# Nickel-Catalyzed Divergent Formylation and Carboxylation of Aryl Halides with Isocyanides

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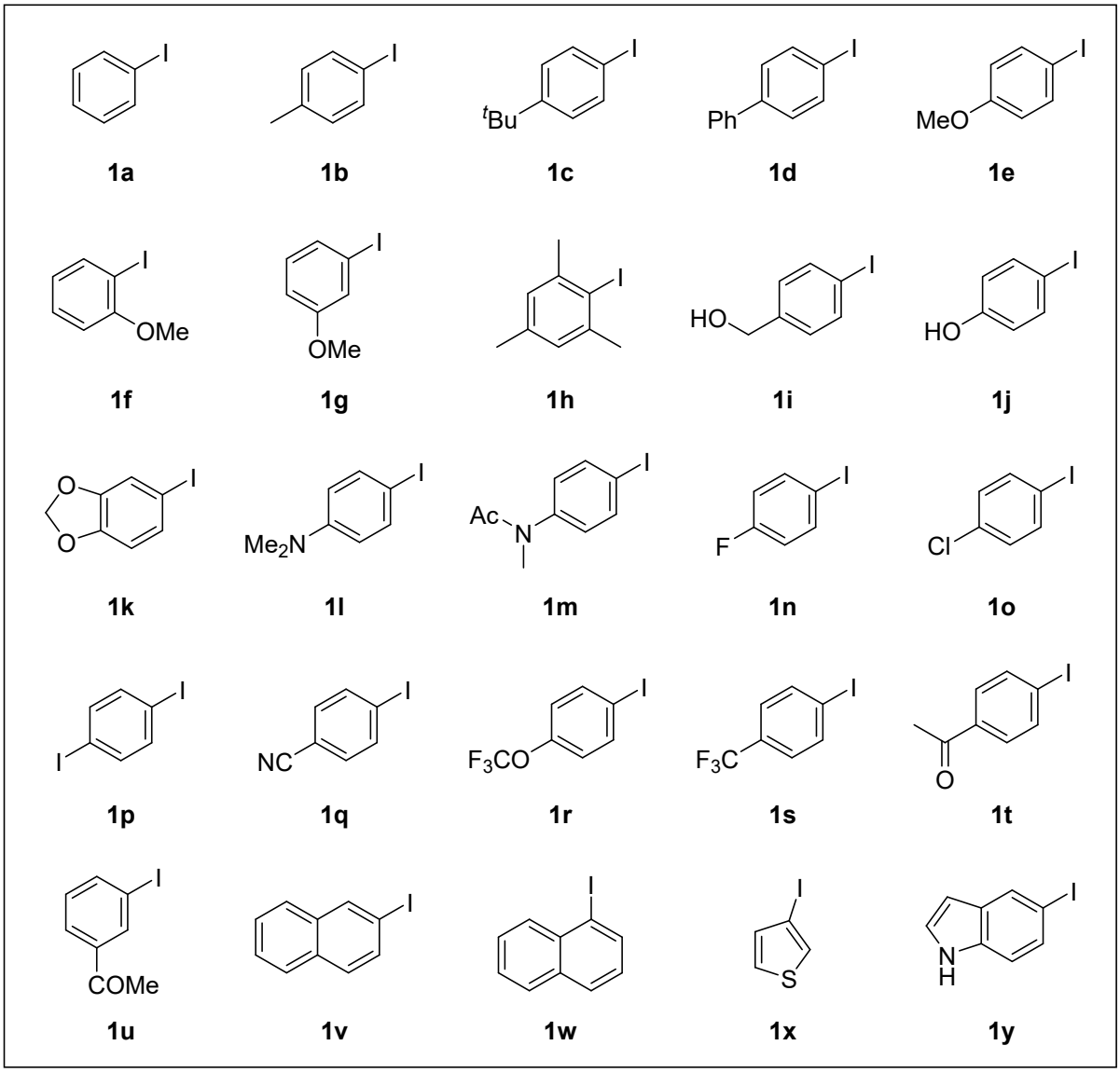
## 1. General Information

Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under nitrogen. Solvents were purified and dried according to standard methods prior to use. All commercially available reagents were obtained from chemical suppliers and used after proper purification if necessary. Flash column chromatography was performed on silica gel (200-300 mesh) with the indicated solvent mixtures. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light.

The $^{1}H$ NMR and spectra were recorded on a Bruker 400 AV or 500 AV spectrometers. Chemical shifts (δ) were reported as parts per million (ppm) downfield from tetramethylsilane and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad and all combinations thereof can be explained by their integral parts. Coupling constant (*J*) was reported in hertz unit (Hz)..

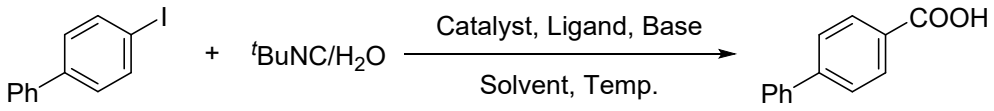
## 2. List of Aryl Iodides




The substrate **1m** was prepared according to the known literature.[1] Other aryl iodides are commercially available and used as received.

# 3. Nickel-Catalyzed Formylation/Carboxylation of Aryl Halides with Isocyanides.

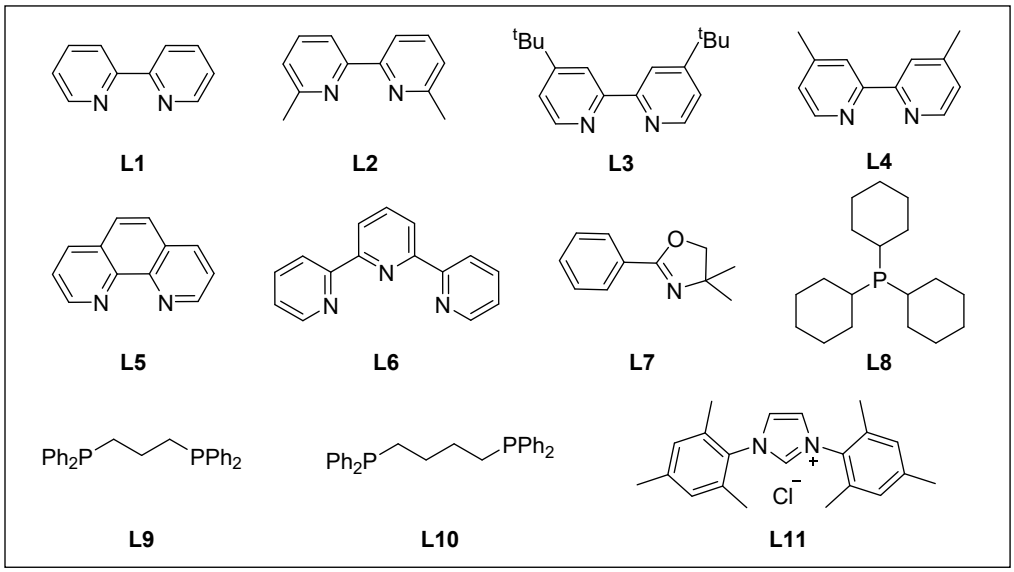
## 3.1 Optimization of the carboxylation reaction




**1d** **2a** **4d**

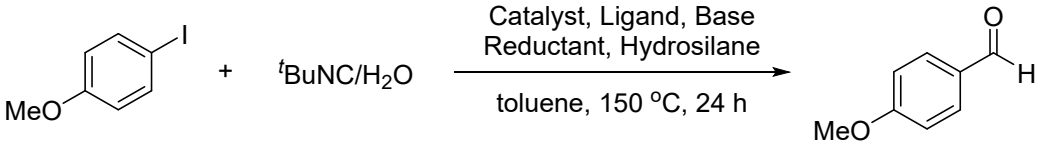
| Entry | Catalyst (mol%) | Ligand (mol%) | Base (equiv) | Solvent | Temp. (°C) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | $NiBr_2$ (5) | **L1** (5) | HCOONa (2) | DMF | 120 | 85 |
| 2 | $NiI_2$ (5) | **L1** (5) | HCOONa (2) | DMF | 120 | 63 |
| 3 | $NiCl_2$ (5) | **L1** (5) | HCOONa (2) | DMF | 120 | 62 |
| 4 | $Ni(OAc)_2 \cdot 4H_2O$ (5) | **L1** (5) | HCOONa (2) | DMF | 120 | 70 |
| 5 | $Ni(OTf)_2$ (5) | **L1** (5) | HCOONa (2) | DMF | 120 | 60 |
| 6 | $Ni(acac)_2$ (5) | **L1** (5) | HCOONa (2) | DMF | 120 | 65 |
| 7 | $NiBr_2$ (10) | **L1** (10) | HCOONa (2) | DMF | 120 | 85 |
| 8 | - | **L1** (5) | HCOONa (2) | DMF | 120 | 0 |
| 9 | $NiBr_2$ (5) | **L2** (5) | HCOONa (2) | DMF | 120 | 75 |
| 10 | $NiBr_2$ (5) | **L3** (5) | HCOONa (2) | DMF | 120 | 80 |
| 11 | $NiBr_2$ (5) | **L4** (5) | HCOONa (2) | DMF | 120 | 78 |
| 12 | $NiBr_2$ (5) | **L5** (5) | HCOONa (2) | DMF | 120 | 42 |
| 13 | $NiBr_2$ (5) | **L6** (5) | HCOONa (2) | DMF | 120 | 45 |
| 14 | $NiBr_2$ (5) | **L7** (5) | HCOONa (2) | DMF | 120 | 50 |
| 15 | $NiBr_2$ (5) | **L8** (5) | HCOONa (2) | DMF | 120 | 62 |
| 16 | $NiBr_2$ (5) | **L9** (5) | HCOONa (2) | DMF | 120 | 55 |
| 17 | $NiBr_2$ (5) | **L10** (5) | HCOONa (2) | DMF | 120 | 50 |
| 18 | $NiBr_2$ (5) | **L11** (5) | HCOONa (2) | DMF | 120 | 53 |
| 19 | $NiBr_2$ (5) | - | HCOONa (2) | DMF | 120 | 55 |
| 20 | $NiBr_2$ (5) | **L1** (5) | AcOONa (2) | DMF | 120 | 45 |
| 21 | $NiBr_2$ (5) | **L1** (5) | EtONa (2) | DMF | 120 | 60 |
| 22 | $NiBr_2$ (5) | **L1** (5) | $Na_2CO_3$ (2) | DMF | 120 | 0 |
| 23 | $NiBr_2$ (5) | **L1** (5) | $^t$BuONa (2) | DMF | 120 | 38 |
| 24 | $NiBr_2$ (5) | **L1** (5) | - | DMF | 120 | 0 |
| 25 | $NiBr_2$ (5) | **L1** (5) | HCOONa (1) | DMF | 120 | 70 |
| 26 | $NiBr_2$ (5) | **L1** (5) | HCOONa (0.5) | DMF | 120 | 55 |
| 27 | $NiBr_2$ (5) | **L1** (5) | HCOONa (2) | NMP | 120 | 68 |
| 28 | $NiBr_2$ (5) | **L1** (5) | HCOONa (2) | DMA | 120 | 65 |
| 29 | $NiBr_2$ (5) | **L1** (5) | HCOONa (2) | DMSO | 120 | 70 |
| 30 | $NiBr_2$ (5) | **L1** (5) | HCOONa (2) | Toluene | 120 | trace |
| 31 | $NiBr_2$ (5) | **L1** (5) | HCOONa (2) | THF | 120 | trace |

| | | | | | | |
|---|---|---|---|---|---|---|
| 32 | $NiBr_2$ (5) | **L1** (5) | HCOONa (2) | DMF | 90 | 68 |
| 33 | $NiBr_2$ (5) | **L1** (5) | HCOONa (2) | DMF | 150 | 84 |
| 34 | $NiBr_2$ (5) | **L1** (5) | HCOONa (2) | DMF | 120 | 75[b] |




[a]Reaction conditions: **1d** (0.4 mmol), **2a** (0.6 mmol), Solvent (1 mL), 12 h. [b]For 24 h.

### 3.2 Optimization of the formylation reaction



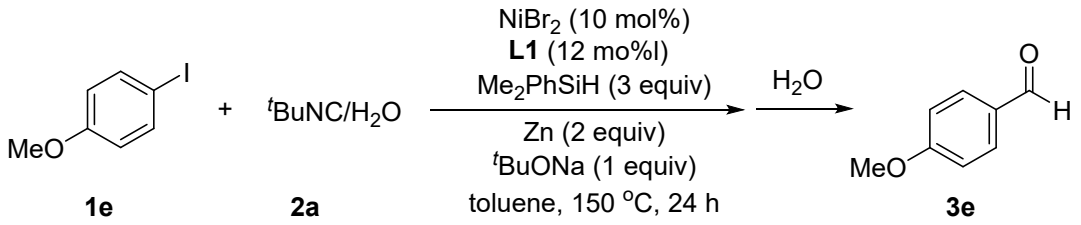

**1d** **2a** **3e**

| Entry | Catalyst/ (mol%) | Ligand/ (mol%) | Base | Hydrosilane | Reductant | Yield of **3e**/% |
|---|---|---|---|---|---|---|
| 1 | $NiBr_2$ (20) | **L1** (24) | *t*-BuONa | $Me_2PhSiH$ | Zn (2) | 80 |
| 2 | $NiBr_2$ (20) | **L1** (24) | *t*-BuONa | $Me_2PhSiH$ | Zn (1) | 69 |
| 3 | $NiBr_2$ (20) | **L1** (24) | *t*-BuONa | $Me_2PhSiH$ | Zn (0.3) | 65 |
| 4 | $NiBr_2$ (20) | **L1** (24) | *t*-BuONa | $Me_2PhSiH$ | - | 57 |
| 5 | $NiBr_2$ (20) | **L1** (24) | *t*-BuOK | $Me_2PhSiH$ | Zn (2) | 25 |
| 6 | $NiBr_2$ (20) | **L1** (24) | *t*-BuOLi | $Me_2PhSiH$ | Zn (2) | 23 |
| 7 | $NiBr_2$ (20) | **L1** (24) | *t*-BuONa | $Me_2PhSiH$ | Mn (2) | 75 |
| 8 | $NiBr_2$ (20) | **L1** (24) | *t*-BuONa | $Me_2PhSiH$ | Mg (2) | 33 |
| 9 | $NiBr_2$ (10) | **L1** (12) | *t*-BuONa | $Me_2PhSiH$ | Zn (2) | 78 |
| 10 | $NiBr_2$ (5) | **L1** (6) | *t*-BuONa | $Me_2PhSiH$ | Zn (2) | 51 |
| 11 | - | **L1** (12) | *t*-BuONa | $Me_2PhSiH$ | Zn (2) | 0 |
| 12 | $NiBr_2$ (10) | **L1** (12) | *t*-BuONa | $Et_3SiH$ | Zn (2) | 57 |
| 13 | $NiBr_2$ (10) | **L1** (12) | *t*-BuONa | $Ph_3SiH$ | Zn (2) | 43 |
| 14 | $NiBr_2$ (10) | **L1** (12) | *t*-BuONa | $(EtO)_2MeSiH$ | Zn (2) | 27 |
| 15 | $NiBr_2$ (10) | **L1** (12) | *t*-BuONa | - | Zn (2) | 0 |
| 16 | $NiBr_2$ (10) | **L1** (12) | *t*-BuONa | $Me_2PhSiH$ | Zn (2) | 62[b] |
| 17 | $NiBr_2$ (10) | **L3** (12) | *t*-BuONa | $Me_2PhSiH$ | Zn (2) | 38 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 18 | $NiBr_2$ (10) | **L4** (12) | *t*-BuONa | $Me_2PhSiH$ | Zn (2) | 53 |
| 19 | $NiBr_2$ (10) | **L5** (12) | *t*-BuONa | $Me_2PhSiH$ | Zn (2) | 48 |
| 20 | $NiBr_2$ (10) | **L8** (12) | *t*-BuONa | $Me_2PhSiH$ | Zn (2) | 36 |
| 21 | $NiBr_2$ (10) | **L11** (12) | *t*-BuONa | $Me_2PhSiH$ | Zn (2) | 0 |

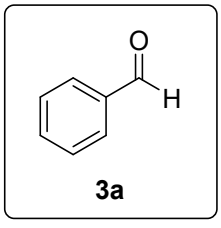
[a]Reaction conditions: **1d** (0.4 mmol), **2a** (0.48 mmol), Catalyst, Ligand (1.2 equiv to catalyst), Base (1 equiv), Zn (2 equiv), Hydrosilane (3 equiv), toluene (1 mL), at 150 °C for 24 h. [b]At 120 °C.

### 3.3 Experimental details and characterization of aromatic aldehydes




To a 25 ml flame-dried Schlenk tube containing a stirring bar was added 1-iodo-4-methoxybenzene (0.4 mmol, 93.6 mg), $NiBr_2$ (10 mol%, 0.04 mmol, 8.8 mg), **L1** (12 mol%, 0.048 mmol, 7.488 mg), Zn (0.8 mmol, 52 mg), *t*-BuONa (0.4 mmol, 38.4 mg), toluene (1 mL), *t*-BuNC (0.48 mmol, 40 mg), and dimethylphenylsilane (1.2 mmol, 163 mg) sequentially under nitrogen. The tube was sealed and stirred at 150 °C for 24 h. After completion, $H_2O$ (0.2 ml) was added to the reaction. The resulting mixture was concentrated and purified by silica gel column chromatography to provide the product **3e** in 78% yield.

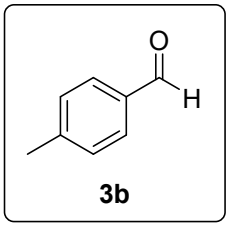
**benzaldehyde (3a)[2]**




Following the general procedure, compound **3a** was obtained as yellow oil (19 mg, 45% yield) .

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.01 (s, 1H), 7.91 – 7.84 (m, 2H), 7.66 – 7.59 (m, 1H), 7.52 (t, *J* = 7.5 Hz, 2H).

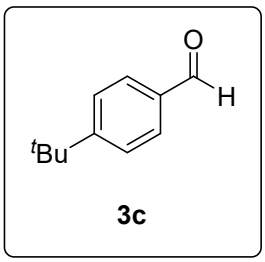
**4-methylbenzaldehyde (3b)[1]**




Following the general procedure, compound **3b** was obtained as yellow oil (30 mg, 63% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.95 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H).

**4-(tert-butyl)benzaldehyde (3c)[1]**

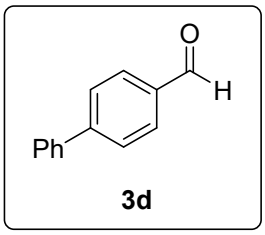


3c

Following the general procedure, compound **3c** was obtained as yellow oil (56 mg, 89% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.98 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 1.36 (s, 9H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 191.90, 158.31, 133.98, 129.59, 125.88, 35.22, 30.95.

**[1,1'-biphenyl]-4-carbaldehyde (3d)[1]**

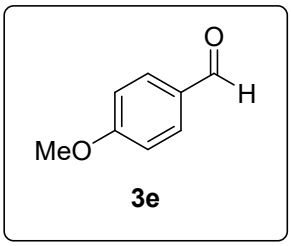


3d

Following the general procedure, compound **3d** was obtained as yellow oil (40 mg, 55% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.05 (s, 1H), 7.98 – 7.92 (m, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.60 (m, 2H), 7.51 – 7.45 (m, 2H), 7.44 – 7.38 (m, 1H).

**4-methoxybenzaldehyde (3e)[1]**

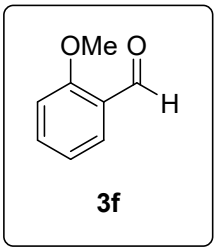


3e

Following the general procedure, compound **3e** was obtained as yellow oil (36 mg, 78% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.89 (s, 1H), 7.86 – 7.82 (m, 2H), 7.03 – 6.99 (m, 2H), 3.89 (s, 3H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 190.67, 164.50, 131.84, 129.83, 114.19, 55.44.

**2-methoxybenzaldehyde (3f) [2]**

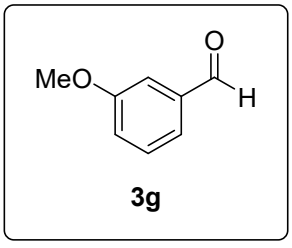


3f

Following the general procedure, compound **3f** was obtained as yellow oil (26 mg, 47% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.44 (d, *J* = 0.7 Hz, 1H), 7.78 (dd, $J_1$ = 7.7, $J_2$ = 1.9 Hz, 1H), 7.53 – 7.48 (m, 1H), 6.96 (dd, $J_1$ = 15.4, $J_2$ = 7.9 Hz, 2H), 3.86 (s, 3H).

**3-methoxybenzaldehyde (3g) [3]**

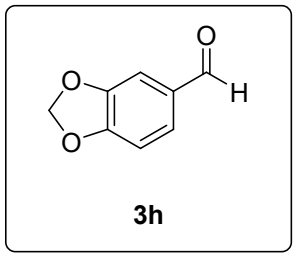


3g

Following the general procedure, compound **3g** was obtained as yellow oil (34 mg, 66% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.96 (s, 1H), 7.47 – 7.42 (m, 2H), 7.38 (d, *J* = 2.1 Hz, 1H), 7.19 – 7.14 (m, 1H), 3.84 (s, 3H).

**benzo[d][1,3]dioxole-5-carbaldehyde (3h)[1]**

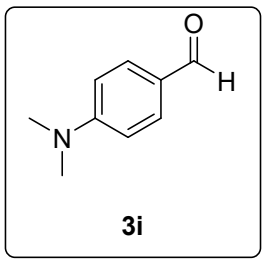



**3h**

Following the general procedure, compound **3h** was obtained as yellow oil (34 mg, 56% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.81 (s, 1H), 7.44 – 7.39 (m, 1H), 7.34 (d, *J* = 1.5 Hz, 1H), 6.96 – 6.92 (m, 1H), 6.08 (d, *J* = 3.1 Hz, 2H).

**4-(dimethylamino)benzaldehyde (3i) [4]**

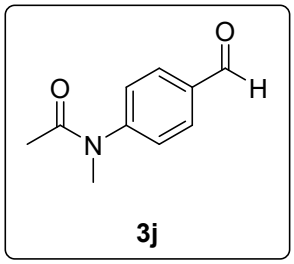



**3i**

Following the general procedure, compound **3i** was obtained as yellow oil (32 mg, 53% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.74 (s, 1H), 7.74 (d, *J* = 8.9 Hz, 2H), 6.70 (d, *J* = 8.9 Hz, 2H), 3.08 (s, 6H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 190.23, 154.27, 131.89, 125.05, 110.91, 39.98.

**N-(4-formylphenyl)-N-methylacetamide (3j) [5]**

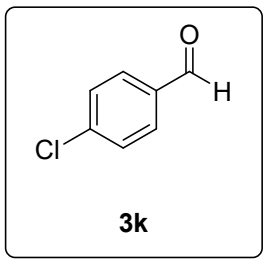



**3j**

Following the general procedure, compound **3j** was obtained as yellow oil (33 mg, 47% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.04 (s, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 3.33 (s, 3H), 1.99 (s, 3H).

**4-chlorobenzaldehyde (3k)[1]**

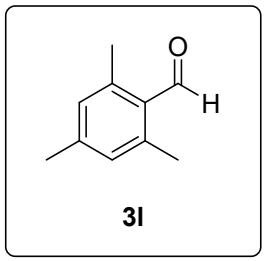



**3k**

Following the general procedure, compound **3k** was obtained as yellow oil (24 mg, 43% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.99 (s, 1H), 7.85 – 7.81 (m, 2H), 7.56 – 7.47 (m, 2H). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 190.85, 140.94, 134.68, 130.89, 129.43.

**2,4,6-trimethylbenzaldehyde (3l) [6]**

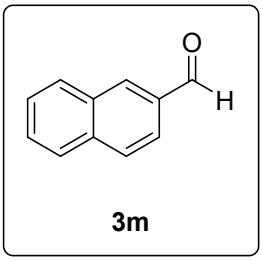



**3l**

Following the general procedure, compound **3l** was obtained as yellow oil (36 mg, 61% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.56 (s, 1H), 6.90 (s, 2H), 2.58 (s, 6H), 2.32 (s, 3H).

**2-naphthaldehyde (3m)[1]**

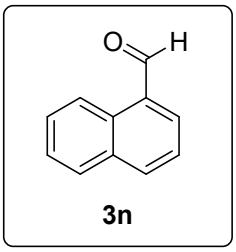


3m

Following the general procedure, compound **3m** was obtained as yellow oil (33 mg, 53% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.13 (s, 1H), 8.30 (s, 1H), 8.00 – 7.86 (m, 4H), 7.66 – 7.54 (m, 2H). **$^{13}$C NMR (126 MHz, CDCl3)** δ 192.21, 136.39, 134.50, 134.05, 132.58, 129.47, 129.07, 129.04, 128.03, 127.04, 122.70.

**1-naphthaldehyde (3n)[1]**

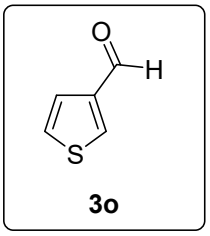


3n

Following the general procedure, compound **3n** was obtained as yellow oil (32 mg, 51% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.32 (d, $J$ = 2.7 Hz, 1H), 9.22 (d, $J$ = 8.6 Hz, 1H), 8.01 (d, $J$ = 8.2 Hz, 1H), 7.87 (dd, $J_1$ = 17.1, $J_2$ = 7.5 Hz, 2H), 7.64 (t, $J$ = 7.6 Hz, 1H), 7.54 (t, $J$ = 7.4 Hz, 2H).

**thiophene-3-carbaldehyde (3o) [7]**

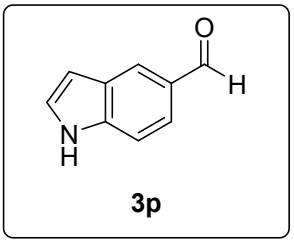


3o

Following the general procedure, compound **3o** was obtained as yellow oil (13 mg, 30% yield).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.93 (s, 1H), 8.14 (dd, $J_1$ = 2.9, $J_2$ = 1.2 Hz, 1H), 7.54 (dd, $J_1$ = 5.1, $J_2$ = 1.1 Hz, 1H), 7.41 – 7.36 (m, 1H).

**1H-indole-5-carbaldehyde (3p) [8]**

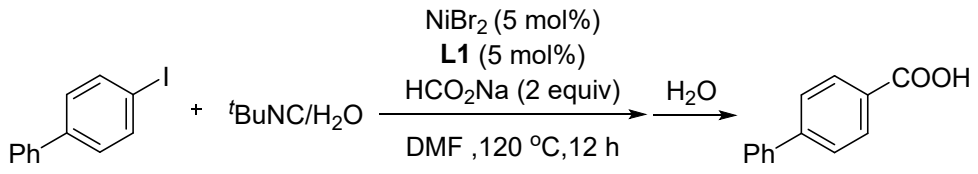


3p

Following the general procedure, compound **3p** was obtained as yellow oil (35 mg, 60% yield).[c]

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.04 (s, 1H), 8.82 (s, 1H), 8.19 (s, 1H), 7.78 (dd, $J_1$ = 8.5, $J_2$ = 1.2 Hz, 1H), 7.49 (d, $J$ = 8.5 Hz, 1H), 7.33 (t, $J$ = 2.8 Hz, 1H), 6.71 (s, 1H).

