Supporting Information

Highly Selective C3-H Iodination of Pyrrolo[1,2-*a*]quinoxaline

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CONTENTS

1. Experimental

Unless otherwise noted, all reactions were performed under an argon atmosphere in Schlenk tubes. Melting points were determined with a fusiometer and are not corrected. The materials obtained from commercial suppliers were used without further purification. For chromatography, Qingdao Ocean Chemical 200-300 mesh silica gel was employed. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance III HD 400 MHz spectrometer in $CDCl_3$ solution and the chemical shifts are reported in ppm (δ) relative to the internal standard tetramethylsilane (TMS) (0 ppm). High-resolution mass spectra (HRMS) were acquired in electrospray ionization (APCI) mode using a TOF mass analyzer.

General procedure for pyrrolo[1,2-*a*]quinoxalines with TBAI (Method A).

A reaction tube (10 mL) was charged with pyrrolo[1,2-*a*]quinoxaline **1** (0.3 mmol), TBAI (0.6 mmol), $TsNHNH_2$ (3 equiv.), TBHP (0.5 mL), and 1,4-dioxane (0.5 mL). Then the mixture was stirred at 80 ^{o}C for 12-16 h. After reaction completion, the solution was quenched the saturated solution of sodium thiosulfate (2 mL) and extracted with dichloromethane (3 × 10 mL). Then, the combined organic layer was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the crude was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the final products **3a-3p**.

General procedure for pyrrolo[1,2-*a*]quinoxalines with I_2 in the presence of PTSA·H_2O (Method B).

A reaction tube (10 mL) was charged with pyrrolo[1,2-*a*]quinoxaline **1** (0.2 mmol), I_2 (0.2 mmol), PTSA·H_2O (15 mol%), and DMSO (2 mL). Then the mixture was stirred at 100 ^{o}C for 12-22 h. After reaction completion, the solution was quenched the saturated solution of sodium thiosulfate (2 mL) and extracted with EtOAc (3 × 10 mL). Then, the combined organic layer was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the crude was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the final products **3a-3q**.

General procedure for the synthesis of 3q'.

A reaction tube (10 mL) was charged with indolo[1,2-*a*]quinoxaline (0.3 mmol), TBAI (0.6 mmol), $TsNHNH_2$ (3 equiv.), TBHP (0.5 mL), and 1,4-dioxane (0.5 mL). Then the mixture was stirred at 80 ^oC for 12 h. After reaction completion, the solution was quenched the saturated solution of sodium thiosulfate (2 mL) and extracted with dichloromethane (3 × 10 mL). Then, the combined organic layer was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the crude was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the corresponding products **3q'**.

General procedure for the gram-scale synthesis of 3a.

A 50 mL round-bottomed flask was charged with **1a** (6 mmol), I_2 (6 mmol), $PTSA{\cdot}H_2O$ (15 mol%), and DMSO (15 mL). The solution was stirred at 100 ^oC for 22 h. After reaction completion, the solution was quenched the saturated solution of sodium thiosulfate (5 mL) and extracted with ethyl acetate (3 × 10 mL). Then, the combined organic layer was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the crude was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the final product **3a** (1.306 g, 74% yield).

Typical procedure for the Pd-catalyzed Suzuki-Miyaura reactions of 3a with arylboronic acids.

To a reaction tube equipped with a magnetic stirring bar, **3a** (0.2 mmol), arylboronic acid (0.4 mmol), $Pd(PPh_3)_4$ (5 mol%), Na_2CO_3 (2 equiv.), and 1,4-dioxane/H_2O (4:1, 2.5 mL) were added. The reaction vessel was allowed to stir at 80 ^oC for 5 h under N_2 atmosphere. After completion of the reaction, the mixture was washed with the saturated NaCl aqueous solution (10 mL) and extracted with dichloromethane (3 × 10 mL). The organic phase was dried over Na_2SO_4 and concentrated in a vacuum. The crude was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the final product **5a-5h**.

Typical procedure for the Pd-catalyzed Sonogashira reactions of 3a with terminal alkynes.

To a reaction tube equipped with a magnetic stirring bar, **3a** (0.2 mmol), terminal alkyne (0.3 mmol), $PdCl_2(PPh_3)_2$ (5 mol%), CuI (20 mol%), and Et_3N (2.0 mL) were added. The reaction vessel was allowed to stir at 65 °C for 12 h under air atmosphere. After completion of the reaction, an appropriate amount of silica gel was added to the solution, and the mixture was concentrated in a vacuum. The crude was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the final product **5i-5n**.

2. Characterization data of the products

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

Light yellow solid (Method A: 77.6 mg, 88%; Method B: 50.6 mg, 86%); mp 177-178 °C. ^{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 145.3, 135.7, 130.2, 128.0, 127.2, 126.4, 125.6, 120.9, 115.4, 113.0, 59.9; HRMS (APCI): m/z calcd for $C_{11}H_7IN_2$ $[M+H]^+$: 294.9723, found: 294.9723.

8-fluoro-3-iodopyrrolo[1,2-a]quinoxaline [3b]

Light yellow solid (Method A: 66.5 mg, 71%; Method B: 62.4 mg, 93%); mp 180-181 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.98 (dd, J = 9.0, 5.8 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.50 (dd, J = 9.0, 2.7 Hz, 1H), 7.20 (ddd, J = 8.9, 8.2, 2.7 Hz, 1H), 7.02 (d, J = 2.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 132.3, 132.2, 121.6, 115.7, 113.9, 113.7, 100.3, 100.1, 60.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.4; HRMS (APCI): m/z calcd for $C_{11}H_6FIN_2$ $[M+H]^+$: 312.9632, found: 312.9624.

4-iodo-8-methylpyrrolo[1,2-a]quinoxaline [3c]

Light yellow solid ((Method A: 62.9 mg, 68%; Method B: 49.3 mg, 80%); mp 175-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.80 (d, J = 2.7 Hz, 2H), 7.56 (s, 1H), 7.28 – 7.21 (m, 1H), 6.94 (d, J = 2.8 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 138.8, 133.9, 130.0, 127.1, 127.0, 126.7, 121.0, 115.2, 113.2, 59.6, 21.9; HRMS (APCI): m/z calcd for $C_{12}H_9IN_2$ $[M+H]^+$: 308.9883, found: 308.9876.

3-iodo-7-methylpyrrolo[1,2-a]quinoxaline [3d]

Light yellow solid (Method A:57.3 mg, 62%; Method B: 61.6 mg, 59%); mp 79-80 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.80 (d, *J* = 2.7 Hz, 1H), 7.74 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.30 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.93 (d, *J* = 2.8 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 135.8, 135.6, 130.0, 129.3, 126.5, 125.2, 120.8, 115.4, 112.9, 59.7, 21.1; HRMS (APCI): m/z calcd for $C_{12}H_9IN_2$ $[M+H]^+$: 308.9883, found: 308.9879.

4-iodo-4-phenylpyrrolo[1,2-a]quinoxaline [3e]

Light yellow solid (Method A: 78.9 mg, 71%; Method B: 40.7 mg, 55%); mp 110-111 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.94 (d, *J* = 2.9 Hz, 1H), 7.81 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.55 – 7.50 (m, 4H), 7.49 – 7.43 (m, 1H), 7.02 (d, *J* = 2.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 137.1, 135.5, 130.3, 129.9, 129.3, 128.2, 127.9, 127.3, 125.8, 124.11, 124.06, 116.3, 113.2, 60.6; HRMS (APCI): m/z calcd for $C_{17}H_{11}IN_2$ $[M+H]^+$: 371.0040, found: 371.0035.

3-iodo-4-(p-tolyl)pyrrolo[1,2-a]quinoxaline [3f]

Light yellow solid (Method A: 61.1 mg, 53%; Method B: 40.0 mg, 52%); mp 152-153 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.92 (d, *J* = 2.9 Hz, 1H), 7.79 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.51 – 7.40 (m, 4H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 2.9 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 139.3, 135.6, 134.3, 130.2, 129.8, 128.8, 127.7, 127.3, 125.7, 124.2, 124.0, 116.2, 113.2, 60.6, 21.6; HRMS (APCI): m/z calcd for $C_{18}H_{13}IN_2$ $[M+H]^+$: 385.0196, found: 385.0188.

3-iodo-4-(4-nitrophenyl)pyrrolo[1,2-a]quinoxaline [3g]

Light yellow solid (Method A: 80.1 mg, 65%; Method B: 59.0 mg, 71%); mp 202-203 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.5 Hz, 2H), 8.06 – 7.97 (m, 2H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.55 (dt, *J* = 34.4, 7.5 Hz, 2H), 7.08 (d, *J* = 3.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 148.6, 143.4, 135.2, 131.2, 130.4, 128.7, 127.4, 126.1, 124.3, 123.5, 123.4, 116.7, 113.4, 60.4; HRMS (APCI): m/z calcd for $C_{17}H_{10}IN_3O_2$ $[M+H]^+$: 415.9890, found: 415.9885.

4-(4-fluorophenyl)-3-iodopyrrolo[1,2-a]quinoxaline [3h]

Light yellow solid (Method A: 94.3 mg, 81%; Method B: 58.2 mg, 75%); mp 140-141 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 7.9, 1.4 Hz, 1H), 7.94 (d, J = 2.9 Hz, 1H), 7.80 (dd, J = 8.2, 1.1 Hz, 1H), 7.60 – 7.42 (m, 4H), 7.20 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 2.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 135.4, 133.2, 133.2, 131.9, 131.8, 130.2, 128.0, 127.3, 125.8, 124.1, 124.0, 116.4, 115.3, 115.1, 113.2, 60.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.0; HRMS (APCI): m/z calcd for $C_{17}H_{10}FIN_2$ $[M+H]^+$: 388.9945, found: 388.9937.

4-iodo-4-(4-methoxyphenyl)pyrrolo[1,2-a]quinoxaline [3i]

Light yellow solid (Method A: 70.8 mg, 59%; Method B: 50.4 mg, 63%); mp 176-177 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 7.9, 1.6 Hz, 1H), 7.93 (d, J = 2.9 Hz, 1H), 7.80 (dd, J = 8.1, 1.4 Hz, 1H), 7.58 – 7.40 (m, 4H), 7.09 – 6.98 (m, 3H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 155.1, 135.6, 131.4, 130.1, 129.7, 127.7, 127.2, 125.7, 124.3, 124.0, 116.3, 113.6, 113.2, 60.6, 55.4; HRMS (APCI): m/z calcd for $C_{18}H_{13}IN_2O$ $[M+H]^+$: 401.0145, found: 401.0142.

5-(4-chlorophenyl)-3-iodopyrrolo[1,2-a]quinoxaline [3j]

Light yellow solid (Method A: 79.0 mg, 65%; Method B: 55.8 mg, 69%); mp 177-178 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.9 Hz, 1H), 7.75 (dd, J = 5.9, 2.9 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.31 (dq, J = 16.3, 7.8 Hz, 6H), 6.83 (t, J = 3.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 135.6, 135.5, 135.4, 131.4, 130.3, 128.4, 128.1, 127.3, 125.9, 124.1, 123.9, 116.4, 113.2, 60.5; HRMS (APCI): m/z calcd for $C_{17}H_{10}ClIN_2$ $[M+H]^+$: 404.9650, found: 404.9643.

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

Light yellow solid (Method A: 110.5 mg, 82%; Method B: 59.3 mg, 66%); mp 163-164 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 1H), 7.73 (s, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.46 (dd, J = 8.0, 2.0 Hz, 2H), 7.34 – 7.22 (m, 4H), 6.84 – 6.80 (m, 1H);^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 136.0, 135.4, 131.7, 131.3, 130.2, 128.1, 127.3, 125.9, 124.1, 123.81, 123.78, 116.5, 113.2, 60.6; HRMS (APCI): m/z calcd for $C_{17}H_{10}BrIN_2$ $[M+H]^+$: 448.9145, found: 448.9134.

4-(3-iodopyrrolo[1,2-a]quinoxalin-4-yl)benzonitrile [3l]

Light yellow solid (Method A: 70.0 mg, 59%); mp 238-249 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.51 – 7.43 (m, 1H), 7.04 (d, *J* = 2.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 140.4, 134.1, 130.9, 129.8, 129.2, 127.5, 126.2, 125.0, 123.1, 122.4, 117.7, 115.7, 112.3, 112.0, 59.3; HRMS (APCI): m/z calcd for $C_{17}H_{10}BrIN_2$ $[M+H]^+$: 395.9992, found: 395.9994.

3-iodo-4-(4-methoxyphenyl)-7-methylpyrrolo[1,2-a]quinoxaline [3m]

Light yellow solid (Method A: 74.6 mg, 60%; Method B: 58.8 mg, 71%); mp 107-108 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.9 Hz, 1H), 7.80 – 7.78 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.32 – 7.25 (m, 1H), 7.07 – 7.02 (m, 2H), 6.99 (d, *J* = 2.9 Hz, 1H), 3.89 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 155.0, 135.6, 135.5, 131.4, 129.9, 129.8, 128.8, 125.1, 124.2, 123.8, 116.1, 113.5, 112.9, 60.1, 55.4, 21.2; HRMS (APCI): m/z calcd for $C_{19}H_{15}IN_2O$ $[M+H]^+$: 415.0302, found: 415.0298.

3-iodo-7-methyl-4-(4-nitrophenyl)pyrrolo[1,2-a]quinoxaline [3n]

Orange solid (Method A: 104.3 mg, 81%; Method B: 55.8 mg, 65%); mp 234-235 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 2.9 Hz, 1H), 7.79 – 7.78 (m, 2H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.75 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.39 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.04 (d, *J* = 2.9 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 148.5, 143.5, 136.1, 135.2, 131.2, 130.1, 129.8, 125.2, 124.0, 123.4, 123.3, 116.6, 113.1, 59.9, 21.2; HRMS (APCI): m/z calcd for $C_{18}H_{12}IN_3O_2$ $[M+H]^+$: 430.0047, found: 430.0044.

4-(2,4-dichlorophenyl)-3-iodopyrrolo[1,2-a]quinoxaline [3o]

Light yellow solid (Method A: 113.3 mg, 86%; Method B: 75.5 mg, 86%); mp 154-155 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.96 (d, *J* = 2.9 Hz, 1H), 7.84 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.56 (d, *J* = 1.9 Hz, 2H), 7.50 – 7.45 (m, 1H), 7.43 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 2.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 135.9, 135.4, 135.3, 134.8, 132.0, 130.4, 129.5, 128.5, 127.7, 127.3, 126.0, 124.0, 123.7, 116.5, 113.4, 60.4; HRMS (APCI): m/z calcd for $C_{17}H_9Cl_2IN_2$ $[M+H]^+$: 438.9260, found: 438.9255.

4-(furan-2-yl)-3-iodopyrrolo[1,2-a]quinoxaline [3p]

Brown solid (Method A: 17.3 mg, 16%; Method B: 17.3 mg, 24%); mp 72-73 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 2.9 Hz, 1H), 7.87 – 7.78 (m, 1H), 7.72 – 7.66 (m, 1H), 7.58 – 7.49 (m, 1H), 7.51 – 7.42 (m, 1H), 7.08 (d, J = 2.9 Hz, 1H), 6.95 (d, J = 3.3 Hz, 1H), 6.63 (dd, J = 3.3, 1.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 145.3, 143.2, 135.2, 130.4, 129.6, 128.5, 128.5, 127.3, 125.9, 124.3, 116.5, 113.4, 113.2, 111.6; HRMS (APCI): m/z calcd for $C_{15}H_9IN_2O$ $[M+H]^+$: 360.9832, found: 360.9823.

7-iodoindolo[1,2-a]quinoxaline [3q]

Orange solid (52.3 mg, 76%); mp 195-196 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.37 – 8.24 (m, 2H), 7.99 (dd, J = 7.9, 1.5 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.55 (ddd, J = 8.5, 5.4, 1.7 Hz, 2H), 7.52 – 7.39 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 136.4, 132.8, 131.3, 130.7, 130.4, 129.1, 129.0, 125.4, 124.6, 123.5, 123.1, 114.7, 114.5, 58.6; HRMS (APCI): m/z calcd for $C_{15}H_9IN_2$ $[M+H]^+$: 344.9883, found: 344.9880.

4-(furan-3-yl)-3-iodopyrrolo[1,2-a]quinoxaline [3q']

Orange solid (101.7 mg, 91%); mp 245-246 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 8.31 (s, 2H), 8.25 (d, J = 9.2 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.56 (t, J = 7.7 Hz, 1H), 7.46 – 7.36 (m, 3H), 7.13 (d, J = 8.2 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 142.9, 139.4, 135.3, 131.3, 130.0, 129.0, 128.8, 128.1, 127.9, 125.3, 125.0, 124.8, 124.7, 124.2, 120.4, 114.5, 114.0, 109.6, 20.4, 0.0; HRMS (APCI): m/z calcd for $C_{22}H_{16}N_2O_2S$ $[M+H]^+$: 373.1005, found: 373.0997.

3-phenylpyrrolo[1,2-a]quinoxaline [5a]

Light yellow solid (44.5 mg, 91%); mp 176-177 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.96 (dd, J = 7.9, 1.6 Hz, 1H), 7.89 (d, J = 2.8 Hz, 1H), 7.80 (dd, J = 8.2, 1.4 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.49 (td, J = 7.6, 1.9 Hz, 3H), 7.43 (td, J = 7.6, 1.5 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.00 (d, J = 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 136.1, 134.4, 130.0, 129.0, 128.2, 127.9, 127.0, 125.3, 123.6, 122.6, 114.1, 113.7, 113.6; HRMS (APCI): m/z calcd for $C_{17}H_{12}N_2$ $[M+H]^+$: 245.1073, found: 245.1069.

3-(p-tolyl)pyrrolo[1,2-a]quinoxaline [5b]

Light yellow solid (50.1 mg, 97%); mp 134-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.96 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.92 (d, *J* = 2.6 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.47 – 7.41 (m, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 2.7 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 136.9, 136.1, 131.5, 130.0, 129.7, 128.1, 128.0, 127.9, 125.3, 123.7, 122.6, 114.0, 113.7, 113.6, 21.2; HRMS (APCI): m/z calcd for $C_{18}H_{14}N_2$ $[M+H]^+$: 259.1230,found: 259.1227.

3-(4-methoxyphenyl)pyrrolo[1,2-a]quinoxaline [5c]

Light yellow solid (33.5 mg, 61%); mp 134-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.95 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.91 (d, *J* = 2.7 Hz, 1H), 7.83 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.56 (d, *J* = 2.1 Hz, 2H), 7.51 (td, *J* = 8.3, 7.8, 1.5 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 2.8 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 145.2, 136.1, 129.9, 129.3, 128.0, 127.9, 126.9, 125.3, 123.6, 122.5, 114.5, 114.0, 113.7, 113.5, 55.4; HRMS (APCI): m/z calcd for $C_{18}H_{14}N_2O$ $[M+H]^+$: 275.1179, found: 275.1172.

4-(pyrrolo[1,2-a]quinoxalin-3-yl)benzonitrile [5d]

Light yellow solid (52.8 mg, 98%); mp 224-225 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.99 (dd, *J* = 9.1, 2.2 Hz, 2H), 7.88 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.79 – 7.70 (m, 4H), 7.58 (td, *J* = 8.3, 7.8, 1.5 Hz, 1H), 7.54 – 7.46 (m, 1H), 7.05 (d, *J* = 2.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 139.2, 136.1, 132.8, 130.2, 128.5, 128.4, 127.6, 125.9, 122.9, 121.3, 119.0, 114.7, 113.9, 113.8, 110.3; HRMS (APCI): m/z calcd for $C_{18}H_{11}N_3$ $[M+H]^+$: 270.1026, found: 270.1020.

methyl 4-(pyrrolo[1,2-a]quinoxalin-3-yl)benzoate [5e]

Light yellow solid (31.4 mg, 52%); mp 198-199 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 2H), 8.02 – 7.95 (m, 2H), 7.88 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.56 (td, *J* = 8.3, 7.8, 1.5 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.08 (d, *J* = 2.8 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 144.7, 139.1, 136.1, 130.4, 130.1, 128.5, 128.3, 127.9, 127.8, 125.7, 122.9, 122.3, 114.5, 113.82, 113.80, 52.2; HRMS (APCI): m/z calcd for $C_{19}H_{14}N_2O_2$ $[M+H]^+$: 303.1128, found: 303.1123.

3-(4-vinylphenyl)pyrrolo[1,2-a]quinoxaline [5f]

Light yellow solid (36.2 mg, 67%); mp 99-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.97 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.94 (d, *J* = 2.7 Hz, 1H), 7.85 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.54 (dt, *J* = 6.4, 1.9 Hz, 3H), 7.48 – 7.43 (m, 1H), 7.03 (d, *J* = 2.8 Hz, 1H), 6.78 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.82 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.30 (dd, *J* = 10.9, 0.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 136.4, 136.1, 133.9, 130.0, 128.3, 128.0, 127.9, 126.9, 125.4, 123.3, 122.7, 114.2, 113.9, 113.7, 113.6; HRMS (APCI): m/z calcd for $C_{19}H_{14}N_2$ $[M+H]^+$: 271.1230, found: 271.1227.

3-(naphthalen-2-yl)pyrrolo[1,2-a]quinoxaline [5g]

Light yellow solid (57.1 mg, 97%); mp 78-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.08 (s, 1H), 7.99 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.88 (dt, *J* = 4.8, 2.4 Hz, 2H), 7.82 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.76 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.45 (td, *J* = 7.7, 1.4 Hz, 1H), 7.10 (d, *J* = 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 136.2, 133.8, 132.4, 131.8, 130.0, 128.7, 128.0, 127.9, 127.8, 126.7, 126.6, 126.5, 125.9, 125.4, 123.6, 122.9, 114.3, 113.8, 113.7; HRMS (APCI): m/z calcd for $C_{21}H_{14}N_2$ $[M+H]^+$: 295.1230, found: 295.1227.

3-(thiophen-3-yl)pyrrolo[1,2-a]quinoxaline [5h]

Light yellow solid (49.6 mg, 99%); mp 64-65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.93 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.84 (d, *J* = 2.7 Hz, 1H), 7.78 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.49 – 7.41 (m, 4H), 7.39 (dd, *J* = 4.6, 1.7 Hz, 1H), 6.96 (d, *J* = 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 136.1, 134.8, 130.0, 128.0, 127.8, 127.5, 126.4, 125.3, 122.6, 120.6, 118.1, 114.0, 113.7, 113.5; HRMS (APCI): m/z calcd for $C_{15}H_{10}N_2S$ $[M+H]^+$: 251.0637, found: 251.0634.

3-(phenylethynyl)pyrrolo[1,2-a]quinoxaline [5i]

Light yellow solid (47.8 mg, 89%); mp 140-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.83 – 7.76 (m, 2H), 7.61 – 7.57 (m, 2H), 7.55 – 7.49 (m, 1H), 7.49 – 7.44 (m, 1H), 7.37 (q, *J* = 7.0, 6.5 Hz, 3H), 7.00 (d, *J* = 2.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 135.3, 130.4, 129.2, 127.3, 127.2, 127.1, 126.54, 126.49, 124.7, 122.4, 115.9, 112.9, 112.7, 101.7, 91.5, 81.0; HRMS (APCI): m/z calcd for $C_{19}H_{12}N_2$ $[M+H]^+$: 269.1073, found: 269.1071.

3-(p-tolylethynyl)pyrrolo[1,2-a]quinoxaline [5j]

Light yellow solid (54.2 mg, 96%); mp 179-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.83 (s, 2H), 7.51 (dd, *J* = 19.3, 7.8 Hz, 4H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.00 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 138.3, 136.4, 131.4, 130.3, 129.2, 128.2, 127.7, 127.6, 125.7, 120.3, 117.0, 113.9, 113.8, 103.1, 92.7, 81.3, 21.6; HRMS (APCI): m/z calcd for $C_{20}H_{14}N_2$ $[M+H]^+$: 283.1230, found: 283.1228.

3-([1,1'-biphenyl]-4-ylethynyl)pyrrolo[1,2-a]quinoxaline [5k]

Light yellow solid (54.4 mg, 79%); mp 157-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.01 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.82 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.64 – 7.61 (m, 3H), 7.61 – 7.58 (m, 1H), 7.55 (td, *J* = 8.2, 7.8, 1.6 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 140.8, 140.4, 136.4, 133.0, 131.9, 130.4, 128.92, 128.89, 128.3, 127.6, 127.12, 127.09, 127.05, 127.0, 125.8, 122.3, 117.1, 114.0, 113.8, 102.9, 92.5, 82.8; HRMS (APCI): m/z calcd for $C_{25}H_{16}N_2$ $[M+H]^+$: 345.1386, found: 345.1384.

3-((4-methoxyphenyl)ethynyl)pyrrolo[1,2-a]quinoxaline [5l]

Light yellow solid (31.0 mg, 52%); mp 187-188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.01 – 7.96 (m, 1H), 7.85 – 7.79 (m, 2H), 7.53 (dd, *J* = 9.0, 2.1 Hz, 3H), 7.49 – 7.45 (m, 1H), 6.99 (d, *J* = 2.8 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 144.7, 136.4, 132.9, 130.3, 128.2, 127.7, 127.5, 125.7, 116.9, 115.5, 114.1, 113.9, 113.8, 103.2, 92.5, 80.6, 55.3; HRMS (APCI): m/z calcd for $C_{20}H_{14}N_2O$ $[M+H]^+$: 299.1179, found: 299.1177.

