Supplementary information

for

Air Oxidized Activated Carbon Catalyst for Aerobic Oxidative Aromatizations of N-Heterocycles

Lukas Enders,[a] David Casadio,[a] Santeri Aikonen,[a] Anna Lenarda,[a] Tom Wirtanen,[a] Tao Hu,[c] Sami Hietala,[a] Lucília S. Ribeiro,[c] Manuel Fernando R. Pereira[c] and Juho Helaja[a]*

a) Department of Chemistry, University of Helsinki, A. I. Virtasen aukio 1, P.O. Box 55, 000014, Helsinki (Finland). Email: juho.helaja@helsinki.fi

b) Research Unit of Sustainable Chemistry, Faculty of Technology, University of Oulu, 90014 Oulu, Finland

c) Laboratory of Separation and Reaction Engineering—Laboratory of Catalysis and Materials (LSRE-LCM), Faculty of Engineering, University of Porto, 4200-465 Porto, Portugal

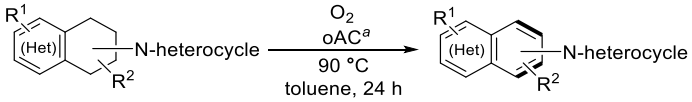
Corresponding author:
juho.helaja@helsinki.fi

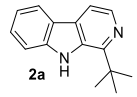
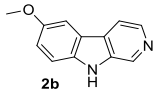
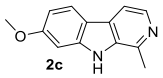
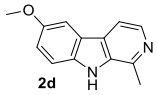
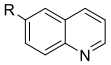
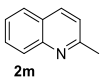
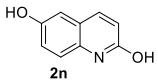
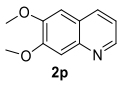
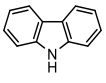
Contents

General remarks

If not described differently, all reactions were performed under air and at RT (18 - 20 °C). Reactions sensitive to water or oxygen were kept under an inert atmosphere of dry argon. They were handled with Schlenck-technique with syringe and septum in absolute and degassed solvents. All HPLC-grade solvents were used without further purification as obtained from the supplier (Honeywell, VWR, Merck, Sigma Aldrich). Distilled water was produced with an Aquatron AS4 (Bibby). All reagents were commercially available and used without further purification as obtained from the supplier. All oxidized active carbon species (oAC) were synthesized in our lab. Oxidized carbon nanotubes (oCNT) were prepared by HNO_3 oxidation.[1] Column chromatography was executed with pressurized air and at RT over silica gel (pore size 40 - 63 µm, VWR). All NMR spectra were measured at a sample temperature of 293 K. The following devices were used: Avance Neo 500 (Bruker, 500 MHz), Avance Neo 400 (Bruker, 400 Mhz), Unity Inova 300 (Varian, 300 MHz). The chemical shift δ in parts per million (ppm) is relative to the shift of tetramethylsilane (δ = 0 ppm) in both ^{1}H and ^{13}C NMR spectra as well as trichloro-fluoromethane (δ = 0 ppm) in ^{19}F spectra. The spectra were calibrated to the residual proton shifts of the corresponding deuterated solvents (^{1}H-NMR: $CDCl_3$ 7.26 ppm, DMSO-d_6: 2.50, ^{13}C-NMR: $CDCl_3$ 77.16 ppm, DMSO-d_6: 39.52). NMR-yields were determined with 1,3,5-trimethoxybenzene as an internal standard using a pulse-width of pw = 3.33 µs and a delay time of d1 = 35 s. High-resolution mass spectra were recorded with a microTOF LC (Bruker),the molecules were ionized with an electron spray ionization source in a positive mode coupled to a time of flight detection method (ESI^{+}-TOF).

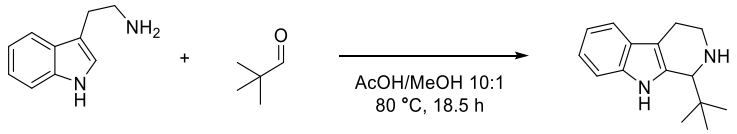
Table S1 Comparison of dehydrogenation of tetrahydro N-heterocycles with oAC_{HNO3} and $oAC_{air(\Delta)}$ catalysts



Entry	Product	Yield[b] (%) oAC_{HNO_3}	Yield[b] (%) $oAC_{air(\Delta)}$
1	 **2a**	36	67[c]
2	 **2b**	16	38
3	 **2c**	9 (15)[d]	12 (3)[d]
4	 **2d**	11 (13)	7
5	 **2e** R = H **2f** R = OMe **2g** R = Me **2h** R = F **2i** R = Cl **2j** R = Br **2k** R = CO_2Me **2l** R = CN	90 (**2e**)	>99 (**2e**) 91 (**2f**)[f] 92 (**2g**)[f] 97 (**2h**)[f] 72 (**2i**)[f] 66 (**2j**)[f] 96 (**2k**)[f] 93 (**2l**)[f]
6	 **2m**	56	53
7[e]	 **2n**	55	47[54][g]
8	 **2o**	49	67
9	 **2p**		30
10	 **2q**	37 (36)[e]	40 (4)[d][67][h]
11	 **2r**		77

[a] 4 eq., one catalyst eq. = 224 mg · $mmol^{-1}$ of SM. [b] Isolated yields. [c] Reaction time 72 h. [d] 3,4-dihydro intermediate, [e] SM is 6-hydroxy-3,4-dihydroquinolin-2(1H)-one [f] Yield as determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [g] at 140 °C, 72 h. [h] at 100 °C, 72 h.

1-*tert*-Butyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (1a)



[160.22] [86.13] **72 %** **1a** [228.34]

The reaction was performed according to a modified method of YE *et al.*[2] Pivaldehyde (1.96 mL, 18.0 mmol, 1.94 eq) was added to a solution of tryptamine (1.50 g, 9.36 mmol, 1.00 eq) in AcOH/MeOH (10:1, 7.50 mL). The reaction was stirred at 80 °C for 18.5 h. After cooling to RT, the solution was basified to pH = 10 with $NH_3 \cdot H_2O$ (aq. 25%). Dist. H_2O (20 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (1 x 40 mL, 3 x 30 mL). The combined organic phases were washed with brine (30 mL), which was then extracted with CH_2Cl_2 (2 x 20 mL). The organic phases were combined, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified via flash chromatography (CH_2Cl_2/MeOH 5% → 15%), which gave an orange oil. Upon adding hexane (20 mL) a pale-yellow solid precipitated, which was filtered off and washed with ice-cold hexane (30 mL). The filtrate-solvent was removed under reduced pressure, giving a pale-yellow solid. Both were combined to give **1a** (1.53 g, 6.70 mmol, 72%). Spectroscopic data matches recorded literature value.[3]

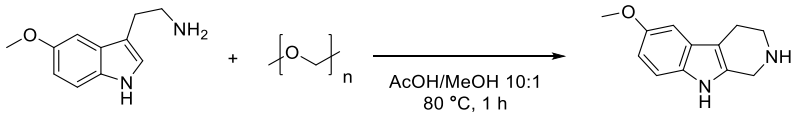
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 10.12 (s, 1H, N*H*), 7.35 (d, ^3J = 8.2 Hz, 2H, 2 x C*H*), 7.00 (ddd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, ^4J = 1.3 Hz, 1H, C*H*), 6.92 (ddd, ^3J = 7.9 Hz, ^3J = 6.8 Hz, ^4J = 1.0 Hz, 1H, C*H*), 3.71 (s, 1H, C*H*), 3.18 (dt, ^2J = 11.8 Hz, ^3J = 4.3 Hz, 1H, C*H*H), 2.73 (dt, ^2J = 12.6 Hz, ^3J = 6.3 Hz, 1H, C*H*H), 2.57-2.58 (m, 2H, CH_2), 1.01 (s, 9H, 3 x CH_3).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 136.0, 135.0, 127, 120.3, 118.0, 117.1, 111.2, 110.0, 61.3, 42.7, 35.6, 3 x 27.4, 22.7.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{15}H_{21}N_2$ $(M+H)^+$: 229.1699, found: 229.1692.

TLC: R_f = 0.32 (CH_2Cl_2/MeOH 10%).

1,2,3,4-Tetrahydro-6-methoxy-1*H*-pyrido[3,4-*b*]indole (1b)



[190.25] [30.03] **60 %** **1b** [202.26]

The reaction was performed according to a method of YE *et al.*[2] Paraformaldehyde (52.1 mg, 1.73 mmol, 1.10 eq) was added to a solution of 5-methoxytryptamine (300 mg, 1.58 mmol, 1.00 eq) in AcOH/MeOH (10:1, 1.10 mL). The reaction was stirred at 80 °C for 1 h under reflux cooling. After cooling to RT, the solution was basified to a pH of 10 with $NH_3 \cdot H_2O$ (aq. 25%, 1.5 mL). Dist. H_2O (10 mL) were added and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL/1 x 20 mL). The combined organic phases were washed with brine (10 mL), which was then extracted with CH_2Cl_2 (3 x 10 mL). The organic phases were again combined, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified via flash chromatography

(CH_2Cl_2/MeOH 10% → 17%), which gave **1b** (193 mg, 954 µmol, 60%) as a grey solid. Spectroscopic data matches recorded literature values.[2]

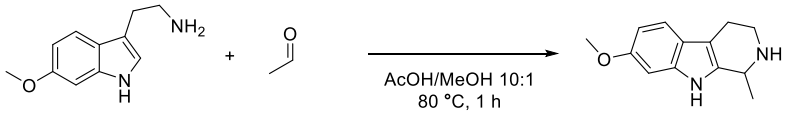
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 10.44 (s, 1H, N*H*-9), 7.13 (d, ^3J = 8.6 Hz, 1H, C*H*-8), 6.84 (d, ^4J = 2.8 Hz, 1H, C*H*-5), 6.62 (dd, ^3J = 8.6 Hz, ^4J = 2.5 Hz, 1H, C*H*-7), 3.82 (s, 2H, CH_2-1), 3.73 (s, 3H, CH_3-10), 2.96 (t, ^3J = 5.6 Hz, 2H, CH_2-3), 2.56 (t, ^3J = 5.6 Hz, 2H, CH_2-4).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 152.9 (*C*-6), 134.9 (*C*-9a), 130.5 (*C*-8a), 127.6 (*C*-4b), 111.3 (*C*H-8), 109.6 (*C*H-7), 106.8 (*C*-4a), 99.6 (*C*H-5), 55.3 (*C*H_3-10), 43.4 (*C*H_2-3), 42.7 (*C*H_2-1), 22.2 (*C*H_2-4).

HRMS (**ESI$^+$**): *m/z* calculated for $C_{12}H_{15}N_2O$ $(M+H)^+$: 203.1179, found: 203.1184.

TLC: R_f = 0.11 (CH_2Cl_2/MeOH 15 %).

2,3,4,9-Tetrahydro-1H-harmine (1c)



[190.25] [44.05] **1c** [216.28]

The reaction was performed according to a modified method of Ye *et al*.[2] Acetaldehyde (44.6 µL, 789 µmol, 1.50 eq) was added to a solution of 6-methoxytryptamine (100 mg, 526 µmol, 1.00 eq) in AcOH/MeOH (10:1, 1.00 mL). The reaction was stirred at 80 °C for 1 h in a sealed tube. After cooling to RT, the solution was basified to a pH of 10 with $NH_3 \cdot H_2O$ (aq. 25%, 1.5 mL). Dist. H_2O (5 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL, 1 x 10 mL). The combined organic phases were washed with brine (10 mL), which was then extracted with CH_2Cl_2 (2 x 10 mL). The organic phases were again combined, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified via flash chromatography (CH_2Cl_2/MeOH 8% → 18%), which gave **1c** (103 mg, 476 µmol, 91%) as a pale-yellow solid. Spectroscopic data matches recorded literature values.[4]

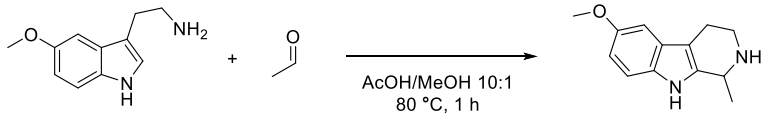
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 10.51 (s, 1H, N*H*), 7.21 (d, ^3J = 8.5 Hz, 1H, C*H*), 6.79 (d, ^4J = 2.9 Hz, 1H, C*H*), 6.59 (dd, ^3J = 8.4 Hz, ^4J = 2.2 Hz, 1H, C*H*), 4.01 (q, ^3J = 6.6 Hz, 1H, C*H*), 3,74 (s, 3H, CH_3), 3.15 (ddd, ^2J = 13.3 Hz, ^3J = 5.3 Hz, ^3J = 3.3 Hz, 1H, C*H*H), 2.87-2.80 (m, 1H, C*H*H), 2.62-2.52 (m, 2H, CH_2), 1.34 (d, ^3J = 6.6 Hz, 1H, CH_3).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 155.0, 136.5, 136.2, 121.5, 117.9, 107.7, 106.4, 94.6, 55.1, 47.8, 42.1, 22.2, 20.4.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{13}H_{17}N_2O$ $(M+H)^+$: 217.1335, found: 217.1325.

TLC: R_f = 0.37 (CH_2Cl_2/MeOH 15%).

1,2,3,4-tetrahydro-isoharmine (1d)



The reaction was performed according to a method of Ye *et al*.[2] Acetaldehyde (98.2 µL, 1.74 mmol, 1.10 eq) was added to a solution of 5-methoxytryptamine (300 mg, 1.58 mmol, 1.00 eq) in AcOH/MeOH (10:1, 1.10 mL). The reaction was stirred at 80 °C for 1 h under reflux cooling. After cooling to RT, the solution was basified to a pH of 10 with $NH_3 \cdot H_2O$ (aq. 25%, 1.5 mL). Dist. H_2O (10 mL) were added and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL, 1 x 20 mL). The combined organic phases were washed with brine (10 mL), which was then extracted with CH_2Cl_2 (3 x 10 mL). The organic phases were again combined, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified via flash chromatography (CH_2Cl_2/MeOH 5% → 17%), which gave **1d** (308 mg, 1.42 mmol, 90%) as a pale-yellow solid. Spectroscopic data matches recorded literature values.[5]

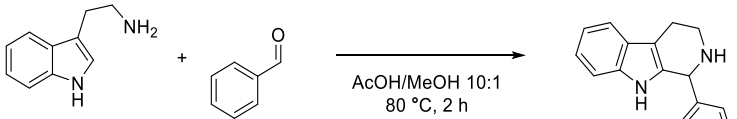
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 10.52 (s, 1H, N*H*-9), 7.15 (d, ^3J = 8.6 Hz, 1H, C*H*-8), 6.84 (d, ^4J = 2.6 Hz, 1H, C*H*-5), 6.64 (dd, ^3J = 8.6 Hz, ^4J = 2.5 Hz, 1H, C*H*-7), 4.05-4.00 (m, 1H, C*H*-1), 3.73 (s, 3H, CH_3-11), 3.27 (s, 1H, N*H*-2), 3.20-3.14 (m, 1H, CH_2-3), 2.88-2.82 (m, 1H, CH_2-3), 2.63-2.54 (m, 2H, CH_2-4), 1.35 (d, ^3J = 6.7 Hz, 3H, CH_3-10).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 152.9 (*C*H-6), 138.6 (*C*-9a), 130.6 (*C*-8a), 127.3 (*C*-4b), 111.4 (*C*H-8), 109.9 (*C*H-7), 106.5 (*C*-4a), 99.8 (*C*H-5), 55.3 (*C*H_3-11), 48.0 (*C*H-1), 42.2 (*C*H_2-3), 22.2 (*C*H_2-4), 20.3 (*C*H_3-10).

HRMS (**ESI$^+$**): *m/z* calculated for $C_{13}H_{17}N_2O$ $(M+H)^+$: 217.1335, found: 217.1329.

TLC: R_f = 0.11 (CH_2Cl_2/MeOH 15%).

1-phenyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (1a)

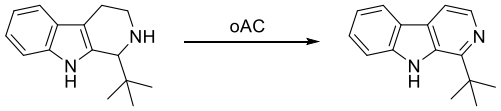


The reaction was performed according to a procedure reported by of Lin *et al*.[6] To a solution of tryptamine (0.5 g, 3.12 mmol, 1.00 eq.) in AcOH:MeOH (10:1, 2 mL) was added benzaldehyde (0.36 g, 3.43 mmol, 1.1 eq.). The reaction mixture was stirred at 80 °C for 1.5 h and then cooled to room temperature. The mixture was then basified to pH 9−10 using NH_4OH (aq.) and extracted with 3x50mL CH_2Cl_2. The combined organic layers were washed with saturated brine, dried with anhydrous Na_2SO_4, and filtered. The solvent was evaporated to give the crude product, which was then purified via flash chromatography (CH_2Cl_2:MeOH 5:1) to give **1x** as a pale yellow solid (348 mg, 49%). Spectroscopic data matches recorded literature values.[7]

^{1}H NMR: (400 MHz, $CDCl_3$): δ = 7.54 (s, 1H, C*H*), 7.49 (s, 1H, C*H*), 7.34 (s, 5H, 5 x C*H*), 7.21 (s, 1H, C*H*), 7.12 (s, 2H, 2 x C*H*), 5.17 (t, *J* = 1.9 Hz, 1H, C*H*), 3.40 (s, 1H, CH_2), 3.16 (s, 1H, CH_2), 2.94 (s, 1H, CH_2), 2.83 (s, 1H, CH_2), 1.87 (s, 1H, N*H*).

^{13}C NMR: (101 MHz, $CDCl_3$): δ = 141.80, 135.86, 134.50, 128.86, 128.51, 128.22, 127.43, 121.75, 119.43, 118.26, 110.83, 110.27, 58.19, 42.97, 22.56.

1-(*tert*-Butyl)-1*H*-pyrido[3,4-*b*]indole (2a)



1a
[228.34]

2a
[224.31]

An example dehydrogenation procedure of 1a to 2a according to the general procedure (main body): 1-*tert*-Butyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (**1a**, 57.1 mg, 250 µmol, 1.00 eq), oAC and a solvent were placed in a reaction tube under an atmosphere of the appropriate gas. It was stirred for n hours at n °C. The reaction was cooled to rt, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7%, 400 mL). The solvent was removed under reduced pressure to give the crude product (**2a**) as a dark-yellow solid.

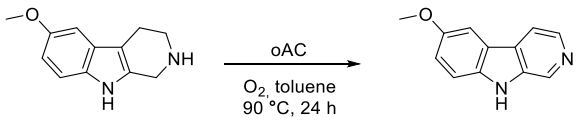
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.14 (s, 1H, N*H*), 8.24 (d, ^3J = 5.2 Hz, 1H, C*H*), 8.18 (d, ^3J = 7.9 Hz, 1H, C*H*), 7.97 (dd, ^3J = 5.2 Hz, ^5J = 0.5 Hz, 1H, C*H*), 7.67 (d, ^3J = 8.2 Hz, 1H, C*H*), 7.52 (ddd, ^3J = 8.2 Hz, ^3J = 7.1 Hz, ^4J = 1.2 Hz, 1H, C*H*), 7.21 (ddd, ^3J = 7.9 Hz, ^3J = 7.0 Hz, ^4J = 0.9 Hz, 1H, C*H*), 1.55 (s, 3 x CH_3).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 151.8, 140.2, 136.5, 132.0, 128.3, 127.7, 121.1, 120.5, 119.1, 113.0, 112.1, 37.5, 3 x 28.9.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{15}H_{17}N_2$ $(M+H)^+$: 225.1386, found: 225.1380.

TLC: R_f = 0.36 (CH_2Cl_2/MeOH 10%).

6-Methoxy-1*H*-pyrido[3,4-*b*]indole (2b)



1b
[202.26]

38 %

2b
[198.23]

The general procedure (main body) was followed. 1,2,3,4-Tetrahydro-6-methoxy-1*H*-pyrido[3,4-*b*]indole (**1b**, 50.6 mg, 250 µmol, 1.00 eq), oAC_{HNO3} (n = 4.00, 224 mg) and toluene (1.00 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7%, 400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2/MeOH 3 % → 8 %), which gave **2b** (8 mg,

40.4 µmol, 16%) as a yellow solid. In a second reaction with $oAC_{air(\Delta)}$ (n = 4.00, 224 mg) in toluene (1.50 mL), an NMR-yield of 38 % was obtained. ^{1}H-NMR data matches recorded literature values.[7]

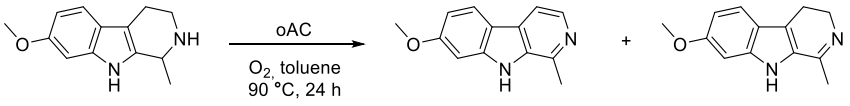
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.41 (s, 1H, N*H*), 8.86 (s, 1H, C*H*), 8.29 (d, ^3J = 5.2 Hz, 1H, C*H*), 8.09 (d, ^3J = 5.2 Hz, 1H, C*H*), 7.78 (d, ^4J = 2.9 Hz, 1H, C*H*), 7.51 (d, ^3J = 8.8 Hz, 1H, C*H*), 7.19 (dd, ^3J = 8.8 Hz, ^4J = 2.6 Hz, 1H, C*H*), 3.86 (s, 3H, CH_3).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 153.3, 137.3, 136.5, 135.4, 134.0, 127.4, 120.9, 118.2, 114.7, 112.8, 103.6, 55.6.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{12}H_{11}N_2O$ $(M+H)^+$: 199.0866, found: 199.0861.

TLC: R_f = 0.39 (CH_2Cl_2/MeOH 10%).

Harmine (2c)



1c [216.28] **2c** [212.25] **2c-int** [214.27]

The general procedure (main body) was followed. 2,3,4,9-Tetrahydro-1*H*-harmine (53.8 mg, 249 µmol, 1.00 eq), oAC_{HNO3} (n = 4.00, 224 mg) and toluene (1.00 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7%, 400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2/MeOH 8% → 15%), which gave the fully oxidized **2c** (5 mg, 23.6 µmol, 9%) as well as the intermediate **2c-int** (8 mg, 37.3 µmol, 15%), both as colorless solids. In a second reaction with $oAC_{air(\Delta)}$ (n = 4.00, 224 mg) in toluene (1.50 mL), NMR-yields of 12 % for **2c** as well as 3 % for **2c-int** were obtained. Spectroscopic data of **2c** matches recorded literature values.[8]

2c (*fully oxidized*)

^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.6 (s, 1H, N*H*), 8.17 (d, ^3J = 5.4 Hz, 1H, C*H*), 8.08 (d, ^3J = 8.7 Hz, 1H, C*H*), 7.87 (d, ^3J = 5.4 Hz, 1H, C*H*), 7.02 (d, ^4J = 2.2 Hz, 1H, C*H*), 6.86 (dd, ^3J = 8.6 Hz, ^4J = 2.4 Hz, 1H, C*H*), 3.88 (s, 3 H, OCH_3), 2.74 (s, 3 H, CH_3).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 160.3, 142.3, 140.8, 136.8, 134.4, 127.7, 122.8, 114.7, 112.1, 109.4, 94.5, 55.3, 19.8.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{13}H_{13}N$ $(M+H)^+$: 213.1022, found: 213.1026.

TLC: R_f = 0.47 (CH_2Cl_2/MeOH 15%).

2c-int (*intermediate*)

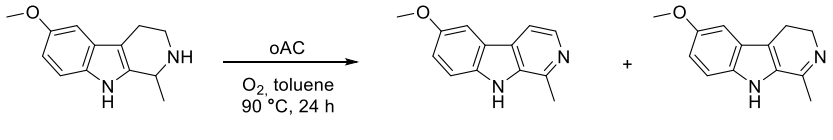
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 12.48 (s, 1H, N*H*), 7.66 (d, ^3J = 9.0 Hz, 1H, C*H*), 6.91 (d, ^4J = 2.1 Hz, 1H, C*H*), 6.84 (dd, ^3J = 8.9 Hz, ^4J = 2.2 Hz, 1H, C*H*), 3.85 (s, 3H, OCH_3), 3.83 (t, ^3J = 8.6 Hz, 2H, CH_2), 3.14 (t, ^3J = 8.8 Hz, 2H, CH_2), 2.69 (s, 3 H, CH_3).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 165.0, 160.6, 142.4, 125.6, 124.3, 123.0, 118.7, 113.9, 93.7, 55.4, 41.5, 18.9, 18.5.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{13}H_{15}N_2$ $(M+H)^+$: 215.1179, found: 215.1171.

TLC: R_f = 0.41 (CH_2Cl_2/MeOH 15%).

Isoharmine (2d)



1d
[216.28]

11 %
2d
[212.25]

13 %
2d-int
[214.27]

The general procedure (main body) was followed. 1,2,3,4-tetrahydroisoharmine (**1d**, 54.0 mg, 250 µmol, 1.00 eq), oAC_{HNO3} (n = 4.00, 224 mg) and toluene (1.00 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7%, 400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2/MeOH 3% → 17%), which gave **2d** (6.1 mg, 28.7 µmol, 11%) as well as the intermediate **2d-int** (6.9 mg, 32.2 µmol, 13 %), both as orange solids. **2d-int** could not be purified. In a second reaction with $oAC_{air(\Delta)}$ (n = 4, 224 mg), an NMR-yield of 7 % was obtained. Spectroscopic data matches recorded literature values.[9]

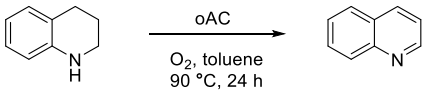
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.42 (s, 1H, N*H*), 8.26 (d, ^3J = 5.4 Hz, 1H, C*H*), 7.93 (d, ^3J = 5.4 Hz, 1H, C*H*), 7.74 (d, ^4J = 2.5 Hz, 1H, C*H*), 7.51 (d, ^3J = 8.8 Hz, 1H, C*H*), 7.18 (dd, ^3J = 8.8 Hz, ^4J = 2.6 Hz, 1H, C*H*), 3.85 (s, 3H, CH_3), 2.75 (s, 3H, CH_3).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 153.3, 142.0, 136.4, 135.4, 135.0, 126.9, 121.3, 118.1, 2 x 112.8, 103.5, 55.6, 20.1.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{13}H_{13}N_2O$ $(M+H)^+$: 213.1022, found: 213.1018.

TLC: R_f = 0.26 (CH_2Cl_2/MeOH 10%).

Quinoline (2e)



[133.19]

90 %

2e
[129.16]

The general procedure (main body) was followed. 1,2,3,4-tetrahydroquinoline (33.3 mg, 250 µmol, 1.00 eq), oAC_{HNO3} (n = 4, 224 mg) and toluene (1.50 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7 %, 400 mL). The solvent was removed under reduced pressure and crude product was purified

via flash chromatography (CH_2Cl_2/MeOH 0% → 10%), which gave **2e** (29 mg, 225 µmol, 90%) as a yellow oil. Spectroscopic data matches recorded literature values.[10] Additional control tests were run: $oAC_{air(\Delta)}$ (n = 4, 225 mg) in the same conditions gave **2e** (33 mg, 255 µmol, >99%). $oAC_{air(\Delta)}$ (n = 4, 225 mg) and a reaction time of 30 min gave an NMR-yield of 53 % **2e**. The same conditions were used to run a test in presence of TEMPO (1 eq) for 3h, the yield was determined with NMR as 52% **2e**. The same conditions were used as well to run a test for 30 minutes in trifluorotoluene. The yield was determined with NMR as 50% **2e**.

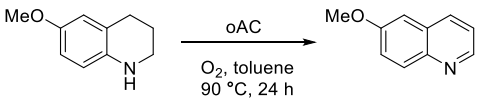
^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 8.93 (dd, ^3J = 4.1 Hz, ^4J = 1.6 Hz, 1H, C*H*), 8.17 (d, ^3J = 8.2 Hz, 1H, C*H*), 8.12 (d, ^3J = 8.5 Hz, 1H, C*H*), 7.82 (d, ^3J = 8.1 Hz, 1H, C*H*), 7.72 (ddd, ^3J = 8.4 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, 1H, C*H*), 7.56 (ddd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1H, C*H*), 7.40 (dd, ^3J = 8.3 Hz, ^3J = 4.1 Hz, 1H, C*H*).

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 150.4, 148.3, 136.1, 2 x 129.5, 128.3, 127.8, 126.6, 121.1.

HRMS (**ESI$^+$**): *m/z* calculated for C_9H_8N $(M+H)^+$: 130.0651, found: 130.0653.

TLC: R_f = 0.56 (CH_2Cl_2/MeOH 10%).

6-Methoxyquinoline (2f)



[163.22] **2f** [159.19]

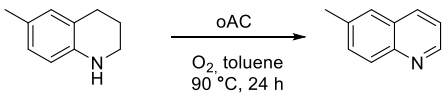
The general procedure (main body) was followed. 6-Methoxy-1,2,3,4-tetrahydroquinoline (40.8 mg, 250 µmol, 1.00 eq), $oAC_{air(\Delta)}$ (n = 4, 224 mg) and toluene (1.50 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7 %, 400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2/MeOH 0% → 10%), which gave **2f** (33.8 mg, 212 µmol, 85 %) as a yellow oil. In a second reaction, an NMR-yield of 91 % was obtained. Spectroscopic data matches recorded literature values.[11] An additional control test was run in the same conditions for 30 minutes. The yield was determined with NMR as 72 % **2f**.

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 8.77 (dd, ^3J = 4.2 Hz, ^4J = 1.6 Hz, 1H, C*H*), 8.03 (dd, ^3J = 8.3 Hz, ^3J = 1.2 Hz, 1H, C*H*), 8.00 (d, ^4J = 9.1 Hz, 1H, C*H*), 7.38-7.33 (m, 2H, 2 x C*H*), 7.06 (d, ^4J = 2.8 Hz, 1H, C*H*), 3.93 (s, 3H, CH_3) .

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 157.8, 148.1, 144.6, 134.9, 131.0, 129.4, 122.4, 121.5, 105.2, 55.7.

TLC: R_f = 0.49 (CH_2Cl_2/MeOH 5 %).

6-Methylquinoline (2g)



[147.22] **2g** [143.19]

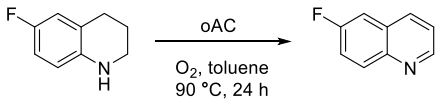
The general procedure (main body) was followed. 1,2,3,4-tetrahydro-6-mehtylquinoline (36.6 mg, 249 µmol, 1.00 eq), $oAC_{air(\Delta)}$ (n = 4, 224 mg) and toluene (1.50 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7 %, 400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2/MeOH 1.5 % → 2 %), which gave **2g** (32.6 mg, 228 µmol, 92 %) as a yellow oil. Spectroscopic data matches recorded literature values.[11] An additional control test was run in the same conditions for 30 minutes. The yield was determined with NMR as 65 % **2g**.

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 8.85 (dd, ^3J = 4.3 Hz, ^4J = 1.7 Hz, 1H, C*H*), 8.06 (d, ^3J = 8.4 Hz, 1H, C*H*), 8.00 (d, ^3J = 8.5 Hz, 1H, C*H*), 7.57 (s, 1H, C*H*), 7.54 (dd, ^3J = 8.5 Hz, ^4J = 1.9 Hz, 1H, C*H*), 7.35 (dd, ^3J = 8.2 Hz, ^3J = 4.2 Hz, 1H, C*H*), 2.54 (s, 3H, CH_3).

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 149.6, 147.0, 136.5, 135.5, 131.9, 129.3, 128.5, 126.7, 121.2, 21.7.

TLC: R_f = 0.47 (CH_2Cl_2/MeOH 5 %).

6-Fluoroquinoline (2h)



[151.18] **2h** [147.15]

The general procedure (main body) was followed. 6-Fluoro-1,2,3,4-tetrahydroquinoline (37.8 mg, 250 µmol, 1.00 eq), $oAC_{air(\Delta)}$ (n = 4, 224 mg) and toluene (1.50 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7 %, 400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2/MeOH 0% → 10%), which gave **2h** (18.2 mg, 124 µmol, 50 %) as a yellow oil. In a second reaction, an NMR-yield of 97 % was obtained. Spectroscopic data matches recorded literature values.[10] An additional control test was run in the same conditions for 30 minutes. The yield was determined with NMR as 64 % **2h**.

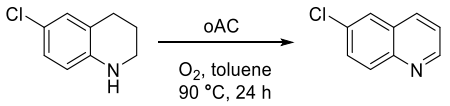
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 8.90 (dd, J = 4.2, 1.7 Hz, 1H, C*H*), 8.37 (dd, J = 8.4, 1.1 Hz, 1H, C*H*), 8.10 (dd, J = 9.2, 5.6 Hz, 1H, C*H*), 7.80 (dd, J = 9.5, 3.0 Hz, 1H, C*H*), 7.69 (ddd, J = 9.2, 8.6, 2.9 Hz, 1H, C*H*), 7.58 (ddd, J = 8.4, 4.2, 0.9 Hz, 1H, C*H*).

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 160.5 (d, ^3J = 248.1 Hz), 149.8 (d, ^3J = 3.3 Hz), 145.5, 135.6 (d, ^3J = 6.1 Hz), 132.2 (d, ^3J = 9.1 Hz), 129.0 (d, ^3J = 9.8 Hz), 121.9, 119.8 (d, ^3J = 26.5 Hz), 110.8 (d, ^3J = 22.2 Hz).

^{19}F-NMR: (376 MHz, $CDCl_3$): δ = 113.8.

TLC: R_f = 0.49 (CH_2Cl_2/MeOH 5 %).

6-Chloroquinoline (2i)



72 %

[167.34] **2i** [163.60]

The general procedure (main body) was followed. 6-Chloro-1,2,3,4-tetrahydroquinoline (16.7 mg, 100 µmol, 1.00 eq), $oAC_{air(\Delta)}$ (n = 4.00, 89.6 mg) and toluene (1.00 mL) were placed in a reaction tube under oxygen atmosphere. It for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of Celite and washed with CH_2Cl_2/MeOH (7 %, 400 mL The solvent was removed under reduced pressure and a yield of 72 % determined through NMR. Spectroscopic data matches recorded literature values.[11] An additional control test was run in the same conditions for 30 minutes. The yield was determined with NMR as 60 % **2i**.

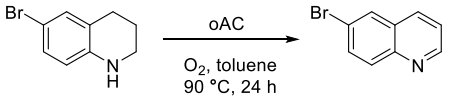
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 8.93 (dd, ^3J = 4.2 Hz, ^3J = 1.7 Hz, 1H, C*H*), 8.36 (dd, ^3J = 8.3 Hz, ^4J = 1.1 Hz, 1H, C*H*), 8.13 (d, ^4J = 2.4 Hz, 1H, C*H*), 8.04 (d, ^3J = 9.0 Hz, 1H, C*H*), 7.77 (dd, ^3J = 8.9 Hz, ^4J = 2.5 Hz, 1H, C*H*), 7.59 (dd, ^3J = 8.3 Hz, ^3J = 4.2 Hz, 1H, C*H*).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 151.1, 146.1, 135.4, 131.1, 130.9, 130.0, 128.7, 126.8, 122.4.

HRMS (**ESI$^+$**): *m/z* calculated for C_9H_7NCl $(M+H)^+$: 164.0262, found: 164.0262.

TLC: R_f = 0.60 (CH_2Cl_2/MeOH 10%).

6-Bromoquinoline (2j)



66 %

[212.09] **2j** [208.06]

The general procedure (main body) was followed. 6-Bromo-1,2,3,4-tetrahydroquinoline (53.7 mg, 253 µmol, 1.00 eq), $oAC_{air(\Delta)}$ (n = 4, 224 mg) and toluene (1.50 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7 %, 400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2) which gave impure **2j** (39.5 mg, 190 µmol, 75 %) as a yellow oil, which could not be further purified. In a second reaction, an NMR-yield of 66 % was obtained. An additional control test was run in the same conditions for 30 minutes. The yield was determined with NMR as 55 % **2j**.

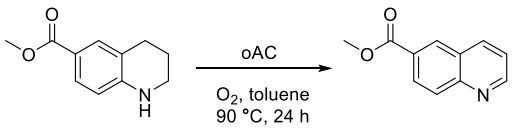
^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 8.93 (dd, ^3J = 4.2 Hz, ^4J = 1.6 Hz, 1H, C*H*), 8.08 (d, ^3J = 8.3 Hz, 1H, C*H*), 7.99 (s, 1H, C*H*), 7.98 (d, ^3J = 7.5 Hz, 1H, C*H*), 7.78 (dd, ^3J = 8.9 Hz, ^3J = 2.3 Hz), 7.43 (dd, ^3J = 8.2 Hz, ^3J = 4.2 Hz, 1H, C*H*).

^{13}C NMR: (101 MHz, DMSO) δ = 151.65, 146.75, 135.77, 133.04, 131.62, 130.53, 129.68, 122.85, 119.94.

HRMS (**ESI$^+$**): *m/z* calculated for C_9H_7NBr $(M+H)^+$: 207.9756, found: 207.9796.

TLC: R_f = 0.49 (CH_2Cl_2/MeOH 5%).

Methyl quinoline-6-carboxylate (2k)



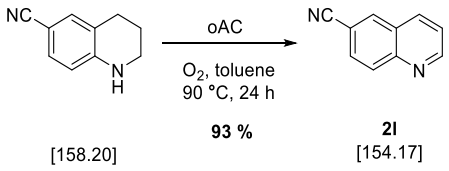
The general procedure (main body) was followed. Methyl 1,2,3,4-tetrahydro-6-quinolinecarboxylate (40.5 mg, 212 µmol, 1.00 eq), oAC (n = 4.7, 224 mg) and toluene (1.50 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7 %, 400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2), which gave **2k** (32.6 mg, 174 µmol, 82 %) as a beige solid. In a second reaction, an NMR-yield of 96 % was obtained. Spectroscopic data matches recorded literature values.[12] An additional control test was run in the same conditions for 30 minutes. The yield was determined with NMR as 34 % **2k**.

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 9.01 (dd, ^3J = 4.3 Hz, ^4J = 1.7 Hz, 1H, C*H*), 8.59 (d, ^4J = 1.9 Hz, 1H, C*H*), 8.29 (dd, ^3J = 8.8 Hz, ^4J = 2.0 Hz, 1H, C*H*), 8.26 (dd, ^3J = 8.3 Hz, ^3J = 1.2 Hz, 1H, C*H*), 8.14 (d, ^3J = 8.8 Hz, 1H, C*H*), 7.48 (dd, ^3J = 8.3 Hz, ^3J = 4.1 Hz, 1H, C*H*), 3.99 (s, 3H, CH_3).

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 166.7, 152.7, 150.2, 137.5, 131.1, 130.0, 129.1, 128.3, 127.6, 122.0, 52.6.

TLC: R_f = 0.49 (CH_2Cl_2/MeOH 5%).

Quinoline-6-carbonitrile (2l)



The general procedure (main body) was followed. 1,2,3,4-tetrahydroquinoline-6-carbonitrile (15.8 mg, 100 µmol, 1.00 eq), $oAC_{air(\Delta)}$ (n = 4.00, 89.6 mg) and toluene (1.00 mL) were placed in a reaction tube under oxygen atmosphere. It for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of Celite and washed with CH_2Cl_2/MeOH (7 %, 400 mL). The solvent was removed under reduced pressure and a yield of 72 % determined through NMR. Spectroscopic data matches recorded literature values.[13] An additional control test was run in the same conditions for 30 minutes. The yield was determined with NMR as 27 % **2l**.

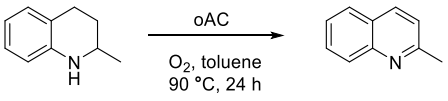
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 9.08 (dd, ^3J = 4.4 Hz, ^3J = 1.7 Hz, 1H, C*H*), 8.67 (d, ^4J = 1.9 Hz, 1H, C*H*), 8.50 (d, ^3J = 8.6 Hz, ^4J = 1.0 Hz, 1H, C*H*), 8.16 (d, ^3J = 8.7 Hz, 1H, C*H*), 8.04 (dd, ^3J = 8.7 Hz, ^4J = 1.9 Hz, 1H, C*H*), 7.70 (dd, ^3J = 8.3 Hz, ^3J = 4.3 Hz, 1H, C*H*).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 153.7, 148.5, 136.8, 135.0, 130.6, 130.2, 127.3, 123.0, 118.6, 109.1.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{10}H_7N_2$ $(M+H)^+$: 155.0604 found: 155.0606.

TLC: R_f = 0.60 (CH_2Cl_2/MeOH 10%).

Quinaldine (2m)



[147.22] **2m** [143.19]

The general procedure (main body) was followed. 1,2,3,4-Tetrahydroquinaldine (36.1 µL, 250 µmol, 1.00 eq), $oAC_{air(\Delta)}$ (n = 4.00, 224 mg) and toluene (1.00 mL) were placed in a reaction tube under oxygen atmosphere. It for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of Celite and washed with CH_2Cl_2/MeOH (7 %, 400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2/MeOH 0% → 5%), which gave **2m** (19 mg, 133 µmol, 53%) as a colorless oil. An additional control test was run in the same conditions for 30 minutes. The yield was determined with NMR as 36 % **2m**. In a reaction with oAC_{HNO3} (n = 4.00, 224 mg) in toluene (1.00 mL), a yield of 56 % (20 mg, 140 µmol) was obtained. Spectroscopic data matches recorded literature values.[11]

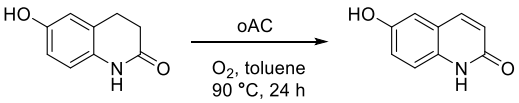
^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 8.05 (d, ^3J = 8.6 Hz, 1H, C*H*), 8.02 (d, ^3J = 8.5 Hz, 1H, C*H*), 7.77 (dd, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 1H, C*H*), 7.68 (ddd, ^3J = 8.5 Hz, ^3J = 6.9 Hz, ^4J = 1.6 Hz, 1H, C*H*), 7.48 (ddd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, ^4J = 1.1 Hz, 1H, C*H*), 7.29 (d, ^3J = 8.3 Hz, 1H, C*H*), 2.75 (s, 3H, CH_3).

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 158.7, 147.3, 136.0, 129.3, 128.2, 127.7, 126.2, 125.6, 122.1, 24.8.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{10}H_{10}N$ $(M+H)^+$: 144.0808, found: 144.0806.

TLC: R_f = 0.56 (CH_2Cl_2/MeOH 10%).

6-Hydroxyquinolin-2(1*H*)-one (2n)



[163.18] **2n** [161.16]

The general procedure (main body) was followed. 6-Hydroxy-3,4-dihydro-2-(1*H*)-quinolinone (40.8 mg, 250 µmol, 1.00 eq), oAC_{HNO3} (n = 4.00, 224 mg) and toluene (1.00 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7%, 400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2/MeOH 3% → 15%), which gave **2n** (22 mg, 137 µmol, 55%) as a colorless solid. In a second reaction with $oAC_{air(\Delta)}$ (n = 4.00, 224 mg) in toluene (1.00 mL), a yield of 47 % (29 mg, 118 µmol) was obtained. A reaction with $oAC_{air(\Delta)}$ (n = 4.00, 224 mg) in anisole (1.50 mL) at 140 °C over 3 d gave an NMR-yield of 47 %. Spectroscopic data matches recorded literature values.[14]

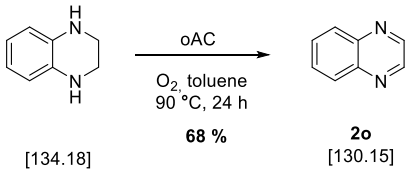
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.49 (s, 1H, O*H*), 10.09 (s, 1H, O*H*), 7.73 (d, ^3J = 9.0 Hz, 1H, C*H*), 7.44 (d, ^3J = 8.5 Hz, 1H, C*H*), 6.68 (d, ^4J = 2.3 Hz, 1H, C*H*), 6.62 (dd, ^3J = 8.5 Hz, ^4J = 2.3 Hz, 1H, C*H*), 6.21 (d, ^3J = 9.5 Hz, 1H, C*H*).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 162.3, 159.3, 140.8, 140.1, 129.3, 117.5, 112.4, 111.5, 99.8.

HRMS (**ESI$^+$**): *m/z* calculated for $C_9H_8NO_2$ $(M+H)^+$: 162.0550, found: 162.0559.

TLC: R_f = 0.28 (CH_2Cl_2/MeOH 10%).

Quinoxaline (2o)



The general procedure (main body) was followed. 1,2,3,4-Tetrahydroquinoxaline (33.4 mg, 249 µmol, 1.00 eq), oAC_{HNO3} (n = 4.00, 224 mg) and toluene (1.00 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of Celite and washed with CH_2Cl_2/MeOH (7%, 400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2/MeOH 0% → 3%), which gave **2o** (16 mg, 123 µmol, 49%) as a red oil. In a second reaction with $oAC_{air(\Delta)}$ (n = 4.00, 224 mg) in toluene (1.00 mL), a yield of 67 % (22 mg, 169 µmol) was obtained. Spectroscopic data matches recorded literature values.[15]

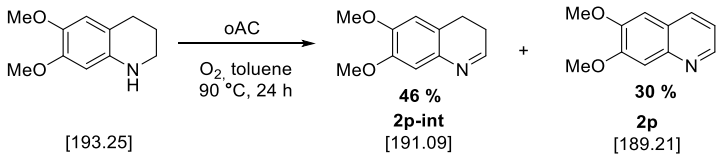
^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 8.87 (s, 2H, 2 x C*H*), 8.14-8.12 (m, 2H, 2 x C*H*), 7.81-7.78 (m, 2H, 2 x C*H*).

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 145.1, 143.2, 130.2, 129.7.

HRMS (**ESI$^+$**): *m/z* calculated for $C_8H_7N_2$ $(M+H)^+$: 131.0604, found: 131.0605.

TLC: R_f = 0.31 (CH_2Cl_2/MeOH 2%).

6,7-Dimethoxyquinoline (2p)



The general procedure (main body) was followed. 1,2,3,4-Tetrahydro-6,7-dimethoxyquinoline (57.1 mg, 295 µmol, 1.18 eq), $oAC_{air(\Delta)}$ (n = 4.00, 224 mg) and toluene (1.50 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7 %, 200 mL/12 %, 100 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2/MeOH 2 % → 5 % → 10 %), which gave **2p** (16.8 mg, 88.7 µmol, 30 %) as well as 3,4-dihydro-6,7-dihydroxyquinoline **2p-int** (25.7 mg, 134 µmol, 49 %) both as a yellow oil. Spectroscopic data for **2p** matches recorded literature values.[16] An additional control test was run in the same conditions for 30 minutes. The yield was determined with NMR as 61% **2p-int** and 3% **2p**.

2p (*fully oxidized*)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 9.05 (s, 1H, C*H*), 8.31 (d, ^3J = 5.7 Hz, 1H, C*H*), 7.64 (d, ^3J = 5.5 Hz, 1H, C*H*), 7.47 (s, 1H, C*H*), 7.33 (s, 1H, C*H*), 3.92 (s, 3H, CH_3), 3.92 (s, 3H, CH_3).

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 152.7, 150.0, 149.7, 141.5, 131.9, 124.4, 119.1, 105.5, 104.8.

TLC: R_f = 0.42 (CH_2Cl_2/MeOH 10 %).

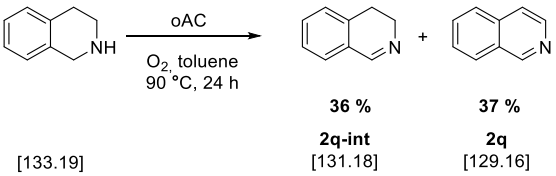
2p-int (*intermediate*)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 8.21 (t, ^3J = 2.0 Hz, 1H, C*H*), 7.03 (s, 1H, C*H*), 6.85 (s, 1H, C*H*), 3.79 (s, 3H, CH_3), 3.76 (s, 3H, CH_3). 3.60-3.55 (m, 2H, CH_2), 2.60 (t, ^3J = 7.9 Hz, 2H, CH_2).

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 159.0, 150.9, 147.5, 129.3, 121.0, 110.9, 110.8, 55.7. 55.6, 46.7, 24.0.

TLC: R_f = 0.28 (CH_2Cl_2/MeOH 10 %).

Isoquinoline (2q)



The general procedure (main body) was followed. 1,2,3,4-Tetrahydroisoquinoline (31.7 µL, 250 µmol, 1.00 eq), oAC_{HNO3} (n = 4.00, 224 mg) and toluene (1.00 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7%, 400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2/MeOH 0% → 5%), which gave the fully oxidized **2q** (12 mg, 93.5 µmol, 37%) as well as the intermediate **2q-int** (12 mg, 91.0 µmol, 36%), both as a yellow oil. In a second reaction with $oAC_{air(\Delta)}$ (n = 4.00, 224 mg) in toluene (1.00 mL), NMR-yields of 40% for **2q** as well as 4% **2q-int** were obtained. An additional control test was run in the same conditions for 30 minutes giving 50% **2q-int** and 2% **2q**. A reaction with $oAC_{air(\Delta)}$ (n = 4.00, 224 mg) at 100 °C in toluene (1.50 mL) over 3 d gave an NMR-yield of 67% **2q**. Spectroscopic data matches recorded literature values.[15]

2m (*fully oxidized*)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 9.27 (s, 1H, C*H*), 8.54 (d, ^3J = 5.4 Hz, 1H, C*H*), 7.98 (dd, ^3J = 8.2 Hz, ^4J = 0.9 Hz, 1H, C*H*), 7.82 (d, ^3J = 7.7 Hz, 1H, C*H*), 7.70 (ddd, ^3J = 8.2 Hz, ^3J = 6.9 Hz, ^4J = 1.3 Hz, 1H, C*H*), 7.66 (d, ^3J = 5.7 Hz, 1H, C*H*) 7.82 (d, ^3J = 7.7 Hz, 1H, C*H*), 7.61 (ddd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1H, C*H*).

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 152.7 (*C*H), 143.2 (*C*H), 135.9 (*C*H), 130.5 (*C*H), 128.9 (*C*H), 127.8 (*C*H), 127.4 (*C*H), 126.6 (*C*H), 120.6 (*C*H).

HRMS (**ESI$^+$**): *m/z* calculated for C_9H_8N $(M+H)^+$: 130.0651, found: 130.0647.

TLC: R_f = 0.59 (CH_2Cl_2/MeOH 10%).

2m-int (*intermediate*)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 8.35 (s, 1H, C*H*), 7.32-7.28 (m, ^3J = 7.7 Hz, 3H, 3 x C*H*), 7.16 (d, ^3J = 7.2 Hz, 1H, C*H*), 3.80-3.76 (d, ^3J = 7.7 Hz, 2H, CH_2), 2.76 (t, ^3J = 7.8 Hz, 1H, C*H*).

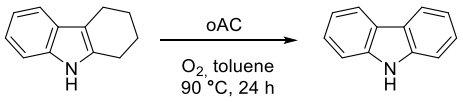
^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 160.5 (*C*H), 136.5 (*C*), 132.3 (*C*), 131.2 (*C*H), 127.6 (*C*H), 127.3 (*C*H), 127.2 (*C*H), 47.5 (*C*H), 25.2 (*C*Ha).

HRMS (**ESI**$^+$): *m/z* calculated for $C_9H_{10}N$ $(M+H)^+$: 132.0808, found: 132.0817.

TLC: R_f = 0.51 (CH_2Cl_2/MeOH 10%).

Due to their close R_f it was not possible to fully separate product and intermediate via flash chromatography, giving a 15% impurity of **2q** in the spectrum of **2q-int**. This value was included into the total yield of both compounds.

Carbazole (2r)



[171.24] **2r** [167.21]

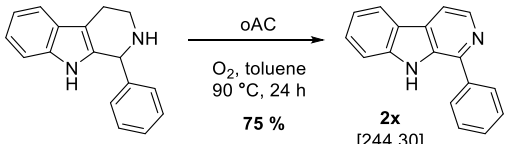
The general procedure (main body) was followed. 1,2,3,4-Tetrahydrocarbazole (43.3 mg, 253 µmol, 1.00 eq), $oAC_{air(\Delta)}$ (n = 4.00, 224 mg) and toluene (1.50 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 24 h at 90 °C. The reaction was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH (7%, 200 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (hexane/EtOAc 9:1 → 6:1 → 4:1), which gave **2r** (32.9 mg, 197 µmol, 78%) as a colorless solid. Spectroscopic data matches recorded literature values.[17]

^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 10.23 (s, 1H, N*H*), 8.09 (d, ^3J = 7.9 Hz, 2H, 2 x C*H*), 7.48 (dt, ^3J = 8.1 Hz, ^3J = 0.8 Hz, 2H, 2 x C*H*), 7.38 (ddd, ^3J = 8.2 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 2H, 2 x C*H*), 7.15 (ddd, ^3J = 7.9 Hz, ^3J = 7.0 Hz, ^4J = 0.9 Hz, 2H, 2 x C*H*).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 139.7, 125.5, 122.3, 120.1, 118.4, 110.8.

TLC: R_f = 0.46 (hexane/EtOAc 4:1).

1-phenyl-1*H*-pyrido[3,4-*b*]indole (2x)



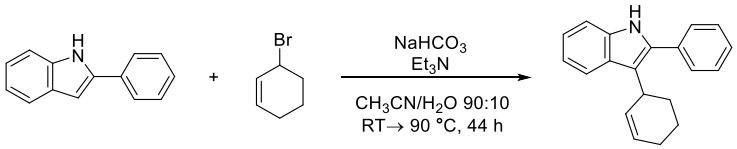
1x [248.13] **2x** [244.30]

The general procedure (main body) was followed. **1x** (20.2 mg, 80 µmol, 1.00 eq), $oAC_{air(\Delta)}$ (n = 4.00, 75 mg) and toluene (1.00 mL) were placed in a reaction tube under oxygen atmosphere. The mixture was stirred for 24 h at 90 °C. The reaction was cooled to room temperature, filtered through a pad of celite and washed with CH_2Cl_2:MeOH (10:1, 150 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (CH_2Cl_2:MeOH 10:1), which gave **2x** (15 mg, 60 µmol, 75%) as a pale yellow solid. A second reaction with $oAC_{air(\Delta)}$ (n = 4.00, 75 mg) in toluene (1 mL) at 90 °C over 3 d gave an isolated yield of 86% (17 mg, 69 µmol). Spectroscopic data matches recorded literature values.[18]

^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.52 (s, 1H, N*H*), 8.47 (d, *J* = 5.2 Hz, 1H, C*H*), 8.27 (d, *J* = 7.9 Hz, 1H, C*H*), 8.13 (d, *J* = 5.2 Hz, 1H, C*H*), 8.04 (d, *J* = 7.0 Hz, 2H, 2 x C*H*), 7.70 – 7.59 (m, 3H, 3 x C*H*), 7.55 (d, *J* = 26.1 Hz, 2H, 2 x C*H*), 7.27 (d, *J* = 14.9 Hz, 1H, C*H*).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 142.64, 141.57, 138.87, 138.84, 133.46, 129.64, 129.20, 128.98, 128.85, 128.63, 122.07, 121.30, 119.97, 114.36, 112.90.

2-Phenyl-3-(1-cyclohexen-3-yl)-indole (3a)



[193.25] [161.04] **3a** [273.38]

The synthesis was performed according to a modified procedure of WESTERMAIER *et al*.[19] 3-Bromocyclohexene (0.69 mL, 6.00 mmol, 1.20 eq) was added to a suspension of 2-phenylindole (966 mg, 5.00 mmol, 1.00 eq) and sodium bicarbonate (840 mg, 10.0 mmol, 2.00 eq) in acetonitrile/dist. H_2O (9:1, 25.0 mL). The reaction was stirred at RT and the pH of the reaction solution was monitored. Sodium bicarbonate (840 mg, 10.0 mmol, 2.00 eq) was added after 50 min and trimethylamine (0.69 mL, 5.00 mmol, 1.00 eq) after 4 h. After stirring for 20 h at RT the reaction was refluxed for 1.5 h at 60 ˚C followed by 22 h at 90 ˚C. The reaction was then cooled to RT and, sequentially, dist. H_2O (2.5 mL), HCl aq. (1 M, 5 mL) and dist. H_2O (30 mL) were added. The aqueous phase was extracted with Et_2O (3 x 30 mL) and the combined organic phases were dried over $MgSO_4$. Flash chromatography (pentane/EtOAc 60:1 → 30:1) gave **3a** (234 mg, 0.86 mmol, 17%) as pale-yellow solid.

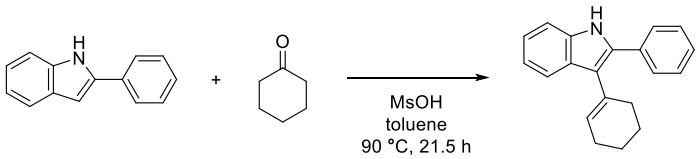
^{1}H-NMR: (300 MHz, DMSO-d_6): δ = 11.11 (s, 1H, N*H*), 7.60-7.48 (m, 5H, 5 x C*H*), 7.42-7.33 (m, 2H, 2 x C*H*), 7.43 (ddd, ^3J = 8.2 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 1H, C*H*), 6.94 (ddd, ^3J = 8.0 Hz, ^3J = 7.1 Hz, ^4J = 1.2 Hz, 1H, C*H*), 5.86-5.80 (m, 1H, CH_{Cy}), 5.67 (d, ^3J = 10.0 Hz, 1H, CH_{Cy}), 3.77-3.68 (m, 1H, CH_{stereo}), 2.27-1.87 (m, 5H, 2 x CH_2, 1 x C*H*H), 1.71-1.56 (m, 1H, 1 x C*H*H).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 136.3, 134.2, 133.0, 132.0, 2 x 128.6, 2 x 128.4, 127.4, 127.2, 126.5, 121.1, 120.0, 118.2, 114.9, 111.3, 33.1, 30.4, 24.5, 22.5.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{20}H_{20}N$ $(M+H)^+$: 274.1590, found: 274.1582.

TLC: R_f = 0.47 (hexane/EtOAc 4:1).

2-Phenyl-3-(1-cyclohexen-1-yl)-indole (3b)



[193.25] [98.15] **3b** [273.38]

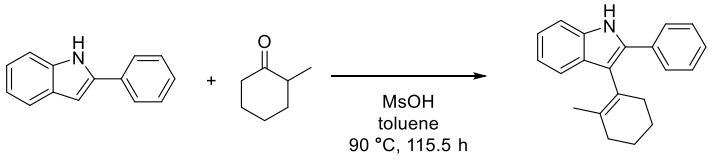
Cyclohexanone (248 µL, 2.40 mmol, 1.20 eq) and methanesulfonic acid (2.58 µL, 0.04 mmol, 0.02 eq) were added to a solution of 2-phenylindole (386 mg, 2.00 mmol, 1.00 eq) in toluene (4.00 mL). The reaction was stirred at 90 °C for 21.5 h and poured into $NaHCO_3$ aq. sat. (20 mL). The aqueous phase was extracted with Et_2O (3 x 20 mL), after which the combined organic phases were washed with dist. H_2O (20 mL) and dried over $MgSO_4$. The solvents were removed under reduced pressure, giving **3b** (375 mg, 1.37 mmol, 69%) as a pale-yellow solid.

