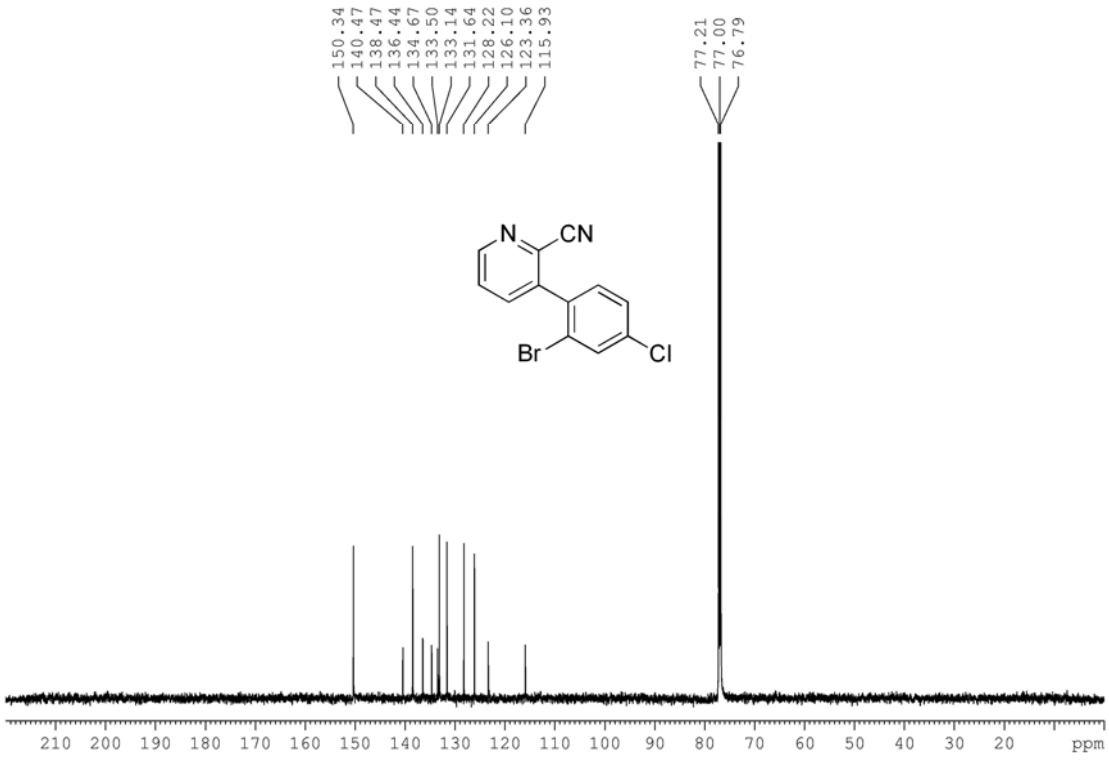
2'-Bromo-4,5-dimethoxy-5'-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile (1P)



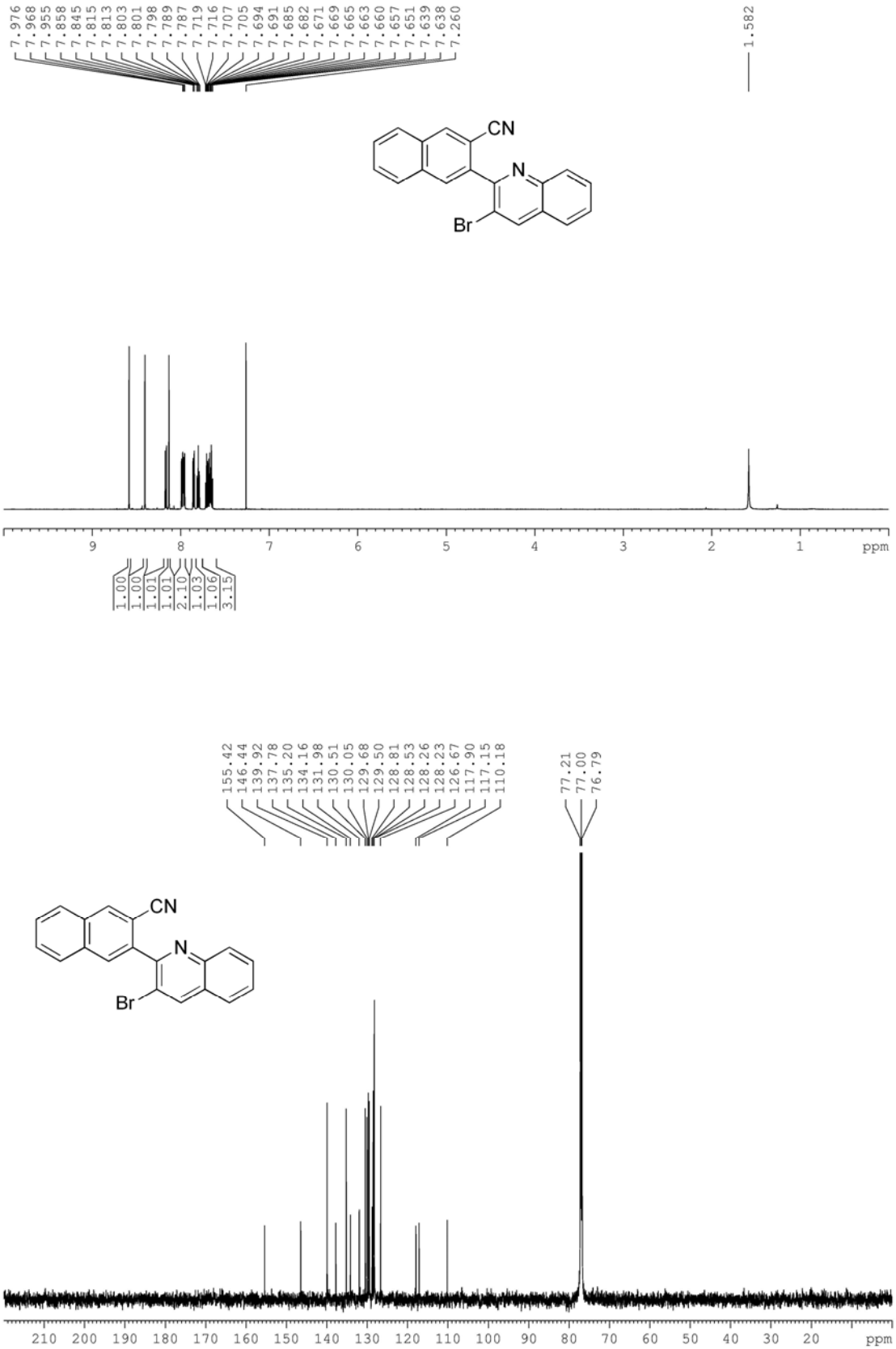


3-(2-Bromo-4-chlorophenyl)picolinonitrile (1Q)



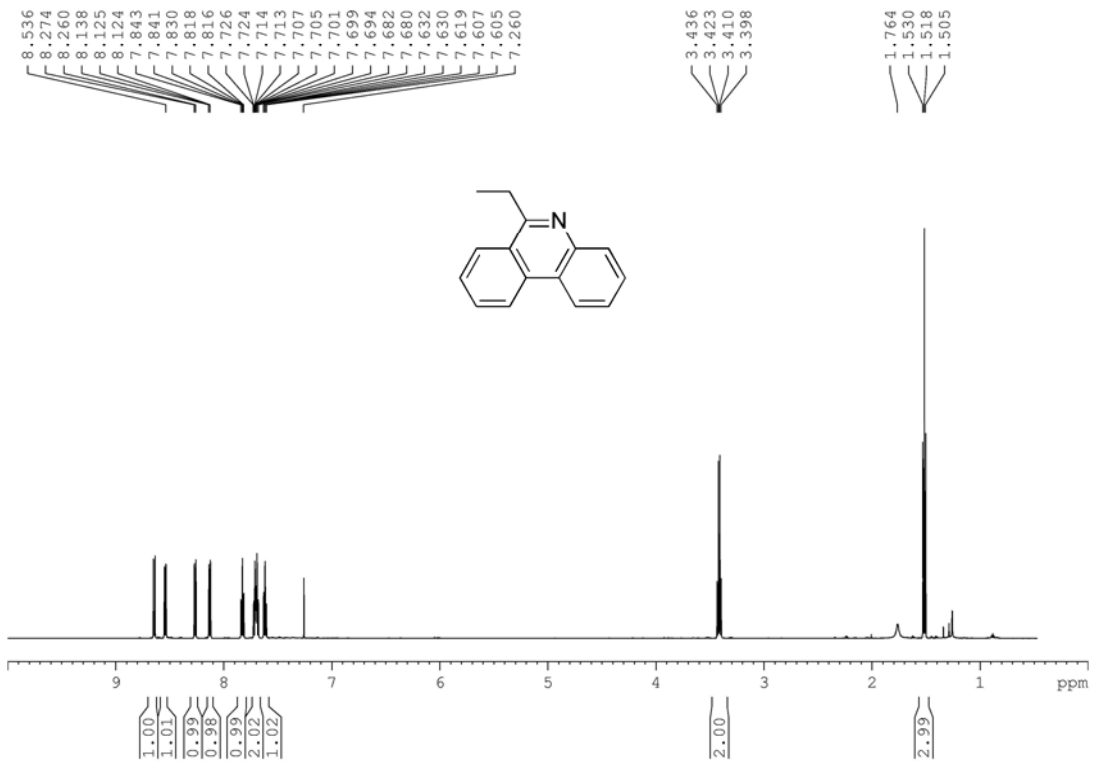


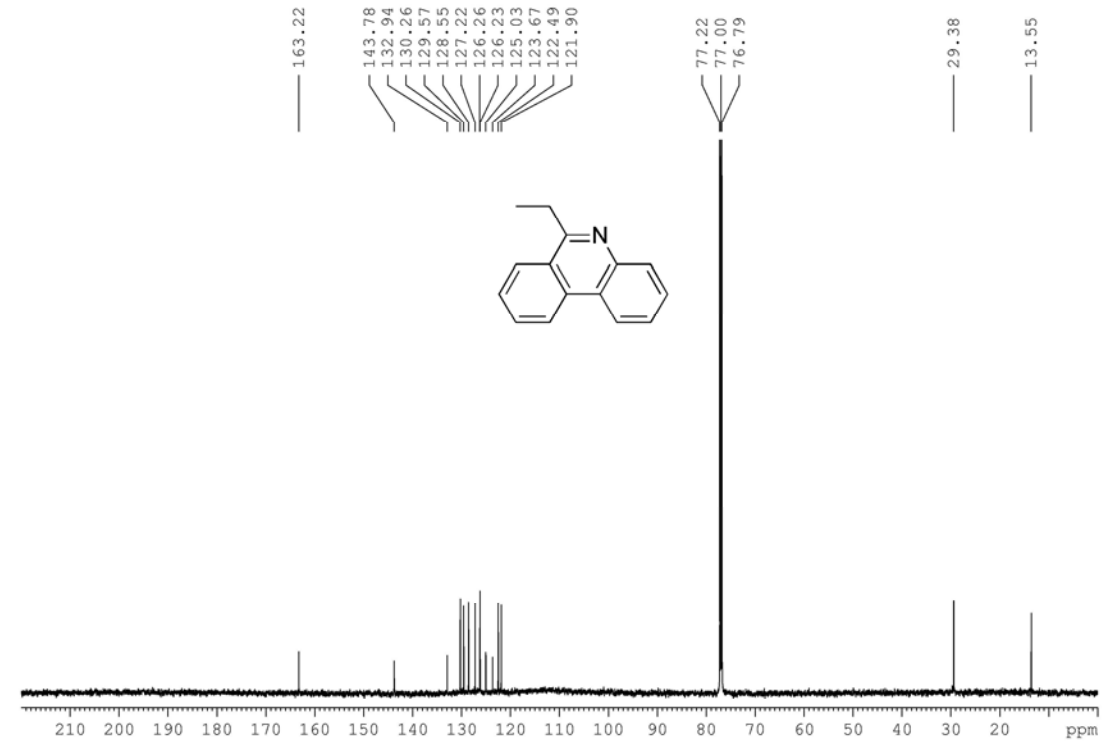
3-(3-Bromoquinolin-2-yl)-2-naphthonitrile (1R)



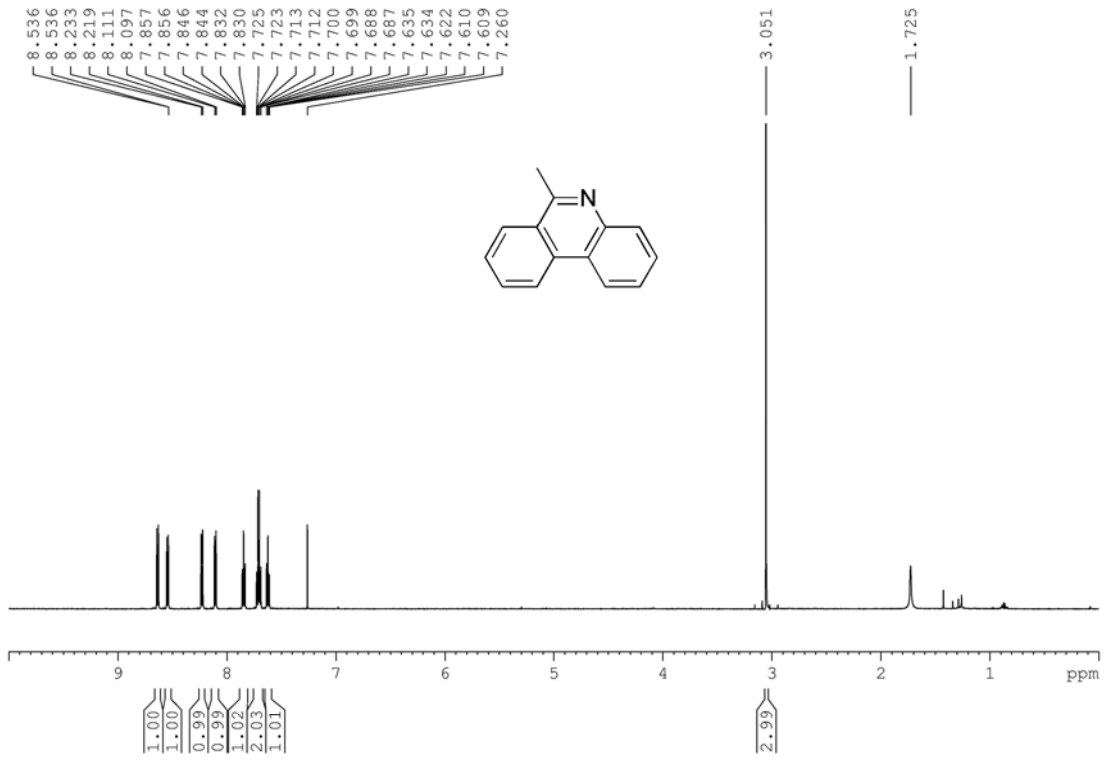
^{1}H and ^{13}C NMR Spectra for Products (600 MHz, $CDCl_3$)

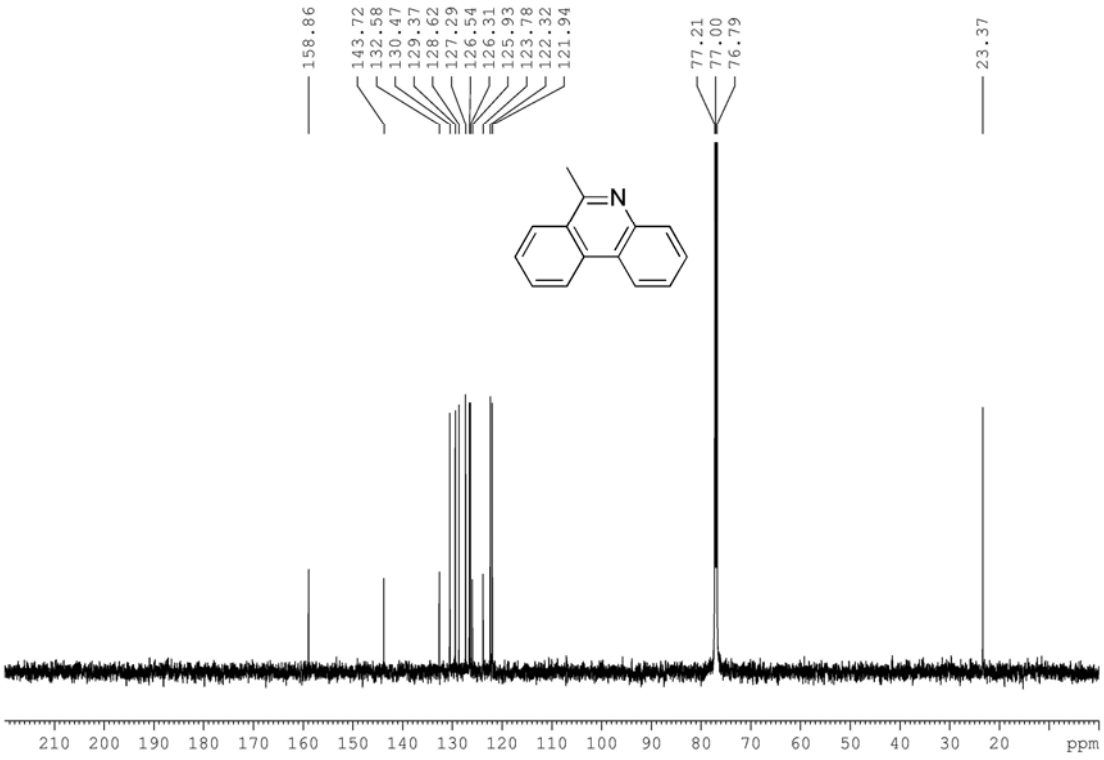
6-Ethylphenanthridine (3a)



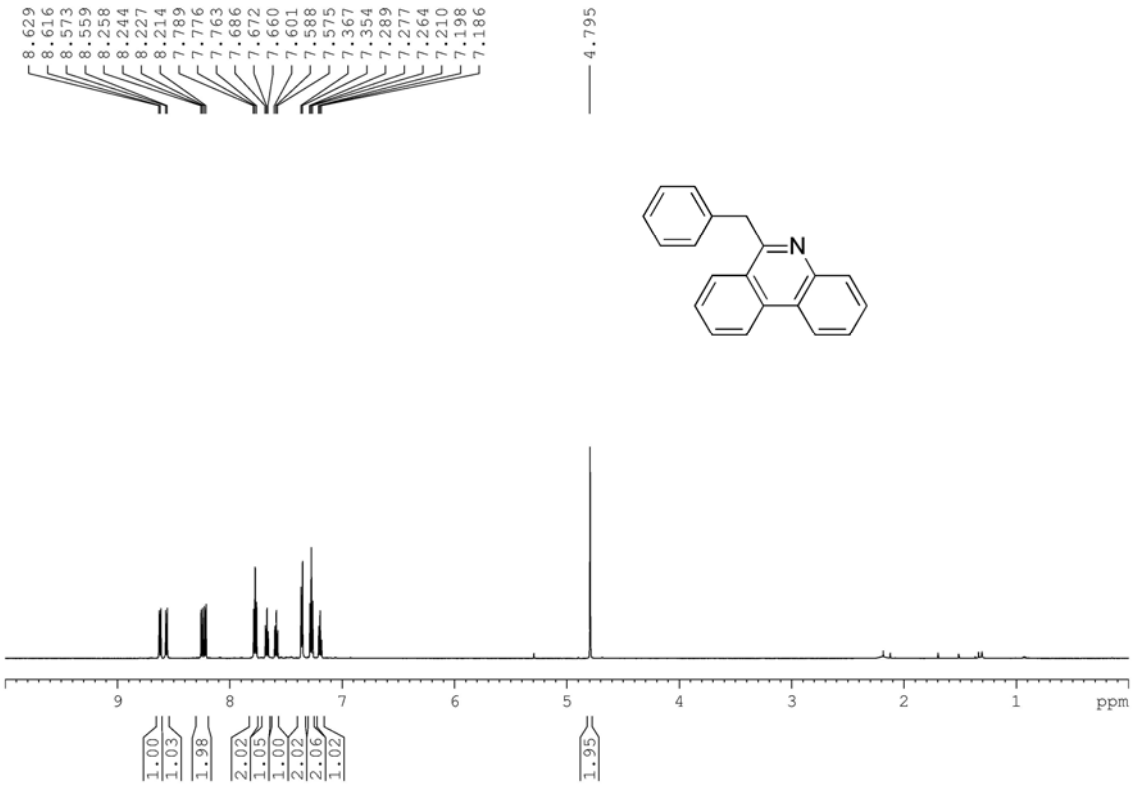


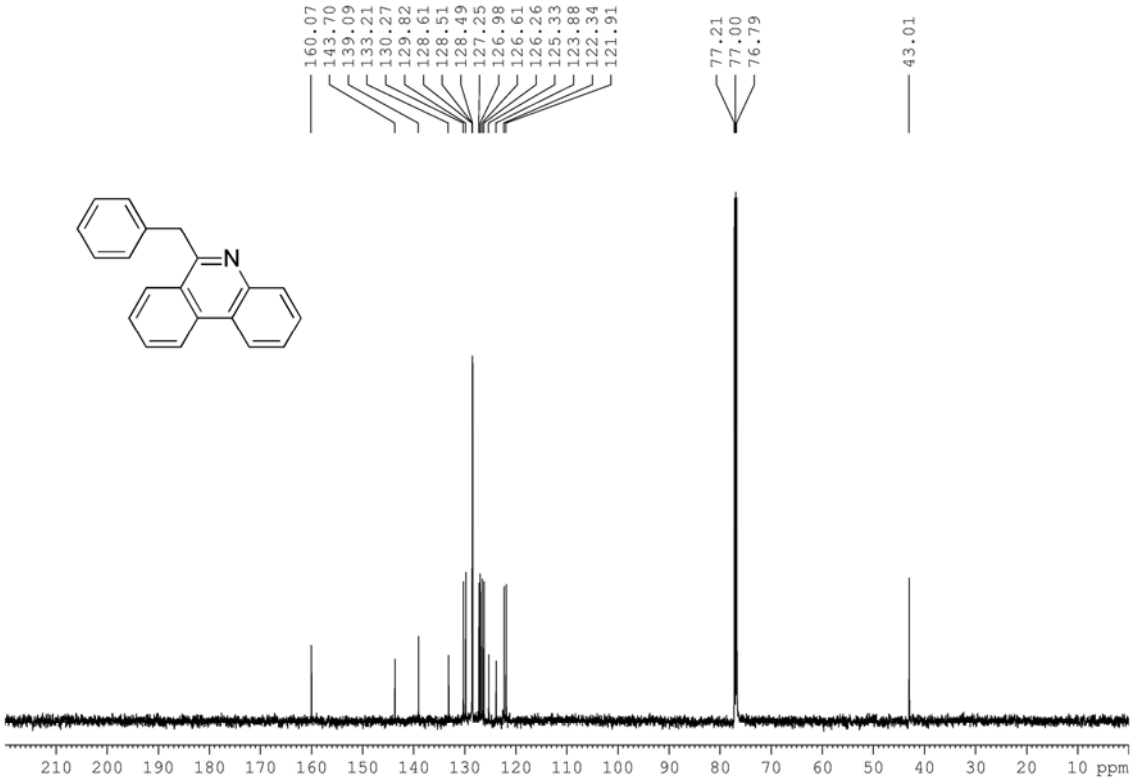
6-Methylphenanthridine (3b)



