Supporting Information

Pd-Catalyzed Direct C−H arylation of Pyrrolo[1,2-a]quinoxalines

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1. Materials and instruments

Unless otherwise noted, all synthetic steps were performed under the air atmosphere using sealed tube. The materials obtained from commercial sources were used without further purification. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Brucker Advance III HD 400 MHz spectrometer in $CDCl_3$ solution. All chemical shifts were reported in ppm (δ) relative to the internal standard TMS (0 ppm). High-resolution mass spectra (HRMS) were acquired in electrospray ionization (APCI) mode using a TOF mass analyzer.

2. Experimental Section

2.1 Typical procedure for Pd-catalyzed arylation of pyrrolo[1,2-a]quinoxalines.

A Schlenk tube (10 mL) was charged with pyrrolo[1,2-*a*]quinoxaline **1** (0.25 mmol), aryl iodides **2** (0.5 mmol), $Pd(OAc)_2$ (10 mol%), X-Phos (15 mol%), and toluene (1 mL). The mixture was stirred at 120 ^{o}C for 24 hours in the air. Subsequently, the solution was concentrated under reduced pressure. The crude was purified by purified by column chromatography on silica gel (PE/EtOAc as eluent) to afford the product **3**.

1,3-Di-p-tolylpyrrolo[1,2-a]quinoxaline (**3a**)

Yield: 63%; Light yellow solid; M.p. = 85-90 ℃;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.98 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.88 (d, *J* = 2.8 Hz, 1H), 7.82 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.53 (td, *J* = 8.2, 7.8, 1.5 Hz, 1H), 7.46 (td, *J* = 7.7, 1.4 Hz, 1H), 6.98 (d, *J* = 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.54, 138.88, 137.63, 137.12, 132.43, 131.27, 130.96, 129.89, 129.85, 129.64, 129.60, 129.15, 128.51, 126.59, 125.07, 123.77, 123.63, 116.81, 116.50, 21.59, 21.35. HRMS (APCI): m/z calcd for $C_{25}H_{21}N_2$ $[M+H]^+$ 349.1699, found: 349.1695.

1,3-Diphenylpyrrolo[1,2-a]quinoxaline (**3b**)

Yield: 54%; Light yellow solid; M.p. = 149-151 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.58 (dd, *J* = 6.6, 3.0 Hz, 3H), 7.54 – 7.48 (m, 4H), 7.41 (t, *J* = 7.4 Hz, 3H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.18 – 7.09 (m, 1H), 6.94 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.46, 137.62, 134.17,

133.88, 132.36, 130.01, 129.79, 129.16, 129.01, 128.95, 128.92, 128.66, 127.35, 126.75, 125.22, 123.93, 123.63, 116.83, 116.68; HRMS (APCI): m/z calcd for $C_{23}H_{17}N_2$ $[M+H]^+$ 321.1386, found: 321.1384.

1,3-Diphenylpyrrolo[1,2-a]quinoxaline (**3c**)

Yield: 57%; Light yellow solid; M.p. = 180-185 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.99 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.84 – 7.70 (m, 8H), 7.46 – 7.35 (m, 2H), 7.23 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 6.98 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.74, 137.54, 137.40, 137.07, 130.93 (d, *J* = 32.8 Hz), 130.66, 130.39, 129.81, 129.34 (d, *J* = 32.8 Hz), 128.61, 128.36, 127.27, 126.05 (q, *J* = 3.7 Hz), 125.85 (q, *J* = 3.7 Hz), 125.72, 125.45 (d, *J* = 23.8 Hz), 124.54, 122.74 (d, *J* = 23.8 Hz), 121.95, 117.16, 116.60; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4, -62.6; HRMS (APCI): m/z calcd for $C_{25}H_{14}F_6N_2$ $[M+H]^+$ 456.1061, found: 456.1063.

1,3-Bis(4-chlorophenyl)pyrrolo[1,2-a]quinoxaline (**3d**)

1. Yield: 49%; Light yellow solid; M.p. = 150-155 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.99 – 7.91 (m, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.52 – 7.44 (m, 6H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.15 (m, 1H), 6.87 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.06, 137.63, 135.13, 133.39, 132.45, 132.12, 130.99, 130.28, 129.75, 129.36, 129.24, 128.72, 127.05, 125.52, 124.10, 122.28, 116.69, 116.63; HRMS (APCI): m/z calcd for $C_{23}H_{15}Cl_2N_2$ $[M+H]^+$ 389.0607, found: 389.0603.

1,3-Bis(4-bromophenyl)pyrrolo[1,2-a]quinoxaline (**3e**)

Yield: 18%; Light yellow solid; M.p. = 172-176 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.64 (dd, J = 15.1, 8.5 Hz, 4H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.46 – 7.36 (m, 4H), 7.20 (td, *J* = 7.7, 1.5 Hz, 1H), 6.88 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.05, 137.62, 132.91, 132.58, 132.33, 132.21, 131.25, 131.06, 130.30, 130.09, 128.71, 127.11, 125.58, 124.10, 123.34, 122.35, 121.52, 116.67, 116.66,; HRMS (APCI): m/z calcd for $C_{23}H_{15}Br_2N_2$ $[M+H]^+$ 476.9602, found:476.9589.

1,3-Bis(4-fluorophenyl)pyrrolo[1,2-a]quinoxaline (**3f**)

Yield: 56%; Light yellow solid; M.p. = 152-155 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.94 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.59 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.54 (dd, *J*

= 8.7, 5.3 Hz, 2H), 7.40 – 7.32 (m, 2H), 7.26 – 7.11 (m, 5H), 6.86 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.01 (d, *J* = 82.1 Hz), 161.55 (d, *J* = 82.1 Hz), 145.16, 137.60, 131.68, 131.59, 131.10, 130.18 (d, *J* = 3.9 Hz), 130.10 (d, *J* = 3.9 Hz), 129.83, 129.79, 128.86, 126.90, 125.36, 123.87, 122.46, 116.65, 116.52, 116.22 (d, *J* = 3.6 Hz), 116.01 (d, *J* = 3.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.8, -114.8; HRMS (APCI): m/z calcd for $C_{23}H_{15}F_2N_2$ $[M+H]^+$ 357.1197, found: 357.1189.

1,3-Bis(4-methoxyphenyl)pyrrolo[1,2-a]quinoxaline (**3g**)

Yield: 53%; Light yellow solid; M.p. = 129-134 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.93 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.44 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.34 (td, *J* = 8.2, 7.8, 1.2 Hz, 1H), 7.14 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.04 (dd, *J* = 8.7, 1.9 Hz, 4H), 6.85 (s, 1H), 3.92 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.02, 159.02, 145.44, 137.58, 132.03, 130.97, 129.79, 129.60, 129.12, 126.59, 126.46, 126.04, 124.91, 123.44, 123.18, 116.56, 116.18, 114.52, 114.22, 55.42, 55.39; HRMS (APCI): m/z calcd for $C_{25}H_{21}N_2O_2$ $[M+H]^+$ 381.1598, found: 381.1590.

1,3-Bis(4-ethoxyphenyl)pyrrolo[1,2-a]quinoxaline (**3h**)

Yield: 52%; Light yellow solid; M.p. = 128-131 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 3H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 4H), 6.84 (s, 1H), 4.13 (dq, *J* = 14.0, 7.0 Hz, 4H), 1.48 (dt, *J* = 13.8, 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.56, 158.53, 145.55, 137.64, 132.30, 131.08, 129.85, 129.72, 129.27, 126.58, 126.55, 125.99, 125.03, 123.54, 116.71, 116.30, 115.19, 114.83, 63.78, 63.72, 15.04, 15.01; HRMS (APCI): m/z calcd for $C_{27}H_{25}N_2O_2$ $[M+H]^+$ 409.1911, found: 409.1903.

1,3-Bis(3-methoxyphenyl)pyrrolo[1,2-a]quinoxaline (**3i**)

Yield: 44%; Light yellow solid; M.p. = 47-52 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 7.94 (d, *J* = 6.5 Hz, 1H), 7.48 – 7.39 (m, 3H), 7.39 – 7.33 (m, 1H), 7.27 – 7.23 (m, 1H), 7.20 – 7.12 (m, 3H), 7.11 – 7.09 (m, 1H), 7.06 (dd, *J* = 7.8, 2.1 Hz, 1H), 6.97 – 6.89 (m, 2H), 3.88 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.19, 159.89, 145.44, 137.61, 135.48, 135.04, 132.08, 130.14, 129.99, 129.97, 128.92,

126.80, 125.24, 123.92, 123.36, 122.16, 121.10, 116.93, 116.57, 115.02, 114.87, 114.05, 113.04, 55.51, 55.44; HRMS (APCI): m/z calcd for $C_{25}H_{21}N_2O_2$ $[M+H]^+$ 381.1598, found: 381.1591.

1,3-Bis(3,5-dimethylphenyl)pyrrolo[1,2-a]quinoxaline (**3j**)

Yield: 36%; Light yellow solid; M.p. = 71-76 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.29 (s, 2H), 7.17 (d, *J* = 13.8 Hz, 4H), 7.03 (s, 1H), 6.90 (s, 1H), 2.41 (d, *J* = 5.2 Hz,12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.65, 138.69, 138.50, 138.25, 137.59, 136.64, 134.08, 133.74, 132.71, 130.56, 129.86, 129.03, 127.45, 126.61, 126.55, 125.07, 123.81, 116.97, 116.54, 21.57, 21.51; HRMS (APCI): m/z calcd for $C_{27}H_{25}N_2$ $[M+H]^+$ 377.2012, found: 377.2006.

8-Methyl-1,3-di-p-tolylpyrrolo[1,2-a]quinoxaline (**3k**)

Yield: 60%; Light yellow solid; M.p. = 281-221 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.29 (m,4H), 7.23 (s, 1H), 7.18 – 7.14 (m, 1H), 6.87 (s, 1H), 2.50 (s, 3H), 2.43 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.61, 138.81, 137.01, 136.85, 135.53, 132.20, 131.40, 131.06, 129.83, 129.65, 129.51, 129.41, 128.89, 128.49, 126.25, 123.85, 123.27, 117.13, 116.34, 21.91, 21.59, 21.35; HRMS (APCI): m/z calcd for $C_{26}H_{23}N_2$ $[M+H]^+$ 363.1856, found: 363.1849.

8-Fluoro-1,3-di-p-tolylpyrrolo[1,2-a]quinoxaline (**3l**)

Yield: 40%; Light yellow solid; M.p. = 78-82 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.90 (d, *J* = 2.4 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.27 (m, 5H), 7.09 (dd, *J* = 9.1, 2.4 Hz, 1H), 6.89 (s, 1H), 2.49 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.50, 139.27, 138.65, 137.43, 132.85, 130.96, 130.52, 130.27, 129.93, 129.81, 129.56, 129.07, 128.54, 127.76, 126.62, 124.48, 123.66, 117.83, 116.76, 21.62, 21.38; ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.6; HRMS (APCI): m/z calcd for $C_{25}H_{20}FN_2$ $[M+H]^+$ 367.1605, found: 367.1603.

7-Chloro-1,3-di-p-tolylpyrrolo[1,2-a]quinoxaline (**3m**)

Yield: 51%; Light yellow solid; M.p. = 81-86 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.89 (dd, *J* = 8.9, 6.2 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz,

2H), 7.33 (dd, *J* = 11.6, 7.8 Hz, 4H), 7.12 (dd, J = 11.1, 2.7 Hz, 1H), 7.10 – 7.04 (m, 1H), 6.89 (s, 1H), 2.50 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.74, 139.33, 137.28, 134.27, 132.48, 131.45, 131.35, 131.08, 130.23, 129.88, 129.77, 129.71, 128.51, 123.69, 123.28, 116.83, 112.99, 112.75, 103.83, 103.54, 21.61, 21.36; HRMS (APCI): m/z calcd for $C_{25}H_{20}ClN_2$ $[M+H]^+$ 383.1310, found: 383.1306.

N-Phenyl-3-(p-tolyl)-1-tosyl-1H-pyrazol-5-amine (**3n**)

Yield: 84%; Light yellow solid; M.p. = 65-70 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 9.4 Hz, 2H), 7.54 – 7.44 (m, 5H), 7.42 – 7.31 (m, 5H), 7.18 – 7.12 (m, 1H), 6.91 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.46, 138.95, 137.63, 134.24, 132.52, 131.23, 130.92, 130.69, 129.95, 129.67, 129.64, 129.15, 128.67, 127.31, 126.68, 125.16, 123.83, 123.59, 116.84, 116.59, 21.61; HRMS (APCI): m/z calcd for $C_{24}H_{19}N_2$ $[M+H]^+$ 335.1543, found: 335.1539.

4-(1-(p-Tolyl)pyrrolo[1,2-a]quinoxalin-3-yl)benzonitrile (**3o**)

Yield: 46%; Light yellow solid; M.p. = 199- NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.83 – 7.65 (m, 4H), 7.48 – 7.42 (m, 3H), 7.39 (t, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.21 – 7.15 (m, 1H), 6.91 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.52, 139.31, 139.08, 137.57, 133.09, 132.91, 130.42, 130.14, 129.74, 129.64, 128.88, 127.18, 125.59, 123.99, 119.08, 116.89, 116.43, 110.52, 21.61; HRMS (APCI): m/z calcd for $C_{25}H_{17}N_3$ $[M+H]^+$ 360.1495, found: 360.1492.

3-(Naphthalen-2-yl)-1-(p-tolyl)pyrrolo[1,2-a]quinoxaline (**3p**)

Yield: 60%; Light yellow solid; M.p. = 89-94 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.80 (t, *J* = 8.4 Hz, 3H), 7.53 – 7.43 (m, 3H), 7.40 (d, *J* = 8.1 Hz, 3H), 7.33 (t, *J* = 6.9 Hz, 1H), 7.24 (dd, *J* = 11.6, 7.4 Hz, 3H), 7.09 – 7.02 (m, 1H), 6.85 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.68, 138.96, 137.62, 134.17, 132.57, 132.19, 131.61, 130.94, 130.06, 129.77, 129.66, 129.15, 128.54, 128.46, 128.19, 126.73, 126.46, 126.17, 126.12, 125.62, 125.32, 125.19, 121.57, 118.86, 116.85, 21.62; HRMS (APCI): m/z calcd for $C_{28}H_{21}N_2$ $[M+H]^+$ 385.1699, found: 385.1696.

1-(p-Tolyl)-3-(5-(p-tolyl)thiophen-2-yl)pyrrolo[1,2-a]quinoxaline (**3q**)

Yield: 60%; Green solid; M.p. = 110-115 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 7.89 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 3H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.23 (d, *J* = 3.7 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.13 – 7.07 (m, 1H), 6.88 (s, 1H), 2.45 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.18, 143.87, 139.13, 137.58, 137.46, 134.92, 132.88, 131.55, 130.55, 129.88, 129.77, 129.67, 129.65, 128.98, 126.89, 125.70, 125.63, 125.34, 123.50, 123.46, 116.78, 116.67, 116.12, 21.62, 21.36; HRMS (APCI): m/z calcd for $C_{29}H_{23}N_2S$ $[M+H]^+$ 431.1576, found: 431.1570.

1-Phenyl-3-(p-tolyl)pyrrolo[1,2-a]quinoxaline (**3r**)

Yield: 55%; Light yellow solid; M.p. = 65-70 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.94 (d, *J* = 9.4 Hz, 1H), 7.59 – 7.54 (m, 3H), 7.54 – 7.50 (m, 2H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.33 (t, *J* = 8.4 Hz, 3H), 7.14 (d, *J* = 7.1 Hz, 1H), 6.92 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.57, 137.63, 137.17, 133.93, 132.50, 132.27, 131.21, 130.92, 129.96, 129.94, 129.87, 129.77, 129.65, 129.62, 129.60, 129.13, 129.05, 128.89, 128.65, 128.52, 126.66, 125.14, 123.87, 123.67, 116.80, 116.60, 21.35; HRMS (APCI): m/z calcd for $C_{24}H_{19}N_2$ $[M+H]^+$ 335.1543, found:335.1538.

4-Phenyl-1-(p-tolyl)pyrrolo[1,2-a]quinoxaline (**3s**)

Yield: 58%; Light yellow solid; M.p. = 122-124 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (ddd, *J* = 11.5, 7.7, 1.6 Hz, 3H), 7.56 (d, *J* = 6.8 Hz, 3H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.30 (m, 3H), 7.14 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.04 (d, *J* = 4.1 Hz, 1H), 6.77 (d, *J* = 4.1 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ154.84, 138.58, 137.57, 132.98, 131.32, 130.16, 129.68, 129.57, 129.46, 128.75, 128.58, 128.31, 126.68, 126.11, 124.95, 116.80, 116.52, 108.93, 21.48; HRMS (APCI): m/z calcd for $C_{24}H_{19}N_2$ $[M+H]^+$ 335.1543, found: 335.1539.

4-(4-Fluorophenyl)-1-(p-tolyl)pyrrolo[1,2-a]quinoxaline (**3t**)

Yield: 68%; Light yellow solid; M.p. = 50-55 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 3H), 7.46 (dd, *J* = 16.1, 8.3 Hz, 3H), 7.39 – 7.29 (m, 3H), 7.27 – 7.19 (m, 2H), 7.17 – 7.08 (m, 1H), 6.99 (d, *J* = 4.1 Hz, 1H), 6.76 (d, *J* = 4.1 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.12, 164.64, 153.80, 144.75, 138.80, 137.53,

134.78, 133.30, 131.33, 130.80 (d, *J* = 8.1 Hz), 130.20, 129.65 (d, *J* = 7.1 Hz), 128.38, 126.61, 126.35, 125.16, 116.98, 116.65, 115.83, 115.61, 108.90, 21.60; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.2; HRMS (APCI): m/z calcd for $C_{24}H_{18}FN_2$ $[M+H]^+$ 353.1449, found: 353.1447.

4-(4-Methoxyphenyl)-1-(p-tolyl)pyrrolo[1,2-a]quinoxaline (**3u**)

Yield: 84%; Light yellow solid; M.p. = 135-140℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 8.4 Hz, 3H), 7.46 (dd, *J* = 12.9, 8.3 Hz, 3H), 7.38 – 7.30 (m, 3H), 7.15 – 7.02 (m, 4H), 6.75 (d, *J* = 4.1 Hz, 1H), 3.91 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.02, 154.43, 138.63, 137.71, 132.99, 131.49, 131.28, 130.30, 130.07, 129.66, 129.55, 128.31, 126.78, 125.92, 125.00, 116.81, 116.59, 114.07, 108.94, 55.56, 21.58; HRMS (APCI): m/z calcd for $C_{25}H_{21}N_2O$ $[M+H]^+$ 365.1648, found: 365.1647.