^{1}H-NMR: (500 MHz, DMSO-d_6): δ = 7.70-7.68 (m, 2H, 2 x C*H*), 7.48-7.44 (m, 3H, 3 x C*H*), 7.36 (d, ^3J = 8.0 Hz, 1H, C*H*), 7.33-7.30 (m, 1H, C*H*), 7.10 (ddd, ^3J = 8.0 Hz, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 1H, C*H*), 6.99 (ddd, ^3J = 7.9 Hz, ^3J = 7.0 Hz, ^4J = 0.9 Hz, 1H, C*H*), 5.78-5.77 (m, 1H, CH_{Cy}), 2.29-2.19 (s, 2H, CH_2), 2.13-2.09 (m, 2H, CH_2), 1.71-1.67 (m, 4H, 2 x CH_2).

^{13}C-NMR: (126 MHz, DMSO-d_6): δ = 135.9, 133.1, 132.6, 131.8, 128.5 (2 x *C*H), 128.2, 127.1, 2 x 127.1, 126.7, 121.6, 2 x 119.0, 116.0, 111.1, 29.3, 25.3, 22.9, 21.9.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{20}H_{10}N$ $(M+H)^+$: 274.1590, found: 274.1584.

2-Phenyl-3-(2-methyl-cylohexene-1-yl)-indole (3c)



[193.25]] [112.17] **3c** [287.41]

MsOH (5.03 µL, 77.5 µmol, 0.05 eq) was added into a solution of 2-methylcyclohexanone (227 µL, 1.86 mmol, 1.20 eq) and 2-phenylindole (300 mg, 1.55 mmol, 1.00 eq) in 5.00 mL toluene. The reaction was refluxed at 90 °C for 115.5 h, cooled to RT and poured into $NaHCO_3$ aq. sat. (30 mL). The aqueous phase was extracted with CH_2Cl_2 (1 x 40 mL, 3 x 30 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was removed under reduced pressure and crude product was purified via flash chromatography (pentane/EtOAc 50:1), which gave **3c** (70.9 mg, 247 µmol, 16%) as a pale-yellow solid.

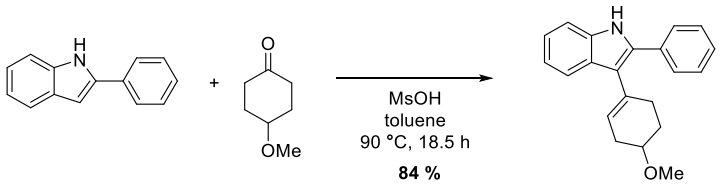
^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 8.14 (s, 1H, N*H*), 7.66-7.64 (m, 2H, 2 x C*H*), 7.44-7.37 (m, 4H, 4 x C*H*), 7.29 (ddd, ^3J = 7.4 Hz, ^3J = 1.8 Hz, ^4J = 1.8 Hz, 1H, C*H*), 7.20 (ddd, ^3J = 8.1 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 1H, C*H*), 7.11 (ddd, ^3J = 8.0 Hz, ^3J = 7.1 Hz, ^4J = 1.1 Hz, 1H, C*H*), 2.27-2.05 (m, 4H, 2 x CH_2), 1.81-1.62 (m, 4H, 2 x CH_2), 1.49 (s, CH_3).

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 136.0, 133.6, 132.7, 132.6, 129.1, 2 x 128.9, 127.3, 2 x 126.3, 124.8, 122.4, 120.2, 119.8, 117.3, 110.8, 31.8, 31.0, 24.0, 23.5, 21.0.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{22}H_{21}N$ $(M+H)^+$: 288.1747, found: 288.1747.

TLC: R_f = 0.42 (hexane/EtOAc 4:1).

2-Phenyl-3-(4-methoxy-cylohexene-1-yl)-indole (3d)



[193.25] [128.17] **3c** [303.41]

MsOH (5.03 µL, 77.5 µmol, 0.05 eq) was added to a solution of 4-methoxycyclohexanone (304 µL, 2.33 mmol, 1.50 eq) and 2-phenylindole (300 mg, 1.55 mmol, 1.00 eq) in 5.00 mL toluene. The reaction was refluxed at 90 °C

for 18.5 h, during which the solution turned red. The reaction mixture was cooled to RT and poured into $NaHCO_3$ aq. sat. (30 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 30 mL, 1 x 40 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was removed under reduced pressure and crude product was purified via flash chromatography (pentane/EtOAc 50:1 → 5:1), which gave **3d** (396 mg, 1.31 mmol, 84%) as a pale-yellow solid.

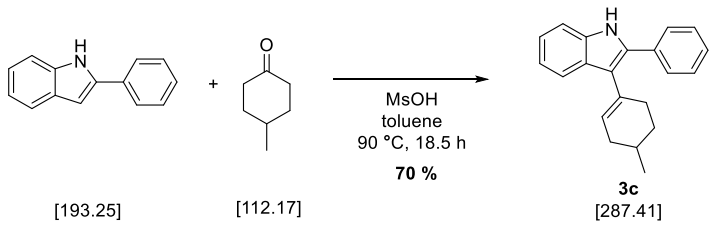
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.31 (s, 1H, N*H*), 7.70-7.67 (m, 2H, 2 x C*H*), 7.48-7.43 (m, 3H, 3 x C*H*), 7.37-7.20 (m, 2H, 2 x C*H*), 7.10 (ddd, ^3J = 8.2 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1H, C*H*), 7.00 (ddd, ^3J = 7.9 Hz, ^3J = 6.9 Hz, ^4J = 1.0 Hz, 1H, C*H*), 5.66 (s, 1H, C*H*), 3.62-3.56 (m, 1H, CH*H*), 3.32 (s, 3H, CH_3), 2.57-2.51 (m, 1H, CH*H*), 2.26-2.21 (m, 3H, CH_2, CH*H*), 1.99-1.91 (m, 1H, CH*H*), 1.72-1.63 (m, 1H, CH*H*).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 135.9, 132.9, 132.7, 131.7, 2 x 128.5, 128.1, 127.2, 2 x 127.1, 124.0, 121.7, 119.1, 119.0, 115.2, 111.2, 74.5, 55.1, 31.4, 27.5, 27.4.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{21}H_{21}NO$ $(M+H)^+$: 304.1696, found: 304.1681.

TLC: R_f = 0.33 (hexane/EtOAc 4:1).

2-Phenyl-3-(4-methyl-cylohexene-1-yl)-indole (3e)



MsOH (5.03 µL, 77.5 µmol, 0.05 eq) was added to a solution of 4-methylcyclohexanone (287 µL, 2.33 mmol, 1.50 eq) and 2-phenylindole (300 mg, 1.55 mmol, 1.00 eq) in 5.00 mL toluene. The reaction was refluxed at 90 °C for 18 h, during which the solution turned red. The reaction mixture was cooled to RT and poured into $NaHCO_3$ aq. sat. (30 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 30 mL, 1 x 40 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was removed under reduced pressure and crude product was purified via flash chromatography (pentane/EtOAc 50:1 → 20:1), which gave **3e** (311 mg, 1.08 mmol, 70%) as a pale-yellow solid.

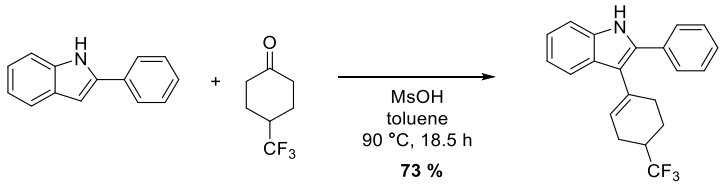
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.28 (s, 1H, N*H*), 7.69-7.66 (m, 2H, 2 x C*H*), 7.48-7.43 (m, 3H, 3 x C*H*), 7.37-7.29 (m, 2H, 2 x C*H*), 7.09 (ddd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1H, C*H*), 6.99 (ddd, ^3J = 7.9 Hz, ^3J = 7.0 Hz, ^4J = 1.0 Hz, 1H, C*H*), 5.74 (s, 1H, C*H*), 2.33-2.08 (m, 3H), 1.89-1.71 (m, 3H), 1.41-1.31 (m, 1H, CH*H*), 1.02 (d, ^3J = 6.2 Hz, 3H, CH_3).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 135.9, 133.1, 132.6, 131.5, 2x 128.5, 128.2, 127.1, 2 x 127.1, 126.3, 121.6, 119.0, 118.9, 115.7, 111.1, 33.9, 31.0, 29.1, 27.7, 21.7.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{21}H_{21}N$ $(M+H)^+$: 288.1747, found: 288.1741.

TLC: R_f = 0.58 (hexane/EtOAc 4:1).

2-Phenyl-3-(4-trifluoromethyl-cylohexene-1-yl)-indole (3f)



[193.25] [166.14] [341.38]

MsOH (5.03 µL, 77.5 µmol, 0.05 eq) was added into a solution of 4-trifluoromethylcyclohexanone (317 µL, 2.33 mmol, 1.50 eq) and 2-phenylindole (300 mg, 1.55 mmol, 1.00 eq) in 5.00 mL toluene. The reaction was refluxed at 90 °C for 17 h, cooled to RT and poured into $NaHCO_3$ aq. sat. (30 mL). The aqueous phase was extracted with CH_2Cl_2 (1 x 40 mL, 2 x 30 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was removed under reduced pressure and crude product was purified via flash chromatography (pentane/EtOAc 40:1 → 10:1), which gave **3f** (387 mg, 1.13 mmol, 73%) as a pale-yellow solid.

^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.35 (s, 1H, N*H*), 7.68-7.65 (m, 2H, 2 x C*H*), 7.52-7.44 (m, 3H, 3 x C*H*), 7.38-7.31 (m, 2H, 2 x C*H*), 7.11 (ddd, ^3J = 8.0 Hz, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 1H, C*H*), 7.01 (ddd, ^3J = 7.9 Hz, ^3J = 7.1 Hz, ^4J = 0.9 Hz, 1H, C*H*), 5.77 (s, 1H, C*H*), 2.74-2.60 (m, 1H, CH*H*), 2.48-2.43 (m, 1H, CH*H*), 2.34-2.17 (m, 3H), 2.01-1.96 (m, 1H, CH*H*), 1.68-1.58 (m, 1H, CH*H*).

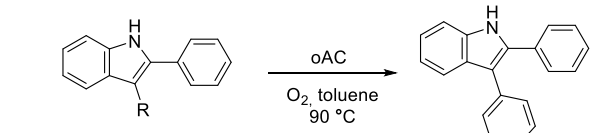
^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 151.8, 140.2, 136.5, 132.0, 128.3, 127.7, 121.1, 120.5, 119.1, 113.0, 112.1, 37.5, 3 x 28.9.

^{19}F-NMR: (400 MHz, DMSO-d_6): δ = 71.5.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{22}H_{18}F_3N$ $(M+H)^+$: 324.1464, found: 324.1464.

TLC: R_f = 0.41 (hexane/EtOAc 4:1).

2,3-Diphenylindole (4a)



3a: R = 1-cyclohexen-3-yl **35%**
3b: R = 1-cyclohexen-1-yl **13 %**

[273.38] **4a** [269.35]

In two separate reactions, 2-Phenyl-3-(1-cyclohexen-3-yl)-indol (**3a**, 50.0 mg, 180 µmol, 1.00 eq) or 2-Phenyl-3-(1-cyclohexen-1-yl)-indol (**3b**, 68.3 mg, 250 µmol, 1.00 eq), oAC_{HNO3} (n = 4, 164 mg **3a,** 224 mg **3b**) and toluene (1.00 mL) were placed in a reaction tube under an oxygen atmosphere. The reactions were stirred at 90 °C for 23 h (**3a**) /73.5 h (**3b**). It was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2 (100 mL). The solvent was removed under reduced pressure and the crude product was purified via flash chromatography (pentane/EtOAc 100:1 → 50:1), giving **4a** (9 mg, 33.4 µmol, 13% from **3b**/ 17 mg, 63.1 µmol, 35% from **3a**) as a yellow oil. In a second reaction with with **3a** (68.5 mg, 251 mmol, 1.00 eq, 24 h reaction time) or **3b** (68.0 mg, 249 mmol, 1.00 eq, 72 h reaction time) with $oAC_{air(\Delta)}$ (n = 4.00, 224 mg) in toluene (1.50 mL), NMR-yields of 61% **3a** as well as 49% **3b** were obtained. Spectroscopic data matches recorded literature values.[20]

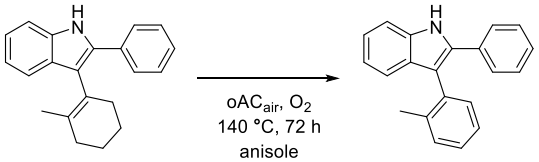
^{1}H-NMR: (300 MHz, $CDCl_3$): δ = 8.24 (s, 1H, N*H*), 7.70-7.68 (m, 1H, C*H*), 7.46-7.23 (m, 12H, 12 x C*H*), 7.16 (ddd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, ^4J = 1.1 Hz, 1H, C*H*).

^{13}C-NMR: (101 MHz, $CDCl_3$): δ = 136.1, 135.2, 134.2, 132.9, 2 x 130.3, 2 x 128.8, 2 x 128.7, 2 x 128.3, 127.8, 126.4, 124.3, 122.9, 120.6, 119.9, 115.3, 111.0.

HRMS (**ESI**$^+$): *m/z* calculated for $C_{20}H_{16}N$ $(M+H)^+$: 270.1277, found: 270.1279.

TLC: R_f = 0.51 (Hexane/EtOAc 4:1).

2-Phenyl-3-(*o*-tolyl)-indole (4c)



3c [287.41] **4c** [283.37]

The general procedure (main body) was followed with **3c** (64.1 mg, 223 µmol, 1.00 eq) and $oAC_{air(\Delta)}$ (200 mg, n = 4) in anisole (1.34 mL). The reaction was stirred at 140 °C for 72 h. It was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH 12% (400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (pentane/EtOAc 50:1), which gave **4c** (36.5 mg, 129 µmol, 58%) as a yellow oil. Spectroscopic data matches recorded literature values.[21]

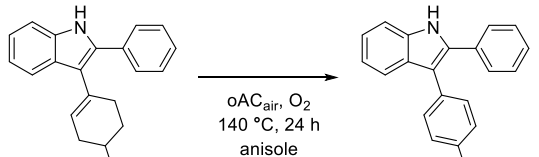
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.55 (s, 1H, N*H*), 7.46 (d, ^3J = 8.2 Hz, 1H, C*H*), 7.40-7.37 (m, 2H, 2 x C*H*), 7.34-7.20 (m, 7H, 7 x C*H*), 7.15 (ddd, ^3J = 8.0 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1H, C*H*), 7.09 (d, ^3J = 7.9 Hz, 1H, C*H*), 6.98 (ddd, ^3J = 8.0 Hz, ^3J = 6.9 Hz, ^4J = 1.0 Hz, 1H, C*H*), 1.94 (s, 1H, CH_3).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 136.9, 136.0, 134.9, 133.6. 132.7, 131.2, 130.2, 128.7, 128.5 (2 x *C*H), 127.2, 127.1, 126.6 (2 x *C*H), 126.0, 121.9, 119.4, 118.7, 113.0, 111.4, 19.8.

HRMS (**ESI**$^+$): *m/z* calculated for $C_{21}H_{18}N$ $(M+H)^+$: 284.1434, found: 284.1427.

TLC: R_f = 0.42 (hexane/EtOAc 4:1).

2-Phenyl-3-(*p*-tolyl)-indole (4e)



3e [287.41] **4e** [283.37]

The general procedure (main body) was followed with **3e** (71.9 mg, 250 µmol, 1.00 eq) and $oAC_{air(\Delta)}$ (224 mg, n = 4) in anisole (1.50 mL). The reaction was stirred at 140 °C for 24 h. It was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH 12% (400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (pentane/EtOAc 50:1 → 40:1), which gave **4e** (51.0 mg, 180 µmol, 72%) as an orange oil. Spectroscopic data matches recorded literature values.[21]

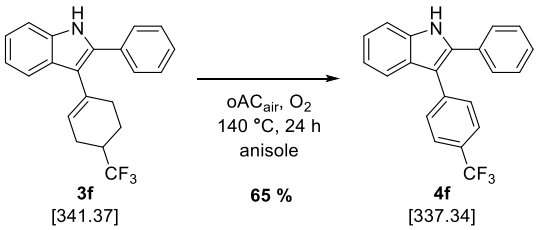
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.50 (s, 1H, N*H*), 7.47-7.42 (m, 4H, 4 x C*H*), 7.38-7.34 (m, 2H, 2 x C*H*), 7.31-7.27 (m, 1H, C*H*), 7.24-7.19 (m, 4H, 4 x C*H*), 7.15 (ddd, ^3J = 8.1 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, 1H, C*H*), 7.02 (ddd, ^3J = 7.9 Hz, ^3J = 7.0 Hz, ^4J = 1.0 Hz, 1H, C*H*), 2.34 (s, 3H, CH_3).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 136.1, 135.1, 133.8, 132.6, 132.2, 129.6, 129.3, 128.5, 128.1, 127.4, 121.9, 119.6, 118.6, 113.2, 111.4, 20.8.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{21}H_{18}N$ $(M+H)^+$: 284.1434, found: 284.1421.

TLC: R_f = 0.49 (hexane/EtOAc 4:1).

2-Phenyl-3-(4-trifluoromethylphenyl)-indole (4f)



3f [341.37] **4f** [337.34]

The general procedure (main body) was followed with **3f** (85.2 mg, 250 µmol, 1.00 eq) and $oAC_{air(\Delta)}$ (224 mg, n = 4) in anisole (1.50 mL). The reaction was stirred at 140 °C for 24 h. It was cooled to 0 °C, filtered through a pad of celite and washed with CH_2Cl_2/MeOH 12% (400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography (pentane/EtOAc 40:1), which gave **4f** (68.8 mg, 204 µmol, 65 %) as a white solid. Spectroscopic data matches recorded literature values.[14]

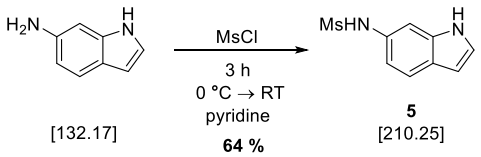
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.73 (s, 1H, N*H*), 7.74-7.72 (m, 2H, 2 x C*H*), 7.58-7.54 (m, 3H, 3 x C*H*), 7.49-7.33 (m, 6H, 6 x C*H*), 7.20 (ddd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, ^4J = 1.1 Hz, 1H, C*H*), 7.09 (ddd, ^3J = 8.0 Hz, ^3J = 7.0 Hz, ^4J = 1.0 Hz, 1H, C*H*).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 140.29, 136.64, 135.77, 132.48, 130.63, 129.21, 128.98, 128.47, 127.86, 126.81, 126.50, 126.34, 126.00, 125.96, 125.92, 125.88, 123.64, 122.77, 120.65, 118.79, 112.20, 112.10.

^{19}F-NMR: (377 MHz, DMSO-d_6): δ = 60.2.

TLC: R_f = 0.35 (hexane/EtOAc 4:1).

***N*-(1*H*-Indol-6-yl)-methanesulfonamide (5)**



[132.17] **5** [210.25]

A procedure of Yudasaka et al. was followed.[22] MsCl (293 µL, 3.78 mmol, 1.00 eq) was added to a stirred solution of 6-aminoindole (500 mg, 3.78 mmol, 1.00 eq) in toluene (20.0 mL) at 0 °C. Upon heating to RT, the solution turned red. After stirring at RT for 3 h pyridine was removed under reduced pressure. Dist. H_2O (20 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (4 x 20 mL). The combined organic phases were dried

over $MgSO_4$. The solvent was removed under reduced pressure and crude product was purified via flash chromatography for three times (CH_2Cl_2/MeOH 1 → 2%, 1 → 1.5%, 0.5 → 1%), giving **5** (507 mg, 2.41 mmol, 64%) as a pale-yellow solid.

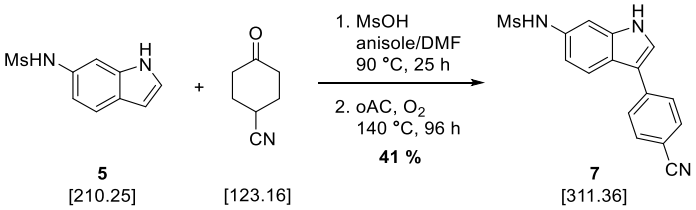
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.05 (s, 1H, N*H*), 9.38 (s, 1H, N*H*), 7.47 (d, ^3J = 8.4 Hz, 1H, C*H*), 7.32-7.39 (m, 2H, 2 x C*H*), 6.90 (dd, ^3J = 8.4 Hz, ^4J = 1.8 Hz, 1H, C*H*), 6.38 (s, 1H, C*H*), 2.88 (s, 3H, CH_3).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 136.0, 132.0, 125.5, 125.0, 120.4, 114.2, 104.3, 100.9, 38.4.

HRMS (**ESI$^+$**): *m/z* calculated for $C_9H_{10}N_2NaO_2S$ $(M+Na)^+$: 233.0355, found: 233.0365.

TLC: R_f = 0.33 (CH_2Cl_2/MeOH 10 %).

***N*-(1*H*-3-(4-Cyanophenyl)-indol-6-yl)-methanesulfonamide (7)**



5 [210.25] [123.16] **7** [311.36]

MsOH (2.39 µL, 36.9 µmol, 0.05 eq) was added to a stirred solution of **5** (155 mg, 737 µmol, 1.00 eq) and 4-oxocyclohexanecarbonitrile (172 µL, 1.47 mmol, 2.00 eq) in anisole/DMF (2.50 mL, 4:1). The reaction was stirred at 90 °C for 25 h. oAC (330 mg) was added to the reaction mixture and it was stirred at 140 °C under oxygen atmosphere for another 96 h. It was cooled to RT, filtered through a pad of celite and washed with CH_2Cl_2/MeOH 12% (400 mL). The solvent was removed under reduced pressure and crude product was purified via flash chromatography twice (CH_2Cl_2/MeOH 0 → 5%, 1%), which gave **7** (94.5 mg, 304 µmol, 41%) as a yellow solid.

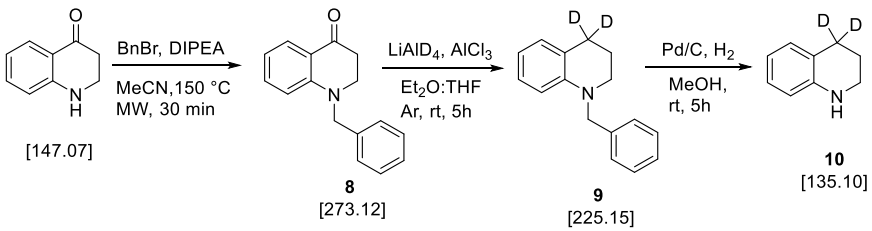
^{1}H-NMR: (400 MHz, DMSO-d_6): δ = 11.62 (s, 1H, N*H*), 9.57 (s, 1H, N*H*), 7.93 (d, ^3J = 2.7 Hz, 1H, C*H*), 7.91-7.87 (m, 3H, 3 x C*H*), 7.85-7.82 (m, 2H, 2 x C*H*), 7.40 (d, ^4J = 1.7 Hz, 1H, C*H*), 7.05 (dd, ^3J = 8.5 Hz, ^4J = 2.1 Hz, 1H, C*H*), 2.93 (s, 3H, CH_3).

^{13}C-NMR: (101 MHz, DMSO-d_6): δ = 140.8, 137.5, 133.0, 2 x 132.7, 2 x 126.3, 125.9, 121.7, 119.7, 119.4, 115.0, 114.0, 107.0, 104.3, 38.6.

HRMS (**ESI$^+$**): *m/z* calculated for $C_{16}H_{13}N_3NaO_2S$ $(M+Na)^+$: 334.0621, found: 334.0615.

TLC: R_f = 0.49 (CH_2Cl_2 10:1).

1,2,3,4-tetrahydroquinoline-4,4-d$_2$ (10)



[147.07] **8** [273.12] **9** [225.15] **10** [135.10]

8 was prepared following a patented procedure.[23] 2,3-dihydroquinolin-4(1H)-one (882 mg, 6 mmol, 1 eq), benzyl bromide (0.72 mL, 6 mmol, 1 eq) and diisopropylethylamine (2.08 mL, 12 mmol, 2 eq) were put in a MW sealed vial with 8 mL MeCN and heated in a microwave at 150 °C for 30 minutes. EtOAc (100 mL) was added and the organic layer was washed with water (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered, concentrated under pressure and purified via flash chromatography (EtoAc/hexane 1:5 → 1:1) to afford compound **8**. (1.3 g, 4.7 mmol, 78%). **10** was prepared according to a modified method by Sakami et al.[25] $LiAlD_4$ (80 mg, 1.90 mmol) was suspended in Et_2O (10 mL) and THF (5 mL), and $AlCl_3$ (240 mg, 18.00 mmol) was added. After 10 min of stirring at room temperature, compound **8** (474 mg, 1.73 mmol), as an Et_2O (10 mL) solution, was added to the suspension and then $AlCl_3$ (200 mg, 15.02 mmol) was added at room temperature. The mixture was stirred at the same temperature for 5 h, and the reaction mixture was quenched by addition of H_2O (100 mL). Saturated aqueous $NaHCO_3$ solution (40 mL) and Et_2O (100 mL) were added, and the organic layer was separated, dried over Na_2SO_4, and concentrated to give **9** (362 mg, 1.60 mmol, 92 %). The benzyl compound obtained above (362 mg) was dissolved n MeOH (40 mL), and Pd on charcoal (5%, 120 mg) was added. The mixture was stirred at room temperature under H_2 and after 5 h, the mixture was filtered through a pad of Celite. The resulting solution was concentrated, and the crude mixture was purified via flash chromatography (CH_2Cl_2) to give the title compound **10** (166 mg, 1.22 mmol, 76 %) as a colorless oil.

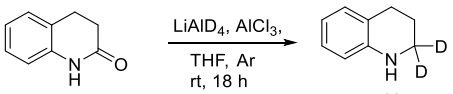
^{1}H-NMR: (400 MHz, DMSO-d_6) δ = 6.88 – 6.76 (m, 2H, 2 x C*H*), 6.45 – 6.34 (m, 2H, 2 x CH), 5.56 (s, 1H, N*H*), 3.22 – 3.09 (m, 2H, CH_2), 1.83 – 1.70 (m, 2H, CH_2).

^{13}C-NMR: (101 MHz, DMSO-d_6) δ = 145.86, 129.38, 126.83, 120.17, 115.45, 113.76, 41.22, 26.44, 21.84.

HRMS (**ESI$^+$**): *m/z* calculated for $C_9H_9ND_2$ $(M+H)^+$: 136.1090, found: 136.1088.

TLC: R_f = 0.78 (CH_2Cl_2).

1,2,3,4-tetrahydroquinoline-2,2-d$_2$ (11)



[147.07] **11** [135.10]

3,4-dihydroquinolin-2(1H)-one (147 mg, 1 mmol, 1 eq) was dissolved in dry THF (10 mL) under Ar atmosphere, and $AlCl_3$ (133 mg, 1 mmol, 1 eq) was added. The solution is stirred for 10 minutes, then $LiAlD_4$ (80 mg, 2 mmol, 2 eq) is added slowly. The reaction is stirred at room temperature for 18 h, then quenched with NaOH 1M, then extracted with EtOAc (3x20 mL). The combined organic layers are washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture is purified with flash chromatography (CH_2Cl_2) to yield the title compound **11** (80 mg, 0.59 mmol, 59%) as a colorless oil.

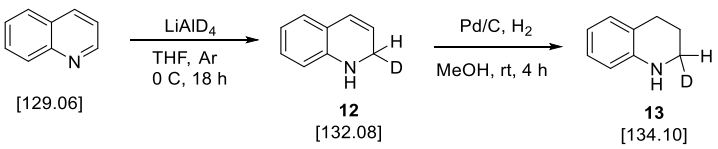
^{1}H-NMR: (400 MHz, $CDCl_3$) δ = 7.01 – 6.94 (m, 2H, 2 x C*H*), 6.65 – 6.59 (m, 1H, C*H*), 6.49 (d, *J* = 7.9 Hz, 1H, C*H*), 3.81 (s, 1H, N*H*), 2.79 (t, *J* = 6.4 Hz, 2H, CH_2), 1.95 (t, *J* = 6.4 Hz, 2H, CH_2).

^{13}C-NMR: (101 MHz, $CDCl_3$) δ = 144.79, 129.51, 126.73, 121.47, 116.93, 114.19, 41.28, 26.92, 21.96.

HRMS (**ESI$^+$**): *m/z* calculated for $C_9H_9ND_2$ $(M+H)^+$: 136.1090, found: 136.1089.

TLC: R_f = 0.78 (CH_2Cl_2).

1,2,3,4- tetrahydroquinoline-2-d (12)



A solution of quinoline (125 µL, 1 mmol, 1 eq) in dry THF (5 mL) was added slowly to a suspension of $LiAlD_4$ (80 mg, 2 mmol, 2 eq) in dry THF (10 mL) at 0 °C under Ar atmosphere. The reaction was left stirring at room temperature for 18 h, then it was quenched with water, filtered, and the filtrate was extracted with EtOAc (3x20 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The resulting white solid was used immediately without purification, and dissolved in 20 mL methanol. 120 mg Pd/C 5% were added and the mixture was stirred at room temperature under H_2 atmosphere for 4 h. It was then filtered and the solvent removed. The crude is purified with flash chromatography (CH_2Cl_2) to yield the title compound **13** (65 mg, 0.48 mmol, 48%) as a colorless oil.

^{1}H NMR: (400 MHz, $CDCl_3$) δ = 7.04 – 6.92 (m, 2H, 2 x C*H*), 6.63 (t, J = 7.4 Hz, 1H, C*H*), 6.50 (d, J = 7.0 Hz, 1H, C*H*), 3.82 (s, 1H, N*H*), 3.32 (dd, J = 13.2, 6.2 Hz, 1H, C*H*D), 2.79 (t, *J* = 6.4 Hz, 2H, CH_2), 1.96 (q, *J* = 6.1 Hz, 2H, CH_2).

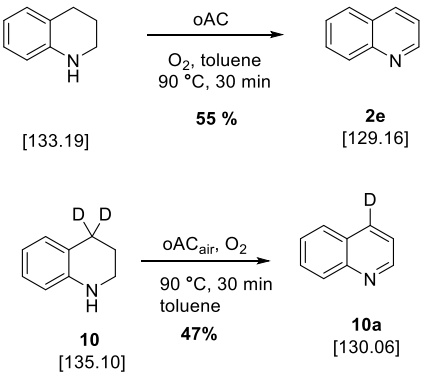
^{13}C NMR: (126 MHz, $CDCl_3$) δ 144.79, 129.52, 126.73, 121.46, 116.94, 114.19, 41.64, 26.95, 22.09.

HRMS (**ESI$^+$**): *m/z* calculated for $C_9H_{10}ND$ $(M+H)^+$: 135.1027, found: 135.1028.

TLC: R_f = 0.78 (CH_2Cl_2).

Kinetic isotope effect tests

For the kinetic isotope effect experiments the general procedure (main body) was followed. 0.1 mmol of the appropriate 1,2,3,4-tetrahydroquinoline, oAC_{HNO3} (n = 4, 89 mg) and toluene (1 mL) were placed in a reaction tube under oxygen atmosphere. It was stirred for 30 minutes at 90 °C. The reaction was cooled to rt, filtered through a pad of celite and washed with CH_2Cl_2 (100 mL). The solvent was removed under reduced pressure and the yield was determined by ^{1}H-NMR. The crude product was then purified via flash chromatography (CH_2Cl_2), to isolate the pure deuterated products **10a** and **11a** as colorless oils.

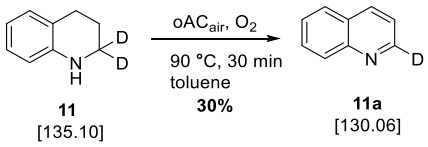


^{1}H NMR: (400 MHz, DMSO-d_6) δ = 8.92 (d, *J* = 4.2 Hz, 1H), 8.08 – 7.96 (m, 2H), 7.78 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.63 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.55 (d, *J* = 4.1 Hz, 1H).

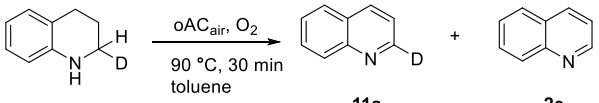
^{13}C NMR: (101 MHz, DMSO-d_6) δ = 151.03, 148.19, 136.15, 129.97, 129.38, 128.52, 128.32, 127.01, 121.82.

HRMS (**ESI**$^+$): *m/z* calculated for C_9H_7ND $(M+H)^+$: 131.0714, found: 131.0715.

TLC: R_f = 0.56 (CH_2Cl_2/MeOH 10%).



11 [135.10] **11a** [130.06]



13 [134.10] **11a** [130.06] **33%** **2e** [129.06] **9%**

^{1}H NMR: (400 MHz, DMSO-d_6) δ = 8.39 (d, *J* = 8.3 Hz, 1H), 8.02 (dd, *J* = 14.8, 8.8 Hz, 2H), 7.78 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.63 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H).

^{13}C NMR: (101 MHz, DMSO) δ = 150.67, 148.15, 136.52, 129.98, 129.36, 128.56, 128.40, 127.02, 121.82.

HRMS (**ESI**$^+$): *m/z* calculated for C_9H_7ND $(M+H)^+$: 131.0714, found: 131.0706.

TLC: R_f = 0.56 (CH_2Cl_2/MeOH 10%).

Carbon material XPS measurements

The X-ray Photoelectron Spectroscopy (XPS) analysis was performed by Thermo Fisher Scientific ESCALAB 250Xi XPS System at the Center of Microscopy and Nanotechnology, University of Oulu (Finland). The monochromatic AlKα radiation (1486.7 eV) operated at 20 mA and 15 kV. The powder samples were put in gold sample holder and O, C, N and Au were measured for all samples. The measurement data were analyzed by Avantage V5 program developed by Thermo Fisher Scientific. Charge compensation was used to determine the presented spectra and the binding energies (BE) were calibrated by the C1s peak position of 284.8 eV. The deconvolution of the peaks was carried out for C1s and O1s with Avantage program utilizing peak BE values for groups as reported for carbon materials by Figueiredo and Pereira.[24]

Table S2. Summary of O1s XPS (surface analysis)

Material	H_2O	O-C=O	C-O esters	C-OH	C=O	O%
Peak BE (eV)	535.9	524.2	533.3	532.3	531.1	
AC (acid washed)	0.16	0.45	1.15	0.75	0.58	3.09
oAC_{HNO3}	0.42	3	4.14	4.71	2.23	14.5
oAC_{HNO3} recycled	0.34	2.09	3.27	3.91	2.53	12.14
$oAC_{HNO3(\Delta)}$	0.46	0.89	3.34	1.92	1.93	8.54
oAC_{air}	0.28	1.39	2.13	1.84	1.66	7.3
$oAC_{air(\Delta)}$	0.74	0.95	3.09	1.98	1.71	8.47
$oAC_{air(\Delta)}$ recycled	0.35	1.37	3.12	2.23	1.85	8.92
$oCNT_{(\Delta)}$	0.1	0.24	0.54	0.43	0.54	1.85

Table S3. Summary of C1s XPS (surface analysis)

Material	Graphitic	Aliphatic	C-OH	C=O	O-C=O	C(π-π*)	C%
Peak BE (eV)	284.6	285.2	286.1	287.6	289.1	291.3	
AC (acid washed)	49.33	20.81	8.83	4.75	2.76	7.74	93.73
oAC_{HNO3}	38.83	20.02	8.73	4.53	6.05	5.63	84.59
oAC_{HNO3} recycled	42.61	17.19	10.48	4.51	4.34	4.91	84.04
$oAC_{HNO3(\Delta)}$	49.46	17.34	9.51	4.72	3.09	6.53	90.56
oAC_{air}	44.55	20.81	11.22	5.3	3.04	7.44	89.32
$oAC_{air(\Delta)}$	42.82	20.68	11.63	5.28	3.26	7.45	87.86
$oAC_{air(\Delta)}$ recycled	42.24	23.56	8.19	5.14	3.14	7.03	89.3
$oCNT_{(\Delta)}$	51.53	30.38	1.7	4.45	2.16	7.63	97.85

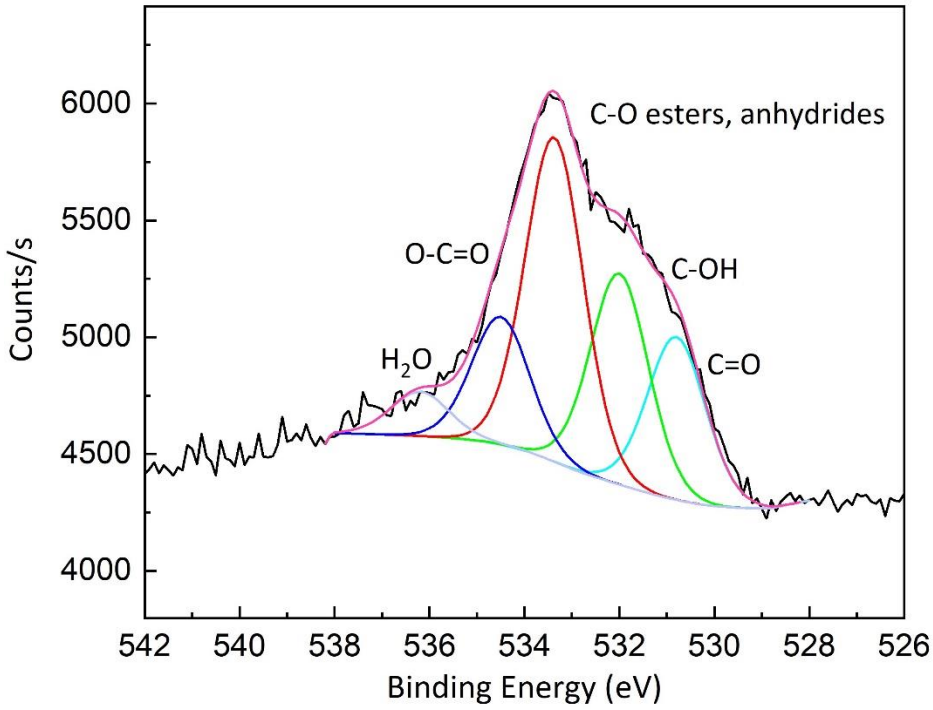


Fig. S1. O1s XPS of $AC_{demetallized}$.

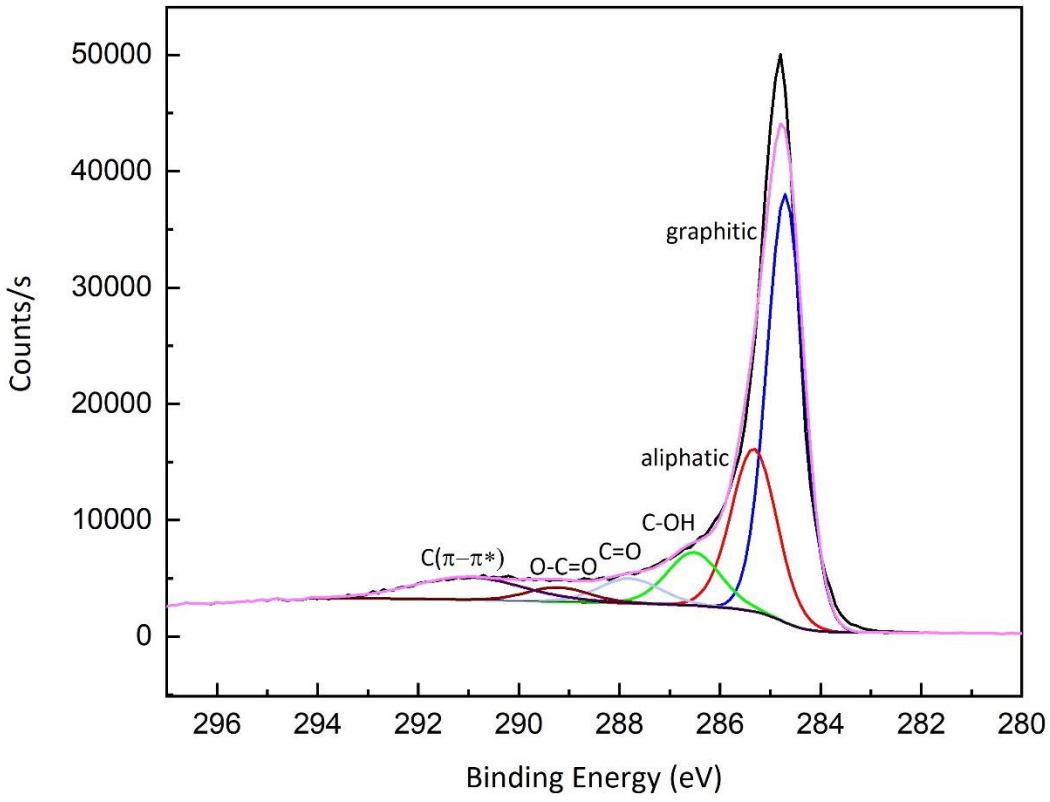


Fig. S2. C1s XPS of $AC_{demetallized}$.

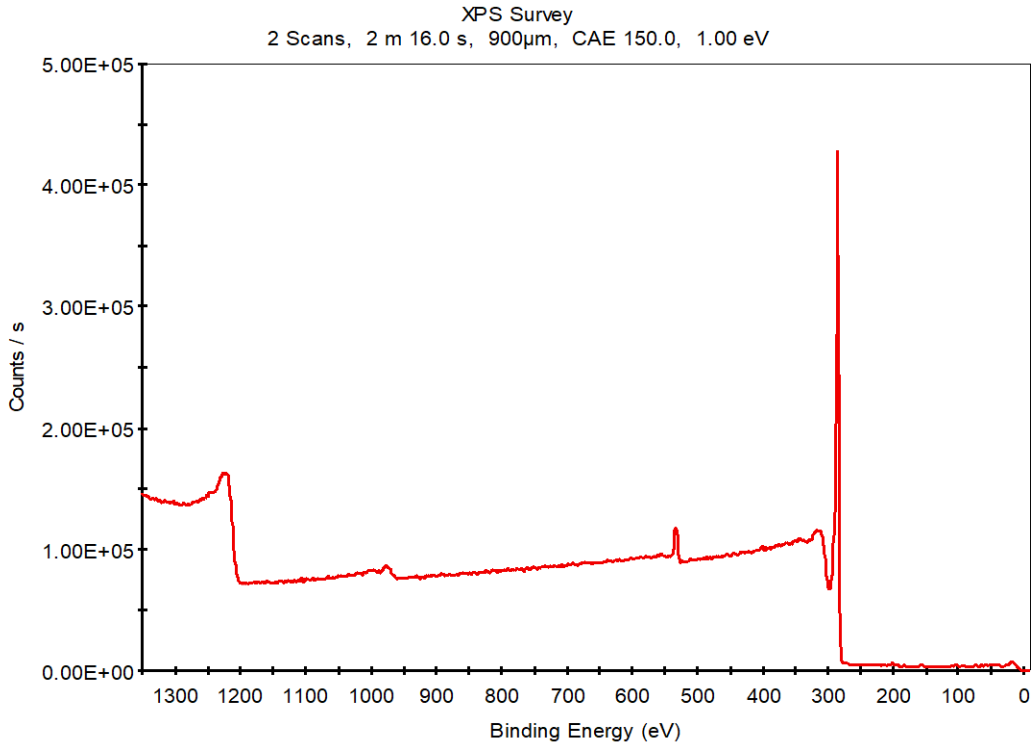


Fig. S3 Survey XPS of $AC_{demetallized}$.

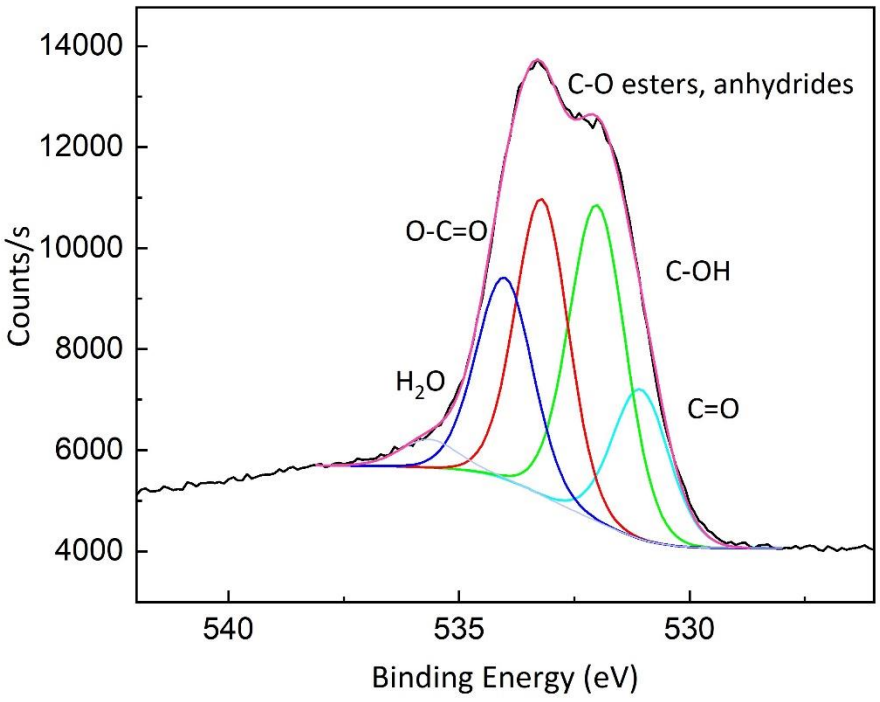


Fig. S4. O1s XPS of oAC_{HNO3}.

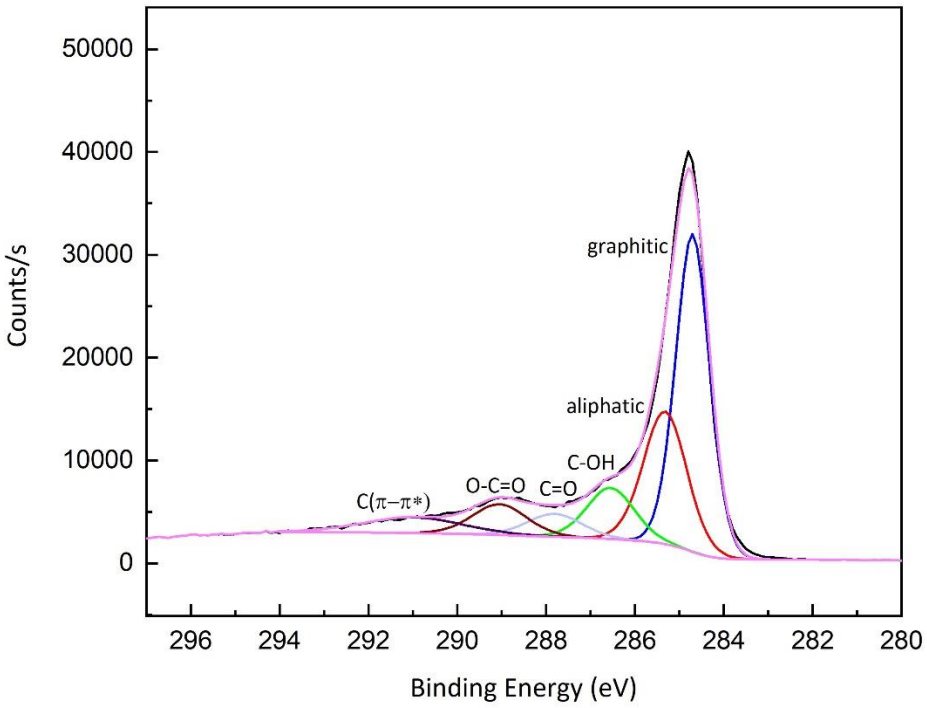


Fig. S5. C1s XPS of oAC_{HNO3}.

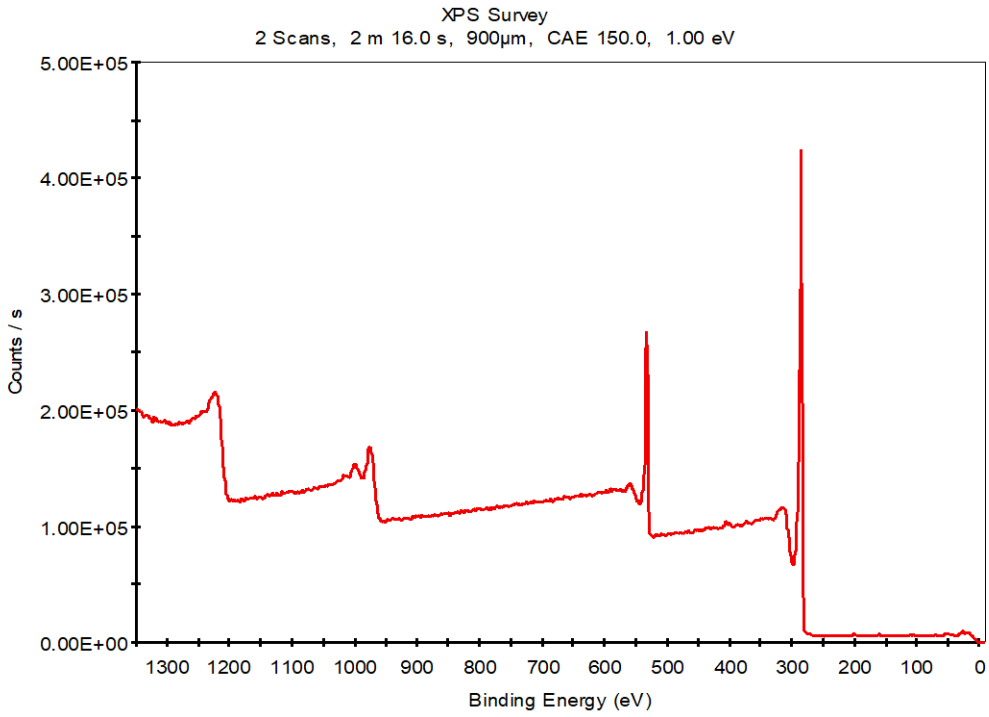


Fig. S6. Survey XPS of oAC_{HNO3}.

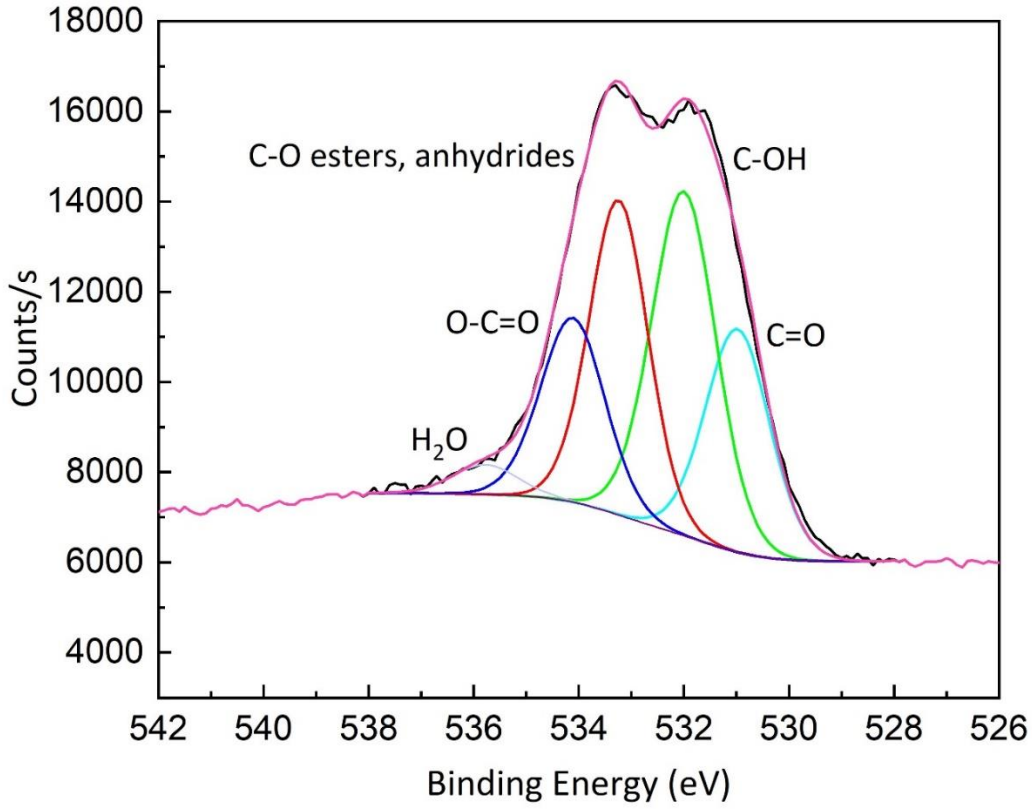


Fig. S7. O1s XPS of oAC$_{HNO3}$ recycled.

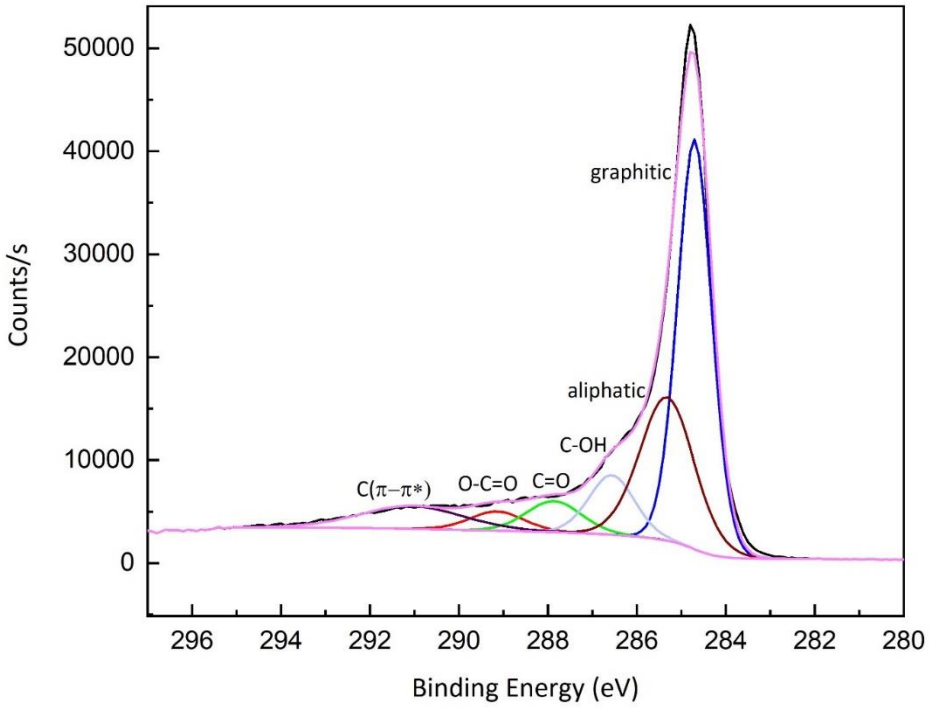


Fig. S8. C1s XPS of oAC$_{HNO3}$ recycled.

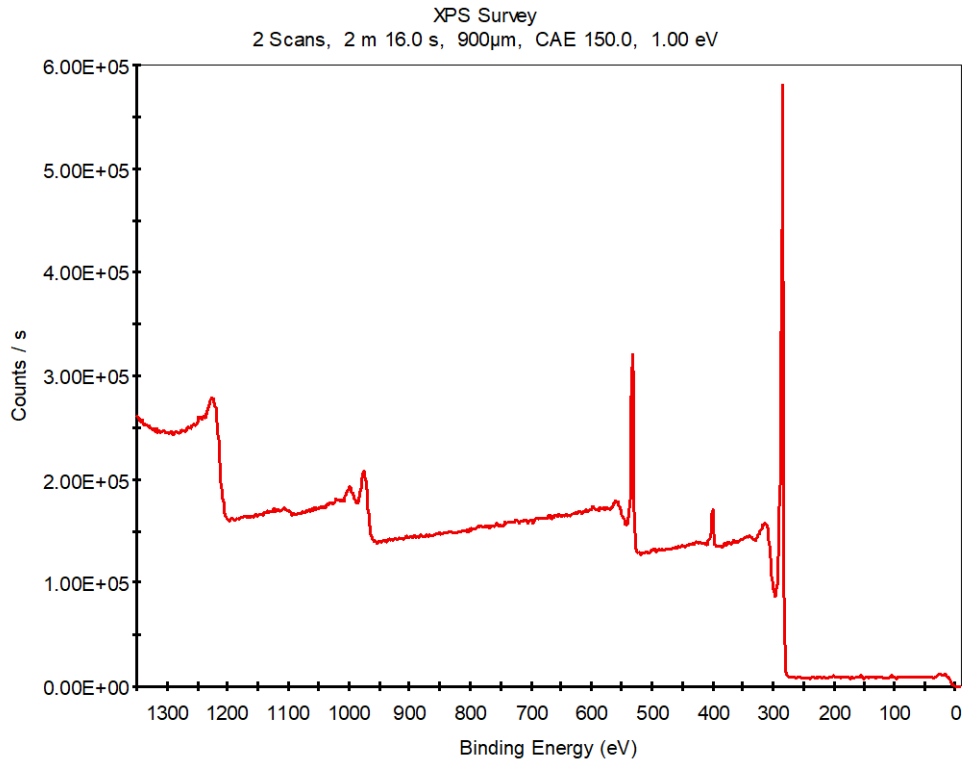


Fig. S9. Survey XPS of oAC_{HNO3} recycled.

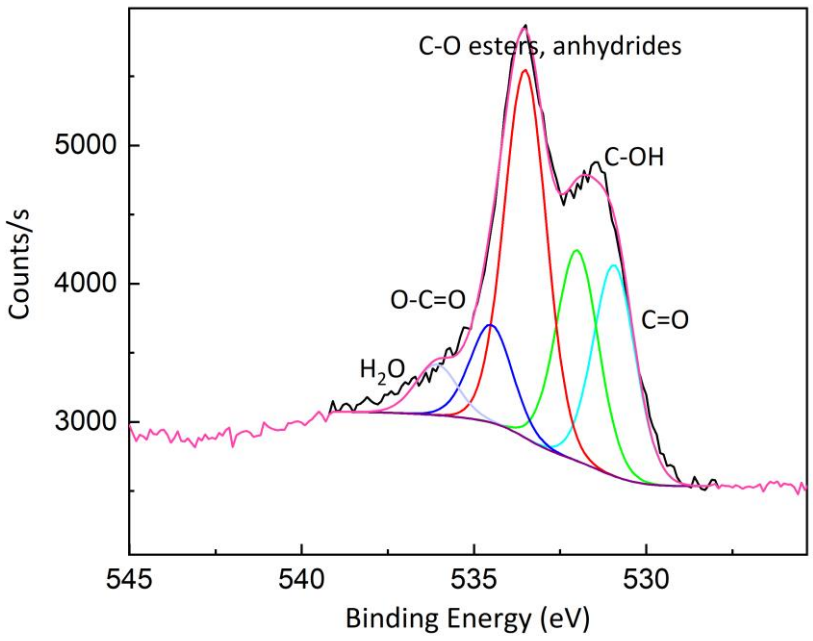


Fig. S10. O1s XPS of $oAC_{HNO3(\Delta)}$.