3-((4-chlorophenyl)ethynyl)pyrrolo[1,2-a]quinoxaline [5m]

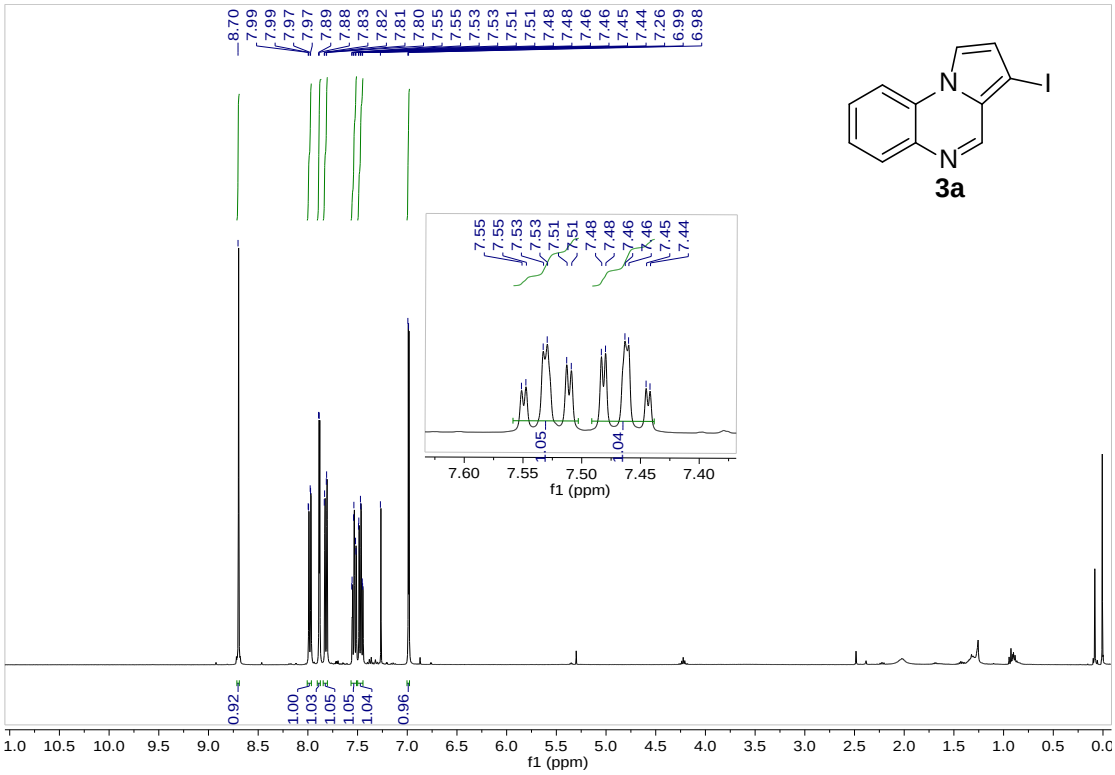
Light yellow solid (44.8 mg, 74%); mp 226-227 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.04 – 7.99 (m, 1H), 7.85 (dd, *J* = 6.2, 1.9 Hz, 2H), 7.56 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.53 – 7.47 (m, 3H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 136.3, 134.1, 132.6, 130.3, 128.8, 128.4, 127.7, 127.6, 125.9, 121.9, 117.1, 114.1, 113.9, 102.5, 91.5, 83.1; HRMS (APCI): m/z calcd for $C_{19}H_{11}ClN_2$ $[M+H]^+$: 303.0684, found: 303.0682.

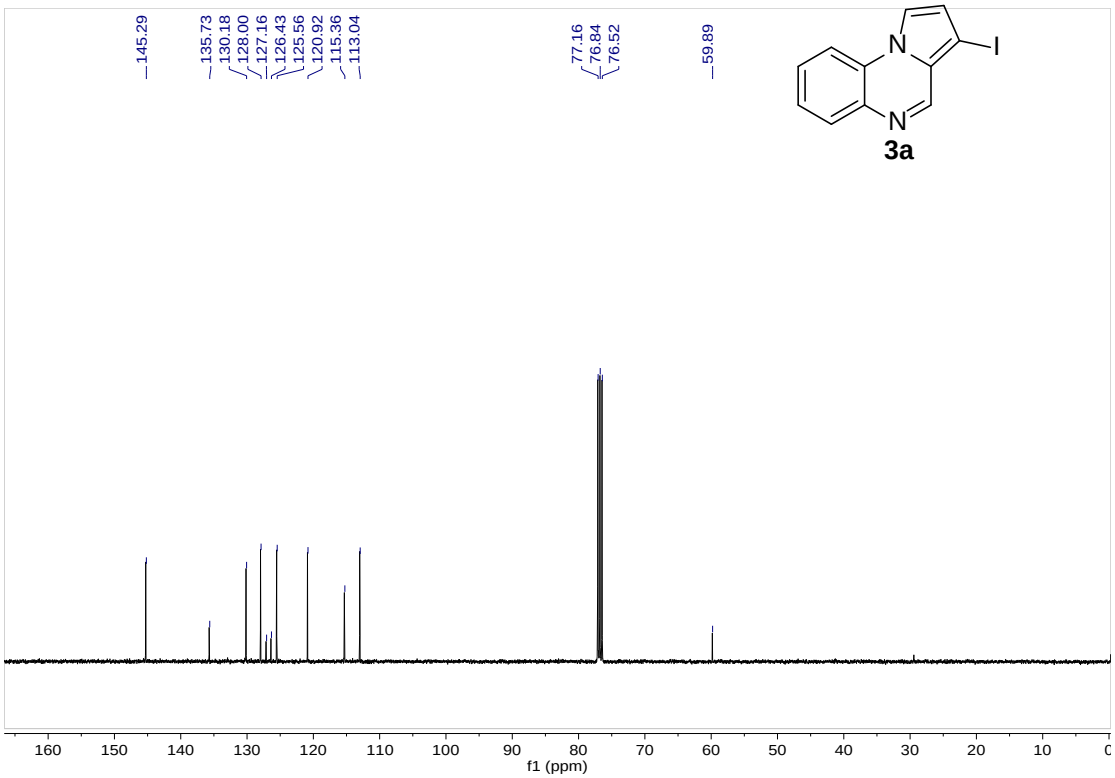
2-methyl-4-(pyrrolo[1,2-a]quinoxalin-3-yl)but-3-yn-2-ol [5n]

Brown liquid (46.1 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.97 (dd, J = 8.0, 1.4 Hz, 1H), 7.71 (dd, J = 8.7, 1.8 Hz, 2H), 7.46 (s, 1H), 7.40 (d, J = 6.7 Hz, 1H), 6.83 (d, J = 2.8 Hz, 1H), 1.69 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 136.0, 130.1, 130.1, 128.3, 127.5, 125.7, 117.2, 113.80, 113.76, 102.6, 97.5, 74.4, 65.6, 31.7; HRMS (APCI): m/z calcd for $C_{16}H_{14}N_2O$ $[M+H]^+$: 251.1179, found: 251.1176.

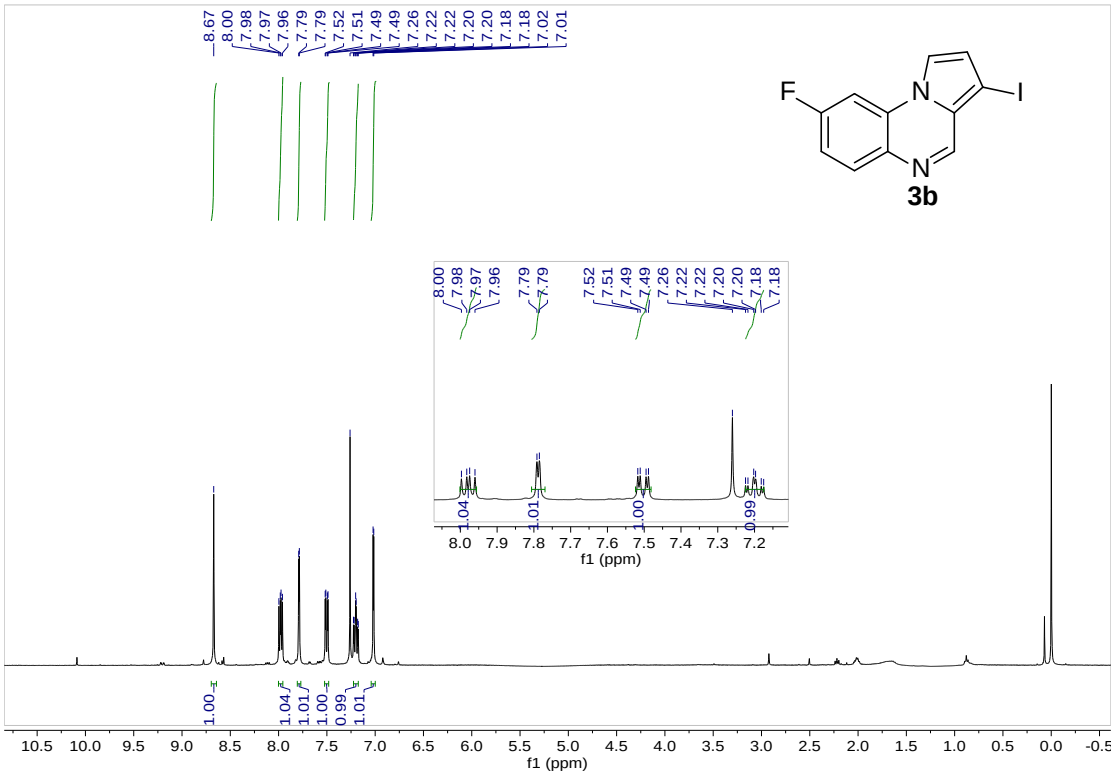
3. NMR spectra of the products

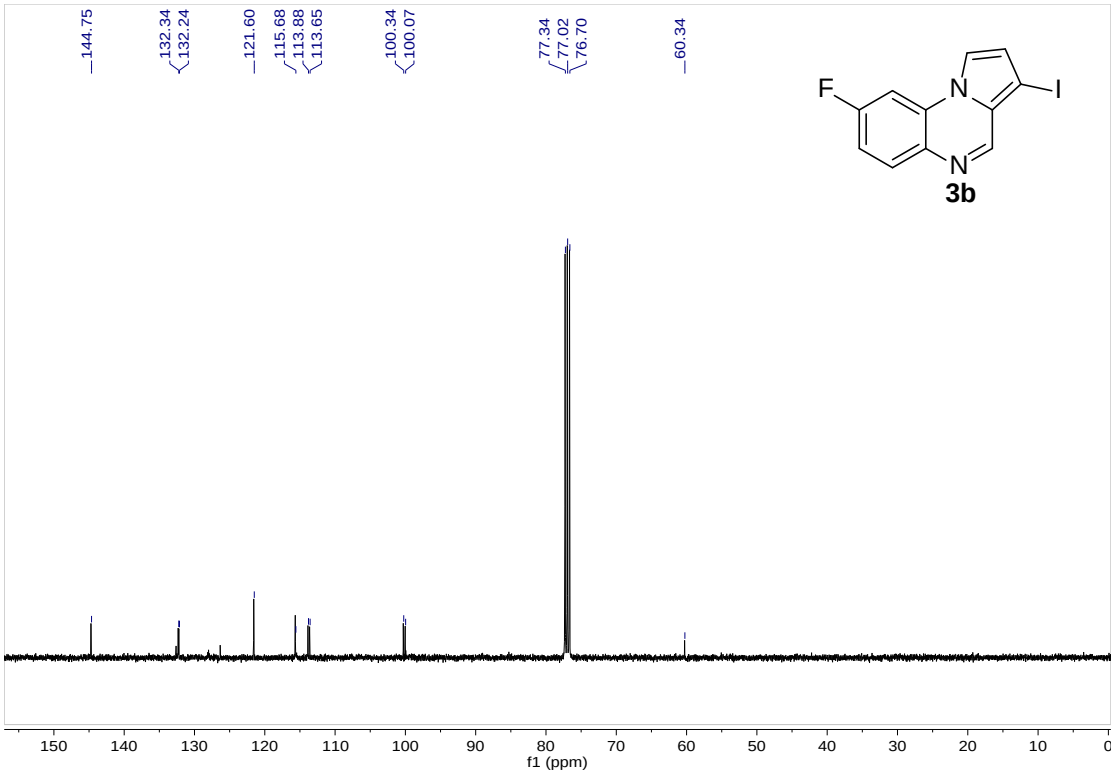
*3-iodopyrrolo[1,2-a]quinoxaline [**3a**]*

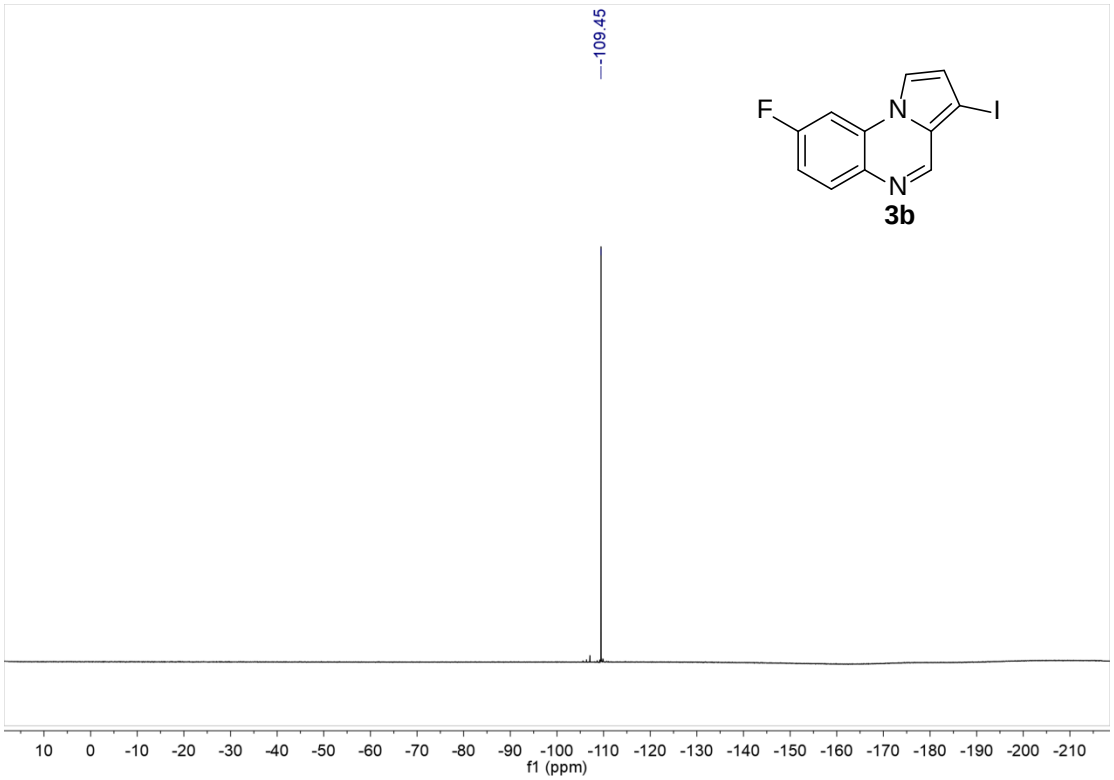




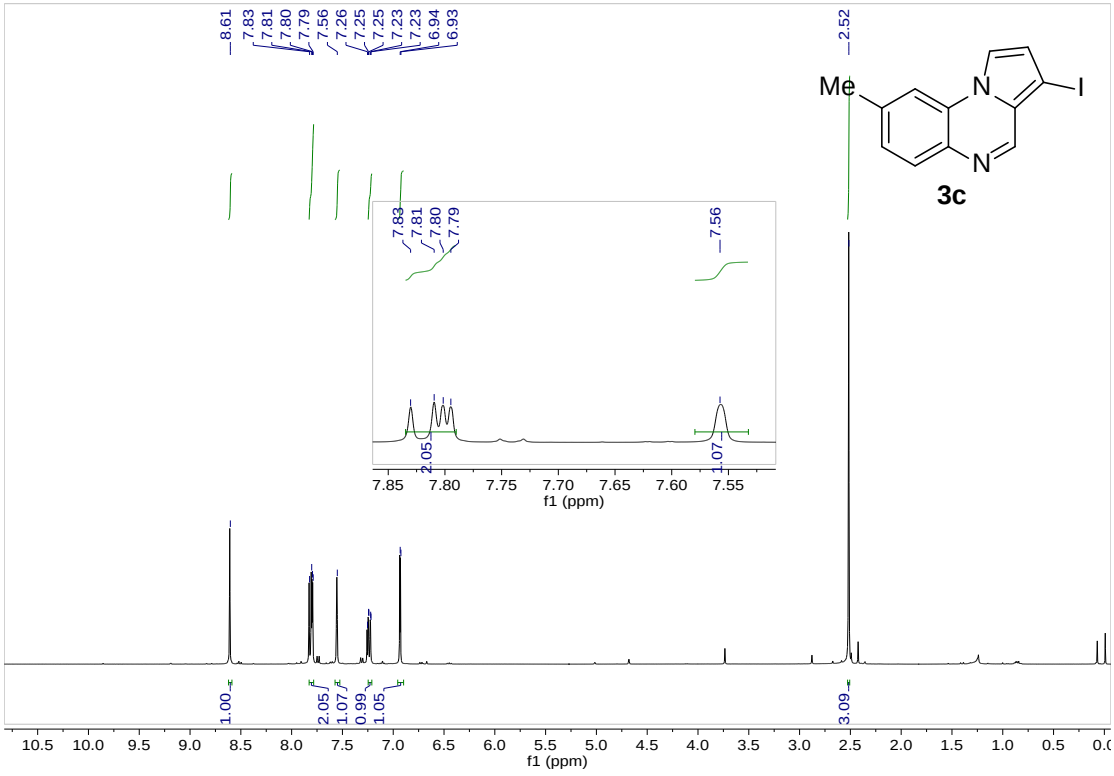
*8-fluoro-3-iodopyrrolo[1,2-a]quinoxaline [**3b**]*

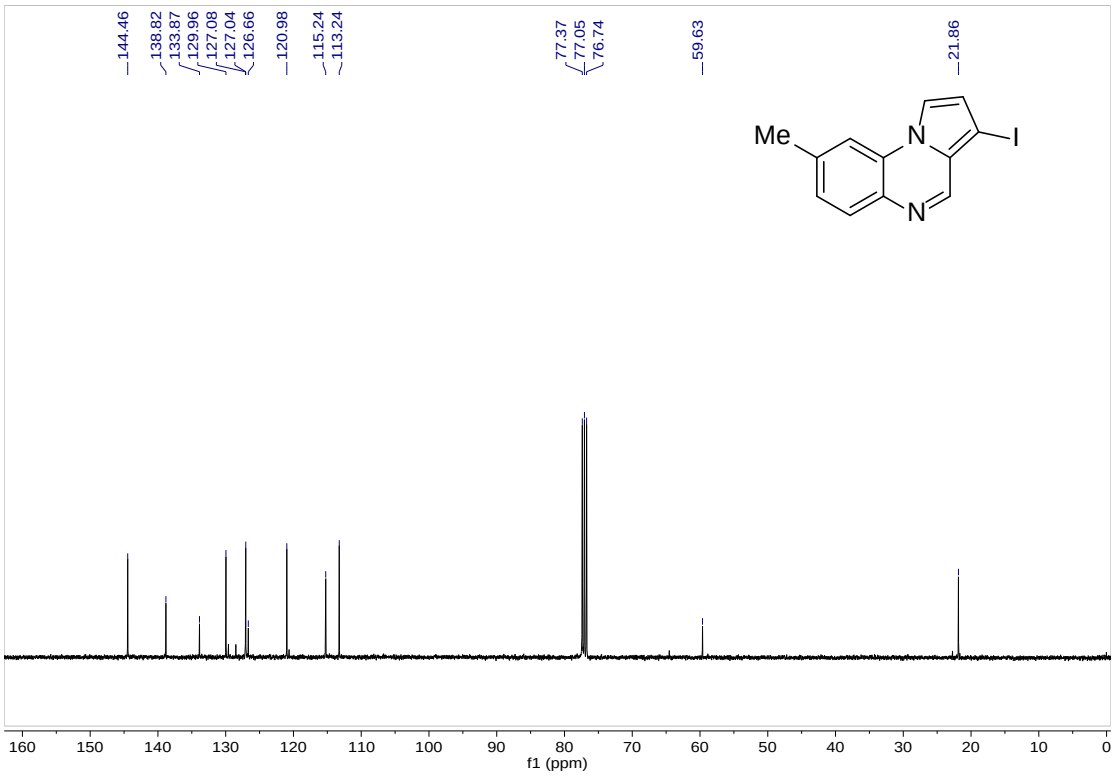




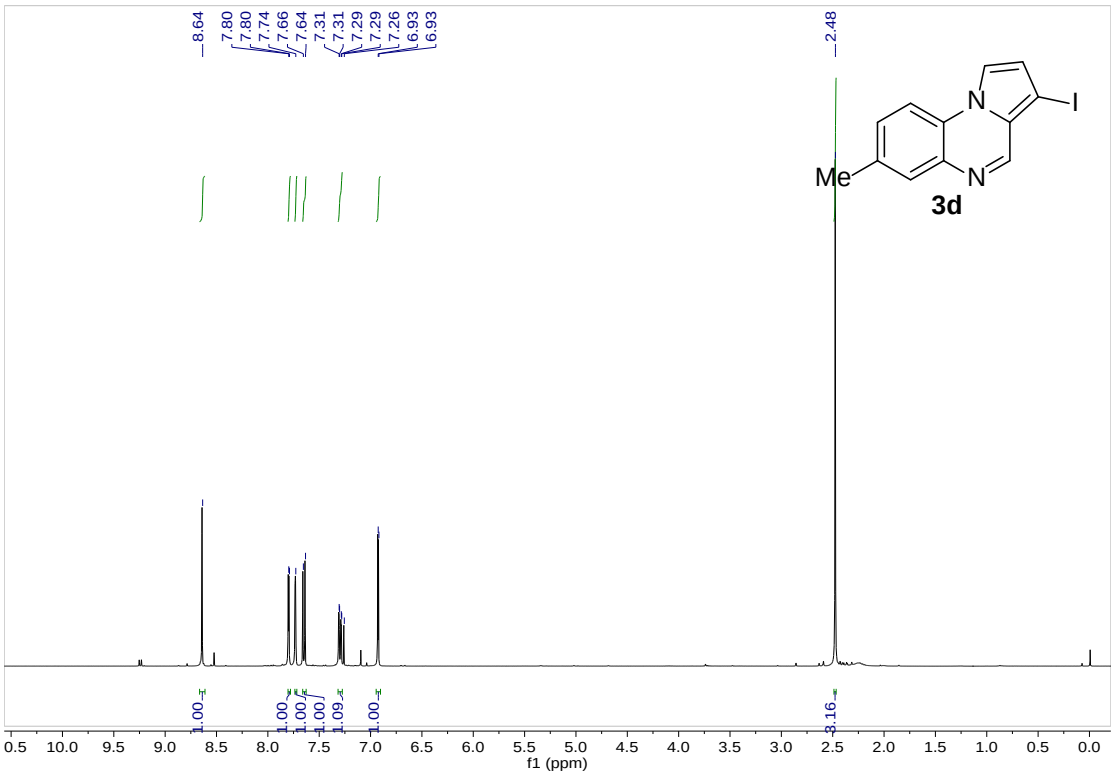


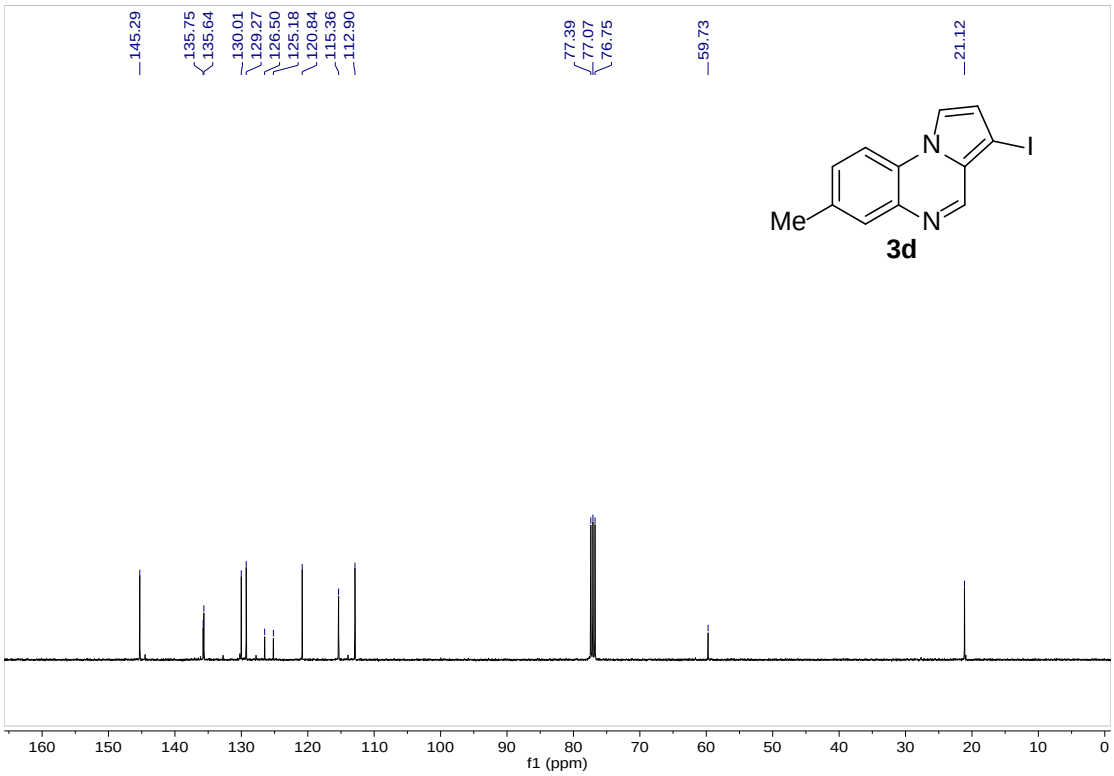
*3-iodo-8-methylpyrrolo[1,2-a]quinoxaline [**3c**]*



