

Supporting Information

**Direct formylation of phenols using difluorocarbene as a  
safe CO surrogate**

Cong-Cong Feng<sup>a</sup> and Song-Lin Zhang\*<sup>a</sup>

*Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of  
Chemical and Material Engineering, Jiangnan University, Wuxi 214122, Jiangsu, China*

**E-mail:** slzhang@jiangnan.edu.cn

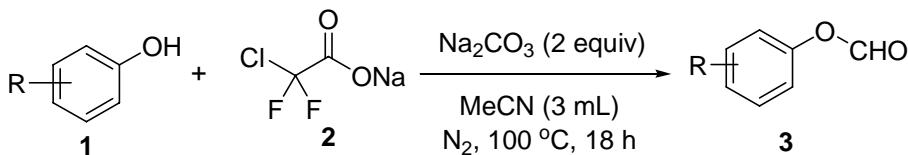
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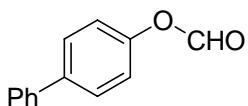
## **1. General experimental details**

All of the chemicals were purchased commercially, and used as received without further purification. All of the reactions were performed in a sealed Schlenk tube under N<sub>2</sub> atmosphere which was realized through evacuation/backfill techniques after three times. Column chromatography on silica gel was used to obtain purified products that are suitable for NMR spectroscopic characterization. NMR spectra were recorded on a 400 MHz spectrometer for <sup>1</sup>H NMR, 101 MHz for <sup>13</sup>C NMR, and 376 MHz for <sup>19</sup>F NMR. Chemical shifts are reported in ppm and referenced to residual solvent peaks. NMR signals are reported as follows to delineate possible splitting: s, singlet; d, doublet; t, triplet; q, quartet; and m, multiple. Coupling constants are reported in Hertz where present. All the <sup>13</sup>C and <sup>19</sup>F NMR spectra were obtained with proton decoupling. Elemental analyses were performed by the Analytic Laboratory of Jiangnan University. High resolution mass spectra (HRMS) were determined on Thermo Scientific LTQ Orbitrap XL with ESI ionization mode.

## 2. Synthesis and characterization of aryl formate products

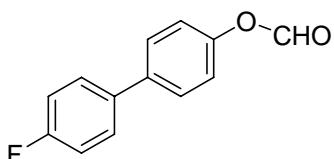


Into a Schlenk tube with a magnetic stirring bar were added  $\text{ClCF}_2\text{CO}_2\text{Na}$  (**2**) (91 mg, 0.6 mmol, 3 equiv) and sodium carbonate (40 mg, 0.4 mmol, 2 equiv). The tube is sealed with a rubber septum, evacuated, and refilled with nitrogen.  $\text{CH}_3\text{CN}$  (1 mL) is injected into the reaction tube, and the tube is placed in an oil bath at 100 °C for half an hour. Then, a solution of phenol **1** (0.2 mmol, 1 equiv.) in  $\text{CH}_3\text{CN}$  (2 mL) was slowly added to the reaction tube, and the mixture was further stirred for 18 h. The reaction mixture was then cooled to room temperature, diluted with dichloromethane (10 mL) and filtrated. The filtrate was washed twice with deionized water (20 mL), and with brine (20 mL). The organic phase is separated and concentrated in vacuum. The residual was purified by column chromatography on silica gel with a mixture of petroleum ether / ethyl acetate = 100:1 (v/v) as the eluent to obtain product **3**.



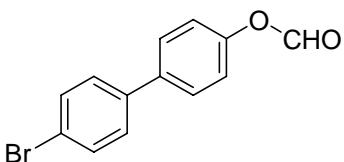
**[1,1'-Biphenyl]-4-yl formate (3a; 33.3 mg, 84%).** Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). White solid; melting point: 57 – 59 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.35 (s, 1H), 7.62 (d,  $J$  = 8.6 Hz, 2H), 7.57 (d,  $J$  = 7.2 Hz, 2H), 7.45 (t,  $J$  = 7.5 Hz, 2H), 7.37 (t,  $J$  = 7.3 Hz, 1H), 7.22 (d,  $J$  = 8.6 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 149.2, 140.1, 139.6, 128.8, 128.4, 127.5, 127.1, 121.4.

These data are in good agreement with literature report.<sup>1</sup>

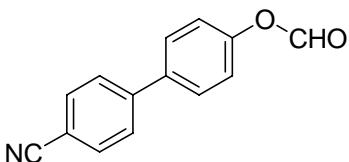


**4'-Fluoro-[1,1'-biphenyl]-4-yl formate (3b; 31.5 mg, 73%).** Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). White solid; melting point: 94 – 97 °C.  $^1\text{H}$  NMR

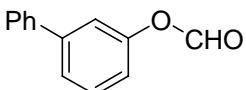
(400 MHz, CDCl<sub>3</sub>) δ 8.34 (s, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.52 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.13 (t, *J* = 8.7 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.6 (d, *J* = 246.9 Hz), 159.2, 149.2, 138.6, 136.2 (d, *J* = 3.2 Hz), 128.7 (d, *J* = 8.1 Hz), 128.2, 121.5, 115.7 (d, *J* = 21.5 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -67.1. HRMS (ESI) m/z calcd for C<sub>13</sub>H<sub>10</sub>FO<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 217.0665, found 217.0660.



**4'-Bromo-[1,1'-biphenyl]-4-yl formate (3c; 29.7 mg, 54%).** Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). Colorless solid; melting point: 82 – 84 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.34 (s, 1H), 7.60 – 7.54 (m, 4H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.1, 149.4, 139.0, 138.3, 131.9, 128.7, 128.2, 121.8, 121.6. HRMS (ESI) m/z calcd for C<sub>13</sub>H<sub>10</sub>BrO<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 276.9864, found 276.9862.

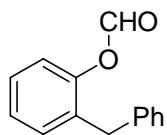


**4'-Cyano-[1,1'-biphenyl]-4-yl formate (3d; 25.1 mg, 57%).** Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). White solid, melting point: 103 – 106 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.34 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.9, 150.2, 144.5, 137.4, 132.7, 128.5, 127.7, 121.9, 116.0, 111.2. HRMS (ESI) m/z calcd for C<sub>14</sub>H<sub>9</sub>NO<sub>2</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 246.0531, found 246.0525.