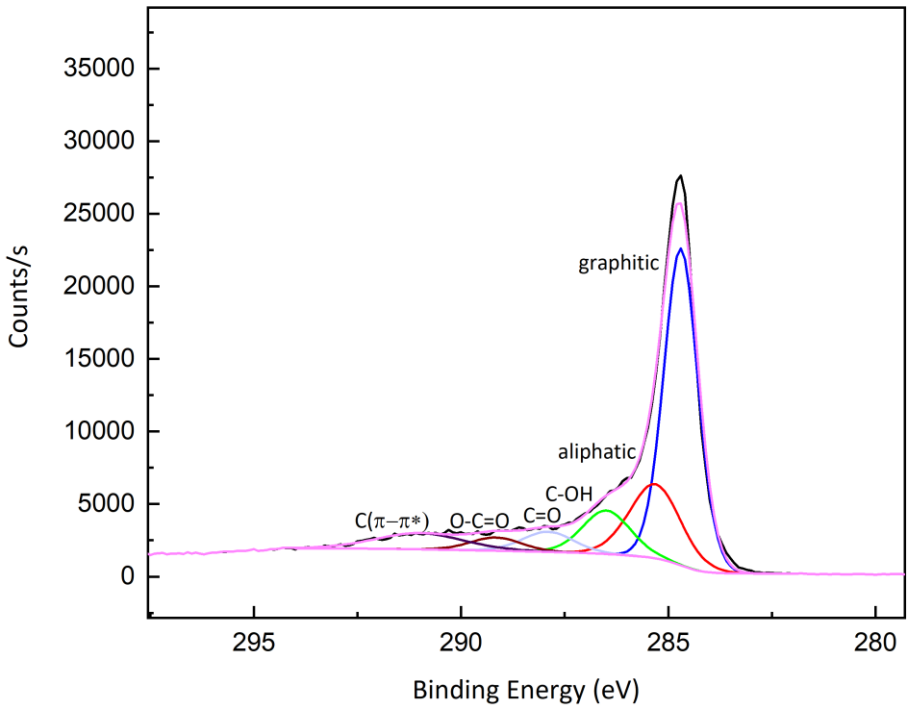


Fig. S11. C1s XPS of $oAC_{HNO3(\Delta)}$.

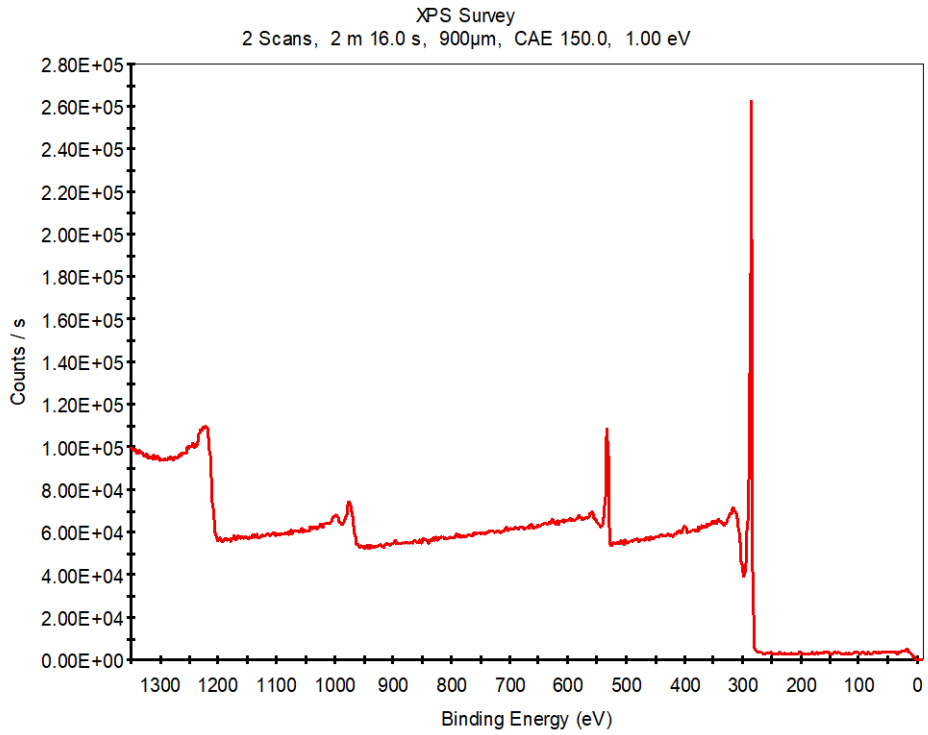


Fig. S12. Survey XPS of $oAC_{HNO3(\Delta)}$.

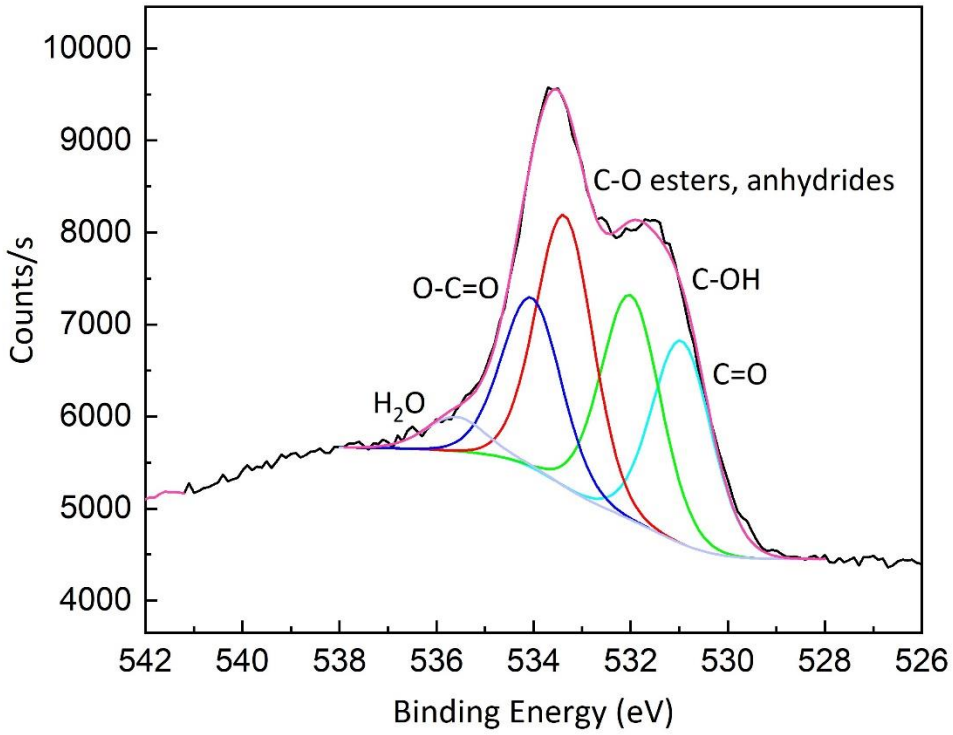


Fig. S13. O1s XPS of oAC_{air}.

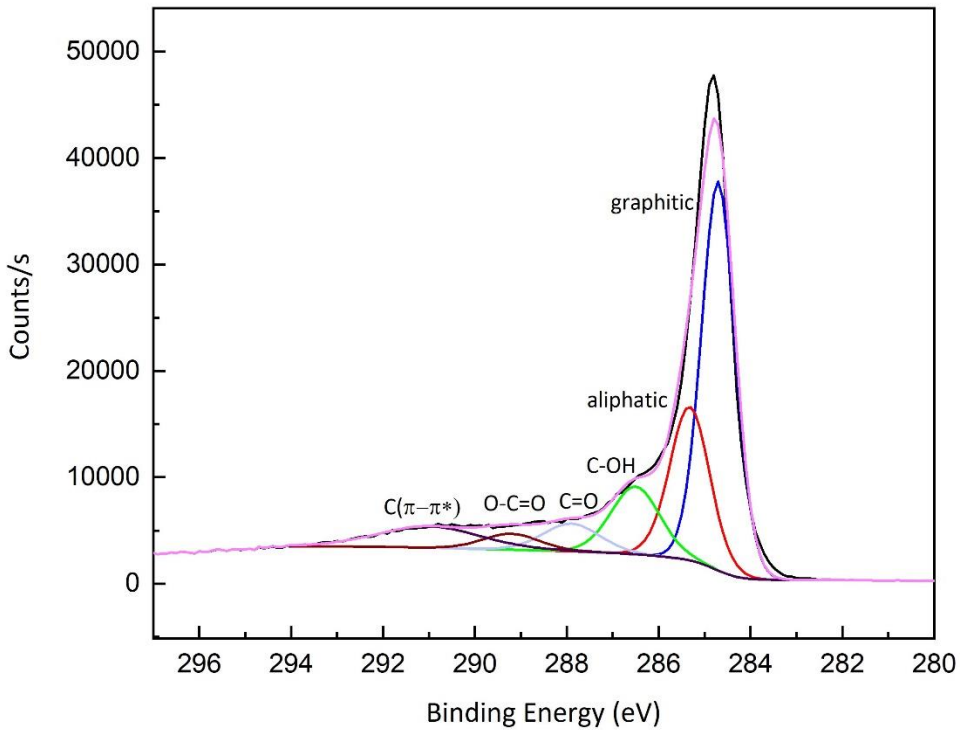


Fig. S14. C1s XPS of oAC_{air}.

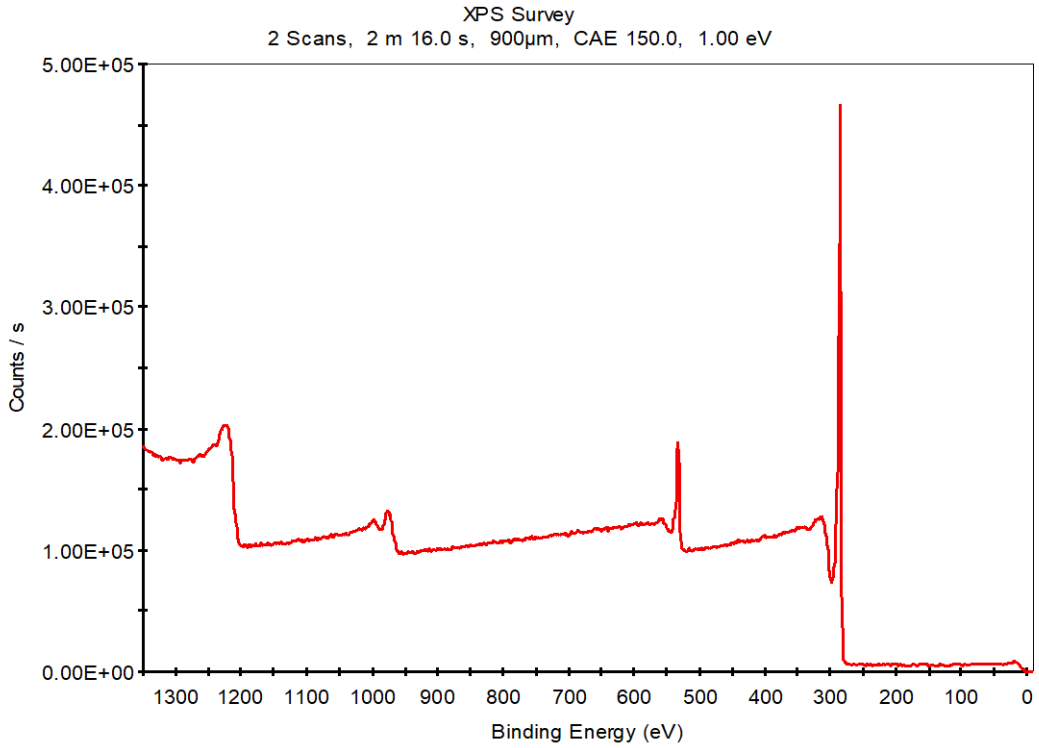


Fig. S15. Survey XPS of oAC$_{air}$.

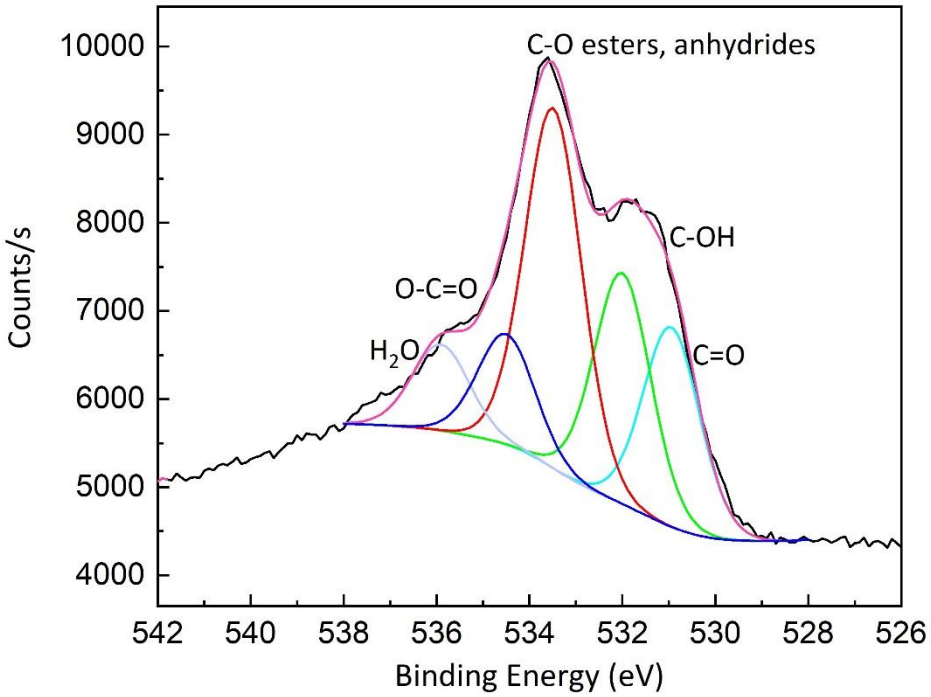


Fig. S16. O1s XPS of oAC$_{air(\Delta)}$.

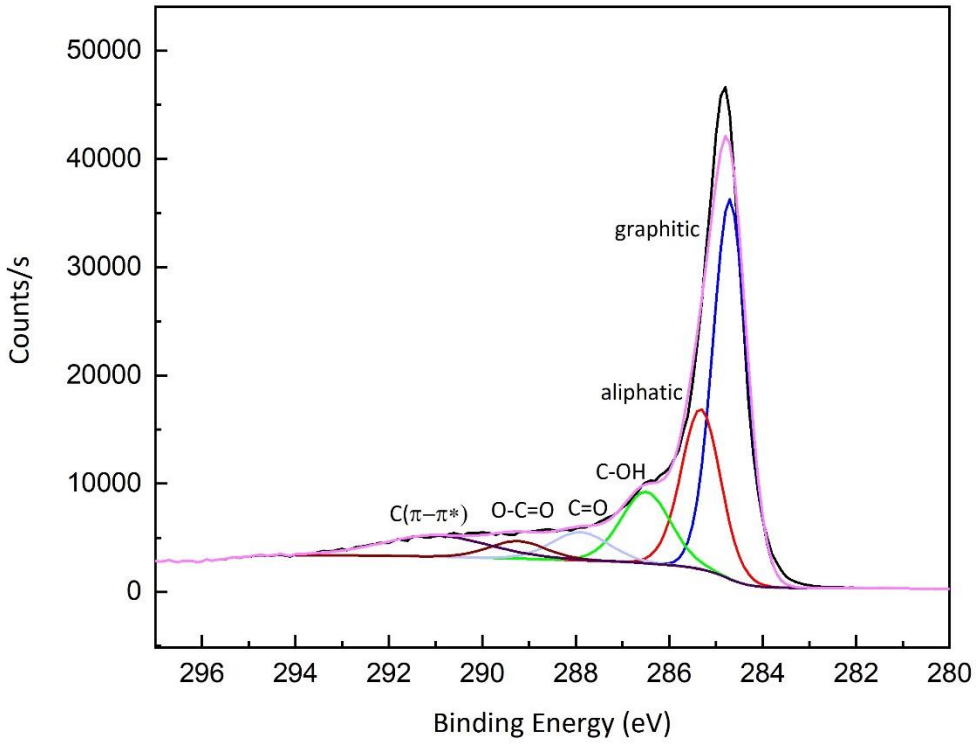


Fig. S17. C1s XPS of oAC$_{air(\Delta)}$.

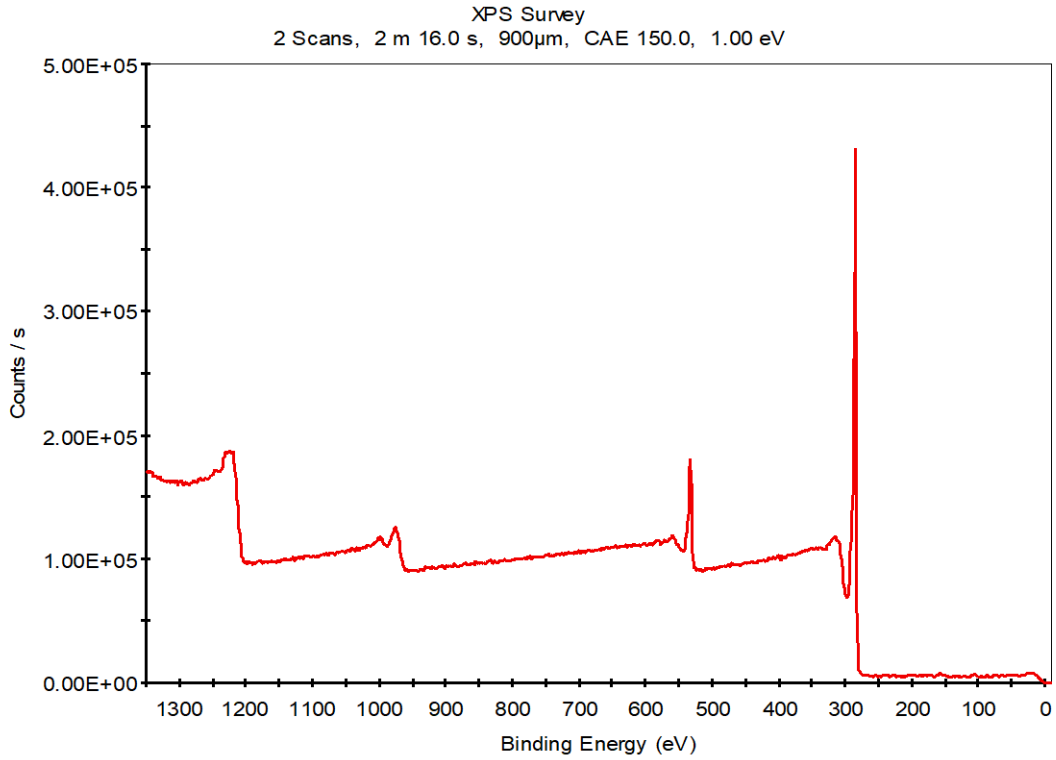


Fig. S18. Survey XPS of oAC$_{air(\Delta)}$.

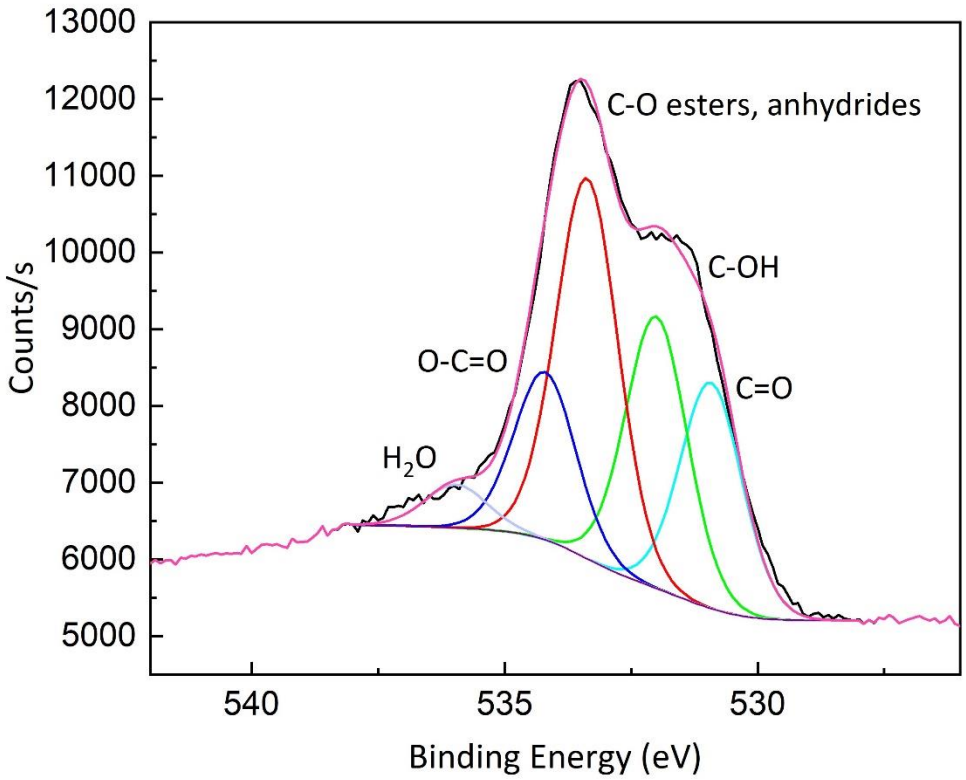


Fig. S19. O1s XPS of $oAC_{air(\Delta)}$ recycled.

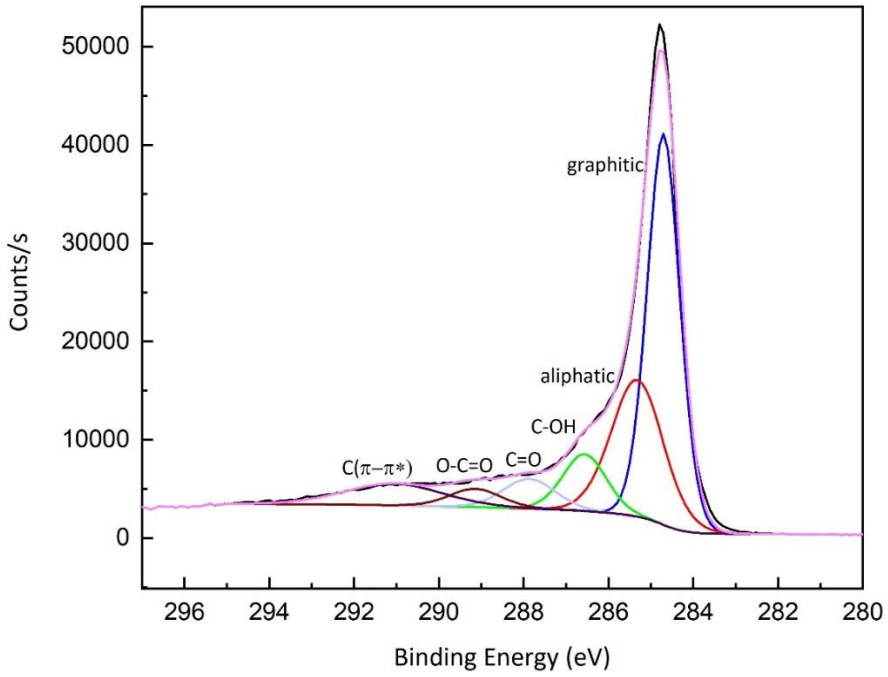


Fig. S20. C1s XPS of $oAC_{air(\Delta)}$ recycled.

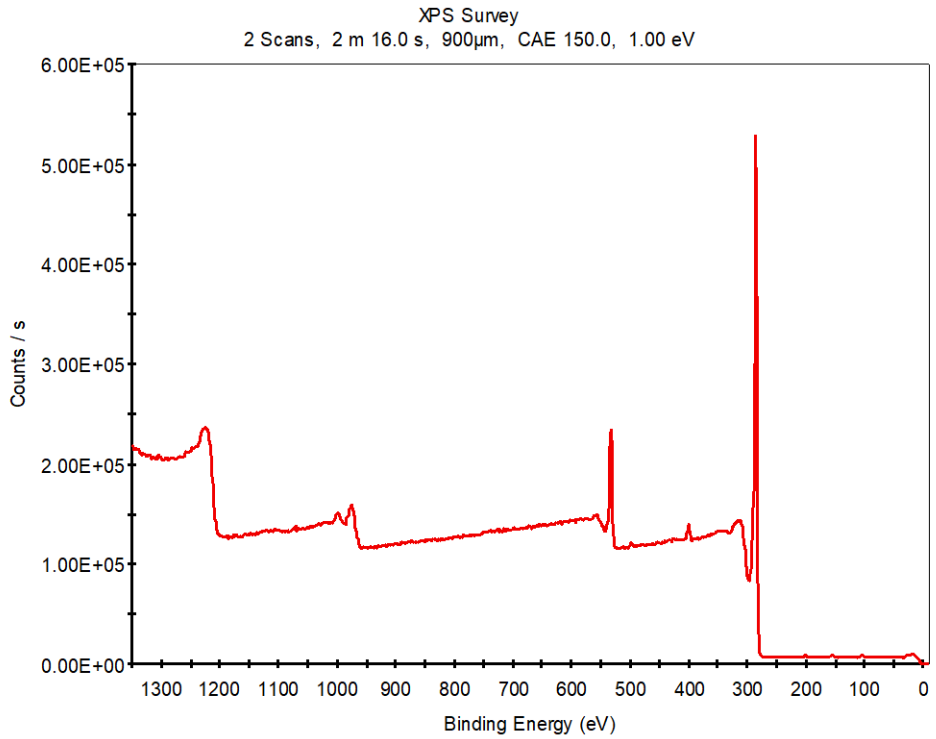


Fig. S21. Survey XPS of $oAC_{air(\Delta)}$ recycled.

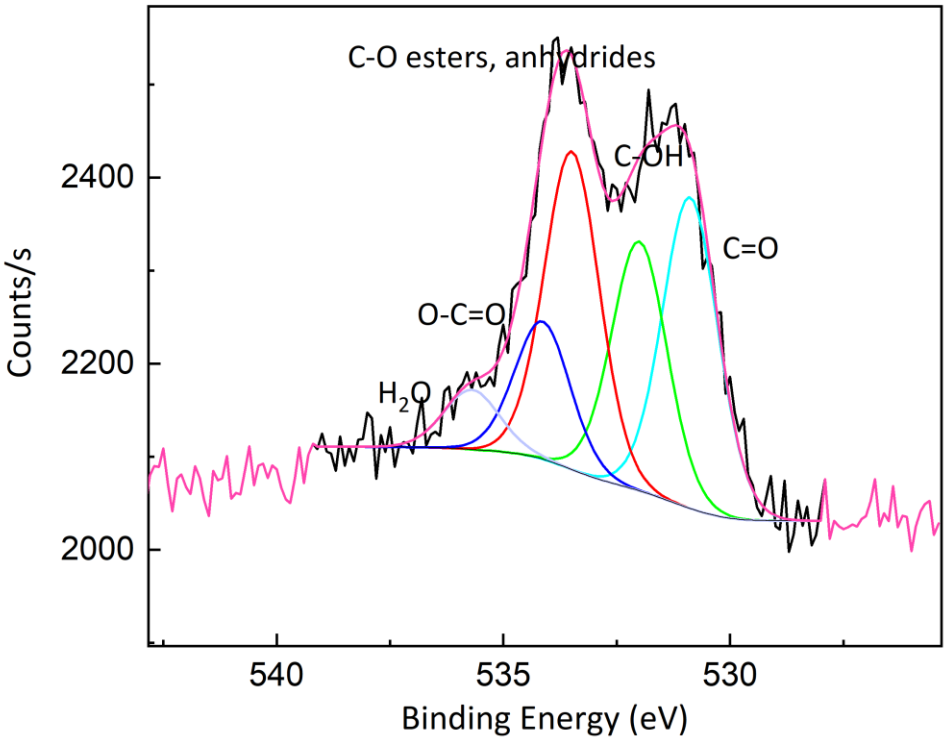


Fig. S22. O1s XPS of $oCNT_{(\Delta)}$.

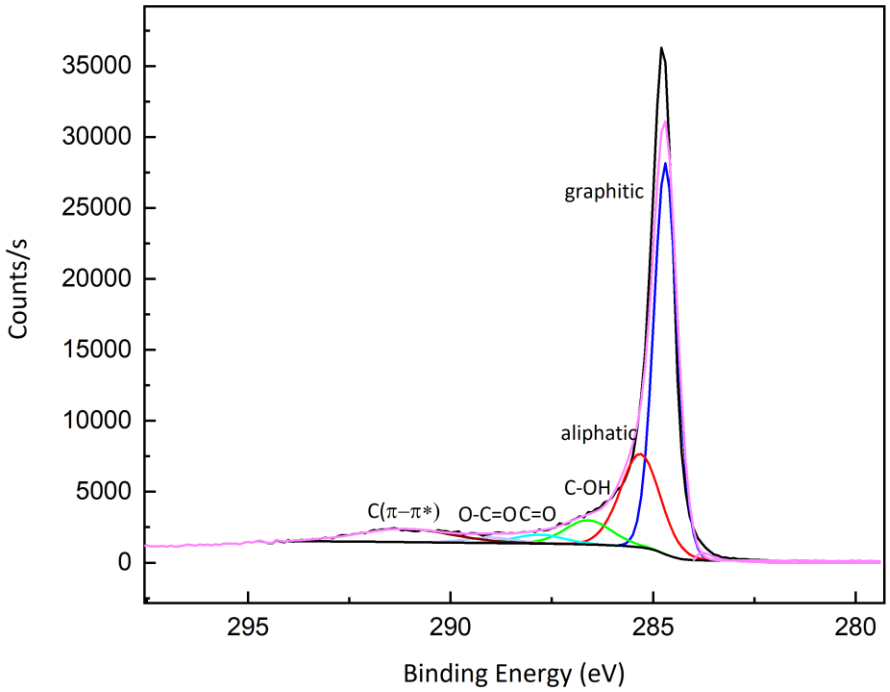


Fig. S23. C1s XPS of oCNT$_{(\Delta)}$.

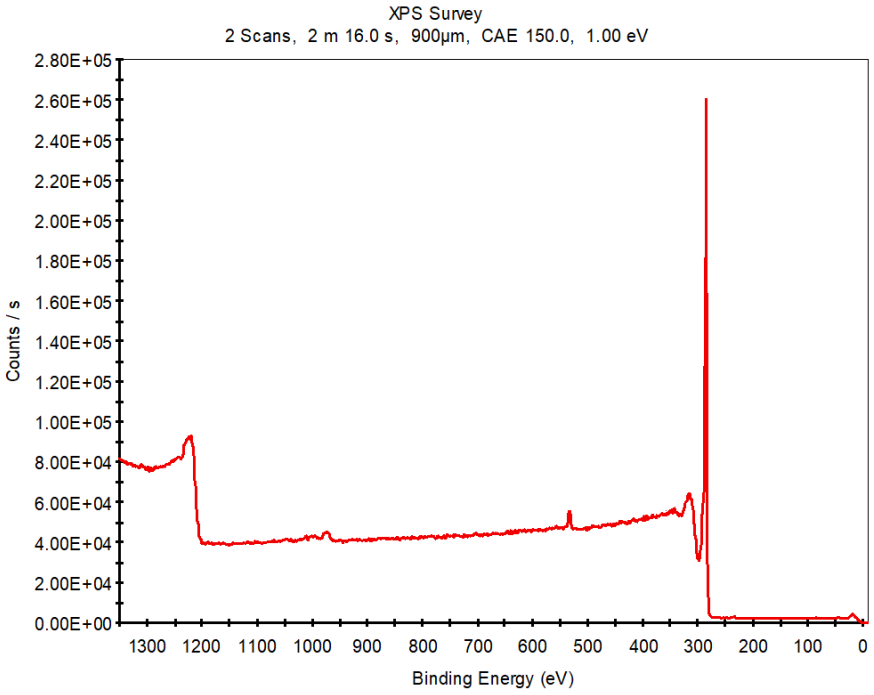


Fig. S24. Survey XPS of oCNT$_{(\Delta)}$.

Carbon material Raman measurements

Raman spectra were recorded on a NT-MDT Ntegra confocal Raman microscope using an excitation wavelength of 532 nm, output power of 22 mW and an ND1 filter. Preparation of the samples was carried out via deposition of the powder onto silicon wafers. For each sample, 3 points were recorded in back scattering mode and averaged.

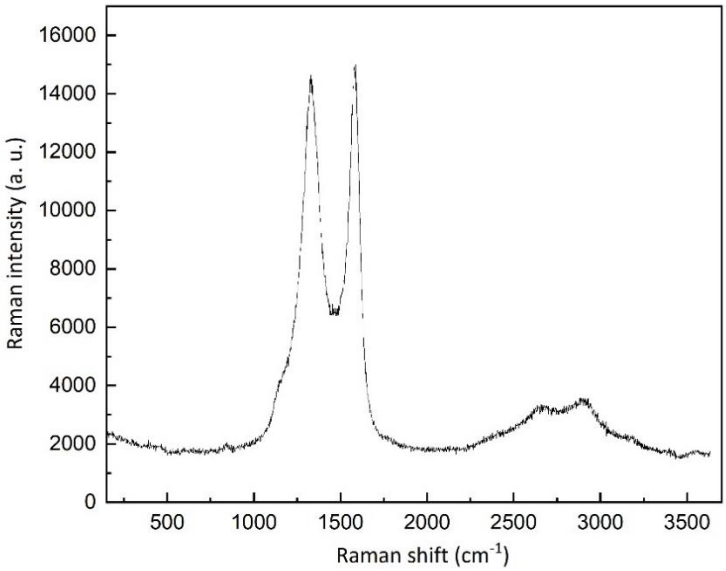


Fig. S25. Raman spectrum of $AC_{demetallized}$.

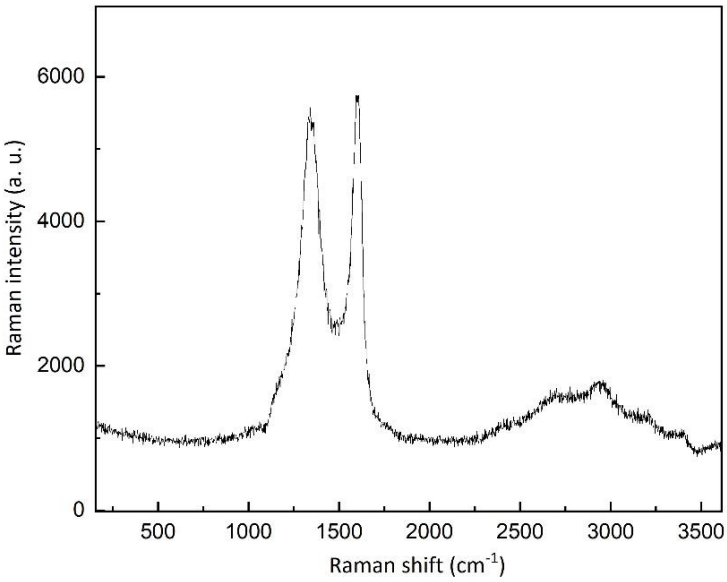


Fig. S26. Raman spectrum of $oAC_{air(\Delta)}$

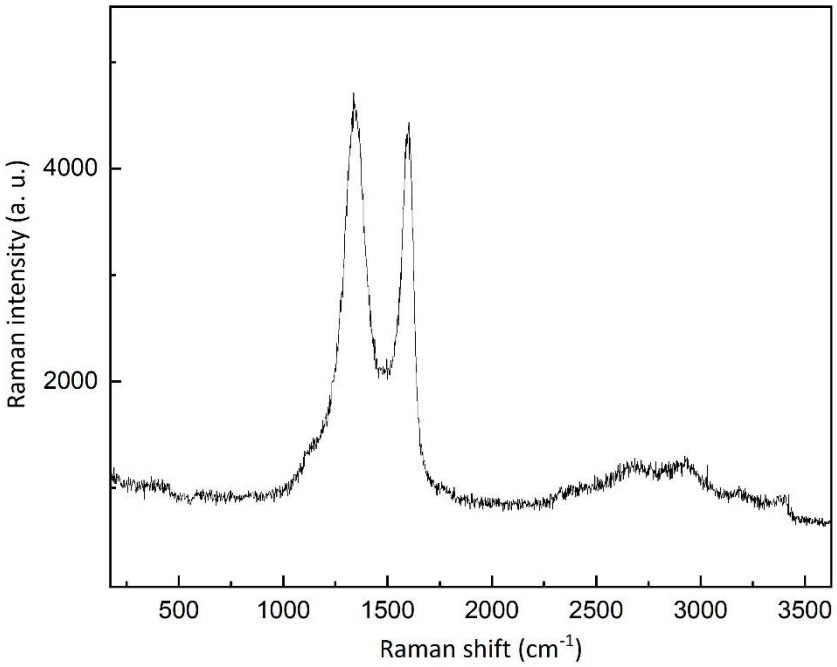


Fig. S27. Raman spectrum of oAC_{HNO3}.

Carbon material ICP-MS measurements

Table S4. ICP-MS determination of metal impurities

Sample	Fe (mg/g)	Ni (mg/g)	Mn (mg/g)	Cu (mg/g)	Co (mg/g)	Pd (mg/g)	Al (mg/g)
AC_{dm}	0.48 ± 0.08	< 0.03	0.020 ± 0.003	0.013 ± 0.002	0.0021 ± 0.0003	< 0.0002	0.47 ± 0.08
oAC_{HNO3}	0.36 ± 0.06	<0.06	0.012 ± 0.002	0.056 ± 0.009	0.0023 ± 0.0004	0.00033 ± 0.00005	0.41 ± 0.07
$oAC_{air(\Delta)}$	0.59 ± 0.09	< 0.03	0.040 ± 0.006	0.020 ± 0.003	0.0057 ± 0.0009	< 0.0002	< 0.6

Carbon material Temperature-programmed desorption measurements

The qualitative and quantitative determination of surface groups was performed by temperature programmed desorption – mass spectrometry (TPD-MS). The analyses were carried out in a fully automated AMI-300 equipment (Altamira Instruments) with a quadrupole mass spectrometry detector (Dycor Dymaxion 200, Ametek). The samples (90 mg) were loaded into a U-shaped quartz cell and submitted to a 5 ºC·min^{-1} heating from room temperature to 1050 °C under helium flow (25 cm^3·min^{-1}). The calibration of CO_2 and CO was performed at the end of each analysis in order to quantify the amounts of these gases released during the TPD experiments.

Table S5. Deconvolution peaks of CO TPD curve of oAC$_{HNO3}$.

	Peak 0	**Peak 1**	**Peak 2**	**Peak 3**	**Peak 4**
		Carboxylic anhydrides	Phenols	Carbonyl/quinones	Pyrones/Chromenes
T (ºC)	247	453	598	732	893
W (ºC)	106	123	136	136	120
A (µmol/g)	138	540	1370	2074	159

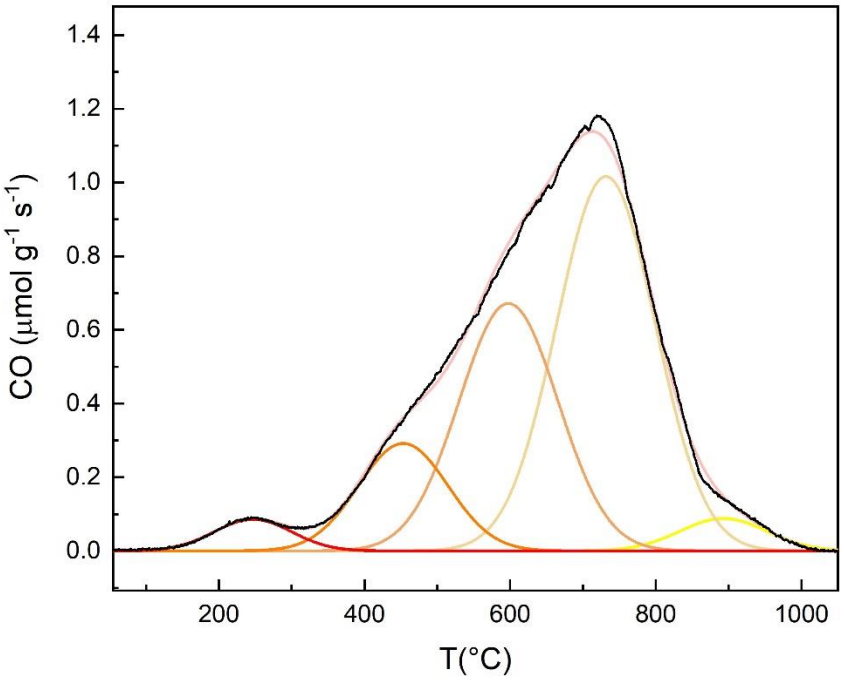


Fig. S28. Deconvolution of CO TPD curve of oAC$_{HNO3}$.

Table S6. Deconvolution peaks of CO_2 TPD curve of oAC_{HNO3}

	Peak 1	Peak 2	Peak 3	Peak 4
	Carboxylic acids (strong)	Carboxylic acids (weak)	Carboxylic anhydrides	Lactones
T (ºC)	246	364	453	636
W (ºC)	98	81	123	172
A (µmol/g)	1143	289	540	388

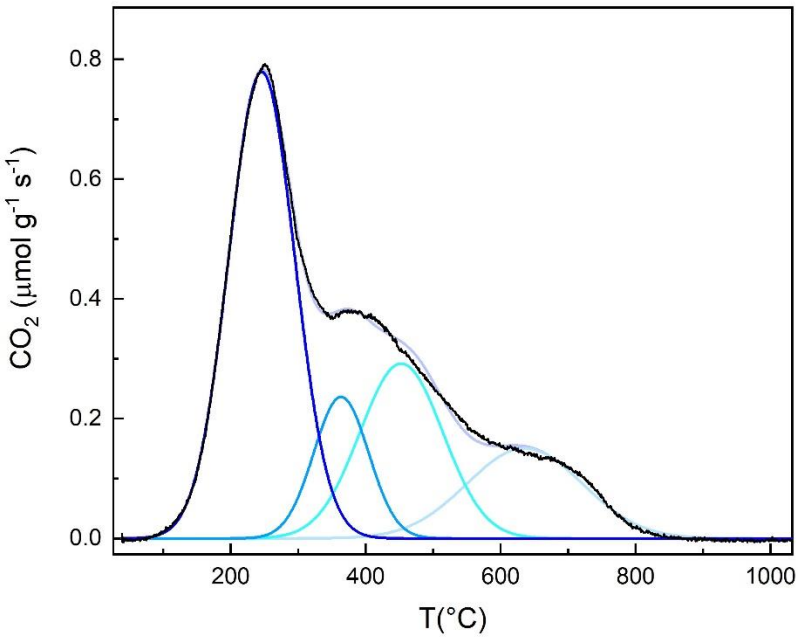


Fig. S29. Deconvolution of CO_2 TPD curve of oAC_{HNO3}.

Table S7. Deconvolution peaks of CO TPD curve of $oAC_{air(\Delta)}$

	Peak 1	Peak 2	Peak 3	Peak 4
	Carboxylic anhydrides	Phenols	Carbonyl/quinones	Pyrones/Chromenes
T (ºC)	563	619	731	868
W (ºC)	189	103	103	106
A (µmol/g)	648	1360	1861	619

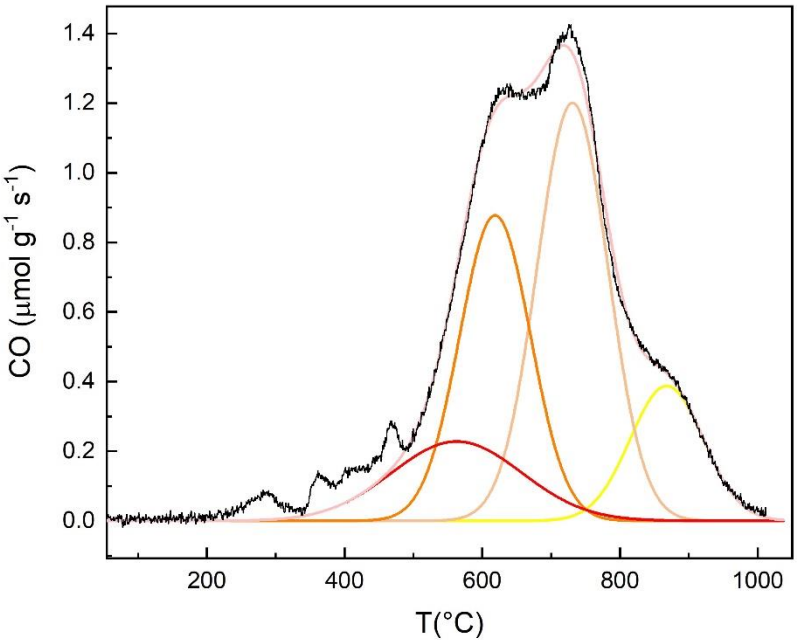


Fig. S30. Deconvolution of CO TPD curve of $oAC_{air(\Delta)}$.

Table S8. Deconvolution peaks of CO_2 TPD curve of $oAC_{air(\Delta)}$

	Peak 1	**Peak 3**	**Peak 4**
	Carboxylic acids	Carboxylic anhydrides	Lactones
T (ºC)	260	563	665
W (ºC)	189	189	189
A (µmol/g)	195	648	243

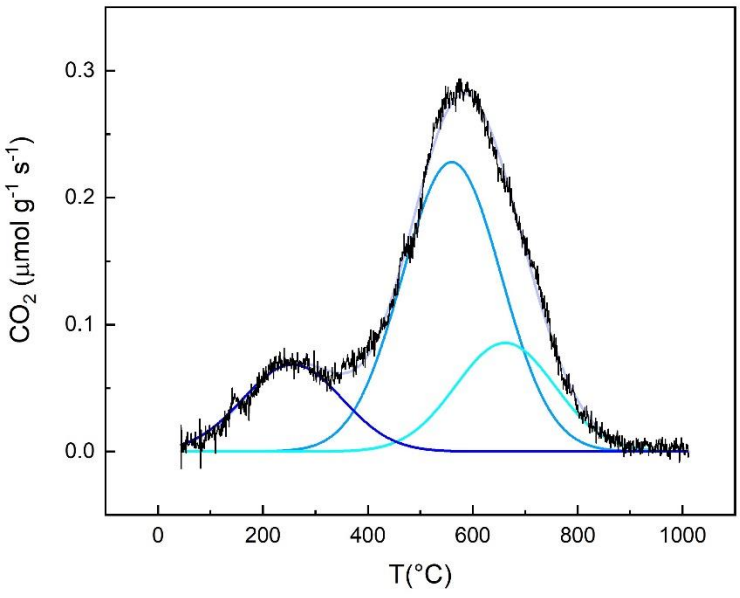


Fig. S31. Deconvolution of CO_2 TPD curve of $oAC_{air(\Delta)}$.

Carbon material BET analysis

Table S9. Textural analysis of $AC_{demetallized}$, oAC_{HNO3} and $oAC_{air(\Delta)}$

Sample	S_{BET} (m^2/g)	$S_{\neq\mu pores}$ (m^2/g)	$V_{\mu pores}$ (cm^3/g)	V^*_p (cm^3/g)
$AC_{demetallized}$	822	335	0.205	0.761
oAC_{HNO3}	738	316	0.179	0.675
$oAC_{air(\Delta)}$	1128	407	0.319	0.868
$oAC_{HNO3(\Delta)}$	802	319	0.202	0.695

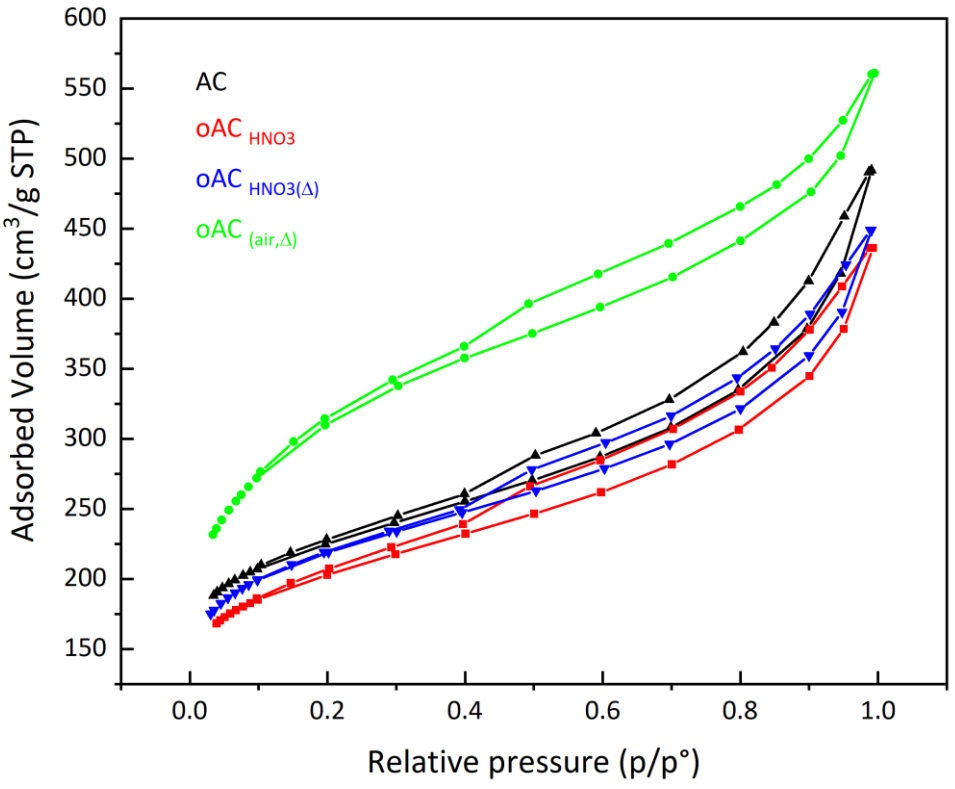
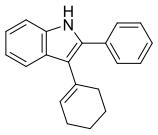
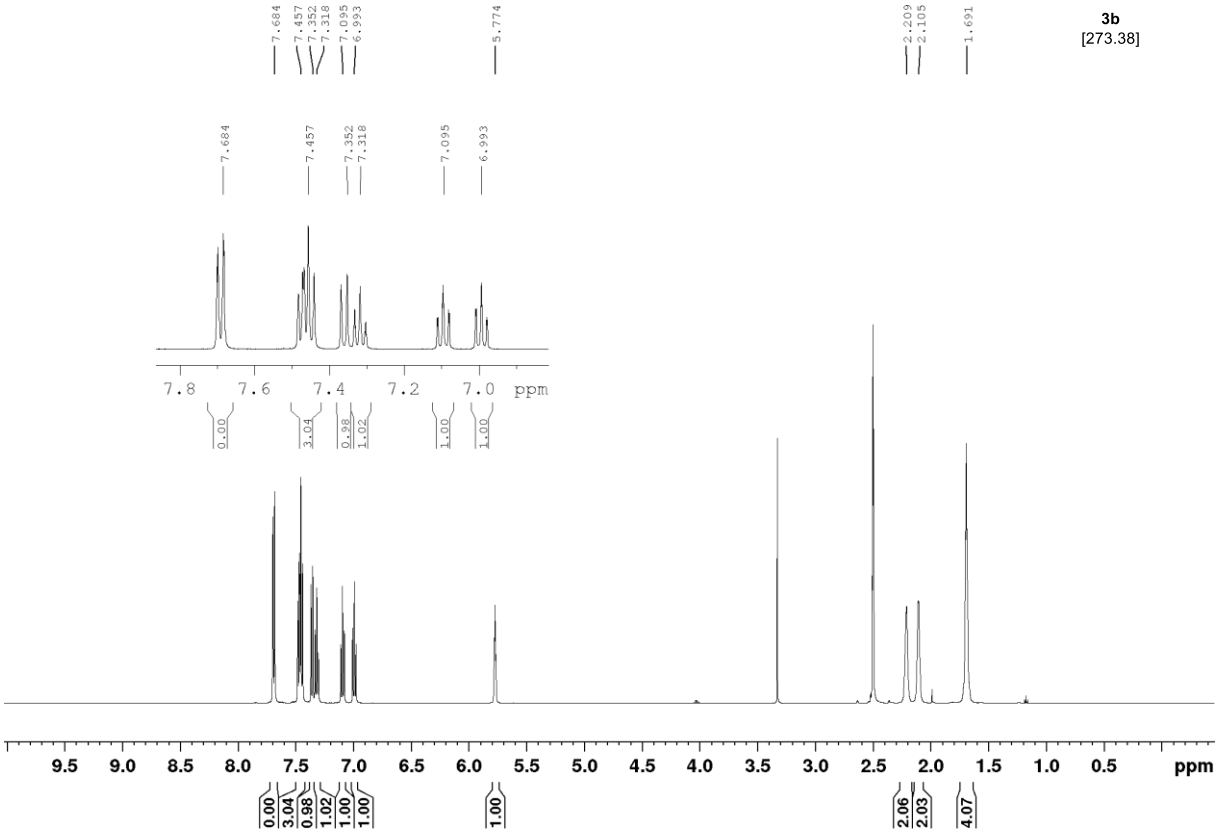


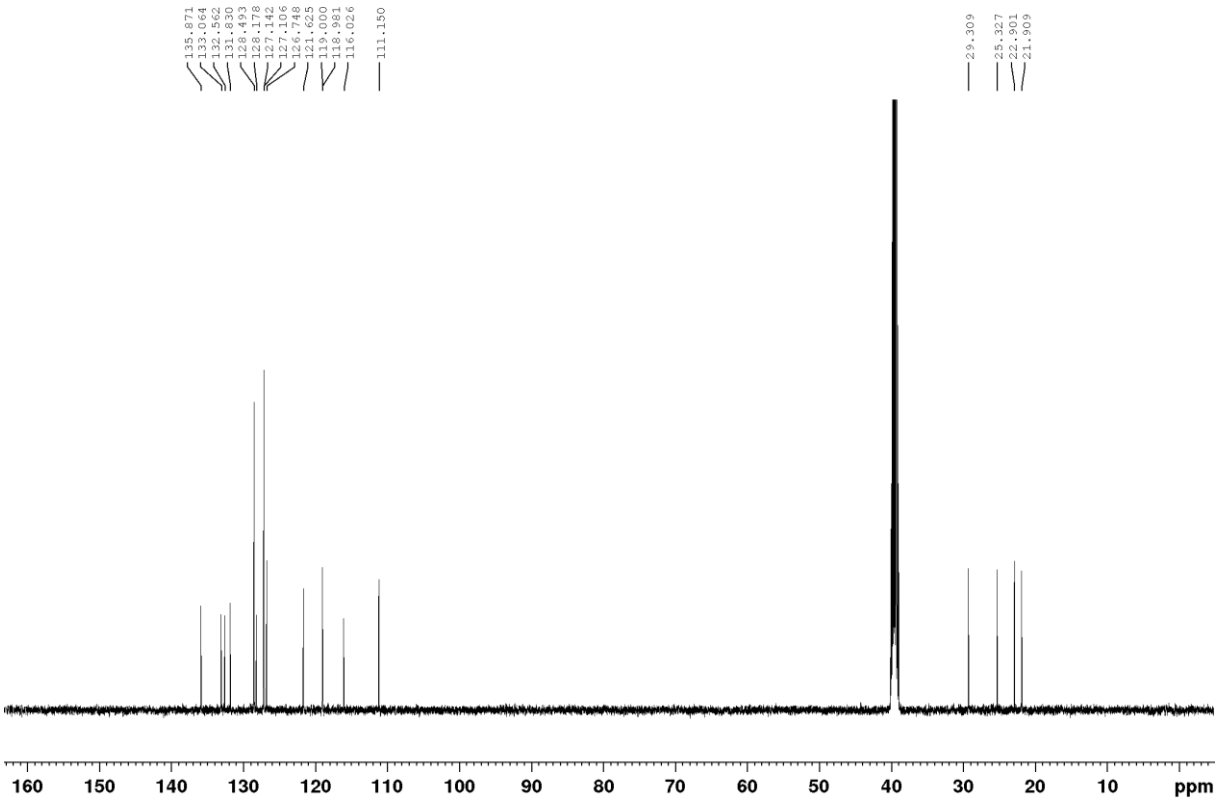
Fig. S32. N_2 physisorption isotherms of $AC_{demetallized}$, oAC_{HNO3}, $oAC_{HNO3(\Delta)}$ and $oAC_{air(\Delta)}$

