Supplementary Information (SI) for ChemComm.

Supporting information

N-Heterocycle-Coordinated λ^5-Iodanes as IBX Alternatives for Alcohol Oxidations

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1. *General information*

Reagents were used as received from their commercial supplier (abcr, Acros Organics, Alfa Aesar, Apollo Scientific, Carbolution Chemicals, Sigma Aldrich, TCI, fluorochem, BLD pharm). All solvents were dried using standard methods.[1] Unless otherwise stated, all yields refer to isolated yields of compounds estimated to be >95% pure as determined by 1H-NMR spectroscopy.

Thin layer chromatography was performed on fluorescence indicator marked precoated silica gel 60 plates (Macherey-Nagel, ALUGRAM Xtra SIL G/UV254) and visualized by UV light (254 nm/366 nm). Column chromatography was performed on silica gel (0.040 – 0.063 mm) with the solvents given in the procedures.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance Neo 600 (600 MHz) or Bruker AVANCE III HD (400 MHz). Chemical shifts for ^{1}H NMR spectra were reported as δ (parts per million) relative to the residual signal of $CDCl_3$ at 7.26 ppm (s) or DMSO-*d₆* at 2.50 ppm. Chemical shifts for ^{13}C NMR spectra were reported as δ (parts per million) relative to the signal of $CDCl_3$ at 77.0 ppm (t) or DMSO-d_6 at 39.5 ppm (sept.). The following abbreviations were used to describe splitting patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext. = sextet, sept = septet, m = multiplet. Coupling constants J are given in Hertz.

HR-ESI mass spectra were recorded on a Bruker impact II (QTOF). APCI mass spectra and reaction control via TLC-MS were recorded on an Advion Expression CMSL via ASAP probe or direct inlet. EI mass spectra were obtained from an Agilent 7890B GC System with an Agilent 5977A MSD mass spectrometer. All signals were reported with m/z ratio. A solvent for HR-ESI mass spectra measurements specified for each compound.

Melting points were determined on a Büchi M-5600 Melting Point apparatus with a heating rate of 1 °C/min. The melting points were reported in °C. Most of the hypervalent iodine compounds underwent changes in appearance (e.g. softening) before final melting/decomposition.

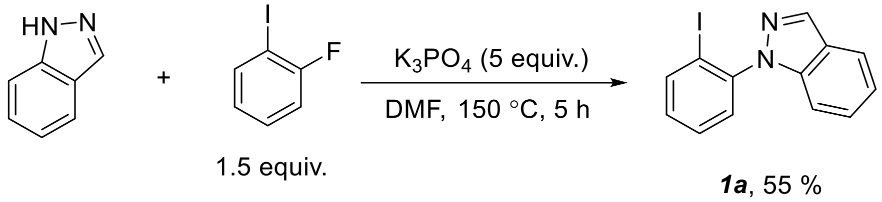
Conditions for single crystal growth specified for each compound. Suitable crystals were selected and measured on a Bruker D8 Venture diffractometer. The crystal was kept at 100 K during data collection. The structures were solved by the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package incorporated in the OLEX2 program package[4] using Least Squares minimization. The ORTEP drawing was made using the program Mercury from the CCDC.

Simultaneous TGA-DSC testing was carried out with Q600 Simultaneous TGA-DTA-DSC analyzer (TA Instruments) or Mettler Toledo TGA/DSC 3+ STAR^e system in an open corundum crucible under air atmosphere at rates specified for each compound. The temperature of oven was held at rt for 1 minute, then heated from rt to temperature specified in the graphs.

IBX was synthesized according to the literature procedure.[5] The analytical data are in accordance with previously reported.[6]

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.14 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 8.00 (t, *J* = 7.8 Hz, 1H), 7.84 (t, *J* = 7.2 Hz, 1H). m.p. = 230-232 °C (lit. 233 °C).[6]

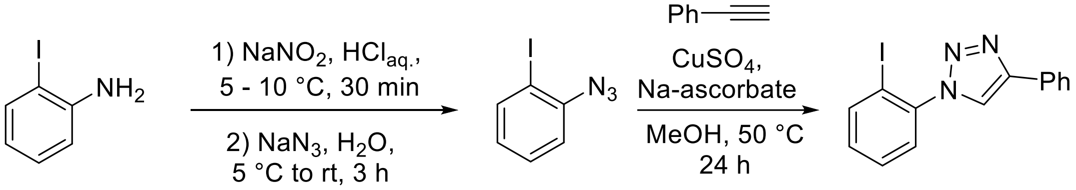
2. Preparation of iodoarenes 1.



1a: According to a modified literature procedure[7] Indazole (7 mmol, 0.827 g) and K_3PO_4 (35 mmol, 7.43 g) were charged in a 250-mL round-bottom flask and DMF (70 mL) was added. 2-Iodofluorobenzene (10.5 mmol, 2.33 g) was added *via* syringe. The reaction mixture was allowed to stir for 5 h at 150 °C (oil bath). Afterwards the mixture was cooled to room temperature and 170 mL of water was added. The water layer was extracted with Et_2O (3 × 100 mL). Combined organic layer was washed with brine (2 × 10 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica (hexane → hexane:EtOAc – 30:1) to give 1-(2-iodophenyl)-*1H*-indazole **1a** as a white slowly crystallizing solid (*It could crystallize over the period of several days to several weeks*), 1.24 g (55 %). mp = 74 – 75 °C. The analytical data are in accordance with previously published.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.25 – 7.20 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 140.4, 140.2, 135.4, 130.7, 129.5, 129.3, 127.1, 124.4, 121.5, 121.3, 110.6, 96.8.



1b, 35 %
over two steps

1b: According to a modified literature procedure[7] 2-iodoaniline (20 mmol, 4.38 g) was suspended in conc. HCl (32 mL) diluted with H_2O (40 mL) and the mixture was cooled with an ice-water bath (approx. 5-10 °C). $NaNO_2$ (22 mmol, 1.52 g) as the water solution (10 mL) was added dropwise. The reaction mixture was stirred for 30 min under cooling. Afterwards the aqueous solution (10 mL) of NaN_3 (30 mmol, 1.95 g) was added under cooling with an ice-water bath and the bath was removed. The reaction proceeded for additional 3 h at room temperature followed by the addition of $NaHCO_3$ sat. solution until slightly basic pH. The water layer was extracted with DCM (4 × 50 mL). Combined organic layer was washed with H_2O (2 × 15 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude residue was used further without any purification.

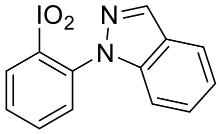
The residue was dissolved in MeOH (40 mL) and phenyl acetylene (30 mmol, 3.3 mL), $CuSO_4·5H_2O$ (4 mmol, 1 g) and sodium ascorbate (10 mmol, 1.98 g) were added to the solution. The mixture was allowed to stir for 24 h at 50 °C (oil bath). Water (160 mL) was added upon cooling to room temperature. The aqueous layer was extracted with DCM (3 × 100 mL). Combined organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude mixture was purified *via* column chromatography on silica (cyclohexane:EtOAc – 9:1 → 4:1) to give 1-(2-iodophenyl)-4-phenyl-*1H*-1,2,3-triazole **1b** as a yellowish solid, 2.43 g (35 %). mp = 152 – 155 °C (lit. 156 – 158 °C).[8] The analytical data are in accordance with previously published.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.57 – 7.43 (m, 4H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.29 – 7.22 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 140.4, 140.2, 131.7, 130.3, 129.4, 129.1, 128.6, 128.0, 126.0, 121.7, 94.1.

3. Preparation of λ^5-Iodanes 2.

General procedure (GP1): iodoarene ***1*** (0.3 mmol) was dissolved in MeCN (3.75 mL). Oxone® (5 equiv., 1.5 mmol, 0.923 g) was added to the mixture neat. Afterwards H_2O (3.75 mL) was added and the mixture was allowed to stir for indicated time at 65 °C (oil bath). Then the reaction was cooled to room temperature and H_2O (15 mL) was added to precipitate the product. The suspension was additionally stored at 4 °C for 3 – 6 h to achieve full precipitation of the solid. Then it was filtered, washed with cold water (3 × 10 mL) and acetone (3 × 3 mL) and dried under vacuum to give iodane ***2***.

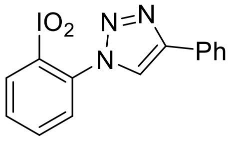


2a: according to ***GP1*** iodoarene ***1a*** (0.3 mmol, 96 mg) reacted with Oxone® for 5 h to give 1-(2-iodylphenyl)-*1H*-indazole ***2a*** as a pale yellow solid, 76 – 86 mg (72 – 81 %). mp = 195 – 196 °C (dec.).

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.62 (s, 1H), 8.27 (dd, *J* = 7.8, 0.6 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.81 – 7.78 (m, 1H), 7.67 – 7.63 (m, 2H), 7.39 (t, *J* = 7.2 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-d_6) δ 141.4, 137.8, 136.9, 136.6, 132.9, 129.1, 126.3, 126.1, 125.7, 122.9, 122.3, 119.6, 111.4.

HRMS (positive mode, MeCN+0.1 % of formic acid) calcd. for $C_{13}H_{10}IN_2O_2^+$ ([M+H$^+$]) 352.97815 (found 352.97821).



2b: according to ***GP1*** iodoarene ***1b*** (0.3 mmol, 104 mg) reacted with Oxone® for 10 h to give 1-(2-iodylphenyl)-4-phenyl-*1H*-1,2,3-triazole ***2b*** as a white solid, 73 mg (64 %). mp = 215 - 216 °C (vigorous dec.; ***handle with care!***).

^{1}H NMR (600 MHz, DMSO-d_6) δ 9.61 (s, 1H), 8.31 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.06 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.85 (td, *J* = 7.2, 1.2 Hz, 1H), 7.81 (td, *J* = 7.8, 1.2 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H).

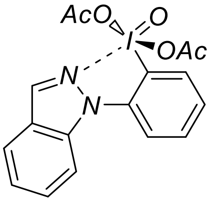
^{13}C NMR (150 MHz, DMSO-d_6) δ 148.2, 140.5, 133.2, 133.0, 129.5, 129.3, 129.2, 128.9, 125.6, 125.5, 119.8, 119.8.

HRMS (positive mode, MeCN+0.1 % of formic acid) calcd. for $C_{14}H_{11}IN_3O_2^+$ ([M+H$^+$]) 379.98905 (found 379.98815).

Gram-scale synthesis of iodane 2a.

1-(2-Iodophenyl)-*1H*-indazole ***1a*** (3.85 mmol, 1.23 g) was dissolved in MeCN (48 mL). Oxone® (9.23 mmol, 11.83 g) was added to the mixture neat. Afterwards H_2O (48 mL) was added and the mixture was allowed to stir for 5 h at 65 °C (oil bath). Then the reaction was cooled to room temperature and H_2O (190 mL) was added to precipitate the product. The suspension was additionally stored at 4 °C overnight to achieve full precipitation of the solid. Then it was filtered, washed with cold water (3 × 100 mL) and acetone (3 × 15 mL) and dried under vacuum to give 1-(2-iodylphenyl)-*1H*-indazole ***2a*** as a yellowish solid, 1.02 g (75 %). mp = 194 – 195 °C. NMR spectra are in accordance with the product ***2a***.

In situ preparation of iodane 2a'



2a’: 1-(2-iodylphenyl)-*1H*-indazole ***2a*** (0.1 mmol, 35 mg) was suspended in $CDCl_3$ (2 mL) and Ac_2O (3 equiv., 28 μL) was added. The reaction mixture was allowed to stir at room temperature for 6 h until the clear solution was observed. The sample from the mixture (approx. 0.3 mL) was diluted with $CDCl_3$ and NMR spectra were recorded.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.4 Hz, 1H), 8.40 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.83 (t, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.41 – 7.39 (m, 1H), 1.78 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.2, 138.4, 137.3, 136.5, 135.7, 133.9, 130.1, 126.9, 126.7, 126.2, 123.9, 122.9, 118.8, 111.4, 20.9.

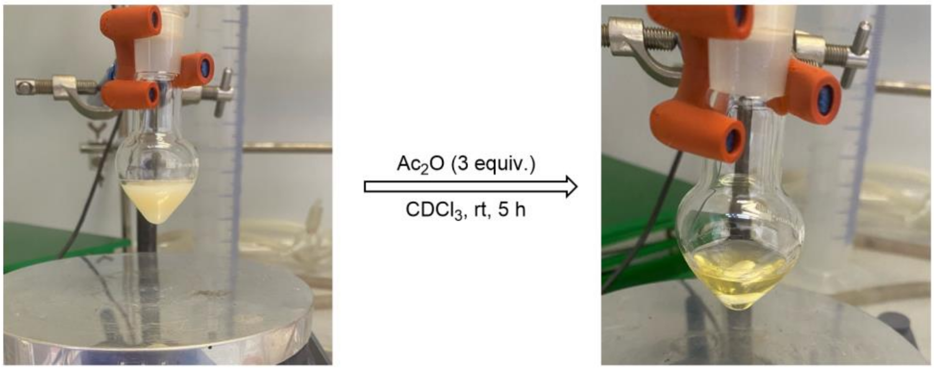


Figure 1. Preparation of iodane ***2a’***.

4. *Preparation of carbonyl compounds 3.*

Table 1. *Optimization of 1-phenylethanol oxidation with iodanes **2***

№	***Iodane***	**Solvent**	**Additive**	**Temp.**	**Yield^{a,b}**
1	***2a***	$CDCl_3$	-	rt	traces
2	***2b***	$CDCl_3$	-	rt	2 %
3^c	***2a***	$CDCl_3$	TFA (2.6 equiv.)	rt	70 %
4^c	***2b***	$CDCl_3$	TFA (2.6 equiv.)	rt	58 %
5	***2a***	MeCN-d_3	-	rt	2 %
6	***2a***	MeCN-d_3	-	50 °C	4 %
7	***2a***	DMSO-d_6	-	rt	6 %
8^c	***2a***	$CDCl_3$	Ac_2O (1.3 equiv.)	rt	10 %^{c}
9^c	***2a***	$CDCl_3$	Ac_2O (2.6 equiv.)	rt	66 %^{c}
10^c	***2a***	**$CDCl_3$**	**Ac_2O (3.9 equiv.)**	**rt**	**quant.^{c}**
11^c	***2a***	$CDCl_3$	TFAA (2.6 equiv.)	rt	75 %^{c}
12^c	***2a***	$CDCl_3$	TFAA (3.9 equiv.)	rt	55 %^{c}
13^c	***2a***	$CDCl_3$	AcOH (7.8 equiv.)	rt	traces

Reaction conditions: ^{a} Reaction conditions: 0.1 mmol of 1-phenylethanol (0.1 mmol, 12 mg), **2** (0.13 mmol), solvent (2 mL). ^{b} Yields were determined by NMR with 1,2-dibromoethane as an internal standard; ^{c} λ^5-iodane was premixed with an additive in 1 mL of the solvent for 30 minutes and the alcohol was added afterwards as the solution in the reaction solvent (1 mL, 2 mL for a reaction in total).

***Supplementary Note 1*:**

Iodanes ***2a*** and ***2b*** were practically inactive without additives (Table 1, entries 1, 2, 5-7). TFA as an additive improved the yields to 70 % and 58 % for ***2a*** and ***2b*** respectively (Table 1, entries 3 and 4). Ac_2O were an additive of choice since three-fold excess of it gave the quant. yield after 24 h (Table 1, entry 10). TFAA as an additive also was a good option yet the acylation of the alcohol lowered the yield of desired ketone ***3i*** (Table 1, entries 11-12). Control experiment with AcOH afforded only traces of the product (Table 1, entry 13).

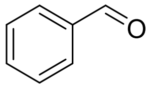
For the preparation of the scope of carbonyl compounds DCM was used instead of $CHCl_3$ since commercial chloroform contains ethanol as a stabilizer which reacts with iodanes itself. To avoid purification of the solvent such replacement was made.

General procedure (GP2): 1-(2-Iodylphenyl)-*1H*-indazole ***2a*** (0.13 mmol, 46 mg) was charged in a reaction vessel and DCM (1 mL) was added. Ac_2O (0.39 mmol, 36.6 µL) was added and the mixture was allowed to stir at room temperature for 30 min following by addition of the solution of an alcohol (0.1 mmol) in DCM (1 mL). The reaction vessel was capped and the reaction was stirred for 24 h at room temperature.

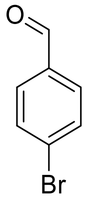
Purification procedure A: after ***GP2*** the solvent was removed under reduced pressure and the residue was purified *via* column chromatography on silica (eluent specified for each compound) to give carbonyl compound ***3***.

Purification procedure B: after ***GP2*** the solution was filtered through a pad of silica (2-3 cm) and washed with hexane:EtOAc – 4:1 (approx. 70-80 mL) to get rid of remaining iodane. Then solvent was removed and 5 mL of sat. $NaHSO_3$ aqueous solution was added. The solution was stirred for at least 3 h at room temperature and all the impurities was extracted with hexane:EtOAc – 4:1 (4 × 5 mL). The water layer was basified with NaOH 50 % solution and extracted with DCM (3 × 5 mL). Combined organic layers were washed with water (2 × 2 mL) and dried over anhydrous Na_2SO_4. The solution was filtered and the solvent was removed under reduced pressure to give carbonyl compounds ***3***.

General procedure (GP3): 1-(2-Iodylphenyl)-*1H*-indazole ***2a*** (0.13 mmol, 46 mg) was charged in a reaction vessel and $CDCl_3$ (1 mL) was added. Ac_2O (0.39 mmol, 36.6 µL) or TFA (0.39 mmol, 30 µL) was added and the mixture was allowed to stir at room temperature for 30 min following by addition of the solution of an alcohol (0.1 mmol) in $CDCl_3$ (1 mL). The reaction vessel was capped and the reaction was stirred for 24 h at room temperature. Then $NaHCO_3$ (0.8 mmol, 67 mg) was added neat and the mixture was allowed to stir for 30 min. 1,2-Dibromoethane (0.1 mmol, 8.7 µL) was added as an internal standard, 0.5 mL of the mixture was filtered and ^1H NMR was recorded to determine the NMR yield (*integration of the aldehyde proton*).



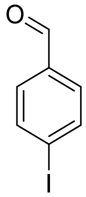
3a: according to ***GP3*** benzyl alcohol (0.1 mmol, 11 mg) reacted with iodane ***2a*** in the presence of Ac_2O to give benzaldehyde ***3a***, NMR yield: 70 %.



3b: according to ***GP2*** 4-bromobenzyl alcohol (0.1 mmol, 19 mg) reacted with iodane ***2a*** followed by column chromatography (cyclohexane:EtOAc – 50:1) (***purification procedure A***) to give 4-bromobenzaldehyde ***3b*** as a colorless solid, 18 mg (96 %). mp = 52 – 53 °C (lit. 51.8 – 53.2°C).[9] The analytical data are in accordance with previously published.[9]

^1H NMR (600 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H).

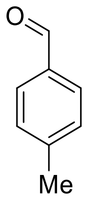
^{13}C NMR (150 MHz, $CDCl_3$) δ 191.2, 135.2, 132.6, 131.1, 129.9.



3c: according to ***GP2*** 4-iodobenzyl alcohol (0.1 mmol, 23.5 mg) reacted with iodane ***2a*** followed by column chromatography (cyclohexane:EtOAc – 30:1) (***purification procedure A***) to give 4-iodobenzaldehyde ***3c*** as a colorless solid, 22.5 mg (97 %). mp = 74 – 74 °C (lit. 74 – 75°C).[10] The analytical data is in accordance with previously published.[11]

^1H NMR (600 MHz, DMSO-d_6) δ 9.96 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H).

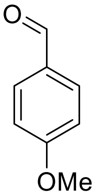
^{13}C NMR (150 MHz, DMSO-d_6) δ 192.7, 138.1, 135.4, 130.9, 103.6.



3d: according to ***GP2*** 4-methylbenzyl alcohol (0.1 mmol, 12 mg) reacted with iodane ***2a*** and after ***purification procedure B*** gave 4-methylbenzaldehyde ***3d*** as a yellowish liquid, 6.5 mg (55 %). The analytical data are in accordance with previously published.[12]

^1H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H).

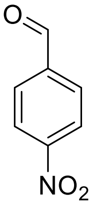
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 145.7, 134.3, 130.0, 129.9, 22.0.



3e: according to ***GP2*** 4-methoxybenzyl alcohol (0.1 mmol, 14 mg) reacted with iodane ***2a*** followed by column chromatography (gradient elution: hexane:EtOAc – 20:1 → hexane:EtOAc – 10:1) (***purification procedure A***) to give 4-methoxybenzaldehyde ***3e*** as a colorless oil, 6.5 mg (55 %). The analytical data is in accordance with previously published.[13]

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.87 (s, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H).

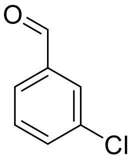
^{13}C NMR (100 MHz, DMSO-d_6) δ 191.3, 164.2, 131.8, 129.7, 114.5, 55.7.



3f: according to ***GP2*** 4-nitrobenzyl alcohol (0.1 mmol, 14 mg) reacted with iodane ***2a*** followed by column chromatography (gradient elution: hexane → hexane:EtOAc – 10:1) (***purification procedure A***) to give 4-nitrobenzaldehyde ***3f*** as a colorless solid, 15 mg (> 99 %). m.p. = 104 – 105 °C (lit. 104 – 105 °C).[14] The analytical data are in accordance with previously published.[15]

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.16 (s, 1H), 8.42 (d, J = 8.4 Hz, 2H), 8.16 (d, J = 8.4 Hz, 2H).

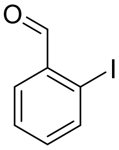
^{13}C NMR (100 MHz, DMSO-d_6) δ 192.4, 150.6, 140.1, 130.6, 124.3.



3g: according to ***GP2*** 3-chlorobenzyl alcohol (0.1 mmol, 14 mg) reacted with iodane ***2a*** and after ***purification procedure B*** gave 3-chlorobenzaldehyde ***3g*** as a yellow liquid, 8 mg (57 %). The analytical data are in accordance with previously published.[16]

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.98 (s, 1H), 7.86 (s, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H).

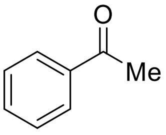
^{13}C NMR (100 MHz, CDCl$_3$) δ 191.0, 137.9, 135.6, 134.6, 130.5, 129.5, 128.1.



3h: according to ***GP2*** 2-iodobenzyl alcohol (0.1 mmol, 23 mg) reacted with iodane ***2a*** followed by column chromatography (hexane:EtOAc – 20:1) (***purification procedure A***) to give 2-iodobenzaldehyde ***3h*** as a colorless solid, 18.5 mg (80 %). m.p. = 32 – 33 °C (lit. 30 – 31 °C).[17] The analytical data are in accordance with previously published.[17]

^{1}H NMR (400 MHz, CDCl$_3$) δ 10.07 (d, J = 0.8 Hz, 1H), 7.96 (dd, J = 8.0, 0.8 Hz, 1H), 7.89 (dd, J = 8.0, 1.6 Hz, 1H), 7.47 (tt, J = 7.6, 0.8 Hz, 1H), 7.31 – 7.27 (m, 1H).

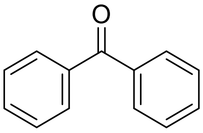
^{13}C NMR (100 MHz, CDCl$_3$) δ 196.0, 140.8, 135.6, 135.3, 130.4, 128.9, 100.9.



3i: according to ***GP2*** 1-phenylethanol (0.1 mmol, 12 mg) reacted with iodane ***2a*** followed by column chromatography (cyclohexane:EtOAc – 50:1) (***purification procedure A***) to give acetophenone ***3i*** as a yellowish liquid, 9.5 mg (79 %). The analytical data are in accordance with previously published.[18]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 2.61 (s, 3H).

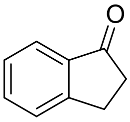
^{13}C NMR (150 MHz, $CDCl_3$) δ 198.3, 137.3, 133.3, 128.7, 128.5, 26.8.



3j: according to ***GP2*** diphenylmethanol (0.1 mmol, 18.5 mg) reacted with iodane ***2a*** followed by column chromatography (hexane:EtOAc – 20:1) (***purification procedure A***) to give benzophenone ***3j*** as an off-white solid, 18 mg (98 %). m.p. = 43 – 44 °C (lit. 46 – 47 °C).[17] The analytical data are in accordance with previously published.[19]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 4H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 4H).

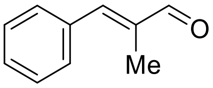
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 137.7, 132.6, 130.2, 128.4.



3k: according to ***GP2*** 2,3-dihydro-*1H*-inden-1-ol (0.1 mmol, 13.5 mg) reacted with iodane ***2a*** followed by column chromatography (gradient elution: hexane → hexane:EtOAc – 20:1) (***purification procedure A***) to give 2,3-dihydro-*1H*-inden-1-one ***3k*** as a yellowish solid, 7.5 mg (57 %). mp = 37 – 38 °C (lit. 37 – 39 °C).[20] The analytical data are in accordance with previously published.[21]

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.66 – 7.63 (m, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 3.10 (t, *J* = 5.6 Hz, 2H), 2.63 (t, *J* = 5.6 Hz, 2H).

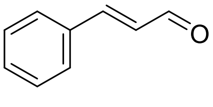
^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 206.3, 155.3, 136.7, 134.6, 127.2, 127.0, 122.9, 35.8, 25.4.



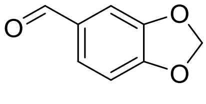
3l: according to ***GP2*** *(E)*-2-methyl-3-phenylprop-2-en-1-ol (0.1 mmol, 15 mg) reacted with iodane ***2a*** followed by column chromatography (PE:EtOAc – 30:1) (***purification procedure A***) to give *(E)*-2-methyl-3-phenylacrylaldehyde ***3l*** as a colorless liquid, 10.5 mg (71 %). The analytical data are in accordance with previously published.[22]

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.58 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.52 – 7.43 (m, 4H), 1.98 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 195.7, 149.7, 137.5, 134.9, 130.1, 129.7, 128.8, 10.6.



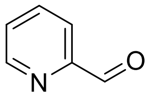
3m: according to ***GP3*** cinnamyl alcohol (0.1 mmol, 14 mg) reacted with iodane ***2a*** in the presence of Ac_2O to give cinnamaldehyde ***3m***, NMR yield: > 99 %.



3n: according to ***GP2*** benzo[*d*][*1,3*]dioxol-5-ylmethanol (0.1 mmol, 15 mg) reacted with iodane ***2a*** and after ***purification procedure B*** gave benzo[*d*][1,3]dioxole-5-carbaldehyde ***3n*** as a yellow oil, 7 mg (47 %). The analytical data are in accordance with previously published.[23]

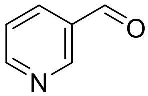
^{1}H NMR (400 MHz, CDCl$_3$) δ 9.81 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.34 (s, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.08 (s, 2H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 190.4, 153.3, 148.9, 132.1, 128.8, 108.5, 107.1, 102.3.



3o: according to ***GP3*** (pyridin-2-yl)methanol (0.1 mmol, 11 mg) reacted with iodane ***2a*** in the presence of TFA to give picolinaldehyde ***3o***, NMR yield: 57 %.

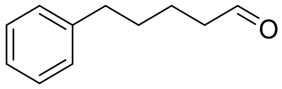
Synthesis of nicotinaldehyde 3p.



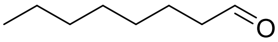
3p: 1-(2-Iodylphenyl)-*1H*-indazole ***2a*** (0.13 mmol, 46 mg) was charged in a reaction vessel and DCM (1 mL) was added. TFA (0.39 mmol, 30 µL) was added and the mixture was allowed to stir at room temperature for 30 min following by addition of the (piridin-3-yl)methanol (0.1 mmol, 11 mg) as DCM (1 mL) solution. The reaction vessel was capped and the reaction was stirred for 24 h at room temperature. Then solvent was removed under reduced pressure and the residue was purified *via* column chromatography on silica (gradient elution DCM → DCM:MeOH – 20:1) to give nicotinaldehyde ***3p*** as a brownish liquid, 8.5 mg (78 %). The analytical data are in accordance with previously published.[24]

^{1}H NMR (600 MHz, CDCl$_3$) δ 10.12 (s, 1H), 9.09 (s, 1H), 8.85 (s, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.48 (m, 1H).

^{13}C NMR (150 MHz, CDCl$_3$) δ 190.9, 154.9, 152.3, 135.9, 131.6, 124.3.



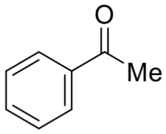
3q: according to ***GP3*** 5-phenylpentan-1-ol (0.1 mmol, 16 mg) reacted with iodane ***2a*** in the presence of Ac$_2$O to give 5-phenylpentanal ***3q***, NMR yield: 40 %.



3r: according to ***GP3*** octan-1-ol (0.1 mmol, 13 mg) reacted with iodane ***2a*** in the presence of Ac$_2$O to give octanal ***3r***, NMR yield: 31 %.

