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Supporting Information

Iron-Catalyzed One-pot Synthesis of Quinoxalines: Transfer Hydrogenative Condensation of 2-Nitroanilines with Vicinal Diols

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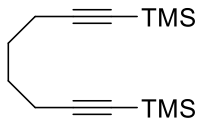
1. General Information.

All catalytic reactions were carried out under an argon atmosphere using a sealed tube. All commercially available reagents and solvents (purchased from Sigma Aldrich, TCI, Alfa Aesar, and Acros Organics) were used without further purification unless otherwise noted. Reactions were monitored by thin-layer chromatography on a silica gel 60 F254 plate using UV illumination at 254 nm. Column chromatography was performed on silica gel (230−400 mesh) using a mixture of *n*-hexane/ethyl acetate or dichloromethane (DCM)/methanol as eluents. Nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR, ^{19}F NMR) spectra were measured on JEOL JNM-ECZ400s [400 MHz (^{1}H), 100 MHz (^{13}C), 376 MHz (^{19}F)] using $CDCl_3$ or DMSO-d_6 as solvent. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.26 ppm, DMSO-d_6 = 2.50 ppm; for $^{13}C\{^{1}H\}$ NMR: $CDCl_3$ = 77.16 ppm, DMSO-d_6 = 39.52 ppm. Coupling constants (J) are expressed in hertz (Hz). IR spectra were recorded on a JASCO, FT/IR-4200 infrared spectrophotometer and are reported in cm^{-1}. All high-resolution mass spectra (HRMS) were acquired under fast atom bombardment (FAB) mode on a JMS-700 MStation mass spectrometer using a doublefocusing magnetic sector. Melting points were measured on a Büchi B540 melting point apparatus and were not corrected.

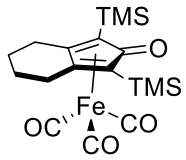
2. Synthesis of Fe 1 catalyst

2.1 Synthesis of 1,8-bis(trimethylsilyl)octa-1,7-diyne [1]



In a round bottom flask, octa-1,7-diyne (1 mmol, 133 µL) was dissolved in dry THF (2 mL) and cooled to –78 °C in a dry ice-acetone bath. *n*-BuLi (2.5M in hexane) (2.2 mmol, 880 µL) was added and reaction mixture was stirred for 15 min at –78 °C, and then 1 h 30 min at room temperature. The trimethylsilylchloride (2.2 mmol, 280 µL) was added and the resulting solution was stirred 4 h at room temperature. Aqueous saturated solution of NH_4Cl was added then aqueous layer was extracted with ether (2x10 mL). Combined organic layers were dried over $MgSO_4$. After filtration, solvent was removed under vacuum. The crude product was purified by silica gel column chromatography using *n*-hexane/ethyl acetate (97/3) to afford the product as colorless oil (243.0 mg, 95% yield).

2.2 Synthesis of (2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)iron tricarbonyl (**Fe 1**)[1]



A mixture of iron complex $Fe_2(CO)_9$ (1 mmol, 363.8 mg) and 1,8-bis(trimethylsilyl)octa-1,7-diyne (1 mmol, 250.5 mg) were placed in dried sealed tube. The tube was degassed and backfilled with argon; then, toluene (7.5 mL) was added using a syringe under argon atmosphere. The reaction tube was capped under argon flow, and then the mixture was stirred and heated at 110 °C in an oil bath for 18 h. After completion, volatiles were removed under reduced pressure, and crude product was purified by column chromatography on neutral alumina using *n*-hexane/ethyl acetate (90/10) to afford the **Fe 1** as yellow crystal (360.2 mg, 86% yield).

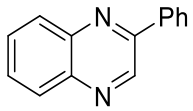
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.48−2.60 (m, 4H), 1.76−1.87 (m, 4H), 0.26 (s, 18H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 209.2, 181.4, 111.1, 71.9, 24.9, 22.5, -0.1.

3. General procedure for the synthesis of quinoxalines 3 from 2-nitroanilines and vicinal diols

A mixture of 2-nitroaniline **1** (0.4 mmol, 1.0 equiv.), diol **2** (0.8 mmol, 2.0 equiv.), **Fe 1** (5.1 mg, 0.012 mmol), and Me_3NO (1.8 mg, 0.024 mmol) was placed in a dry 10 mL tube and sealed. The tube was then degassed and backfilled with argon three times, and toluene (1 mL) was added using a syringe under argon atmosphere. The reaction tube was capped under argon flow, and then the mixture was stirred and heated at 150 ℃ using an oil bath. After 24 h, the reaction mixture was cooled to room temperature, and volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography using *n*-hexane/ethyl acetate as an eluent to afford the desired quinoxaline derivatives **3**.

2-Phenylquinoxaline (**3a**)

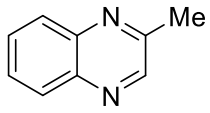


Following the general procedure, reaction of 2-nitro aniline **1a** (0.4 mmol, 55.3 mg) with 1-phenylethane-1,2-diol **2a** (0.8 mmol, 111.0 mg) produced **3a** as a yellow solid (71.6 mg, 87% yield). mp 75−77 ℃. Eluent: *n*-hexane/ethyl acetate (90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.34 (s, 1H), 8.12−8.22 (m, 4H), 7.76−7.80 (m, 2H), 7.54−7.60 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 151.9, 143.5, 142.4, 141.7, 136.8, 130.4, 130.3, 129.7, 129.6, 129.3, 129.2, 127.6. IR (neat) υ 1652, 1547,1489, 1313, 1123, 1049, 956, 796, 767 cm^{-1}.

HRMS (FAB^+) m/z calcd for $C_{14}H_{11}N_2$ $[M + H]^+$: 207.0922, found: 207.0924.

2-Methylquinoxaline (**3b**)

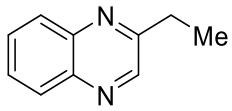


Following the general procedure, reaction of 2-nitro aniline **1a** (0.4 mmol, 55.3 mg) with propane-1,2-diol **2b** (0.8 mmol, 59 μL) produced **3b** as a yellow oil (46.8 mg, 81% yield). Eluent: *n*-hexane/ethyl acetate (85/15).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.73 (s, 1H), 7.99−8.07 (m, 2H), 7.67−7.75 (m, 2H), 2.77 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 153.8, 146.1, 142.1, 141.0, 130.1, 129.2, 129.0, 128.7, 22.6. IR (neat) υ 3064, 2990, 1700, 1652,1559, 1490, 1200, 1127, 963, 758 cm^{-1}.

HRMS (FAB^+) m/z calcd for $C_9H_9N_2$ $[M + H]^+$: 145.0766, found: 145.0772.

2-Ethylquinoxaline (**3c**)

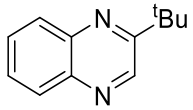


Following the general procedure, reaction of 2-nitro aniline **1a** (0.4 mmol, 55.3 mg) with butane-1,2-diol **2c** (0.8 mmol, 73 μL) produced **3c** as a yellow oil (49.3 mg, 78% yield). Eluent: *n*-hexane/ethyl acetate (90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.75 (s, 1H), 8.02−8.08 (m, 2H), 7.71 (m, 2H), 3.05 (q, J = 7.5 Hz, 2H), 1.43 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 158.6, 145.7, 142.2, 141.3, 130.0, 129.3, 129.0, 128.9, 29.7, 13.5. IR (neat) υ 2971, 2890, 1700, 1645,1559, 1198, 1127, 960, 919, 758 cm^{-1}

HRMS (FAB$^+$) m/z calcd for $C_{10}H_{11}N_2$ [M + H]$^+$: 159.0922, found: 159.0923.

2-(tert-Butyl)quinoxaline (**3d**)[2]

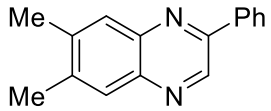


Following the general procedure, reaction of 2-nitro aniline **1a** (0.4 mmol, 55.3 mg) with 3,3-dimethylbutane-1,2-diol **2d** (0.8 mmol, 94.6 mg) produced **3d** as a yellow oil (59.4 mg, 80% yield). Eluent: *n*-hexane/ethyl acetate (90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.98 (s, 1H), 8.04−8.07 (m, 2H), 7.69−7.73 (m, 2H), 1.51 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 163.8, 143.5, 141.7, 140.8, 129.8, 129.4, 129.0, 37.3, 29.9. IR (neat) υ 3064, 2965, 2868, 2330, 1706, 1652, 1557, 1097, 968, 800, 759 cm^{-1}

HRMS (FAB$^+$) m/z calcd for $C_{12}H_{15}N_2$ [M + H]$^+$: 187.1235, found: 187.1229.

6,7-Dimethyl-2-phenylquinoxaline (**3e**)

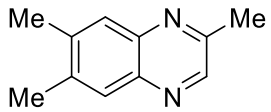


Following the general procedure, reaction of 6,7-dimethyl-2-phenylquinoxaline **1b** (0.4 mmol, 66.5 mg) with 1-phenylethane-1,2-diol **2a** (0.8 mmol, 111.0 mg) produced **3e** as a pale-yellow solid (88.1 mg, 94% yield). mp 128−130°C. Eluent: *n*-hexane/ethyl acetate (90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.23 (s, 1H), 8.16−8.18 (m, 2H), 7.91 (s, 1H), 7.86 (s, 1H), 7.53 (m, 3H), 2.52 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 151.2, 142.5, 141.4, 141.0, 140.6, 140.3, 137.2, 130.0, 129.2, 128.8, 128.2, 127.5, 20.58, 20.54. IR (neat) υ 2988, 2895, 2357, 1706, 1662, 1557, 1267, 1024, 870, 749 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{16}H_{15}N_2$ $[M + H]^+$: 235.1235, found: 235.1227.

2,6,7-Trimethylquinoxaline (**3f**)

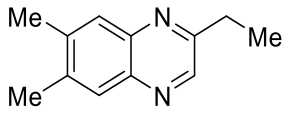


Following the general procedure, reaction of 6,7-dimethyl-2-phenylquinoxaline **1b** (0.4 mmol, 66.5 mg) with propane-1,2-diol **2b** (0.8 mmol, 59 μL) produced **3f** as a pale-yellow solid (60.1 mg, 87% yield). mp 112−114 °C. Eluent: *n*-hexane/ethyl acetate (85/15).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.64 (s, 1H), 7.80 (s, 1H), 7.75 (s, 1H), 2.74 (s, 3H), 2.48 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 152.8, 145.2, 141.1, 140.6, 140.0, 139.4, 128.3, 127.8, 22.6, 20.5, 20.4. IR (neat) υ 2992, 2891, 2352, 1700, 1645, 1506, 1340, 1274, 764, 749 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{11}H_{13}N_2$ $[M + H]^+$: 173.1079, found: 173.1080.

2-Ethyl-6,7-dimethylquinoxaline (**3g**)

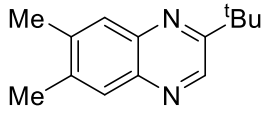


Following the general procedure, reaction of 6,7-dimethyl-2-phenylquinoxaline **1b** (0.4 mmol, 66.5 mg) with butane-1,2-diol **2c** (0.8 mmol, 73 μL) produced **3g** as a yellow solid (61.3 mg, 82% yield). mp 113−115 °C. Eluent: *n*-hexane/ethyl acetate (90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.66 (s, 1H), 7.81 (s, 1H), 7.79 (s, 1H), 3.02 (q, J = 7.8 Hz, 2H), 2.48 (s, 6H), 1.42 (t, J = 7.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 157.6, 144.7, 141.1, 140.6, 140.3, 139.5, 128.3, 128.0, 29.6, 20.5, 20.4, 13.7. IR (neat) υ 2995, 2820, 2340, 1695, 1635, 1506, 1340, 1267, 764, 758, 749 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{12}H_{15}N_2$ $[M + H]^+$: 187.1235, found: 187.1230.

2-(tert-Butyl)-6,7-dimethylquinoxaline (**3h**) [2]



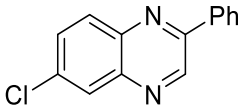
Following the general procedure, reaction of 6,7-dimethyl-2-phenylquinoxaline **1b** (0.4 mmol, 66.5 mg) with 3,3-dimethylbutane-1,2-diol **2d** (0.8 mmol, 94.6 mg) produced **3h** as a yellow solid (70.9 mg, 83% yield). mp 39−41 °C. Eluent: *n*-hexane/ethyl acetate (90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.87 (s, 1H), 7.82 (s, 1H), 7.80 (s, 1H), 2.48 (s, 6H), 1.49

(s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 162.8, 142.4, 140.6, 140.2, 139.7, 139.3, 128.4, 128.0, 37.1, 29.9, 20.4. IR (neat) υ 3012, 2920, 2868, 2339, 1704, 1675, 1550, 1088, 805, 763, 749 cm^{-1}.

HRMS (FAB^+) m/z calcd for $C_{14}H_{19}N_2$ $[M + H]^+$: 215.1548, found: 215.1544.

6-Chloro-2-phenylquinoxaline (**3i**)[3]

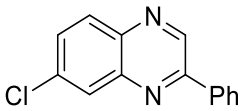


Following the general procedure, reaction of 4-chloro-2-nitroaniline **1c** (0.4 mmol, 69.1 mg) with 1-phenylethane-1,2-diol **2a** (0.8 mmol, 111.0 mg) produced **3i** as a yellow solid (28.3 mg, 29% yield). mp 142−144 °C. Eluent: *n*-hexane/ethyl acetate (90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.33 (s, 1H), 8.18−8.20 (m, 2H), 8.09−8.13 (m, 2H), 7.74 (dd, J = 9.2, 2.5 Hz, 1H), 7.54−7.60 (m, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 152.1, 144.3, 141.9, 141.0, 136.5, 135.4, 131.5, 131.0, 130.6, 129.4, 128.2, 127.7. IR (neat) υ 1684, 1635, 1557, 1506, 1170, 874, 829, 757 cm^{-1}.

HRMS (FAB^+) m/z calcd for $C_{14}H_{10}ClN_2$ $[M + H]^+$: 241.0533, found: 241.0530.

7-Chloro-2-phenylquinoxaline (**3i′**)[3]

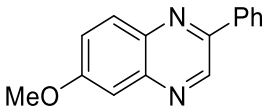


Following the general procedure, reaction of 4-chloro-2-nitroaniline **1c** (0.4 mmol, 69.1 mg) with 1-phenylethane-1,2-diol **2a** (0.8 mmol, 111.0 mg) produced **3i′** as a yellow solid (42.8 mg, 45% yield). mp 121−123 °C. Eluent: *n*-hexane/ethyl acetate (90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.32 (s, 1H), 8.16−8.21 (m, 3H), 8.06 (d, J = 9.2 Hz, 1H), 7.69 (dd, J = 9.2, 2.4 Hz, 1H), 7.55−7.60 (m, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 152.6, 143.4, 142.6, 140.0, 136.3, 136.1, 130.6, 130.6, 130.3, 129.2, 128.5, 127.6. IR (neat) υ 1681, 1636, 1562, 1511, 1167, 879, 829, 756 cm^{-1}.

HRMS (FAB^+) m/z calcd for $C_{14}H_{10}ClN_2$ $[M + H]^+$: 241.0533, found: 241.0530.

6-Methoxy-2-phenylquinoxaline (**3j**)[3]



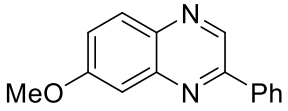
Following the general procedure, reaction of 4-methoxy-2-nitroaniline **1d** (0.4 mmol, 67.3 mg)

with 1-phenylethane-1,2-diol **2a** (0.8 mmol, 111.0 mg) produced **3j** as a yellow solid (32.2 mg, 34% yield). mp 108−110 ℃. Eluent: *n*-hexane/ethyl acetate (90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.25 (s, 1H), 8.15−8.17 (m, 2H), 8.06 (d, J = 8.6 Hz, 1H), 7.44−7.59 (m, 5H), 4.00 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 160.7, 149.7, 143.3, 143.2, 138.5, 137.1, 130.7, 129.8, 129.2, 127.3, 123.7, 106.6, 55.94. IR (neat) υ 2941, 1697, 1545, 1481, 1352, 1181, 1062, 896, 786 cm^{-1}

HRMS (FAB$^+$) m/z calcd for $C_{15}H_{13}N_2O$ [M + H] $^+$: 237.1028, found: 237.1033.

7-Methoxy-2-phenylquinoxaline (**3j′**)[3]

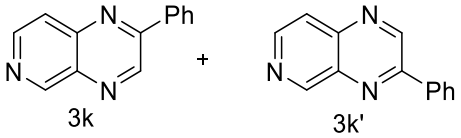


Following the general procedure, reaction of 4-methoxy-2-nitroaniline **1d** (0.4 mmol, 67.3 mg) with 1-phenylethane-1,2-diol **2a** (0.8 mmol, 111.0 mg) produced **3j′** as a yellow solid (60.3 mg, 64% yield). mp 85−87 ℃. Eluent: *n*-hexane/ethyl acetate (90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.17 (s, 1H), 8.17 (d, J = 6.7 Hz, 2H), 8.00 (d, J = 9.2 Hz, 1H), 7.52−7.59 (m, 3H), 7.45 (d, J = 1.8 Hz, 1H), 7.40 (dd, J = 9.2, 2.4 Hz, 1H), 4.00 (s, 3H), ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 161.1, 152.0, 144.1, 140.9, 137.9, 137.1, 130.2, 130.1, 129.2, 127.6, 123.0, 106.9, 55.94. IR (neat) υ 2925, 1684, 1516, 1464, 1345, 1175, 1056, 874, 770 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{15}H_{13}N_2O$ [M + H] $^+$: 237.1028, found: 237.1031.

3-Phenylpyrido[3,4-*b*]pyrazine (**3k**) / 3-phenylpyrido[3,4-*b*]pyrazine (**3k′**) [4]

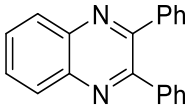


Following the general procedure, reaction of 3-nitropyridin-4-amine **1f** (0.4 mmol, 55.7 mg) with 1-phenylethane-1,2-diol **2a** (0.8 mmol, 111.0 mg) produced **3k: 3k′** = 1: 4.3 mixture as a white solid (65.3 mg, 79% yield). mp 108−110 ℃. Eluent: *n*-hexane/ethyl acetate (70/30).

Major product **3k′**. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.56 (s, 1H), 9.45 (s, 1H), 8.85 (d, J = 5.5 Hz, 1H), 8.24−8.26 (m, 2H), 7.99−8.00 (m, 1H), 7.60 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 156.0, 154.4, 147.9, 147.0, 145.2, 135.9, 131.5, 129.5, 128.1, 127.7, 122.0. IR (neat) υ 3050, 3031, 2348, 1700, 1652, 1559,1506, 1022, 959, 831, 762 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{13}H_{10}N_3$ [M + H] $^+$: 208.0875, found: 208.0871.

2,3-Diphenylquinoxaline (**3l**)



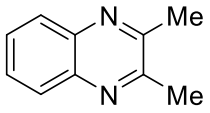
Following the general procedure, reaction of 2-nitroaniline **1a** (0.4 mmol, 55.3 mg) with (*R*, *R*) 1,2-diphenylethane-1,2-diol **2e** (0.8 mmol, 171.5 mg) produced **3l** as a yellow solid (56.2 mg, 50% yield) and 2-phenyl-1*H*-benzo[*d*]imidazole as a white solid (13.6 mg, 18% yield). mp 121−123 ℃. Eluent: *n*-hexane/ethyl acetate (90/10).

Following the general procedure, reaction of 2-nitroaniline **1a** (0.4 mmol, 55.3 mg) with meso-1,2-diphenylethane-1,2-diol **2e′** (0.8 mmol, 171.5 mg) produced **3l** as a yellow solid (58.3 mg, 52% yield) and 2-phenyl-1*H*-benzo[*d*]imidazole as a white solid (15.3 mg, 20% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (dd, J = 6.4, 3.6 Hz, 2H), 7.78 (dd, J = 6.4, 3.4 Hz, 2H), 7.51−754 (m, 4H), 7.32−7.37 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 153.6, 141.4, 139.2, 130.1, 130.0, 129.3, 129.0, 128.4. IR (neat) υ 2925, 1645, 1449,1399, 1212, 1175, 1024, 874, 770, 717 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{20}H_{15}N_2$ [M + H] $^+$: 283.1235, found: 283.1236.

2,3-Dimethylquinoxaline (**3m**)

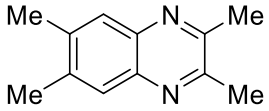


Following the general procedure, reaction of 2-nitroaniline **1a** (0.4 mmol, 55.3 mg) with butane-2,3-diol **2f** (0.8 mmol, 74 μL) produced **3m** as a pale-yellow solid (50.4 mg, 80% yield). mp 104−106 ℃. Eluent: *n*-hexane/ethyl acetate (85/15).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.99 (dd, J = 6.1, 3.7 Hz, 2H), 7.67 (dd, J = 6.1, 3.7 Hz, 2H), 2.74 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 153.6, 141.2, 129.0, 128.4, 23.34. IR (neat) υ 3050, 2991, 2357, 1700, 1652, 1554, 1217, 750 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{10}H_{11}N_2$ [M + H] $^+$: 159.0922, found: 159.0924.

2,3,6,7-Tetramethylquinoxaline (**3o**)



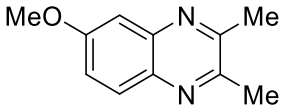
Following the general procedure, reaction of 4,5-dimethyl-2-nitroaniline **1b** (0.4 mmol, 66.5 mg) with butane-2,3-diol **2f** (0.8 mmol, 74 μL) produced **3o** as a pale-yellow solid (59.1 mg, 79% yield). mp 189−191℃. Eluent: *n*-hexane/ethyl acetate (80/20).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 (s, 2H), 2.70 (s, 6H), 2.46 (s, 6H). ^{13}C{^{1}H} NMR

(100 MHz, $CDCl_3$) δ (ppm) 152.4, 140.0, 139.2, 127.6, 23.2, 20.4. IR (neat) υ 2987, 2886, 2360, 1700, 1652, 1516,1419, 1260, 976, 763, 749 cm^{-1}.

HRMS (FAB^+) m/z calcd for $C_{12}H_{15}N_2$ $[M + H]^+$: 187.1235, found: 187.1233.

6-Methoxy-2,3-dimethylquinoxaline (**3p**)

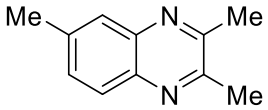


Following the general procedure, reaction of 4-methoxy-2-nitroaniline **1e** (0.4 mmol, 67.3 mg) with butane-2,3-diol **2f** (0.8 mmol, 74 μL) produced **3p** as a yellow solid (62.7 mg, 83% yield). mp 99−101℃. Eluent: *n*-hexane/ethyl acetate (75/25).

^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.85−7.87 (m, 1H), 7.30−7.33 (m, 2H), 3.94 (s, 3H), 2.71 (s, 3H), 2.69 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 160.1, 153.5, 150.8, 142.5, 137.1, 129.4, 121.9, 106.2, 55.8, 23.2, 22.9. IR (neat) υ 2953, 2872, 2328, 1695, 1645, 1218, 1156, 948, 824, 751 cm^{-1}.

HRMS (FAB^+) m/z calcd for $C_{11}H_{13}N_2O$ $[M + H]^+$: 189.1028, found: 189.1027.

2,3,6-Trimethylquinoxaline (**3q**)

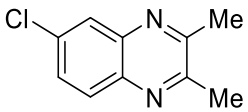


Following the general procedure, reaction of 5-methyl-2-nitroaniline **1g** (0.4 mmol, 60.9 mg) with butane-2,3-diol **2f** (0.8 mmol, 74 μL) produced **3q** as a white solid (56.0 mg, 81% yield). mp 91−93 ℃. Eluent: *n*-hexane/ethyl acetate (80/20).

^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (d, J = 8.6 Hz, 1H), 7.75 (s, 1H), 7.49 (dd, J = 8.6, 1.8 Hz, 1H), 2.72 (s, 6H), 2.56 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 153.4, 152.5, 141.2, 139.5, 139.2, 131.1, 127.9, 127.4, 23.3, 23.2, 21.8. IR (neat) υ 2941, 2845, 2349, 1690, 1616, 1429, 1260, 1166, 831, 763, 749 cm^{-1}

HRMS (FAB^+) m/z calcd for $C_{11}H_{13}N_2$ $[M + H]^+$: 173.1079, found: 173.1074.

6-Chloro-2,3-dimethylquinoxaline (**3r**)

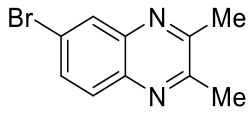


Following the general procedure, reaction of 5-chloro-2-nitroaniline **1h** (0.4 mmol, 69.1 mg) with butane-2,3-diol **2f** (0.8 mmol, 74 μL) produced **3r** as a yellow solid (59.4 mg, 77% yield). mp 88−90 ℃. Eluent: *n*-hexane/ethyl acetate (85/15).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (d, J = 2.3 Hz, 1H), 7.91 (d, J = 8.7 Hz, 1H), 7.61 (dd, J = 8.7, 2.3 Hz, 1H), 2.73 (s, 3H), 2.73 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 154.7, 153.9, 141.5, 139.7, 134.5, 129.9, 129.7, 127.5, 23.4, 23.3. IR (neat) υ 2937, 2836, 2339, 1600, 1387, 1244, 1145, 853, 749, 705 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{10}H_{10}ClN_2$ [M + H] $^+$: 193.0533, found: 193.0532.

6-Bromo-2,3-dimethylquinoxaline (**3s**)

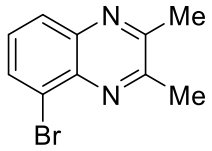


Following the general procedure, reaction of 5-bromo-2-nitroaniline **1i** (0.4 mmol, 86.8 mg) with butane-2,3-diol **2f** (0.8 mmol, 74 µL) produced **3s** as a yellow solid (67.2 mg, 71% yield). mp 84−86 °C. Eluent: *n*-hexane/ethyl acetate (85/15).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 (d, J = 1.8 Hz, 1H), 7.85 (d, J = 8.7 Hz 1H), 7.74 (dd, J = 8.7, 1.8 Hz, 1H), 2.73 (s, 3H), 2.72 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 154.6, 154.0, 141.8, 139.9, 132.4, 130.8, 129.8, 122.6, 23.3. IR (neat) υ 2958, 2843, 2352, 1616, 1404, 1217, 922, 849, 703 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{10}H_{10}BrN_2$ [M + H] $^+$: 237.0027, found: 237.0028.