1,4-Di-p-tolylpyrrolo[1,2-a]quinoxaline (**3v**)

Yield: 76%; Light yellow solid; M.p. = 167-172 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.54 – 7.41 (m, 3H), 7.34 (dd, *J* = 16.4, 8.1 Hz, 4H), 7.12 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.04 (d, *J* = 4.0 Hz, 1H), 6.75 (d, *J* = 4.0 Hz, 1H), 2.48 (d, *J* = 7.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.92, 139.86, 138.65, 137.71, 135.87, 133.01, 131.50, 130.18, 129.68, 129.56, 129.36, 128.80, 128.38, 126.06, 125.02, 116.84, 116.61, 109.02, 21.62, 21.59.; HRMS (APCI): m/z calcd for $C_{25}H_{21}N_2$ $[M+H]^+$ 349.1699, found: 349.1697.

2.2 Typical procedure for the gram-scale synthesis of 3u.

A mixture of 4-(4-methoxyphenyl)-1-(*p*-tolyl)pyrrolo[1,2-*a*]quinoxaline (**1**, 5 mmol), 1-iodo-4-methylbenzene (**2**, 10 mmol), $Pd(OAc)_2$ (10 mol%), X-Phos (15 mol%), and toluene (20 mL) was stirred at 120 ^{o}C for 24 hours in air. Upon completion, the solution was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOH as eluent) to afford target product **3u** (1.175 g, 65% yield).

2.3 Typical procedure for the synthesis of 3ua.

A Schlenk tube (10 mL) was charged with **3u** (0.5 mmol), NH_4SCN (1.0 mmol), NCS

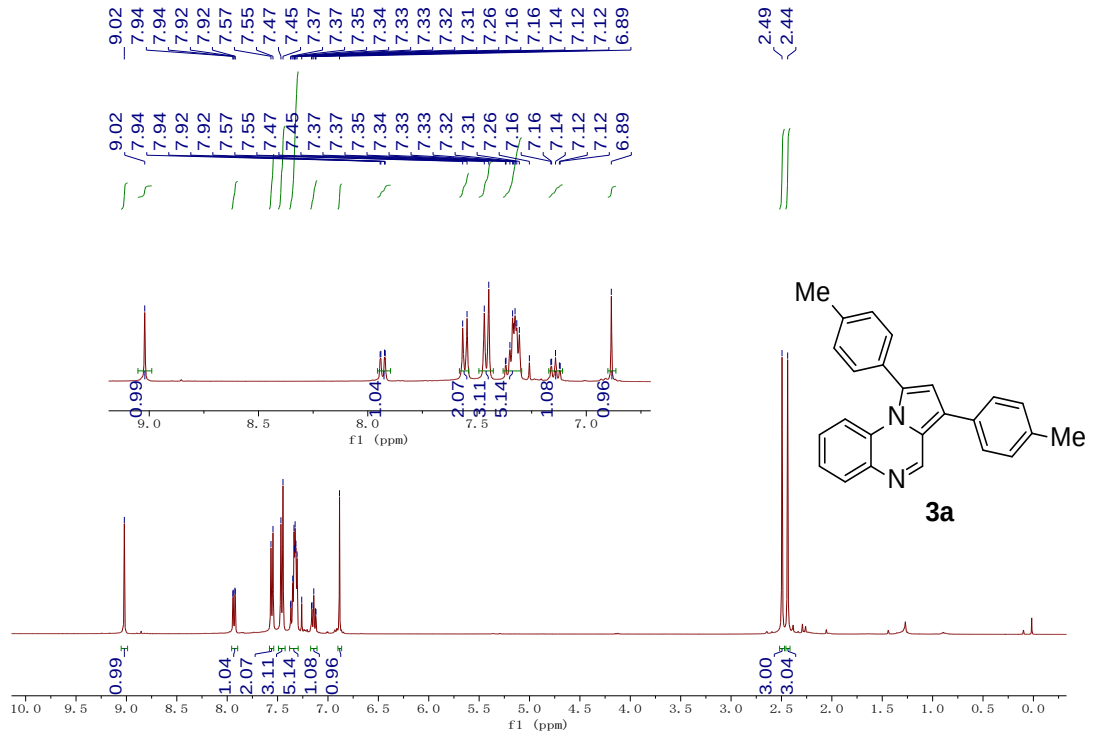
(0.75 mmol) and MeCN (2 mL). The mixture was stirred at room temperature for 24 h. After completion of the reaction, the solution was concentrated in vacuo. The crude was purified by flash chromatography on silica gel (PE/EtOAc as eluent) to afford target product **3ua** in a 58% yield.

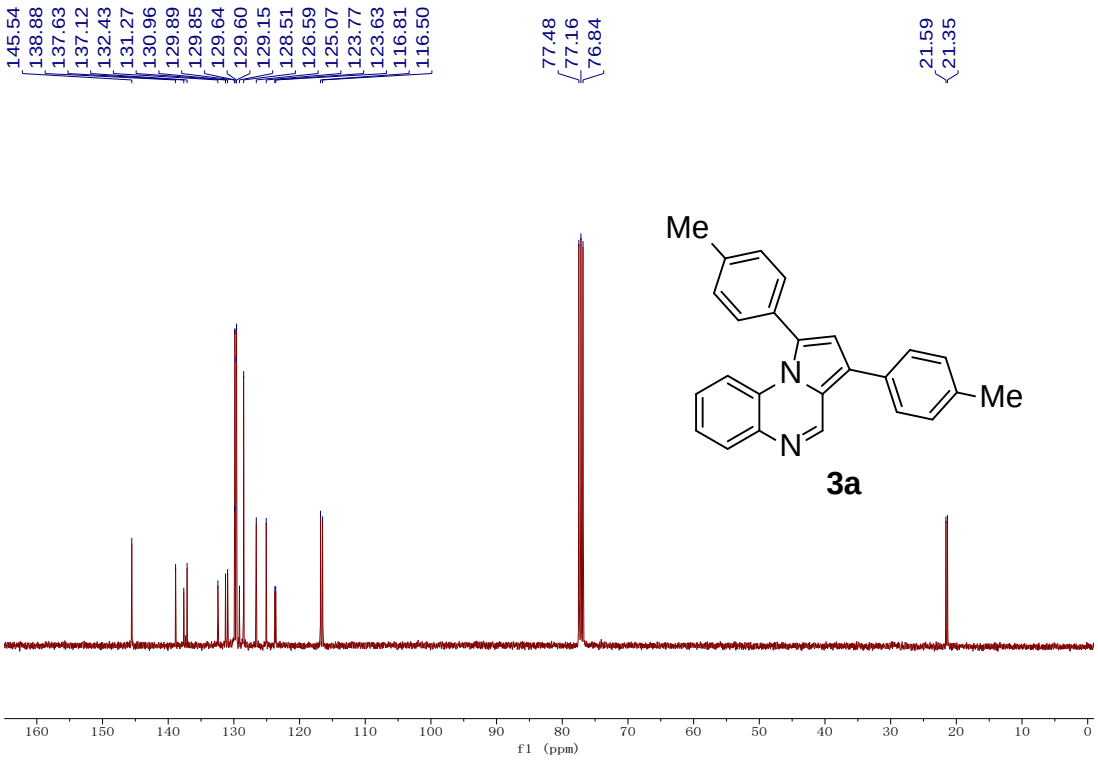
4-(4-Methoxyphenyl)-3-thiocyanato-1-(p-tolyl)pyrrolo[1,2-a]quinoxaline (**3 ua**)

Yield: 58%; Brown solid; M.p. = 218-221 ℃; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.3 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.46 – 7.37 (m, 4H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.21 – 7.14 (m, 1H), 7.11 (s, 1H), 7.08 (s, 1H), 6.97 (s, 1H), 3.92 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.28, 153.91, 139.66, 133.73, 130.44, 130.36, 129.85, 129.82, 129.62, 127.98, 127.10, 126.09, 125.33, 119.95, 116.60, 114.42, 111.23, 55.60, 21.63; HRMS (APCI): m/z calcd for $C_{26}H_{19}N_3OS$ $[M+H]^+$ 422.1322, found: 422.1329.

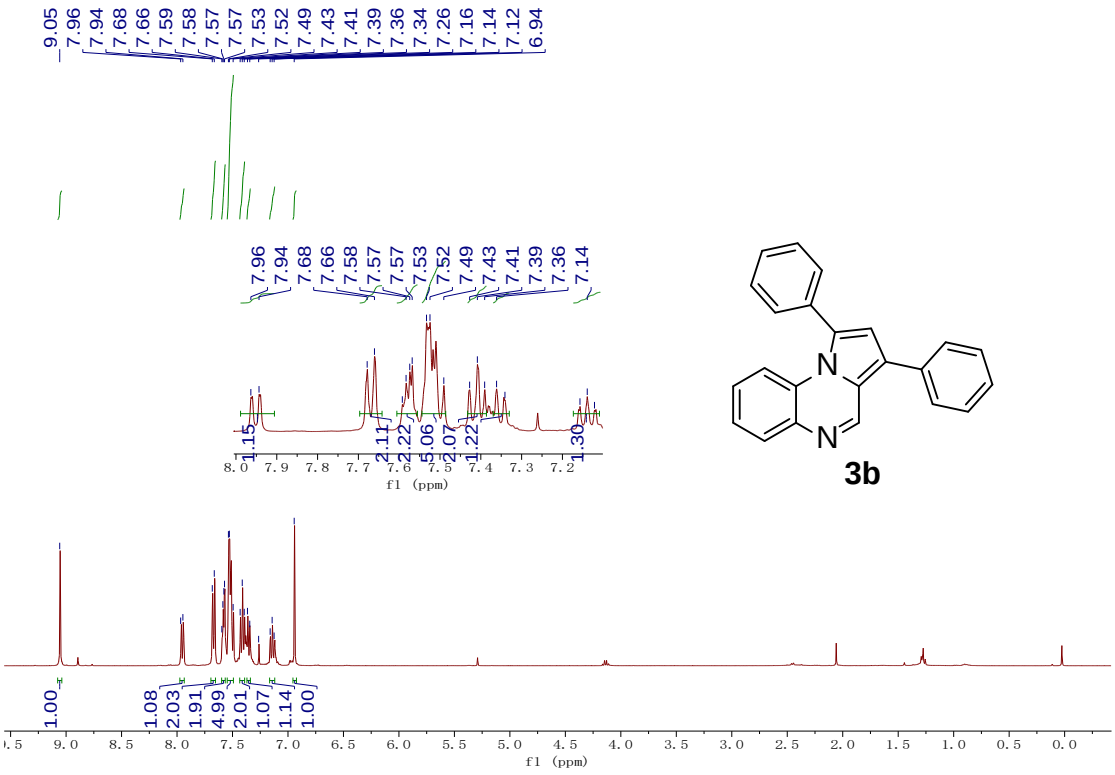
3. NMR spectra of the products

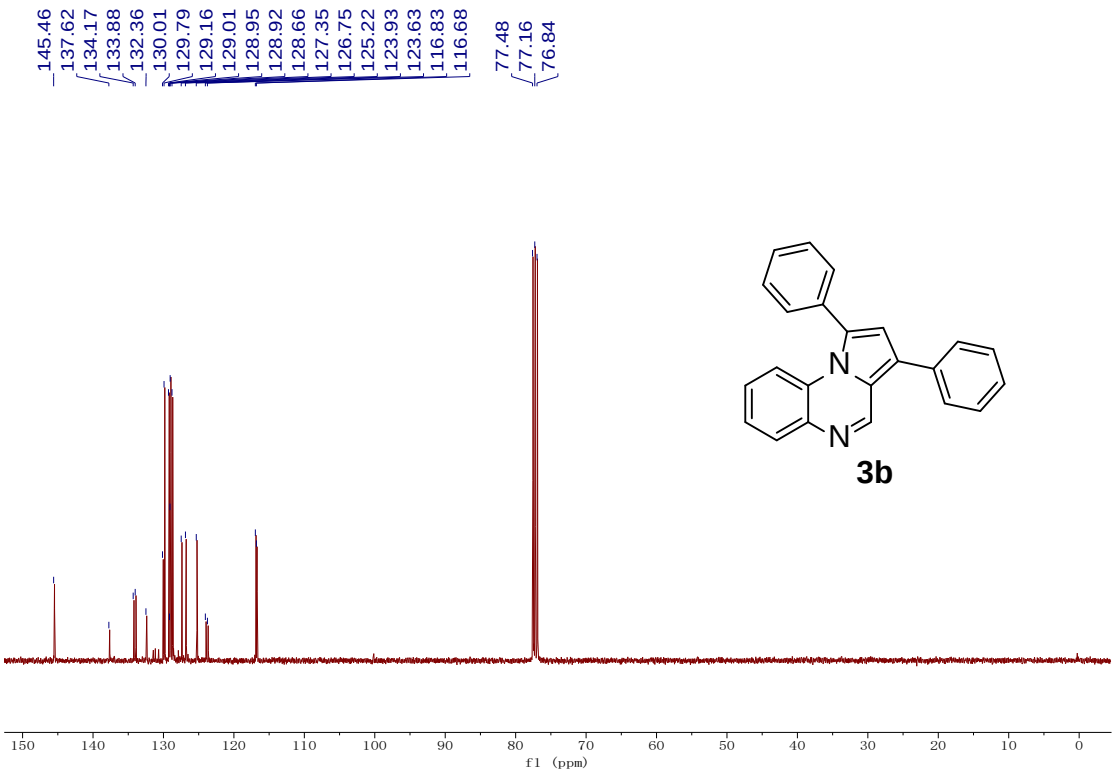
*1,3-iodopyrrolo[1,2-a]quinoxaline [**3a**]*



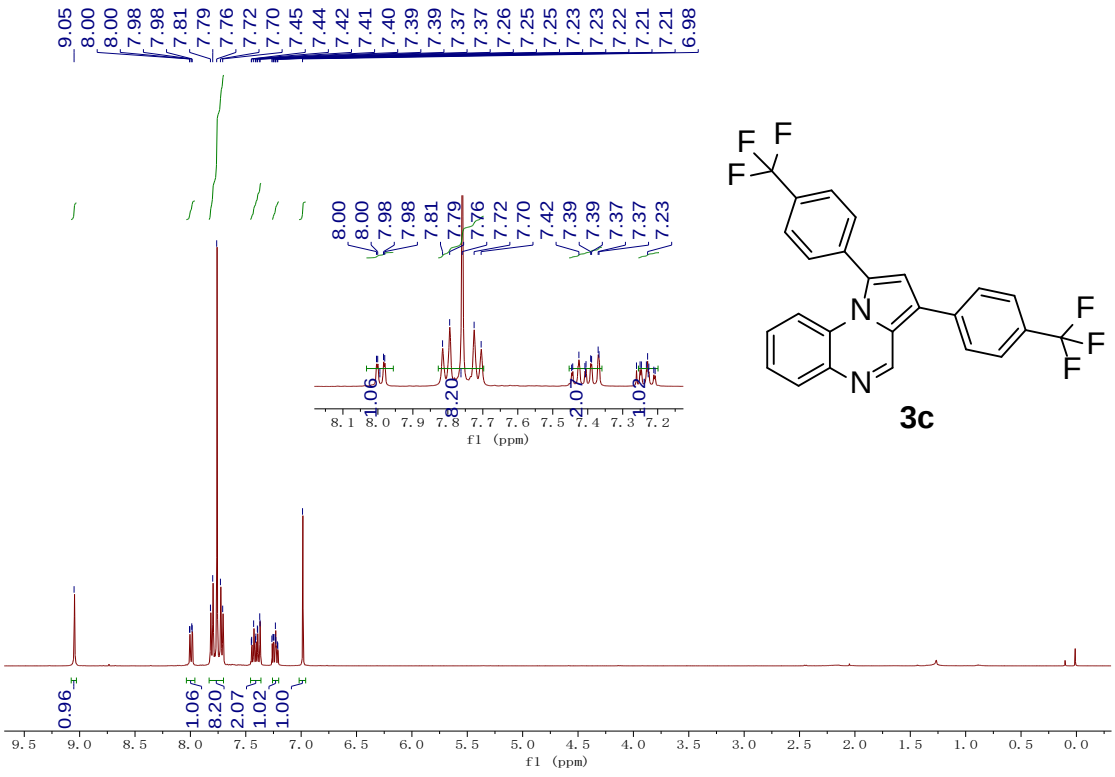


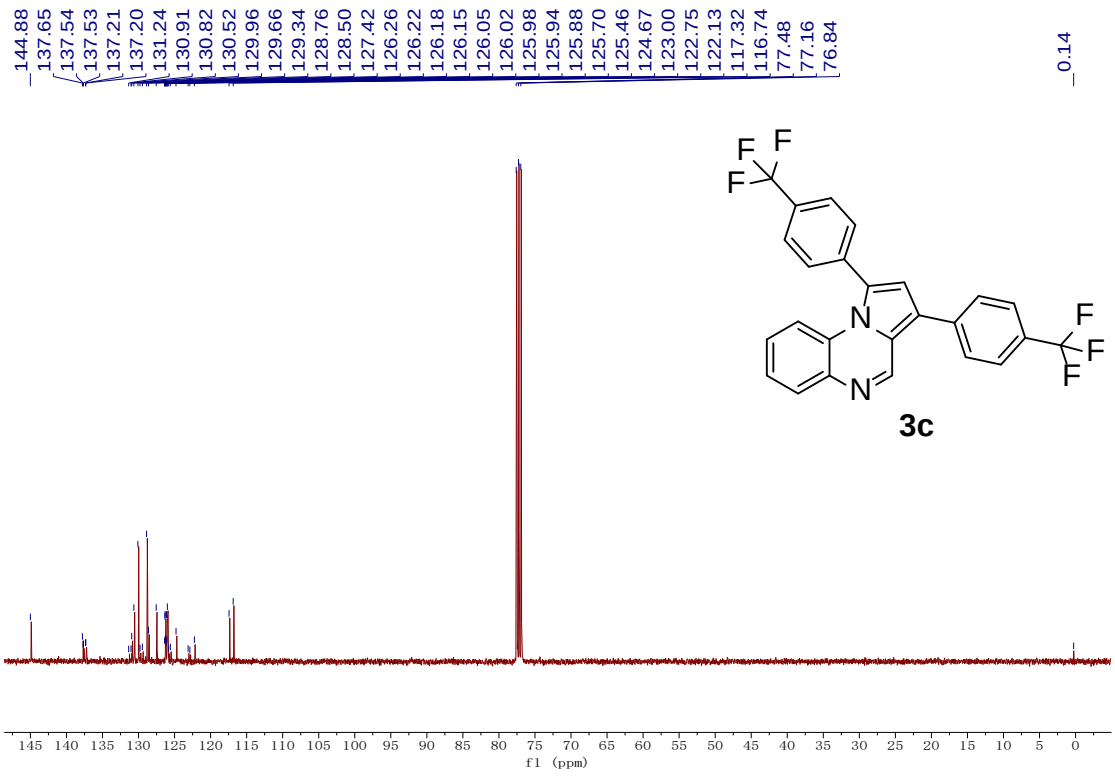
*1,3-diphenylpyrrolo[1,2-a]quinoxaline [**3b**]*

