Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthesis of Quinoxaline Derivatives via Aromatic Nucleophilic Substitution of Hydrogen

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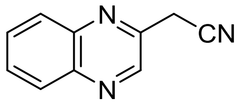
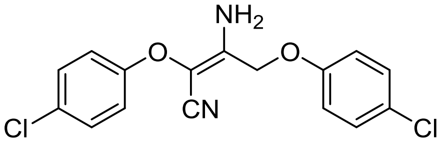
General information. Analytical grade solvents were used as received. Hexanes used for extraction and chromatography was distilled before use. Commercially available dry THF and DMF were used KHMDS 1M THF solution was prepared by dissolving solid KHMDS (weighted in a glove-box) in anhydrous THF in a Schlenk flask under Ar atmosphere. All ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at 298 K in $CDCl_3$ using a 400 MHz or a 500 MHz NMR spectrometer. The ^{1}H and ^{13}C NMR chemical shifts are given relative to the TMS signal at 0.0 ppm and relative to $CFCl_3$ for ^{19}F spectra. Mass spectra and HRMS measurements were obtained using a mass spectrometer equipped with an electrospray ion source and q-TOF type mass analyzer (ESI), or a magnetic sector mass spectrometer equipped with an electron impact (EI) ion source and the EBE double focusing geometry mass analyzer. Column chromatography was performed using silica gel 60 (0.040−0.063 mm). Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plates (0.20 mm thickness) and visualized under a UV lamp.

Experimental procedures and characterization data for new compounds

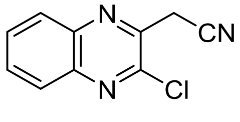
Cyanomethylation of quinoxaline 1 with 4-chlorophenoxyacetonitrile (4). In a dry Schlenk flask under Ar atmosphere DMF (3 mL) was cooled to 0 °C and *tert*-BuOK (4.5 mmol, 504 mg) was added with stirring. The resulting suspension was cooled to -20 °C and quinoxaline **1** (1.5 mmol, 195 mg) solution in DMF (1.5 mL) was added, followed by drop-wise addition (duration 15 min) of solution of **4** (1.5 mmol, 251 mg) in DMF (1.5 mL). After 2 h, 3% aqueous HCl (1.5 mL) was added, followed by saturated aqueous $NaHCO_3$ (10 mL). The products was extracted with AcOEt (3 x 5 mL) and the combined organic phases washed with brine (3x 20 mL). After evaporation and column chromatography on silica gel with hexanes/AcOEt 3:1 as eluent, **2-Cyanomethylquinoxaline (5)**[1] was isolated as brown crystalline solid, 115 mg (45%) yield. δ_H (200 MHz; $CDCl_3$; Me_4Si) 8.92 (s, 1H), 8.12 (m, 2H), 7.83 (m, 2H), 4.15 (s, 2H). δ_C (101 MHz; $CDCl_3$; Me_4Si) 145.6, 143.5, 141.9, 141.8, 130.9, 130.5, 129.3, 129.1, 115.7, 25.1.





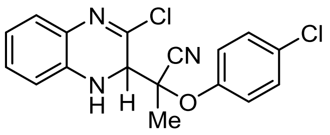
3-Amino-2,4-bis(4-chlorophenoxy)crotonitrile (6)[2] was isolated as beige crystalline solid, 125 mg (50%) yield. δ_H (400 MHz; $CDCl_3$; Me_4Si) 7.28 (m, 4H), 6.94 (m, 4H), 4.83 (s, 2H), 4.76 (bs, 2H). δ_C (101 MHz; $CDCl_3$; Me_4Si) 155.7, 154.3, 145.7, 129.8, 129.7, 128.5, 127.5, 116.8, 116.3, 115.4, 102.2, 64.4.

Cyanomethylation of 2-chloroquinoxaline (2) with nitrile 4. Performed as above for quinoxaline, but **2** (1.5 mmol, 241 mg) and **4** (1.5 mmol, 251 mg) were dissolved together in DMF (3.0 mL) and added drop-wise.

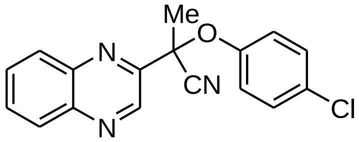


2-Chloro-3-cyanomethylquinoxaline (7a)[3] was isolated as light brown crystalline solid, 169 mg (55%) yield. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.16 (m, 1H), 8.05 (m, 1H), 7.84 (m, 2H), 4.28 (s, 2H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 145.4, 144.3, 141.7, 140.6, 131.7, 131.0, 129.1, 128.2, 114.6, 25.7. MS (EI) *m/z* 203 (97%, M^+), 168 (100%), 102 (64%), 76 (35%), 50 (34%).

Preparation of nitriles 9b, 10b. A solution of KO*t*-Bu (1.5 mmol, 168 mg, 3 equiv.) in THF (1 mL) was placed in a flame-dried Schlenk flask under argon atmosphere and cooled to -78 °C. A solution of **2** (0.5 mmol, 83 mg, 1 equiv.) and 2-(*p*-chlorophenoxy)propionitrile **8** (0.6 mmol, 109 mg, 1.2 equiv.) in THF (1 mL) was added dropwise with vigorous magnetic stirring. After 5 min brine (10 mL) was added, followed by AcOEt (10 mL). The phases were separated, the organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4 and evaporated. Column chromatography on silica gel using hexanes-ethyl acetate (5:1) as eluent gave an inseparable 1:1.2 mixture of **9b** (one diastereoisomer) and **10b** as brown oil in 105 mg (64%) combined yield.

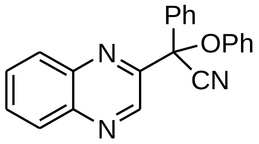


9b: δ_H (400 MHz; $CDCl_3$; Me_4Si) 7.7 (dm, J = 9.0 Hz, 2H), 7.25 (m, 1H), 7.13 (td, J = 7.7 Hz, 1.5 Hz, 1H), 7.05 (dm, J = 9.0 Hz, 2H), 6.83 (td, J = 7.6 Hz, 1.3 Hz, 1H), 6.73 (dd, J = 7.9 Hz, 1.1 Hz, 1H), 4.88 (d, J = 3.4 Hz, 1H), 4.79 (d, J = 3.4 Hz, 1H), 1.52 (s, 3H).



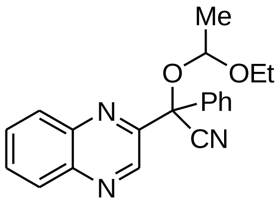
The same reaction performed at -78 °C to -20 °C over 15 min gave only **2-(4'-chlorophenoxy)-2-(2'-quinoxalinyl)propionitrile 10b**, isolated in 84 mg (54%) yield, pale yellow oil. δ_H (400 MHz; $CDCl_3$; Me_4Si) 9.05 (s, 1H), 8.19 (m, 1H), 8.14 (m, 1H), 7.85 (m, 2H), 7.19 (d, J = 9.1 Hz, 2H), 6.97 (d, J = 9.1 Hz, 2H), 2.20 (s, 3H). δ_C (101 MHz; $CDCl_3$; Me_4Si) 152.7, 151.3, 142.4, 141.6, 140.9, 131.2, 131.1, 129.6, 129.6, 129.4, 129.3, 120.6, 117.7, 78.0, 28.8. HRMS (APCI): Calcd for $C_{17}H_{13}N_3OCl$ ($[M+H]^+$) 310.0747, found: 310.0752.

Preparation of nitriles 10c, 10d. A 1M THF solution of KHMDS (1.1 mmol, 1.1 mL, 2.2 equiv.) was placed in a flame-dried Schlenk flask under argon atmosphere and cooled to -78 °C. A solution of **2** (0.5 mmol, 83 mg, 1 equiv.) and carbanion precursor (0.5 mmol, 1 equiv.) in DMF (1 mL) was added dropwise with vigorous magnetic stirring. After 15 min 2M $HCl_{(aq)}$ (5 mL) was added, followed by AcOEt (10 mL) and brine (5 mL). The phases were separated, the organic phase was washed with brine (1x10 mL), dried over anhydrous Na_2SO_3 and evaporated. The products were purified by column chromatography on silica gel using hexanes-ethyl acetate (5:1) as eluent.



Nitrile 10c. Prepared from 2-phenoxy-2-phenylacetonitrile in 152 mg (90%), pale yellow oil. δ_H (400 MHz; $CDCl_3$; Me_4Si) 9.15 (s, 1H), 8.21 (m, 1H), 8.10 (m, 1H), 7.79 (m, 4H), 7.41 (m, 3H), 7.23 (t, J = 7.7 Hz, 2H), 7.10 (m, 2H), 7.04 (m, 1H). δ_C (101 MHz; $CDCl_3$; Me_4Si) 154.1, 151.9, 142.2, 142.0, 140.8, 136.9, 130.9, 130.8,

129.7, 129.6, 129.5, 129.2, 129.2, 126.0, 123.8, 118.9, 116.9, 82.4. MS (EI) *m/z* 337 (5%, M$^+$), 244 (100%), 216 (11%), 190 (9%). HRMS (ESI): Calcd for $C_{22}H_{15}N_3O$ (M$^+$) 337.1215, found: 337.1218.



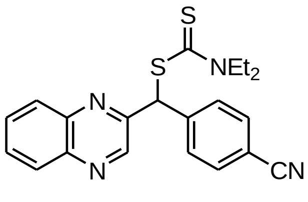
Nitrile 10d. Prepared from 2-(1-ethoxyethoxy)-2-phenylacetonitrile in 145 mg (87%) yield as 1.7: 1 mixture of diastereoisomers, pale yellow oil.

Major diastereoisomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 9.02 (s, 1H), 8.15 (m, 1H), 8.07 (m, 1H), 7.76 (m, 2H), 7.61 (m, 2H), 7.35 (m, 3H), 5.27 (q, J = 5.2 Hz, 1H), 3.35 (m, 2H), 1.49 (d, J = 5.2 Hz, 3H), 0.71 (t, J = 7.0 Hz, 3H). δ_C (101 MHz; $CDCl_3$; Me_4Si) 153.4, 143.4, 141.6, 140.3, 137.3, 130.7, 130.3, 129.5, 129.4, 129.0, 128.9, 126.0, 117.2, 99.5, 81.0, 61.5, 20.6, 14.4.

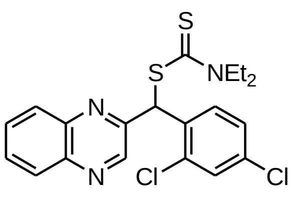
Minor diastereoisomer: δ_H (400 MHz; $CDCl_3$; Me_4Si) 8.96 (s, 1H), 8.15 (m, 1H), 8.07 (m, 1H), 7.76 (m, 2H), 7.66 (m, 2H), 7.35 (m, 3H), 5.19 (q, J = 5.2 Hz, 1H), 3.67 (dq, J = 9.1 Hz, 7.0 Hz, 1H), 3.53 (dq, J = 9.2 Hz, 7.0 Hz, 1H), 1.35 (d, J = 5.2 Hz, 3H), 1.13 (t, J = 7.0 Hz, 3H). δ_C (101 MHz; $CDCl_3$; Me_4Si) 152.4, 142.9, 141.9, 140.5, 137.9, 130.8, 130.4, 129.7, 129.3, 129.0, 128.8, 126.1, 117.5, 99.5, 80.5, 62.0, 21.2, 14.8.

HRMS (ESI): Calcd for $C_{20}H_{19}N_3O_2Na$ ([M+Na]$^+$) 356.1375, found: 356.1378.

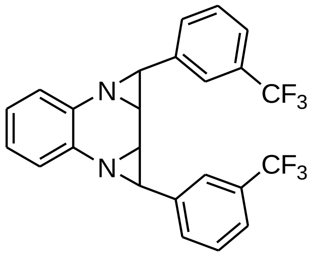
Preparation of dithiocarbamates 10e, 10f. A solution of KO*t*-Bu (2 mmol, 224 mg, 4 equiv.) in THF (2 mL) was placed in a flame-dried Schlenk flask under argon atmosphere and cooled to -30 °C. A solution of **2** (0.5 mmol, 83 mg, 1 equiv.) and 4-cyanobenzyl or 2,4-dichlorobenzyl *N,N*-diethyldithiocarbamate (0.6 mmol, 1.2 equiv.) in THF (1 mL) was added dropwise with vigorous magnetic stirring. After 90 min brine (20 mL) was added, followed by AcOEt (15 mL). The phases were separated, the organic phase was washed with brine (10 mL), dried over anhydrous Na_2SO_4 and evaporated. The products were purified by column chromatography on silica gel using hexanes-ethyl acetate (5:1) as eluent.



Dithiocarbamate 10e. Obtained in 120 mg (61%) yield, yellow oil. δ_H (400 MHz; $CDCl_3$; Me_4Si) 9.00 (s, 1H), 8.09 (m, 1H), 8.07 (m, 1H), 7.75 (m, 4H), 7.60 (d, J = 8.4 Hz, 2H), 7.00 (s, 1H), 3.97 (m, 2H), 3.76 (m, 2H), 1.29 (m, 3H), 1.23 (m, 3H). δ_C (101 MHz; $CDCl_3$; Me_4Si) 192.1, 154.1, 145.4, 143.9, 142.0, 141.4, 132.2, 130.3, 130.1, 130.0, 129.3, 129.2, 118.5, 111.6, 58.5, 50.0, 47.0, 12.7, 11.4. HRMS (ESI): Calcd for $C_{21}H_{20}N_4S_2Na$ ([M+Na]$^+$) 415.1027, found: 415.1022.



Dithiocarbamate 10f. Obtained in 124 mg (57%) yield, yellow oil. δ_H (400 MHz; $CDCl_3$; Me_4Si) 9.07 (s, 1H), 8.08 (m, 1H), 8.04 (m, 1H), 7.71 (m, 3H), 7.41 (d, J = 2.2 Hz, 1H), 7.24 (s, 1H), 7.23 (dd, J = 8.4, 2.2 Hz, 1H), 3.97 (m, 2H), 3.77 (m, 2H), 1.32 (m, 3H), 1.23 (m, 3H). δ_C (101 MHz; $CDCl_3$; Me_4Si) 192.5, 154.1, 146.0, 142.1, 141.4, 134.9, 134.7, 134.3, 132.2, 129.9, 129.8, 129.6, 129.3, 129.2, 127.2, 55.6, 49.9, 47.0, 12.8, 11.5. HRMS (ESI): Calcd for $C_{20}H_{20}N_3S_2Cl_2$ ($[M+H]^+$) 436.0476, found: 436.0474.

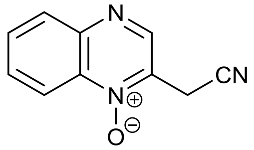


Bis(aziridine) 11. A 1M THF solution of KHMDS (1.75 mmol, 1.75 mL, 3.5 equiv.) was placed in a flame-dried Schlenk flask under argon atmosphere and cooled to -78 °C. A solution of **1** (0.5 mmol, 65 mg, 1 equiv.) and 3-trifluoromethylbenzyl chloride (1.5 mmol, 292 mg, 3 equiv.) in DMF (1 mL) was added dropwise with vigorous magnetic stirring. After 15 min 2M $HCl_{(aq)}$ (5 mL) was added, followed by AcOEt (10 mL) and brine (5 mL). The phases were separated, the organic phase was washed with brine (1x10 mL), dried over anhydrous Na_2SO_3 and evaporated. Compound **11** was isolated by column chromatography on silica gel using hexanes-ethyl acetate (20:1) as eluent in 69 mg (31%) yield, yellow oil. δ_H (400 MHz; $CDCl_3$; Me_4Si) 7.65 (s, 2H), 7.56 (m, 4H), 7.49 (m, 2H), 7.31 (m, 2H), 7.07 (m, 2H), 3.17 (d, J = 3.3 Hz, 2H), 3.11 (d, J = 3.3 Hz, 2H). δ_C (101 MHz; $CDCl_3$; Me_4Si) 139.0, 137.2, 131.1 (q, $^2J_{CF}$ = 32.4 Hz), 129.4, 129.0, 127.0, 125.6, 124.4 (q, $^3J_{CF}$ = 3.7 Hz), 124.1 (q, $^1J_{CF}$ = 272.1 Hz), 122.8 (q, $^3J_{CF}$ = 3.8 Hz), 53.5, 40.0. HRMS (ESI): Calcd for $C_{24}H_{16}F_6N_2Na$ ($[M+Na]^+$) 469.1115, found: 469.1109.

VNS reactions with quinoxaline *N*-oxide (3) – preparation of *N*-oxides 12.

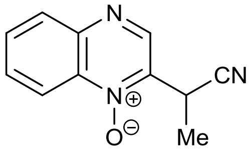
1M solution of ^{t}BuOK in THF (3.5 mL, 3.5 equiv) was introduced into a flame-dried Schlenk flask under argon atmosphere was cooled to -20 °C (brine/dry ice bath). A solution of **3** (1 mmol, 146 mg) and the appropriate carbanion precursor (1.3 mmol) in dry THF (1.5 mL) was then added drop-wise with vigorous stirring. After 10 minutes, the reaction was quenched with 2M HCl, diluted with brine (20 mL) and AcOEt (20 mL) and transferred to a separatory funnel. The phases were separated and the aqueous phase was washed with AcOEt (2 x 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated using a rotary evaporator. The products were purified by column chromatography on silica gel with 10% – 30% AcOEt in hexanes as eluent.

In some cases the reaction temperature and time were different than given above, see Scheme 4 in the main text for details.

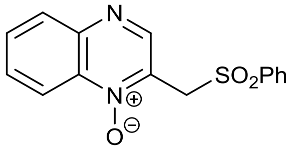


2-Cyanomethylquinoxaline-1-oxide (12a). Obtained in 112 mg (60%) yield, yellow solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.94 (s, 1H), 8.56 (d, 1H, J = 8.5

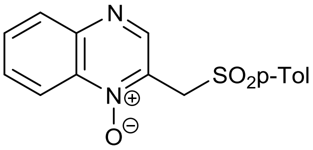
Hz), 8.17 (d, 1H, J = 8.4 Hz), 7.86 (m, 1H), 7.80 (m, 1H), 4.17 (s, 2H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 145.4, 144.8, 136.5, 132.2, 132.0, 131.0, 130.4, 118.6, 114.1, 18.4. HRMS (ESI): Calcd for $C_{10}H_7N_3ONa$ ($[M+Na]^+$) 208.0487, found: 208.0478.



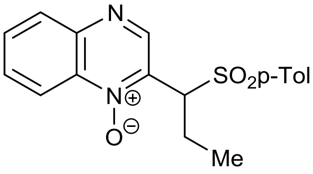
2-(1-Cyanoethyl)quinoxaline-1-oxide (12b). Obtained in 128 mg (64%) yield, yellow solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.96 (s, 1H), 8.57 (dd, J = 8.7, 1.6 Hz, 1H), 8.16 (dd, J = 8.4, 1.5 Hz, 1H), 7.85 (ddd, J = 8.4, 6.9, 1.6 Hz, 1H), 7.79 (ddd, J = 8.5, 7.0, 1.4 Hz, 1H), 4.82 (q, J = 7.1 Hz, 1H), 1.80 (d, J = 7.1 Hz, 3H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 145.2, 144.1, 137.1, 136.6, 131.8, 130.9, 130.3, 118.8, 118.3, 25.1, 15.8. HRMS (ESI): Calcd for $C_{11}H_9N_3ONa$ ($[M+Na]^+$) 222.0643, found: 222.0633.



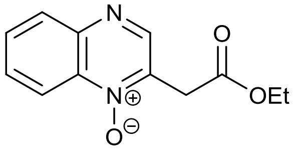
2-(Phenylsulfonyl)methylquinoxaline-1-oxide (12c). Obtained in 232 mg (77%) yield, white solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.84 (s, 1H), 8.36 (d, 1H, J = 8.6 Hz), 8.13 (d, 1H, J = 8.5 Hz), 7.82 (m, 3H), 7.71 (t, 1H, J = 7.4 Hz), 7.61 (t, 1H, J = 7.5 Hz), 7.46 (m, 2H), 5.02 (s, 2H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 147.5, 145.3, 138.8, 136.7, 134.3, 131.9, 131.0, 130.6, 130.3, 129.3, 128.2, 119.0, 54.5. HRMS (ESI): Calcd for $C_{15}H_{12}N_2O_3SNa$ ($[M+Na]^+$) 323.0466, found: 323.0479.



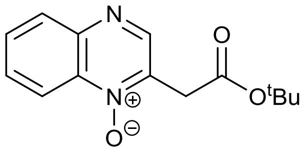
2-(*p*-Tolylsulfonylmethyl)quinoxaline-1-oxide (12d). Obtained in 280 mg (89%) yield, yellow solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.82 (s, 1H), 8.39 (dd, 1H, J = 8.7, 1.4 Hz), 8.12 (dd, 1H, J = 8.4, 1.3 Hz), 7.82 (m, 1H), 7.71 (m, 1H), 7.70 (d, 2H, J = 8.3 Hz), 7.25 (d, 2H, J = 8.2 Hz), 5.00 (s, 2H), 2.40 (s, 3H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 147.5, 145.4, 145.2, 136.8, 135.9, 131.9, 131.2, 130.5, 130.3, 129.9, 128.2, 119.0, 54.5, 21.7. HRMS (ESI): Calcd for $C_{16}H_{14}N_2O_3SNa$ ($[M+Na]^+$) 337.0623, found: 337.0630.



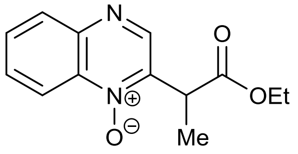
2-(1-*p*-Tolylsulfonylpropyl)quinoxaline-1-oxide (12e). Obtained in 140 mg (41%) yield, yellow solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.93 (s, 1H), 8.35 (d, 1H, J = 8.6 Hz), 8.12 (d, 1H, J = 8.4 Hz), 7.81 (m, 1H), 7.70 (m, 1H), 7.63 (d, 2H, J = 8.2 Hz), 7.17 (d, 2H, J = 8.0 Hz), 5.73 (m, 1H), 2.56 (m, 1H), 2.33 (s, 3H), 2.29 (m, 1H), 0.95 (t, 3H, J = 7.5 Hz). δ_C (126 MHz; $CDCl_3$; Me_4Si) 145.7, 145.2, 144.8, 136.6, 135.0, 134.8, 131.8, 130.4, 130.2, 129.7, 128.5, 119.2, 62.1, 21.6, 21.0, 11.2. HRMS (ESI): Calcd for $C_{18}H_{18}N_2O_3SNa$ ($[M+Na]^+$) 365.0936, found: 365.0943.



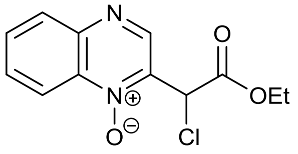
***N*-Oxide 12f.** Obtained in 170 mg (73%) yield, yellow oil. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.74 (s, 1H), 8.57 (dd, 1H, J = 8.6, 0.9 Hz), 8.12 (dm, 1H, J = 8.3 Hz), 7.80 (m, 1H), 7.74 (m, 1H), 4.23 (q, 2H, J = 7.1 Hz), 4.03 (s, 2H), 1.27 (t, 3H, J = 7.1 Hz). δ_C (126 MHz; $CDCl_3$; Me_4Si) 167.7, 147.1, 145.1, 136.9, 136.5, 131.2, 130.3, 130.1, 118.8, 61.7, 34.9, 14.1. HRMS (ESI): Calcd for $C_{12}H_{12}N_2O_3Na$ ([M+Na]$^+$) 255.0746, found: 255.0753.



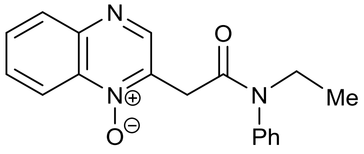
***N*-Oxide 12g.** Obtained in 210 mg (81%) yield, white solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.71 (s, 1H), 8.58 (dd, 1H, J = 8.6, 1.0 Hz), 8.11 (dd, 1H, J = 8.2, 1.1 Hz), 7.78 (m, 1H), 7.73 (m, 1H), 3.96 (s, 2H), 1.46 (s, 9H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 166.9, 147.2, 145.0, 136.93, 136.87, 131.1, 130.2, 130.1, 118.9, 82.3, 36.0, 28.0. HRMS (ESI): Calcd for $C_{14}H_{16}N_2O_3Na$ ([M+Na]$^+$) 283.1059, found: 283.1072.



***N*-Oxide 12h.** Obtained in 158 mg (64%) yield, yellow oil. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.74 (s, 1H), 8.58 (dd, J = 8.5, 1.7 Hz, 1H), 8.14 (m, 1H), 7.81 (m, 1H), 7.75 (m, 1H), 4.39 (q, J = 7.3 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 1.70 (d, J = 7.3 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 171.0, 145.3, 144.5, 140.8, 136.5, 130.9, 130.1, 129.8, 118.6, 61.2, 39.4, 13.9, 13.6. HRMS (ESI): Calcd for $C_{13}H_{14}N_2O_3Na$ ([M+Na]$^+$) 269.0902, found: 269.0907.

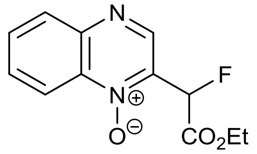


***N*-Oxide (12i).** Obtained in 104 mg (39%) yield, yellow oil. δ_H (500 MHz; $CDCl_3$; Me_4Si) 9.04 (s, 1H), 8.56 (d, 1H, J = 8.5 Hz), 8.17 (d, 1H, J = 8.3 Hz), 7.87 (t, 1H, J = 7.4 Hz), 7.79 (t, 1H, J = 7.8 Hz), 5.98 (s, 1H), 4.32 (q, 2H, J = 7.1 Hz), 1.31 (t, 3H, J = 7.1 Hz). δ_C (126 MHz; $CDCl_3$; Me_4Si) 165.5, 145.5, 145.2, 136.7, 136.3, 132.1, 130.8, 130.3, 118.8, 63.2, 51.7, 13.9. HRMS (ESI): Calcd for $C_{12}H_{11}N_2O_3ClNa$ ([M+Na]$^+$) 289.0356, found: 289.0347.

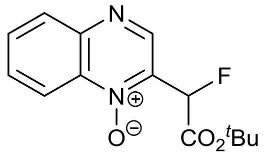


***N*-Oxide 12j.** Obtained in 170 mg (55%) yield, brown solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.67 (s, 1H), 8.55 (dd, J = 8.5, 1.6 Hz, 1H), 8.13 (dd, J = 8.4, 1.4 Hz, 1H), 7.78 (ddd, J = 8.4, 7.0, 1.5 Hz, 1H), 7.73 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.48 (m, 2H), 7.40 (m, 3H), 3.83 (q, J = 7.1 Hz, 2H), 3.77 (s, 2H), 1.17 (t, J = 7.1 Hz, 3H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 166.2, 147.2, 144.4, 141.9, 138.4, 137.0, 131.1, 130.2, 130.0, 129.7, 128.5, 128.4, 118.8, 44.4, 35.3, 13.0. HRMS

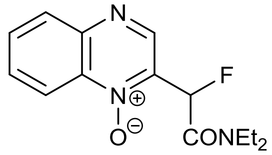
(ESI): Calcd for $C_{18}H_{17}N_3O_2Na$ ($[M+Na]^+$) 330.1218, found: 330.1205.



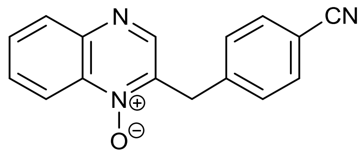
***N*-Oxide 12k.** Obtained in 40 mg (16%) yield, brown solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.87 (s, 1H), 8.57 (d, J = 8.6 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.88 (t, J = 7.4 Hz, 1H), 7.79 (t, J = 7.9 Hz, 1H), 6.37 (d, $^2J_{HF}$ = 46.0 Hz, 1H), 4.35 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 165.2 (d, $^2J_{CF}$ = 24.7 Hz), 145.7, 144.7 (d, $^3J_{CF}$ = 6.2 Hz), 136.6, 132.3, 130.8, 130.3, 118.8, 84.5 (d, $^1J_{CF}$ = 184.4 Hz), 62.7, 14.0. HRMS (ESI): Calcd for $C_{12}H_{11}N_2O_3FNa$ ($[M+Na]^+$) 273.0651, found: 273.0663.



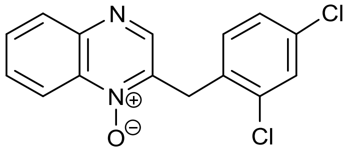
***N*-Oxide 12k'.** Obtained in 78 mg (28%) yield, brown solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.83 (s, 1H), 8.57 (dd, J = 8.7, 1.5 Hz, 1H), 8.16 (dd, J = 8.4, 1.3 Hz, 1H), 7.86 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H), 7.78 (ddd, J = 8.5, 7.0, 1.4 Hz, 1H), 6.27 (d, $^2J_{HF}$ = 46.2 Hz, 1H), 1.50 (s, 9H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 164.1 (d, $^2J_{CF}$ = 24.4 Hz), 145.5, 144.6 (d, $^3J_{CF}$ = 6.0 Hz), 136.7, 135.9 (d, $^2J_{CF}$ = 25.0 Hz), 132.2, 130.6, 130.2, 118.8, 84.3 (d, $^1J_{CF}$ = 184.5 Hz), 84.3, 27.8. HRMS (ESI): Calcd for $C_{14}H_{15}N_2O_3FNa$ ($[M+Na]^+$) 301.0964, found: 301.0960.



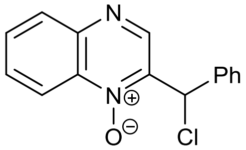
***N*-Oxide 12l.** Obtained in 166 mg (60%) yield, yellow solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.99 (s, 1H), 8.54 (dd, J = 8.7, 1.5 Hz, 1H), 8.18 (dd, J = 8.4, 1.4 Hz, 1H), 7.85 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.77 (ddd, J = 8.5, 6.9, 1.4 Hz, 1H), 6.81 (d, $^2J_{HF}$ = 46.4 Hz, 1H), 3.70 (m, 1H), 3.58 (m, 1H), 3.50 (m, 1H), 3.43 (m, 1H), 1.38 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 163.3 (d, $^2J_{CF}$ = 20.8 Hz) 145.2, 144.5 (d, $^3J_{CF}$ = 7.8 Hz) 137.3 (d, $^2J_{CF}$ = 28.6 Hz), 136.1, 131.8, 130.5, 130.3, 118.4, 83.2 (d, $^1J_{CF}$ = 178.7 Hz), 42.3, 41.2, 14.7, 12.7. HRMS (ESI): Calcd for $C_{14}H_{16}N_3O_2FNa$ ($[M+Na]^+$) 300.1124, found: 300.1137.



2-(4-Cyanobenzyl)quinoxaline-1-oxide (12m). Obtained in 220 mg (84%) yield, yellow solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.65 (s, 1H), 8.56 (dd, J = 8.5, 1.6 Hz, 1H), 8.11 (dd, J = 8.3, 1.5 Hz, 1H), 7.80 (m 1H), 7.75 (m, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.47 (d, J = 8.3 Hz, 1H), 4.43 (s, 2H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 146.5, 144.9, 141.0, 140.1, 137.0, 132.6, 131.2, 130.6, 130.2, 130.0, 118.8, 118.6, 111.3, 34.9. HRMS (ESI): Calcd for $C_{16}H_{12}N_3O$ ($[M+H]^+$) 262.0980, found: 262.0985.

