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Quinoxaline as Integrated Directing Group in Palladium-Catalyzed *Ortho* C–H Bond Arylation of the Aryl Unit of 2-Arylquinoxalines

Imane Idris,[a,b] Fazia Derridj,[a,b] Thierry Roisnel,[a] Henri Doucet,[a]* and Jean-François Soulé[a]*

[a] Univ Rennes, CNRS, ISCR UMR 6226, F-35000 Rennes, France
email : henri.doucet@univ-rennes1.fr and jean-francois.soule@univ-rennes1.fr

[b] Laboratoire de physique et chimie des Matériaux (LPCM), UMMTO University, BP 17 RP, 15000
Tizi-Ouzou, Algeria.

Table of Content

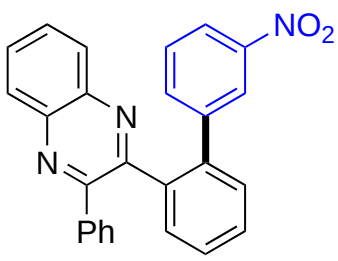
1. General information

All reactions were carried out under argon atmosphere with standard Schlenk techniques. DMA was purchased from Acros Organics and was not purified before use. ^{1}H NMR spectra were recorded on Bruker GPX (400 MHz) spectrometer. Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.28 ppm for ^{1}H; 77.23 ppm for ^{13}C), constants were reported in Hertz. ^{1}H NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). ^{13}C NMR spectra were recorded at 100 MHz on the same spectrometer and reported in ppm. All reagents were weighed and handled in air. HRMS were recorded on a Waters Q-Tof 2 mass spectrometer at the corresponding facilities of the CRMPO, Centre Régional de Mesures Physiques de l'Ouest, Université de Rennes 1. Melting points were performed on a LEICA VMHB Kofler system.

2. Procedure

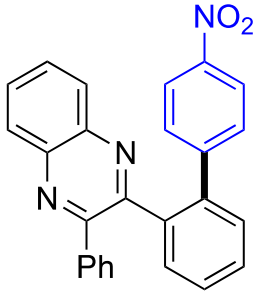
A (Palladium-catalyzed direct C4 arylation): To a 5 mL oven dried Schlenk tube, 2,3-diphenylquinoxaline derivative (1.5 mmol), aryl bromide (1 mmol), KOAc (196 mg, 2 mmol), 4 mL of a freshly prepared solution of $Pd(OAc)_2$ in DMA [using 2.8 mg of $Pd(OAc)_2$ (0.0125 mmol) and 100 mL of DMA under argon]. The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 150 °C for 48 hours. After cooling the reaction at room temperature and concentration, the crude mixture was purified by silica column chromatography to afford the desired arylated products.

3. Product characterizations

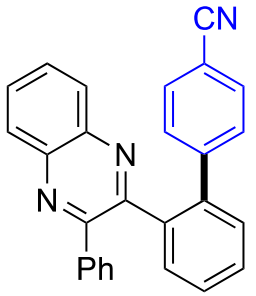


2-(3'-Nitro-[1,1'-biphenyl]-2-yl)-3-phenylquinoxaline (1): Following the general procedure using 3-bromonitrobenzene (202 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **1** (274 mg, 68%) as a yelow solid (Mp = 202-204 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.30 – 8.23 (m, 1H), 8.15 – 8.09 (m, 1H), 7.99 – 7.93 (m, 2H), 7.88 – 7.79 (m, 2H), 7.70 (td, *J* = 1.3, 7.6 Hz, 1H), 7.60 (td, *J* = 1.4, 7.6 Hz, 1H), 7.28 – 7.23 (m, 3H), 7.07 (ddd, *J* = 1.5, 7.7, 9.0 Hz, 3H), 6.86 (dd, *J* = 1.3, 8.3 Hz, 2H), 6.79 (ddd, *J* = 1.1, 1.8, 7.7 Hz,

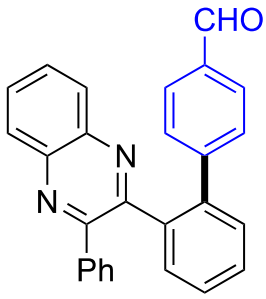
1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.5, 153.2, 148.2, 141.8, 141.5, 141.1, 138.6, 138.3, 137.5, 134.7, 131.7, 130.3, 130.1, 129.8, 129.6, 129.4, 129.3, 129.2, 128.9, 128.4, 127.8, 123.9, 121.4. Elemental analysis: calcd (%) for $C_{26}H_{17}N_3O_2$ (403.44): C 77.41, H 4.25; found: C 77.29, H 4.31. HRMS (ESI) Calcd for: $C_{26}H_{17}N_3O_2Na^+$: 426.1218; Found: 426.1219 $[M+Na]^+$.



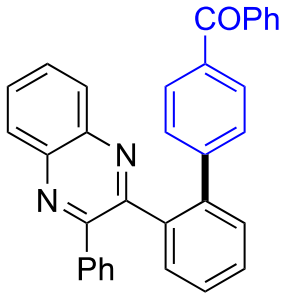
2-(4'-Nitro-[1,1'-biphenyl]-2-yl)-3-phenylquinoxaline (2): Following the general procedure using 4-bromonitrobenzene (202 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **2** (258 mg, 64%) as a white solid (Mp = 210-212 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.27 – 8.22 (m, 1H), 8.19 – 8.12 (m, 1H), 7.94 (dd, *J* = 1.4, 7.6 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.70 (td, *J* = 1.3, 7.5 Hz, 1H), 7.59 (td, *J* = 1.4, 7.6 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.10 (dd, *J* = 7.1, 8.6 Hz, 2H), 6.89 (dd, *J* = 1.3, 8.3 Hz, 2H), 6.62 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.5, 153.2, 146.8, 146.3, 141.5, 141.0, 138.8, 138.3, 137.7, 131.7, 130.4, 130.2, 129.7, 129.6, 129.6, 129.4, 129.1, 129.1, 128.6, 128.0, 123.1. Elemental analysis: calcd (%) for $C_{26}H_{17}N_3O_2$ (403.44): C 77.41, H 4.25; found: C 77.68, H 4.42.



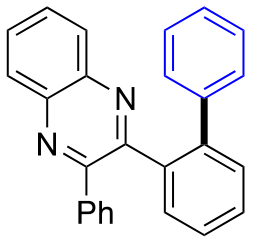
2'-(3-Phenylquinoxalin-2-yl)-[1,1'-biphenyl]-4-carbonitrile (3): Following the general procedure using 4-bromobenzonitrile (182 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **3** (253 mg, 66%) as a white solid (Mp = 180-184 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.27 – 8.21 (m, 1H), 8.18 – 8.13 (m, 1H), 7.93 (dd, *J* = 1.4, 7.6 Hz, 1H), 7.88 – 7.81 (m, 2H), 7.68 (td, *J* = 1.3, 7.6 Hz, 1H), 7.57 (td, *J* = 1.4, 7.6 Hz, 1H), 7.28 – 7.19 (m, 4H), 7.11 (t, *J* = 7.8 Hz, 2H), 6.94 – 6.88 (m, 2H), 6.56 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.6, 153.2, 144.8, 141.5, 141.0, 139.2, 138.2, 137.8, 131.6, 131.6, 130.3, 130.1, 129.7, 129.5, 129.4, 129.4, 129.2, 129.1, 128.5, 127.9, 110.2. Elemental analysis: calcd (%) for $C_{27}H_{17}N_3$ (383.45): C 84.57, H 4.47; found: C 84.61, H 4.40.



2'-(3-Phenylquinoxalin-2-yl)-[1,1'-biphenyl]-4-carbaldehyde (4): Following the general procedure using 4-bromobenzaldehyde (185 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **4** (236 mg, 61%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.92 (s, 1H), 8.29 – 8.22 (m, 1H), 8.17 – 8.10 (m, 1H), 7.93 (dd, *J* = 1.4, 7.6 Hz, 1H), 7.87 – 7.79 (m, 2H), 7.71 – 7.63 (m, 1H), 7.57 (td, *J* = 1.4, 7.6 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.25 (tt, *J* = 1.4, 7.1 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 2H), 6.86 (dt, *J* = 1.4, 6.8 Hz, 2H), 6.63 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.0, 154.0, 153.4, 146.4, 141.4, 141.0, 139.8, 138.2, 137.8, 134.3, 131.5, 130.2, 130.0, 129.7, 129.6, 129.5, 129.5, 129.4, 129.3, 129.1, 129.0, 128.5, 127.8. Elemental analysis: calcd (%) for $C_{27}H_{18}N_2O$ (386.45): C 83.92, H 4.69; found: C 84.08, H 4.47.

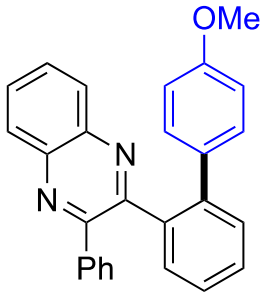


Phenyl(2'-(3-phenylquinoxalin-2-yl)-[1,1'-biphenyl]-4-yl)methanone (5): Following the general procedure using 4-bromobenzophenone (261 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **5** (273 mg, 59%) as a yellow solid (Mp = 168-171 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.29 – 8.22 (m, 1H), 8.18 – 8.11 (m, 1H), 7.93 (dd, *J* = 1.4, 7.6 Hz, 1H), 7.85 – 7.80 (m, 2H), 7.78 – 7.72 (m, 2H), 7.67 (td, *J* = 1.3, 7.5 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.52 – 7.46 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.23 (m, 2H), 7.11 (t, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 7.2 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.3, 154.2, 153.5, 144.3, 141.4, 141.0, 140.1, 138.3, 138.0, 137.6, 135.4, 132.3, 131.4, 130.1, 130.0, 130.0, 129.9, 129.7, 129.6, 129.4, 129.2, 129.1, 128.8, 128.5, 128.4, 128.2, 127.8. Elemental analysis: calcd (%) for $C_{33}H_{22}N_2O$ (462.55): C 85.69, H 4.79; found: C 85.90, H 4.91. HRMS (ESI) Calcd for: $C_{33}H_{22}N_2ONa^+$: 485.1630; Found: 424.1632 $[M+Na]^+$.

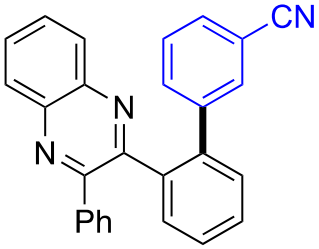


2-([1,1'-Biphenyl]-2-yl)-3-phenylquinoxaline (6): Following the general procedure using bromobenzene (157 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **6** (240 mg, 67%) as a yellow solid (Mp = 140-144 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.30 – 8.22 (m, 1H), 8.17 – 8.09 (m, 1H), 7.89 (dd, *J* = 1.3,

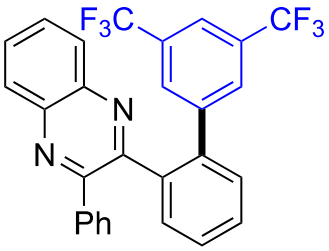
7.6 Hz, 1H), 7.85 – 7.76 (m, 2H), 7.60 (td, *J* = 1.4, 7.5 Hz, 1H), 7.53 (td, *J* = 1.5, 7.6 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.12 – 7.05 (m, 3H), 6.93 (t, *J* = 7.7 Hz, 2H), 6.89 – 6.85 (m, 2H), 6.46 (dd, *J* = 1.1, 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.8, 153.9, 141.3, 141.2, 141.0, 140.0, 138.1, 131.2, 129.9, 129.8, 129.7, 129.4, 129.3, 129.1, 129.0, 129.0, 128.2, 128.0, 127.9, 127.6, 126.5. Elemental analysis: calcd (%) for $C_{26}H_{18}N_2$ (358.44): C 87.12, H 5.06; found: C 87.30, H 5.01.



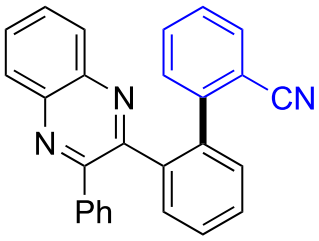
2-(4'-Methoxy-[1,1'-biphenyl]-2-yl)-3-phenylquinoxaline (7): Following the general procedure using 4-bromoanisole (187 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 85-15) to afford the desired compound **7** (175 mg, 45%) as a white solid (Mp = 148-151 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.29 – 8.23 (m, 1H), 8.17 – 8.10 (m, 1H), 7.87 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.81 (td, *J* = 2.2, 4.8, 5.3 Hz, 2H), 7.58 (dd, *J* = 1.4, 7.5 Hz, 1H), 7.50 (td, *J* = 1.5, 7.5 Hz, 1H), 7.26 – 7.17 (m, 2H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.94 – 6.88 (m, 2H), 6.49 (d, *J* = 8.7 Hz, 2H), 6.37 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.4, 155.0, 153.9, 141.3, 141.1, 140.8, 138.1, 137.9, 132.7, 131.1, 130.1, 129.8, 129.7, 129.7, 129.4, 129.3, 129.1, 128.9, 128.2, 127.6, 127.6, 113.5, 55.2. Elemental analysis: calcd (%) for $C_{27}H_{20}N_2O$ (388.47): C 83.48, H 5.19; found: C 83.21, H 5.34.



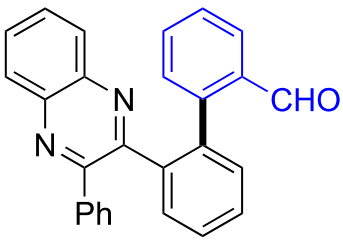
2'-(3-Phenylquinoxalin-2-yl)-[1,1'-biphenyl]-3-carbonitrile (8): Following the general procedure using 3-bromobenzonitrile (182 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **8** (219 mg, 57%) as a white solid (Mp = 165-167 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.29 – 8.22 (m, 1H), 8.18 – 8.10 (m, 1H), 7.93 (dd, *J* = 1.3, 7.6 Hz, 1H), 7.89 – 7.79 (m, 2H), 7.68 (td, *J* = 1.3, 7.6 Hz, 1H), 7.58 (td, *J* = 1.4, 7.6 Hz, 1H), 7.39 (dt, *J* = 1.4, 7.8 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.20 – 7.12 (m, 3H), 7.00 (td, *J* = 0.6, 7.8 Hz, 1H), 6.91 – 6.83 (m, 2H), 6.69 (ddd, *J* = 1.2, 1.8, 7.8 Hz, 1H), 6.67 – 6.65 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.6, 153.2, 141.5, 141.4, 141.0, 138.9, 138.2, 137.7, 133.1, 132.4, 131.6, 130.3, 130.1, 130.0, 129.8, 129.6, 129.4, 129.2, 129.1, 129.0, 128.8, 128.3, 128.0, 118.4, 112.5. Elemental analysis: calcd (%) for $C_{27}H_{17}N_3$ (383.45): C 84.57, H 4.47; found: C 84.74, H 4.62.



2-(3',5'-Bis(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-3-phenylquinoxaline (9): Following the general procedure using 1-bromo-3,5-bis(trifluoromethyl)benzene (293 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 90-10) to afford the desired compound **9** (346 mg, 70%) as a white solid (Mp = 112-114 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.29 – 8.22 (m, 1H), 8.15 – 8.10 (m, 1H), 8.00 (dd, *J* = 1.3, 7.6 Hz, 1H), 7.89 – 7.80 (m, 2H), 7.73 (td, *J* = 1.3, 7.6 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.29 – 7.23 (m, 2H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.91 – 6.84 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.2, 152.9, 141.9, 141.5, 140.9, 138.6, 137.9, 137.4, 131.5, 131.1 (q, *J* = 34.1 Hz), 130.4, 130.2, 129.8, 129.6, 129.4, 129.2, 129.0, 128.8, 128.0, 122.8 (q, *J* = 273.1 Hz), 120.3 (m). Elemental analysis: calcd (%) for $C_{28}H_{16}F_6N_2$ (494.44): C 68.02, H 3.26; found: C 68.14, H 3.55.

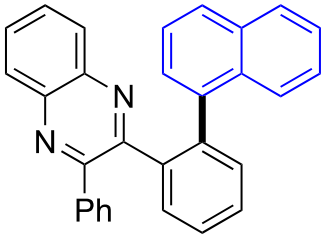


2'-(3-Phenylquinoxalin-2-yl)-[1,1'-biphenyl]-2-carbonitrile (10): Following the general procedure using 2-bromobenzonitrile (182 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **10** (196 mg, 51%) as a white solid (Mp = 212-215 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.26 – 8.20 (m, 1H), 8.16 – 8.09 (m, 1H), 7.97 (dd, *J* = 1.3, 7.7 Hz, 1H), 7.81 (qd, *J* = 3.5, 7.2 Hz, 2H), 7.71 (td, *J* = 1.3, 7.6 Hz, 1H), 7.61 (td, *J* = 1.4, 7.6 Hz, 1H), 7.49 (dd, *J* = 1.3, 7.7 Hz, 1H), 7.42 (dd, *J* = 1.3, 7.8 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.25 – 7.16 (m, 3H), 7.08 (td, *J* = 1.4, 7.7 Hz, 1H), 7.02 (dd, *J* = 1.3, 8.3 Hz, 2H), 6.57 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.4, 143.0, 141.3, 140.9, 138.9, 137.8, 136.6, 133.7, 131.7, 131.4, 131.0, 130.6, 130.2, 130.0, 129.6, 129.4, 129.3, 129.3, 129.2, 128.8, 128.5, 127.1, 117.8, 112.4. Elemental analysis: calcd (%) for $C_{27}H_{17}N_3$ (383.45): C 84.57, H 4.47; found: C 84.64, H 4.53.

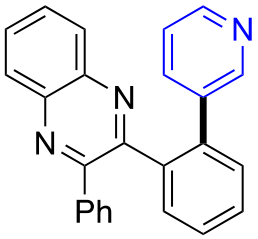


2'-(3-Phenylquinoxalin-2-yl)-[1,1'-biphenyl]-2-carbaldehyde (11): Following the general procedure using 2-bromobenzaldehyde (185 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **11** (182 mg, 47%) as a yellow solid (Mp = 162-165 ºC). ^{1}H NMR

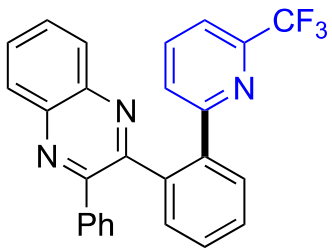
(400 MHz, $CDCl_3$) δ (ppm) 9.00 (s, 1H), 8.27 – 8.19 (m, 1H), 8.14 – 8.06 (m, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.85 – 7.76 (m, 2H), 7.73 – 7.66 (m, 2H), 7.54 (td, *J* = 1.4, 7.6 Hz, 1H), 7.34 – 7.23 (m, 2H), 7.19 – 7.07 (m, 4H), 7.04 – 6.95 (m, 2H), 6.53 (dd, *J* = 1.2, 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 191.4, 153.5, 153.4, 143.2, 141.3, 140.8, 139.3, 138.2, 136.4, 134.2, 132.4, 131.5, 130.2, 130.1, 129.4, 129.3, 129.3, 129.1, 129.1, 129.0, 128.7, 128.1, 127.6, 127.0. Elemental analysis: calcd (%) for $C_{27}H_{18}N_2O$ (386.45): C 83.92, H 4.69; found: C 83.81, H 4.74.



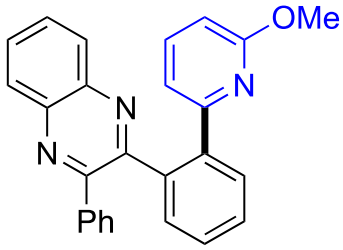
2-(2-(Naphthalen-1-yl)phenyl)-3-phenylquinoxaline (12): Following the general procedure using 1-bromonaphthalene (207 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 90-10) to afford the desired compound **12** (220 mg, 54%) as a brown oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (dd, *J* = 1.5, 8.4 Hz, 1H), 8.00 (ddd, *J* = 1.5, 7.9, 13.0 Hz, 2H), 7.75 (ddd, *J* = 1.7, 6.0, 13.3 Hz, 1H), 7.72 – 7.65 (m, 3H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.38 (dd, *J* = 1.3, 7.7 Hz, 1H), 7.27 – 7.16 (m, 2H), 7.09 – 7.04 (m, 1H), 7.03 – 6.96 (m, 2H), 6.94 – 6.87 (m, 2H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.47 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.5, 153.5, 141.0, 140.8, 139.8, 139.1, 138.3, 137.2, 133.3, 131.8, 131.2, 131.2, 129.7, 129.6, 129.1, 129.0, 129.0, 128.7, 128.6, 128.5, 128.1, 127.6, 127.5, 127.5, 125.8, 125.6, 125.1, 124.6. Elemental analysis: calcd (%) for $C_{30}H_{20}N_2$ (408.50): C 88.21, H 4.94; found: C 88.46, H 5.10.



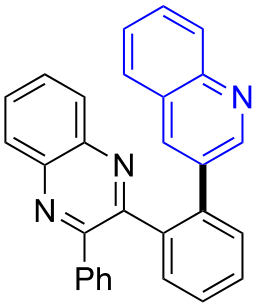
2-Phenyl-3-(2-(pyridin-3-yl)phenyl)quinoxaline (13): Following the general procedure using 3-bromopyridine (158 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel ((heptane-AcOEt, 70-30) to afford the desired compound **13** (205 mg, 57%) as a white solid (Mp = 196-199 ºC). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.39 (brs, 1H), 8.28 – 8.21 (m, 1H), 8.14 (dd, *J* = 2.1, 7.7 Hz, 1H), 7.93 (dd, *J* = 1.4, 7.6 Hz, 1H), 7.88 – 7.77 (m, 2H), 7.67 (td, *J* = 1.2, 7.6 Hz, 1H), 7.58 (td, *J* = 1.4, 7.6 Hz, 1H), 7.35 – 7.25 (m, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.90 (d, *J* = 7.3 Hz, 3H), 6.77 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.7, 153.3, 149.4, 147.5, 141.5, 141.1, 138.4, 137.9, 137.6, 135.8, 131.6, 130.2, 130.0, 129.9, 129.8, 129.7, 129.4, 129.1, 128.9, 128.9, 128.6, 127.9. Elemental analysis: calcd (%) for $C_{25}H_{17}N_3$ (359.43): C 83.54, H 4.77; found: C 83.70, H 5.03.



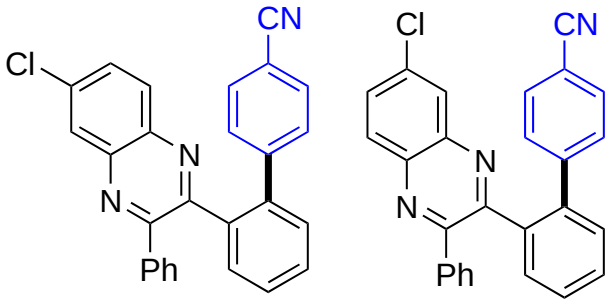
2-Phenyl-3-(2-(6-(trifluoromethyl)pyridin-2-yl)phenyl)quinoxaline (14): Following the general procedure using 2-bromo-6-(trifluoromethyl)pyridine (225 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **14** (291 mg, 68%) as a yellow solid (Mp = 120-123 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 – 8.12 (m, 2H), 7.85 – 7.76 (m, 3H), 7.68 – 7.54 (m, 4H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.08 (dt, *J* = 7.5, 13.6 Hz, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.0, 154.7, 153.3, 147.2 (d, *J* = 34.7 Hz), 141.3, 141.2, 139.0, 138.2, 138.1, 137.6, 131.8, 129.8, 129.7, 129.6, 129.3, 129.2, 129.2, 129.0, 128.4, 127.8, 125.2, 120.7(q, *J* = 137.7 Hz), 117.8 (q, *J* = 2.8 Hz). Elemental analysis: calcd (%) for $C_{26}H_{16}F_3N_3$ (427.43): C 73.06, H 3.77; found: C 73.19, H 3.56.



2-(2-(6-Methoxypyridin-2-yl)phenyl)-3-phenylquinoxaline (15): Following the general procedure using 2-bromo-6-methoxypyridine (188 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **15** (210 mg, 54%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 – 8.10 (m, 2H), 7.81 – 7.72 (m, 2H), 7.71 – 7.67 (m, 1H), 7.58 – 7.49 (m, 3H), 7.32 (dd, *J* = 7.4, 8.2 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.20 – 7.16 (m, 2H), 7.15 – 7.09 (m, 2H), 6.55 (dd, *J* = 0.7, 7.3 Hz, 1H), 6.46 (dd, *J* = 0.7, 8.2 Hz, 1H), 2.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.7, 155.8, 155.3, 154.0, 141.2, 141.1, 139.8, 138.8, 138.4, 138.3, 131.5, 129.6, 129.5, 129.2, 129.2, 129.1, 129.1, 128.9, 128.8, 128.3, 127.7, 115.7, 108.8, 52.3. Elemental analysis: calcd (%) for $C_{26}H_{19}N_3O$ (389.46): C 80.18, H 4.92; found: C 80.08, H 5.13.



2-Phenyl-3-(2-(quinolin-3-yl)phenyl)quinoxaline (16): Following the general procedure using 3-bromoquinoline (208 mg, 1 mmol) and 2,3-diphenylquinoxaline (424 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 70-30) to afford the desired compound **16** (241 mg, 59%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.27 (dd, *J* = 1.6, 7.9 Hz, 1H), 8.10 – 8.04 (m, 2H), 8.00 – 7.95 (m, 2H), 7.88 – 7.76 (m, 2H), 7.73 – 7.57 (m, 3H), 7.49 – 7.43 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 1.2, 7.7 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 2.1 Hz, 1H), 7.01 – 6.95 (m, 2H), 6.74 – 6.68 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.7, 153.3, 150.4, 146.4, 141.5, 141.2, 138.5, 137.9, 137.7, 135.2, 133.3, 131.6, 130.2, 130.2, 130.1, 129.9, 129.8, 129.4, 129.1, 129.0, 128.9, 128.9, 128.5, 128.3, 127.8, 127.5, 126.6. Elemental analysis: calcd (%) for $C_{29}H_{19}N_3$ (409.49): C 85.06, H 4.68; found: C 85.16, H 4.34.



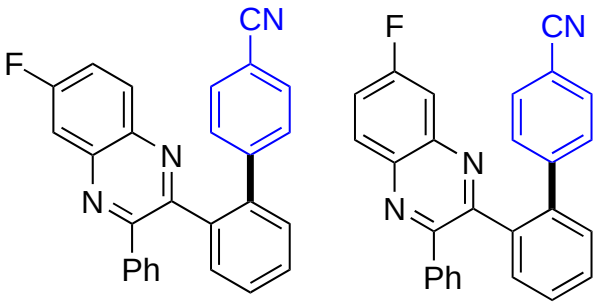
2'-(6-Chloro-3-phenylquinoxalin-2-yl)-[1,1'-biphenyl]-4-carbonitrile (17a) & 2'-(7-chloro-3-phenylquinoxalin-2-yl)-[1,1'-biphenyl]-4-carbonitrile (17b) Following the general procedure using 4-bromobenzonitrile (182 mg, 1 mmol) and 6-chloro-2,3-diphenylquinoxaline (475 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 70-30) to afford the desired compound **17a**&**17b** in 1:1 ratio (234 mg, 56%) as a white solid (Mp = 120-122 &220-222 ºC).

17a or 17b ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.23 (d, *J* = 2.3 Hz, 1H), 8.08 (d, *J* = 8.9 Hz, 1H), 7.91 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.77 (dd, *J* = 2.3, 8.9 Hz, 1H), 7.69 (td, *J* = 1.3, 7.6 Hz, 1H), 7.59 (td, *J* = 1.4, 7.6 Hz, 1H), 7.28 – 7.19 (m, 4H), 7.11 (t, *J* = 7.8 Hz, 2H), 6.91 – 6.86 (m, 2H), 6.54 (d, *J* = 8.4 Hz, 2H). **17a or 17b** ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.5, 153.4, 144.7, 141.3, 140.0, 139.2, 137.9, 137.4, 135.9, 131.7, 131.6, 131.4, 130.6, 129.9, 129.6, 129.4, 129.3, 129.1, 128.8, 128.0, 128.0, 118.7, 110.3.

17a or 17b ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8 8.20 – 8.11 (m, 2H), 7.91 (dd, *J* = 1.4, 7.6 Hz, 1H), 7.78 (dd, *J* = 2.3, 8.9 Hz, 1H), 7.68 (td, *J* = 1.3, 7.6 Hz, 1H), 7.58 (td, *J* = 1.4, 7.6 Hz, 1H), 7.27 – 7.18 (m, 4H), 7.16 – 7.08 (m, 2H), 6.92 – 6.84 (m, 2H), 6.54 (d, *J* = 8.4 Hz, 2H). **17a or 17b** ^{13}C NMR (100 MHz, $CDCl_3$) 154.1, 153.8, 144.7, 141.7, 139.5, 139.2, 137.9, 137.4,

136.1, 131.7, 131.5, 131.2, 130.3, 129.9, 129.6, 129.4, 129.3, 129.1, 128.9, 128.3, 128.0, 118.7, 110.3.

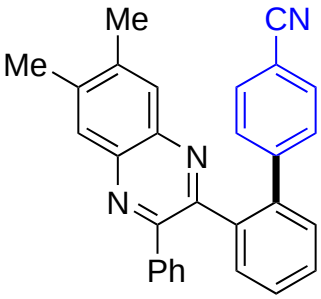
Elemental analysis: calcd (%) for $C_{27}H_{16}ClN_3$ (417.90): C 77.60, H 3.86; found: C 77.42, H 3.99.