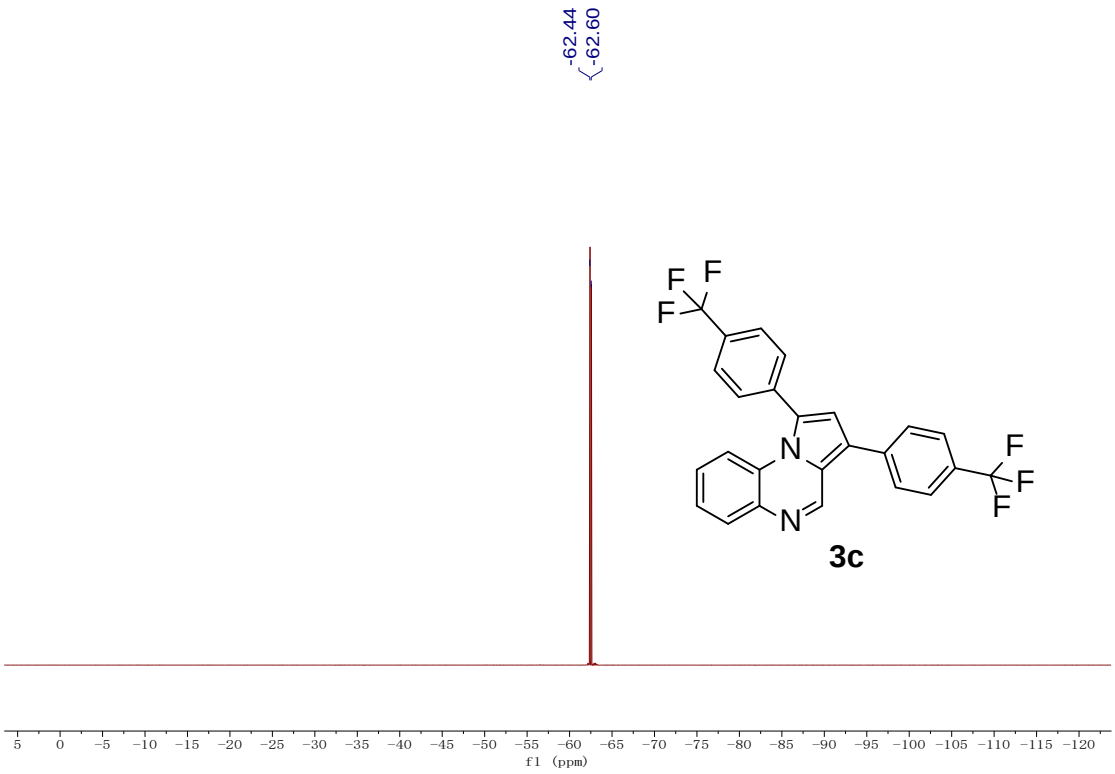




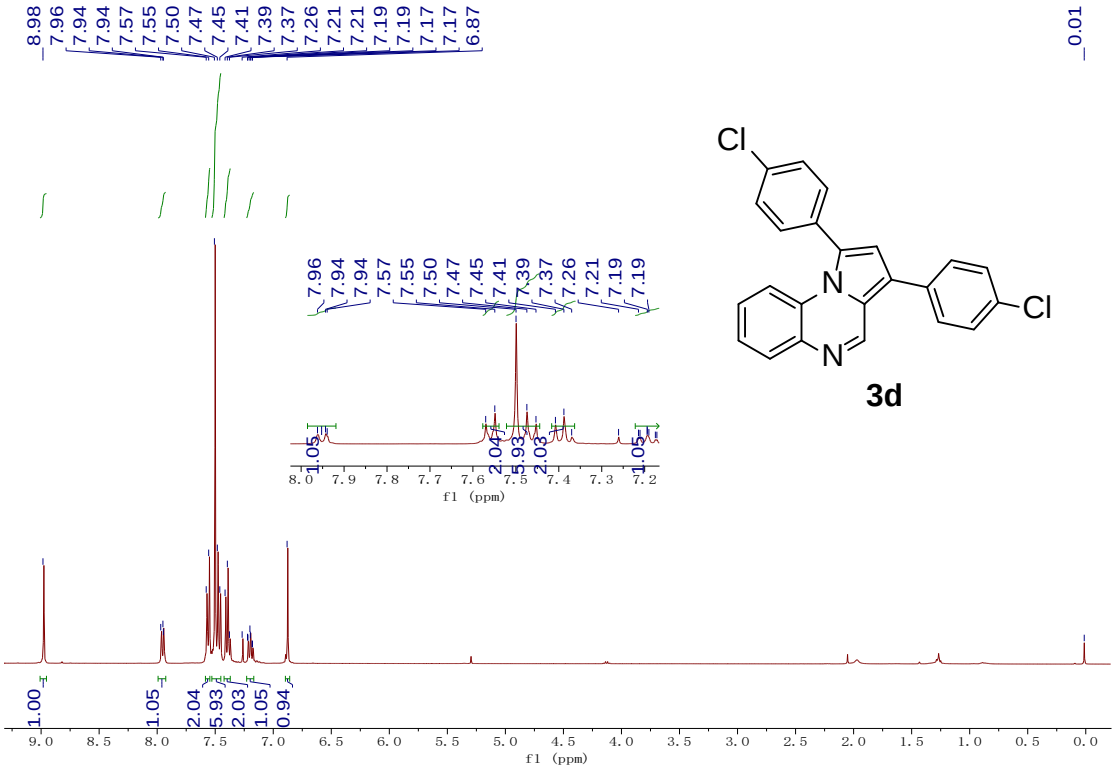
*1,3-bis(4-(trifluoromethyl)phenyl)pyrrolo[1,2-a]quinoxaline [**3c**]*

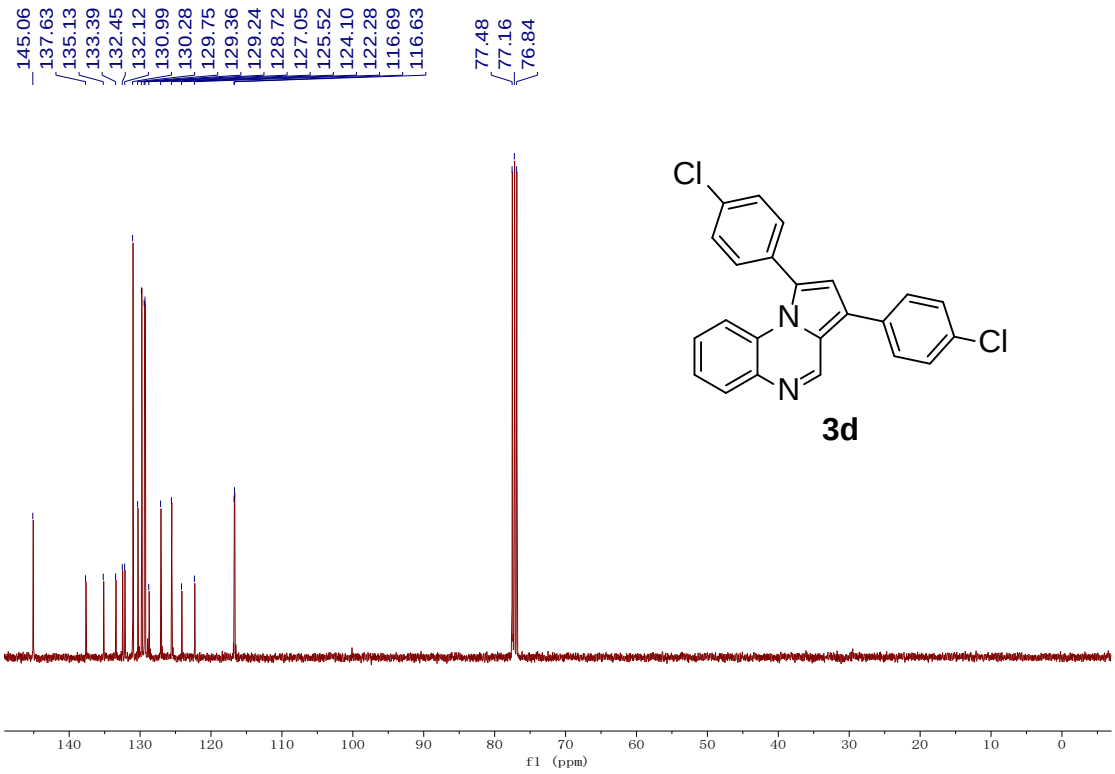




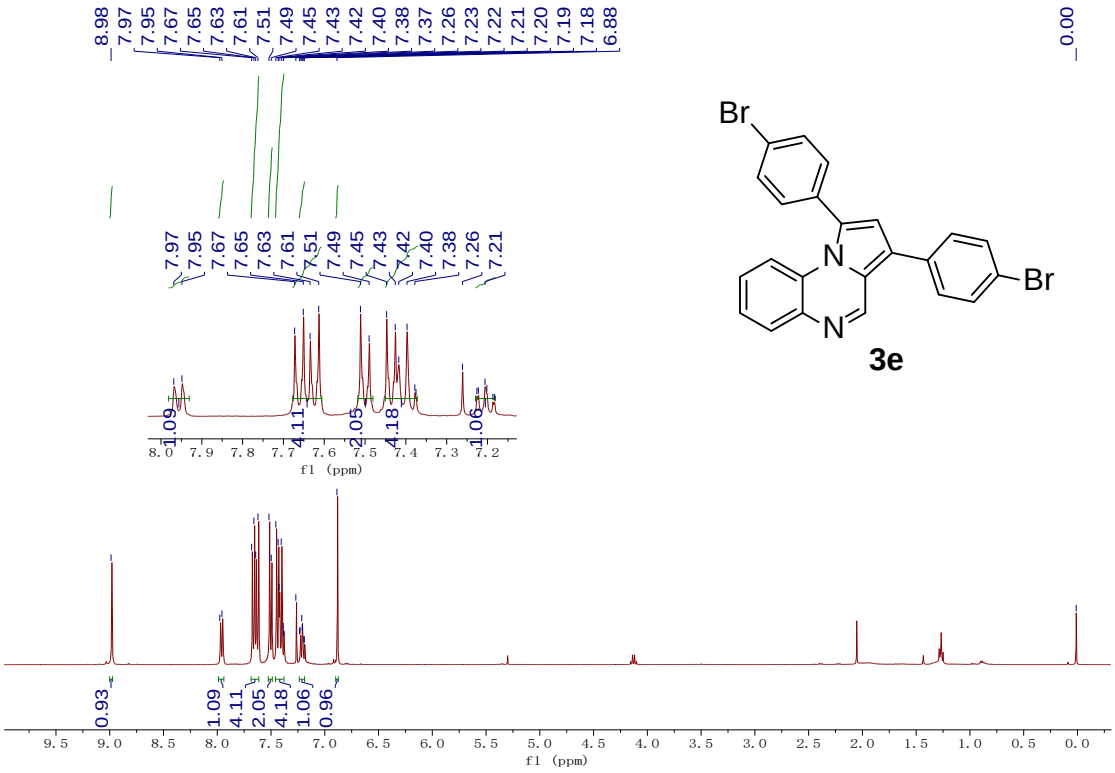


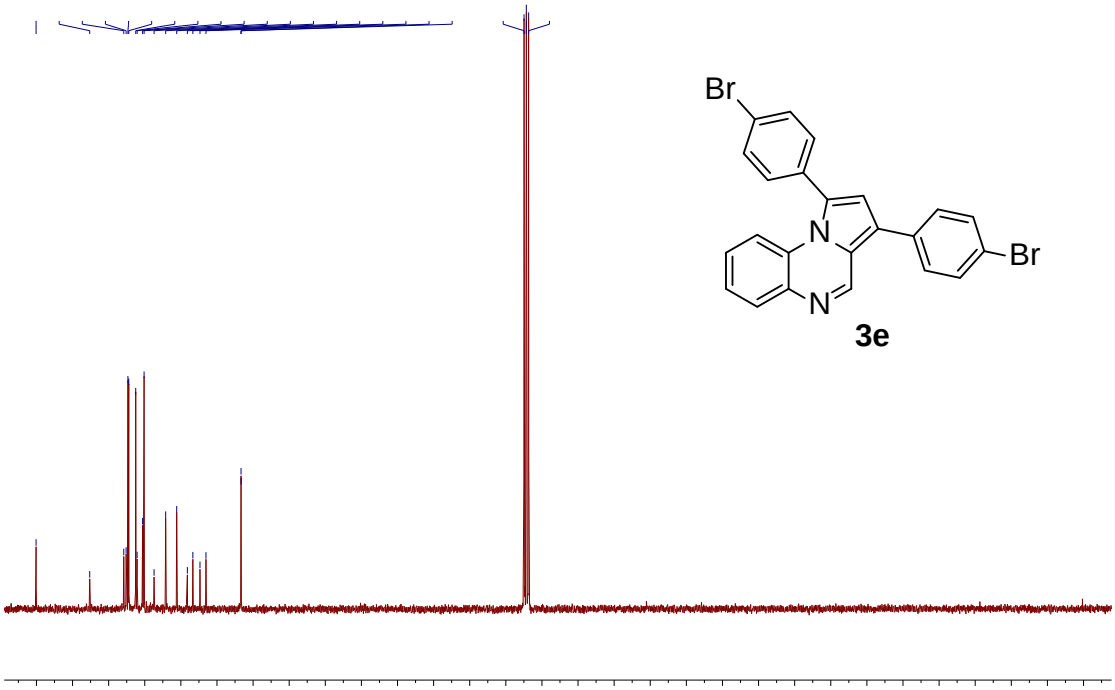
*1,3-bis(4-chlorophenyl)pyrrolo[1,2-a]quinoxaline [**3d**]*





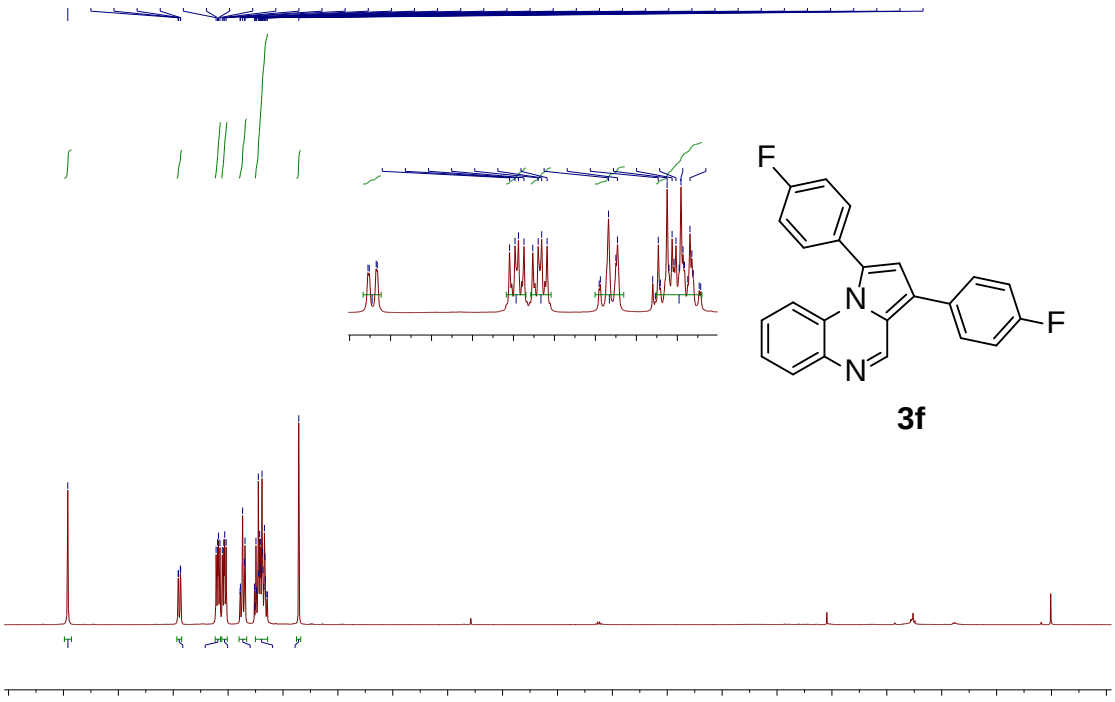
*1,3-bis(4-bromophenyl)pyrrolo[1,2-a]quinoxaline [**3e**]*