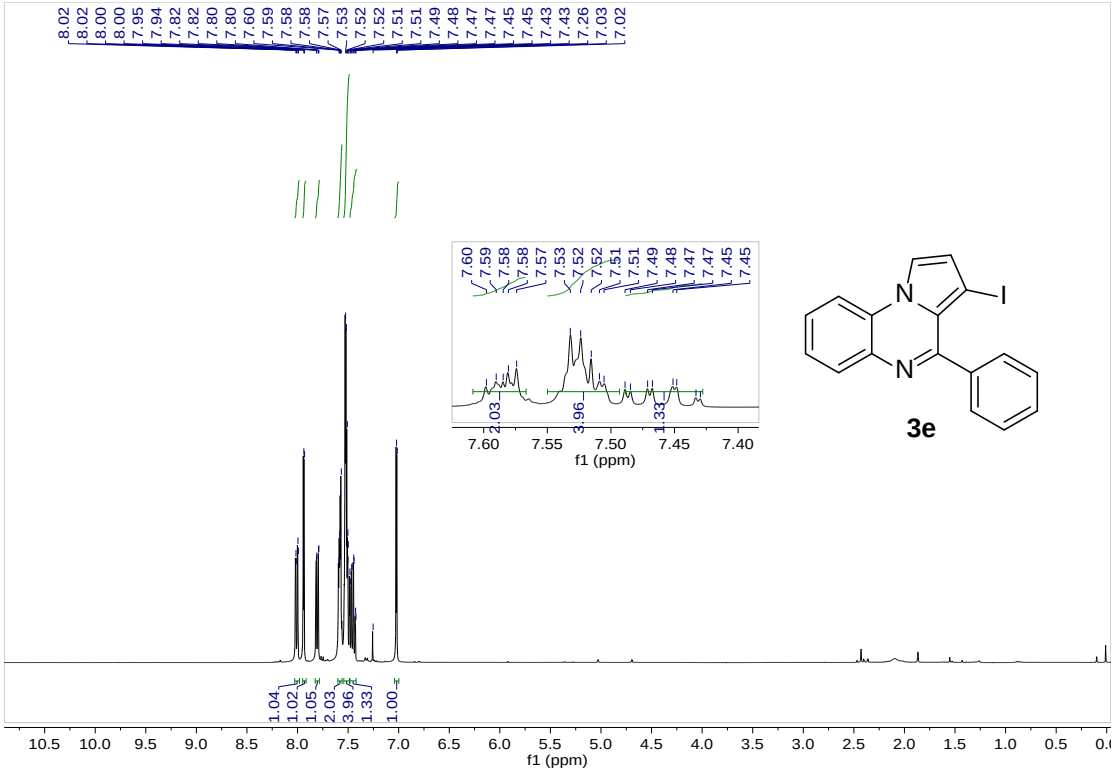


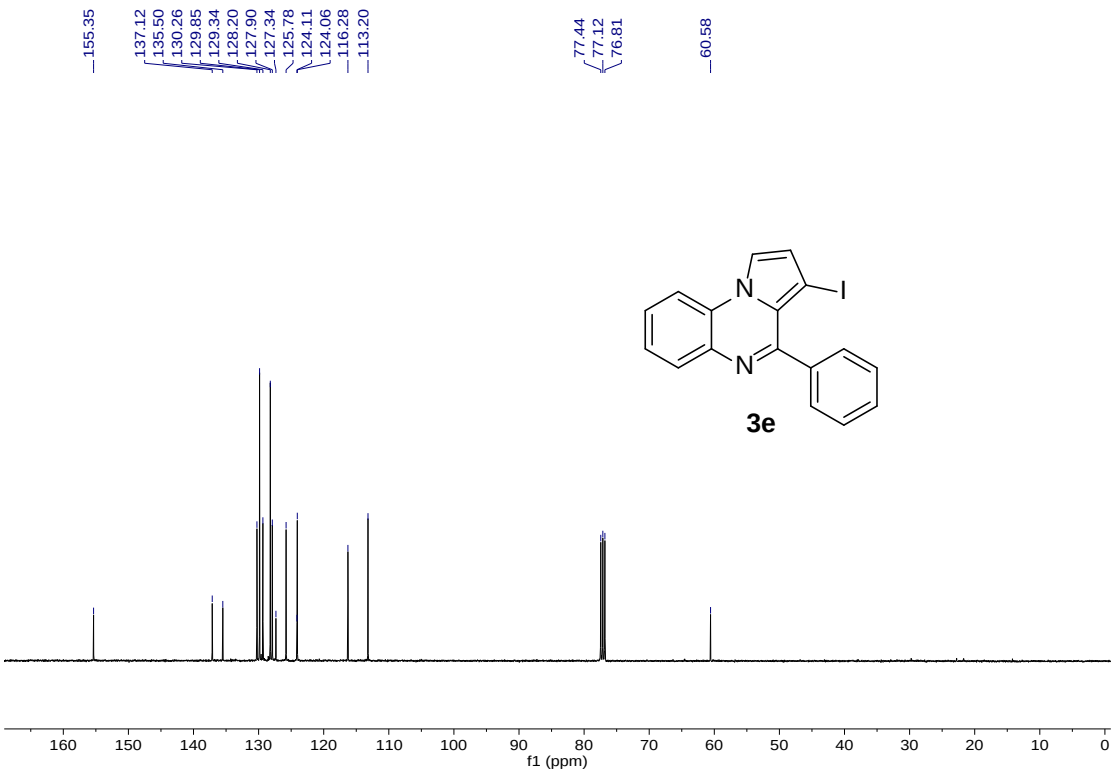
*3-iodo-7-methylpyrrolo[1,2-a]quinoxaline [**3d**]*



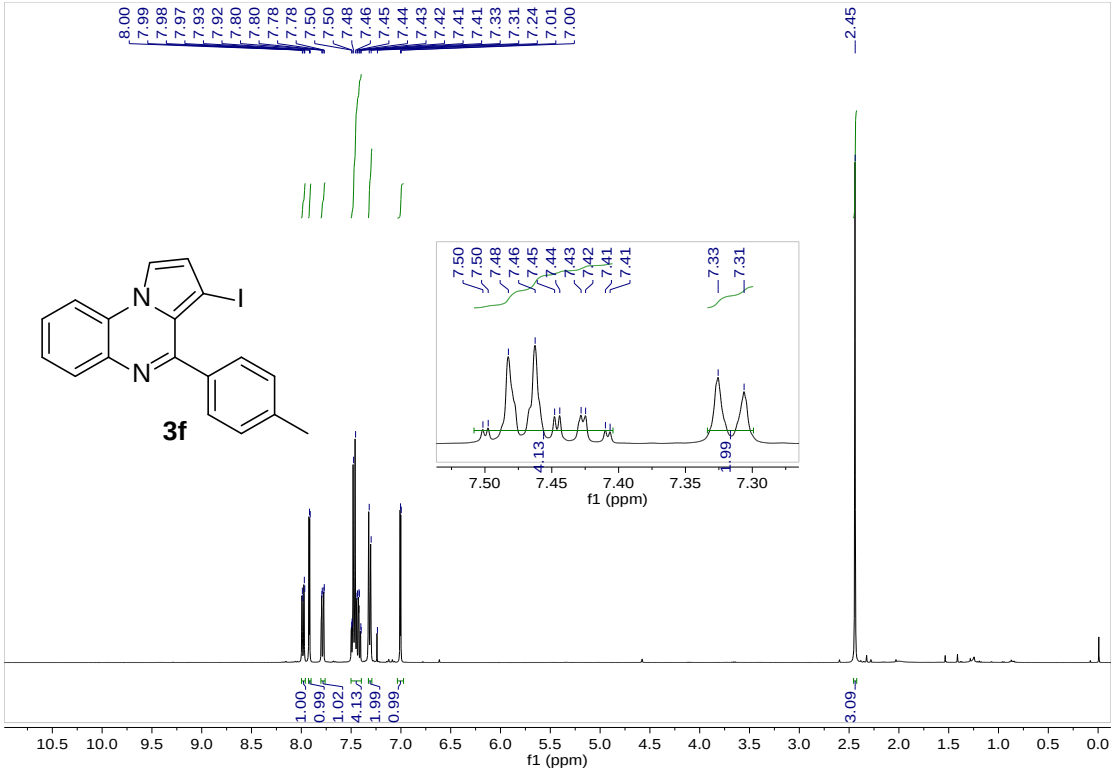


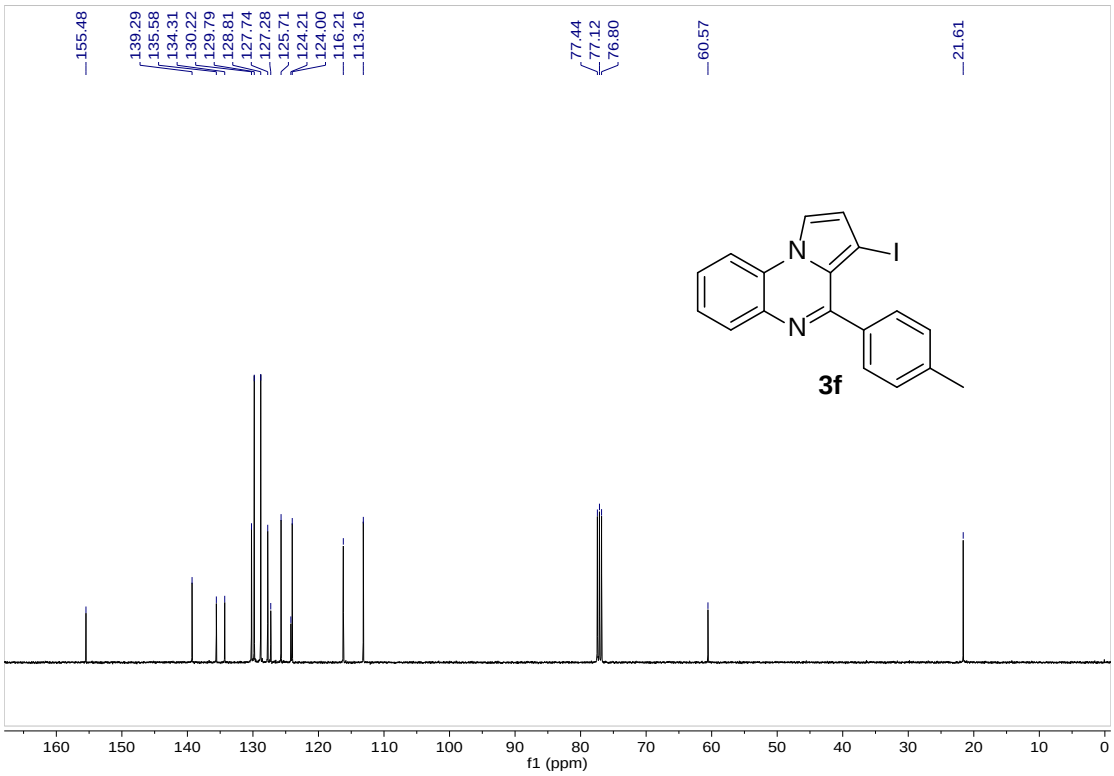
*3-iodo-4-phenylpyrrolo[1,2-a]quinoxaline [**3e**]*



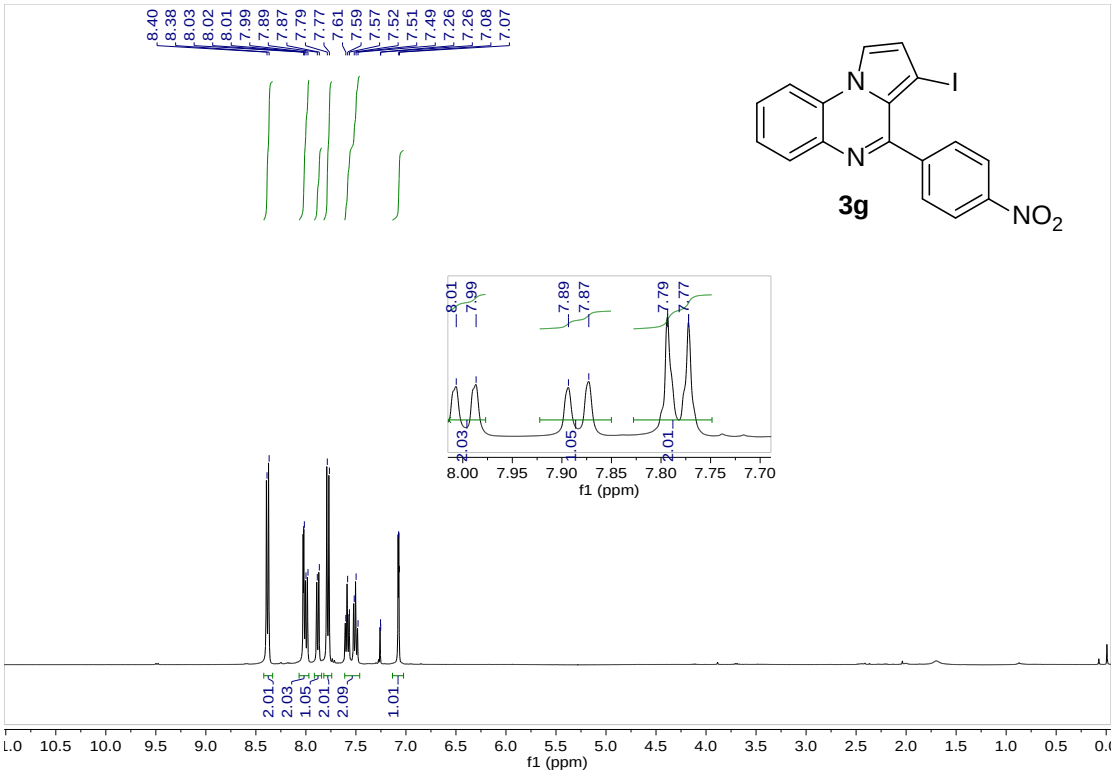


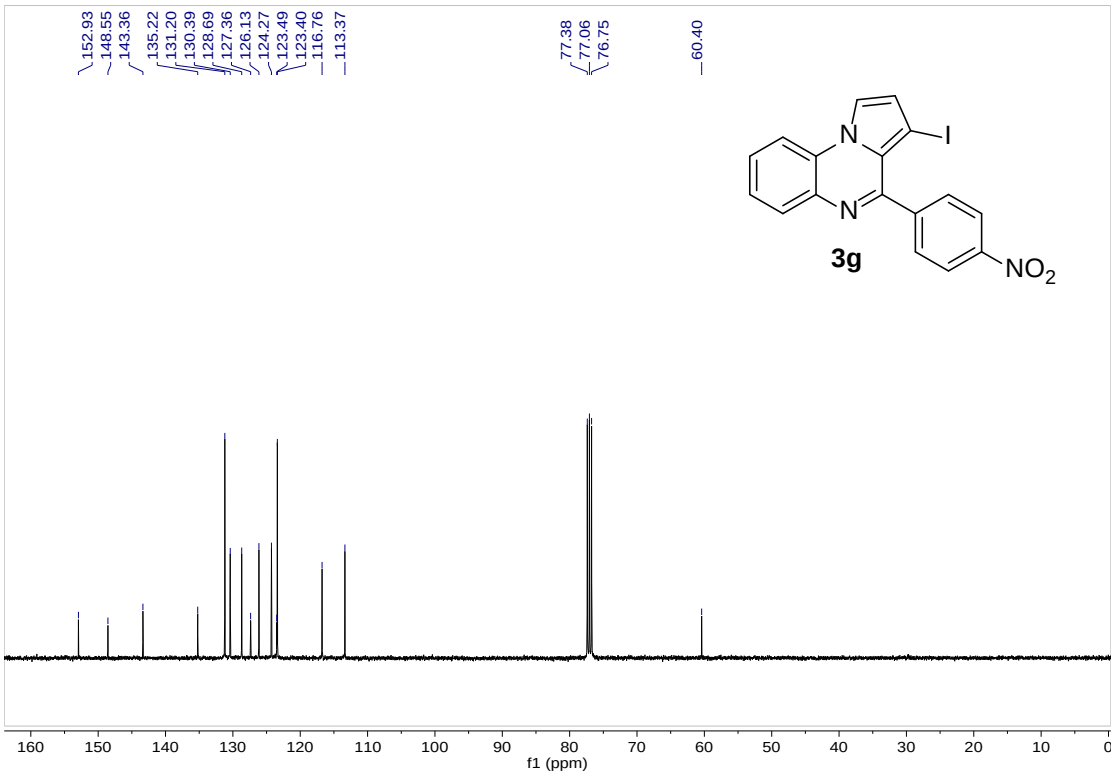
*3-iodo-4-(p-tolyl)pyrrolo[1,2-a]quinoxaline [**3f**]*



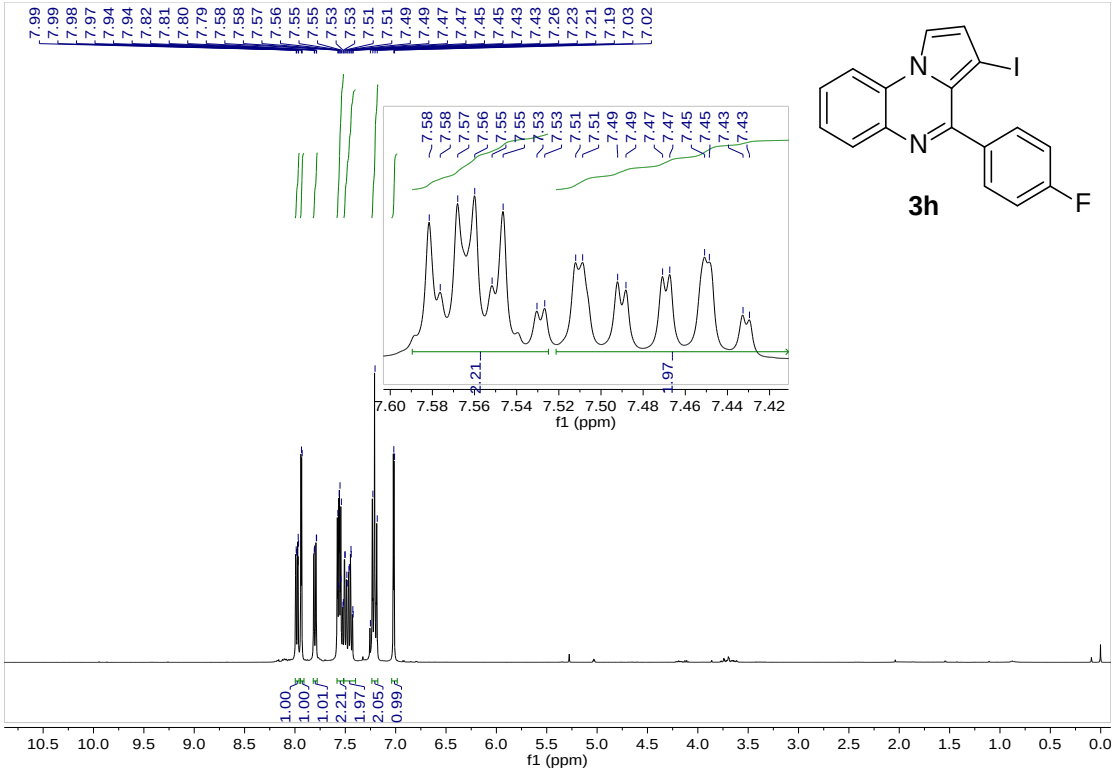


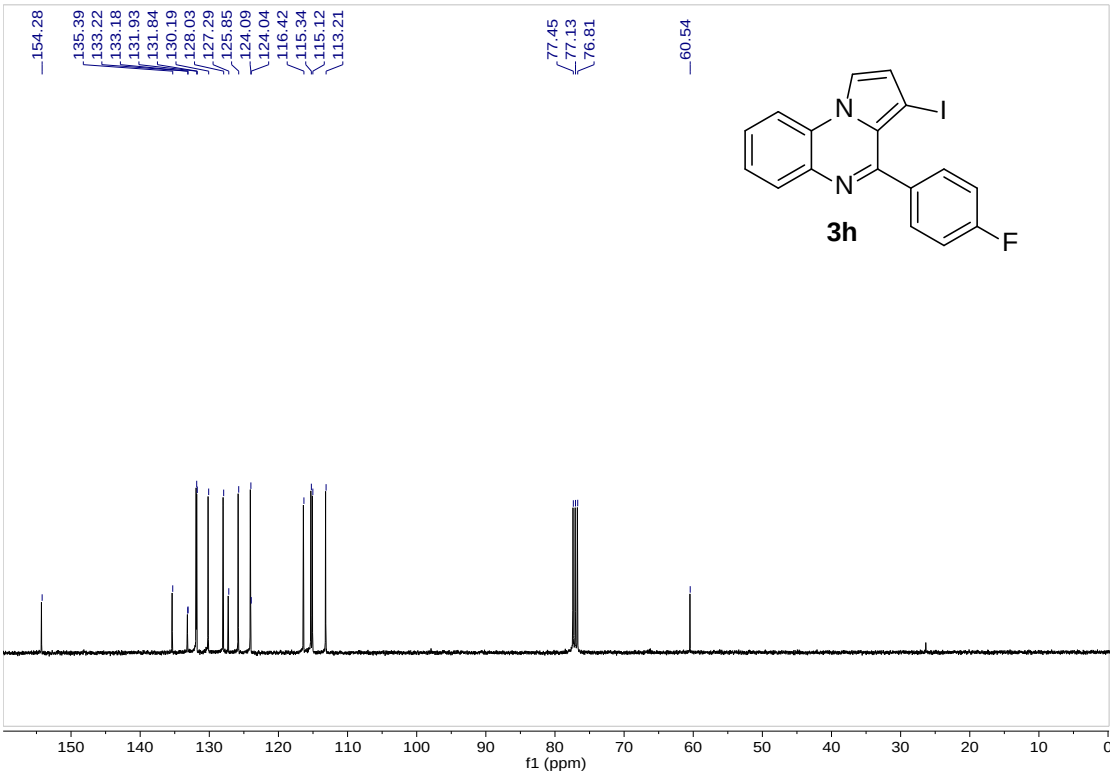
*3-iodo-4-(4-nitrophenyl)pyrrolo[1,2-a]quinoxaline [**3g**]*





