Rhodium-Catalyzed Asymmetric Functionalization of Quinoxalinium Salts

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Supporting Information

A. Materials and Methods

Reactions were performed in flame-dried sealed tubes or modified Schlenk (Kjeldahl shape) flasks fitted with a glass stopper under a positive pressure of nitrogen or inside a nitrogen filled glovebox using 4 mL vials unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred *via* syringe. The appropriate starting materials and reagents were dried *via* azeotropic removal of water with toluene. Molecular sieves were activated at 350 °C and were crushed immediately prior to use, then flame-dried under vacuum. Organic solutions were concentrated by rotary evaporation at 45 °C. Flash column chromatography was performed employing Silicycle P60 230–400 mesh silica gel.

Dichloromethane, tetrahydrofuran, diethyl ether, DMF and toluene were purified by passage through two packed columns of neutral alumina under an argon atmosphere.[1] Methanol was distilled from magnesium at 760 Torr. All other chemicals were obtained from commercial vendors and were used without further purification unless otherwise noted.

Automated flash chromatography was performed with a Teledyne Isco Combiflash® R*f* system with Redi*sep* Gold™ silica columns. Thin-layer chromatography was performed using glass plates pre-coated to a depth of 0.25 mm with 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm) and visualized under UV light (254 and 360 nm), or stained with vanillin in acidic EtOH.

Proton-1, Carbon-13, Phosphorous-31 and Fluorine-19 nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and ^{19}F NMR) spectra were recorded on a Bruker Advance III instrument; chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual isotopes in the NMR solvent (d-chloroform: δ 7.26 for ^{1}H NMR, δ 77.2 for ^{13}C NMR; d4-methanol: δ 3.31 for ^{1}H NMR, δ 49.0 for ^{13}C NMR; d6-DMSO: δ 2.50 for ^{1}H NMR, δ 39.5 for ^{13}C NMR; d6-benzene: δ 7.16 for ^{1}H NMR, δ 128.1 for ^{13}C NMR). Data are presented as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), coupling constant in Hertz (Hz), integration.

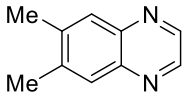
HPLC analysis for the determination of enantiomeric access (*ee*) was performed using a Waters 1515 isocratic solvent pump, 2489 UV-Vis detector, and CHIRALPAK® columns (IA, IC, ID, and IG columns), or Agilent Technologies 1260 Infinity II HPLC system and InfinityLab Poroshell 120 columns (Chiral-CD, Chiral-V, Chiral-T, and Chiral-CF)

Optical rotations are calculated and reported in concentrations of g/mL and were recorded using a Rudolph Research Analytical Autopol® IV Automatic Polarimeter with a 0.5 dm path length.

High resolution mass spectrometry (HRMS) was performed using an Orbitrap Exploris 120 quadrupole orbitrap.

Melting points were obtained on a Barnstead/Electrothermal Mel-Temp Model 1001D.

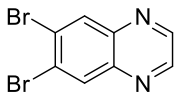
B. Synthesis of Quinoxaline Starting Materials



S1

6,7-Dimethylquinoxaline (S1)

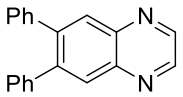
A modified version of a previously reported procedure was used.[2] A 50 mL round-bottom flask was charged with a magnetic stir bar, 4,5-dimethyl-1,2-phenylenediamine (1.00 g, 7.34 mmol, 1.00 equiv.), and MeOH (45.0 mL). The mixture was sonicated to ensure 4,5-dimethyl-1,2-phenylenediamine was fully solvated in MeOH. While stirring, glyoxal (40.0 wt % in H_2O, 0.922 mL, 8.07 mmol, 1.10 equiv.) was added to the MeOH solution by syringe. The reaction was let stir, open to air, for 1 minute. After 1 minute, the reaction was diluted with H_2O (40.0 mL). The now opaque mixture was transferred to a separatory and EtOAc (45.0 mL) was added. Brine solution (20.0 mL) was added to the separatory funnel to aid in layer separation. The layers were separated, and the aqueous layer was extracted with EtOAc (1x45.0 mL). The organic extracts were combined and dried with Na_2SO_4. The solids were removed by filtration and the resulting filtrate was purified via isocratic column chromatography on silica gel to yield **S1** as an orange solid. The NMR spectra matched those of the reported compound.[2] **Yield**: 624 mg (54%); **TLC:** R*f*=0.29 (30/70 EtOAc/Hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.74 (s, 2H), 7.85 (s, 2H), 2.51 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.2, 142.1, 140.7, 128.6, 20.4; **HRMS:** (ESI) *m/z* Calcd for $C_{10}H_{11}N_2$ $[M+H]^+$: 159.0916, Found: 159.0916.



S2

6,7-Dibromoquinoxaline (S2)

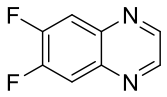
A modified version of a previously reported procedure was used.[2] A 100 mL round-bottom flask was charged with a magnetic stir bar, 4,5-dibromo-1,2-diaminobenzene (500 mg, 1.88 mmol, 1.00 equiv.), and MeOH (11.8 mL). While stirring, glyoxal (40.0 wt % in H_2O, 0.237 mL, 2.07 mmol, 1.10 equiv.) was added to the solution by syringe. The reaction was let stir, open to air, for 1 minute. After 1 minute, the reaction was diluted with H_2O (30.0 mL). The now opaque mixture was transferred to a separatory funnel and DCM (20.0 mL) was added. The layers were separated, and the aqueous layer was extracted with DCM (2x20.0 mL). The organic extracts were combined and dried with Na_2SO_4. The solids were removed by filtration and the resulting filtrate was purified via isocratic column chromatography on silica gel to yield **S2** as a light orange solid. The NMR spectra matched those of the reported compound.[3] **Yield:** 267 mg (49%); **TLC**: R*f*=0.34 (EtOAc/Hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.86 (s, 2H), 8.45 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.9, 142.1, 133.5, 126.8; **HRMS:** (ESI) *m/z* Calcd for $C_8H_5{}^{79}Br_2N_2$ $[M+H]^+$: 286.8814, Found: 286.8817.



S3

6,7-Diphenylquinoxaline (S3)

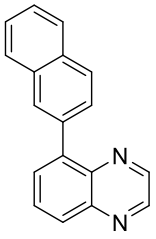
A 10 mL Schlenk tube was charged with **S2** (249 mg, 0.870 mmol, 1.00 equiv.), K_2CO_3 (241 mg, 1.74, 2.00 equiv.), $PhB(OH)_2$ (424 mg, 3.48 mmol, 4.00 equiv.), and a magnetic stir bar. The Schlenk tube was transferred into a nitrogen glovebox where $Pd(PPh_3)_4$ (50.8 mg, 0.0440 mmol, 0.0500 equiv.) and dioxane (3.48 mL) were added. The Schlenk tube was sealed and brought to the bench where it was placed under N_2 on a Schlenk line. Water (1.74 mL), degassed by sparging with N_2, was added to the reaction mixture under N_2. The reaction mixture was sealed under N_2 and allowed to stir at 80 °C for 23 hours in an oil bath. The reaction was then let cool to room temperature and added to a separatory funnel containing water (30.0 mL). The layers were separated, and the aqueous layer was extracted with DCM (3x30.0 mL). The organic extracts were combined and dried with Na_2SO_4. The solids were removed by filtration and the resulting filtrate was purified via isocratic column chromatography on silica gel to yield **S3** as a yellow solid. **Yield:** 125 mg (51%); **TLC**: R*f*=0.40 (20/80 EtOAc/Hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.87 (s, 2H), 8.17 (s, 2H), 7.30 – 7.26 (m, 6H), 7.26 – 7.21 (m, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.5, 143.7, 142.5, 140.2, 130.7, 130.1, 128.2, 127.5; **HRMS:** (ESI) *m/z* Calcd for $C_{20}H_{15}N_2$ $[M+H]^+$: 283.1229, Found: 283.1230.



S4

6,7-Difluoroquinoxaline (S4)

A modified version of a previously reported procedure was used.[2] A 100 mL round-bottom flask was charged with a magnetic stir bar, 4,5-difluoro-1,2-diaminobenzene (1.00 g, 6.94 mmol, 1.00 equiv.), and MeOH (45.0 mL). While stirring, glyoxal (40.0 wt % in H_2O, 0.872 mL, 7.63 mmol, 1.10 equiv.) was added to the MeOH solution by syringe. The reaction was let stir, open to air, for 1 minute. After 1 minute, the reaction was diluted with H_2O (40.0 mL). The now opaque mixture was transferred to a separatory and EtOAc (100 mL) was added. Brine solution (50 mL) was added to the separatory funnel to aid in layer separation. The layers were separated, and the aqueous layer was extracted with EtOAc (1x50.0 mL). The organic extracts were combined and dried with Na_2SO_4. The solids were removed by filtration and the resulting filtrate was purified via isocratic column chromatography on silica gel to yield **S4** as a light orange solid. **Yield**: 465 mg (40%); **TLC:** R*f*=0.27 (20/80 EtOAc/Hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.84 (s, 2H), 7.87 (t, J = 9.3 Hz, 2H); **^{13}C NMR** (126 MHz, CDCl3) δ 146.0, 141.9, 135.0, 130.3; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -129.2 (t, J = 9.5 Hz); **HRMS:** (ESI) *m/z* Calcd for $C_8H_5F_2N_2$ $[M+H]^+$: 167.0415, Found: 167.0414.



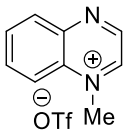
S5

5-(Naphthalen-2-yl)quinoxaline (S5)

A 50 mL Schlenk flask was charged with 5-bromoquinoxaline (500 mg, 2.39 mmol, 1.00 equiv.), K_2CO_3 (661 mg, 4.78, 2.00 equiv.), 2-naphthylboronic acid (822 mg, 4.78 mmol, 2.00 equiv.), and a magnetic stir bar. The Schlenk flask was transferred into a nitrogen glovebox where $Pd(PPh_3)_4$ (139 mg, 0.120 mmol, 0.0500 equiv.) was added. The Schlenk flask was sealed and brought to the bench where it was placed under N_2 on a Schlenk line. Dry toluene (9.56 mL) and water (4.78 mL), degassed by sparging with N_2, was added to the reaction mixture under N_2. The reaction mixture was sealed under N_2 and allowed to stir at 115 °C for 19 hours in an oil bath. The reaction was then let cool to room temperature and added to a separatory funnel containing water (30.0 mL). The layers were separated, and the aqueous layer was extracted with DCM (2x30.0 mL). The organic extracts were combined and dried with Na_2SO_4. The solids were removed by filtration and the resulting filtrate was purified via isocratic column chromatography on silica gel to yield **S5** as an orange solid. **Yield:** 440 mg (72%); **TLC**: R*f*=0.28 (20/80 EtOAc/Hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.93 – 8.86 (m, 2H), 8.17 (dd, J = 8.2, 1.7 Hz, 1H), 8.14 – 8.10 (m, 1H), 7.97 (d, J = 8.5 Hz, 1H), 7.95 – 7.87 (m, 4H), 7.82 (dd, J = 8.4, 1.8 Hz, 1H), 7.53 (dt, J = 6.2, 3.4 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.9, 144.8, 143.5, 141.4, 141.4, 136.0, 133.5, 133.0, 131.0, 130.0, 129.6, 129.3, 128.9, 128.4, 127.8, 127.5, 126.4, 126.3; **HRMS:** (ESI) *m/z* Calcd for $C_{18}H_{13}N_2$ $[M+H]^+$: 257.1073, Found: 257.1074.

C. Synthesis of Quinoxalinium Salts

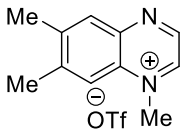
Safety warning: We have found that most of the quinoxalinium salts were potent nasal irritants. This effect was particularly prominent for N-Bn quinoxalinium salts. Thus, all salts should be handled with appropriate safety precautions.



3

1-Methylquinoxalin-1-ium trifluoromethanesulfonate (3)

A 100 mL Schlenk flask was charged with quinoxaline (5.00 g, 38.4 mmol, 1.00 equiv.) and a magnetic stir bar. The Schlenk flask was evacuated and backfilled with N_2 three times. (It should be noted that while this reaction was carried out under N_2, variations were carried out under standard atmospheric conditions without a noticeable impact to yield. This reaction is likely tolerable to atmospheric conditions as well.) Dry DCM (49.9 mL) was added to the Schlenk flask under N_2. The reaction was cooled to 0 °C in an ice bath and methyl trifluoromethanesulfonate (3.91 mL, 34.6 mmol, 0.900 equiv.) was added to the reaction drop-wise over 10 minutes. The reaction was let warm to room temperature and stirred, sealed under N_2, for 20 hours. After stirring, the now opaque white reaction mixture was added to rapidly stirring Et_2O (400 mL). The precipitated solids were collected by filtration and rinsed with Et_2O (200 mL). The resulting off-white solids **3** were allowed to air dry and then used as-is without further purification. **Yield:** 9.91 g (88%); **^{1}H NMR** (500 MHz, MeOD) δ 9.60 (d, J = 2.9 Hz, 1H), 9.40 (dd, J = 3.0, 1.1 Hz, 1H), 8.64 – 8.55 (m, 2H), 8.41 – 8.28 (m, 2H), 4.82 (s, 3H); **^{13}C NMR** (126 MHz, MeOD) δ 148.6, 147.4, 142.2 (t, J = 10 Hz), 137.6, 135.1, 132.9, 132.7, 121.7 (q, J = 318 Hz), 120.2, 46.7; **^{19}F NMR** (471 MHz, MeOD) δ -80.1; **HRMS** (ESI) *m/z:* $[M\text{-}OTf]^+$ Calcd for $C_9H_9N_2$: 145.0760, Found: 145.0760; **m. p. =** 96 °C.

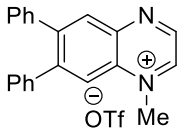


5a

1,6,7-Trimethylquinoxalin-1-ium trifluoromethanesulfonate (5a)

A 10 mL Schlenk flask was charged with **S1** (250 mg, 1.58 mmol, 1.00 equiv.) and a magnetic stir bar. The Schlenk flask was evacuated and backfilled with N_2 three times. (It should be noted that while this reaction was carried out under N_2, variations were carried out under standard atmospheric conditions without a noticeable impact to yield. This reaction is likely tolerable to atmospheric conditions as well.) Dry DCM (2.05 mL) was added to the Schlenk flask under N_2. The reaction was cooled to 0 °C in an ice bath and methyl trifluoromethanesulfonate (0.161 mL, 1.42 mmol, 0.900 equiv.) was added to the reaction drop-wise over 10 minutes. The reaction was let warm to room temperature and stirred, sealed under N_2, for 22 hours. After stirring, the now opaque yellow reaction mixture was added to rapidly stirring Et_2O (100 mL). The precipitated solids were collected by filtration and rinsed with Et_2O (100 mL). The resulting tan solids **5a** were allowed to air dry and then used as-is without further purification. **Yield:** 467 mg (92%); **^{1}H NMR** (500 MHz, MeOD) δ 9.44 (s, 1H), 9.20 (s, 1H), 8.38 (s, 1H), 8.32 (s, 1H), 4.74 (s, 3H), 2.74 (s, 3H), 2.67 (s, 3H); **^{13}C NMR** (126 MHz, MeOD) δ

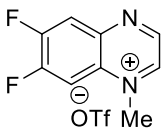
151.0, 147.2, 147.1, 146.8, 140.2, 131.7, 131.2, 121.7 (q, J = 319 Hz), 118.9, 46.4, 21.34, 20.3; **^{19}F NMR** (471 MHz, MeOD) δ -80.1; **HRMS** (ESI) *m/z*: $[M\text{-}OTf]^+$ Calcd for $C_{11}H_{13}N_2$: 173.1073, Found: 173.1073; **m. p. =** 158 °C.



5b

1-Methyl-6,7-diphenylquinoxalin-1-ium trifluoromethanesulfonate (5b)

A 4 mL vial was charged with **S3** (125 mg, 0.442 mmol, 1.00 equiv.), a magnetic stir bar, and sealed with a septa cap. The vial was evacuated and backfilled with N_2 three times. (It should be noted that while this reaction was carried out under N_2, variations were carried out under standard atmospheric conditions without a noticeable impact to yield. This reaction is likely tolerable to atmospheric conditions as well.) The vial was cooled to -78 °C in an acetone/dry ice bath and dry DCM (1.17 mL) was added by syringe. Methyl trifluoromethanesulfonate (0.161 mL, 1.42 mmol, 0.900 equiv.) was added to the reaction drop-wise over 10 minutes at -78 °C. The reaction was let warm to 4 °C and stirred, sealed under N_2, for 16 hours. After stirring at 4 °C, the now translucent red reaction mixture was added to rapidly stirring hexanes (125 mL). The precipitated dark red solids were collected by filtration upon which they turned into a dark red goo on the filter paper. The dark red goo was solvated in DCM (20 mL) and concentrated down into a vial. All volatiles were removed by evaporation under reduced pressure, upon which **5b** was collected as a reddish-orange crystalline solid and used as-is without further purification. **Yield:** 191 mg (97%); **^{1}H NMR** (500 MHz, MeOD) δ 9.58 (d, J = 2.9 Hz, 1H), 9.37 (d, J = 2.9 Hz, 1H), 8.54 (d, J = 10.1 Hz, 2H), 7.48 – 7.27 (m, 10H), 4.84 (s, 3H); **^{13}C NMR** (126 MHz, MeOD) δ 151.4, 148.9, 148.6, 146.9, 141.8, 140.0, 139.7, 133.2, 132.2, 131.2, 130.9, 129.9, 129.6, 129.6, 129.3, 121.8 (q, J = 319 Hz), 121.0, 46.5; **^{19}F NMR** (471 MHz, MeOD) δ -80.1; **HRMS** (ESI) *m/z*: $[M\text{-}OTf]^+$ Calcd for $C_{21}H_{17}N_2$: 297.1386, Found: 297.1385; **m. p. =** 56 °C.

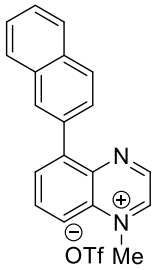


5c

6,7-difluoro-1-methylquinoxalin-1-ium trifluoromethanesulfonate (5c)

A 10 mL Schlenk flask was charged with **S4** (250 mg, 1.50 mmol, 1.00 equiv.) and a magnetic stir bar. The Schlenk flask was evacuated and backfilled with N_2 three times. (It should be noted that while this reaction was carried out under N_2, variations were carried out under standard atmospheric conditions without a noticeable impact to yield. This reaction is likely tolerable to atmospheric conditions as well.) Dry DCM (1.95 mL) was added to the Schlenk flask under N_2. The reaction was cooled to 0 °C in an ice bath and methyl trifluoromethanesulfonate (0.153 mL, 1.35 mmol, 0.900 equiv.) was added to the reaction drop-wise over 10 minutes. The reaction was let warm to room temperature and stirred, sealed under N_2, for 21 hours. After stirring, the reaction mixture was added to rapidly stirring Et_2O (100 mL). The precipitated solids were collected by filtration and rinsed with Et_2O (50 mL). The resulting off-white solids **5c** were allowed to air dry and then used as-is without further

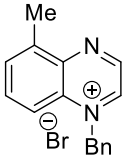
purification. **Yield:** 495 mg (90%); **^{1}H NMR** (500 MHz, MeOD) δ 9.61 (d, J = 3.0 Hz, 1H), 9.44 (d, J = 2.9 Hz, 1H), 8.80 – 8.73 (m, 1H), 8.57 (td, J = 8.9, 2.2 Hz, 1H), 4.77 (s, 3H); **^{13}C NMR** (126 MHz, MeOD) δ 156.9 (dd, J = 265, 16 Hz), 155.6 (dd, J = 263, 16 Hz), 149.0 (d, J = 3 Hz), 145.7 (d, J = 12 Hz), 142.3, 131.5, 121.6 (q, J = 319 Hz), 119.0 (dd, J = 19, 3 Hz), 108.7 (dd, J = 24, 2 Hz), 47.3; **^{19}F NMR** (471 MHz, MeOD) δ -80.2, -118.6 (dp, J = 19.6, 9.9 Hz), -125.1 (ddt, J = 23.6, 19.9, 8.1 Hz); **HRMS** (ESI) *m/z*: [M-OTf]$^+$ Calcd for $C_9H_7F_2N_2$: 181.0571, Found: 181.0571; **m. p. =** 102-105°C.



5d

1-Methyl-5-(naphthalen-2-yl)quinoxalin-1-ium trifluoromethanesulfonate (5d)

A 20 mL vial was charged with **S5** (440 mg, 1.72 mmol, 1.00 equiv.) and a magnetic stir bar. Dry DCM (2.29) mL was added to the vial. The reaction was cooled to 0 °C in an ice bath and methyl trifluoromethanesulfonate (0.175 mL, 1.55 mmol, 0.900 equiv.) was added to the reaction drop-wise over 10 minutes. The reaction was capped, let warm to room temperature, and stirred, for 19 hours. After stirring, the reaction mixture was added to rapidly stirring hexanes (125 mL). The precipitated solids were collected by filtration and rinsed with hexanes (50.0 mL). The resulting yellow-orange solids **5d** were allowed to air dry and then used as-is without further purification. **Yield:** 680 mg (94%); **^{1}H NMR** (500 MHz, DMSO) δ 9.70 (d, J = 2.8 Hz, 1H), 9.62 (d, J = 2.9 Hz, 1H), 8.66 (dd, J = 8.0, 2.0 Hz, 1H), 8.50 – 8.41 (m, 2H), 8.23 (d, J = 1.8 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.07 – 8.00 (m, 2H), 7.80 (dd, J = 8.5, 1.8 Hz, 1H), 7.67 – 7.58 (m, 2H), 4.79 (s, 3H); **^{13}C NMR** (126 MHz, DMSO) δ 147.4, 143.1, 141.9, 141.2, 135.4, 133.9, 133.8, 132.7, 132.5, 131.6, 130.0, 128.8, 128.3, 127.6, 127.4, 127.0, 126.6, 120.7 (q, J = 322 Hz), 118.9, 46.1; **^{19}F NMR** (471 MHz, MeOD) δ -80.1; **HRMS** (ESI) *m/z*: [M-OTf]$^+$ Calcd for $C_{19}H_{15}N_2$: 271.1229, Found: 271.1229; **m. p. =** 165-170°C.

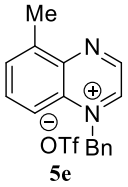


S6

1-Benzyl-5-methylquinoxalin-1-ium bromide (S6)

A 25 mL round-bottom flask was charged with 5-methylquinoxaline (2.21 mL, 17.3 mmol, 1.00 equiv.), a magnetic stir bar, and sealed with a 24/40 rubber septum. The round-bottom flask was evacuated and backfilled with N_2 three times. (It should be noted that while this reaction was carried out under N_2, variations were carried out under standard atmospheric conditions without a noticeable impact to yield. This reaction is likely tolerable to atmospheric conditions as well.) Dry MeCN (5.78 mL) was added to the round-bottom flask under N_2. Benzyl bromide (2.26 mL, 19.1 mmol, 1.10 equiv.) was added to the reaction drop-wise over 10 minutes at room temperature, under N_2. The reaction was let stir at room temperature, sealed under N_2, for 36 hours. After stirring, the opaque yellow reaction mixture was added to rapidly stirring hexanes (200 mL). The precipitated solids were collected by filtration and rinsed with hexanes (50.0 mL). The resulting bright green solids **S6** were allowed to air dry and then used as-is without further purification. **Yield:** 1.47 g (28%); **^{1}H NMR** (500 MHz, MeOD) δ 9.63

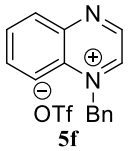
(d, J = 3.0 Hz, 1H), 9.36 (d, J = 2.9 Hz, 1H), 8.48 (dd, J = 8.8, 1.3 Hz, 1H), 8.19 (dd, J = 8.8, 7.2 Hz, 1H), 8.13 (dt, J = 7.2, 1.1 Hz, 1H), 7.53 – 7.45 (m, 5H), 6.41 (s, 2H), 2.96 (t, J = 0.8 Hz, 3H); **^{13}C NMR** (126 MHz, MeOD) δ 147.4, 147.2, 142.8, 140.6, 137.5, 134.9, 132.9, 132.5, 131.0, 130.8, 129.9, 118.1, 62.9, 17.7; **HRMS** (ESI) *m/z*: $[M\text{-}Br]^+$ Calcd for $C_{16}H_{15}N_2$: 235.1229, Found: 235.1228; **m. p. =** 129-132 °C.



5e

1-Benzyl-5-methylquinoxalin-1-ium trifluoromethanesulfonate (5e)

A 125 mL Erlenmeyer flask was charged with **S6** (1.00 g, 3.17 mmol, 1.00 equiv.), acetone (50 mL), and a magnetic stir bar. Silver trifluoromethanesulfonate (AgOTf) (0.940 g, 3.66 mmol, 1.15 equiv.) in acetone (5 mL) was added to the Erlenmeyer flask while stirring. Grey solids precipitated immediately upon addition of (AgOTf) and the reaction mixture was quickly filtered over a sand/celite/sand plug. The filtrate was collected, and all volatiles were removed by evaporation under reduced pressure. The resulting dark solid was solvated in DCM (6.00 mL) and added to rapidly stirring hexanes (200 mL). The precipitated solids were collected by filtration and rinsed with hexanes (100 mL). The resulting pale green solids **5e** were allowed to air dry and then used as-is without further purification. **Yield:** 1.17 g (92%); **^{1}H NMR** (500 MHz, MeOD) δ 9.62 (d, J = 2.9 Hz, 1H), 9.32 (d, J = 2.9 Hz, 1H), 8.47 (d, J = 8.9 Hz, 1H), 8.18 (dd, J = 8.8, 7.3 Hz, 1H), 8.13 (dt, J = 7.1, 1.2 Hz, 1H), 7.49 (s, 5H), 6.39 (s, 2H), 2.96 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.5 – 147.2 (m), 142.8, 140.4, 137.5, 134.9, 132.8, 132.5, 131.0, 130.8, 129.8, 123.0 (q, J = 319 Hz), 118.0, 62.8, 17.7; **^{19}F NMR** (471 MHz, MeOD) δ -80.1; **HRMS** (ESI) *m/z*: $[M\text{-}OTf]^+$ Calcd for $C_{16}H_{15}N_2$: 235.1229, Found: 235.1229; **m. p. =** 75 °C.

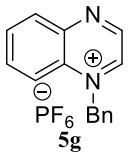


5f

1-Benzylquinoxalin-1-ium trifluoromethanesulfonate (5f)

A 50 mL Erlenmeyer flask was charged with **5h** (1.00 g, 3.32 mmol, 1.00 equiv.), acetone (40 mL), and a magnetic stir bar. Silver trifluoromethanesulfonate (AgOTf) (0.398 g, 3.65 mmol, 1.10 equiv.) in acetone (5 mL) was added to the Erlenmeyer flask while stirring. Grey solids precipitated immediately upon addition of (AgOTf) and the reaction mixture was quickly filtered over a sand/celite/sand plug. The filtrate was collected, and all volatiles were removed by evaporation under reduced pressure. The resulting yellow mixture was solvated in DCM (3.00 mL) and added to rapidly stirring hexanes (200 mL), upon which an opaque white oil crashed out. The organic solution was decanted off and the oil was solvated in minimal DCM (3.00 mL). Hexanes (100 mL) were added to the DCM and the resulting solution was placed in a -20 °C freezer for 1 hour. The precipitated solids were collected by filtration and the resulting grey-brown solids **5f** were then used as-is without further purification. **Yield:** 420 mg (34%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.57 (dd, J = 20.7, 3.0 Hz, 2H), 8.54 (dd, J = 14.8, 8.6 Hz, 2H), 8.19 (dt, J = 26.1, 7.5 Hz, 2H), 7.49 – 7.39 (m, 5H), 6.43 (s, 2H); **^{13}C NMR** (126

MHz, MeOD) δ 149.0, 148.0, 141.0, 137.6, 135.1, 133.1, 132.5, 132.2, 131.1, 130.8, 130.0, 121.7 (q, J = 319 Hz), 120.4, 62.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.5; **HRMS** (ESI) *m/z*: $[M\text{-}OTf]^+$ Calcd for $C_{15}H_{13}N_2$: 221.1073, Found: 221.1073; **m. p. =** 66 °C.



5g

1-Benzylquinoxalin-1-ium hexafluorophosphate (5g)

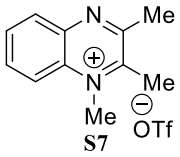
A 250 mL round-bottom flask was charged with **5h** (1.00 g, 3.32 mmol. 1.00 equiv.), DCM (50.0 mL), and two magnetic stir bars. Potassium hexafluorophosphate (1.22 g, 6.64 mmol. 2.00 equiv.) was solvated in water (50.0 mL) and added to the round-bottom flask. The reaction mixture was capped and stirred rapidly, at ambient temperature, to mix the separate organic and aqueous layers. The reaction was stirred for 25 hours, transferred into a separatory funnel, and DCM (10.0 mL) and water (20.0 mL) were added. The layers were separated, and the aqueous layer was extracted with DCM (3x25.0 mL). The organic extracts were combined and dried with Na_2SO_4. The solids were removed by filtration and the resulting filtrate was concentrated under reduced pressure. The resulting mixture was solvated in DCM (10.0 mL) and added to rapidly stirring hexanes (200 mL). The precipitated solids were collected by filtration and the resulting pale green crystalline solids **5g** were then used as-is without further purification. **Yield:** 323 mg (27%); **^{1}H NMR** (500 MHz, DMSO) δ 9.78 (d, J = 2.8 Hz, 1H), 9.68 (d, J = 2.8 Hz, 1H), 8.60 (dd, J = 25.0, 8.3 Hz, 2H), 8.33 – 8.23 (m, 2H), 7.54 (d, J = 7.0 Hz, 2H), 7.48 – 7.38 (m, 3H), 6.43 (s, 2H); **^{13}C NMR** (126 MHz, DMSO) δ 148.7, 145.6, 141.4, 135.9, 133.7, 132.4, 131.4, 130.1, 129.3, 129.2, 128.3, 119.6, 60.6; **^{19}F NMR** (471 MHz, DMSO) δ -69.4, -70.9; **^{31}P NMR** (203 MHz, DMSO) δ -142.4 (p); **HRMS** (ESI) *m/z*: $[M\text{-}PF_6]^+$ Calcd for $C_{15}H_{13}N_2$: 221.1073, Found: 221.1073; **m. p. =** 185 °C.

5h

1-Benzylquinoxalin-1-ium bromide (5h)

A 50 mL Schlenk flask was charged with quinoxaline (5.00 g, 38.4 mmol, 1.00 equiv.) and a magnetic stir bar. The Schlenk flask was evacuated and backfilled with N_2 three times. (It should be noted that while this reaction was carried out under N_2, variations were carried out under standard atmospheric conditions without a noticeable impact to yield. This reaction is likely tolerable to atmospheric conditions as well.) Dry MeCN (12.64 mL) and benzyl bromide (5.02 mL, 42.3 mmol, 1.10 equiv.) were added to the Schlenk flask sequentially, under N_2. The reaction was allowed to stir at ambient temperature, sealed under N_2, for 22 hours. After 22 hours of stirring, the yellow opaque reaction mixture was added into rapidly stirring hexanes (450 mL). The precipitated solids were collected by filtration and the resulting yellow solids **5g** were then used as-is without further purification. **Yield:** 6.34 g (55%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.73 (s, 1H), 9.64 (s, 1H), 8.57 – 8.48 (m, 2H), 8.23 – 8.11 (m, 2H), 7.57 – 7.51 (m, 2H), 7.43 – 7.36 (m, 3H), 6.76 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.7, 146.3,

140.4, 136.5, 133.6, 132.3, 131.7, 130.3, 130.0, 129.8, 128.7, 119.8, 61.6; **HRMS** (ESI) *m/z*: $[M\text{-}Br]^+$ Calcd for $C_{15}H_{13}N_2$: 221.1073, Found: 221.1072; **m. p. =** 127-129 °C.



S7

1,2,3-trimethylquinoxalin-1-ium trifluoromethanesulfonate (S7)

A 50 mL Schlenk flask was charged with 2,3-dimethylquinoxaline (1.00 g, 6.32 mmol, 1.00 equiv.) and a magnetic stir bar. The Schlenk flask was evacuated and backfilled with N_2 three times. (It should be noted that while this reaction was carried out under N_2, variations were carried out under standard atmospheric conditions without a noticeable impact to yield. This reaction is likely tolerable to atmospheric conditions as well.) Dry DCM (8.21 mL) was added to the flask. The reaction was cooled to 0 °C in an ice bath and methyl trifluoromethanesulfonate (0.644 mL, 5.69 mmol, 0.900 equiv.) was added to the reaction drop-wise over 10 minutes. The reaction was sealed, let warm to room temperature, and stirred, for 19 hours. After stirring, the resulting reaction solution was concentrated under reduced pressure to give a crude residue. The residue was solvated in DCM (4 mL) and added to rapidly stirring Et_2O (100 mL). The precipitated solids were collected by filtration and rinsed with hexanes (50.0 mL). The resulting pale green solids **S7** were allowed to air dry and then used as-is without further purification. **Yield:** 521 mg (26%); **^{1}H NMR** (500 MHz, MeOD) δ 8.52 (d, J = 8.6 Hz, 1H), 8.34 (d, J = 8.0 Hz, 1H), 8.14 (dt, J = 19.7, 7.3 Hz, 2H), 4.62 (s, 3H), 3.13 (s, 3H), 3.01 (s, 3H); **^{13}C NMR** (126 MHz, MeOD) δ 159.1, 155.6, 143.9, 135.2, 133.4, 132.3, 131.9, 121.6 (q, J = 318.8 Hz), 119.7, 41.2, 24.8, 19.7; **^{19}F NMR** (471 MHz, MeOD) δ -80.03; **HRMS** (ESI) *m/z*: $[M\text{-}OTf]^+$ Calcd for $C_{11}H_{13}N_2$: 173.1073, Found: 173.1073; **m. p. =** 102-106 °C.

D. Asymmetric Synthesis of Dihydroquinoxalines (Boronic Acid Scope)

Preparation of Rh/Ligand catalyst stock solution for dearomatization reactions:

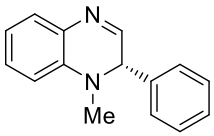
The procedure below is an example of making 5 reaction equivalents worth of rhodium catalyst stock solution. 2 mL of the total 10 mL solution below is equivalent to 6 mol% (1 reaction equivalent) of the rhodium catalyst for a 0.2 mmol scale dearomatization reaction.

In a nitrogen filled glovebox, $Rh(COD)_2BF_4$ (24.4 mg, 0.0600 mmol, 1.00 equiv.), (R,R)-QuinoxP* (23.4 mg, 0.0700 mmol, 1.17 equiv.) and dioxane (10.0 mL) were added to a 20 mL vial containing a stir bar. The resulting heterogenous dioxane solution was stirred for 30 minutes to promote the formation of the catalyst. The resulting homogeneous Rh/(R,R)-QuinoxP* solution was an opaque orange-red color. The catalyst solution was then used as-is in the general procedure below (2 mL of catalyst solution per dearomatization reaction).

For racemic dearomatization products, the same catalyst formation procedure above was followed. In a glovebox, to a 20 mL vial was added $Rh(COD)_2BF_4$ (20.3 mg, 0.0500 mmol, 1.00 equiv.), the achiral ligand 1,2-Bis(diphenylphosphino)benzene (DPPBz) (22.3 mg, 0.0500 mmol, 1.00 equiv.), and dioxane (10.0 mL) to form a Rh/DPPBz catalyst solution. The resulting opaque dark-yellow solution was then used as-is in the general procedure below to yield the racemic version of the generated dihydroquinoxalines.

General procedure for the asymmetric dearomatization of quinoxalinium salts using the Rh/(R,R)-QuinoxP catalyst system:

The specified quinoxalinium salt (0.200 mmol, 1.00 equiv.), boronic acid (0.500 mmol, 2.50 equiv.), and Na_2CO_3 (63.6 mg, 0.600 mmol, 3.00 equiv.) were measured into a 4 mL scintillation vial on the benchtop. The vial containing quinoxalinium salt, boronic acid, and Na_2CO_3 were transferred into a nitrogen filled glovebox where the above pre-formed Rh/(R,R)-QuinoxP stock solution of catalyst (2.00 mL, 0.012 mmol, 0.06 equiv.) was added into the 4 mL vial. The vial was then sealed with a PTFE-lined septa cap and brought outside the glovebox. Water (0.200 mL), degassed by sparging with nitrogen, was added to the reaction mixture via syringe and the reaction mixture was heated at 80 °C for 2 hours using an aluminum heating block. The vial was then removed from the heating block and allowed to cool to room temperature. The resulting room temperature reaction mixture was diluted with EtOAc (1.00 mL) and dried with $MgSO_4$ (1.00 g). The reaction was filtered over Al_2O_3, the solids were rinsed with EtOAc (2.00 mL) and the resulting filtrate was concentrated under reduced pressure to give a crude reaction residue. The residue was purified by isocratic flash column chromatography with silica gel using the given TLC solvent conditions, and the solvents were removed under reduced pressure to give the desired dihydroquinoxaline product.

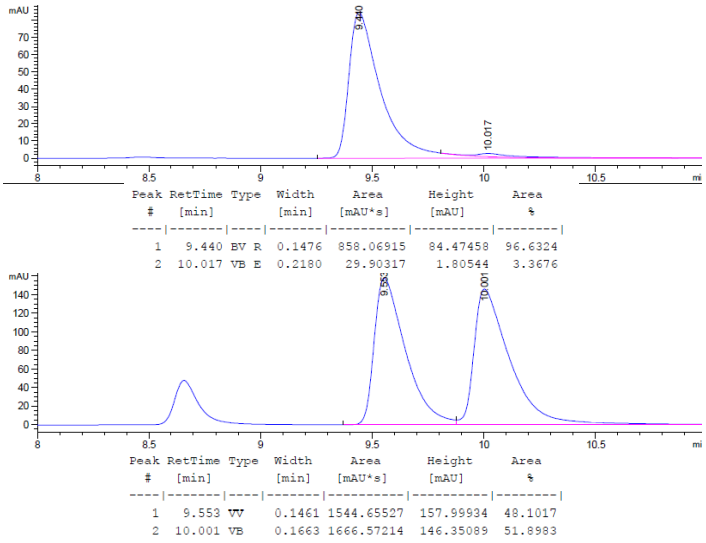


4a

(2S)-1-Methyl-2-phenyl-1,2-dihydroquinoxaline (4a)

Dihydroquinoxaline **4a** (yellow crystalline solid) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and phenyl boronic acid (61.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 80% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 30.2 mg (68%); **ee**: 94% (Chiral-CD, MeCN/water gradient 15/85 to 35/65 - 10 minutes, 35/65 to 95/5 – 5 minutes, flow rate = 0.750 mL/min, I = 254 nm) tR = 9.4 min (major), 10.0 min (minor); **TLC:** R*f* = 0.34 (20/80 EtOAc/Hexanes); $[\alpha]_D^{20}$: +544° (*c* 0.00150 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, J = 3.4 Hz, 1H), 7.39 – 7.24 (m, 6H), 7.13 (td, J = 7.8, 1.6 Hz, 1H), 6.72 (td, J = 7.5, 1.2 Hz, 1H), 6.55 (dd, J = 8.1, 1.1 Hz, 1H), 4.99 (d, J = 3.3 Hz, 1H), 2.71 (s, 3H); (500 MHz, C_6D_6) δ 7.65 (dd, J = 7.5, 1.6 Hz, 1H), 7.26 (d, J = 3.3 Hz, 1H), 7.04 (td, J = 7.8, 1.7 Hz, 1H), 6.97 (s, 5H), 6.72 (td, J = 7.5, 1.2 Hz, 1H), 6.32 (dd, J = 8.1, 1.2 Hz, 1H), 4.26 (d, J = 3.2 Hz, 1H), 2.19 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.0, 139.4, 138.5, 132.1, 129.9, 129.2, 128.7, 128.4, 127.2, 117.6, 110.2, 64.4, 35.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{14}N_2$: 223.1229, Found: 223.1230; **Melting Point** 100-104°C.

Single crystals suitable for **X-Ray** analysis were obtained by vapor diffusion recrystallization from a solution of **4a** in a mixture of dichloromethane and *n*-heptane. CCDC registry number 2237393.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.440	BV R	0.1476	858.06915	84.47458	96.6324
2	10.017	VB E	0.2180	29.90317	1.80544	3.3676

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.553	VV	0.1461	1544.65527	157.99934	48.1017
2	10.001	VB	0.1663	1666.57214	146.35089	51.8983

Figure S1. Thermal ellipsoid plot of the X-ray crystallographic structure of **4a** (CCDC: 2237393) with an ellipsoid contour probability level of 50%.

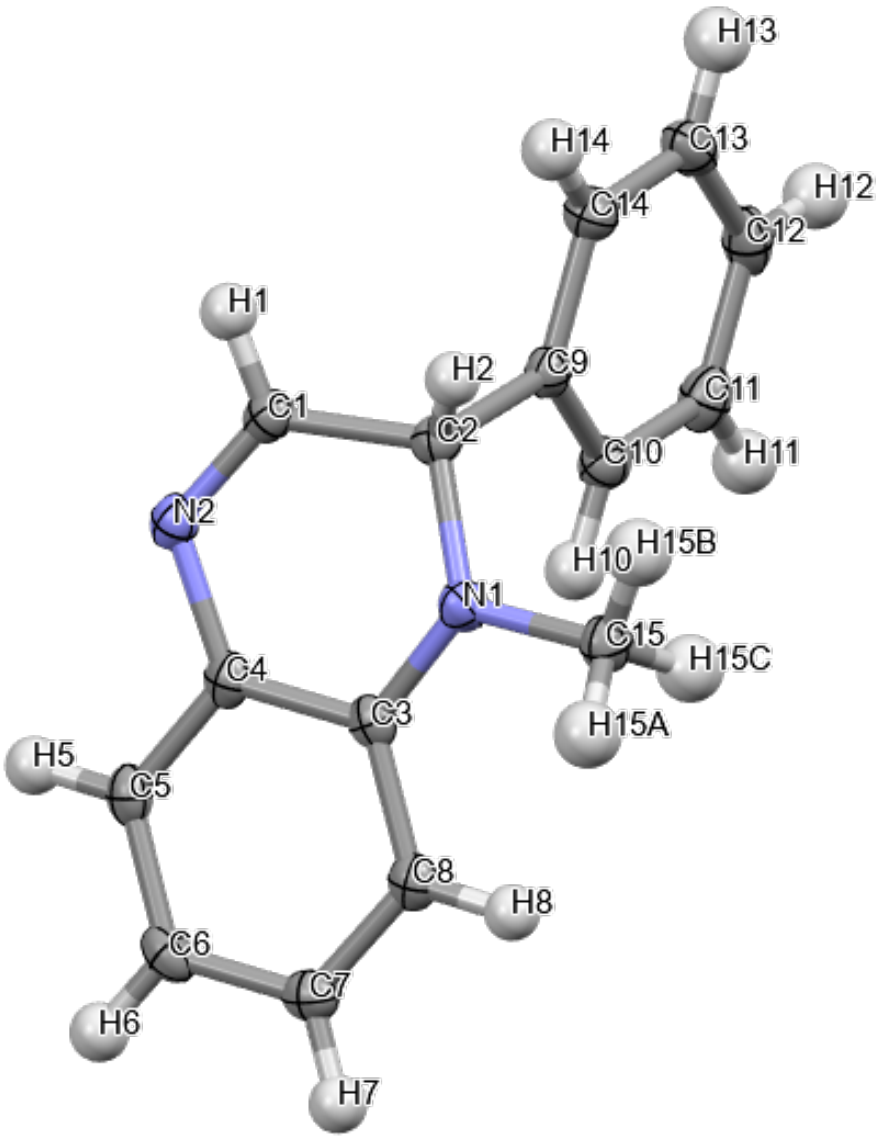
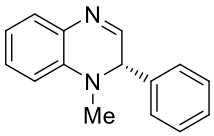


Table S1. Crystallographic data acquisition and analysis parameters used to collect the structure of **4a** (CCDC: 2237393)

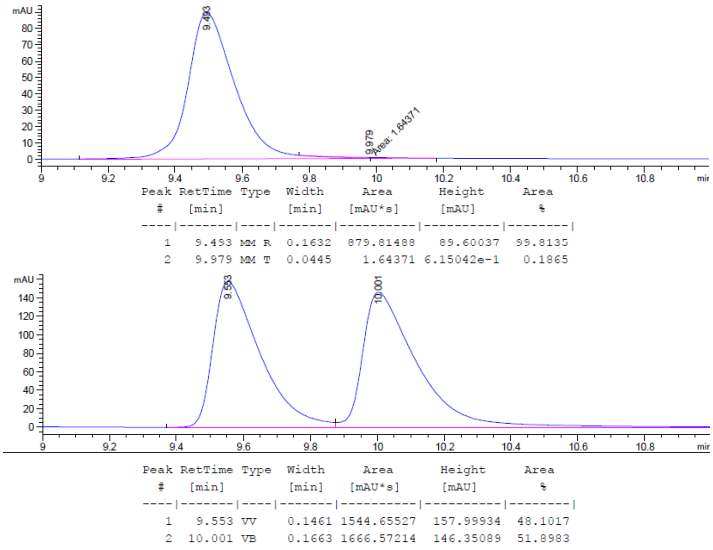
Chemical formula	$C_{15}H_{14}N_2$	
Formula weight	222.28 g/mol	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal size	0.025 x 0.075 x 0.160 mm	
Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 9.2003(5) Å	α = 90°
	b = 6.2609(3) Å	β = 96.663(2)°
	c = 9.8991(5) Å	γ = 90°
Volume	566.36(5) $Å^3$	
Z	2	
Density (calculated)	1.303 g/cm^3	
Absorption coefficient	0.602 mm^{-1}	
F(000)	376	
Diffractometer	Bruker D8 VENTURE κ-geometry	
Radiation source	Incoatec IμS DIAMOND microfocus	
Theta range for data collection	4.50 to 70.06°	
Index ranges	-11<=h<=11, -7<=k<=7, -11<=l<12	
Reflections collected	8177	
Independent reflections	2124 [R(int) = 0.0261]	
Coverage of independent reflections	99.70%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9850 and 0.9100	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2124 / 1 / 155	
Goodness-of-fit on F^2	1.055	
Final R indices (2686 data; I>2σ(I))	R1 = 0.0250, wR2 = 0.0632	
Final R indices (all data)	R1 = 0.0251, wR2 = 0.0633	
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0259P)^2+0.1142P]$	
	where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.10(9)	
Largest diff. peak and hole	0.150 and -0.136 $eÅ^{-3}$	
R.M.S. deviation from mean	0.029 $eÅ^{-3}$	

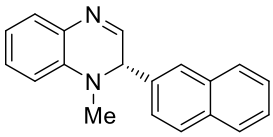


(PhBpin): **4a**

(2S)-1-Methyl-2-phenyl-1,2-dihydroquinoxaline (4a)

Dihydroquinoxaline **4a** (yellow crystalline solid) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and phenylboronic acid pinacol ester (102 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 35% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 14.4 mg (32%); **ee**: >99% (Chiral-CD, MeCN/water gradient 15/85 to 35/65 - 10 minutes, 35/65 to 95/5 – 5 minutes, flow rate = 0.750 mL/min, I = 254 nm) tR = 9.5 min (major), 10.0 min (minor); See above entry of **4a** for full characterization data.

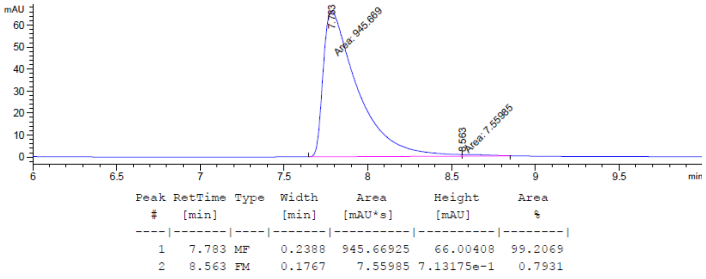




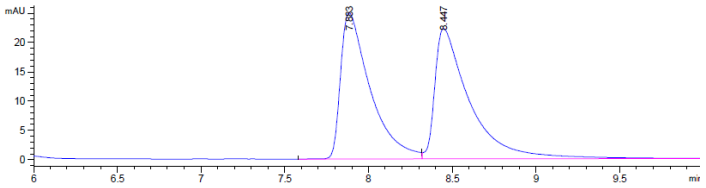
4b

(2S)-1-Methyl-2-(naphthalen-2-yl)-1,2-dihydroquinoxaline (4b)

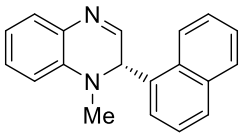
Dihydroquinoxaline **4b** (yellow solid) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and naphthalene-2-boronic acid (86.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 91% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 45.2 mg (83%); **ee**: 98% (Chiral-CD, MeCN/water gradient 20/80 to 30/70 - 10 minutes, 30/70 to 95/5 – 5 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 7.8 min (major), 8.6 min (minor); **TLC:** R*f* = 0.34 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +565° (*c* 0.00456 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 3H), 7.72 – 7.68 (m, 1H), 7.54 (d, J = 3.2 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.43 (dd, J = 8.5, 1.8 Hz, 1H), 7.29 (dd, J = 7.6, 1.6 Hz, 1H), 7.15 (td, J = 7.8, 1.7 Hz, 1H), 6.75 (td, J = 7.5, 1.3 Hz, 1H), 6.58 (dd, J = 8.1, 1.2 Hz, 1H), 5.18 (d, J = 3.2 Hz, 1H), 2.73 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.9, 139.4, 136.0, 133.5, 133.5, 132.0, 130.0, 129.4, 128.5, 128.2, 127.9, 126.7, 126.5, 126.2, 125.0, 117.6, 110.2, 64.8, 35.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{17}N_2$: 273.1386, Found: 273.1383.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.783	MF	0.2388	945.66925	66.00408	99.2069
2	8.563	FM	0.1767	7.55985	7.13175e-1	0.7931



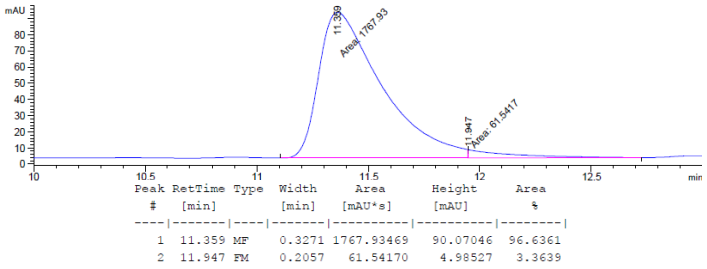
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.883	BV	0.1767	306.40317	24.96350	48.6422
2	8.447	VB	0.2060	323.50879	22.25070	51.3578



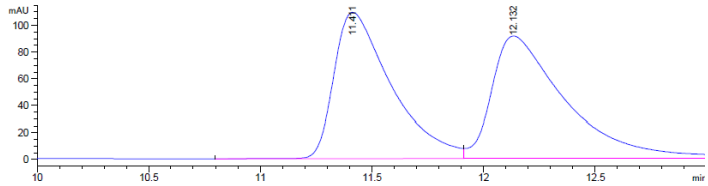
4c

(2S)-1-Methyl-2-(naphthalen-1-yl)-1,2-dihydroquinoxaline (4c)

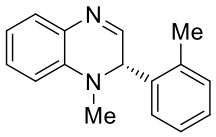
Dihydroquinoxaline **4c** (yellow-orange solid) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and naphthalene-1-boronic acid (86.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 79% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 34.3 mg (63%); **ee**: 94% (Chiral-CD, MeCN/water gradient 20/80 to 20/80 - 10 minutes, 20/80 to 95/5 – 5 minutes, flow rate = 0.750 mL/min, I = 254 nm) tR = 11.4 min (major), 11.9 min (minor); **TLC:** R*f* = 0.39 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +723° (*c* 0.00324 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.34 – 8.28 (m, 1H), 7.95 – 7.88 (m, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.50 – 7.40 (m, 2H), 7.28 (dd, J = 7.6, 1.6 Hz, 1H), 7.18 (td, J = 7.8, 1.6 Hz, 1H), 6.76 (td, J = 7.5, 1.2 Hz, 1H), 6.65 (dd, J = 8.0, 1.3 Hz, 1H), 5.82 (d, J = 2.9 Hz, 1H), 2.70 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.1, 139.8, 134.4, 134.4, 131.8, 130.6, 130.0, 129.3 (s, 2C), 128.6, 127.0, 126.7, 126.1, 125.8, 123.1, 117.7, 110.1, 61.8, 35.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{17}N_2$: 273.1386, Found: 273.1386.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.359	MF	0.3271	1767.93469	90.07046	96.6361
2	11.947	FM	0.2057	61.54170	4.98527	3.3639



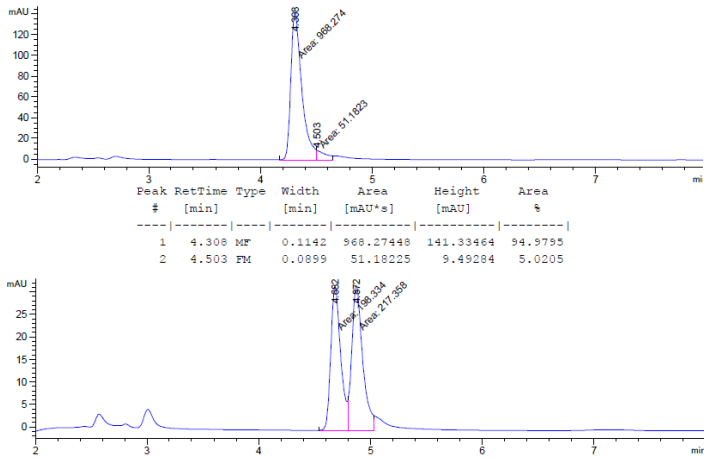
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.411	BV	0.2625	1951.52734	109.12074	47.7698
2	12.132	VV	0.3365	2133.74536	91.38922	52.2302



4d

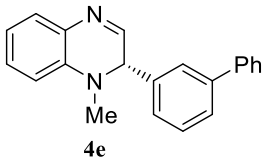
(2S)-1-Methyl-2-(2-methylphenyl)-1,2-dihydroquinoxaline (4d)

Dihydroquinoxaline **4d** (tan solid) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 2-methylphenylboronic acid (68.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 48% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 20.8 mg (44%); **ee**: 90% (Chiral-CD, MeCN/water gradient 20/80 to 30/70 - 10 minutes, 30/70 to 95/5 – 5 minutes, flow rate = 0.750 mL/min, I = 254 nm) tR = 11.9 min (major), 12.9 min (minor); **TLC:** R*f* = 0.31 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +422° (*c* 0.00310 g/mL, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 (d, J = 2.9 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.25 – 7.10 (m, 5H), 6.73 – 6.67 (m, 1H), 6.57 (d, J = 8.0 Hz, 1H), 5.36 (d, J = 2.9 Hz, 1H), 2.65 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.4, 139.7, 137.3, 135.2, 131.6, 131.4, 130.0, 128.5, 128.4 (s, 2C), 127.0, 117.4, 109.7, 61.7, 35.0, 19.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{17}N_2$: 237.1386, Found: 237.1387.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.308	MF	0.1142	968.27448	141.33464	94.9795
2	4.503	FM	0.0899	51.18225	9.49284	5.0205

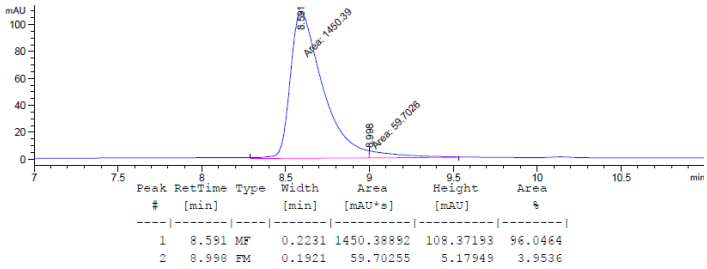
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.682	MF	0.1037	198.33388	31.88921	47.7118
2	4.872	FM	0.1127	217.35788	32.14089	52.2882



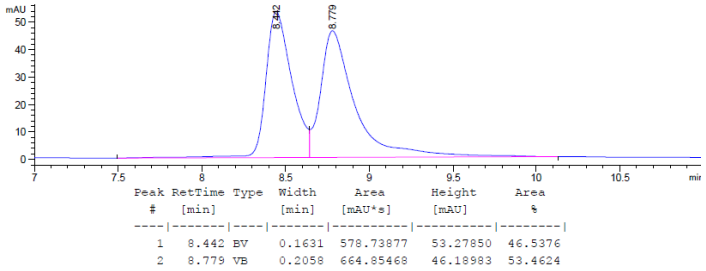
4e

(2S)-2-([1,1'-Biphenyl]-3-yl)-1-methyl-1,2-dihydroquinoxaline (4e)

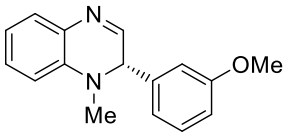
Dihydroquinoxaline **4e** (yellow oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 3-biphenylboronic acid (99.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 68% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 89.1 mg (67%); **ee**: 92% (Chiral-CD, MeCN/water gradient 20/80 to 25/75 - 10 minutes, 25/75 to 95/5 – 5 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 8.6 min (major), 9.0 min (minor); **TLC:** R*f* = 0.31 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +468° (*c* 0.00310 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 4H), 7.48 (t, J = 1.8 Hz, 1H), 7.42 (q, J = 7.3 Hz, 3H), 7.37 – 7.33 (m, 1H), 7.29 – 7.24 (m, 2H), 7.14 (td, J = 7.8, 1.6 Hz, 1H), 6.73 (td, J = 7.5, 1.2 Hz, 1H), 6.58 (dd, J = 8.1, 1.2 Hz, 1H), 5.07 (d, J = 3.2 Hz, 1H), 2.75 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.9, 142.2, 140.7, 139.4, 139.2, 132.1, 129.9, 129.8, 129.0, 128.4, 127.7, 127.5, 127.3, 126.2, 125.9, 117.7, 110.2, 64.5, 35.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{19}N_2$: 299.1542, Found: 299.1542.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.591	MF	0.2231	1450.38892	108.37193	96.0464
2	8.998	FM	0.1921	59.70255	5.17949	3.9536



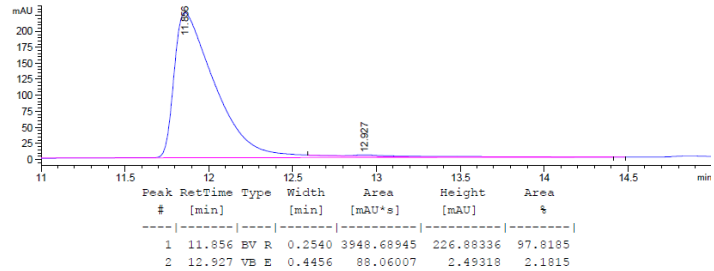
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.442	BV	0.1631	578.73877	53.27850	46.5376
2	8.779	VB	0.2058	664.85468	46.18983	53.4624



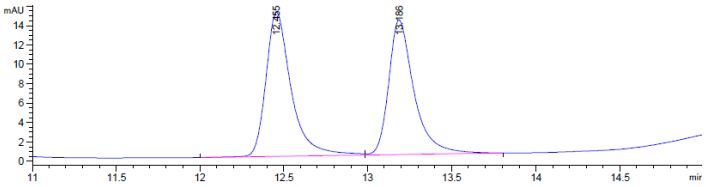
4f

(2S)-2-(3-methoxyphenyl)-1-methyl-1,2-dihydroquinoxaline (4f)

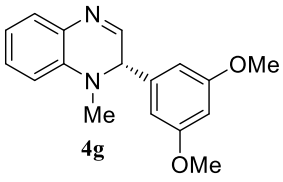
Dihydroquinoxaline **4f** (yellow-green oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 3-methoxyphenylboronic acid (76.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 74% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 29.3 mg (58%); **ee**: 96% (Chiral-CD, MeCN/water gradient 20/80 to 30/70 - 10 minutes, 30/70 to 95/5 – 5 minutes, flow rate = 0.750 mL/min, I = 254 nm) tR = 11.9 min (major), 12.9 min (minor); **TLC:** R*f* = 0.25 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +465° (*c* 0.00328 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, J = 3.3 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.13 (td, J = 7.8, 1.6 Hz, 1H), 6.88 – 6.83 (m, 2H), 6.82 – 6.79 (m, 1H), 6.72 (td, J = 7.5, 1.2 Hz, 1H), 6.56 (dd, J = 8.1, 1.2 Hz, 1H), 4.96 (d, J = 3.2 Hz, 1H), 3.75 (s, 3H), 2.71 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.3, 154.9, 140.2, 139.4, 132.1, 130.3, 129.9, 128.3, 119.5, 117.6, 113.9, 112.8, 110.1, 64.4, 55.4, 35.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{17}N_2O$: 253.1335, Found: 253.1336.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.856	BV R	0.2540	3948.68945	226.88336	97.8185
2	12.927	VB E	0.4456	88.06007	2.49318	2.1815



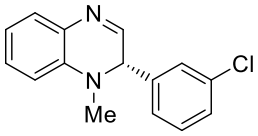
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.455	BV	0.1563	156.57953	14.87080	51.7707
2	13.186	VB	0.1559	145.86890	13.90312	48.2293



4g

(2S)-2-(3,5-Dimethoxyphenyl)-1-methyl-1,2-dihydroquinoxaline (4g)

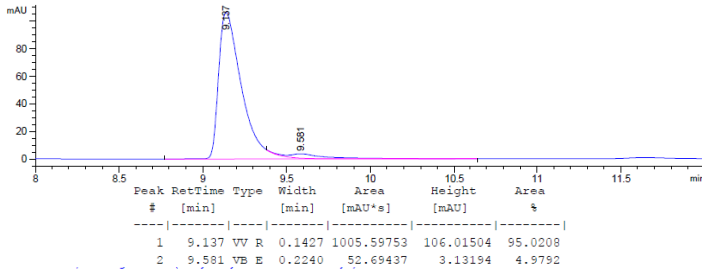
Dihydroquinoxaline **4g** (yellow oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 3,5-dimethoxyphenylboronic acid (91.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 78% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 35.6 mg (63%); **ee**: 94% (See reduced compound **S8** for HPLC separation conditions); **TLC:** R*f* = 0.35 (30/70 EtOAc/Hexanes); $[\alpha]_D^{20}$: +641° (*c* 0.00267 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, J = 3.2 Hz, 1H), 7.24 (dd, J = 7.6, 1.7 Hz, 1H), 7.12 (td, J = 7.8, 1.6 Hz, 1H), 6.71 (td, J = 7.5, 1.2 Hz, 1H), 6.57 (dd, J = 8.1, 1.2 Hz, 1H), 6.44 – 6.38 (m, 3H), 4.92 (d, J = 3.1 Hz, 1H), 3.73 (s, 6H), 2.72 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.5, 154.9, 141.2, 139.4, 132.0, 129.9, 128.3, 117.7, 110.1, 105.3, 100.2, 64.5, 55.5, 35.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{19}N_2O_2$: 283.1441, Found: 283.1439.



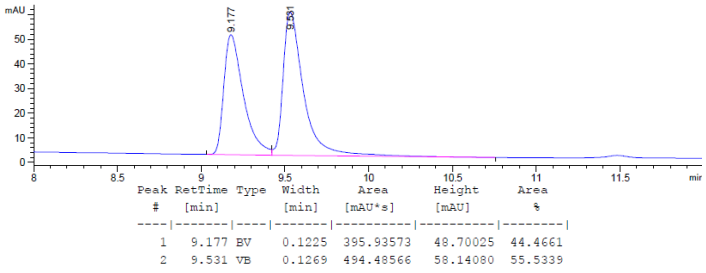
4h

(2S)-2-(3-Chlorophenyl)-1-methyl-1,2-dihydroquinoxaline (4h)

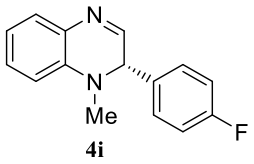
Dihydroquinoxaline **4h** (orange oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 3-chlorophenylboronic acid (78.2 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 63% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 29.8 mg (58%); **ee**: 90% (Chiral-CD, MeCN/water gradient 10/90 to 30/70 - 10 minutes, 30/70 to 95/5 – 5 minutes, flow rate = 1.00mL/min, I = 254 nm) tR = 9.1 min (major), 9.6 min (minor); **TLC:** R*f* = 0.28 (20/80 EtOAc/Hexanes); $[\alpha]_D^{20}$: +362° (*c* 0.00353 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, J = 3.3 Hz, 1H), 7.32 – 7.23 (m, 4H), 7.20 – 7.11 (m, 2H), 6.74 (td, J = 7.5, 1.2 Hz, 1H), 6.57 (dd, J = 8.1, 1.2 Hz, 1H), 4.99 (d, J = 3.3 Hz, 1H), 2.72 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.9, 140.6, 139.0, 135.2, 131.9, 130.6, 130.1, 128.9, 128.5, 127.3, 125.4, 117.9, 110.2, 64.0, 35.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{14}{}^{35}ClN_2$: 257.0840, Found: 257.0840.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.137	VV R	0.1427	1005.59753	106.01504	95.0208
2	9.581	VB E	0.2240	52.69437	3.13194	4.9792



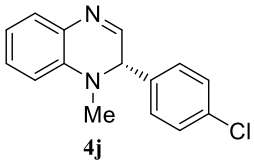
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.177	BV	0.1225	395.93573	48.70025	44.4661
2	9.531	VB	0.1269	494.48566	58.14080	55.5339



4i

(2S)-2-(4-Fluorophenyl)-1-methyl-1,2-dihydroquinoxaline (4i)

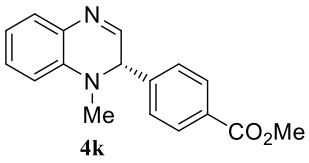
Dihydroquinoxaline **4i** (yellow oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 4-fluorophenylboronic acid (70.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 75% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 23.5 mg (49%); **ee**: 92% (See reduced compound **7a** for HPLC separation conditions); **TLC:** R*f* = 0.19 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$: +574° (*c* 0.00420 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, J = 3.4 Hz, 1H), 7.30 – 7.20 (m, 3H), 7.14 (td, J = 7.7, 1.6 Hz, 1H), 7.06 – 6.98 (m, 2H), 6.74 (td, J = 7.5, 1.2 Hz, 1H), 6.55 (dd, J = 8.1, 1.2 Hz, 1H), 4.98 (d, J = 3.3 Hz, 1H), 2.70 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.0, 162.1, 154.6, 139.2, 134.3 (d, J = 3 Hz), 132.0, 130.0, 129.0, 128.9, 128.4, 117.8, 116.2 (d, J = 22 Hz), 110.3, 63.6, 35.0; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{14}FN_2$: 241.1135, Found: 241.1136.



4j

(2S)-2-(4-Chlorophenyl)-1-methyl-1,2-dihydroquinoxaline (4j)

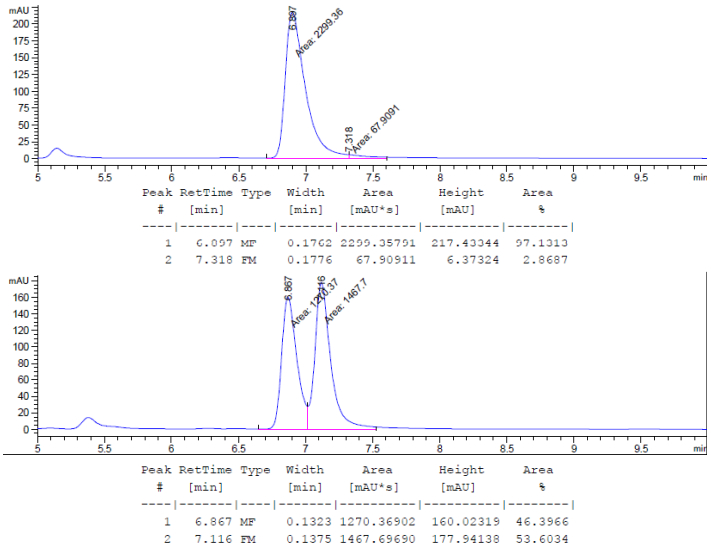
Dihydroquinoxaline **4j** (orange oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 4-chlorophenylboronic acid (78.2 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 76% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 30.8 mg (60%); **ee:** 96% (See reduced compound **S9** for HPLC separation conditions); **TLC:** R*f* = 0.22 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$: +511° (*c* 0.00350 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, J = 3.3 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 7.22 – 7.18 (m, 2H), 7.14 (td, J = 7.8, 1.6 Hz, 1H), 6.74 (td, J = 7.5, 1.2 Hz, 1H), 6.55 (dd, J = 8.1, 1.2 Hz, 1H), 4.97 (d, J = 3.3 Hz, 1H), 2.70 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.2, 139.1, 136.9, 134.7, 132.0, 130.0, 129.5, 128.5, 128.5, 117.8, 110.3, 63.7, 35.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{14}{}^{35}ClN_2$: 257.0840, Found: 257.0839.

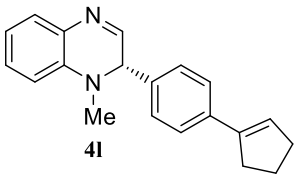


4k

Methyl 4-[(2S)-1-methyl-1,2-dihydroquinoxalin-2-yl]benzoate (4k)

Dihydroquinoxaline **4k** (yellow oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 4-methoxycarbonylphenylboronic acid (90.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 44% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 24.1 mg (43%); **ee:** 94% (Chiral-CD, MeCN/water gradient 20/80 to 30/70 - 12 minutes, 30/70 to 95/5 – 5 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 6.9 min (major), 7.3 min (minor); **TLC:** R*f* = 0.28 (30/70 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +445° (*c* 0.00356 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.47 (d, J = 3.4 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.28 – 7.26 (m, 1H), 7.15 (td, J = 7.8, 1.6 Hz, 1H), 6.75 (t, J = 1.0 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 5.07 (d, J = 3.3 Hz, 1H), 3.91 (s, 3H), 2.72 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.7, 153.8, 143.2, 139.1, 131.9, 130.6, 130.5, 130.1, 128.5, 127.1, 117.9, 110.3, 64.2, 52.4, 35.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2O_2$: 281.1284, Found: 281.1285.

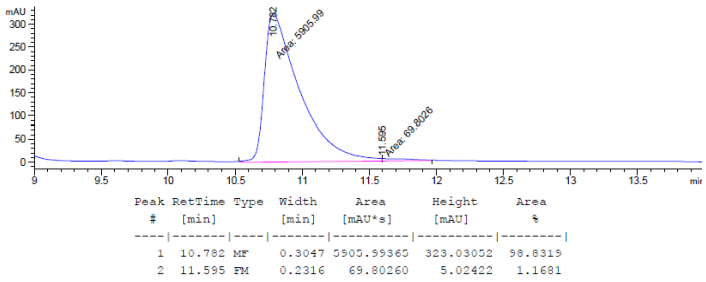




4l

(2S)-2-[4-(Cyclopent-1-en-1-yl)phenyl]-1-methyl-1,2-dihydroquinoxaline (4l)

Dihydroquinoxaline **4l** (yellow solid) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 4-cyclopentenylbenzeneboronic acid (94.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 85% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 48.4 mg (84%); **ee:** 98% (Chiral-CD, MeCN/water gradient 35/65 to 35/65 - 10 minutes, 35/65 to 95/5 – 5 minutes, flow rate = 0.50 mL/min, I = 254 nm) tR = 10.8 min (major), 11.6 min (minor); **TLC:** R*f* = 0.41 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +441° (*c* 0.00344 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, J = 3.3 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.27 – 7.24 (m, 1H), 7.22 – 7.18 (m, 2H), 7.12 (td, J = 7.8, 1.6 Hz, 1H), 6.72 (td, J = 7.6, 1.2 Hz, 1H), 6.54 (dd, J = 8.1, 1.2 Hz, 1H), 6.21 – 6.15 (m, 1H), 4.96 (d, J = 3.3 Hz, 1H), 2.70 (s, 3H), 2.71 – 2.63 (m, 2H), 2.52 (tq, J = 7.5, 2.5 Hz, 2H), 2.08 – 1.96 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.0, 142.0, 139.4, 137.4, 136.8, 132.2, 129.8, 128.3, 127.3, 127.1, 126.4, 117.6, 110.2, 64.2, 35.0, 33.5, 33.3, 23.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{21}N_2$: 289.1669, Found: 289.1698.