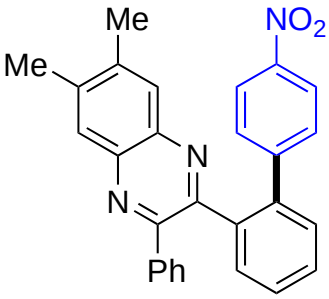
2'-(6-Fluoro-3-phenylquinoxalin-2-yl)-[1,1'-biphenyl]-4-carbonitrile (18a) & 2'-(7-fluoro-3-phenylquinoxalin-2-yl)-[1,1'-biphenyl]-4-carbonitrile (18b): Following the general procedure using 4-bromobenzonitrile (182 mg, 1 mmol) and 6-fluoro-2,3-diphenylquinoxaline (448 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 85-15) to afford the desired compound **18a**&**18b** in 1:1 ratio (249 mg, 62%) as a white solid (Mp = 140-143 &198-200 ºC). **18a** or **18b** ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.15 (dd, *J* = 5.7, 9.2 Hz, 1H), 7.92 (dd, *J* = 1.1, 7.6 Hz, 1H), 7.88 – 7.82 (m, 1H), 7.69 (td, *J* = 1.3, 7.6 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.27 – 7.20 (m, 4H), 7.16 – 7.07 (m, 2H), 6.88 (dd, *J* = 1.3, 7.0 Hz, 2H), 6.55 (d, *J* = 8.5 Hz, 2H). **18a** or **18b** ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.0 (d, *J* = 254.2 Hz), 152.6 (m), 154.5, 144.7, 139.2, 138.7, 137.9, 137.5, 131.7, 131.6, 131.5, 131.4, 129.9, 129.6, 129.4, 129.3, 129.0, 128.6, 128.0, 120.7 (d, *J* = 23.5 Hz), 118.7, 112.6 (d, *J* = 21.8 Hz), 110.2

18a or **18b** ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.24 (dd, *J* = 5.7, 9.2 Hz, 1H), 7.92 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.76 (dd, *J* = 2.8, 9.1 Hz, 1H), 7.70 (td, *J* = 1.3, 7.6 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.28 – 7.22 (m, 2H), 7.15 – 7.07 (m, 2H), 6.89 (dd, *J* = 1.3, 7.9 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H). **18a** or **18b** ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.1 (d, *J* = 254.2 Hz), 153.9, 152.8 (m), 146.7, 146.3, 138.9, 138.2, 138.0, 127.4, 131.6, 131.2, 131.1, 129.8, 129.6, 129.5, 129.4, 129.2, 128.9, 128.0, 123.1, 120.6 (d, *J* = 23.6 Hz), 112.9 6 (d, *J* = 20.1 Hz).

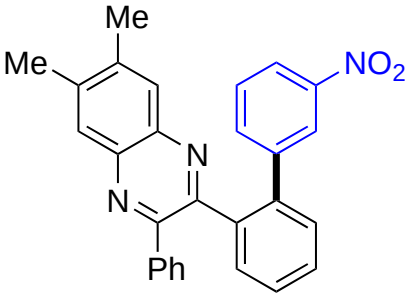
Elemental analysis: calcd (%) for $C_{27}H_{16}FN_3$ (401.44): C 80.78, H 4.02; found: C 80.91, H 3.87.



2'-(6,7-Dimethyl-3-phenylquinoxalin-2-yl)-[1,1'-biphenyl]-4-carbonitrile (19): Following the general procedure using 4-bromobenzonitrile (182 mg, 1 mmol) and 6,7-dimethyl-2,3-diphenylquinoxaline (465 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **19** (267 mg, 65%) as a yellow solid (Mp = 210-203 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (s, 1H), 7.93 – 7.87 (m, 2H), 7.65 (td, *J* = 1.3, 7.5 Hz, 1H), 7.54 (td, *J* = 1.4, 7.6 Hz, 1H), 7.21 (dt, *J* = 5.7, 7.2 Hz, 4H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.90 – 6.84 (m, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 2.57 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.5, 152.3, 145.0, 141.0, 140.8, 140.5, 140.0, 139.2, 138.5, 138.0, 131.6, 131.5, 129.5, 129.5, 129.2, 129.1, 128.4, 128.3, 128.1, 127.8, 118.8, 110.0, 20.5, 20.5. Elemental analysis: calcd (%) for $C_{29}H_{21}N_3$ (411.51): C 84.64, H 5.14; found: C 84.70, H 5.32. HRMS (ESI) Calcd for: $C_{29}H_{21}N_3Na^+$: 434.1633; Found: 434.1633 $[M+Na]^+$.

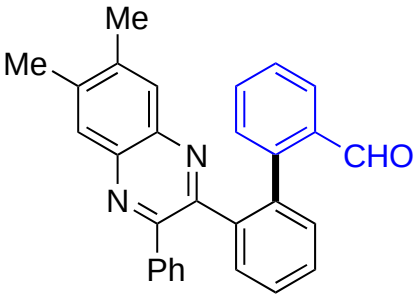


6,7-Dimethyl-2-(4'-nitro-[1,1'-biphenyl]-2-yl)-3-phenylquinoxaline (20): Following the general procedure using 4-bromonitrobenzene (202 mg, 1 mmol) and 6,7-dimethyl-2,3-diphenylquinoxaline (465 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 90-10) to afford the desired compound **20** (289 mg, 67%) as a yellow solid (Mp = 219-221 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (s, 1H), 7.94 – 7.86 (m, 2H), 7.82 – 7.75 (m, 2H), 7.68 (td, *J* = 1.3, 7.6 Hz, 1H), 7.56 (td, *J* = 1.4, 7.6 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.89 – 6.83 (m, 2H), 6.67 – 6.55 (m, 2H), 2.58 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.4, 152.2, 147.0, 146.2, 141.1, 140.9, 140.5, 140.0, 138.8, 138.6, 138.0, 131.7, 129.6, 129.5, 129.5, 129.4, 129.1, 128.4, 128.3, 128.1, 127.9, 123.0, 20.5, 20.4. Elemental analysis: calcd (%) for $C_{28}H_{21}N_3O_2$ (431.50): C 77.94, H 4.91; found: C 77.61, H 5.12.

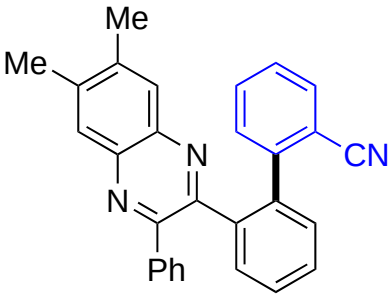


6,7-Dimethyl-2-(3'-nitro-[1,1'-biphenyl]-2-yl)-3-phenylquinoxaline (21): Following the general procedure using 3-bromonitrobenzene (202 mg, 1 mmol) and 6,7-dimethyl-2,3-diphenylquinoxaline (465 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **21**

(272 mg, 63%) as a yellow solid (Mp = 207-210 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00 (s, 1H), 7.96 – 7.90 (m, 2H), 7.87 (s, 1H), 7.68 (td, *J* = 1.3, 7.6 Hz, 1H), 7.57 (td, *J* = 1.4, 7.6 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.04 (td, *J* = 5.5, 7.9 Hz, 3H), 6.87 – 6.82 (m, 2H), 6.77 (ddd, *J* = 1.0, 1.7, 7.7 Hz, 1H), 2.57 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.4, 152.2, 148.1, 141.9, 141.0, 140.8, 140.5, 140.1, 138.6, 138.5, 137.8, 134.7, 131.7, 129.6, 129.6, 129.2, 128.9, 128.6, 128.4, 128.3, 128.2, 127.7, 123.9, 121.3, 20.5, 20.4. Elemental analysis: calcd (%) for $C_{28}H_{21}N_3O_2$ (431.50): C 77.94, H 4.91; found: C 78.05, H 5.11.

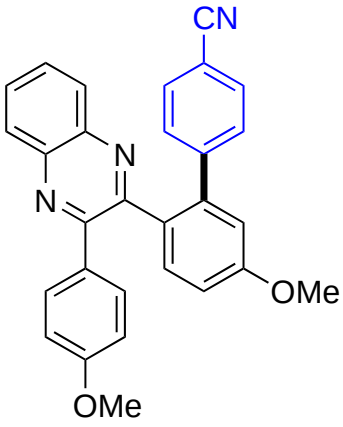


2'-(6,7-Dimethyl-3-phenylquinoxalin-2-yl)-[1,1'-biphenyl]-2-carbaldehyde (22): Following the general procedure using 2-bromobenzaldehyde (185 mg, 1 mmol) and 6,7-dimethyl-2,3-diphenylquinoxaline (465 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **22** (216 mg, 52%) as a yellow solid (Mp = 208-211 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.98 (s, 1H), 8.00 – 7.92 (m, 2H), 7.84 (s, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.52 (td, *J* = 1.4, 7.6 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.17 – 7.02 (m, 4H), 6.96 (d, *J* = 7.8 Hz, 2H), 6.50 (dd, *J* = 1.2, 7.7 Hz, 1H), 2.56 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 191.5, 152.4, 143.4, 140.9, 140.7, 140.3, 139.8, 139.7, 138.5, 136.4, 134.2, 132.3, 131.5, 131.4, 129.4, 129.0, 128.8, 128.5, 128.3, 128.1, 128.0, 127.5, 126.9, 20.5, 20.4. Elemental analysis: calcd (%) for $C_{29}H_{22}N_2O$ (414.51): C 84.03, H 5.35; found: C 82.86, H 5.12. HRMS (ESI) Calcd for: $C_{29}H_{22}N_2ONa^+$: 437.1630; Found: 437.1631 $[M+Na]^+$.

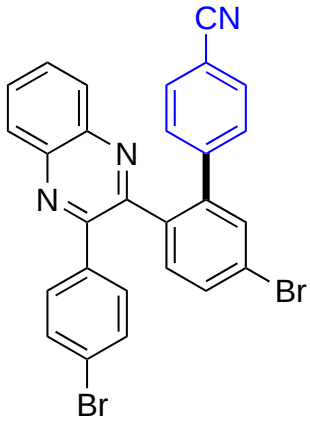


2'-(6,7-dimethyl-3-phenylquinoxalin-2-yl)-[1,1'-biphenyl]-2-carbonitrile (23): Following the general procedure using 2-bromobenzonitrile (182 mg, 1 mmol) and 6,7-dimethyl-2,3-diphenylquinoxaline (465 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **23** (243 mg, 59%) as a yellow solid (Mp = 198-200 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (s, 1H), 7.95 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.87 (s, 1H), 7.69 (td, *J* = 1.3, 7.6 Hz, 1H), 7.59 (td, *J* = 1.5, 7.6 Hz, 1H), 7.47 (dd, *J* = 1.2, 7.8 Hz, 1H), 7.40 (dd, *J* = 1.3, 7.7 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.24 – 7.15 (m, 3H), 7.05 (td, *J* = 1.4, 7.7 Hz, 1H), 7.01 – 6.96 (m, 2H), 6.54 (dd, *J* = 1.1, 7.9 Hz, 1H), 2.56 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.5, 152.3, 143.2, 140.8, 140.6, 140.3, 139.9, 139.2, 138.1, 136.5, 133.6, 131.7, 131.3, 131.0, 130.5, 129.5, 129.1,

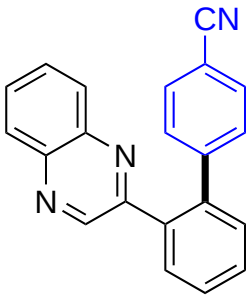
129.1, 128.8, 128.4, 128.3, 128.2, 127.0, 117.8, 112.3, 20.5, 20.4. Elemental analysis: calcd (%) for $C_{29}H_{21}N_3$ (411.51): C 84.64, H 5.14; found: C 84.89, H 5.27.



5'-Methoxy-2'-(3-(4-methoxyphenyl)quinoxalin-2-yl)-[1,1'-biphenyl]-4-carbonitrile (24): Following the general procedure using 4-bromobenzonitrile (182 mg, 1 mmol) and 2,3-bis(4-methoxyphenyl)quinoxaline (514 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-20) to afford the desired compound **24** (328 mg, 74%) as a yellow solid (Mp = 210-213 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.22 – 8.16 (m, 1H), 8.15 – 8.06 (m, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.20 (dd, *J* = 2.6, 8.5 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 2.6 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.3 Hz, 2H), 3.93 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.5, 160.1, 153.3, 153.1, 144.9, 141.4, 140.8, 140.5, 133.0, 131.6, 131.0, 130.6, 130.5, 130.0, 129.7, 129.2, 129.2, 129.0, 118.8, 115.2, 114.5, 113.4, 110.3, 55.6, 55.4. Elemental analysis: calcd (%) for $C_{29}H_{21}N_3O_2$ (443.51): C 78.54, H 4.77; found: C 78.80, H 4.76.



5'-Bromo-2'-(3-(4-bromophenyl)quinoxalin-2-yl)-[1,1'-biphenyl]-4-carbonitrile (25): Following the general procedure using 4-bromobenzonitrile (182 mg, 1 mmol) and 2,3-bis(4-bromophenyl)quinoxaline (660 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 80-40) to afford the desired compound **25** (270 mg, 50%) as a yellow solid (Mp = 203-206 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.27 – 8.19 (m, 1H), 8.17 – 8.10 (m, 1H), 7.90 – 7.84 (m, 2H), 7.83 – 7.79 (m, 2H), 7.42 (s, 1H), 7.31 – 7.26 (m, 4H), 6.79 (d, *J* = 9.1 Hz, 2H), 6.59 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.1, 151.8, 143.2, 141.4, 141.1, 140.7, 136.9, 136.5, 133.3, 132.5, 132.5, 131.9, 131.3, 130.8, 130.6, 130.5, 129.4, 129.3, 129.2, 124.0, 123.5, 118.4, 111.0. Elemental analysis: calcd (%) for $C_{27}H_{15}Br_2N_3$ (541.24): C 59.92, H 2.79; found: C 60.10, H 3.06.

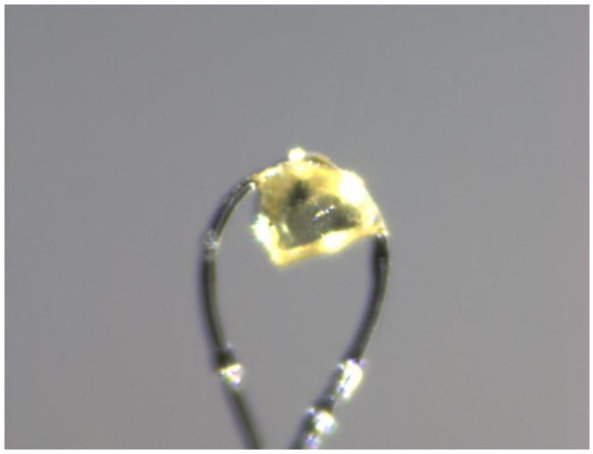


2'-(quinoxalin-2-yl)-[1,1'-biphenyl]-4-carbonitrile (27): Following the general procedure using 4-bromobenzonitrile (182 mg, 1 mmol) and 2-phenylquinoxaline (309 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel (heptane-AcOEt, 70-30) to afford the desired compound **27** (190 mg, 62%) as a yellow solid (Mp = 152-155 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.39 (s, 1H), 8.11 (dd, *J* = 1.7, 7.2 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.94 – 7.90 (m, 1H), 7.87 – 7.77 (m, 2H), 7.70 – 7.63 (m, 2H), 7.59 – 7.52 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.8, 146.2, 145.4, 142.3, 140.7, 139.3, 136.5, 132.3, 131.4, 130.5, 130.4, 130.4, 130.0, 129.4, 129.2, 118.6, 111.3. Elemental analysis: calcd (%) for $C_{21}H_{13}N_3$ (307.35): C 82.06, H 4.26; found: C 81.85.10, H 4.51. HRMS (ESI) Calcd for: $C_{21}H_{13}N_3Na^+$: 330.1007; Found: 330.1007 $[M+Na]^+$.

4. Crystal structure report of compound **1**

a. X-ray crystallographic study

b.



(C26 H17 N3 O2); M = 403.42. D8 VENTURE Bruker AXS diffractometer [*], Mo-Kα radiation (λ = 0.71073 Å), T = 150(2) K; monoclinic P 21/c (I.T.#14), a = 9.3417(7), b = 9.4841(9), c = 22.2977(18) Å, β = 90.720(3) °, V = 1975.4(3) Å3. Z = 4, d = 1.357 g.cm-3, μ = 0.088 mm-1. The structure was solved by dual-space algorithm using the SHELXT program [1], and then refined with full-matrix least-squares methods based on F2 (SHELXL) [2]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F2 with 4518 unique intensities and 280 parameters converged at ωR(F2) = 0.1060 (R(F) = 0.0413) for 4011 observed reflections with I > 2σ(I).

[1] G. M. Sheldrick, Acta Cryst. A71 (2015) 3-8
[2] Sheldrick G.M., Acta Cryst. C71 (2015) 3-8

[*] Thanks to FEDER founds

c. Structural data

Empirical formula	C26 H17 N3 O2
Formula weight	403.42 g/mol

Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P 21/c
Unit cell dimensions	a = 9.3417(7) Å, α = 90 °
	b = 9.4841(9) Å, β = 90.720(3) °
	c = 22.2977(18) Å, γ = 90 °
Volume	1975.4(3) Å3
Z, Calculated density	4, 1.357 g.cm-3
Absorption coefficient	0.088 mm-1
F(000)	840
Crystal size	0.300 x 0.220 x 0.130 mm
Crystal color	colourless
Theta range for data collection	3.061 to 27.482 °
h_min, h_max	-10, 12
k_min, k_max	-12, 11
l_min, l_max	-28, 28
Reflections collected / unique	19478 / 4518 [R(int)a = 0.0252]
Reflections [I>2σ]	4011
Completeness to theta_max	0.997
Absorption correction type	multi-scan
Max. and min. transmission	0.989 , 0.906
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	4518 / 0 / 280
bS (Goodness-of-fit)	1.067
Final R indices [I>2σ]	R1c = 0.0413, wR2d = 0.1060
R indices (all data)	R1c = 0.0470, wR2d = 0.1117
Largest diff. peak and hole	0.256 and -0.222 e-.Å-3

aRint = ∑ |Fo2 - < Fo2>| / ∑[Fo2]

bS = {∑ [w(Fo2 - Fc2)2] / (n - p)}1/2

cR1 = ∑ | |Fo| - |Fc| | / ∑ |Fo|

dwR2 = {∑ [w(Fo2 - Fc2)2] / ∑ [w(Fo2)2]}1/2

w = 1 / [σ(Fo2) + aP2 + bP] where P = [2Fc2 + MAX(Fo2, 0)] /3

Atomic coordinates, site occupancy (%) and equivalent isotropic displacement parameters (Å2). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	occ.	U(eq)
C1	0.52175(14)	0.65075(14)	0.41182(6)	1	0.0236(3)
H1	0.441418	0.610163	0.431018	1	0.028
C2	0.51148(16)	0.78509(15)	0.38757(6)	1	0.0293(3)
H2	0.424136	0.835934	0.390084	1	0.035
C3	0.62842(17)	0.84547(15)	0.35964(6)	1	0.0304(3)
H3	0.621574	0.938097	0.343640	1	0.036
C4	0.75517(15)	0.77052(15)	0.35510(6)	1	0.0286(3)
H4	0.834450	0.810889	0.335084	1	0.034
C5	0.76642(14)	0.63648(14)	0.37977(6)	1	0.0240(3)
H5	0.854217	0.586388	0.377310	1	0.029
C6	0.64954(13)	0.57465(13)	0.40821(5)	1	0.0194(2)
C7	0.66588(12)	0.43192(13)	0.43497(5)	1	0.0190(2)
N8	0.78608(11)	0.40855(12)	0.46532(5)	1	0.0217(2)
C9	0.80304(13)	0.27925(14)	0.49162(5)	1	0.0216(3)
C10	0.92777(14)	0.25280(16)	0.52686(6)	1	0.0280(3)
H10	0.999531	0.323141	0.531264	1	0.034
C11	0.94335(15)	0.12449(17)	0.55446(6)	1	0.0315(3)
H11	1.026568	0.106296	0.578142	1	0.038
C12	0.83785(15)	0.01915(16)	0.54826(6)	1	0.0310(3)
H12	0.850795	-0.068691	0.568071	1	0.037
C13	0.71679(14)	0.04123(15)	0.51411(6)	1	0.0271(3)
H13	0.647033	-0.031035	0.509668	1	0.033
C14	0.69731(13)	0.17347(14)	0.48556(5)	1	0.0214(3)
N15	0.57444(11)	0.19744(11)	0.45283(5)	1	0.0218(2)

C16	0.55868(12)	0.32303(13)	0.42827(5)	1	0.0187(2)
C17	0.42271(13)	0.34749(13)	0.39369(5)	1	0.0195(2)
C18	0.29405(13)	0.33974(14)	0.42461(6)	1	0.0250(3)
H18	0.294775	0.311394	0.465474	1	0.030
C19	0.16478(14)	0.37293(16)	0.39642(7)	1	0.0289(3)
H19	0.077999	0.369128	0.418126	1	0.035
C20	0.16331(14)	0.41153(15)	0.33657(6)	1	0.0280(3)
H20	0.075416	0.434968	0.317125	1	0.034
C21	0.29048(13)	0.41602(14)	0.30488(6)	1	0.0241(3)
H21	0.288229	0.440692	0.263586	1	0.029
C22	0.42146(13)	0.38489(13)	0.33271(5)	1	0.0194(2)
C23	0.55489(13)	0.39273(13)	0.29698(5)	1	0.0193(2)
C24	0.57813(14)	0.50645(14)	0.25818(6)	1	0.0235(3)
H24	0.508601	0.579323	0.255363	1	0.028
C25	0.70060(15)	0.51481(15)	0.22378(6)	1	0.0282(3)
H25	0.713687	0.592716	0.197638	1	0.034
C26	0.80402(14)	0.41013(15)	0.22735(6)	1	0.0273(3)
H26	0.887841	0.414265	0.203726	1	0.033
C27	0.78088(13)	0.29931(13)	0.26654(6)	1	0.0227(3)
C28	0.65927(13)	0.28787(13)	0.30133(5)	1	0.0200(2)
H28	0.647306	0.210055	0.327620	1	0.024
N29	0.89051(12)	0.18844(12)	0.27220(6)	1	0.0294(3)
O30	0.99079(12)	0.19049(13)	0.23755(6)	1	0.0460(3)
O31	0.87630(12)	0.09830(12)	0.31116(6)	1	0.0409(3)

Anisotropic displacement parameters (Å2)

The anisotropic displacement factor exponent takes the form: -2π2 [h2 a*2 U11 + ... + 2 h k a* b* U12].

Atom	U11	U22	U33	U23	U13	U12
C1	0.0260(6)	0.0248(6)	0.0201(6)	-0.0002(5)	0.0042(5)	0.0016(5)
C2	0.0352(7)	0.0259(7)	0.0270(6)	0.0009(5)	0.0040(5)	0.0083(5)
C3	0.0435(8)	0.0219(6)	0.0257(6)	0.0033(5)	0.0014(6)	-0.0012(6)
C4	0.0320(7)	0.0273(7)	0.0264(6)	0.0019(5)	0.0012(5)	-0.0094(5)
C5	0.0212(6)	0.0259(6)	0.0249(6)	-0.0008(5)	-0.0009(5)	-0.0036(5)
C6	0.0218(6)	0.0206(6)	0.0158(5)	-0.0018(4)	-0.0018(4)	-0.0020(4)
C7	0.0182(5)	0.0226(6)	0.0161(5)	-0.0012(4)	0.0015(4)	0.0001(4)
N8	0.0195(5)	0.0258(5)	0.0199(5)	-0.0001(4)	-0.0007(4)	0.0000(4)
C9	0.0193(6)	0.0264(6)	0.0191(5)	-0.0006(5)	0.0011(4)	0.0029(5)
C10	0.0226(6)	0.0340(7)	0.0273(6)	-0.0005(5)	-0.0042(5)	0.0022(5)
C11	0.0260(7)	0.0393(8)	0.0290(7)	0.0011(6)	-0.0064(5)	0.0093(6)
C12	0.0316(7)	0.0300(7)	0.0312(7)	0.0064(6)	-0.0005(5)	0.0110(6)
C13	0.0255(6)	0.0251(6)	0.0307(7)	0.0036(5)	0.0009(5)	0.0041(5)
C14	0.0193(6)	0.0249(6)	0.0202(6)	0.0015(5)	0.0018(4)	0.0040(5)
N15	0.0187(5)	0.0235(5)	0.0231(5)	0.0020(4)	0.0007(4)	0.0012(4)
C16	0.0165(5)	0.0221(6)	0.0176(5)	0.0002(4)	0.0015(4)	0.0002(4)
C17	0.0178(5)	0.0180(5)	0.0227(6)	0.0006(4)	-0.0010(4)	-0.0010(4)
C18	0.0207(6)	0.0282(7)	0.0263(6)	0.0040(5)	0.0021(5)	-0.0012(5)
C19	0.0171(6)	0.0327(7)	0.0372(7)	0.0028(6)	0.0042(5)	-0.0001(5)
C20	0.0170(6)	0.0313(7)	0.0355(7)	0.0010(6)	-0.0055(5)	0.0026(5)
C21	0.0225(6)	0.0256(6)	0.0241(6)	-0.0004(5)	-0.0043(5)	0.0014(5)
C22	0.0191(6)	0.0176(5)	0.0216(6)	-0.0017(4)	-0.0006(4)	0.0001(4)
C23	0.0187(5)	0.0206(6)	0.0186(5)	-0.0033(4)	-0.0027(4)	-0.0015(4)
C24	0.0251(6)	0.0222(6)	0.0230(6)	0.0002(5)	-0.0031(5)	0.0007(5)
C25	0.0316(7)	0.0257(7)	0.0273(6)	0.0046(5)	0.0019(5)	-0.0051(5)
C26	0.0246(6)	0.0277(7)	0.0297(7)	-0.0024(5)	0.0064(5)	-0.0055(5)
C27	0.0197(6)	0.0196(6)	0.0287(6)	-0.0058(5)	0.0009(5)	-0.0015(5)
C28	0.0203(6)	0.0178(6)	0.0219(6)	-0.0021(4)	-0.0004(4)	-0.0023(4)
N29	0.0215(5)	0.0229(6)	0.0440(7)	-0.0062(5)	0.0048(5)	-0.0010(4)
O30	0.0301(6)	0.0406(7)	0.0679(8)	-0.0009(6)	0.0226(5)	0.0058(5)
O31	0.0340(6)	0.0303(6)	0.0587(7)	0.0106(5)	0.0084(5)	0.0091(4)

Bond lengths [Å]

C1	- C2	= 1.3870(19)
C1	- C6	= 1.3982(18)
C1	- H1	= 0.9500
C2	- C3	= 1.388(2)
C2	- H2	= 0.9500
C3	- C4	= 1.386(2)
C3	- H3	= 0.9500
C4	- C5	= 1.3886(19)
C4	- H4	= 0.9500
C5	- C6	= 1.3984(17)
C5	- H5	= 0.9500
C6	- C7	= 1.4864(17)
C7	- N8	= 1.3225(15)
C7	- C16	= 1.4450(17)
N8	- C9	= 1.3676(17)
C9	- C14	= 1.4132(18)
C9	- C10	= 1.4195(17)
C10	- C11	= 1.371(2)
C10	- H10	= 0.9500
C11	- C12	= 1.409(2)
C11	- H11	= 0.9500
C12	- C13	= 1.3714(19)
C12	- H12	= 0.9500
C13	- C14	= 1.4172(18)
C13	- H13	= 0.9500
C14	- N15	= 1.3714(16)
N15	- C16	= 1.3185(16)
C16	- C17	= 1.4957(16)
C17	- C18	= 1.3950(17)
C17	- C22	= 1.4050(17)
C18	- C19	= 1.3904(18)
C18	- H18	= 0.9500
C19	- C20	= 1.384(2)
C19	- H19	= 0.9500
C20	- C21	= 1.3905(19)
C20	- H20	= 0.9500
C21	- C22	= 1.3966(17)
C21	- H21	= 0.9500
C22	- C23	= 1.4896(16)
C23	- C28	= 1.3952(17)
C23	- C24	= 1.4013(18)
C24	- C25	= 1.3876(19)
C24	- H24	= 0.9500
C25	- C26	= 1.387(2)
C25	- H25	= 0.9500
C26	- C27	= 1.3857(19)
C26	- H26	= 0.9500
C27	- C28	= 1.3878(17)
C27	- N29	= 1.4721(17)
C28	- H28	= 0.9500
N29	- O30	= 1.2220(16)
N29	- O31	= 1.2273(17)

Angles [°]

C2	- C1	- C6	=	120.44(12)
C2	- C1	- H1	=	119.80
C6	- C1	- H1	=	119.80
C1	- C2	- C3	=	120.20(13)
C1	- C2	- H2	=	119.90
C3	- C2	- H2	=	119.90
C4	- C3	- C2	=	119.95(13)
C4	- C3	- H3	=	120.00
C2	- C3	- H3	=	120.00
C3	- C4	- C5	=	120.07(13)
C3	- C4	- H4	=	120.00
C5	- C4	- H4	=	120.00