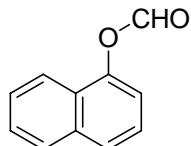


**[1,1'-Biphenyl]-3-yl formate (3e; 34.5 mg, 87%).** Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.36 (s, 1H), 7.59 (d,

*J* = 7.1 Hz, 2H), 7.54 – 7.43 (m, 4H), 7.42 – 7.35 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 150.3, 143.2, 139.8, 129.9, 128.9, 127.8, 127.1, 125.1, 119.83, 119.81. HRMS (ESI) m/z calcd for  $\text{C}_{13}\text{H}_{10}\text{O}_2\text{Na}^+$  ( $\text{M}+\text{Na}$ )<sup>+</sup> 221.0578, found 221.0571.

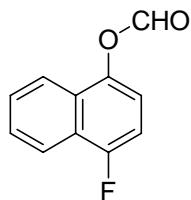


**2-Benzylphenyl formate (3f; 39.2 mg, 93%).** Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (s, 1H), 7.35 – 7.29 (m, 3H), 7.28 – 7.24 (m, 3H), 7.20 (d, *J* = 7.3 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 1H), 3.99 (s, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 148.2, 139.4, 132.8, 131.2, 128.8, 128.5, 127.6, 126.6, 126.3, 121.9, 36.1. HRMS (ESI) m/z calcd for  $\text{C}_{14}\text{H}_{12}\text{O}_2\text{Na}^+$  ( $\text{M}+\text{Na}$ )<sup>+</sup> 235.0735, found 235.0730.



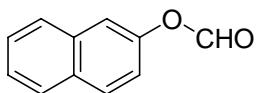
**Naphthalen-1-yl formate (3g; 28.4 mg, 83%).** Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.52 (s, 1H), 8.00 – 7.94 (m, 1H), 7.93 – 7.87 (m, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.48 (t, *J* = 7.9 Hz, 1H) 7.29 (d, *J* = 7.5, 0.6 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 145.9, 134.7, 128.0, 126.8, 126.7, 126.6, 126.4, 125.3, 121.1, 117.4.

These data are in good agreement with literature report.<sup>2</sup>



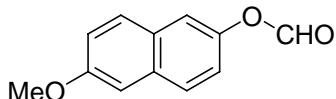
**4-Fluoronaphthalen-1-yl formate (3h; 22.4 mg, 60%).** Eluted with petroleum

ether/ethyl acetate = 100:1 (v/v). Brown oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.49 (s, 1H), 8.17 – 8.10 (m, 1H), 7.95 – 7.88 (m, 1H), 7.66 – 7.58 (m, 2H), 7.22 (dd,  $J$  = 8.3, 4.4 Hz, 1H), 7.14 (dd,  $J$  = 9.7, 8.3 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 156.7 (d,  $J$  = 251.3 Hz), 141.6 (d,  $J$  = 3.9 Hz), 127.8, 127.4 (d,  $J$  = 5.2 Hz), 127.1 (d,  $J$  = 1.9 Hz), 124.5 (d,  $J$  = 18.1 Hz), 121.2 (d,  $J$  = 2.4 Hz), 121.0 (d,  $J$  = 4.8 Hz), 117.2 (d,  $J$  = 8.8 Hz), 108.7 (d,  $J$  = 22.5 Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -124.05. HRMS (ESI) m/z calcd for  $\text{C}_{11}\text{H}_8\text{FO}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  191.0508; found 191.0502.

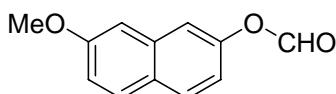


**Naphthalen-2-yl formate (3i;** 21.6 mg, 63%). Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (s, 1H), 7.92 – 7.79 (m, 3H), 7.61 (d,  $J$  = 2.2 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.30 – 7.26 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 147.5, 133.7, 131.6, 129.8, 127.8, 127.7, 126.9, 126.0, 120.4, 118.2.

These data are in good agreement with literature report.<sup>3</sup>



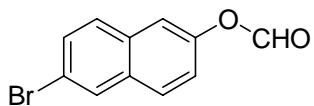
**6-Methoxynaphthalen-2-yl formate (3j;** 30 mg, 75%). Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). White solid, melting point: 93 – 95 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (s, 1H), 7.76 (d,  $J$  = 8.9 Hz, 1H), 7.71 (d,  $J$  = 8.9 Hz, 1H), 7.53 (d,  $J$  = 1.8 Hz, 1H), 7.25 – 7.12 (m, 3H), 3.92 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.6, 157.8, 145.9, 132.8, 129.0, 128.9, 128.4, 120.7, 119.8, 118.1, 105.8, 55.3. HRMS (ESI) m/z calcd for  $\text{C}_{12}\text{H}_{10}\text{O}_3\text{Na}^+$  ( $\text{M}+\text{Na}$ ) $^+$  225.0528, found 225.0524.



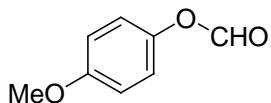
**7-Methoxynaphthalen-2-yl formate (3k;** 29.3 mg, 73%). Eluted with petroleum

ether/ethyl acetate = 100:1 (v/v). Yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (s, 1H), 7.79 (d,  $J$  = 8.8 Hz, 1H), 7.74 (d,  $J$  = 8.9 Hz, 1H), 7.49 (d,  $J$  = 1.9 Hz, 1H), 7.18 – 7.08 (m, 3H), 3.92 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 158.4, 148.2, 135.1, 129.5, 129.3, 127.1, 118.9, 117.9, 117.1, 105.6, 55.3.

These data are in good agreement with literature report.<sup>4</sup>

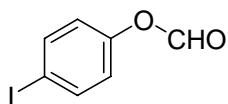


**6-Bromonaphthalen-2-yl formate (3l; 32 mg, 64%).** Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). White solid, melting point: 76 – 79 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (s, 1H), 8.02 (d,  $J$  = 1.5 Hz, 1H), 7.79 (d,  $J$  = 8.9 Hz, 1H), 7.68 (d,  $J$  = 8.8 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.29 (dd,  $J$  = 8.9, 2.3 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.0, 147.7, 132.6, 132.1, 130.3, 129.9, 129.2, 128.9, 121.6, 120.0, 118.3. HRMS (ESI) m/z calcd for  $\text{C}_{11}\text{H}_7\text{BrO}_2\text{Na}^+$  ( $\text{M}+\text{Na}$ )<sup>+</sup> 272.9527, found 272.9522.