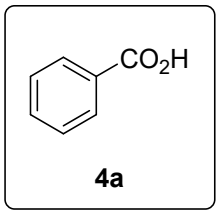
**3.4 Experimental details and characterization of aromatic carboxylic acids**




**1d** **2a** **4d**

Under the positive nitrogen atmosphere, **1d** (0.4 mmol, 112 mg), **2a** (0.6 mmol, 49.8 mg), $NiBr_2$ (5 mol%, 4.4 mg), **L1** (5 mol%, 3.1 mg), $HCO_2Na$ (0.8 mmol, 54.4 mg), and DMF (1 mL) were added to 25 mL Schlenk tube. The reaction mixture was stirred at 120 °C for 12 hours. After the completion, $H_2O$ (1 mL) was added to the reaction and the resulting mixture was extracted with ethyl acetate (5 mL×2). The combined organic layer was dried over the anhydrous $Na_2SO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography (PE : EA = 5:1) to give the desired product in 84% yield as white solid.

**benzoic acid (4a)[9]**

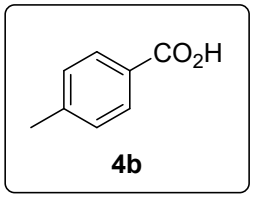



**4a**

Following the general procedure: 10 mol% of $NiBr_2$ and 10 mol% bipyridine were used. Compound **4a** was obtained as a white solid in 68% yield (33 mg); mp = 120 °C.

**$^1$H NMR (500 MHz, DMSO-*d*$_6$)**: δ 12.96 (br, 0.7H), 7.95 (d, *J* = 7.0 Hz, 2H), 7.63 (t, *J* = 6.9 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H). **$^{13}$C NMR (126 MHz, DMSO-*d*$_6$)** δ 167.37, 132.85, 130.85, 129.27, 128.57.

**p-methylacetyl urea benzoic acid (4b)[9]**

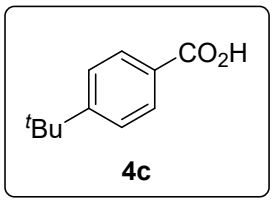



**4b**

Following the general procedure: 10 mol% of $NiBr_2$ and 10 mol% bipyridine were used. Compound **4b** was obtained as a white solid in 65% yield (35 mg); mp = 175 °C.

**$^1$H NMR (400 MHz, DMSO-*d*$_6$)**: δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H).

**4-(tert-butyl)benzoic acid (4c)[10]**

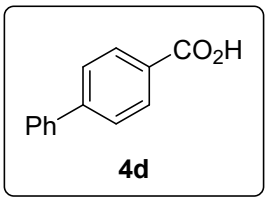



**4c**

Following the general procedure: 10 mol% of $NiBr_2$ and 10 mol% bipyridine were used. Compound **4c** was obtained as a white solid in 65% yield (46 mg); mp = 160 °C.

**$^1$H NMR (500 MHz, DMSO-$d_6$)**: δ 12.78 (br, 0.56H), 7.88 (d, $J$ = 8.5 Hz, 2H), 7.51 (d, $J$ = 8.4 Hz, 2H), 1.29 (s, 9H).

**[1,1'-biphenyl]-4-carboxylic acid (4d)[10]**

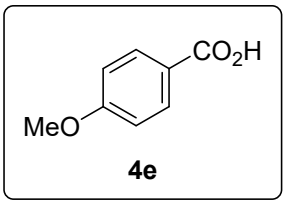


**4d**

Following the general procedure: 10 mol% of $NiBr_2$ and 10 mol% bipyridine were used. Compound **4d** was obtained as a white solid in 84% yield (66 mg); mp = 220 °C.

**$^1$H NMR (500 MHz, DMSO-$d_6$)**: δ 13.00 (br, 0.58H), 8.04 (d, $J$ = 8.3 Hz, 2H), 7.81 (d, $J$ = 8.3 Hz, 2H), 7.74 (d, $J$ = 7.4 Hz, 2H), 7.51 (t, $J$ = 7.6 Hz, 2H), 7.43 (t, $J$ = 7.3 Hz, 1H).

**4-methoxybenzoic acid (4e)[9]**

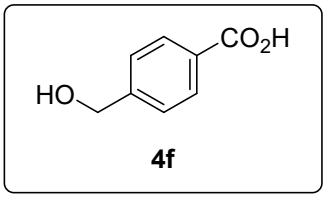


**4e**

Following the general procedure, compound **4e** was obtained as a white solid in 69% yield (42 mg); mp = 180 °C.

**$^1$H NMR (500 MHz, DMSO-$d_6$)**: δ 12.63 (br, 0.89H), 7.90 (d, $J$ = 8.9 Hz, 2H), 7.02 (d, $J$ = 8.8 Hz, 2H), 3.83 (s, 3H).

**4-(hydroxymethyl)benzoic acid (4f) [11]**

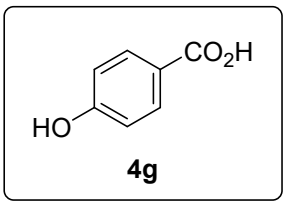


**4f**

Following the general procedure, compound **4f** was obtained as a white solid in 72% yield (43 mg); mp = 175 °C.

**$^1$H NMR (400 MHz, DMSO-$d_6$)**: δ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.44 (d, $J$ = 8.0 Hz, 2H), 5.41 (br, 1H), 4.58 (s, 2H). **$^{13}$C NMR (126 MHz, DMSO-$d_6$)** δ 167.69, 147.92, 129.50, 129.38, 126.52, 62.72.

**5-((trimethylsilyl)oxy)benzoic acid (4g)[10]**

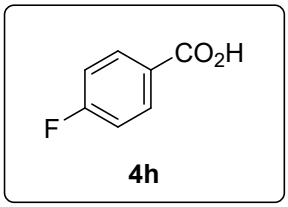


**4g**

Following the general procedure, compound **4g** was obtained as a white solid in 53% yield (29 mg); mp = 278 °C.

**$^1$H NMR (500 MHz, DMSO-$d_6$)**: δ 11.08 (br, 1.72H), 7.84 (d, $J$ = 7.9 Hz, 2H), 7.30 (d, $J$ = 7.9 Hz, 2H), 2.36 (s, 3H).

**4-fluorobenzoic acid (4h)[9]**

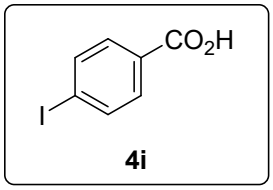


**4h**

Following the general procedure, compound **4h** was obtained as a white solid in 42% yield (24 mg); mp = 180 °C;

**$^1$H NMR (500 MHz, DMSO-$d_6$)**: δ 8.00 (dd, *J* = 8.0, 5.9 Hz, 2H), 7.30 (t, *J* = 8.6 Hz, 2H).

**4-iodobenzoic acid (4i)[12]**

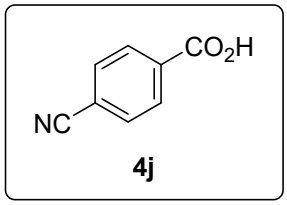


**4i**

Following the general procedure, compound **4i** was obtained as a white solid in 61% yield (61 mg); mp = 265 °C.

**$^1$H NMR (500 MHz, DMSO-$d_6$)**: δ 13.14 (br, 0.79H), 7.89 (t, *J* = 9.9 Hz, 2H), 7.71 (t, *J* = 7.9 Hz, 2H).

**4-cyanobenzoic acid (4j) [10]**

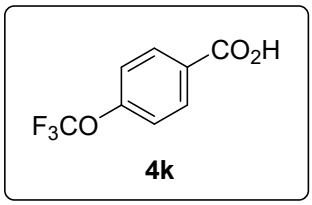


**4j**

Following the general procedure, compound **4j** was obtained as a white solid in 72% yield (42 mg); mp = 215 °C.

**$^1$H NMR (400 MHz, DMSO-$d_6$)**: δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H).

**4-(trifluoromethoxy)benzoic acid (4k)[13]**

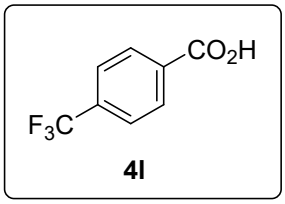


**4k**

Following the general procedure, compound **4k** was obtained as a white solid in 58% yield (48 mg); mp = 150 °C.

**$^1$H NMR (400 MHz, DMSO-$d_6$)**: δ 8.09 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H).

**4-(trifluoromethyl)benzoic acid (4l)[9]**

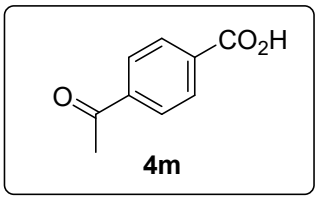


**4l**

Following the general procedure, compound **4l** was obtained as a white solid in 48% yield (37 mg); mp = 210 °C.

**$^1$H NMR (400 MHz, DMSO-$d_6$)**: δ 13.43 (br, 0.55H), 8.16 (d, *J* = 8.1 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 2H).

**4-acetylbenzoic acid (4m) [14]**



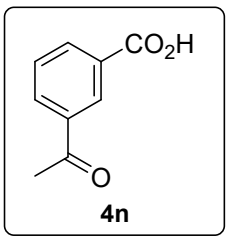
**4m**

Following the general procedure, compound **4m** was obtained as a white solid in 57% yield (37 mg); mp = 205 °C.

**$^1$H NMR (400 MHz, DMSO-$d_6$)**: δ 8.06 (s, 4H), 2.64 (s, 3H).

**$^{13}$C NMR (126 MHz, DMSO-$d_6$)** δ 197.76, 166.68, 139.82, 134.61, 129.56, 128.31, 26.99.

**5-(methoxycarbonyl)benzoic acid (4n)[15]**

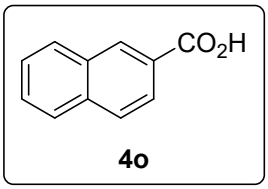


4n

Following the general procedure, compound **4n** was obtained as a white solid in 76% yield (50 mg); mp = 234 °C.

**$^1$H NMR (400 MHz, DMSO-$d_6$)**: δ 8.43 (s, 1H), 8.17 (t, *J* = 7.2 Hz, 2H), 7.65 (t, *J* = 7.7 Hz, 1H), 2.61 (s, 3H).

**2-naphthoic acid (4o)** [13]

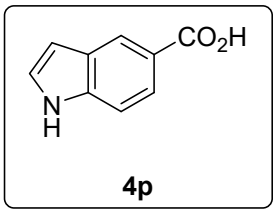


4o

Following the general procedure, compound **4o** was obtained as a white solid in 56% yield (39 mg); mp = 180 °C.

**$^1$H NMR (400 MHz, DMSO-$d_6$)**: δ 8.62 (s, 1H), 8.12 (d, *J* = 7.9 Hz, 1H), 8.03 – 7.97 (m, 3H), 7.69 – 7.58 (m, 2H).

**1H-indole-5-carboxylic acid (4p)**[9]



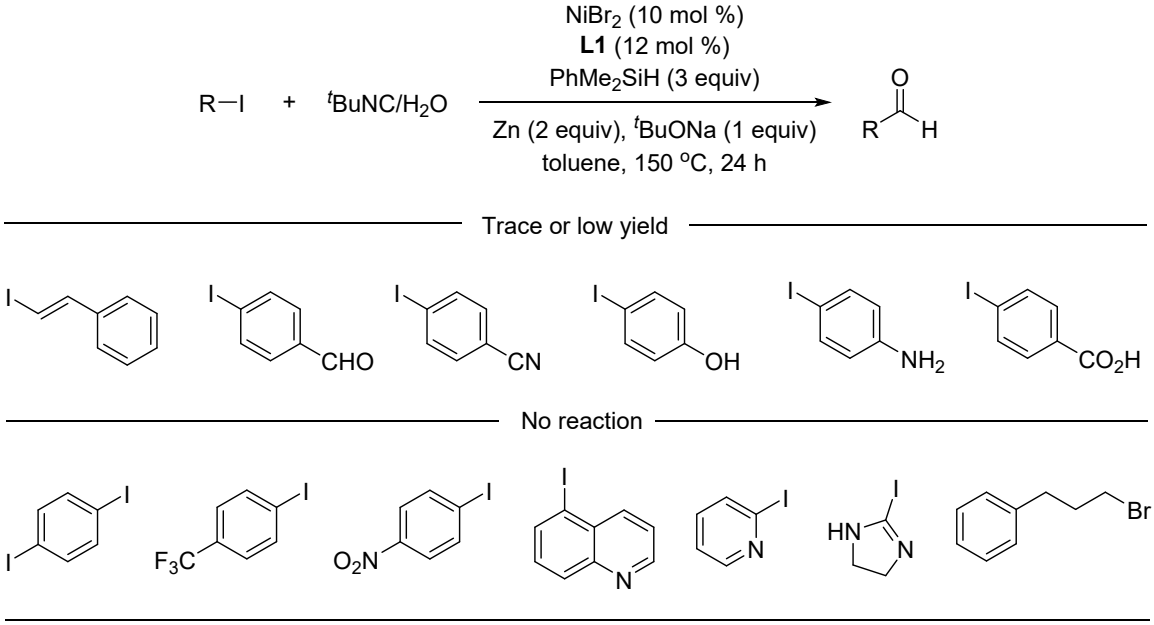
4p

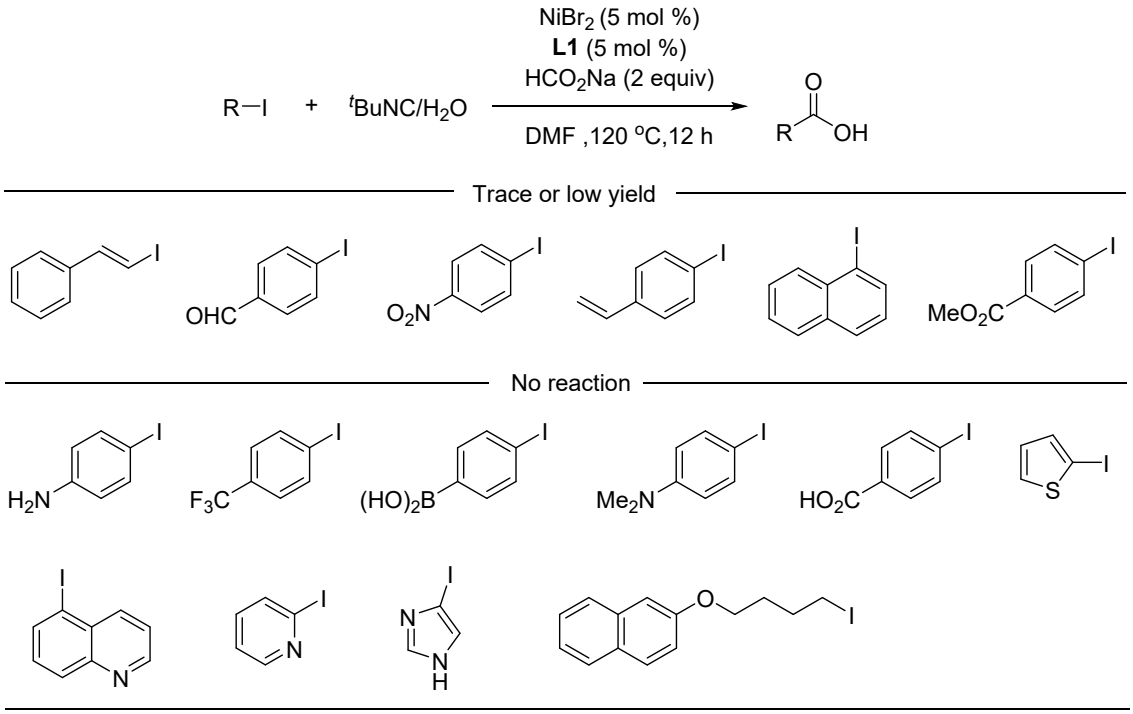
Following the general procedure, compound **4p** was obtained as a white solid in 70% yield (45 mg); mp = 205 °C.

**$^1$H NMR (400 MHz, DMSO-$d_6$)**: δ 12.41 (br, 1H), 11.44 (s, 1H), 8.26 (s, 1H), 7.73 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.46 (dd, *J* = 5.9, 2.7 Hz, 2H), 6.98 – 6.33 (m, 1H). **$^{13}$C NMR (126 MHz, DMSO-$d_6$)** δ 169.18, 138.82, 127.66, 127.41, 123.39, 122.74, 121.74, 111.68, 103.11.

### 3.5 Unsuccessful examples

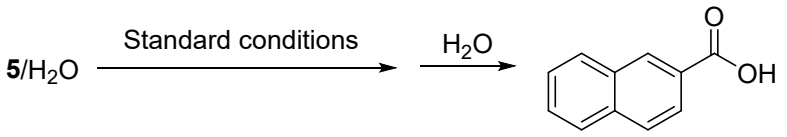
In addition the above examples, other aryl halides bearing various functional groups, heteroaromatic halides, and alkenyl/alkyl halides were investigated under the standard reaction conditions. Unfortunately, we failed to get a satisfying yield both in the formylation and carboxylation reactions.



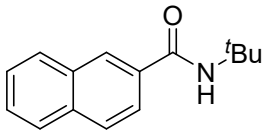



## 4. Mechanistic studies

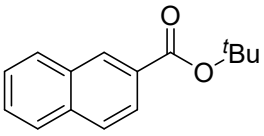
### 4.1 Investigation of the possible intermediate in the carboxylation reaction



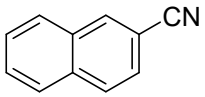

**4o**




**5a**: NR




**5b**: NR

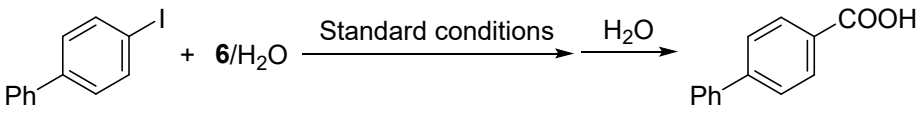



**5c**: NR

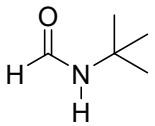
**Experimental procedure:**

Under the positive nitrogen atmosphere, **5** (0.4 mmol), $NiBr_2$ (5 mol%, 4.4 mg), 2,2-bipyridine **L1** (5 mol%, 3.1 mg), $HCO_2Na$ (0.8 mmol, 54.4 mg), and DMF (1 mL) were added to 25-mL Schlenk tube. The reaction mixture was stirred at 120 °C for 12 hours. After the completion, $H_2O$ (2 ml) was added to the reaction mixture and no product **4o** was detected by TLC analysis.

### 4.2 Investigation of the other possible carbonyl sources




**1d** **4d**



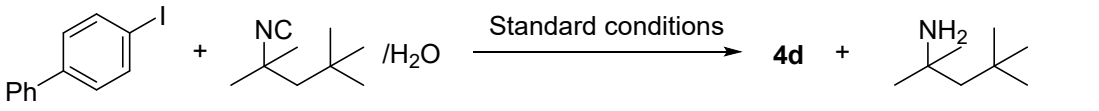

TMSCN CuCN CO (1 atm)

**6a**: NR **6b**: NR **6c**: NR **6d**: 40% (**4d**)

**Experimental procedure:**

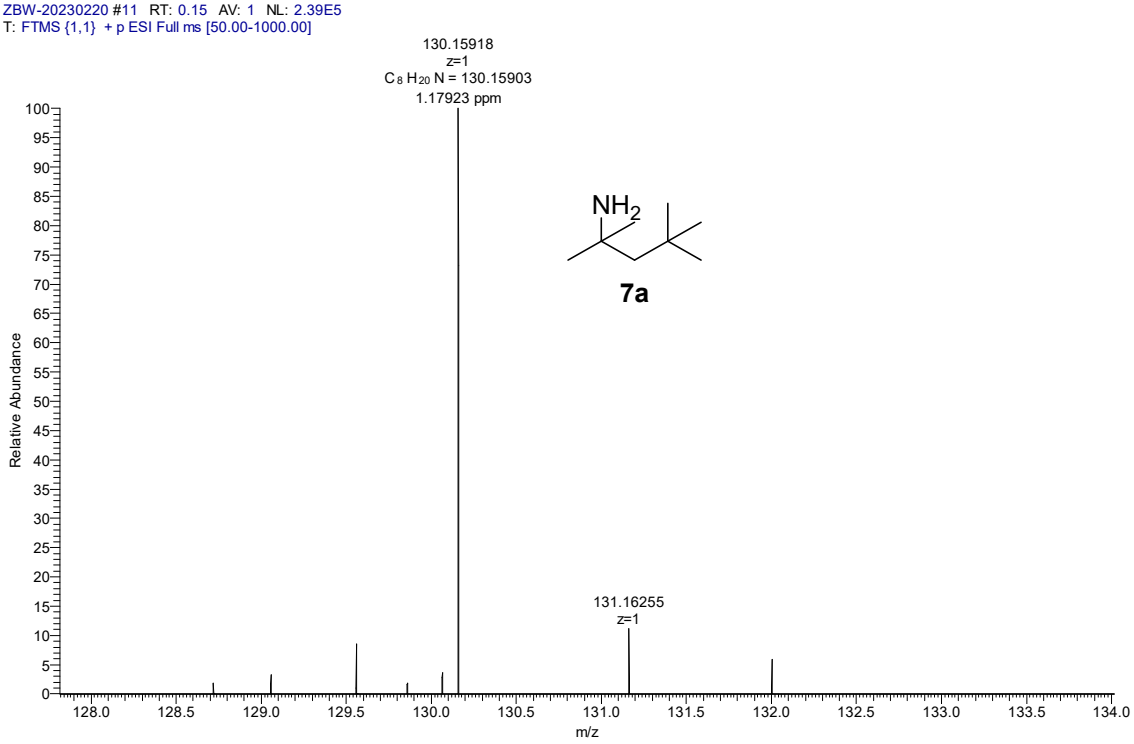
Under the positive nitrogen atmosphere, **1d** (0.4 mmol, 112 mg), $NiBr_2$ (10 mol%, 8.8 mg), **L1** (10 mol%, 6.2 mg), $HCO_2Na$ (0.8 mmol, 54.4 mg), **6a-d** (0.6 mmol, **6d**: CO balloon used ) and DMF (1 mL) were added to 25-mL Schlenk tube. The reaction mixture was stirred at 120 °C for 12 hours. After the completion, $H_2O$ (2 ml) was added to the reaction mixture and only the reaction of **1d** with **6d** proceeded smoothly. The product was isolated in 40% yield.

### 4.3 Detection of *tert*-octylamine 7a

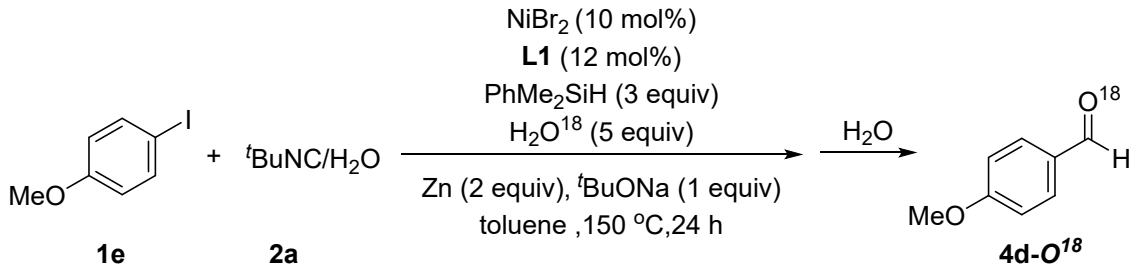



**1d** **2b** **7a**: Detected by HRMS

Under the positive nitrogen atmosphere, **1d** (0.4 mmol, 112 mg), **2b** (0.6 mmol, 83.4 mg), $NiBr_2$ (5 mol%, 4.4 mg), **L1** (5 mol%, 3.1 mg), $HCO_2Na$ (0.8 mmol, 54.4 mg), $H_2O$ (2 mmol, 40 mg) and DMF (1 mL) were added to 25 mL Schlenk tube. The reaction mixture was stirred at 120 °C for 12 hours. After the completion, the reaction mixture was directly subjected to the HRMS analysis.