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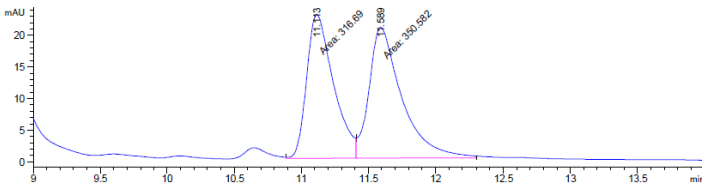
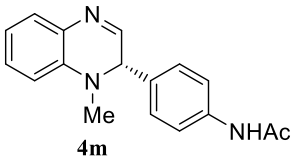
1	10.782	MF	0.3047	5905.99365	323.03052	98.8319
2	11.595	FM	0.2316	69.80260	5.02422	1.1681



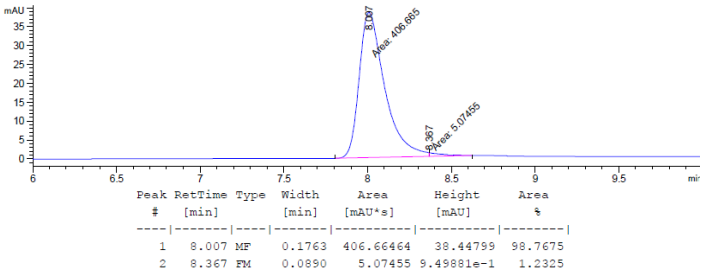
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.113	MF	0.2316	316.69003	22.79478	47.4604
2	11.589	FM	0.2816	350.58182	20.74840	52.5396



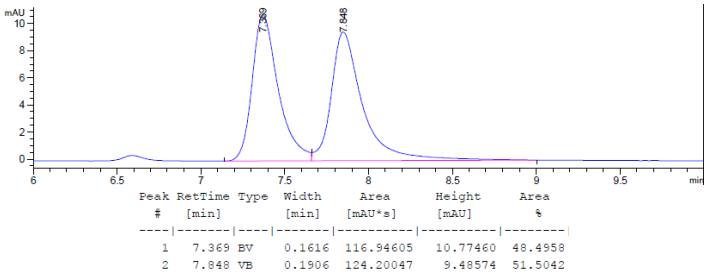
4m

***N*-{4-[(2S)-1-Methyl-1,2-dihydroquinoxalin-2-yl]phenyl}acetamide (4m)**

Dihydroquinoxaline **4m** (yellow solid) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 4-acetylaminophenylboronic acid (89.5 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 72% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 40.2 mg (72%); **ee:** 98% (Chiral-CD, MeCN/water gradient 20/80 to 30/70 - 10 minutes, 30/70 to 95/5 – 5 minutes, flow rate = 0.75 mL/min, I = 254 nm) tR = 8.0 min (major), 8.4 min (minor); **TLC:** R*f* = 0.36 (80/20 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +470° (*c* 0.00329 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 3H), 7.27 – 7.24 (m, 1H), 7.23 – 7.20 (m, 2H), 7.16 – 7.09 (m, 2H), 6.72 (td, J = 7.5, 1.2 Hz, 1H), 6.54 (dd, J = 8.1, 1.4 Hz, 1H), 4.95 (d, J = 3.4 Hz, 1H), 2.69 (s, 3H), 2.17 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.5, 154.9, 139.3, 138.4, 134.2, 132.0, 129.9, 128.3, 128.0, 120.5, 117.6, 110.3, 63.8, 35.0, 24.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{18}N_3O$: 280.1444, Found: 280.1442.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.007	MF	0.1763	406.66464	38.44799	98.7675
2	8.367	FM	0.0890	5.07455	9.49881e-1	1.2325



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.369	BV	0.1616	116.94605	10.77460	48.4958
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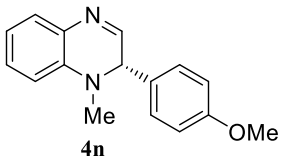
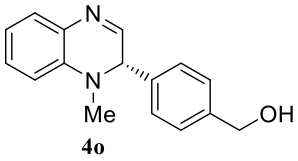


4n

(2S)-2-(4-methoxyphenyl)-1-methyl-1,2-dihydroquinoxaline (4n)

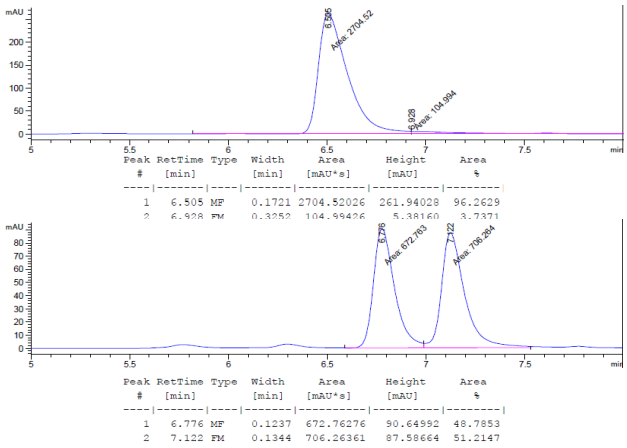
Dihydroquinoxaline **4n** (yellow oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 4-methoxyphenylboronic acid (76.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 63% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 26.7 mg (53%); **ee:** 94% (See reduced compound **S10** for HPLC separation conditions); **TLC:** R*f* = 0.20 (20/80 EtOAc/Hexanes); $[\alpha]_D^{20}$: +284° (*c* 0.00312 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, J = 3.3 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.20 – 7.16 (m, 2H), 7.12 (td, J = 7.7, 1.6 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.72 (td, J = 7.5, 1.2 Hz, 1H), 6.53 (dd, J = 8.1, 1.2 Hz, 1H), 4.92 (d, J = 3.3 Hz, 1H), 3.79 (s, 3H), 2.69 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.0, 155.3, 139.4, 132.2, 130.6, 129.8, 128.6, 128.3, 117.5, 114.5, 110.2, 63.7, 55.4, 34.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{17}N_2O$: 253.1335, Found: 253.1334.

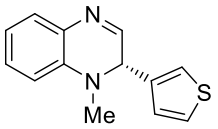


4o

{4-[(2S)-1-Methyl-1,2-dihydroquinoxalin-2-yl]phenyl}methanol (4o)

Dihydroquinoxaline **4o** (yellow waxy semi-solid) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 4-hydroxymethylphenylboronic acid (76.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 71% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 32.3 mg (64%); **ee:** 92% (Chiral-CD, MeCN/water gradient 10/90 to 35/65 - 10 minutes, 35/65 to 95/5 – 5 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 6.5 min (major), 6.9 min (minor); **TLC:** R*f* = 0.31 (60/40 EtOAc/Hexanes); $[\alpha]_D^{20}$: +419° (*c* 0.00331 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, J = 3.3 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.28 – 7.23 (m, 3H), 7.13 (td, J = 7.7, 1.6 Hz, 1H), 6.72 (td, J = 7.5, 1.3 Hz, 1H), 6.55 (dd, J = 8.2, 1.3 Hz, 1H), 4.99 (d, J = 3.3 Hz, 1H), 4.68 (d, J = 5.4 Hz, 2H), 2.70 (s, 3H), 1.84 – 1.78 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.9, 141.7, 139.3, 137.6, 131.8, 130.0, 128.2, 127.8, 127.4, 117.6, 110.2, 64.8, 64.1, 35.0; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{17}N_2O$: 253.1335, Found: 253.1336.

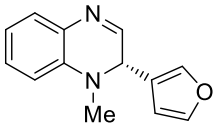




4p

(2S)-1-methyl-2-(thiophen-3-yl)-1,2-dihydroquinoxaline (4p)

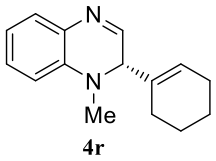
Dihydroquinoxaline **4p** (yellow-brown oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 3-thienylboronic acid (63.98 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 78% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 28.3 mg (62%); **ee** 88% (See reduced compound **7b** for HPLC separation conditions) **TLC:** R*f* = 0.24 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$: +453° (*c* 0.00352 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, J = 3.6 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.17 – 7.10 (m, 2H), 6.93 (dd, J = 5.0, 1.3 Hz, 1H), 6.75 (td, J = 7.5, 1.2 Hz, 1H), 6.55 (dd, J = 8.1, 1.3 Hz, 1H), 5.03 (d, J = 3.5 Hz, 1H), 2.76 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.5, 139.3, 138.5, 132.7, 129.7, 128.2, 127.1, 126.6, 123.0, 117.9, 110.8, 59.1, 35.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{13}N_2{}^{32}S$: 229.0794, Found: 229.0791.



4q

(2S)-2-(Furan-3-yl)-1-methyl-1,2-dihydroquinoxaline (4q)

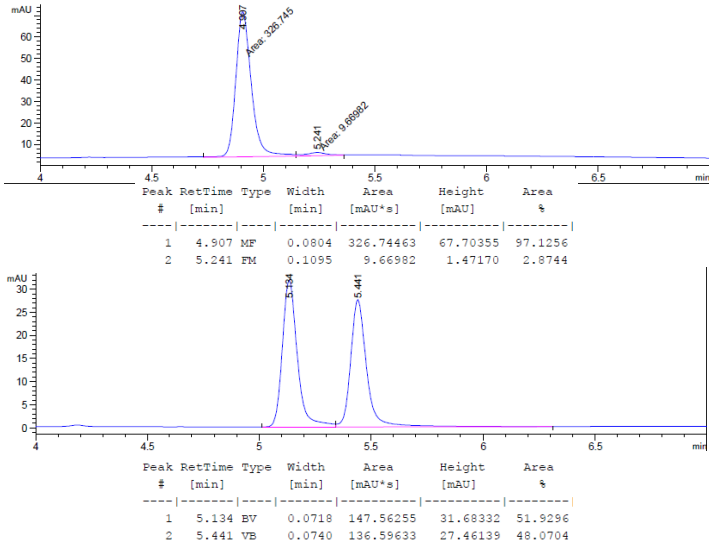
Dihydroquinoxaline **4q** (orange oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 3-furanylboronic acid (55.9 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 66% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 28.0 mg (66%); **ee** 76% (See reduced compound **S11** for HPLC separation conditions); **TLC:** R*f* = 0.21 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$: +191° (*c* 0.00283 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, J = 3.6 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.29 (dd, J = 7.6, 1.6 Hz, 1H), 7.13 (ddd, J = 8.8, 7.6, 1.6 Hz, 1H), 6.77 (td, J = 7.5, 1.2 Hz, 1H), 6.57 (dd, J = 8.1, 1.2 Hz, 1H), 6.20 (dd, J = 1.8, 0.9 Hz, 1H), 4.85 (d, J = 3.6 Hz, 1H), 2.77 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.2, 144.0, 140.2, 139.4, 133.0, 129.6, 128.1, 121.2, 118.2, 111.2, 109.6, 54.8, 34.9; **HRMS:** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{13}N_2O$: 213.1022, Found: 213.1020.

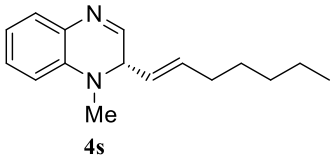


4r

(2S)-2-(Cyclohex-1-en-1-yl)-1-methyl-1,2-dihydroquinoxaline (4r)

Dihydroquinoxaline **4r** (yellow oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and cyclohex-1-enylboronic acid (62.98 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 69% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 15.4 mg (34%); **ee:** 94% (Chiral-CD, MeCN/water gradient 30/70 to 70/30 - 10 minutes, 70/30 to 95/5 – 5 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 4.9 min (major), 5.2 min (minor); **TLC:** R*f* = 0.35 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +463° (*c* 0.00326 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 2H), 7.16 (dd, J = 7.5, 1.6 Hz, 1H), 7.06 (td, J = 7.7, 1.6 Hz, 1H), 6.63 (td, J = 7.5, 1.3 Hz, 1H), 6.48 (dd, J = 8.1, 1.2 Hz, 1H), 5.70 – 5.64 (m, 1H), 4.36 (d, J = 3.2 Hz, 1H), 2.68 (s, 3H), 2.13 – 2.01 (m, 2H), 1.95 – 1.79 (m, 2H), 1.65 – 1.51 (m, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.8, 140.1, 135.6, 131.9, 129.6, 128.2, 125.9, 116.9, 109.3, 67.3, 34.1, 25.3, 24.5, 22.5, 22.3; **HRMS:** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2$: 227.1542, Found: 227.1542.

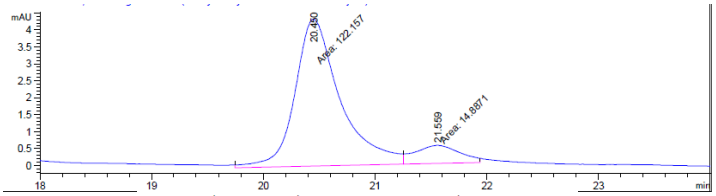




4s

(2S)-2-[(1E)-hept-1-en-1-yl]-1-methyl-1,2-dihydroquinoxaline (4s)

Dihydroquinoxaline **4s** (yellow oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and trans-1-heptenylboronic acid (71.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 48% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 23.3 mg (48%); **ee:** 78% (Chiral-CD, MeCN/water gradient 20/80 to 30/70 - 60 minutes, 30/70 to 95/5 – 5 minutes, flow rate = 0.150 mL/min, I = 254 nm) tR = 20.5 min (major), 21.6 min (minor); **TLC:** R*f* = 0.34 (15/85 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +208° (*c* 0.00375 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, J = 3.6 Hz, 1H), 7.22 (dd, J = 7.6, 1.6 Hz, 1H), 7.11 (td, J = 7.7, 1.6 Hz, 1H), 6.71 (td, J = 7.5, 1.2 Hz, 1H), 6.54 (dd, J = 8.1, 1.2 Hz, 1H), 5.69 (dt, J = 15.3, 6.7 Hz, 1H), 5.46 (ddt, J = 15.3, 8.7, 1.5 Hz, 1H), 4.23 (dd, J = 8.7, 3.6 Hz, 1H), 2.76 (s, 3H), 2.05 – 1.97 (m, 2H), 1.40 – 1.18 (m, 6H), 0.87 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.4, 139.6, 135.8, 132.8, 129.3, 128.0, 123.8, 117.6, 110.8, 62.3, 34.6, 32.2, 31.4, 28.8, 22.6, 14.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{23}N_2$: 243.1855, Found: 243.1856.



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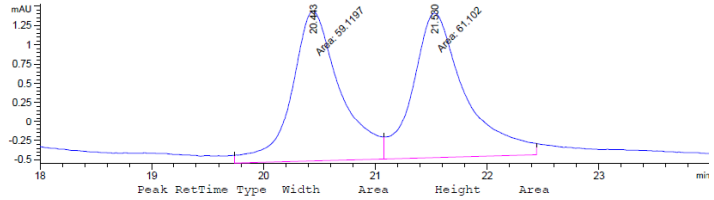

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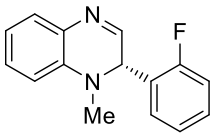
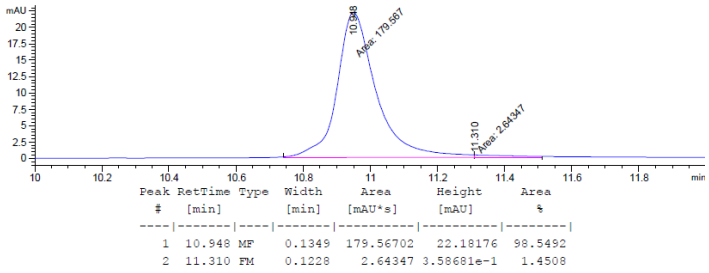
2	21.530	FM	0.5411	61.10203	1.88219	50.8245



4t

(2S)-2-(2-Fluorophenyl)-1-methyl-1,2-dihydroquinoxaline (4t)

Dihydroquinoxaline **4t** (yellow-brown semi-solid) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 2-fluorophenylboronic acid (70.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 30% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 9.13 mg (19%); **ee:** >99% (Chiral-CD, MeCN/water gradient 10/90 to 30/70 - 10 minutes, 30/70 to 95/5 – 5 minutes, flow rate = 0.750 mL/min, I = 254 nm) tR = 10.9 min (major), 11.3 min (minor); **TLC:** R*f* = 0.22 (10/90 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +642° (*c* 0.00125 g/mL, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.54 (d, J = 3.6 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.21 (td, J = 7.6, 1.8 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.11 – 7.02 (m, 2H), 6.77 – 6.71 (m, 1H), 6.58 (d, J = 8.0 Hz, 1H), 5.45 (d, J = 3.7 Hz, 1H), 2.79 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.0, 158.1, 153.2, 139.3, 132.1, 130.2 (d, J = 8 Hz), 129.9, 129.1 (d, J = 4 Hz), 128.4, 126.0 – 123.8 (m), 117.8, 115.9 (d, J = 22 Hz), 110.4, 56.6 (d, J = 3 Hz), 35.2; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -119.78; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{14}FN_2$: 241.1135, Found: 241.1133.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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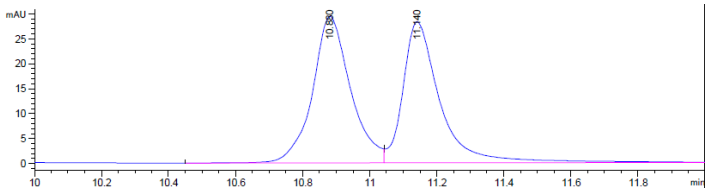
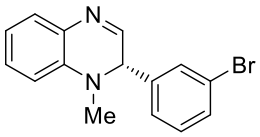
2	11.310	FM	0.1228	2.64347	3.58681e-1	1.4508



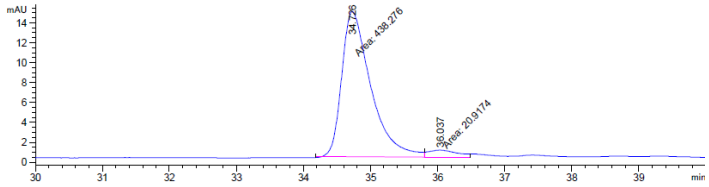
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.880	BV	0.1171	232.50635	29.38496	51.1945
2	11.140	VB	0.1146	221.65669	28.31454	48.8055



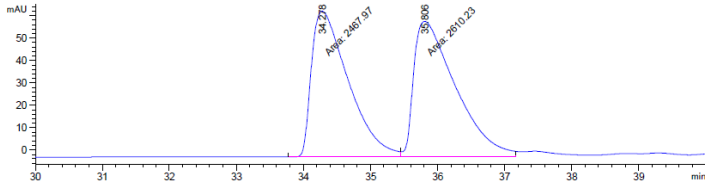
4u

(2S)-2-(3-Bromophenyl)-1-methyl-1,2-dihydroquinoxaline (4u)

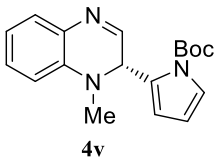
Dihydroquinoxaline **4u** (orange oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and 3-bromophenylboronic acid (100 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 33% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 19.9 mg (33%); **ee:** 90% (Chiral-CD, MeCN/water gradient 10/90 to 30/70 - 60 minutes, 30/70 to 95/5 – 10 minutes, flow rate = 0.500 mL/min, I = 254 nm) tR = 34.7 min (major), 36.0 min (minor); **TLC:** R*f* = 0.30 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +383° (*c* 0.00254 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.41 (t, J = 1.4 Hz, 1H), 7.26 (dd, J = 7.6, 1.6 Hz, 1H), 7.22 – 7.19 (m, 2H), 7.14 (td, J = 7.8, 1.6 Hz, 1H), 6.74 (td, J = 7.5, 1.3 Hz, 1H), 6.57 (dd, J = 8.1, 1.2 Hz, 1H), 4.98 (d, J = 3.3 Hz, 1H), 2.72 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.9, 140.8, 139.0, 131.8, 131.8, 130.9, 130.1, 130.1, 128.5, 125.9, 123.4, 117.9, 110.3, 64.0, 35.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{14}{}^{79}BrN_2$: 301.0334, Found: 301.0335.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.726	MF	0.5016	438.27582	14.56134	95.4447
2	36.037	FM	0.5061	20.91745	6.88882e-1	4.5553



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.278	MF	0.6337	2467.97339	64.90430	48.5993
2	35.806	FM	0.7209	2610.23267	60.34596	51.4007

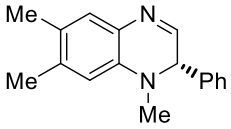


4v

(2S)-2-(Furan-3-yl)-1-methyl-1,2-dihydroquinoxaline (4v)

Dihydroquinoxaline **4v** (yellow oil) was synthesized using quinoxalinium salt **3** (58.8 mg, 0.200 mmol, 1.00 equiv.) and *N*-Boc-2-pyrroleboronic acid (106 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 77% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 46.1 mg (74%); **ee** 2% (See reduced compound **S12** for HPLC separation conditions) **TLC:** R*f* = 0.50 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$: +26° (*c* 0.00225 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, J = 3.9 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.20 – 7.13 (m, 2H), 6.74 (td, J = 7.5, 1.2 Hz, 1H), 6.64 (dd, J = 8.1, 1.2 Hz, 1H), 5.97 (t, J = 3.4 Hz, 1H), 5.91 – 5.86 (m, 1H), 5.79 (d, J = 3.9 Hz, 1H), 2.92 (s, 3H), 1.63 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.8, 149.4, 139.6, 132.7, 130.6, 129.5, 128.0, 122.2, 117.6, 113.3, 110.8, 110.5, 84.5, 56.2, 35.8, 28.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{22}N_3O_2$: 312.1706, Found: 312.1704.

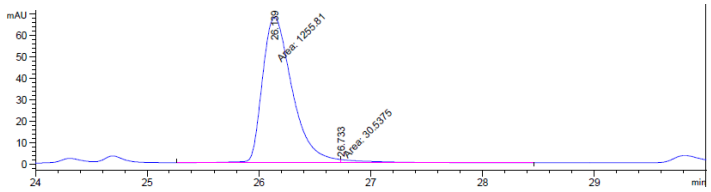
E. Asymmetric Synthesis of Dihydroquinoxalines (Quinoxaline Derivative Scope)



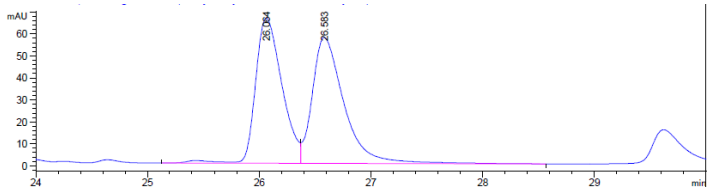
6a

(2S)-1,6,7-Trimethyl-2-phenyl-1,2-dihydroquinoxaline (6a)

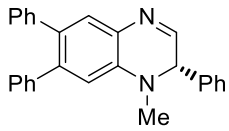
Dihydroquinoxaline **6a** (yellow-orange solid) was synthesized using quinoxalinium salt **5a** (64.5 mg, 0.200 mmol, 1.00 equiv.) and phenylboronic acid (61.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 40% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 20.0 mg (40%); **ee:** 96% (Chiral-CD, MeCN/water gradient 10/90 to 50/50 - 16 minutes, 50/50 to 77/33 – 24 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 26.1 min (major), 26.7 min (minor); **TLC:** R*f* = 0.26 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +498° (*c* 0.00234 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, J = 3.4 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.28 – 7.24 (m, 2H), 7.03 (s, 1H), 6.36 (s, 1H), 4.91 (d, J = 3.3 Hz, 1H), 2.68 (s, 3H), 2.22 (s, 3H), 2.18 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.2, 138.6, 138.1, 137.2, 130.3, 129.3, 129.1, 128.6, 127.3, 125.3, 111.7, 64.4, 35.1, 20.3, 18.7; **HRMS** (ESI) *m/z* $[M+H]^+$ Calcd for $C_{17}H_{19}N_2$: 251.1542, Found: 251.1543.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.139	MF	0.3084	1255.80933	67.86665	97.6260
2	26.733	FM	0.3304	30.53748	1.54041	2.3740



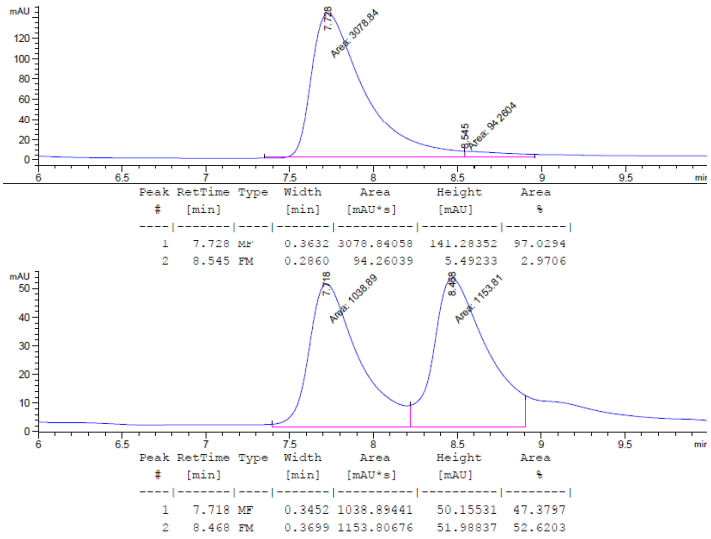
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.064	VV R	0.2533	1087.44104	66.02066	49.0860
2	26.583	VB	0.2954	1127.93933	57.23740	50.9140

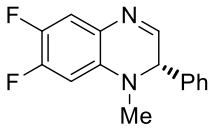


6b

(2S)-6,7-diphenyl-1-methyl-2-phenyl-1,2-dihydroquinoxaline (6b)

Dihydroquinoxaline **6b** (bright yellow solid) was synthesized using quinoxalinium salt **5b** (89.3 mg, 0.200 mmol, 1.00 equiv.) and phenylboronic acid (61.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 55% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 41.2 mg (55%); **ee:** 94% (Chiral-CD, MeCN/water gradient 26/78 to 28/72 - 10 minutes, 28/72 to 95/5 – 5 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 7.7 min (major), 8.5 min (minor); **TLC:** R*f* = 0.37 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: +306° (*c* 0.00295 g/mL, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 (d, J = 3.2 Hz, 1H), 7.42 – 7.33 (m, 6H), 7.25 – 7.10 (m, 9H), 6.58 (s, 1H), 5.06 (d, J = 3.2 Hz, 1H), 2.76 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.4, 142.0, 141.9, 141.2, 138.6, 138.4, 131.3, 130.4, 130.0, 130.0, 129.9, 129.3, 128.8, 128.0, 127.9, 127.4, 126.7, 125.9, 112.4, 64.6, 35.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{23}N_2$: 375.1855, Found: 375.1854.



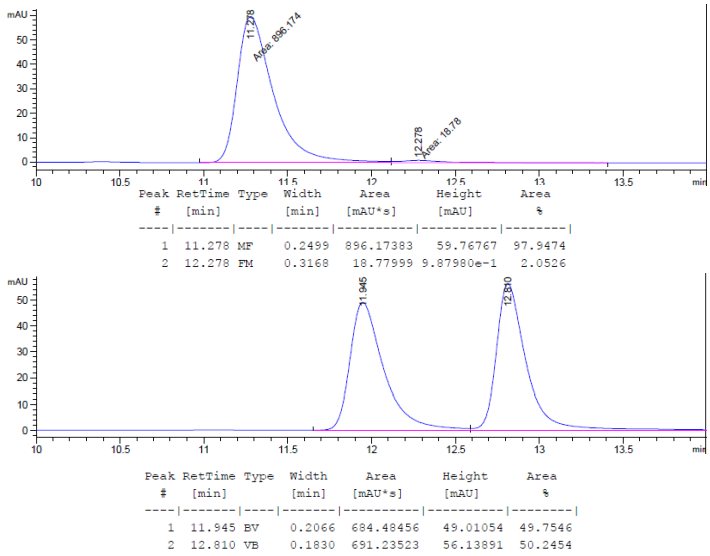


6c

(2S)-6,7-difluoro-1-methyl-2-phenyl-1,2-dihydroquinoxaline (6c)

Dihydroquinoxaline **6c** (off-white crystalline solid) was synthesized using quinoxalinium salt **5c** (66.0 mg, 0.200 mmol, 1.00 equiv.) and phenylboronic acid (61.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 43% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 20.7 mg (40%); **ee:** 96% (Chiral-CD, MeCN/water gradient 20/80 to 30/70 - 12 minutes, 30/70 to 95/5 – 5 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 11.3 min (major), 12.3 min (minor); **TLC:** R*f* = 0.36 (20/80 EtOAc/Hexanes); $[\alpha]_D^{20}$: +516° (*c* 0.00247 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, J = 3.4 Hz, 1H), 7.35 (ddd, J = 5.0, 3.8, 2.2 Hz, 3H), 7.25 – 7.20 (m, 2H), 7.11 (dd, J = 10.6, 8.5 Hz, 1H), 6.31 (dd, J = 12.4, 7.1 Hz, 1H), 4.94 (d, J = 3.4 Hz, 1H), 2.67 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.4 (d, J = 3 Hz), 150.8 (dd, J = 246.4, 13 Hz), 142.5 (dd, J = 237, 14 Hz), 137.7, 136.5 (dd, J = 9.3, 2 Hz), 129.4, 129.0, 127.9 (dd, J = 8, 3 Hz), 127.2, 116.9 (dd, J = 19, 2 Hz), 99.0 (d, J = 23 Hz), 63.6, 35.3; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -136.1 (ddd, J = 21.6, 12.5, 8.6 Hz), -153.3 (ddd, J = 22.0, 10.5, 6.9 Hz); **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{13}F_2N_2$: 259.1041, Found: 259.1042; **Melting Point** 76.0-80.0 °C.

Single crystals suitable for **X-Ray** analysis were obtained by vapor diffusion recrystallization from a solution of **6c** in a mixture of diethyl ether and *n*-heptane. CCDC registry number 2237394.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.278	MF	0.2499	896.17383	59.76767	97.9474
2	12.278	FM	0.3168	18.77999	9.87980e-1	2.0526

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.945	BV	0.2066	684.48456	49.01054	49.7546
2	12.810	VB	0.1830	691.23523	56.13891	50.2454

Figure S2. Thermal ellipsoid plot of the X-ray crystallographic structure of **6c** (CCDC: 2237394) with an ellipsoid contour probability level of 50%.

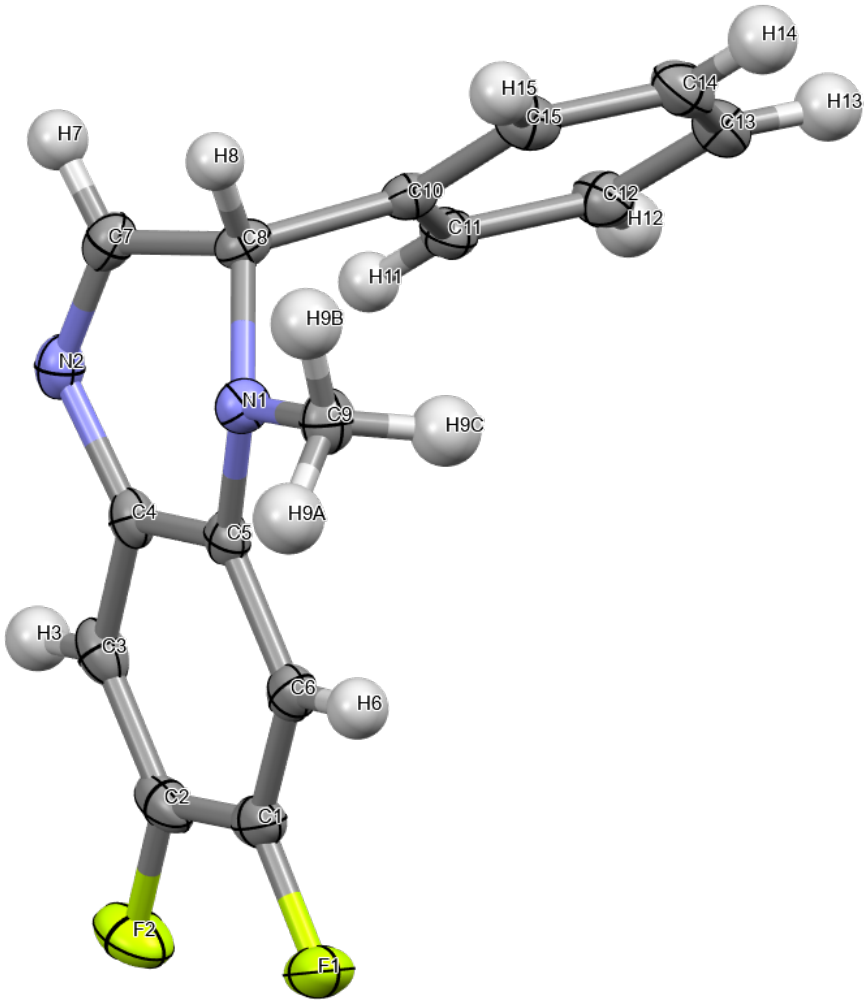
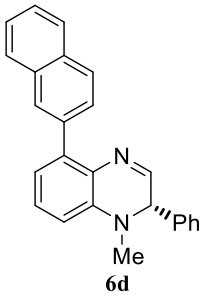


Table S2. Crystallographic data acquisition and analysis parameters used to collect the structure of **6c** (CCDC: 2237394).

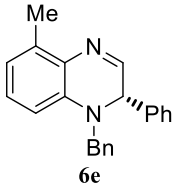
Chemical formula	$C_{15}H_{12}F_2N_2$	
Formula weight	258.27 g/mol	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal size	0.040 x 0.080 x 0.160 mm	
Crystal system	orthohombric	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.3491(2) Å	α = 90°
	b = 10.4486(4) Å	β = 90°
	c = 21.5259(9) Å	γ = 90°
Volume	1203.10(8) $Å^3$	
Z	4	
Density (calculated)	1.426 g/cm^3	
Absorption coefficient	0.897 mm^{-1}	
F(000)	536	
Diffractometer	Bruker D8 VENTURE κ-geometry	
Radiation source	Incoatec IμS DIAMOND microfocus	
Theta range for data collection	4.11 to 74.36°	
Index ranges	-5<=h<=6, -12<=k<=10, -26<=l<=25	
Reflections collected	11770	
Independent reflections	2413 [R(int) = 0.0278]	
Coverage of independent reflections	99.30%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9650 and 0.8700	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2413 / 0 / 173	
Goodness-of-fit on F^2	1.052	
Final R indices (2686 data; I>2σ(I))	R1 = 0.0237, wR2 = 0.0640	
Final R indices (all data)	R1 = 0.0240, wR2 = 0.0645	
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0349P)^2+0.1976P]$	
	where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.03(2)	
Largest diff. peak and hole	0.168 and -0.129 $eÅ^{-3}$	
R.M.S. deviation from mean	0.030 $eÅ^{-3}$	



6d

(2S)-1-Methyl-5-(naphthalen-2-yl)-2-phenyl-1,2-dihydroquinoxaline (6d)

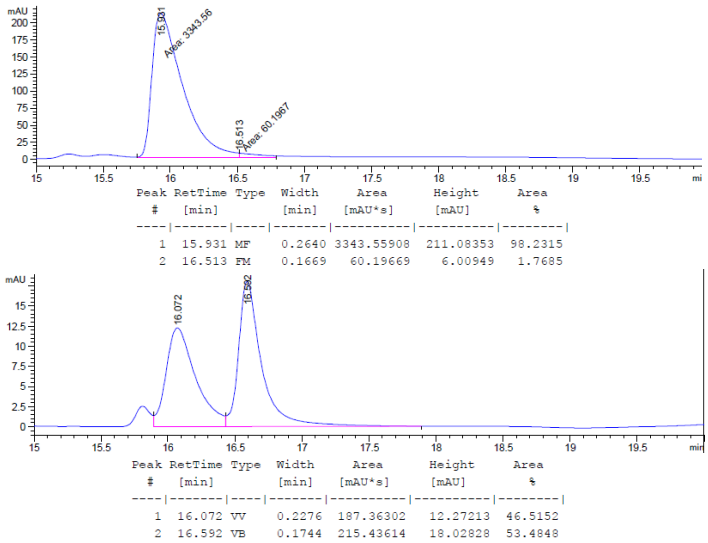
Dihydroquinoxaline **6d** (yellow solid) was synthesized using quinoxalinium salt **5d** (84.1 mg, 0.200 mmol, 1.00 equiv.) and phenylboronic acid (61.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 63% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 43.9 mg (63%); **ee:** 96% (See reduced compound **S13** for HPLC separation conditions); **TLC:** R*f* = 0.13 (10/90 EtOAc/Hexanes); $[\alpha]_D^{20}$: +26° (*c* 0.00271 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.91 – 7.80 (m, 3H), 7.63 (dd, J = 8.4, 1.8 Hz, 1H), 7.54 (d, J = 3.5 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.40 – 7.29 (m, 5H), 7.23 (t, J = 7.8 Hz, 1H), 6.89 (d, J = 7.7 Hz, 1H), 6.65 (d, J = 8.1 Hz, 1H), 4.98 (d, J = 3.5 Hz, 1H), 2.83 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.8, 140.1, 139.8, 138.6, 137.7, 133.4, 132.7, 129.6, 129.3, 129.2, 129.2, 128.8, 128.7, 128.3, 127.7, 127.2, 127.0, 125.9, 125.8, 119.7, 109.9, 63.7, 35.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{21}N_2$: 349.1699, Found: 349.1699.

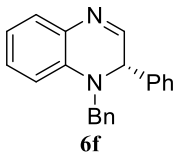


6e

(2S)-1-Benzyl-5-methyl-2-phenyl-1,2-dihydroquinoxaline (6e)

Dihydroquinoxaline **6e** (yellow oil) was synthesized using quinoxalinium salt **5e** (76.9 mg, 0.200 mmol, 1.00 equiv.) and phenylboronic acid (61.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **qNMR Yield**: 61% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 30.6 mg (49%); **ee:** 96% (Chiral-CD, MeCN/water gradient 10/90 to 30/70 - 15 minutes, 30/70 to 95/5 – 5 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 15.9 min (major), 16.5 min (minor); **TLC:** R*f* = 0.26 (5/95 EtOAc/Hexanes); $[\alpha]_D^{20}$: +636° (*c* 0.00281 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, J = 3.6 Hz, 1H), 7.35 – 7.18 (m, 10H), 6.94 (t, J = 7.9 Hz, 1H), 6.60 (d, J = 7.5 Hz, 1H), 6.47 (d, J = 8.1 Hz, 1H), 5.02 (d, J = 3.6 Hz, 1H), 4.60 (d, J = 16.1 Hz, 1H), 4.06 (d, J = 16.1 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.1, 138.9, 138.7, 136.9, 136.5, 130.7, 129.2, 128.9, 128.8, 128.6, 127.4, 127.3, 119.8, 109.1, 61.5, 51.1, 17.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{21}N_2$: 313.1699, Found: 313.1699.





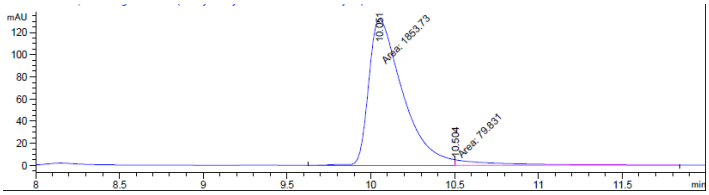
6f

(2S)-1-benzyl-2-phenyl-1,2-dihydroquinoxaline (6f)

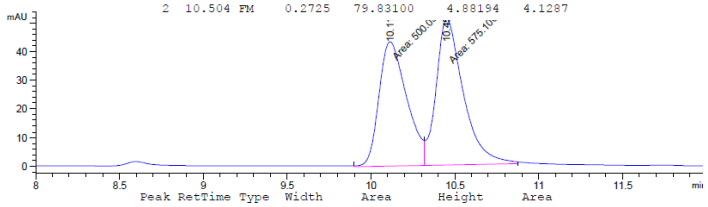
Dihydroquinoxaline **6f** (yellow oil) was synthesized using one of three quinoxalinium salts **5f** (74.1 mg, 0.200 mmol, 1.00 equiv.), or **5g** (73.3 mg, 0.200 mmol, 1.00 equiv.) or **5h** (60.2 mg, 0.200 mmol, 1.00 equiv.) and phenylboronic acid (61.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. **TLC:** R*f* = 0.31 (20/80 EtOAc/Hexanes); $[\alpha]_D^{20}$: +609° (*c* 0.00316 g/mL, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, J = 3.5 Hz, 1H), 7.40 – 7.20 (m, 11H), 7.05 (td, J = 7.8, 1.7 Hz, 1H), 6.72 (td, J = 7.5, 1.2 Hz, 1H), 6.59 (dd, J = 8.2, 1.2 Hz, 1H), 5.06 (d, J = 3.5 Hz, 1H), 4.59 (d, J = 16.1 Hz, 1H), 4.04 (d, J = 16.1 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.9, 138.8, 136.7, 132.2, 129.8, 129.3, 128.9, 128.8, 128.7, 127.5, 127.4, 127.4, 117.7, 110.9, 62.1, 50.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{19}N_2$: 299.1542, Found: 299.1539.

Yield & ee from **5f**

qNMR Yield: 53% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 28.0 mg (47%); **ee:** 92% (Chiral-CD, MeCN/water gradient 20/80 to 30/70 - 12 minutes, 30/70 to 95/5 – 5 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 11.3 min (major), 12.3 min (minor)



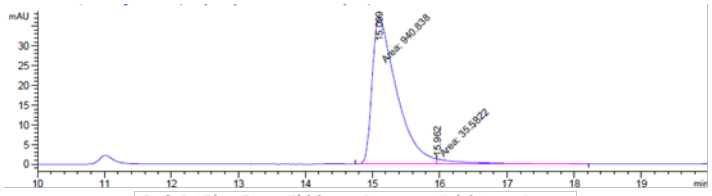
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.051	MF	0.2342	1853.73425	131.94322	95.8713
2	10.504	FM	0.2725	79.83100	4.88194	4.1287



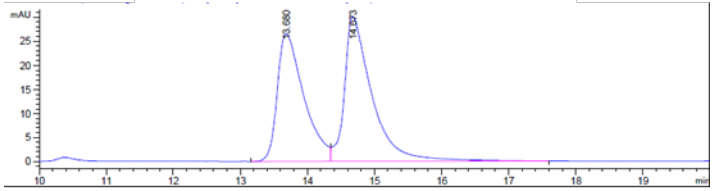
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.112	MF	0.1922	500.05023	43.36677	46.5096
2	10.450	FM	0.1877	575.10571	51.06128	53.4904

Yield & ee from **5g**

qNMR Yield: 55% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 32.8 mg (55%); **ee:** 92% (Chiral-CD, MeCN/water gradient 20/80 to 30/70 - 60 minutes, 30/70 to 95/5 – 5 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 15.1 min (major), 16.0 min (minor)



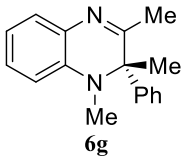
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.099	MF	0.4246	940.83795	36.92711	96.3559
2	15.962	FM	0.4600	35.58219	1.28929	3.6441



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.690	BV	0.4117	730.64008	26.51987	46.0500
2	14.673	VB	0.4084	855.98315	30.01667	53.9500

Yield from **5h**

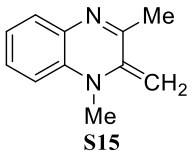
qNMR Yield: 7% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 4.18 mg (7%) ; **ee**: n/a



6g

(2S)-1,2,3-trimethyl-2-phenyl-1,2-dihydroquinoxaline (6g)

The synthesis of dihydroquinoxaline **6g** was attempted using quinoxalinium salt **S7** (64.5 mg, 0.200 mmol, 1.00 equiv.) and phenylboronic acid (61.0 mg, 0.500 mmol, 2.50 equiv.) according to the **general procedure** above. Analysis of the crude reaction mixture found that an elimination product (**S15**) of the starting material was obtained in an NMR yield of 95% (1,3,5-trimethoxybenzene as the internal standard).

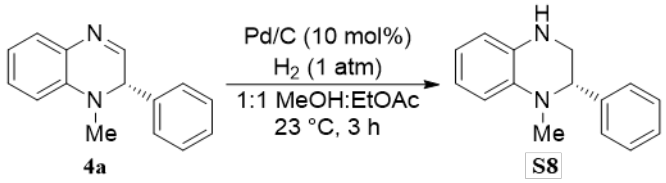


S15

1,3-dimethyl-2-methylidene-1,2-dihydroquinoxaline (S15)

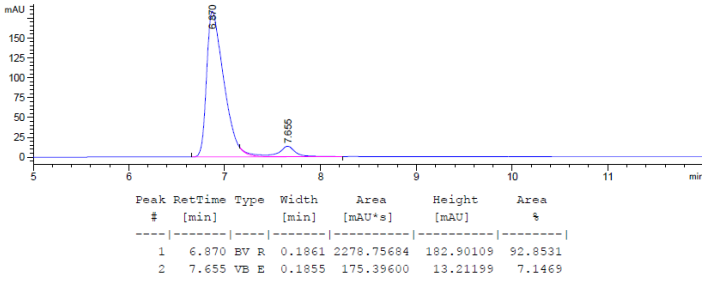
Compound **S15** was confirmed by isolation and characterization of the elimination product as a dark red oil. **Yield:** 23.6 mg (69%); **TLC:** R_f = 0.07 (20/80EtOAc/Hexanes); **^{1}H NMR** (500 MHz, C_6D_6) δ 7.69 (dd, J = 7.7, 1.6 Hz, 1H), 6.97 (ddd, J = 8.5, 7.4, 1.7 Hz, 1H), 6.78 (td, J = 7.5, 1.2 Hz, 1H), 6.35 (dd, J = 8.1, 1.2 Hz, 1H), 4.09 (d, J = 2.1 Hz, 1H), 3.68 (d, J = 2.1 Hz, 1H), 2.40 (s, 3H), 2.16 (s, 3H); **^{13}C NMR** (126 MHz, C_6D_6) δ 158.6, 140.8, 135.5, 134.1, 129.1, 128.6, 120.1, 110.8, 82.7, 31.8, 23.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{13}N_2$: 173.1073, Found: 173.1073.

F. Synthesis of Tetrahydroquinoxalines (Dihydroquinoxaline Functionalization Scope)

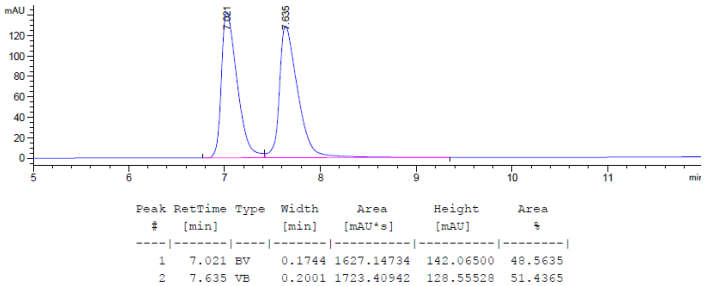


(2S)-1-Methyl-2-phenyl-1,2,3,4-tetrahydroquinoxaline (S8)

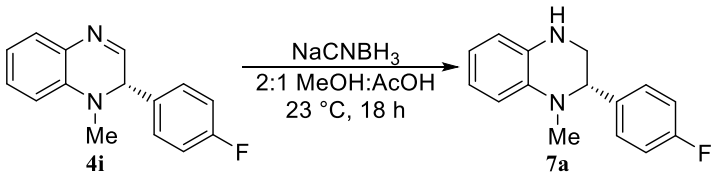
A 20 mL vial with a magnetic stir bar was charged with **4a** (11.4 mg, 0.0510 mmol, 1.00 equiv.), 5% Pd/C (10.9 mg, 0.00510 mmol, 0.100 equiv.), EtOAc (1.00 mL) and methanol (1.00 mL). The vial was sealed with a 14/20 rubber septum, which was further sealed with parafilm and electrical tape. The reaction mixture was degassed with H_2 (1.00 atm) for 10 minutes and then let stir at ambient temperature, under H_2 (1.00 atm) for 3 hours. After 3 hours, the reaction mixture was filtered over a plug of Al_2O_3 and Na_2SO_4. The resulting filtrate was purified via isocratic column chromatography on silica gel to yield **S8** as a green oil. **Yield** 4.80 mg (42%); **ee**: 86% (Chiral-CD, MeCN/water (0.1% formic acid) gradient 10/90 to 20/80 - 10 minutes, 20/80 to 95/5 – 5 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 6.9 min (major), 7.7 min (minor); **TLC:** R_f = 0.35 (15/85 EtOAc/Hexanes); $[\alpha]_D^{20}$**:** -19° (*c* 0.00160 g/mL, $CDCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.29 – 7.20 (m, 3H), 6.82 – 6.75 (m, 1H), 6.67 (dd, J = 8.1, 1.3 Hz, 1H), 6.61 (td, J = 7.4, 1.3 Hz, 1H), 6.56 (dd, J = 7.6, 1.6 Hz, 1H), 4.43 (t, J = 4.2 Hz, 1H), 3.69 (s, 1H), 3.57 (dd, J = 11.1, 3.6 Hz, 1H), 3.33 (dd, J = 11.1, 4.8 Hz, 1H), 2.81 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.3, 136.8, 133.8, 128.6, 127.5, 127.1, 119.9, 117.2, 114.3, 111.0, 62.8, 48.1, 37.3; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{17}N_2$: 225.1386, Found: 225.1376.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.870	BV R	0.1861	2278.75684	182.90109	92.8531
2	7.655	VB E	0.1855	175.39600	13.21199	7.1469

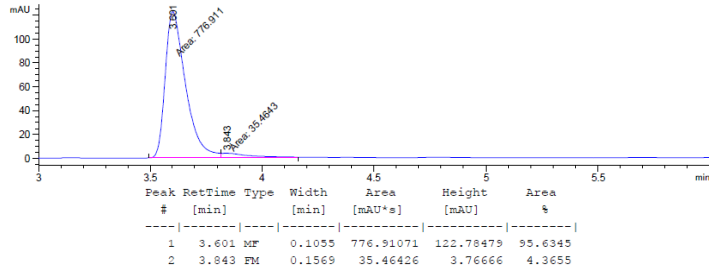


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.021	BV	0.1744	1627.14734	142.06500	48.5635
2	7.635	VB	0.2001	1723.40942	128.55528	51.4365

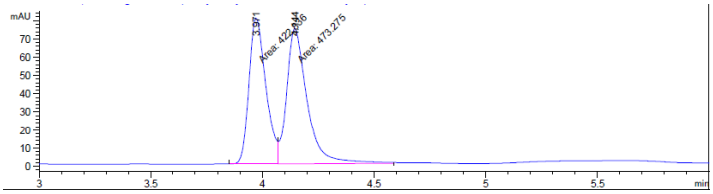


(2S)-2-(4-Fluorophenyl)-1-methyl-1,2,3,4-tetrahydroquinoxaline (7a)

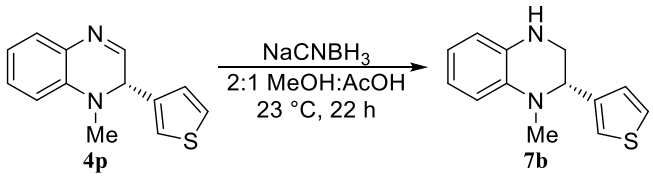
A 20 mL vial was charged with **4i** (36.0 mg, 0.150 mmol, 1.00 equiv.), $NaCNBH_3$ (11.3 mg, 0.180 mmol, 1.20 equiv.) and a magnetic stir bar. Methanol (1.50 mL) and AcOH (0.750 mL) were added to the vial in succession. The reaction mixture was allowed to stir at room temperature for 18 hours. The reaction mixture was cooled to 0 °C in an ice bath and quenched by slow addition of sat. $NaHCO_3$ (6.0 mL). The resulting reaction mixture was extracted with DCM (3x3.00 mL) and the organic layer was dried with Na_2SO_4 which was removed by filtration. The filtrate was concentrated under reduced pressure and purified via isocratic flash column chromatography with silica gel to afford **7a** as a grey crystalline solid. **Yield:** 25.1 mg (69%); **ee**: 92% (Chiral-CD, MeCN/water (0.1% formic acid) gradient 10/90 to 15/85 - 10 minutes, 15/85 to 95/5 – 5 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 3.6 min (major), 3.8 min (minor); **TLC:** R*f* = 0.35 (15/85 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$: -36° (*c* 0.00507 g/mL, MeCN); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 2H), 7.00 (t, J = 8.7 Hz, 2H), 6.81 – 6.74 (m, 1H), 6.68 – 6.53 (m, 3H), 4.41 (t, J = 4.1 Hz, 1H), 3.70 (s, 1H), 3.56 (dd, J = 11.0, 3.6 Hz, 1H), 3.28 (dd, J = 11.1, 4.6 Hz, 1H), 2.79 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.2, 161.3, 138.0, 136.4, 133.7, 128.6 (d, J = 8.1 Hz), 117.4, 115.6 (d, J = 1114.2 Hz), 115.4 (d, J = 21.3 Hz), 114.2, 62.2, 48.0, 37.3; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.5; **HRMS:**(ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{16}FN_2$: 243.1292, Found: 243.1282.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.601	MF	0.1055	776.91071	122.78479	95.6345
2	3.843	FM	0.1569	35.46426	3.76666	4.3655

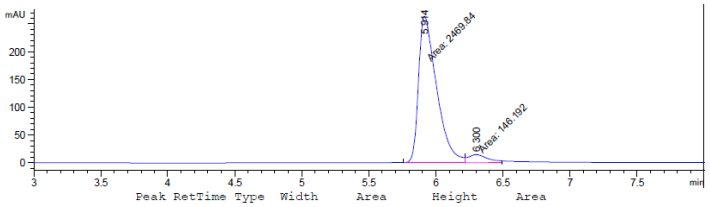


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.971	MF	0.0879	422.83594	80.19186	47.1857
2	4.144	FM	0.1060	473.27484	74.42779	52.8143

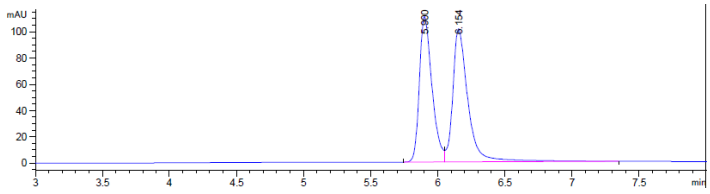


(2S)-1-Methyl-2-(thiophen-3-yl)-1,2,3,4-tetrahydroquinoxaline (7b)

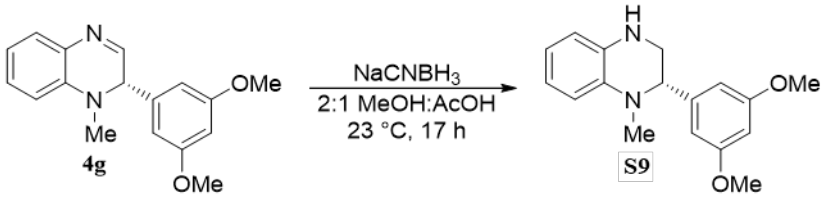
A 10 mL pear flask was charged with **4p** (45.7 mg, 0.2 mmol, 1.00 equiv.), $NaCNBH_3$ (15.1 mg, 0.240 mmol, 1.20 equiv.) and a magnetic stir bar. Methanol (1.50 ml) and AcOH (0.750 mL) were added to the flask in succession. The reaction mixture was allowed to stir at room temperature for 22 hours. The reaction mixture was cooled to 0 °C in an ice bath and quenched by slow addition of sat. $NaHCO_3$ (6.0 mL). The resulting reaction mixture was extracted with DCM (2 x 4.00 mL) and the organic layer was dried with Na_2SO_4 which was removed by filtration. The filtrate was concentrated under reduced pressure and purified via isocratic flash column chromatography with silica gel to afford **7b** as a white solid. **Yield:** 31.8 mg (69%); **ee**: 88% (Chiral-CD, MeCN/water (0.1% formic acid) gradient 10/90 to 10/90 - 10 minutes, 10/90 to 95/5 – 3 minutes, flow rate = 0.75 mL/min, I = 254 nm) tR = 5.9 min (major), 6.3 min (minor); **TLC:** R_f = 0.34 (15/85 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$**:** -19° (*c* 0.00160 g/mL $CDCl_3$); **^{1}H NMR** (500 MHz, C_6D_6) δ 6.88 (td, J = 7.6, 1.5 Hz, 1H), 6.84 – 6.74 (m, 3H), 6.72 (dd, J = 3.0, 1.3 Hz, 1H), 6.57 (dd, J = 7.9, 1.4 Hz, 1H), 6.37 (dd, J = 7.6, 1.5 Hz, 1H), 3.99 (t, J = 3.8 Hz, 1H), 3.13 (dd, J = 10.9, 3.5 Hz, 1H), 2.88 – 2.77 (m, 2H), 2.48 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.0, 136.0, 133.6, 126.8, 125.8, 121.7, 119.7, 117.6, 114.1, 111.5, 58.3, 47.2, 37.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{15}{}^{32}SN_2$: 231.0950, Found: 231.0946.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.914	MF	0.1562	2469.83740	263.49899	94.4117
2	6.300	FM	0.1690	146.19200	14.41971	5.5883

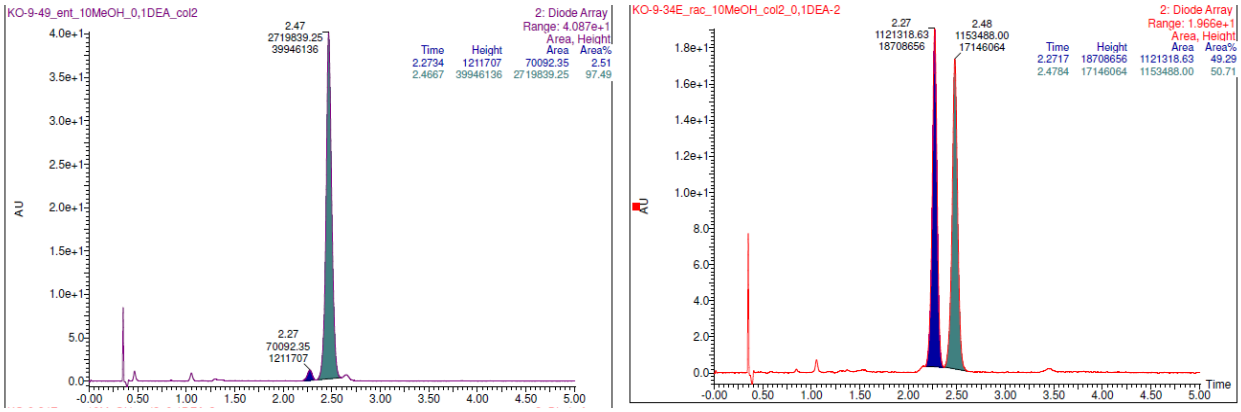


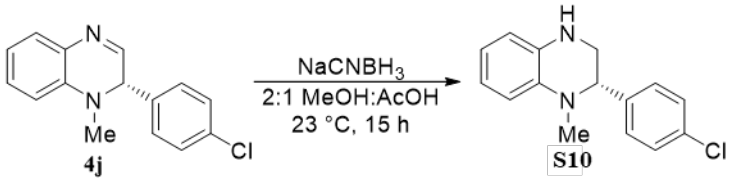
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.900	BV	0.0979	722.67242	110.81659	47.4674
2	6.154	VB	0.1154	799.78802	101.36273	52.5326



(2S)-2-(3,5-Dimethoxyphenyl)-1-methyl-1,2,3,4-tetrahydroquinoxaline (S9)

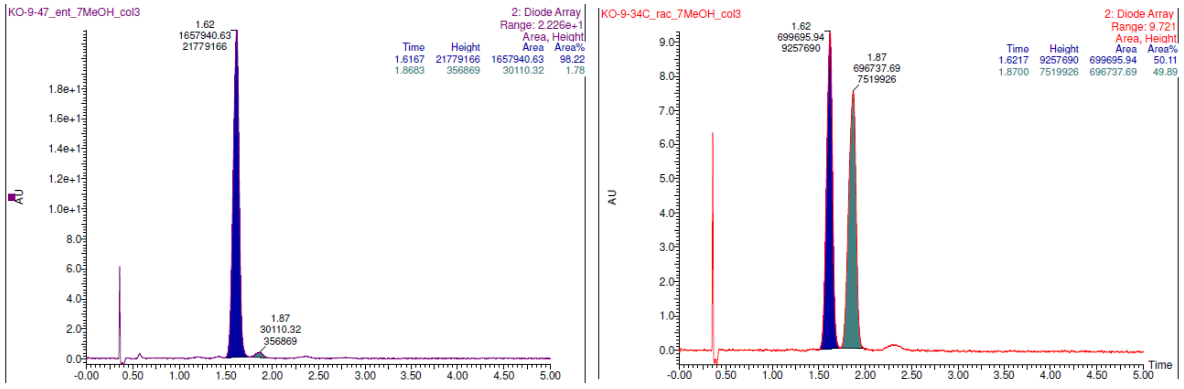
A 20 mL vial was charged with **4g** (35.5 mg, 0.126 mmol, 1.00 equiv.), $NaCNBH_3$ (9.49 mg, 0.151 mmol, 1.20 equiv.) and a magnetic stir bar. Methanol (2.00 ml) and AcOH (1.00 mL) were added to the vial in succession. The reaction mixture was allowed to stir at room temperature for 17 hours. The reaction mixture was cooled to 0 °C in an ice bath and quenched by slow addition of sat. $NaHCO_3$ (4.00 mL). The resulting reaction mixture was extracted with DCM (3 x 2.00 mL) and the organic layer was dried with Na_2SO_4 which was removed by filtration. The filtrate was concentrated under reduced pressure and purified via isocratic flash column chromatography with silica gel to afford **S9** as a green oil. **Yield:** 30.1 mg (84%); **ee**: 94% Chiralpak IB-3, MeOH/$scCO_2$ (0.1% diethylamine) isocratic 10/90 to 10/90 - 5 minutes, flow rate = 2.50 mL/min, I = 254 nm) tR = 2.5 min (major), 2.3 min (minor); **TLC:** R_f = 0.42 (20/80 EtOAc/Hexanes); $[\alpha]_D^{20}$**:** -1° (*c* 0.00247 g/mL $CDCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.76 (td, J = 7.6, 1.6 Hz, 1H), 6.67 (d, J = 7.9 Hz, 1H), 6.60 (td, J = 7.4, 1.3 Hz, 1H), 6.55 (dd, J = 7.7, 1.5 Hz, 1H), 6.43 – 6.39 (m, 2H), 6.38 – 6.36 (m, 1H), 4.34 (dd, J = 5.3, 3.6 Hz, 1H), 3.74 (s, 6H), 3.53 (dd, J = 11.1, 3.6 Hz, 1H), 3.36 (dd, J = 11.1, 5.3 Hz, 1H), 2.81 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 144.8, 136.8, 133.8, 119.9, 117.4, 114.4, 111.3, 105.2, 99.2, 63.0, 55.4, 48.2, 37.3; **HRMS** (ESI) *m/z*:$[M+H]^+$ Calcd for $C_{17}H_{21}N_2O_2$: 285.1597, Found: 285.1590.

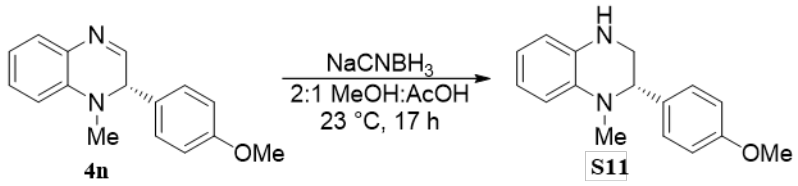




(2S)-2-(4-Chlorophenyl)-1-methyl-1,2,3,4-tetrahydroquinoxaline (S10)

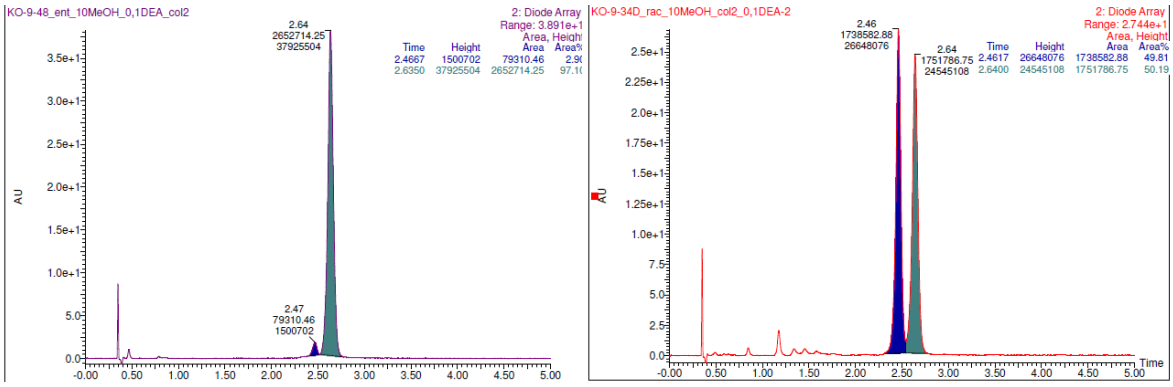
A 20 mL vial was charged with **4j** (30.7 mg, 0.120 mmol, 1.00 equiv.), $NaCNBH_3$ (9.05 mg, 0.144 mmol, 1.20 equiv.) and a magnetic stir bar. Methanol (2.00 ml) and AcOH (1.00 mL) were added to the vial in succession. The reaction mixture was allowed to stir at room temperature for 15 hours. The reaction mixture was cooled to 0 °C in an ice bath and quenched by slow addition of sat. $NaHCO_3$ (4.00 mL). The resulting reaction mixture was extracted with DCM (3 x 2.00 mL) and the organic layer was dried with Na_2SO_4 which was removed by filtration. The filtrate was concentrated under reduced pressure and purified via isocratic flash column chromatography with silica gel to afford **S10** as an off-white solid. **Yield:** 21.8 mg (70%); **ee**: 96% Chiralpak IC-3, MeOH/$scCO_2$ isocratic 7/93 to 7/93 - 5 minutes, flow rate = 2.50 mL/min, I = 254 nm) tR = 1.6 min (major), 1.9 min (minor); **TLC:** R_f = 0.63 (20/80 EtOAc/Hexanes); $[\alpha]_D^{20}$**:** -45° (*c* 0.00230 g/mL $CDCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.20 – 7.14 (m, 2H), 6.79 (td, J = 7.7, 1.6 Hz, 1H), 6.68 – 6.59 (m, 2H), 6.56 (dd, J = 7.6, 1.6 Hz, 1H), 4.41 (t, J = 4.0 Hz, 1H), 3.69 (s, 1H), 3.56 (dd, J = 11.1, 3.6 Hz, 1H), 3.28 (dd, J = 11.1, 4.5 Hz, 1H), 2.80 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.9, 136.3, 133.7, 133.2, 128.8, 128.4, 120.0, 117.4, 114.3, 111.1, 62.3, 47.8, 37.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{16}N_2{}^{35}Cl$: 259.0996, Found: 259.0991.

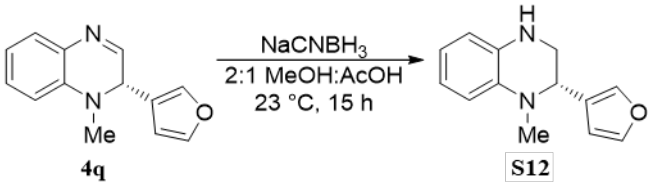




(2S)-2-(4-Methoxyphenyl)-1-methyl-1,2,3,4-tetrahydroquinoxaline (S11)

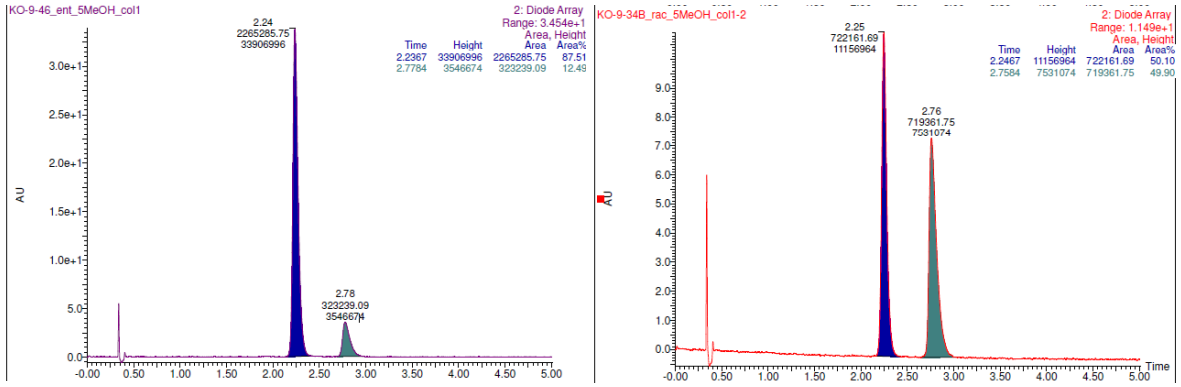
A 20 mL vial was charged with **4n** (26.6 mg, 0.105 mmol, 1.00 equiv.), $NaCNBH_3$ (7.92 mg, 0.126 mmol, 1.20 equiv.) and a magnetic stir bar. Methanol (2.00 ml) and AcOH (1.00 mL) were added to the vial in succession. The reaction mixture was allowed to stir at room temperature for 17 hours. The reaction mixture was cooled to 0 °C in an ice bath and quenched by slow addition of sat. $NaHCO_3$ (4.00 mL). The resulting reaction mixture was extracted with DCM (3 x 2.00 mL) and the organic layer was dried with Na_2SO_4 which was removed by filtration. The filtrate was concentrated under reduced pressure and purified via isocratic flash column chromatography with silica gel to afford **S11** as an off-white solid. **Yield:** 29.5 mg (58%); **ee**: 94% Chiralpak IB-3, MeOH/$scCO_2$ (0.1% diethylamine) isocratic 10/90 to 10/90 - 5 minutes, flow rate = 2.50 mL/min, I = 254 nm) tR = 2.6 min (major), 2.5 min (minor); **TLC:** R_f = 0.53 (20/80 EtOAc/Hexanes); $[\alpha]_D^{20}$**:** -35° (*c* 0.00385 g/mL $CDCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 – 7.12 (m, 2H), 6.89 – 6.82 (m, 2H), 6.77 (ddd, J = 8.6, 7.3, 1.6 Hz, 1H), 6.65 (dd, J = 8.0, 1.3 Hz, 1H), 6.60 (td, J = 7.4, 1.3 Hz, 1H), 6.55 (dd, J = 7.5, 1.6 Hz, 1H), 4.37 (dd, J = 4.9, 3.5 Hz, 1H), 3.79 (s, 3H), 3.54 (dd, J = 11.0, 3.5 Hz, 1H), 3.30 (dd, J = 11.0, 4.9 Hz, 1H), 2.78 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.1, 136.8, 134.3, 133.9, 128.2, 119.9, 117.2, 114.2, 114.0, 111.1, 62.2, 55.4, 48.3, 37.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{19}N_2O$: 255.1491, Found: 255.1488.

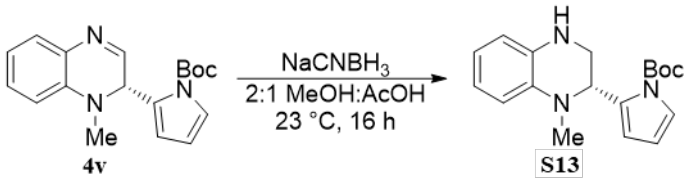




(2S)-2-(Furan-3-yl)-1-methyl-1,2,3,4-tetrahydroquinoxaline (S12)

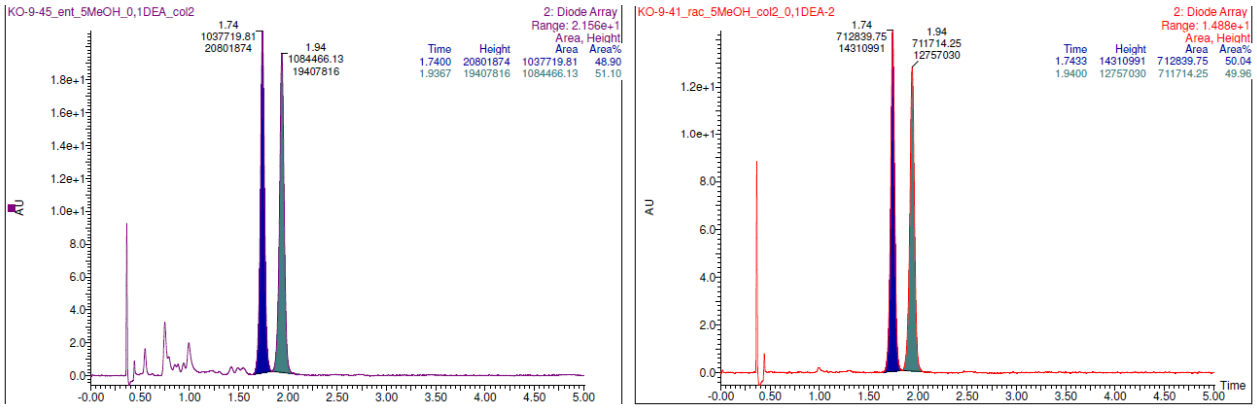
A 20 mL vial was charged with **4q** (19.3 mg, 0.0910 mmol, 1.00 equiv.), $NaCNBH_3$ (6.86 mg, 0.109 mmol, 1.20 equiv.) and a magnetic stir bar. Methanol (1.50 ml) and AcOH (0.750 mL) were added to the vial in succession. The reaction mixture was allowed to stir at room temperature for 15 hours. The reaction mixture was cooled to 0 °C in an ice bath and quenched by slow addition of sat. $NaHCO_3$ (4.00 mL). The resulting reaction mixture was extracted with DCM (3 x 2.00 mL) and the organic layer was dried with Na_2SO_4 which was removed by filtration. The filtrate was concentrated under reduced pressure and purified via isocratic flash column chromatography with silica gel to afford **S12** as an off-white solid. **Yield:** 15.9 mg (82%); **ee**: 76% Chiralpak IA-3, MeOH/$scCO_2$ isocratic 5/95 to 5/95 - 5 minutes, flow rate = 2.50 mL/min, I = 254 nm) tR = 2.2 min (major), 2.8 min (minor); **TLC:** R_f = 0.46 (20/80 EtOAc/Hexanes); $[\alpha]_D^{20}$**:** -58° (*c* 0.00250 g/mL $CDCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 6.72 (td, J = 7.6, 1.6 Hz, 1H), 6.65 – 6.51 (m, 3H), 6.33 – 6.29 (m, 1H), 4.33 (t, J = 3.7 Hz, 1H), 3.76 (s, 1H), 3.64 (dd, J = 10.9, 3.4 Hz, 1H), 3.36 (dd, J = 10.9, 4.1 Hz, 1H), 2.80 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.2, 140.0, 135.7, 133.7, 125.4, 119.6, 117.9, 114.0, 111.8, 109.9, 54.1, 47.1, 37.3; **HRMS:** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{15}N_2O$: 215.1178, Found: 215.1174.