5. Additional experiments

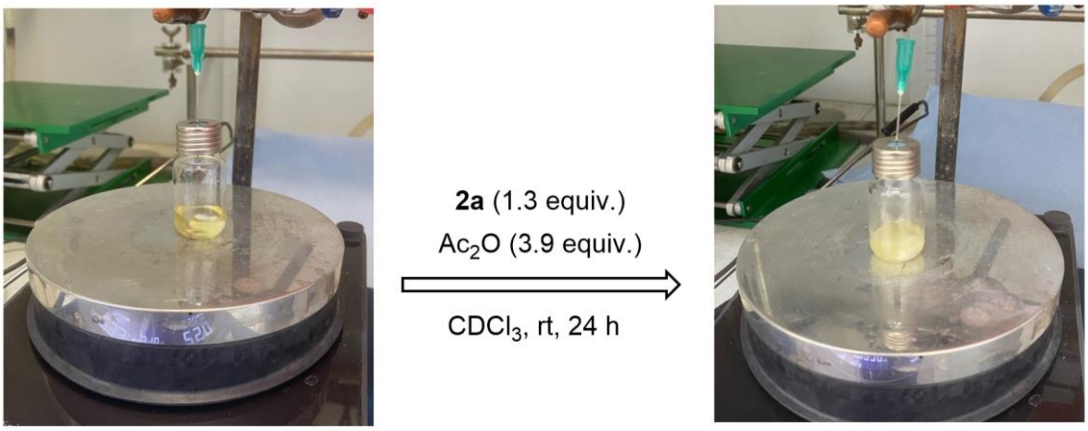
Oxidation with an open vessel



3i: 1-(2-Iodylphenyl)-*1H*-indazole ***2a*** (0.13 mmol, 46 mg) was charged in a reaction vessel and $CDCl_3$ (1 mL) was added. Ac_2O (0.39 mmol, 36.6 µL) was added and the mixture was allowed to stir at room temperature for 30 min following by addition of the 1-phenylehtanol (0.1 mmol, 12 mg) as $CDCl_3$ (1 mL) solution. The reaction vessel was capped, pierced with a needle and the reaction was stirred for 24 h at room temperature to give acetophenone ***3i***. After than the 1,2-dibromoethane was added as an internal standard, sample of aprrox. 0.5 mL was transferred to the NMR tube and the ^{1}H NMR spectrum was recorded to determine the yield. NMR yield: 96 %.

Supplementary note 2

We observed full dissolution of the starting materials after approx. 4 h after the start of the reaction. After 24 h there were a small amount of the precipitate (Fig.2), presumably iodane ***2a*** after the hydrolysis of *in situ* formed diacetate ***2a’***. It seems that the rate of hydrolysis was lower under given conditions than the rate of alcohol oxidation since the moisture from air did not change the yield substantially. Thus, we believe that deviation between the yield of ***3i*** in the optimization table (Table 1, entry 10) is a little higher compared to the one in the comparison experiment (Fig. 2 in the main text) due to the fact that samples in the first several hours contained unreacted iodane ***2a*** in solid form.

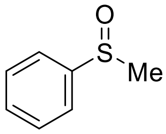


after 4 h

after 24 h

Figure 2. Preparation of acetophenone ***3i*** in the vessel opened to air

Preparation of methyl phenyl sulfoxide



4: 1-(2-Iodylphenyl)-*1H*-indazole ***2a*** (0.11 mmol, 39 mg) was charged in a reaction vessel and MeCN (1 mL) was added. Thioanisole (0.1 mmol, 11.7 µL) was added neat. The reaction vessel was capped, placed in the preheated aluminium block and stirred for 10 h. Solvent was removed under reduced pressure and the residue was purified via column on silica (eluent: DCM:MeOH – 20:1) to give methyl phenyl sulfoxide **4** as a slightly yellow oil (freezes in a refrigerator), 10.4 mg (75 %). The analytical data are in accordance with previously published.[25]

1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.2 Hz, 2H), 7.54 – 7.48 (m, 3H), 2.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 131.2, 129.5, 123.6, 44.1.

α,β – Dehydrogenation of carbonyl compounds (unsuccessful experiments)

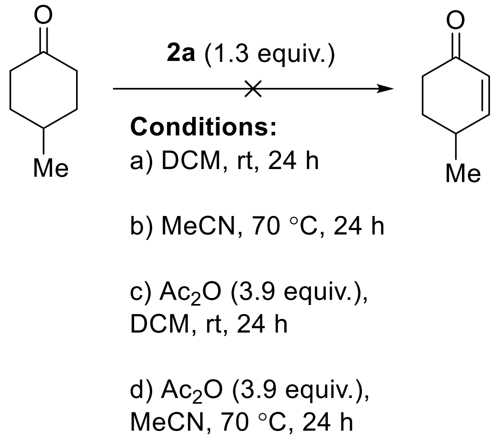
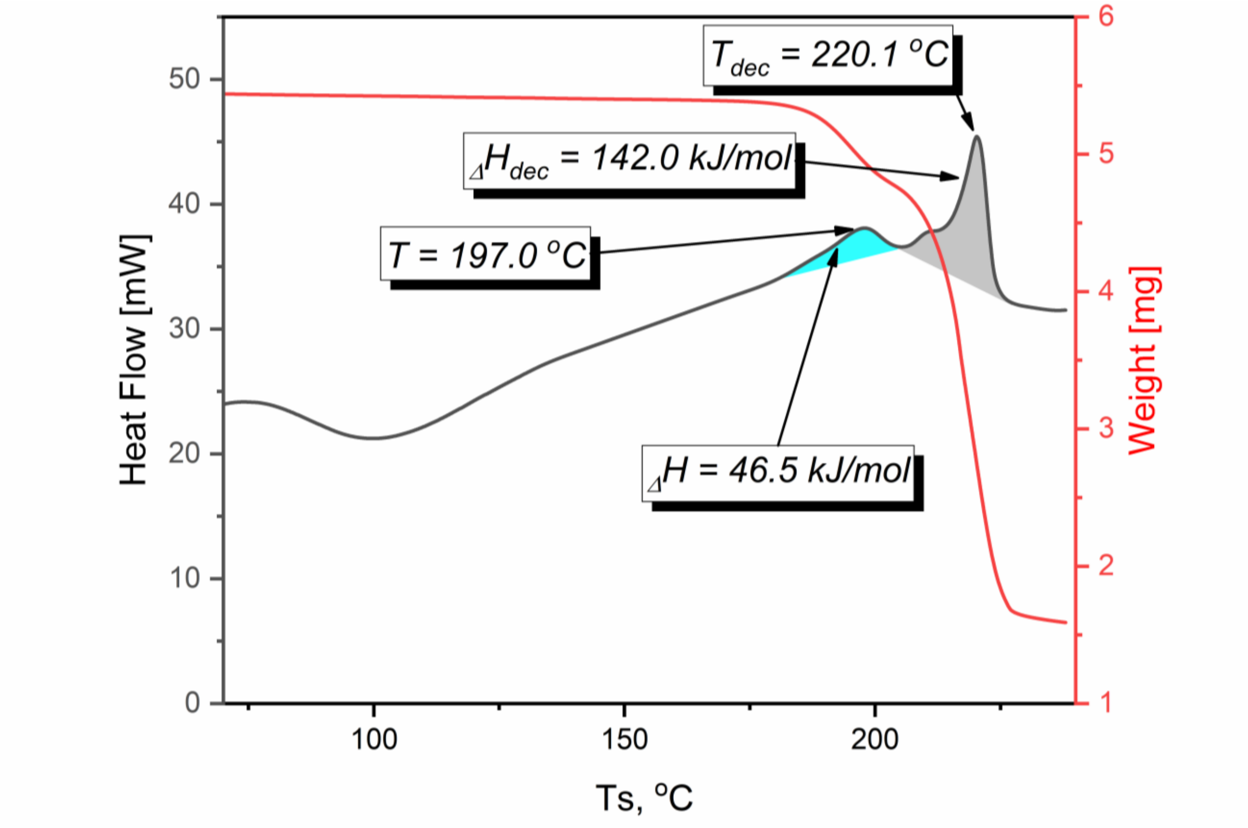


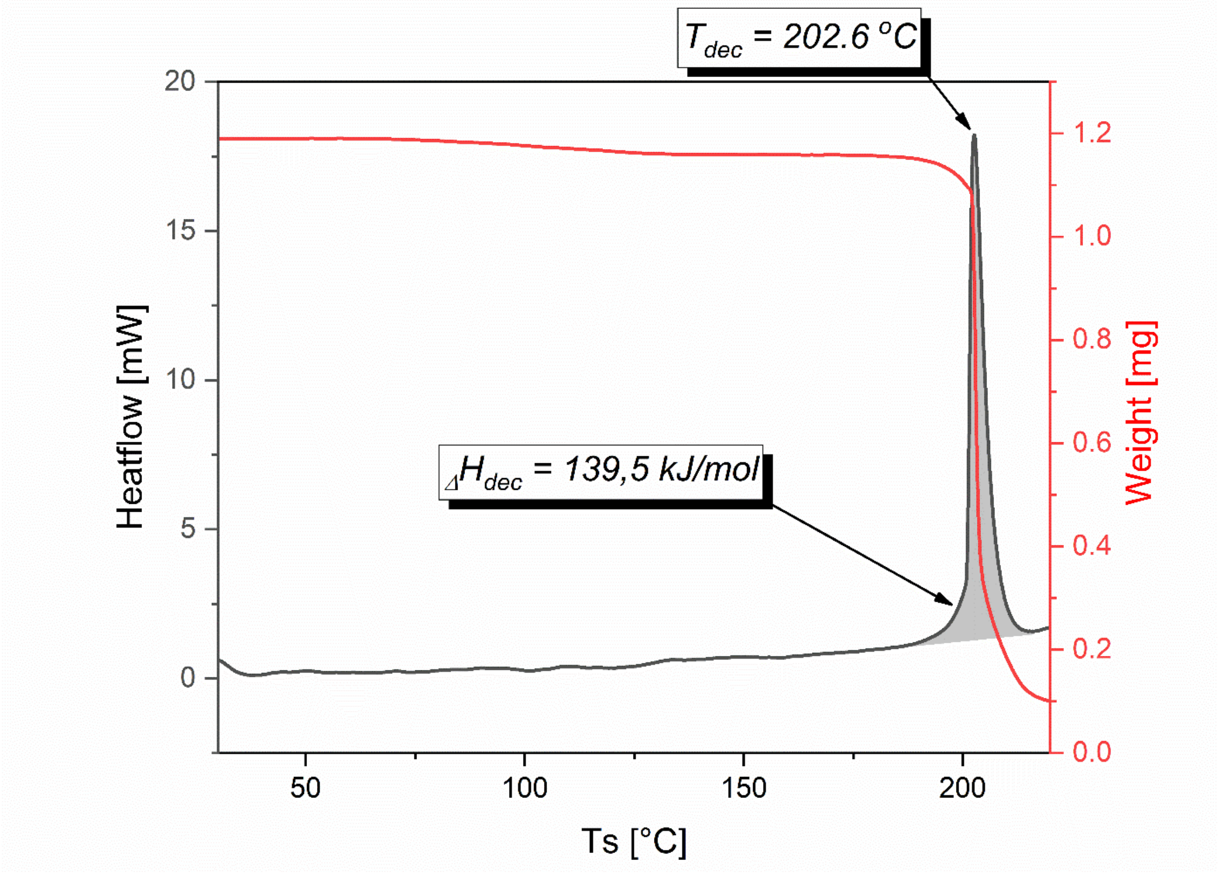
Figure 3. Conditions for the unsuccessful experiments on dehydrogenation of 4-methylcyclohexanone

6. Thermal analysis plots

a) ***IBX*** (rt to 238°C, 10 °C/min; air atmosphere)

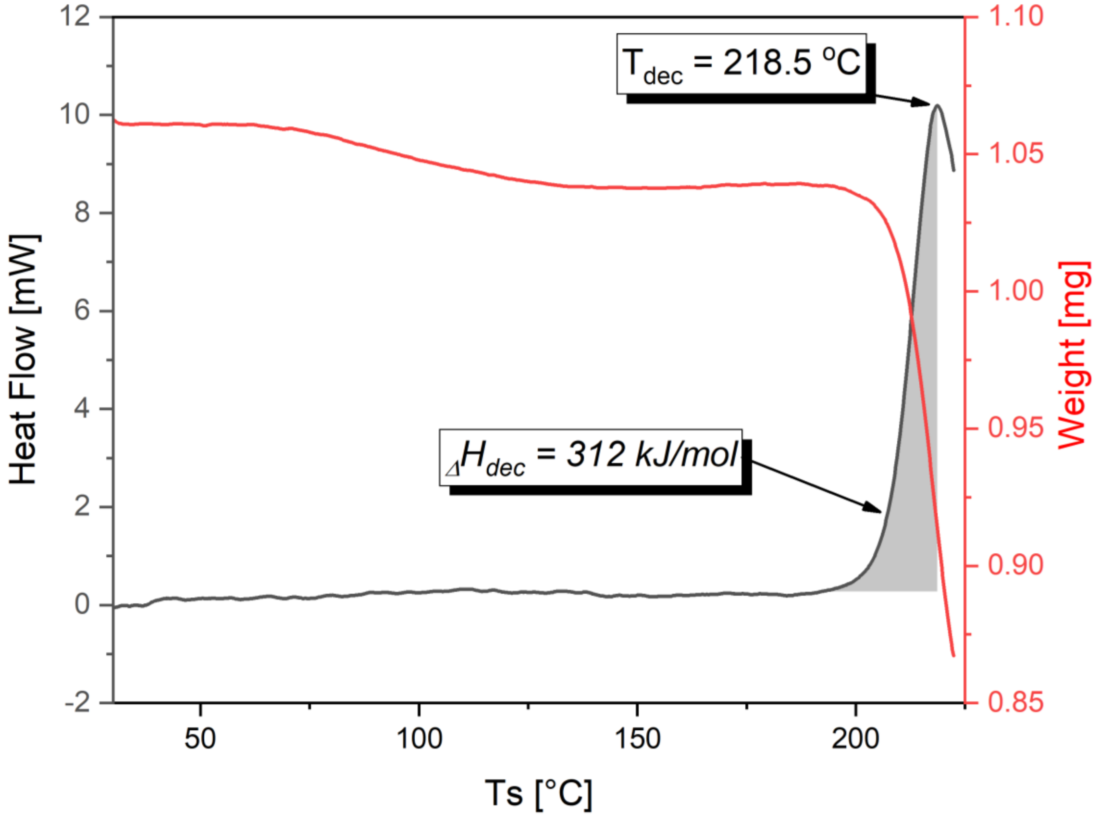


b) ***Iodane 2a*** (rt to 225 °C; 10 °C/min; air atmosphere)



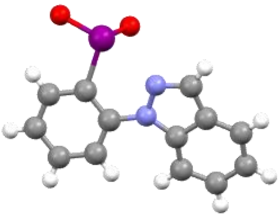
c) ***Iodane 2b*** (rt to 225 °C; 10 °C/min; air atmosphere).

Integration was done for half of the peak and then doubled due to explosion at the temperature where the plot ends.



7. Crystal data

2a (CCDC 2364396). Crystal was grown by slow evaporation of AcOH:H_2O – 3:2 solution of *2a*.



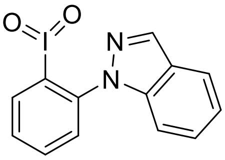


Table 2 Crystal data and structure refinement for 2a.

Empirical formula	$C_{13}H_9IN_2O_2$
Formula weight	352.12
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.5622(6)
b/Å	11.6742(8)
c/Å	15.1234(11)
α/°	90
β/°	92.555(3)
γ/°	90
Volume/Å^3	1157.43(16)
Z	4
ρ_{calc}g/cm^3	2.021
μ/mm^{-1}	2.761
F(000)	680.0
Crystal size/mm^3	0.6 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.214 to 72.702
Index ranges	$-10 \leq h \leq 10$, $-19 \leq k \leq 19$, $-25 \leq l \leq 20$
Reflections collected	33426
Independent reflections	5599 [R_{int} = 0.0342, R_{sigma} = 0.0235]
Data/restraints/parameters	5599/0/163
Goodness-of-fit on F^2	1.049

Final R indexes [I>=2σ (I)]	R_1 = 0.0185, wR_2 = 0.0411
Final R indexes [all data]	R_1 = 0.0216, wR_2 = 0.0424
Largest diff. peak/hole / e Å^{-3}	0.62/-0.54

Table 3 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	2501.8(2)	5349.7(2)	4532.8(2)	9.67(2)
O1	1143.9(14)	5924.2(8)	5452.7(6)	14.79(16)
O2	4851.9(14)	6152.5(8)	4654.5(6)	14.92(16)
N2	4125.2(16)	4988.3(10)	2984.6(7)	13.13(17)
N1	3411.3(16)	5823.5(9)	2416.8(7)	11.50(16)
C5	563.5(19)	7109.7(11)	2052.1(8)	13.7(2)
C6	1681.8(17)	6437.1(10)	2663.3(7)	10.67(18)
C1	1021.8(18)	6370.4(10)	3533.1(7)	11.03(18)
C13	5752(2)	4534.8(11)	2643.8(9)	14.5(2)
C4	-1151(2)	7697.7(11)	2307.2(8)	15.5(2)
C3	-1803.0(19)	7627.3(12)	3169.5(9)	15.9(2)
C12	6143.6(19)	5054.8(11)	1818.7(8)	13.6(2)
C7	4623.9(18)	5903.5(10)	1693.4(8)	11.54(18)
C2	-708.4(19)	6951.1(11)	3781.2(8)	13.7(2)
C9	6076(2)	6459.1(12)	350.4(9)	17.3(2)
C10	7550(2)	5590.9(13)	451.9(9)	20.3(3)
C11	7619(2)	4888.4(12)	1186.5(9)	18.2(2)
C8	4599.8(19)	6638.2(11)	958.7(8)	14.5(2)

Table 4 Anisotropic Displacement Parameters (Å^2×10^3) for 2a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	8.87(3)	11.16(3)	8.97(3)	1.10(2)	0.23(2)	-1.32(2)
O1	15.5(4)	18.4(4)	10.6(3)	-2.0(3)	2.4(3)	-1.0(3)
O2	11.1(4)	13.9(4)	19.6(4)	1.9(3)	-1.6(3)	-4.5(3)

Table 4 Anisotropic Displacement Parameters (Å^2×10^3) for 2a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	12.7(4)	13.3(4)	13.5(4)	3.5(3)	1.6(3)	2.3(3)
N1	11.9(4)	11.9(4)	11.0(4)	2.3(3)	2.8(3)	2.4(3)
C5	13.4(5)	16.1(5)	11.5(5)	2.3(4)	1.2(4)	1.9(4)
C6	9.0(4)	11.6(4)	11.4(4)	0.1(3)	1.2(3)	-0.1(3)
C1	10.7(4)	11.7(5)	10.7(4)	1.1(3)	1.1(3)	0.0(3)
C13	14.1(5)	13.8(5)	15.8(5)	2.4(4)	3.1(4)	3.1(4)
C4	14.3(5)	17.6(5)	14.7(5)	3.8(4)	0.8(4)	4.3(4)
C3	13.5(5)	18.2(6)	16.1(5)	1.9(4)	3.6(4)	5.1(4)
C12	12.4(5)	12.5(5)	16.1(5)	0.7(4)	2.9(4)	1.7(4)
C7	11.7(5)	11.9(5)	11.2(4)	0.1(3)	2.4(3)	1.1(4)
C2	13.2(5)	15.7(5)	12.5(5)	0.8(4)	3.4(4)	2.2(4)
C9	18.1(6)	19.3(6)	15.2(5)	2.9(4)	7.0(4)	2.7(4)
C10	20.7(6)	22.2(6)	18.7(6)	2.0(5)	9.4(5)	5.4(5)
C11	16.1(6)	18.7(6)	20.4(6)	2.0(4)	6.9(4)	5.3(4)
C8	15.3(5)	14.3(5)	14.1(5)	2.3(4)	3.9(4)	2.3(4)

Table 5 Bond Lengths for 2a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	O1	1.8138(9)	C1	C2	1.3883(16)
I1	O2	1.8070(9)	C13	C12	1.4213(18)
I1	C1	2.1256(11)	C4	C3	1.3929(18)
N2	N1	1.3680(14)	C3	C2	1.3913(18)
N2	C13	1.3172(16)	C12	C7	1.4126(17)
N1	C6	1.4064(15)	C12	C11	1.4039(18)
N1	C7	1.3843(15)	C7	C8	1.4032(17)
C5	C6	1.3961(17)	C9	C10	1.4047(19)
C5	C4	1.3872(17)	C9	C8	1.3811(17)
C6	C1	1.4052(16)	C10	C11	1.380(2)

Table 6 Bond Angles for 2a.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	I1	C1	96.53(4)	N2	C13	C12	110.68(11)
O2	I1	O1	100.16(4)	C5	C4	C3	121.20(11)
O2	I1	C1	98.19(4)	C2	C3	C4	119.00(11)
C13	N2	N1	107.56(10)	C7	C12	C13	105.26(10)
N2	N1	C6	117.03(9)	C11	C12	C13	134.09(12)
N2	N1	C7	110.57(9)	C11	C12	C7	120.65(12)
C7	N1	C6	132.39(10)	N1	C7	C12	105.90(10)
C4	C5	C6	120.20(11)	N1	C7	C8	132.88(11)
C5	C6	N1	121.17(10)	C8	C7	C12	121.19(11)
C5	C6	C1	118.43(11)	C1	C2	C3	120.10(11)
C1	C6	N1	120.40(10)	C8	C9	C10	122.43(12)
C6	C1	I1	123.14(8)	C11	C10	C9	120.97(12)
C2	C1	I1	115.77(8)	C10	C11	C12	117.84(12)
C2	C1	C6	121.06(11)	C9	C8	C7	116.84(11)

Table 7 Torsion Angles for 2a.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
I1	C1	C2	C3	-178.98(10)	C13	N2	N1	C6	-178.97(11)
N2	N1	C6	C5	-165.06(11)	C13	N2	N1	C7	-0.06(14)
N2	N1	C6	C1	13.94(16)	C13	C12	C7	N1	-1.61(14)
N2	N1	C7	C12	1.09(14)	C13	C12	C7	C8	176.65(12)
N2	N1	C7	C8	-176.88(13)	C13	C12	C11	C10	-178.57(15)
N2	C13	C12	C7	1.66(15)	C4	C5	C6	N1	179.28(12)
N2	C13	C12	C11	-178.69(15)	C4	C5	C6	C1	0.26(18)
N1	N2	C13	C12	-1.01(15)	C4	C3	C2	C1	0.9(2)
N1	C6	C1	I1	-0.77(16)	C12	C7	C8	C9	2.60(19)
N1	C6	C1	C2	-178.57(11)	C7	N1	C6	C5	16.3(2)
N1	C7	C8	C9	-179.69(13)	C7	N1	C6	C1	-164.67(12)
C5	C6	C1	I1	178.26(9)	C7	C12	C11	C10	1.0(2)

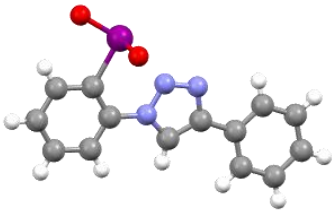
Table 7 Torsion Angles for 2a.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C5	C6	C1	C2	0.46(18)	C9	C10	C11	C12	1.3(2)
C5	C4	C3	C2	-0.1(2)	C10	C9	C8	C7	-0.3(2)
C6	N1	C7	C12	179.77(12)	C11	C12	C7	N1	178.69(12)
C6	N1	C7	C8	1.8(2)	C11	C12	C7	C8	-3.05(19)
C6	C5	C4	C3	-0.4(2)	C8	C9	C10	C11	-1.7(2)
C6	C1	C2	C3	-1.03(19)					

Table 8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2a.

Atom	*x*	*y*	*z*	U(eq)
H5	977.96	7164.99	1459.73	16
H13	6553.95	3941.55	2912.53	17
H4	-1893.6	8156.64	1886.17	19
H3	-2977.51	8035.01	3337.42	19
H2	-1145.65	6886.51	4369.54	16
H9	6094.7	6940.9	-155.41	21
H10	8512.98	5485.83	8.41	24
H11	8631.34	4310.85	1262.02	22
H8	3614.99	7230.72	883.32	17

2b (CCDC: 2364398). Crystal was grown by slow evaporation of AcOH solution of 2b.



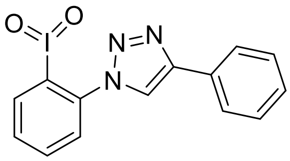


Table 9 Crystal data and structure refinement for 2b.

Empirical formula	$C_{14}H_{10}IN_3O_2$
Formula weight	379.15
Temperature/K	100.00

Crystal system	trigonal
Space group	R3c
a/Å	26.9537(8)
b/Å	26.9537(8)
c/Å	9.8807(5)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	6216.6(5)
Z	18
ρ_{calc}g/cm^3	1.823
μ/mm^{-1}	2.322
F(000)	3312.0
Crystal size/mm^3	0.11 × 0.04 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.046 to 61.124
Index ranges	$-38 \le h \le 38$, $-38 \le k \le 38$, $-14 \le l \le 14$
Reflections collected	64874
Independent reflections	4233 [R_{int} = 0.0626, R_{sigma} = 0.0269]
Data/restraints/parameters	4233/1/181
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0273, wR_2 = 0.0523
Final R indexes [all data]	R_1 = 0.0290, wR_2 = 0.0528
Largest diff. peak/hole / e Å^{-3}	0.72/-1.02
Flack parameter	0.003(9)

Table 10 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2b. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	248.7(2)	3243.1(2)	3342.0(4)	14.24(6)

Table 10 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2b. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	17.1(15)	2711.8(15)	4698(3)	18.2(7)
N1	1598.5(17)	3732.4(18)	4332(4)	18.0(8)
O2	-266.4(15)	2815.9(15)	2060(4)	19.4(7)
N2	1199.4(18)	3853.9(19)	4783(5)	19.4(8)
C4	1154(2)	2569(2)	1102(5)	21.7(10)
C7	2098(2)	4047(2)	5007(5)	19.6(9)
C5	1687(2)	2793(2)	1722(6)	22.1(10)
N3	1426.8(18)	4239.6(19)	5730(4)	21.7(9)
C2	907(2)	3099(2)	2645(5)	17.0(9)
C3	762(2)	2724(2)	1562(6)	20.9(10)
C8	1981(2)	4367(2)	5908(5)	19.6(9)
C6	1836(2)	3174(2)	2794(5)	21.4(10)
C1	1447(2)	3332(2)	3257(6)	18.5(9)
C10	2881(2)	4873(2)	7276(5)	22.6(10)
C14	2146(2)	5121(2)	7576(6)	27.7(11)
C9	2345(2)	4795(2)	6925(5)	21.3(9)
C11	3207(2)	5272(2)	8256(6)	28.5(11)
C13	2468(3)	5509(3)	8562(7)	33.1(13)
C12	3001(2)	5592(3)	8901(6)	30.9(12)

Table 11 Anisotropic Displacement Parameters (Å^2×10^3) for 2b. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	13.17(12)	15.20(13)	13.58(10)	0.70(11)	0.02(10)	6.51(11)
O1	20.6(17)	18.1(17)	16.7(19)	3.9(13)	2.3(13)	10.3(14)
N1	14.0(18)	17.7(19)	20(2)	0.1(15)	-1.2(15)	6.2(15)
O2	15.7(16)	20.2(17)	18.9(17)	-1.8(13)	-4.0(13)	6.4(14)
N2	14.7(18)	24(2)	19(2)	-3.9(16)	-1.9(15)	9.3(16)
C4	21(2)	25(3)	20(2)	-2.4(19)	1.0(19)	12(2)

Table 11 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2b. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C7	16(2)	18(2)	22(2)	-0.7(18)	-2.0(18)	6.3(18)
C5	19(2)	23(2)	27(3)	3(2)	7(2)	12(2)
N3	19(2)	24(2)	22(2)	-2.2(17)	-3.3(16)	10.4(17)
C2	14(2)	19(2)	20(2)	4.4(18)	3.4(17)	9.4(18)
C3	20(2)	21(2)	22(3)	1.0(19)	-1.1(19)	9(2)
C8	16(2)	22(2)	22(2)	1.3(18)	-0.9(18)	9.7(19)
C6	16(2)	21(2)	25(3)	1(2)	-2(2)	8.0(19)
C1	17(2)	18(2)	16(2)	2.4(17)	-0.3(17)	6.0(18)
C10	20(2)	22(2)	26(3)	-3(2)	-1.4(19)	10(2)
C14	22(2)	26(3)	36(3)	-8(2)	-5(2)	13(2)
C9	18(2)	19(2)	24(2)	-2.1(19)	-3.2(19)	7.5(19)
C11	22(2)	32(3)	30(3)	-6(2)	-6(2)	12(2)
C13	31(3)	25(3)	44(4)	-11(2)	-2(3)	14(2)
C12	26(3)	29(3)	33(3)	-12(2)	-4(2)	10(2)

Table 12 Bond Lengths for 2b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	O1	1.828(3)	N3	C8	1.365(6)
I1	O2	1.806(3)	C2	C3	1.388(7)
I1	C2	2.113(5)	C2	C1	1.400(7)
N1	N2	1.347(6)	C8	C9	1.473(7)
N1	C7	1.354(6)	C6	C1	1.392(7)
N1	C1	1.421(7)	C10	C9	1.394(7)
N2	N3	1.302(6)	C10	C11	1.386(7)
C4	C5	1.393(7)	C14	C9	1.397(7)
C4	C3	1.391(7)	C14	C13	1.373(8)
C7	C8	1.383(7)	C11	C12	1.389(8)
C5	C6	1.388(7)	C13	C12	1.382(8)

Table 13 Bond Angles for 2b.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	I1	C2	94.83(17)	C7	C8	C9	131.0(5)
O2	I1	O1	99.34(16)	N3	C8	C7	108.7(4)
O2	I1	C2	95.92(18)	N3	C8	C9	120.2(4)
N2	N1	C7	110.4(4)	C5	C6	C1	119.6(5)
N2	N1	C1	118.1(4)	C2	C1	N1	120.2(4)
C7	N1	C1	131.5(4)	C6	C1	N1	120.2(4)
N3	N2	N1	108.5(4)	C6	C1	C2	119.6(5)
C3	C4	C5	120.0(5)	C11	C10	C9	119.9(5)
N1	C7	C8	104.1(4)	C13	C14	C9	120.6(5)
C6	C5	C4	120.7(5)	C10	C9	C8	121.6(5)
N2	N3	C8	108.2(4)	C10	C9	C14	119.0(5)
C3	C2	I1	115.4(4)	C14	C9	C8	119.3(5)
C3	C2	C1	120.7(5)	C10	C11	C12	120.4(5)
C1	C2	I1	123.8(4)	C14	C13	C12	120.4(5)
C2	C3	C4	119.4(5)	C13	C12	C11	119.6(5)

Table 14 Torsion Angles for 2b.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
I1	C2	C3	C4	-175.1(4)	C5	C6	C1	N1	-178.4(5)
I1	C2	C1	N1	-6.2(7)	C5	C6	C1	C2	0.7(8)
I1	C2	C1	C6	174.6(4)	N3	C8	C9	C10	170.2(5)
N1	N2	N3	C8	-0.6(5)	N3	C8	C9	C14	-8.3(7)
N1	C7	C8	N3	-0.7(6)	C3	C4	C5	C6	-0.4(8)
N1	C7	C8	C9	-179.7(5)	C3	C2	C1	N1	177.6(5)
N2	N1	C7	C8	0.4(5)	C3	C2	C1	C6	-1.5(7)
N2	N1	C1	C2	3.6(7)	C1	N1	N2	N3	-178.0(4)
N2	N1	C1	C6	-177.3(5)	C1	N1	C7	C8	178.2(5)
N2	N3	C8	C7	0.8(6)	C1	C2	C3	C4	1.4(8)
N2	N3	C8	C9	179.9(5)	C10	C11	C12	C13	0.1(9)

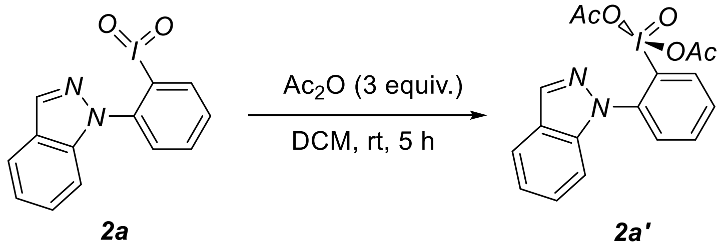
Table 14 Torsion Angles for 2b.