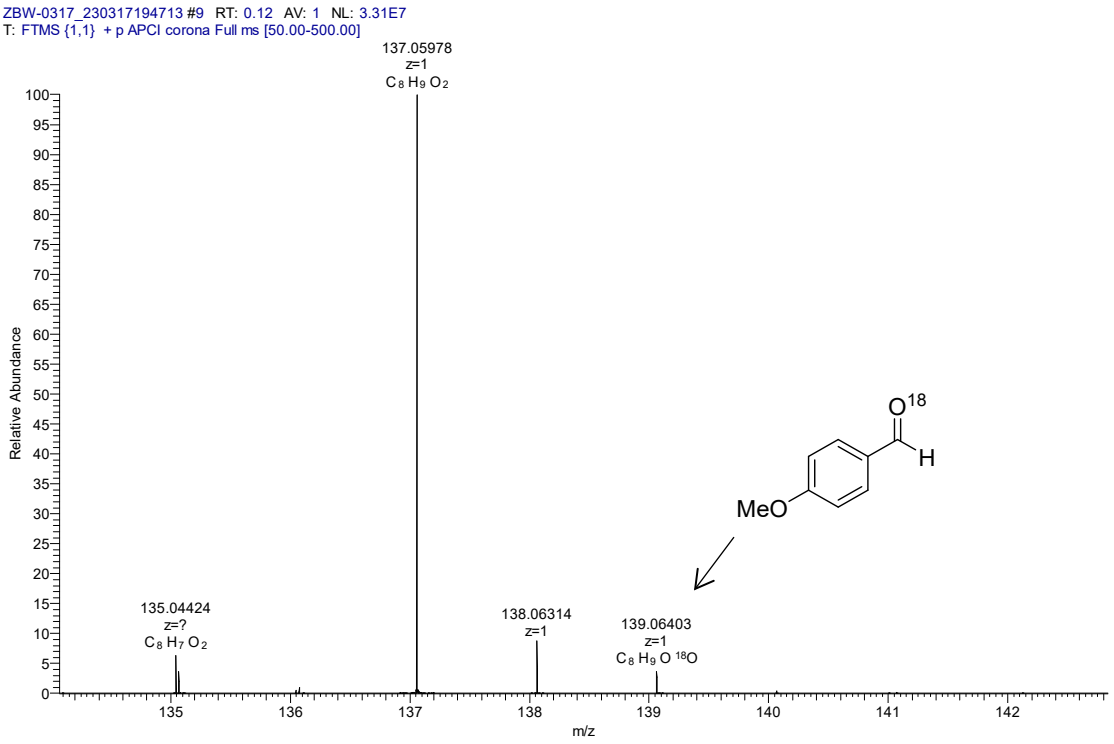

### 4.4 $O^{18}$-labelling experiment

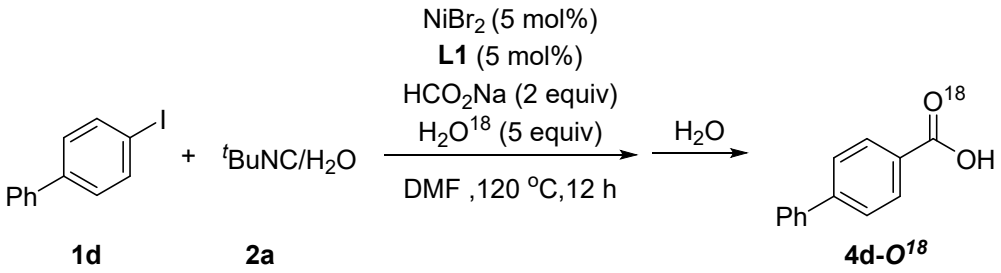



**1e** **2a** **4d-*O*$^{18}$**

Under the positive nitrogen atmosphere, **1e** (0.4 mmol, 94 mg), **2a** (0.48 mmol, 40 mg), $NiBr_2$ (10 mol%, 8.8 mg), **L1** (12 mol%, 7.5 mg), $PhMe_2SiH$ (1.2 mmol, 163 mg),

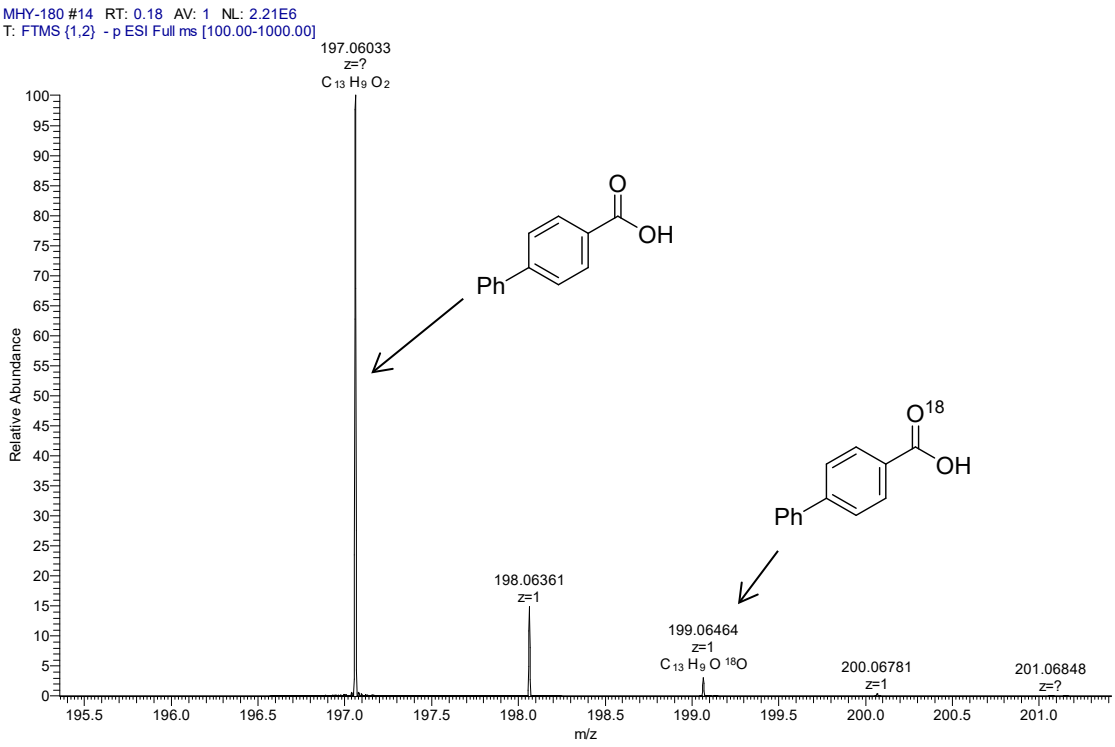
Zn (0.8 mmol, 52 mg), $^{t}$BuONa (0.4 mmol, 38.4 mg), $H_2O^{18}$ (2 mmol, 40 mg) and toluene (1 mL) were added to 25 mL Schlenk tube. The reaction mixture was stirred at 150 r the completion,



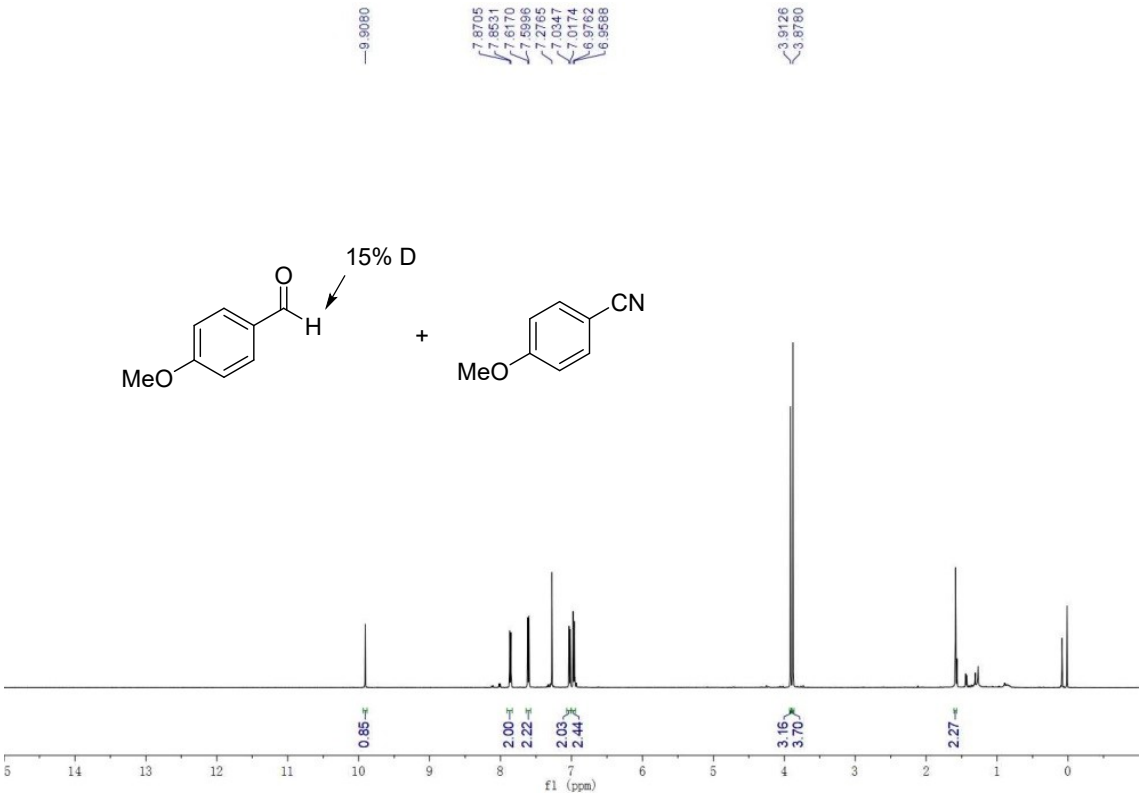

**1d** **2a** **4d-*O*$^{18}$**

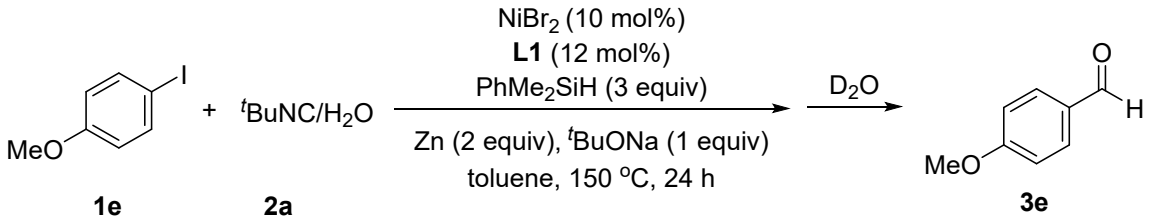
Under the positive nitrogen atmosphere, **1d** (0.4 mmol, 112 mg), $NiBr_2$ (5 mol%, 4.4 mg), **L1** (5 mol%, 3.1 mg), $HCO_2Na$ (0.8 mmol, 54.4 mg), $H_2O^{18}$ (2 mmol, 40 mg) and DMF (1 mL) were added to 25 mL Schlenk tube. The reaction mixture was stirred at 120 °C for 12 hours. After the completion, the product was isolated in 75% yield and subjected to the HRMS analysis.




## 4.5 Deuterium-labelling experiment

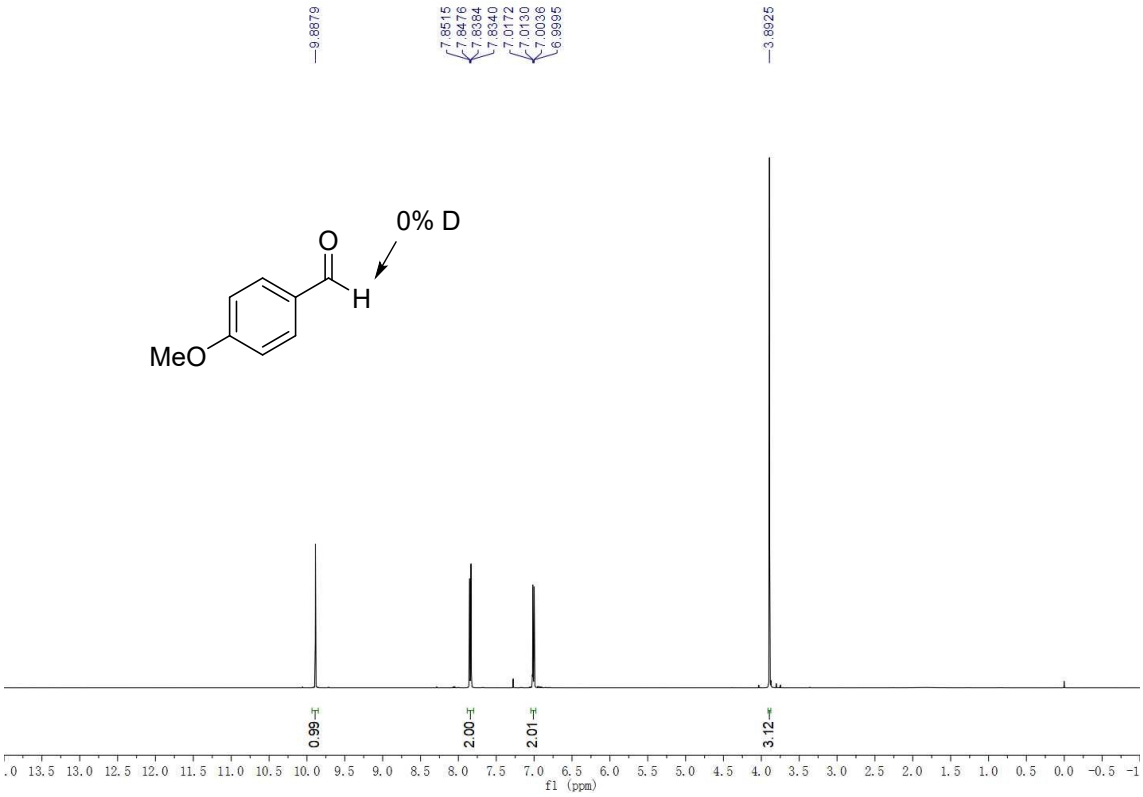

Under the positive nitrogen atmosphere, **1e** (0.4 mmol, 94 mg), **2a** (0.48 mmol, 40 mg), $NiBr_2$ (10 mol%, 8.8 mg), **L1** (12 mol%, 7.5 mg), $PhMe_2SiH$ (1.2 mmol, 163 mg), Zn (0.8 mmol, 52 mg), $^t$BuONa (0.4 mmol, 38.4 mg), $D_2O$ (2 mmol, 40 mg) and toluene (1 mL) were added to 25 mL Schlenk tube. The reaction mixture was stirred at 150 °C for 24 hours. After the completion, the inseparable mixture of **3e-*d*** and **8e** was isolated and directly subjected to the $^1$H NMR analysis.




**1e** **2a** **3e**

Under the positive nitrogen atmosphere, **1e** (0.4 mmol, 94 mg), **2a** (0.48 mmol, 40 mg), $NiBr_2$ (10 mol%, 8.8 mg), **L1** (12 mol%, 7.5 mg), $PhMe_2SiH$ (1.2 mmol, 163 mg), Zn (0.8 mmol, 52 mg), $^t$BuONa (0.4 mmol, 38.4 mg) and toluene (1 mL) were added to 25 mL Schlenk tube. The reaction mixture was stirred at 150 °C for 24 hours. After the completion, $D_2O$ (2 mmol, 40 mg) was added to the 25 mL Schlenk tube and the reaction mixture was stirred at 150 °C for 1 hours. The product was isolated in 70% yield and characterized by $^1$H NMR analysis.


9.8879
7.8515
7.8476
7.8384
7.8340
7.0172
7.0130
7.0036
6.9995
3.8925
0% D
O
H
MeO
0.99
2.00
2.01
3.12
f1 (ppm)

## 5. References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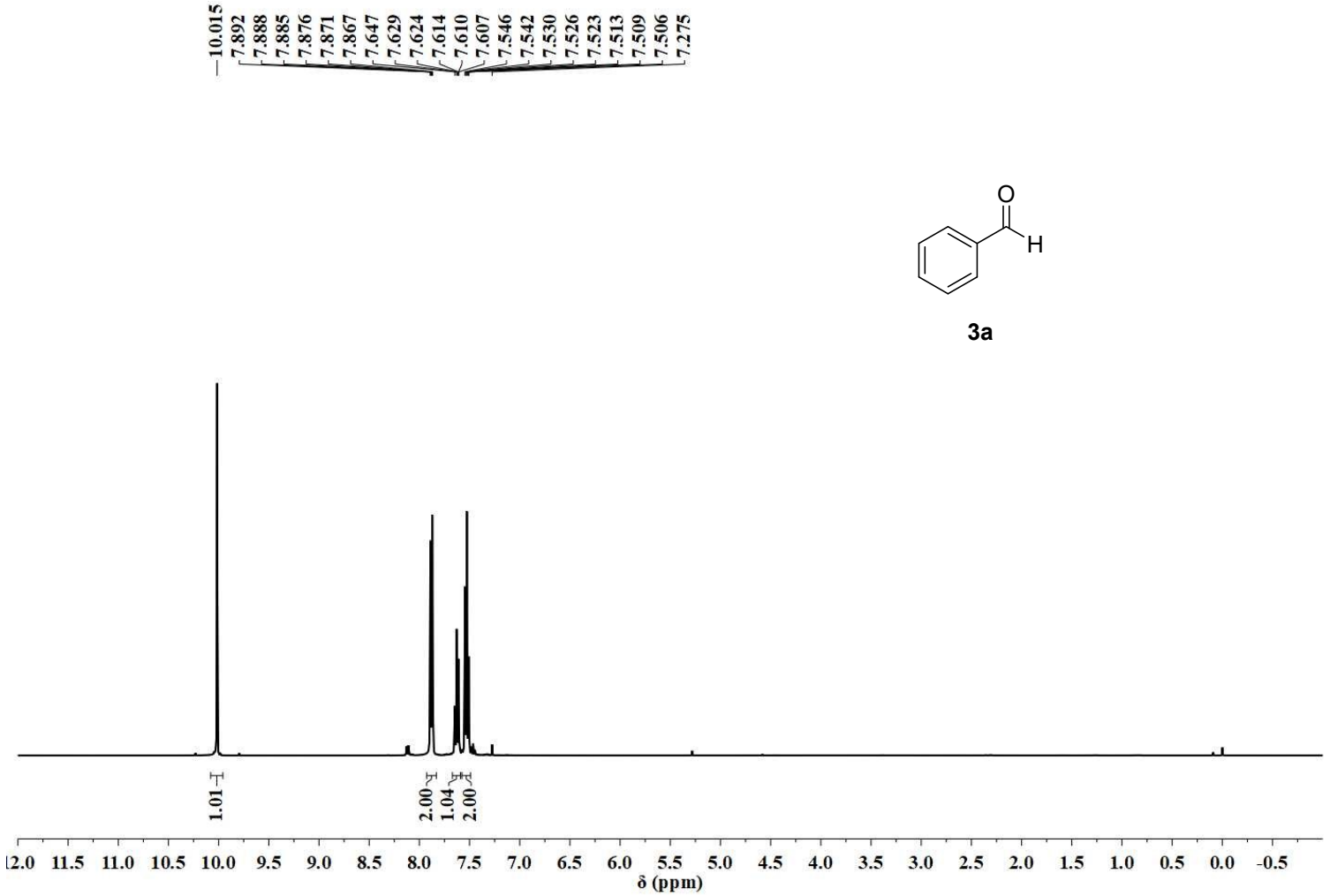
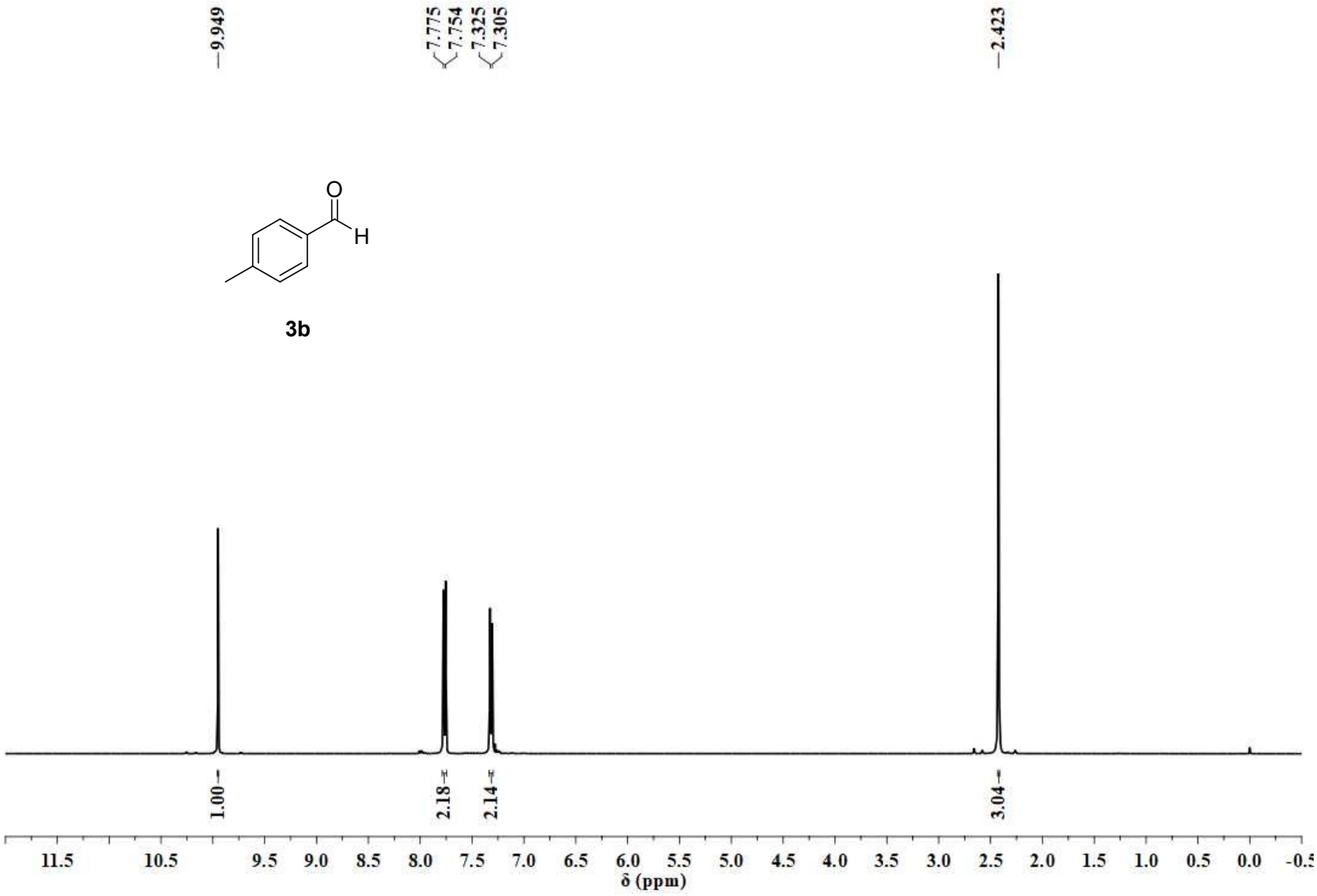
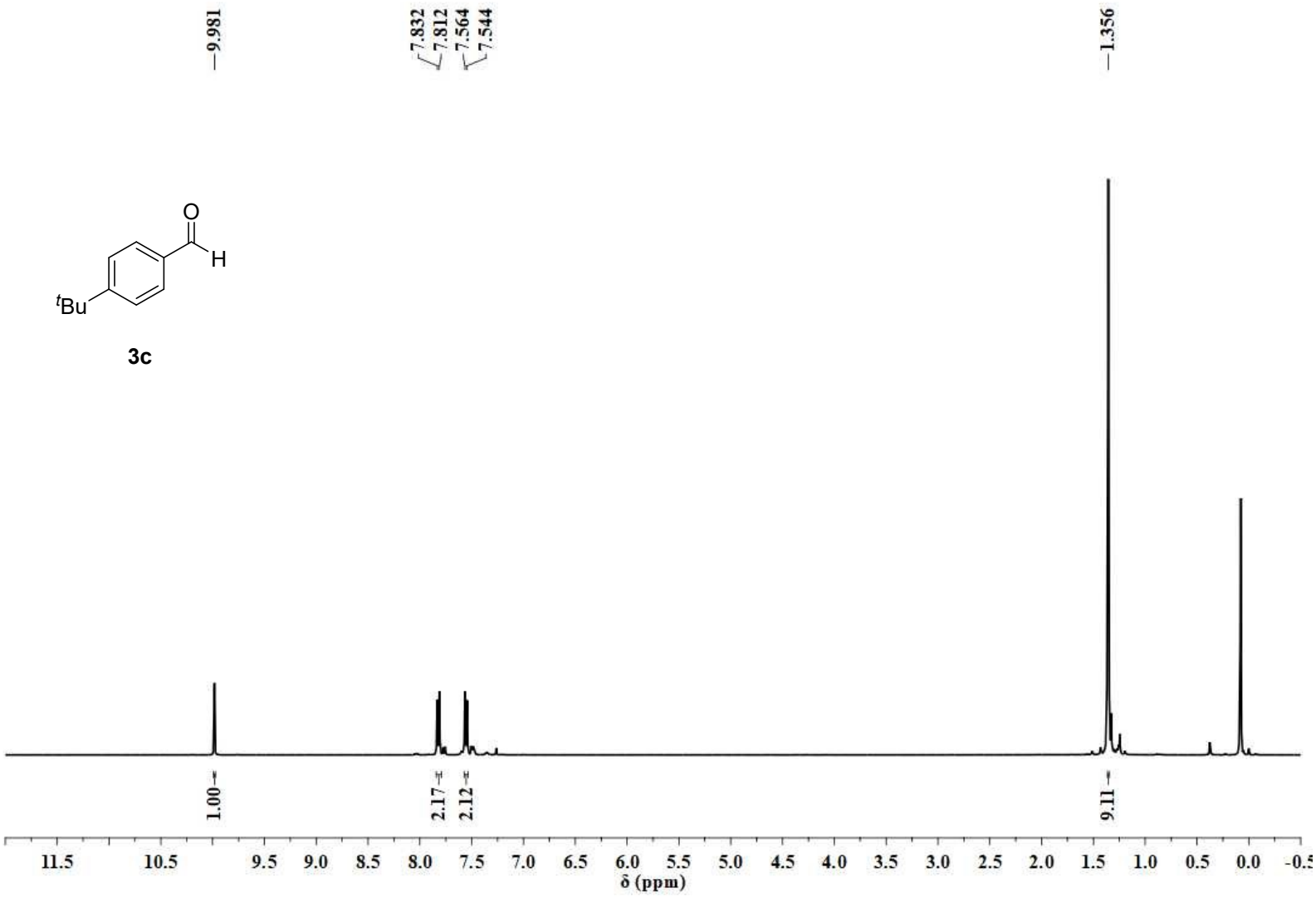
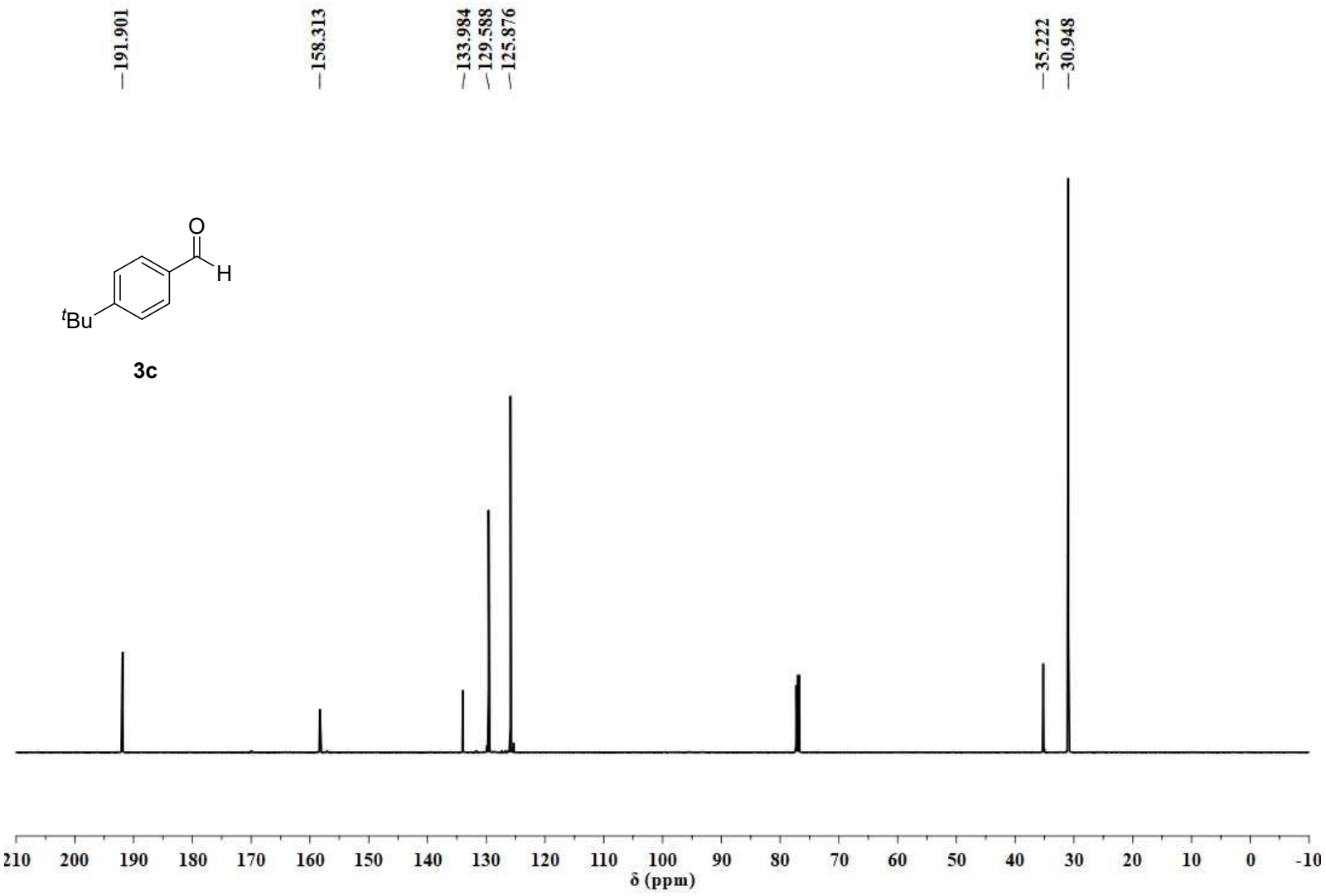
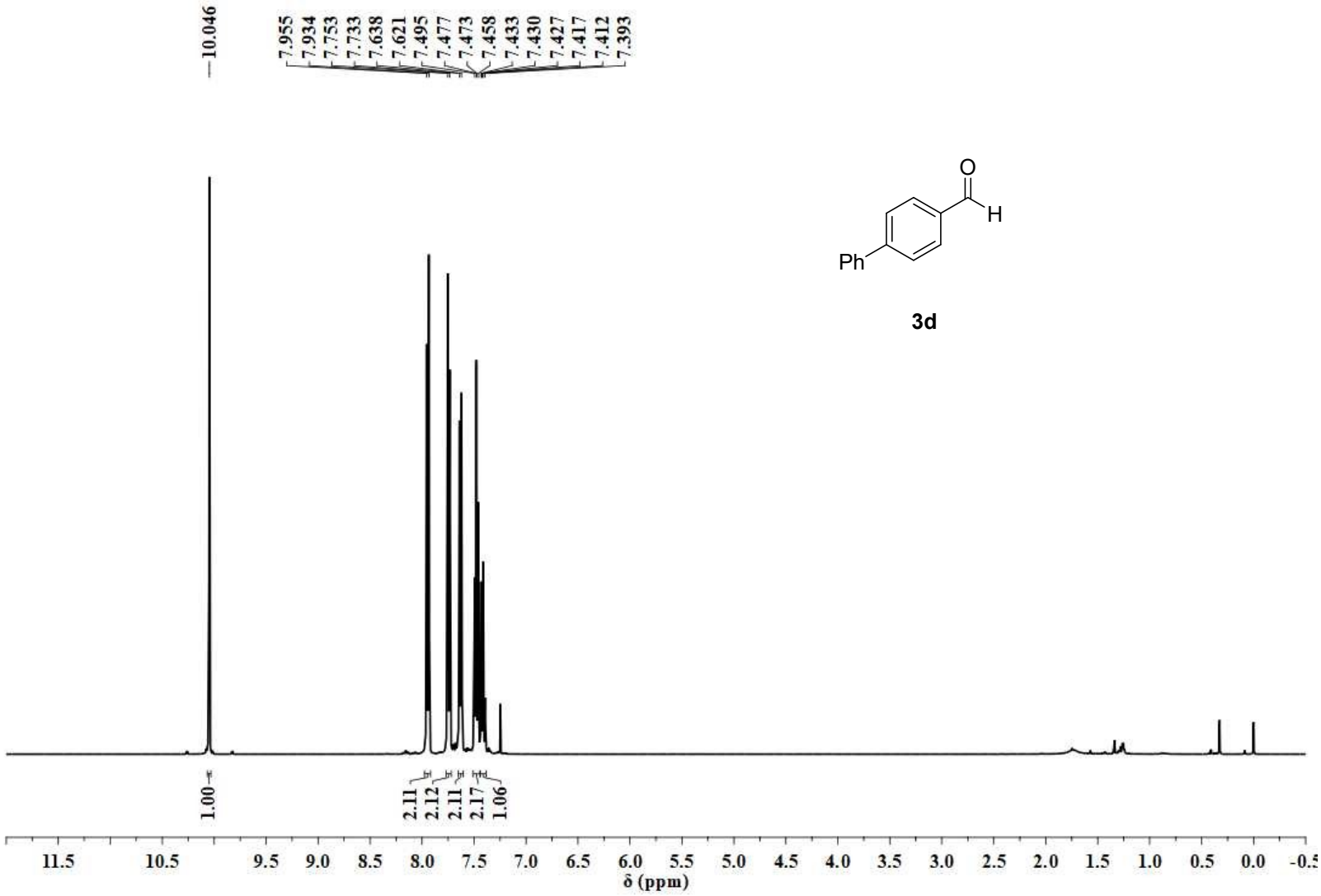
## 6. $^{1}$H NMR Spectra