C4 - C5 - C6 = 120.52(12)
C4 - C5 - H5 = 119.70
C6 - C5 - H5 = 119.70
C1 - C6 - C5 = 118.80(12)
C1 - C6 - C7 = 122.03(11)
C5 - C6 - C7 = 119.15(11)
N8 - C7 - C16 = 121.07(11)
N8 - C7 - C6 = 116.13(11)
C16 - C7 - C6 = 122.81(10)
C7 - N8 - C9 = 117.57(11)
N8 - C9 - C14 = 121.23(11)
N8 - C9 - C10 = 119.06(12)
C14 - C9 - C10 = 119.69(12)
C11 - C10 - C9 = 119.16(13)
C11 - C10 - H10 = 120.40
C9 - C10 - H10 = 120.40
C10 - C11 - C12 = 121.01(13)
C10 - C11 - H11 = 119.50
C12 - C11 - H11 = 119.50
C13 - C12 - C11 = 121.15(13)
C13 - C12 - H12 = 119.40
C11 - C12 - H12 = 119.40
C12 - C13 - C14 = 119.00(13)
C12 - C13 - H13 = 120.50
C14 - C13 - H13 = 120.50
N15 - C14 - C9 = 120.83(11)
N15 - C14 - C13 = 119.19(12)
C9 - C14 - C13 = 119.98(11)
C16 - N15 - C14 = 117.34(11)
N15 - C16 - C7 = 121.94(11)
N15 - C16 - C17 = 116.36(10)
C7 - C16 - C17 = 121.69(11)
C18 - C17 - C22 = 119.66(11)
C18 - C17 - C16 = 117.92(11)
C22 - C17 - C16 = 122.33(11)
C19 - C18 - C17 = 120.89(12)
C19 - C18 - H18 = 119.60
C17 - C18 - H18 = 119.60
C20 - C19 - C18 = 119.59(12)
C20 - C19 - H19 = 120.20
C18 - C19 - H19 = 120.20
C19 - C20 - C21 = 120.00(12)
C19 - C20 - H20 = 120.00
C21 - C20 - H20 = 120.00
C20 - C21 - C22 = 121.14(12)
C20 - C21 - H21 = 119.40
C22 - C21 - H21 = 119.40
C21 - C22 - C17 = 118.68(11)
C21 - C22 - C23 = 119.09(11)
C17 - C22 - C23 = 122.23(11)
C28 - C23 - C24 = 118.55(11)
C28 - C23 - C22 = 121.07(11)
C24 - C23 - C22 = 120.38(11)
C25 - C24 - C23 = 121.36(12)
C25 - C24 - H24 = 119.30
C23 - C24 - H24 = 119.30
C26 - C25 - C24 = 120.40(12)
C26 - C25 - H25 = 119.80
C24 - C25 - H25 = 119.80
C27 - C26 - C25 = 117.72(12)
C27 - C26 - H26 = 121.10
C25 - C26 - H26 = 121.10
C26 - C27 - C28 = 123.16(12)
C26 - C27 - N29 = 118.81(11)
C28 - C27 - N29 = 118.02(11)
C27 - C28 - C23 = 118.80(11)
C27 - C28 - H28 = 120.60

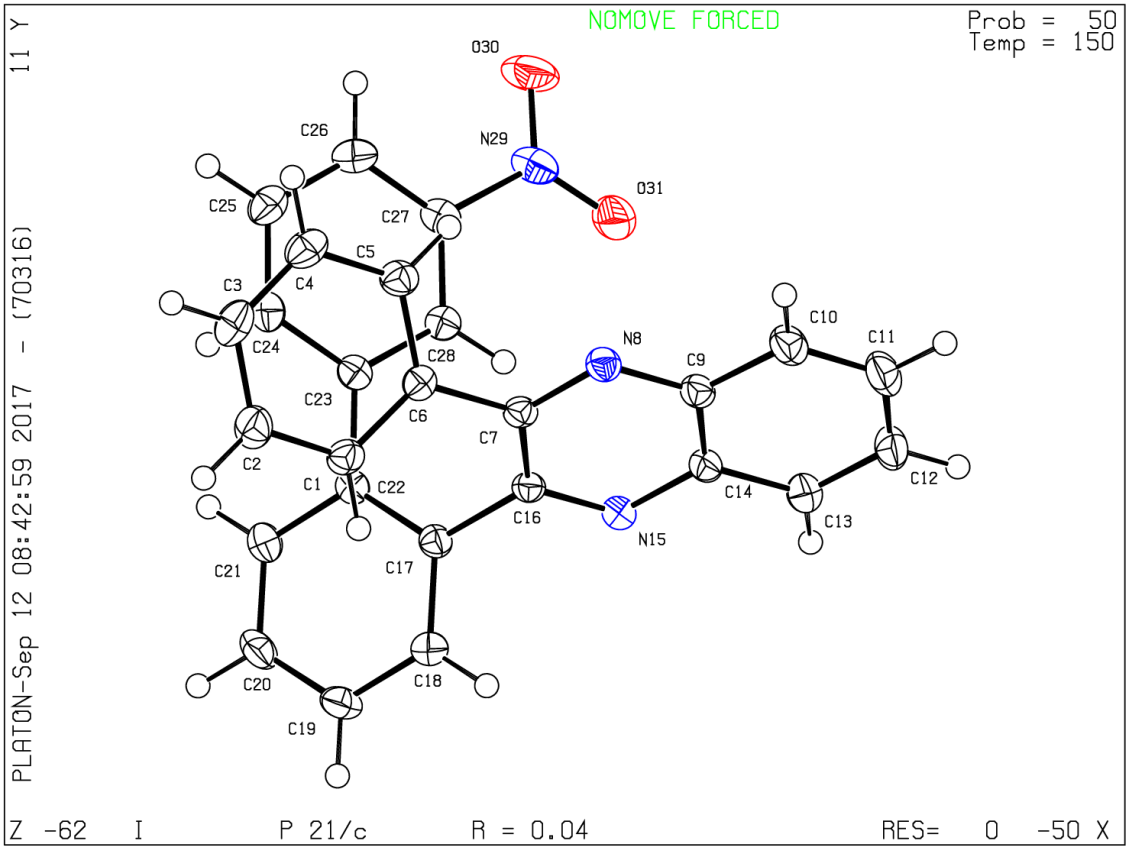
C23	- C28	- H28	= 120.60
O30	- N29	- O31	= 123.32(12)
O30	- N29	- C27	= 118.20(12)
O31	- N29	- C27	= 118.48(11)

Torsion angles [°]

C6	- C1	- C2	- C3	= -0.20(2)
C1	- C2	- C3	- C4	= 1.00(2)
C2	- C3	- C4	- C5	= -1.60(2)
C3	- C4	- C5	- C6	= 1.40(2)
C2	- C1	- C6	- C5	= 0.02(18)
C2	- C1	- C6	- C7	= 178.45(11)
C4	- C5	- C6	- C1	= -0.59(18)
C4	- C5	- C6	- C7	= -179.07(11)
C1	- C6	- C7	- N8	= -135.58(12)
C5	- C6	- C7	- N8	= 42.85(15)
C1	- C6	- C7	- C16	= 45.02(17)
C5	- C6	- C7	- C16	= -136.55(12)
C16	- C7	- N8	- C9	= -1.99(16)
C6	- C7	- N8	- C9	= 178.60(10)
C7	- N8	- C9	- C14	= 1.27(17)
C7	- N8	- C9	- C10	= -177.10(11)
N8	- C9	- C10	- C11	= 178.42(12)
C14	- C9	- C10	- C11	= 0.03(19)
C9	- C10	- C11	- C12	= 0.10(2)
C10	- C11	- C12	- C13	= 0.50(2)
C11	- C12	- C13	- C14	= -1.10(2)
N8	- C9	- C14	- N15	= 0.24(18)
C10	- C9	- C14	- N15	= 178.59(11)
N8	- C9	- C14	- C13	= -178.99(11)
C10	- C9	- C14	- C13	= -0.64(18)
C12	- C13	- C14	- N15	= -178.09(12)
C12	- C13	- C14	- C9	= 1.15(19)
C9	- C14	- N15	- C16	= -0.97(17)
C13	- C14	- N15	- C16	= 178.27(11)
C14	- N15	- C16	- C7	= 0.25(17)
C14	- N15	- C16	- C17	= -178.97(10)
N8	- C7	- C16	- N15	= 1.30(18)
C6	- C7	- C16	- N15	= -179.33(11)
N8	- C7	- C16	- C17	= -179.52(11)
C6	- C7	- C16	- C17	= -0.15(17)
N15	- C16	- C17	- C18	= 62.27(15)
C7	- C16	- C17	- C18	= -116.96(13)
N15	- C16	- C17	- C22	= -121.19(13)
C7	- C16	- C17	- C22	= 59.59(16)
C22	- C17	- C18	- C19	= -2.10(2)
C16	- C17	- C18	- C19	= 174.55(12)
C17	- C18	- C19	- C20	= 1.30(2)
C18	- C19	- C20	- C21	= 0.40(2)
C19	- C20	- C21	- C22	= -1.30(2)
C20	- C21	- C22	- C17	= 0.51(19)
C20	- C21	- C22	- C23	= -179.33(12)
C18	- C17	- C22	- C21	= 1.18(18)
C16	- C17	- C22	- C21	= -175.31(11)
C18	- C17	- C22	- C23	= -178.99(11)
C16	- C17	- C22	- C23	= 4.52(18)
C21	- C22	- C23	- C28	= -135.98(13)
C17	- C22	- C23	- C28	= 44.19(17)
C21	- C22	- C23	- C24	= 44.10(17)
C17	- C22	- C23	- C24	= -135.73(13)
C28	- C23	- C24	- C25	= 1.08(18)
C22	- C23	- C24	- C25	= -178.99(12)
C23	- C24	- C25	- C26	= -0.30(2)
C24	- C25	- C26	- C27	= -0.60(2)
C25	- C26	- C27	- C28	= 0.90(2)
C25	- C26	- C27	- N29	= -178.64(12)

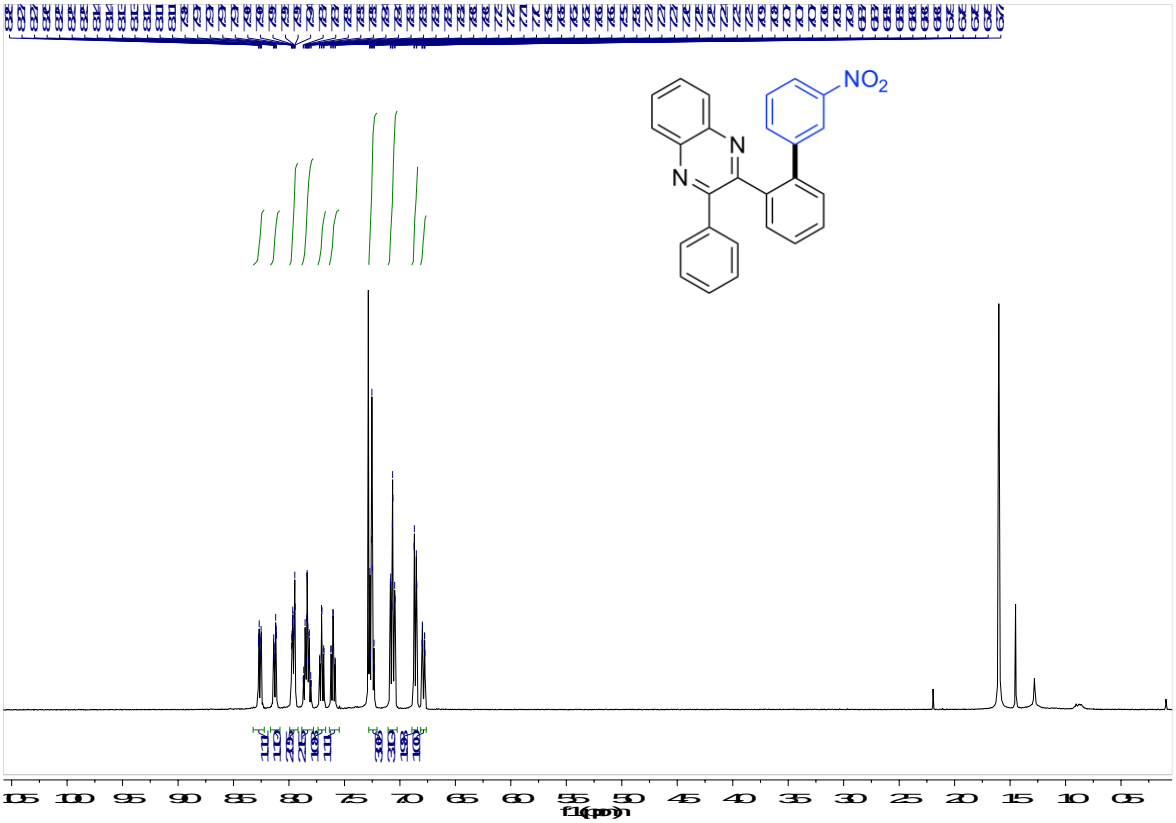
C26 - C27 - C28 - C23 = -0.14(19)
N29 - C27 - C28 - C23 = 179.38(11)
C24 - C23 - C28 - C27 = -0.83(17)
C22 - C23 - C28 - C27 = 179.25(11)
C26 - C27 - N29 - O30 = -7.53(18)
C28 - C27 - N29 - O30 = 172.93(12)
C26 - C27 - N29 - O31 = 172.85(13)
C28 - C27 - N29 - O31 = -6.69(18)

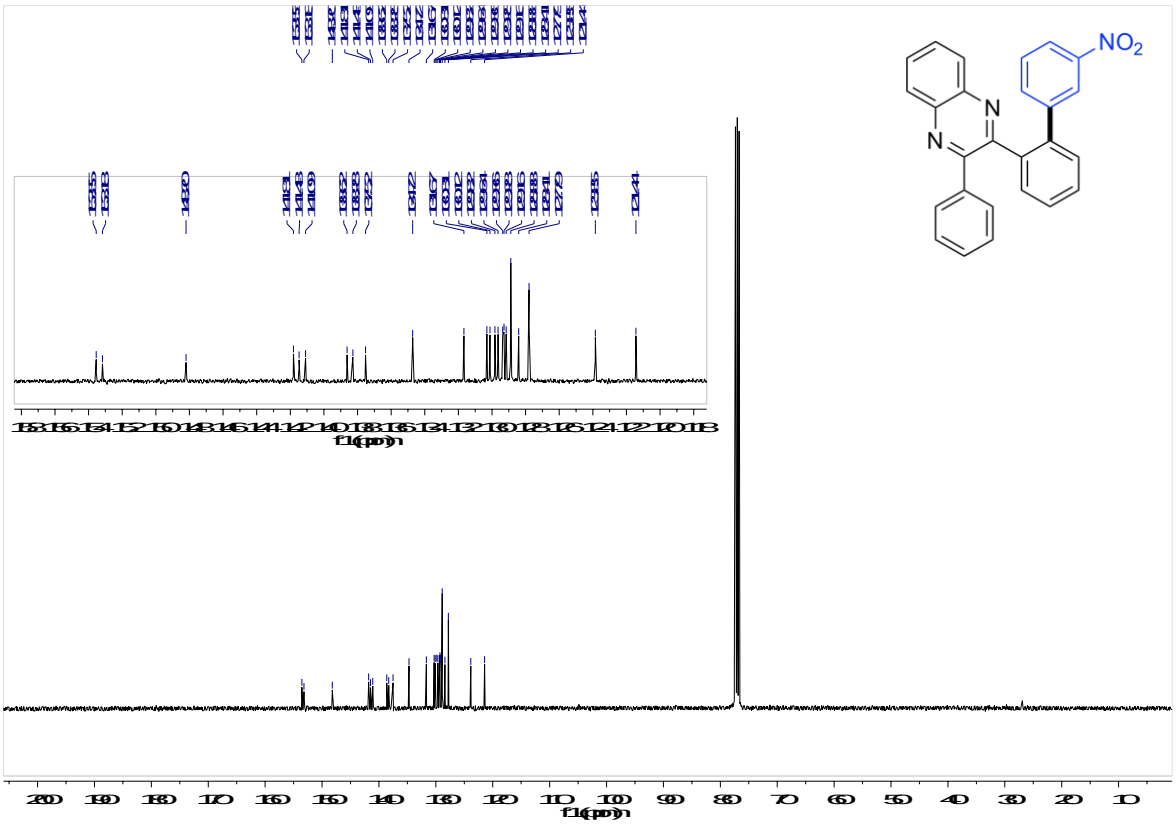
d. Structure visualisation



5. NMR Charts

1





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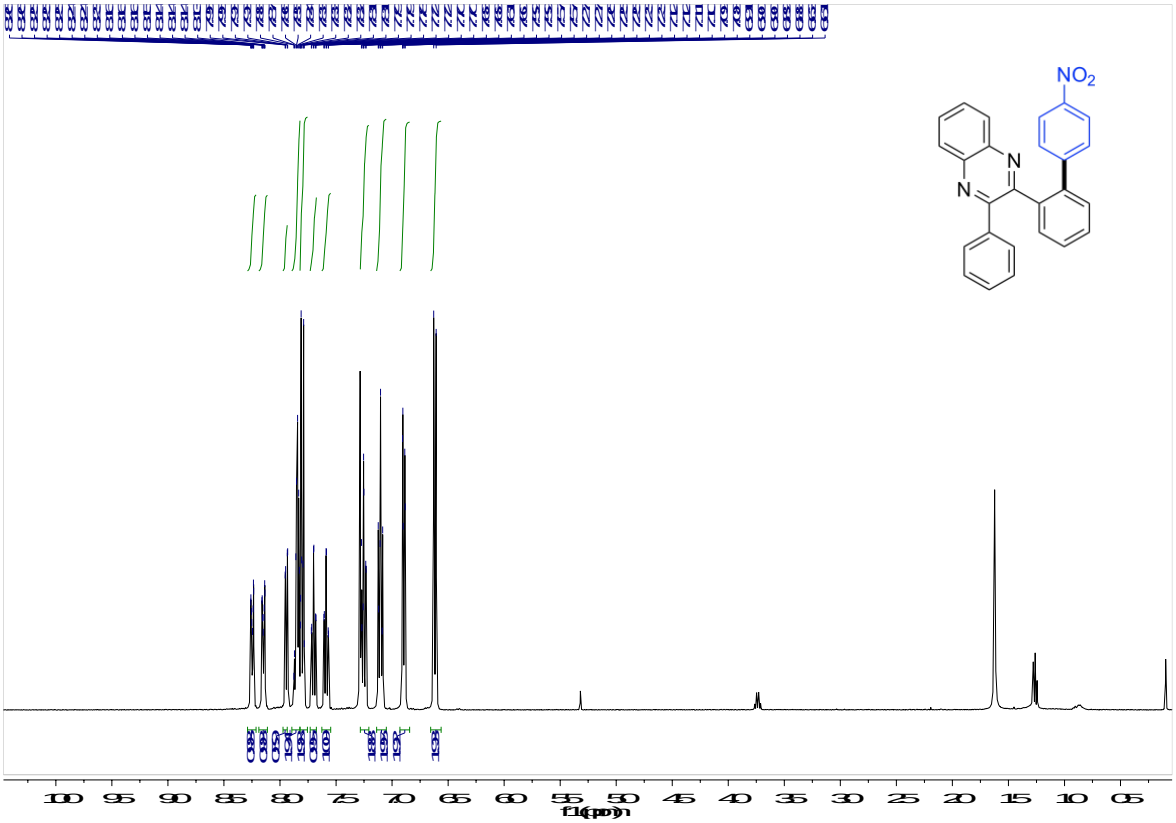

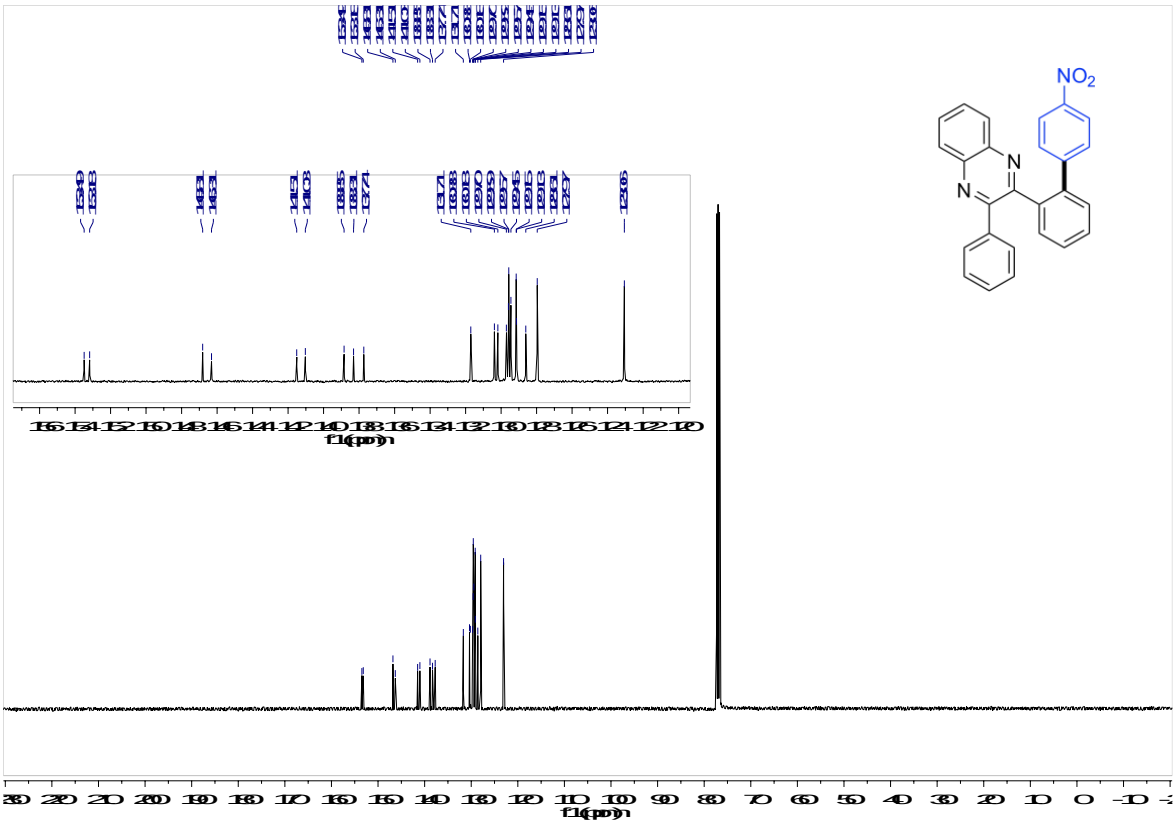

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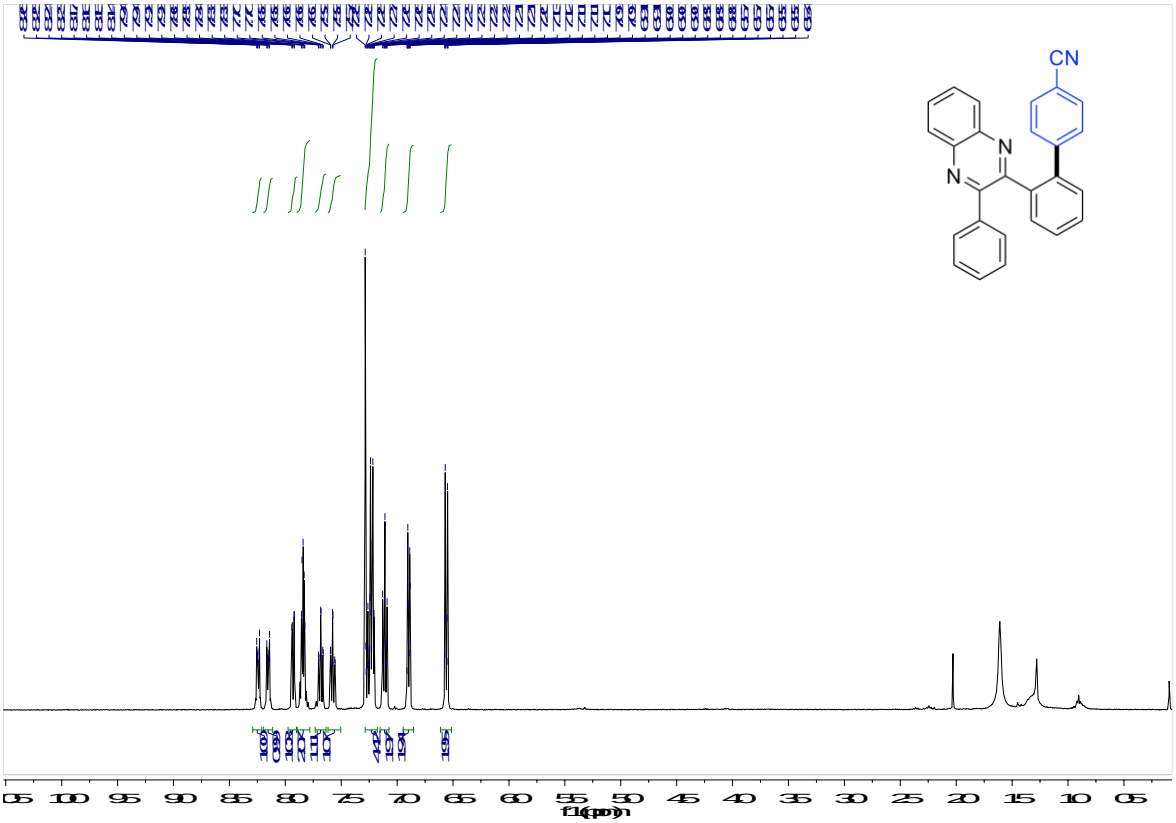

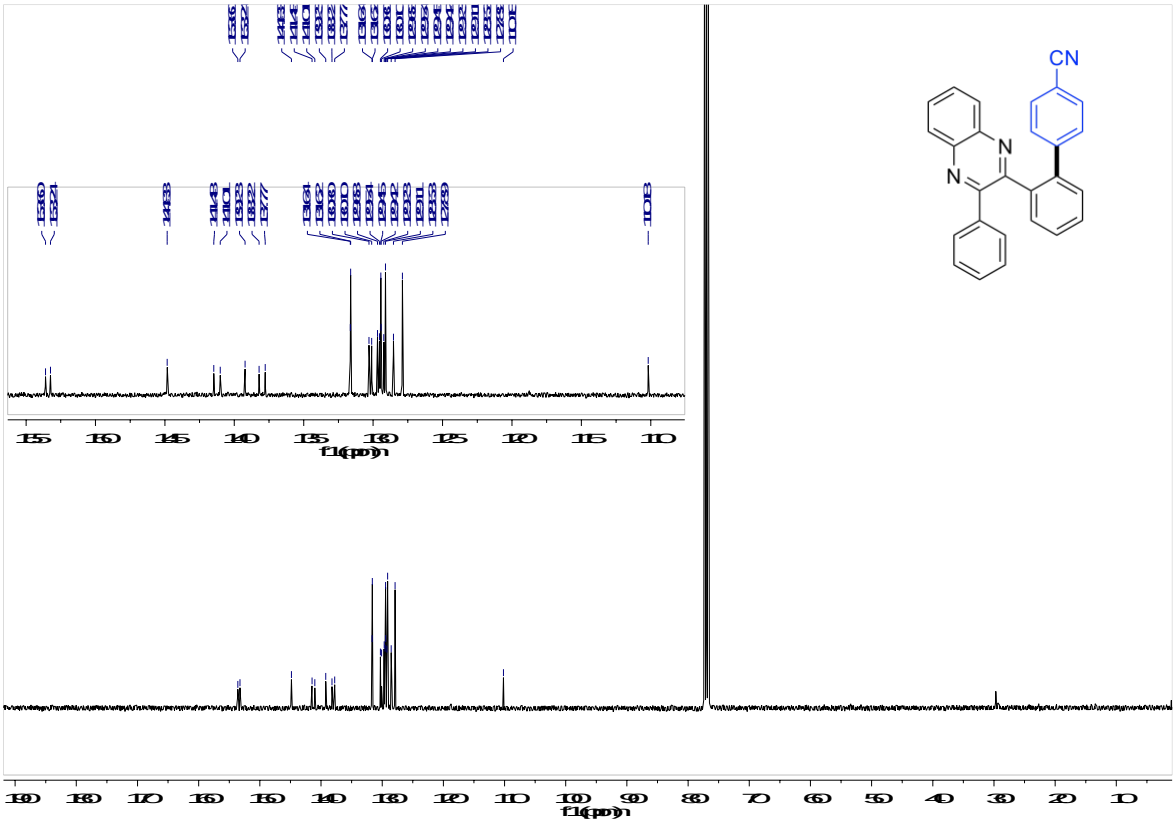

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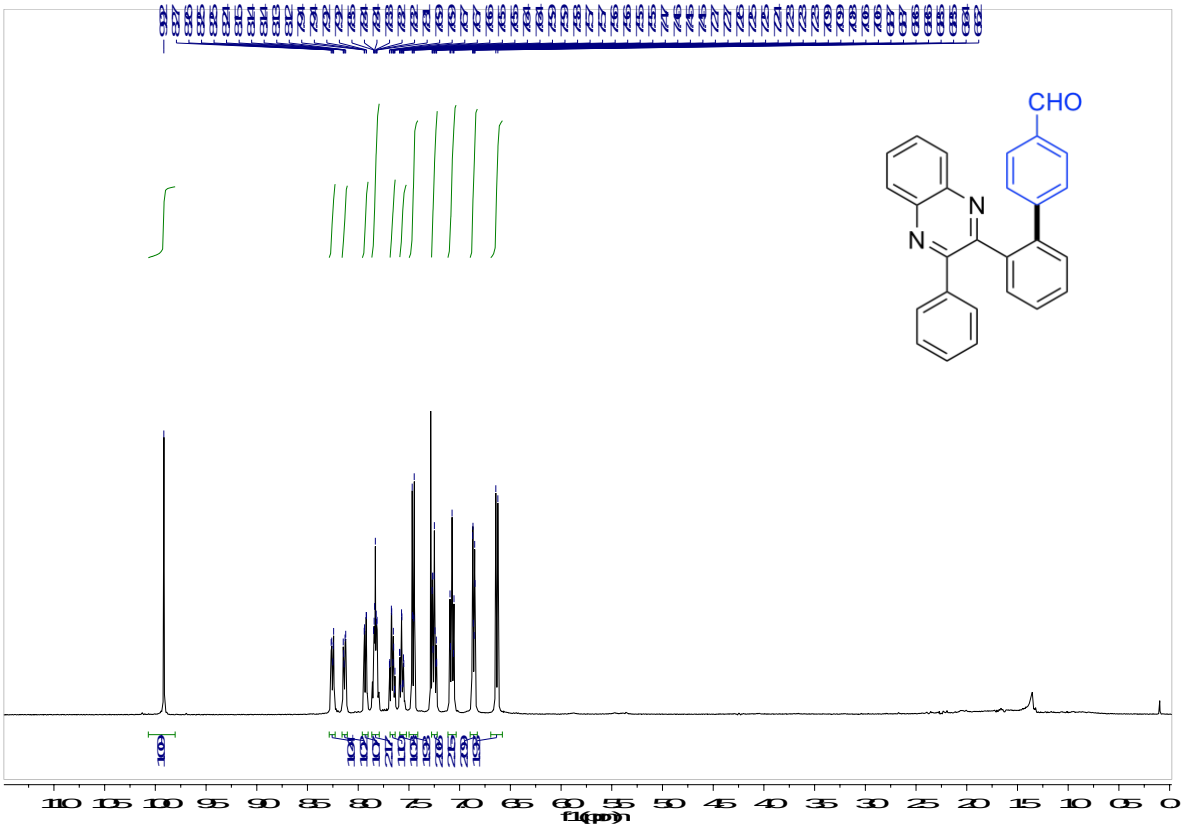