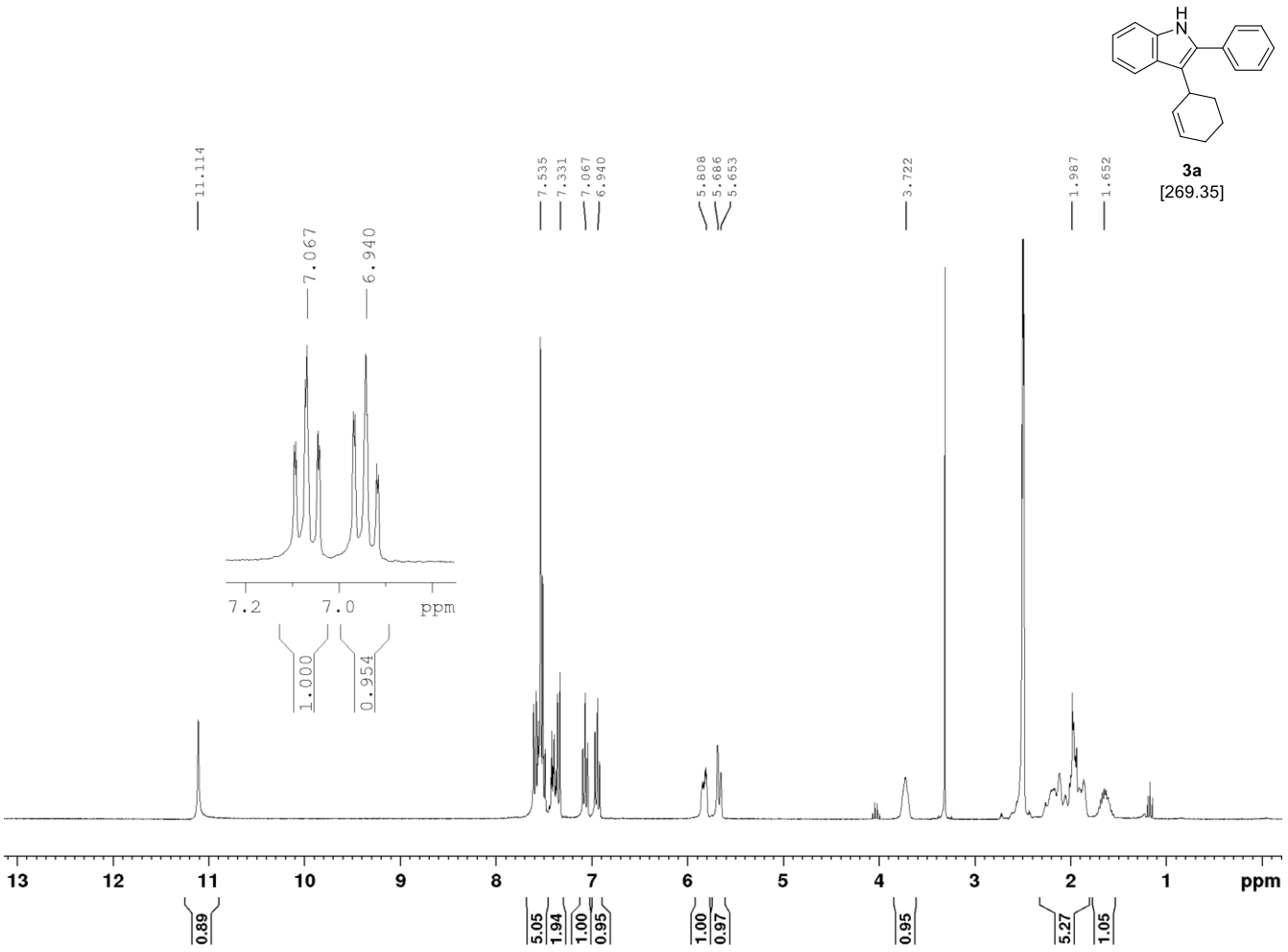
NMR Spectra



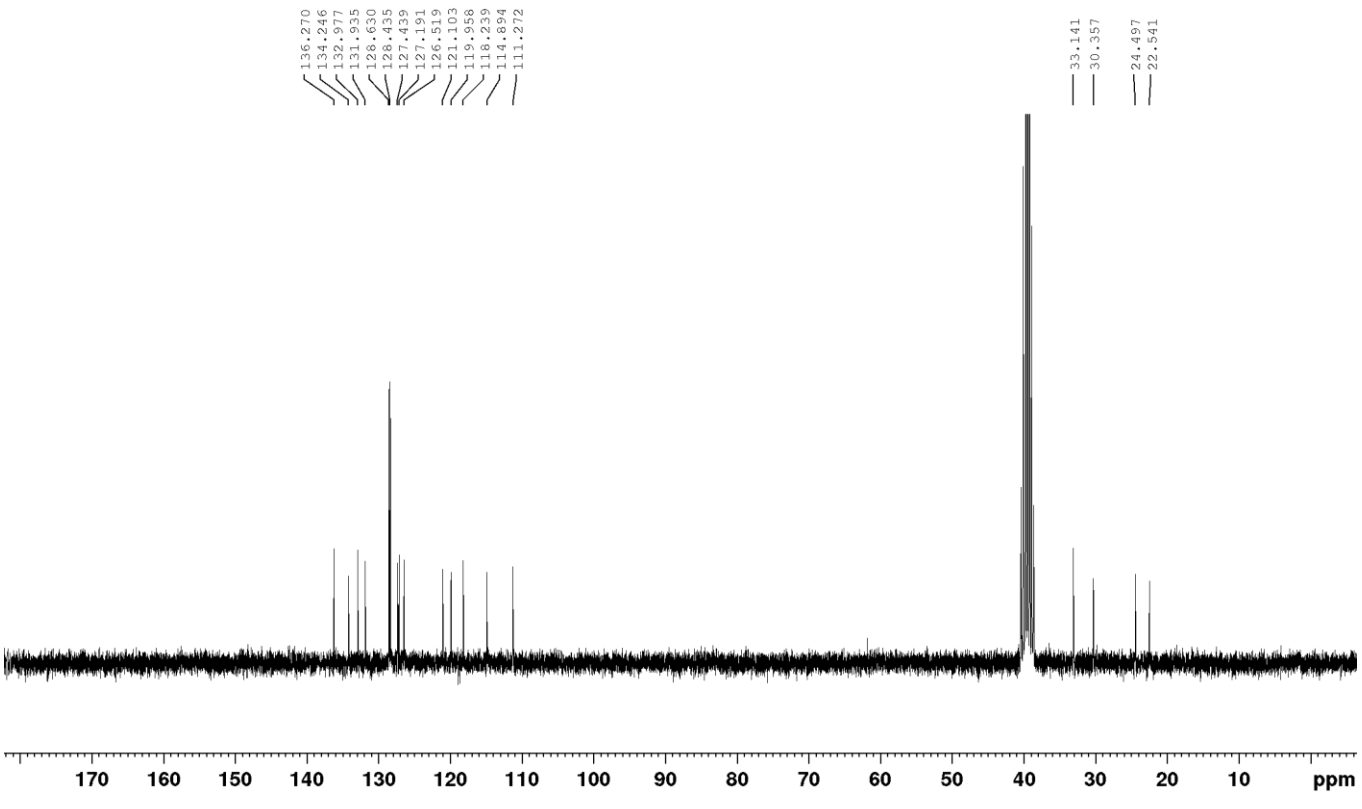
3b
[273.38]

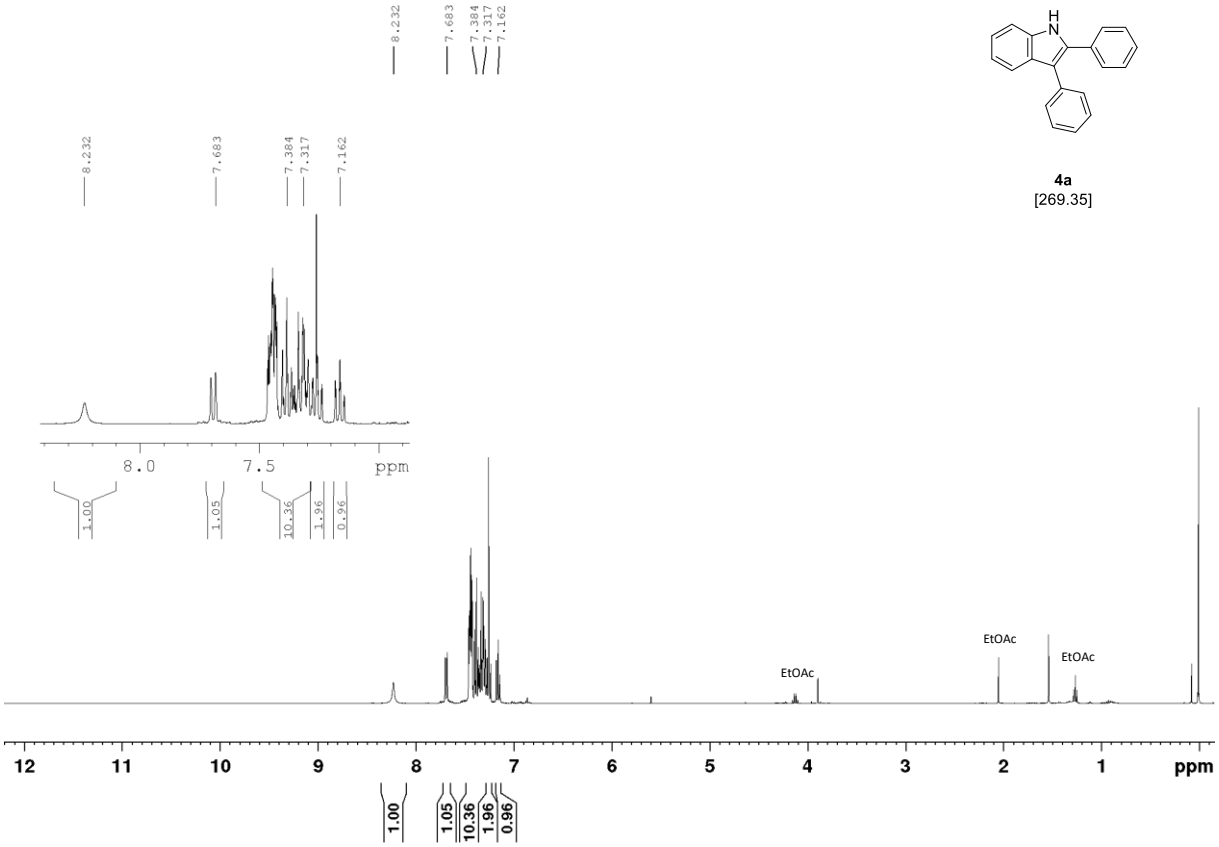


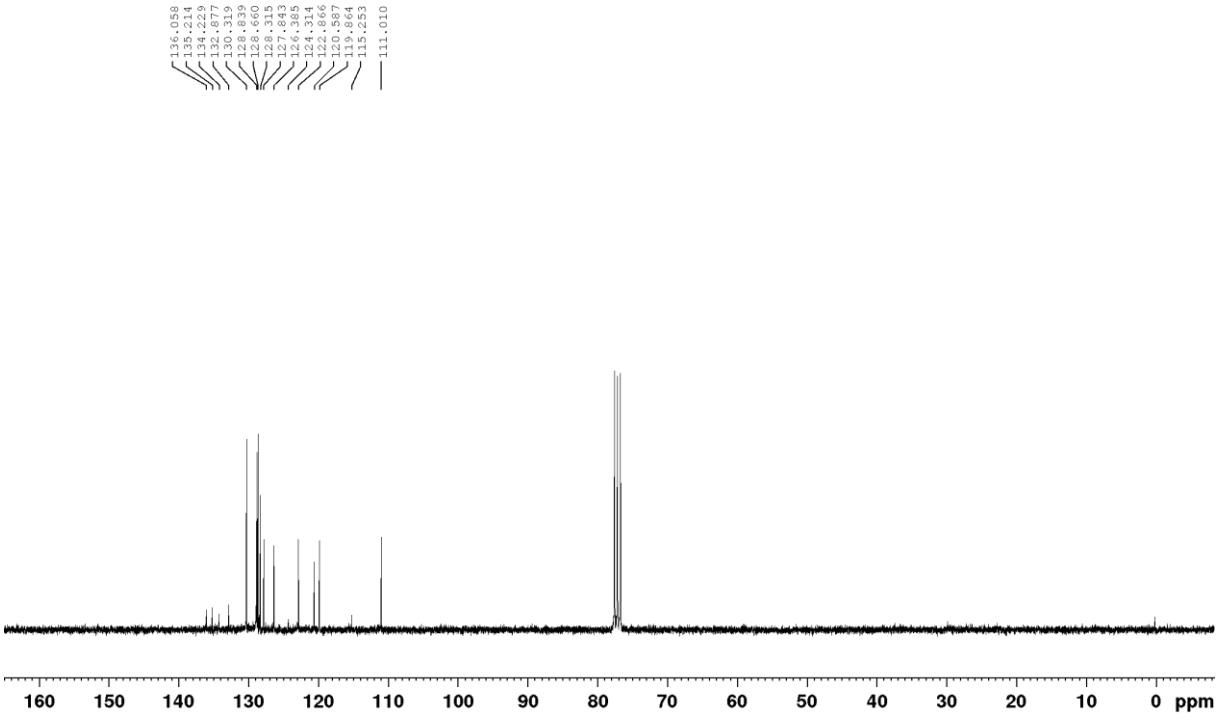


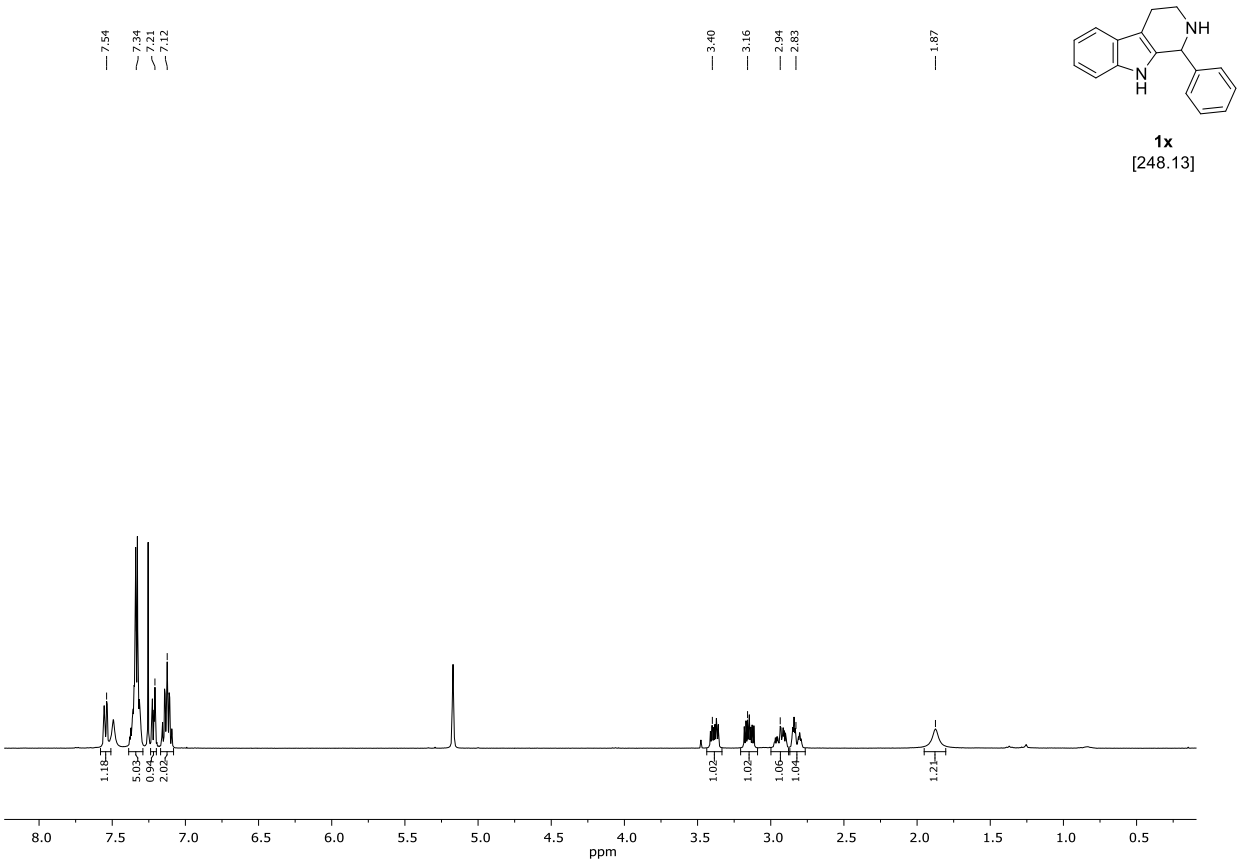

11.114
7.535
7.331
7.067
6.940
5.808
5.686
5.653
3.722
1.987
1.652
7.067
6.940
7.2
7.0
ppm
1.000
0.954
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.89
5.05
1.94
1.00
0.95
1.00
0.97
0.95
5.27
1.05

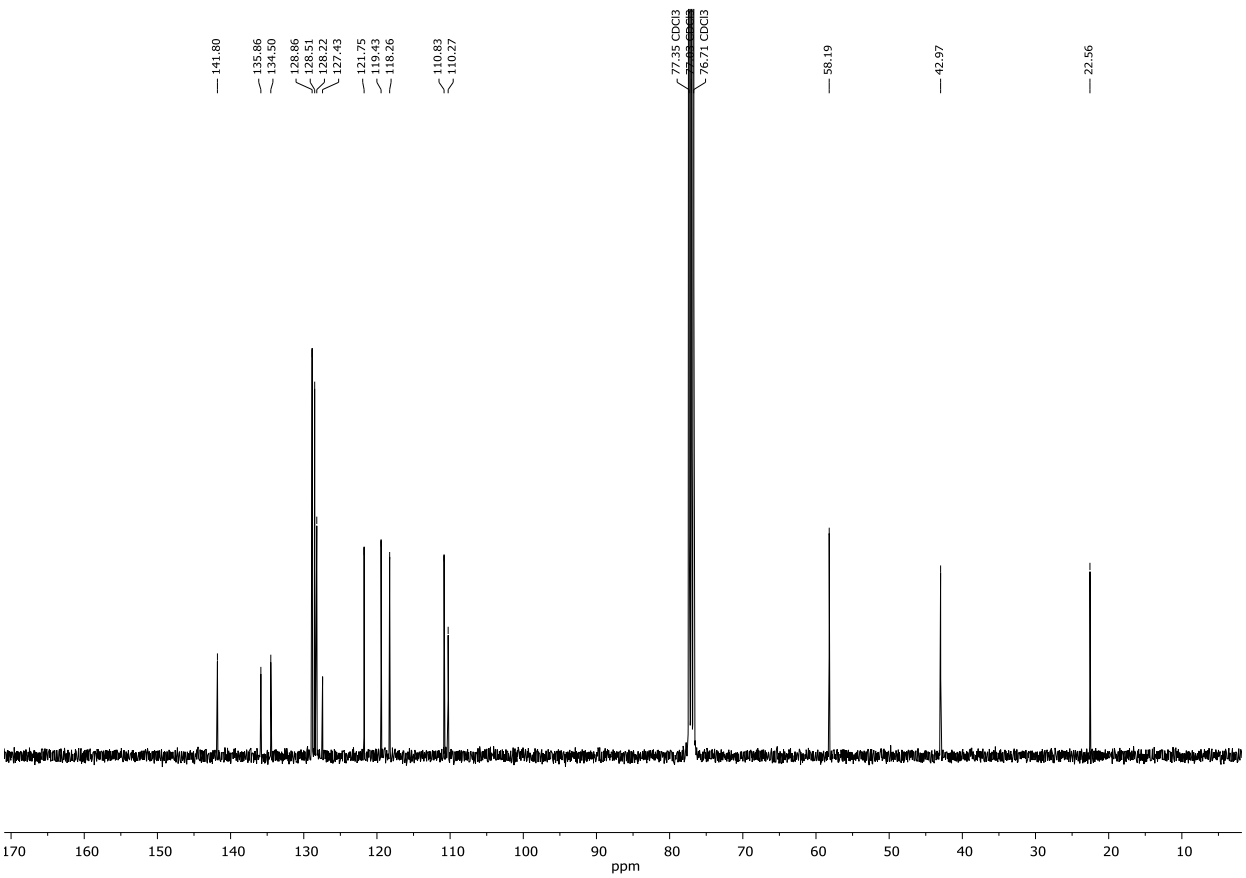
3a
[269.35]

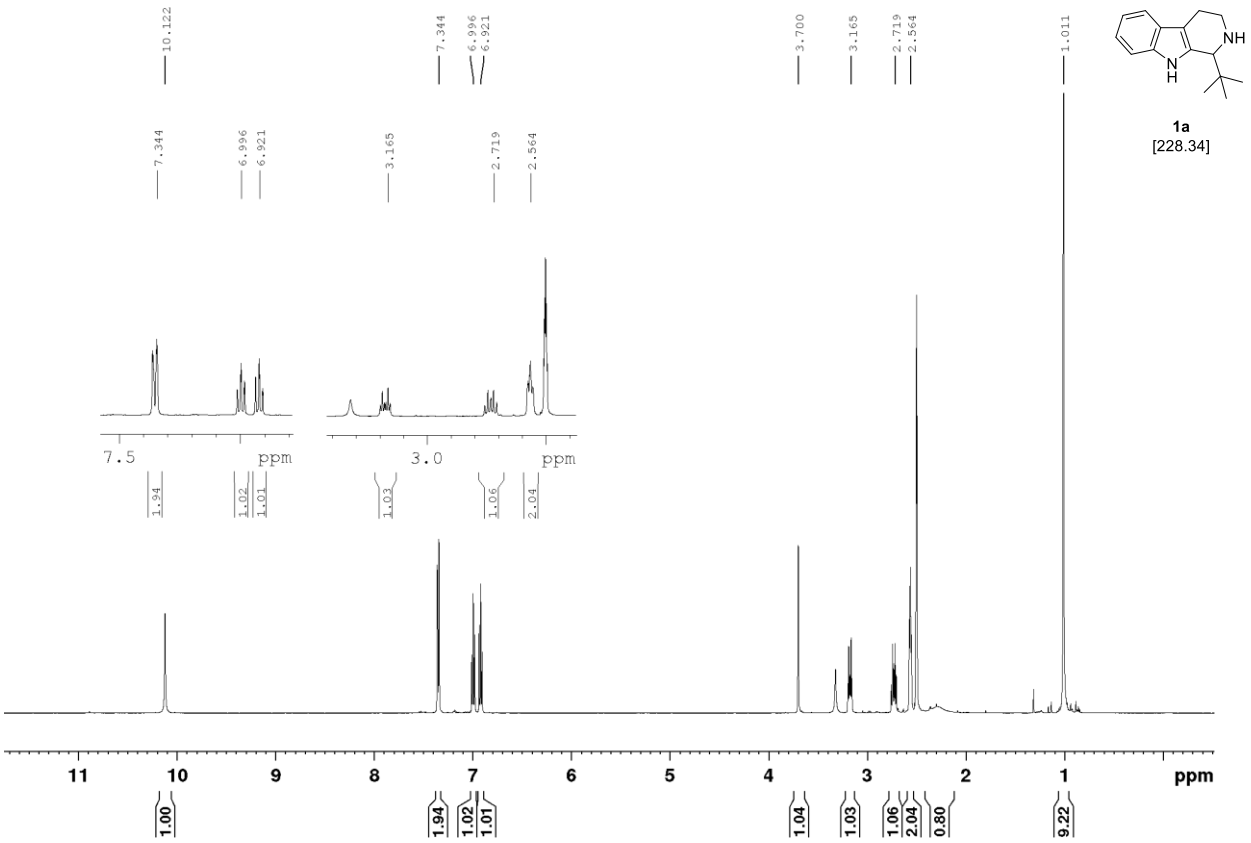

136.270
134.246
132.977
131.935
128.630
128.435
127.439
127.191
126.519
121.103
119.958
118.239
114.894
111.272
33.141
30.357
24.497
22.541
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

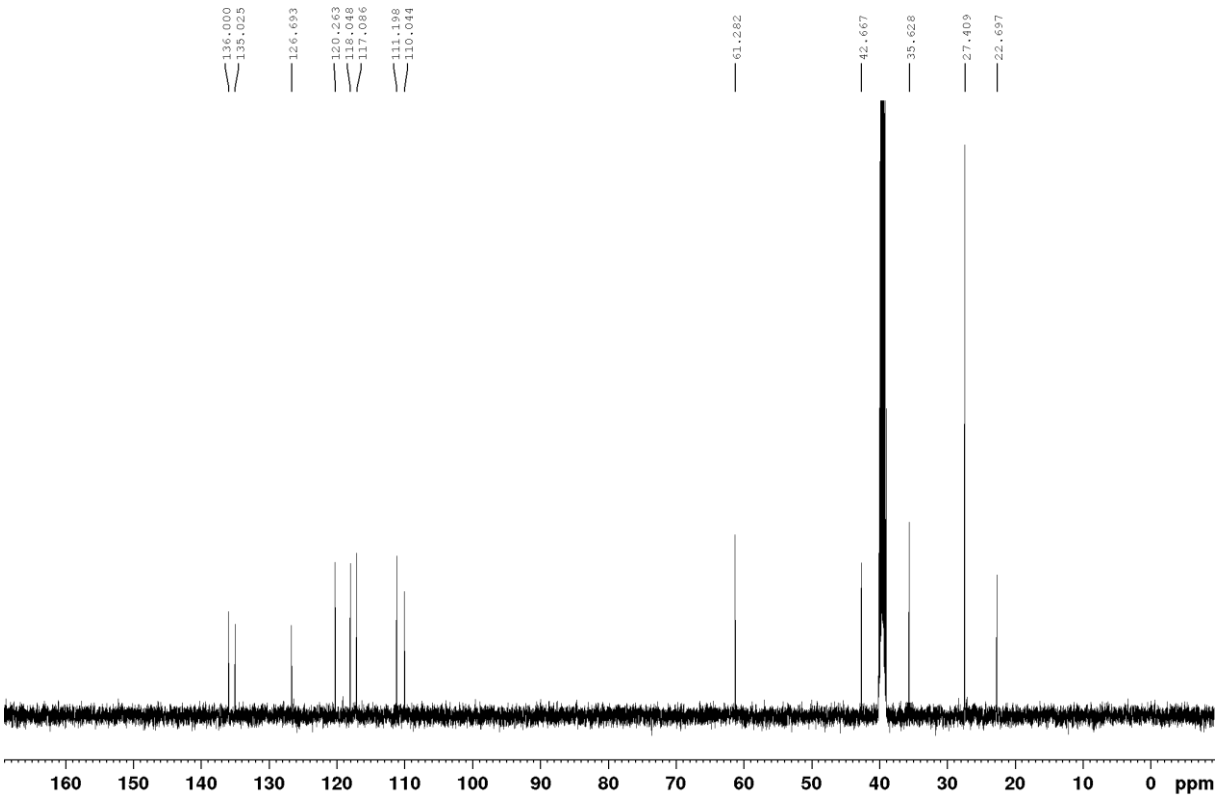

8.232
7.683
7.384
7.317
7.162
4a
[269.35]
8.0
7.5
ppm
1.00
1.05
10.36
1.96
0.96
EtOAc
EtOAc
EtOAc
12
11
10
9
8
7
6
5
4
3
2
1
ppm

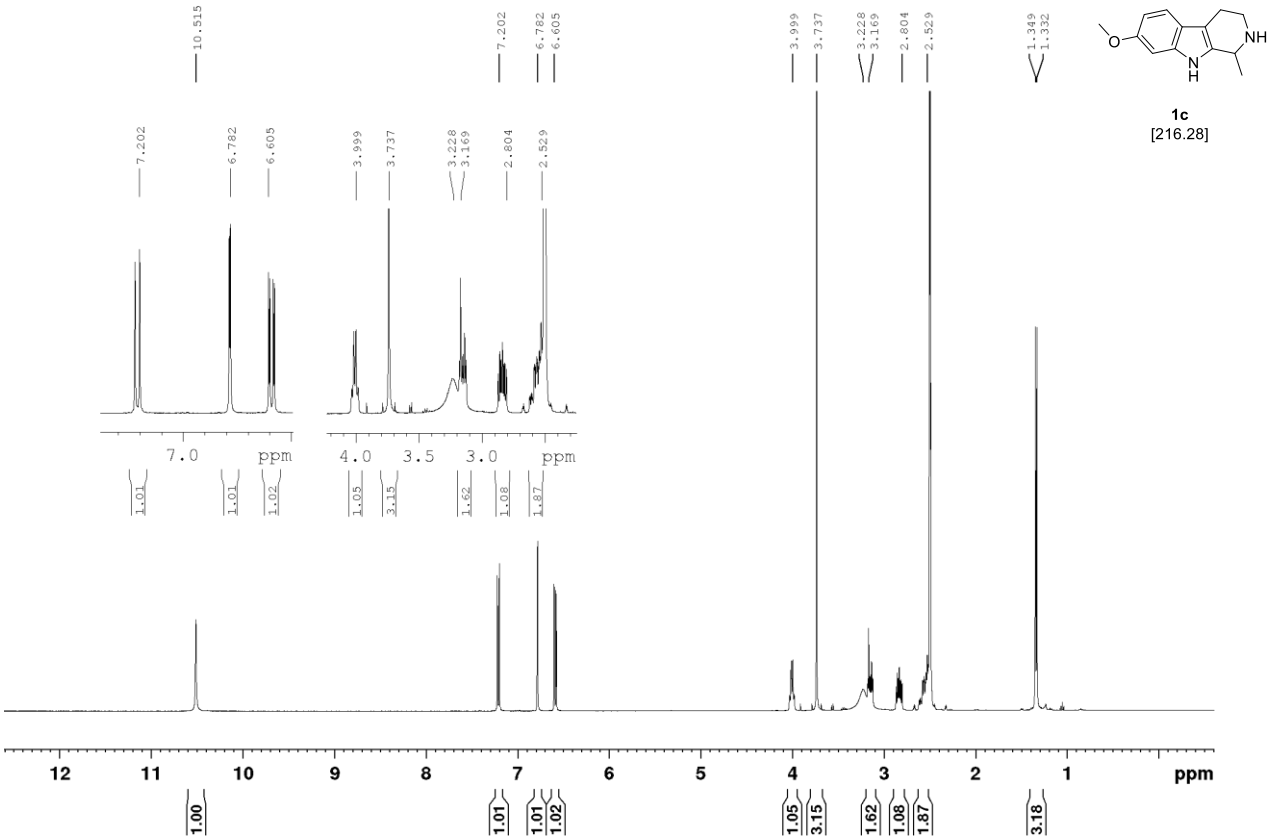

136.058
135.214
134.229
132.877
130.319
128.839
128.660
128.315
127.843
126.385
124.314
122.866
120.587
119.864
115.253
111.010
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.54
7.34
7.21
7.12
3.40
3.16
2.94
2.83
1.87
NH
N
H
1x
[248.13]
1.18
5.03
0.94
2.02
1.02
1.02
1.06
1.04
1.21
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
ppm

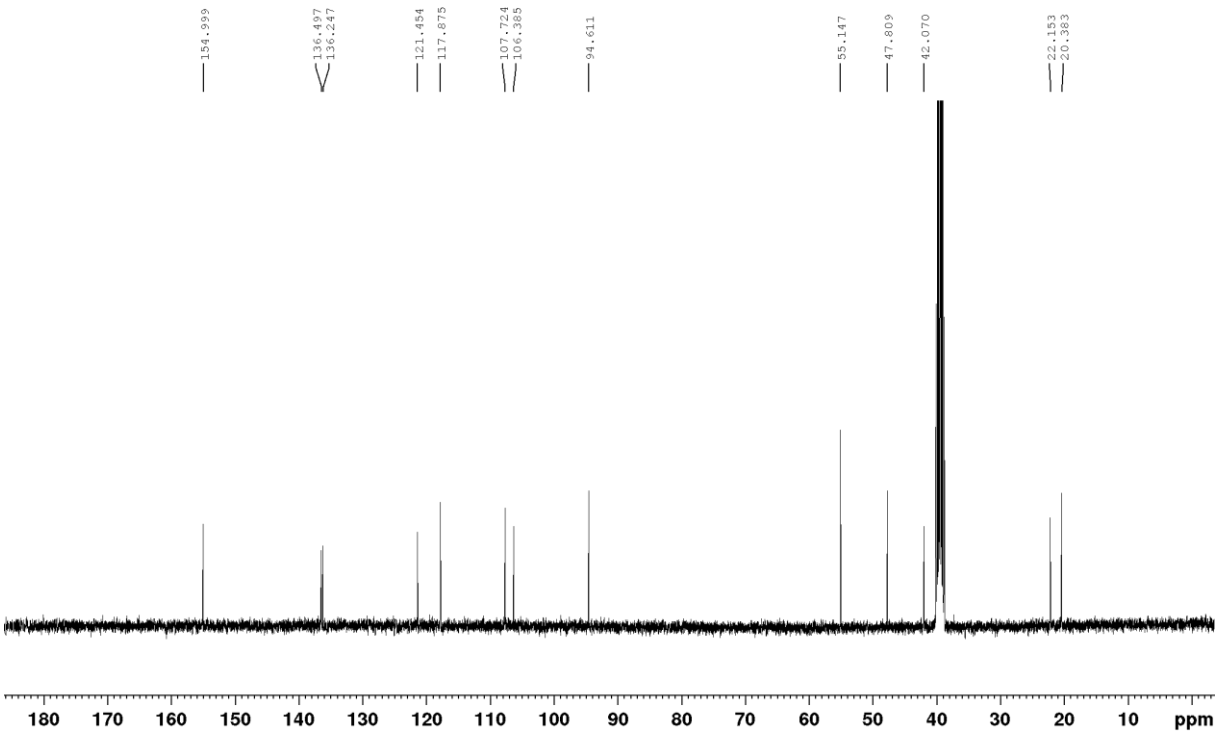

141.80
135.86
134.50
128.86
128.51
128.22
127.43
121.75
119.43
118.26
110.83
110.27
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
58.19
42.97
22.56
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

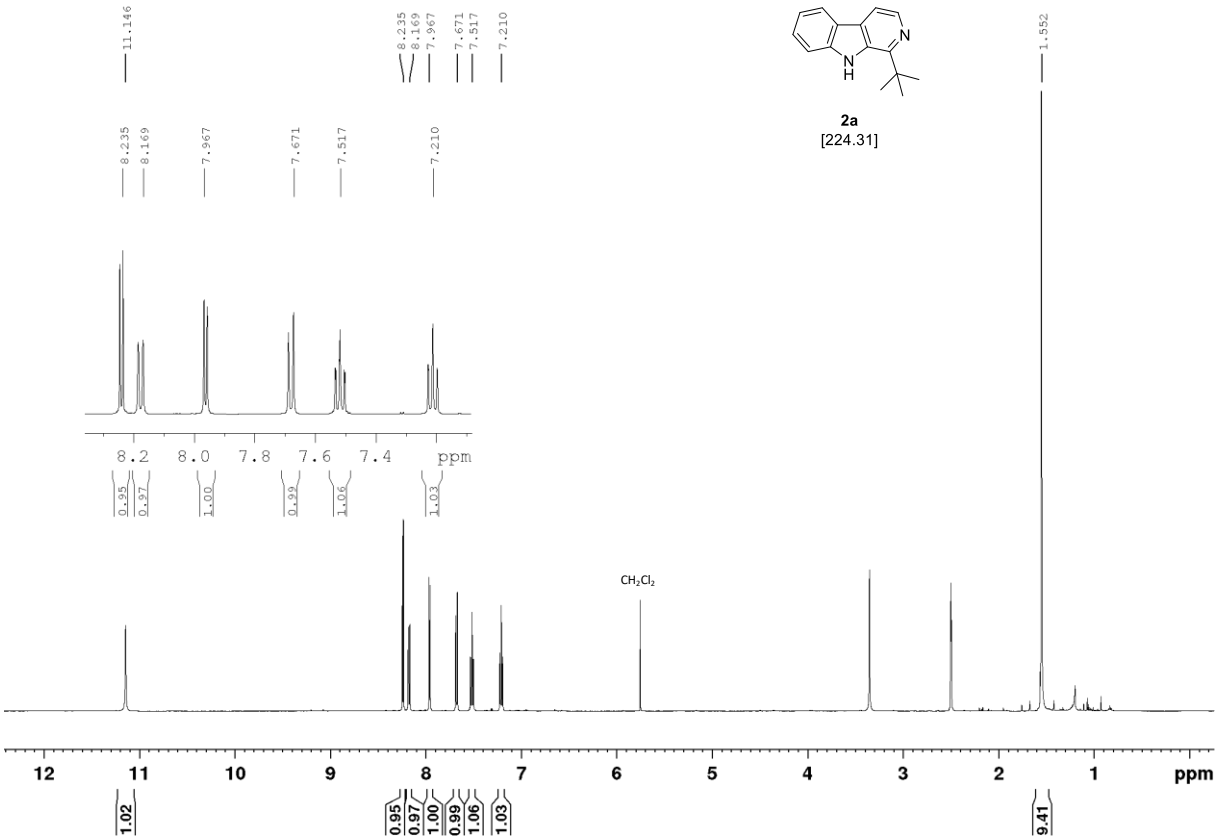

10.122
7.344
6.996
6.921
3.700
3.165
2.719
2.564
1.011
NH
N
H
1a
[228.34]
7.5
ppm
3.0
ppm
1.94
1.02
1.01
1.03
1.06
2.04
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.94
1.02
1.01
1.04
1.03
1.06
2.04
0.80
9.22

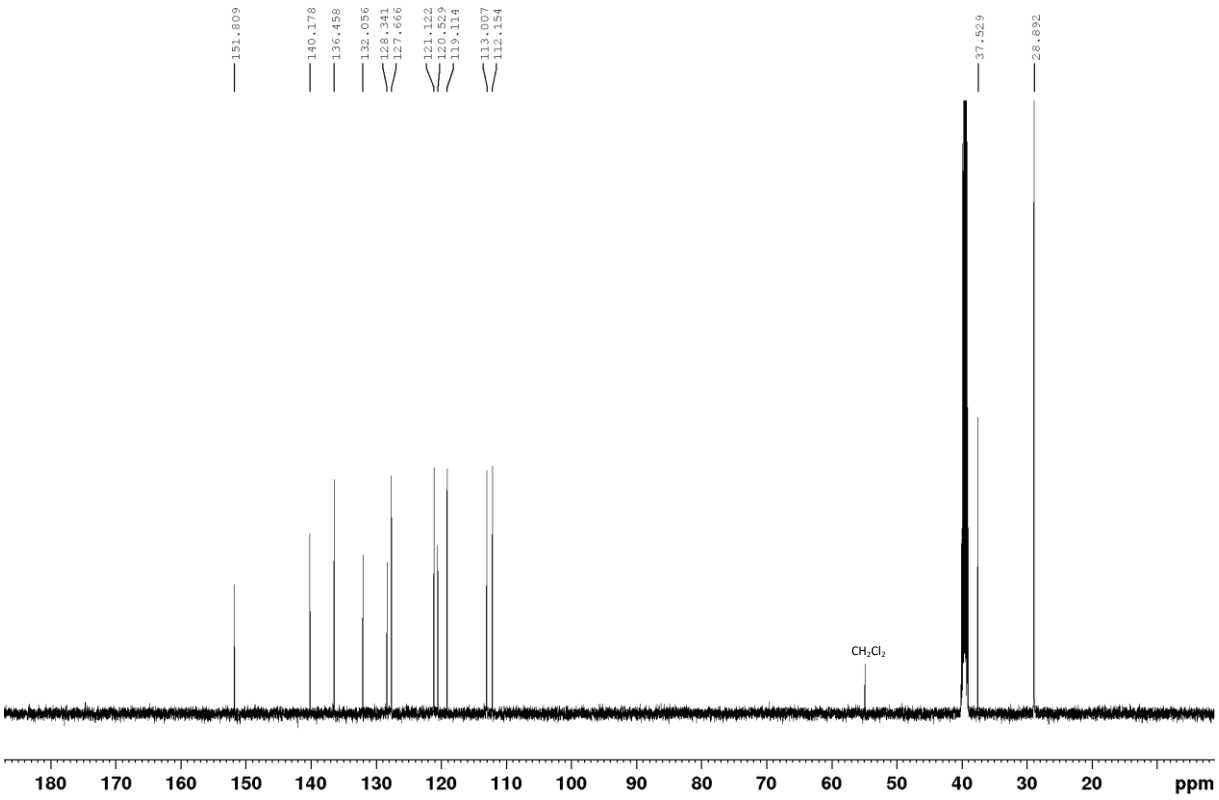

136.000
135.025
126.693
120.263
118.048
117.086
111.198
110.044
61.282
42.667
35.628
27.409
22.697
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

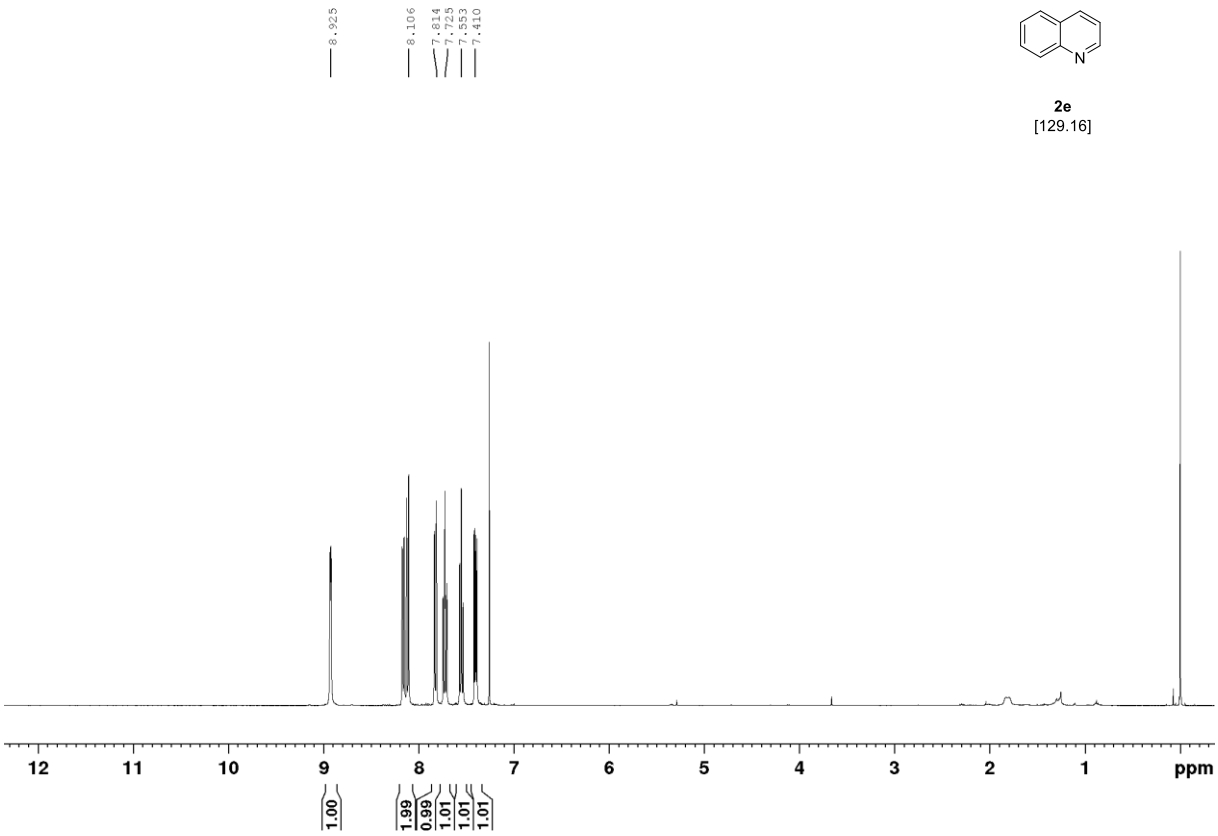

10.515
7.202
6.782
6.605
3.999
3.737
3.228
3.169
2.804
2.529
1.349
1.332
1.00
1.01
1.01
1.02
1.05
3.15
1.62
1.08
1.87
3.18
ppm

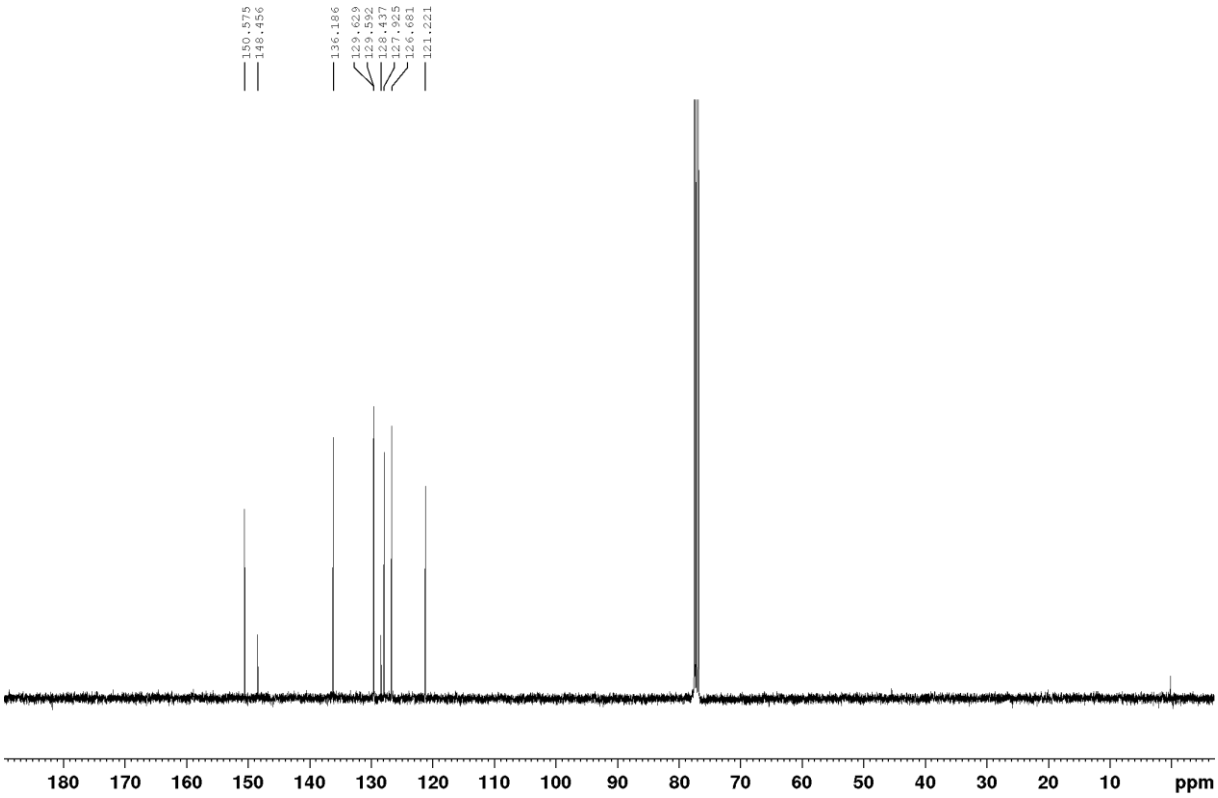
1c
[216.28]

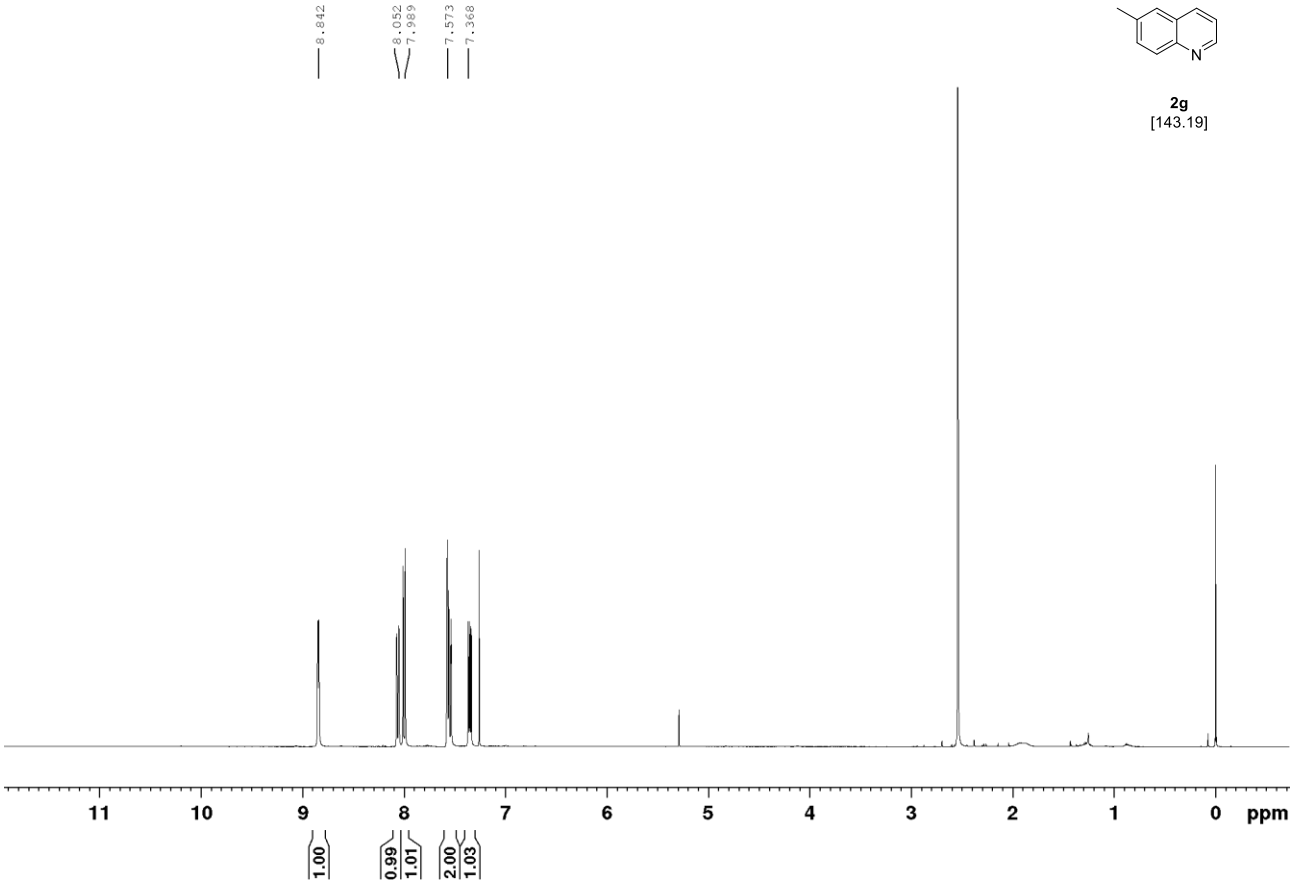

154.999
136.497
136.247
121.454
117.875
107.724
106.385
94.611
55.147
47.809
42.070
22.153
20.383
ppm

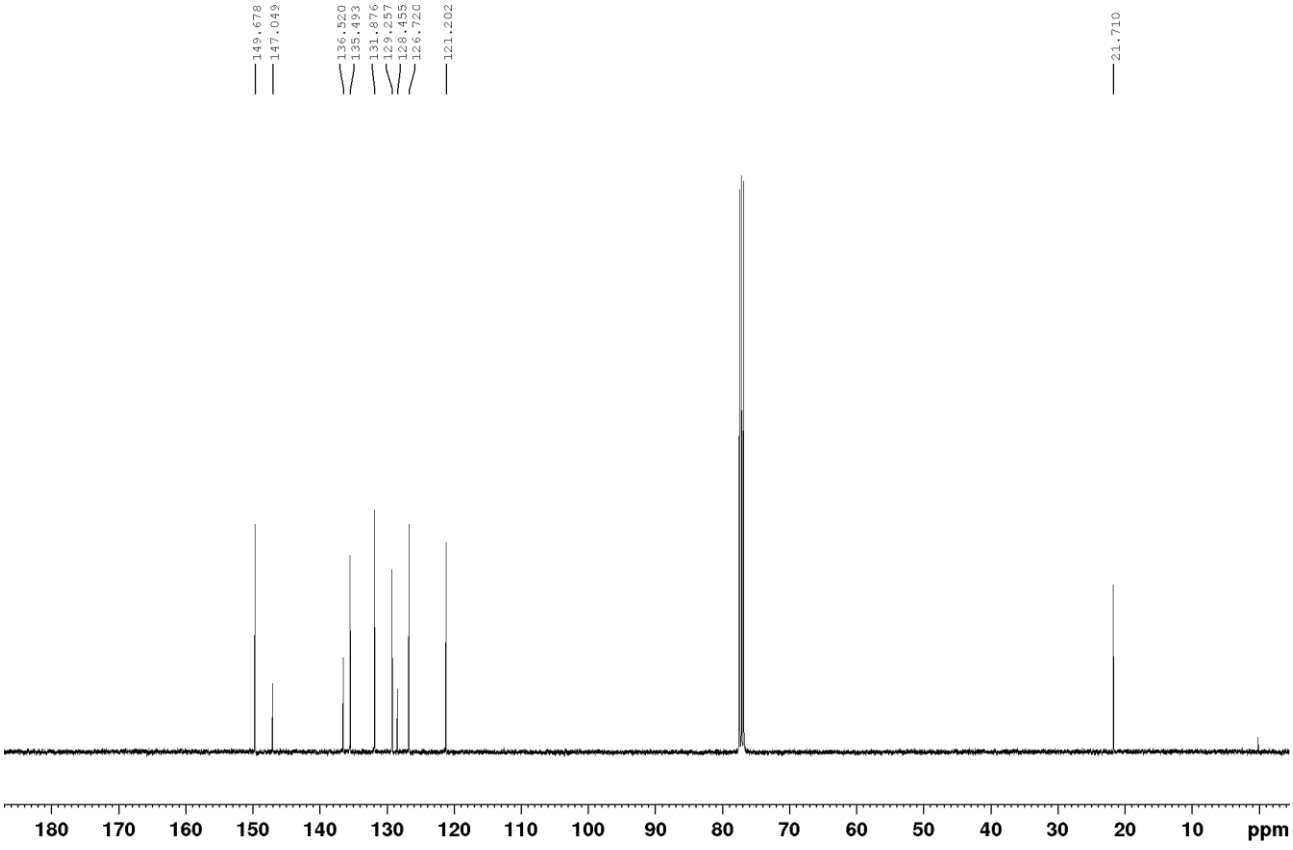

11.146
8.235
8.169
7.967
7.671
7.517
7.210
1.552
2a
[224.31]
CH2Cl2
ppm

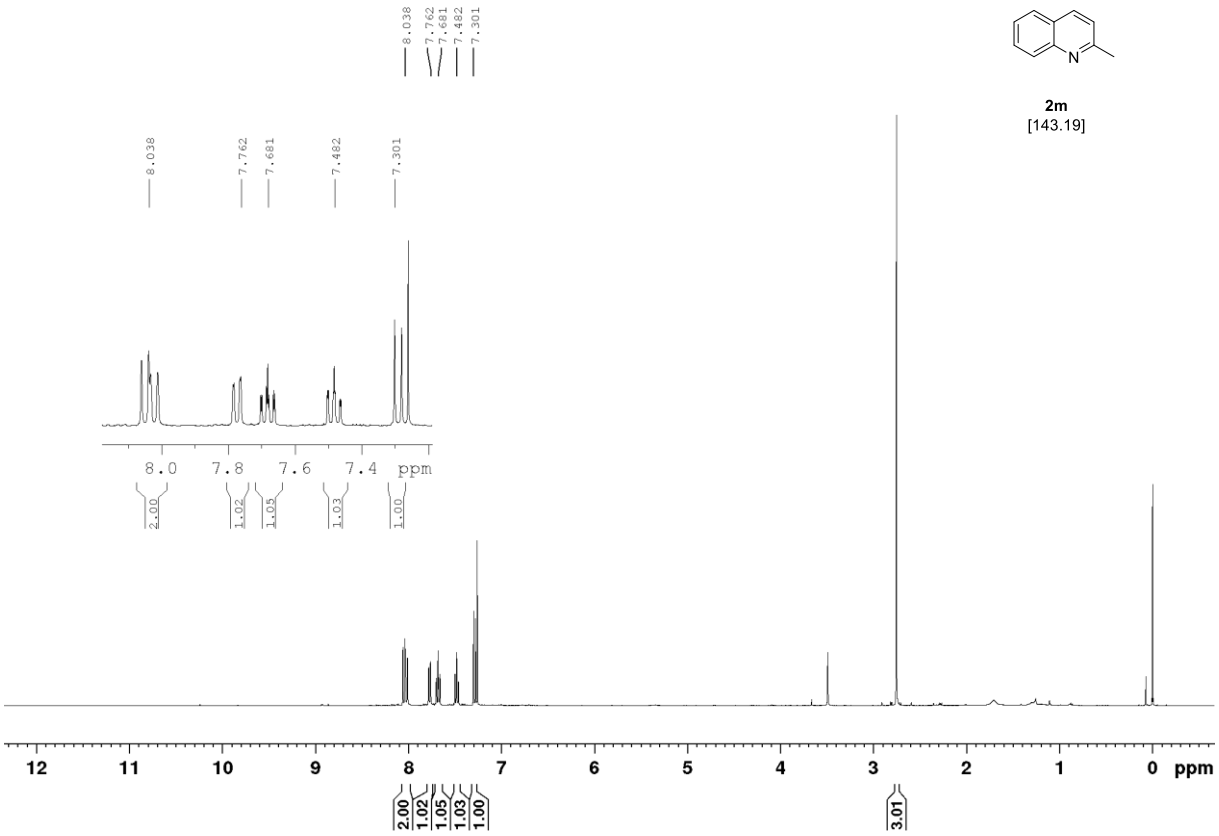

151.809
140.178
136.458
132.056
128.341
127.666
121.122
120.529
119.114
113.007
112.154
37.529
28.892
CH2Cl2
ppm

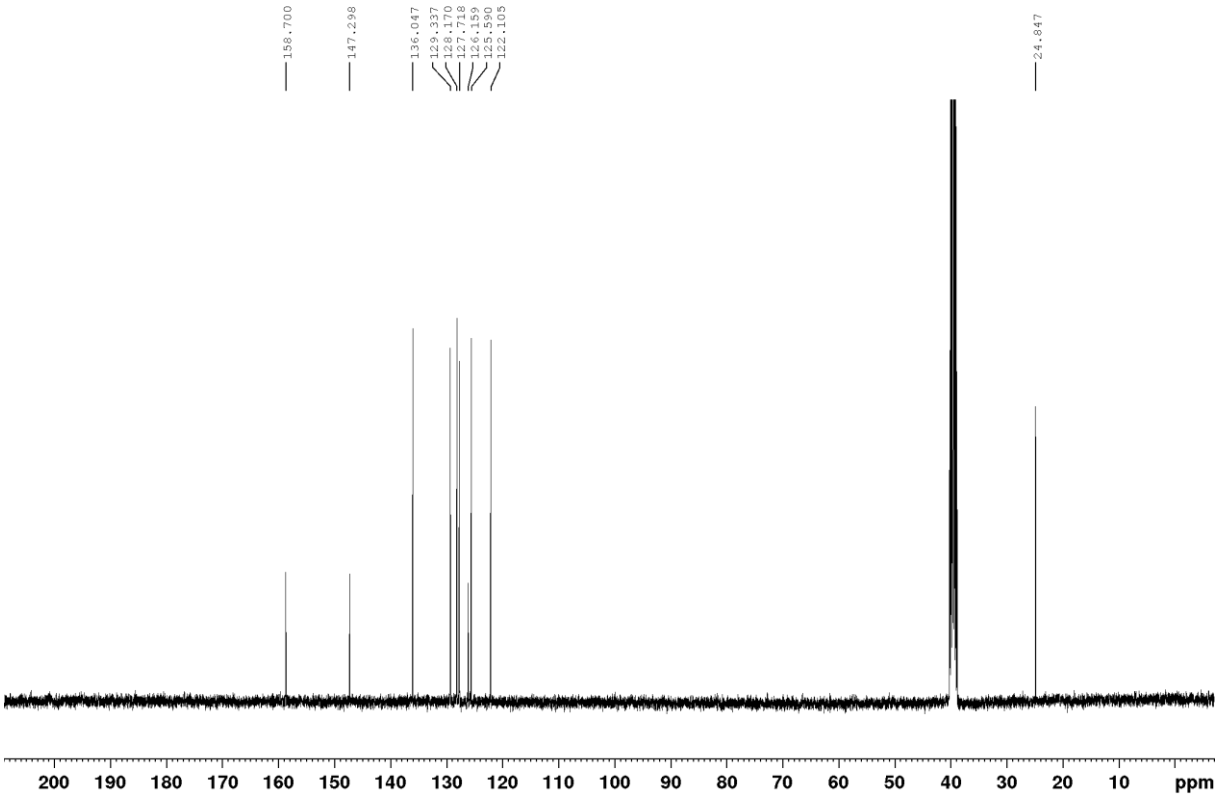

8.925
8.106
7.814
7.725
7.553
7.410
N
2e
[129.16]
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.99
0.99
1.01
1.01
1.01

