# Electronic Supporting Information

# Carbon Nitride as a Heterogeneous Visible-Light Photocatalyst for the Minisci Reaction and Coupling to $H_2$ Production

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## Table of Contents

## General information

Reagents used throughout this study were of the highest available purity purchased from commercial suppliers and used directly without any further purification, unless mentioned otherwise. Pristine and cyanamide functionalised carbon nitride were synthesised according to a previously reported procedure.[1,2] Amorphous carbon dots and graphitic nitrogen doped carbon dots were prepared as previously described.[3] All photocatalytic experiments were performed with LEDXON MODULAR 14.4 W blue LEDs (470 nm wavelength). Products were purified by flash column chromatography on silica gel 60 (0.040-0.063 mm mesh) from Material Harvest. Thin layer chromatography (TLC) was carried out on aluminium Merck Kieselgel 60 F254 sheets, visualised by ultraviolet irradiation (254 and 365). The amount of $H_2$ was quantified against $CH_4$ as the internal standard with a Shimadzu Tracera GC-2010 Plus gas chromatograph equipped with Hayesep D (2m * 1/8'' OD * 2mm ID, 80/100 mesh, Analytical Columns) precolumn and a RT-Molsieve 5A (30m * 0.53 mm ID, Restek) main column. $^{1}H$ and $^{13}C$ NMR spectroscopy were recorded on Bruker DPX 400 spectrometer at room temperature. Chemical shifts (δ) of $^{1}H$ and $^{13}C$ NMR spectra are given in ppm and the peaks were internally referenced against the residual solvent peak (note: $CDCl_3$ referenced δ 7.26 ppm for $^{1}H$ and 77.16 ppm for $^{13}C$). NMR data were reported in the following form: Chemical shift, multiplicity, coupling constant and integration. Attenuated total reflection Fourier transform infrared (ATR-IR) spectra were recorded on a Nicolet iS50 spectrometer and reported in terms of frequency of absorption ($cm^{-1}$). Mass spectra were recorded on a Waters LCT premier Time of Flight mass spectrometer or Micromass Quadrupole-Time of Flight mass spectrometer. Reported mass values are within the error limits of 5 ppm.

## Experimental Procedures

### General procedure for photocatalytic reactions

In a 10 mL borosilicate photoreactor charged with a magnetic stir bar carbon nitride (10 mg), heteroarenes (0.5 mmol) and trifluoroacetic acid (0.75 mmol, 1.5 equiv.) were dissolved in solvent/substrate (3 mL). The reaction mixture was then stirred rapidly and irradiated with 470 nm blue LEDs open to air (a fan was used for cooling). The reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was quenched with 1 M NaOH (2.5 mL) and extracted with DCM (3 x 20 mL). The combined organic extract was dried over $MgSO_4$, filtered and concentrated under reduced pressure on a rotavapor. To the crude product, 1,3,5-trimethoxy benzene (0.1 mmol) was added as an internal standard for NMR analysis. The crude product was purified by flash column chromatography.

### General procedure for hydrogen production experiment

In a 10 mL borosilicate photoreactor charged with a magnetic stir bar carbon nitride (5 mg), isoquinoline (50 μmol), trifluoroacetic acid (75 μmol, 1.5 equiv.) and 15 μL of a Pt nanoparticle dispersion (1000 ppm in $H_2O$) were dissolved in an aqueous phosphate solution (pH 4.5, 2.7 mL, 0.1 M) and THF or DMA as a substrate (0.3 mL). The reaction vessel was then tightly sealed with a rubber septum and purged with $N_2$ containing 2% $CH_4$ as the internal gas chromatography standard. The reaction mixture was stirred rapidly and irradiated with 470 nm

blue LEDs. Periodically, the amount of accumulated $H_2$ was quantified via headspace injections into a gas chromatograph. After 10 h, the reaction was quenched with 1 M NaOH (0.5 mL) and extracted with DCM (3 x 10 mL). The combined organic extract was dried over $MgSO_4$, filtered and concentrated under reduced pressure on a rotavapor. To the crude product, 1,3,5-trimethoxy benzene (0.1 mmol) was added as an internal standard for NMR analysis. Note: only up to 20 μmol of compounds were trackable in the NMR analysis.

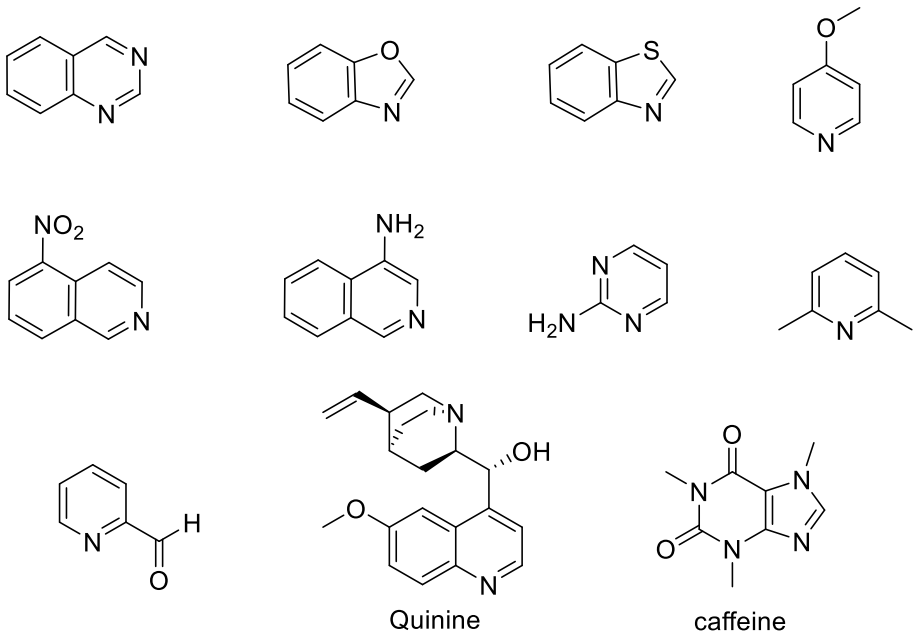



**Table S1. List of unsuccessful substrates**

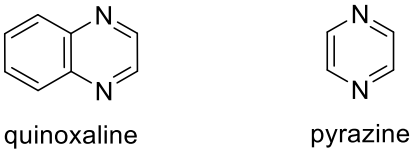
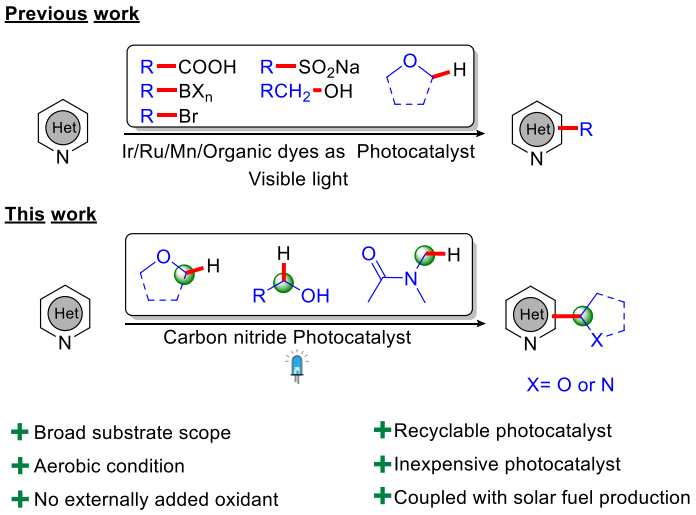



**Table S2. List of substrates with slower kinetics.** Note: These substrates have less than 15% conversion in 48h. The solvent was found to be mostly evaporated in 48h since reactions are performed in open atmosphere.

## Supporting Scheme




**Scheme S1.** Photocatalysed Minisci coupling

## Supporting Figures

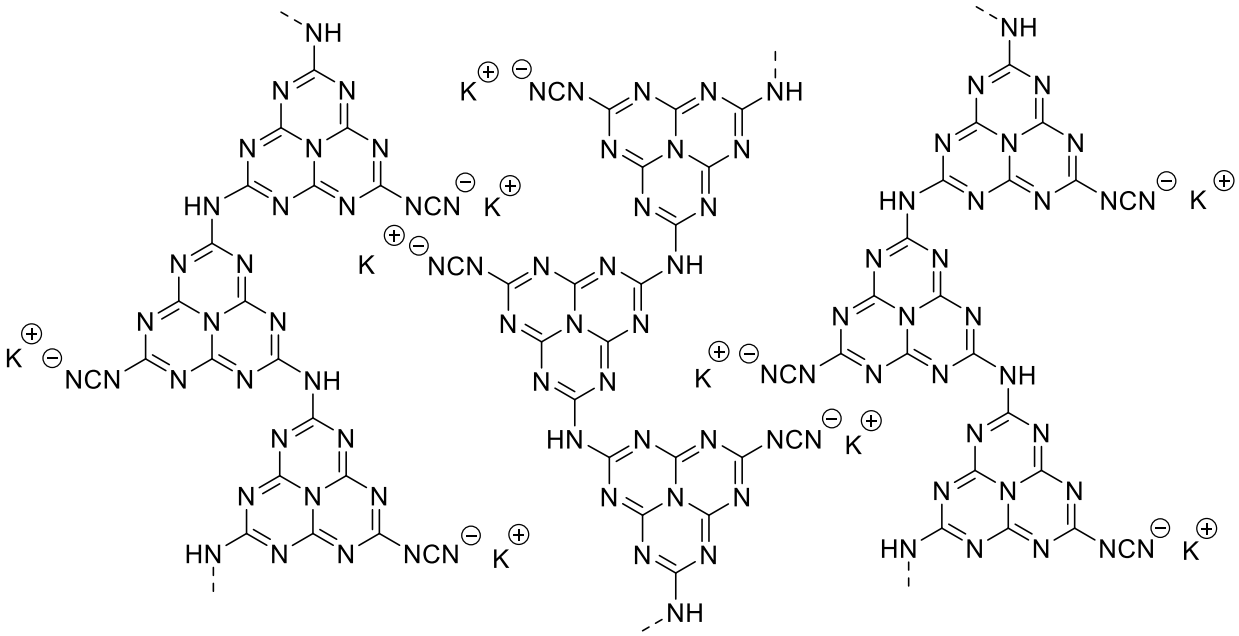


**Figure S1.** Structure of cyanamide functionalised graphitic carbon nitride used in this study.

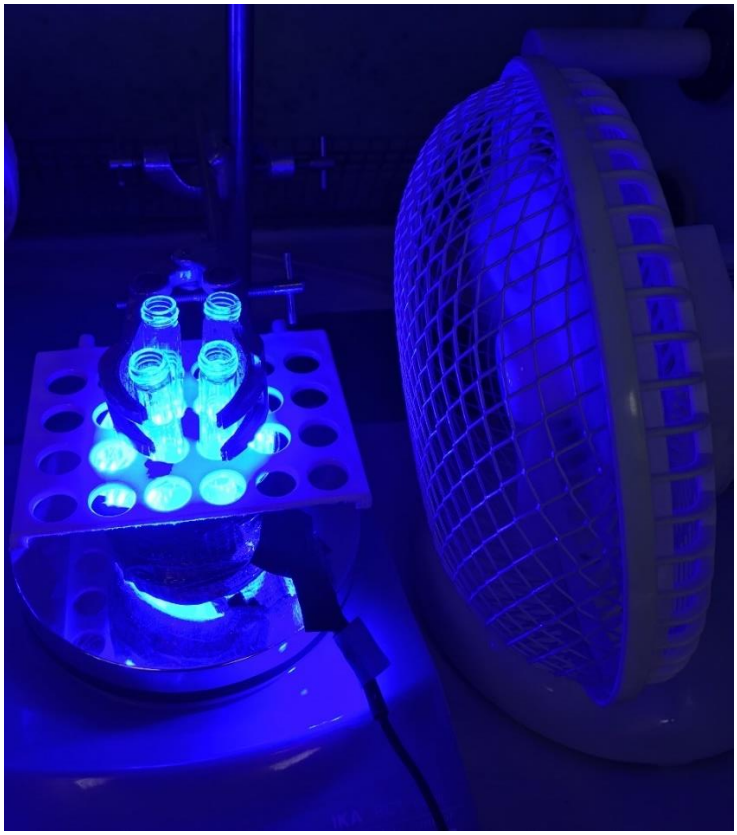


**Figure S2.** Experimental set-up.

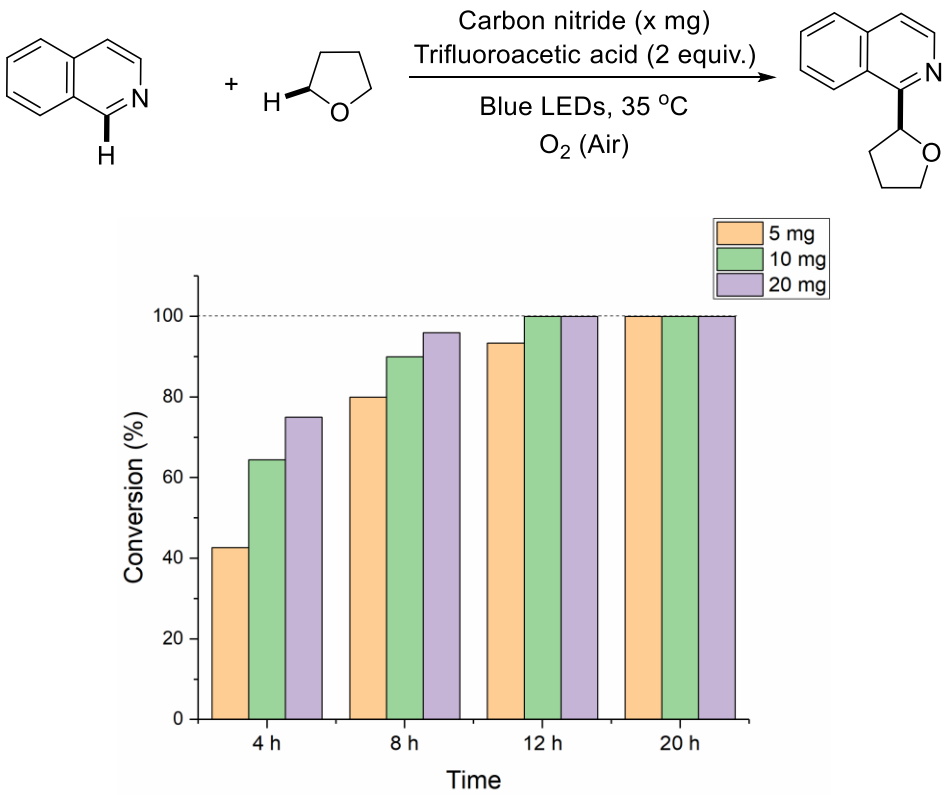



**Figure S3.** Optimization of carbon nitride loading. Reaction condition: Isoquinoline (0.5 mmol), carbon nitride (mg given in legend) in THF (3 mL), TFA (2 equiv.), unless otherwise noted. Conversion yield were obtained from $^{1}$H NMR.

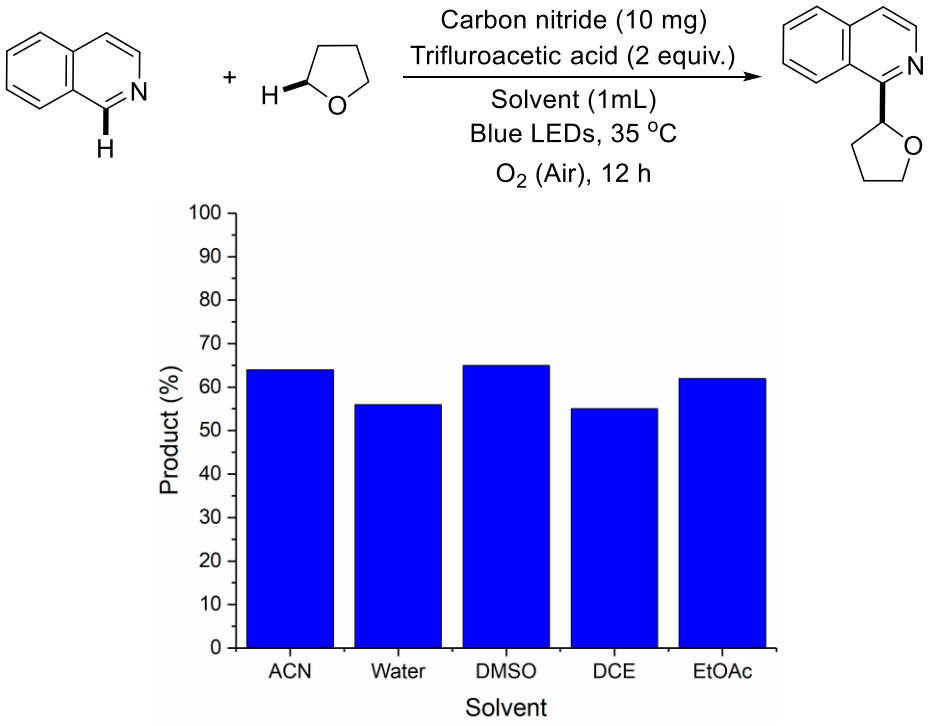



**Figure S4.** Screening of solvents. Isoquinoline (0.5 mmol), THF (2 mL), solvent (1 mL), TFA (2 equiv.), carbon nitride (10 mg) irradiated for 12 h, unless otherwise noted. Product yields were obtained from $^{1}$H NMR spectroscopy using 1,3,5 trimethoxybenzene (0.1mmol) as an internal standard. ACN= acetonitrile, DMSO= dimethyl sulfoxide, DCE= dichloroethane, EtOAc= ethyl acetate.

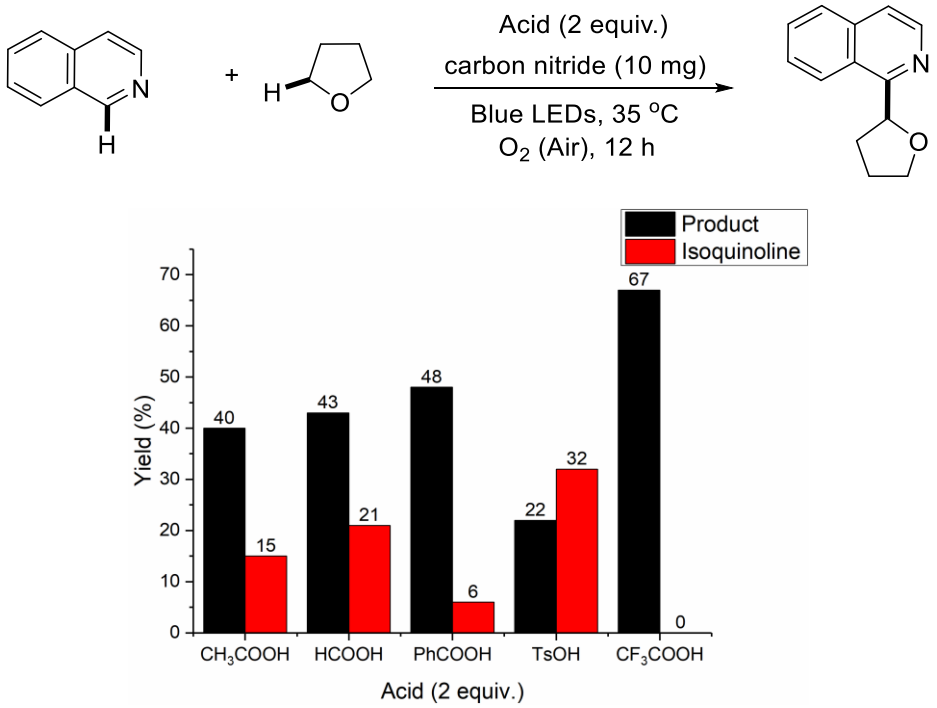



**Figure S5.** Investigation of various acids. Isoquinoline (0.5 mmol), THF (3 mL), acids (2 equiv.), carbon nitride (10 mg) irradiated for 12 h, unless otherwise noted. Product yields were obtained from $^{1}$H NMR spectroscopy using 1,3,5 trimethoxybenzene (0.1 mmol) as an internal standard. PhCOOH= benzoic acid and TsOH= p-toluenesulfonic acid.

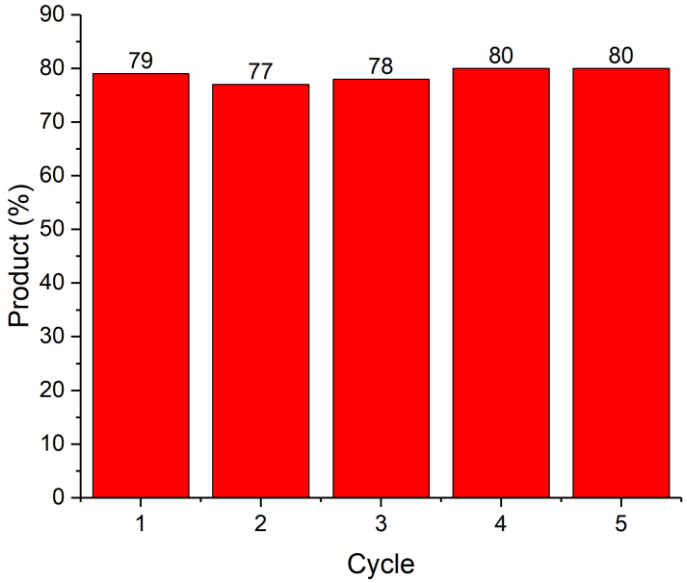



**Figure S6** Reusability of carbon nitride. Reaction condition: isoquinoline (0.5 mmol), THF (3 mL), TFA (1.5 equiv.) and carbon nitride (10 mg) irradiated for 10 h, unless otherwise noted. Product yields were obtained from $^{1}$H NMR spectroscopy.

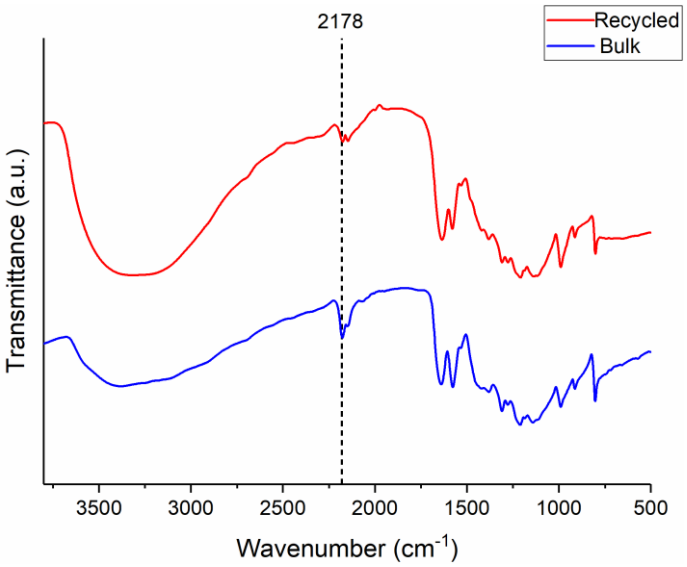



**Figure S7.** ATR-IR spectra of carbon nitride before (blue) and after (red) five-times recycling

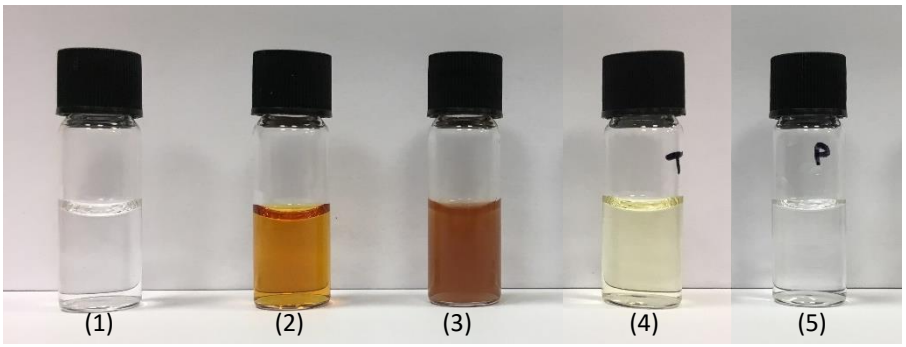
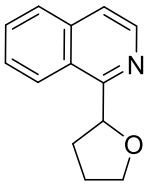


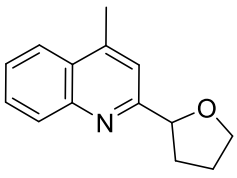

**Figure S8**. Iodine test. A solution of KI (0.1 M,0.5 mL) and $CH_3COOH$ (0.1 M, 0.5 mL) in samples 1 to 4 along with (1) water (10 μL), (2) $H_2O_2$ (30 wt.%, 1 μL), (3) photocatalytic reaction mixture (10 μL) after 10h irradiation (4) THF (10 μL), (5) photocatalytic reaction mixture (10 μL) after 10h irradiation in water (1 mL).

## Product Characterisation



**1-(Tetrahydrofuran-2-yl)isoquinoline (1a)**

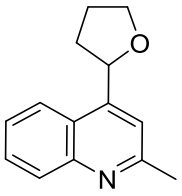
The reaction was completed in 10 hours and the desired product (colourless oil, 78 mg, 78% yield) was obtained by flash chromatography (15% ethyl acetate/hexane). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 5.8 Hz, 1H), 8.24 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 5.8 Hz, 1H), 5.62 (t, *J* = 7.1 Hz, 1H), 4.13 – 4.06 (m, 1H), 3.99 – 3.89 (m, 1H), 2.49-2.40 (m, 1H), 2.33-2.25 (m, 1H), 2.13 – 1.93 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 159.62, 141.57, 136.53, 129.83, 127.32, 127.11, 126.61, 125.29, 120.52, 79.13, 69.00, 30.79, 26.16. ATR-IR (neat) 2970, 2868, 1622, 1563, 1082, 823 $cm^{-1}$. HRMS (ESI) calculated for $C_{13}H_{13}NaO^+$ [$(M+Na)^+$] 222.0889, found 222.0890.



**4-Methyl-2-(tetrahydrofuran-2-yl)quinoline (1b)**

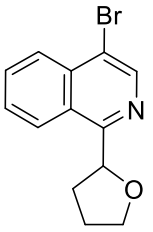
The reaction was completed in 12 hours and the desired product (colourless oil, 71 mg, 67% yield) was obtained by flash chromatography (17% ethyl acetate/hexane). $^1$H NMR (400 MHz, Chloroform-*d*): δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.43 (s, 1H), 5.13 (t, *J* = 6.9 Hz, 1H), 4.16 (q, *J* = 6.7 Hz, 1H), 4.02 (q, *J* = 7.9, 7.3 Hz, 1H), 2.68 (s, 3H), 2.54 – 2.43 (m, 1H), 2.11 – 1.94 (m, 3H). $^{13}$C NMR (101

MHz, $CDCl_3$): δ 163.15, 147.41, 144.97, 129.63, 129.17, 127.52, 125.87, 123.75, 118.66, 82.15, 69.31, 33.37, 26.04, 18.95. ATR-IR (neat) 2963, 2868, 1600, 1507, 1446, 1063, 880, 755 $cm^{-1}$. HRMS (ESI) calculated for $C_{14}H_{16}NO^+$ [$(M+H)^+$] 214.1226, found 214.1225.



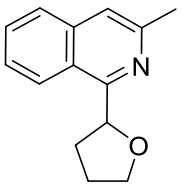
**2-Methyl-4-(tetrahydrofuran-2-yl)quinoline (1c)**

The reaction was completed in 40 hours and the desired product (colourless oil, 88 mg, 83% yield) was obtained by flash chromatography (25% ethyl acetate/hexane). $^1H$ NMR (400 MHz, Chloroform-*d*): δ 8.03 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.42 (s, 1H), 5.54 (t, J = 7.1 Hz, 1H), 4.22 – 4.17 (m, 1H), 4.04 – 3.98 (m, 1H), 2.71 (s, 3H), 2.63 – 2.47 (m, 1H), 2.11 – 1.87 (m, 2H), 1.85 – 1.76 (m, 1H). $^{13}C$ NMR (101 MHz, $CDCl_3$): δ 159.13, 149.33, 147.97, 129.44, 128.98, 125.52, 123.92, 123.05, 117.24, 76.83, 69.02, 33.93, 26.04, 25.59. ATR-IR (neat) 2975, 2867, 1600, 1509, 1442, 1076, 884, 757 $cm^1$. HRMS (ESI) calculated for $C_{14}H_{16}NO^+$ [$(M+H)^+$] 214.1226, found 214.1225.



**4-Bromo-1-(tetrahydrofuran-2-yl)isoquinoline (1d)**

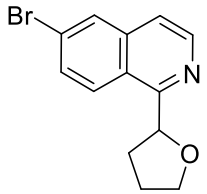
The reaction was completed in 10 hours and the desired product (yellow oil, 80 mg, 58% yield) was obtained by flash chromatography (14% ethyl acetate/hexane). $^1H$ NMR (400 MHz, Chloroform-*d*): δ 8.65 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 8.4 Hz, 1H), 5.65 (t, *J* = 7.0 Hz, 1H), 4.17 – 4.07 (m, 1H), 4.03 –3.97 (m, 1H), 2.53 – 2.46 (m, 1H), 2.40 – 2.33 (m , 1H), 2.20 – 2.02 (m, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 159.24, 143.26, 135.12, 131.13, 128.08, 127.94, 126.67, 125.75, 119.35, 78.80, 69.10, 30.62, 26.15. ATR-IR (neat) 2948, 2869, 1615, 1563, 1447, 1047, 920, 757, 664 $cm^{-1}$. HRMS (ESI) calculated for $C_{13}H_{12}BrNNaO^+$ [$(M+Na)^+$] 299.9994, found 300.0006.



**3-Methyl-1-(tetrahydrofuran-2-yl)isoquinoline (1e)**

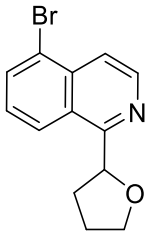
The reaction was completed in 6 hours and the desired product (colourless oil, 70 mg, 66% yield) was obtained by flash chromatography (13% ethyl acetate/hexane). $^1H$ NMR (400 MHz, Chloroform-*d*): δ 8.33 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.61 (t, *J* = 7.1 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.40 (s, 1H), 5.67 (t, *J* = 7.2 Hz, 1H), 4.22 – 4.17 (m, 1H), 4.04 –3.99 (m, 1H), 2.70 (s, 3H), 2.63 – 2.52 (m, 1H), 2.43 – 2.32 (m, 1H), 2.26 – 2.03 (m, 2H). $^{13}C$ NMR (101 MHz, $CDCl_3$): δ 158.88, 150.21, 137.46, 129.67, 126.76, 126.04, 125.36, 124.78, 118.48,

79.84, 68.96, 30.72, 26.15, 24.44. ATR-IR (neat) 2951, 2870, 1622, 1591,1440, 1052, 876, 748 $cm^{-1}$. HRMS (ESI) calculated for $C_{14}H_{16}NO^+$ [$(M+H)^+$] 214.1226, found 214.1226.