5-Bromo-2,3-dimethylquinoxaline (**3t**)

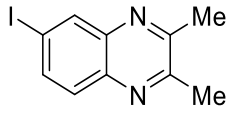


Following the general procedure, reaction of 3-bromo-2-nitroaniline **1j** (0.4 mmol, 86.8 mg) with butane-2,3-diol **2f** (0.8 mmol, 74 µL) produced **3t** as a yellow solid (58.8 mg, 59% yield). mp 57−59 °C. Eluent: *n*-hexane/ethyl acetate (85/15).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.99 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 8.0 Hz, 1H), 2.82 (s, 3H), 2.78 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 154.9, 154.4, 141.7, 139.1, 132.6, 129.4, 128.2, 123.4, 23.5, 22.9. IR (neat) υ 2969, 2863, 2359, 1627, 1423, 1228, 933, 873, 748 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for C10H10BrN2 [M + H] $^+$: 237.0027, found: 237.0030.

6-Iodo-2,3-dimethylquinoxaline (**3u**)

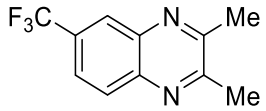


Following the general procedure, reaction of 5-iodo-2-nitroaniline **1k** (0.4 mmol, 105.6 mg) with butane-2,3-diol **2f** (0.8 mmol, 74 µL) produced **3t** as a yellow solid (69.3 mg, 61% yield). mp 77−79 °C. Eluent: *n*-hexane/ethyl acetate (85/15).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.39 (d, J = 1.4 Hz, 1H), 7.90 (dd, J = 8.7, 1.8 Hz, 1H), 7.68 (d, J = 9.2 Hz, 1H), 2.72 (s, 3H), 2.70 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 154.4, 154.2, 142.0, 140.3, 137.7, 137.4, 129.7, 94.3, 23.4, 23.3. IR (neat) υ 2944, 2831, 2349, 1609, 1550, 1260, 830, 758, 720 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{10}H_{10}IN_2$ [M + H] $^+$: 284.9889, found: 284.9882.

2,3-Dimethyl-6-(trifluoromethyl)quinoxaline (**3v**)

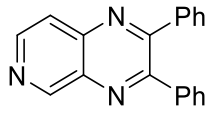


Following the general procedure, reaction of 2-nitro-5-(trifluoromethyl)aniline **1l** (0.4 mmol, 82.5 mg) with butane-2,3-diol **2f** (0.8 mmol, 74 µL) produced **3v** as a yellow solid (59.4 mg, 66% yield). mp 88−90 °C. Eluent: *n*-hexane/ethyl acetate (90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.30 (s, 1H), 8.10 (d, J = 8.7 Hz, 1H), 7.84 (dd, J = 8.7, 2.3 Hz, 1H), 2.78 (s, 3H), 2.77 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 156.0, 155.4, 142.3, 140.2, 130.7 (q, $J_{C\text{-}F}$=32.6 Hz), 129.66, 126.6 (q, $J_{C\text{-}F}$=4.8 Hz), 125.3, 124.7 (q, $J_{C\text{-}F}$=2.9 Hz), 123.9 ($J_{C\text{-}F}$=271.0 Hz), 23.5, 23.4. ^{19}F-NMR (376 MHz, $CDCl_3$) δ (ppm) -62.36. IR (neat) υ 2940, 2857, 2357, 1623, 1419, 1113, 935, 846, 749 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{11}H_{10}F_3N_2$ [M + H] $^+$: 227.0796, found: 227.0797.

2,3-Diphenylpyrido[3,4-*b*]pyrazine (**3x**)[3]



Following the general procedure, reaction of 3-nitropyridin-4-amine **1f** (0.4 mmol, 55.7 mg) with 1,2-diphenylethane-1,2-diol **2f** (0.8 mmol, 74 µL) produced **3x** as a yellow solid (55.1 mg, 49% yield). mp 165−167 °C. Eluent: *n*-hexane/ethyl acetate (75/25).

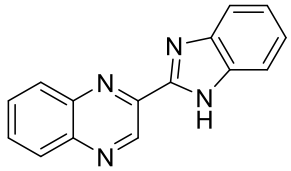
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.62 (s, 1H), 8.84 (d, J = 5.5 Hz, 1H), 8.02 (d, J = 6.0 Hz, 1H), 7.53−7.56 (m, 4H), 7.34−7.44 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 158.3, 155.7, 154.2, 146.9, 143.9, 138.3, 136.5, 130.0, 129.9, 129.7, 128.6, 121.8. IR (neat) υ 2344, 1669, 1554, 1464, 1394, 1260, 1033, 764,749 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{19}H_{14}N_3$ [M + H] $^+$: 284.1188, found: 284.1188.

4. General procedure for the synthesis of 2-(1*H*-benzo[*d*]imidazol-2-yl)-quinoxaline (5)

A mixture of 2-nitroaniline **1** (0.4 mmol, 1.0 eq), glycerol **4** (0.8 mmol, 2.0 equiv.), **Fe 1** (8.4 mg, 0.02 mmol), and Me_3NO (1.8 mg, 0.04 mmol) was placed in a dried 10 mL sealed tube. The tube was degassed and backfilled with argon three times; then, toluene (1 mL) was added using a syringe under argon atmosphere. The reaction tube was capped under argon flow, and then the mixture was stirred and heated at 150 ℃ in an oil bath 24 h. After completion, the reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography using *n*-hexane/ethyl acetate as an eluent to afford the desired product **5**.

2-(1*H*-benzo[*d*]imidazol-2-yl)quinoxaline (**5a**)

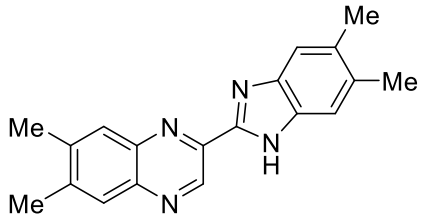


Following the general procedure, reaction of 2-nitroaniline **1a** (0.4 mmol, 55.3 mg) with glycerol **4** (0.8 mmol, 59 μL) produced **5a** as a yellow solid (22.1 mg, 45% yield). mp 241−243 ℃. Eluent: *n*-hexane/ethyl acetate (75/25).

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 13.49 (bs, 1H), 9.82 (s, 1H), 8.18−8.23 (m, 2H), 7.92−8.00 (m, 2H), 7.73 (bs, 2H), 7.32 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm) 148.8, 144.1, 143.6, 142.0, 141.1, 131.3, 130.9, 129.3, 129.0. IR (neat) υ 3447, 2334, 1704, 1669, 1506, 1456, 1267, 1152, 819,763, 720 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{15}H_{11}N_4$ [M + H] $^+$: 247.0984, found: 247.0986.

2-(5,6-dimethyl-1H-benzo[*d*]imidazol-2-yl)-6,7-dimethylquinoxaline (**5b**)



Following the general procedure, reaction of 4,5-dimethyl-2-nitroaniline **1b** (0.4 mmol, 66.5 mg) with glycerol **4** (0.8 mmol, 59 μL) produced **5b** as a yellow solid (27.6 mg, 47% yield). mp 301−303 ℃. Eluent: *n*-hexane/ethyl acetate (75/25).

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 13.13 (bs, 1H), 9.63 (s, 1H), 7.90 (s, 1H), 7.89 (s, 1H), 7.44 (bs, 2H), 2.48 (s, 6H), 2.32 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ (ppm) 148.09, 142.94, 142.83, 141.44, 141.07, 140.76, 139.90, 128.09, 127.58, 20.08, 19.96, 19.84. IR (neat) υ 3445, 2324, 1700, 1660, 1498, 1429, 1260, 1033, 758, 720, 703 cm^{-1}.

HRMS (FAB$^+$) m/z calcd for $C_{19}H_{19}N_4$ [M + H] $^+$: 303.1610, found: 303.1609.

5. Synthesis of quinoxaline 3a from 1,2-dinitrobenzene and vicinal diol

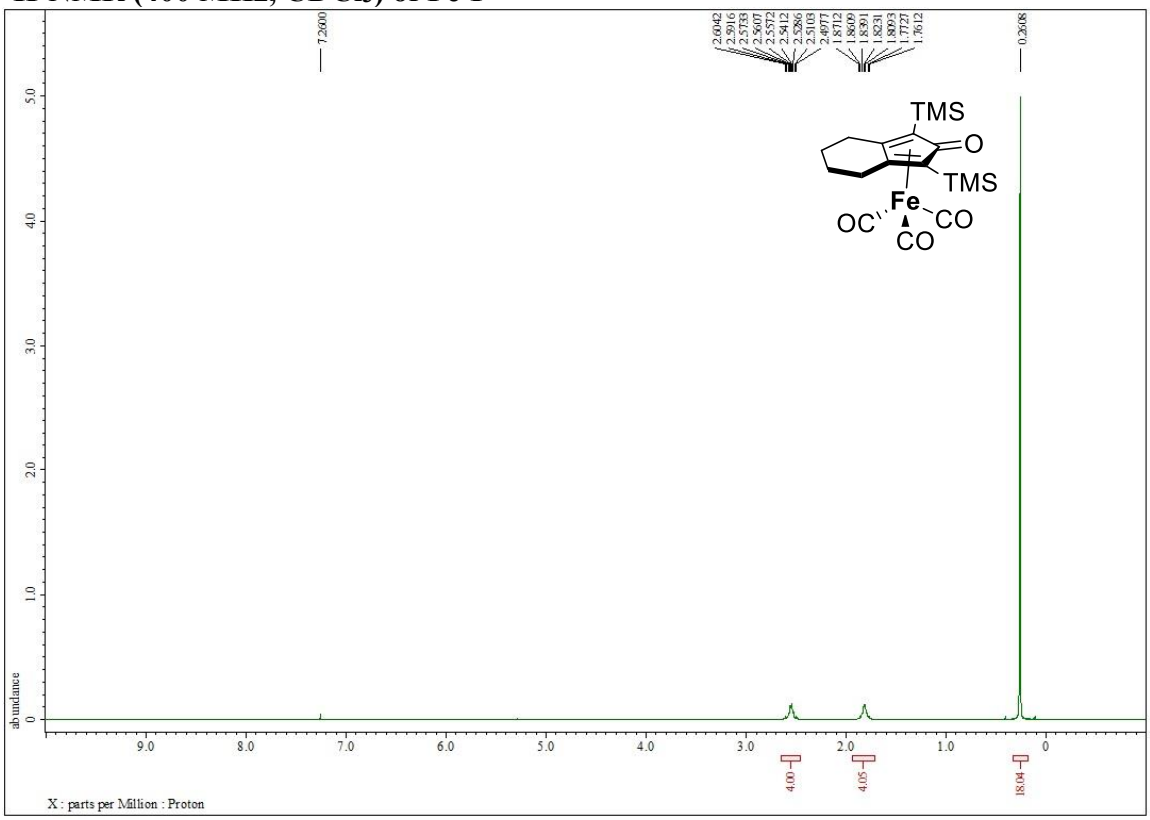
A mixture of 1,2-dinitrobenzene **6** (0.4 mmol, 67.3 mg), diol **2a** (1.6 mmol, 221 mg), **Fe 1** (5.1 mg, 0.012 mmol), and Me_3NO (1.8 mg, 0.024 mmol) was placed in a dried 10 mL sealed tube. The tube was degassed and backfilled with argon three times; then, toluene (1 mL) was added using a syringe under argon atmosphere. The reaction tube was capped under argon flow, and then the mixture was stirred and heated at 150 °C in an oil bath 24 h. After completion, the reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography using *n*-hexane/ethyl acetate (90/10) as an eluent to afford the desired product **3a** as a yellow solid (67.0 mg, 81% yield).

6. References

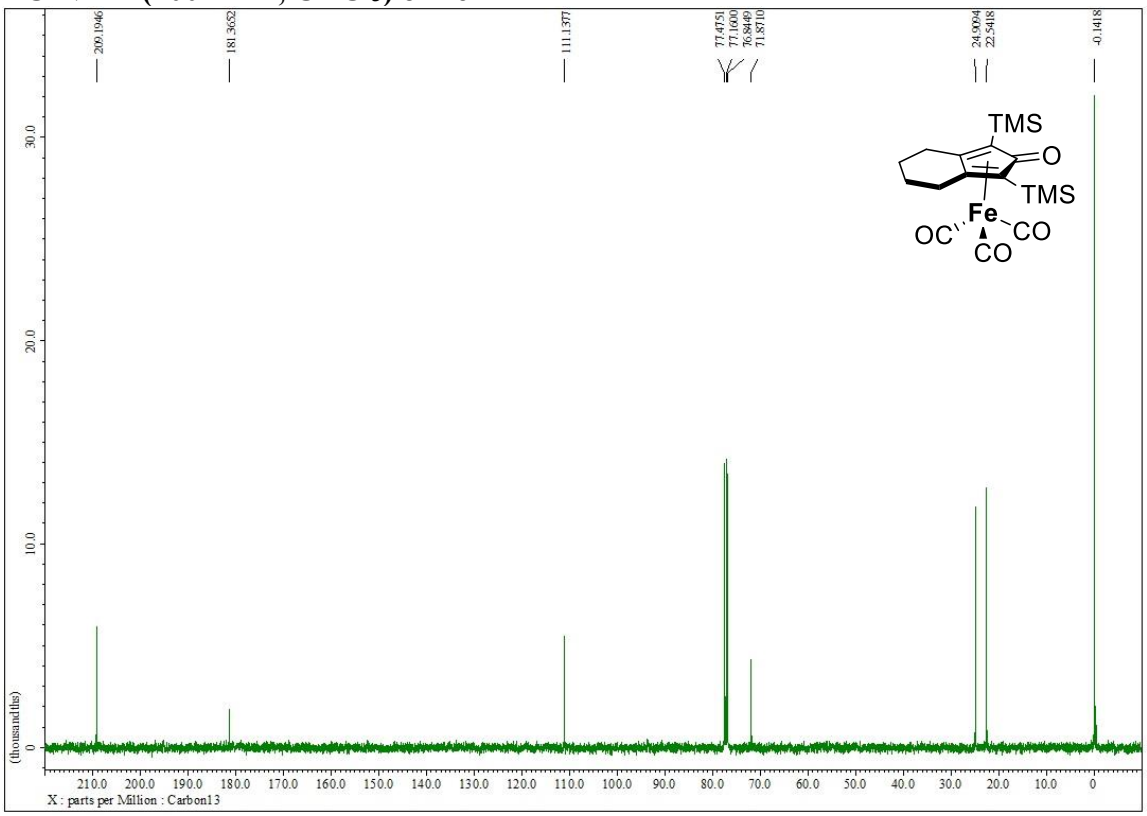
1. S. Moulin, H. Dentel, A. P. -Ozherelyeva, S. Gaillard, A. Poater, L. Cavallo, J. F. Lohier and J. L. Renaud, *Chem.–Eur. J.,* 2013, **19**, 17881−17890.
2. S. Shee, D. Panja and S. Kundu, *J. Org. Chem.,* 2020, **85**, 2775−2784.
3. F. Xie, M. Zhang, H. Jiang, M. Chen, W. Lv, A. Zhenga and X. Jiana, *Green Chem.,* 2015, **17**, 279–284.
4. X. Meng, X. Bi, C. Yu, G. Chen, B. Chen, Z. Jing and P. Zhao, *Green Chem.,* 2018, **20**, 4638–4644.