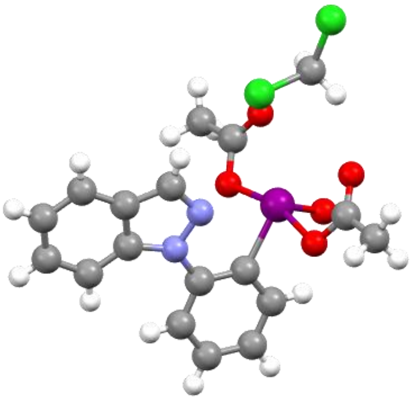
A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C4	C5	C6	C1	0.2(8)	C14	C13	C12	C11	-1.3(10)
C7	N1	N2	N3	0.1(6)	C9	C10	C11	C12	0.6(9)
C7	N1	C1	C2	-174.2(5)	C9	C14	C13	C12	1.6(10)
C7	N1	C1	C6	5.0(8)	C11	C10	C9	C8	-178.8(5)
C7	C8	C9	C10	-10.9(9)	C11	C10	C9	C14	-0.3(8)
C7	C8	C9	C14	170.6(6)	C13	C14	C9	C8	177.7(5)
C5	C4	C3	C2	-0.4(8)	C13	C14	C9	C10	-0.8(9)

Table 15 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2b.

Atom	*x*	*y*	*z*	U(eq)
H4	1057.51	2310.43	364.65	26
H7	2447.43	4047.03	4888.29	23
H5	1952.4	2684.36	1407.6	27
H3	398.9	2573.71	1138.68	25
H6	2201.53	3326.3	3210.2	26
H10	3022.03	4653.2	6845.73	27
H14	1783.82	5074.76	7334.53	33
H11	3573.44	5327.98	8488.48	34
H13	2322.82	5720.72	9013.43	40
H12	3226.45	5865.37	9570.23	37

2a' (CCDC: 2364397). Crystal was grown by cooling the reaction mixture to -30 °C in a closed vial after the formation of *2a'* from *2a (reaction below)*.





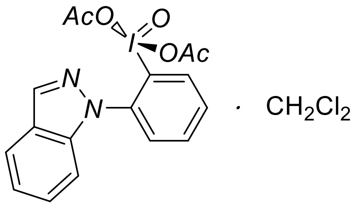


Table 16 Crystal data and structure refinement for 2a’.

Empirical formula	$C_{18}H_{17}Cl_2IN_2O_5$
Formula weight	539.14
Temperature/K	100.00
Crystal system	orthorhombic
Space group	Pbca
a/Å	15.2341(4)
b/Å	14.6267(4)
c/Å	17.4417(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3886.44(18)
Z	8
ρ_{calc}g/cm^3	1.843
μ/mm^{-1}	1.957
F(000)	2128.0
Crystal size/mm^3	0.121 × 0.117 × 0.113
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.348 to 72.688
Index ranges	$-20 \le h \le 25$, $-15 \le k \le 24$, $-29 \le l \le 29$
Reflections collected	61224
Independent reflections	9432 [R_{int} = 0.0290, R_{sigma} = 0.0194]
Data/restraints/parameters	9432/0/255

Goodness-of-fit on F^2	1.119
Final R indexes [I>=2σ (I)]	$R_1 = 0.0211$, $wR_2 = 0.0460$
Final R indexes [all data]	$R_1 = 0.0239$, $wR_2 = 0.0469$
Largest diff. peak/hole / e Å^{-3}	0.54/-0.88

Table 17 Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2\times10^3$) for 2a'. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
I1	6286.4(2)	6100.8(2)	7035.9(2)	9.00(2)
Cl1	4414.0(2)	6244.5(2)	8567.2(2)	19.52(5)
Cl2	4818.3(2)	6243.0(3)	10205.2(2)	24.53(6)
O1	7423.2(5)	6204.5(7)	7245.4(5)	18.22(16)
O3	6297.2(6)	4880.6(6)	8298.2(5)	20.10(17)
O2	6323.9(6)	4644.7(6)	7036.2(5)	16.76(15)
O4	6188.8(6)	7488.3(5)	6689.8(5)	14.50(14)
O5	6026.3(7)	7717.9(7)	7946.1(5)	21.87(18)
N2	4714.8(6)	6016.7(6)	6381.9(5)	11.54(14)
N1	4841.1(6)	6152.1(6)	5611.4(5)	10.16(14)
C2	7243.7(7)	5733.9(7)	5599.1(6)	12.77(17)
C14	6316.9(8)	4352.5(8)	7753.3(7)	15.63(18)
C5	5875.1(7)	5937.1(7)	4552.3(6)	11.96(16)
C13	3886.6(7)	6195.8(7)	6531.2(6)	12.40(16)
C12	3435.2(7)	6458.2(7)	5853.9(6)	10.61(15)
C11	2566.8(7)	6724.4(8)	5704.9(6)	13.48(17)
C1	6398.1(6)	5914.6(7)	5845.4(6)	10.05(15)
C8	3844.0(7)	6648.6(8)	4507.6(6)	13.61(17)
C9	2984.8(7)	6904.3(8)	4375.3(6)	15.99(18)
C6	5694.4(6)	6008.0(6)	5333.9(5)	9.09(14)
C16	6085.5(8)	8022.1(7)	7295.8(7)	14.67(17)
C15	6342.8(10)	3334.8(9)	7837.7(8)	24.4(3)

Table 17 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2a'. U$_{eq}$ is defined as 1/3 of the trace of the orthogonalised U$_{IJ}$ tensor.

Atom	*x*	*y*	*z*	U(eq)
C18	5244.5(8)	6359.9(9)	9268.2(7)	17.50(19)
C3	7412.7(7)	5659.9(8)	4819.3(6)	13.81(17)
C7	4066.0(6)	6422.4(7)	5264.1(6)	9.93(15)
C4	6730.6(7)	5772.9(7)	4303.2(6)	13.18(17)
C10	2350.2(7)	6940.7(8)	4960.9(7)	15.46(18)
C17	6067.4(10)	9023.5(8)	7108.3(8)	23.0(2)

Table 18 Anisotropic Displacement Parameters (Å^2×10^3) for 2a'. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
I1	9.17(3)	10.86(3)	6.97(3)	0.00(2)	-1.42(2)	-0.09(2)
Cl1	17.74(11)	24.86(13)	15.95(11)	-3.87(9)	-2.40(9)	-2.69(9)
Cl2	24.88(14)	34.69(16)	14.03(11)	0.66(11)	1.24(10)	3.58(12)
O1	9.7(3)	28.8(4)	16.2(4)	-1.6(3)	-4.8(3)	-1.2(3)
O3	29.6(5)	19.5(4)	11.2(3)	0.6(3)	-1.1(3)	6.0(3)
O2	27.6(4)	12.7(3)	10.0(3)	1.1(3)	-0.1(3)	2.4(3)
O4	20.7(4)	11.3(3)	11.5(3)	0.2(2)	0.6(3)	-1.5(3)
O5	34.5(5)	18.4(4)	12.7(3)	-2.6(3)	-0.7(3)	-1.8(4)
N2	10.8(3)	16.6(4)	7.2(3)	0.4(3)	0.2(3)	-0.2(3)
N1	8.7(3)	14.3(3)	7.5(3)	0.7(3)	0.0(3)	0.1(3)
C2	9.7(4)	16.2(4)	12.5(4)	-0.7(3)	0.0(3)	0.9(3)
C14	19.0(5)	15.2(4)	12.8(4)	2.7(3)	0.6(4)	4.4(4)
C5	12.2(4)	15.0(4)	8.7(4)	-0.1(3)	0.1(3)	0.9(3)
C13	10.8(4)	16.7(4)	9.7(4)	-0.3(3)	0.8(3)	0.0(3)
C12	9.8(4)	11.4(4)	10.6(4)	-0.5(3)	0.0(3)	0.2(3)
C11	10.1(4)	15.3(4)	15.0(4)	-0.5(3)	-0.2(3)	1.8(3)
C1	9.6(4)	12.0(4)	8.6(4)	0.1(3)	-0.4(3)	0.1(3)
C8	13.5(4)	17.6(4)	9.7(4)	1.9(3)	-0.8(3)	2.4(3)
C9	15.0(4)	19.7(5)	13.2(4)	2.0(4)	-3.3(4)	3.1(4)

Table 18 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2a'. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6	9.1(3)	10.1(3)	8.1(3)	0.2(3)	0.2(3)	-0.3(3)
C16	16.4(4)	12.6(4)	15.0(4)	-1.6(3)	-2.7(4)	-1.2(3)
C15	37.7(7)	14.3(5)	21.3(5)	5.0(4)	3.7(5)	5.5(5)
C18	14.1(4)	24.1(5)	14.3(4)	-2.1(4)	0.0(4)	-0.5(4)
C3	11.4(4)	16.7(4)	13.3(4)	-1.6(3)	2.9(3)	0.5(3)
C7	9.4(4)	10.6(4)	9.7(4)	-0.2(3)	-1.4(3)	0.3(3)
C4	13.8(4)	15.7(4)	10.1(4)	-0.3(3)	2.7(3)	0.3(3)
C10	12.0(4)	17.5(4)	17.0(4)	1.2(4)	-2.2(4)	3.5(3)
C17	34.9(7)	11.7(4)	22.3(5)	-1.0(4)	-7.5(5)	-0.2(4)

Table 19 Bond Lengths for 2a'.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	O1	1.7765(8)	C2	C3	1.3885(15)
I1	O2	2.1306(9)	C14	C15	1.4963(18)
I1	O4	2.1226(8)	C5	C6	1.3946(14)
I1	C1	2.1011(10)	C5	C4	1.3946(15)
Cl1	C18	1.7675(12)	C13	C12	1.4198(15)
Cl2	C18	1.7669(12)	C12	C11	1.4032(14)
O3	C14	1.2252(15)	C12	C7	1.4087(14)
O2	C14	1.3217(14)	C11	C10	1.3759(16)
O4	C16	1.3234(14)	C1	C6	1.4014(14)
O5	C16	1.2217(14)	C8	C9	1.3806(15)
N2	N1	1.3720(12)	C8	C7	1.4016(14)
N2	C13	1.3146(14)	C9	C10	1.4075(16)
N1	C6	1.4030(13)	C16	C17	1.5011(16)
N1	C7	1.3848(13)	C3	C4	1.3847(15)
C2	C1	1.3834(14)			

Table 20 Bond Angles for 2a’.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	I1	O2	93.39(4)	C7	C12	C13	105.49(9)
O1	I1	O4	92.59(4)	C10	C11	C12	117.69(10)
O1	I1	C1	97.78(4)	C2	C1	I1	114.02(7)
O4	I1	O2	163.29(3)	C2	C1	C6	122.23(9)
C1	I1	O2	82.44(3)	C6	C1	I1	123.68(7)
C1	I1	O4	81.29(4)	C9	C8	C7	116.75(10)
C14	O2	I1	108.86(7)	C8	C9	C10	122.69(10)
C16	O4	I1	110.20(7)	C5	C6	N1	122.09(9)
C13	N2	N1	107.45(9)	C5	C6	C1	117.65(9)
N2	N1	C6	116.50(8)	C1	C6	N1	120.25(9)
N2	N1	C7	110.49(8)	O4	C16	C17	113.82(10)
C7	N1	C6	133.01(9)	O5	C16	O4	122.37(10)
C1	C2	C3	119.45(10)	O5	C16	C17	123.80(11)
O3	C14	O2	122.03(11)	Cl2	C18	Cl1	111.56(6)
O3	C14	C15	123.47(11)	C4	C3	C2	119.23(10)
O2	C14	C15	114.49(10)	N1	C7	C12	105.83(8)
C6	C5	C4	120.12(9)	N1	C7	C8	133.23(9)
N2	C13	C12	110.73(9)	C8	C7	C12	120.93(9)
C11	C12	C13	133.29(10)	C3	C4	C5	121.29(10)
C11	C12	C7	121.21(9)	C11	C10	C9	120.73(10)

Table 21 Torsion Angles for 2a’.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
I1	O2	C14	O3	-0.42(14)	C13	C12	C7	C8	-179.60(10)
I1	O2	C14	C15	-179.91(9)	C12	C11	C10	C9	-0.72(17)
I1	O4	C16	O5	-2.48(14)	C11	C12	C7	N1	179.05(9)
I1	O4	C16	C17	176.34(9)	C11	C12	C7	C8	-0.27(15)
I1	C1	C6	N1	-6.06(13)	C1	C2	C3	C4	0.28(16)
I1	C1	C6	C5	174.98(7)	C8	C9	C10	C11	0.45(18)

Table 21 Torsion Angles for 2a'.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
N2	N1	C6	C5	166.55(9)	C9	C8	C7	N1	-179.13(11)
N2	N1	C6	C1	-12.36(13)	C9	C8	C7	C12	-0.02(16)
N2	N1	C7	C12	0.30(11)	C6	N1	C7	C12	-178.89(10)
N2	N1	C7	C8	179.51(11)	C6	N1	C7	C8	0.32(19)
N2	C13	C12	C11	-179.05(11)	C6	C5	C4	C3	1.23(16)
N2	C13	C12	C7	0.17(12)	C3	C2	C1	I1	-175.61(8)
N1	N2	C13	C12	0.02(12)	C3	C2	C1	C6	1.38(16)
C2	C1	C6	N1	177.24(9)	C7	N1	C6	C5	-14.29(17)
C2	C1	C6	C5	-1.71(15)	C7	N1	C6	C1	166.80(10)
C2	C3	C4	C5	-1.58(17)	C7	C12	C11	C10	0.64(16)
C13	N2	N1	C6	179.14(9)	C7	C8	C9	C10	-0.06(17)
C13	N2	N1	C7	-0.20(12)	C4	C5	C6	N1	-178.53(9)
C13	C12	C11	C10	179.76(11)	C4	C5	C6	C1	0.40(15)
C13	C12	C7	N1	-0.28(11)					

Table 22 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2a'.

Atom	*x*	*y*	*z*	U(eq)
H2	7704.96	5660.93	5960.55	15
H5	5414.62	6000.76	4188.97	14
H13	3625.84	6155.12	7024.77	15
H11	2143.31	6754.31	6103.92	16
H8	4264.18	6627.04	4105.59	16
H9	2815.11	7062.07	3868.16	19
H15A	6939.53	3114.99	7737.39	37
H15B	5936.01	3055.78	7470.67	37
H15C	6169.84	3167.17	8360.29	37
H18A	5700.36	5888.54	9182.14	21
H18B	5524.83	6967.32	9215.87	21
H3	7989.6	5533.32	4641.87	17

Table 22 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2a'.

Atom	***x***	***y***	***z***	**U(eq)**
H4	6847.61	5737.91	3769.05	16
H10	1765.74	7116.62	4841.14	19
H17A	6668.52	9243.57	7030.92	34
H17B	5795.96	9360.02	7532.41	34
H17C	5725.93	9120.84	6639.17	34

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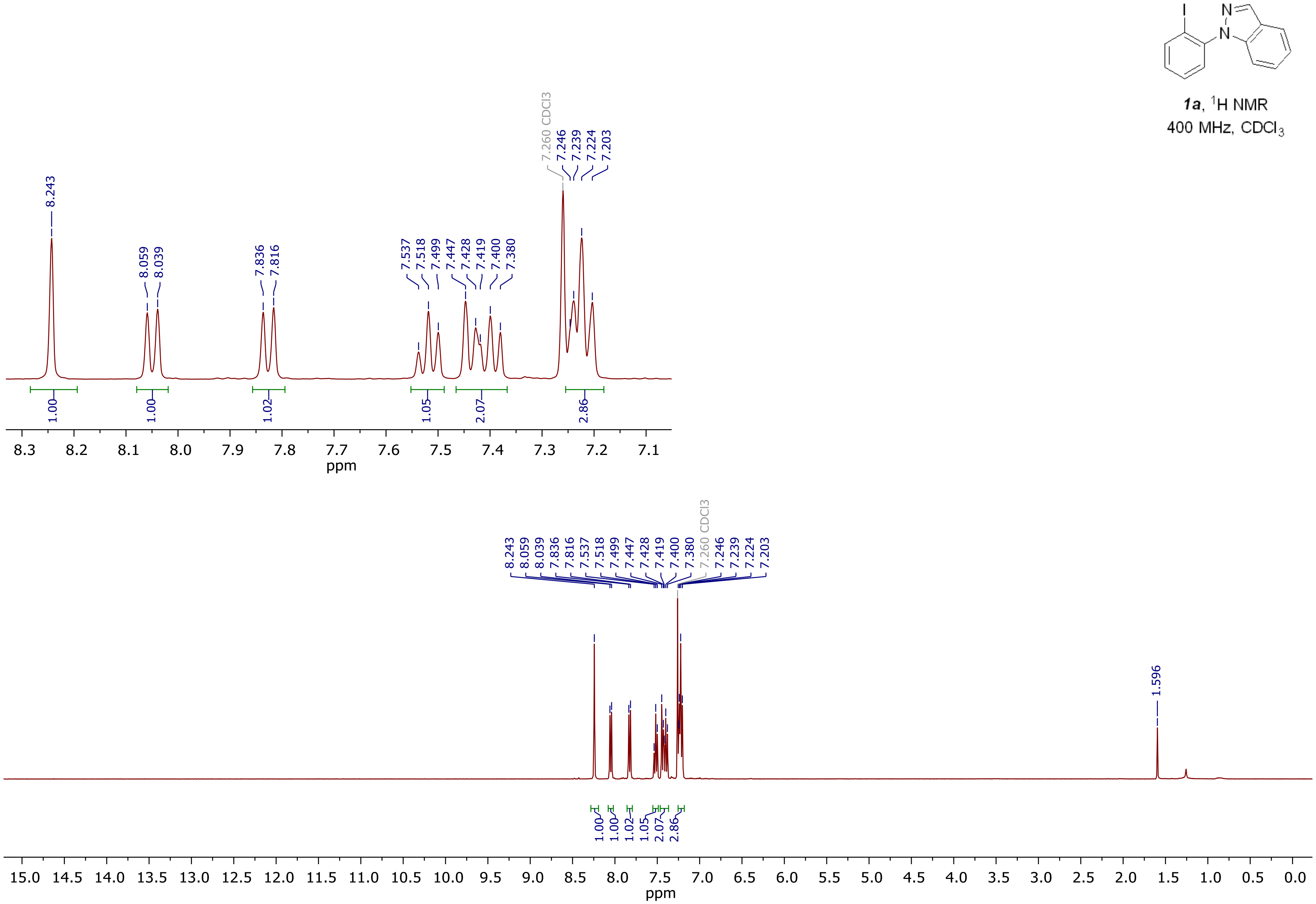
Spectral data



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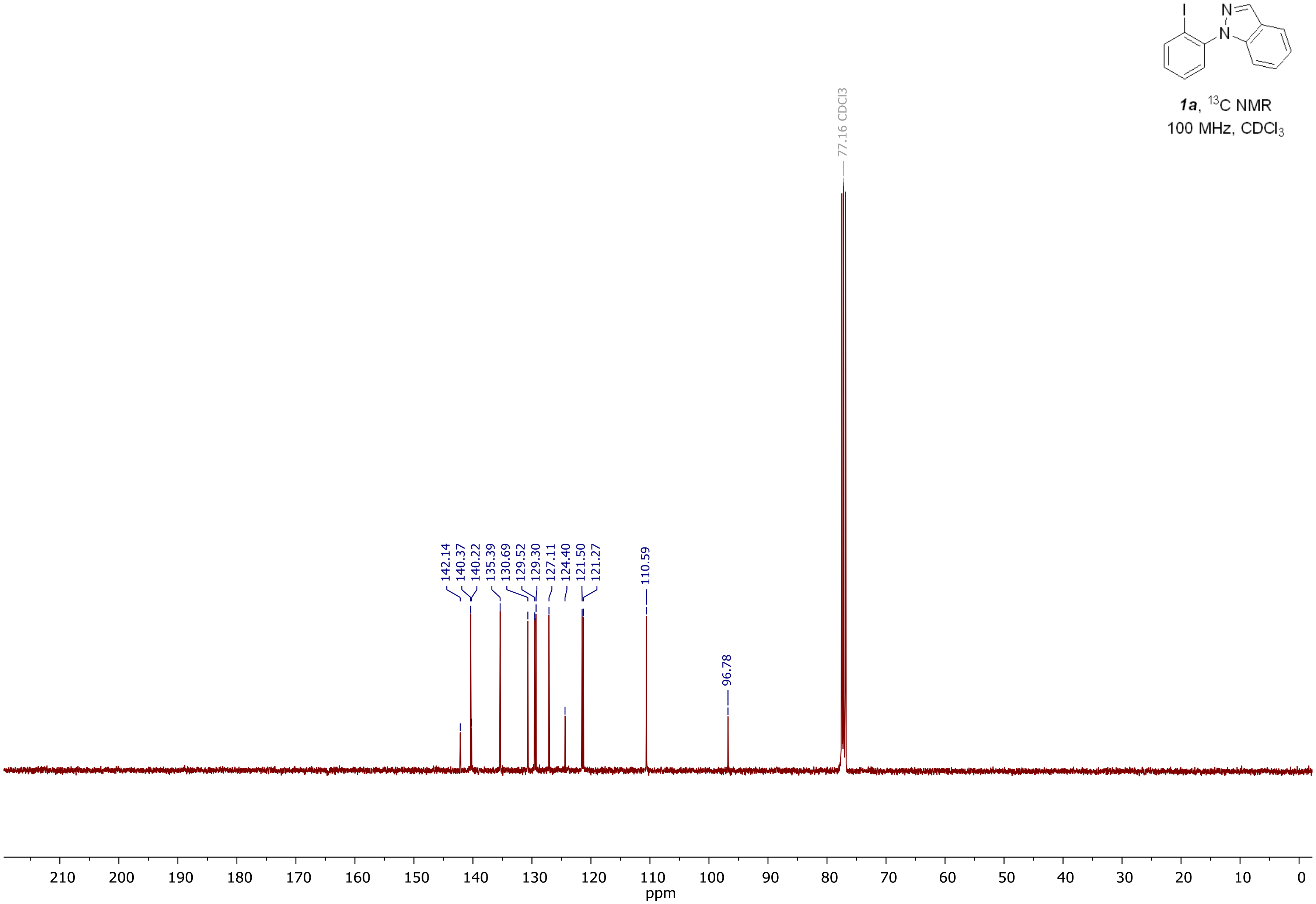

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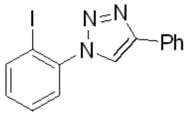

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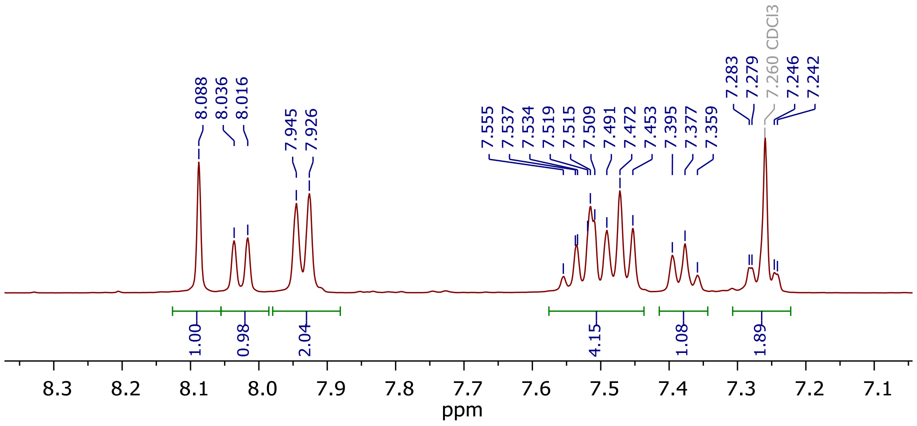