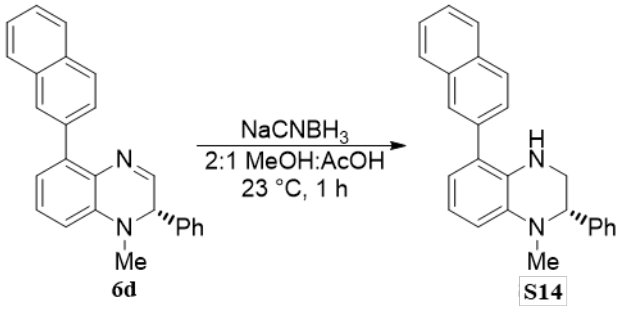




Tert-butyl 2-[(2R)-1-methyl-1,2,3,4-tetrahydroquinoxalin-2-yl]-1H-pyrrole-1-carboxylate (S13)

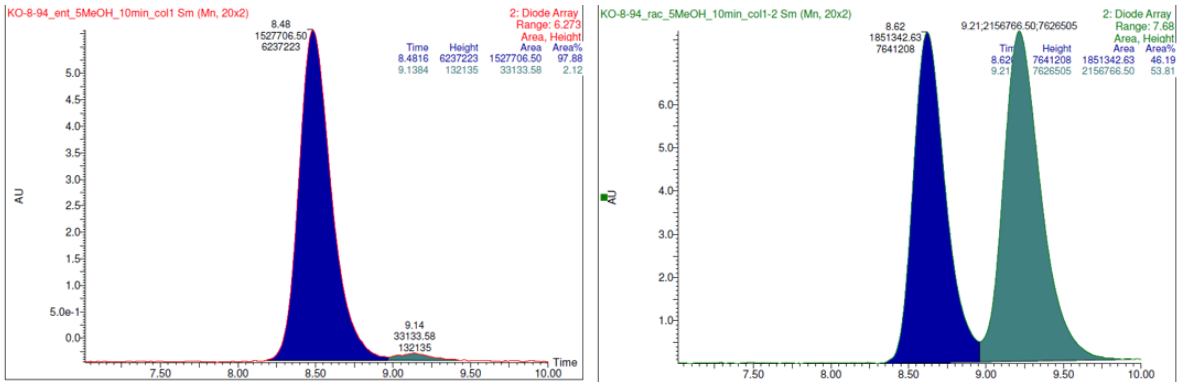
A 20 mL vial was charged with **4v** (28.7 mg, 0.0920 mmol, 1.00 equiv.), $NaCNBH_3$ (6.94 mg, 0.110 mmol, 1.20 equiv.) and a magnetic stir bar. Methanol (1.50 ml) and AcOH (0.750 mL) were added to the vial in succession. The reaction mixture was allowed to stir at room temperature for 16 hours. The reaction mixture was cooled to 0 °C in an ice bath and quenched by slow addition of sat. $NaHCO_3$ (4.00 mL). The resulting reaction mixture was extracted with DCM (3 x 2.00 mL) and the organic layer was dried with Na_2SO_4 which was removed by filtration. The filtrate was concentrated under reduced pressure and purified via isocratic flash column chromatography with silica gel to afford **S13** as an yellow oil. **Yield:** 25.7 mg (90%); **ee**: 2% Chiralpak IB-3, MeOH/$scCO_2$ (0.1% diethylamine) isocratic 5/95 to 5/95 - 5 minutes, flow rate = 2.50 mL/min, I = 254 nm) tR = 2.6 min (major), 2.5 min (minor); **TLC:** R_f = 0.38 (10/90 EtOAc/Hexanes); $[\alpha]_D^{20}$**:** +3° (*c* 0.00303 g/mL $CDCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (dd, J = 3.4, 1.8 Hz, 1H), 6.75 (td, J = 7.7, 1.6 Hz, 1H), 6.58 (ddd, J = 8.3, 6.2, 1.5 Hz, 2H), 6.51 (dd, J = 7.8, 1.6 Hz, 1H), 6.03 (t, J = 3.3 Hz, 1H), 5.86 (dt, J = 2.9, 1.3 Hz, 1H), 5.15 (t, J = 2.9 Hz, 1H), 3.68 – 3.59 (m, 2H), 3.51 (dd, J = 11.3, 2.2 Hz, 1H), 2.92 (s, 3H), 1.60 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.6, 136.0, 134.4, 133.1, 121.4, 119.8, 117.0, 114.2, 112.7, 110.5, 110.1, 83.9, 56.8, 45.2, 38.0, 28.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{24}N_3O_2$: 314.1863, Found: 314.1858.

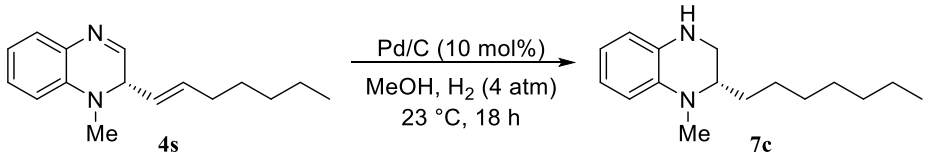




(2S)-1-Methyl-5-(naphthalen-2-yl)-2-phenyl-1,2,3,4-tetrahydroquinoxaline (S14)

A 20 mL vial was charged with **6d** (25.0 mg, 0.0720 mmol, 1.00 equiv.), $NaCNBH_3$ (5.28 mg, 0.0840 mmol, 1.20 equiv.) and a magnetic stir bar. Methanol (2.00 ml) and AcOH (1.00 mL) were added to the vial in succession. The reaction mixture was allowed to stir at room temperature for 1 hours. The reaction mixture was cooled to 0 °C in an ice bath and quenched by slow addition of 10% aq. NaOH (2.00 mL). The resulting reaction mixture was extracted with EtOAc (3 x 2.00 mL) and the organic layer was dried with $MgSO_4$ which was removed by filtration. The filtrate was concentrated under reduced pressure and purified via isocratic flash column chromatography with silica gel to afford **S14** as a white solid. **Yield:** 20.8 mg (82%); **ee**: 96% Chiralpak IA-3, MeOH/$scCO_2$ isocratic 5/95 to 5/95 - 5 minutes, flow rate = 2.50 mL/min, I = 254 nm) tR = 8.5 min (major), 9.1 min (minor); **TLC:** R_f = 0.19 (5/95 EtOAc/Hexanes); $[\alpha]_D^{20}$**:** -97° (*c* 0.00225 g/mL $CDCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 – 7.82 (m, 4H), 7.58 (dd, J = 8.4, 1.7 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.39 – 7.32 (m, 2H), 7.29 (d, J = 7.1 Hz, 3H), 6.86 (t, J = 7.8 Hz, 1H), 6.71 (ddd, J = 13.1, 7.8, 1.4 Hz, 2H), 4.47 (t, J = 4.4 Hz, 1H), 4.14 (s, 1H), 3.48 (ddd, J = 11.1, 3.8, 1.6 Hz, 1H), 3.25 (ddd, J = 11.1, 5.1, 2.1 Hz, 1H), 2.86 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.4, 137.2, 136.8, 133.7, 132.5, 131.3, 128.6, 128.4, 128.1, 127.9, 127.8, 127.6, 127.3, 126.7, 126.3, 126.1, 119.1, 119.1, 110.5, 63.1, 48.1, 37.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{23}N_2$: 351.1855, Found: 351.1864.

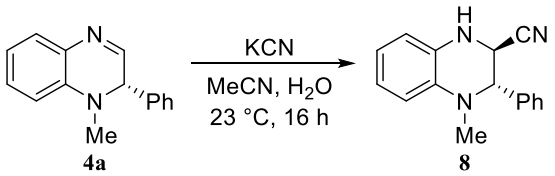




4s **7c**

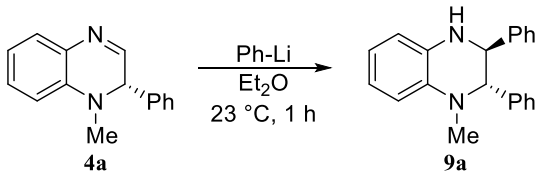
(2S)-2-Heptyl-1-methyl-1,2,3,4-tetrahydroquinoxaline (7c)

A 20 mL vial with a magnetic stir bar was charged with **4s** (28.3 mg, 0.117 mmol, 1.00 equiv.), 10% Pd/C (12.5 mg, 0.0117 mmol, 0.100 equiv.), and methanol (2.00 mL). The vial was sealed with a 14/20 rubber septum, which was further sealed with parafilm and electrical tape. The septum was pierced with two 18 G needles and the vial was placed inside of a Parr pressure reactor, which was then pressurized with H_2 (4.00 atm). The reaction was let stir at ambient temperature for 18 hours. The resulting reaction mixture was filtered over a plug of sand and celite. The resulting filtrate was purified via isocratic column chromatography on silica gel to yield **7c** as a translucent colorless oil. **Yield:** 19.0 mg (66%); **TLC:** R_f = 0.45 (10/90 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$**:** -52° (*c* 0.00244 g/mL EtOAc); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.68 (td, J = 7.6, 1.6 Hz, 1H), 6.55 (td, J = 7.5, 1.3 Hz, 1H), 6.49 (dt, J = 8.0, 1.8 Hz, 2H), 3.63 (s, 1H), 3.38 (ddd, J = 10.8, 3.1, 0.8 Hz, 1H), 3.25 – 3.14 (m, 2H), 2.89 (s, 3H), 1.63 – 1.48 (m, 2H), 1.39 – 1.21 (m, 10H), 0.90 – 0.85 (m, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 135.3, 133.6, 119.2, 117.0, 113.5, 111.4, 58.5, 43.0, 38.0, 32.0, 29.9, 29.9, 29.5, 26.7, 22.8, 14.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{27}N_2$: 247.2168, Found: 247.2166.



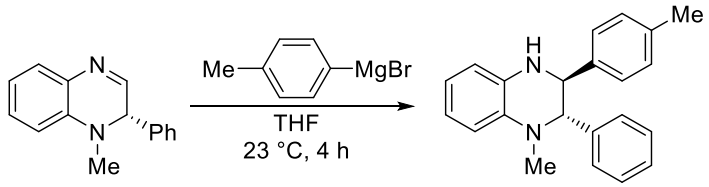
(2R,3S)-4-methyl-3-phenyl-1,2,3,4-tetrahydroquinoxaline-2-carbonitrile (8)

A 4 mL vial with a magnetic stir bar and septa cap was charged with **4a** (44.5 mg, 0.200 mmol, 1.00 equiv.), KCN (26.1 mg, 0.400 mmol, 2.00 equiv.), and dry MeCN (1.00 mL). The reaction was stirred at ambient temperature for 1 hour, after which water (1.00 mL) was added to the reaction by syringe through the septa. The reaction stirred for an additional 15 hours at ambient temperature. After stirring the reaction was quenched by addition by sat. Na_2CO_3 (1.00 mL) and extracted with EtOAc (3x2.00 mL). The aqueous layer was slowly added to a 30% bleach solution to ensure any potential residual HCN would be safely quenched. The EtOAc extracts were combined and dried with $MgSO_4$. The solids were removed by filtration and the resulting filtrate was purified via isocratic column chromatography on silica gel to yield **8** as a white solid. **Yield:** 25.5 mg (51% over 2 steps); **TLC:** R_f = 0.24 (20/80 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$**:** -197° (*c* 0.00221 g/mL $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 3H), 7.18 – 7.13 (m, 2H), 6.92 (ddd, J = 8.1, 7.3, 1.5 Hz, 1H), 6.74 – 6.65 (m, 2H), 6.62 (dd, J = 7.7, 1.6 Hz, 1H), 4.75 (t, J = 2.0 Hz, 1H), 4.35 (dd, J = 3.4, 2.5 Hz, 1H), 3.99 (t, J = 2.3 Hz, 1H), 2.98 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.2, 134.5, 128.9, 128.6, 128.5, 126.7, 122.0, 11168.9, 117.8, 115.3, 110.9, 64.6, 47.1, 37.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{16}N_3$: 250.1338, Found: 250.1339.



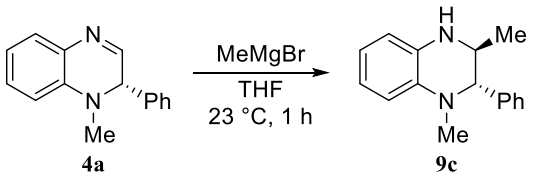
(2S,3S)-1-methyl-2,3-diphenyl-1,2,3,4-tetrahydroquinoxaline (9a)

In a glovebox, a 4 mL vial, with a magnetic stir bar, was charged with **4a** (44.5 mg, 0.200 mmol, 1.00 equiv.), Et_2O (1.00 mL), sealed with a septa cap, and brought outside the glovebox. On the bench, PhLi (0.316 mL, 0.600 mmol, 3.00 equiv., 1.90 M solution in dibutyl ether) was added to the 4 mL vial. The resulting reaction mixture was allowed to stir at ambient temperature for 1 hour. After stirring, the reaction was quenched with sat. NH_4Cl (2.00 mL) and extracted with EtOAc (3x2.00 mL). The EtOAc extracts were combined and dried with $MgSO_4$. The solids were removed by filtration and the resulting filtrate was purified via isocratic column chromatography on silica gel to yield **9a** as a colorless oil. **Yield:** 40.3 mg (64% over 2 steps); **TLC:** R_f = 0.33 (5/95 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$**:** -73° (*c* 0.00270 g/mL $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 6H), 7.14 – 7.10 (m, 2H), 7.09 – 7.01 (m, 2H), 6.80 (ddd, J = 7.9, 7.2, 1.5 Hz, 1H), 6.73 (dd, J = 7.9, 1.4 Hz, 1H), 6.67 (td, J = 7.4, 1.4 Hz, 1H), 6.60 (dd, J = 7.6, 1.5 Hz, 1H), 4.36 (dd, J = 5.8, 1.6 Hz, 1H), 4.26 (d, J = 5.8 Hz, 1H), 4.07 (s, 1H), 2.74 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.2, 140.7, 136.5, 134.1, 128.4, 128.4, 127.9, 127.7, 127.6, 127.5, 119.4, 117.8, 113.5, 111.7, 69.2, 61.8, 37.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{21}N_2$: 301.1699, Found: 301.1687.



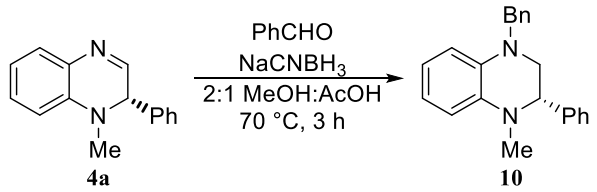
(2S,3S)-1-methyl-3-(4-methylphenyl)-2-phenyl-1,2,3,4-tetrahydroquinoxaline (9b)

A 20 mL vial with a magnetic stir bar was charged with **4a** (19.4 mg, 0.0870 mmol, 1.00 equiv.) and sealed with a 14/20 septa, which was further sealed with parafilm and electrical tape. The vial was evacuated and backfilled with N_2 three times. Under N_2, dry THF (1.00 mL) was added to the vial. Under N_2, TolMgBr (0.348 mL, 0.174 mmol, 2.00 equiv., 0.500 M solution in diethyl ether) was added to the vial. The reaction was allowed to stir at ambient temperature for 4 hours. After stirring, the reaction was quenched with sat. NH_4Cl (6.00 mL) and extracted with Et_2O (3x4.00 mL). The Et_2O extracts were combined and dried with Na_2SO_4. The solids were removed by filtration and the resulting filtrate was purified via isocratic column chromatography on silica gel to yield **9b** as a yellow oil. **Yield:** 22.5 mg (82%); **TLC:** R_f = 0.29 (5/95 EtOAc/Hexanes); $[\alpha]_D^{20}$**:** -101° (*c* 0.00375 g/mL $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.16 (m, 3H), 7.09 – 6.97 (m, 6H), 6.79 (td, J = 7.6, 1.6 Hz, 1H), 6.71 (dd, J = 8.1, 1.4 Hz, 1H), 6.66 (td, J = 7.4, 1.5 Hz, 1H), 6.58 (dd, J = 7.6, 1.6 Hz, 1H), 4.32 (dd, J = 5.9, 1.2 Hz, 1H), 4.25 (d, J = 5.9 Hz, 1H), 4.02 (s, 1H), 2.74 (s, 3H), 2.29 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.8, 139.3, 137.3, 136.5, 134.1, 129.1, 128.4, 127.9, 127.5, 127.4, 119.3, 117.7, 113.4, 111.6, 69.2, 61.5, 37.4, 21.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{23}N_2$: 315.1855, Found: 315.1848.



(2S,3S)-1,3-Dimethyl-2-phenyl-1,2,3,4-tetrahydroquinoxaline (9c)

In a glovebox, a 10 mL Schlenk tube was charged with **4a** (29.9 mg, 0.135 mmol, 1.00 equiv.), and dry THF (1.35 mL). The Schlenk tube was brough outside of the glovebox and placed under N_2. Under N_2, MeMgBr (0.180 mL, 0.540 mmol, 4.00 equiv., 3.0 M solution in diethyl ether) was added to the Schlenk tube slowly by syringe. The reaction was allowed to stir at ambient temperature for 1 hour. Cooled the Schlenk tube to 0 °C in an ice-bath and quenched the reaction with sat. NH_4Cl. The reaction mixture was extracted with DCM (3x4.00 mL) and dried with Na_2SO_4. The solids were removed by filtration and the resulting filtrate was concentrated down to yield **9c** as a bright yellow oil, which was clean by NMR without column purification. **Yield:** 31.4 mg (98%); **TLC:** R_f = 0.31 (10/90 EtOAc/Hexanes); $\boldsymbol{[\alpha]_D^{20}}$**:** -27° (*c* 0.00234 g/mL $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.30 – 7.27 (m, 1H), 7.23 – 7.17 (m, 2H), 6.79 – 6.72 (m, 1H), 6.67 (dd, J = 7.9, 1.3 Hz, 1H), 6.62 (td, J = 7.4, 1.3 Hz, 1H), 6.55 (dd, J = 7.6, 1.6 Hz, 1H), 3.94 (d, J = 5.8 Hz, 1H), 3.64 (s, 1H), 3.42 (p, J = 6.2 Hz, 1H), 2.72 (s, 3H), 1.10 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.7, 136.8, 133.4, 128.7, 127.7, 127.7, 119.5, 117.6, 114.0, 111.4, 69.2, 52.2, 37.3, 20.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{19}N_2$: 239.1542, Found: 239.1536.



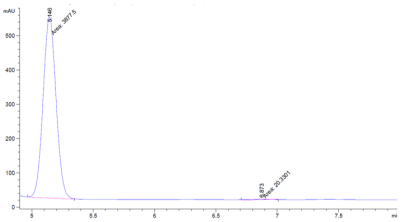
(2S)-4-benzyl-1-methyl-2-phenyl-1,2,3,4-tetrahydroquinoxaline (10)

A 4 mL vial was charged with **4a** (16.8 mg, 0.0760 mmol, 1.00 equiv.), $NaCNBH_3$ (11.3 mg, 0.180 mmol, 1.20 equiv.), a magnetic stir bar and a septa cap. Methanol (0.500 ml) and AcOH (0.250 mL) were added to the vial in succession. Benzaldehyde (0.0100 mL, 0.0990 mmol, 1.20 equiv.) was added to the vial by syringe through the septa cap. The reaction was then heated at 70 °C in an aluminum heating block, while stirring, for 3 hours. After 3 hours, the reaction was let cool to ambient temperature, quenched with sat. NH_4Cl (1.00 mL), and extracted with DCM (3x2.00 mL). The DCM extracts were combined and dried with $MgSO_4$. The solids were removed by filtration and the resulting filtrate was purified via isocratic column chromatography on silica gel to yield **10** as an off-white solid. **Yield:** 19.3 mg (81%); **TLC:** R_f = 0.23 (5/95 EtOAc/Hexanes); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$**:** -16° (*c* 0.00255 g/mL $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 3H), 7.23 – 7.13 (m, 5H), 7.10 – 7.05 (m, 2H), 6.79 (t, J = 7.6 Hz, 1H), 6.69 (d, J = 7.9 Hz, 1H), 6.67 – 6.58 (m, 2H), 4.46 (t, J = 4.2 Hz, 1H), 4.38 (d, J = 15.6 Hz, 1H), 4.26 (d, J = 15.6 Hz, 1H), 3.46 (dd, J = 11.4, 3.7 Hz, 1H), 3.24 (dd, J = 11.4, 4.9 Hz, 1H), 2.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.3, 138.5, 137.0, 135.7, 128.5 (2 Cs), 127.4, 127.4, 127.2, 126.9, 119.0, 117.3, 111.4, 110.4, 62.9, 55.5, 54.2, 37.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{23}N_2$: 315.1855, Found: 315.1852.

G. Preparative Scale Synthesis of (2S)-1-Methyl-2-phenyl-1,2-dihydroquinoxaline (4a)

(2S)-1-Methyl-2-phenyl-1,2-dihydroquinoxaline (4a)

In a glovebox, a 20 mL vial, with a magnetic stir bar, was charged with $Rh(COD)_2BF_4$ (24.4 mg, 0.0600 mmol, 0.0600 equiv.), (R,R)-QuinoxP* (23.4 mg, 0.0700 mmol, 0.0700 equiv.) and dioxane (10 mL). The resulting heterogenous dioxane solution was stirred for 30 minutes to promote the formation of the catalyst. The resulting homogeneous opaque orange-red color Rh/(R,R)-QuinoxP* solution was added to a 20 mL vial containing quinoxalinium salt **3** (294 mg, 1.00 mmol, 1.00 equiv.), Na_2CO_3 (318 mg, 3.00 mmol, 3.00 equiv.) and phenyl boronic acid (305 mg, 2.50 mmol, 2.50 equiv.). The 20 mL vial was sealed with a PTFE-lined septa cap and brought outside the glovebox. Water (1.00 mL), degassed by sparging with nitrogen, was added to the reaction mixture via syringe and the reaction mixture was heated at 80 °C for 2 hours using an aluminum heating block. The vial was then removed from the heating block and allowed to cool to room temperature. The resulting room temperature reaction mixture was diluted with EtOAc (5.00 mL) and dried with MgSO4 (2.00 g). The reaction was filtered over Al_2O_3, the solids were rinsed with EtOAc (5.00 mL) and the resulting filtrate was concentrated under reduced pressure to give a crude reaction residue. The residue was purified by flash column chromatography with silica gel using a 0 to 100% gradient of EtOAc/Hexanes. The solvents were removed under reduced pressure to give the desired dihydroquinoxaline product **4a**. **qNMR Yield:** 78% (1,3,5-trimethoxybenzene as internal standard); **Isolated Yield:** 170 mg (76%); **ee:** 98% (Chiralpak IG, IPA/MTBE gradient 2.5/97.5 to 2.5/97.5 - 15 minutes, 2.5/97.5 to 95/5 – 2 minutes, flow rate = 1.00 mL/min, I = 254 nm) tR = 5.1 min (major), 6.9 min (minor). See compound **4a** for full characterization of the product.



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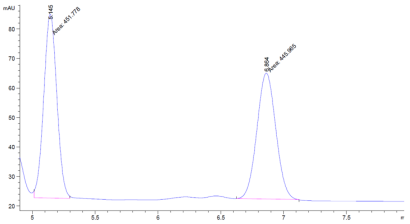
2	6.873	MM	0.2029	20.33012	1.66987	0.5216



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1	5.145	MM	0.1208	451.77844	62.30877	50.3238
2	6.864	MM	0.1744	445.96548	42.63000	49.6762

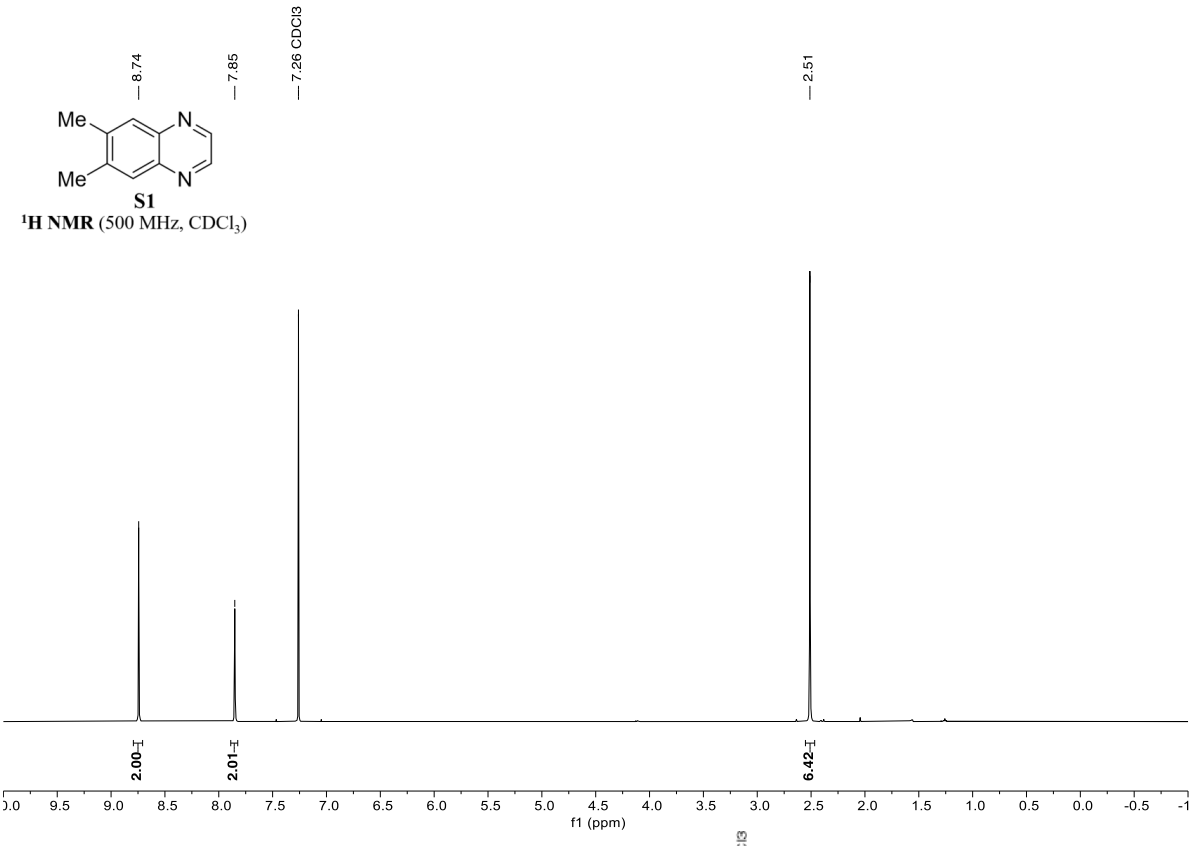
H. References

[1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518–1520.

[2] V. Elumalai, J. H. Hansen, *SynOpen* **2021**, *05*, 43–48.

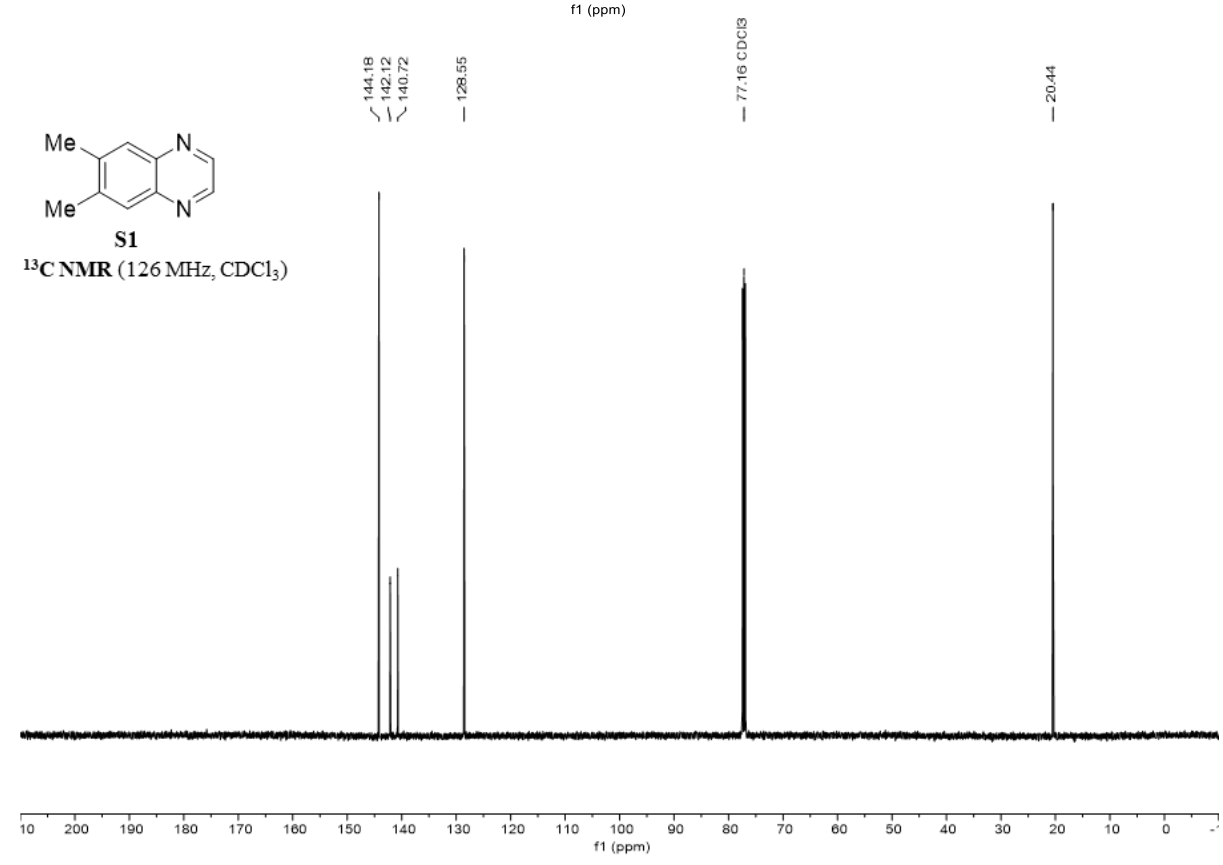
[3] S. Yang, B. Shan, X. Xu, Q. Miao, *Chemistry – A European Journal* **2016**, *22*, 6637–6642.

I. NMR Spectra



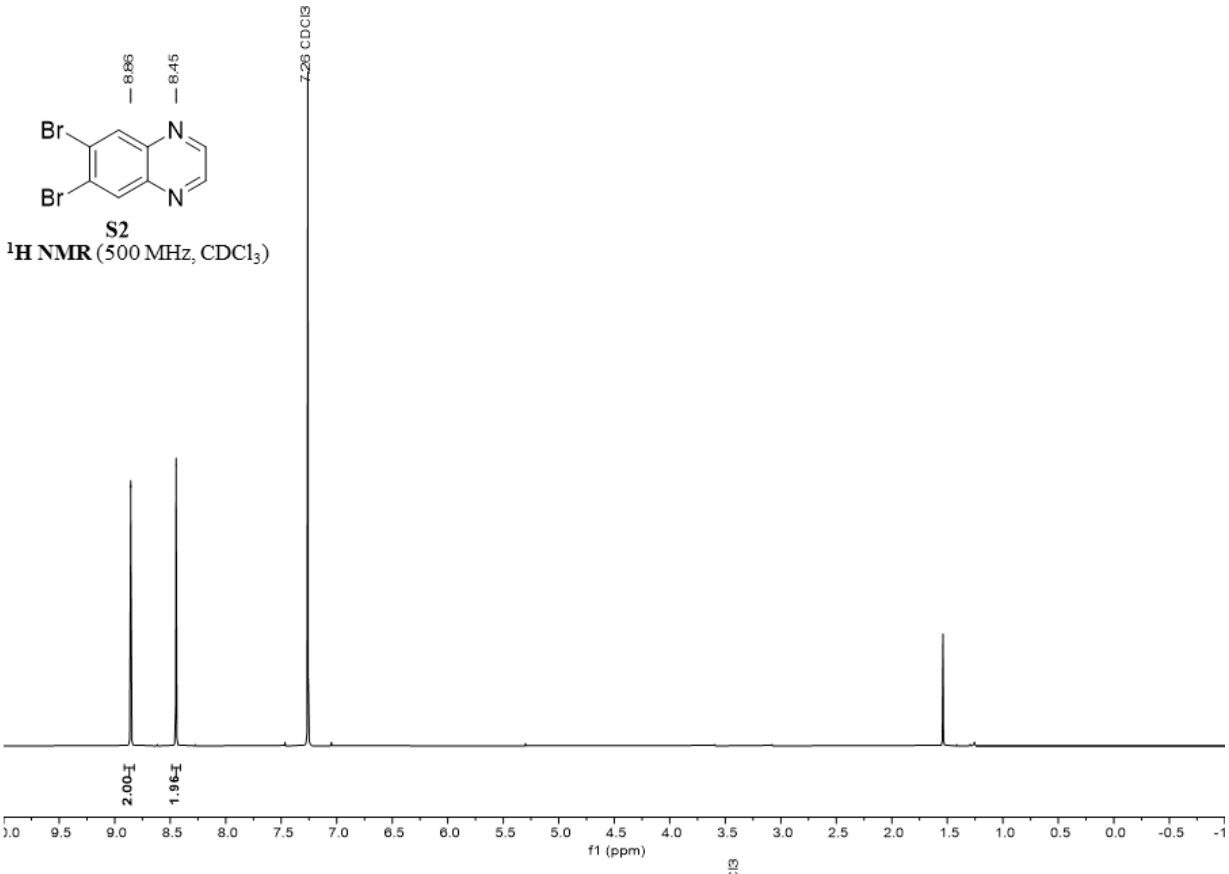
S1

^{1}H NMR (500 MHz, $CDCl_3$)



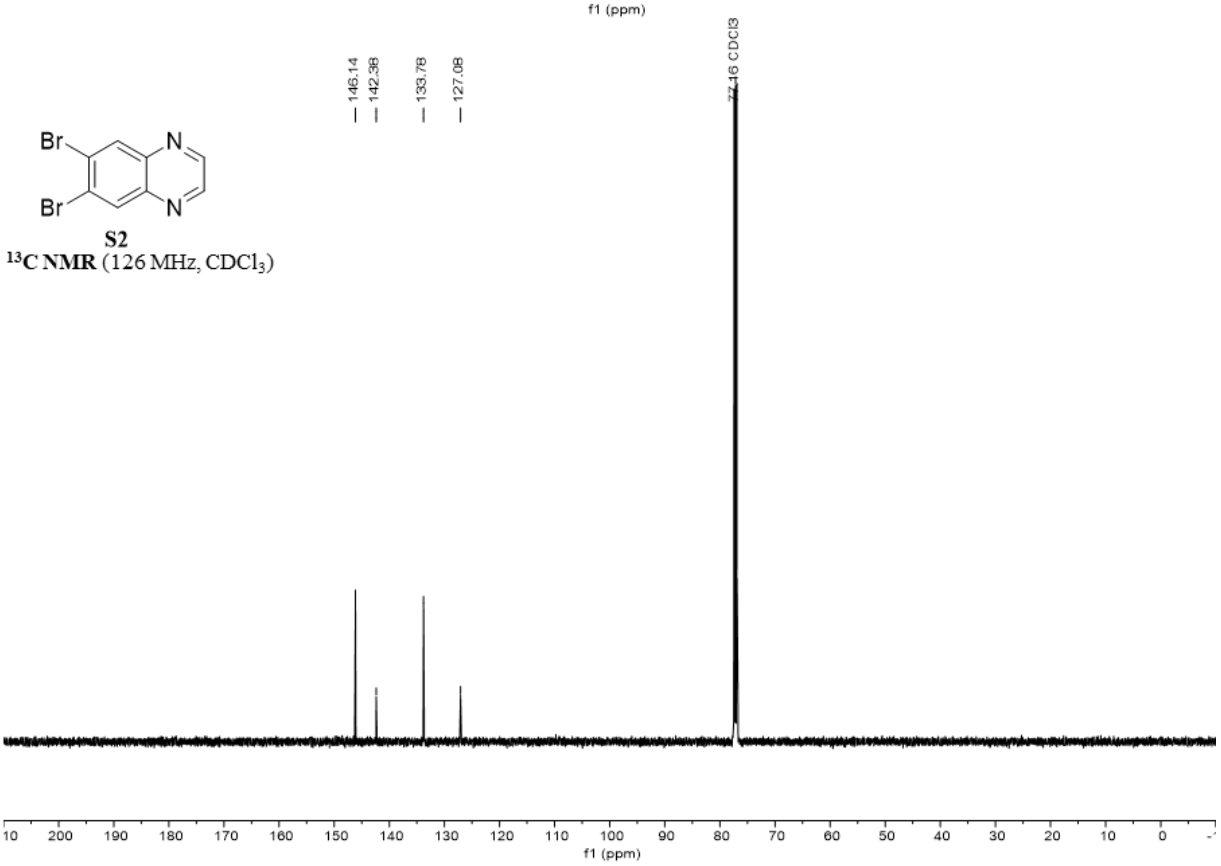
S1

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



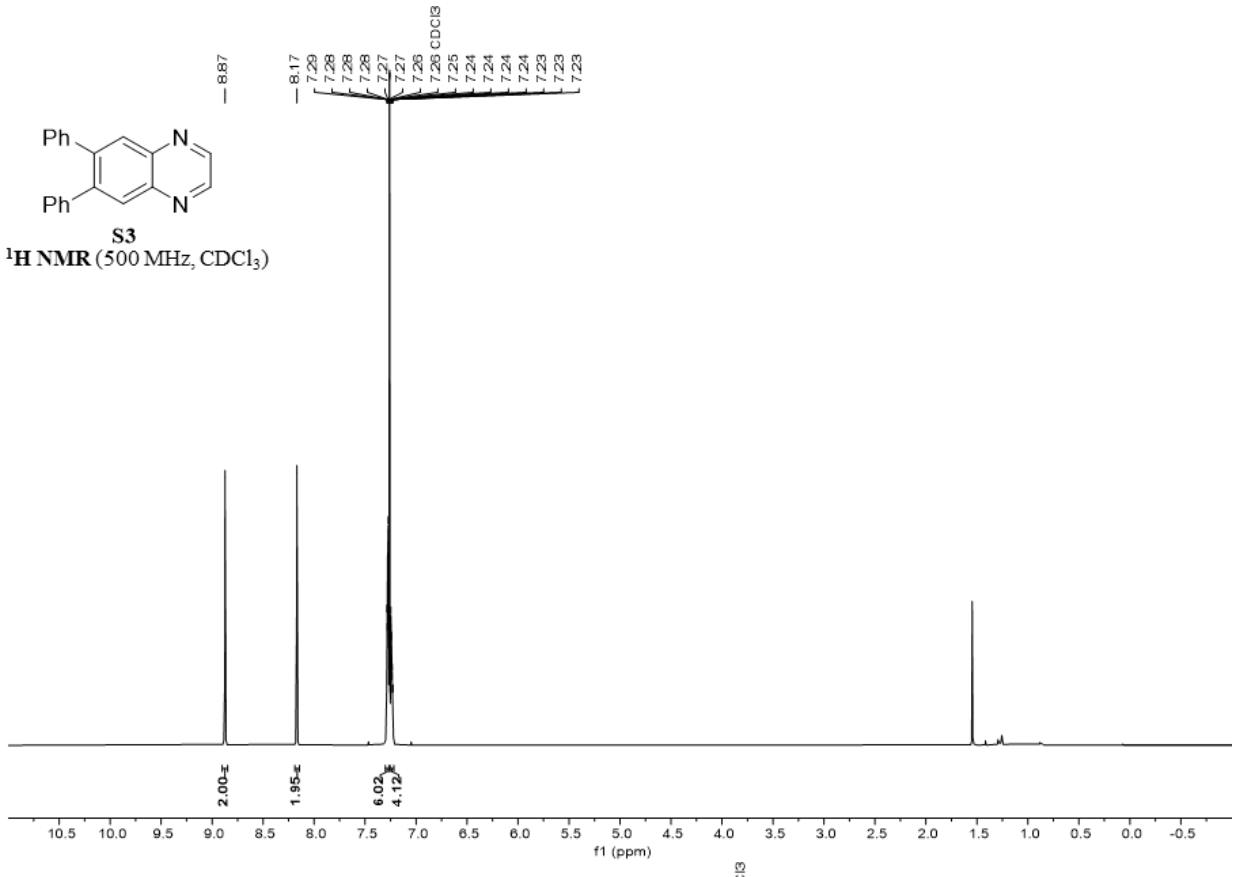
S2

^{1}H NMR (500 MHz, $CDCl_3$)



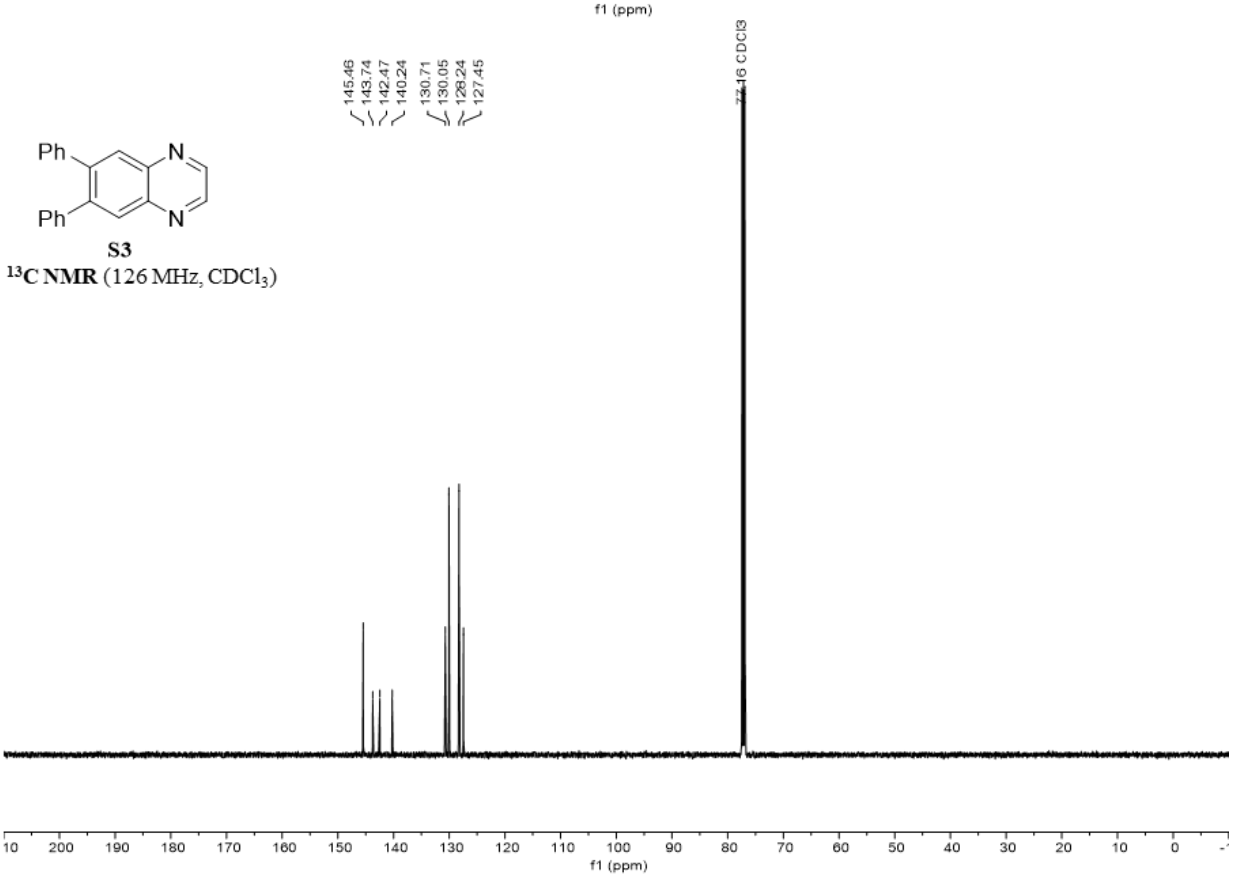
S2

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



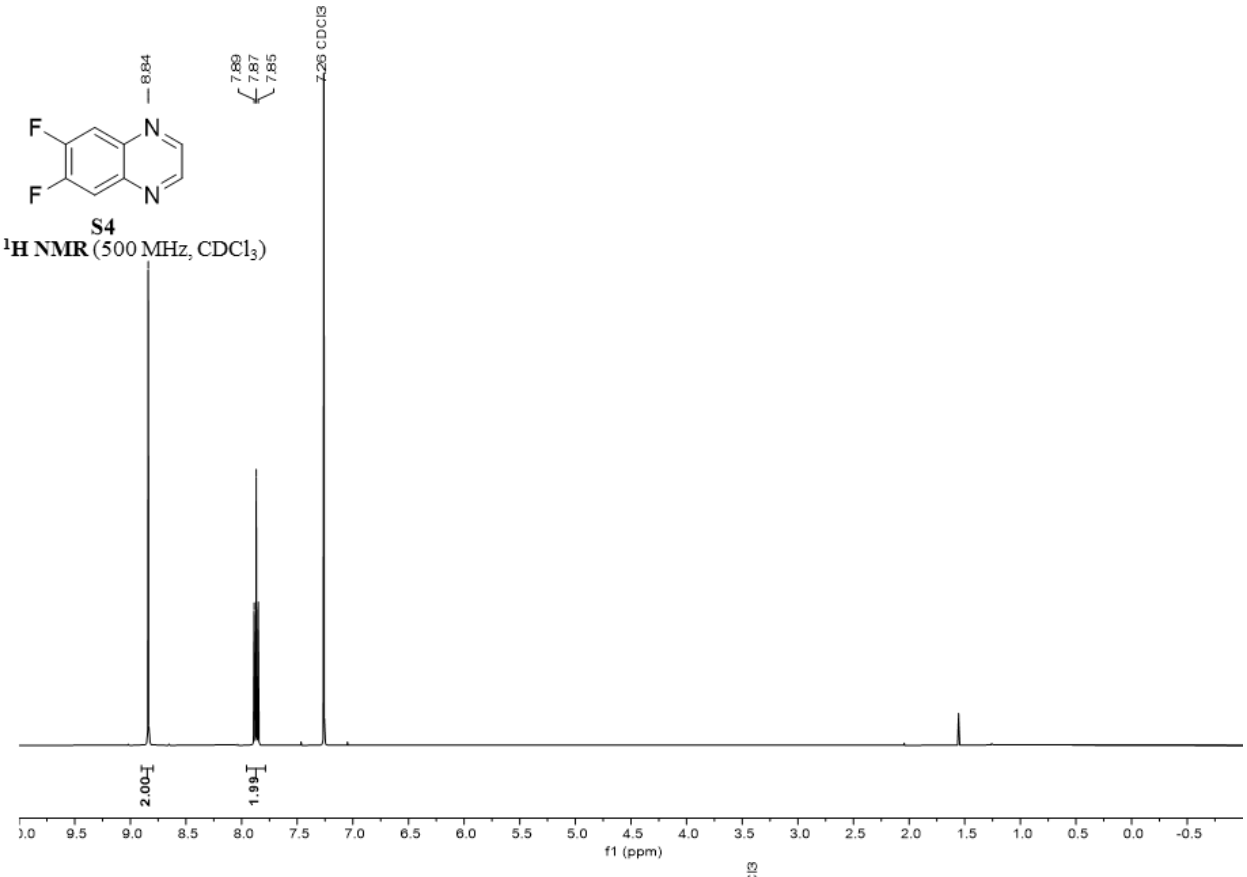
S3

^{1}H NMR (500 MHz, $CDCl_3$)



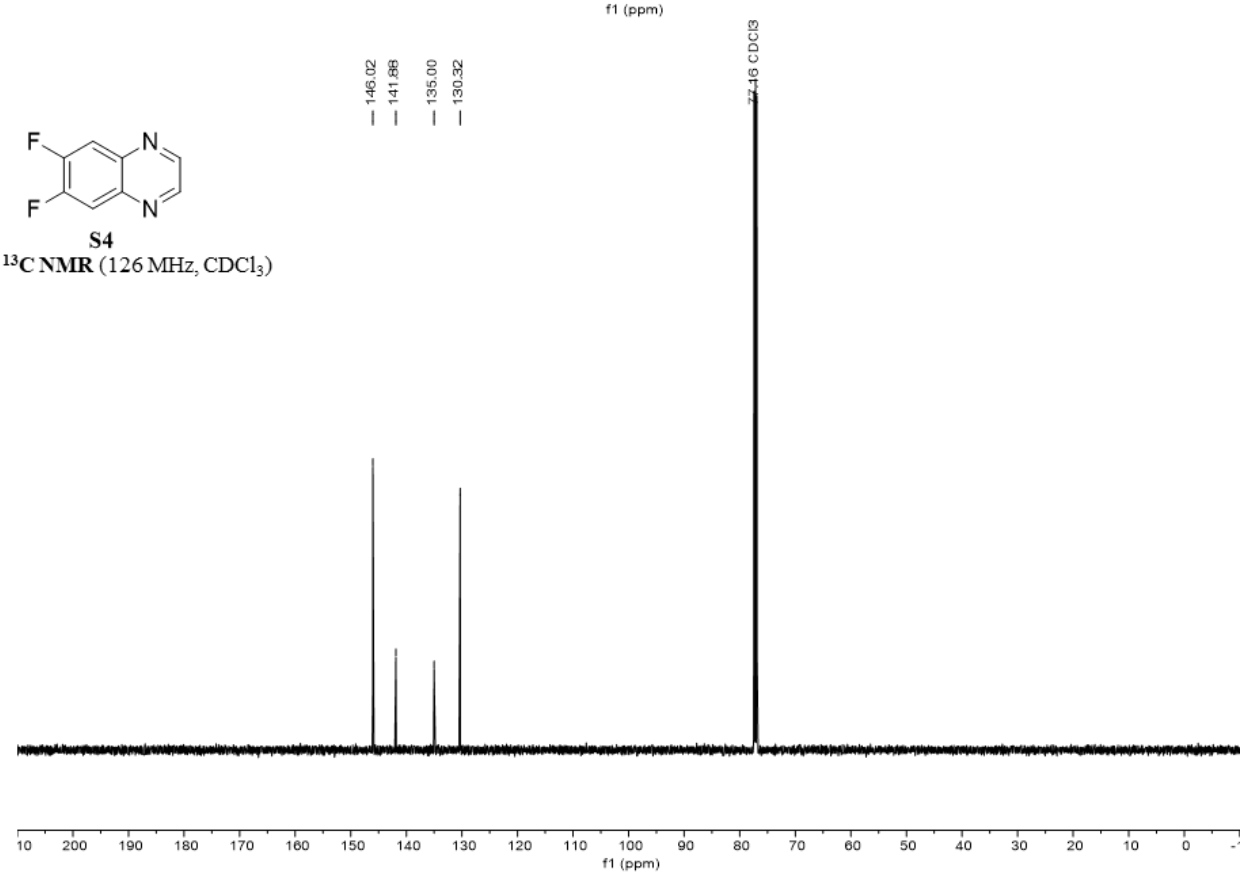
S3

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



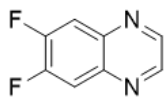
S4

^{1}H NMR (500 MHz, $CDCl_3$)



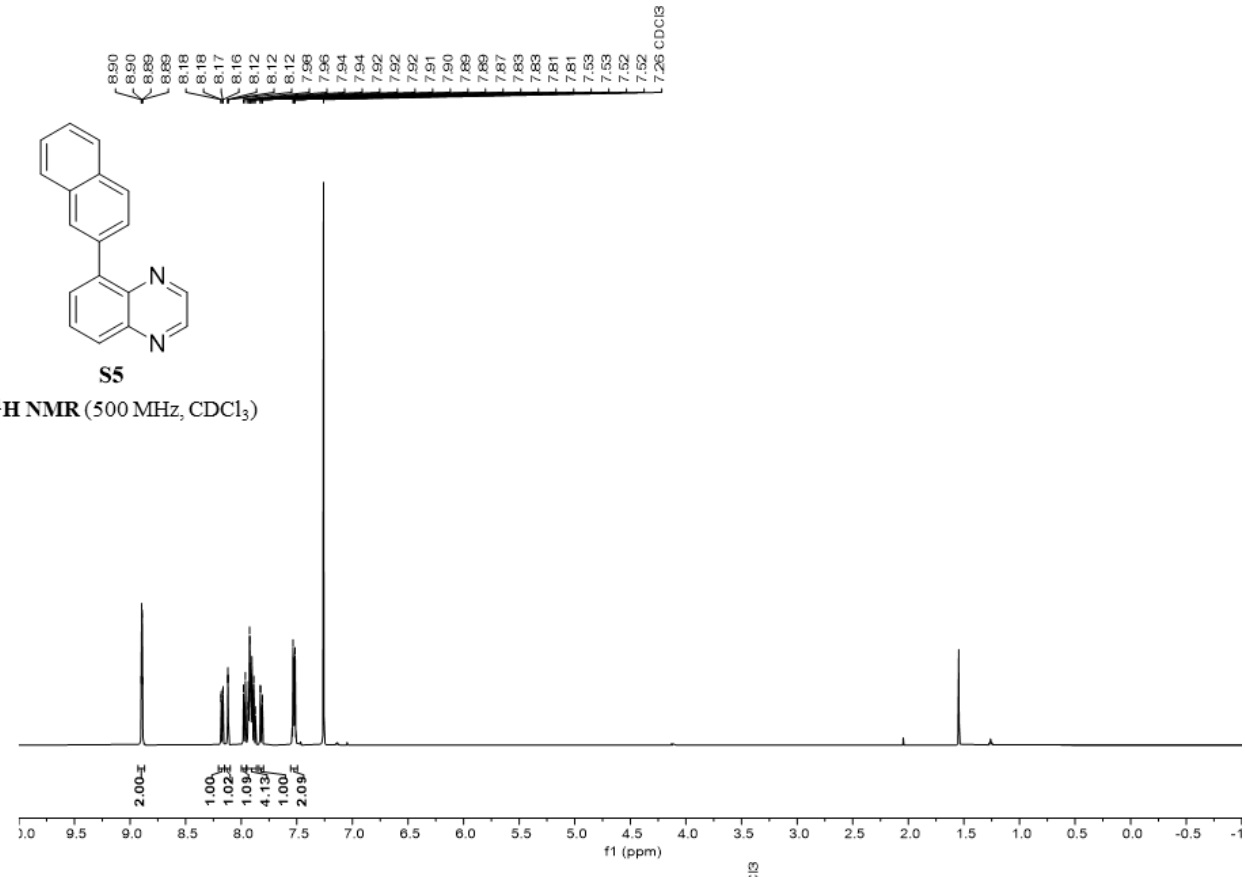
S4

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



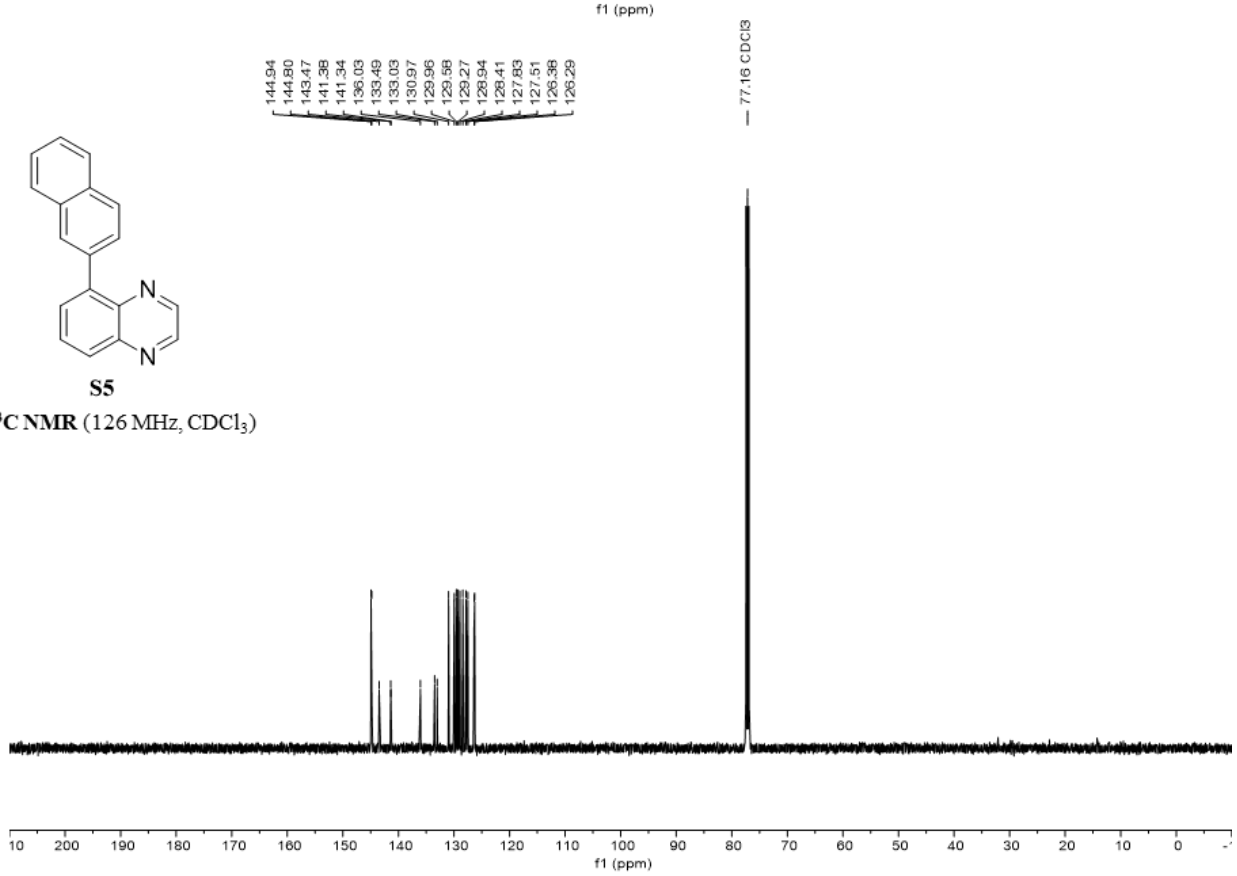
S4

^{19}F NMR (471 MHz, $CDCl_3$)



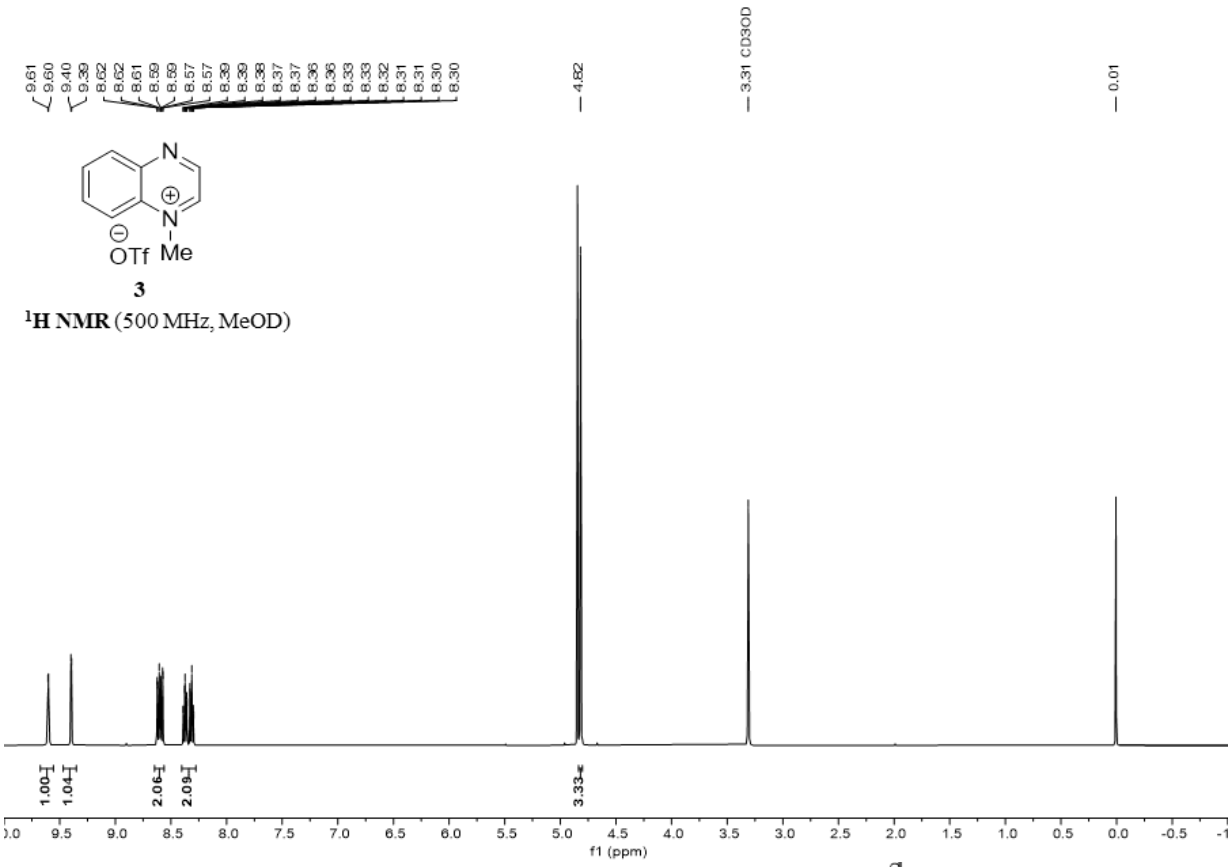
S5

^{1}H NMR (500 MHz, $CDCl_3$)



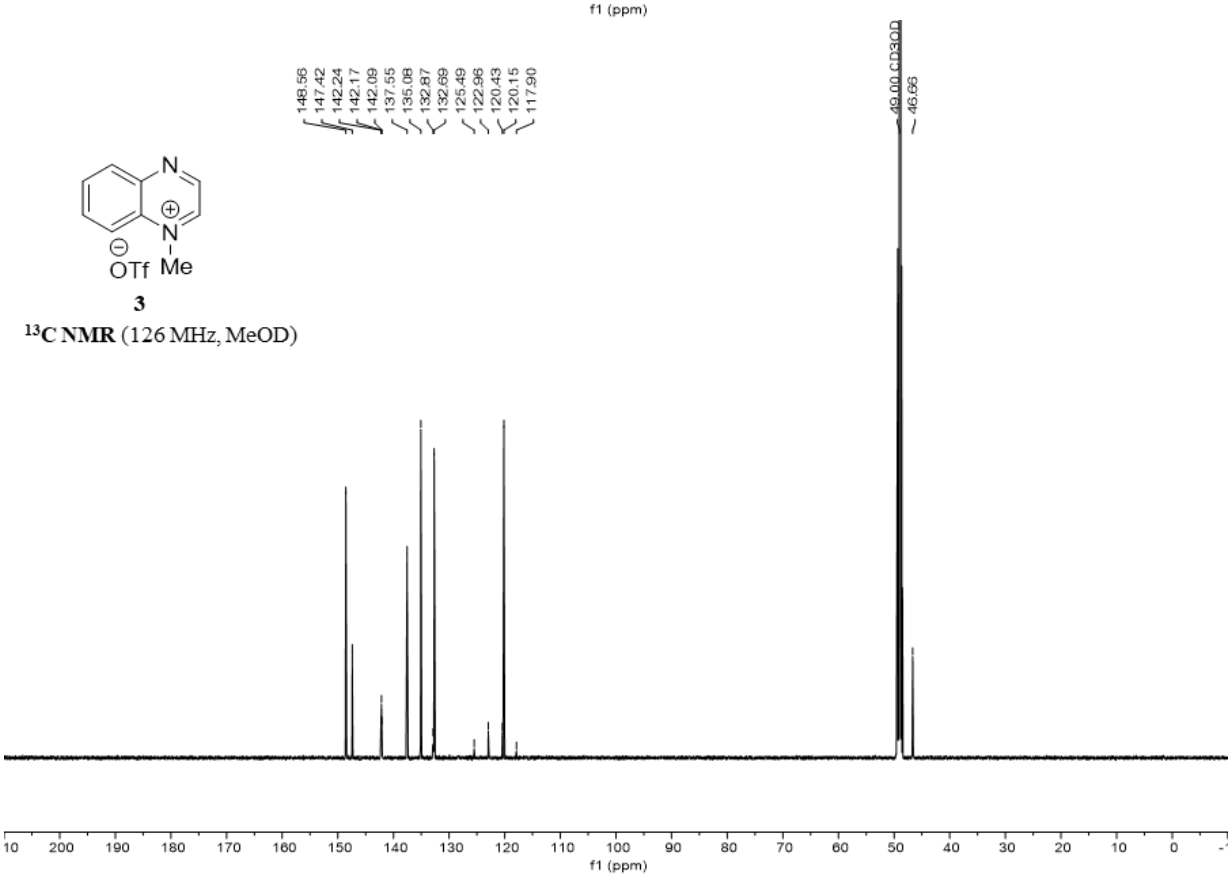
S5

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



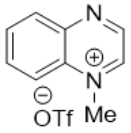
3

^{1}H NMR (500 MHz, MeOD)



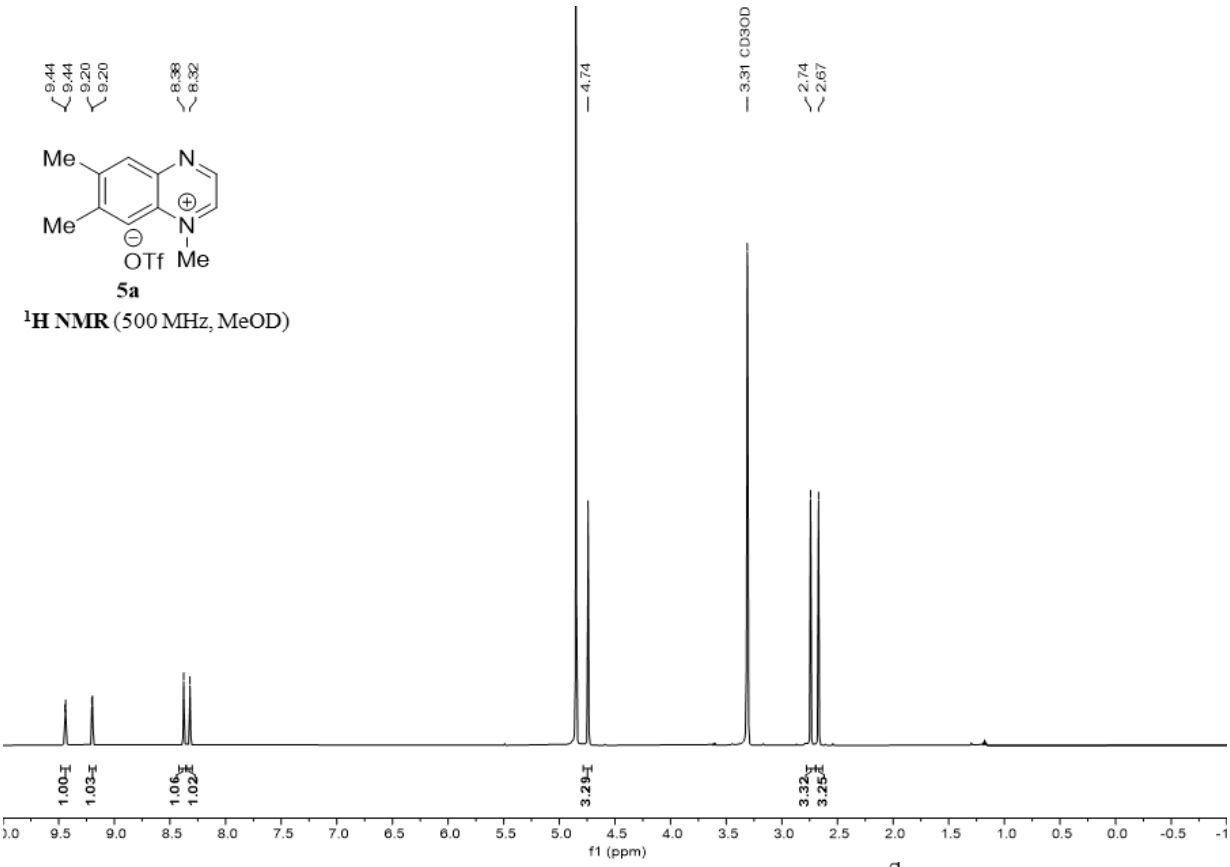
3

^{13}C NMR (126 MHz, MeOD)



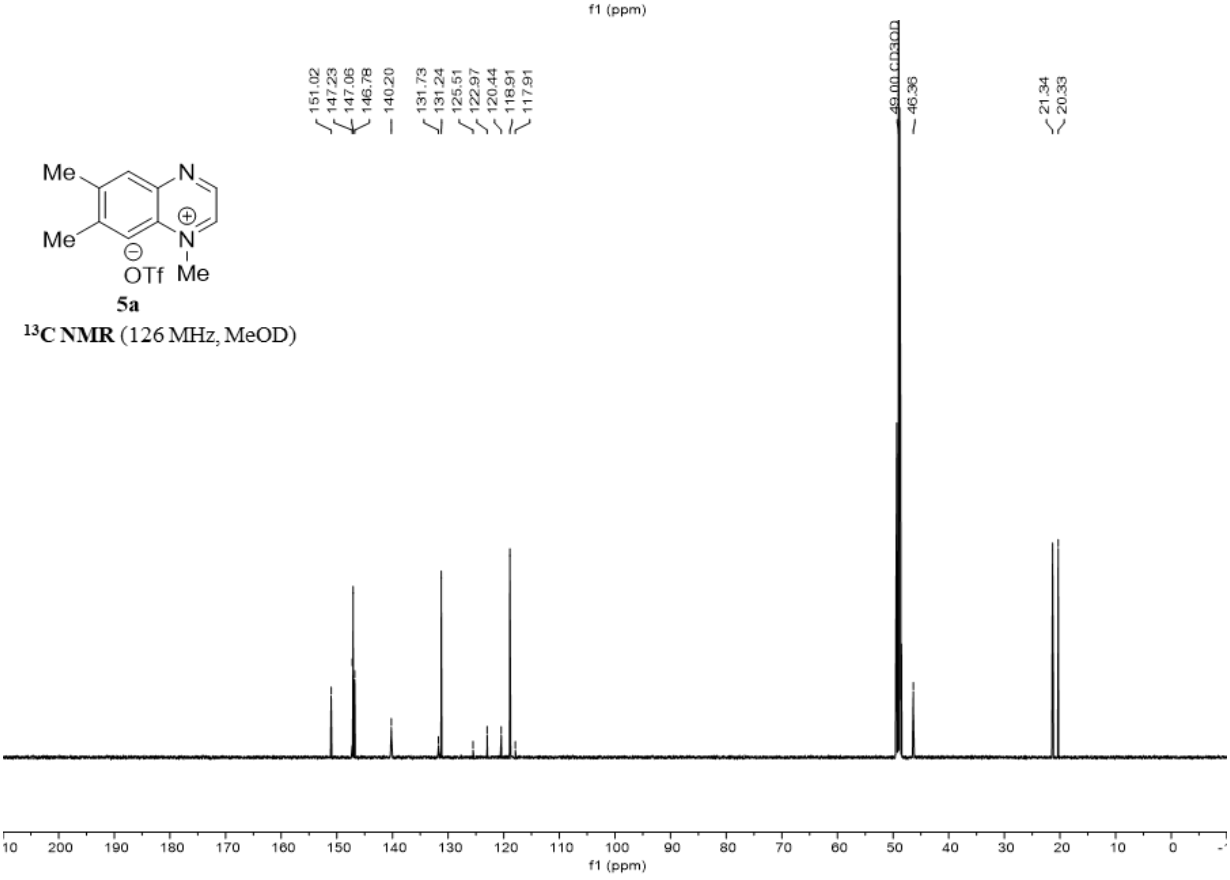
3

^{19}F NMR (471 MHz, MeOD)



5a

^{1}H NMR (500 MHz, MeOD)



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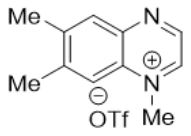
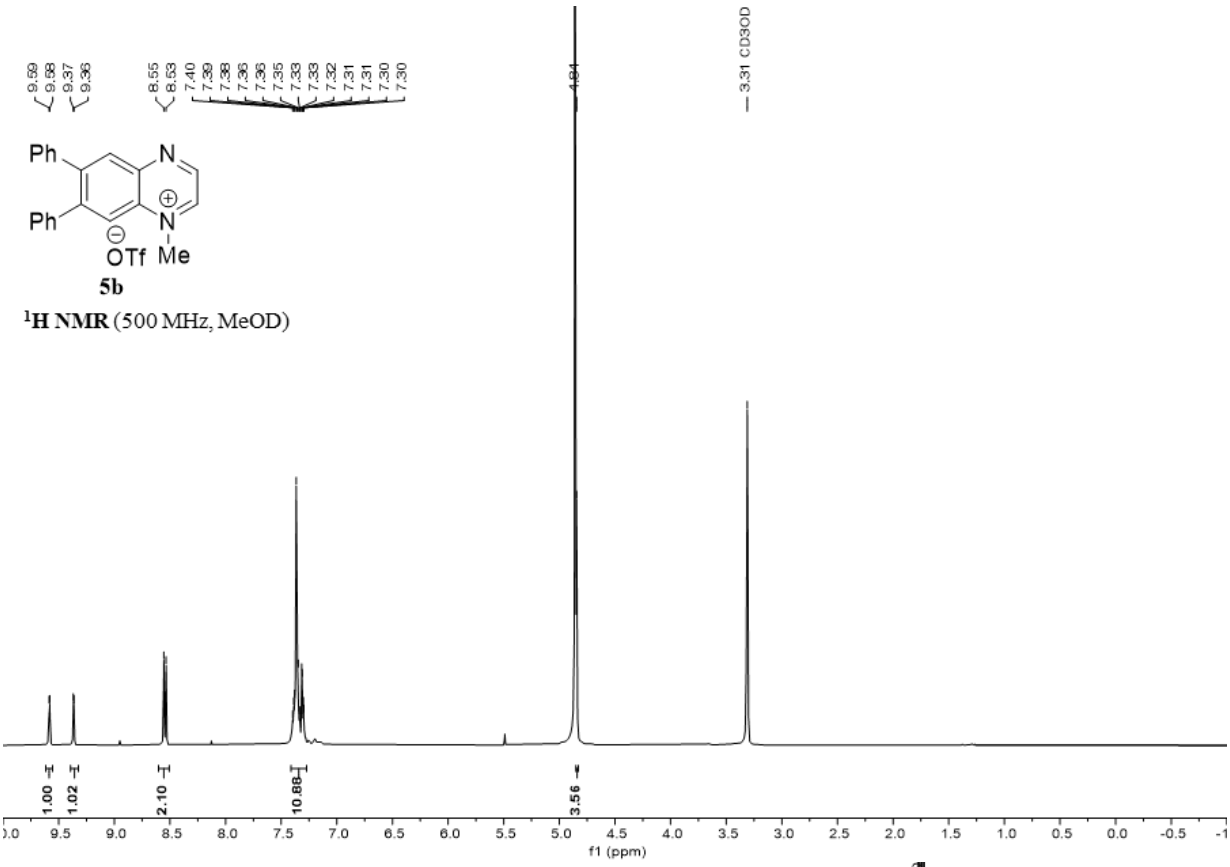