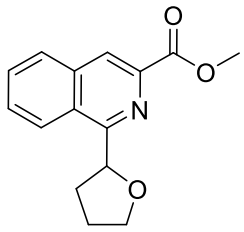

**6-Bromo-1-(tetrahydrofuran-2-yl)isoquinoline (1f)**

The reaction was completed in 10 hours and the desired product (yellow oil, 62 mg, 52% yield) was obtained by flash chromatography (14% ethyl acetate/hexane). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 5.7 Hz, 1H), 8.25 (d, *J* = 9.0 Hz, 1H), 7.99 (d, *J* = 2.1 Hz, 1H), 7.67 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.48 (d, *J* = 5.7 Hz, 1H), 5.65 (t, *J* = 7.1 Hz, 1H), 4.16 (q, *J* = 7.4 Hz, 1H), 4.03 (q, *J* = 7.4 Hz, 1H), 2.60 – 2.49 (m, 1H), 2.44 – 2.31 (m, 1H), 2.24 – 2.04 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.96, 142.69, 137.81, 130.66, 129.43, 127.38, 125.19, 124.69, 119.54, 79.32, 69.10, 30.62, 26.20. ATR-IR (neat) 2969, 2867, 1610, 1557, 1451, 1049, 822, 774, 665 $cm^{-1}$. HRMS (ESI) calculated for $C_{13}H_{13}BrNO^+$ [$(M+H)^+$] 278.0175, found 278.0178.




**5-Bromo-1-(tetrahydrofuran-2-yl)isoquinoline (1g)**

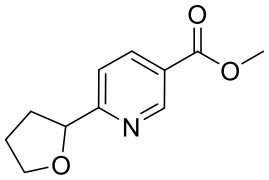
The reaction was completed in 4 hours and the desired product (white powder, 68 mg, 50% yield) was obtained by flash chromatography (14% ethyl acetate/hexane). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 5.9 Hz, 1H), 8.33 (d, *J* = 8.5 Hz, 1H), 7.94 – 7.92 (m, 2H), 7.43 (dd, *J* = 8.5, 7.5 Hz, 1H), 5.69 (t, *J* = 7.0 Hz, 1H), 4.16 – 3.99 (m, 1H), 4.07 – 3.94 (m, 1H), 2.59 – 2.50 (m, 1H), 2.44 – 2.29 (m, 1H), 2.23 – 1.96 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 160.08, 143.01, 135.72, 133.70, 127.91, 127.47, 125.23, 122.36, 119.44, 79.11, 69.13, 30.69, 26.20. ATR-IR (neat) 2964, 2881, 1609, 1575, 1487, 1055, 836, 748, 663 $cm^{-1}$ HRMS (ESI) calculated for $C_{13}H_{12}BrNNaO^+$ [$(M+Na)^+$] 299.9994, found 300.0013.




**Methyl 1-(tetrahydrofuran-2-yl)isoquinoline-3-carboxylate (1h)**

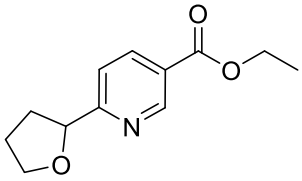
The reaction was completed in 7 hours and the desired product (colourless oil, 68 mg, 60% yield) was obtained by flash chromatography (14% ethyl acetate/hexane). $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 5.7 Hz, 2H), 8.05 – 7.95 (m, 1H), 7.85 – 7.68 (m, 2H), 5.70 (t, *J* = 7.2 Hz, 1H), 4.19 (q, *J* = 7.4 Hz, 1H), 4.09 – 4.03 (m, 4H), 2.73 (m, 1H), 2.44 (m, 1H), 2.20

(m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.63, 160.13, 140.15, 136.51, 130.63, 129.43, 128.89, 128.30, 126.13, 124.27, 80.55, 69.10, 52.82, 30.37, 26.22. ATR-IR (neat) 2946, 2873, 1713, 1568, 1450, 1052, 909, 750 $cm^{-1}$. HRMS (ESI) calculated for $C_{15}H_{16}NO_3^+$ [$(M+H)^+$] 258.1125, found 258.1130.



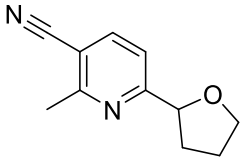
**Methyl 6-(tetrahydrofuran-2-yl)nicotinate (1i)**

The reaction was completed in 5.5 hours and the desired product (colourless oil, 77 mg, 75% yield) was obtained by flash chromatography (14% ethyl acetate/hexane). $^1$H NMR (400 MHz, Chloroform-*d*) δ 9.12 (d, *J* = 2.0 Hz, 1H), 8.25 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 5.05 (m, 1H), 4.10 (m, 1H), 4.01 – 3.95 (m, 1H), 3.92 (s, 3H), 2.50 – 2.40 (m, 1H), 1.95 (m, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.84, 165.92, 150.44, 137.85, 124.52, 119.35, 81.26, 69.33, 52.41, 33.24, 25.83. ATR-IR (neat) 2952, 2873, 1722, 1596, 1435, 1284, 1066, 737 $cm^{-1}$. HRMS (ESI) calculated for $C_{11}H_{13}NO_3Na^+$ [$(M+Na)^+$] 230.0788, found 230.0786.



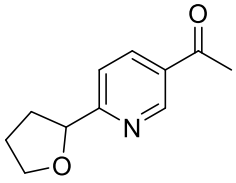
**Ethyl -6-(tetrahydrofuran-2-yl)nicotinate (1j)**

The reaction was completed in 7 hours and the desired product (colourless oil, 66 mg, 60% yield) was obtained by flash chromatography (20% ethyl acetate/hexane). $^1$H NMR (400 MHz, Chloroform-*d*) δ 9.09 (dd, *J* = 2.2, 0.8 Hz, 1H), 8.22 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.49 (dt, *J* = 8.2, 0.8 Hz, 1H), 5.02 (dd, *J* = 7.4, 5.6 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.10 – 4.02 (m, 1H), 3.98 – 3.92 (m, 1H), 2.47 – 2.36 (m, 1H), 2.00 – 1.88 (m, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.65, 165.36, 150.36, 137.72, 124.76, 119.22, 81.20, 69.25, 61.31, 33.18, 25.76, 14.33. ATR-IR (neat) 2980, 2873, 1717, 1596, 1267, 1067, 737 $cm^{-1}$. HRMS (ESI) calculated for $C_{12}H_{16}NO_3^+$ [$(M+H)^+$] 222.1125, found 222.1122.



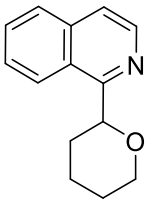
**2-Methyl-6-(tetrahydrofuran-2-yl)nicotinonitrile (1k)**

The reaction completed in 6 hours and the desired product (white powder, 66 mg, 70% yield) was obtained by flash chromatography (15% ethyl acetate/hexane). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 4.97 (dd, *J* = 7.6, 5.3 Hz, 1H), 4.07 (td, *J* = 8.4, 8.0, 3.9 Hz, 1H), 3.96 (dt, *J* = 8.2, 6.5 Hz, 1H), 2.72 (s, 3H), 2.42 (dddt, *J* = 9.1, 6.2, 4.4, 2.5 Hz, 1H), 2.00 – 1.85 (m, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.24, 160.98, 140.65, 117.27, 116.89, 107.20, 81.08, 69.35, 33.18, 25.71, 23.66. ATR–IR (neat) 2984, 2918, 2230, 1587, 1565, 1451, 1072, 847 $cm^{-1}$. HRMS (ESI) calculated for $C_{11}H_{13}N_2O^+$ [(M+H)+] 189.1022, found 189.1024.



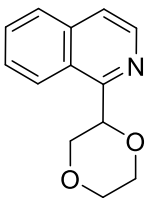
**1-(6-(Tetrahydrofuran-2-yl)pyridin-3-yl)ethan-1-one (1l)**

The reaction completed in 5 hours and the desired product (colourless oil, 65 mg, 69% yield) was obtained by flash chromatography (30% ethyl acetate/hexane). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 9.06 (d, *J* = 2.0 Hz, 1H), 8.19 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 5.05 (dd, *J* = 7.4, 5.6 Hz, 1H), 4.14 – 4.04 (m, 1H), 4.03 – 3.93 (m, 1H), 2.60 (s, 3H), 2.50 – 2.39 (m, 1H), 2.01 – 1.90 (m, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 196.65, 167.97, 149.54, 136.33, 131.01, 119.66, 81.24, 69.34, 33.22, 26.81, 25.83. ATR–IR (neat) 2977, 2872, 1684, 1590, 1266, 1065, 847 $cm^{-1}$. HRMS (ESI) calculated for $C_{11}H_{14}NO_2^+$ [$(M+H)^+$] 192.1019, found 192.1022.



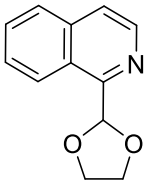
**1-(Tetrahydro-2H-pyran-2-yl)Isoquinoline**[4] **(2a)**

The reaction was completed in 48 hours and the desired product (yellow oil, 54 mg, 50% yield) was obtained by flash chromatography (20% ethyl acetate/hexane). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 5.7 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 5.7 Hz, 1H), 5.16 (dd, *J* = 11.0, 2.3 Hz, 1H), 4.25 (ddt, *J* = 11.5, 4.0, 1.8 Hz, 1H), 3.76 (td, *J* = 11.7, 2.4 Hz, 1H), 2.17 – 2.01 (m, 2H), 1.97 (dq, *J* = 12.8, 2.1 Hz, 1H), 1.89 – 1.73 (m, 2H), 1.68 – 1.61 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.68, 141.80, 136.65, 129.74, 127.37, 126.98, 126.07, 125.25, 120.51, 79.32, 69.43, 31.07, 25.92, 23.90. HRMS (ESI) calculated for $C_{14}H_{15}NNaO^+$ [$(M+Na)^+$] 236.1046, found 236.1045.



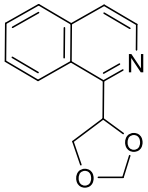
**1-(1,4-Dioxan-2-yl)isoquinoline**[4] **(2b)**

The reaction was completed in 48 hours and the desired product (yellow oil, 64 mg, 60% yield) was obtained by flash chromatography (20% ethyl acetate/hexane). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 5.7 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.66 – 7.56 (m, 2H), 5.46 (dd, *J* = 9.6, 3.0 Hz, 1H), 4.20 – 4.04 (m, 4H), 3.94 – 3.81 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.09, 141.96, 136.58, 130.13, 127.58, 126.61, 124.80, 121.16, 75.96, 70.40, 67.69, 66.63. HRMS (ESI) calculated for $C_{13}H_{14}NO_2^+$ [$(M+H)^+$] 216.1019, found 216.1025.



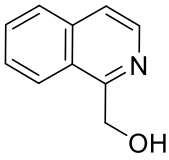
**1-(1,3-Dioxolan-2-yl)isoquinoline**[4] **(2c)**

The reaction was completed in 14 hours and the desired product (colourless oil, 73 mg, 64% yield) was obtained by flash chromatography (25% ethyl acetate/hexane). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 5.7 Hz, 1H), 8.39 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.63 (m, 2H), 7.60 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 6.46 (s, 1H), 4.38 – 4.26 (m, 2H), 4.23 – 4.14 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 154.74, 141.63, 136.86, 130.17, 127.47, 127.34, 126.46, 125.32, 122.06, 103.62, 65.63. HRMS (ESI) calculated for $C_{12}H_{12}NO_2^+$ [$(M+H)^+$] 202.0863, found 202.0860.



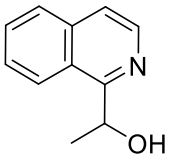
**1-(1,3-Dioxolan-4-yl)isoquinoline**[4] **(2c')**

The reaction was completed in 14 hours and the desired product (colourless oil, 24 mg, 19% yield) was obtained by flash chromatography (15% ethyl acetate/hexane). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 5.7 Hz, 1H), 8.37 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.71 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.68 – 7.60 (m, 2H), 5.80 (t, *J* = 6.7 Hz, 1H), 5.29 (s, 1H), 5.20 (s, 1H), 4.59 (dd, *J* = 8.1, 6.4 Hz, 1H), 4.42 (t, *J* = 7.5 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.48, 141.64, 136.78, 130.29, 127.70, 127.61, 127.06, 125.14, 121.38, 96.19, 76.36, 68.60. HRMS (ESI) calculated for $C_{12}H_{12}NO_2^+$ [$(M+H)^+$] 202.0863, found 202.0861.



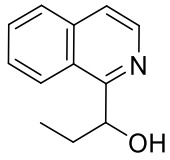
**Isoquinolin-1-ylmethanol (3a)**

The reaction was completed in 14 hours and the desired product (white solid, 19 mg, 25% yield) was obtained by flash chromatography (20% ethyl acetate/hexane). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.45 (d, *J* = 5.8 Hz, 1H), 7.91 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.71 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.66 – 7.56 (m, 2H), 5.24 (s, 2H), 5.05 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.55, 140.53, 135.99, 130.59, 127.66, 127.49, 123.29, 120.43, 61.54. ATR-IR (neat) 3139, 2925, 2847, 1622, 1588, 1346, 1022, 829, 746 $cm^{-1}$. HRMS (ESI) calculated for $C_{10}H_{10}NO^+$ [$(M+H)^+$] 160.0757, found 160.0758.



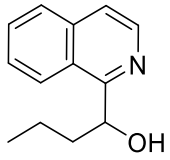
**1-(Isoquinolin-1-yl)ethan-1-ol (3b)**

The reaction was completed in 28 hours and the desired product (white powder, 43 mg, 50% yield) was obtained by flash chromatography (20% ethyl acetate/hexane). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.70 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.67 – 7.54 (m, 2H), 5.59 (q, *J* = 6.5 Hz, 1H), 5.23 (s, 1H), 1.60 (d, *J* = 6.5 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.30, 140.56, 136.58, 130.37, 127.66, 127.45, 124.72, 124.31, 120.60, 66.09, 25.53. ATR-IR (neat) 3147, 2974, 2876, 1622, 1591, 1442, 1069, 874, 748 cm$^{-1}$.HRMS (ESI) calculated for $C_{11}H_{12}NO^{+}$ [(M+H)$^{+}$] 174.0914, found 174.0914.




**1-(Isoquinolin-1-yl)propan-1-ol (3c)**

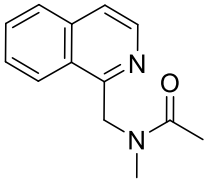
The reaction was completed in 36 hours and the desired product (colourless oil, 50 mg, 53% yield) was obtained by flash chromatography (20% ethyl acetate/hexane). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 5.7 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.69 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.66 – 7.55 (m, 2H), 5.42 (dt, *J* = 8.0, 3.6 Hz, 1H), 5.14 (d, *J* = 6.1 Hz, 1H), 2.06 (dqd, *J* = 14.8, 7.4, 3.4 Hz, 1H), 1.71 (dp, *J* = 14.6, 7.3 Hz, 1H), 1.00 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 161.36, 140.44, 136.51, 130.32, 127.62, 127.35, 124.97, 124.27, 120.50, 70.76, 32.10, 9.81. ATR-IR(neat) 3392, 2963, 2874, 1623, 1564, 1376, 1050, 823, 743 cm$^{-1}$. HRMS (ESI) calculated for $C_{12}H_{14}NO^{+}$ [(M+H)+] 188.1070, found 188.1070.




**1-(Isoquinolin-1-yl)butan-1-ol (3d)**

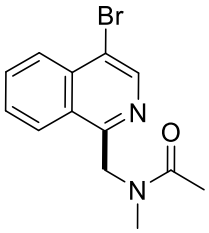
The reaction was completed in 48 hours and the desired product (colourless oil, 53 mg, 53% yield) was obtained by flash chromatography (25% ethyl acetate/hexane). $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 5.7 Hz, 1H), 8.07 – 7.98 (m, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.70 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.65 – 7.52 (m, 2H), 5.54 – 5.40 (m, 1H), 5.12 (s, 1H), 1.99 – 1.90 (m, 1H), 1.64 (dtdd, *J* = 20.4, 10.0, 6.4, 4.5 Hz, 2H), 1.55 – 1.45 (m, 1H), 0.95 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 161.69, 140.51, 136.54, 130.32, 127.65, 127.39, 124.91, 124.25, 120.49, 69.56, 41.57, 18.96, 14.14. ATR-IR(neat) 3395, 2957, 2870, 1623, 1564, 1377, 1011, 822, 744 cm$^{-1}$. HRMS (ESI) calculated for $C_{13}H_{16}NO^{+}$ [(M+H)$^{+}$] 202.1226, found 202.1227.

**Note:** A mixture of isomers were observed for the Minisci-type coupling of amides with *N*-heteroarenes and thus NMR spectra are not analysed but the spectra are reported in the next section.



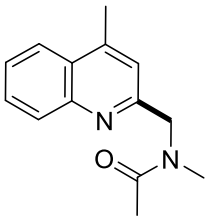
**N-(Isoquinolin-1-ylmethyl)-N-methylacetamide[5] (4a)**

(a mixture of anti and syn isomers) The reaction was completed in 11 hours and the desired product (white solid, 101 mg, 95% yield) was obtained by flash chromatography (5% MeOH/ethyl acetate). ATR-IR (neat) 3447, 2929, 1623, 1583, 1402, 1008, 747 $cm^{-1}$. HRMS (ESI) calculated for $C_{13}H_{15}N_2O^+$ [$(M+H)^+$] 215.1179, found 215.1179.



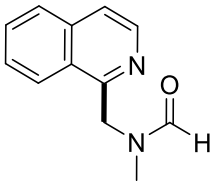
**N-((4-Bromoisoquinolin-1-yl)methyl)-N-methylacetamide (4b)**

(a mixture of anti and syn isomers) The reaction was completed in 15 hours and the desired product (yellow solid, 140 mg, 96% yield) was obtained by flash chromatography (10% MeOH/ethyl acetate). ATR-IR (neat) 3404, 2952, 1628, 1613, 1412, 1016, 748 $cm^{-1}$. HRMS (ESI) calculated for $C_{13}H_{13}BrNO_2Na^+$ [$(M+Na)^+$] 293.0284, found 293.0282.



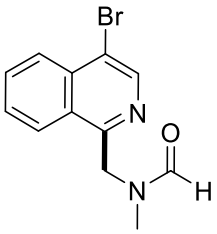
**N-Methyl-N-((4-methylquinolin-2-yl)methyl)acetamide (4c)**

(a mixture of anti and syn isomers) The reaction was completed in 12 hours and the desired product (yellow solid, 82 mg, 72% yield) was obtained by flash chromatography (5% MeOH/ethyl acetate). ATR-IR (neat) 3453, 2930, 1628, 1613, 1398, 1030, 758 $cm^{-1}$. HRMS (ESI) calculated for $C_{14}H_{17}NO_2^+$ [$(M+H)^+$] 229.1335, found 229.1334.



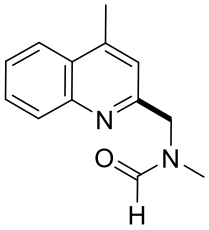
**N-(Isoquinolin-1-ylmethyl)-N-methylformamide (4d)**

(a mixture of anti and syn isomers) The reaction was completed in 12 hours and the desired product (colourless oil, 140 mg, 75% yield) was obtained by flash chromatography (5% MeOH/ethyl acetate). ATR-IR (neat) 3317, 2924, 1664, 1600, 1397, 1063, 854, 771 $cm^{-1}$. HRMS (ESI) calculated for $C_{12}H_{13}N_2O^+$ [$(M+H)^+$] 201.1022, found 201.1022.



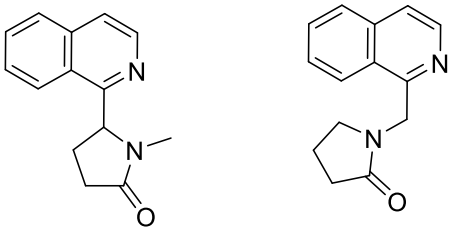

**N-((4-Bromoisoquinolin-1-yl)methyl)-N-methylformamide (4e)**

(a mixture of anti and syn isomers) The reaction was completed in 16 hours and the desired product (yellow solid, 129 mg, 93% yield) was obtained by flash chromatography (5% MeOH/ethyl acetate). ATR-IR(neat) 2924, 1653, 1560, 1393, 1087, 898, 756 $cm^{-1}$. HRMS (ESI) calculated for $C_{12}H_{11}NONa^+$ [$(M+Na)^+$] 300.9947, found 300.9944.




**N-Methyl-N-((4-methylquinolin-2-yl)methyl)formamide (4f)**

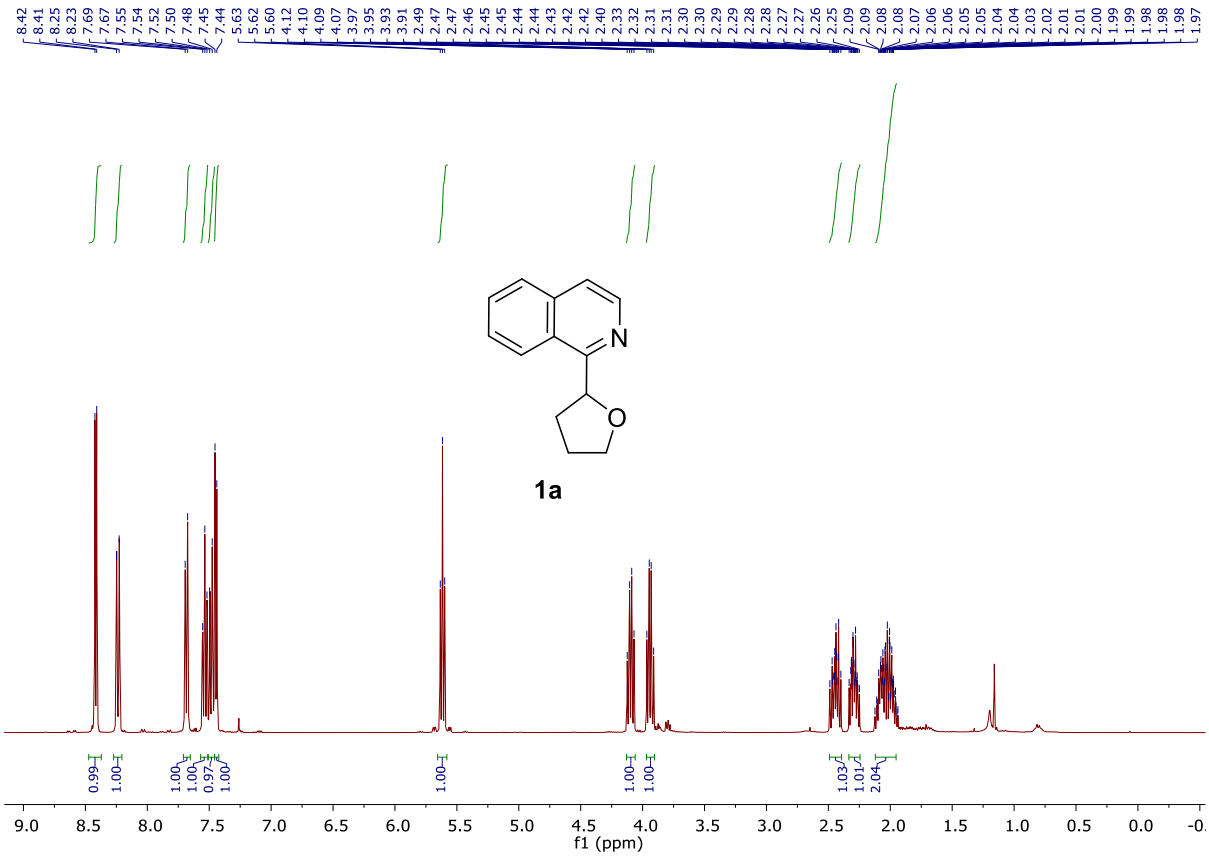
(a mixture of anti and syn isomers) The reaction was completed in 19 hours and the desired product (white solid, 75 mg, 71% yield) was obtained by flash chromatography (5% MeOH/ethyl acetate). ATR-IR(neat) 3450, 2923, 1659, 1585, 1387, 1081, 826, 748 $cm^{-1}$. HRMS (ESI) calculated for $C_{13}H_{14}NO_2Na^+$ [$(M+Na)^+$] 237.0998, found 237.0995.

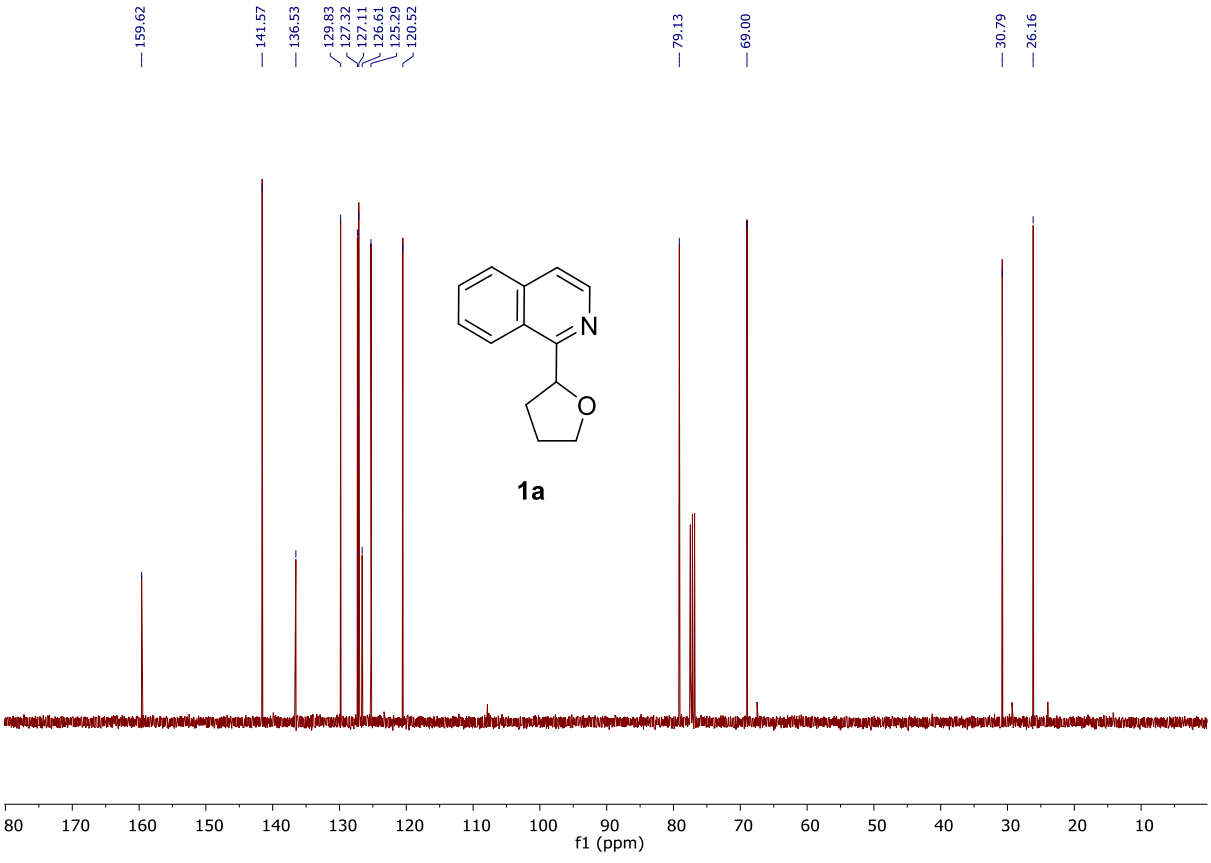


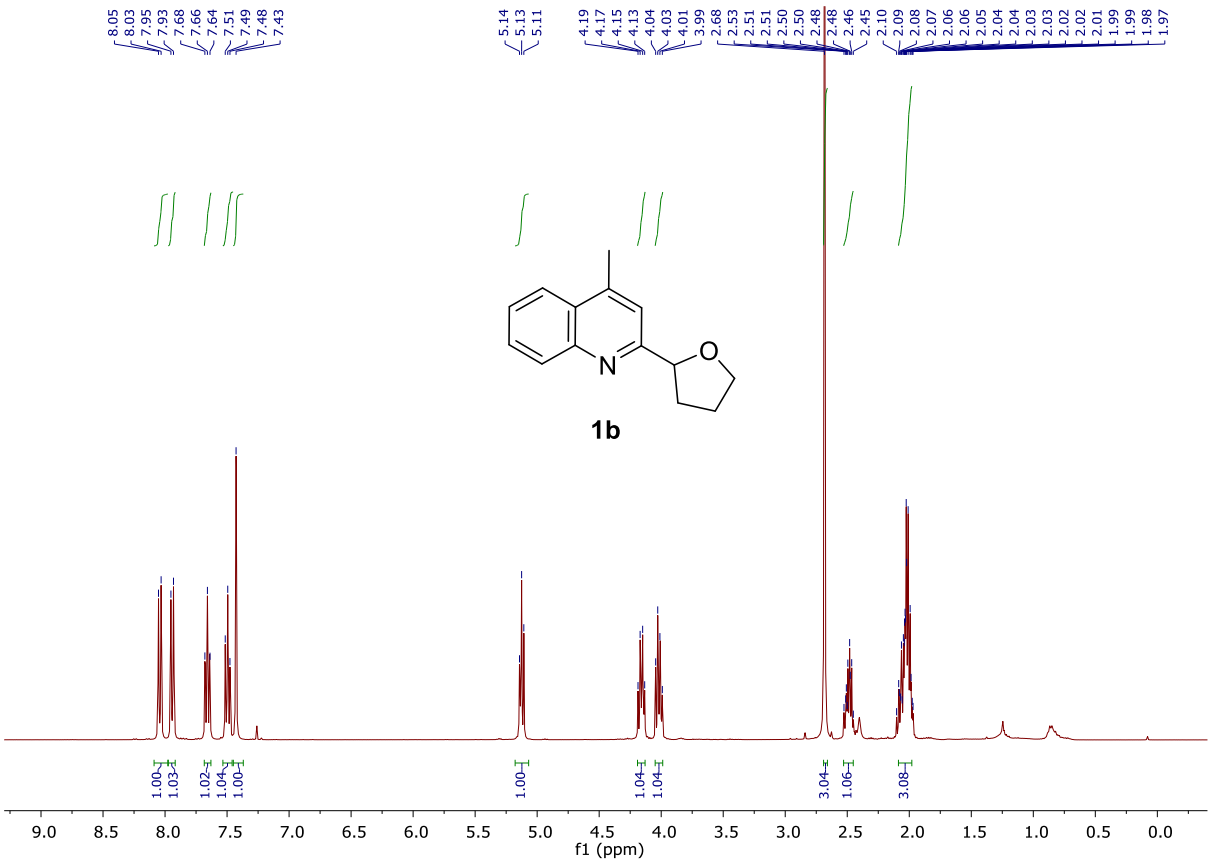

**1-[(Isoquinolin-1′-yl)methyl]pyrrolidin-2-one** and **5-(Isoquinolin-1′-yl)-1-methylpyrrolidin-2-one (4g)**

(a mixture of isomers) The reaction was completed in 20 hours and the desired product (colourless oil, 109 mg, 97% yield) was obtained by flash chromatography (5% MeOH/ethyl acetate). ATR-IR(neat) 3455, 2925, 1667,1623, 1394, 1112, 826, 749 $cm^{-1}$. HRMS (ESI) calculated for $C_{14}H_{15}N_2O^+$ [$(M+H)^+$] 227.1179, found 227.1177.