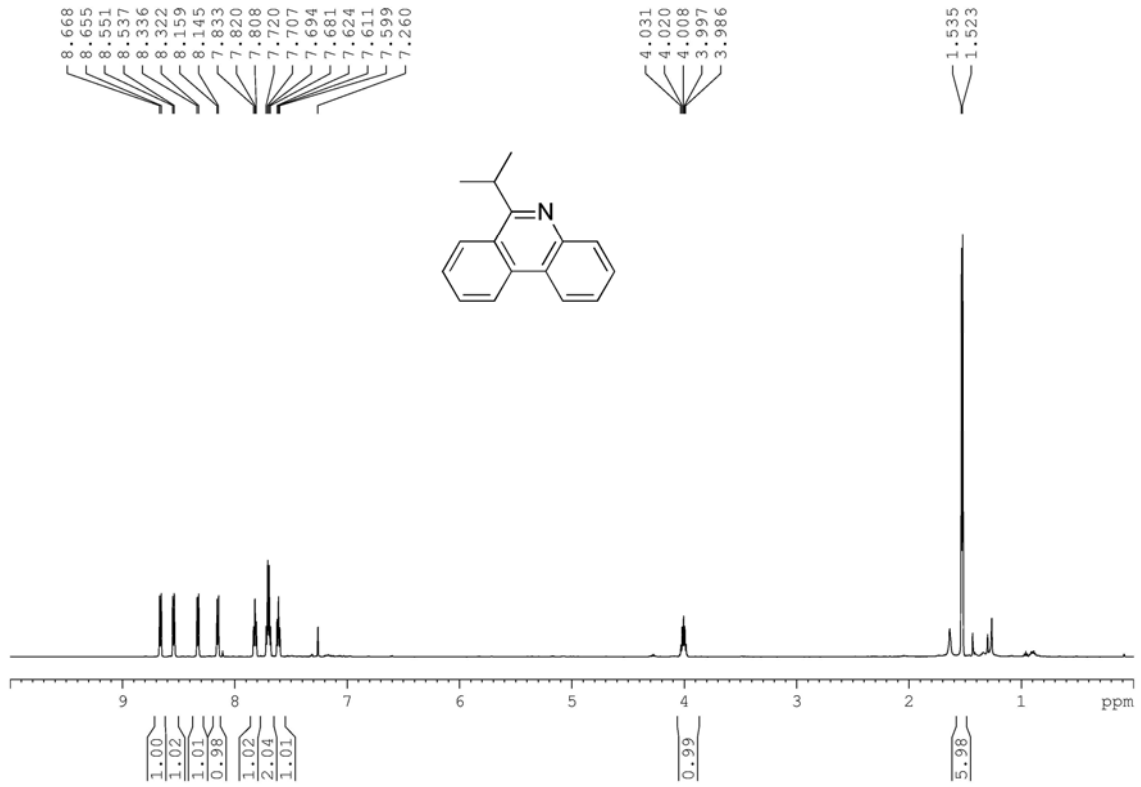


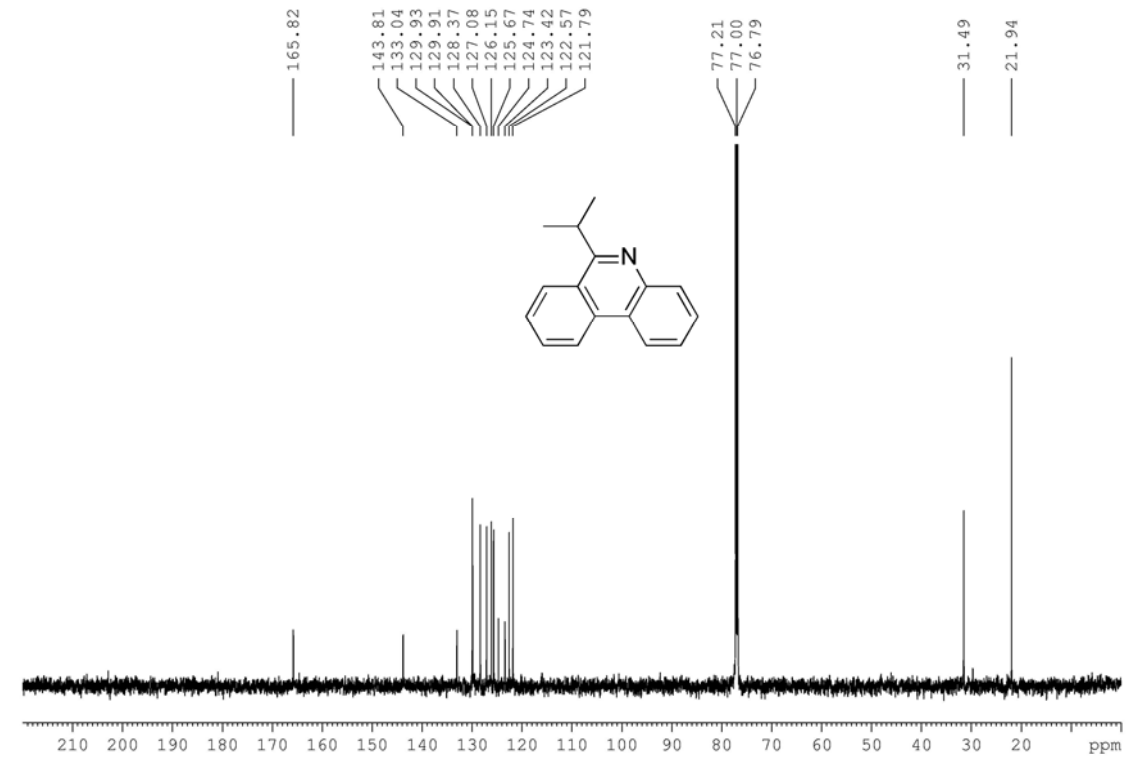
6-Benzylphenanthridine (3c)



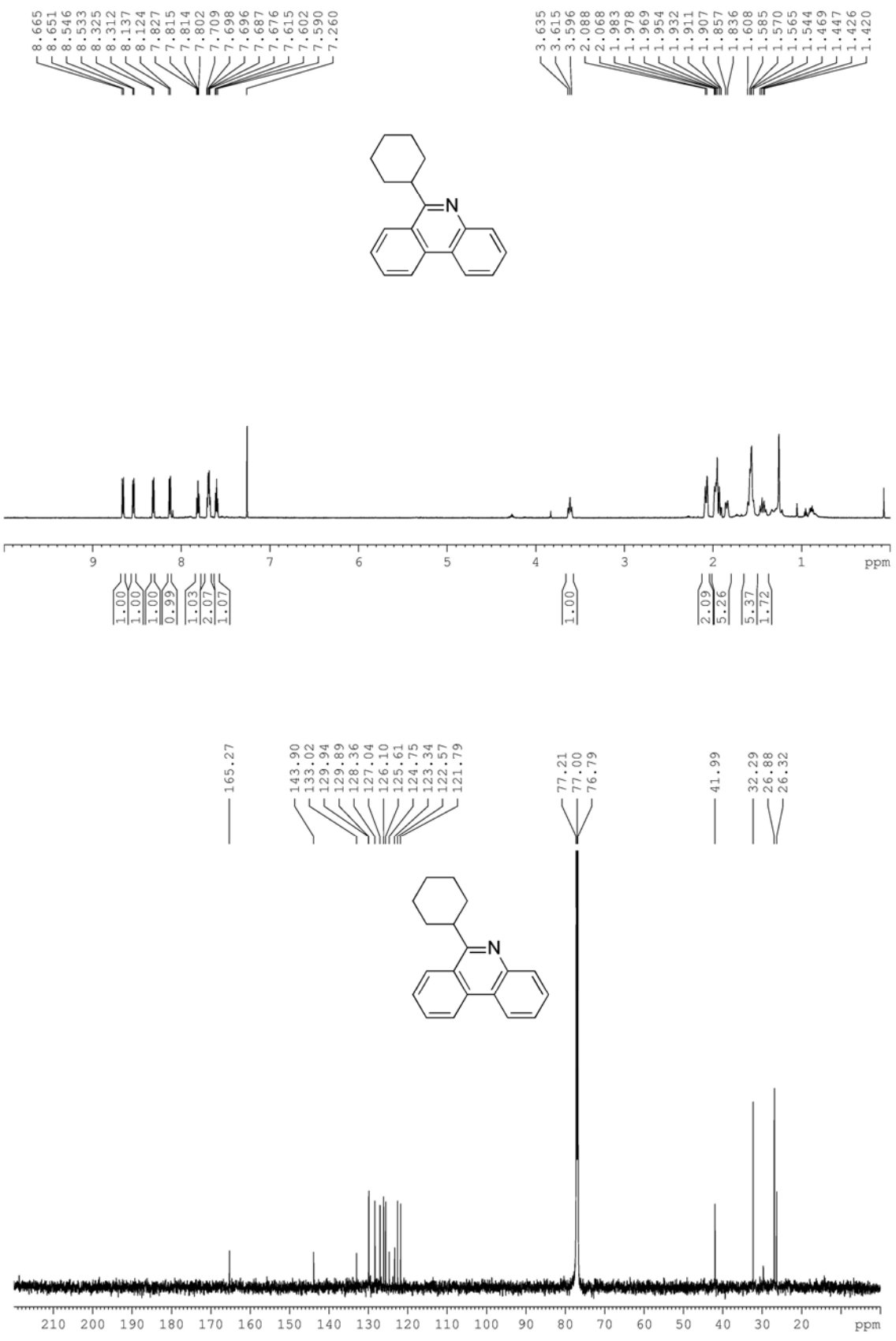


6-Isopropylphenanthridine (3d)

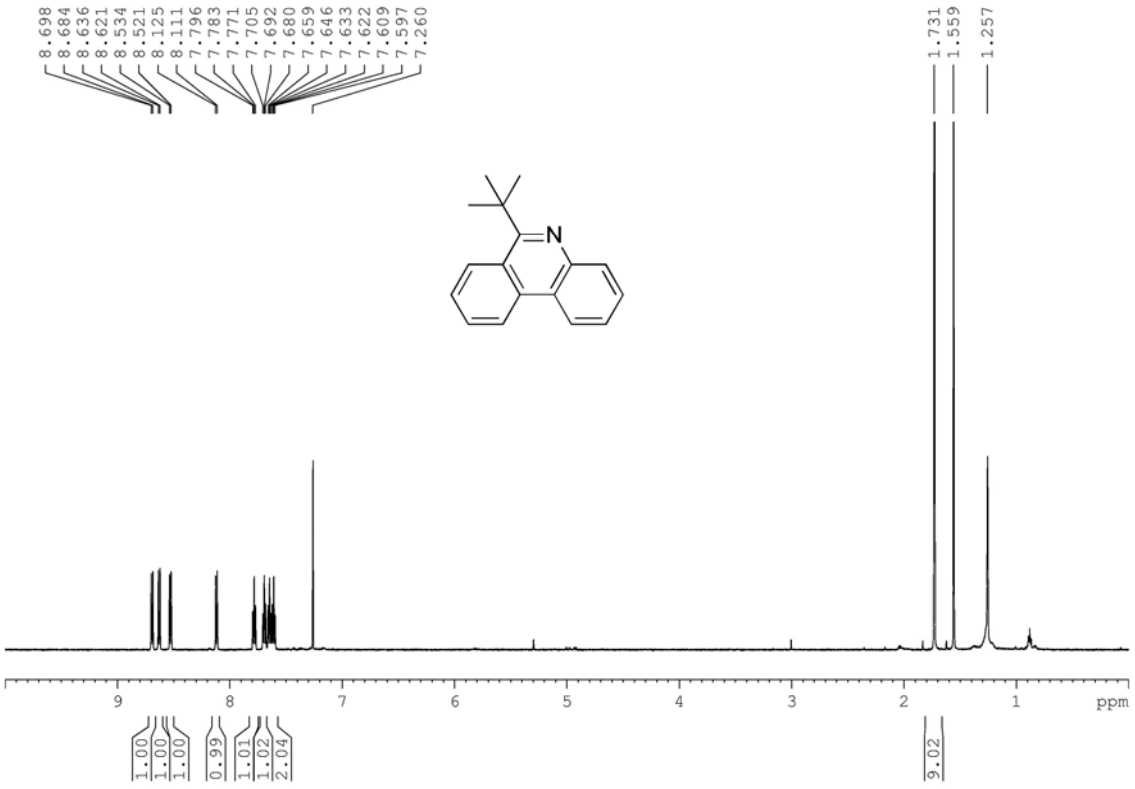


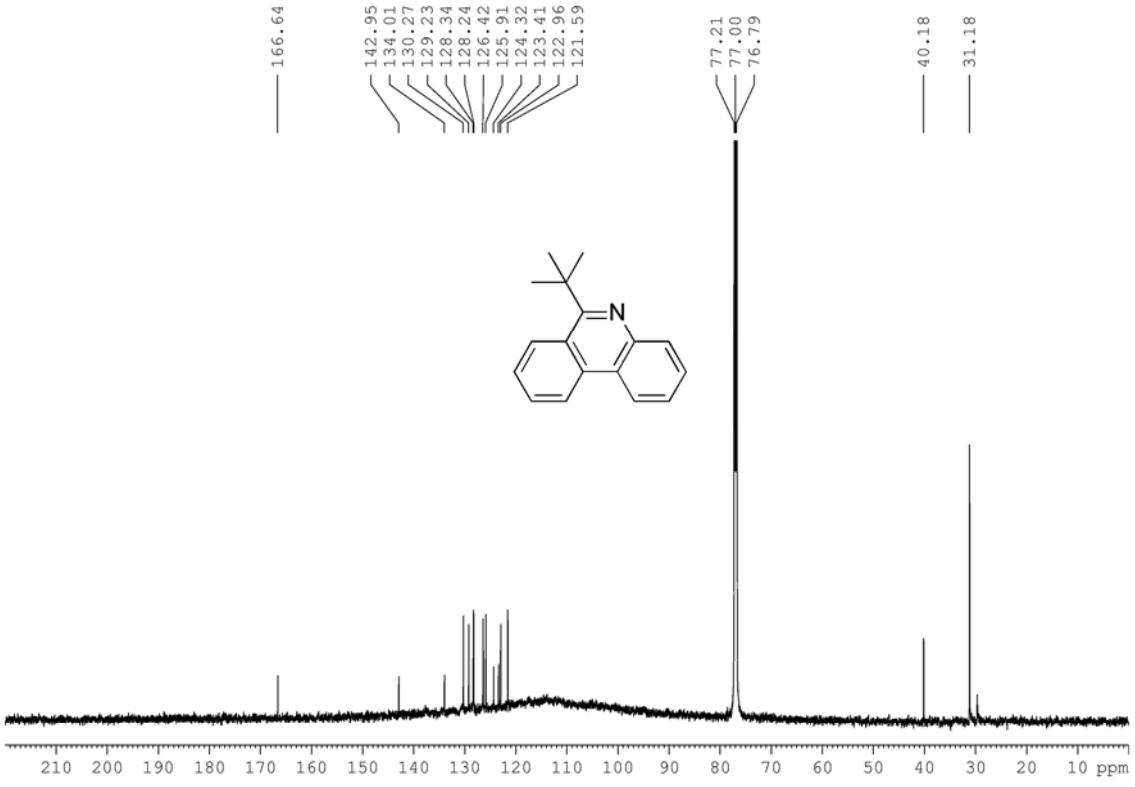


6-Cyclohexylphenanthridine (3e)

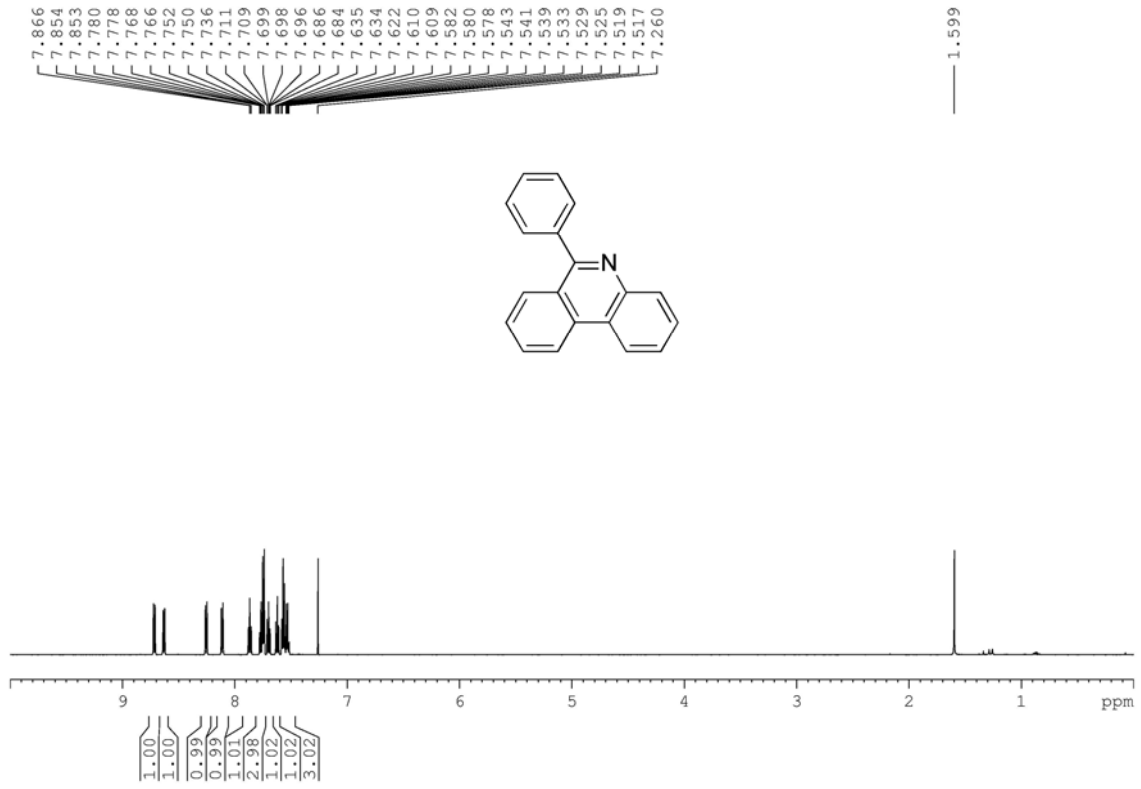


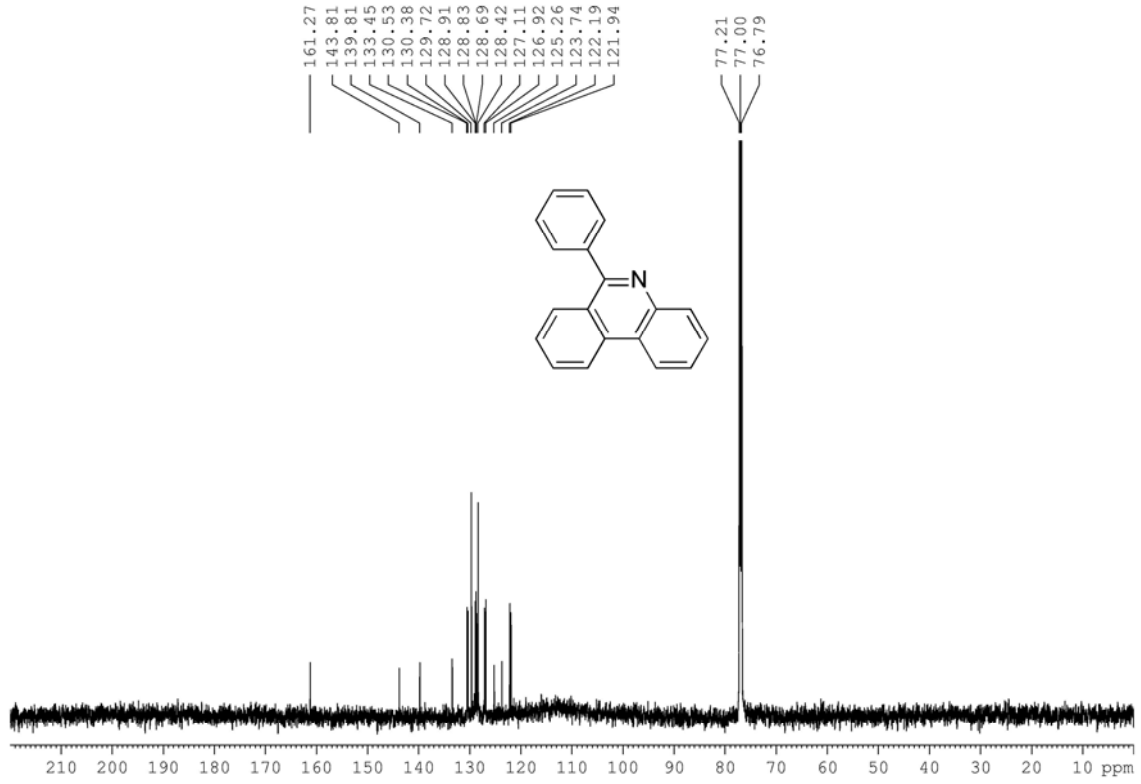
6-(*tert*-Butyl)phenanthridine (3f)



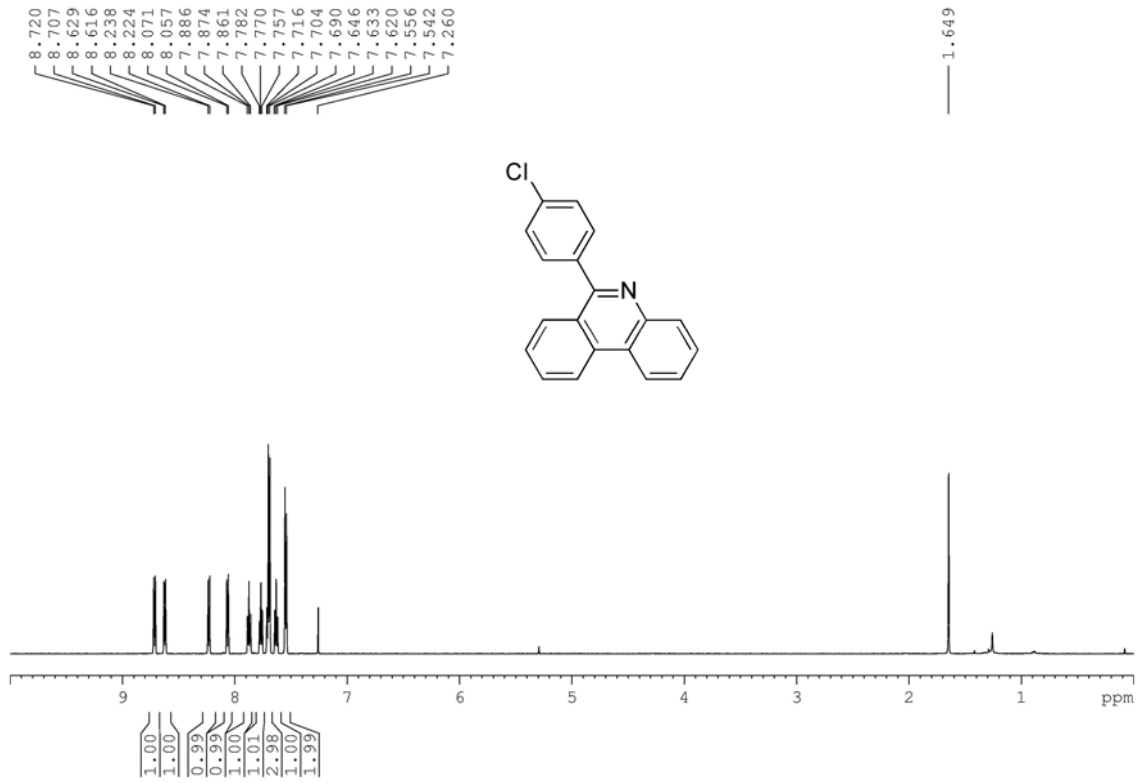


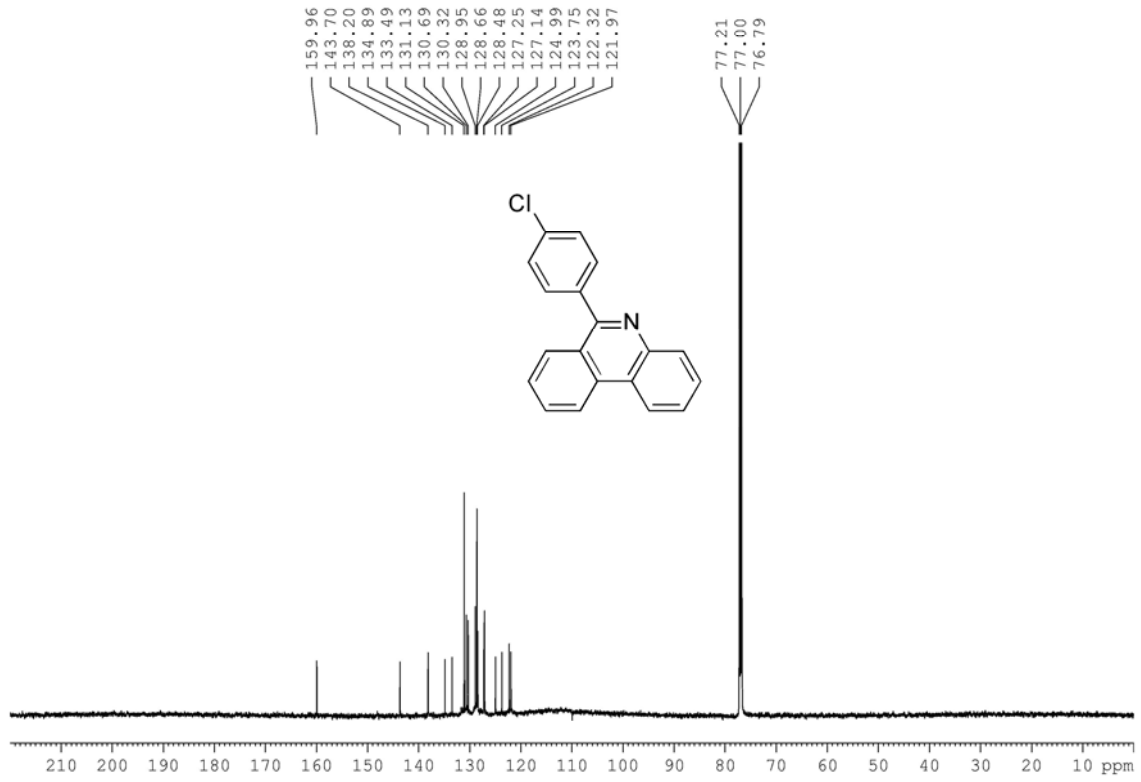
6-Phenylphenanthridine (3g)