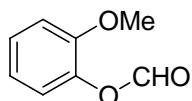
**4-Methoxyphenyl formate (3m; 9.6 mg, 32%).** Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). Colorless solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (s, 1H), 7.06 (d,  $J$  = 9.0 Hz, 2H), 6.91 (d,  $J$  = 9.1 Hz, 2H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 157.7, 143.4, 121.9, 114.7, 55.6.

These data are in good agreement with literature report.<sup>5</sup>

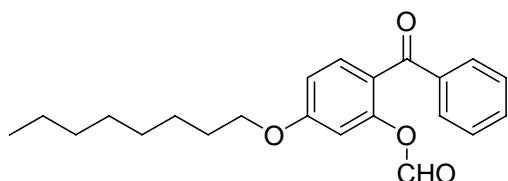


**4-Iodophenyl formate (3n; 24.5 mg, 50%).** Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (s, 1H), 7.72 (d,  $J$  = 8.8 Hz, 2H), 6.92 (d,  $J$  = 8.8 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 149.6, 138.7,

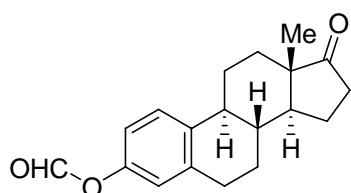
123.3, 90.4. Anal. Calcd for C<sub>7</sub>H<sub>5</sub>IO<sub>2</sub>: C, 33.90; H, 2.03. Found: C, 33.68; H, 1.90.



**2-Methoxyphenyl formate (3o; 8 mg, 26%).** Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (s, 1H), 7.23 (dd, J = 7.5, 1.6 Hz, 1H), 7.10 (dd, J = 7.9, 1.6 Hz, 1H), 7.02 – 6.94 (m, 2H), 3.85 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.2, 150.9, 138.9, 127.4, 122.6, 120.9, 112.6, 55.9. These data are in good agreement with literature report.<sup>6</sup>



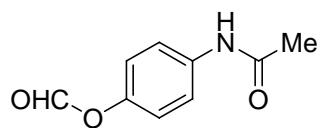
**2-Benzoyl-5-(octyloxy)phenyl formate (4; 34 mg, 48%).** Eluted with petroleum ether/ethyl acetate = 100:1 (v/v). Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 (s, 1H), 7.75 (dd, J = 8.3, 1.3 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.49 (d, J = 8.7 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 6.84 (dd, J = 8.6, 2.4 Hz, 1H), 6.75 (d, J = 2.4 Hz, 1H), 4.02 (t, J = 6.5 Hz, 2H), 1.86 – 1.77 (m, 2H), 1.52 – 1.43 (m, 2H), 1.41 – 1.23 (m, 8H), 0.89 (d, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 193.7, 162.6, 158.7, 149.8, 138.0, 132.7, 129.8, 128.3, 123.4, 111.9, 109.3, 68.7, 31.8, 29.3, 29.2, 29.0, 25.9, 22.6, 14.1. HRMS (ESI) m/z calcd for C<sub>22</sub>H<sub>27</sub>O<sub>4</sub><sup>+</sup> (M+H)<sup>+</sup> 355.1909, found 355.1905.



**(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl formate (5; 51.7 mg, 87%).** Eluted with petroleum ether/ethyl acetate = 5:1 (v/v). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (s, 1H),

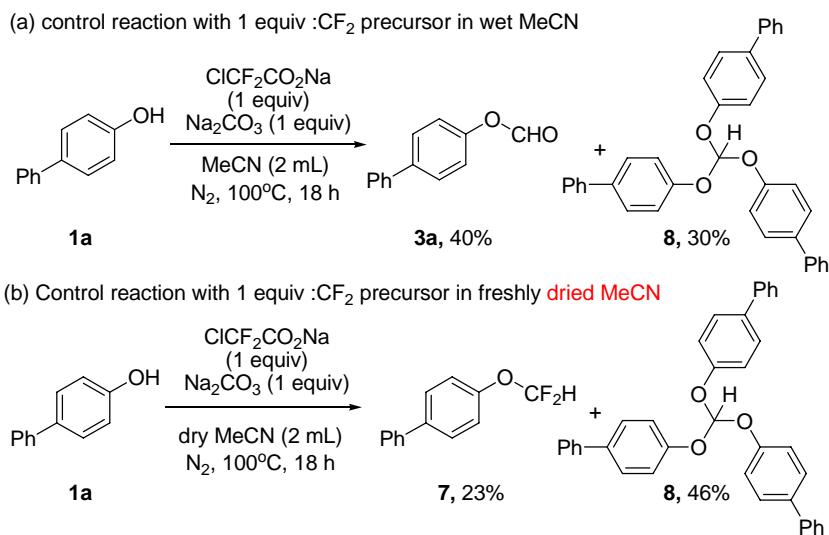
7.30 (d,  $J = 8.5$  Hz, 1H), 6.90 (dd,  $J = 8.5, 2.3$  Hz, 1H), 6.86 (s, 1H), 2.92 (dd,  $J = 8.6, 4.0$  Hz, 2H), 2.51 (dd,  $J = 18.8, 8.6$  Hz, 1H), 2.45 – 2.35 (m, 1H), 2.34 – 2.24 (m, 1H), 2.20 – 1.93 (m, 4H), 1.70 – 1.40 (m, 6H), 0.91 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  220.5, 159.5, 147.8, 138.4, 138.0, 126.6, 121.1, 118.2, 77.0, 50.4, 47.8, 44.1, 37.9, 35.8, 31.5, 29.3, 26.2, 25.7, 21.5, 13.8.

These data are in good agreement with literature report.<sup>7</sup>



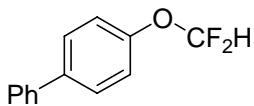
**4-Acetamidophenyl formate (6; 18.6 mg, 52%).** Eluted with petroleum ether/ethyl acetate = 1:1 (v/v). Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (s, 1H), 7.53 (d,  $J = 8.8$  Hz, 2H), 7.31 (br s, 1H), 7.09 (d,  $J = 8.8$  Hz, 2H), 2.17 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 159.3, 146.0, 136.1, 121.6, 121.0, 24.5. HRMS (ESI) m/z calcd for  $\text{C}_9\text{H}_{10}\text{NO}_3^+$  ( $\text{M}+\text{H})^+$  180.0661, found 180.0656.

