Sodium Sulfide-Promoted Regio-Defined Redox Condensation of *o*-Nitroanilines with Aryl Ketones to Benzo[*a*]phenazines and Quinoxalines

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General information

Reagents were obtained from commercial supplier and used without further purification. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or phosphomolybdic acid or vanilline stains. Flash column chromatography was carried out using kieselgel 35-70 µm particle sized silica gel (230-400 mesh). NMR Chemical shifts are reported in (δ) ppm relative to tetramethylsilane (TMS) with the residual solvent as internal reference ($CDCl_3$, δ 7.26 ppm for ^1H, 77.0 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration.

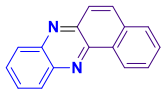
General procedure

General procedure for the synthesis of quinoxaline

A mixture of *o*-nitroaniline (1 mmol), α-tetralone/acetophenone (1.2 mmol) and $Na_2S•3H_2O$ (1 mmol) in DMSO (0.2 mL) was heated at 130 ºC for 1-4 h. The crude mixture was partitioned between H_2O (2 mL) and dichloromethane (4 mL). The combined dichloromethane layer was separated. The aqueous layer was extracted with dichloromethane (4 mL). The combined dichloromethane layers were dried (Na_2SO_4), concentrated and purified by column chromatography on silica gel (EtOAc:Hexane 3:97) to provide the expected benzo[a]phenazine/quinoxaline as pale yellow solid.

Product characterization

Benzo[a]phenazine (3a)[1]



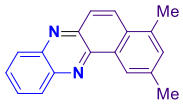
Purification of the crude mixture by column chromatography on silica gel (DCM to DCM:EtOAc 99:1) (pale yellow solid, pale yellow solid, 125 mg, 54%).

^1H NMR (600 MHz, $CDCl_3$) δ 9.42-9.40 (m, 1H), 8,38-8,35 (m, 1H), 8.3-8.27 (m, 1H), 8.01-7.95 (m, 2H), 7.91-7.85 (m, 3H), 7.81-7.76 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.8, 142.9, 142.8, 142.1, 133.4, 131.3, 130.1, 130.0, 129.9, 129.8, 129.4, 128.3, 128.1, 127.4, 125.5 (1 signals missing due to overlap).

2,4-Dimethylbenzo[a]phenazine (3b)

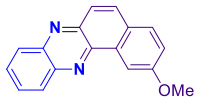
[1] S. Wang, R. Li, S. Jiang, H. Huang, W. Shao and G. Deng *Adv. Synth. Catal.*, 2022, **364**, 1481.



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 1:99) (pale yellow solid, pale yellow solid, 106 mg, 41%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.38-8.35 (m, 1H), 8.29-8.26 (m, 1H), 8.21 (d, J = 9.4 Hz, 1H), 7.93 (d, J = 9.5 Hz, 1H), 7.87-7.84 (m, 2H), 7.45 (s, 1H), 2.75 (s, 3H), 2.65 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.6, 143.0, 142.9, 142.1, 137.9, 135.0, 132.9, 131.6, 130.0, 129.9, 129.8, 129.6, 129.3, 125.8, 123.4, 22.0, 19.6 (1 signals missing due to overlap).
HRMS (ESI+) calcd for $C_{18}H_{15}N_2$ [M + H]+ 259.1235. Found: 259.1240

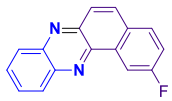
2-Methoxybenzo[a]phenazine (3c)[2]



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 122 mg, 47%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (d, J = 2.7, 1H), 8.37-8.35 (m, 1H), 8.28-8.25 (m, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.86-7.79 (m, 4H), 7.35 (dd, J = 8.6 Hz, J = 2.7 Hz, 1H), 4.12 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 144.1, 143.0, 142.3, 141.8, 133.0, 132.9, 130.1, 129.8, 129.9, 129.7, 129.3, 127.7, 124.6, 119.8, 106.6, 55.9.

2-Fluorobenzo[a]phenazine (3d)[3]

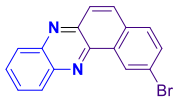


Purification of the crude mixture by column chromatography on silica gel (DCM to DCM:EtOAc 99:1) (pale yellow solid, 126 mg, 51%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.06 (dd, J = 2.7 Hz, J = 10.0 Hz, 1H), 8.38-8.36 (m, 1H), 8.31-8.28 (m, 1H), 7.99 (d, J = 9.3 Hz, 1H), 7.95-7.88 (m, 4H), 7.52-7.49 (m, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.6 (d, J = 248.7 Hz), 143.9, 143.3, 142.0, 142.0, 133.4 (d, J = 8.5 Hz), 132.5, 130.6, 130.4 (d, J = 9.0 Hz), 130.2, 130.0 (d, J = 2.1 Hz), 129.9, 129.4, 126.6 (d, J = 2.3 Hz), 118,4 (d, J = 24.1 Hz), 111.1 (d, J = 23.2 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ -111.13 (dd, J = 15.3, 8.7 Hz).

[2] L. A. Nguyen, T. T. T. Nguyen, Q. A. Ngo and T. B. Nguyen, *Adv. Synth. Catal.*, 2022, **364**, 2748.
[3] S. J. Lou, D. Q. Xu, D. F. Shen, Y. F. Wang, Y. K. Liu and Z. Y. Xu, *Chem. Comm.*, 2012, **48**, 11993.

2-Bromobenzo[a]phenazine (3e)[4]

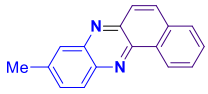


Purification of the crude mixture by column chromatography on silica gel (DCM to DCM:EtOAc 99:1) (pale yellow solid, 163 mg, 53%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.57 (d, J = 2.0 Hz, 1H), 8.39-8.37 (m, 1H), 8.31-8.28 (m, 1H), 8.01-7.96 (m, 2H), 7.91-7.87 (m, 3H), 7.79 (d, J = 8.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 143.4, 142.0, 141.9, 137.1, 137.1, 135.4, 133.0, 131.1, 131.0, 130.7, 128.4, 120.8, 120.7, 117.5, 117.5.

9-Methylbenzo[a]phenazine (3g)[4]

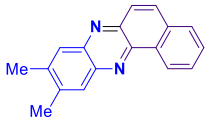


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 112 mg, 46%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.40-9.39 (m, 1H), 8.25 (d, J = 8.7 Hz, 1H), 8.04-8.03 (m, 1H), 8.00 (d, J = 9.2 Hz, 1H), 7.95 (d, J = 9.2 Hz, 1H), 7.91-7.90 (m, 1H), 7.81-7.75 (m, 2H), 7.70 (dd, J = 8.7, 1.95 Hz, 1H), 2.67 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.6, 142.9, 142.0, 140.7, 133.1, 133.0, 132.6, 131.3, 129.5, 129.2, 128.2, 127.8, 127.6, 127.2, 125.2, 22.2 (1 signals missing due to overlap).

9,10-Dimethylbenzo[a]phenazine (3f)[4]

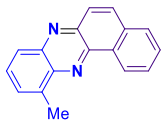


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 98 mg, 38%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.38-9.36 (m, 1H), 8.08-8.07 (m, 1H), 7.99-7.98 (m, 1H), 7.96-7.88 (m, 3H), 7.78-7.72 (m, 2H), 2.56 (s, 3H), 2.55 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.0, 142.0, 142.0, 141.2, 141.0, 140.9, 133.1, 132.3, 131.3, 129.3, 128.4, 128.1, 127.9, 127.7, 127.3, 125.1, 20.6, 20.5.

11-Methylbenzo[a]phenazine (3h)

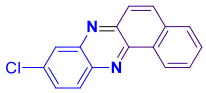


[4] S. Wang, R. Li, S. Jiang, H. Huang, W. Shao and G. Deng, *Adv. Synth. Catal.*, 2022, **364**, 1481.

Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 125 mg, 51%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.46-9.44 (m, 1H), 8.12-8.10 (m, 1H), 8.01 (d, J = 9.2 Hz, 1H), 7.96 (d, J = 9.3 Hz, 1H), 7.92-7.90 (m, 1H), 7.81-7.73 (m, 3H), 7.70-7.68 (m, 1H), 3.04 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 142.9, 141.4, 141.3, 138.0, 133.2, 133.0, 131.6, 130.0, 129.6, 129.4, 128.2, 127.8, 127.2, 127.1, 125.3, 17.5.
HRMS (ESI+) calcd for $C_{17}H_{13}N_2$ [M + H]+ 245.1079. Found: 245.1083.

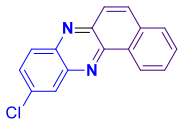
9-Chlorobenzo[a]phenazine (3i)[5]



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 58 mg, 22%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.42-9.36 (m, 1H), 8.31 (d, J = 9.1 Hz, 1H), 8.28 (d, J = 2.3 Hz, 1H), 8.04 (d, J = 9.3 Hz, 1H), 7.96-7.91 (m, 2H), 7.84-7.78 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 143.0, 142.9, 140.6, 136.1, 134.2, 133.5, 131.2, 131.1, 130.2, 128.5, 128.3, 128.0, 127.2, 125.6 (1 signals missing due to overlap).

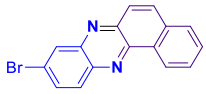
10-Chlorobenzo[a]phenazine (3j)[5]



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 111 mg, 42%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.34-9.31 (m, 1H), 8.31 (d, J = 2.3 Hz, 1H), 8.17 (d, J = 9.0 Hz, 1H), 7.98 (d, J = 9.2 Hz, 1H), 7.90-7.87 (m, 2H), 7.80-7.75 (m, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.7, 143.1, 141.9, 141.2, 135.7, 133.6, 133.4, 131.2, 130.9, 130.4, 130.2, 128.3, 128.2, 128.1, 127.0, 125.5.

9-Bromobenzo[a]phenazine (3k)



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 96 mg, 31%).

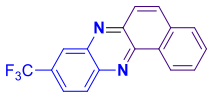
[5] A. Kwast, K. Stachowska, A. Trawczyński and Z. Wróbel, *Tetrahedron Lett.*, 2011, **52**, 6484.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.34-9.31 (m, 1H), 8.43 (d, J = 2.2 Hz, 1H), 8.18 (d, J = 9.1 Hz, 1H), 7.99 (d, J = 9.3 Hz, 1H), 7.90-7.87 (m, 3H), 7.80-7.76 (m, 2H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 143.1, 142.7, 140.5, 134.0, 133.4, 133.3, 131.3, 131.0, 130.9, 130.0, 128.3, 128.1, 127.0, 125.4, 124.1.

HRMS (ESI+) calcd for $C_{16}H_{10}BrN_2$ [M + H]+ 309.0027. Found: 309.0032.

9-(Trifluoromethyl)benzo[a]phenazine (3l)



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 167 mg, 56%).

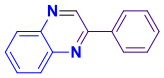
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.38-9.34 (m, 1H), 8.57 (s, 1H), 8.43 (d, J = 8.9 Hz, 1H), 8.02 (d, J = 9.3 Hz, 1H), 7.98 (dd, J = 8.9, J = 1.9 Hz, 1H), 7.92 (d, J = 9.3 Hz, 1H), 7.91-7.88 (m, 1H), 7.82-7.79 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.6, 144.0, 142.5, 141.4, 134.3, 133.5, 131.4 (d, J = 32.9 Hz), 131.0, 130.7, 130.5, 128.4, 128.2, 127.4 (q, J = 4.4 Hz), 126.9, 125.7, 125.0 (q, J = 3.0 Hz), 123.8 (d, J = 272.4 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.73.

HRMS (ESI+) calcd for $C_{17}H_{10}F_3N_2$ [M + H]+ 299.0796. Found: 299.0881.

2-Phenylquinoxaline (5a)[6]

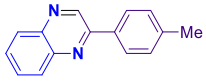


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 126 mg, 61%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.20-8.18 (m, 2H), 8.17-8.11 (m, 2H), 7.78-7.72 (m, 2H), 7.58-7.50 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.0, 143.5, 142.5, 141.7, 136.9, 130.4, 130.3, 129.8, 129.7, 129.3, 129.2, 127.7.

2-(*p*-Tolyl)quinoxaline (5b)[7]



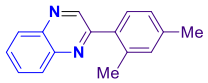
Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 125 mg, 57%).

[6] C. Zhang, Z. Xu, L. Zhang and N. Jiao, *Tetrahedron.*, 2012, **68**, 5258.
[7] Z. Zhan, H. Ma, X. Cui, P. Jiang, J. Pu, Y. Zhang and G. Huang, *Org. Biomol. Chem.*, 2019, **17**, 5148.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.15-8.10 (m, 4H), 7.78-7.70 (m, 2H), 7.36 (d, J = 7.9 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.0, 143.4, 142.5, 141.6, 140.6, 134.1, 130.3, 130.0, 129.7, 129.4, 129.2, 127.6, 21.5.

2-(2,4-dimethylphenyl)quinoxaline (5c)[8]

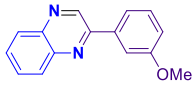


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 124 mg, 53%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.0 (s, 1H), 8.15-8.13 (m, 2H), 7.81-7.76 (m, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7,19 (s, 1H), 7,18 (d, J = 7.3 Hz, 2H), 2.46 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 146.2, 142.2, 141.1, 139.6, 136.6, 134.5, 132.2, 130.3, 130.2, 129.7, 129.3, 127.2, 21.2, 20.5 (1 signals missing due to overlap).

2-(3-Methoxyphenyl)quinoxaline (5d)[9]

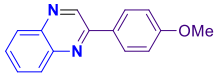


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 146 mg, 62%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.17-8.11 (m, 2H), 7.8-7.73 (m, 4H), 7.49-7.46 (m, 1H), 7.08-7.06 (m, 1H), 3.94 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.5, 151.8, 143.6, 142.4, 141.8, 138.3, 130.4, 130.3, 129.8, 129.7, 129.3, 120.1, 116.4, 112.9, 55.6.

2-(4-Methoxyphenyl)quinoxaline (5e)[2]



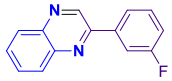
Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 120 mg, 51%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.18-8.17 (m, 2H), 8.12-8.08 (m, 2H), 7.77-7.69 (m, 2H), 7.09-7.06 (m, 2H), 3.90 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.6, 151.6, 143.2, 142.5, 141.4, 130.3, 129.6, 129.5, 129.3, 129.2, 129.1, 114.8, 55.7.

[8] C. Neochoritis, J. Stephanidou-Stephanatou and C. A. Tsoleridis, *Synlett*., 2009, 302.
[9] J. Qin, F. Chen, Z. Ding, Y. He, Q. Fan and L.Xu, *Org. Lett.,* 2011, **13**, 6568.

2-(3-Fluorophenyl)quinoxaline (5f)[10]



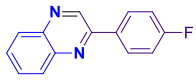
Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 101 mg, 45%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.16-8.12 (m, 2H), 7.97-7.94 (m, 2H), 7.81-7.75 (m, 2H), 7.54-7.51 (m, 1H), 7.23-7.20 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6 (d, J = 247 Hz), 150.5 (d, J = 2.43 Hz), 143.1, 142.3, 142.0, 139.2 (d, J = 7.5 Hz), 130.8 (d, J = 8.0 Hz), 130.6, 130.1, 129.8, 129.3, 123.2 (d, J = 2.8 Hz), 117.3 (d, J = 21.5 Hz), 114.6 (d, J = 23.0 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -111.76.

2-(4-Fluorophenyl)quinoxaline (5g)[1]



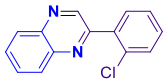
Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 121 mg, 54%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.23-8.20 (m, 2H), 8.15-8.12 (m, 2H), 7.81-7.74 (m, 2H), 7.28-7.24 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4 (d, J = 252.3 Hz), 150.9, 143.0, 142.3, 141.6, 133.1 (d, J = 3.02 Hz), 130.5, 129.8, 129.7, 129.6, 129.3, 116.4 (d, J = 22.7 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -110.57 (p, J = 6.7 Hz).

2-(2-Chlorophenyl)quinoxaline (5h)[11]



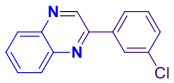
Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane) (pale yellow solid, 125 mg, 52%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.19-8.16 (m, 2H), 7.82-7.79 (m, 2H), 7.74-7.72 (m, 1H), 7.56-7.54 (m, 1H), 7.47-7.43 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.5, 146.3, 142.4, 141.5, 136.7, 132.8, 132.1, 131.0, 130.4, 130.4, 130.3, 130.0, 129.4, 127.6.

2-(3-Chlorophenyl)quinoxaline (5i)[12]

[10] Q. A. Chen, D. S. Wang, Y. G. Zhou, Y. Duan, H. J. Fan, Y. Yang and Z. Zhang, *J. Am. Chem. Soc*., 2011, **133**, 6126.
[11] T. T. T. Nguyen, L. A. Nguyen, Q. A. Ngo, M. Koleski and T. B. Nguyen, *Org. Chem. Front*., 2021, **8**, 1593.
[12] J. Pu, X. Liu, X. Luo, Z. Zhan, Y. Zhang and G. Huang, *Chem. Select*, 2018, **3**, 12219.

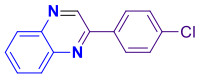


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 1:99) (pale yellow solid, 134 mg, 56%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.21 (s, 1H), 8.14-8.1 (m, 2H), 8.06-8.03 (m, 1H), 7.79-7.73 (m, 2H), 7.49-7.46 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.4, 143.0, 142.3, 141.9, 138.6, 135.5, 130.6, 130.4, 130.3, 130.0, 129.8, 129.3, 127.8, 125.6.

2-(4-Chlorophenyl)quinoxaline (5j)[2]

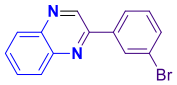


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 1:99) (pale yellow solid, 130 mg, 54%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.329 (s, 1H), 8.16-8.11 (m, 4H), 7.80-7.74 (m, 2H), 7.74-7.52 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 143.0, 142.3, 141.8, 136.7, 135.3, 130.6, 129.9, 129.7, 129.5, 129.3, 128.9.

2-(3-Bromophenyl)quinoxaline (5k)[13]

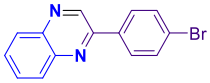


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 116 mg, 41%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.40-8.39 (m, 1H), 8.17-8.11 (m, 3H), 7.83-7.76 (m, 2H), 7.67-7.65 (m, 1H), 7.44 (t, J = 7.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 143.1, 142.4, 142.0, 138.9, 133.3, 130.8 (2C), 130.7, 130.1, 129.8, 129.3, 126.1, 123.6.

2-(4-Bromophenyl)quinoxaline (5l)[2]



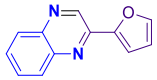
Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 158 mg, 56%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.15-8.07 (m, 4H), 7.8-7.74 (m, 2H), 7.7-7.68 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.8, 142.9, 142.4, 141.9, 135.8, 132.5, 130.6, 129.9, 129.8, 129.3, 129.1, 125.1.

[13] M. Jeganathan, A. Dhakshinamoorthy and K. Pitchumani, *Tetrahedron Lett.*, 2014, **55**, 1616.

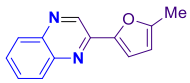
2-(Furan-2-yl)quinoxaline (5m)[14]



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 1:99) (pale yellow solid, 82 mg, 42%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.09-8.04 (m, 2H), 7.75-7.72 (m, 1H), 7.70-7.67 (m, 2H), 7.30 (dd, J = 0.6 Hz, J = 3.5 Hz, 1H), 6.61 (dd, J = 1.7 Hz, J = 3.5 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 151.8, 145.2, 144.0, 142.2, 141.4, 130.6, 129.4, 129.3, 112.6, 111.9 (2 signals missing due to overlap).

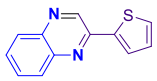
2-(5-Methylfuran-2-yl)quinoxaline (5n)[15]



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 103 mg, 49%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.07-8.01 (m, 2H), 7.72-7.69 (m, 1H), 7.66-7.63 (m, 1H), 7.20 (d, J = 3.3 Hz, 1H), 6.21-6.20 (m, 1H), 2.46 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 150.2, 144.1, 142.2, 142.2, 141.1, 130.5, 129.2, 129.2, 129.0, 113.5, 109.2, 14.2.

2-(Thiophen-2-yl)quinoxaline (5o)[16]

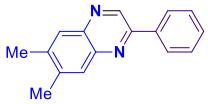


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 117 mg, 55%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.07-8.05 (m, 2H), 7.86-7.85 (m, 1H), 7.75-7.72 (m, 1H), 7.70-7.67 (m, 1H), 7.54-7.53 (m, 1H), 7.20-7.19 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 142.4, 142.3, 142.2, 141.5, 130.5, 129.9, 129.3, 129.2, 128.6, 127.1 (1 signals missing due to overlap).

6,7-Dimethyl-2-phenylquinoxaline (5p)[12]

[14] Y. Yang, F. Ni, W. M. Shu and A. X. Wu, *Chem. Eur. J.*, 2014, **20**, 11776.
[15] N. O. Saldabol, J. Popelis and V. Slavinska. *Chem. Heterocycl. Compd.*, 2002, **38**, 783.
[16] X. T. Wang, J. L. Song, M. Zhong, H. J. Kang, H. Xie, T. Che, B. Shu, D. Peng, L. Zhang and S. S. Zhang, *Eur. J. Org. Chem.*, 2020, **24**, 3635.

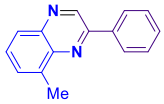


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 89 mg, 38%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.18-8.17 (m, 2H), 7.91 (s, 1H), 7.86 (s, 1H),7.57-7.55 (m, 2H), 7.52-7.49 (m, 1H), 2.52 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.2, 142.6, 141.4, 141.0, 140.8, 140.3, 137.3, 130.0, 129.2, 128.8, 128.3, 127.6, 20.6, 20.5.

8-Methyl-2-phenylquinoxaline (5q)[17]

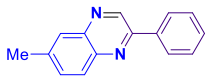


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 1:99) (pale yellow solid, 84 mg, 38%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.26-8.24 (m, 2H), 7.95 (dd, 1H, J = 1.6 Hz, J = 7.9 Hz), 7.63-7.58 (m, 2H), 7.57-7.54 (m, 2H), 7.52-7.49 (m, 1H), 2.87 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.3, 142.7, 141.8, 141.4, 138.1, 137.2, 130.2, 130.1, 129.4, 129.2, 127.5, 127.0, 17.2.

6-Methyl-2-phenylquinoxaline (5r)[18]



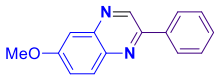
Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 88 mg, 40%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.22-8.15 (m, 2H), 8.05 (d, J = 8.5 Hz, 1H), 7.89 (s, 1H), 7.62 (dd, J = 8.5, J = 1.8 Hz, 1H), 7.58-7.55 (m, 2H), 7.53-7.49 (m, 1H), 2.61 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.2, 143.4, 141.8, 140.9, 140.3, 137.1, 132.7, 130.1, 129.3, 129.3, 128.1, 127.6, 22.0.

6-Methoxy-2-phenylquinoxaline (5s)[19]

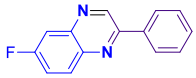
[17] T. B. Nguyen, P. Retailleau and A. Al-Mourabit, *Org. Lett*., 2013, **15**, 5238.
[18] K. Gopalaiah, A. Saini, S. N. Chrudu, D. C. Rao, H. Yadav and B. Kumar, *Org. Biomol. Chem.*, 2017, **15**, 2259.
[19] T. Chen, X. Chen, J. Wei, D. Lin, Y. Xie and W. Zeng, *Org. Lett*., 2016, **18**, 2078.



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 94 mg, 40%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.16 (d, J = 0.3, 1H), 8.17 (d, J = 8.1 Hz, 2H), 7.99 (d, J = 9.1 Hz, 1H), 7.56 (t, J = 7.7 Hz, 2H), 7.53-7.49 (m, 1H), 7.44 (d, J = 2.6 Hz, 1H), 7.40-7.37 (m, 1H), 3.99 (d, J = 0.4, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.2, 152.1, 144.1, 140.9, 138.0, 137.2, 130.2, 129.3, 127.7, 123.0, 107.1, 56.0 (1 signals missing due to overlap).

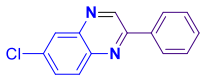
6-Fluoro-2-phenylquinoxaline (5t)[19]



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 114 mg, 51%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.18 – 8.15 (m, 2H), 8.14 (dd, J = 9.2, J = 5.8 Hz, 1H), 7.74 (dd, J = 9.0, J = 2.8 Hz, 1H), 7.58 – 7.51 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5 (d, J = 251.9 Hz), 151.3 (d, J = 3.3 Hz), 144.1, 142.3 (d, J = 13.0 Hz), 139.5, 136.5, 131.7 (d, J = 9.8 Hz), 130.3, 129.2, 127.4, 120.7 (d, J = 25.8 Hz), 112.7 (d, J = 21.7 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ -108.57.

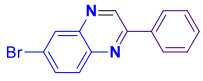
6-Chloro-2-phenylquinoxaline (5u)[20]



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 1:99) (pale yellow solid, 91 mg, 38%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.3 (s, 1H), 8.18-8.16 (m, 2H), 8.1-8.06 (m, 2H), 7.70 (dd, J = 2.3 Hz, J = 8.9 Hz, 1H), 7.57-7.51 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 144.2, 141.9, 140.9, 136.5, 135.3, 131.4, 130.9, 130.6, 129.3, 128.2, 127.6.

6-Bromo-2-phenylquinoxaline (5v)[20]



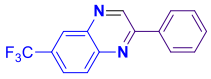
Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 1:99) (pale yellow solid, 108 mg, 38%).

[20] R. Zhang, Y. Qin, L. Zhang and S. Luo, *Org. Lett.*, 2017, **19**, 5629.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.3 (s, 1H), 8.28 (d, J = 2.2 Hz, 1H), 8.18-8.16 (m, 2H), 7.99 (d, J = 8.9 Hz, 1H), 7.83 (dd, J = 2.2 Hz, J = 8.9 Hz, 1H), 7.57-7.51 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 144.2, 142.2, 141.2, 136.5, 133.9, 131.6, 131.0, 130.6, 129.3, 127.6, 123.5.

2-Phenyl-6-(trifluoromethyl)quinoxaline (5w)[21]



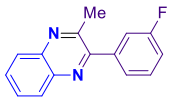
Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 110 mg, 40%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.40 (s, 1H), 8.41 (s, 1H), 8.24 (d, J = 8.7 Hz, 1H), 8.23-8.20 (m, 2H), 7.94 (dd, J = 8.7, J = 2.0 Hz, 1H), 7.60-7.55 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 144.6, 143.4, 140.6, 136.0, 131.1 (d, J = 33.0 Hz), 130.9, 130.8, 129.3, 128.8, 127.7, 127.2 (q, J = 4.3 Hz), 125.9 (q, J = 3.1 Hz), 123.7 (d, J = 272.7 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.56.

2-(3-Fluorophenyl)-3-methylquinoxaline (7a)[22]



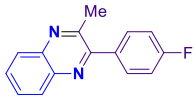
Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 1:99) (pale yellow solid, 98 mg, 41%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10-8.09 (m, 1H), 8.06-8.04 (m, 1H), 7.76-7.70 (m, 2H), 7.51-7.47 (m, 1H), 7.44-7.43 (m, 1H) 7.21-7.18 (m, 2H), 2.77 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9 (d, J = 247.4 Hz), 153.6 (d, J = 1.8 Hz), 152.3, 141.5, 141.3 (d, J = 7.9 Hz), 141.0, 130.3 (d, J = 8.2), 130.2, 129.5 (d, J = 25.6 Hz), 128.5, 124.6 (d, J = 2.4 Hz), 116.4, 116.2 (d, J = 7.8 Hz), 116.1, 24.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.31.

2-(4-Fluorophenyl)-3-methylquinoxaline (7b)[22]



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 71 mg, 30%).

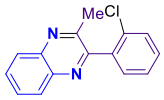
[21] J. Pu, X. Liu, X. Luo, Z. Zhan, Y. Zhang and G. Huang, *Chem. Select*, ***2018***, **3**, 12219.
[22] D. M. Cui, D. W. Zhuang, Y. Chen and C. Zhang, *J. Org. Chem*., 2011**, 7**, 860.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11-8.02 (m, 2H), 7.76-7.68 (m, 2H), 7.67-7.63 (m, 2H), 7.24-7.18 (m, 2H), 2.76 (s, 3H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.4 (d, J = 248.9 Hz), 153.9, 152.4, 141.4, 141.1, 135.2 (d, J = 3.3 Hz), 131.1 (d, J = 8.7 Hz), 130.0, 129.4, 129.3, 128.5, 115.7 (d, J = 22.1 Hz), 24.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.15.

2-(2-Chlorophenyl)-3-methylquinoxaline (7c)[23]

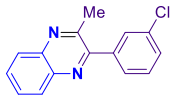


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 104 mg, 41%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11-8.07 (m, 2H), 7.77-7.70 (m, 2H), 7.52-7.50 (m, 1H), 7.43-7.41 (m, 3H), 2.60 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 153.3, 141.8, 140.7, 138.1, 132.9, 130.4, 130.2, 129.8, 129.4, 129.3, 128.6, 127.4, 23.1 (1 signals missing due to overlap).

2-(3-Chlorophenyl)-3-methylquinoxaline (7d)[23]

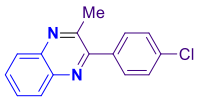


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 1:99) (pale yellow solid, 97 mg, 38%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11-8.09 (m, 1H), 8.07-8.05 (m, 1H), 7.77-7.71 (m, 2H), 7.67-7.66 (m, 1H), 7.55-7.53 (m, 1H) 7.49-7.44 (m, 2H), 2.77 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.5, 152.3, 141.5, 141.0, 140.9, 134.8, 130.2, 129.9, 129.6, 129.4, 129.3, 129.2, 128.5, 127.3, 24.4.

2-(4-Chlorophenyl)-3-methylquinoxaline (7e)[24]

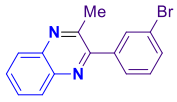


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 51 mg, 20%).

[23] Y. Chen, K. Li, M. Zhao, Y. Li, and B. Chen, *Tetrahedron Lett.*, 2013, **54**, 1627.
[24] C. Li, F. Zhang, Z. Yang and C. Qi, *Tetrahedron Lett.*, 2014, **55**, 5430.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10-8.08 (m, 1H), 8.07-8.04 (m, 1H), 7.76-7.70 (m, 2H), 7.62-7.60 (m, 2H), 7.52-7.50 (m, 2H), 2.77 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 153.8, 152.3, 141.5, 141.1, 137.6, 135.4, 130.5, 130.1, 129.5, 129.3, 128.9, 128.5, 24.5.

2-(3-Bromophenyl)-3-methylquinoxaline (7f)

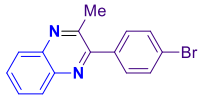


Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 1:99) (pale yellow solid, 104 mg, 35%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10-8.09 (m, 1H), 8.06-8.04 (m, 1H), 7.82 (t, J = 1.8 Hz, 1H), 7.77-7.71 (m, 2H), 7.64-7.61 (m, 1H), 7.59-7.57 (m, 1H), 7.39 (t, J = 7.8 Hz, 1H), 2.77 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 153.4, 152.3, 141.6, 141.1, 141, 132.2, 130.2, 130.1, 129.6, 129.4, 128.5, 127.7, 122.9, 24.4 (1 signals missing due to overlap).

HRMS (ESI+) calcd for $C_{15}H_{12}BrN_2$ [M + H]+ 299.0184. Found: 299.0192.

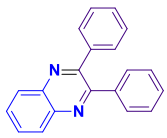
2-(4-Bromophenyl)-3-methylquinoxaline (7g)[24]



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 83 mg, 28%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (dd, J = 1.3 Hz, J = 8.0 Hz, 1H), 8.05 (dd, J = 1.6 Hz, J = 8.5 Hz, 1H), 7.77-7.71 (m, 2H), 7.68-7.66 (m, 2H), 7.56-7.54 (m, 2H), 2.77 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 152.3, 141.5, 141.1, 138.1, 131.9, 130.8, 130.1, 129.6, 129.3, 128.5, 123.7, 24.5.

2,3-Diphenylquinoxaline (7h)[25]



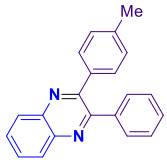
Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 127 mg, 45%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20-8.17 (m, 2H), 7.79-7.76 (m, 2H), 7.54-7.52 (m, 4H), 7.38-7.32 (m, 6H).

[25] C. Qi, H. Jiang, L. Huang, Z. Chen and H. Chen, *Synthesis*., 2011, **3**, 387.

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 141.4, 139.3, 130.1, 130, 129.4, 128.9, 128.4.

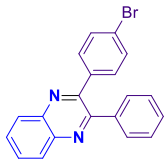
2-Phenyl-3-(*p*-tolyl)quinoxaline (7i)[26]



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 1:99) (pale yellow solid, 121 mg, 41%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19-8.16 (m, 2H), 7.77-7.74 (m, 2H), 7.56-7.55 (m, 2H), 7.44-7.33 (m, 5H), 7.14 (d, J = 7.97 Hz, 2H), 2.37 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 153.6, 141.4, 141.2, 139.4, 138.9, 136.3, 129.9, 129.8 (2C), 129.7, 129.3, 129.1, 128.8, 128.3, 21.4 (2 signals missing due to overlap).

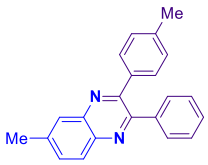
2-(4-Bromophenyl)-3-phenylquinoxaline (7j)[27]



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 184 mg, 51%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19-8.16 (m, 2H), 7.80-7.77 (m, 2H), 7.52-7.51 (m, 2H), 7.49-7.46 (m, 2H), 7.42-7.36 (m, 5H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 152.3, 141.4, 141.3, 139.0, 138.1, 131.6, 130.4, 130.3, 129.9, 129.4, 129.3, 129.2, 128.6, 123.6 (1 signals missing due to overlap).

6-Methyl-2-phenyl-3-(p-tolyl)quinoxaline (7k)[28]



Purification of the crude mixture by column chromatography on silica gel (EtOAc:Hexane 3:97) (pale yellow solid, 171 mg, 56%).

[26] K. B. Harsha and K. S. Rangappa, *RSC Adv*., 2016, **6**, 57154.
[27] T. B. Nguyen, D. H. Mac, T. M. C. Tran, B. N. Nguyen and H. T. Cao, *Org. Biomol. Chem*., 2022, **20**, 7226-7231.
[28] W. Zhang, X. Yang, Z. Cao, X. Min, H. Zhou, J. Zhong, T. Gong, L. Wang, Q. Huang and W. Yang, *Chem. Select*., 2023, **8**, e202302634.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J = 8.5 Hz, 1H), 7.94-7.93 (m, 1H), 7.59-7.57 (m, 1H), 7.53-7.51 (m, 2H), 7.41-7.38 (m, 2H), 7.37-7.31 (m, 3H), 7.12 (d, J = 7.8 Hz, 2H), 2.61 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 152.6, 141.4, 141.2, 140.4, 140.2, 139.8, 139.5, 138.7, 138.6, 136.4, 132.2, 132.1, 129.8, 129.8, 129.8, 128.9, 128.7, 128.2, 128.0, 21.9, 21.3.

HRMS (ESI+) calcd for $C_{22}H_{19}N_2$ [M + H]+ 311.1548. Found: 311.1557.

Crystallographic data collection, structure determination and refinement

Suitable crystals for single crystal X-ray diffraction (SCXRD) analyses were obtained for the four quinoxaline compounds (**3f**, **3h**, **5u**, **5v**) (pale yellow solid, see Table S1) by slow evaporation in the presence of deuterated chloroform solvent.

X-ray diffraction data were measured at room temperature using a RIGAKU *XtaLabPro* diffractometer equipped with a Mo microfocus sealed tube *MM003* generator coupled to a double-bounce confocal Max-Flux® multilayer optics and a HPAD *PILATUS3R 200K* detector. *CrysAlisPro* [1] was employed for the data processing, with a combination of absorption correction including a numerical one based on Gaussian integration over a multifaceted crystal and an empirical one using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. Out of the four samples, only crystal **3k** did not meet the iUCr recommendations for diffraction quality. The tiny needles we managed to grow weakly diffracted, intensities falling short of the atomic resolution limit while also yielding a high Rint ≥ 12%. The presence of Br atom in the compound helped us to solve the structure by intrinsic phasing methods (*SHELXT* program),[2] and to refine it by full-matrix least-squares methods on F^2 using *SHELX-L*.[3] No evidence of twinning could be detected retrospectively. The three remaining structures were obtained using the same method. Regarding compound **3h**, a preliminary solution in the centrosymmetric space group, $P2_{1\&}/c$, showed an apparent benzopyrene form on a center of inversion. To resolve the overlapped structures of 11-methylbenzo[*a*]phenazine squeezed in the unit cell between the two-fold rotation screw axes along the b-direction, we switched to the non-centrosymmetric space group P 2_1 and refined independently, two molecules each with a half-occupancy factor (see figure S1). Displacement parameters for all non-hydrogen atoms of the molecules of interest were refined anisotropically. Independent Atom (IAM) models of **5u**[4] and **5v**[5] were previously reported in the CSD[6] (Refcode 3x *FEPYOQ* and *EYIRUC*, respectively). The final structure refinements for **3h** and **3k** were pursued by Hirshfeld atom refinement (HAR)[7] with aspherical scattering factors using *NoSpherA2* [8] partitioning in *Olex2* [9] based on electron density from iterative single-determinant SCF single-point DFT calculations using *ORCA* [10] with a B3LYP[11] functional using non-relativistic Hamiltonian, and a Jorge-TZP basis set.[12] Any of these wavefunctions were read by the *NoSpherA2* software; the related electron-density was partitioned into Hirshfeld atoms, whose Fourier transforms are the non-spherical scattering factors, which were then tabulated in a .tsc file and handed over to *olex2.refine* [13] for the least-squares refinement. In this HAR approach, all H atoms molecule present in **5v**, were refined anisotropically and independently.

Crystal data, data collection and structure refinement details are summarized in Table S1. Ortep views for each structure are shown in figure S2.

CCDC 2310625-2310628 (compounds **3h**, **3k**, **5v**, and **5u**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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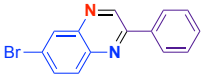
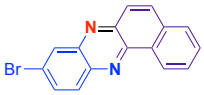
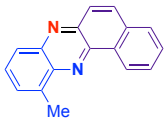
Table S1 Crystal data, data collection and structure refinement details for the four quinoxaline derivatives.