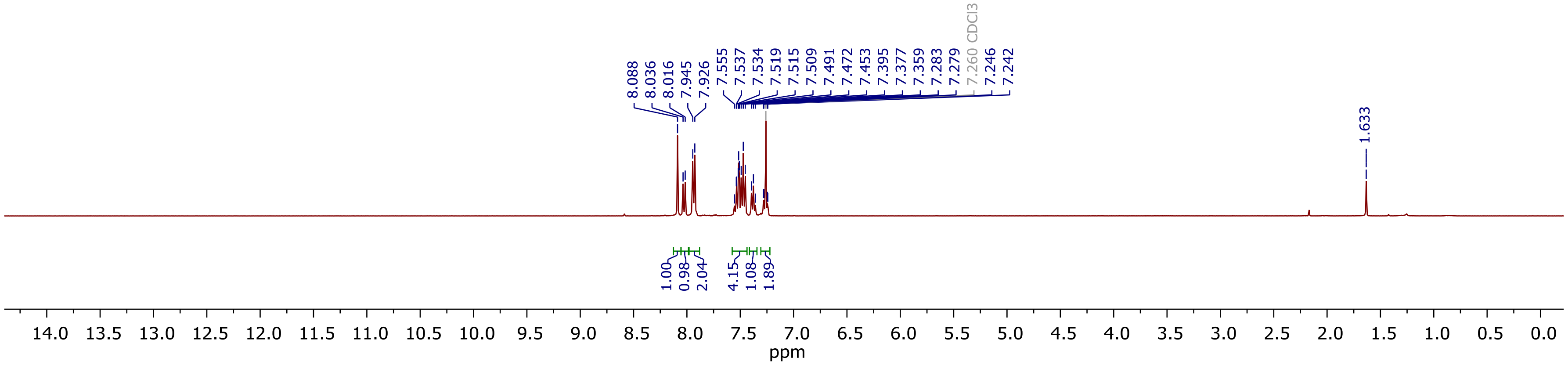

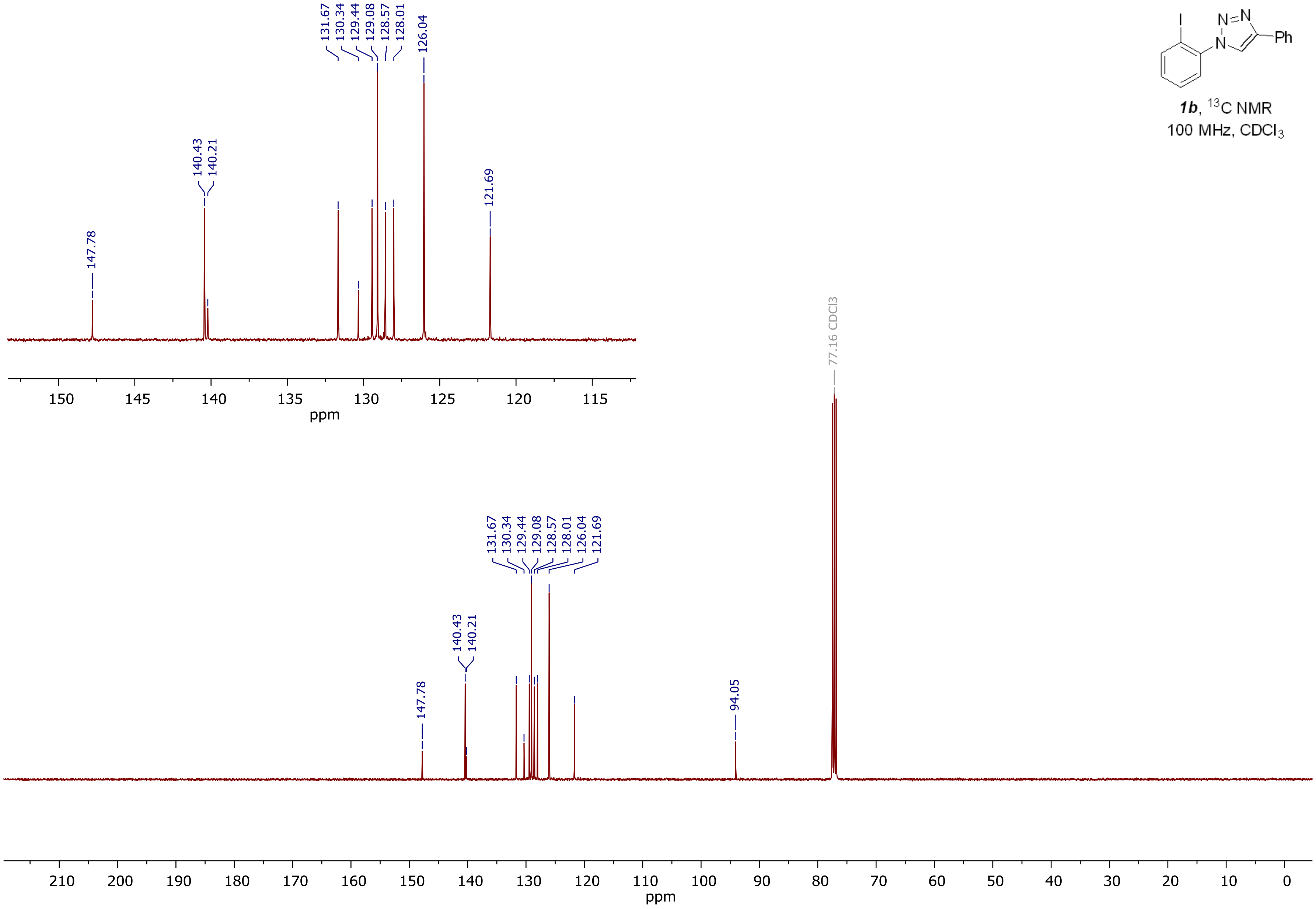

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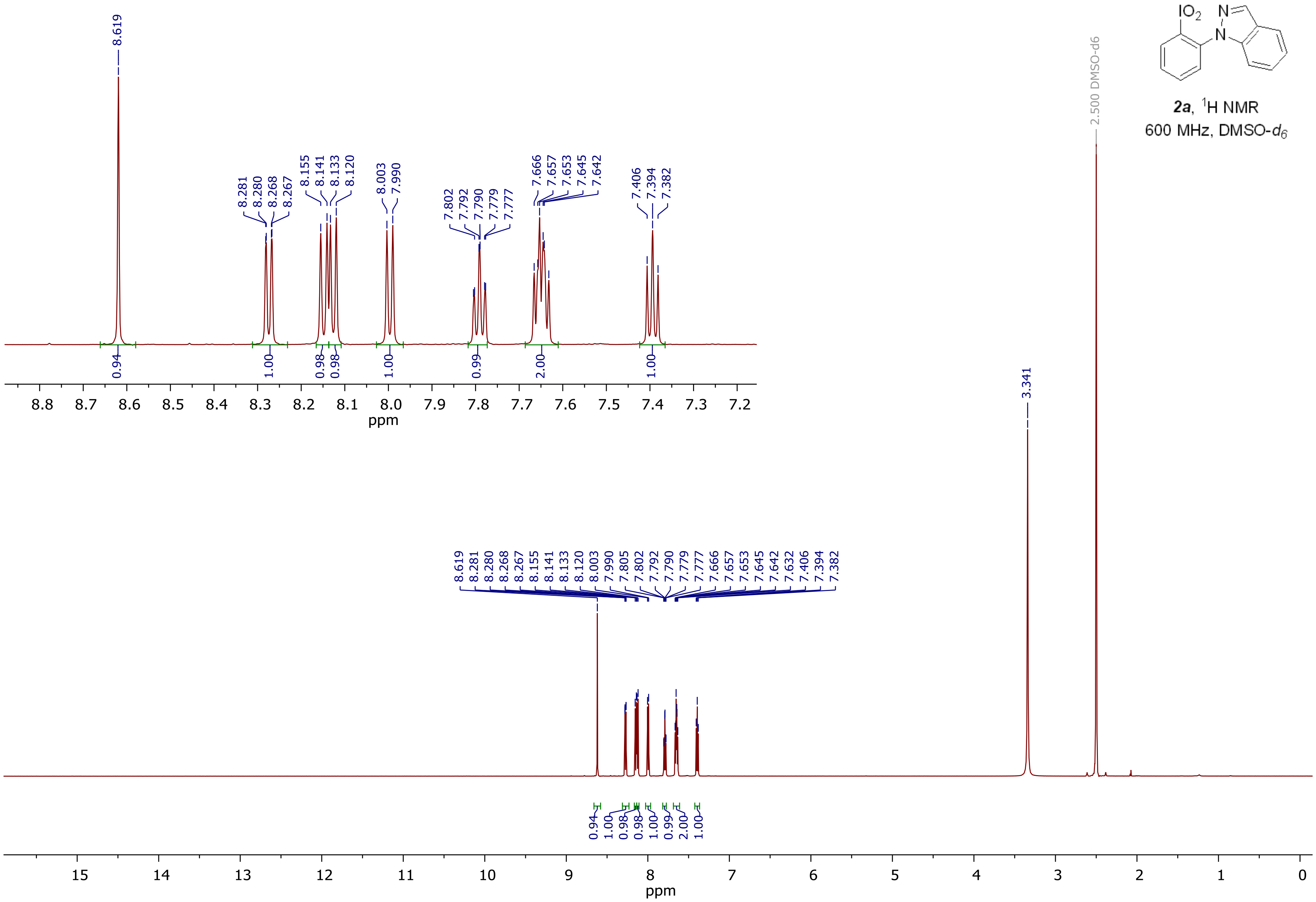

2a, ^{1}H NMR
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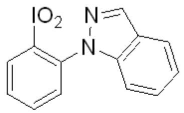

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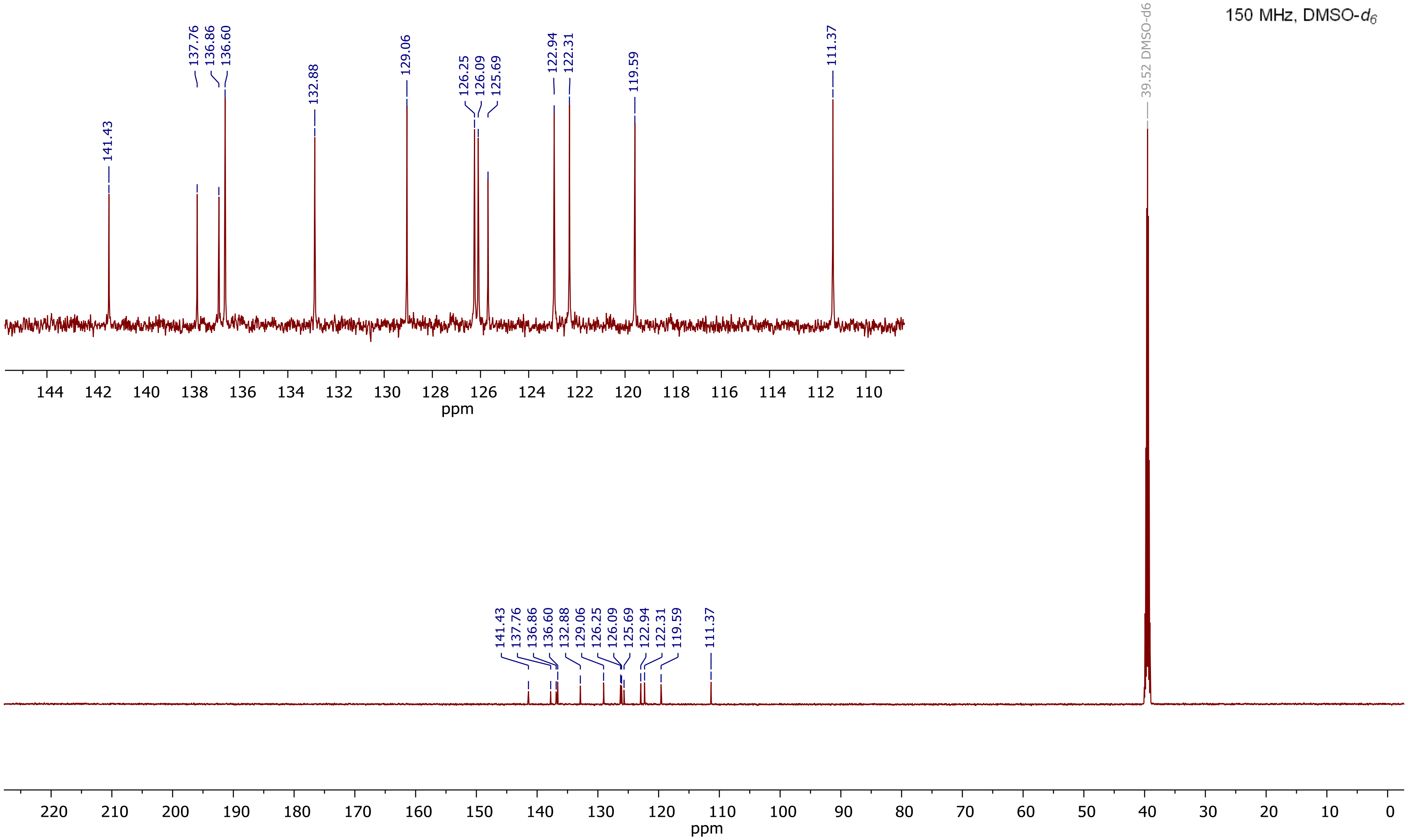

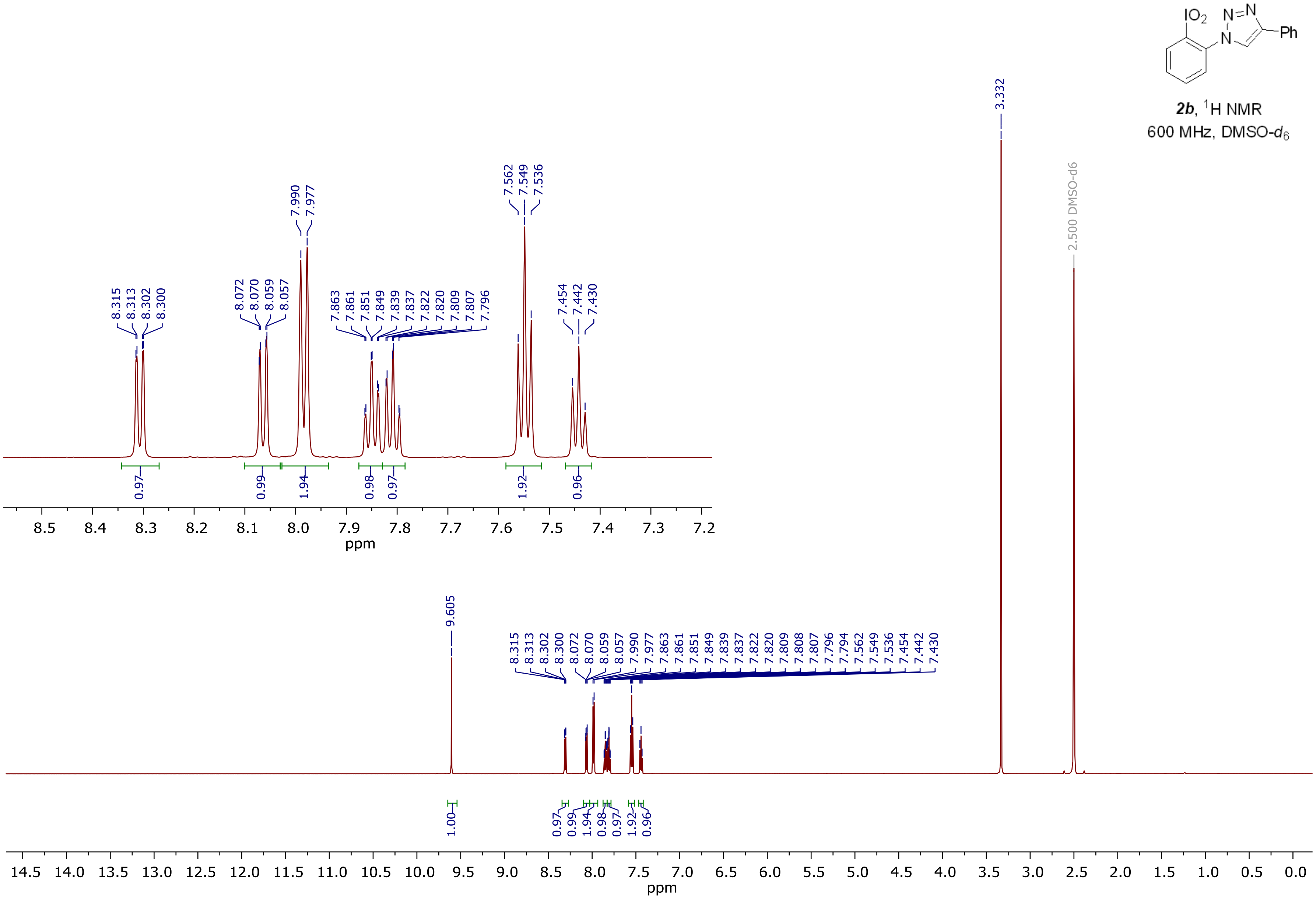

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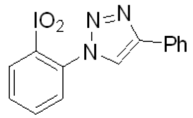

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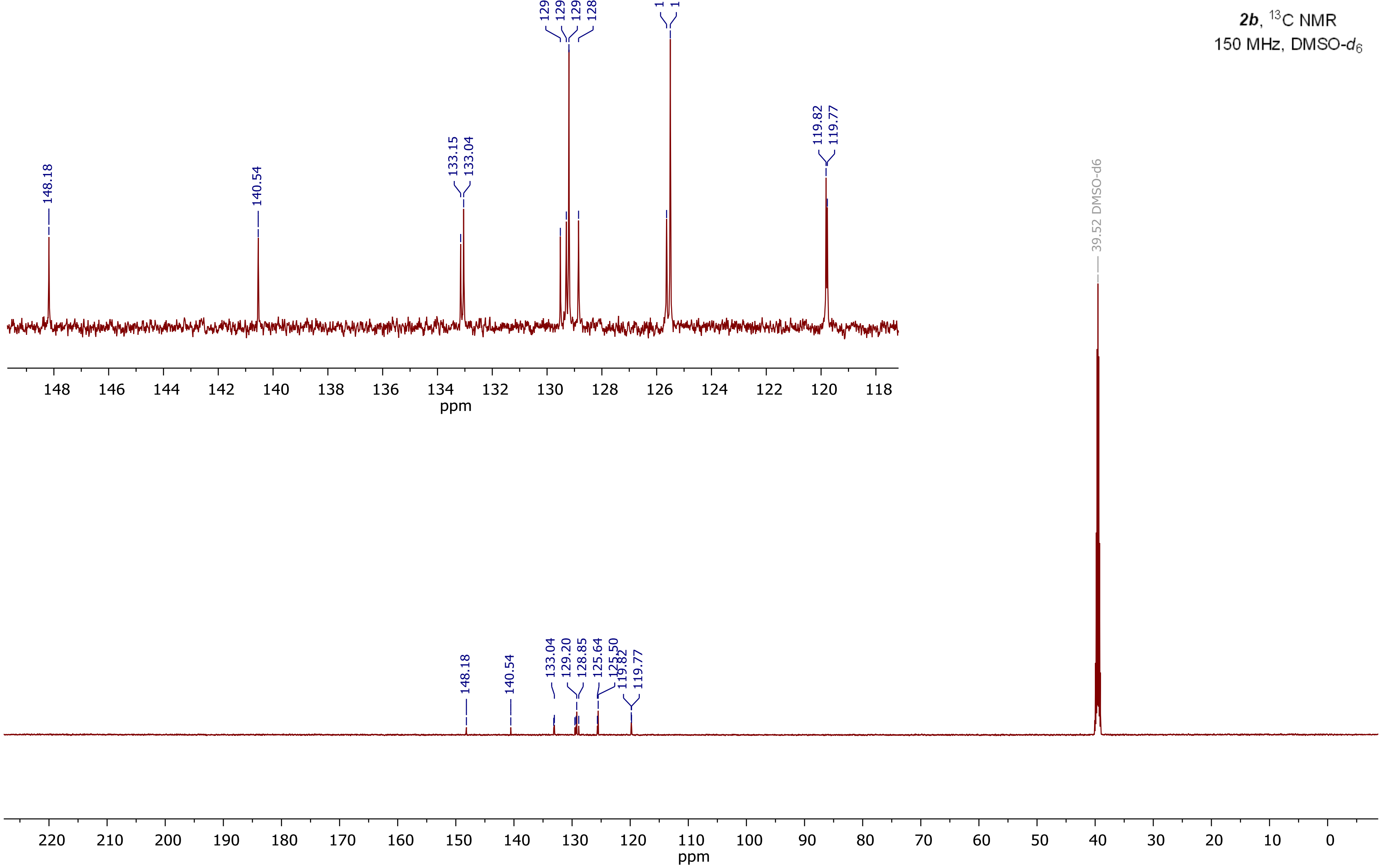
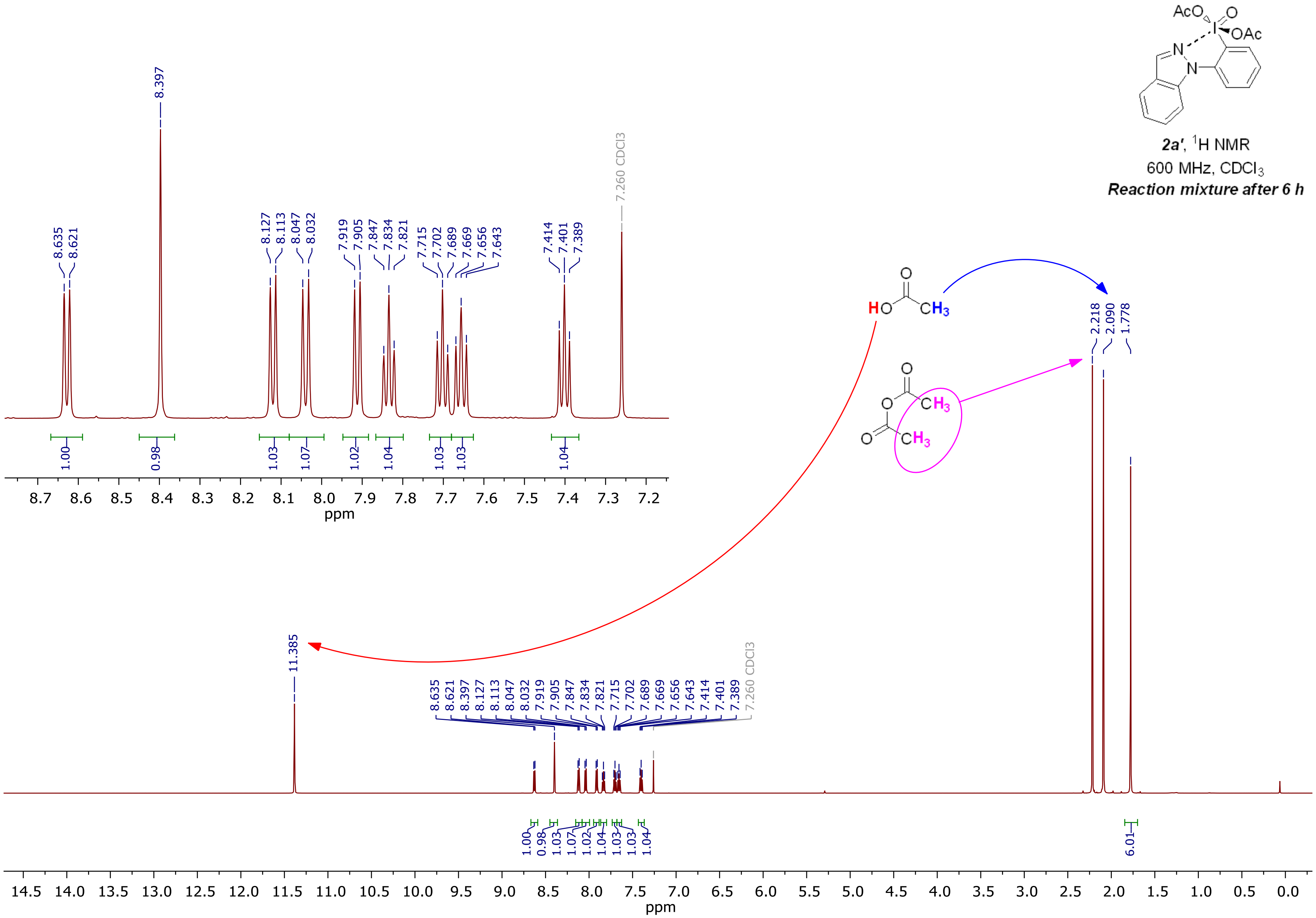
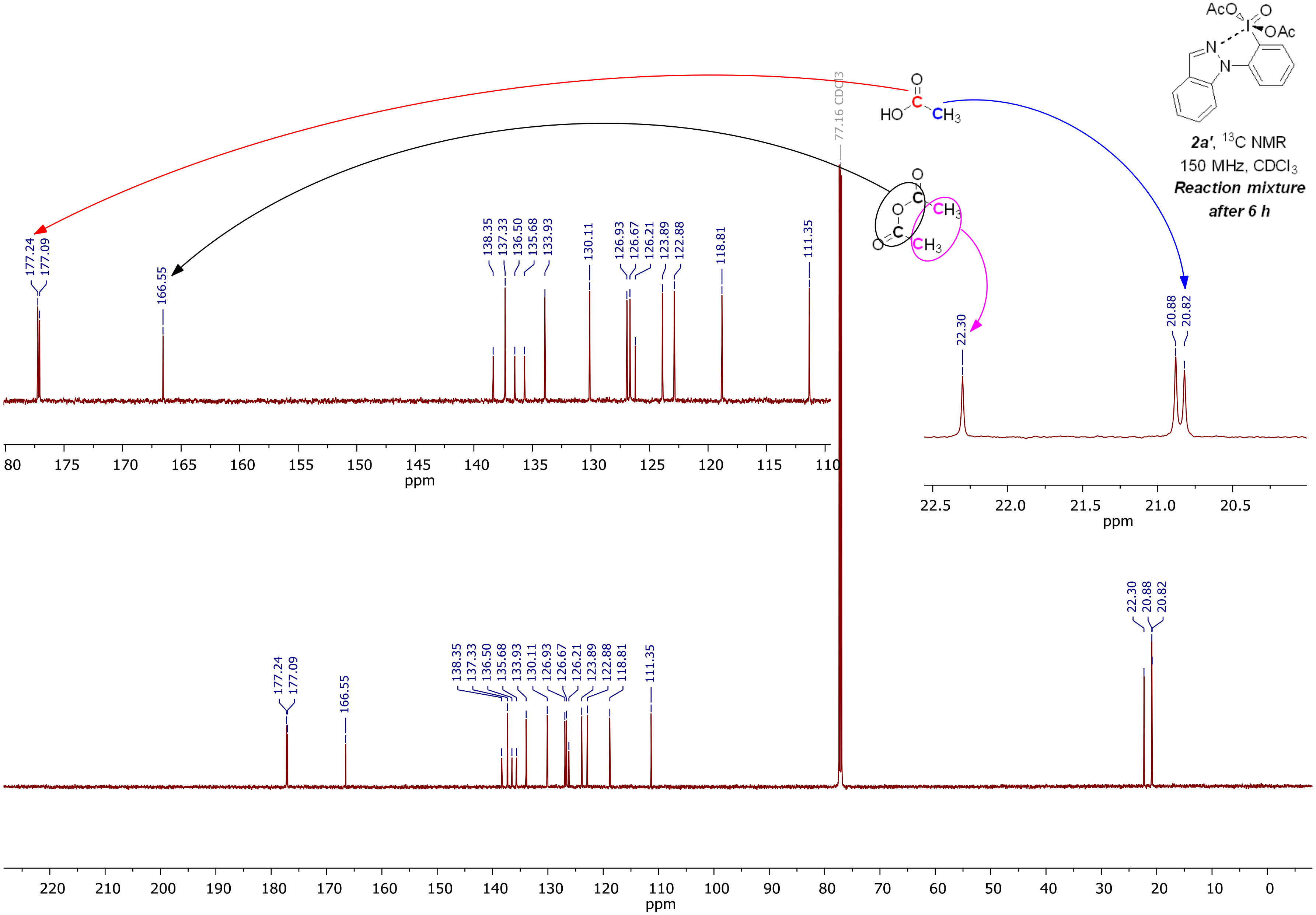