7. NMR spectra

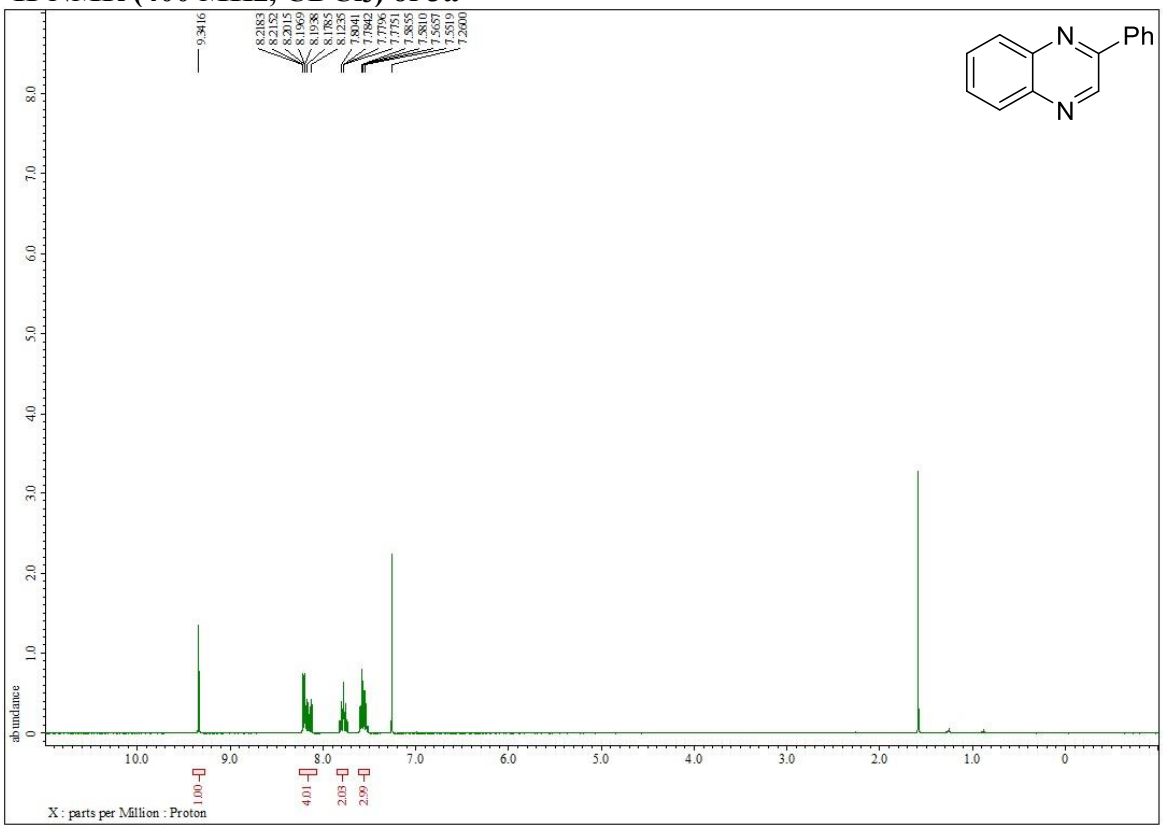
^{1}H-NMR (400 MHz, $CDCl_3$) of Fe 1



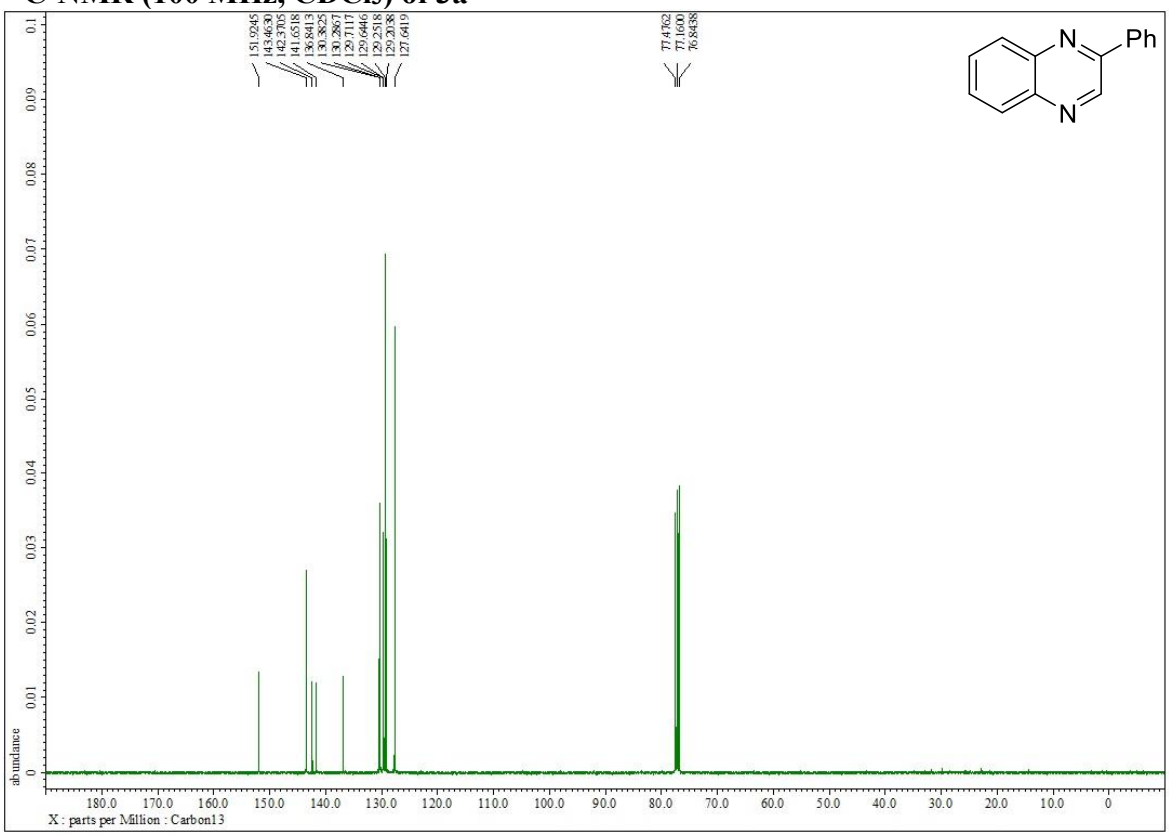
^{13}C-NMR (100 MHz, $CDCl_3$) of Fe 1



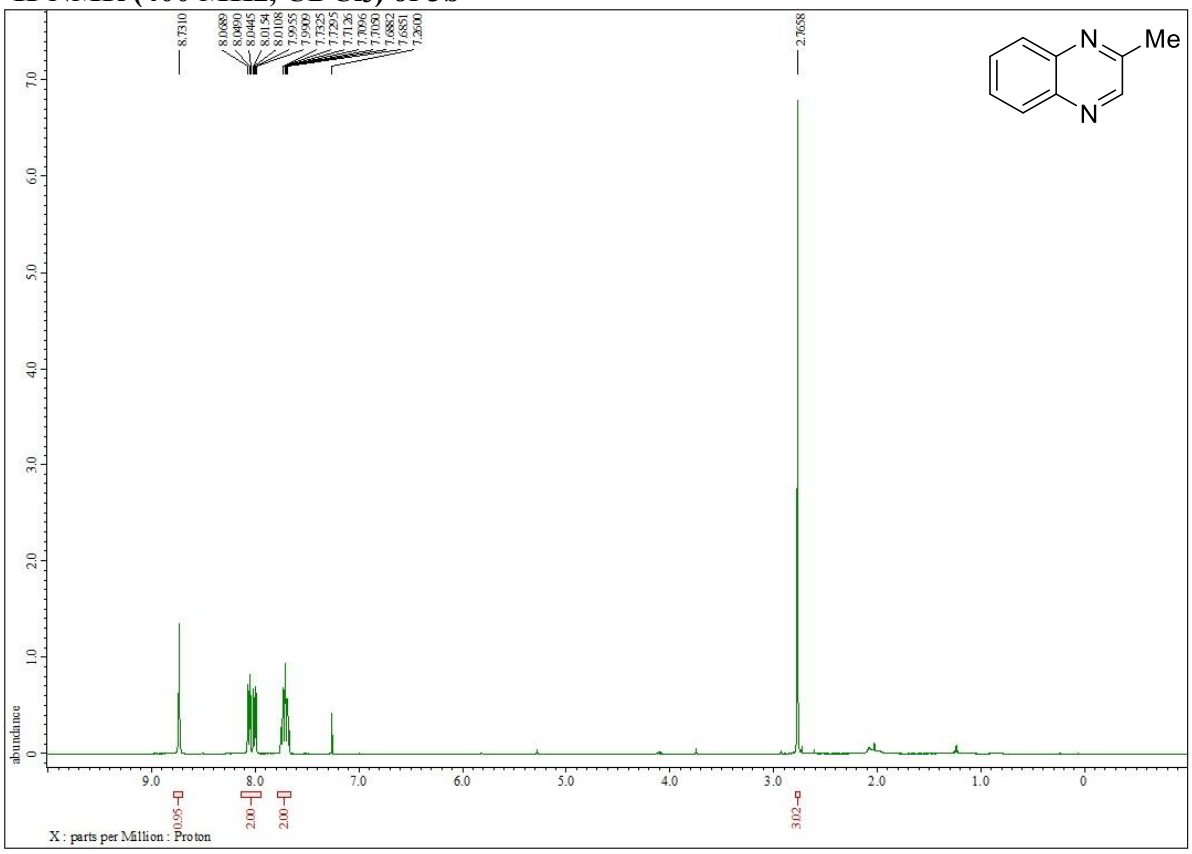
^{1}H-NMR (400 MHz, $CDCl_3$) of 3a



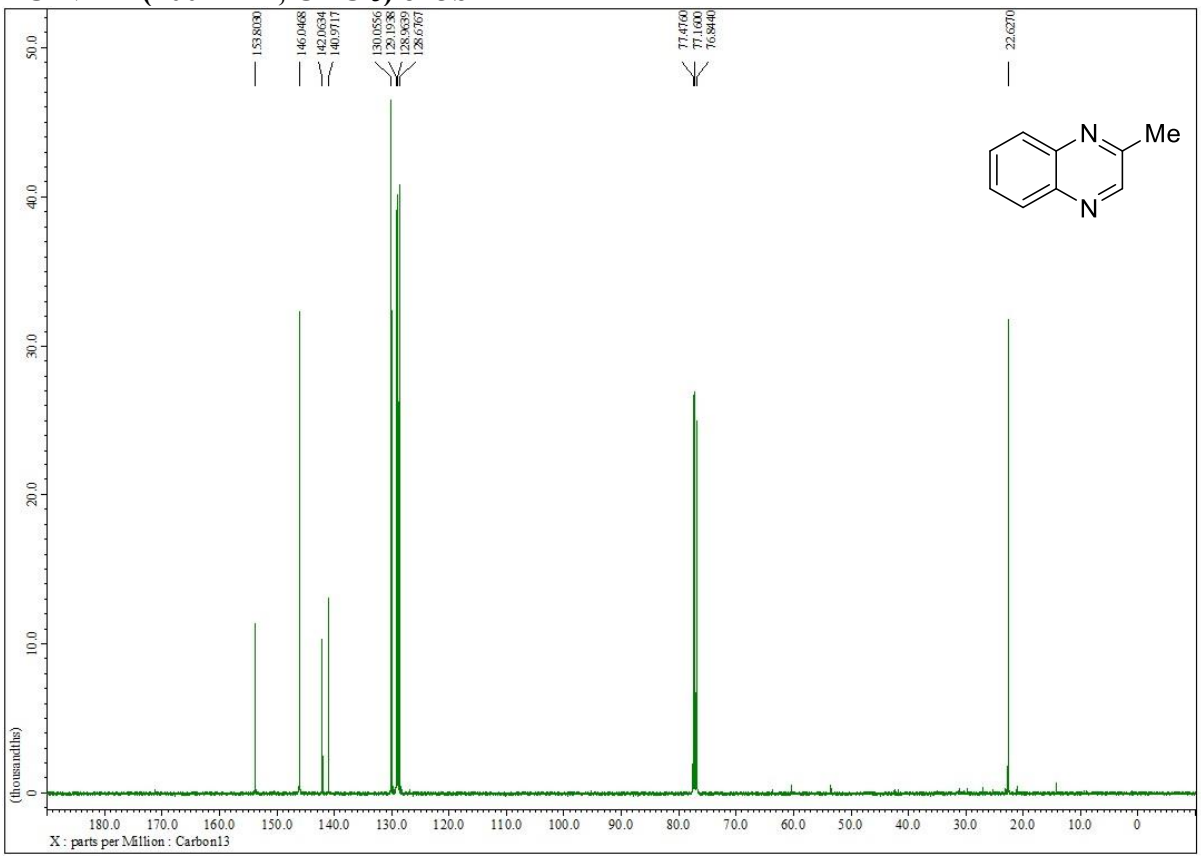
^{13}C-NMR (100 MHz, $CDCl_3$) of 3a



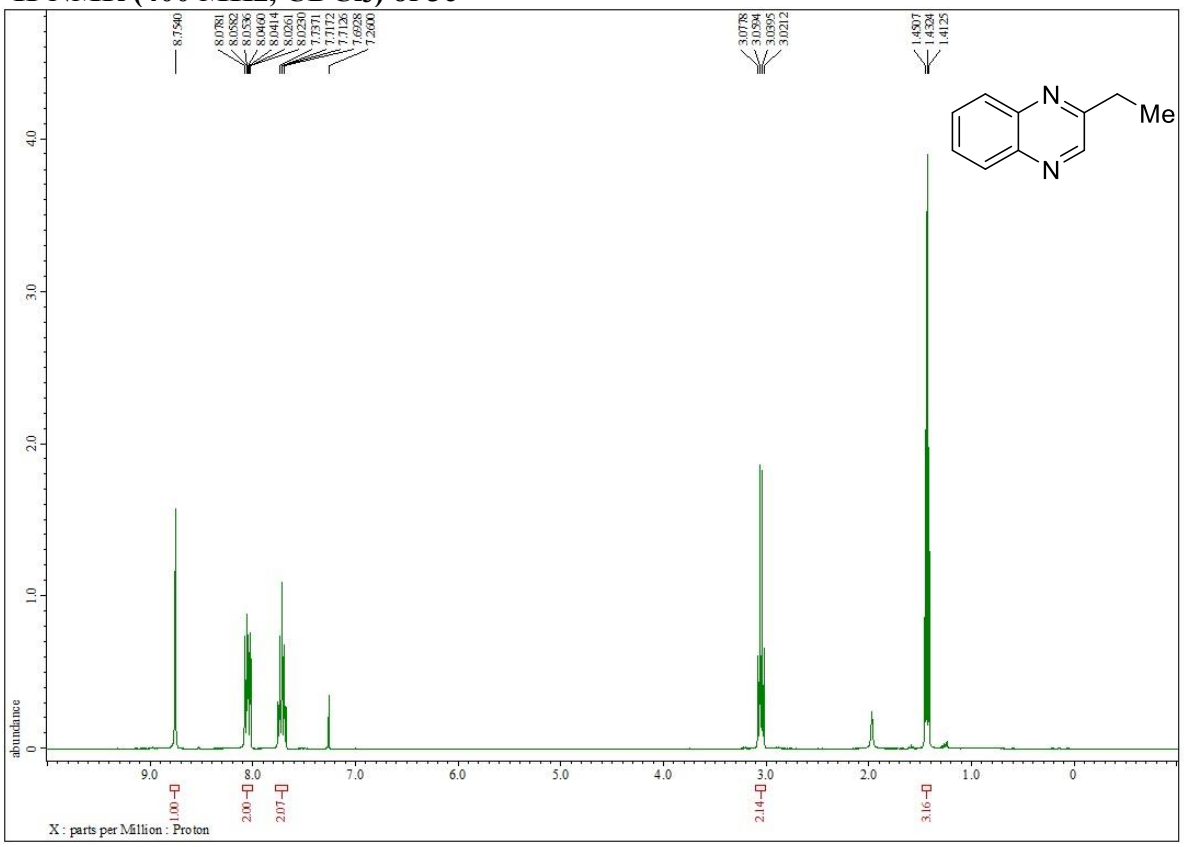
^{1}H-NMR (400 MHz, $CDCl_3$) of 3b



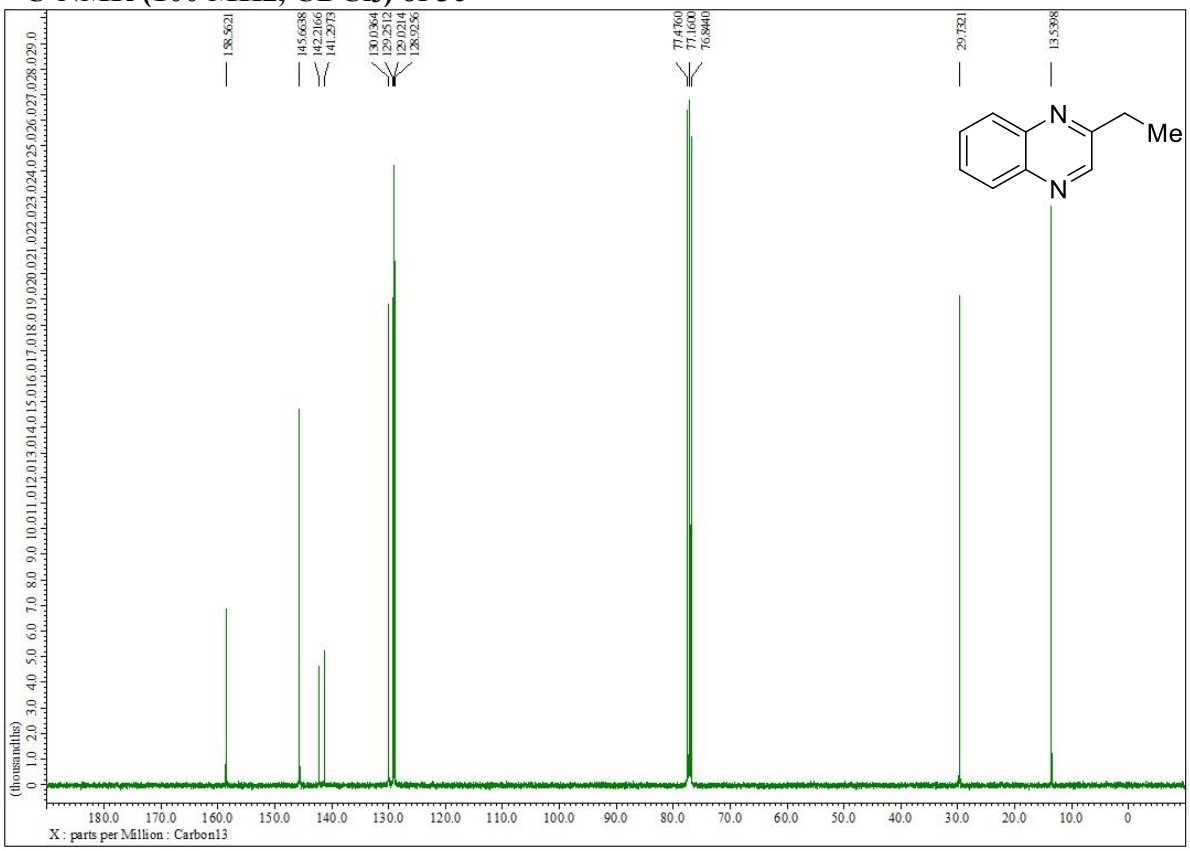
^{13}C-NMR (100 MHz, $CDCl_3$) of 3b



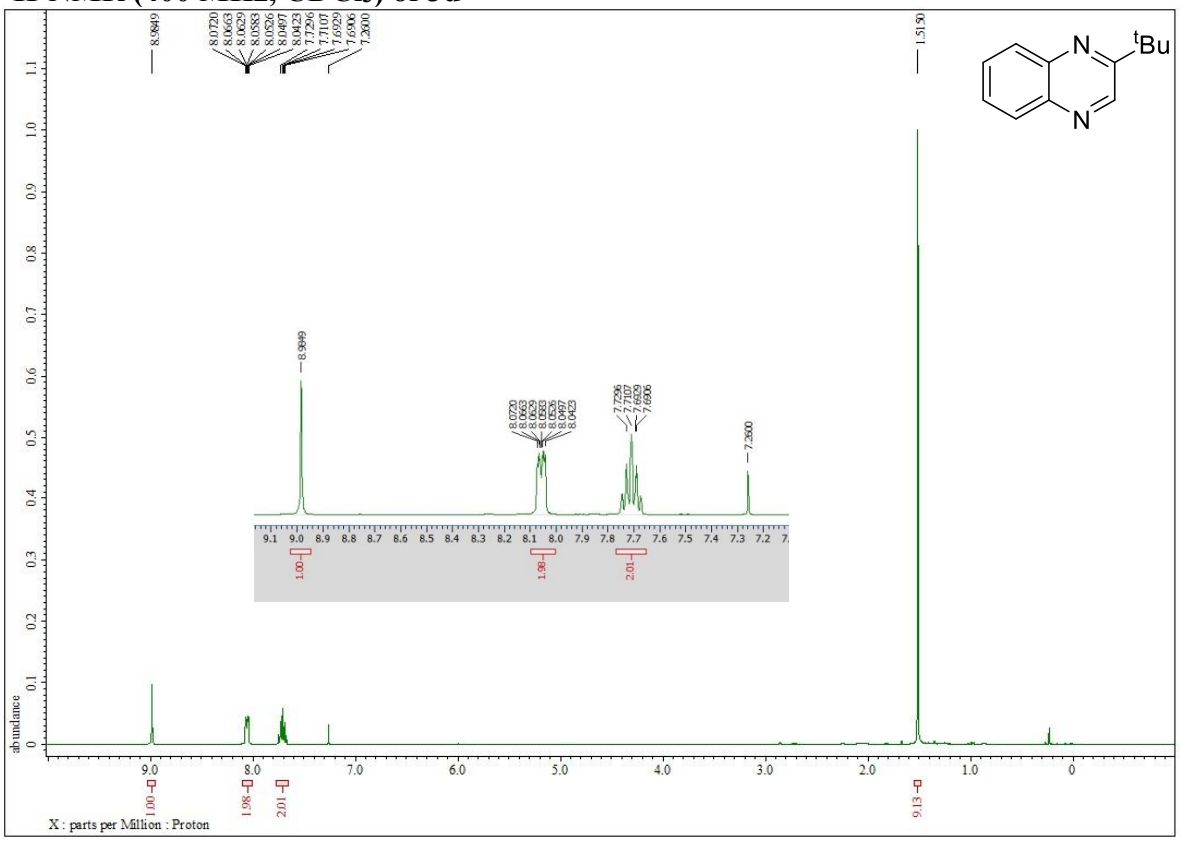
^{1}H-NMR (400 MHz, $CDCl_3$) of 3c



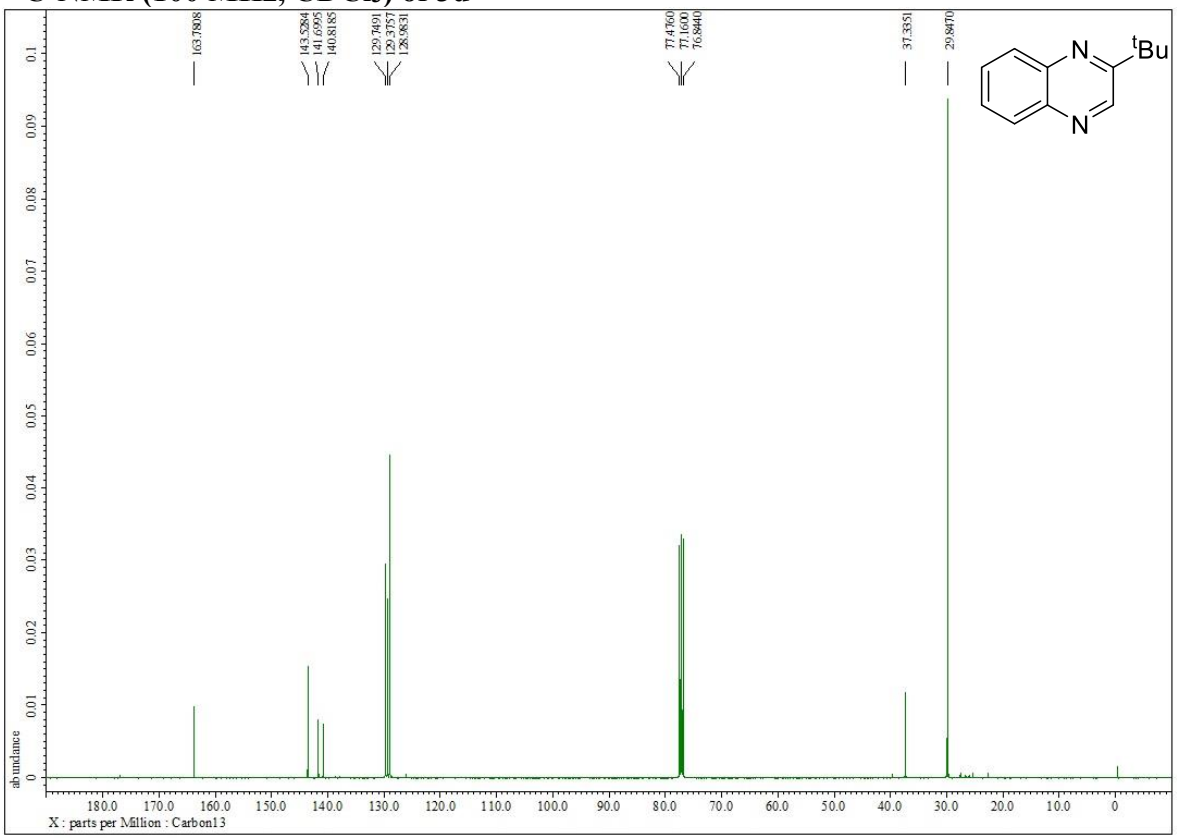
^{13}C-NMR (100 MHz, $CDCl_3$) of 3c



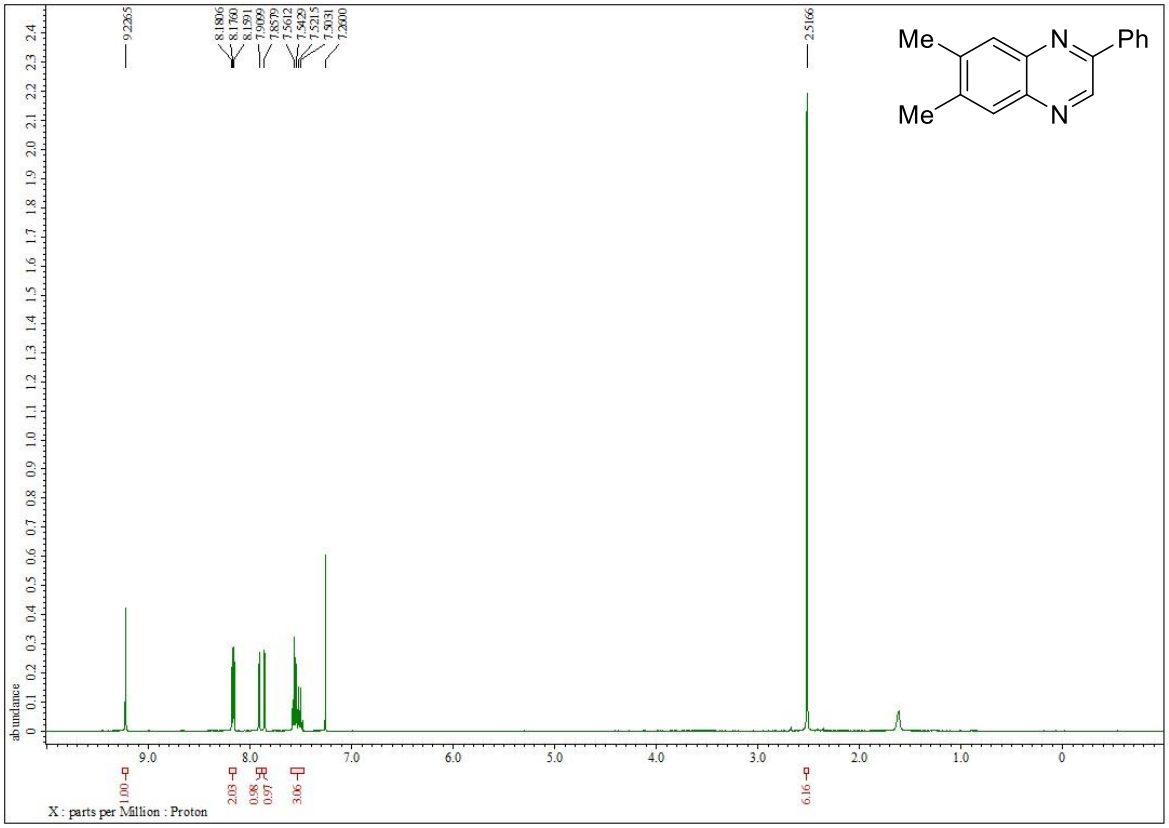
^{1}H-NMR (400 MHz, $CDCl_3$) of 3d