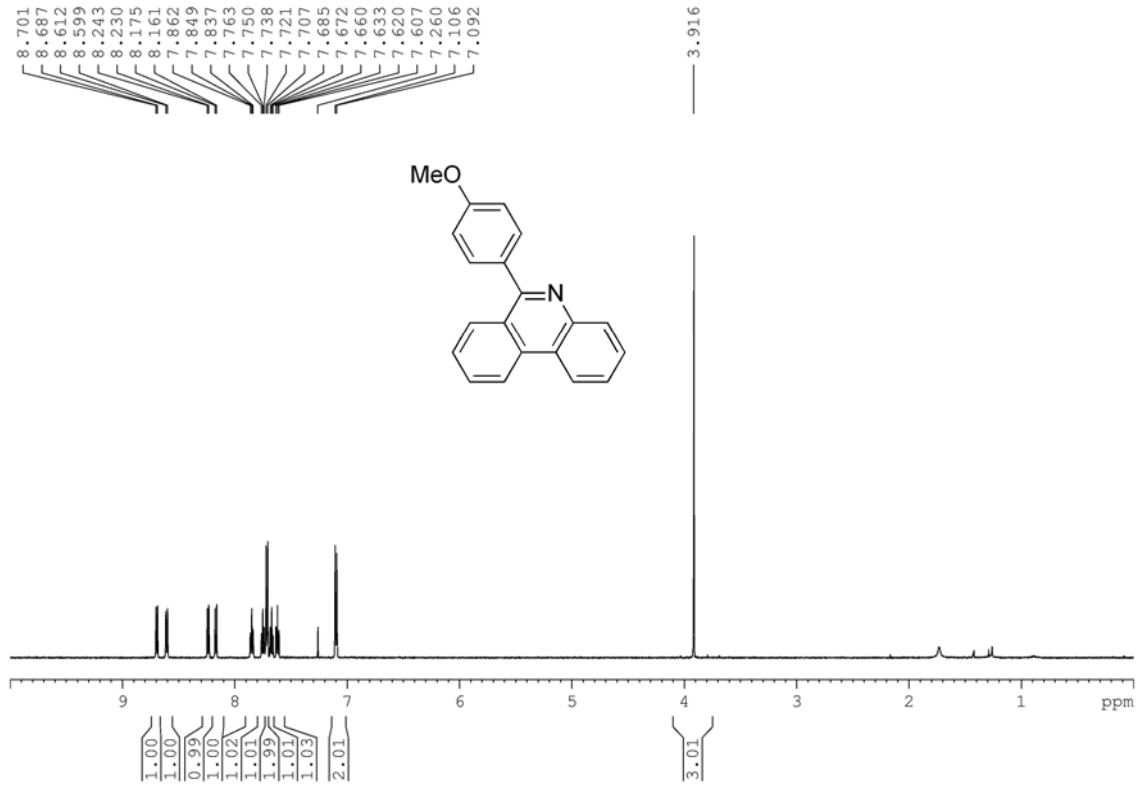


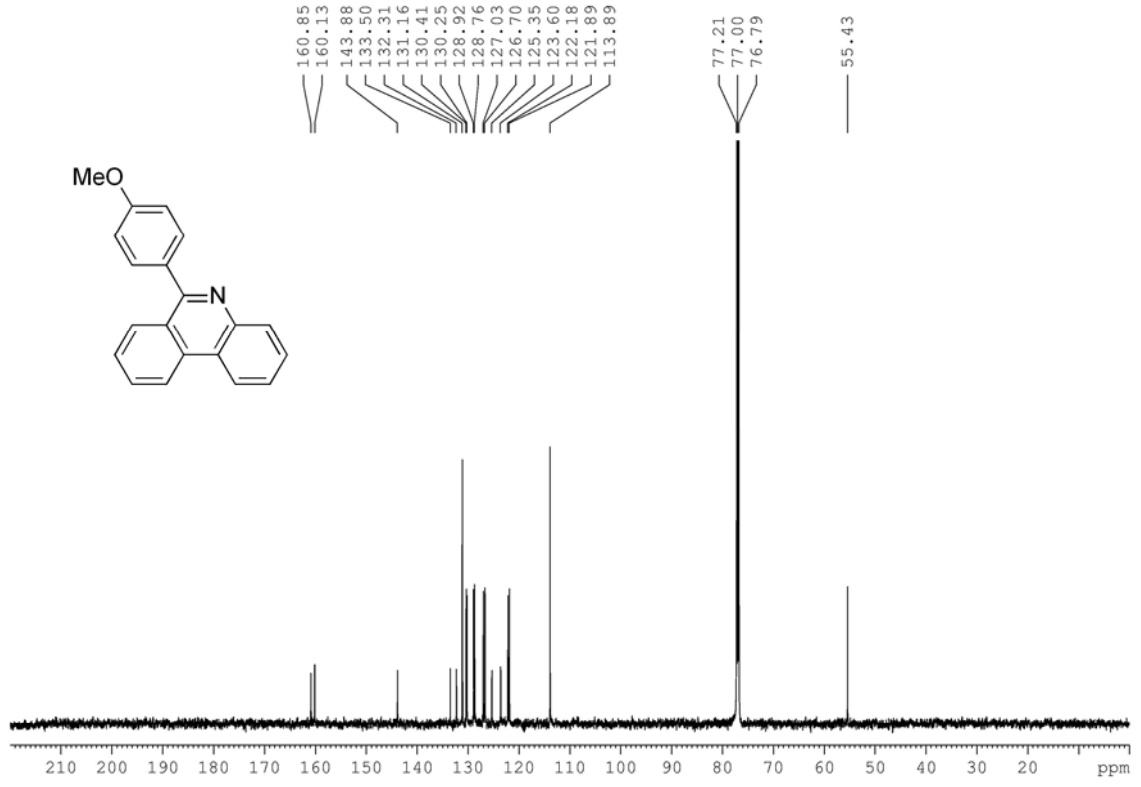
6-(4-Chlorophenyl)phenanthridine (3h)



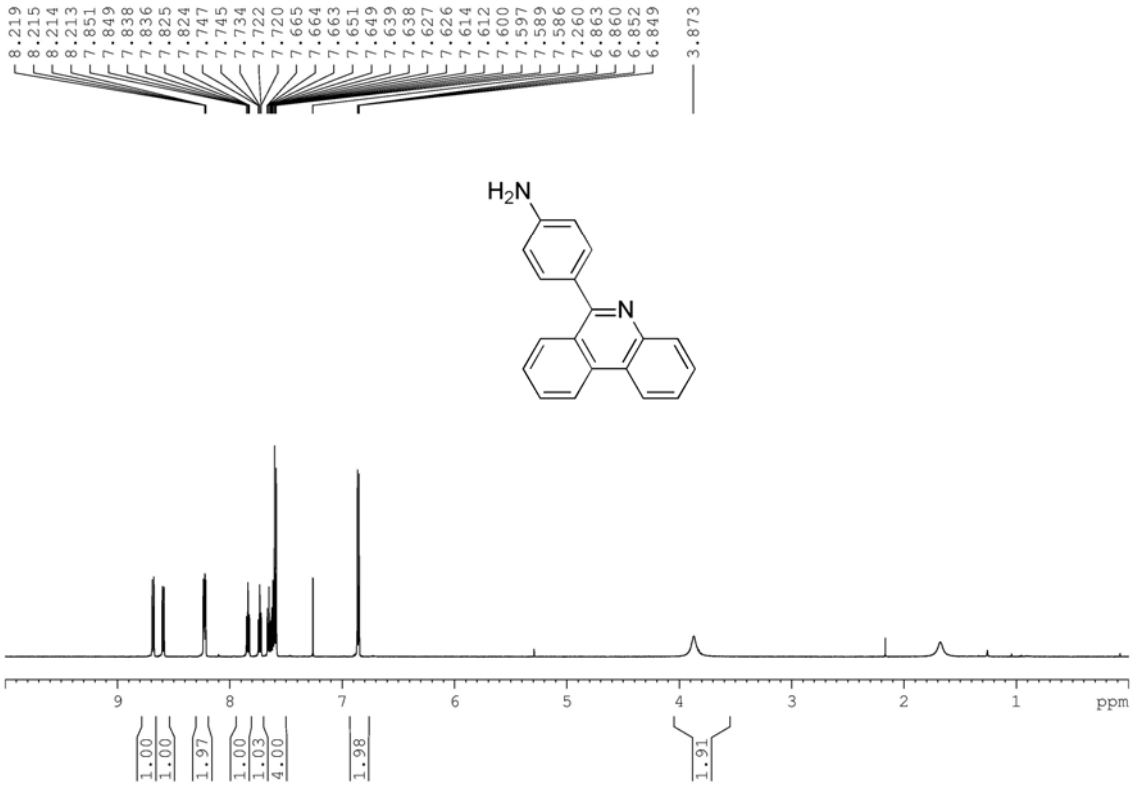


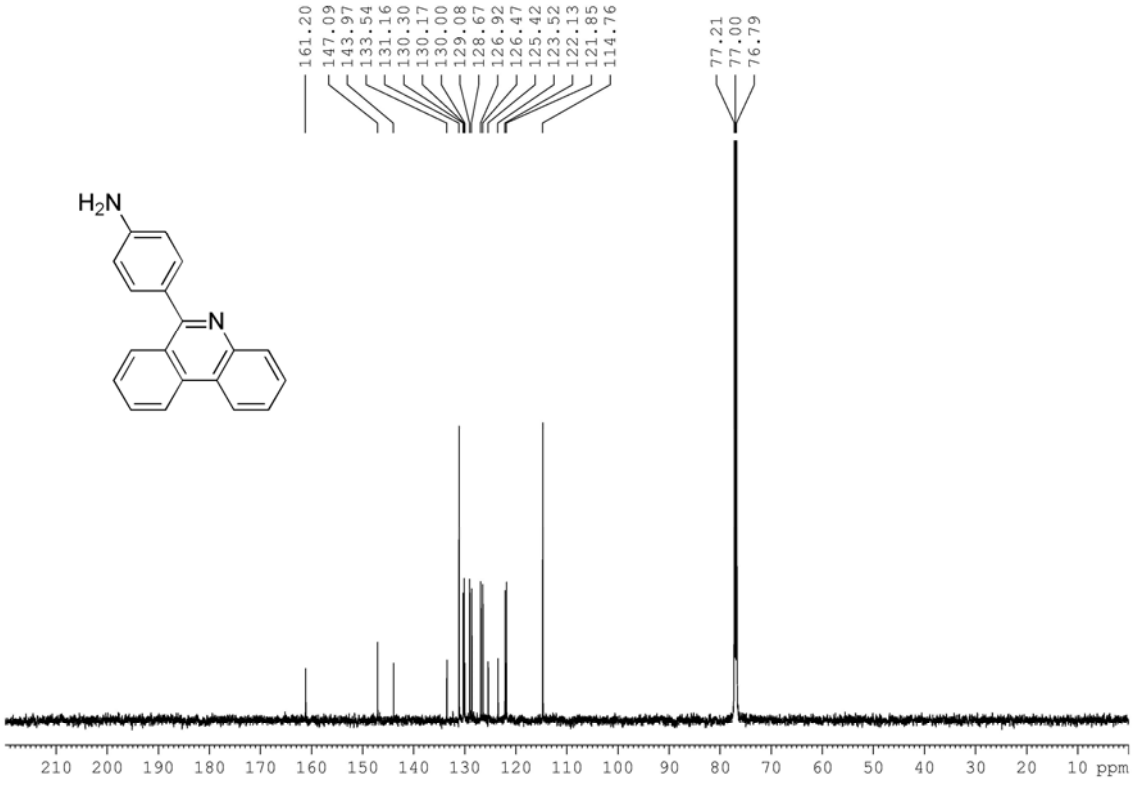
6-(4-Methoxyphenyl)phenanthridine (3i)



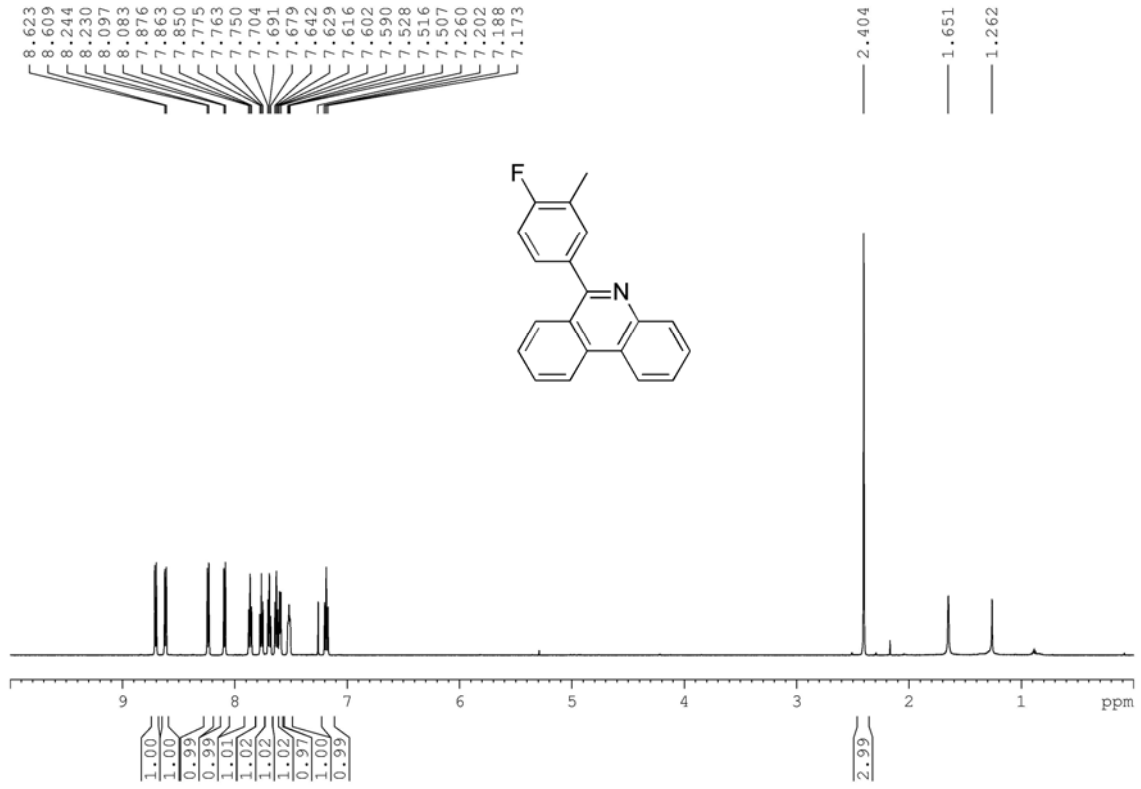


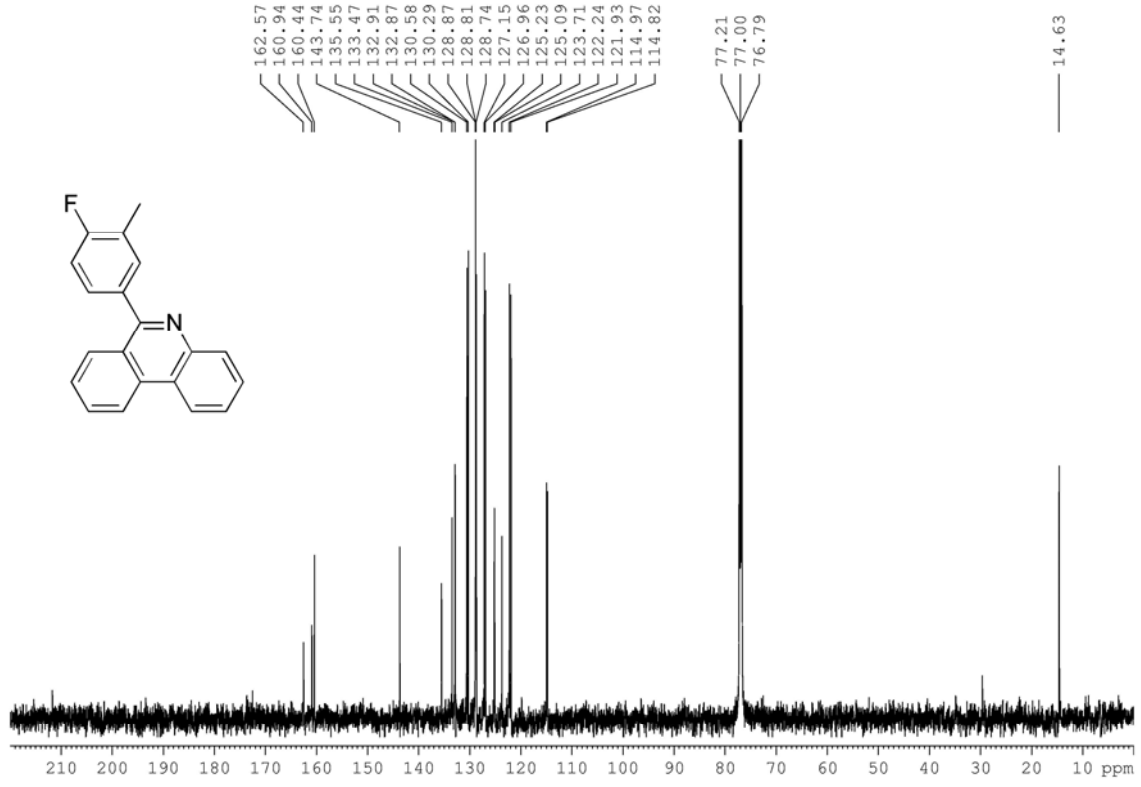
6-(4-Aminophenyl)phenanthridine (3j)



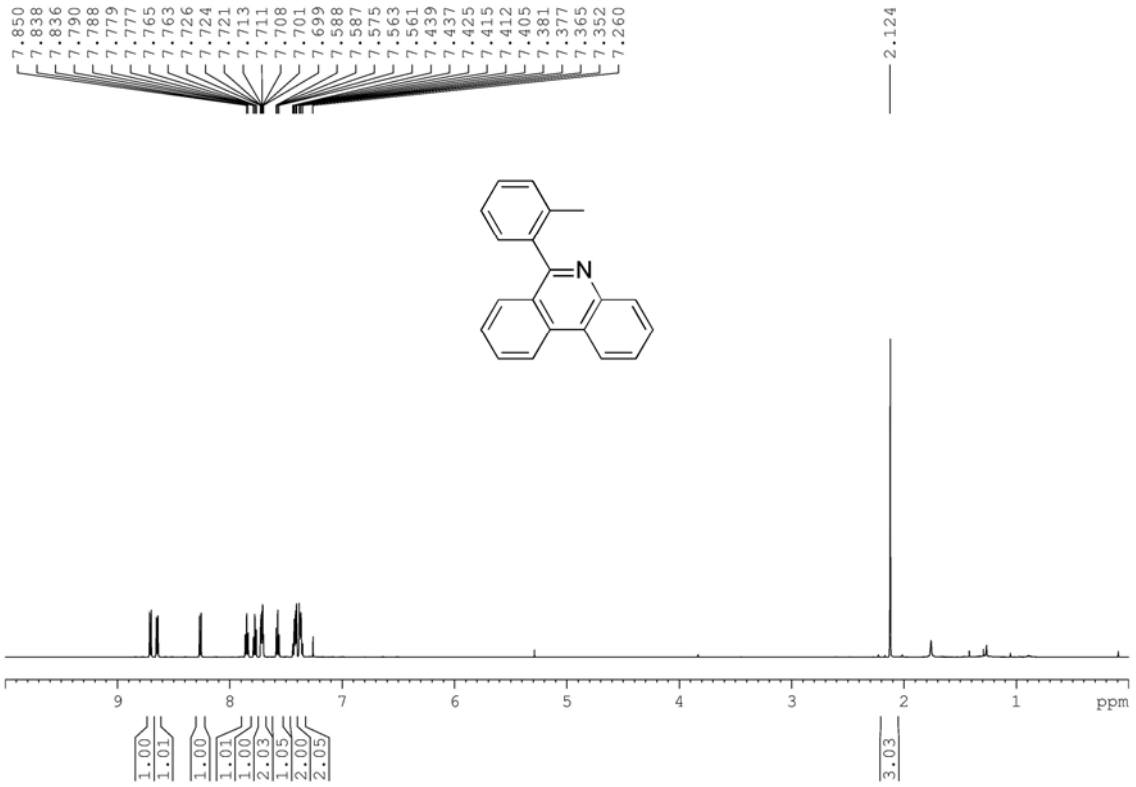


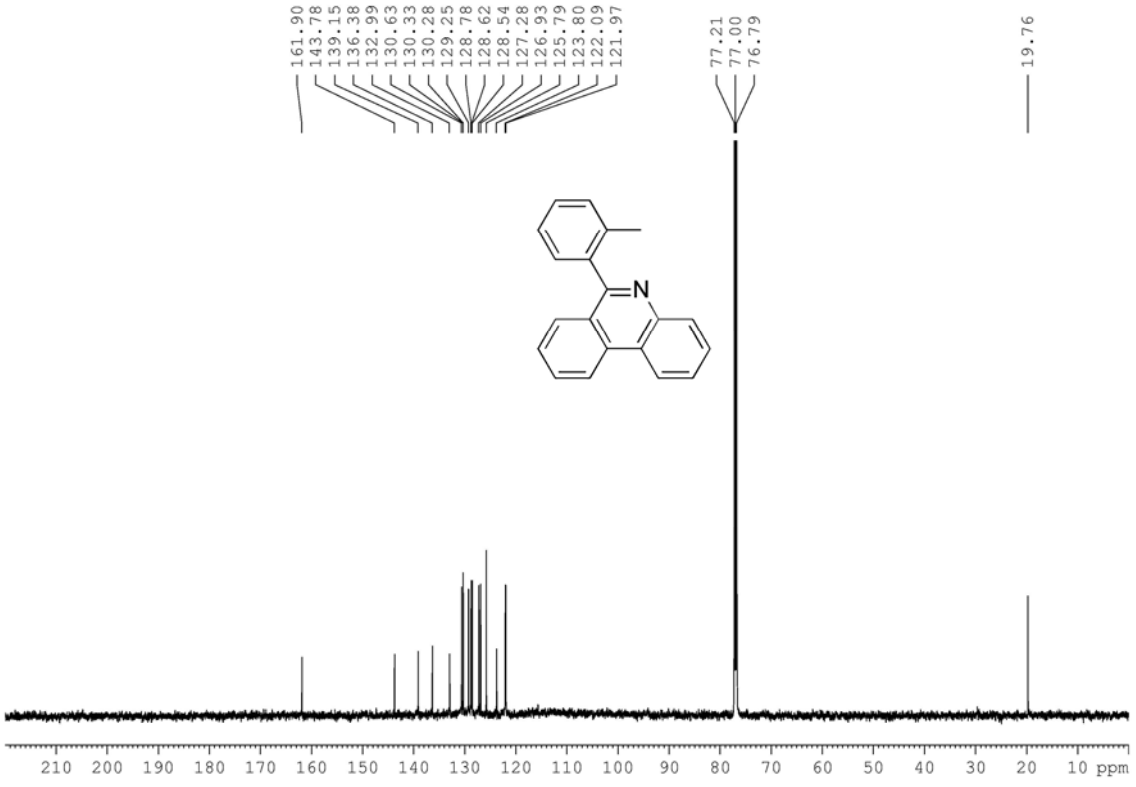
6-(4-Fluoro-3-methylphenyl)phenanthridine (3k)