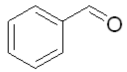
2a′, ^{1}H NMR

600 MHz, $CDCl_3$

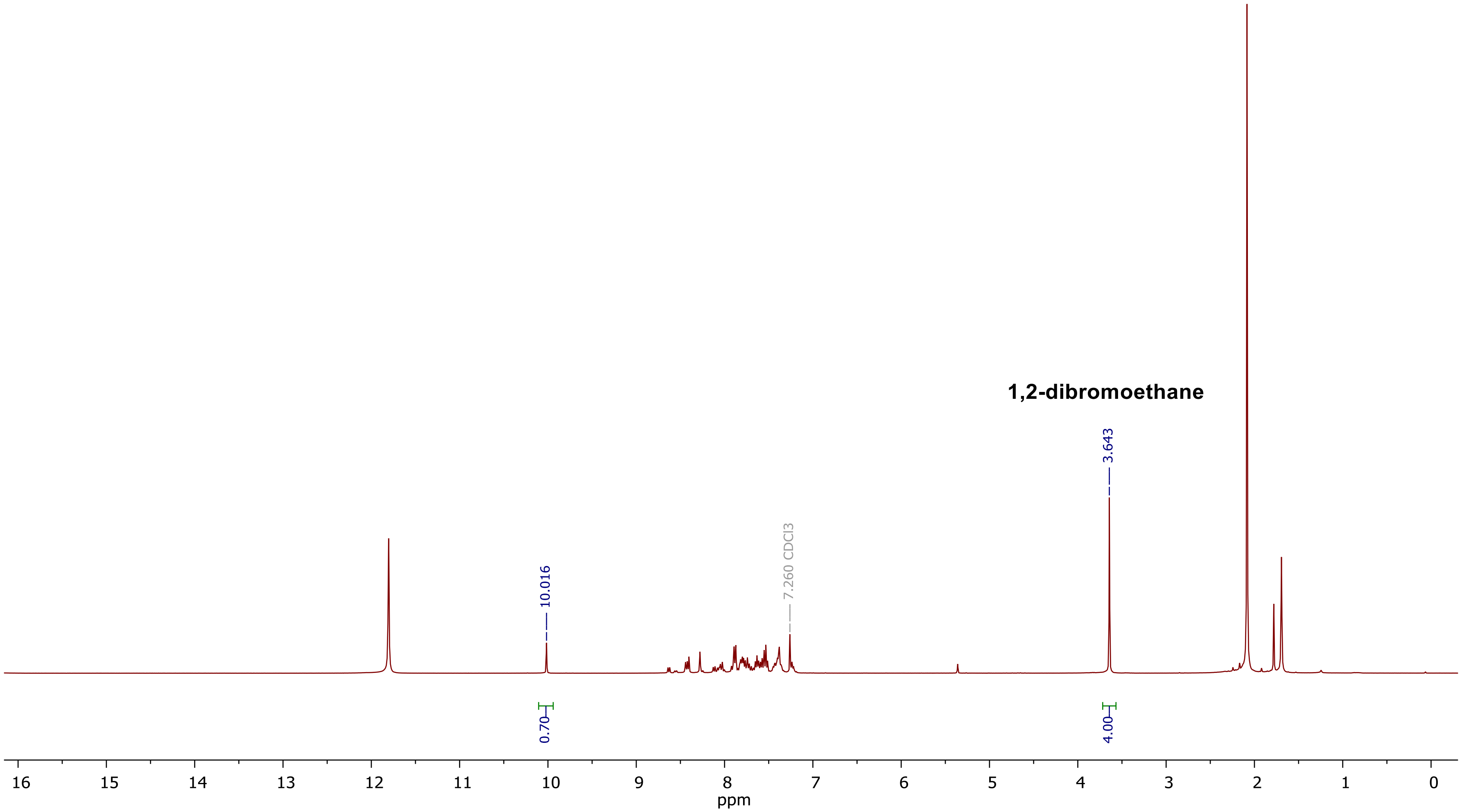
Reaction mixture after 6 h

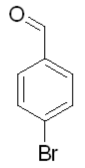


2a', ^{13}C NMR
150 MHz, $CDCl_3$
Reaction mixture
after 6 h



3a, ^{1}H NMR
400 MHz, $CDCl_3$
NMR yield





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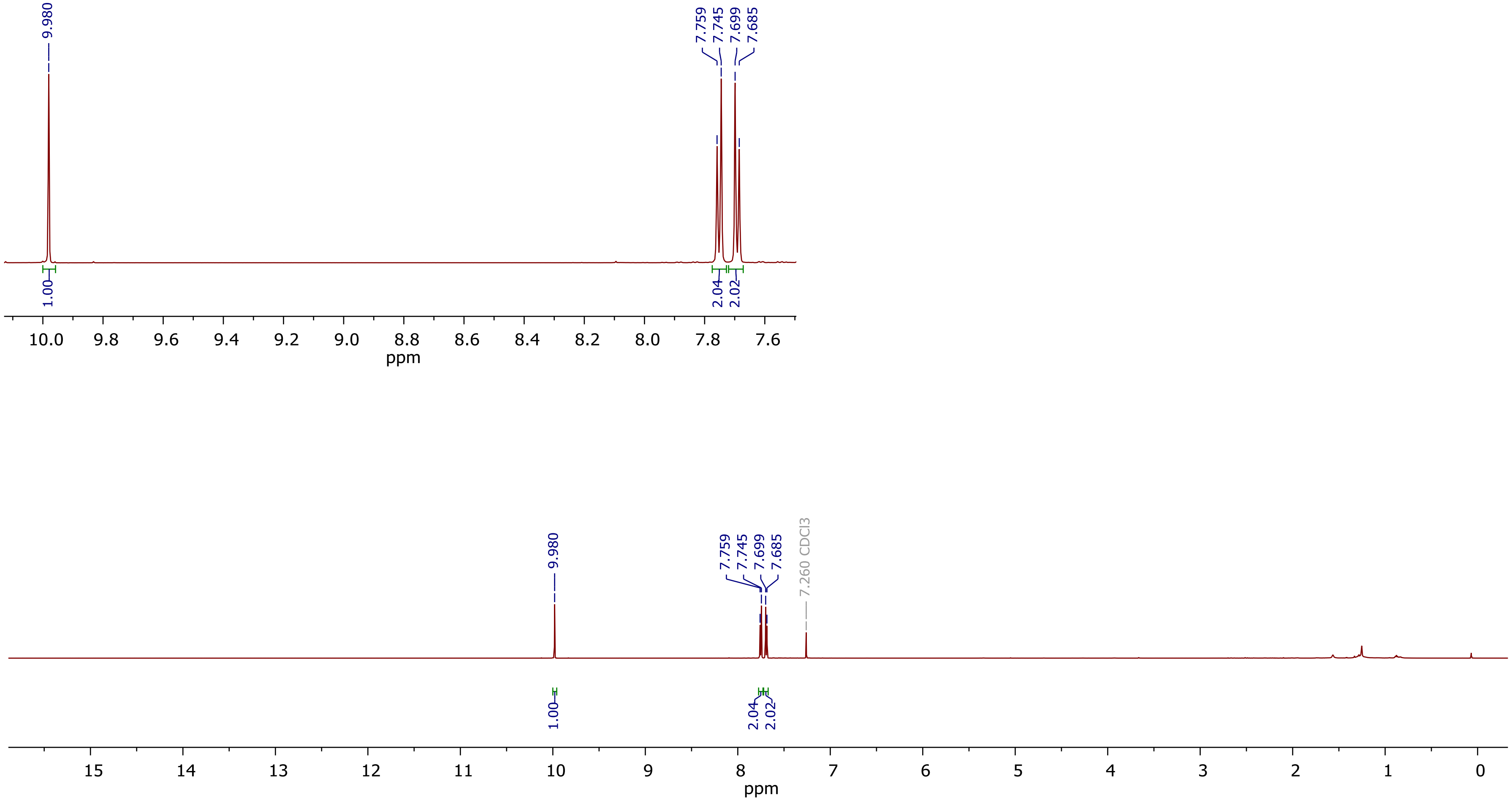

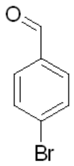

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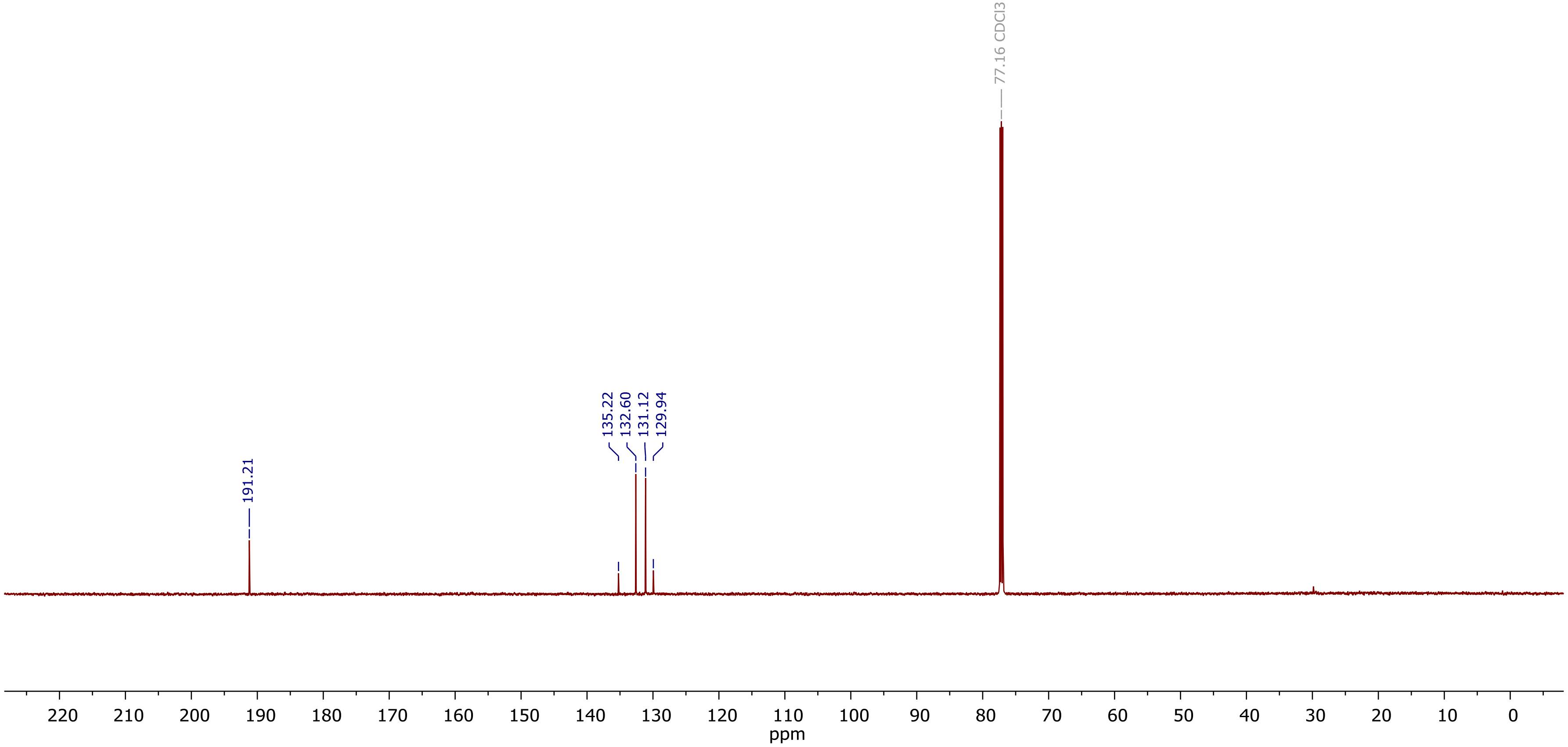

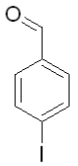

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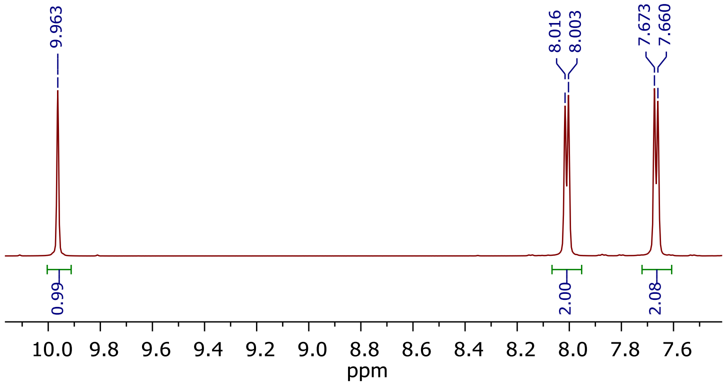

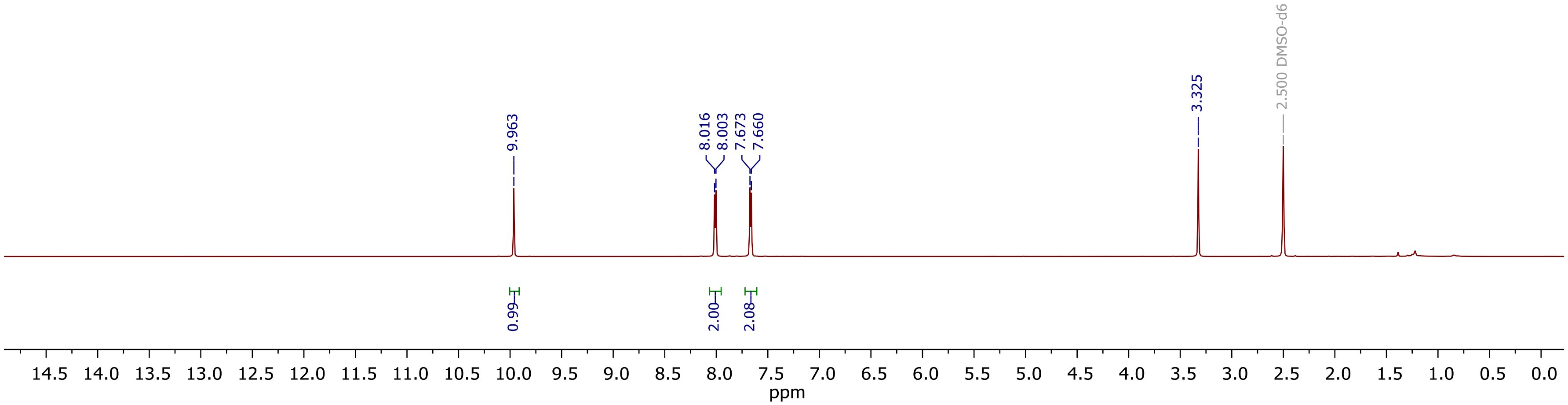

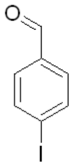

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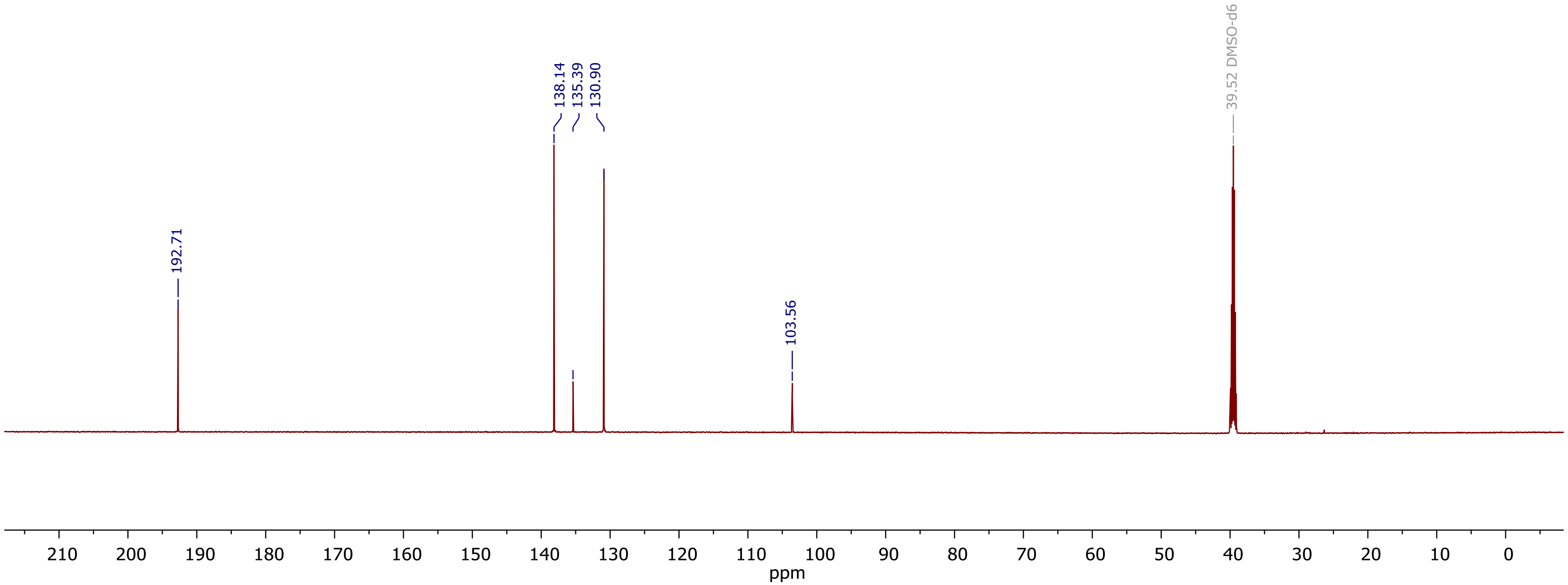
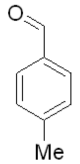
150 MHz, DMSO-d_6





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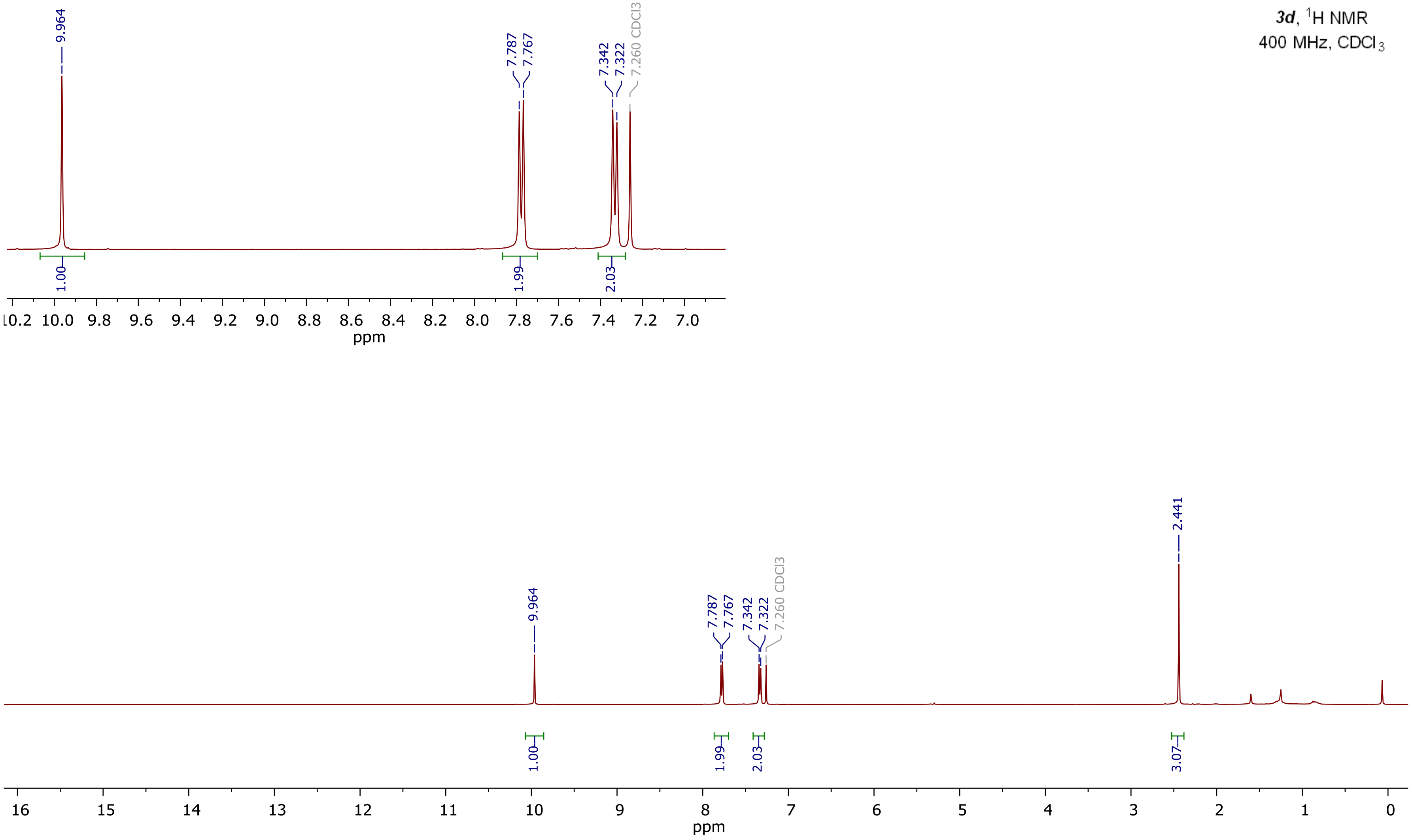
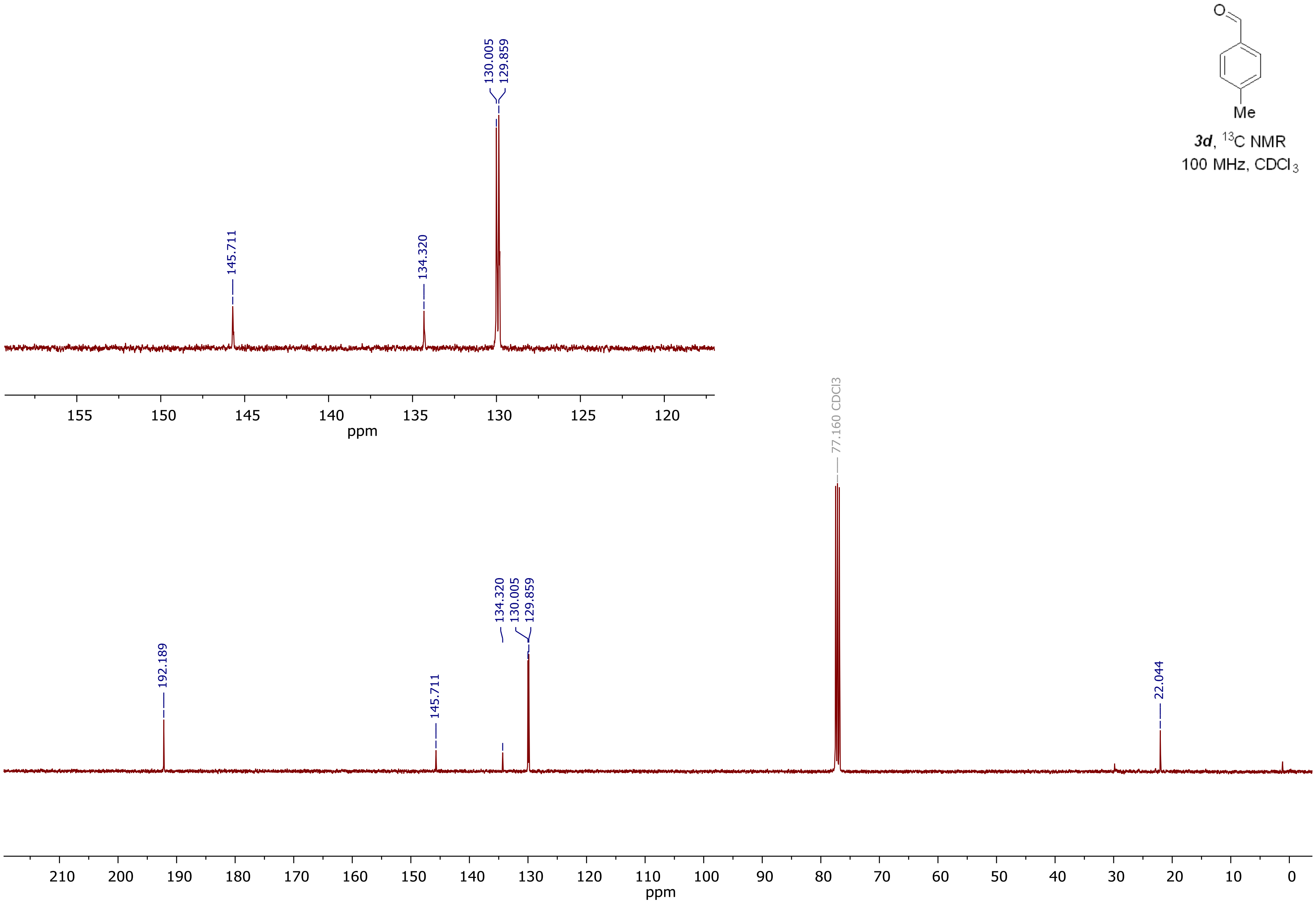
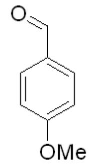
400 MHz, $CDCl_3$





3d, ^{13}C NMR
100 MHz, $CDCl_3$



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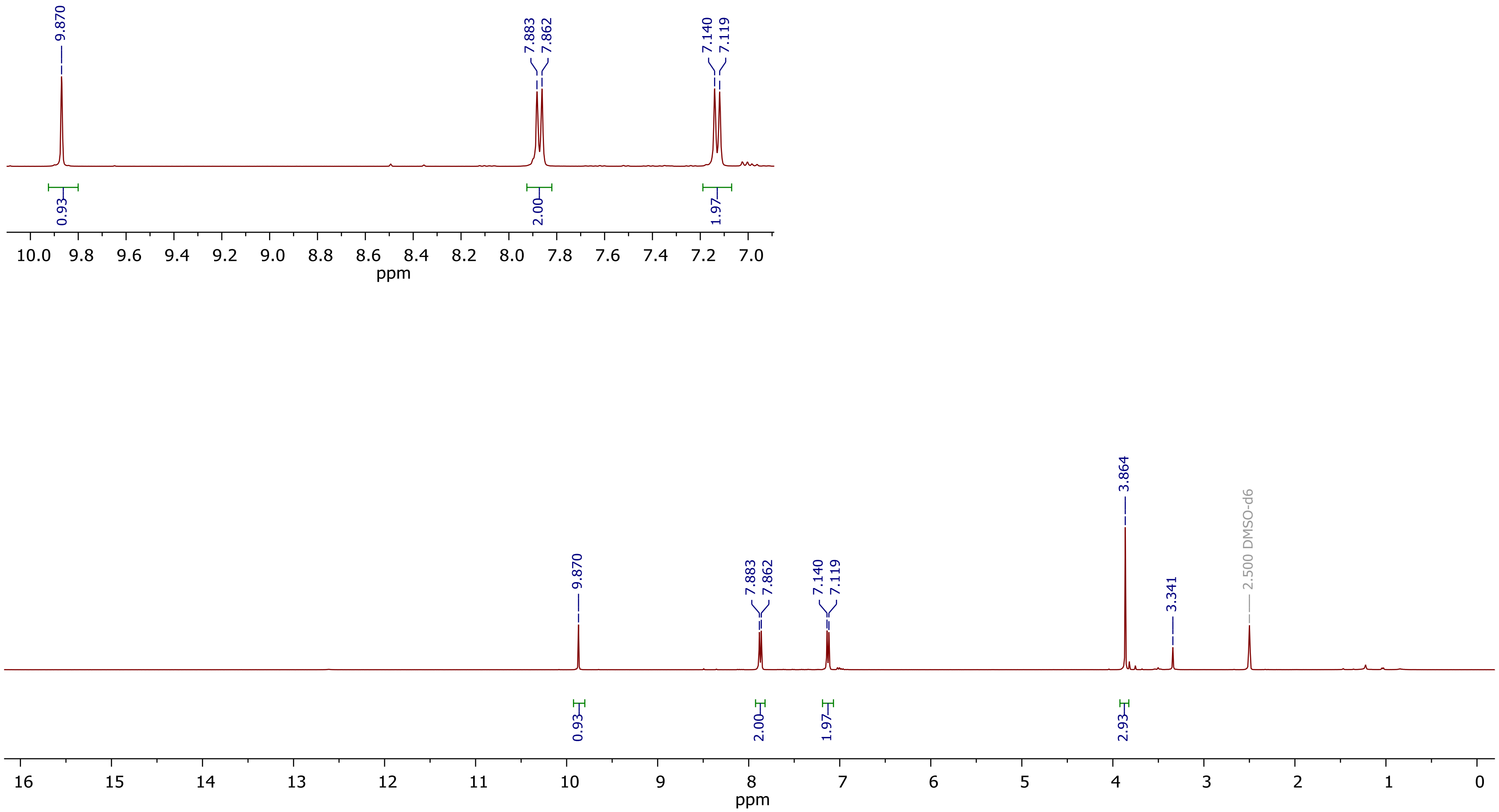
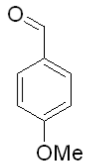
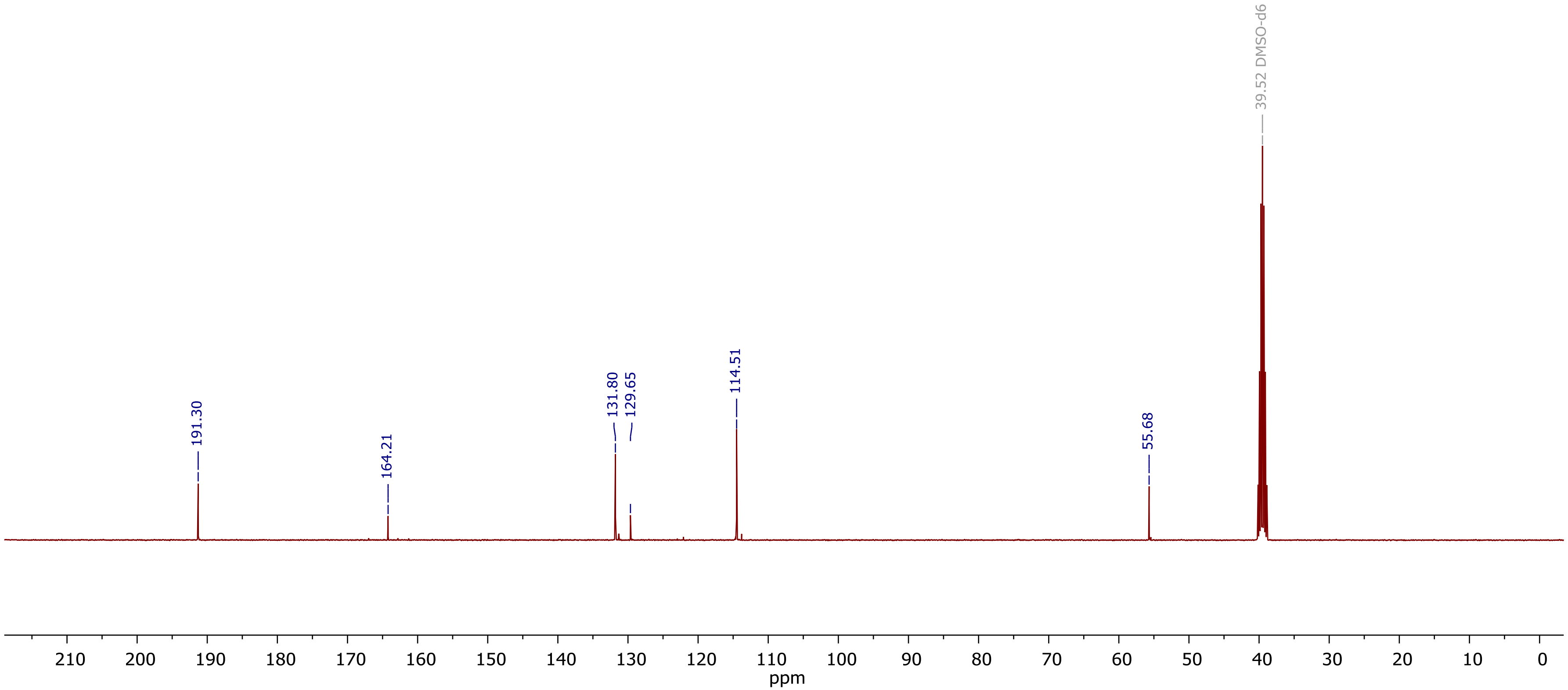
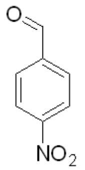
400 MHz, DMSO-d_6