# Spectral Data for Products

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5.11
4.19
4.17
4.15
4.13
4.04
4.03
4.01
3.99
2.68
2.53
2.51
2.51
2.50
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2.48
2.46
2.45
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2.09
2.08
2.07
2.06
2.06
2.05
2.04
2.04
2.03
2.03
2.02
2.02
2.01
1.99
1.99
1.98
1.97
N
O
1b
1.00
1.03
1.02
1.04
1.00
1.00
1.04
1.04
3.04
1.06
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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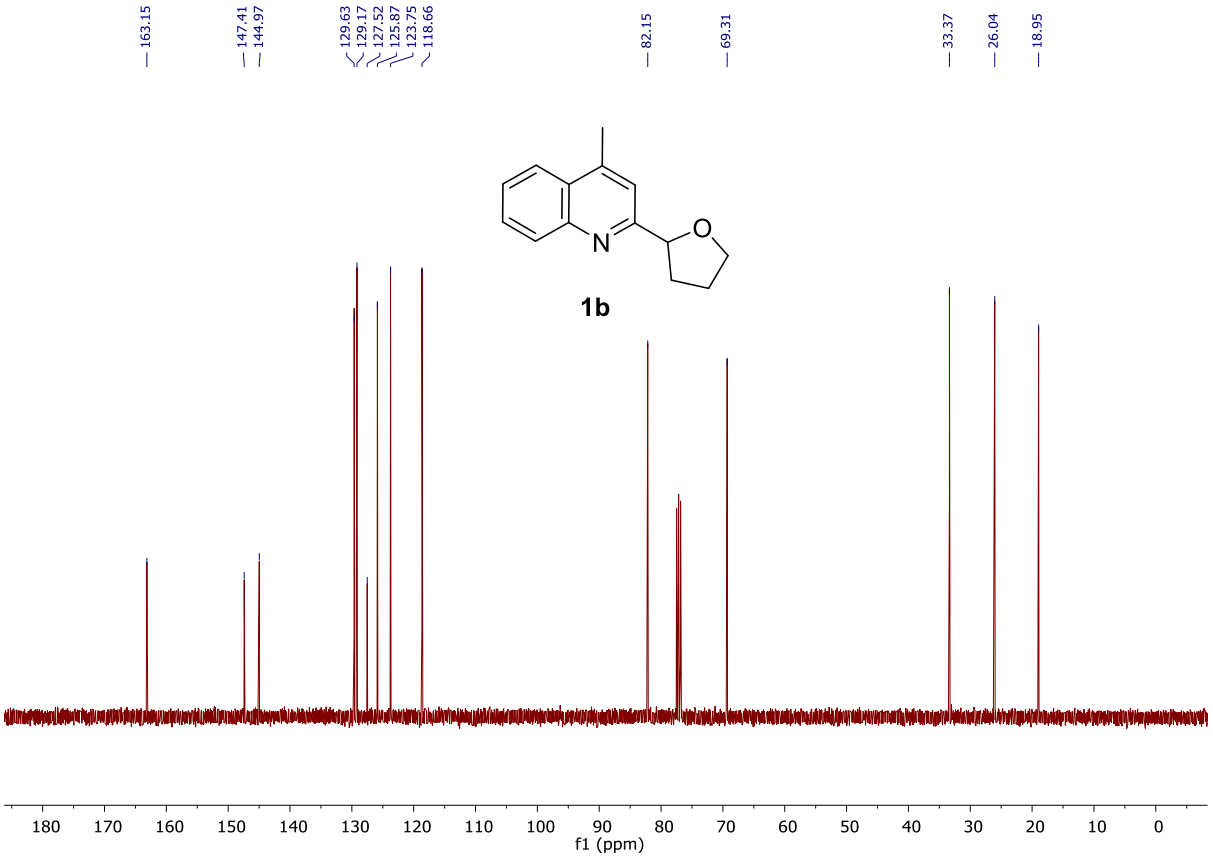
0.0
f1 (ppm)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123.75
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82.15
69.31
33.37
26.04
18.95
N
O
1b
180
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130
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90
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50
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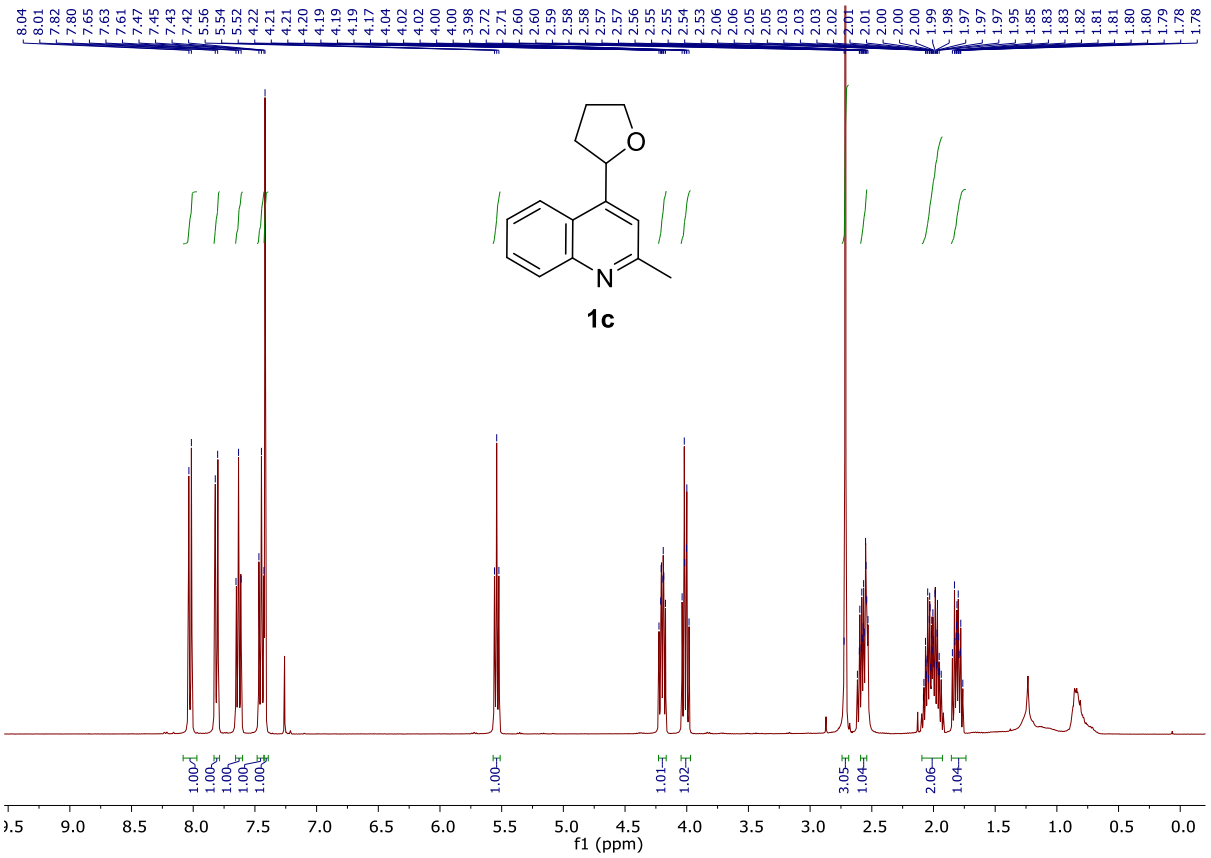
30
20
10
0
f1 (ppm)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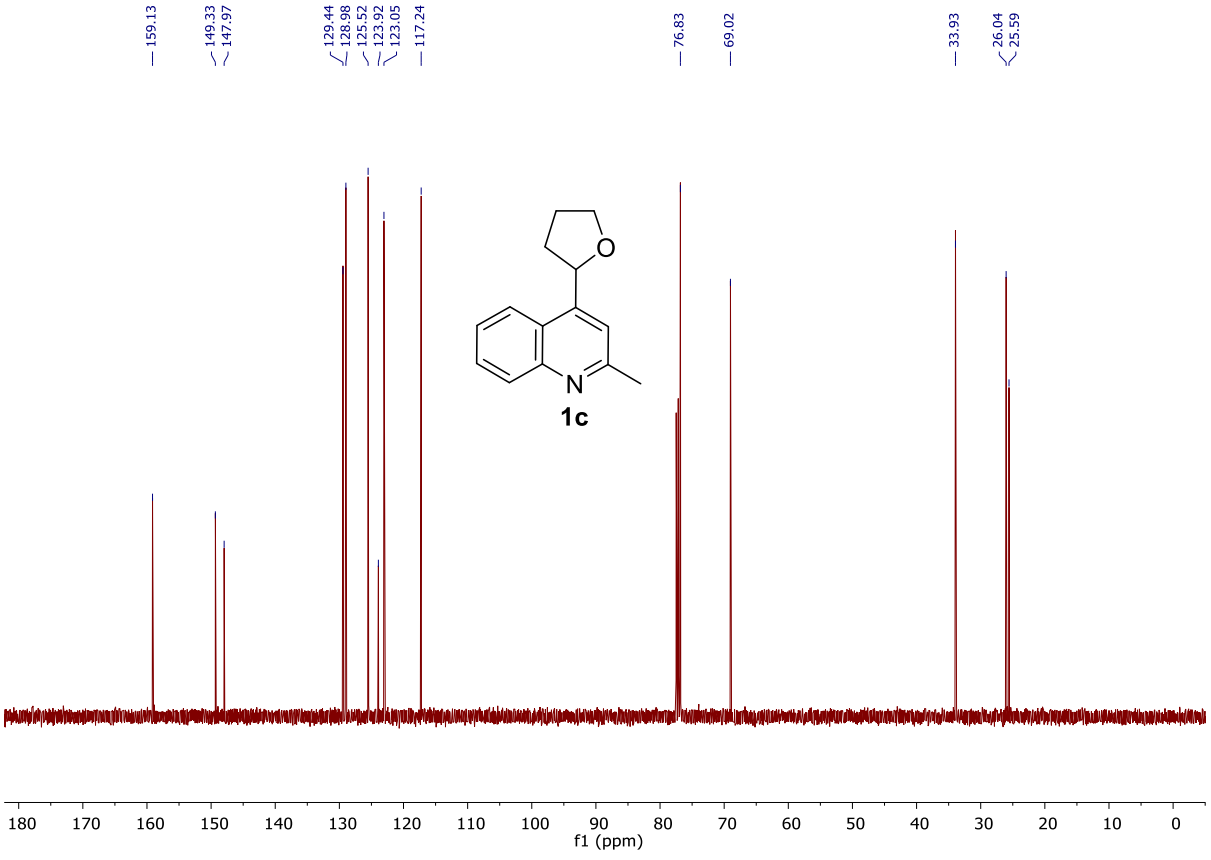
O
N
1c
1.00 1.00 1.00 1.00 1.00 1.00 1.01 1.02 3.05 1.04 2.06 1.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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123.92
123.05
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26.04
25.59
O
N
1c
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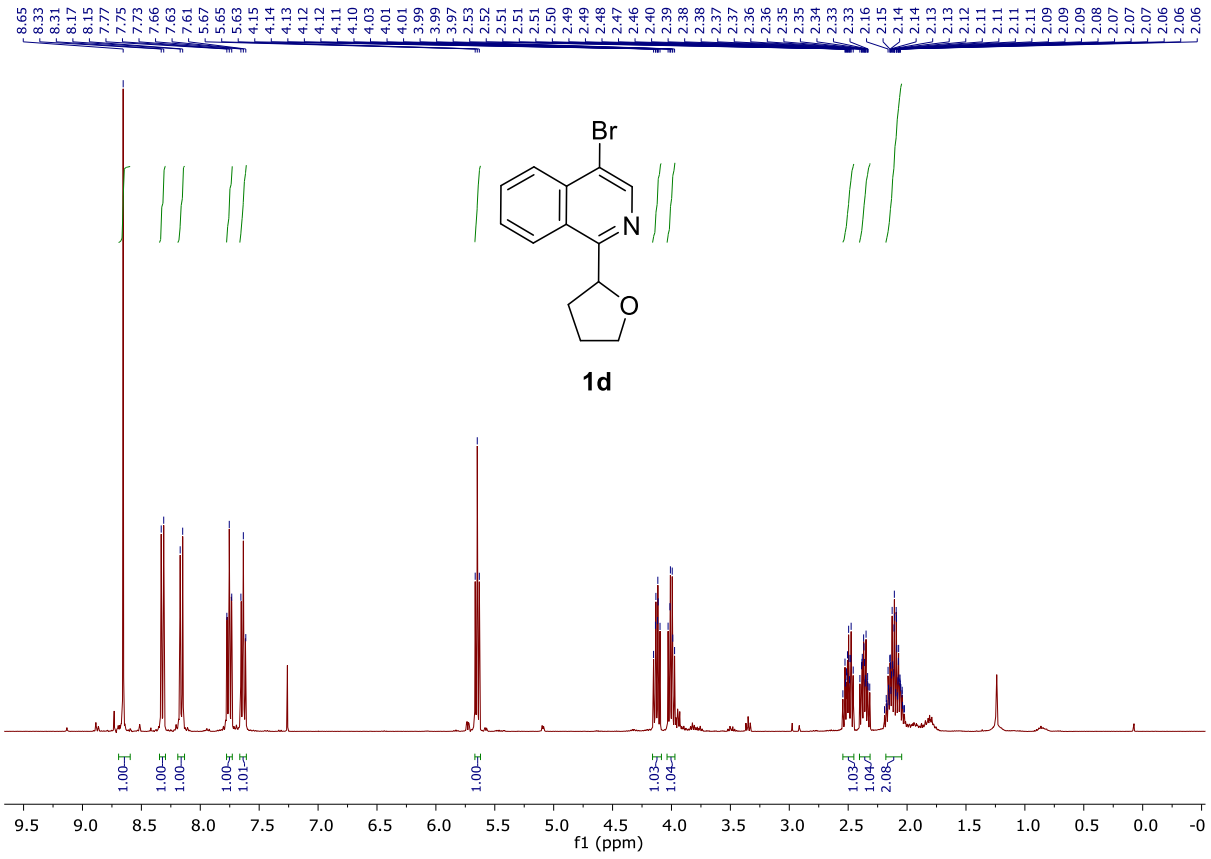
f1 (ppm)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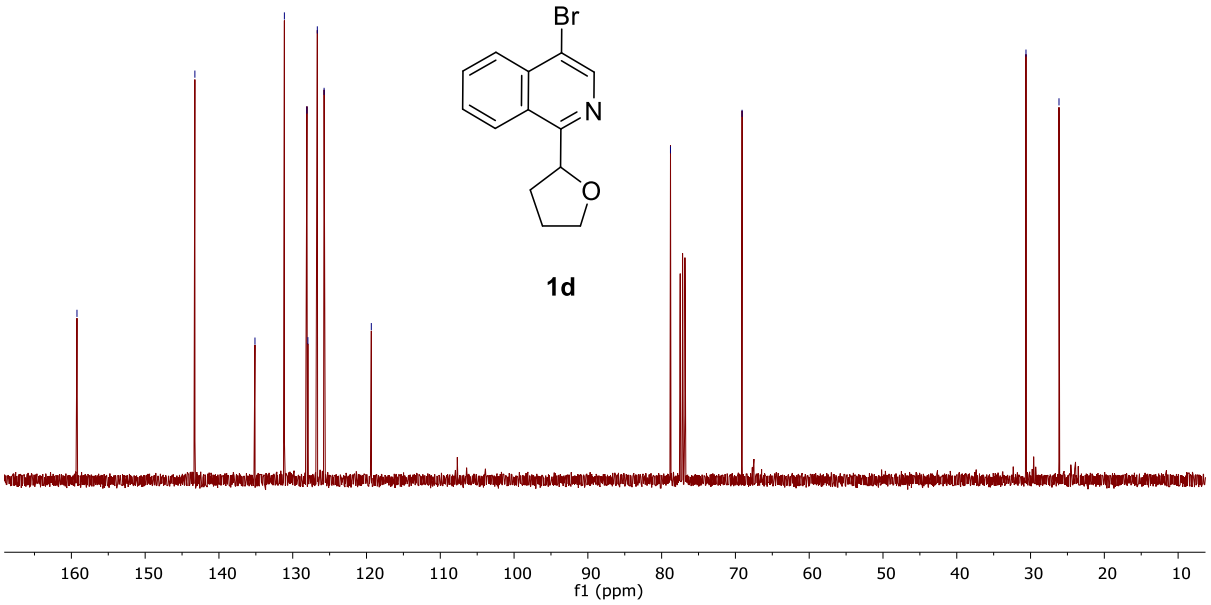
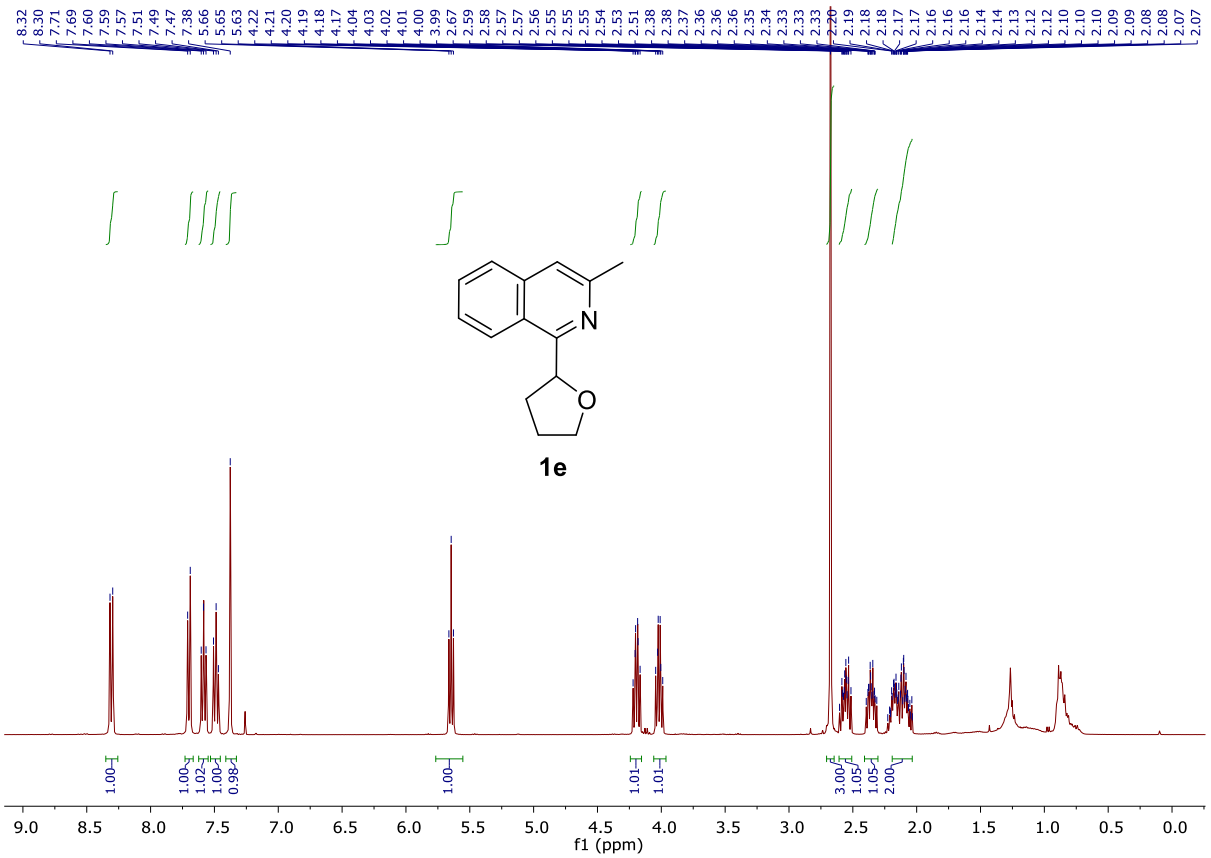
O
1d
f1 (ppm)