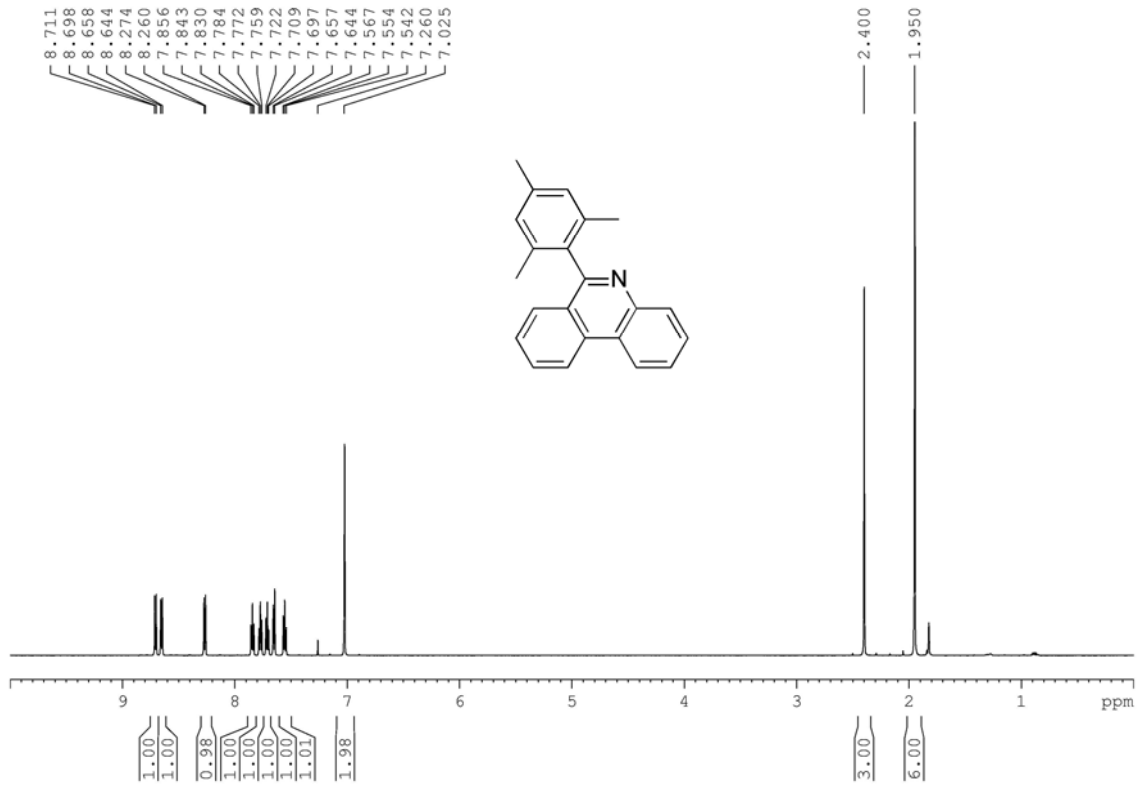


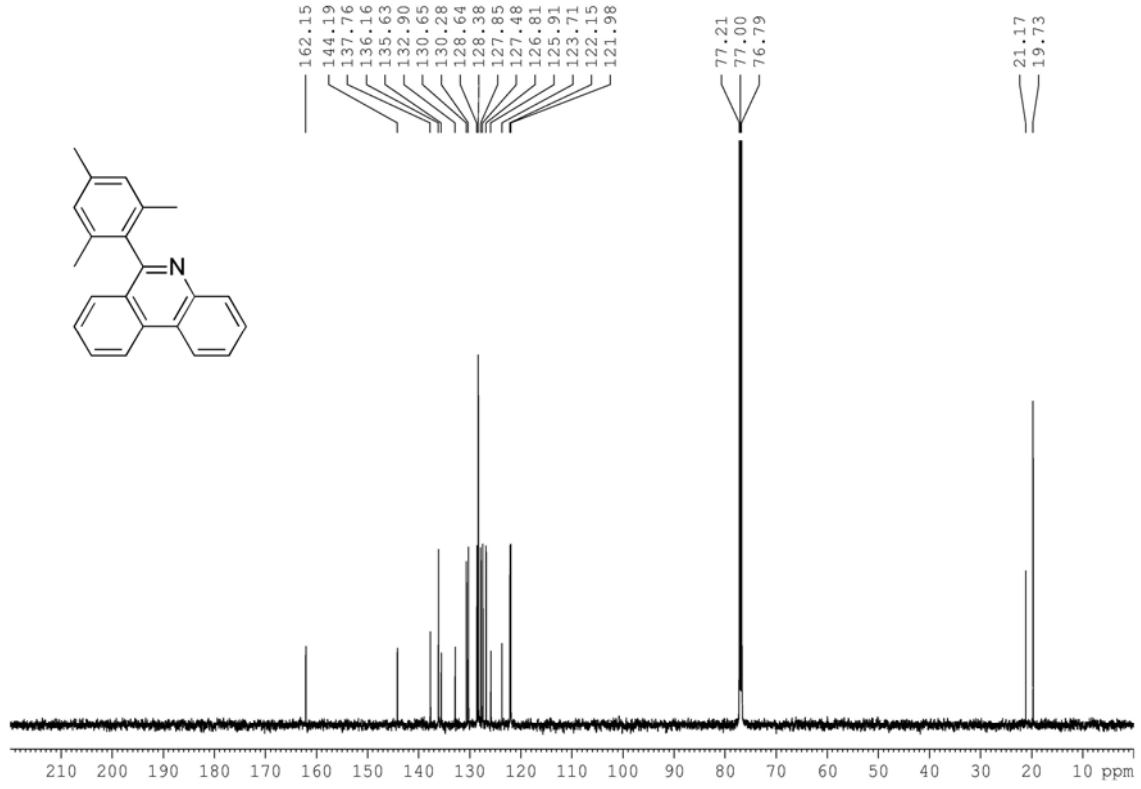
6-(*o*-Tolyl)phenanthridine (3l)



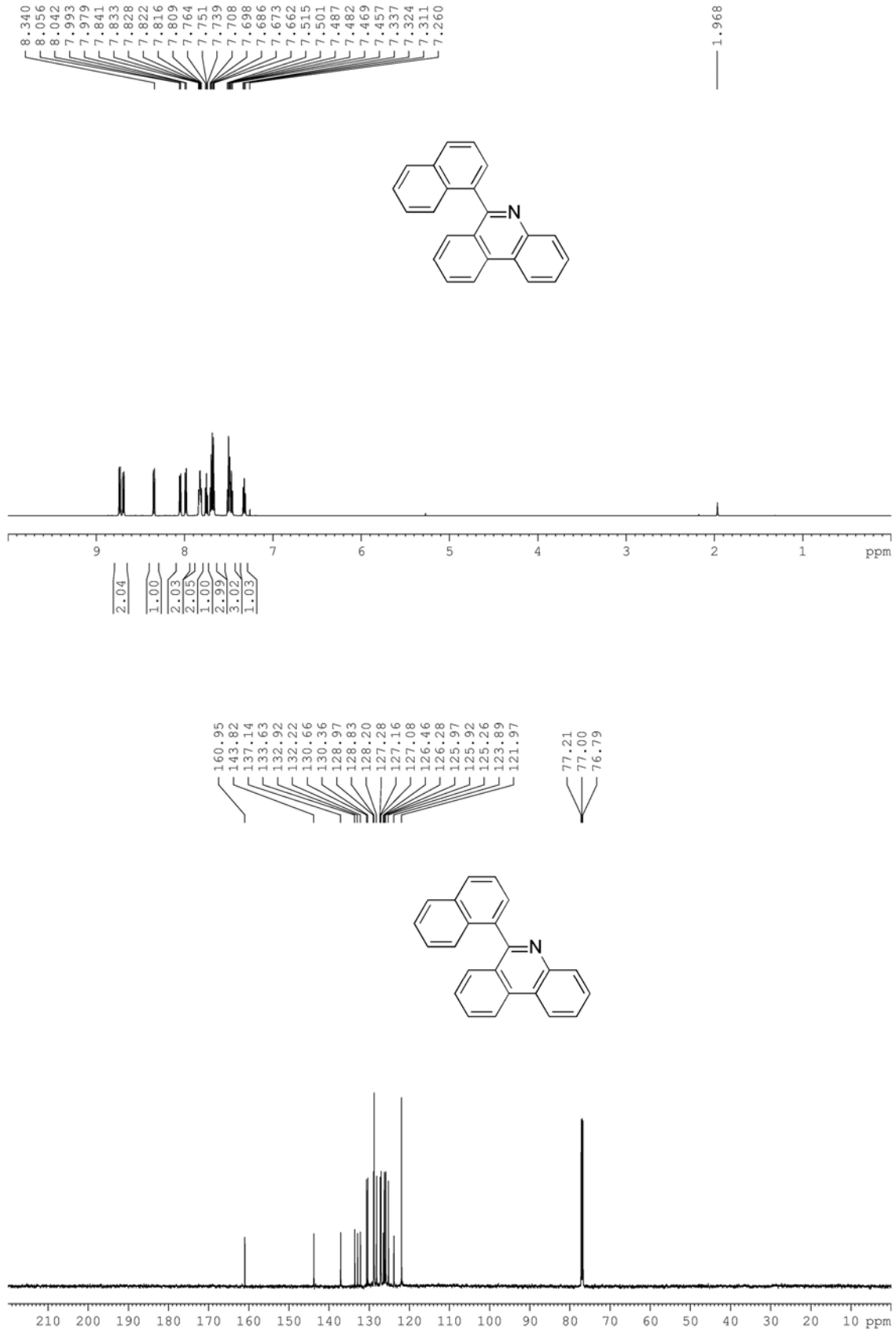


6-Mesitylphenanthridine (3m)

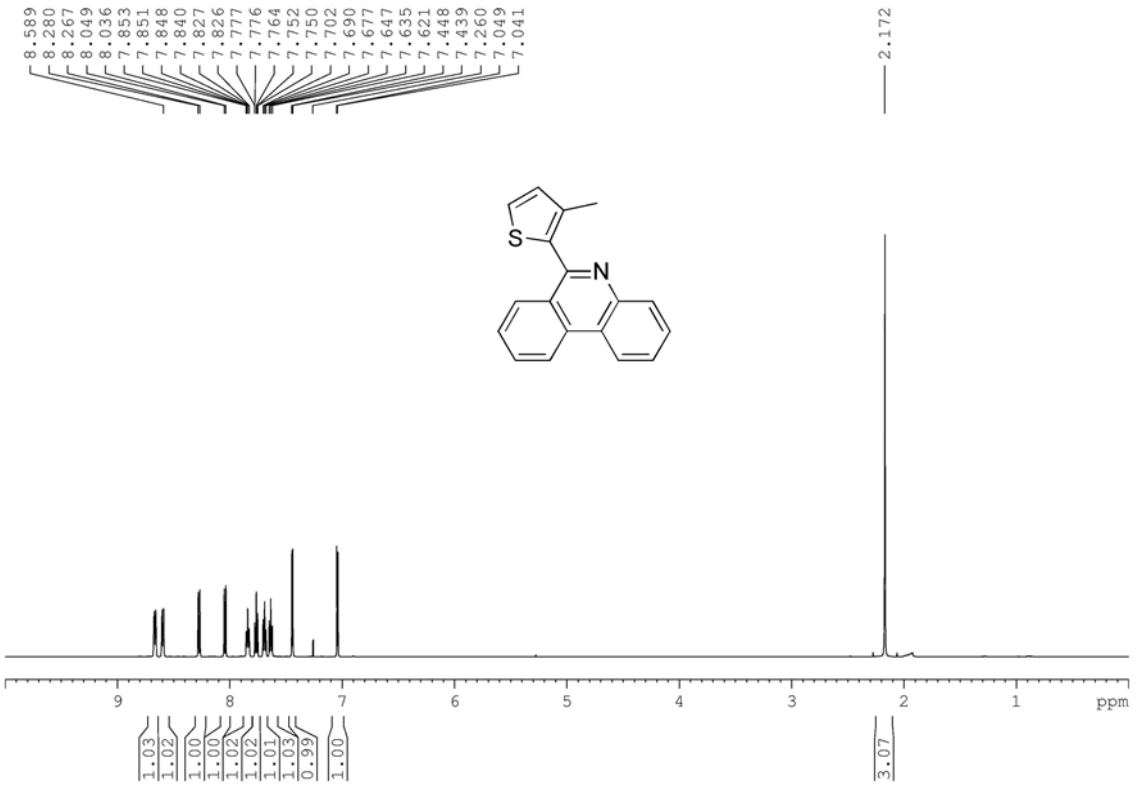


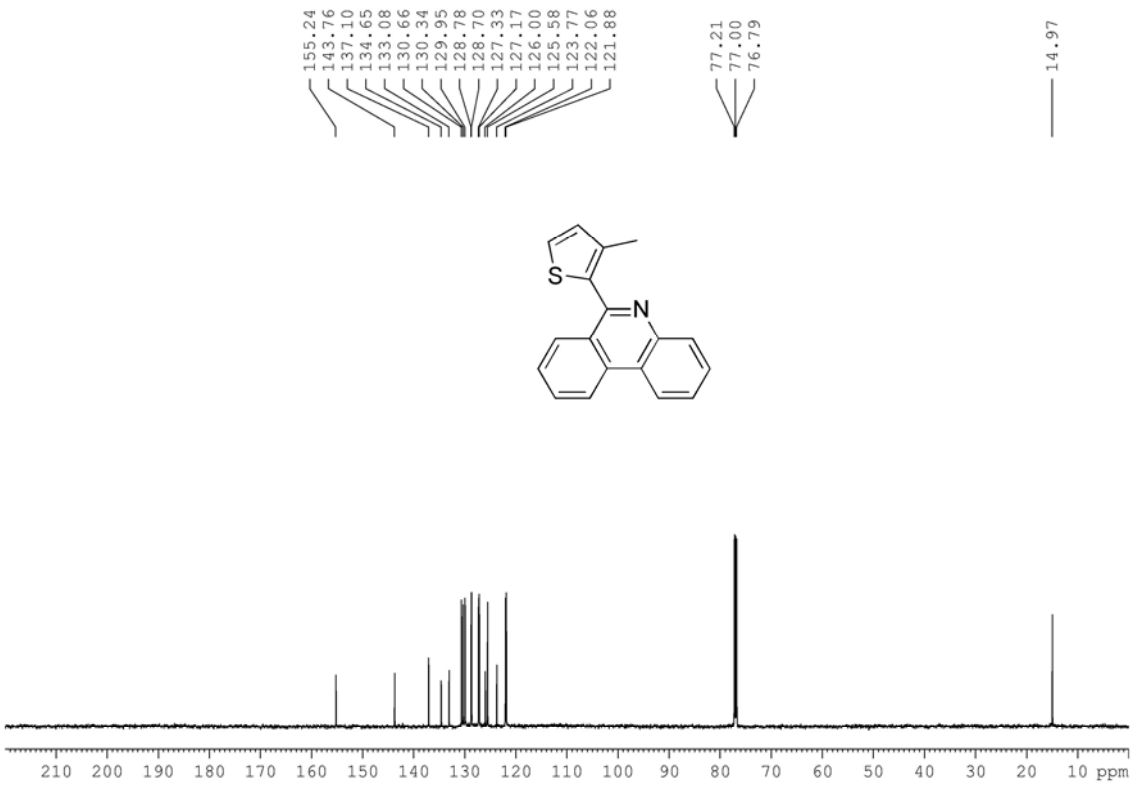


6-(Naphthalen-1-yl)phenanthridine (3n)

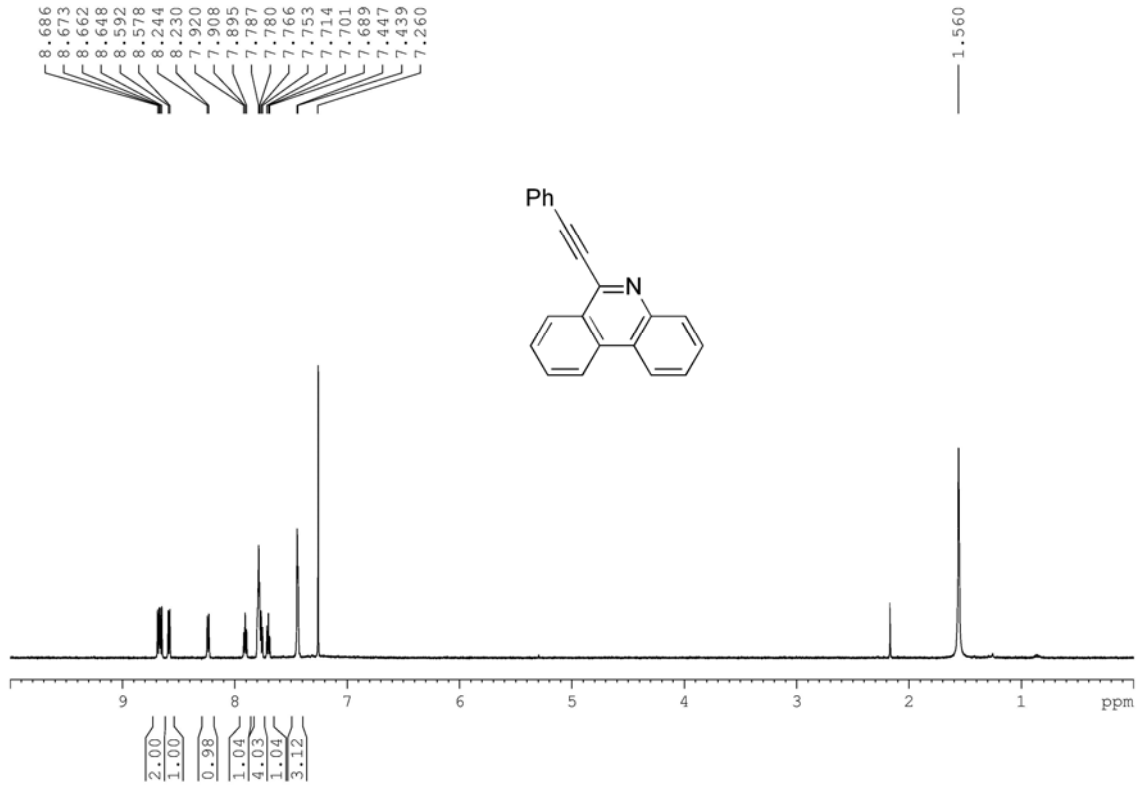


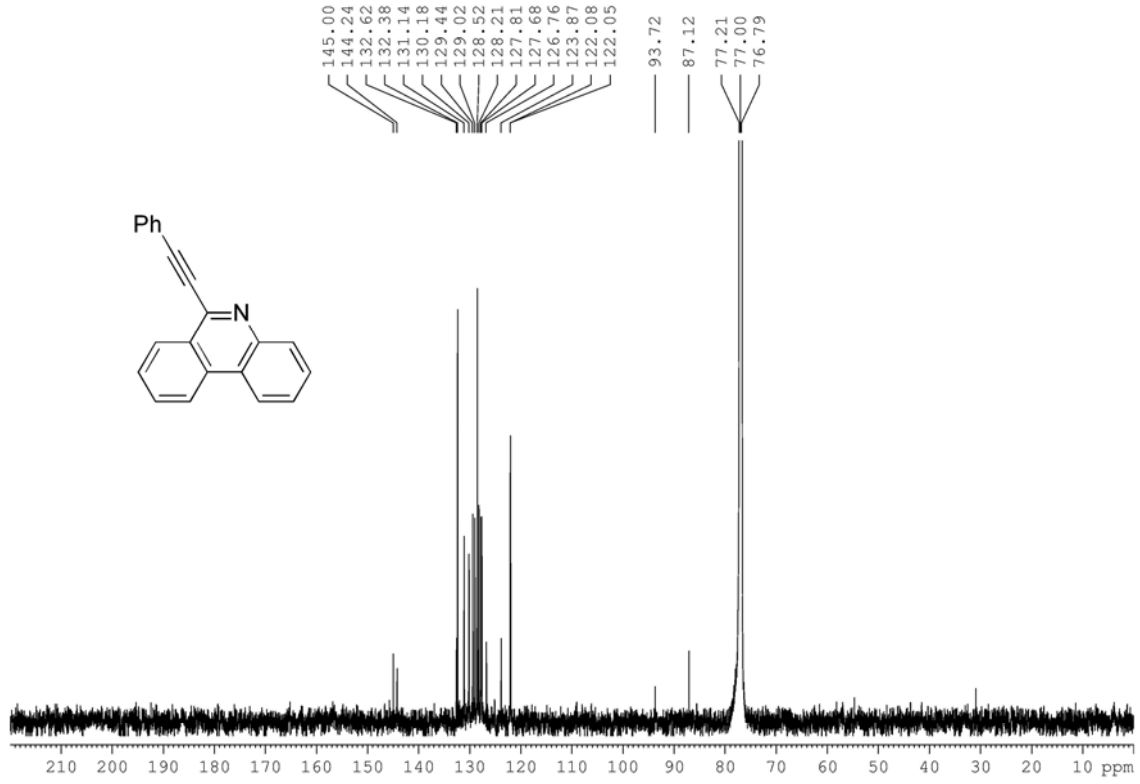
6-(3-Methylthiophen-2-yl)phenanthridine (3o)



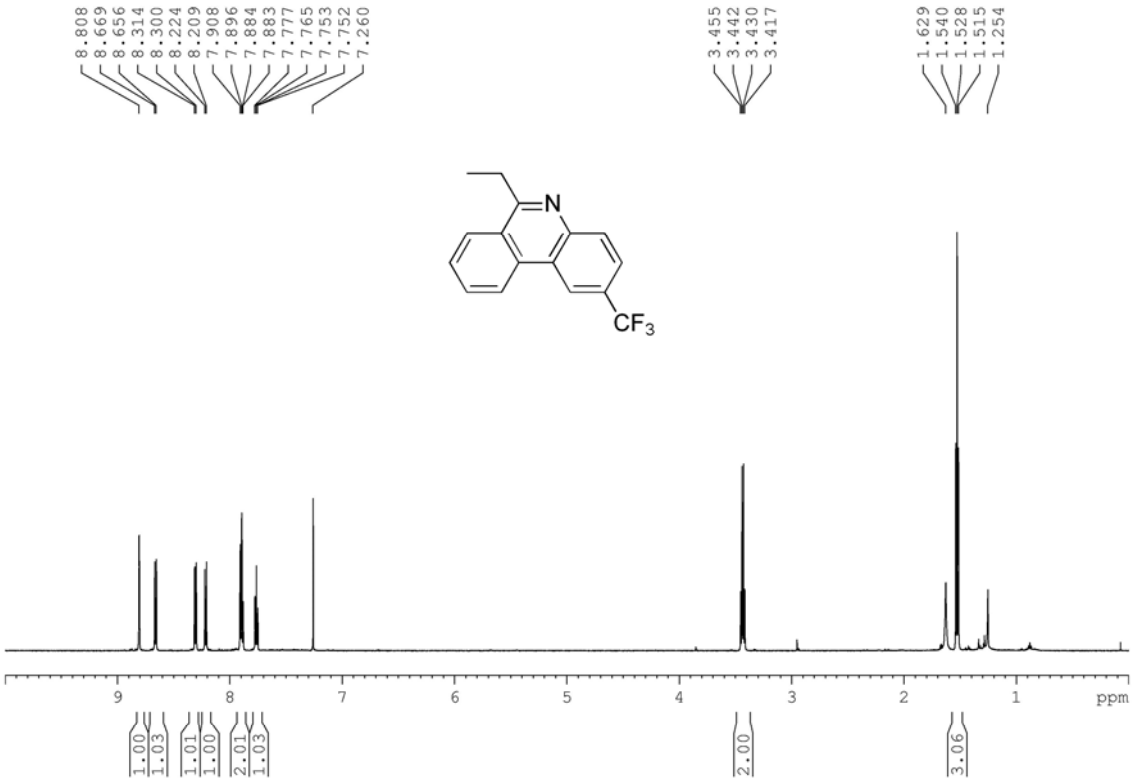


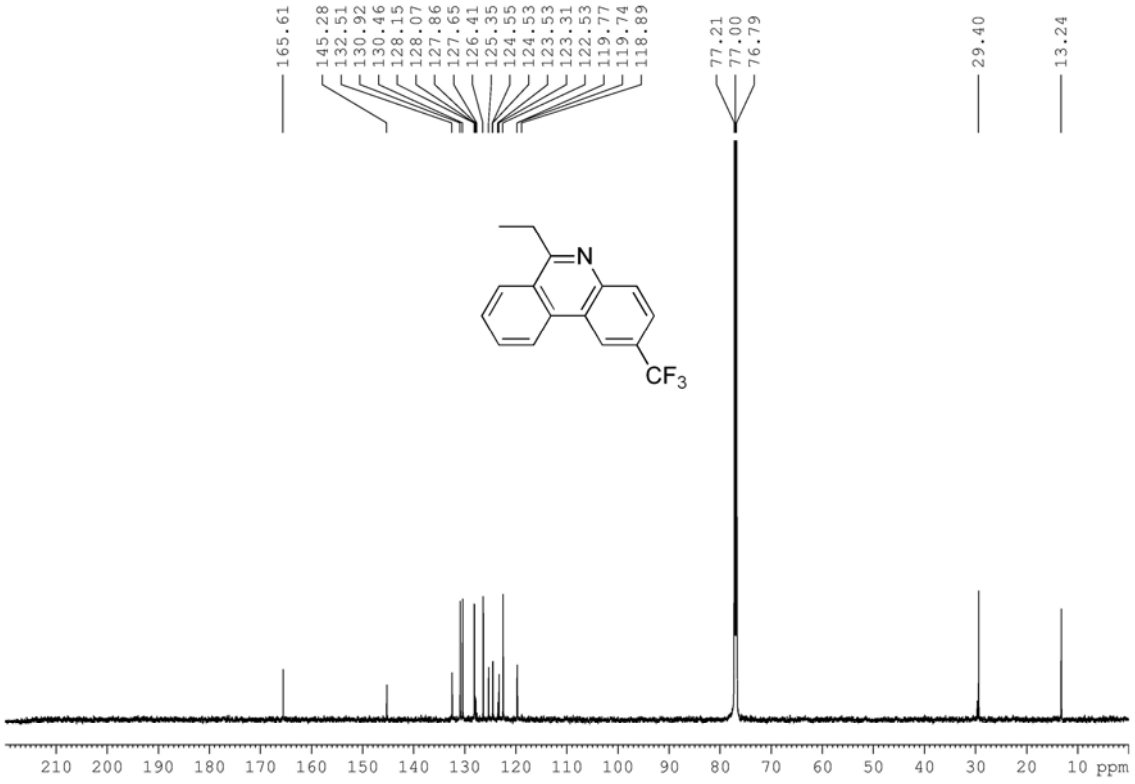
6-(Phenylethynyl)phenanthridine (3p)