*4-(4-fluorophenyl)-3-iodopyrrolo[1,2-a]quinoxaline [**3h**]*

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135.39
133.22
133.18
131.93
131.84
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128.03
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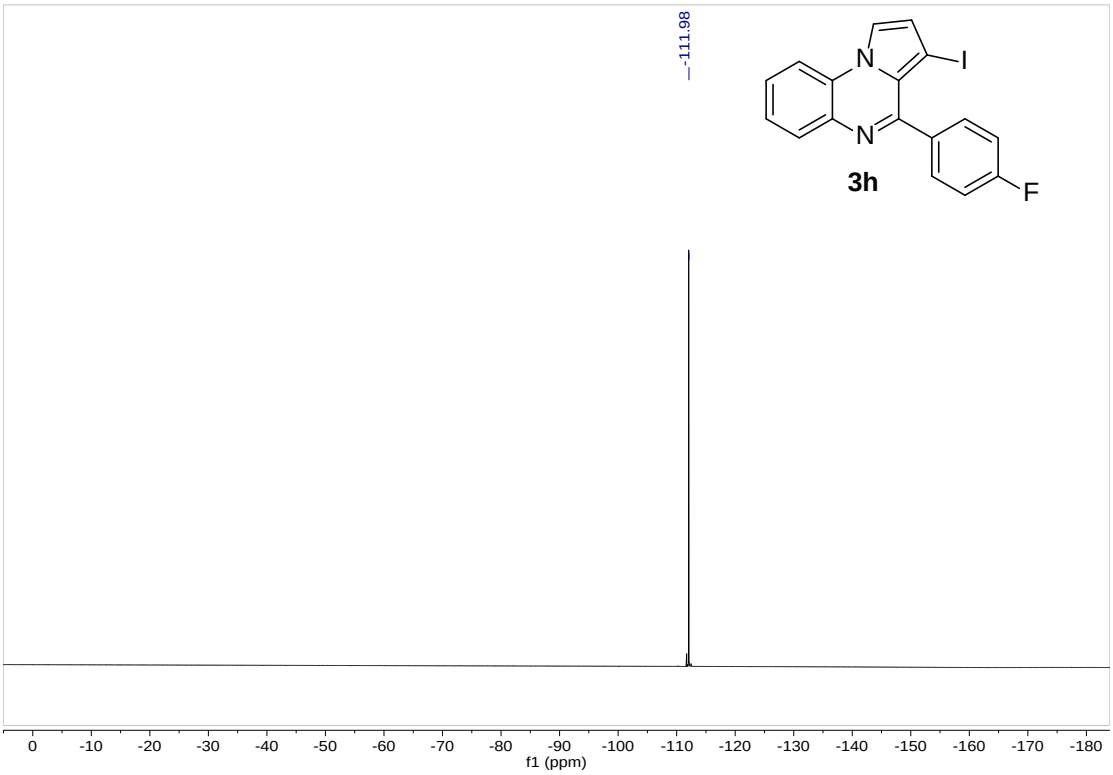
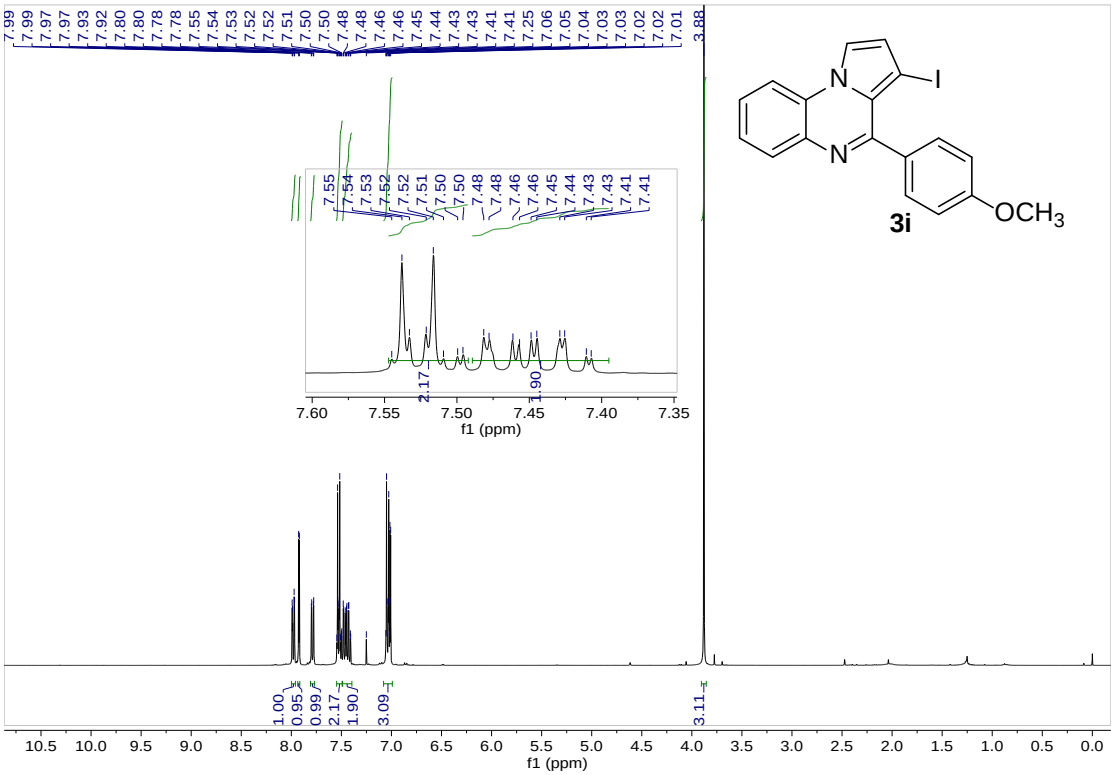
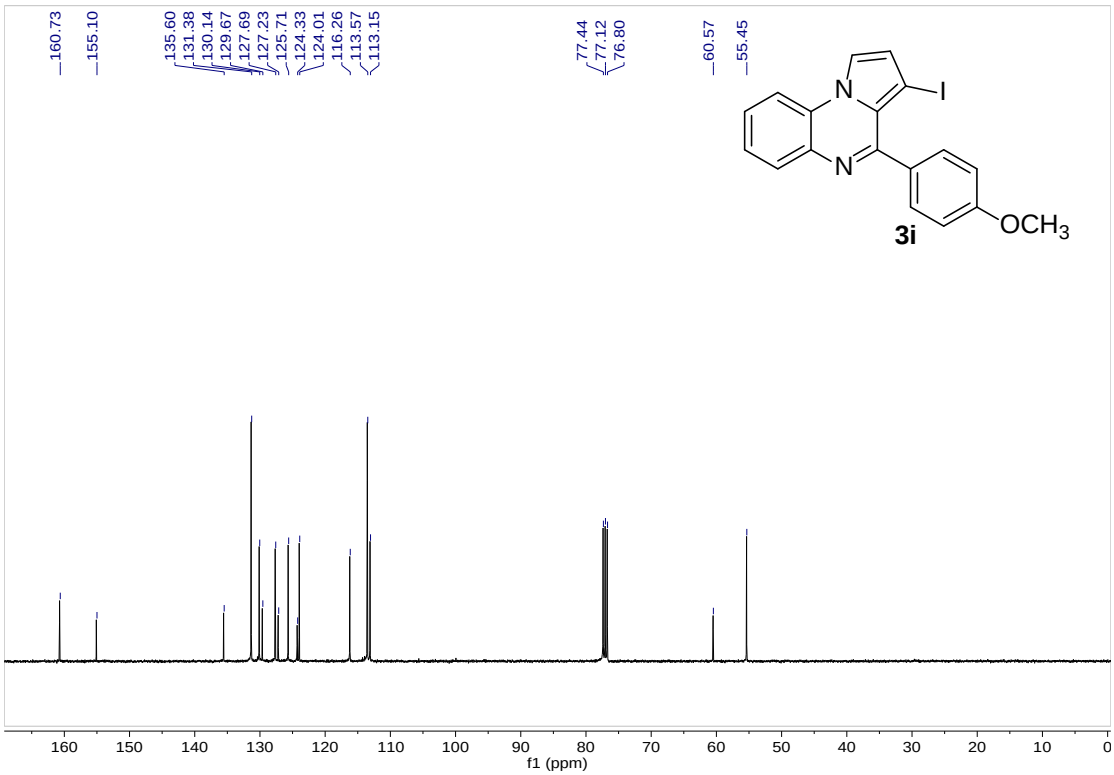
125.85
124.09
124.04
116.42
115.34
115.12
113.21
77.45
77.13
76.81
60.54
N
N
I
F
3h
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

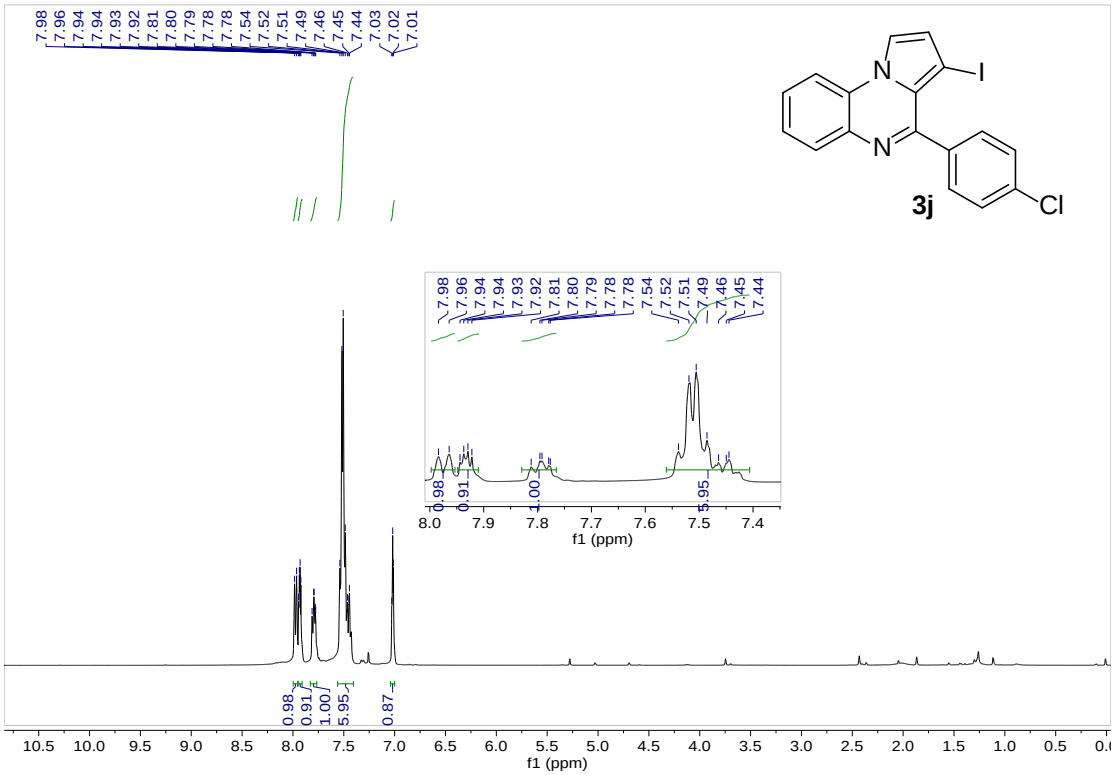

-111.98
N
N
I
F
3h
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

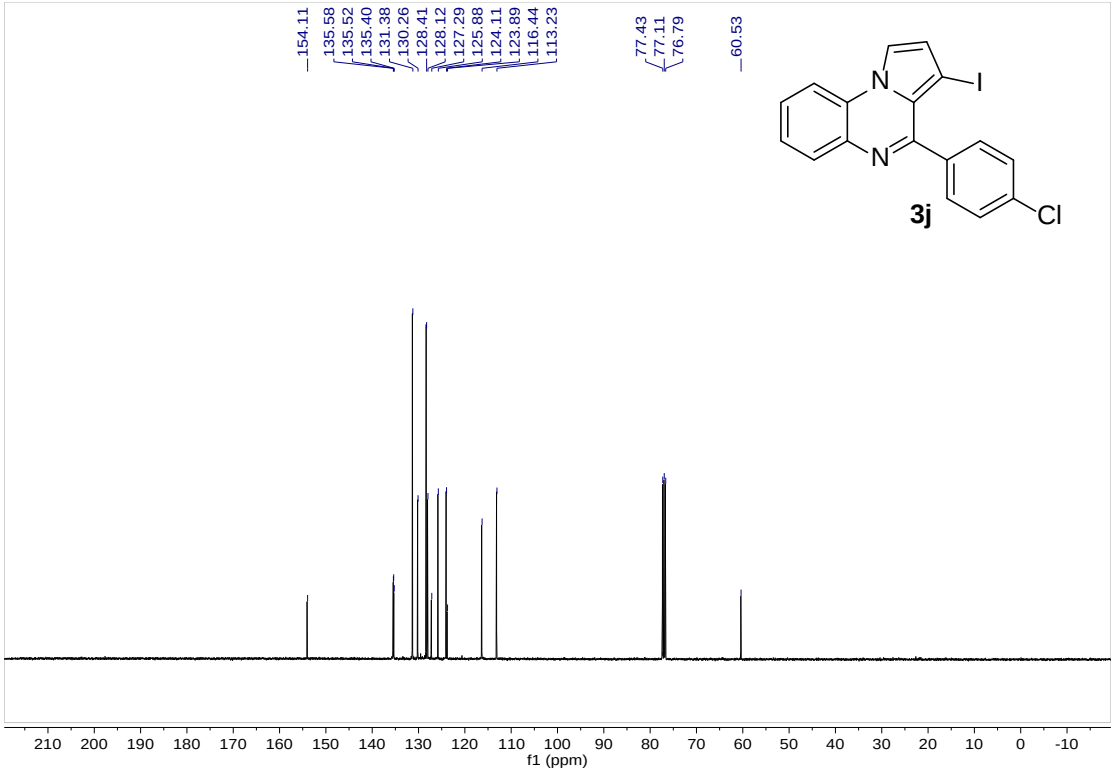
*3-iodo-4-(4-methoxyphenyl)pyrrolo[1,2-a]quinoxaline [**3i**]*



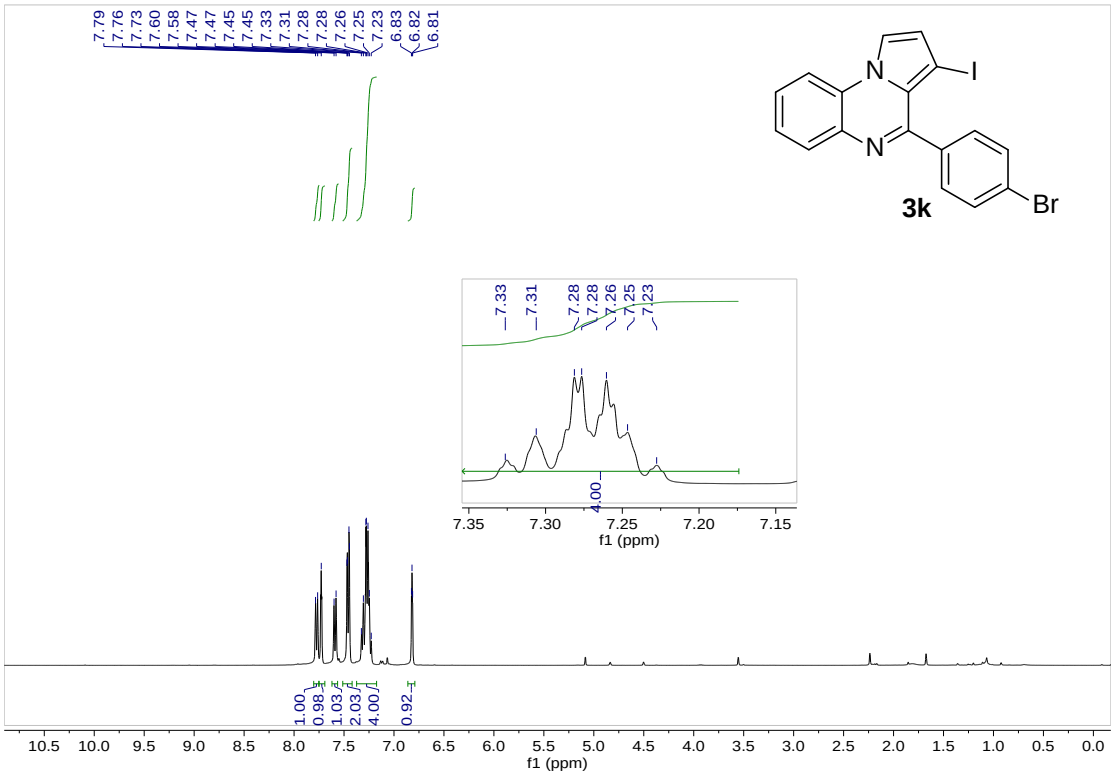


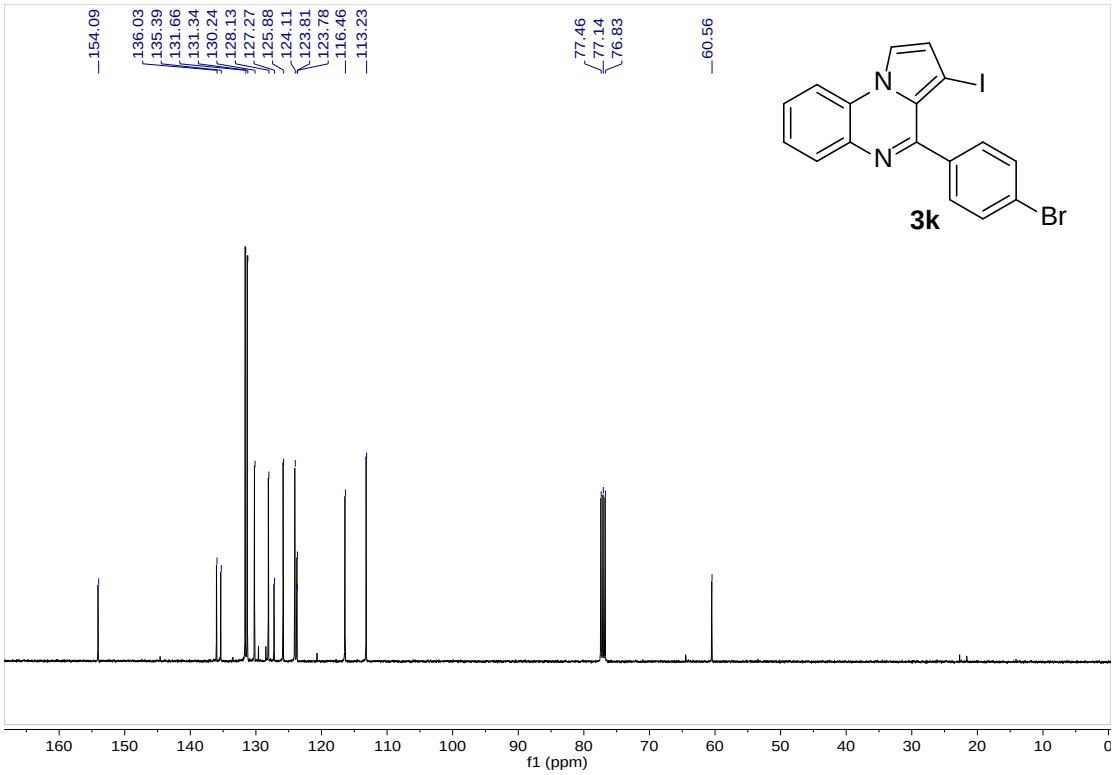
*4-(4-chlorophenyl)-3-iodopyrrolo[1,2-a]quinoxaline [**3j**]*



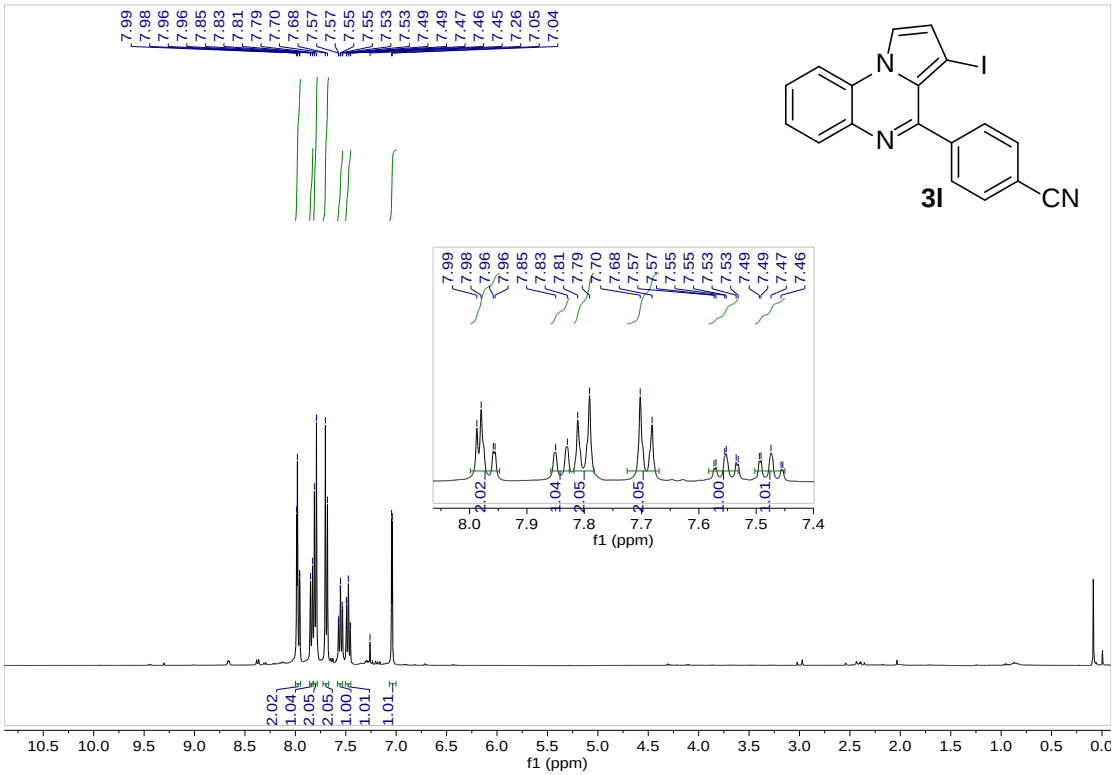


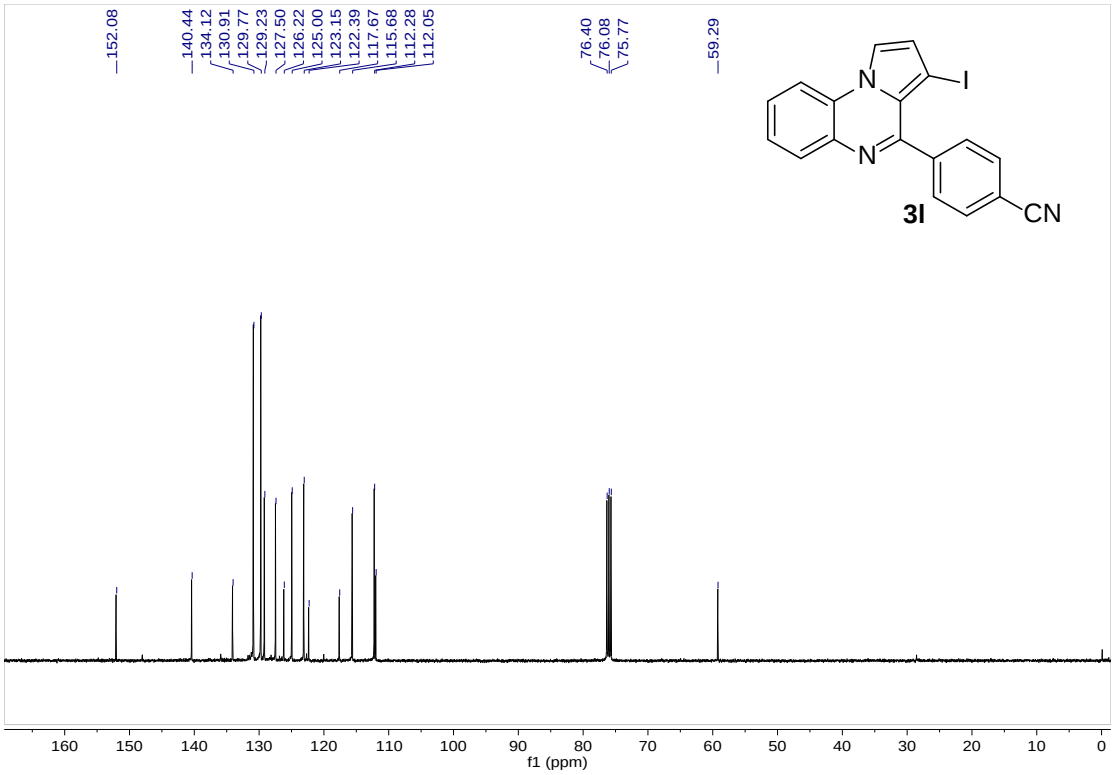
*4-(4-bromophenyl)-3-iodopyrrolo[1,2-a]quinoxaline [**3k**]*



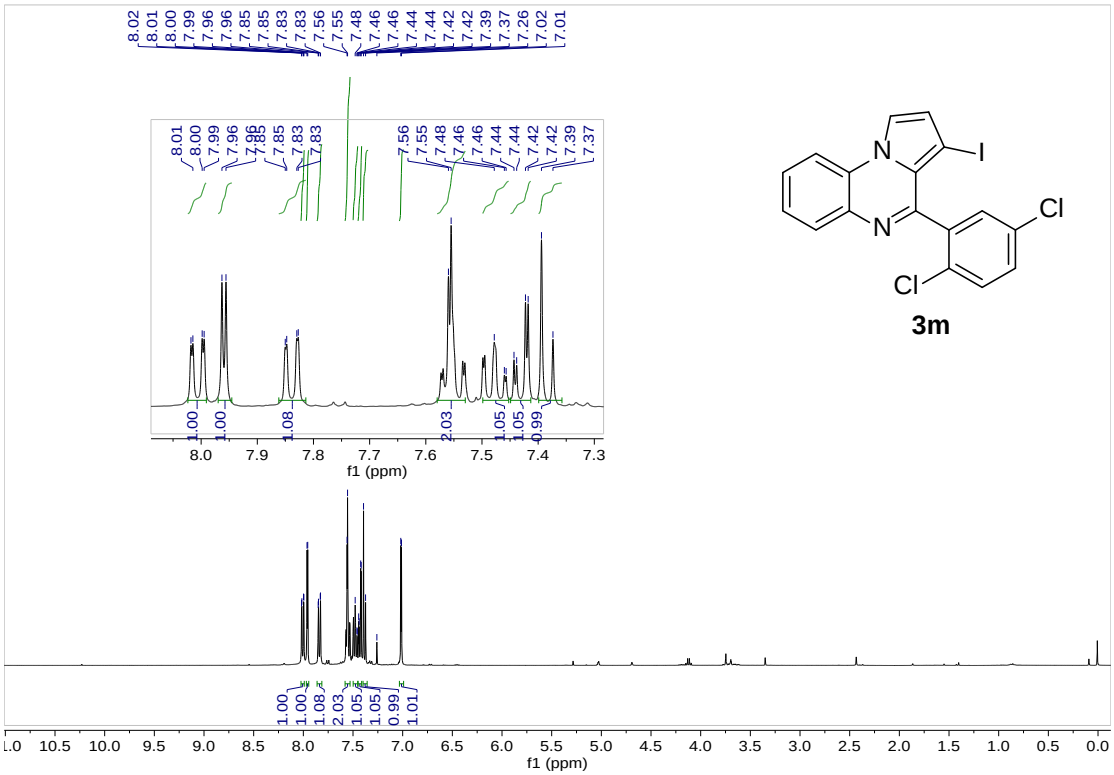


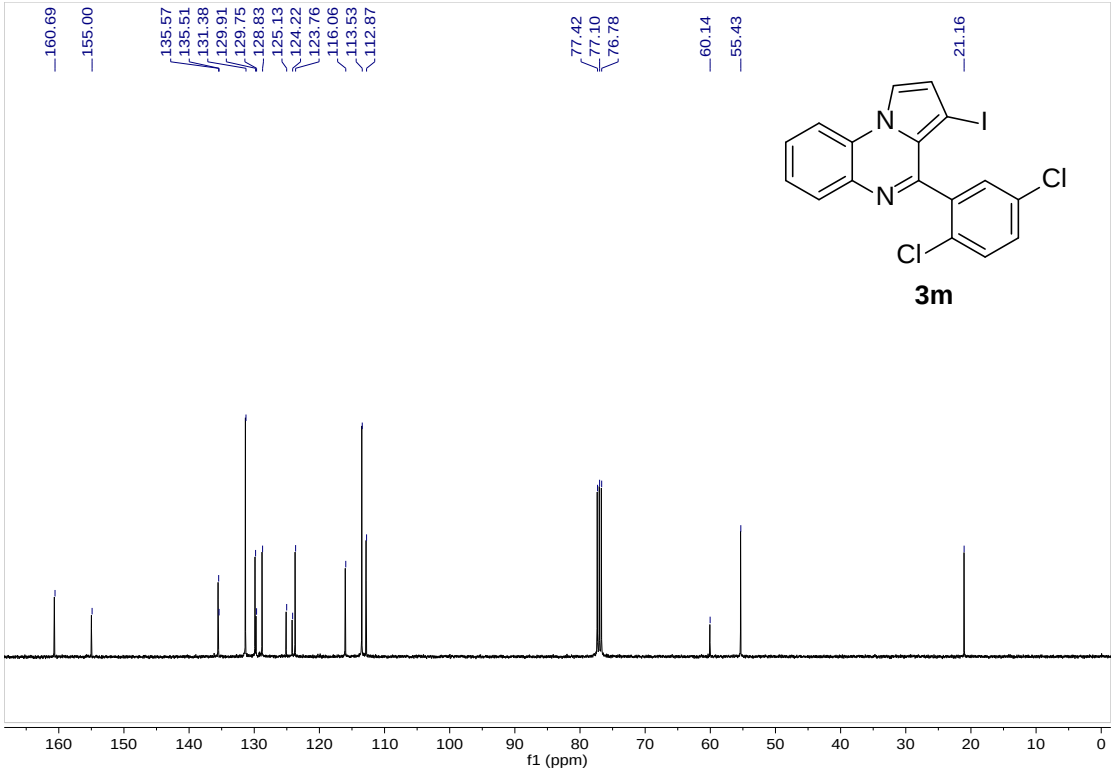
*4-(3-iodopyrrolo[1,2-a]quinoxalin-4-yl)benzonitrile [**3l**]*



