**Electronic supplementary materials** *Mendeleev Commun.*, 2021, **31**, 271–273

# Nickel catalyzed hydrosilane reduction of (het)arenecarboxylic acids into aldehydes

**Liang Wang, Yaoyao Wang, Yu Tao, Nana Zhang and Shubai Li**

**Contents**



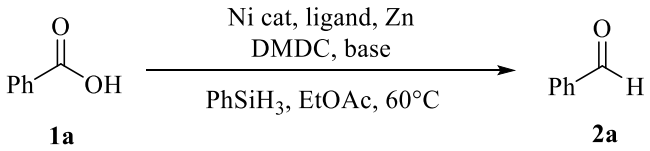
## General Experimental

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Aladdin and Sigma Aldrich) and used without further purification. Ni catalysts, diphenylsilane, Zn, Mn and ligands were purchased from Sigma Aldrich (>95%). Other organic compounds and dry solvents were used as received from Aladdin. $^{1}$H NMR and $^{13}$C NMR spectra were recorded at ambient temperature on an AVANCE 500 MHz spectrometer. Chemical shifts are reported in $\delta$ units, parts per million (ppm), and were referenced to $CDCl_3$ (7.26 or 77.0 ppm) as the internal standard. The coupling constants *J* are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). The GC−MS analyses were performed on a Thermo Scientific™ equipment (TSQ 8000 Evo). Melting points (m.p.) are determined with an Optimelt MPA 100 apparatus and are not corrected. All the products are known compounds and were identified by comparing of their physical and spectra data with those reported in the literature.

**CAUTION**: $NiCl_2$(dme) and $NiBr_2 \cdot 3H_2O$ can cause cancer and allergy or asthma symptoms. They are also very toxic to aquatic life with long lasting effects.

**Experimental Procedures, Spectral and Analytical data**

**Table S1** Ni source, ligand and base screening.[a]

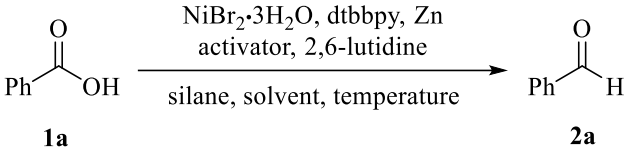



**1a** **2a**

| Entry | [Ni] source | Ligand | Base | Yield(%)[b] |
|---|---|---|---|---|
| 1 | $Ni(COD)_2$ | dtbbpy | 2,6-lutidine | 12 |
| 2 | $NiCl_2(dme)$ | dtbbpy | 2,6-lutidine | 39 |
| 3 | $NiCl_2•(H_2O)_6$ | dtbbpy | 2,6-lutidine | 15 |
| 4 | $NiI_2$ | dtbbpy | 2,6-lutidine | 5 |
| 5 | $Ni(OAc)_2•(H_2O)_4$ | dtbbpy | 2,6-lutidine | 4 |
| 6 | $Ni(acac)_2$ | dtbbpy | 2,6-lutidine | trace |
| 7 | $Ni(ClO_4)_2$ | dtbbpy | 2,6-lutidine | 0 |
| 8 | $Ni(OTf)_2$ | dtbbpy | 2,6-lutidine | 4 |
| 9 | $NiBr_2·3H_2O$ | dtbbpy | 2,6-lutidine | 45 |
| 10 | $NiBr_2·3H_2O$ | bpy | 2,6-lutidine | 20 |
| 11 | $NiBr_2·3H_2O$ | 4,4'-diOMebpy | 2,6-lutidine | 8 |
| 12 | $NiBr_2·3H_2O$ | phen | 2,6-lutidine | 14 |
| 13 | $NiBr_2·3H_2O$ | neocuproine | 2,6-lutidine | 6 |
| 14 | $NiBr_2·3H_2O$ | dtbbpy | 2,4,6-collidine | 31 |
| 15 | $NiBr_2·3H_2O$ | dtbbpy | DBU | 11 |
| 16 | $NiBr_2·3H_2O$ | dtbbpy | DIPEA | 24 |
| 17 | $NiBr_2·3H_2O$ | dtbbpy | DMAP | 0 |
| 18 | $NiBr_2·3H_2O$ | dtbbpy | $K_2CO_3$ | 8 |
| 19 | $NiBr_2·3H_2O$ | dtbbpy | 2,6-lutidine | 51[c], 38[d] |

[a] Reaction conditions: **1a** (0.2 mmol), [Ni] (10 mol%), ligand (20 mol%), Zn(20 mol%), $PhSiH_3$ (1.5 equiv), DMDC (2 equiv), base (1.2 equiv), EtOAc (4 mL), 60 °C, 24 h. [b] GC yield using *n*-dodecane as the internal standard. [c] 20 mol% catalyst. [d] 5 mol% catalyst.

**Table S2** Further optimization of the reaction conditions.[a]




**1a** **2a**

| Entry | Activator | Silane | Solvent | Temperature (°C) | Yield(%)[b] |
|---|---|---|---|---|---|
| 1 | DMDC | $PhSiH_3$ | EtOAc | 60 | 51 |
| 2 | DMDC | $Ph_2SiH_2$ | EtOAc | 60 | 65 |
| 3 | DMDC | $MePhSiH_2$ | EtOAc | 60 | 52 |
| 4 | DCC | $Ph_2SiH_2$ | EtOAc | 60 | trace |
| 5 | DIC | $Ph_2SiH_2$ | EtOAc | 60 | trace |
| 6 | $Piv_2O$ | $Ph_2SiH_2$ | EtOAc | 60 | 31 |
| 7 | $Boc_2O$ | $Ph_2SiH_2$ | EtOAc | 60 | 12 |
| 8 | DMDC | $Ph_2SiH_2$ | MeCN | 60 | 14 |
| 9 | DMDC | $Ph_2SiH_2$ | THF | 60 | 39 |
| 10 | DMDC | $Ph_2SiH_2$ | 1,4-Dioxane | 60 | 46 |
| 11 | DMDC | $Ph_2SiH_2$ | DMSO | 60 | 0 |
| 12 | DMDC | $Ph_2SiH_2$ | DCM | 60 | 6 |
| 13 | DMDC | $Ph_2SiH_2$ | EtOAc | 40 | 42 |
| 14 | DMDC | $Ph_2SiH_2$ | EtOAc | 80 | 58 |
| 15 | DMDC | $Ph_2SiH_2$ | EtOAc | 60 | 69[c],77[d],75[e] |
| 16 | DMDC | $Ph_2SiH_2$ | EtOAc | 60 | 33[f] |

[a] Reaction conditions: **1a** (0.2 mmol), $NiBr_2·3H_2O$ (20 mol%), dtbbpy (20 mol%), Zn(20 mol%), silane (1.5 equiv), activator (2 equiv), 2,6-lutidine (1.2 equiv), solvent (4 mL), 24 h. [b] GC yield. [c] $Ph_2SiH_2$ (2.0 equiv). [d] $Ph_2SiH_2$ (2.25 equiv.). [e] $Ph_2SiH_2$ (2.5 equiv). [f] Mn instead of Zn.