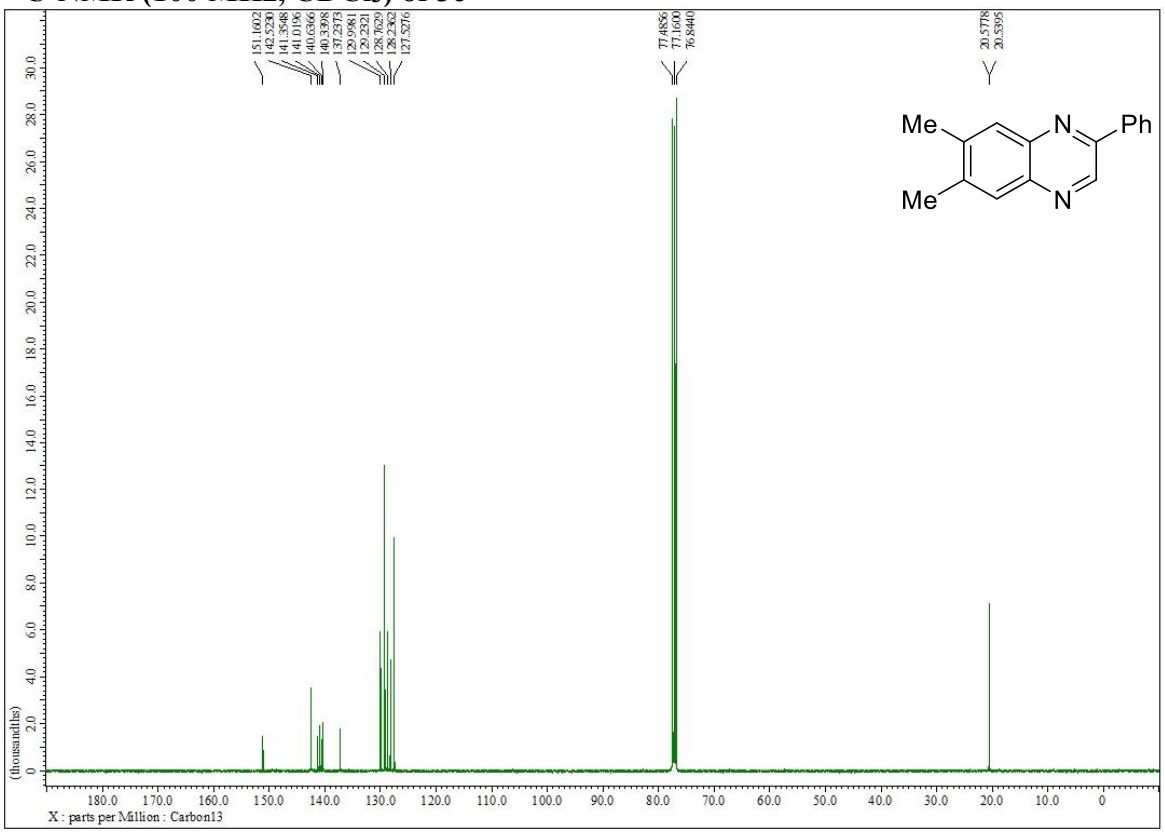
^{13}C-NMR (100 MHz, $CDCl_3$) of 3d



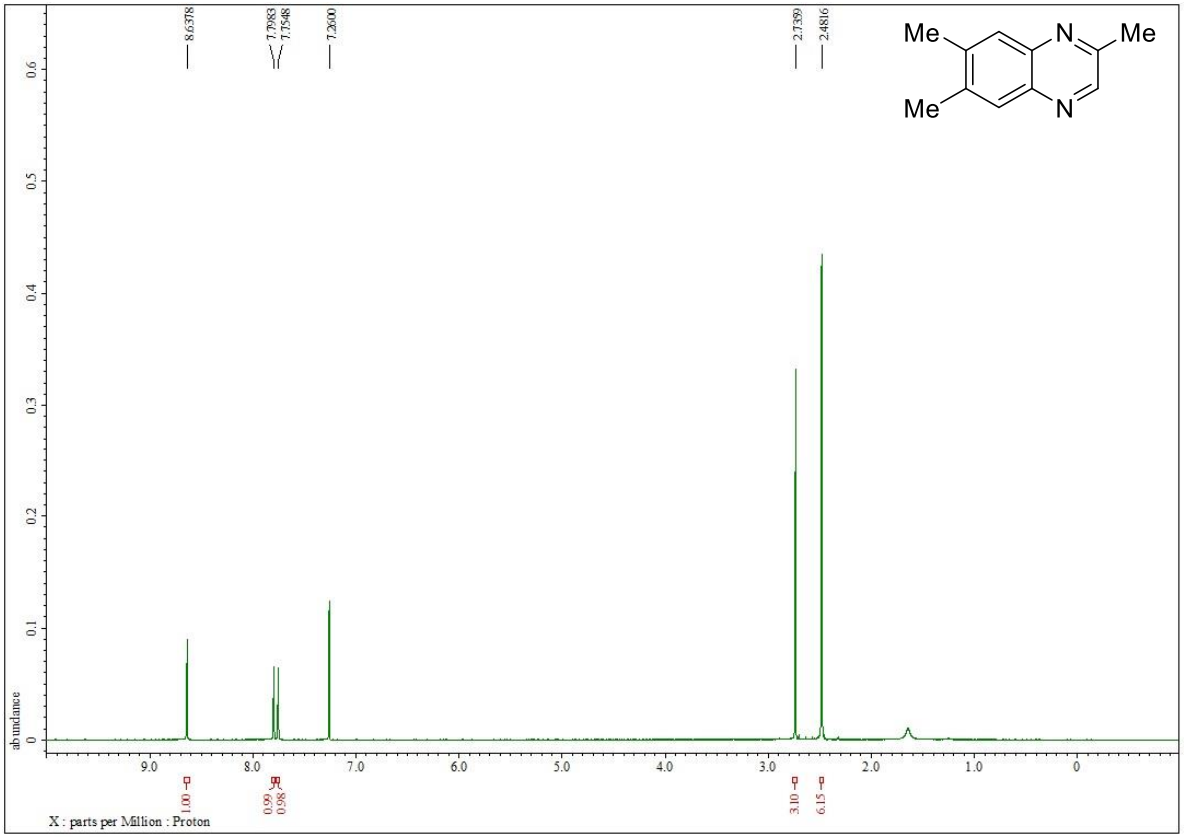
^{1}H-NMR (400 MHz, $CDCl_3$) of 3e



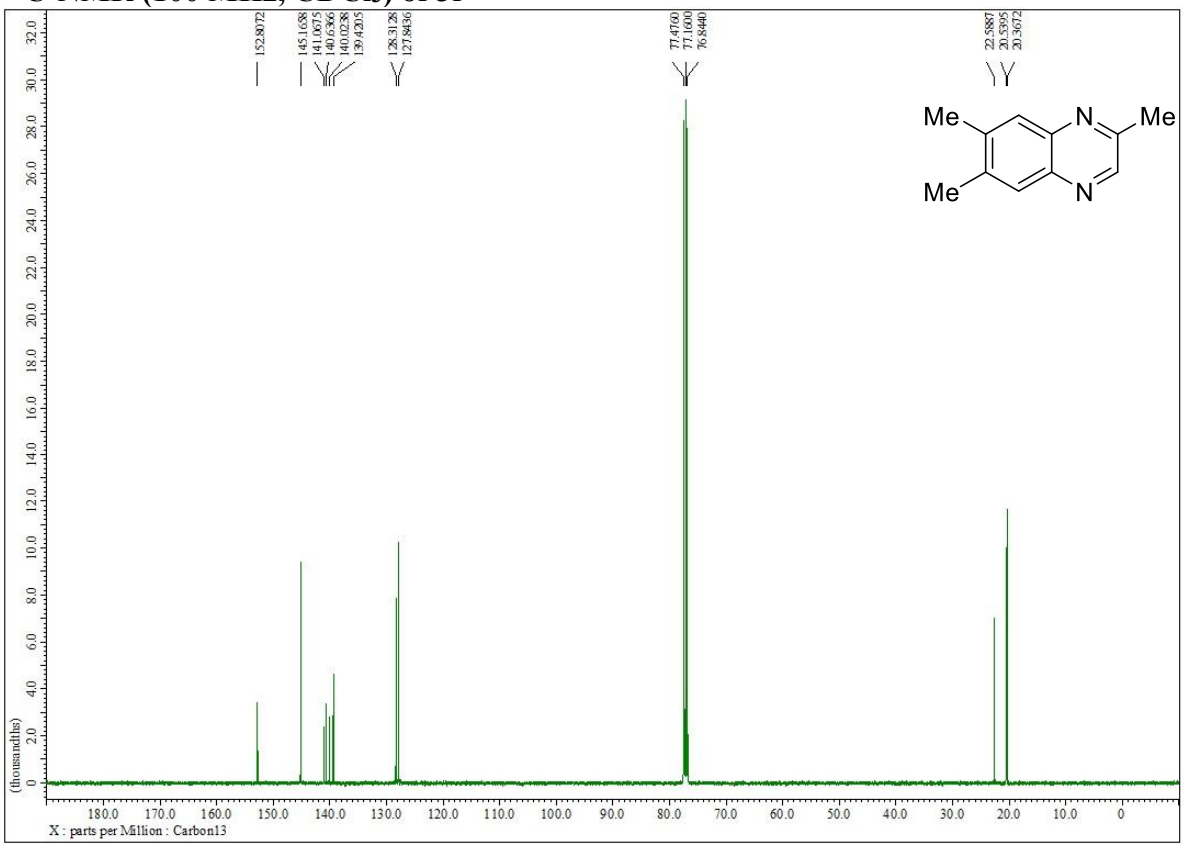
^{13}C-NMR (100 MHz, $CDCl_3$) of 3e



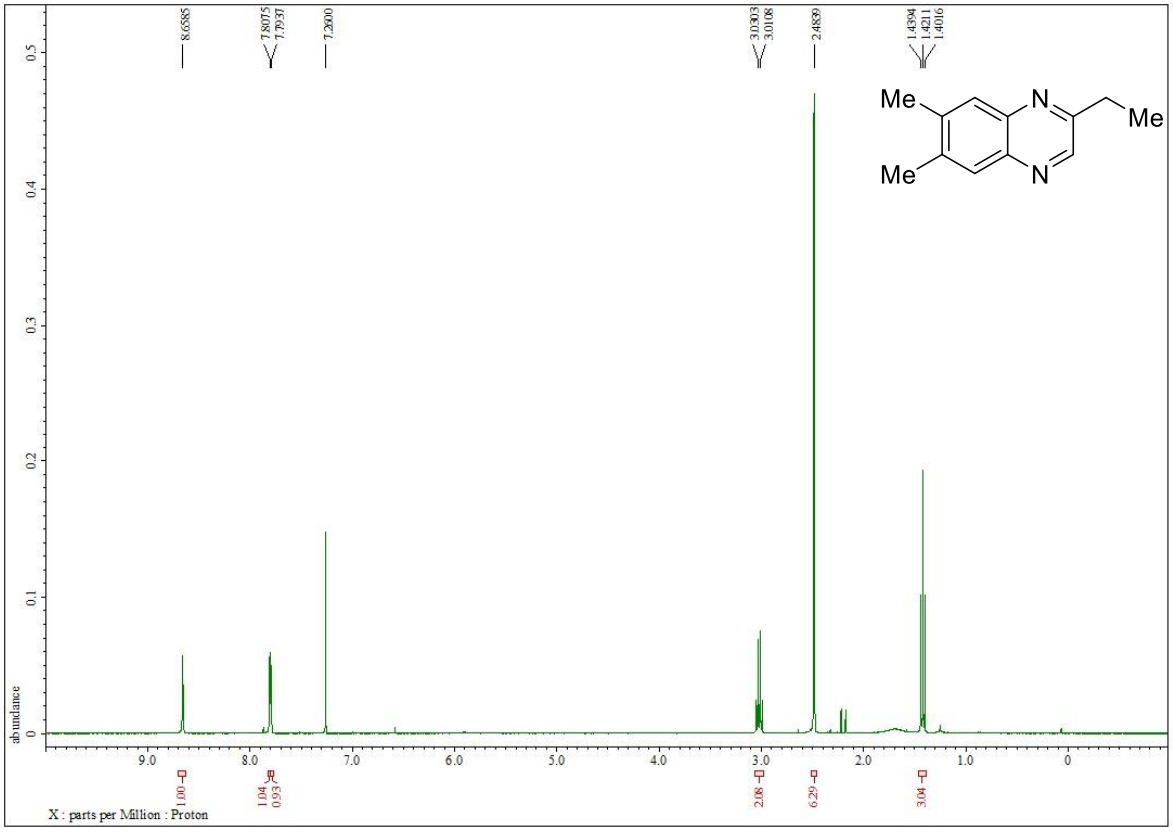
^{1}H-NMR (400 MHz, $CDCl_3$) of 3f



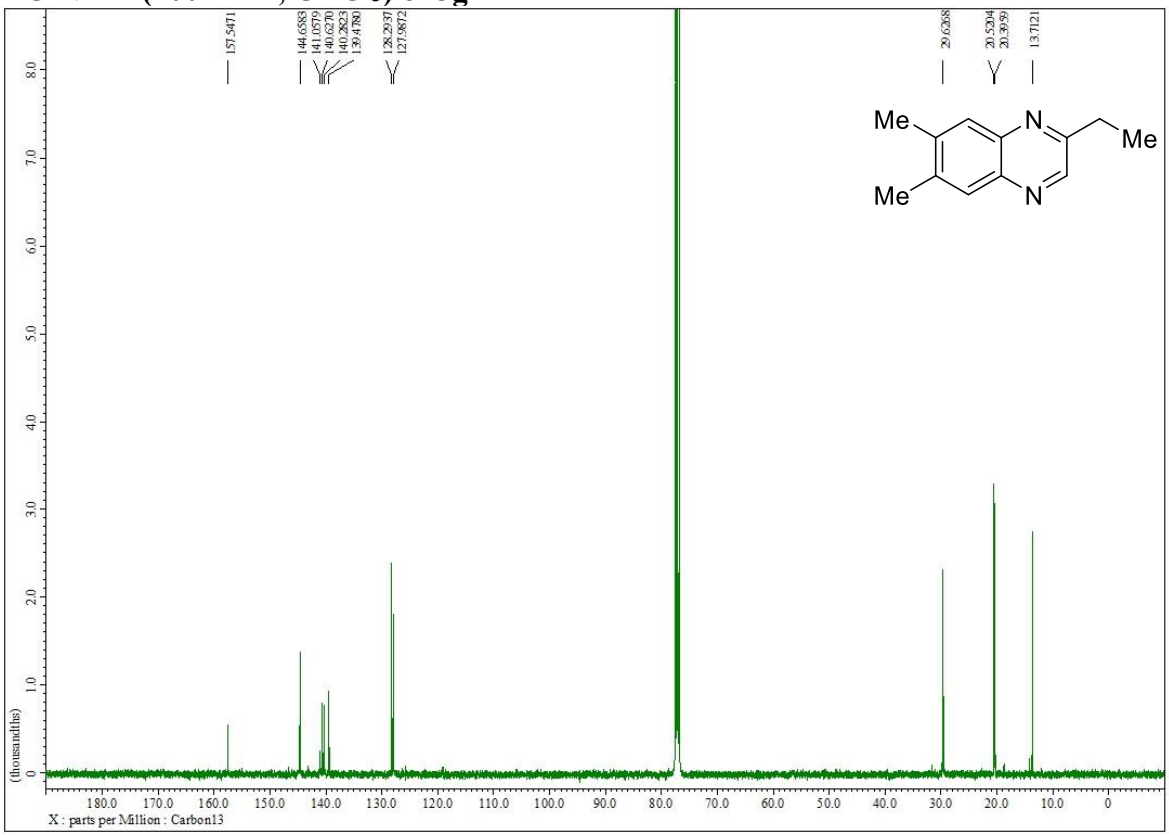
^{13}C-NMR (100 MHz, $CDCl_3$) of 3f



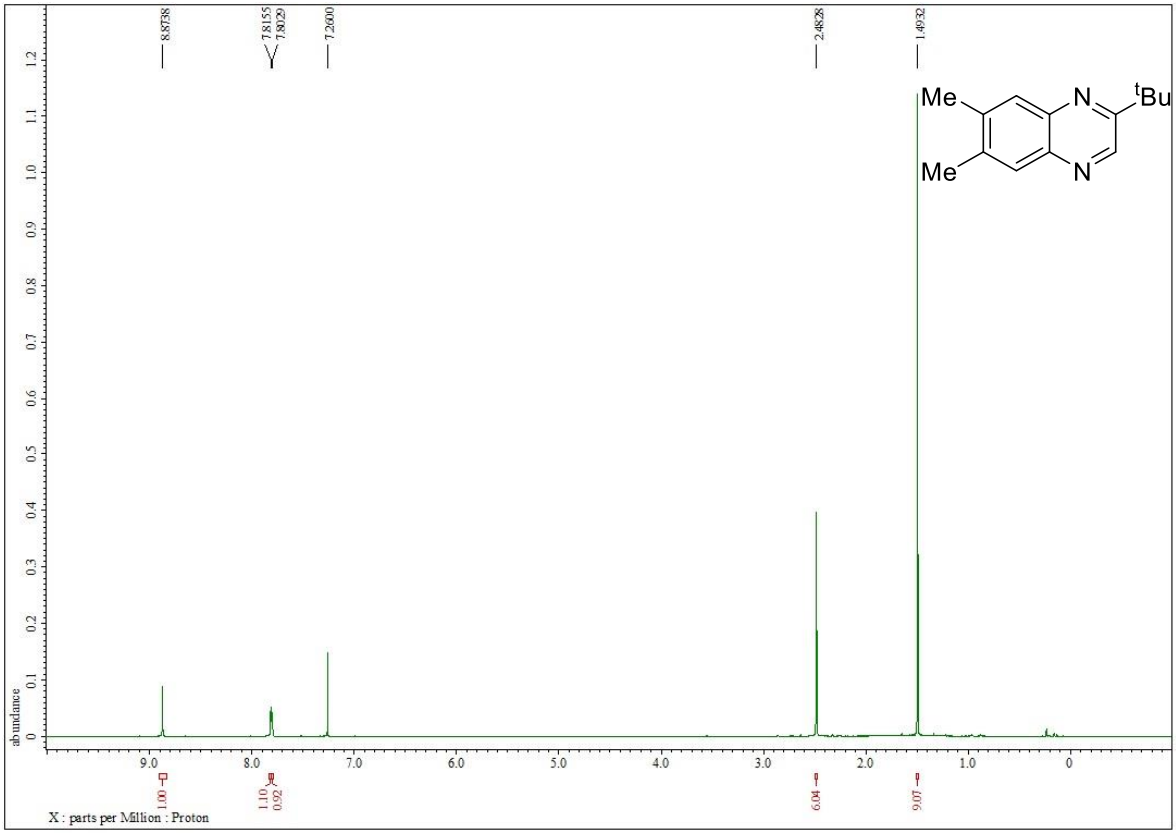
^{1}H-NMR (400 MHz, $CDCl_3$) of 3g



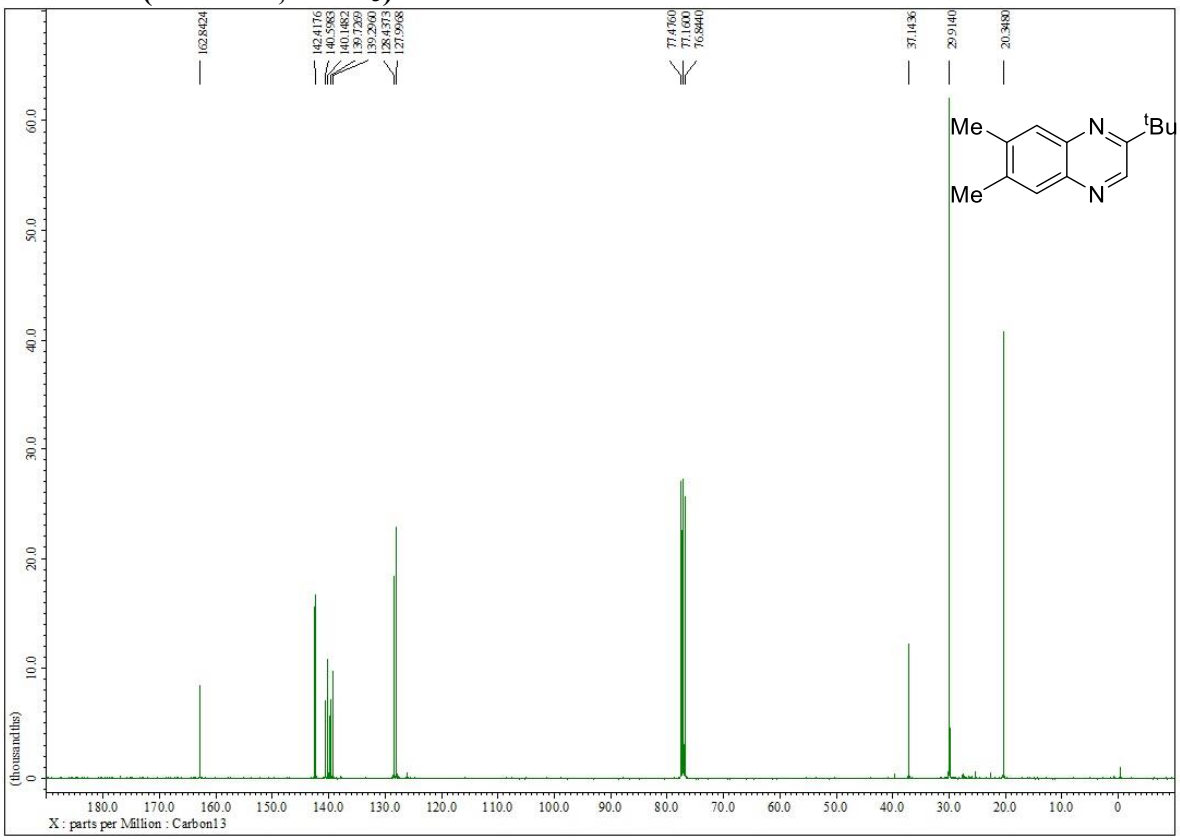
^{13}C-NMR (100 MHz, $CDCl_3$) of 3g



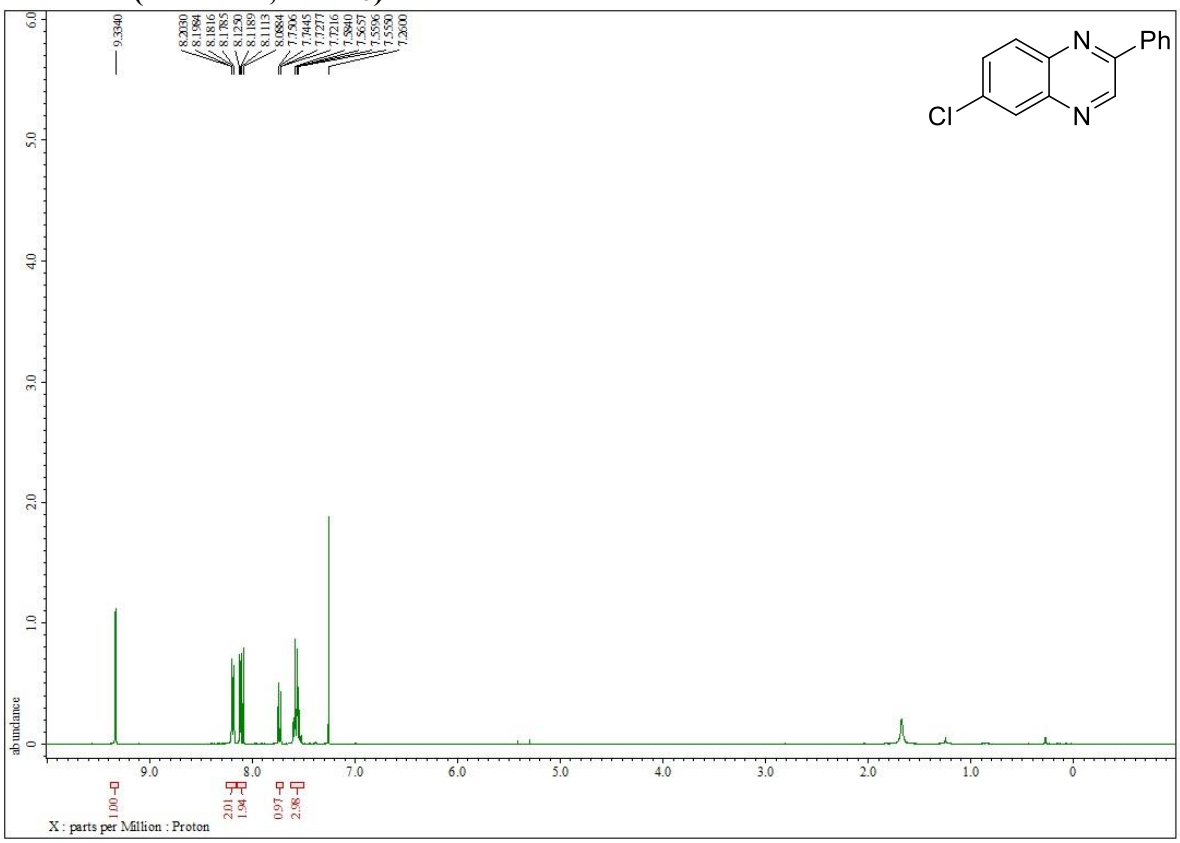
^{1}H-NMR (400 MHz, $CDCl_3$) of 3h



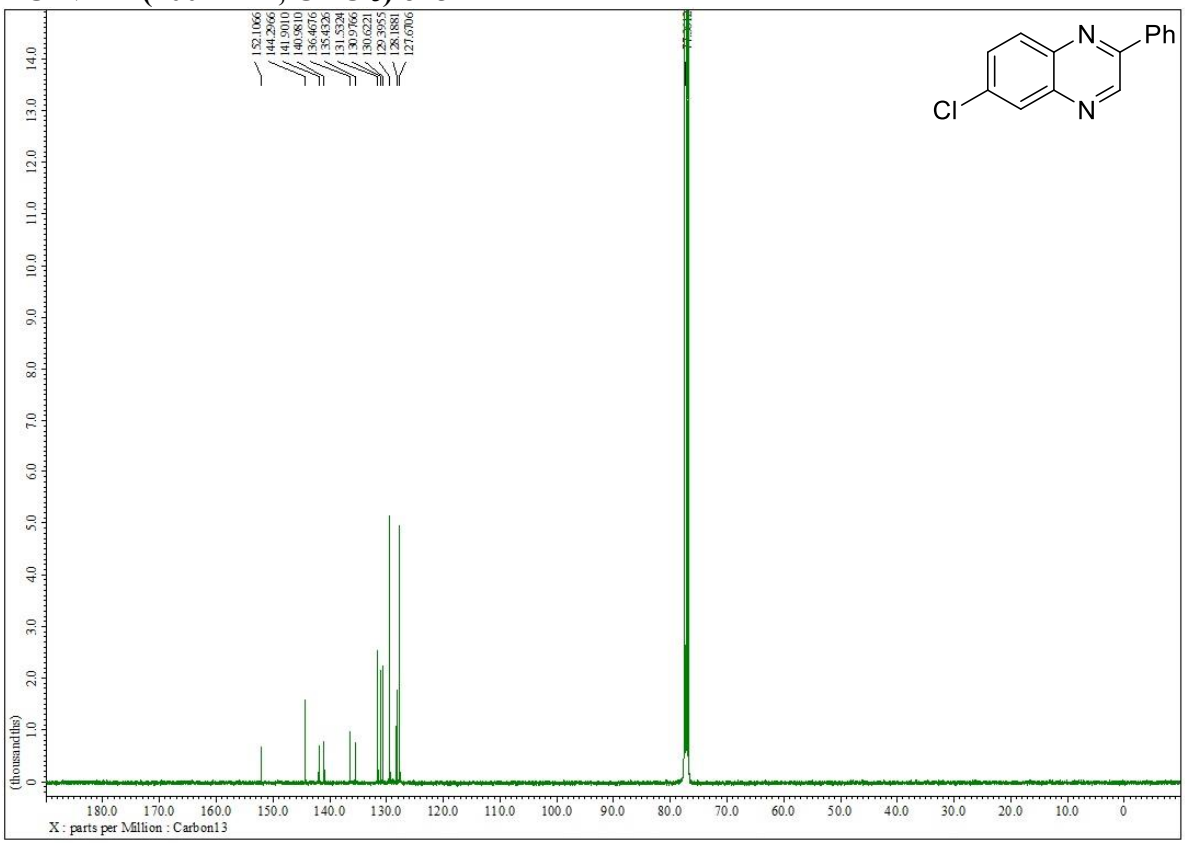
^{13}C-NMR (100 MHz, $CDCl_3$) of 3h



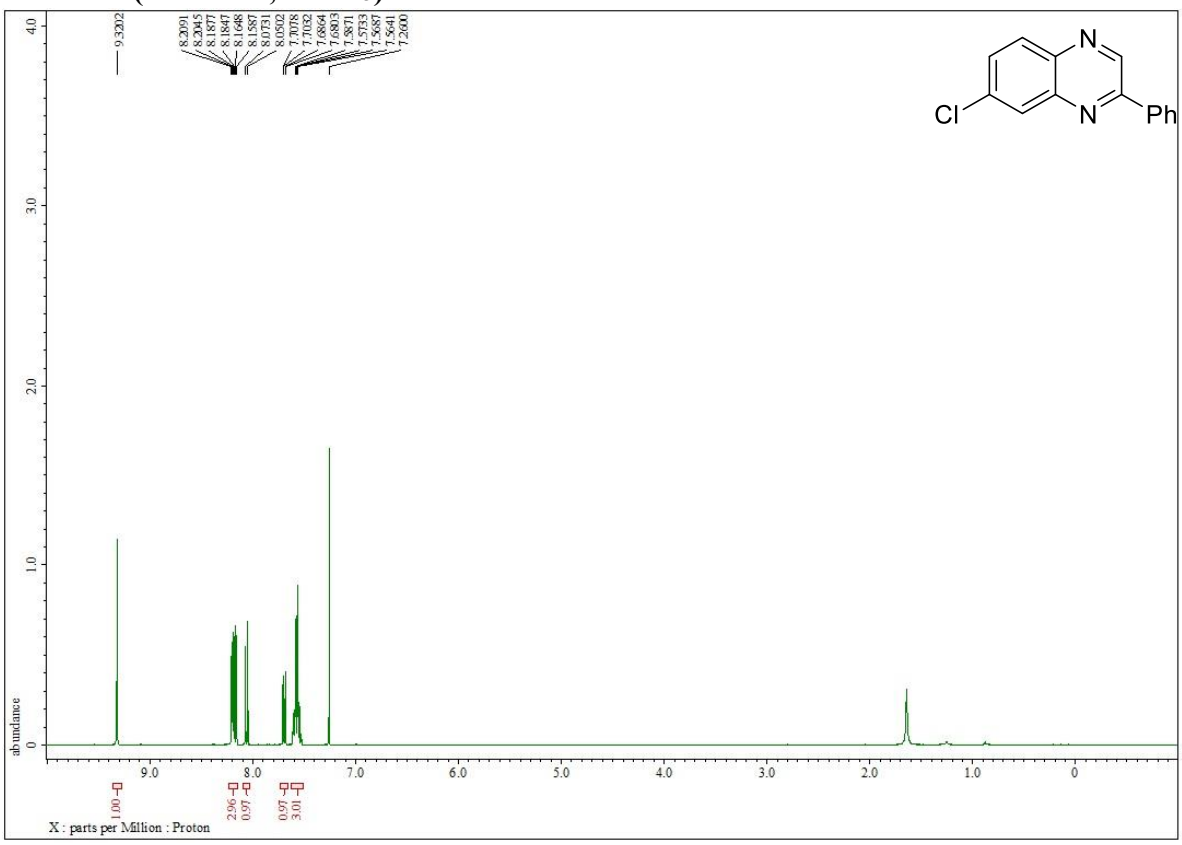