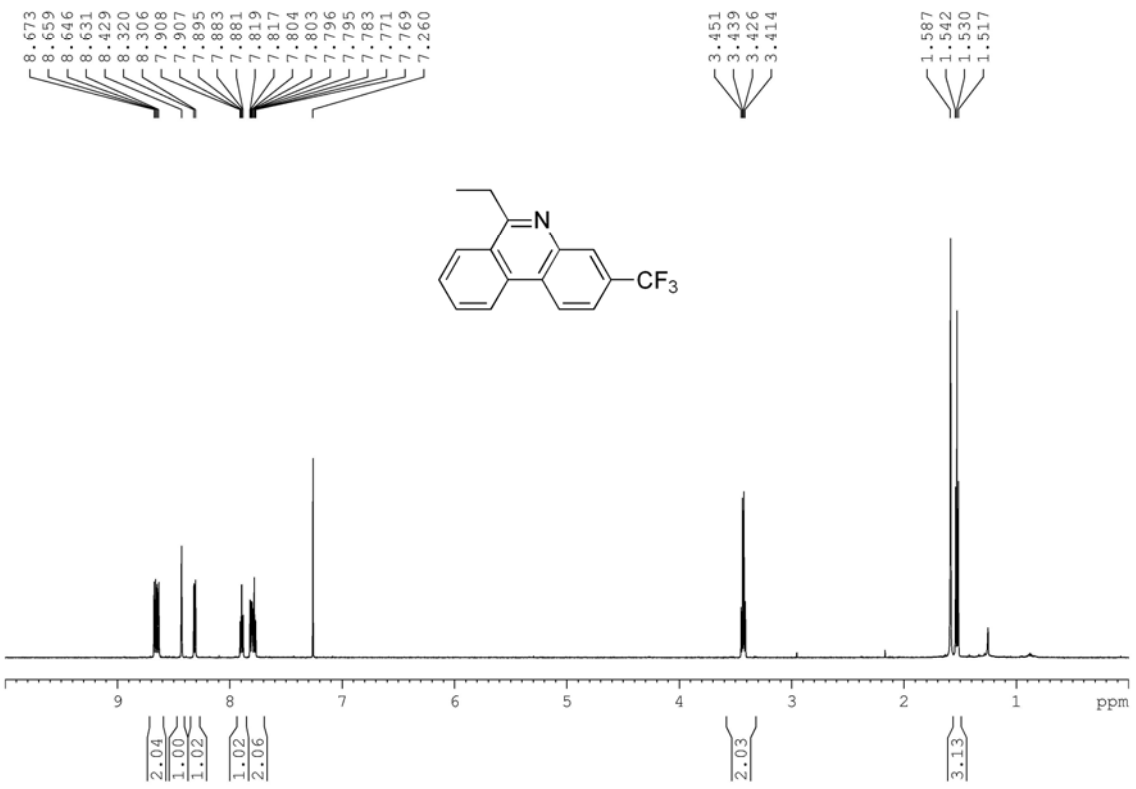


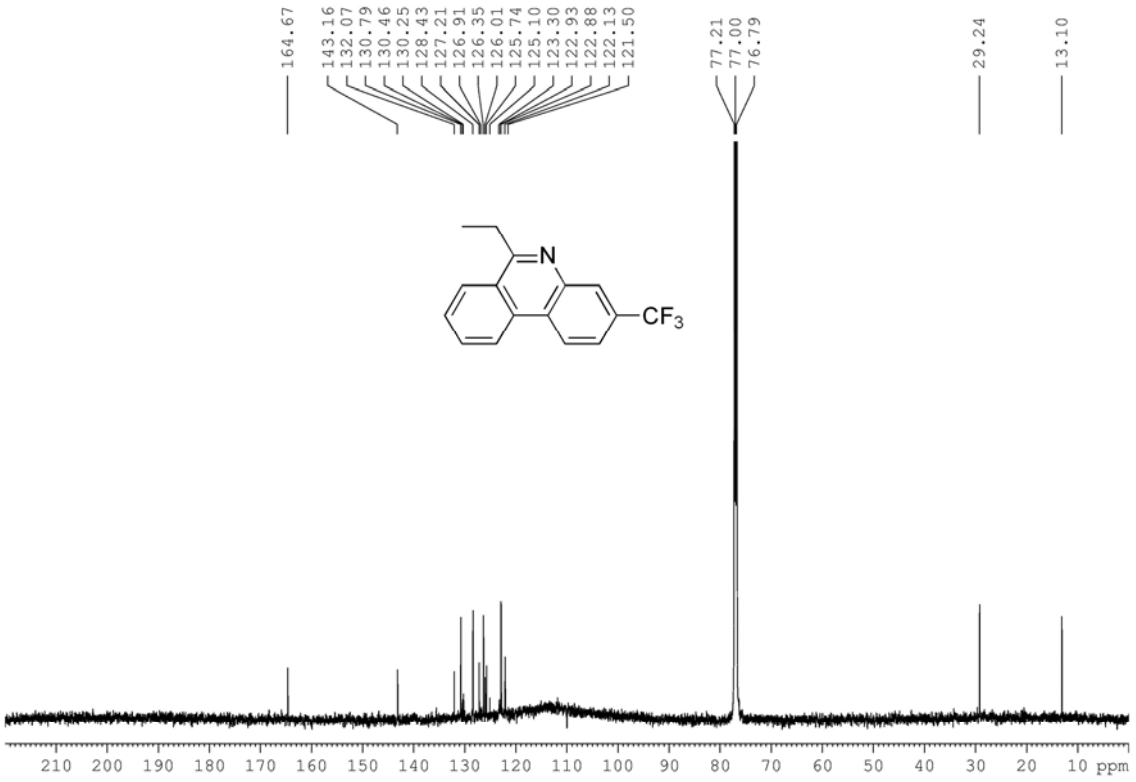
6-Ethyl-2-(trifluoromethyl)phenanthridine (3A)



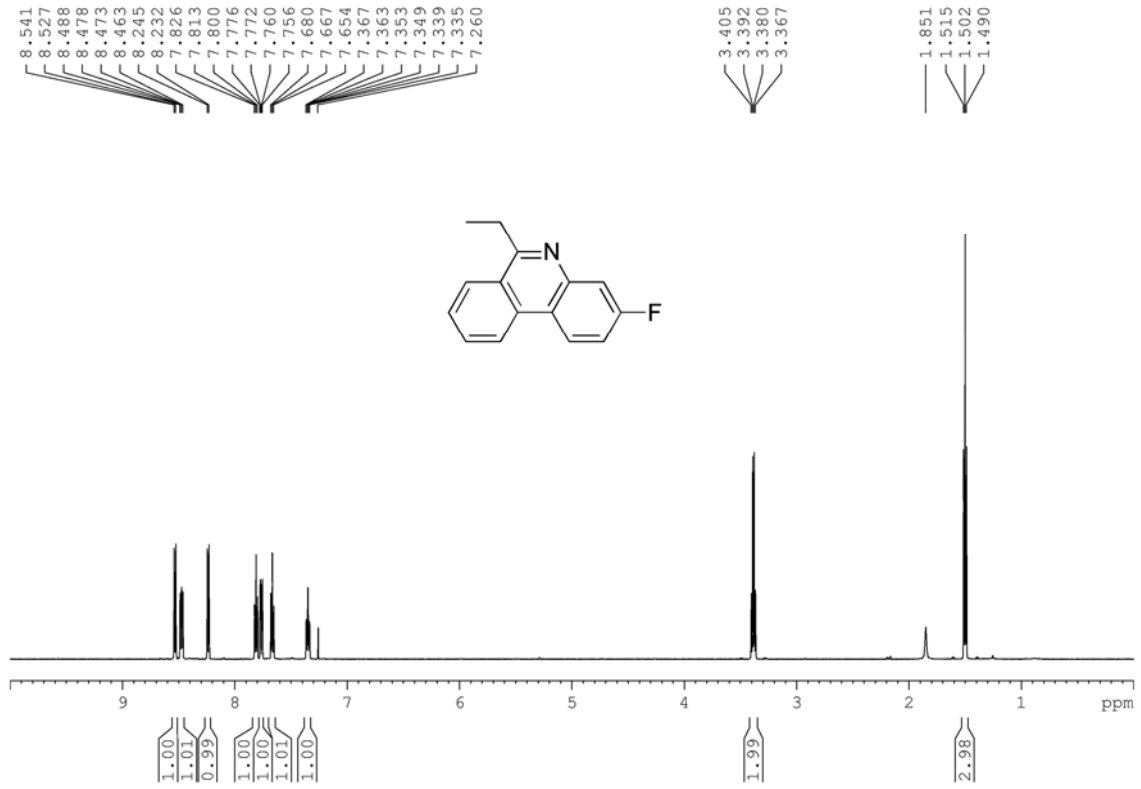


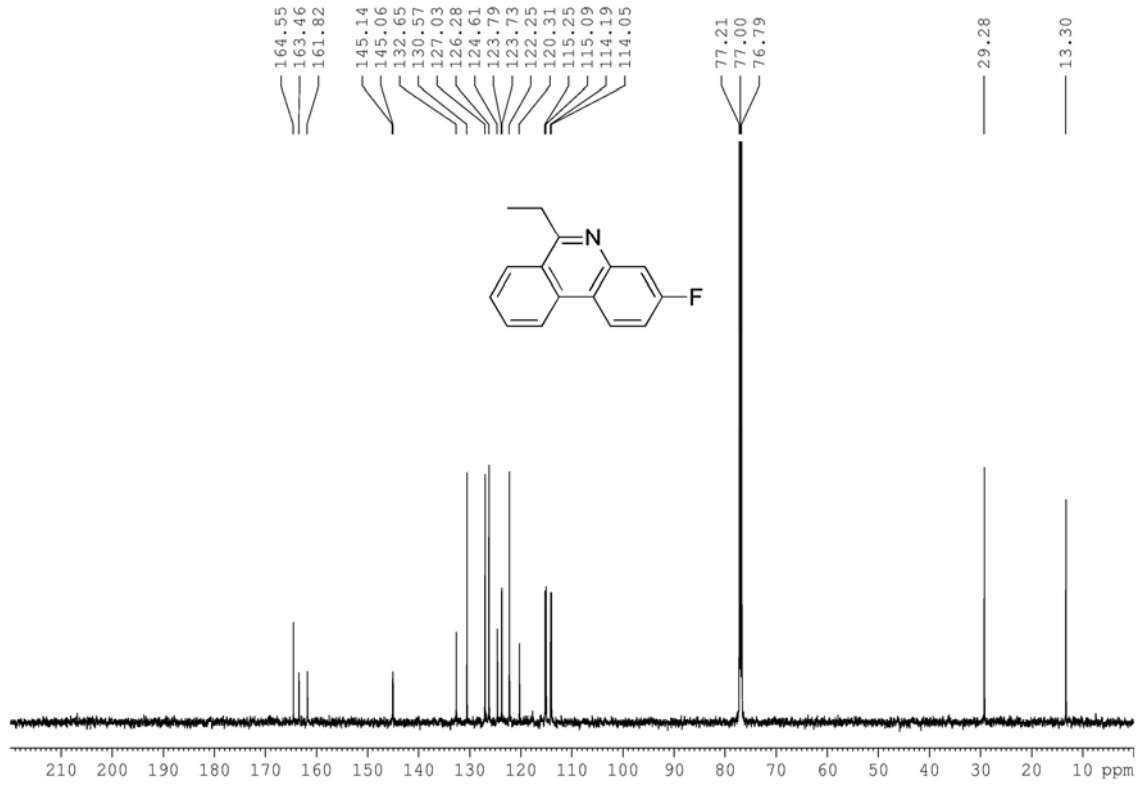
6-Ethyl-3-(trifluoromethyl)phenanthridine (3B)



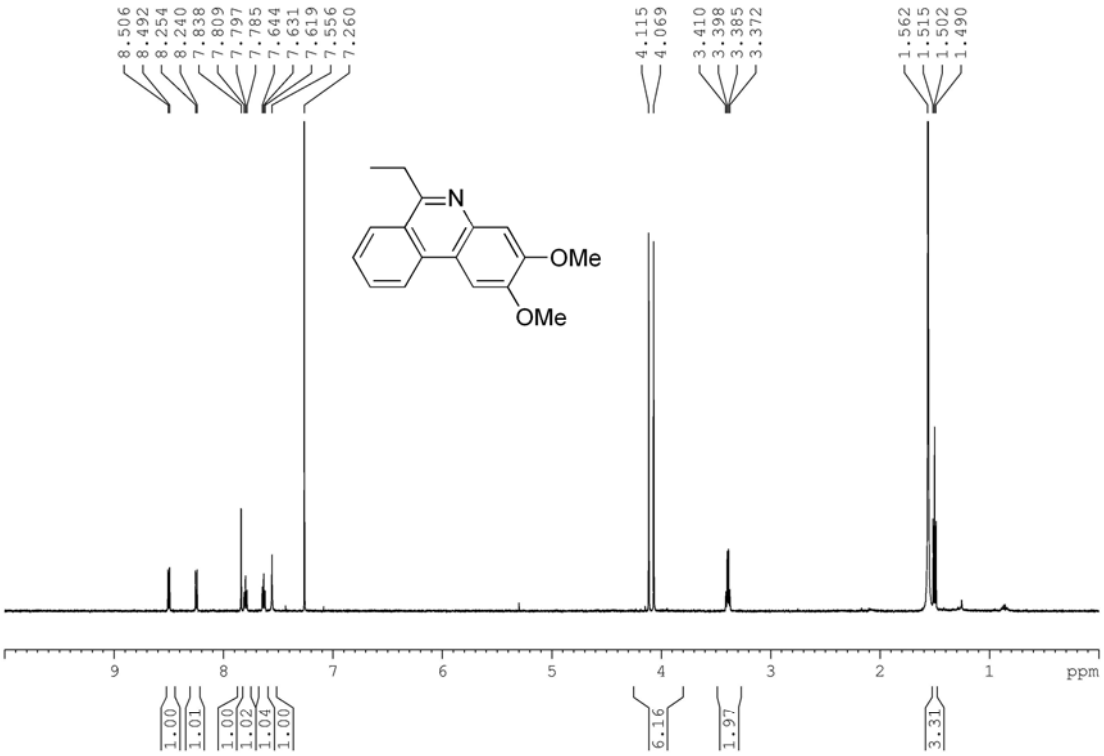


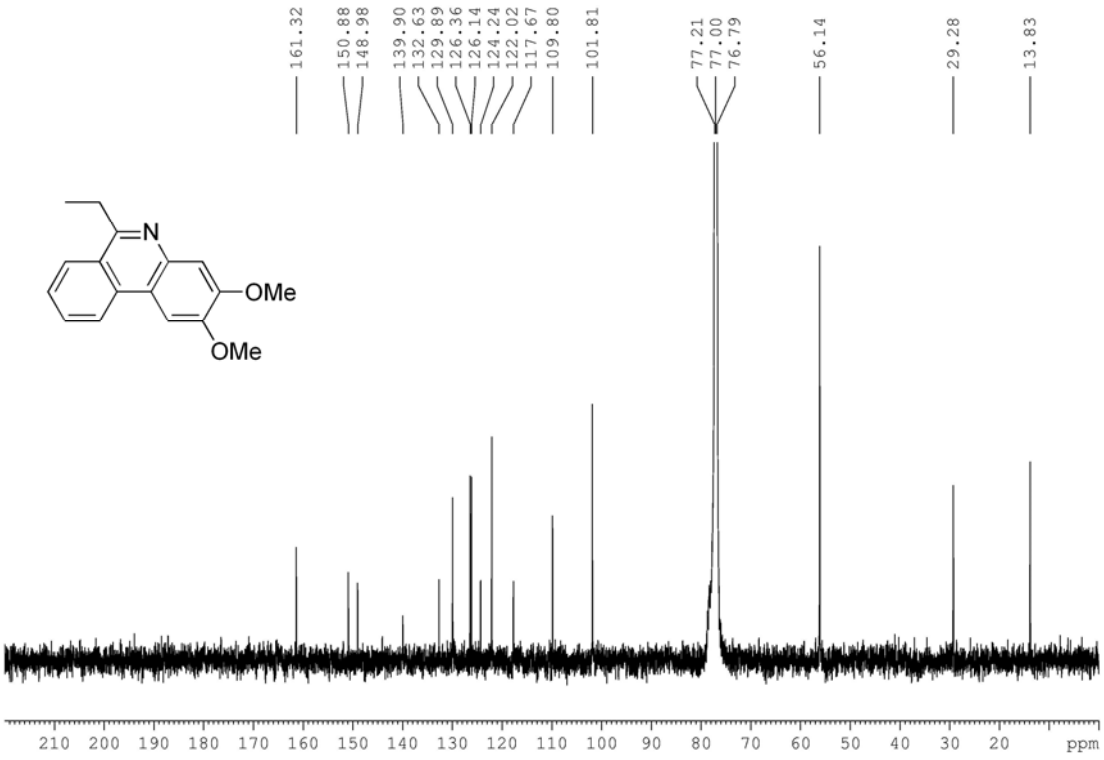
6-Ethyl-3-fluorophenanthridine (3C)



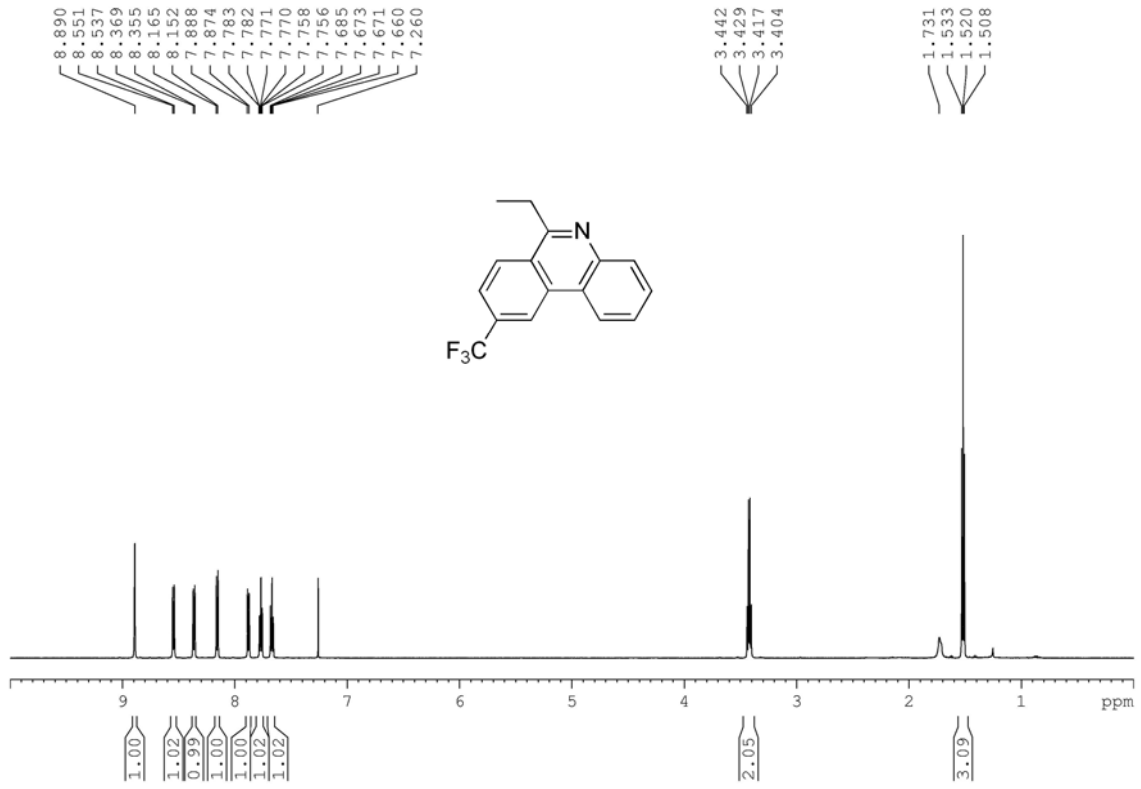


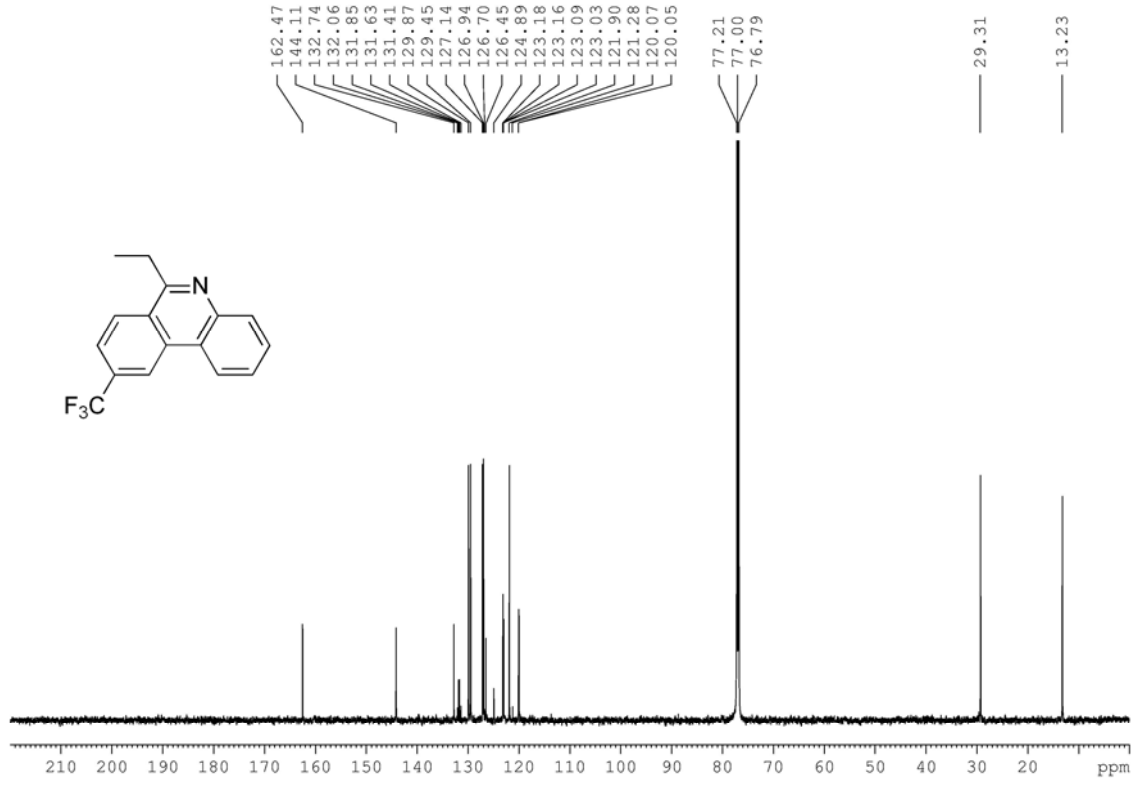
6-Ethyl-2,3-dimethoxyphenanthridine (3D)



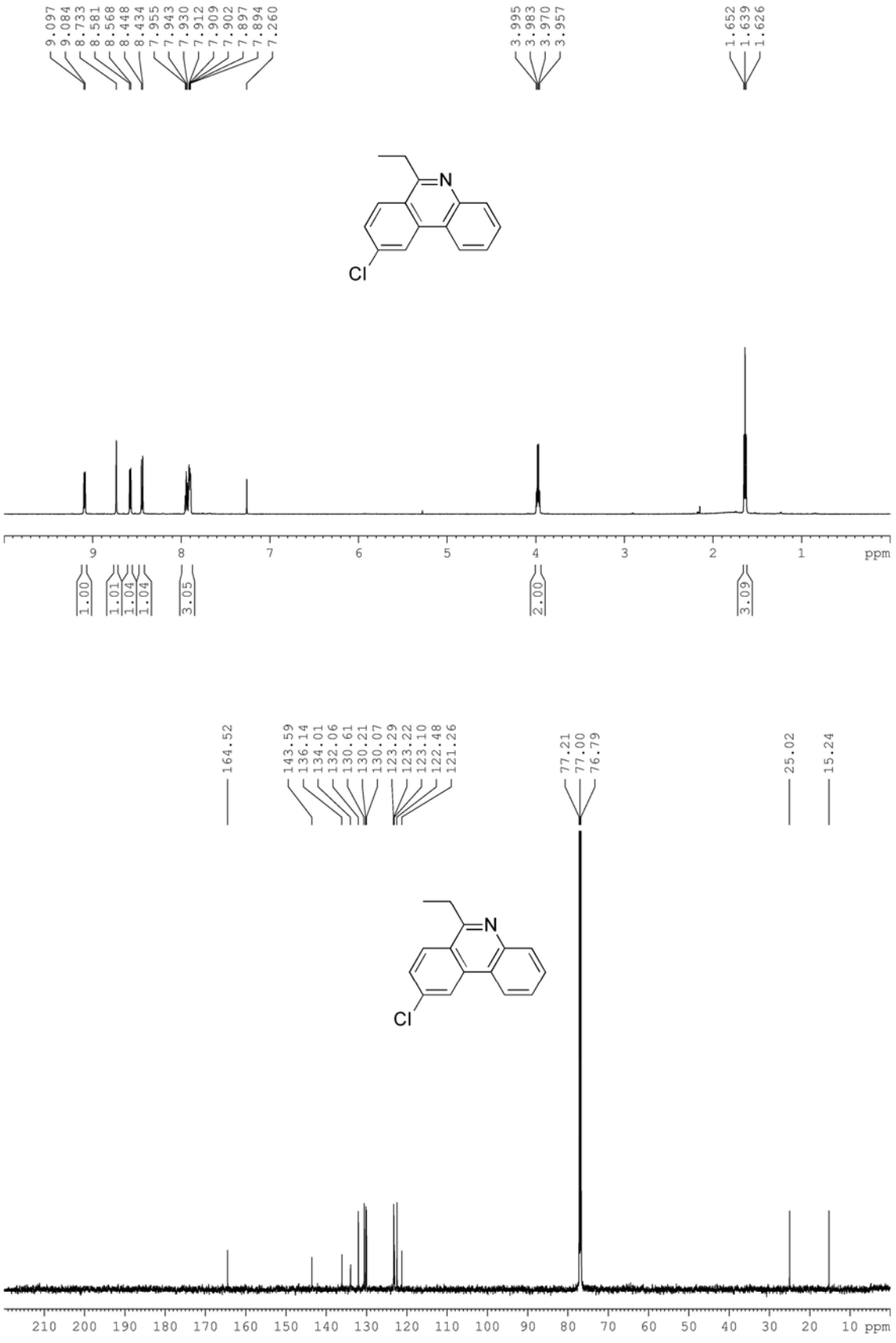


6-Ethyl-9-(trifluoromethyl)phenanthridine (3E)