**General procedure for the synthesis of 2**

In an oven-dried 10 ml vial, $NiBr_2·3H_2O$ (11 mg, 0.04 mmol) was stirred vigorously with ligand dtbbpy (11 mg, 0.04 mmol) in a dry solvent (4 ml) for 10 minutes. Then acid **1** (0.2 mmol) and Zn (3 mg, 0.04 mmol) were added to a 10 ml Schlenk flask with a magnetic stir bar. The flask was evacuated and backfilled with nitrogen three times. To this was added the solution of Ni/ligand prepared above (4 ml), 2,6-lutidine (0.24 mmol) and DMDC (0.4 mmol). Then, $Ph_2SiH_2$ (0.45 mmol) was added via microsyringe, and the reaction mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with diethyl ether (5.0 ml) and *n*-dodecane as an internal standard was added. The yield of product **2** was analyzed by gas chromatography using *n*-dodecane as the internal standard.

**Characterization data of product 2**

Benzaldehyde (**2a**).[S1] Colourless liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.86 (dd, *J* = 5.0, 3.2 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H). GC-MS (m/z):106.

4-Methylbenzaldehyde (**2b**).[S1] Colourless liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H). GC-MS (m/z):120.

4-Ethylbenzaldehyde (**2c**).[S2] Colourless liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H). GC-MS (m/z):134.

4-Methoxybenzaldehyde (**2d**).[S1] Colourless liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H). GC-MS (m/z):136.

4-(*tert*-Butyl)benzaldehyde (**2e**).[S3] Colourless liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 1.35 (s, 9H). GC-MS (m/z):162.

4-(Dimethylamino)benzaldehyde (**2f**).[S4] Light yellow solid. M.p.70~72 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.71 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 3.05 (s, 6H). GC-MS (m/z):149.

4-(Methylthio)benzaldehyde (**2g**).[S5] Light yellow liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.74 – 7.71 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 2.49 (s, 3H). GC-MS (m/z):152.

2-Methoxybenzaldehyde (**2h**).[S5] Light yellow solid. M.p. 38~40 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.82 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.03 – 6.97 (m, 2H), 3.92 (s, 3H). GC-MS (m/z):136.

2-Methylbenzaldehyde (**2i**).[S6] Light yellow liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.77 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.45 (td, *J* = 7.5, 1.3 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 2.65 (s, 3H). GC-MS (m/z):120.

3-Methylbenzaldehyde (**2j**).[S7] Light yellow liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.70 – 7.64 (m, 2H), 7.46 – 7.37 (m, 2H), 2.42 (s, 3H). GC-MS (m/z):120.

3,4-Dimethoxybenzaldehyde (**2k**).[S8] Light yellow solid. M.p. 43~45 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.42 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.36 (d, *J* = 1.7 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H). GC-MS (m/z):166.

2-Naphthaldehyde (**2l**).[S5] Light yellow solid. M.p. 58~60 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.32 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.96 – 7.88 (m, 3H), 7.67 – 7.61 (m, 1H), 7.60 – 7.54 (m, 1H). GC-MS (m/z):156.

Methyl 4-formylbenzoate (**2m**).[S2] Light yellow solid. M.p. 63~65 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.18 (d, *J* = 8.2 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 2H), 3.95 (s, 3H). GC-MS (m/z):164.

1-Methyl-1*H*-indole-3-carbaldehyde (**2n**).[S9] Light yellow solid. M.p. 70~73 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.29 (dd, *J* = 6.6, 1.8 Hz, 1H), 7.61 (s, 1H), 7.36 – 7.29 (m, 3H), 3.82 (s, 3H). GC-MS (m/z):159.

Furan-2-carbaldehyde (**2o**).[S5] Light yellow liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.67 – 7.63 (m, 1H), 7.23 – 7.19 (m, 1H), 6.56 (dd, *J* = 3.6, 1.6 Hz, 1H). GC-MS (m/z):96.

Cinnamaldehyde (**2p**).[S2] Light yellow liquid. $^1$H NMR (500 MHz, $CDCl_3$) δ 9.71 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.48 (d, *J* = 16.0 Hz, 1H), 7.45 – 7.34 (m, 3H), 6.72 (dd, *J* = 15.9, 7.7 Hz, 1H). GC-MS (m/z):132.