Identification code		**5u**	**5v**	**3h**	**3f**
Empirical formula		$C_{14}H_9ClN_2$	$C_{14}H_9BrN_2$	$C_{16}H_9BrN_2$	$C_{17}H_{12}N_2$
2D-scheme					
Chemical name		6-chloro-2-phenylquinoxaline	6-bromo-2-phenylquinoxaline	9-bromobenzo[*a*]phenazine	11-methylbenzo[*a*]phenazine
Formula weight		240.693	285.144	309.16	244.29
Temperature	(K)	293.0(2)			
Diffractometer,		Rigaku XtaLABpro mm003 Pilatus 200,			
Wavelength	(λ)	0.71073			
Crystal system,		Monoclinic,	Monoclinic,	Monoclinic,	Monoclinic,
space group		P 2_1	P 2_1	P 2_1/n	P 2_1
Unit cell dimensions	a (Å)	9.5508(6)	9.6512(5)	16.013(2)	4.3756(4)
	b (Å)	4.7677(3)	4.9125(2)	4.6349(7)	10.0848(9)
	c (Å)	12.4996(9)	12.4349(9)	16.5622(19)	14.3422(12)
	β (°)	103.508(7)	104.633(6)	96.230(13)	98.393(8)
Volume	Å^3	553.43(7)	570.43(6)	1222.0(3)	626.1(1)
Z,		2,	2,	4,	2,
Calculated density	(g.cm^{-3})	1.444	1.660	1.681	1.296
Absorption coefficient	(mm^{-1})	0.319	3.578	3.348	0.077
F(000)		248	284	616	256
Crystal size	(mm)	0.50 x 0.13 x 0.08	0.59 x 0.12 x 0.08	0.21 x 0.04 x 0.02	0.51 x 0.15 x 0.07
Theta range for data collection	(°)	3.35 to 30.51	3.39 to 29.13	3.362 to 20.807	2.871 to 29.566
Limiting indices		-13 ≤ h ≤ 12,	-13 ≤ h ≤ 14,	-16 ≤ h ≤ 15,	-6 ≤ h ≤ 6,
		-6 ≤ k ≤ 6,	-6 ≤ k ≤ 7,	-4 ≤ k ≤ 4,	-13 ≤ k ≤ 14
		-17 ≤ l ≤ 18	-17 ≤ l ≤ 17	-16 ≤ l ≤ 16	-19 ≤ l ≤ 19
Reflections collected / unique		10590 / 3070	10735 / 2878	6207 / 1276	14319 / 3331
Rint		0.0383	0.0285	0.1278	0.0375
Completeness to θ = 25.24°		99.6	99.7	99.2	99.8
Absorption correction		Gaussian			
Max. and min. transmission		1.000 and 0.650	1.000 and 0.356	1.000 and 0.614	1.000 and 0.724
Refinement method		Full-matrix least-squares on F^2			
Data / restraints / parameters		3070 / 1 / 235	2878 / 13 / 236	1276 / 0 / 172	3329 / 379 / 346
Goodness-of-fit on F^2		1.1208	1.0575	1.109	1.010
Final R indices [$I>2\sigma(I)$]	R1	0.0295,	0.0240,	0.0723,	0.0373,

	wR2	0.0539	0.0400	0.1744	0.0967
Final R indices	R1	0.0427,	0.0338,	0.0992,	0.0662,
(all data)	wR2	0.0573	0.0419	0.1919	0.1122
Absolute structure		-0.01(3)	0.002(5)	n/a	0(6)
Extinction coefficient		n/a	0.0165(14)	n/a	n/a
Largest diff. peak and hole	($e.Å^{-3}$)	0.1845 and -0.2707	0.6002 and -0.4865	1.400 and -0.888	0.088 and -0.114
CCDC Deposit number		2310625	2310626	2310627	2310628

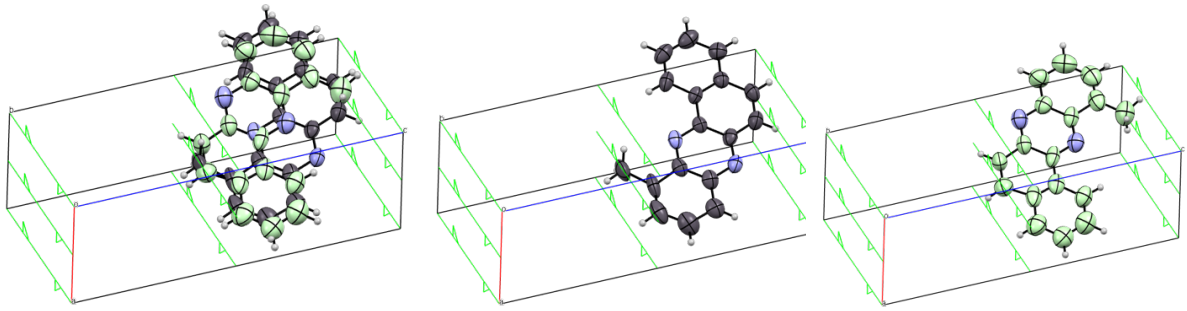


Figure S1 View of the content of the asymmetric unit of **3f** (left). The overlapped structure orientation with half-occupancy factor are separate in the subsequent two figures.

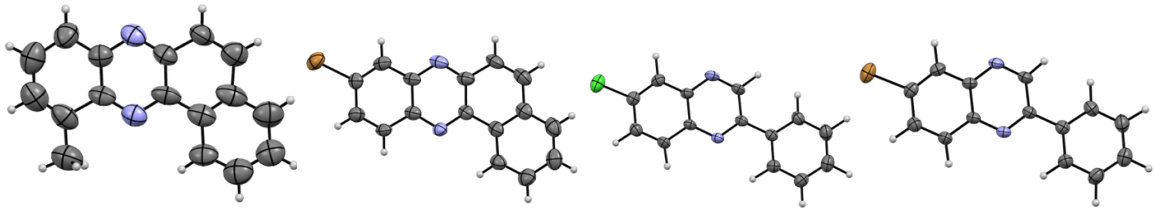
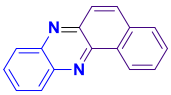


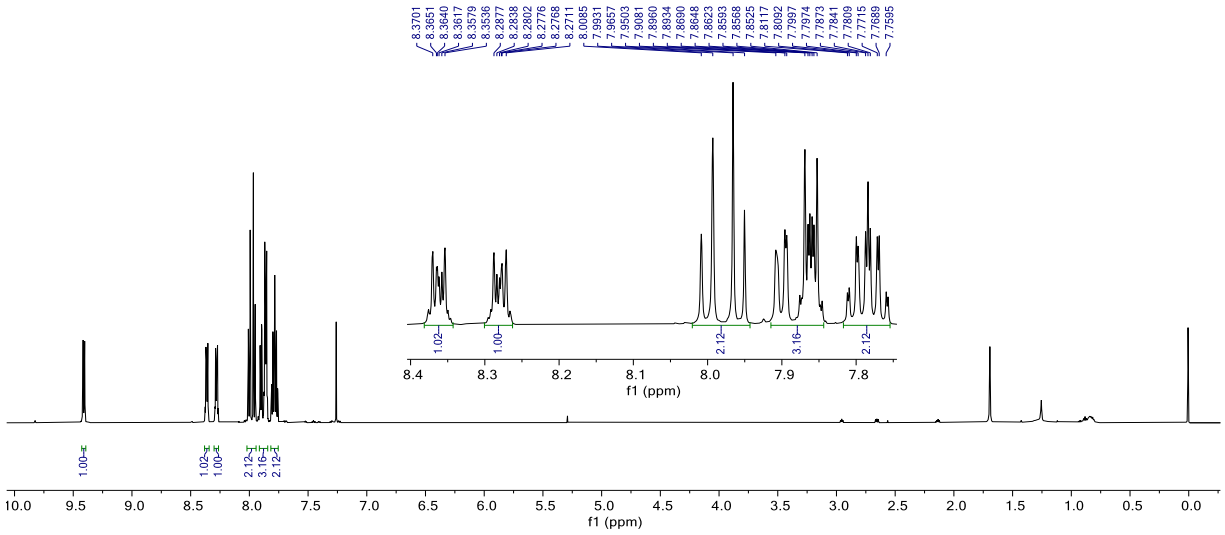
Figure S2 (From left to right) Ortep views of the molecular structures: **3h**, **3k**, **5u**, and **5v**. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms with an arbitrary radius size.

Copies of NMR spectra

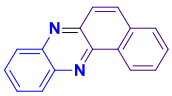
Benzo[a]phenazine (3a)

^{1}H NMR (600 MHz, $CDCl_3$)

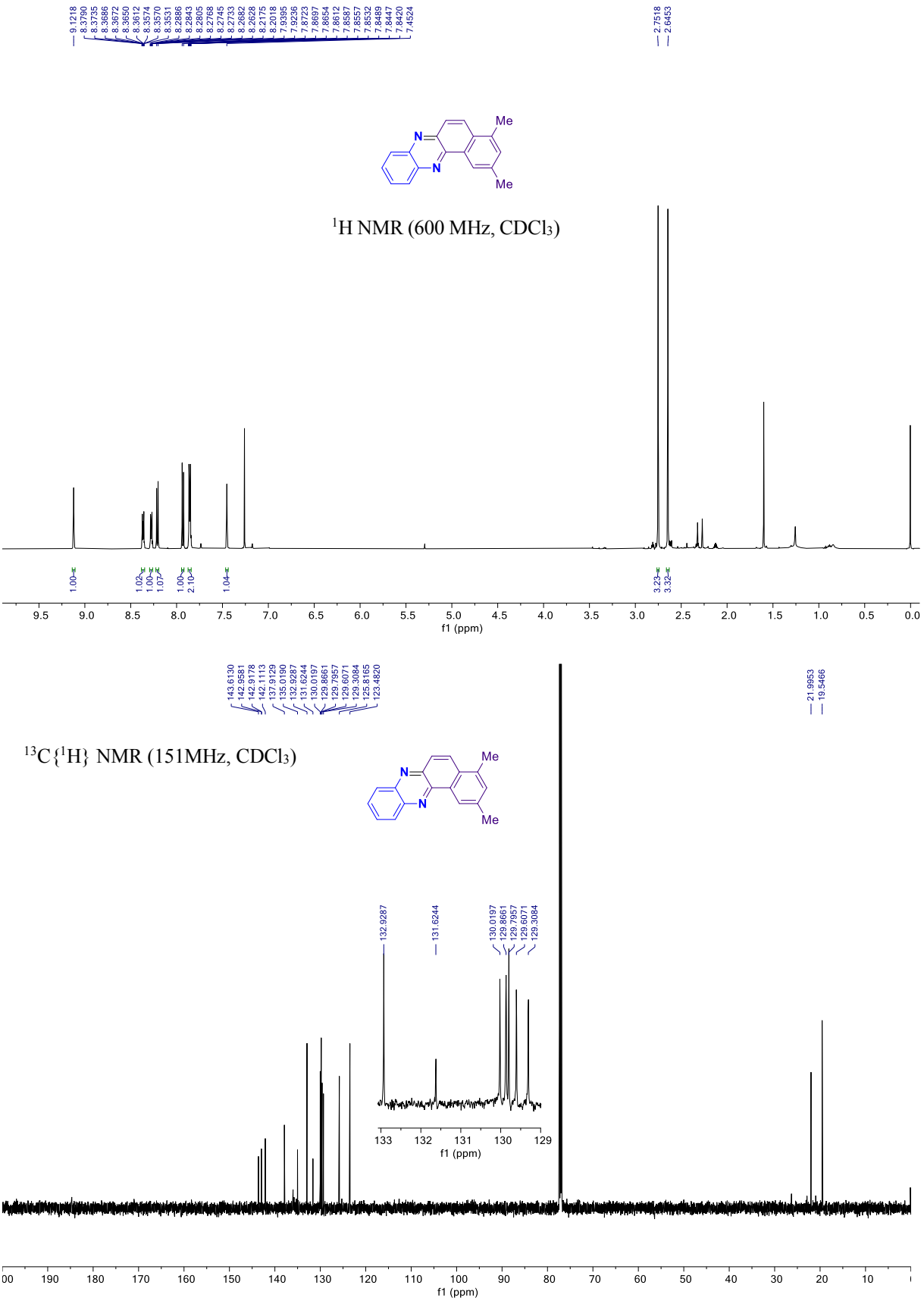




^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

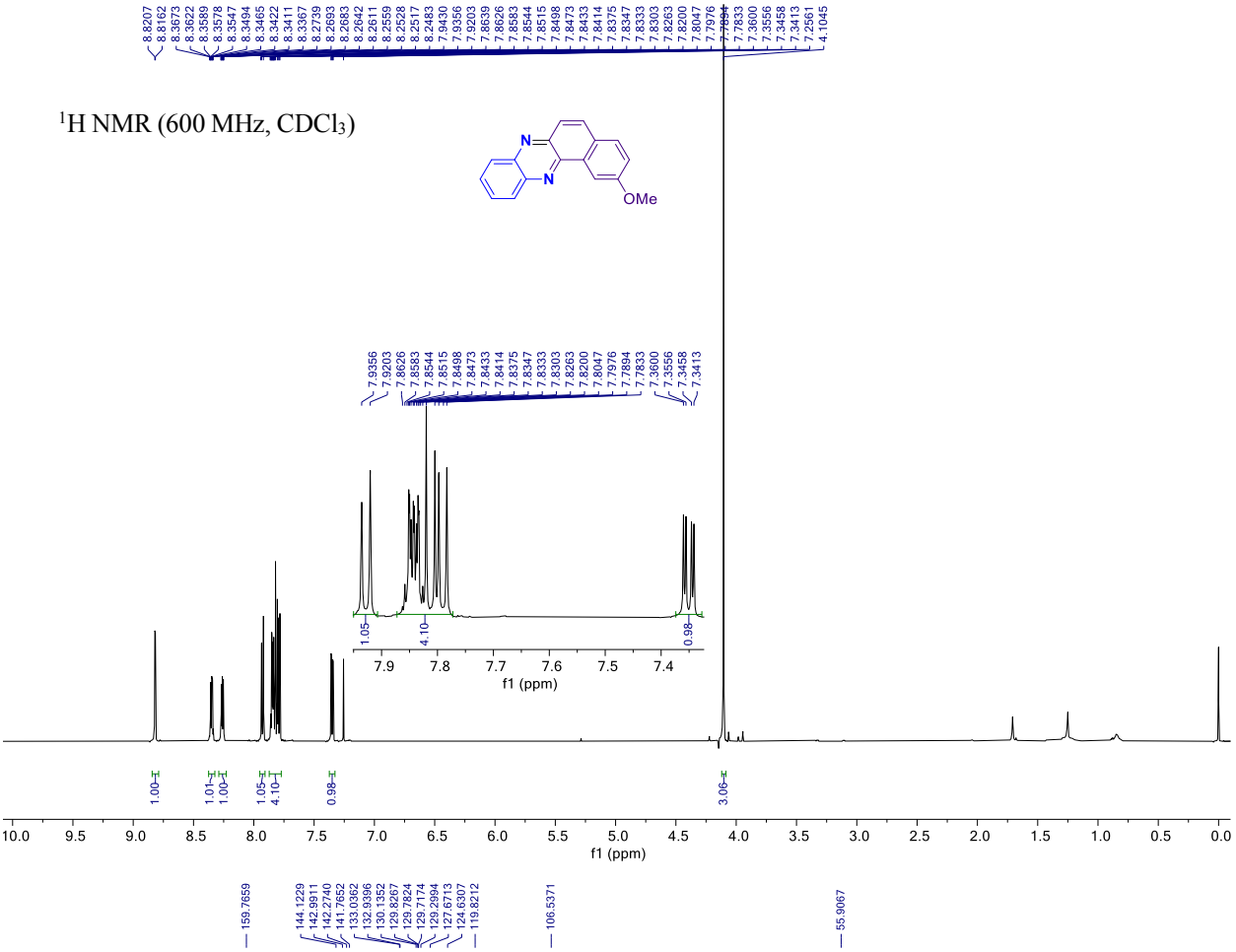


2,4-Dimethylbenzo[a]phenazine (3b)

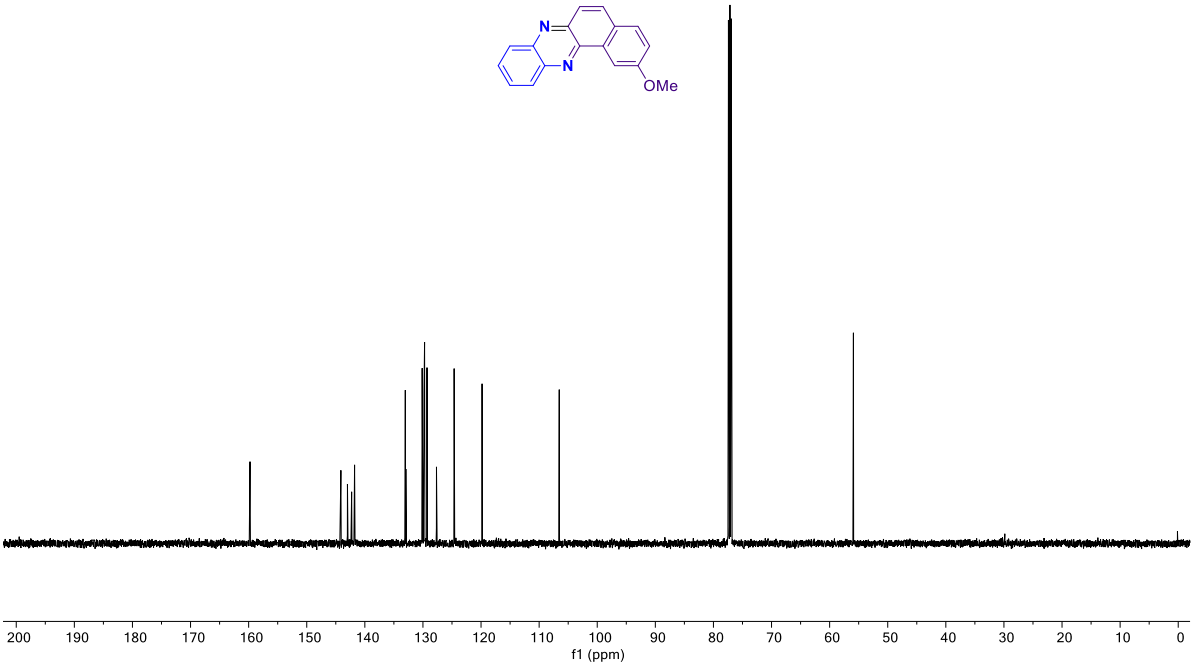


2-Methoxybenzo[a]phenazine (3c)

^{1}H NMR (600 MHz, $CDCl_3$)

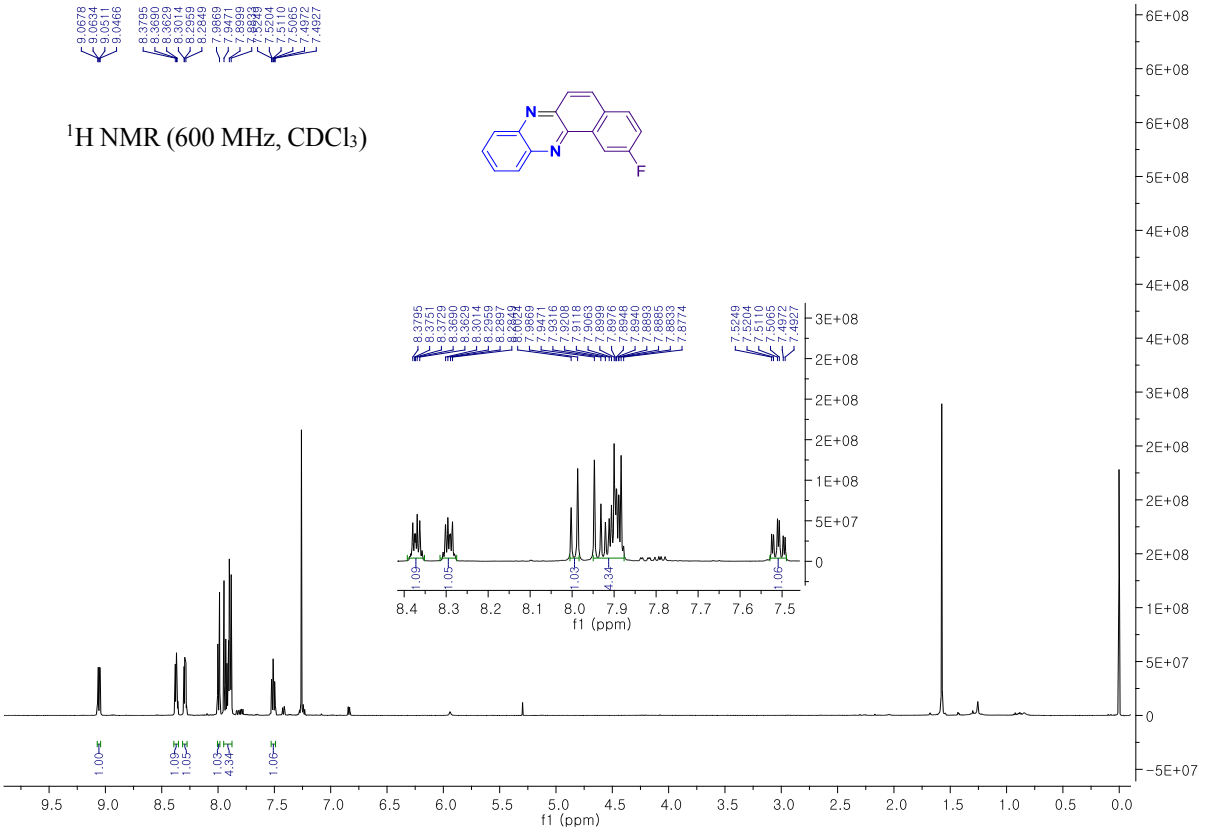


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

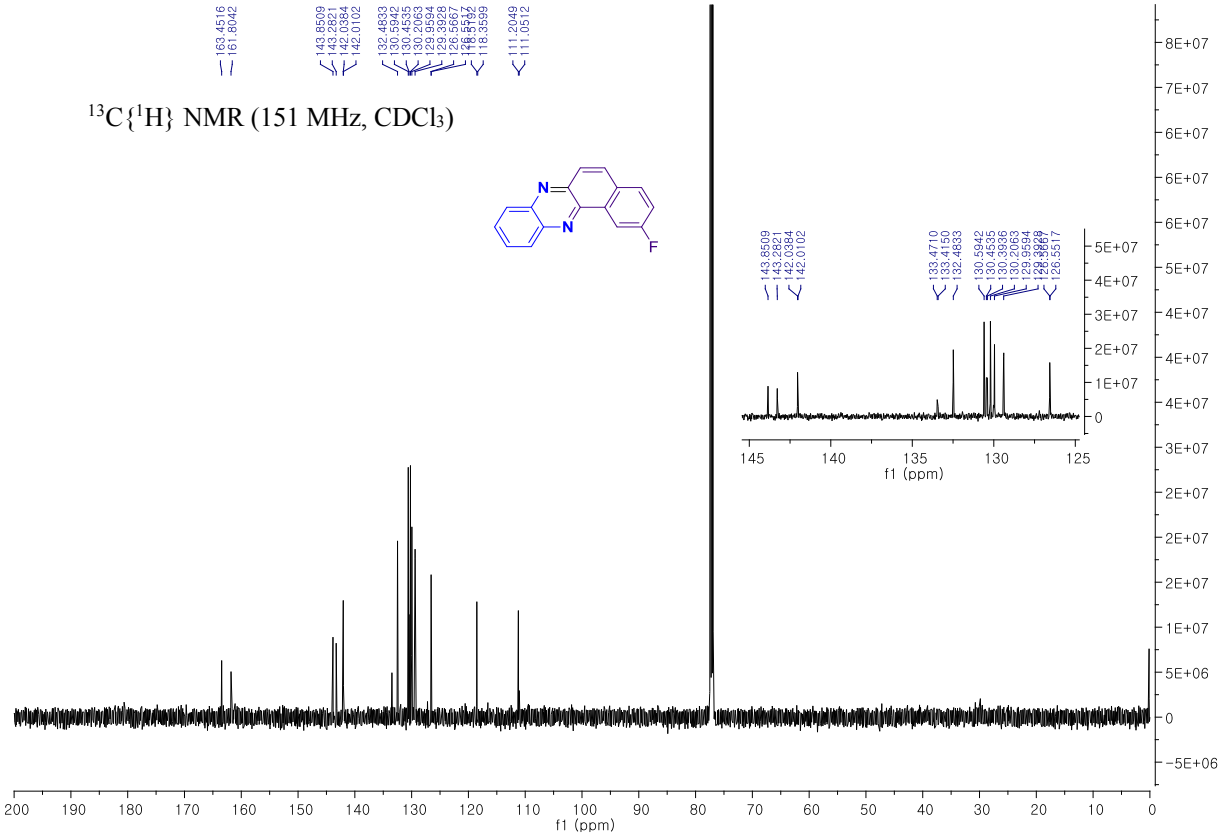


2-Fluorobenzo[a]phenazine (3d)

^{1}H NMR (600 MHz, $CDCl_3$)

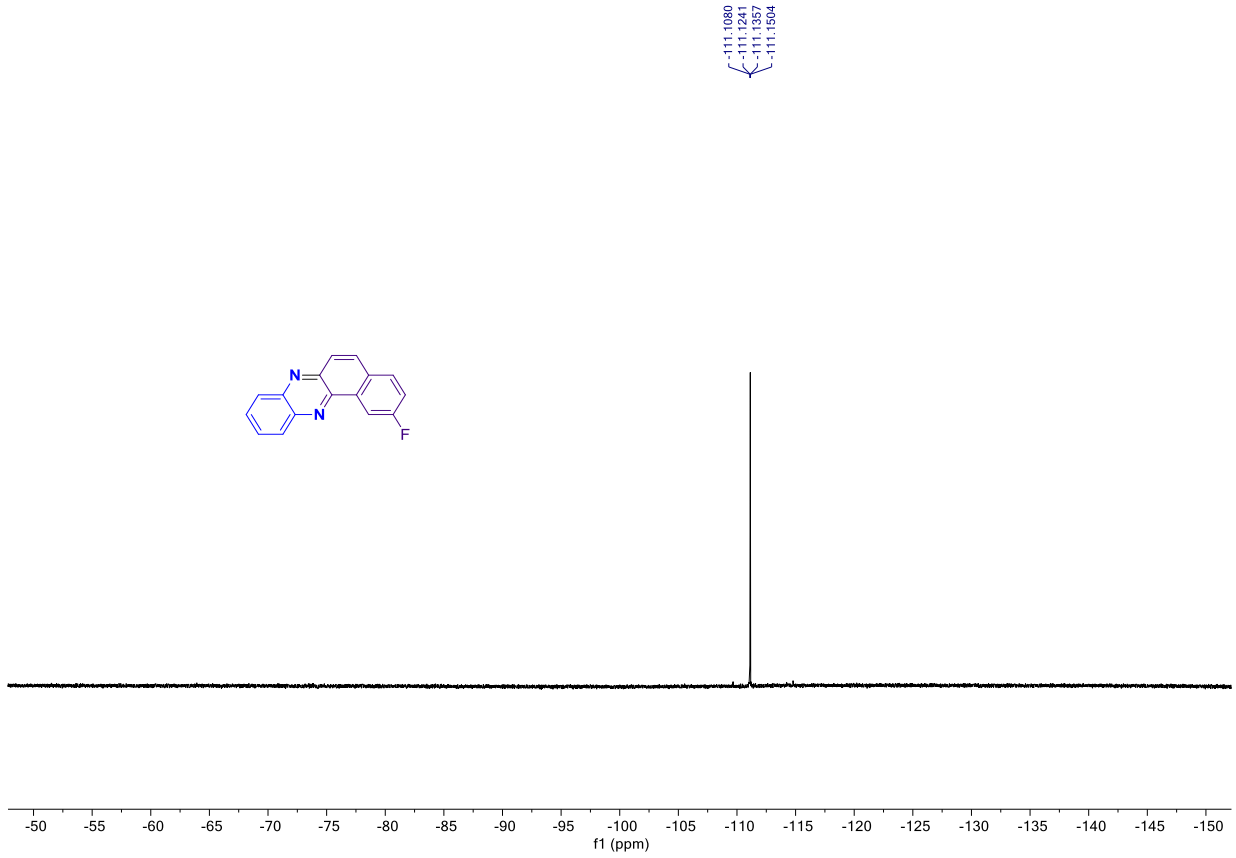


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



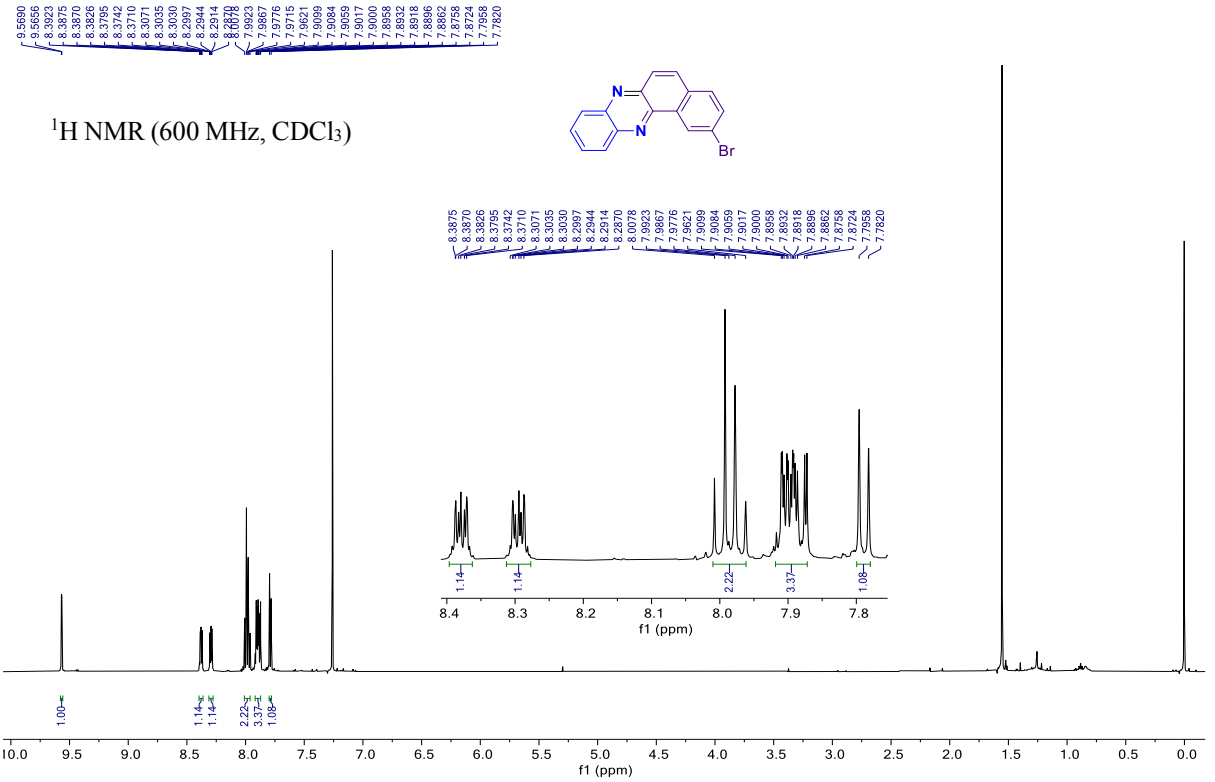
2-Fluorobenzo[a]phenazine (3d)

^{19}F NMR (565 MHz, $CDCl_3$)

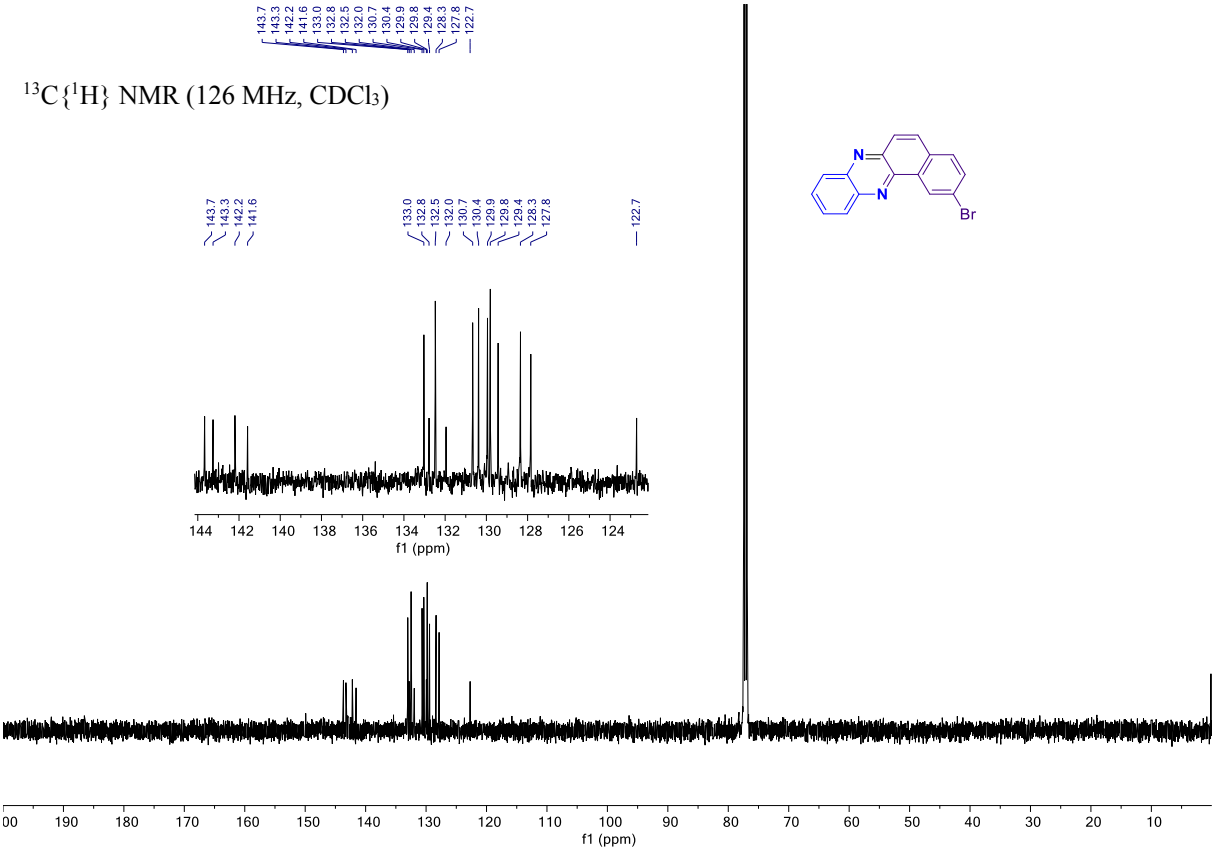


2-Bromobenzo[a]phenazine (3e)

^{1}H NMR (600 MHz, $CDCl_3$)

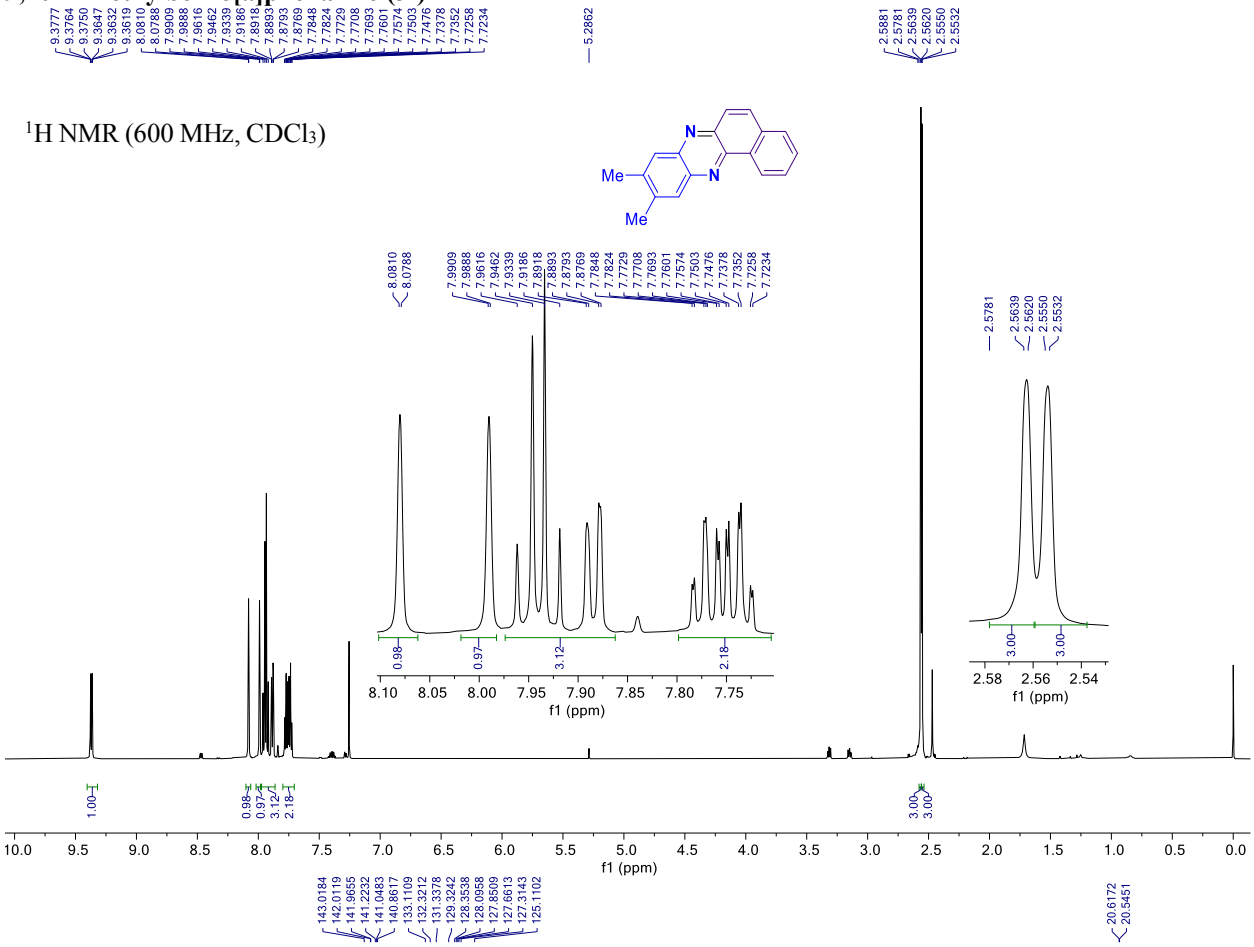


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

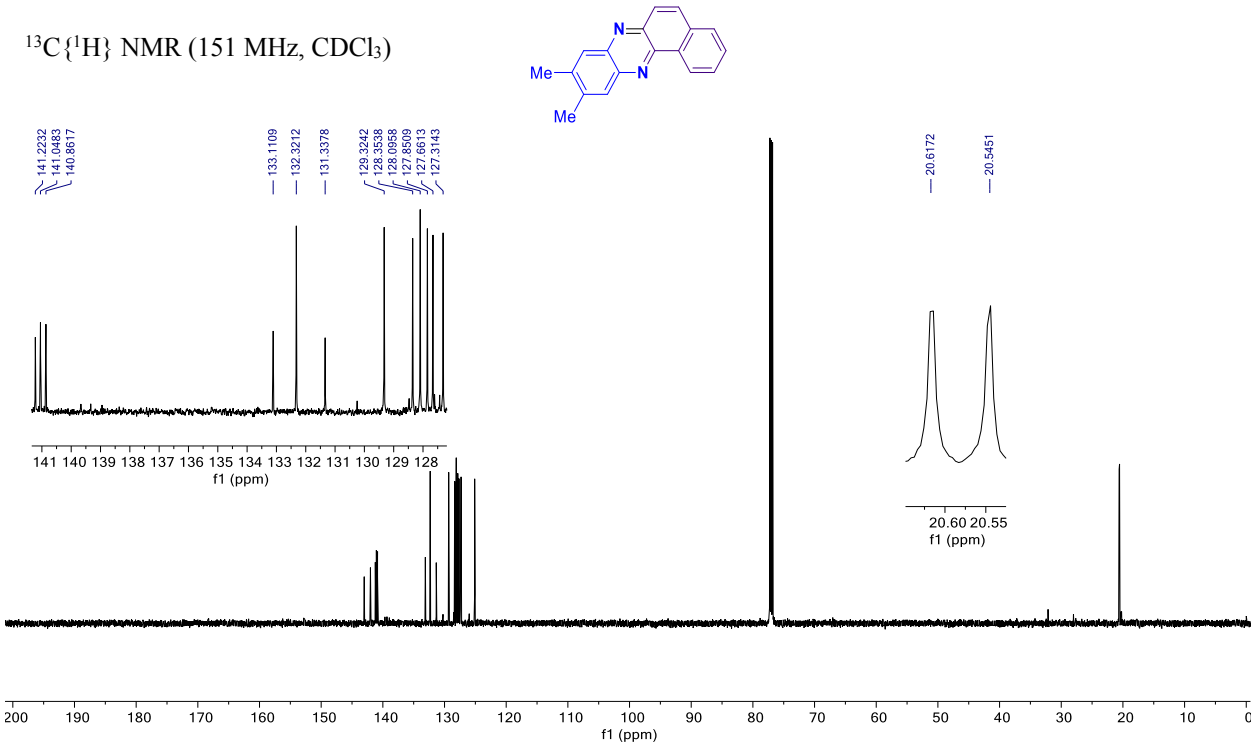


9,10-Dimethylbenzo[a]phenazine (3f)