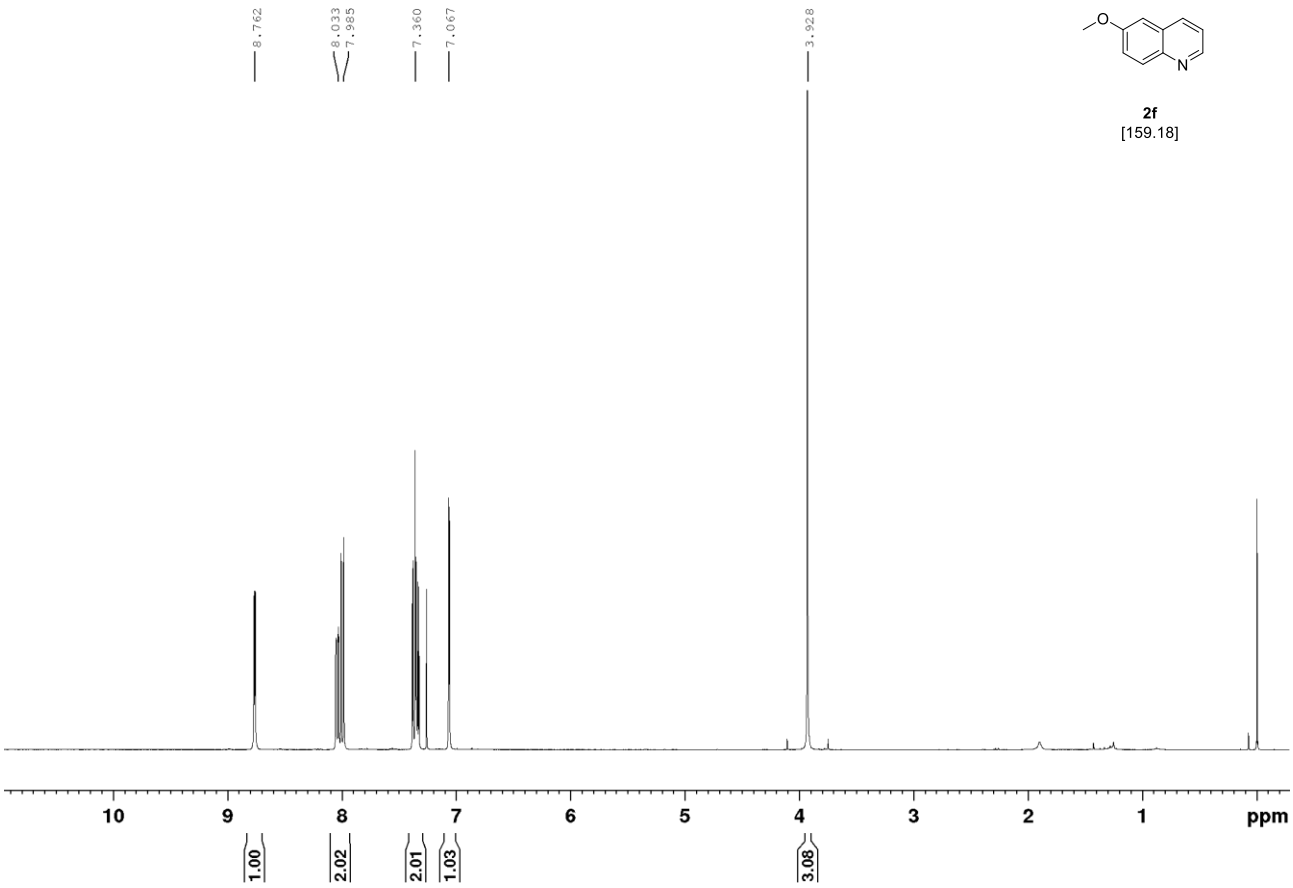

150.575
148.456
136.186
129.629
129.592
128.437
127.925
126.681
121.221
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

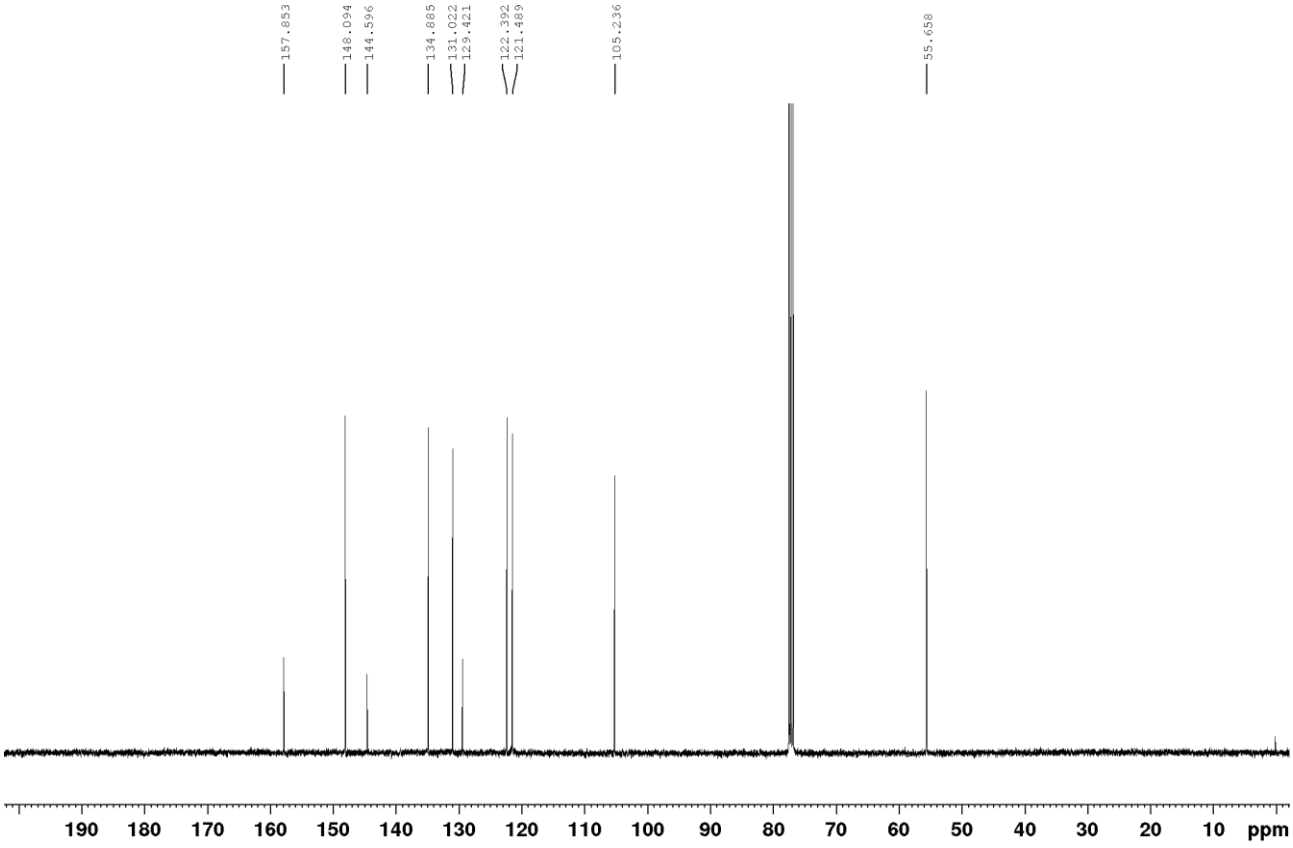

8.842
8.052
7.989
7.573
7.368
2g
[143.19]
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
1.01
2.00
1.03

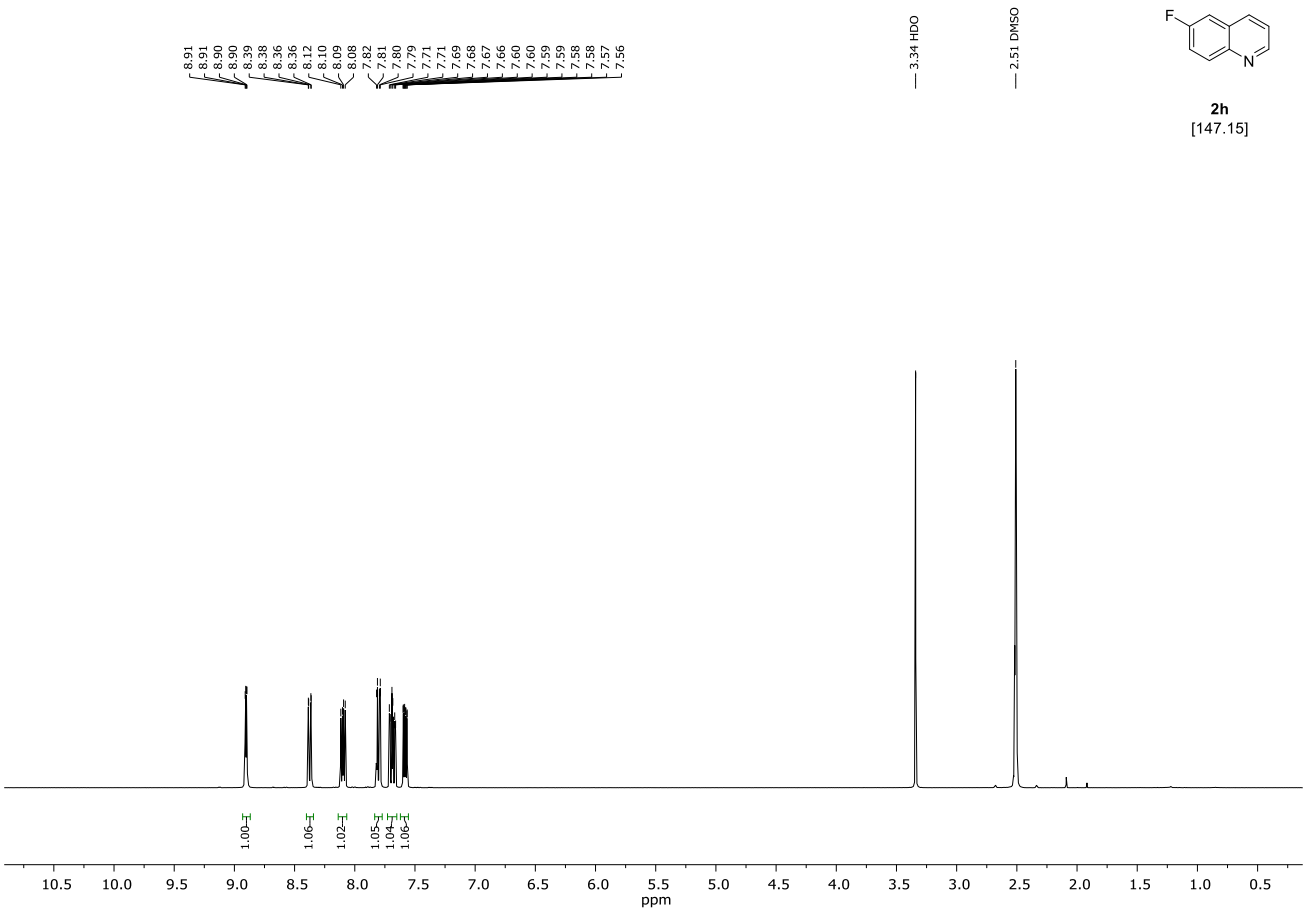

149.678
147.049
136.520
135.493
131.876
129.257
128.455
126.720
121.202
21.710
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

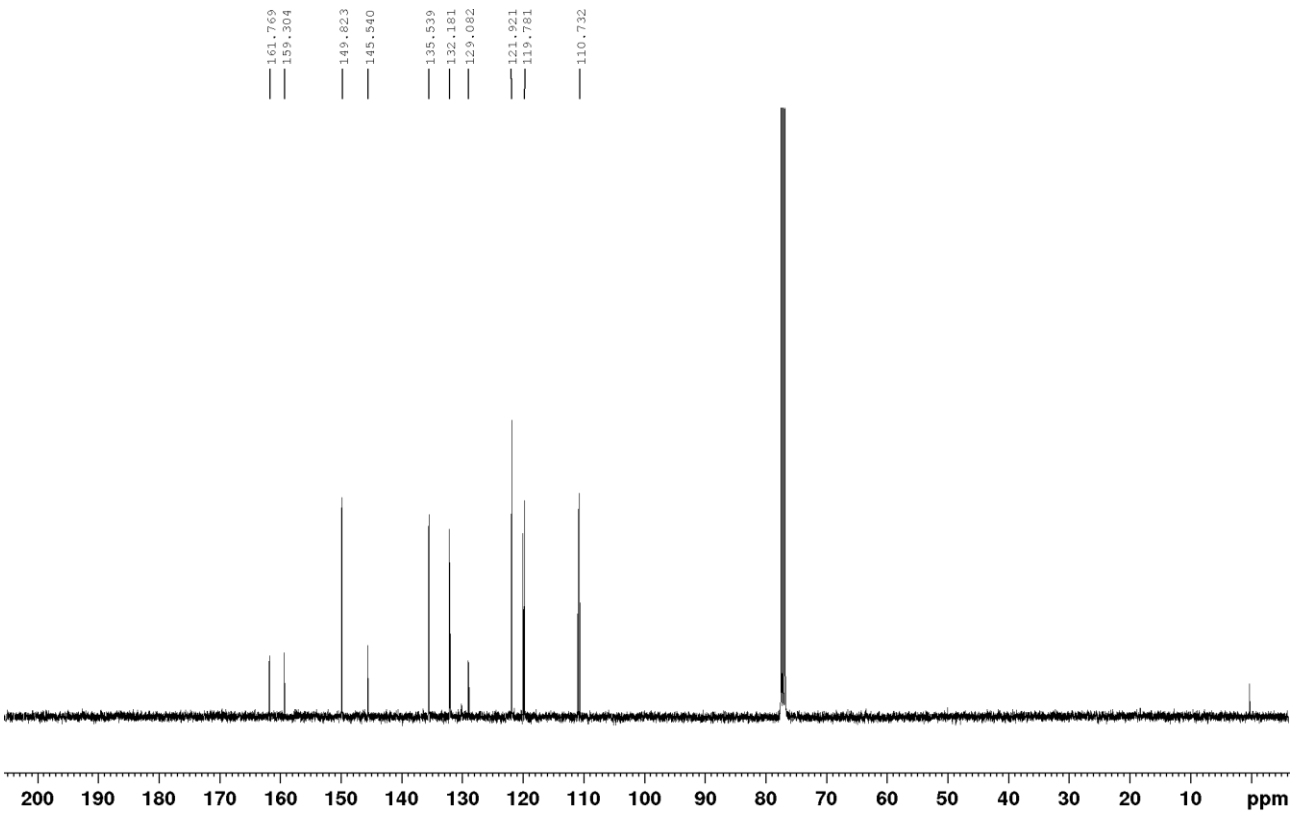

8.038
7.762
7.681
7.482
7.301
2m
[143.19]
8.0
7.8
7.6
7.4
ppm
2.00
1.02
1.05
1.03
1.00
3.01
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

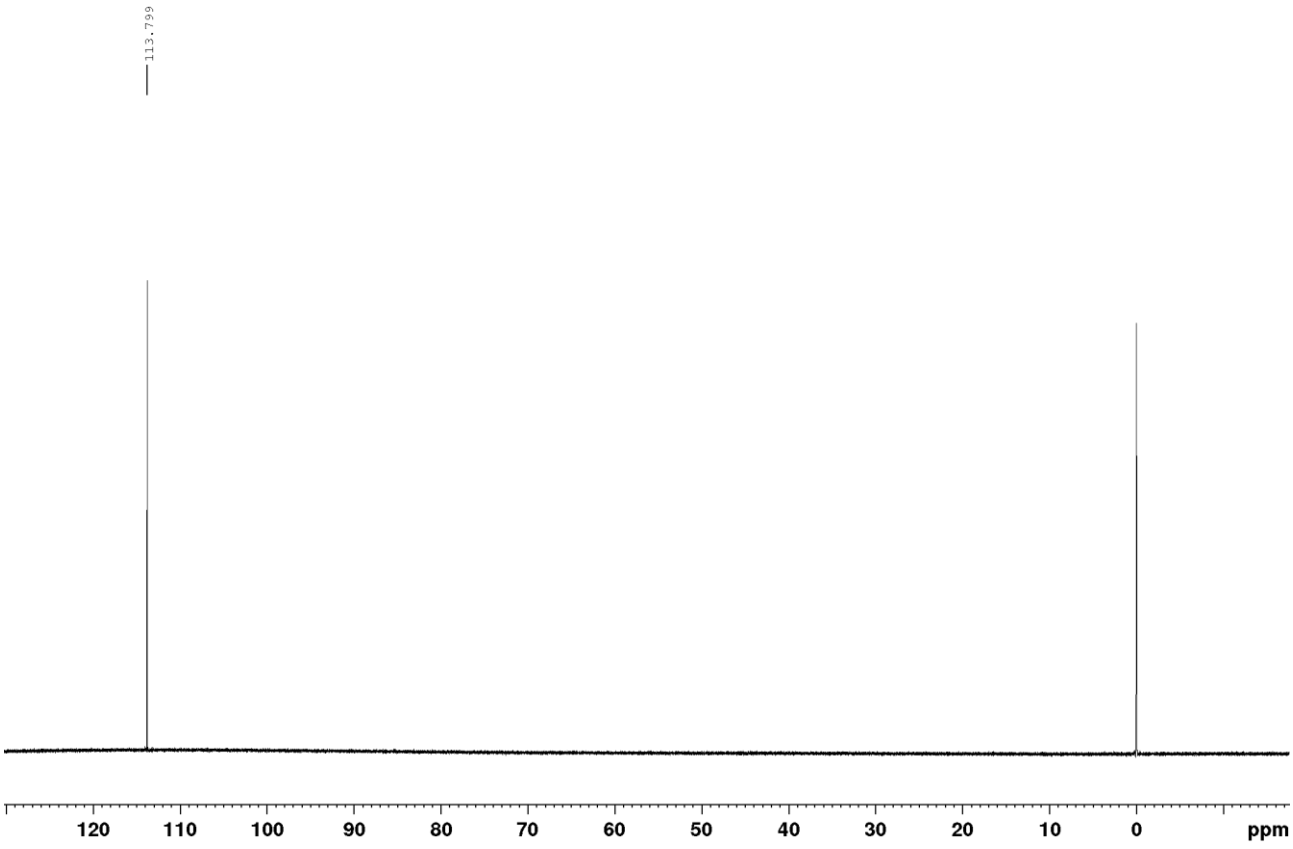

158.700
147.298
136.047
129.337
128.170
127.718
126.159
125.590
122.105
24.847
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

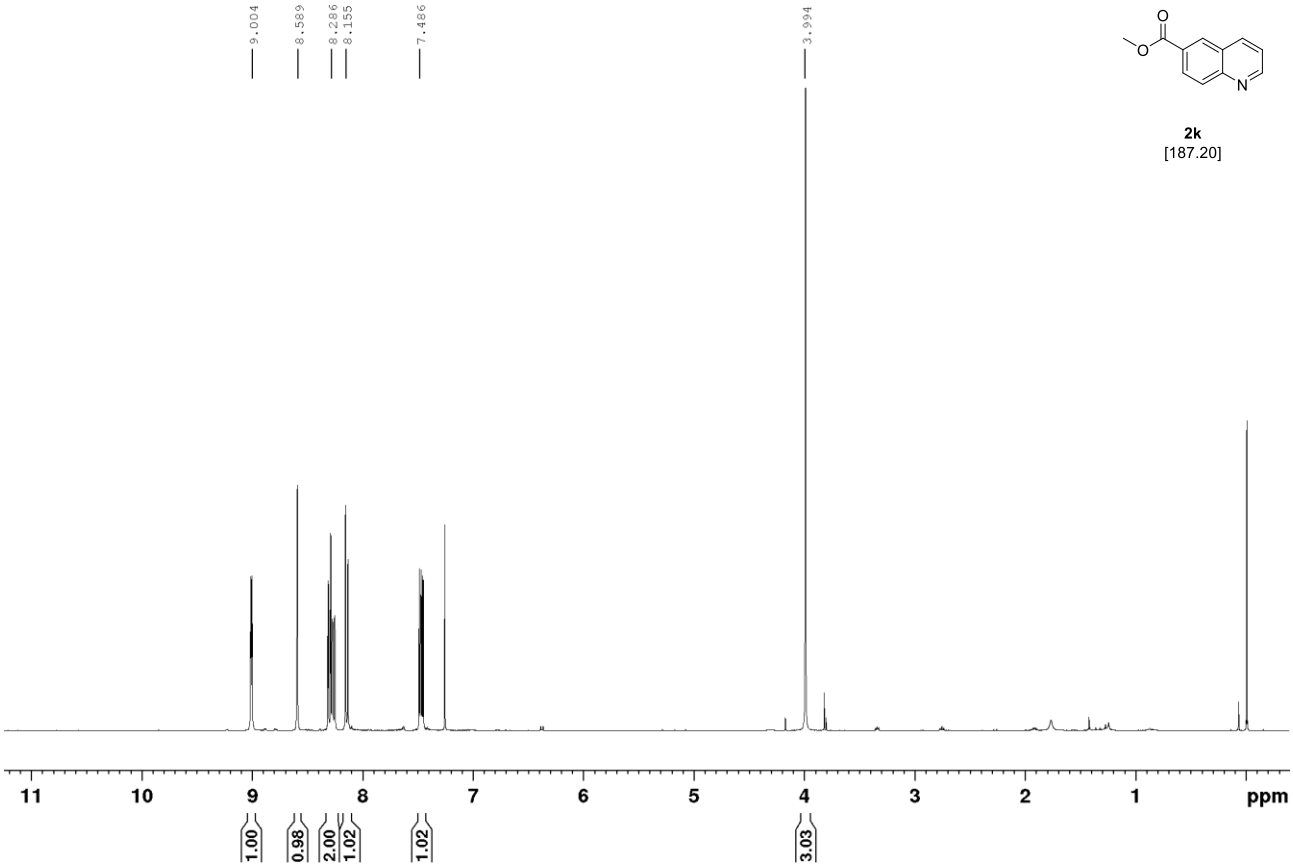

8.762
8.033
7.985
7.360
7.067
3.928
2f
[159.18]
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.02
2.01
1.03
3.08

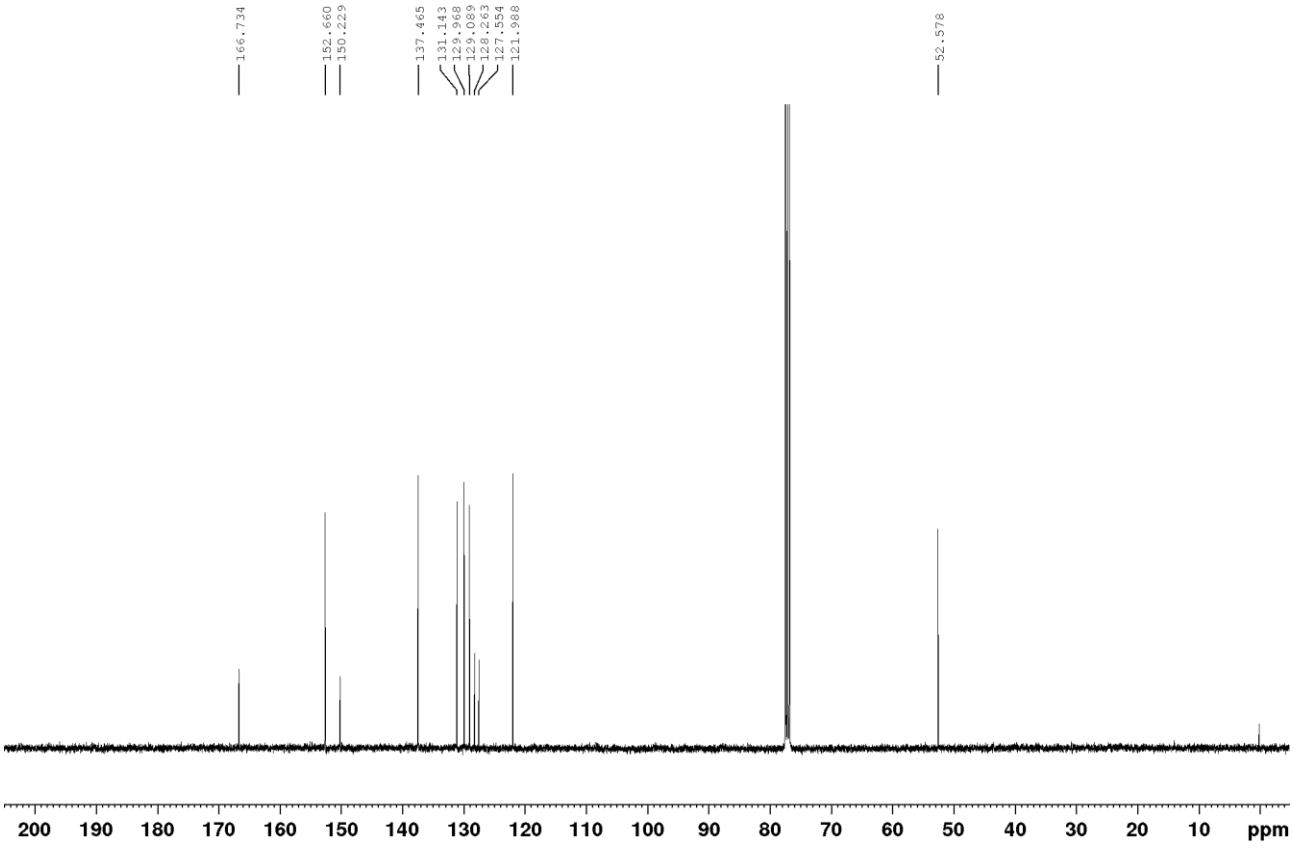

157.853
148.094
144.596
134.885
131.022
129.421
122.392
121.489
105.236
55.658
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

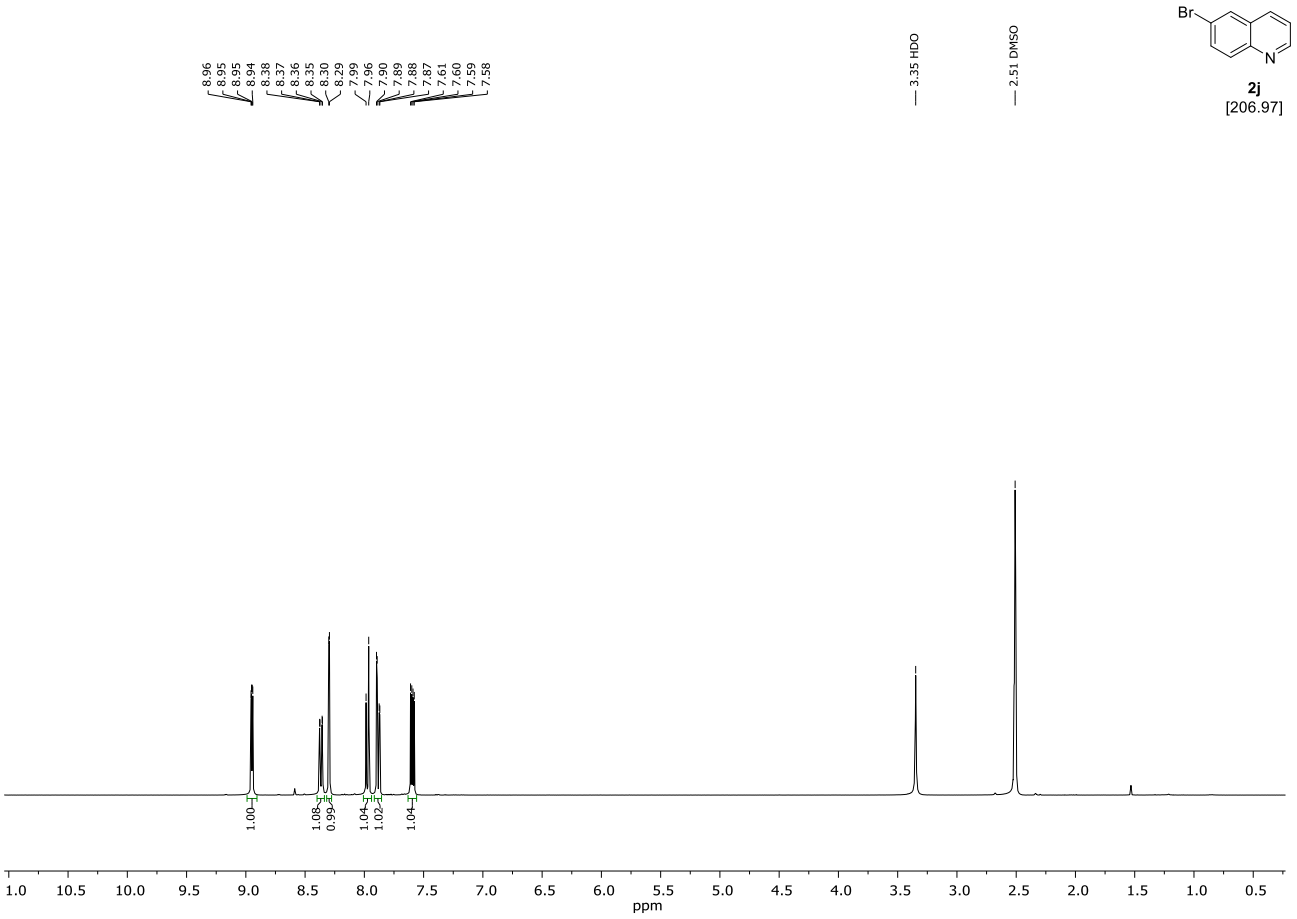

8.91
8.91
8.90
8.90
8.39
8.38
8.36
8.36
8.12
8.10
8.09
8.08
7.82
7.81
7.80
7.79
7.71
7.71
7.69
7.68
7.67
7.66
7.60
7.60
7.59
7.59
7.58
7.58
7.57
7.56
3.34 HDO
2.51 DMSO
F
N
2h
[147.15]
1.00
1.06
1.02
1.05
1.04
1.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

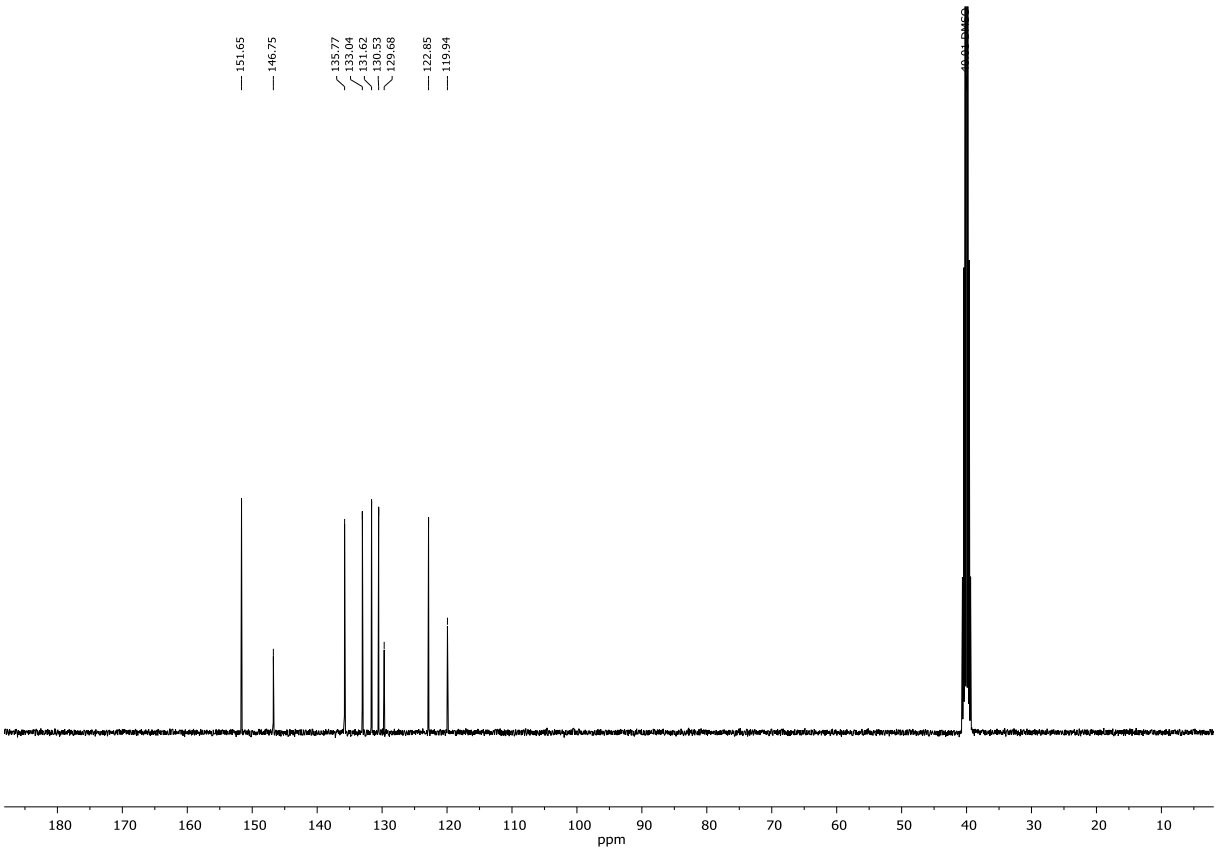

161.769
159.304
149.823
145.540
135.539
132.181
129.082
121.921
119.781
110.732
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

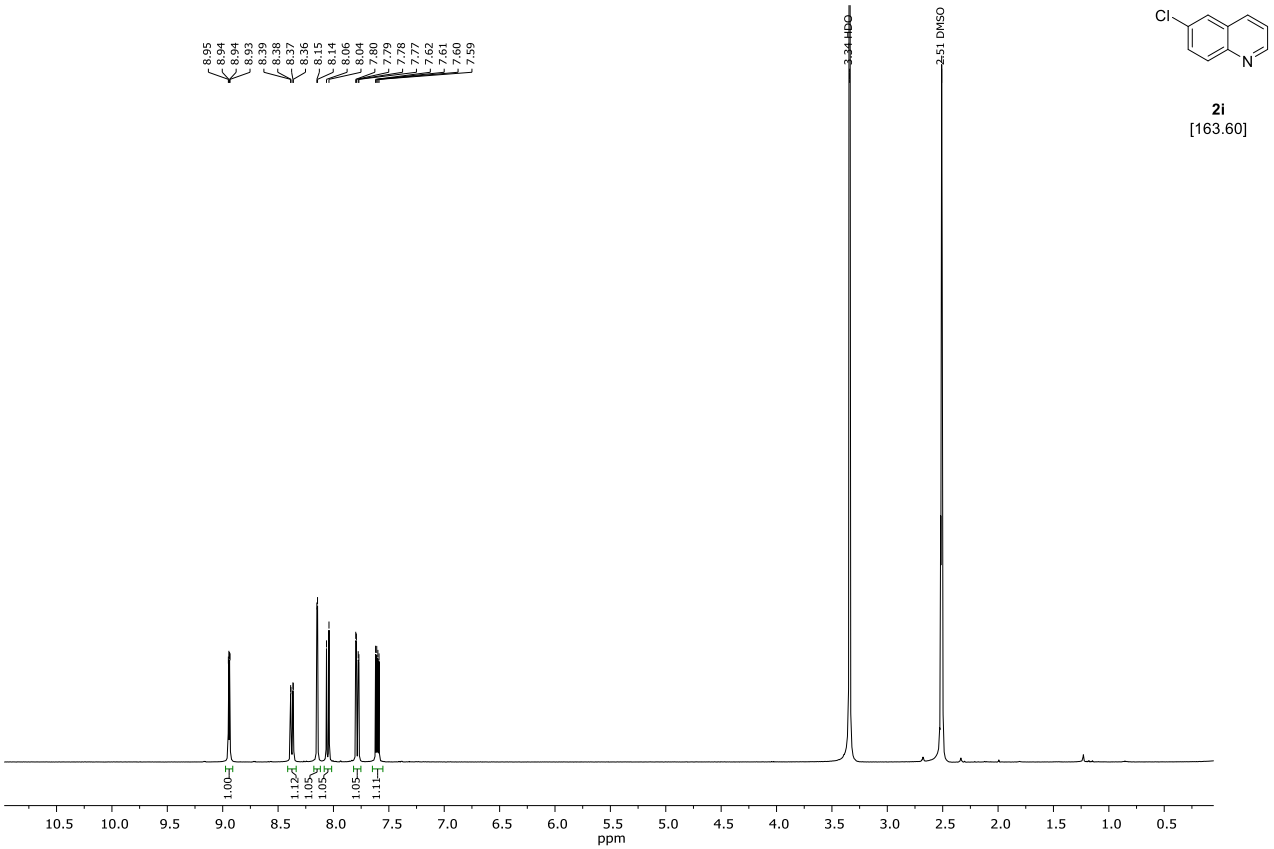

113.799
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

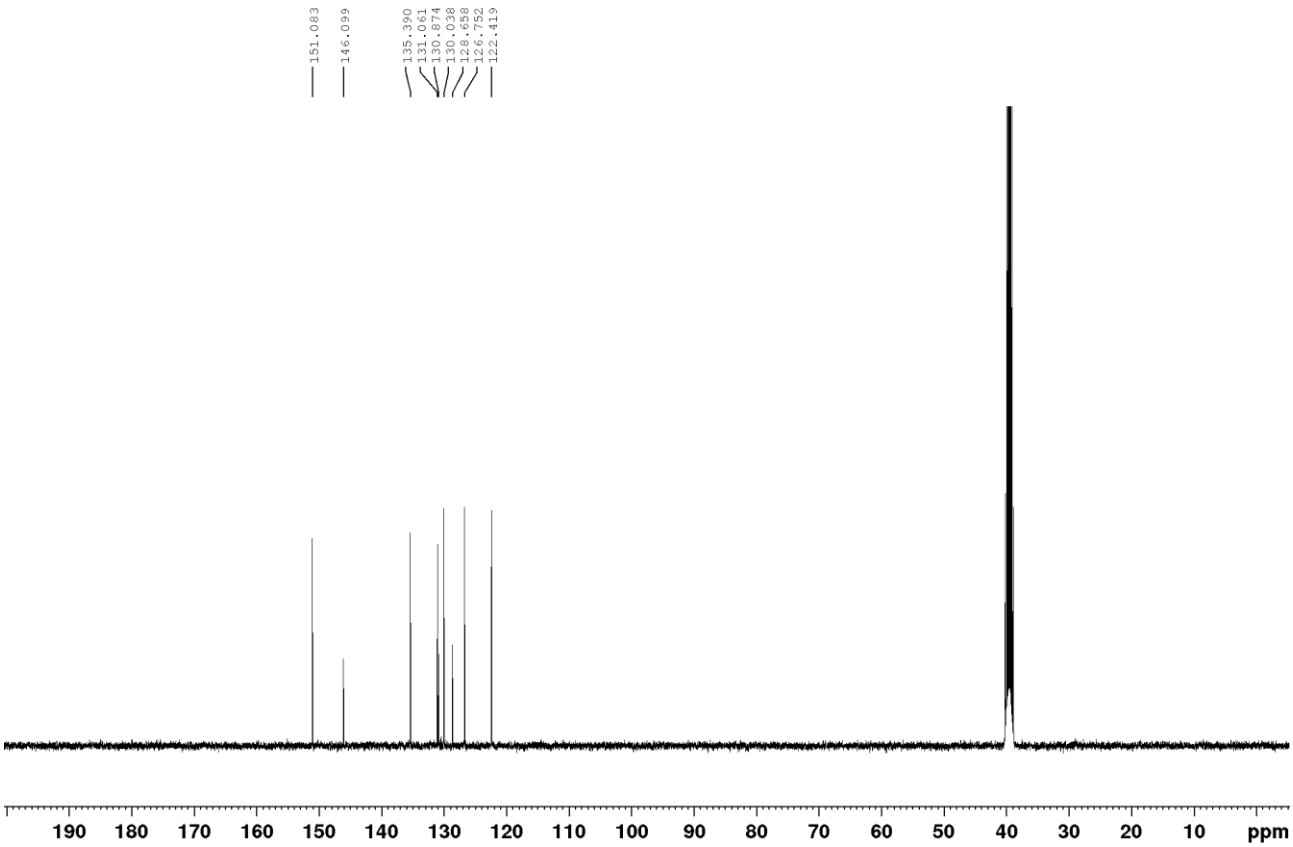

9.004
8.589
8.286
8.155
7.486
3.994
O
O
N
2k
[187.20]
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.98
2.00
1.02
1.02
3.03

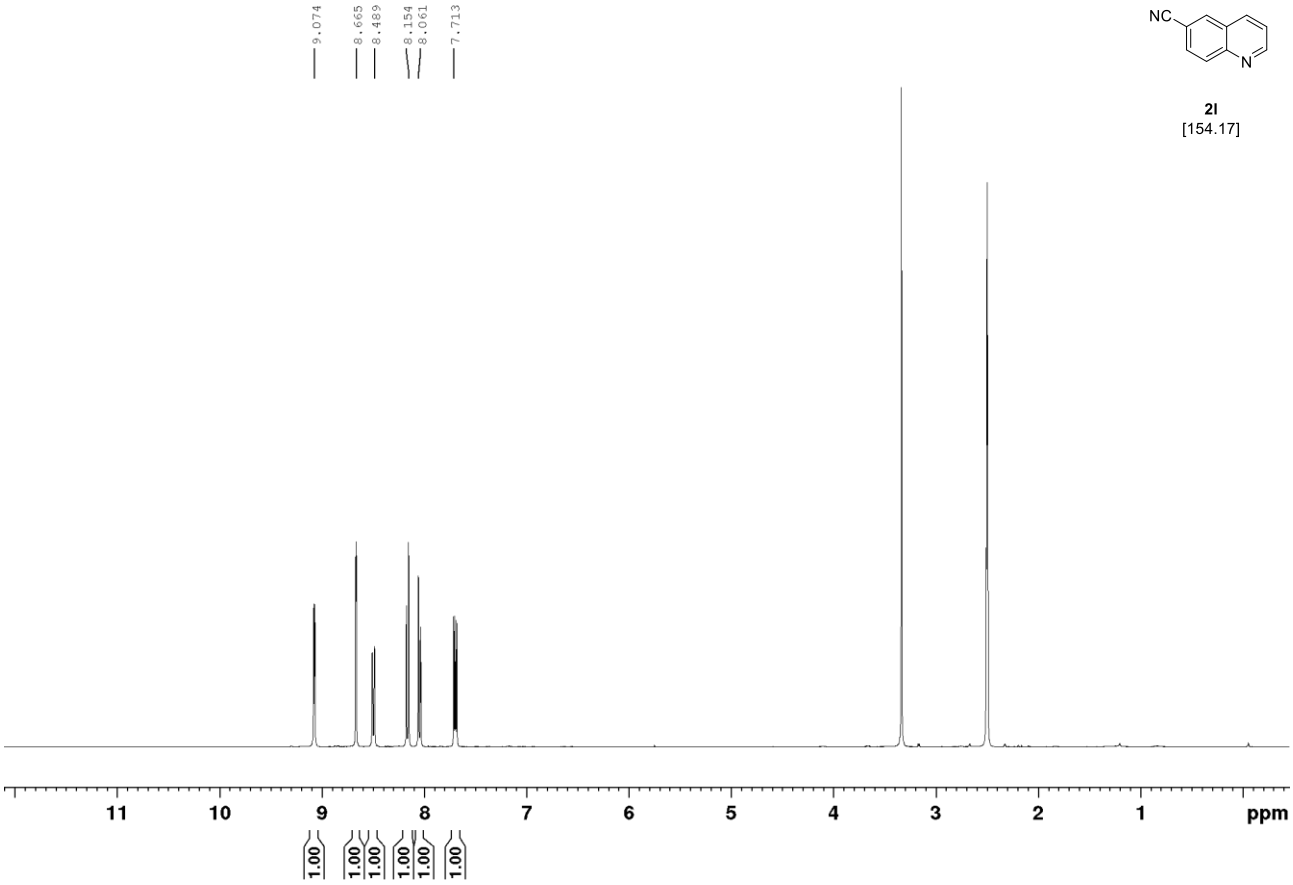

166.734
152.660
150.229
137.465
131.143
129.968
129.089
128.263
127.554
121.988
52.578
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

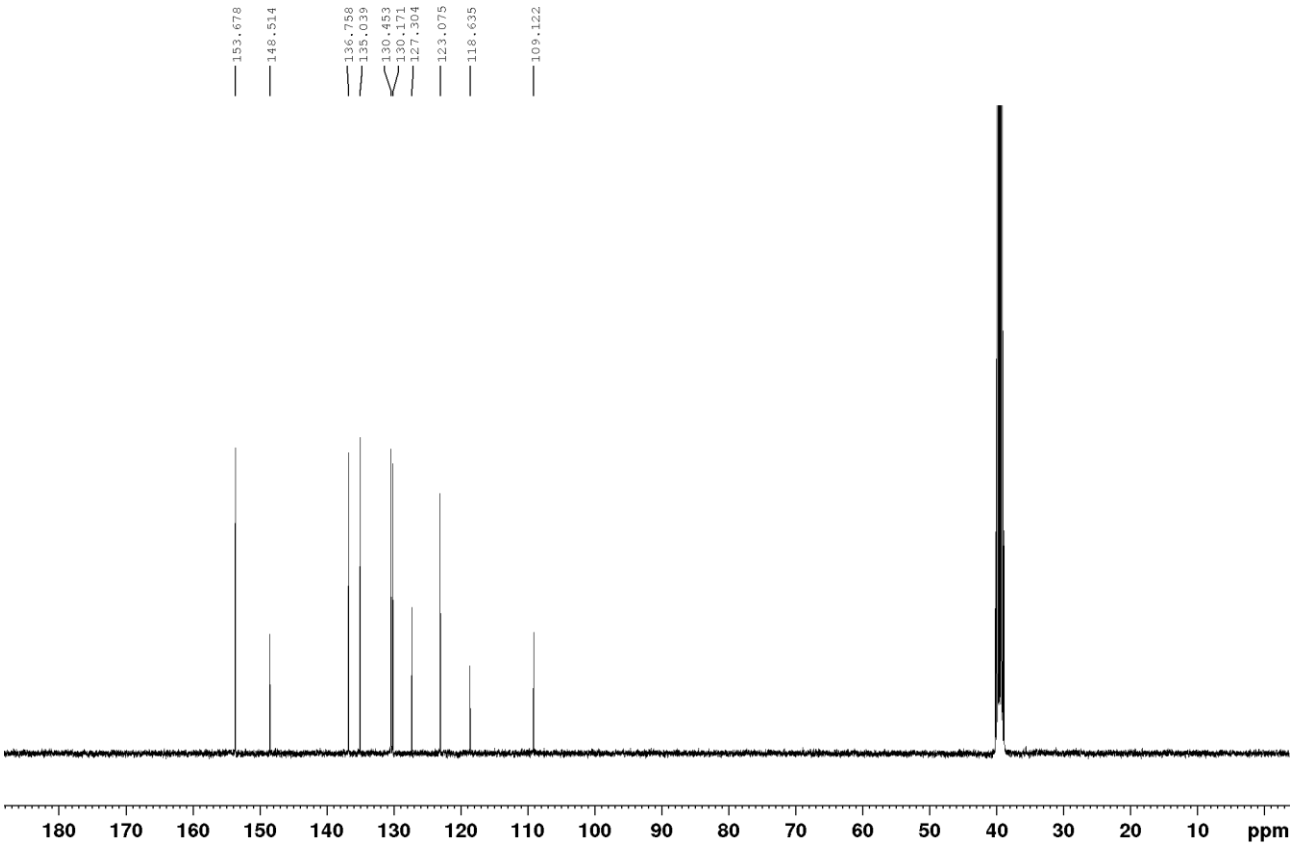

8.96
8.95
8.95
8.94
8.38
8.37
8.36
8.35
8.30
8.29
7.99
7.96
7.90
7.89
7.88
7.87
7.61
7.60
7.59
7.58
3.35 HDO
2.51 DMSO
Br
N
2j
[206.97]
1.00
1.08
0.99
1.04
1.02
1.04
ppm

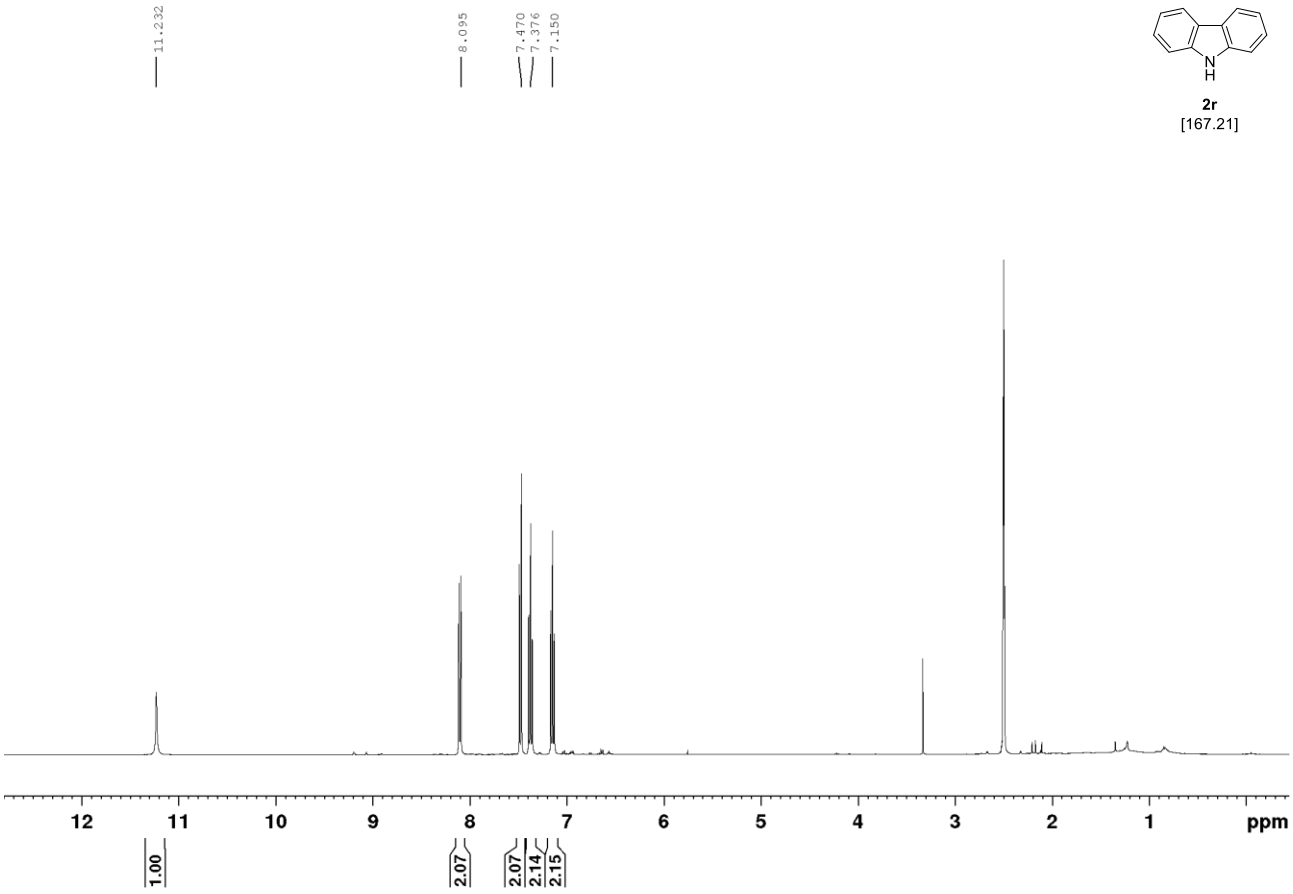

151.65
146.75
135.77
133.04
131.62
130.53
129.68
122.85
119.94
ppm

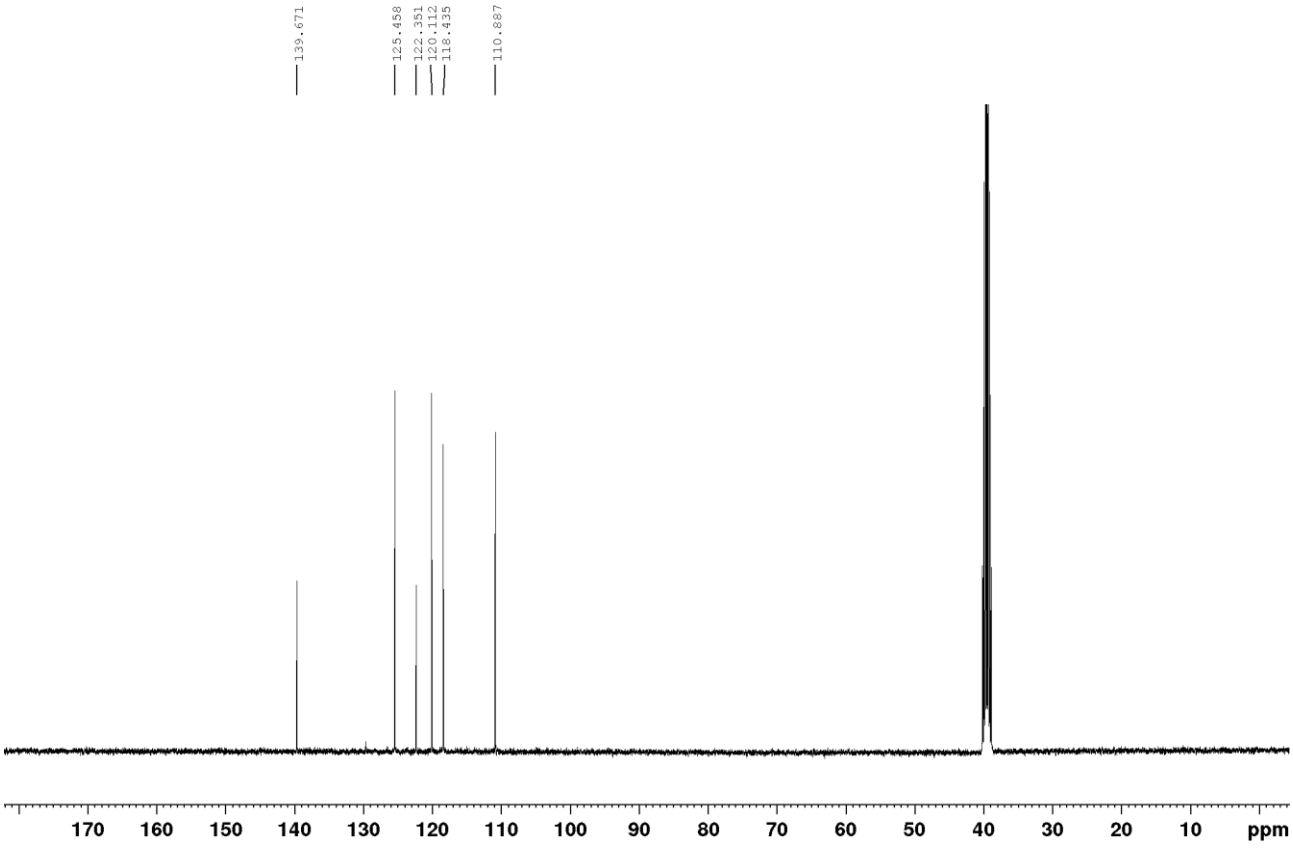

8.95
8.94
8.94
8.93
8.39
8.38
8.37
8.36
8.15
8.14
8.06
8.04
7.80
7.79
7.78
7.77
7.62
7.61
7.60
7.59
3.34 HDO
2.51 DMSO
Cl
N
2i
[163.60]
1.00
1.12
1.05
1.05
1.05
1.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

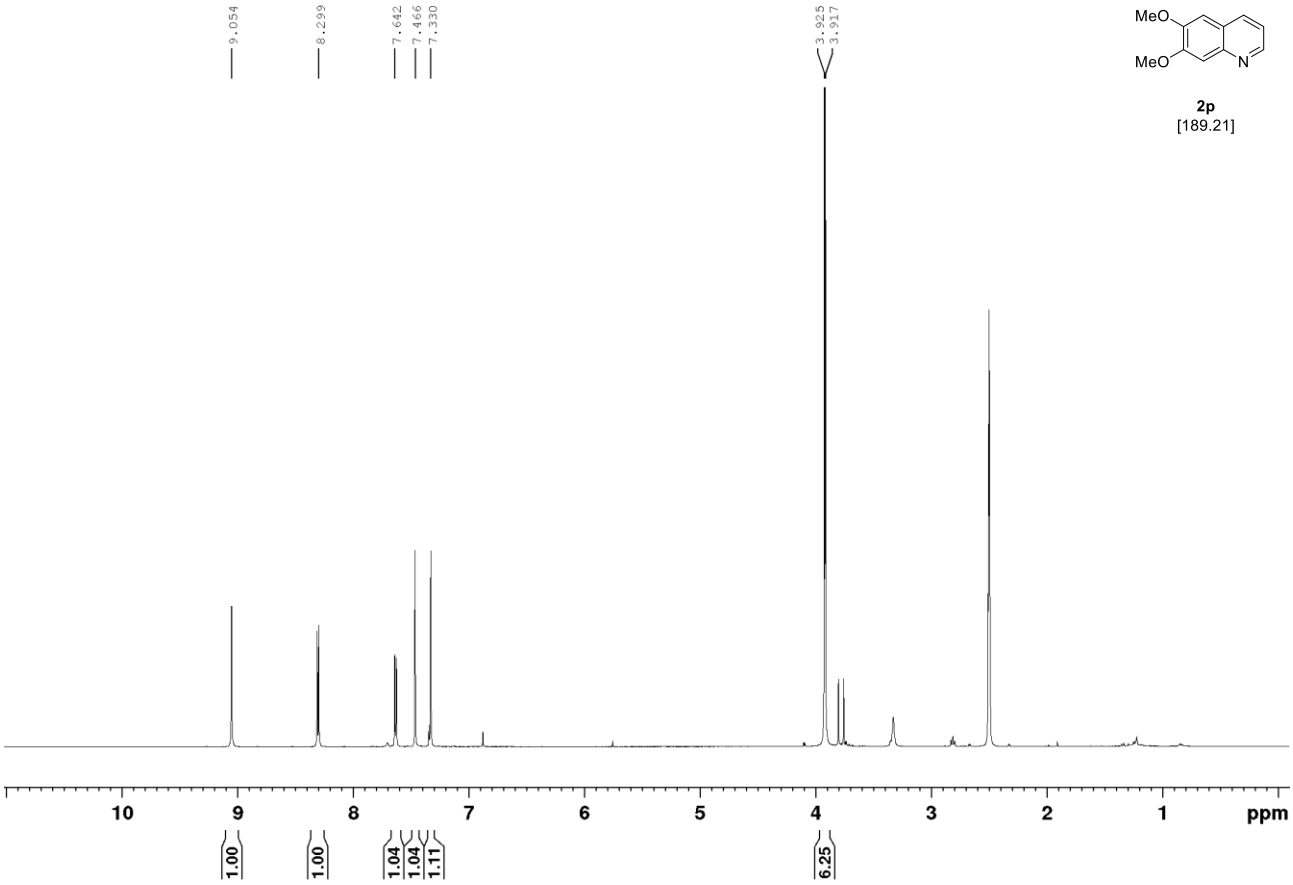

151.083
146.099
135.390
131.061
130.874
130.038
128.658
126.752
122.419
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