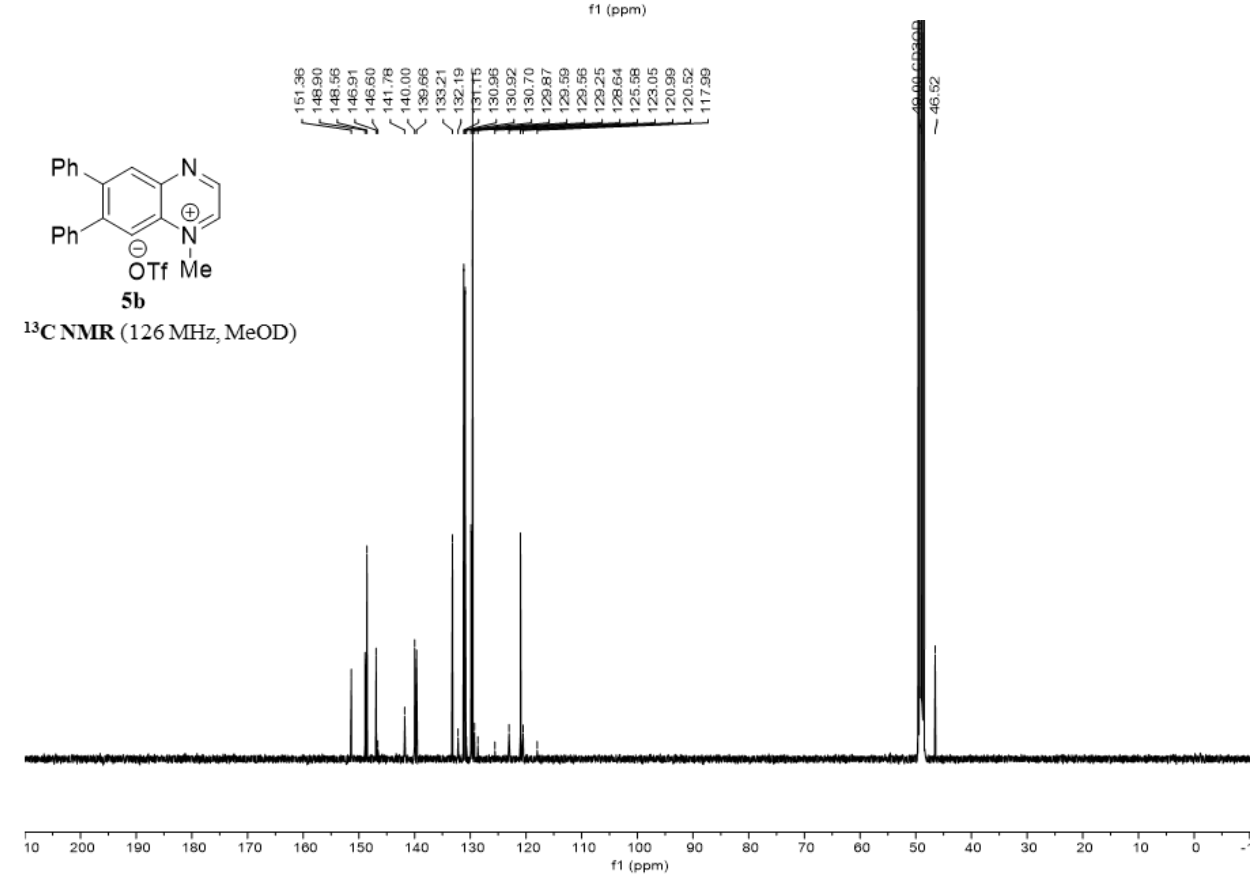
5a

^{19}F NMR (471 MHz, MeOD)



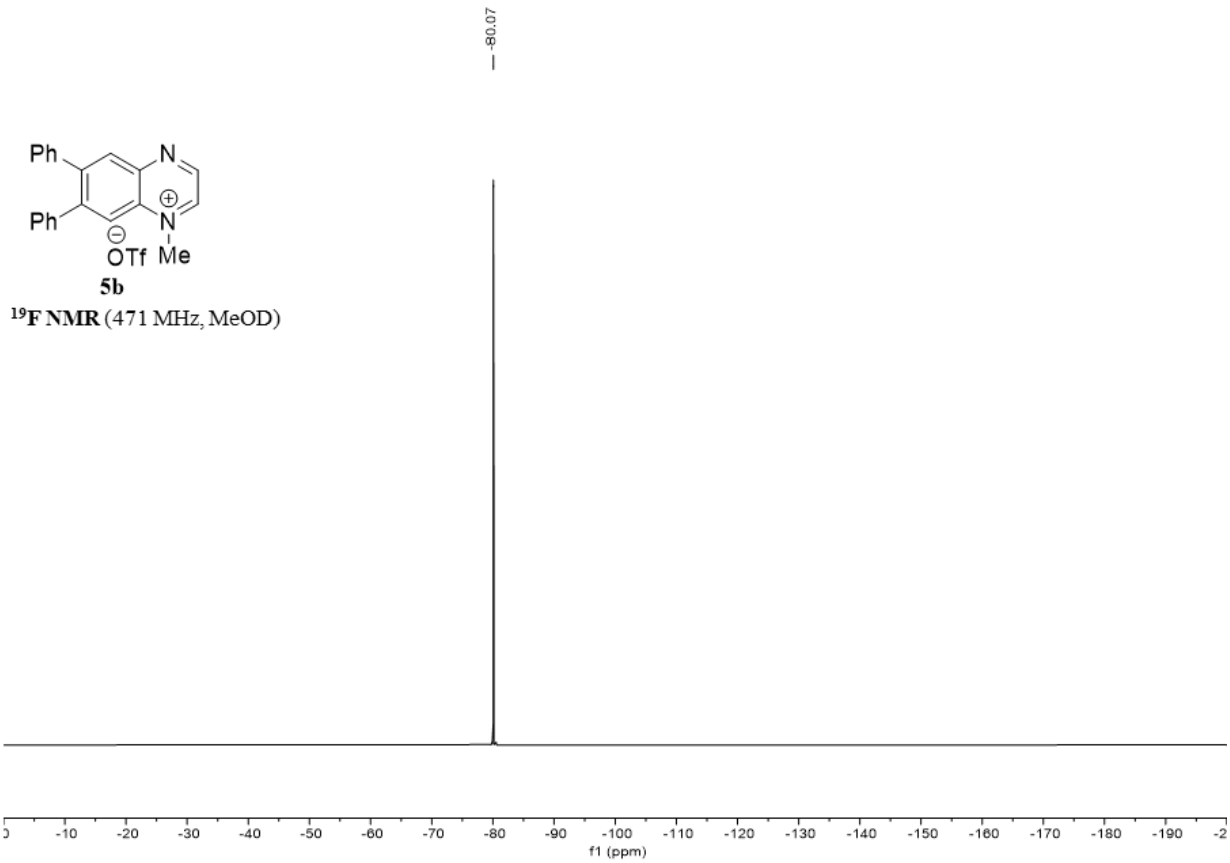
5b

^{1}H NMR (500 MHz, MeOD)



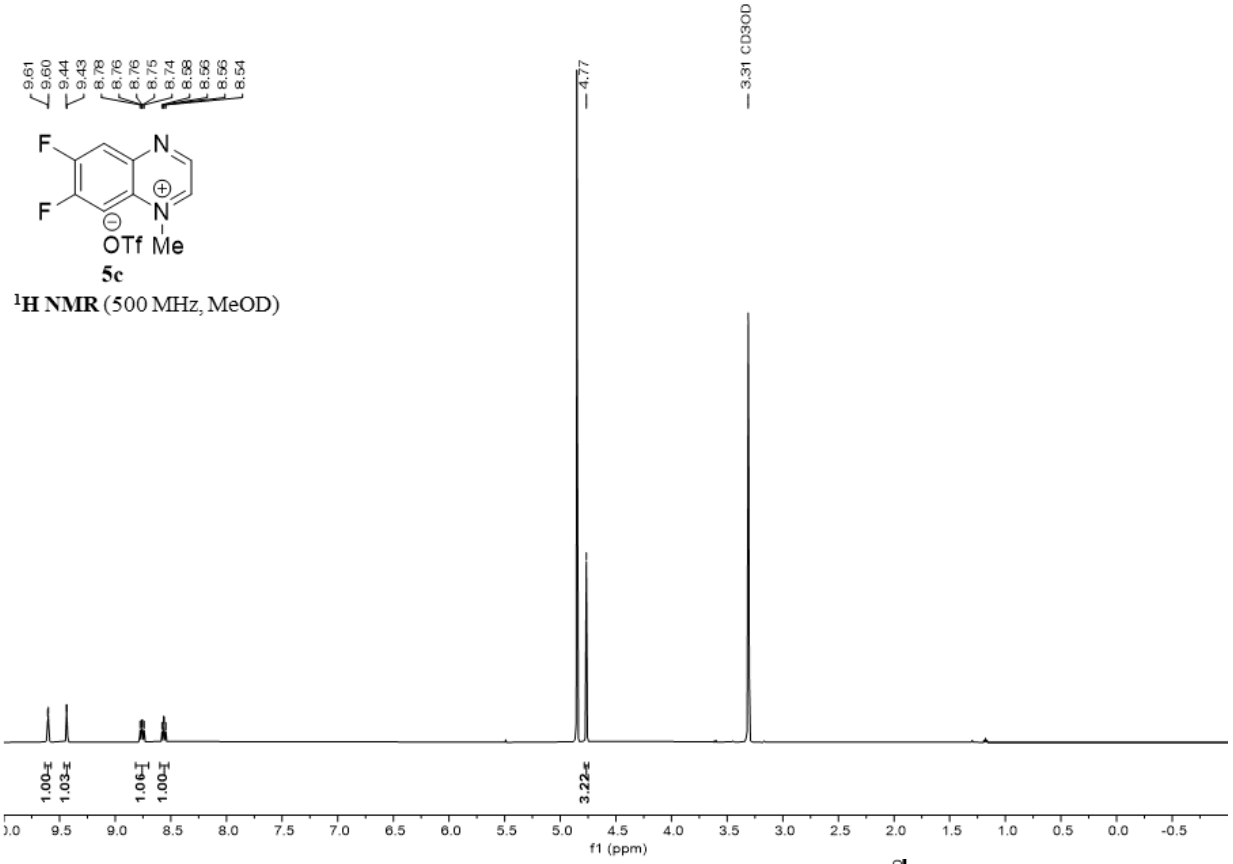
5b

^{13}C NMR (126 MHz, MeOD)



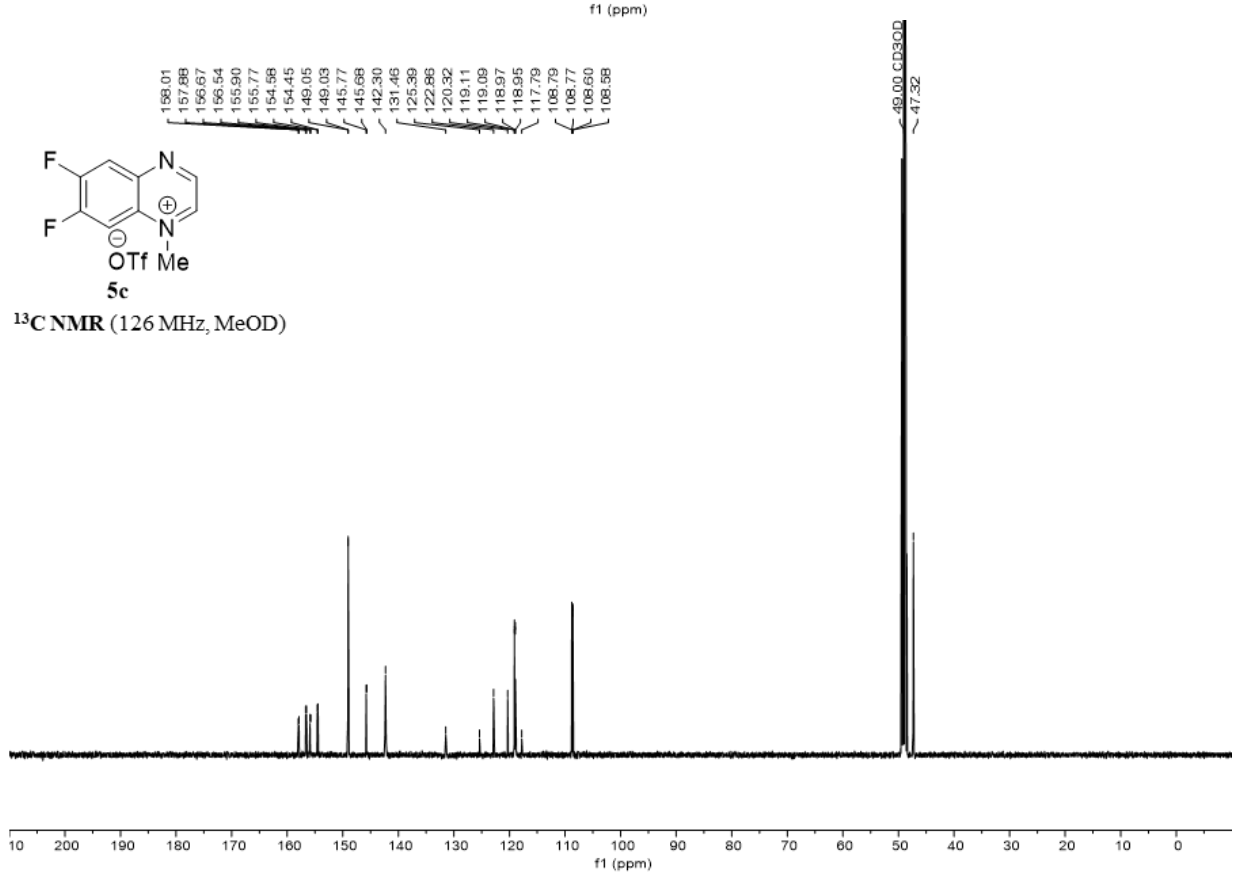
5b

^{19}F NMR (471 MHz, MeOD)



5c

^{1}H NMR (500 MHz, MeOD)



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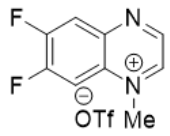

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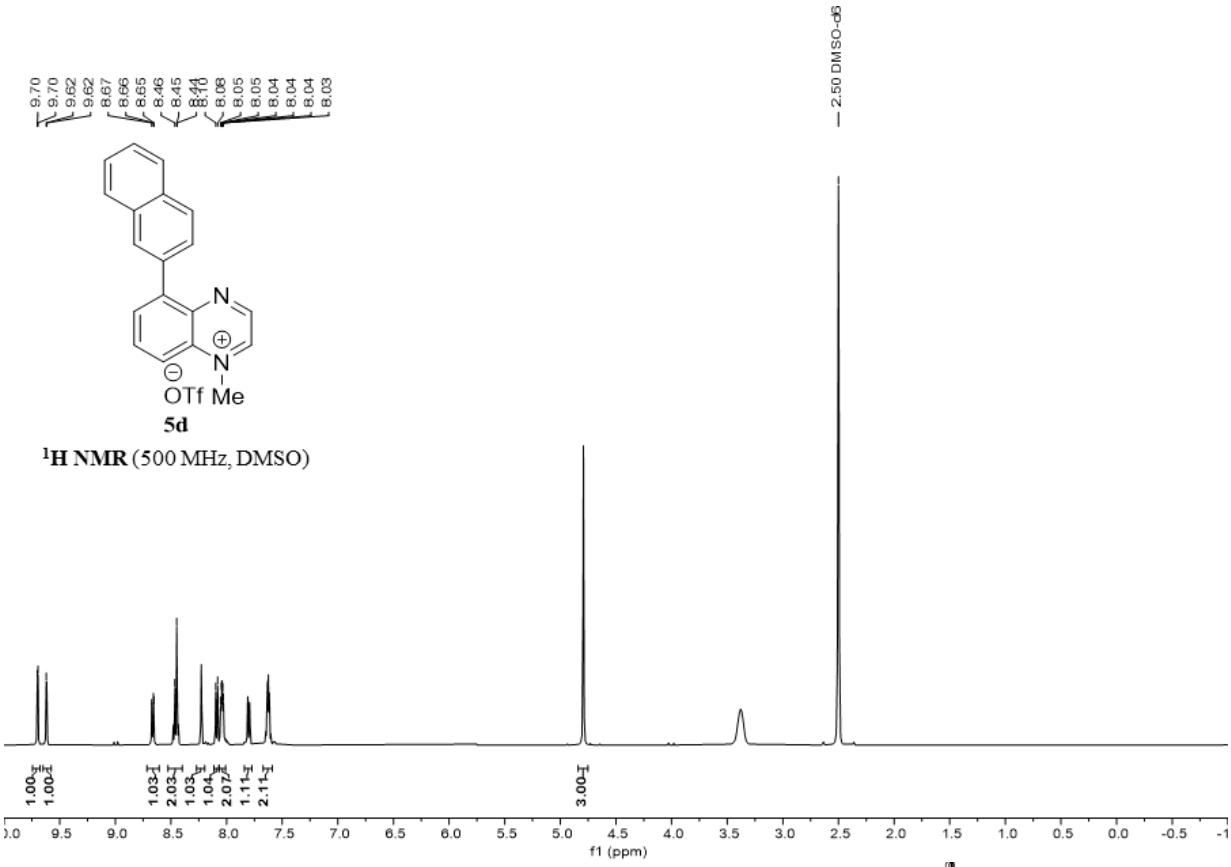
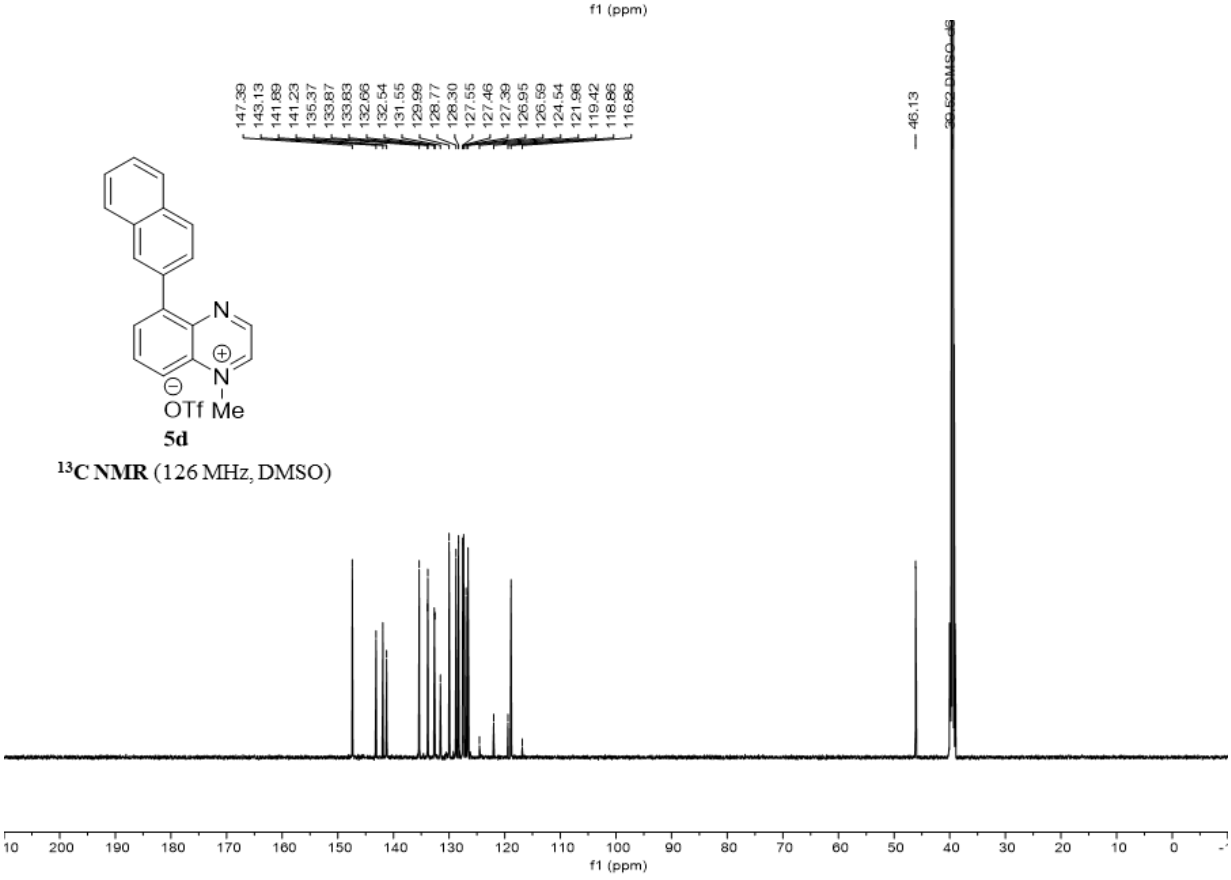


5d

^{1}H NMR (500 MHz, DMSO)



5d

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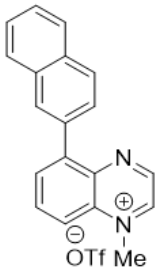
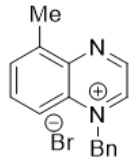


5d

^{19}F NMR (471 MHz, MeOD)



S6

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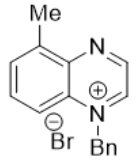

S6

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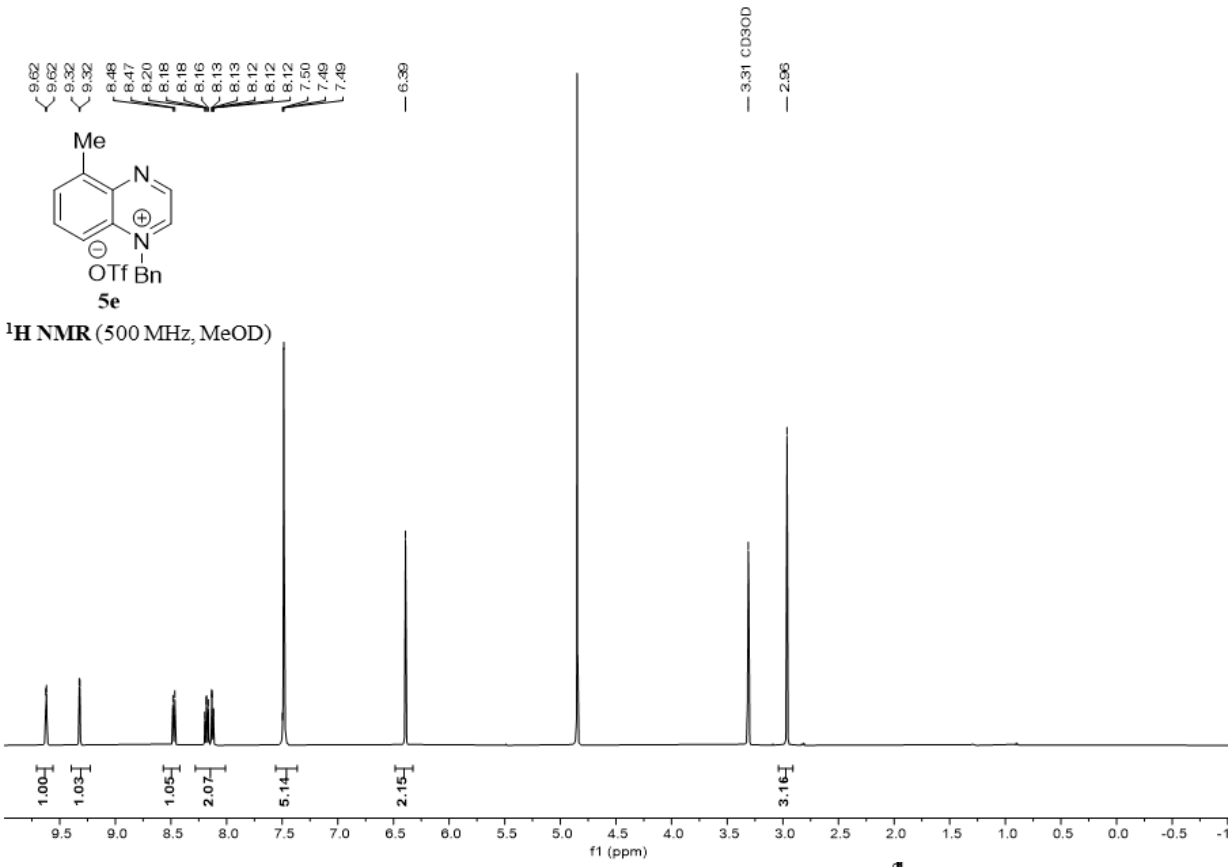

5e

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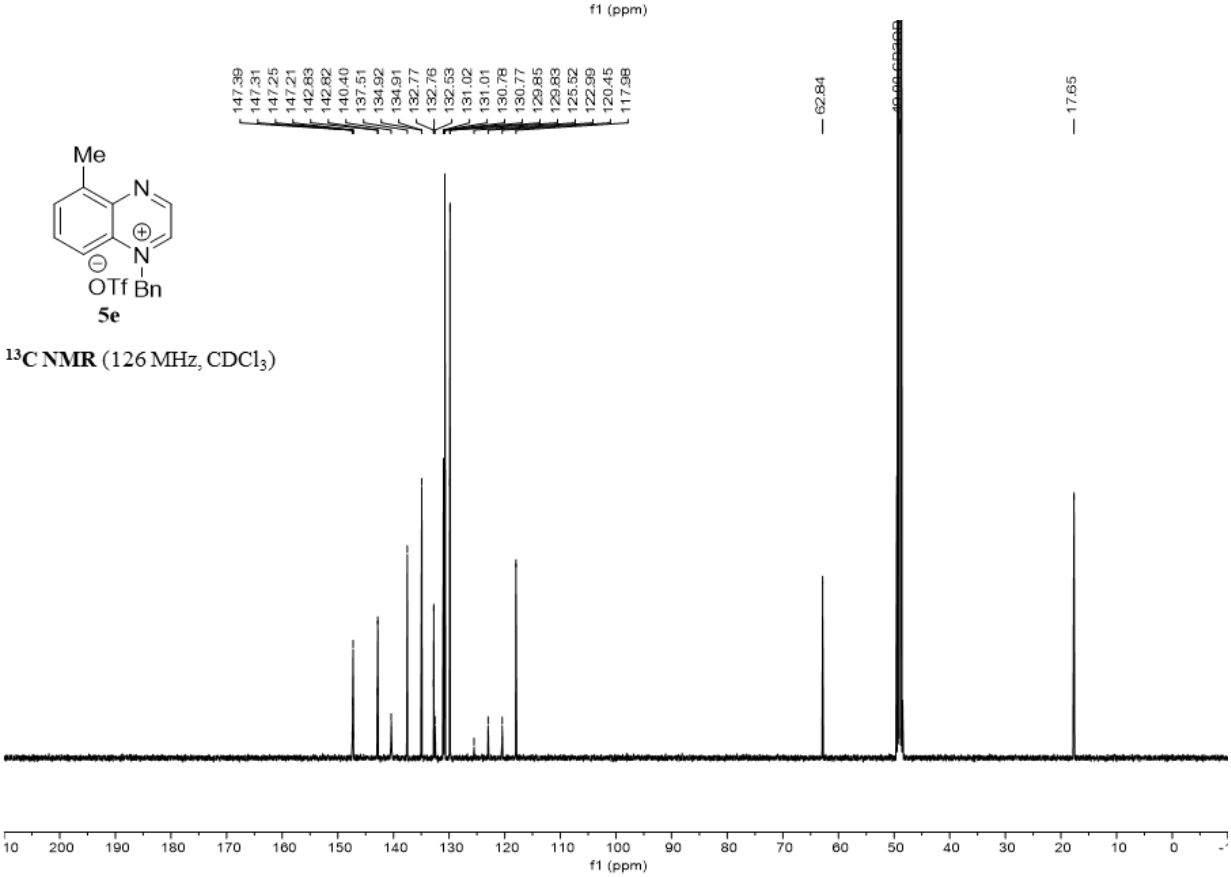
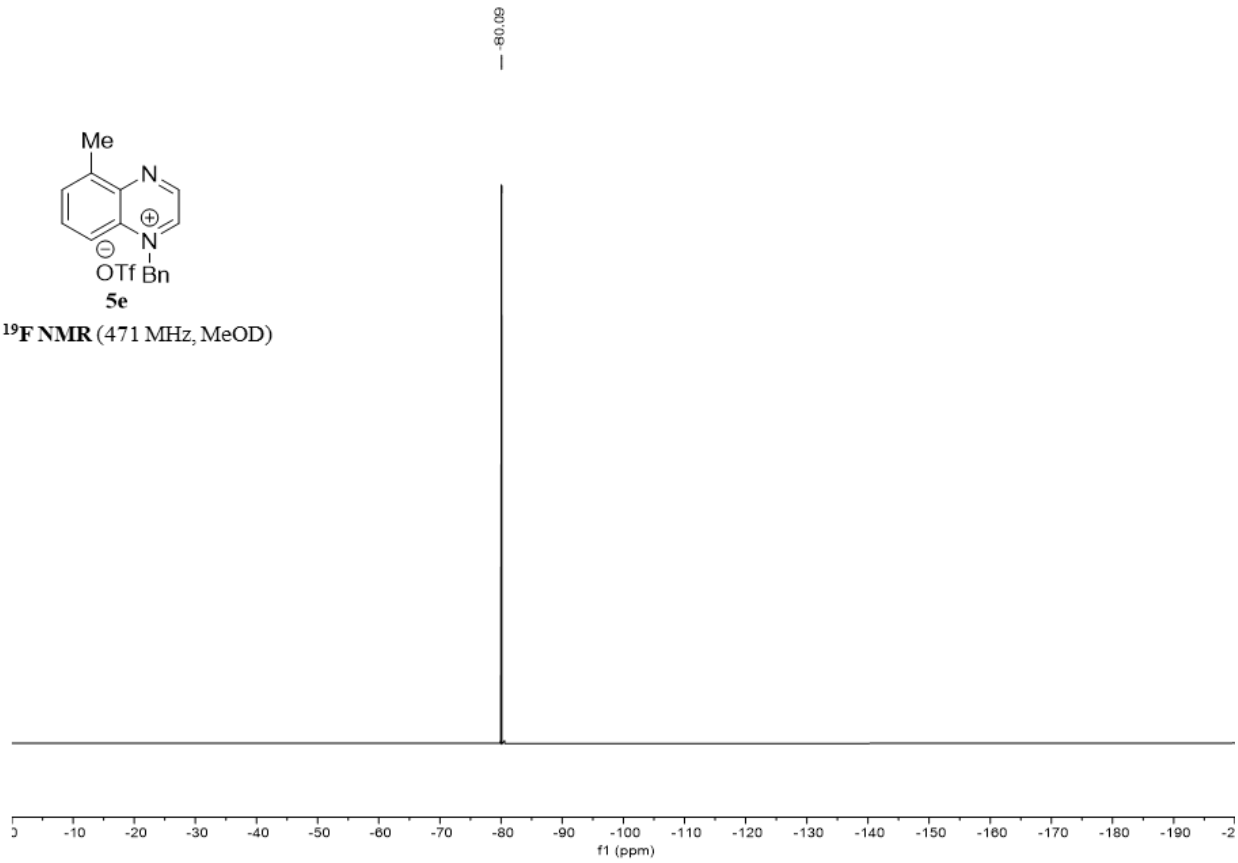


5e

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

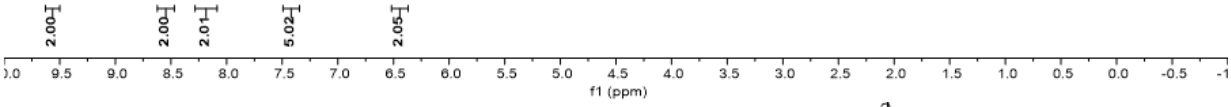


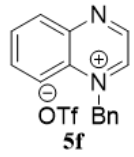
5e

^{19}F NMR (471 MHz, MeOD)

5f

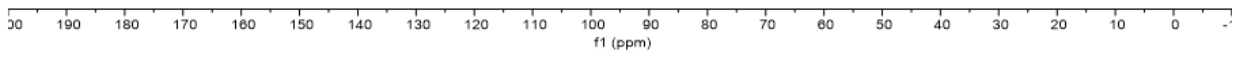
^{1}H NMR (500 MHz, $CDCl_3$)

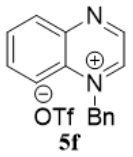




5f

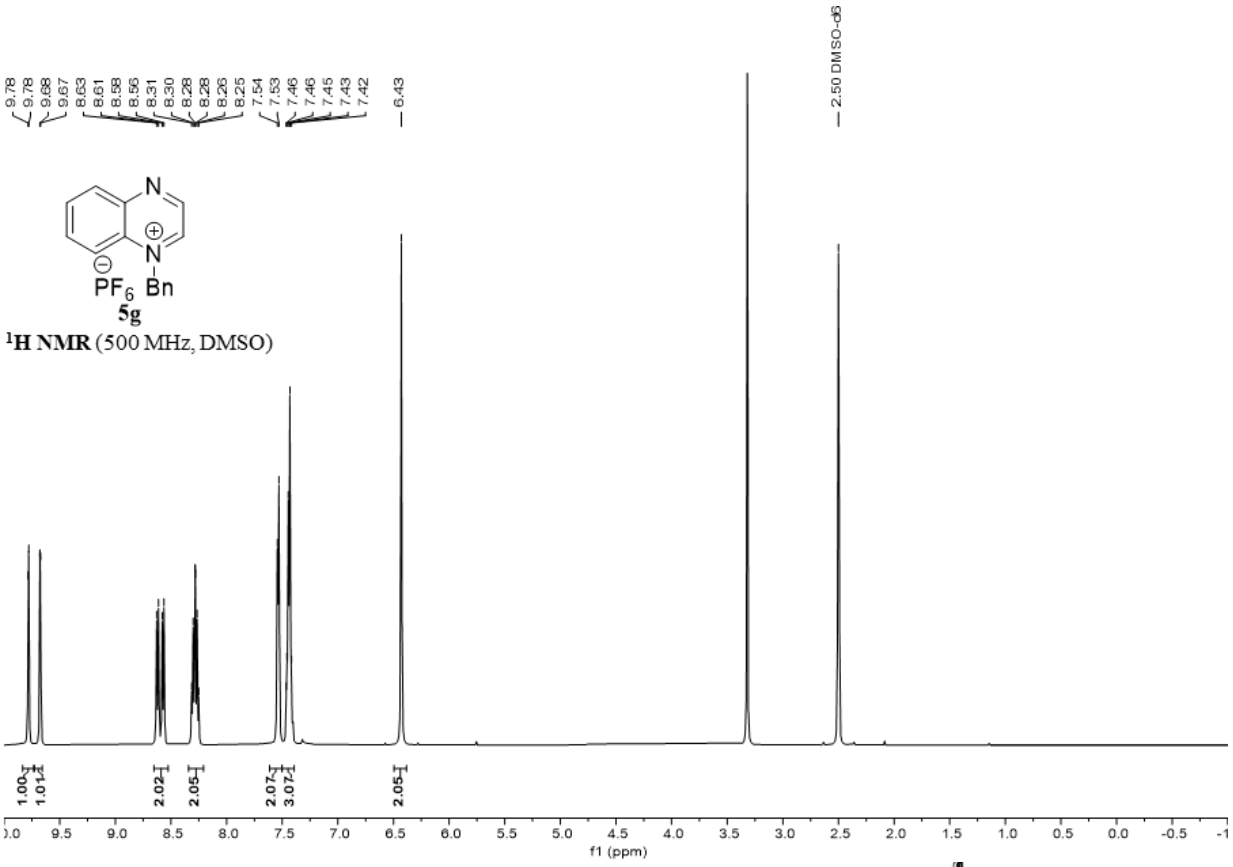
^{13}C NMR (126 MHz, MeOD)





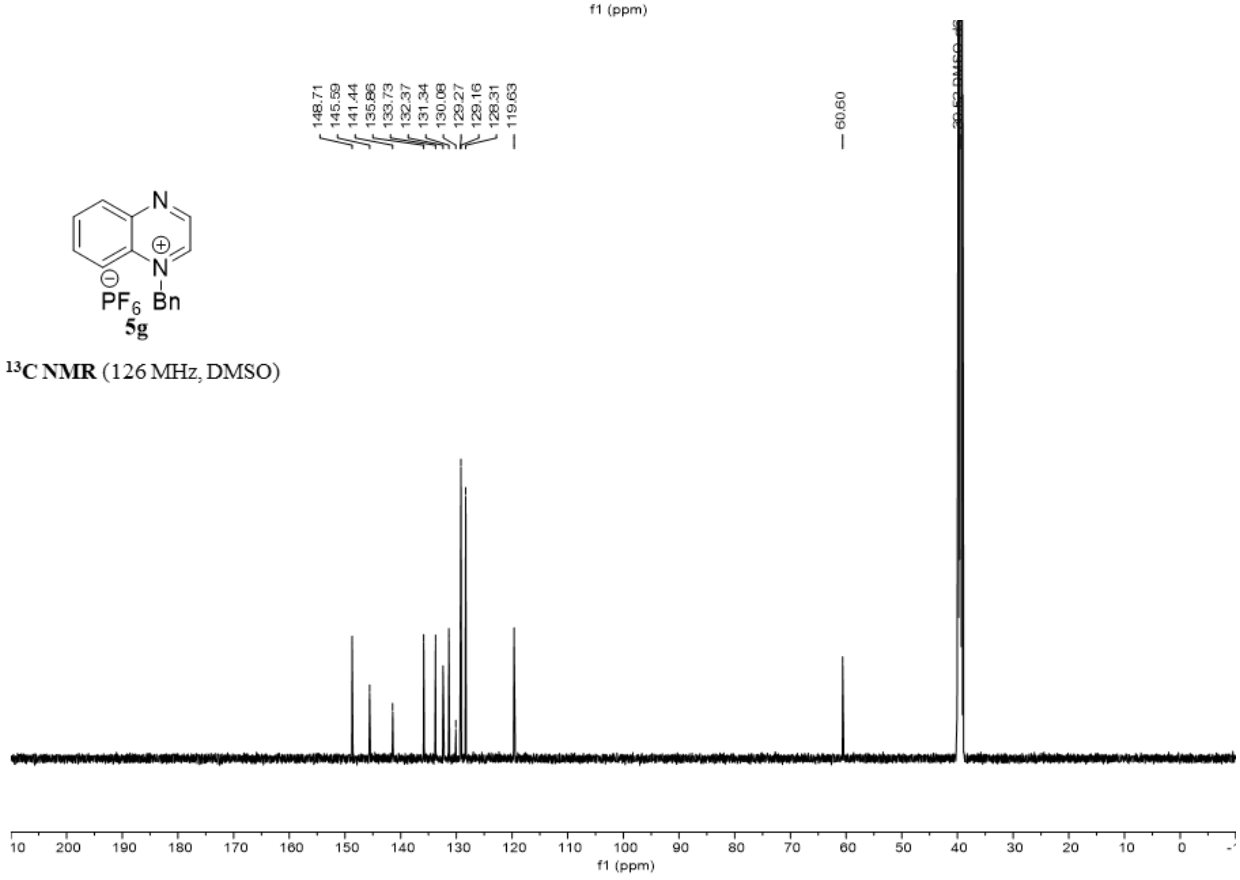
5f

^{19}F NMR (471 MHz, $CDCl_3$)



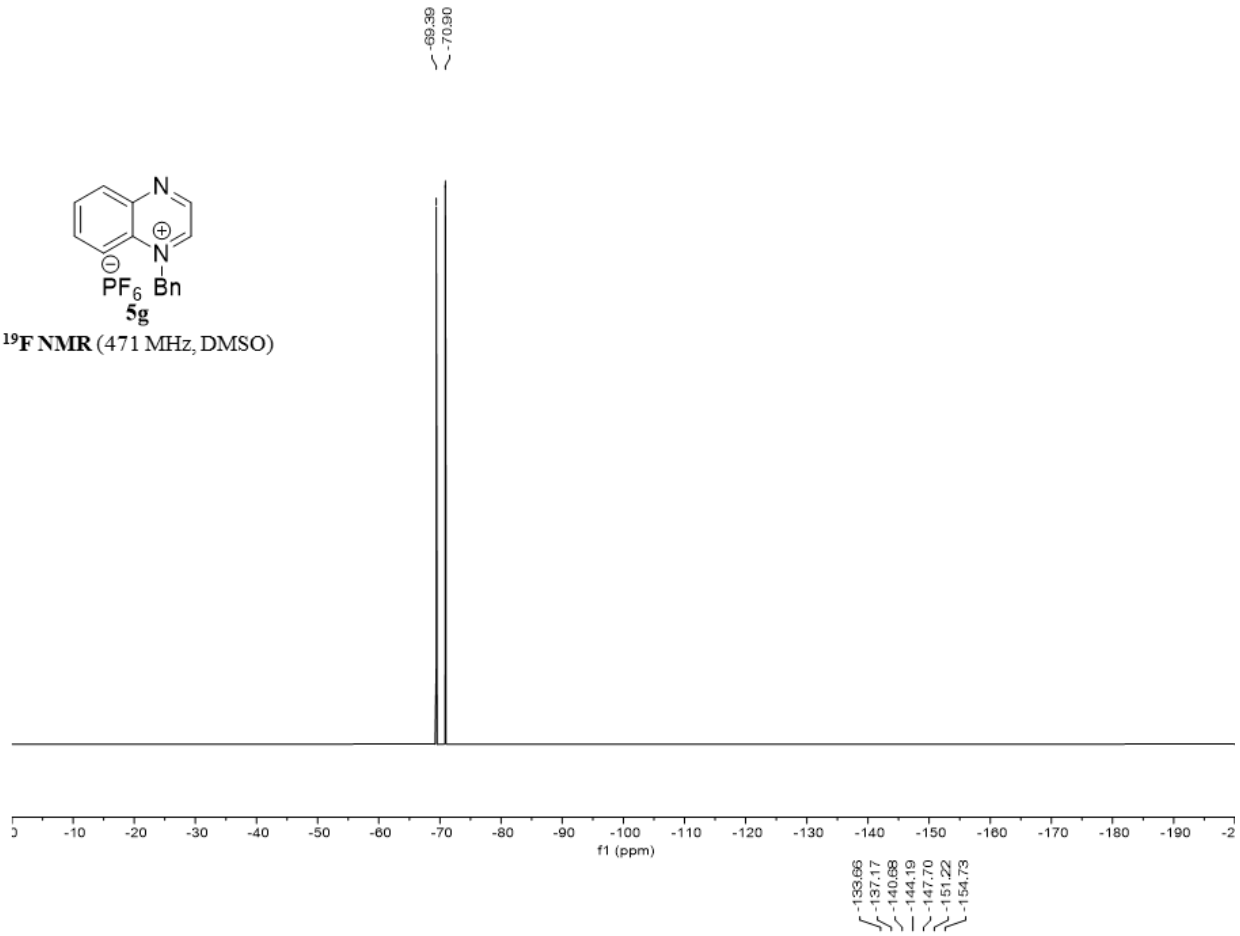
5g

^{1}H NMR (500 MHz, DMSO)

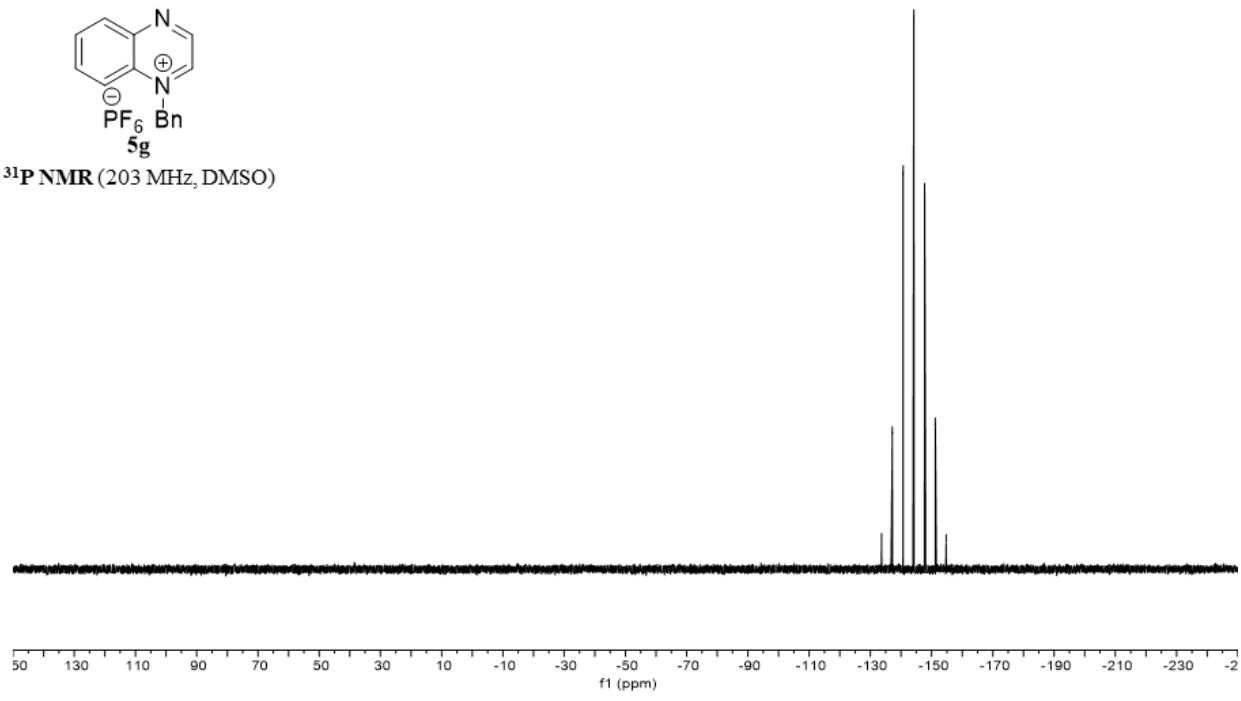


5g

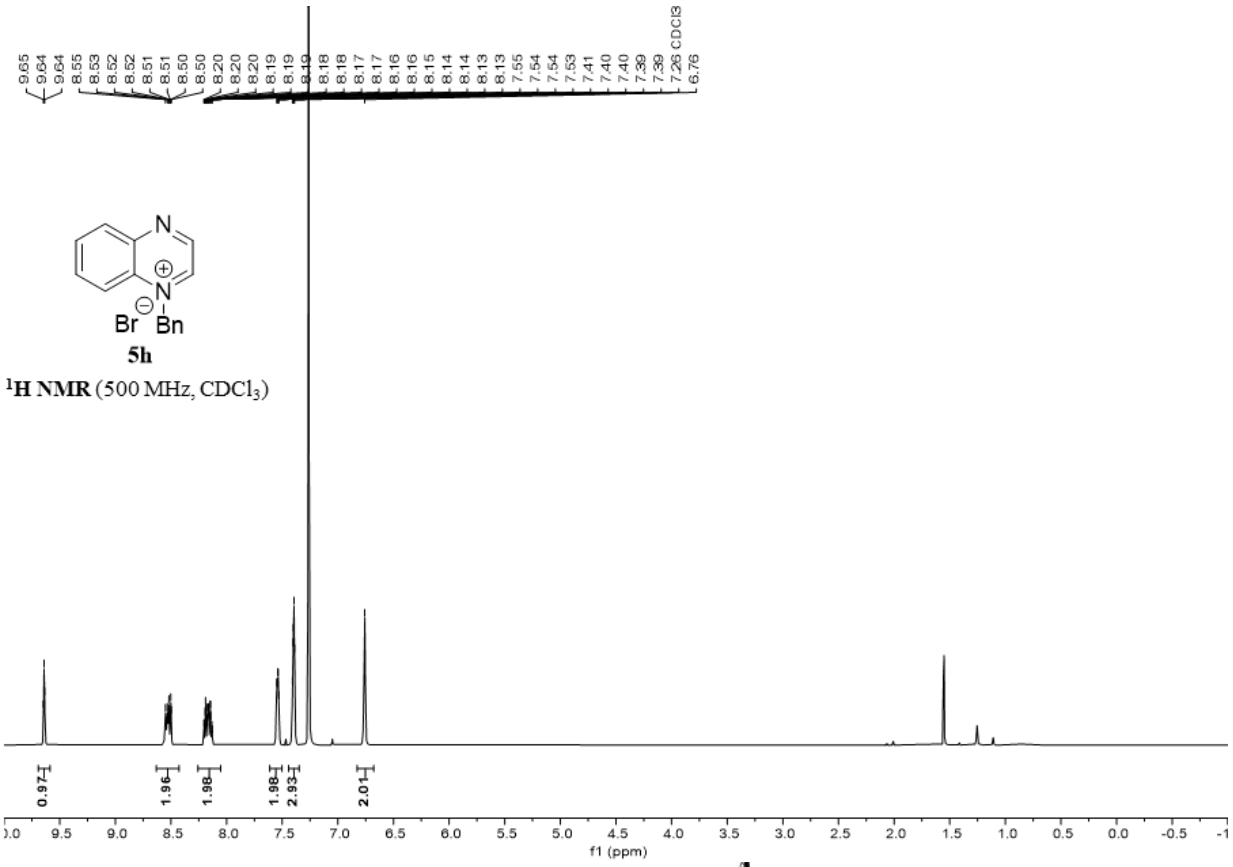
^{13}C NMR (126 MHz, DMSO)



^{19}F NMR (471 MHz, DMSO)

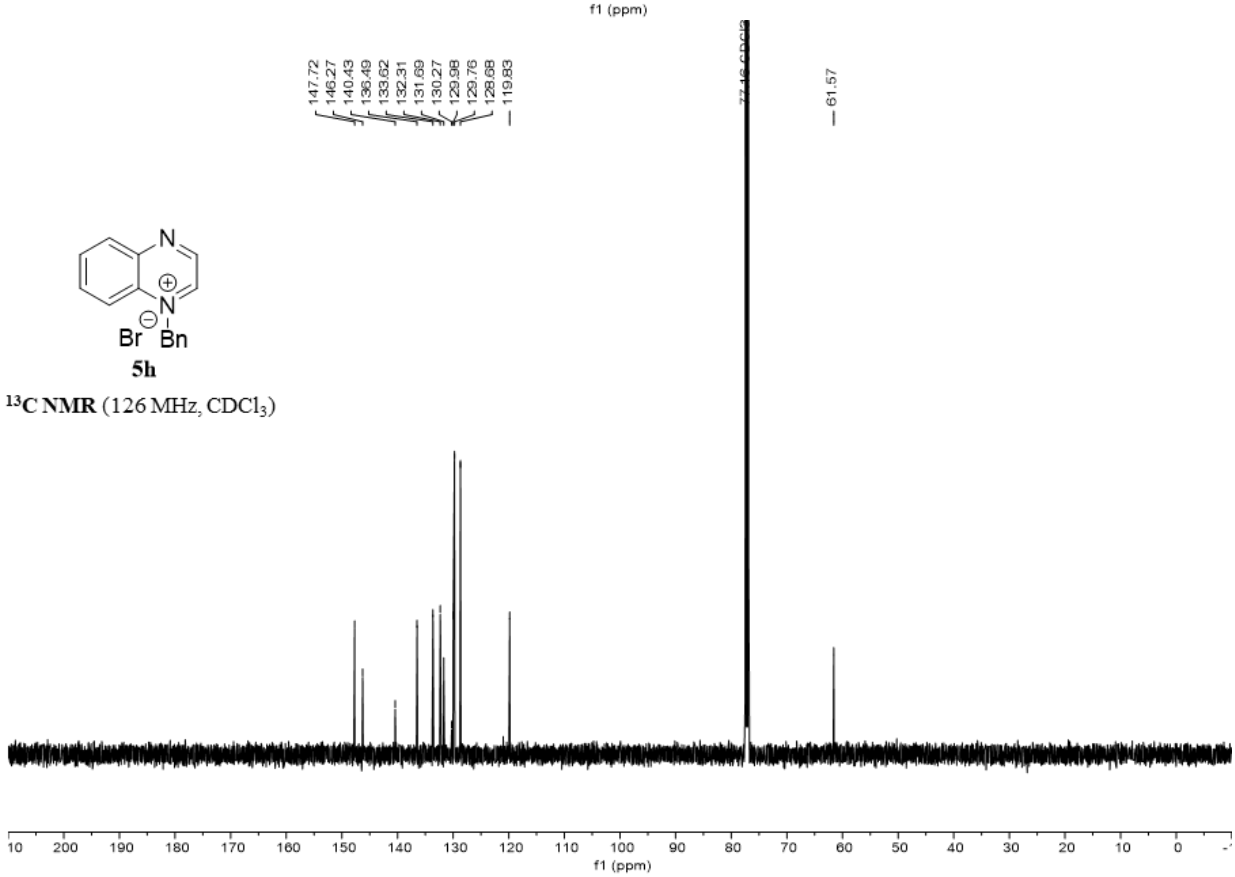


^{31}P NMR (203 MHz, DMSO)



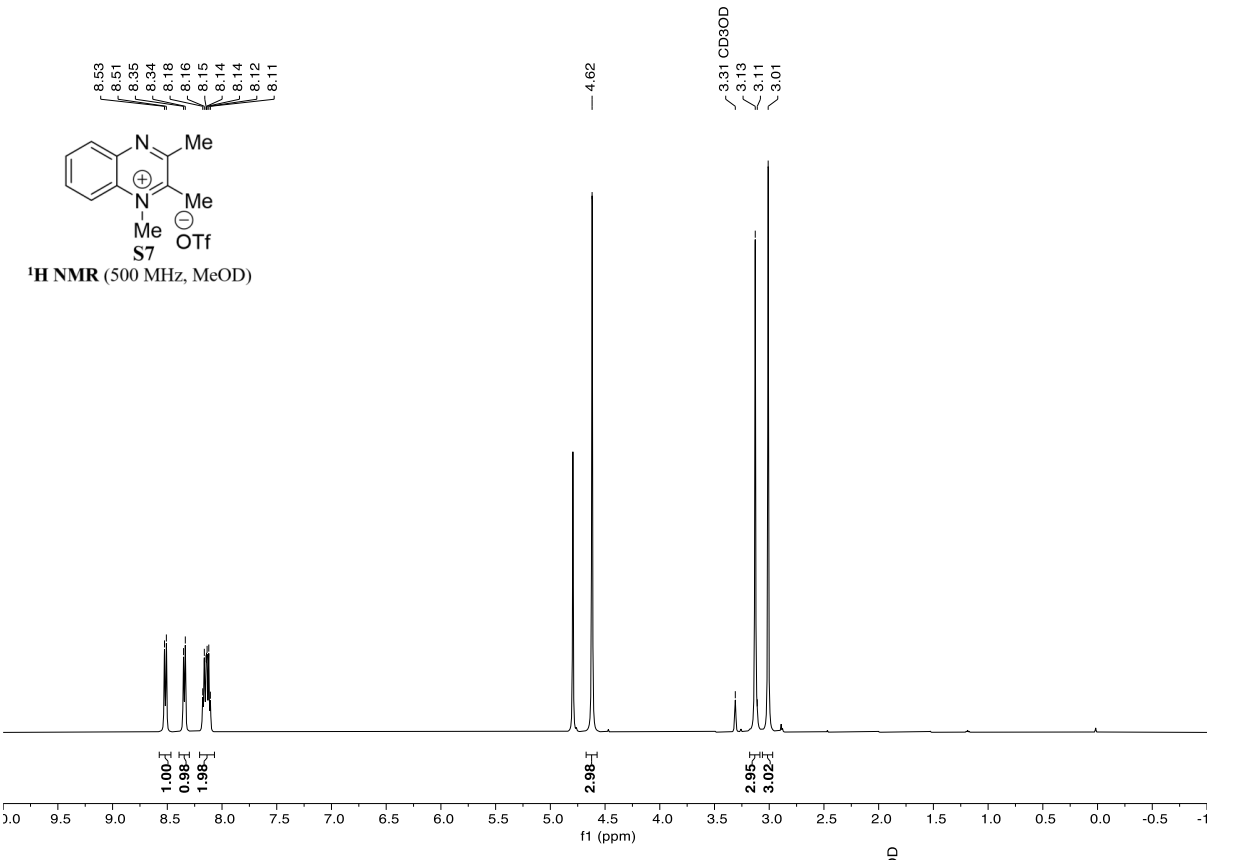
5h

^{1}H NMR (500 MHz, $CDCl_3$)



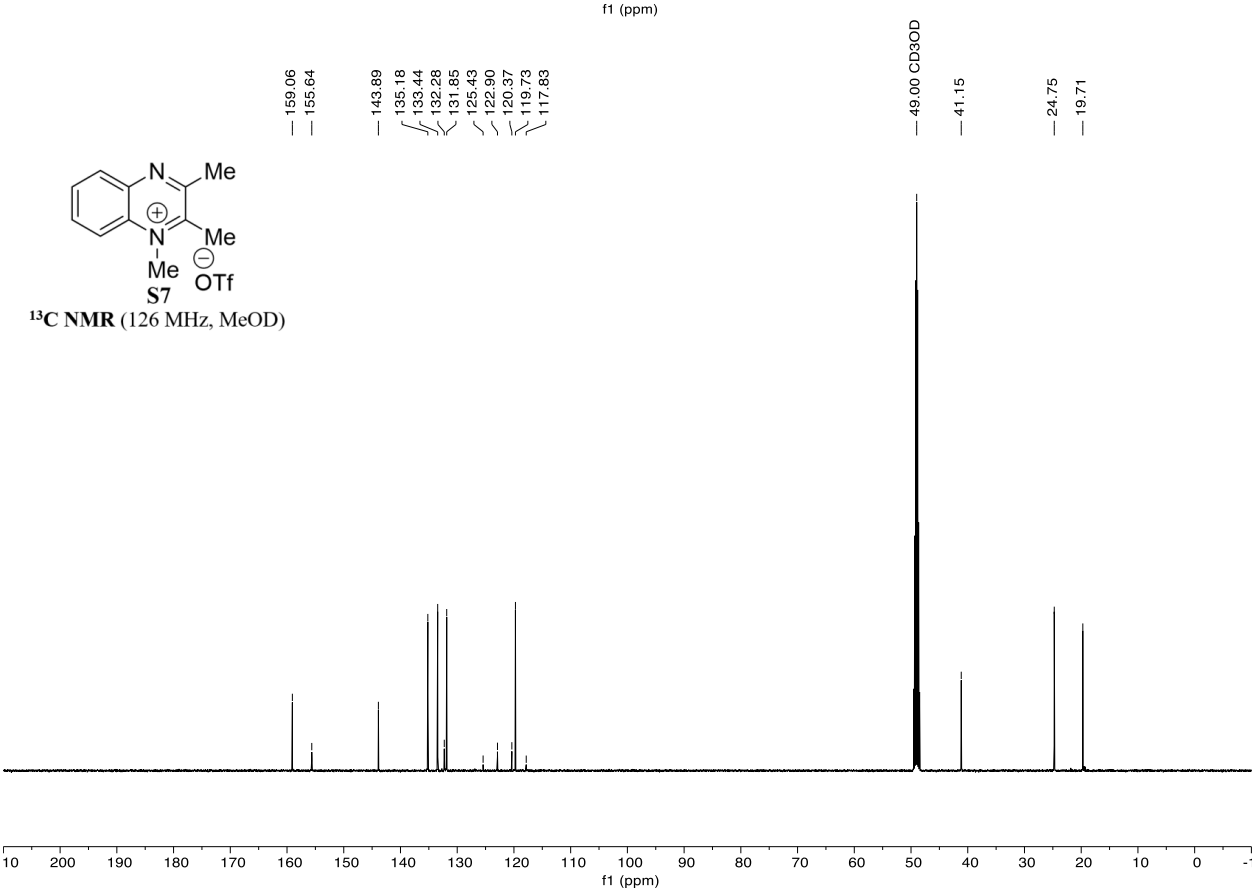
5h

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



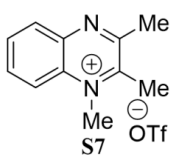
S7

^{1}H NMR (500 MHz, MeOD)



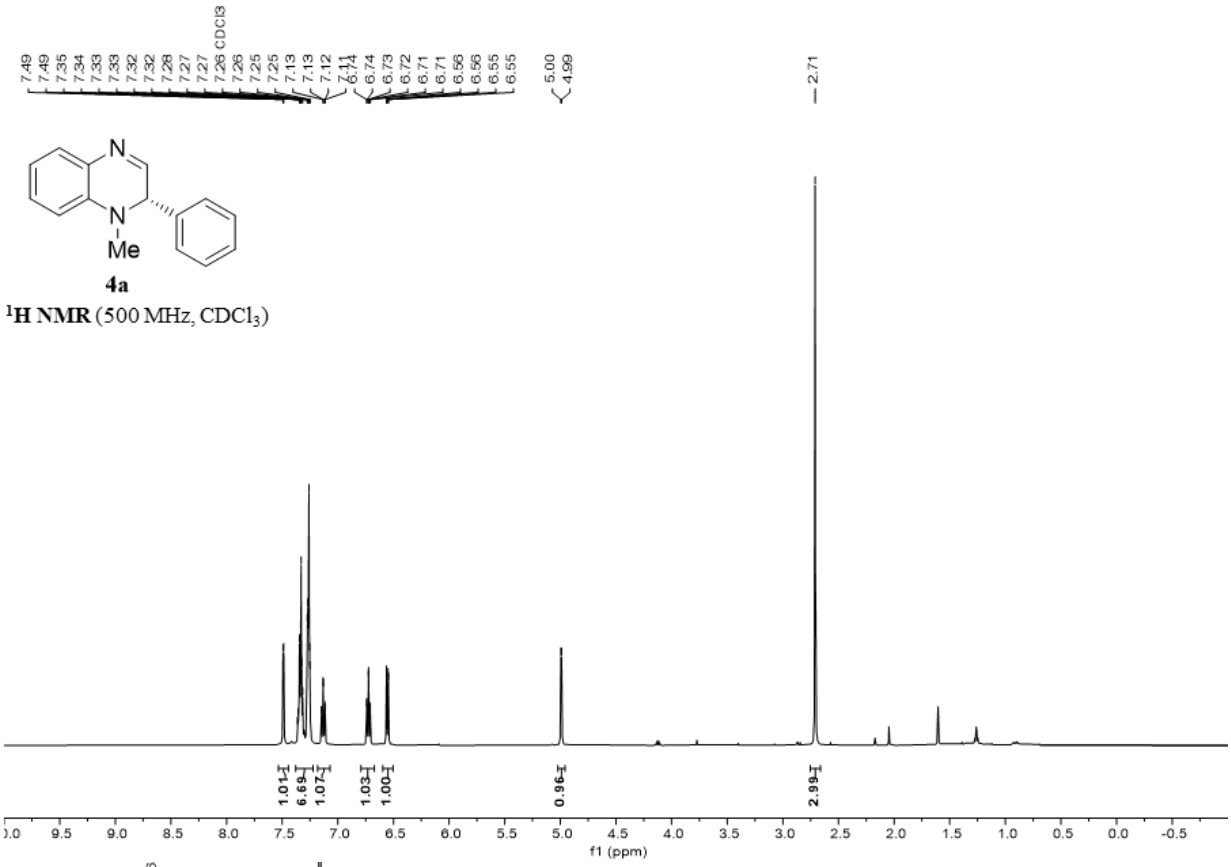
S7

^{13}C NMR (126 MHz, MeOD)



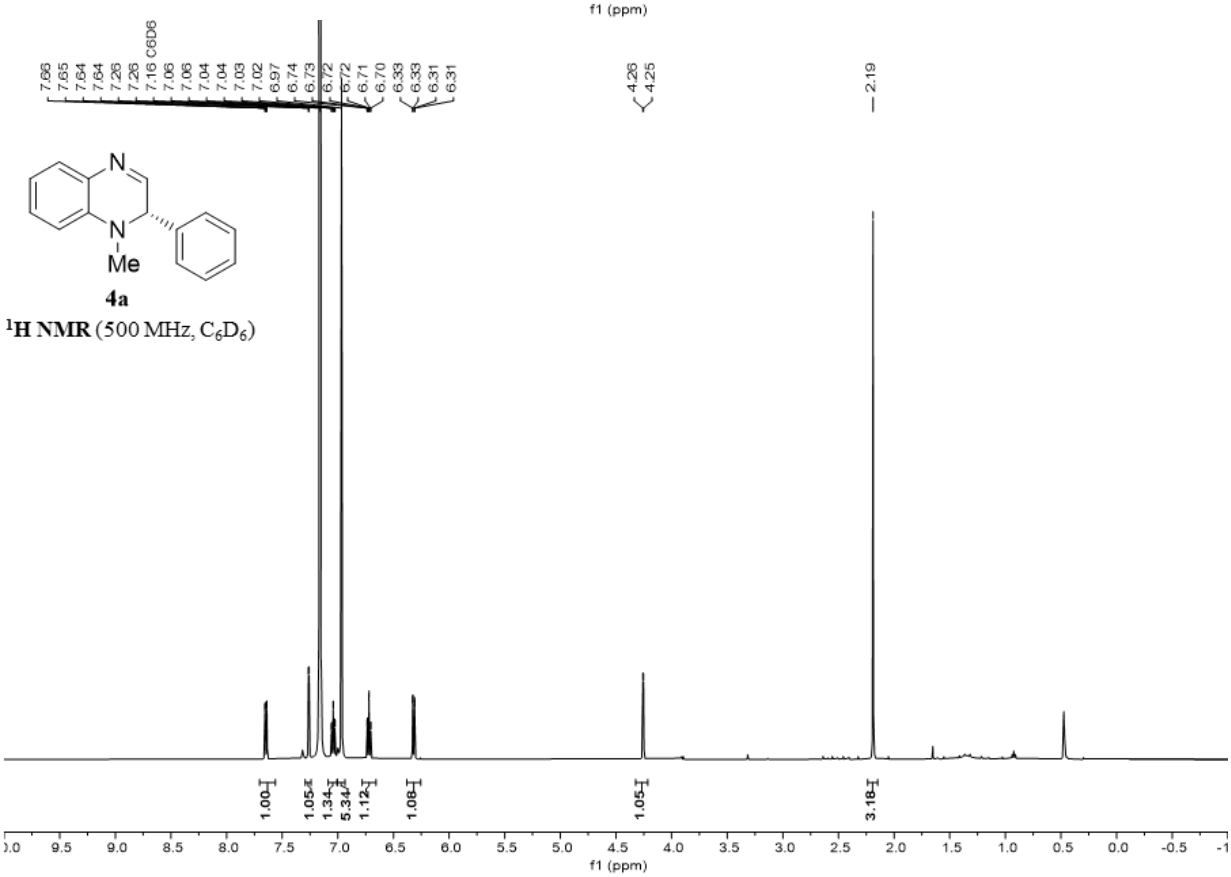
S7

^{19}F NMR (471 MHz, MeOD)



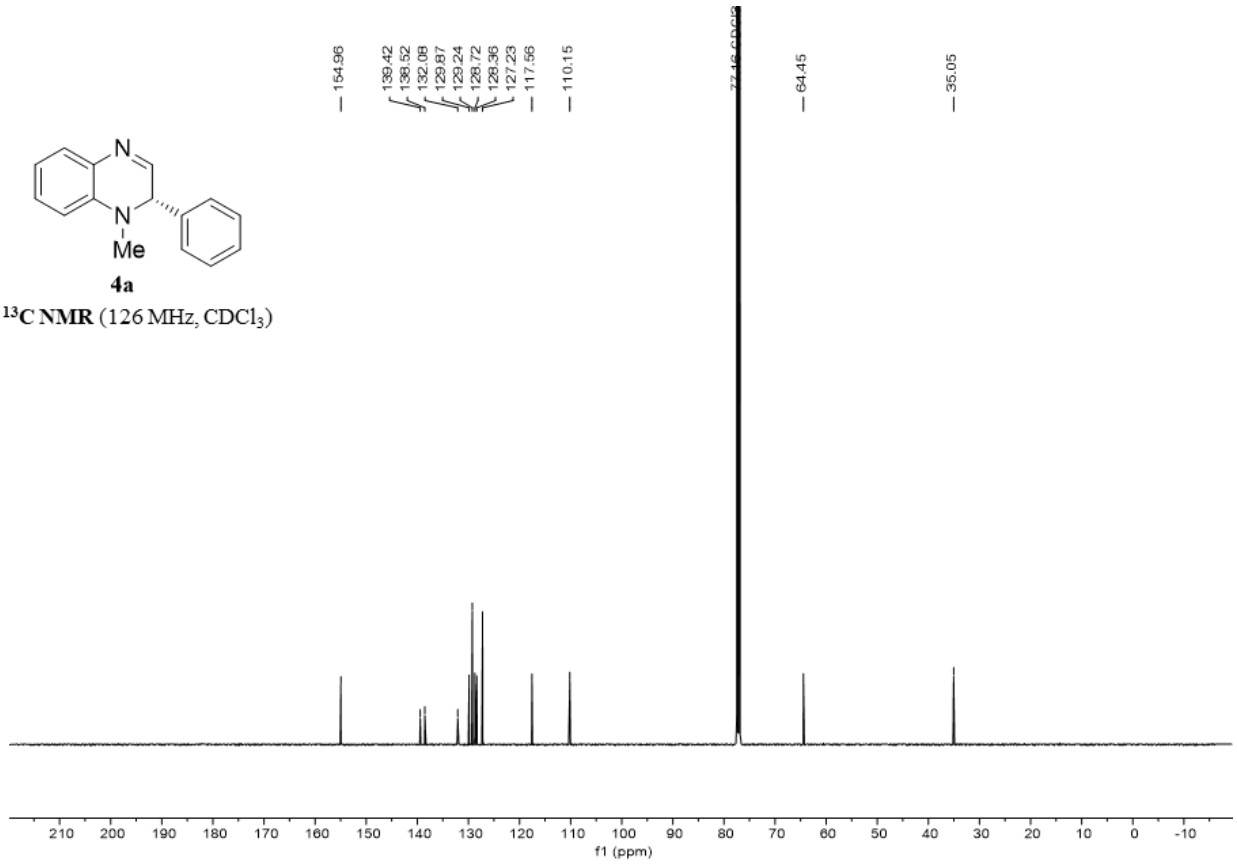
4a

^{1}H NMR (500 MHz, $CDCl_3$)



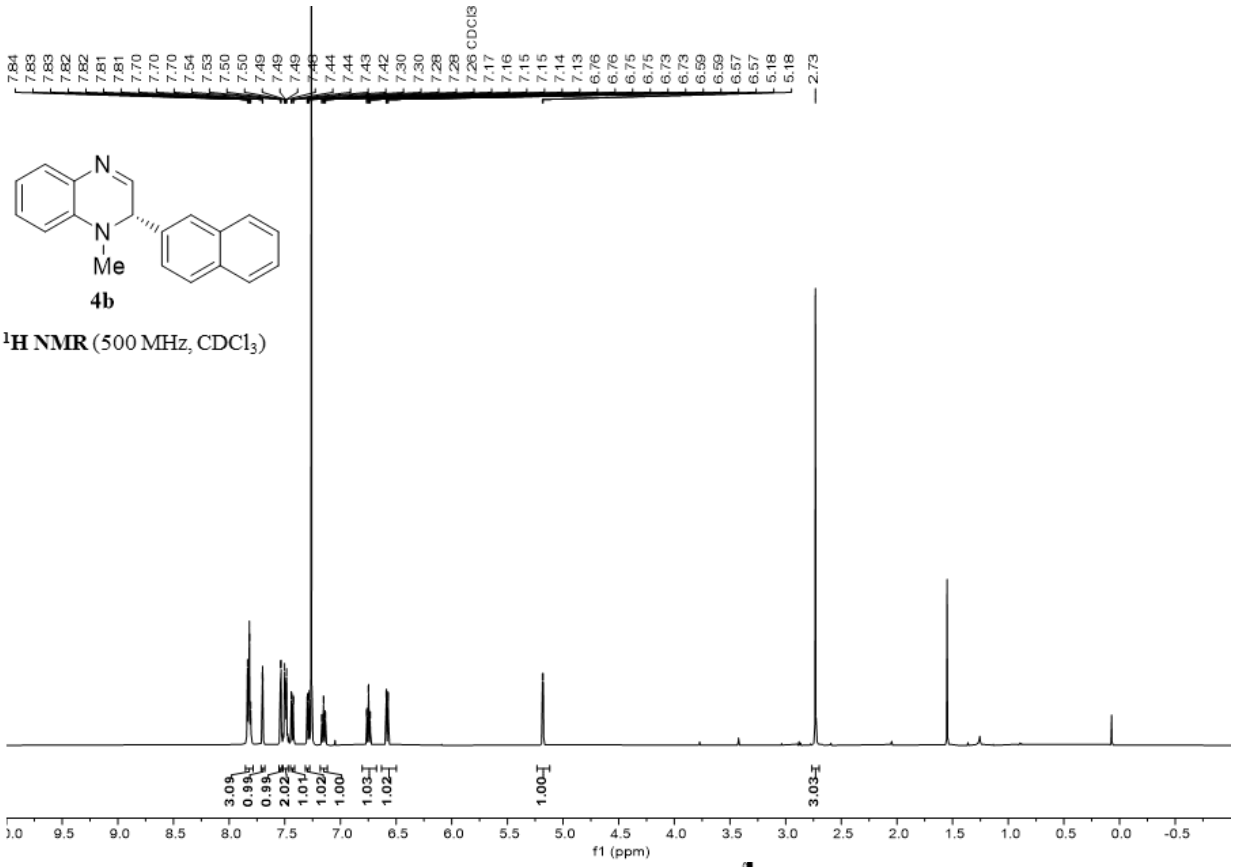
4a

^{1}H NMR (500 MHz, C_6D_6)