## References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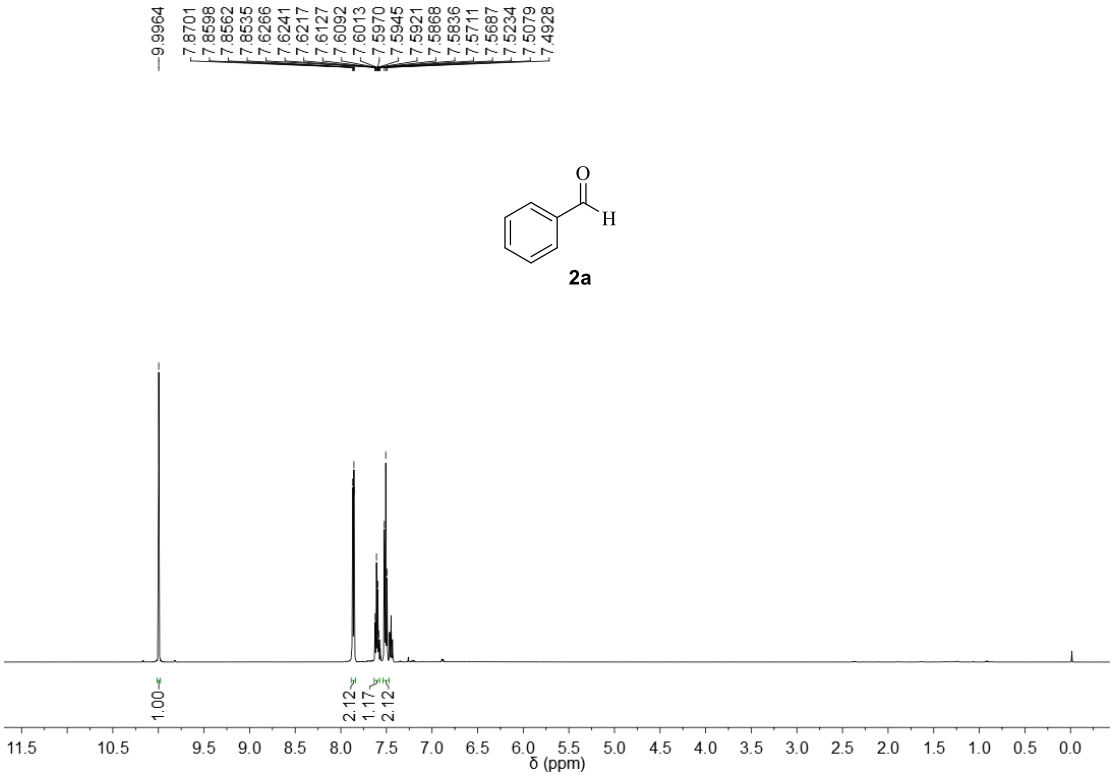
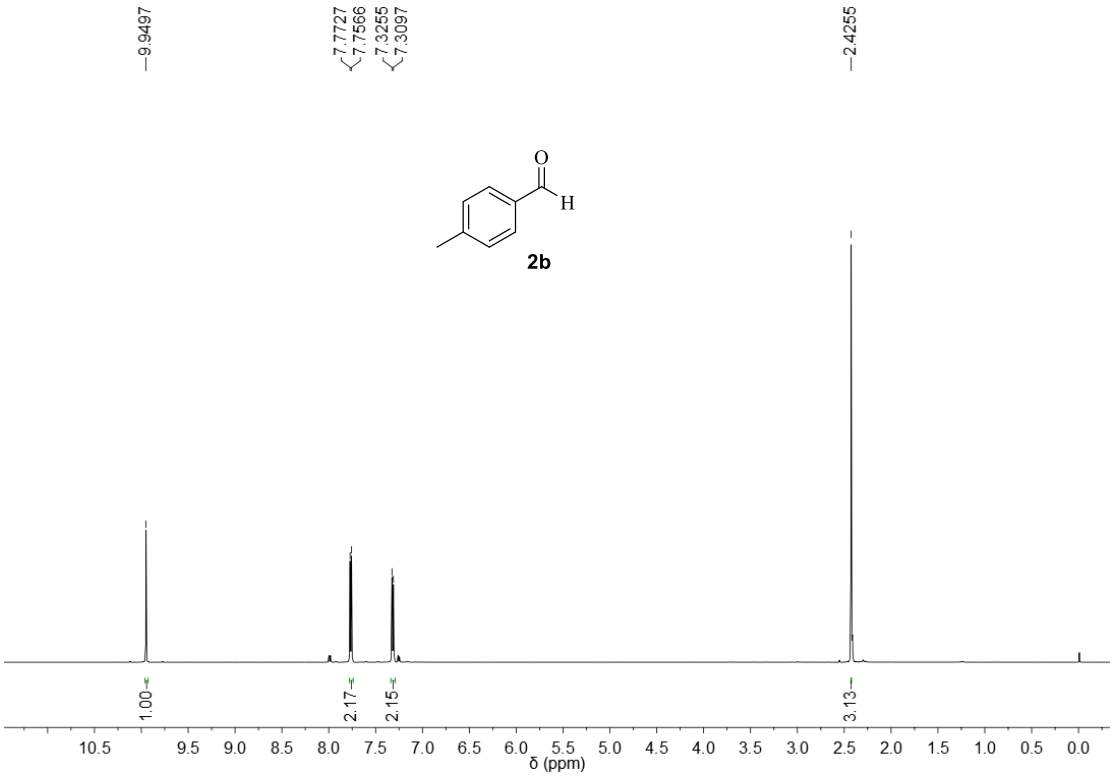
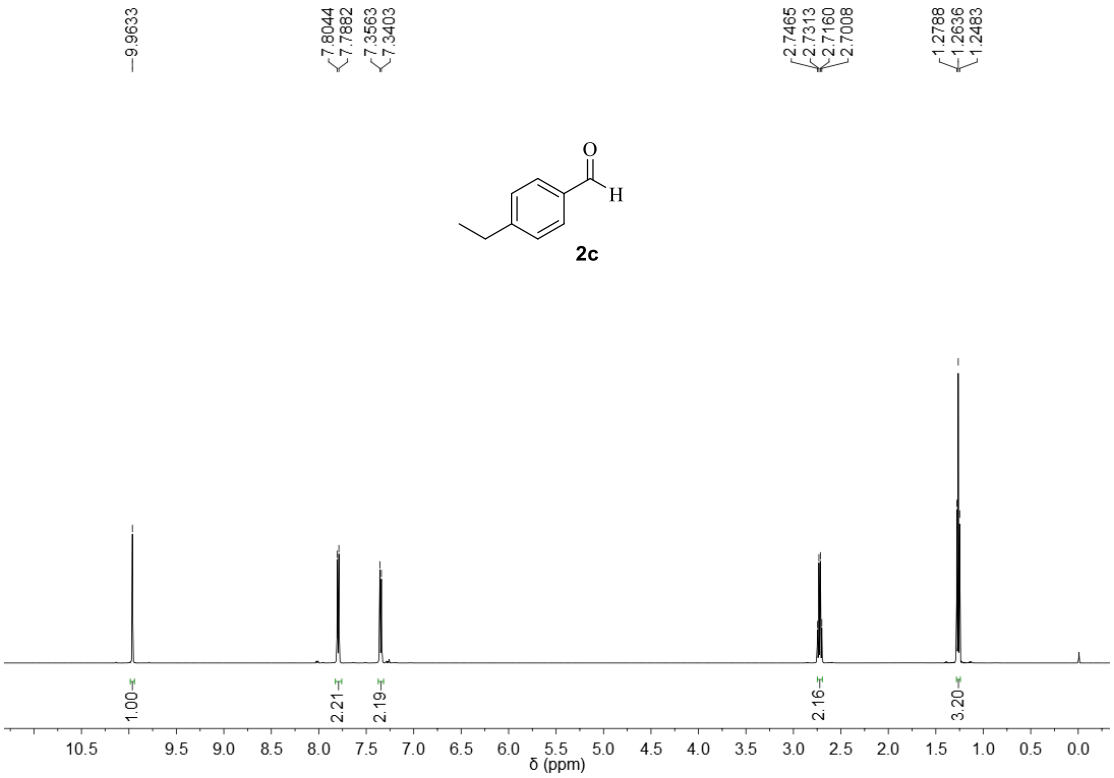
## Copies of $^{1}$H NMR Spectra

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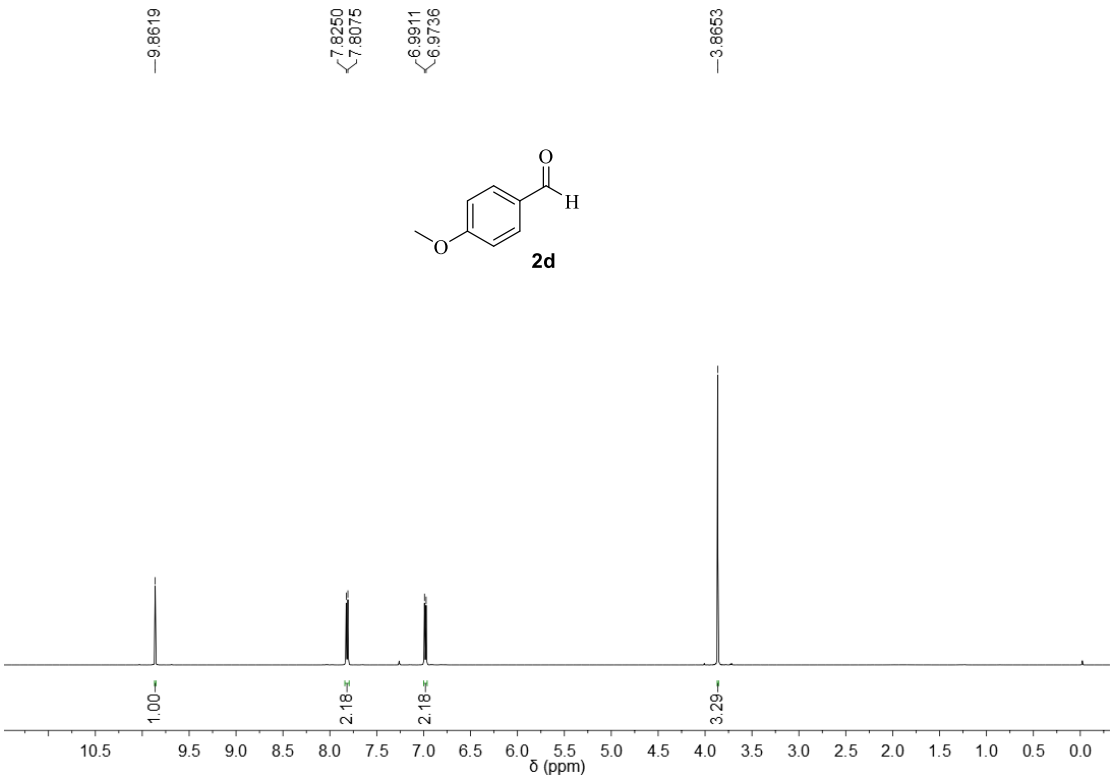
2.21
2.19
2.16
3.20
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