^{1}H-NMR (400 MHz, $CDCl_3$) of 3i



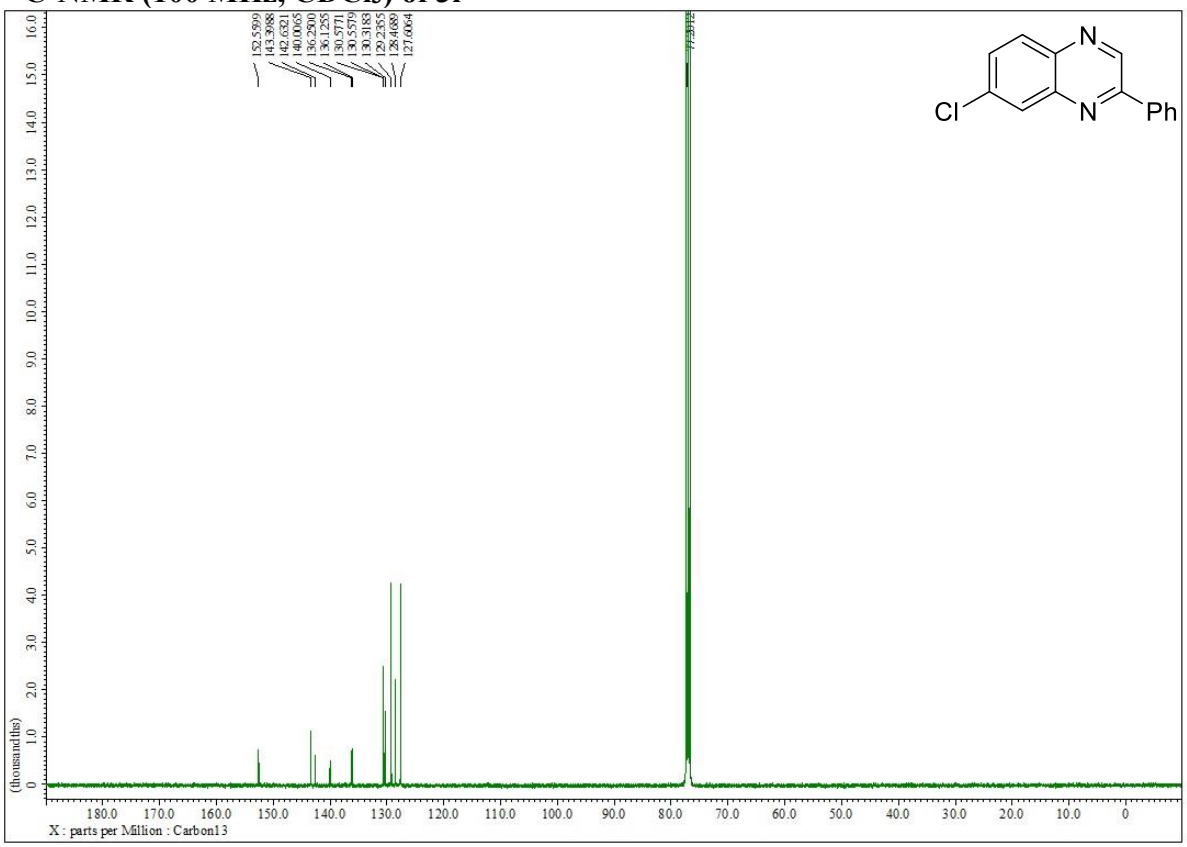
^{13}C-NMR (100 MHz, $CDCl_3$) of 3i



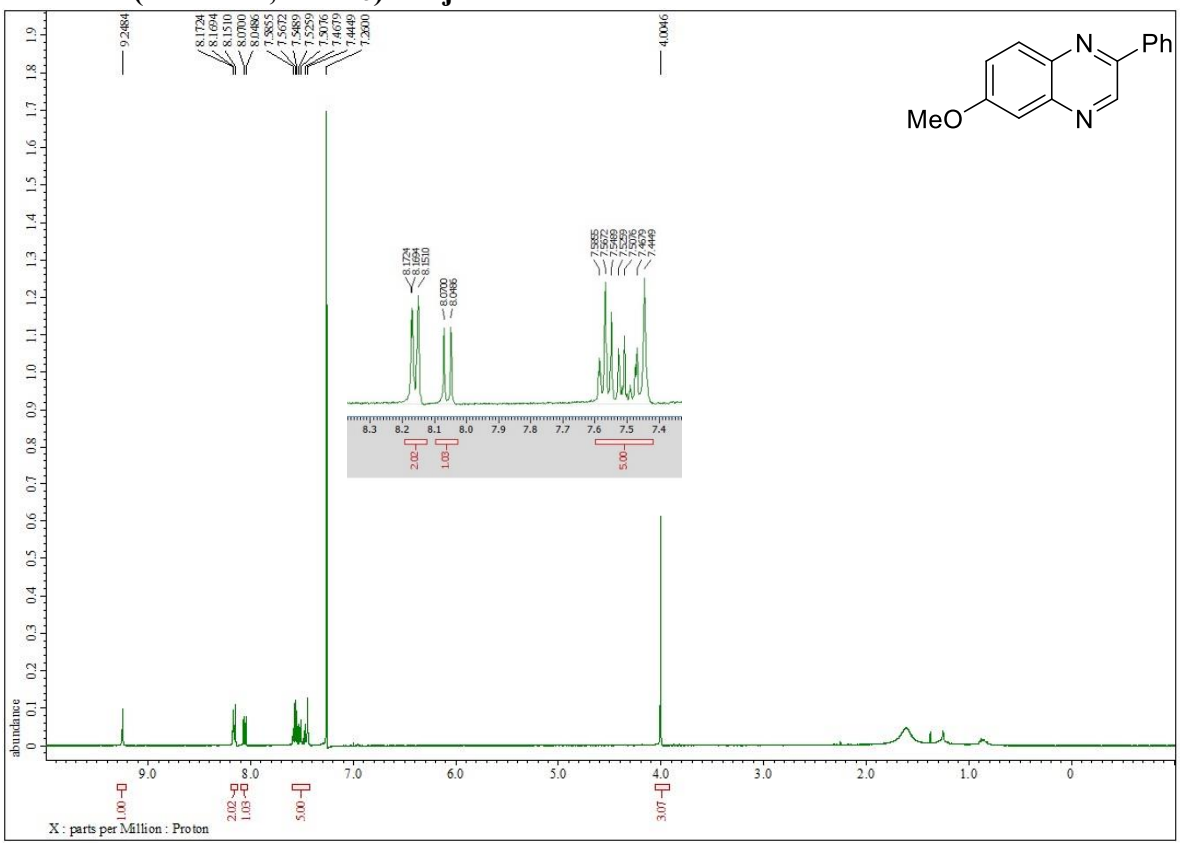
^{1}H-NMR (400 MHz, $CDCl_3$) of 3i′



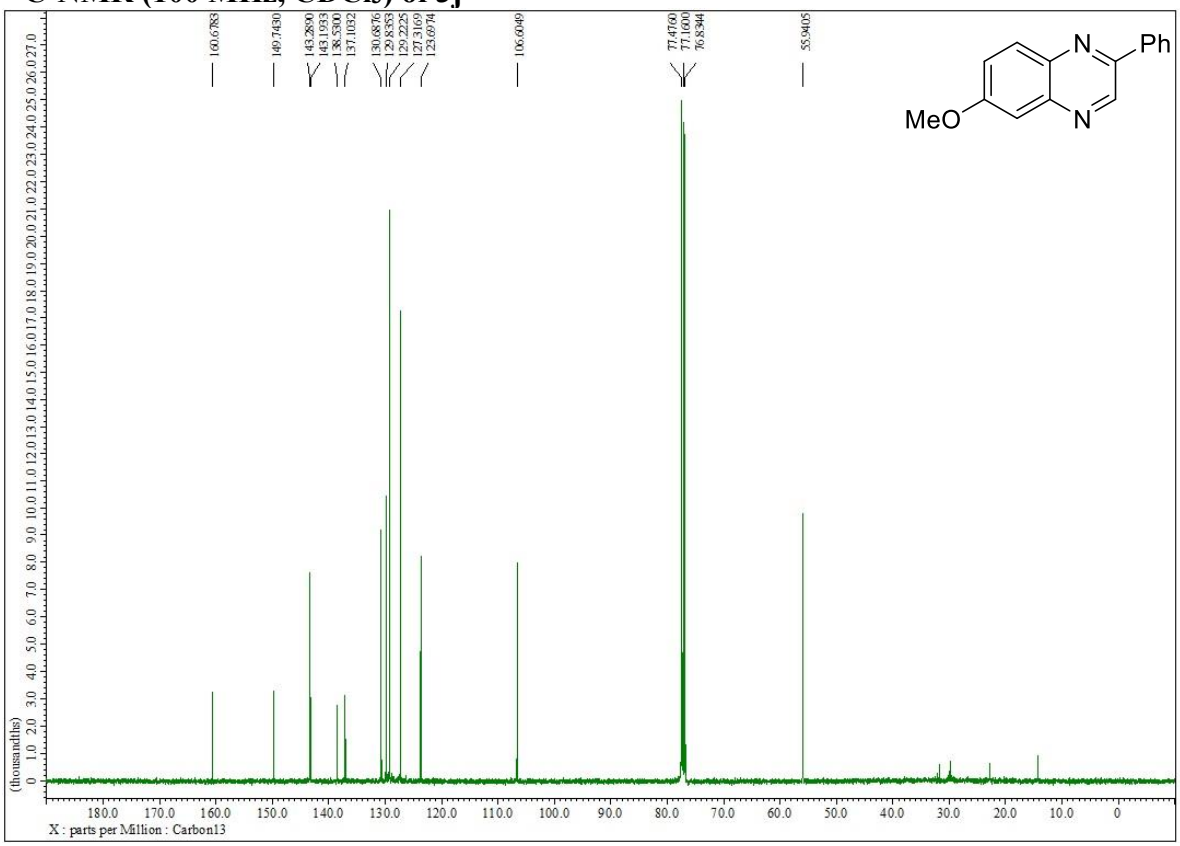
^{13}C-NMR (100 MHz, $CDCl_3$) of 3i′



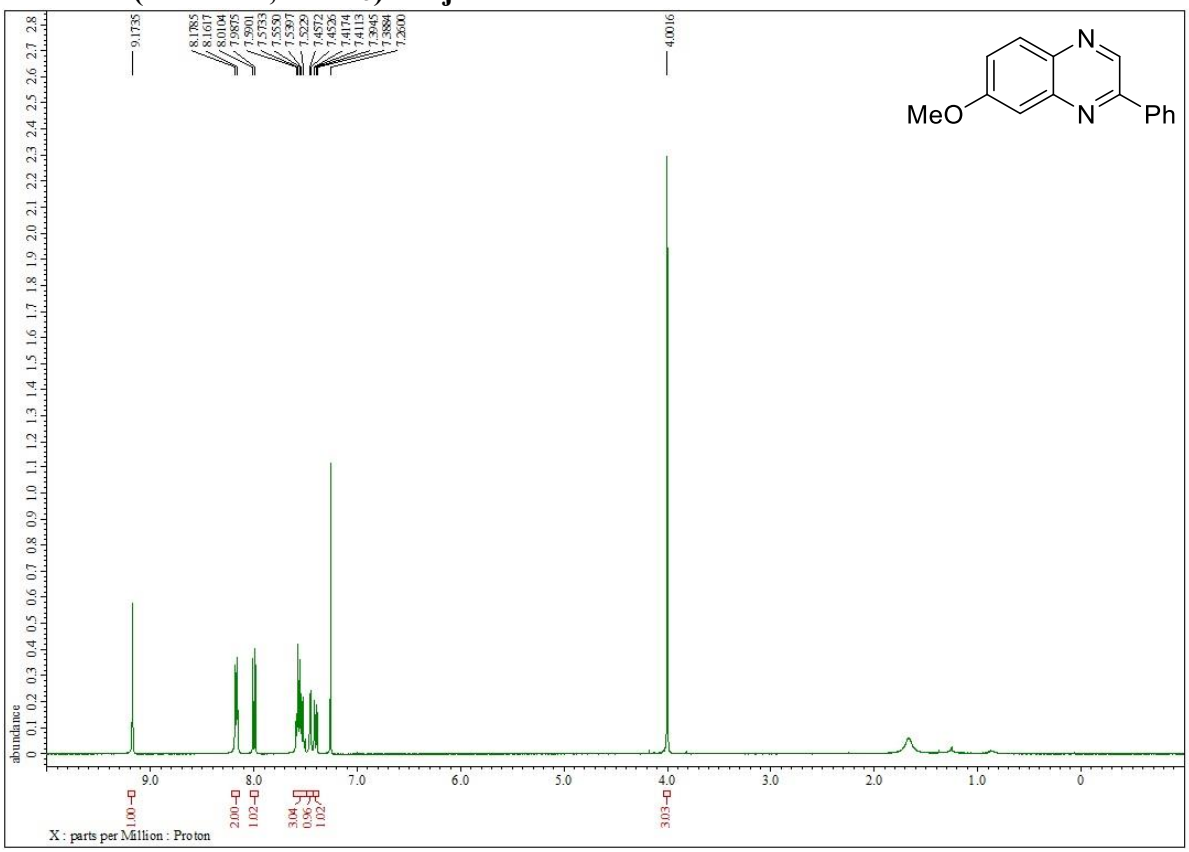
^{1}H-NMR (100 MHz, $CDCl_3$) of 3j



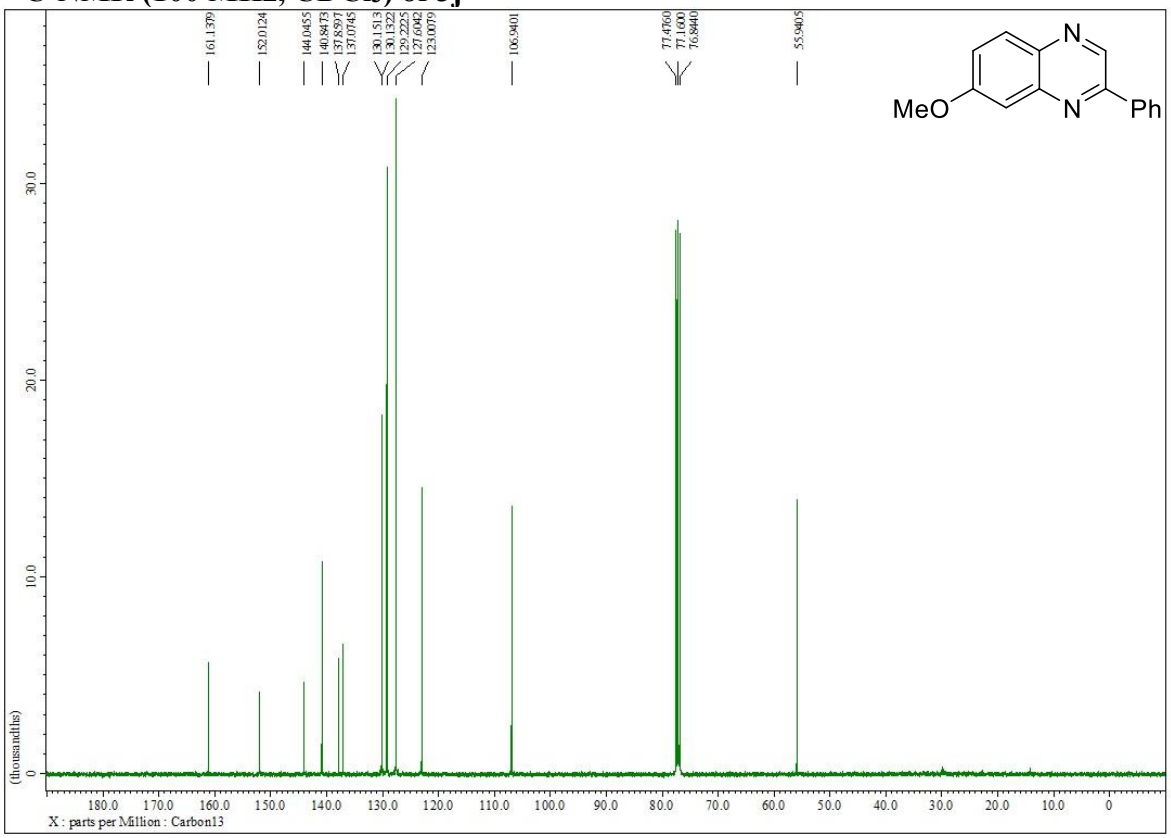
^{13}C-NMR (100 MHz, $CDCl_3$) of 3j



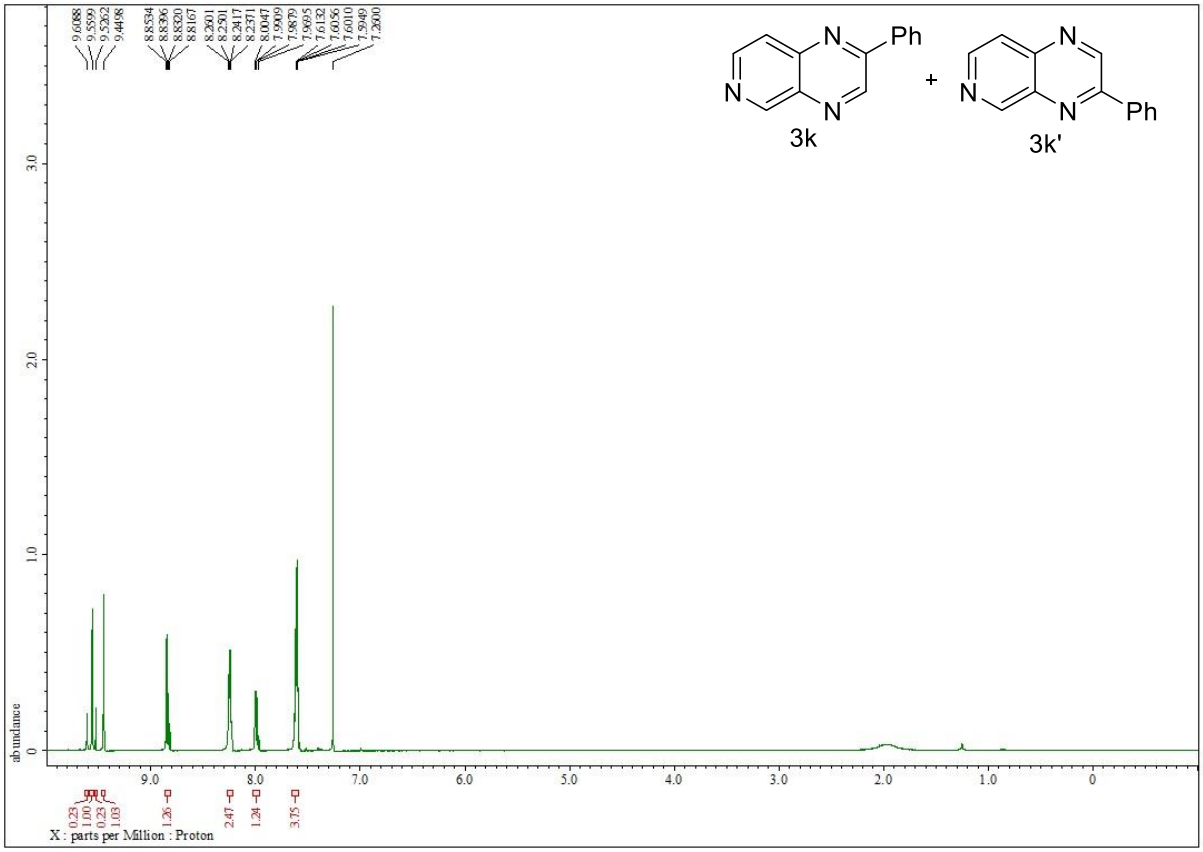
^{1}H-NMR (100 MHz, $CDCl_3$) of 3j′



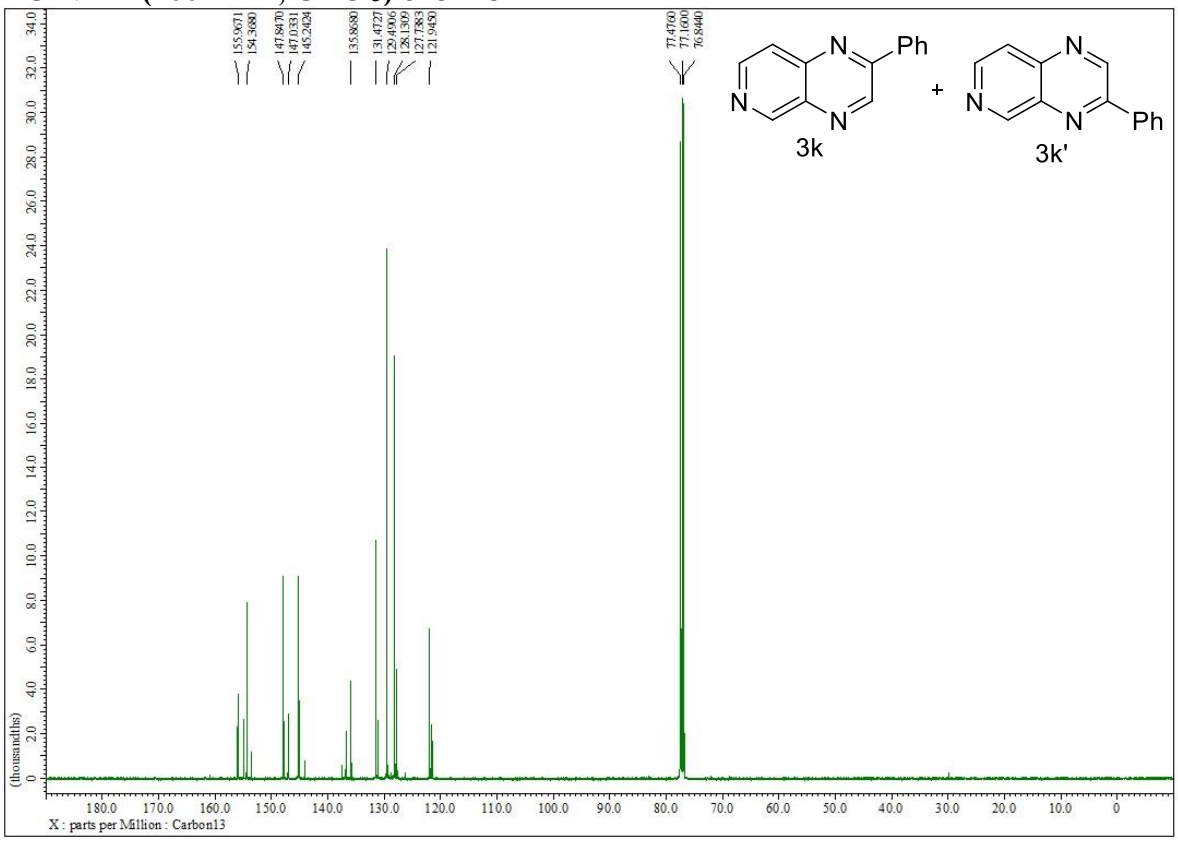
^{13}C-NMR (100 MHz, $CDCl_3$) of 3j′



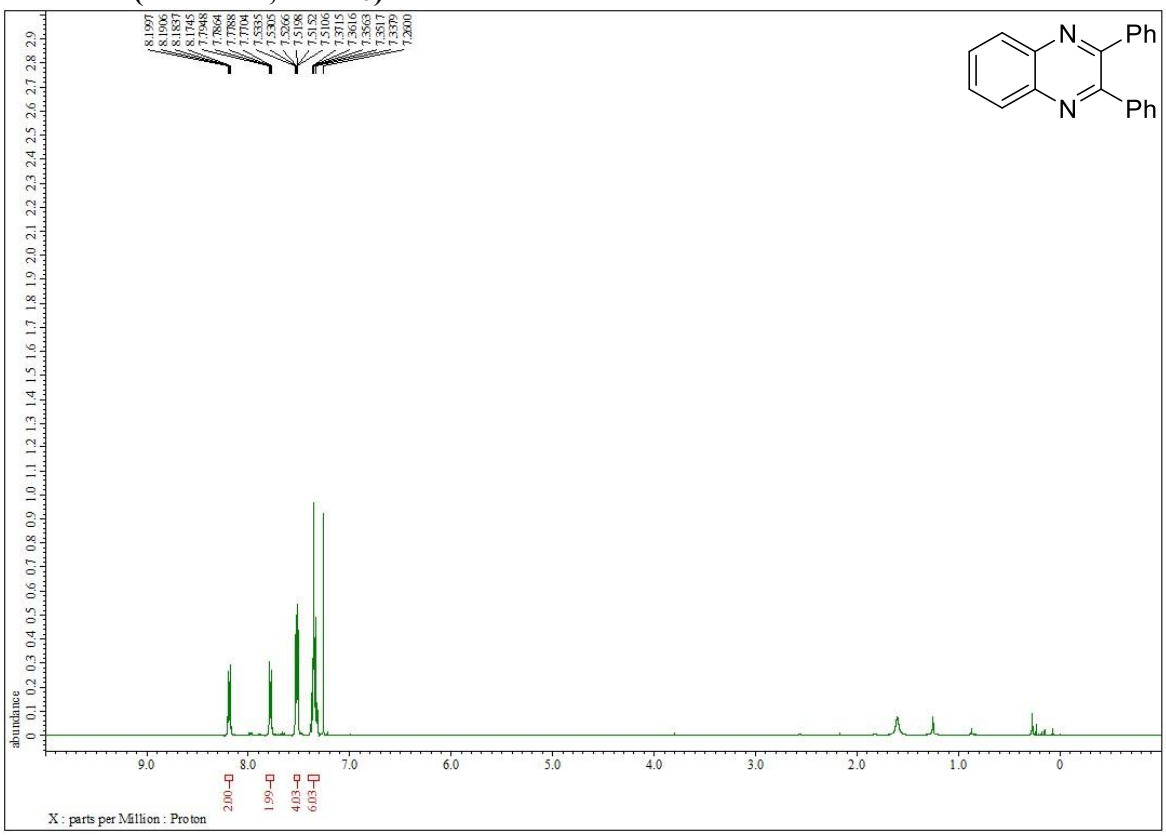
^{1}H-NMR (400 MHz, $CDCl_3$) of 3k+3k′



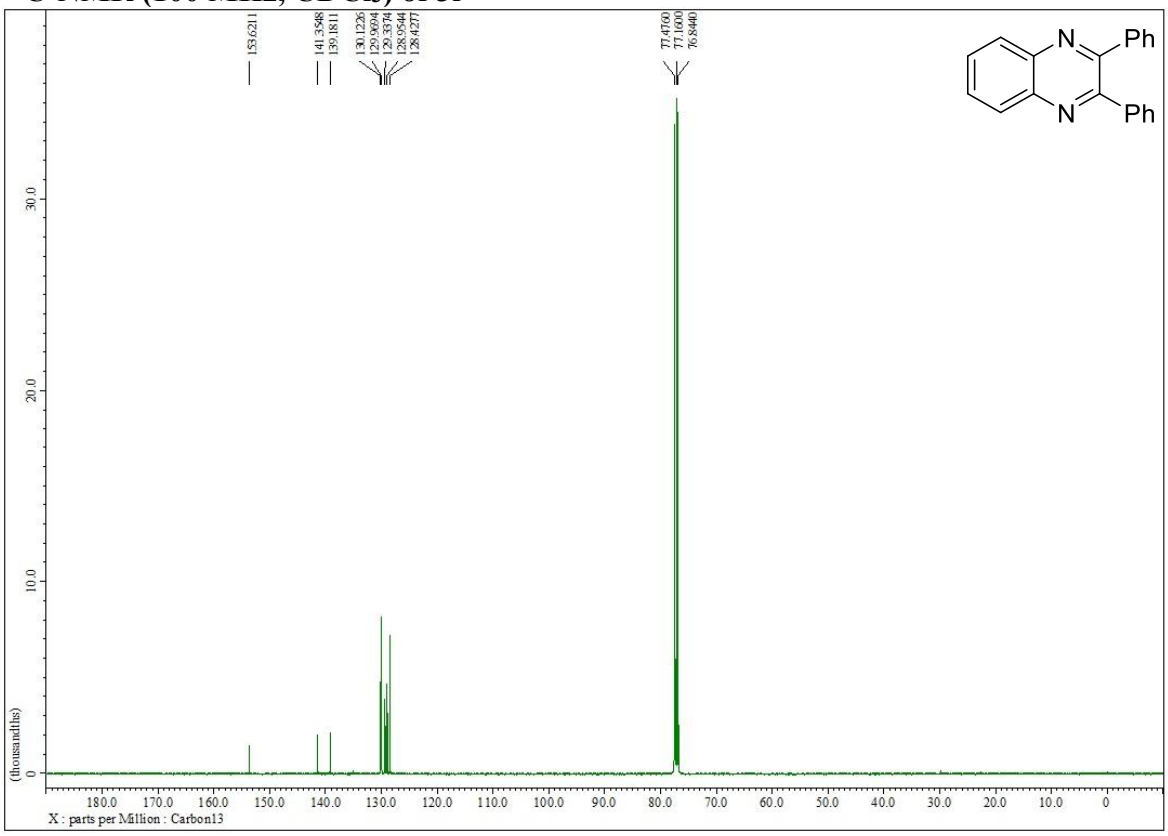
^{13}C-NMR (100 MHz, $CDCl_3$) of 3k+3k′