### 3. Control experiments



**Scheme S1.** Control experiments with the observation of difluoromethylated intermediate **7** and orthoformate **8**.

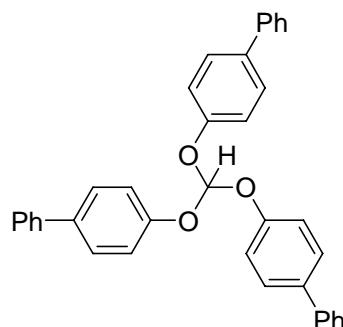
When performing the model reaction under a slightly different condition compared to the optimal conditions, that is, with only 1 equivalent of ClCF<sub>2</sub>CO<sub>2</sub>Na and base in wet MeCN. This reaction produced **3a** in a 40% yield, together with an orthoformate product **8** in a 30% yield (Scheme S1a). Interestingly, performing this same reaction in a freshly dried MeCN solvent did not produce formate **3a** at all, but instead produced a O-difluoromethylated product **7** and the orthoformate **8** in 23% and 46% yield, respectively. These results strongly imply that difluoromethylated **7** is the intermediate initially generated, which can undergo subsequent C-F functionalization by either moisture or phenol to eventually give the desired formate product **3**.



**4-(difluoromethoxy)-1,1'-biphenyl (7; 10 mg, 23%).** Eluted with petroleum ether. White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.53 (m, 4H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 8.7 Hz, 2H), 6.55 (t, *J* = 73.9 Hz, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -80.66. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.6 (t, *J* = 2.8

Hz), 140.1, 138.6, 128.9, 128.5, 127.4, 127.0, 119.8, 116.0 (t,  $J$  = 259.7 Hz).

These data are in good agreement with literature report.<sup>8</sup>



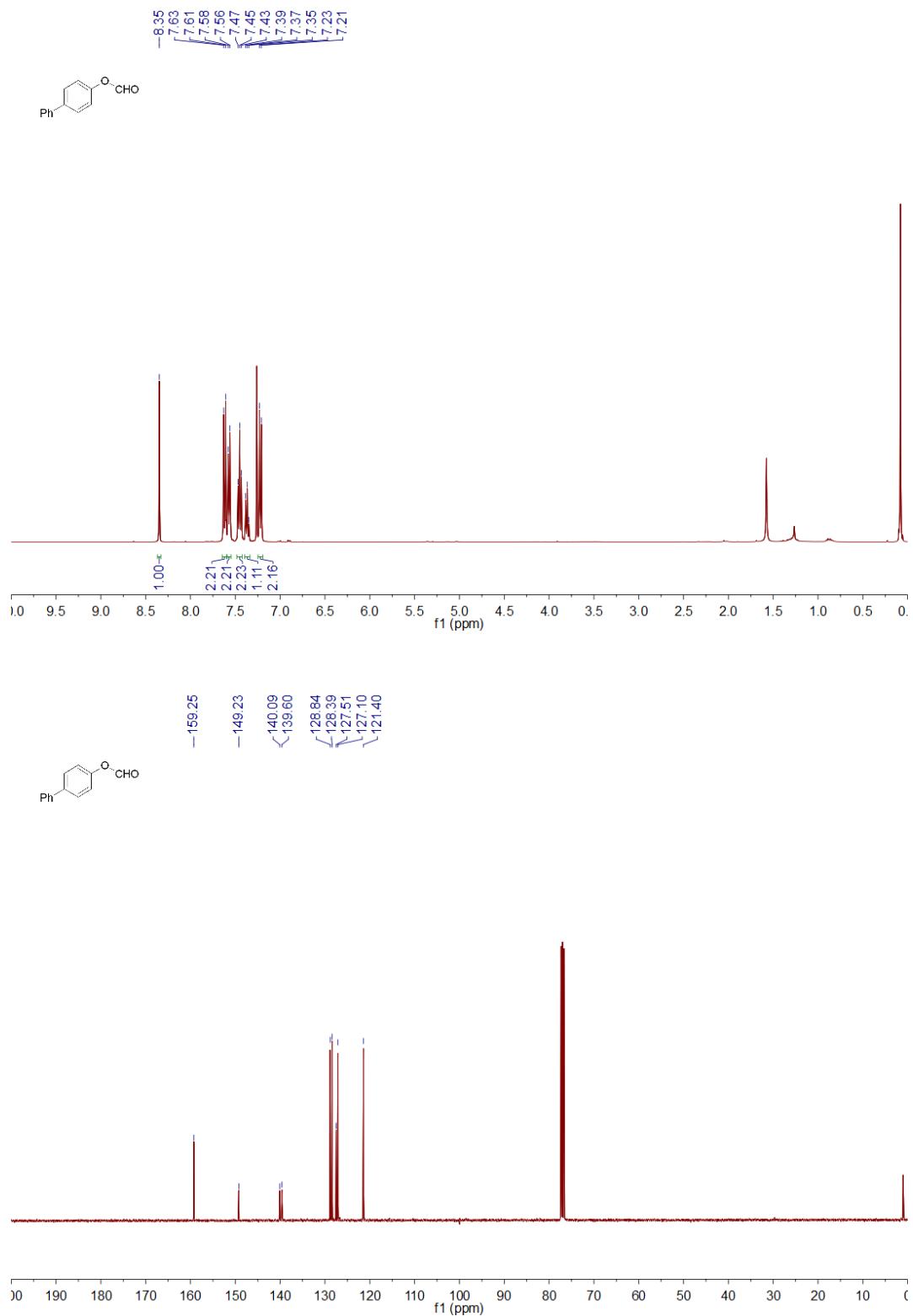
**Tris([1,1'-biphenyl]-4-yloxy)methane (8;** 16 mg, 46%); Eluted with petroleum ether/ethyl acetate = 100:1 (v/v); White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (dd,  $J$  = 7.9, 5.9 Hz, 12H), 7.44 (t,  $J$  = 7.6 Hz, 6H), 7.34 (t,  $J$  = 7.3 Hz, 3H), 7.25 (d,  $J$  = 8.6 Hz, 6H), 6.74 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.2, 140.4, 136.8, 128.8, 128.4, 127.1, 126.9, 118.4, 110.9. HRMS (ESI) m/z calcd for C<sub>37</sub>H<sub>29</sub>O<sub>3</sub><sup>+</sup> (M+H)<sup>+</sup> 521.2117, found 521.2114.