Br
N
O
1d
f1 (ppm)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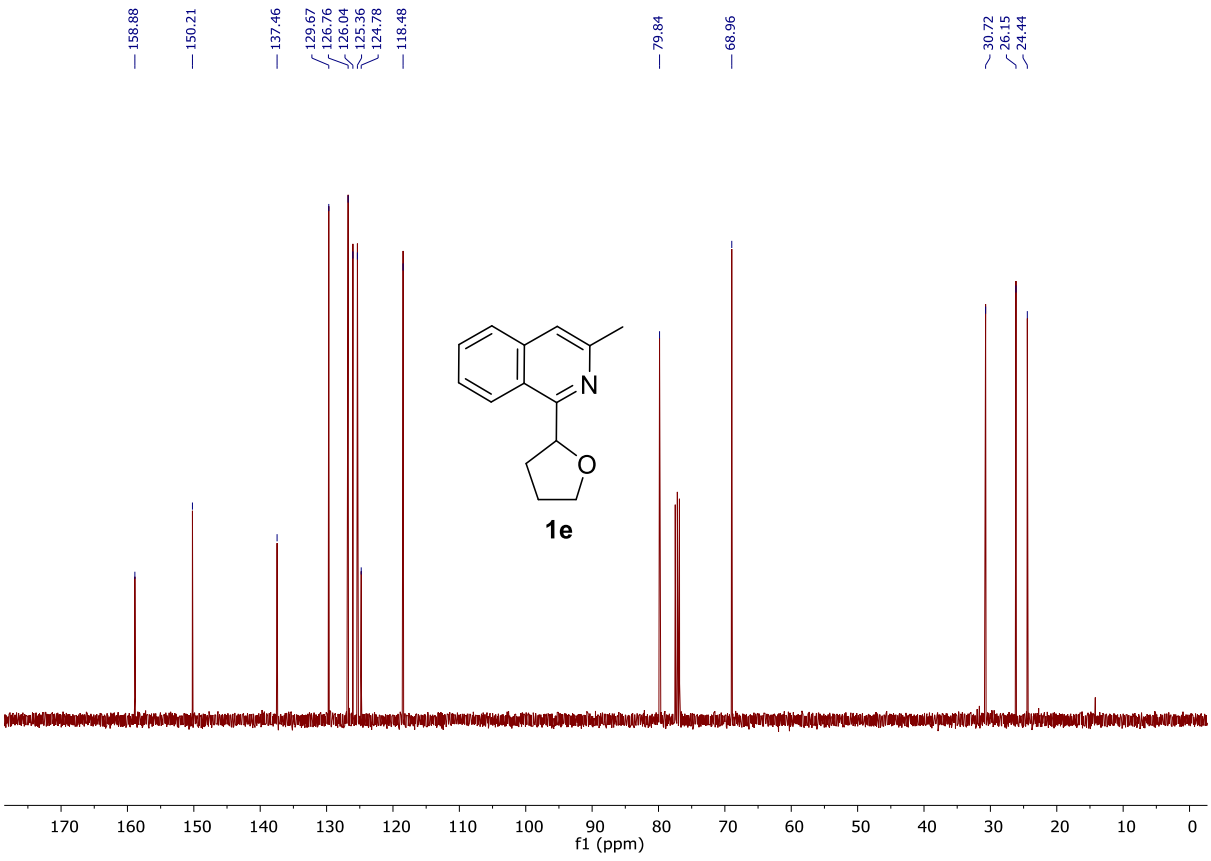
N
O
1e
1.00 1.00 1.02 1.00 0.98 1.00 1.01 1.01 3.00 1.05 1.05 2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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N
O
1e
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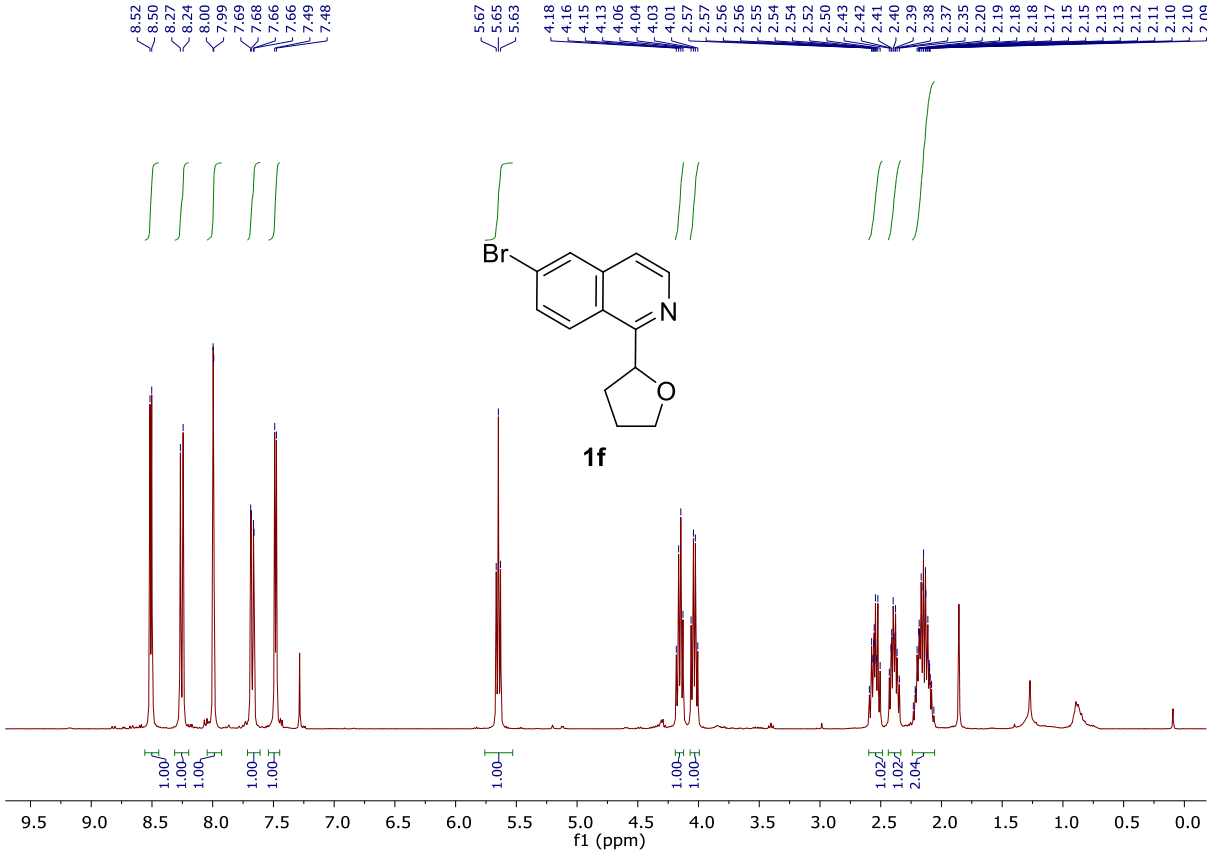
f1 (ppm)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7.68
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7.66
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7.48
5.67
5.65
5.63
4.18
4.16
4.15
4.13
4.06
4.04
4.03
4.01
2.57
2.57
2.56
2.56
2.55
2.54
2.54
2.52
2.50
2.43
2.42
2.41
2.40
2.39
2.38
2.37
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2.19
2.18
2.18
2.17
2.15
2.15
2.13
2.13
2.12
2.11
2.10
2.10
Br
N
O
1f
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.02
1.02
2.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
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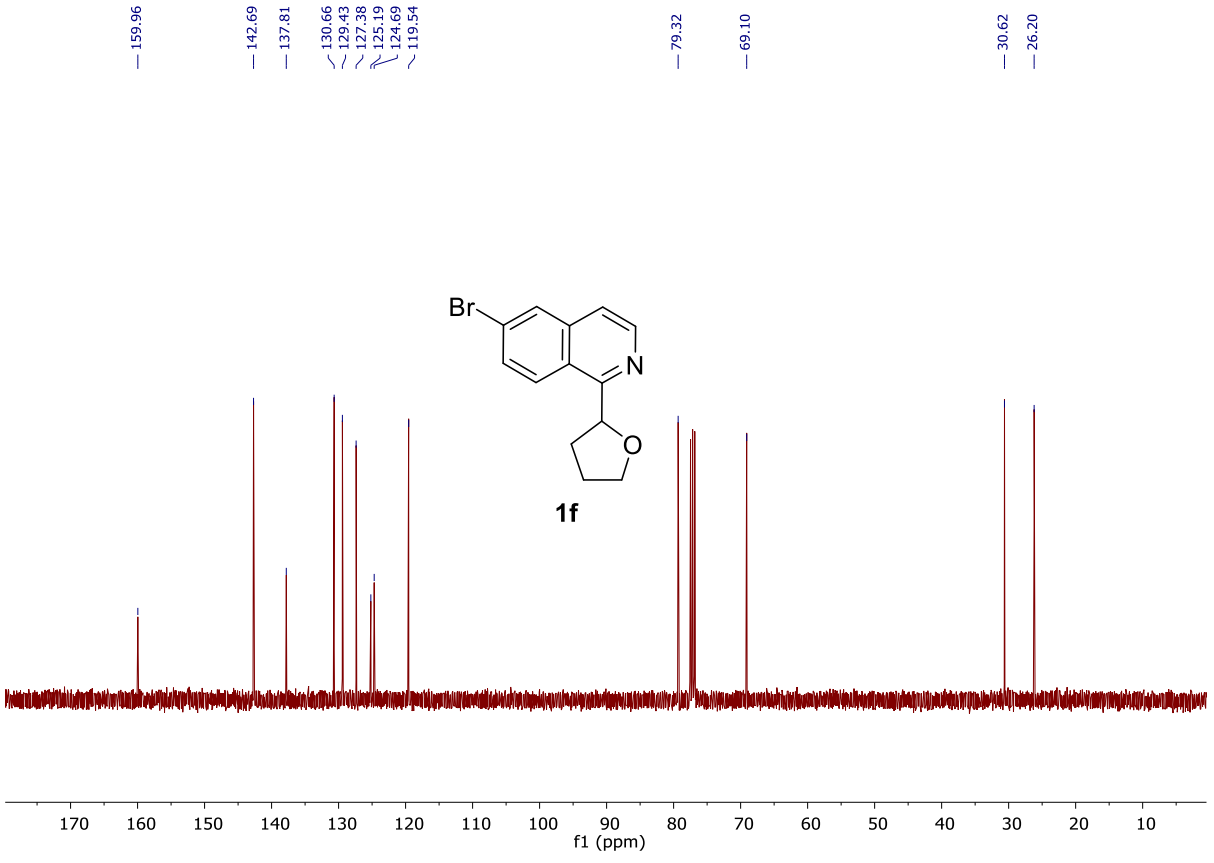
f1 (ppm)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124.69
119.54
79.32
69.10
30.62
26.20
Br
N
O
1f
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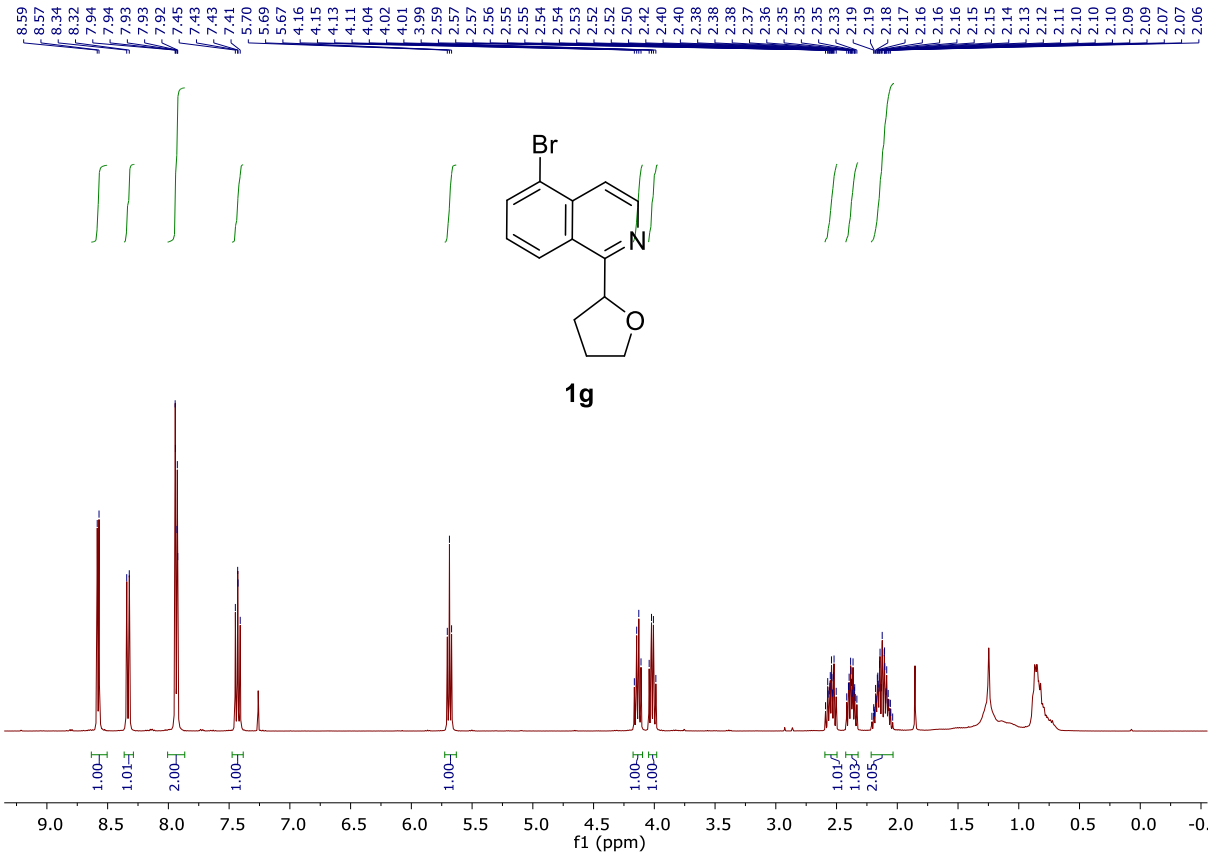
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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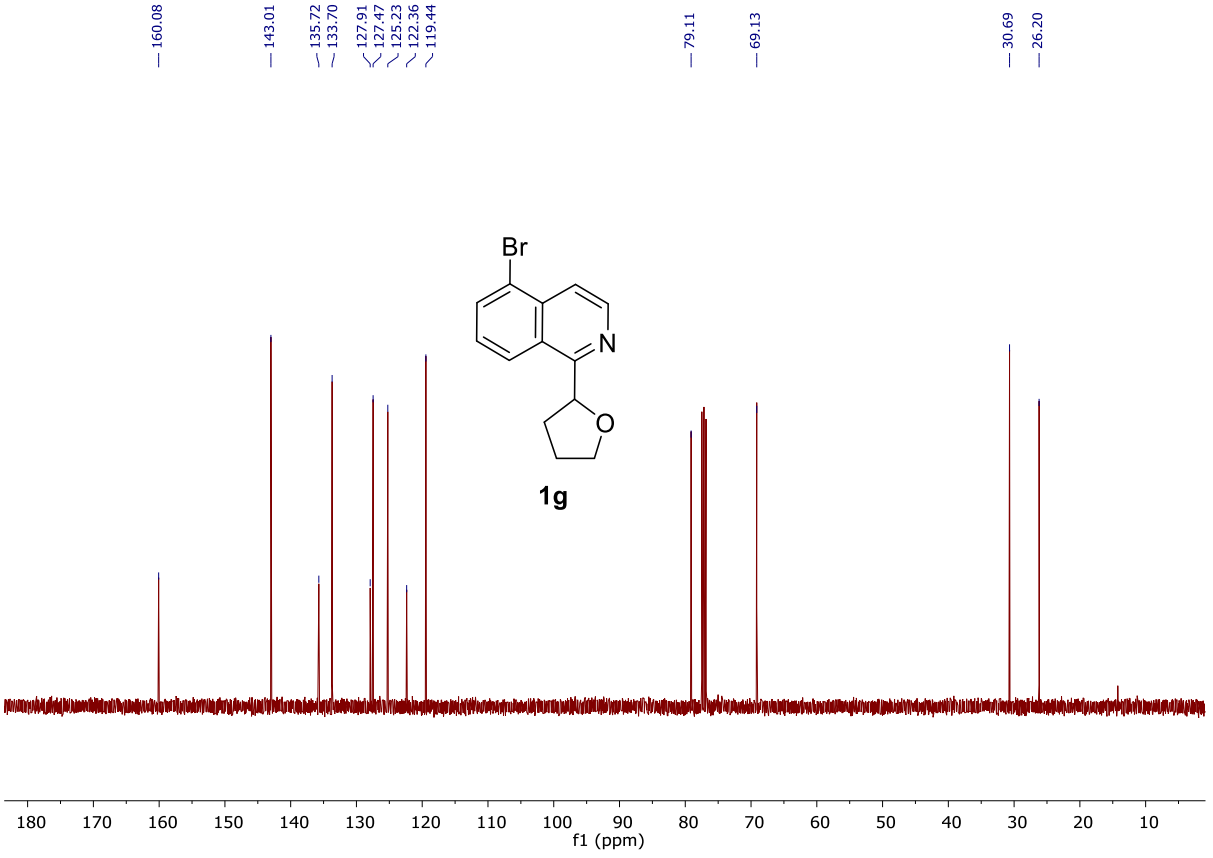
N
O
1g
f1 (ppm)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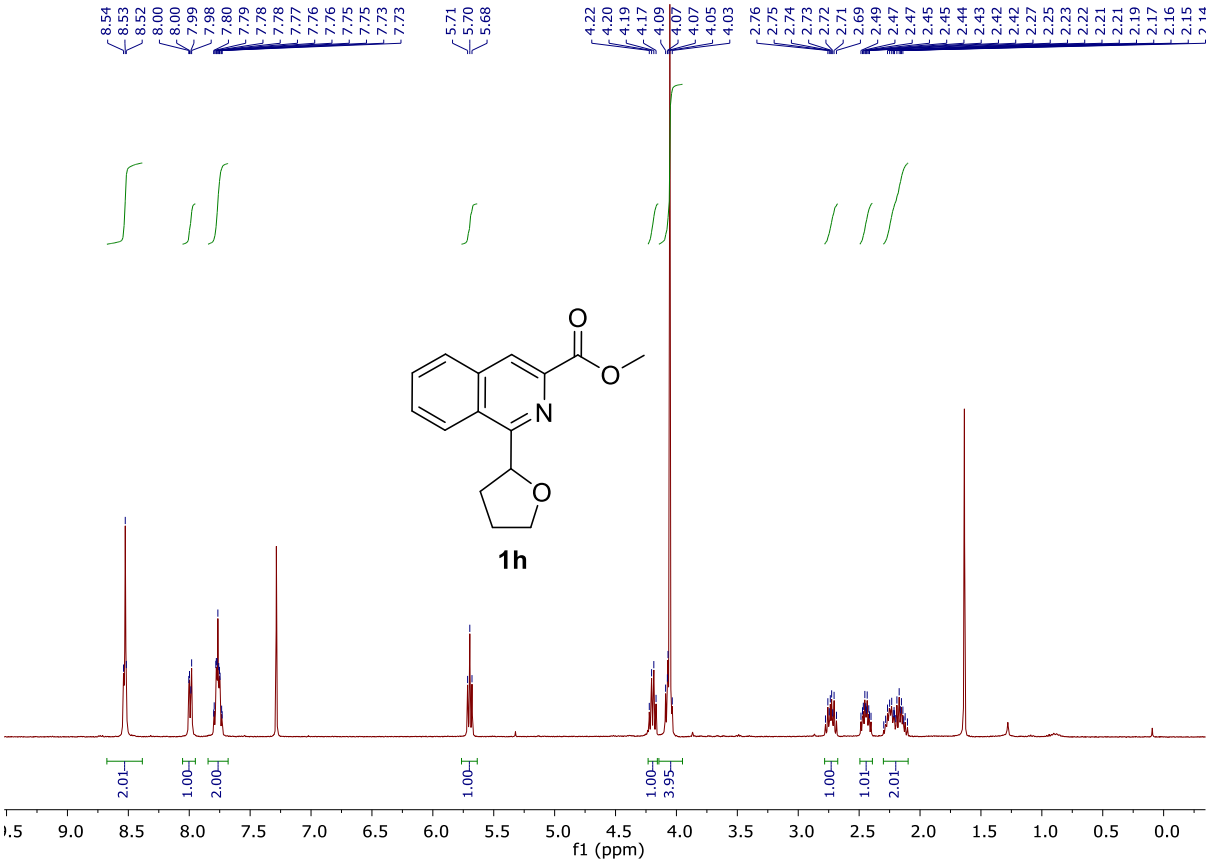
N
O
1g
f1 (ppm)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7.76
7.76
7.75
7.75
7.73
7.73
5.71
5.70
5.68
4.22
4.20
4.19
4.17
4.09
4.07
4.07
4.05
4.03
2.76
2.75
2.74
2.73
2.72
2.71
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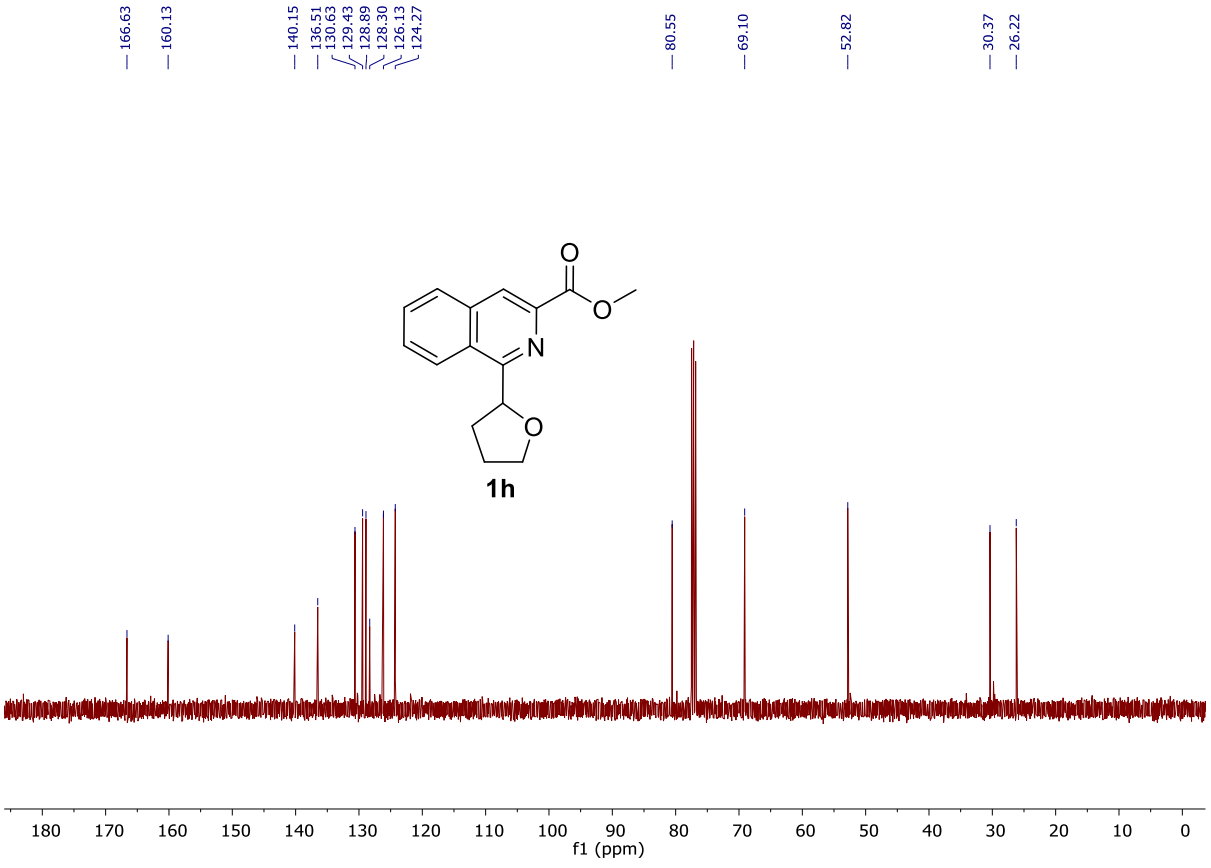
2.01
f1 (ppm)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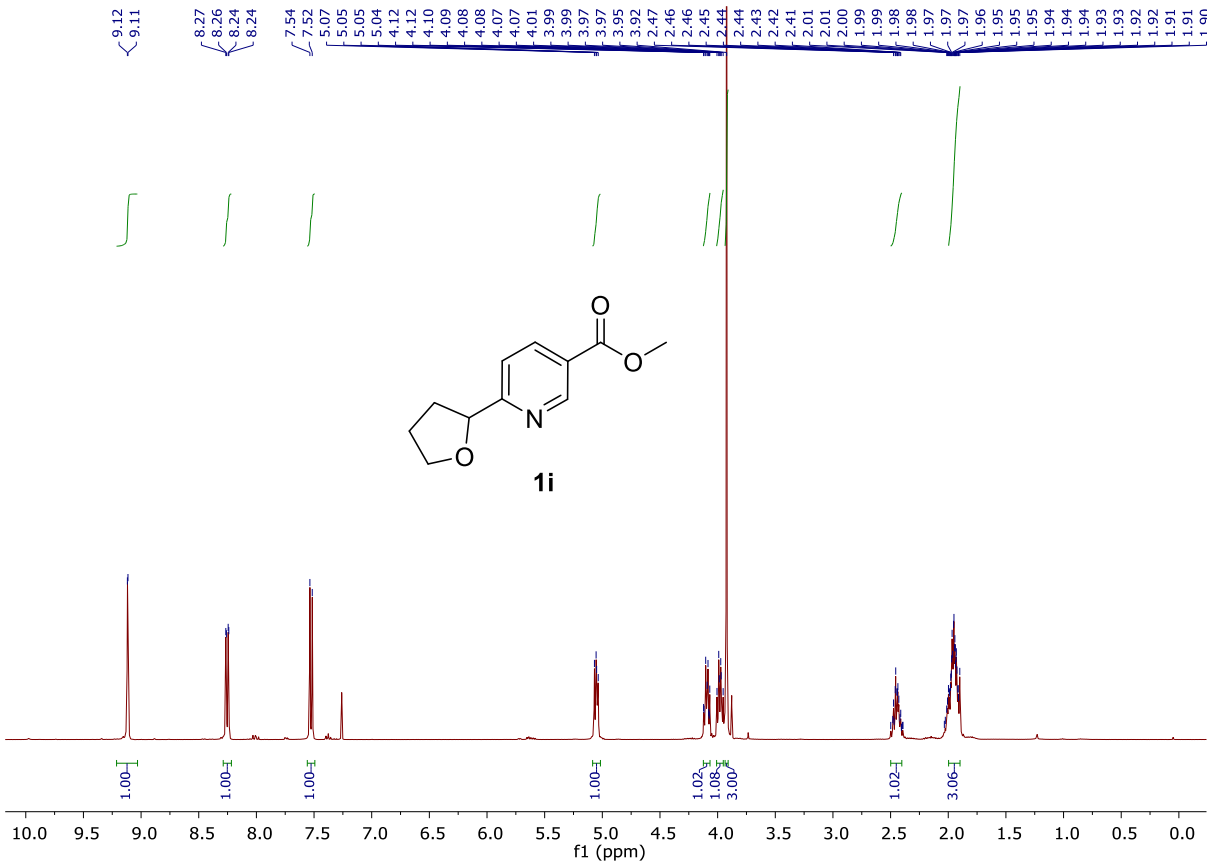
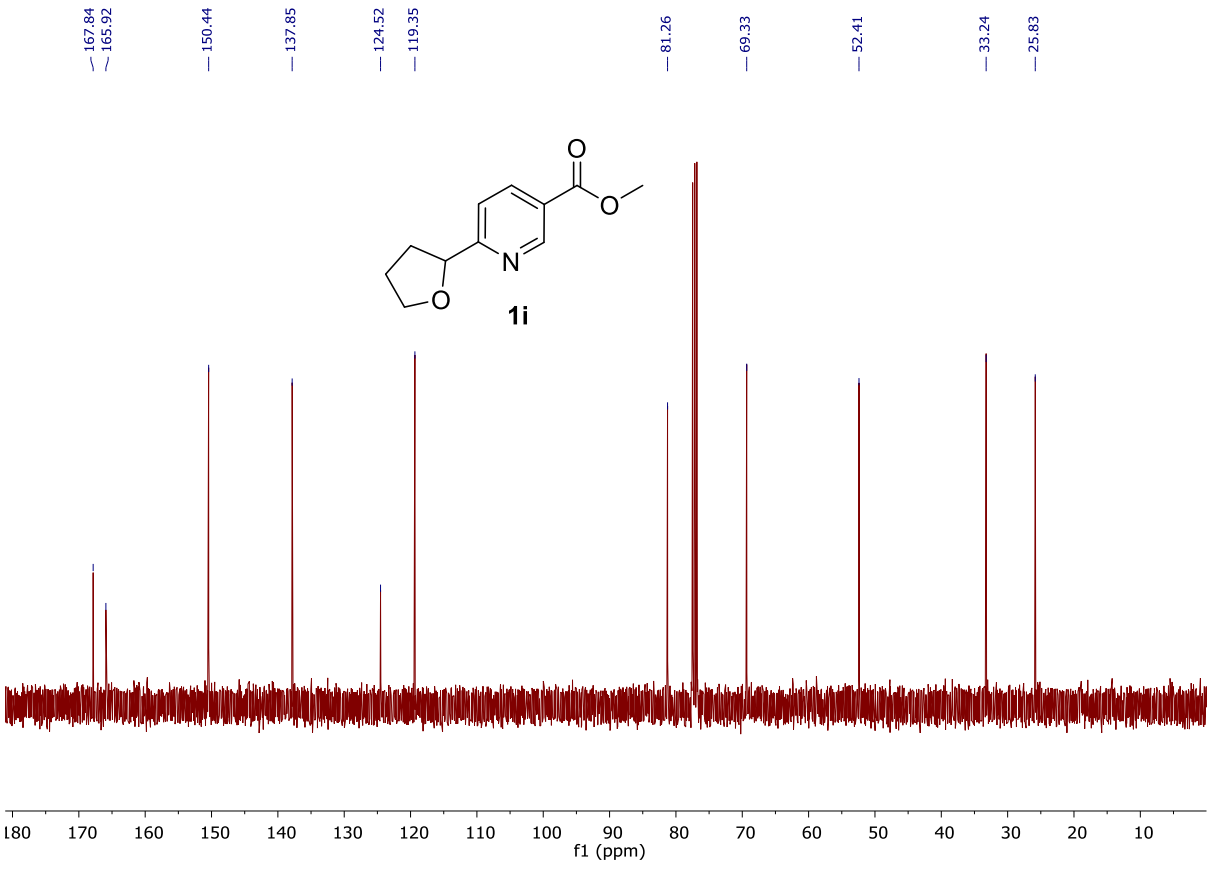
69.10
52.82
30.37
26.22
O
O
N
O
1h
f1 (ppm)