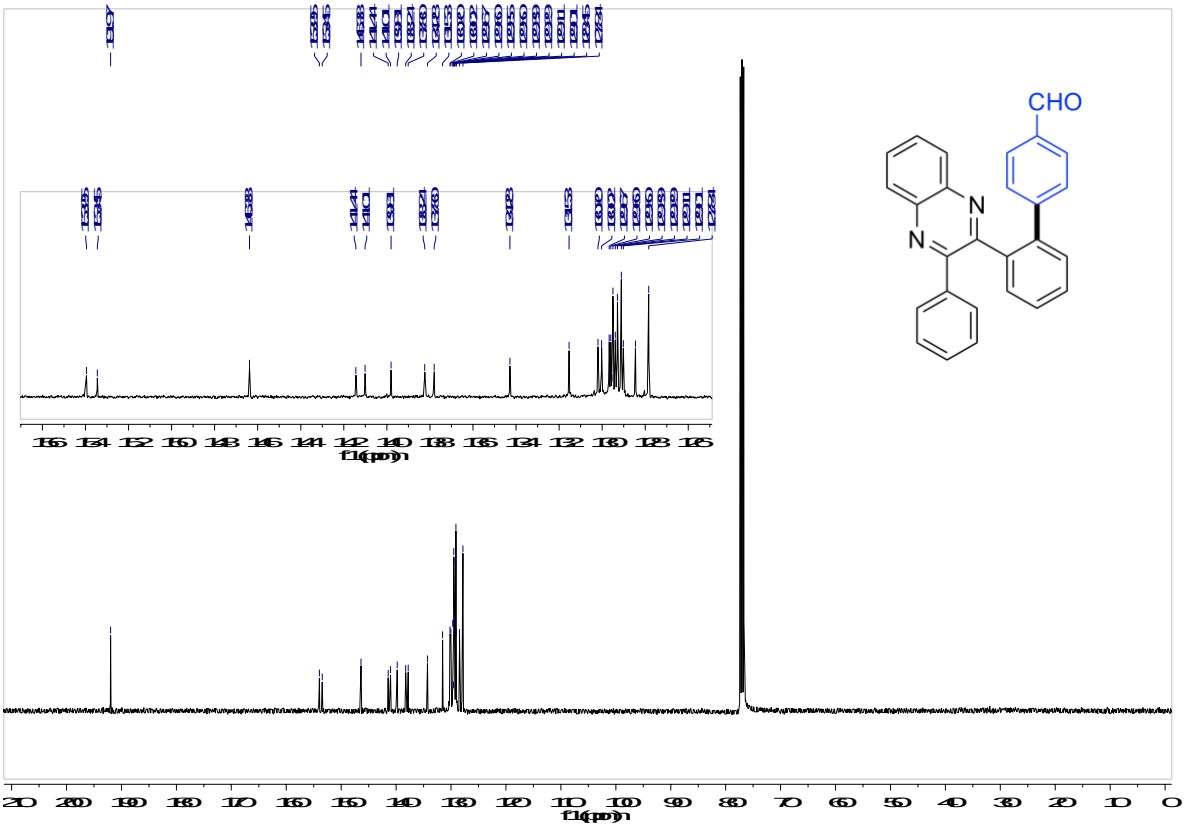

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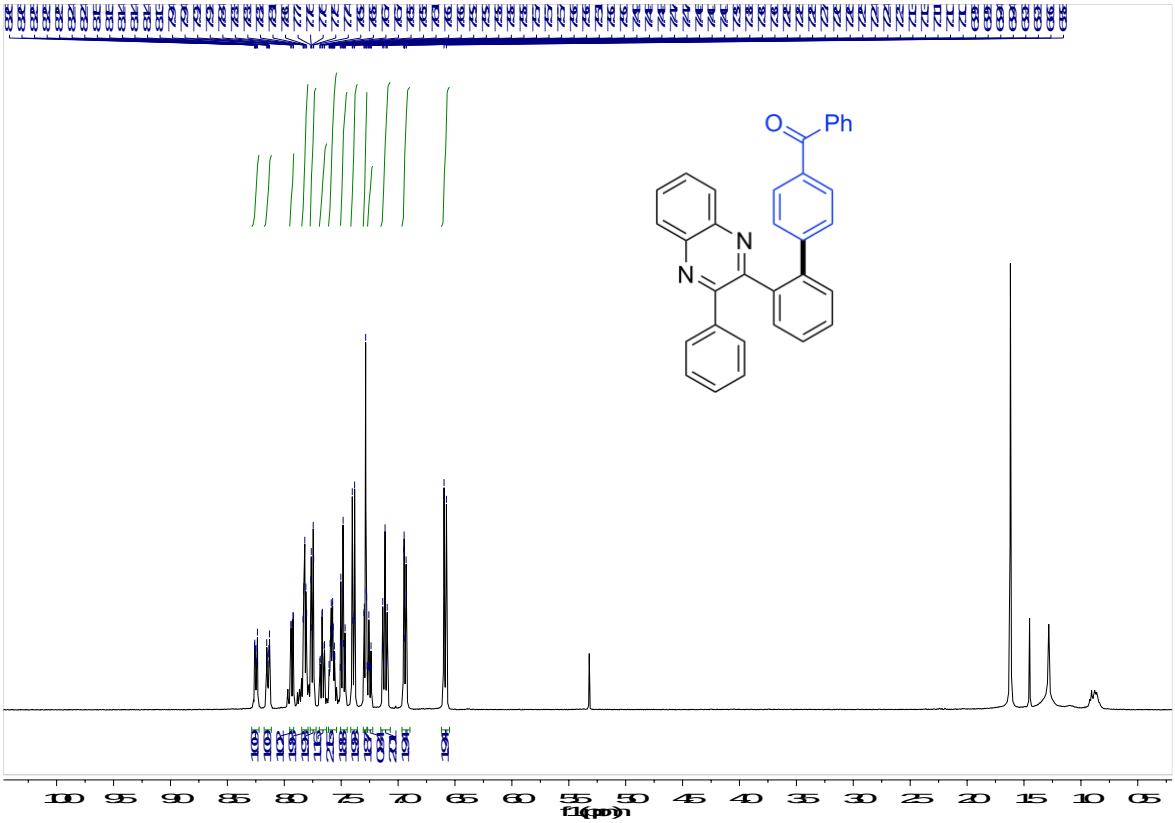

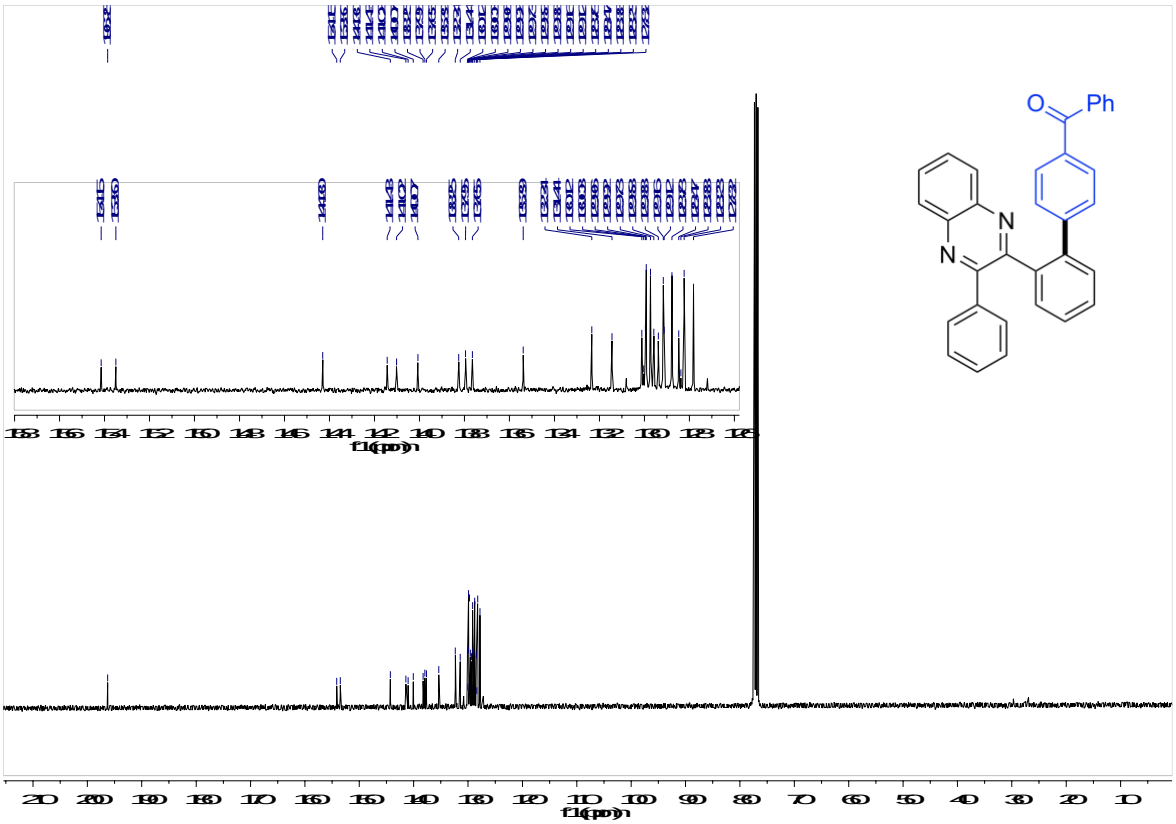

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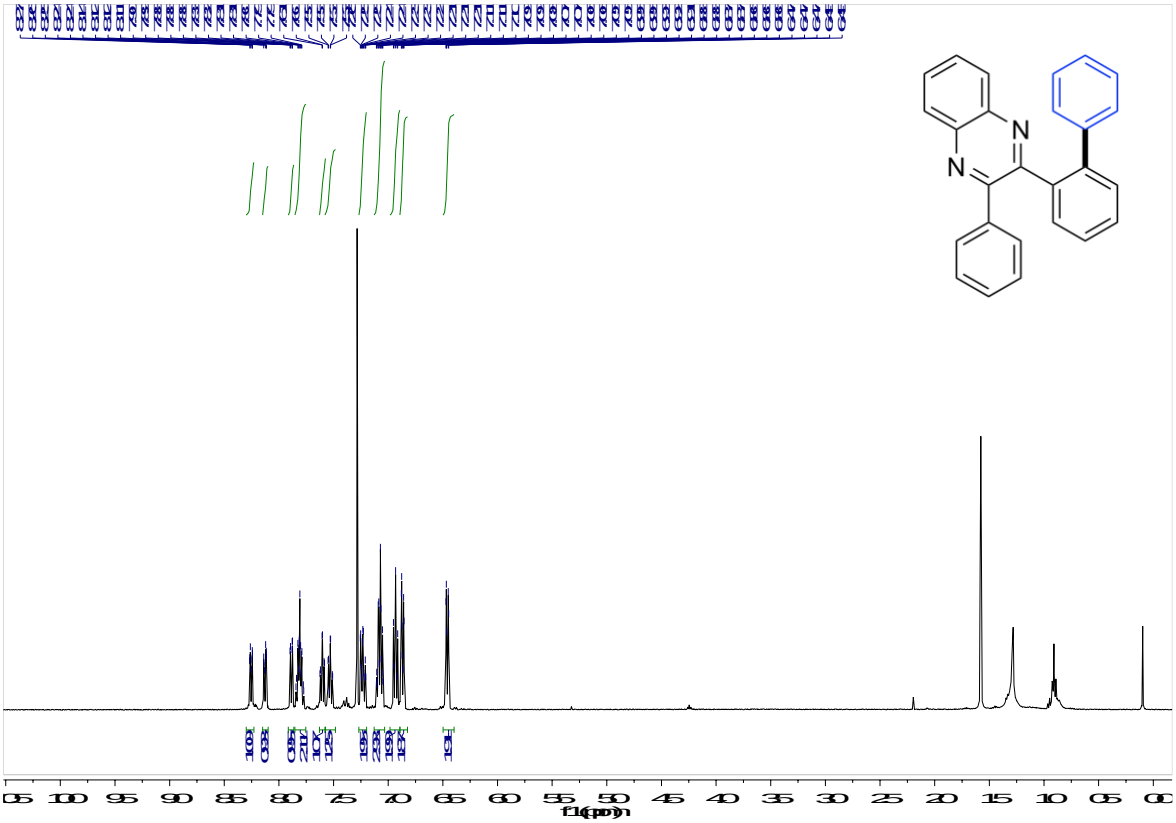

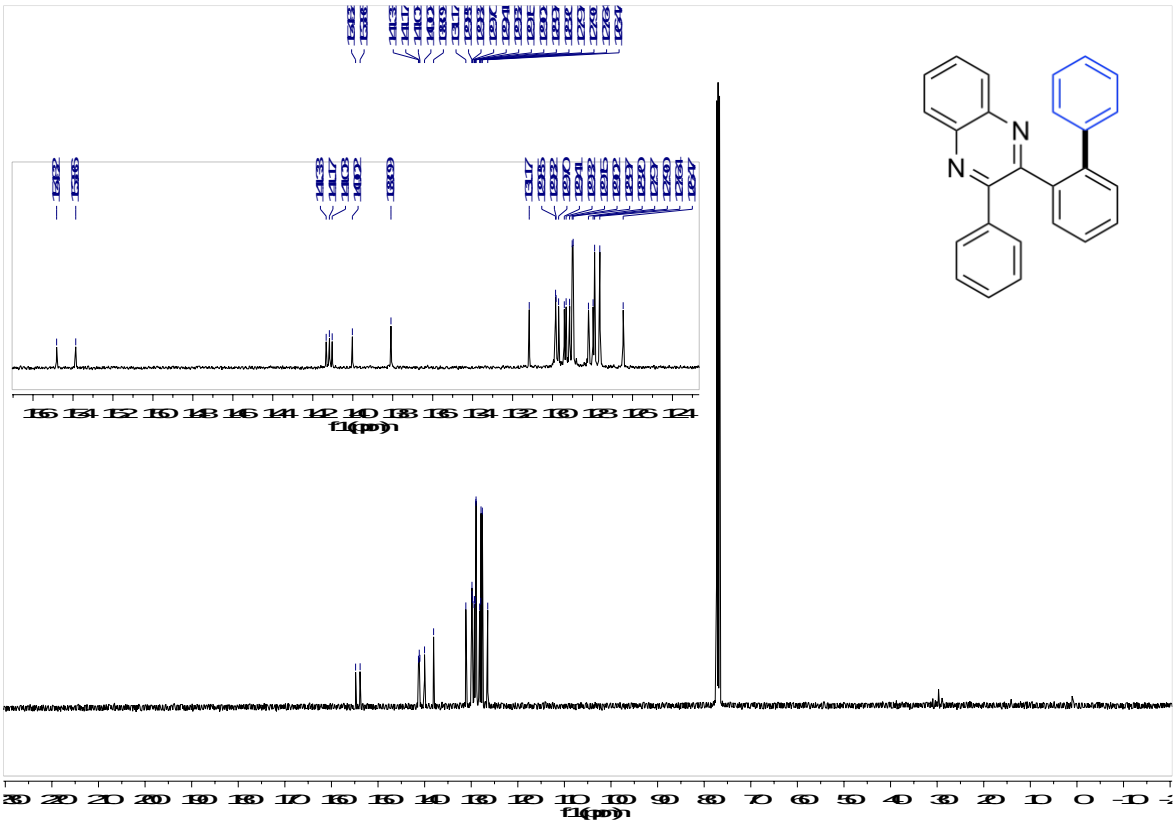

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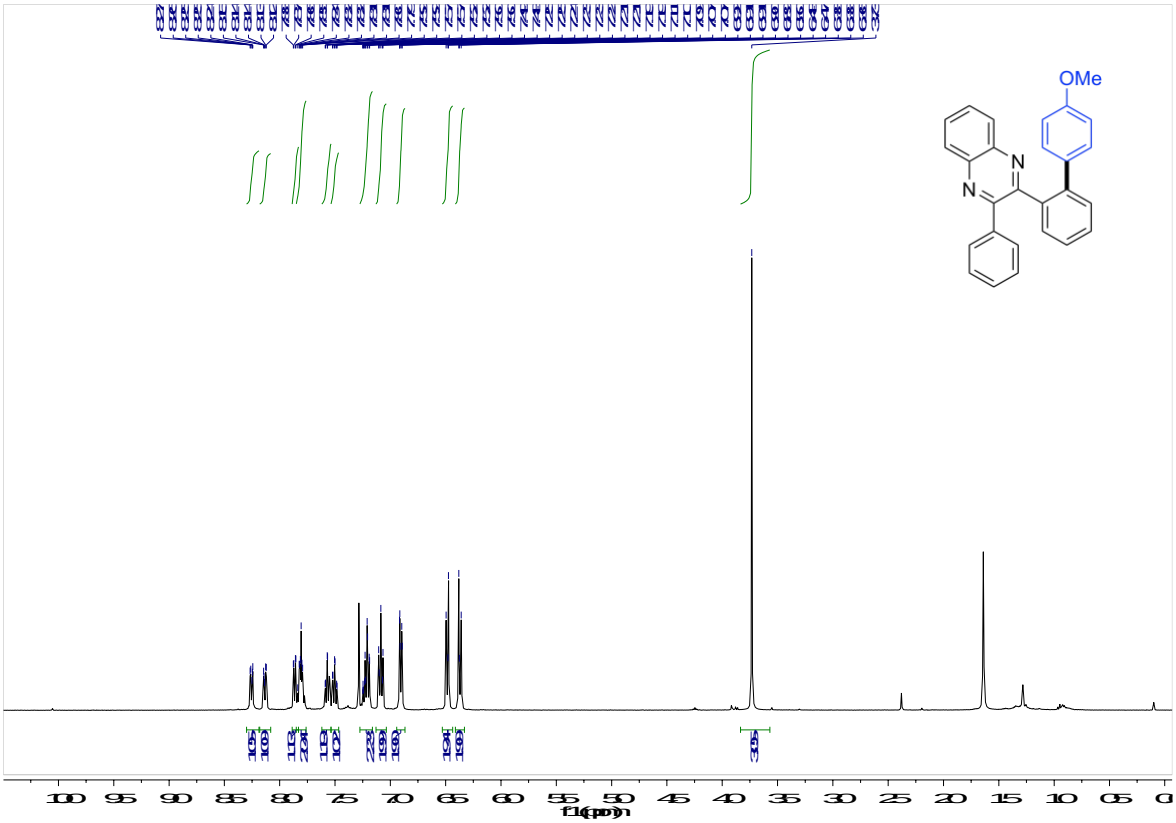

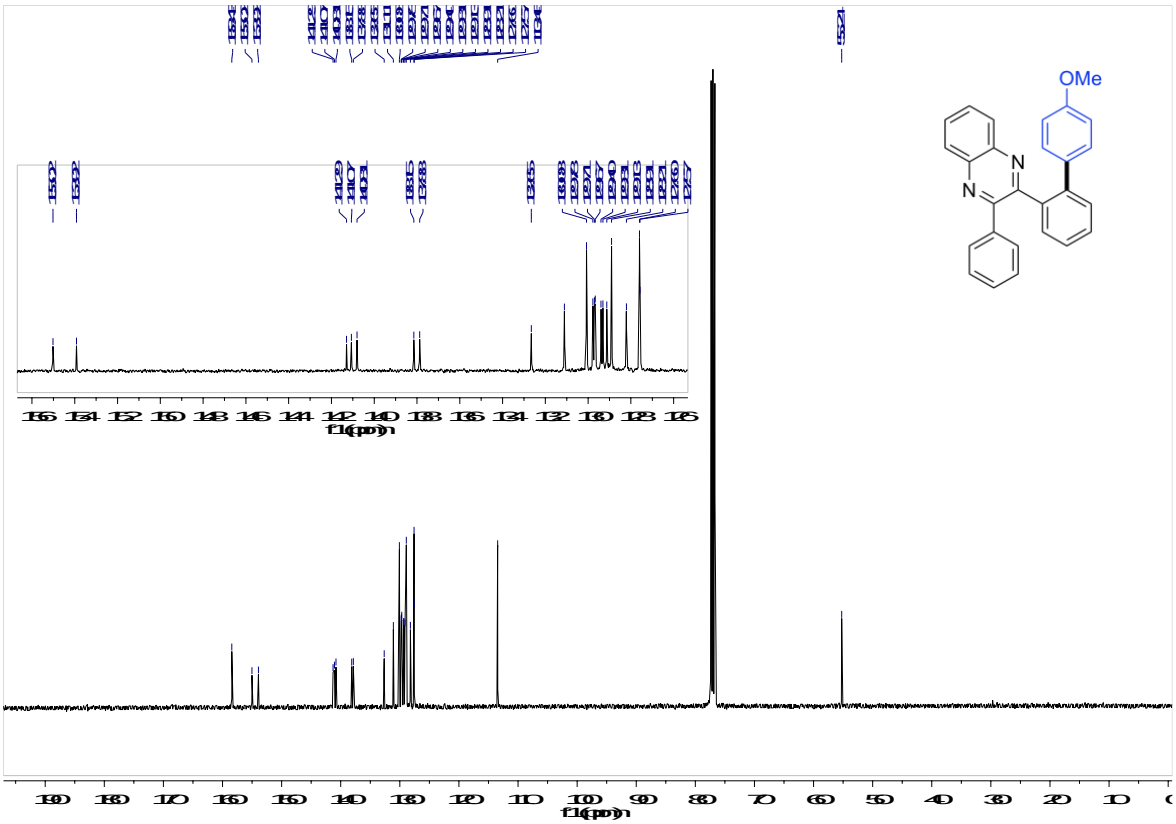

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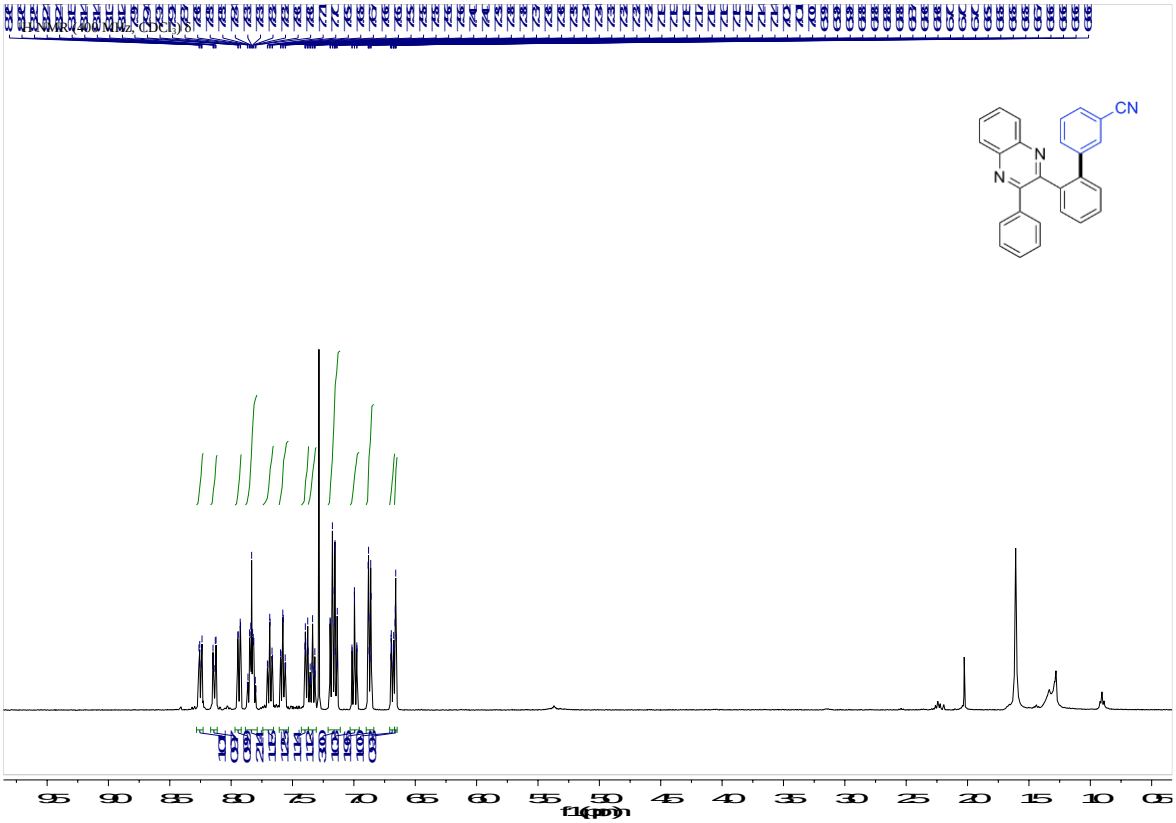