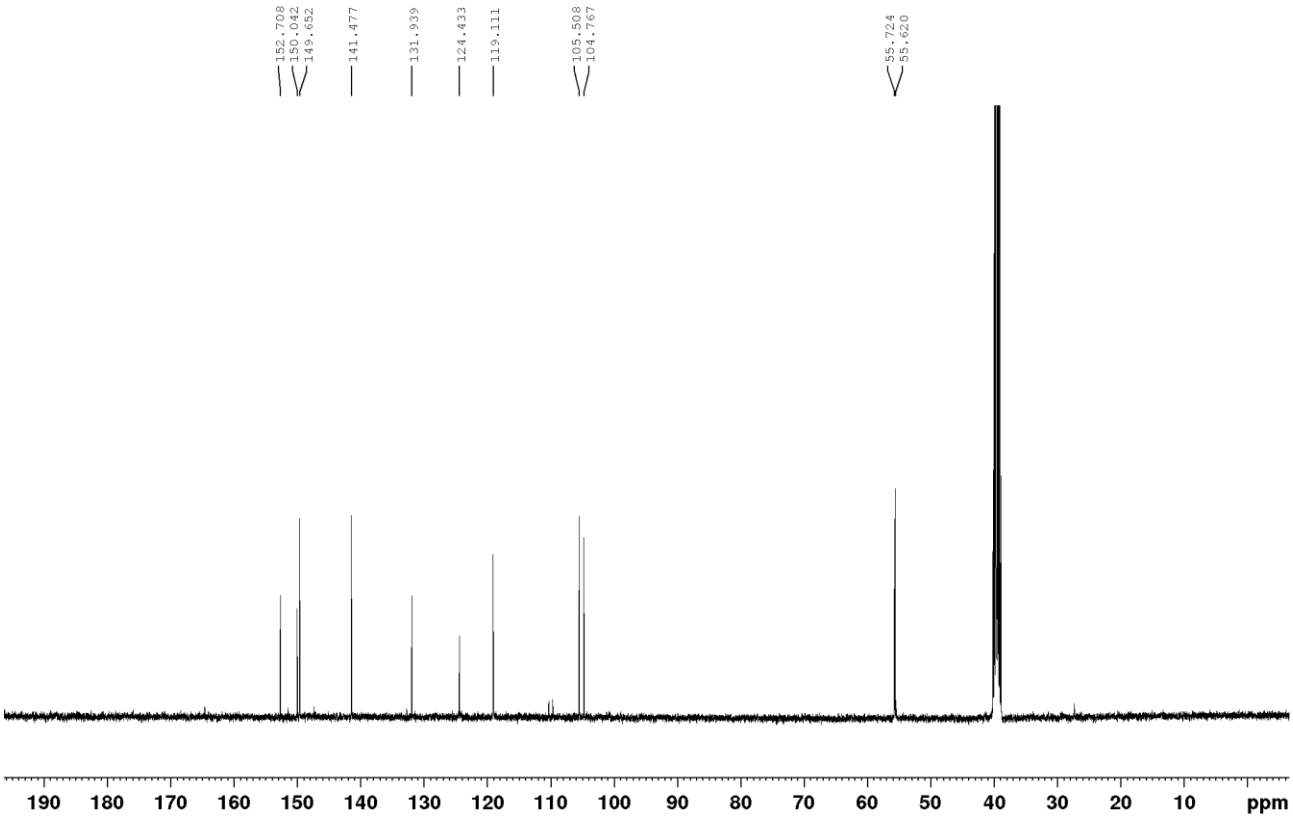

9.074
8.665
8.489
8.154
8.061
7.713
NC
N
2l
[154.17]
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.00
1.00
1.00
1.00

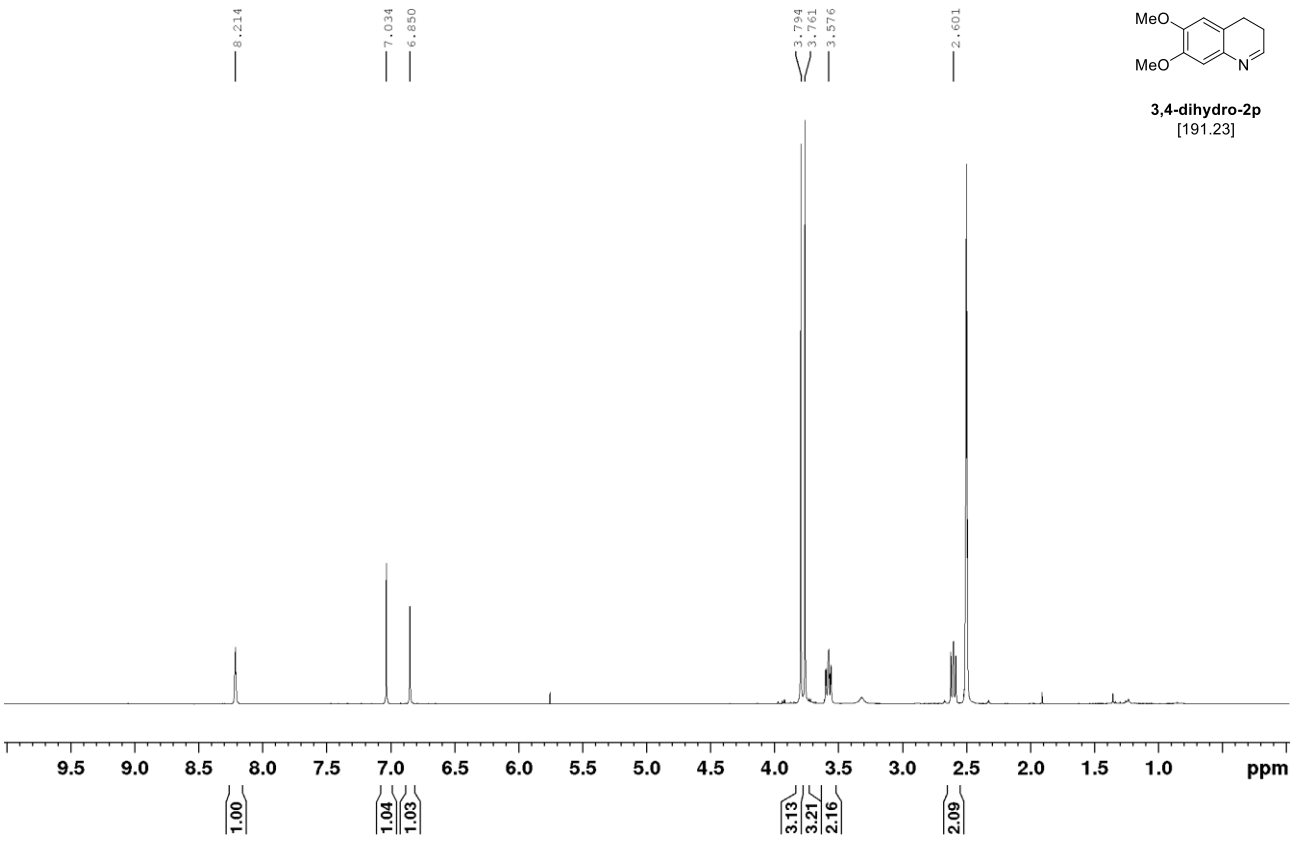

153.678
148.514
136.758
135.039
130.453
130.171
127.304
123.075
118.635
109.122
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

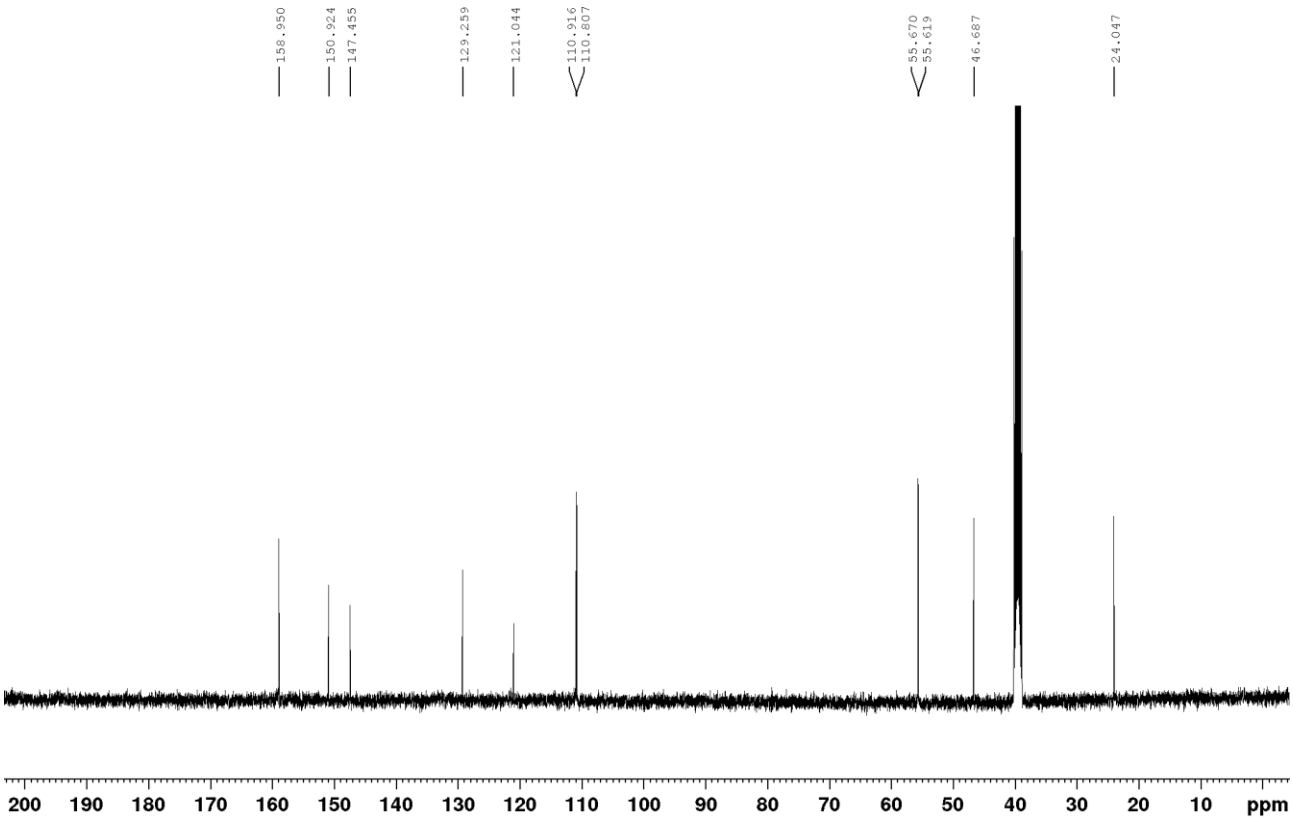

11.232
8.095
7.470
7.376
7.150
N
H
2r
[167.21]
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.07
2.07
2.14
2.15

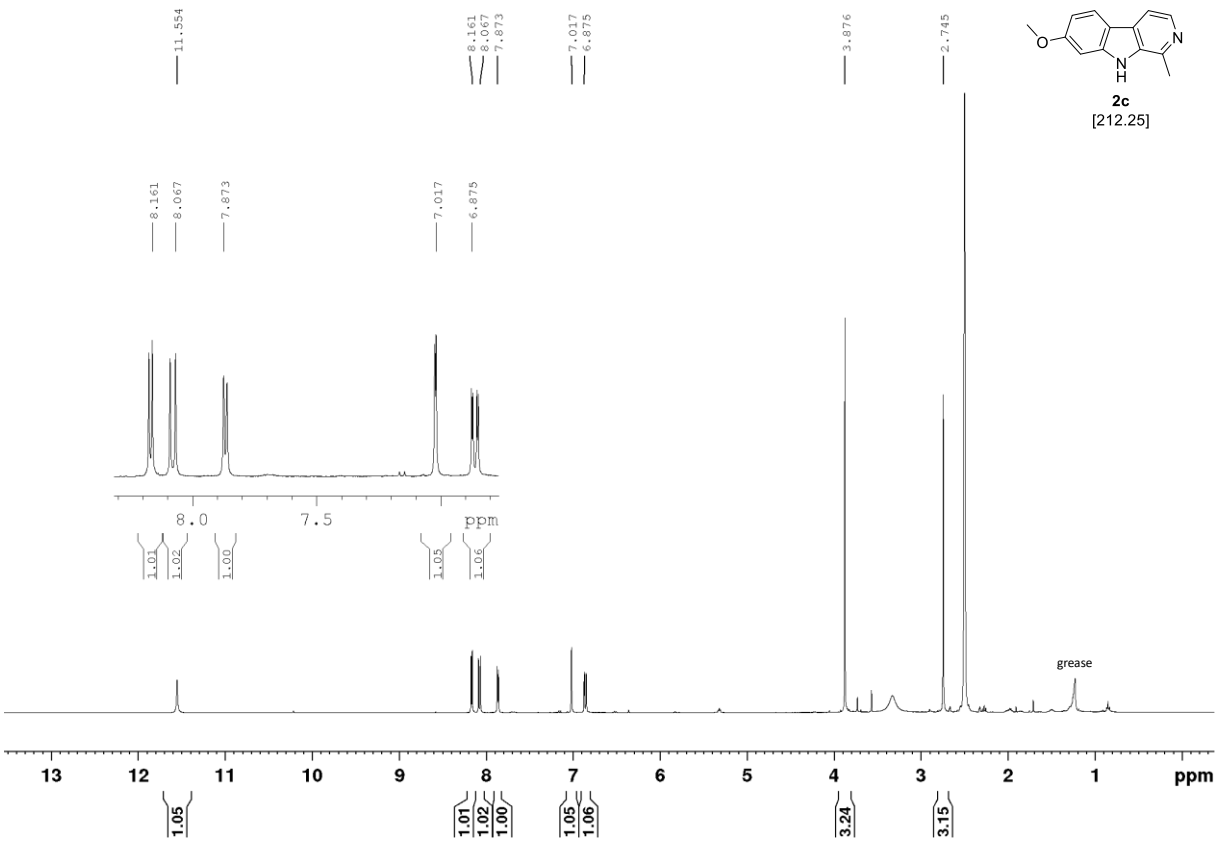

139.671
125.458
122.351
120.112
118.435
110.887
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

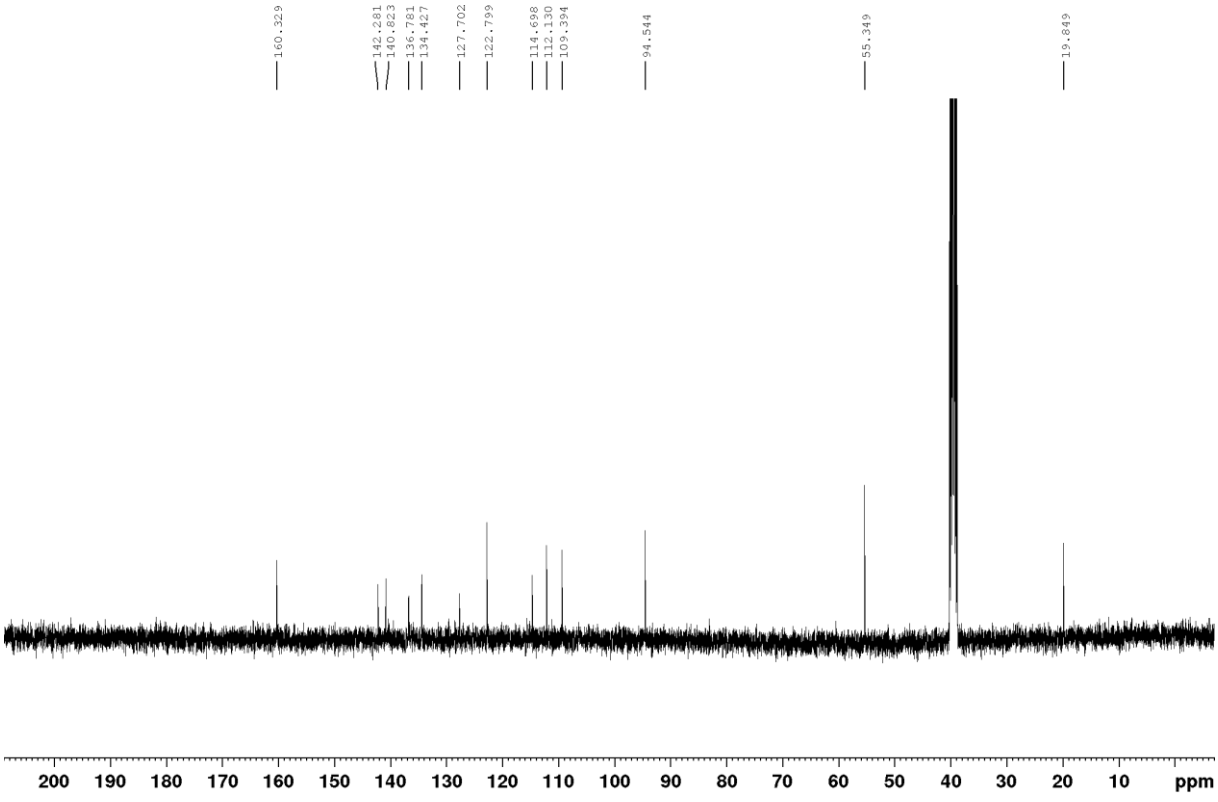

9.054
8.299
7.642
7.466
7.330
3.925
3.917
MeO
MeO
N
2p
[189.21]
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.04
1.04
1.11
6.25

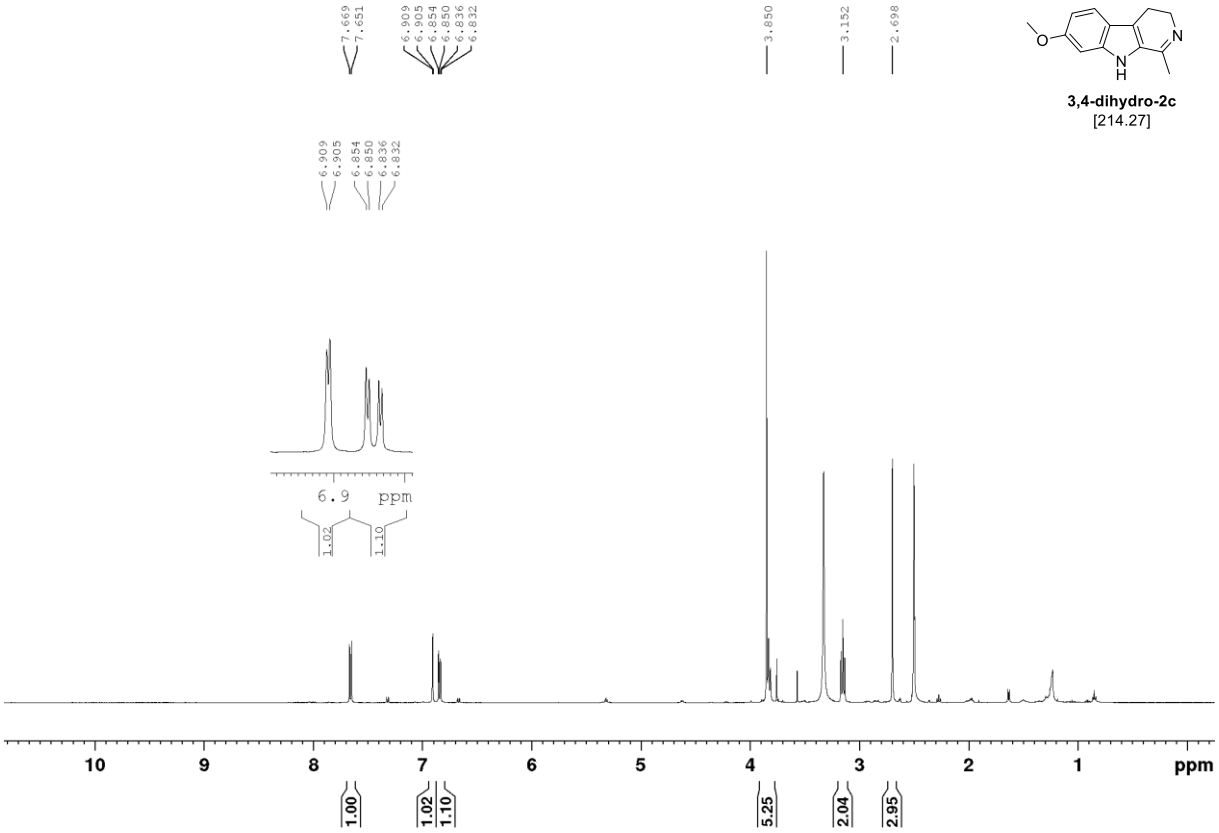

152.708
150.042
149.652
141.477
131.939
124.433
119.111
105.508
104.767
55.724
55.620
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.214
7.034
6.850
3.794
3.761
3.576
2.601
MeO
MeO
N
3,4-dihydro-2p
[191.23]
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 ppm
1.00
1.04
1.03
3.13
3.21
2.16
2.09

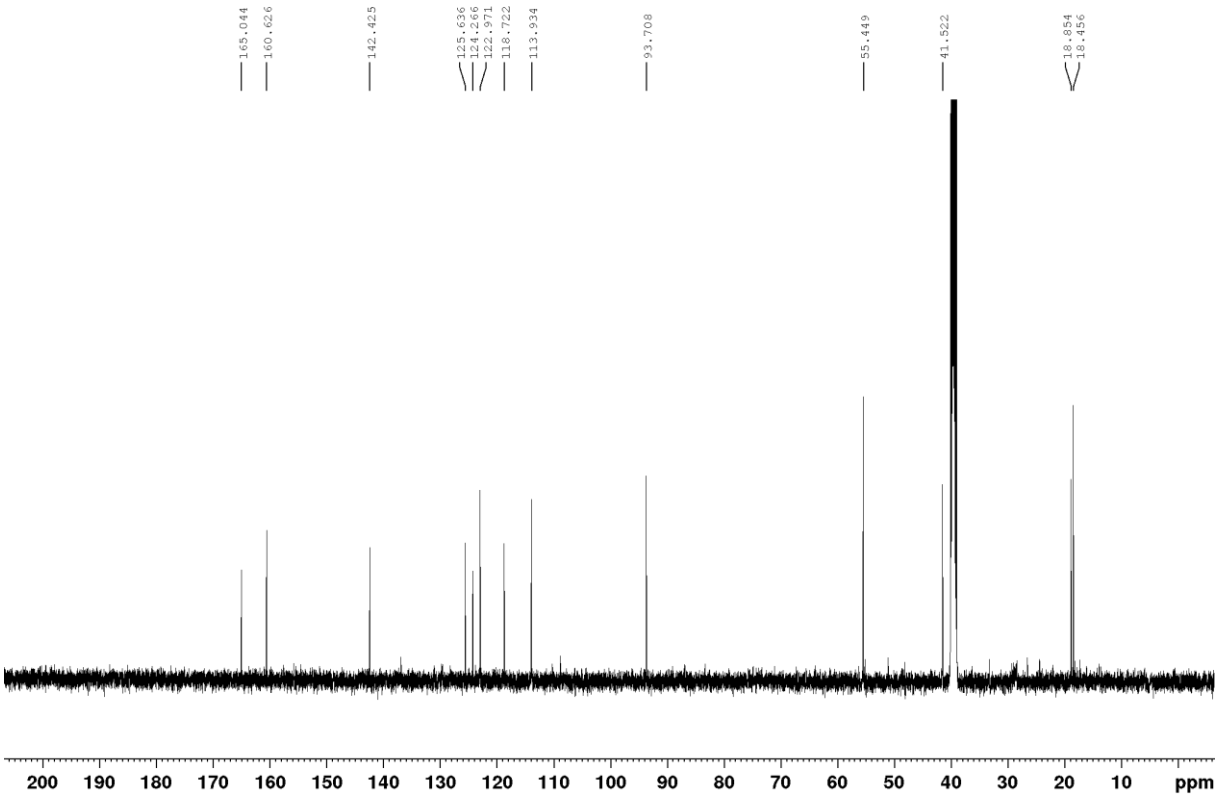

158.950
150.924
147.455
129.259
121.044
110.916
110.807
55.670
55.619
46.687
24.047
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

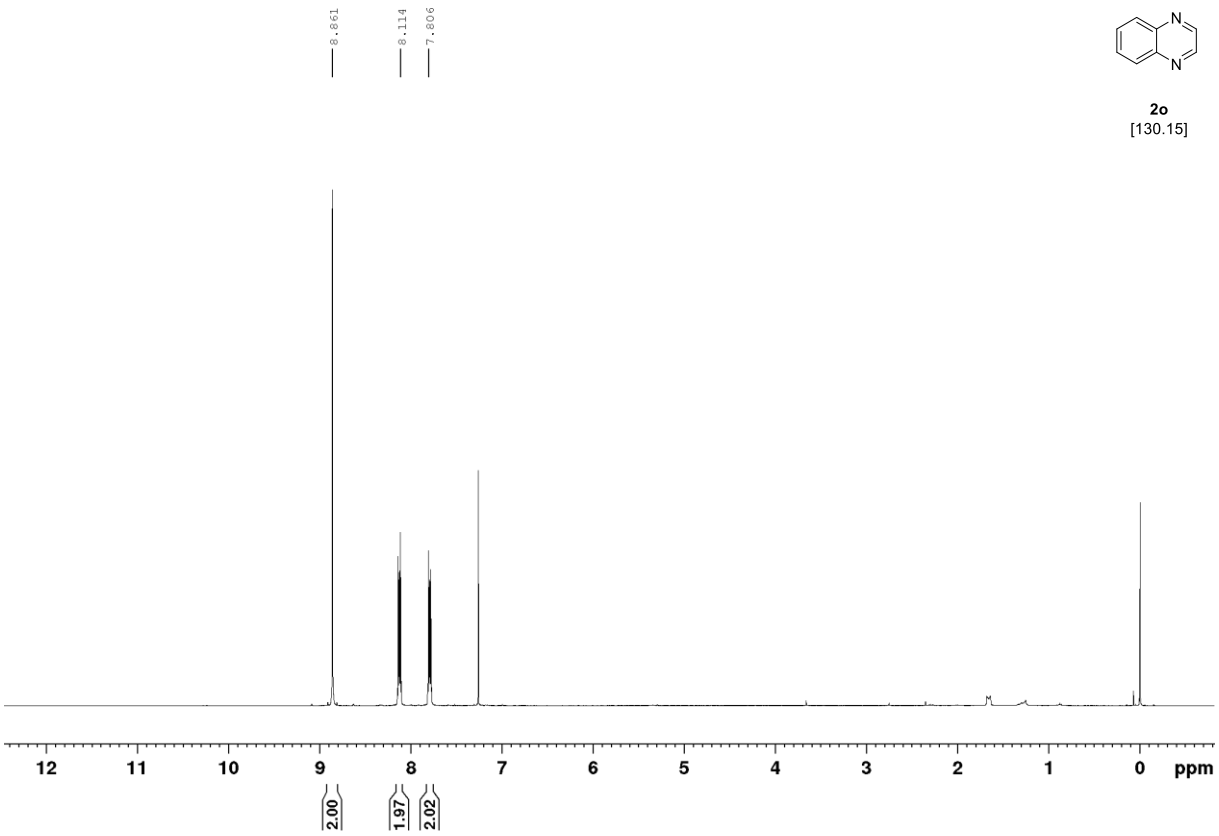

11.554
8.161
8.067
7.873
7.017
6.875
3.876
2.745
O
N
H
2c
[212.25]
grease
ppm
1.05
1.01
1.02
1.00
1.05
1.06
3.24
3.15

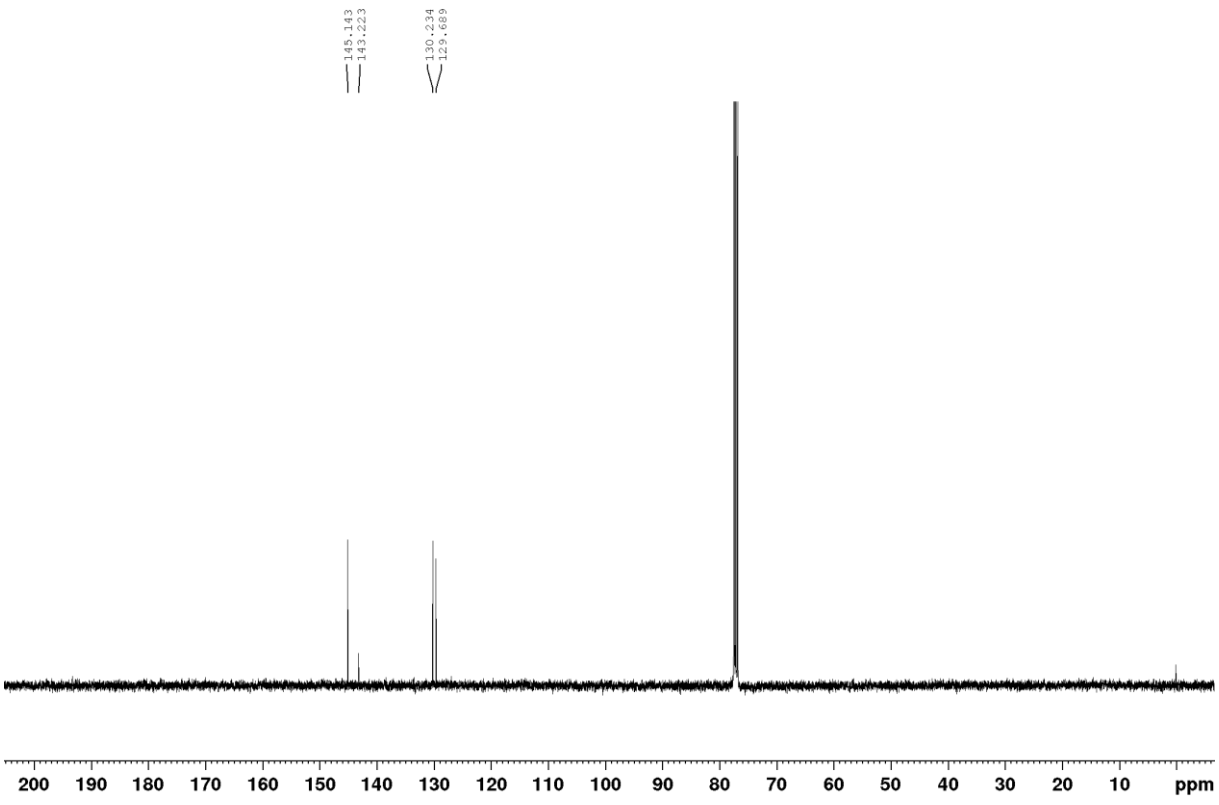

160.329
142.281
140.823
136.781
134.427
127.702
122.799
114.698
112.130
109.394
94.544
55.349
19.849
ppm

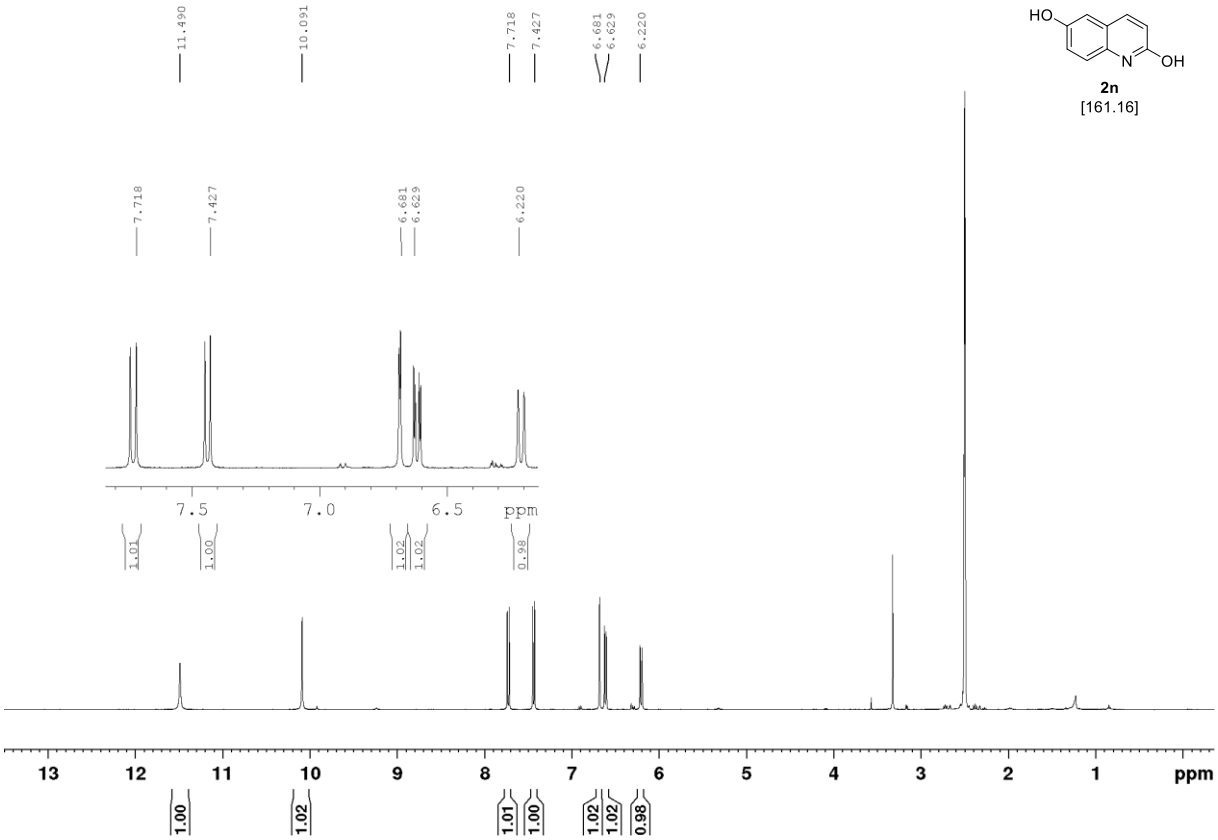


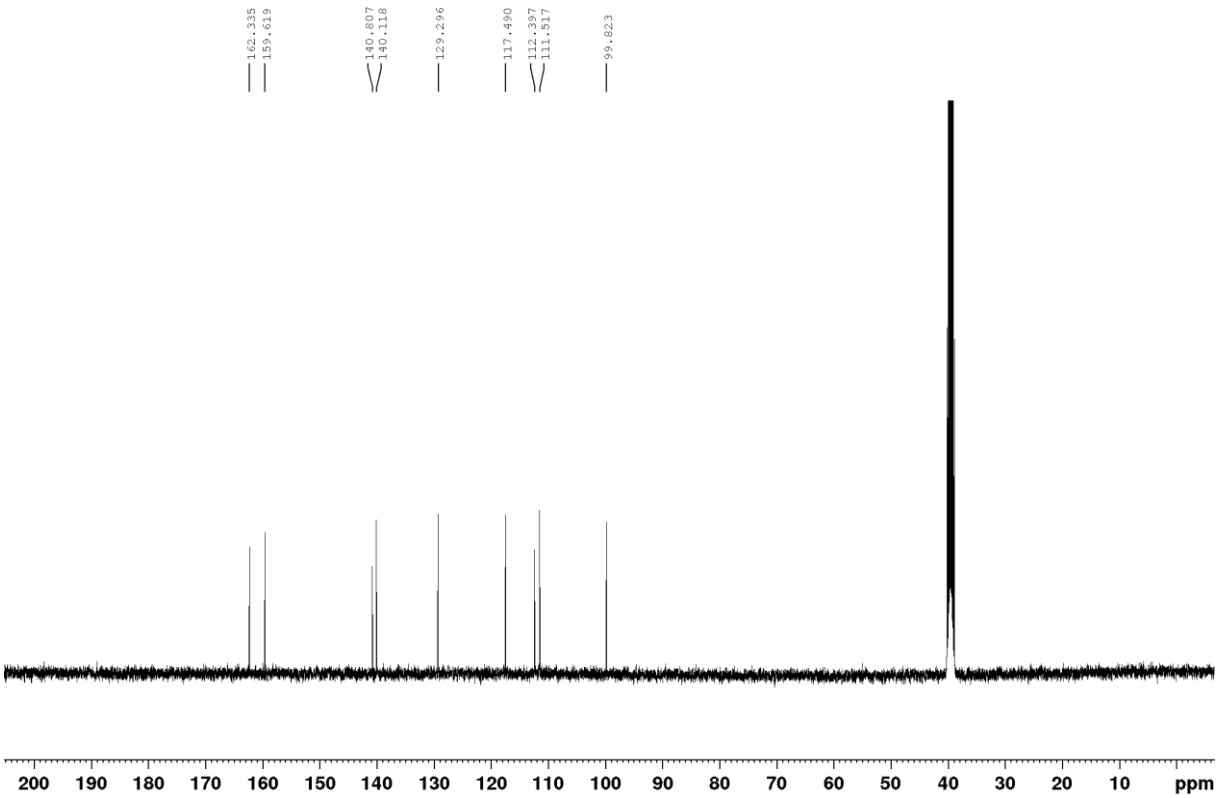
3,4-dihydro-2c
[214.27]

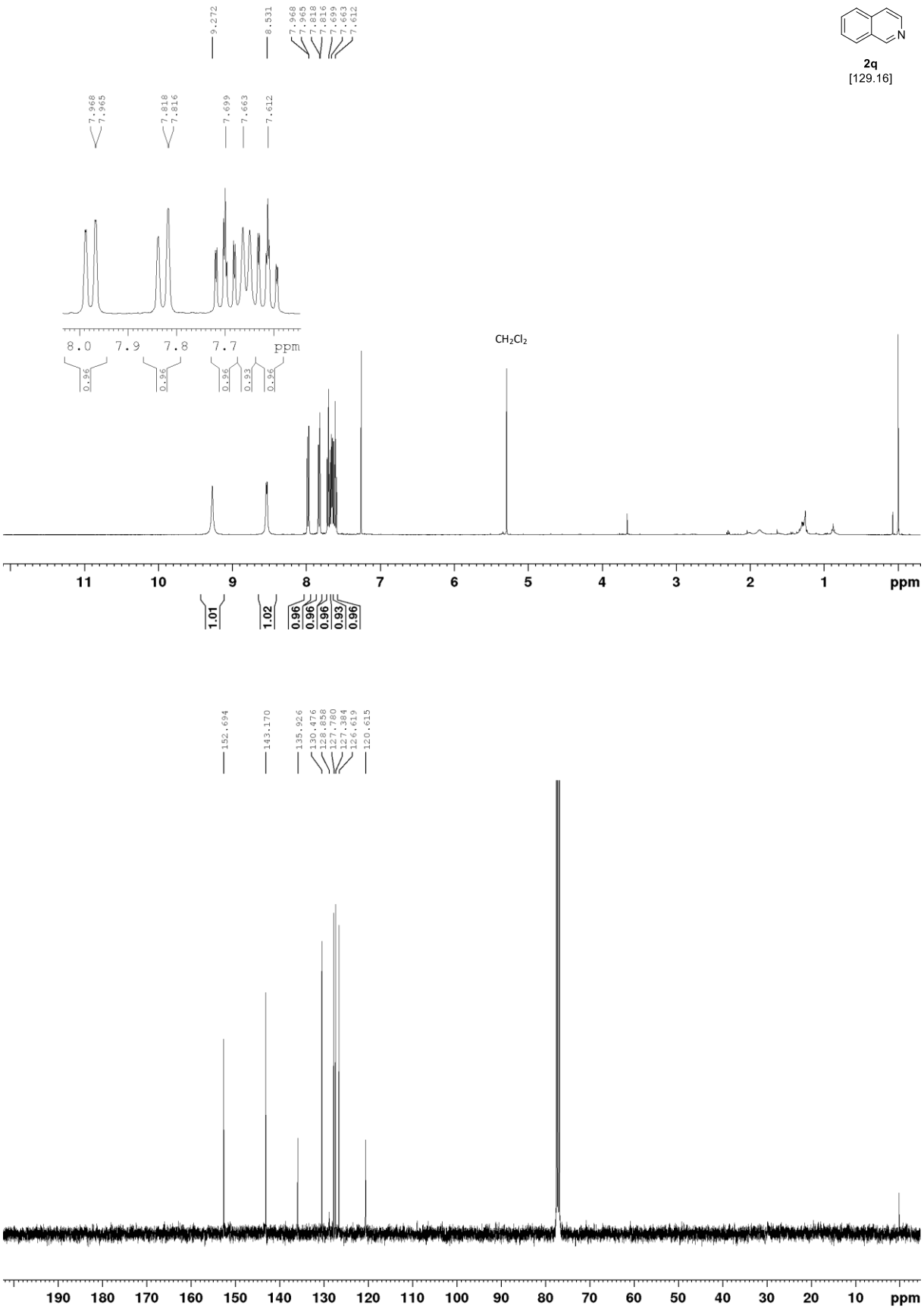


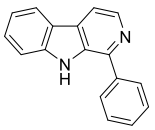

8.861
8.114
7.806
2o
[130.15]
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.97
2.02


145.143
143.223
130.234
129.689
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

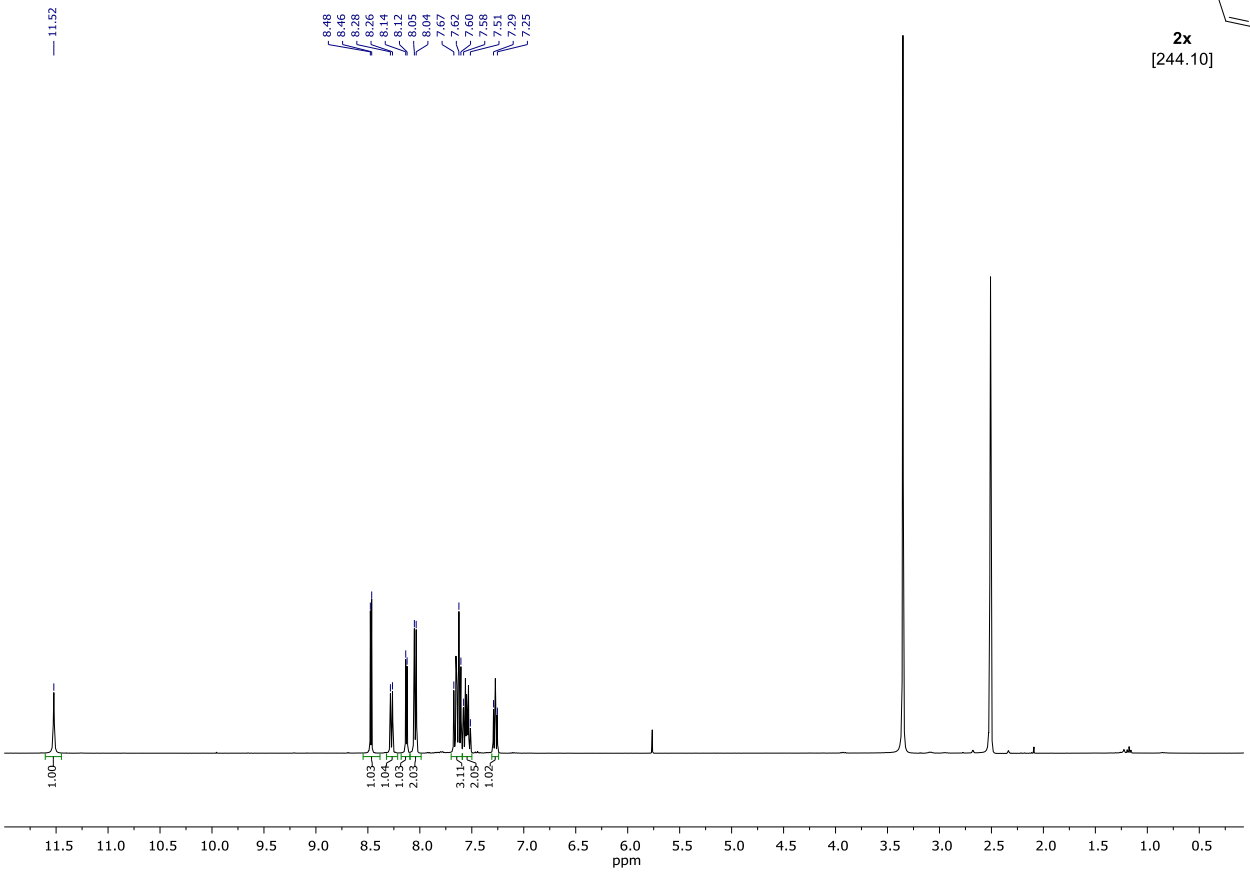

11.490
10.091
7.718
7.427
6.681
6.629
6.220
HO
N
OH
2n
[161.16]
7.5
7.0
6.5
ppm
1.01
1.00
1.02
1.02
0.98
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
1.01
1.00
1.02
1.02
0.98

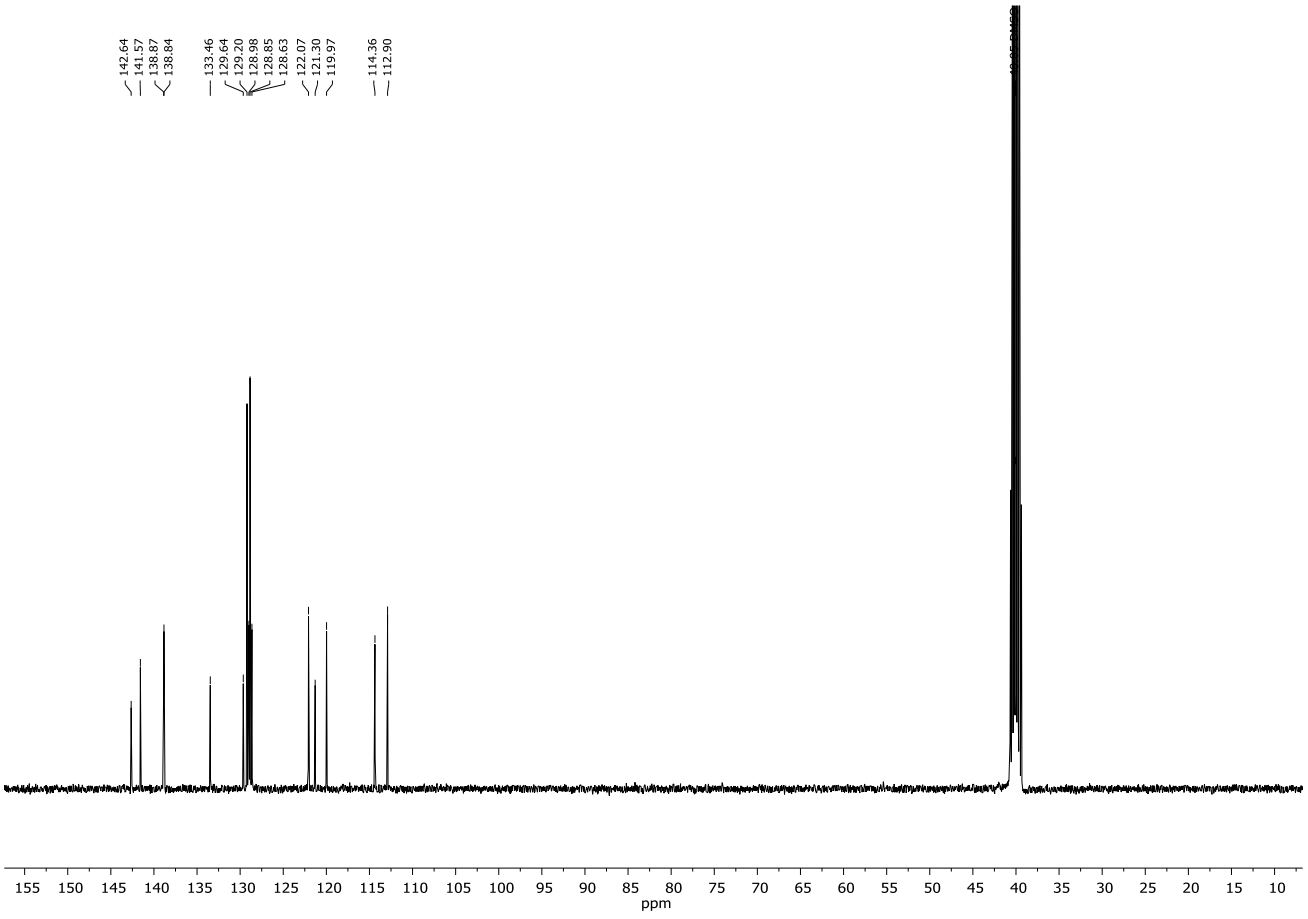

162.335
159.619
140.807
140.118
129.296
117.490
112.397
111.517
99.823
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

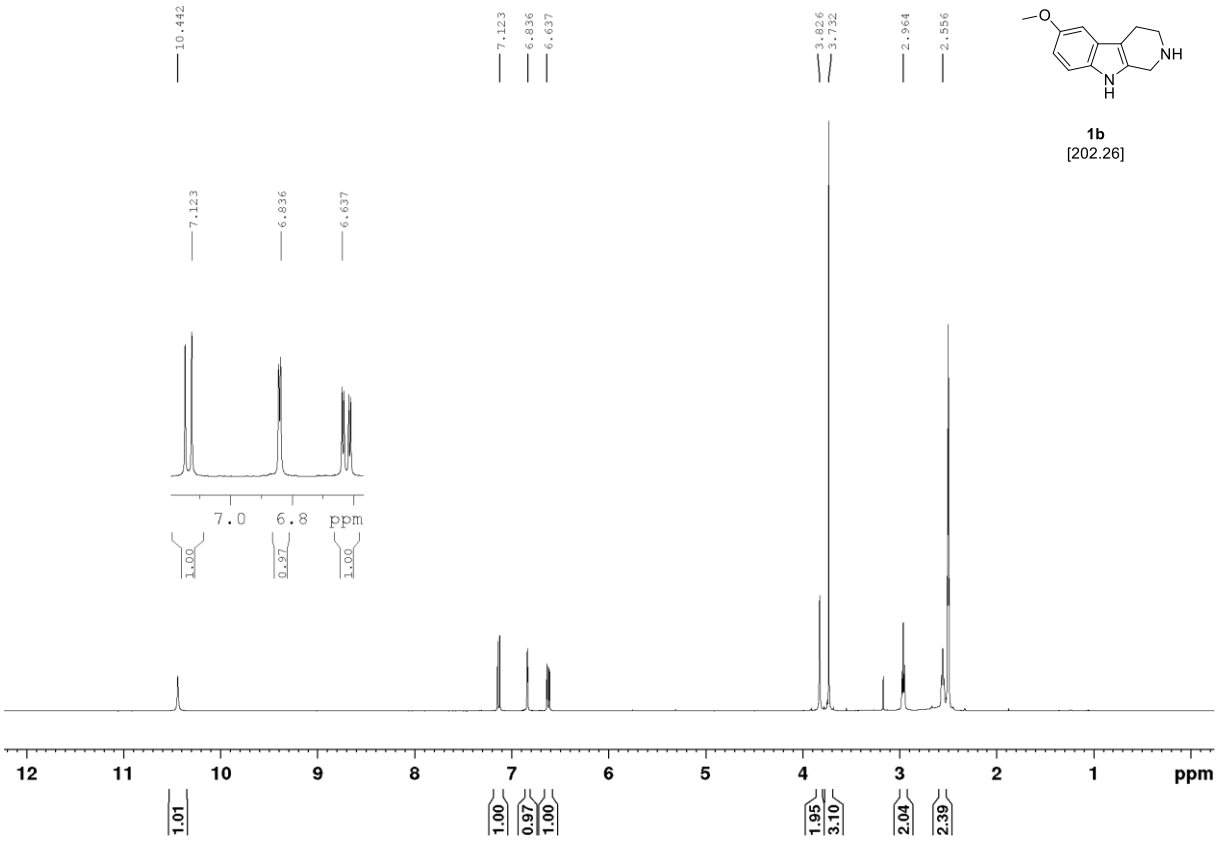

9.272
8.531
7.968
7.965
7.818
7.816
7.699
7.663
7.612
N
2q
[129.16]
CH2Cl2
ppm
1.01
1.02
0.96
0.96
0.96
0.93
0.96
152.694
143.170
135.926
130.476
128.858
127.780
127.384
126.619
120.615

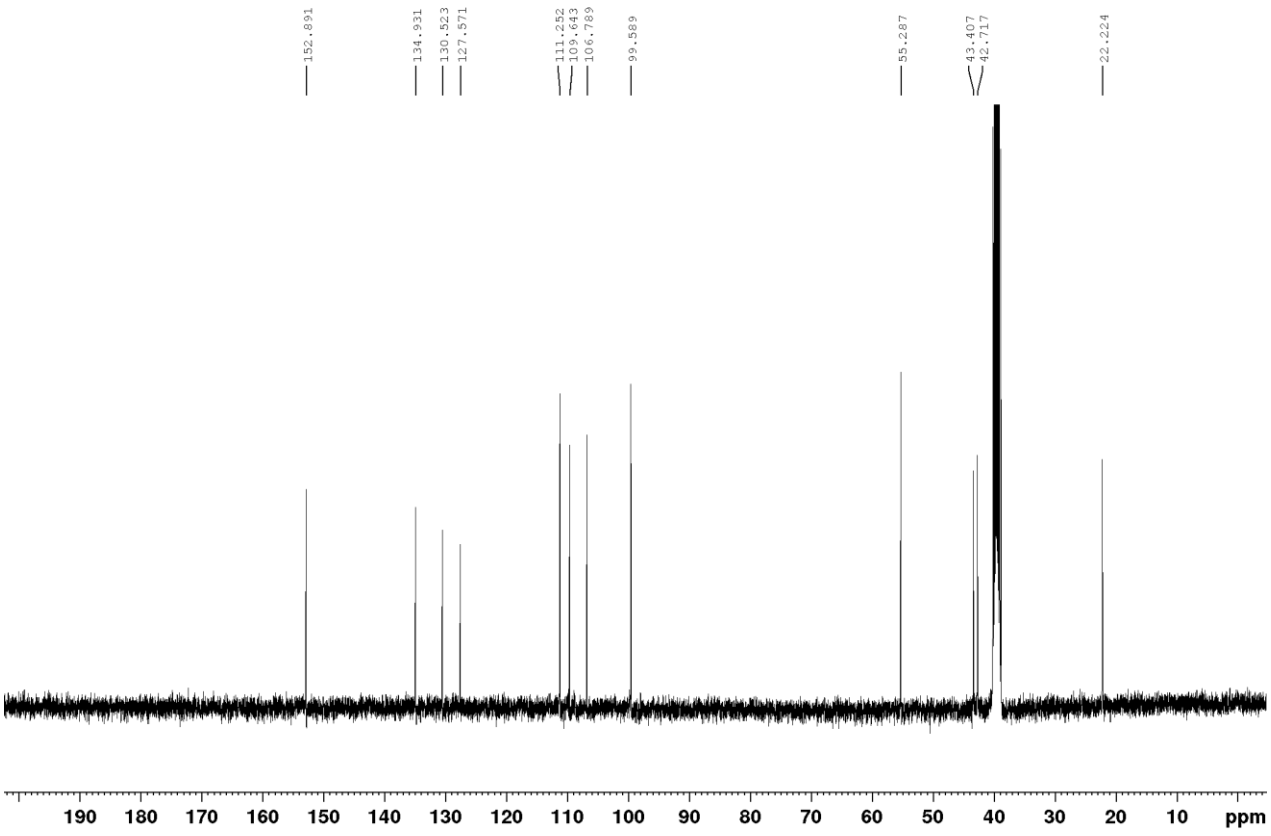


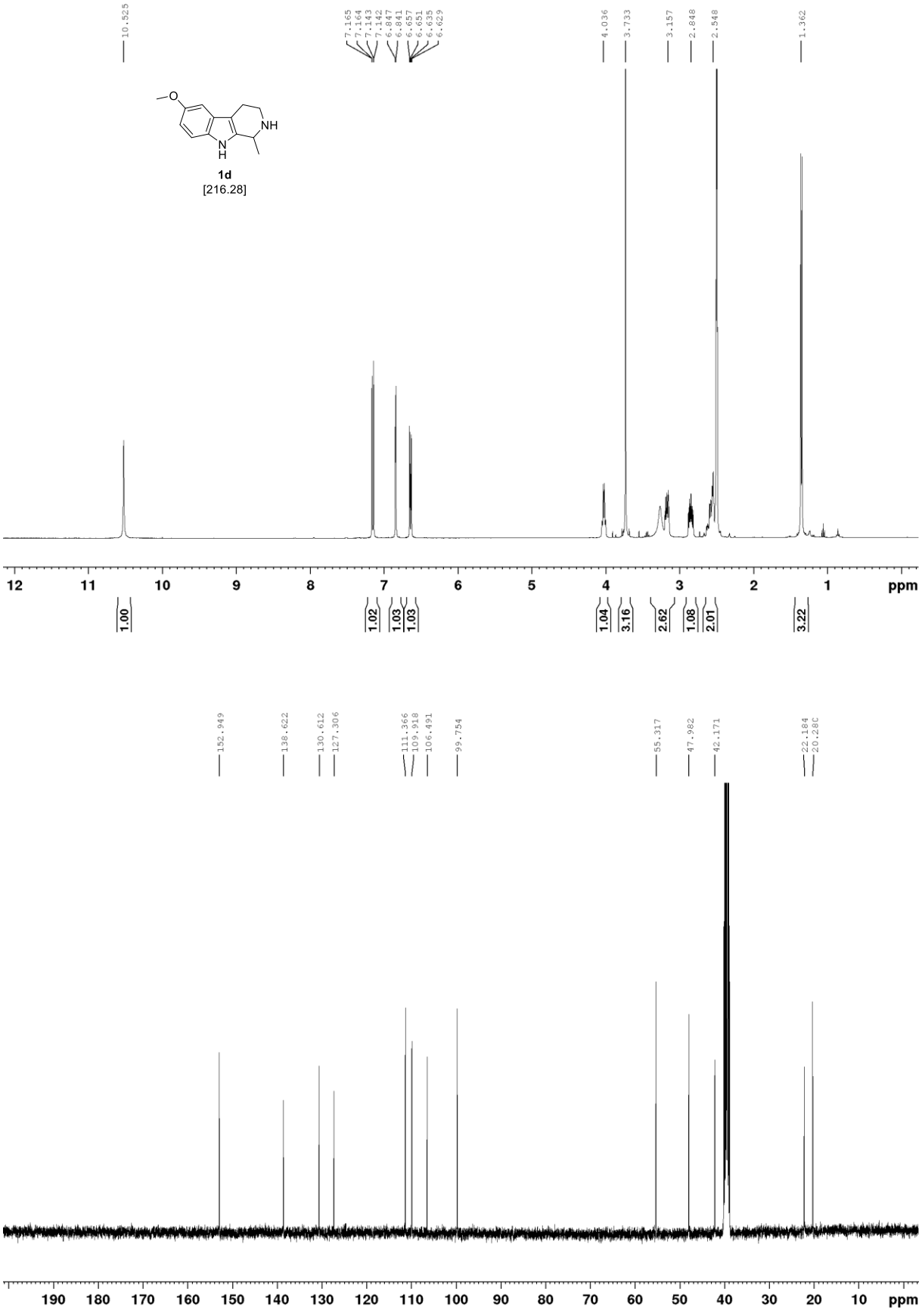
2x
[244.10]