**2c**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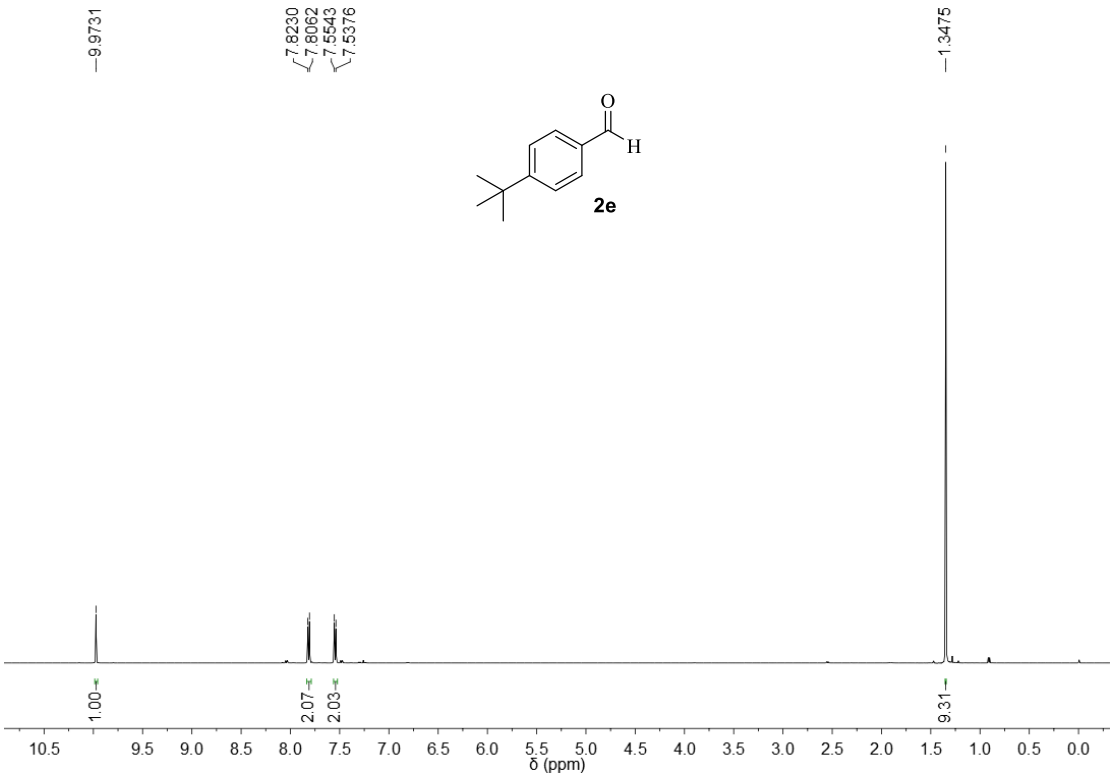
δ (ppm)

**2d**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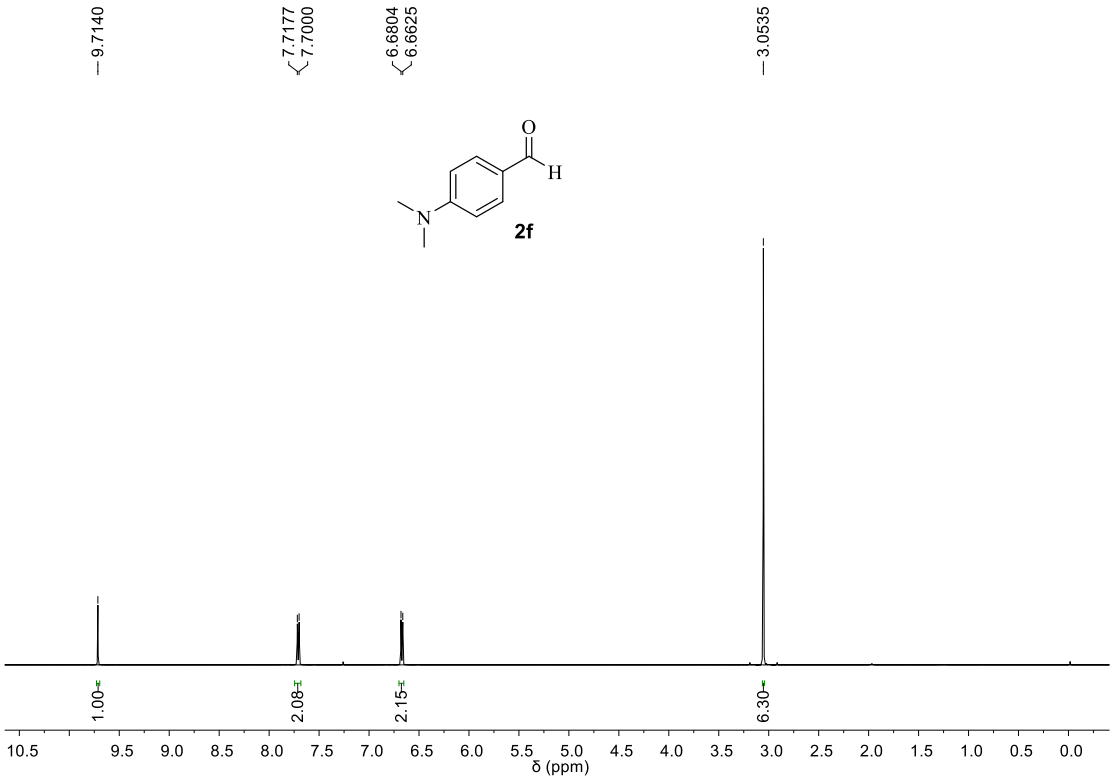
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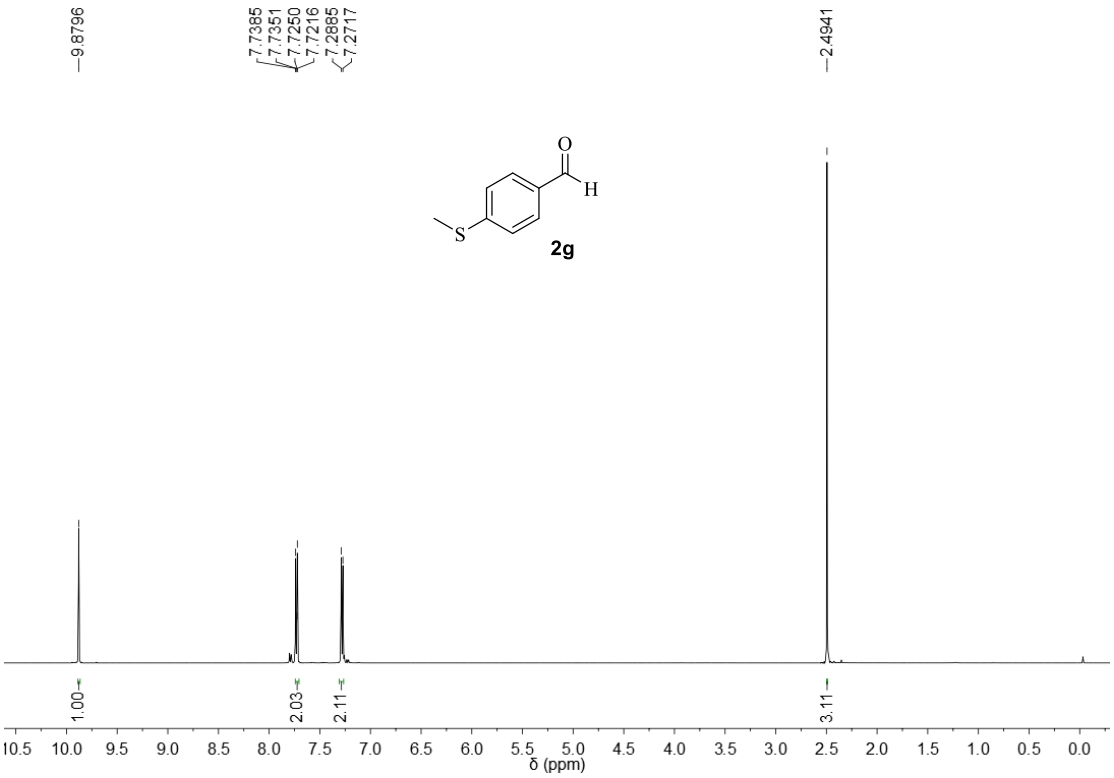