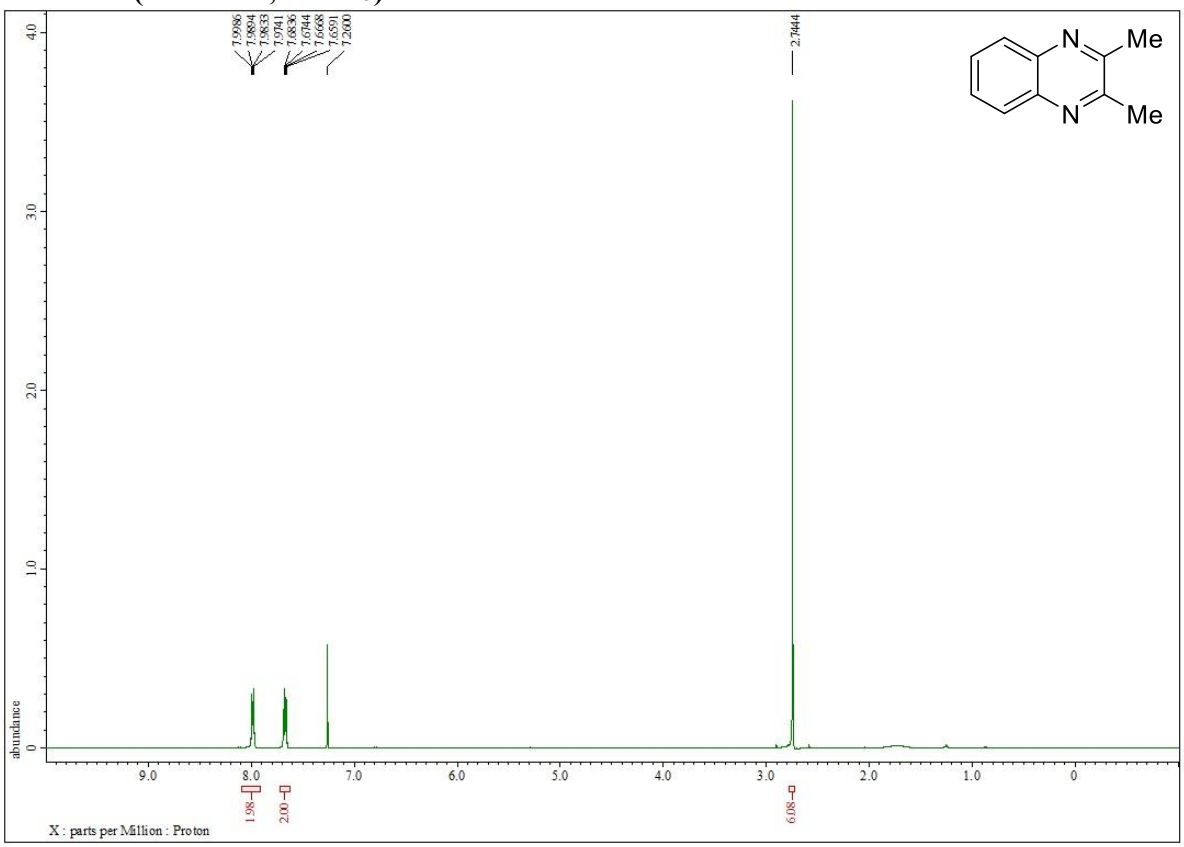
^{1}H-NMR (400 MHz, $CDCl_3$) of 3l



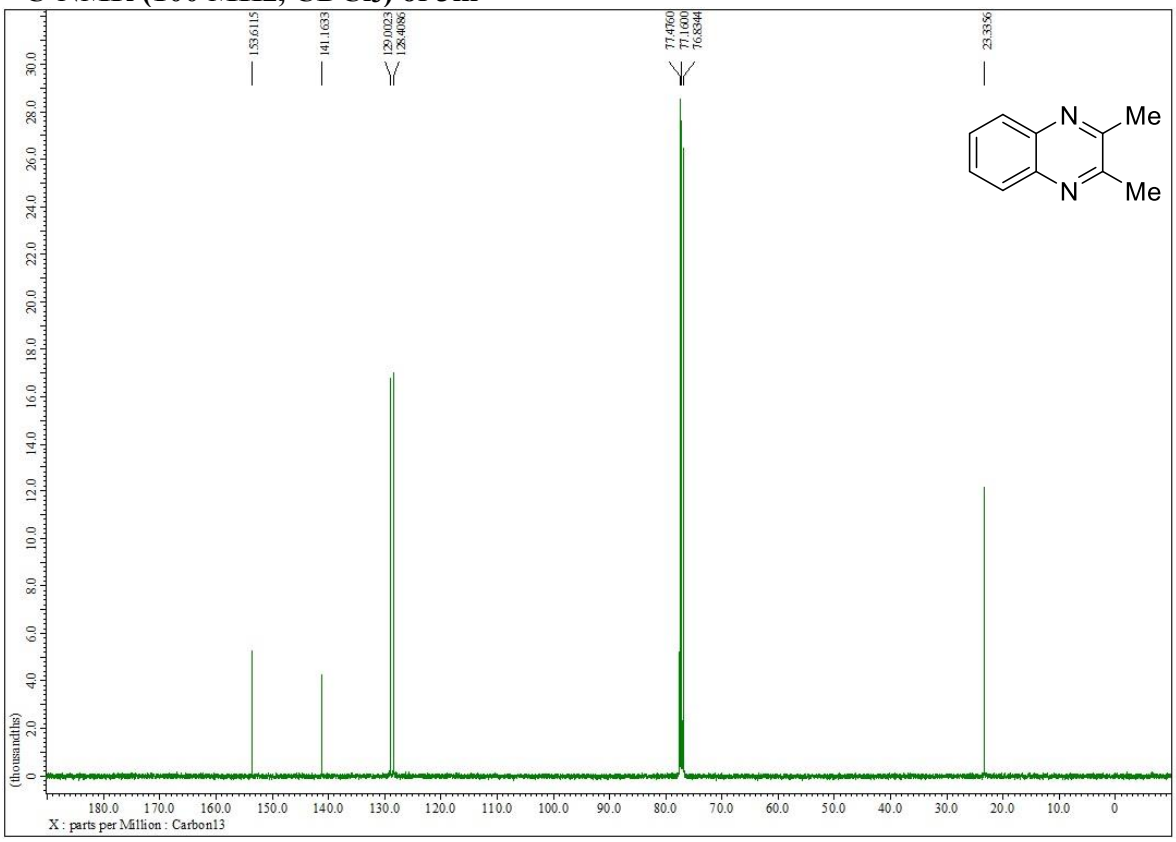
^{13}C-NMR (100 MHz, $CDCl_3$) of 3l



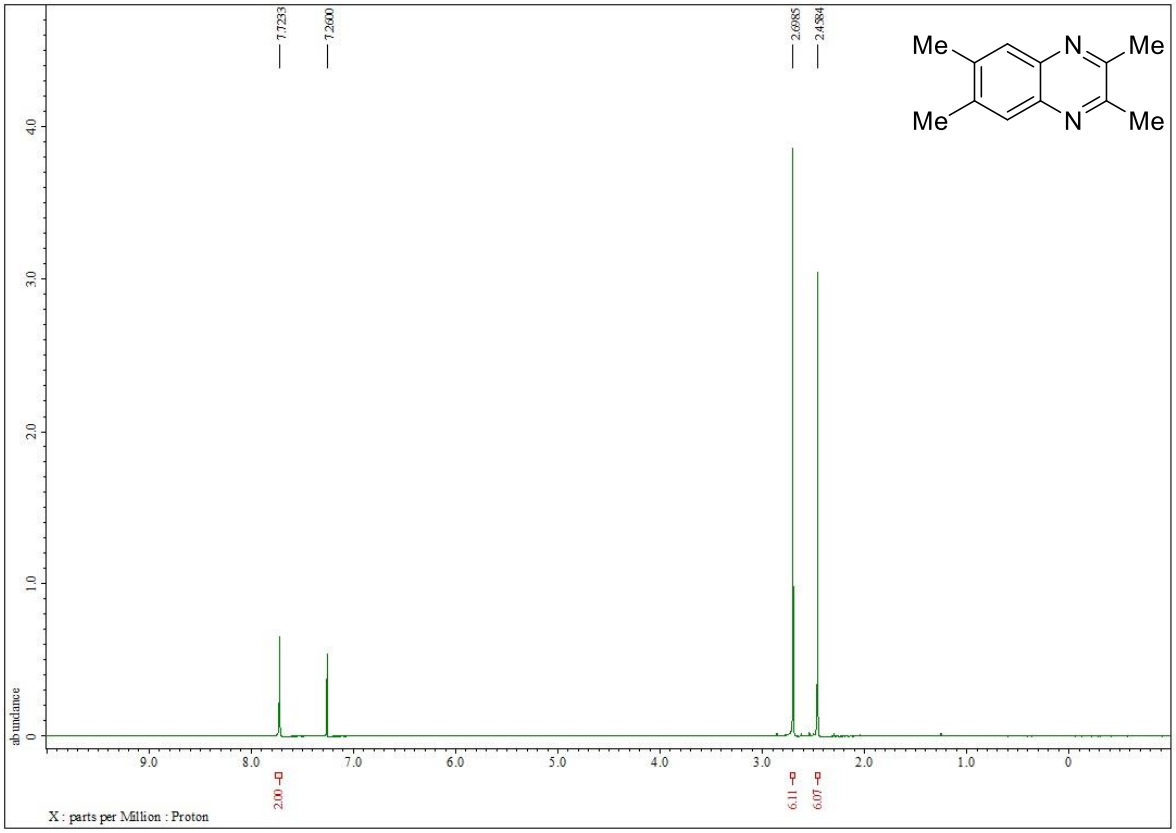
^{1}H-NMR (400 MHz, $CDCl_3$) of 3m



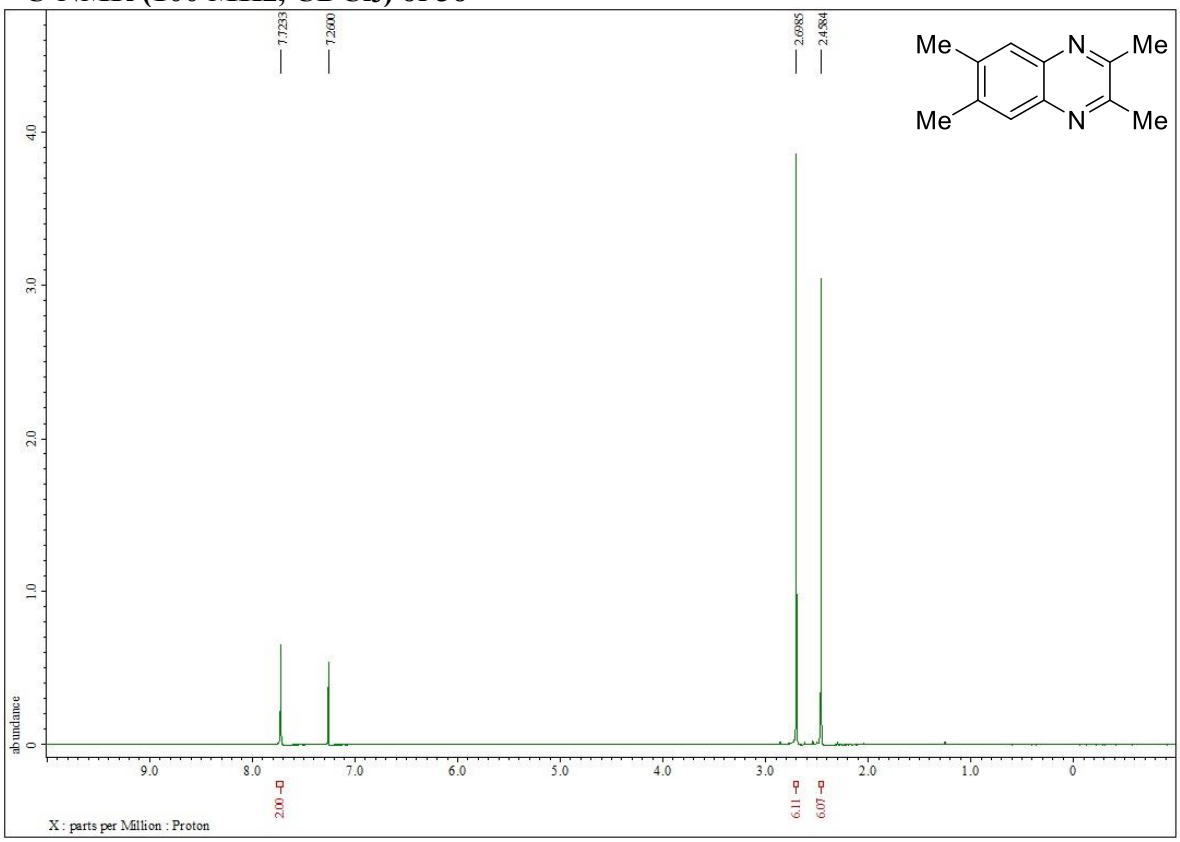
^{13}C-NMR (100 MHz, $CDCl_3$) of 3m



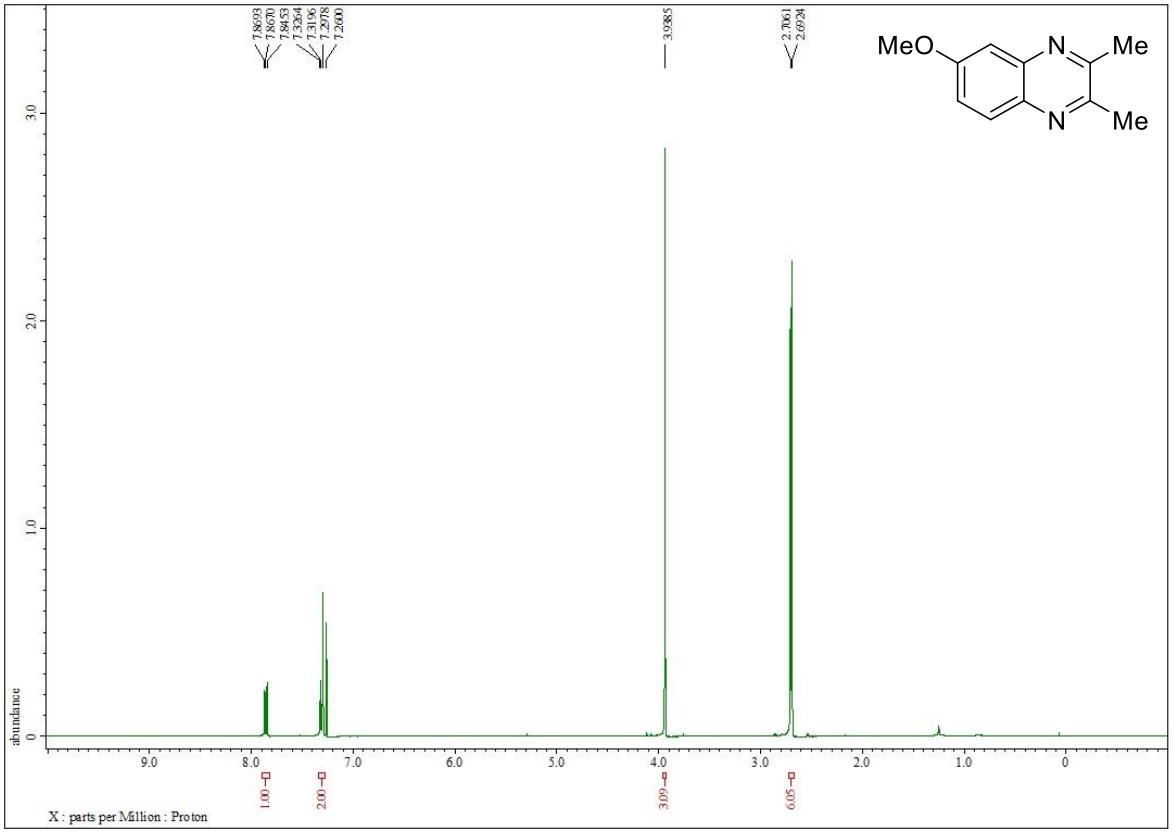
^{1}H-NMR (400 MHz, $CDCl_3$) of 3o



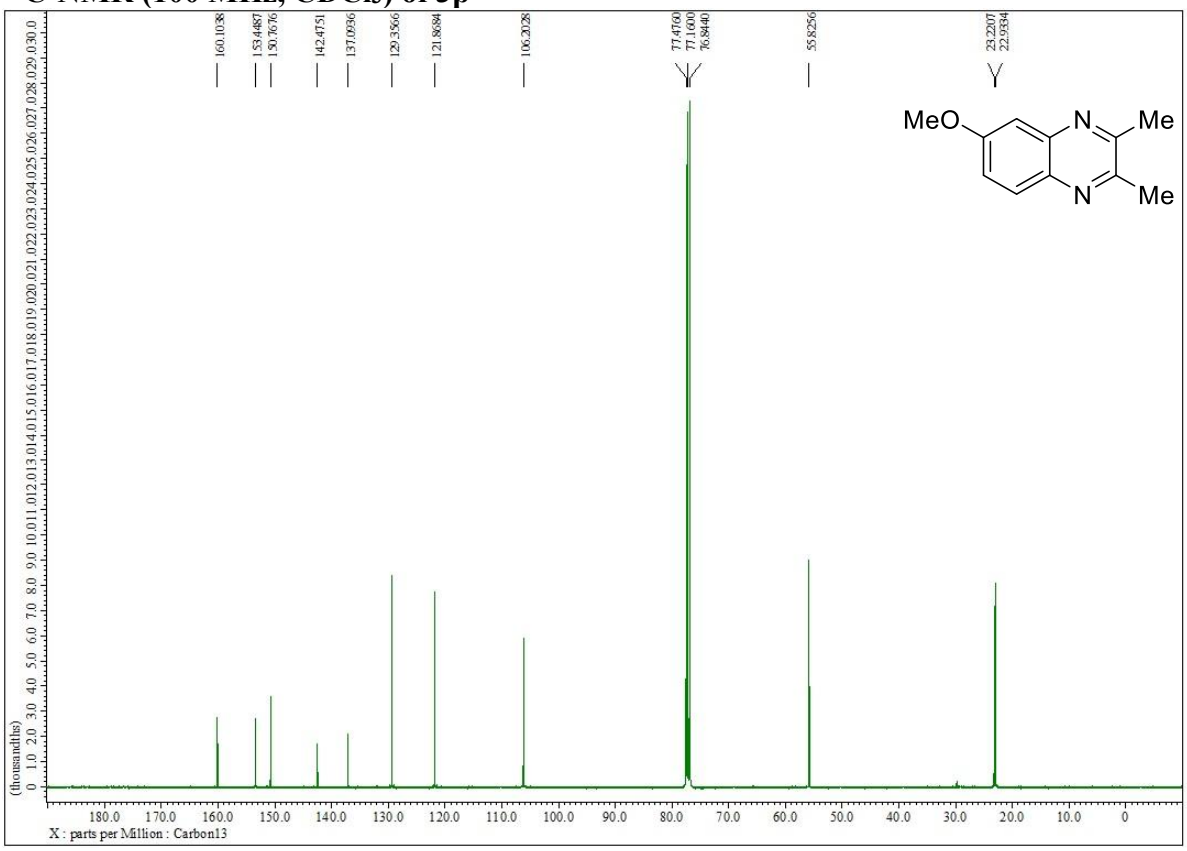
^{13}C-NMR (100 MHz, $CDCl_3$) of 3o



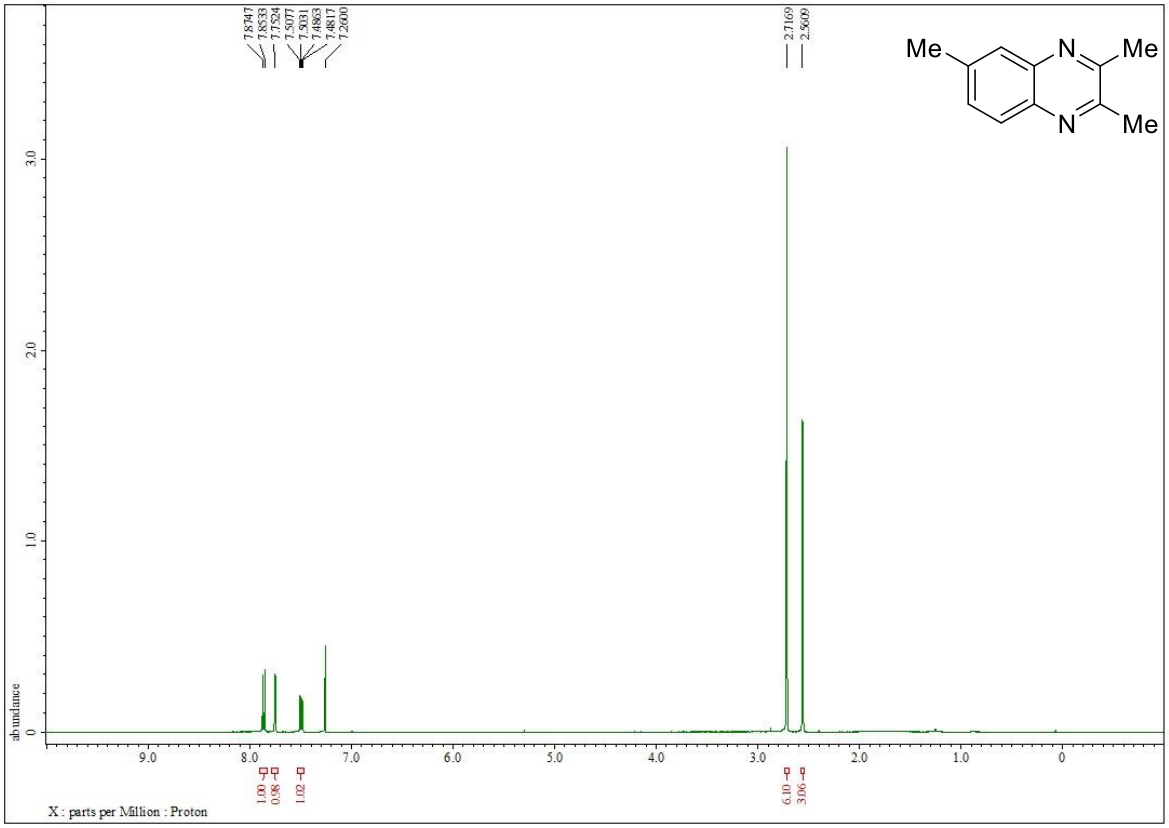
^{1}H-NMR (400 MHz, $CDCl_3$) of 3p



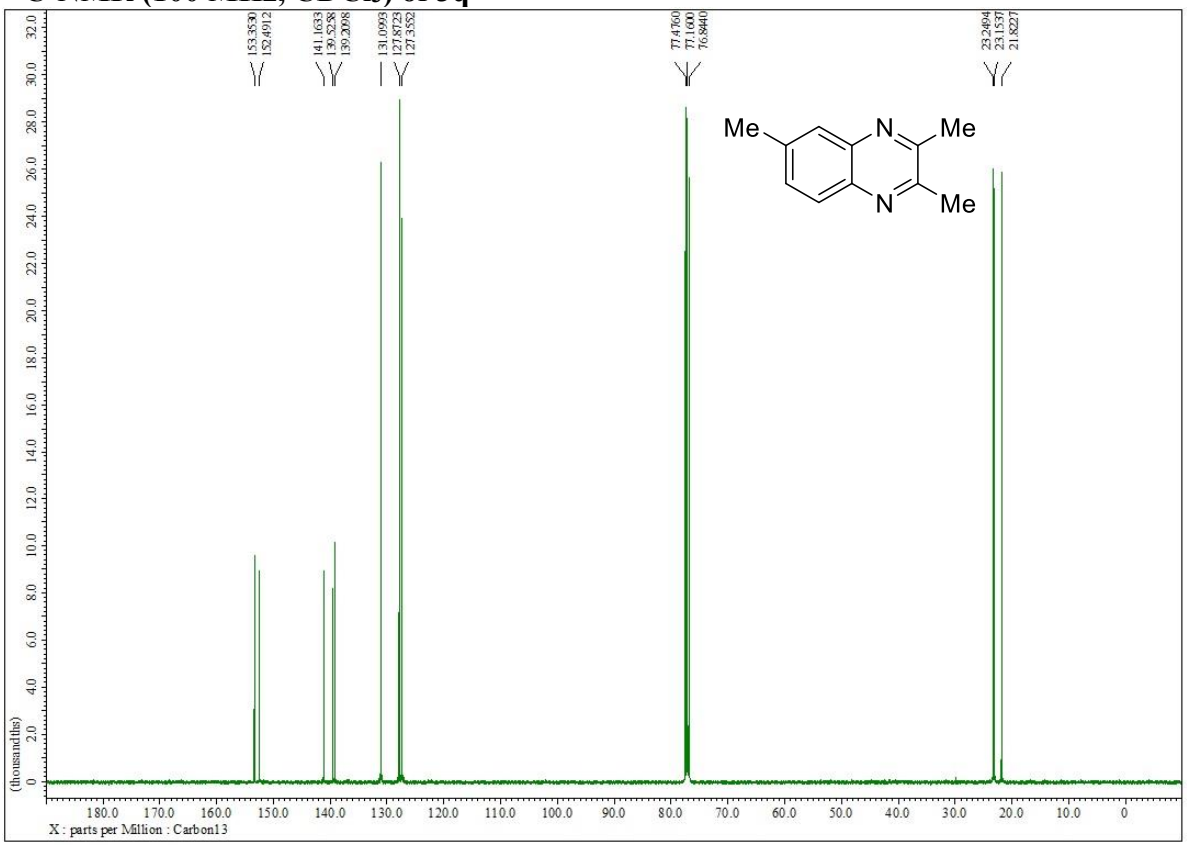
^{13}C-NMR (100 MHz, $CDCl_3$) of 3p



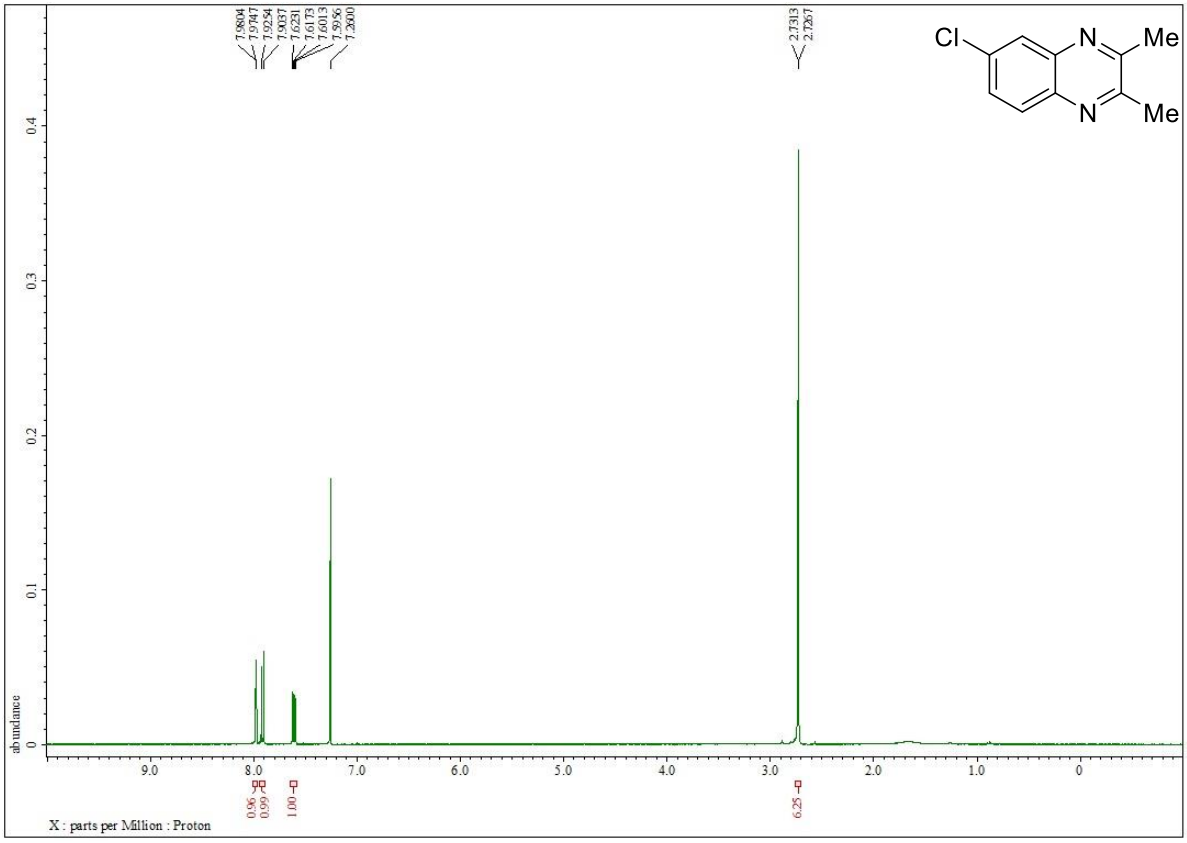