**References:**

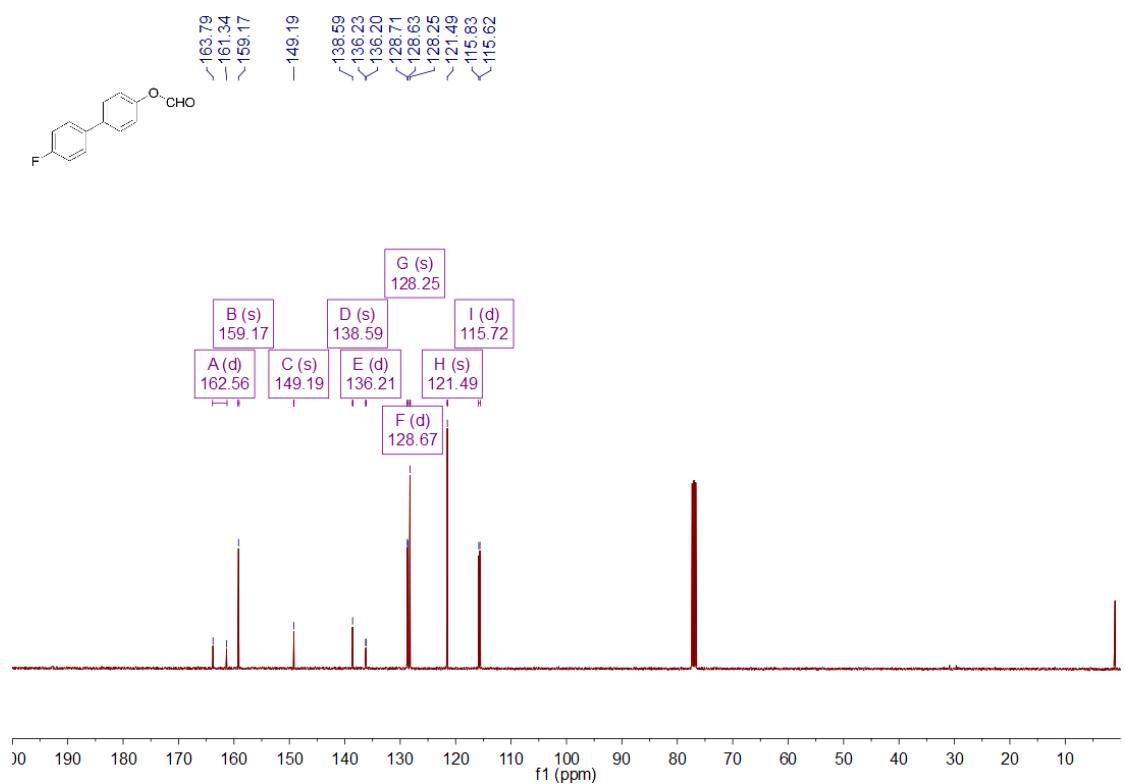
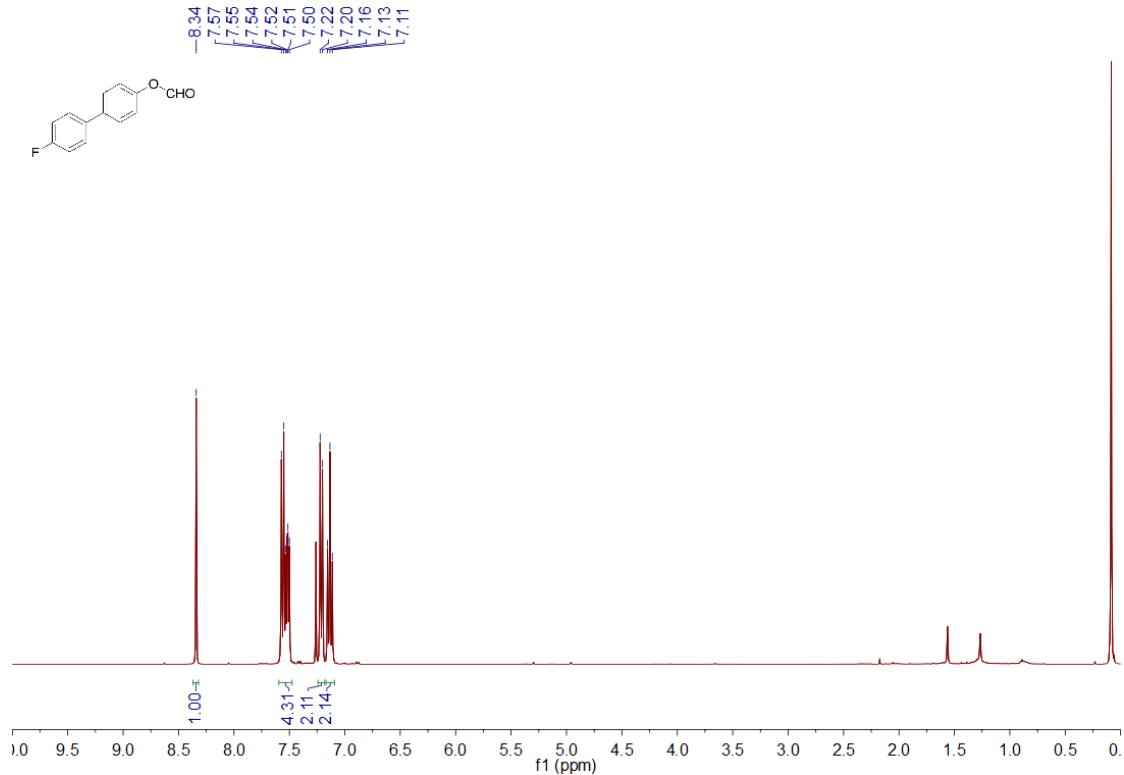
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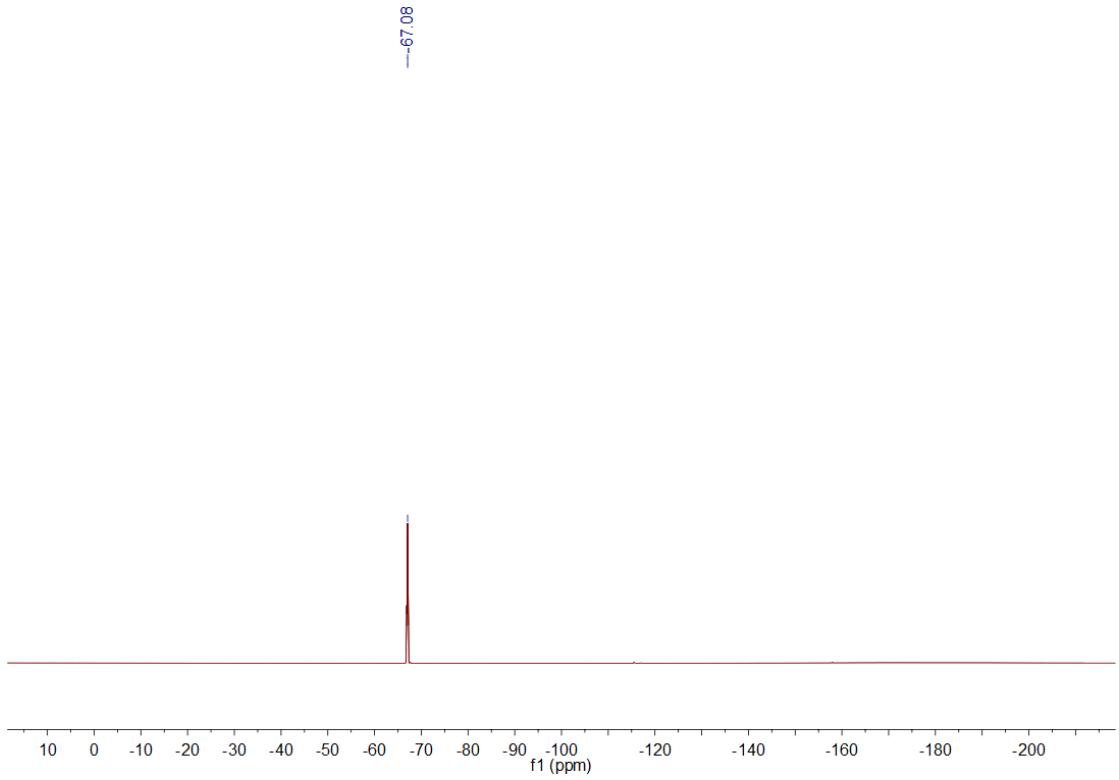
#### 4. Copies of NMR spectra for all the products