^{1}H NMR (600 MHz, $CDCl_3$)

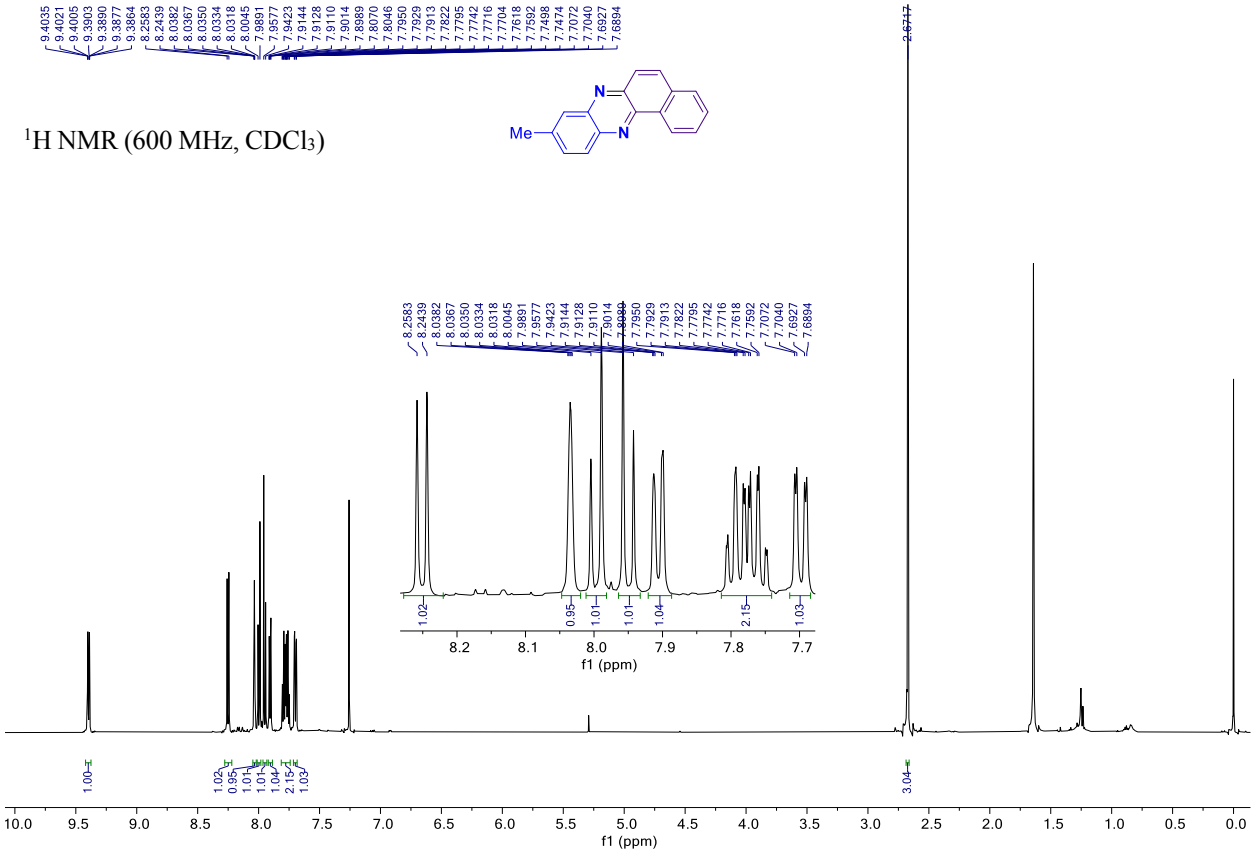


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

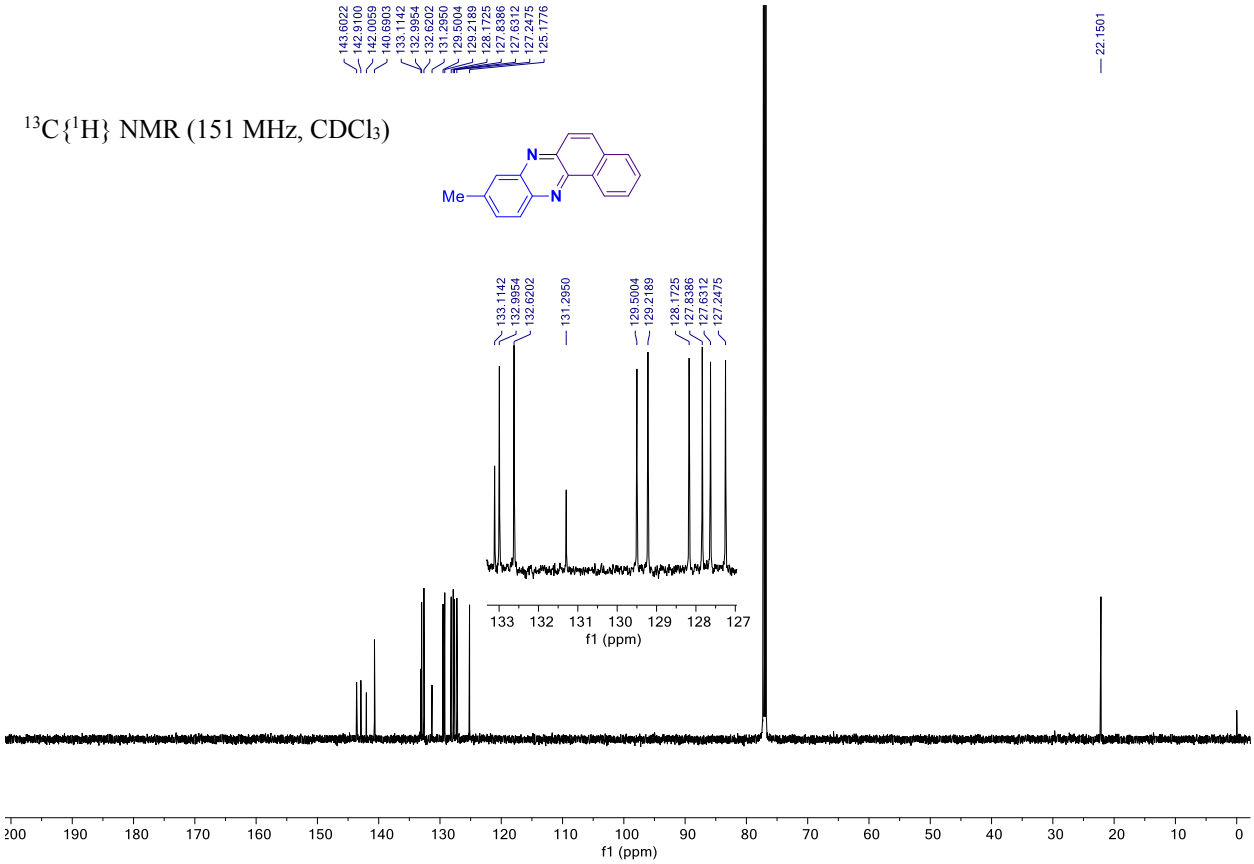


9-Methylbenzo[a]phenazine (3g)

^{1}H NMR (600 MHz, $CDCl_3$)

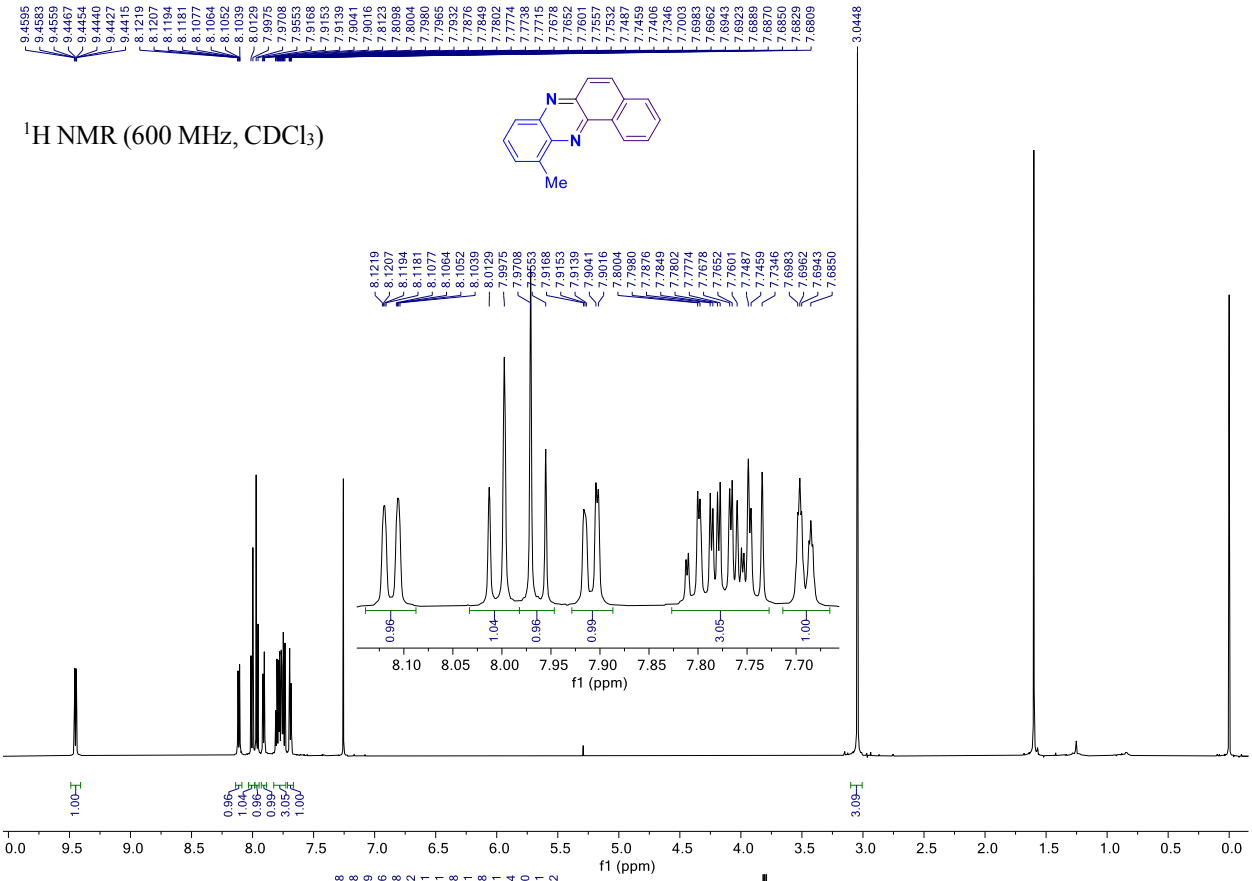


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

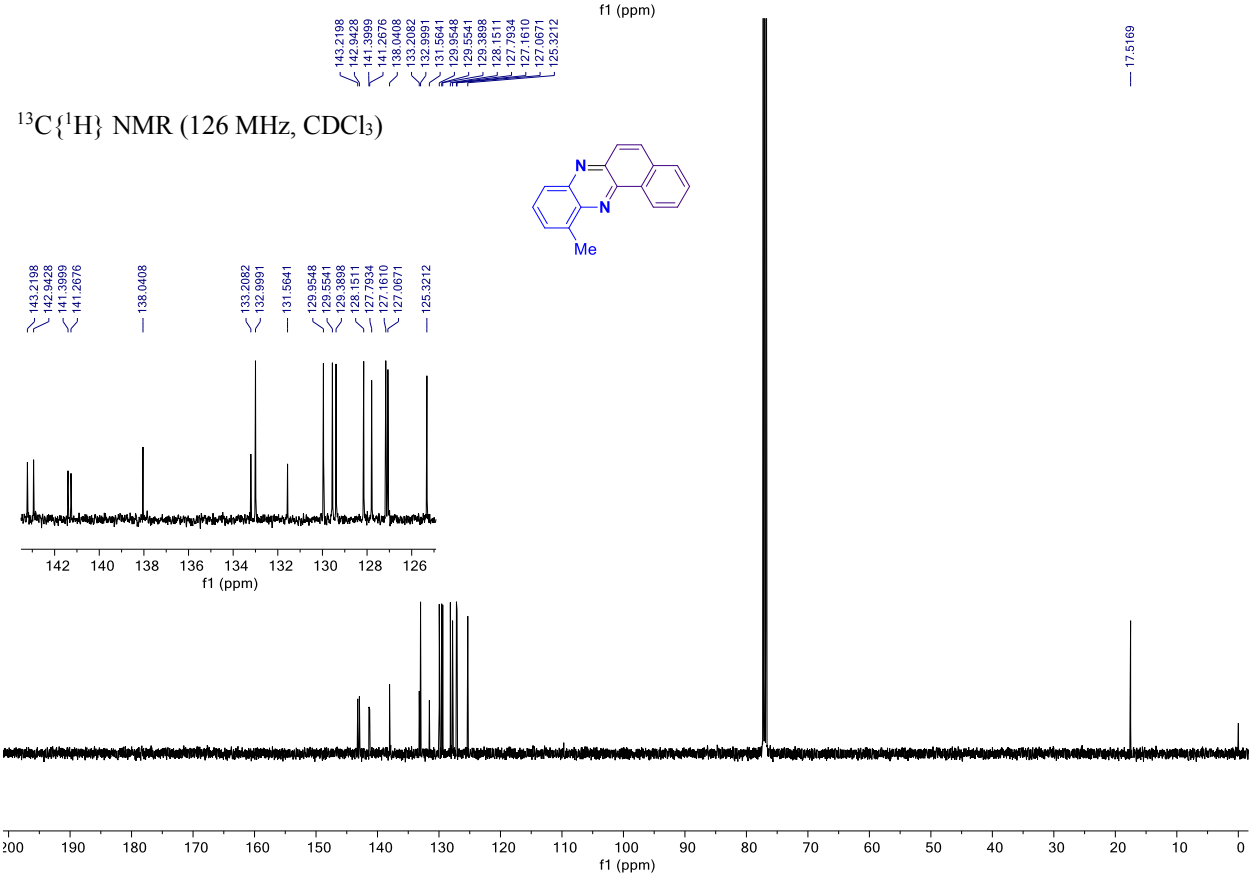


11-Methylbenzo[a]phenazine (3h)

^{1}H NMR (600 MHz, $CDCl_3$)

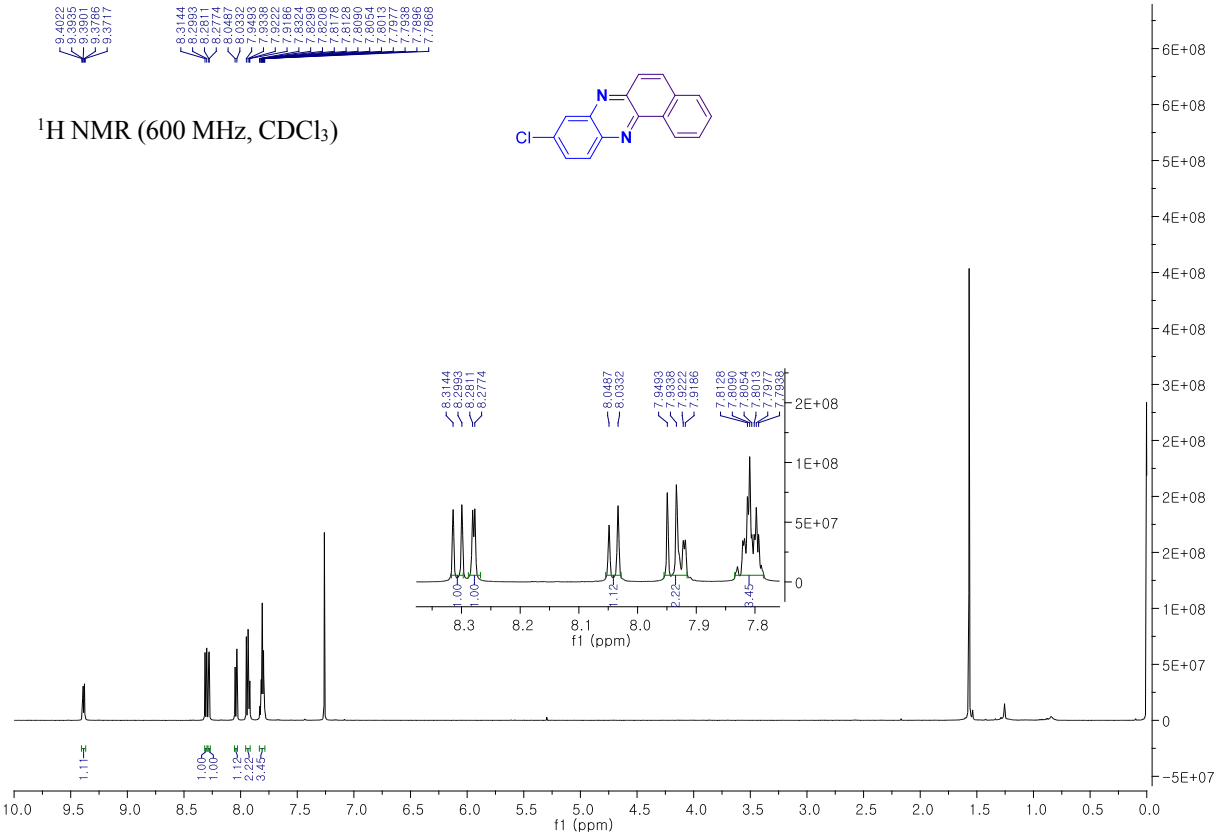


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

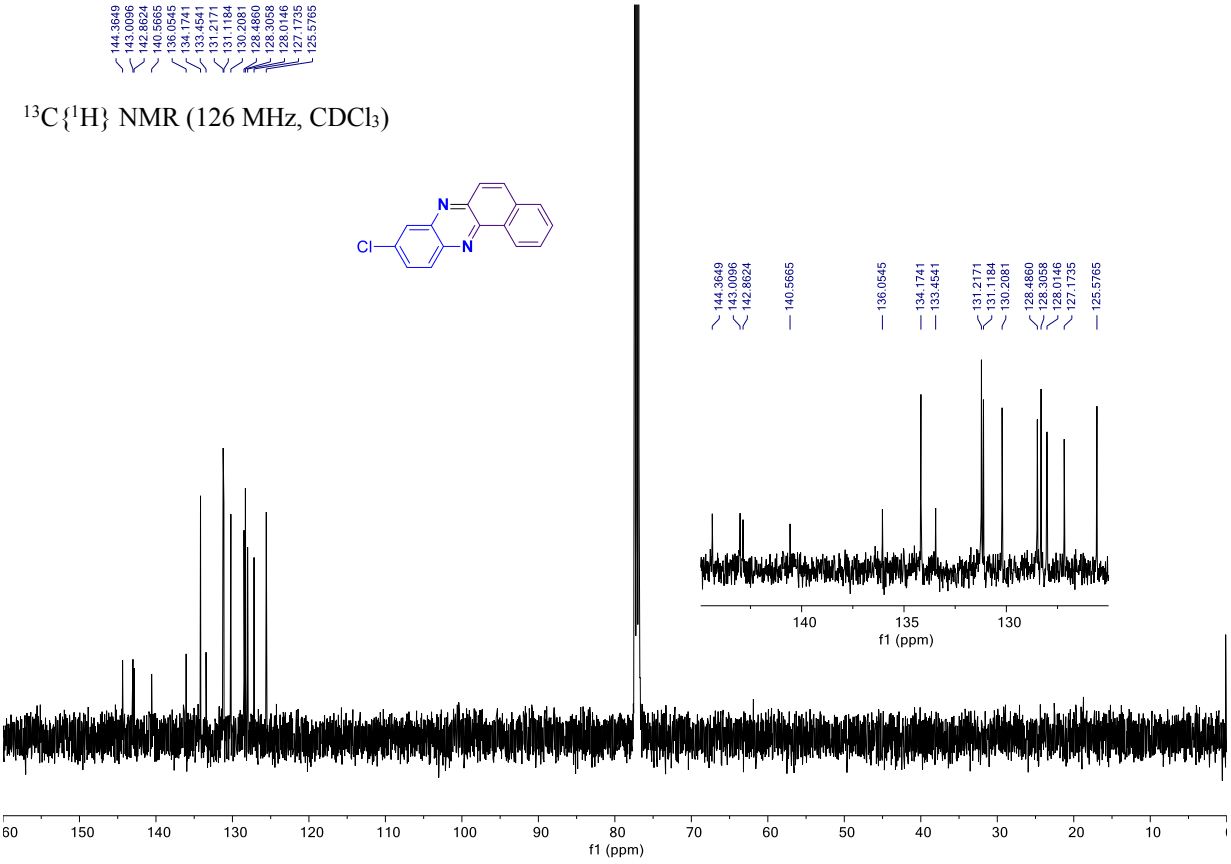


9-Chlorobenzo[a]phenazine (3i)

^{1}H NMR (600 MHz, $CDCl_3$)

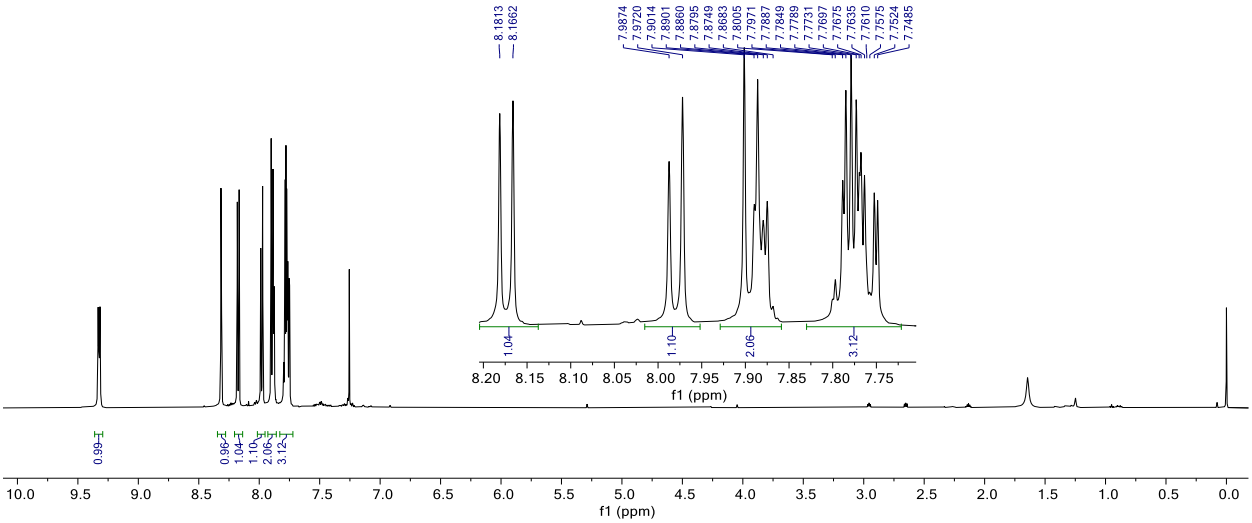


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

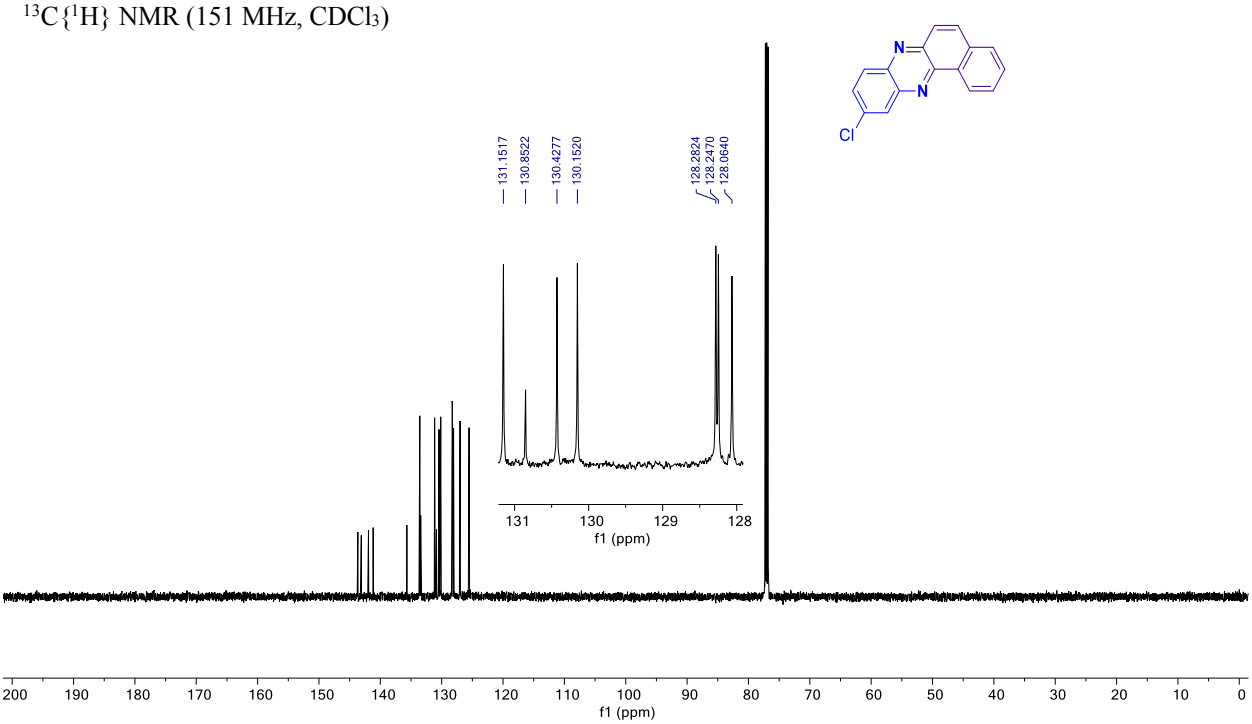


10-Chlorobenzo[a]phenazine (3j)

^{1}H NMR (600 MHz, $CDCl_3$)

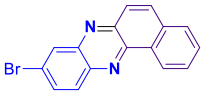


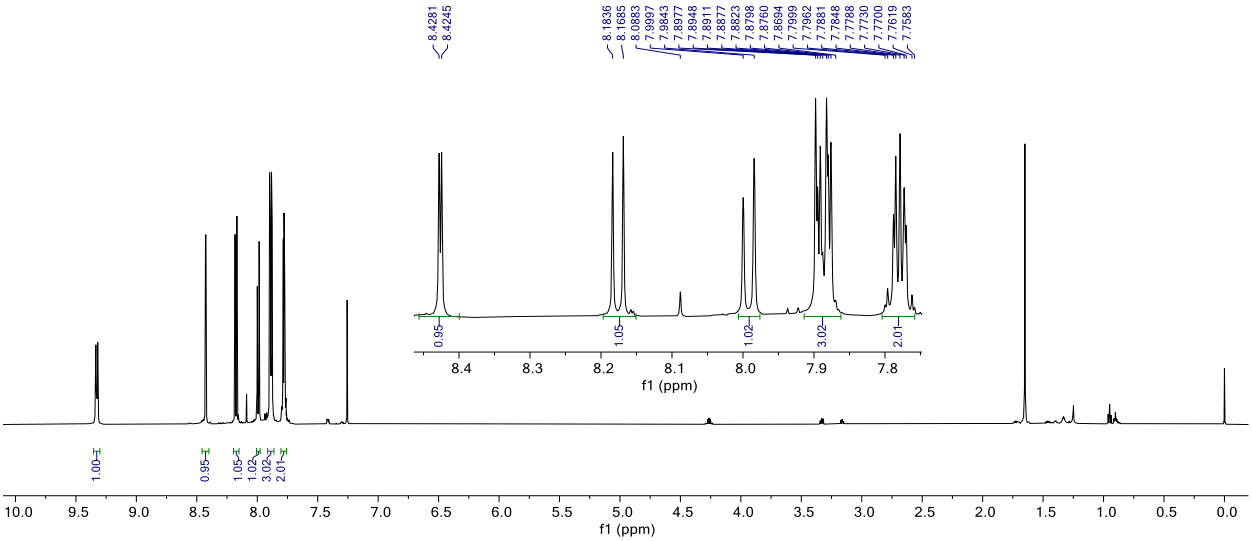
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



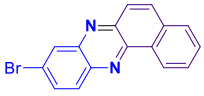
9-Bromobenzo[a]phenazine (3k)

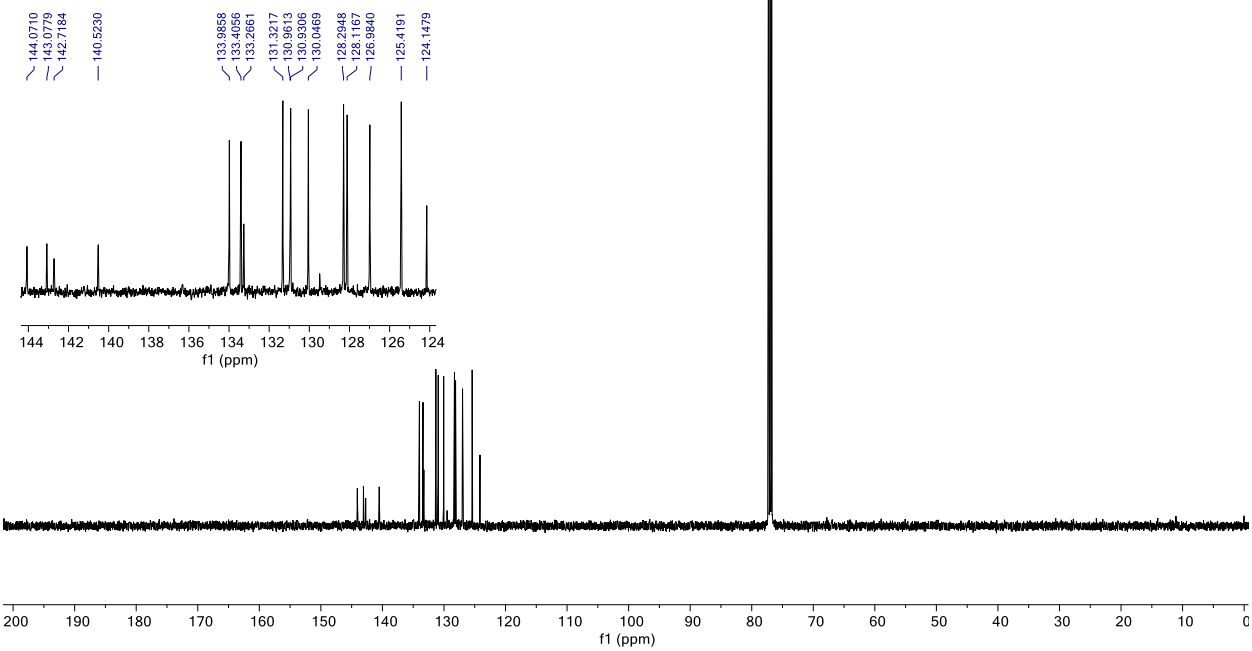
^{1}H NMR (600 MHz, $CDCl_3$)





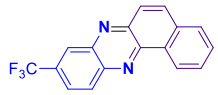
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

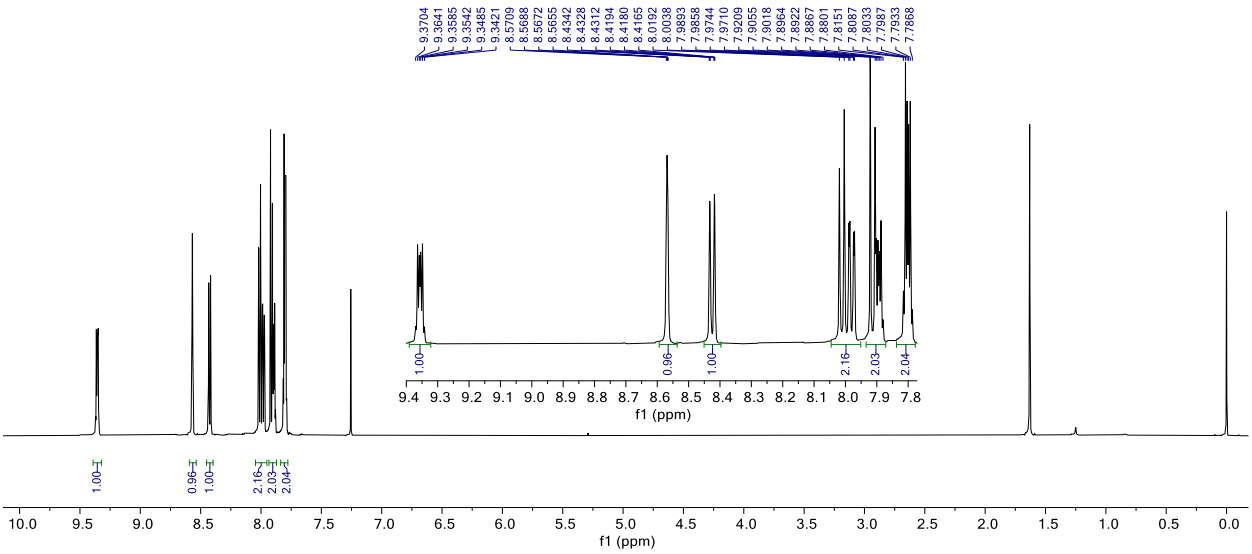




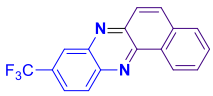
9-(Trifluoromethyl)benzo[a]phenazine (3l)

^{1}H NMR (600 MHz, $CDCl_3$)



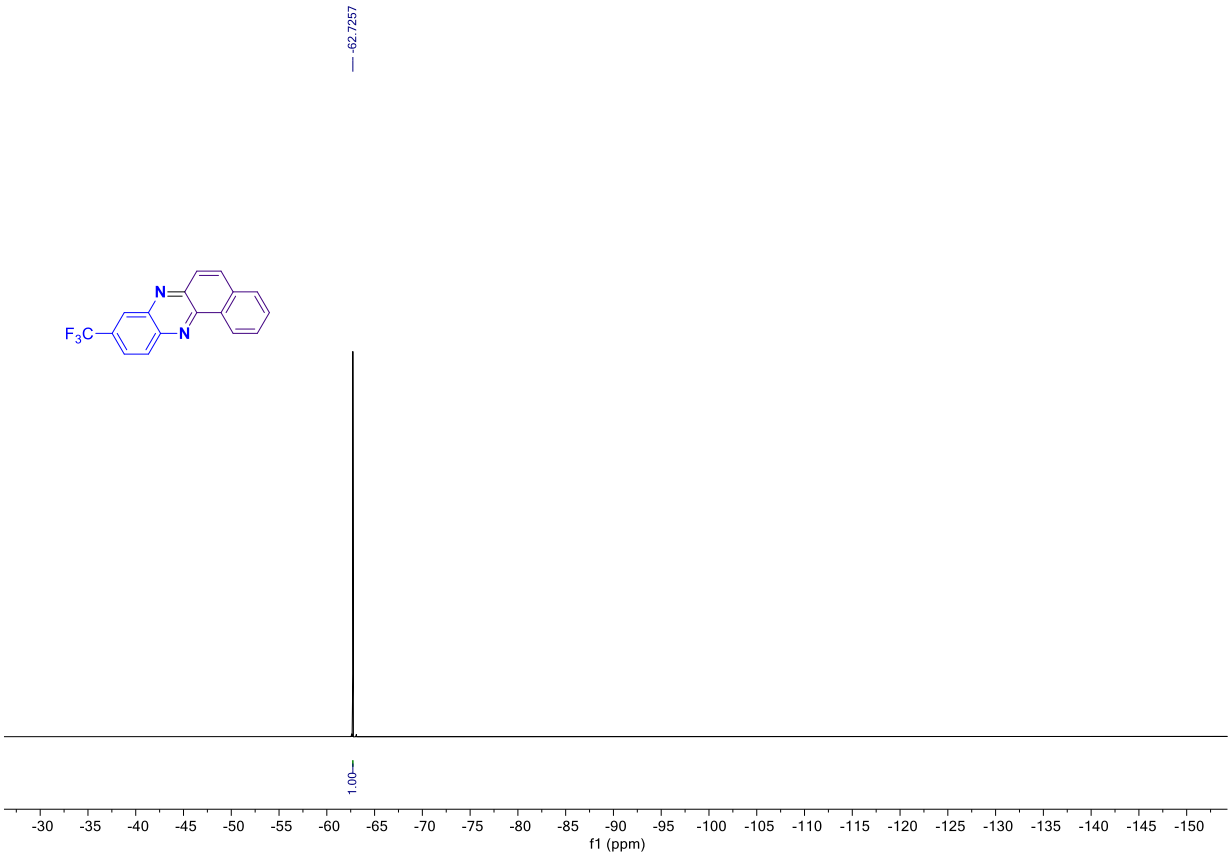


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



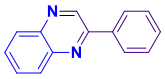
9-(Trifluoromethyl)benzo[a]phenazine (3l)

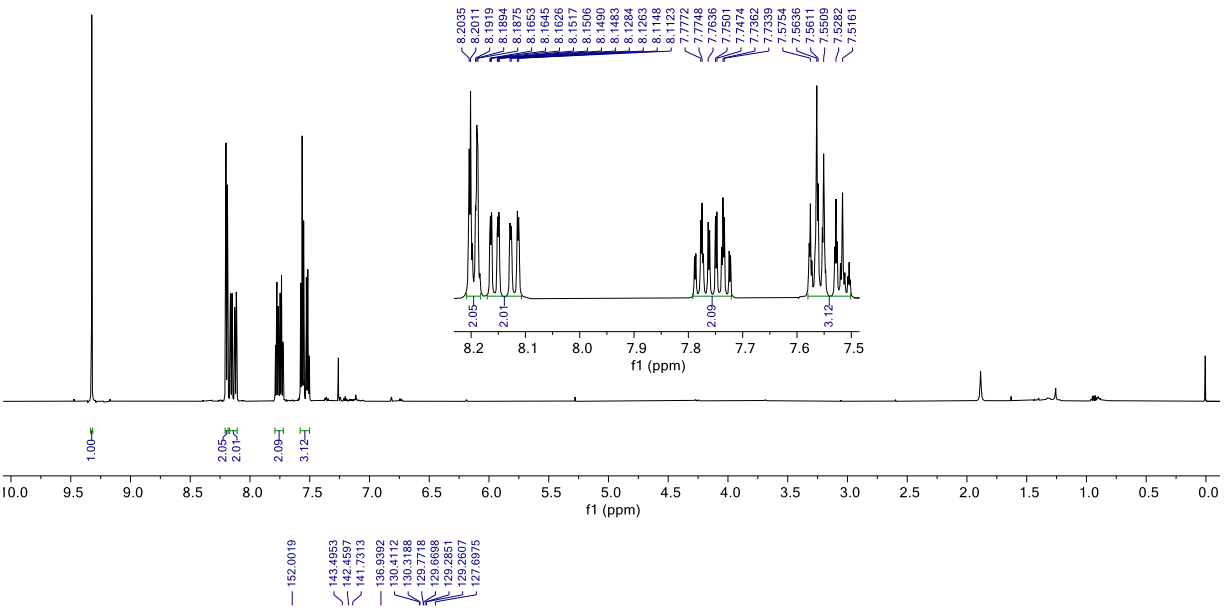
^{19}F NMR (565 MHz, $CDCl_3$)