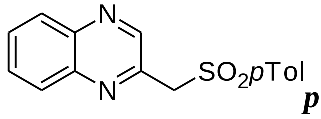


2-(2,4-Dichlorobenzyl)quinoxaline-1-oxide (12n). Obtained in 150 mg (49%) yield, brown solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.59 – 8.55 (m, 2H), 8.09 (dd, J = 8.2, 1.5 Hz, 1H), 7.77 (ddd, J = 8.3, 7.6, 1.6 Hz, 1H), 7.73 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 2.2 Hz, 1H), 7.25 (dd, *J* = 8.3, 2.2 Hz, 1H), 4.44 (s, 2H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 146.8, 144.6, 139.6, 137.0, 135.1, 134.1, 132.9, 131.5, 131.0, 130.3, 130.1, 129.6, 127.5, 118.8, 32.6. HRMS (ESI): Calcd for $C_{15}H_{11}N_2OCl_2$ ($[M+H]^+$) 305.0248, found: 305.0241.

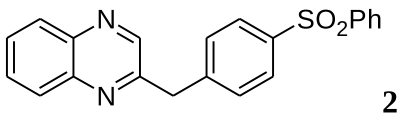


***N*-Oxide 12o.** Obtained in 110 mg (41%) yield, yellow oil. δ_H (600 MHz; $CDCl_3$; Me_4Si) 9.01 (s, 1H), 8.55 (d, J = 8.7 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.80 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.73 (ddd, J = 8.5, 7.0, 1.4 Hz, 1H), 7.56 (m, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 6.91 (s, 1H). δ_C (151 MHz; $CDCl_3$; Me_4Si) 145.7, 144.6, 141.0, 136.6, 136.4, 131.7, 130.6, 130.2, 129.1, 129.0, 127.8, 119.0, 54.6. HRMS (ESI): Calcd for $C_{15}H_{12}N_2OCl$ ($[M+H]^+$) 271.0638, found: 271.0634.

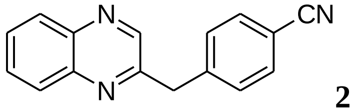
Preparation of quinoxalines 13. 1M solution of ^{t}BuOK in THF (3.5 mL, 3.5 equiv) was introduced into a flame-dried Schlenk flask under argon atmosphere was cooled to -20 °C (brine/dry ice bath). A solution of **3** (1 mmol, 146 mg) and the appropriate carbanion precursor (1.3 mmol) in dry DMF (1.5 mL) was then added drop-wise with vigorous stirring. After 10 minutes, the reaction was quenched with 2M HCl, diluted with brine (20 mL) and AcOEt (20 mL) and transferred to a separatory funnel. The phases were separated and the aqueous phase was washed with AcOEt (2 x 20 mL). The combined organic extracts were washed with brine (3 x 20 mL), dried over Na_2SO_4 and concentrated using a rotary evaporator. The products were purified by column chromatography on silica gel with 10% – 30% AcOEt in hexanes as eluent.



***p*-Tolyl (quinoxalin-2-yl)methyl sulfone (13a).** Obtained in 132 mg (44%) yield, yellow solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.87 (s, 1H), 8.12 (dd, J = 8.2, 1.6 Hz, 1H), 7.93 (dd, J = 7.9, 1.9 Hz, 1H), 7.83 – 7.72 (m, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 7.3 Hz, 2H), 4.75 (s, 2H), 2.41 (s, 3H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 146.1, 145.3, 144.7, 142.1, 141.9, 135.1, 130.6, 130.5, 129.9, 129.32, 129.29, 128.5, 63.0, 21.6. HRMS (ESI): Calcd for $C_{16}H_{14}N_2O_2SNa$ ($[M+Na]^+$) 321.0674, found: 321.0688.



2-(4-Phenylsulfonylbenzyl)quinoxaline (13b). Obtained in 198 mg (55%) yield, yellow solid. δ_H (500 MHz; $CDCl_3$; Me_4Si) 8.72 (s, 1H), 8.08 (m, 2H), 7.93 (m, 4H), 7.77 (m, 2H), 7.56 (m, 1H), 7.50 (m, 4H), 4.43 (s, 2H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 154.2, 145.5, 143.7, 142.1, 141.6, 141.4, 140.2, 133.2, 130.3, 130.0, 129.6, 129.3, 129.2, 129.1, 128.2, 127.6, 42.5. HRMS (ESI): Calcd for $C_{21}H_{16}N_2O_2SNa$ ($[M+Na]^+$) 383.0830, found: 383.0836.



2-(4-Cyanobenzyl)quinoxaline (13c). Obtained in 126 mg (51%) yield, yellow solid, along with **12m** (26 mg, 10% yield). δ_H (500 MHz; $CDCl_3$; Me_4Si) δ 8.73 (s, 1H), 8.08 (m, 2H), 7.77 (m, 2H), 7.62 (d, 2H, J = 8.1 Hz), 7.45 (d, 2H, J = 8.1 Hz), 4.43 (s, 2H). δ_C (126 MHz; $CDCl_3$; Me_4Si) 154.1, 145.5, 143.3, 142.1, 141.4, 132.6, 130.4, 129.9, 129.7, 129.3, 129.1, 118.7, 110.9, 42.7. HRMS (ESI): Calcd for $C_{16}H_{12}N_3$ ($[M+H]^+$) 246.1031, found: 243.1039.

References

1. G. M. Fischer, M. Isomaki-Krondahl, I. Gottker-Schnetmann, E. Daltrozzo and A. Zumbusch, *Chem. Eur. J.*, 2009, **15**, 4857–4864.

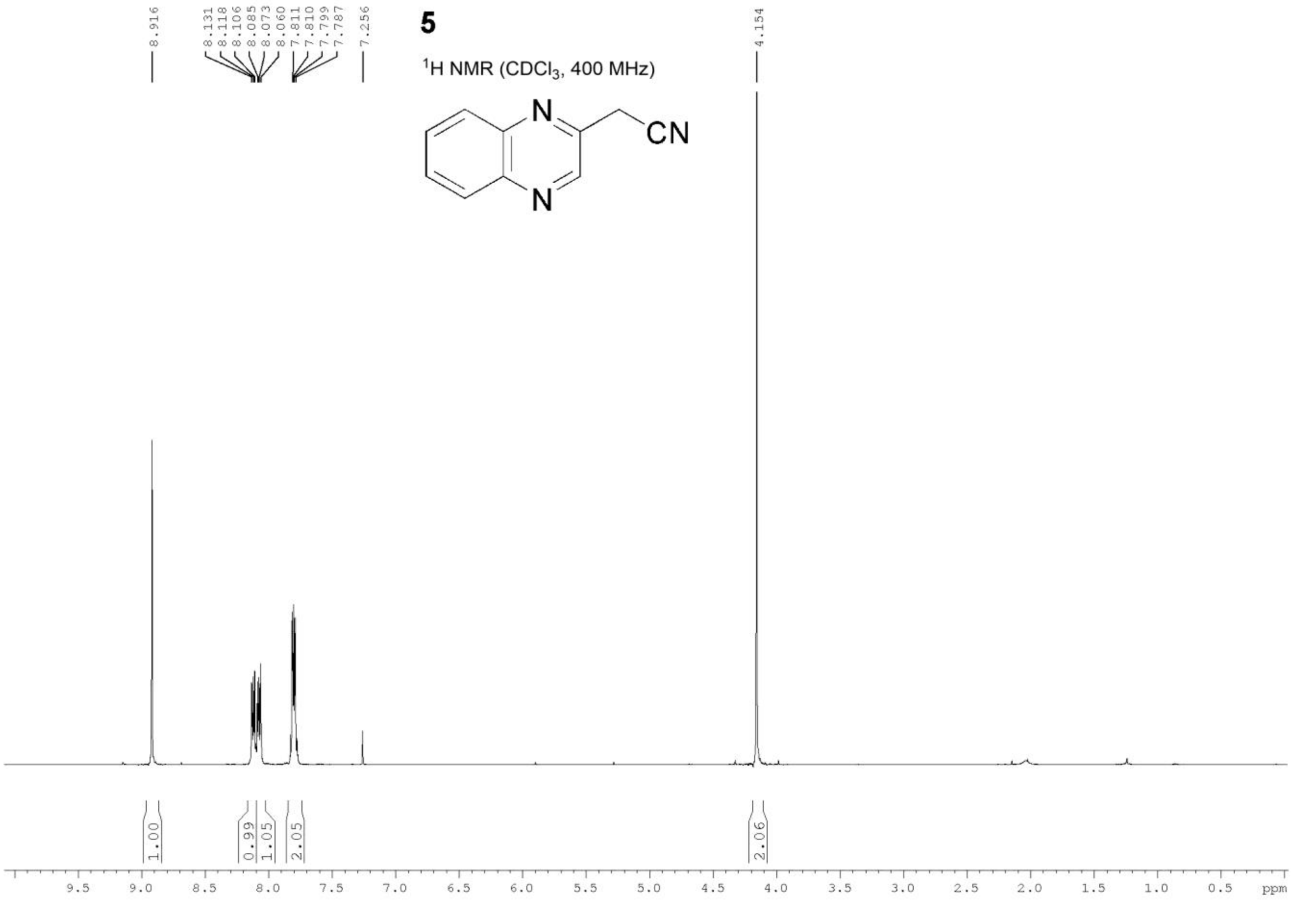
2. M. Mąkosza, T. Ziobrowski, M. Serebriakov and A. Kwast, *Tetrahedron*, 1997, **53**, 4739–4750.

3. C. A. Obafemi and W. Pfleiderer, *Molecules*, 2004, **9**, 223–231.

Copies of NMR spectra

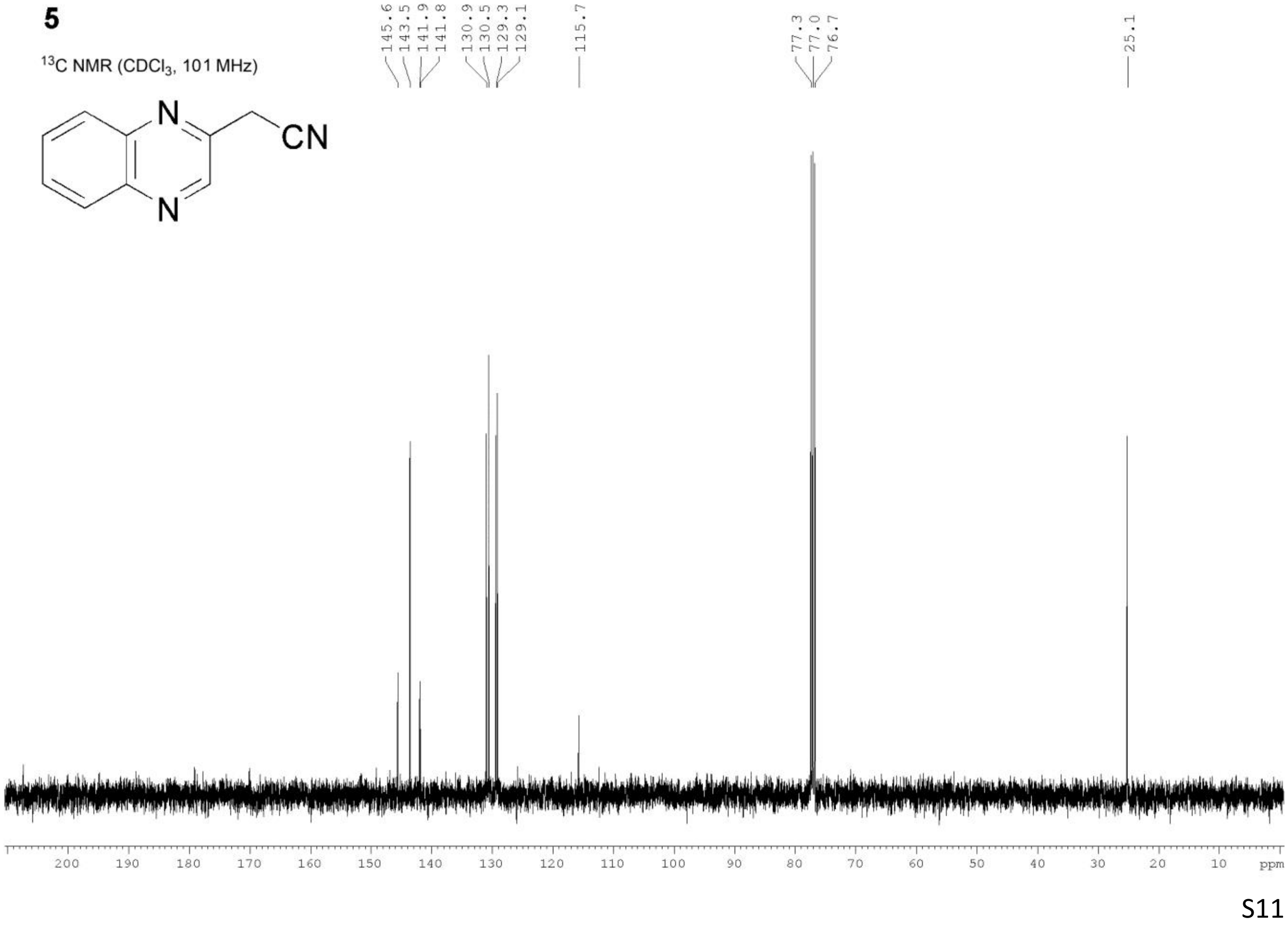
5

^{1}H NMR (CDCl$_3$, 400 MHz)



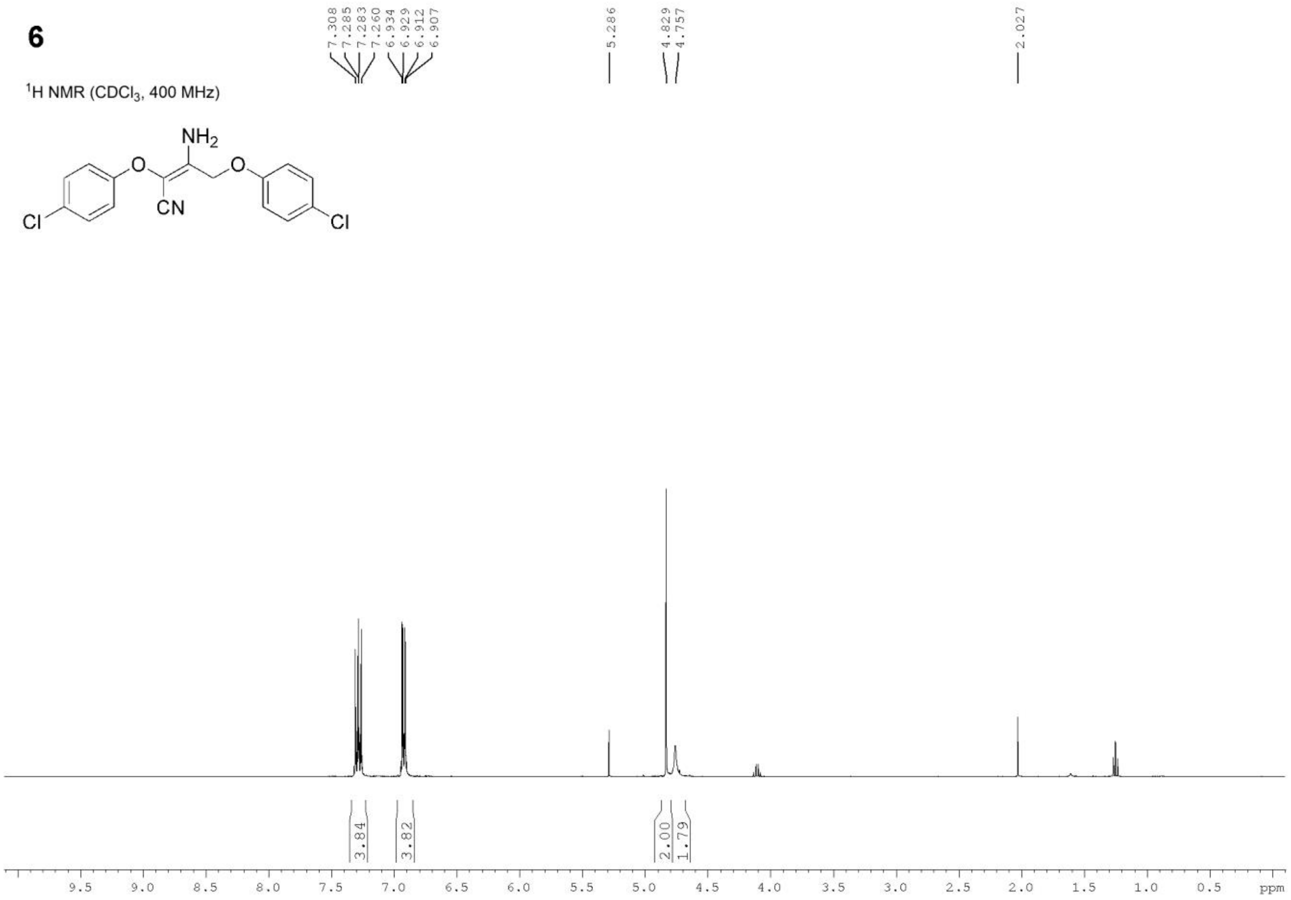
5

^{13}C NMR (CDCl$_3$, 101 MHz)



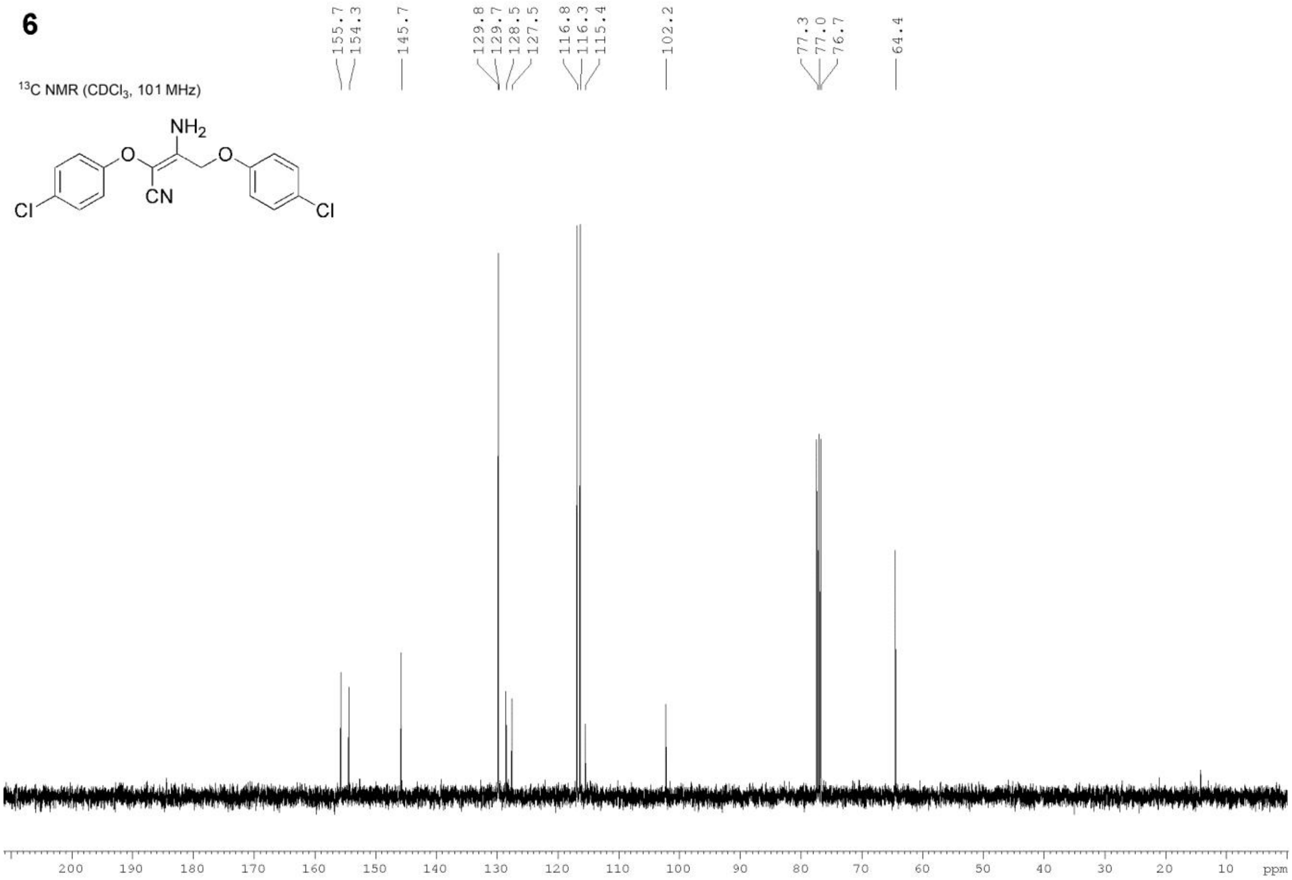
6

^{1}H NMR (CDCl$_3$, 400 MHz)

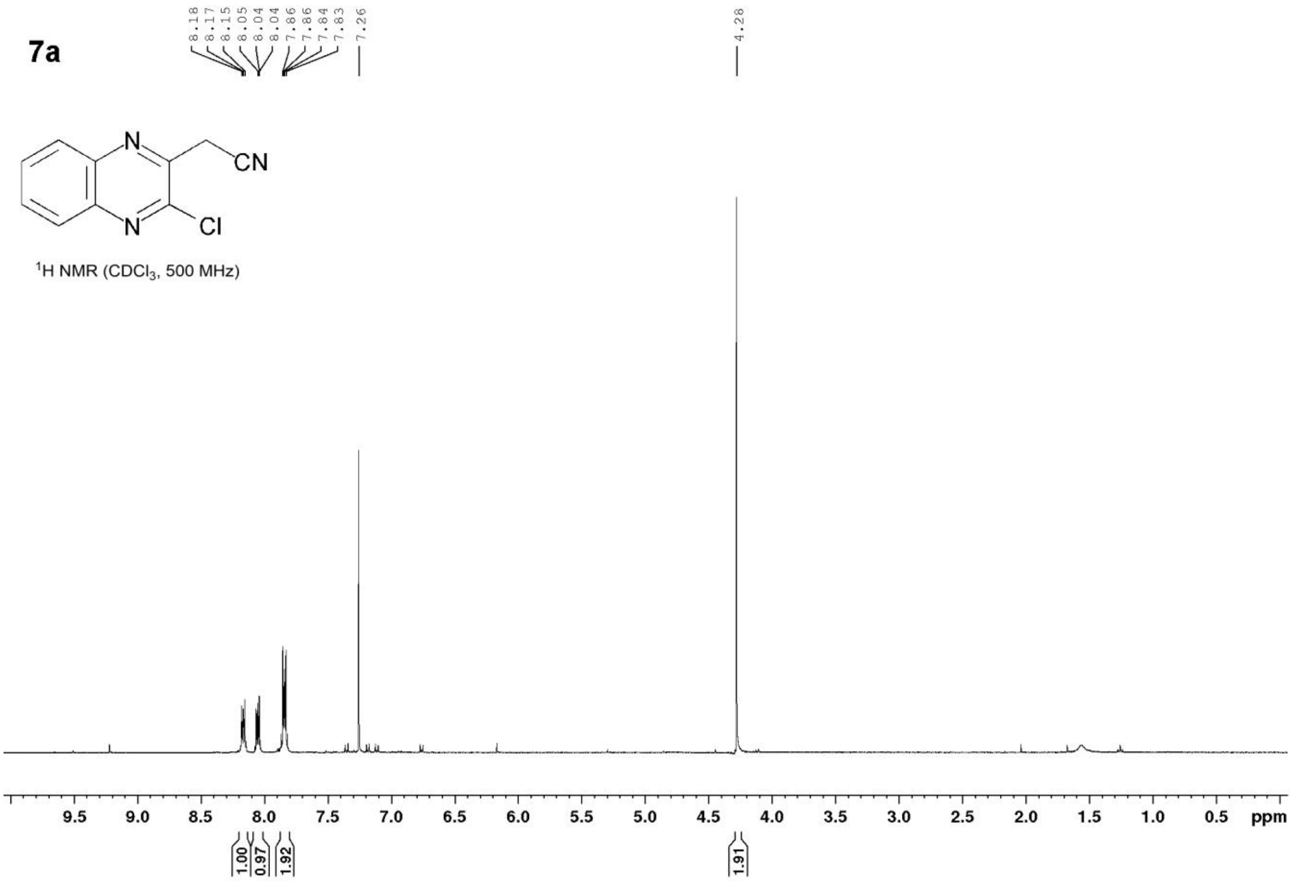


6

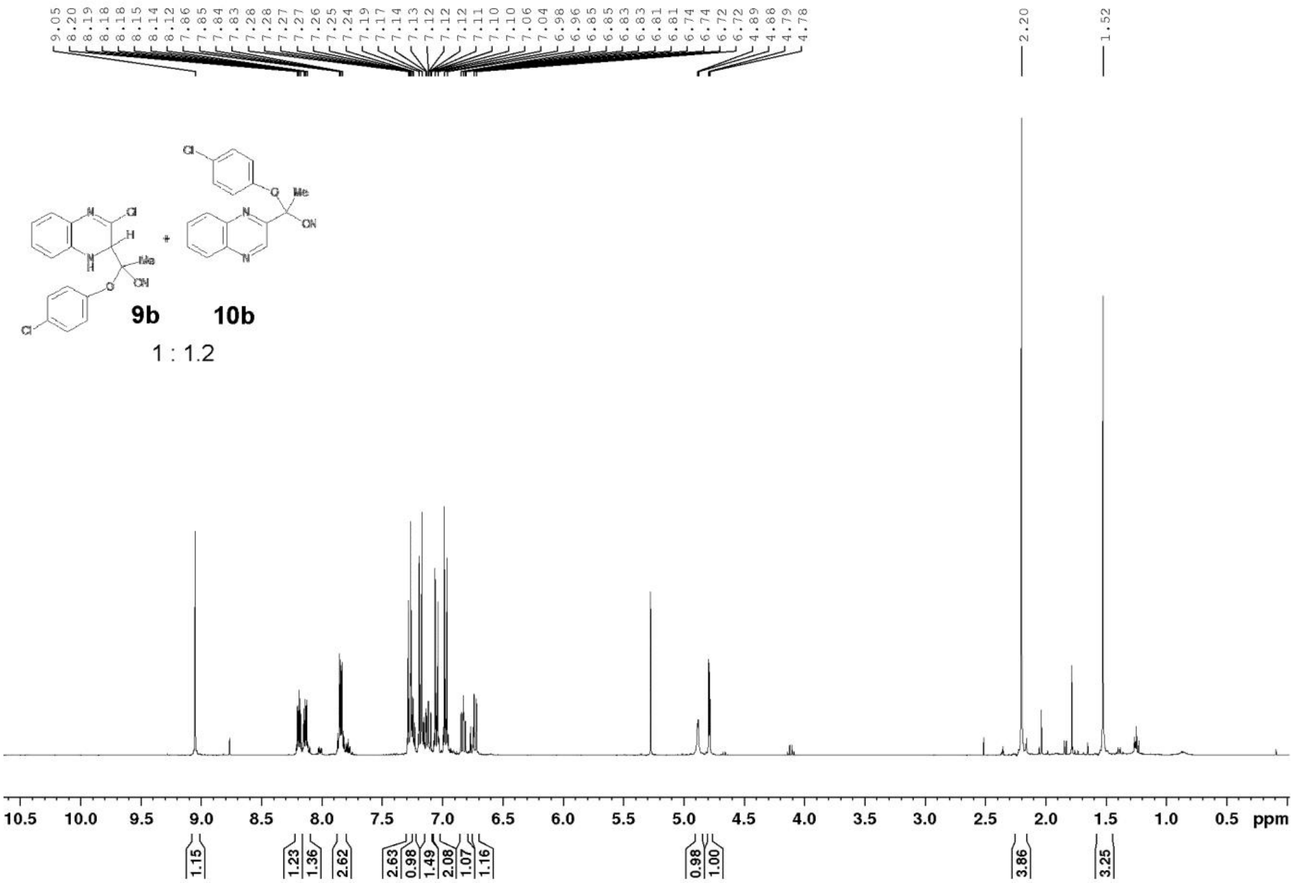
^{13}C NMR (CDCl$_3$, 101 MHz)



7a



^{1}H NMR (CDCl$_3$, 500 MHz)