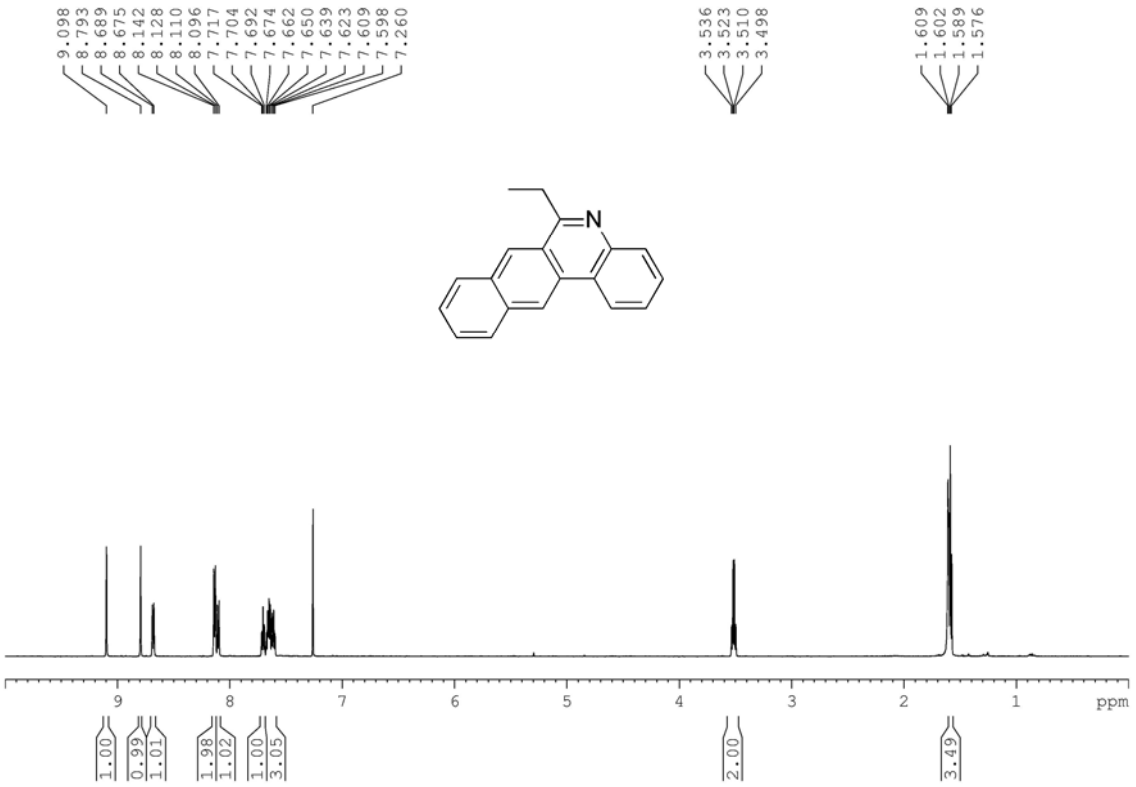


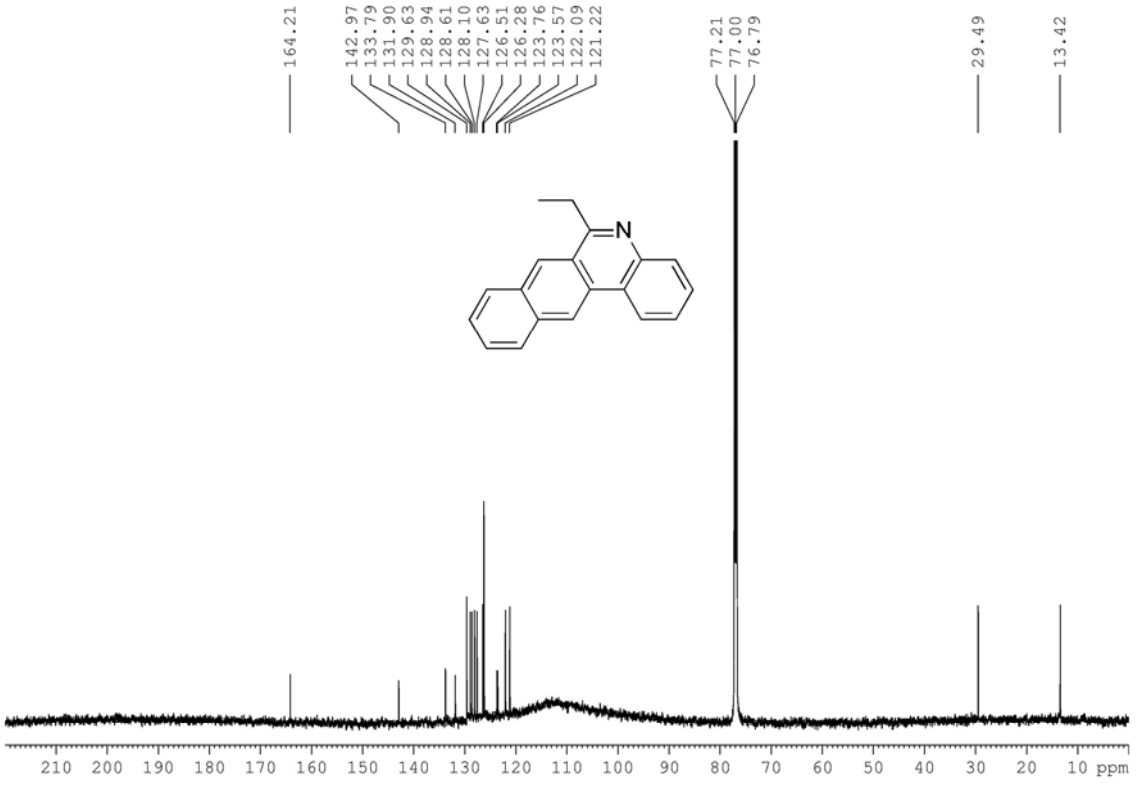


9-Chloro-6-ethylphenanthridine (3F)

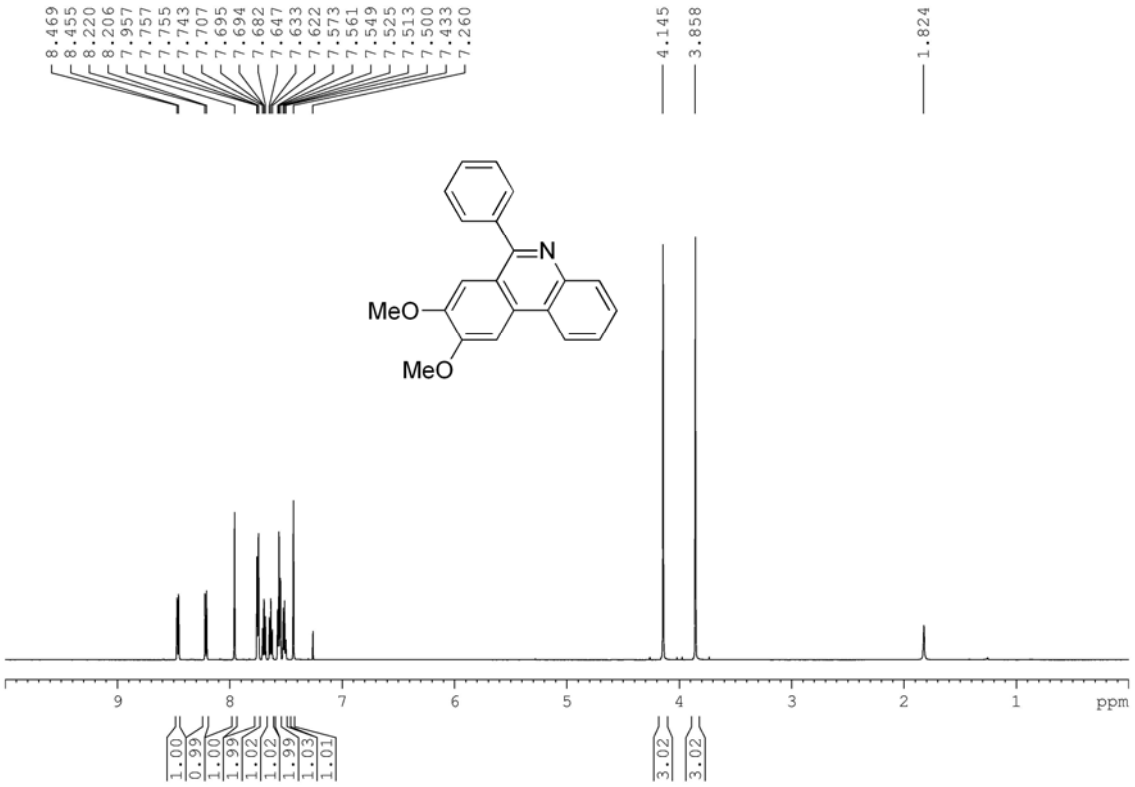


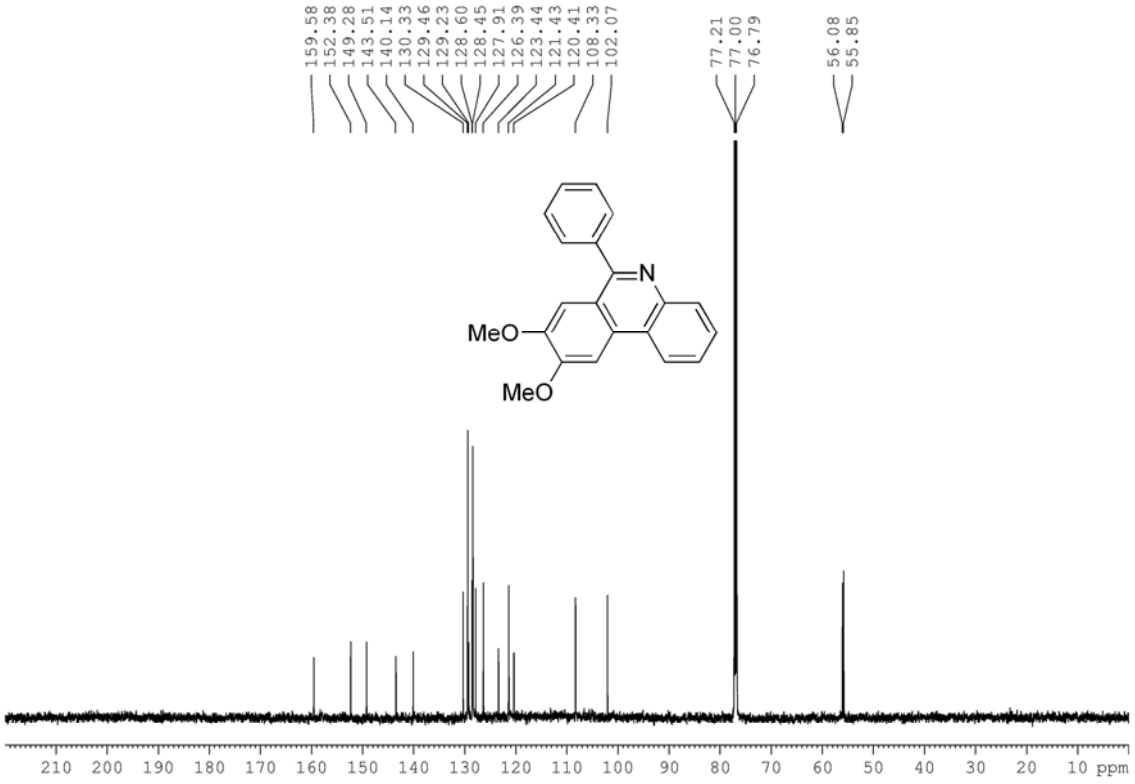
6-Ethylbenzo[*j*]phenanthridine (3G)



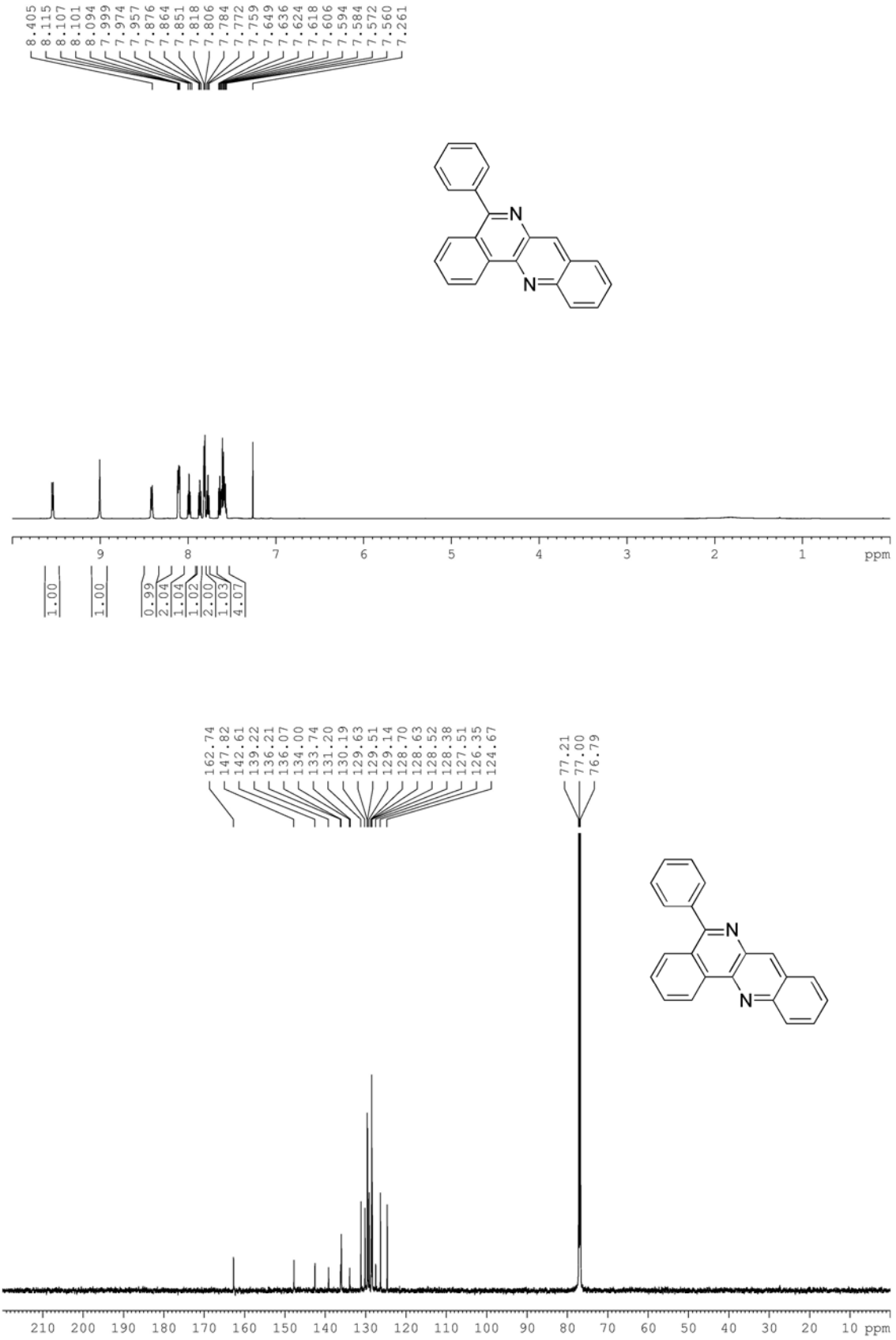


8,9-Dimethoxy-6-phenylphenanthridine (3H)

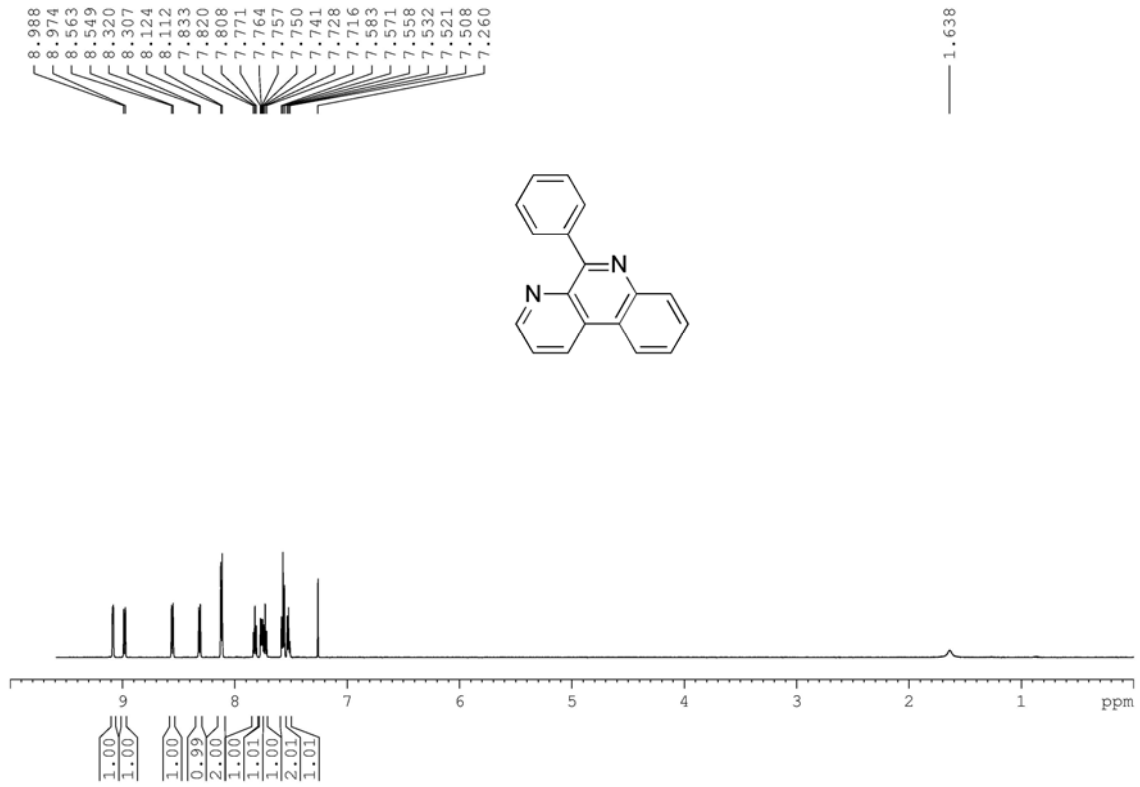


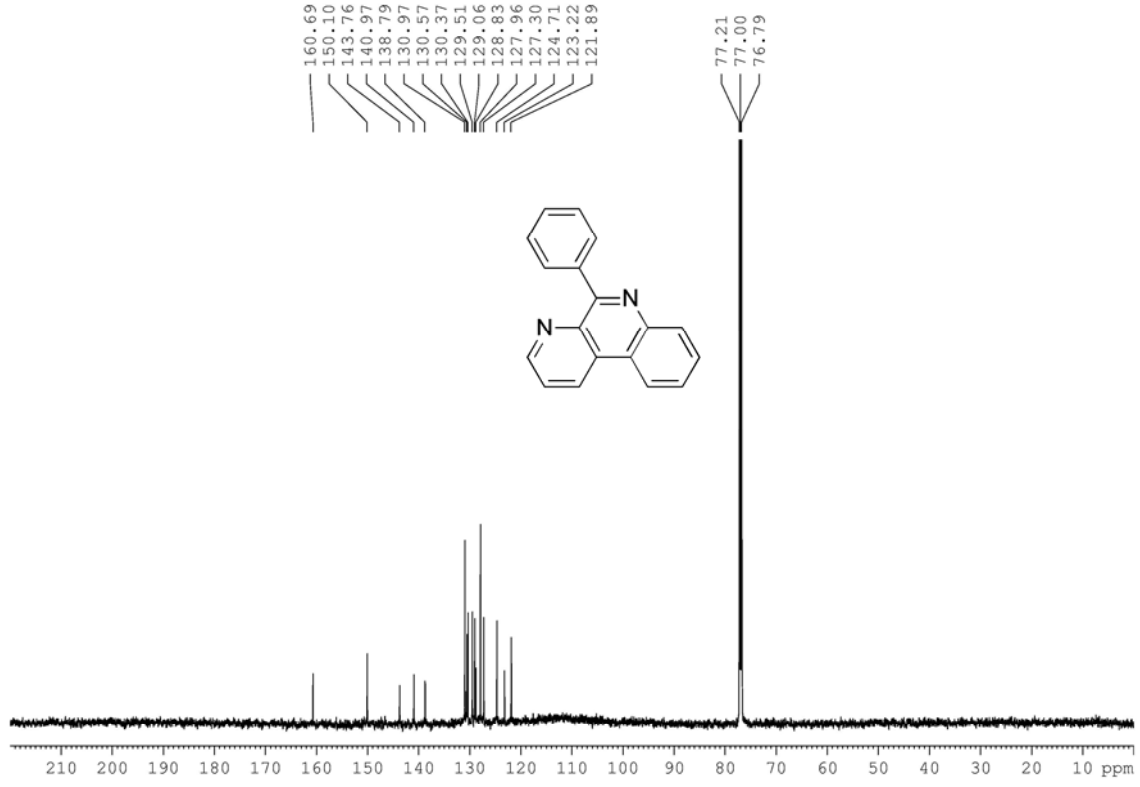


5-Phenyldibenzo[*b*,*h*][1,5]naphthyridine (3I)