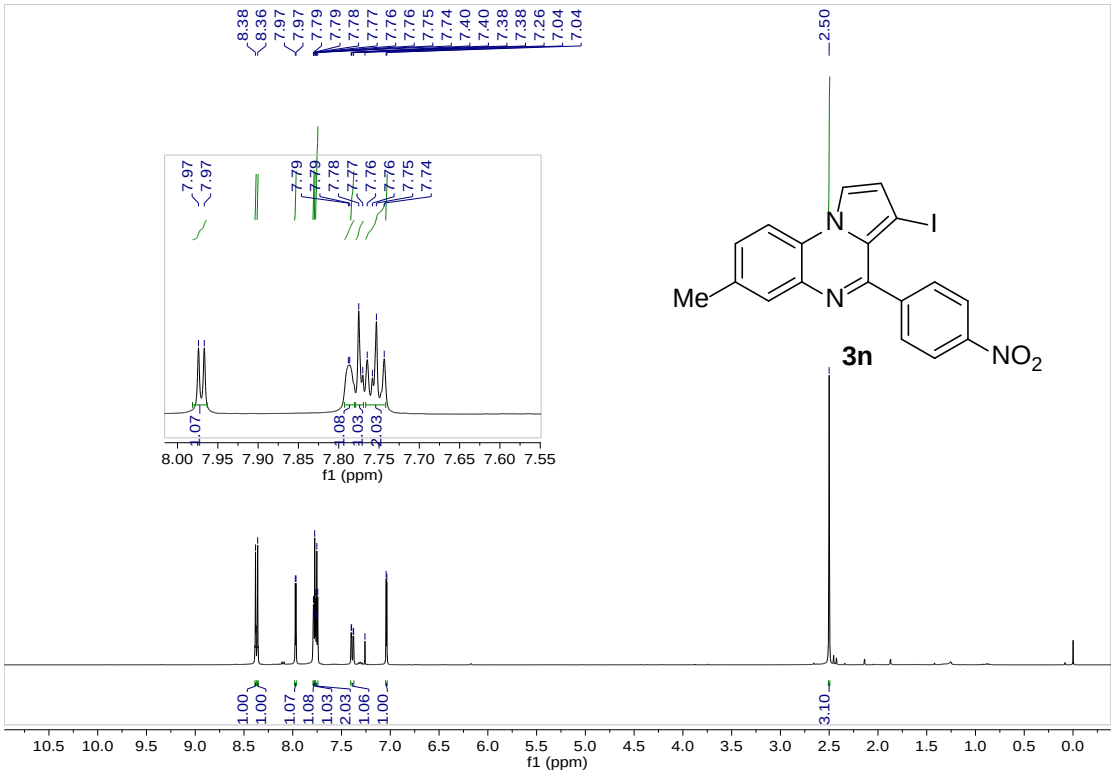


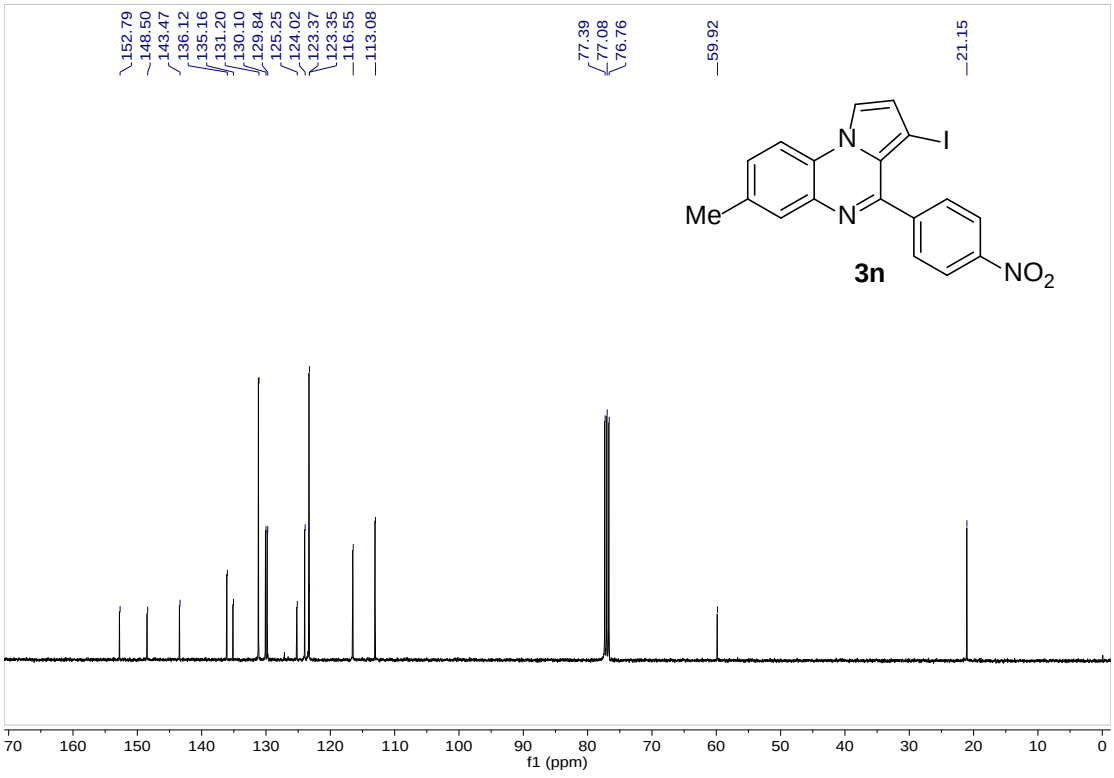
*3-iodo-4-(4-methoxyphenyl)-7-methylpyrrolo[1,2-a]quinoxaline [**3m**]*



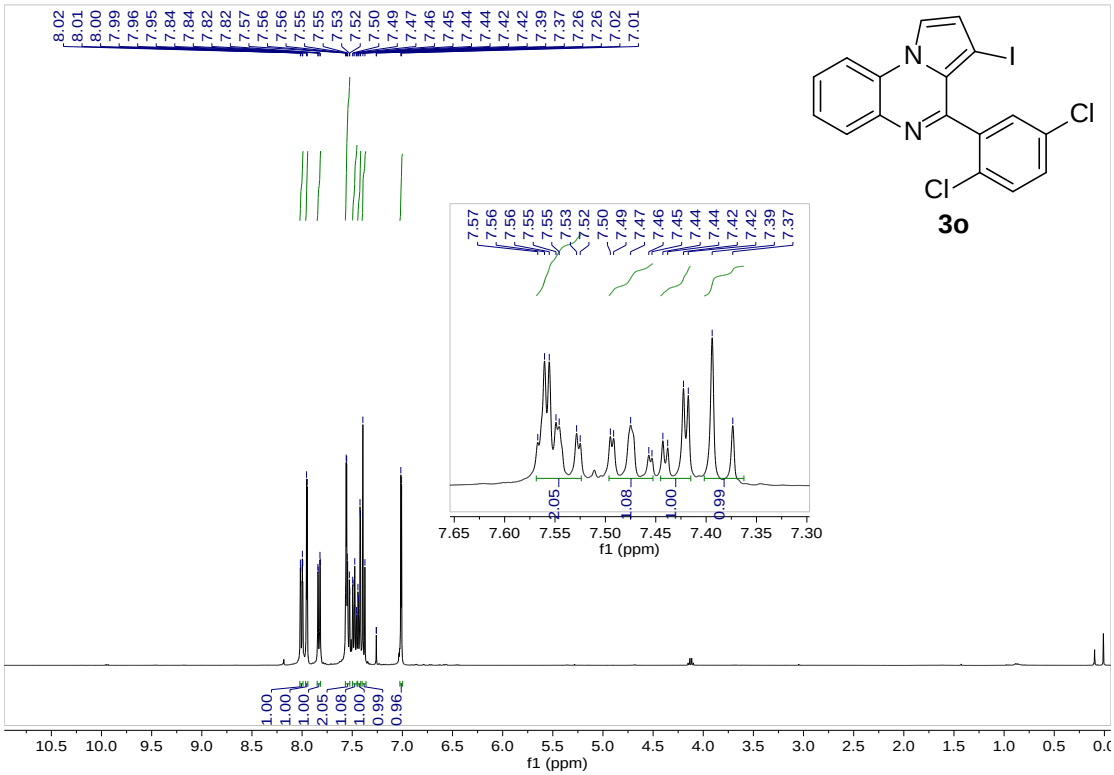


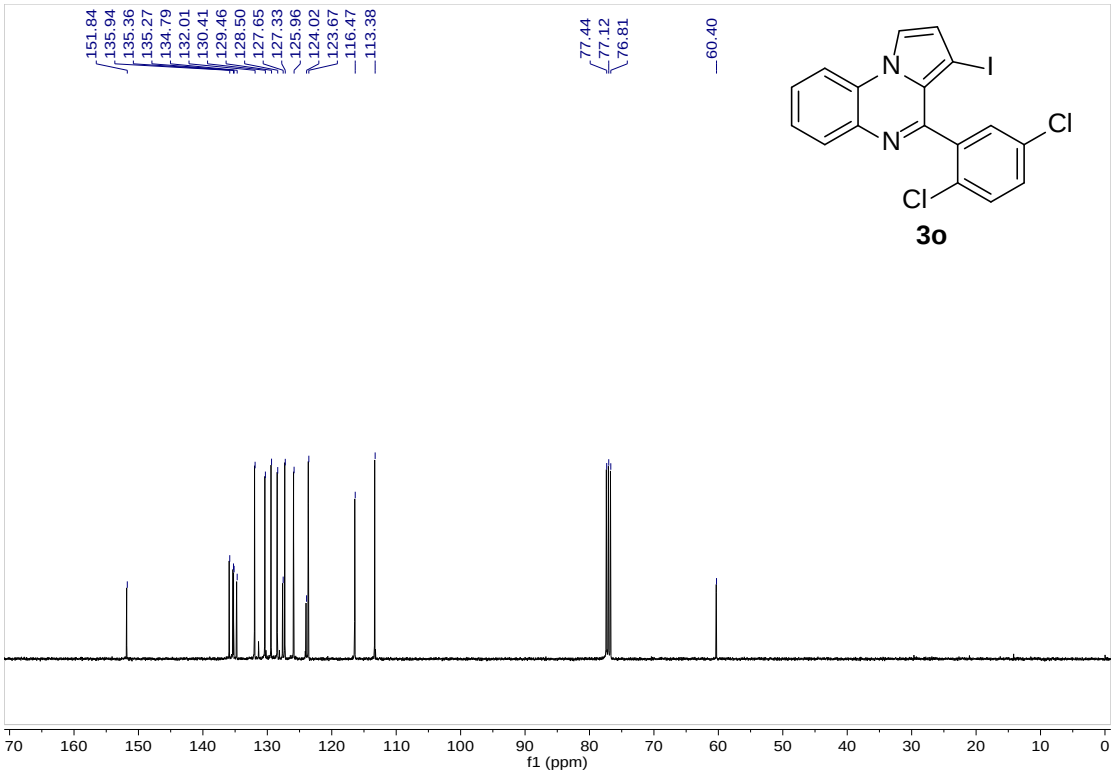
*3-iodo-7-methyl-4-(4-nitrophenyl)pyrrolo[1,2-a]quinoxaline [**3n**]*



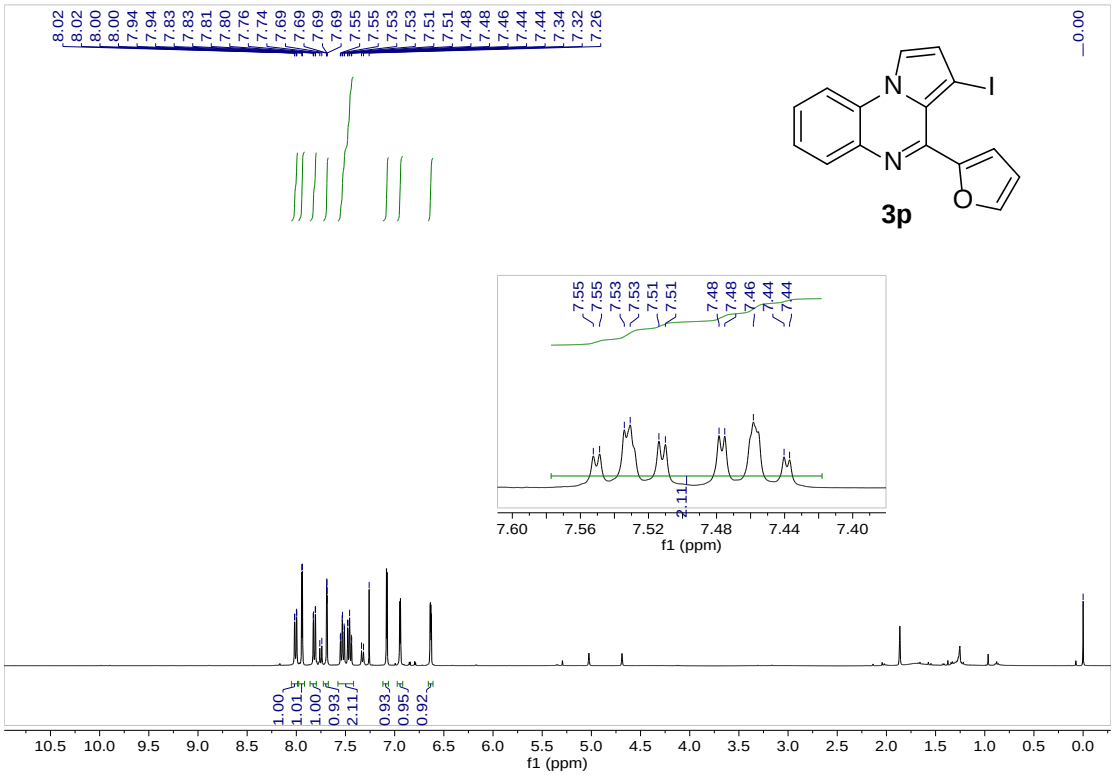


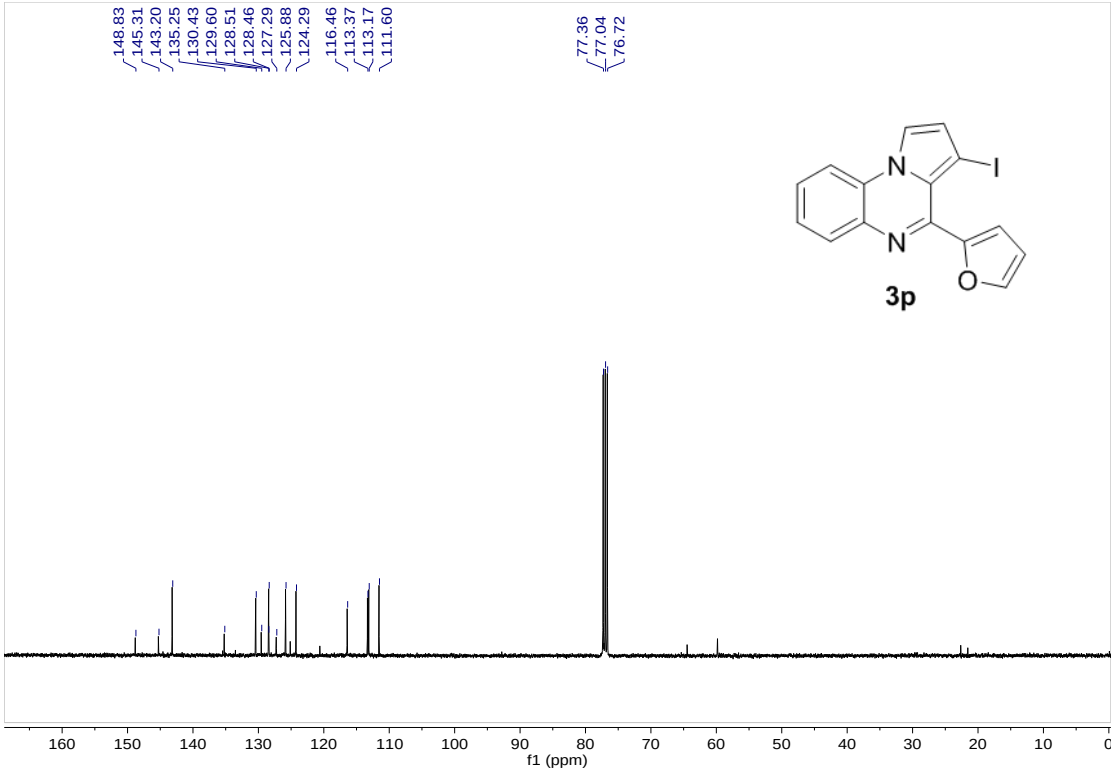
*4-(2,4-dichlorophenyl)-3-iodopyrrolo[1,2-a]quinoxaline [**3o**]*



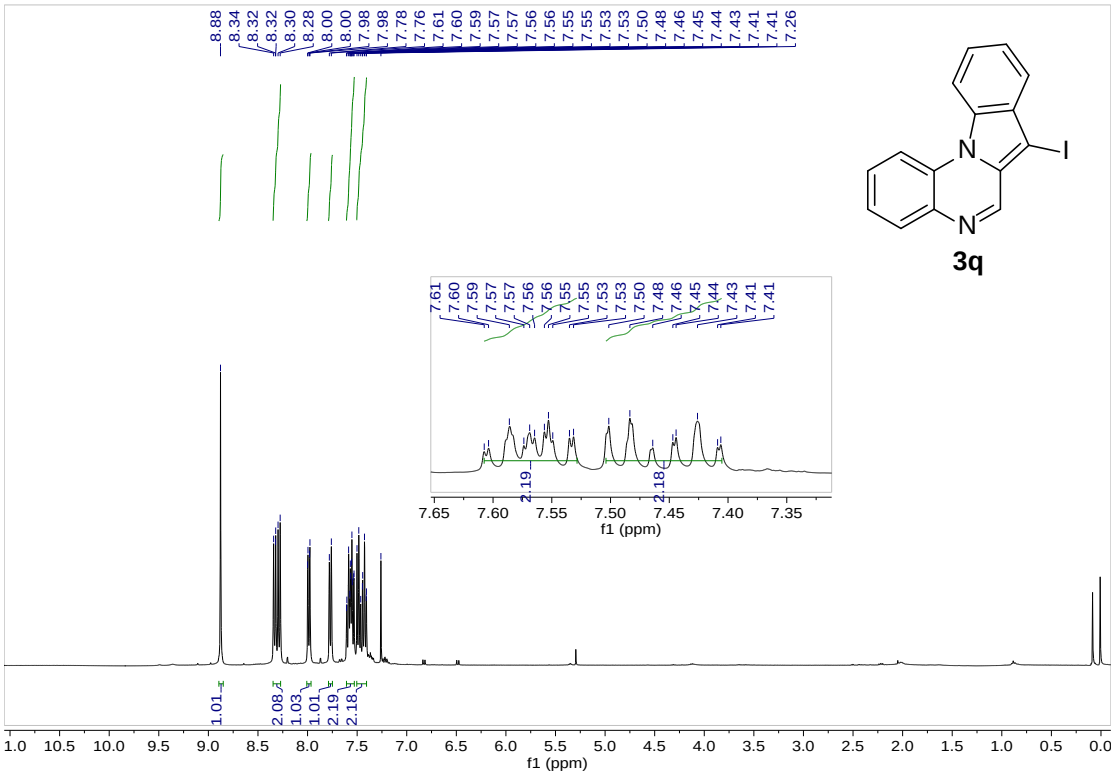


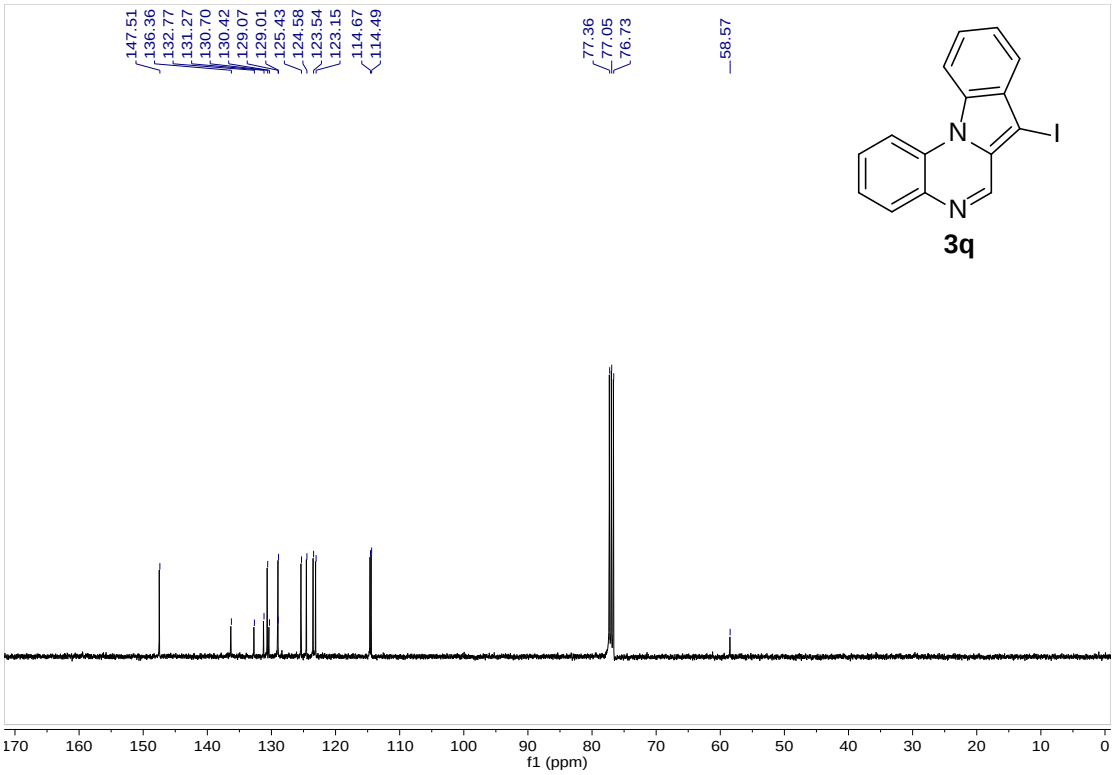
*4-(furan-3-yl)-3-iodopyrrolo[1,2-a]quinoxaline [**3p**]*