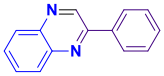
2-Phenylquinoxaline (5a)

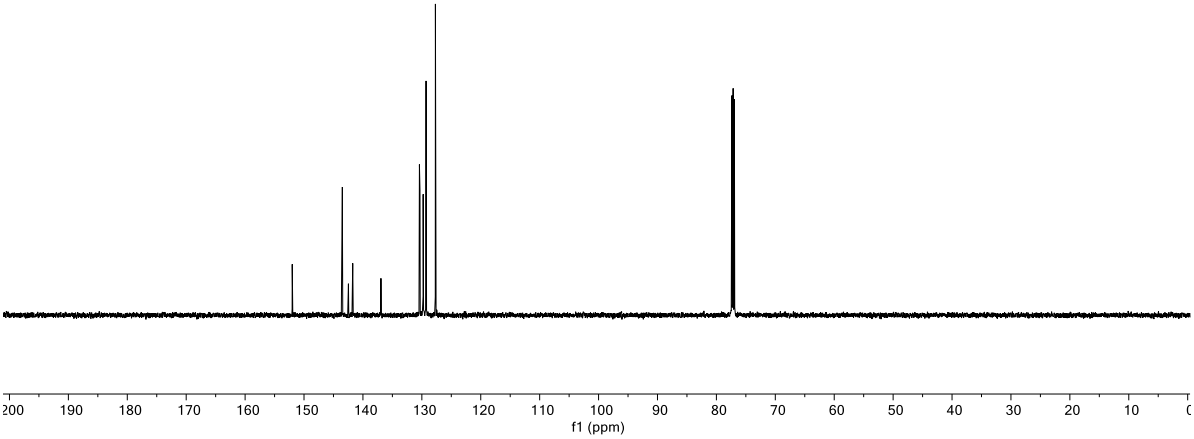
^{1}H NMR (600 MHz, $CDCl_3$)





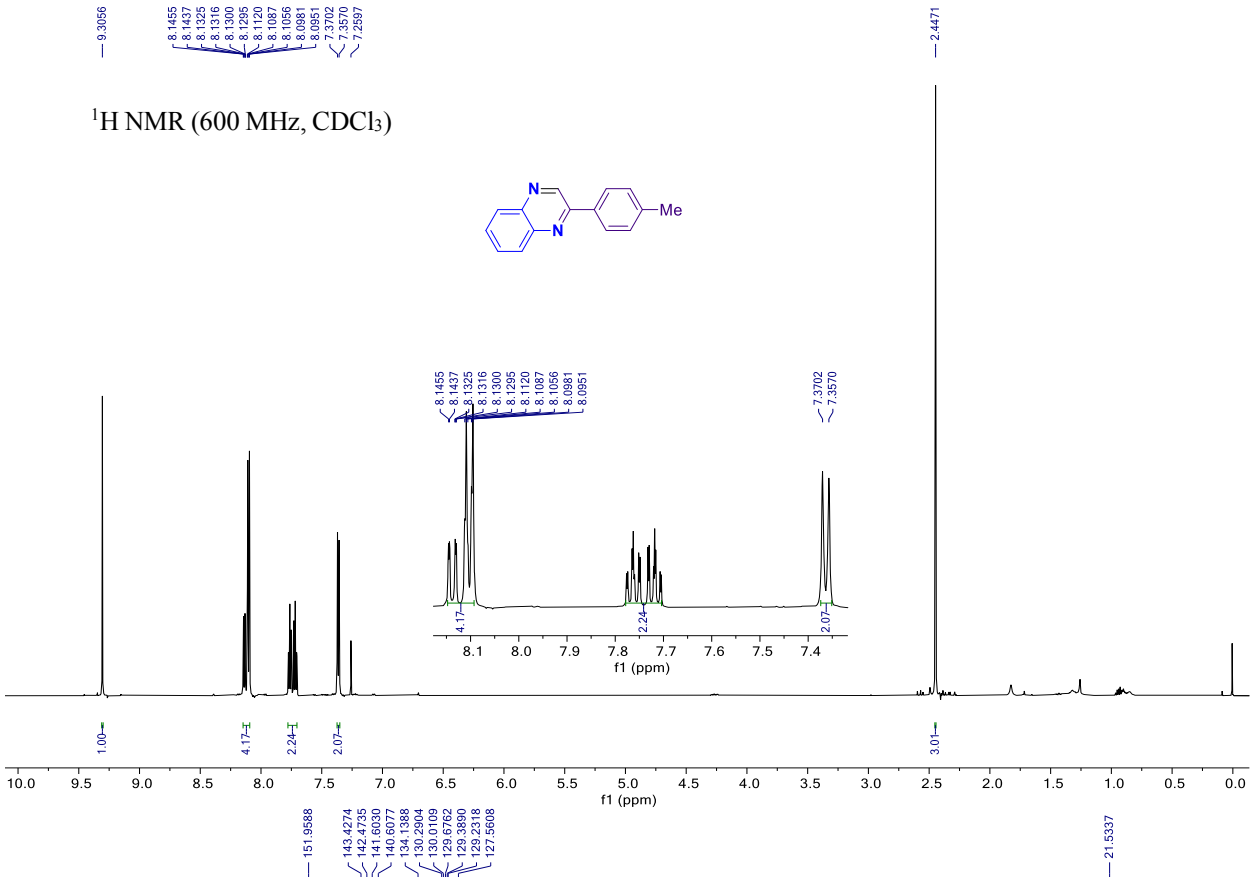
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



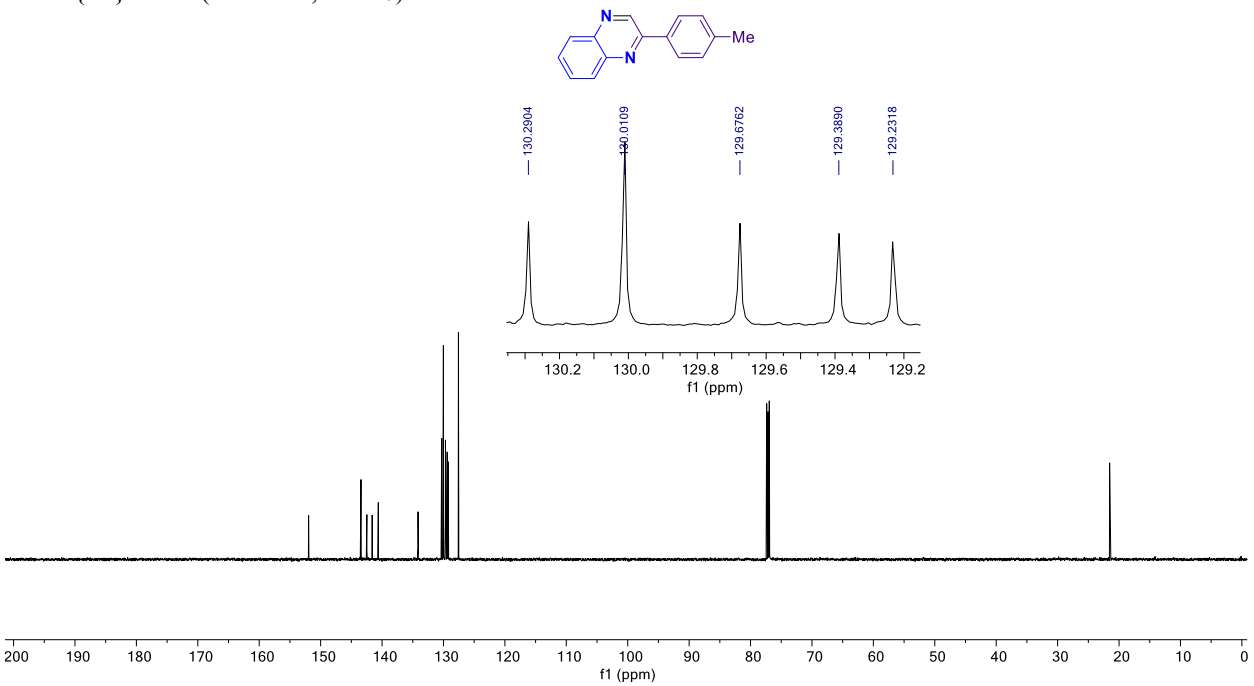


2-(*p*-Tolyl)quinoxaline (5b

^{1}H NMR (600 MHz, $CDCl_3$)

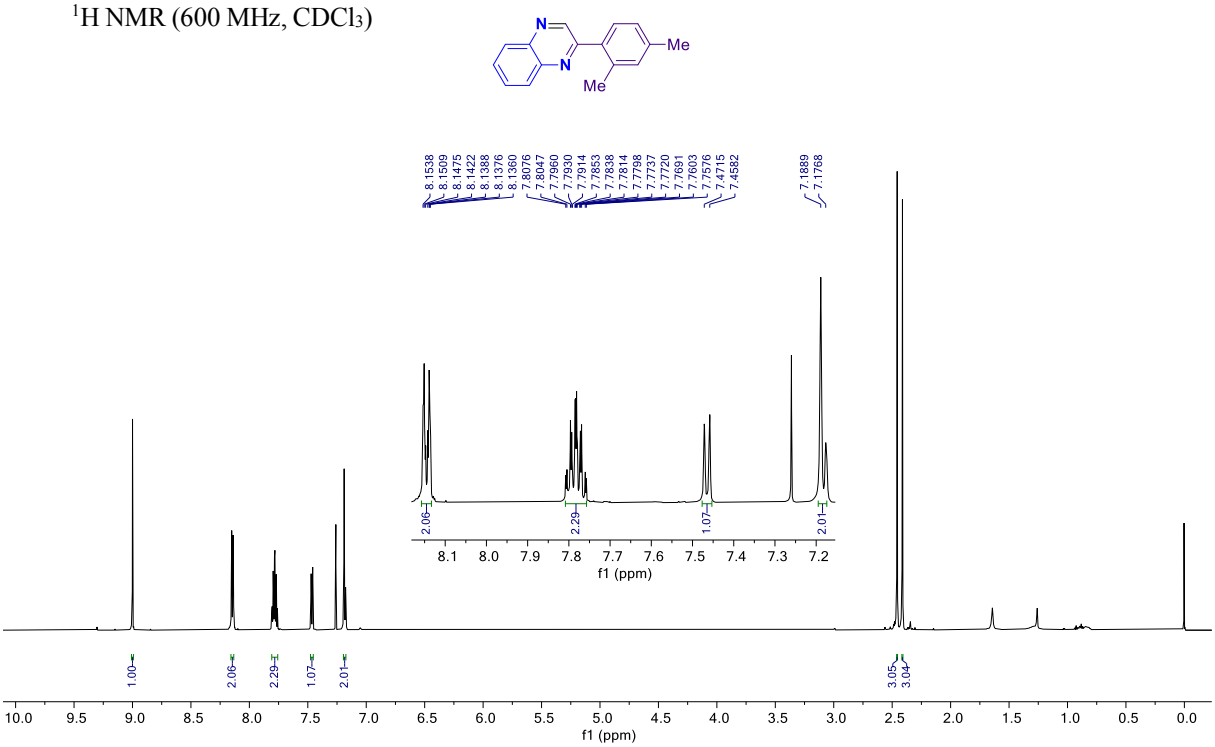


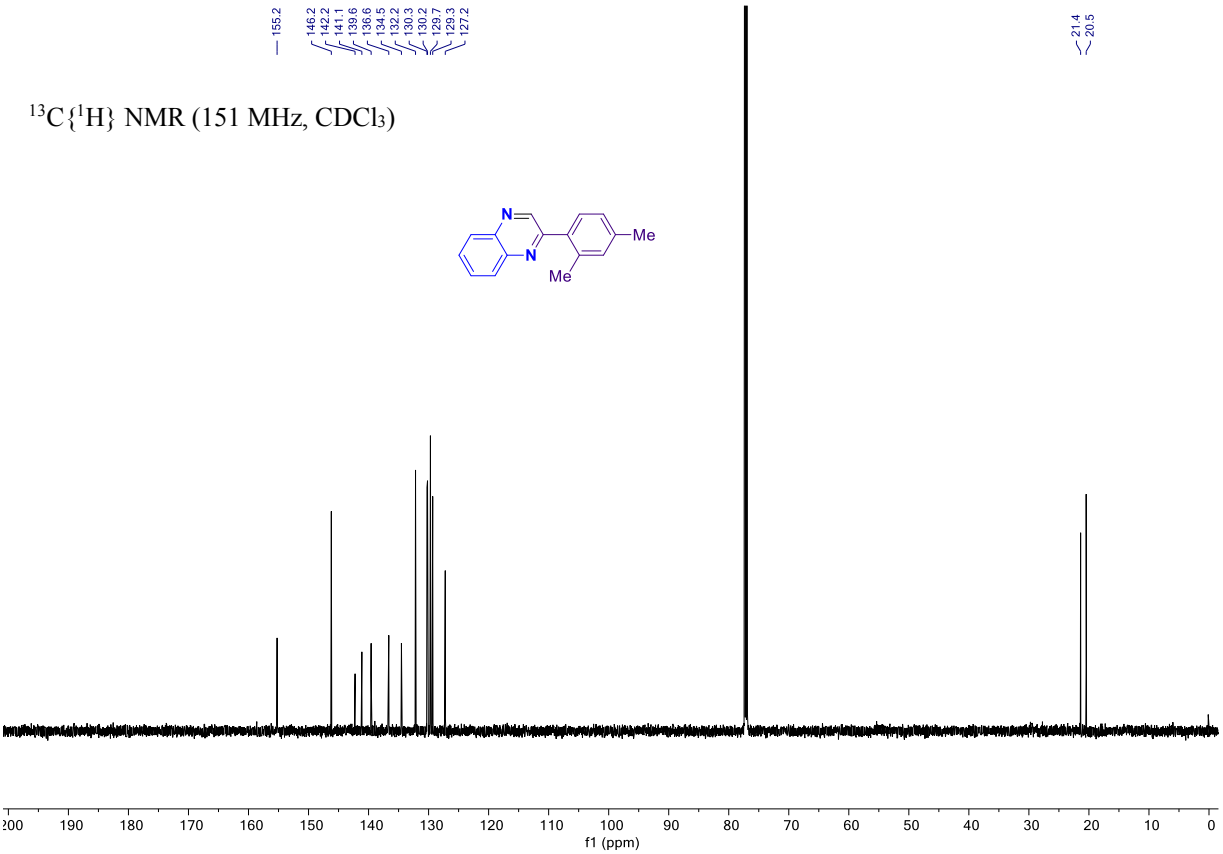
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



2-(2,4-Dimethylphenyl)quinoxaline (5c)

^{1}H NMR (600 MHz, $CDCl_3$)

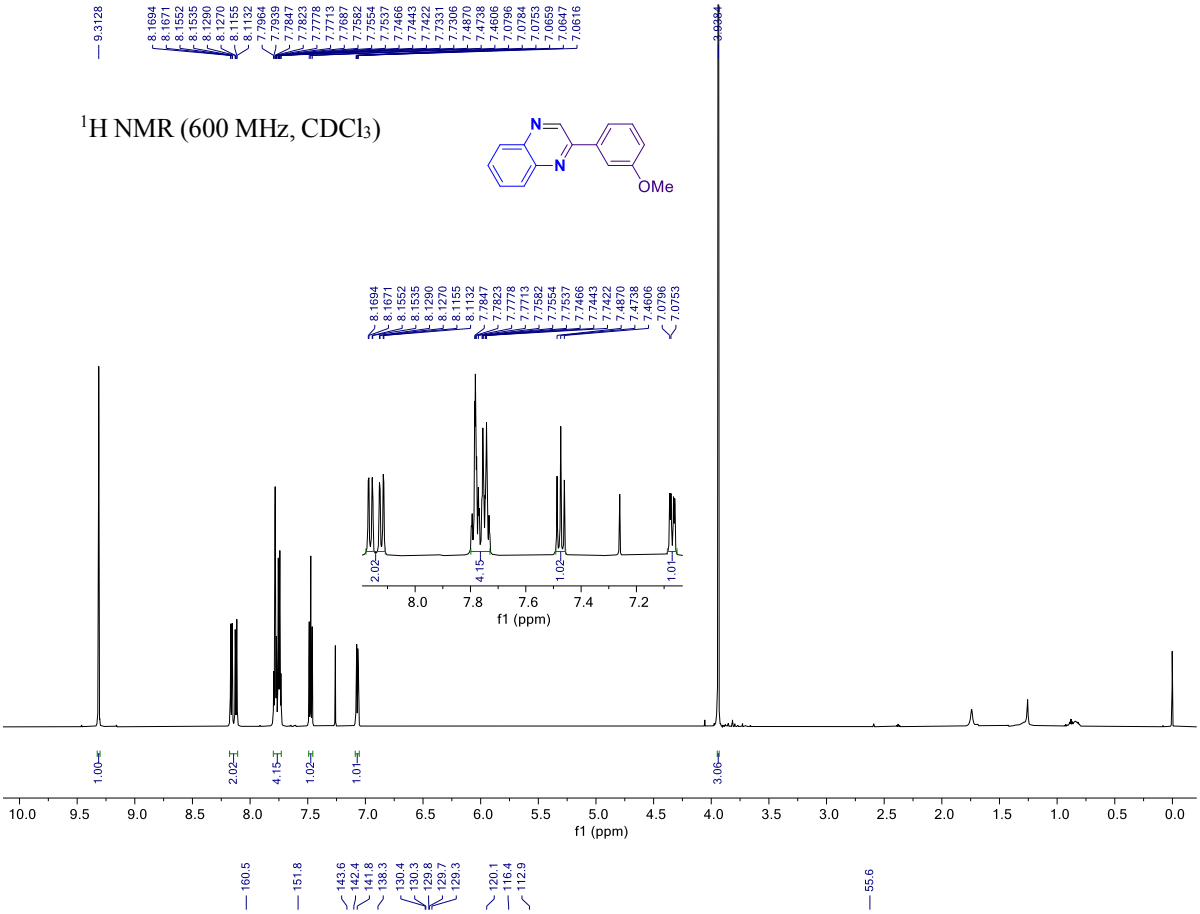




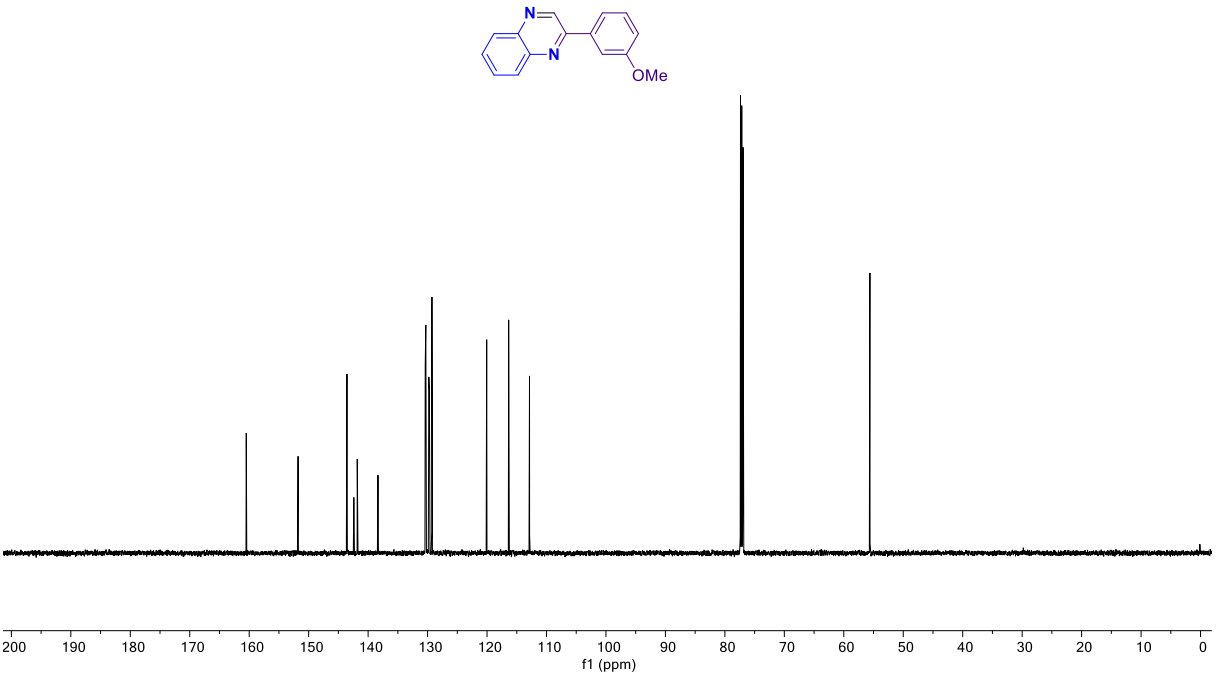
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

2-(3-Methoxyphenyl)quinoxaline (5d)

^{1}H NMR (600 MHz, $CDCl_3$)

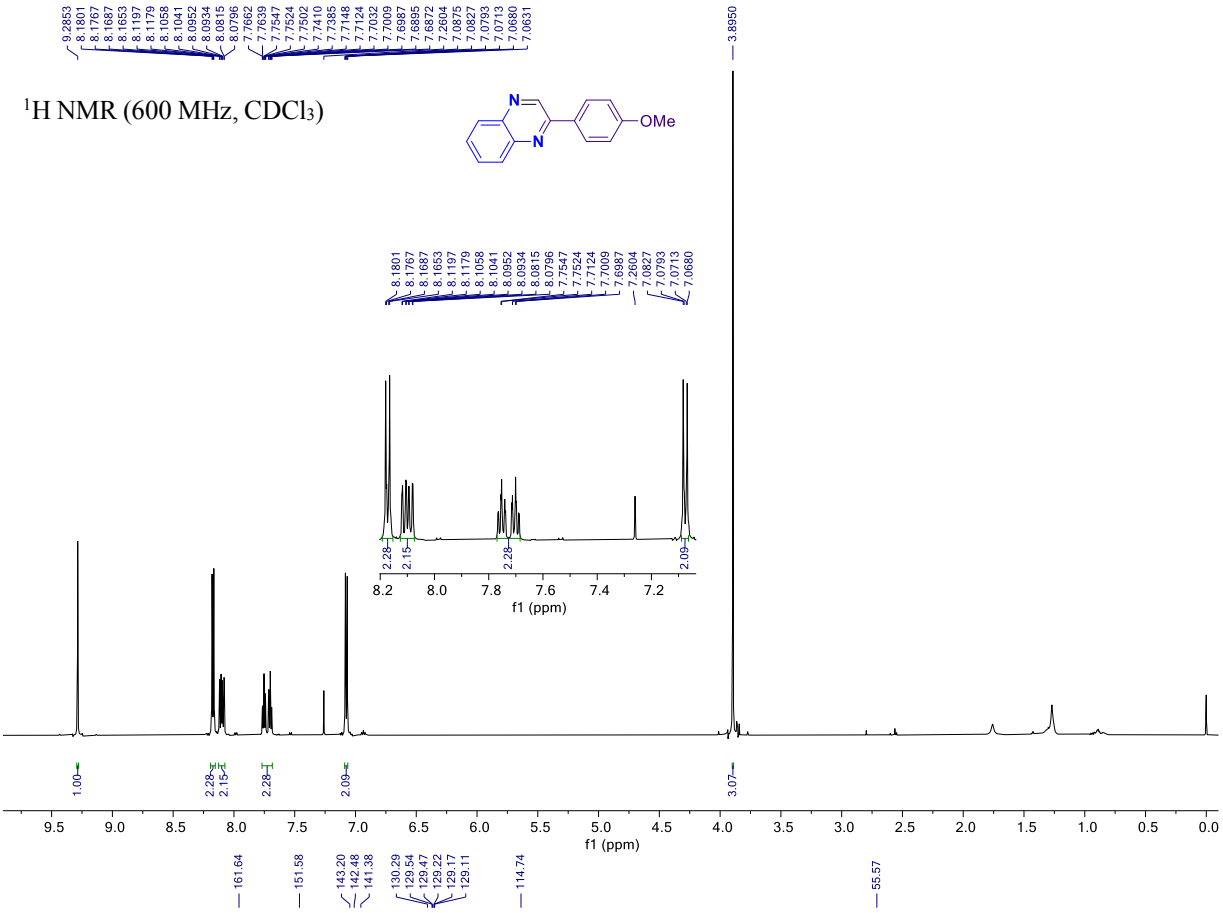


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

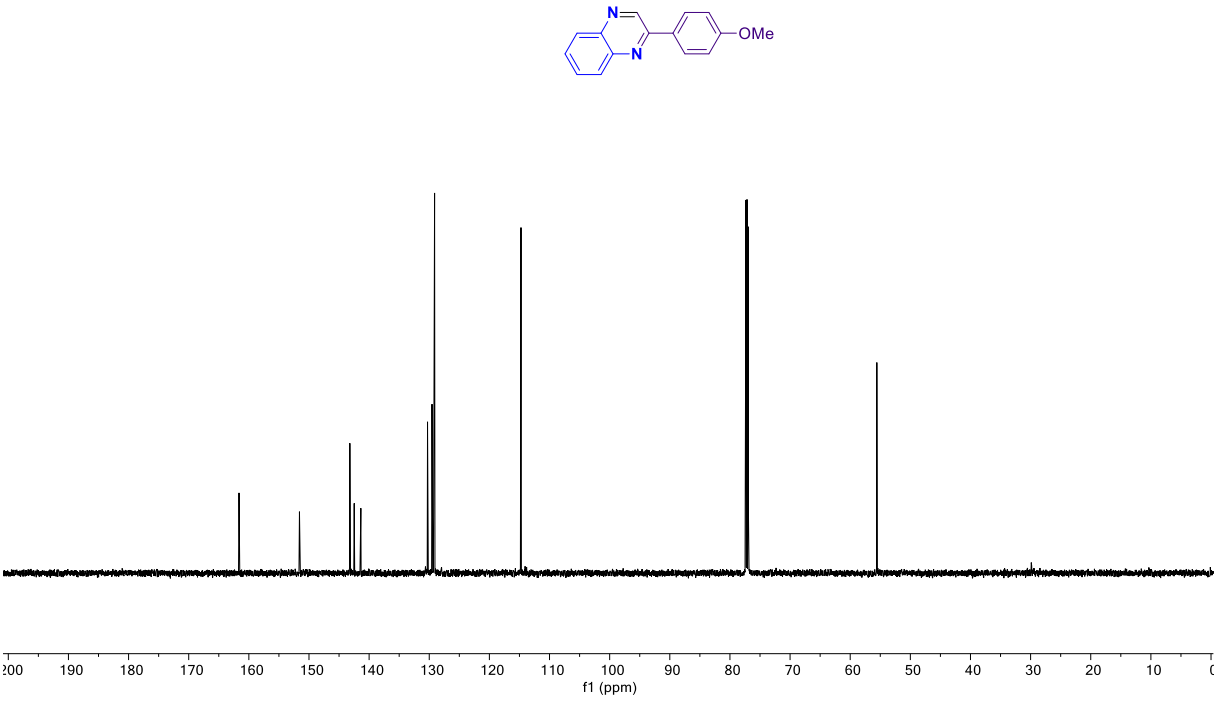


2-(4-Methoxyphenyl)quinoxaline (5e)

^{1}H NMR (600 MHz, $CDCl_3$)

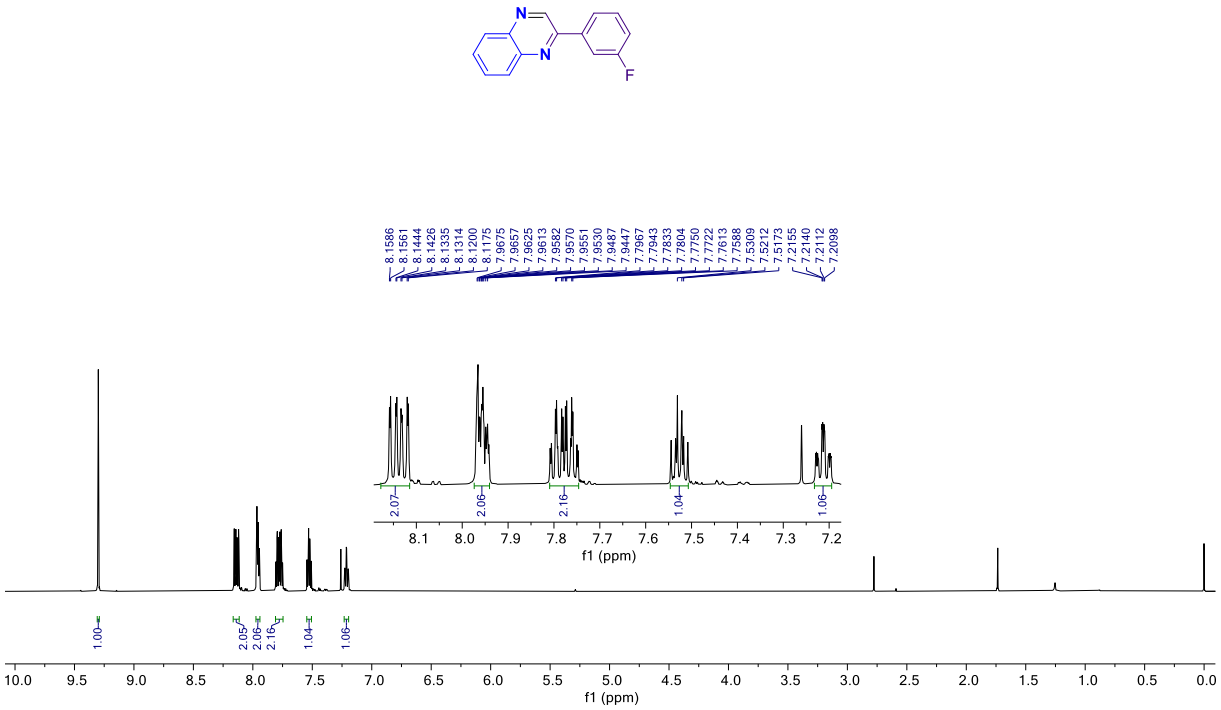


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

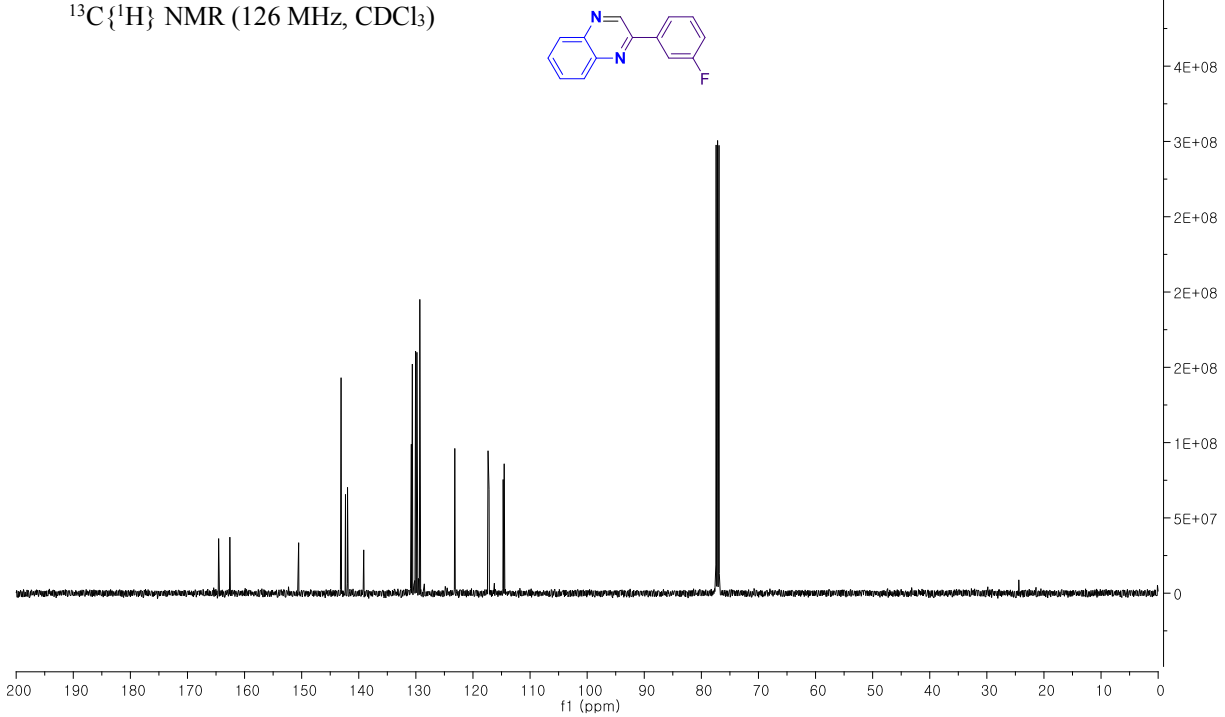


2-(3-Fluorophenyl)quinoxaline (5f)

^{1}H NMR (600 MHz, $CDCl_3$)

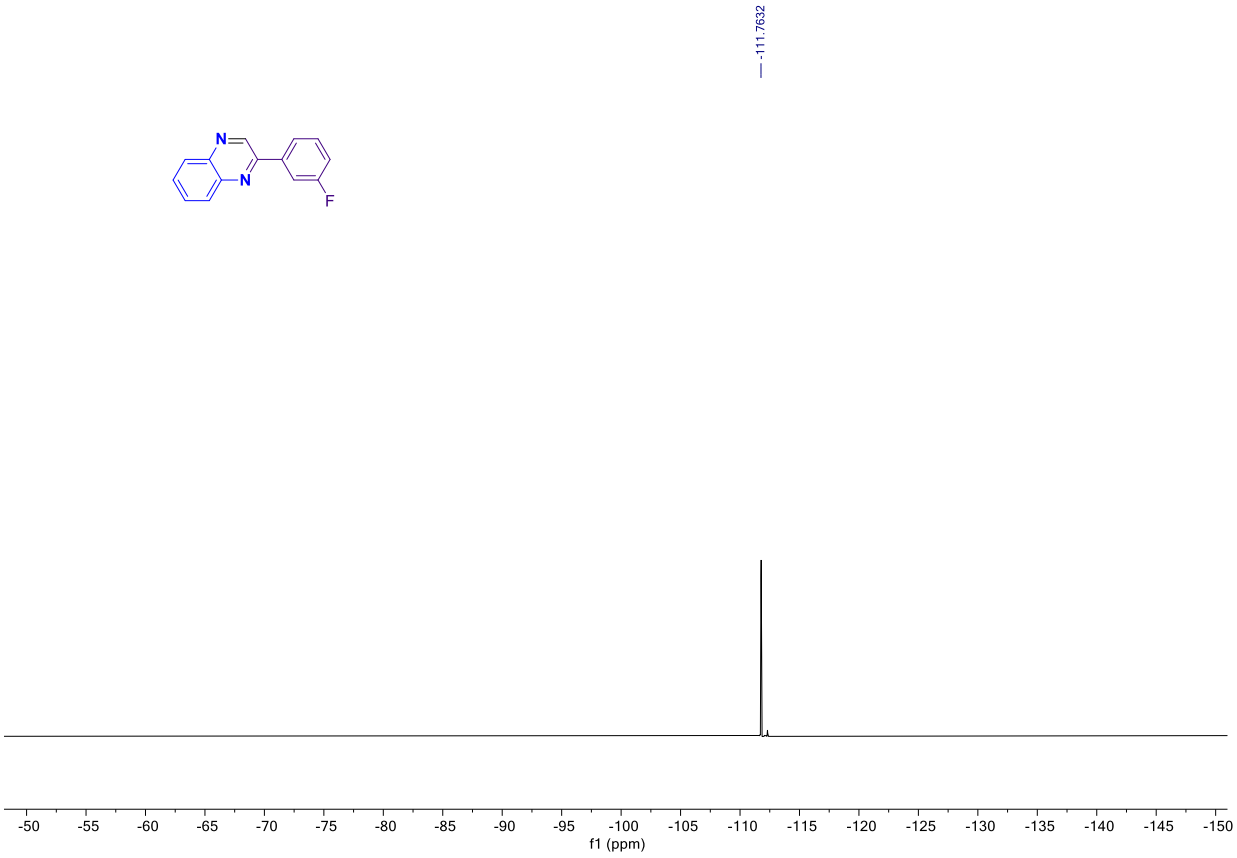


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



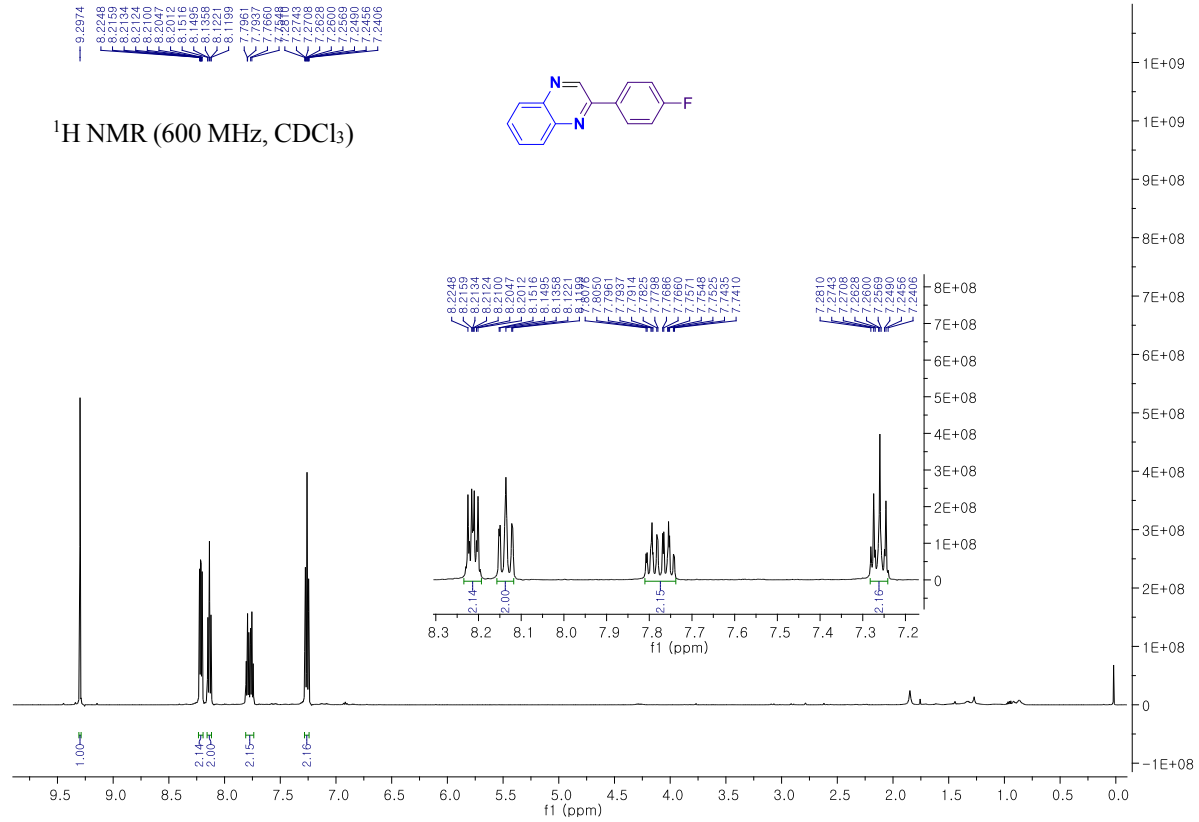
2-(3-Fluorophenyl)quinoxaline (5f)