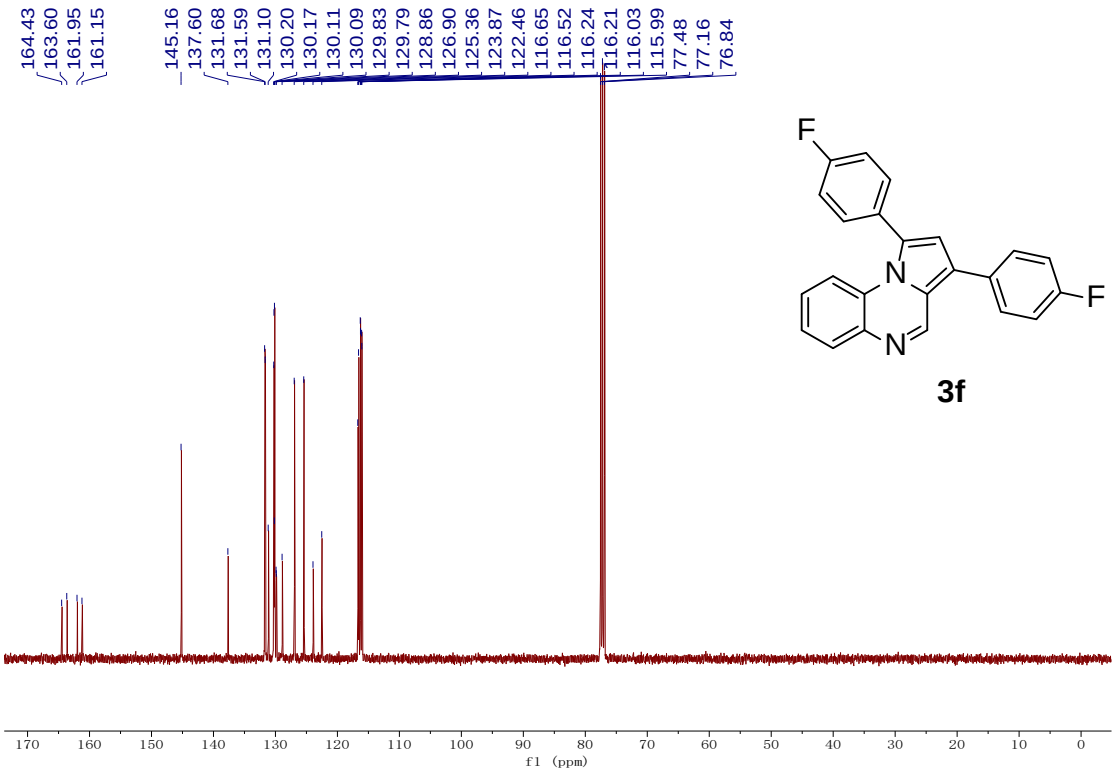


3e

*1,3-bis(4-fluorophenyl)pyrrolo[1,2-a]quinoxaline [**3f**]*



3f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129.79
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125.36
123.87
122.46
116.65
116.52
116.24
116.21
116.03
115.99
77.48
77.16
76.84
F
N
N
F
3f
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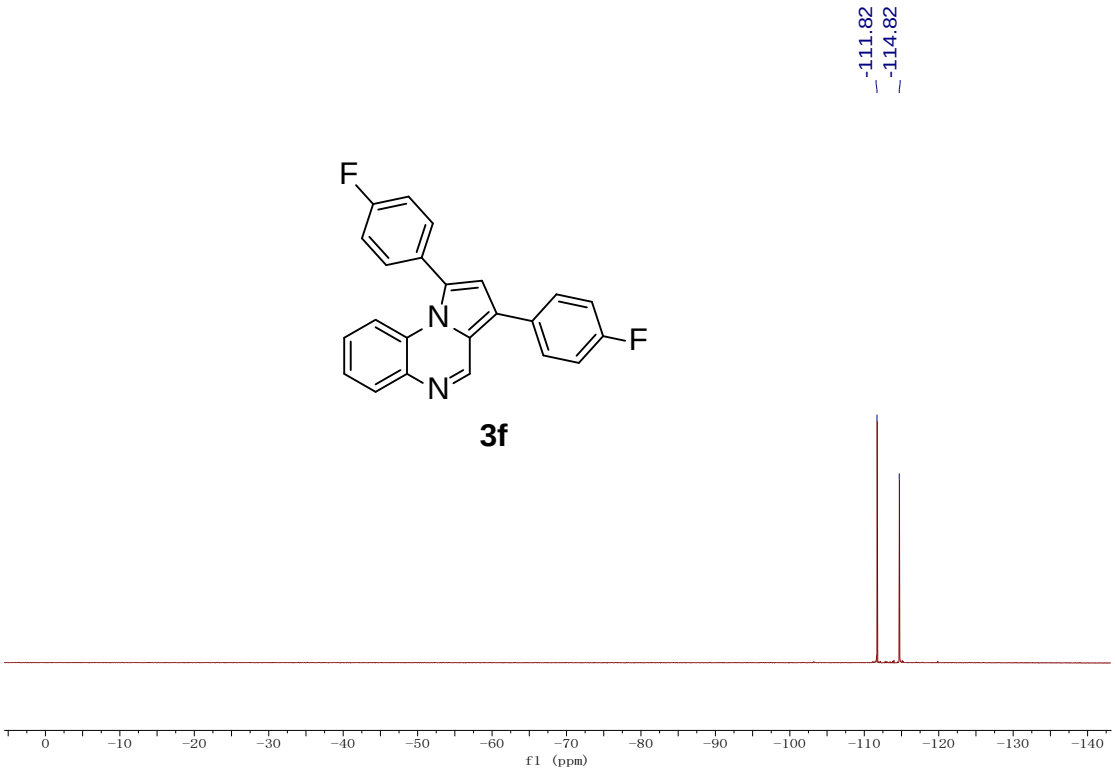
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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F
N
N
F
3f
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−30
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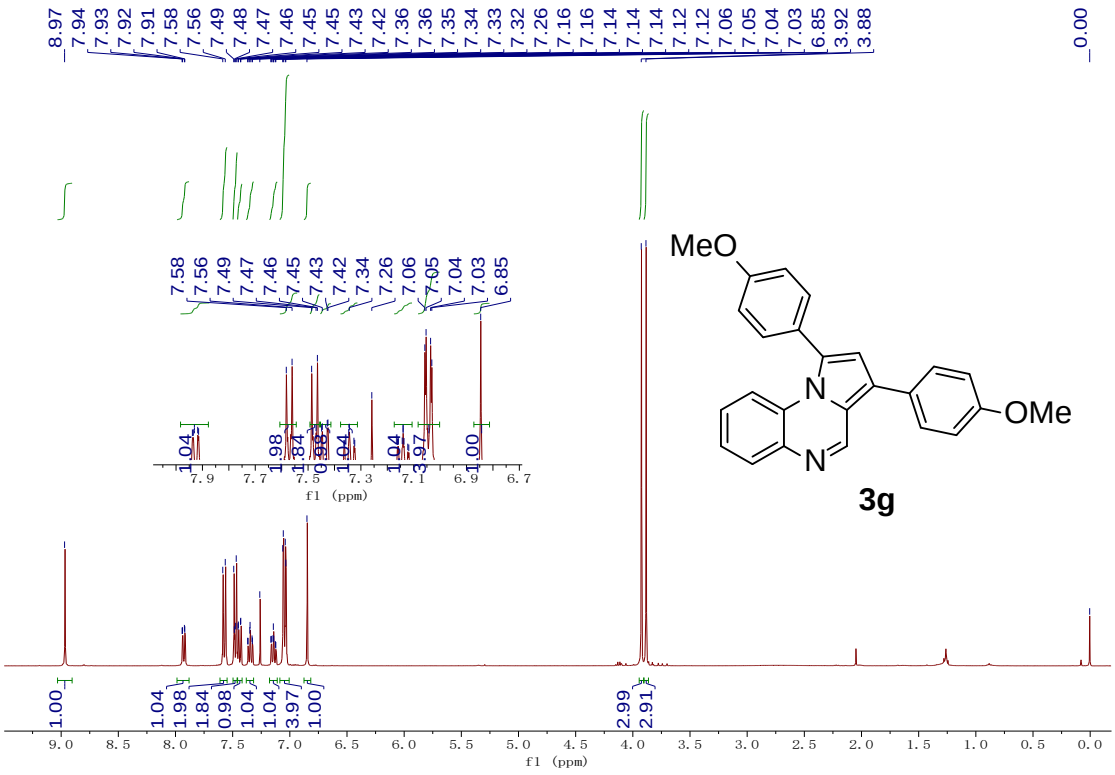
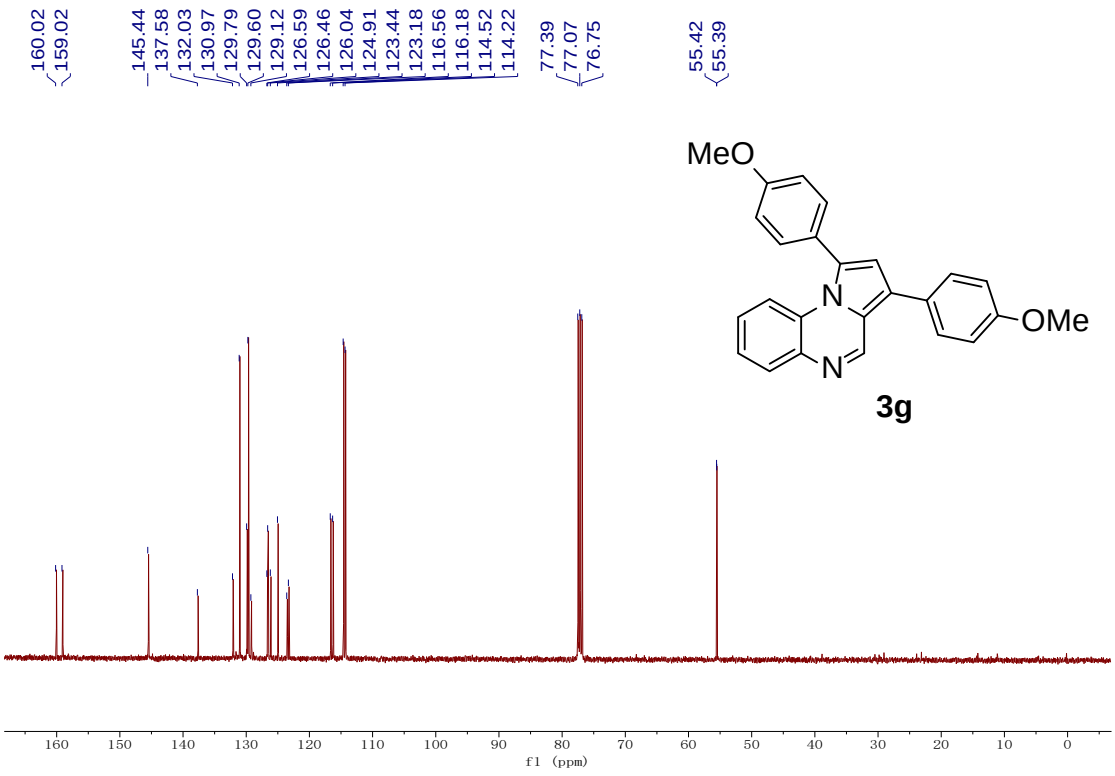
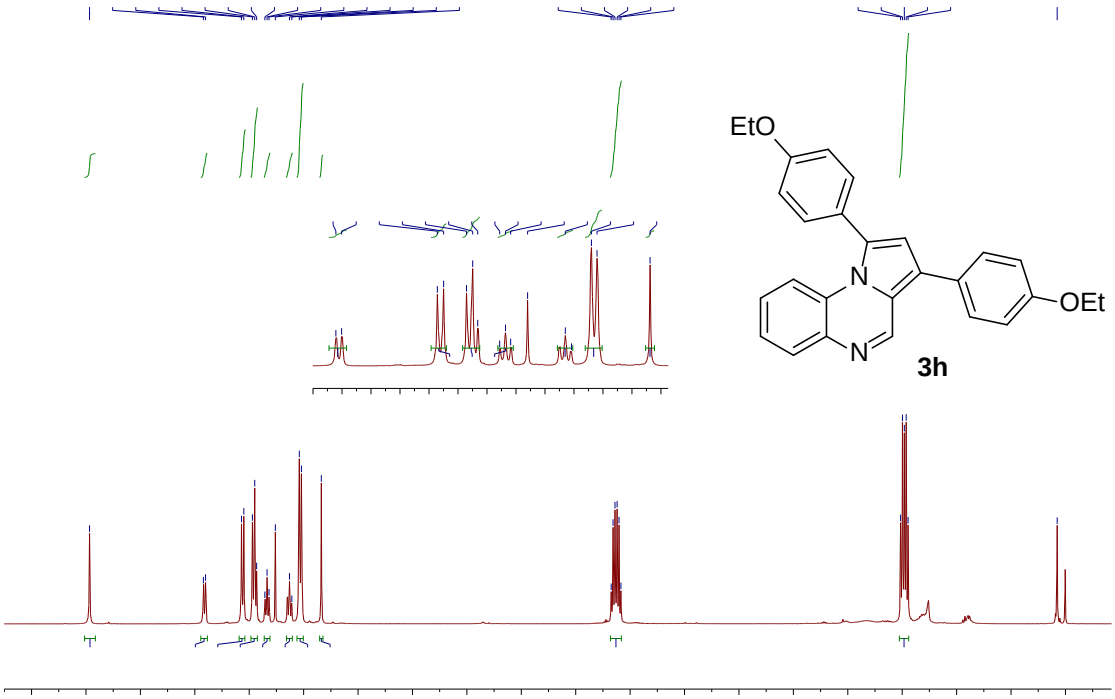
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
f1 (ppm)

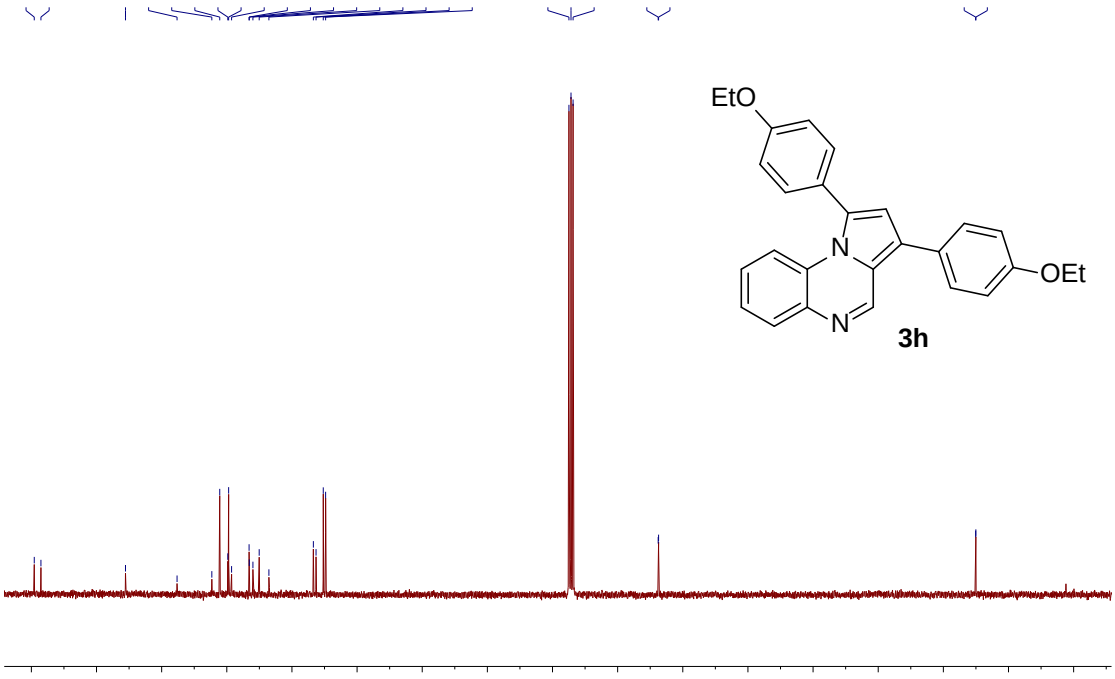
*1,3-bis(4-methoxyphenyl)pyrrolo[1,2-a]quinoxaline [**3g**]*