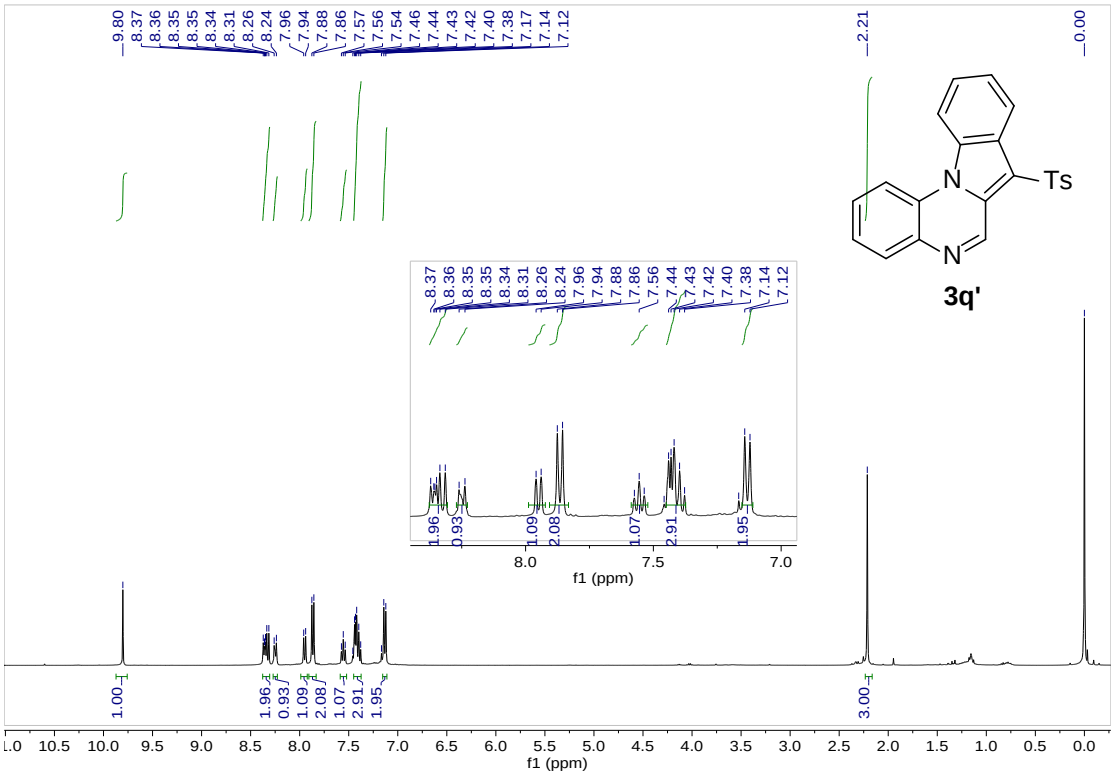


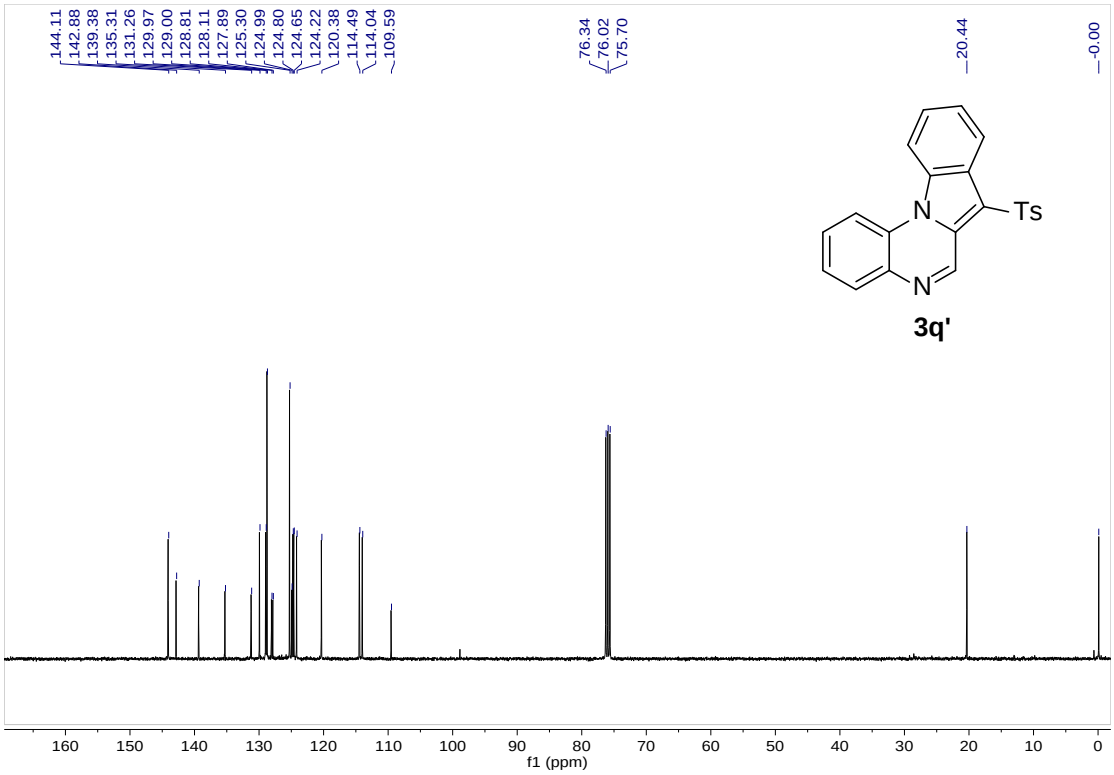
*7-iodoindolo[1,2-a]quinoxaline [**3q**]*



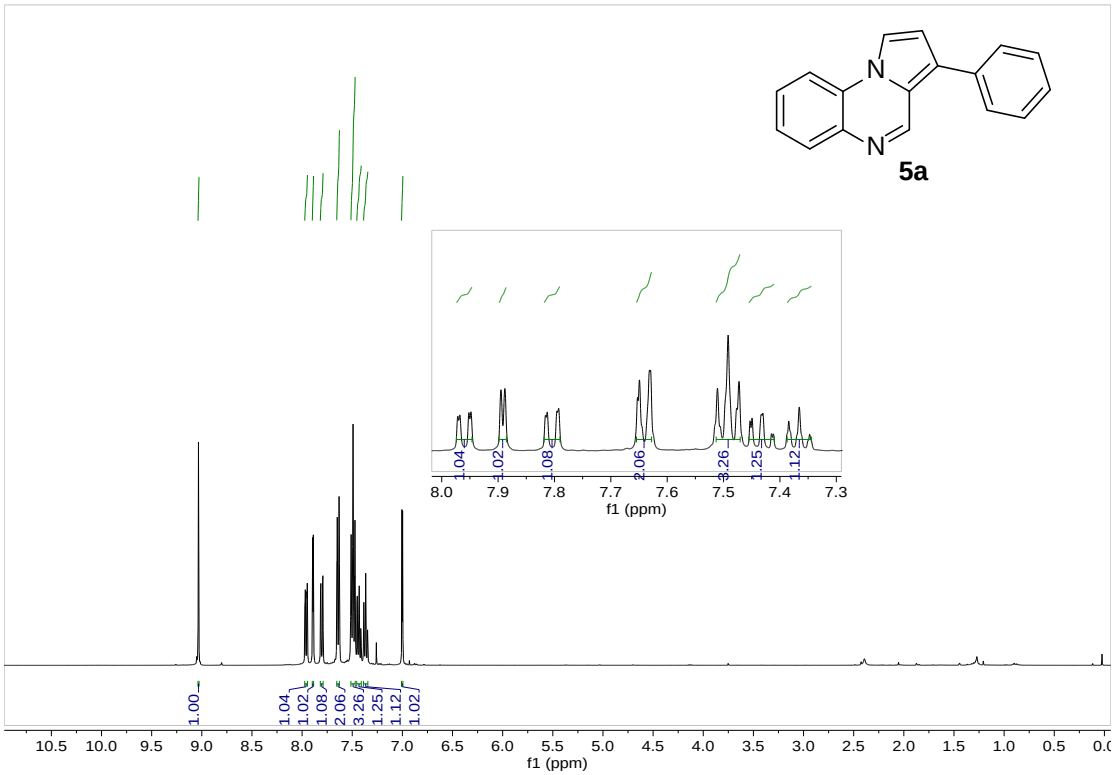


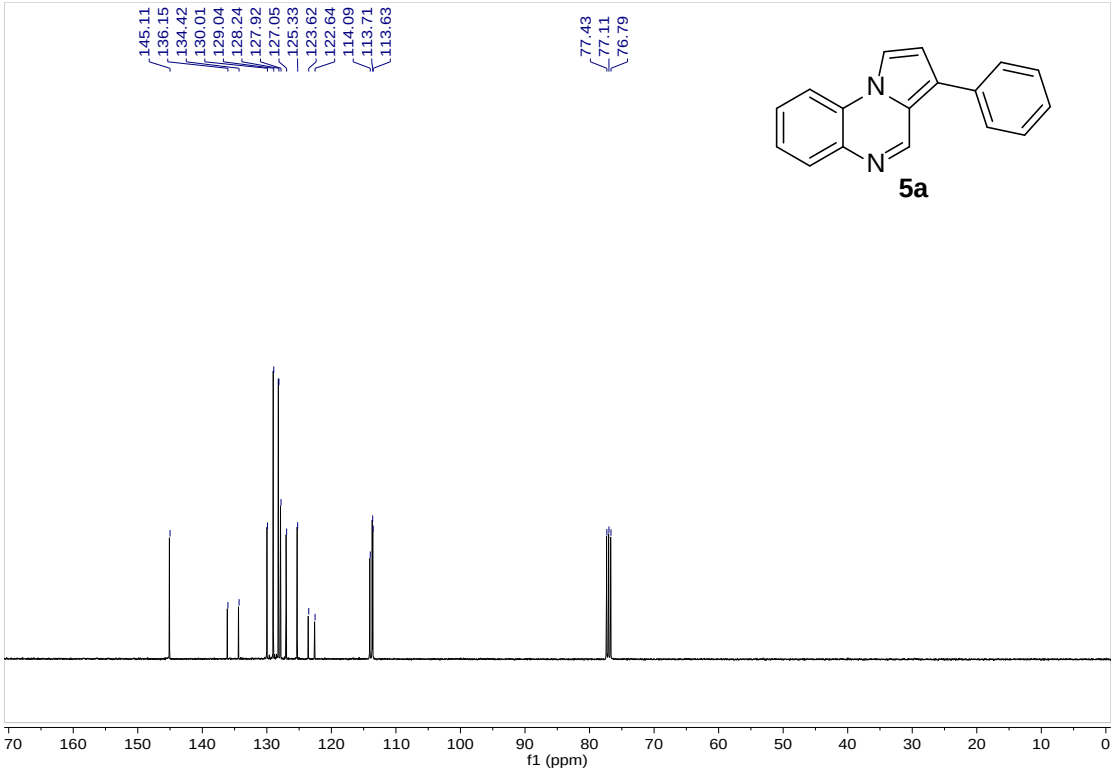
*4-(furan-3-yl)-3-iodopyrrolo[1,2-a]quinoxaline [**3q'**]*



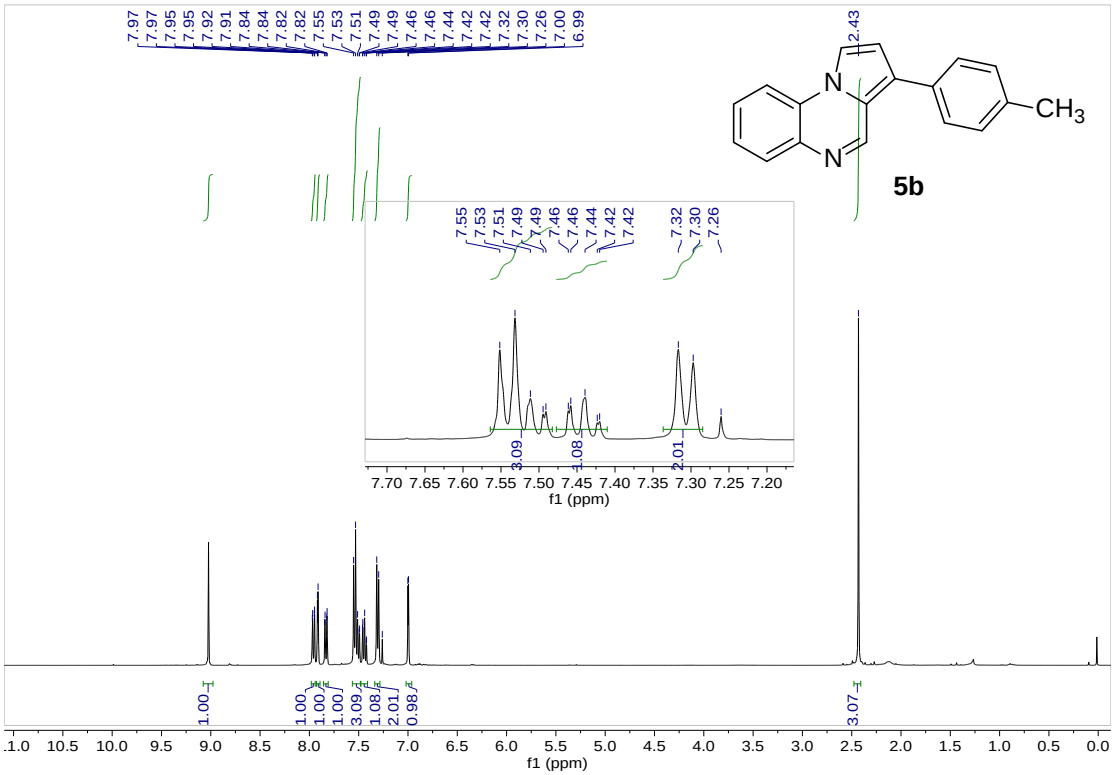


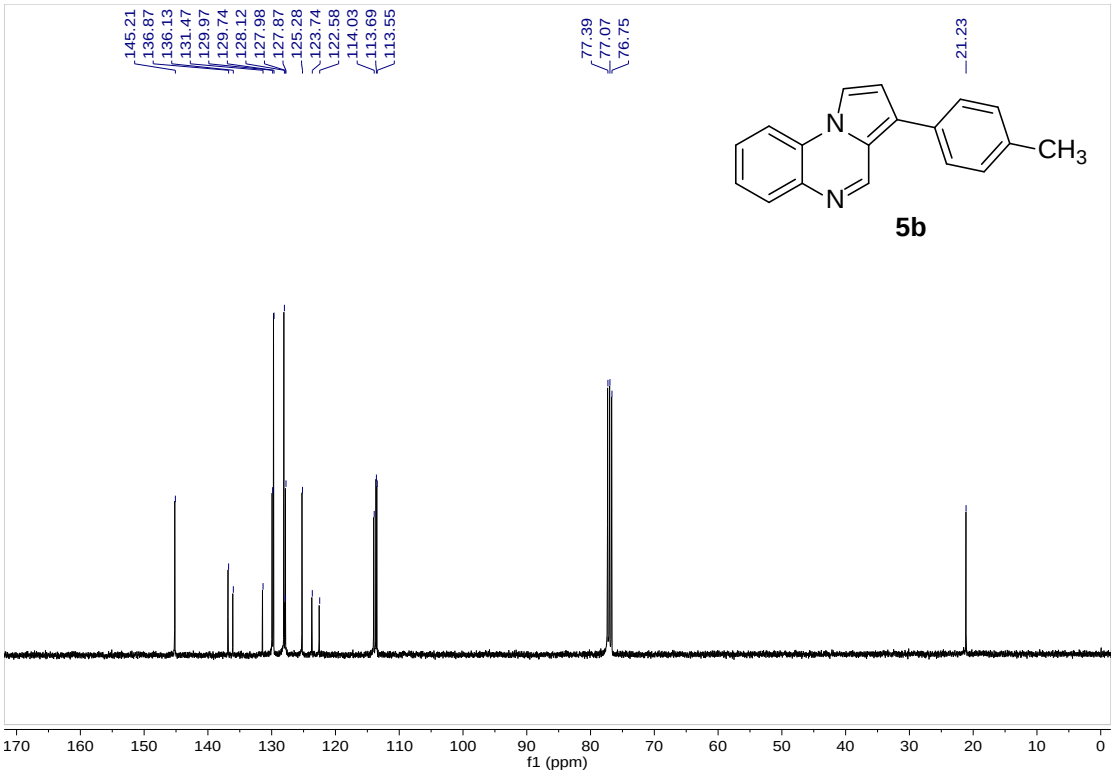
*3-phenylpyrrolo[1,2-a]quinoxaline [**5a**]*



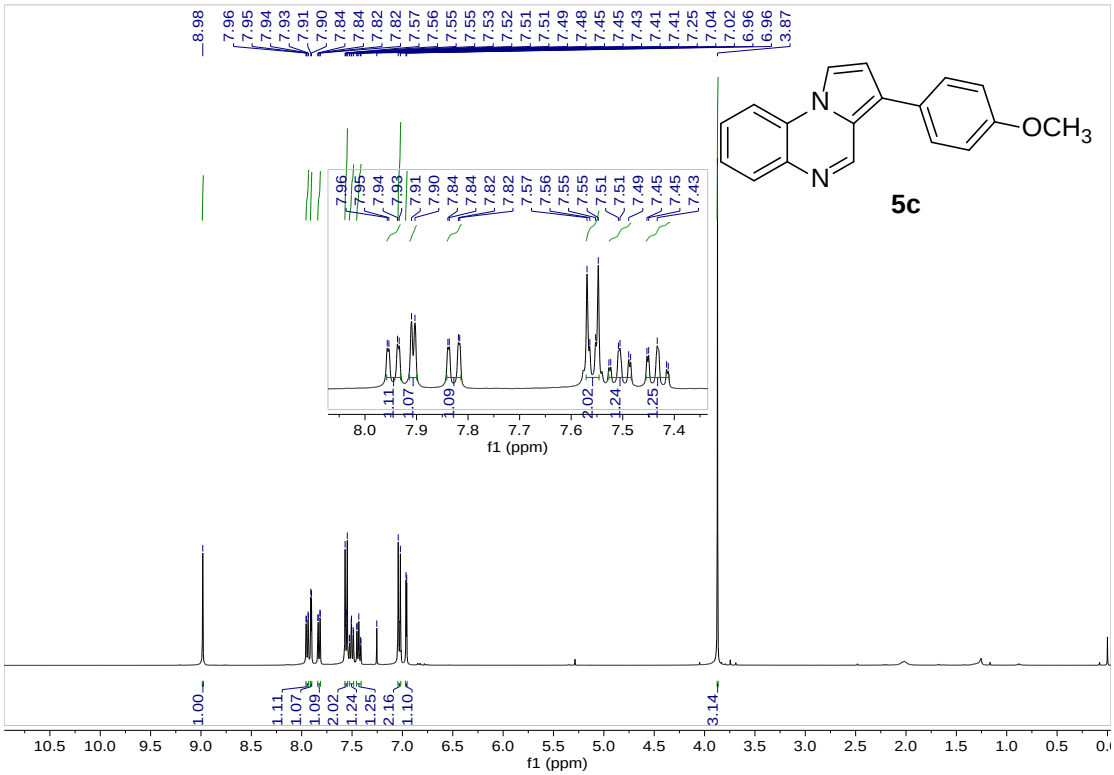


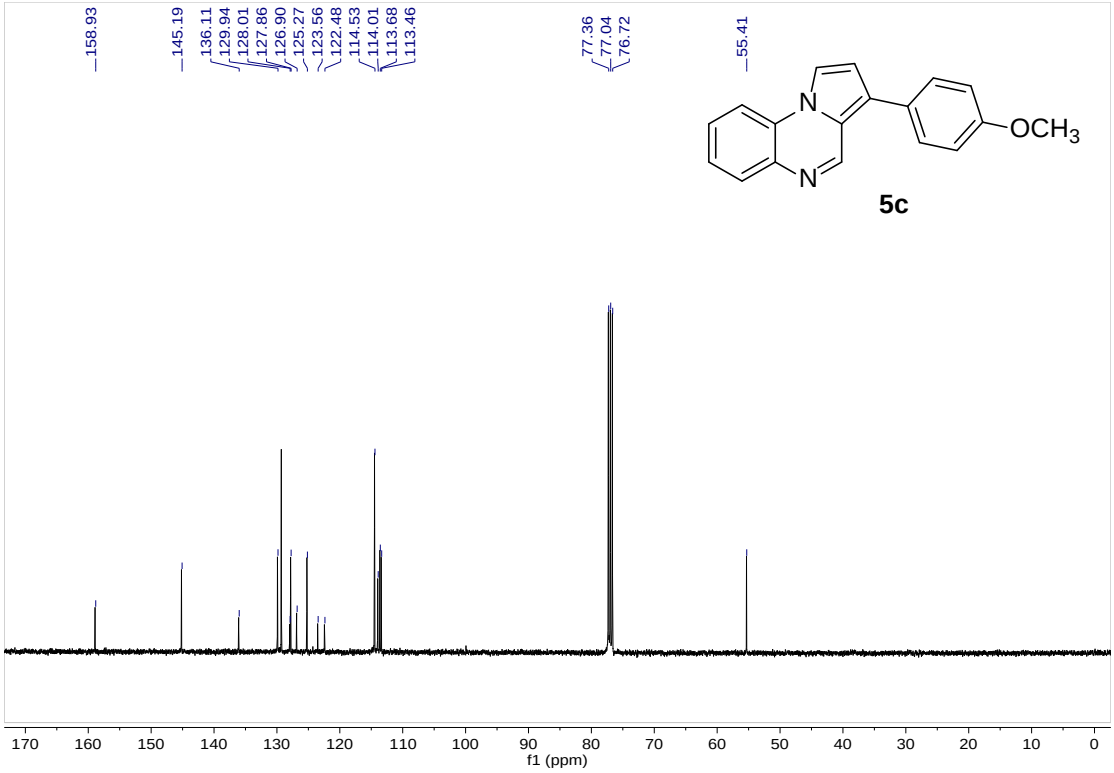
*3-(p-tolyl)pyrrolo[1,2-a]quinoxaline [**5b**]*



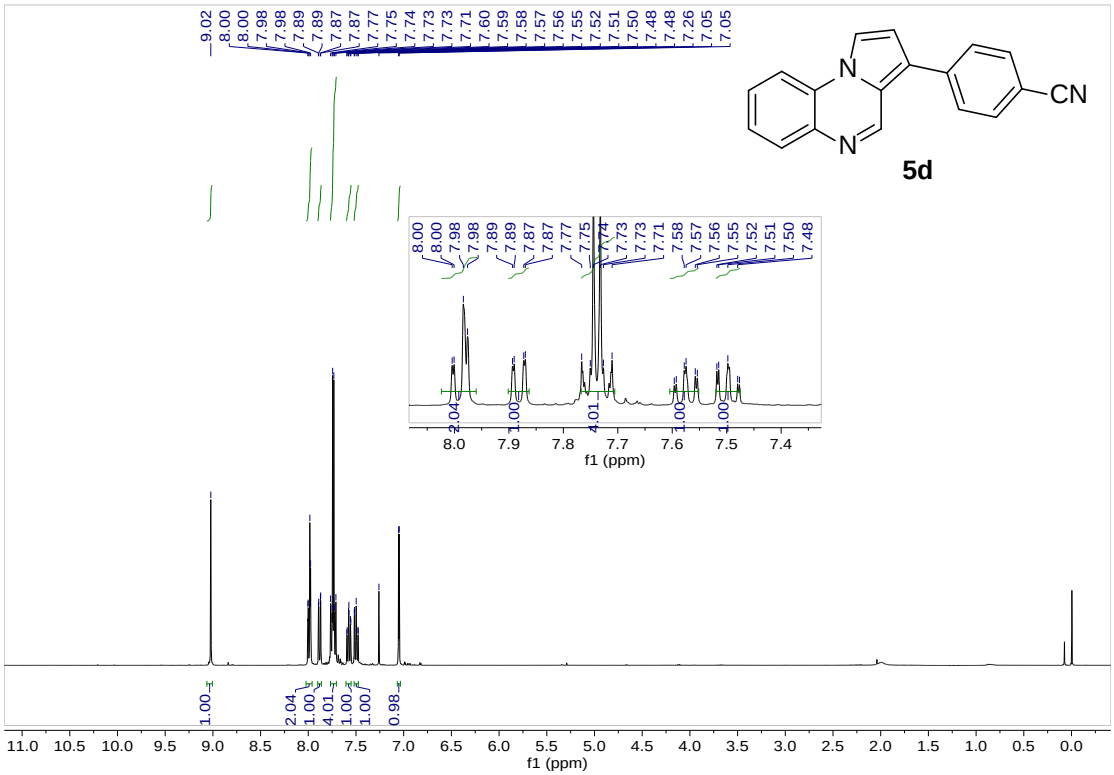


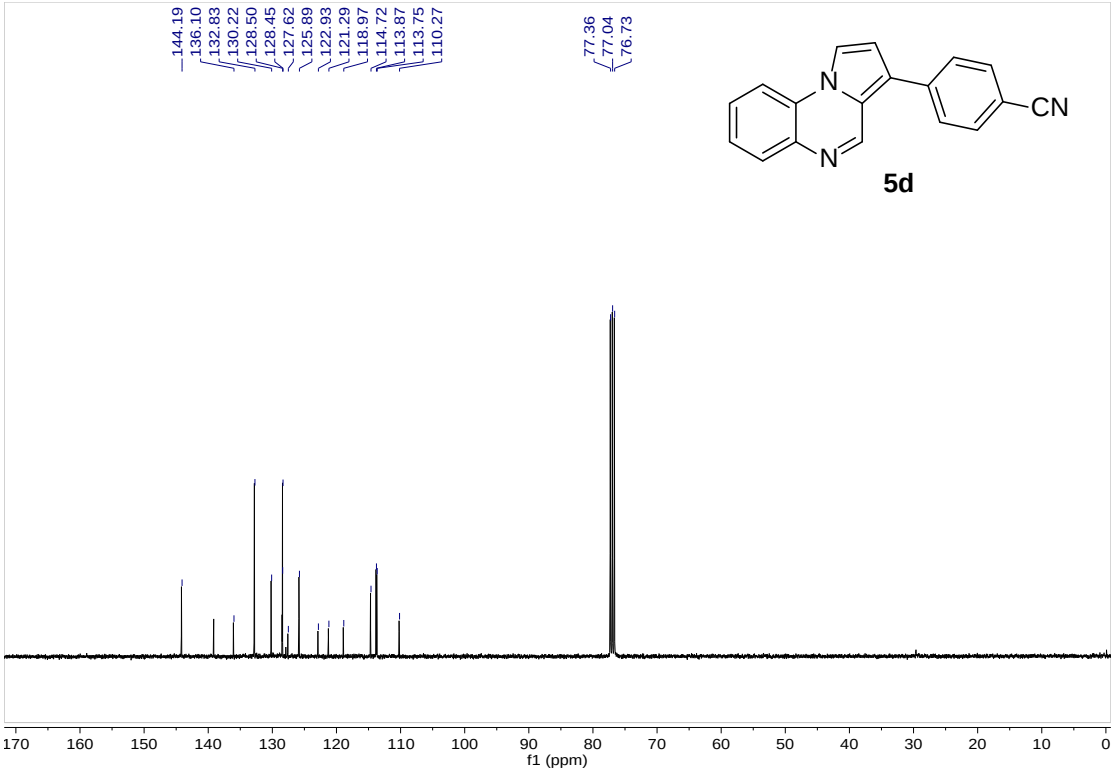
*3-(4-methoxyphenyl)pyrrolo[1,2-a]quinoxaline [**5c**]*