^{19}F NMR (565 MHz, $CDCl_3$)

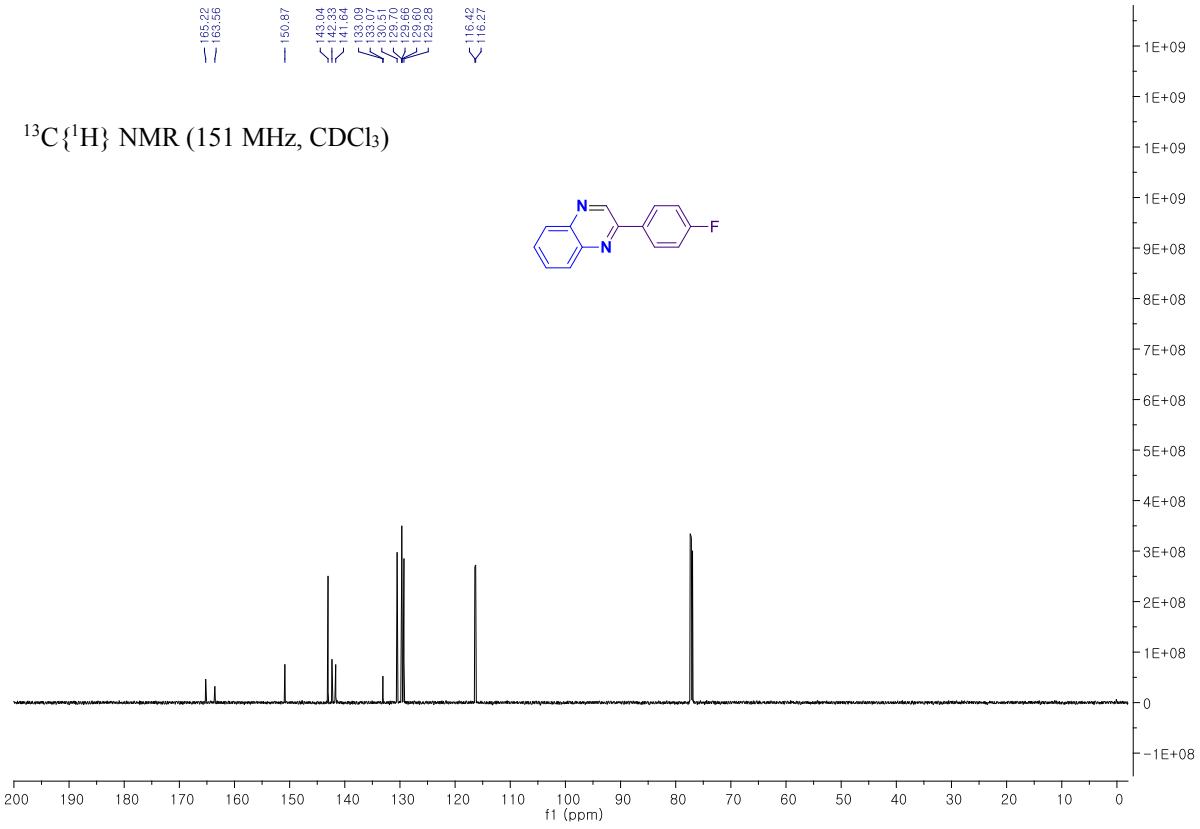


2-(4-Fluorophenyl)quinoxaline (5g)

^{1}H NMR (600 MHz, $CDCl_3$)

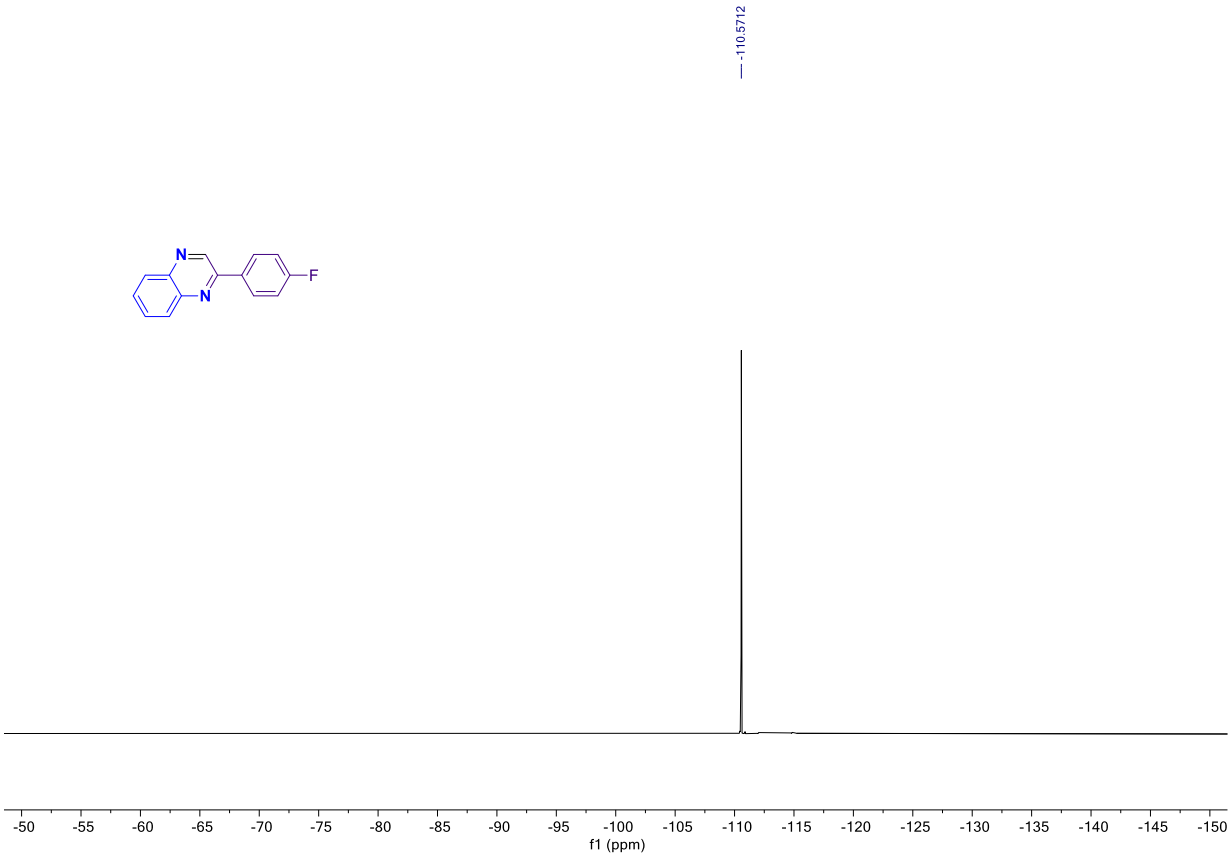


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



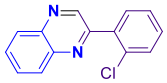
2-(4-Fluorophenyl)quinoxaline (5g)

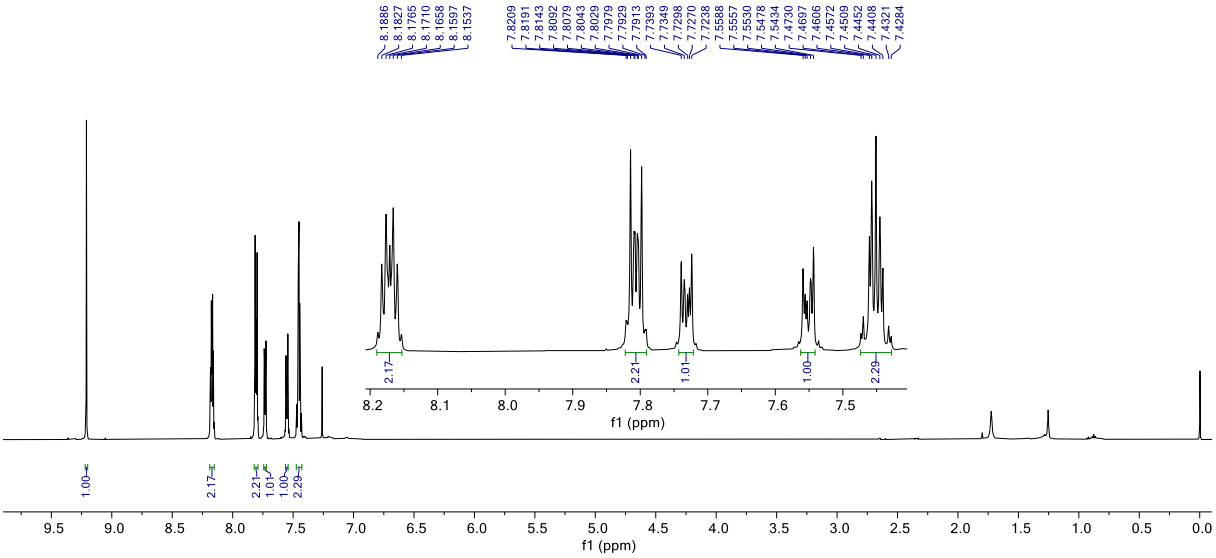
^{19}F NMR (565 MHz, $CDCl_3$)



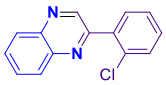
2-(2-Chlorophenyl)quinoxaline (5h)

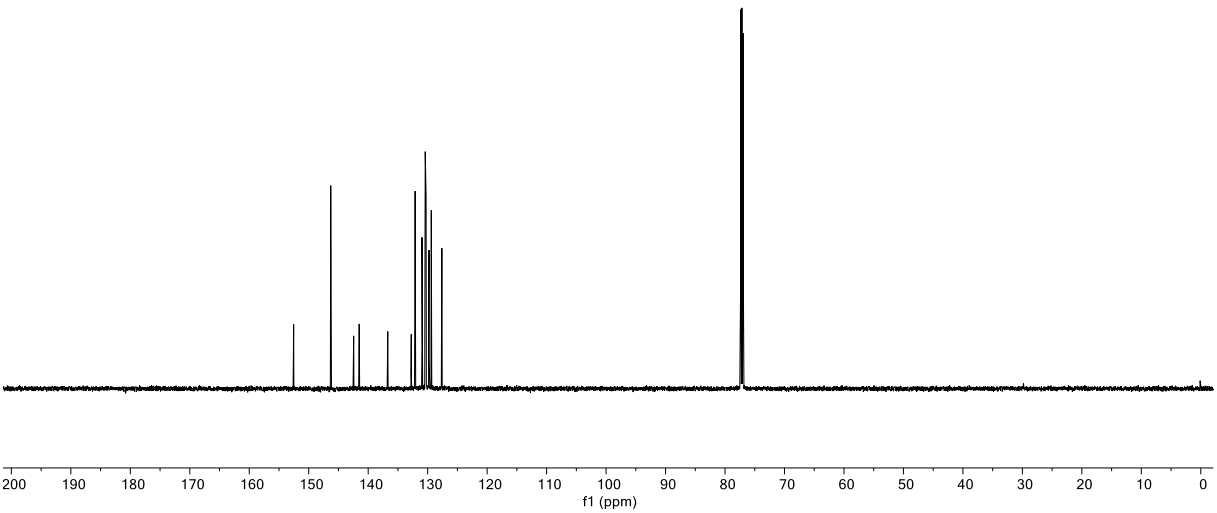
^{1}H NMR (600 MHz, $CDCl_3$)





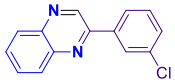
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

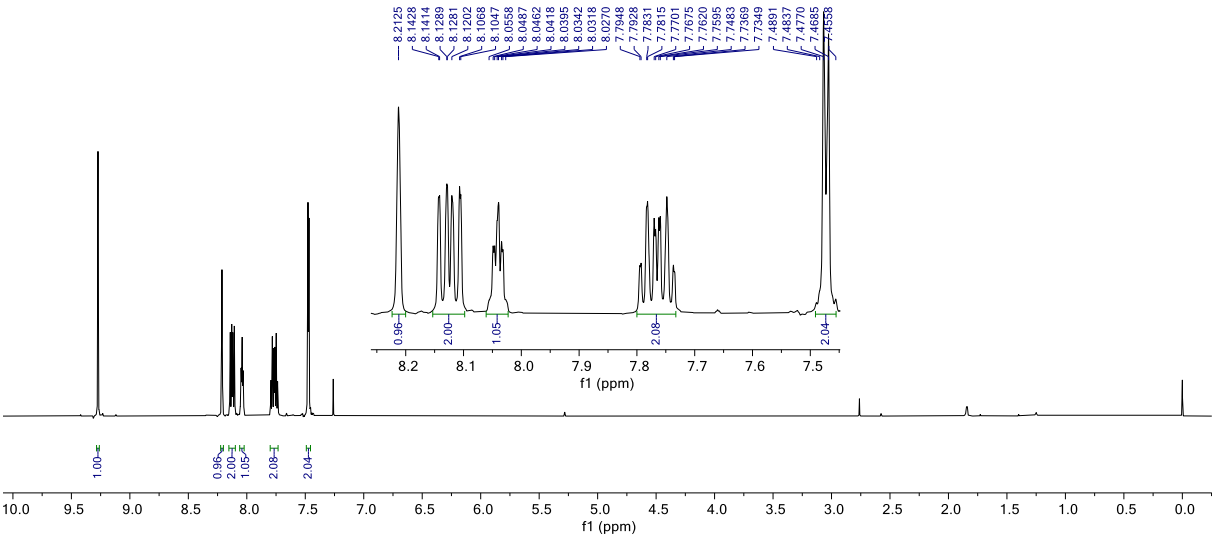




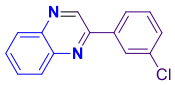
2-(3-Chlorophenyl)quinoxaline (5i)

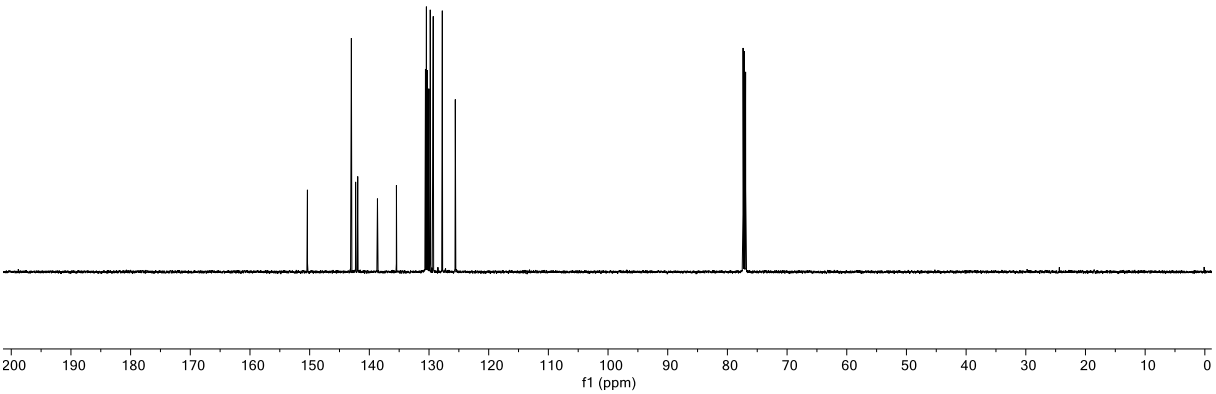
^{1}H NMR (600 MHz, $CDCl_3$)





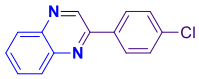
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

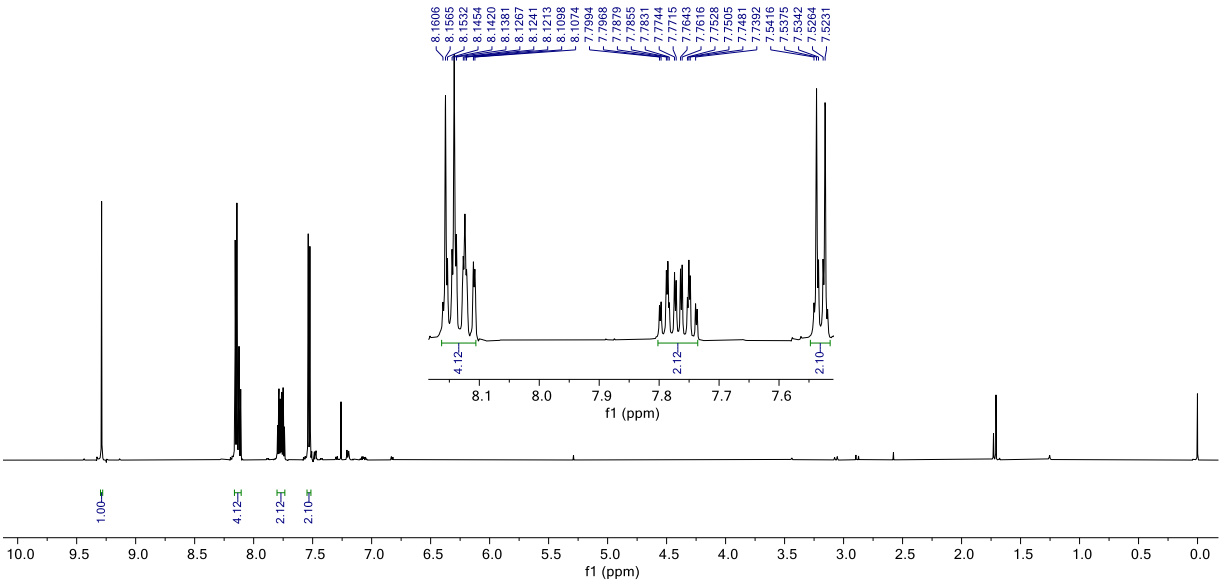




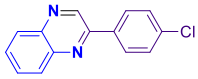
2-(4-Chlorophenyl)quinoxaline (5j)

^{1}H NMR (600 MHz, $CDCl_3$)



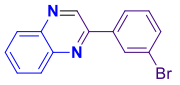


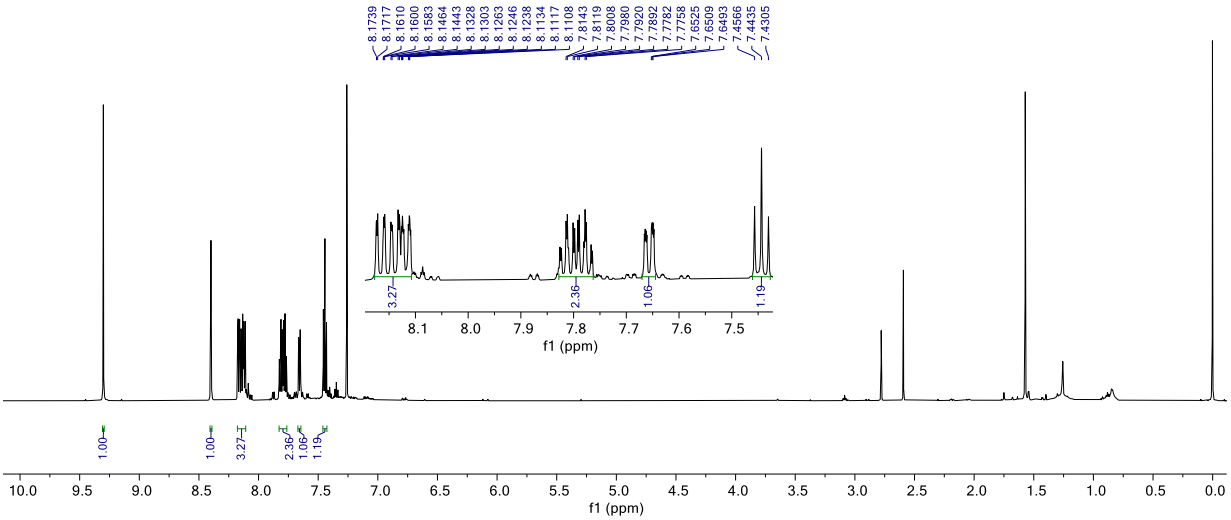
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



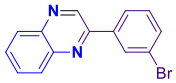
2-(3-Bromophenyl)quinoxaline (5k)

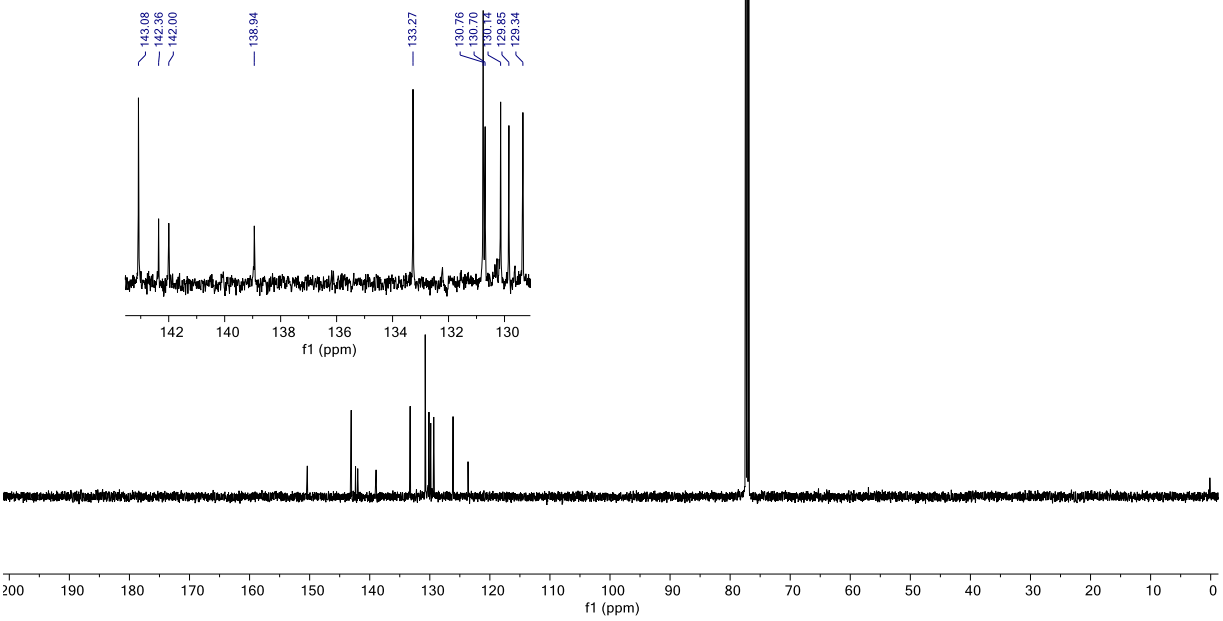
^{1}H NMR (600 MHz, $CDCl_3$)





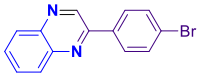
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

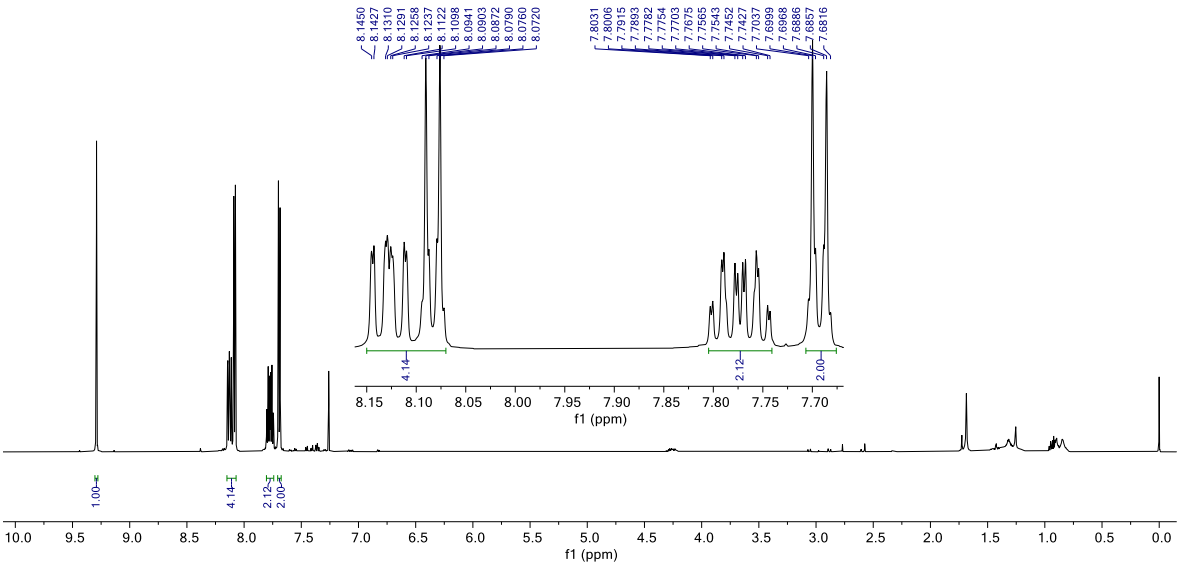




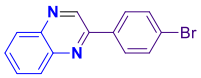
2-(4-Bromophenyl)quinoxaline (5l)

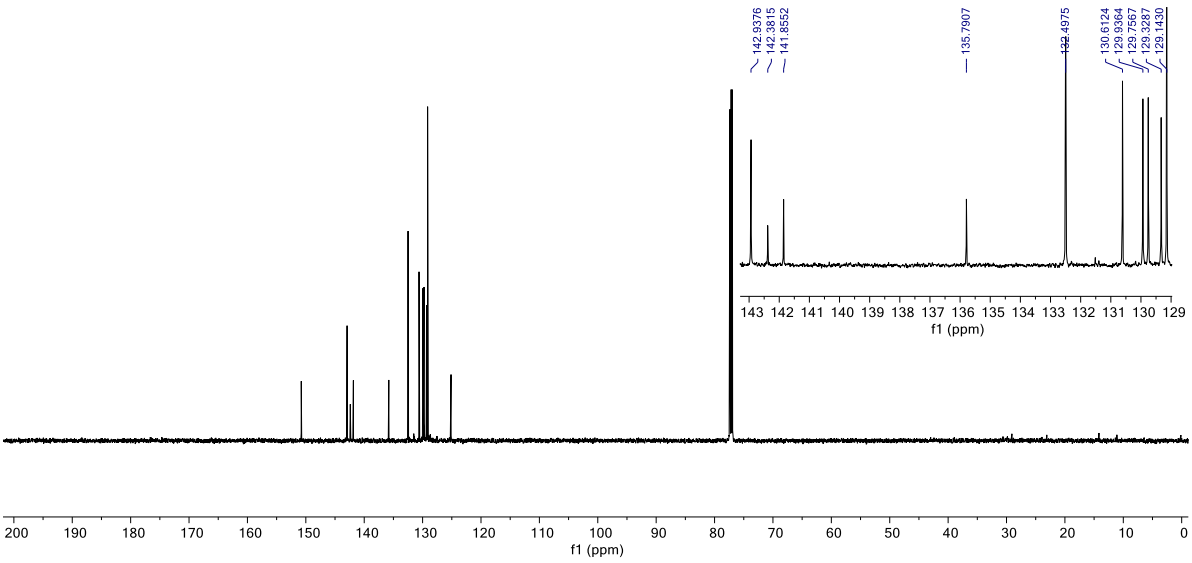
^{1}H NMR (600 MHz, $CDCl_3$)





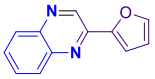
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

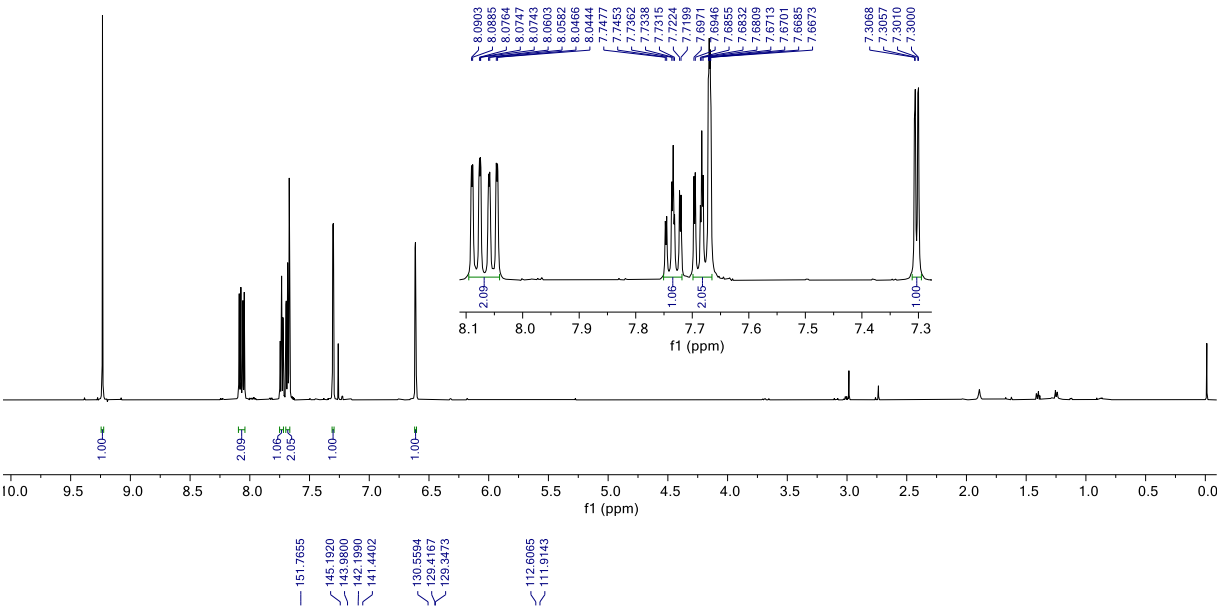




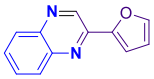
2-(Furan-2-yl)quinoxaline (5m)

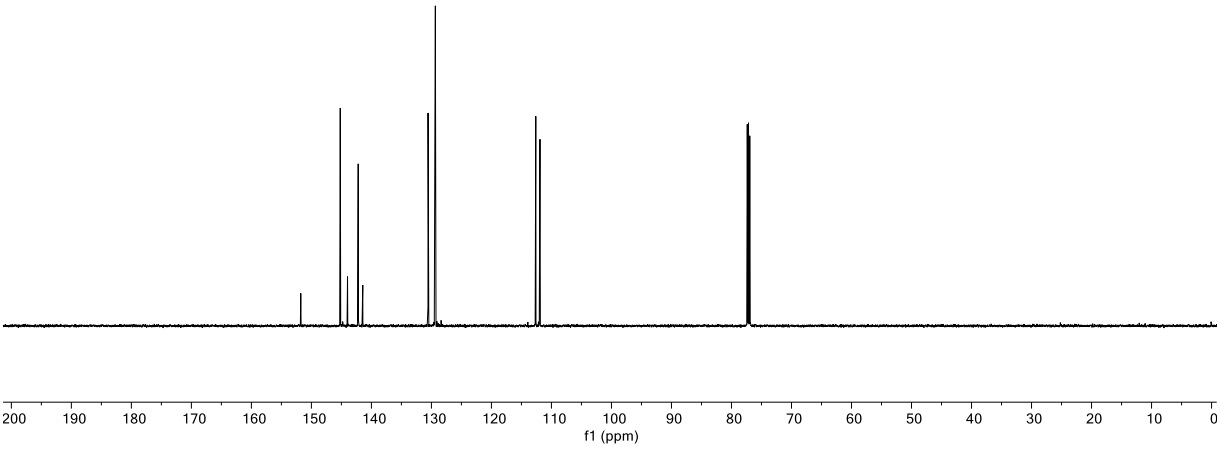
^{1}H NMR (600 MHz, $CDCl_3$)





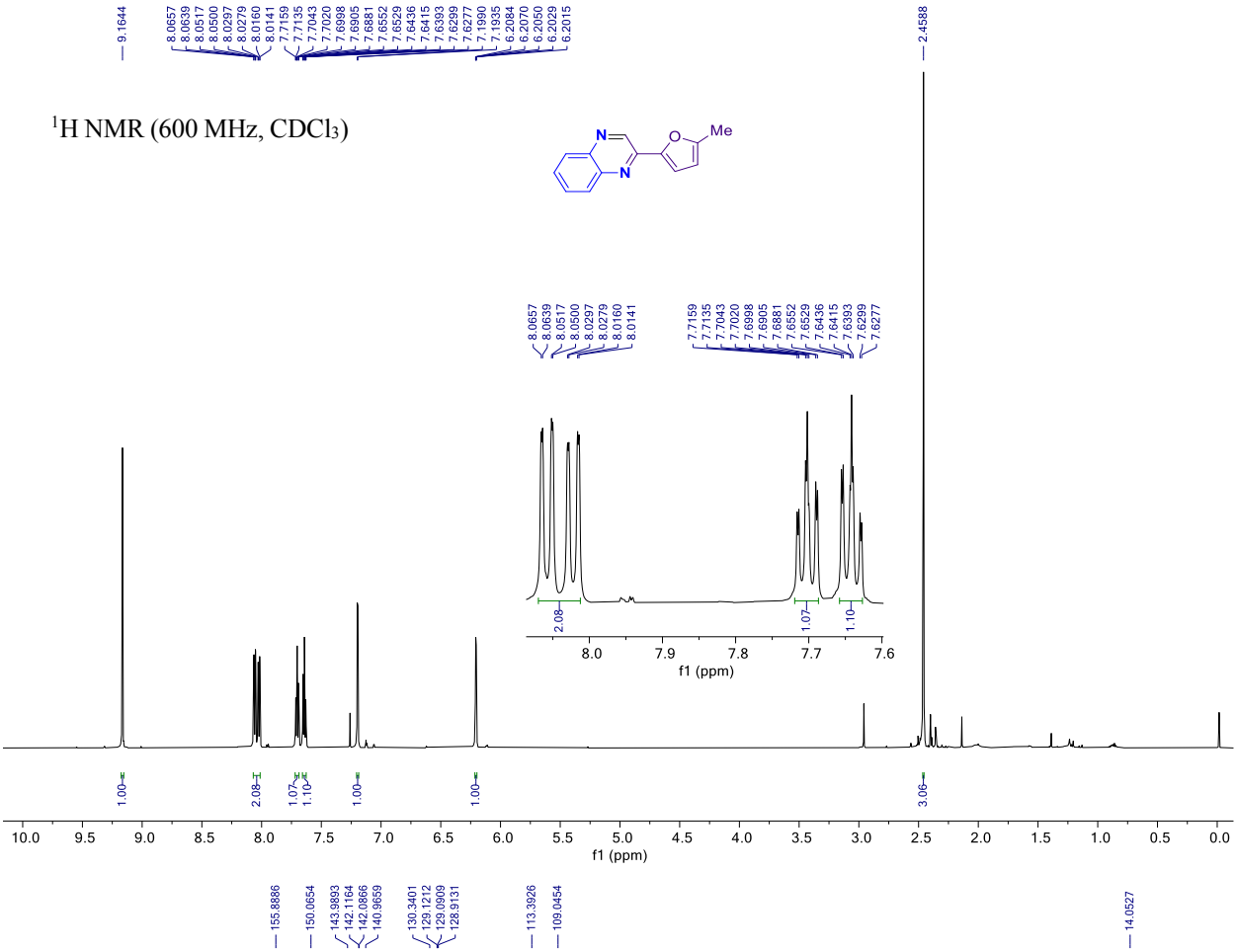
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



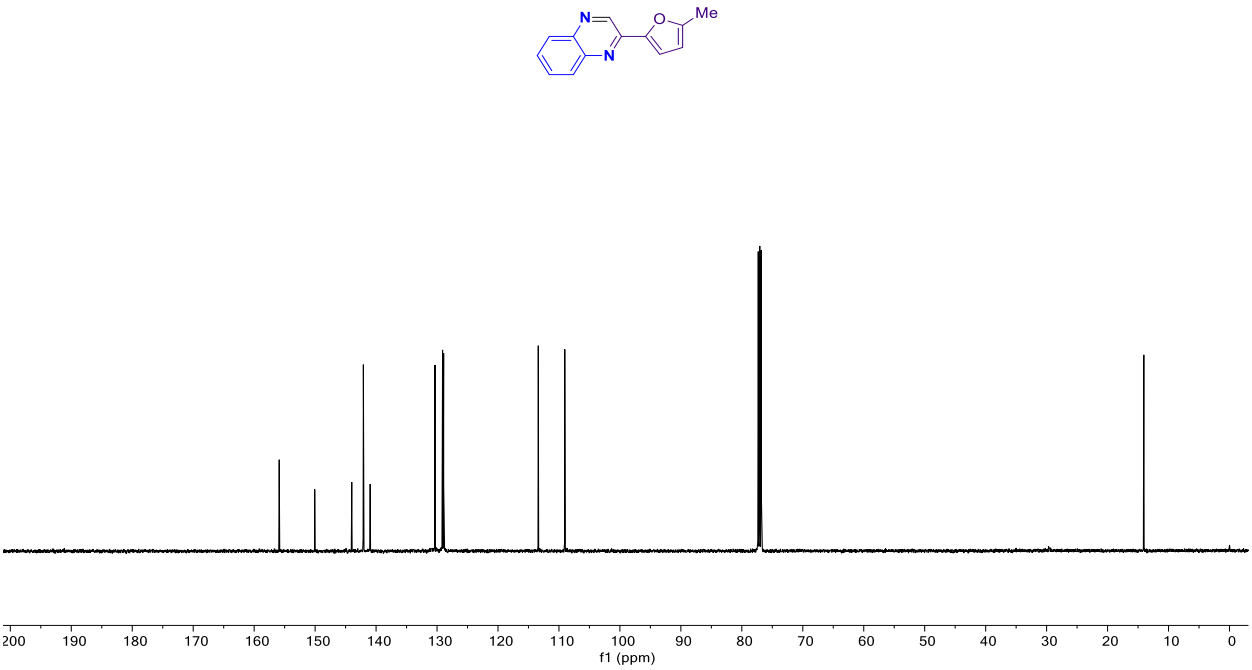


2-(5-Methylfuran-2-yl)quinoxaline (5n)

^{1}H NMR (600 MHz, $CDCl_3$)

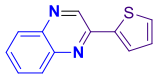


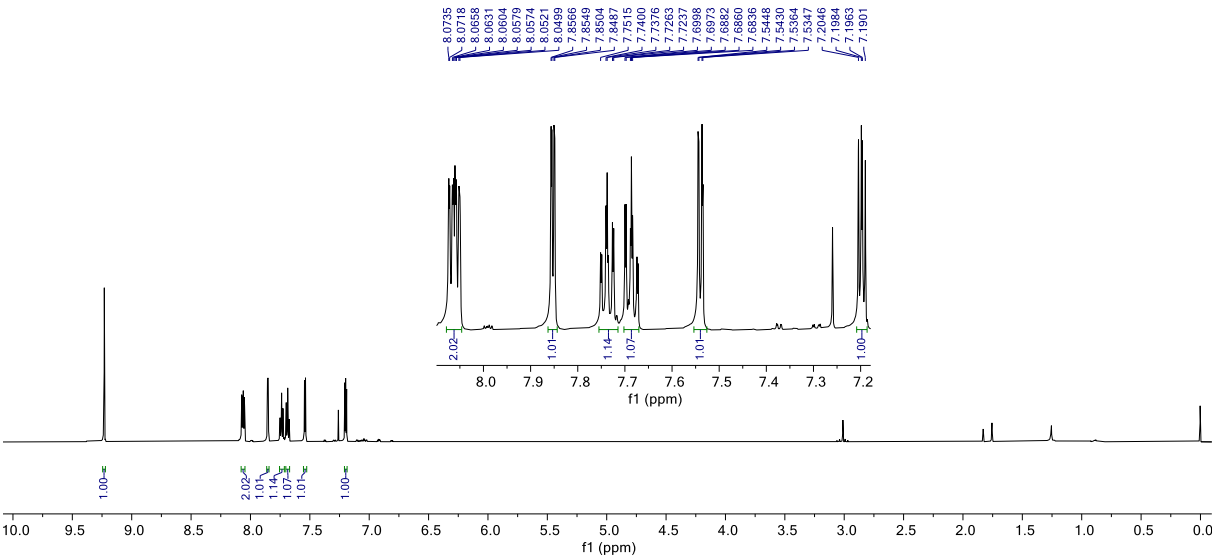
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