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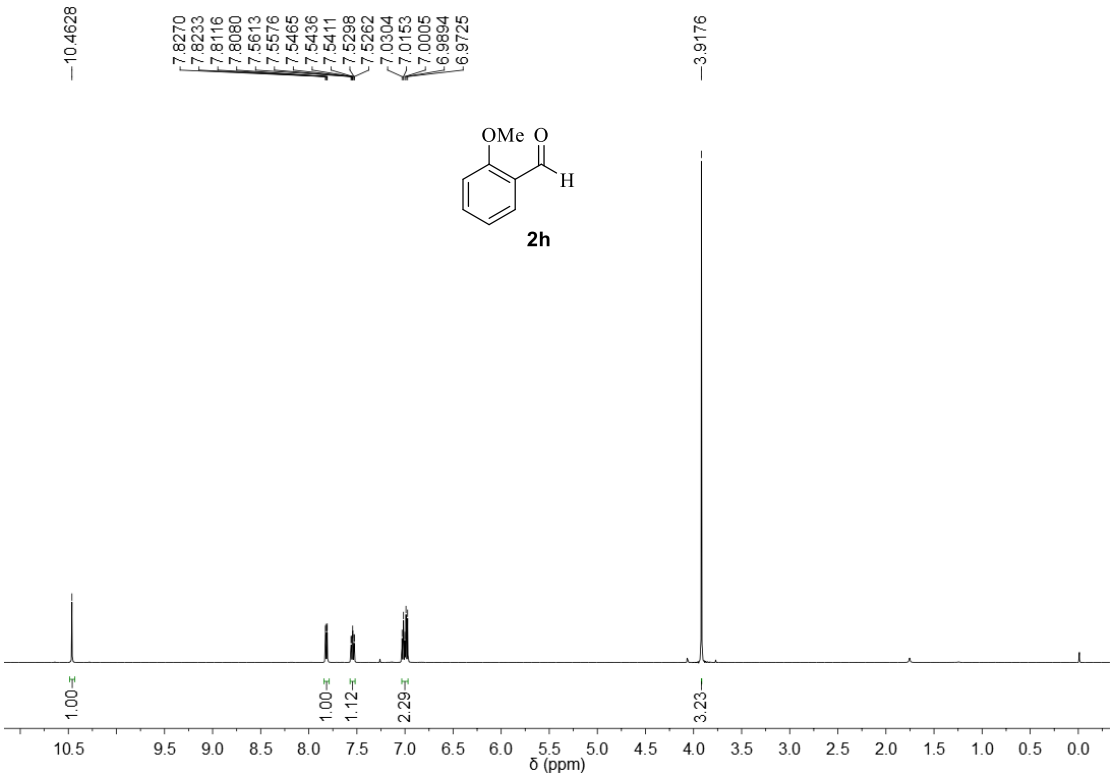
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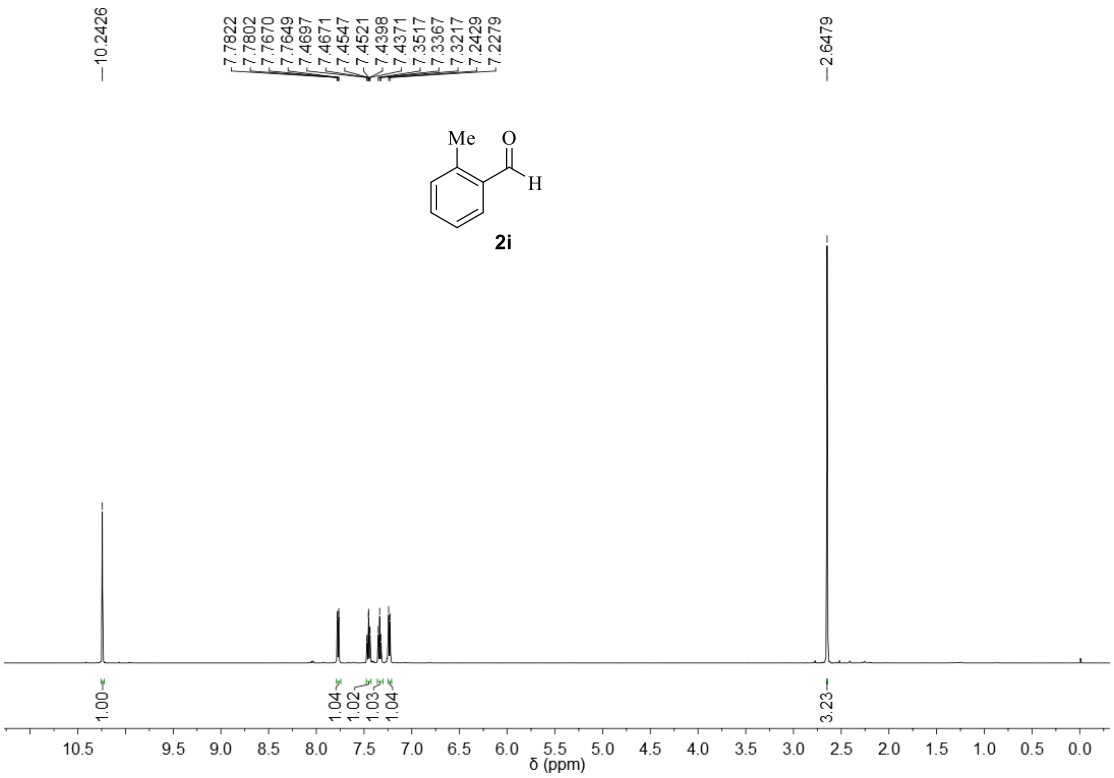
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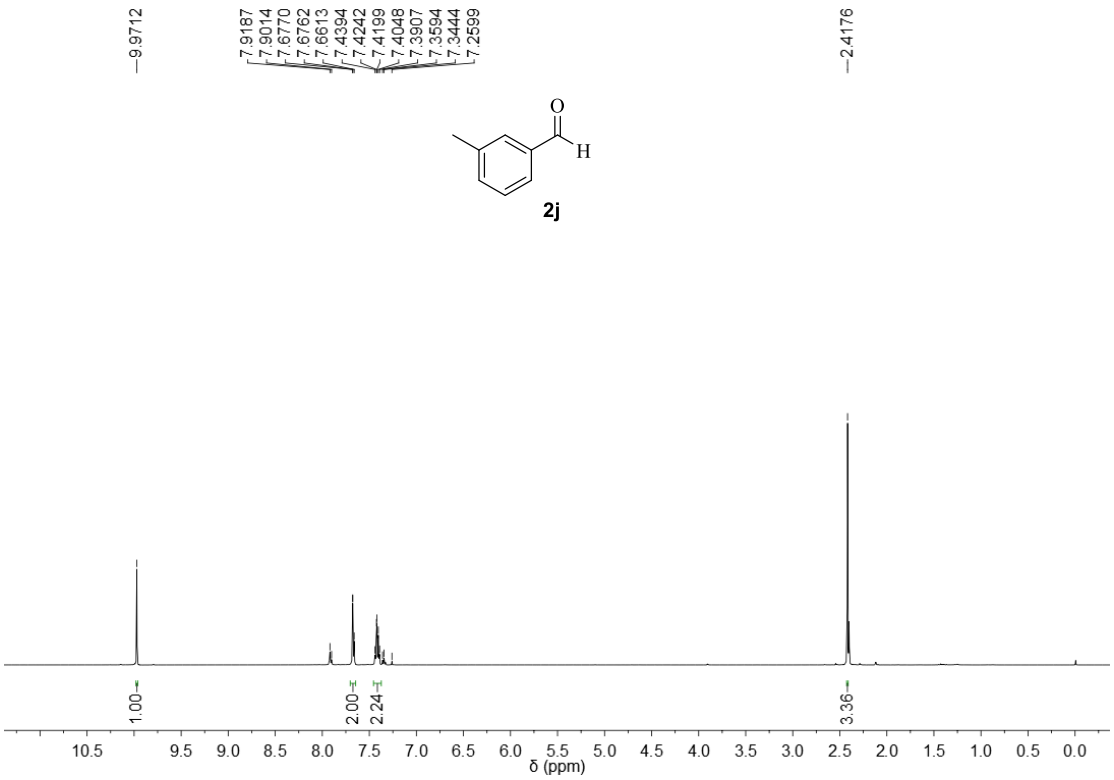