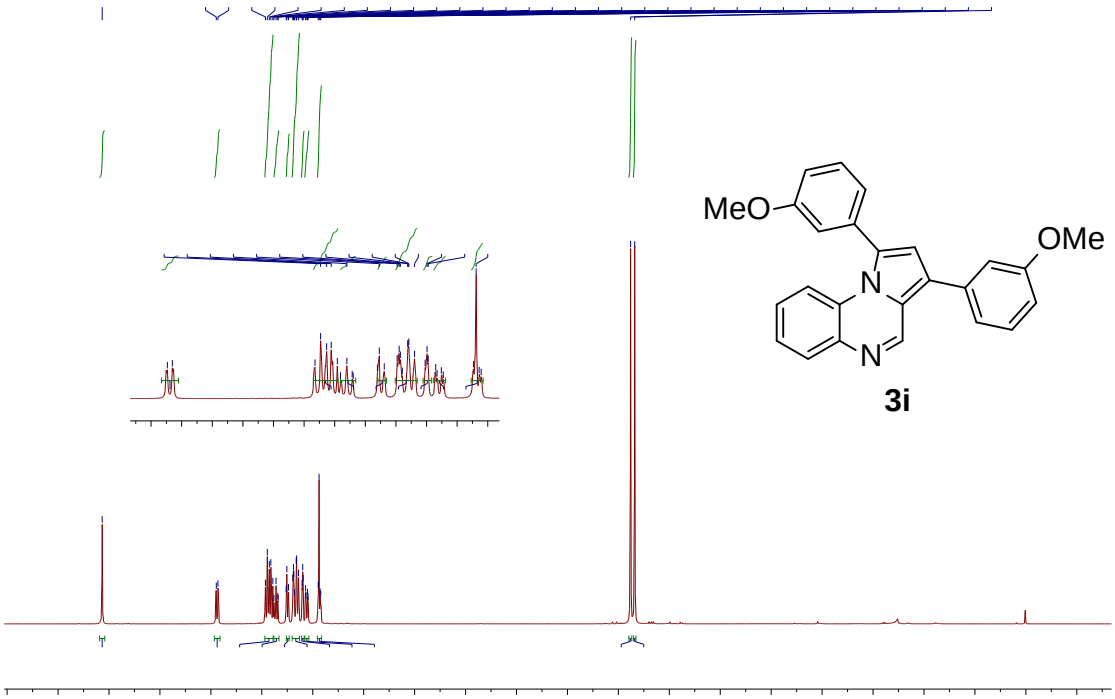


*1,3-bis(4-ethoxyphenyl)pyrrolo[1,2-a]quinoxaline [**3h**]*

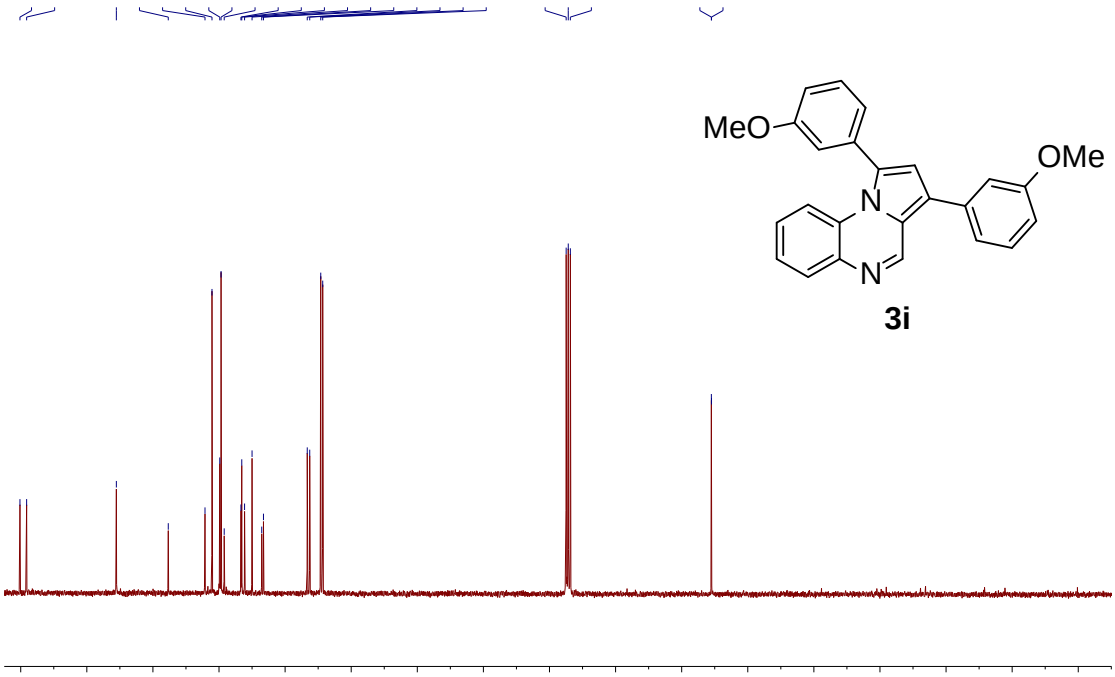




*4-(4-bromophenyl)-3-iodopyrrolo[1,2-a]quinoxaline [**3i**]*

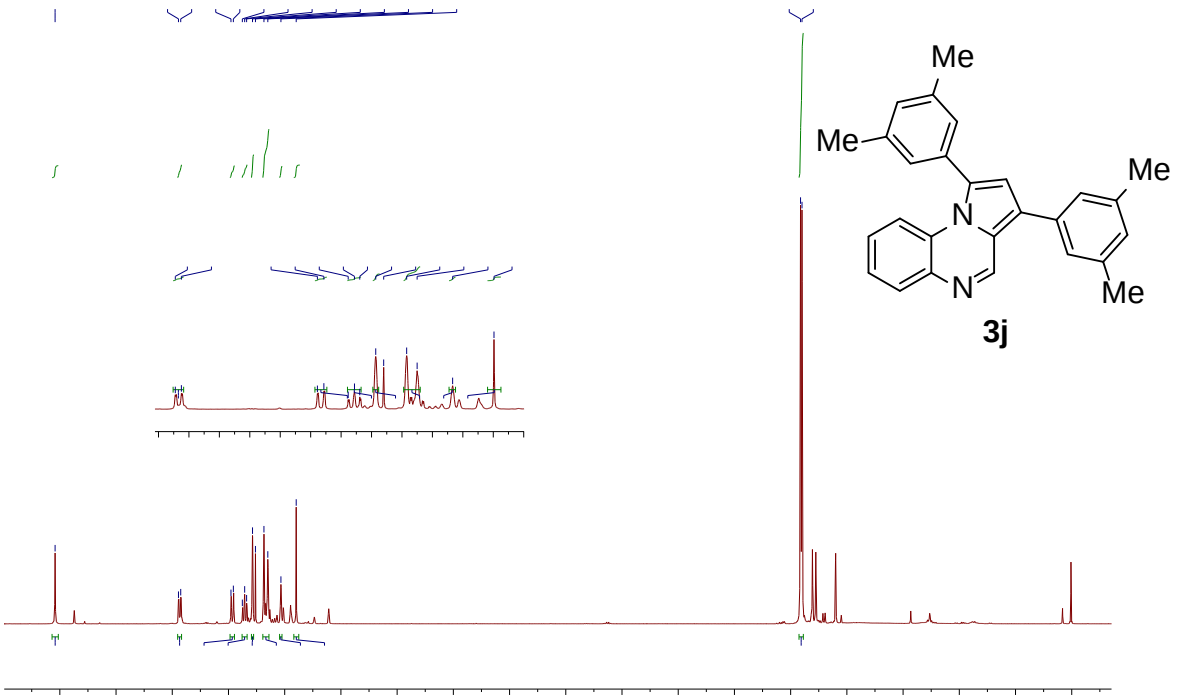


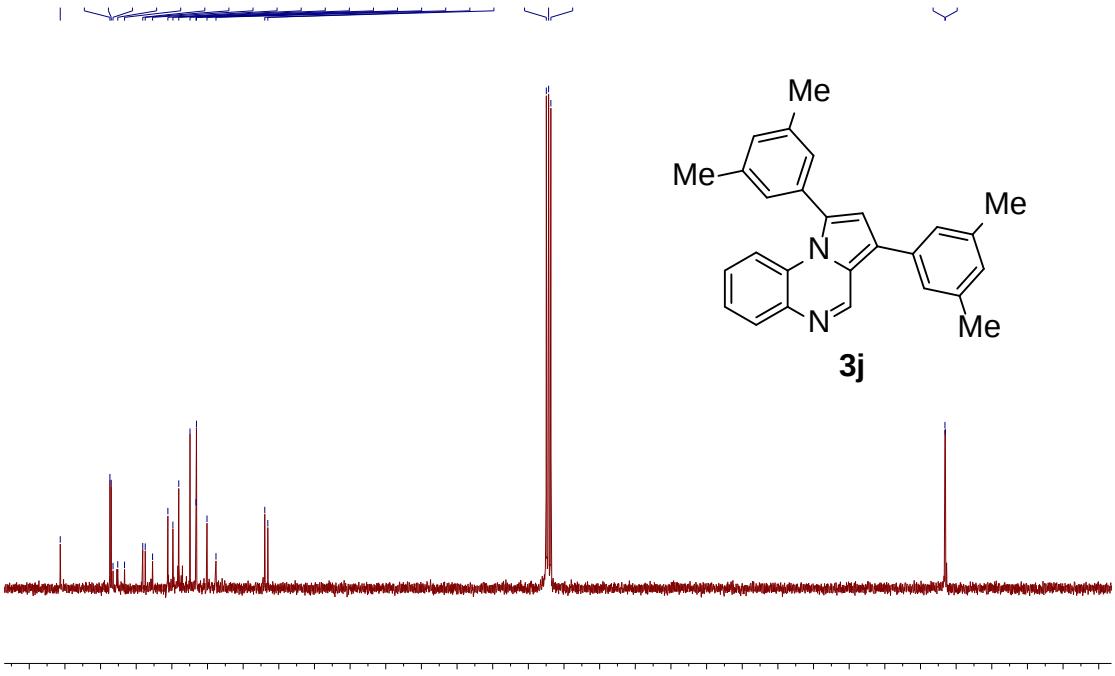
3i



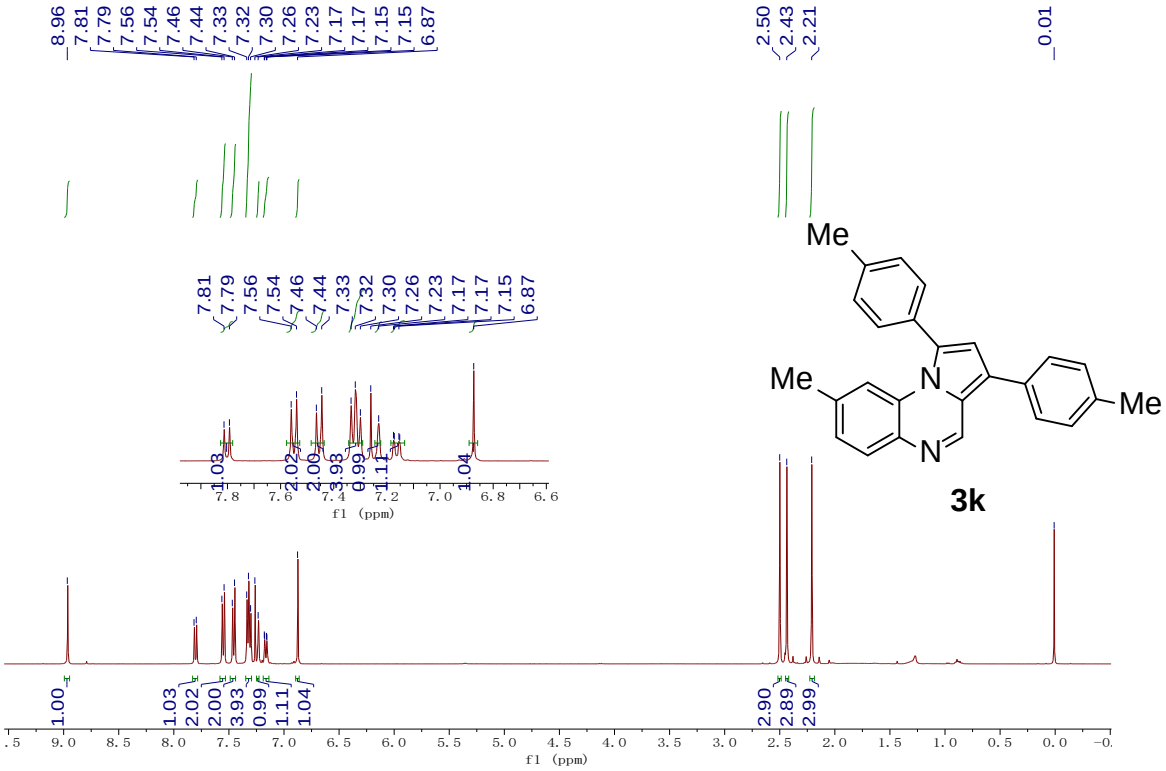
3i

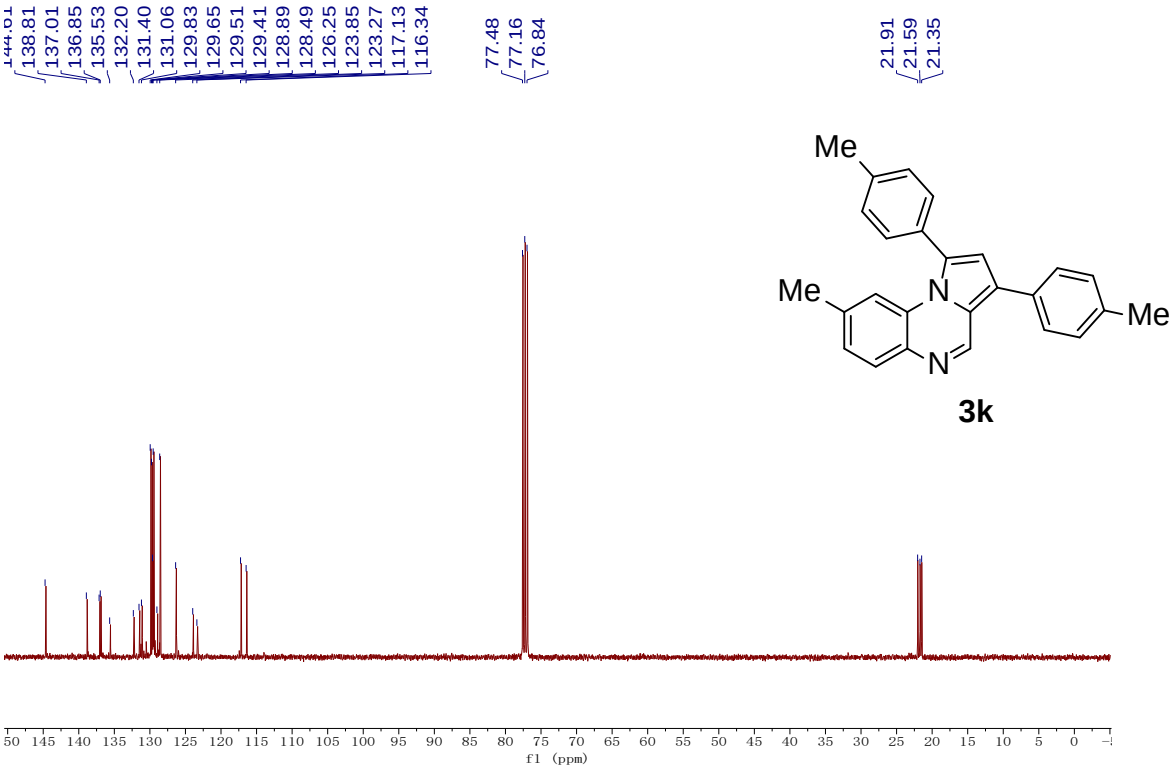
*1,3-bis(3,5-dimethylphenyl)pyrrolo[1,2-a]quinoxaline [**3j**]*



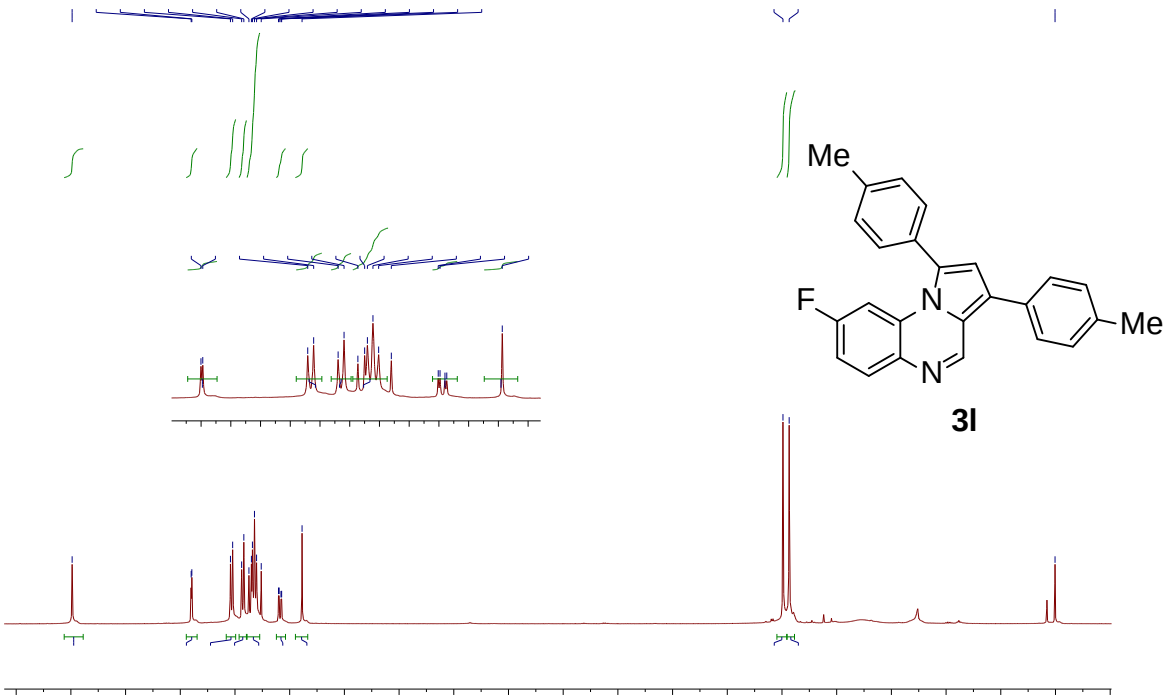


*8-methyl-1,3-di-p-tolylpyrrolo[1,2-a]quinoxaline [**3k**]*

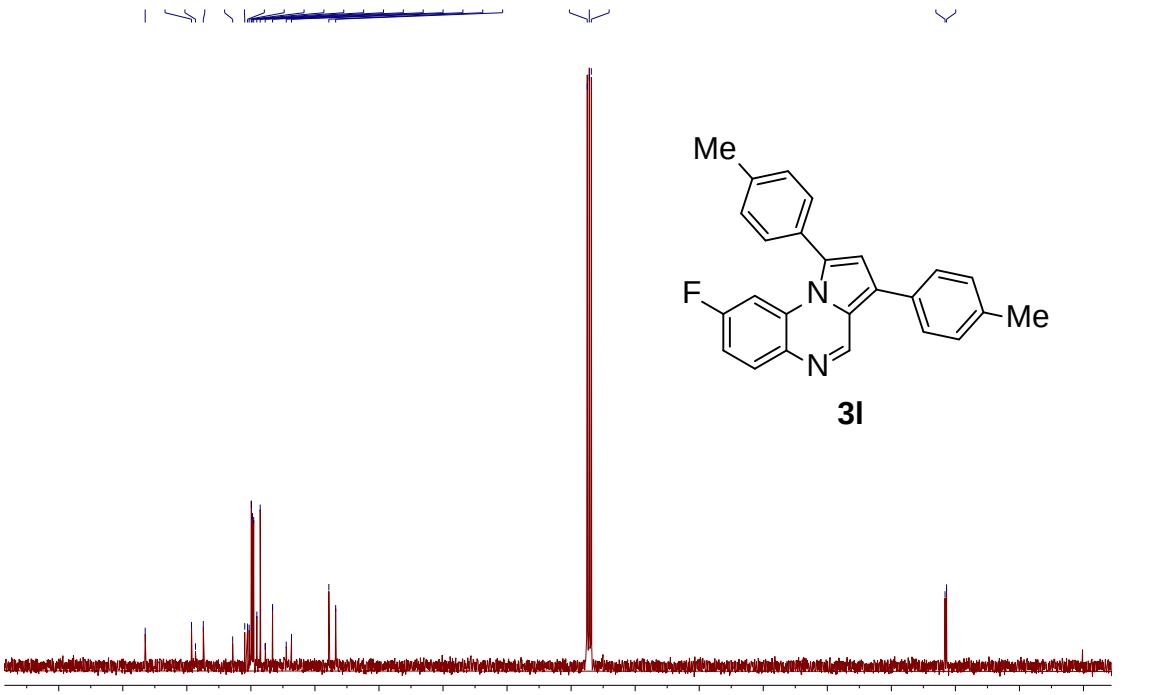




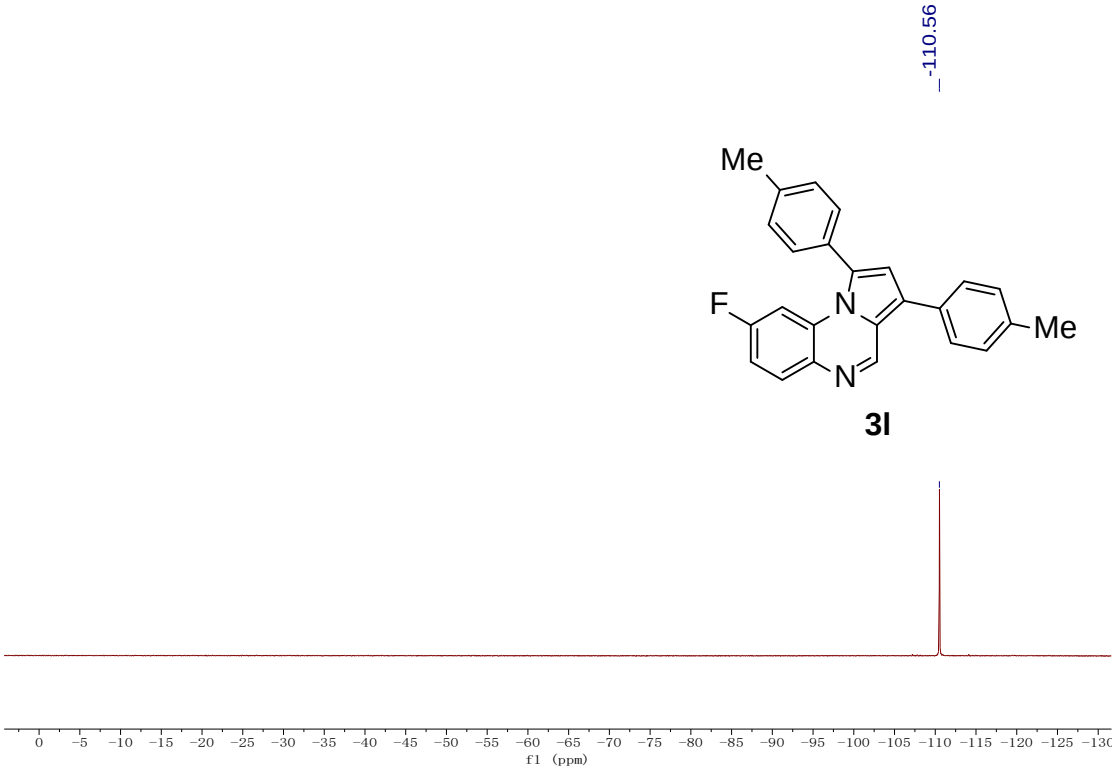
*8-fluoro-1,3-di-p-tolylpyrrolo[1,2-a]quinoxaline [**3l**]*