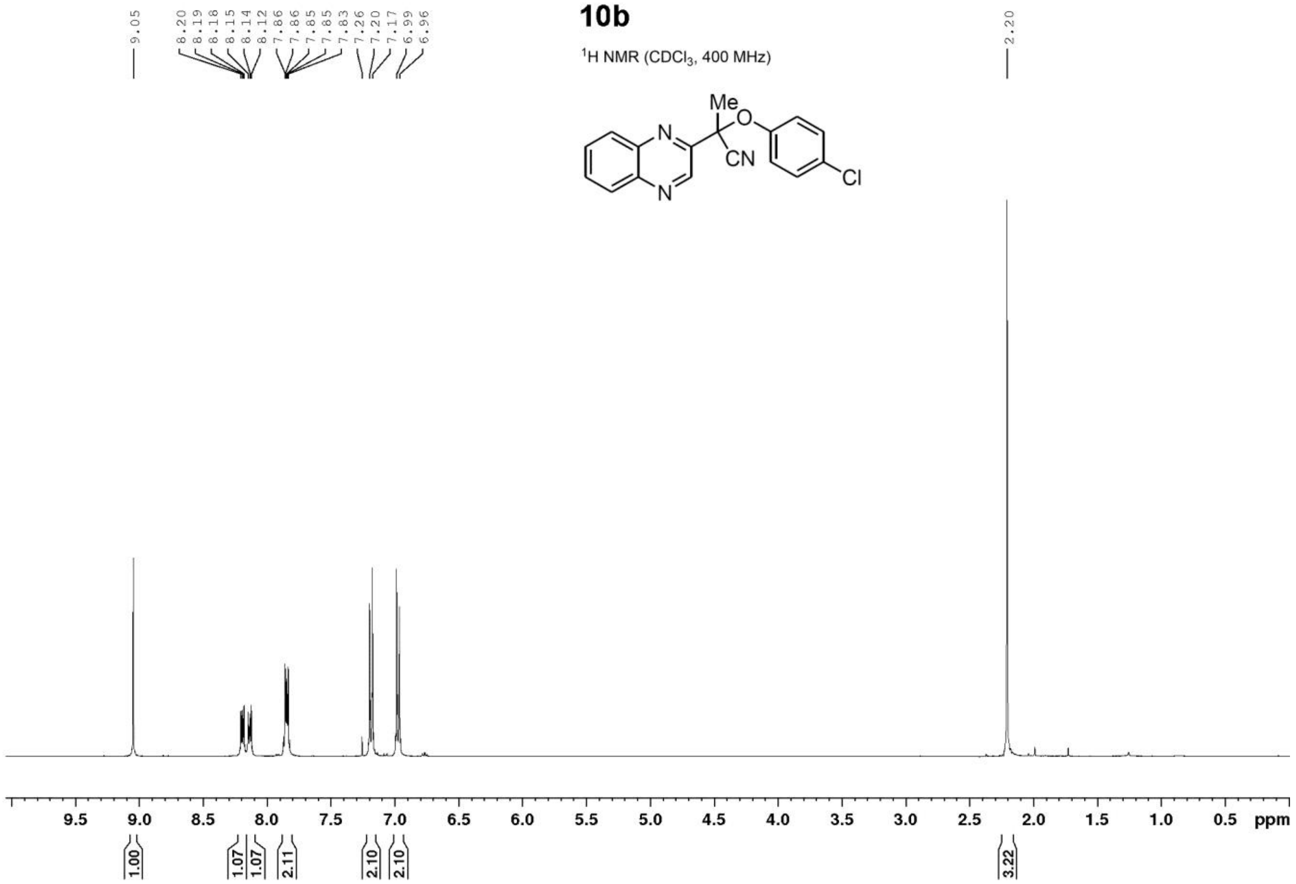


9b **10b**

1 : 1.2

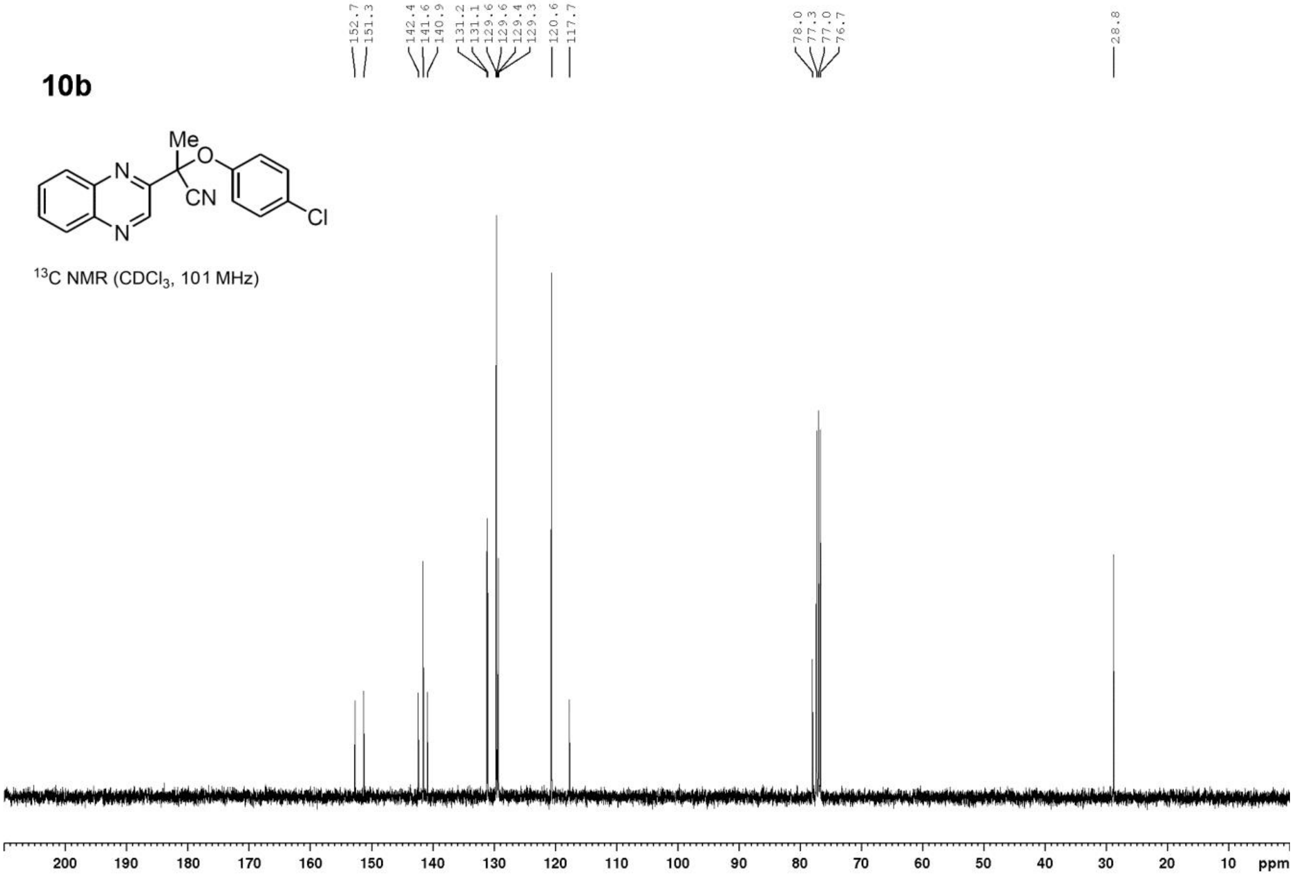
10b

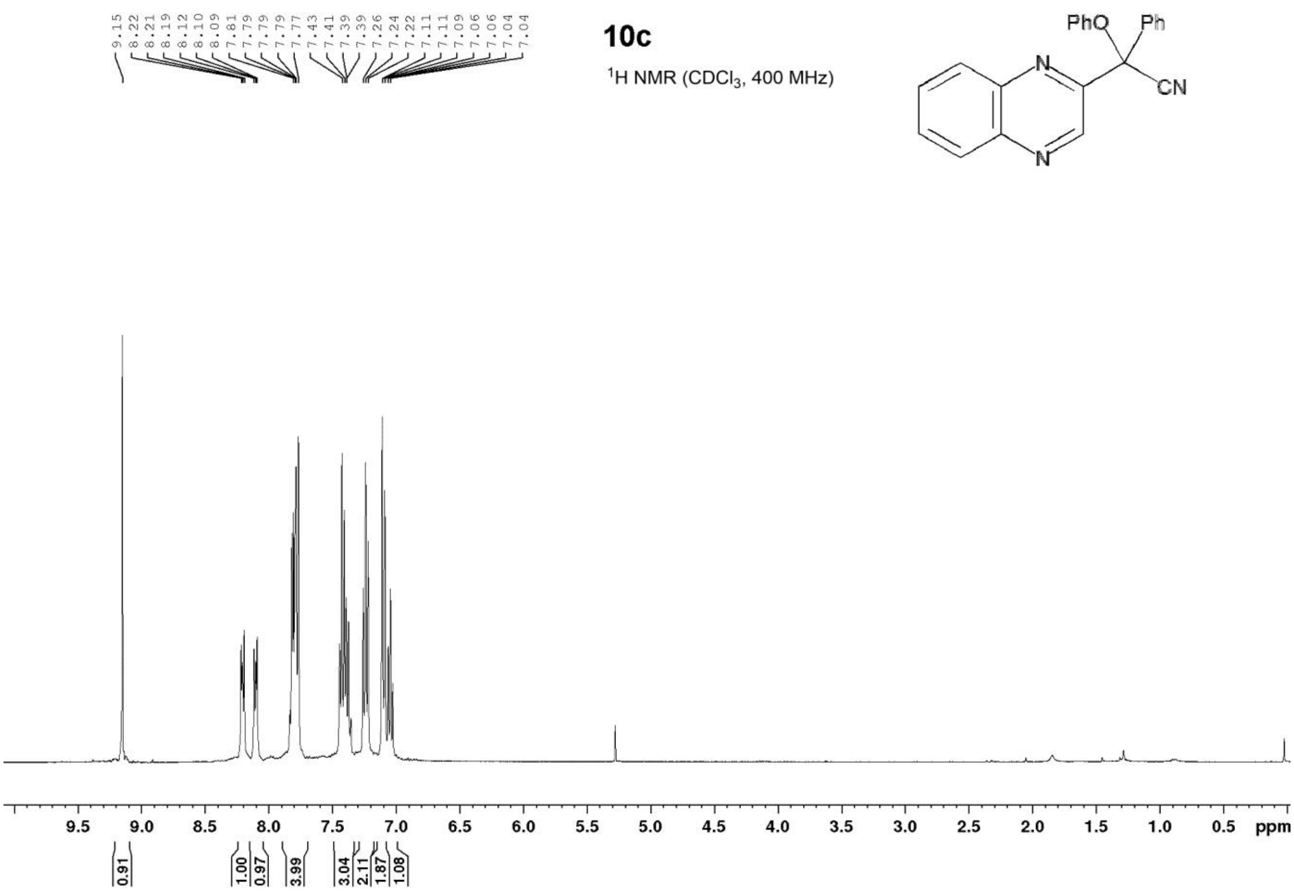
^1H NMR ($CDCl_3$, 400 MHz)



10b

^{13}C NMR ($CDCl_3$, 101 MHz)



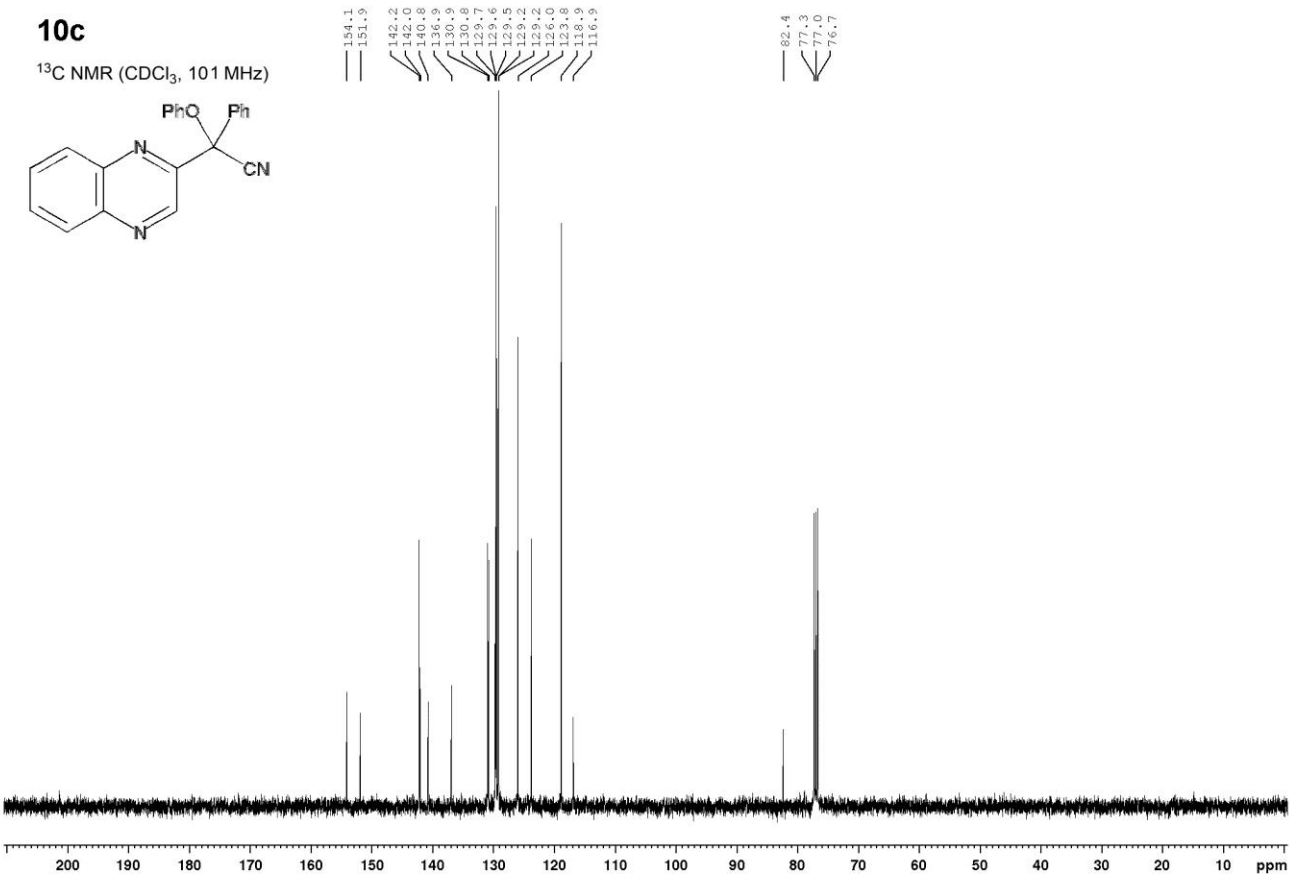


10c

^{1}H NMR (CDCl$_3$, 400 MHz)

10c

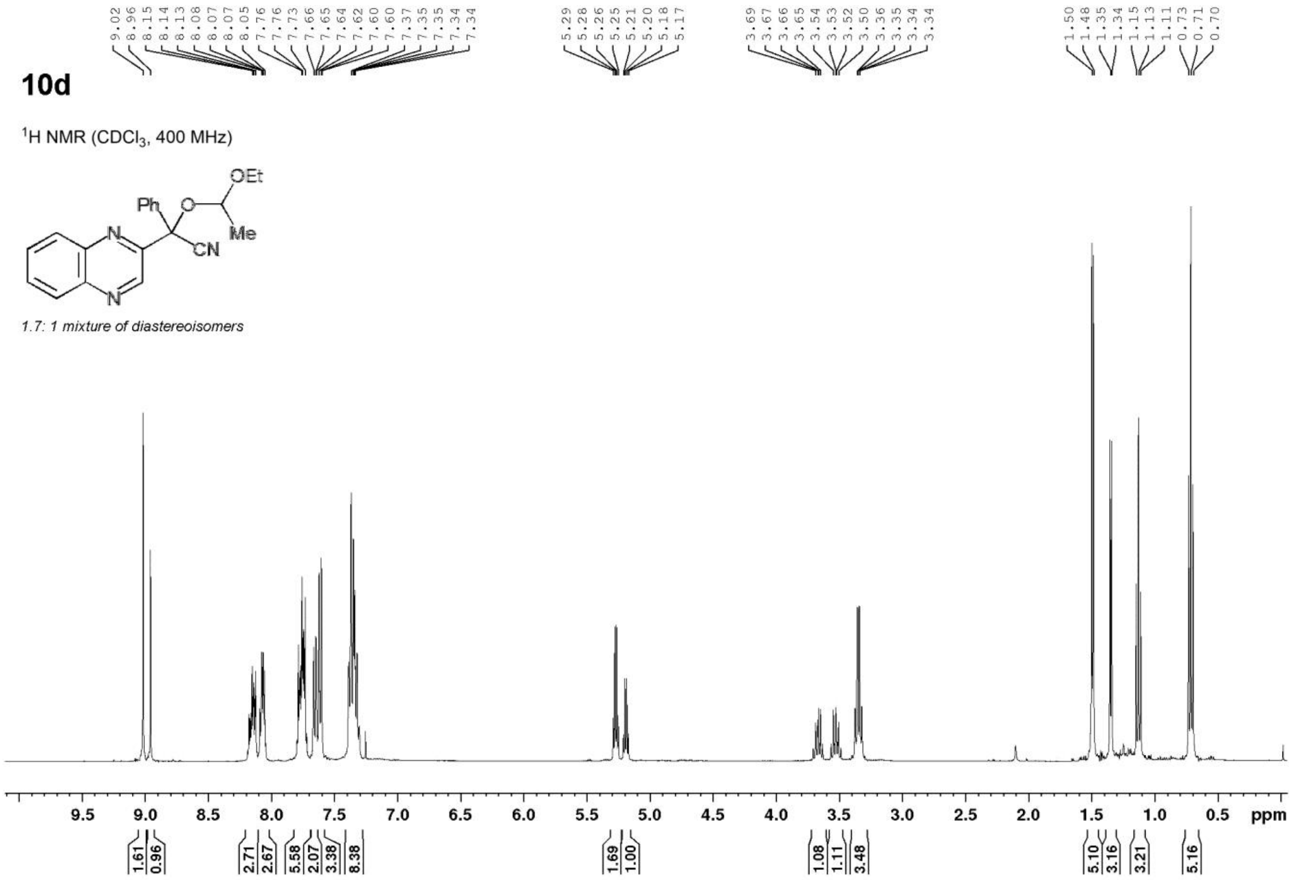
^{13}C NMR (CDCl$_3$, 101 MHz)



10d

^{1}H NMR (CDCl$_3$, 400 MHz)

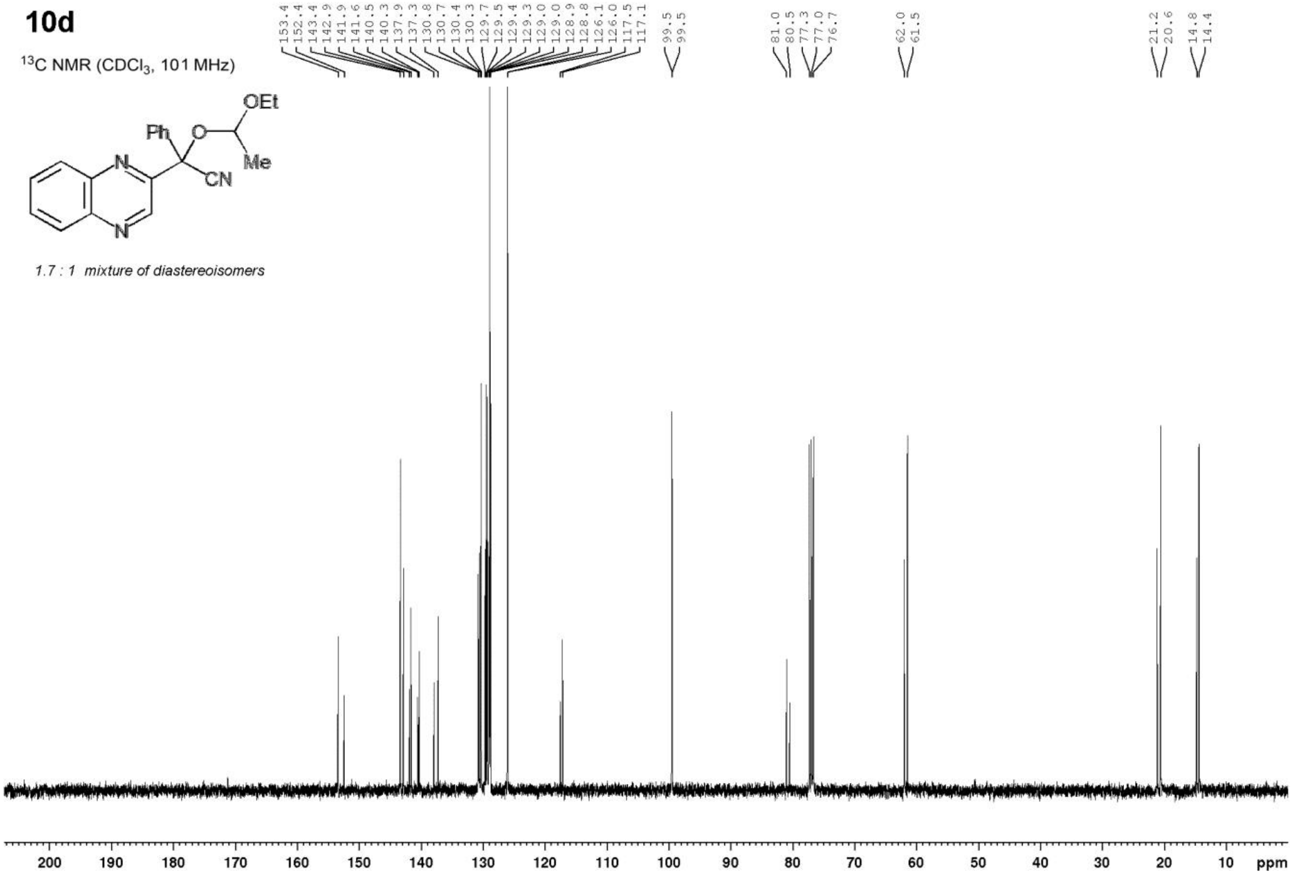
1.7: 1 mixture of diastereoisomers

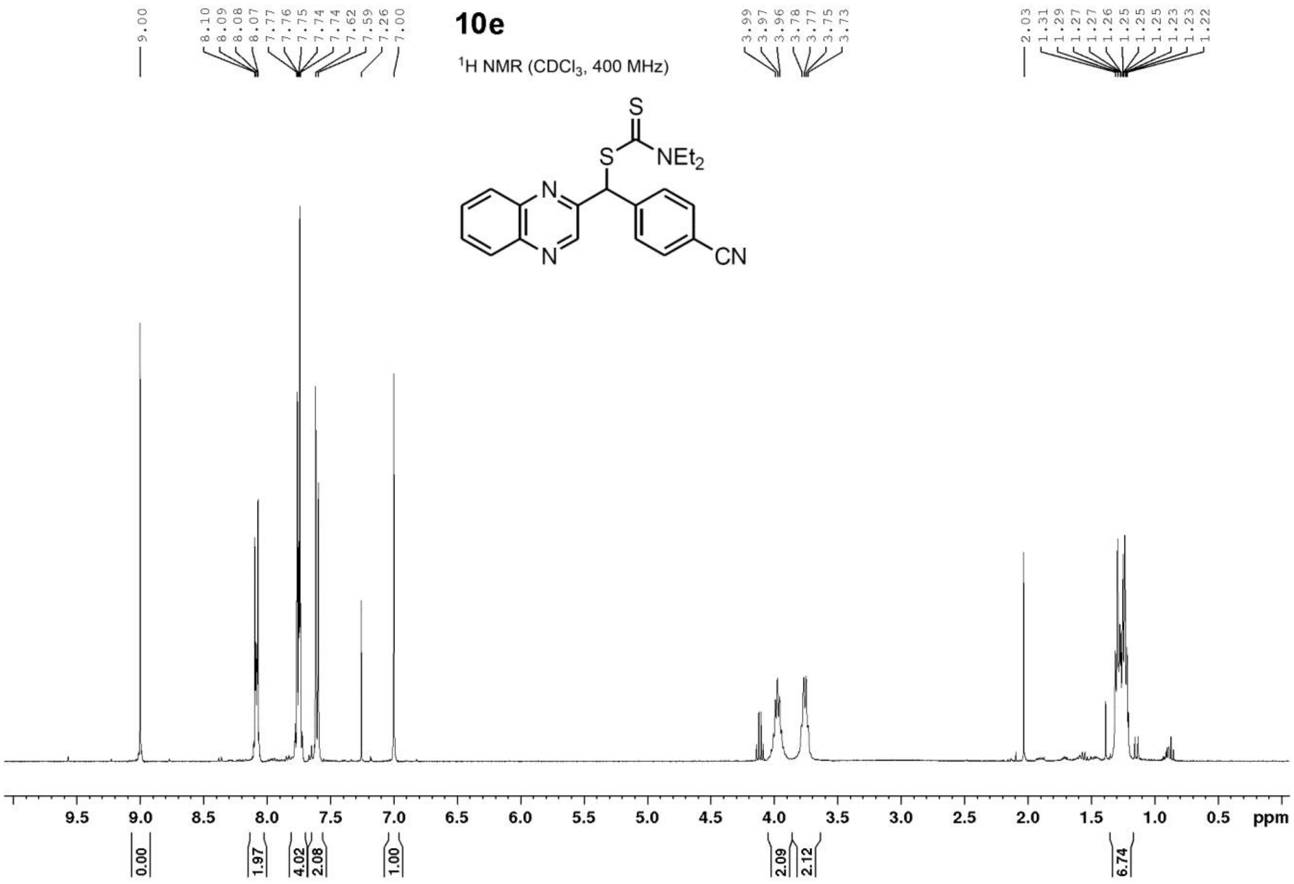


10d

^{13}C NMR (CDCl$_3$, 101 MHz)

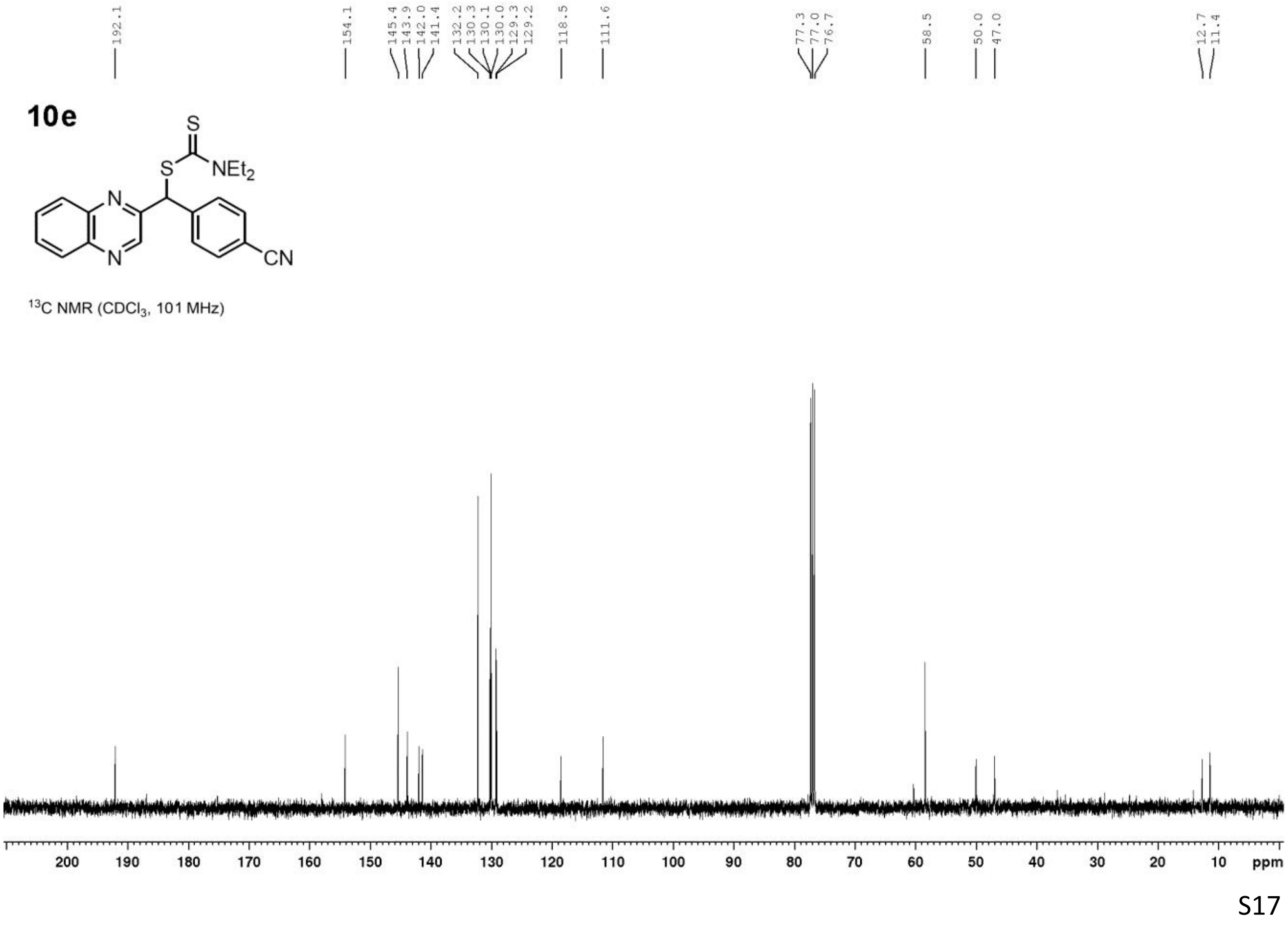
1.7 : 1 mixture of diastereoisomers





10e

^{1}H NMR (CDCl$_3$, 400 MHz)

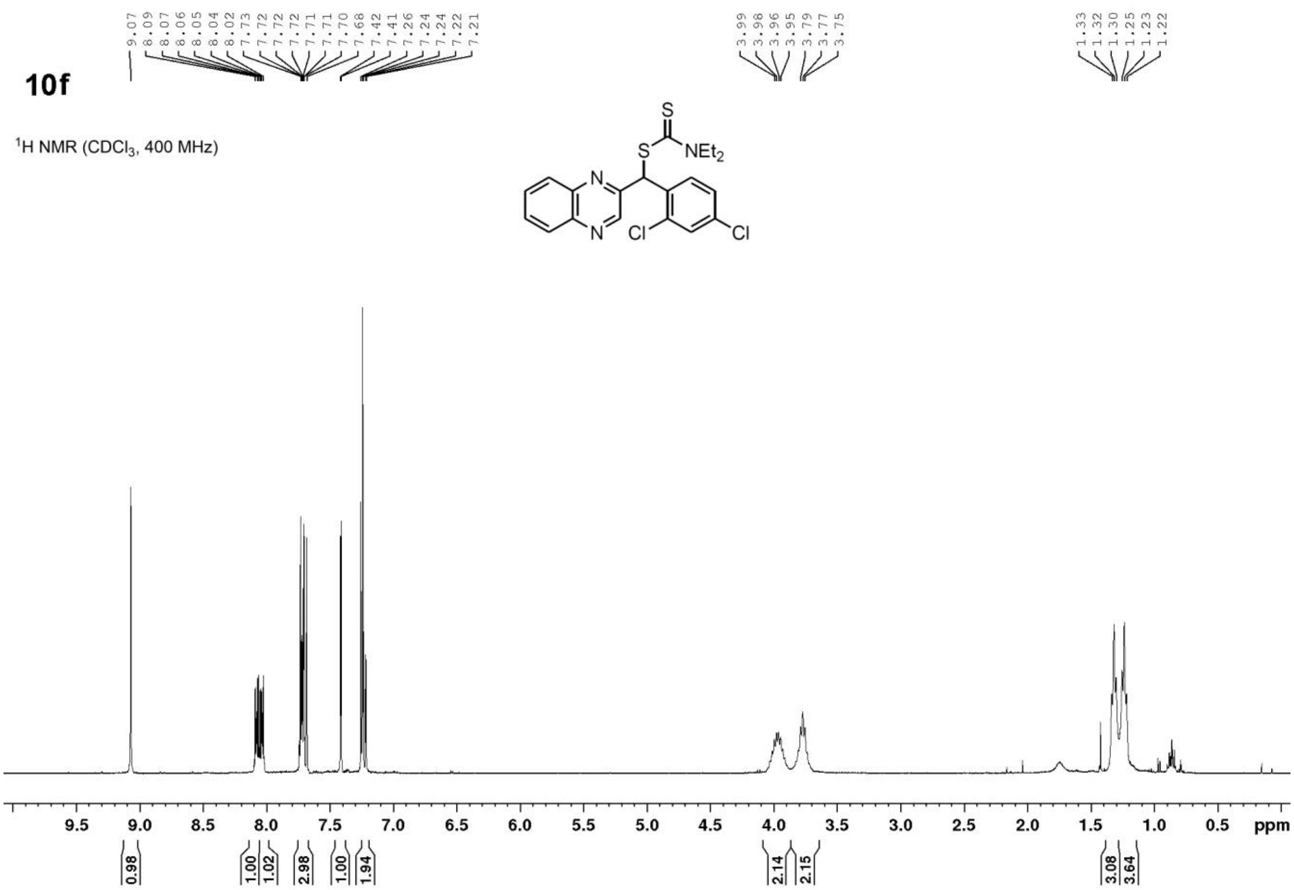


10e

^{13}C NMR (CDCl$_3$, 101 MHz)