1i
f1 (ppm)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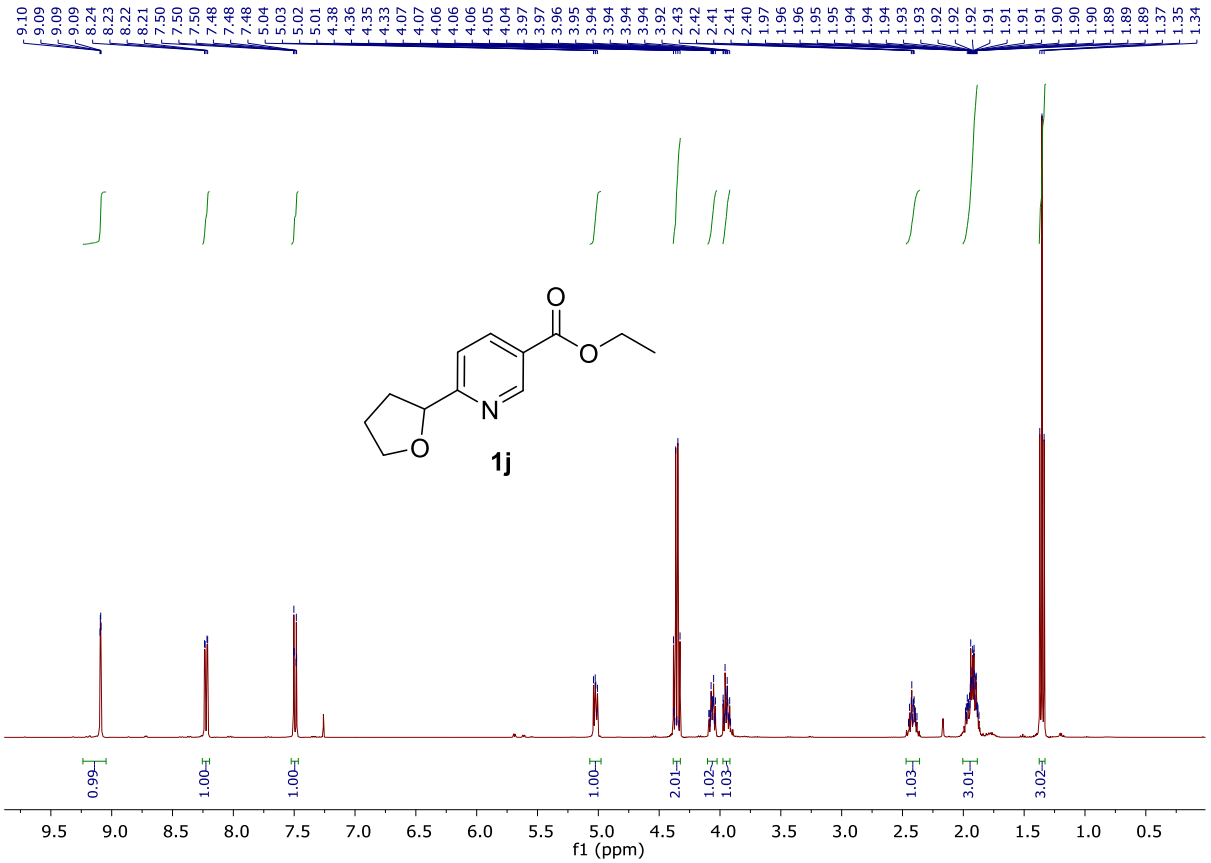
f1 (ppm)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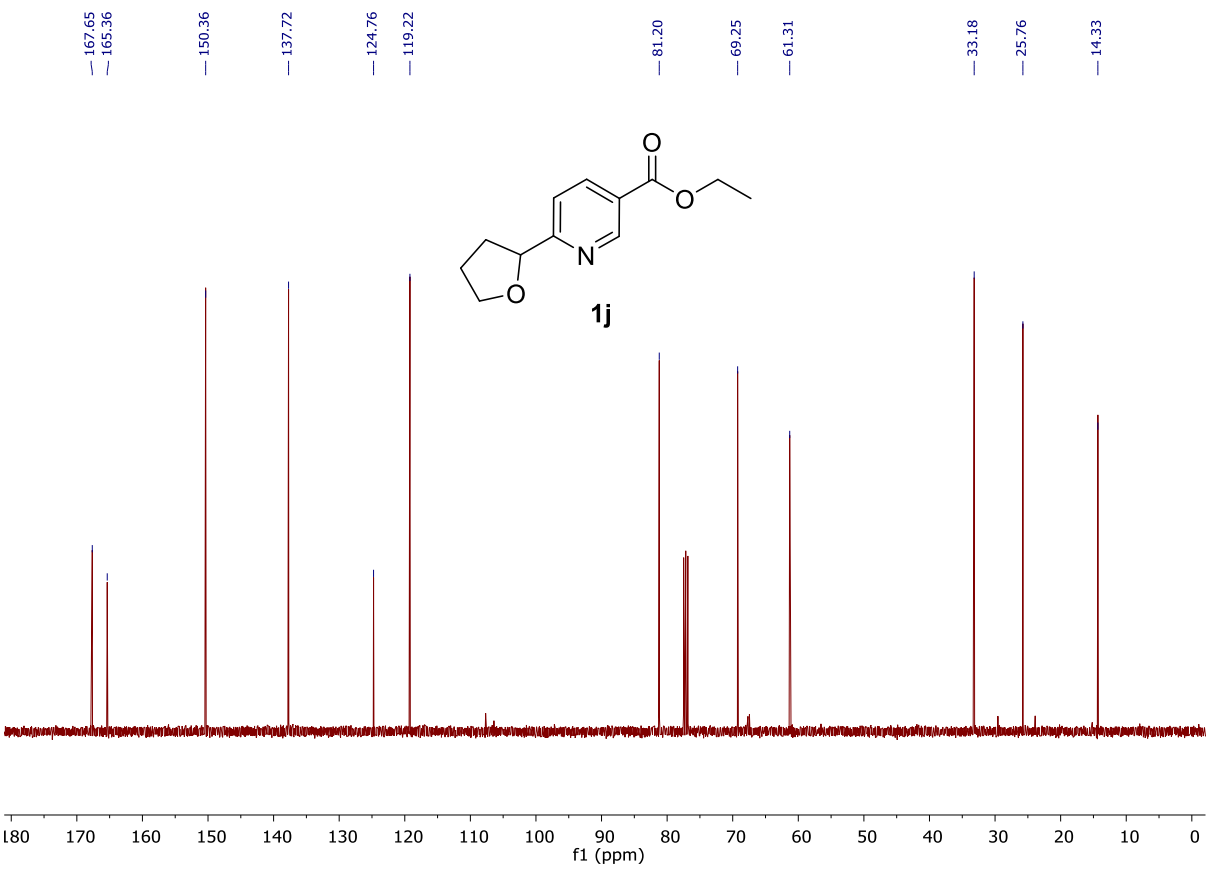
O
O
N
O
1j
0.99 1.00 1.00 1.00 2.01 1.02 1.03 1.03 3.01 3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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N
O
1j
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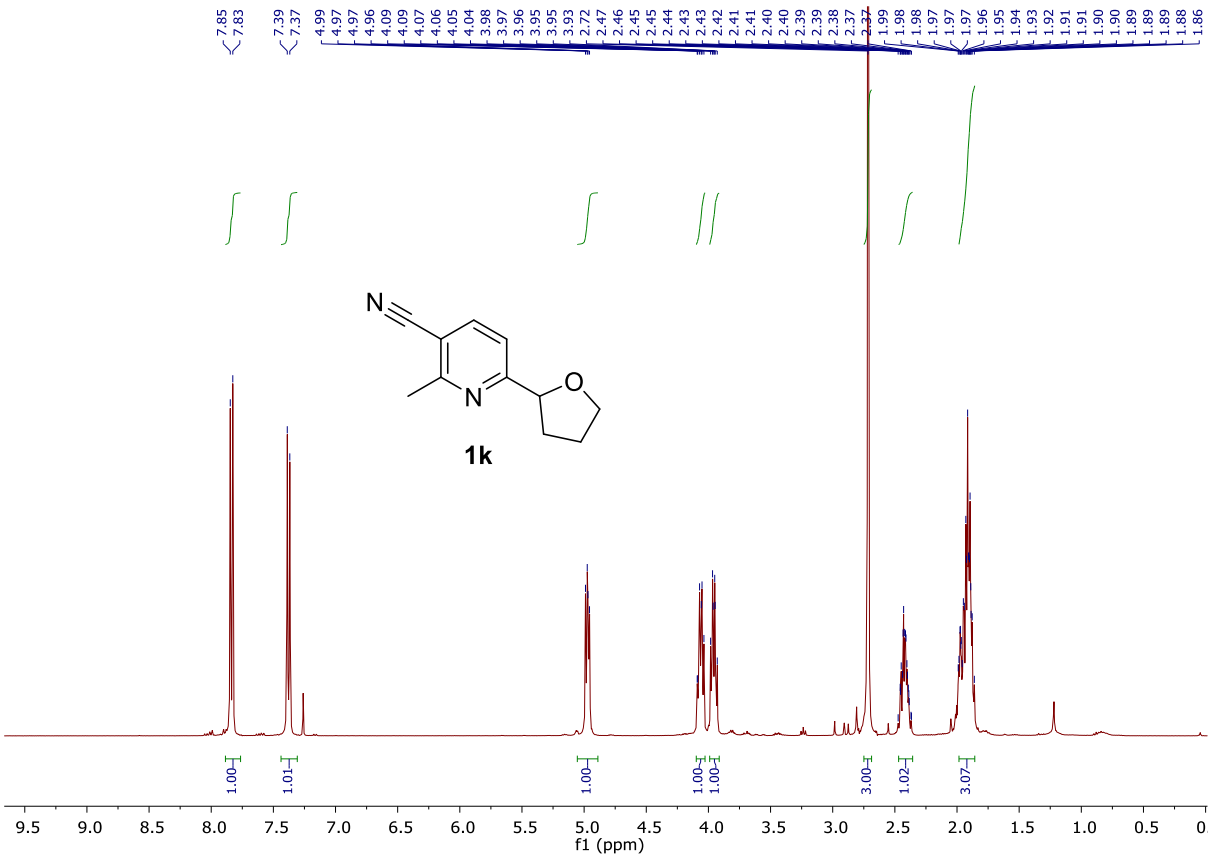
f1 (ppm)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1.00
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1.02
3.07
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6.5
6.0
5.5
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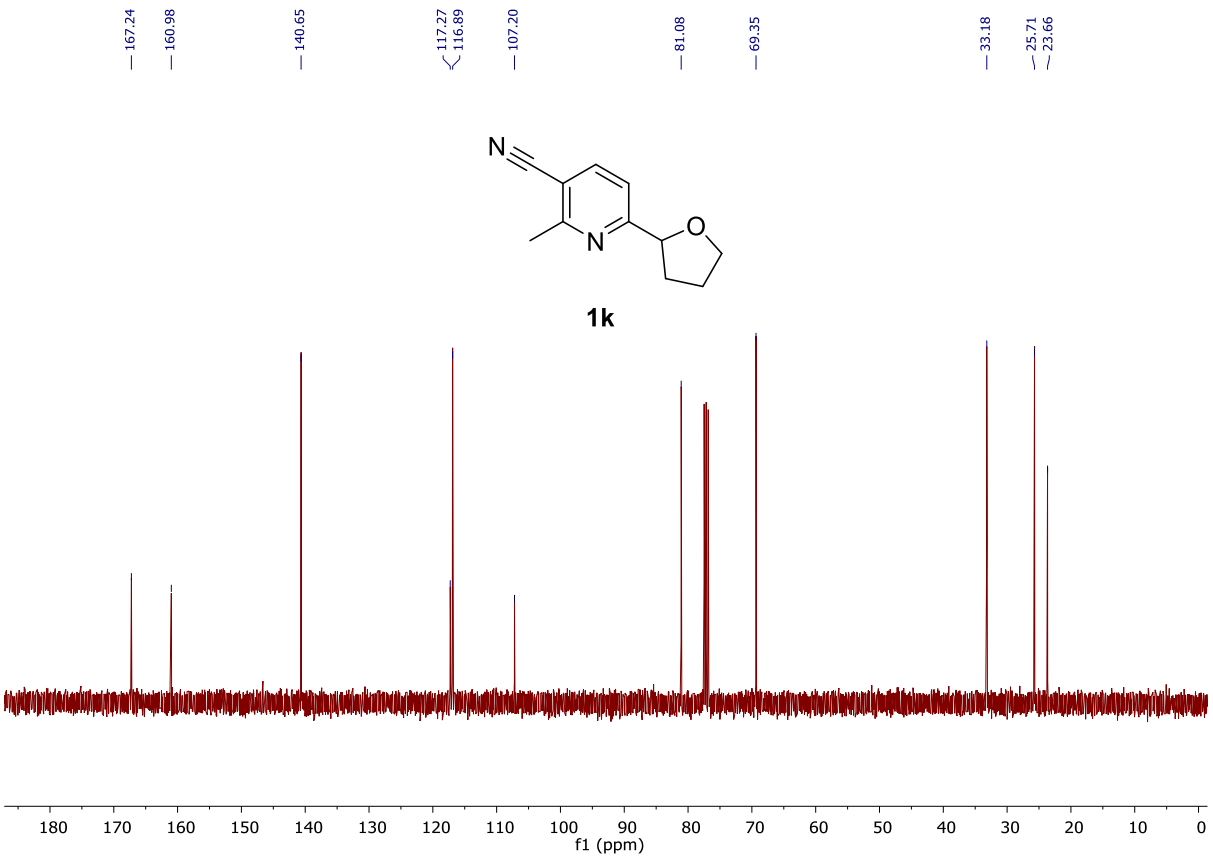
f1 (ppm)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117.27
116.89
107.20
81.08
69.35
33.18
25.71
23.66
N
O
N
1k
180
170
160
150
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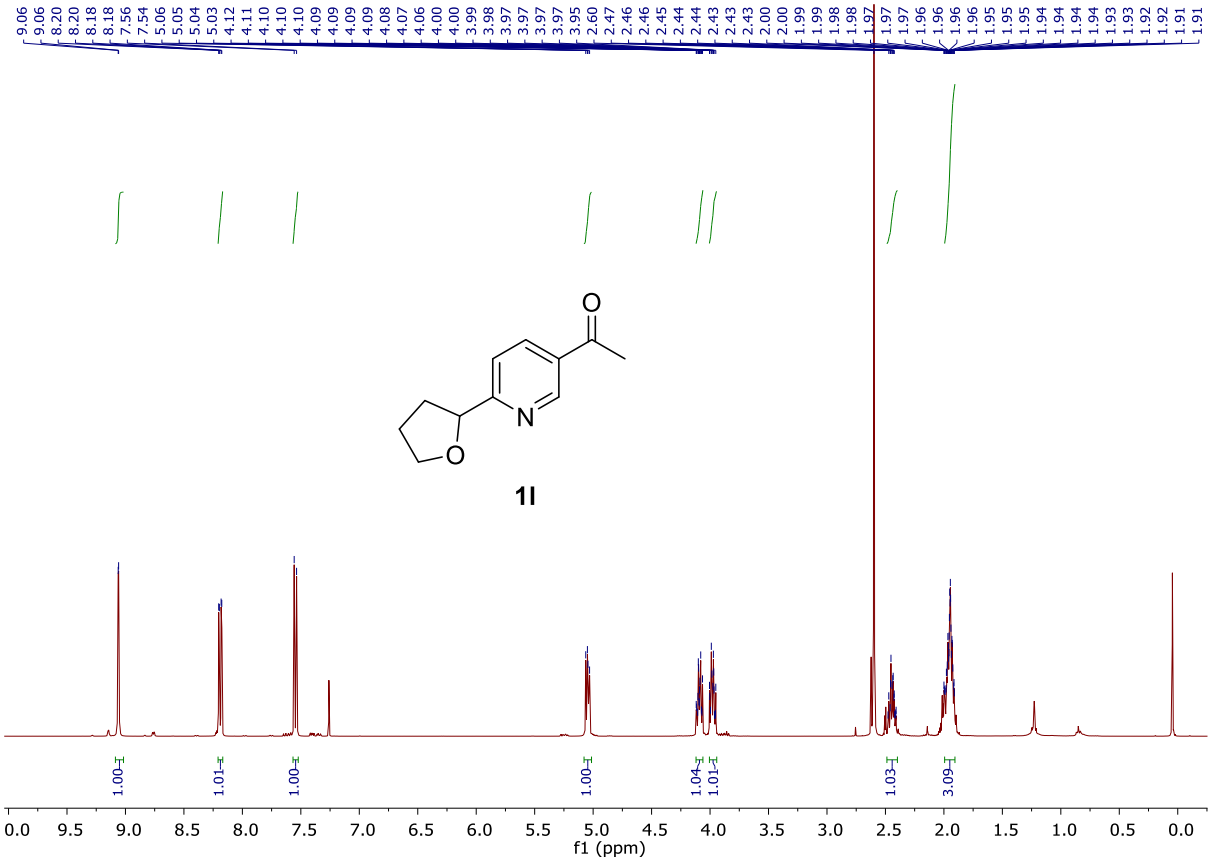
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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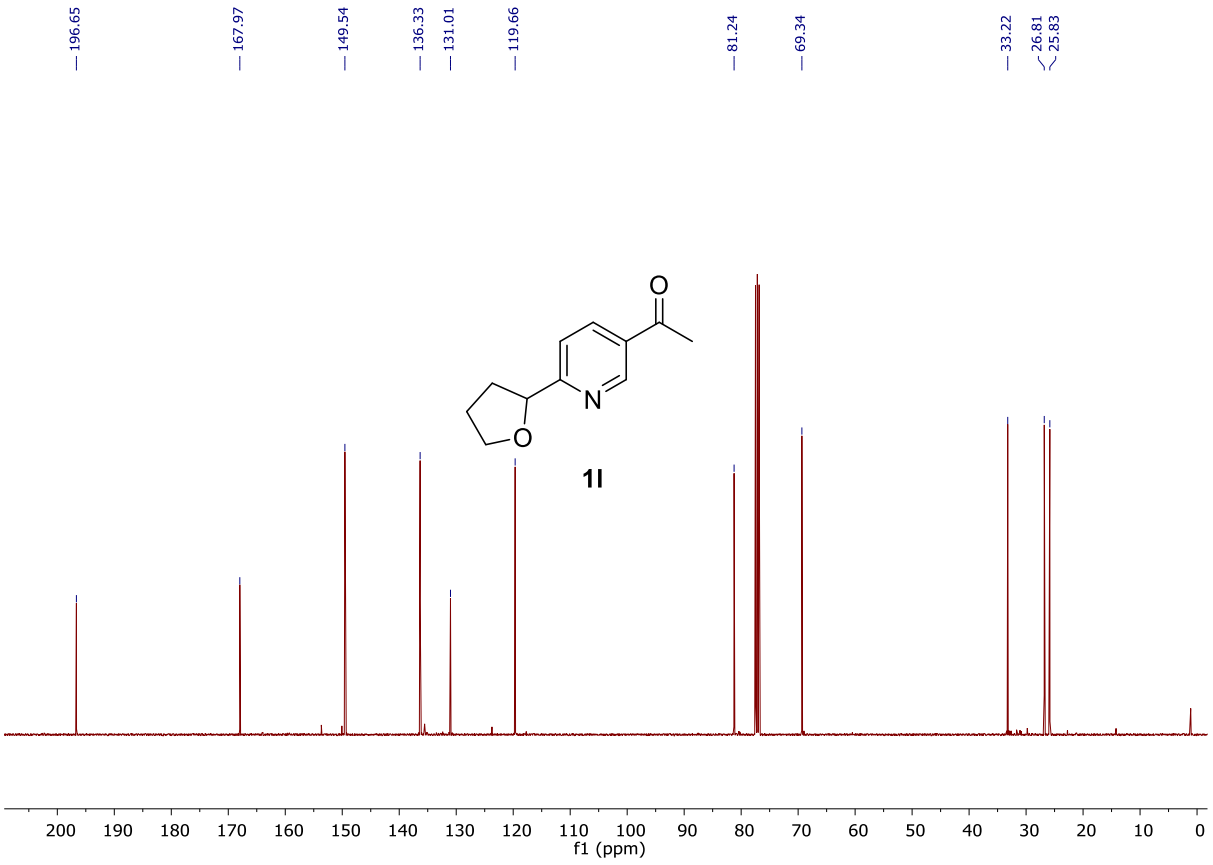
O
N
O
1l
1.00 1.01 1.00 1.00 1.04 1.01 1.03 3.09
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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O
N
O
1l
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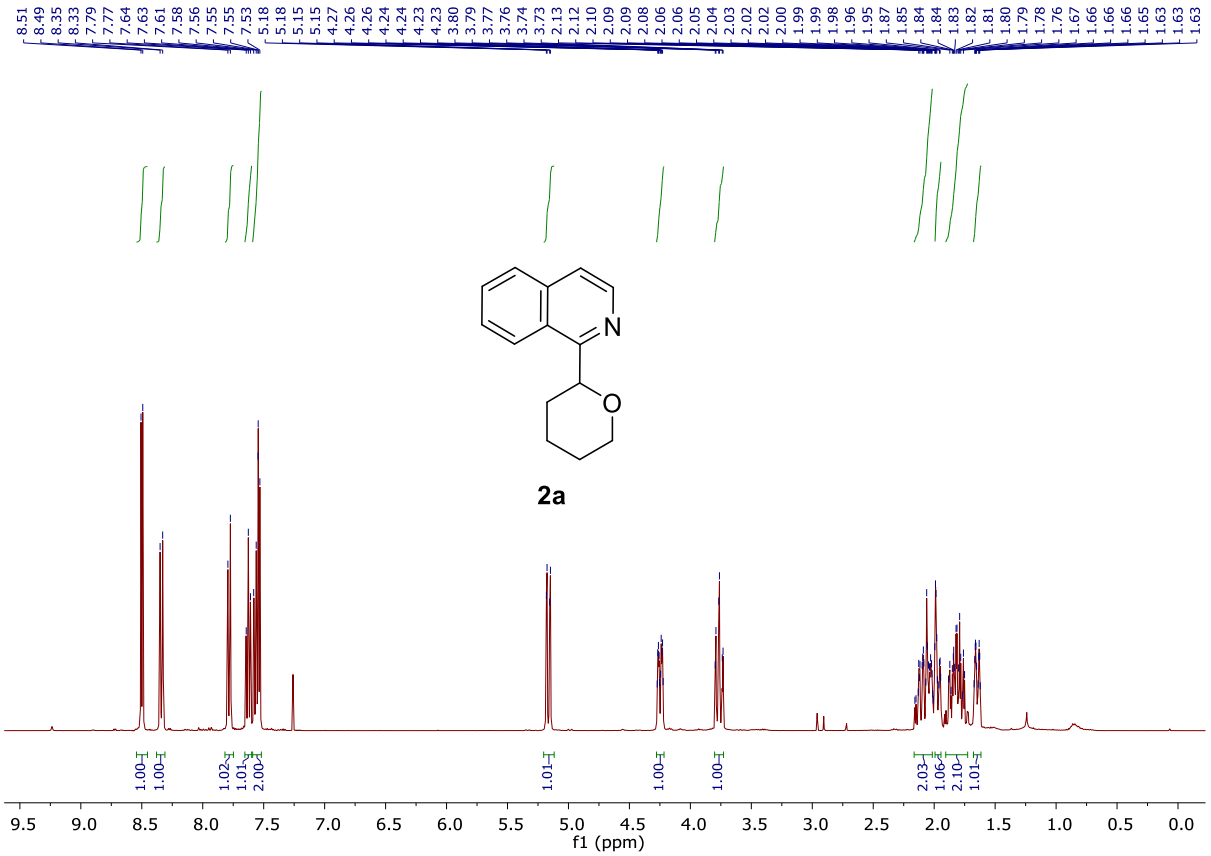
f1 (ppm)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2.00
1.01
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1.00
2.03
1.06
2.10
1.01
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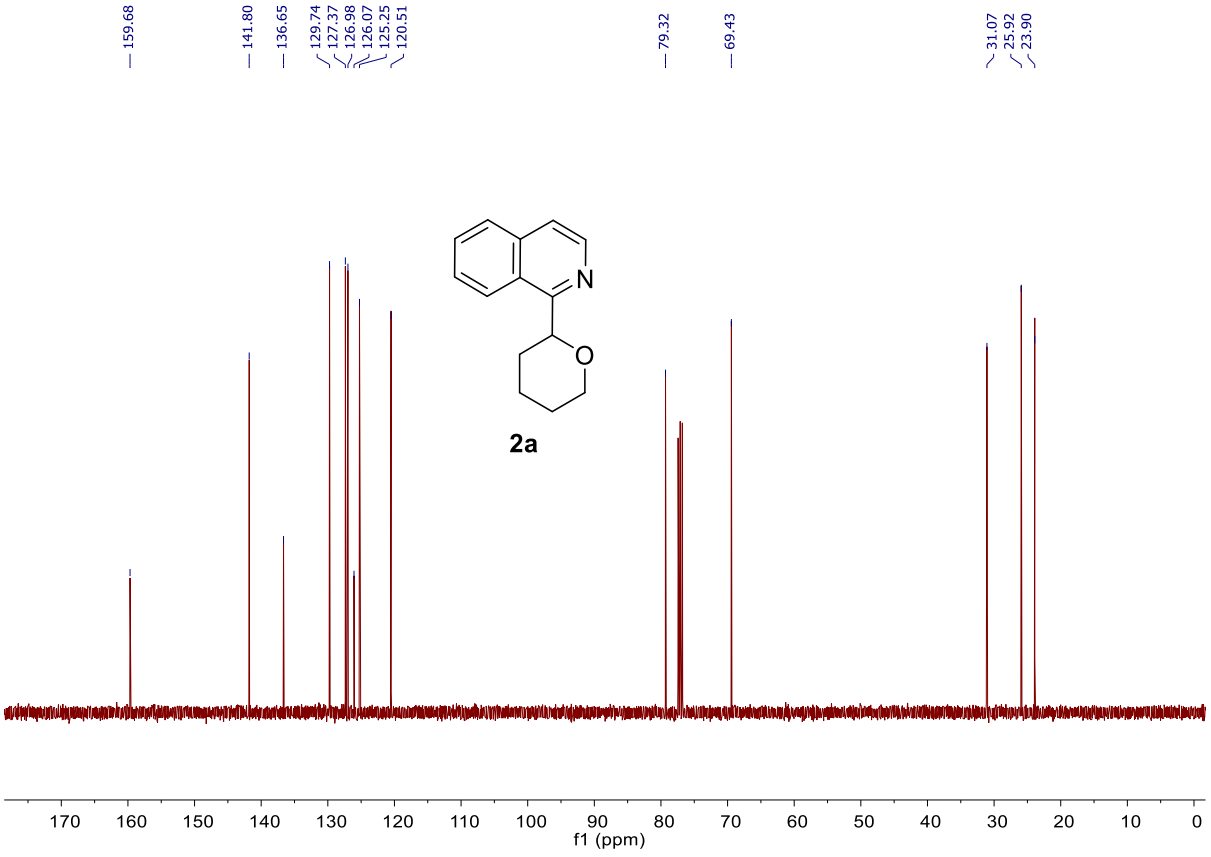
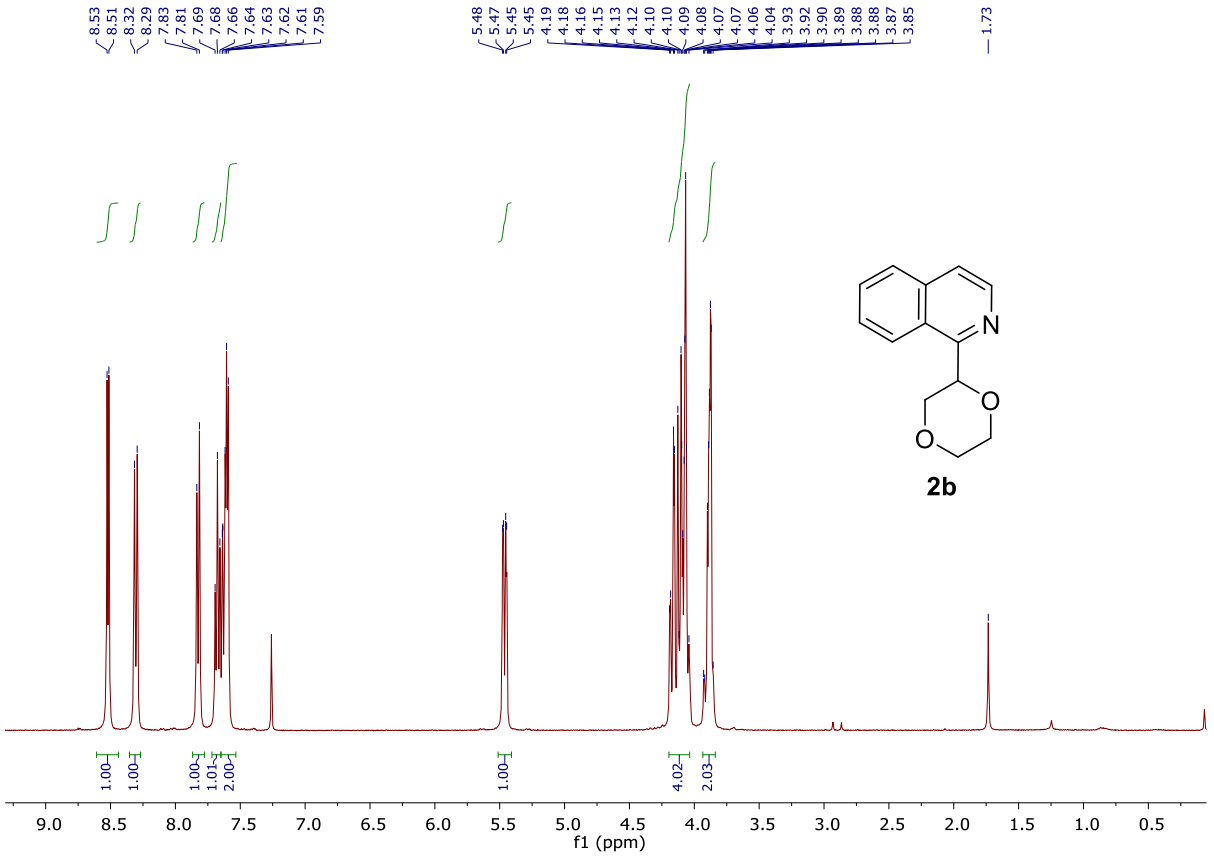
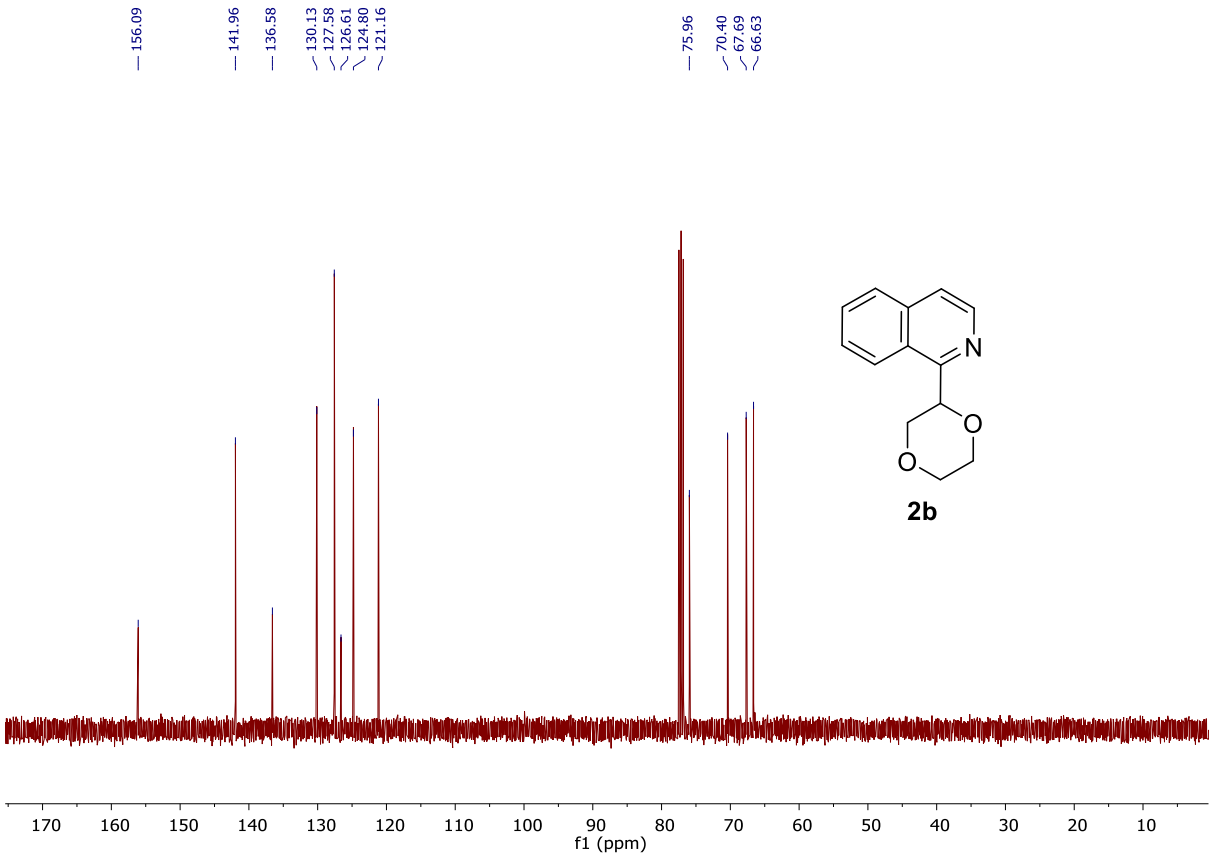
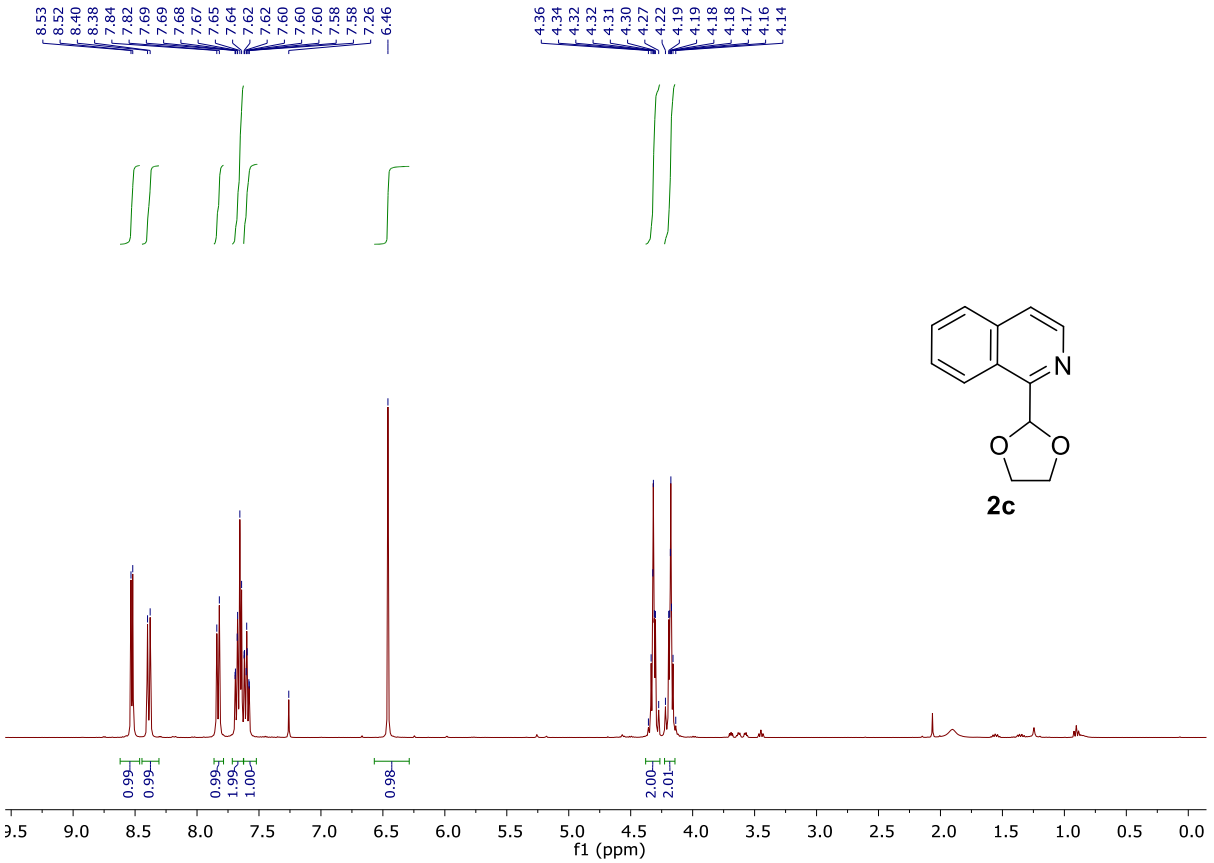
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.68
141.80
136.65
129.74
127.37
126.98
126.07
125.25
120.51
79.32
69.43
31.07
25.92
23.90
N
O
2a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

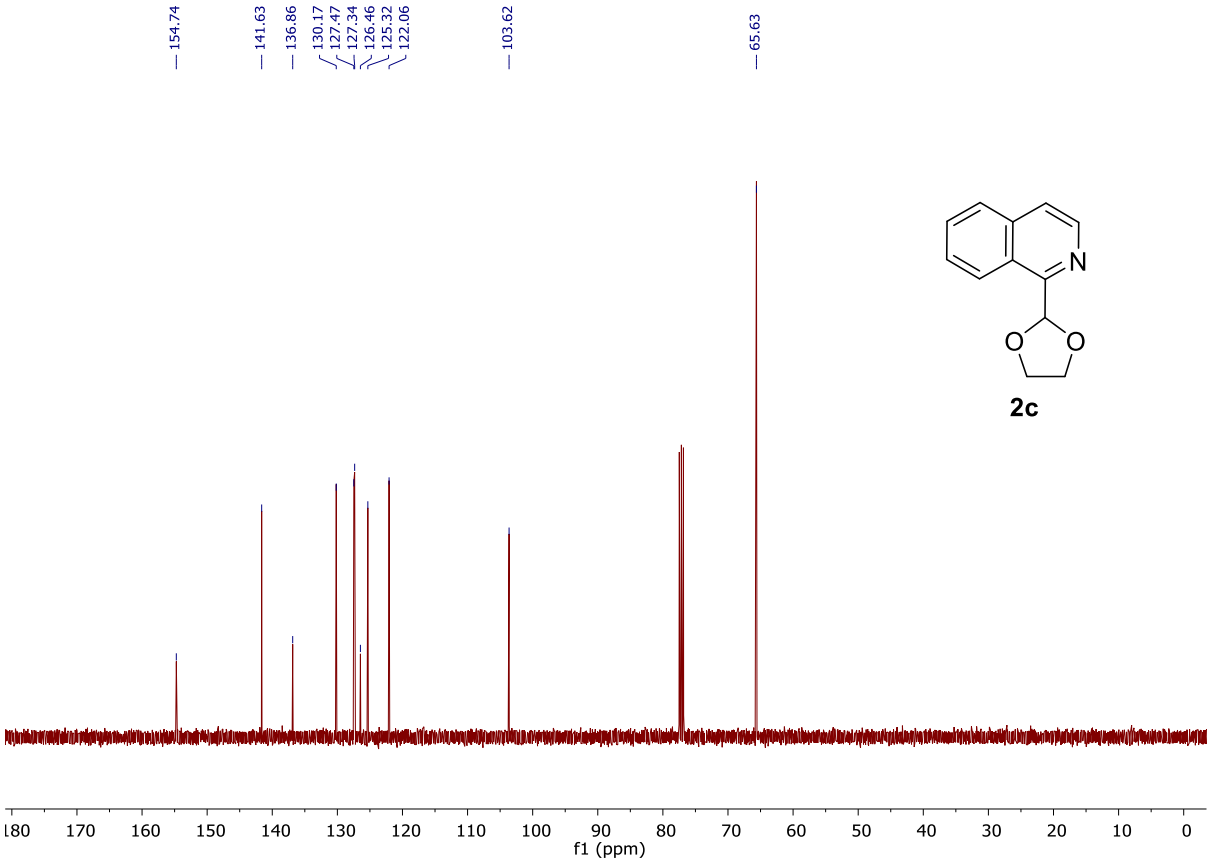

8.53
8.51
8.32
8.29
7.83
7.81
7.69
7.68
7.66
7.64
7.63
7.62
7.61
7.59
5.48
5.47
5.45
5.45
4.19
4.18
4.16
4.15
4.13
4.12
4.10
4.10
4.09
4.08
4.07
4.07
4.06
4.04
3.93
3.92
3.90
3.89
3.88
3.88
3.87
3.85
1.73
1.00
1.00
1.00
1.01
2.00
1.00
4.02
2.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
N
O
O
2b