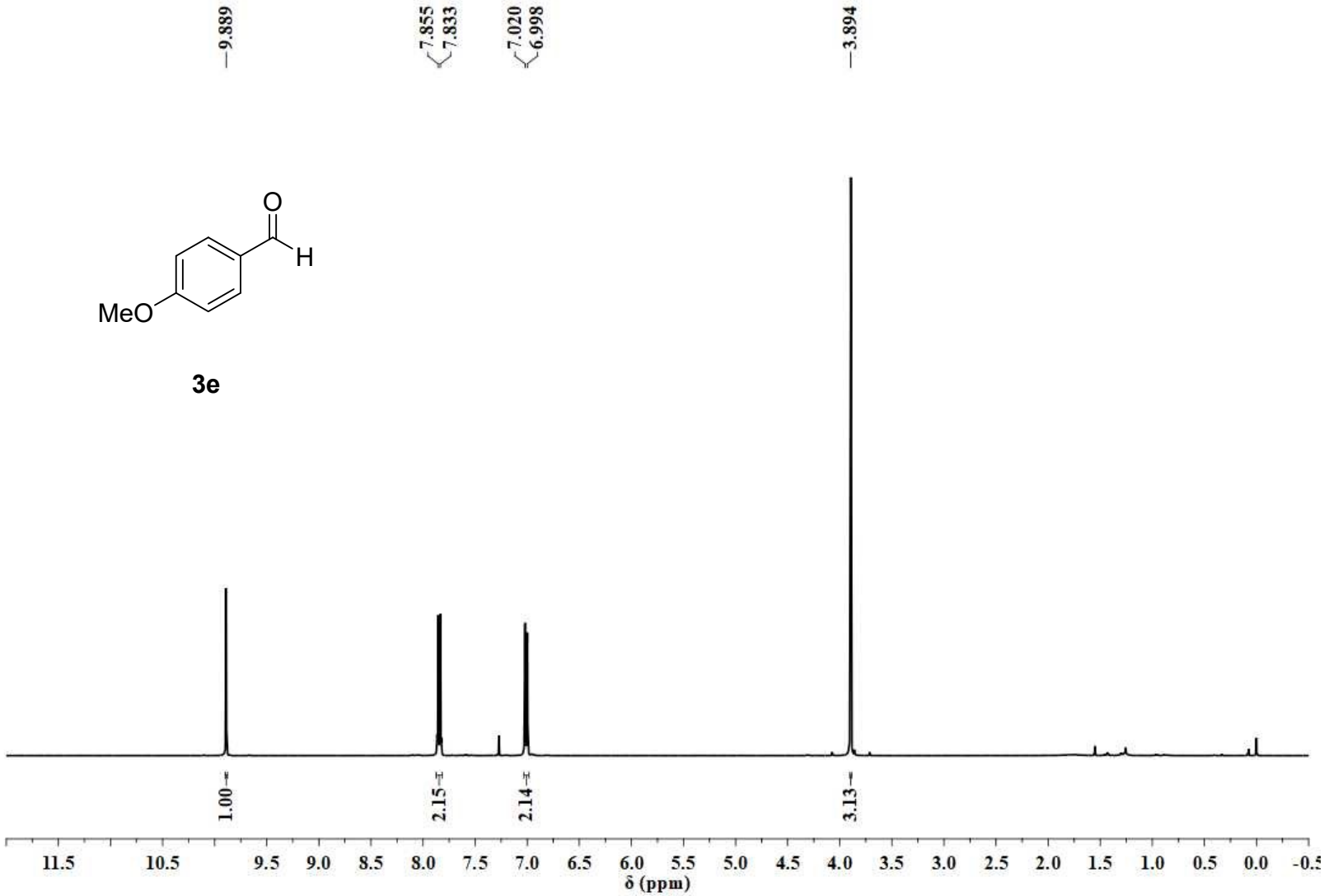



9.949
7.775
7.754
7.325
7.305
2.423
O
H
3b
1.00
2.18
2.14
3.04
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

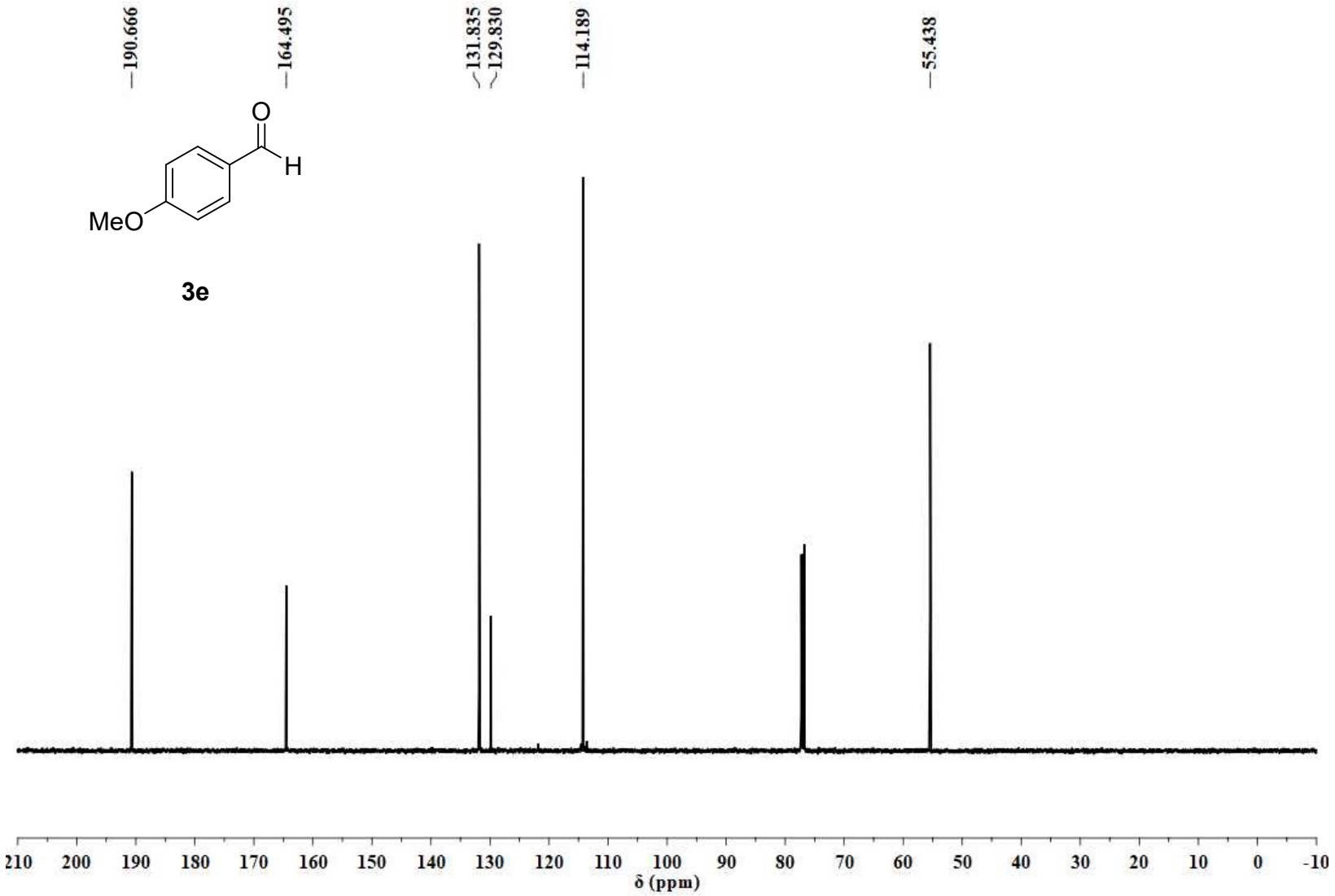

9.981
7.832
7.812
7.564
7.544
1.356
O
H
tBu
3c
1.00
2.17
2.12
9.11
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

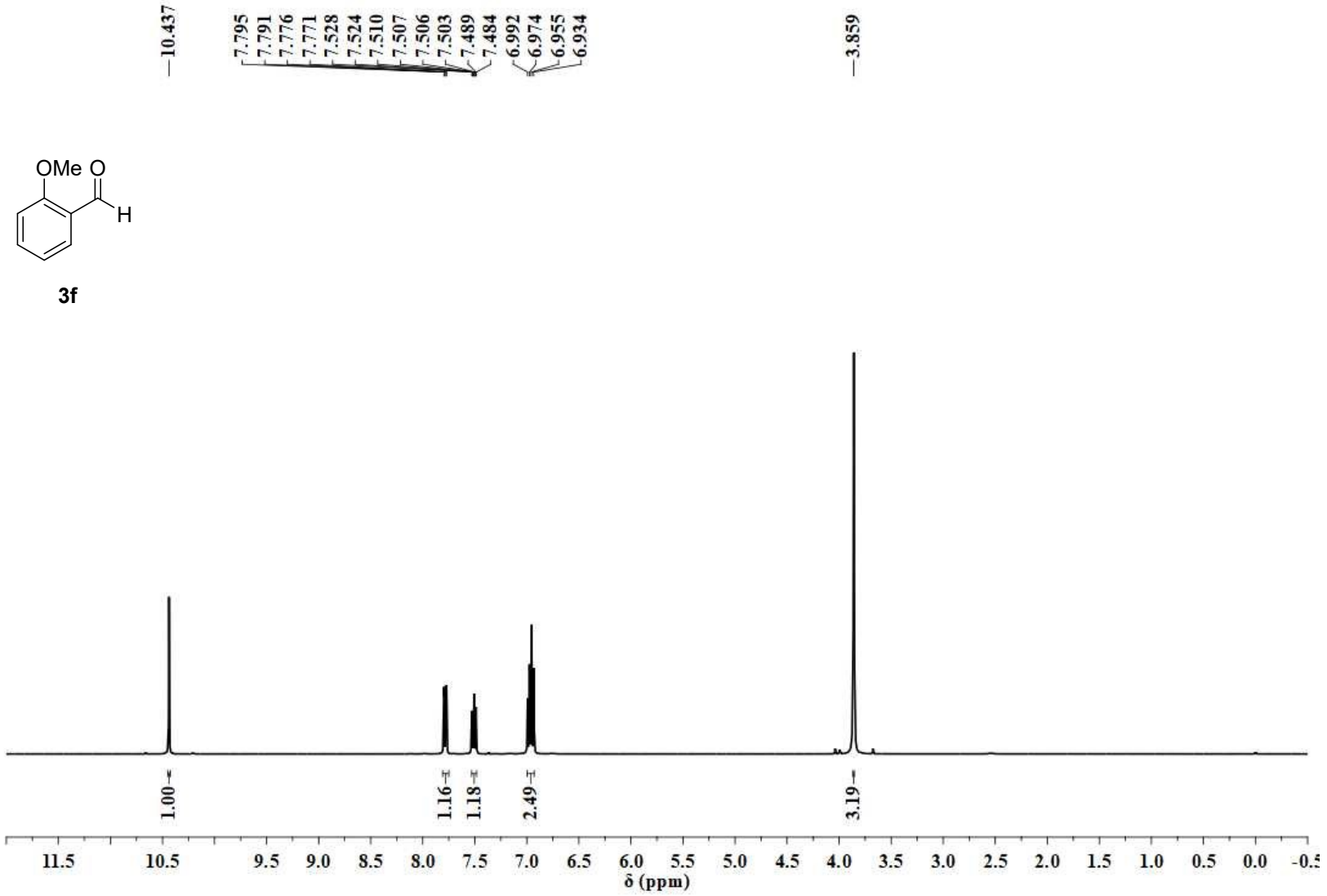

191.901
158.313
133.984
129.588
125.876
35.222
30.948
O
H
tBu
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


10.046
7.955
7.934
7.753
7.733
7.638
7.621
7.495
7.477
7.473
7.458
7.433
7.430
7.427
7.417
7.412
7.393
O
H
Ph
3d
1.00
2.11
2.12
2.11
2.17
1.06
11.5
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)

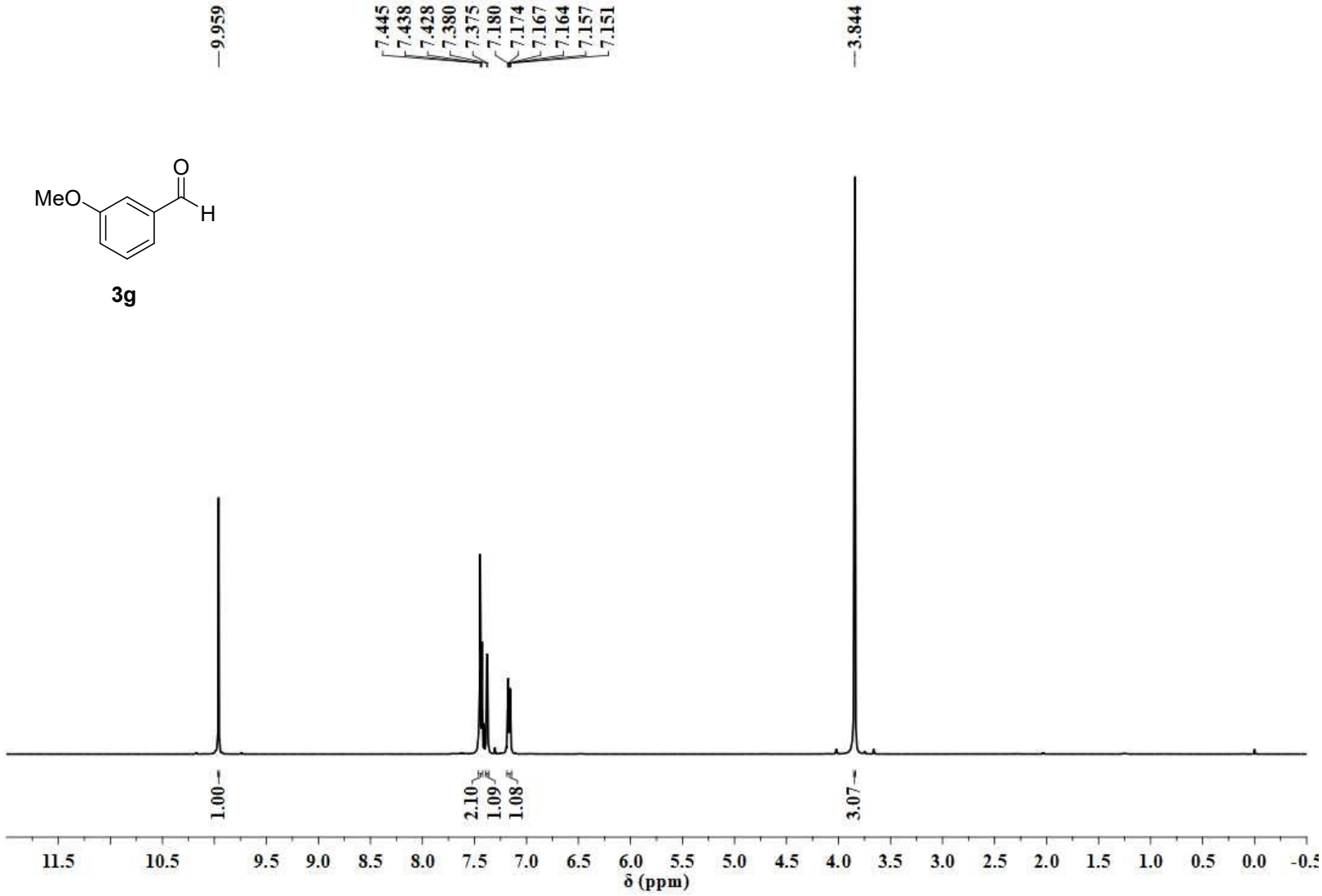

9.889
7.855
7.833
7.020
6.998
3.894
O
H
MeO
1.00
2.15
2.14
3.13
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

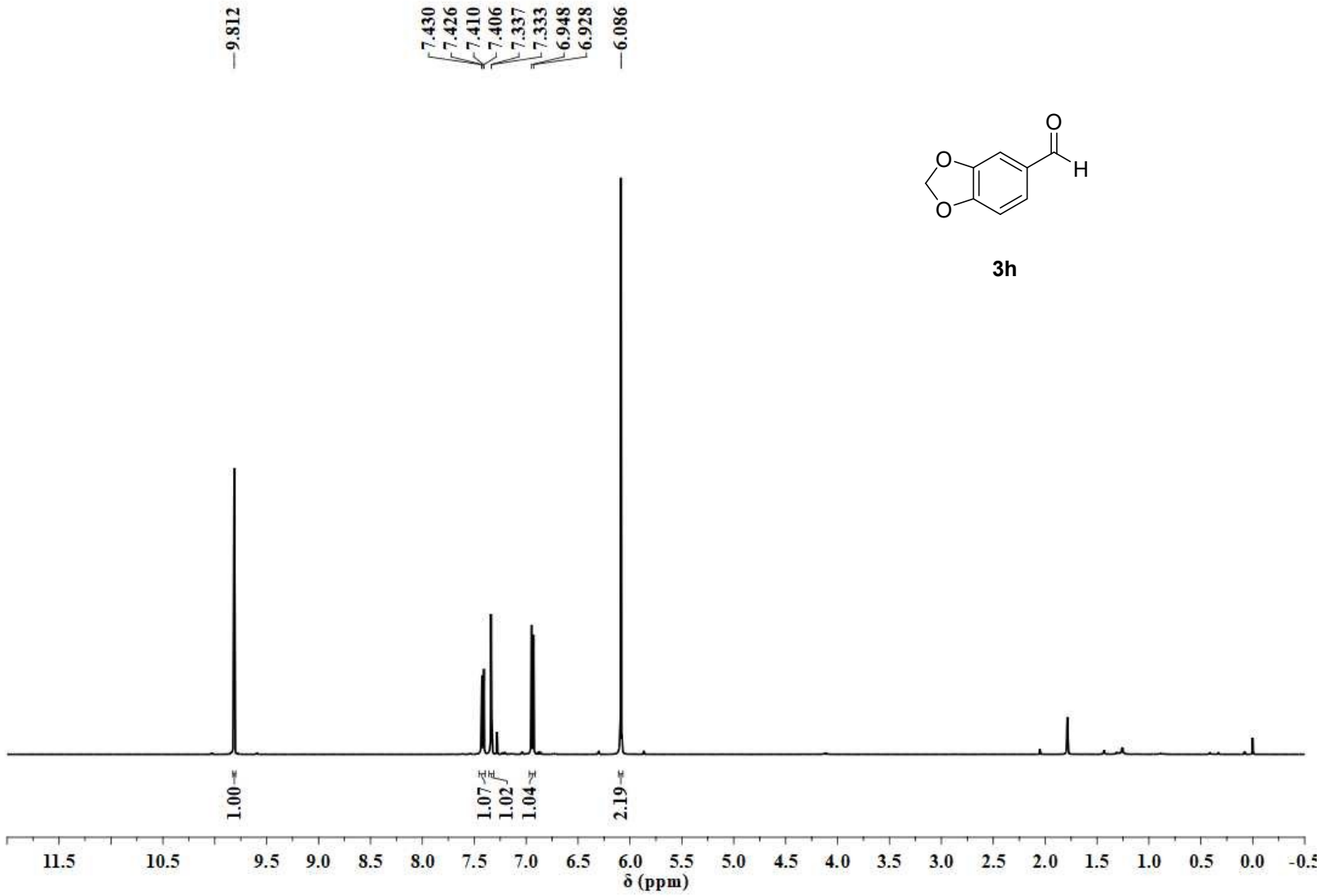
**3e**


190.666
164.495
131.835
129.830
114.189
55.438
O
H
MeO
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

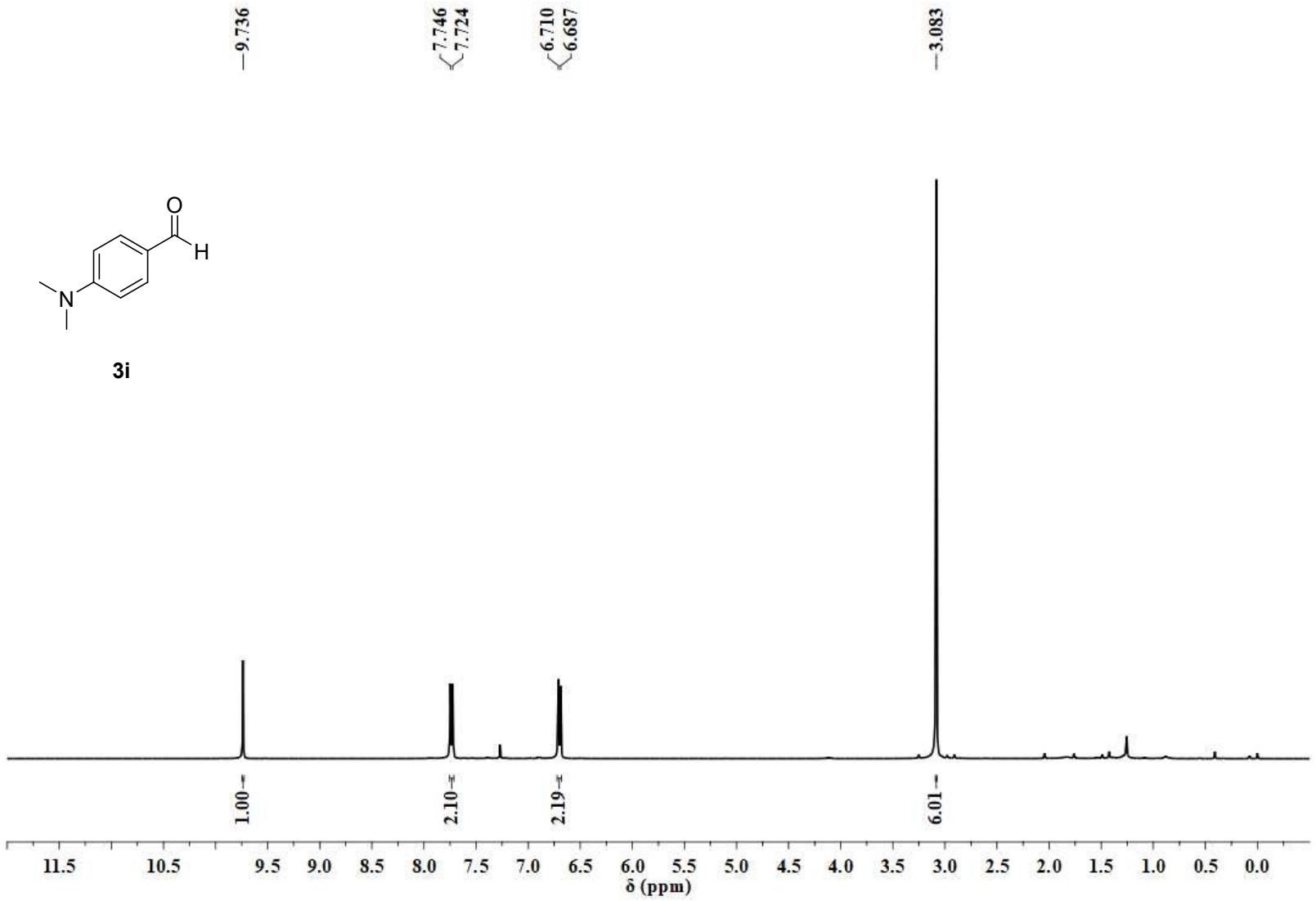

10.437
7.795
7.791
7.776
7.771
7.528
7.524
7.510
7.507
7.506
7.503
7.489
7.484
6.992
6.974
6.955
6.934
3.859
OMe O
H
1.00
1.16
1.18
2.49
3.19
δ (ppm)