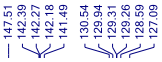


2-(Thiophen-2-yl)quinoxaline (5o)

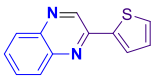
^{1}H NMR (600 MHz, $CDCl_3$)

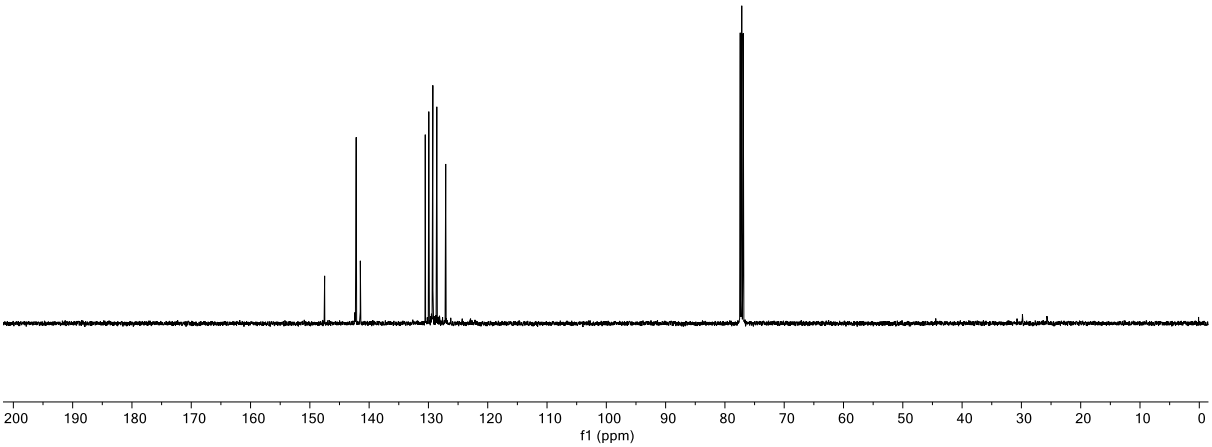






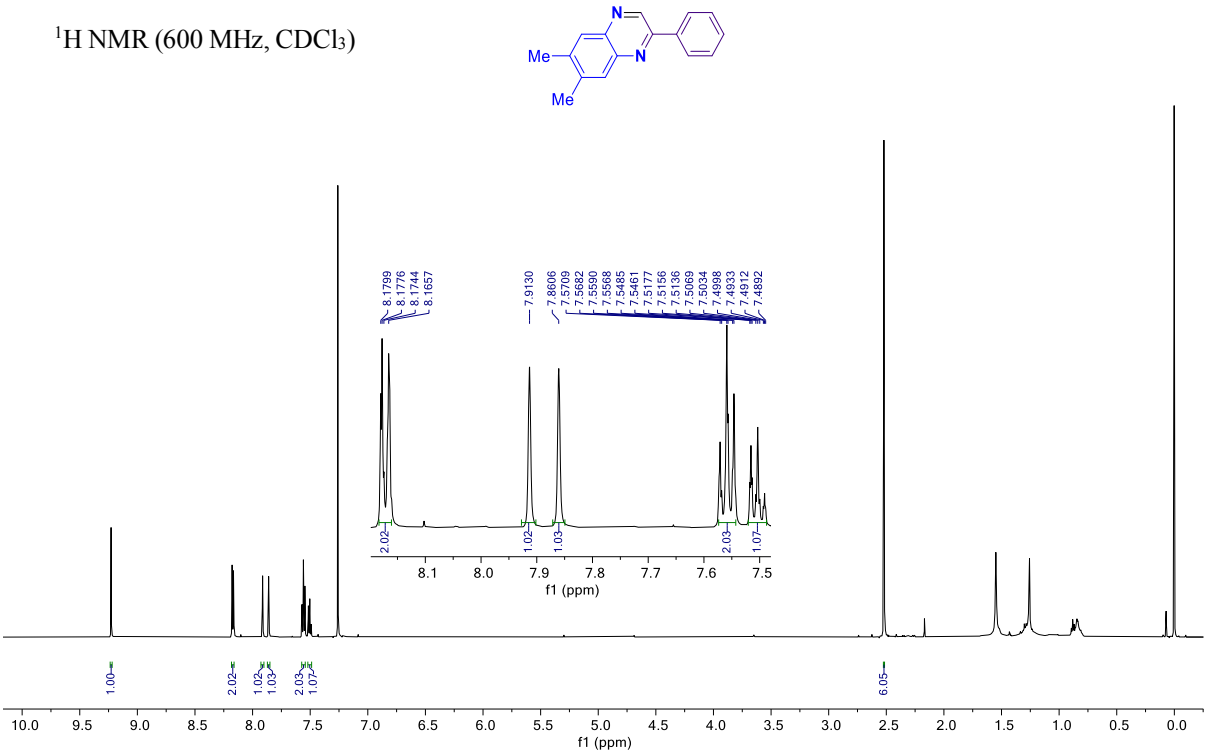
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



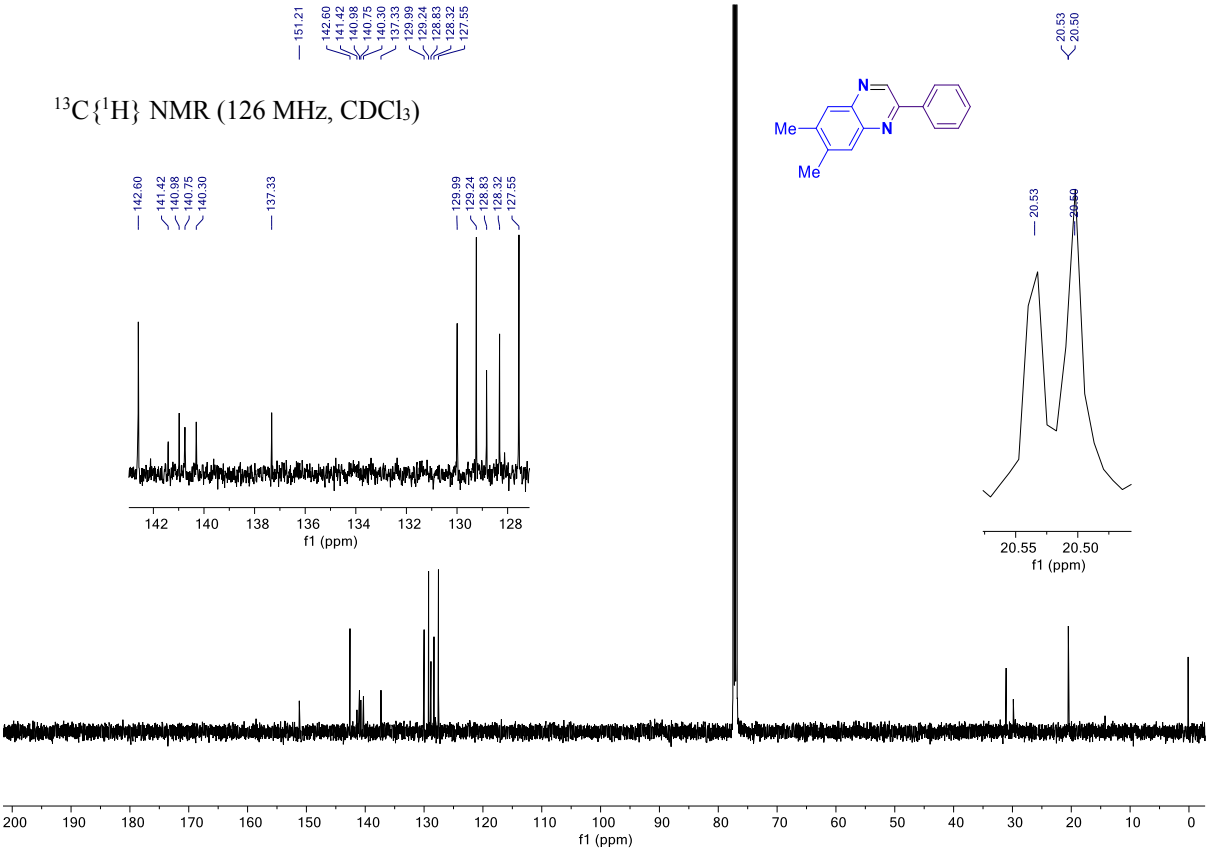


6,7-Dimethyl-2-phenylquinoxaline (5p)

^{1}H NMR (600 MHz, $CDCl_3$)

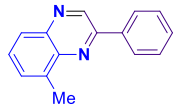


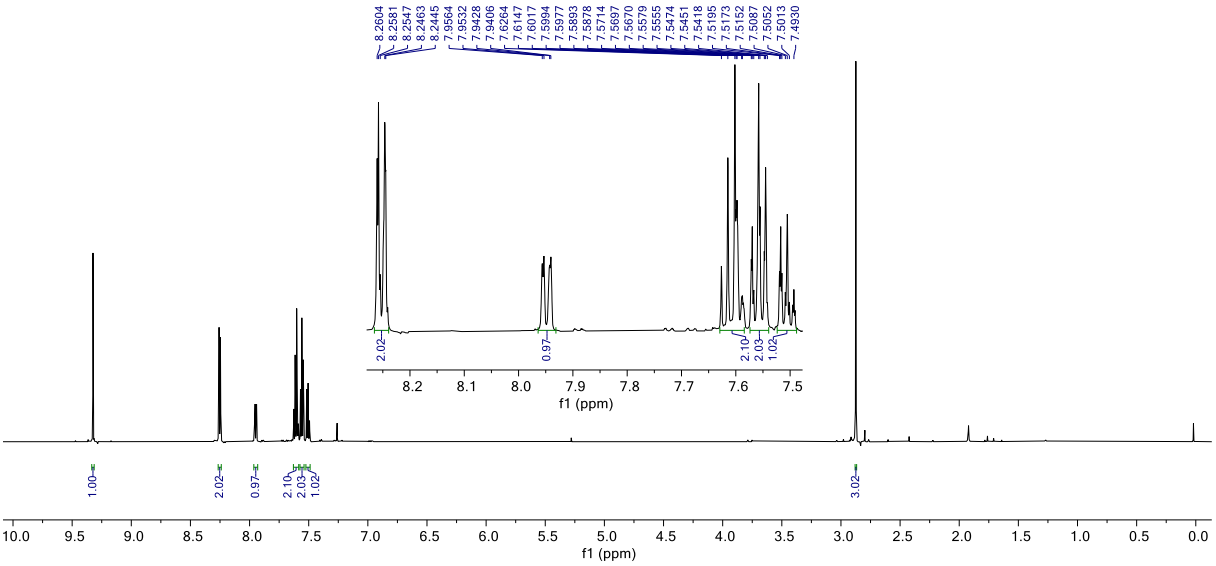
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



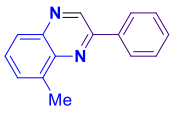
8-Methyl-2-phenylquinoxaline (5q)

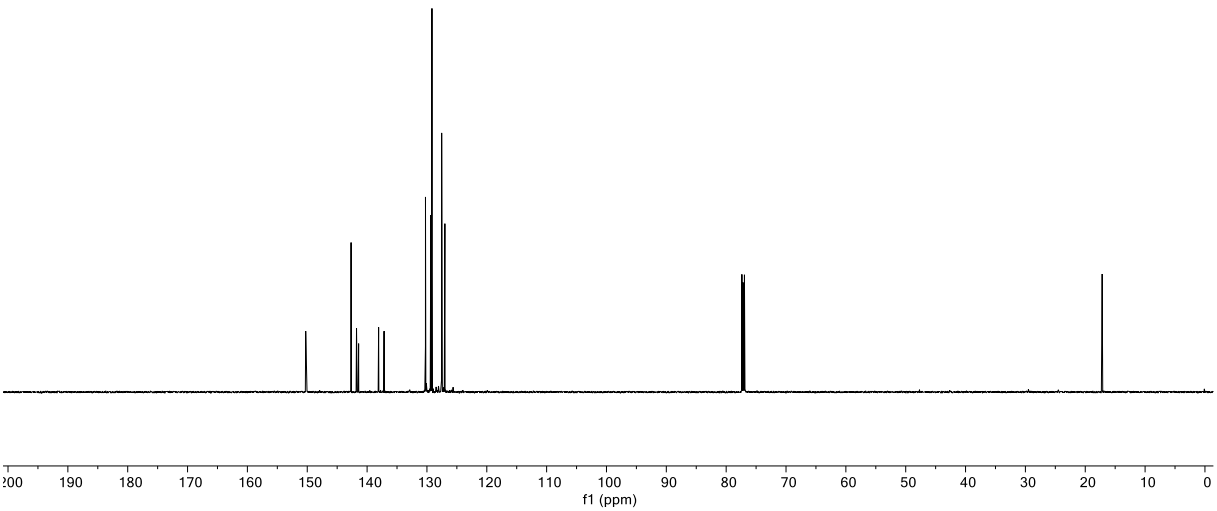
^{1}H NMR (600 MHz, $CDCl_3$)





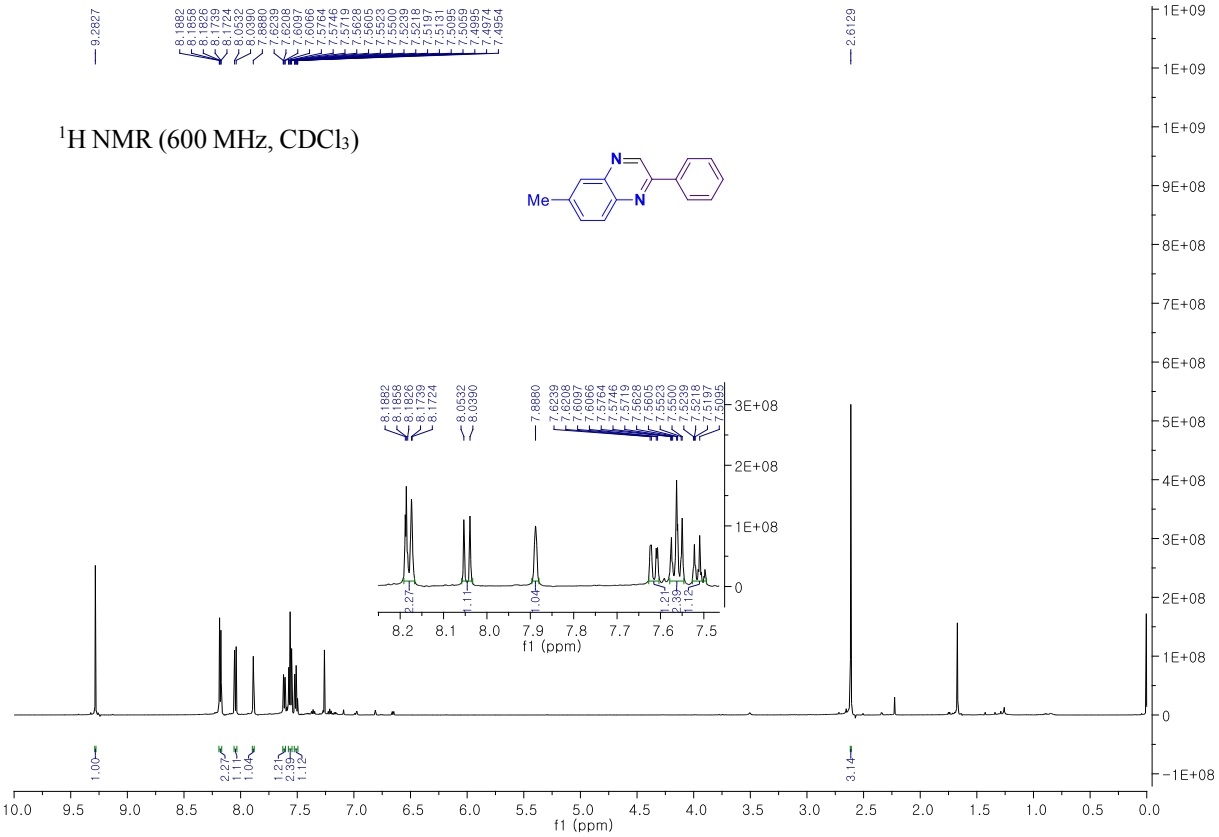
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



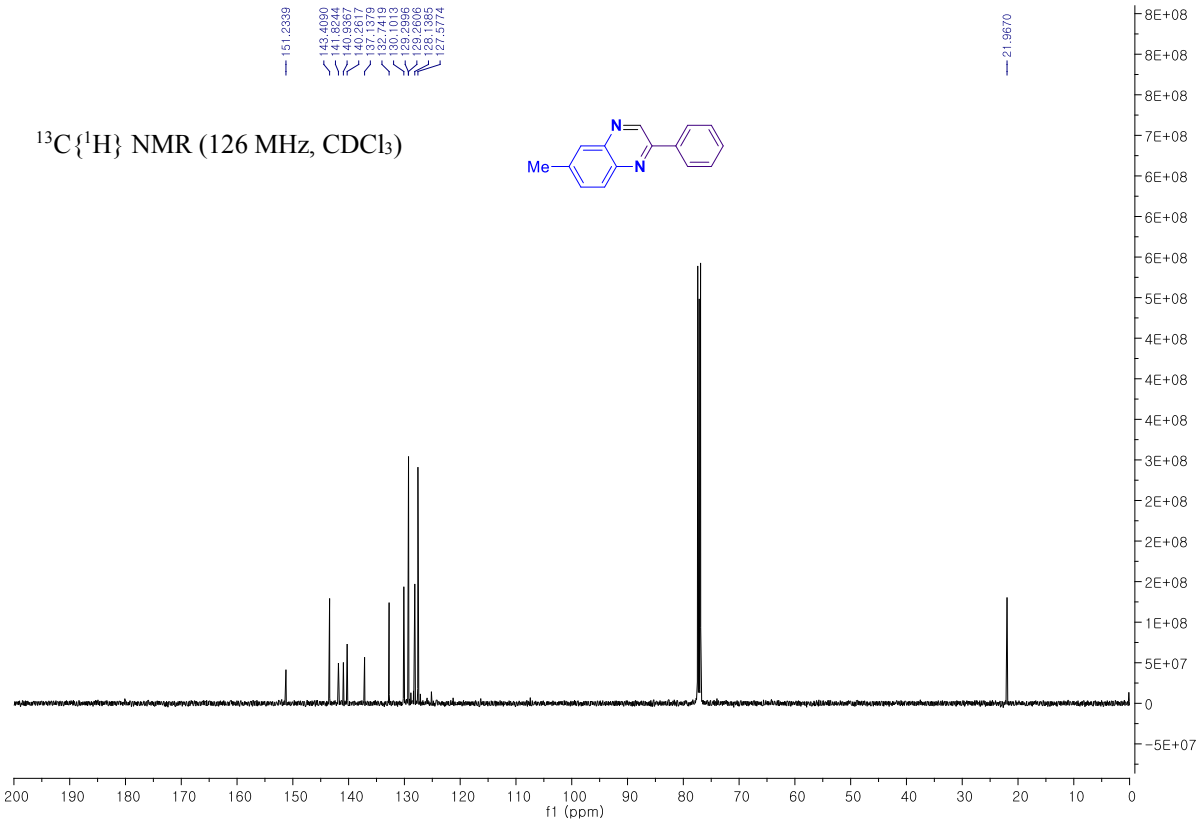


6-Methyl-2-phenylquinoxaline (5r)

^{1}H NMR (600 MHz, $CDCl_3$)

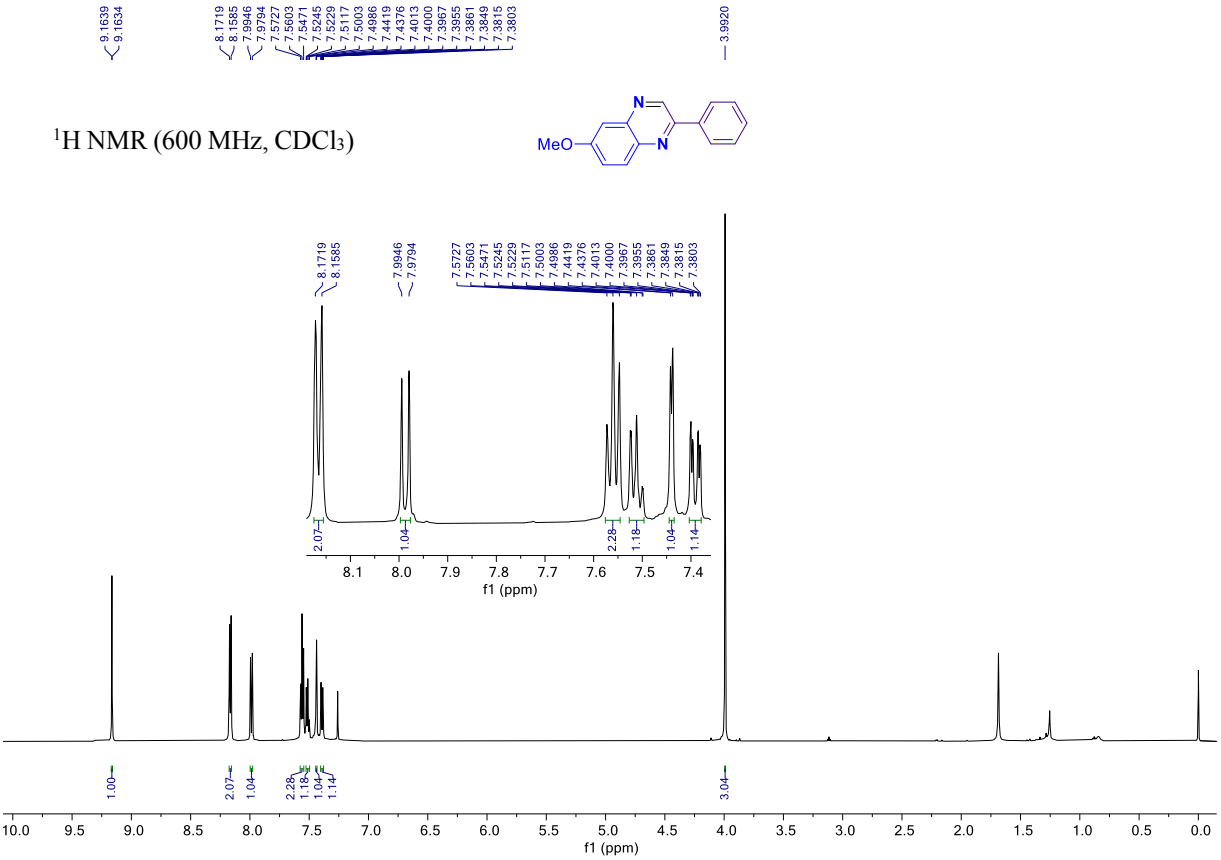


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

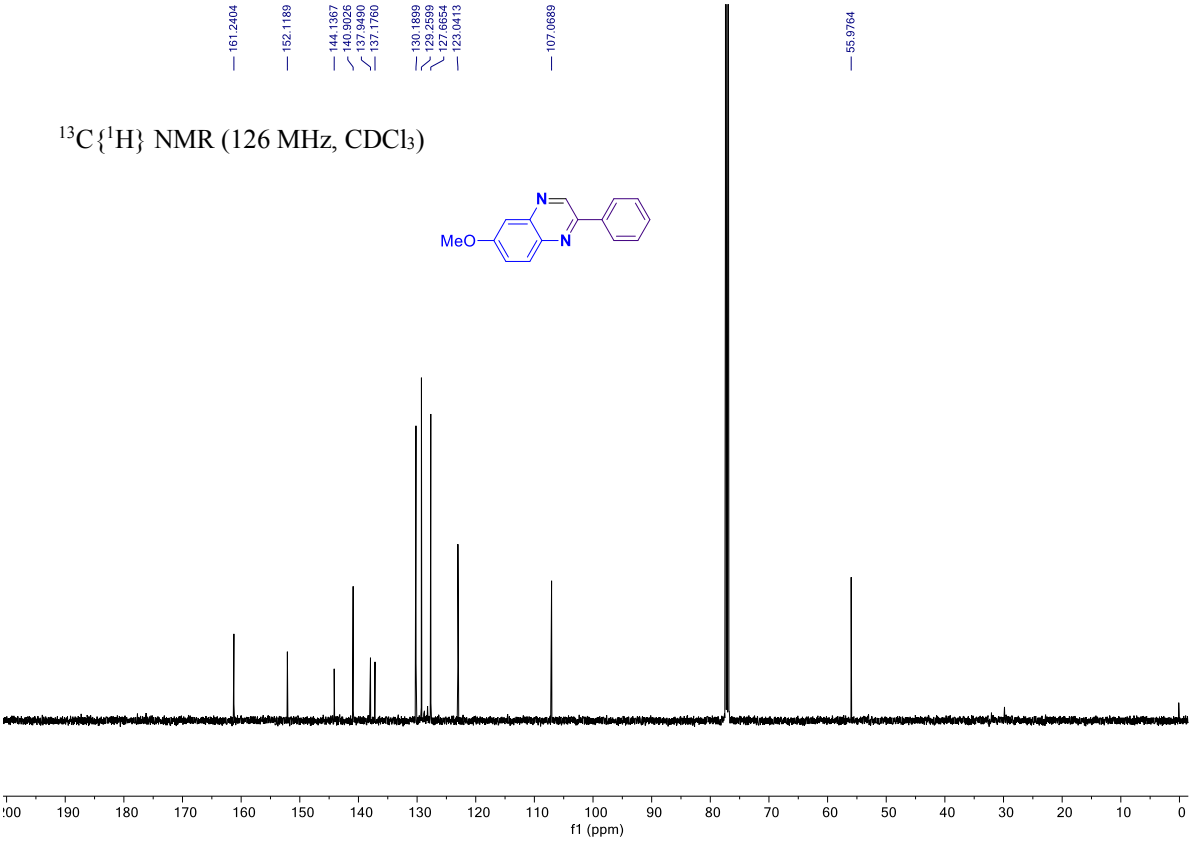


6-Methoxy-2-phenylquinoxaline (5s)

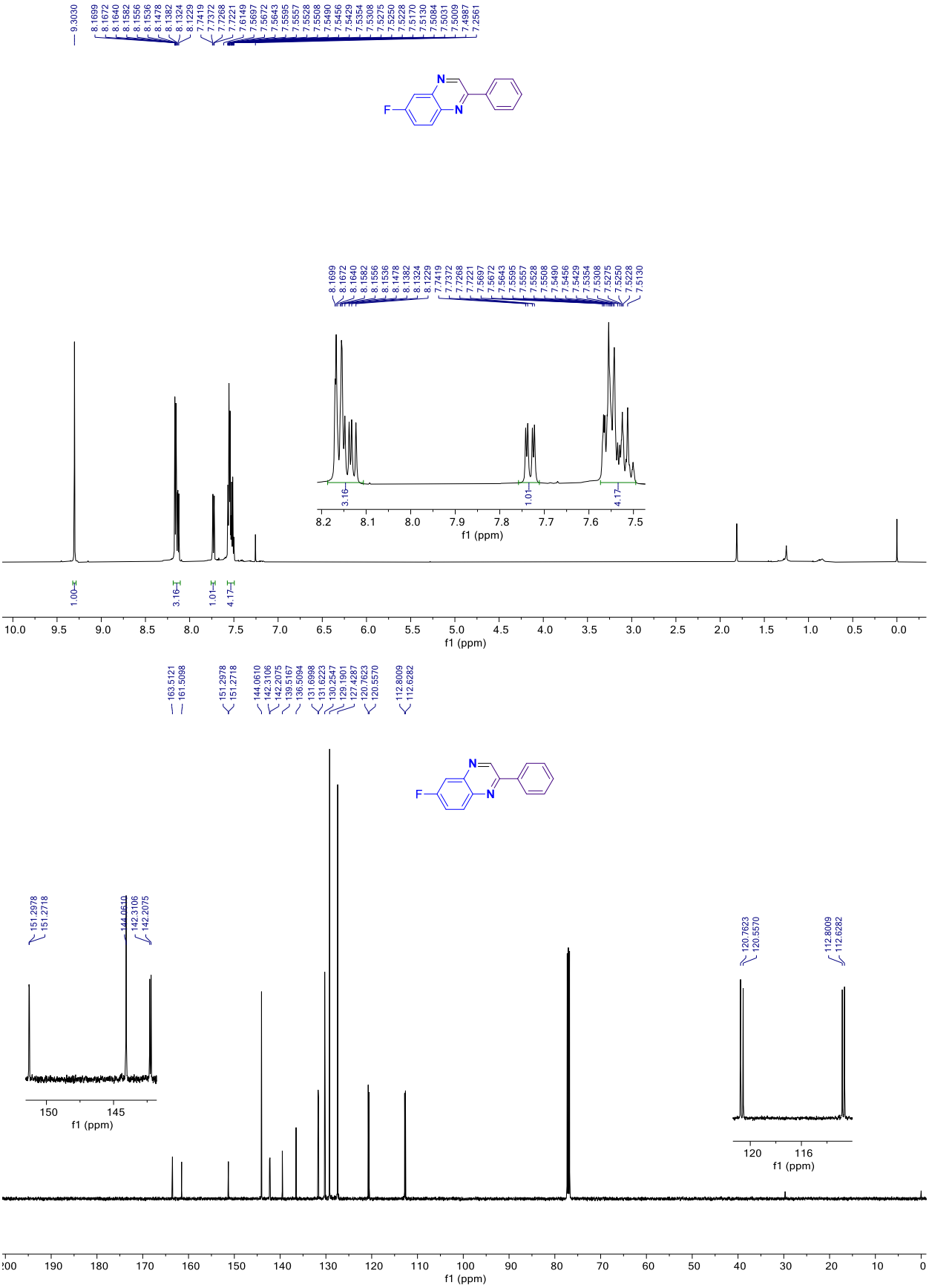
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

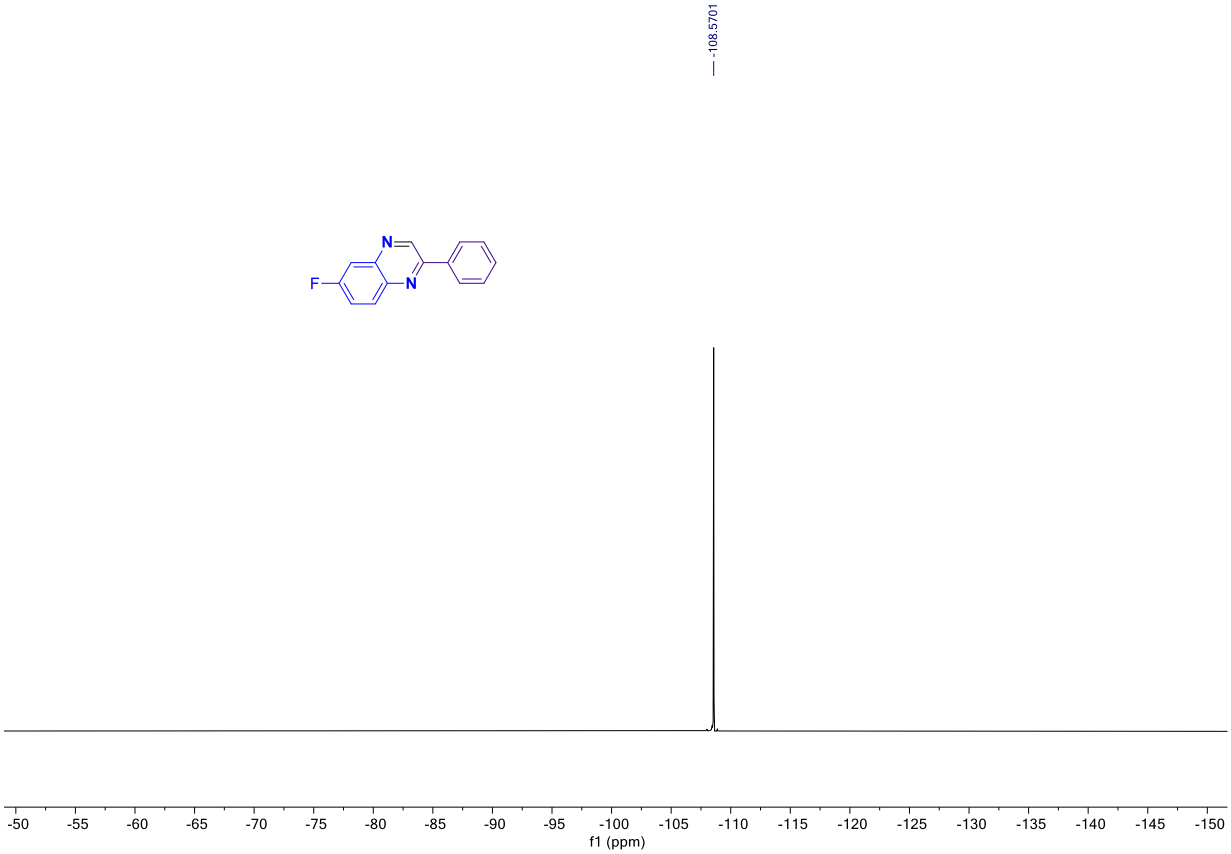


6-Fluoro-2-phenylquinoxaline (5t)



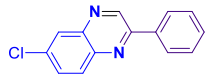
6-Fluoro-2-phenylquinoxaline (5t)

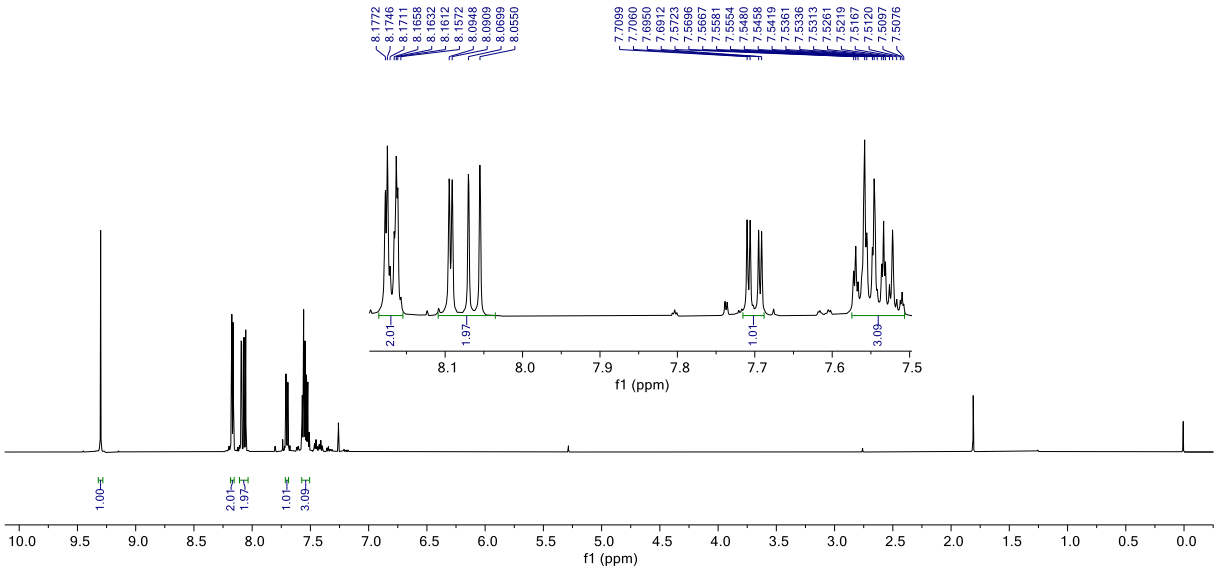
^{19}F NMR (565 MHz, $CDCl_3$)

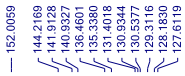


6-Chloro-2-phenylquinoxaline (5u)

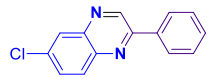
^{1}H NMR (600 MHz, $CDCl_3$)

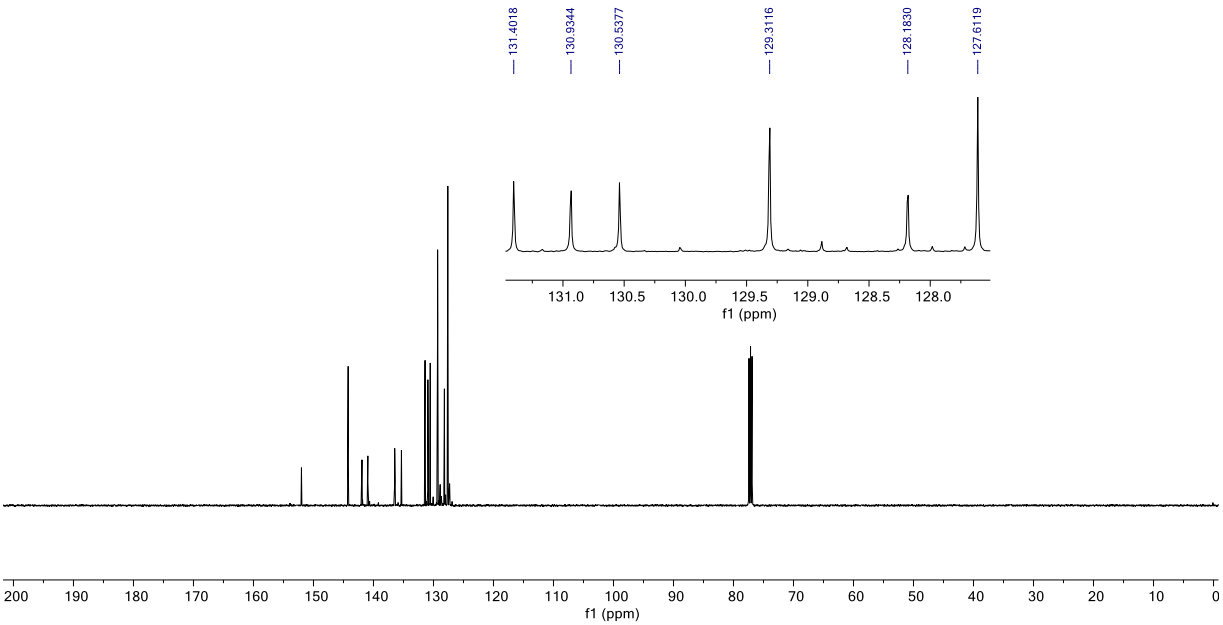






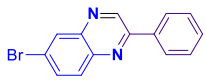
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