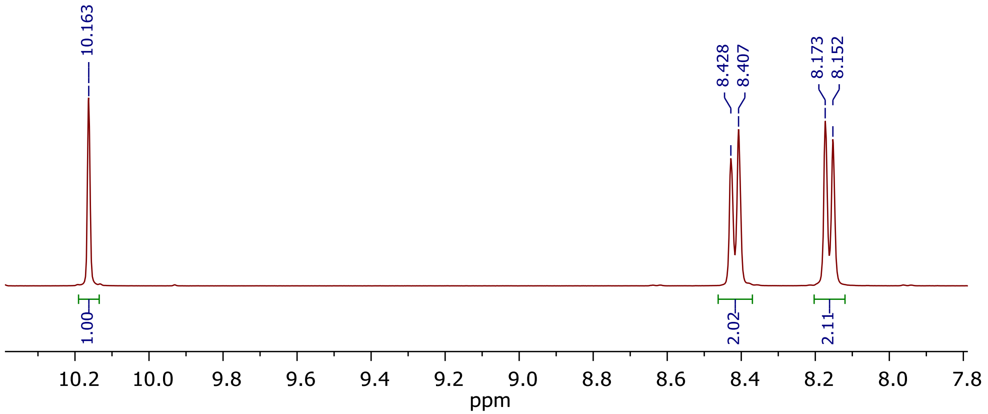


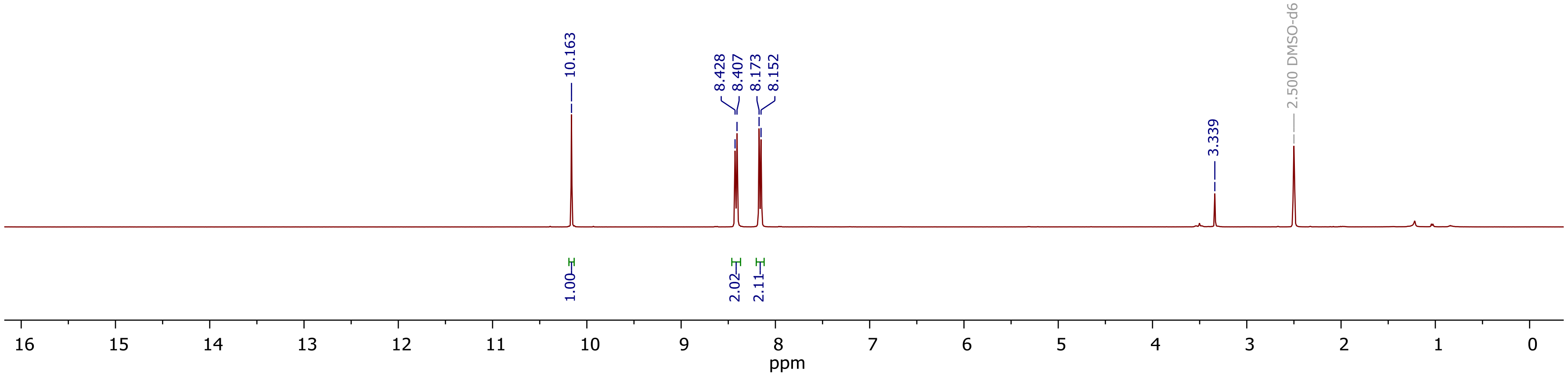
3e, ^{13}C NMR
100 MHz, DMSO-d_6

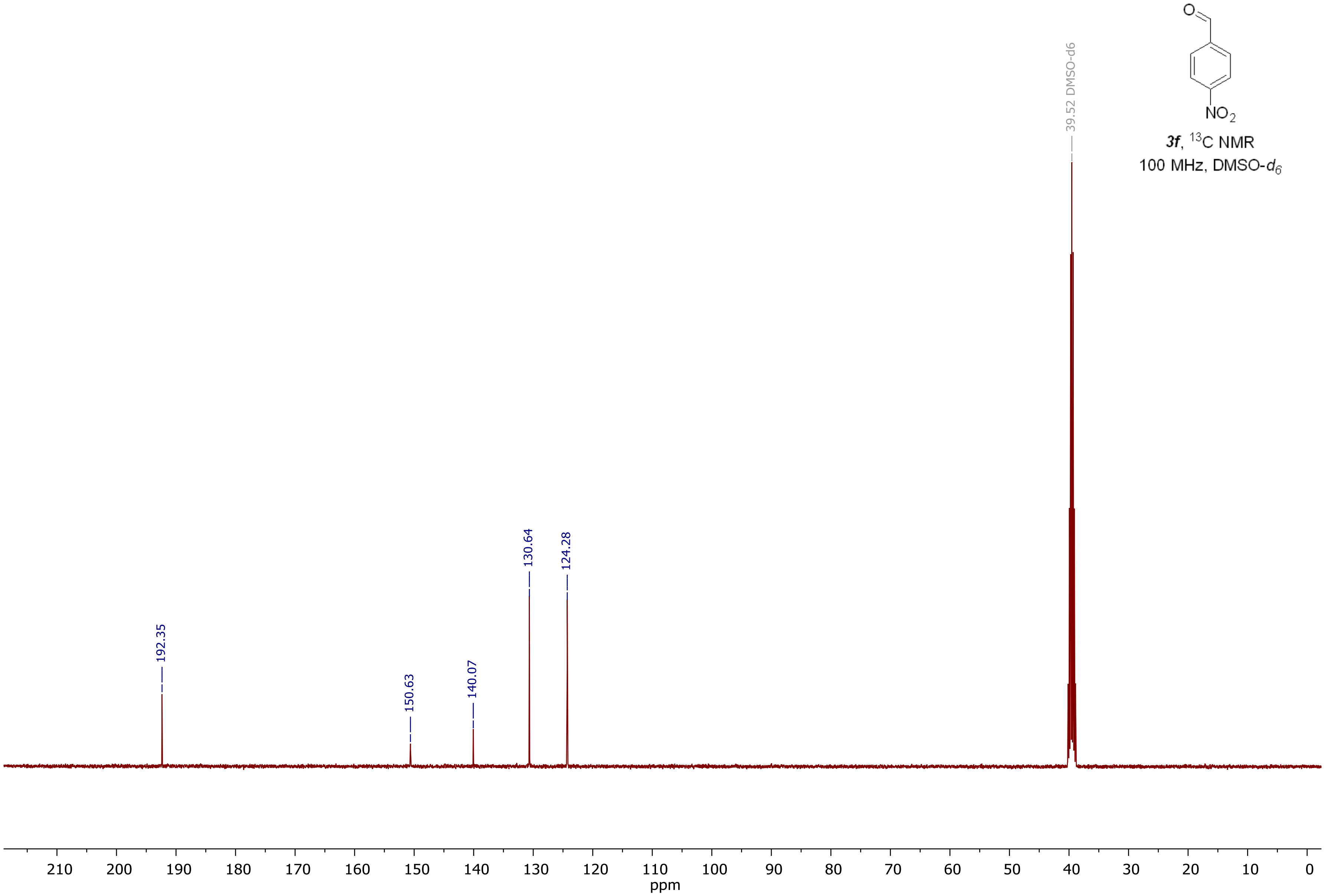




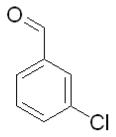
3f, ^{1}H NMR
400 MHz, DMSO-d_6



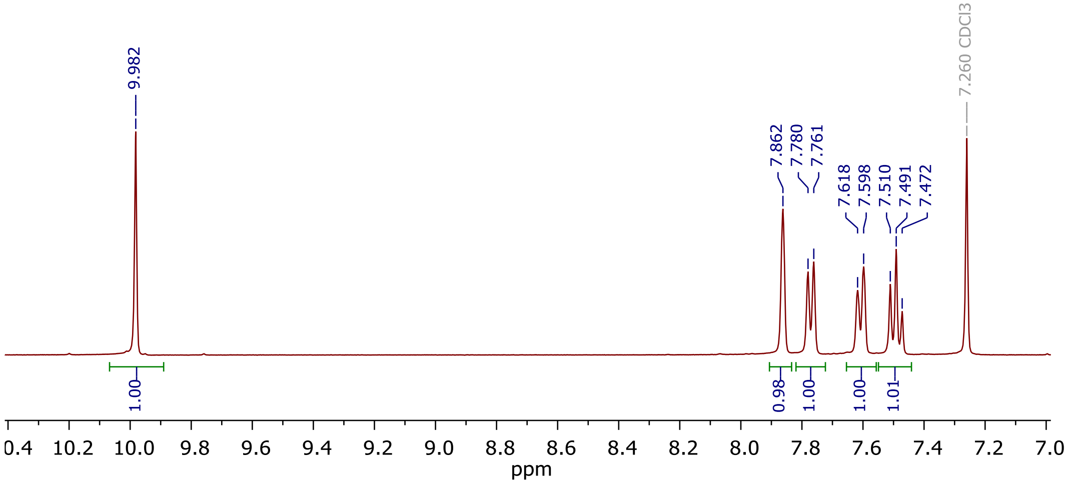


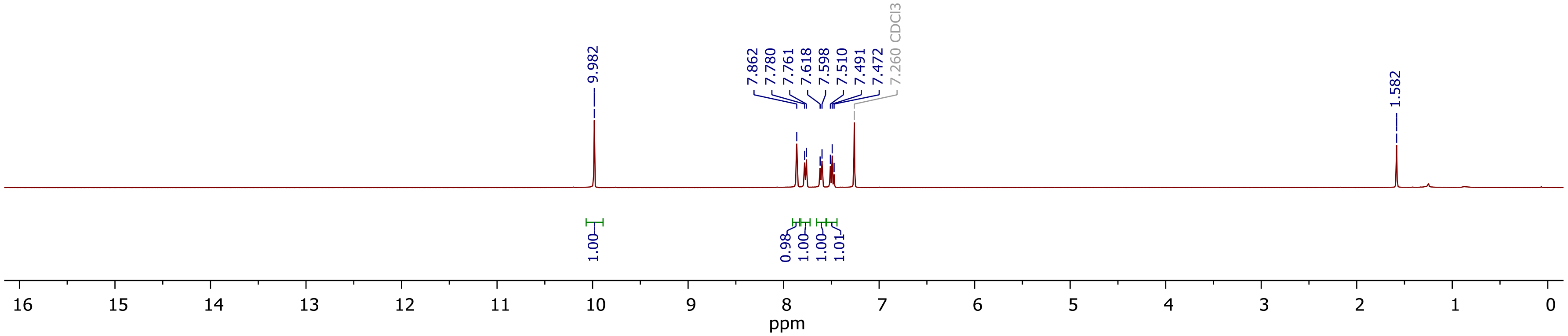


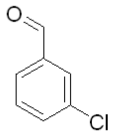
3f, ^{13}C NMR
100 MHz, DMSO-d_6



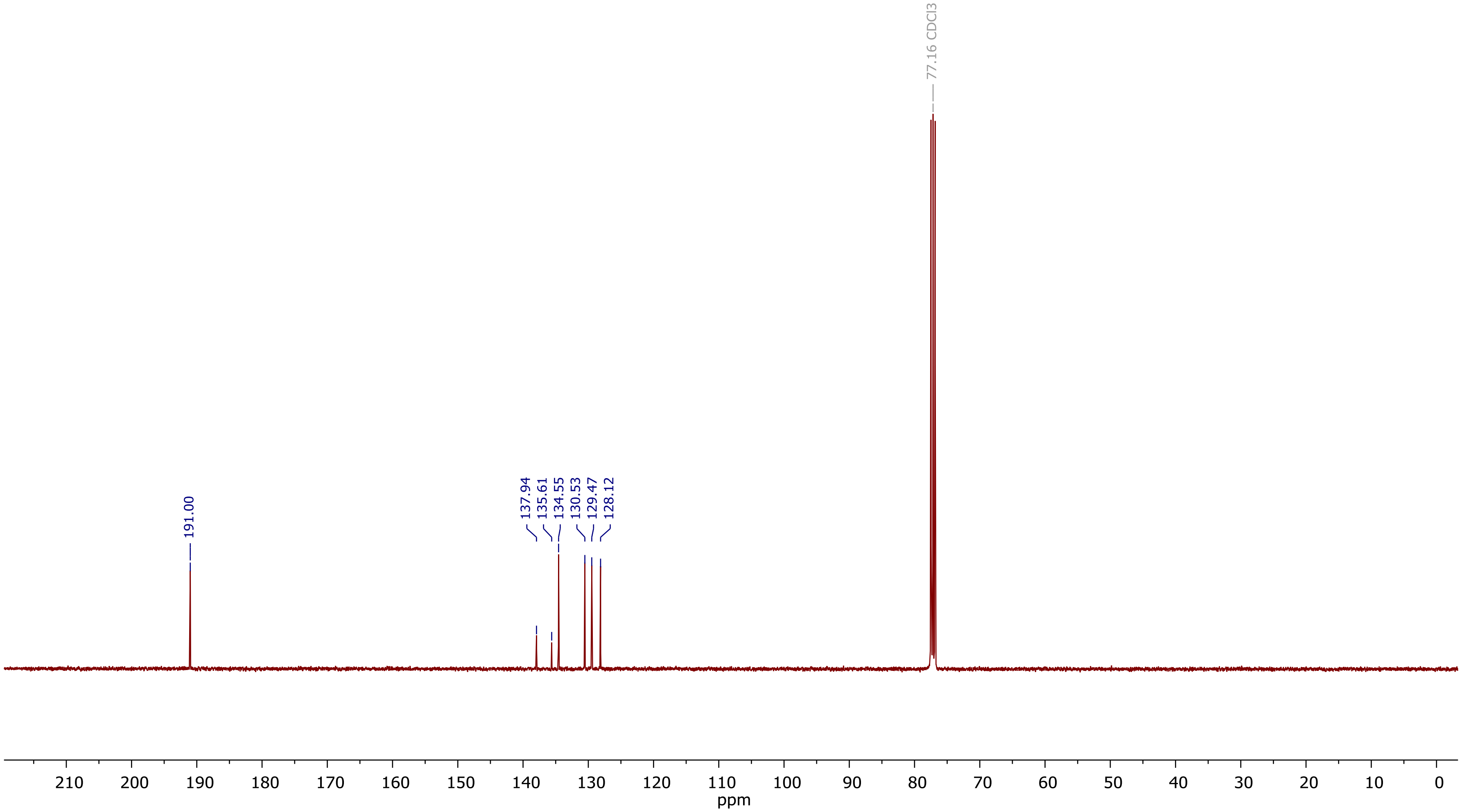
3g, ^{1}H NMR
400 MHz, $CDCl_3$

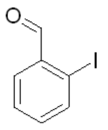




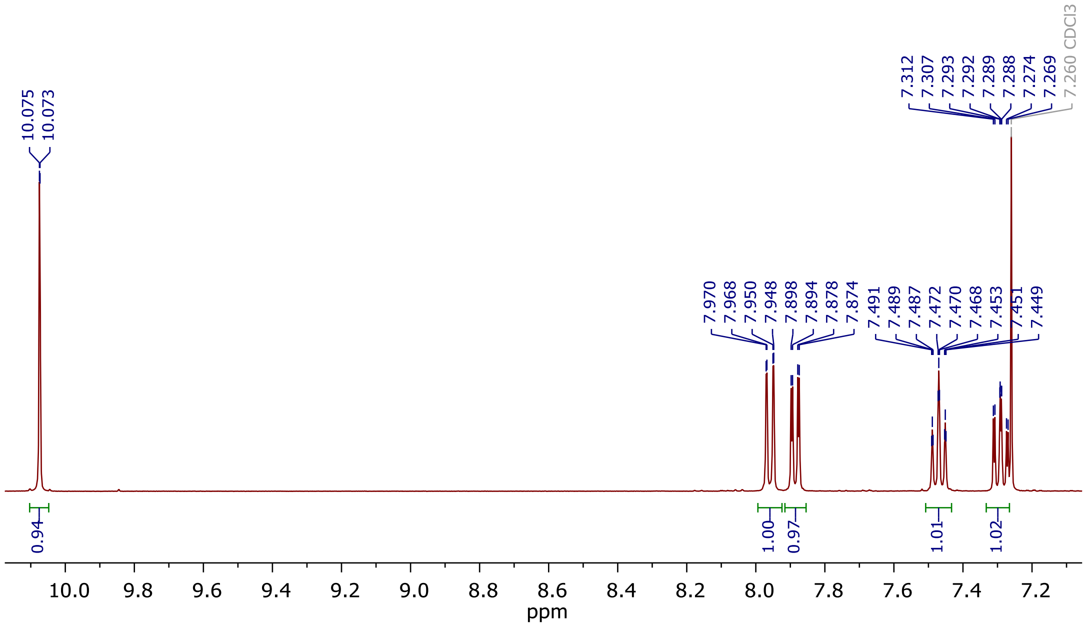


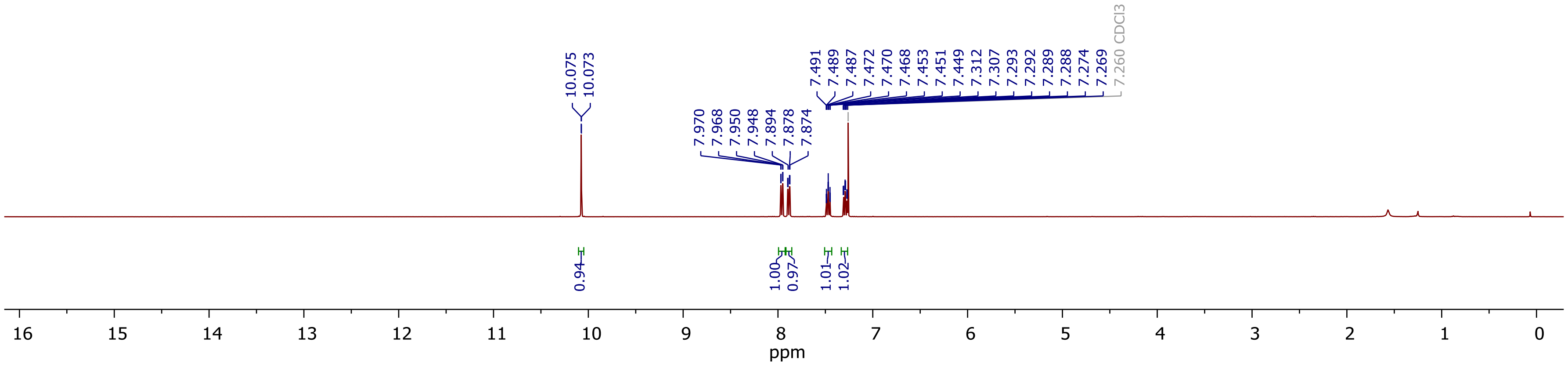
3g, ^{13}C NMR
100 MHz, $CDCl_3$

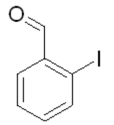




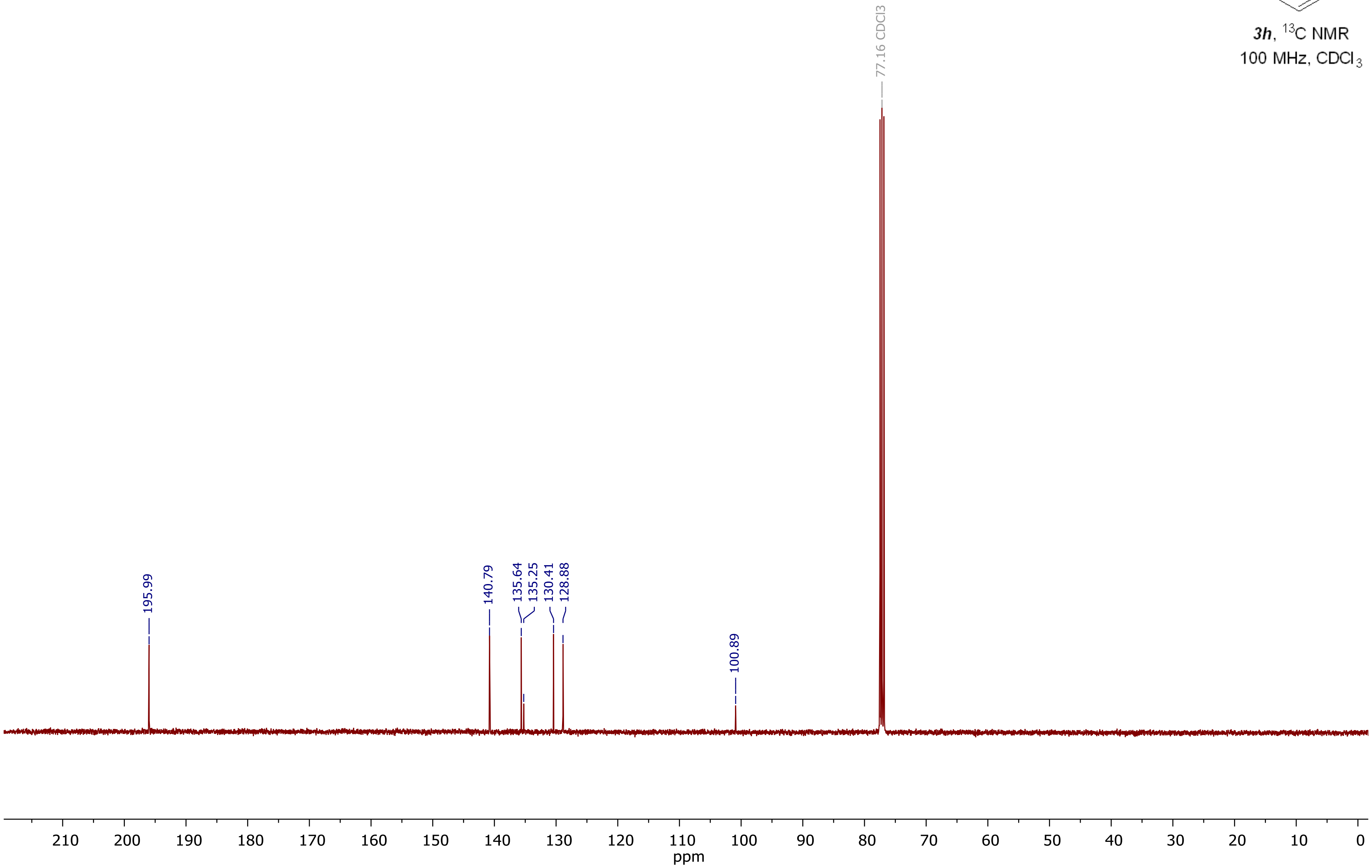
3h, ^{1}H NMR
400 MHz, $CDCl_3$

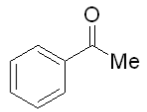




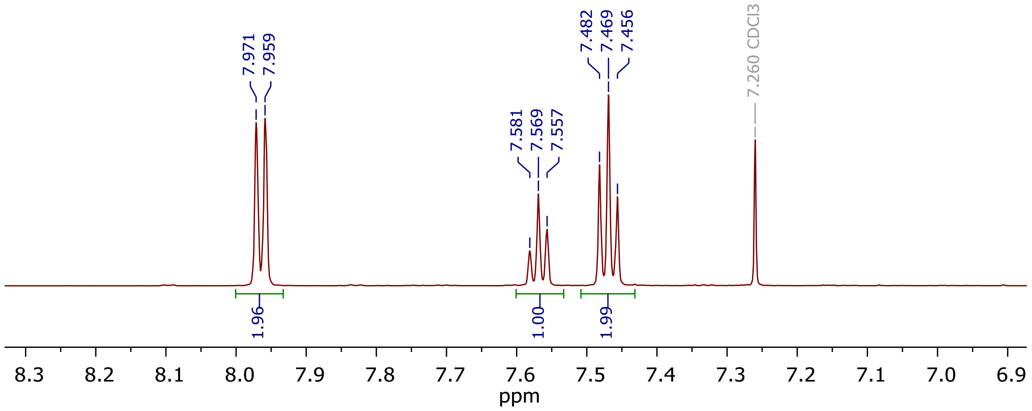


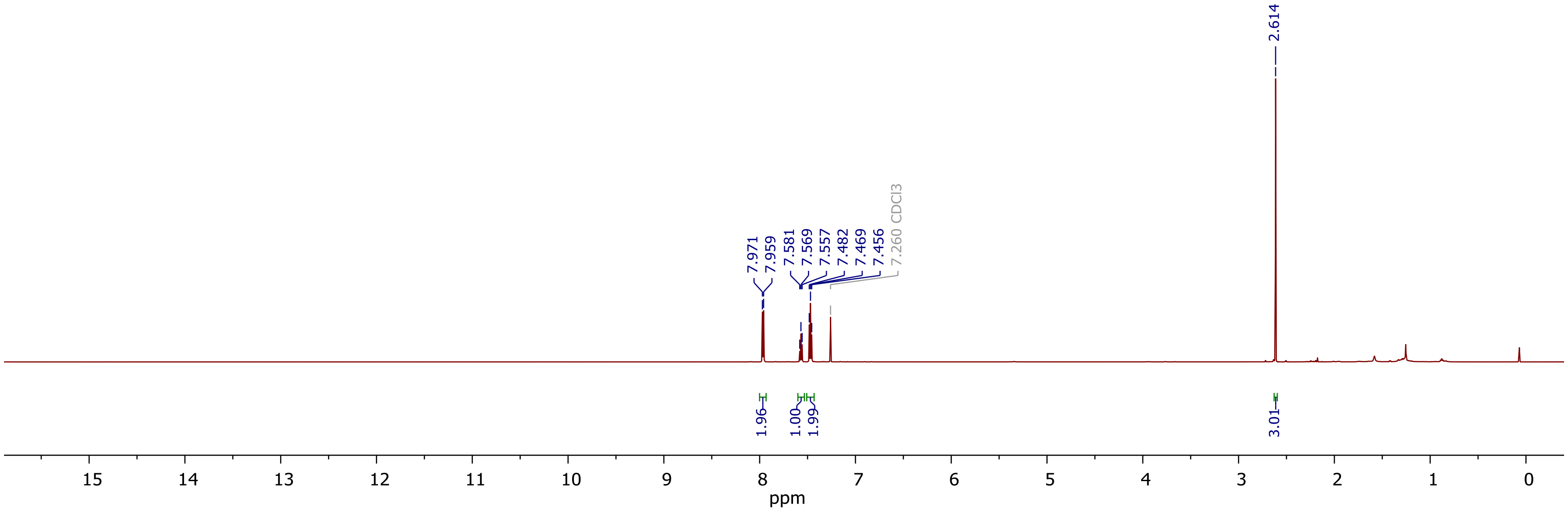
3h, ^{13}C NMR
100 MHz, $CDCl_3$

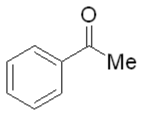




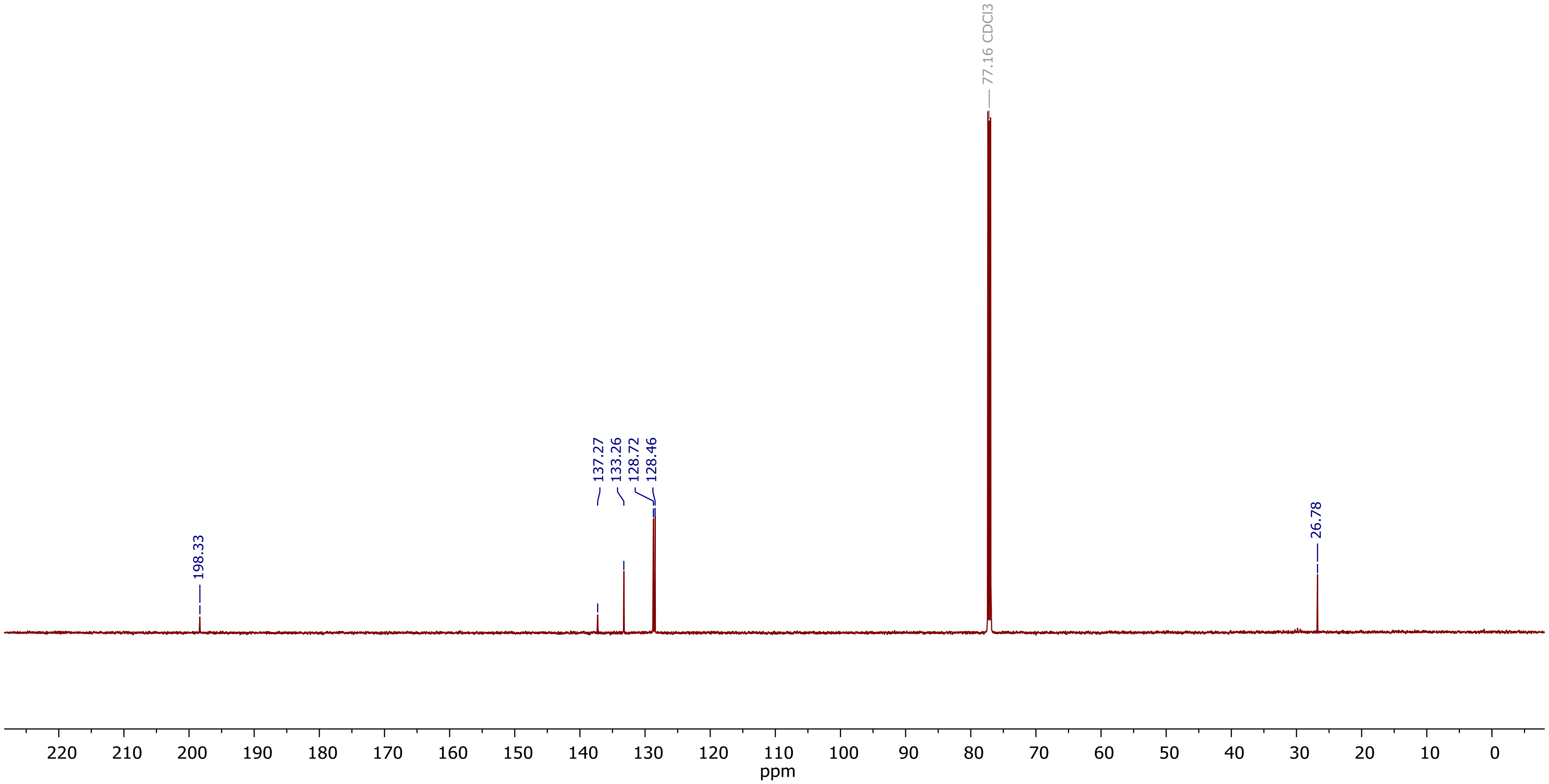
3i, ^{1}H NMR
600 MHz, $CDCl_3$

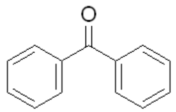