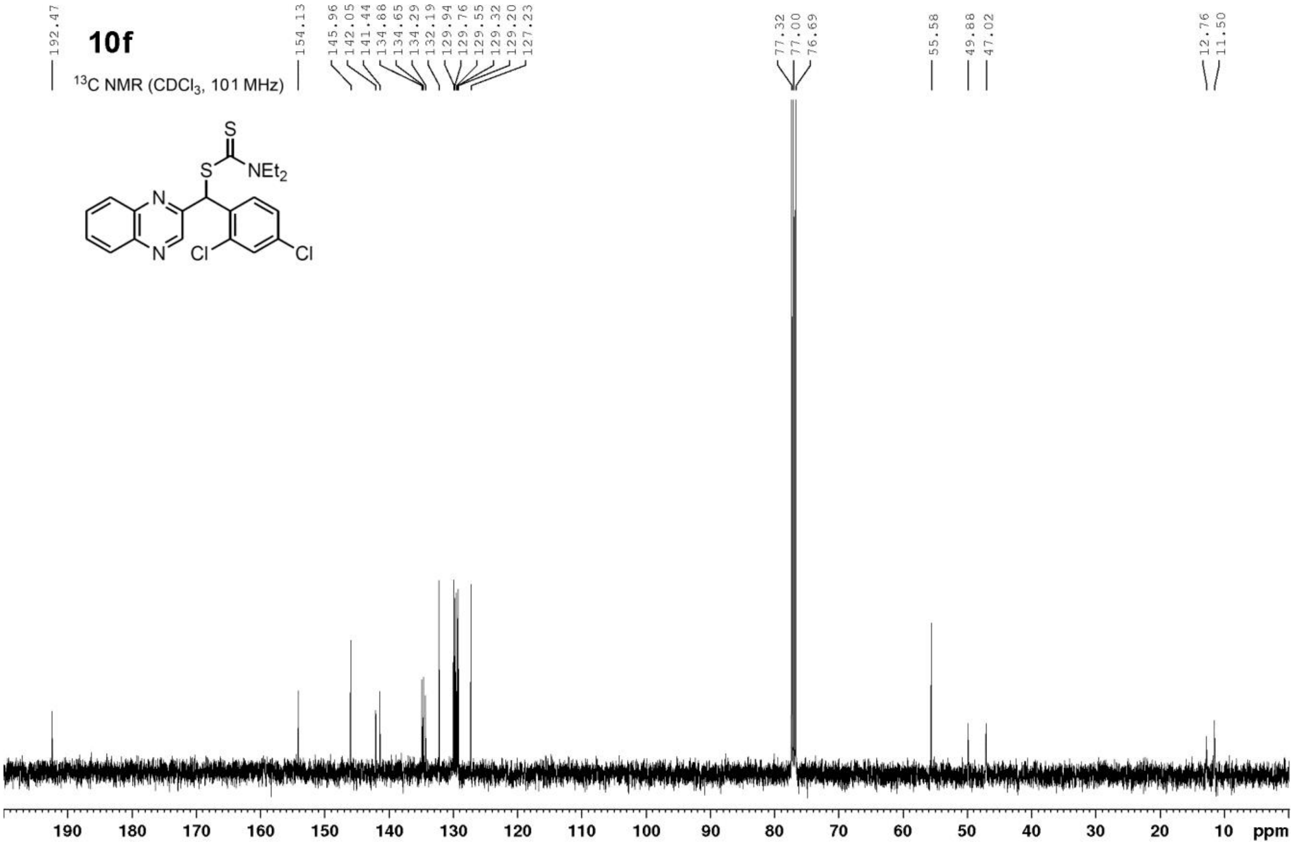
10f

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



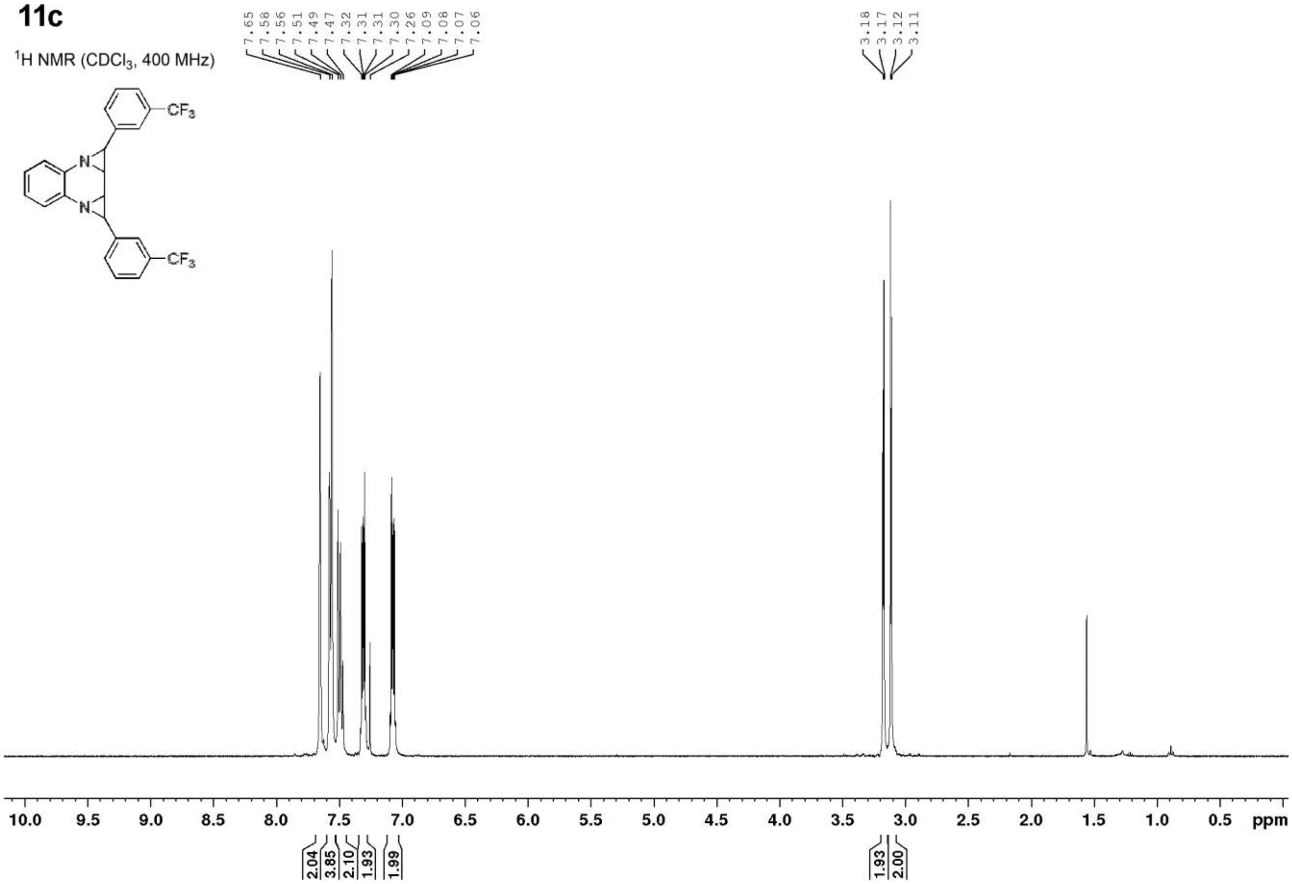
10f

^{13}C NMR ($CDCl_3$, 101 MHz)



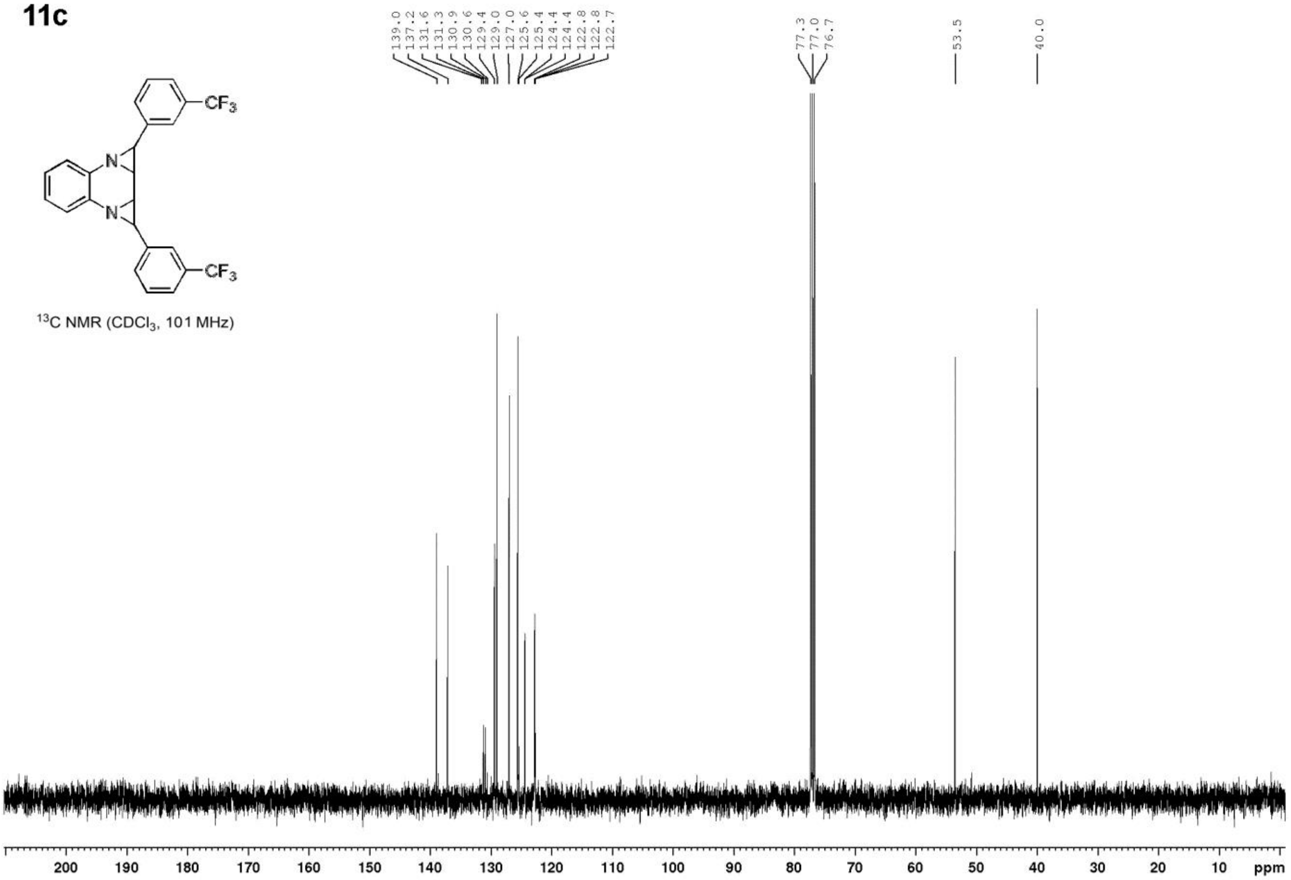
11c

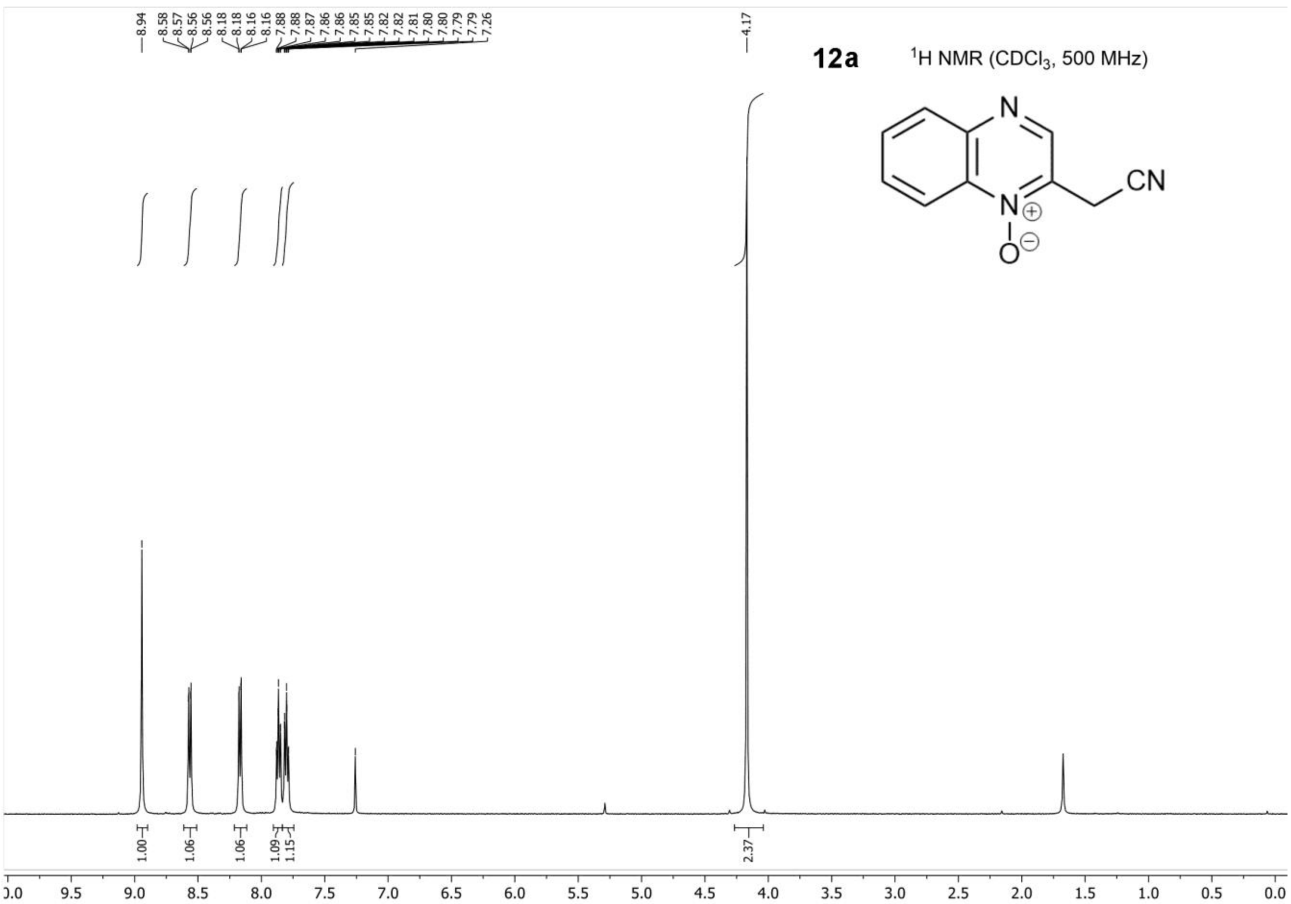
^{1}H NMR ($CDCl_3$, 400 MHz)

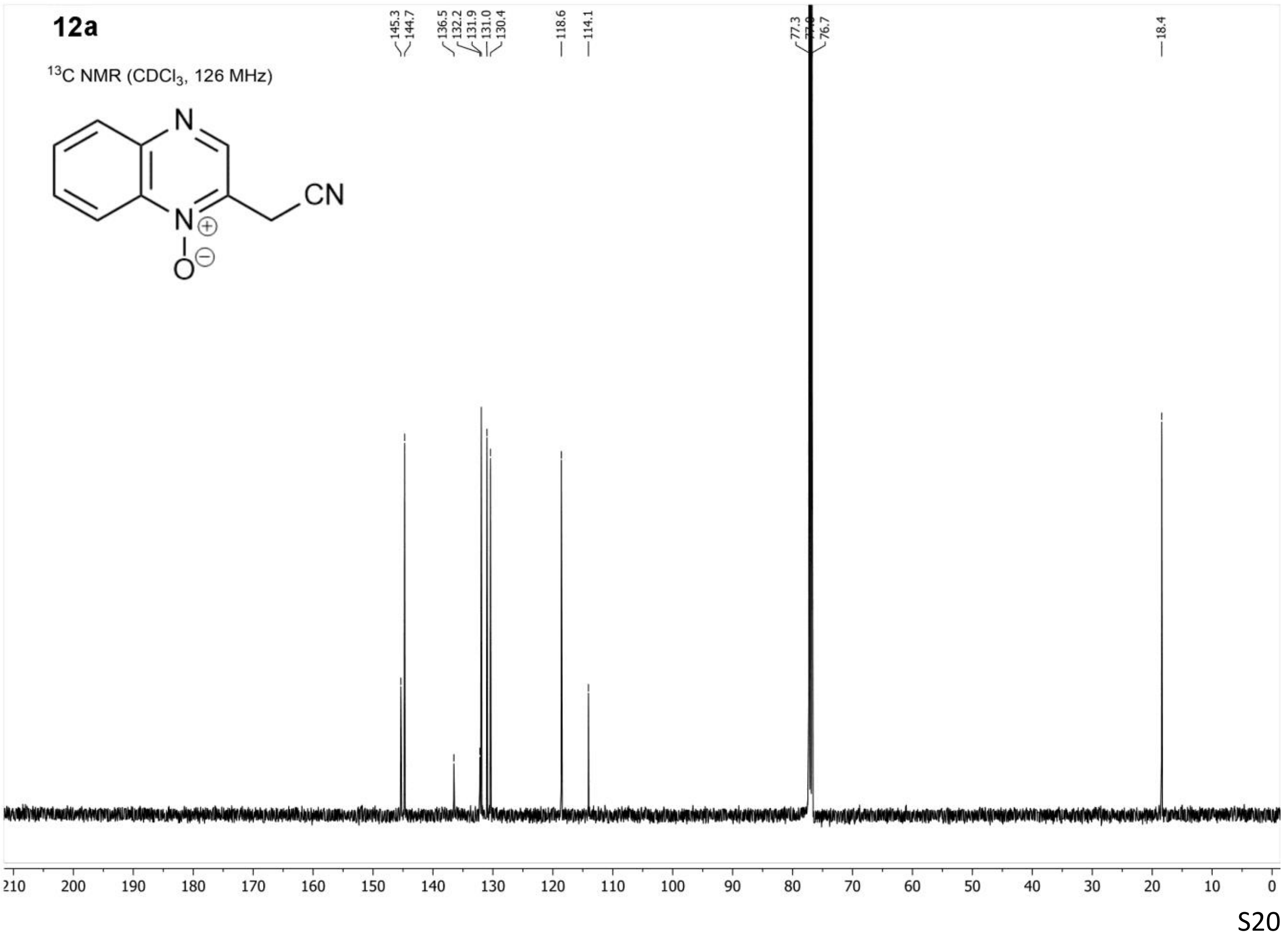


11c

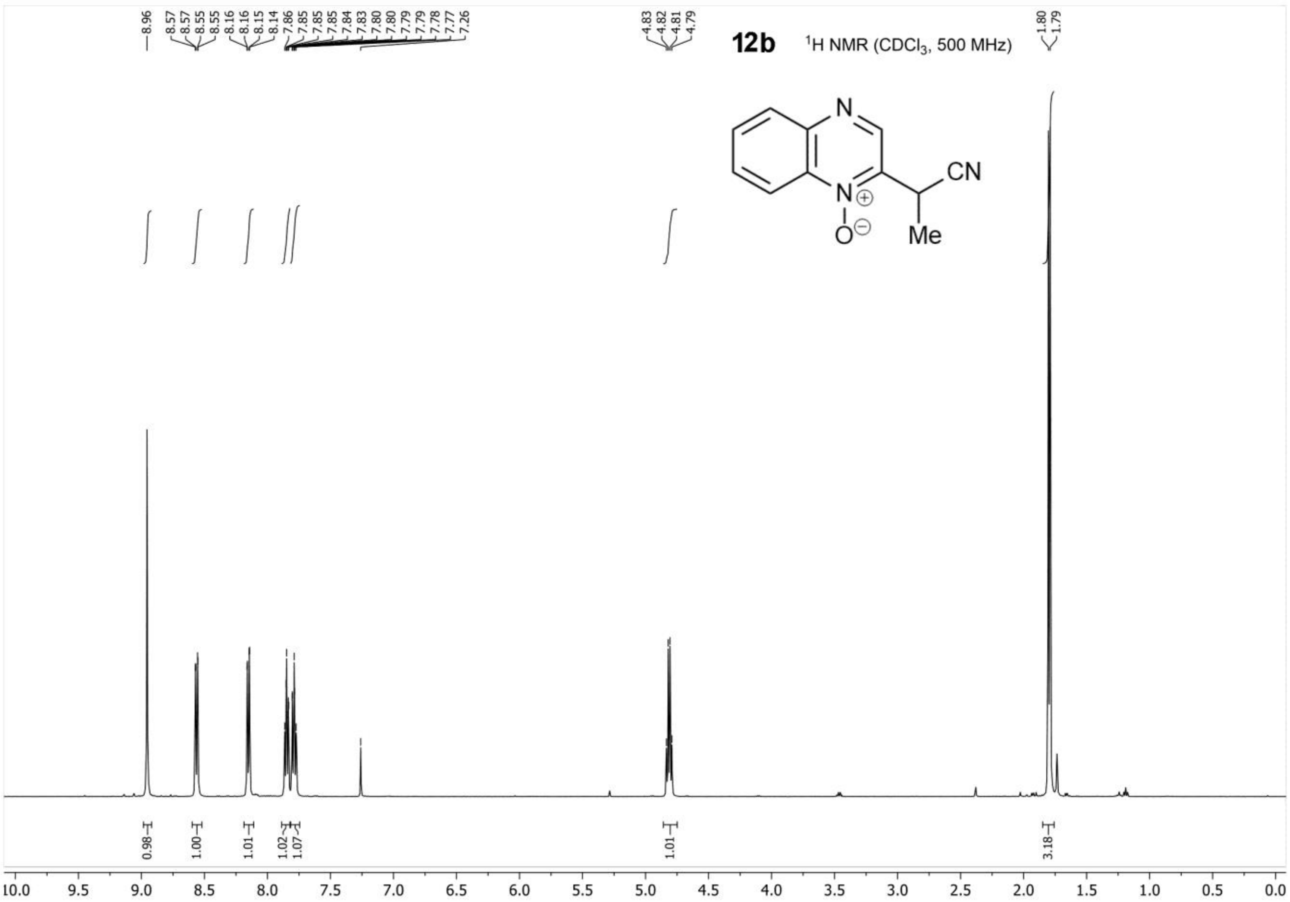
^{13}C NMR ($CDCl_3$, 101 MHz)

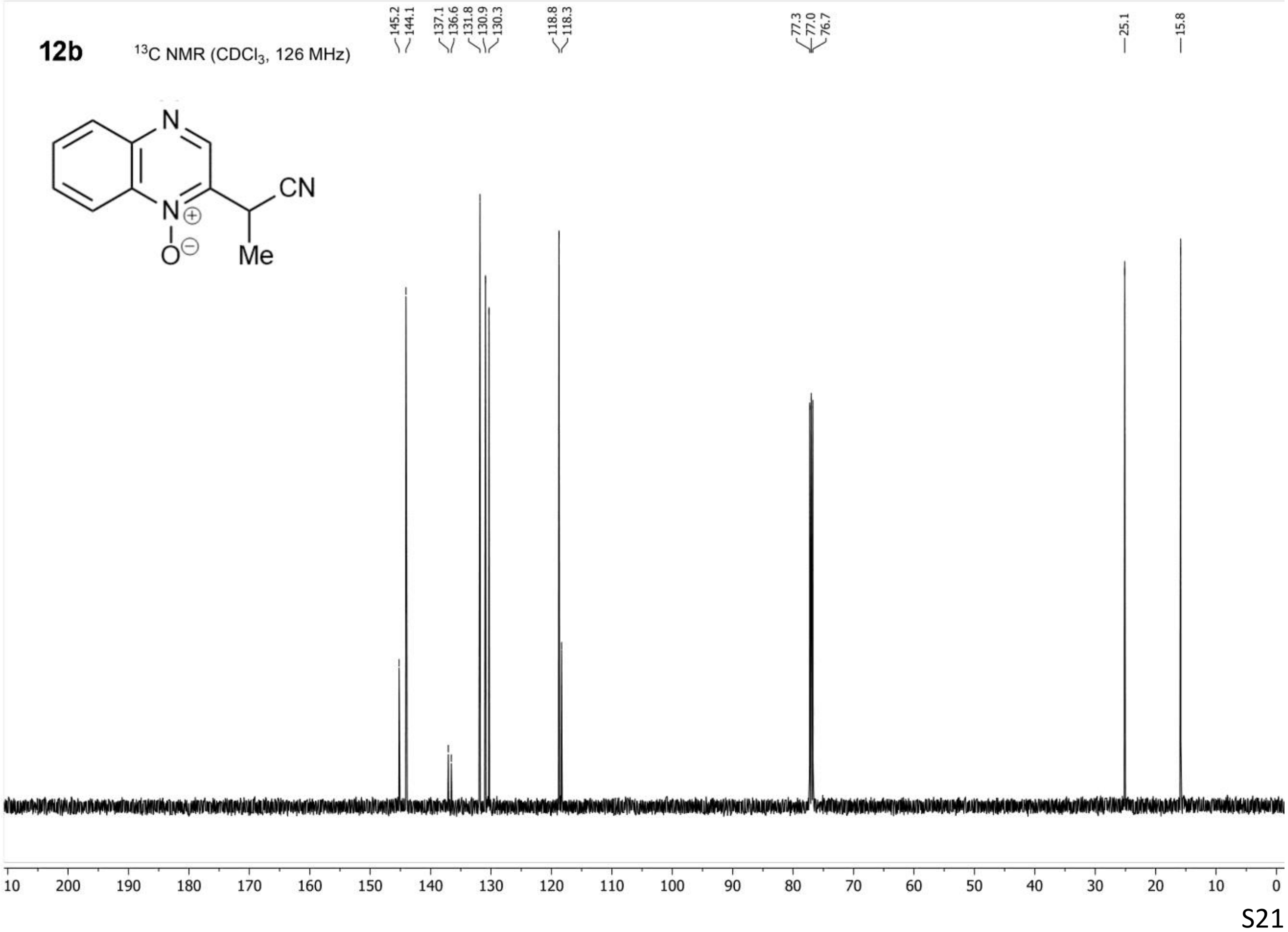


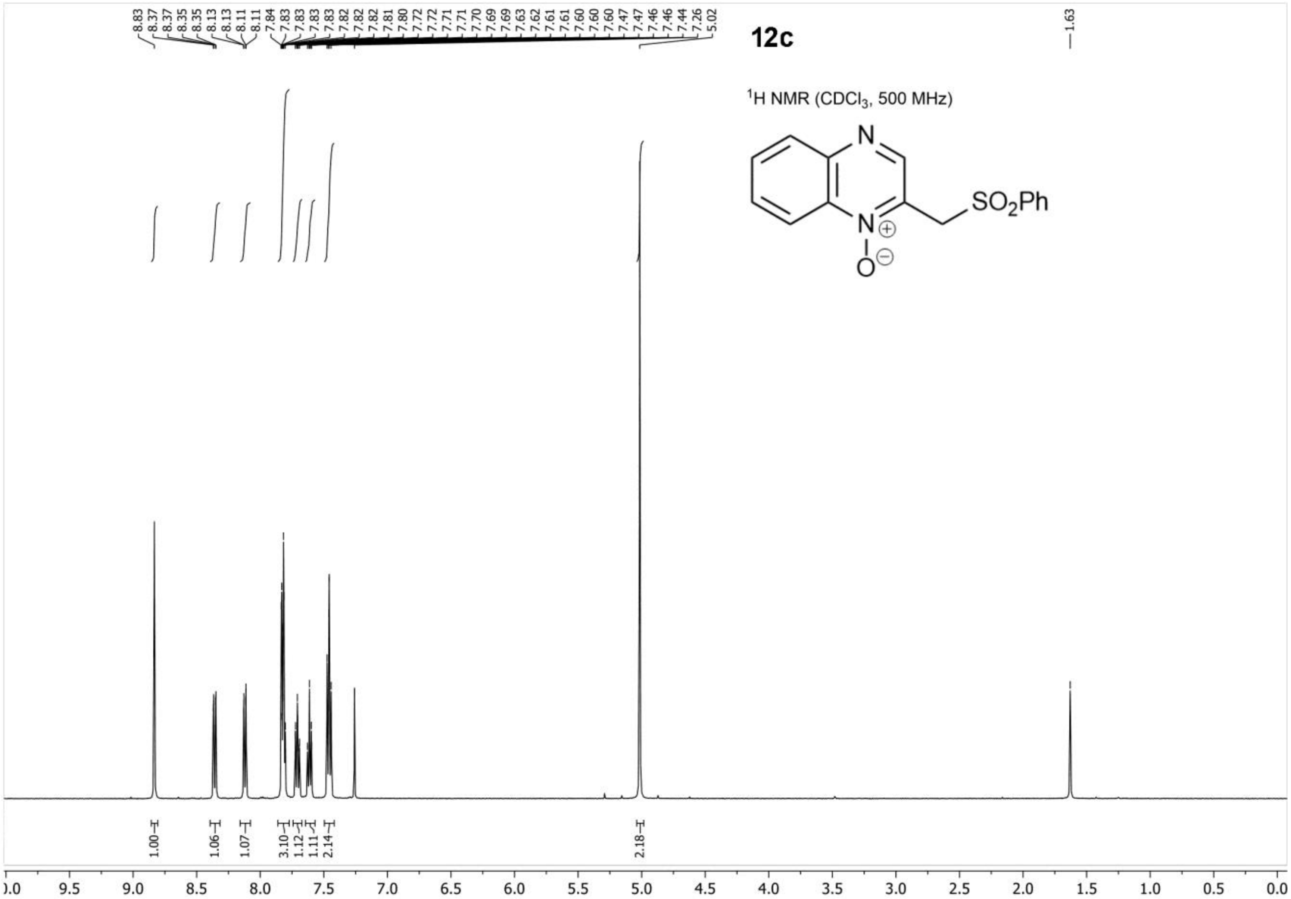

12a ^1H NMR ($CDCl_3$, 500 MHz)


12a

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

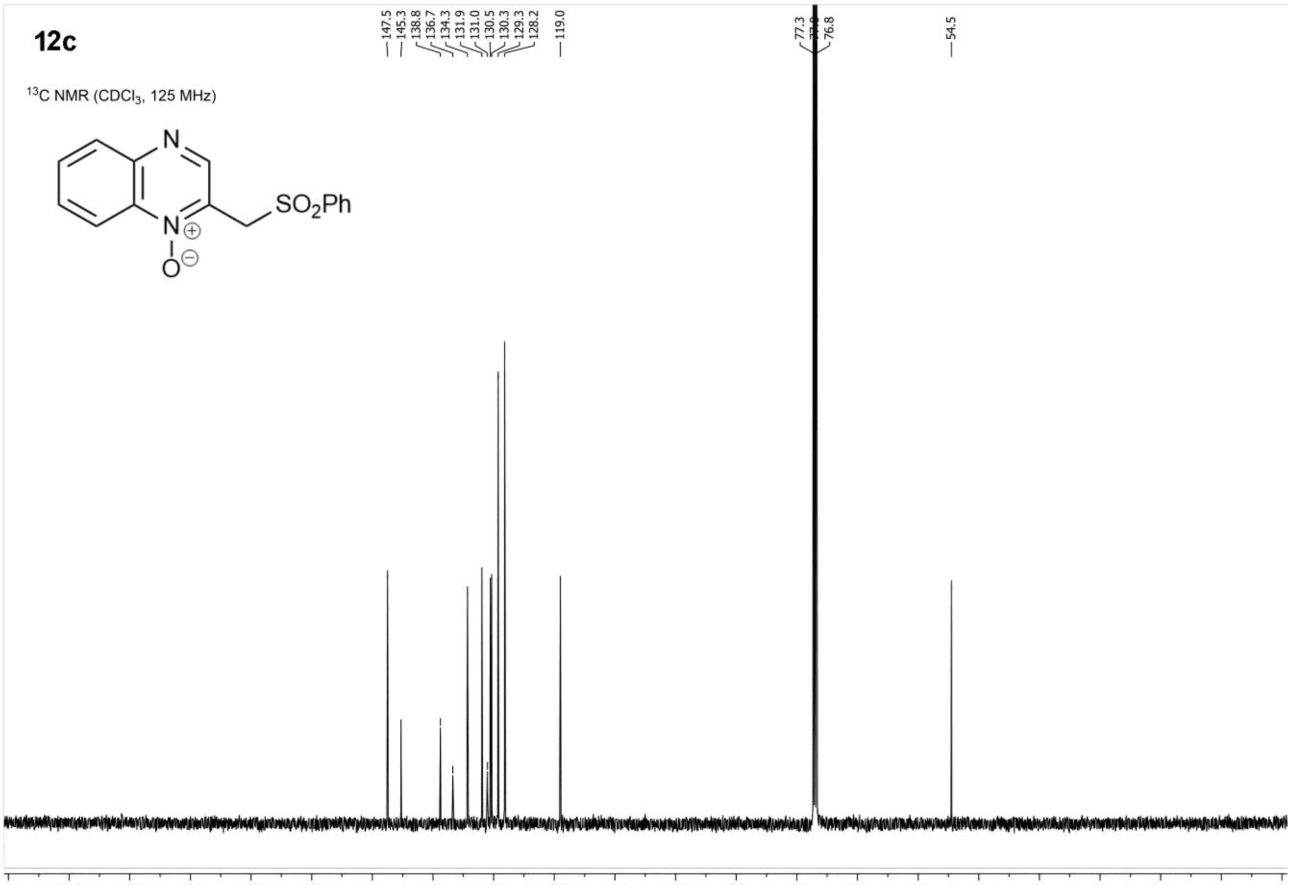

12b ^{1}H NMR (CDCl$_3$, 500 MHz)