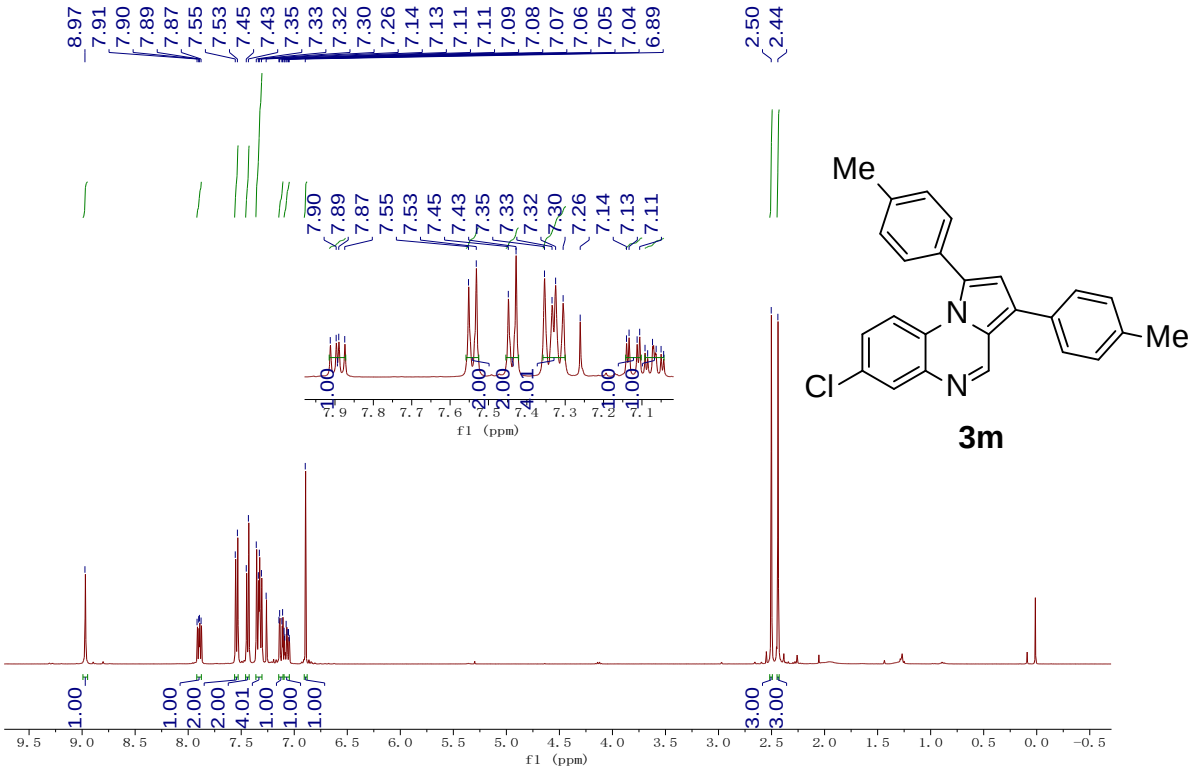
3l

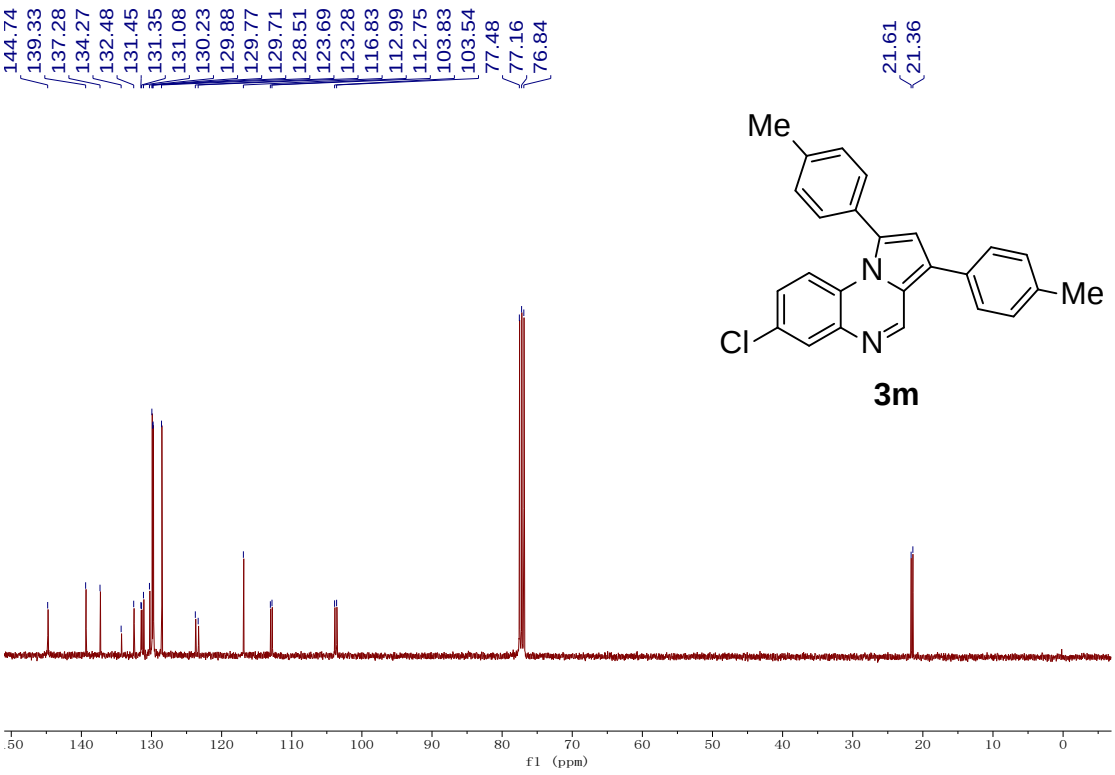


3l

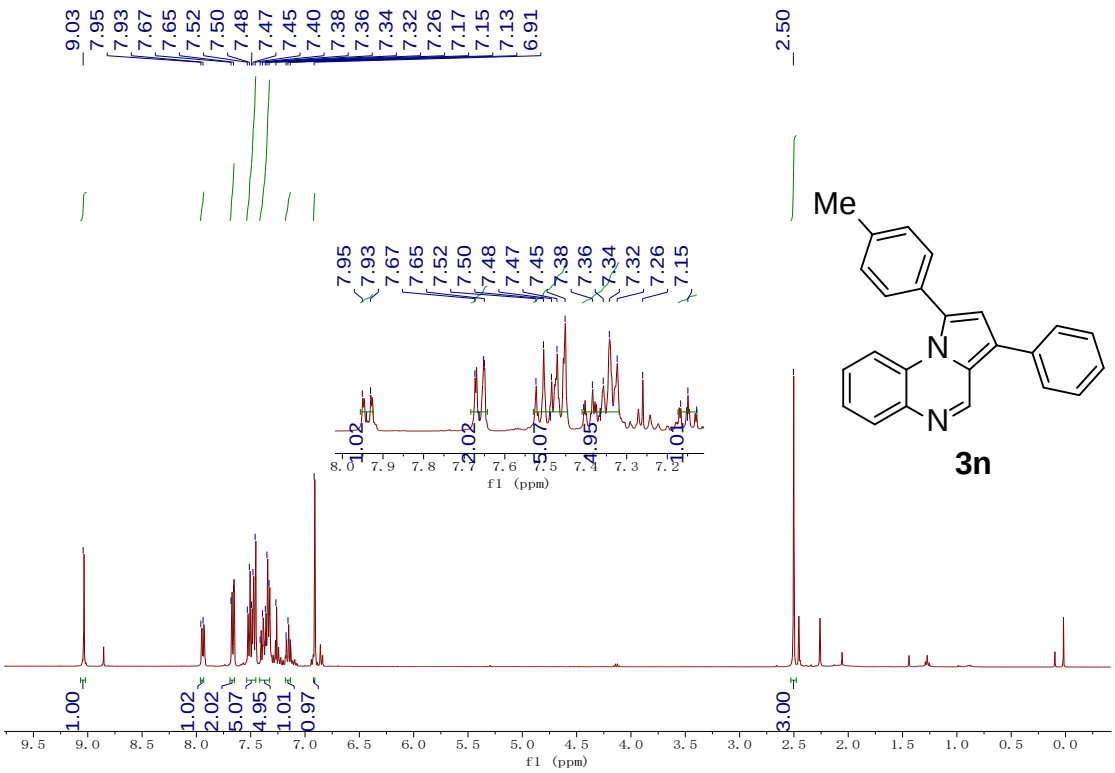


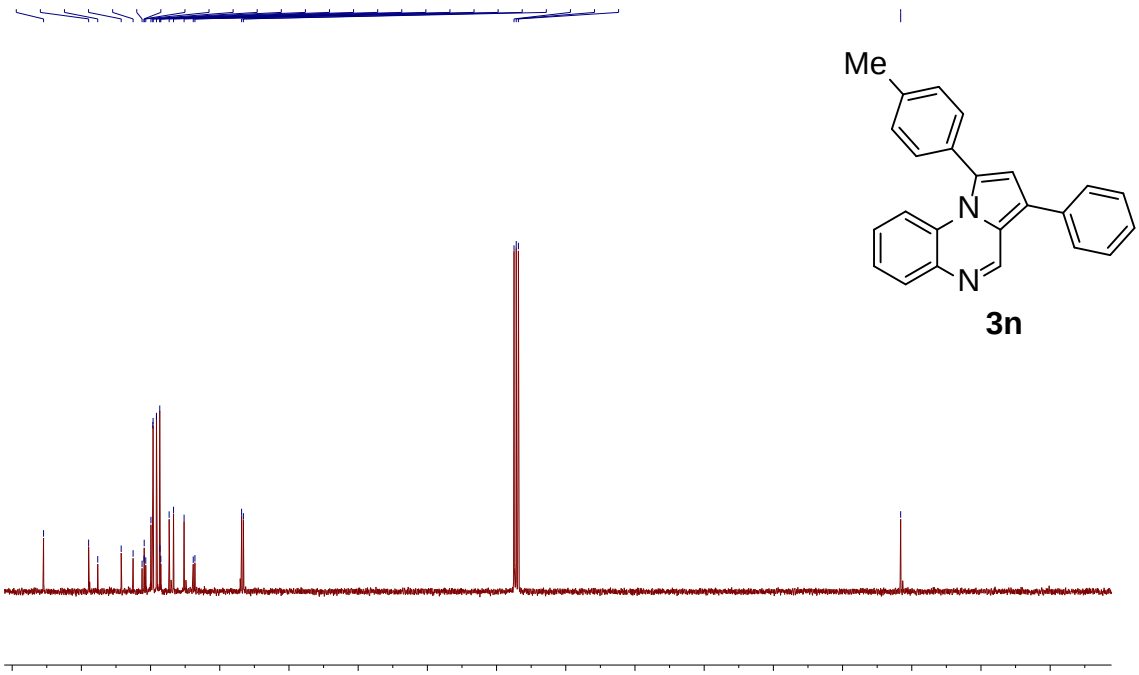
*7-chloro-1,3-di-p-tolylpyrrolo[1,2-a]quinoxaline [**3m**]*



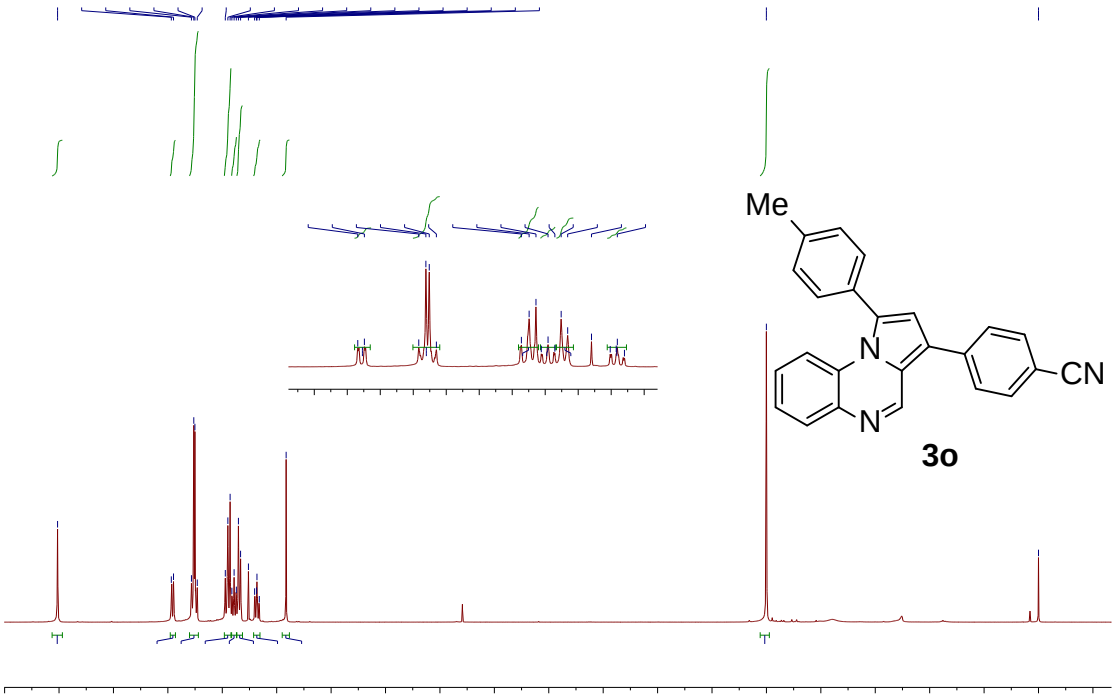


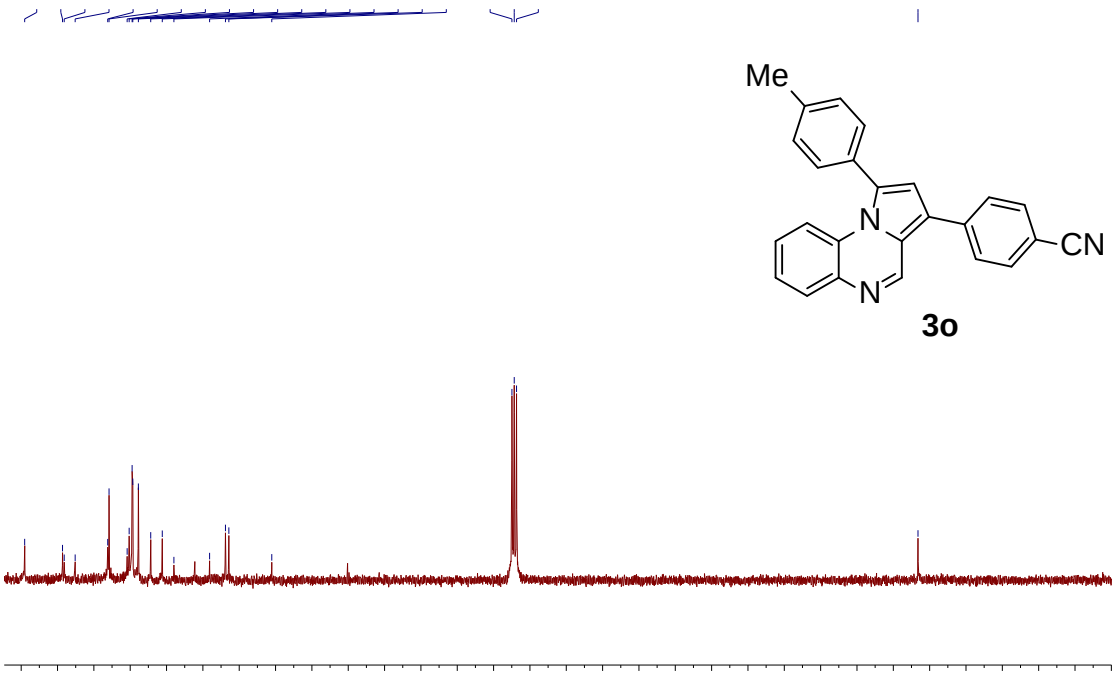
*3-phenyl-1-(p-tolyl)pyrrolo[1,2-a]quinoxaline [**3n**]*