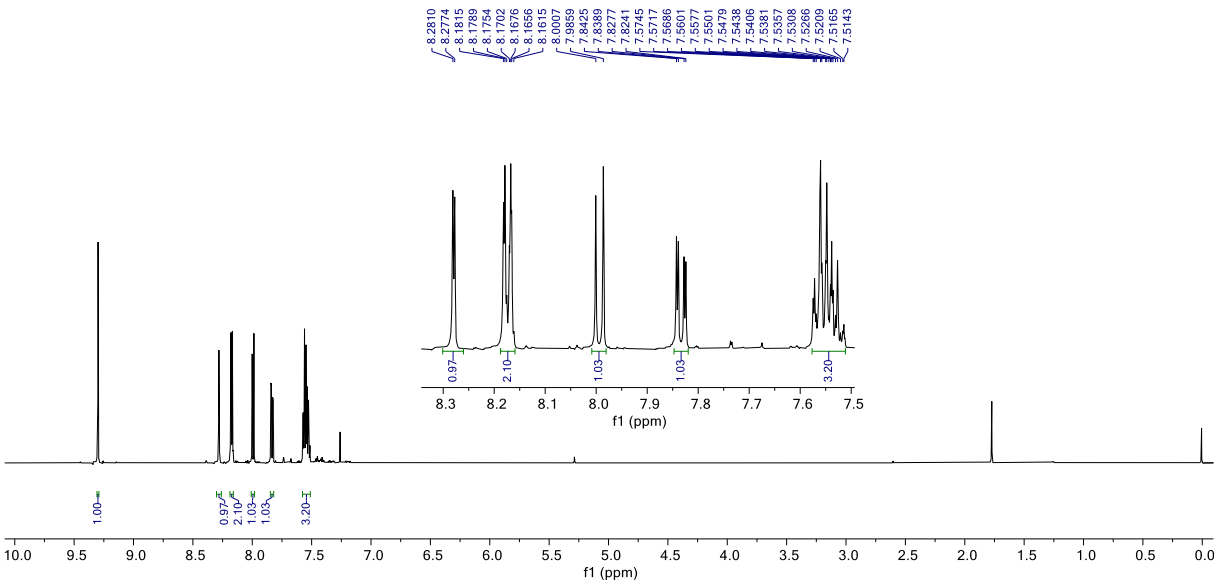




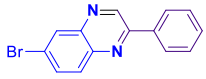
6-Bromo-2-phenylquinoxaline (5v)

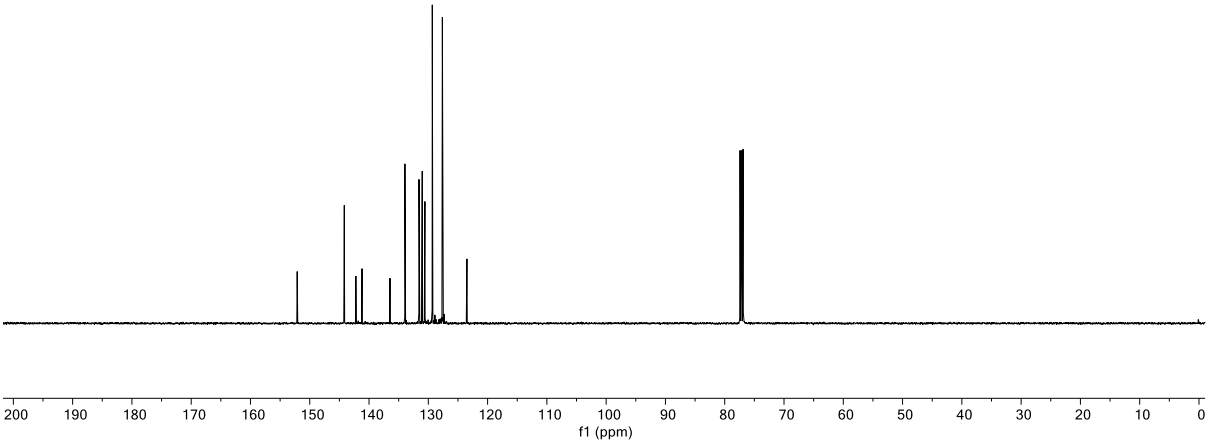
^{1}H NMR (600 MHz, $CDCl_3$)





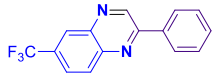
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

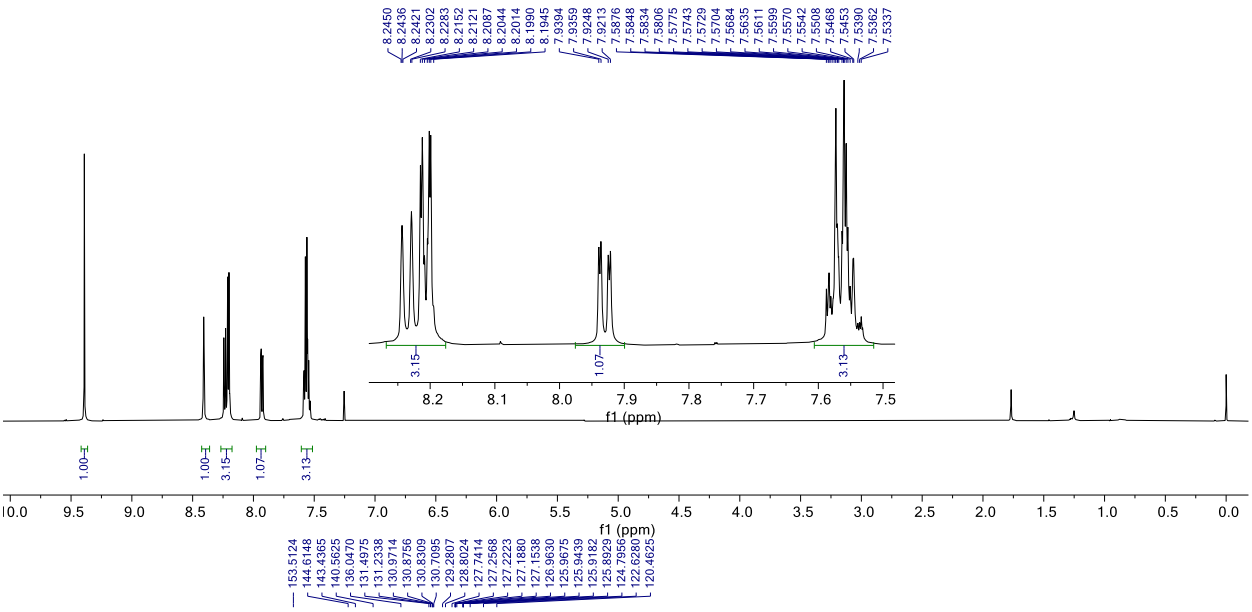




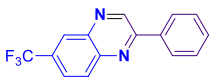
2-Phenyl-6-(trifluoromethyl)quinoxaline (5w)

^{1}H NMR (600 MHz, $CDCl_3$)



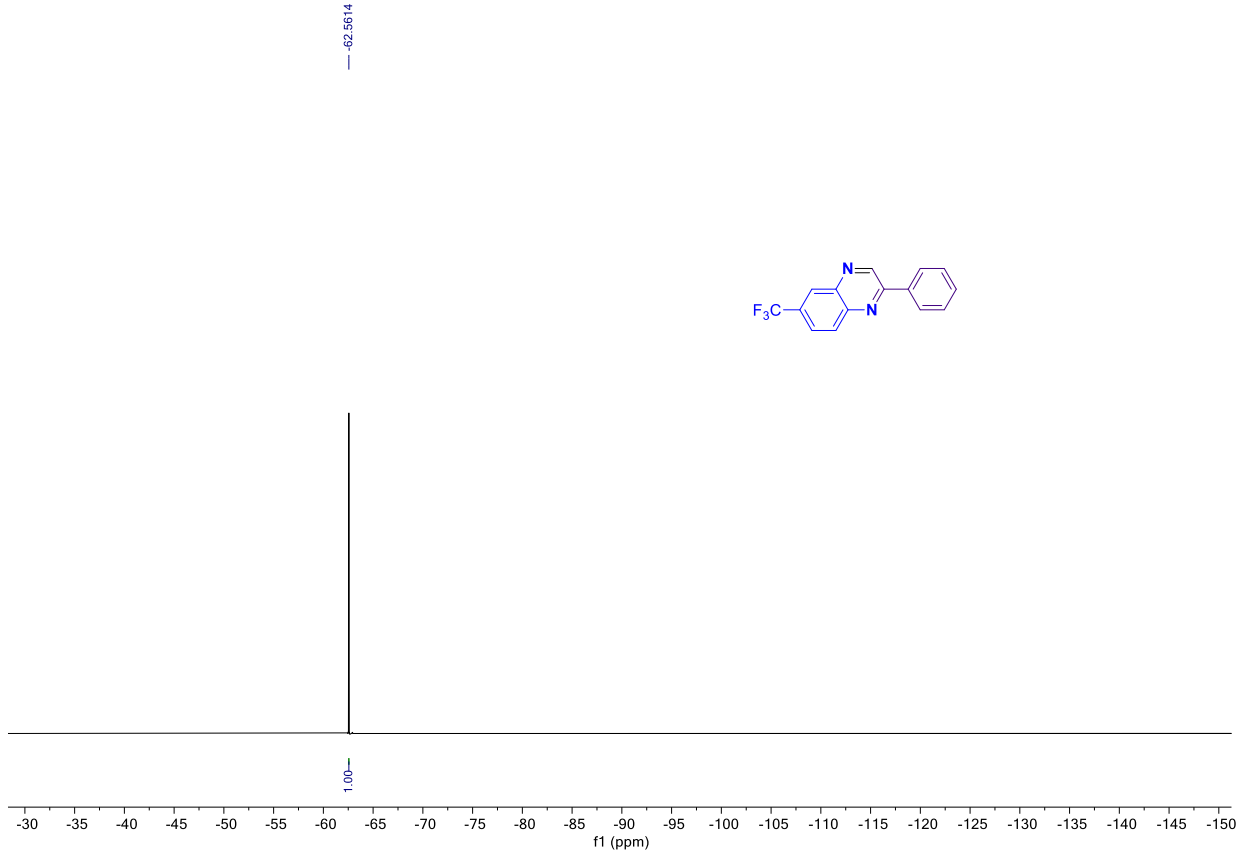


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



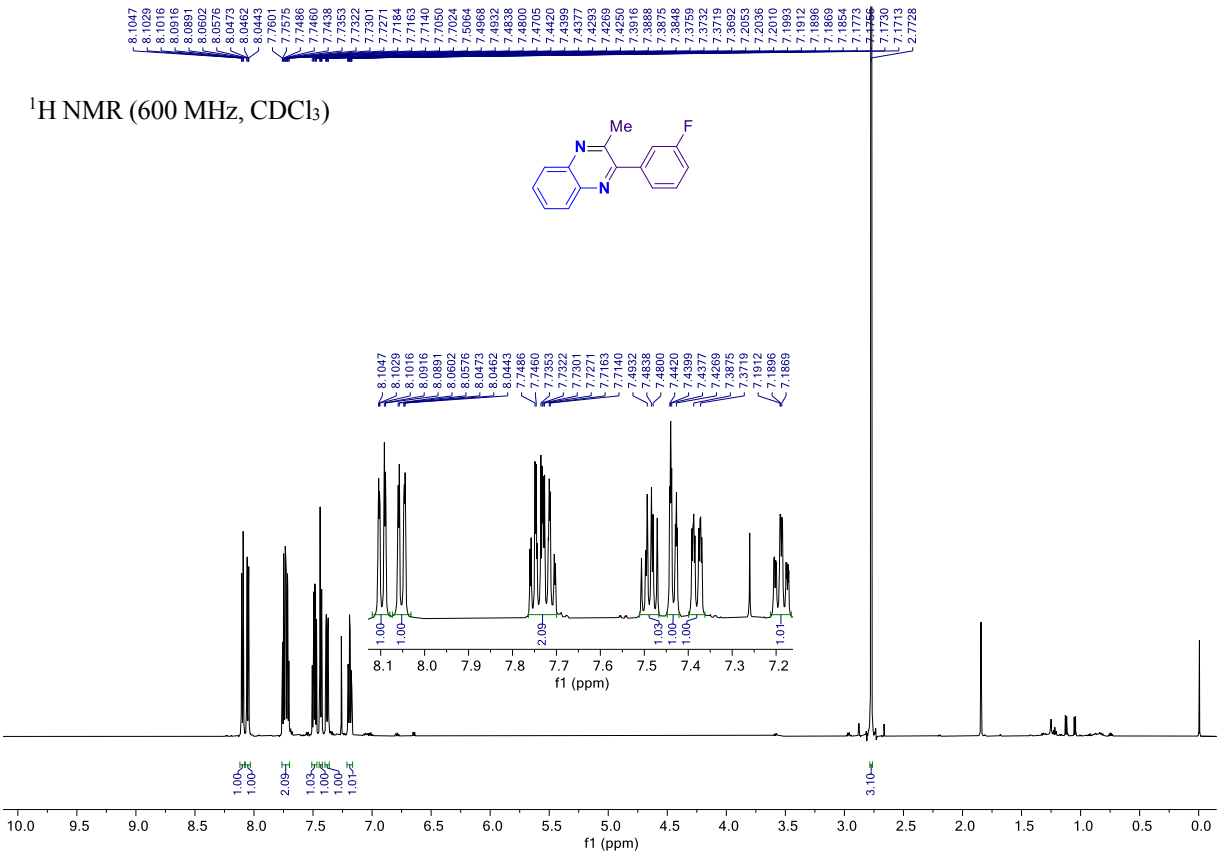
6-(trifluoromethyl)-2-phenylquinoxaline (5w)

^{19}F NMR (565 MHz, $CDCl_3$)

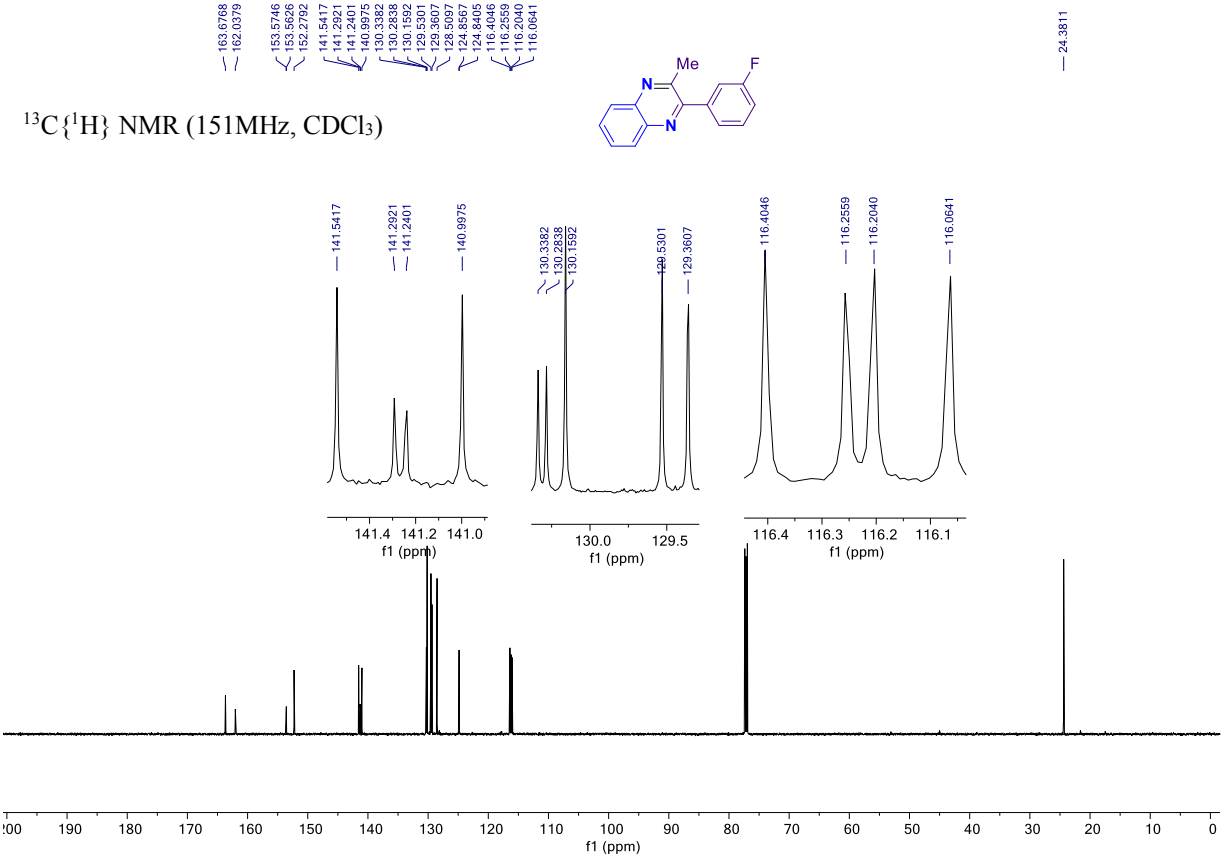


2-(3-Fluorophenyl)-3-methylquinoxaline (7a)

^{1}H NMR (600 MHz, $CDCl_3$)

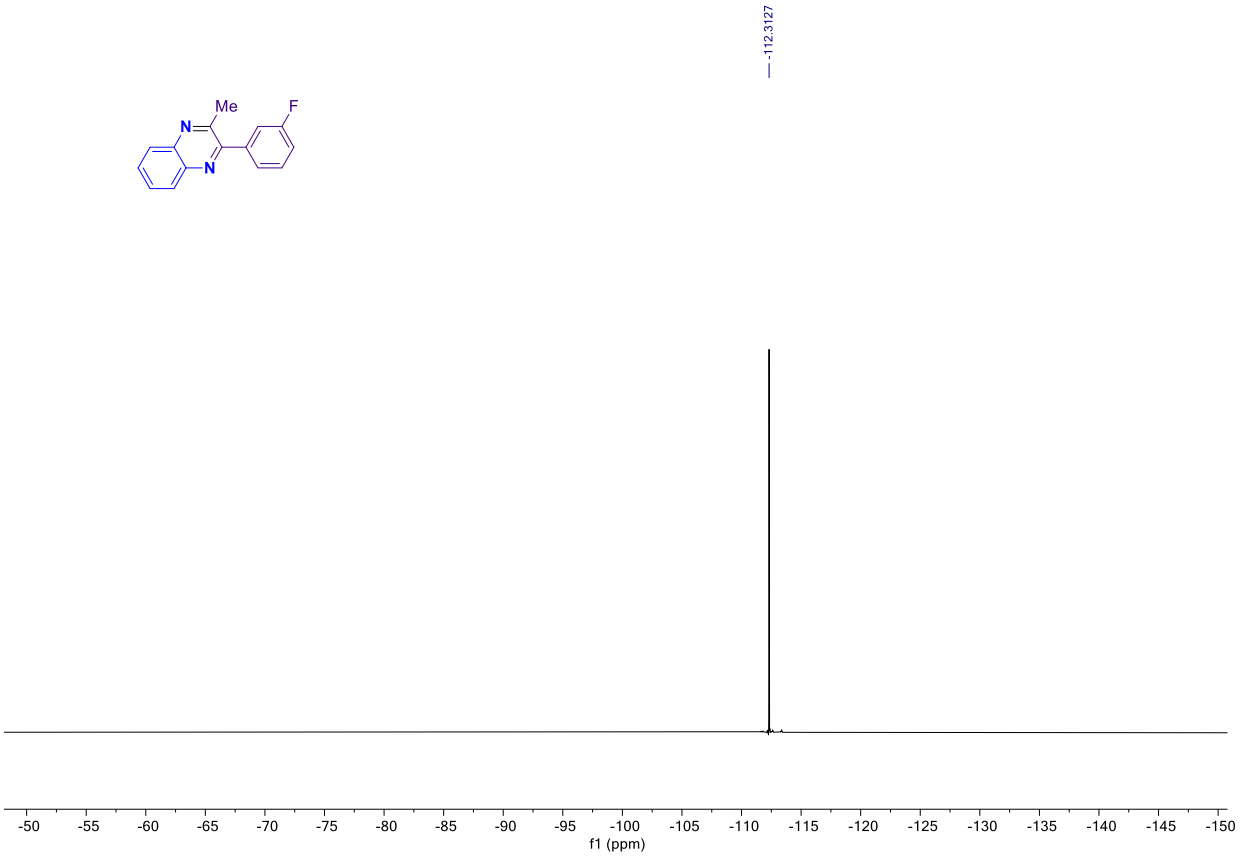


^{13}C{^{1}H} NMR (151MHz, $CDCl_3$)



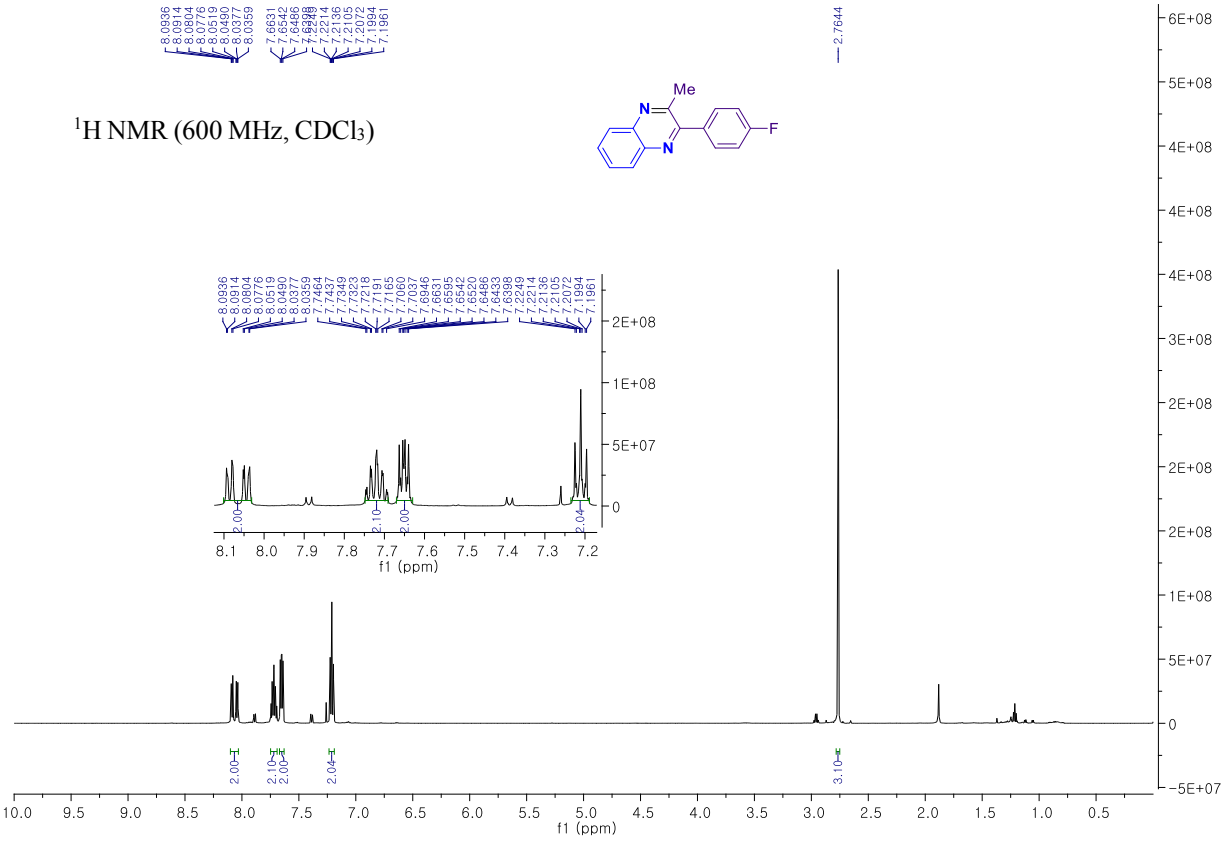
2-(3-Fluorophenyl)-3-methylquinoxaline (7a)

^{19}F NMR (565 MHz, $CDCl_3$)

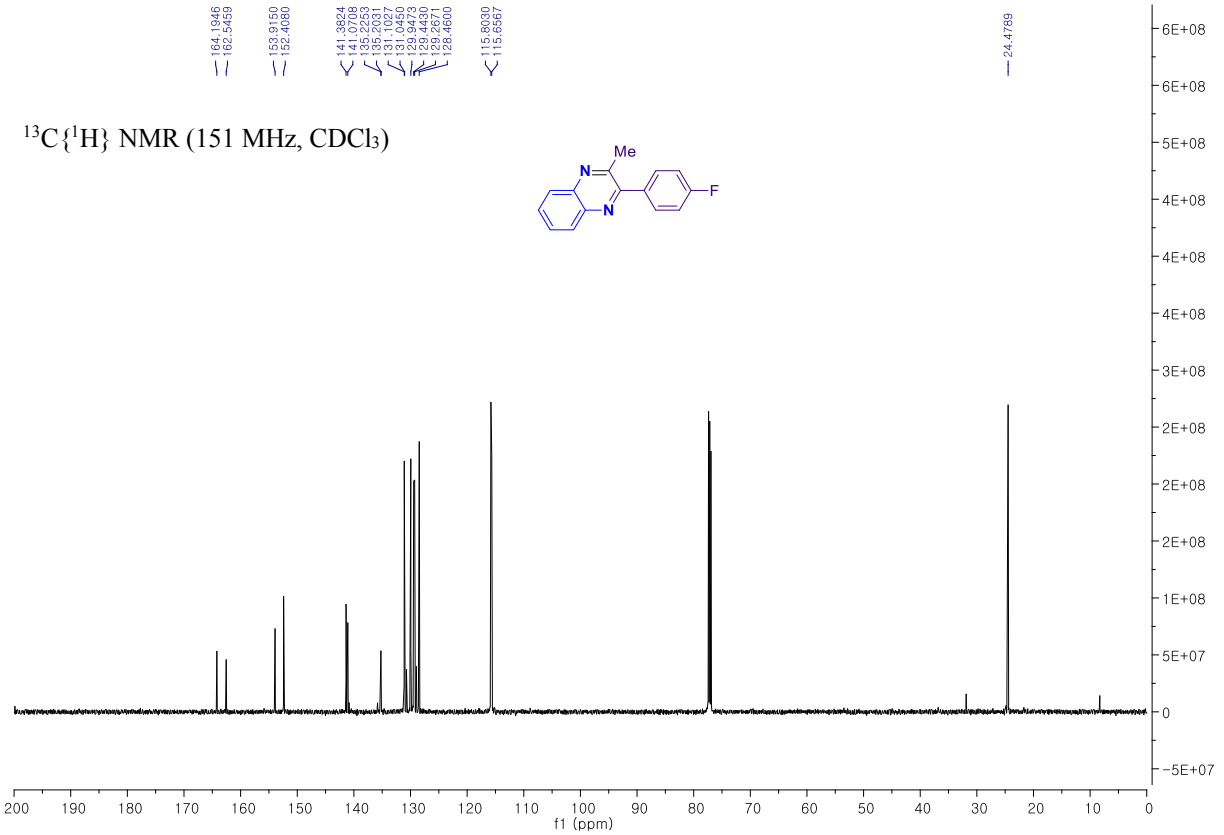


2-(4-Fluorophenyl)-3-methylquinoxaline (7b)

^{1}H NMR (600 MHz, $CDCl_3$)

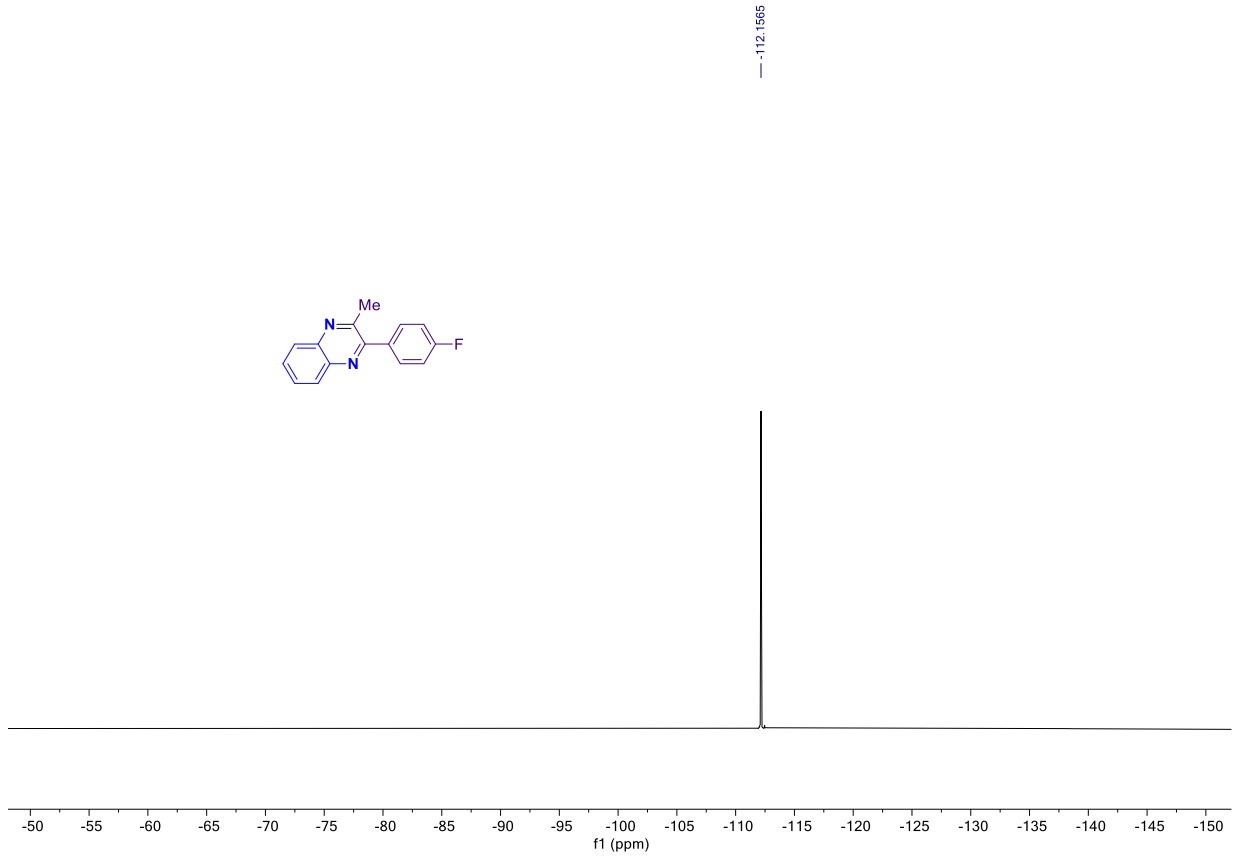


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



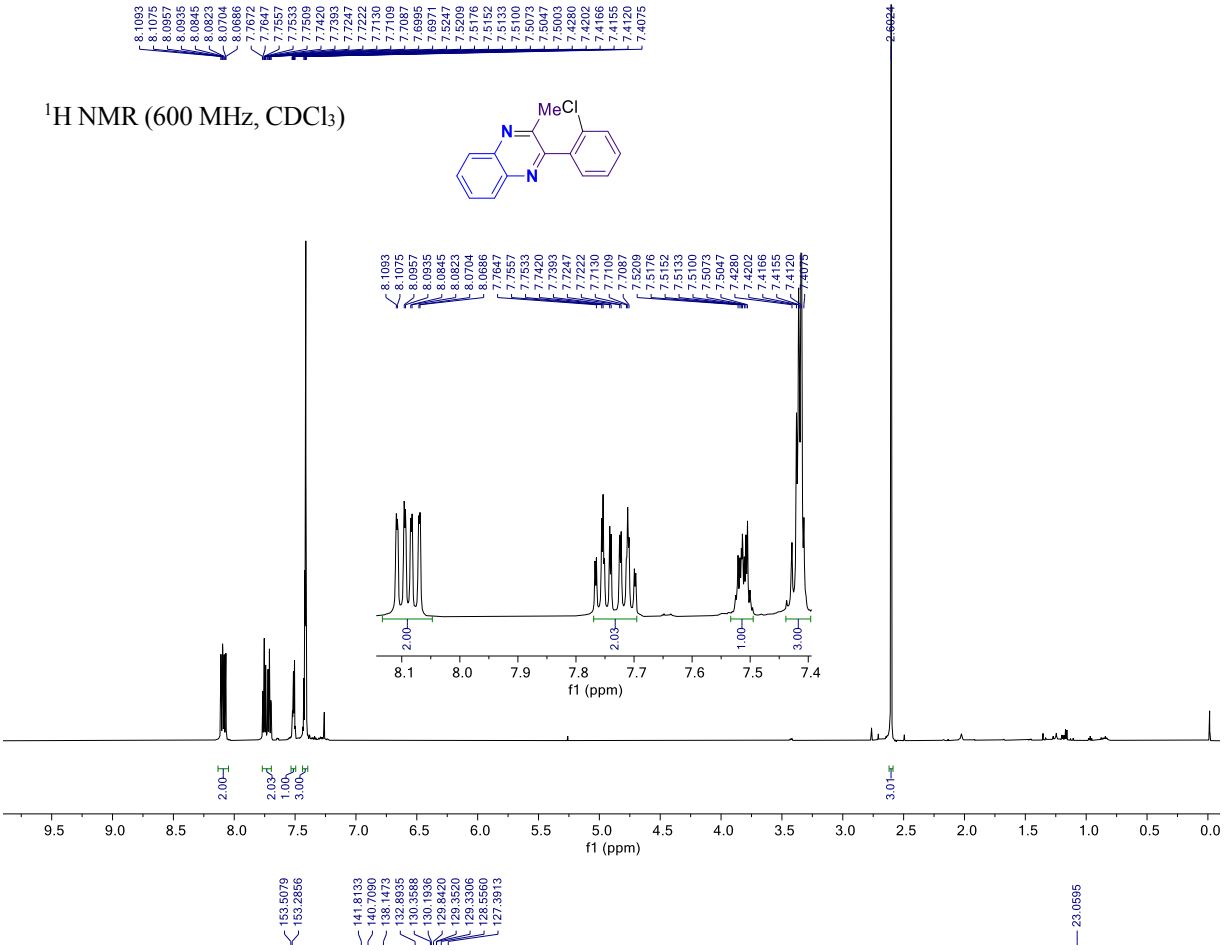
2-(4-Flourophenyl)-3-methylquinoxaline (7b)

^{19}F NMR (565 MHz, $CDCl_3$)

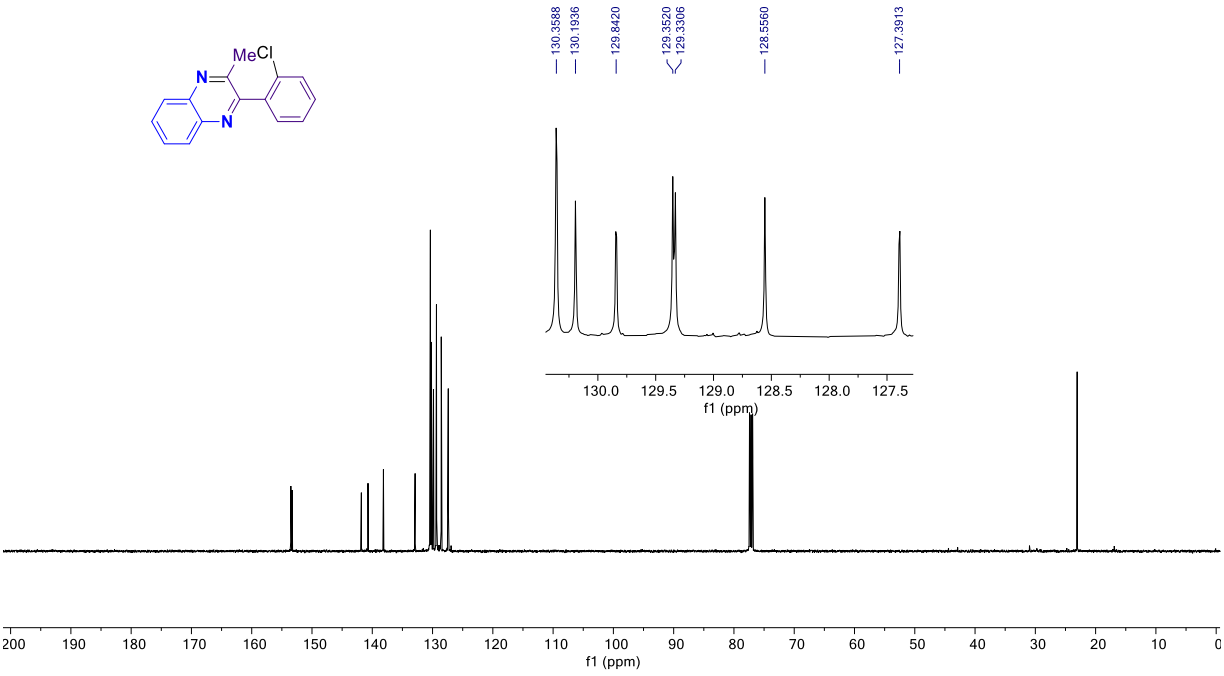


2-(2-Chlorophenyl)-3-methylquinoxaline (7c)

^{1}H NMR (600 MHz, $CDCl_3$)

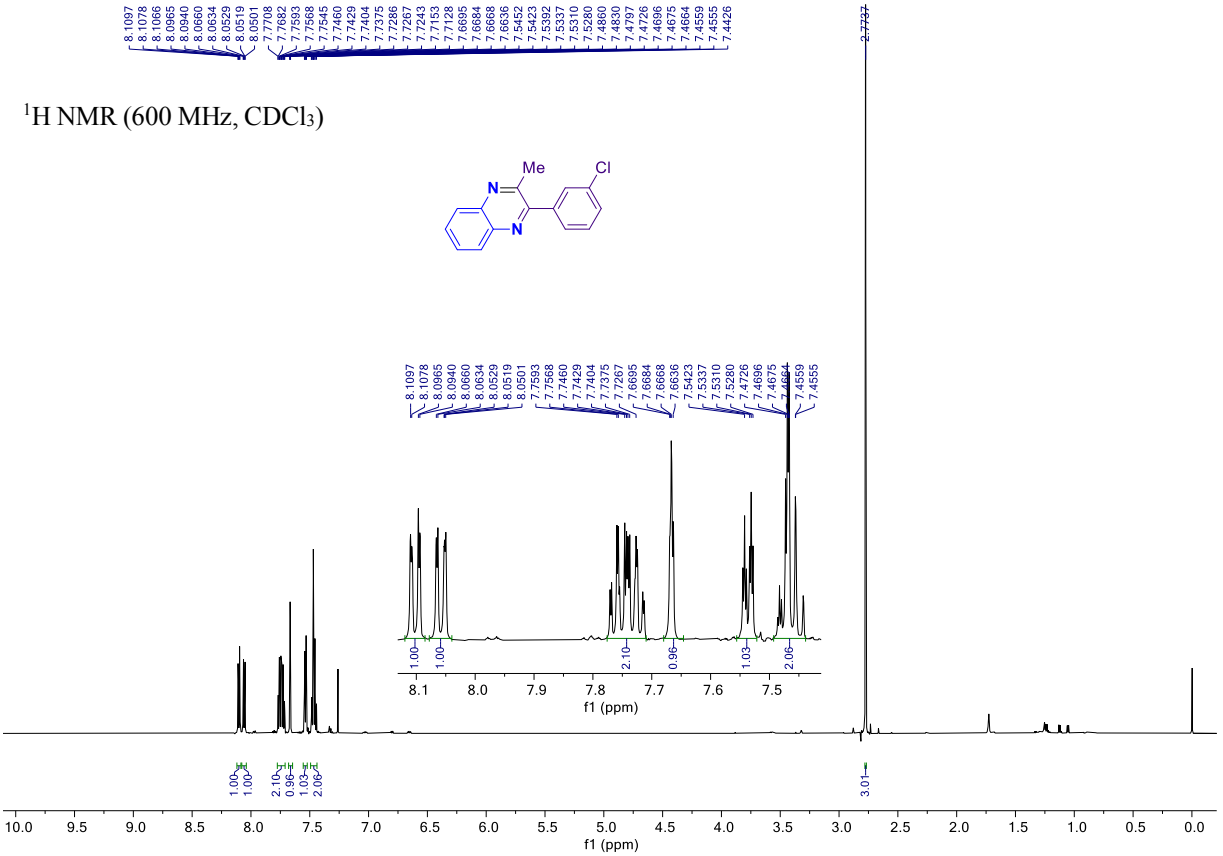


^{13}C{^{1}H} NMR (126MHz, $CDCl_3$)