**[1,1'-biphenyl]-4-yl formate (3a.**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )

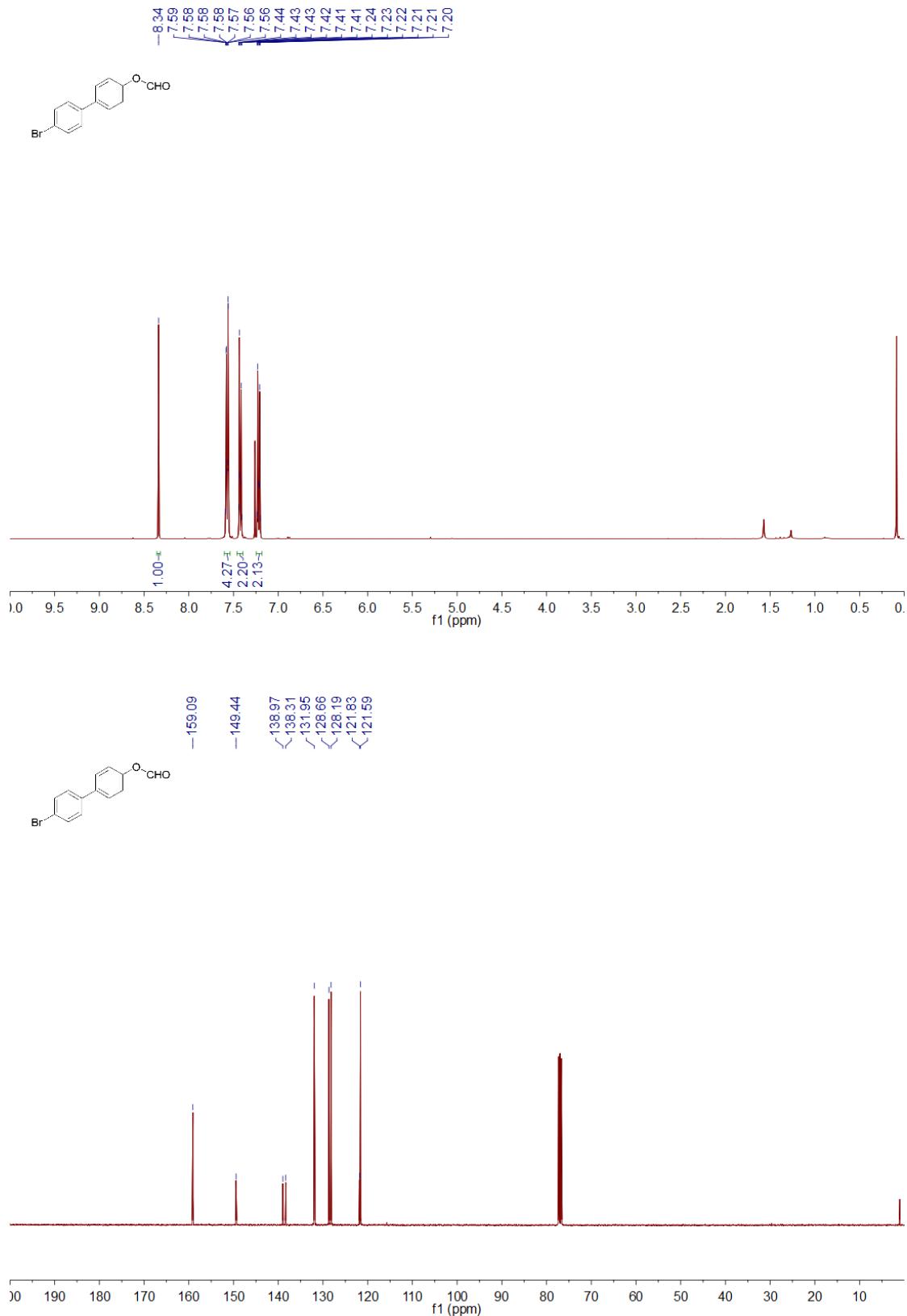


**4'-fluoro-[1,1'-biphenyl]-4-yl formate (3b.**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ ;  $^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ )