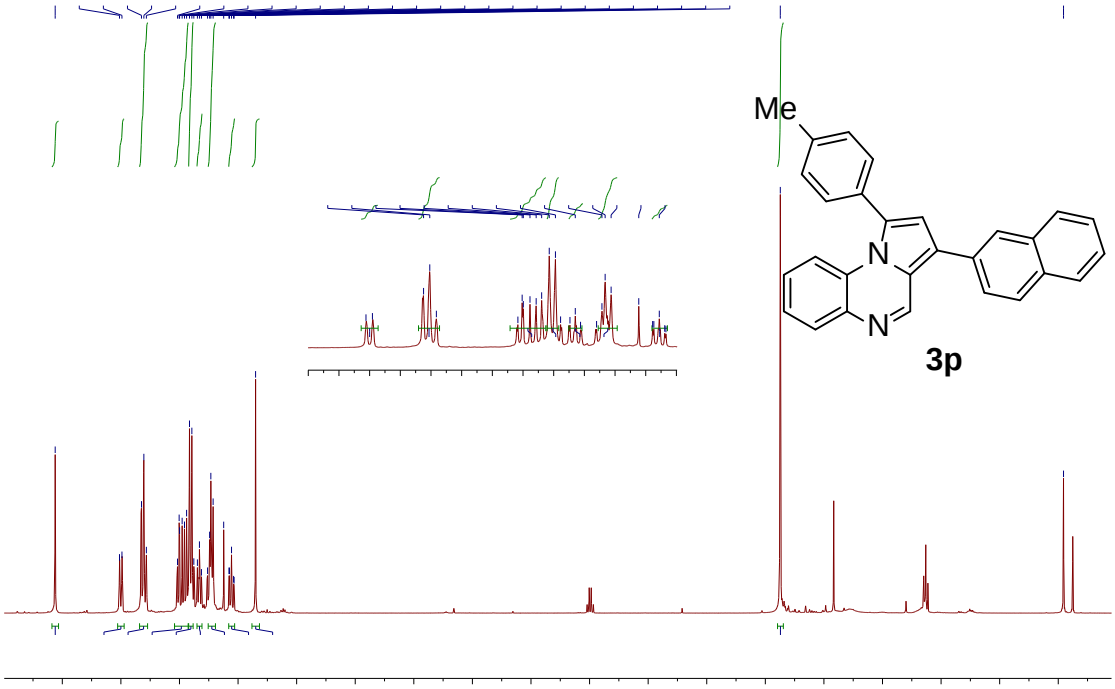


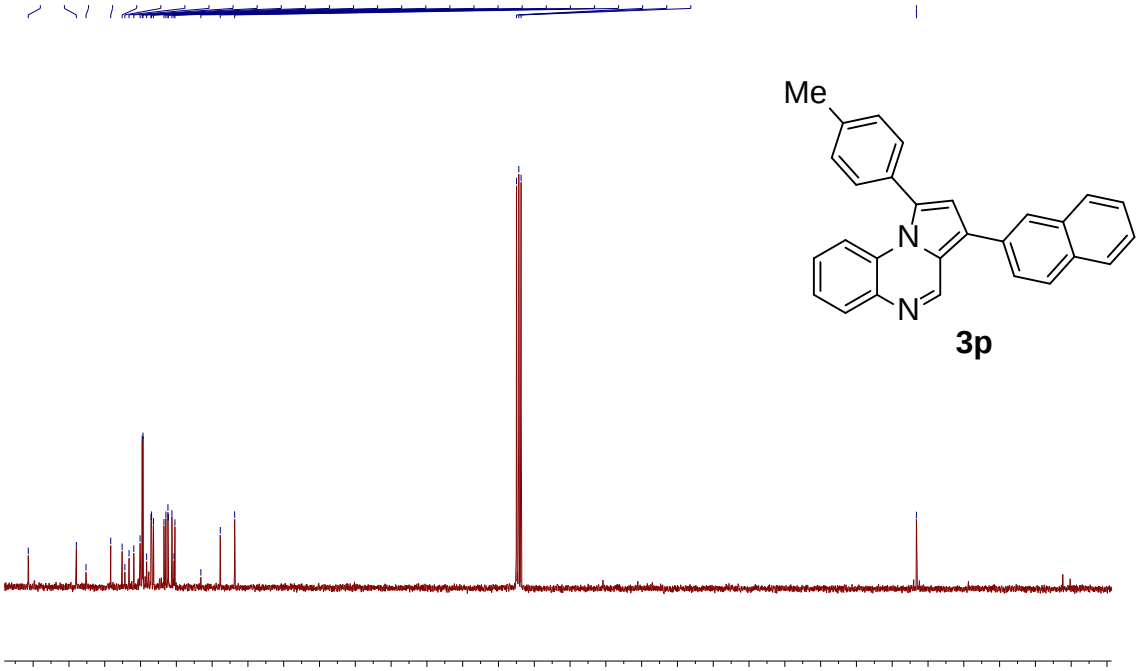
*4-(1-(p-tolyl)pyrrolo[1,2-a]quinoxalin-3-yl)benzonitrile [**3o**]*



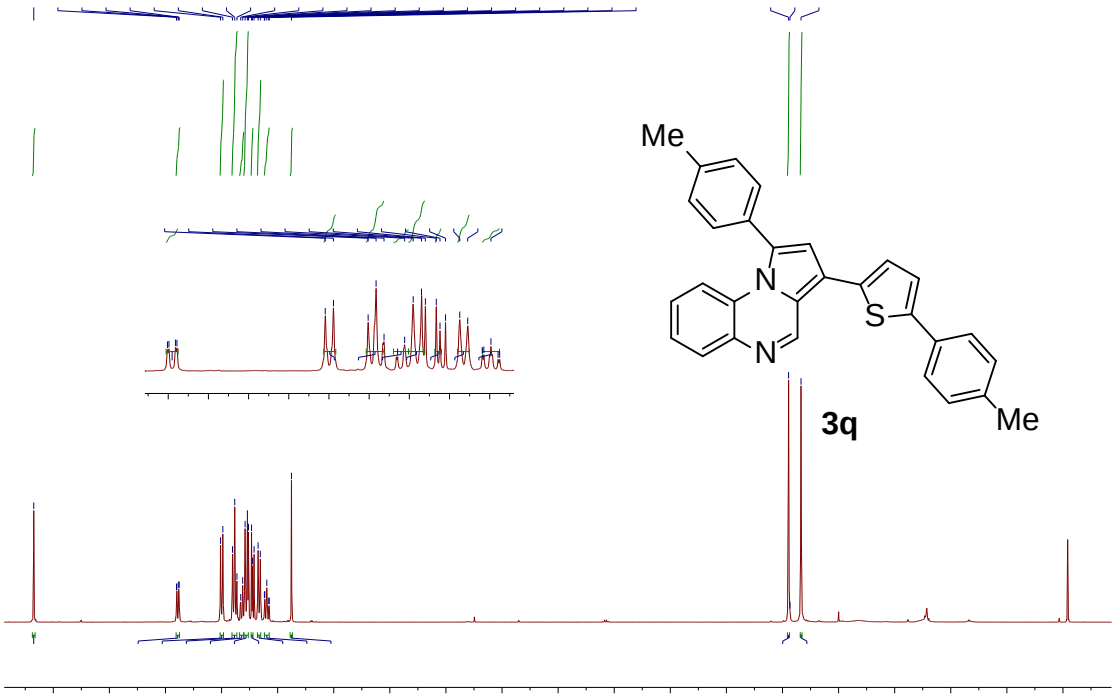


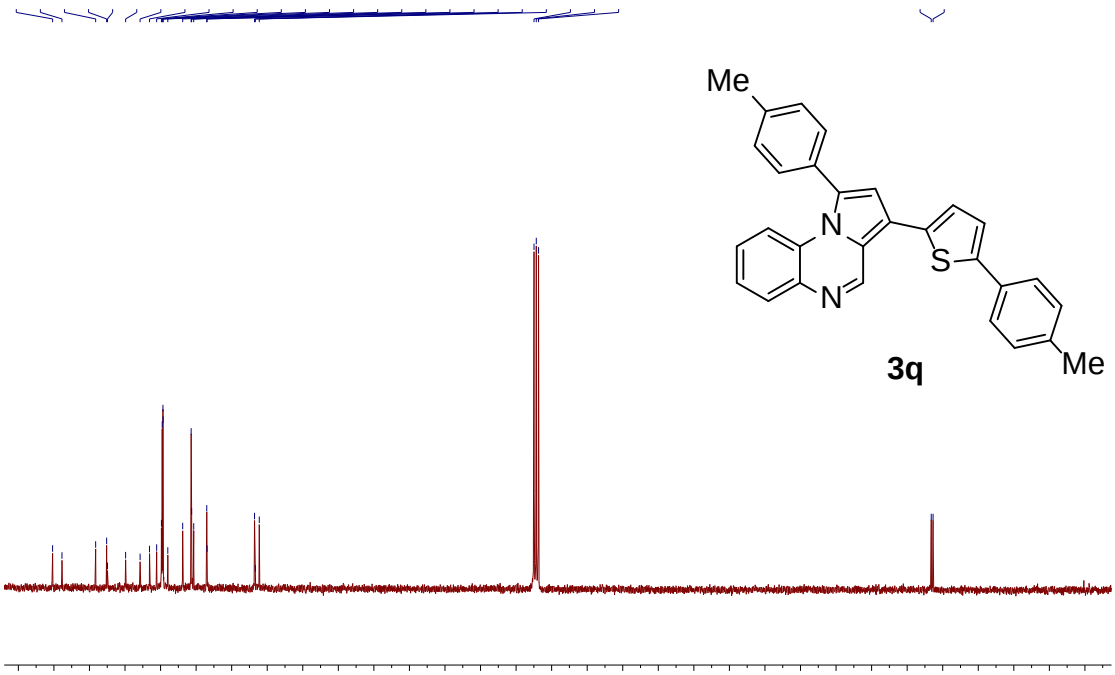
*3-(naphthalen-2-yl)-1-(p-tolyl)pyrrolo[1,2-a]quinoxaline [**3p**]*



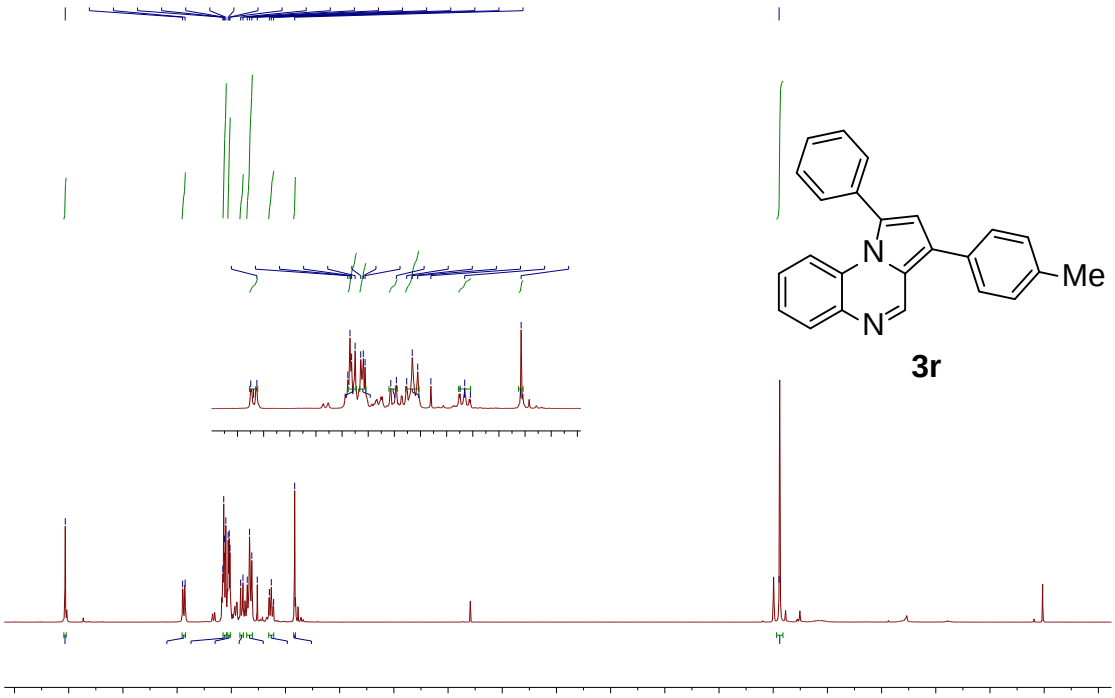


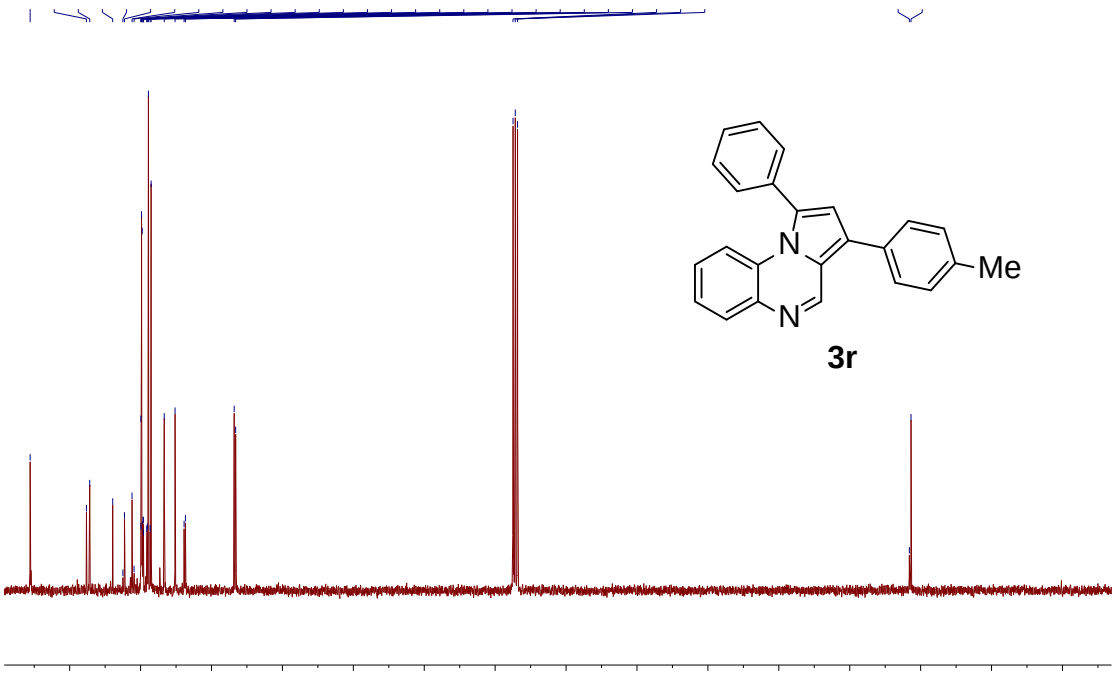
*1-(p-tolyl)-3-(5-(p-tolyl)thiophen-2-yl)pyrrolo[1,2-a]quinoxaline [**3q**]*



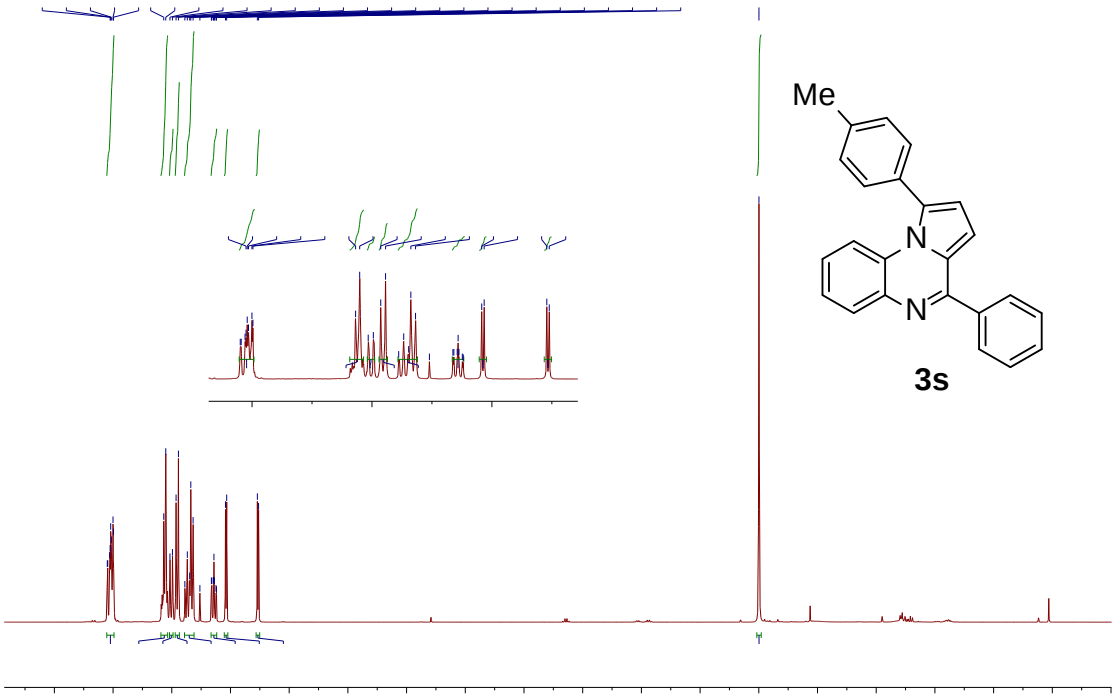


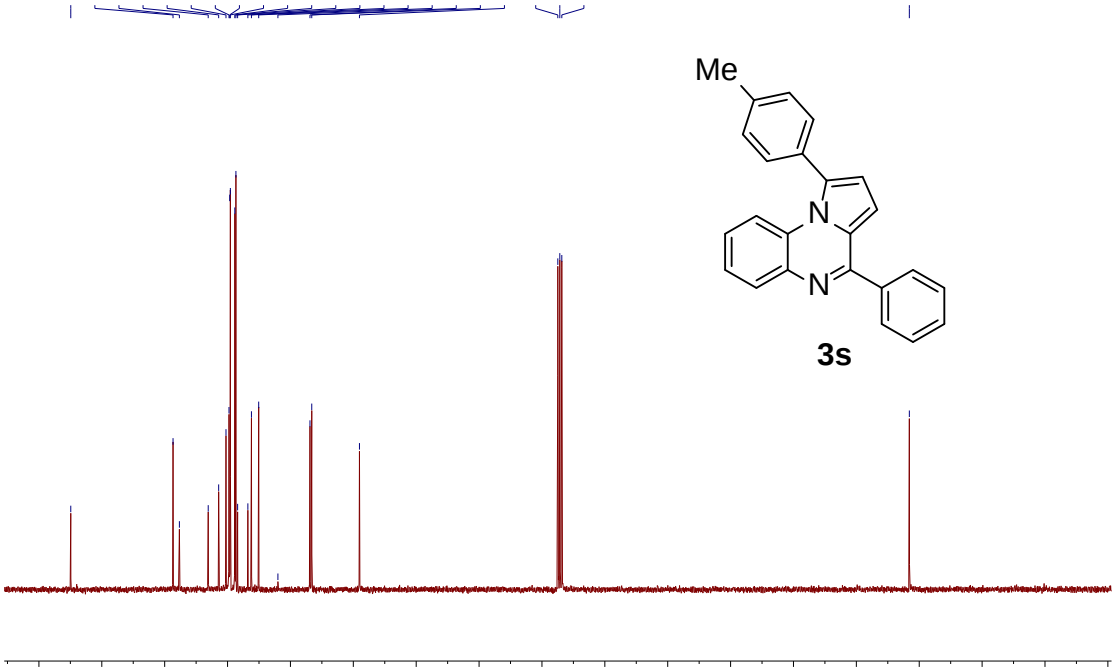
*1-phenyl-3-(p-tolyl)pyrrolo[1,2-a]quinoxaline [**3r**]*