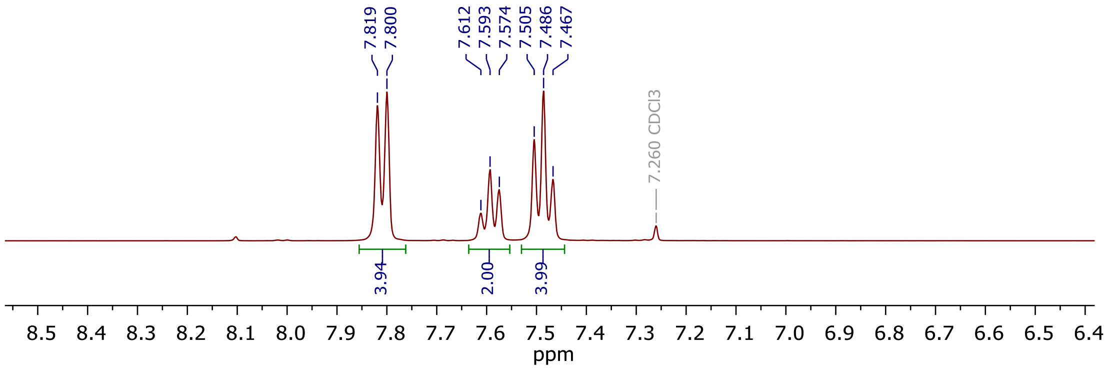


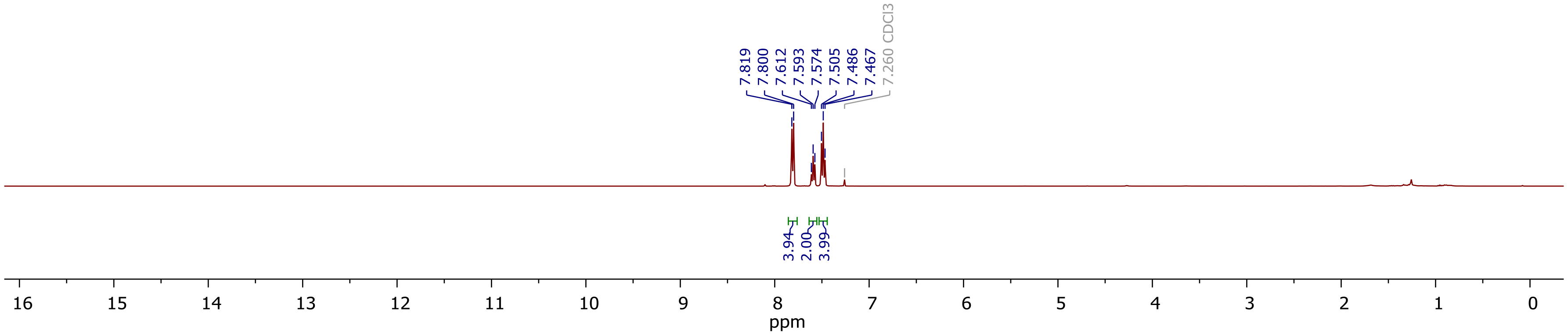
3i, ^{13}C NMR
150 MHz, $CDCl_3$

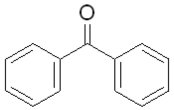




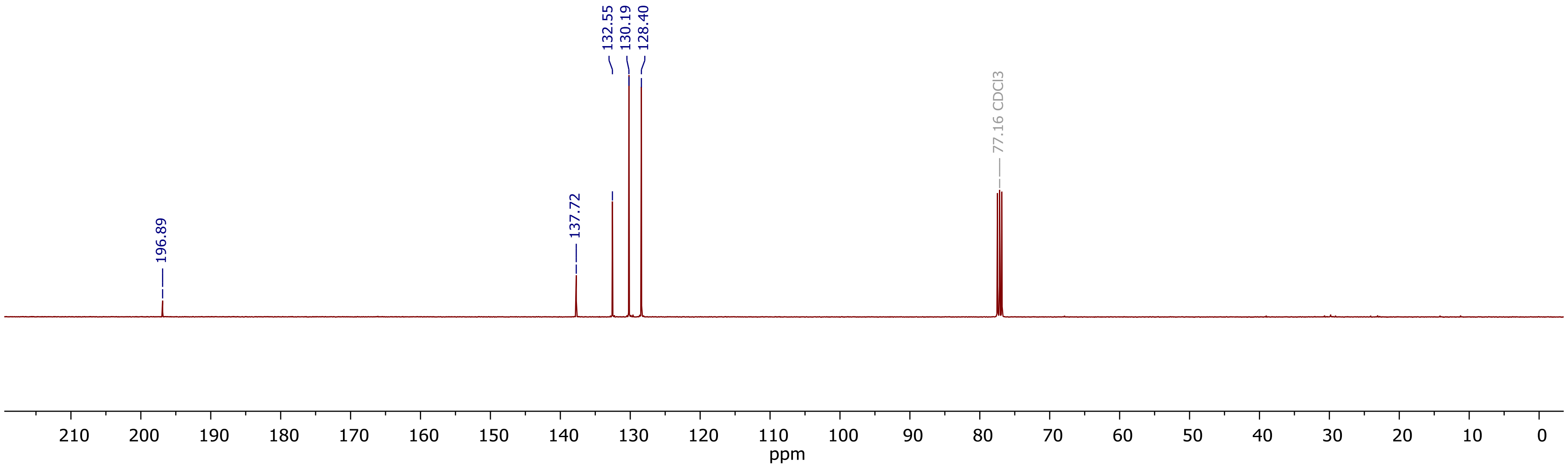
3j, ^{1}H NMR
400 MHz, $CDCl_3$

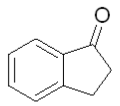




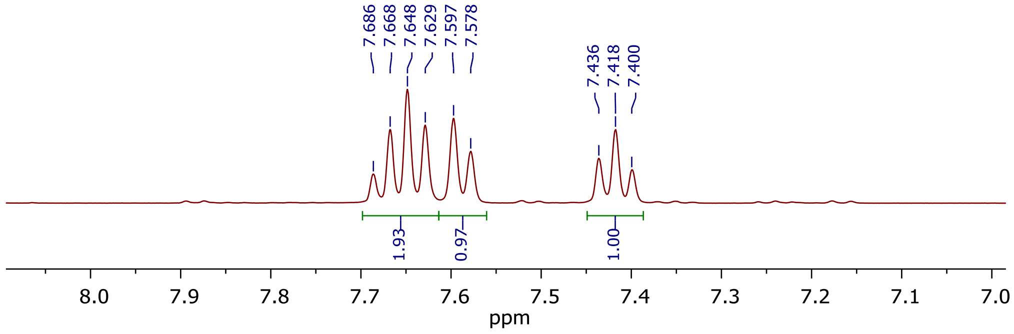


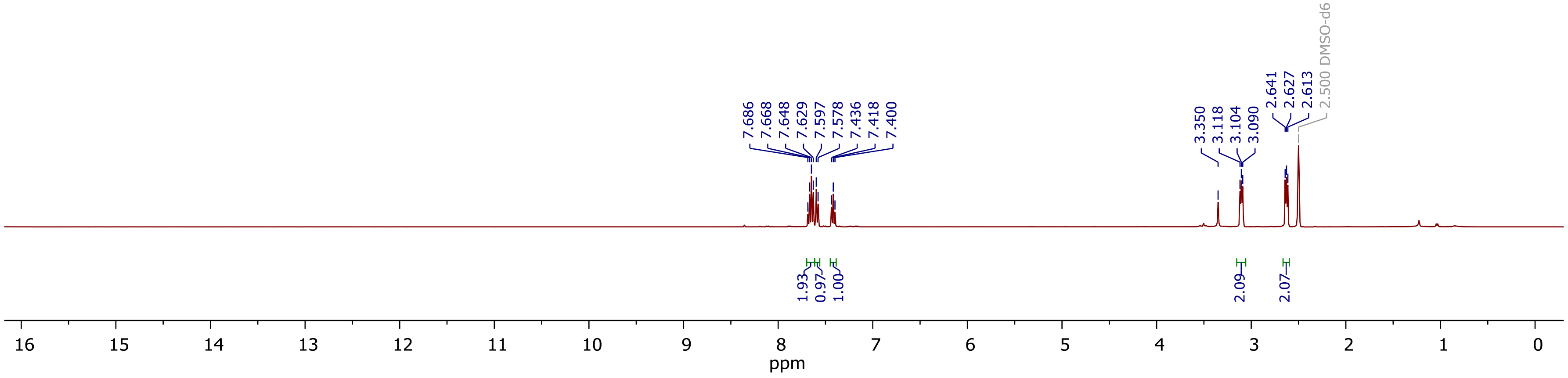
3j, ^{13}C NMR
100 MHz, $CDCl_3$

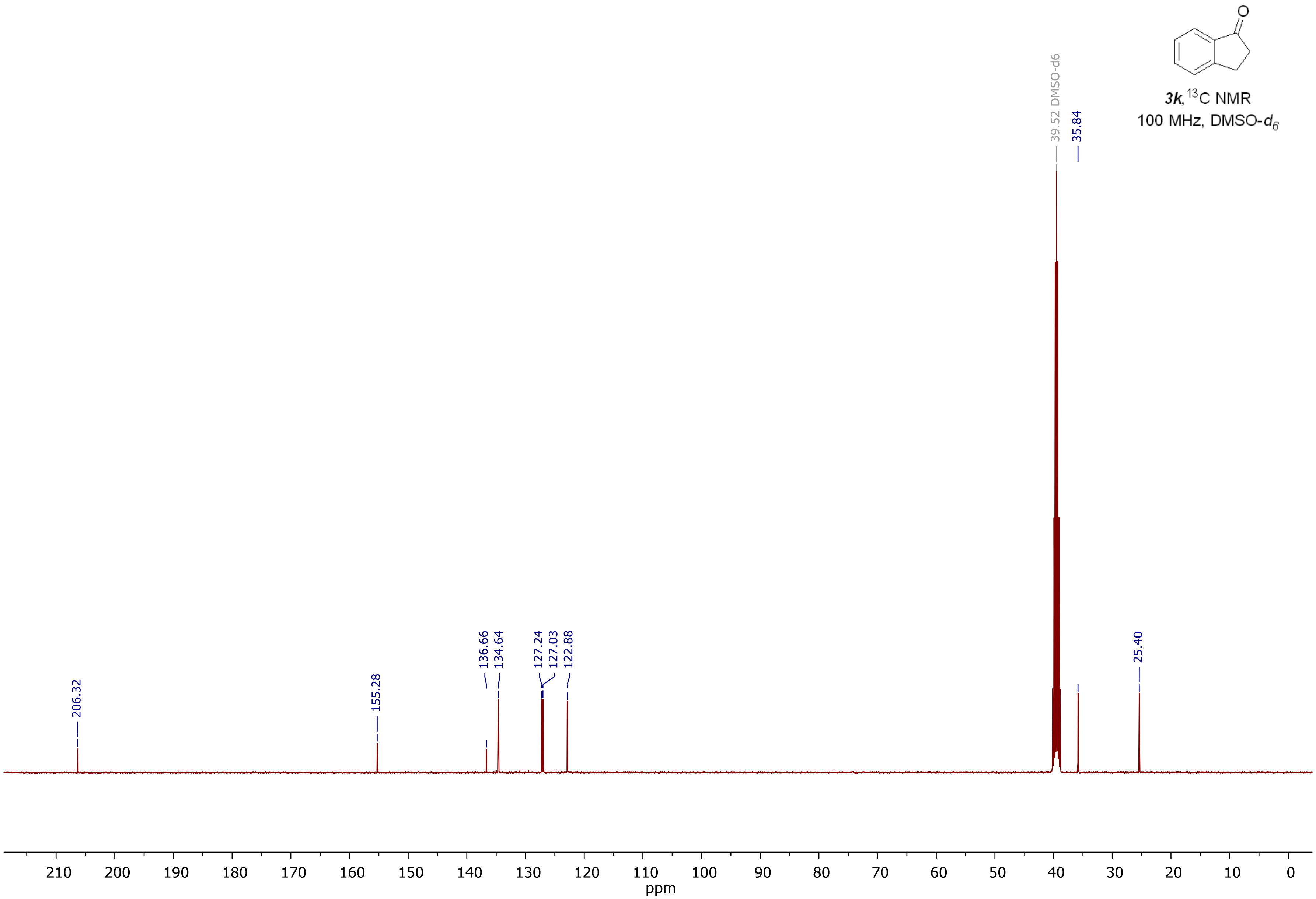




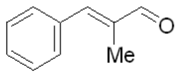
3k, ^{1}H NMR
400 MHz, DMSO-d_6



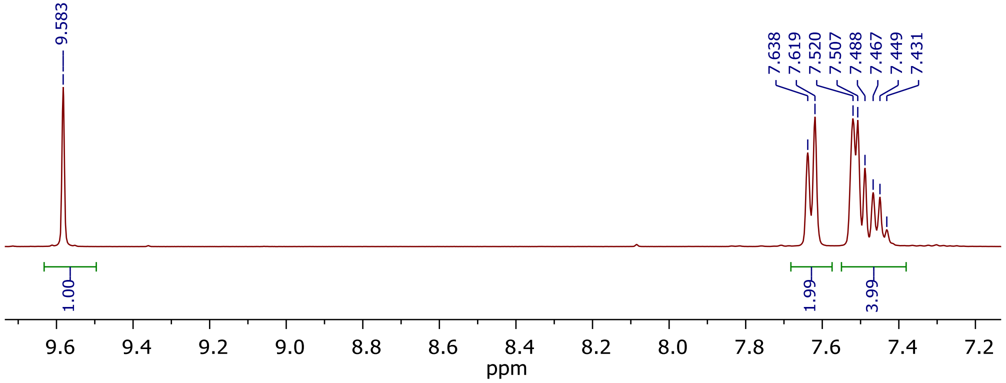


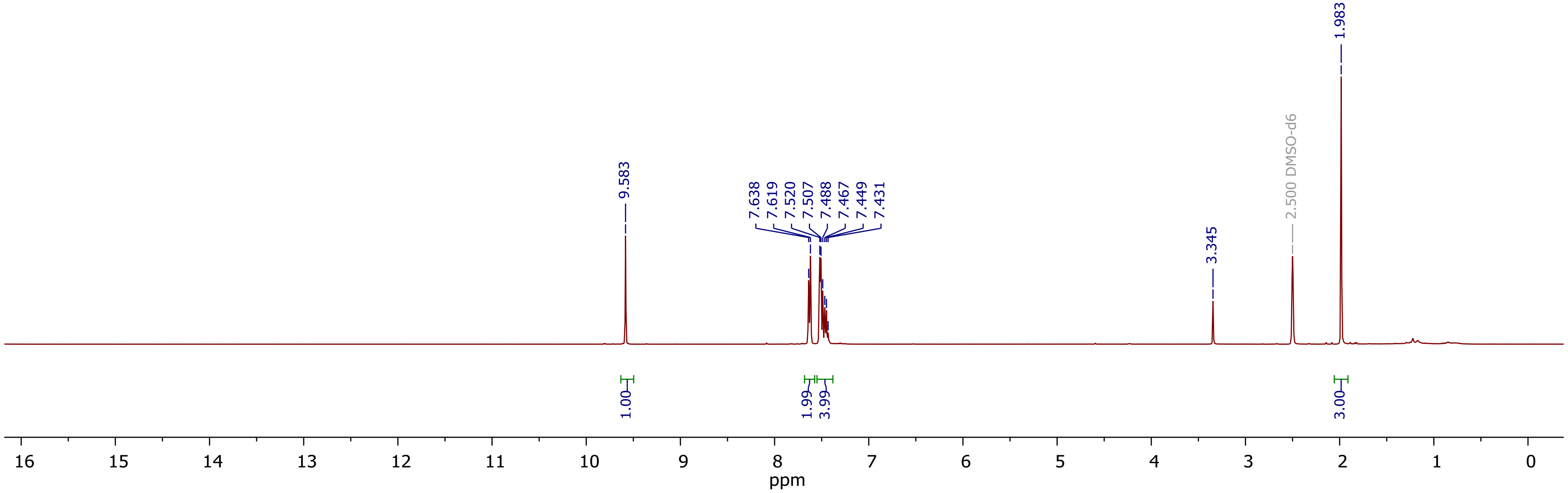


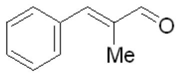
3k, ^{13}C NMR
100 MHz, DMSO-d_6



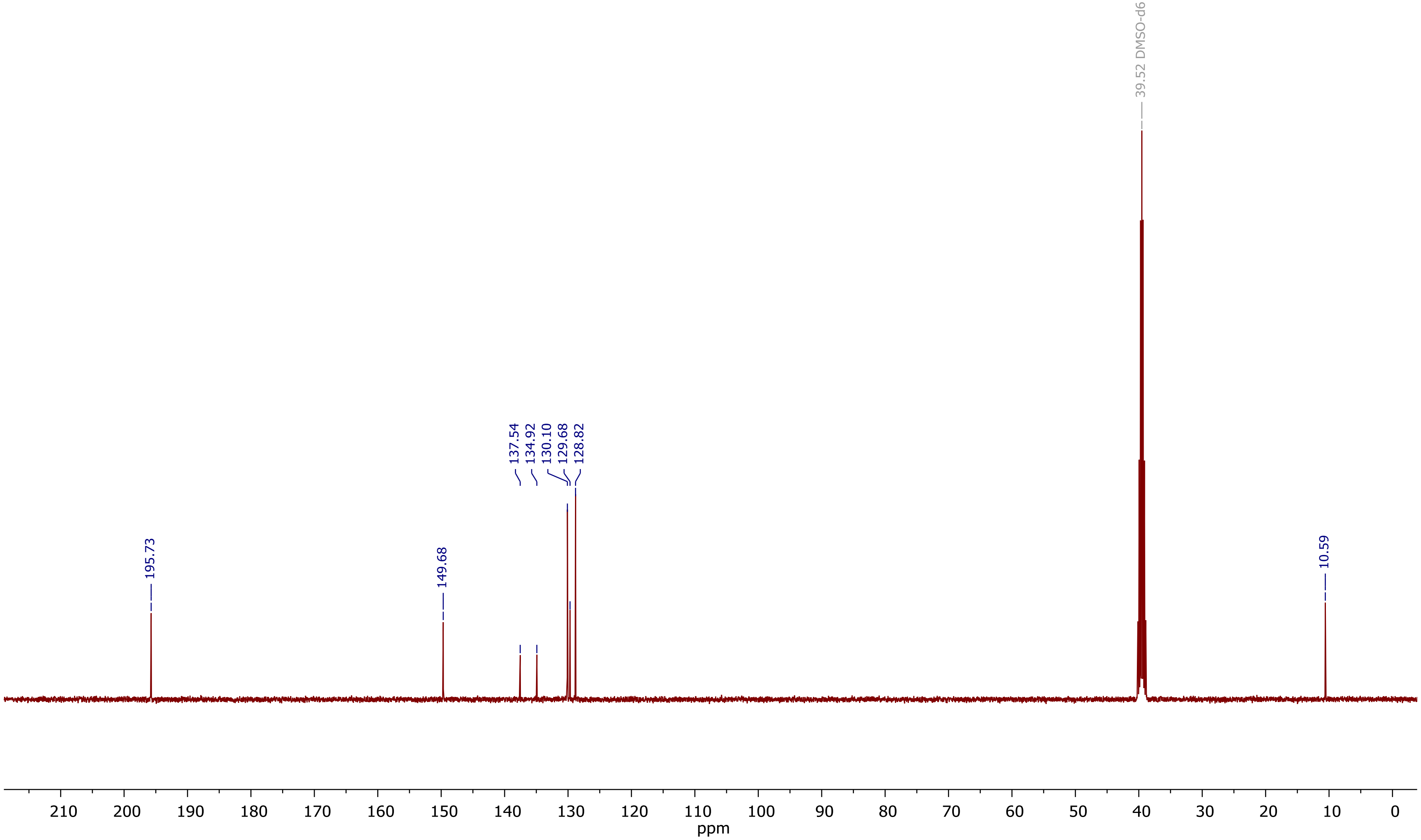
3l, ^{1}H NMR
400 MHz, DMSO-d_6

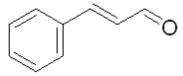




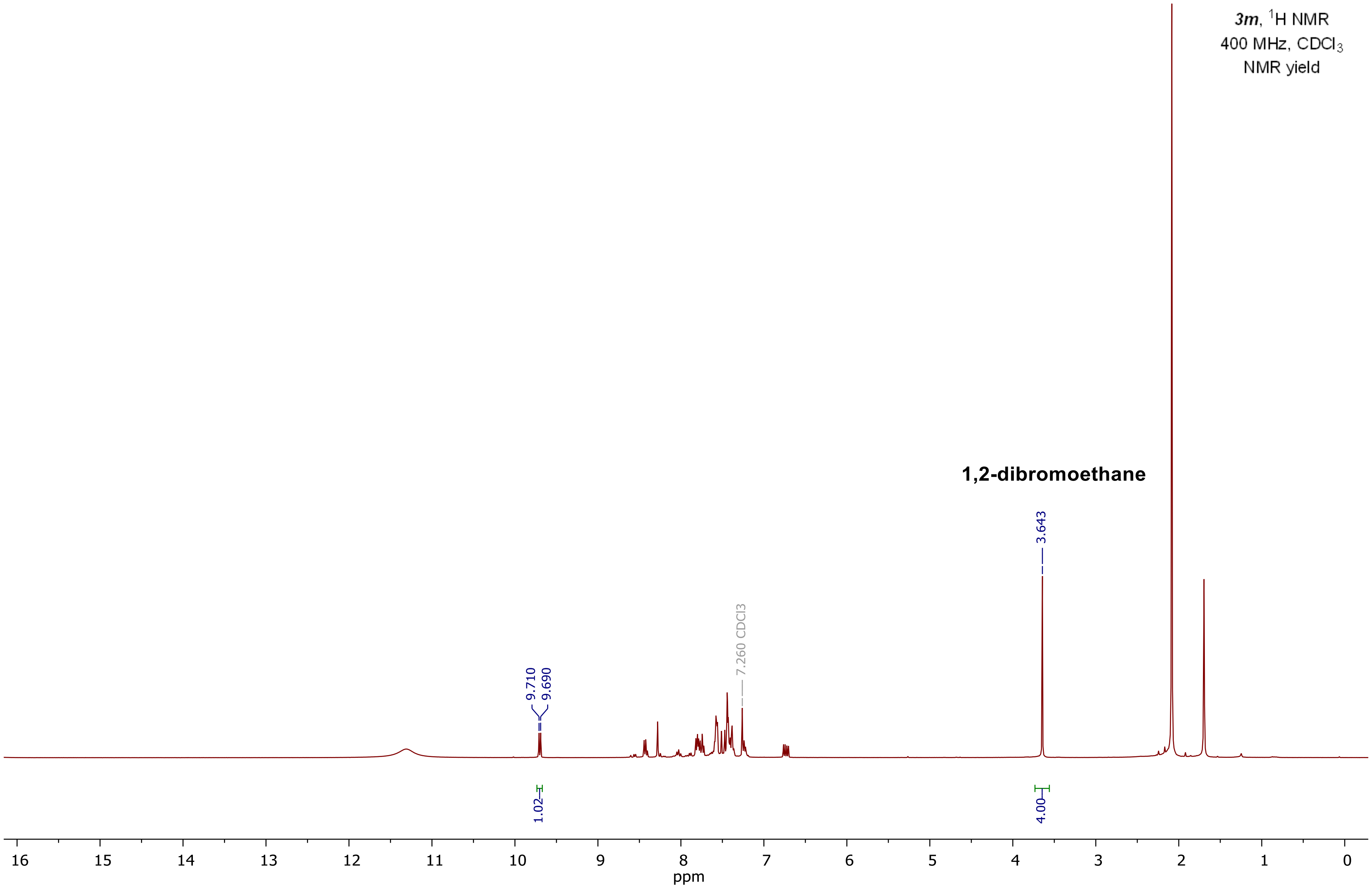


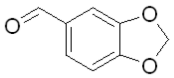
3l, ^{13}C NMR
100 MHz, DMSO-d_6



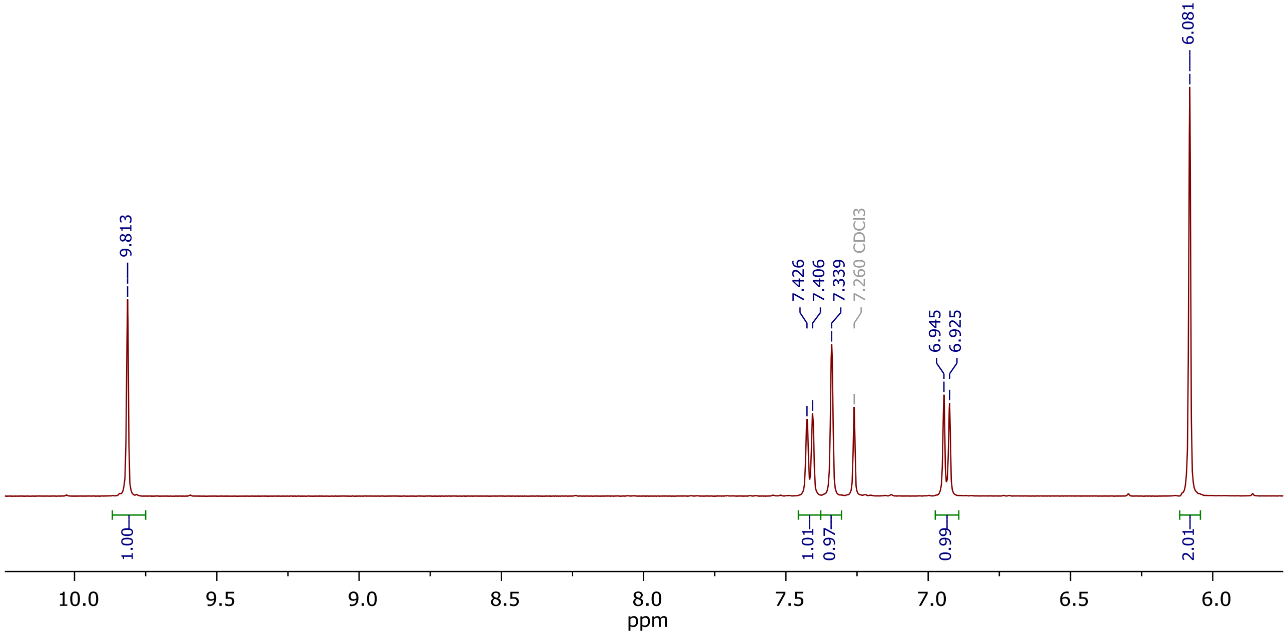


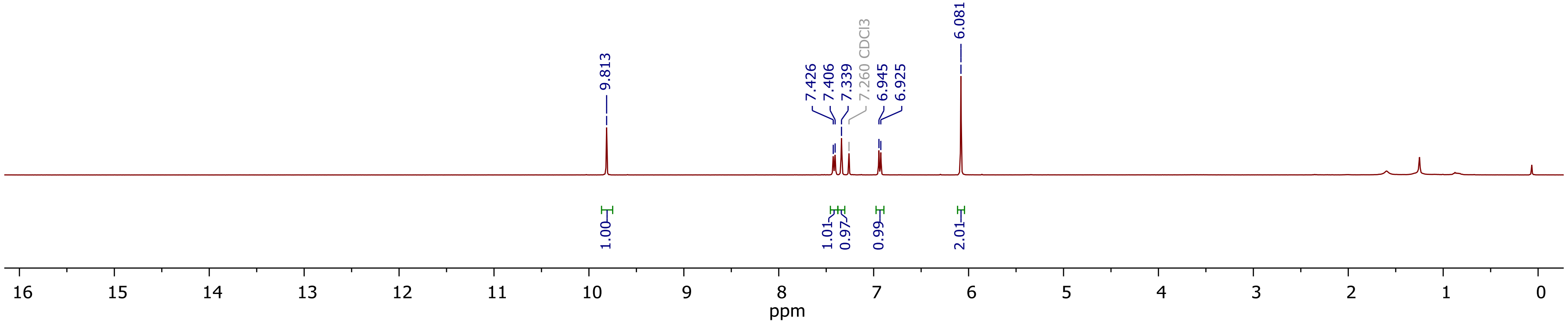
3m, ^{1}H NMR
400 MHz, CDCl$_3$
NMR yield