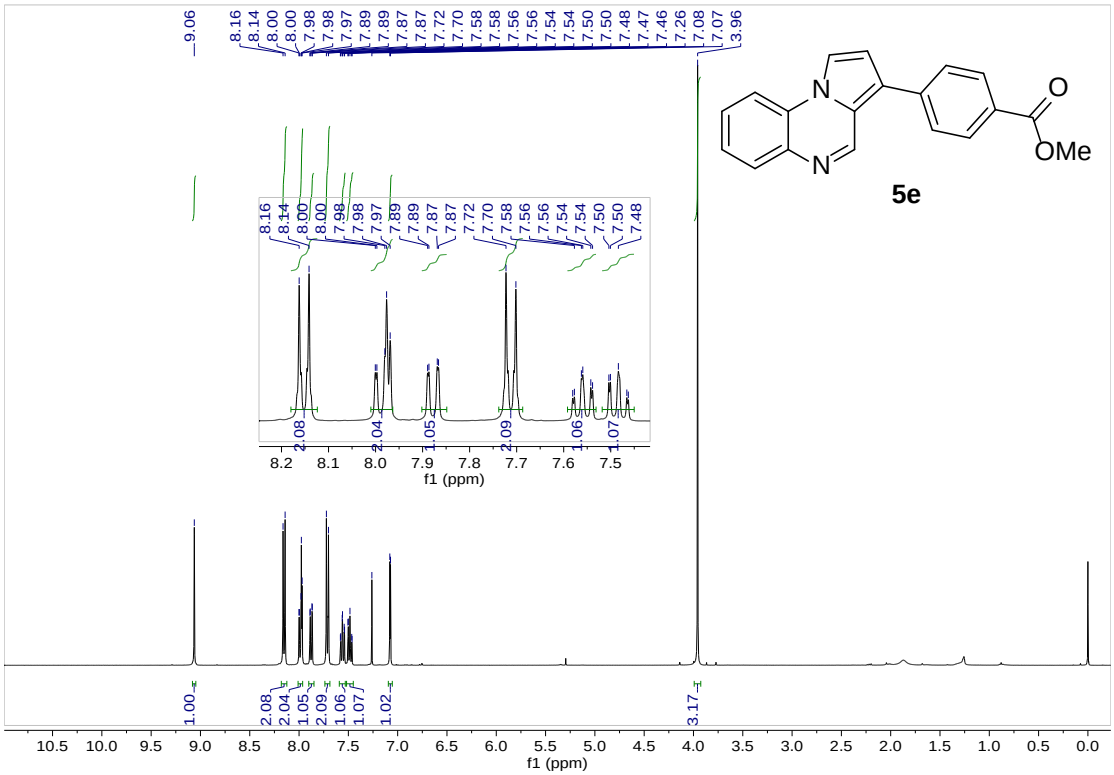


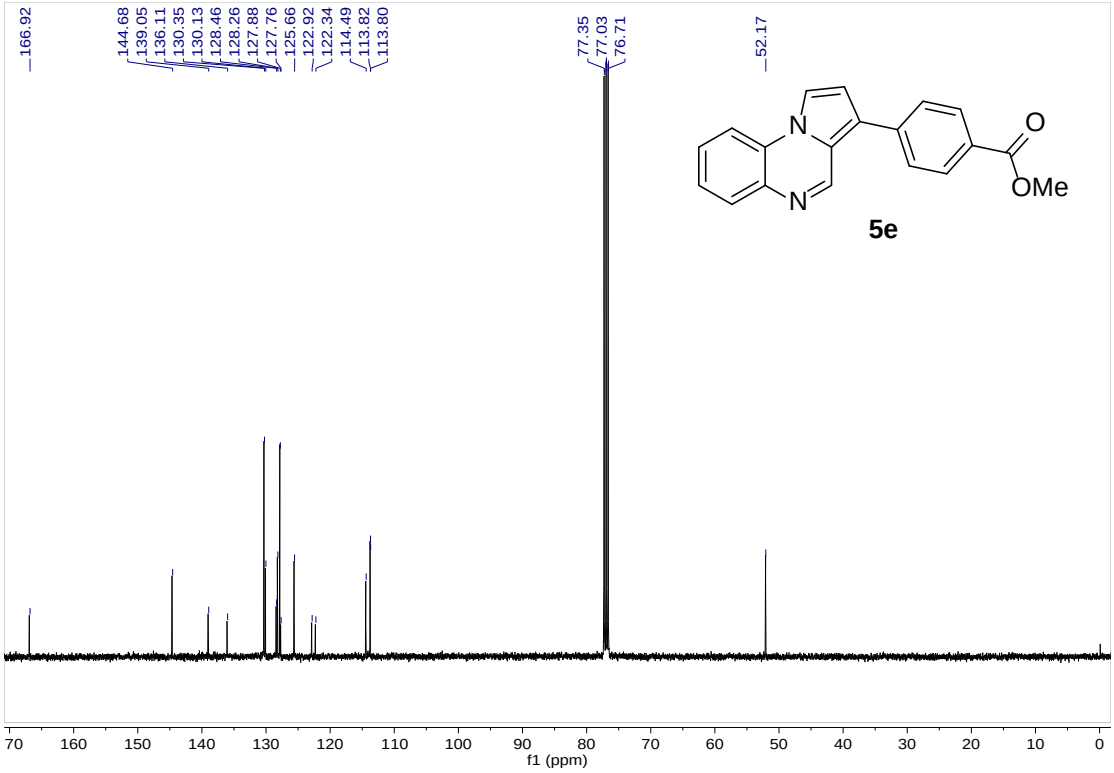
*4-(pyrrolo[1,2-a]quinoxalin-3-yl)benzonitrile [**5d**]*



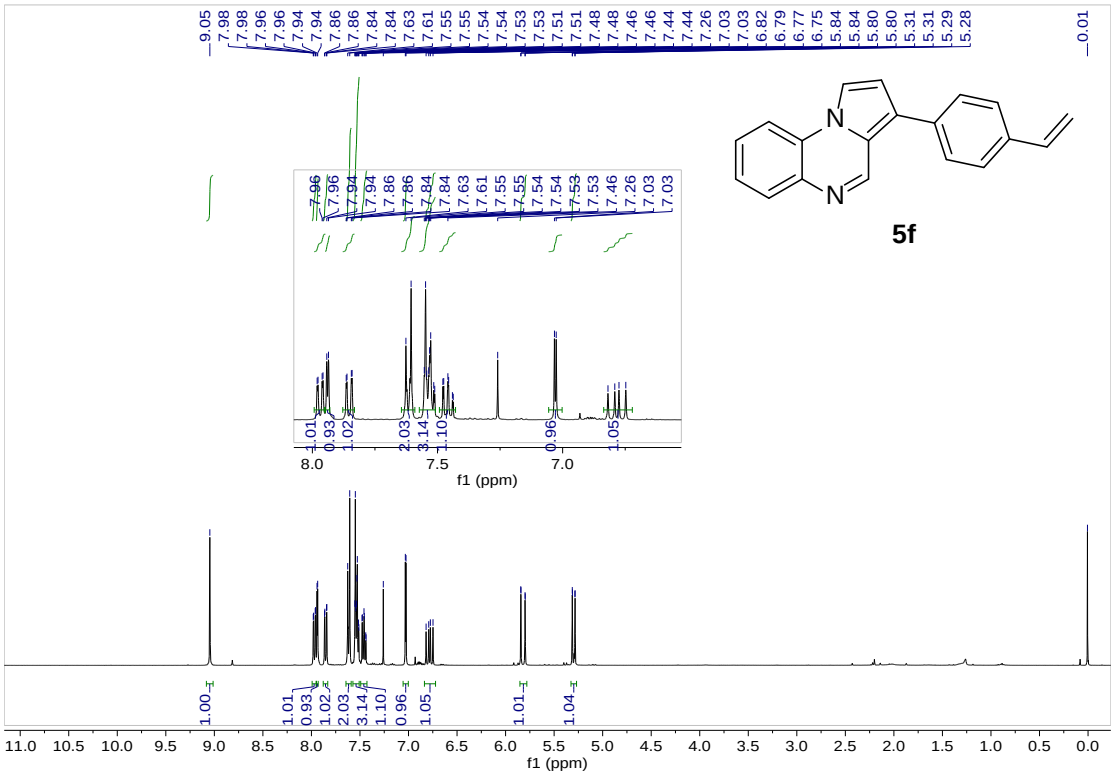


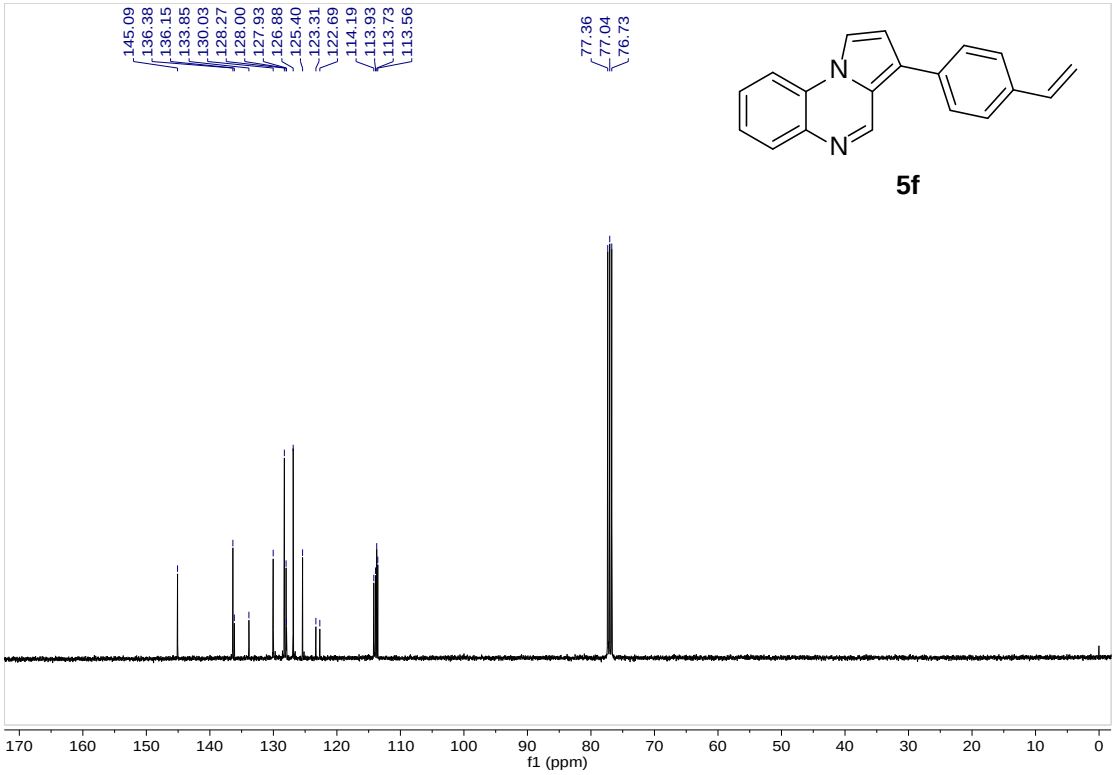
*methyl 4-(pyrrolo[1,2-a]quinoxalin-3-yl)benzoate [**5e**]*



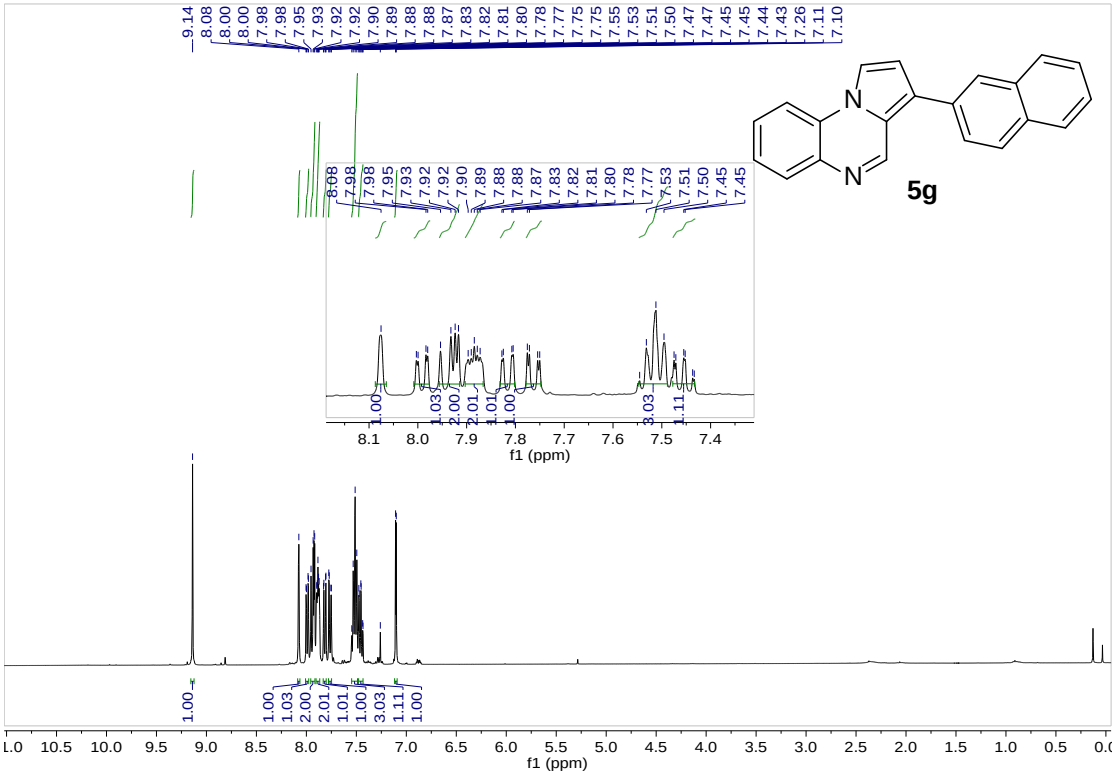


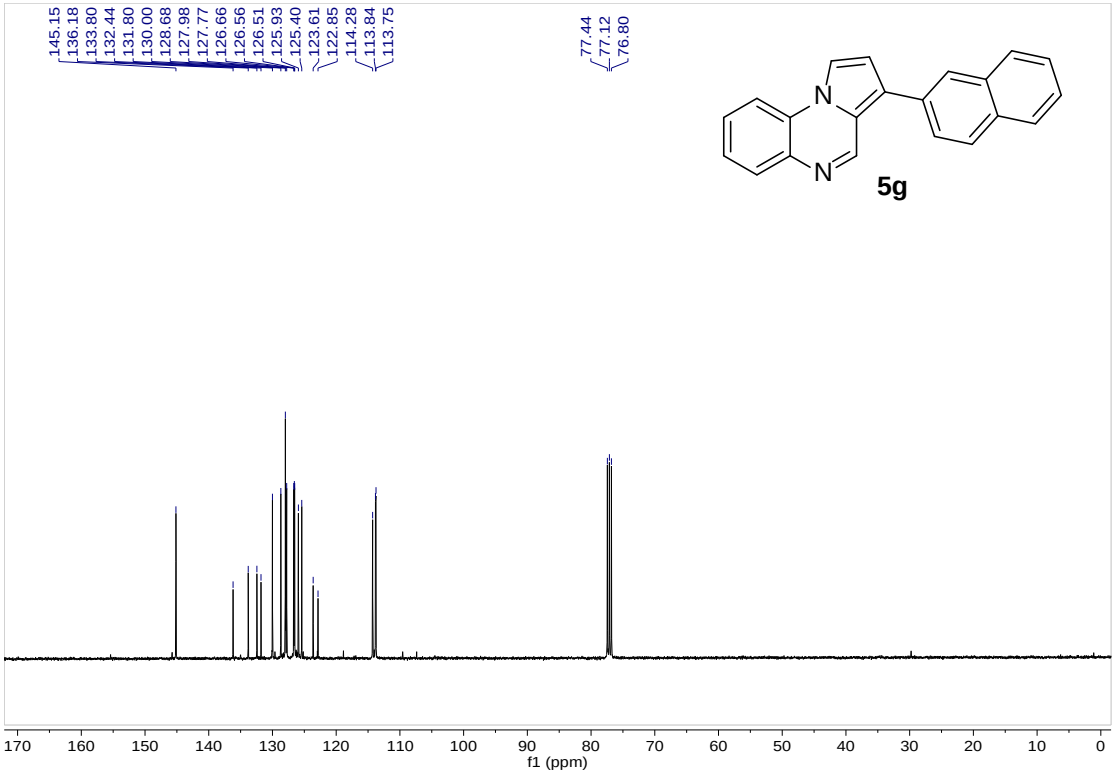
*3-(4-vinylphenyl)pyrrolo[1,2-a]quinoxaline [**5f**]*



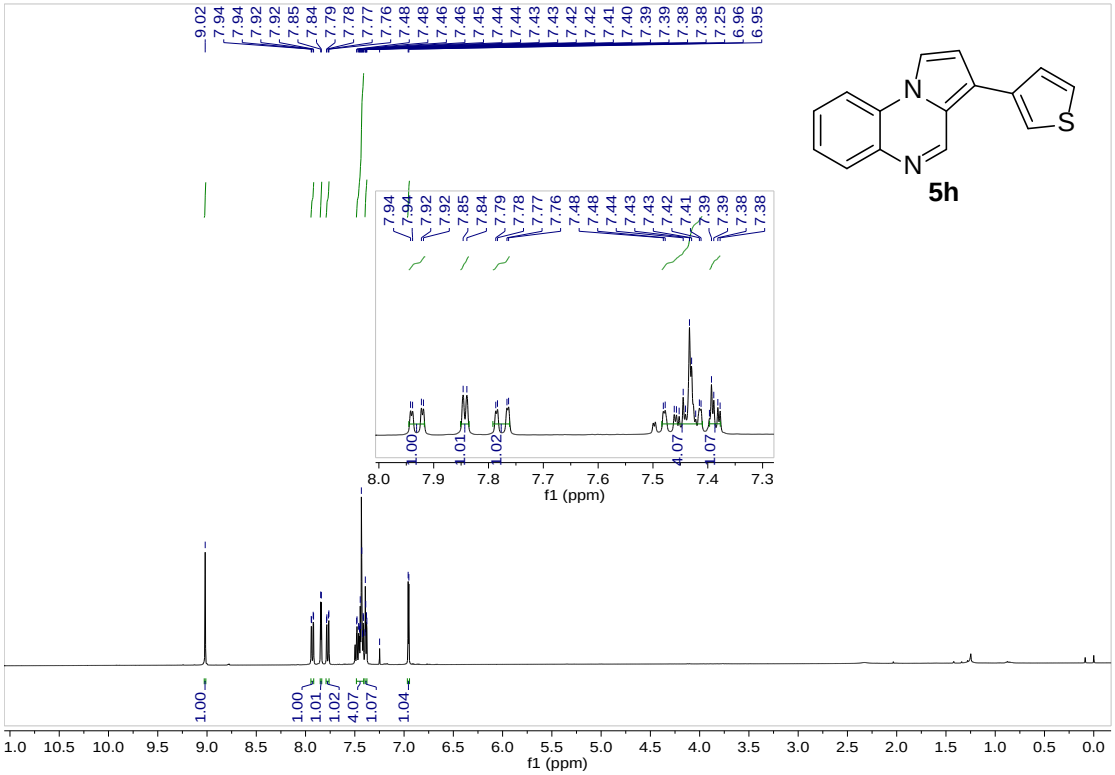


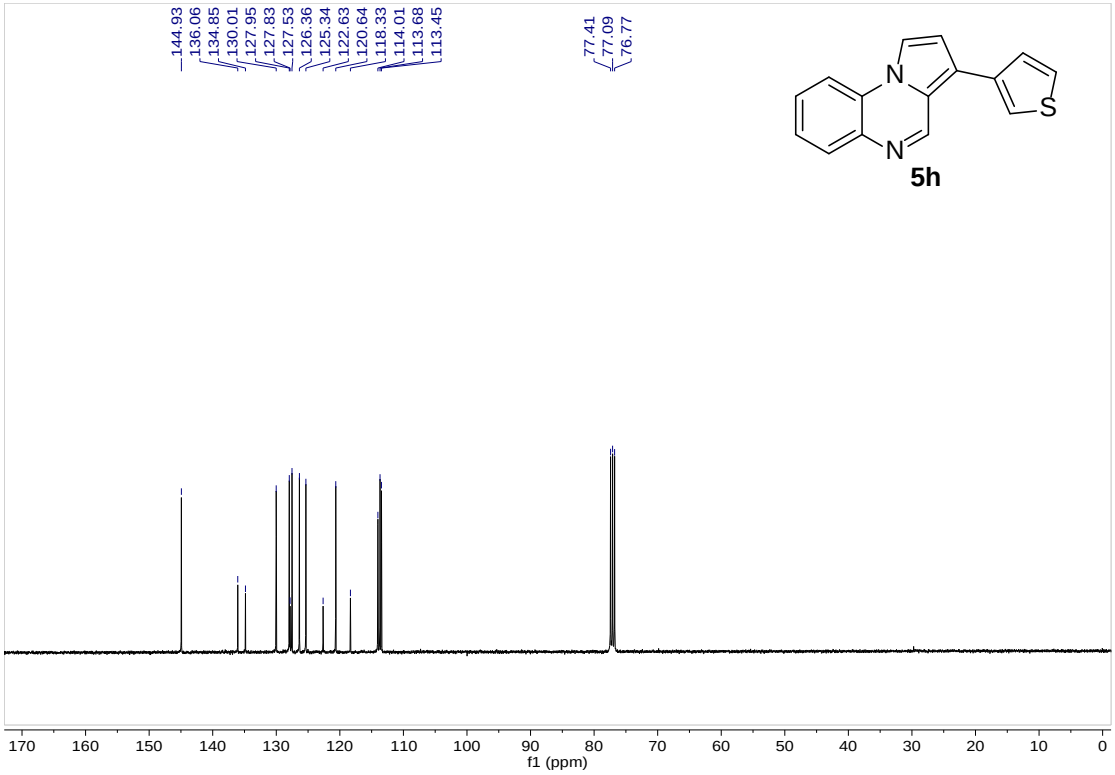
*3-(naphthalen-2-yl)pyrrolo[1,2-a]quinoxaline [**5g**]*