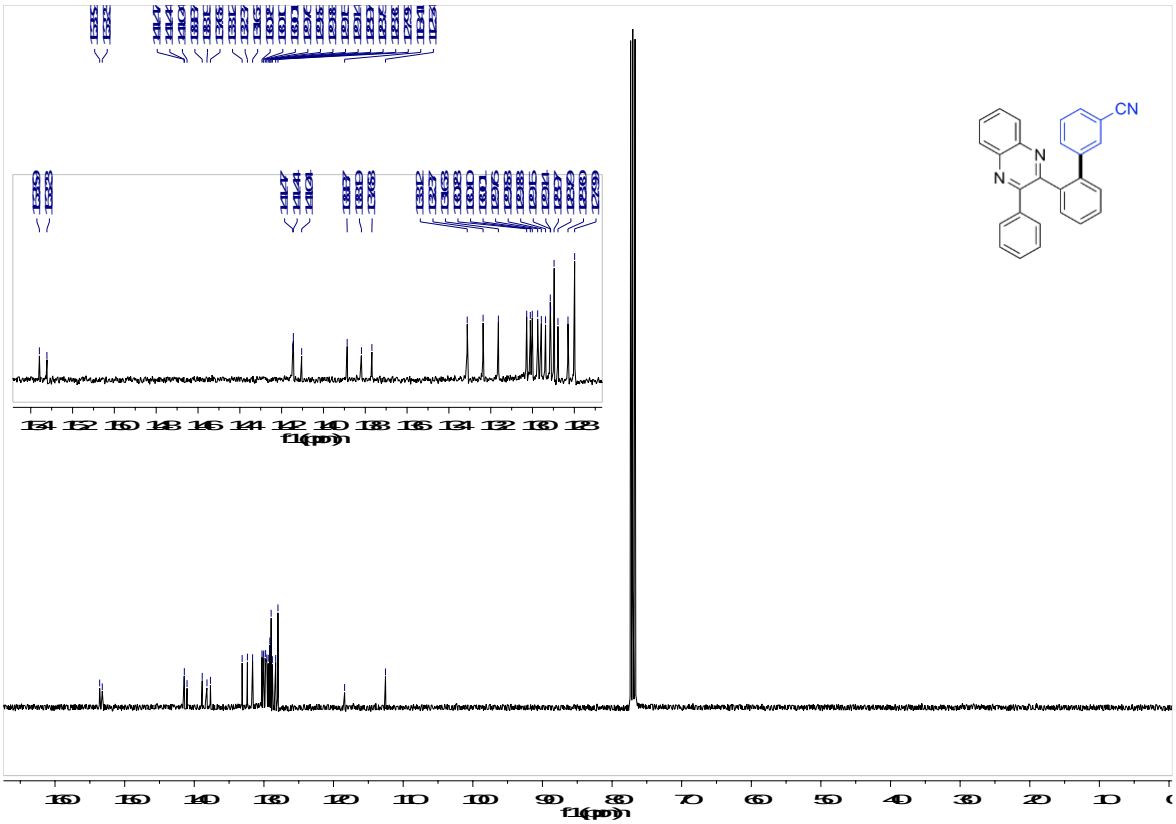

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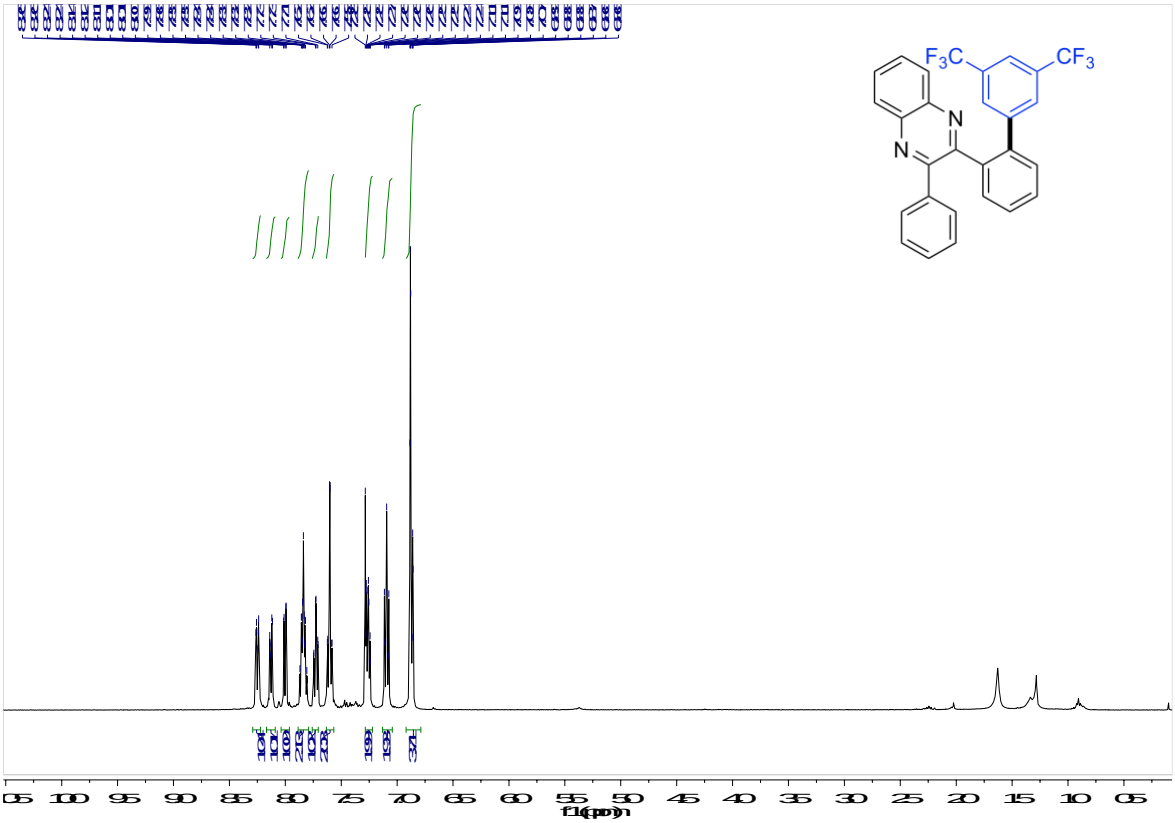

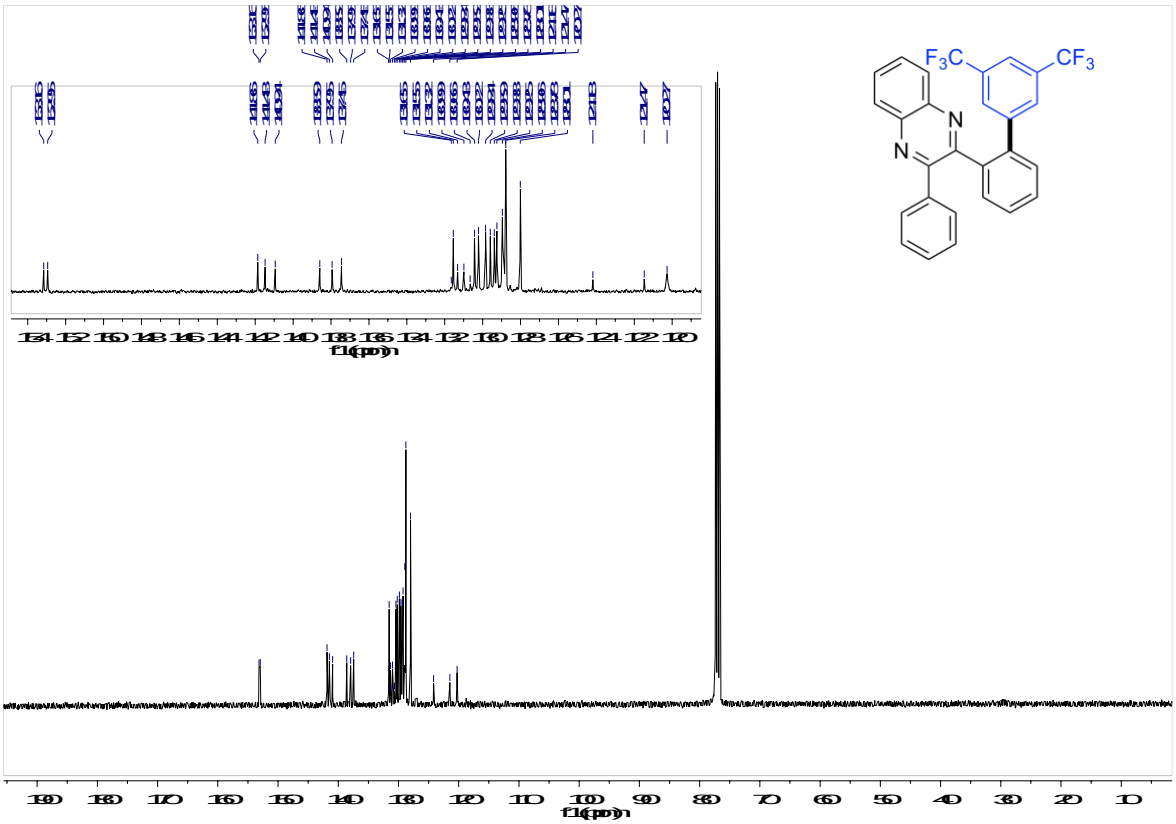

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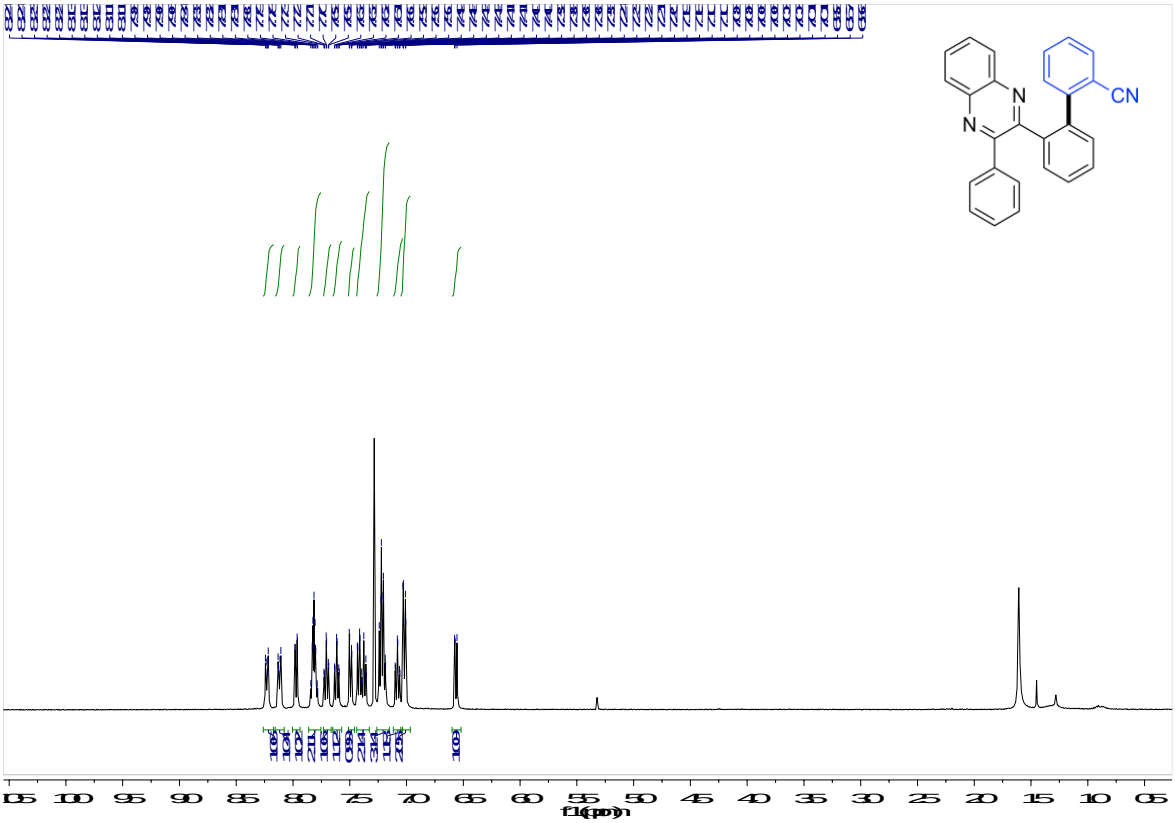
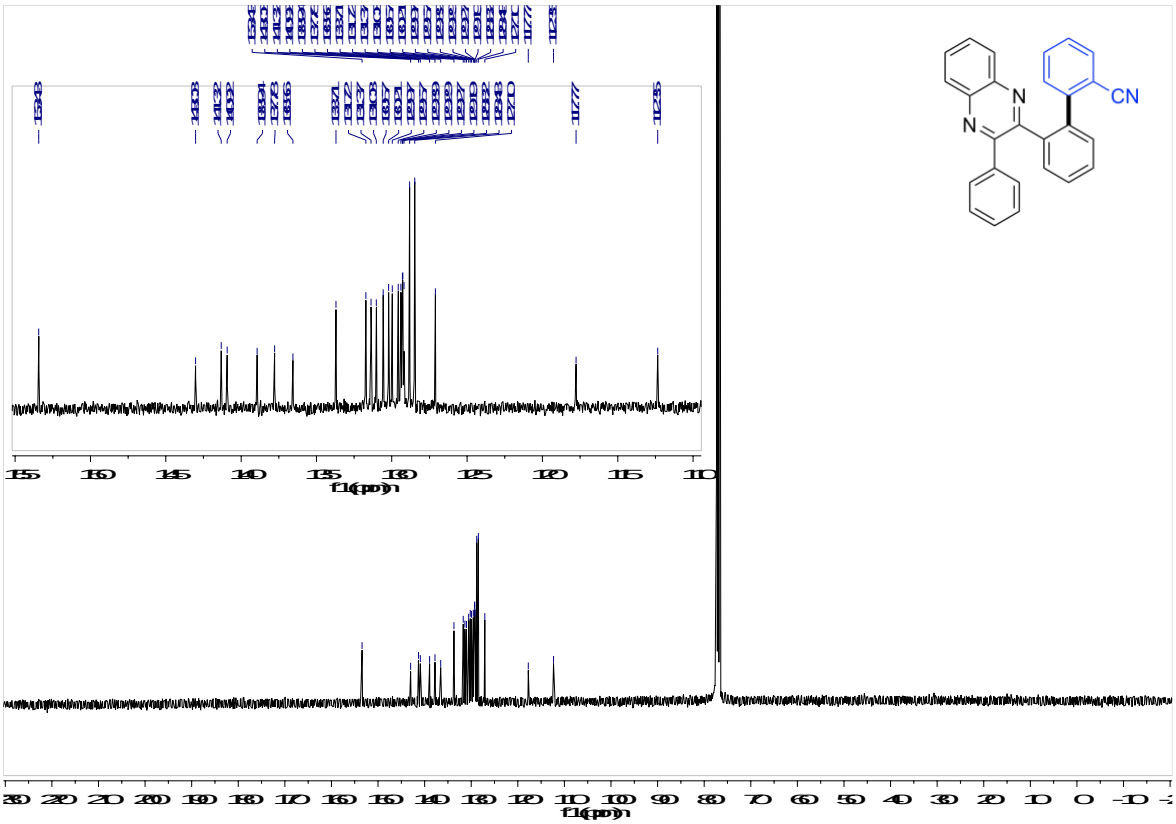
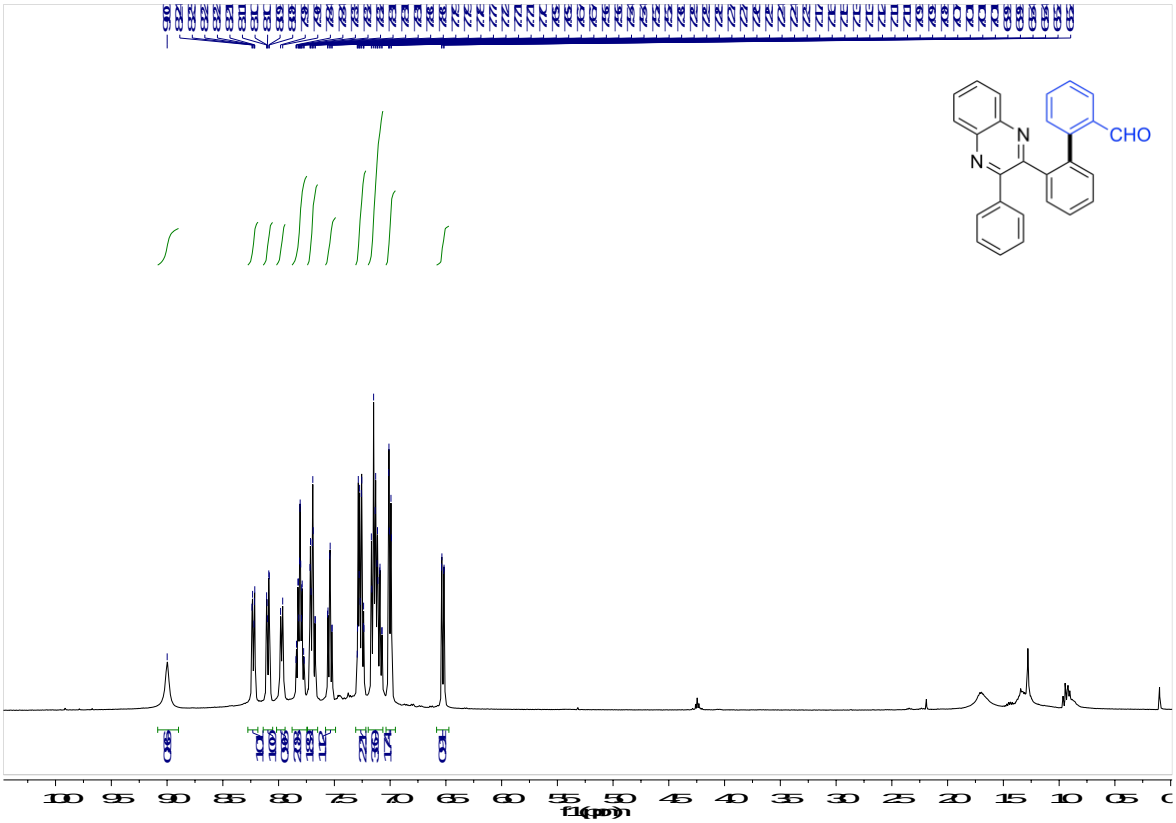
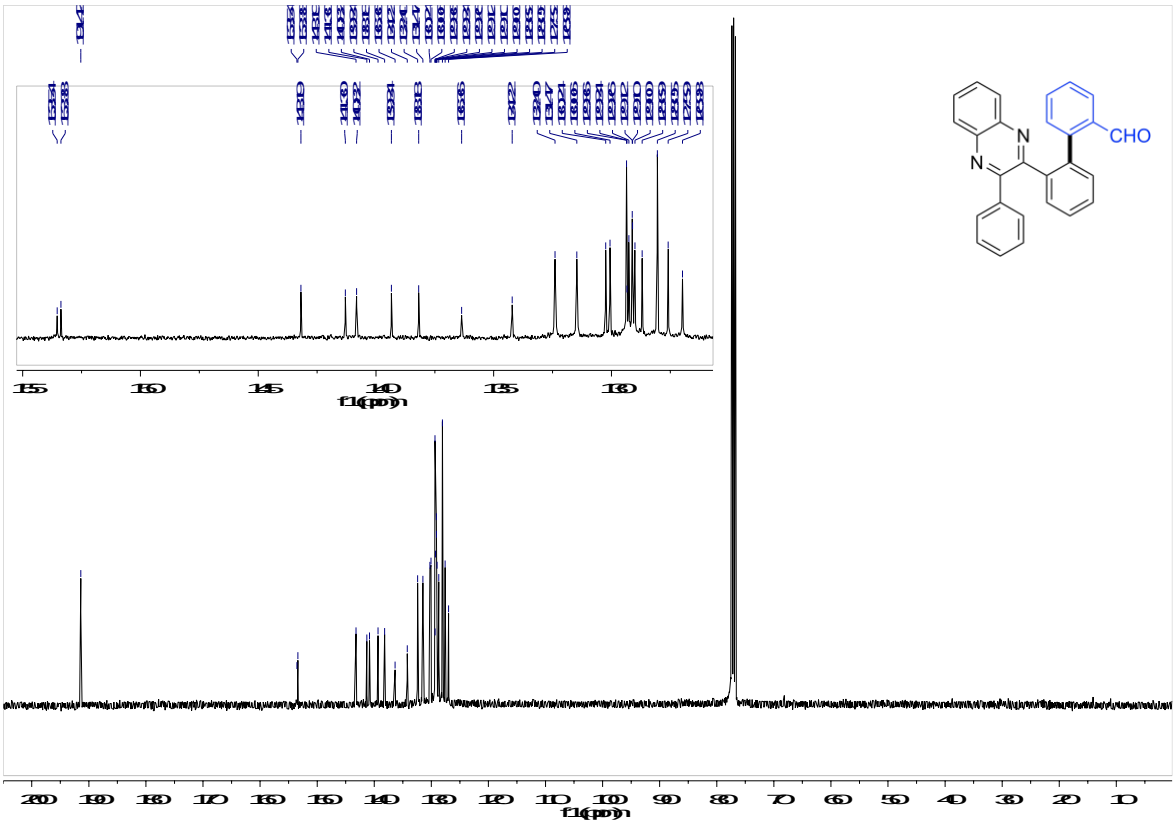




11





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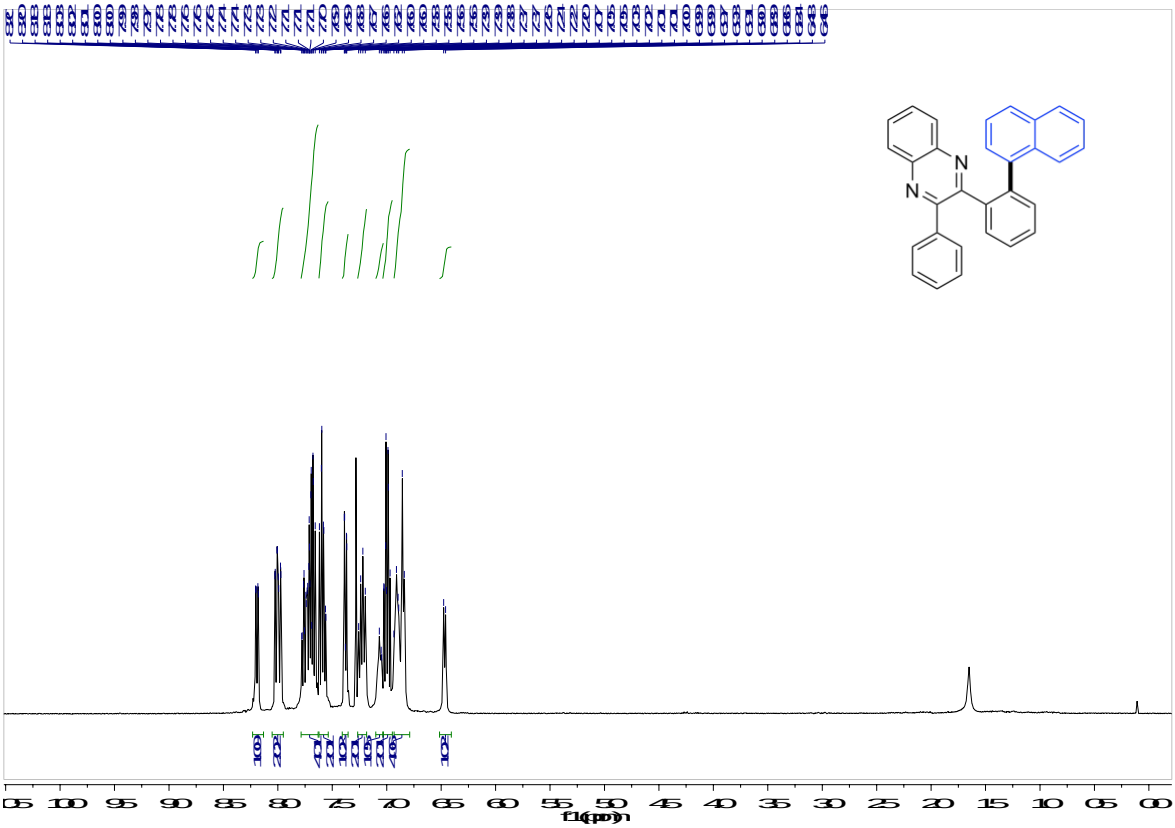