**3f**

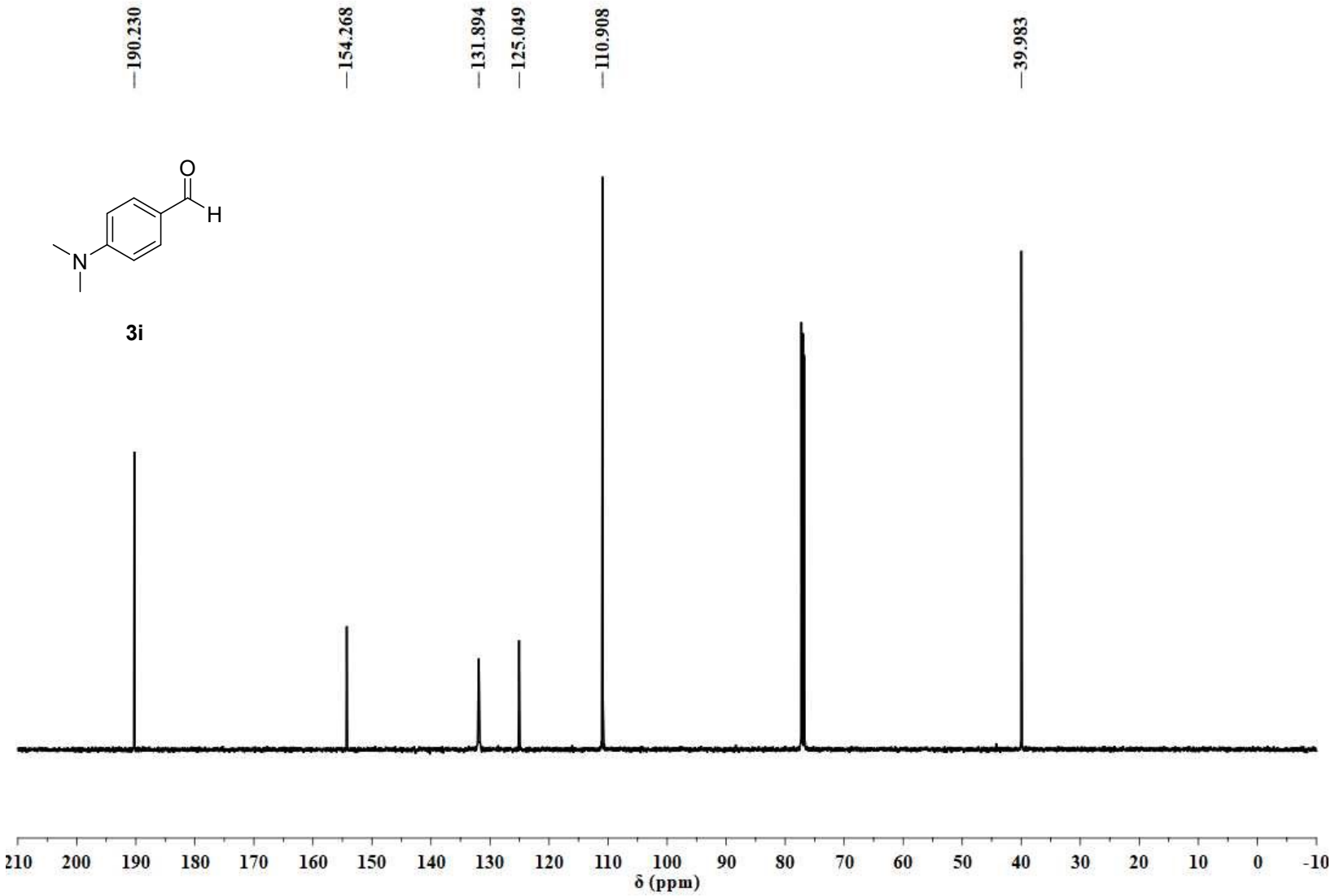

9.959
7.445
7.438
7.428
7.380
7.375
7.180
7.174
7.167
7.164
7.157
7.151
3.844
MeO
O
H
3g
1.00
2.10
1.09
1.08
3.07
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

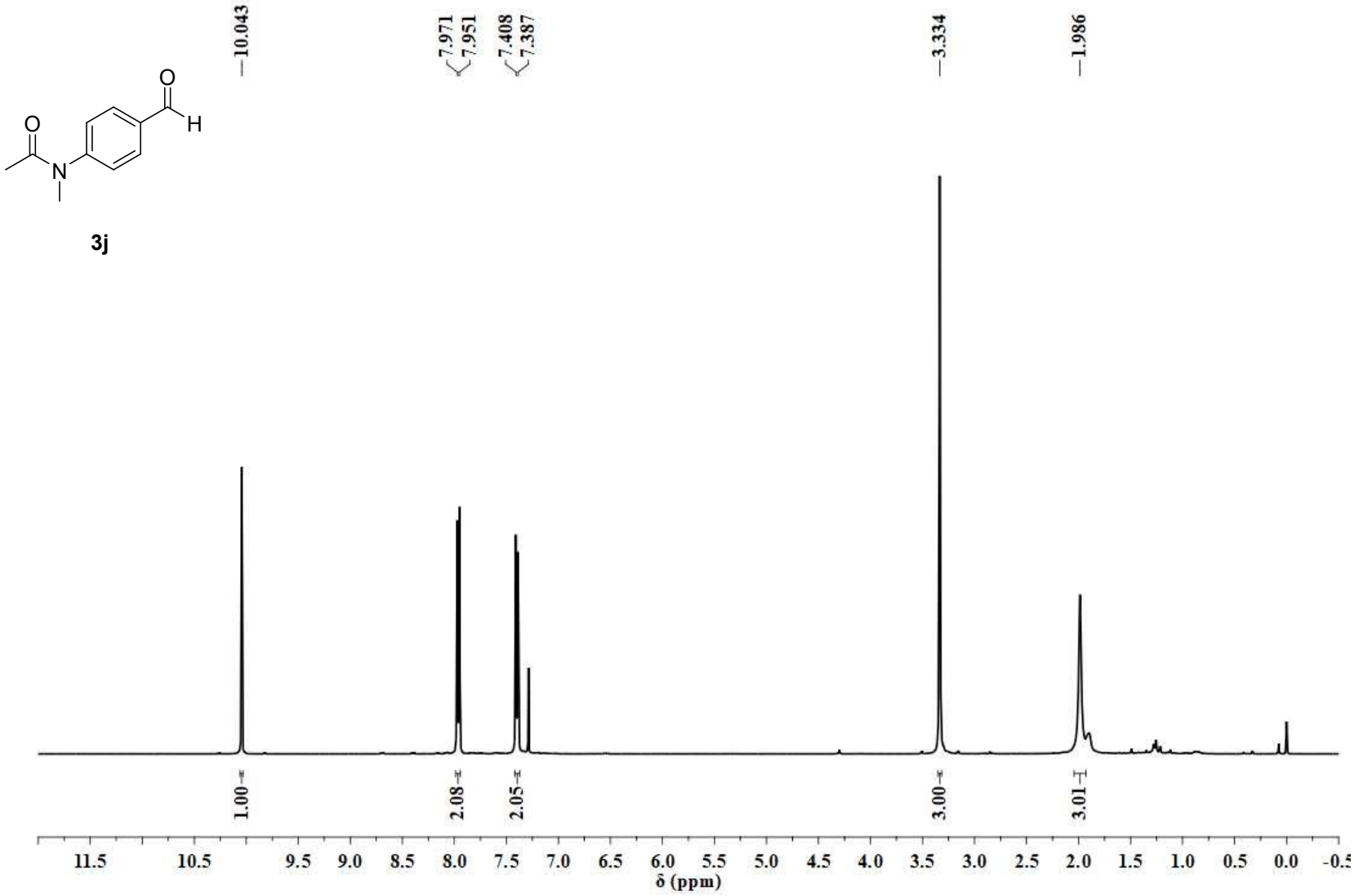

9.812
7.430
7.426
7.410
7.406
7.337
7.333
6.948
6.928
6.086
O
O
O
H
1.00
1.07
1.02
1.04
2.19
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

**3h**

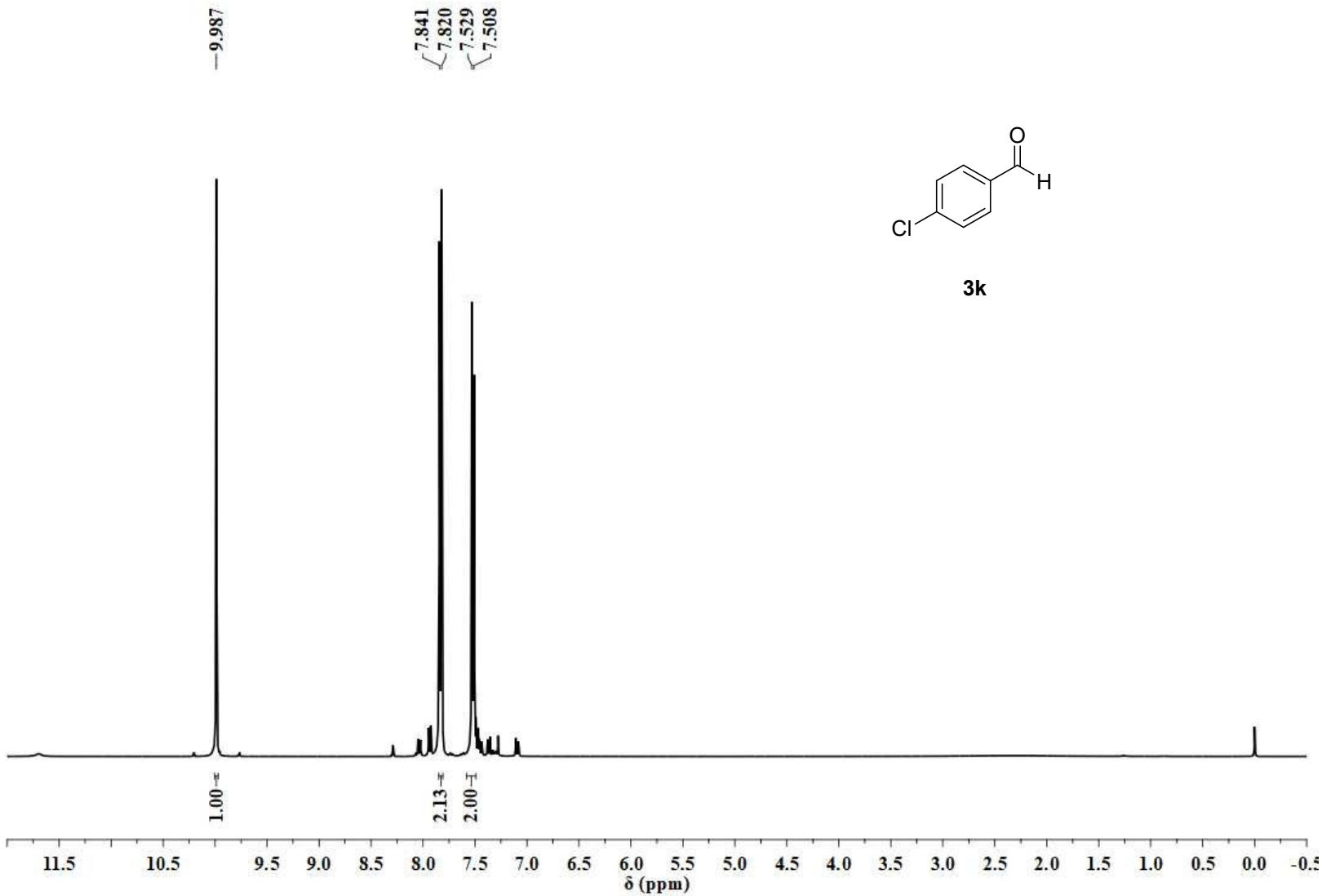

9.736
7.746
7.724
6.710
6.687
3.083
O
H
N
1.00
2.10
2.19
6.01
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

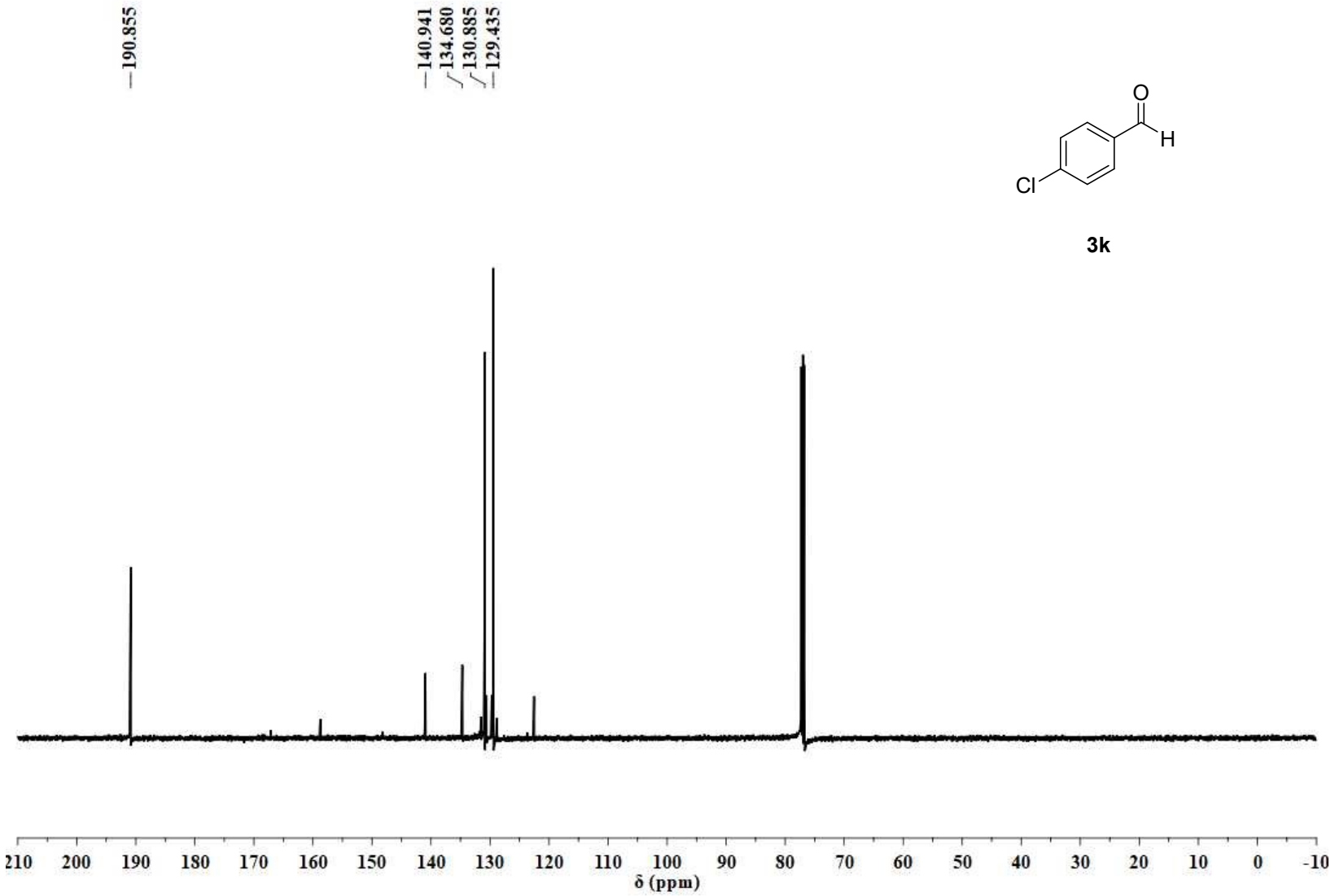
**3i**

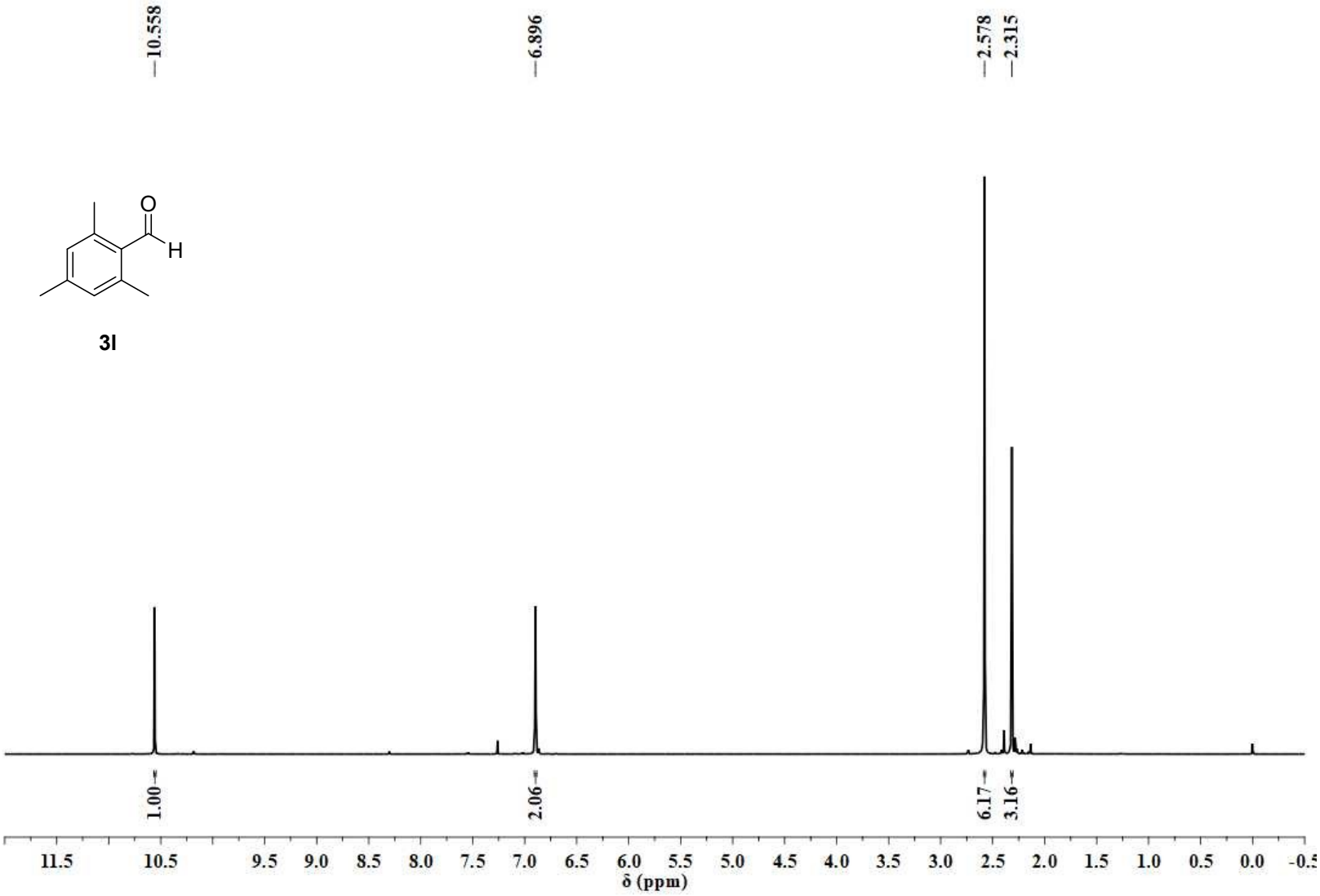

190.230
154.268
131.894
125.049
110.908
39.983
O
H
N
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

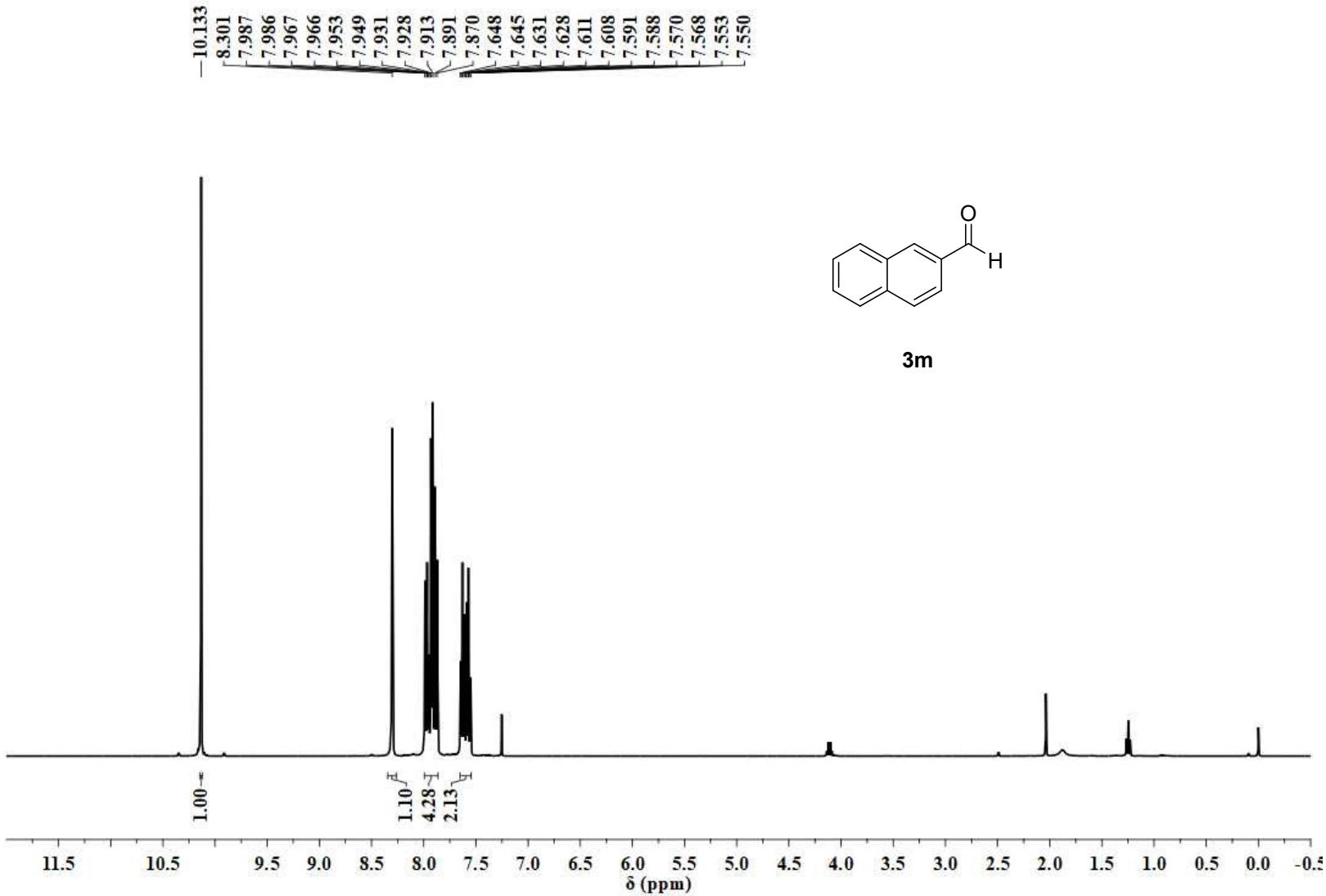

10.043
7.971
7.951
7.408
7.387
3.334
1.986
O
O
H
N
1.00
2.08
2.05
3.00
3.01
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

**3j**

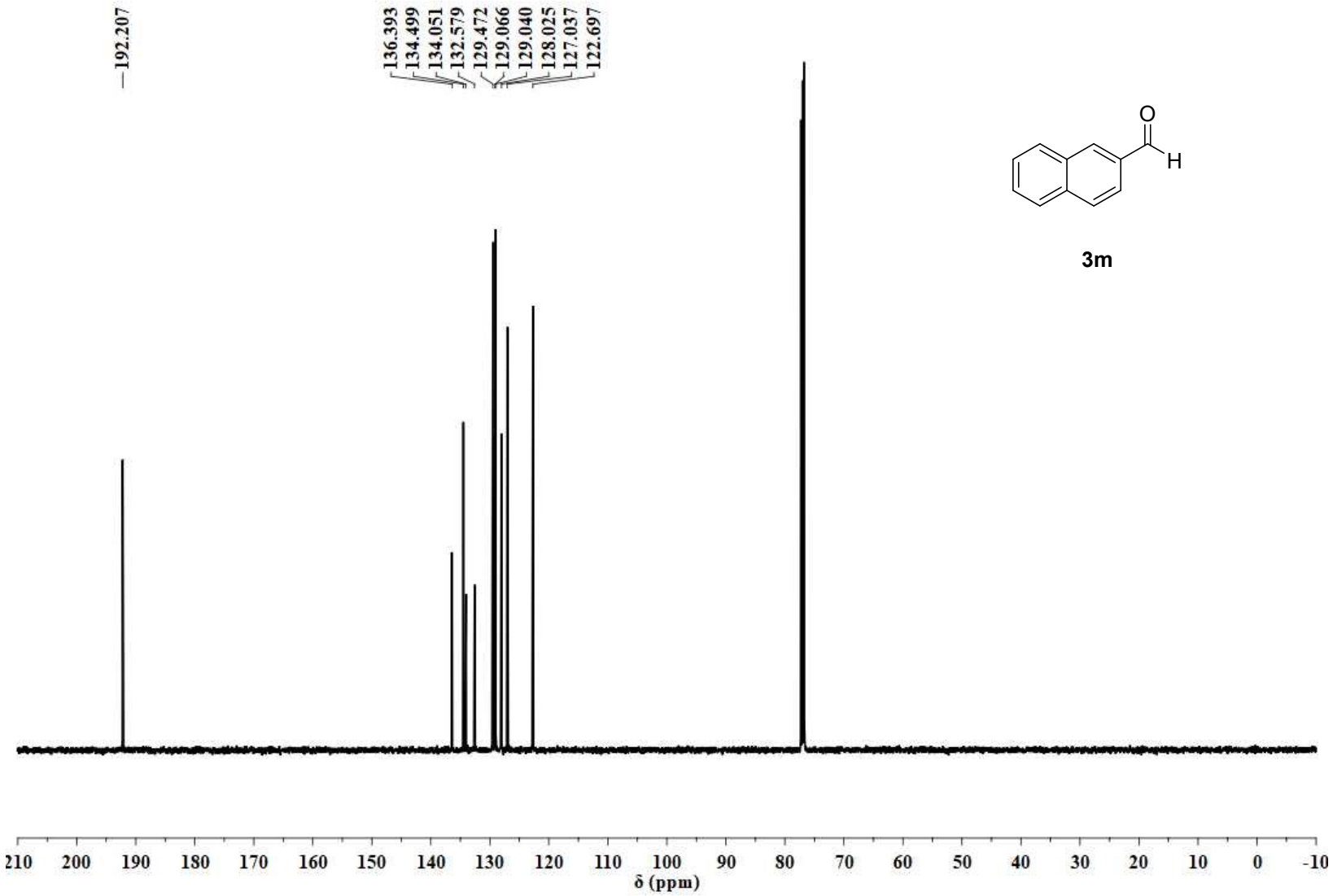

9.987
7.841
7.820
7.529
7.508
O
H
Cl
3k
1.00
2.13
2.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