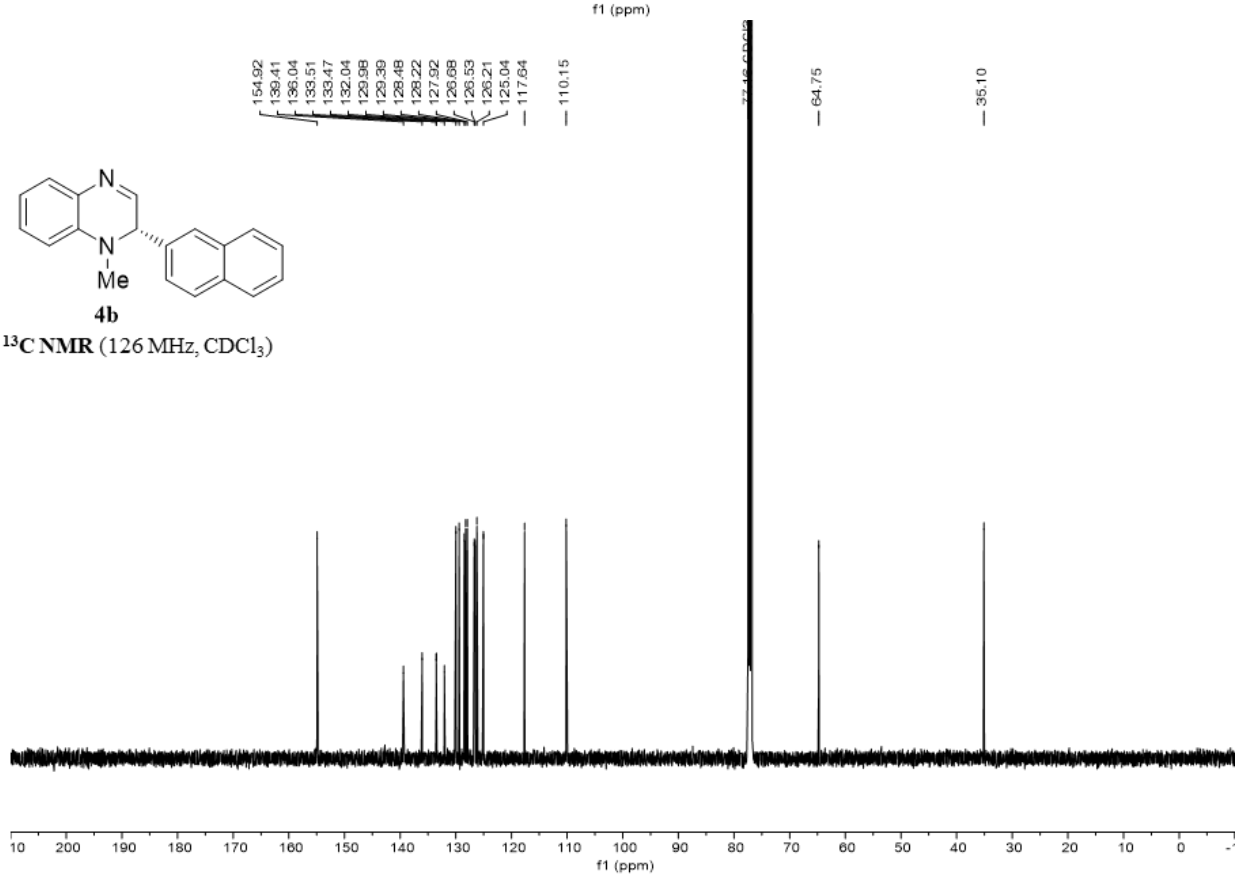
4a

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



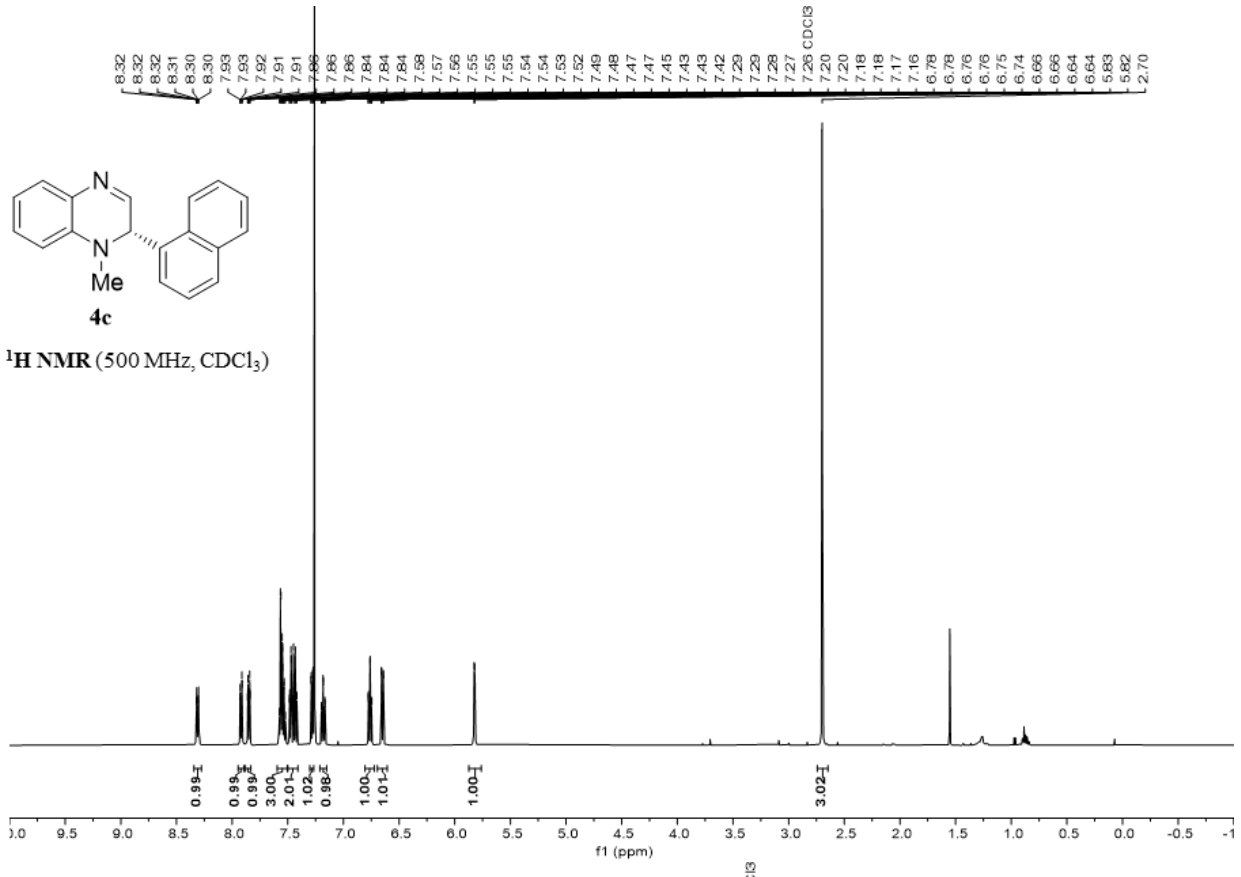
4b

^{1}H NMR (500 MHz, $CDCl_3$)



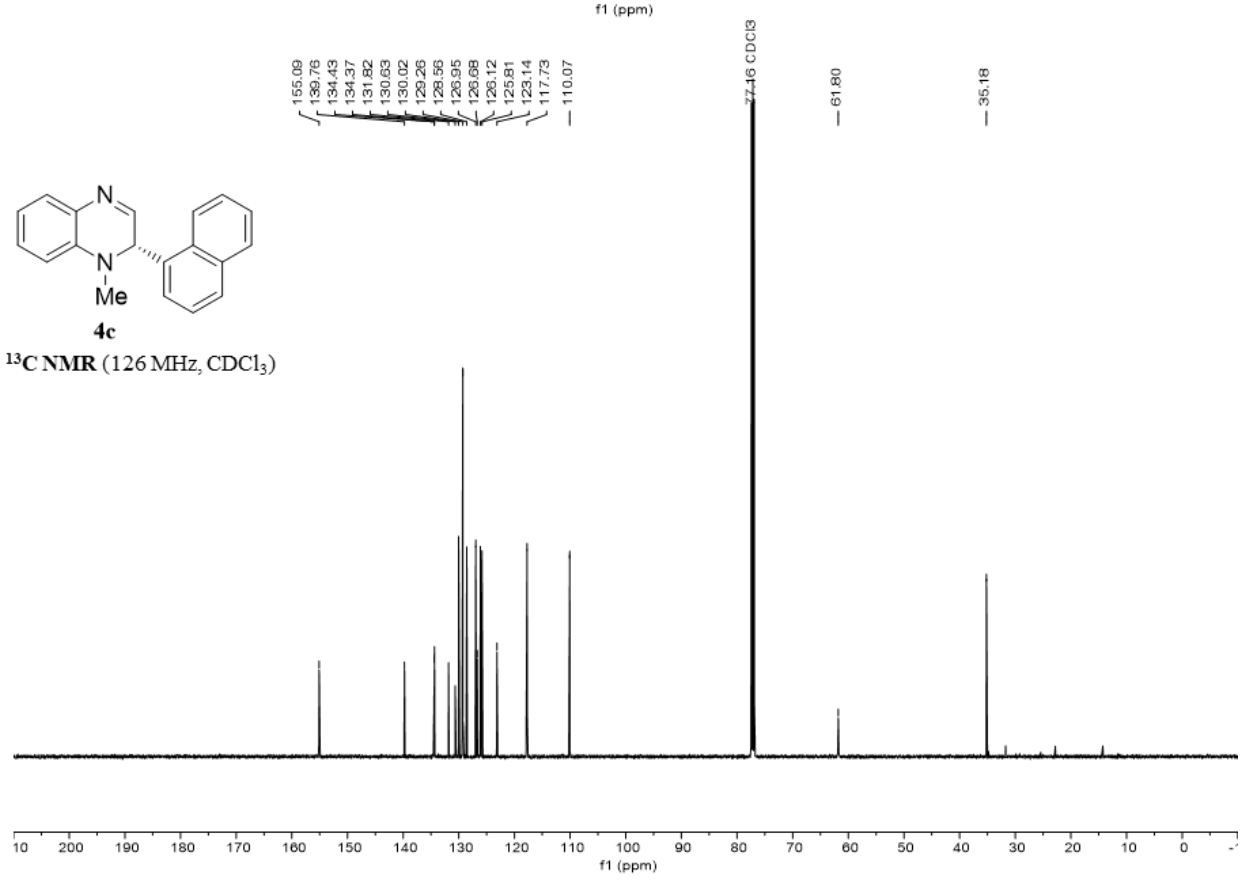
4b

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



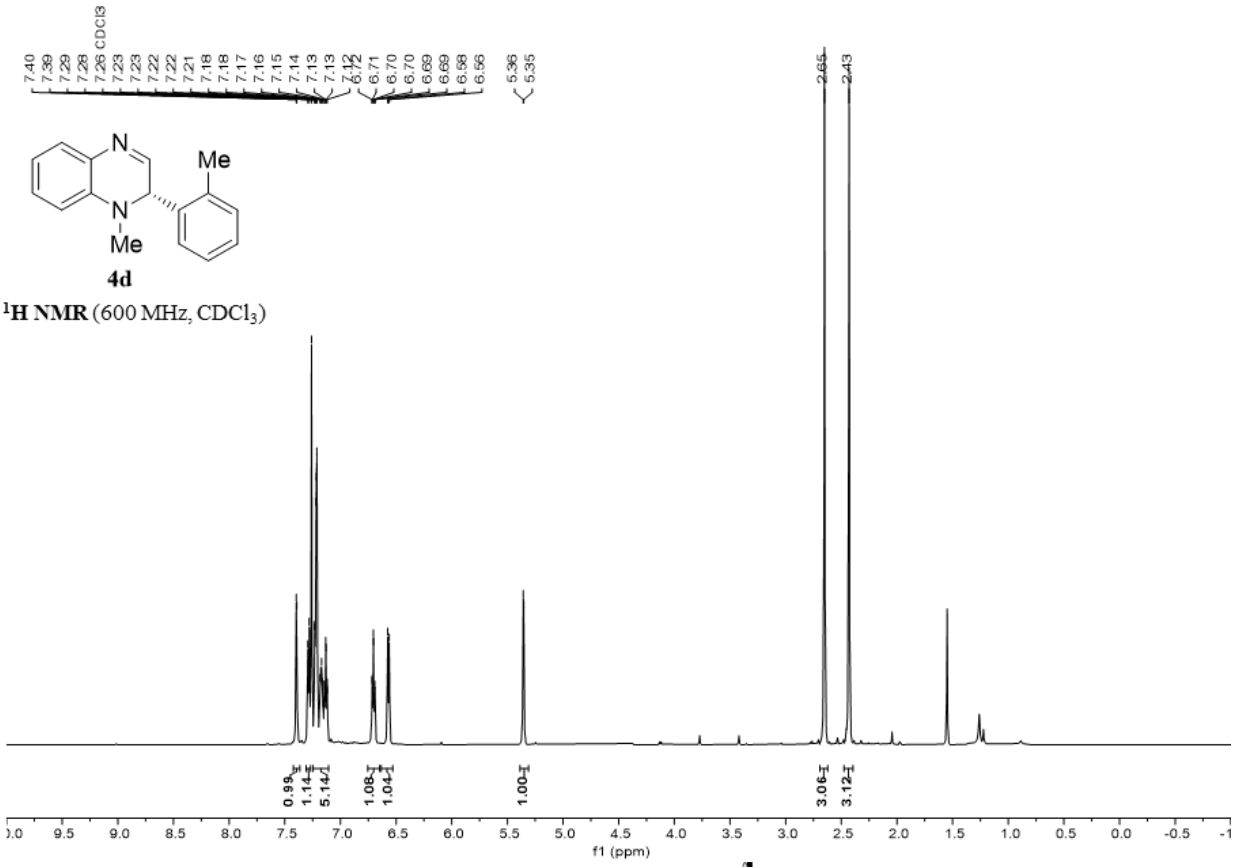
4c

^{1}H NMR (500 MHz, $CDCl_3$)



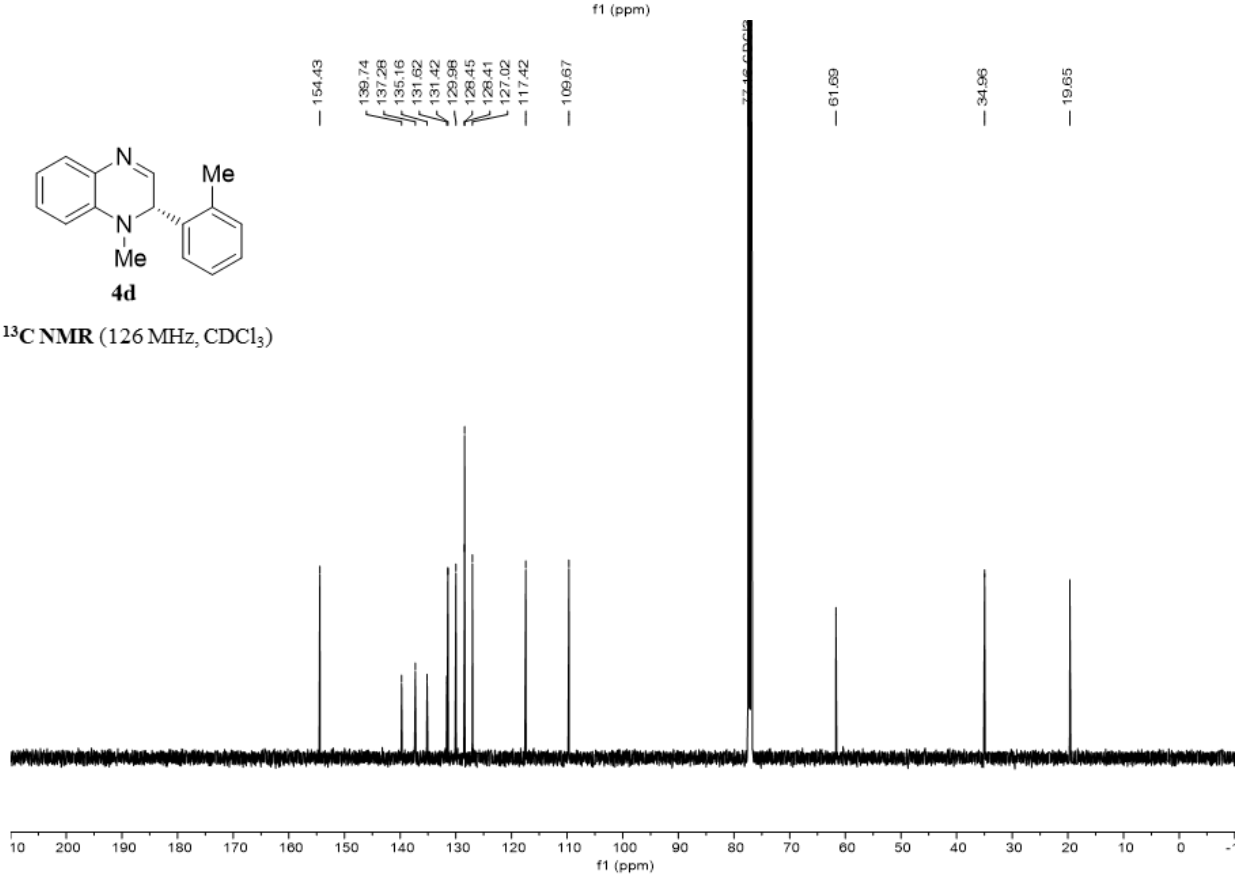
4c

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



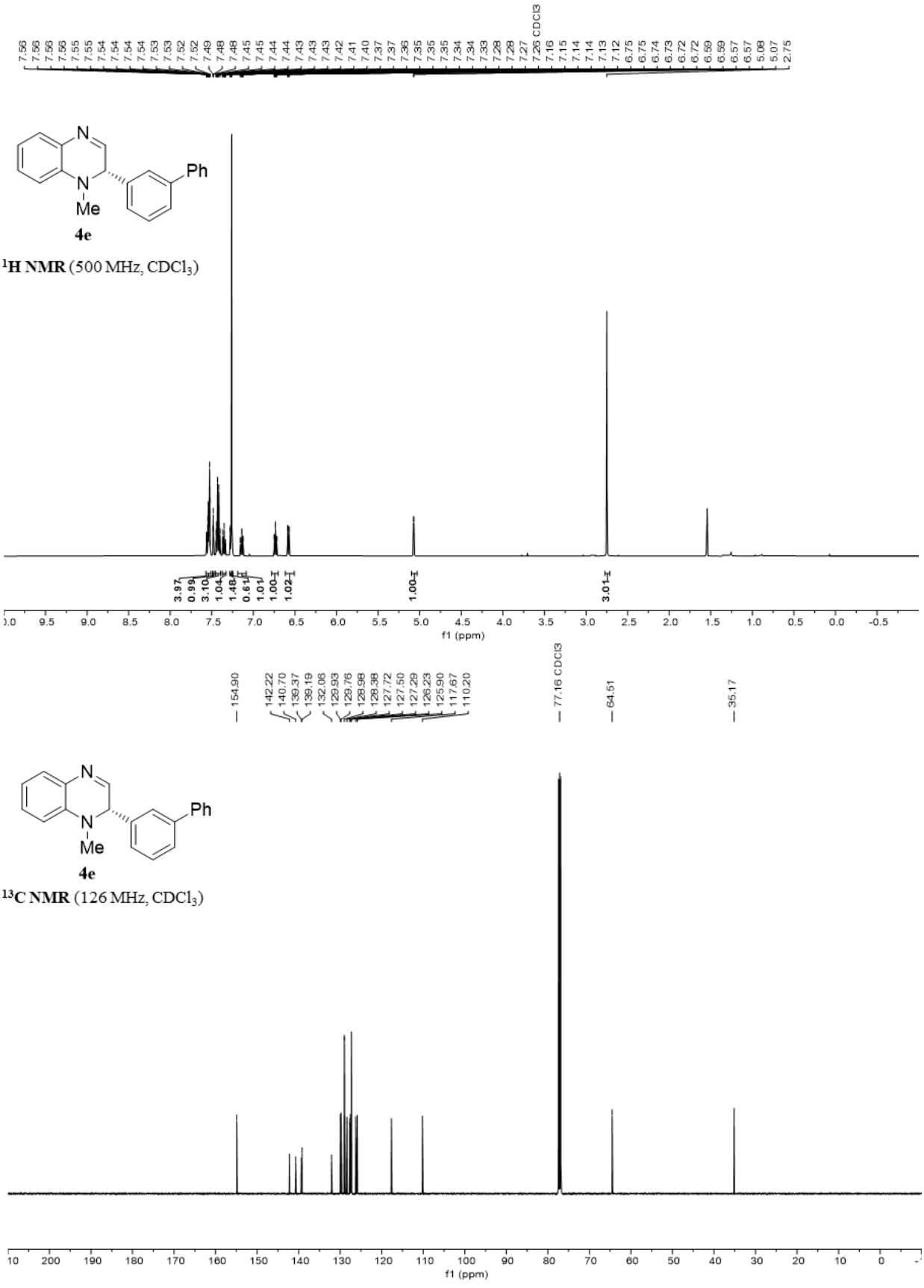
4d

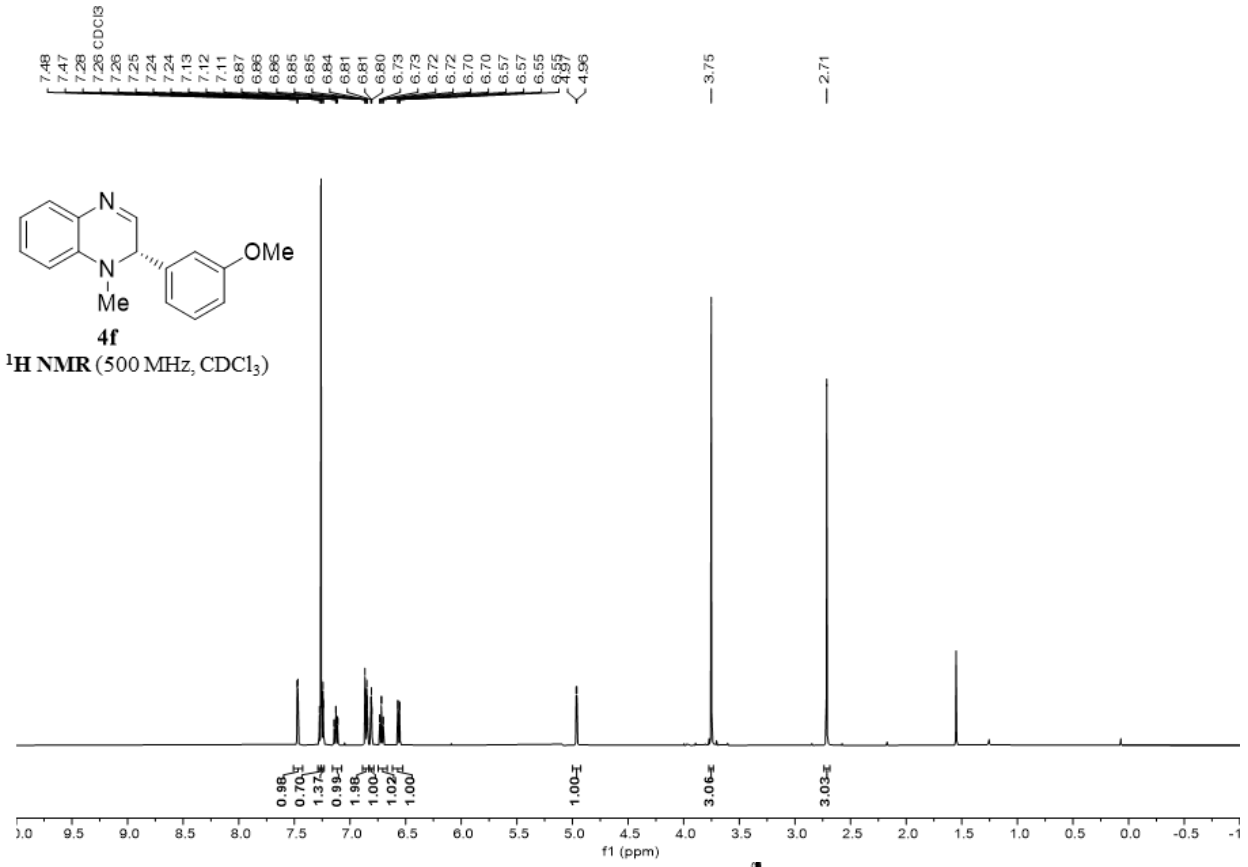
^{1}H NMR (600 MHz, $CDCl_3$)



4d

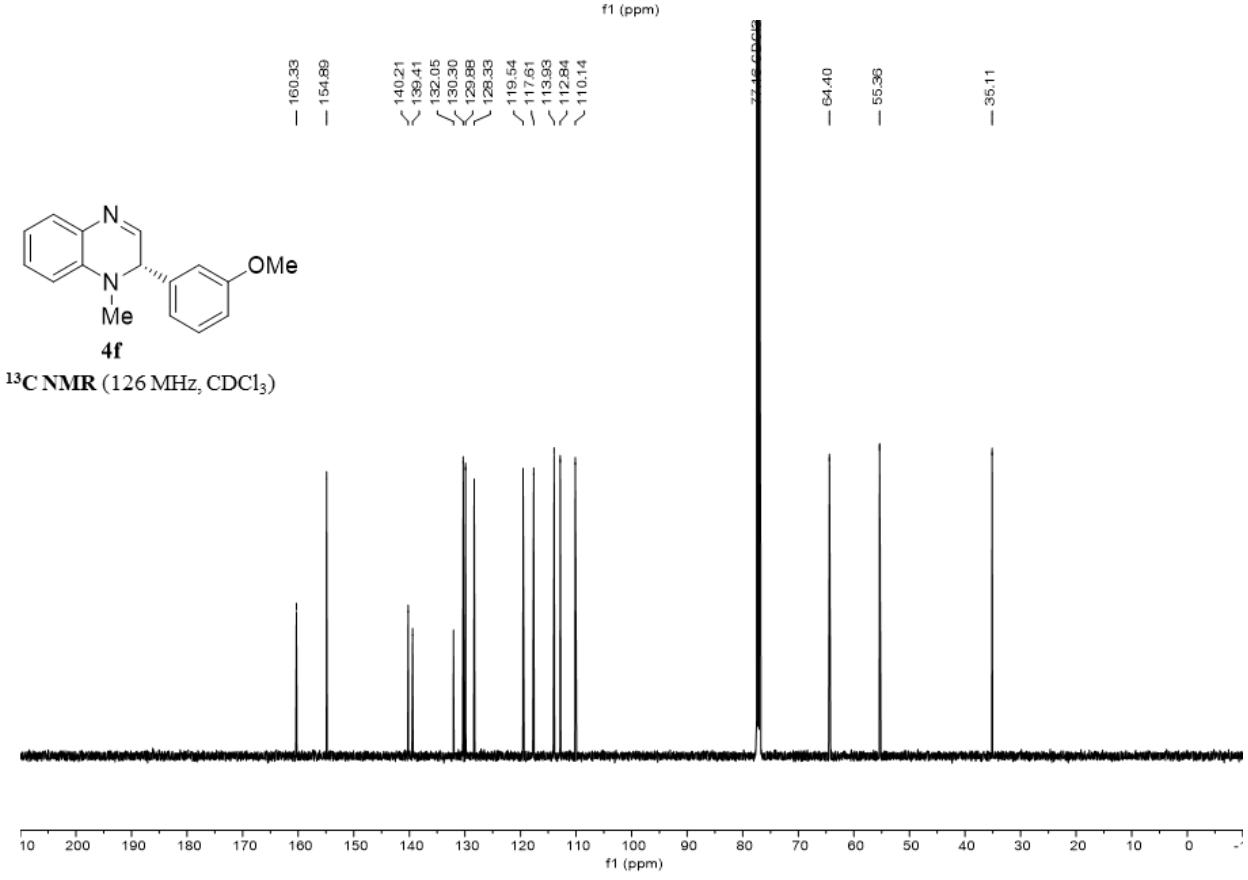
^{13}C NMR (126 MHz, $CDCl_3$)


7.56 7.56 7.56 7.56 7.55 7.55 7.54 7.54 7.54 7.54 7.53 7.53 7.52 7.52 7.49 7.48 7.48 7.48 7.45 7.45 7.44 7.44 7.43 7.43 7.43 7.42 7.41 7.40 7.37 7.37 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.28 7.28 7.27 7.26 CDCl3 7.16 7.15 7.14 7.14 7.13 7.12 6.75 6.75 6.74 6.73 6.72 6.72 6.59 6.59 6.57 6.57 5.08 5.07 2.75
N
N
Me
Ph
4e
1H NMR (500 MHz, CDCl3)
3.97 0.99 3.10 1.04 1.48 0.61 1.01 1.00 1.02 1.00 3.01
f1 (ppm)
154.90 142.22 140.70 139.37 139.19 132.06 129.93 129.76 128.98 128.36 127.72 127.50 127.29 126.23 125.90 117.67 110.20 77.16 CDCl3 64.51 35.17
N
N
Me
Ph
4e
13C NMR (126 MHz, CDCl3)
f1 (ppm)



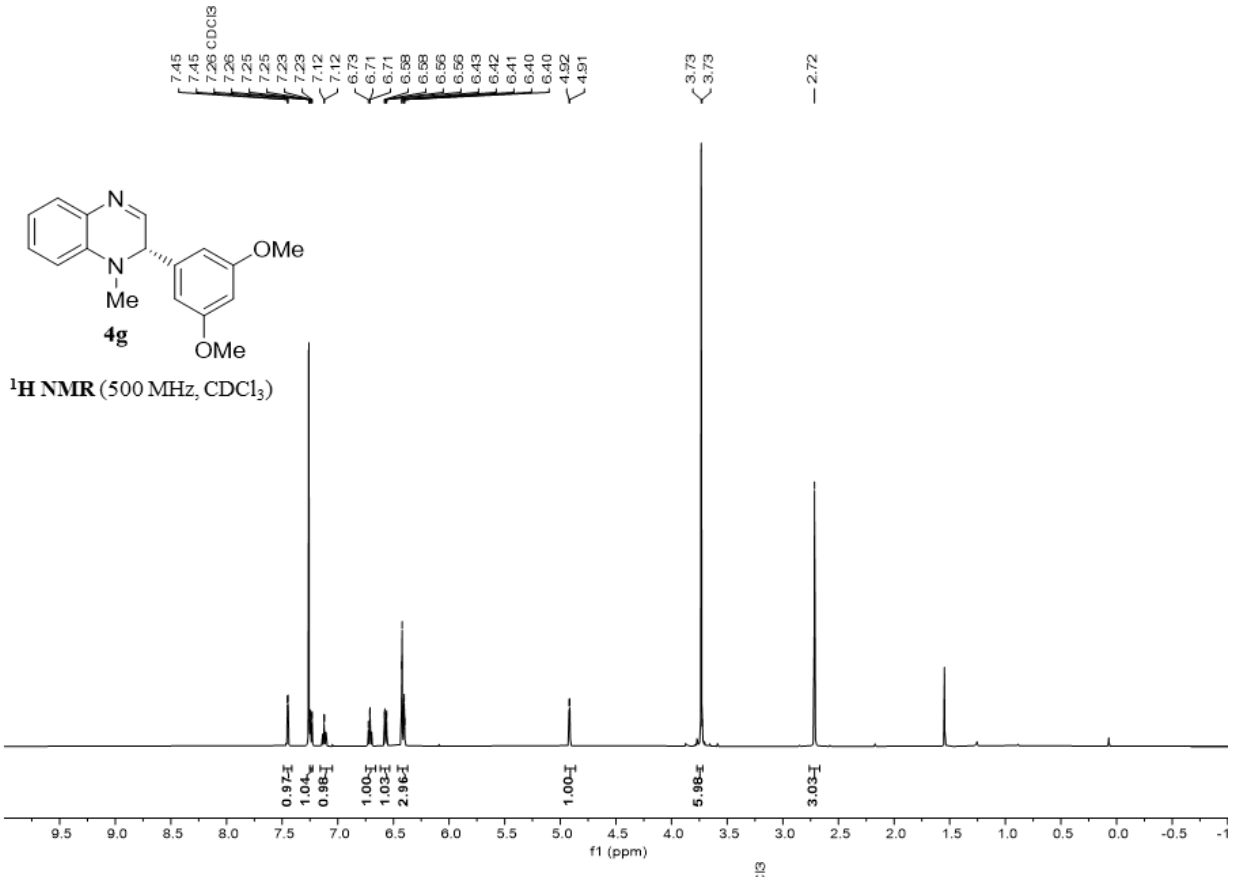
4f

^{1}H NMR (500 MHz, $CDCl_3$)

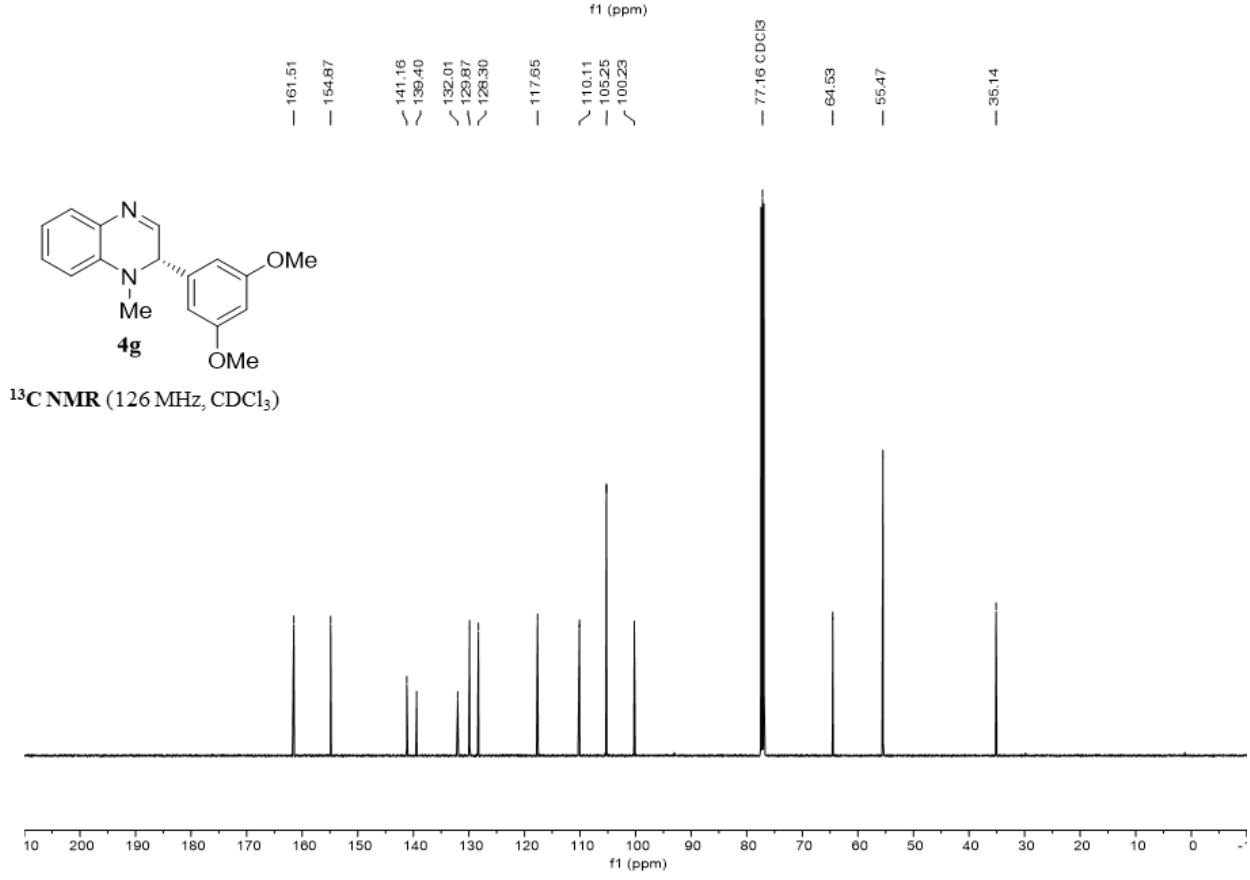


4f

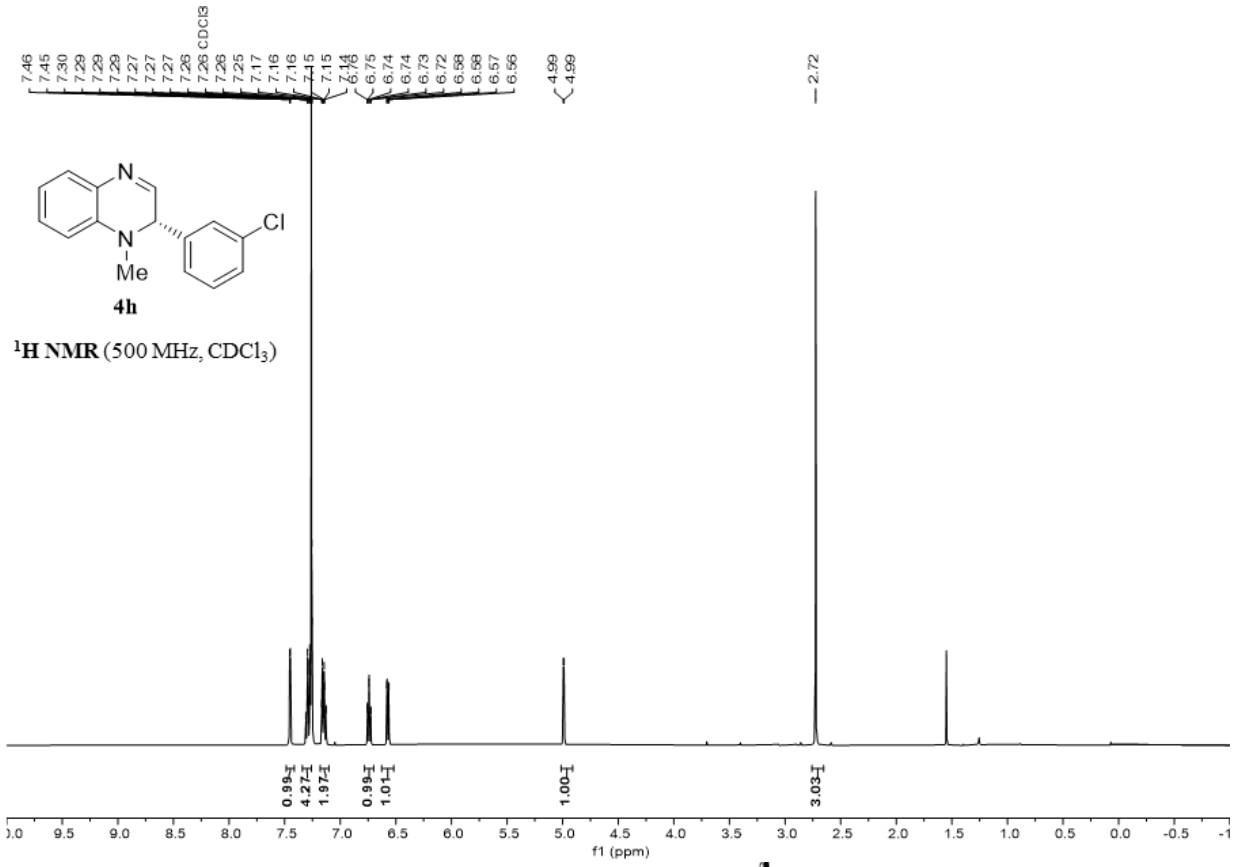
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

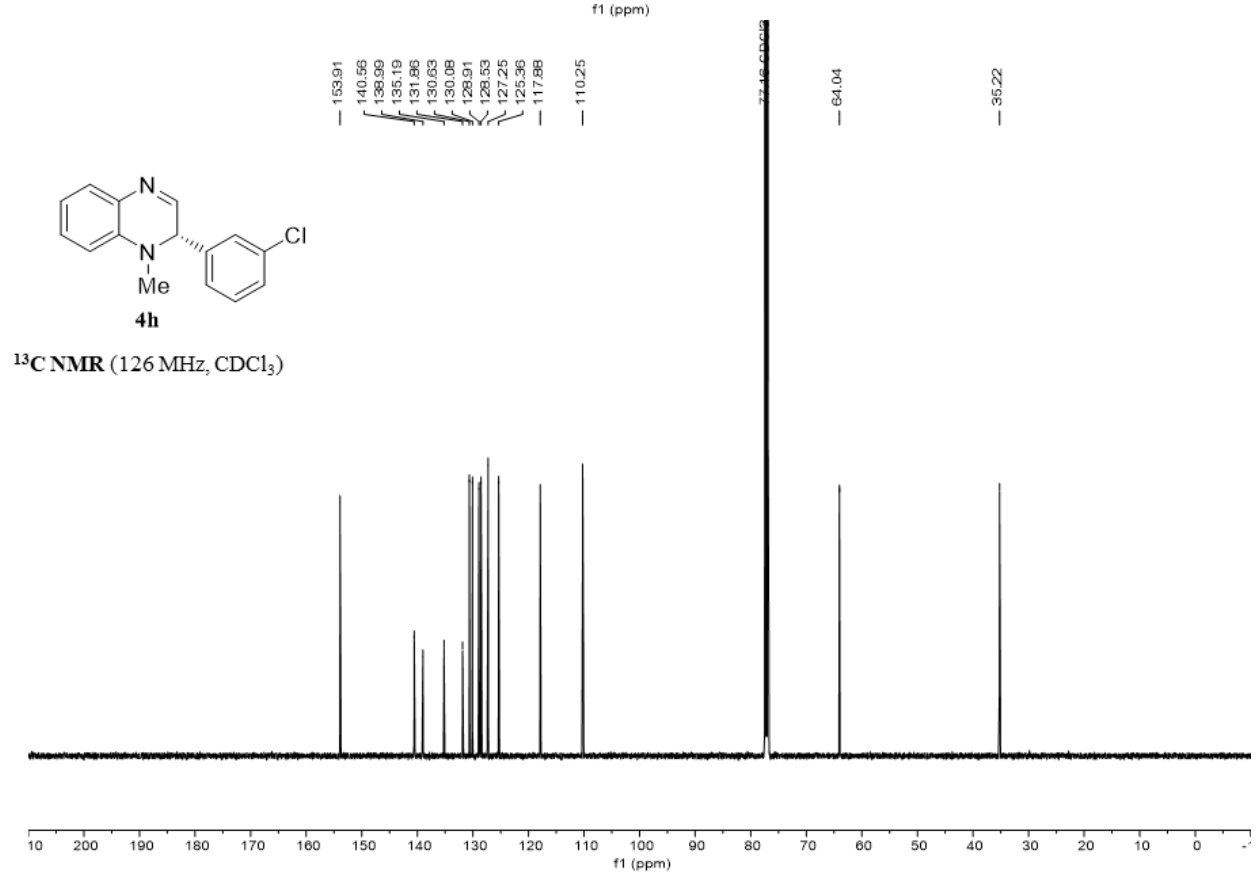


^{13}C NMR (126 MHz, $CDCl_3$)



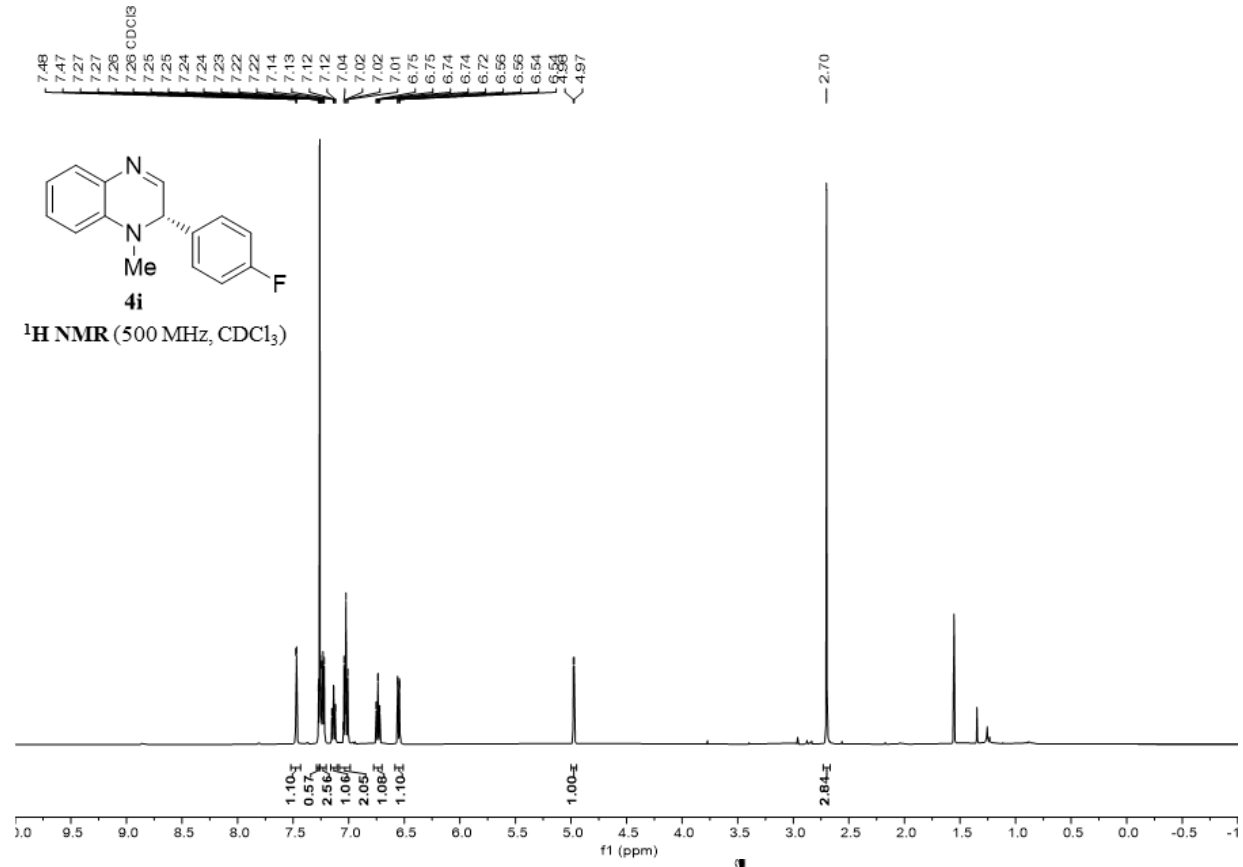
4h

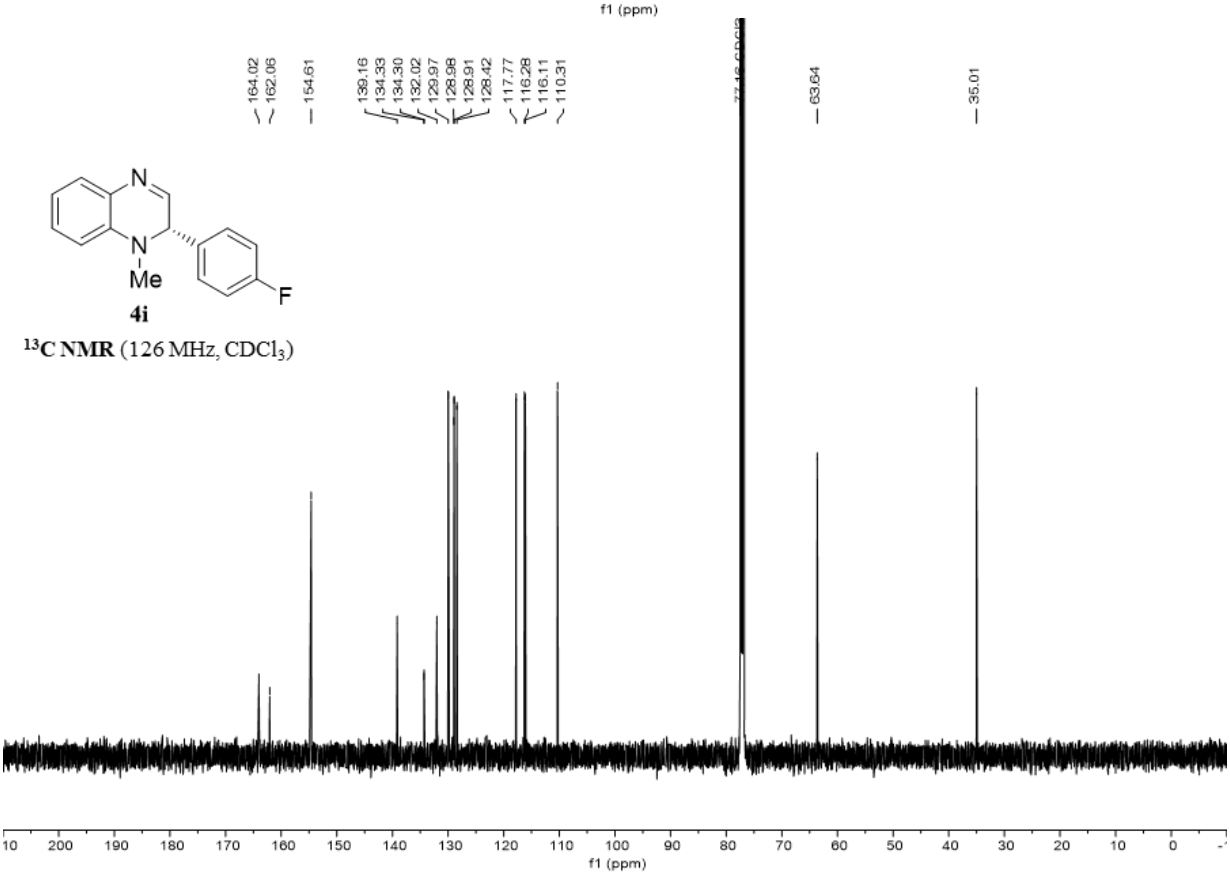
^{1}H NMR (500 MHz, $CDCl_3$)

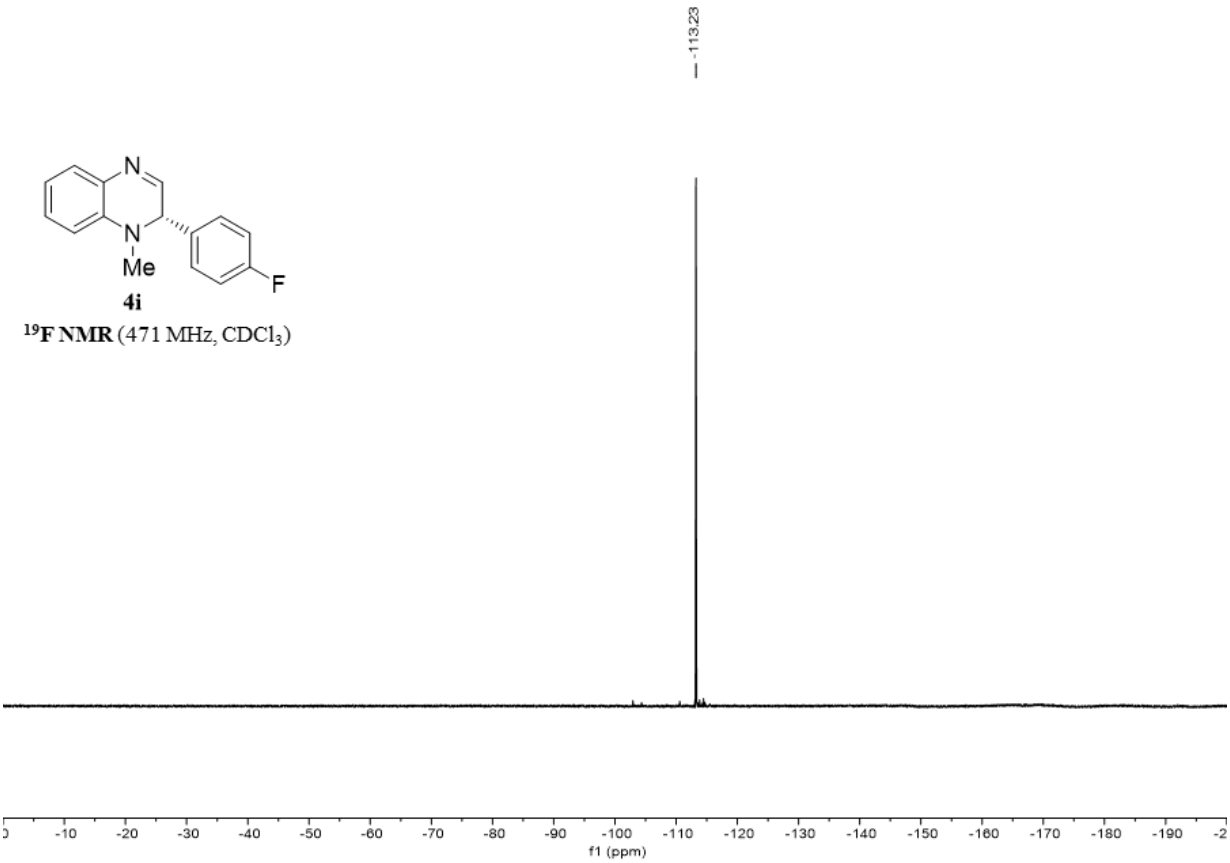


4h

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

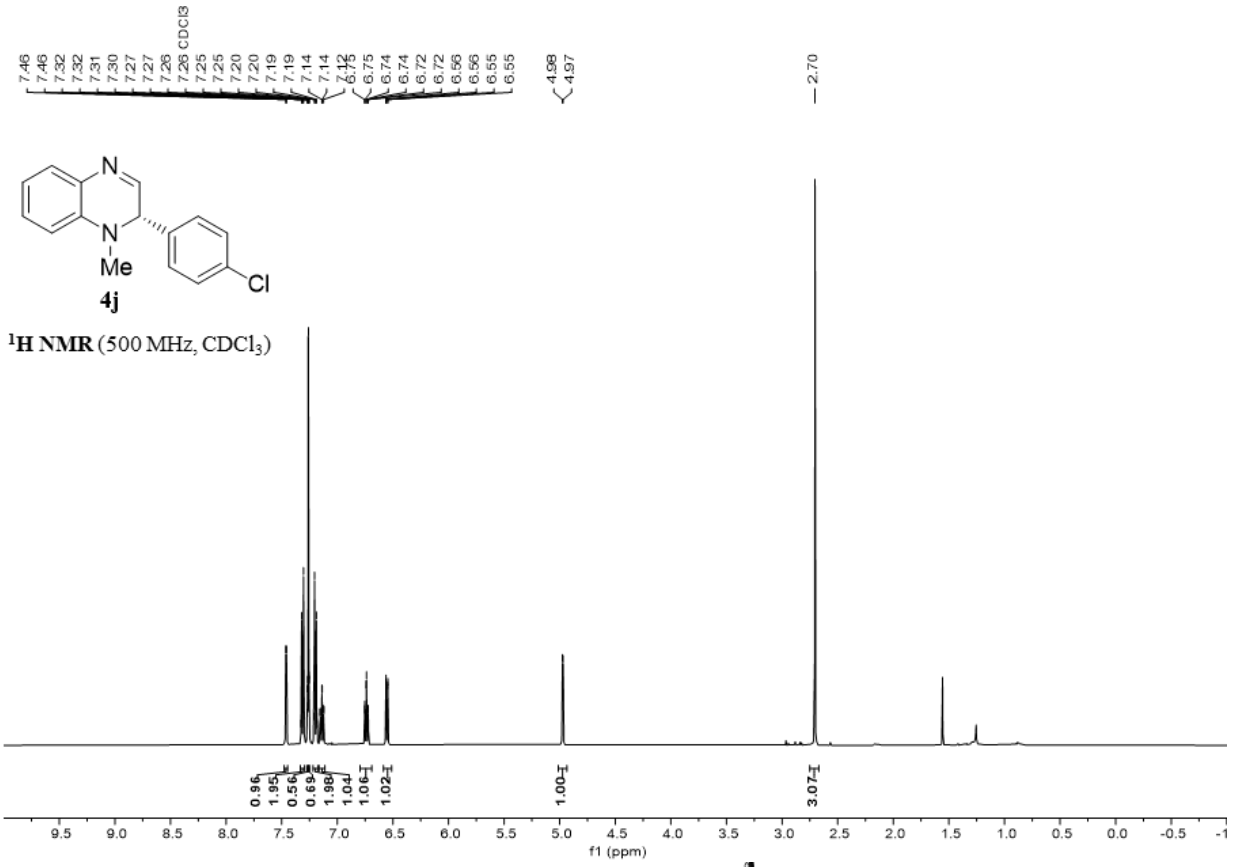

7.48
7.47
7.27
7.27
7.26
7.26 CDCl3
7.25
7.25
7.24
7.24
7.23
7.22
7.22
7.14
7.13
7.12
7.12
7.04
7.02
7.02
7.01
6.75
6.75
6.74
6.74
6.72
6.56
6.56
6.54
4.97
2.70
N
N
Me
F
4i
1H NMR (500 MHz, CDCl3)
1.10
0.57
2.56
1.06
2.05
1.08
1.10
1.00
2.84
f1 (ppm)


164.02
162.06
154.61
139.16
134.33
134.30
132.02
129.97
128.98
128.91
128.42
117.77
116.28
116.11
110.31
77.48 CDCl3
63.64
35.01
N
N
Me
F
4i
13C NMR (126 MHz, CDCl3)
f1 (ppm)

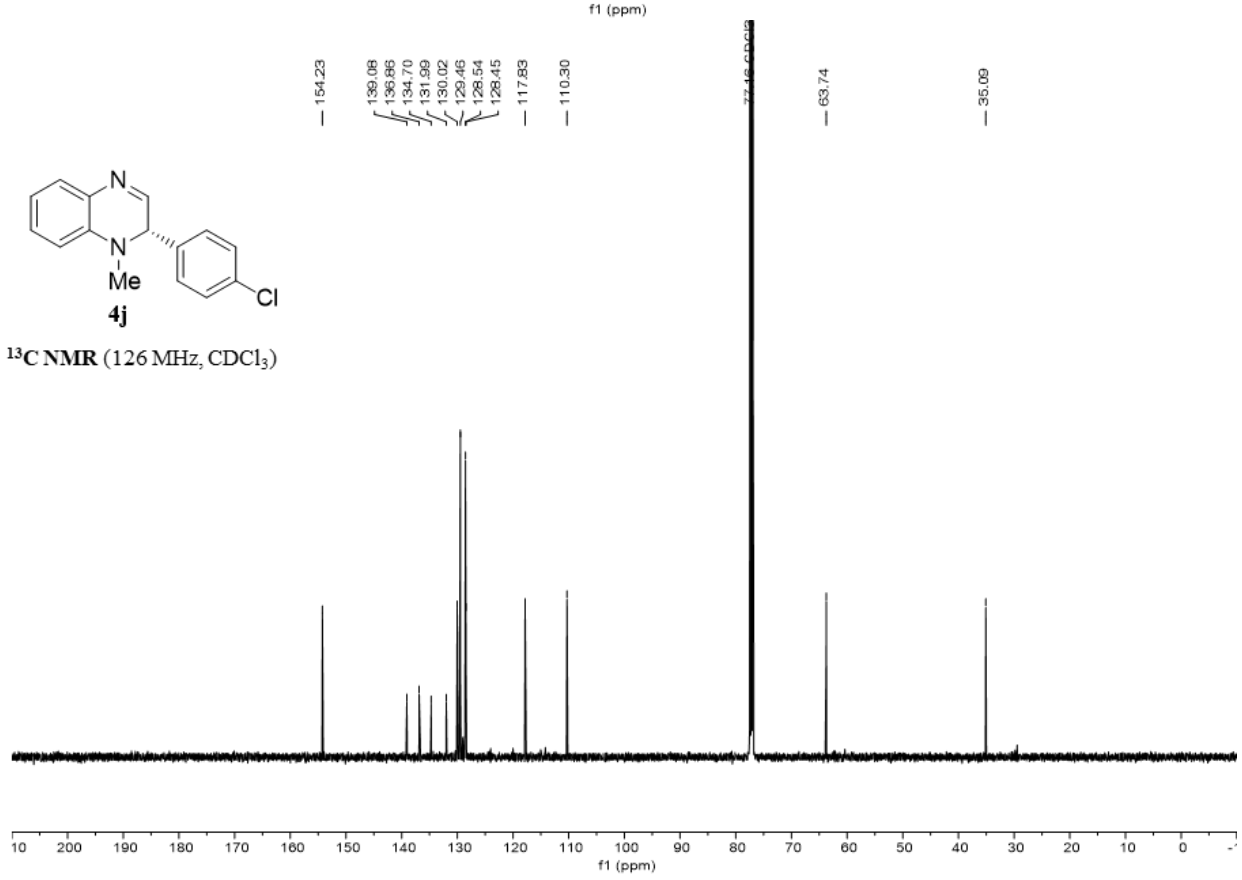


4i

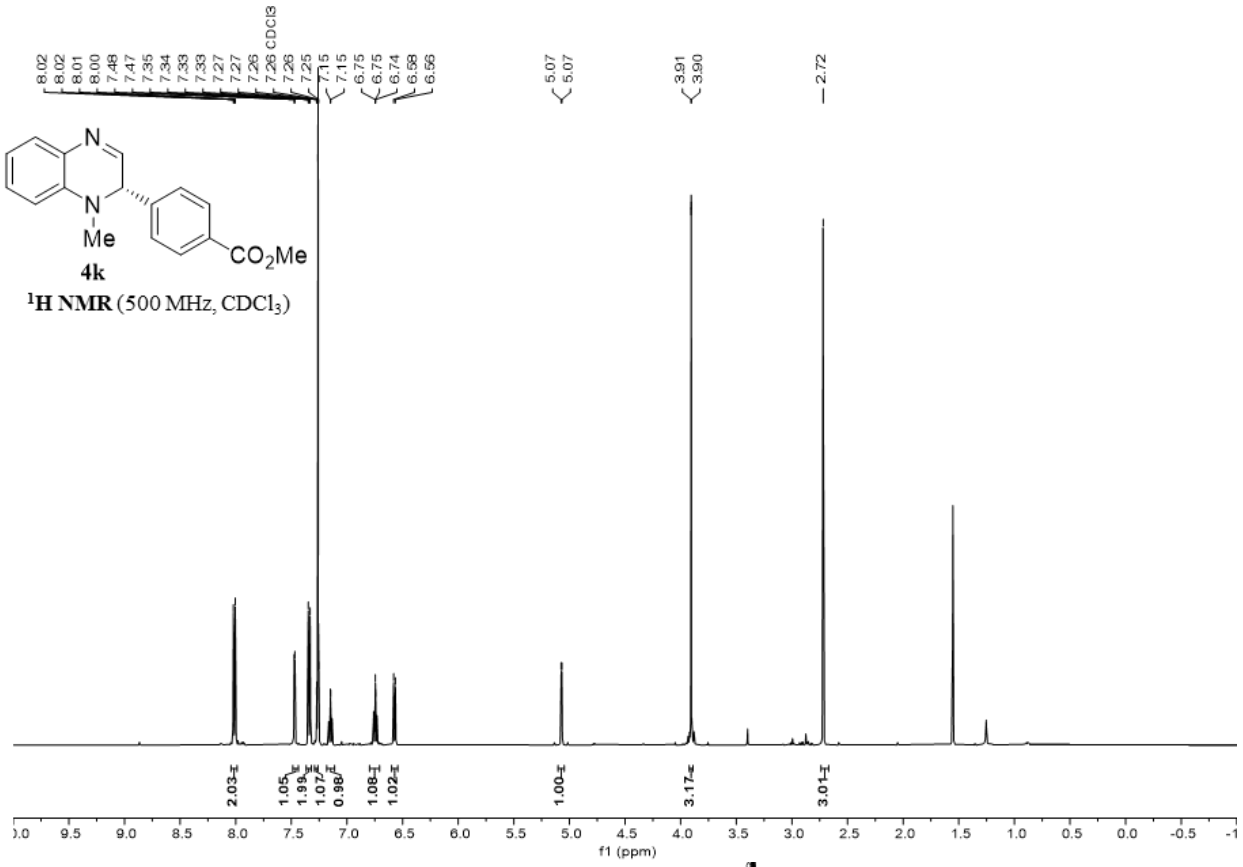
^{19}F NMR (471 MHz, $CDCl_3$)

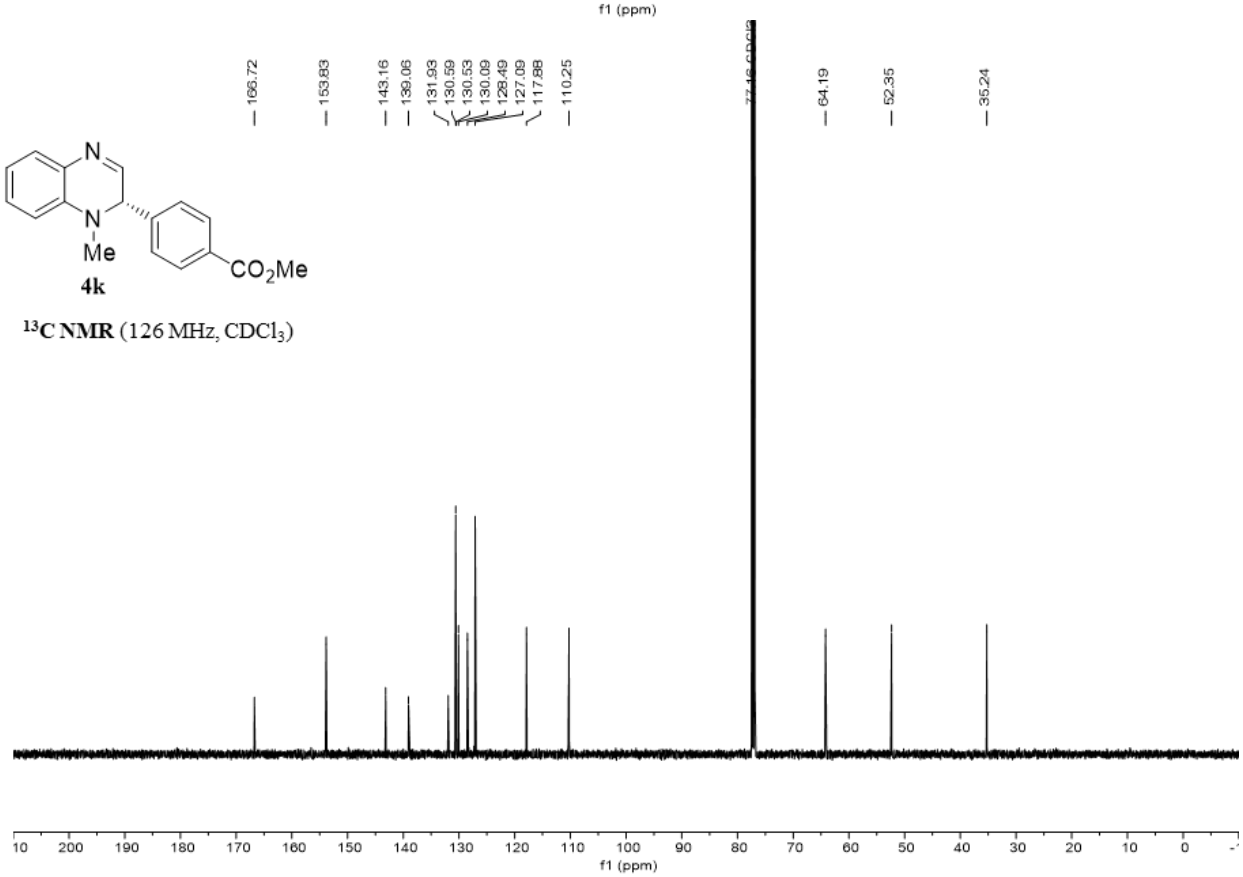


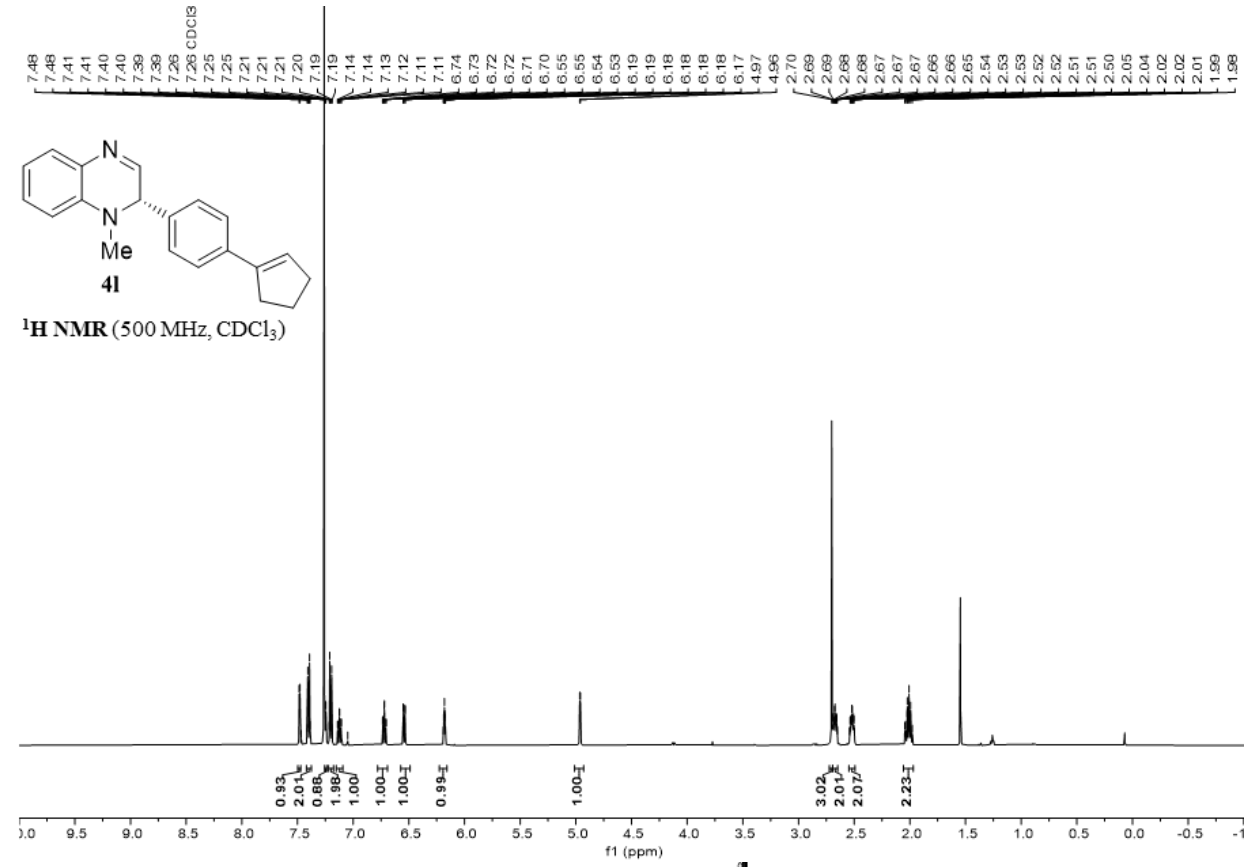
^{1}H NMR (500 MHz, $CDCl_3$)



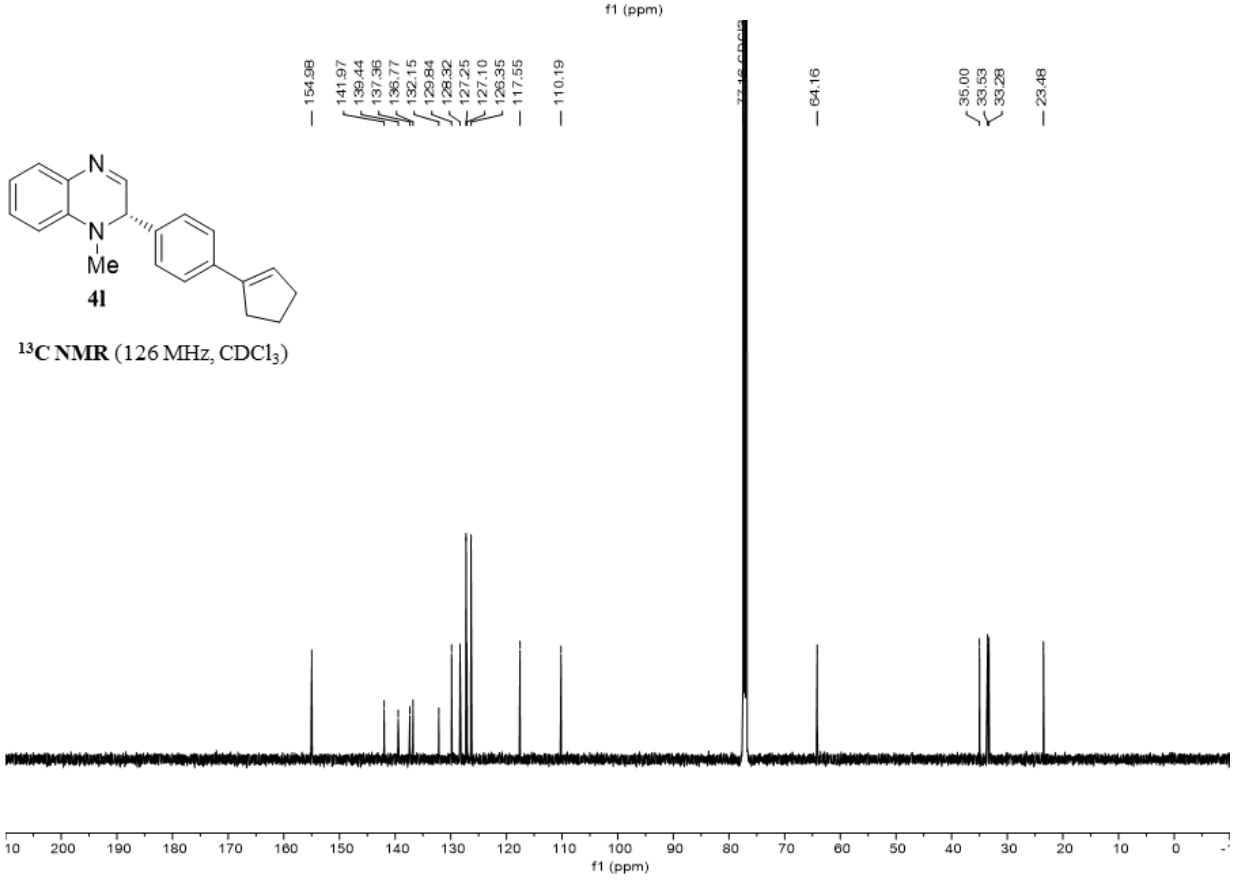
^{13}C NMR (126 MHz, $CDCl_3$)