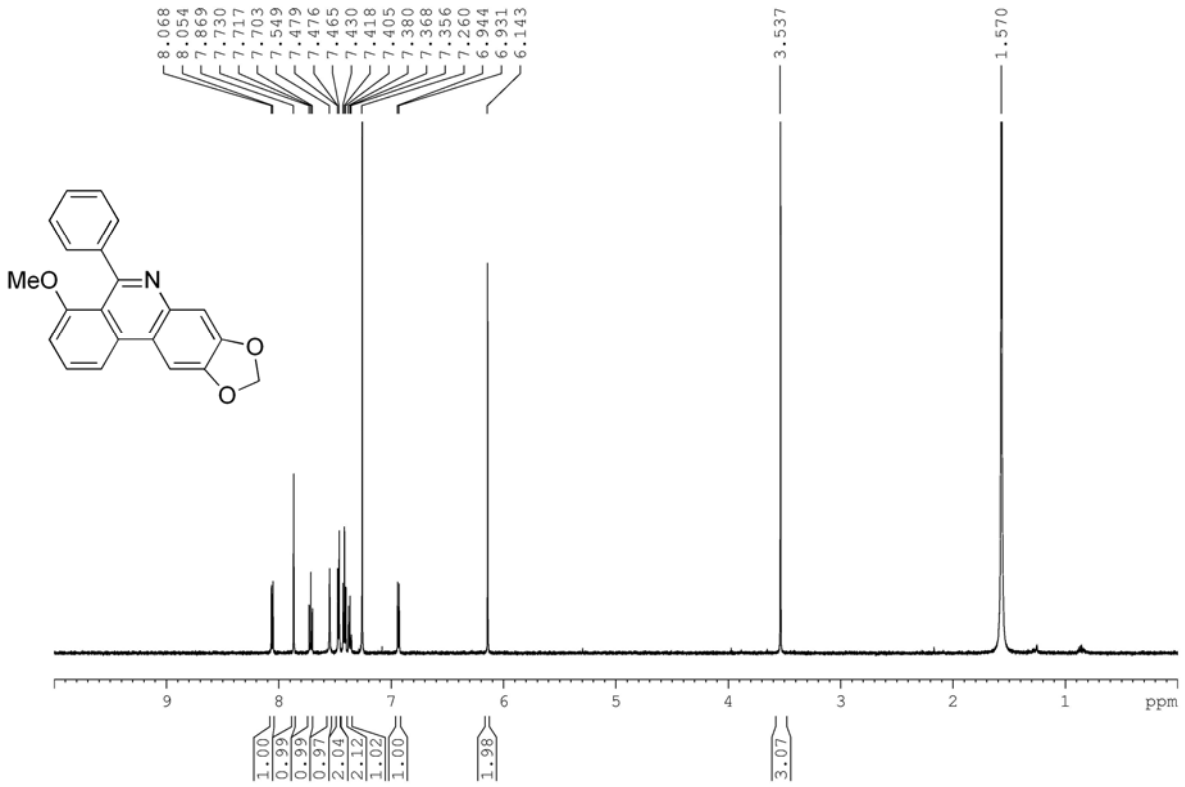


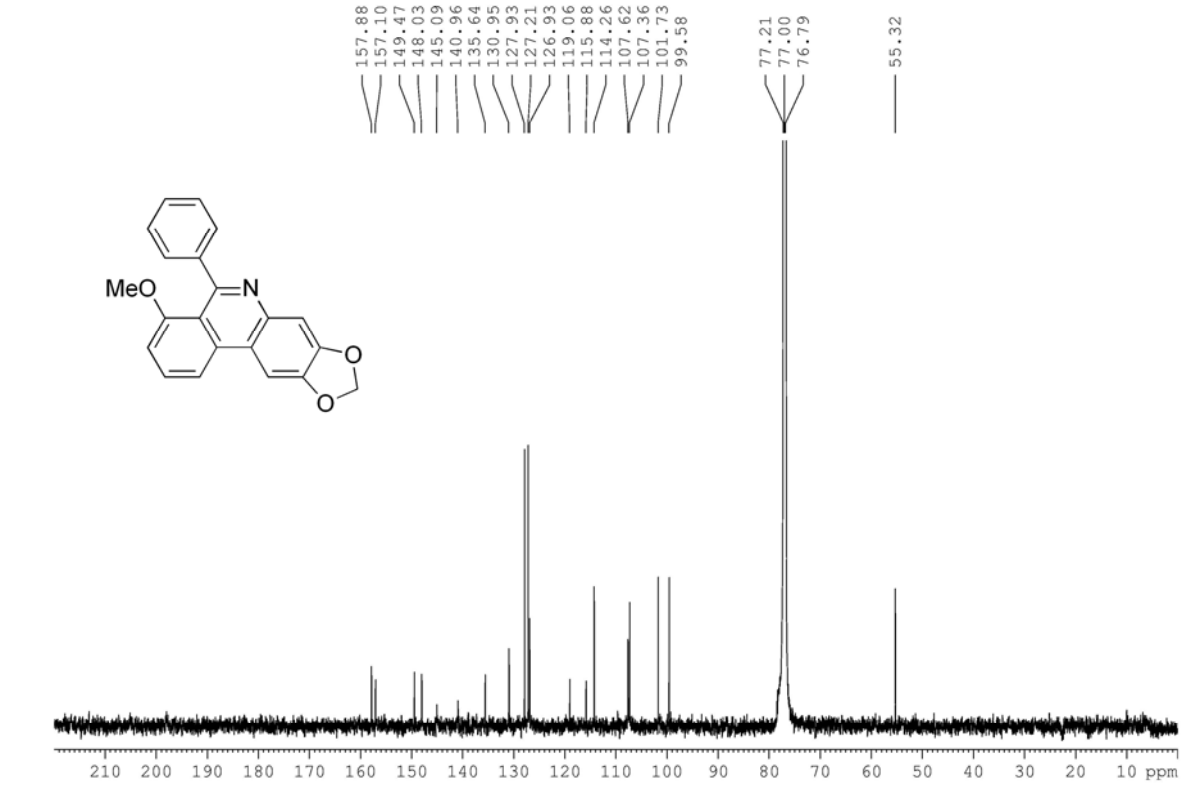
5-Phenylbenzo[*f*][1,7]naphthyridine (3J)



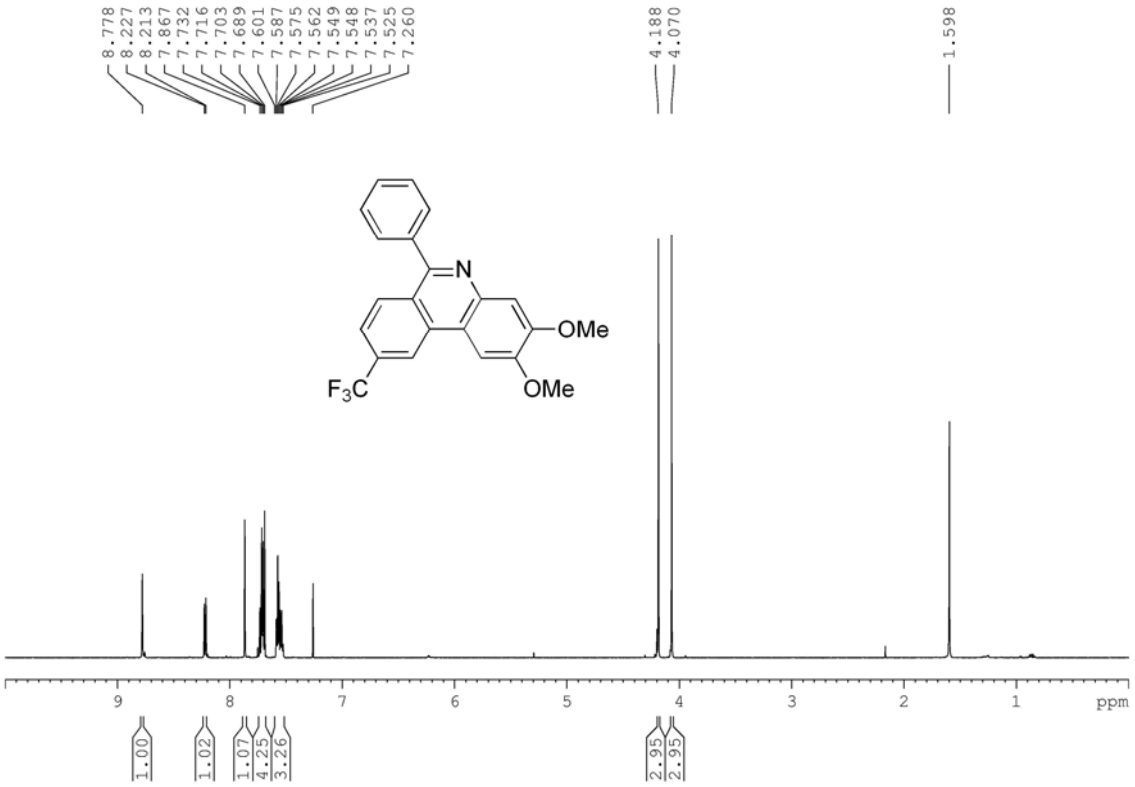


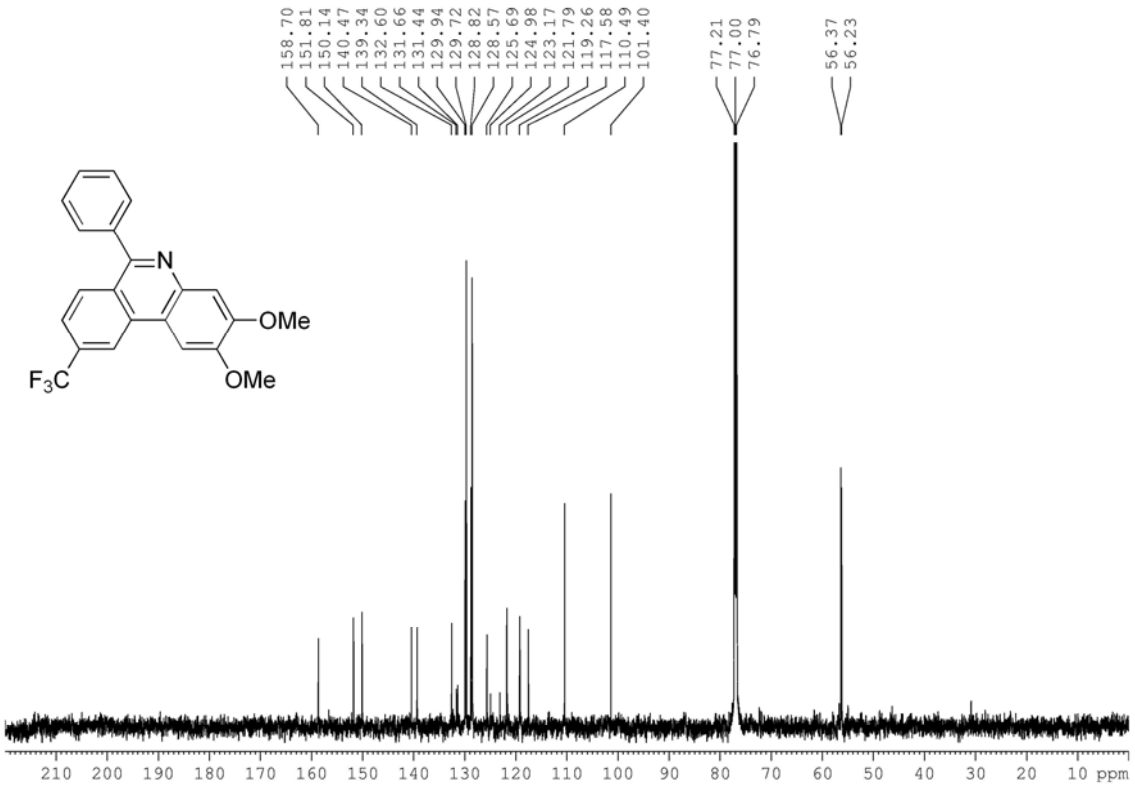
4-Methoxy-5-phenyl-[1,3]dioxolo[4,5-*b*]phenanthridine (3K)



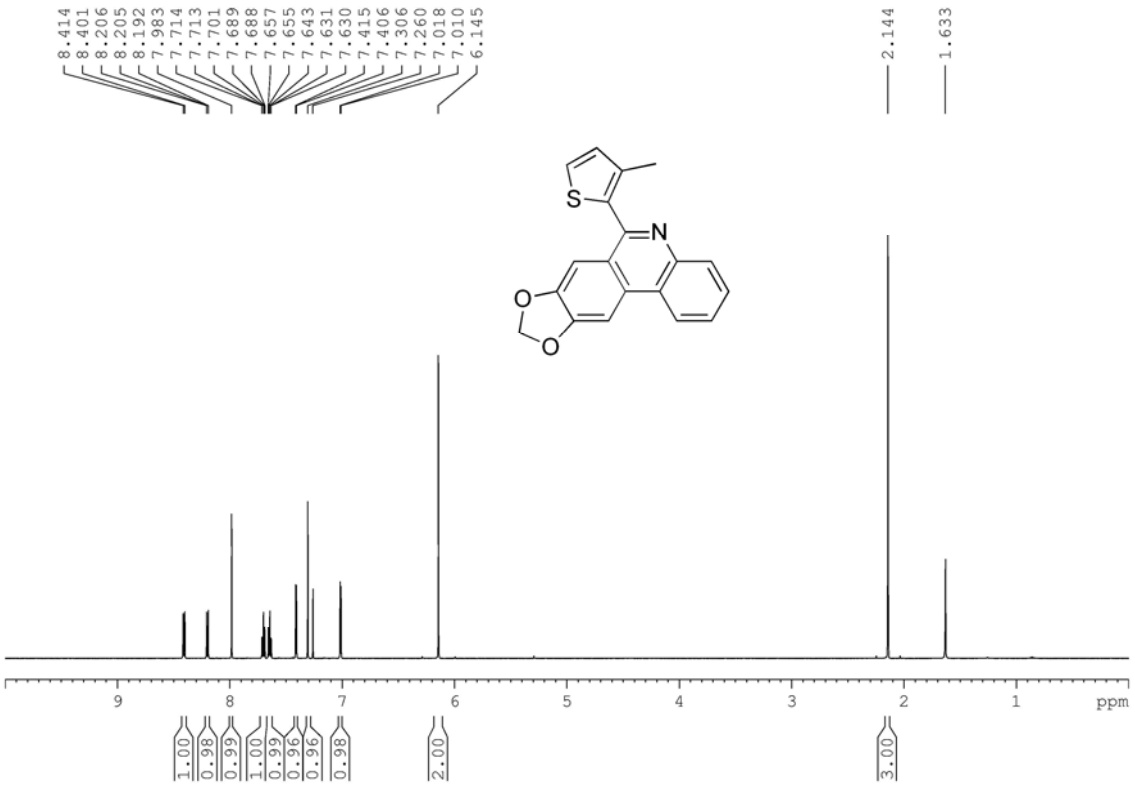


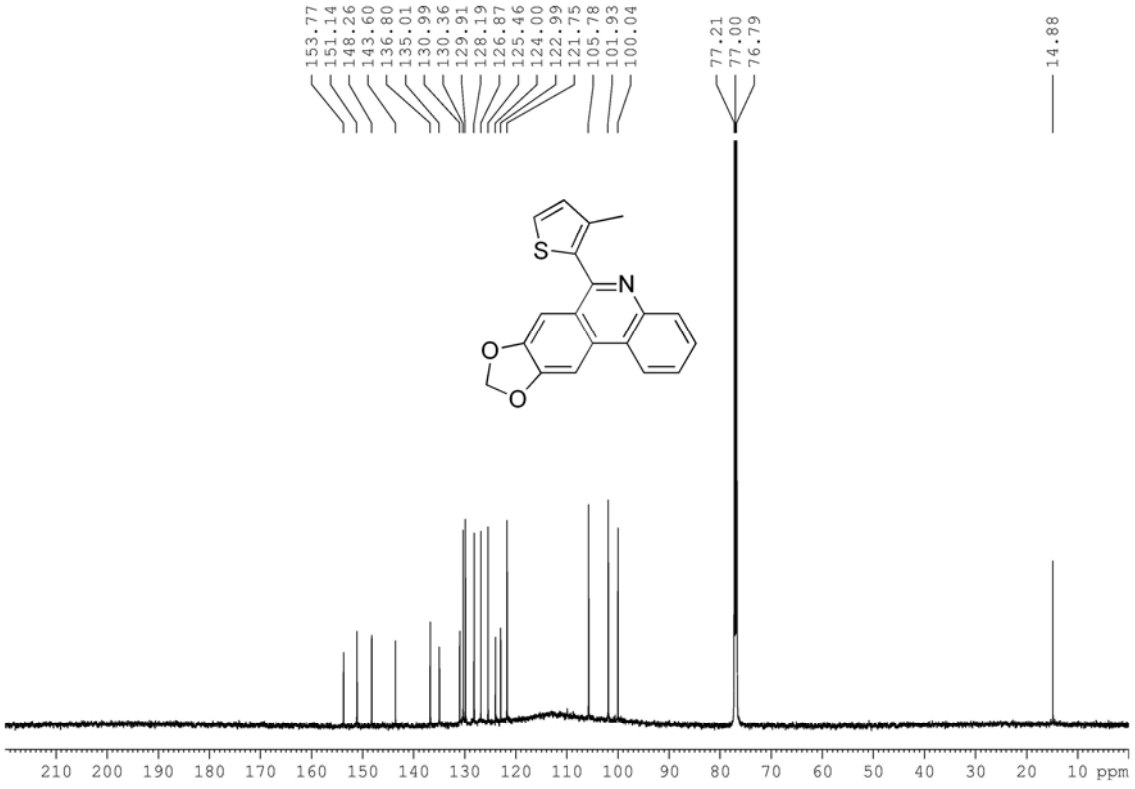
2,3-Dimethoxy-6-phenyl-9-(trifluoromethyl)phenanthridine (3L)



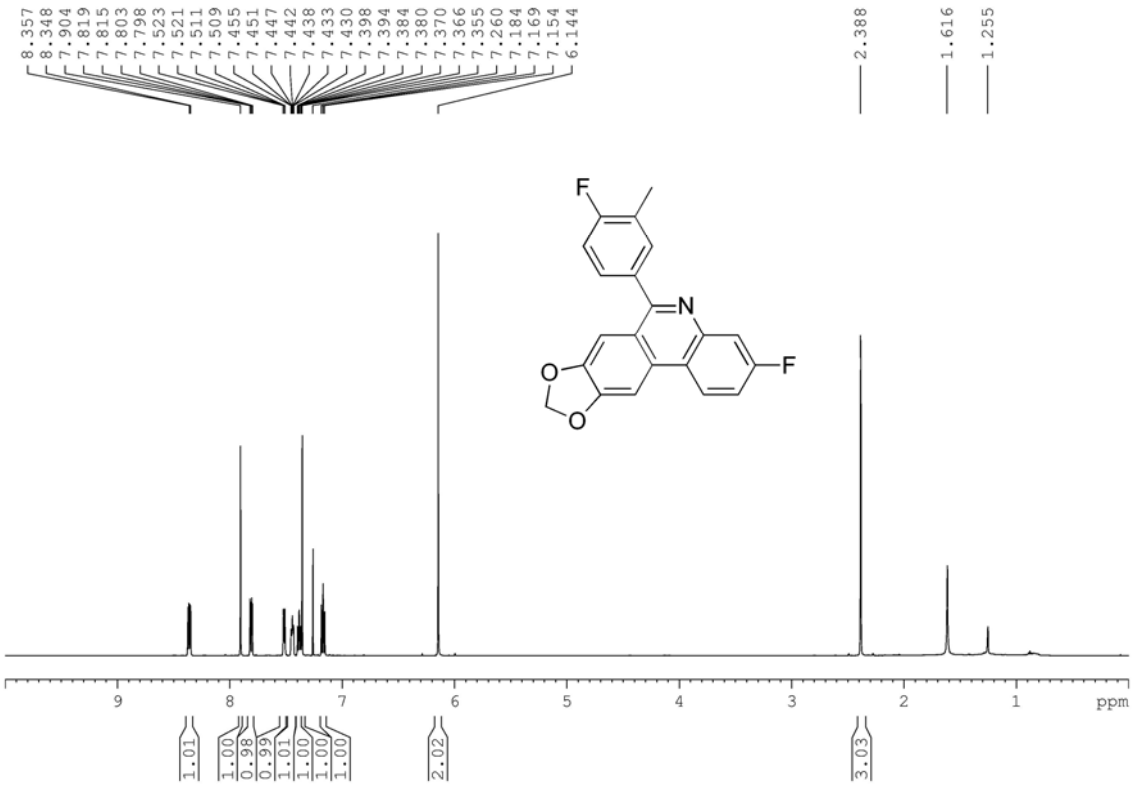


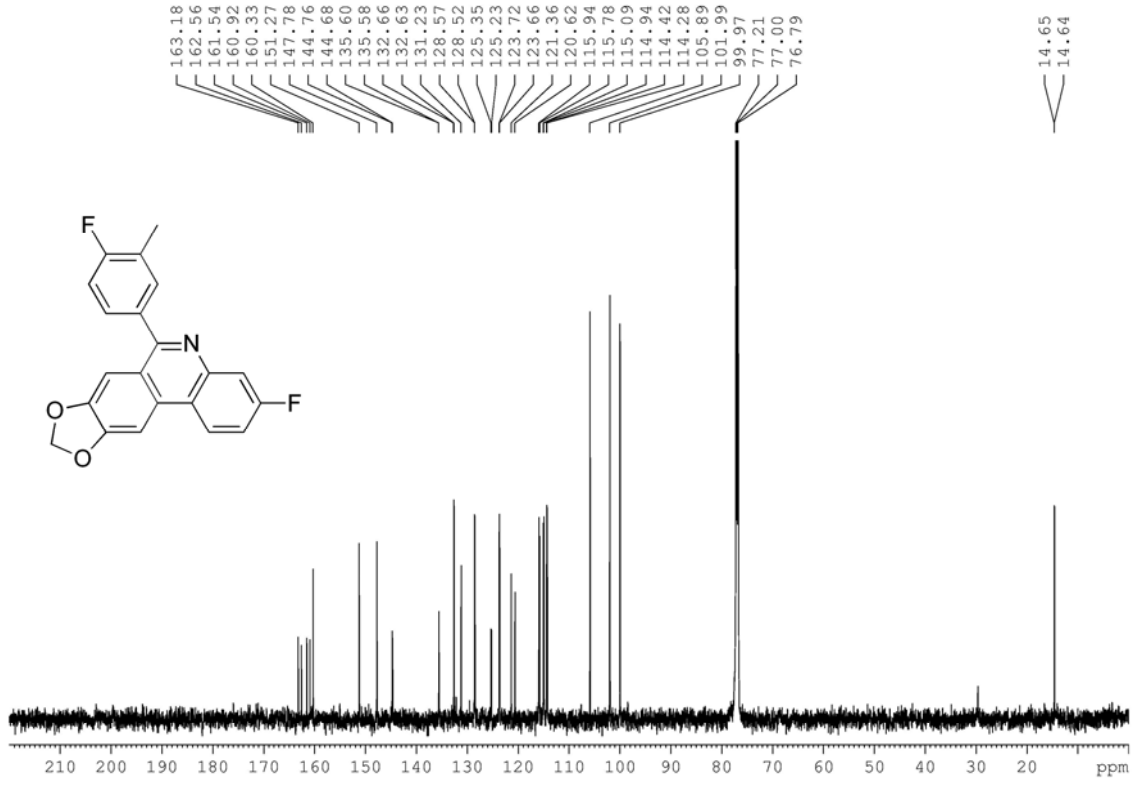
6-(3-Methylthiophen-2-yl)-[1,3]dioxolo[4,5-*j*]phenanthridine (3M)



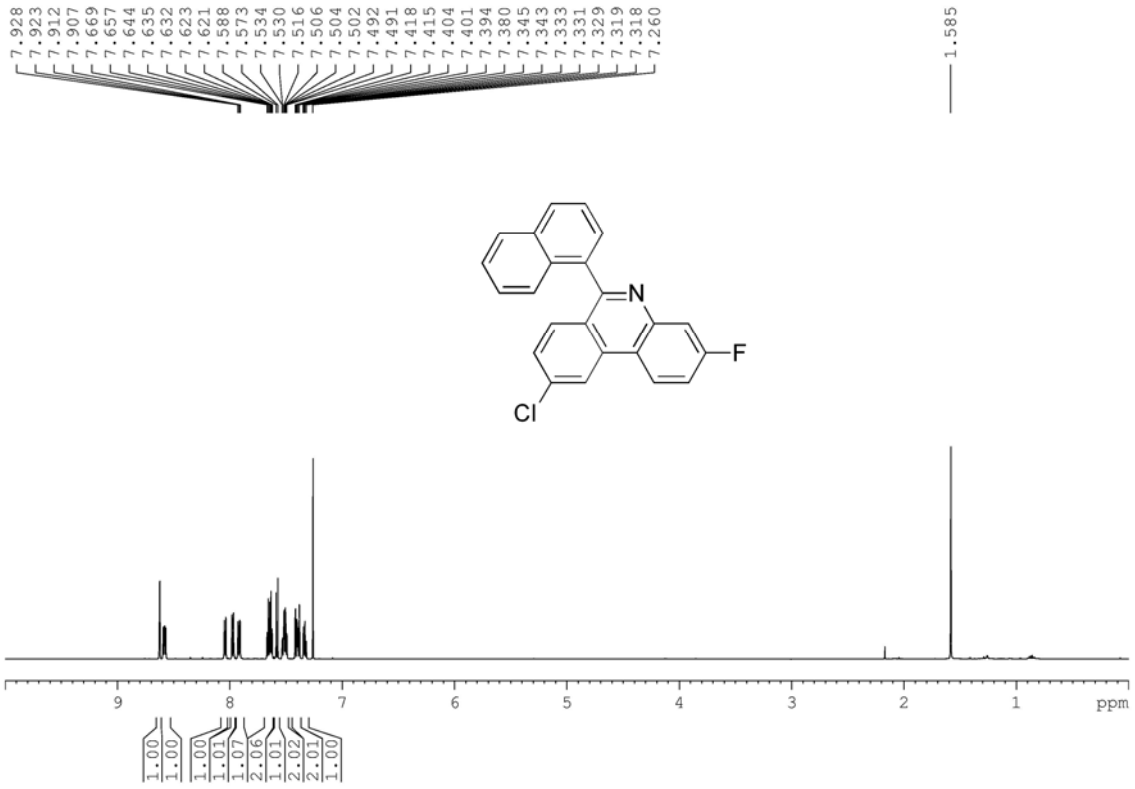


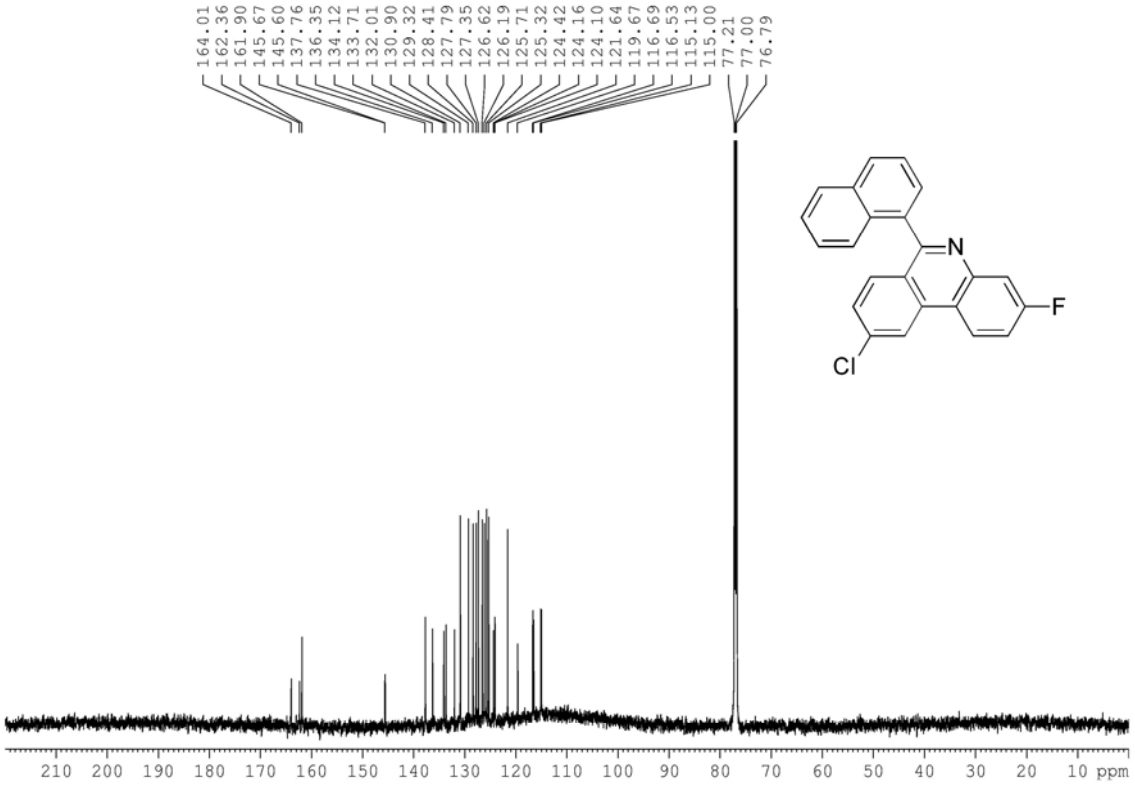
3-Fluoro-6-(4-fluoro-3-methylphenyl)-[1,3]dioxolo[4,5-*j*]phenanthridine (3N)