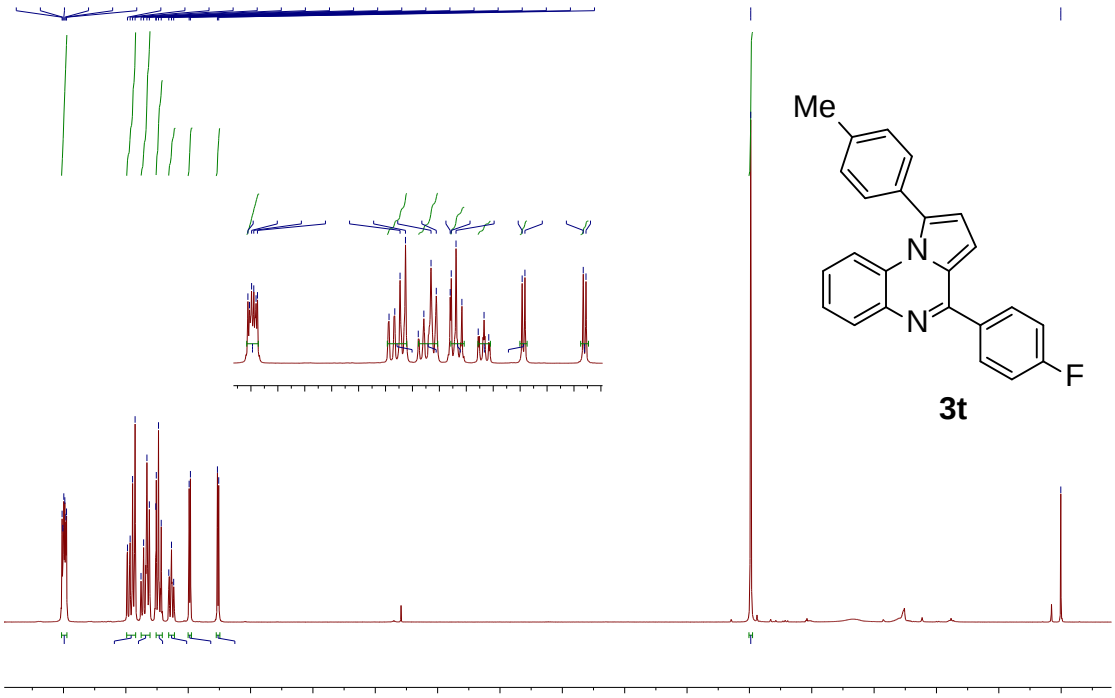


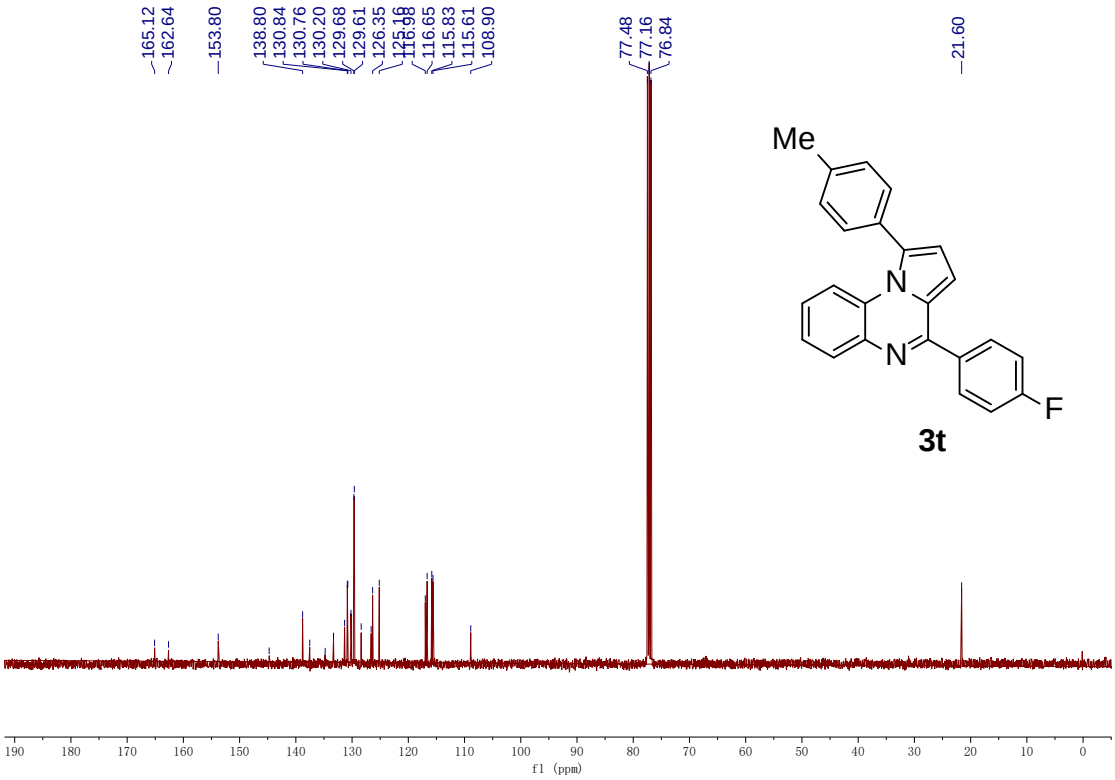
*4-phenyl-1-(p-tolyl)pyrrolo[1,2-a]quinoxaline [**3s**]*





*4-(4-fluorophenyl)-1-(p-tolyl)pyrrolo[1,2-a]quinoxaline [**3t**]*

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77.16
76.84
21.60
Me
N
N
F
3t
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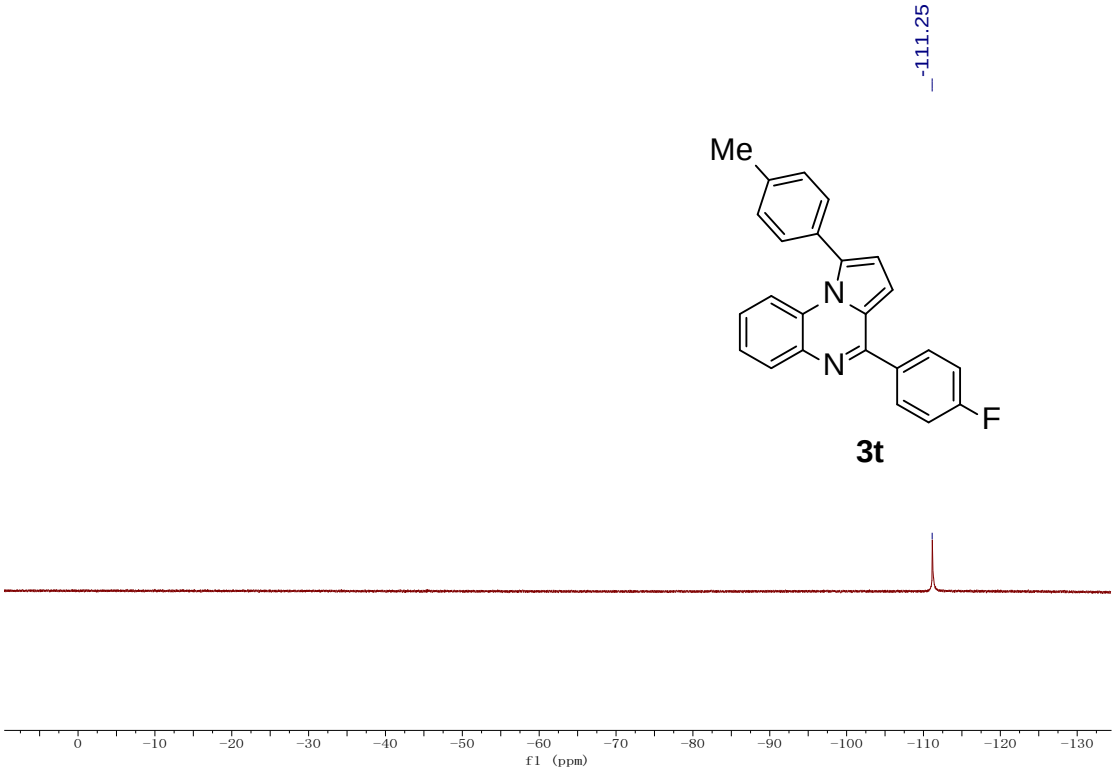
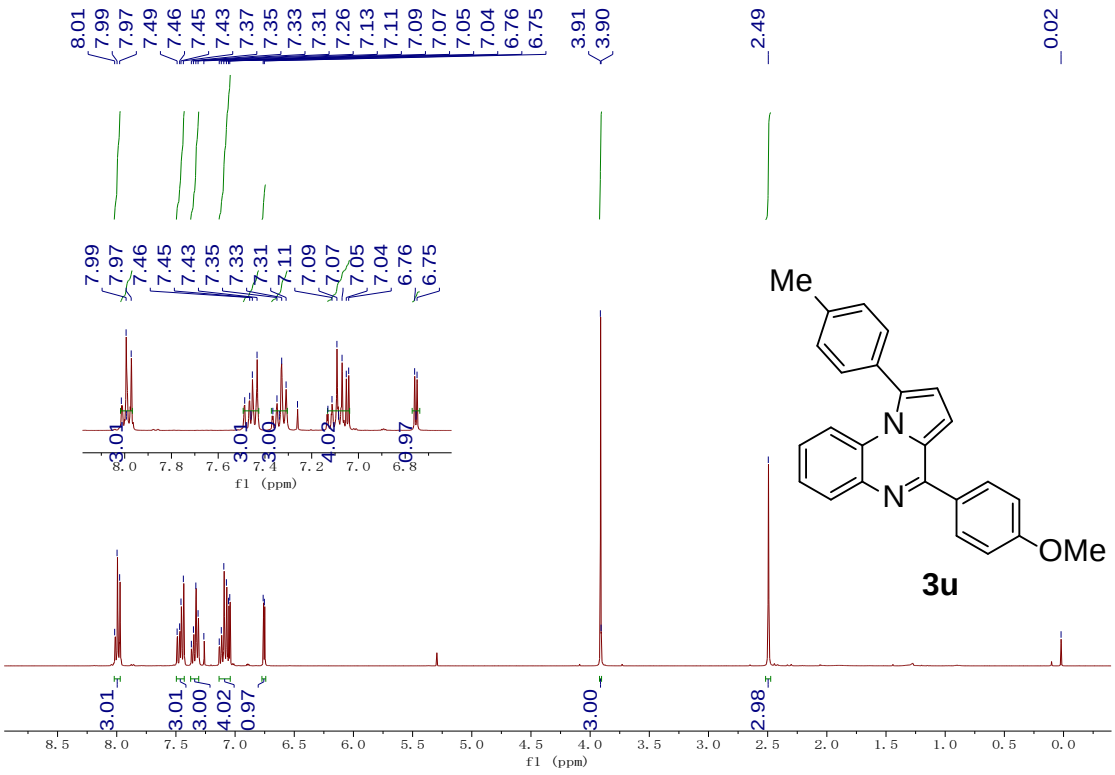
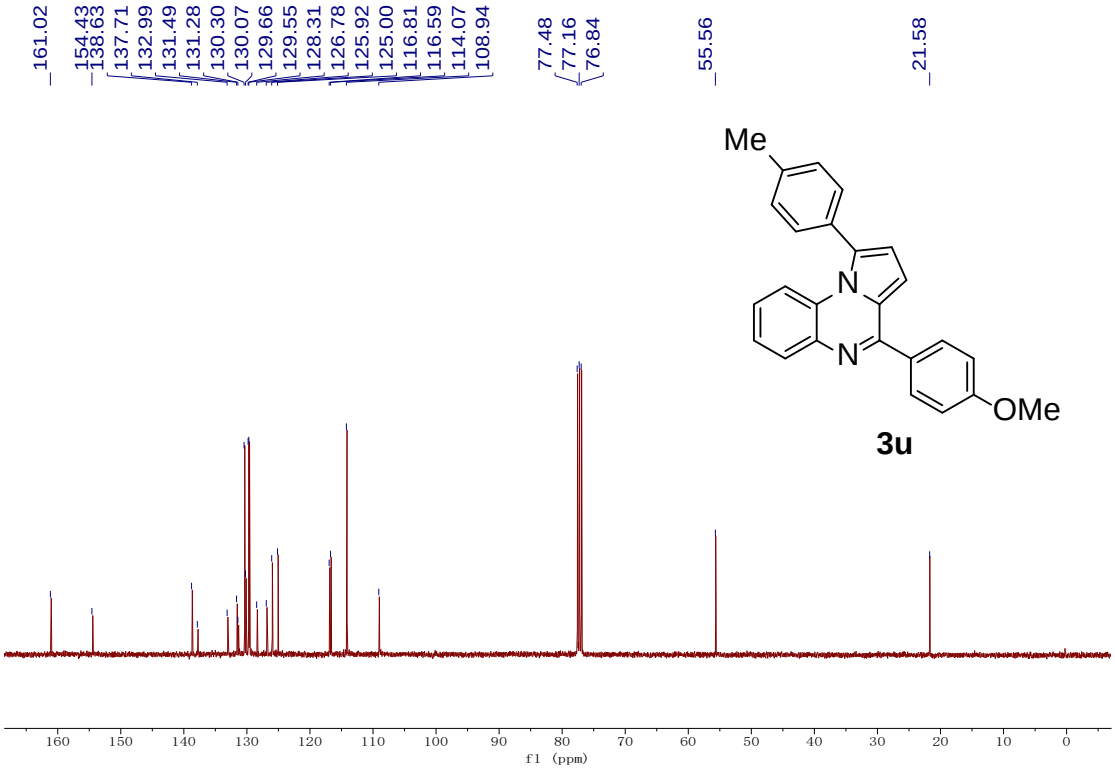
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

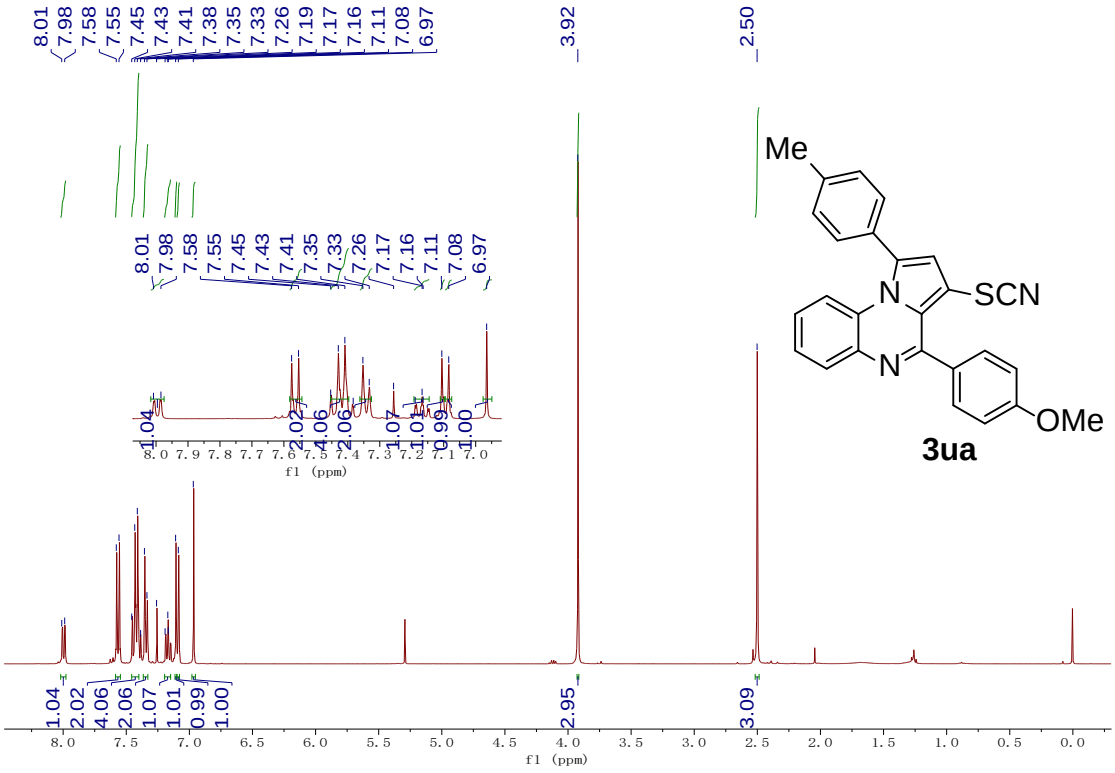

-111.25
Me
N
N
F
3t
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
f1 (ppm)

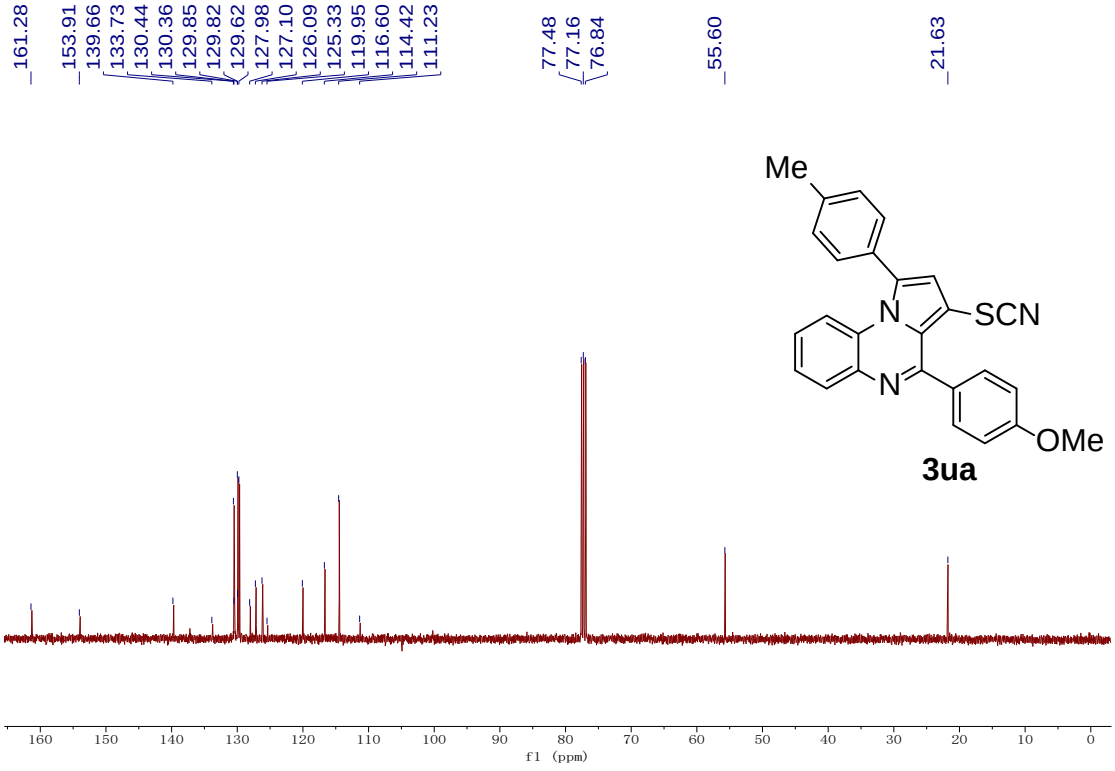
4-(4-methoxyphenyl)-1-(p-tolyl)pyrrolo[1,2-a]quinoxaline [3u]





*4-(4-methoxyphenyl)-3-thiocyanato-1-(p-tolyl)pyrrolo[1,2-a]quinoxaline [**3ua**]*





*1,4-di-p-tolylpyrrolo[1,2-a]quinoxaline [**3v**]*