8.02
8.02
8.01
8.00
7.48
7.47
7.35
7.34
7.33
7.33
7.27
7.27
7.26
7.26 CDCl3
7.26
7.25
7.15
7.15
6.75
6.75
6.74
6.58
6.56
5.07
5.07
3.91
3.90
2.72
N
N
Me
CO2Me
4k
1H NMR (500 MHz, CDCl3)
2.03
1.05
1.99
1.07
0.98
1.08
1.02
1.00
3.17
3.01
f1 (ppm)

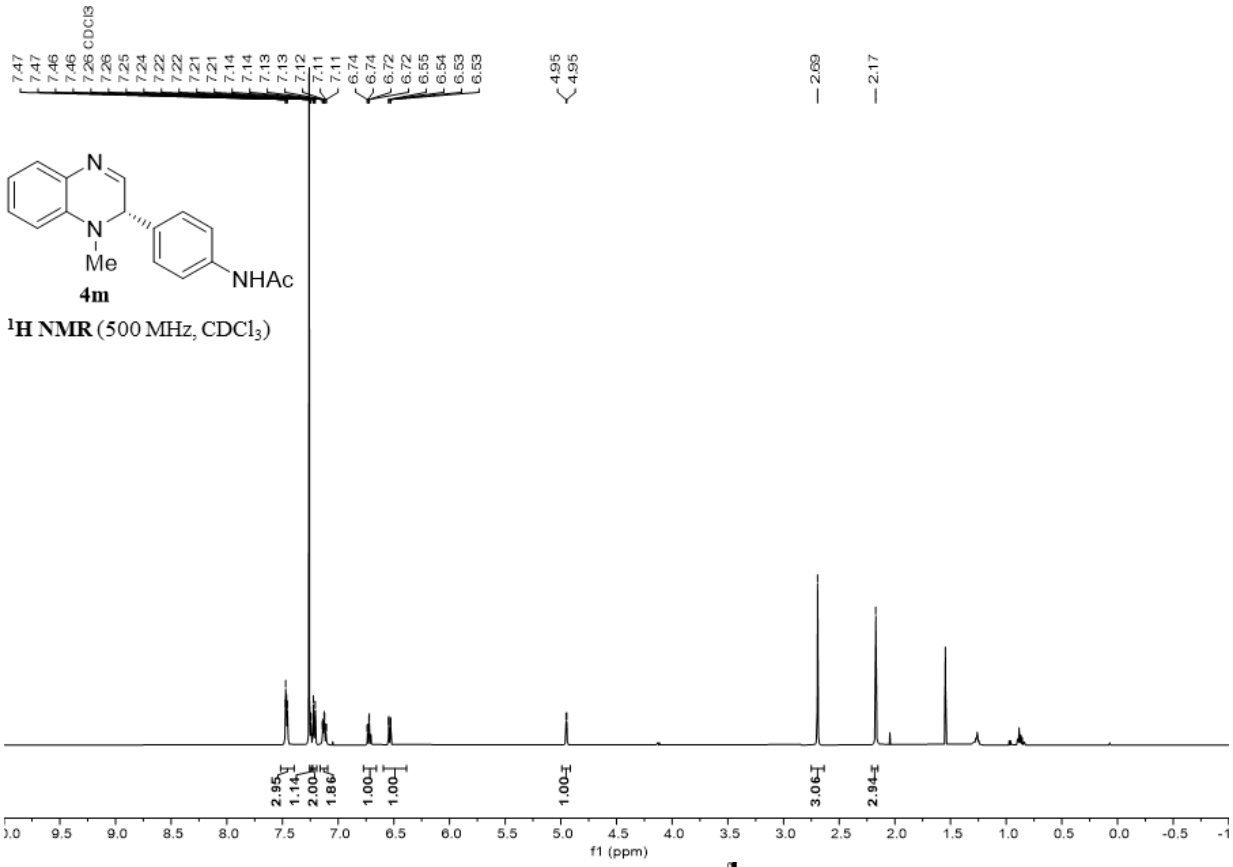

166.72
153.83
143.16
139.06
131.93
130.59
130.53
130.09
128.49
127.09
117.88
110.25
77.16 CDCl3
64.19
52.35
35.24
N
N
Me
CO2Me
4k
13C NMR (126 MHz, CDCl3)
f1 (ppm)



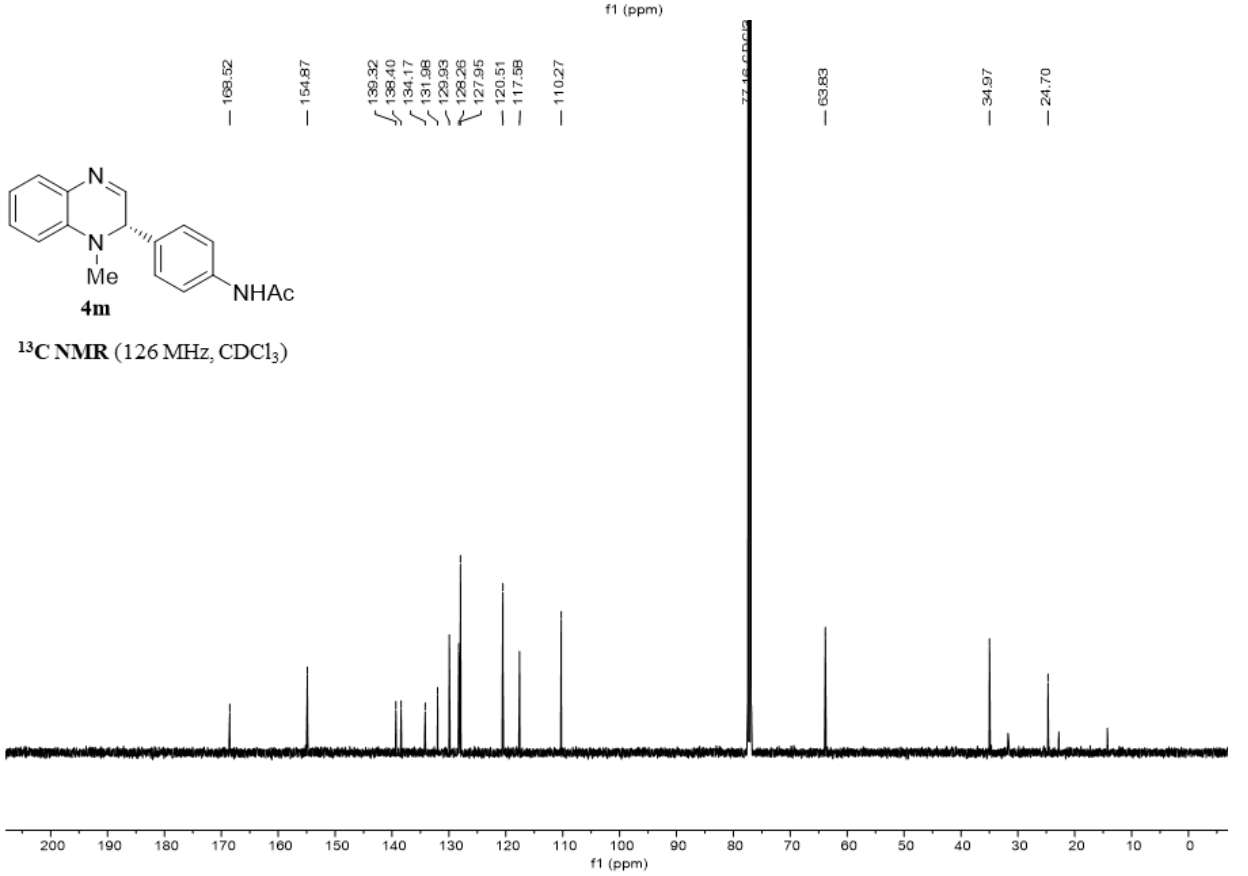
^{1}H NMR (500 MHz, $CDCl_3$)



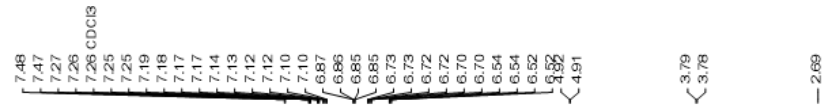
^{13}C NMR (126 MHz, $CDCl_3$)

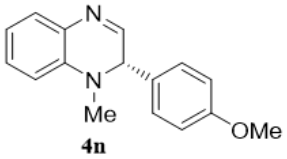


^{1}H NMR (500 MHz, $CDCl_3$)



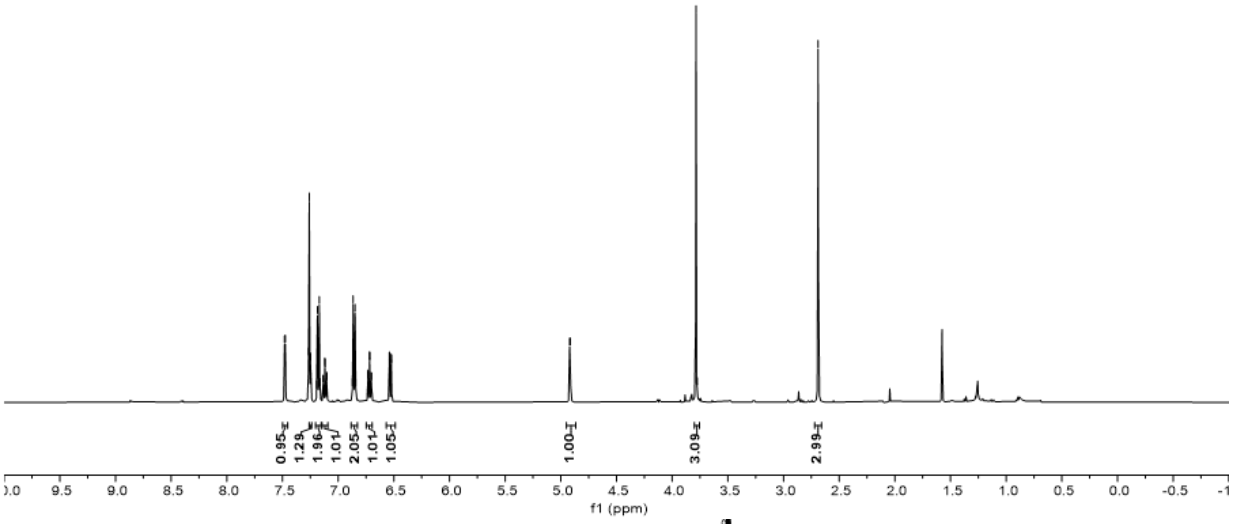
^{13}C NMR (126 MHz, $CDCl_3$)

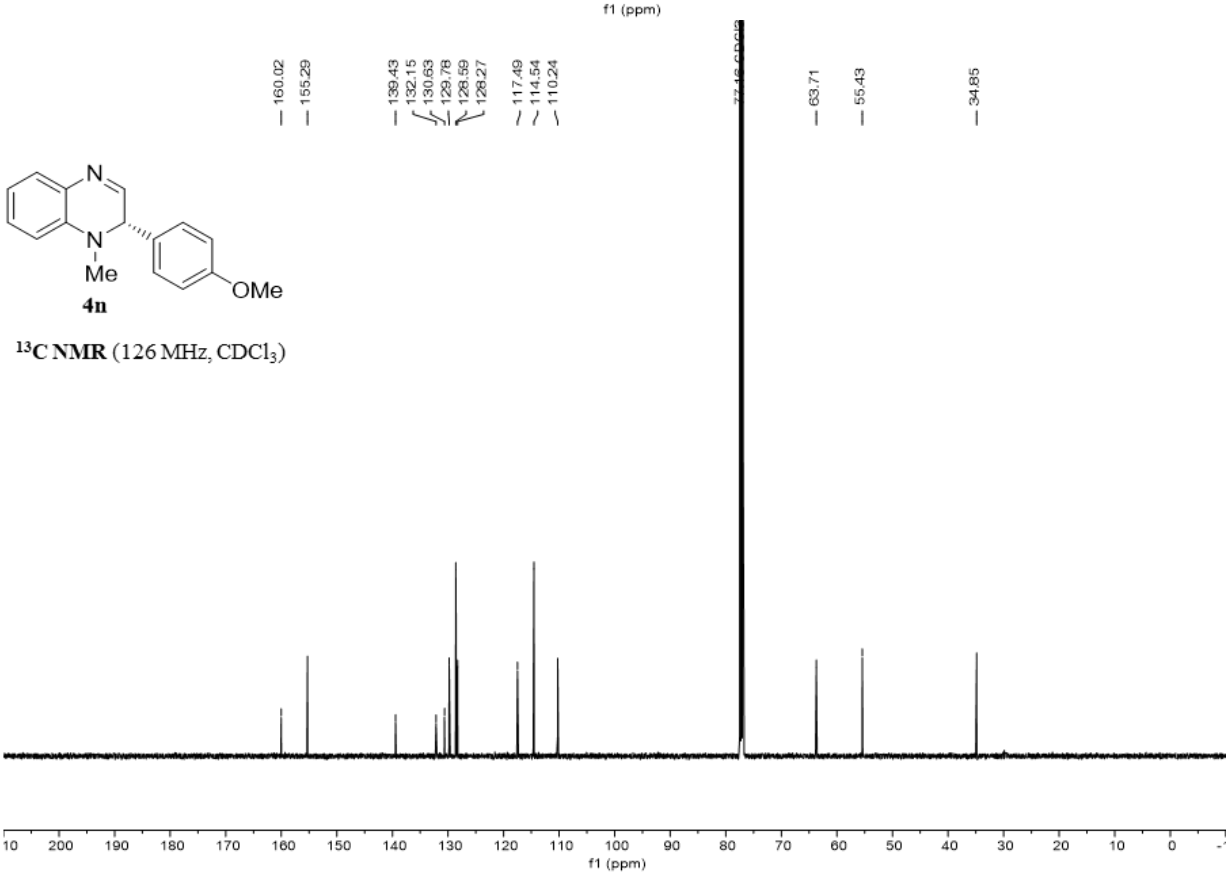




4n

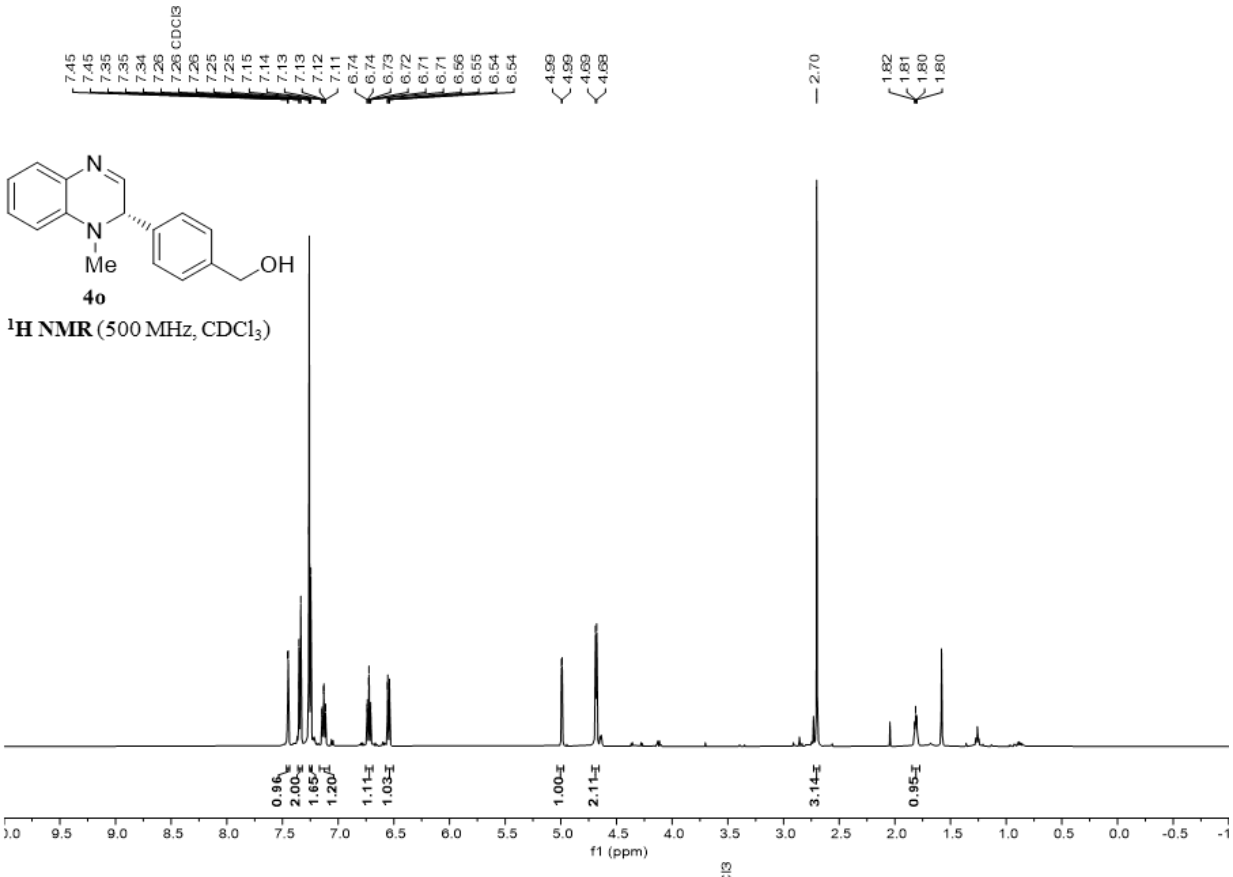
^{1}H NMR (500 MHz, $CDCl_3$)



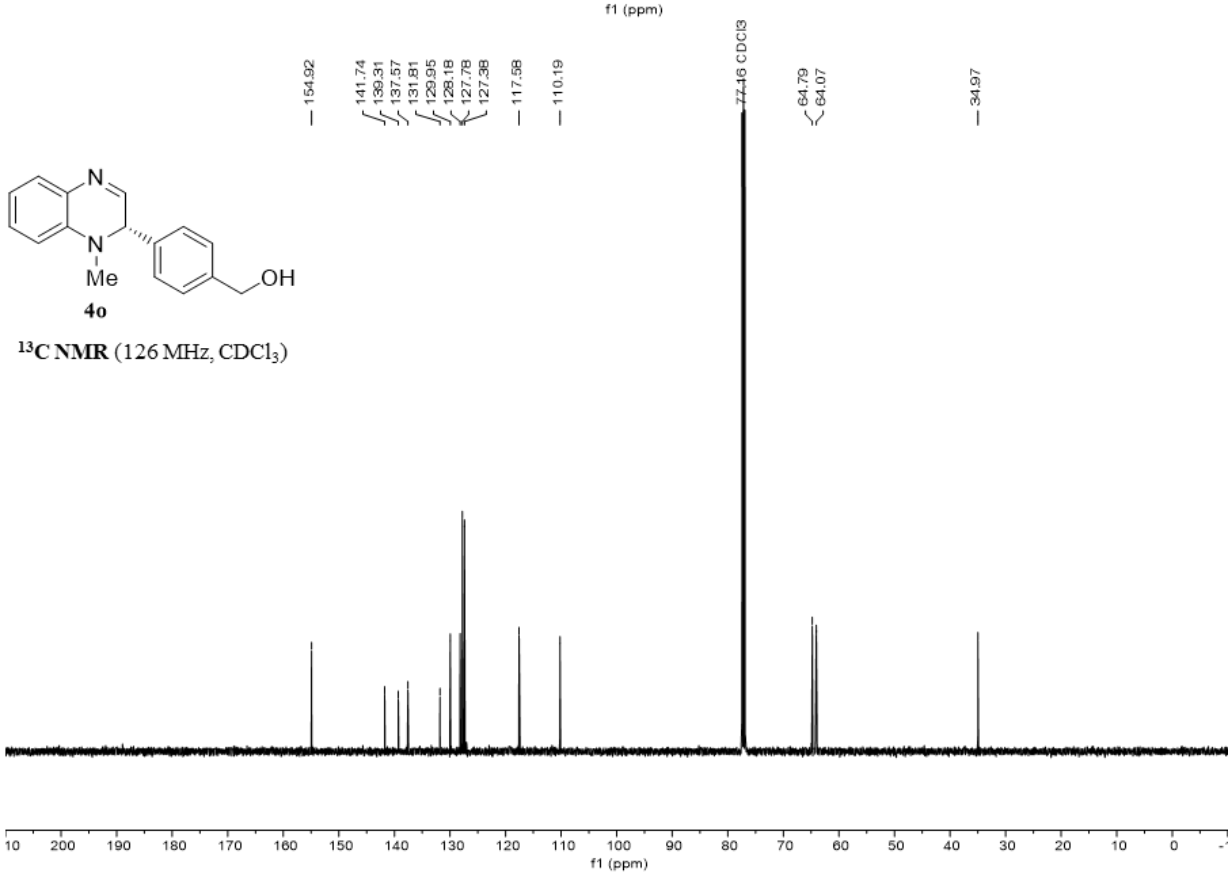


4n

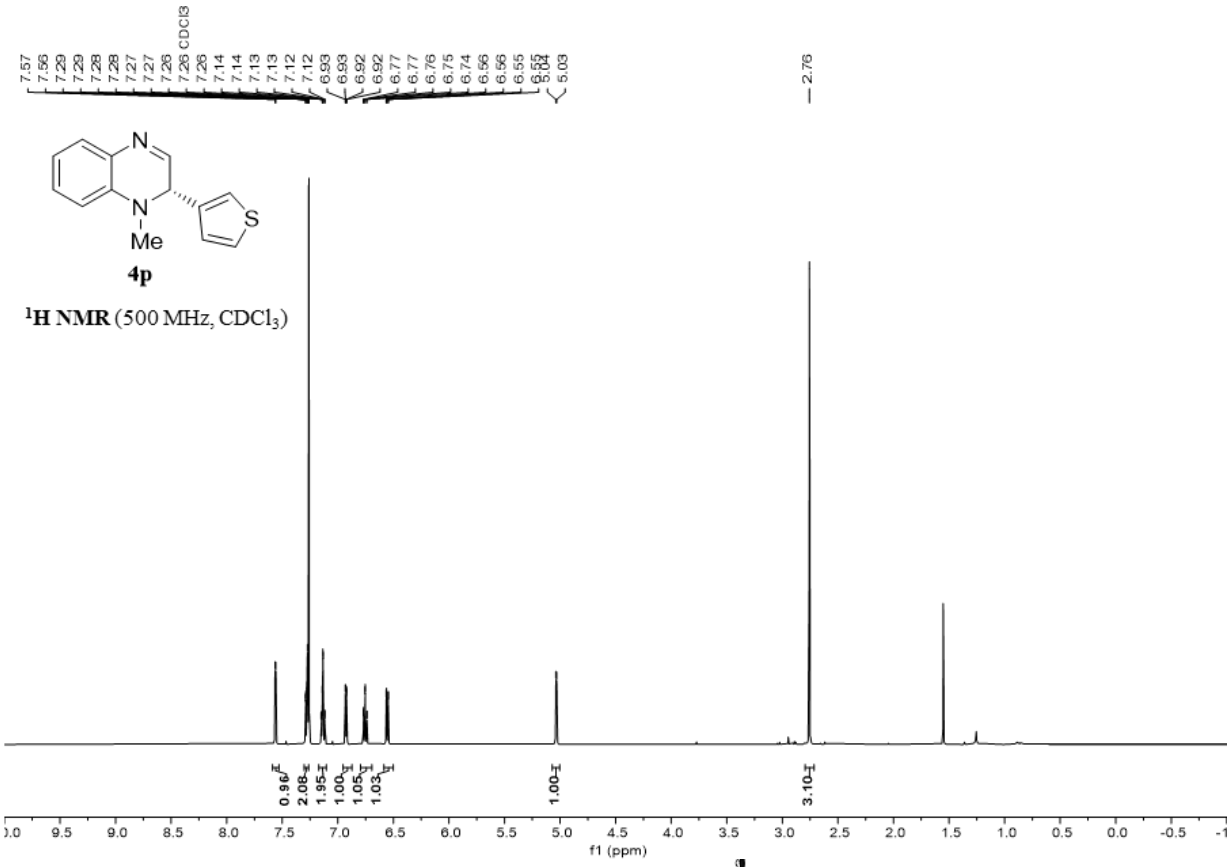
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

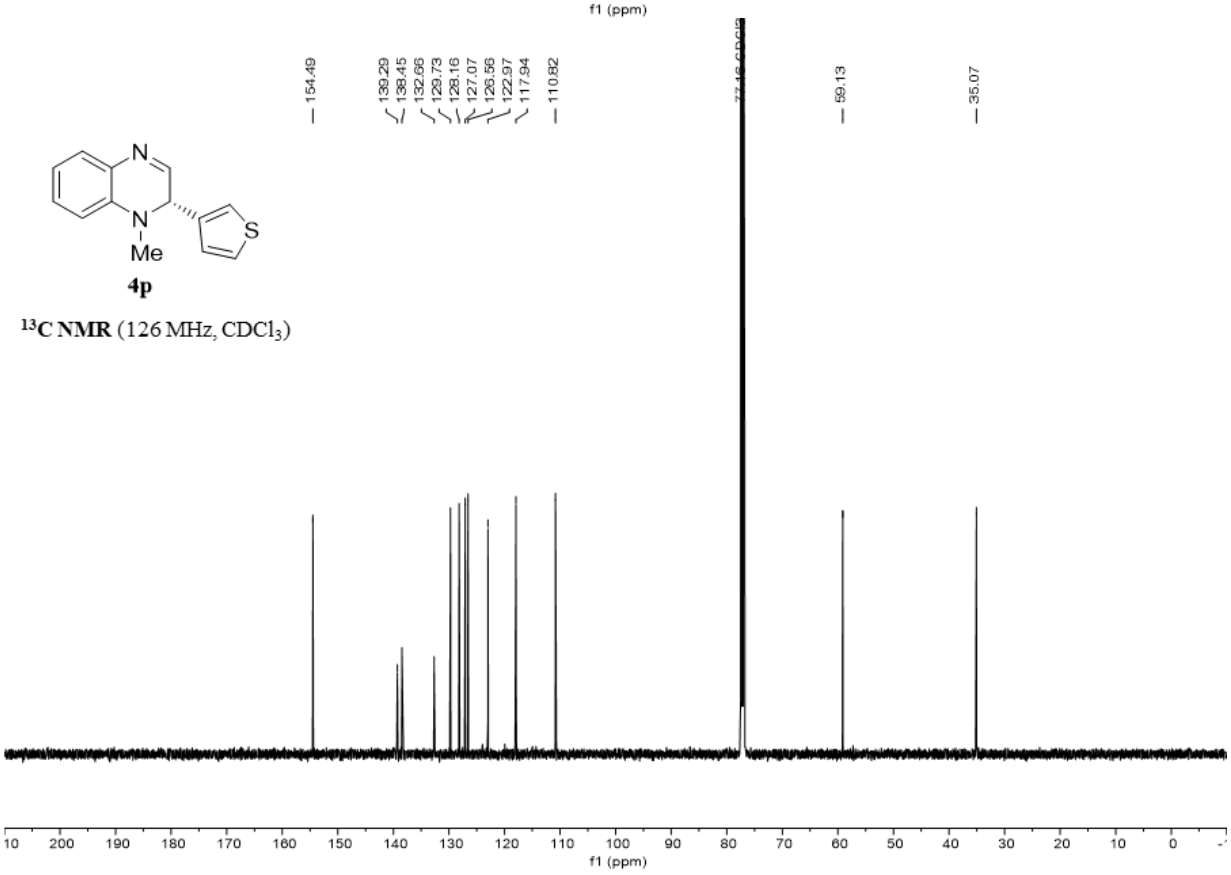


^{13}C NMR (126 MHz, $CDCl_3$)



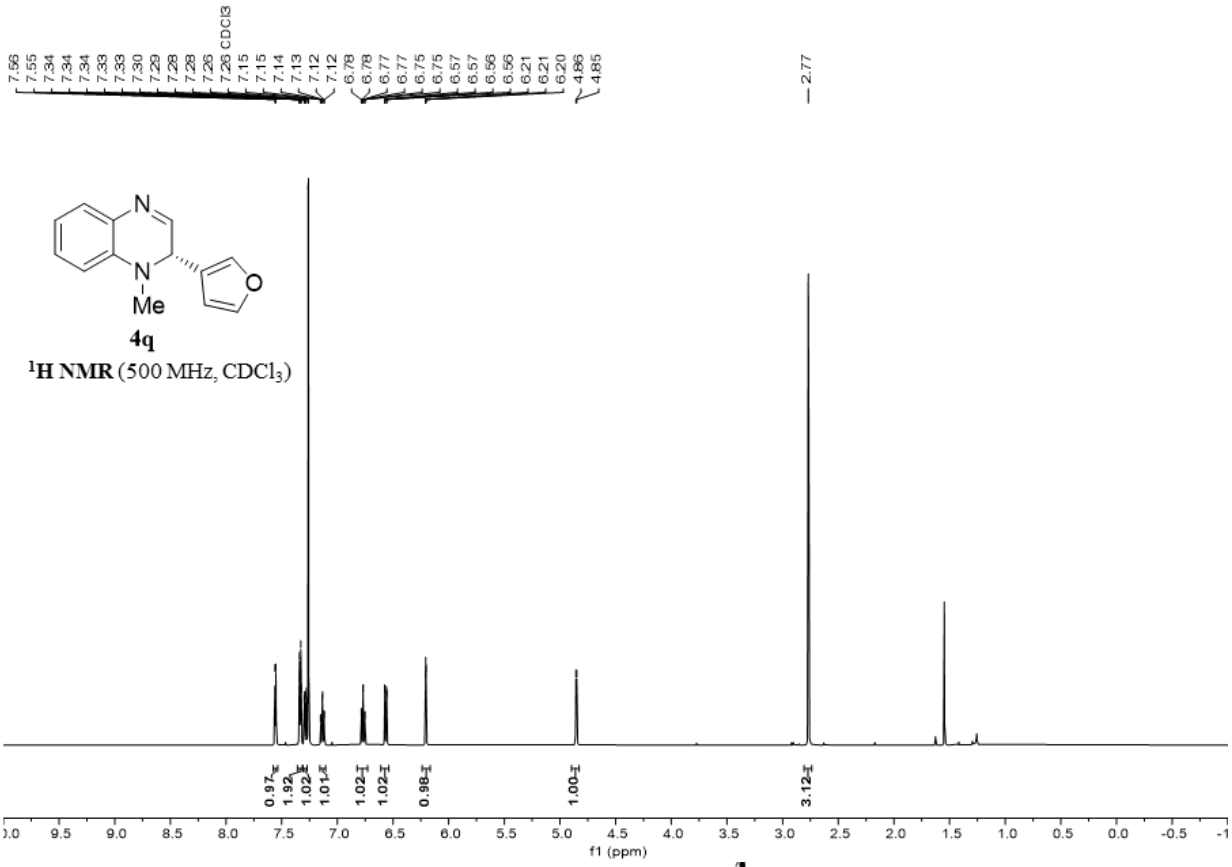
4p

^{1}H NMR (500 MHz, $CDCl_3$)

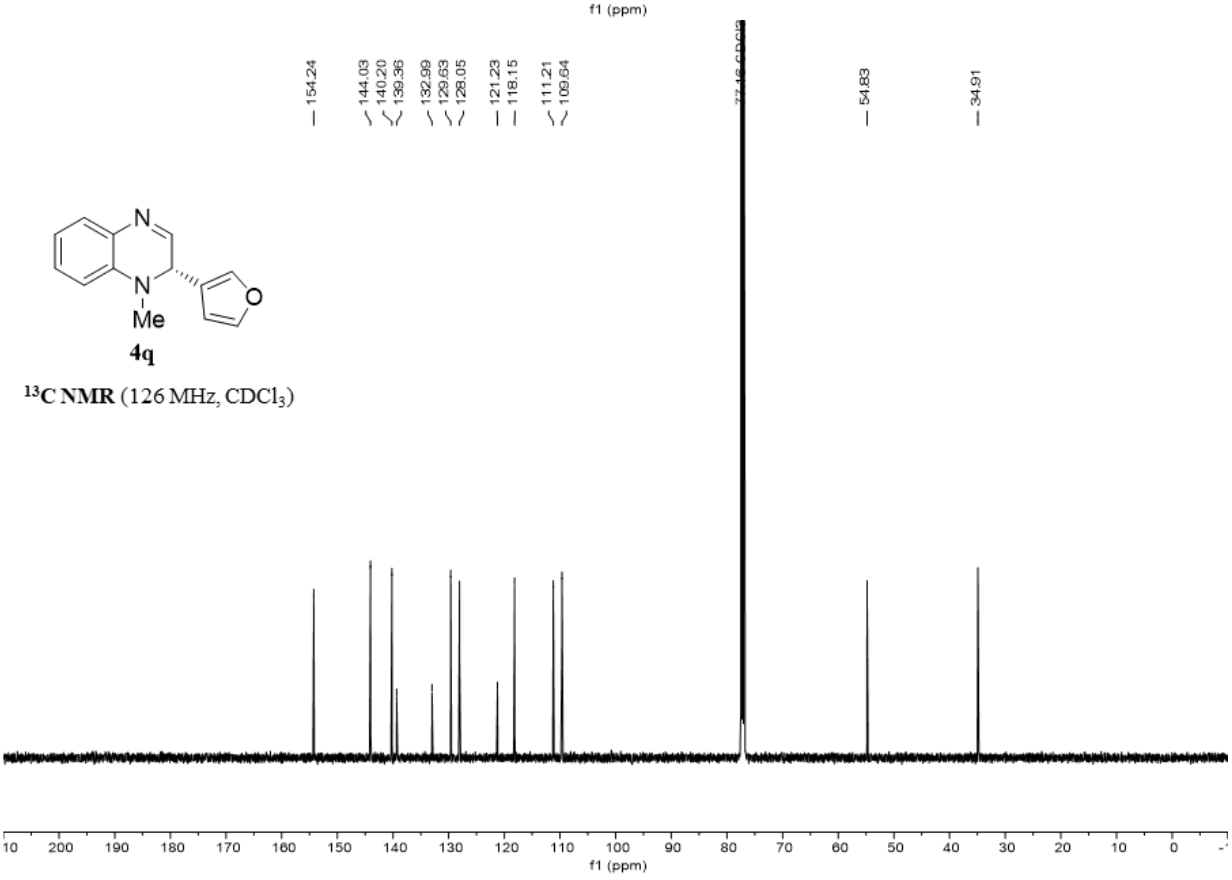


4p

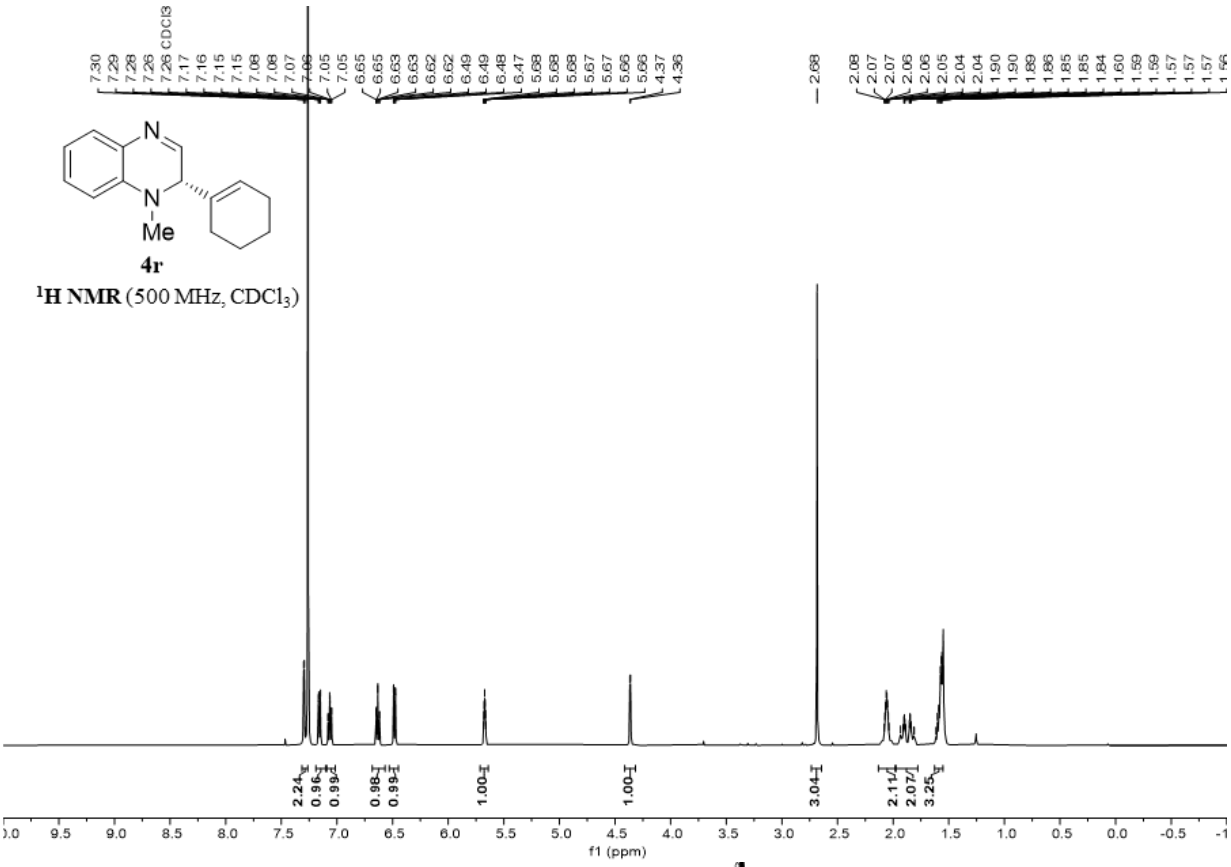
^{13}C NMR (126 MHz, $CDCl_3$)



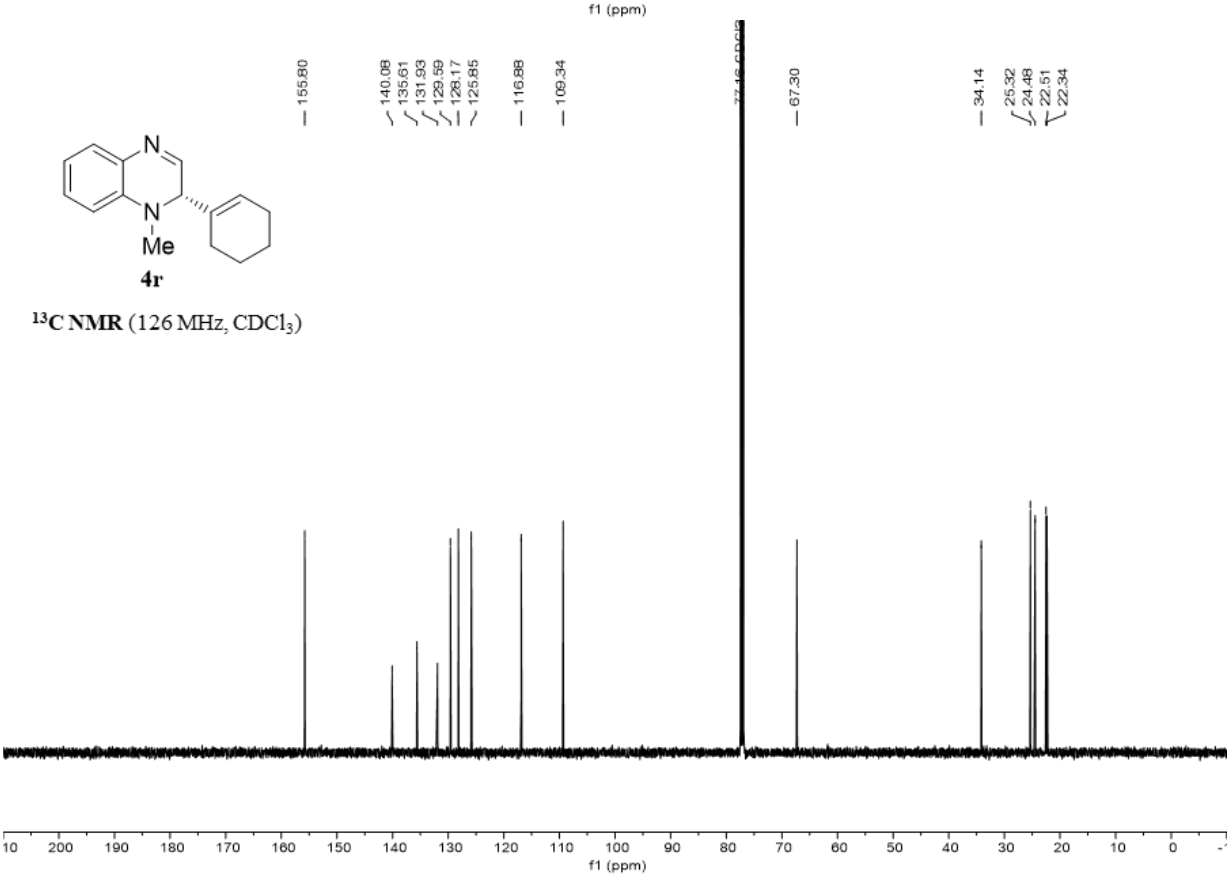
^{1}H NMR (500 MHz, $CDCl_3$)



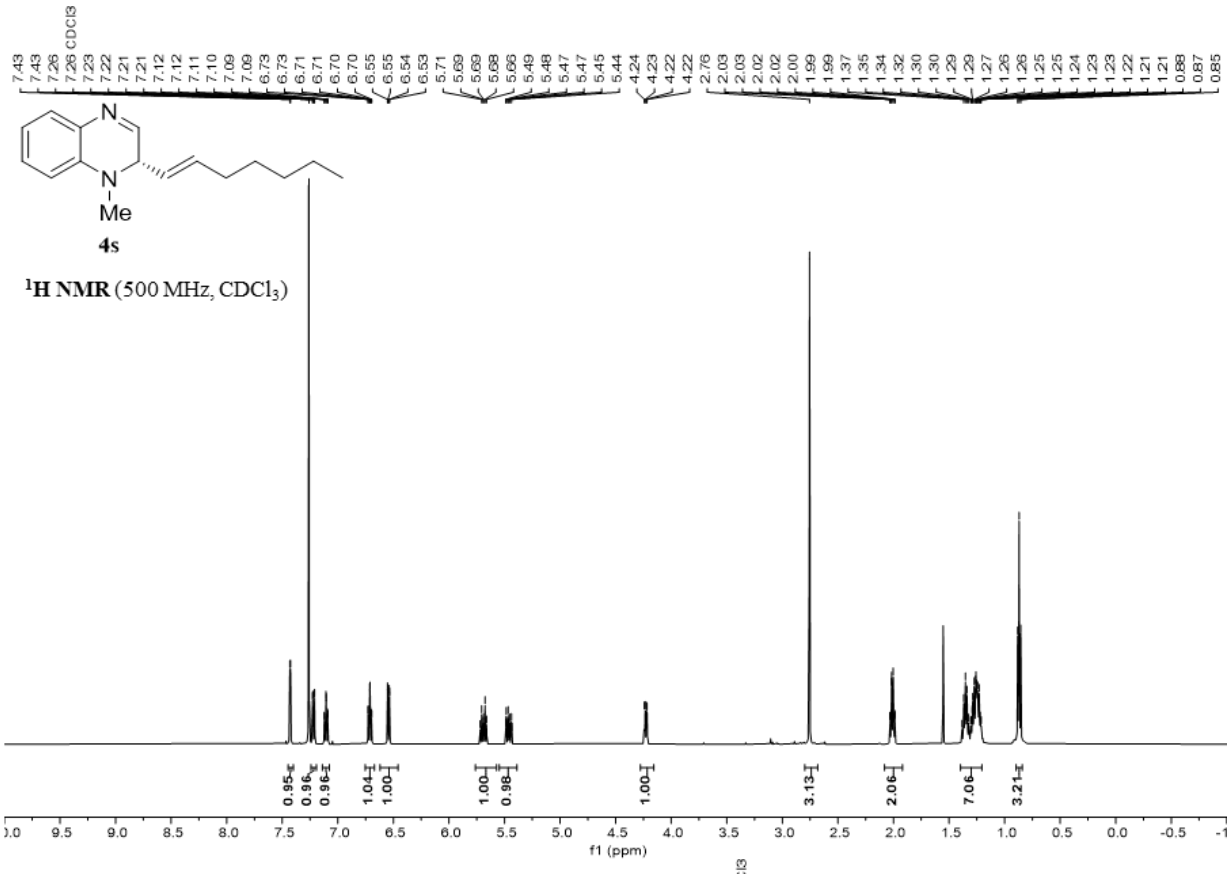
^{13}C NMR (126 MHz, $CDCl_3$)



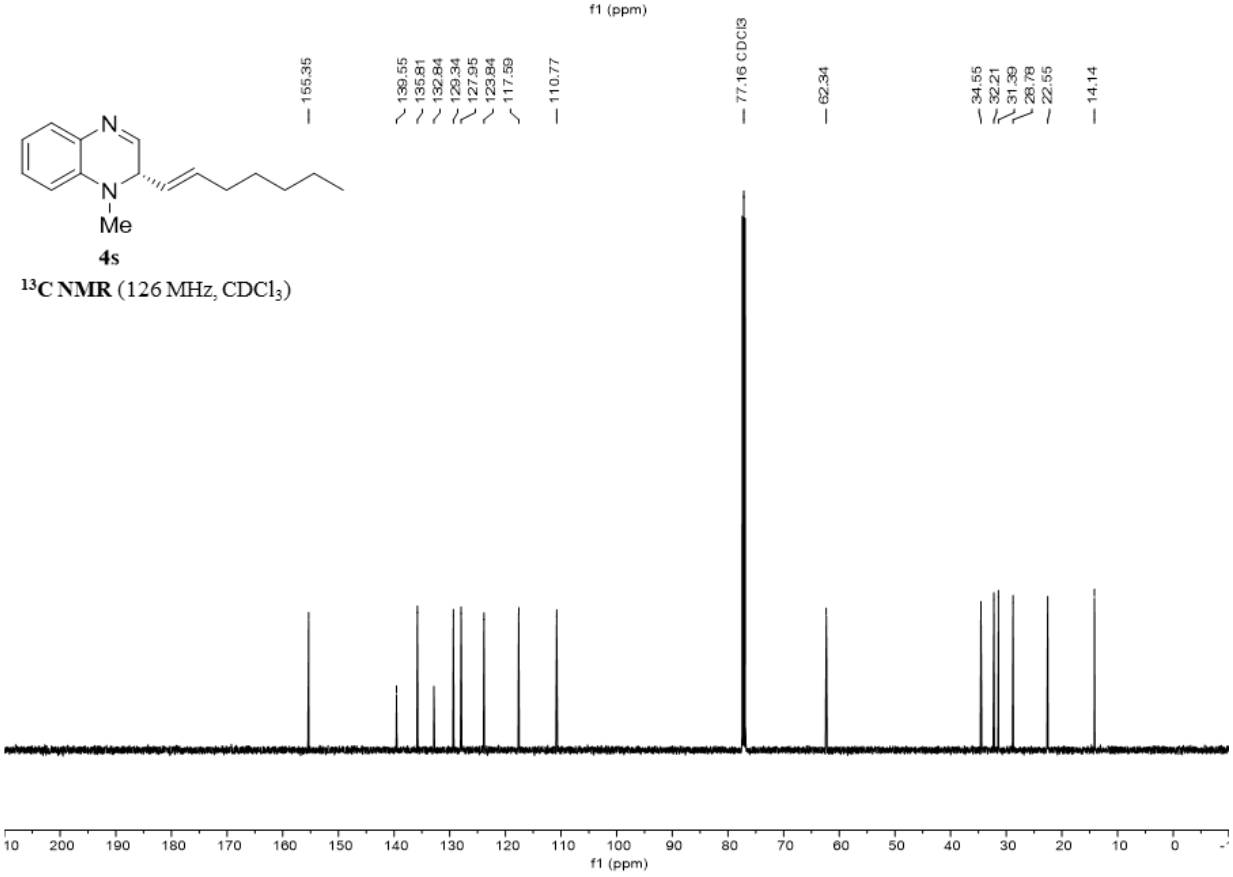
^{1}H NMR (500 MHz, $CDCl_3$)



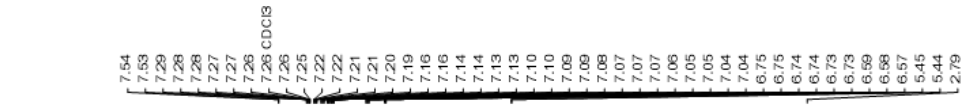
^{13}C NMR (126 MHz, $CDCl_3$)

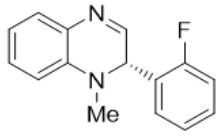


^{1}H NMR (500 MHz, $CDCl_3$)



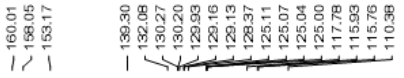
^{13}C NMR (126 MHz, $CDCl_3$)

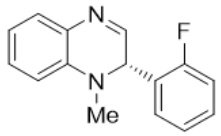




4t

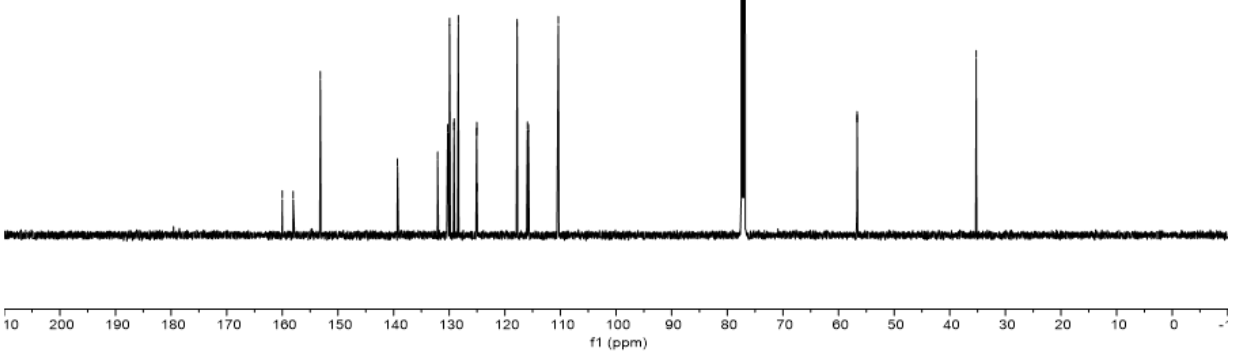
^{1}H NMR (600 MHz, $CDCl_3$)

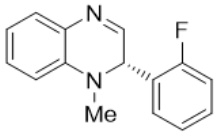




4t

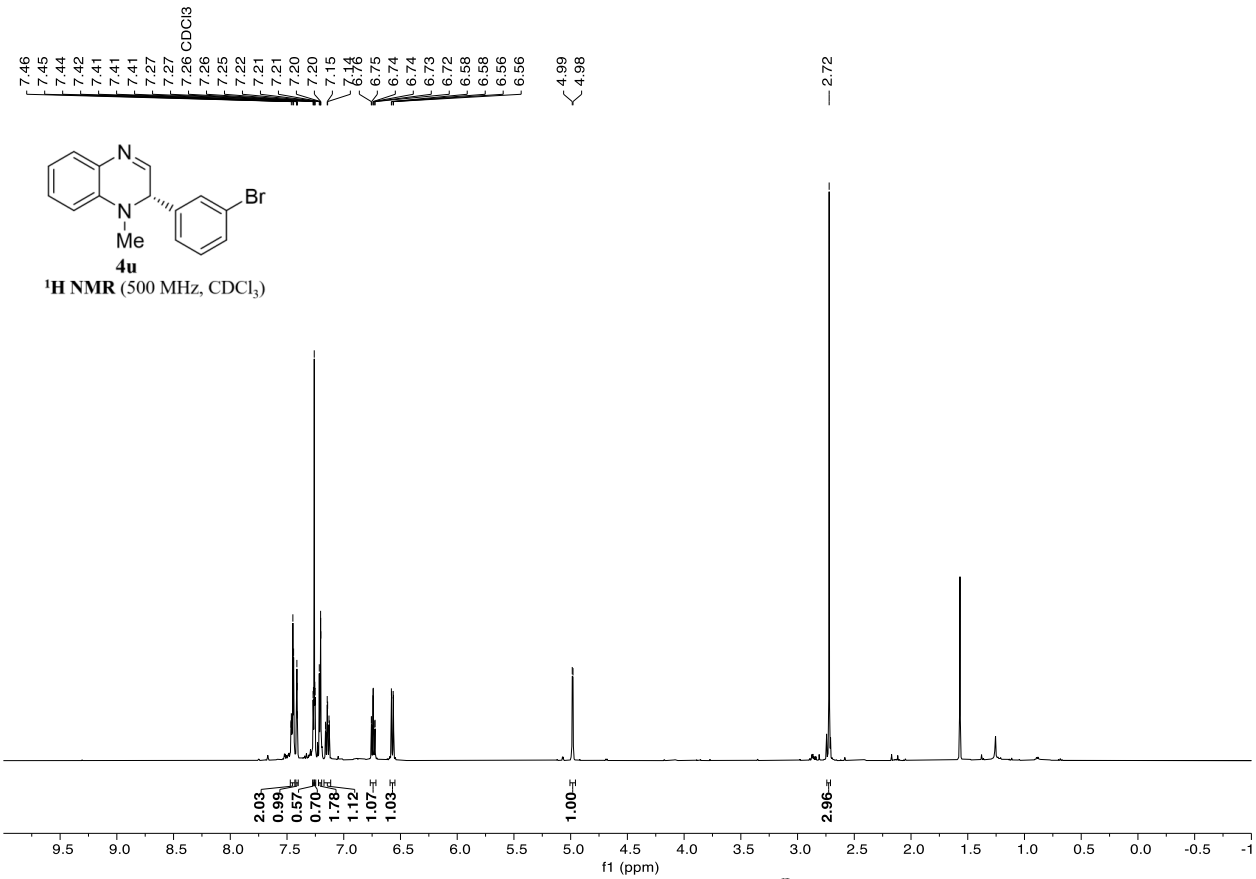
^{13}C NMR (126 MHz, $CDCl_3$)





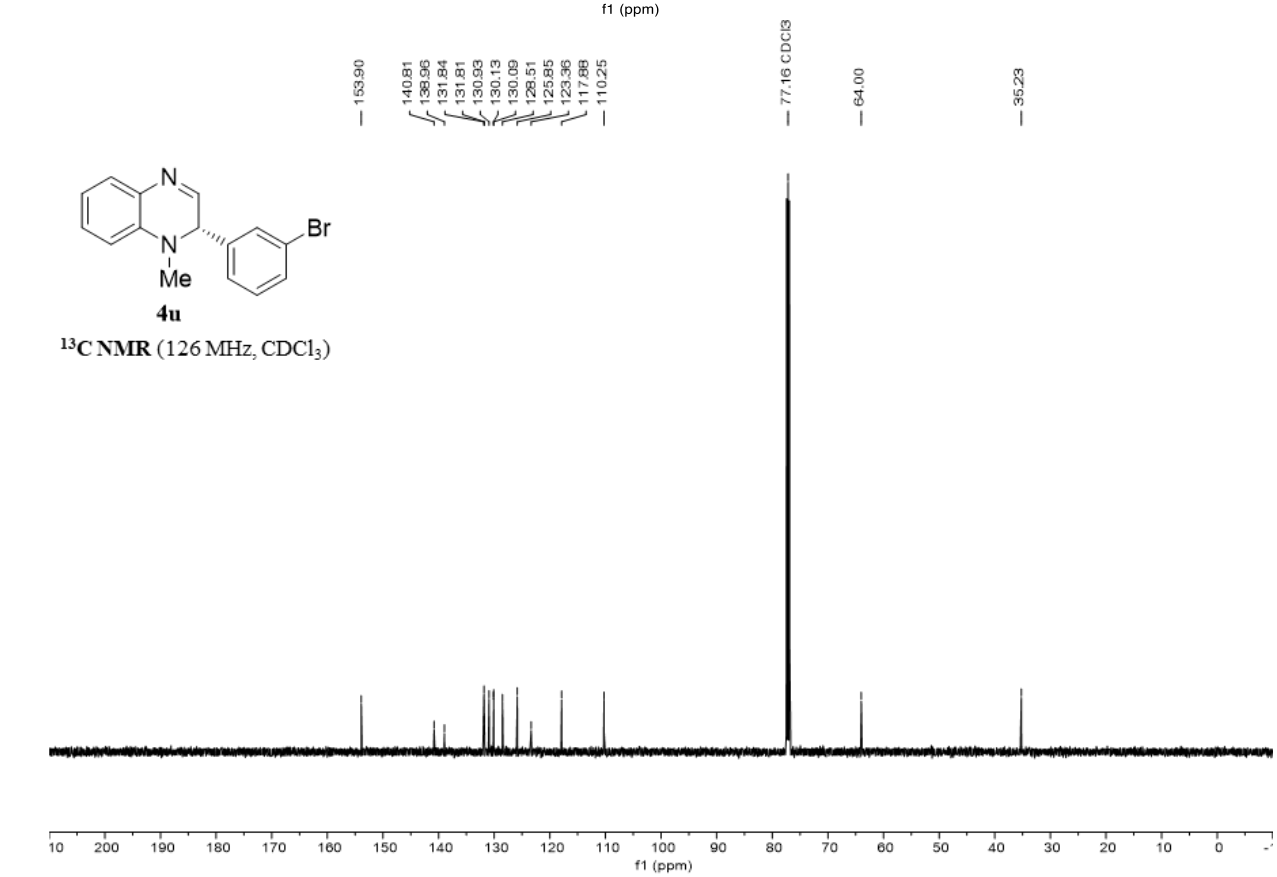
4t

^{19}F NMR (471 MHz, $CDCl_3$)



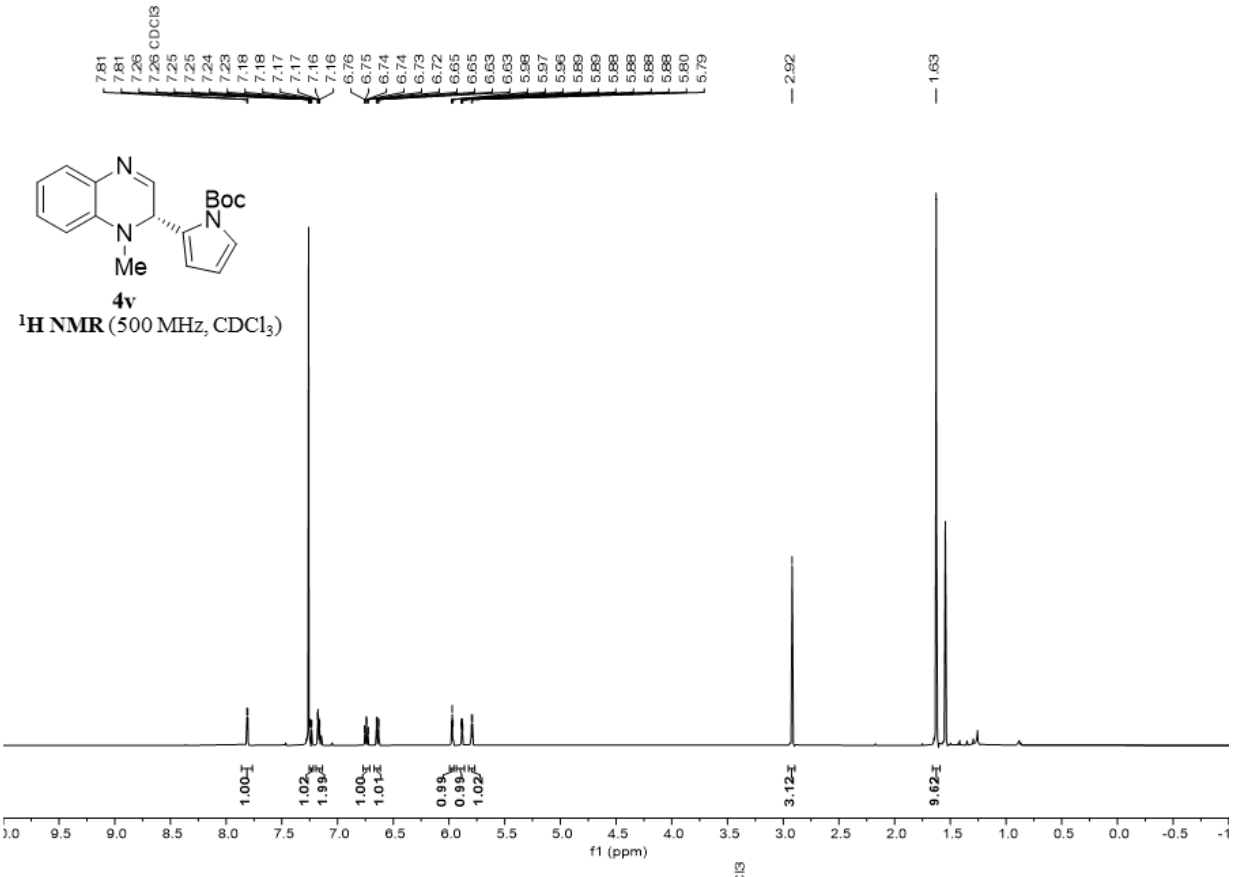
4u

^{1}H NMR (500 MHz, $CDCl_3$)



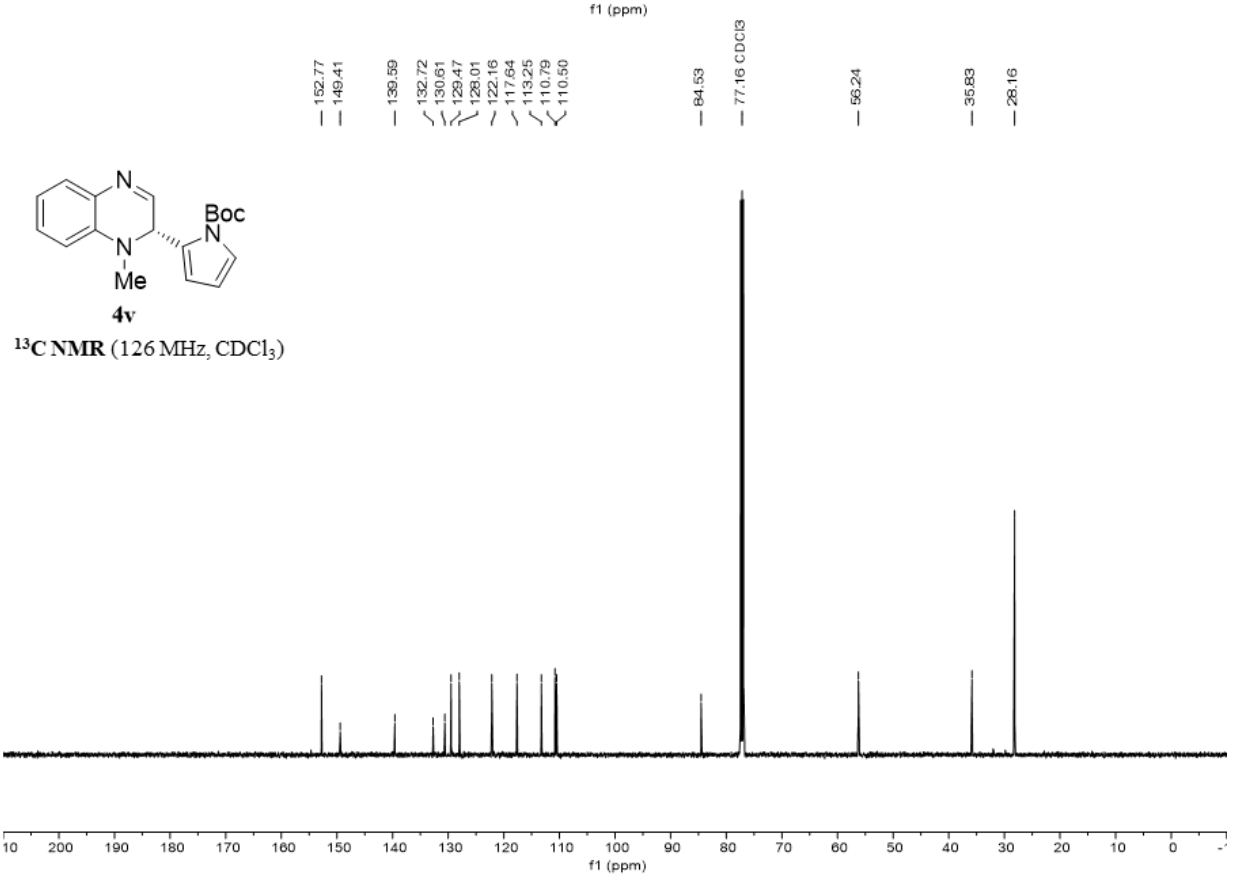
4u

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



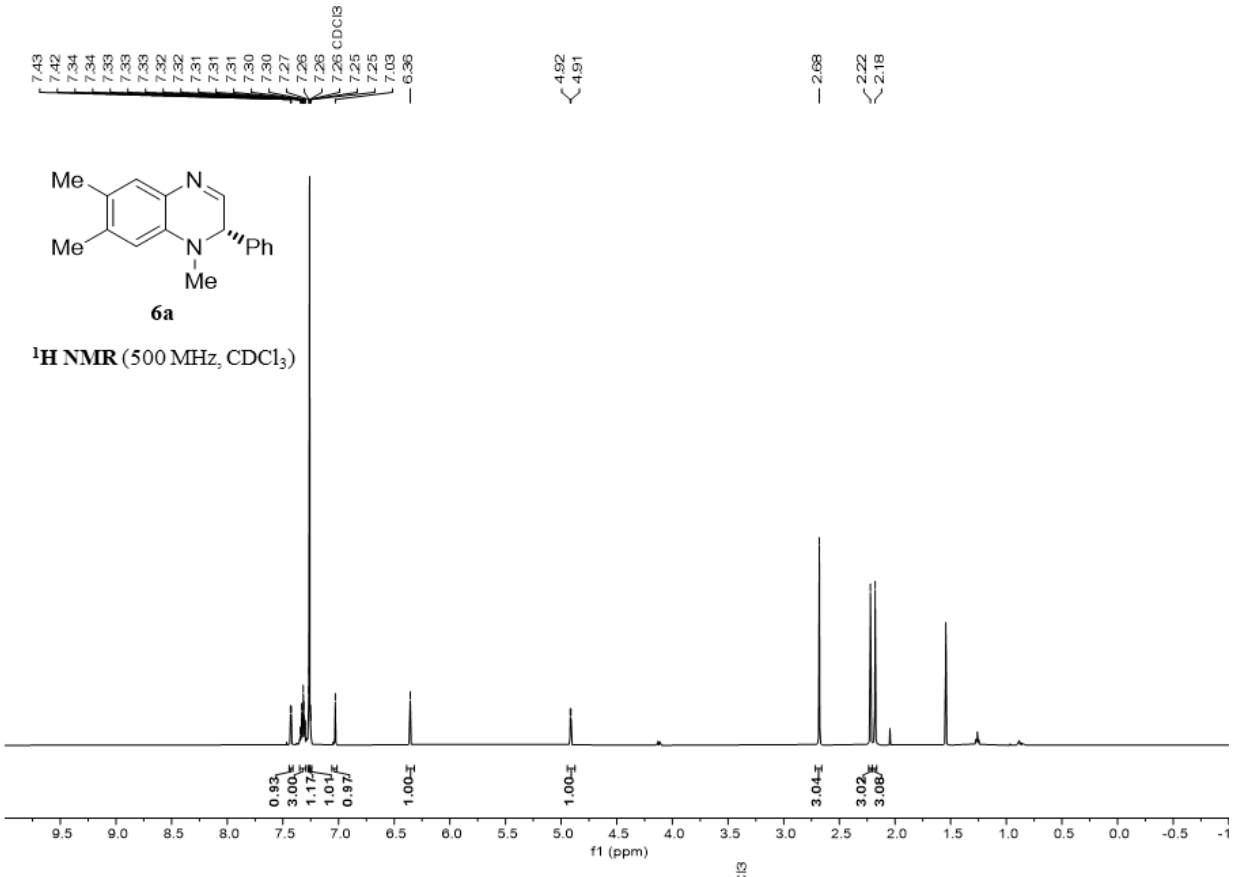
4v

^{1}H NMR (500 MHz, $CDCl_3$)



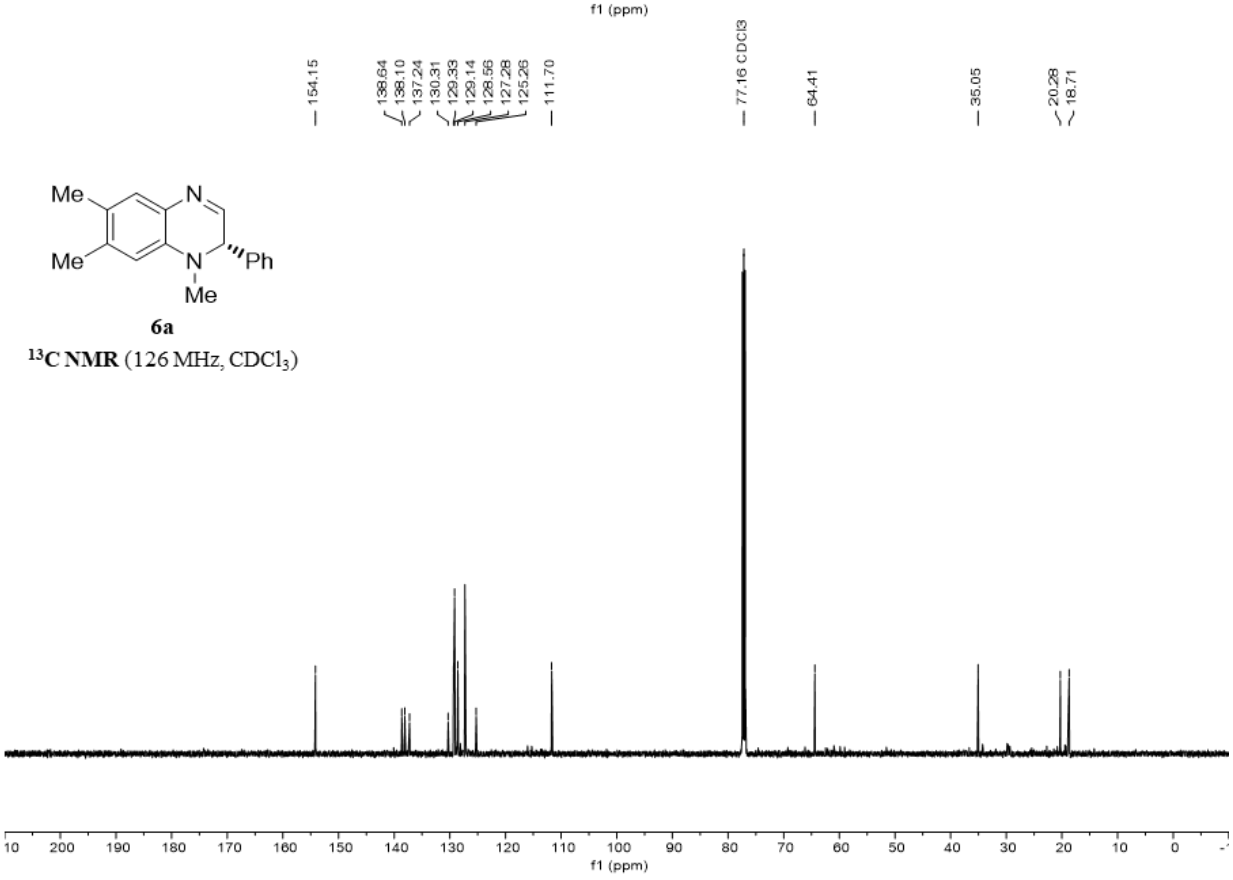
4v

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



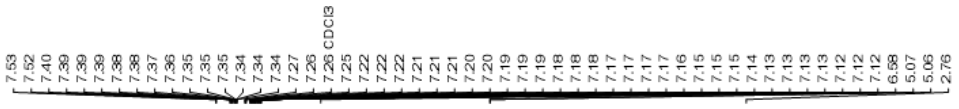
6a

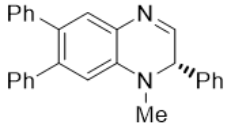
^{1}H NMR (500 MHz, $CDCl_3$)



6a

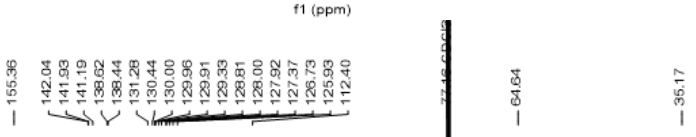
^{13}C NMR (126 MHz, $CDCl_3$)