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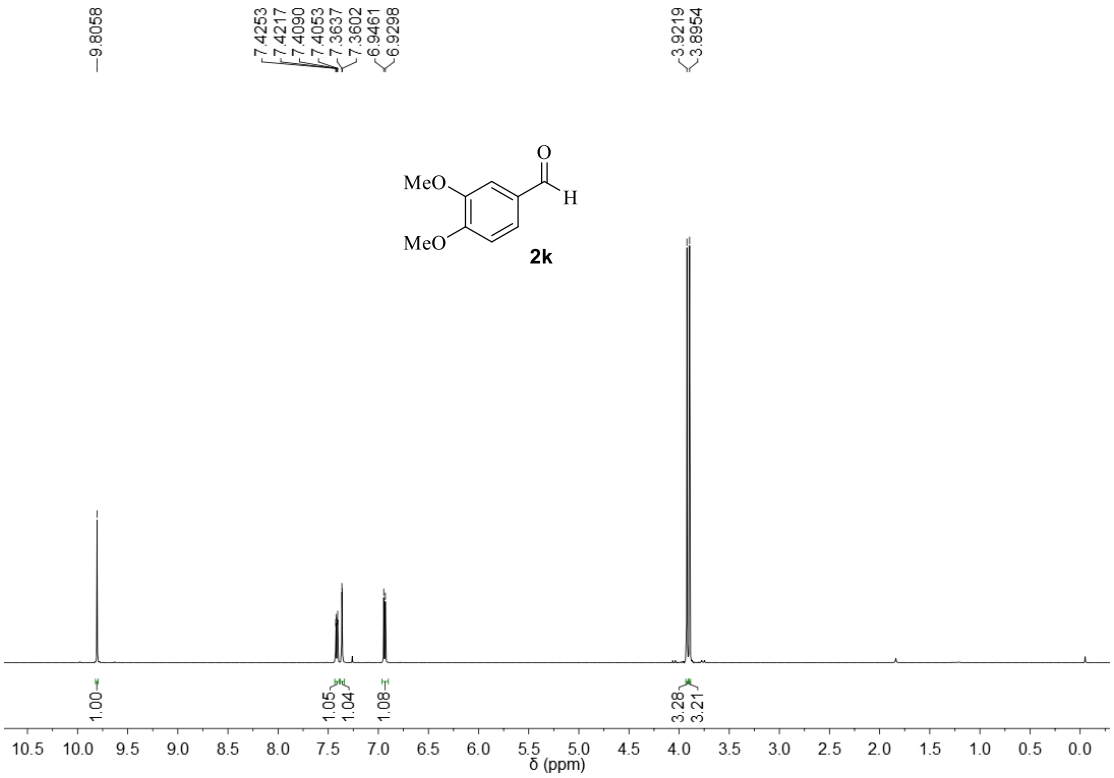
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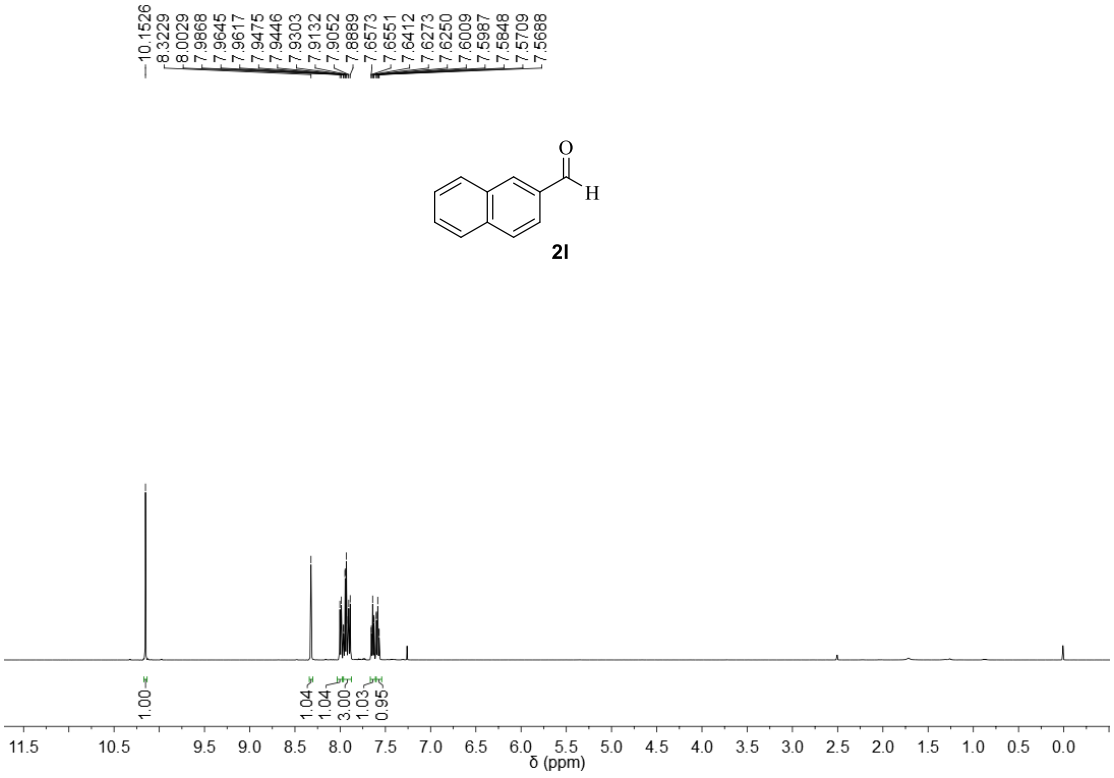
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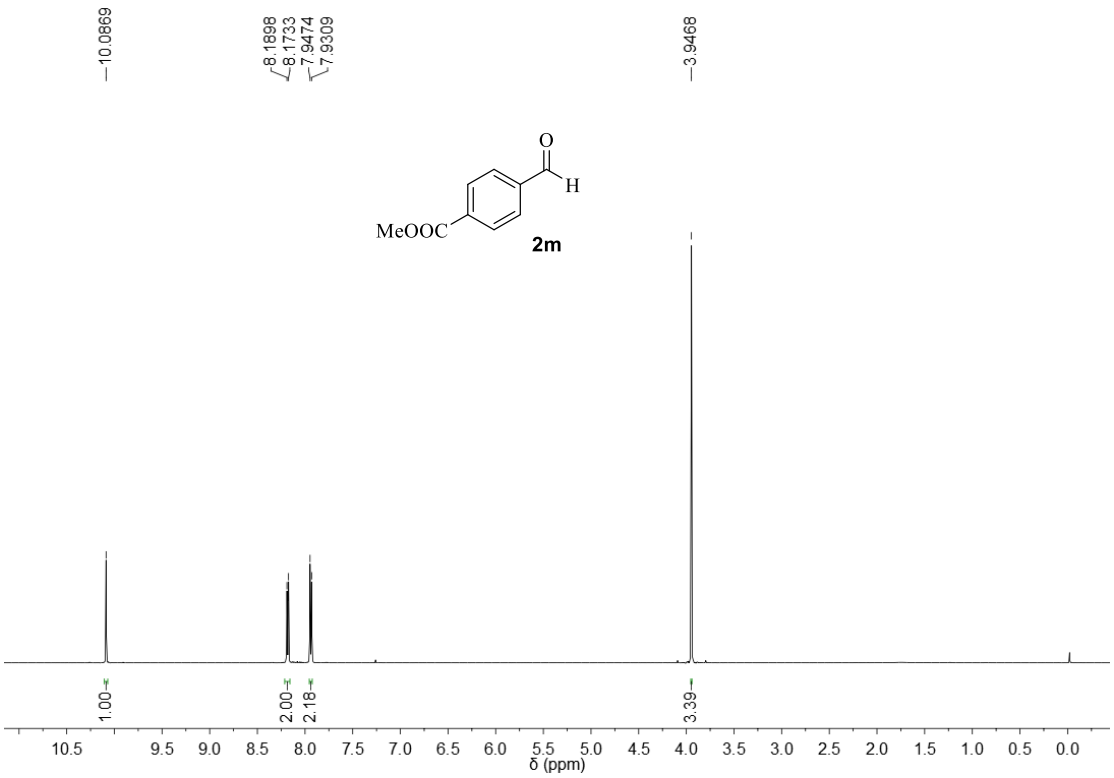