156.09
141.96
136.58
130.13
127.58
126.61
124.80
121.16
75.96
70.40
67.69
66.63
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
N
O
O
2b


8.53
8.52
8.40
8.38
7.84
7.82
7.69
7.69
7.68
7.67
7.65
7.64
7.62
7.62
7.60
7.60
7.60
7.58
7.58
7.26
6.46
4.36
4.34
4.32
4.32
4.31
4.30
4.27
4.22
4.19
4.19
4.18
4.18
4.17
4.16
4.14
0.99
0.99
0.99
1.99
1.00
0.98
2.00
2.01
f1 (ppm)

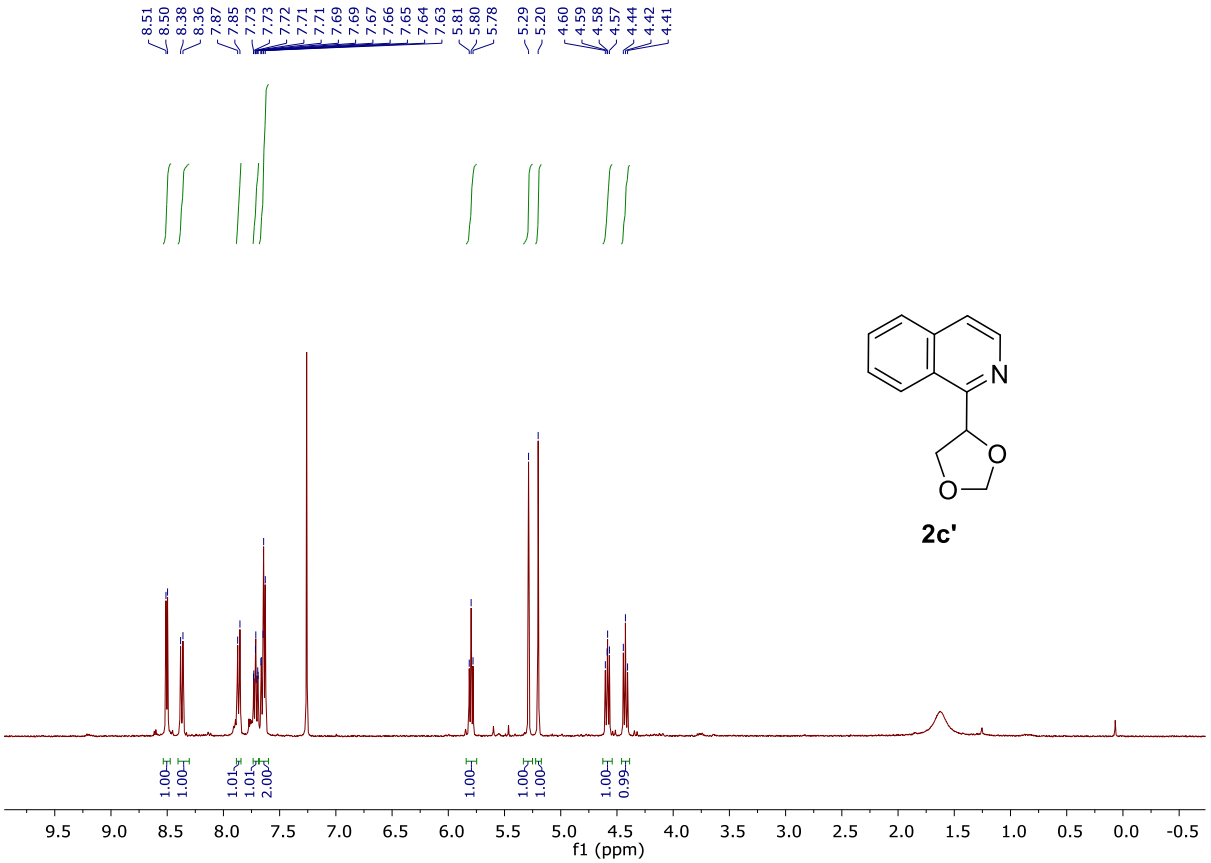


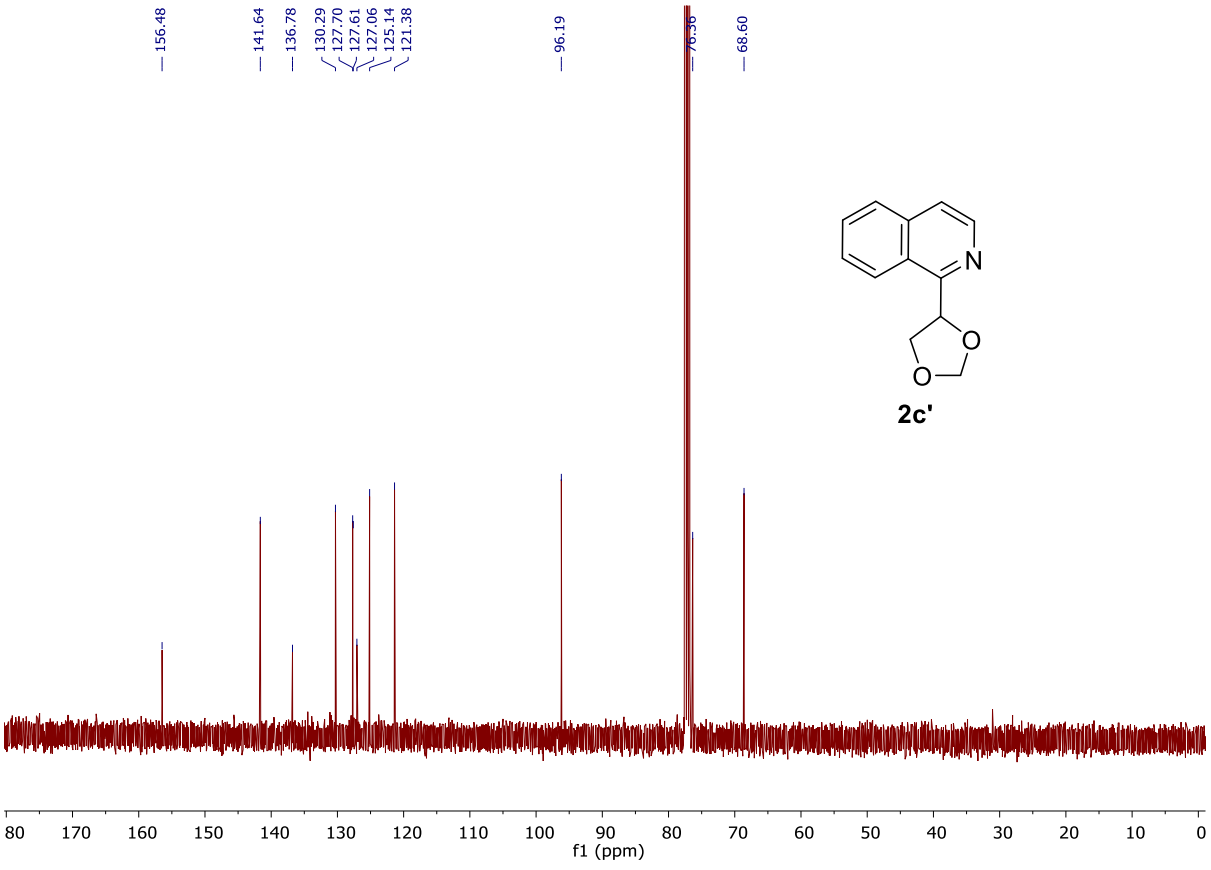
**2c**

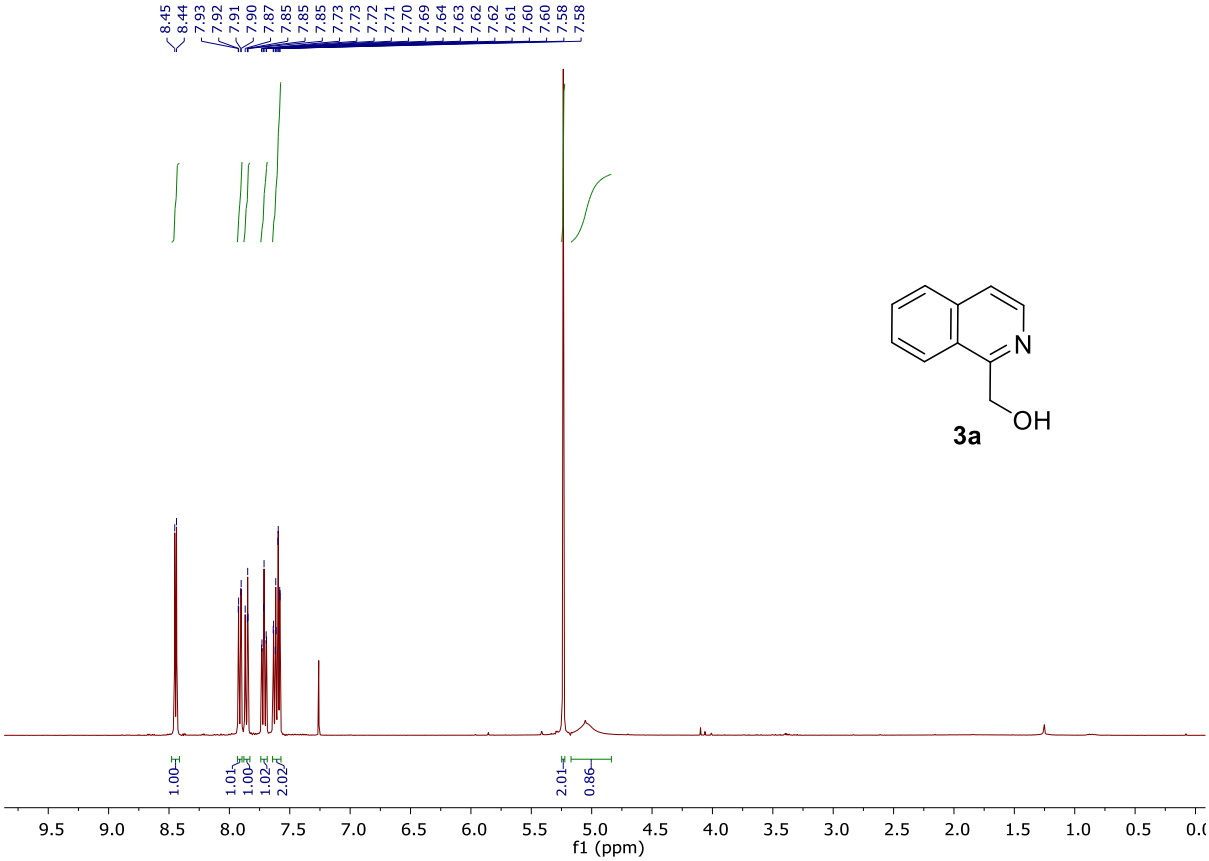

154.74
141.63
136.86
130.17
127.47
127.34
126.46
125.32
122.06
103.62
65.63
f1 (ppm)

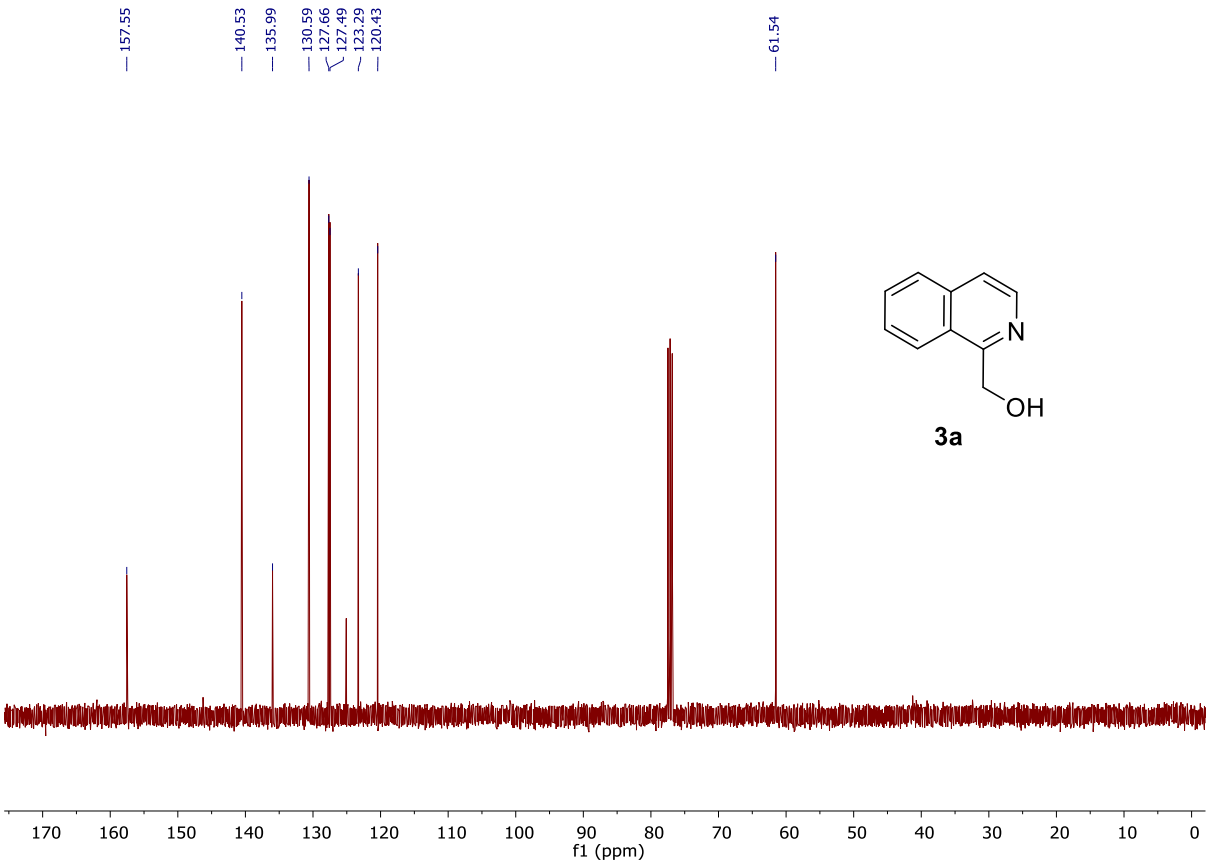


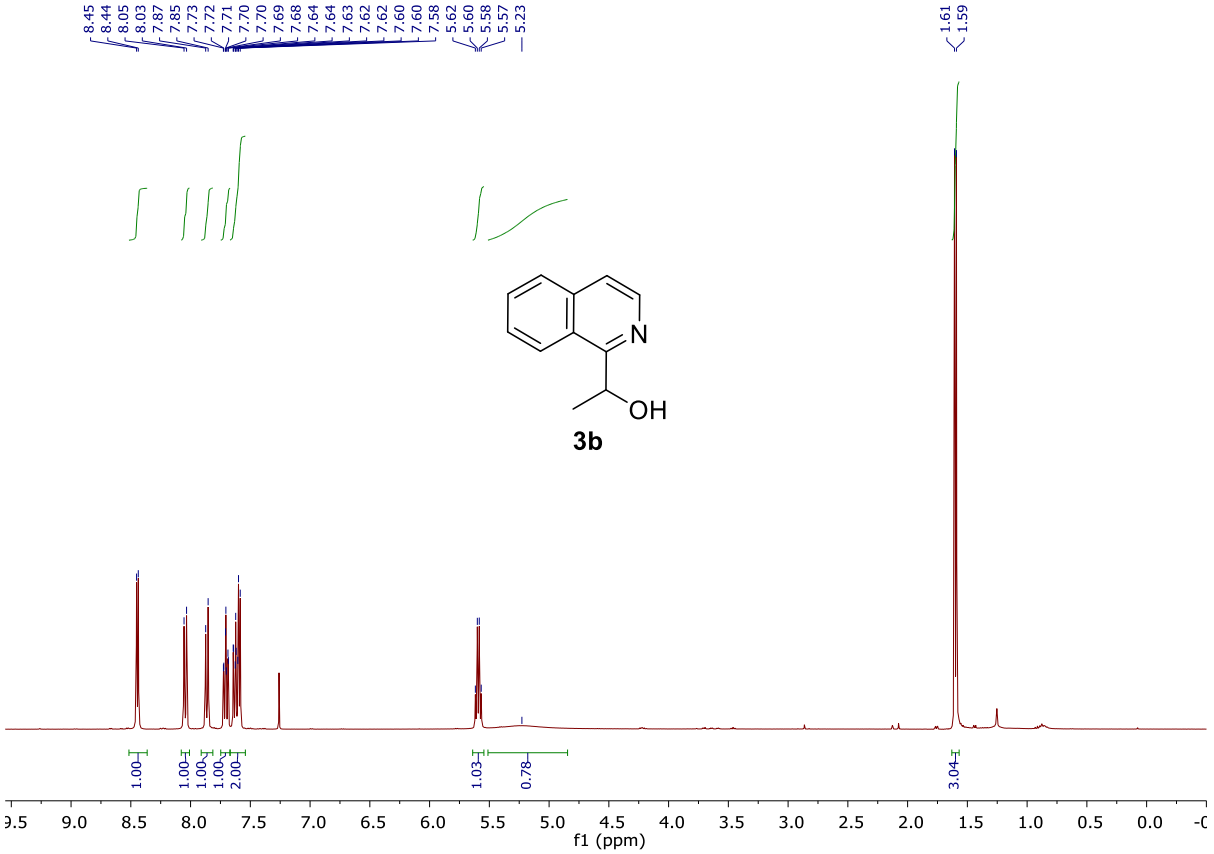
**2c**

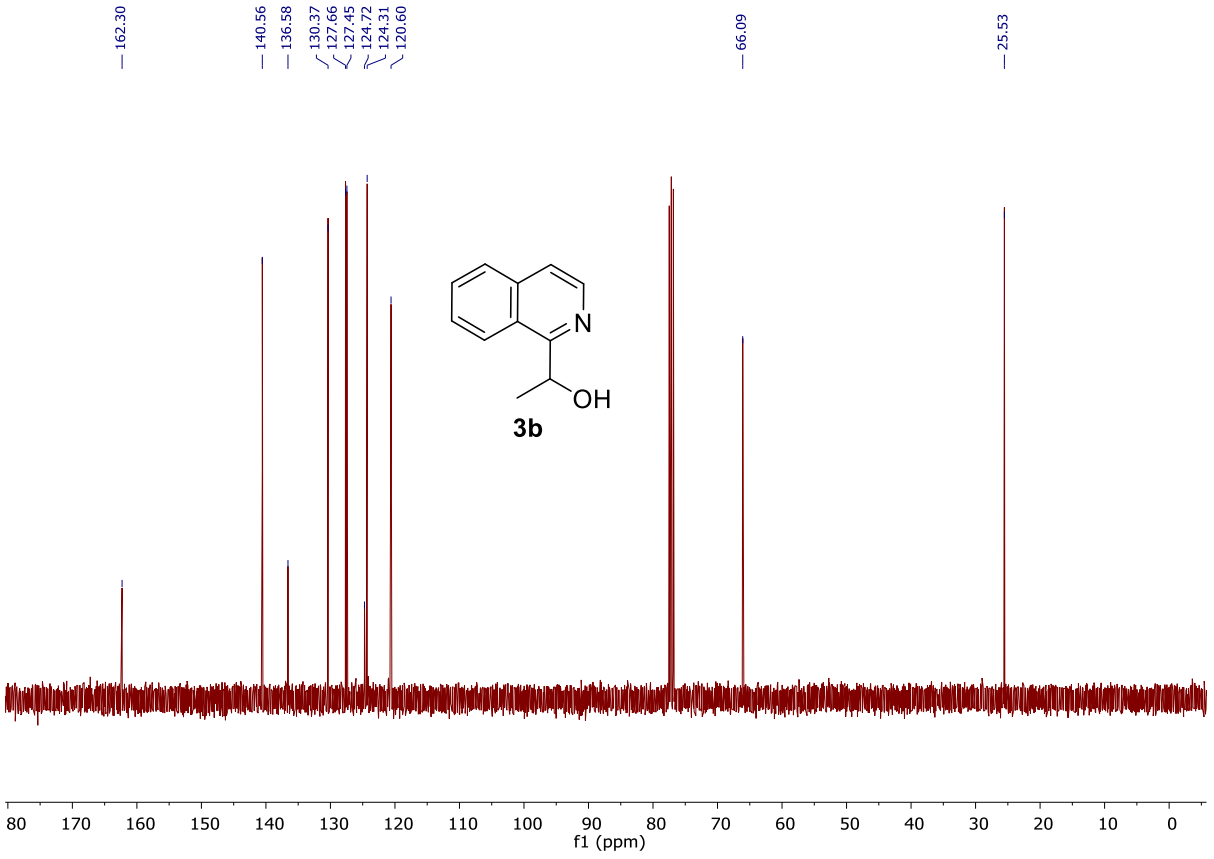

8.51
8.50
8.38
8.36
7.87
7.85
7.73
7.73
7.72
7.71
7.71
7.69
7.69
7.67
7.66
7.65
7.64
7.63
5.81
5.80
5.78
5.29
5.20
4.60
4.59
4.58
4.57
4.44
4.42
4.41
1.00
1.00
1.01
1.01
2.00
1.00
1.00
1.00
1.00
0.99
N
O
O
2c'
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

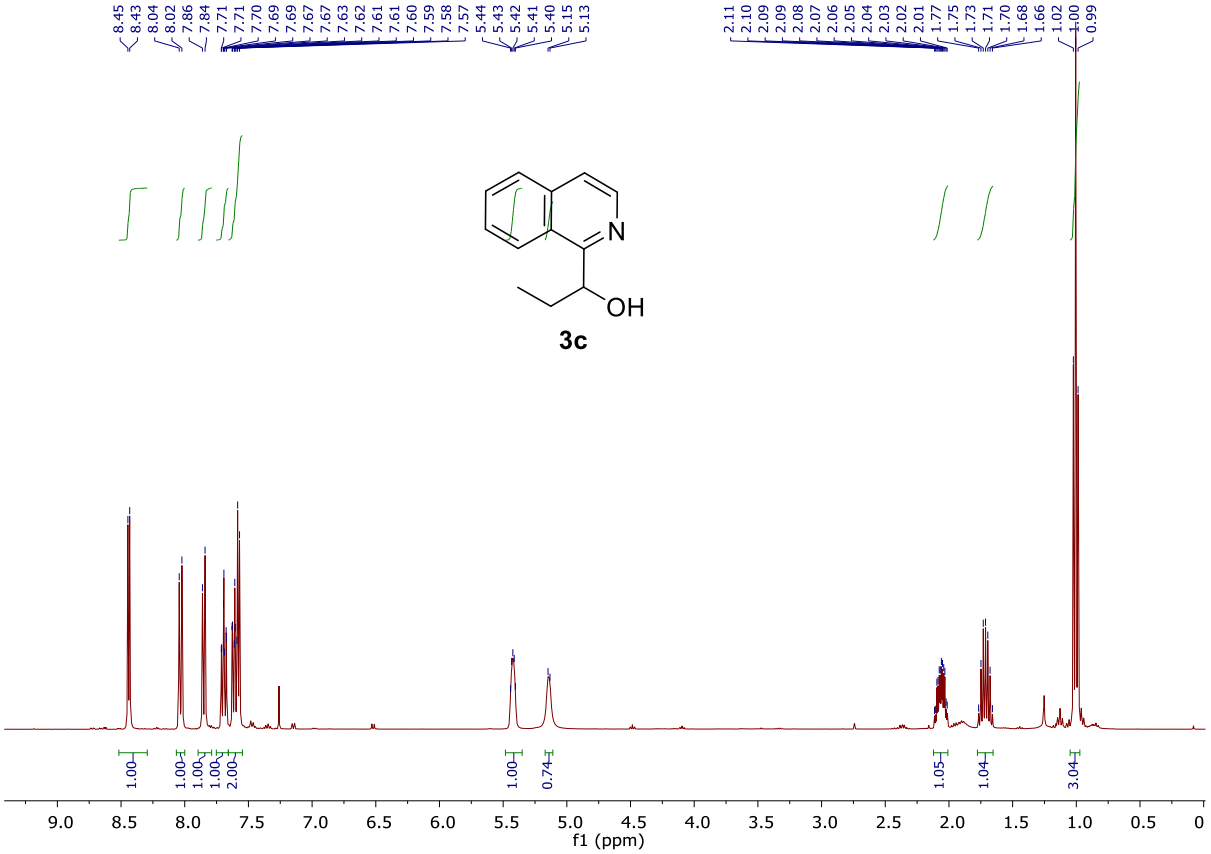

156.48
141.64
136.78
130.29
127.70
127.61
127.06
125.14
121.38
96.19
76.36
68.60
N
O
O
2c'
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

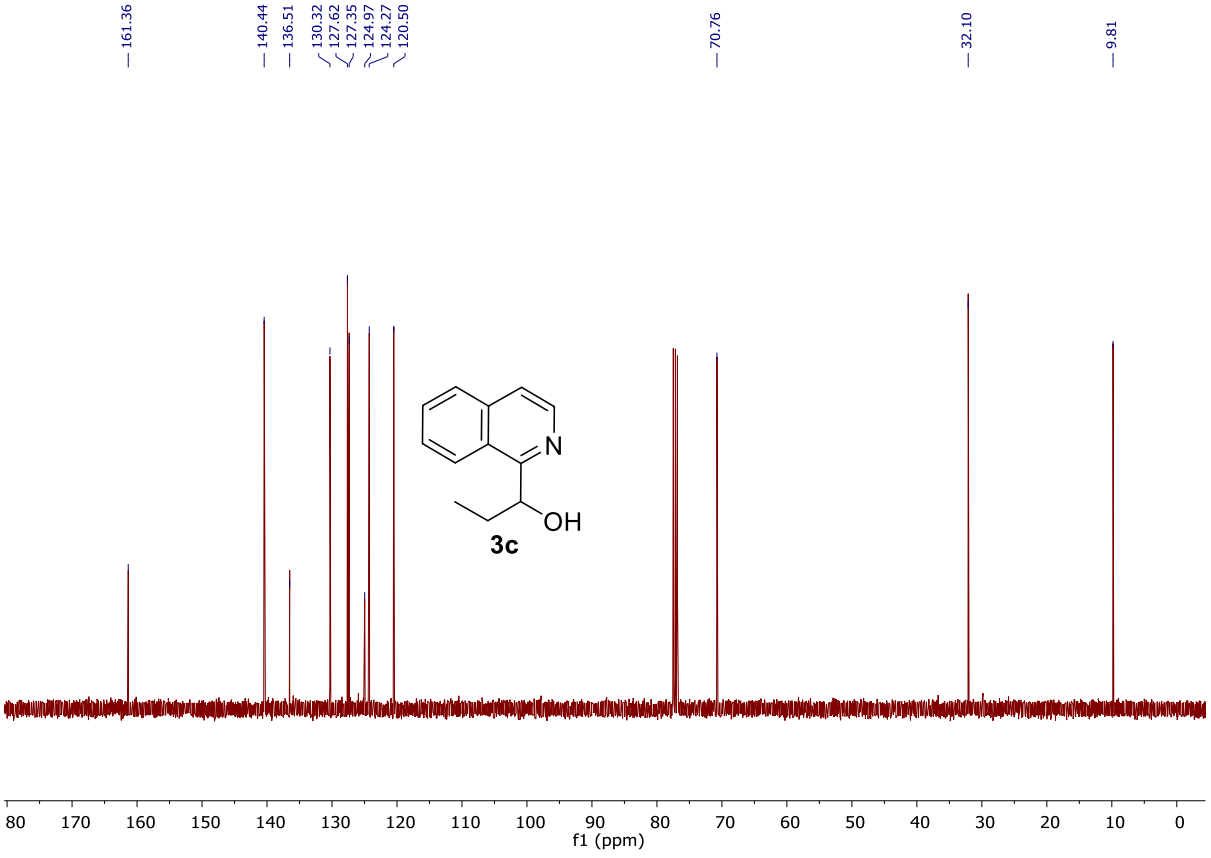

8.45
8.44
7.93
7.92
7.91
7.90
7.87
7.85
7.85
7.85
7.73
7.73
7.72
7.71
7.70
7.69
7.64
7.63
7.62
7.62
7.61
7.60
7.60
7.58
7.58
1.00
1.01
1.00
1.02
2.02
2.01
0.86
N
OH
3a
f1 (ppm)