^{1}H-NMR (400 MHz, $CDCl_3$) of 3q



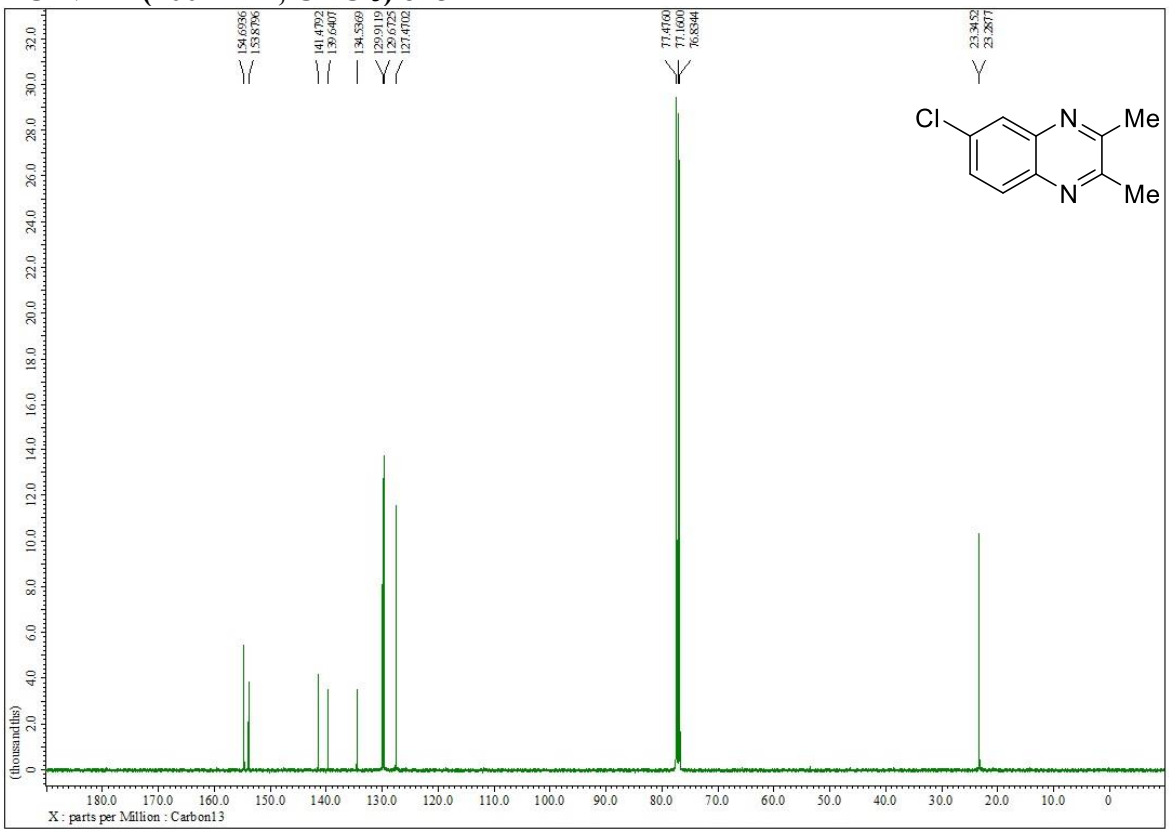
^{13}C-NMR (100 MHz, $CDCl_3$) of 3q



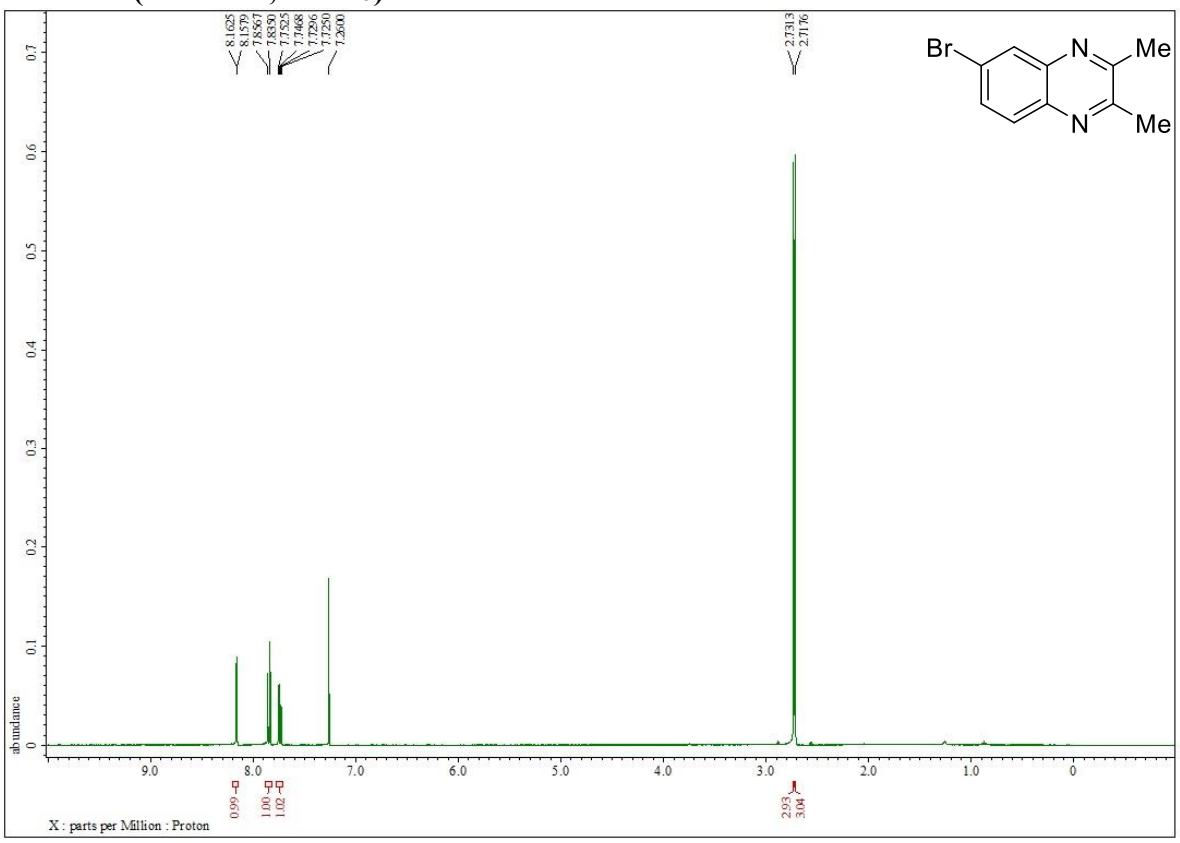
^{1}H-NMR (400 MHz, $CDCl_3$) of 3r



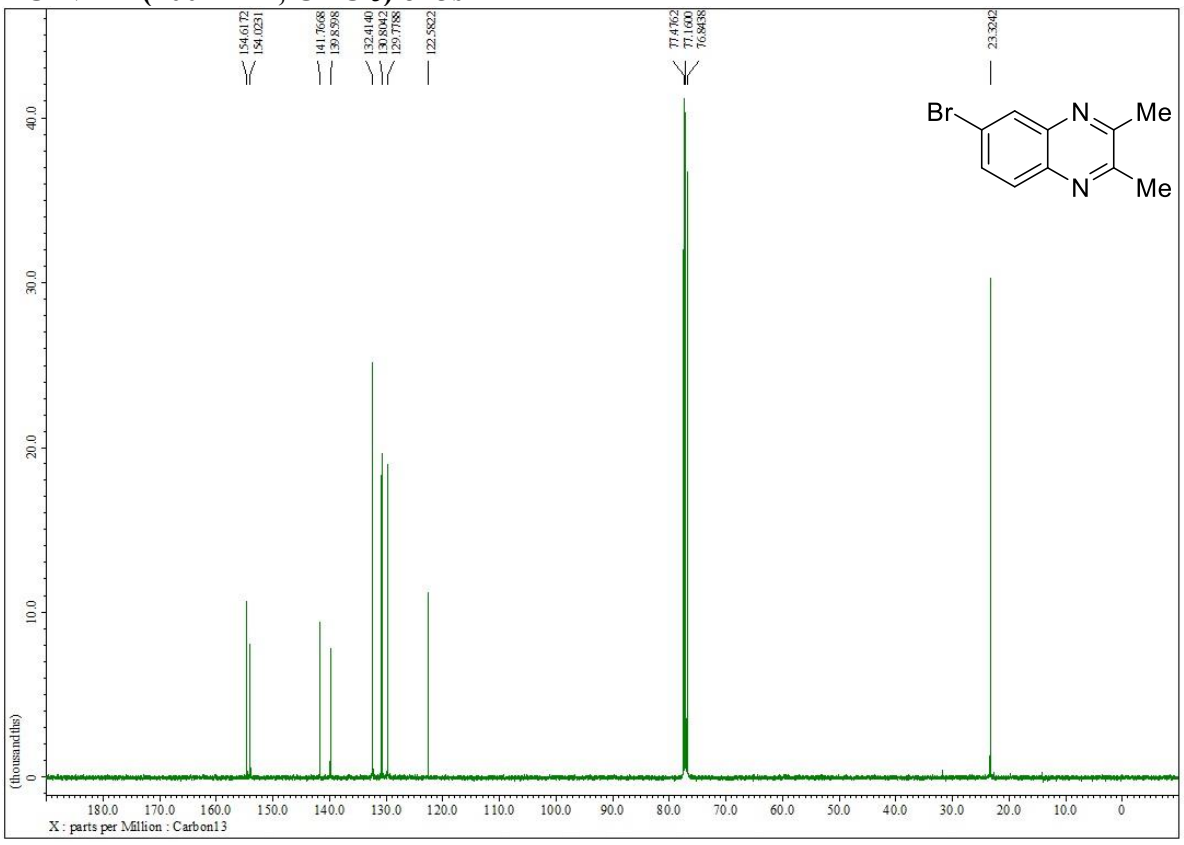
^{13}C-NMR (100 MHz, $CDCl_3$) of 3r



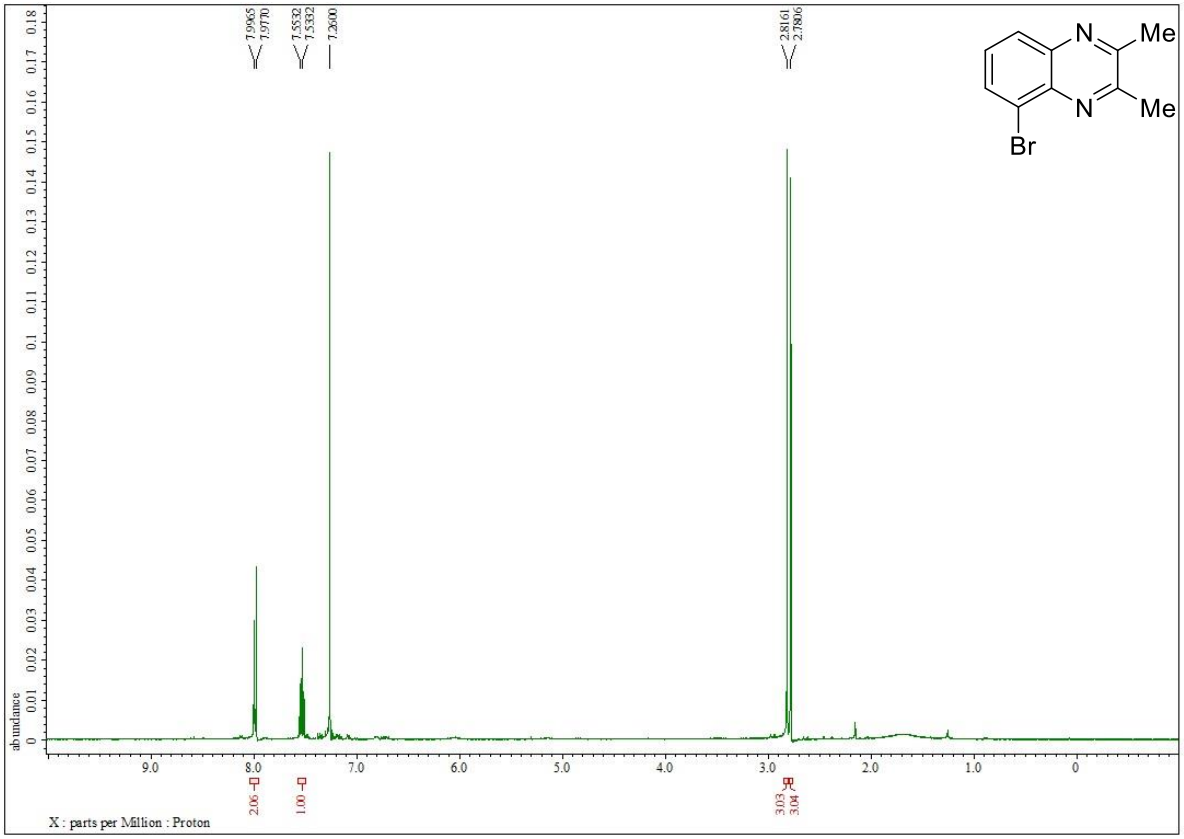
^{1}H-NMR (400 MHz, $CDCl_3$) of 3s



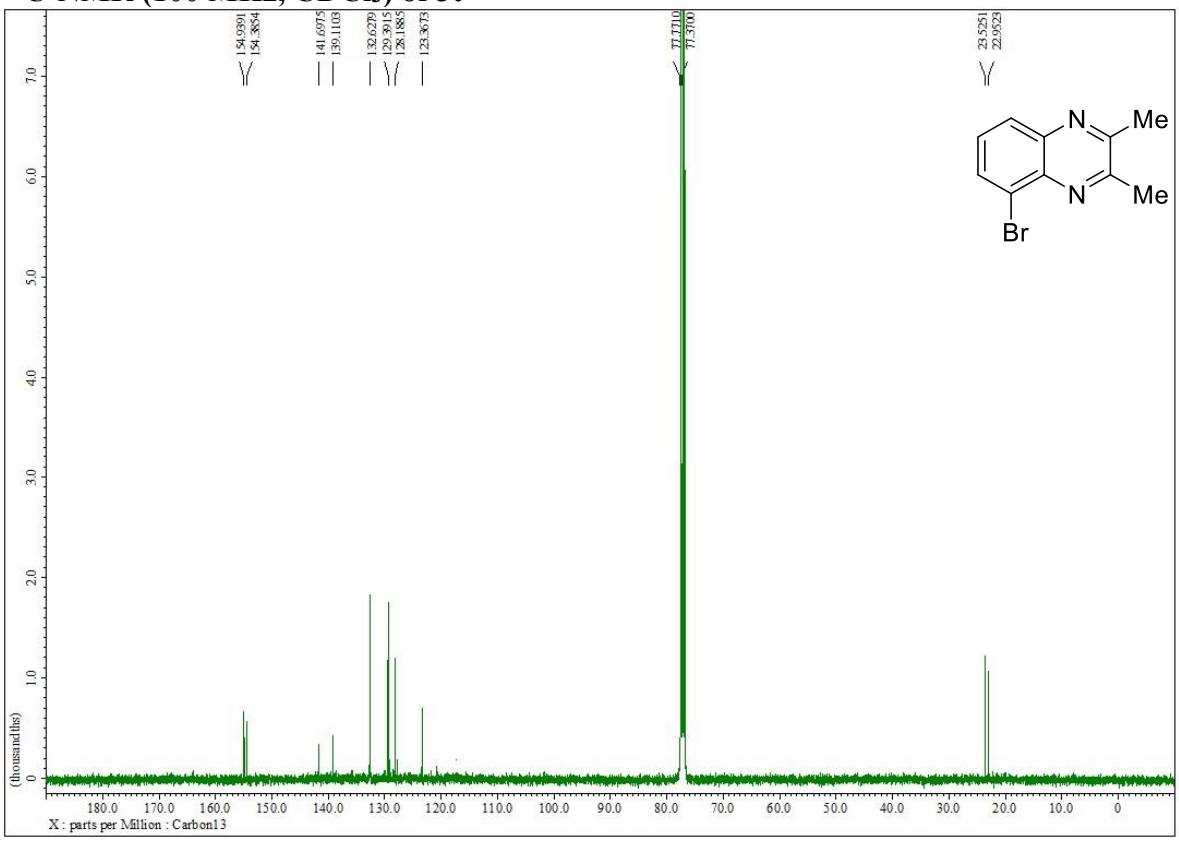
^{13}C-NMR (100 MHz, $CDCl_3$) of 3s



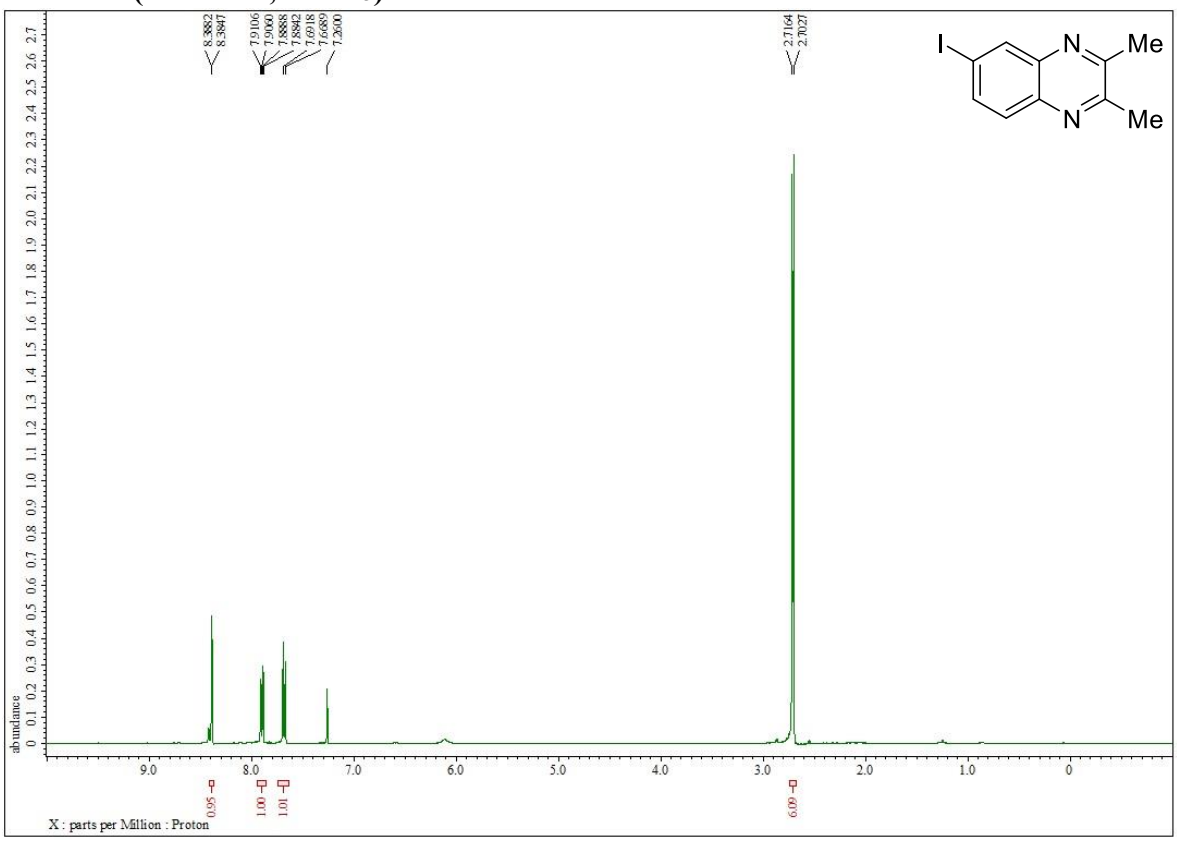
^{1}H-NMR (400 MHz, $CDCl_3$) of 3t



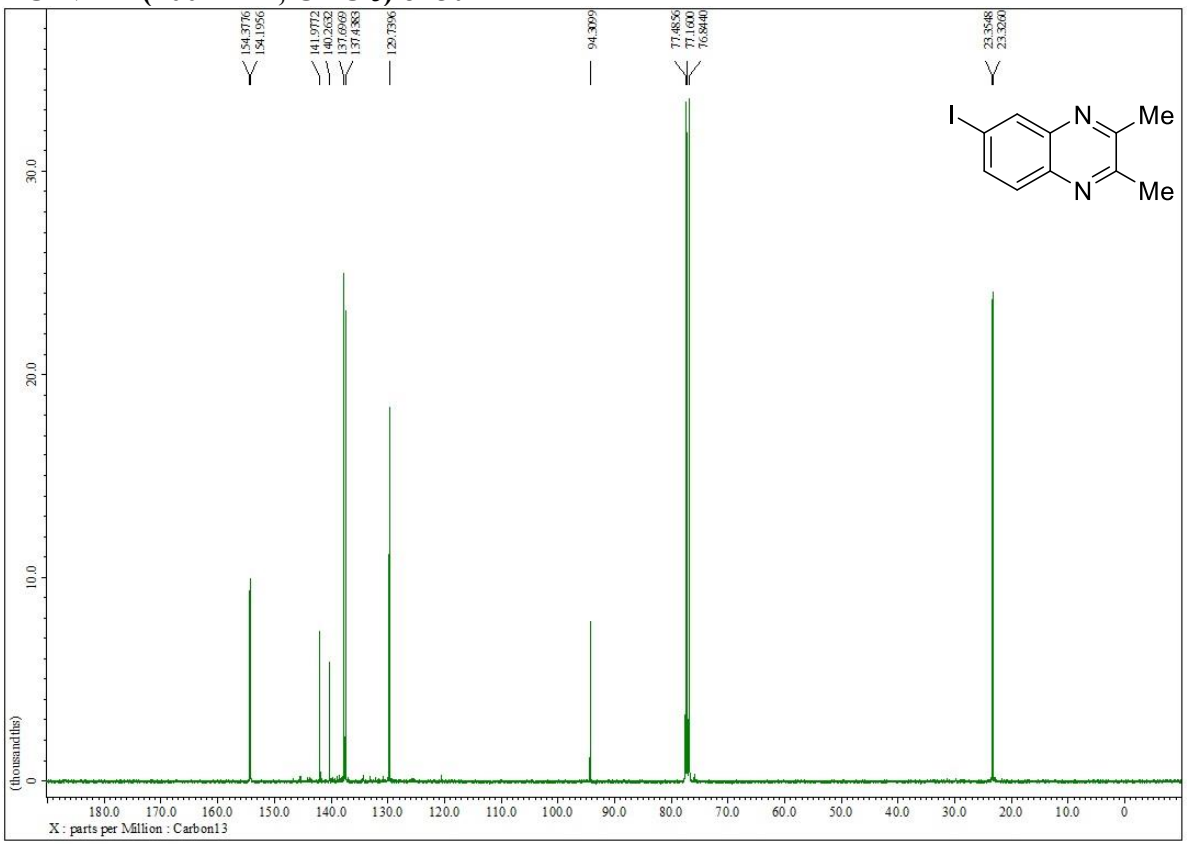
^{13}C-NMR (100 MHz, $CDCl_3$) of 3t



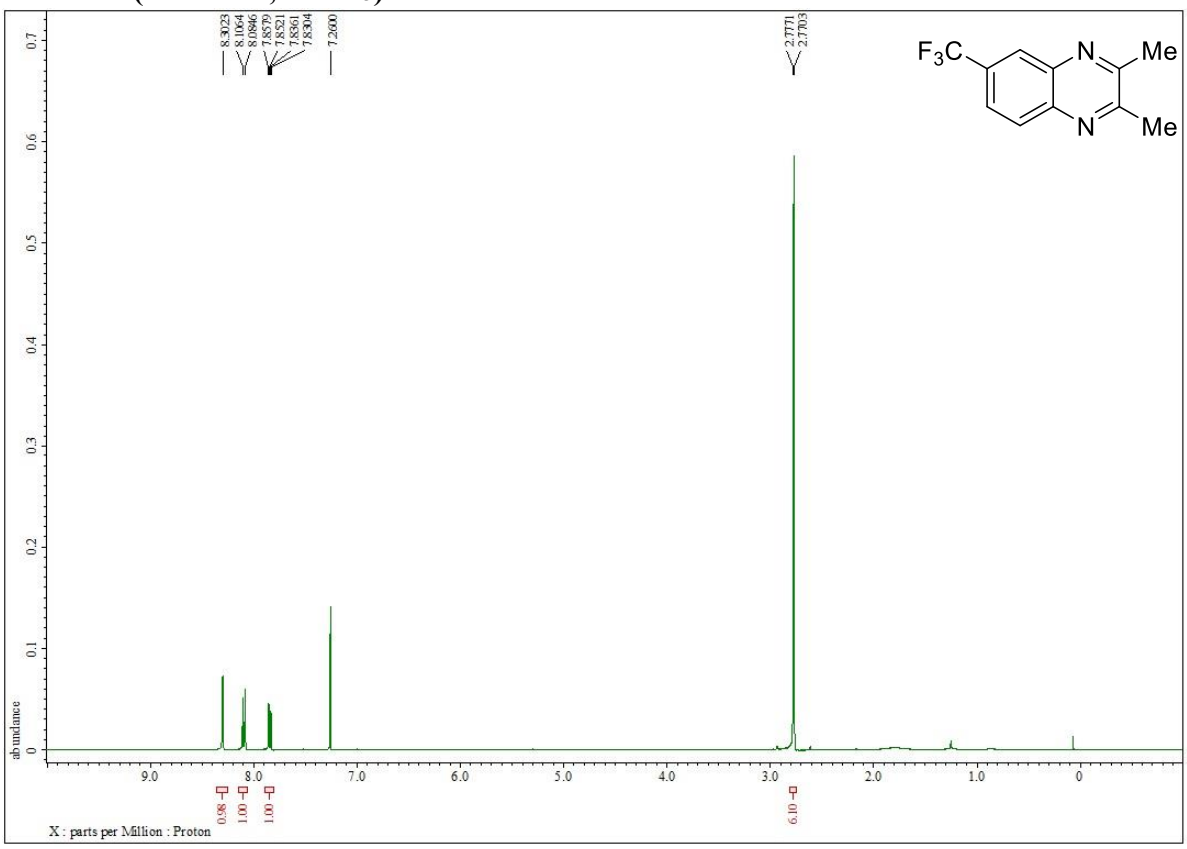
^{1}H-NMR (400 MHz, $CDCl_3$) of 3u