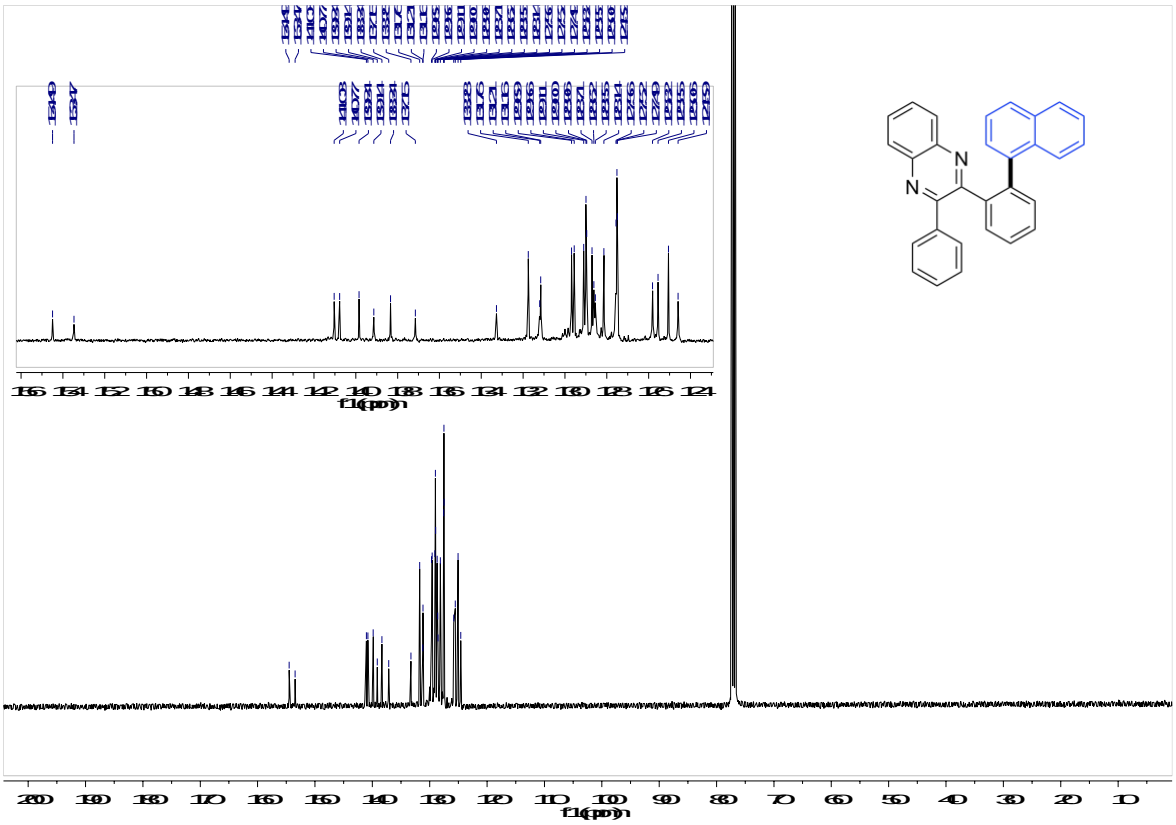

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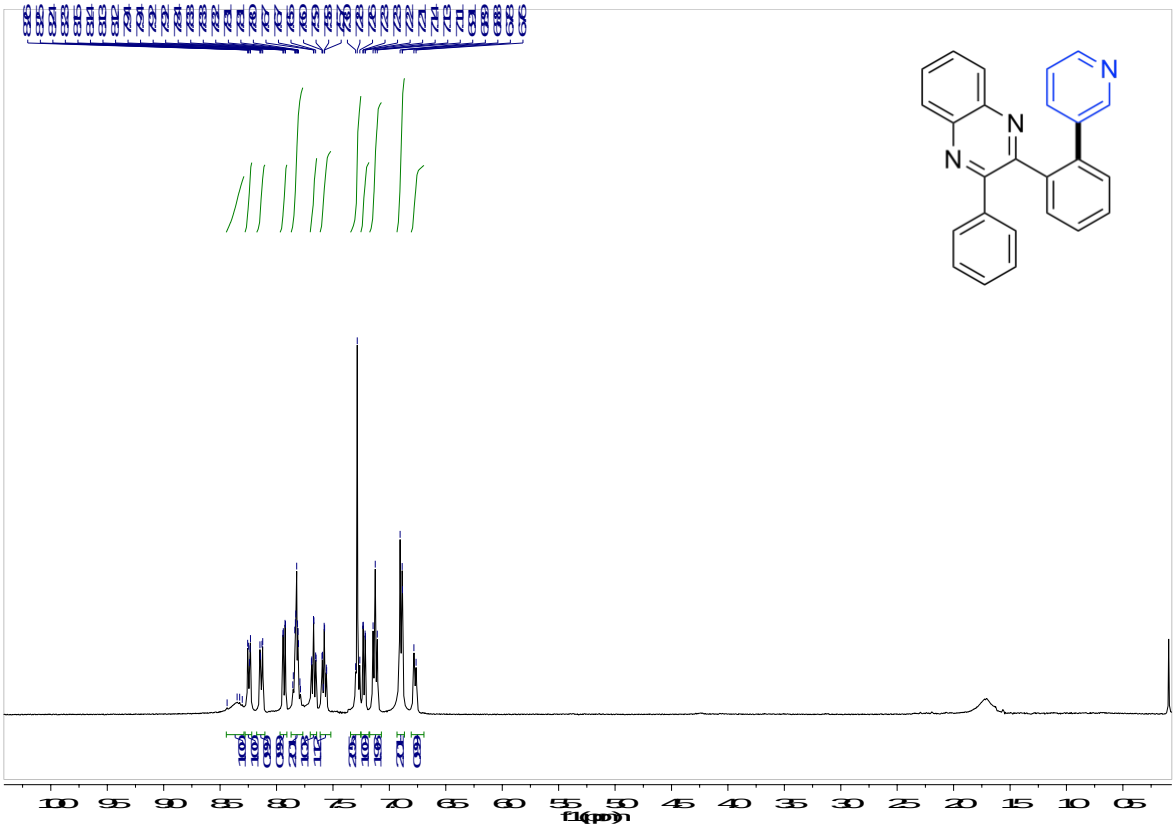
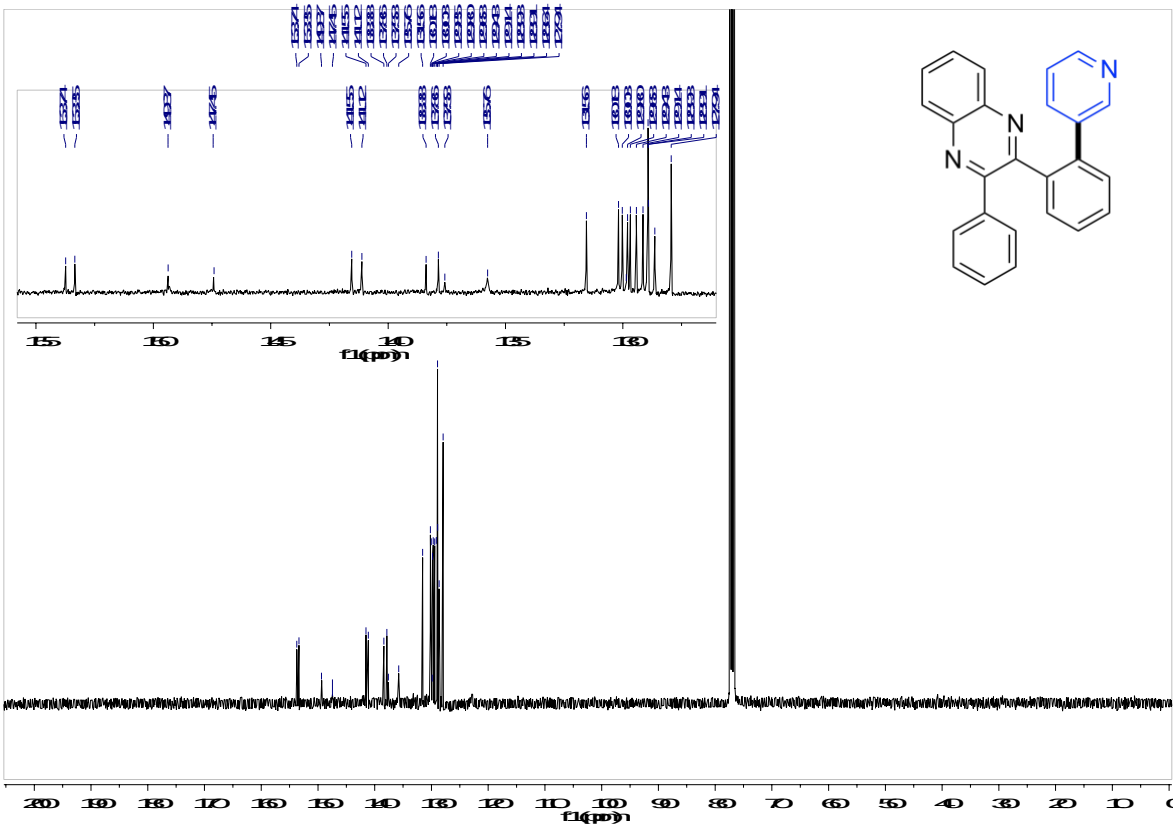
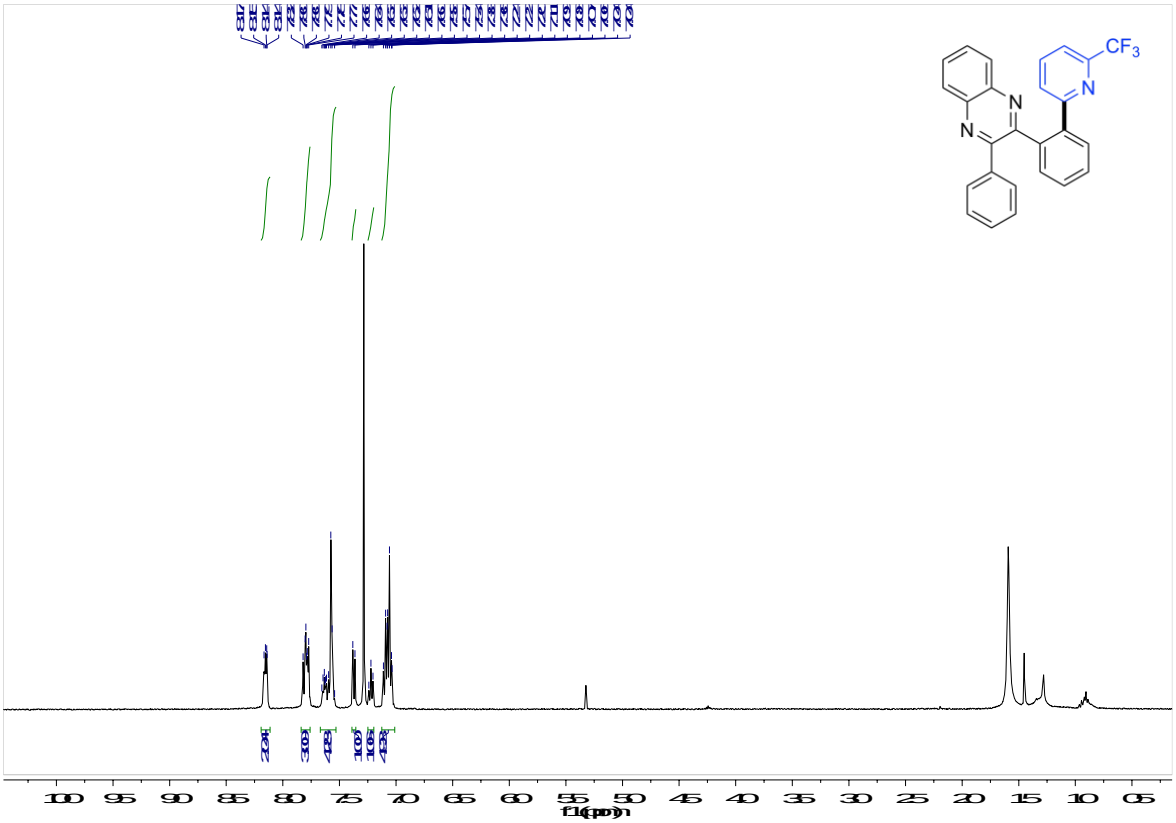
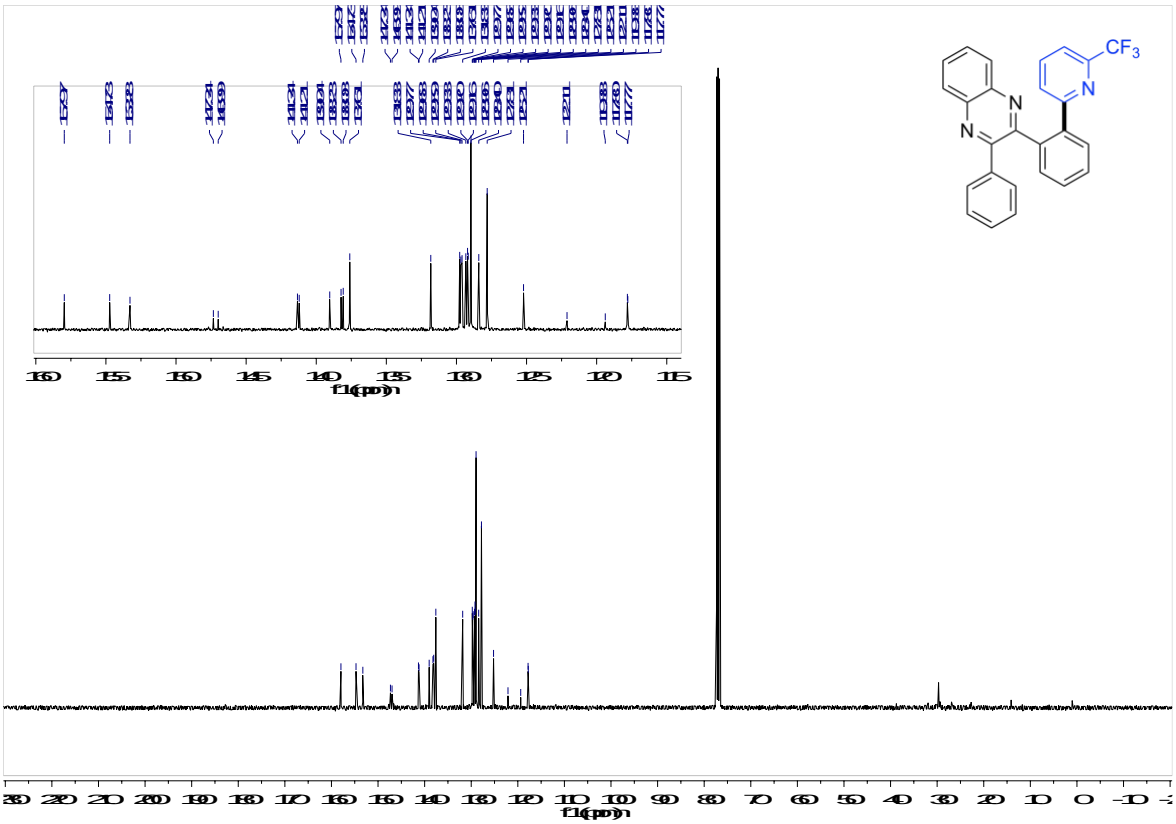