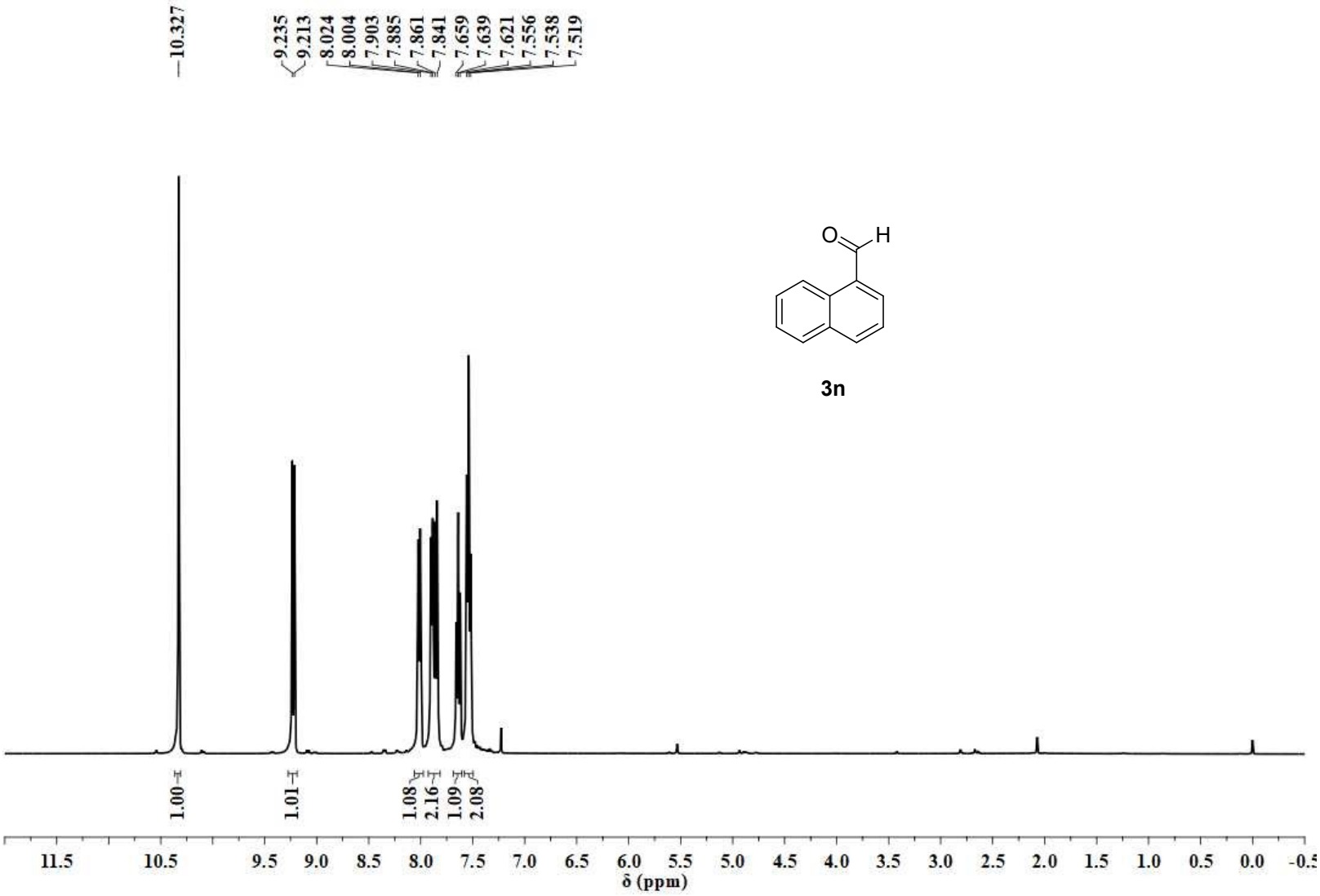

190.855
140.941
134.680
130.885
129.435
O
H
Cl
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

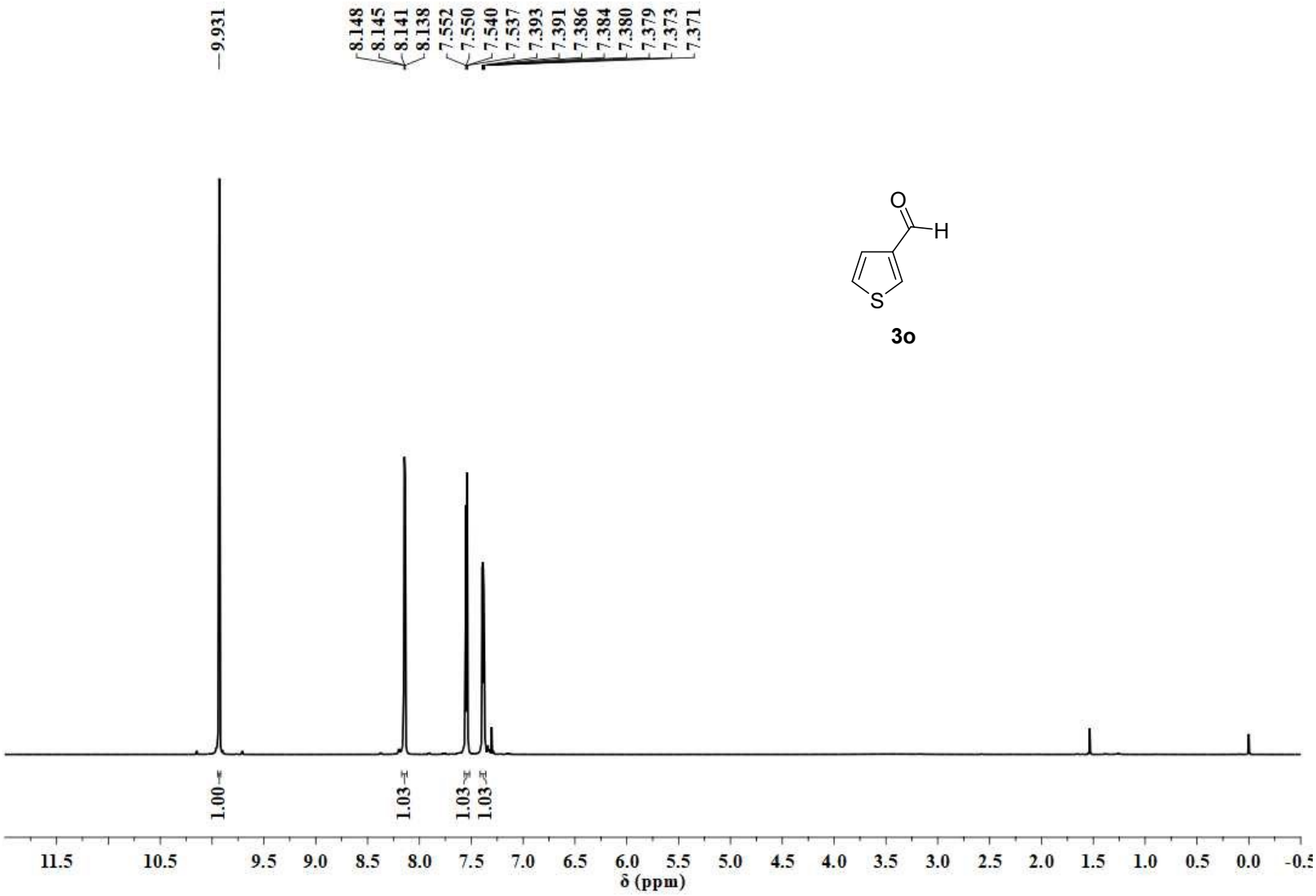

10.558
6.896
2.578
2.315
O
H
3l
1.00
2.06
6.17
3.16
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


10.133
8.301
7.987
7.986
7.967
7.966
7.953
7.949
7.931
7.928
7.913
7.891
7.870
7.648
7.645
7.631
7.628
7.611
7.608
7.591
7.588
7.570
7.568
7.553
7.550
O
H
1.00
1.10
4.28
2.13
11.5
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)

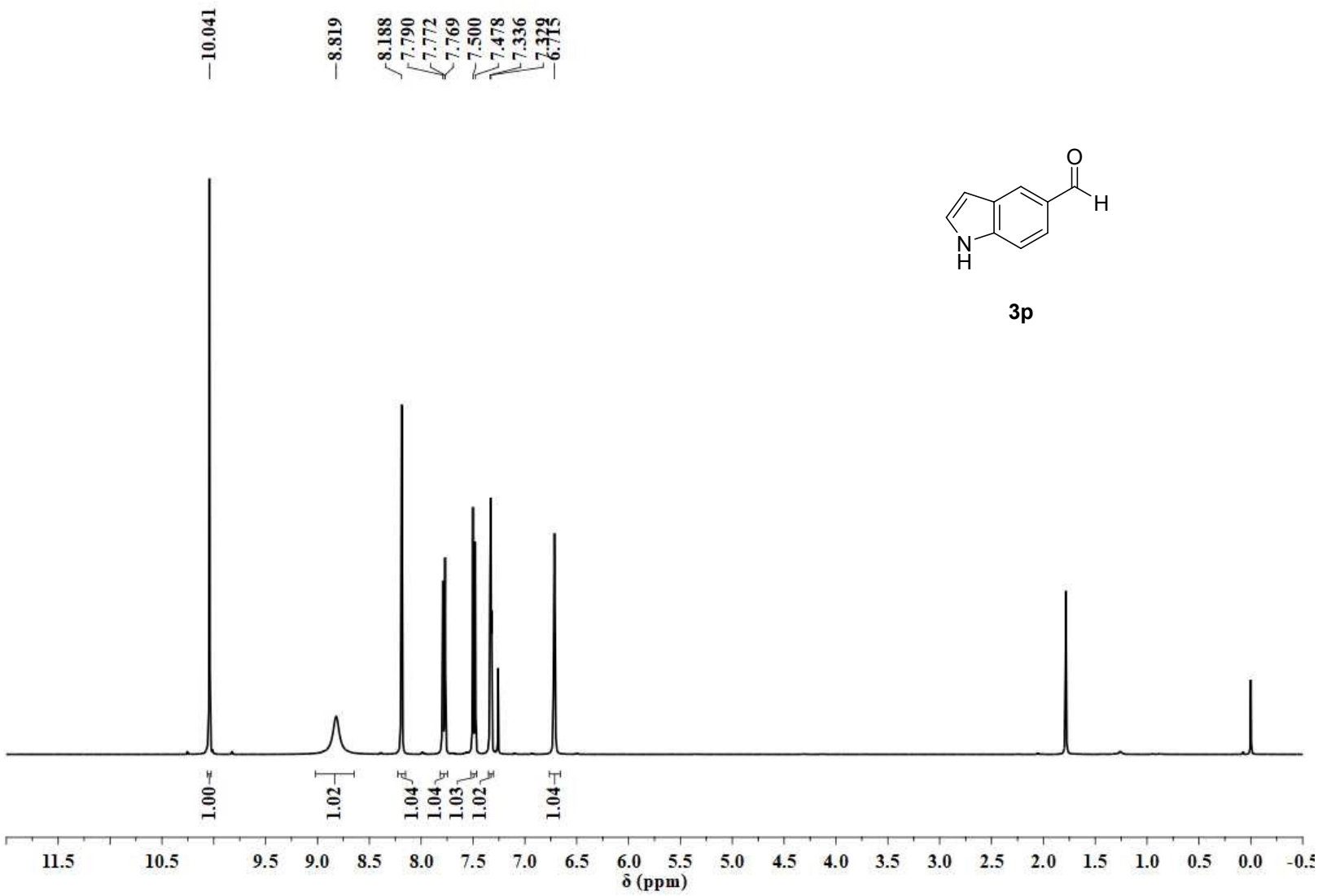
**3m**

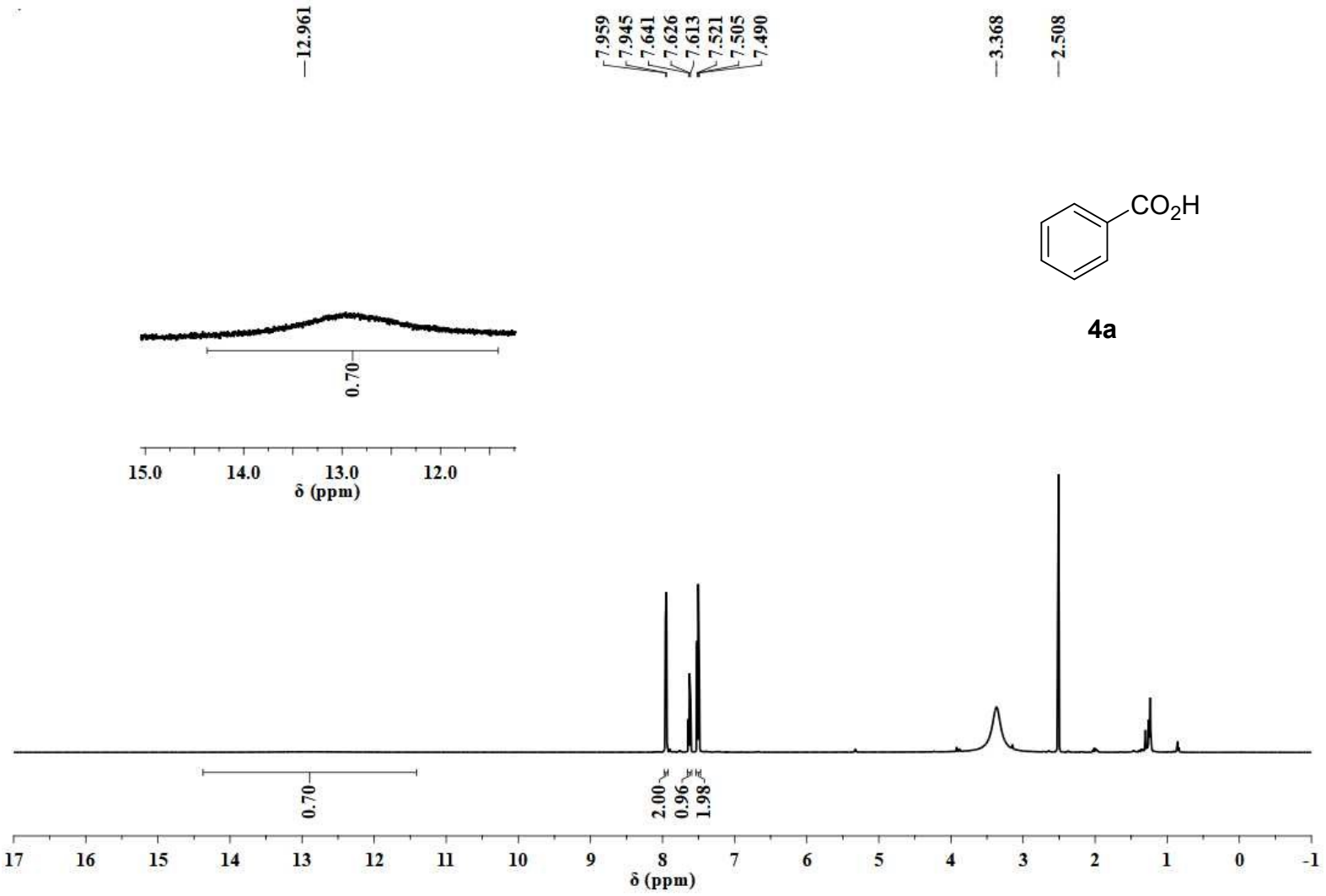

192.207
136.393
134.499
134.051
132.579
129.472
129.066
129.040
128.025
127.037
122.697
O
H
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

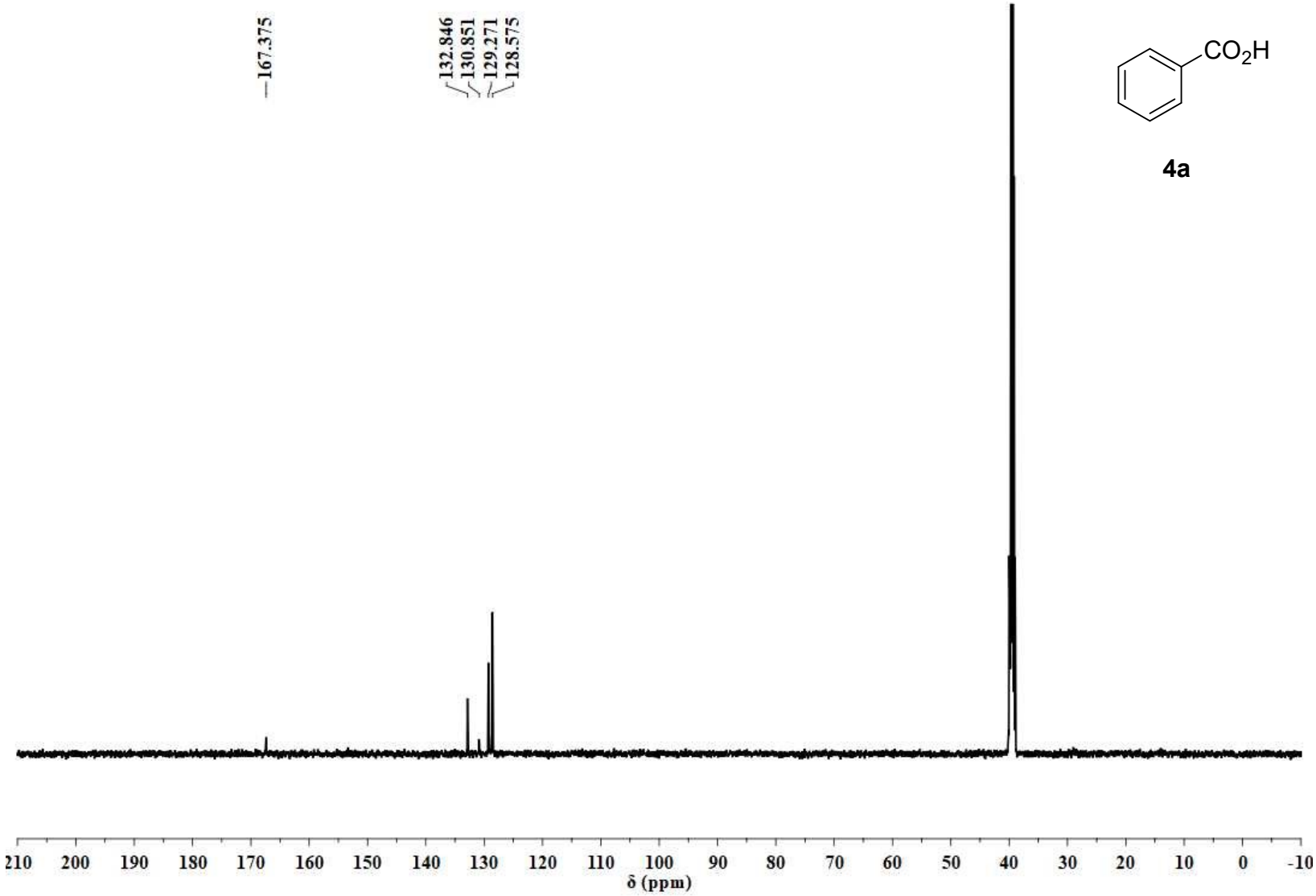

10.327
9.235
9.213
8.024
8.004
7.903
7.885
7.861
7.841
7.659
7.639
7.621
7.556
7.538
7.519
O
H
3n
1.00
1.01
1.08
2.16
1.09
2.08
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

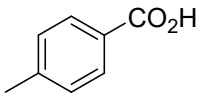

9.931
8.148
8.145
8.141
8.138
7.552
7.550
7.540
7.537
7.393
7.391
7.386
7.384
7.380
7.379
7.373
7.371
O
H
S
1.00
1.03
1.03
1.03
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

**3o**


10.041
8.819
8.188
7.790
7.772
7.769
7.500
7.478
7.336
7.329
6.715
O
H
N
H
3p
1.00
1.02
1.04
1.04
1.03
1.02
1.04
11.5
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)

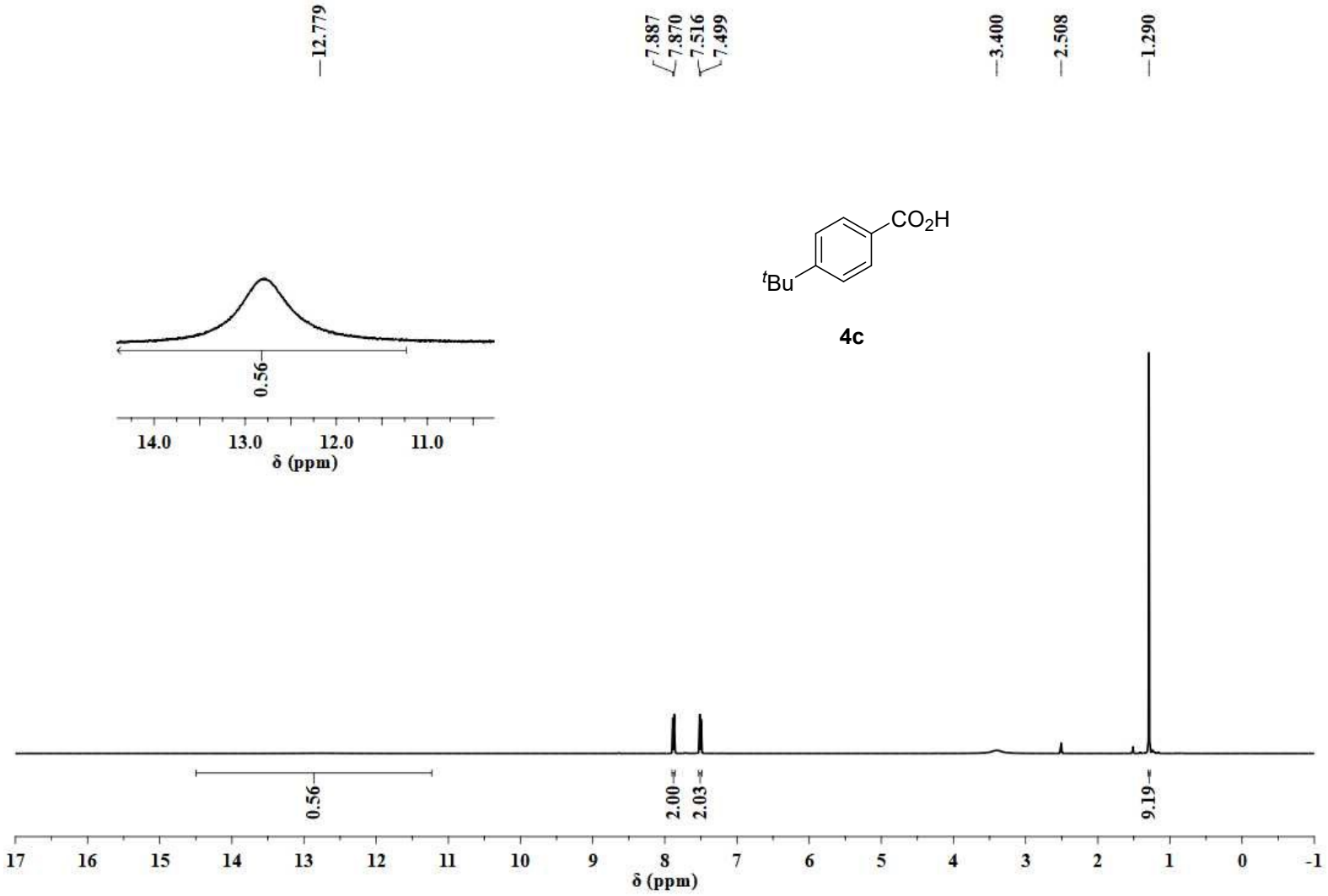

12.961
7.959
7.945
7.641
7.626
7.613
7.521
7.505
7.490
3.368
2.508
CO2H
4a
0.70
15.0
14.0
13.0
12.0
δ (ppm)
0.70
2.00
0.96
1.98
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