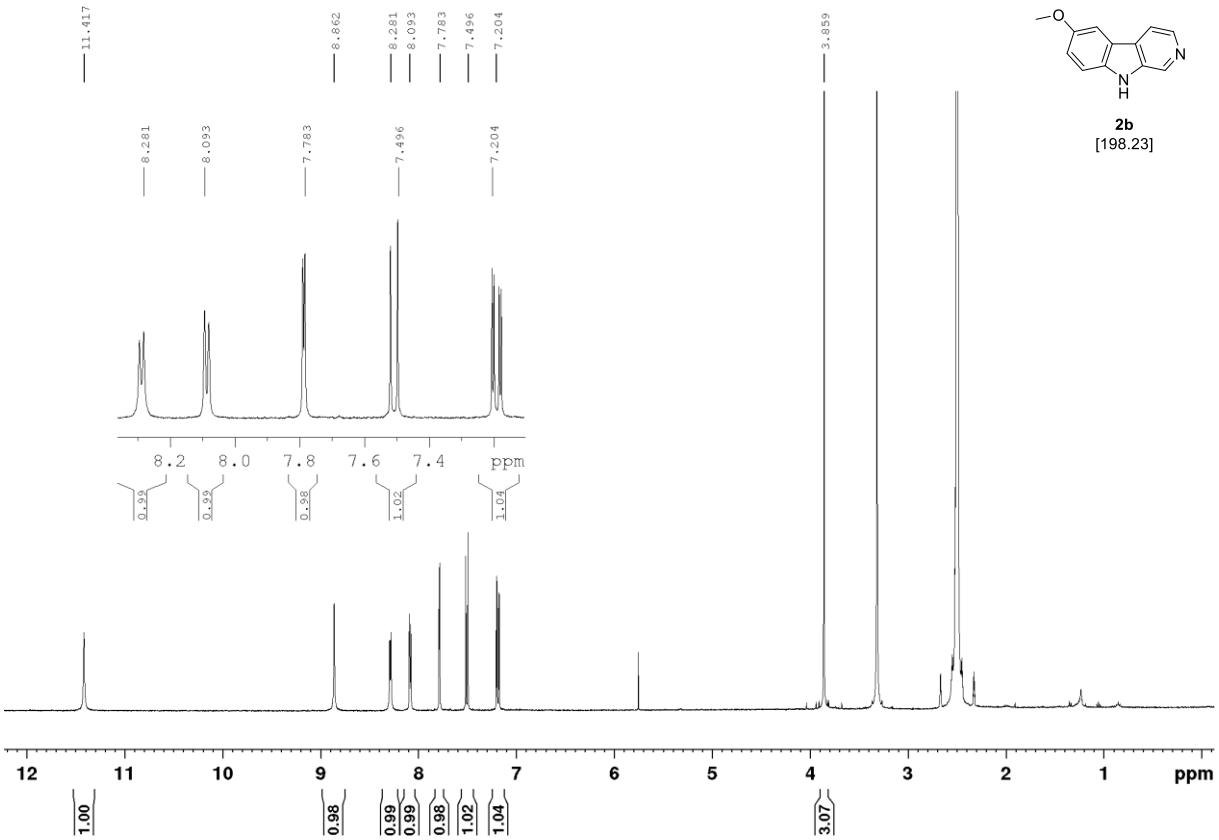

11.52
8.48
8.46
8.28
8.26
8.14
8.12
8.05
8.04
7.67
7.62
7.60
7.58
7.51
7.29
7.25
1.00
1.03
1.04
1.03
2.03
3.11
2.05
1.02
ppm

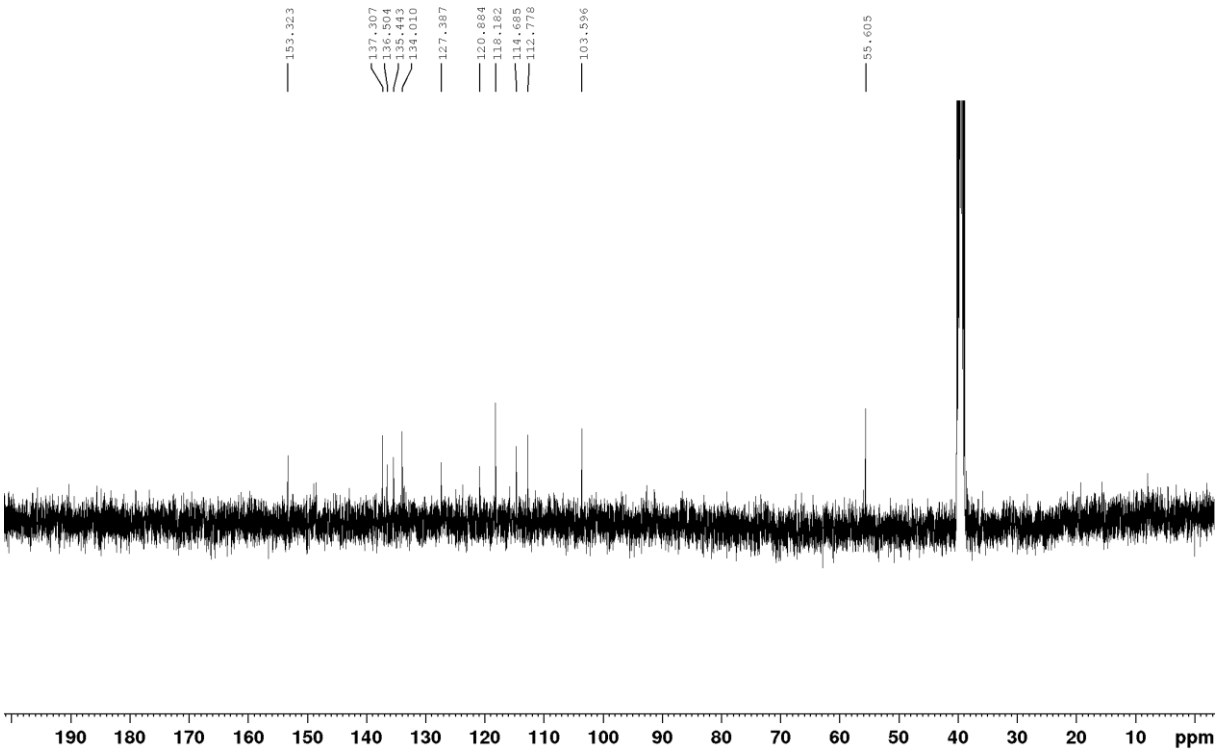

142.64
141.57
138.87
138.84
133.46
129.64
129.20
128.98
128.85
128.63
122.07
121.30
119.97
114.36
112.90
ppm

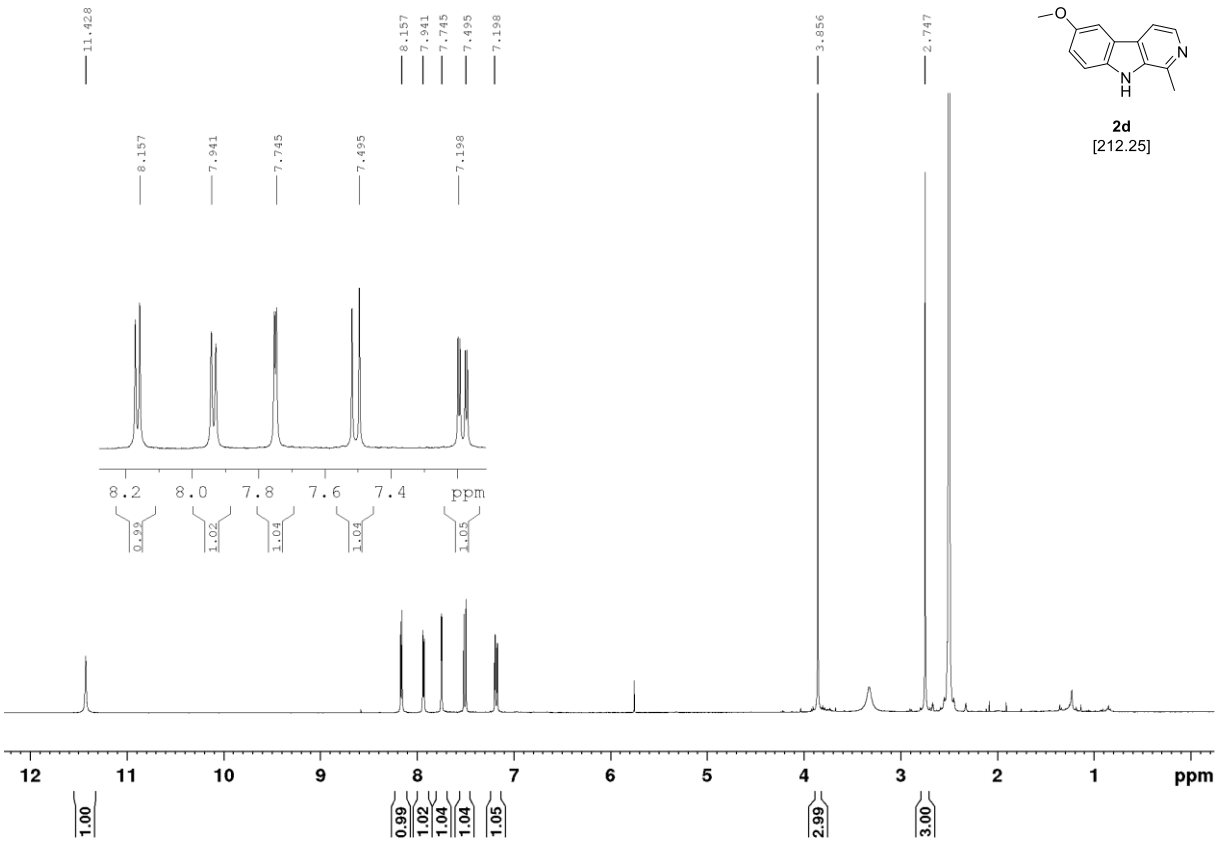

10.442
7.123
6.836
6.637
3.826
3.732
2.964
2.556
O
NH
N
H
1b
[202.26]
7.0
6.8
ppm
1.00
0.97
1.00
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
1.00
0.97
1.00
1.95
3.10
2.04
2.39

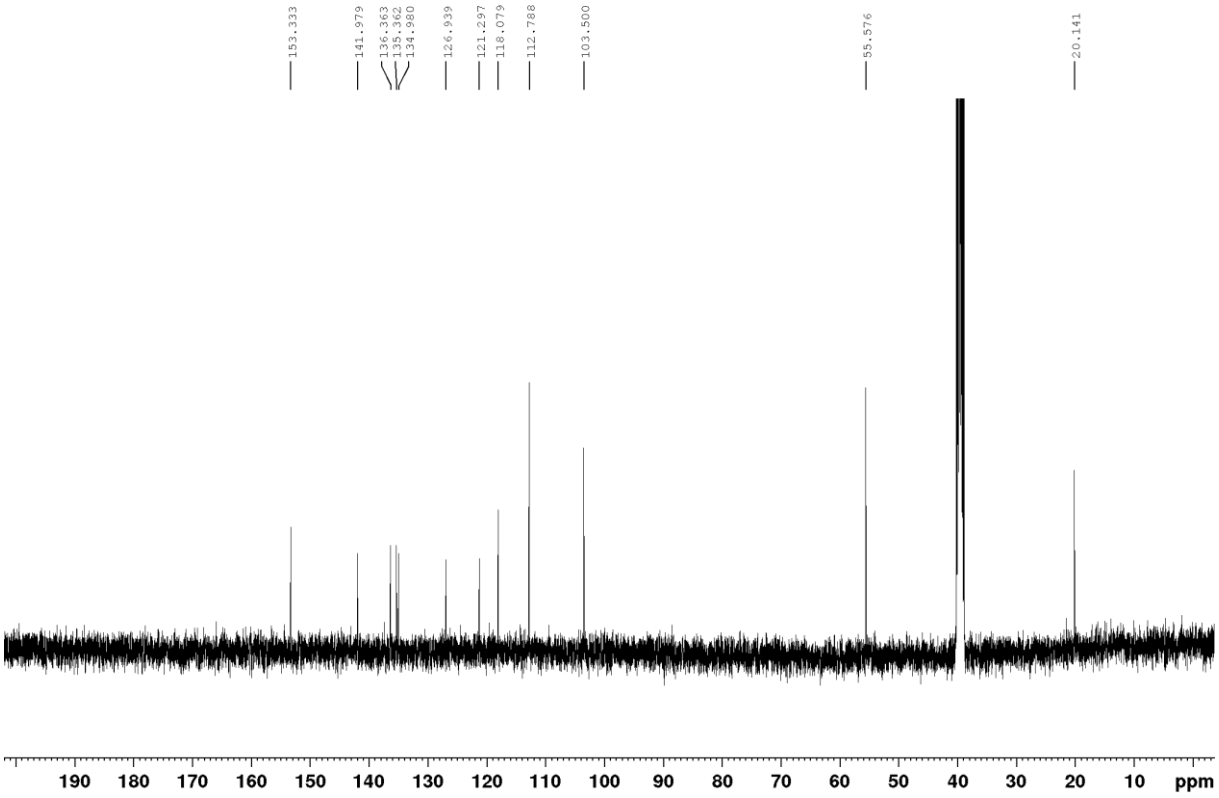

152.891
134.931
130.523
127.571
111.252
109.643
106.789
99.589
55.287
43.407
42.717
22.224
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

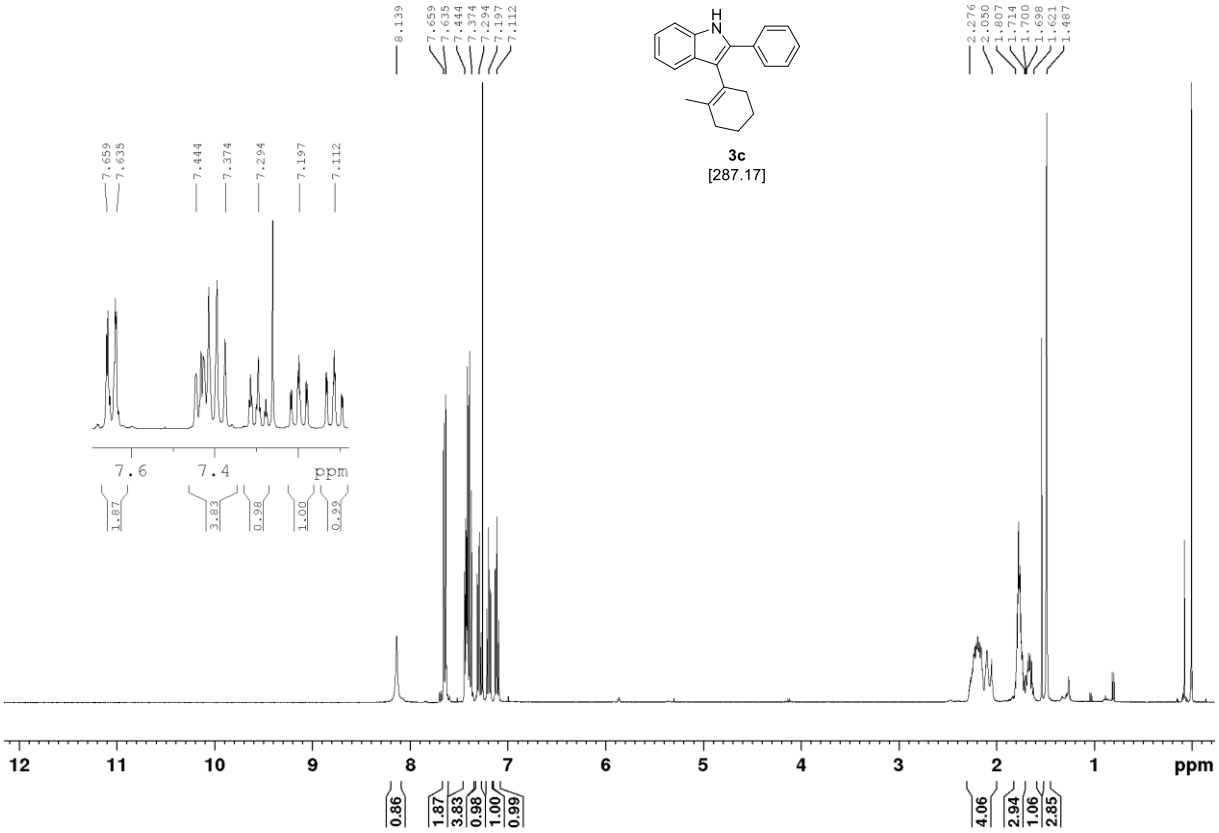

10.525
7.165
7.164
7.143
7.142
6.847
6.841
6.657
6.651
6.635
6.629
4.036
3.733
3.157
2.848
2.548
1.362
O
NH
N
H
1d
[216.28]
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
1.03
1.03
1.04
3.16
2.62
1.08
2.01
3.22
152.949
138.622
130.612
127.306
111.366
109.918
106.491
99.754
55.317
47.982
42.171
22.184
20.280
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

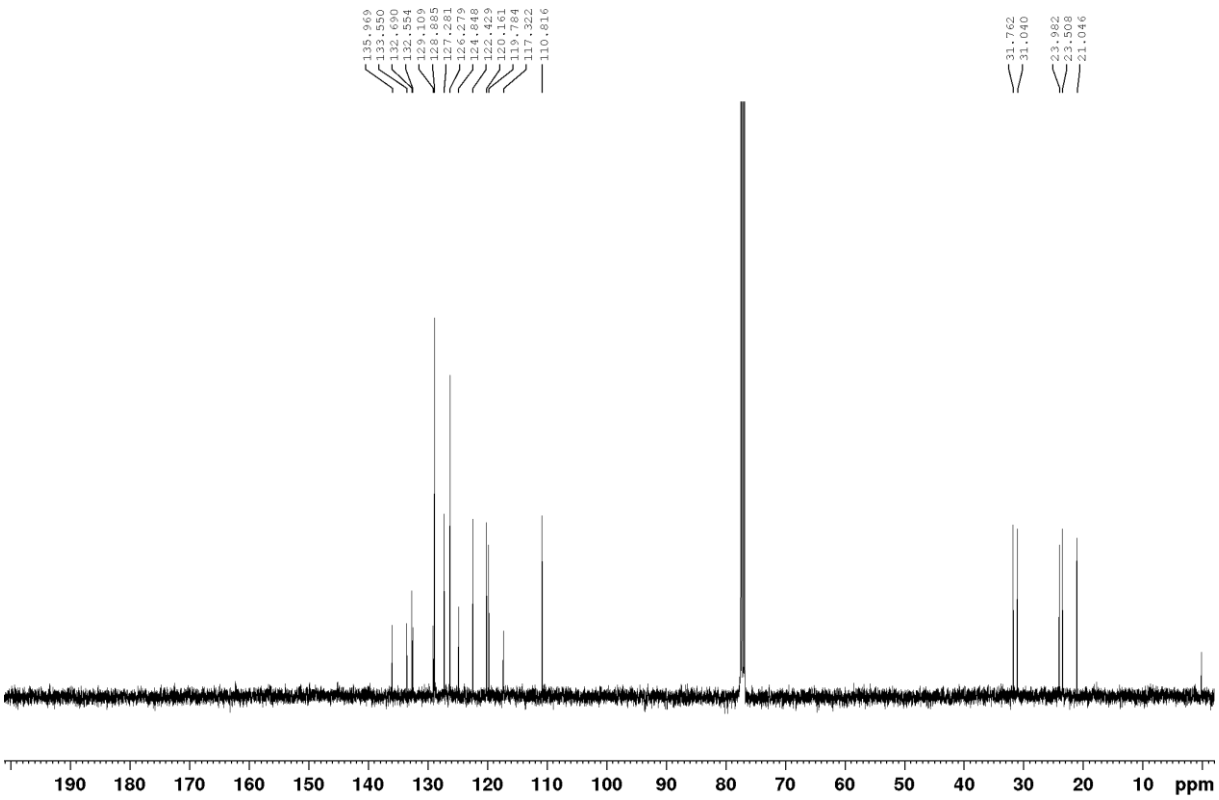

11.417
8.862
8.281
8.093
7.783
7.496
7.204
3.859
8.281
8.093
7.783
7.496
7.204
8.2
8.0
7.8
7.6
7.4
ppm
0.99
0.99
0.98
1.02
1.04
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.98
0.99
0.99
0.98
1.02
1.04
3.07
O
N
H
2b
[198.23]

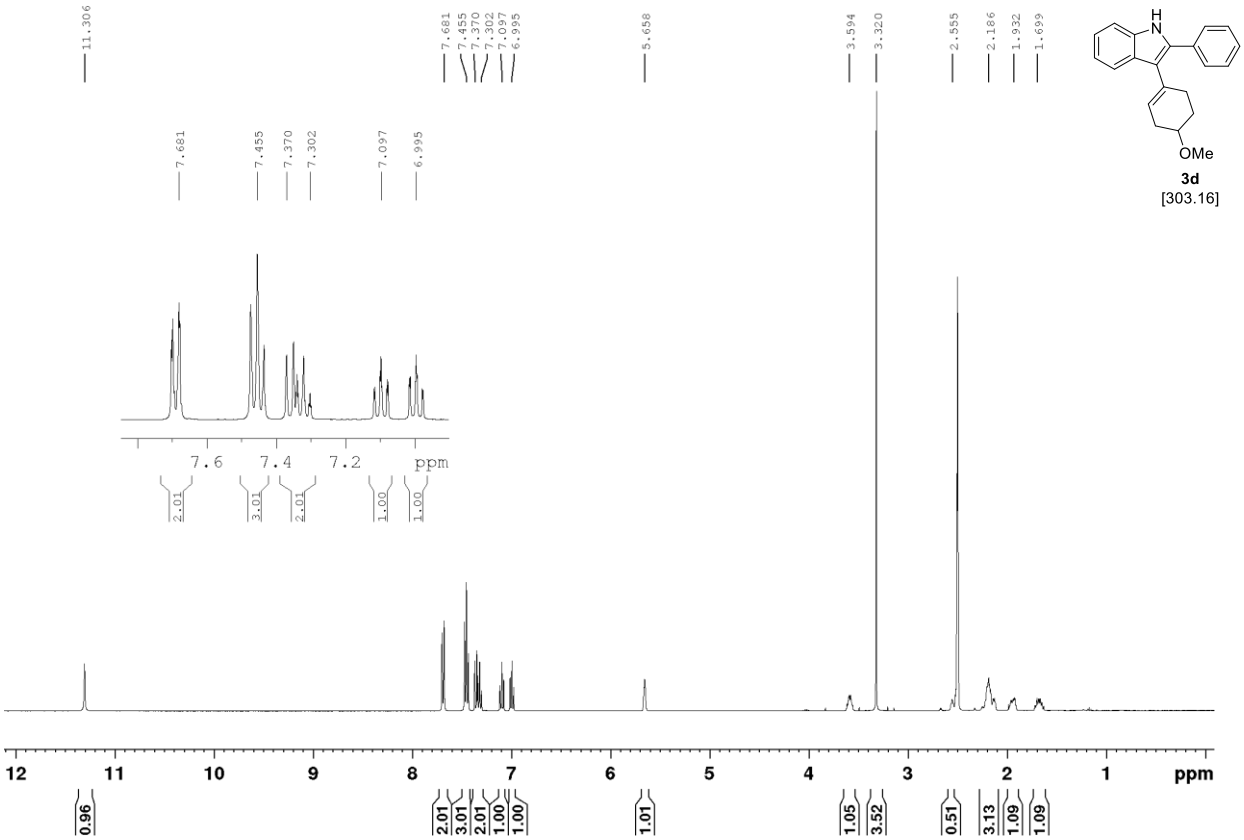

153.323
137.307
136.504
135.443
134.010
127.387
120.884
118.182
114.685
112.778
103.596
55.605
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

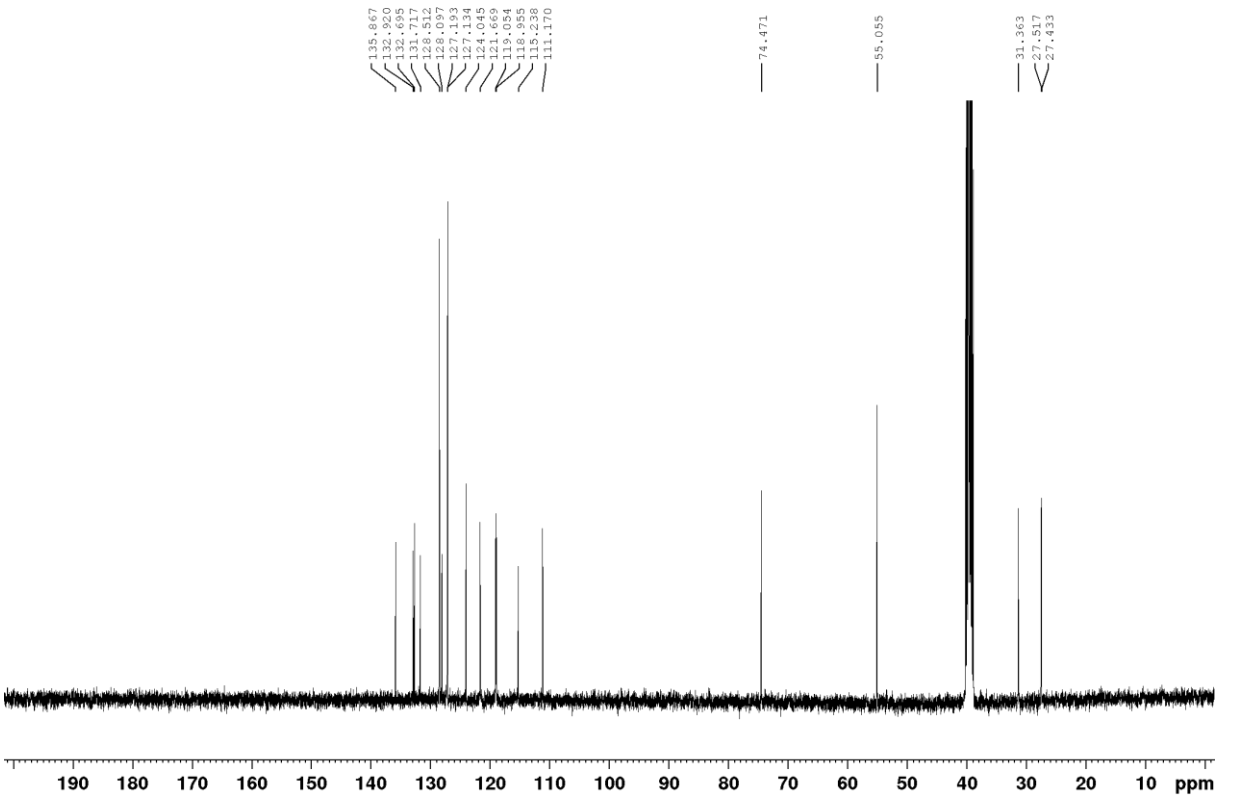

11.428
8.157
7.941
7.745
7.495
7.198
3.856
2.747
8.2
8.0
7.8
7.6
7.4
ppm
0.99
1.02
1.04
1.04
1.05
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.99
1.02
1.04
1.04
1.05
2.99
3.00
2d
[212.25]

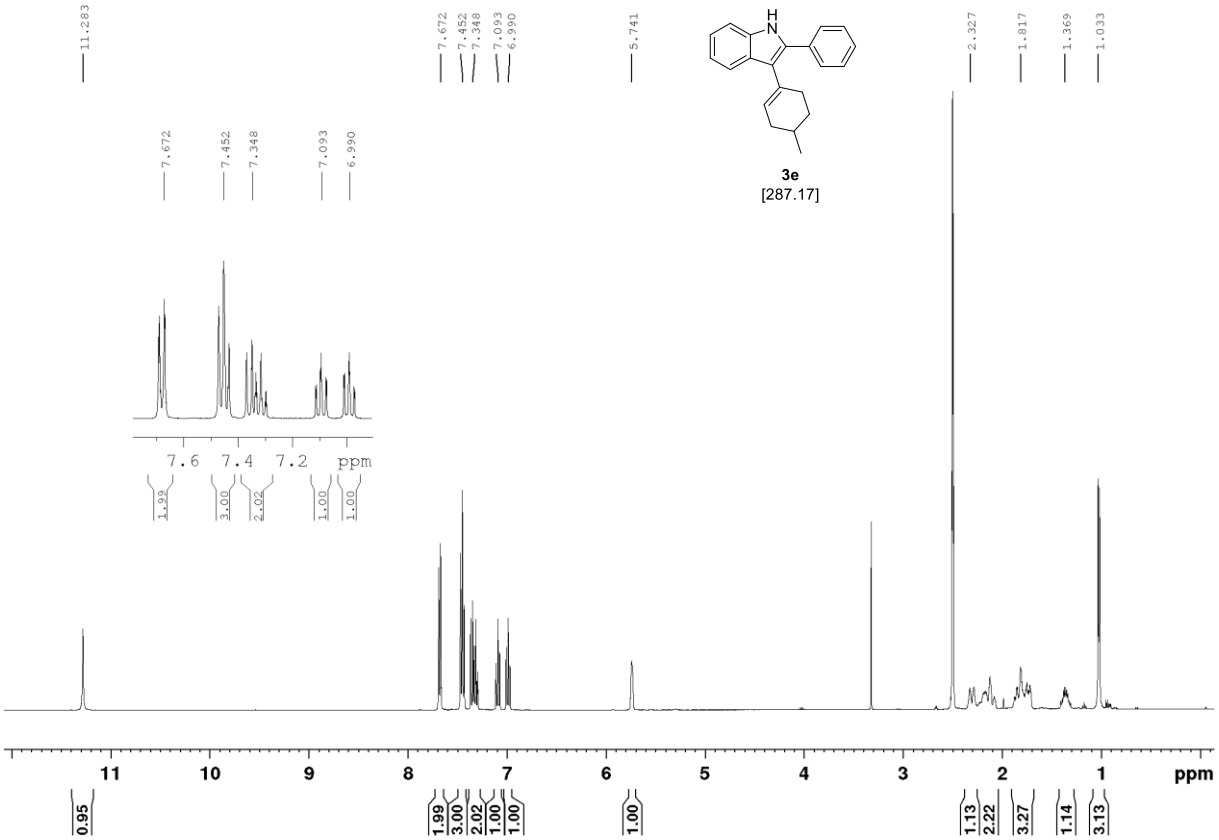

153.333
141.979
136.363
135.362
134.980
126.939
121.297
118.079
112.788
103.500
55.576
20.141
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

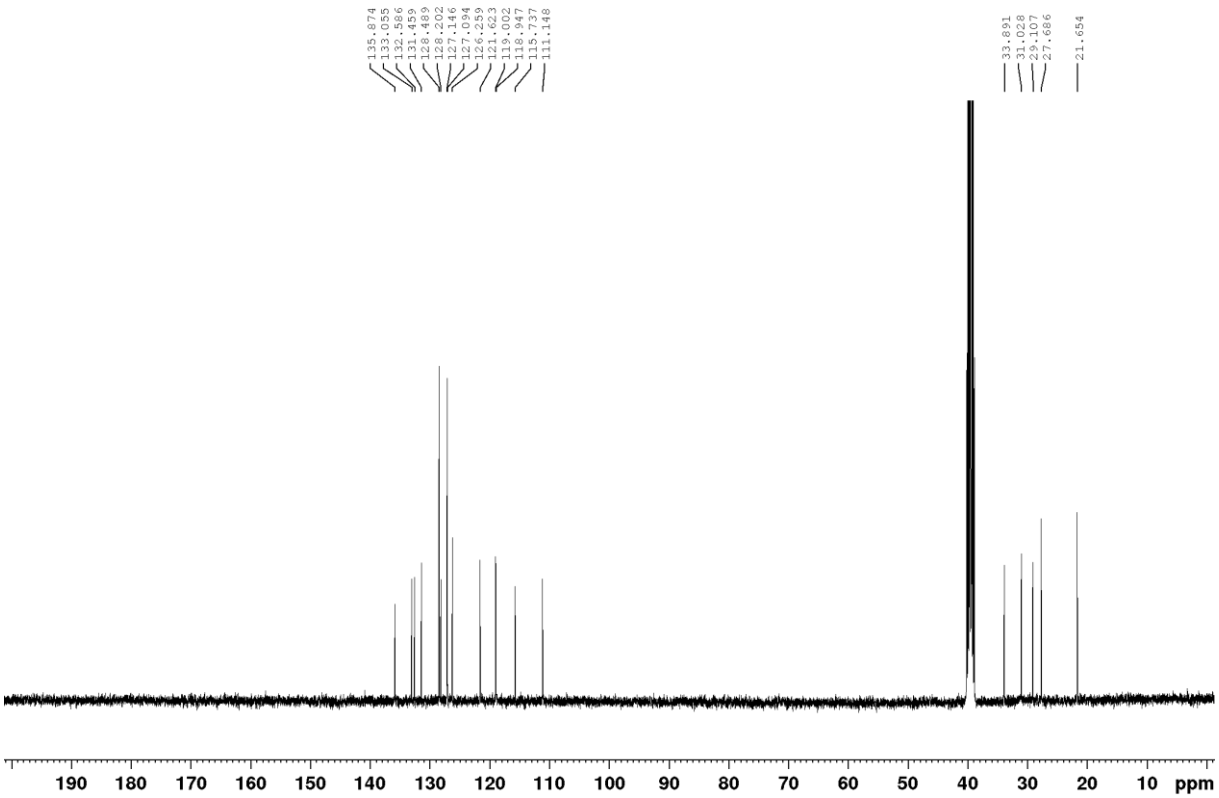

8.139
7.659
7.635
7.444
7.374
7.294
7.197
7.112
2.276
2.050
1.807
1.714
1.700
1.698
1.621
1.487
H
N
3c
[287.17]
7.6
7.4
ppm
1.87
3.83
0.98
1.00
0.99
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.86
1.87
3.83
0.98
1.00
0.99
4.06
2.94
1.06
2.85

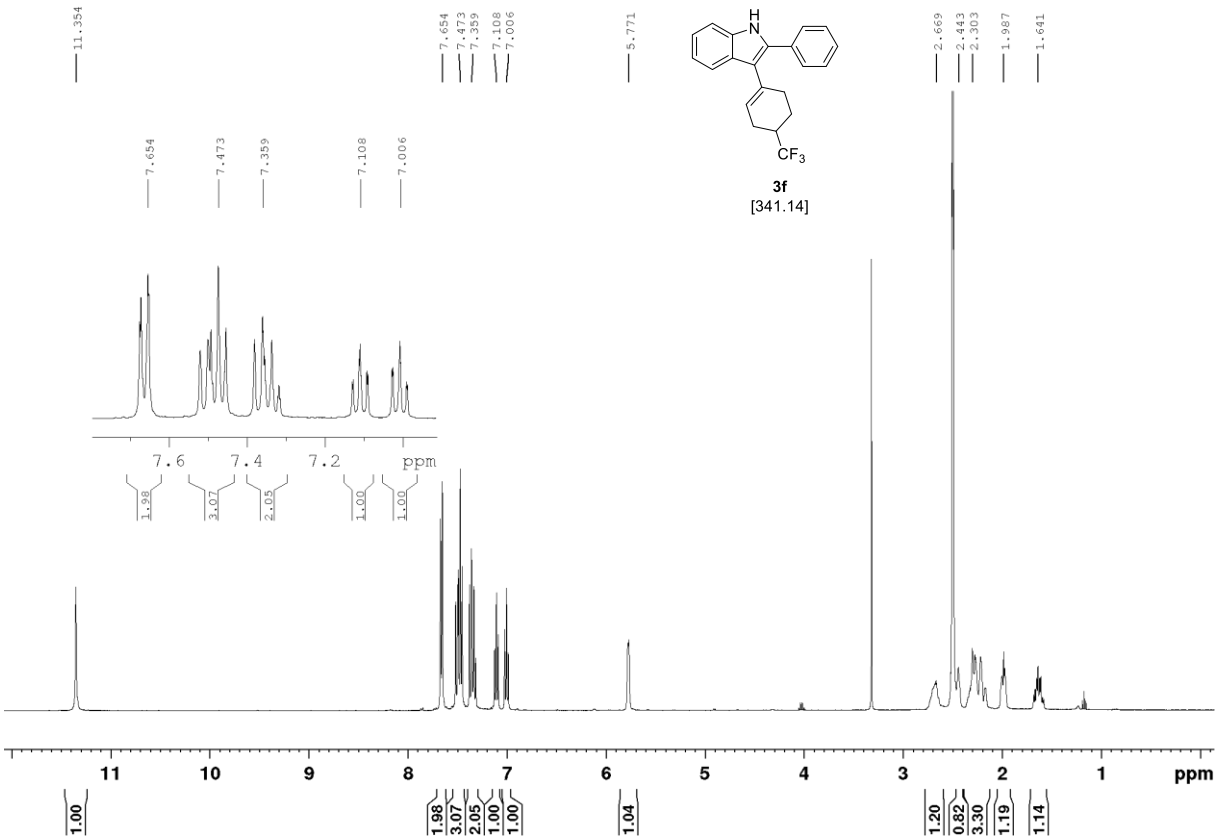

135.969
133.550
132.690
132.554
129.109
128.885
127.281
126.279
124.848
122.429
120.161
119.784
117.322
110.816
31.762
31.040
23.982
23.508
21.046
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

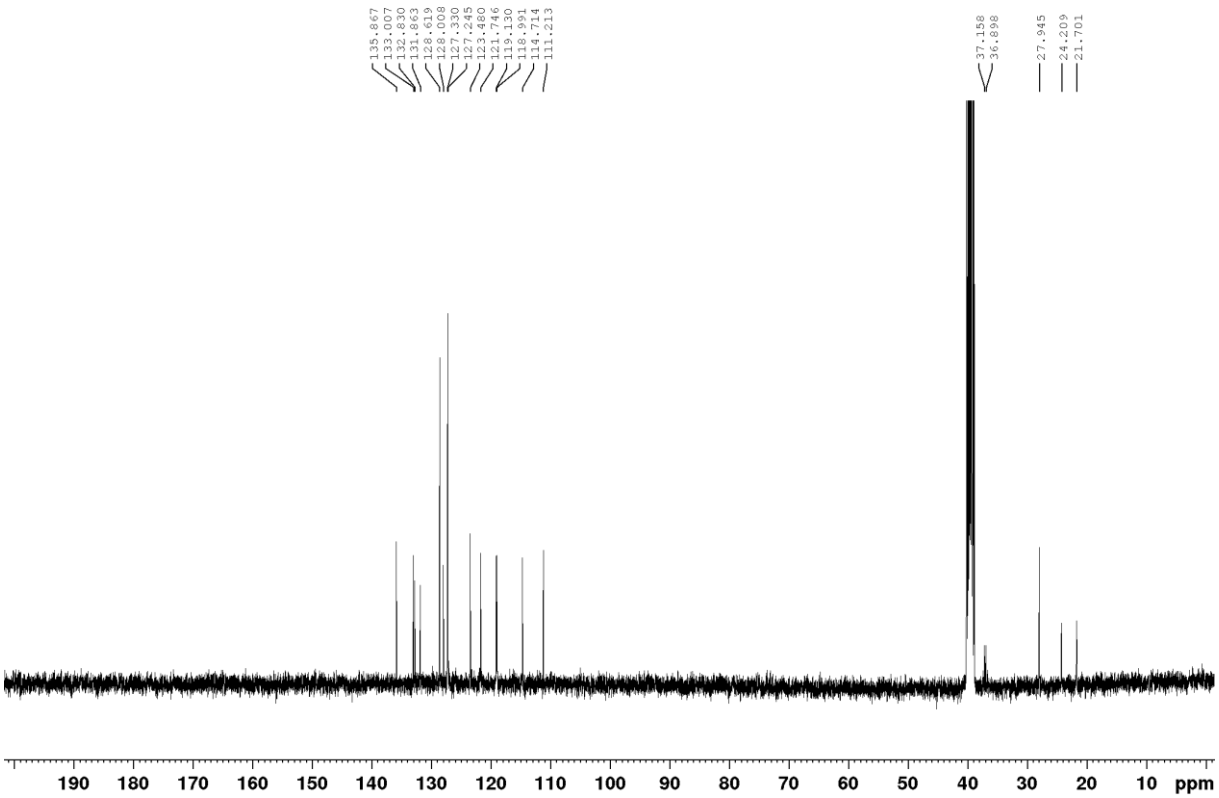

11.306
7.681
7.455
7.370
7.302
7.097
6.995
5.658
3.594
3.320
2.555
2.186
1.932
1.699
7.6
7.4
7.2
ppm
2.01
3.01
2.01
1.00
1.00
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.96
2.01
3.01
2.01
1.00
1.00
1.01
1.05
3.52
0.51
3.13
1.09
1.09
OMe
3d
[303.16]

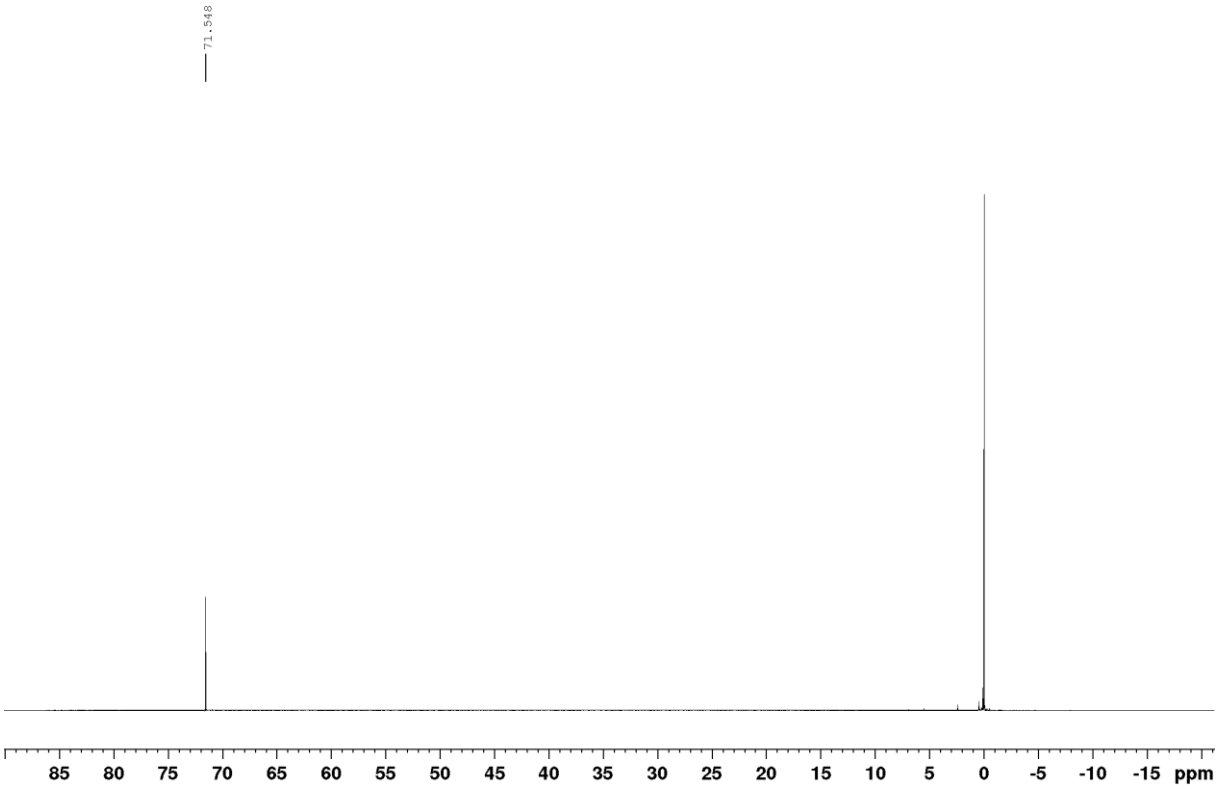

135.867
132.920
132.695
131.717
128.512
128.097
127.193
127.134
124.045
121.669
119.054
118.955
115.238
111.170
74.471
55.055
31.363
27.517
27.433
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

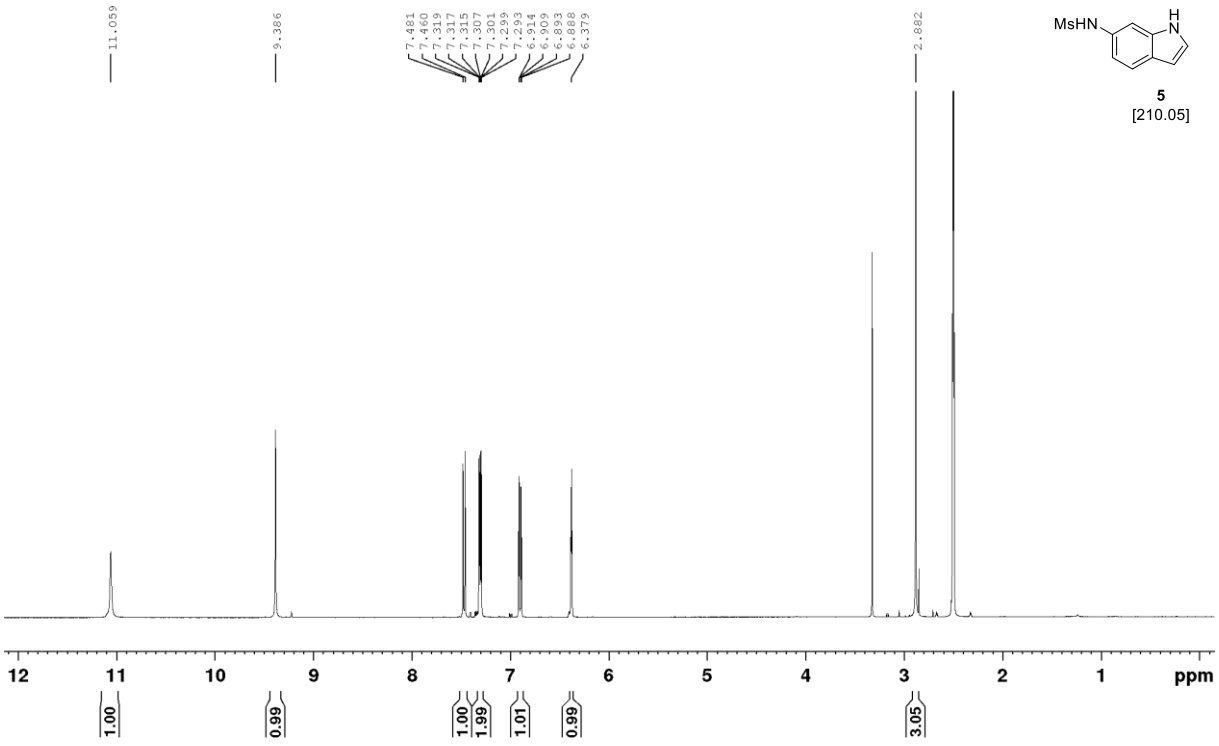

11.283
7.672
7.452
7.348
7.093
6.990
5.741
2.327
1.817
1.369
1.033
3e
[287.17]
7.6 7.4 7.2 ppm
11 10 9 8 7 6 5 4 3 2 1 ppm
0.95
1.99
3.00
2.02
1.00
1.00
1.00
1.13
2.22
3.27
1.14
3.13

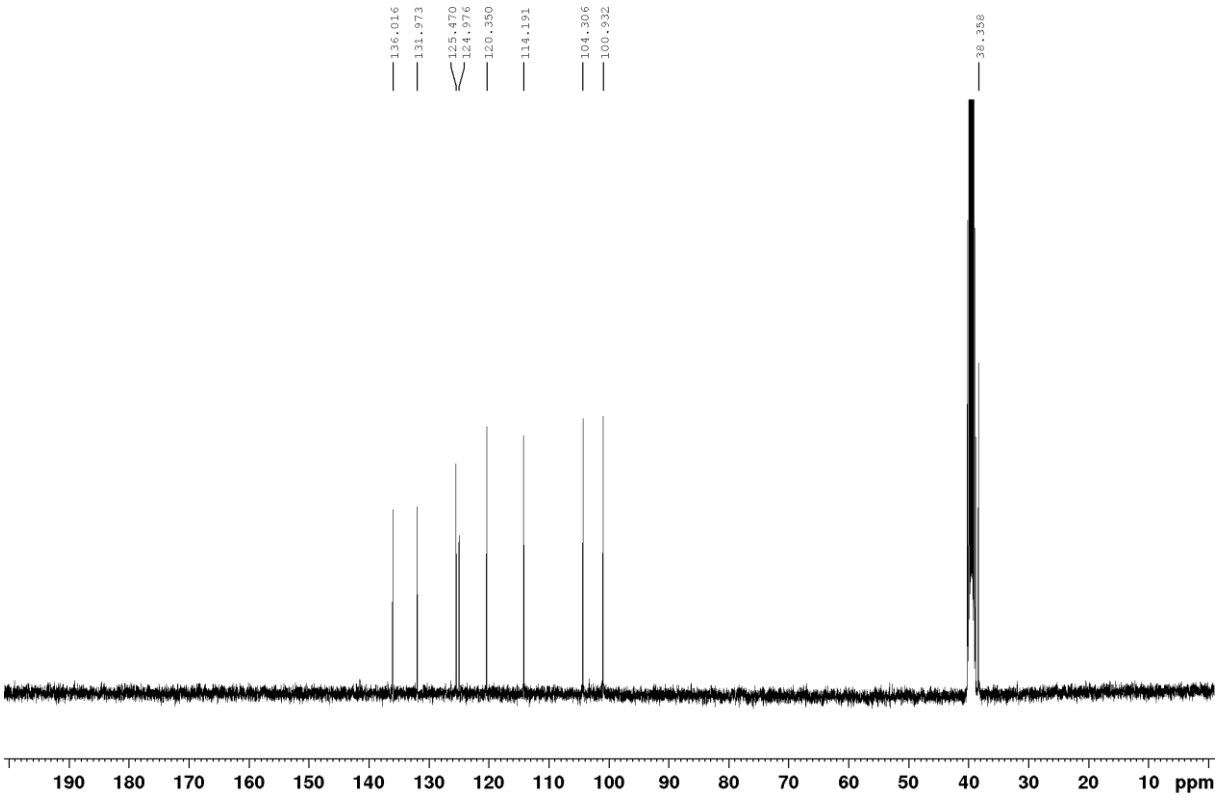

135.874
133.055
132.586
131.459
128.489
128.202
127.146
127.094
126.259
121.623
119.002
118.947
115.737
111.148
33.891
31.028
29.107
27.686
21.654
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

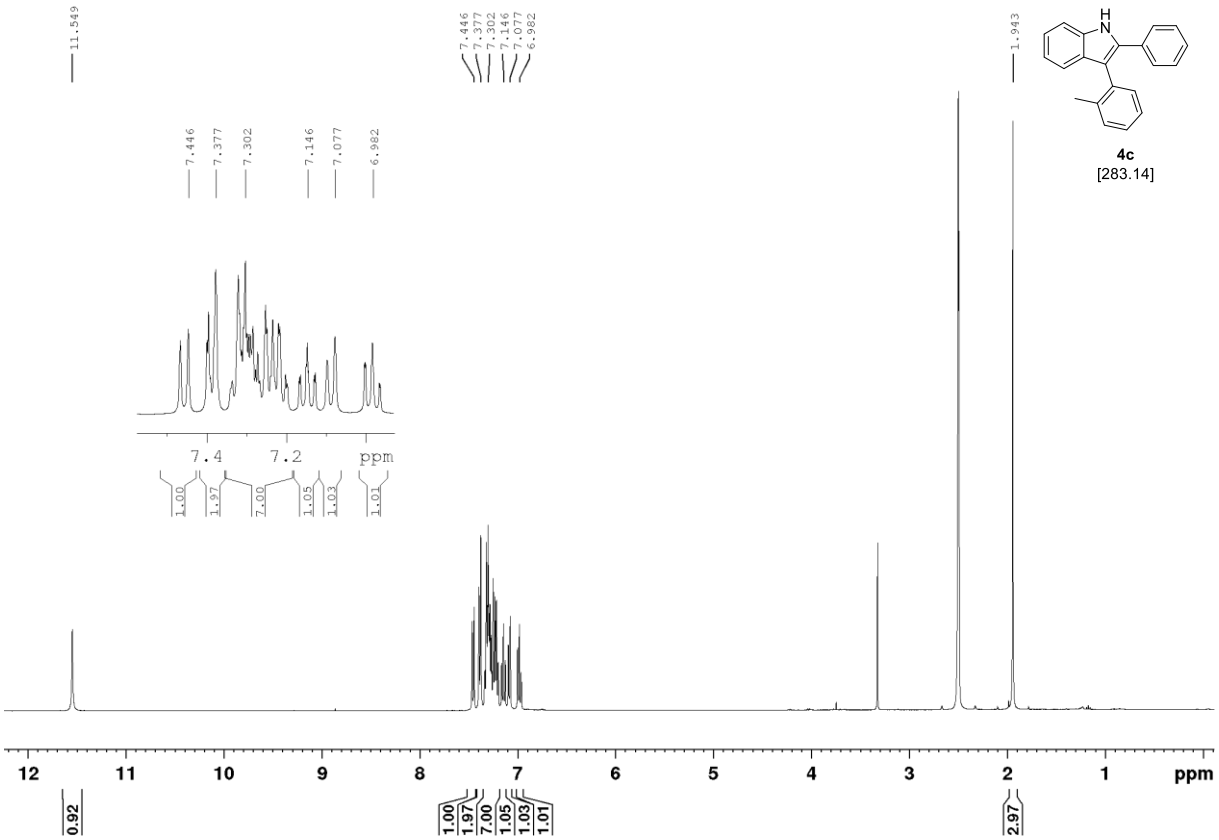

11.354
7.654
7.473
7.359
7.108
7.006
5.771
2.669
2.443
2.303
1.987
1.641
3f
[341.14]
7.6
7.4
7.2
ppm
1.98
3.07
2.05
1.00
1.00
1.00
1.98
3.07
2.05
1.00
1.00
1.04
1.20
0.82
3.30
1.19
1.14
11
10
9
8
7
6
5
4
3
2
1
ppm

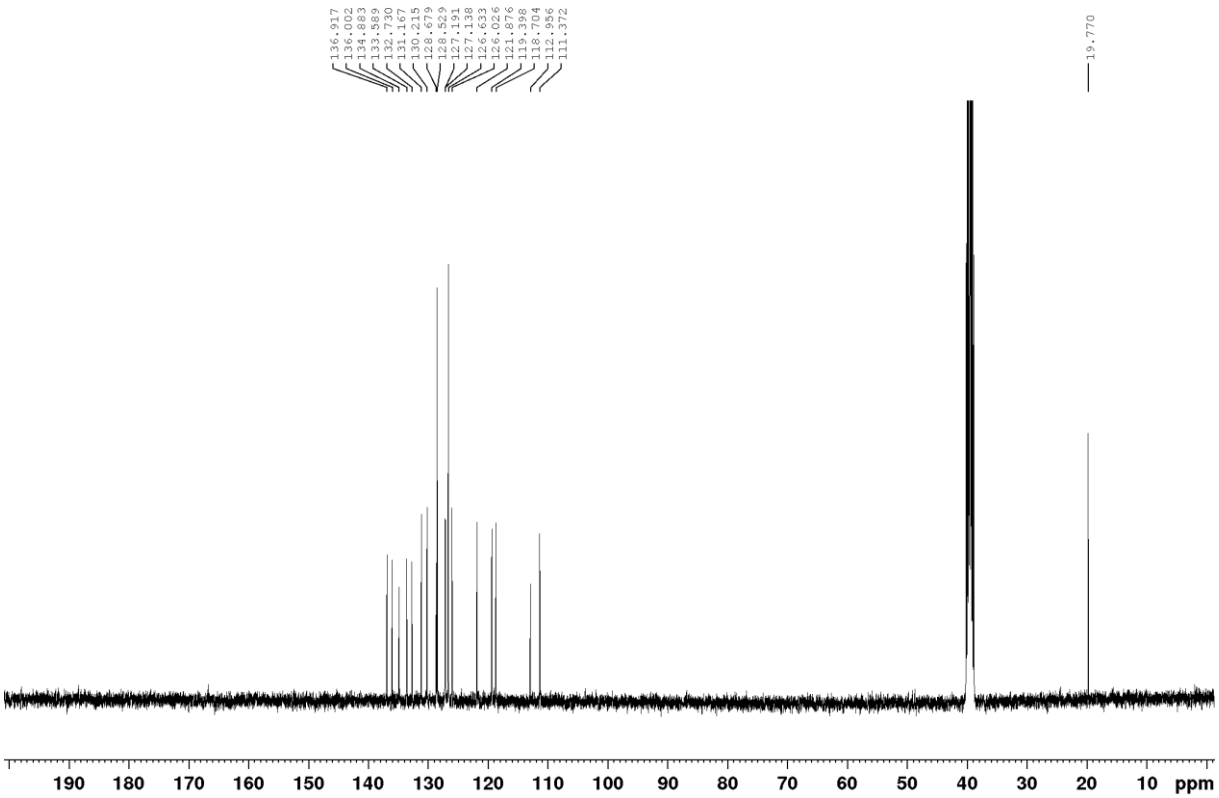

135.867
133.007
132.830
131.863
128.619
128.008
127.330
127.245
123.480
121.746
119.130
118.991
114.714
111.213
37.158
36.898
27.945
24.209
21.701
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