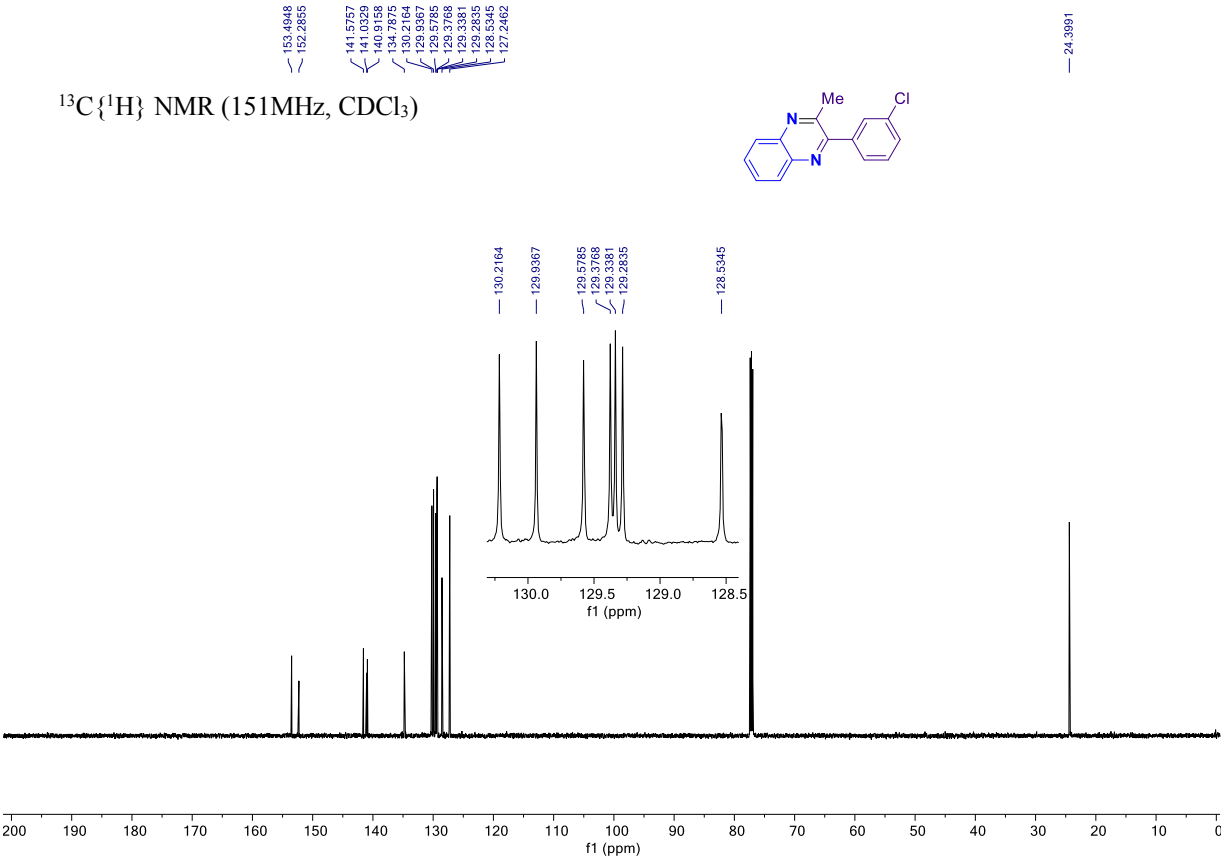


2-(3-Chlorophenyl)-3-methylquinoxaline (7d)

^{1}H NMR (600 MHz, $CDCl_3$)

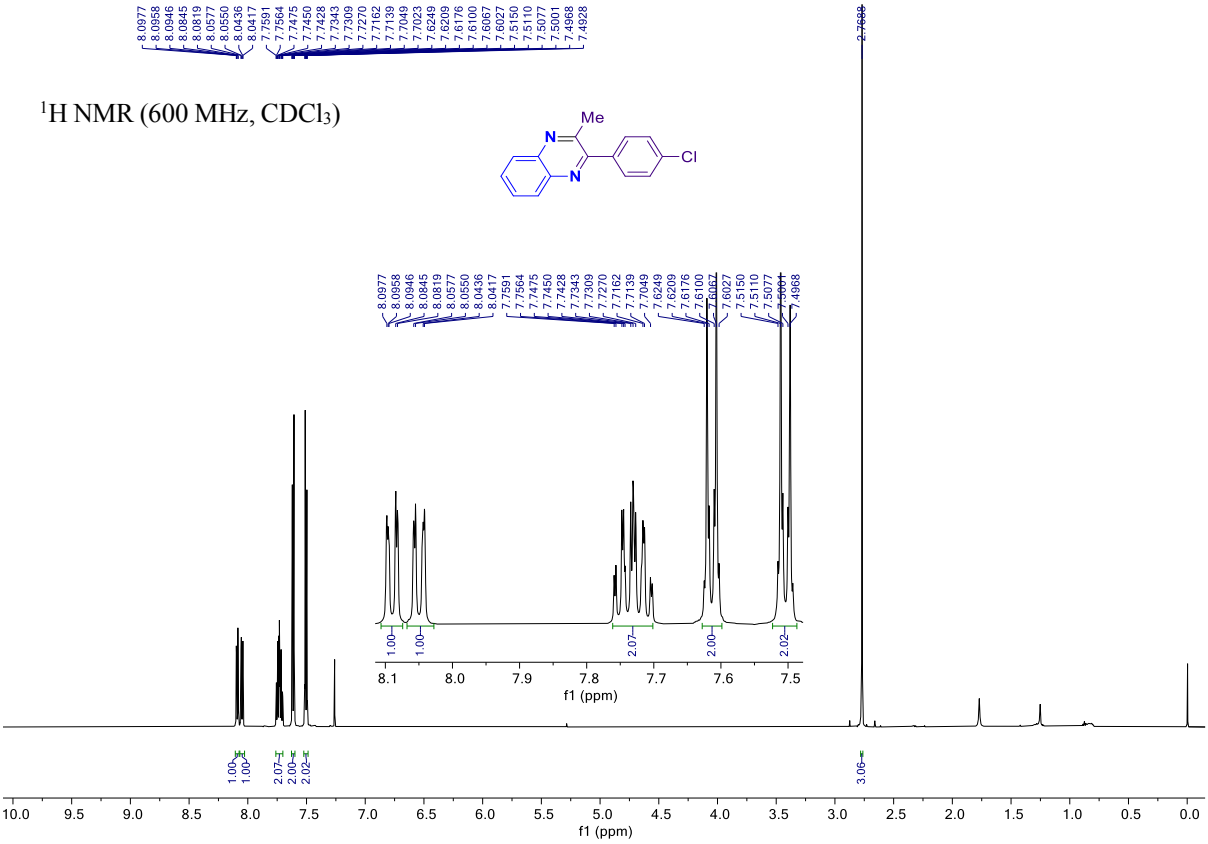


^{13}C{^{1}H} NMR (151MHz, $CDCl_3$)

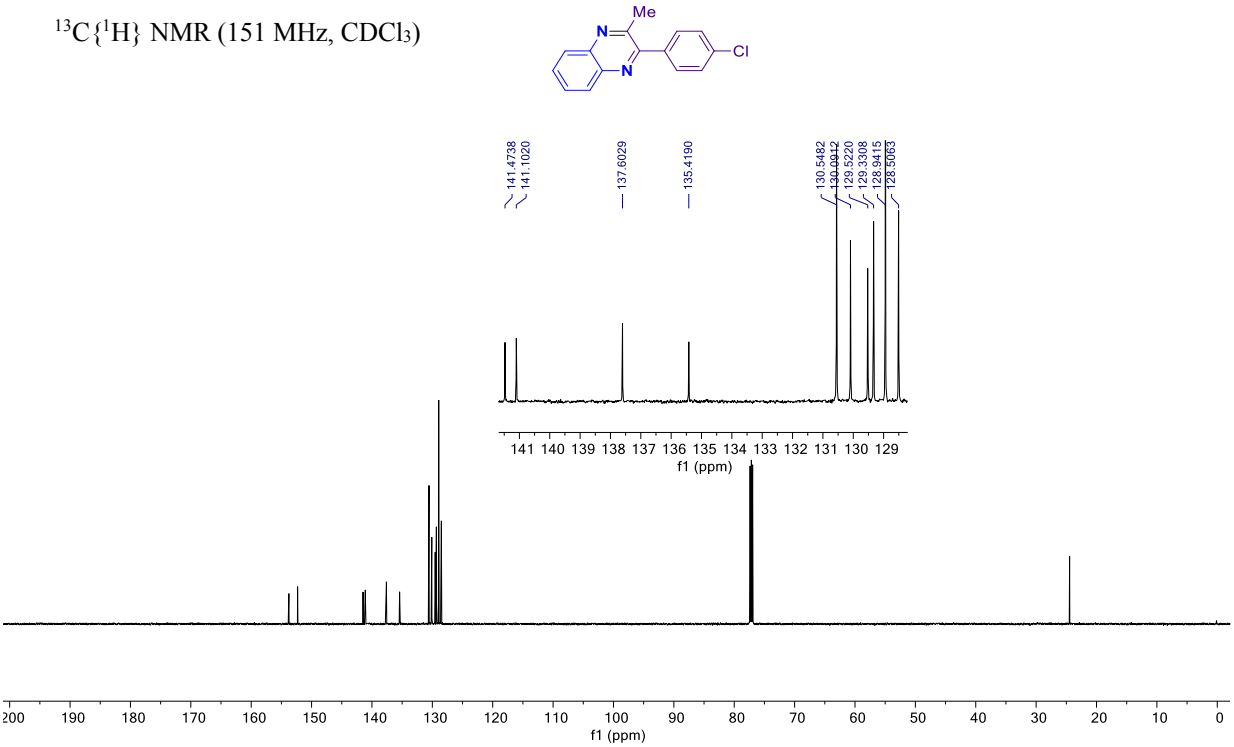


2-(4-Chlorophenyl)-3-methylquinoxaline (7e)

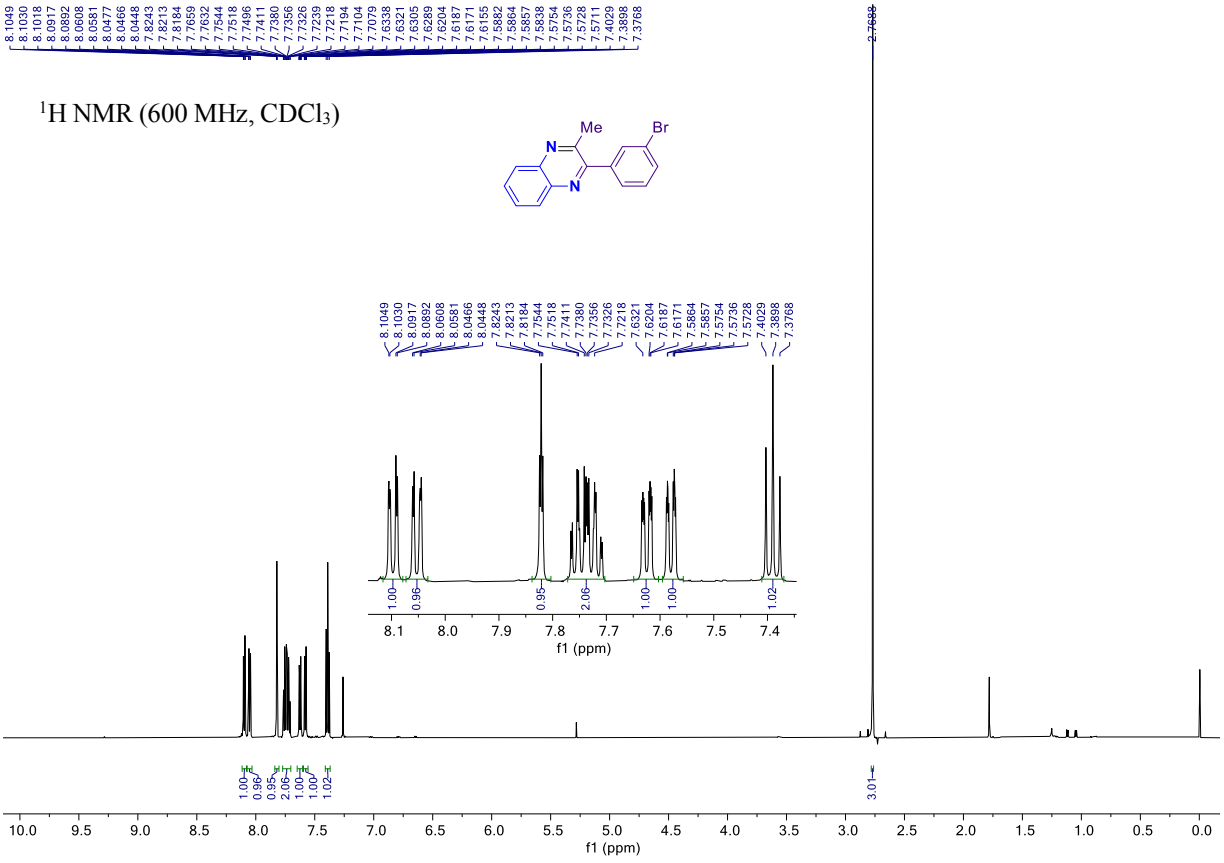
^{1}H NMR (600 MHz, $CDCl_3$)



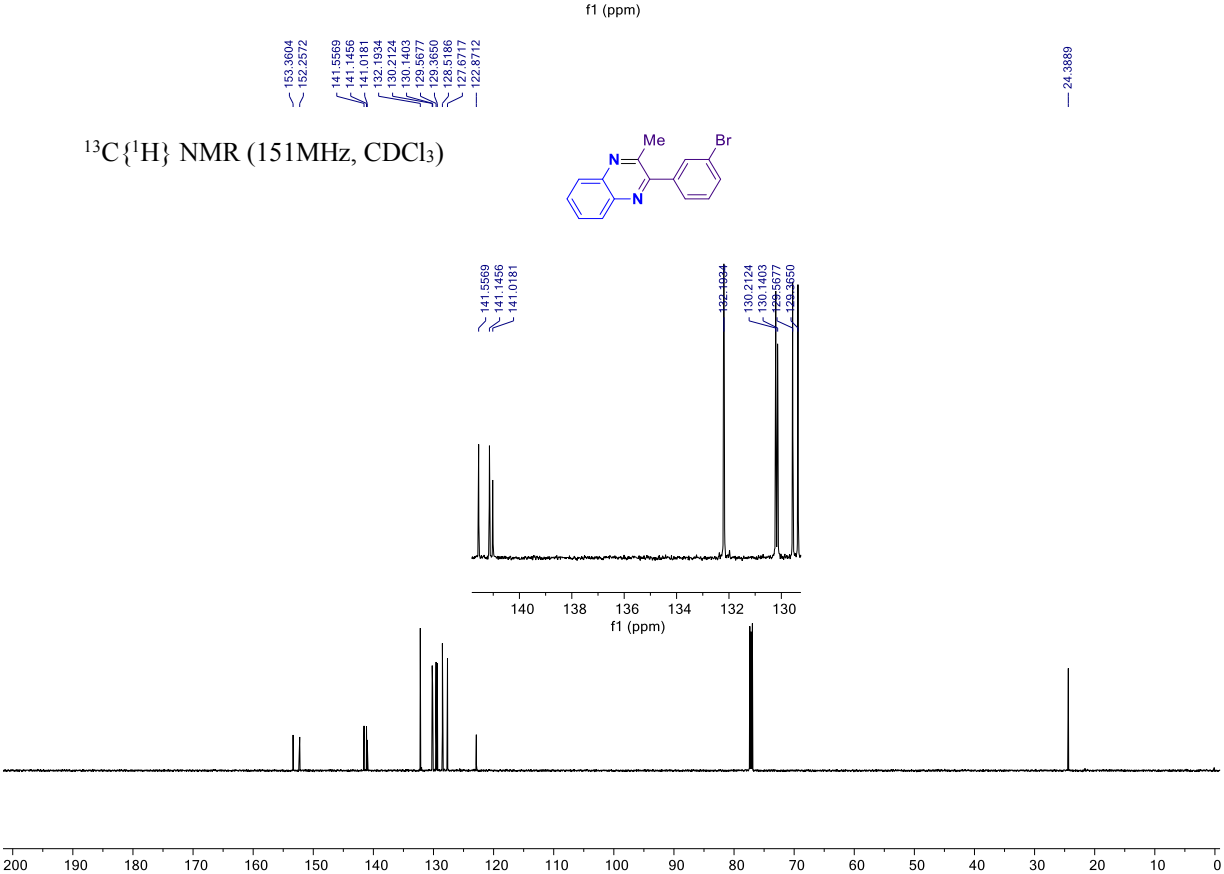
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



2-(3-Bromophenyl)-3-methylquinoxaline (7f)



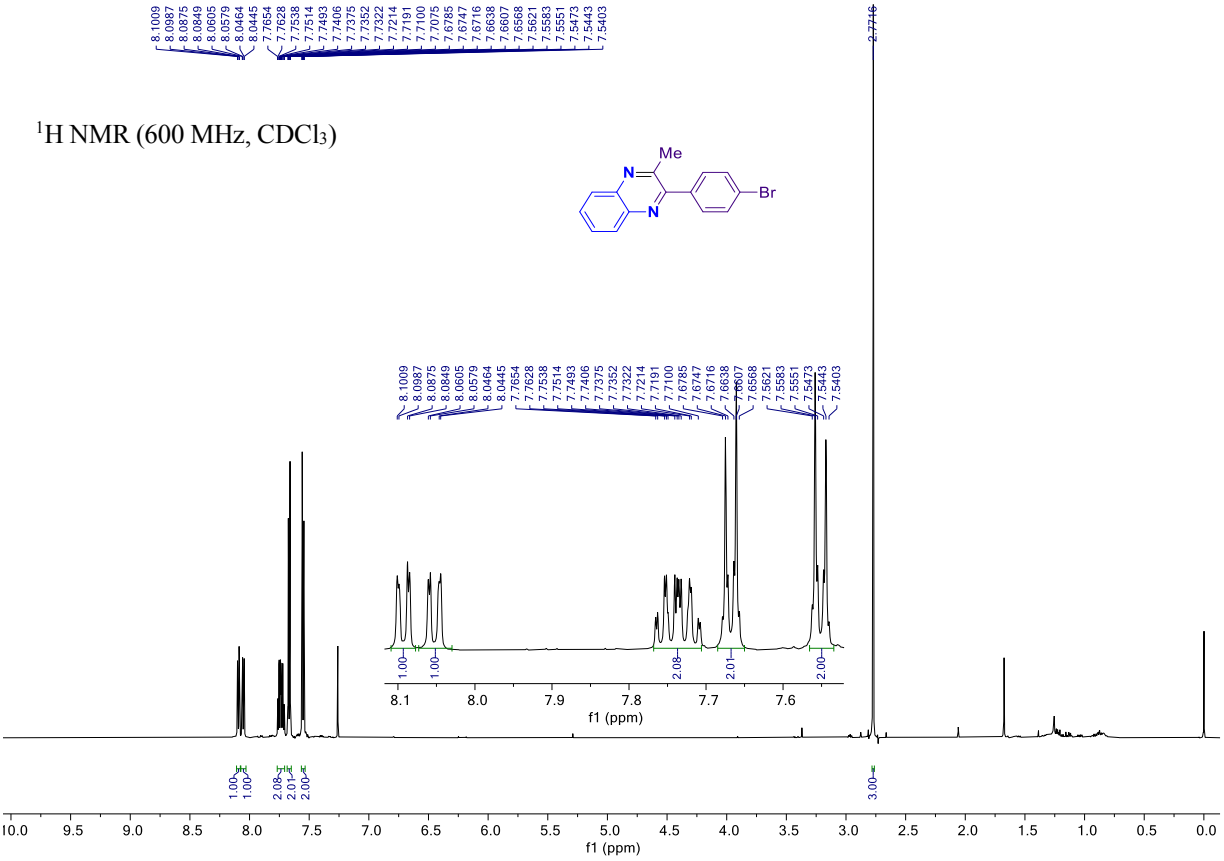
^{1}H NMR (600 MHz, $CDCl_3$)



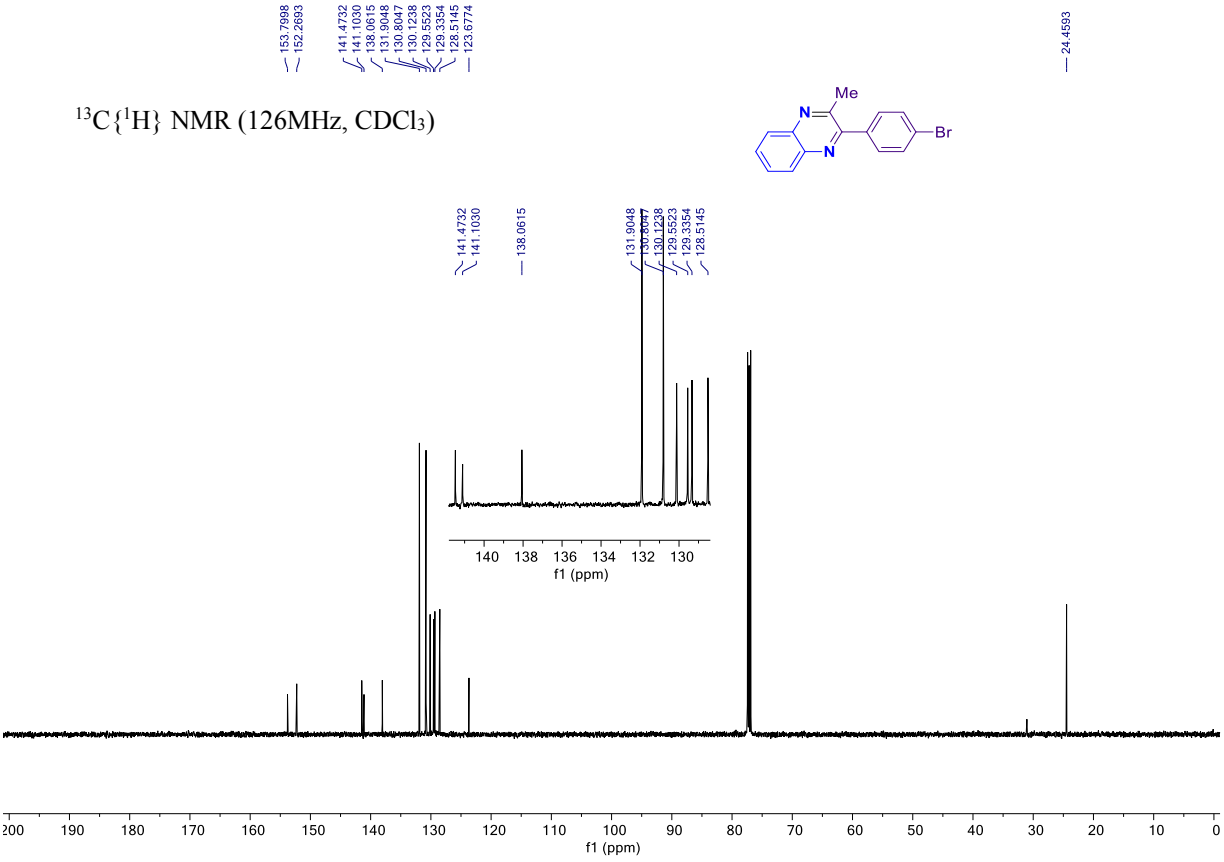
^{13}C{^{1}H} NMR (151MHz, $CDCl_3$)

2-(4-Bromophenyl)-3-methylquinoxaline (7g)

^{1}H NMR (600 MHz, $CDCl_3$)

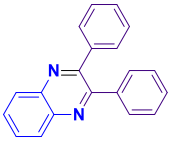


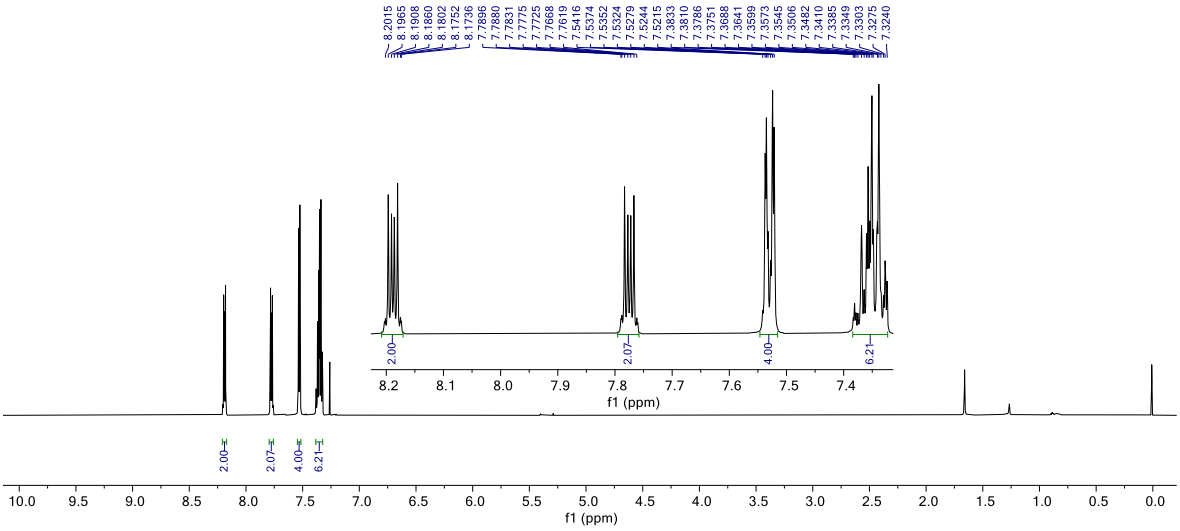
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$)



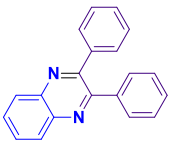
2,3-Diphenylquinoxaline (7h)

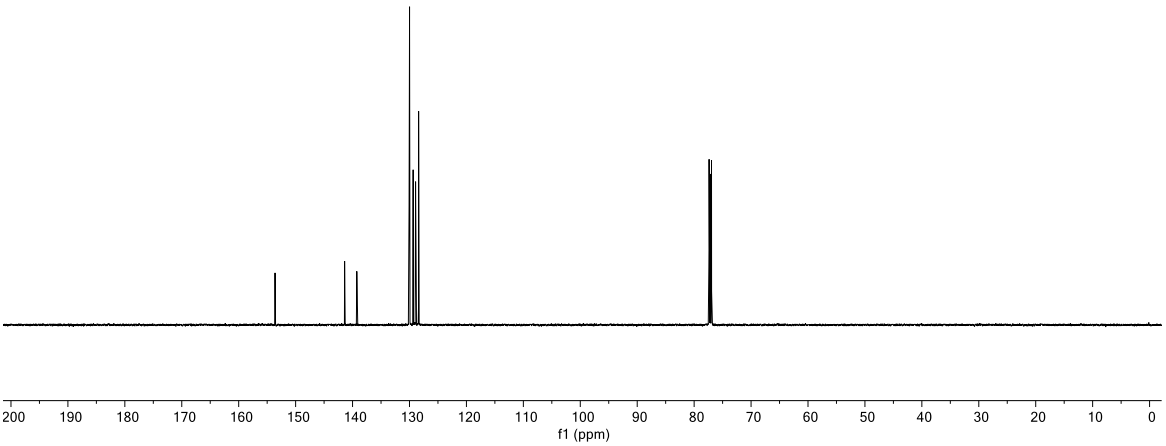
^{1}H NMR (600 MHz, $CDCl_3$)





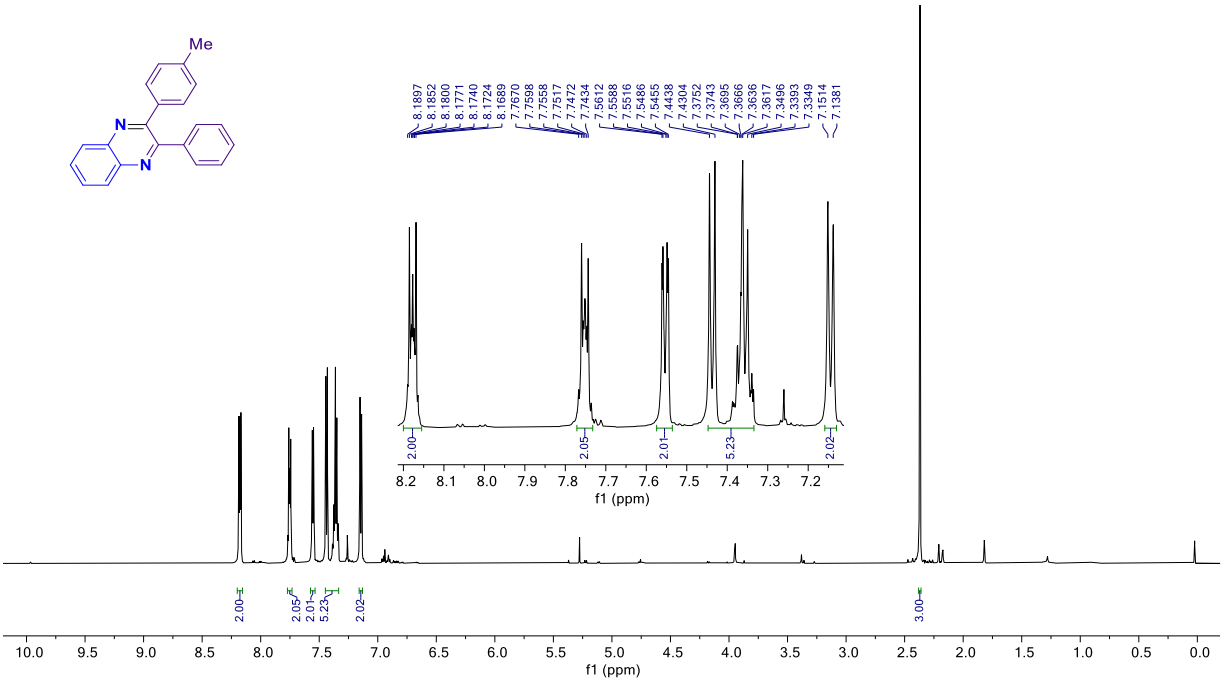
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



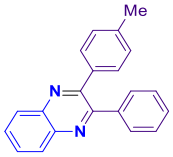


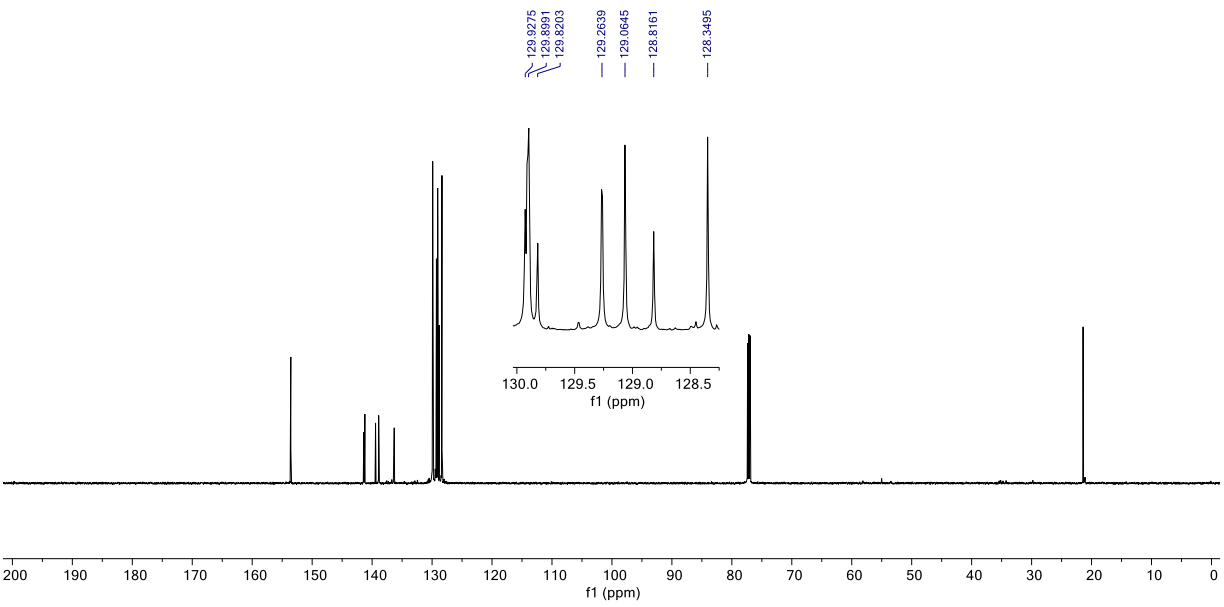
2-Phenyl-3-(*p*-tolyl)quinoxaline (7i)

^{1}H NMR (600 MHz, $CDCl_3$)



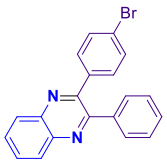
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

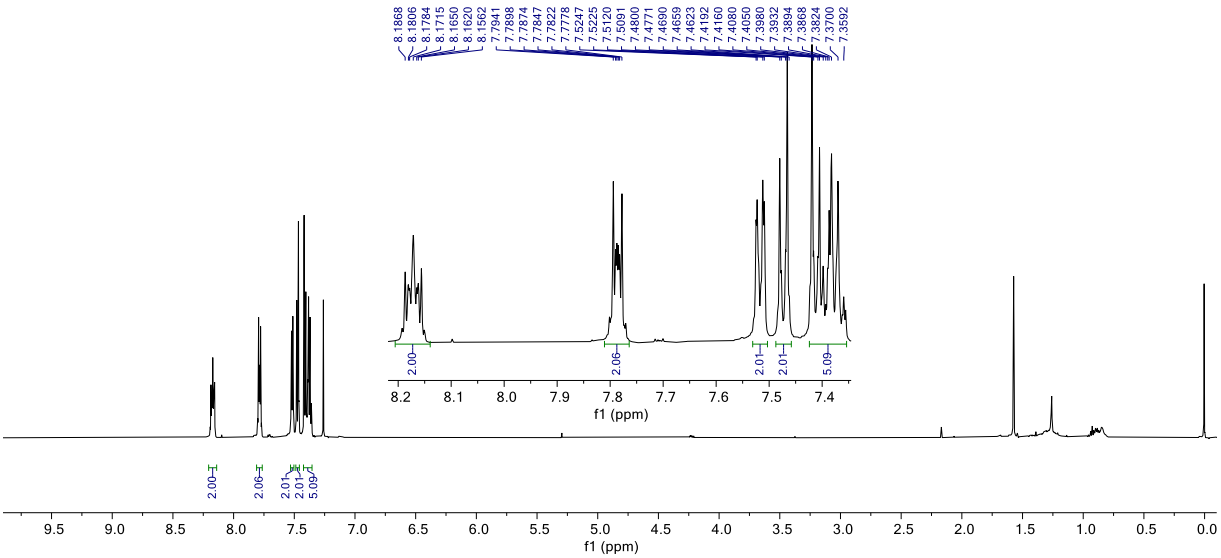




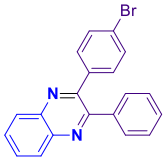
2-(4-Bromophenyl)-3-phenylquinoxaline (7j)

^{1}H NMR (600 MHz, $CDCl_3$)



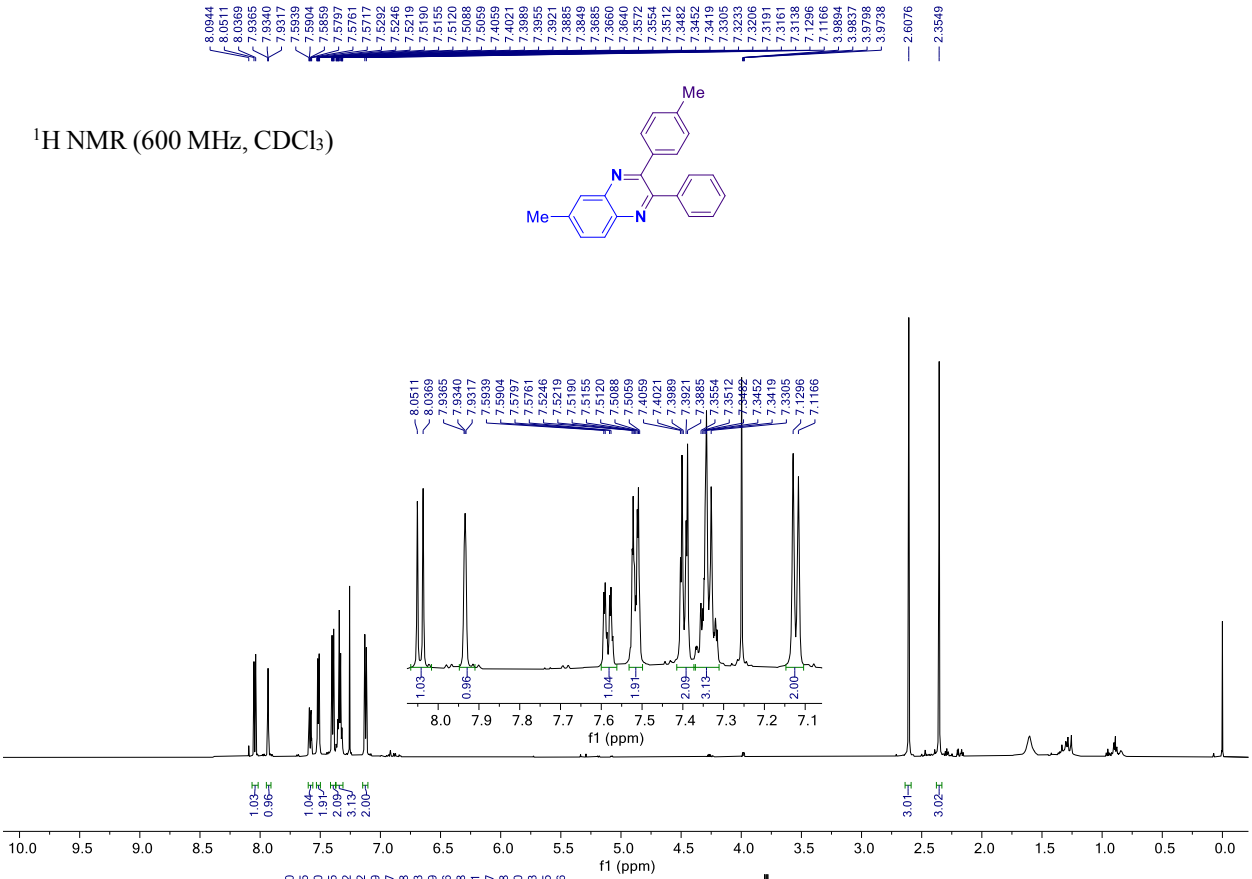


^{13}C{^{1}H} NMR (126MHz, $CDCl_3$)



6-Methyl-2-phenyl-3-(p-tolyl)quinoxaline (7k)

^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (126MHz, $CDCl_3$)