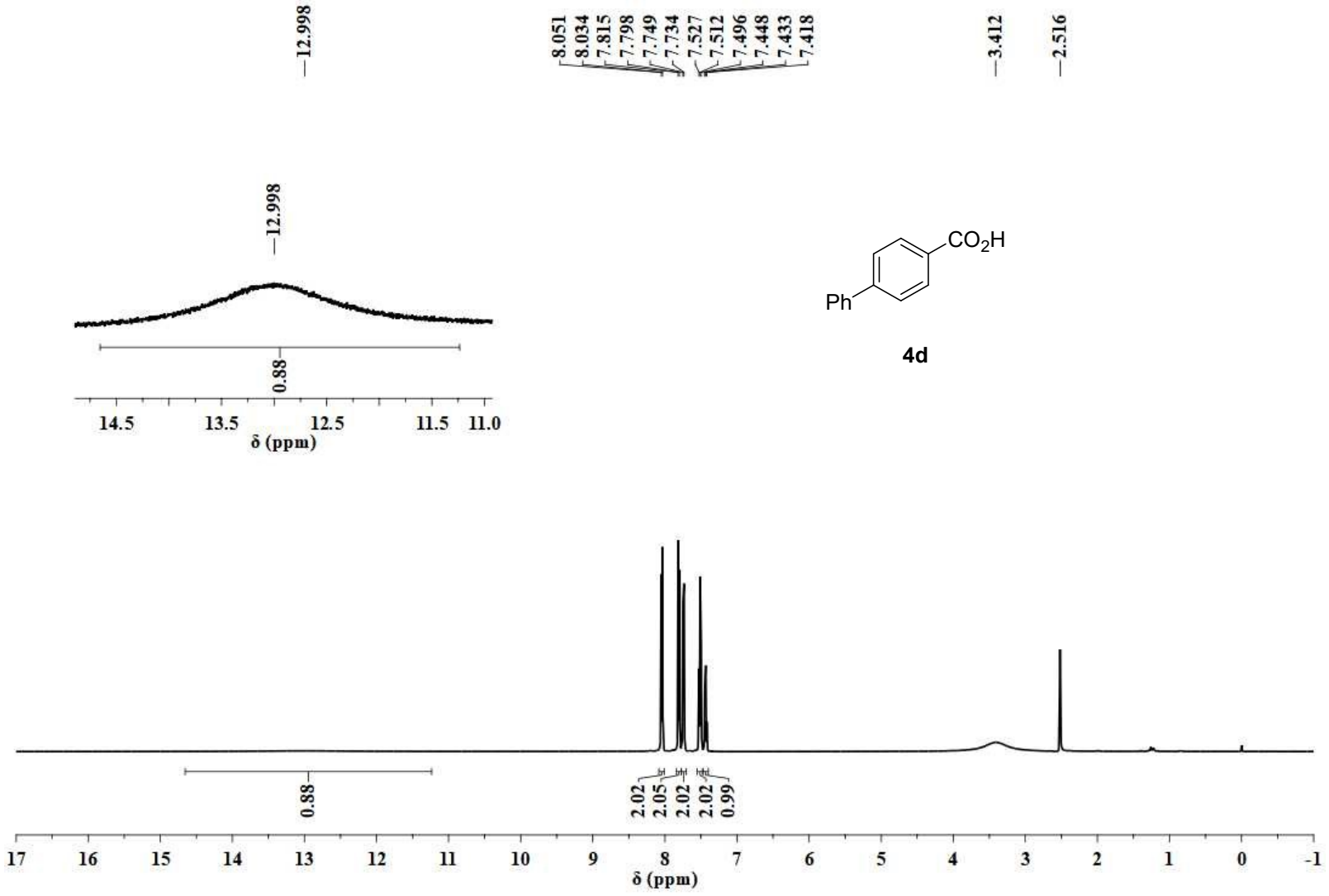

167.375
132.846
130.851
129.271
128.575
CO2H
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

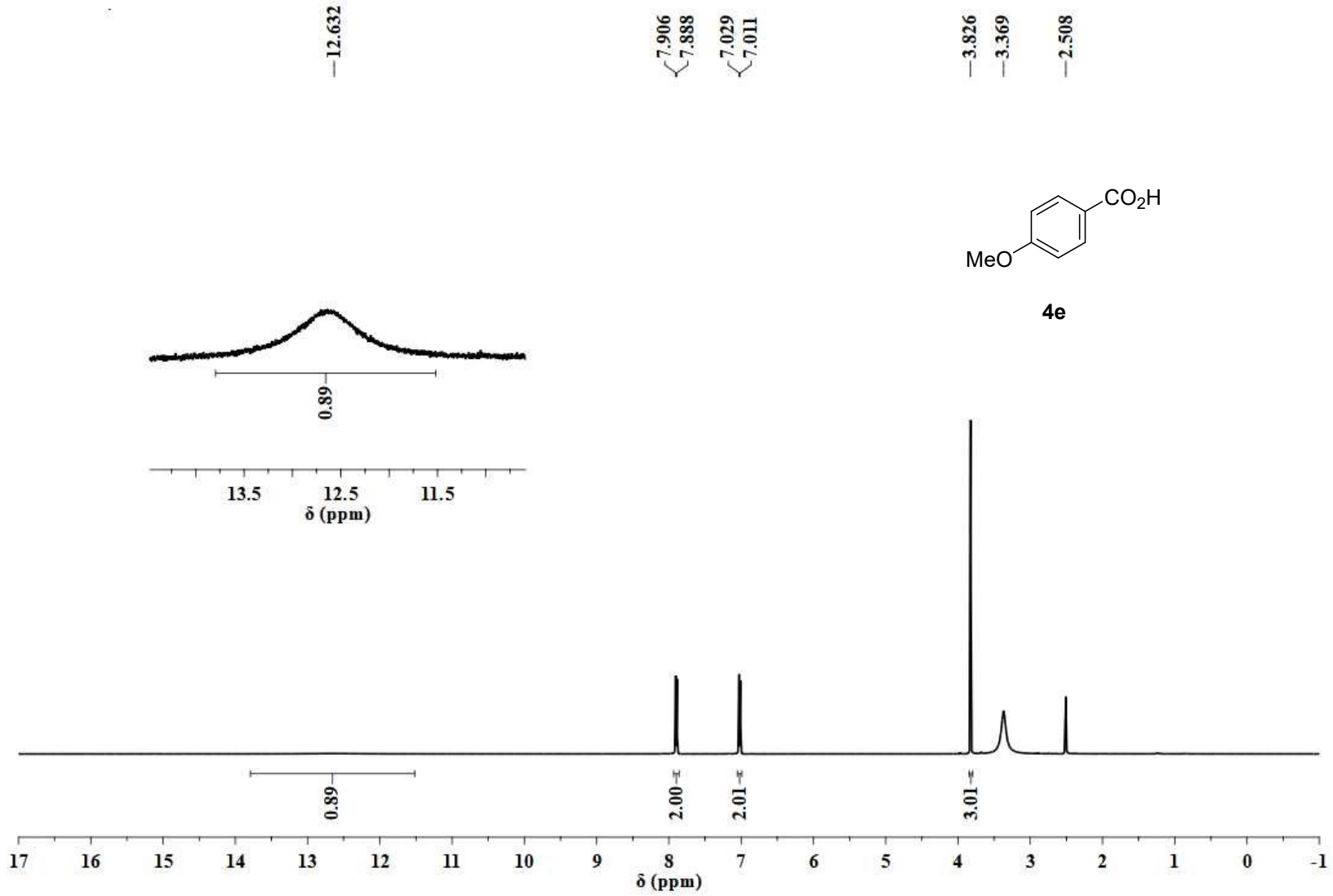

CO2H

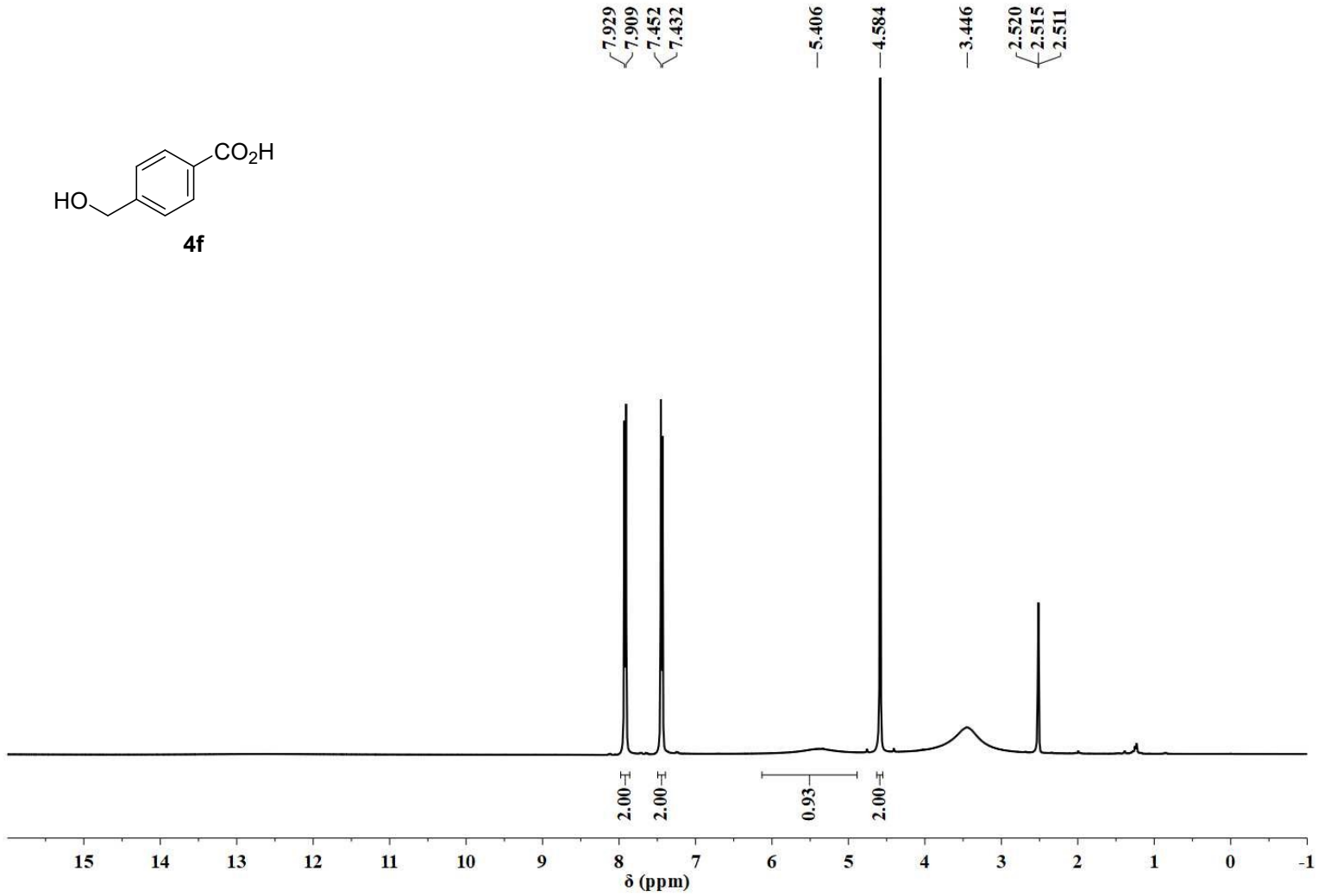
**4b**

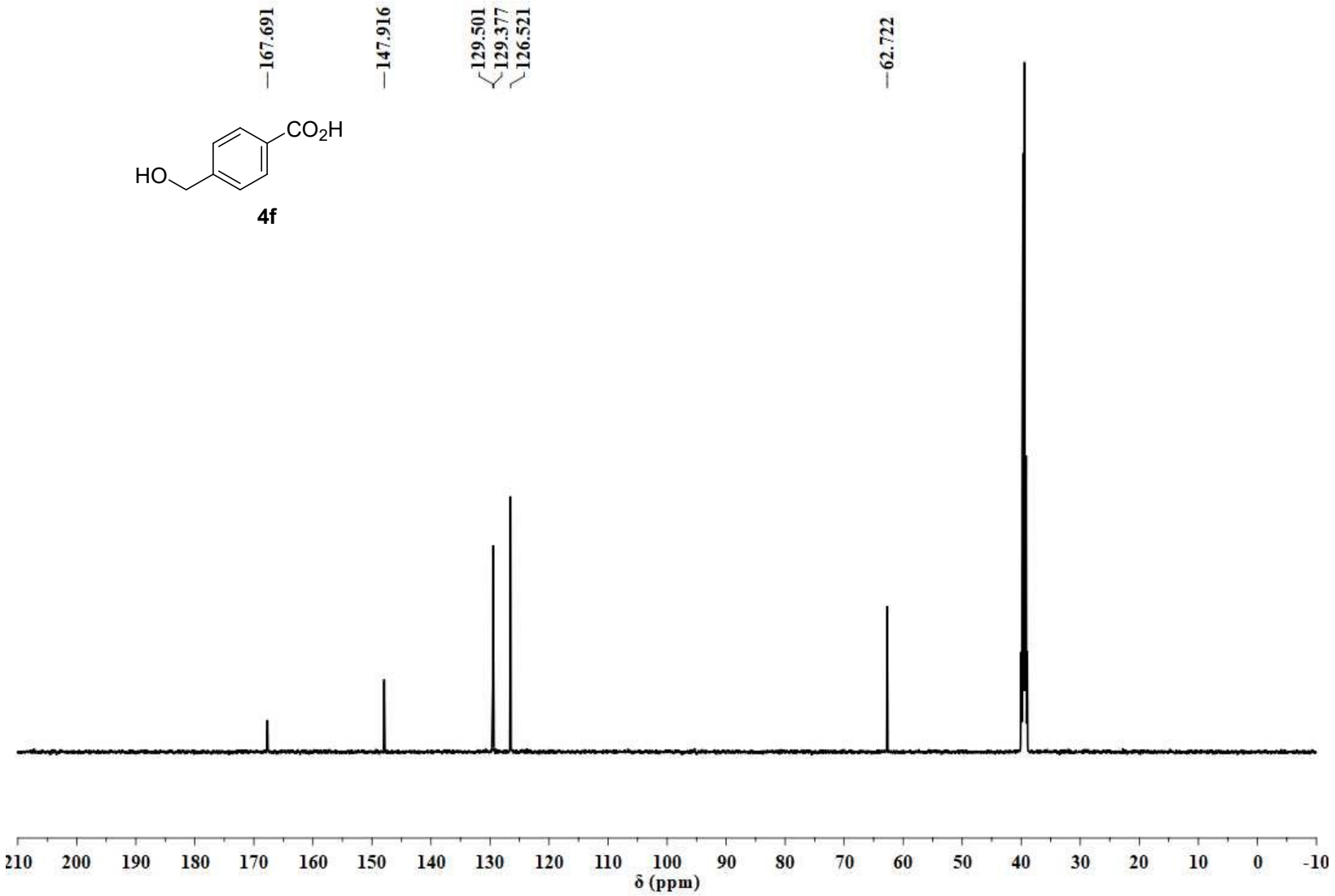

7.836
7.816
7.294
7.274
3.451
2.495
2.352
1.97
1.96
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

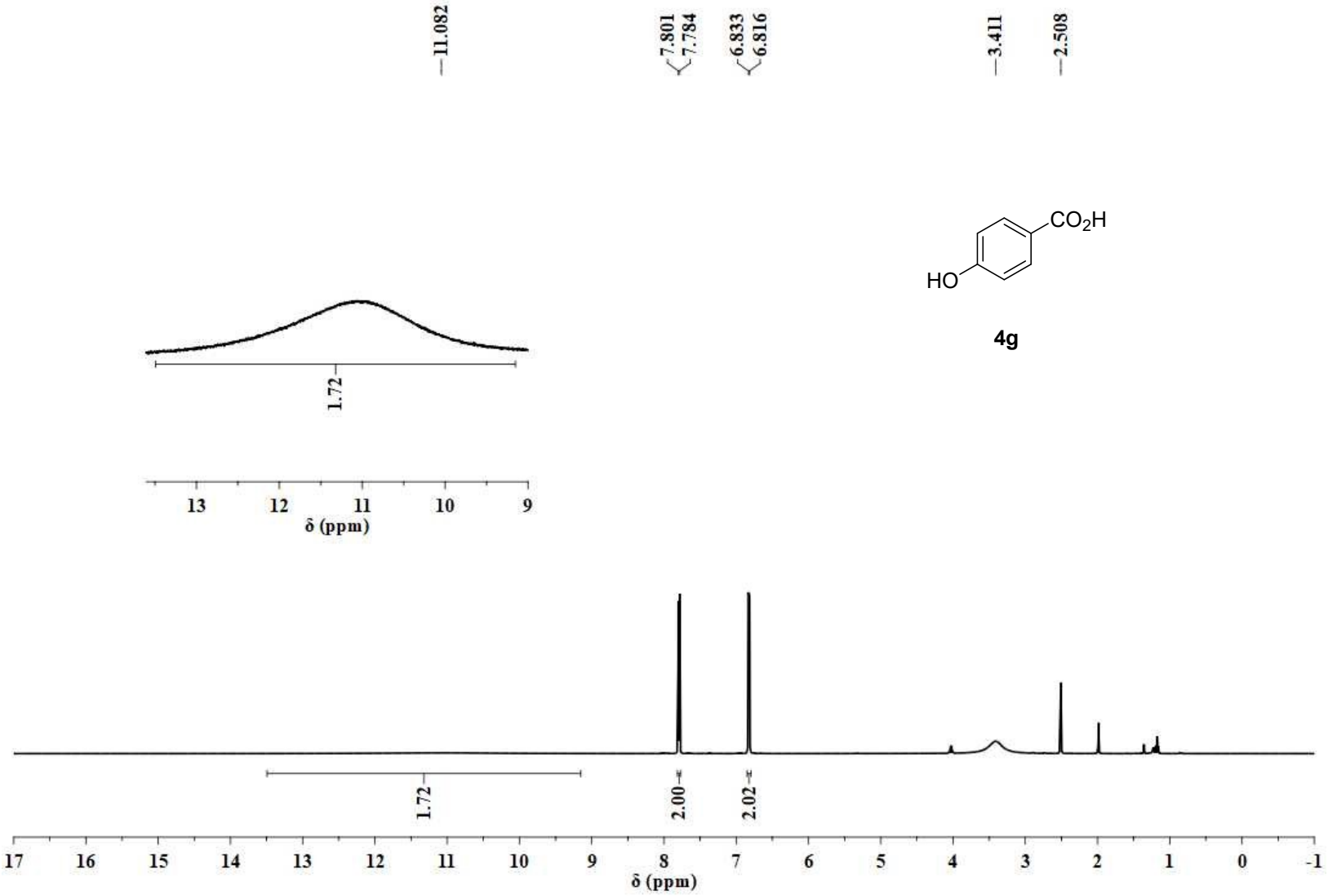

12.779
7.887
7.870
7.516
7.499
3.400
2.508
1.290
CO2H
tBu
4c
0.56
14.0
13.0
12.0
11.0
δ (ppm)
0.56
2.00
2.03
9.19
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

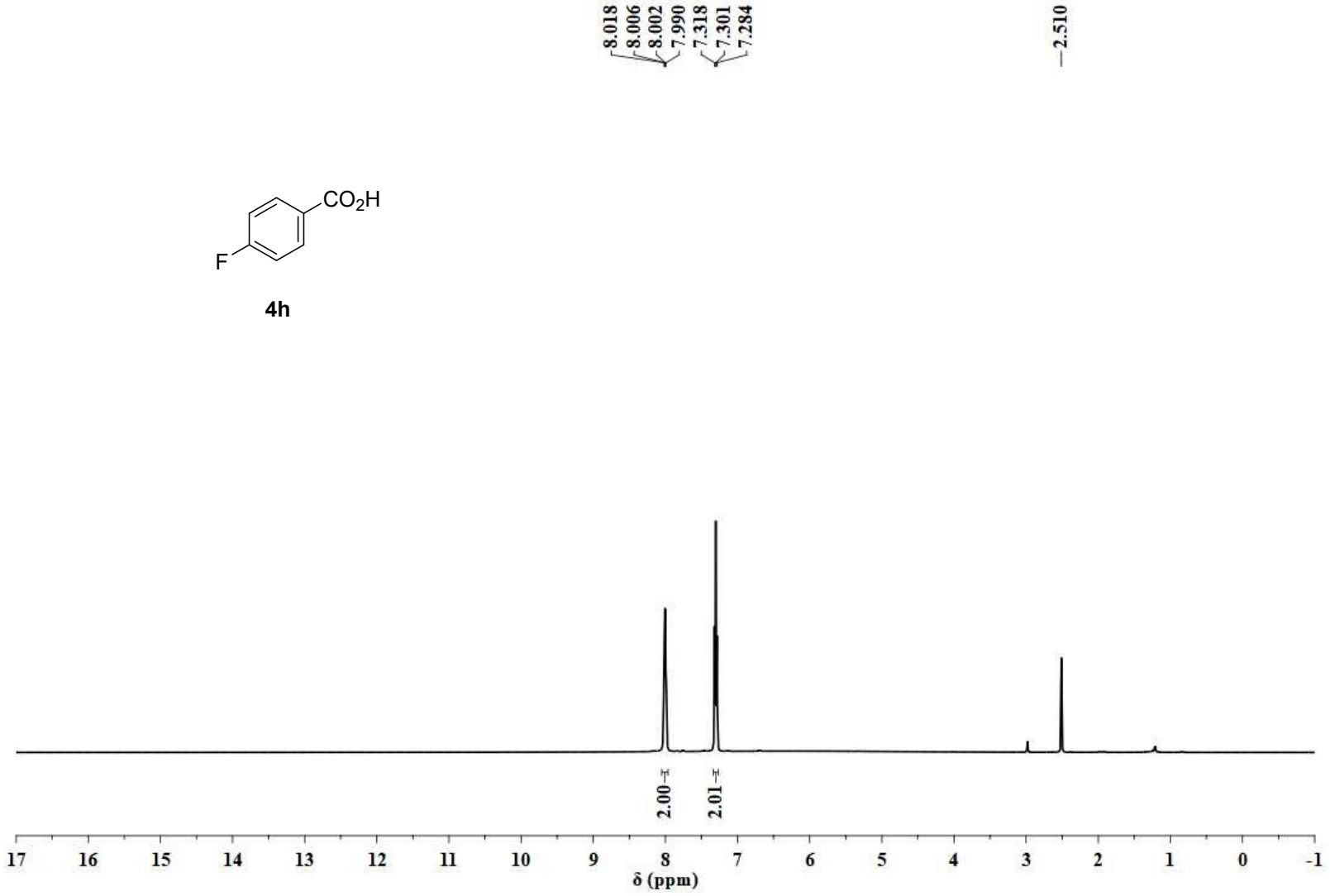

12.998
8.051
8.034
7.815
7.798
7.749
7.734
7.527
7.512
7.496
7.448
7.433
7.418
3.412
2.516
CO2H
Ph
4d
0.88
δ (ppm)
2.02
2.05
2.02
2.02
0.99

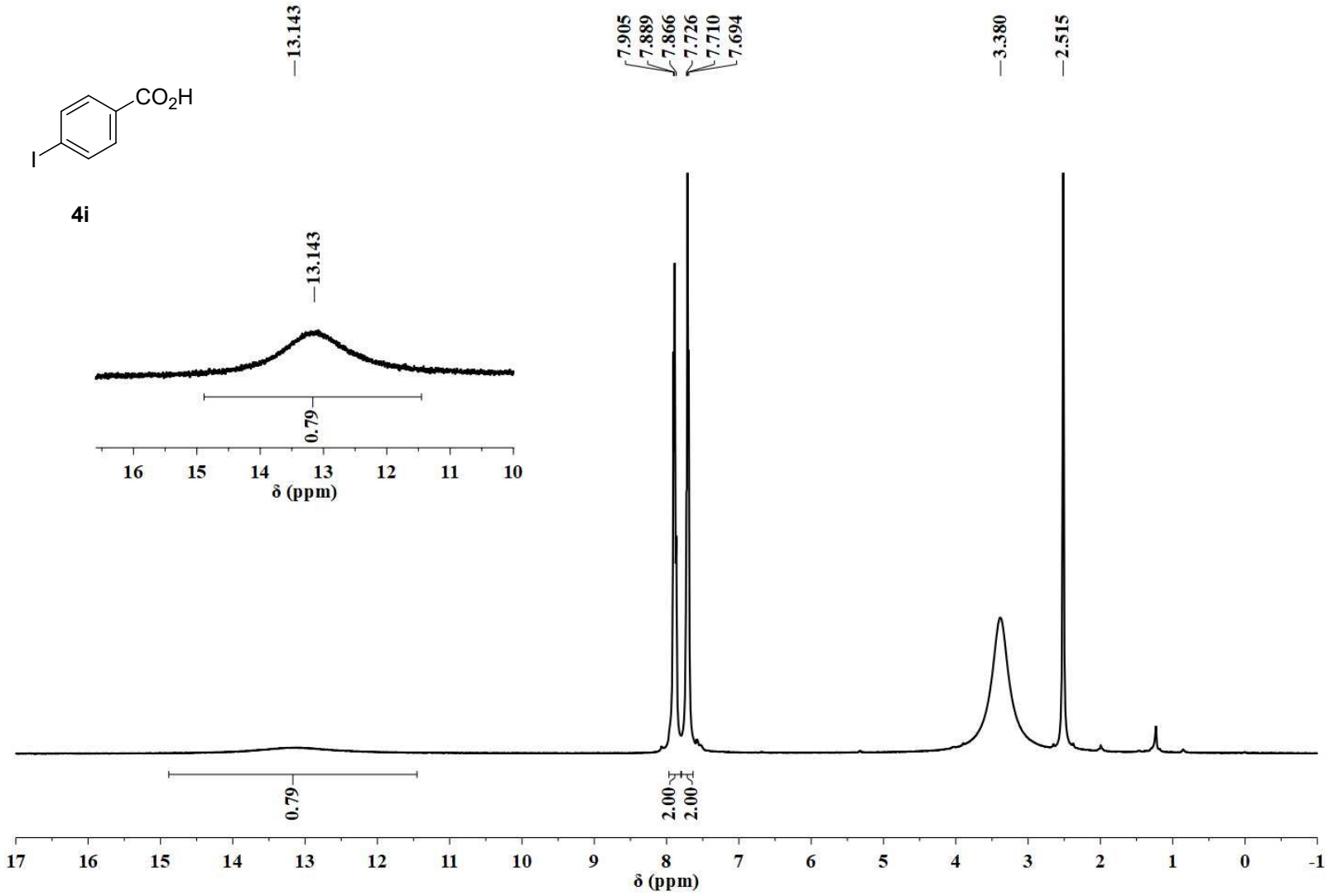

12.632
7.906
7.888
7.029
7.011
3.826
3.369
2.508
CO2H
MeO
4e
0.89
13.5
12.5
11.5
δ (ppm)
0.89
2.00
2.01
3.01
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