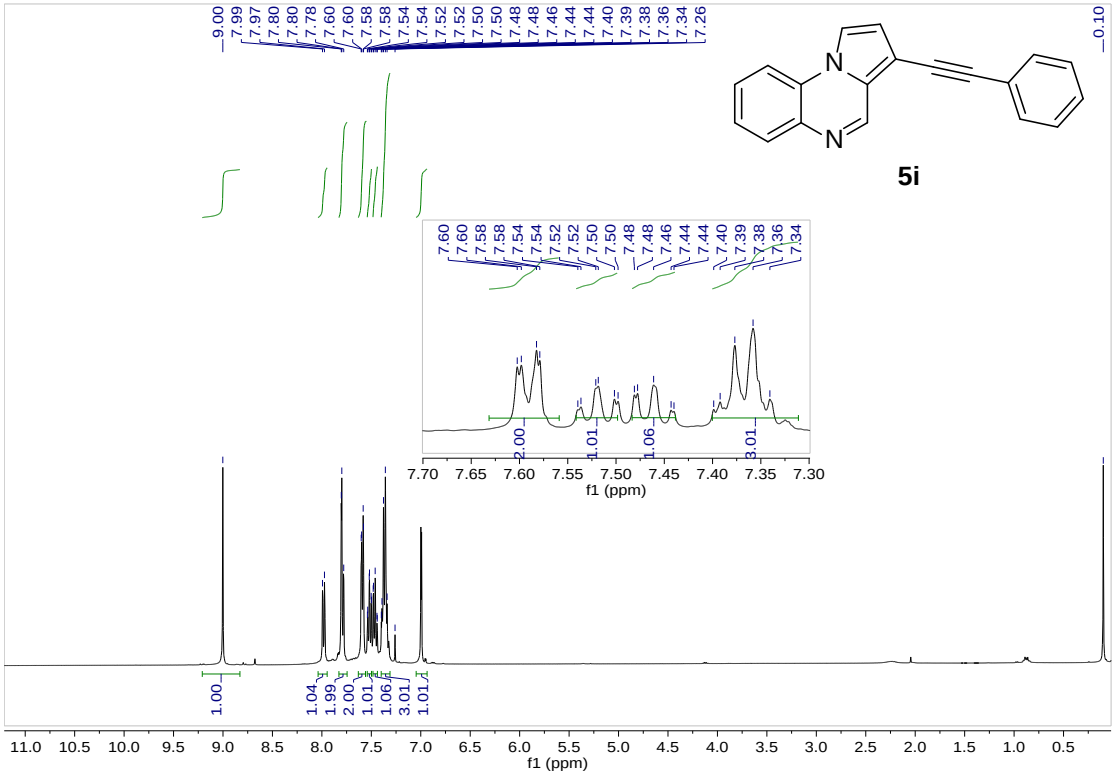


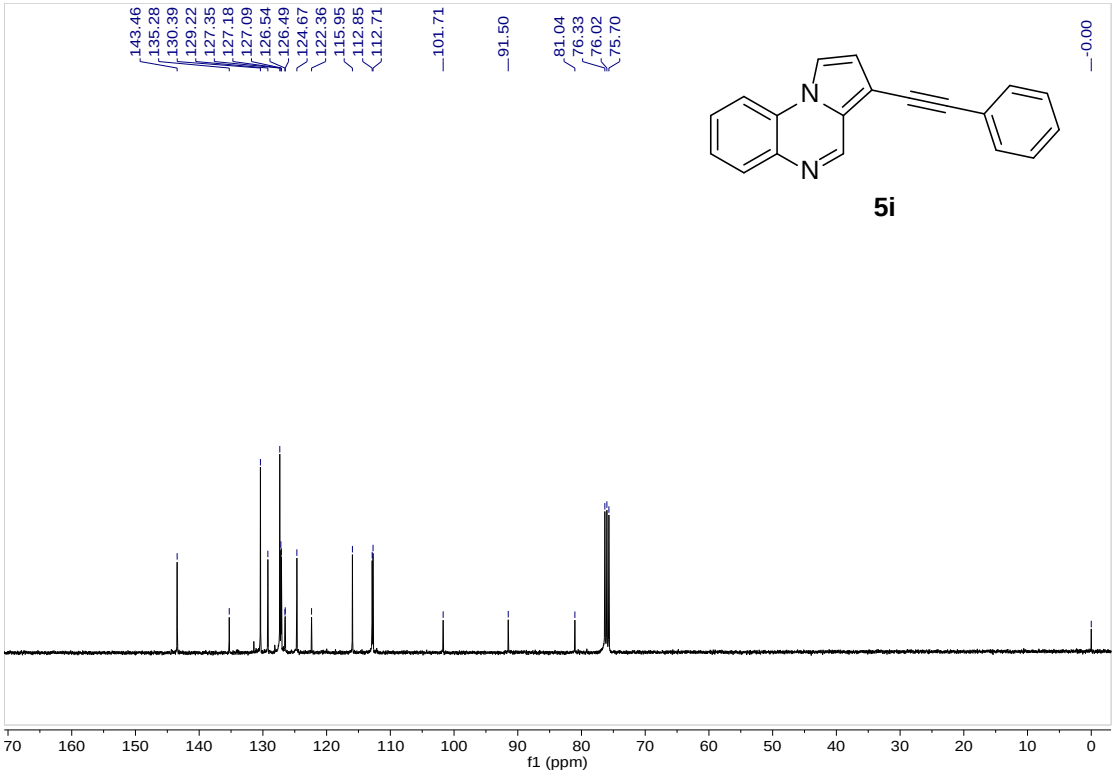
*3-(thiophen-3-yl)pyrrolo[1,2-a]quinoxaline [**5h**]*



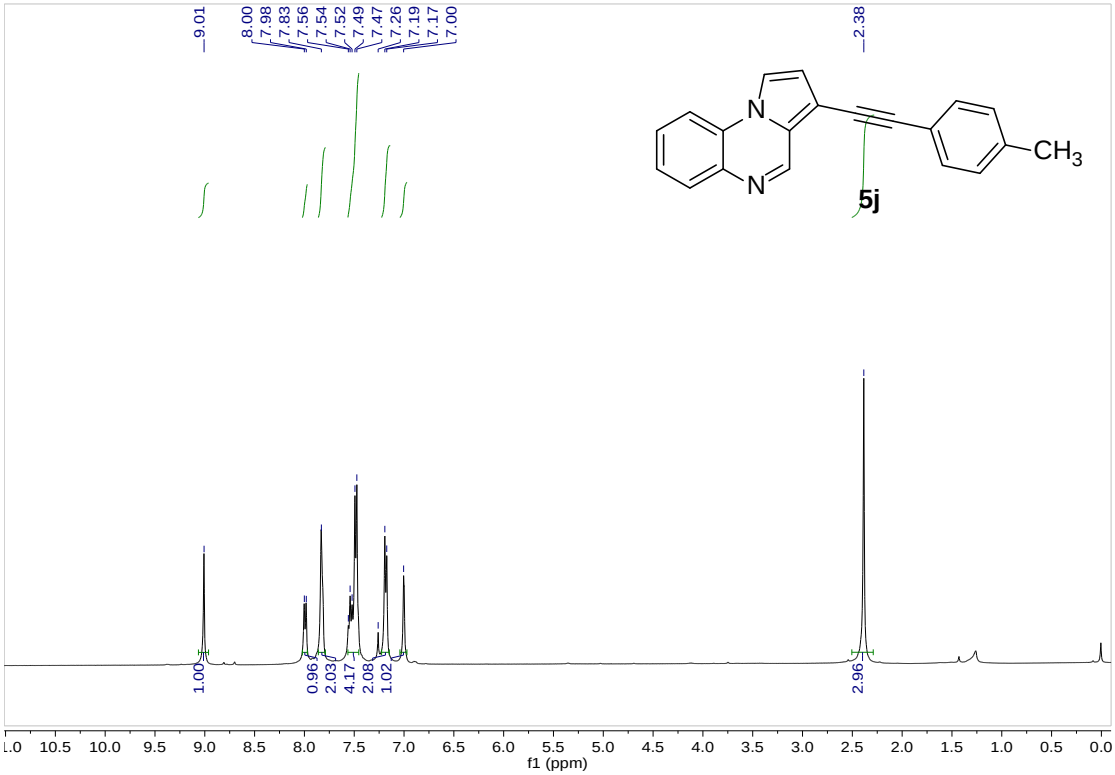


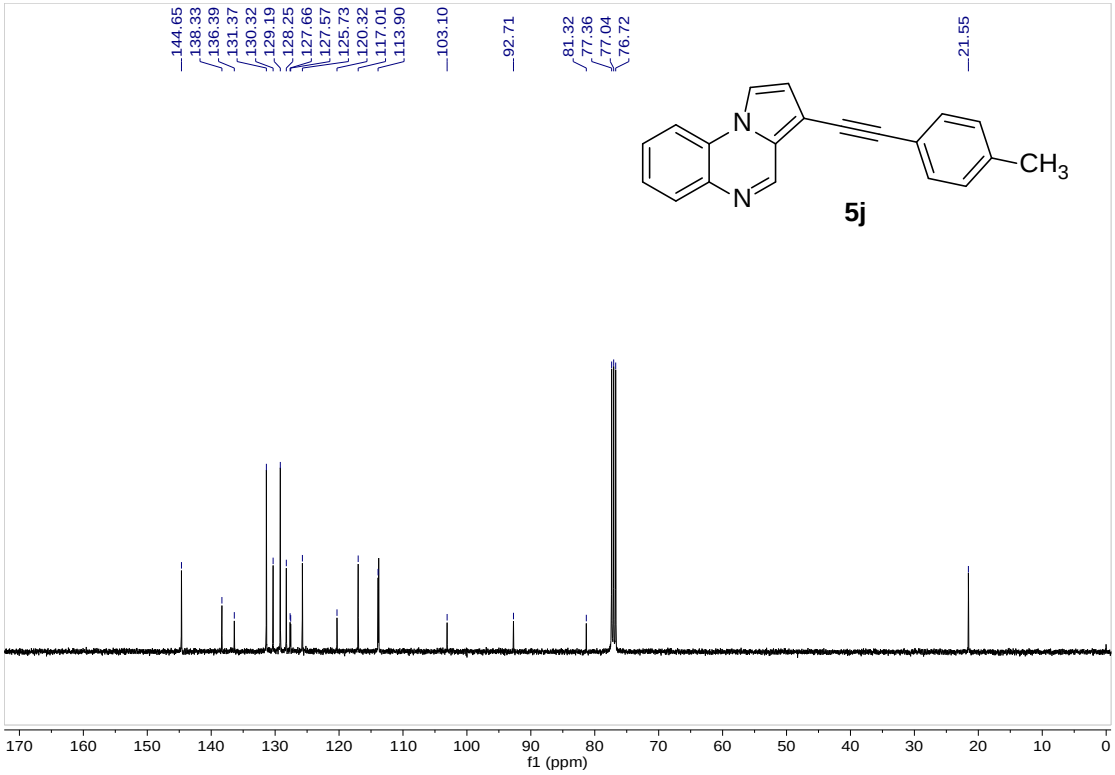
*3-(phenylethynyl)pyrrolo[1,2-a]quinoxaline [**5i**]*



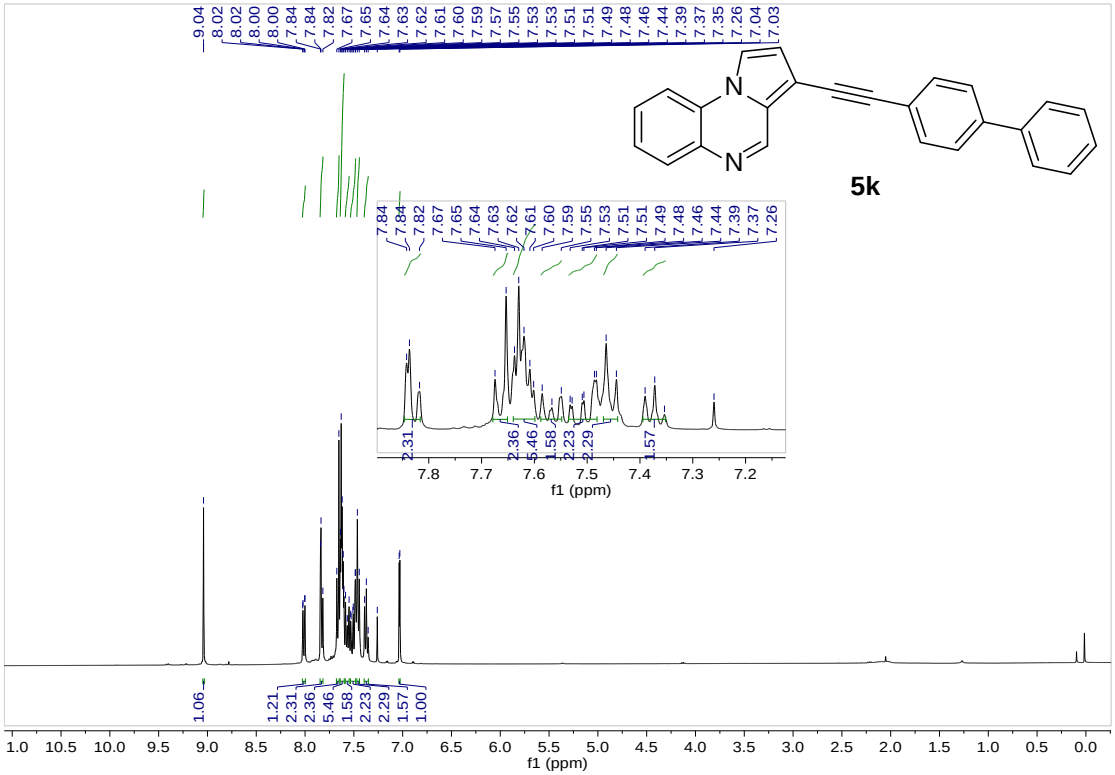


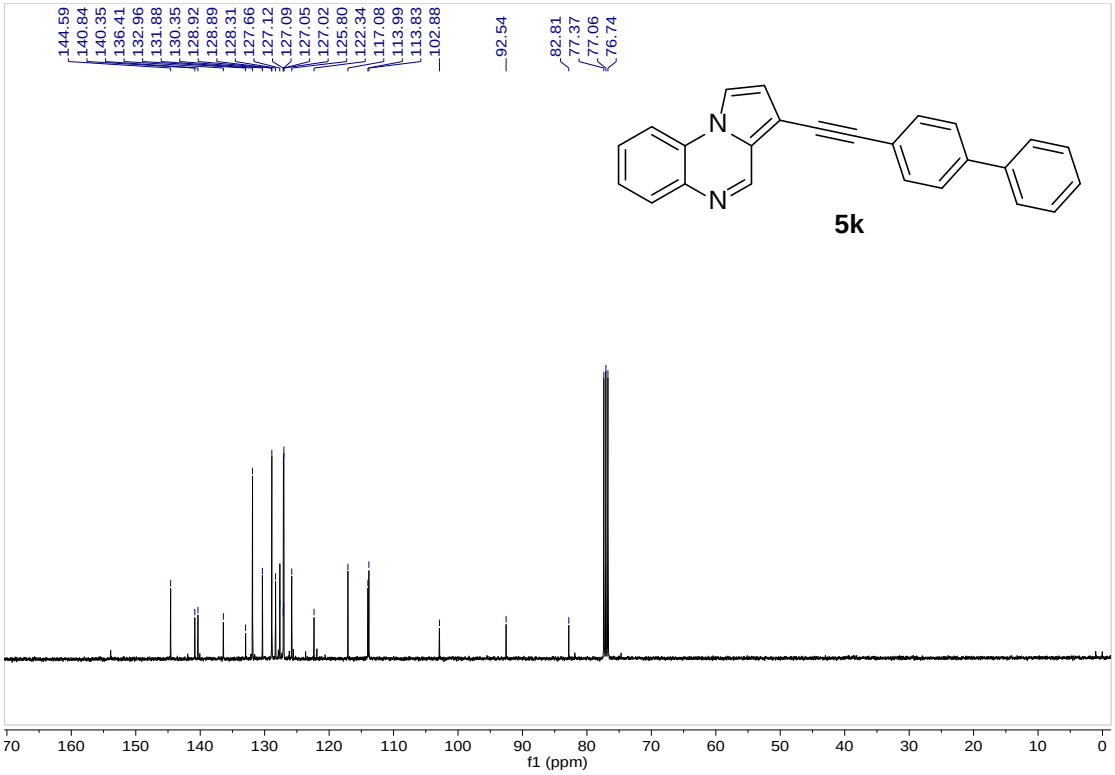
*3-(p-tolylethynyl)pyrrolo[1,2-a]quinoxaline [**5j**]*



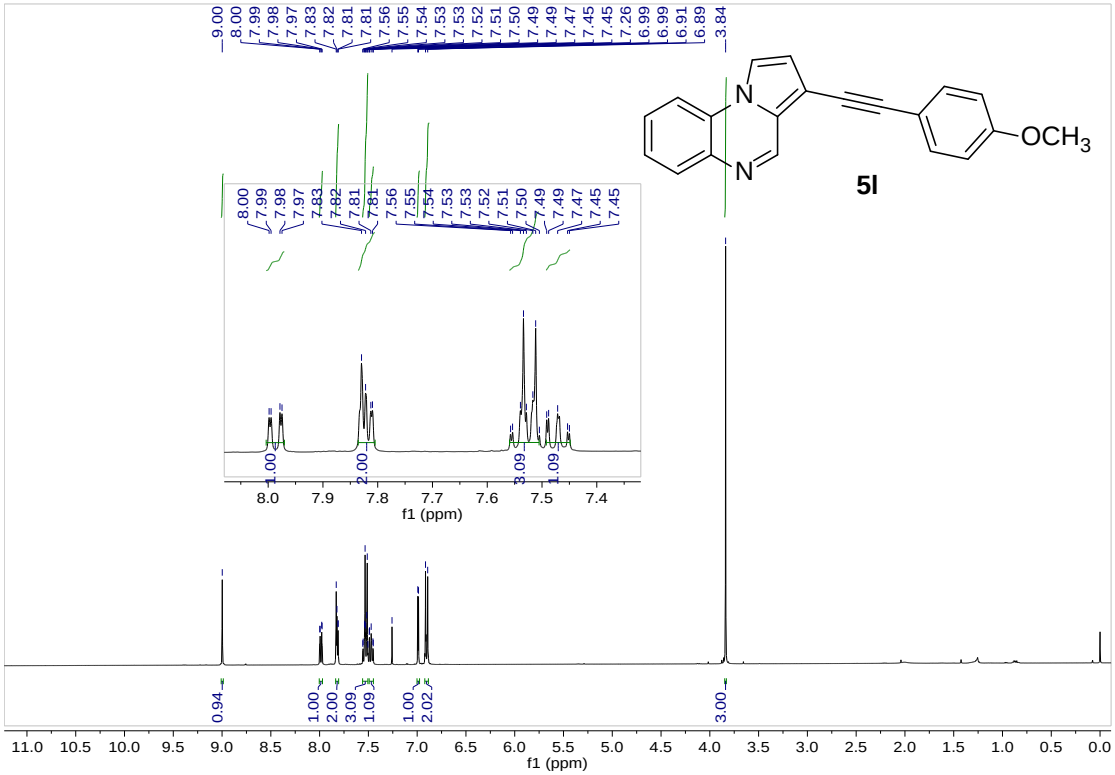


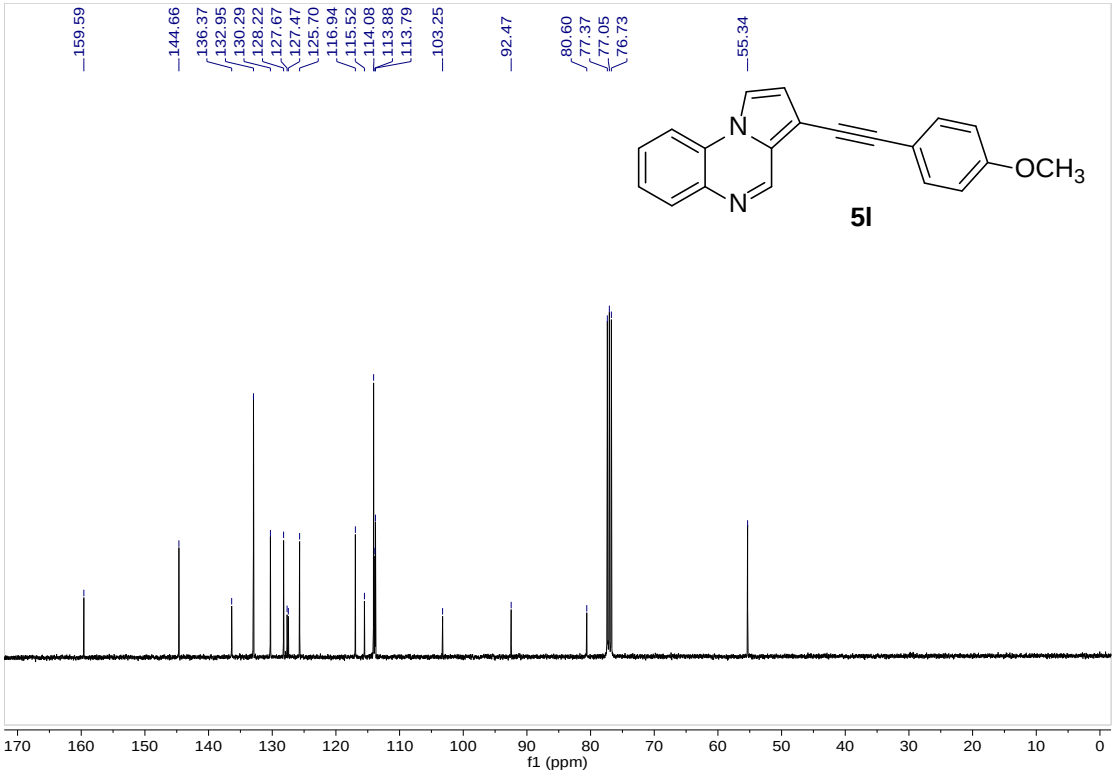
*3-([1,1'-biphenyl]-4-ylethynyl)pyrrolo[1,2-a]quinoxaline [**5k**]*



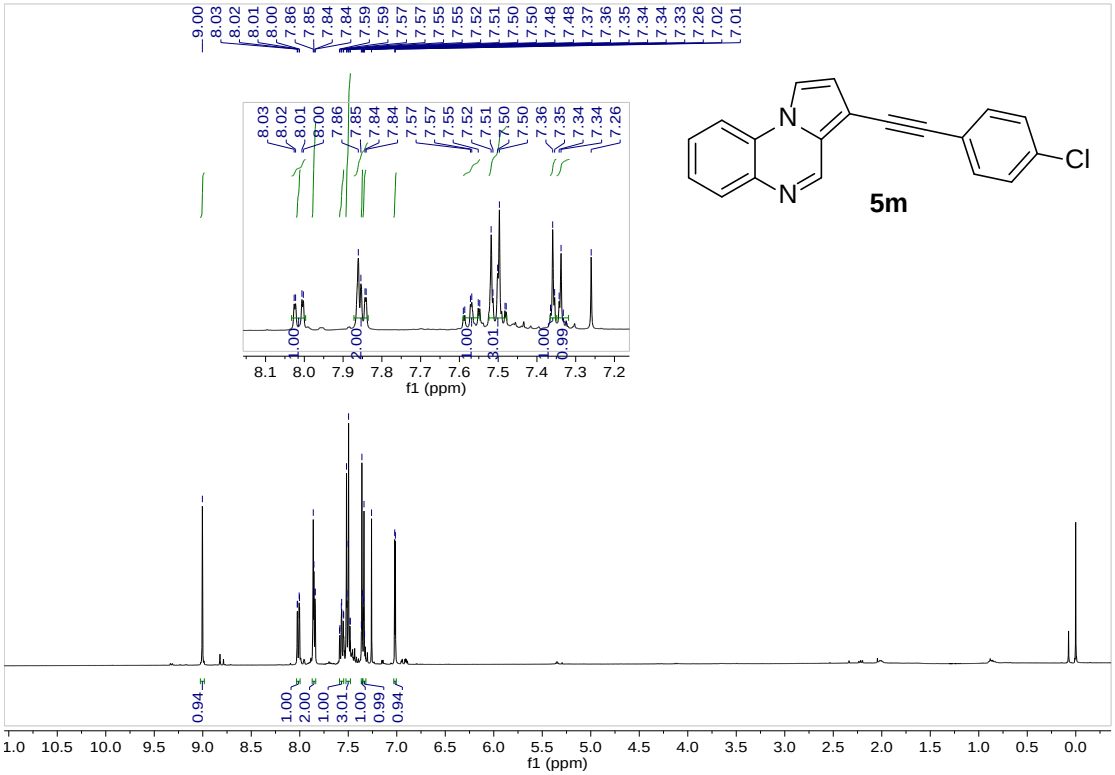


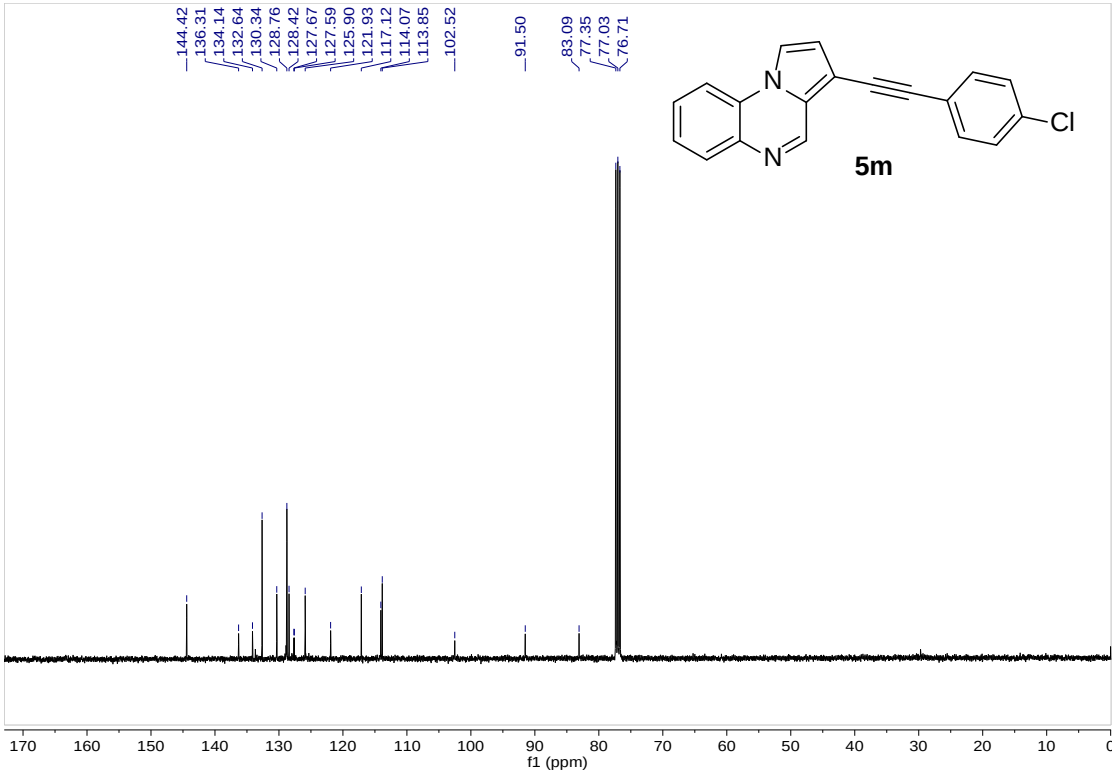
*3-((4-methoxyphenyl)ethynyl)pyrrolo[1,2-a]quinoxaline [**5l**]*





*3-((4-chlorophenyl)ethynyl)pyrrolo[1,2-a]quinoxaline [**5m**]*





*2-methyl-4-(pyrrolo[1,2-a]quinoxalin-3-yl)but-3-yn-2-ol [**5n**]*