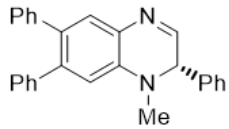




6b

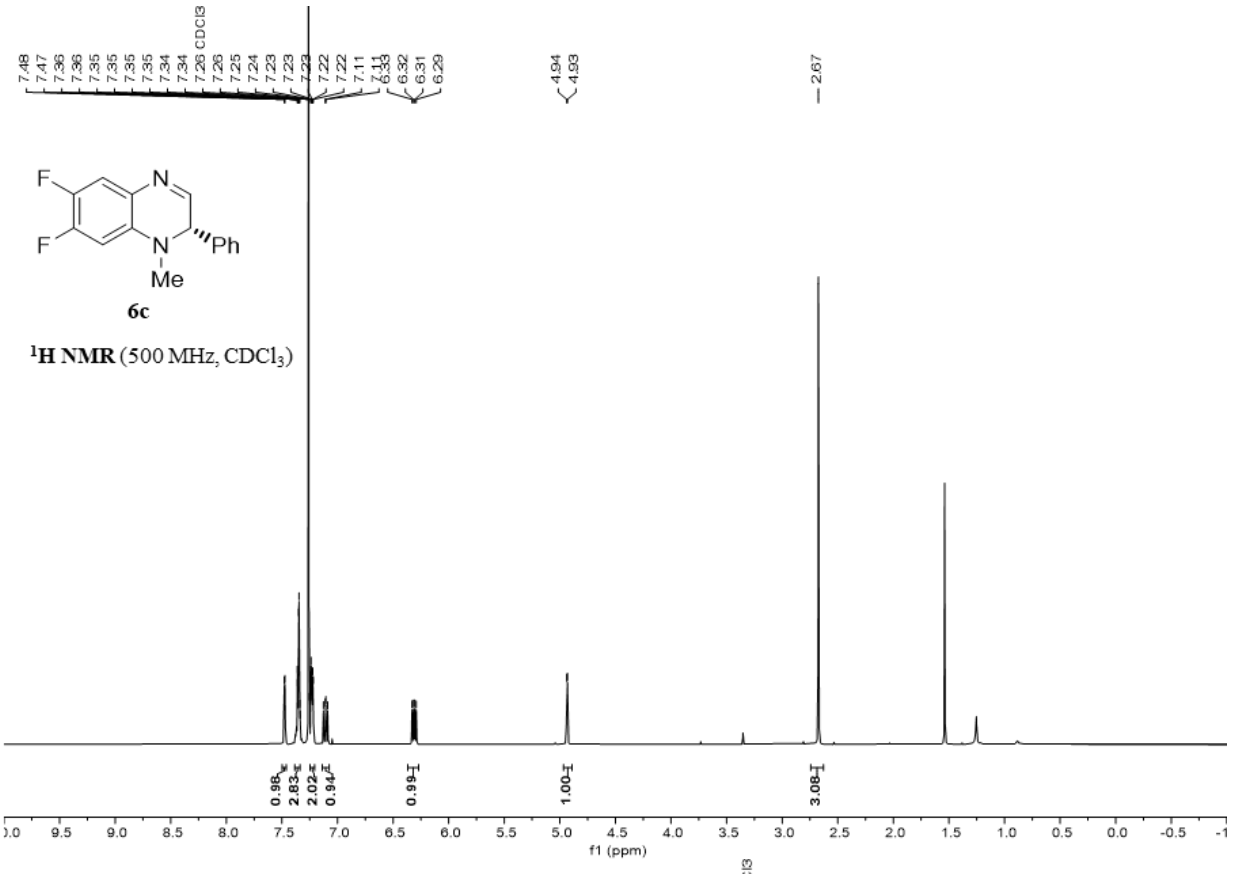
^{1}H NMR (600 MHz, $CDCl_3$)





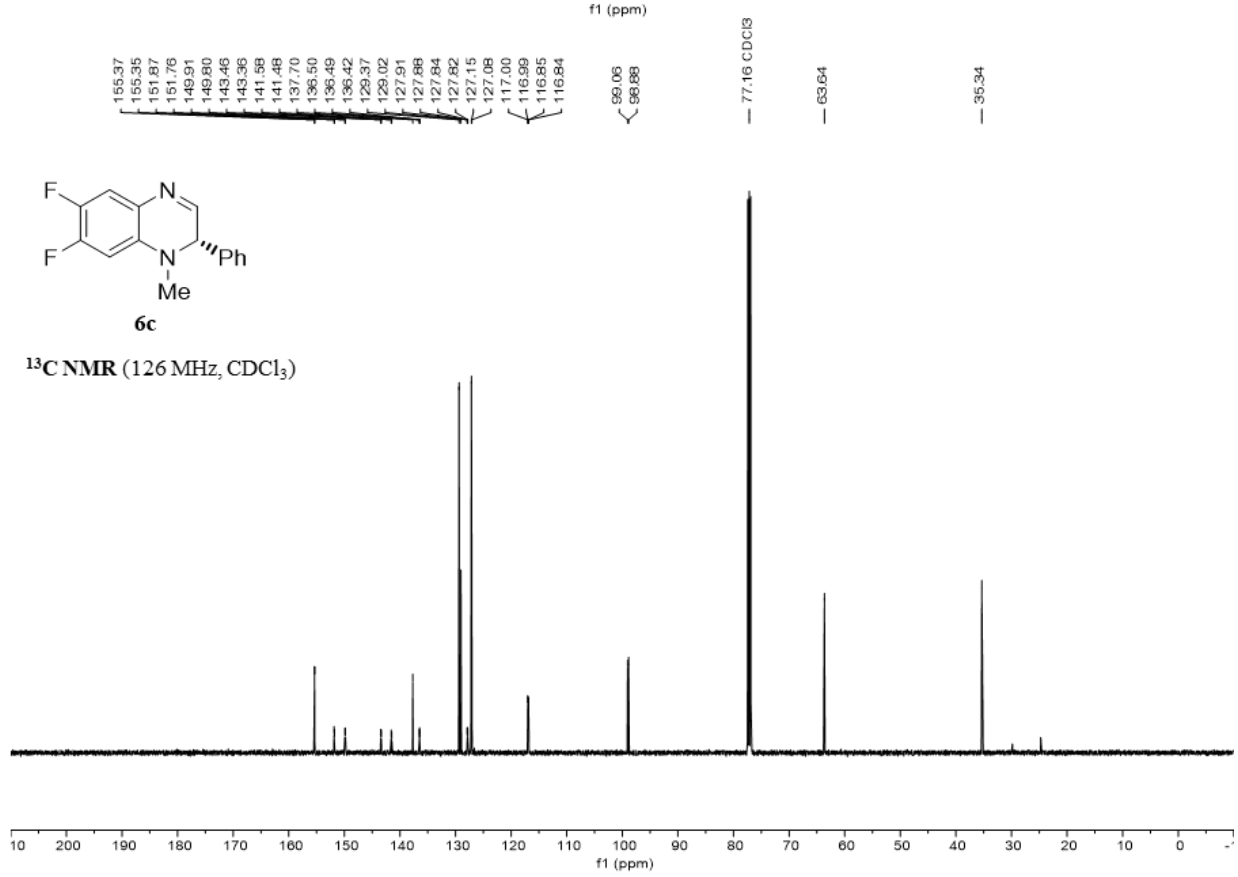
6b

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



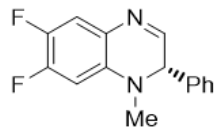
6c

^{1}H NMR (500 MHz, $CDCl_3$)



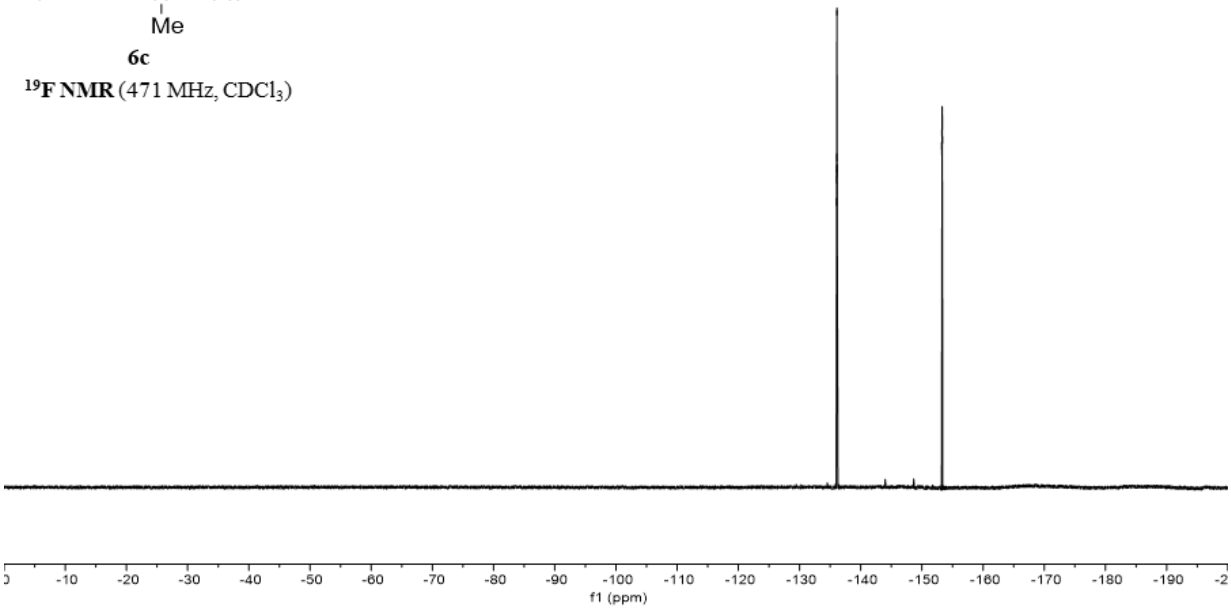
6c

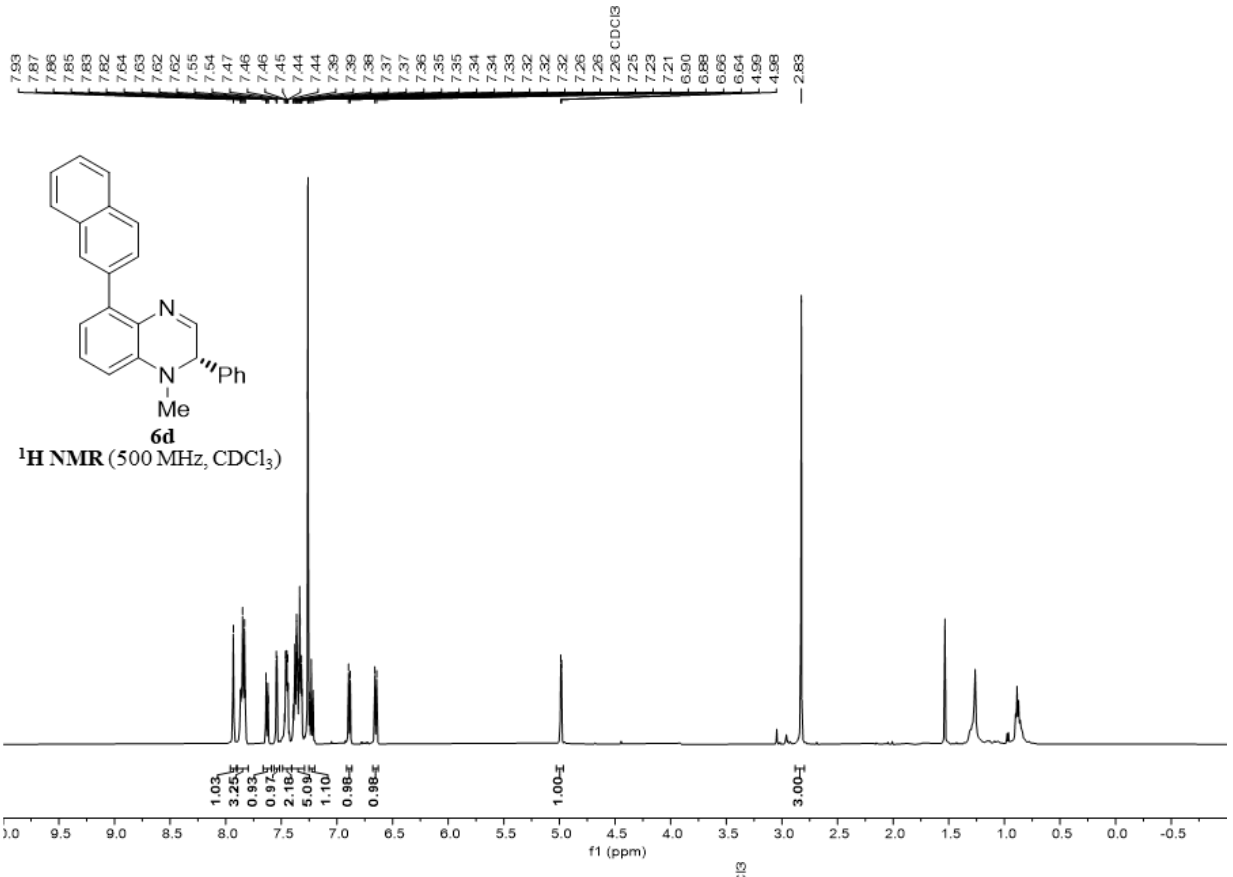
^{13}C NMR (126 MHz, $CDCl_3$)



6c

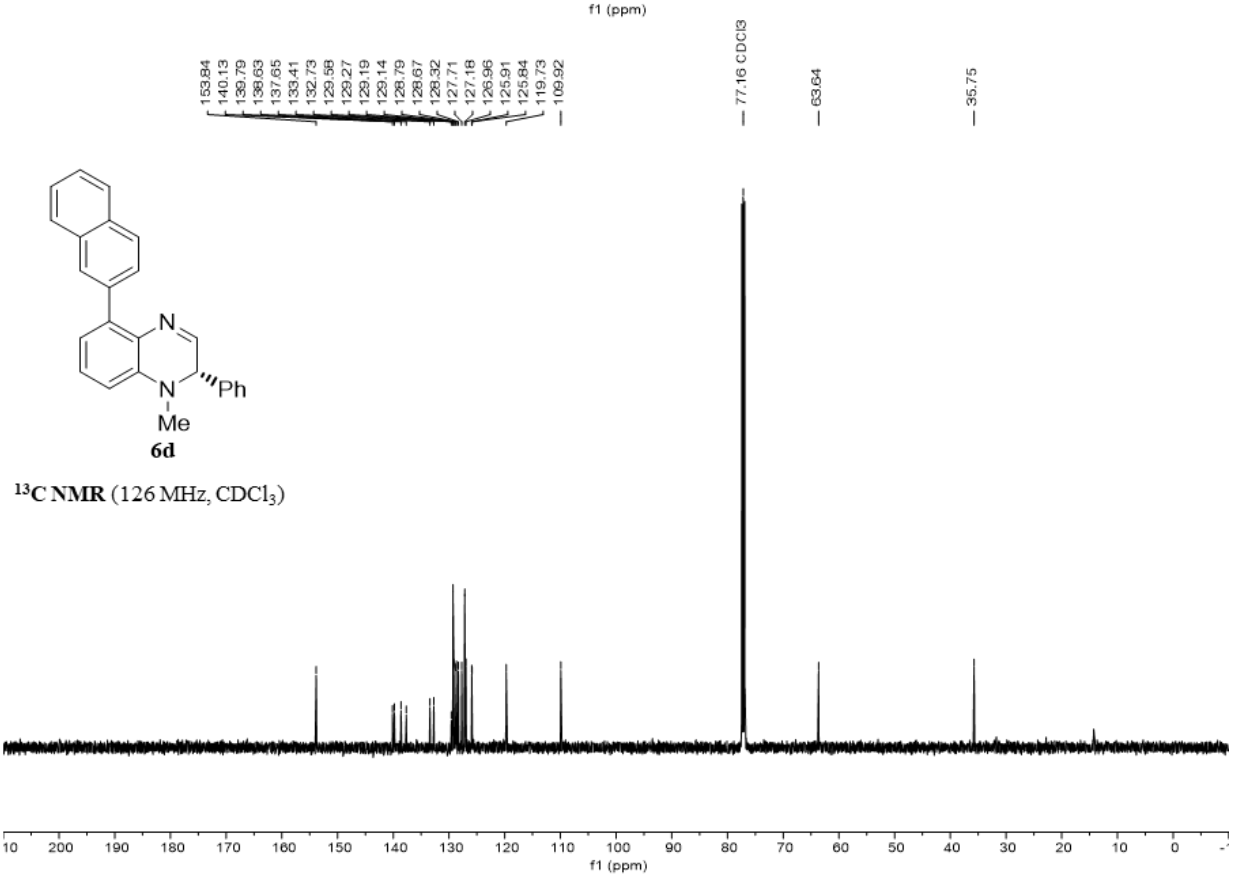
^{19}F NMR (471 MHz, $CDCl_3$)





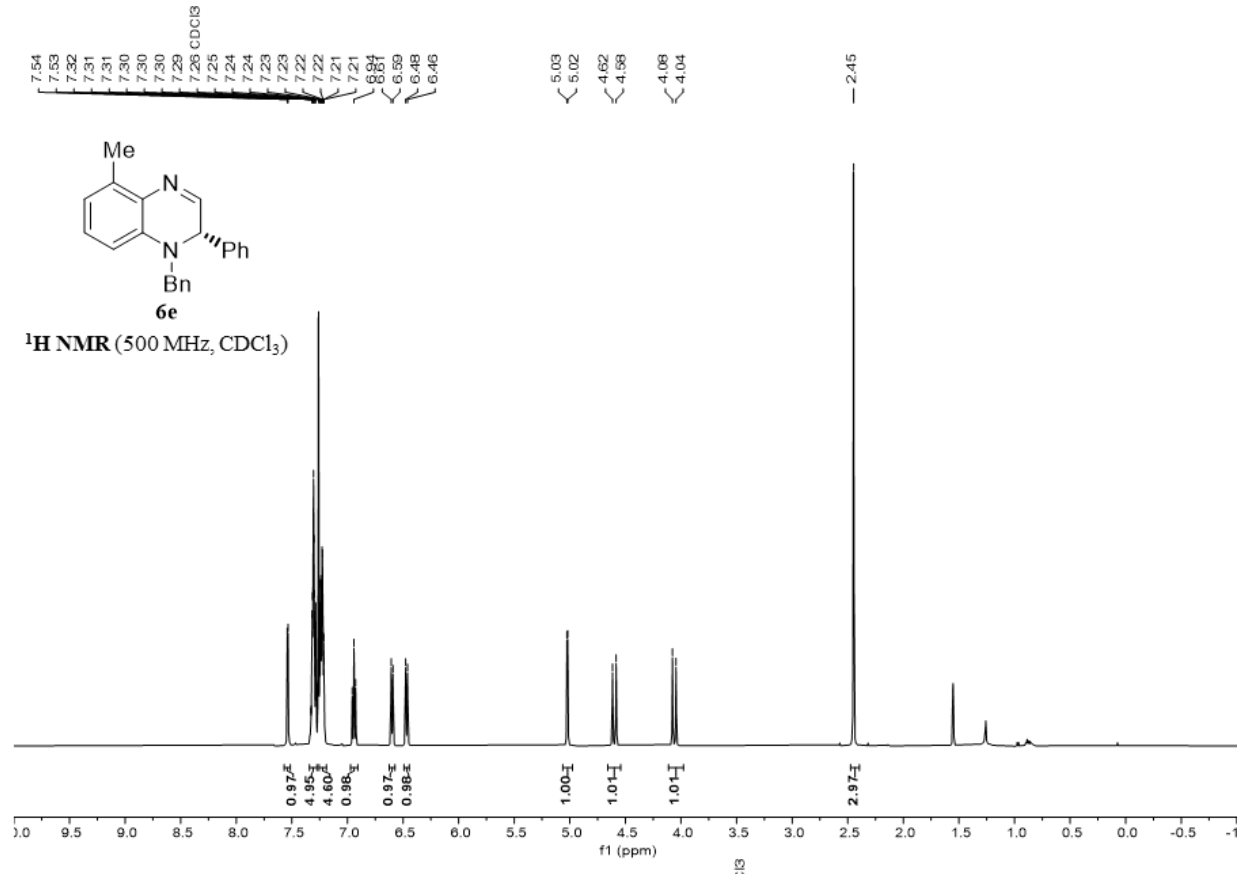
6d

^{1}H NMR (500 MHz, $CDCl_3$)



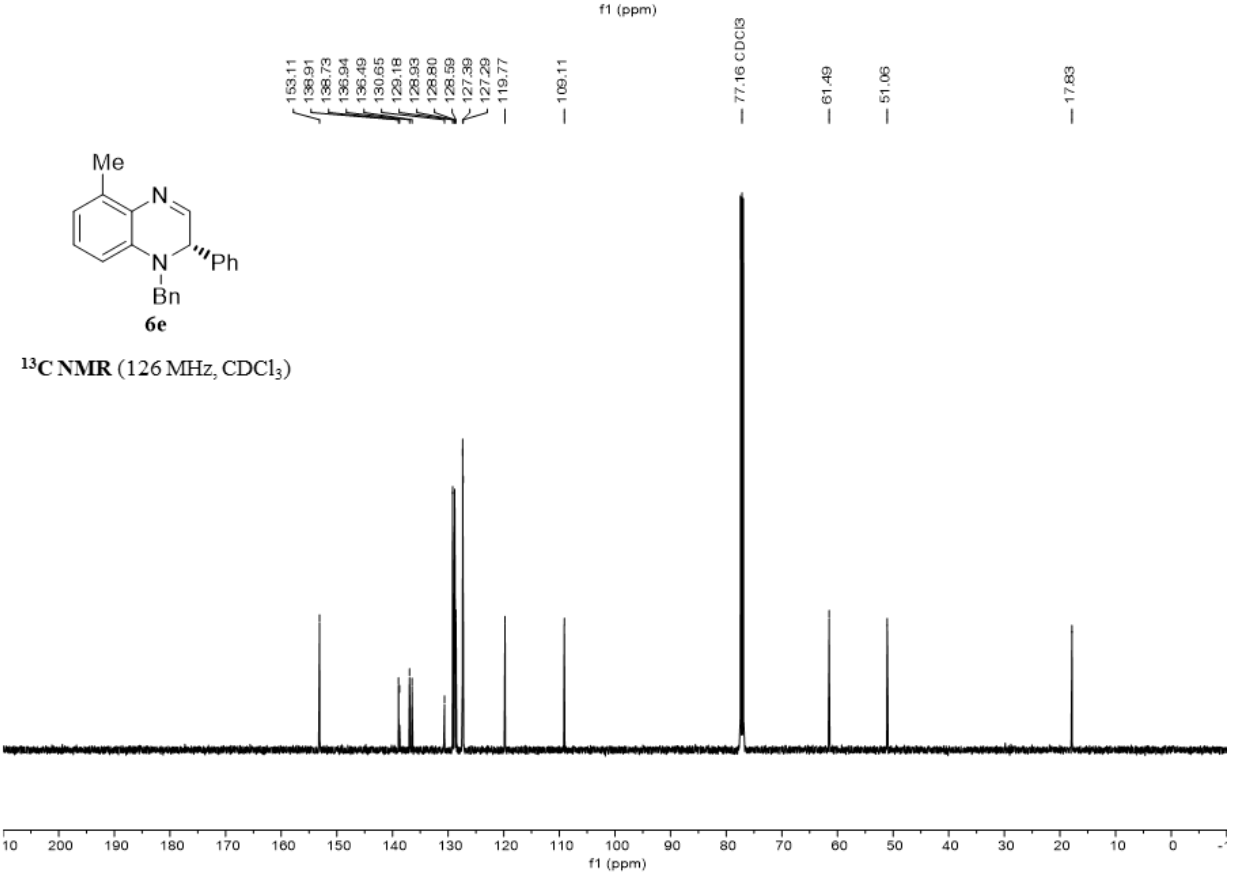
6d

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



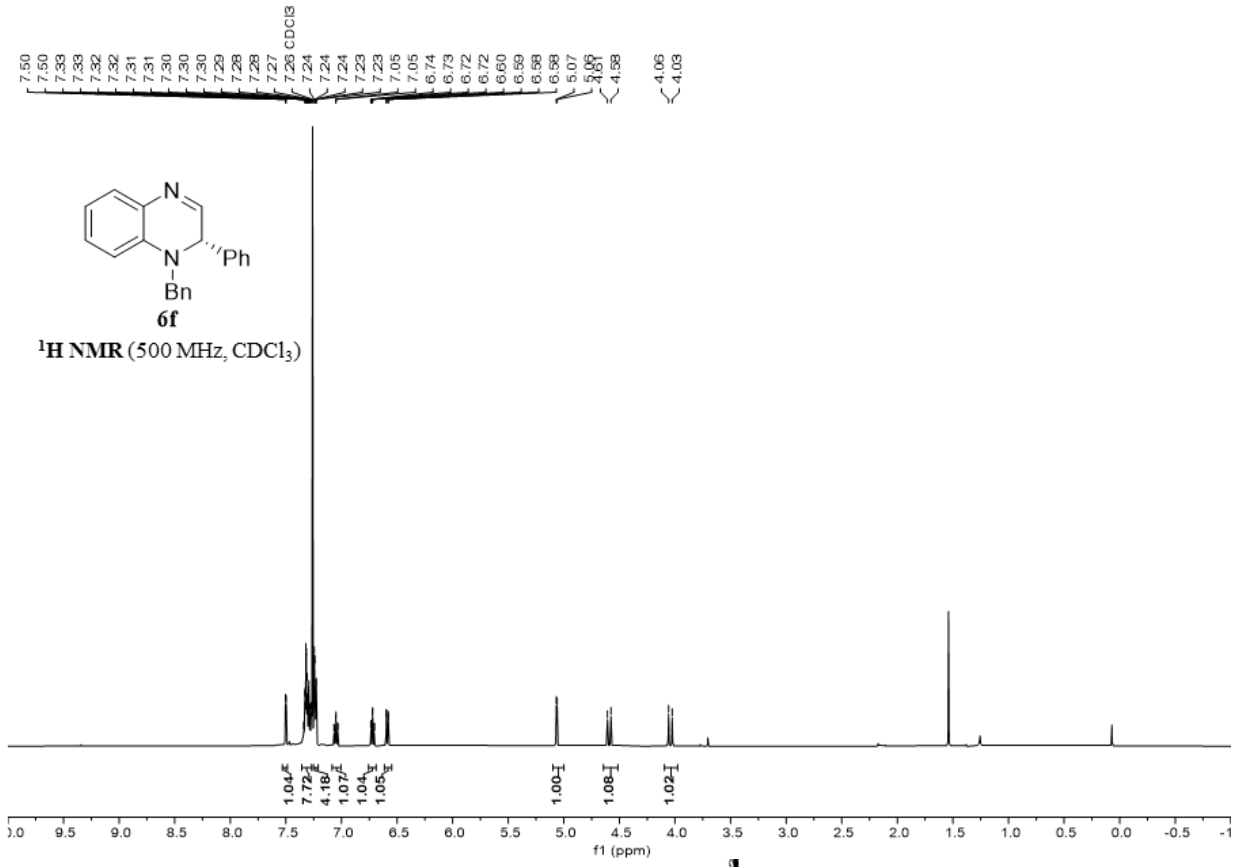
6e

^{1}H NMR (500 MHz, $CDCl_3$)



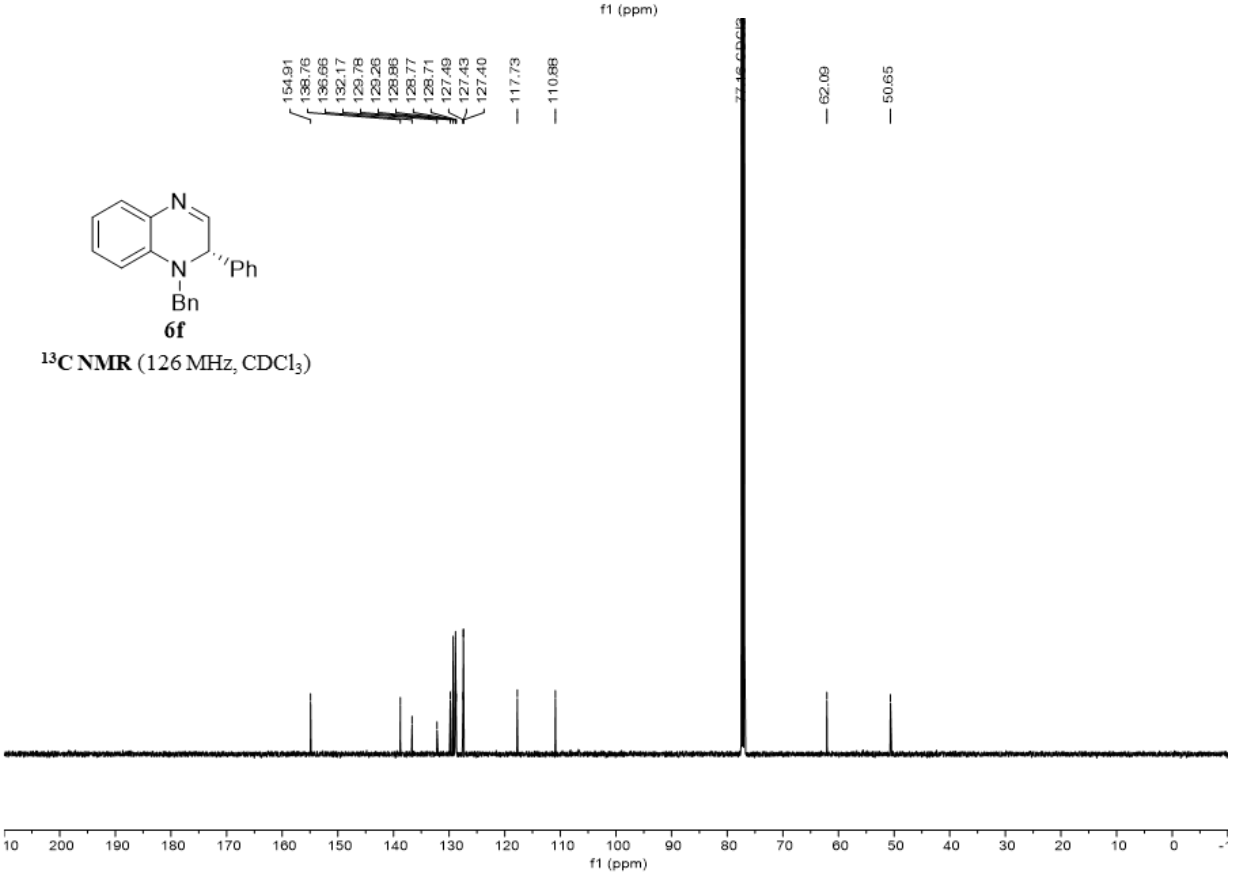
6e

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



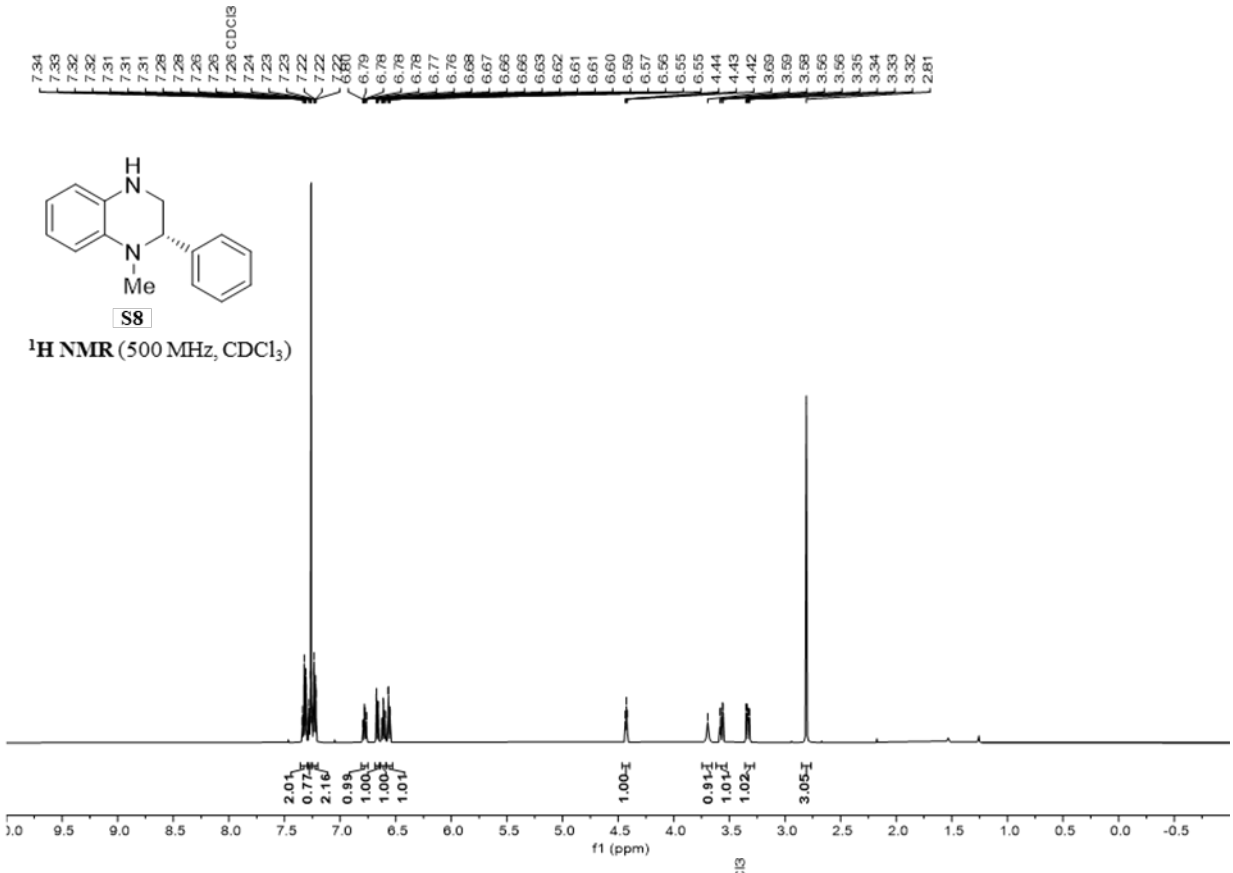
6f

^{1}H NMR (500 MHz, $CDCl_3$)

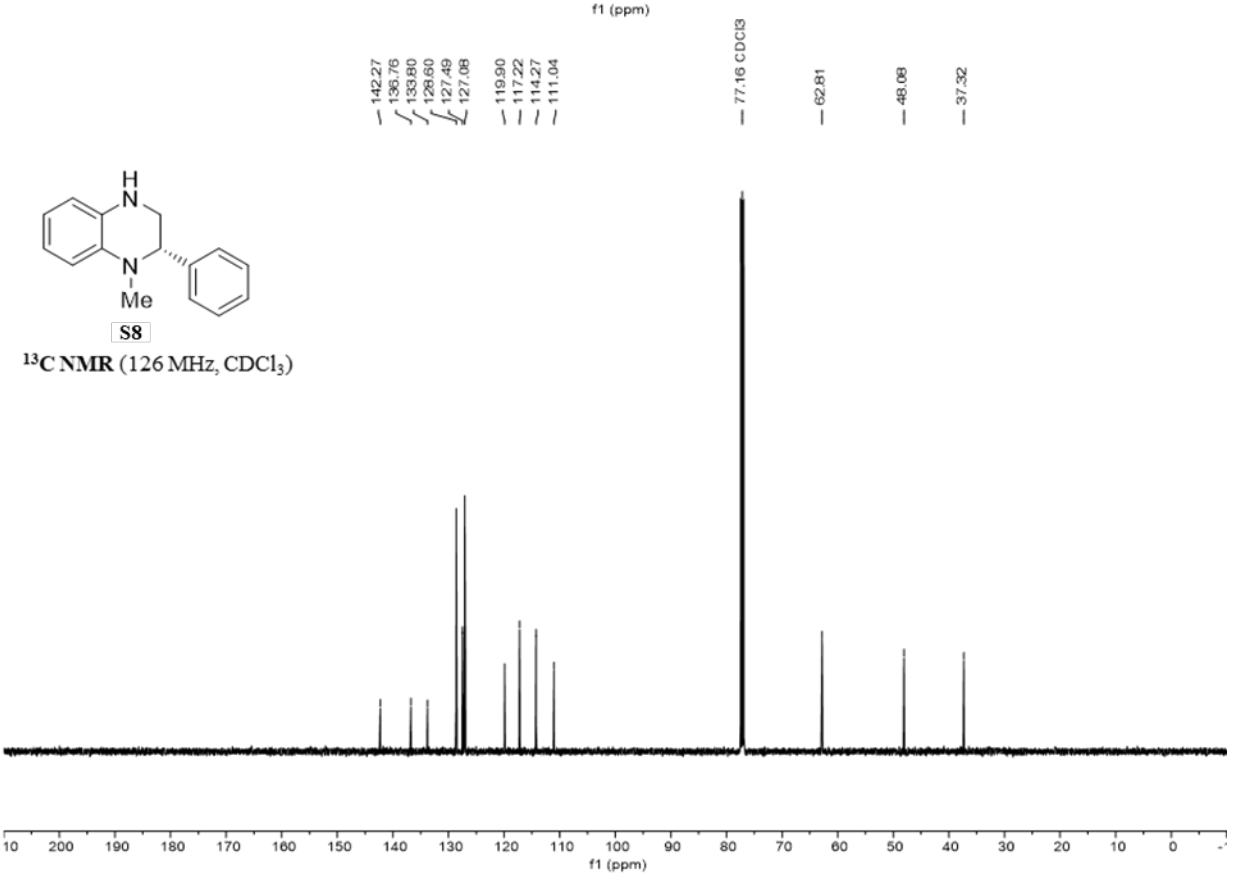


6f

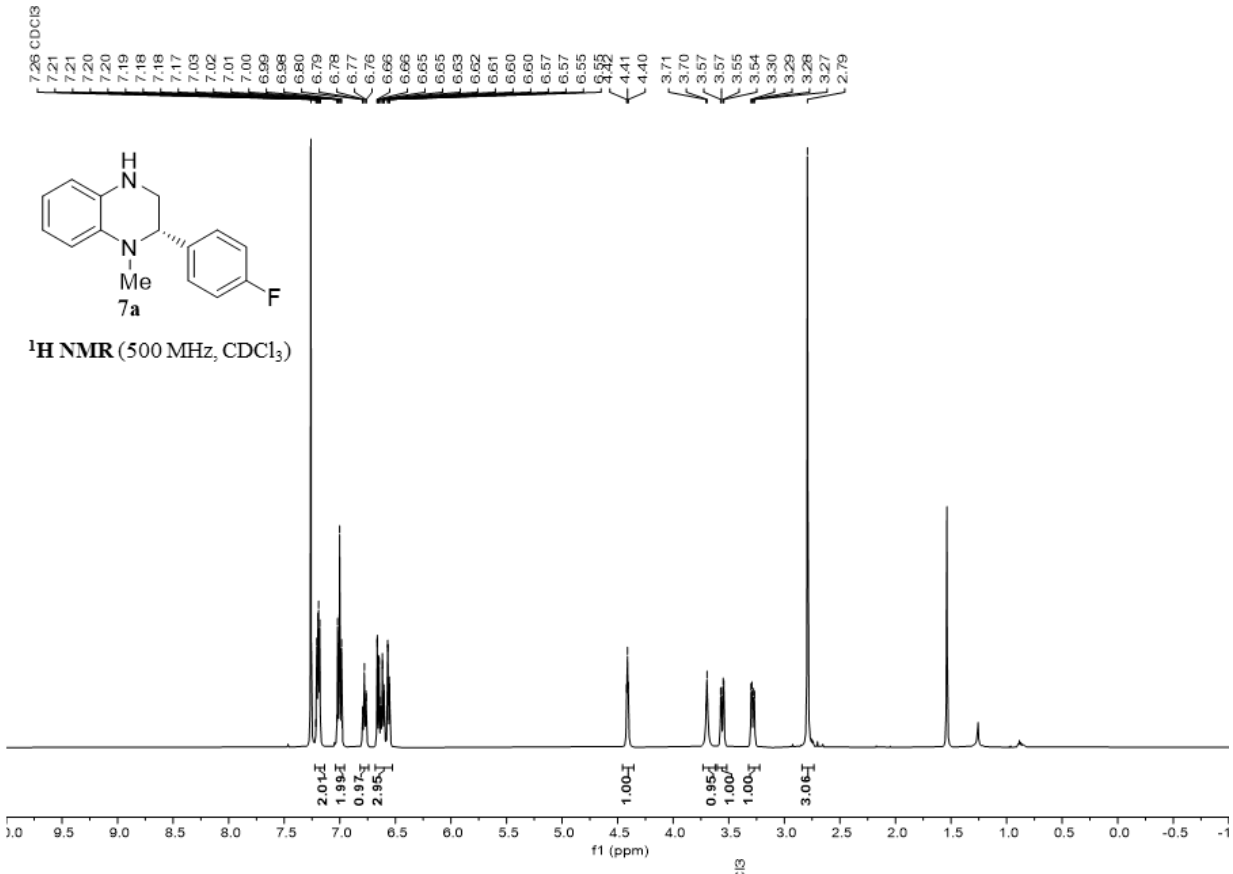
^{13}C NMR (126 MHz, $CDCl_3$)



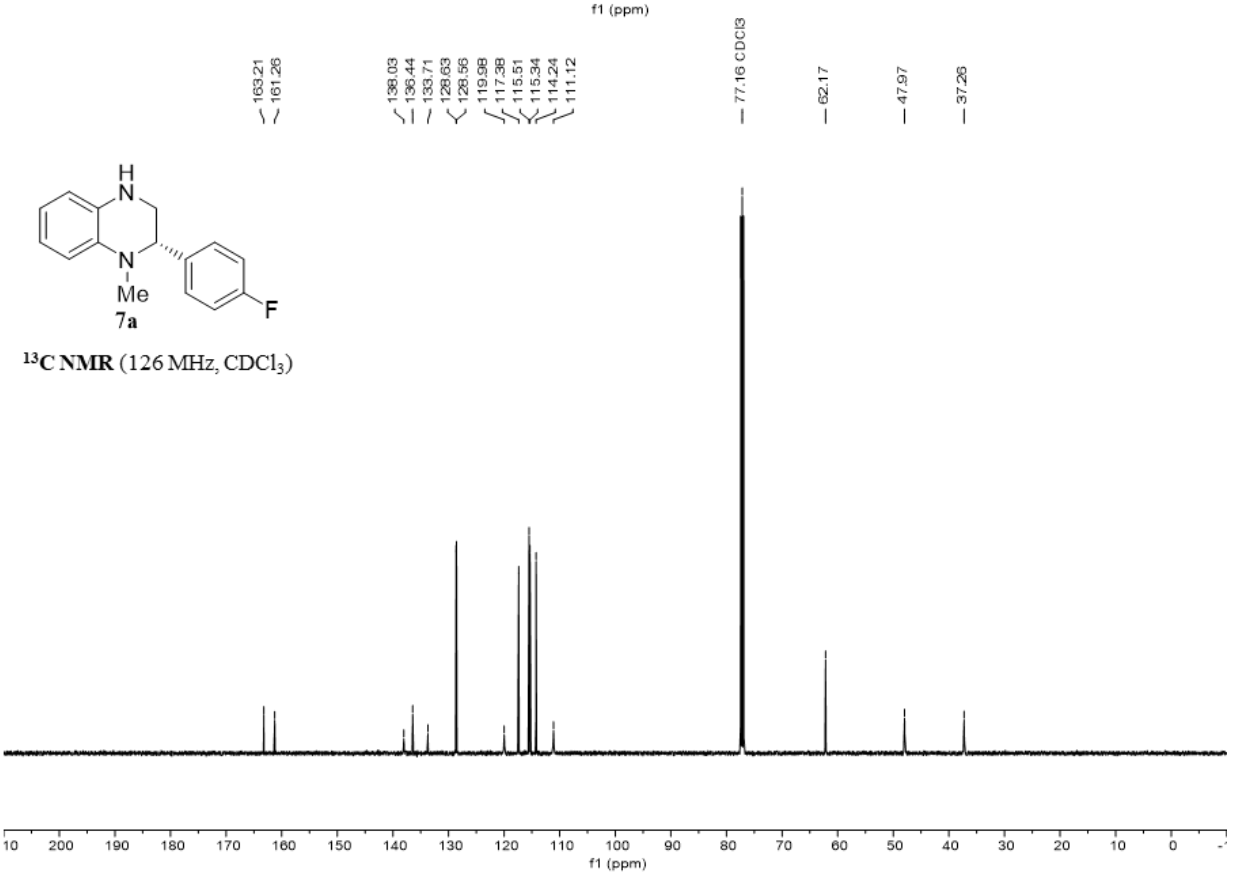
^{1}H NMR (500 MHz, $CDCl_3$)



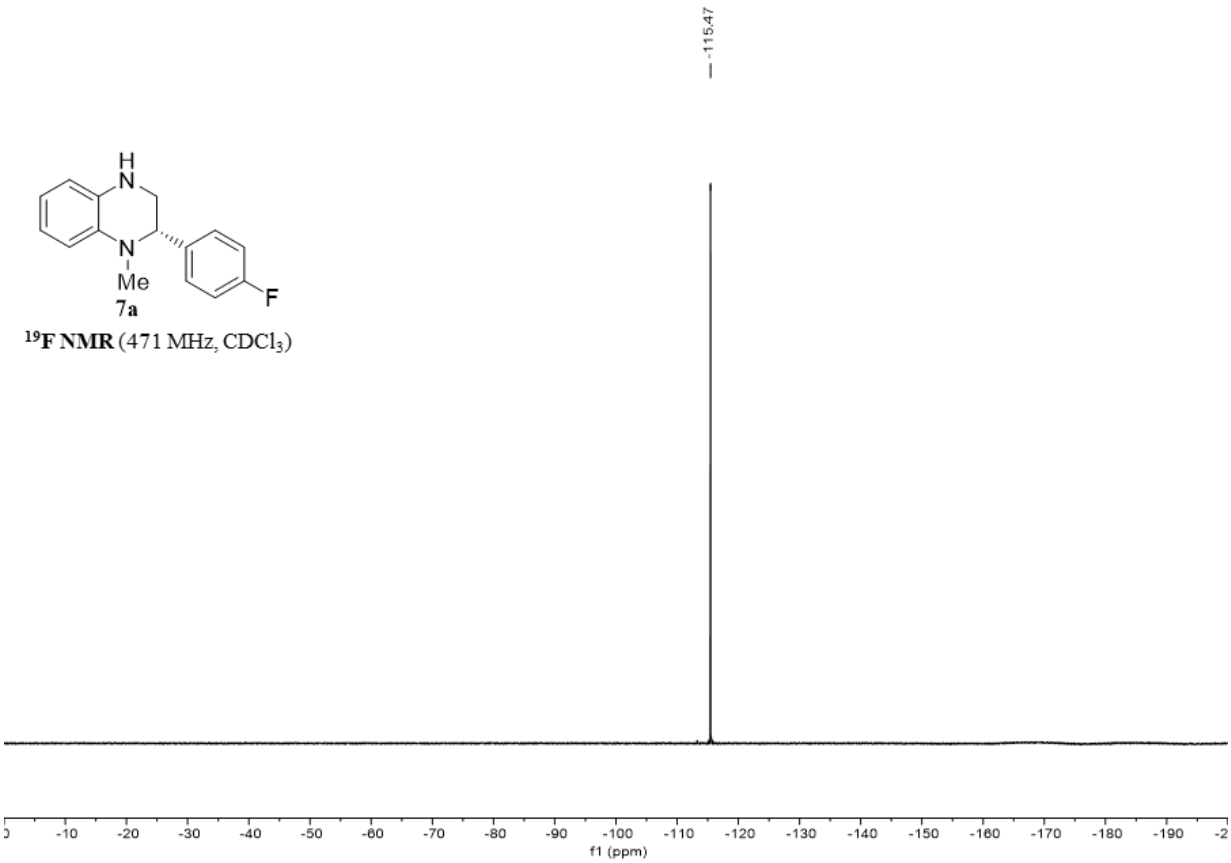
^{13}C NMR (126 MHz, $CDCl_3$)



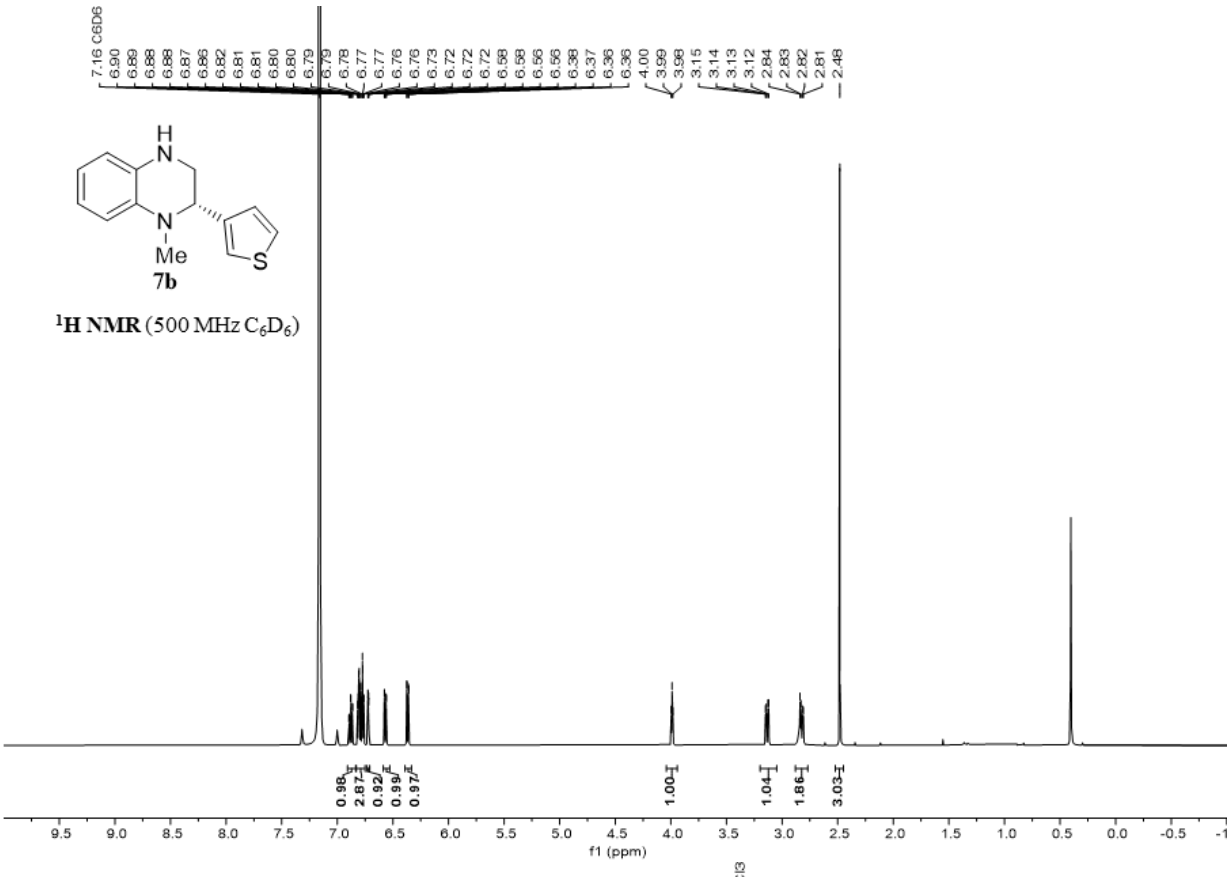
^{1}H NMR (500 MHz, $CDCl_3$)



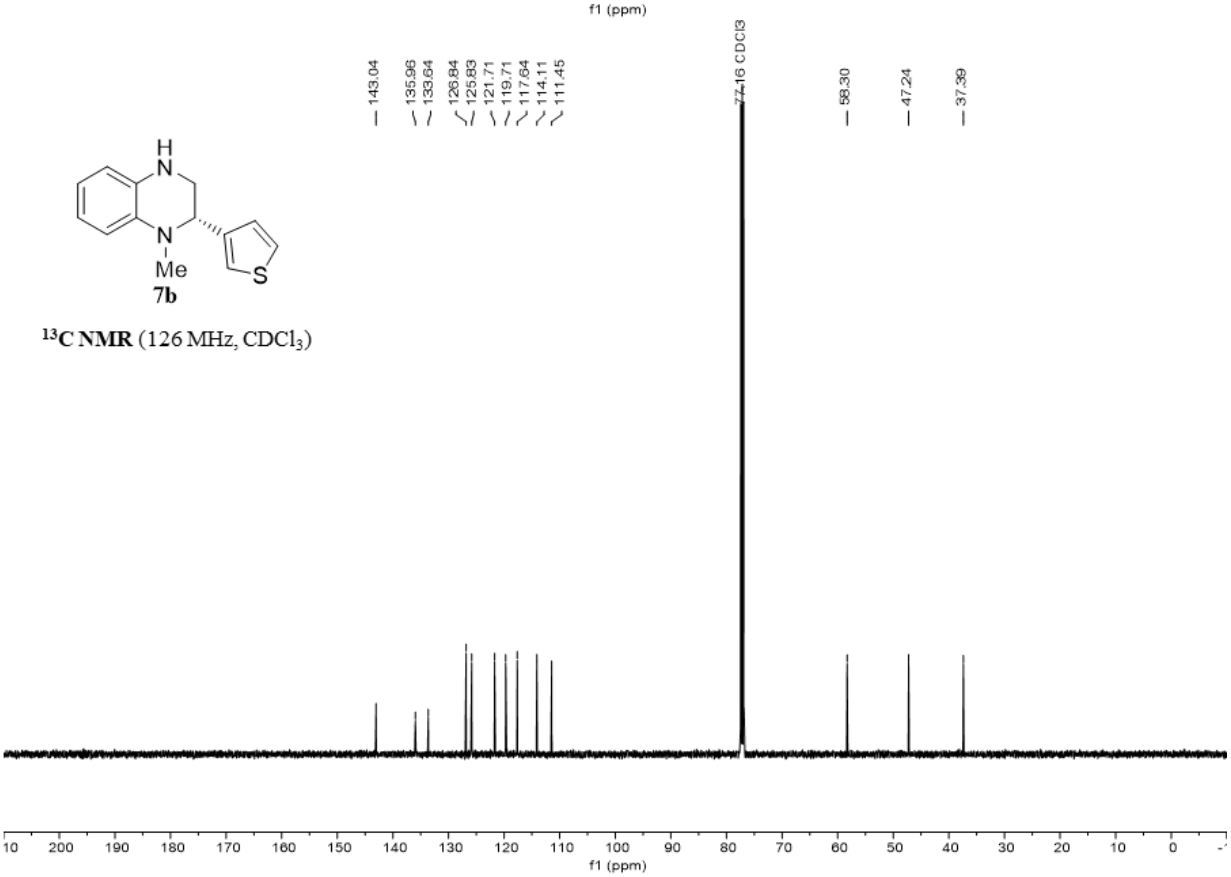
^{13}C NMR (126 MHz, $CDCl_3$)



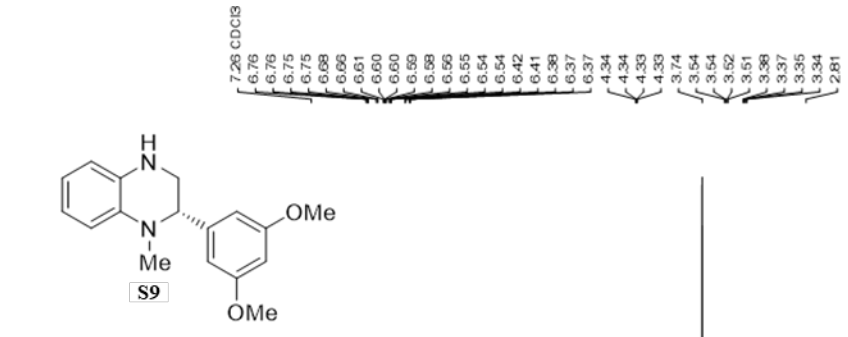
^{19}F NMR (471 MHz, $CDCl_3$)



^{1}H NMR (500 MHz C_6D_6)

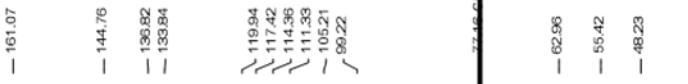


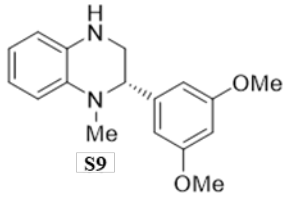
^{13}C NMR (126 MHz, $CDCl_3$)



S9

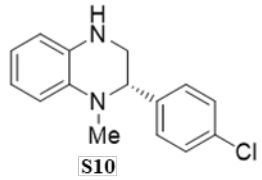
^{1}H NMR (500 MHz, $CDCl_3$)





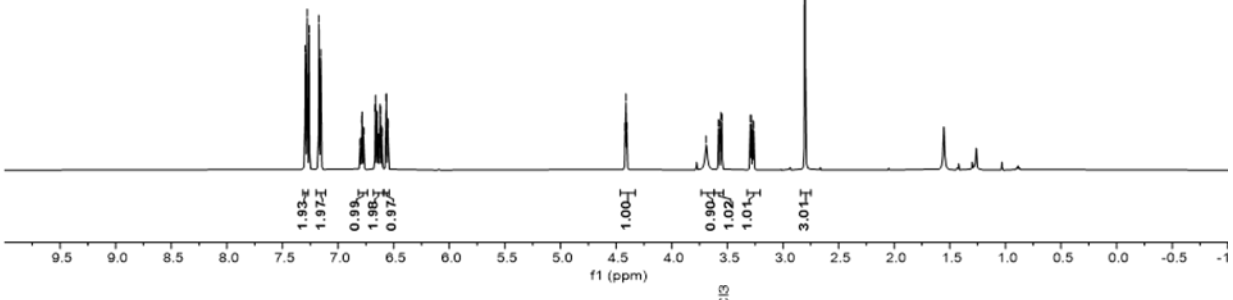
S9

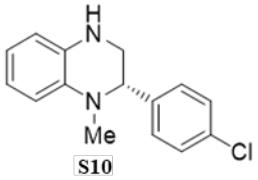
^{13}C NMR (126 MHz, $CDCl_3$)



S10

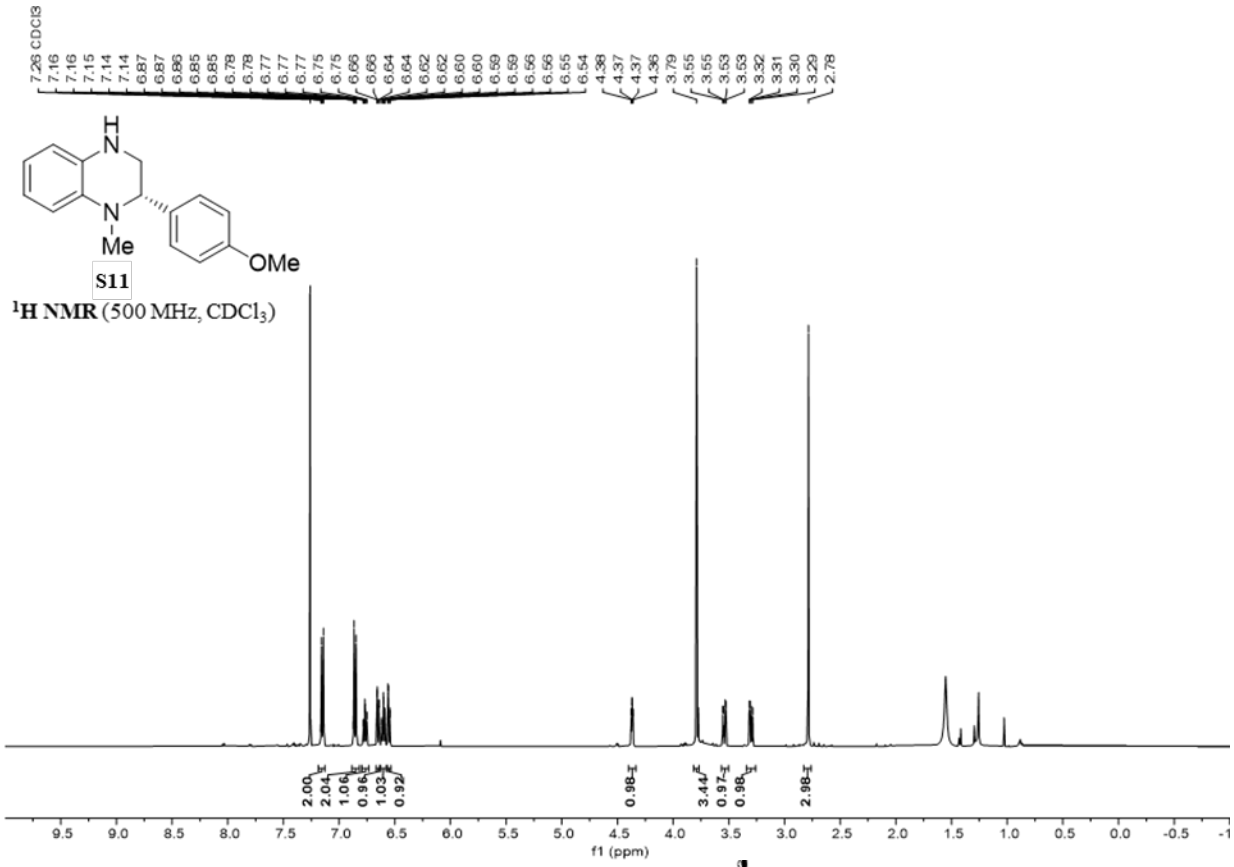
^{1}H NMR (500 MHz, $CDCl_3$)



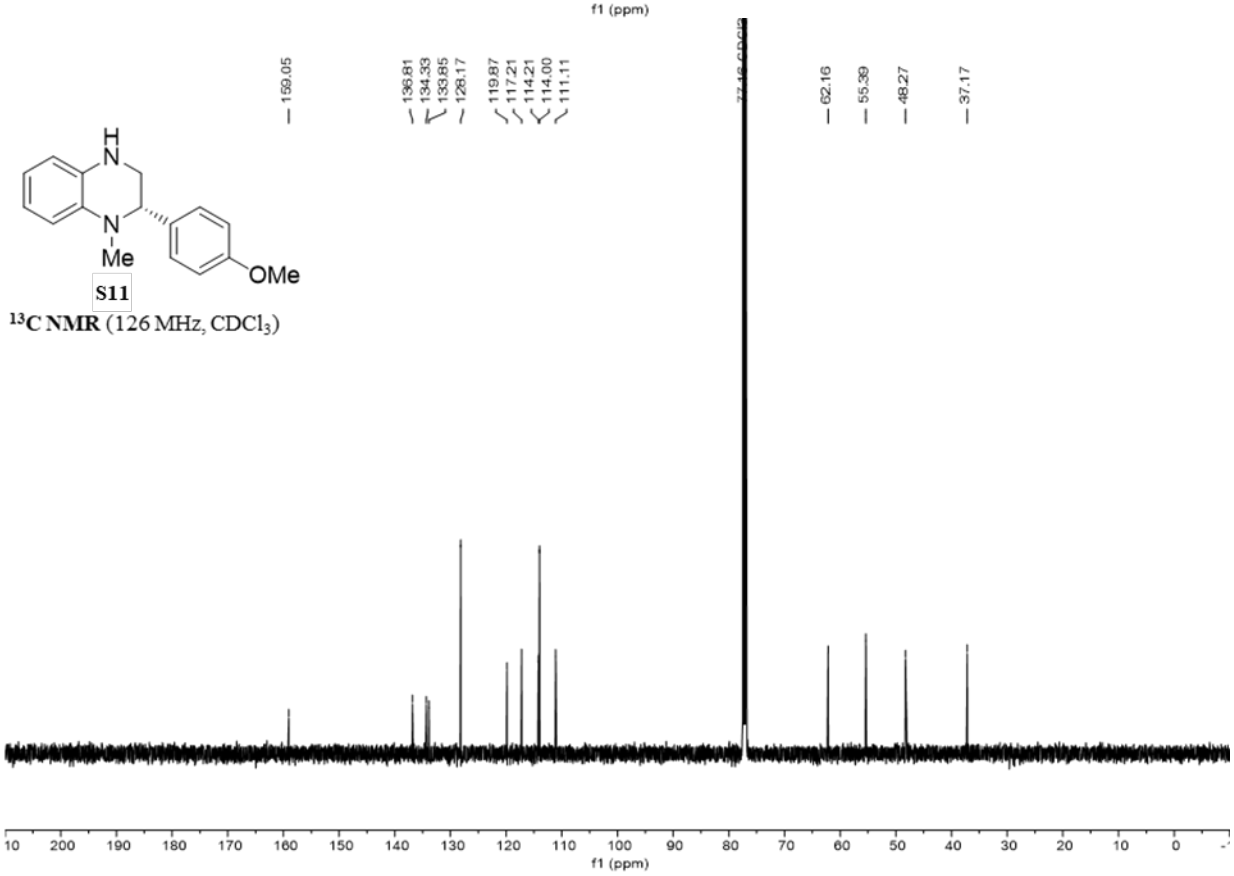


S10

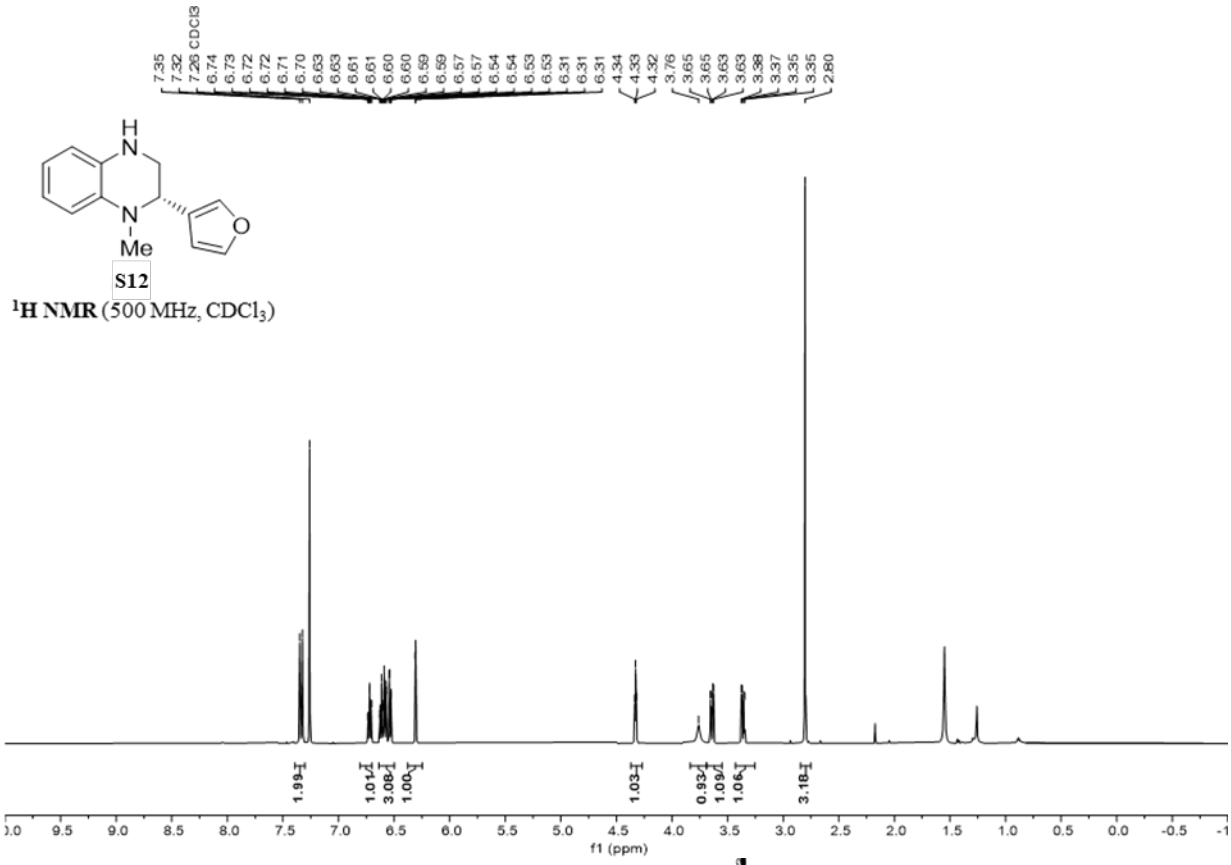
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

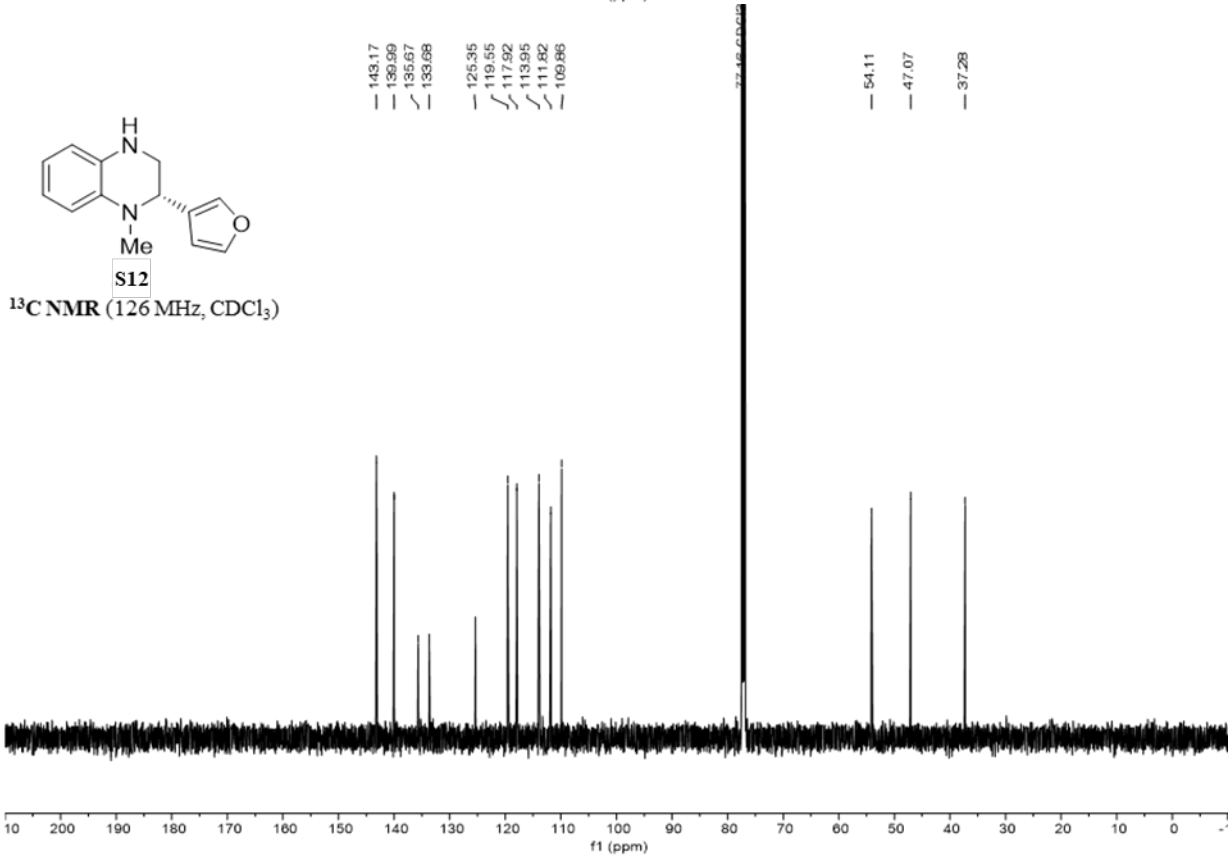


^{13}C NMR (126 MHz, $CDCl_3$)



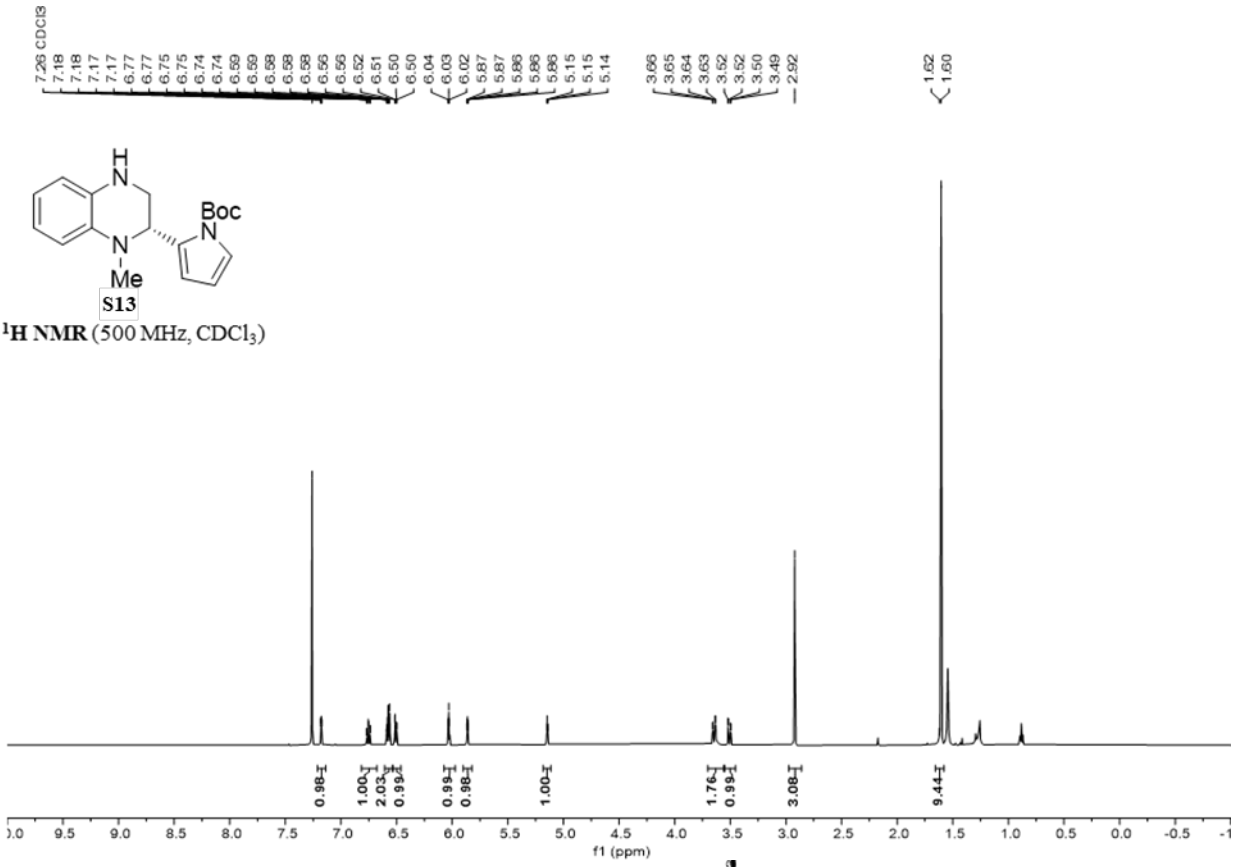
S12

^{1}H NMR (500 MHz, $CDCl_3$)