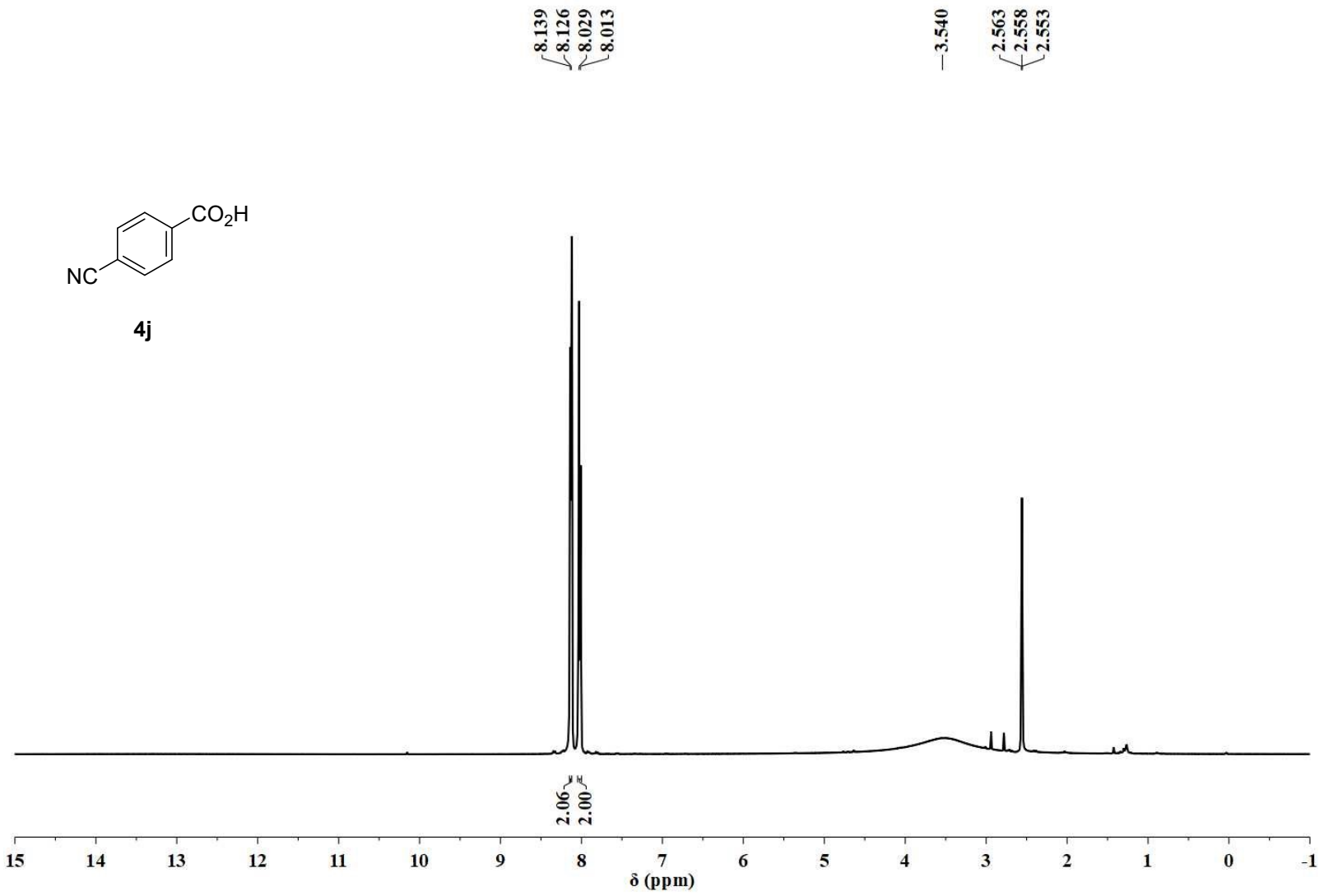

CO2H
HO
4f
7.929
7.909
7.452
7.432
5.406
4.584
3.446
2.520
2.515
2.511
2.00
2.00
0.93
2.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

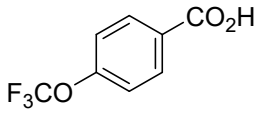

167.691
147.916
129.501
129.377
126.521
62.722
CO2H
HO
4f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


11.082
7.801
7.784
6.833
6.816
3.411
2.508
CO2H
HO
4g
1.72
13
12
11
10
9
δ (ppm)
1.72
2.00
2.02
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


8.018
8.006
8.002
7.990
7.318
7.301
7.284
2.510
CO2H
F
4h
2.00
2.01
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

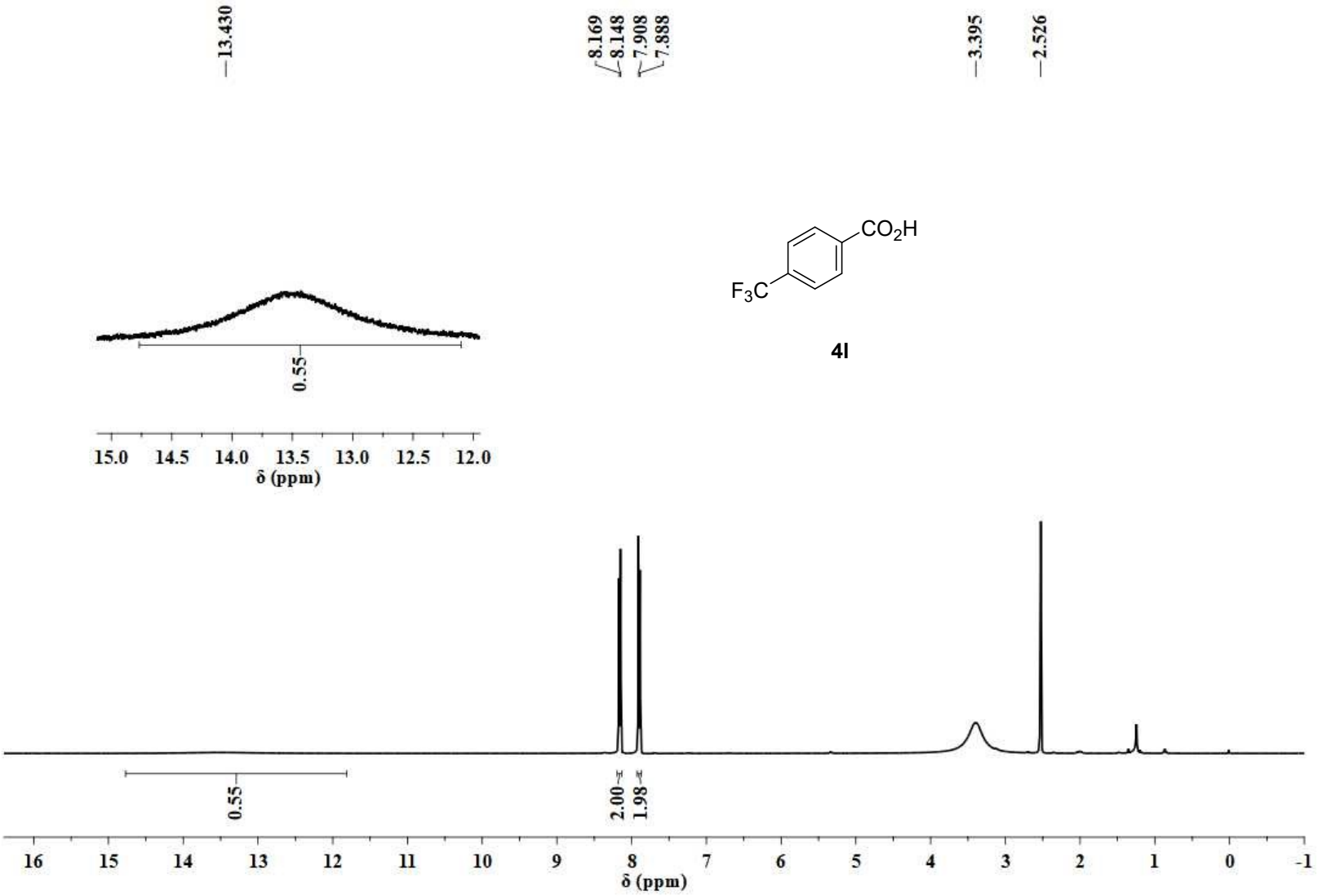

13.143
7.905
7.889
7.866
7.726
7.710
7.694
3.380
2.515
CO2H
I
4i
13.143
0.79
16 15 14 13 12 11 10
δ (ppm)
0.79
2.00
2.00
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
δ (ppm)

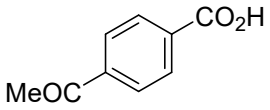

8.139
8.126
8.029
8.013
3.540
2.563
2.558
2.553
CO2H
NC
4j
2.06
2.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


CO2H
F3CO

**4k**

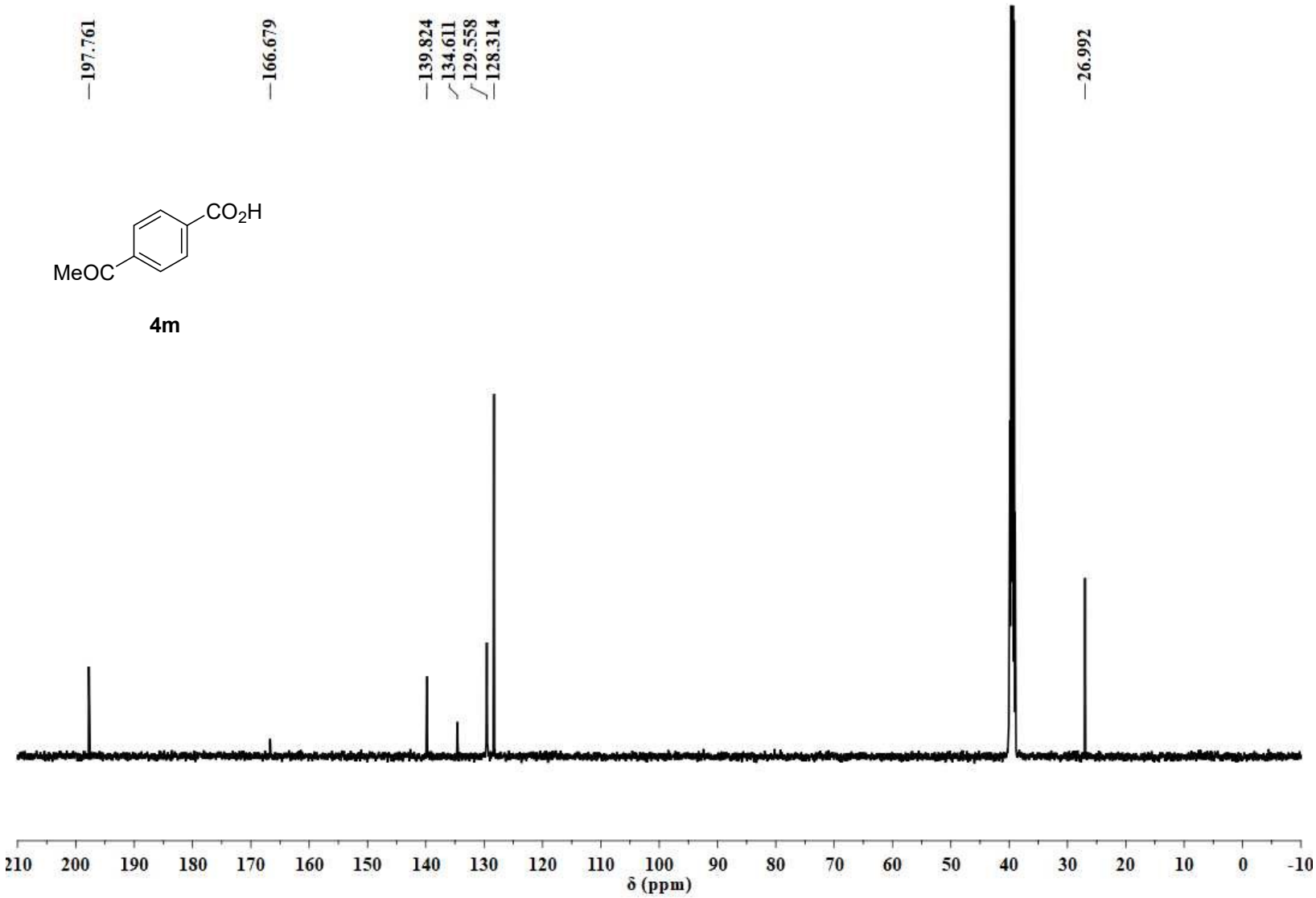

8.104
8.085
7.516
7.495
3.414
2.536
2.00
1.97
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

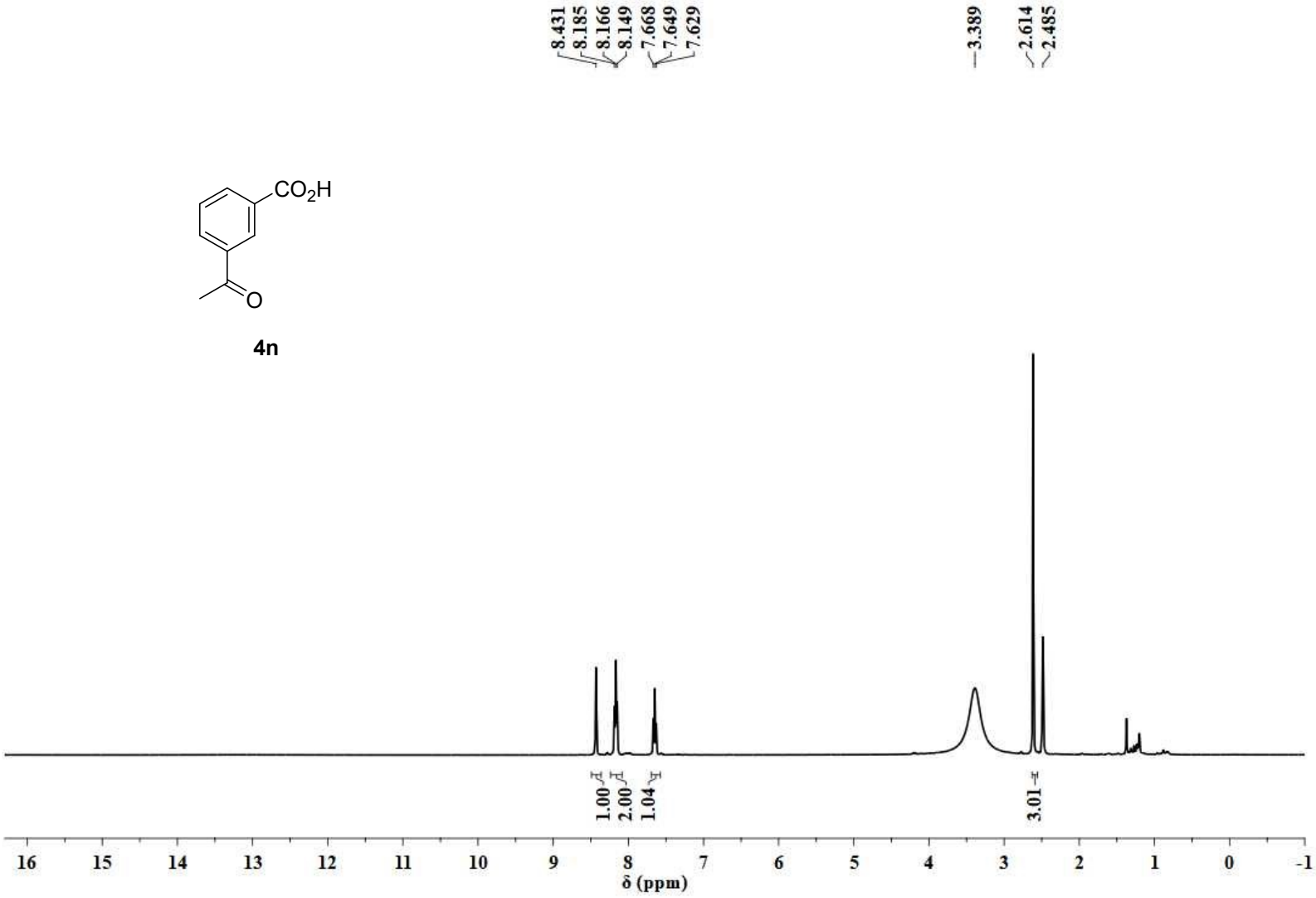

13.430
8.169
8.148
7.908
7.888
3.395
2.526
CO2H
F3C
4l
0.55
15.0 14.5 14.0 13.5 13.0 12.5 12.0
δ (ppm)
0.55
2.00
1.98
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
δ (ppm)

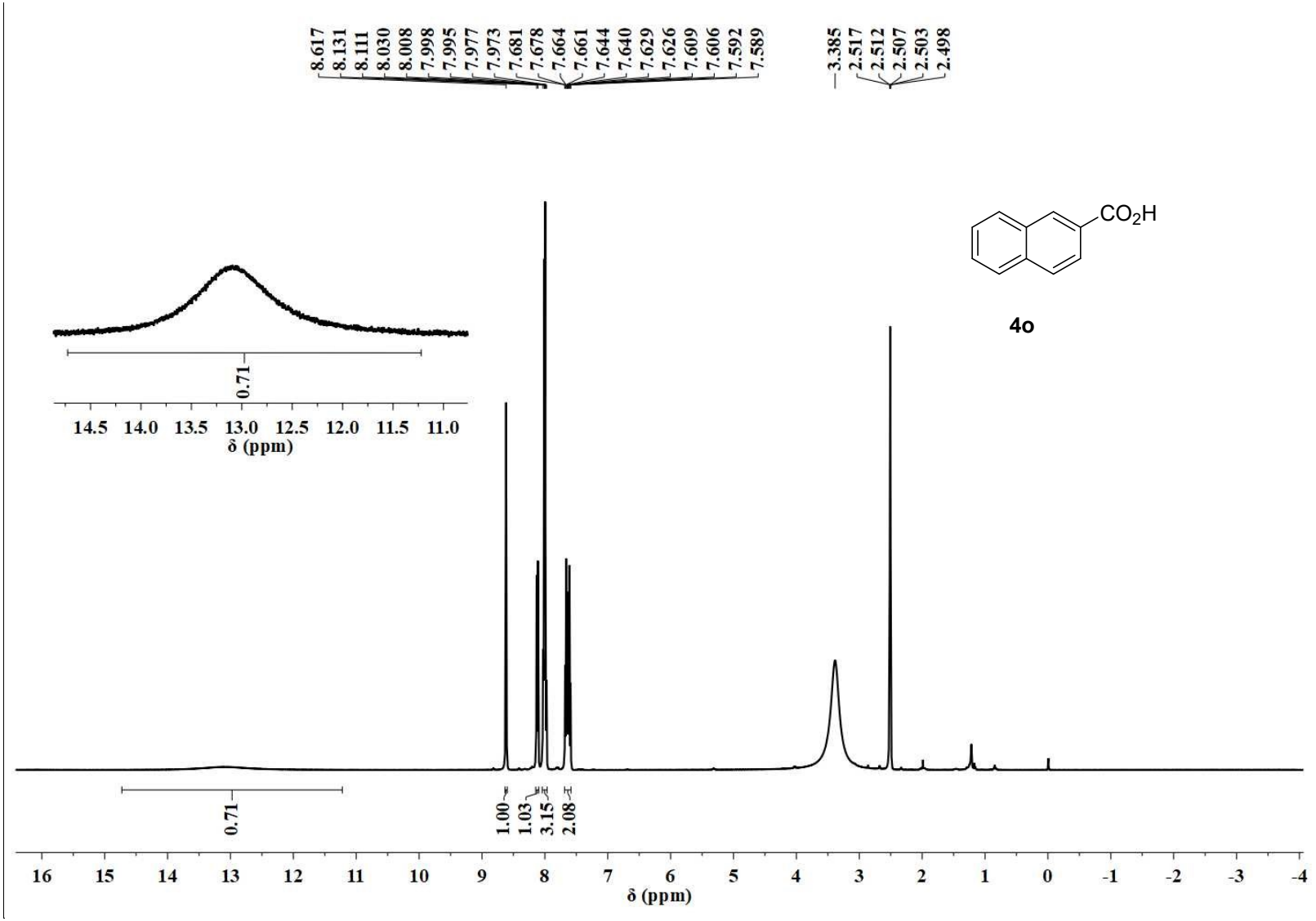

CO2H
MeOC

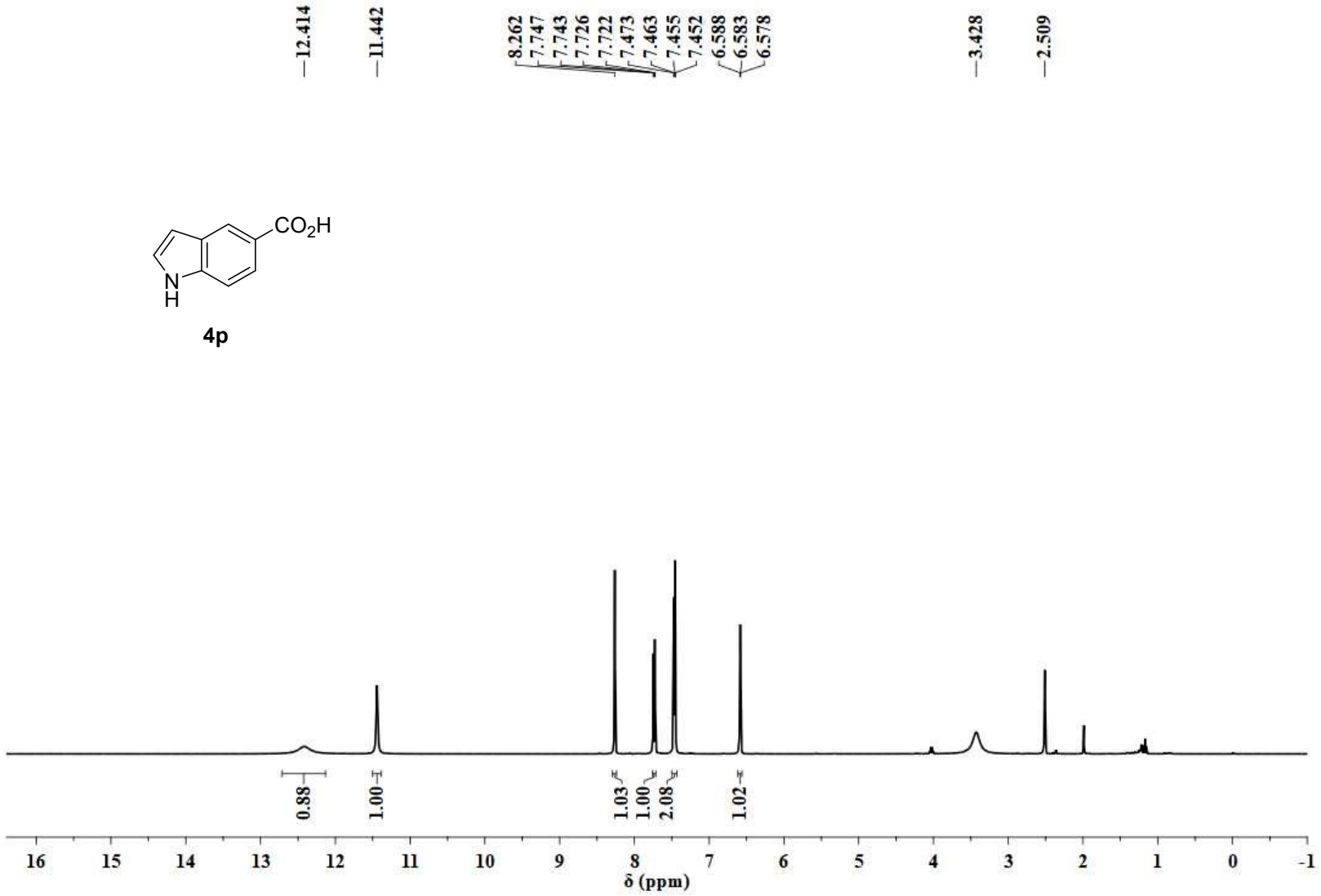
**4m**


8.062
3.424
2.636
2.514
4.02
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

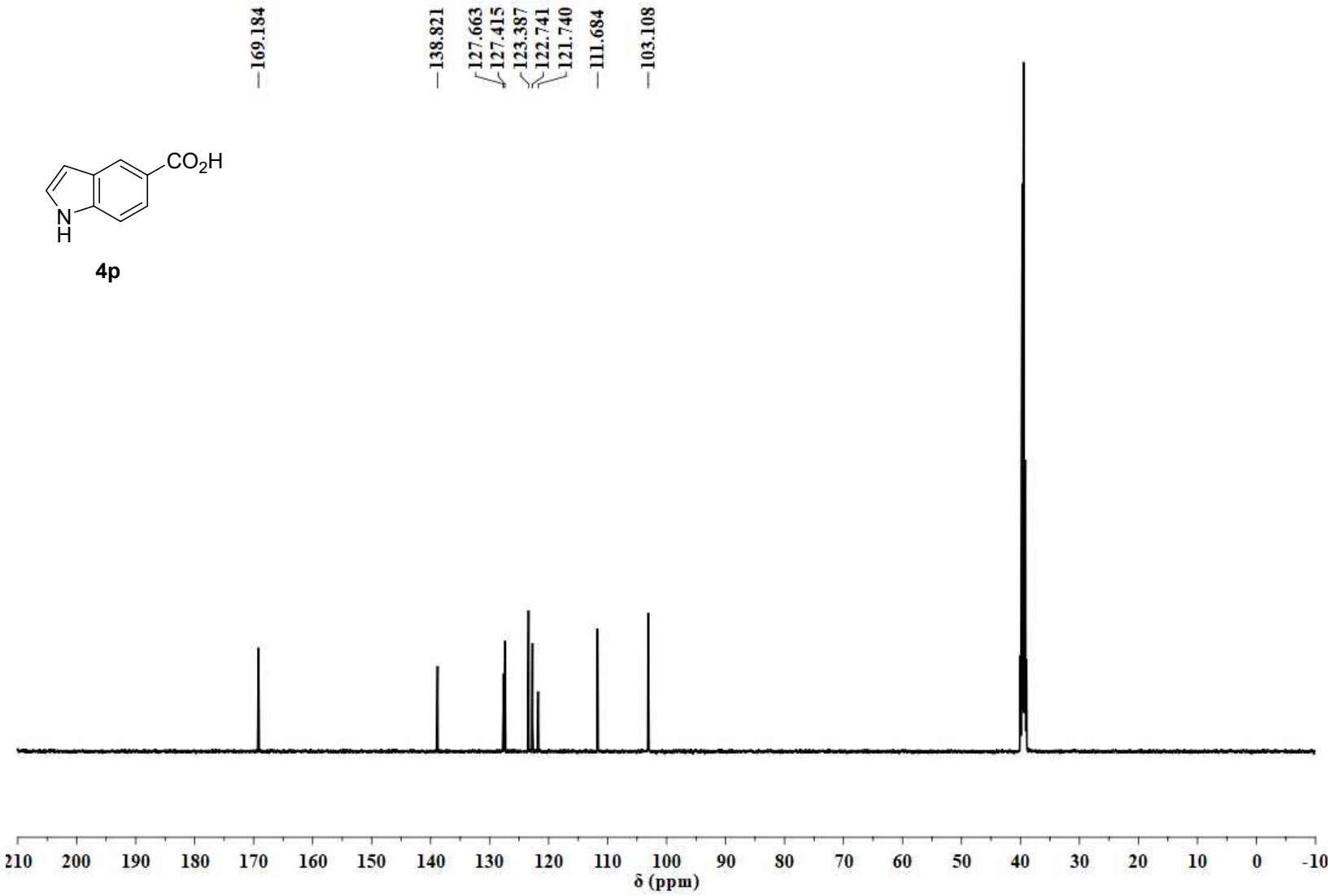

197.761
166.679
139.824
134.611
129.558
128.314
26.992
CO2H
MeOC
4m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)


8.431
8.185
8.166
8.149
7.668
7.649
7.629
3.389
2.614
2.485
CO2H
O
4n
1.00
2.00
1.04
3.01
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


8.617
8.131
8.111
8.030
8.008
7.998
7.995
7.977
7.973
7.681
7.678
7.664
7.661
7.644
7.640
7.629
7.626
7.609
7.606
7.592
7.589
3.385
2.517
2.512
2.507
2.503
2.498
CO2H
4o
0.71
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0
δ (ppm)
0.71
1.00
1.03
3.15
2.08
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
δ (ppm)


12.414
11.442
8.262
7.747
7.743
7.726
7.722
7.473
7.463
7.455
7.452
6.588
6.583
6.578
3.428
2.509
CO2H
N
H
0.88
1.00
1.03
1.00
2.08
1.02
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

**4p**


169.184
138.821
127.663
127.415
123.387
122.741
121.740
111.684
103.108
CO2H
N
H
4p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)