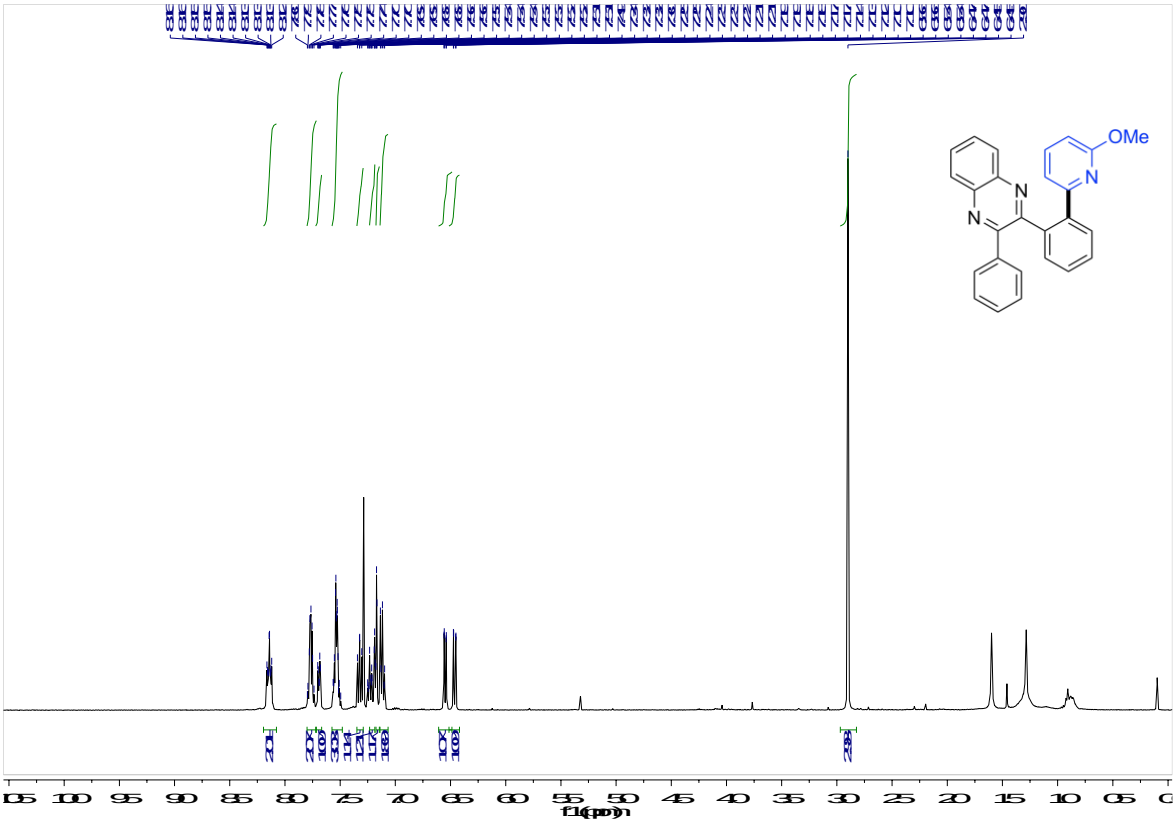


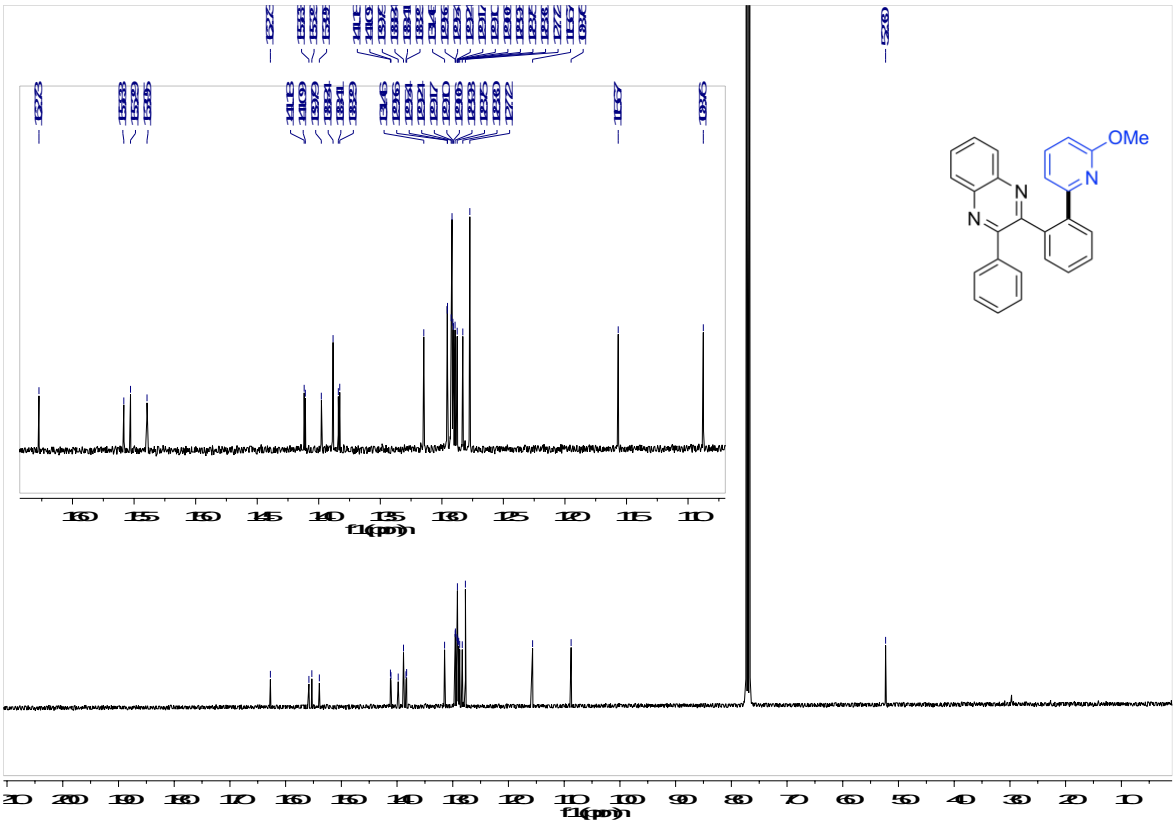
14



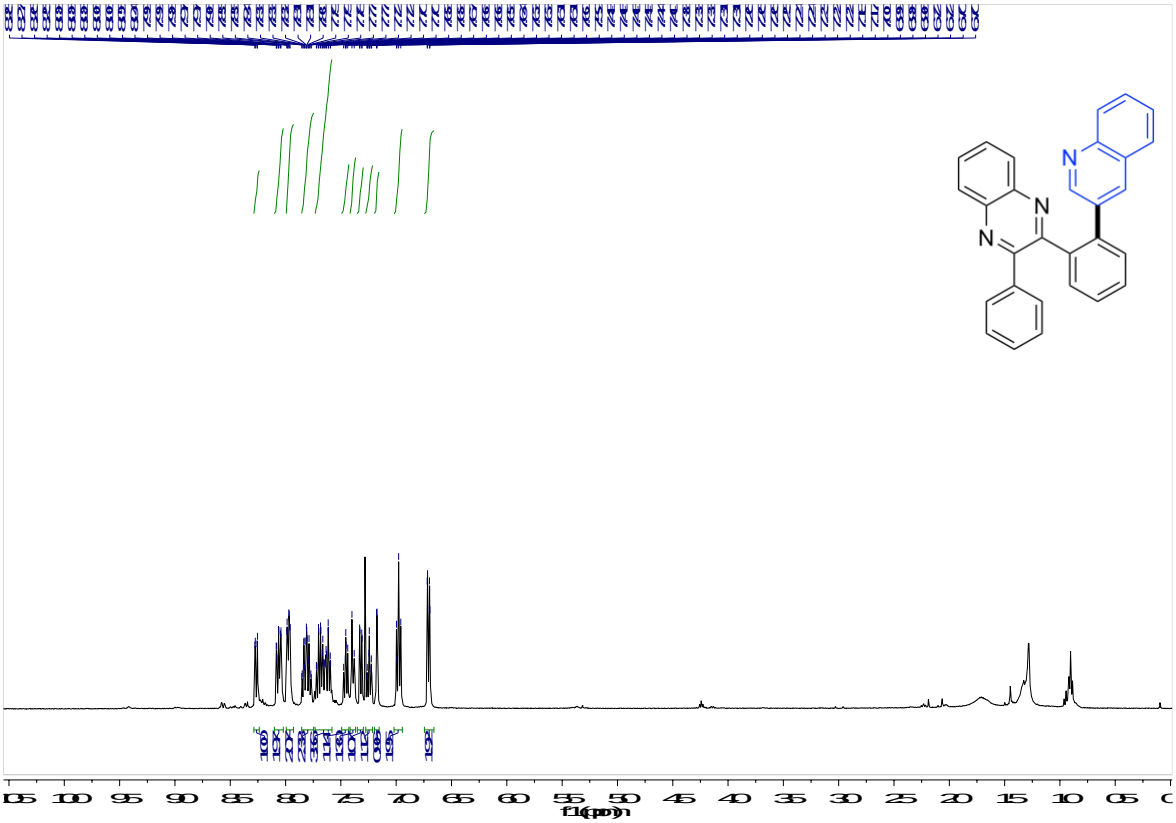


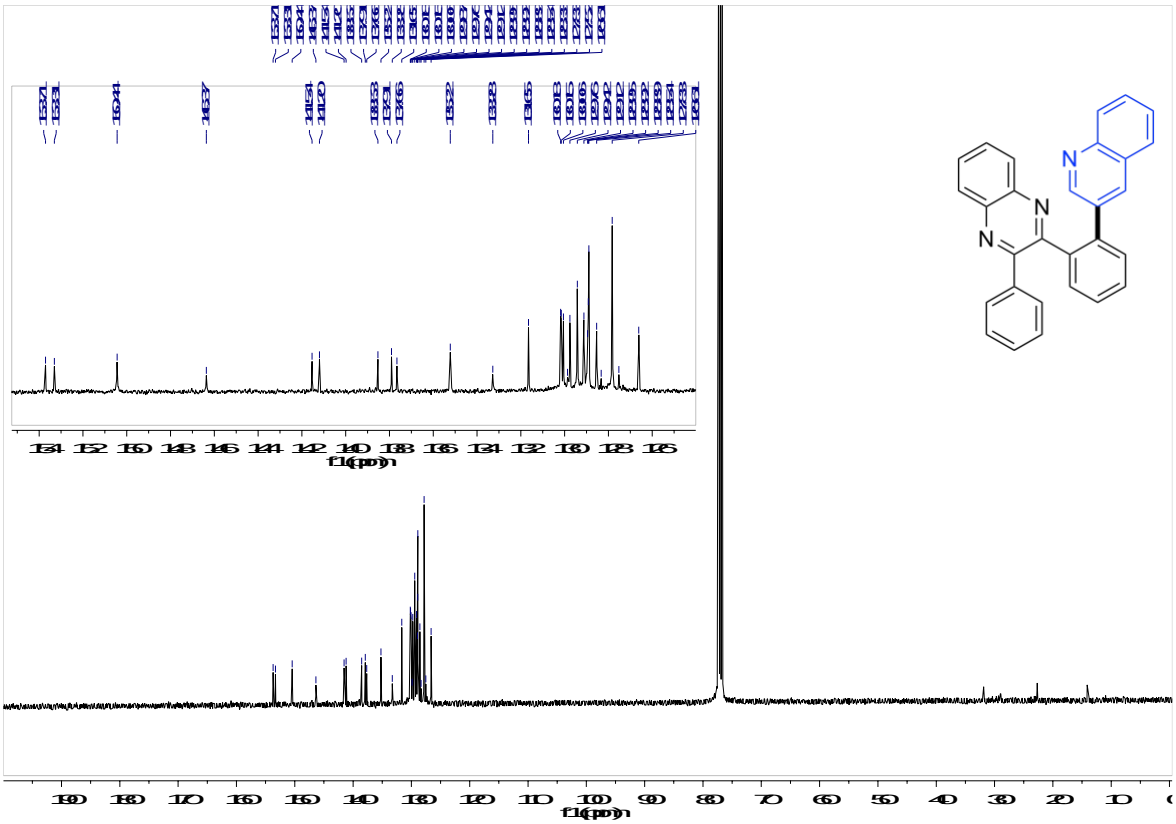
15



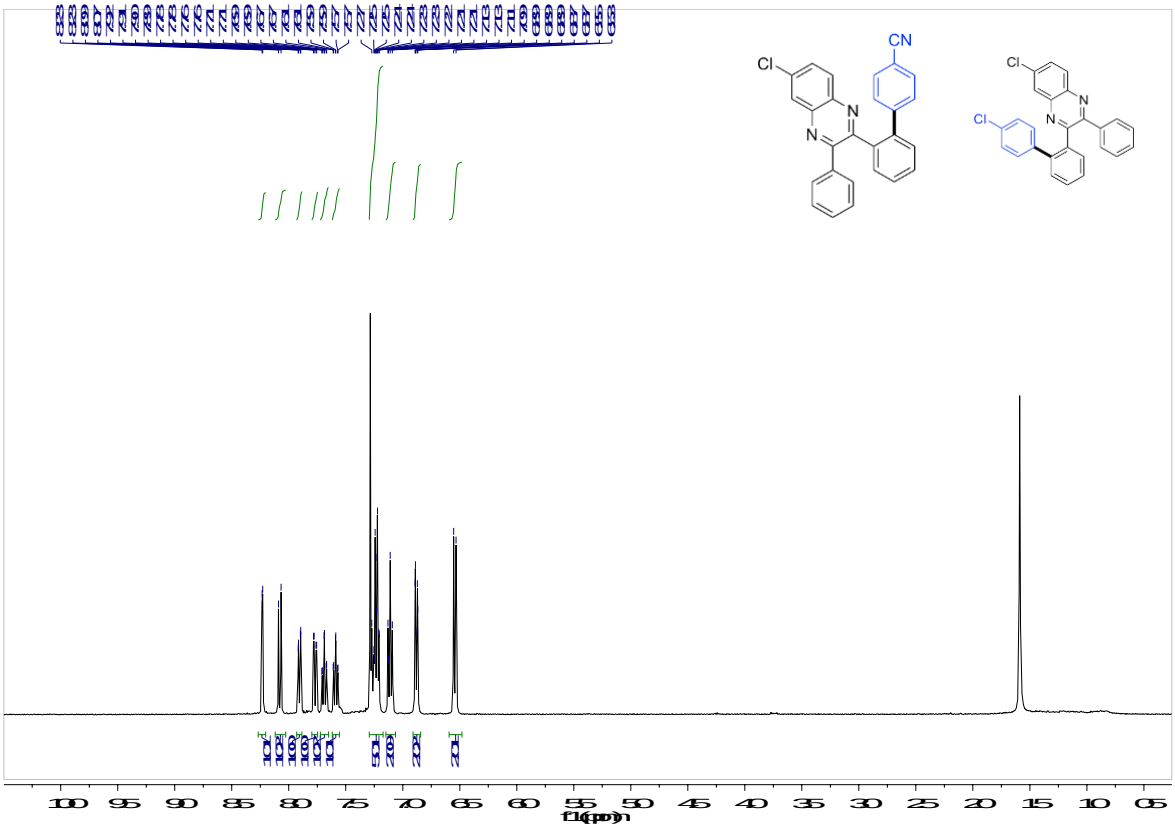


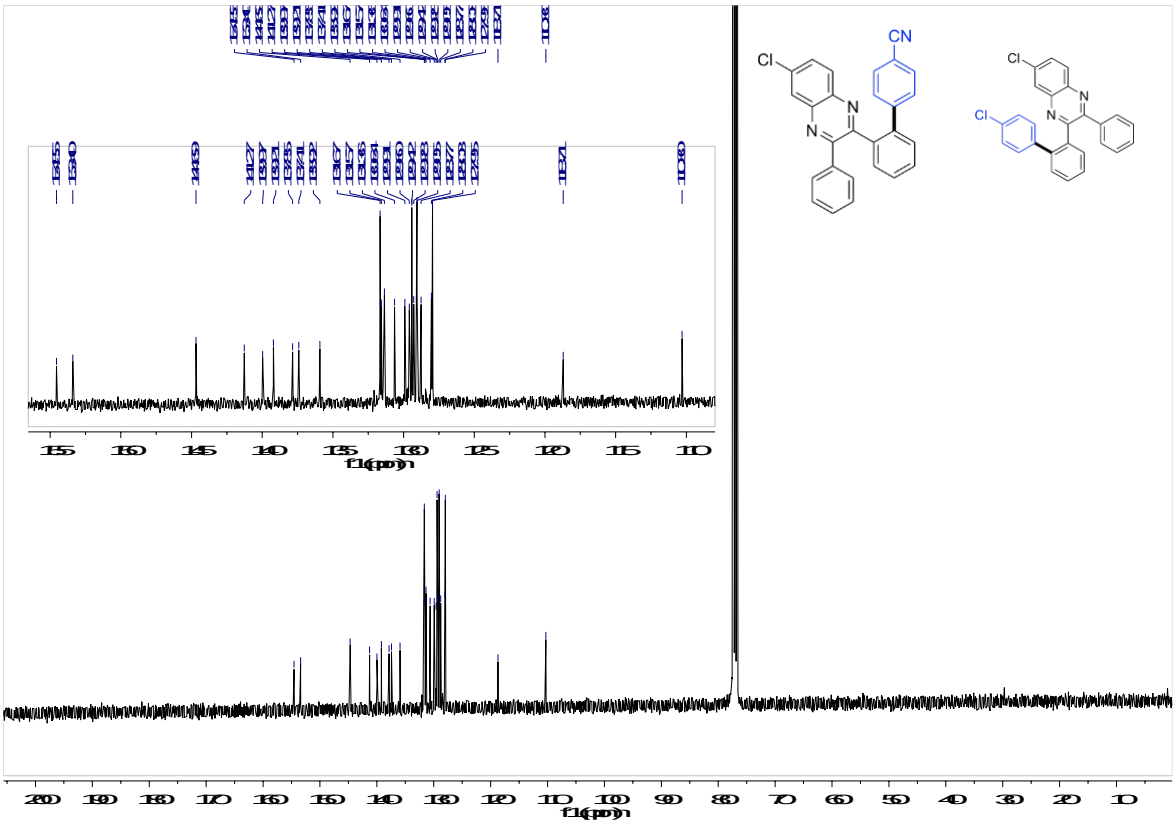
16



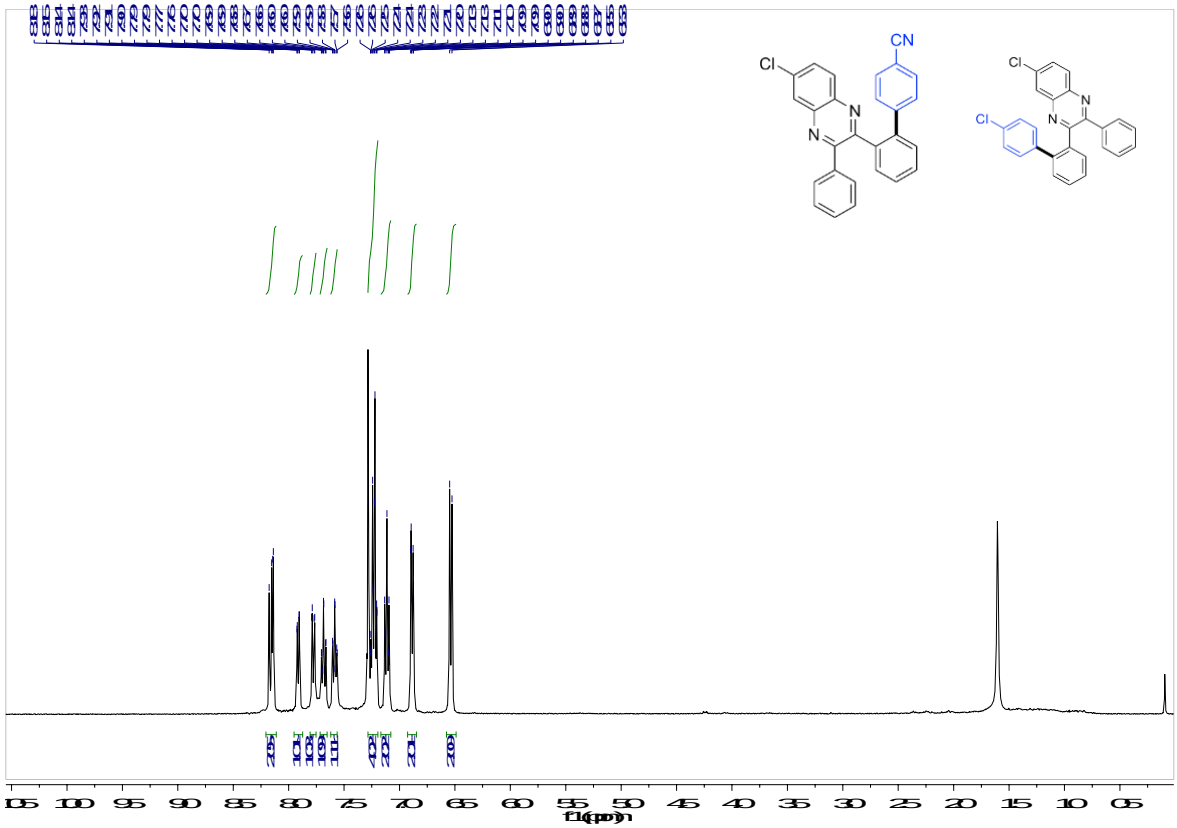


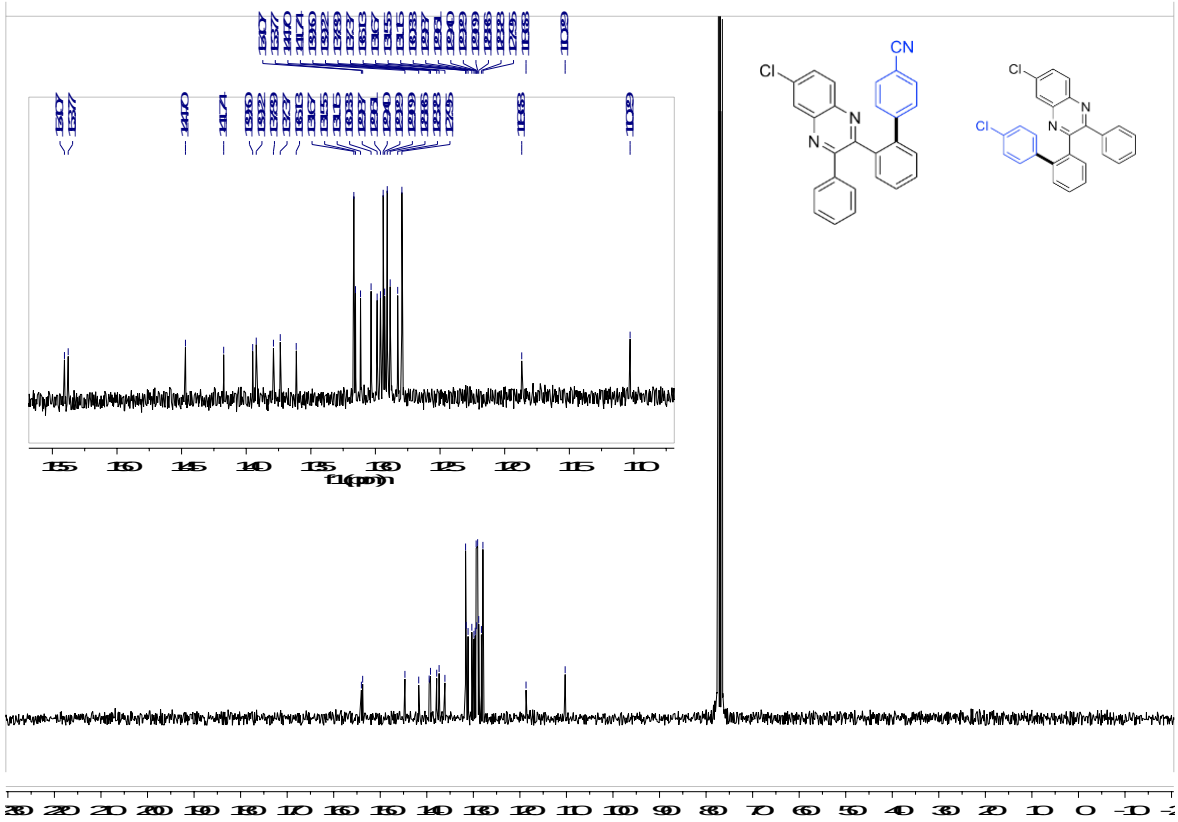
17a or 17b



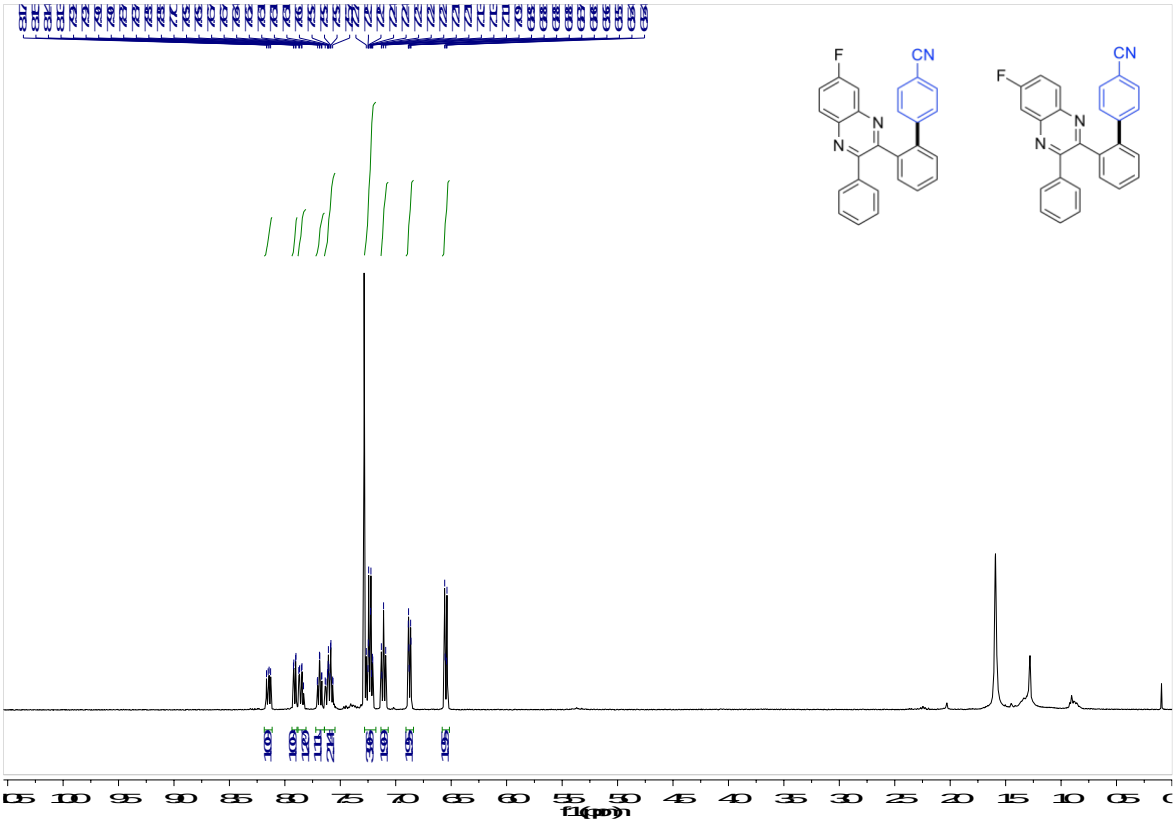


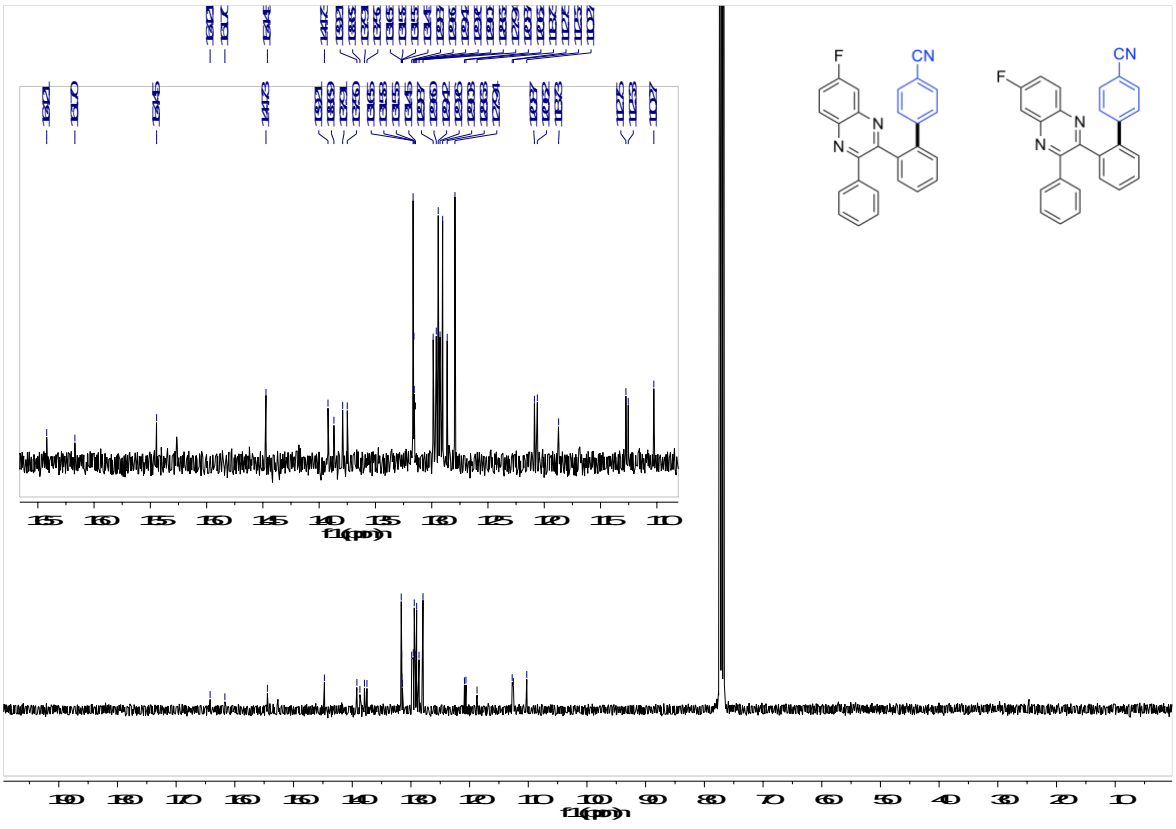
17a or 17b





18a or 18b





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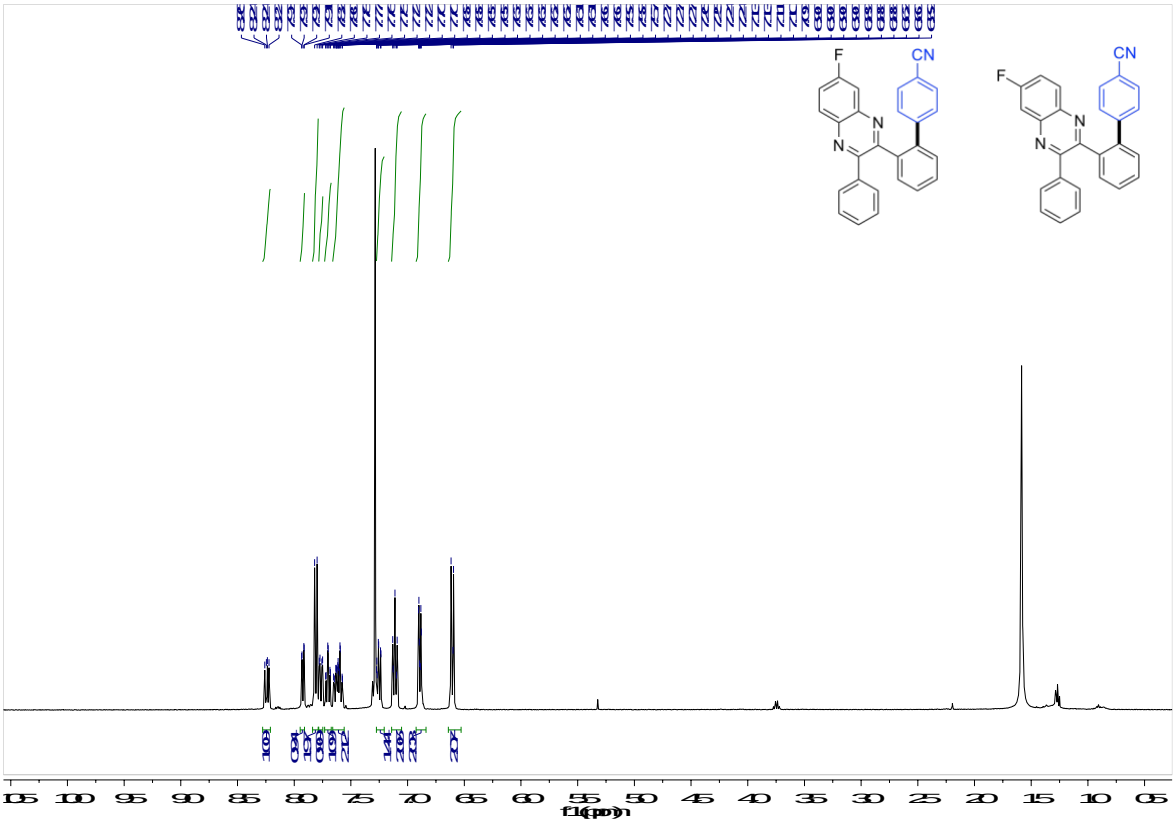
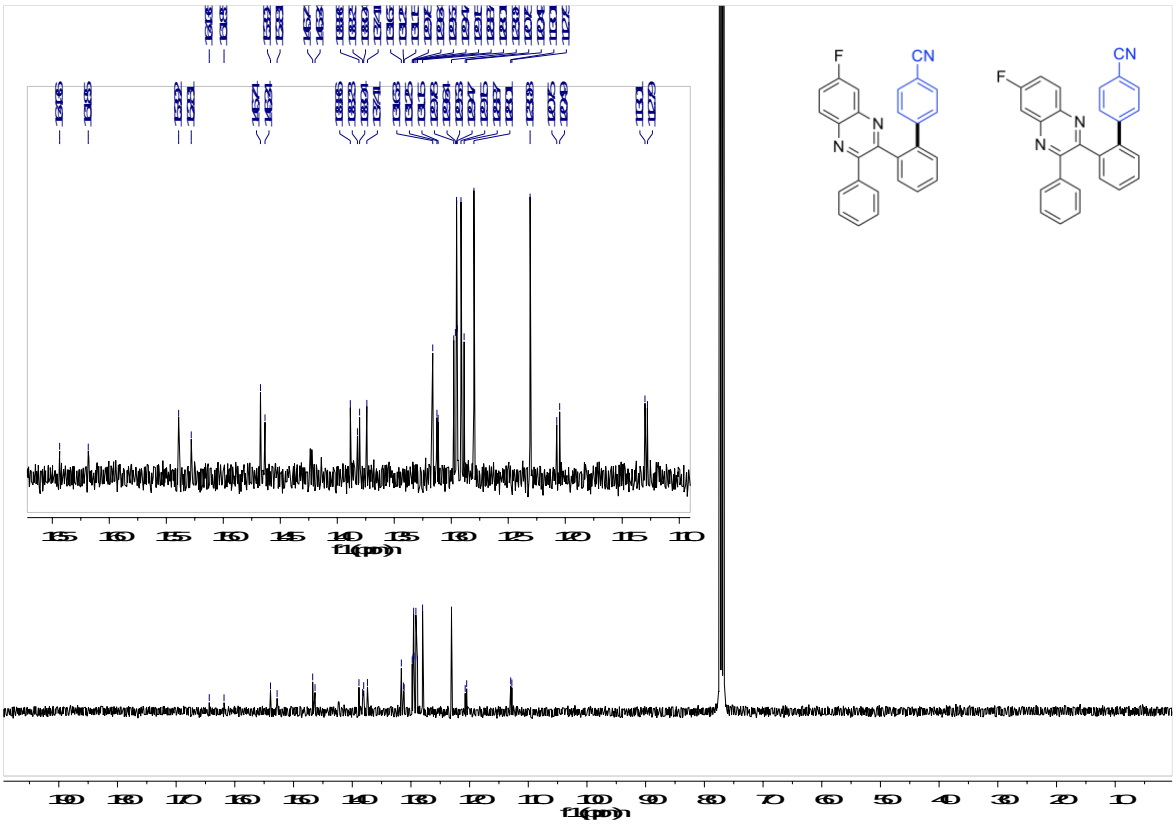
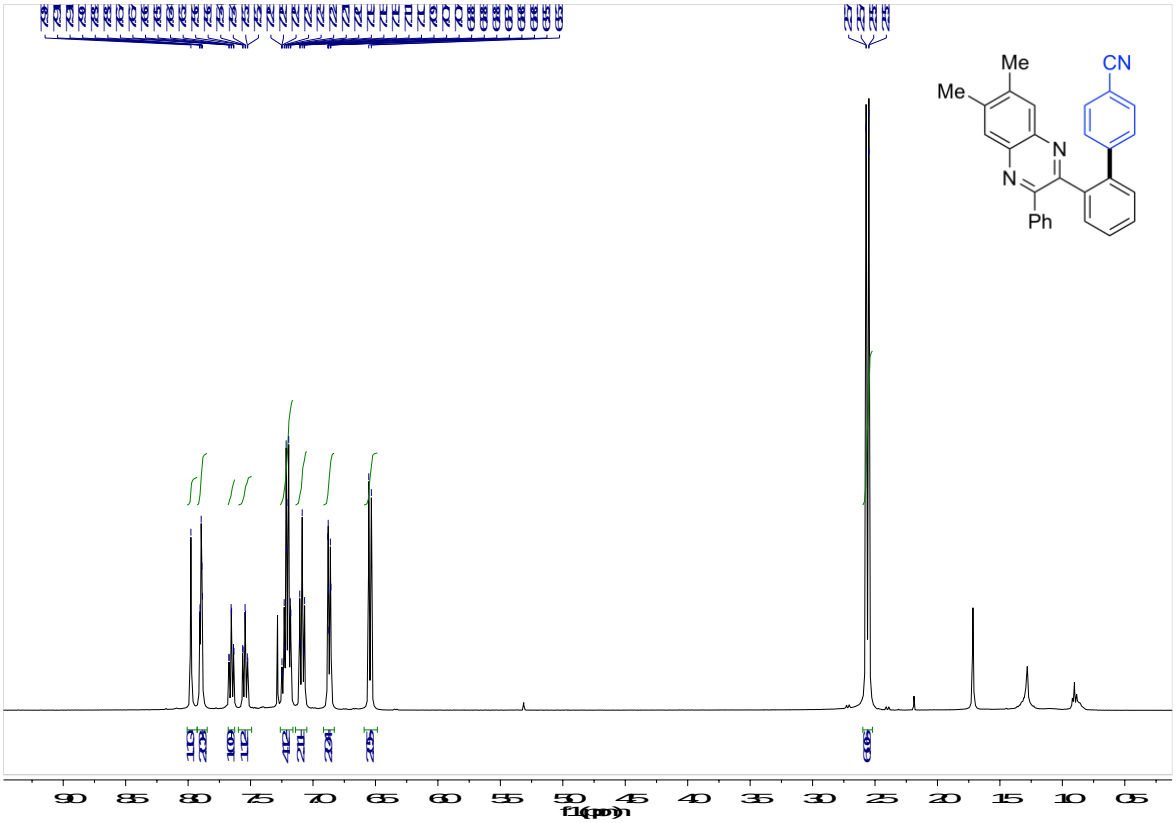
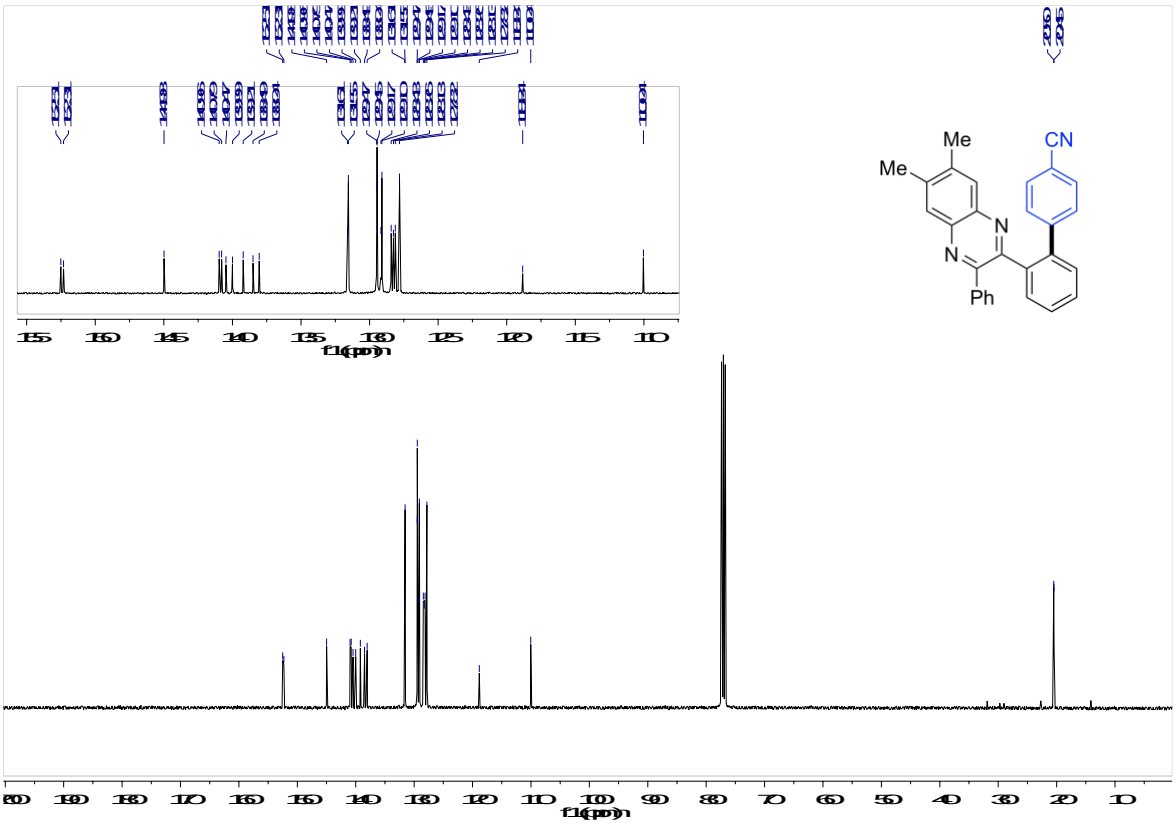




19





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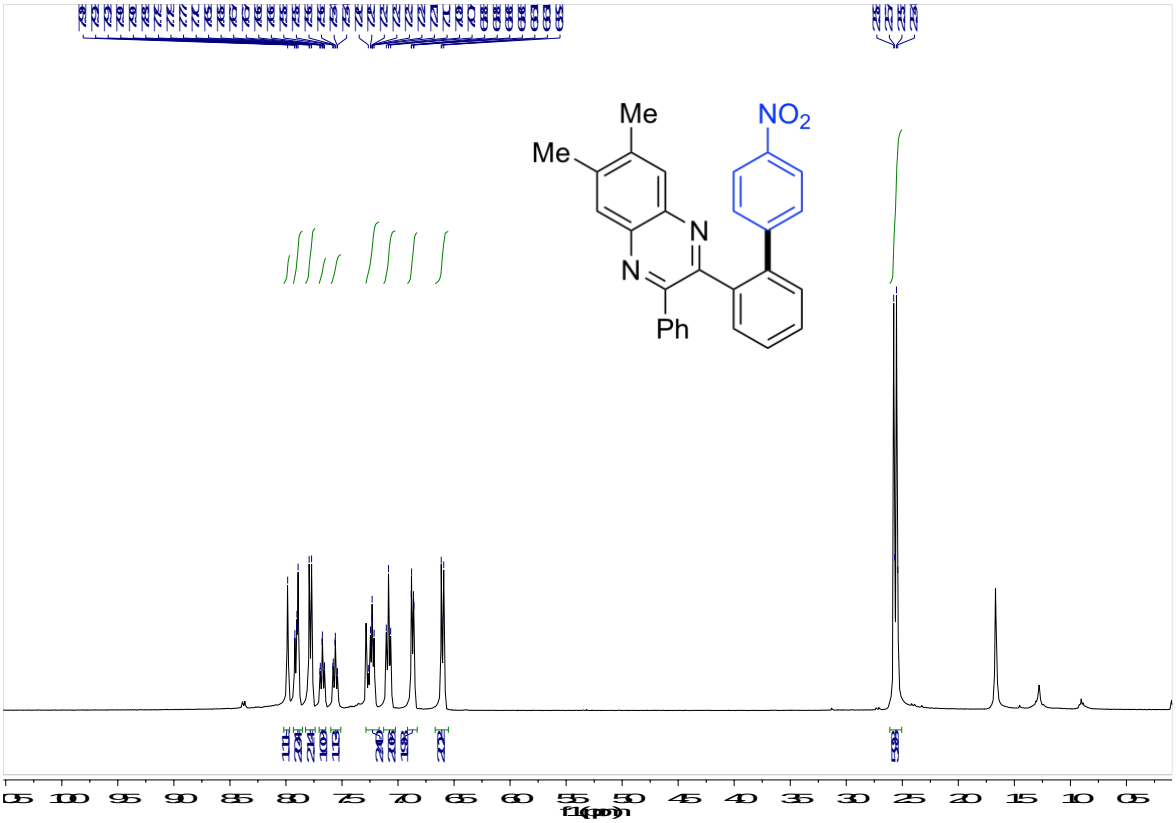

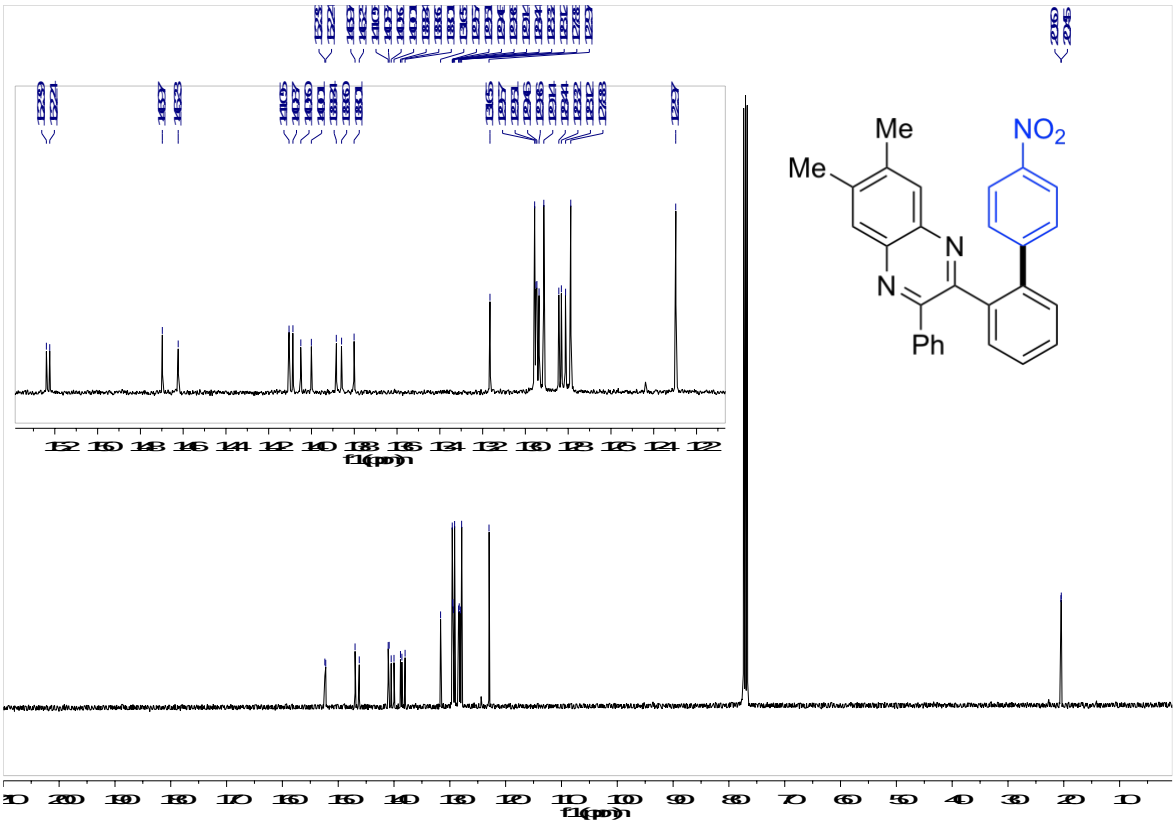

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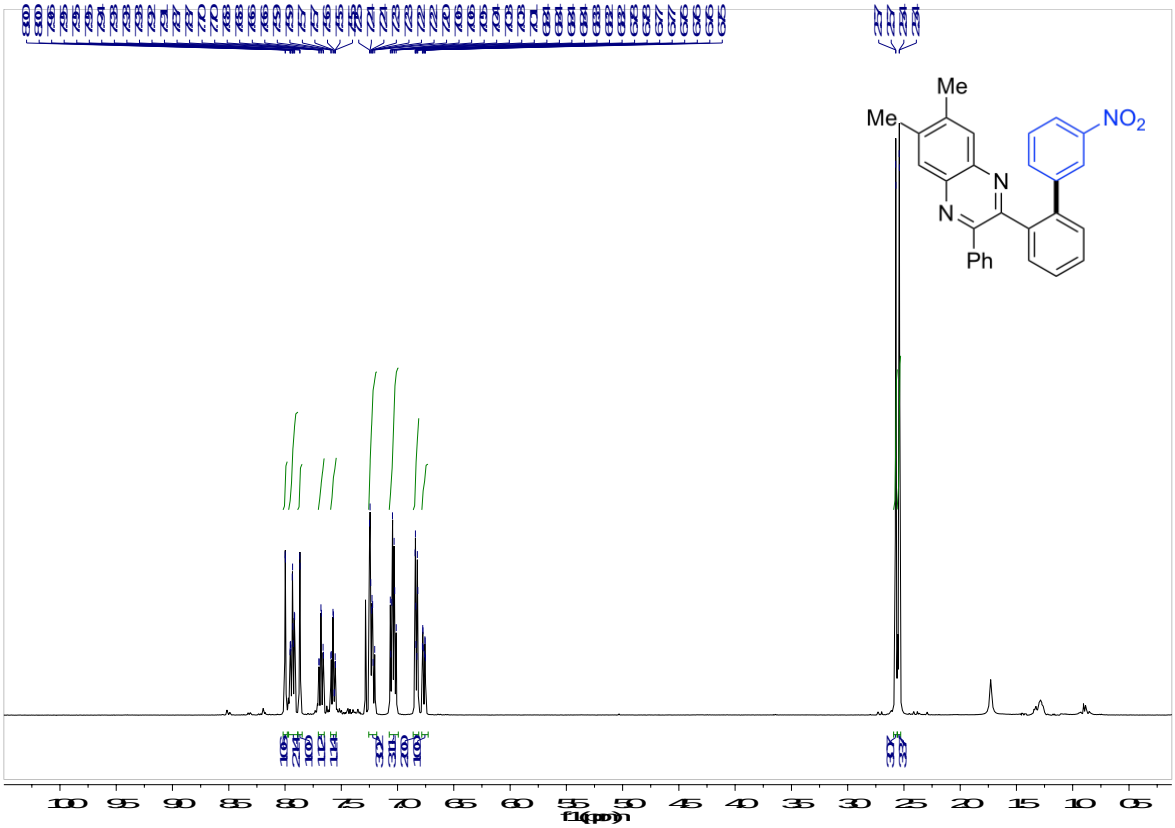