12b ^{13}C NMR (CDCl$_3$, 126 MHz)



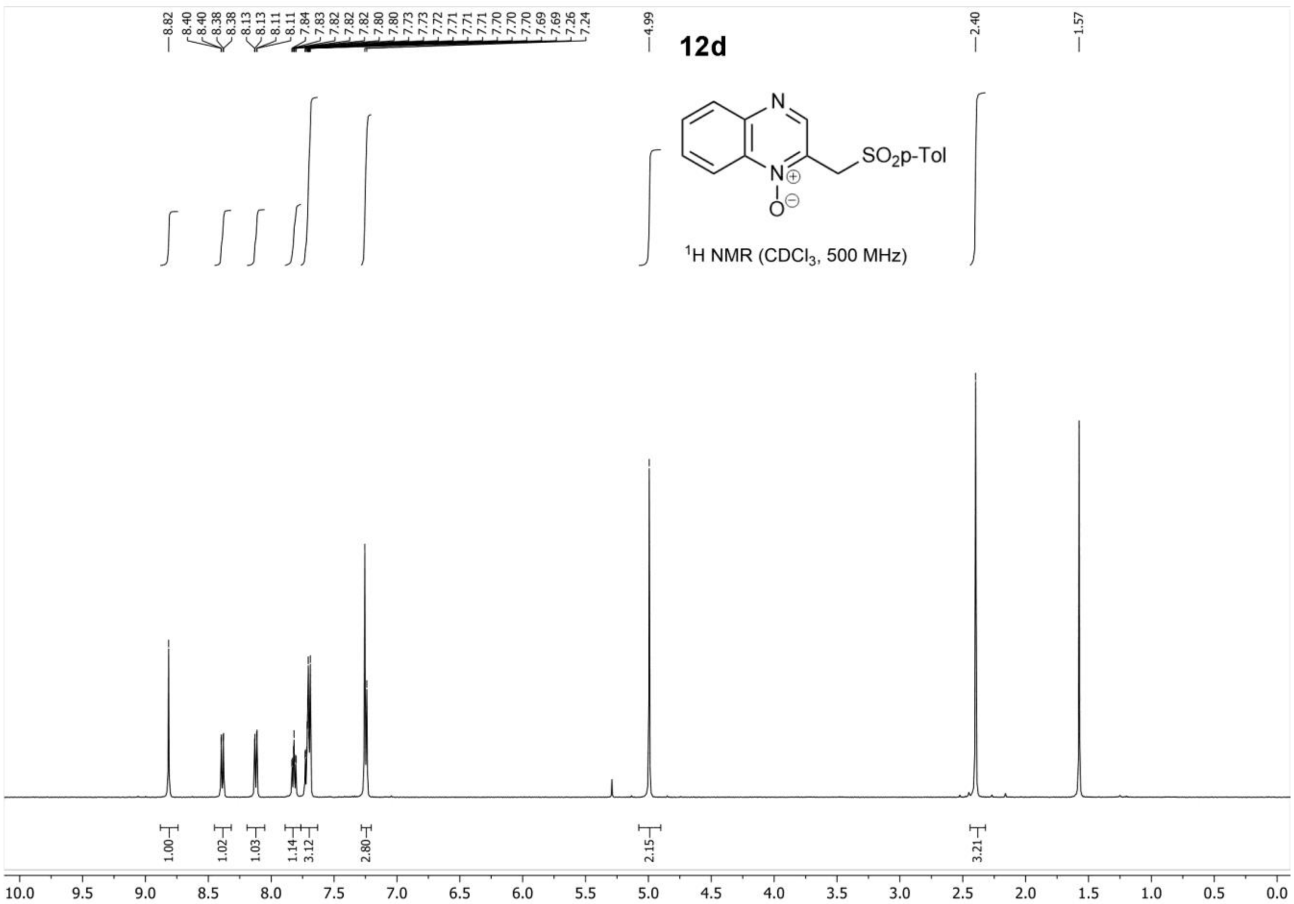
12c

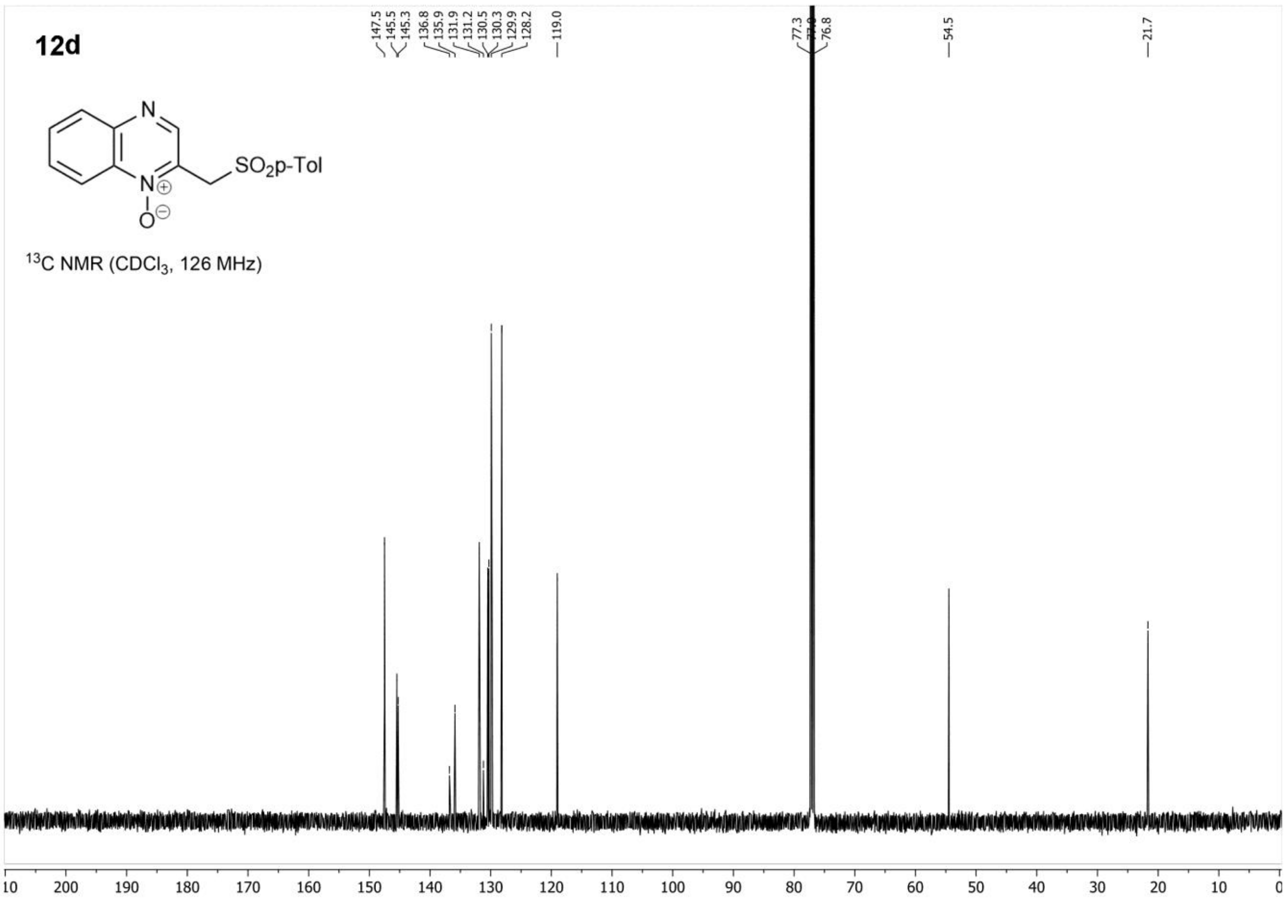
^{1}H NMR (CDCl$_3$, 500 MHz)

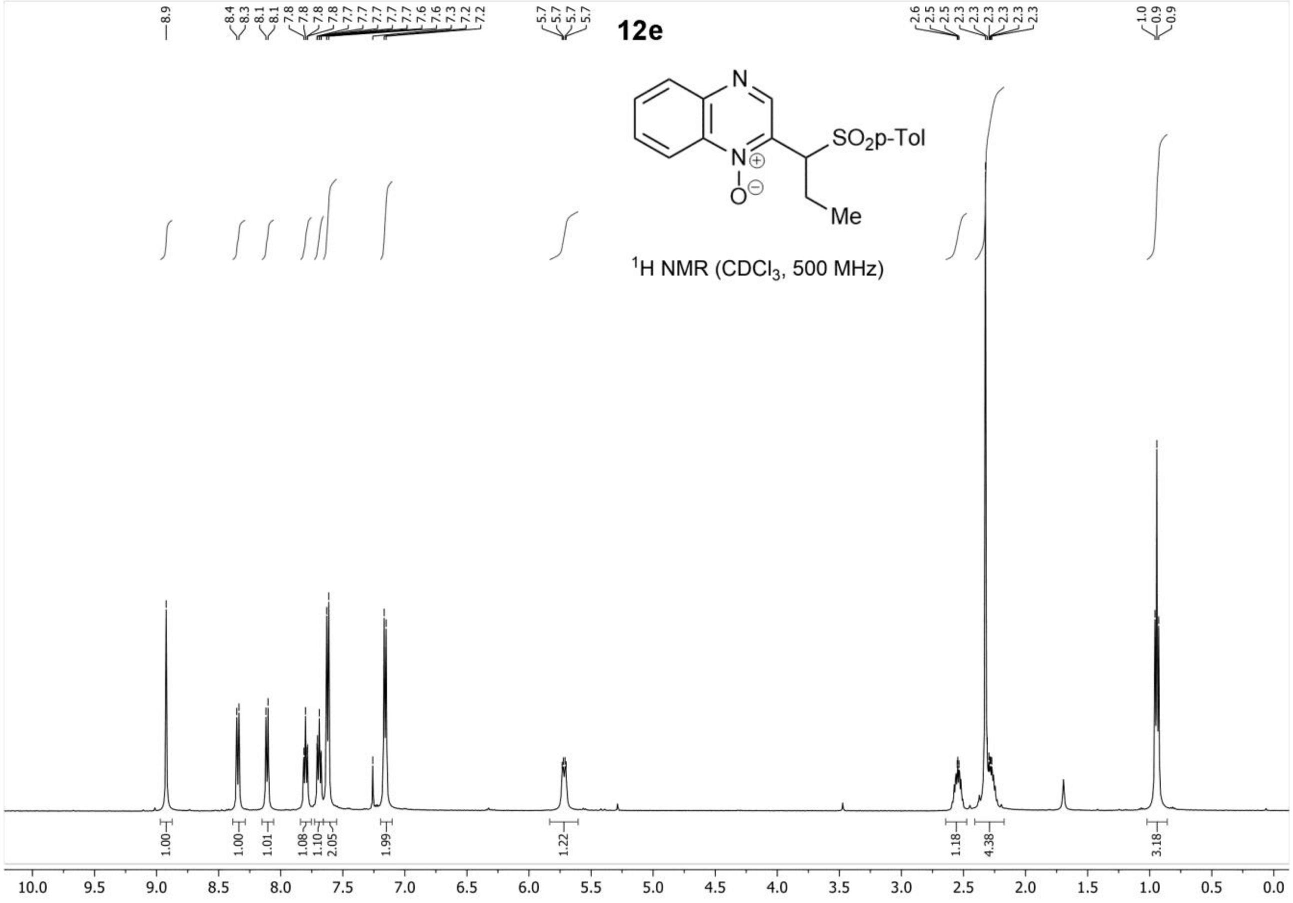


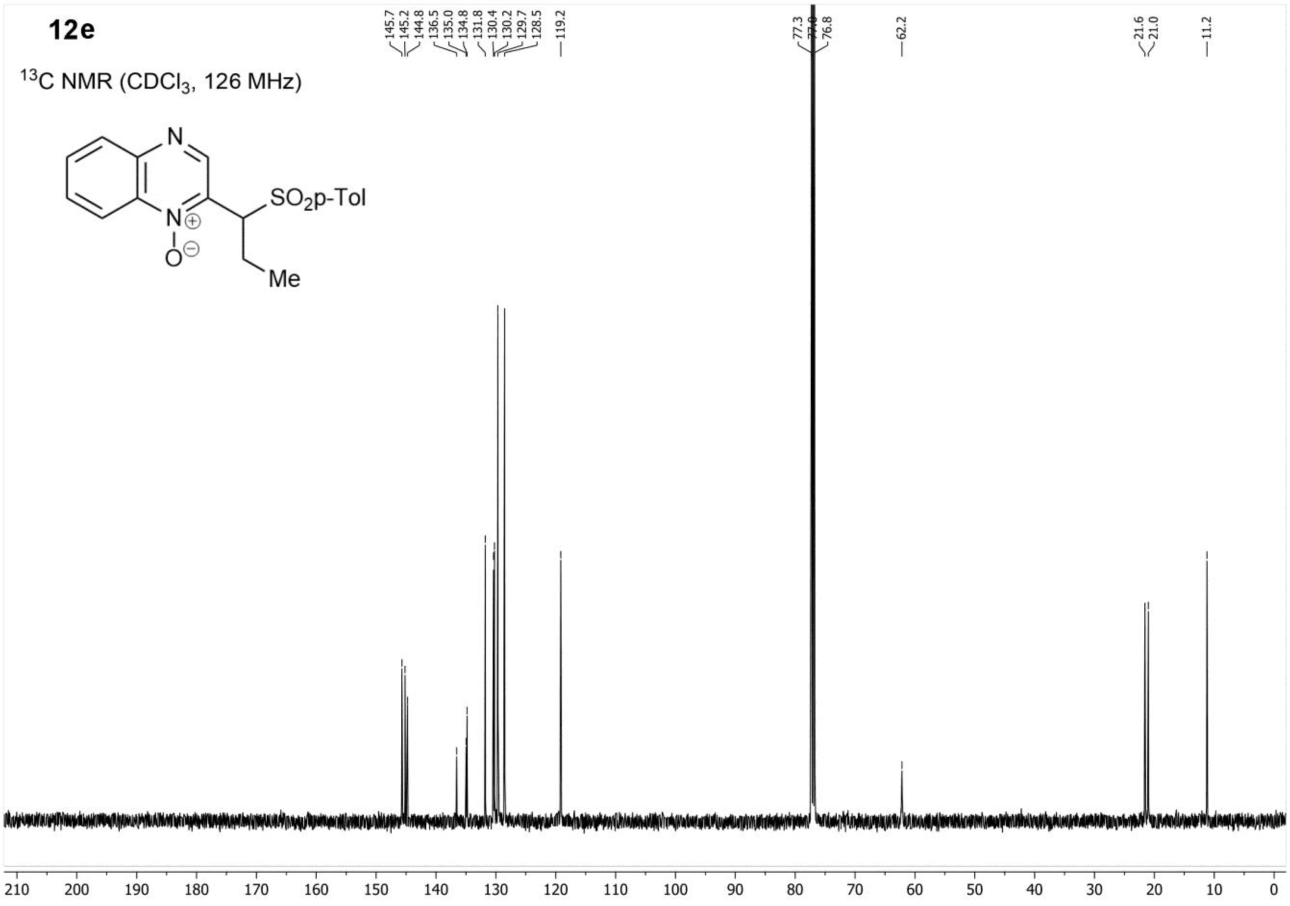
12c

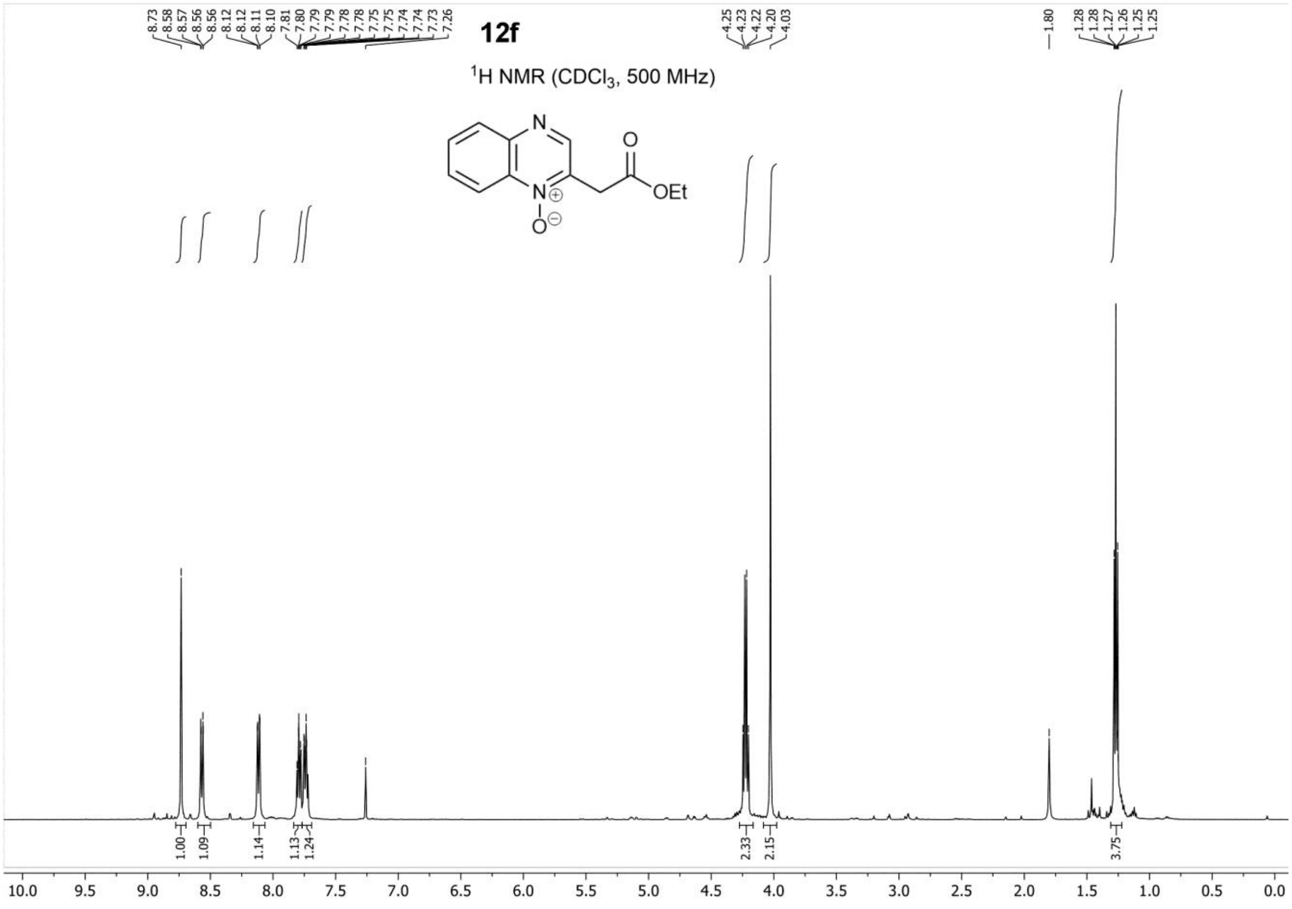
^{13}C NMR (CDCl$_3$, 125 MHz)

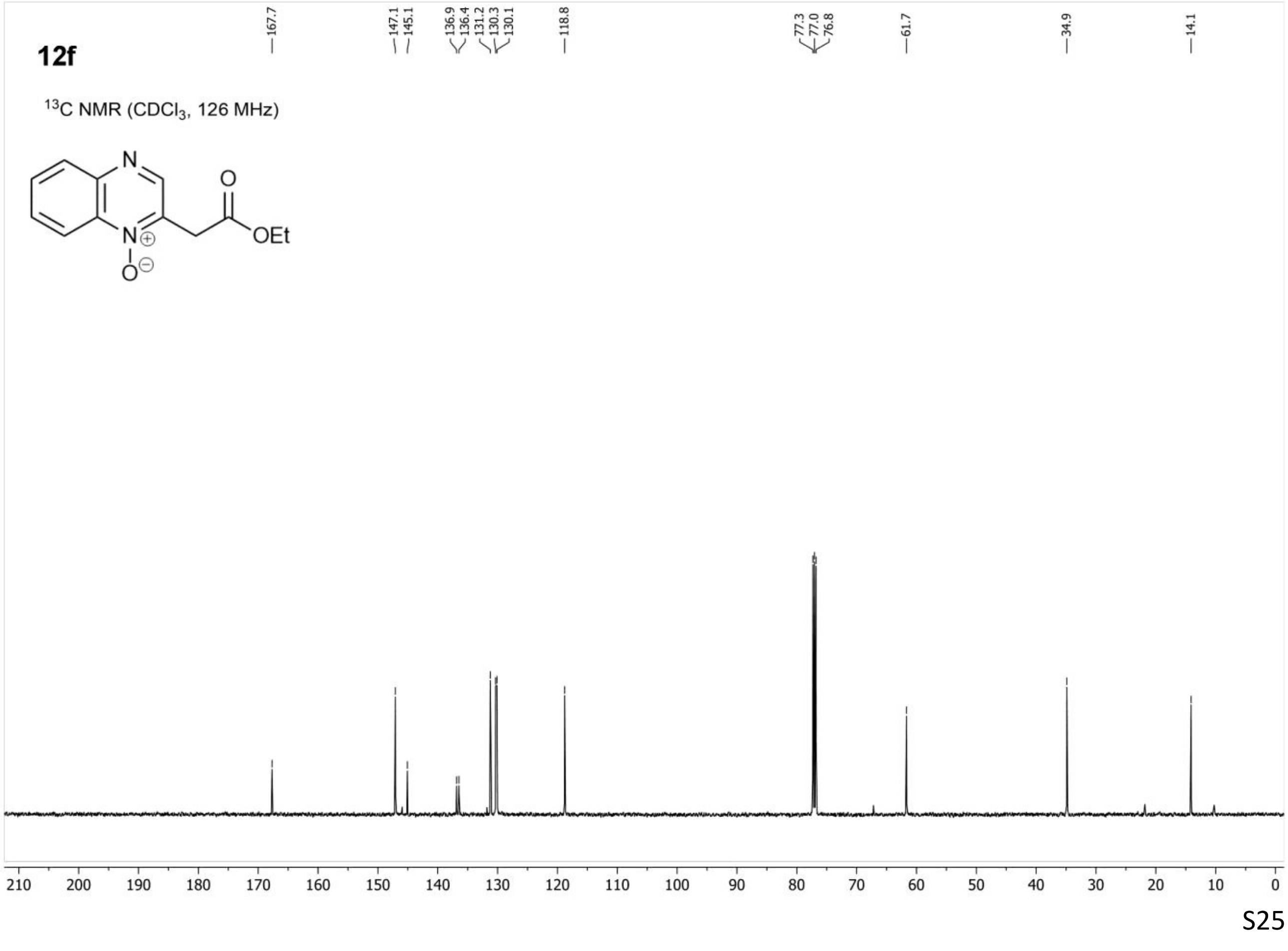

8.82
8.40
8.40
8.38
8.38
8.13
8.13
8.11
8.11
7.84
7.83
7.82
7.82
7.82
7.80
7.80
7.73
7.73
7.72
7.71
7.71
7.71
7.70
7.70
7.69
7.26
7.24
4.99
2.40
1.57
12d
N
SO2p-Tol
N⊕
O⊖
1H NMR (CDCl3, 500 MHz)
1.00
1.02
1.03
1.14
3.12
2.80
2.15
3.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

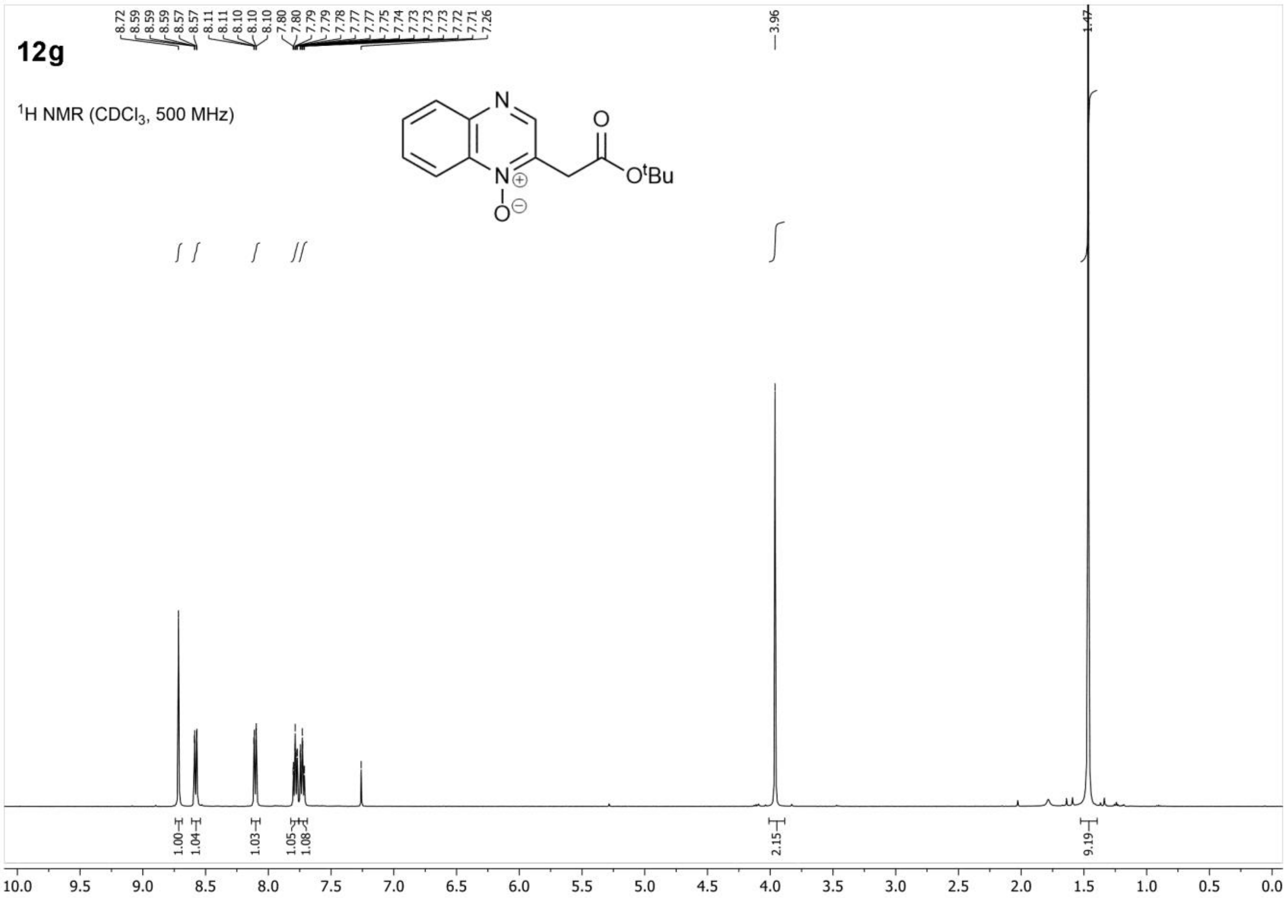

12d
N
SO2p-Tol
N⊕
O⊖
13C NMR (CDCl3, 126 MHz)
147.5
145.5
145.3
136.8
135.9
131.9
131.2
130.5
130.3
129.9
128.2
119.0
77.3
77.0
76.8
54.5
21.7
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

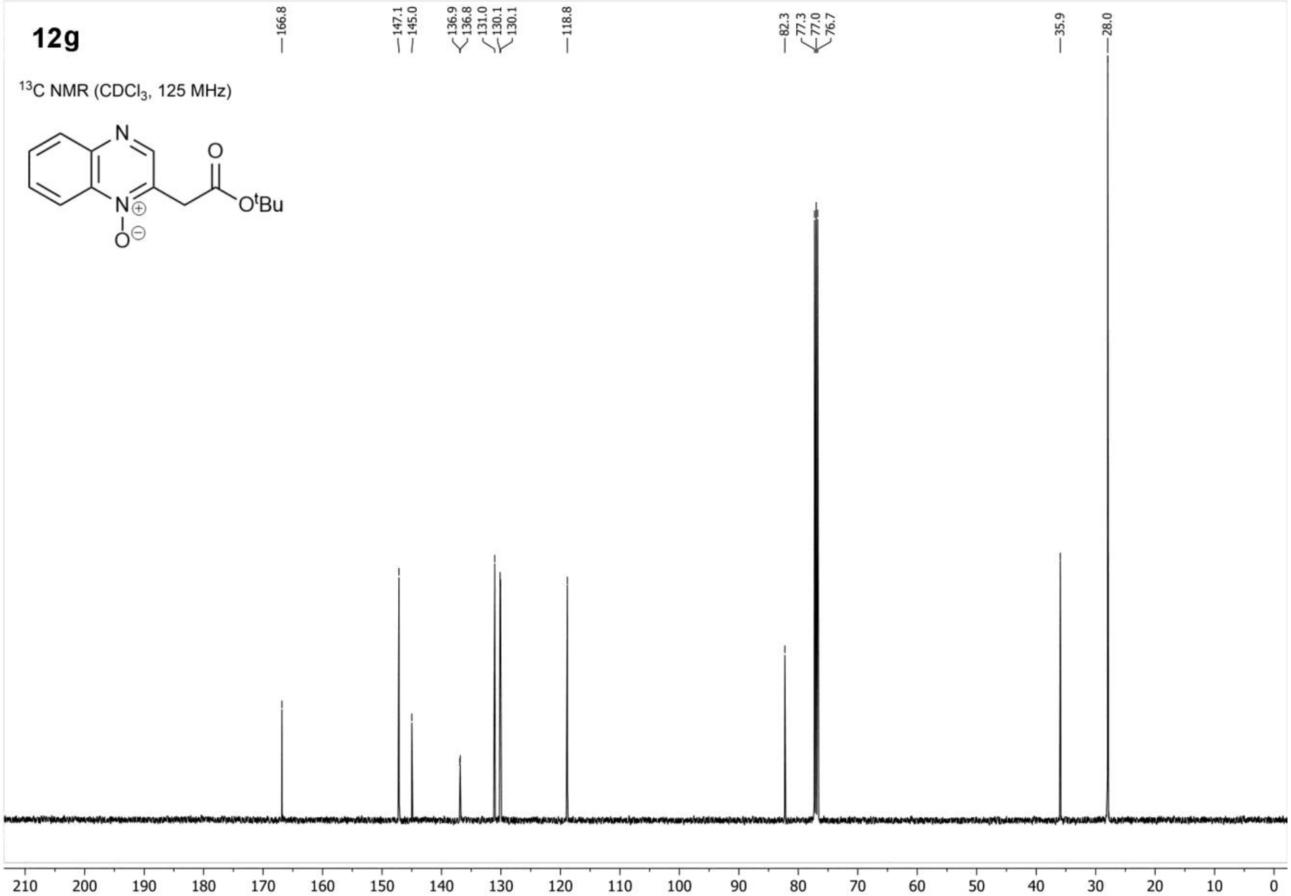

12e
SO2p-Tol
N
N⊕
O⊖
Me
1H NMR (CDCl3, 500 MHz)
8.9
8.4
8.3
8.1
8.1
7.8
7.8
7.8
7.7
7.7
7.7
7.7
7.7
7.6
7.6
7.3
7.2
7.2
5.7
5.7
5.7
5.7
2.6
2.5
2.5
2.3
2.3
2.3
2.3
2.3
2.3
1.0
0.9
0.9
1.00
1.00
1.01
1.08
1.10
2.05
1.99
1.22
1.18
4.38
3.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