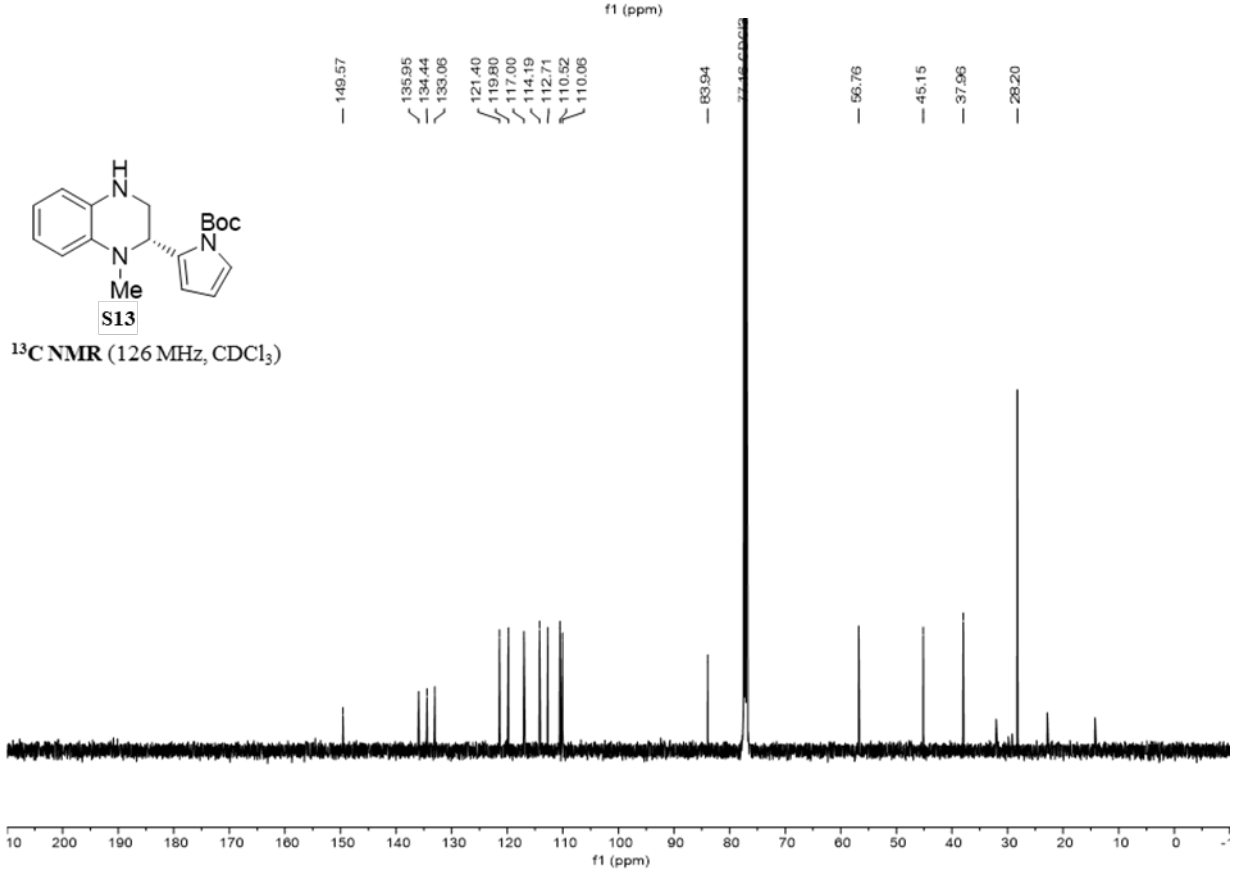


S12

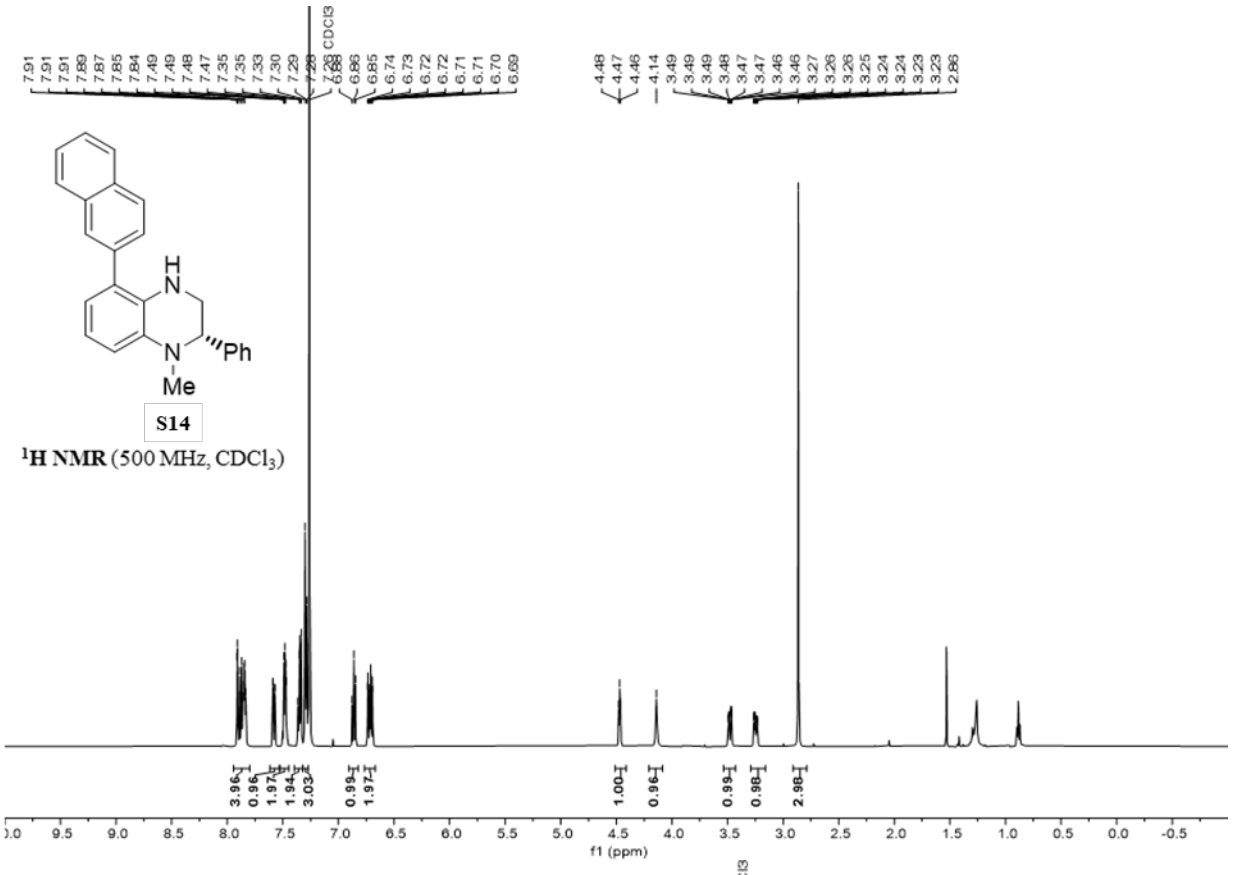
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

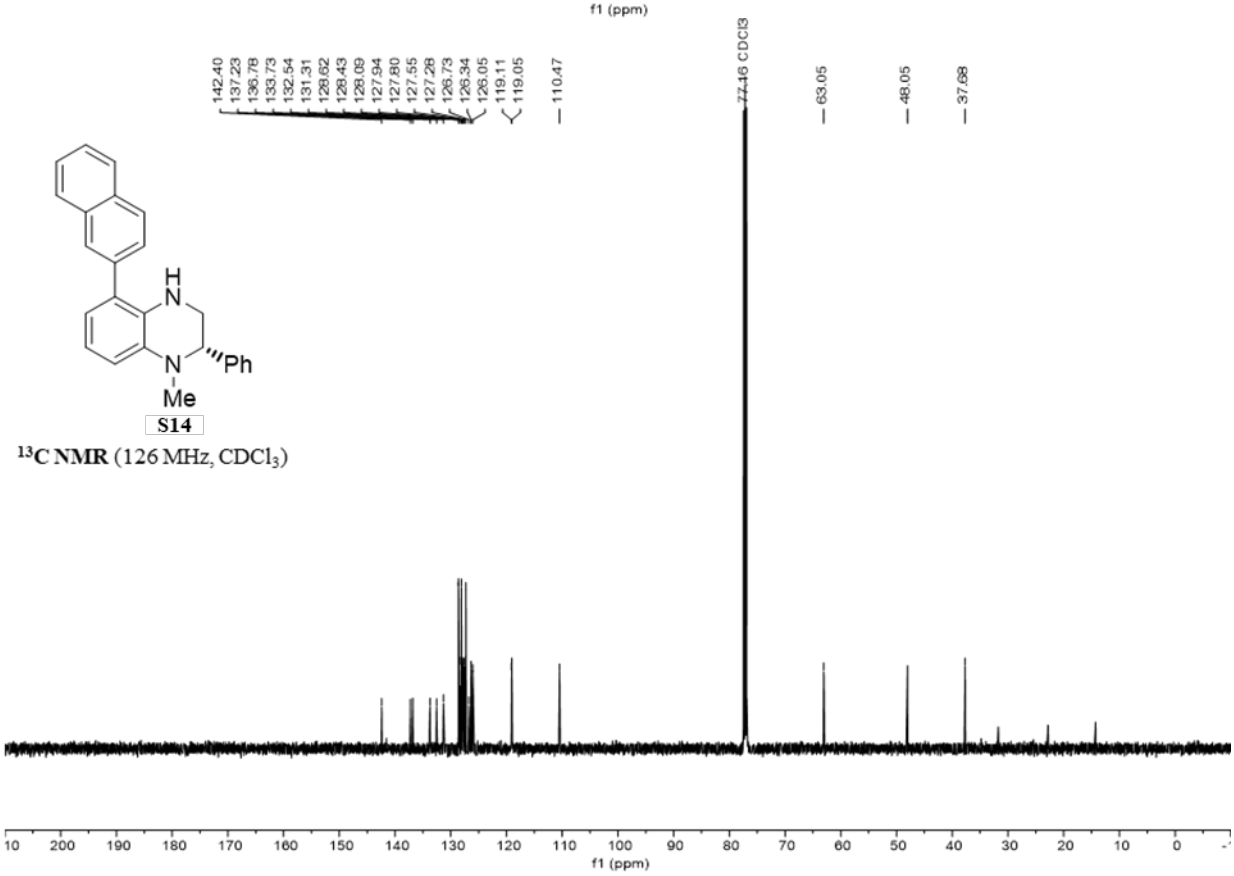


^{13}C NMR (126 MHz, $CDCl_3$)



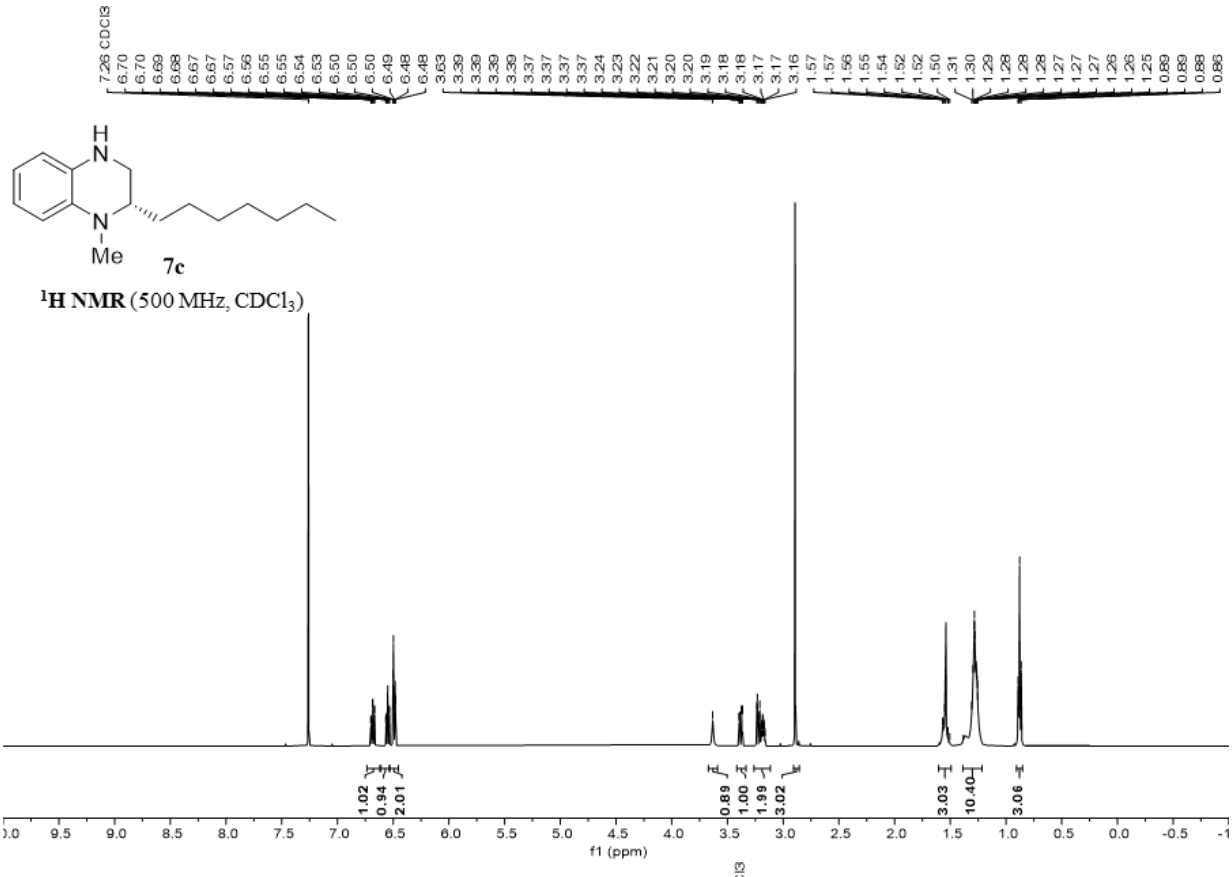
S14

^{1}H NMR (500 MHz, $CDCl_3$)



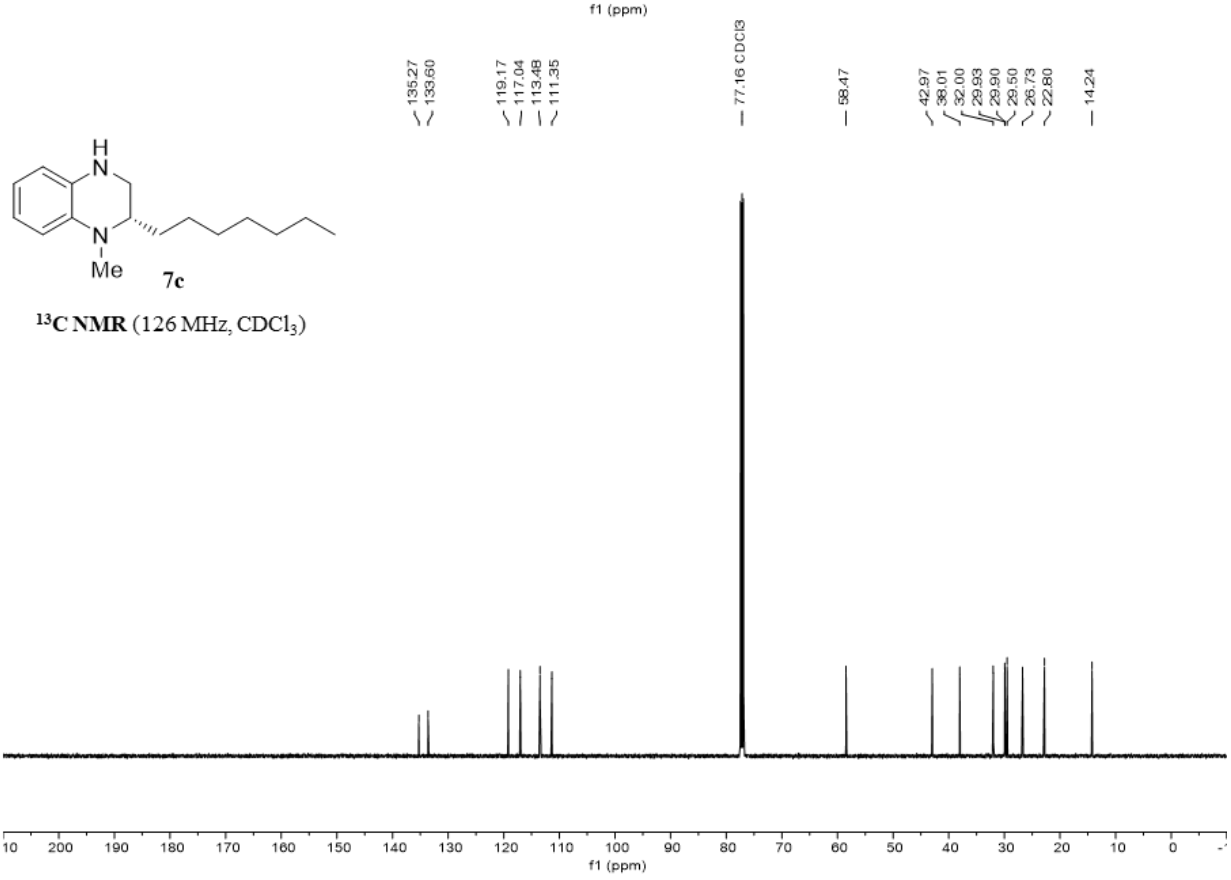
S14

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



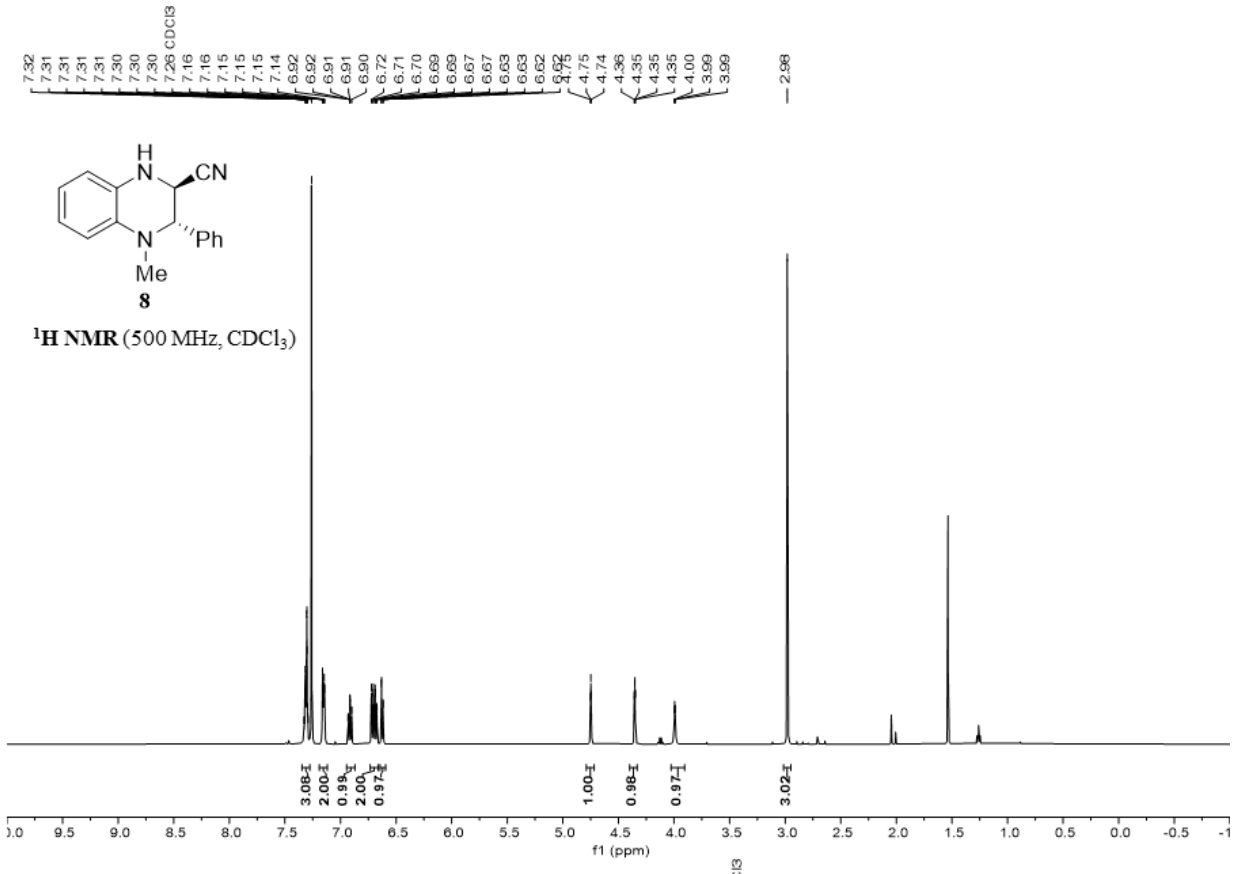
7c

^{1}H NMR (500 MHz, $CDCl_3$)



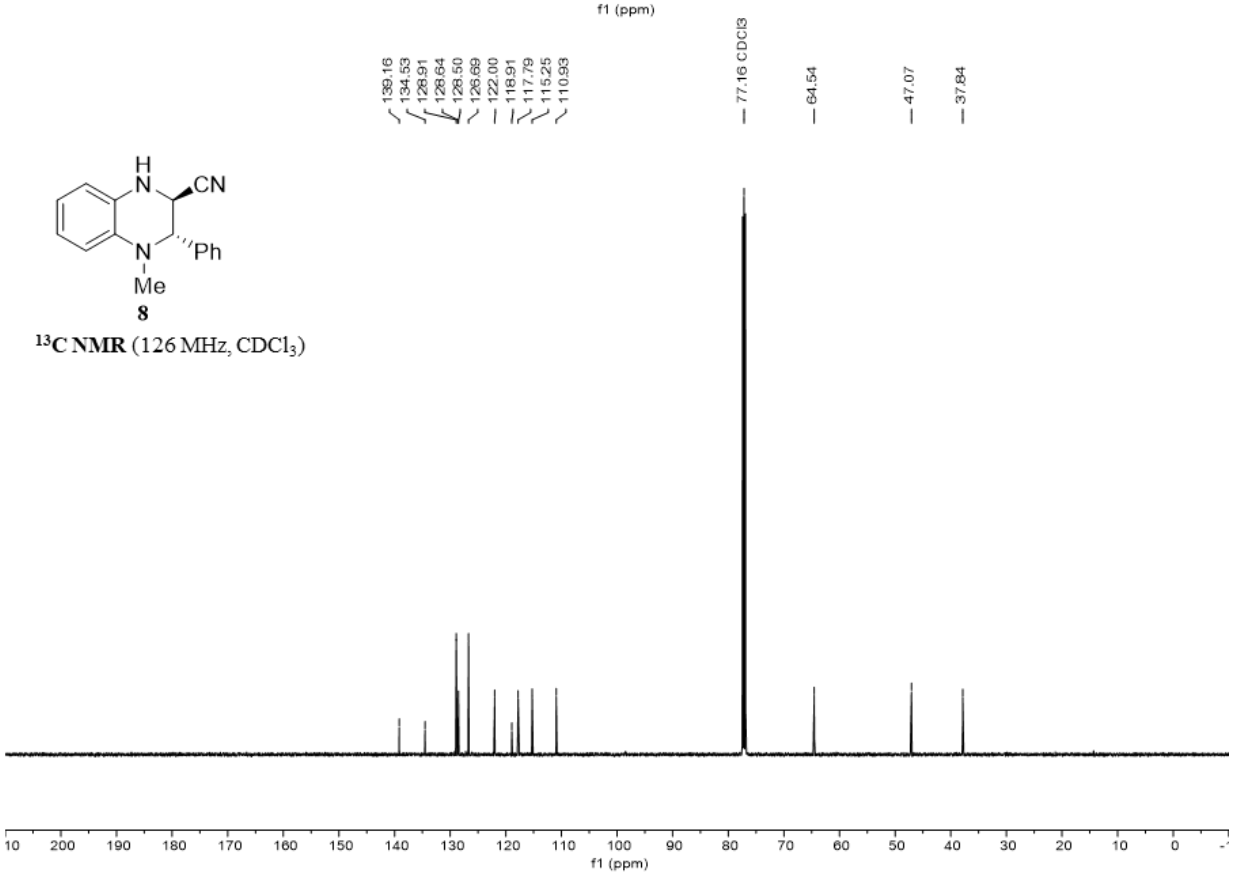
7c

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



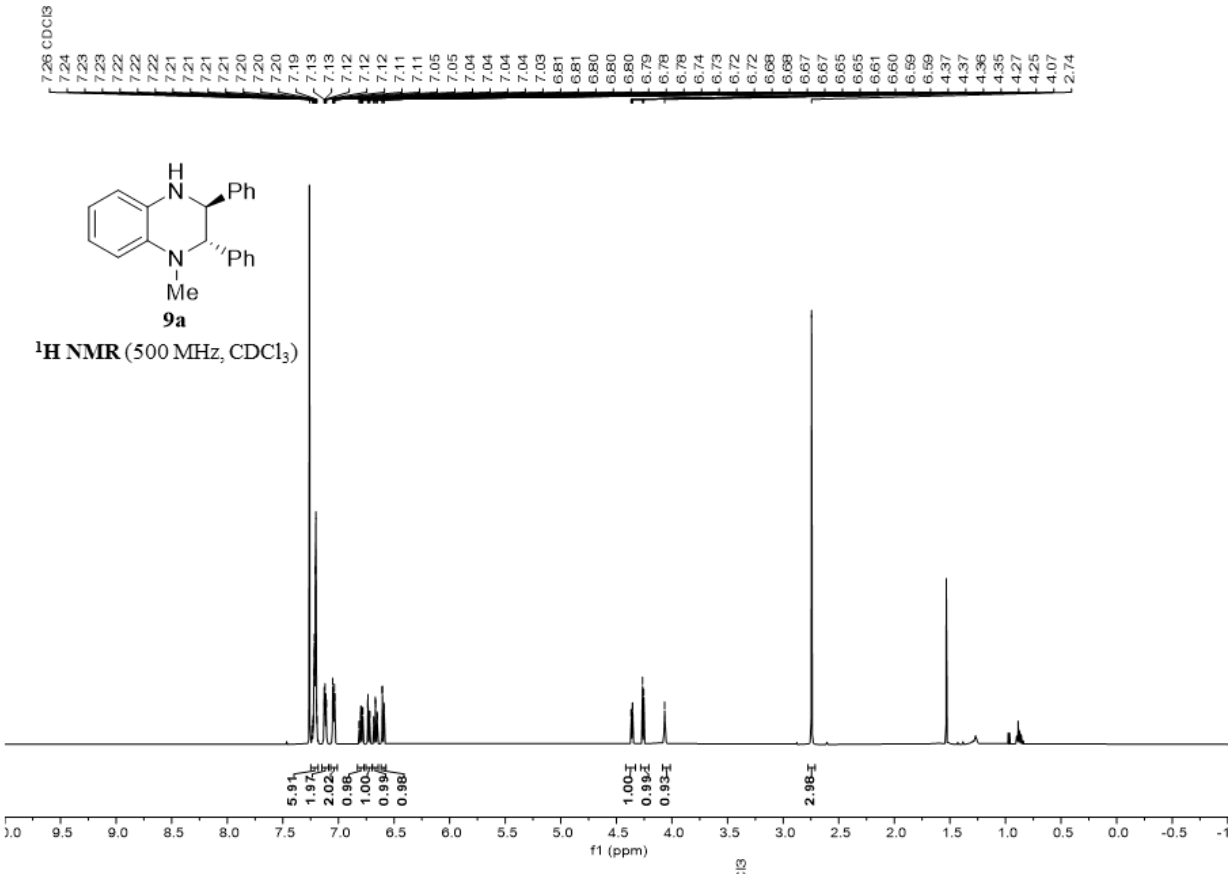
8

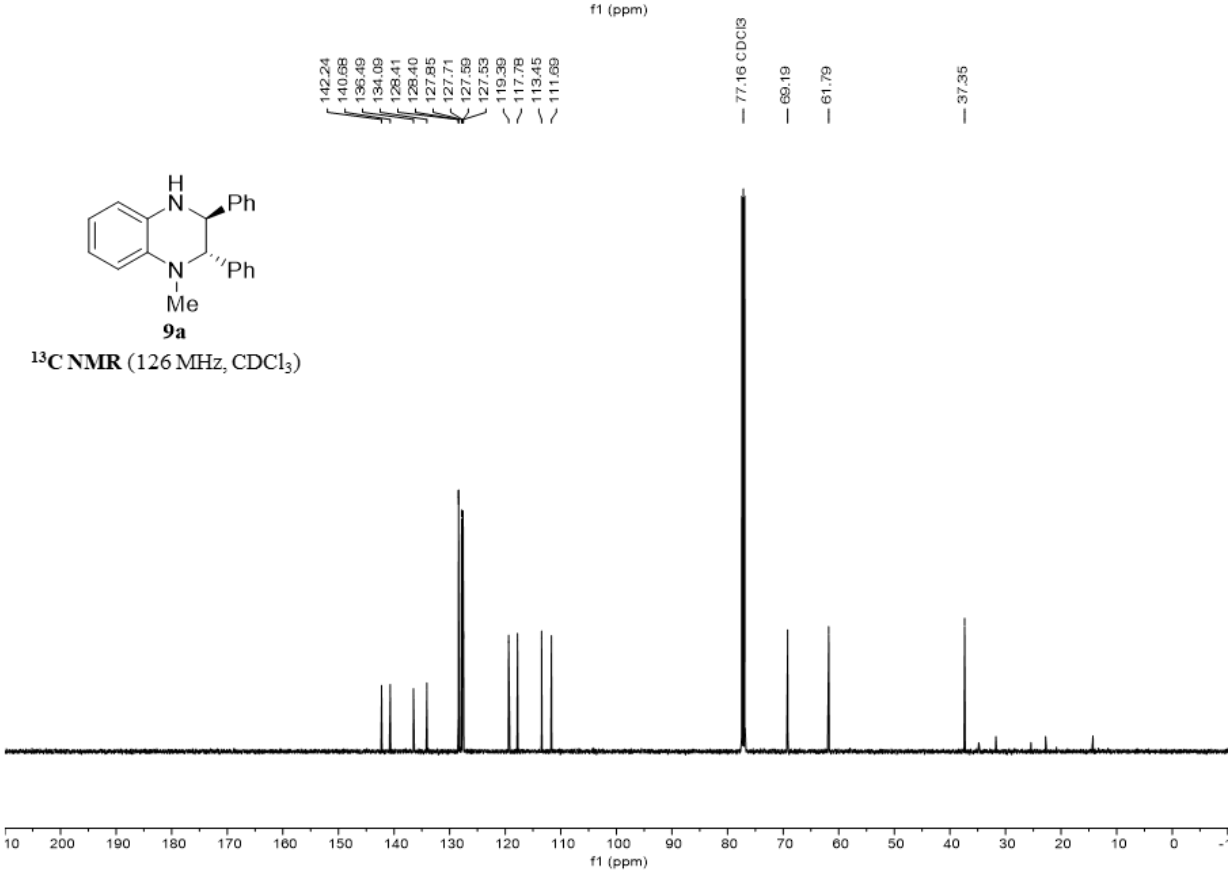
^{1}H NMR (500 MHz, $CDCl_3$)

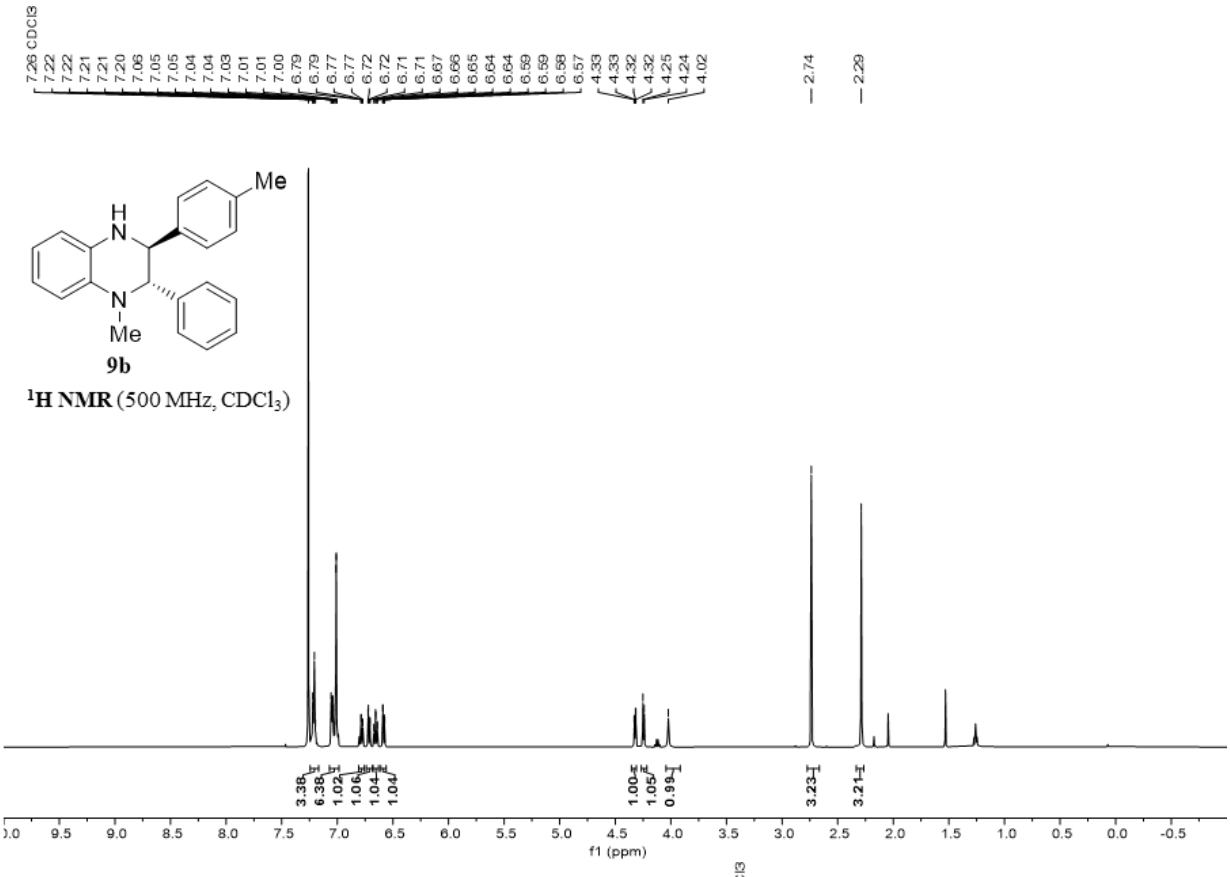


8

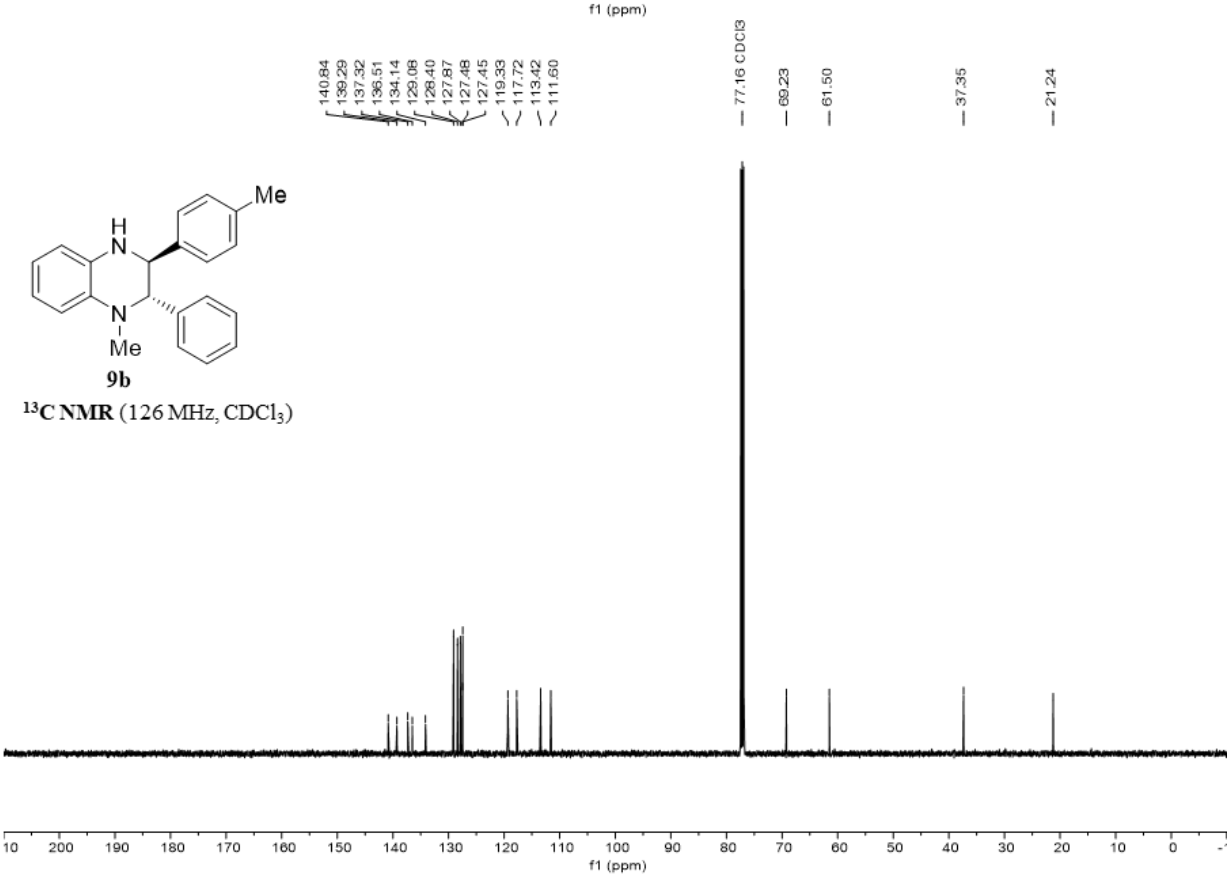
^{13}C NMR (126 MHz, $CDCl_3$)


7.26 CDCl3
7.24
7.23
7.23
7.22
7.22
7.22
7.21
7.21
7.21
7.21
7.20
7.20
7.20
7.19
7.13
7.13
7.12
7.12
7.12
7.11
7.11
7.05
7.05
7.04
7.04
7.04
7.04
7.03
6.81
6.81
6.80
6.80
6.80
6.79
6.78
6.78
6.74
6.73
6.72
6.72
6.68
6.68
6.67
6.67
6.65
6.65
6.61
6.60
6.59
6.59
4.37
4.37
4.36
4.35
4.27
4.25
4.07
2.74
H
N
Ph
N
Ph
Me
9a
1H NMR (500 MHz, CDCl3)
5.91
1.97
2.02
0.98
1.00
0.99
0.98
1.00
0.99
0.93
2.98
f1 (ppm)

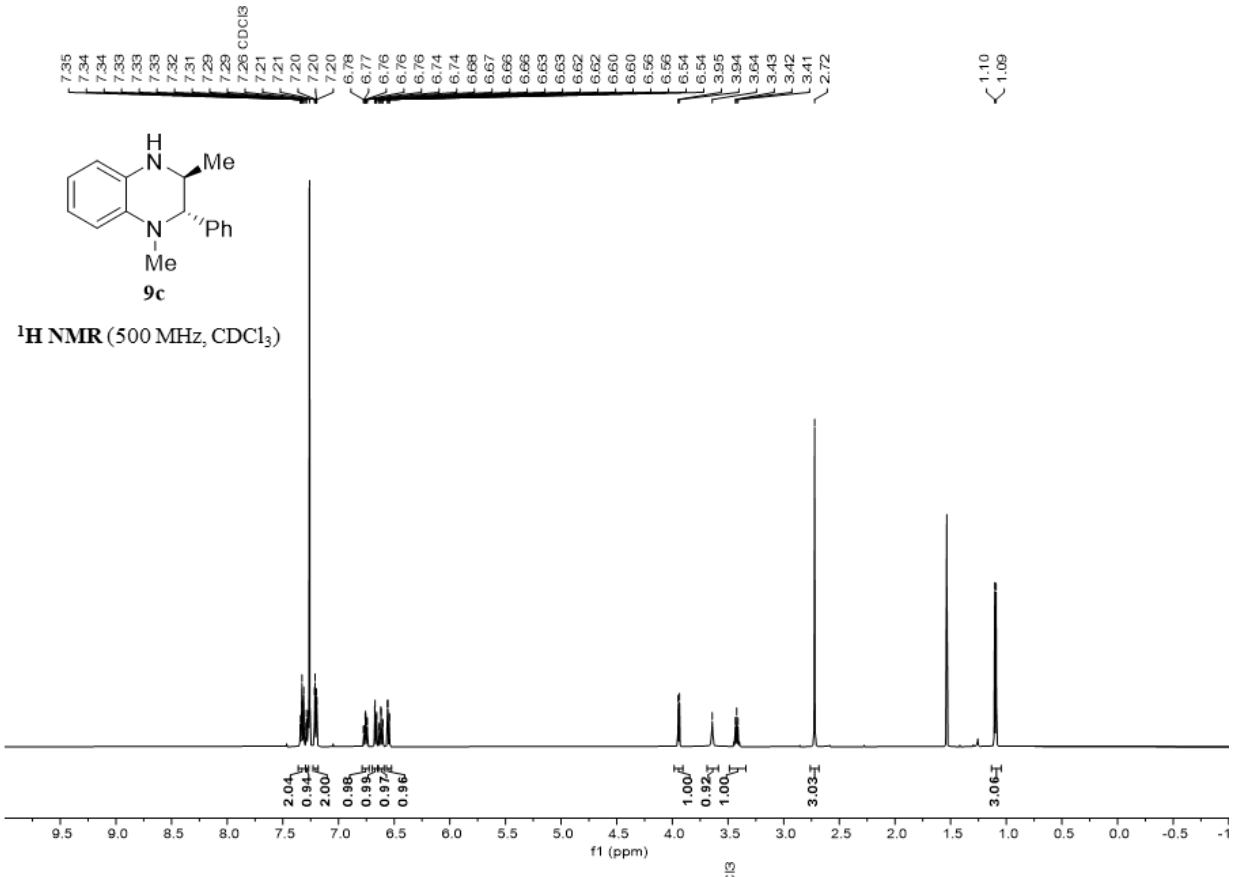

142.24
140.68
136.49
134.09
128.41
128.40
127.85
127.71
127.59
127.53
119.39
117.78
113.45
111.69
77.16 CDCl3
69.19
61.79
37.35
H
N
Ph
N
Ph
Me
9a
13C NMR (126 MHz, CDCl3)
f1 (ppm)



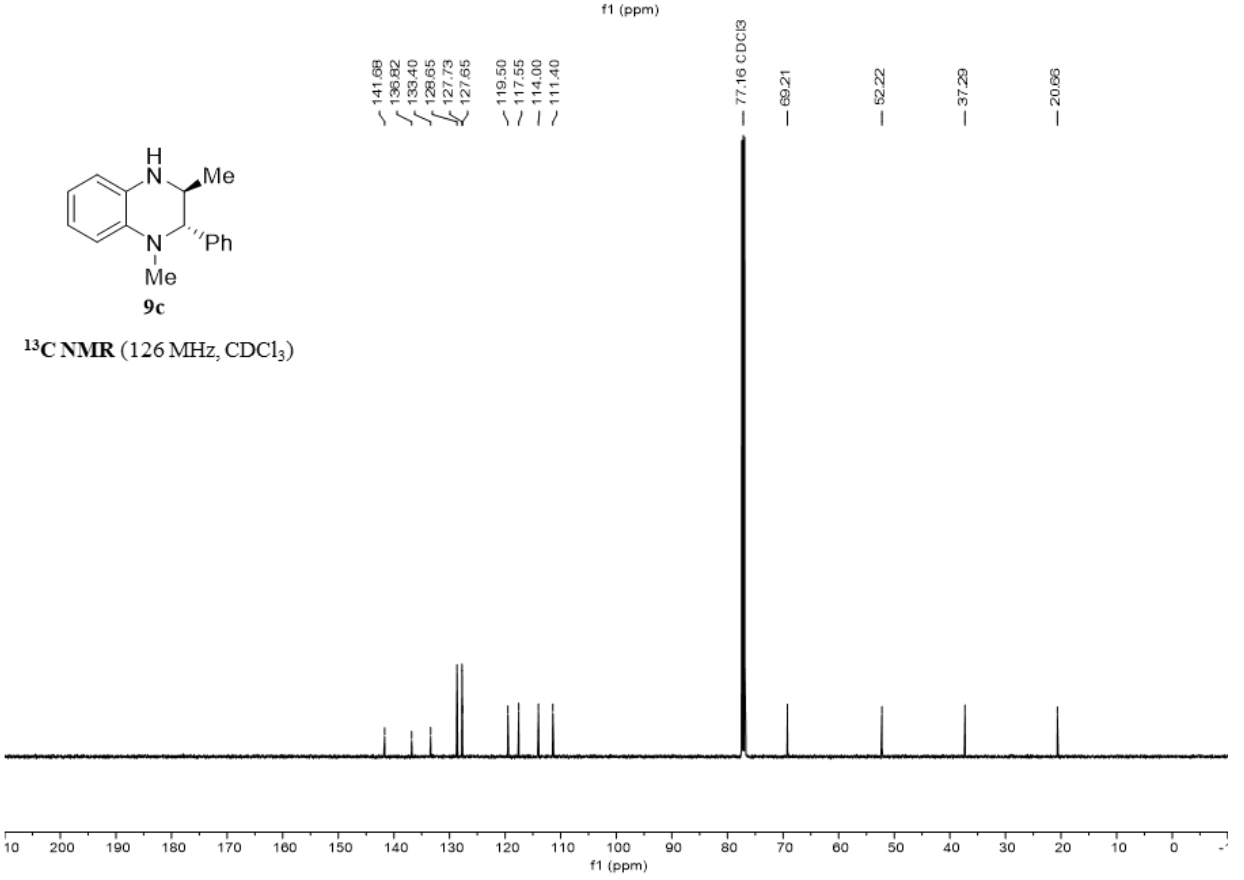
^{1}H NMR (500 MHz, $CDCl_3$)



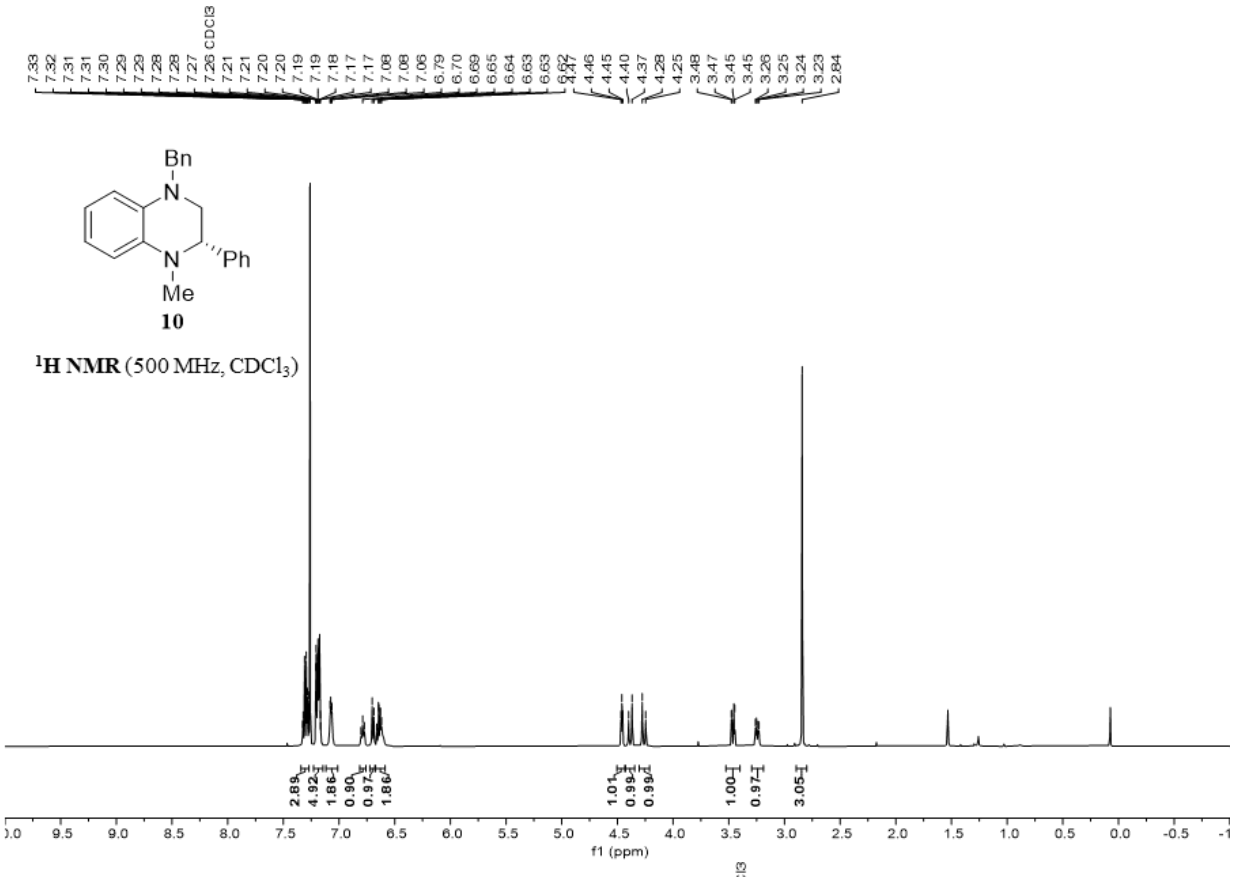
^{13}C NMR (126 MHz, $CDCl_3$)

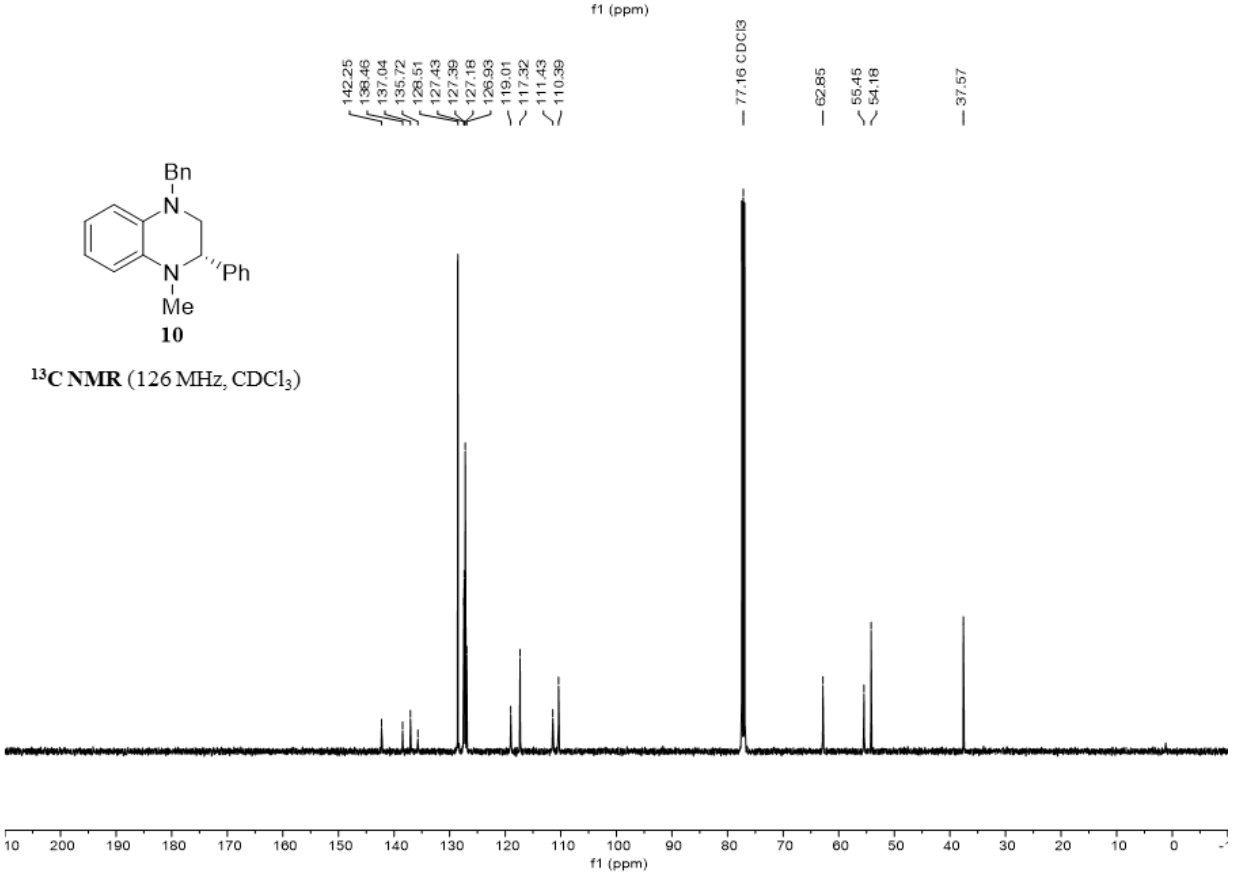


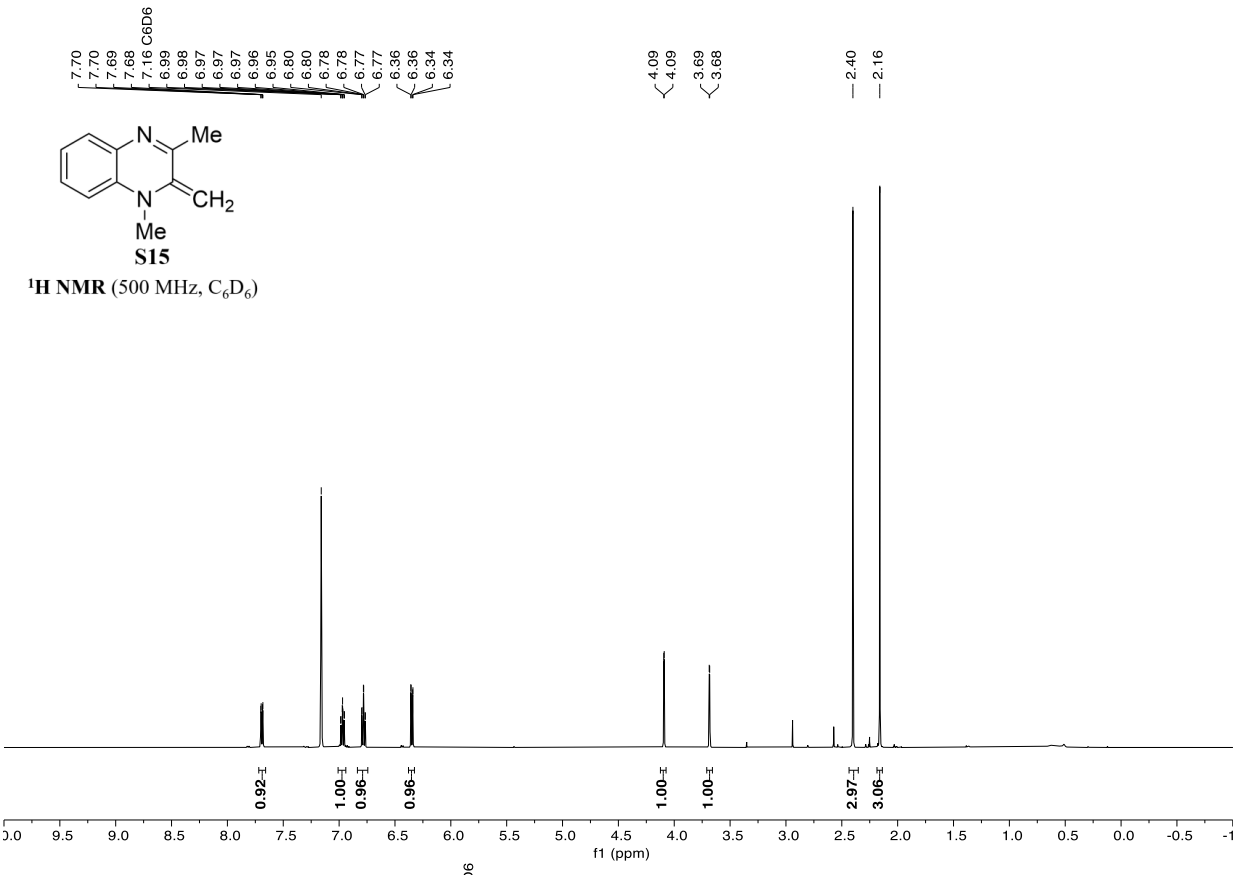
^{1}H NMR (500 MHz, $CDCl_3$)



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

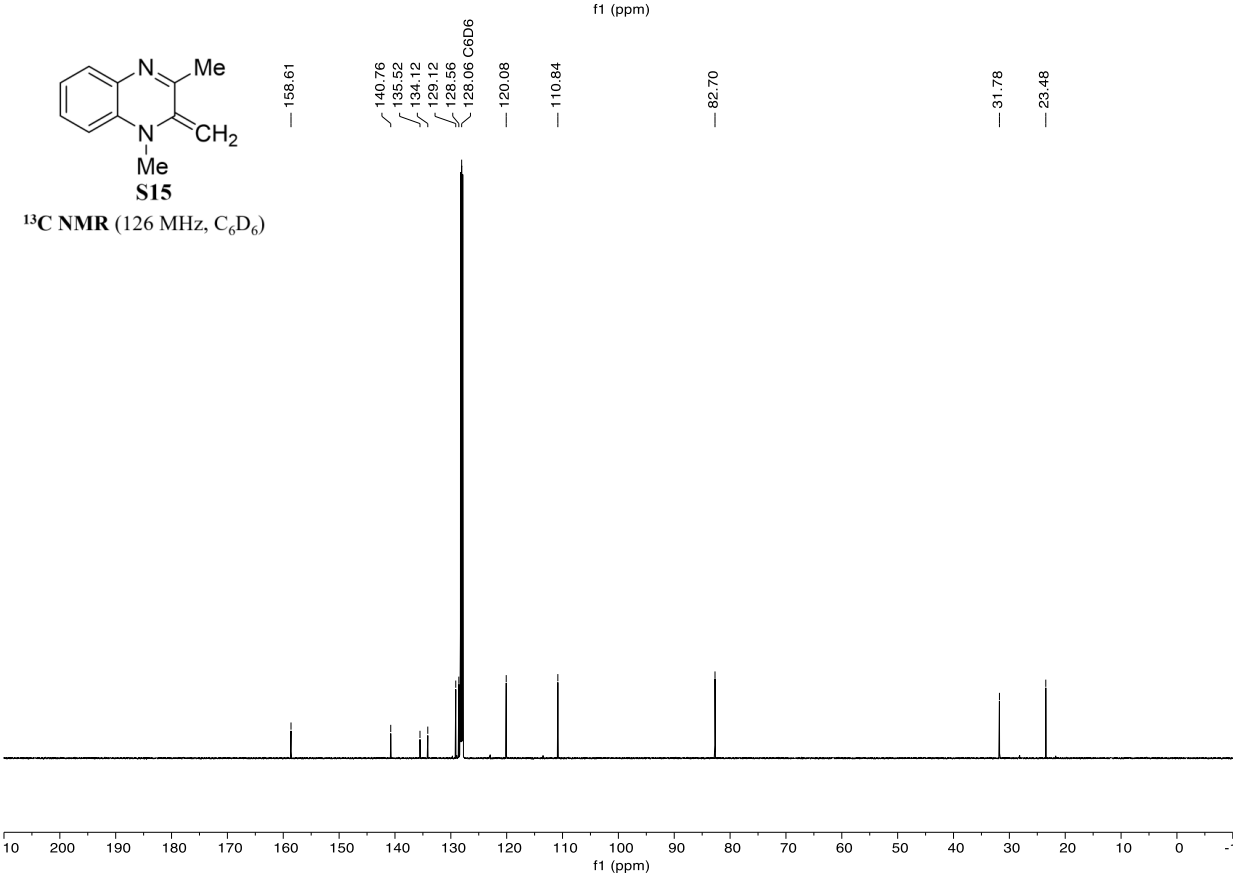

7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.26 CDCl3
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.08
7.08
7.06
6.79
6.70
6.69
6.65
6.64
6.63
6.63
6.62
4.47
4.46
4.45
4.40
4.37
4.28
4.25
3.48
3.47
3.45
3.45
3.26
3.25
3.24
3.23
2.84
Bn
N
N
Ph
Me
10
1H NMR (500 MHz, CDCl3)
2.89
4.92
1.86
0.90
0.97
1.80
1.01
0.99
0.99
1.00
0.97
3.05
f1 (ppm)


142.25
138.46
137.04
135.72
128.51
127.43
127.39
127.18
126.93
119.01
117.32
111.43
110.39
77.16 CDCl3
62.85
55.45
54.18
37.57
Bn
N
N
Ph
Me
10
13C NMR (126 MHz, CDCl3)
f1 (ppm)



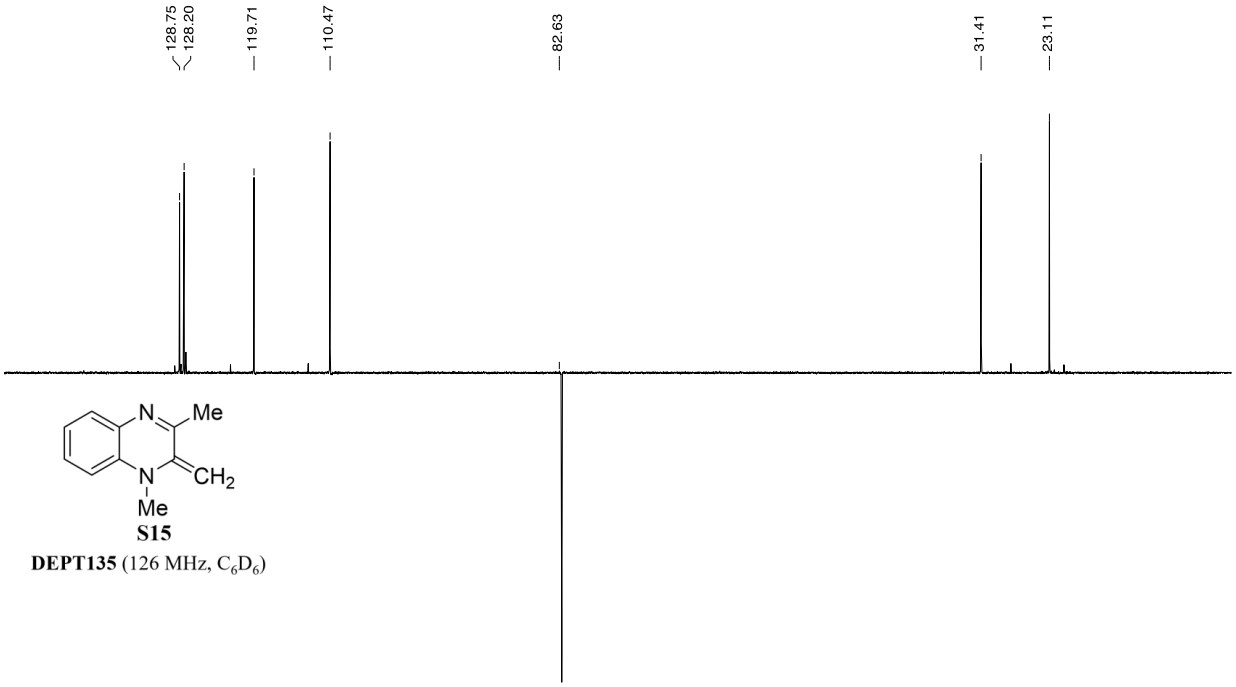
S15

^{1}H NMR (500 MHz, C_6D_6)



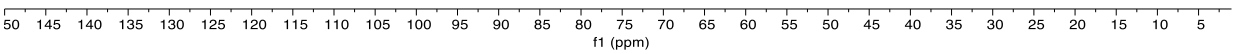
S15

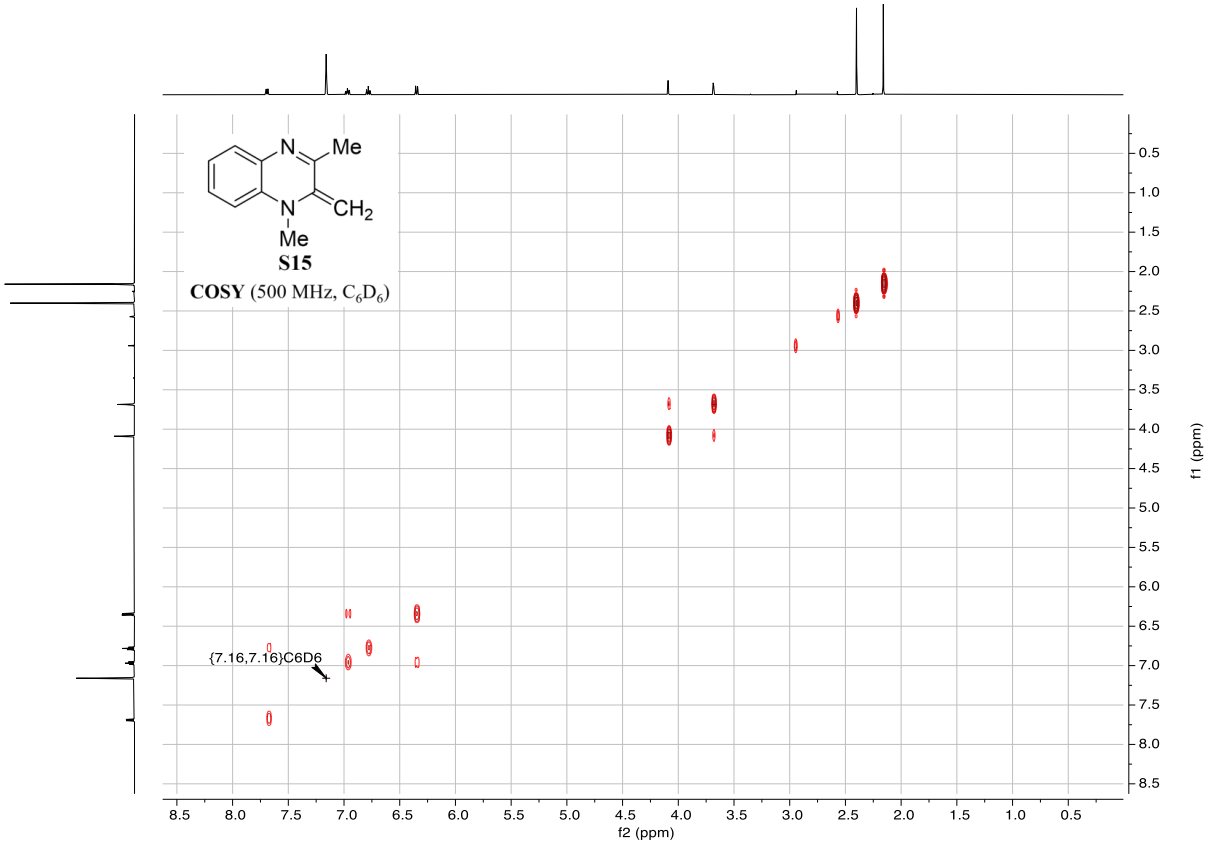
^{13}C NMR (126 MHz, C_6D_6)



S15

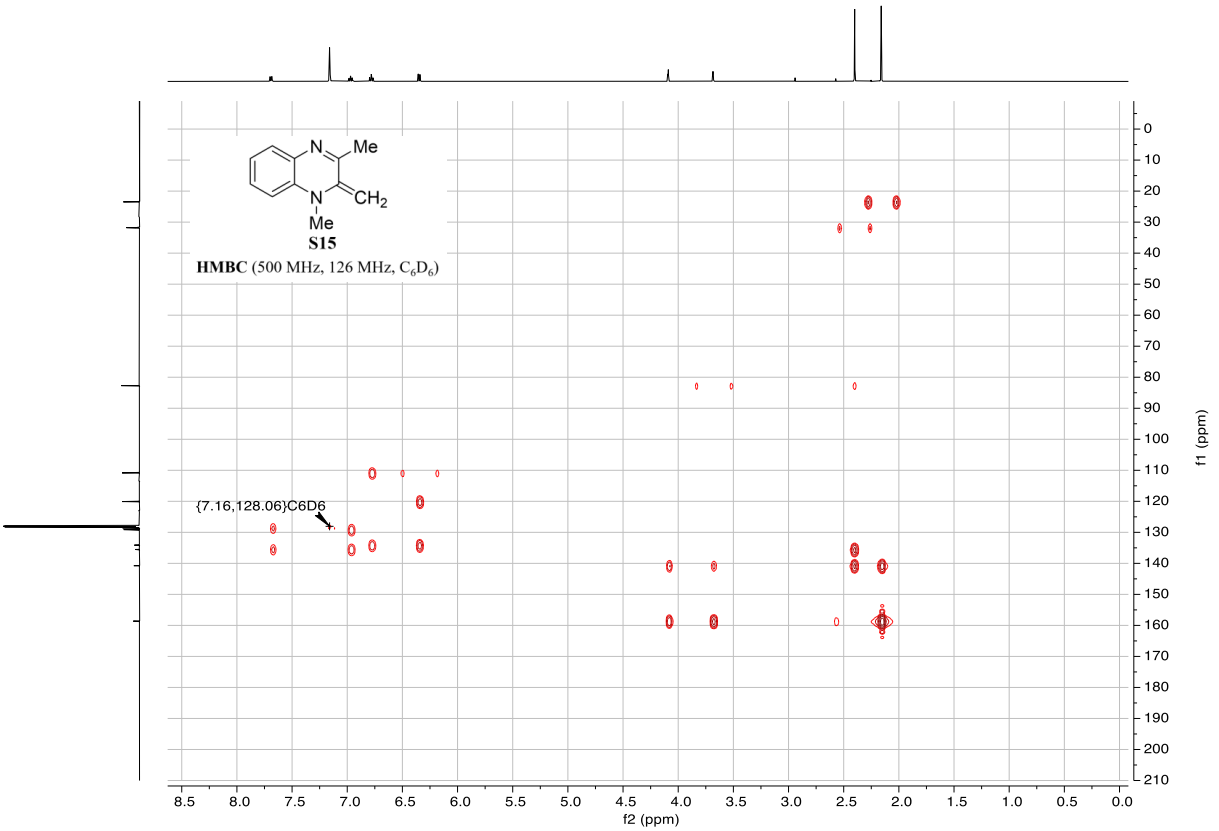
DEPT135 (126 MHz, C_6D_6)

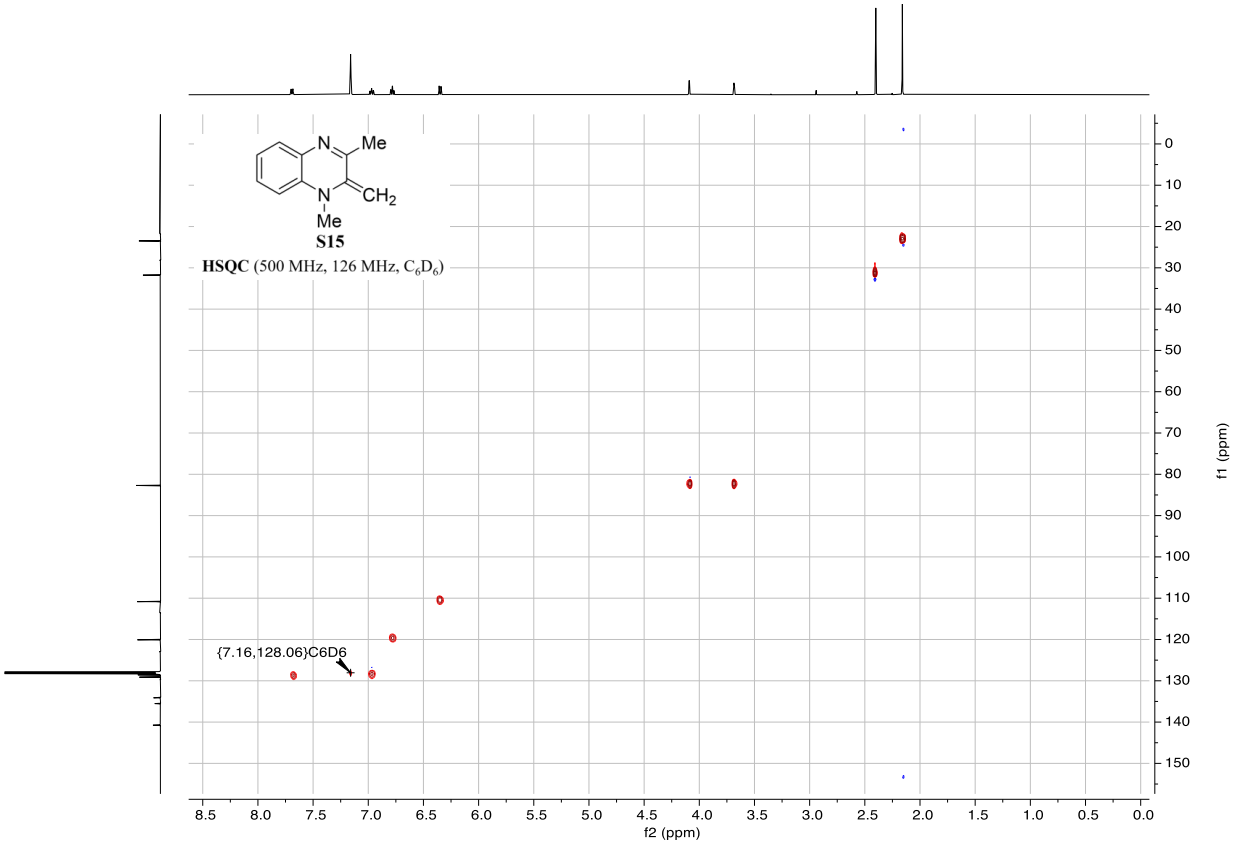




S15

COSY (500 MHz, C_6D_6)


Me
N
CH2
N
Me
S15
HMBC (500 MHz, 126 MHz, C6D6)
{7.16,128.06}C6D6
f2 (ppm)
f1 (ppm)


Me
N
CH2
N
Me
S15
HSQC (500 MHz, 126 MHz, C6D6)
{7.16,128.06}C6D6
f2 (ppm)
f1 (ppm)