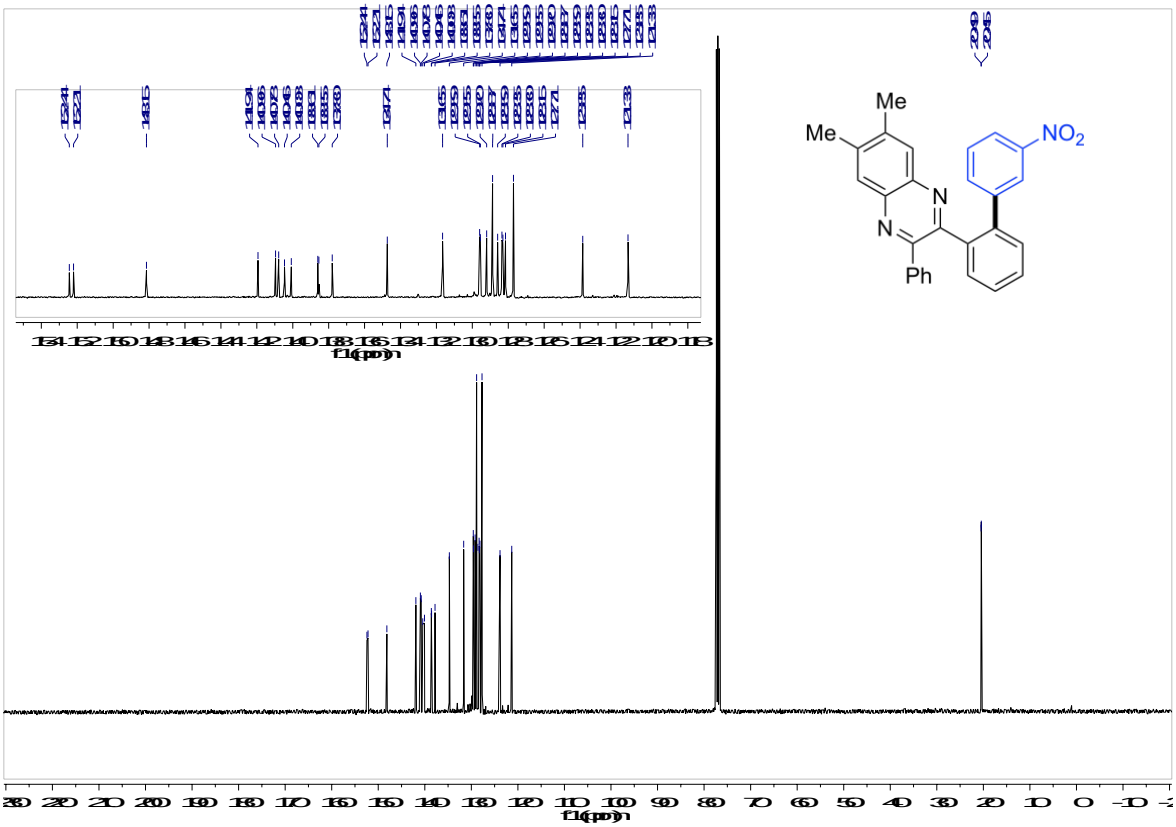

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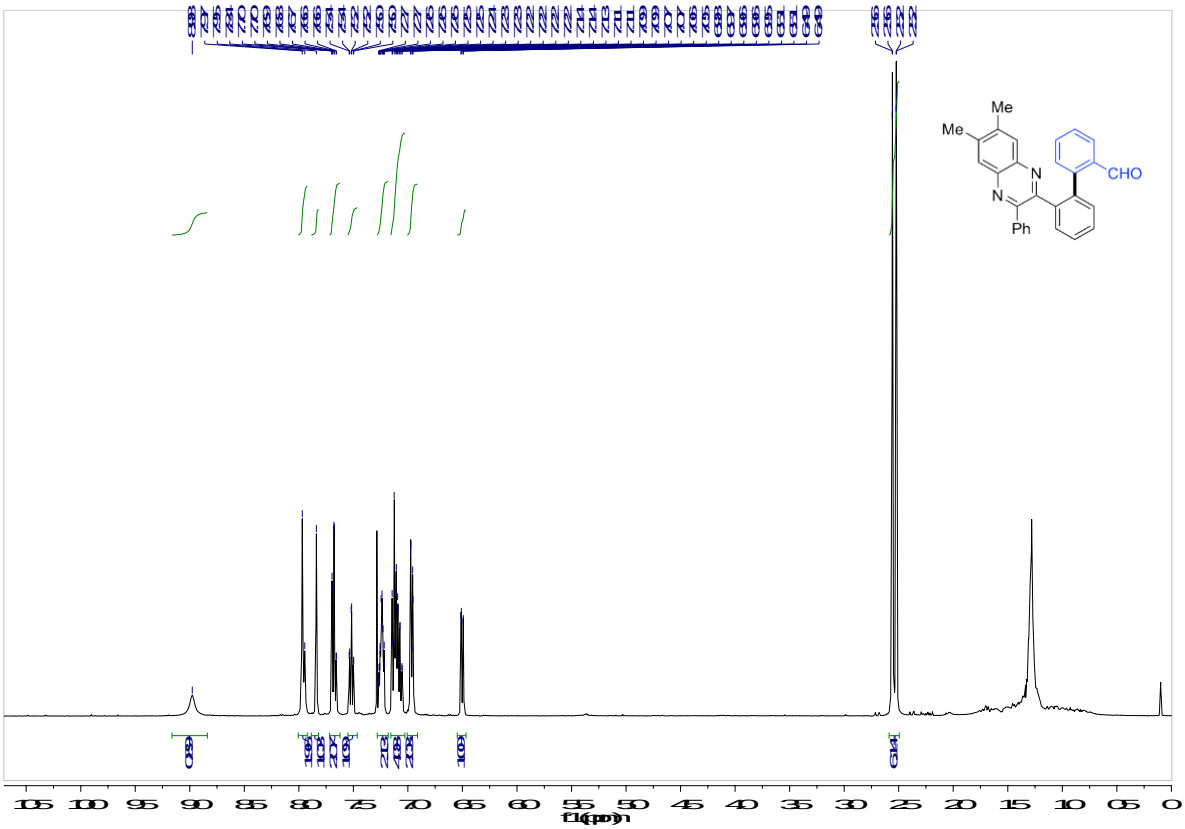

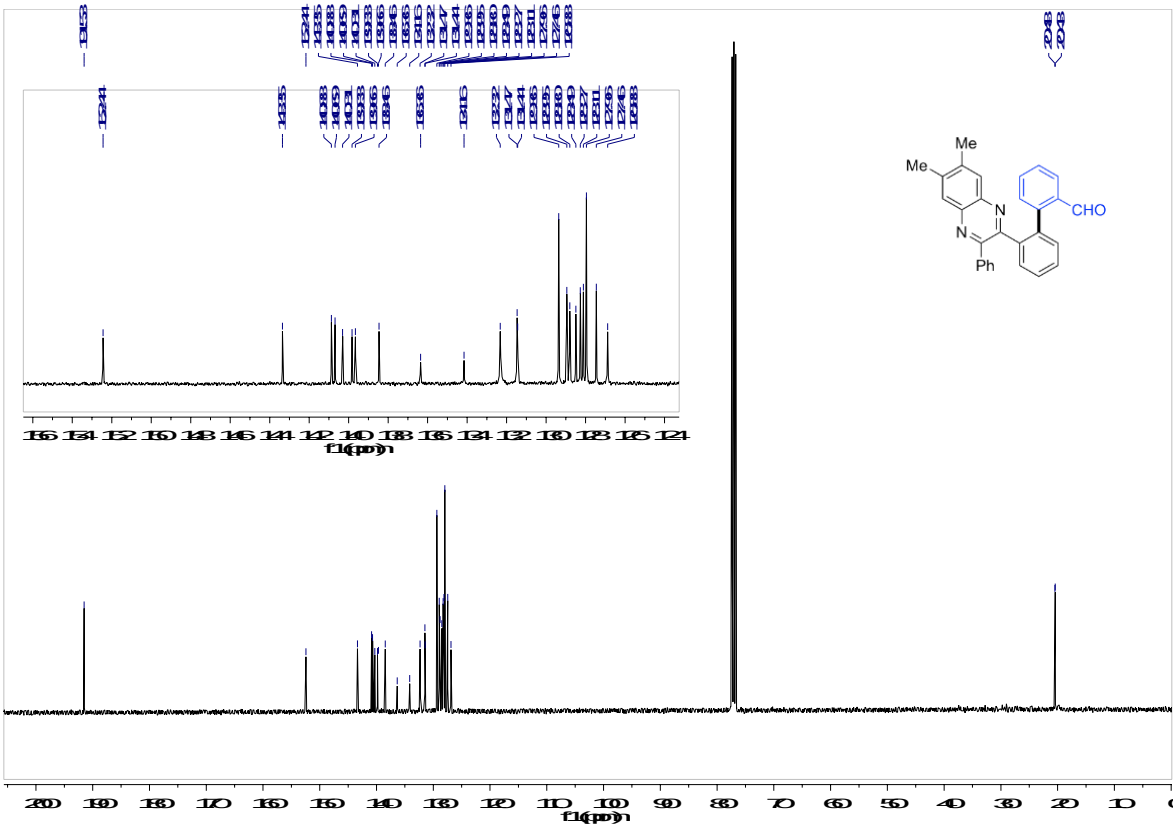

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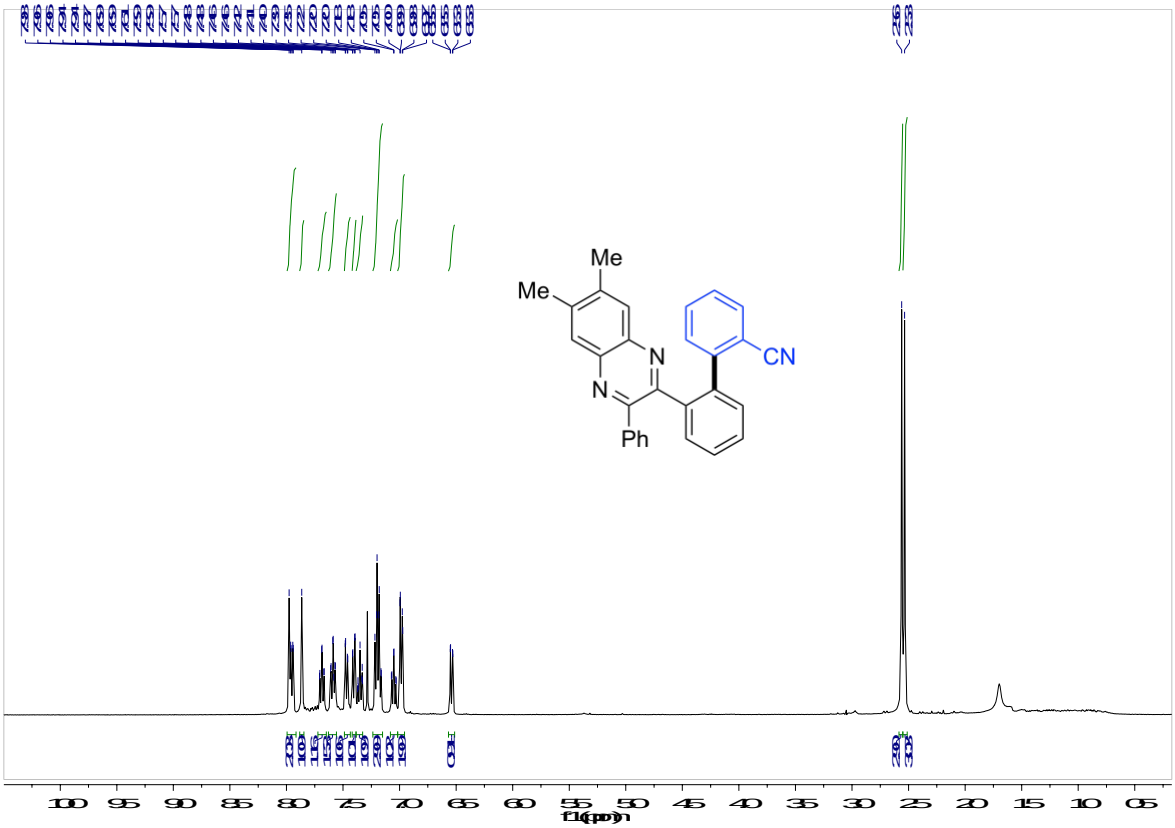

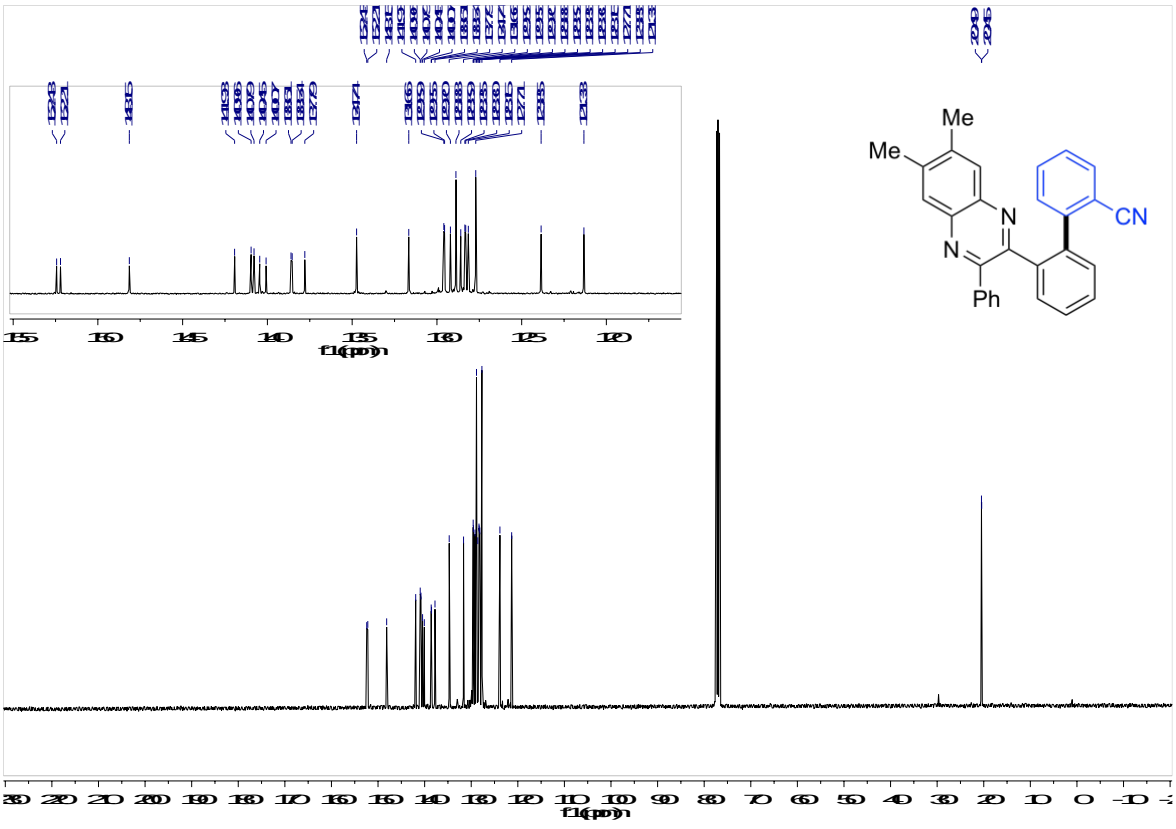

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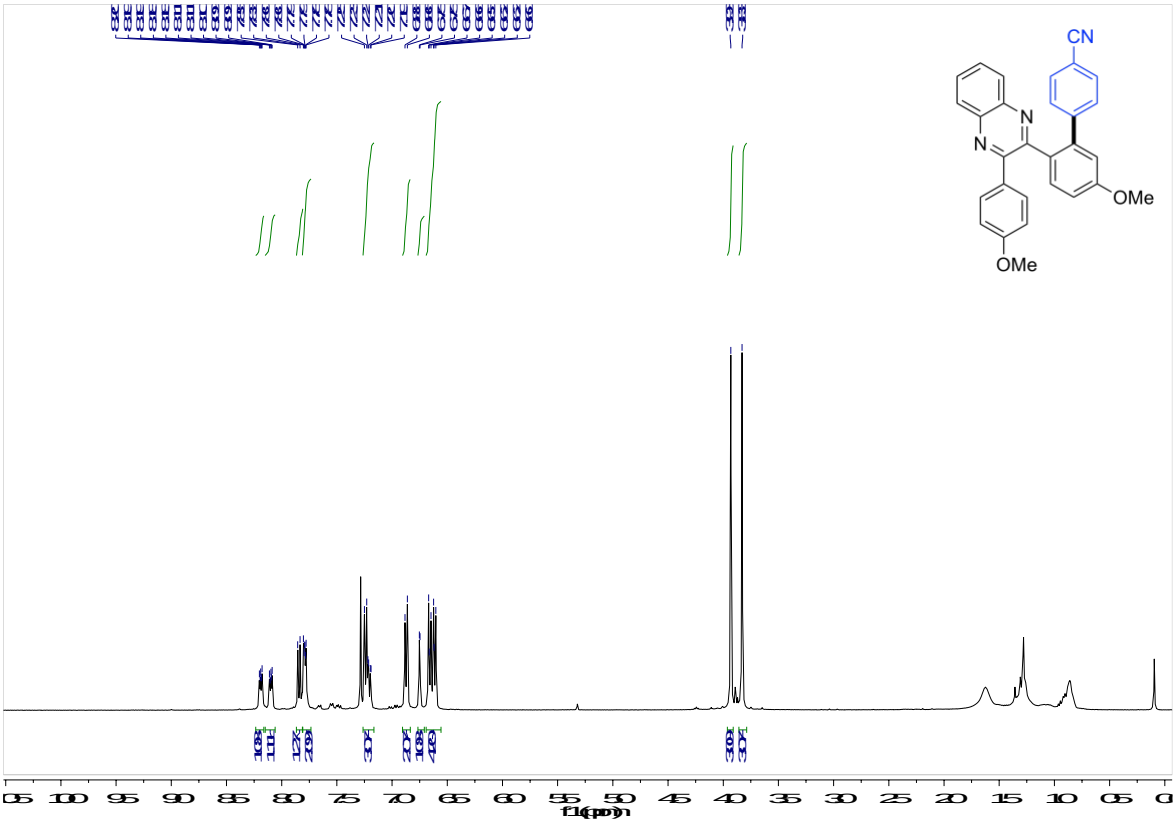

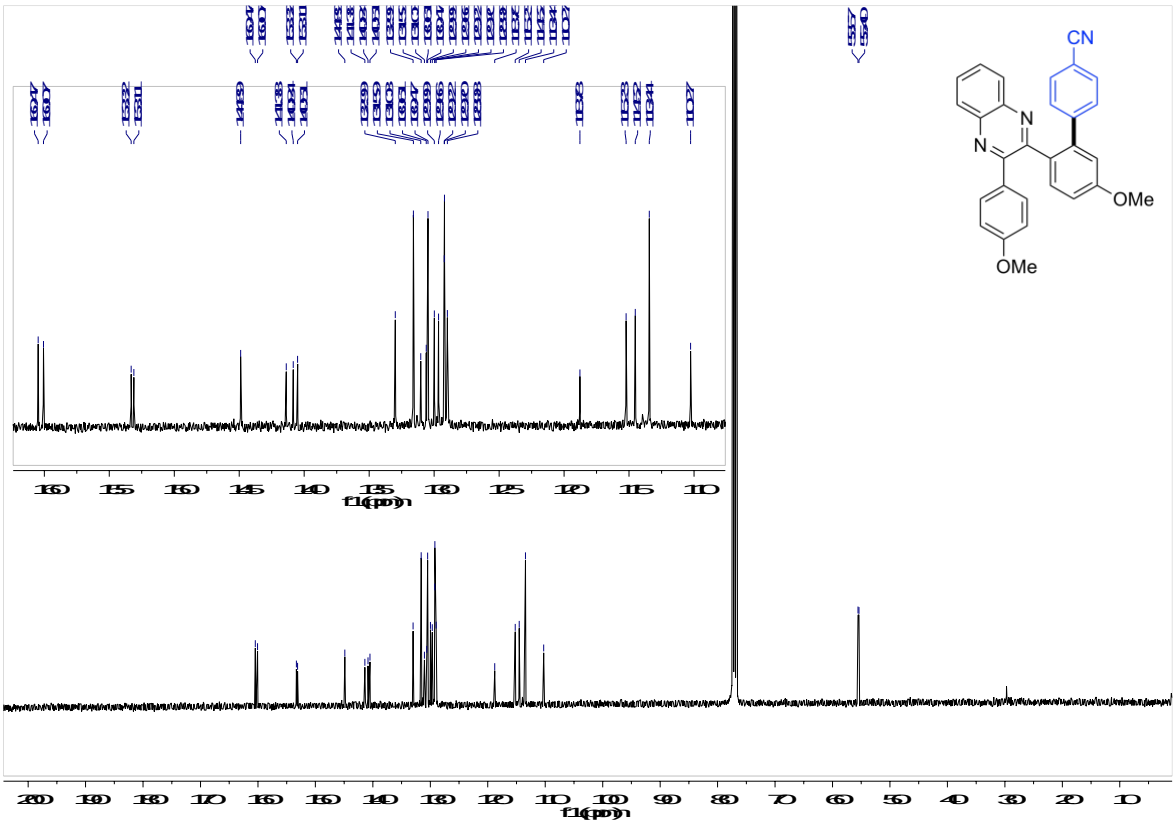

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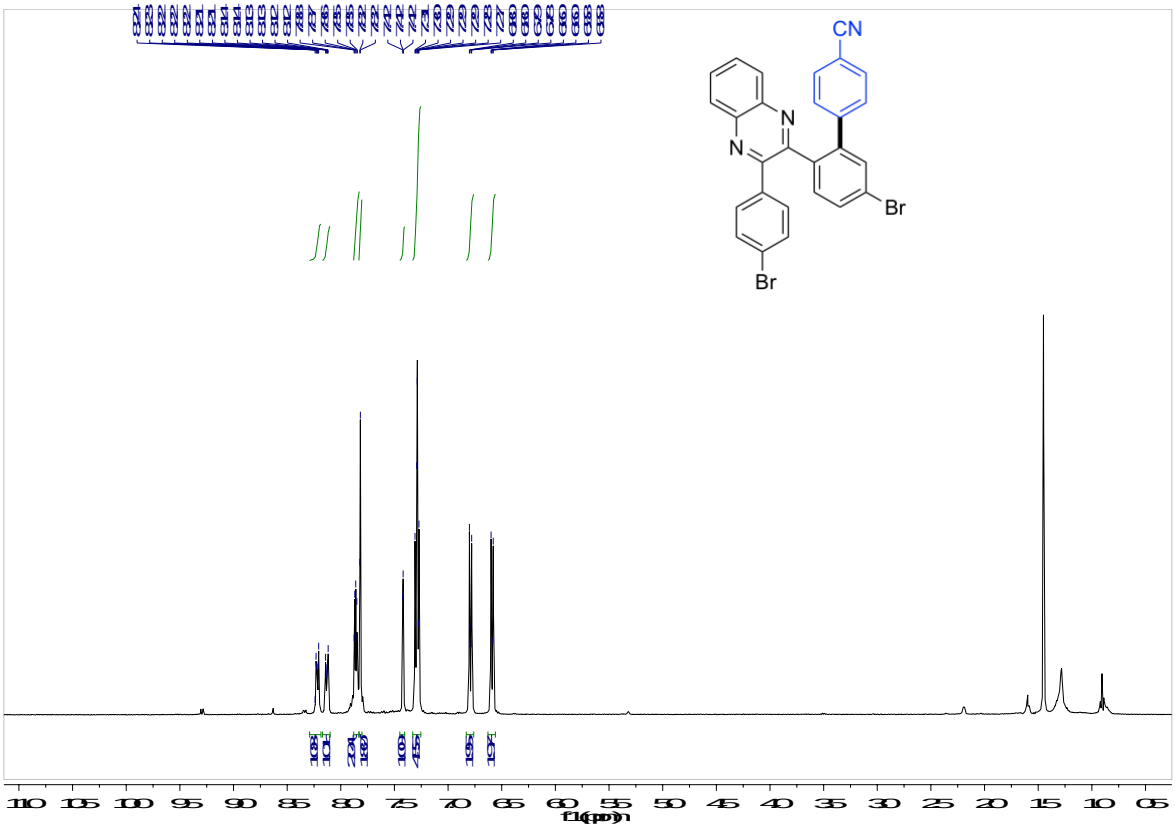

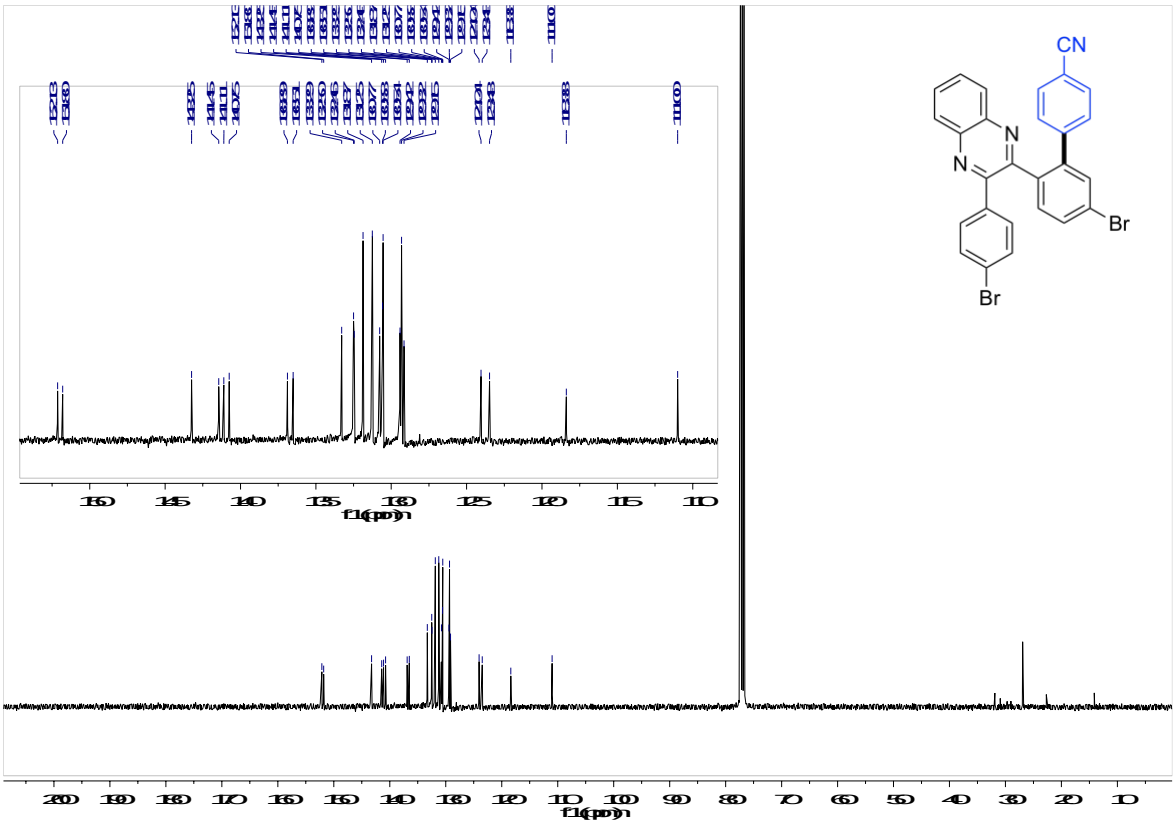

27