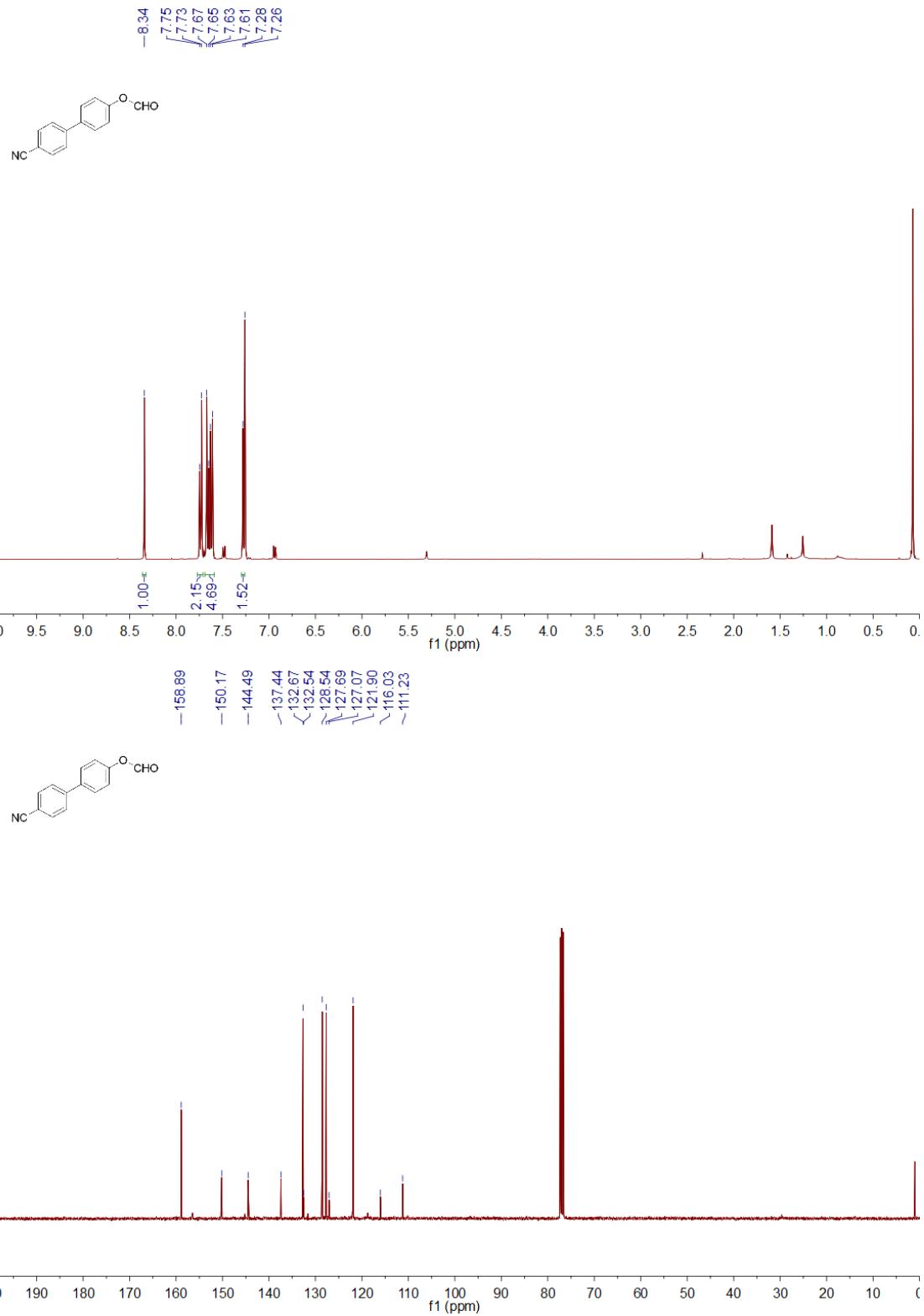




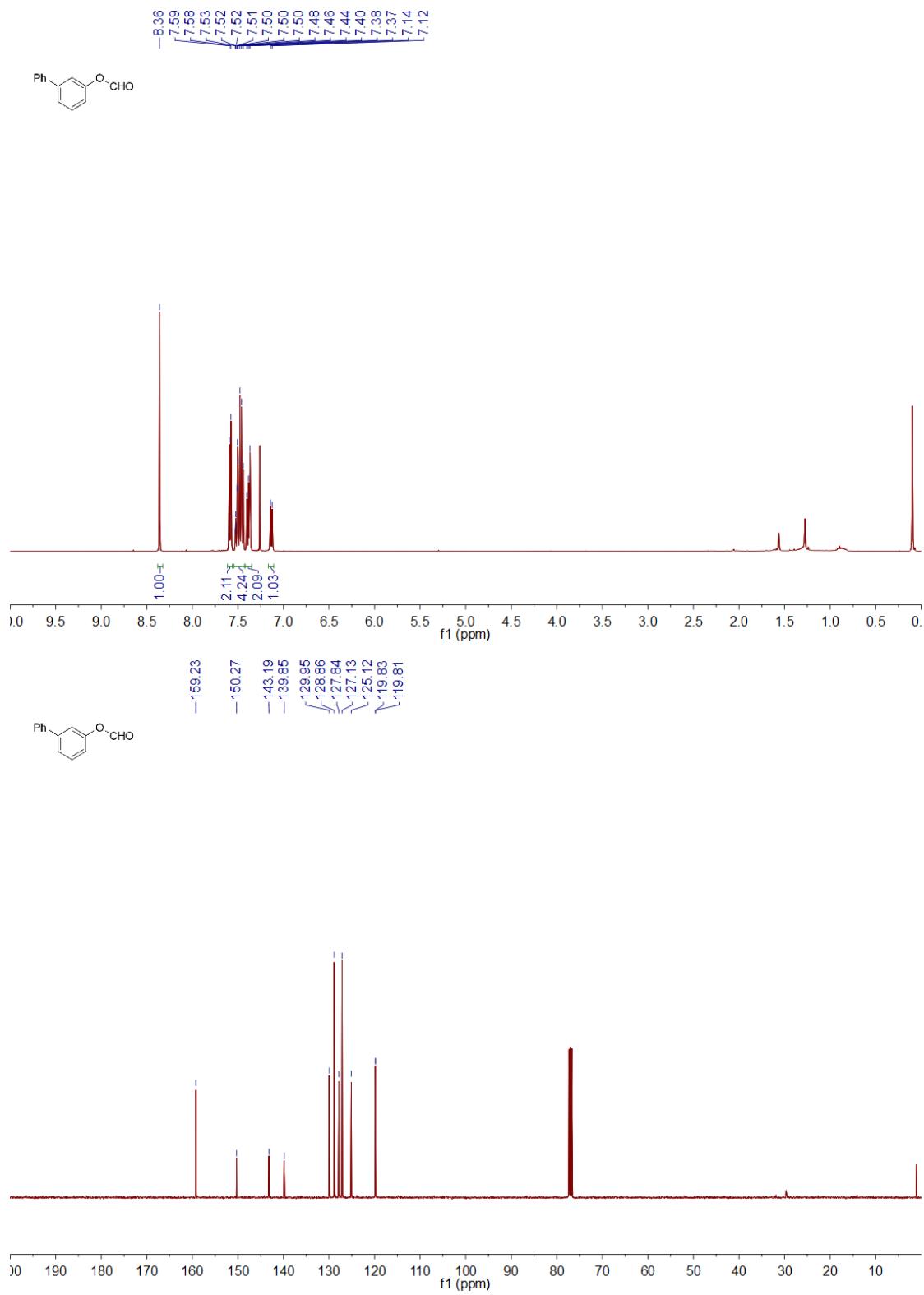
**4'-bromo-[1,1'-biphenyl]-4-yl formate (3c.**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )