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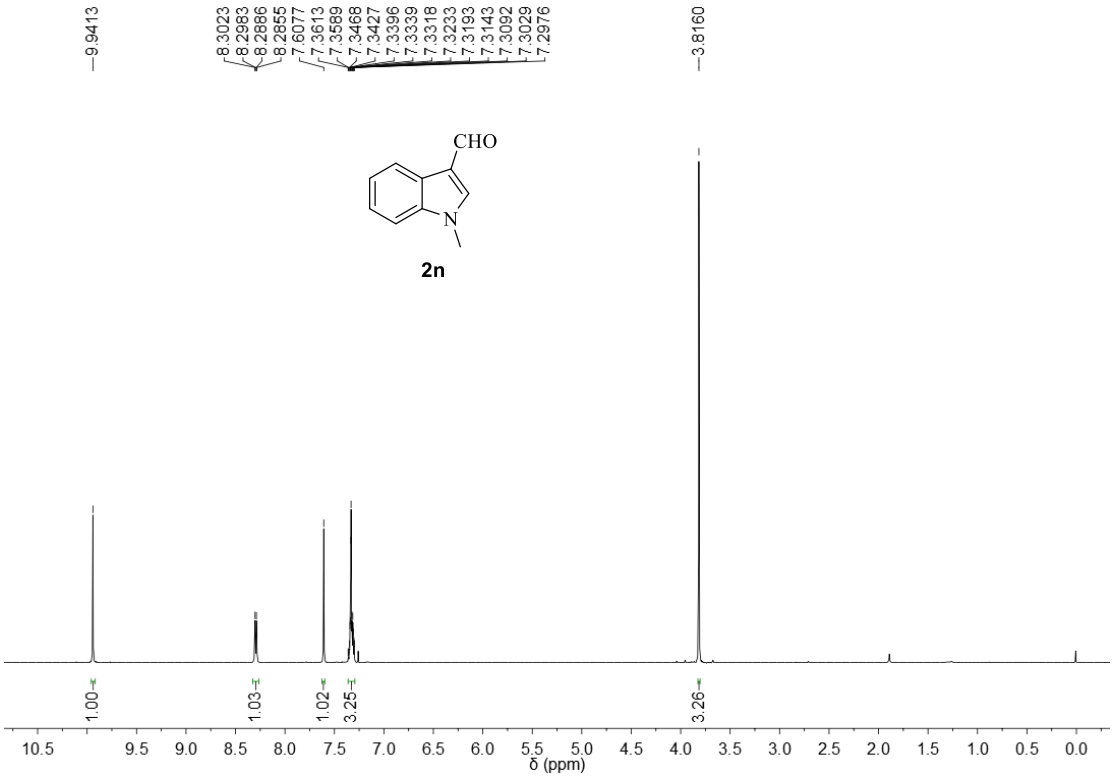
δ (ppm)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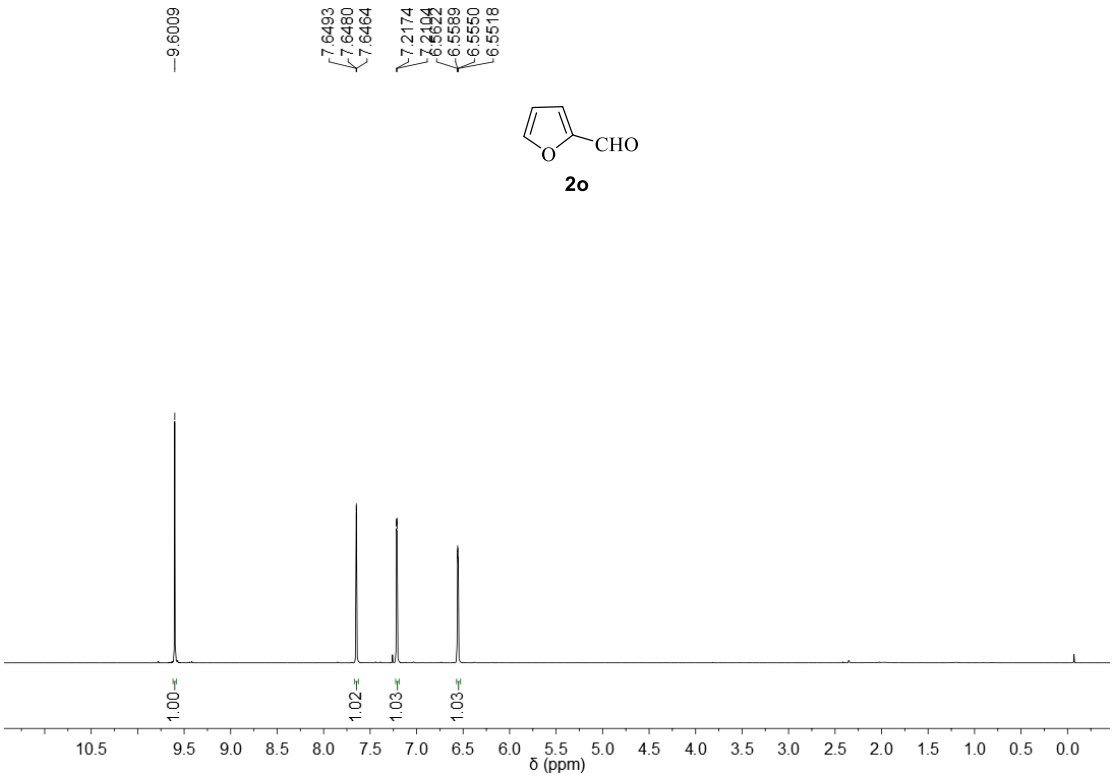
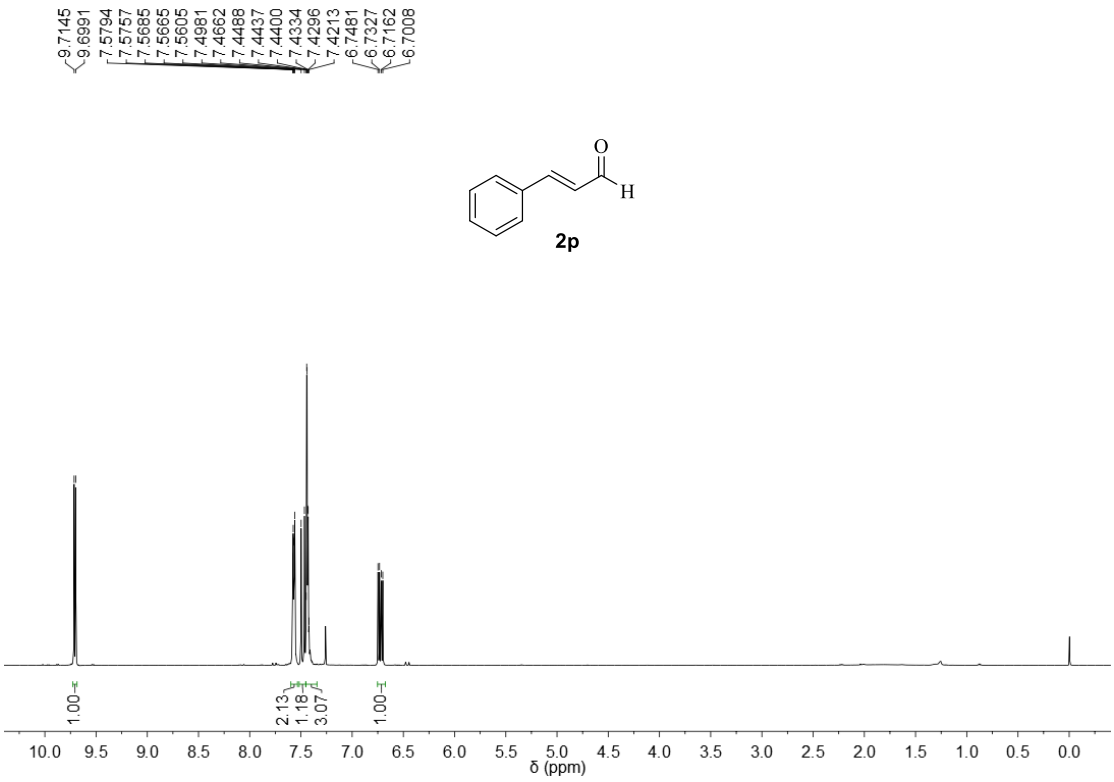
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)


9.6009
7.6493
7.6480
7.6464
7.2174
6.5589
6.5550
6.5518
O
CHO
1.00
1.02
1.03
1.03
δ (ppm)

**2o**


9.7145
9.6991
7.5794
7.5757
7.5685
7.5665
7.5605
7.4981
7.4662
7.4488
7.4437
7.4400
7.4334
7.4296
7.4213
6.7481
6.7327
6.7162
6.7008
O
H
1.00
2.13
1.18
3.07
1.00
δ (ppm)

**2p**