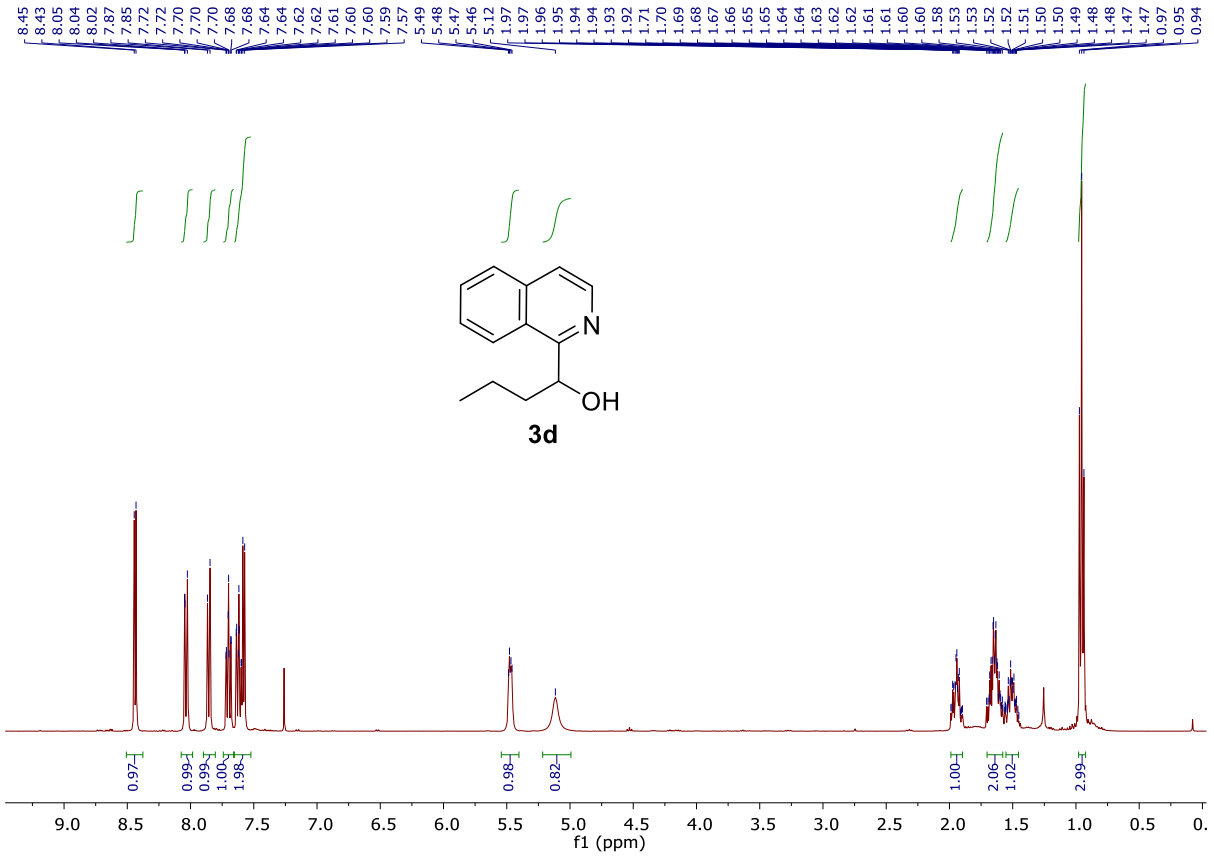

157.55
140.53
135.99
130.59
127.66
127.49
123.29
120.43
61.54
N
OH
3a
f1 (ppm)

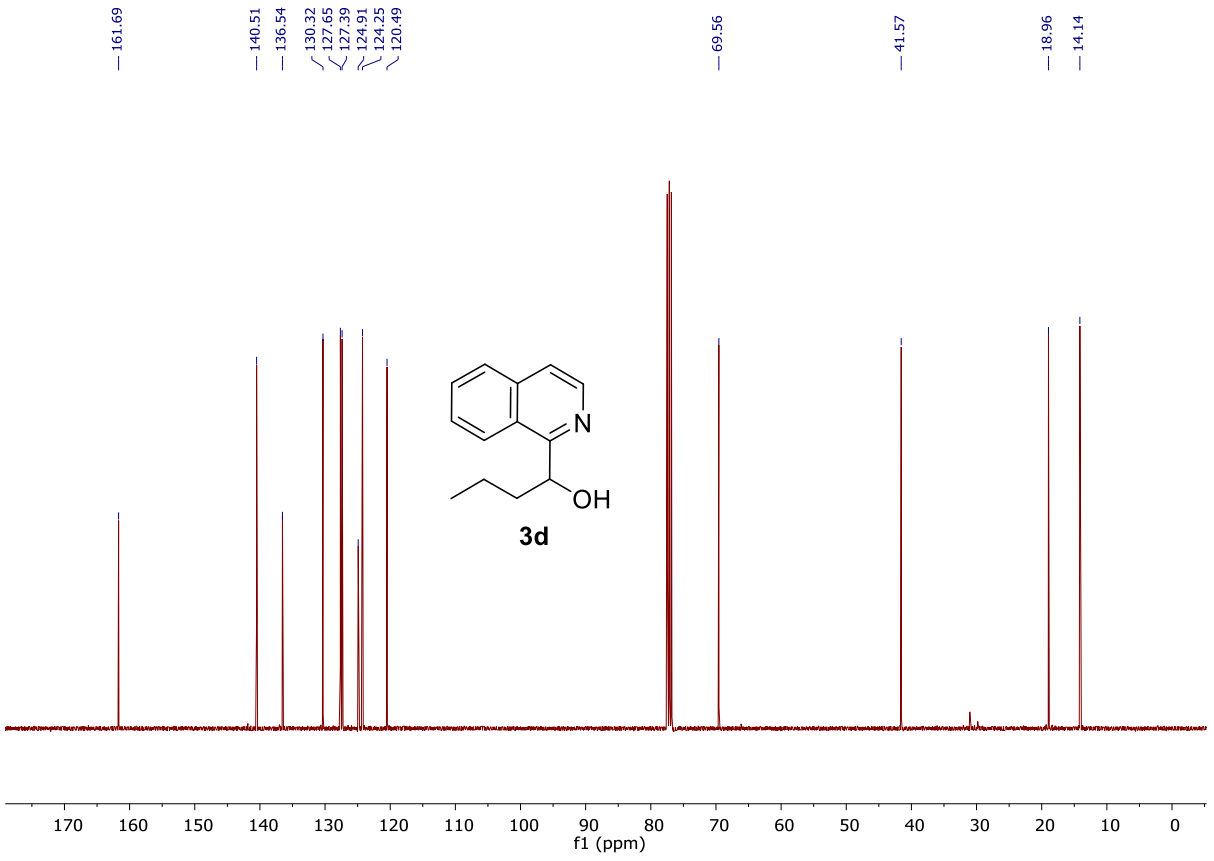

8.45
8.44
8.05
8.03
7.87
7.85
7.73
7.72
7.71
7.70
7.70
7.69
7.68
7.64
7.64
7.63
7.62
7.62
7.60
7.60
7.58
5.62
5.60
5.58
5.57
5.23
1.61
1.59
N
OH
3b
1.00
1.00
1.00
1.00
2.00
1.03
0.78
3.04
f1 (ppm)

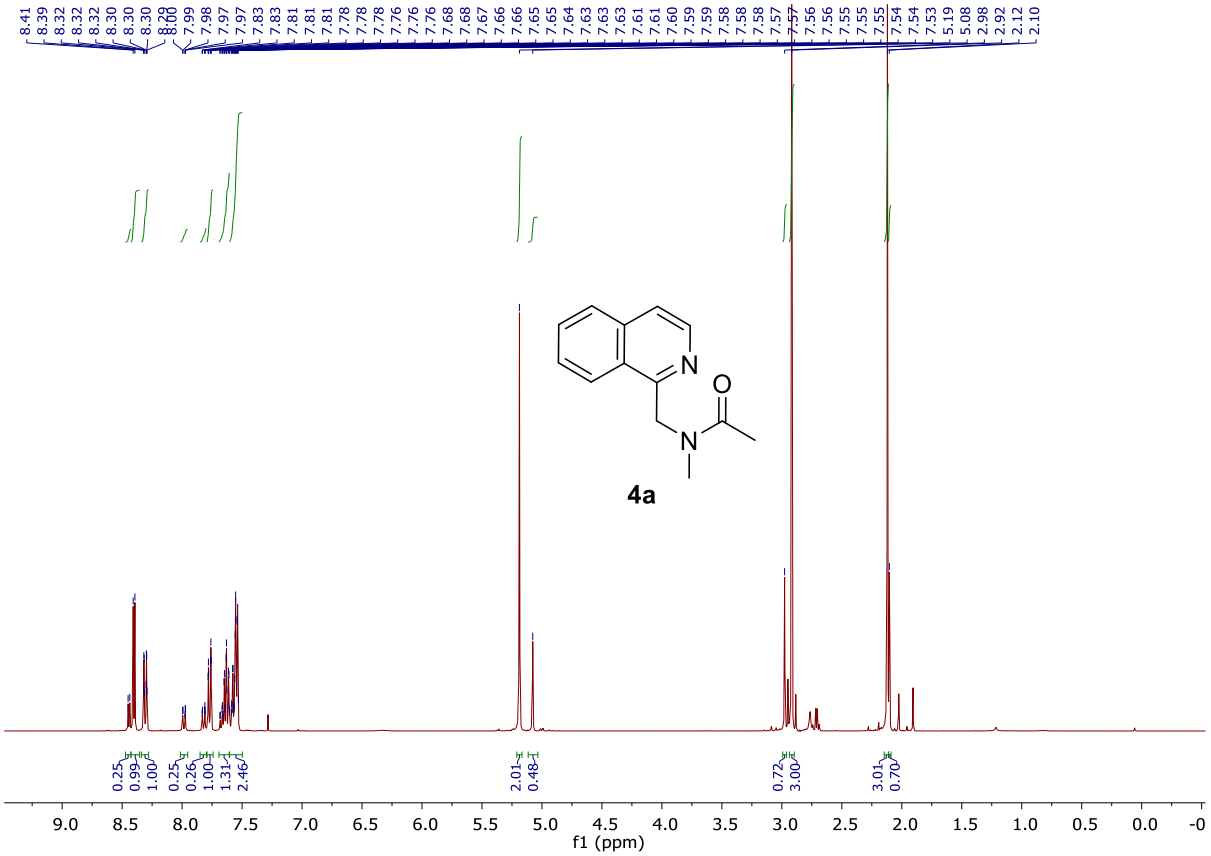

162.30
140.56
136.58
130.37
127.66
127.45
124.72
124.31
120.60
66.09
25.53
N
OH
3b
f1 (ppm)

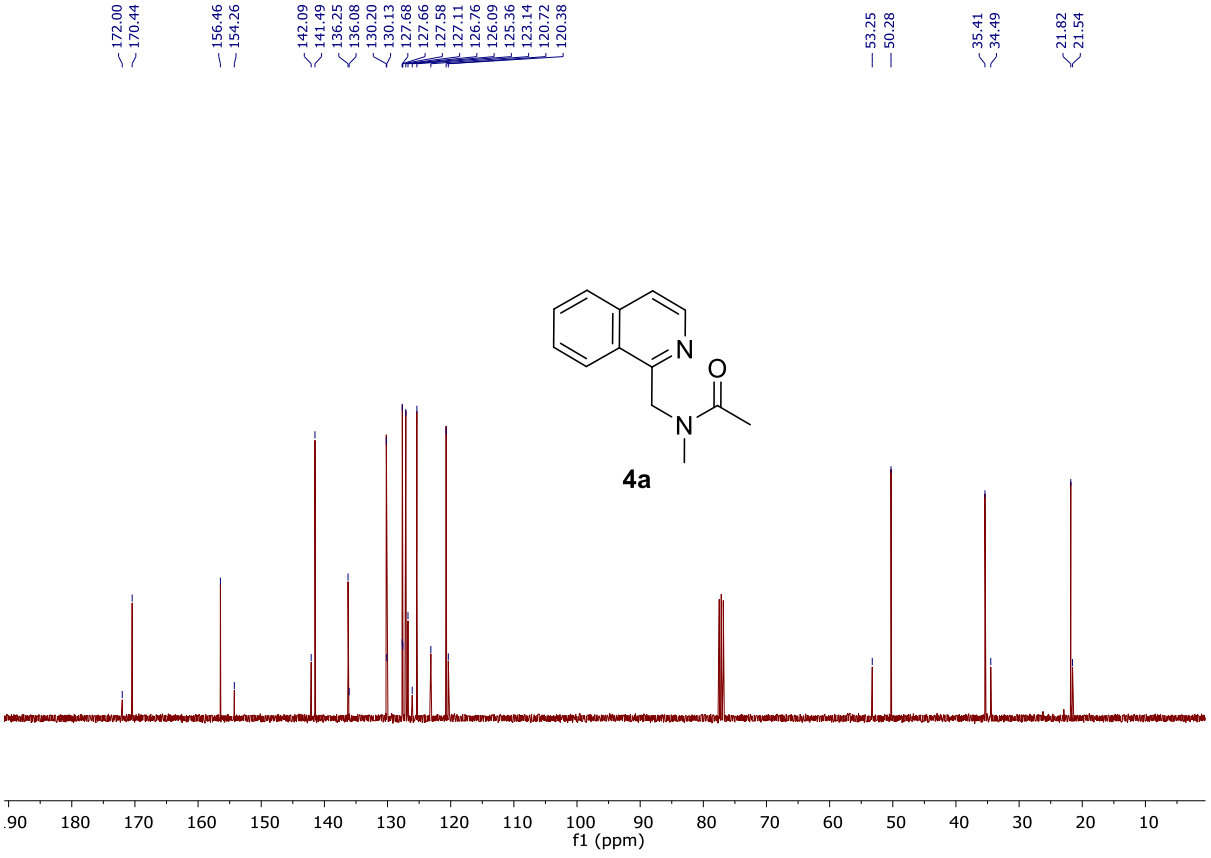

8.45
8.43
8.04
8.02
7.86
7.84
7.71
7.71
7.70
7.69
7.69
7.67
7.67
7.63
7.62
7.61
7.61
7.60
7.59
7.58
7.57
5.44
5.43
5.42
5.41
5.40
5.15
5.13
2.11
2.10
2.09
2.09
2.08
2.07
2.06
2.05
2.04
2.03
2.02
2.01
1.77
1.75
1.73
1.71
1.70
1.68
1.66
1.02
1.00
0.99
N
OH
3c
1.00
1.00
1.00
1.00
2.00
1.00
0.74
1.05
1.04
3.04
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
f1 (ppm)

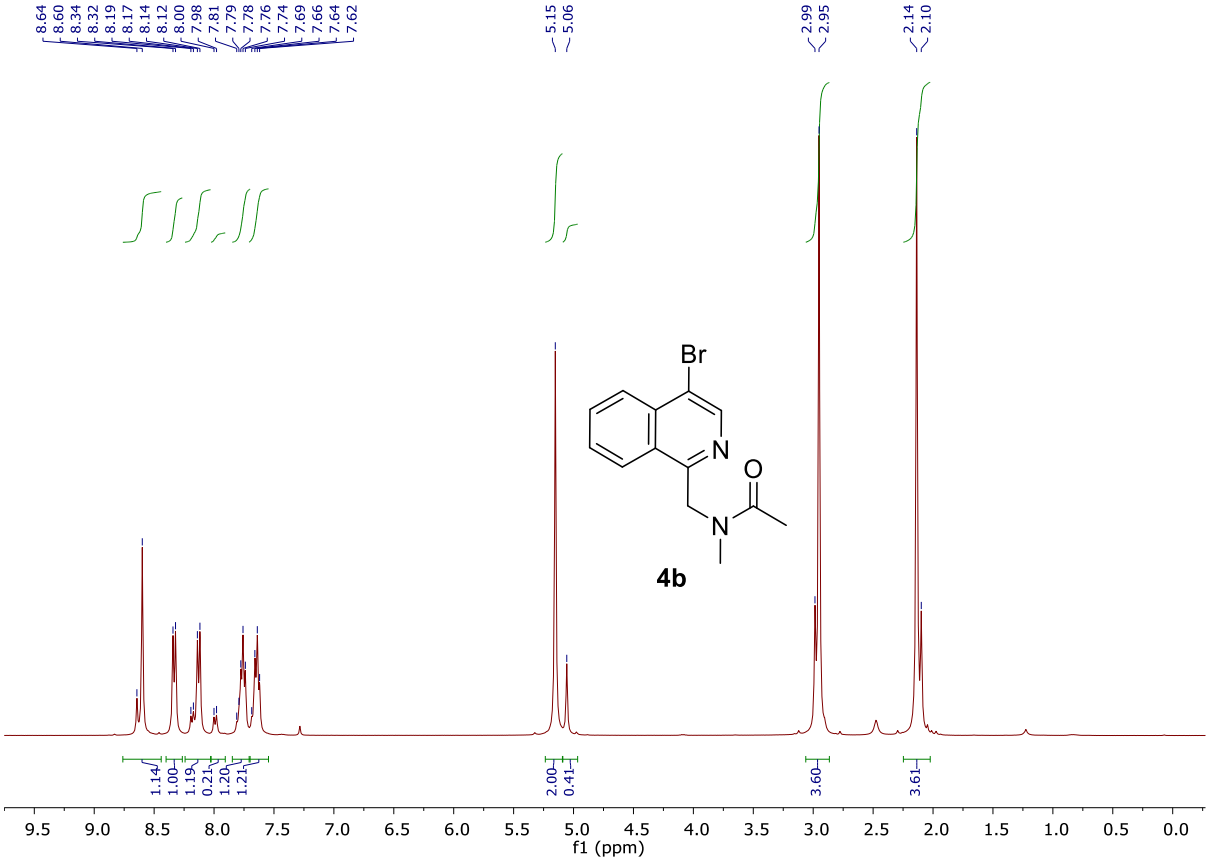

161.36
140.44
136.51
130.32
127.62
127.35
124.97
124.27
120.50
70.76
32.10
9.81
N
OH
3c
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.45 8.43 8.05 8.04 8.02 7.87 7.85 7.72 7.72 7.70 7.70 7.70 7.68 7.68 7.64 7.64 7.62 7.62 7.61 7.60 7.60 7.59 7.57
5.49 5.48 5.47 5.46 5.12 1.97 1.97 1.96 1.95 1.94 1.94 1.93 1.92 1.71 1.70 1.69 1.68 1.67 1.66 1.65 1.65 1.64 1.64 1.63 1.62 1.62 1.61 1.61 1.60 1.60 1.58 1.53 1.53 1.52 1.52 1.51 1.50 1.50 1.49 1.48 1.48 1.47 1.47 0.97 0.95 0.94
N
OH
3d
0.97 0.99 0.99 1.00 1.98 0.98 0.82 1.00 2.06 1.02 2.99
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.
f1 (ppm)


161.69 140.51 136.54 130.32 127.65 127.39 124.91 124.25 120.49 69.56 41.57 18.96 14.14
N
OH
3d
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.41 8.39 8.32 8.32 8.32 8.30 8.30 8.30 8.29 8.00 7.99 7.98 7.97 7.97 7.83 7.83 7.81 7.81 7.81 7.78 7.78 7.78 7.76 7.76 7.76 7.68 7.68 7.67 7.66 7.66 7.65 7.65 7.64 7.63 7.63 7.63 7.61 7.61 7.60 7.59 7.59 7.58 7.58 7.58 7.57 7.57 7.56 7.56 7.55 7.55 7.55 7.54 7.54 7.53 5.19 5.08 2.98 2.92 2.12 2.10
N
O
N
4a
0.25 0.99 1.00 0.25 0.26 1.00 1.31 2.46 2.01 0.48 0.72 3.00 3.01 0.70
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 -0
f1 (ppm)


172.00 170.44 156.46 154.26 142.09 141.49 136.25 136.08 130.20 130.13 127.68 127.66 127.58 127.11 126.76 126.09 125.36 123.14 120.72 120.38 53.25 50.28 35.41 34.49 21.82 21.54
N
O
N
4a
.90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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8.60
8.34
8.32
8.19
8.17
8.14
8.12
8.00
7.98
7.81
7.79
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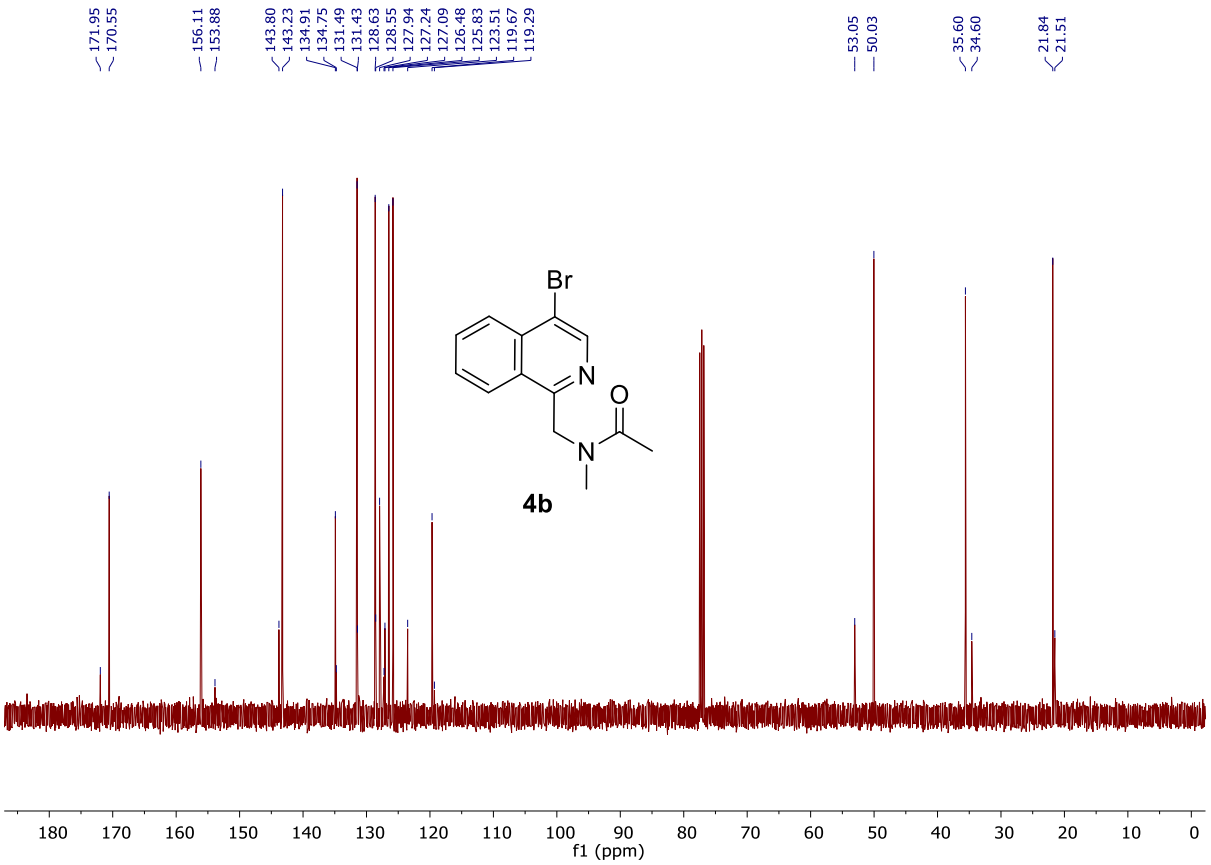
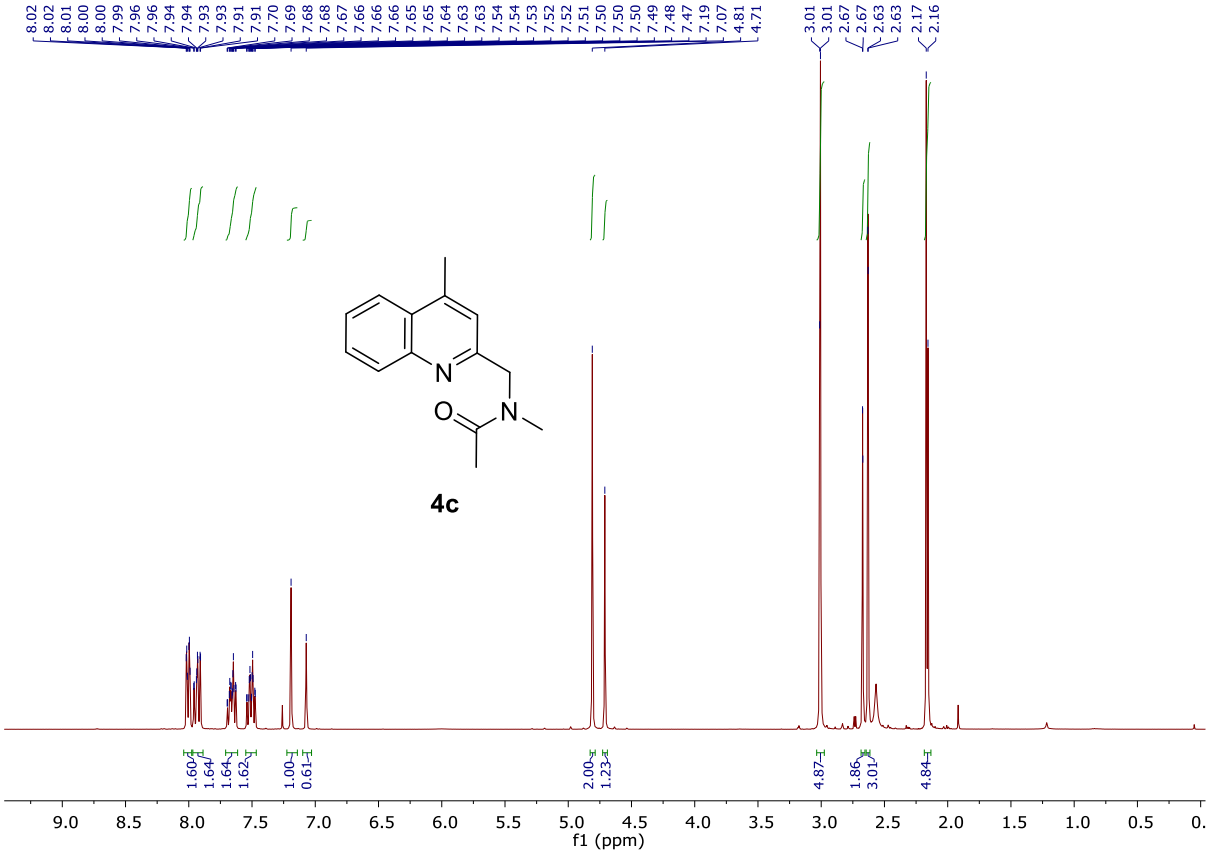
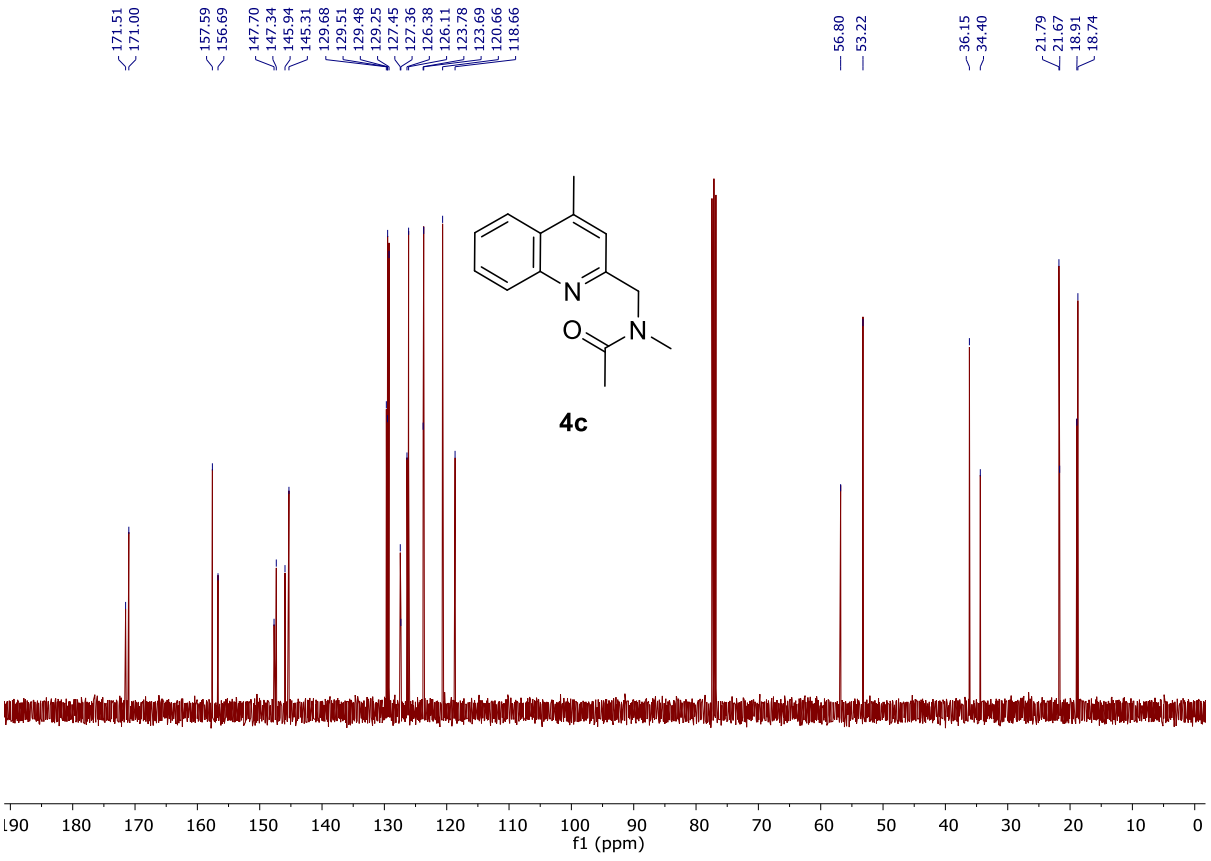
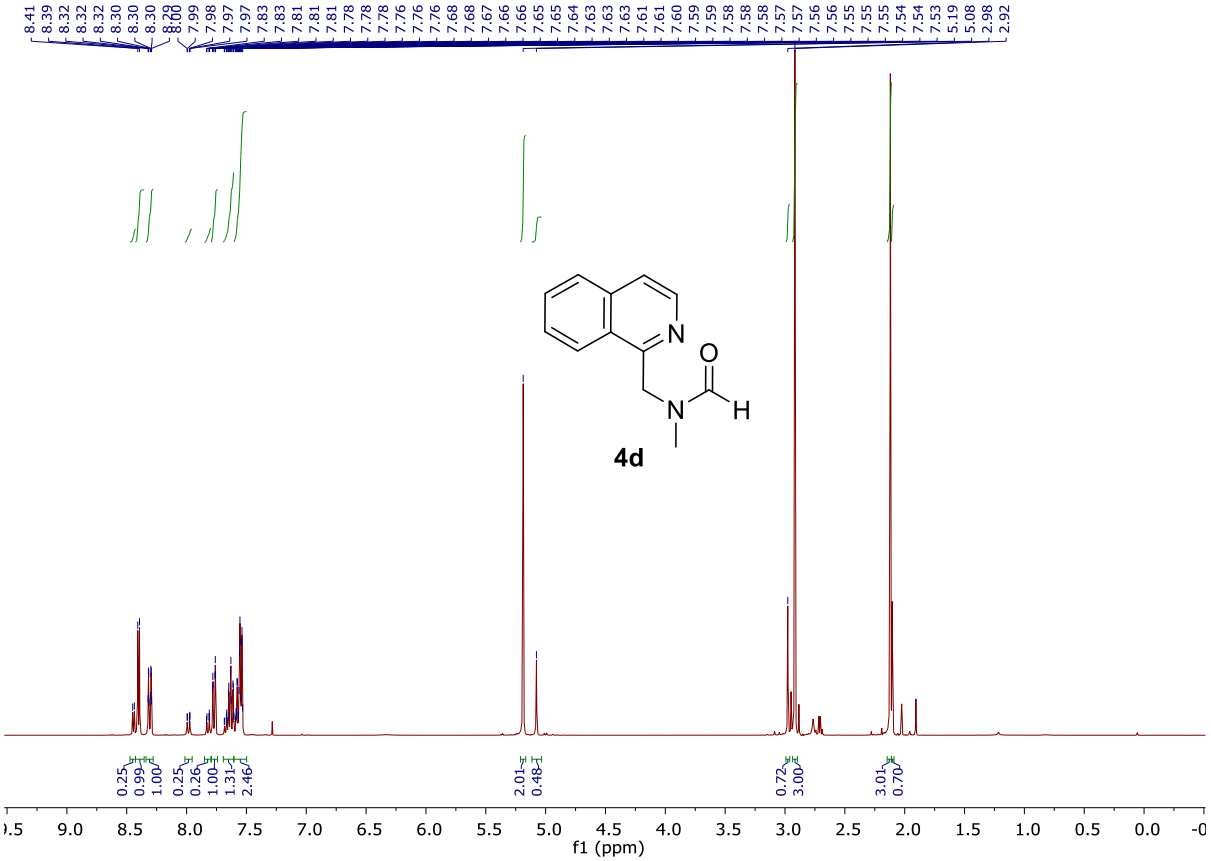
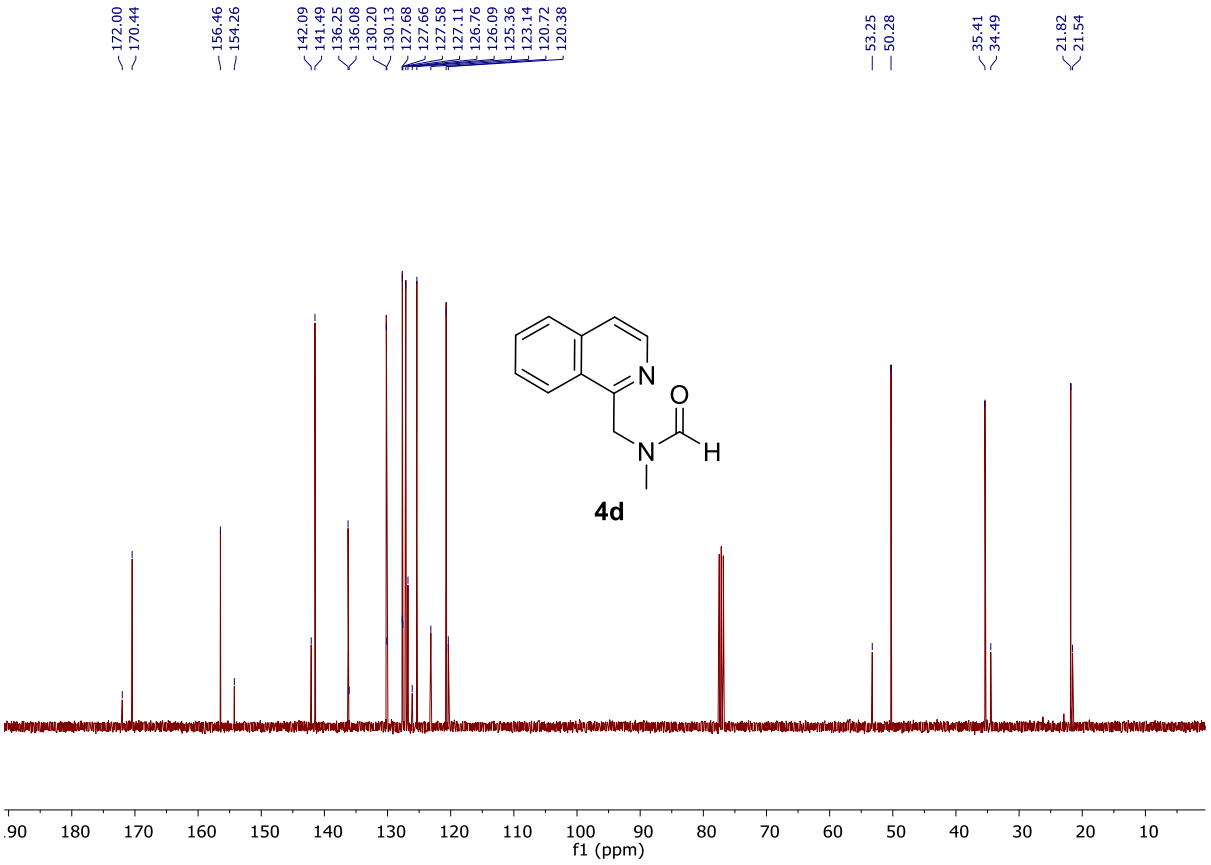
7.76
7.74
7.69
7.66
7.64
7.62
5.15
5.06
2.99
2.95
2.14
2.10
Br
N
O
N
4b
1.14
1.00
1.19
0.21
1.20
1.21
2.00
0.41
3.60
3.61
f1 (ppm)