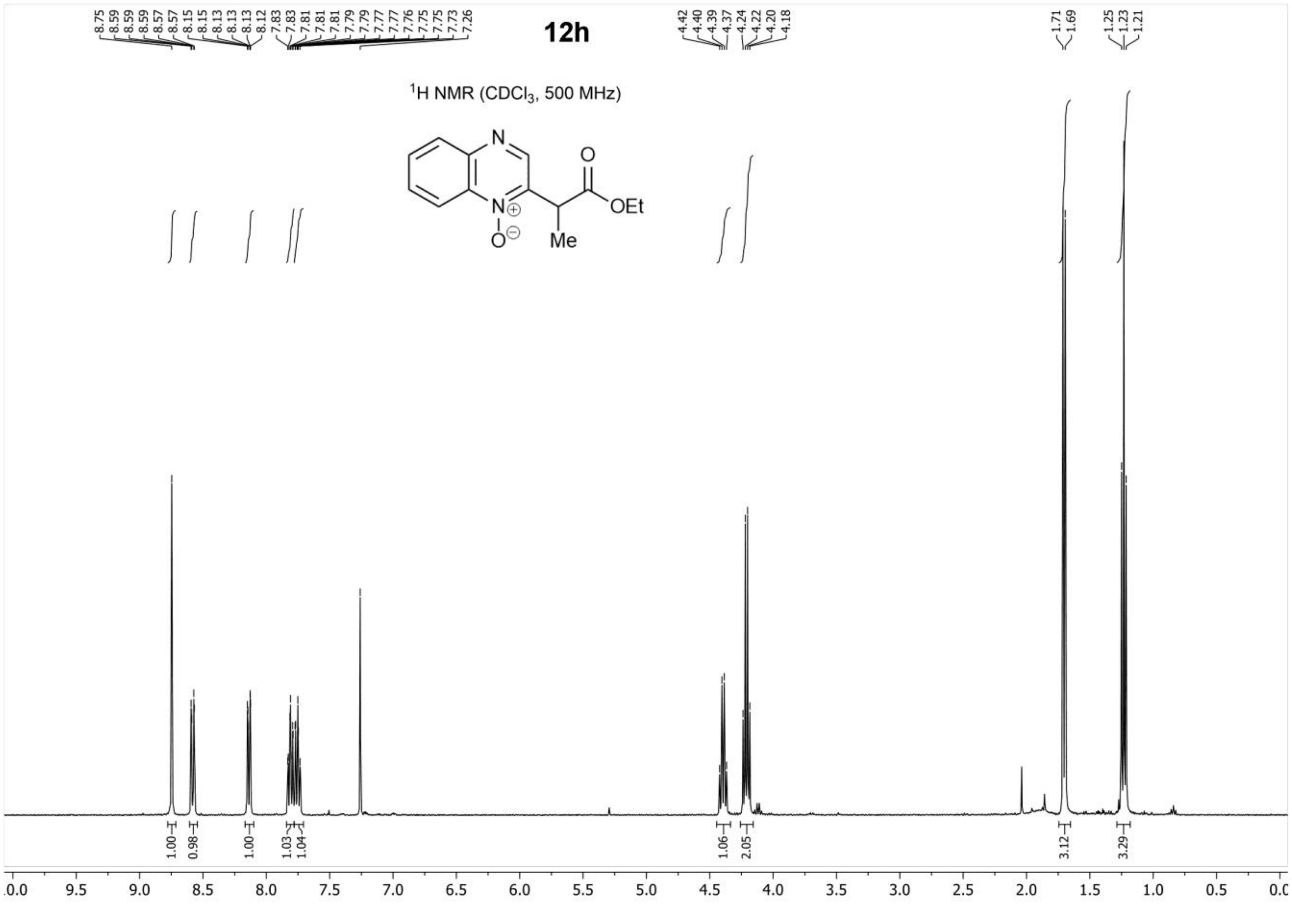

12e
13C NMR (CDCl3, 126 MHz)
SO2p-Tol
N
N⊕
O⊖
Me
145.7
145.2
144.8
136.5
135.0
134.8
131.8
130.4
130.2
129.7
128.5
119.2
77.3
77.0
76.8
62.2
21.6
21.0
11.2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.73 8.58 8.57 8.56 8.56 8.12 8.11 8.10 7.81 7.80 7.79 7.78 7.78 7.75 7.75 7.74 7.73 7.26
12f
^{1}H NMR (CDCl$_3$, 500 MHz)
N
N⊕
O⊖
O
OEt
4.25 4.23 4.22 4.20 4.03
1.80
1.28 1.28 1.27 1.26 1.25 1.25
1.00
1.09
1.14
1.13
1.24
2.33
2.15
3.75
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


167.7
147.1 145.1
136.9 136.4 131.2 130.3 130.1
118.8
77.3 77.0 76.8
61.7
34.9
14.1
12f
^{13}C NMR (CDCl$_3$, 126 MHz)
N
N⊕
O⊖
O
OEt
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

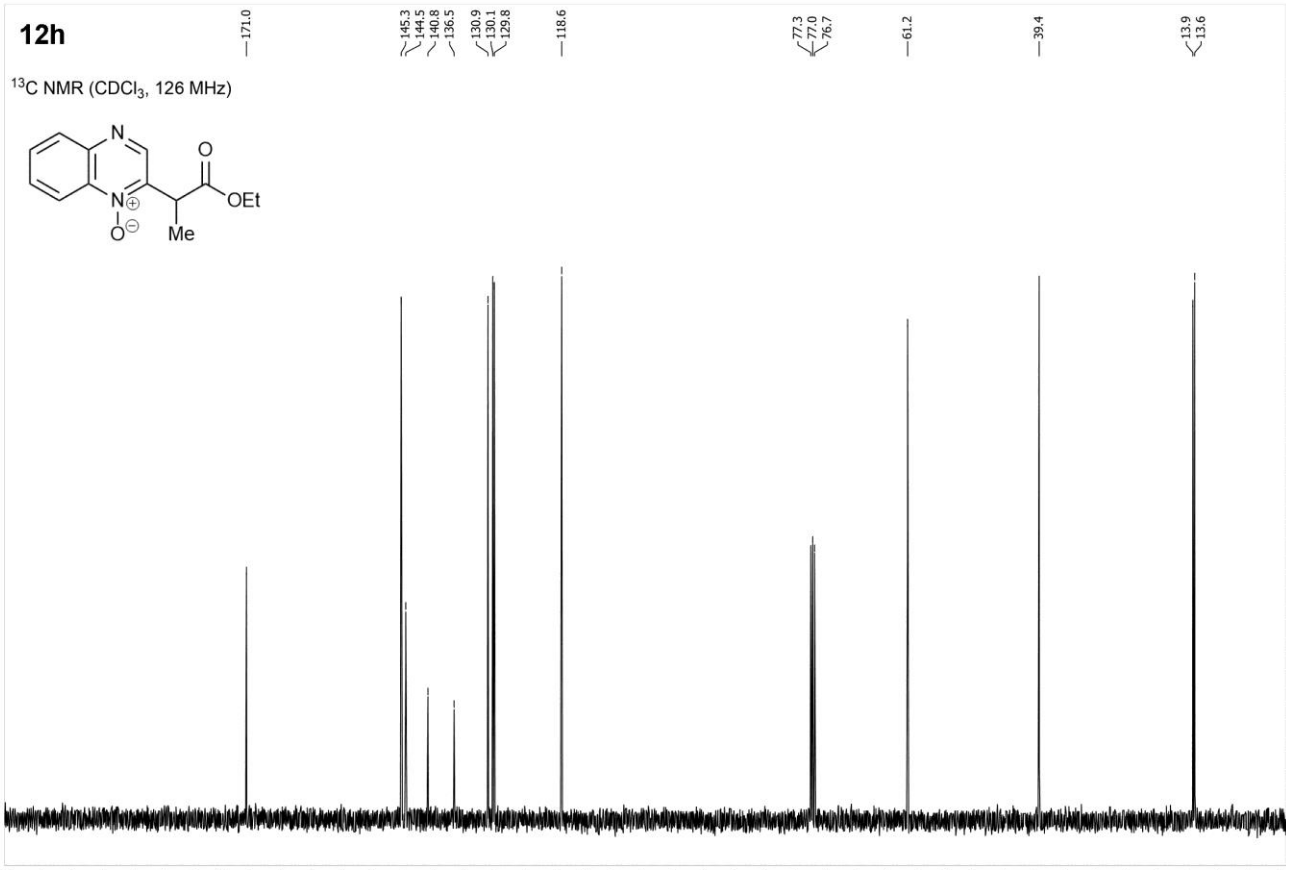

12g
^{1}H NMR (CDCl$_3$, 500 MHz)
8.72
8.59
8.59
8.57
8.57
8.11
8.11
8.10
8.10
8.10
7.80
7.79
7.79
7.78
7.77
7.77
7.75
7.74
7.73
7.73
7.73
7.72
7.71
7.26
3.96
1.47
N
N⊕
O⊖
O
O^{t}Bu
1.00
1.04
1.03
1.05
1.08
2.15
9.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


12g
^{13}C NMR (CDCl$_3$, 125 MHz)
166.8
147.1
145.0
136.9
136.8
131.0
130.1
130.1
118.8
82.3
77.3
77.0
76.7
35.9
28.0
N
N⊕
O⊖
O
O^{t}Bu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



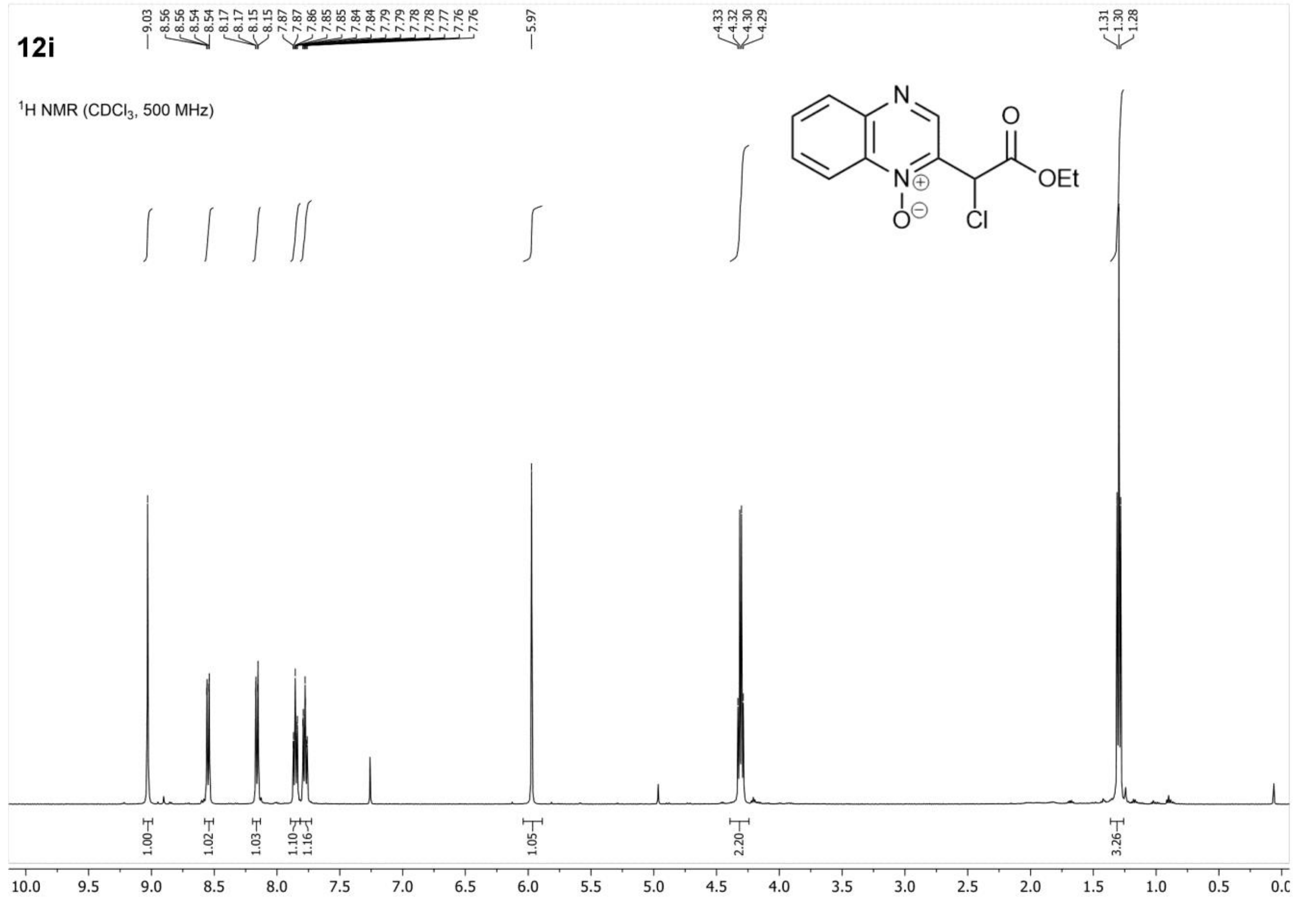
12h

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

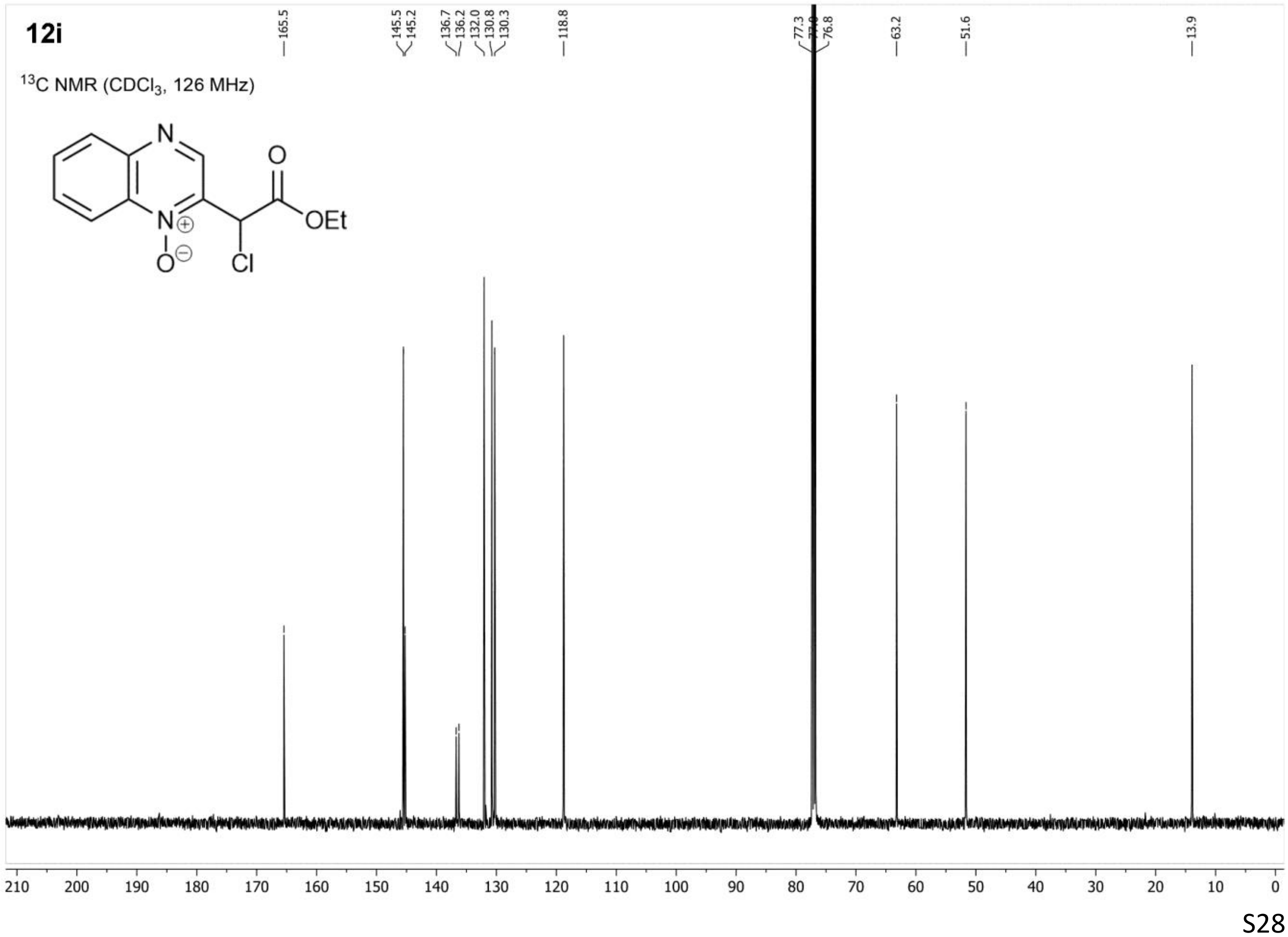


12h

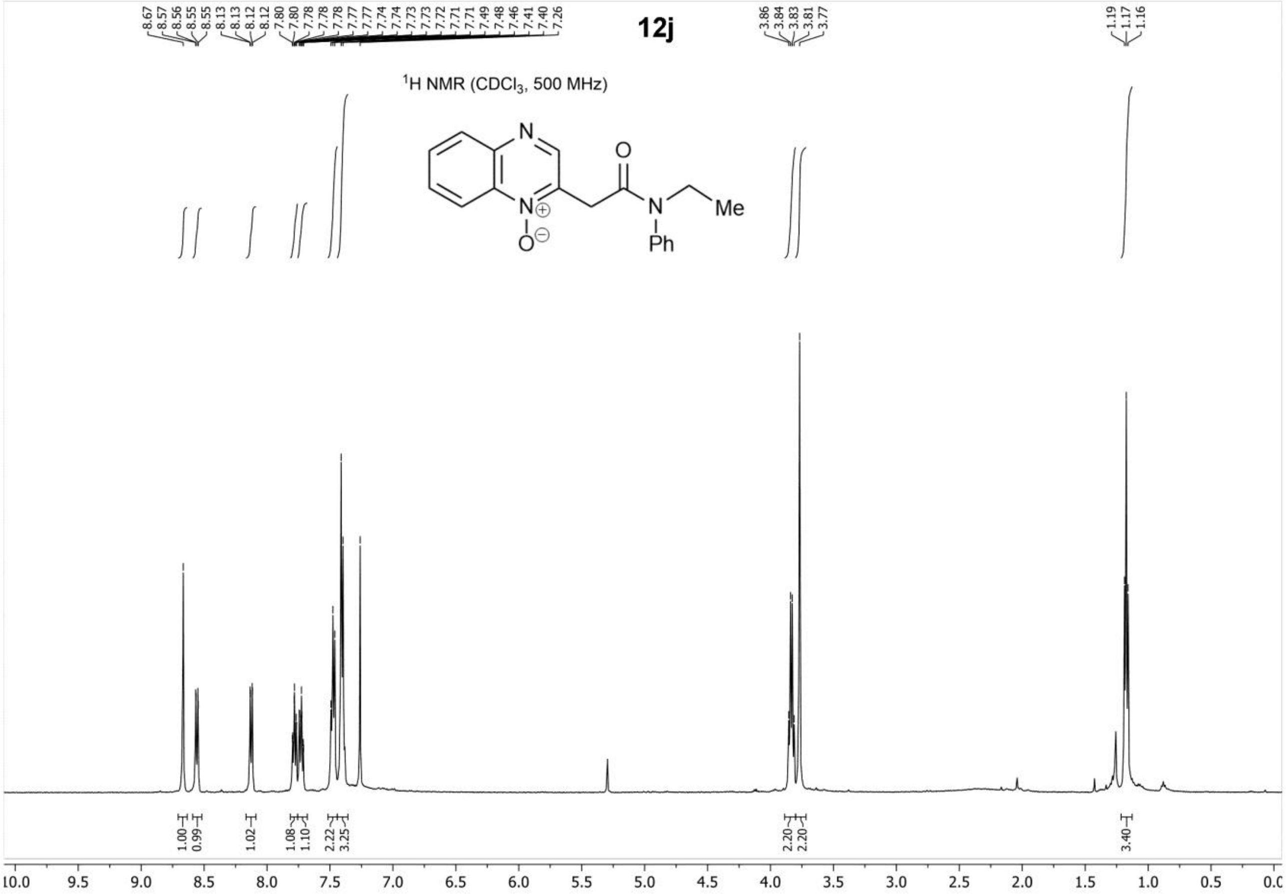
^{13}C NMR ($CDCl_3$, 126 MHz)

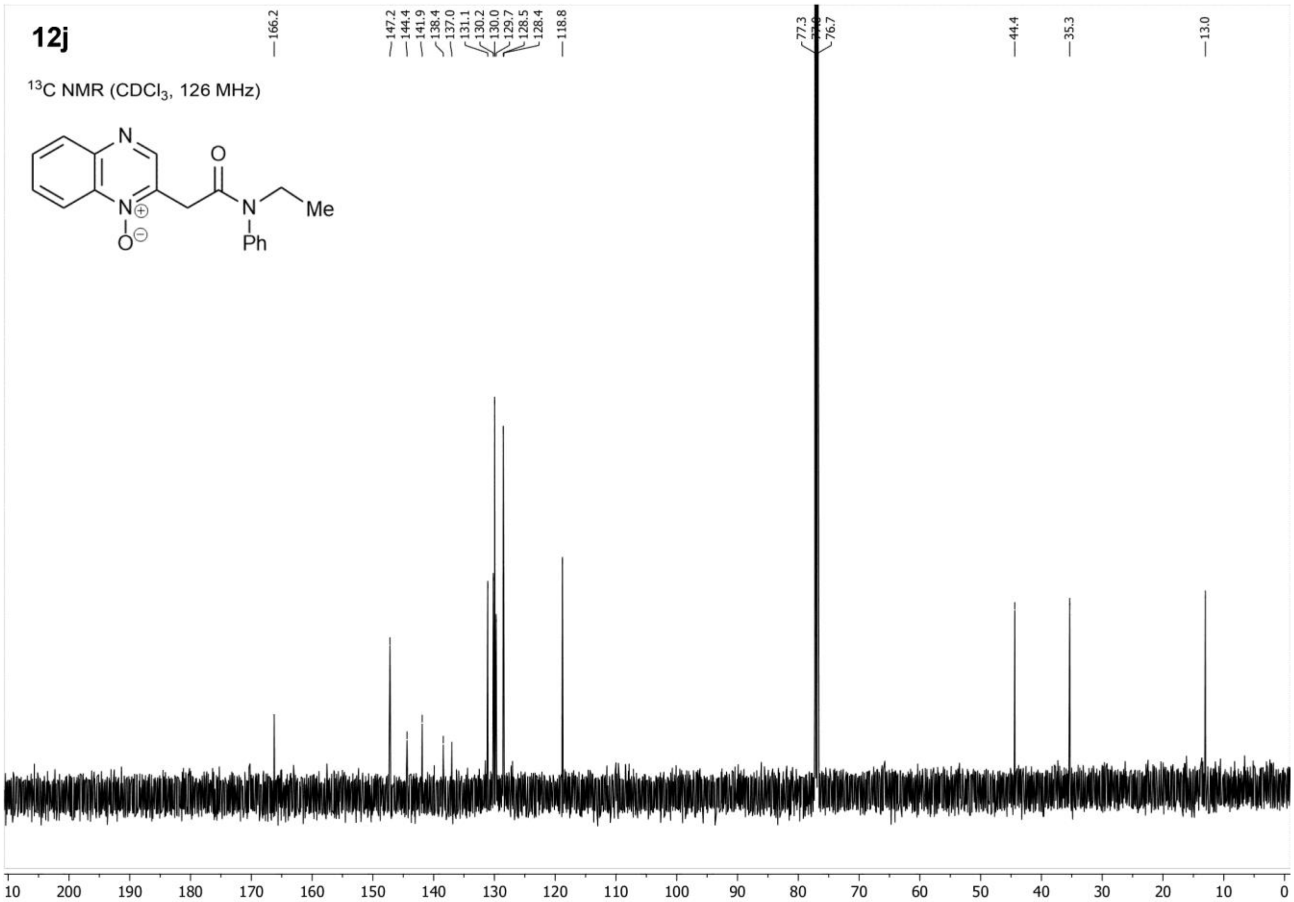

12i

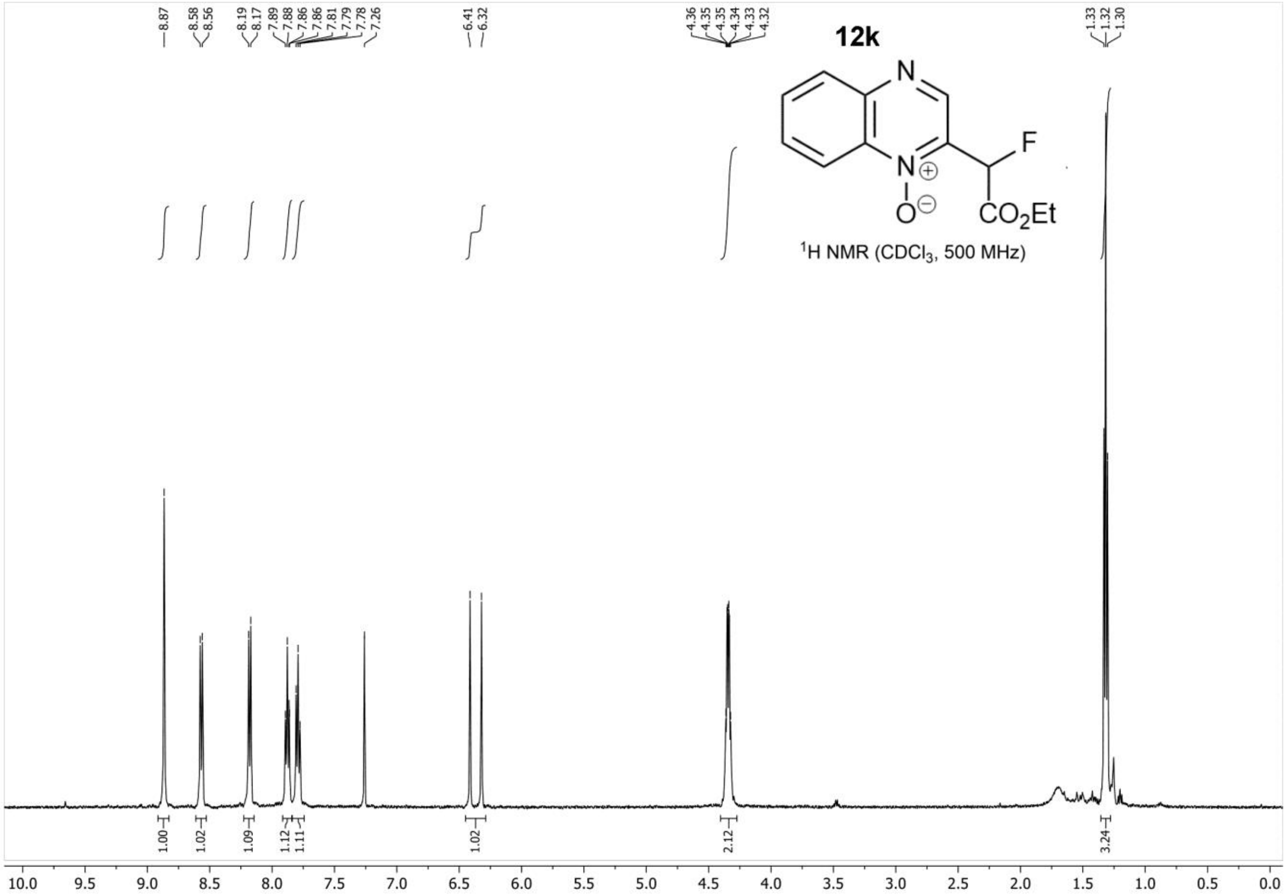
^{1}H NMR ($CDCl_3$, 500 MHz)


12i

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

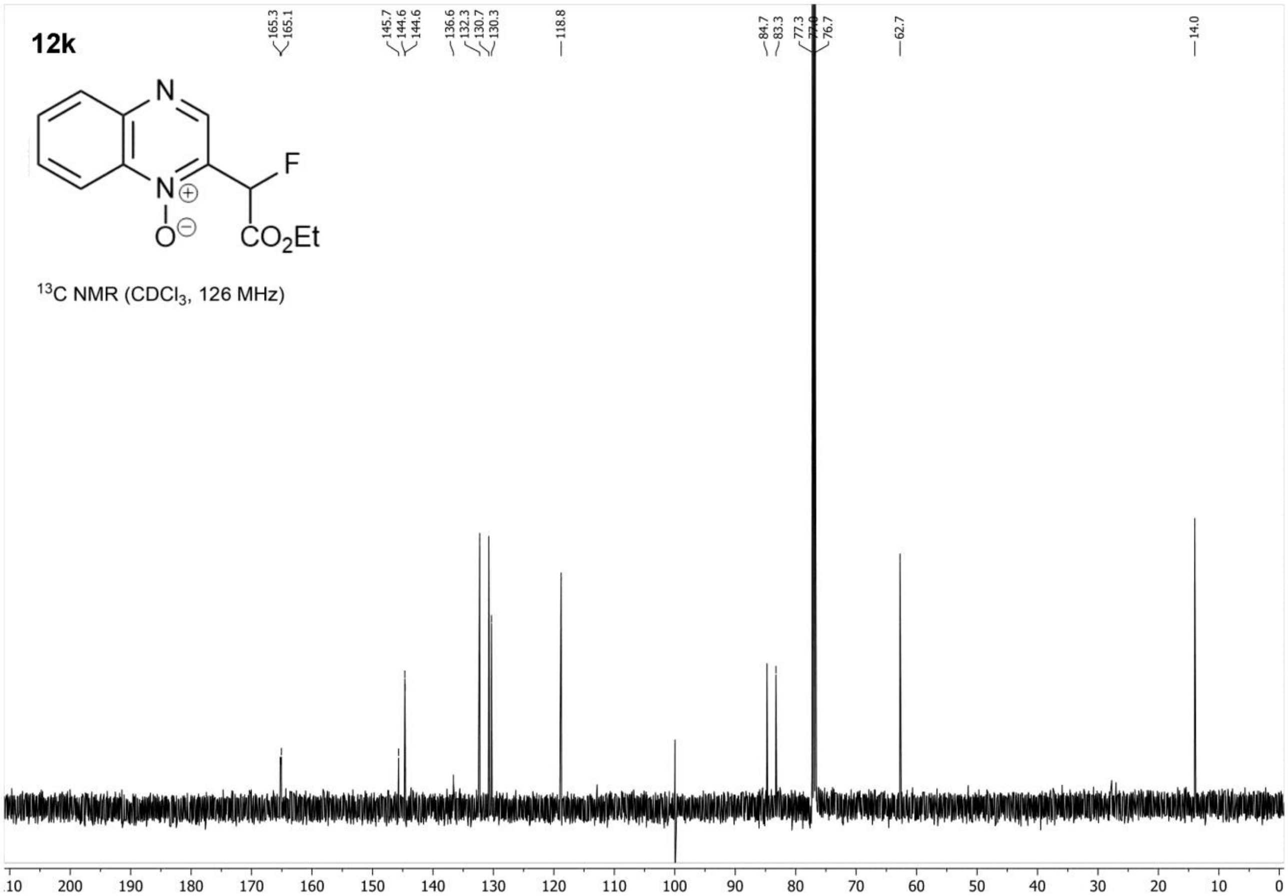

12j
^{1}H NMR (CDCl$_3$, 500 MHz)
N
O
N
Me
N
Ph
O
8.67
8.57
8.56
8.55
8.55
8.13
8.13
8.12
8.12
7.80
7.78
7.78
7.78
7.77
7.77
7.74
7.74
7.73
7.73
7.72
7.71
7.71
7.49
7.48
7.46
7.41
7.40
7.26
3.86
3.84
3.83
3.81
3.77
1.19
1.17
1.16
1.00
0.99
1.02
1.08
1.10
2.22
3.25
2.20
2.20
3.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