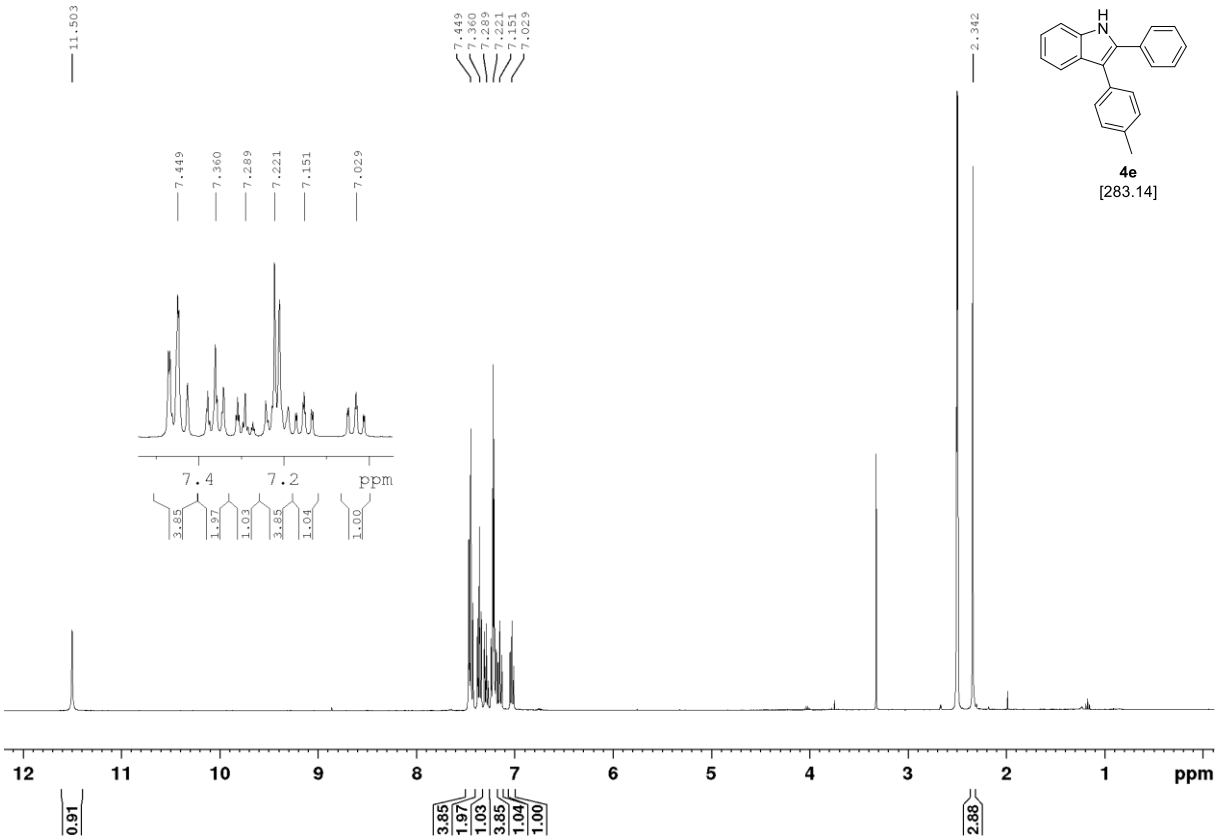

71.548
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 ppm

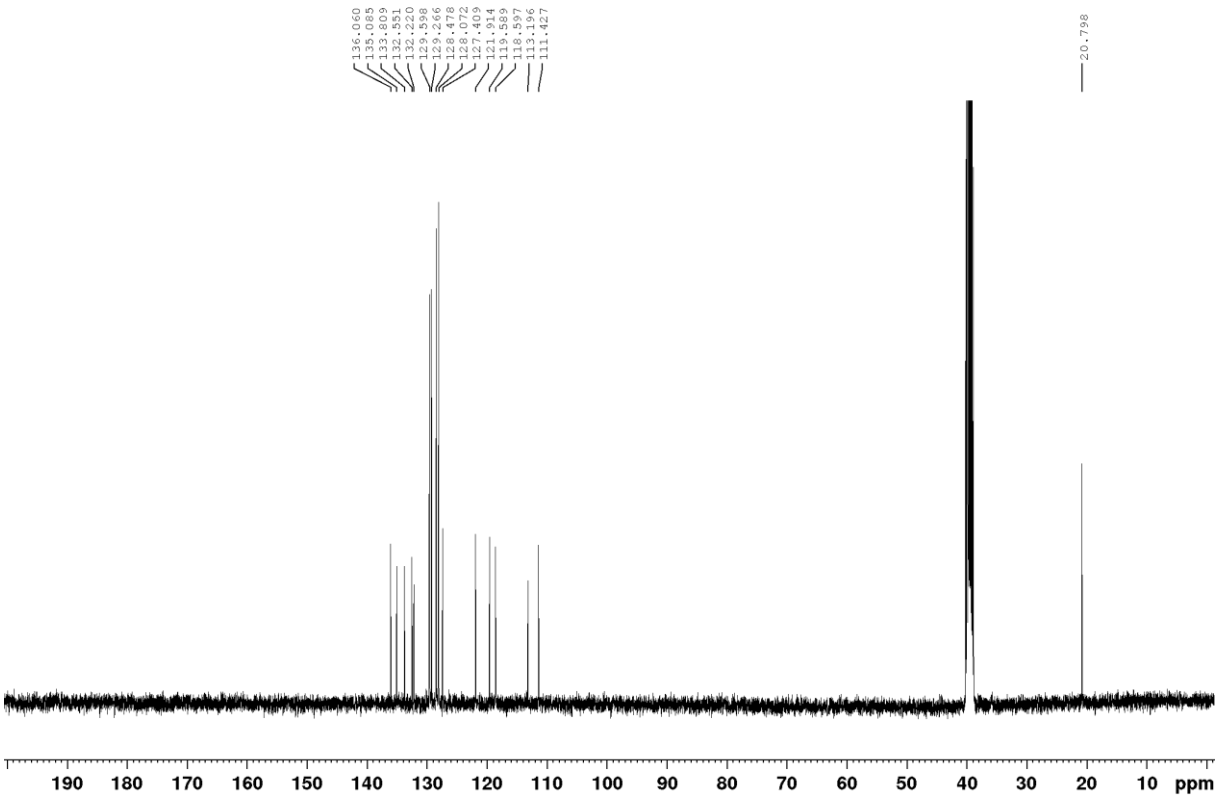

11.059
9.386
7.481
7.460
7.319
7.317
7.315
7.307
7.301
7.299
7.293
6.914
6.909
6.893
6.888
6.379
2.882
MsHN
H
N
5
[210.05]
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.99
1.00
1.99
1.01
0.99
3.05

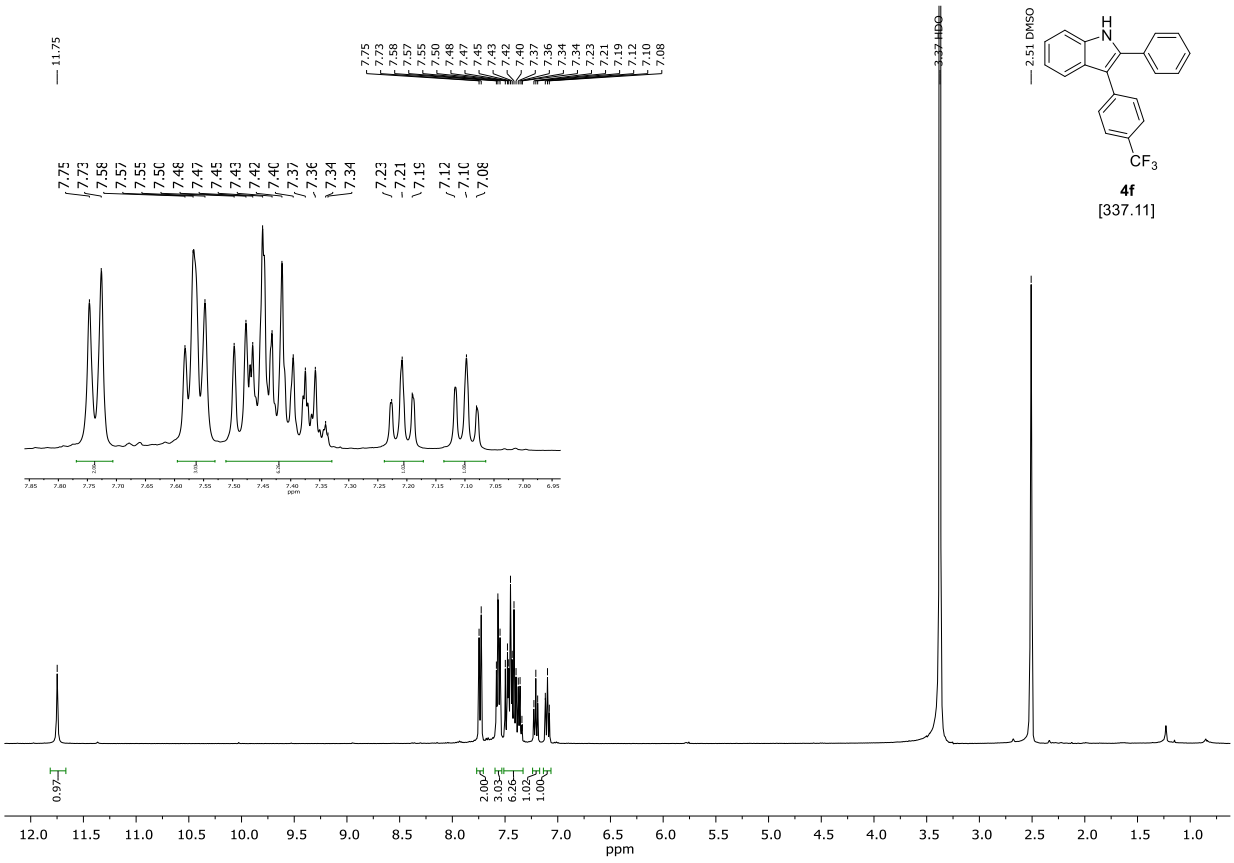

136.016
131.973
125.470
124.976
120.350
114.191
104.306
100.932
38.358
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

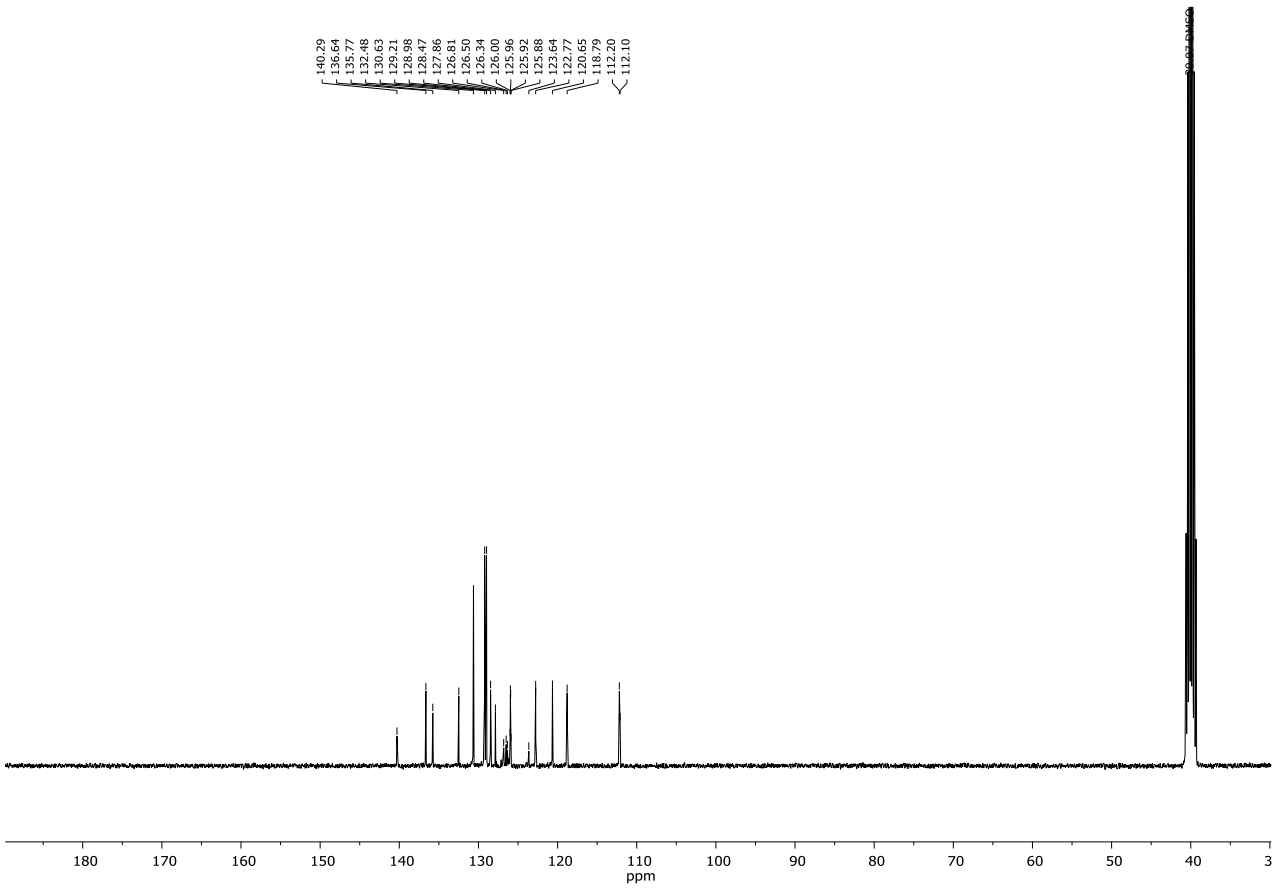

11.549
7.446
7.377
7.302
7.146
7.077
6.982
1.943
4c
[283.14]
7.4
7.2
ppm
1.00
1.97
7.00
1.05
1.03
1.01
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.92
1.00
1.97
7.00
1.05
1.03
1.01
2.97

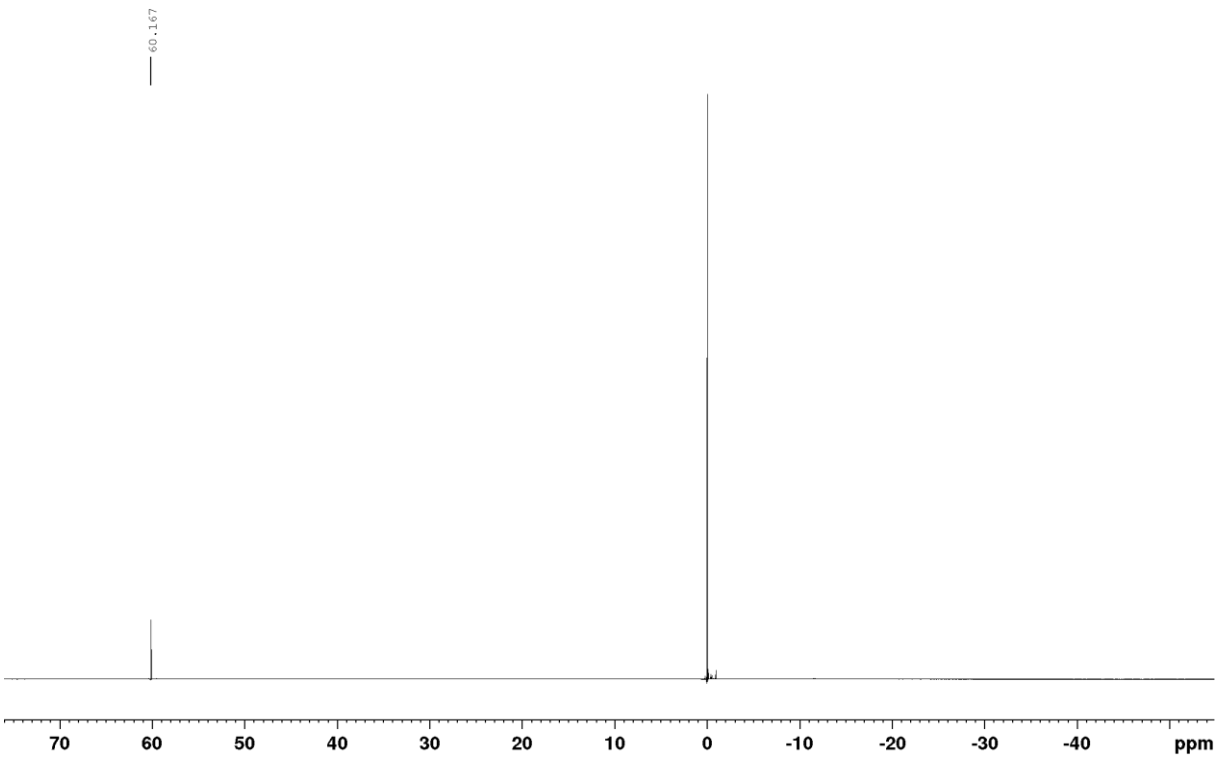

136.917
136.002
134.883
133.989
132.770
131.167
130.215
128.679
128.529
127.191
127.138
126.633
126.026
121.876
119.398
118.704
112.956
111.372
19.770
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

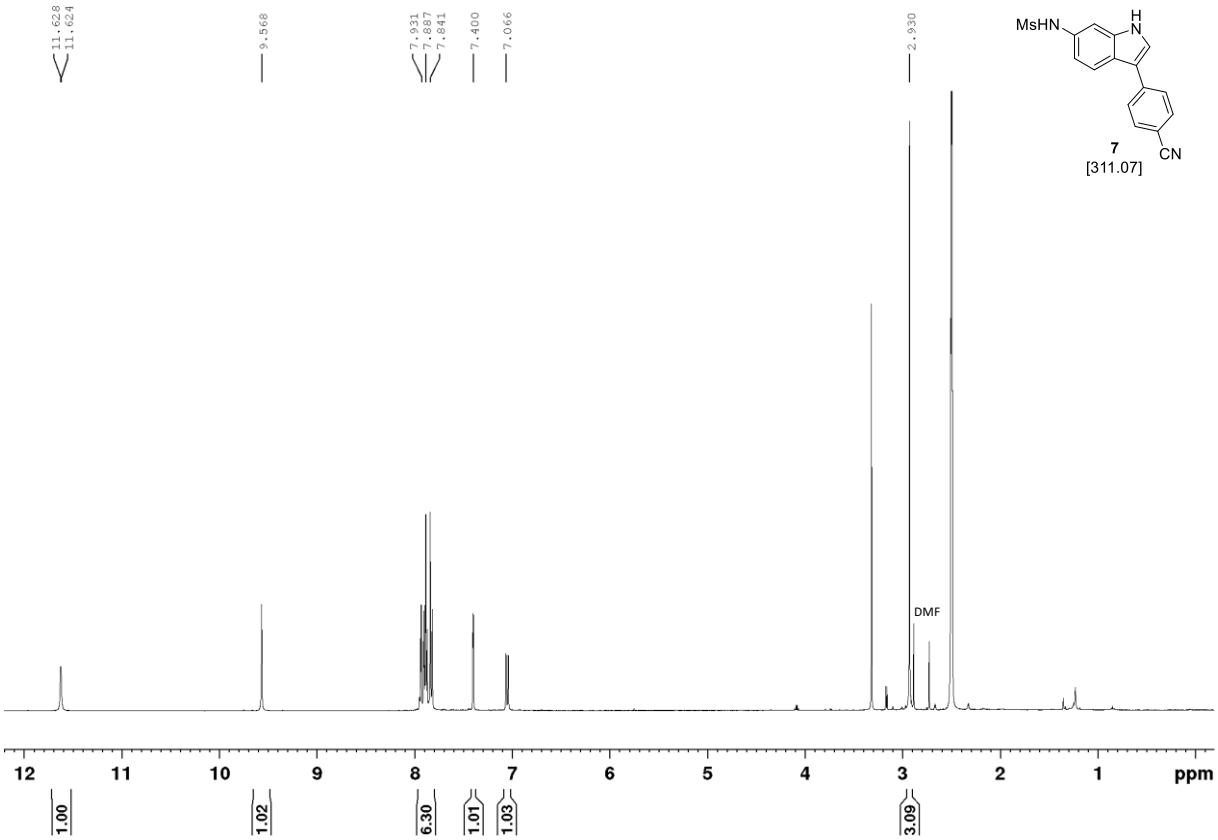

11.503
7.449
7.360
7.289
7.221
7.151
7.029
2.342
4e
[283.14]
7.4
7.2
ppm
3.85
1.97
1.03
3.85
1.04
1.00
0.91
2.88

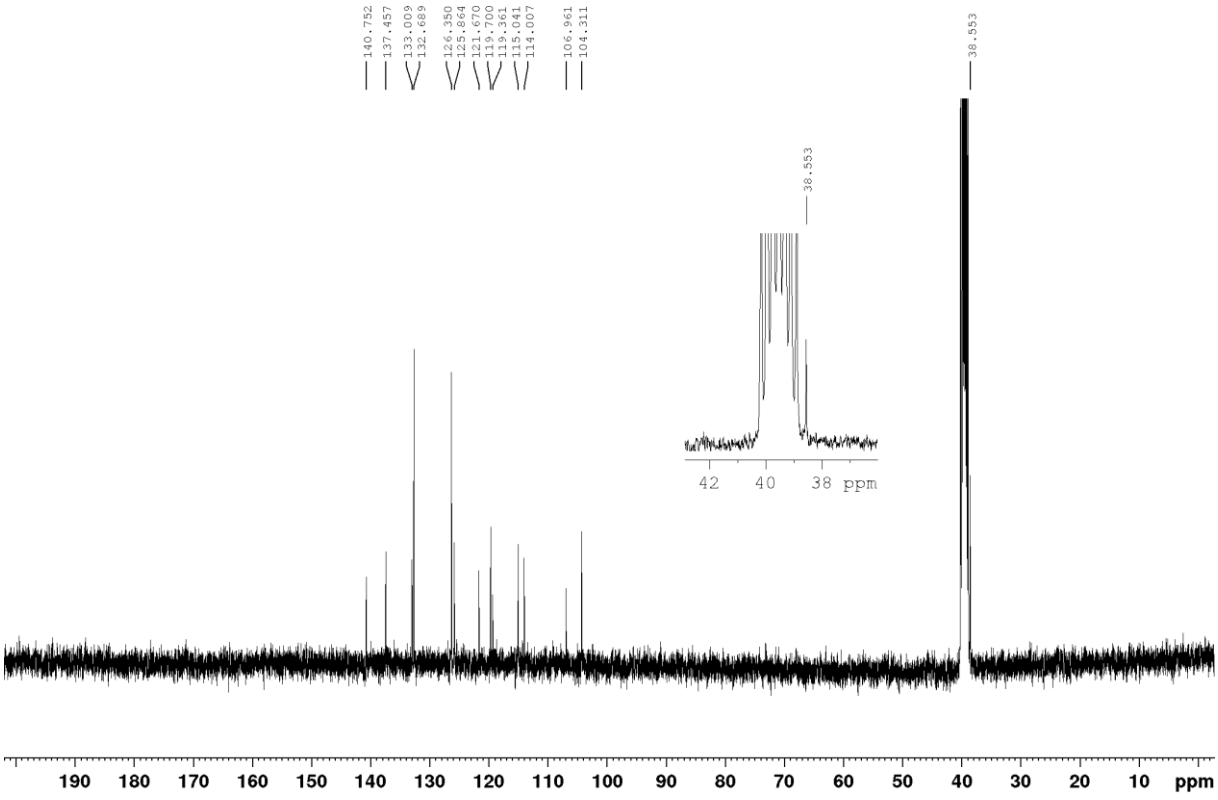

136.060
135.085
133.809
132.551
132.220
129.598
129.266
128.478
128.072
127.409
121.914
119.589
118.597
113.196
111.427
20.798
ppm

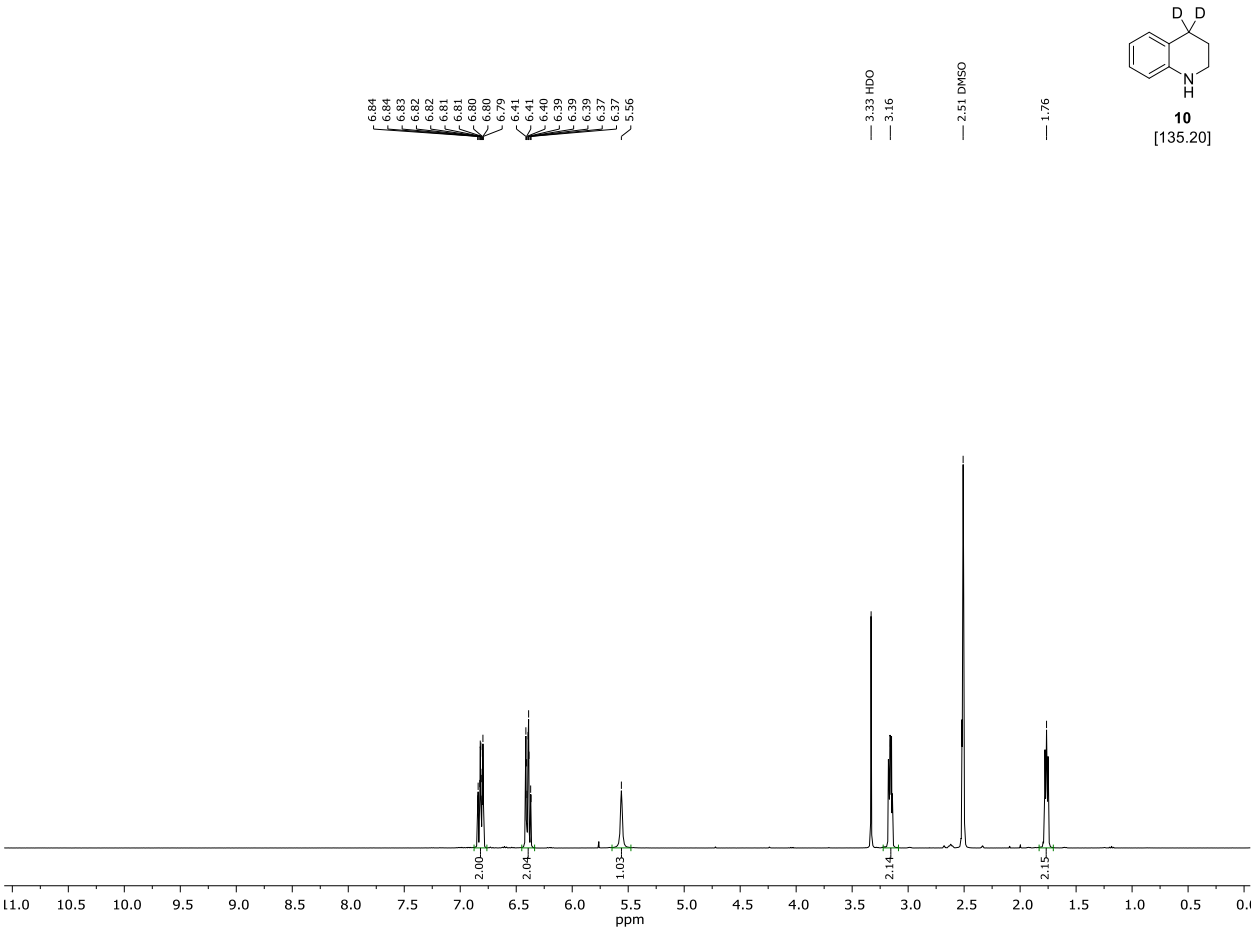

11.75
7.75
7.73
7.58
7.57
7.55
7.50
7.48
7.47
7.45
7.43
7.42
7.40
7.37
7.36
7.34
7.34
7.23
7.21
7.19
7.12
7.10
7.08
3.37 H2O
2.51 DMSO
4f
[337.11]
0.97
2.00
3.03
6.26
1.02
1.00
ppm

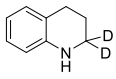

140.29
136.64
135.77
132.48
130.63
129.21
128.98
128.47
127.86
126.81
126.50
126.34
126.00
125.96
125.92
125.88
123.64
122.77
120.65
118.79
112.20
112.10
39.52 DMSO
ppm


60.167
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm

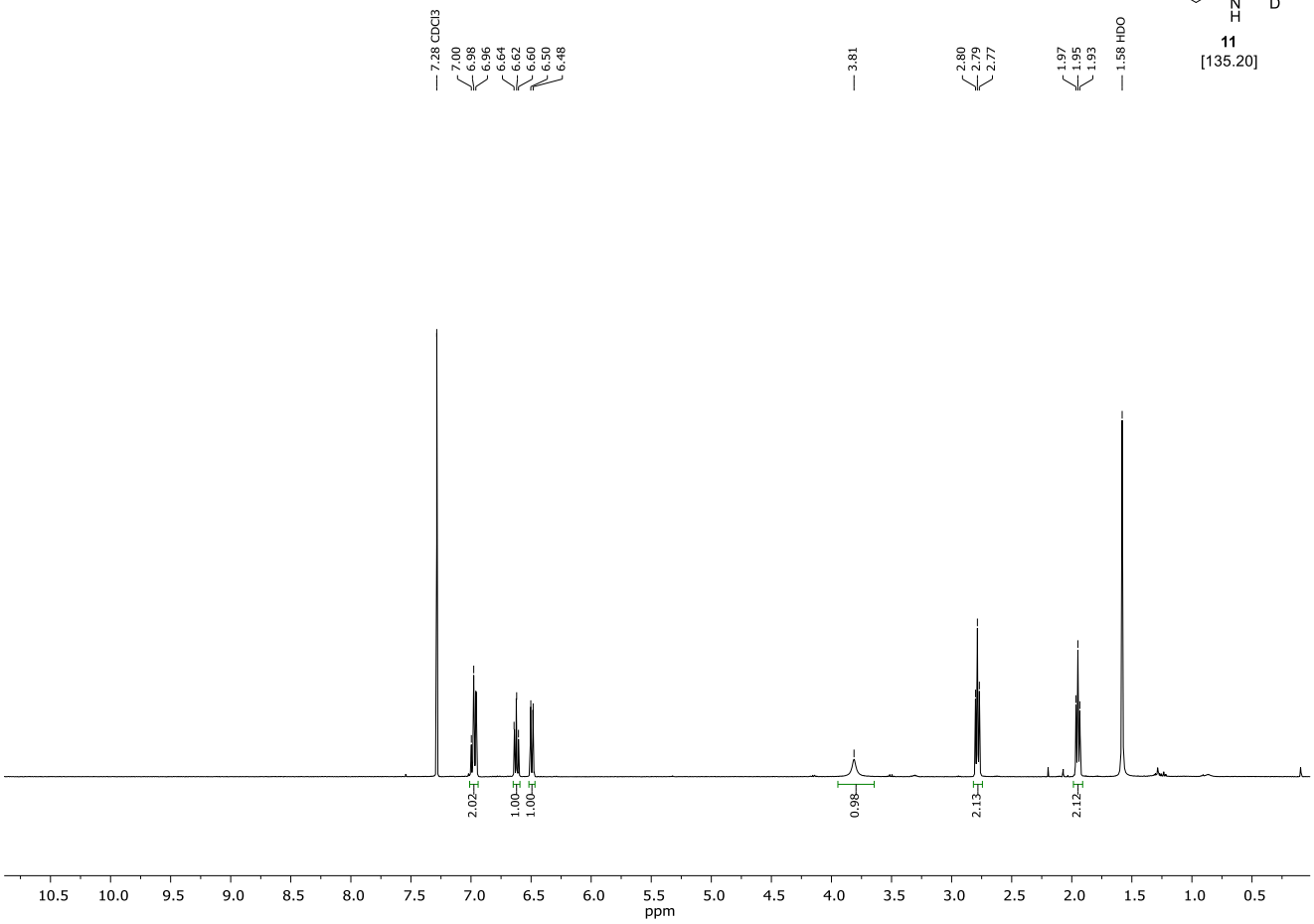

11.628
11.624
9.568
7.931
7.887
7.841
7.400
7.066
2.930
MsHN
H
N
CN
7
[311.07]
DMF
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
6.30
1.01
1.03
3.09

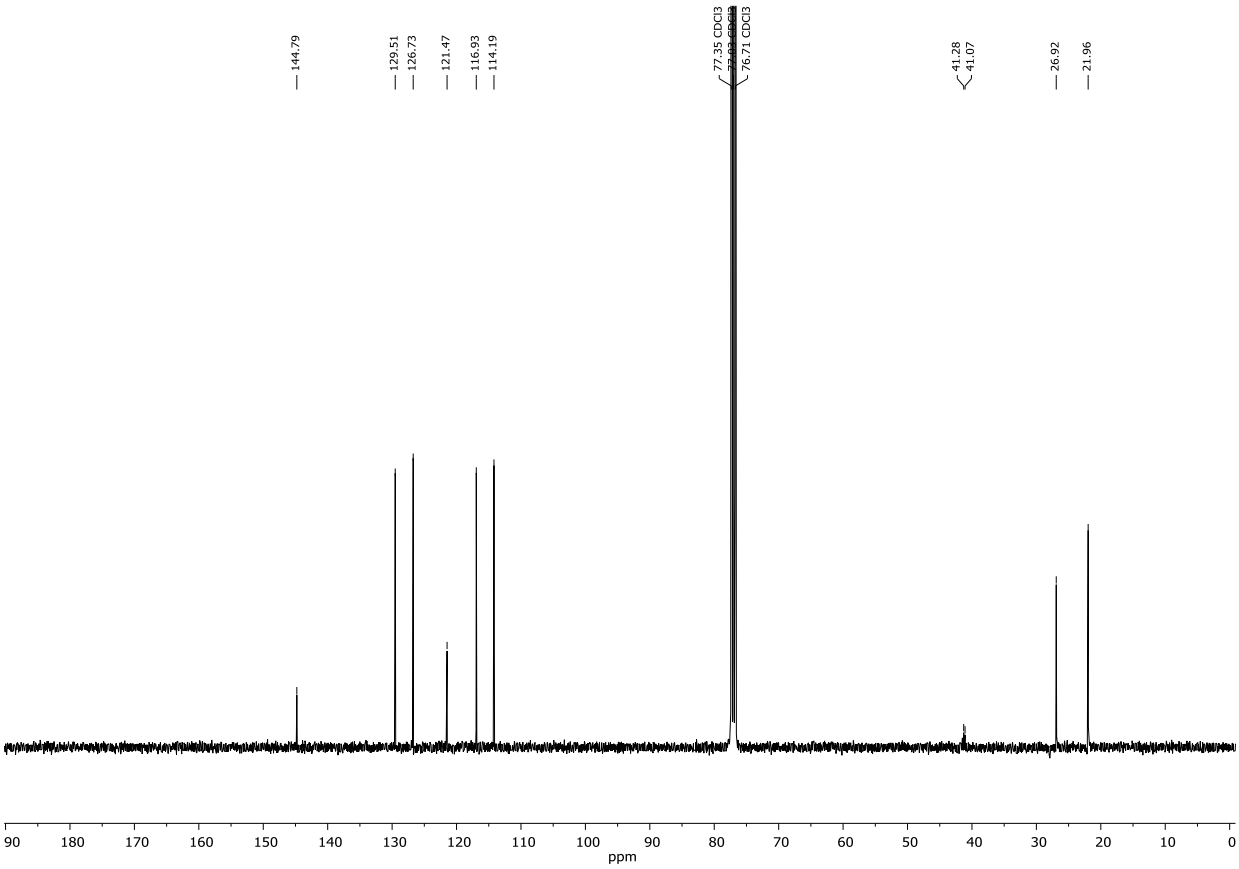

140.752
137.457
133.009
132.689
126.350
125.864
121.670
119.700
119.361
115.041
114.007
106.961
104.311
38.553
38.553
42
40
38 ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

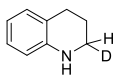

6.84
6.84
6.83
6.82
6.82
6.81
6.81
6.80
6.80
6.79
6.79
6.41
6.41
6.40
6.39
6.39
6.39
6.37
6.37
5.56
3.33 HDO
3.16
2.51 DMSO
1.76
D
D
N
H
10
[135.20]
2.00
2.04
1.03
2.14
2.15
ppm
145.86
129.38
126.83
120.17
115.45
113.76
41.22
26.63
26.44
26.25
21.84
ppm


D
D
N
H

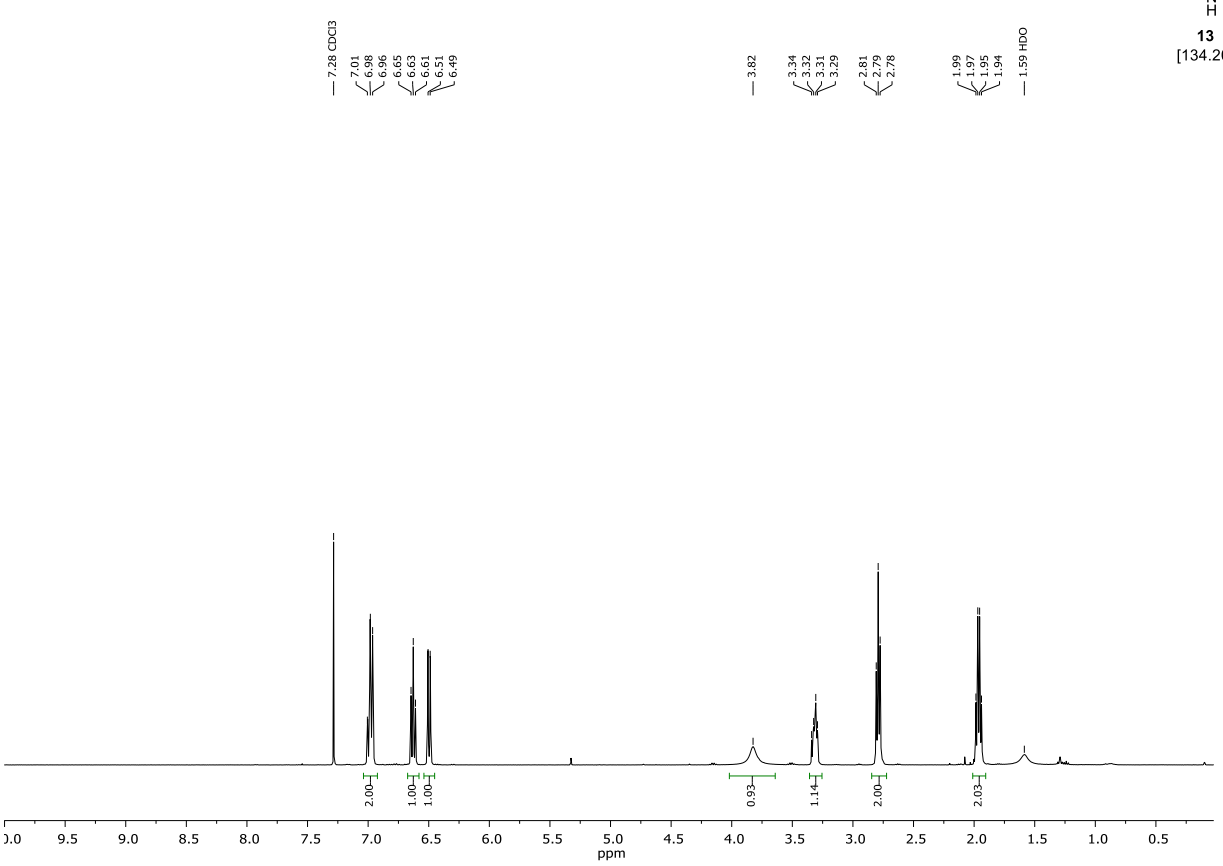
11
[135.20]

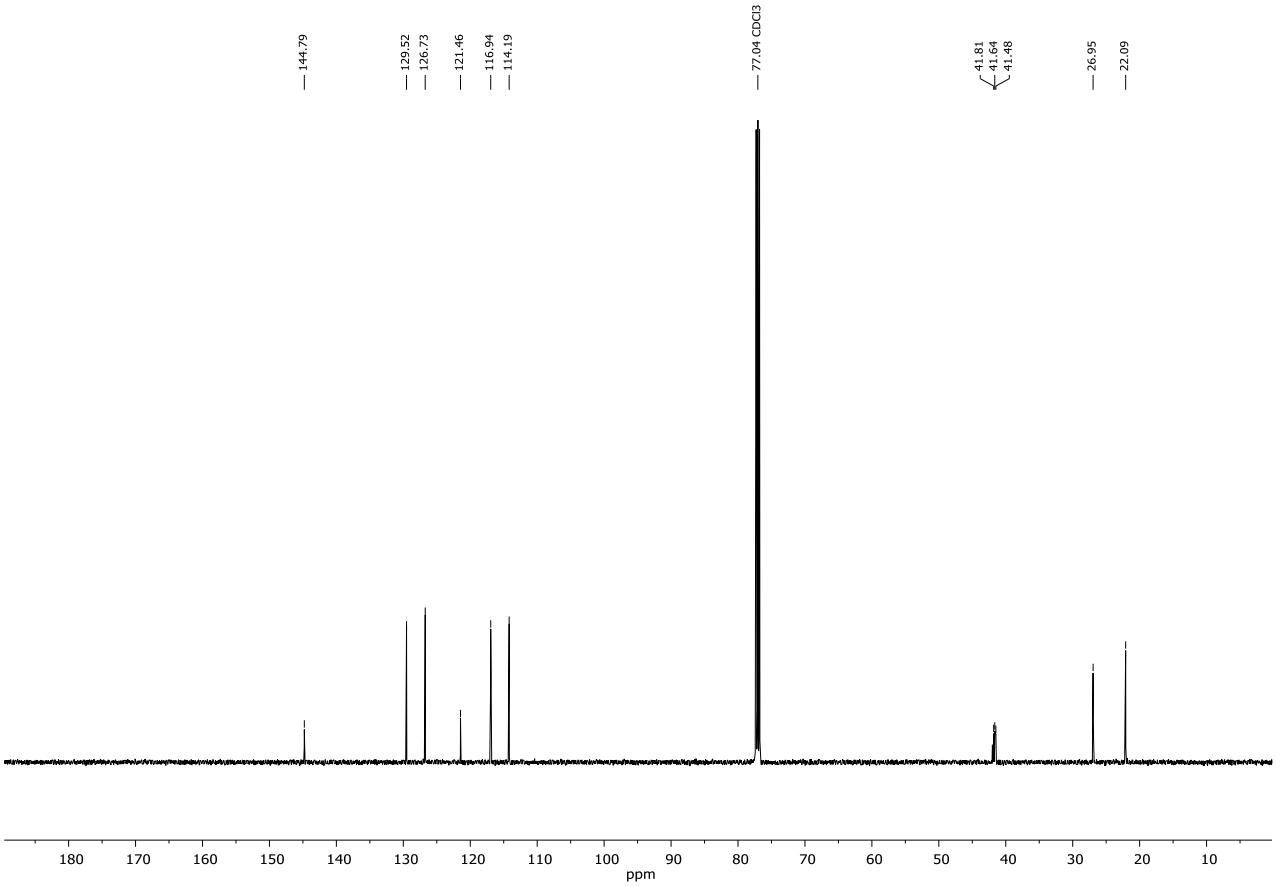

7.28 CDCl3
7.00
6.98
6.96
6.64
6.62
6.60
6.50
6.48
3.81
2.80
2.79
2.77
1.97
1.95
1.93
1.58 HDO
2.02
1.00
1.00
0.98
2.13
2.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

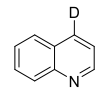

144.79
129.51
126.73
121.47
116.93
114.19
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
41.28
41.07
26.92
21.96
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


H
D
N
H

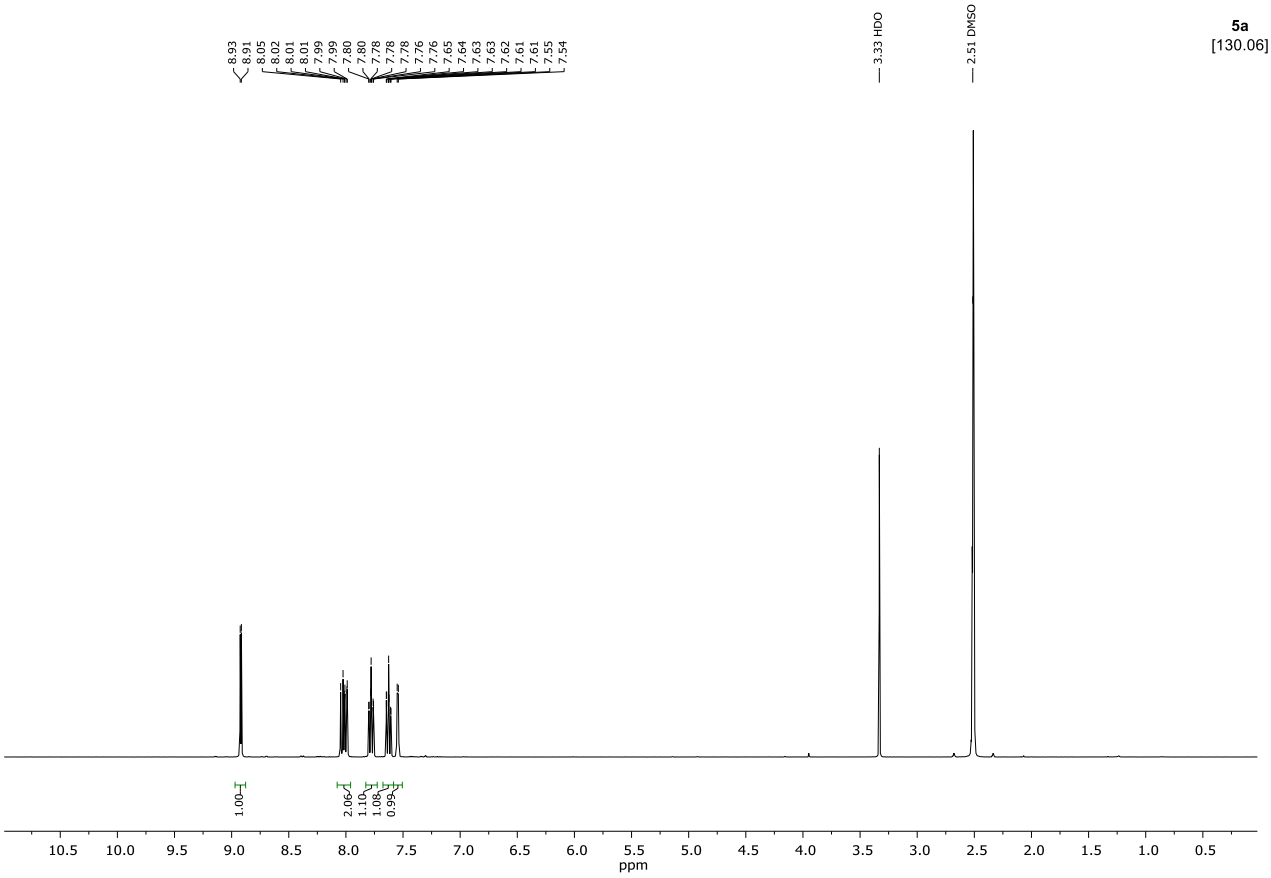
13
[134.20]

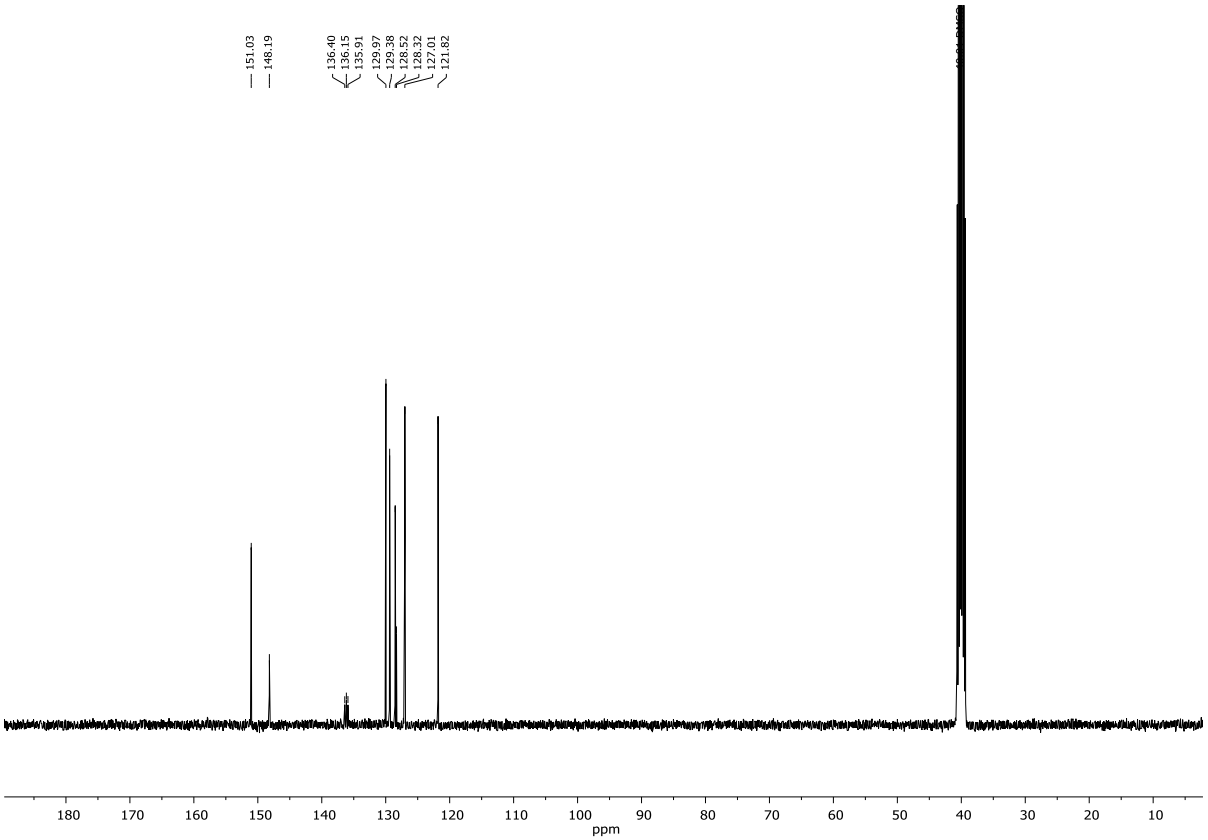

7.28 CDCl3
7.01
6.98
6.96
6.65
6.63
6.61
6.51
6.49
3.82
3.34
3.32
3.31
3.29
2.81
2.79
2.78
1.99
1.97
1.95
1.94
1.59 HDO
2.00
1.00
1.00
0.93
1.14
2.00
2.03
ppm

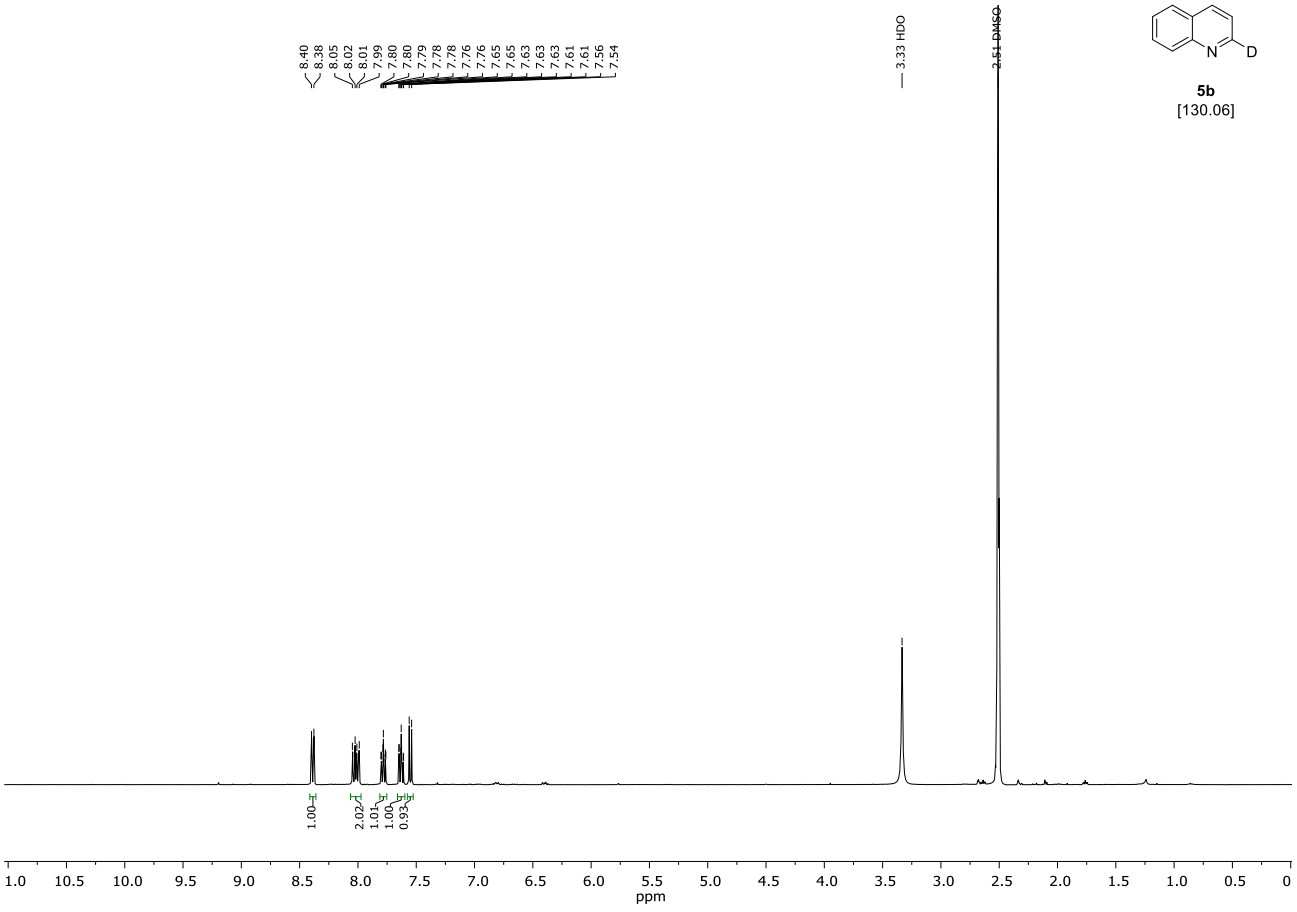

144.79
129.52
126.73
121.46
116.94
114.19
77.04 CDCl3
41.81
41.64
41.48
26.95
22.09
ppm

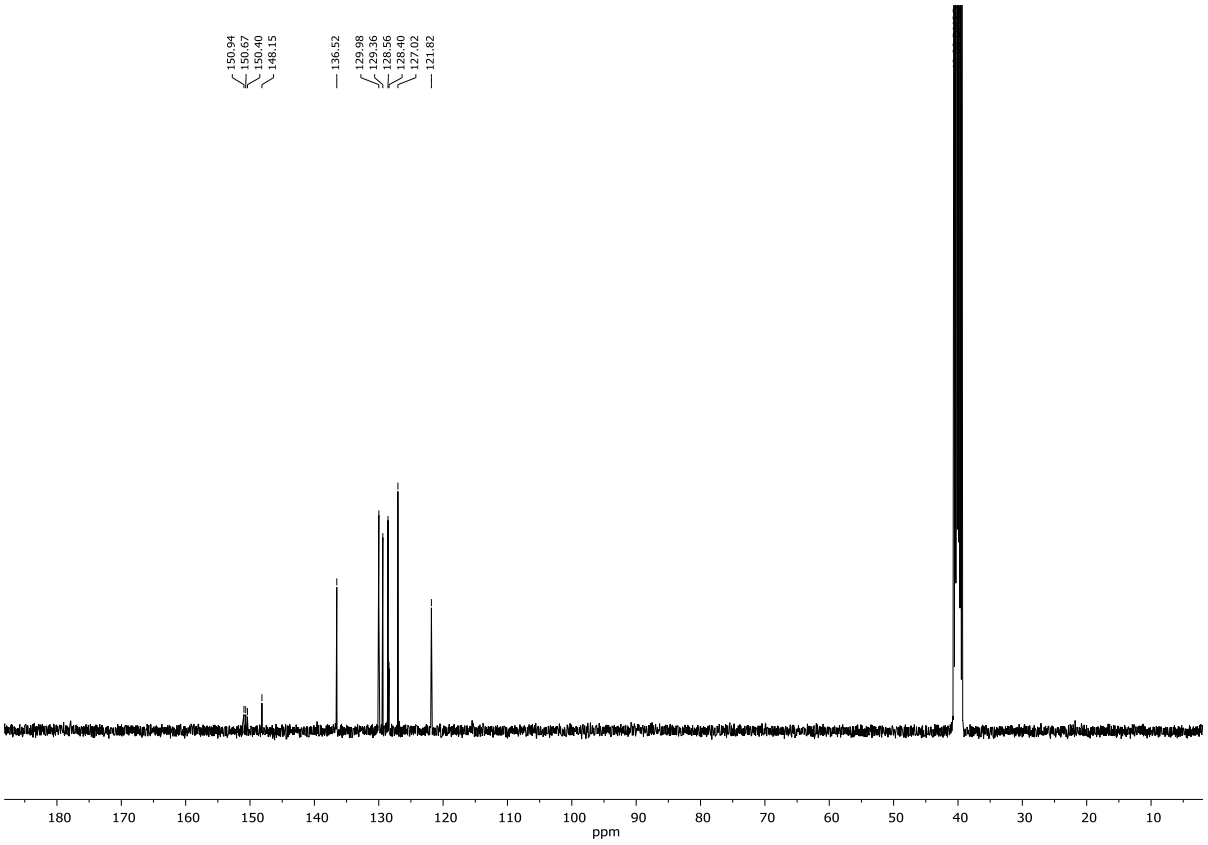

D
N

5a
[130.06]


8.93
8.91
8.05
8.02
8.01
8.01
7.99
7.99
7.80
7.80
7.78
7.78
7.78
7.78
7.76
7.76
7.65
7.64
7.63
7.63
7.62
7.61
7.61
7.55
7.54
3.33 HDO
2.51 DMSO
1.00
2.06
1.10
1.08
0.99
10.5
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
ppm


151.03
148.19
136.40
136.15
135.91
129.97
129.38
128.52
128.32
127.01
121.82
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.40
8.38
8.05
8.02
8.01
7.99
7.80
7.80
7.79
7.78
7.78
7.76
7.76
7.65
7.65
7.63
7.63
7.63
7.61
7.61
7.56
7.54
3.33 HDO
2.51 DMSO
N
D
5b
[130.06]
1.00
2.02
1.01
1.00
0.93
1.0 10.5 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
ppm


150.94
150.67
150.40
148.15
136.52
129.98
129.36
128.56
128.40
127.02
121.82
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

References

1 T. Wirtanen, M. K. Mäkelä, J. Sarfraz, P. Ihalainen, S. Hietala, M. Melchionna and J. Helaja, *Adv. Synth. Catal.*, 2015, **357**, 3718–3726.

2 J. Ye, J. Wu, T. Lv, G. Wu, Y. Gao and H. Chen, *Angew. Chem., Int. Ed.*, 2017, **56**, 14968–14972.

3 M. Desroses, T. Koolmeister, S. Jacques, S. Llona-Minguez, M.-C. Jacques-Cordonnier, A. Cázares-Körner, T. Helleday and M. Scobie, *Tetrahedron Lett.*, 2013, **54**, 3554–3557.

4 F. Leipold, S. Hussain, D. Ghislieri and N. J. Turner, *ChemCatChem*, 2013, **5**, 3505–3508.

5 T. B. Goh, M. N. Mordi, M. R. H. Mas Haris and S. M. Mansor, *Magn. Reson. Chem.*, 2015, **53**, 857–859.

6 Y. Lin, J. Ye, W. Zhang, Y. Gao and H. Chen, *Adv. Synth. Catal.*, 2019, **361**, 432–435.

7 J. Dai, W. Dan, Y. Zhang, M. He and J. Wang, *Bioorganic & Medicinal Chemistry Letters*, 2018, **28**, 3123–3128.

8 Y.-Q. Huang, H.-J. Song, Y.-X. Liu and Q.-M. Wang, *Chem. Eur. J.*, 2018, **24**, 2065–2069.

9 S. Eagon and M. O. Anderson, *Eur. J. Org. Chem.*, 2014, **2014**, 1653–1665.

10 A. Sharma, R. Kumar, N. Sharma, V. Kumar and A. K. Sinha, *Adv. Synth. Catal.*, 2008, **350**, 2910–2920.

11 A. V. Iosub and S. S. Stahl, *Organic letters*, 2015, **17**, 4404–4407.

12 M. K. Sahoo, G. Jaiswal, J. Rana and E. Balaraman, *Chem. Eur. J.*, 2017, **23**, 14167–14172.

13 P. Y. Yeung, C. M. So, C. P. Lau and F. Y. Kwong, *Angew. Chem., Int. Ed.*, 2010, **49**, 8918–8922.

14 T.-C. Wang, Y.-L. Chen, K.-H. Lee and C.-C. Tzeng, *Synthesis*, 1997, **1997**, 87–90.

15 S. Chakraborty, W. W. Brennessel and W. D. Jones, *J. Am. Chem. Soc.*, 2014, **136**, 8564–8567.

16 C. Venkateswarlu, P. V. Balaji, K. De, B. Crousse, B. Figadère and J. Legros, *J. Fluor. Chem.*, 2013, **152**, 94–98.

17 S. M. Bonesi, M. A. Ponce and R. Erra-Balsells, *Journal of Heterocyclic Chemistry*, 2004, **41**, 161–171.

18 A. Kamlah, F. Lirk and F. Bracher, *Tetrahedron*, 2016, **72**, 837–845.

19 M. Westermaier and H. Mayr, *Org. lett.*, 2006, **8**, 4791–4794.

20 H. A. Houck, K. de Bruycker, C. Barner-Kowollik, J. M. Winne and F. E. Du Prez, *Macromolecules*, 2018, **51**, 3156–3164.

21 S. Cacchi, G. Fabrizi, D. Lamba, F. Marinelli and L. M. Parisi, *Synthesis*, 2003, 728–734.

22 M. Yudasaka, D. Shimbo, T. Maruyama, N. Tada and A. Itoh, *Org. lett.*, 2019, **21**, 1098–1102.

23 Abbott Laboratories (2008): US2008/153871, 2008, A1.

24 J. L. Figueiredo and M. F. R. Pereira, *Cat. Today*, 2010, **150**, 2–7.