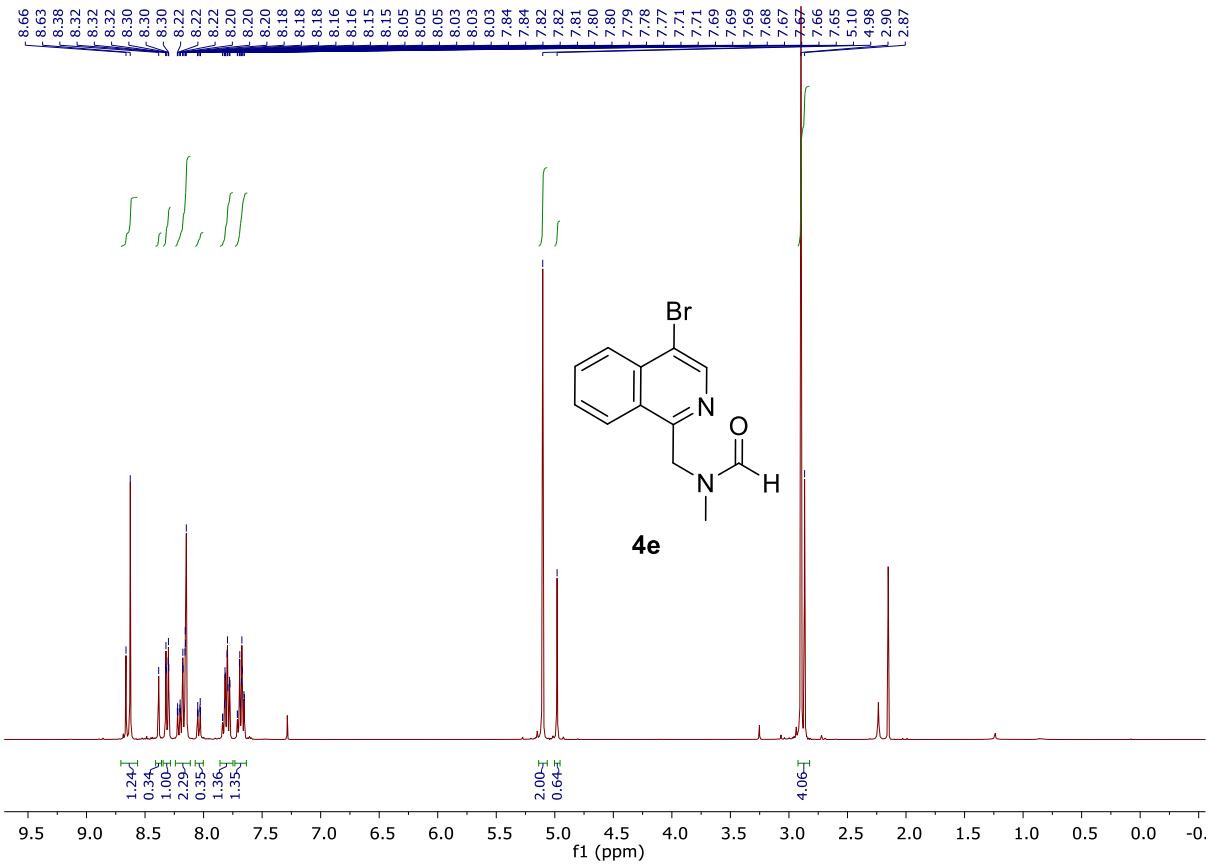

171.95
170.55
156.11
153.88
143.80
143.23
134.91
134.75
131.49
131.43
128.63
128.55
127.94
127.24
127.09
126.48
125.83
123.51
119.67
119.29
53.05
50.03
35.60
34.60
21.84
21.51
Br
N
O
N
4b
f1 (ppm)

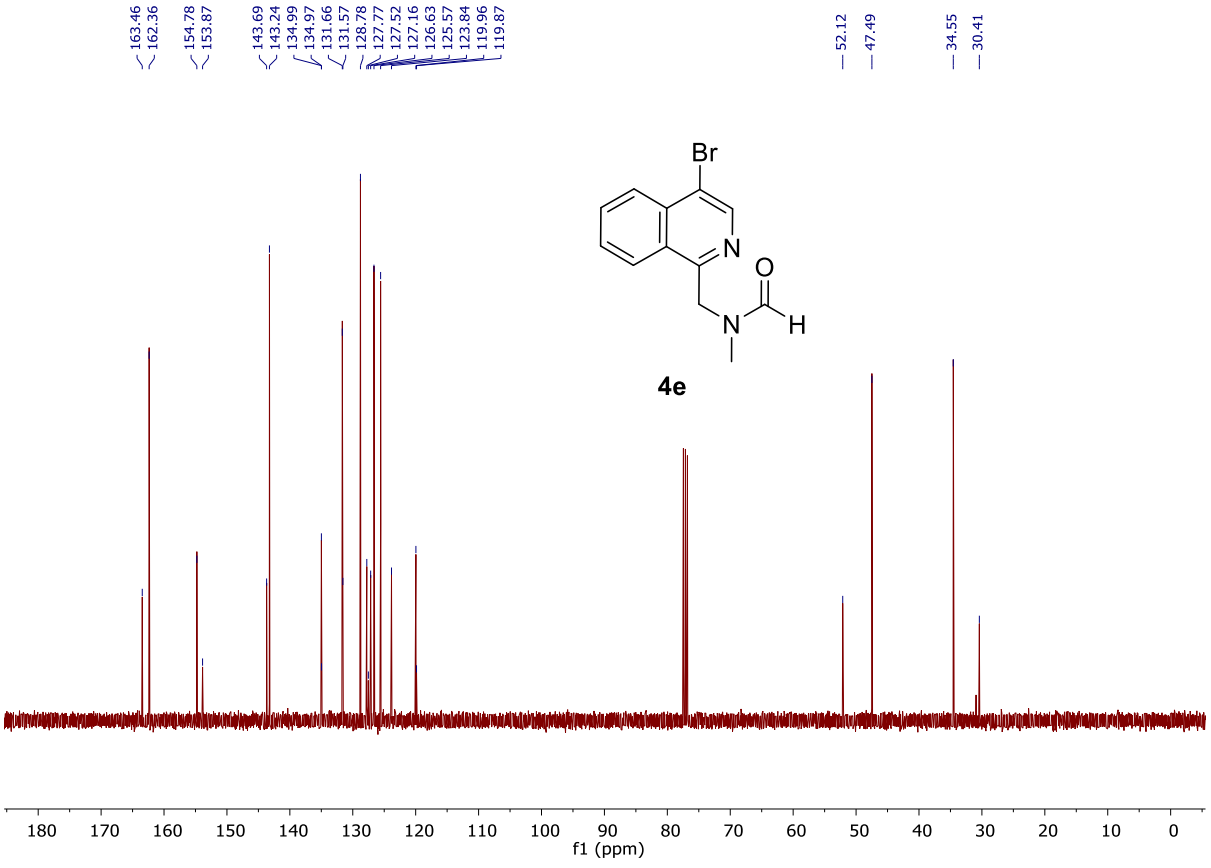

8.02 8.02 8.01 8.00 8.00 7.99 7.96 7.96 7.94 7.94 7.93 7.93 7.91 7.91 7.70 7.69 7.68 7.68 7.67 7.66 7.66 7.66 7.65 7.64 7.63 7.63 7.54 7.54 7.53 7.52 7.52 7.51 7.50 7.50 7.50 7.49 7.48 7.47 7.19 7.07 4.81 4.71
3.01 3.01 2.67 2.67 2.63 2.63 2.17 2.16
1.60 1.64 1.64 1.62 1.00 0.61 2.00 1.23 4.87 1.86 3.01 4.84
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.
f1 (ppm)
4c

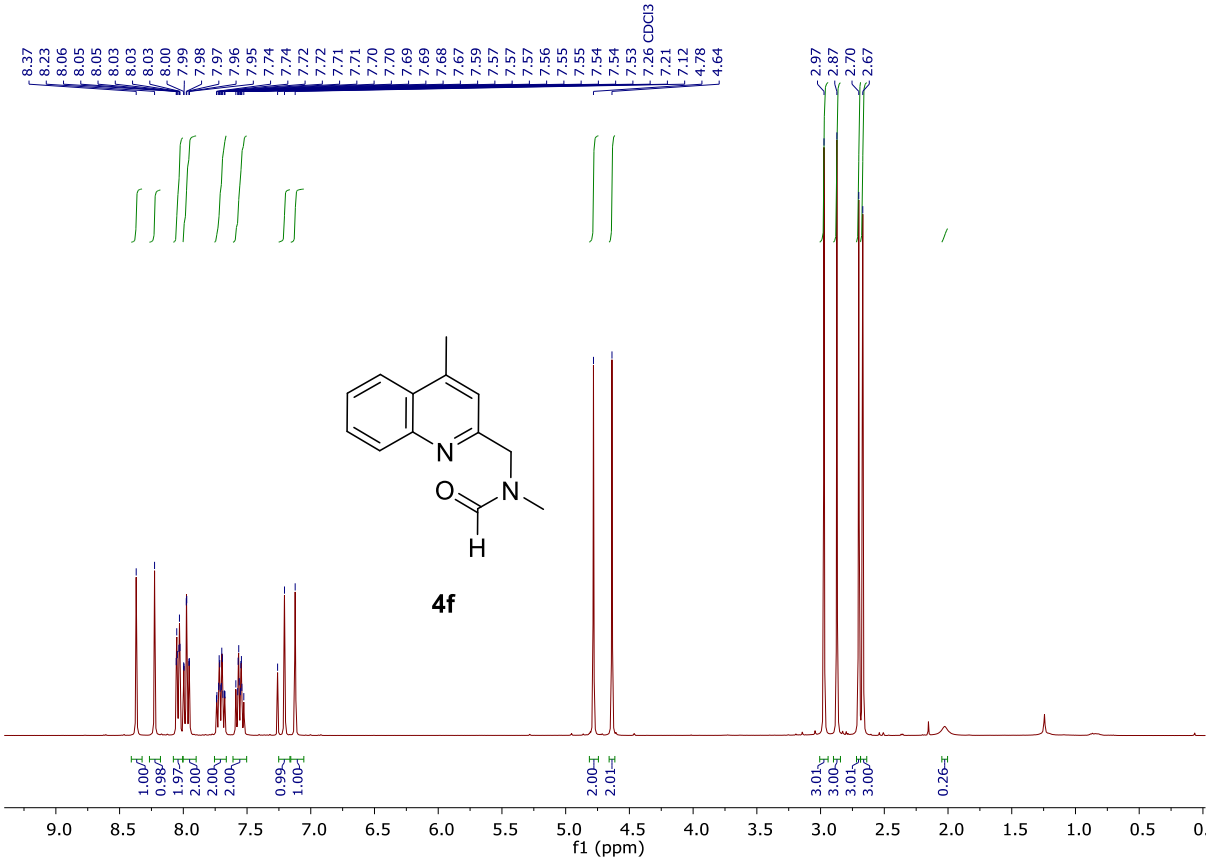

171.51 171.00 157.59 156.69 147.70 147.34 145.94 145.31 129.68 129.51 129.48 129.25 127.45 127.36 126.38 126.11 123.78 123.69 120.66 118.66
56.80 53.22 36.15 34.40 21.79 21.67 18.91 18.74
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
4c


8.41 8.39 8.32 8.32 8.32 8.30 8.30 8.30 8.28 8.00 7.99 7.98 7.97 7.97 7.83 7.83 7.81 7.81 7.81 7.78 7.78 7.78 7.76 7.76 7.76 7.68 7.68 7.67 7.66 7.66 7.65 7.65 7.64 7.63 7.63 7.63 7.61 7.61 7.60 7.59 7.59 7.58 7.58 7.58 7.57 7.57 7.56 7.56 7.55 7.55 7.55 7.54 7.54 7.53 5.19 5.08 2.98 2.92
0.25 0.99 1.00 0.25 0.26 1.00 1.31 2.46 2.01 0.48 0.72 3.00 3.01 0.70
f1 (ppm)
4d

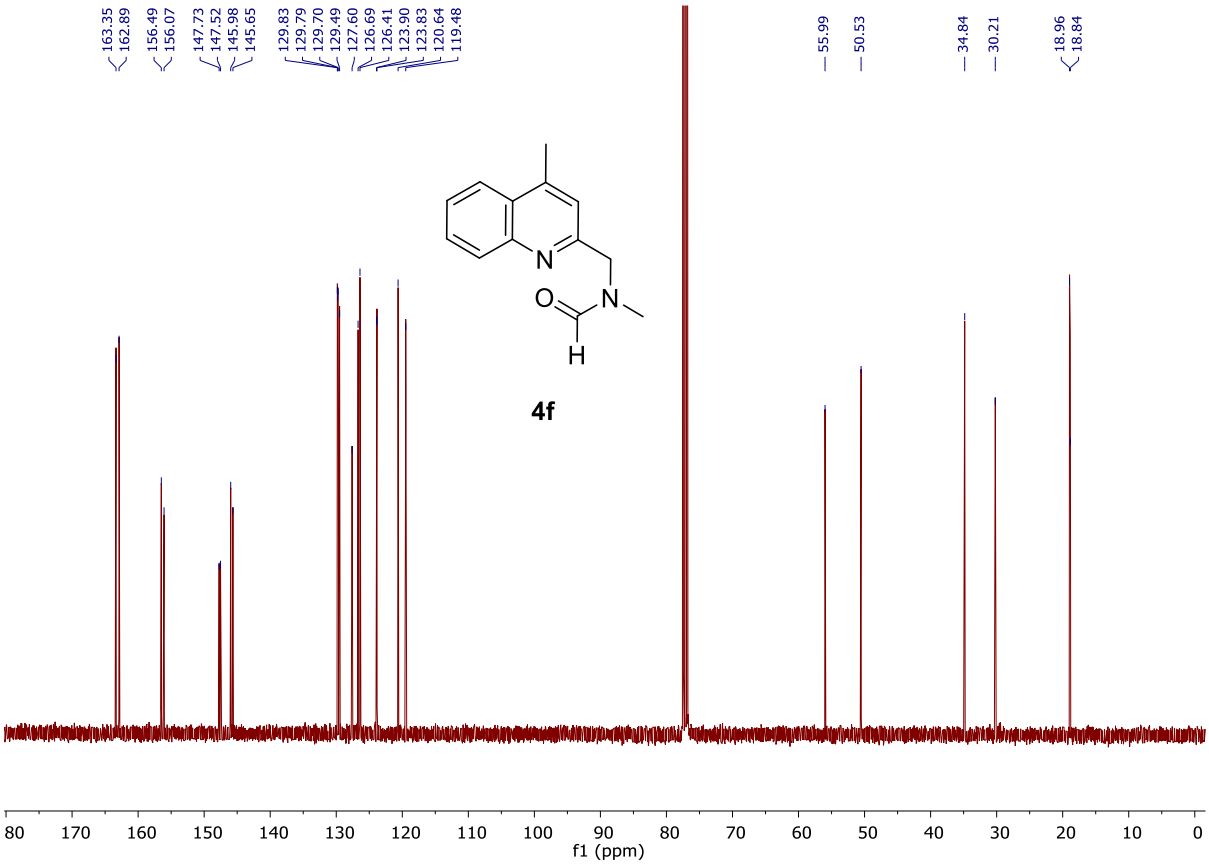

172.00 170.44 156.46 154.26 142.09 141.49 136.25 136.08 130.20 130.13 127.68 127.66 127.58 127.11 126.76 126.09 125.36 123.14 120.72 120.38 53.25 50.28 35.41 34.49 21.82 21.54
f1 (ppm)
4d


8.66 8.63 8.38 8.32 8.32 8.32 8.30 8.30 8.30 8.22 8.22 8.22 8.20 8.20 8.20 8.18 8.18 8.18 8.16 8.16 8.15 8.15 8.05 8.05 8.05 8.03 8.03 8.03 7.84 7.84 7.82 7.82 7.81 7.80 7.80 7.79 7.78 7.77 7.71 7.71 7.69 7.69 7.69 7.68 7.67 7.67 7.66 7.65 5.10 4.98 2.90 2.87
Br
N
O
N
H
4e
1.24 0.34 1.00 2.29 0.35 1.36 1.35 2.00 0.64 4.06
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
f1 (ppm)

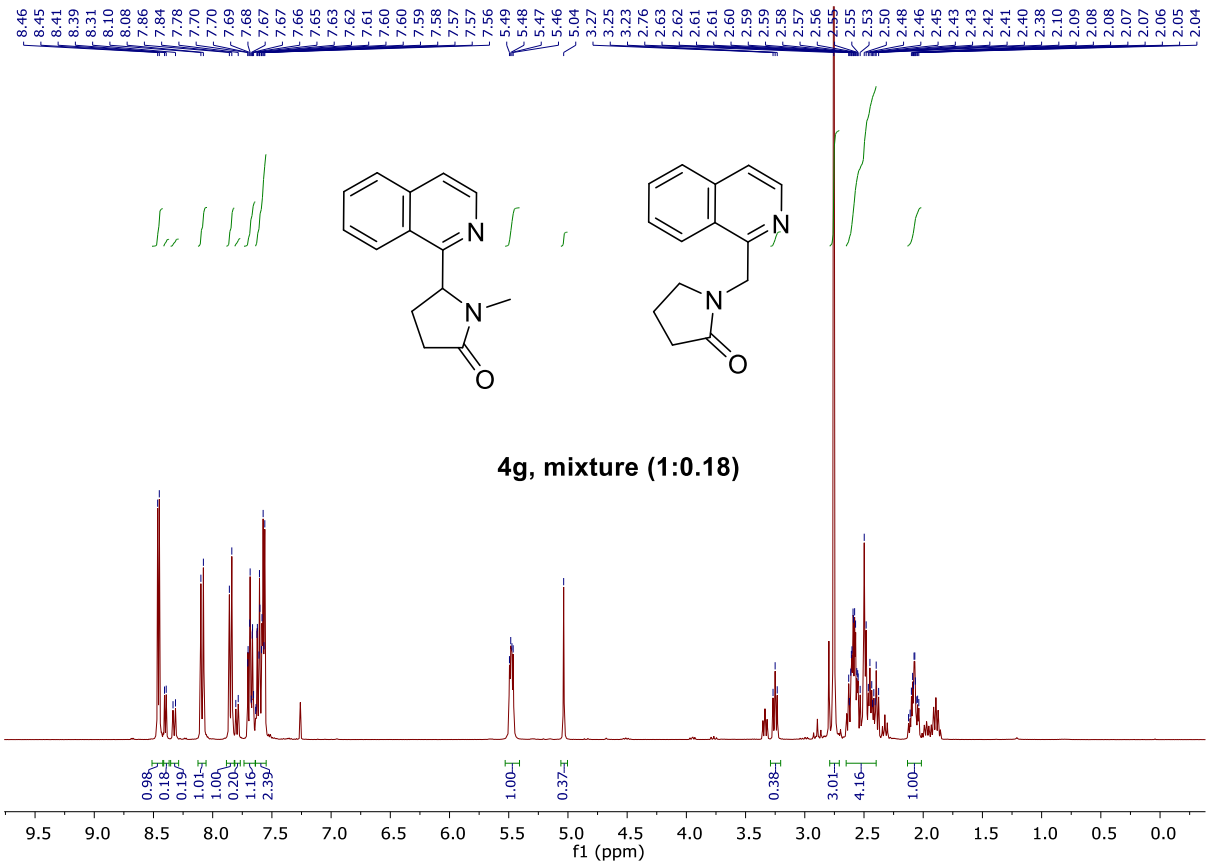

163.46 162.36 154.78 153.87 143.69 143.24 134.99 134.97 131.66 131.57 128.78 127.77 127.52 127.16 126.63 125.57 123.84 119.96 119.87 52.12 47.49 34.55 30.41
Br
N
O
N
H
4e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

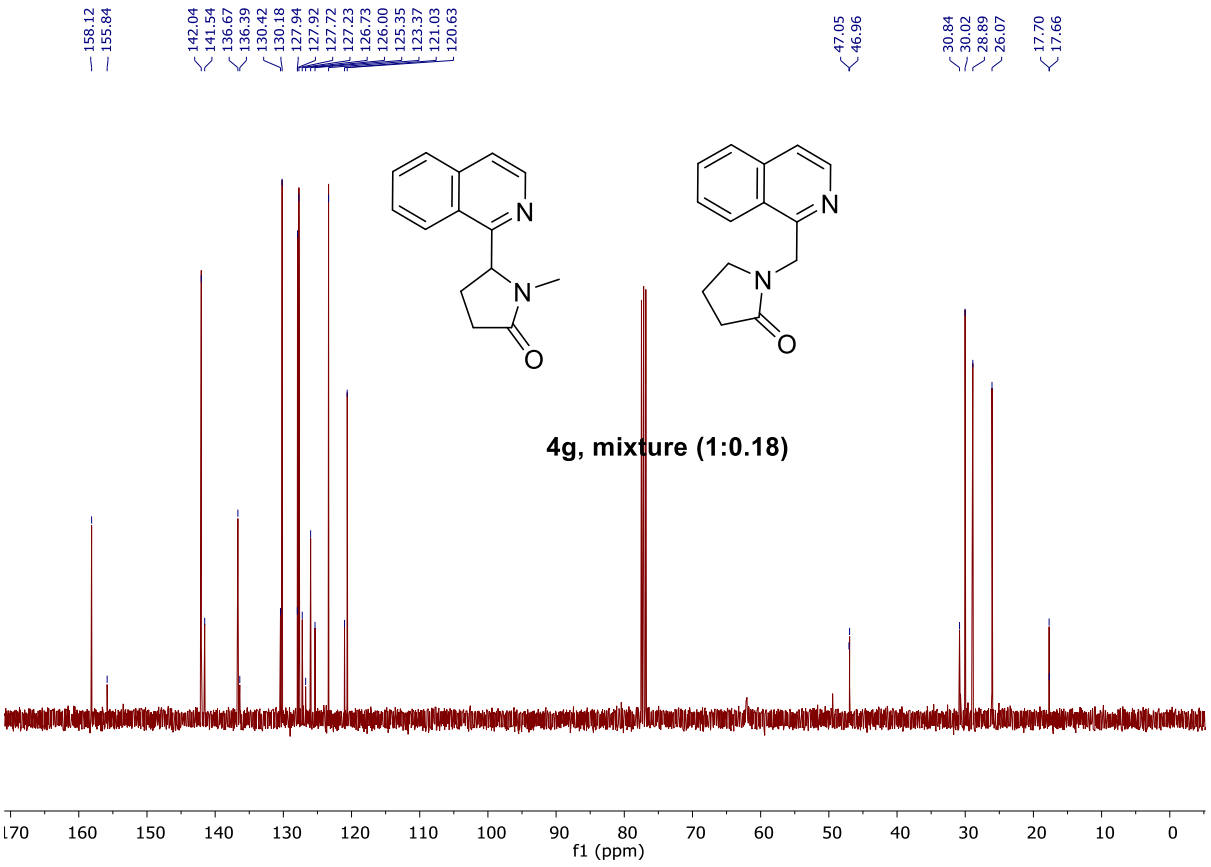

8.37
8.23
8.06
8.05
8.05
8.03
8.03
8.03
8.00
7.99
7.98
7.97
7.96
7.95
7.74
7.74
7.72
7.72
7.71
7.71
7.70
7.70
7.69
7.69
7.68
7.67
7.59
7.57
7.57
7.57
7.56
7.55
7.55
7.54
7.54
7.53
7.26 CDCl3
7.21
7.12
4.78
4.64
2.97
2.87
2.70
2.67
1.00
0.98
1.97
2.00
2.00
2.00
0.99
1.00
2.00
2.01
3.01
3.00
3.01
3.00
0.26
f1 (ppm)

**4f**


163.35
162.89
156.49
156.07
147.73
147.52
145.98
145.65
129.83
129.79
129.70
129.49
127.60
126.69
126.41
123.90
123.83
120.64
119.48
55.99
50.53
34.84
30.21
18.96
18.84
f1 (ppm)

**4f**


8.46 8.45 8.41 8.39 8.31 8.10 8.08 7.86 7.84 7.78 7.70 7.70 7.69 7.68 7.67 7.67 7.66 7.65 7.63 7.62 7.61 7.60 7.60 7.59 7.58 7.57 7.57 7.56 5.49 5.48 5.47 5.46 5.04 3.27 3.25 3.23 2.76 2.63 2.62 2.61 2.61 2.60 2.59 2.59 2.58 2.57 2.56 2.55 2.55 2.53 2.50 2.48 2.46 2.45 2.43 2.43 2.42 2.41 2.40 2.38 2.10 2.09 2.08 2.08 2.07 2.07 2.06 2.05 2.04
N
N
O
4g, mixture (1:0.18)
0.98 0.18 0.19 1.01 1.00 0.20 1.16 2.39 1.00 0.37 0.38 3.01 4.16 1.00
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
f1 (ppm)


158.12 155.84 142.04 141.54 136.67 136.39 130.42 130.18 127.94 127.92 127.72 127.23 126.73 126.00 125.35 123.37 121.03 120.63 47.05 46.96 30.84 30.02 28.89 26.07 17.70 17.66
N
N
O
4g, mixture (1:0.18)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

**Supporting References**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End of Supporting Information