12j
^{13}C NMR (CDCl$_3$, 126 MHz)
N
O
N
Me
N
Ph
O
166.2
147.2
144.4
141.9
138.4
137.0
131.1
130.2
130.0
129.7
128.5
128.4
118.8
77.3
77.0
76.7
44.4
35.3
13.0
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



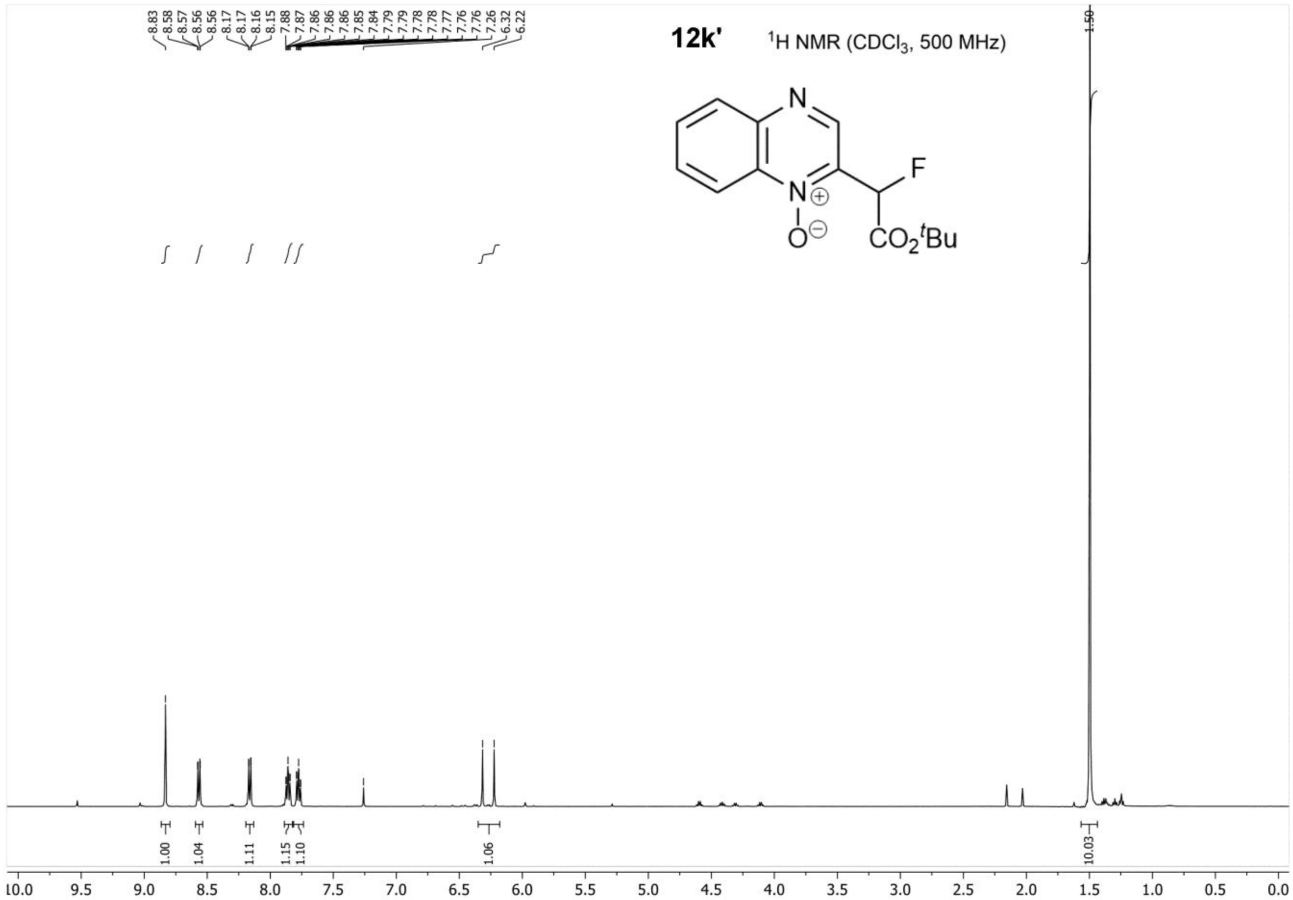
12k

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

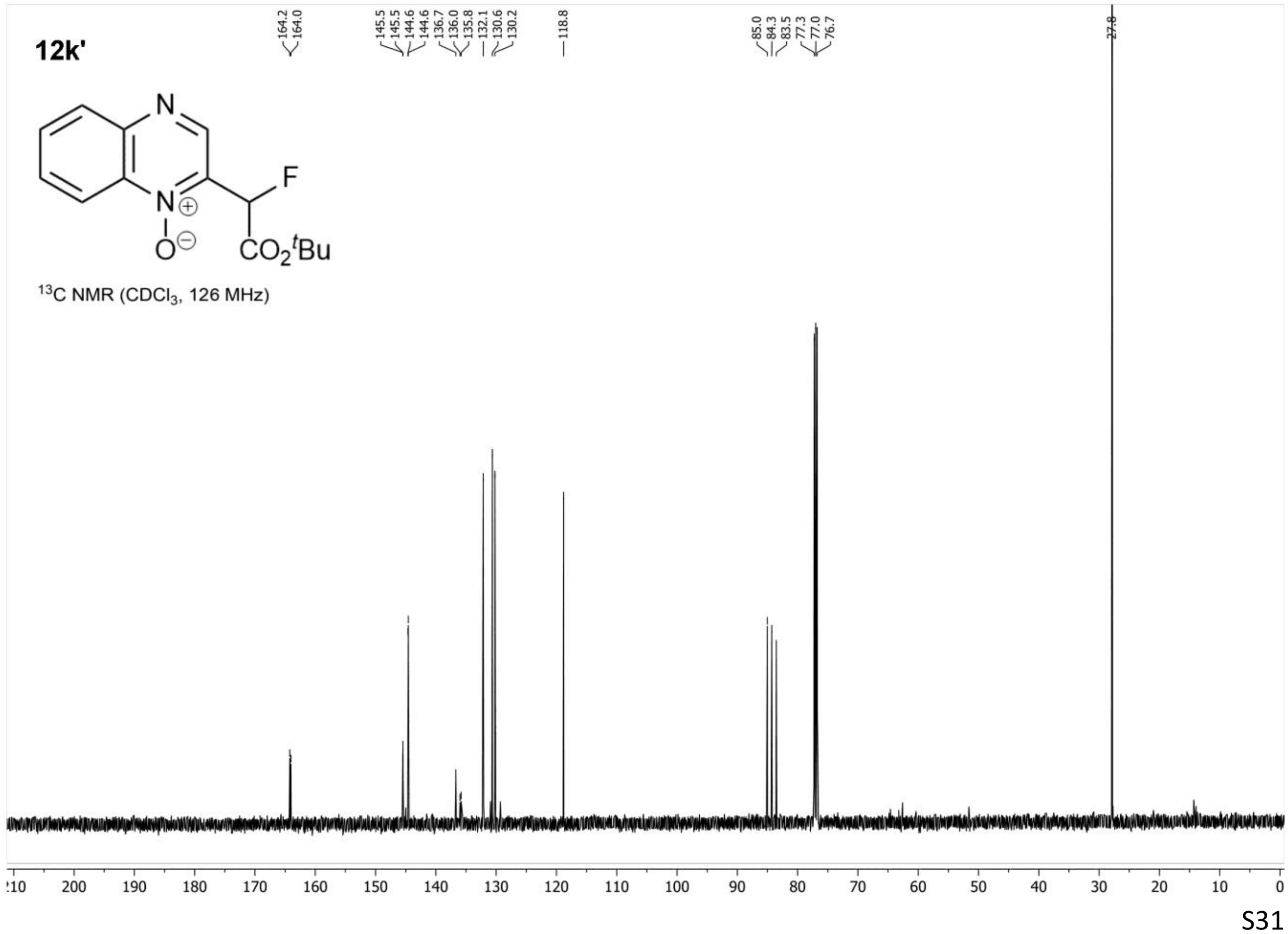


12k

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

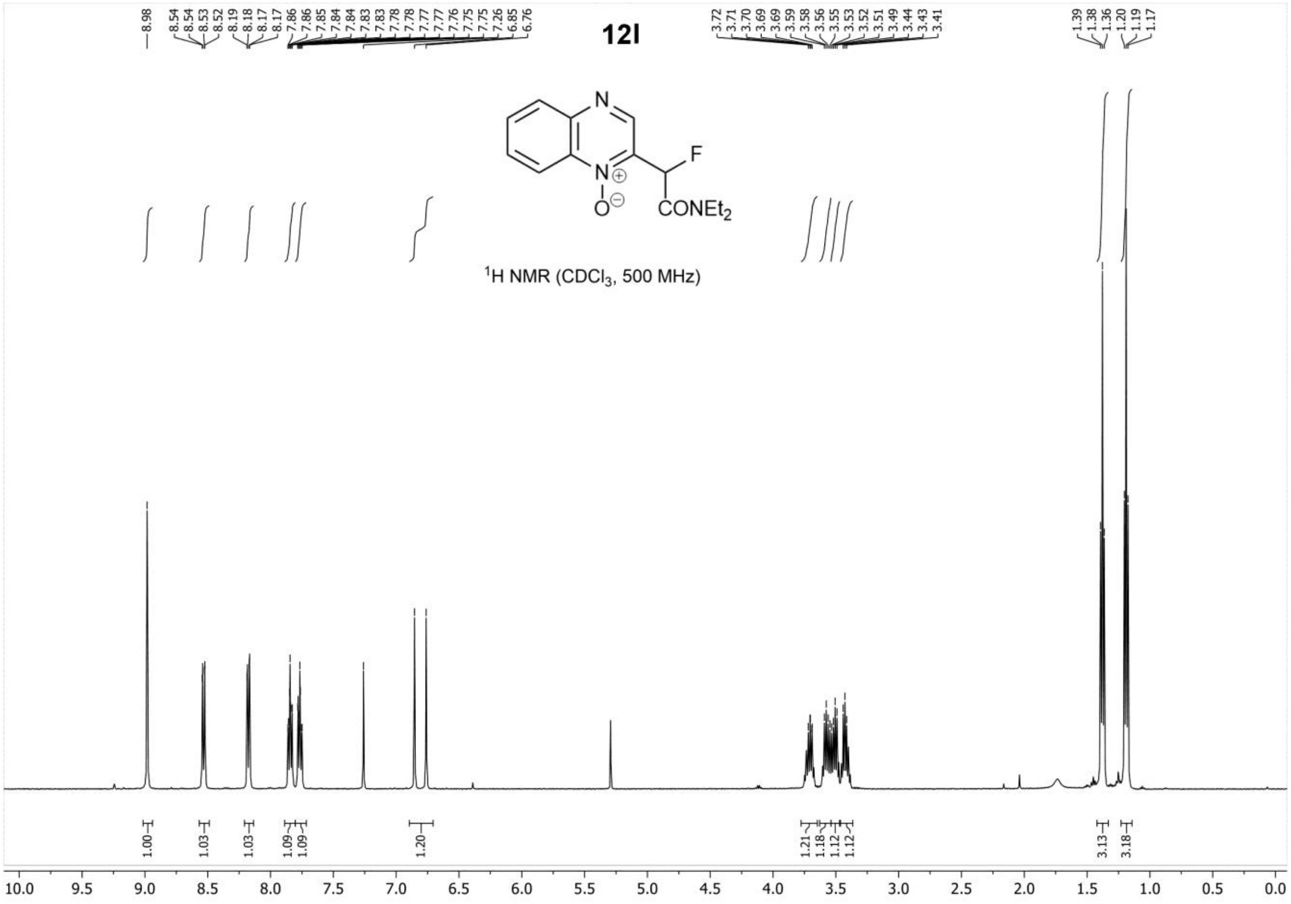


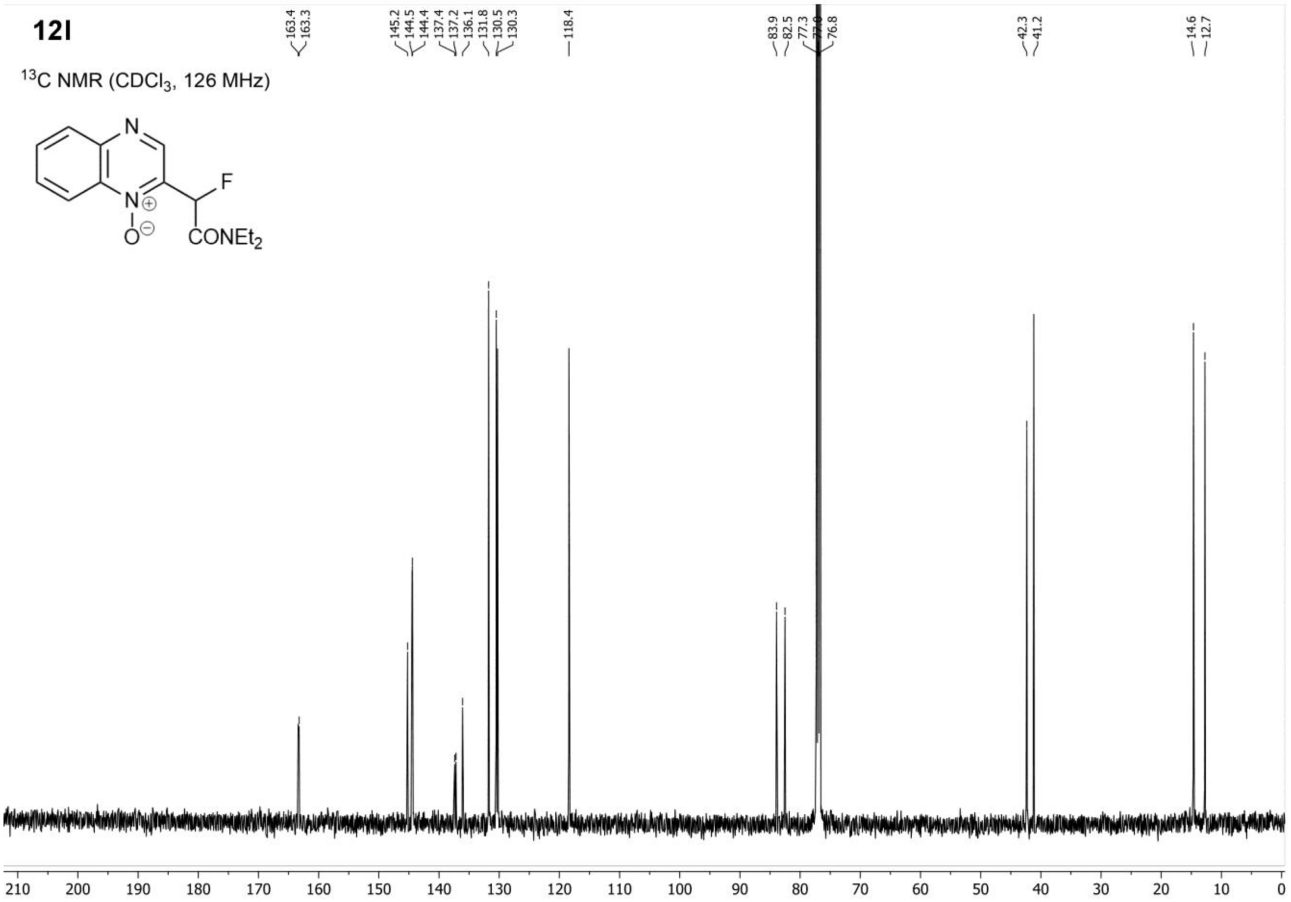
12k' ^{1}H NMR ($CDCl_3$, 500 MHz)

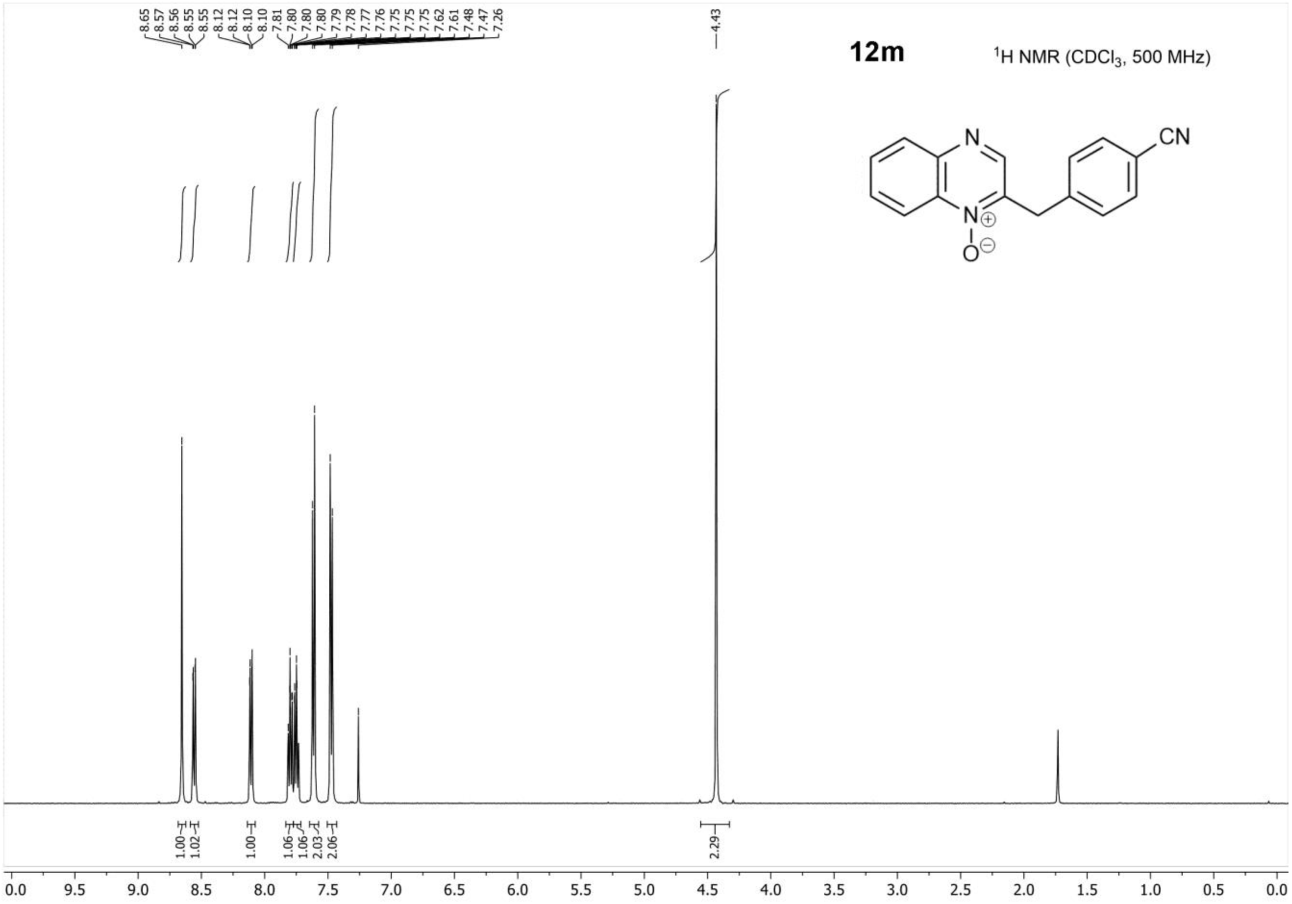


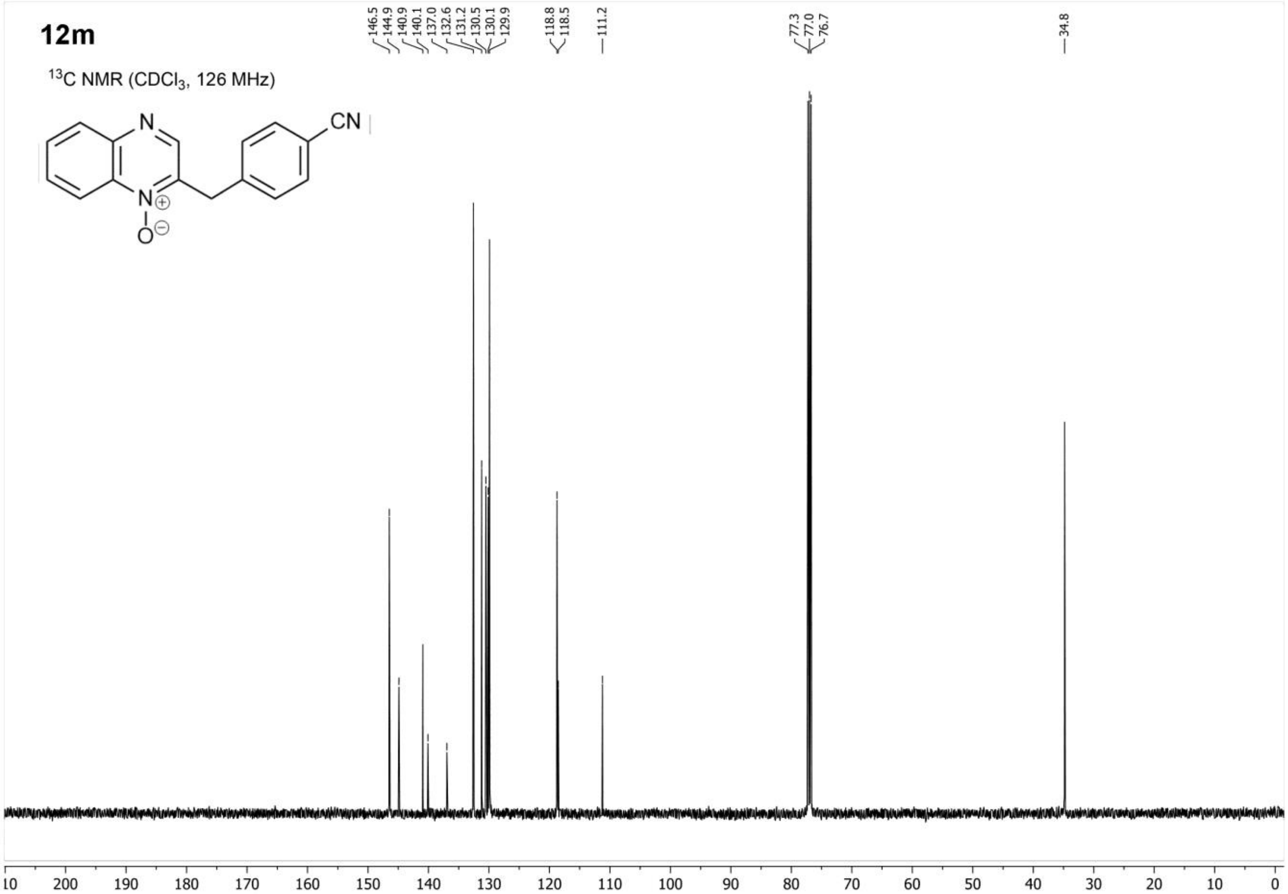
12k'

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

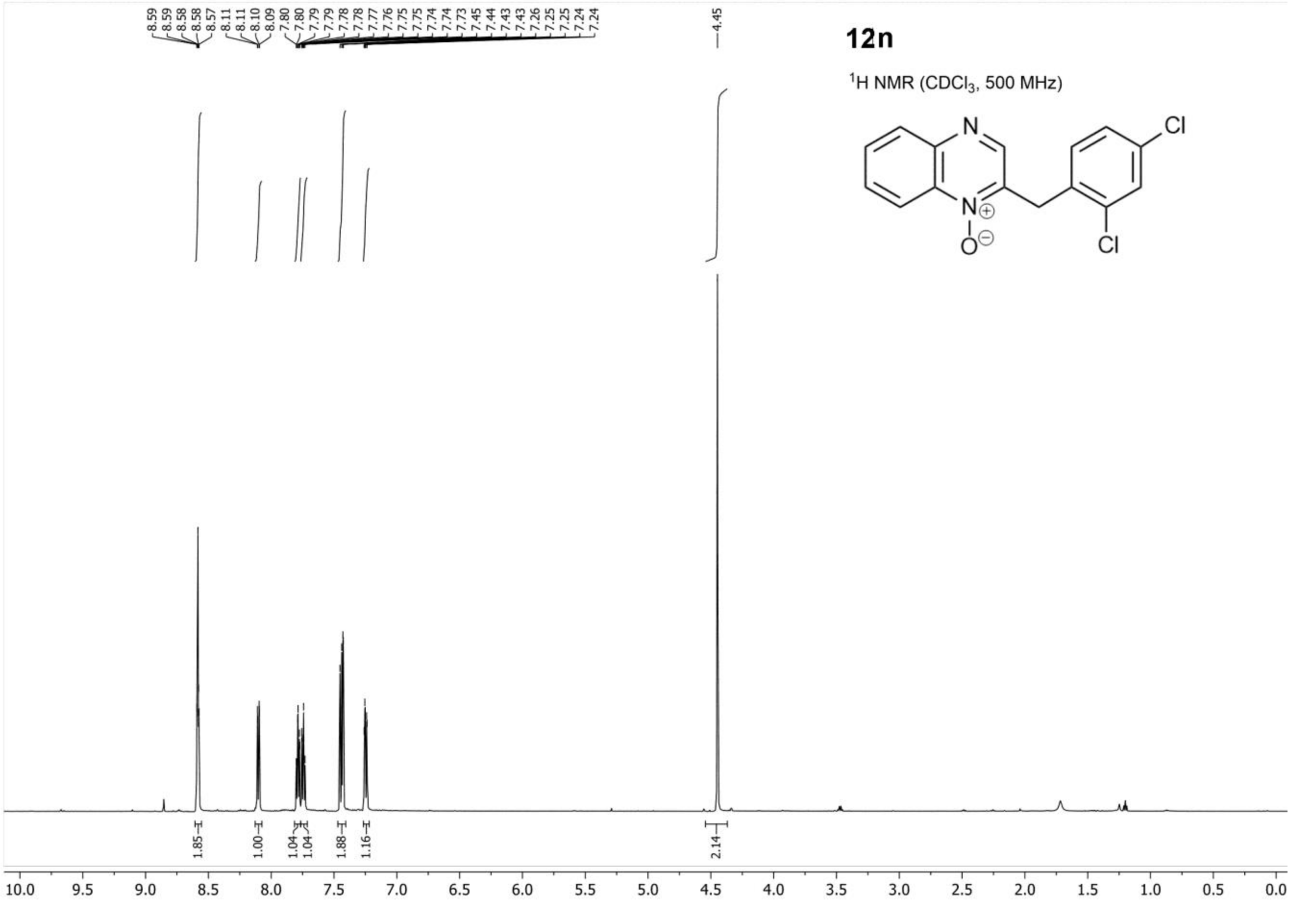

12l
1H NMR (CDCl3, 500 MHz)
N
N⊕
O⊖
F
CONEt2
8.98
8.54
8.54
8.53
8.52
8.19
8.18
8.17
8.17
7.86
7.86
7.85
7.84
7.84
7.83
7.83
7.78
7.78
7.77
7.77
7.76
7.75
7.75
7.26
6.85
6.76
3.72
3.71
3.70
3.69
3.69
3.59
3.58
3.56
3.55
3.53
3.52
3.51
3.49
3.44
3.43
3.41
1.39
1.38
1.36
1.20
1.19
1.17
1.00
1.03
1.03
1.09
1.09
1.20
1.21
1.18
1.12
1.12
3.13
3.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


12l
13C NMR (CDCl3, 126 MHz)
N
N⊕
O⊖
F
CONEt2
163.4
163.3
145.2
144.5
144.4
137.4
137.2
136.1
131.8
130.5
130.3
118.4
83.9
82.5
77.3
77.0
76.8
42.3
41.2
14.6
12.7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


12m ^{1}H NMR (CDCl$_3$, 500 MHz)

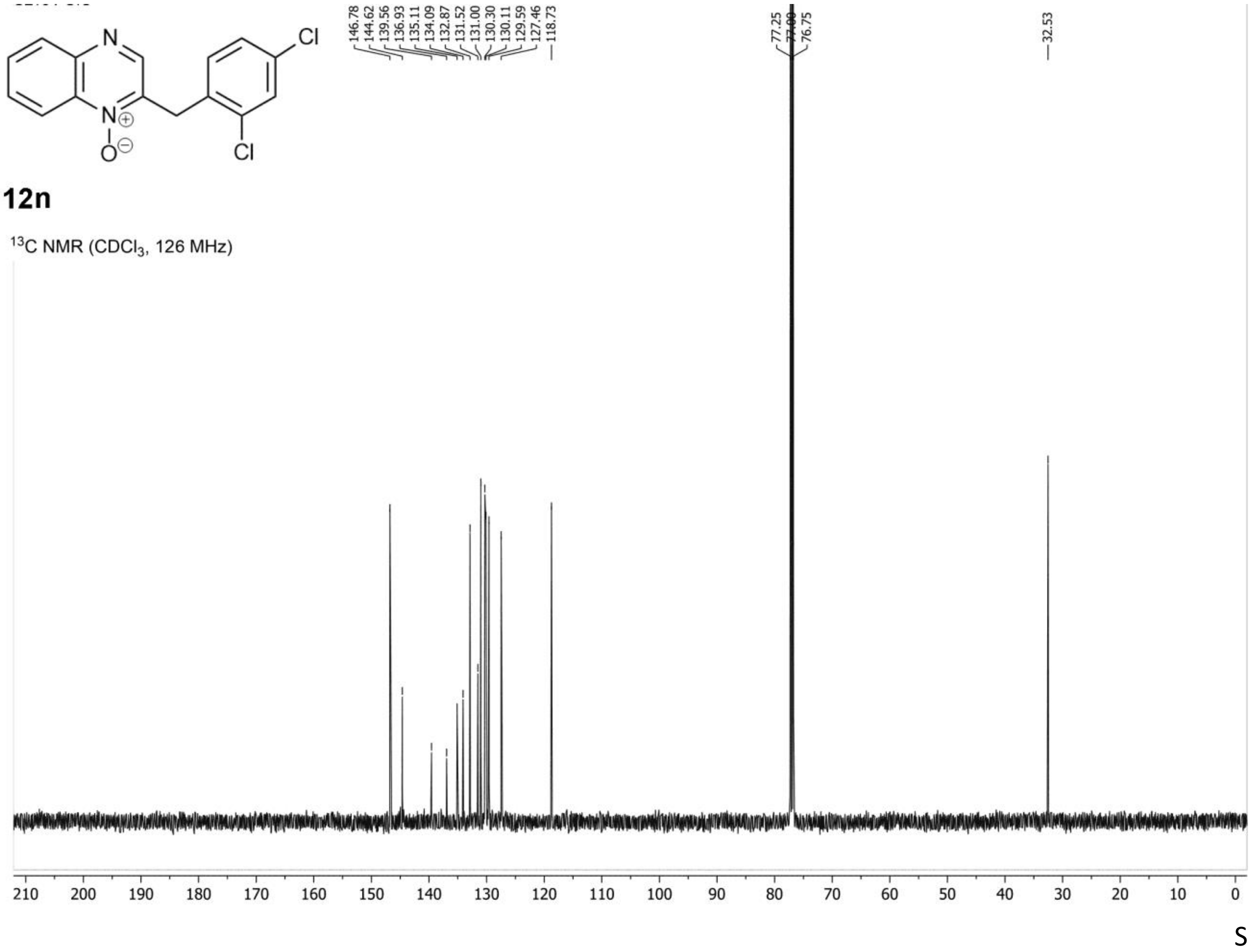

12m

^{13}C NMR (CDCl$_3$, 126 MHz)