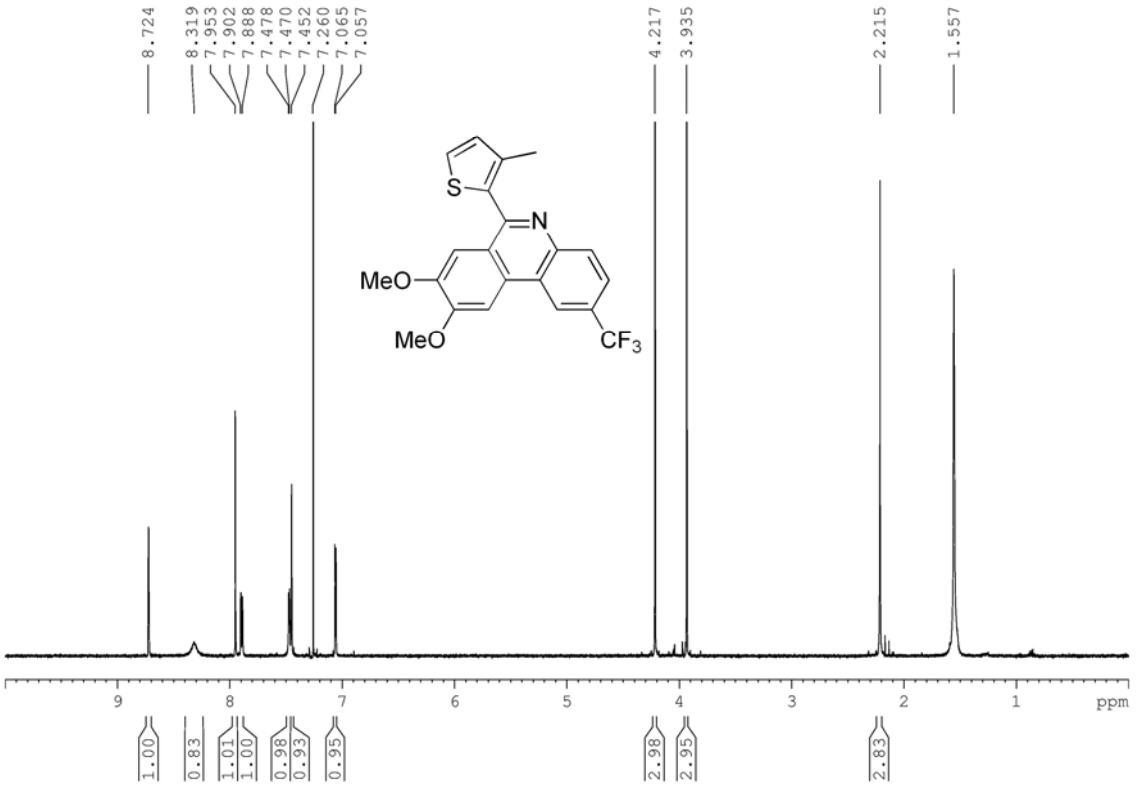


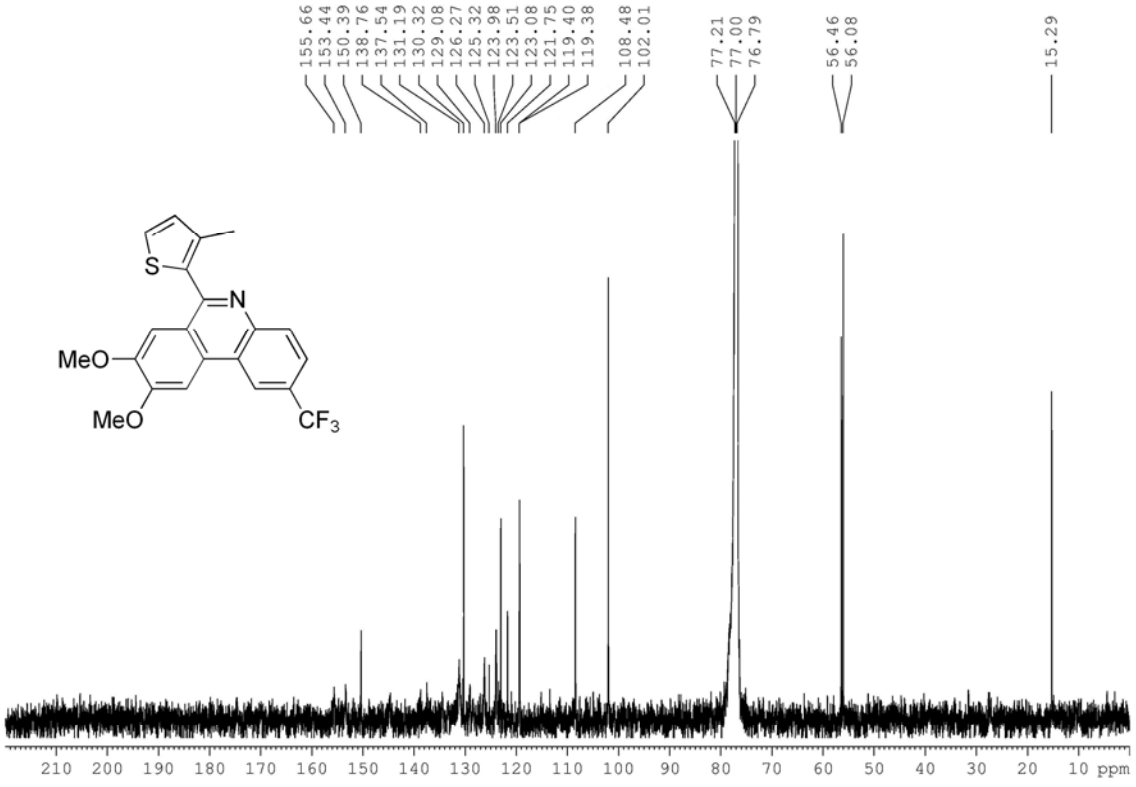
9-Chloro-3-fluoro-6-(naphthalen-1-yl)phenanthridine (3O)



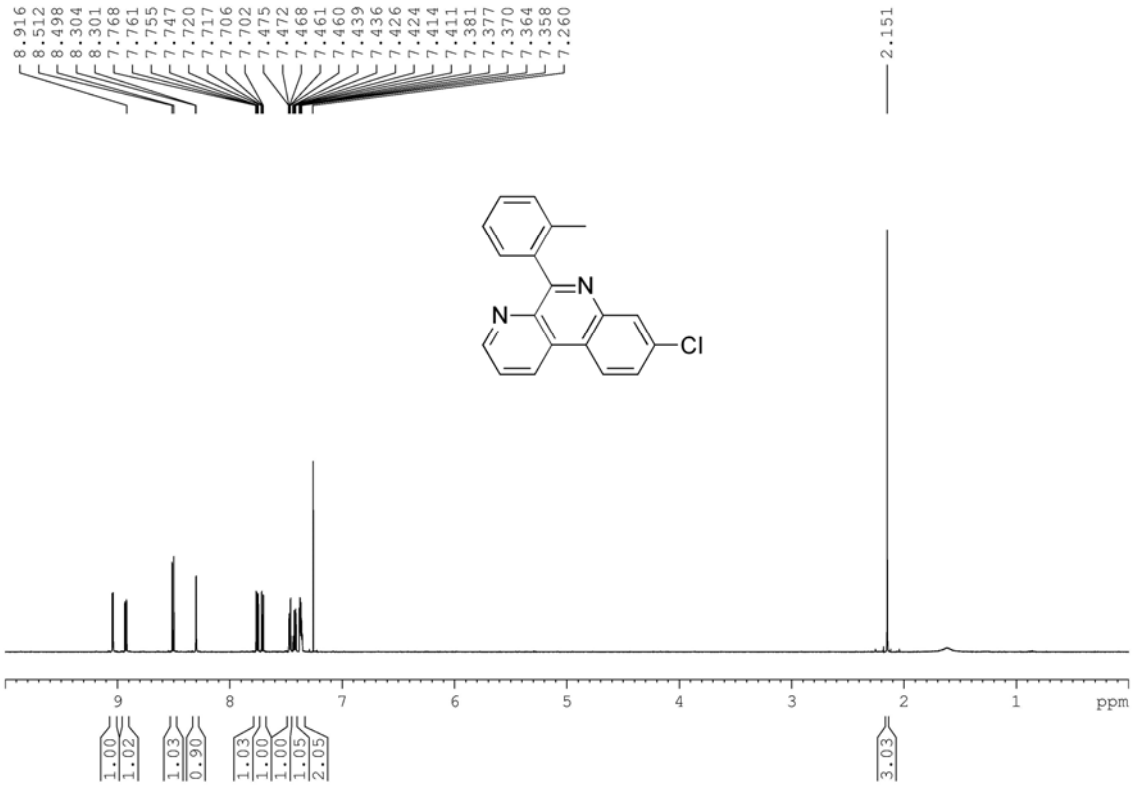


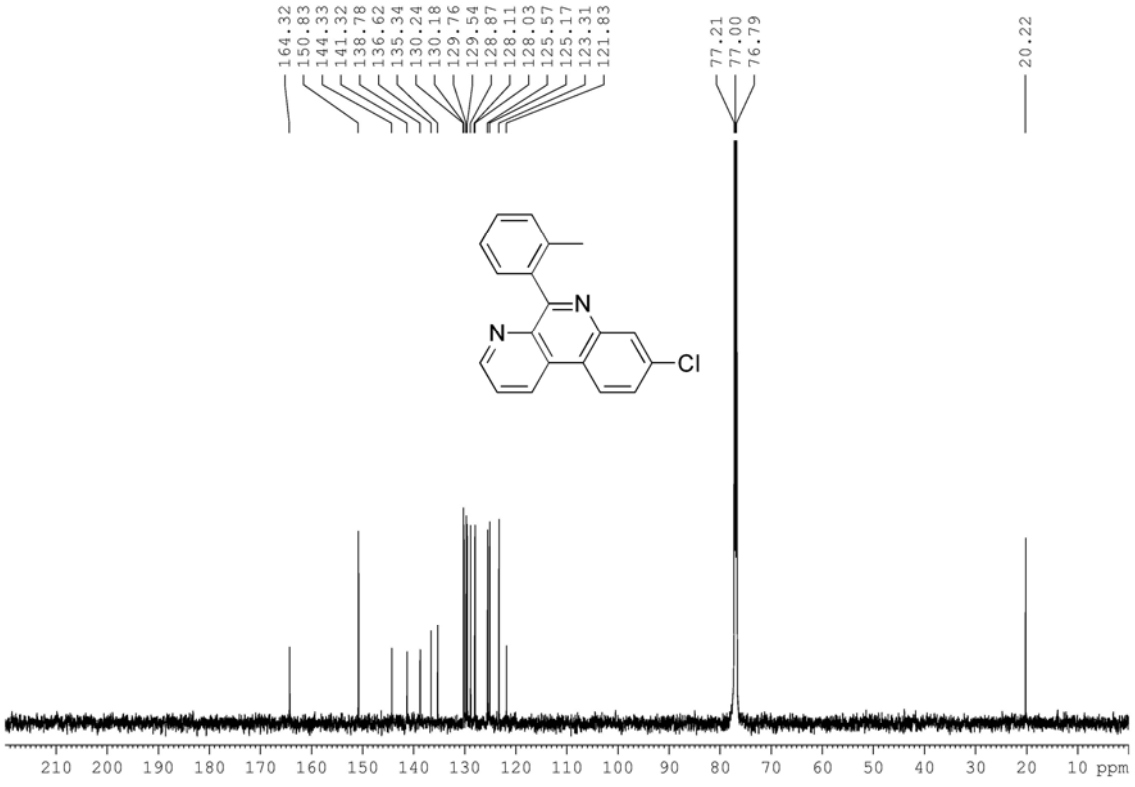
8,9-Dimethoxy-6-(3-methylthiophen-2-yl)-3-(trifluoromethyl)phenanthridine (3P)



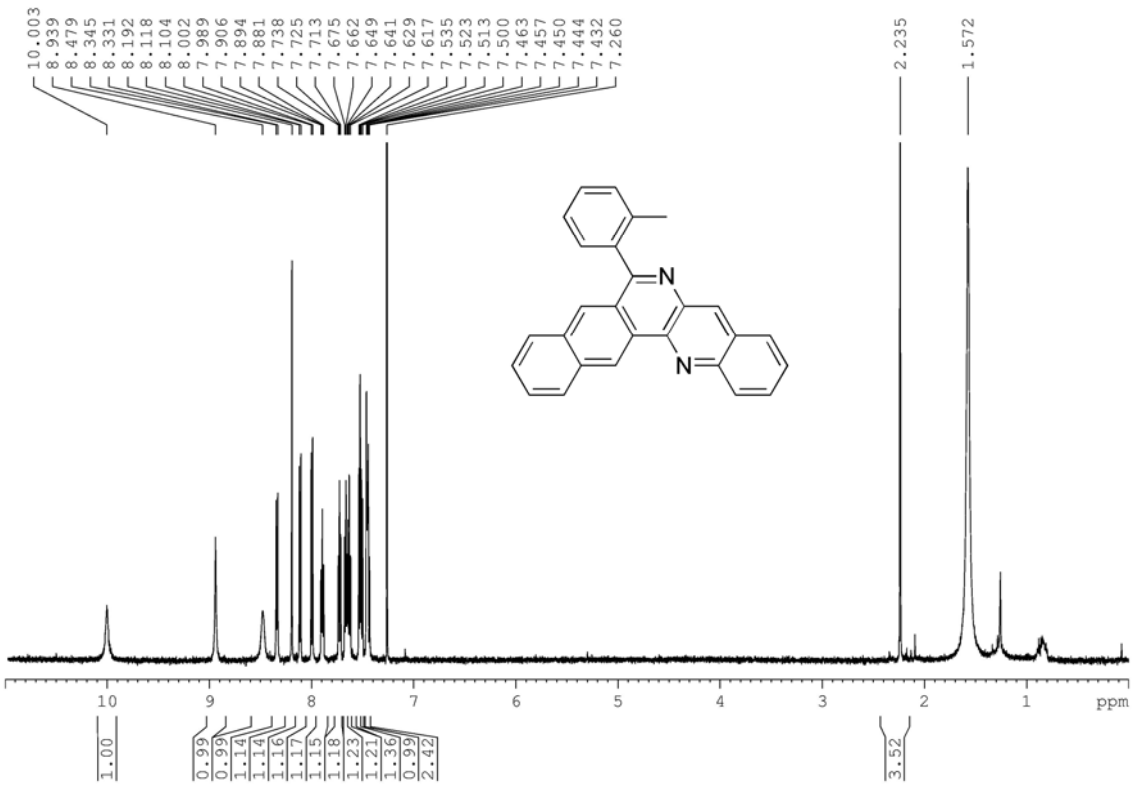


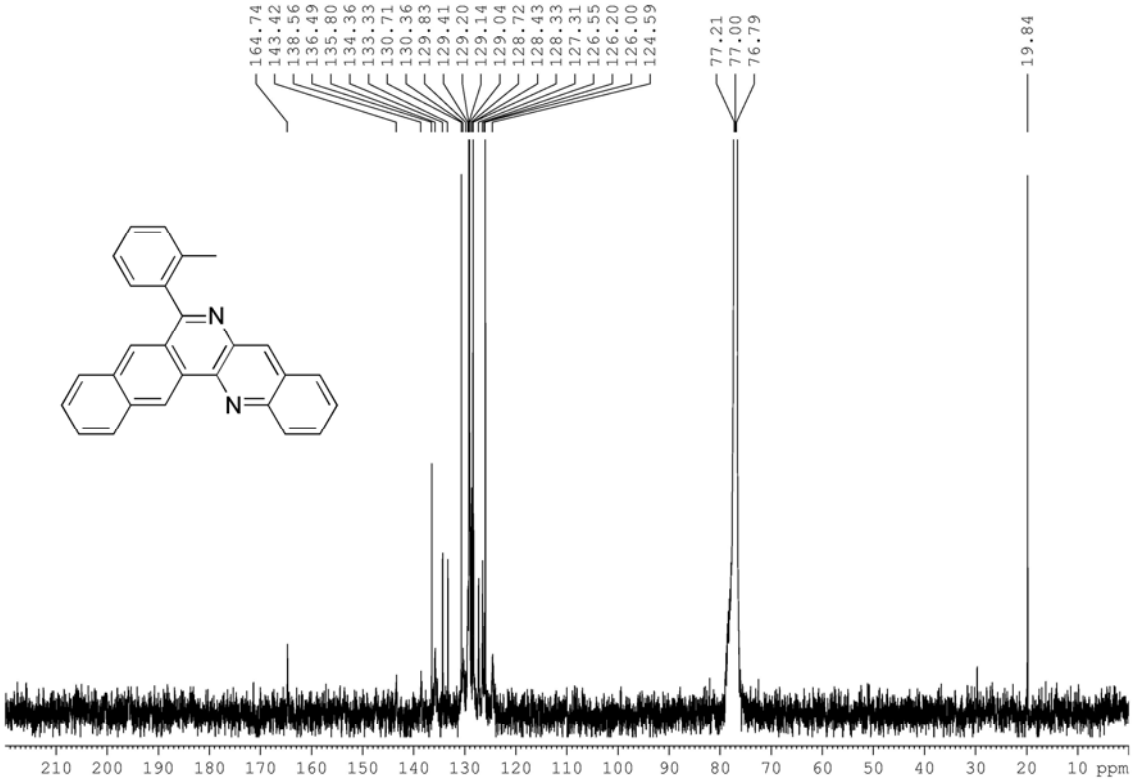
8-Chloro-5-(*o*-tolyl)benzo[*f*][1,7]naphthyridine (3Q)



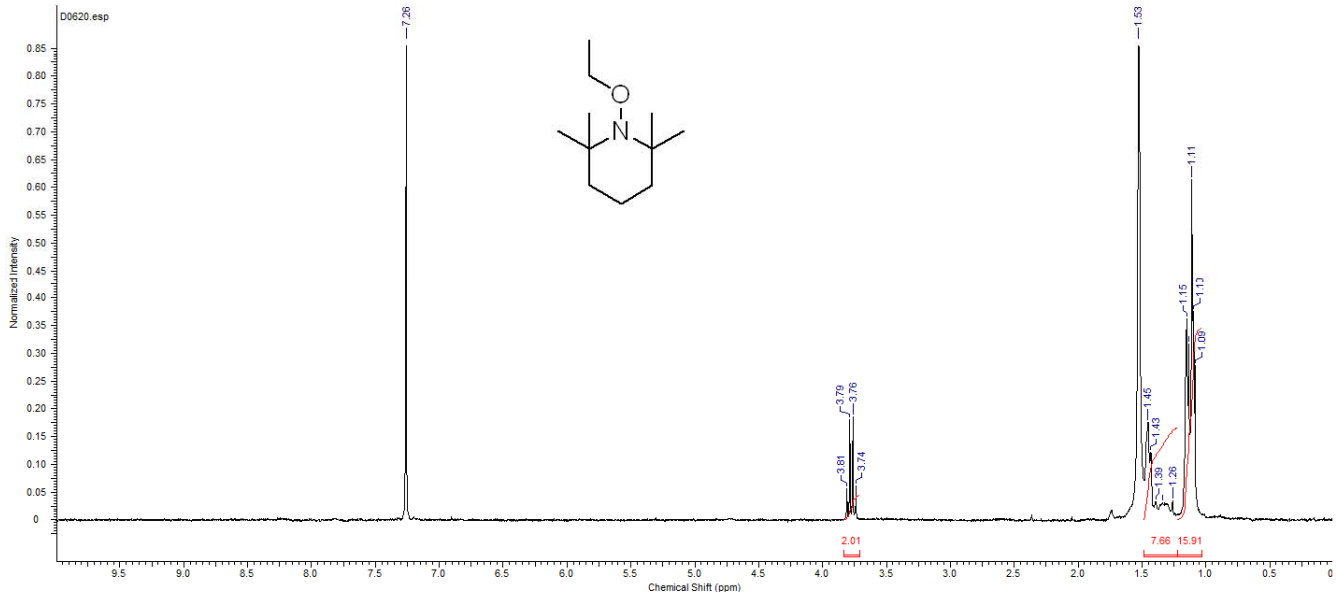


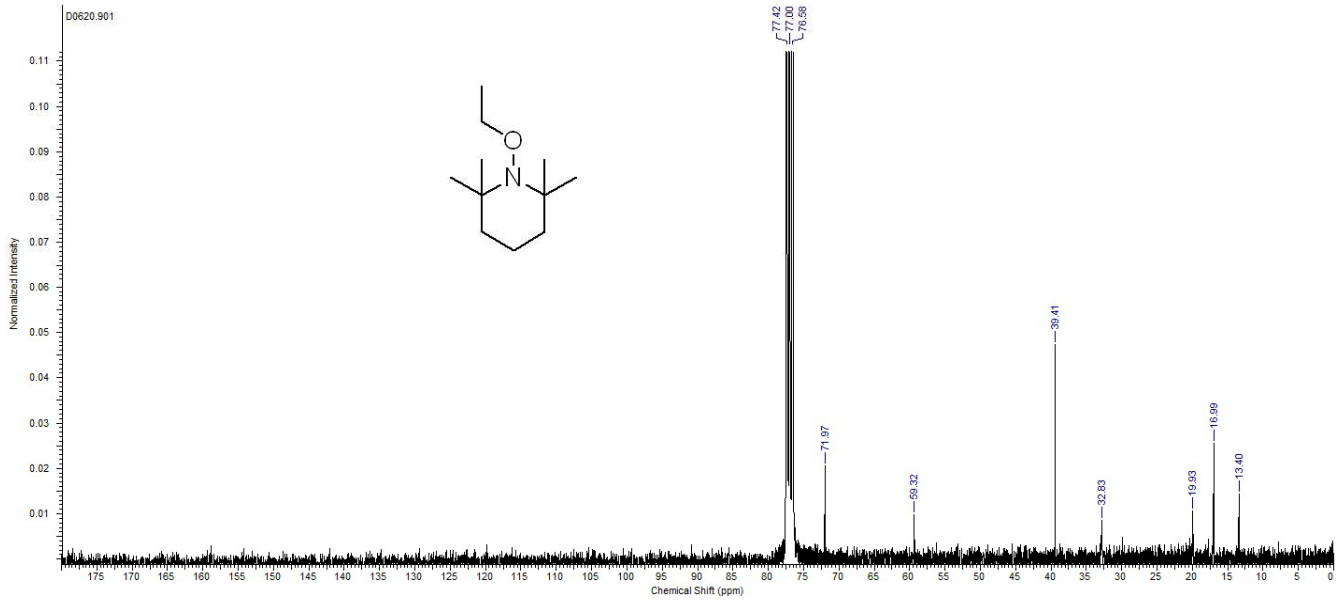
7-(*o*-Tolyl)benzo[*b*]naphtho[2,3-*h*][1,5]naphthyridine (3R)





1-Ethoxy-2,2,6,6-tetramethylpiperidine (4a) (300 MHz, $CDCl_3$)





1-Ethoxy-2,2,6,6-tetramethylpiperidine (4a) (GC-MS)