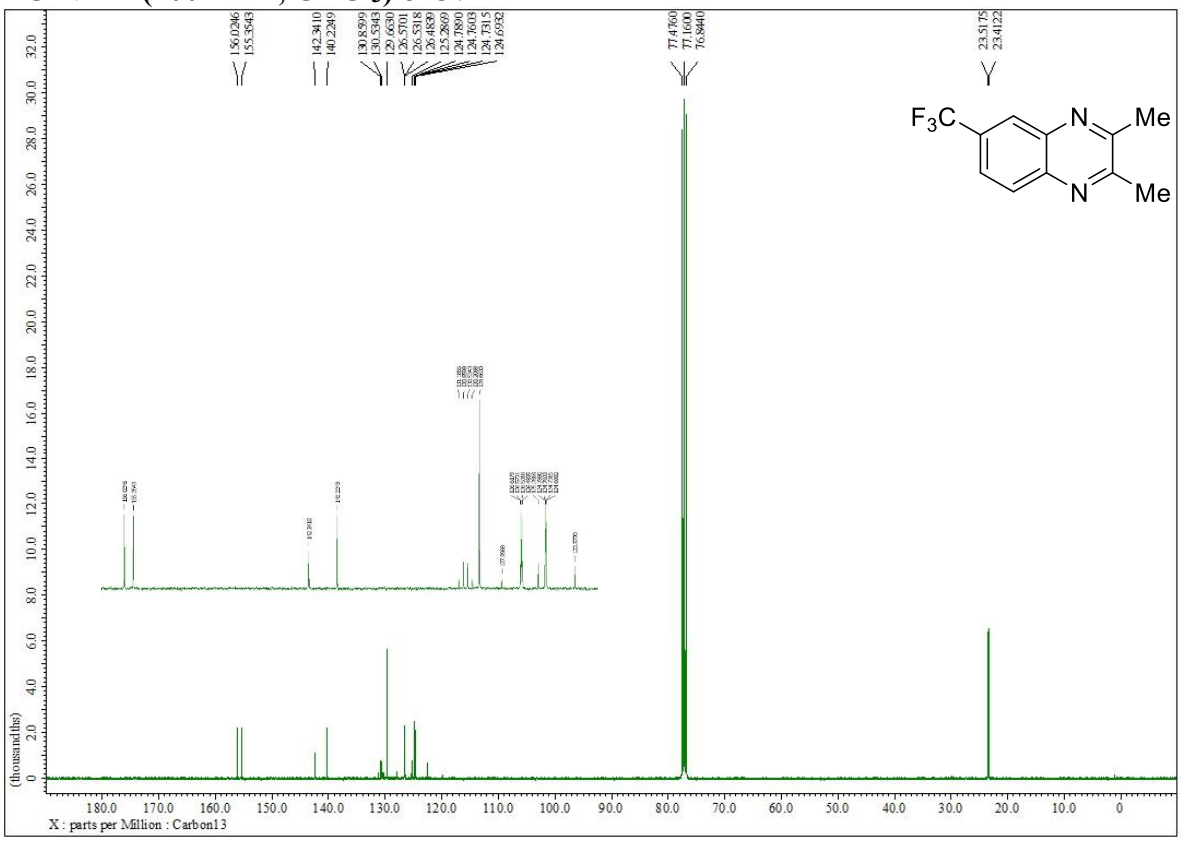
^{13}C-NMR (100 MHz, $CDCl_3$) of 3u



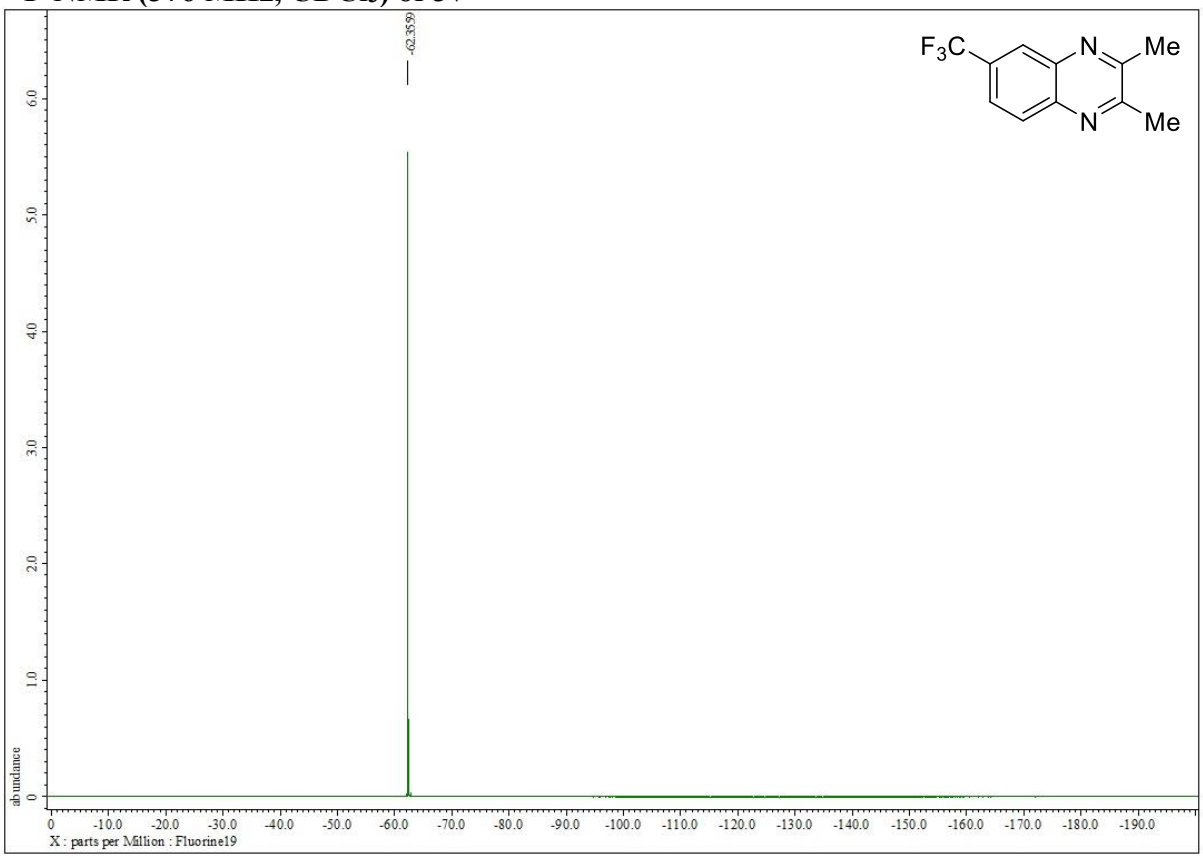
^{1}H-NMR (400 MHz, $CDCl_3$) of 3v



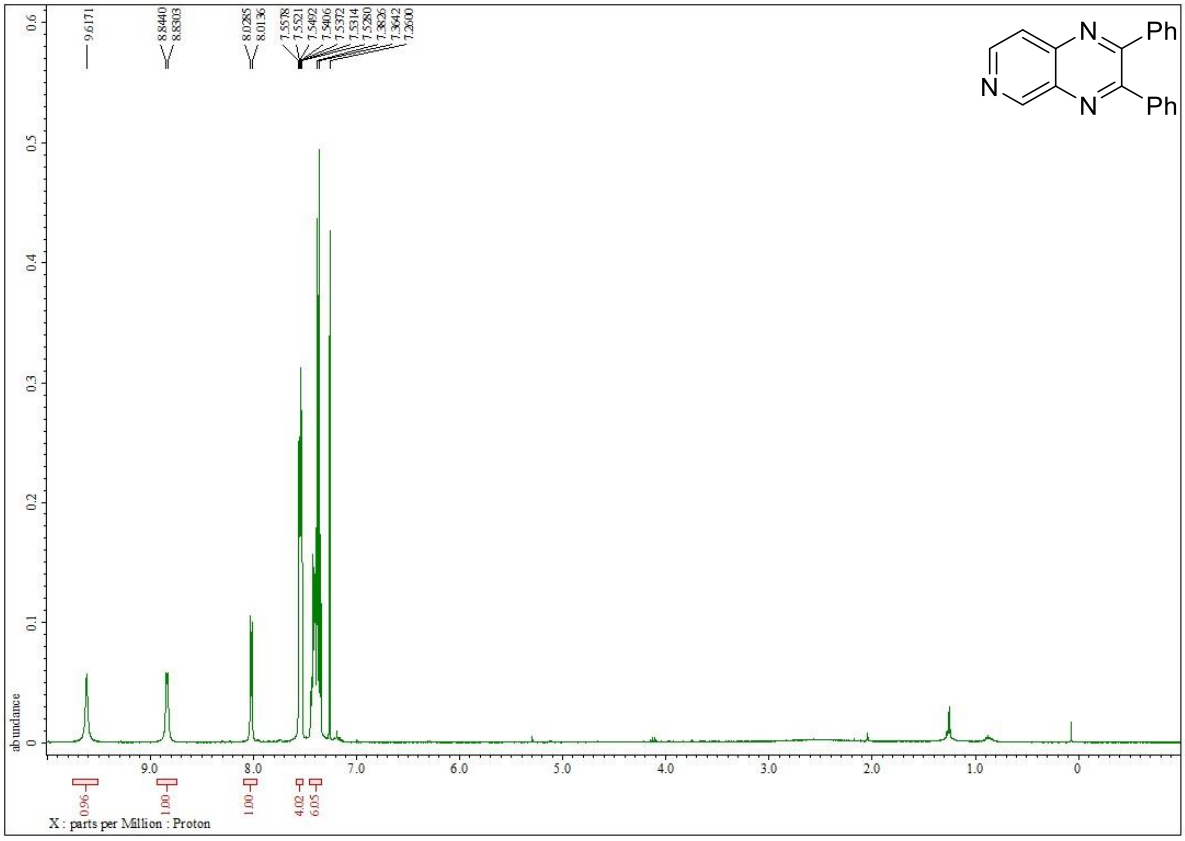
^{13}C-NMR (100 MHz, $CDCl_3$) of 3v



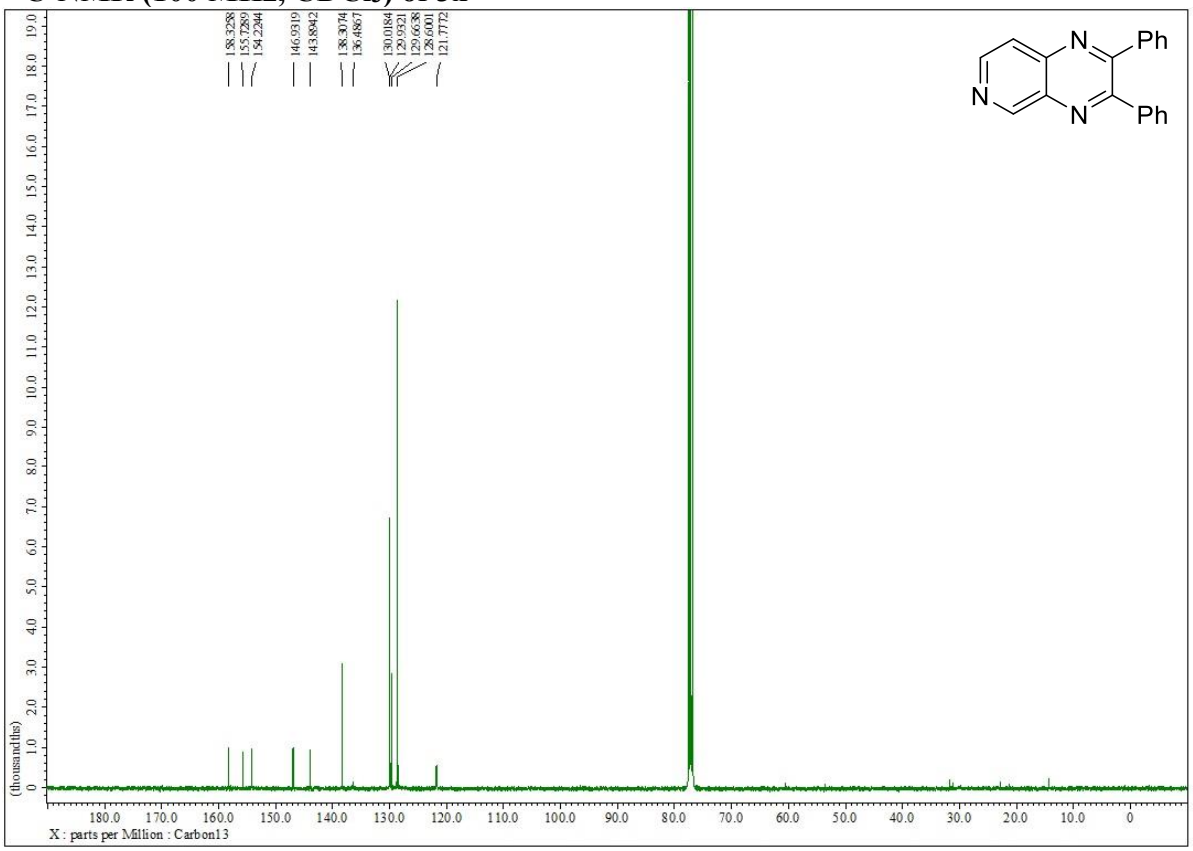
^{19}F-NMR (376 MHz, $CDCl_3$) of 3v



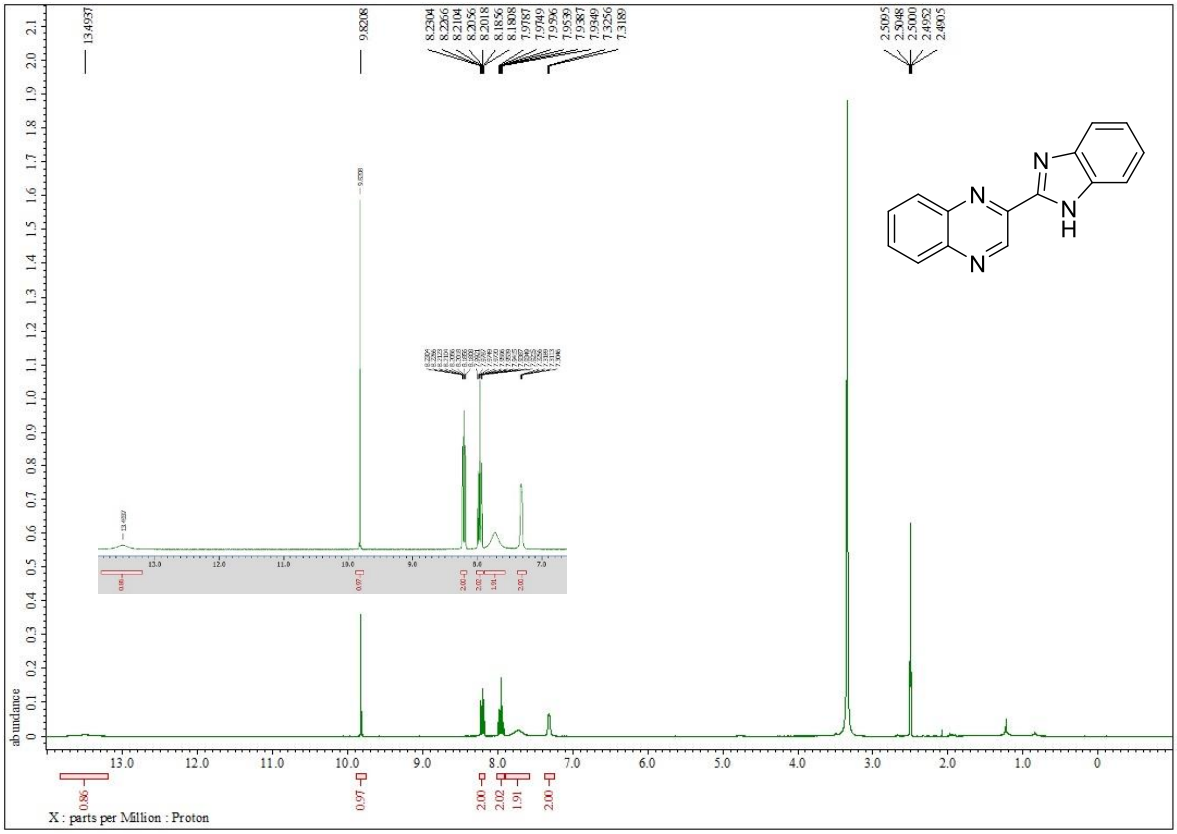
^{1}H-NMR (400 MHz, $CDCl_3$) of 3x



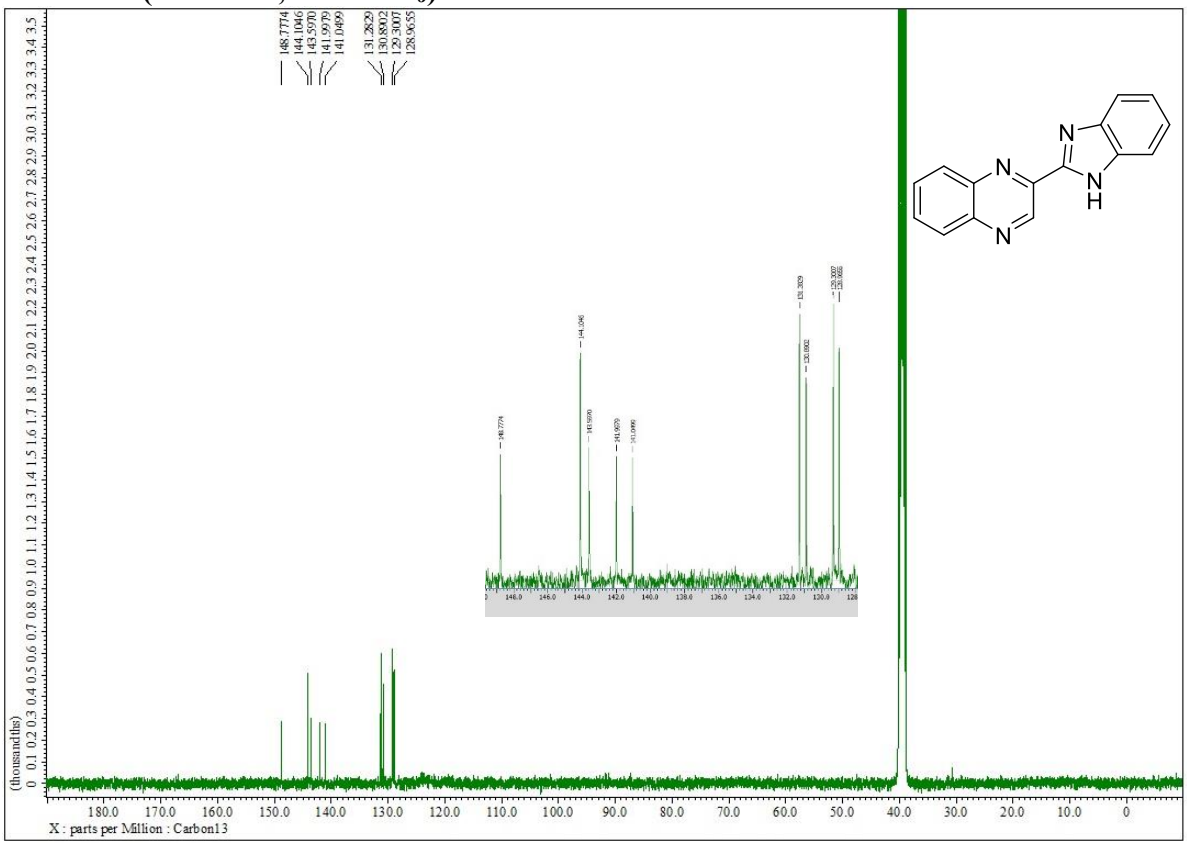
^{13}C-NMR (100 MHz, $CDCl_3$) of 3x



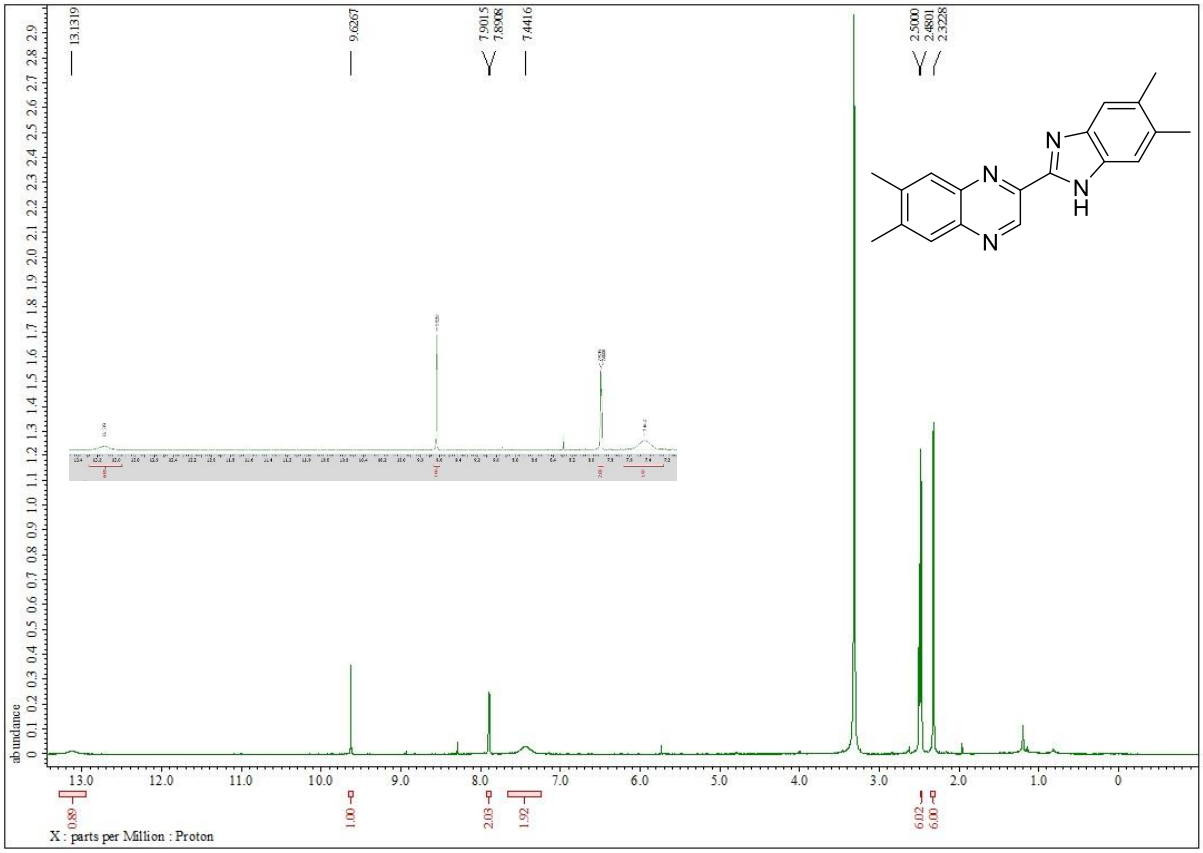
^{1}H-NMR (400 MHz, DMSO-d_6) of 5a



^{13}C-NMR (100 MHz, DMSO-d_6) of 5a



^{1}H-NMR (400 MHz, DMSO-d_6) of 5b



^{13}C-NMR (125 MHz, DMSO-d_6) of 5b