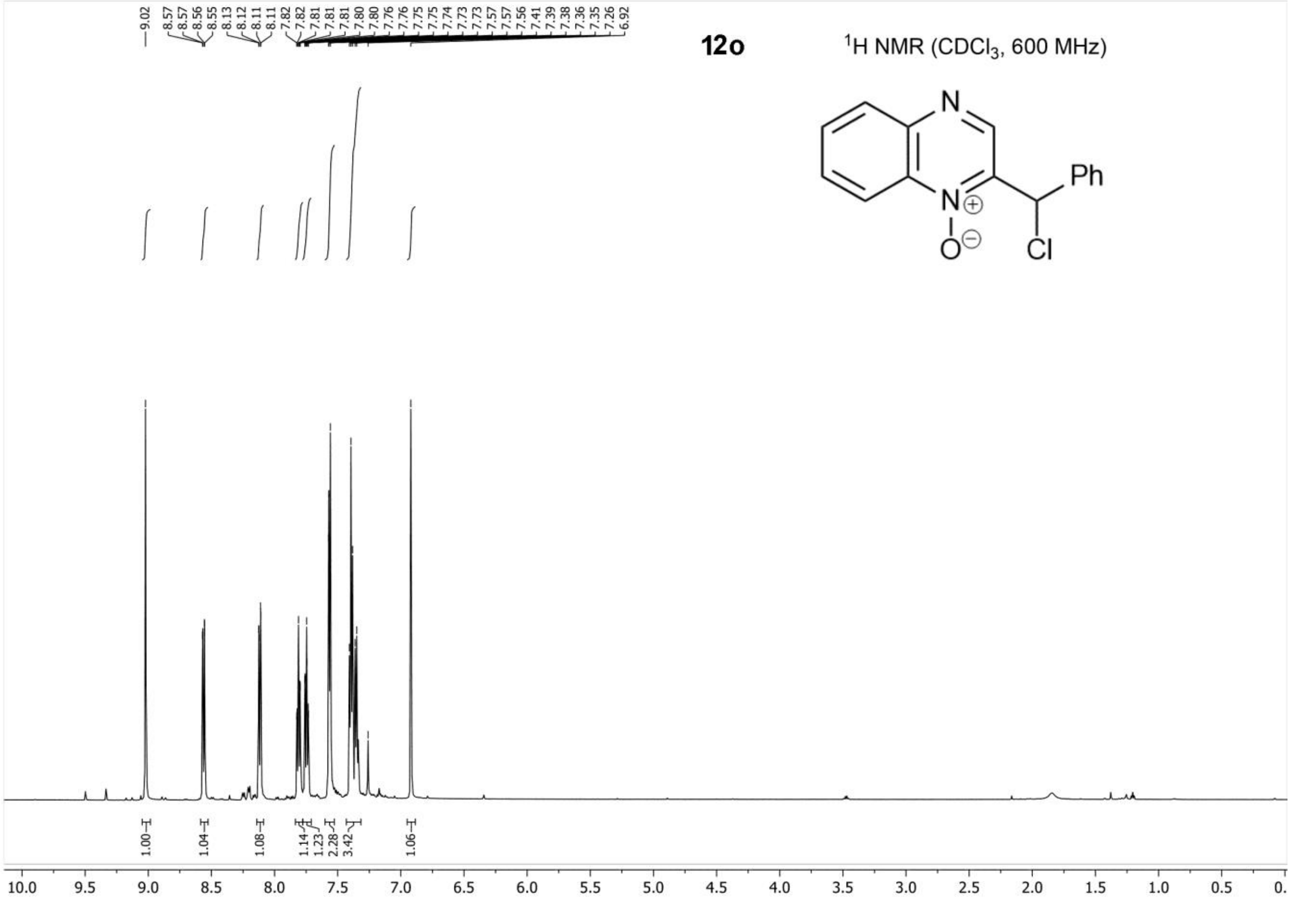
12n

^{1}H NMR (CDCl$_3$, 500 MHz)

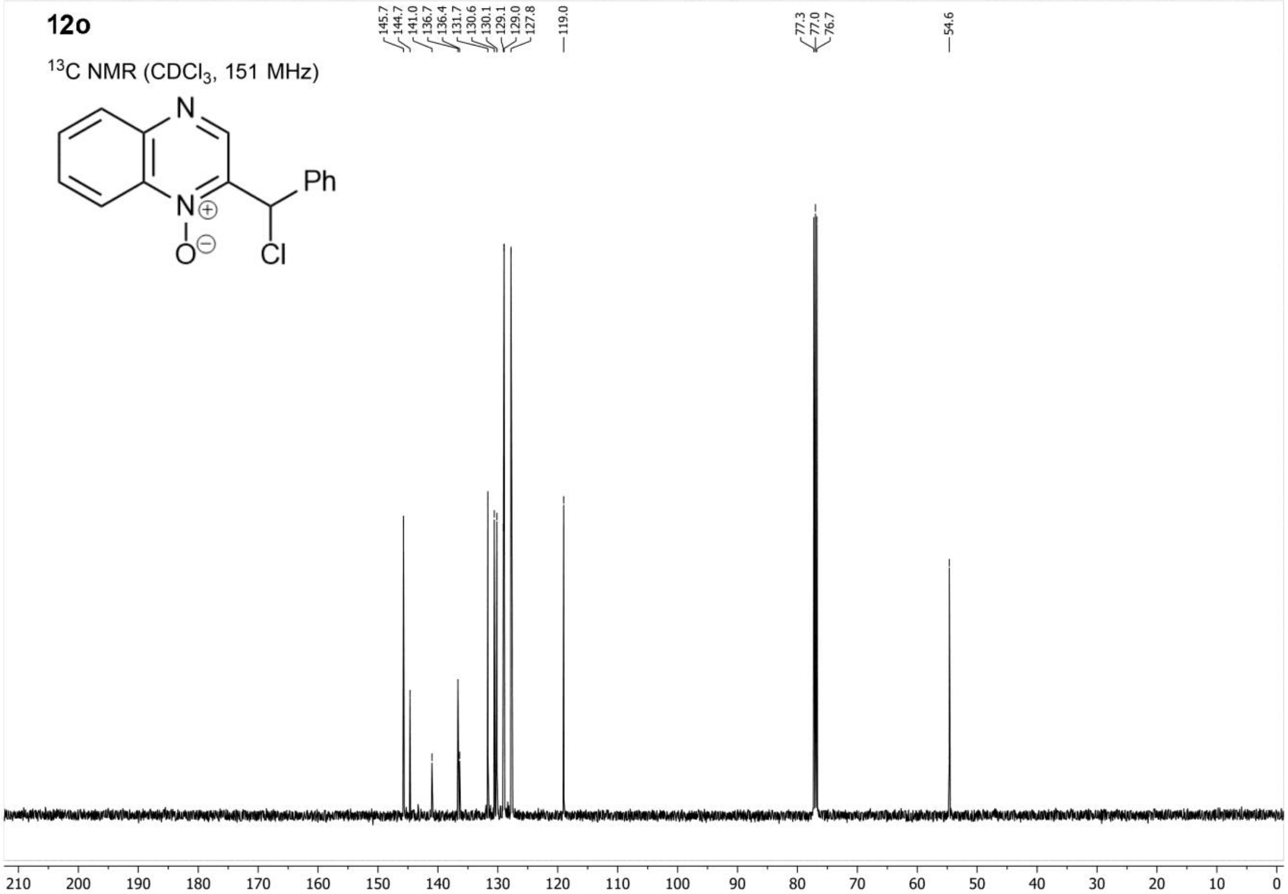


12n

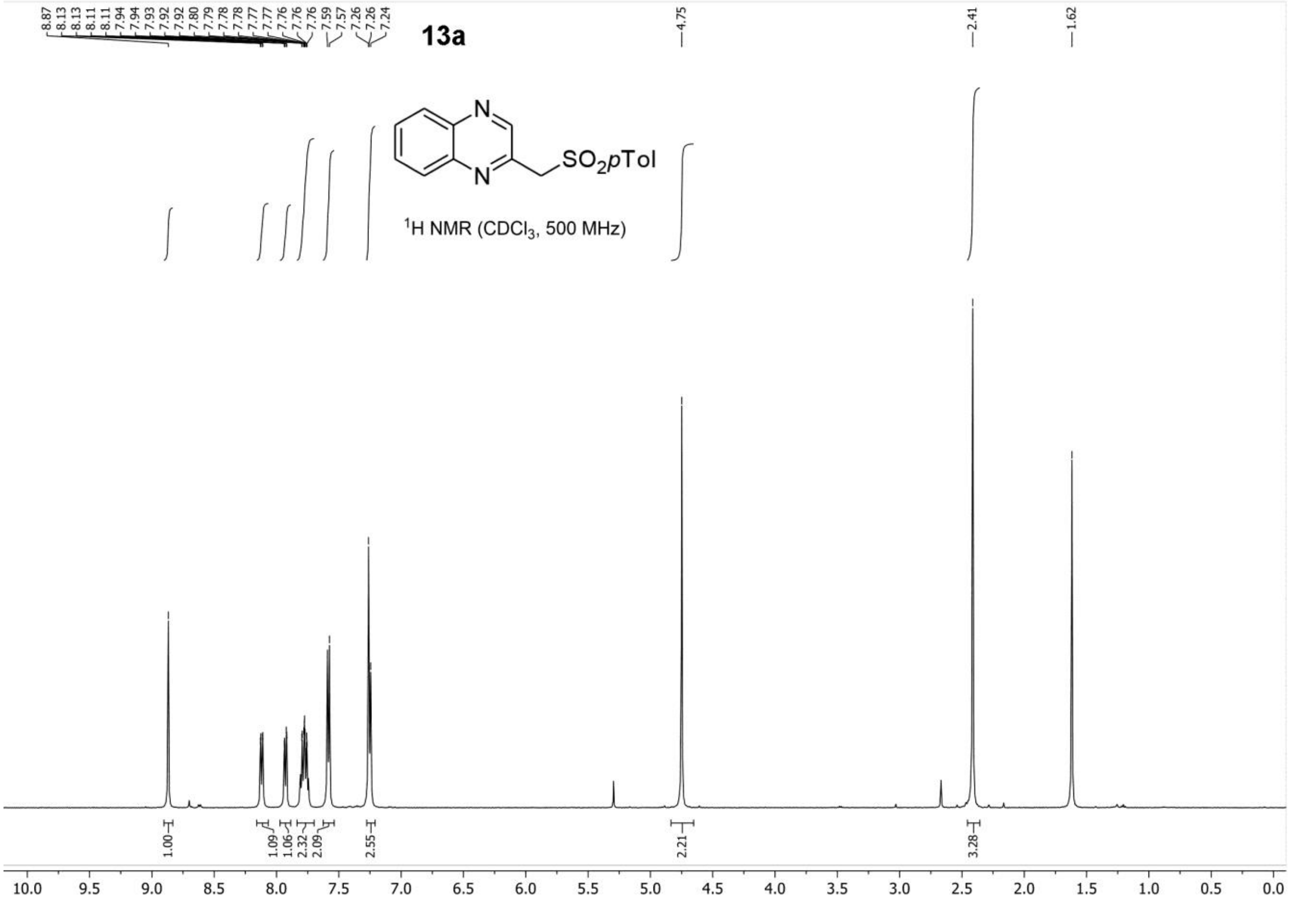
^{13}C NMR (CDCl$_3$, 126 MHz)

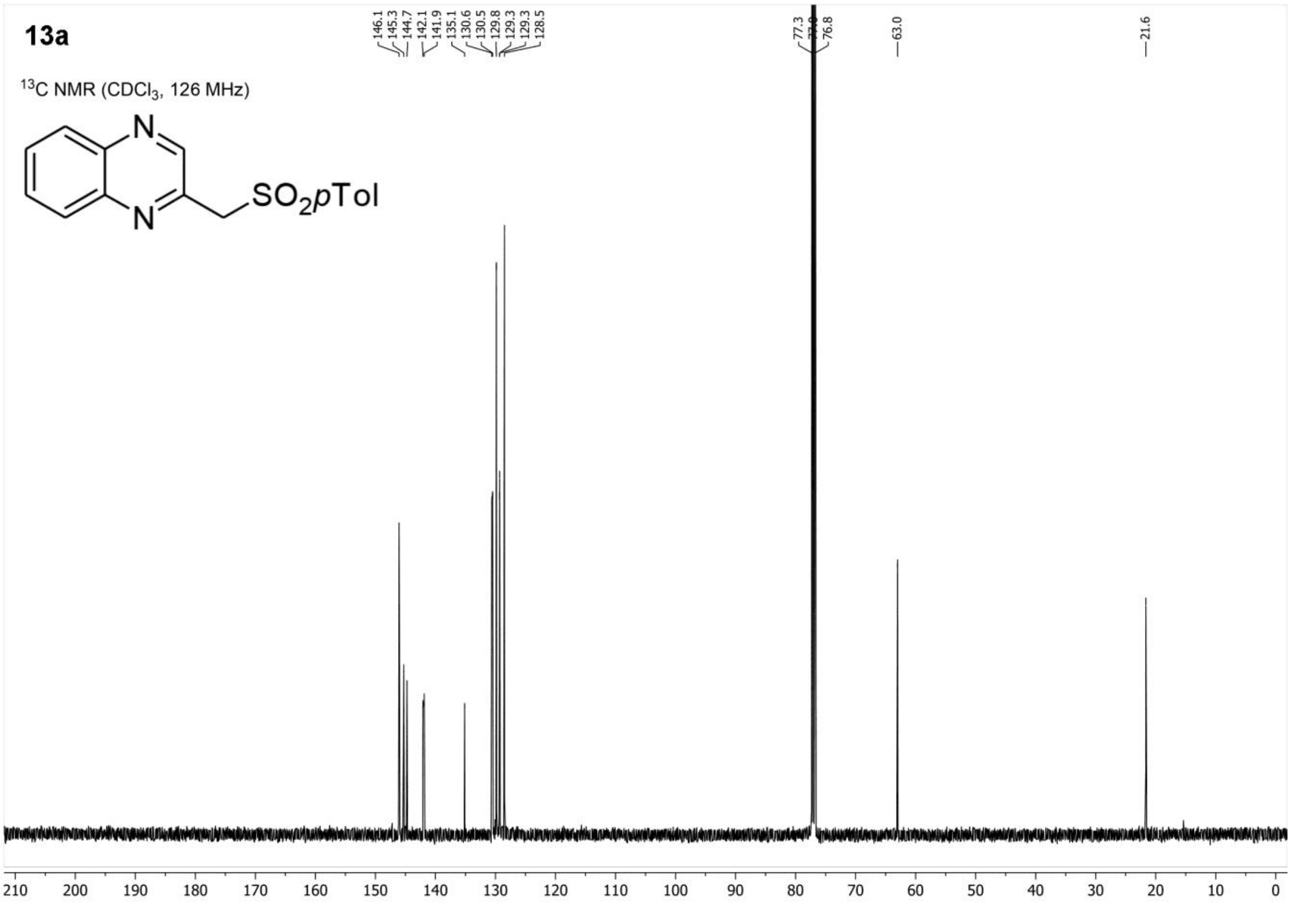

12o

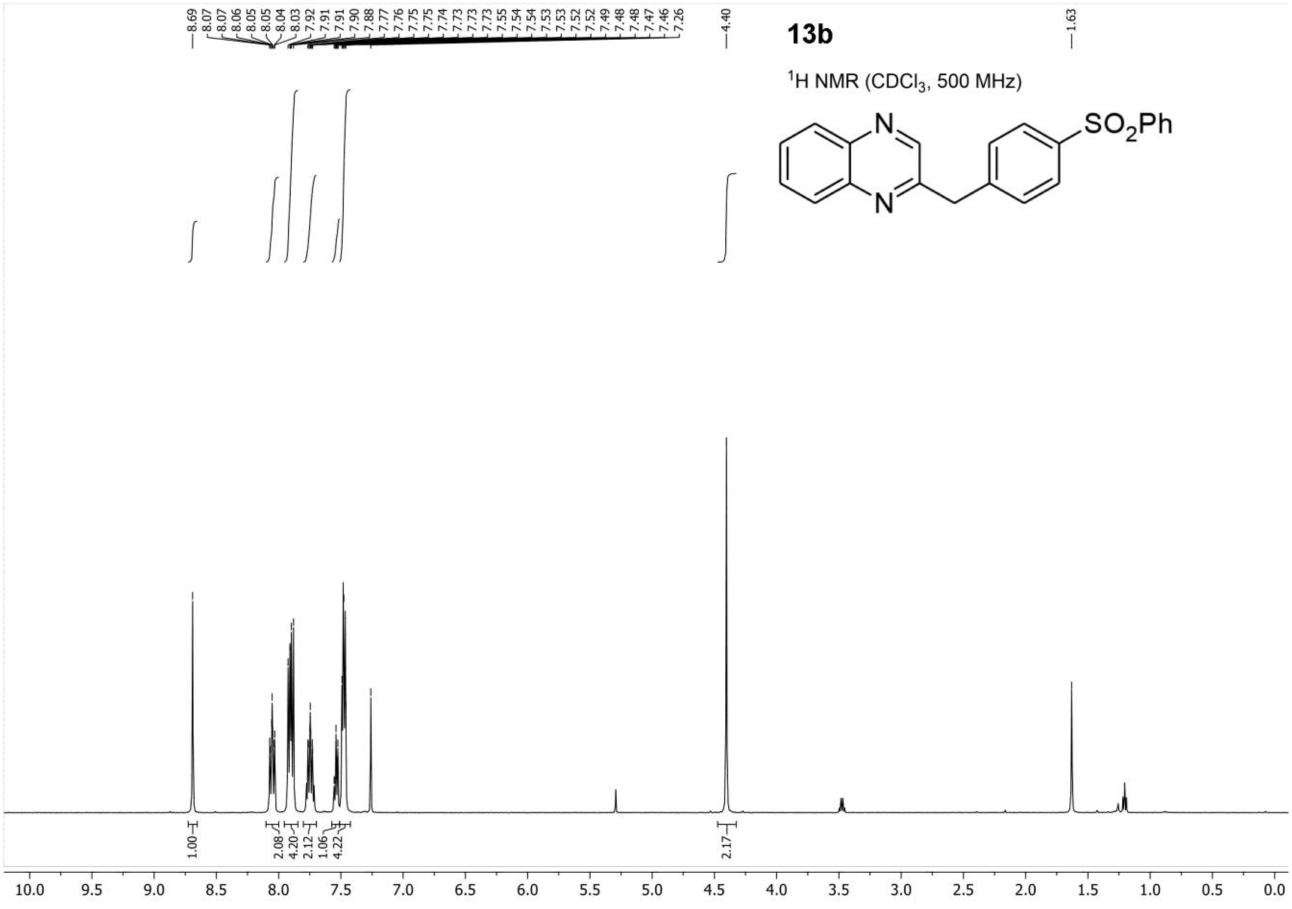
^{1}H NMR (CDCl$_3$, 600 MHz)


12o

^{13}C NMR (CDCl$_3$, 151 MHz)

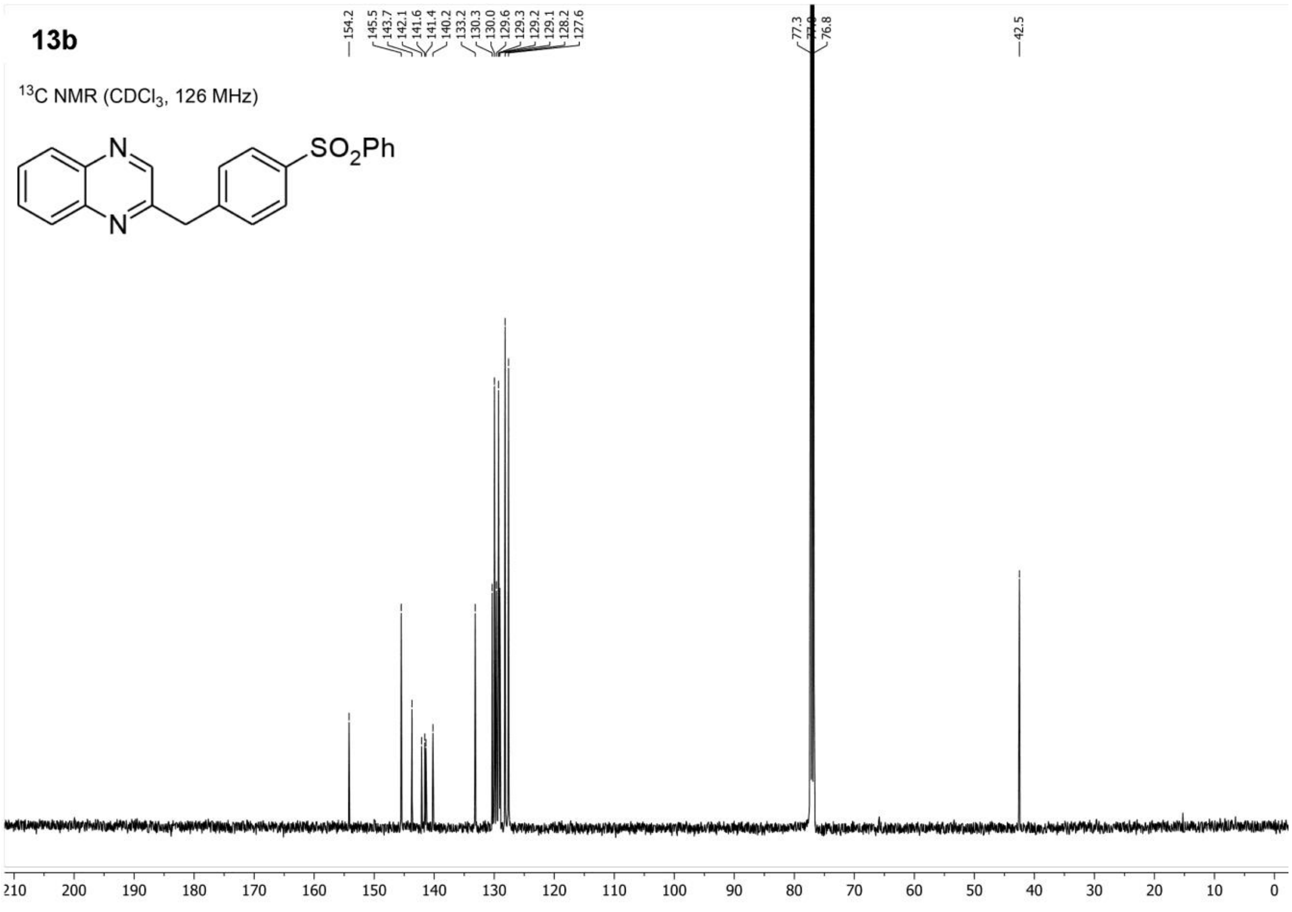

13a
SO2pTol
N
N
1H NMR (CDCl3, 500 MHz)
8.87
8.13
8.13
8.11
8.11
7.94
7.93
7.92
7.92
7.80
7.79
7.78
7.78
7.77
7.77
7.76
7.76
7.76
7.59
7.57
7.26
7.26
7.24
4.75
2.41
1.62
1.00
1.09
1.06
2.32
2.09
2.55
2.21
3.28
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


13a
13C NMR (CDCl3, 126 MHz)
SO2pTol
N
N
146.1
145.3
144.7
142.1
141.9
135.1
130.6
130.5
129.8
129.3
129.3
128.5
77.3
77.0
76.8
63.0
21.6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



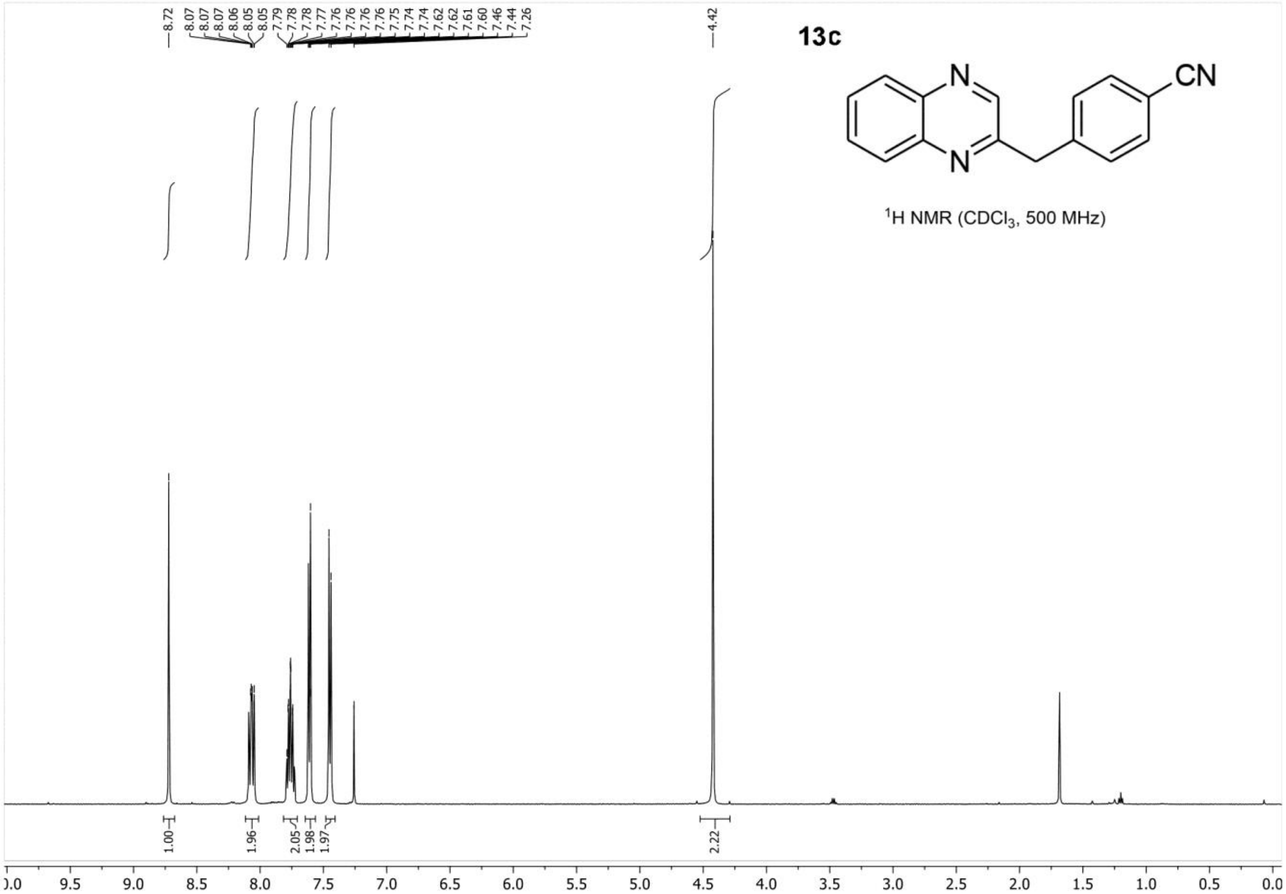
13b

^{1}H NMR (CDCl$_3$, 500 MHz)



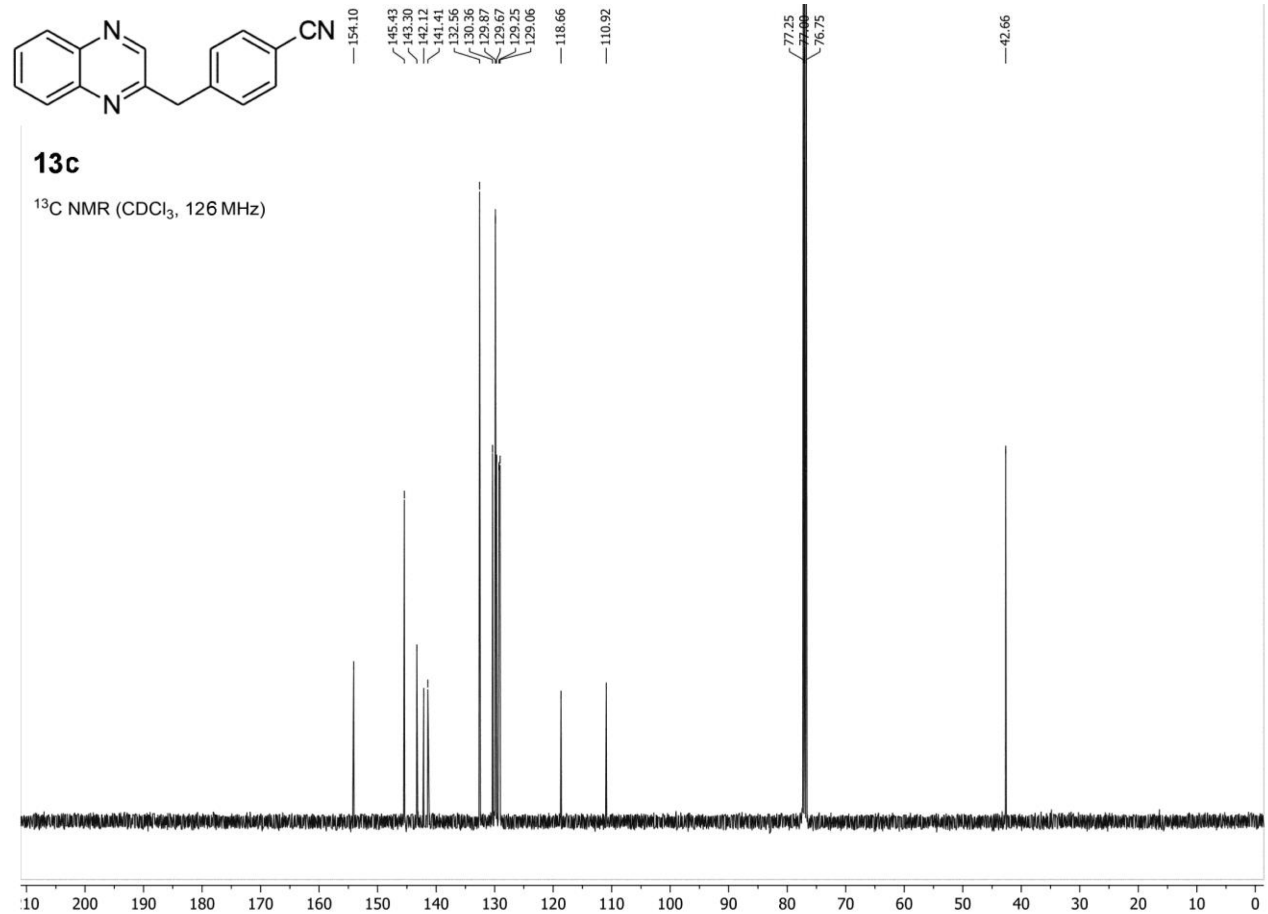
13b

^{13}C NMR (CDCl$_3$, 126 MHz)



13c

^{1}H NMR (CDCl$_3$, 500 MHz)



13c

^{13}C NMR (CDCl$_3$, 126 MHz)