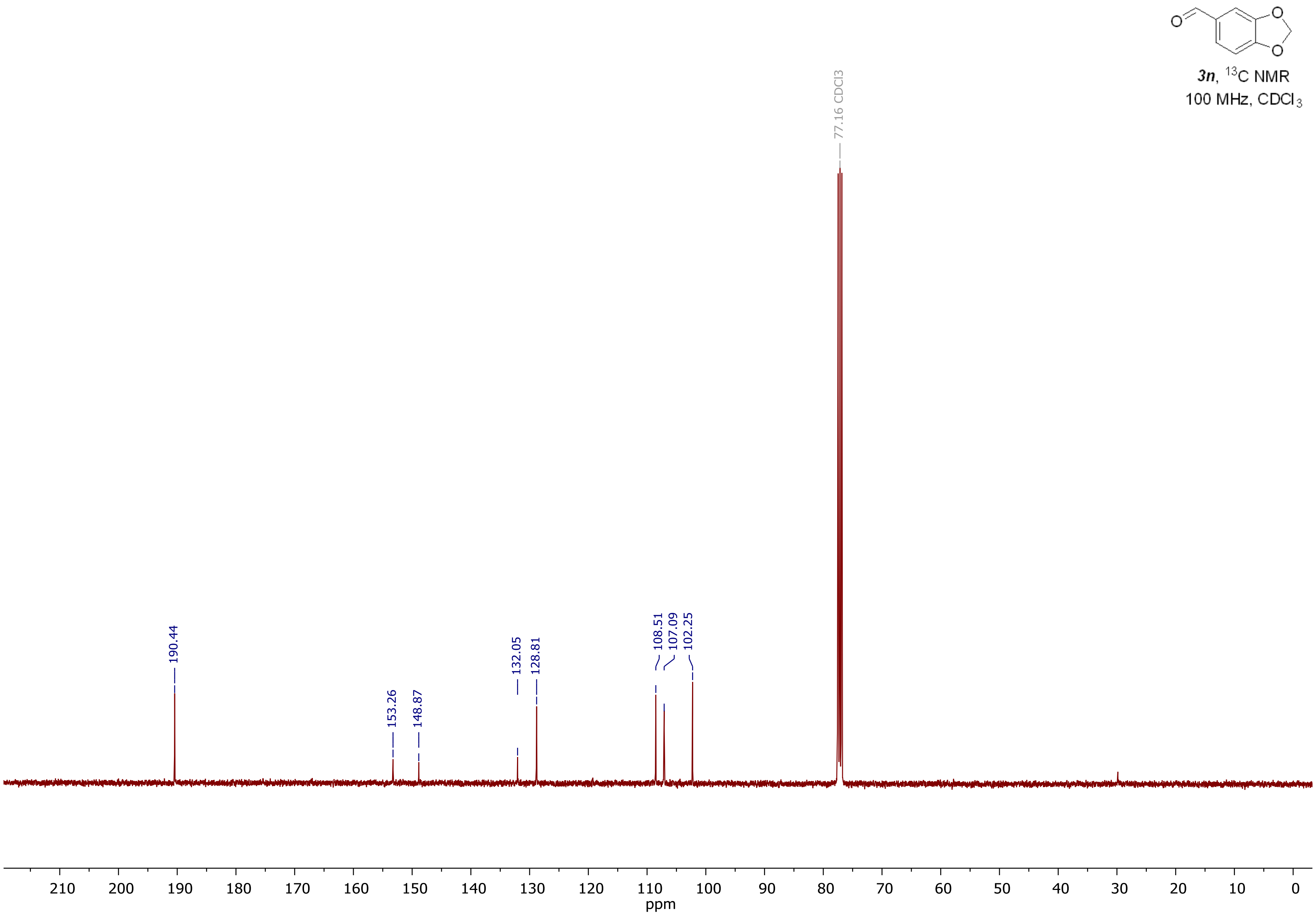


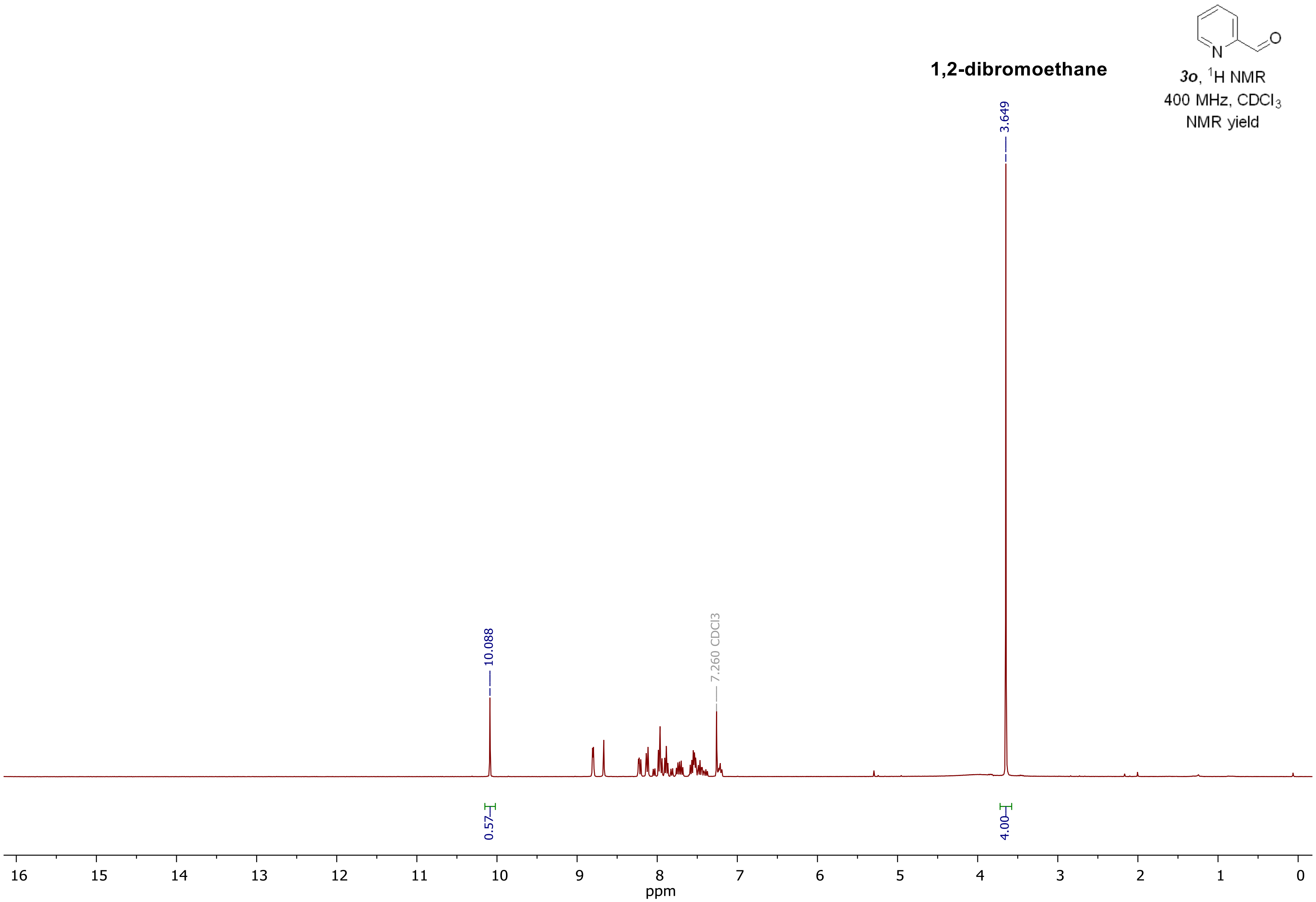


3n, ^{1}H NMR
400 MHz, CDCl$_3$

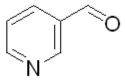




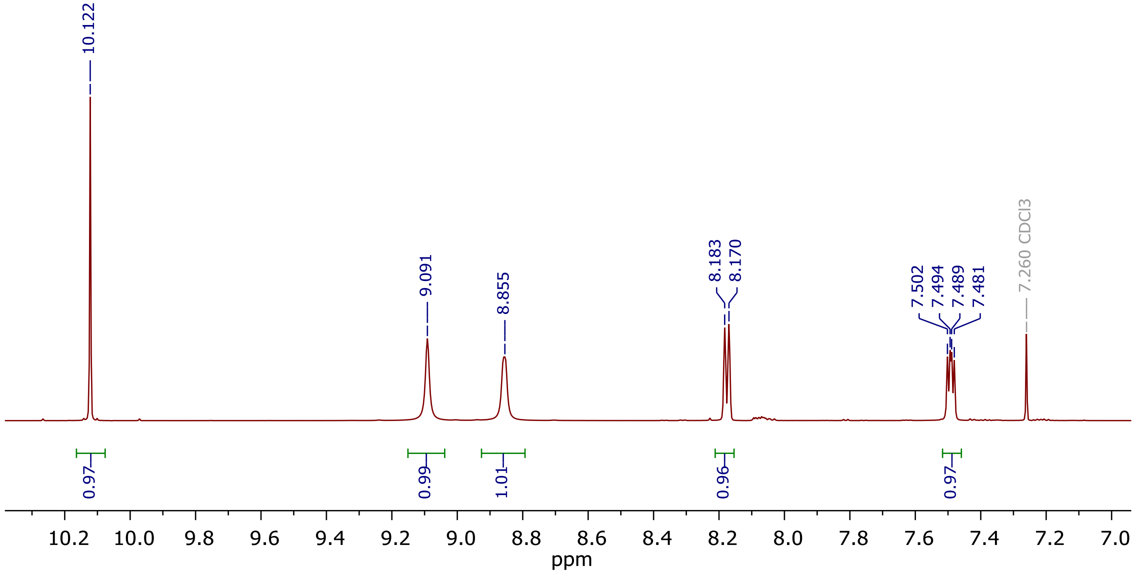

3n, ^{13}C NMR
100 MHz, CDCl$_3$
O
O
O
77.16 CDCl3
190.44
153.26
148.87
132.05
128.81
108.51
107.09
102.25
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

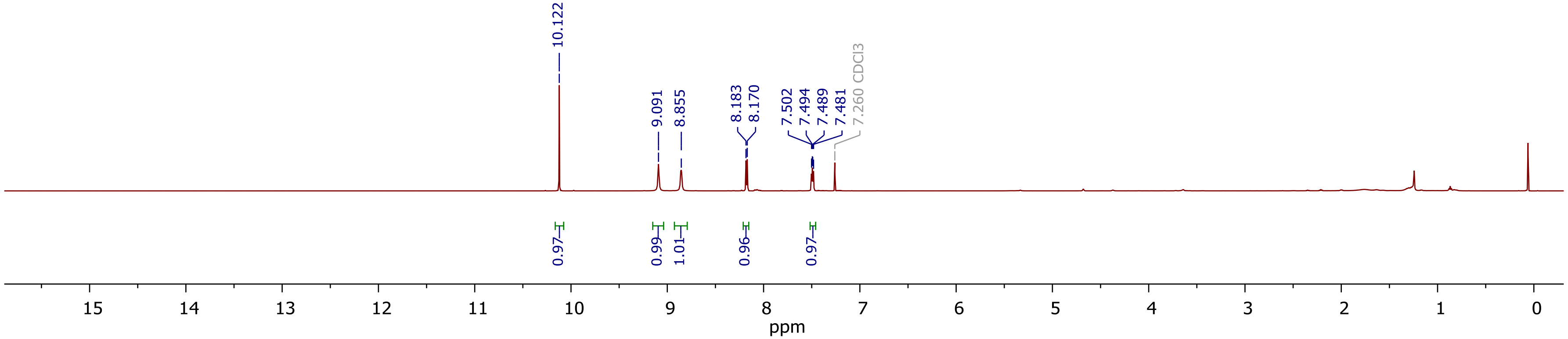


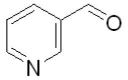
3o, ^{1}H NMR
400 MHz, $CDCl_3$
NMR yield



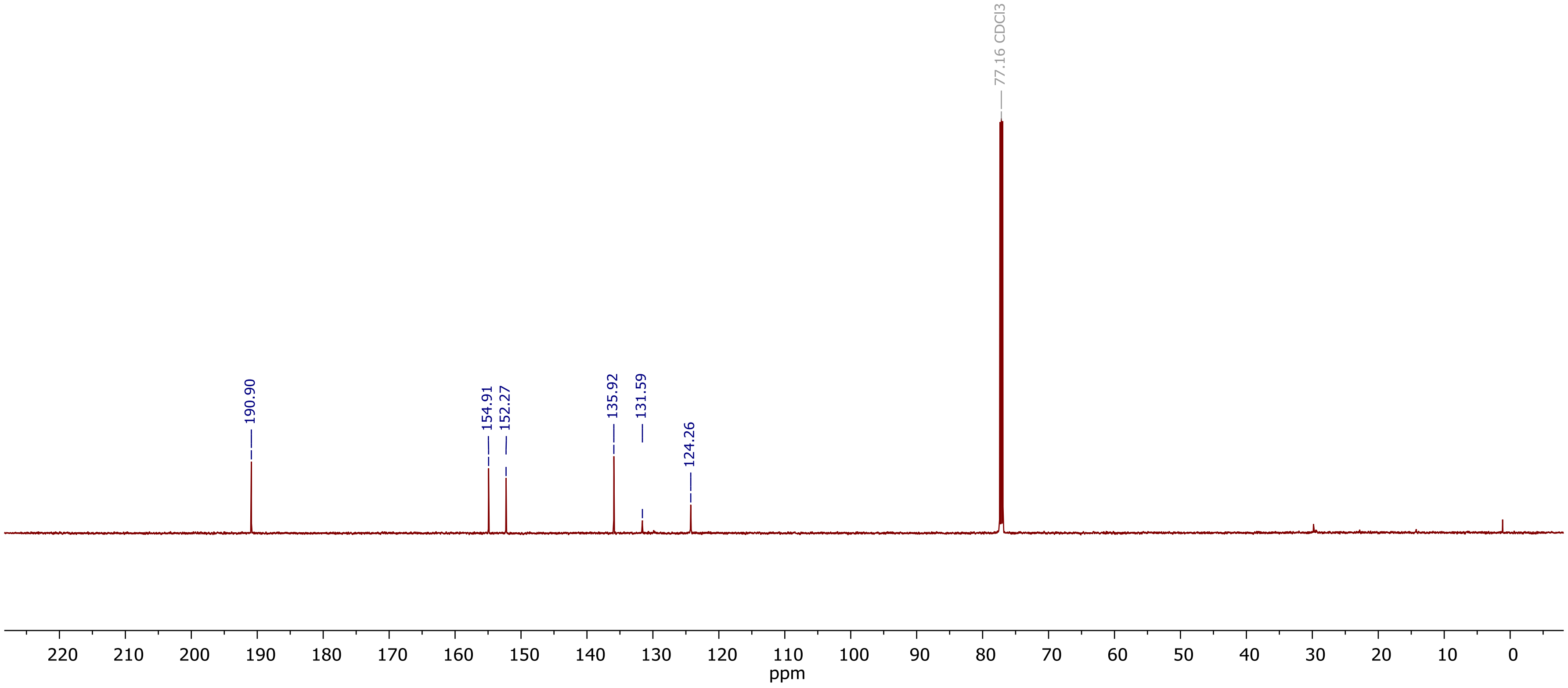
3p, ^{1}H NMR
600 MHz, $CDCl_3$

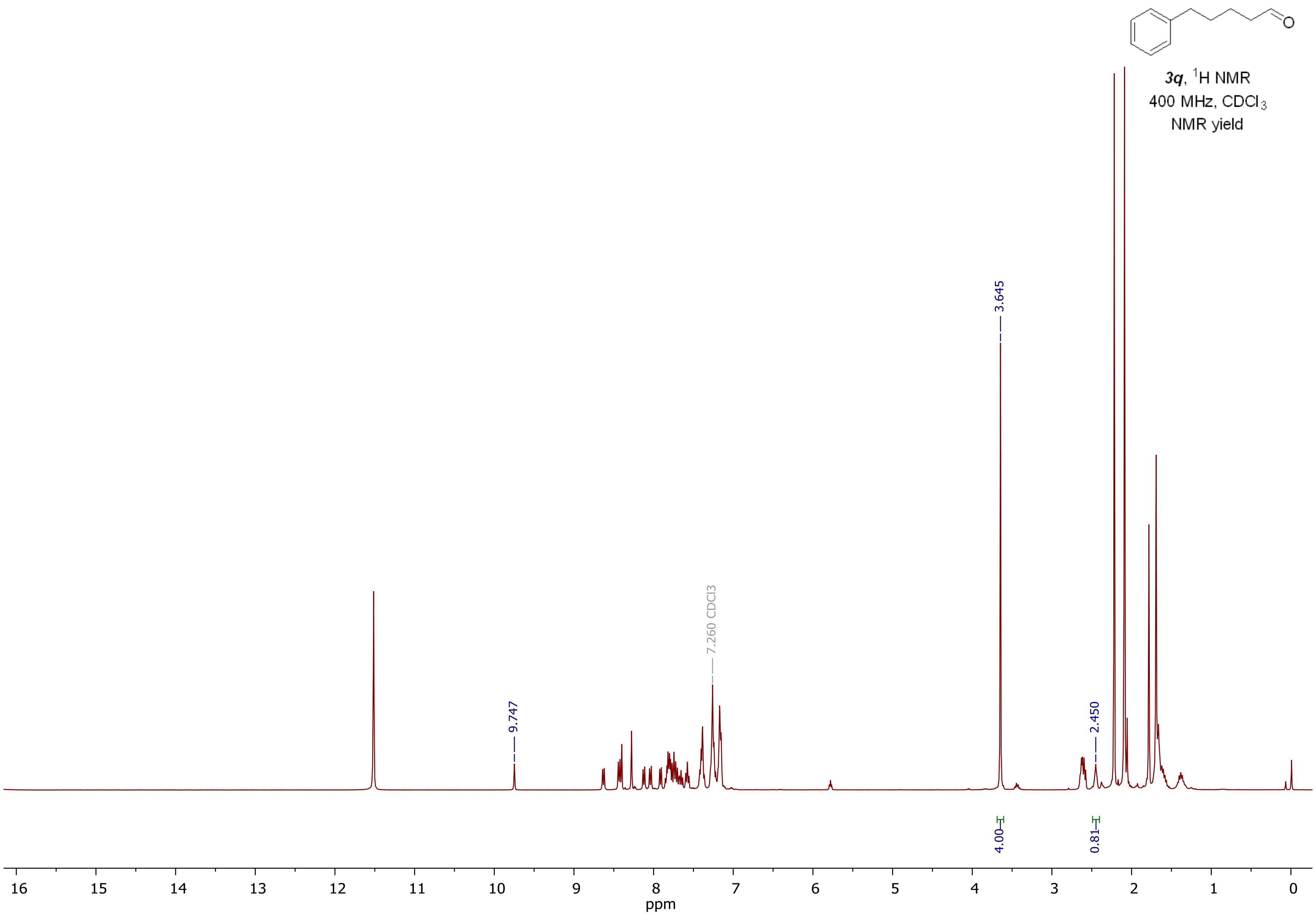


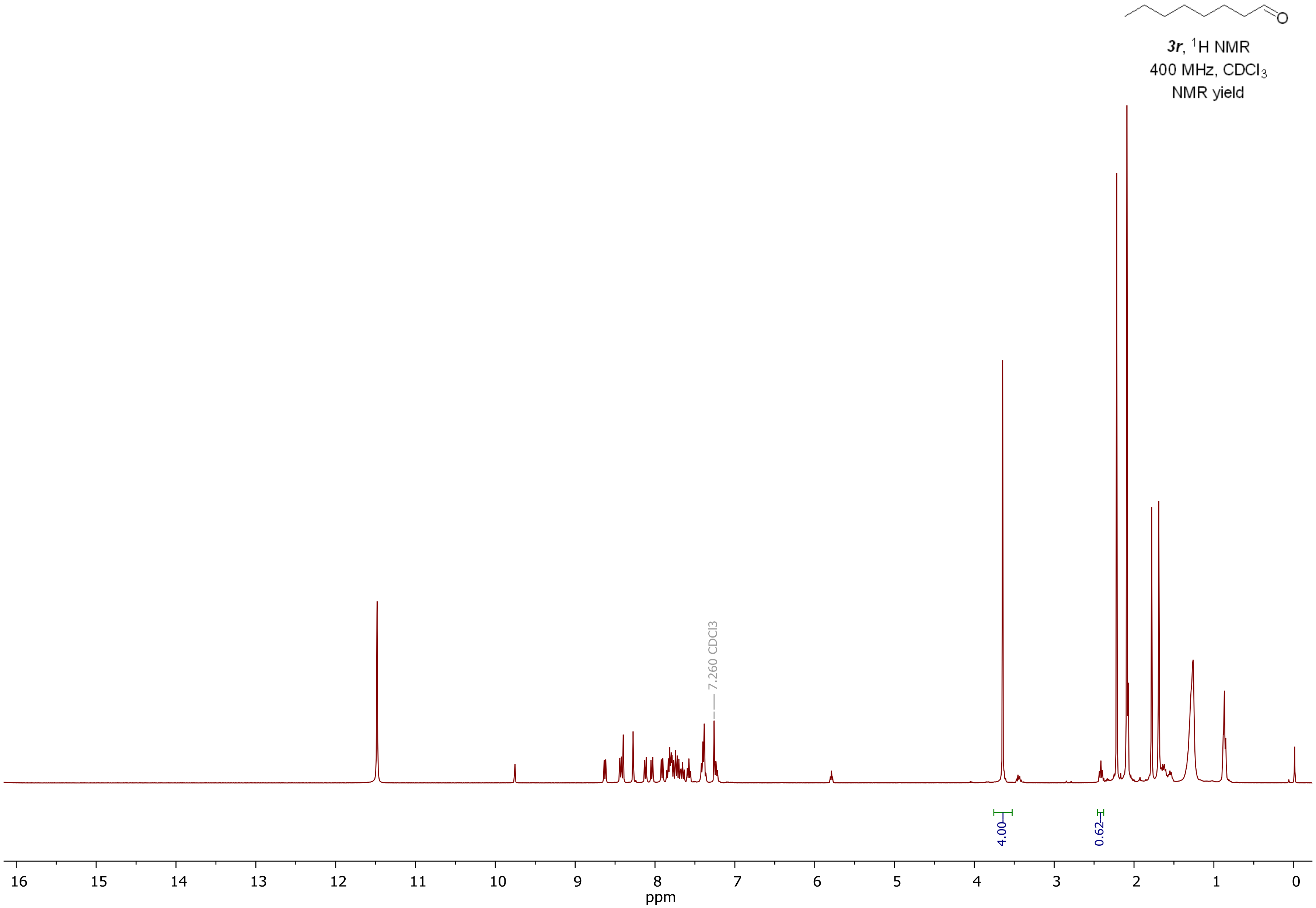




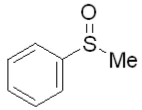
3p, ^{13}C NMR
150 MHz, $CDCl_3$



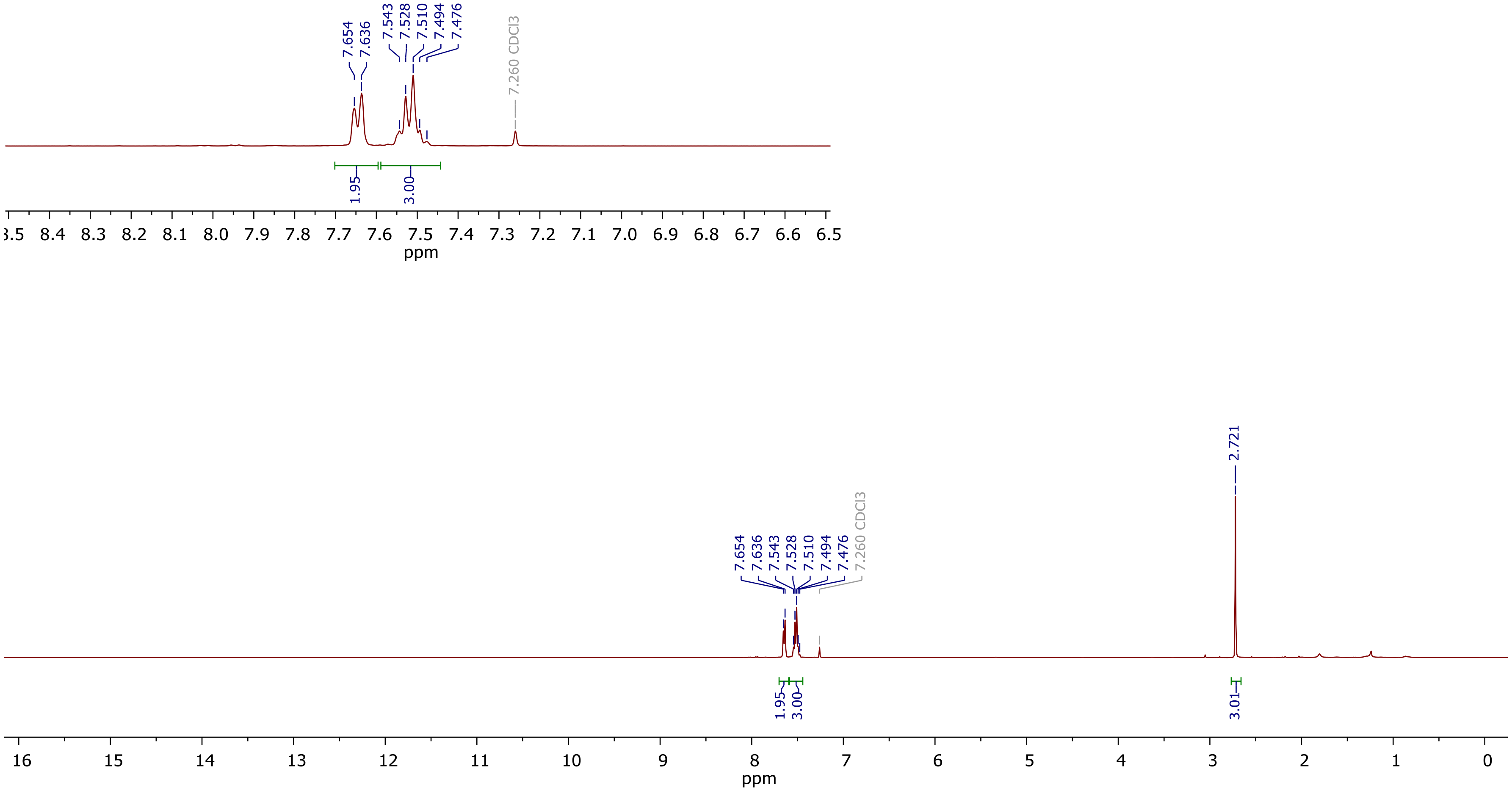

3q, ^{1}H NMR
400 MHz, $CDCl_3$
NMR yield
9.747
7.260 CDCl3
3.645
2.450
4.00
0.81
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

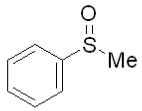


3r, ^{1}H NMR
400 MHz, $CDCl_3$
NMR yield



4, ¹H NMR
400 MHz, $CDCl_3$





4, ^{13}C NMR
100 MHz, CDCl$_3$