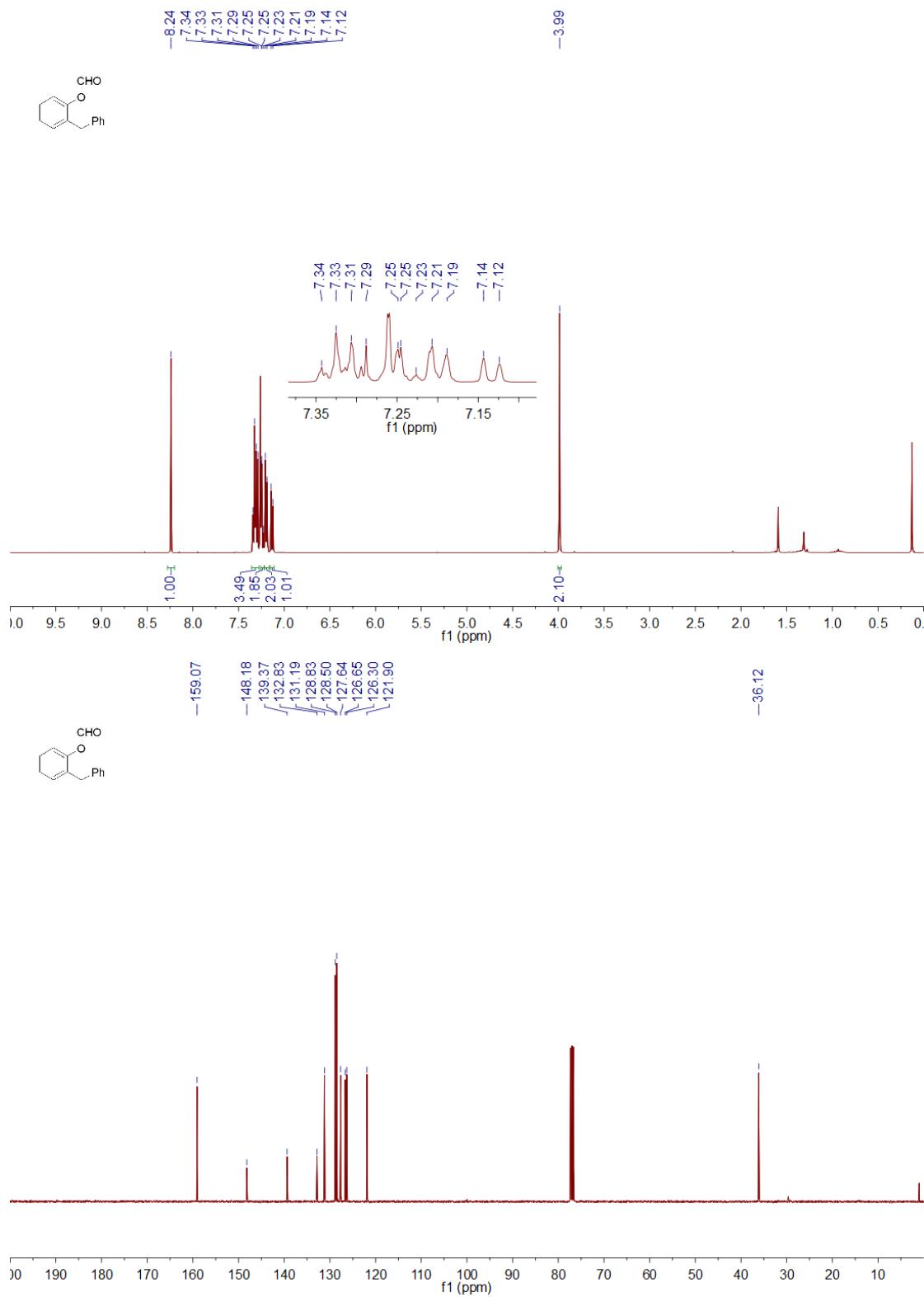
**4'-cyano-[1,1'-biphenyl]-4-yl formate (3d).**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )



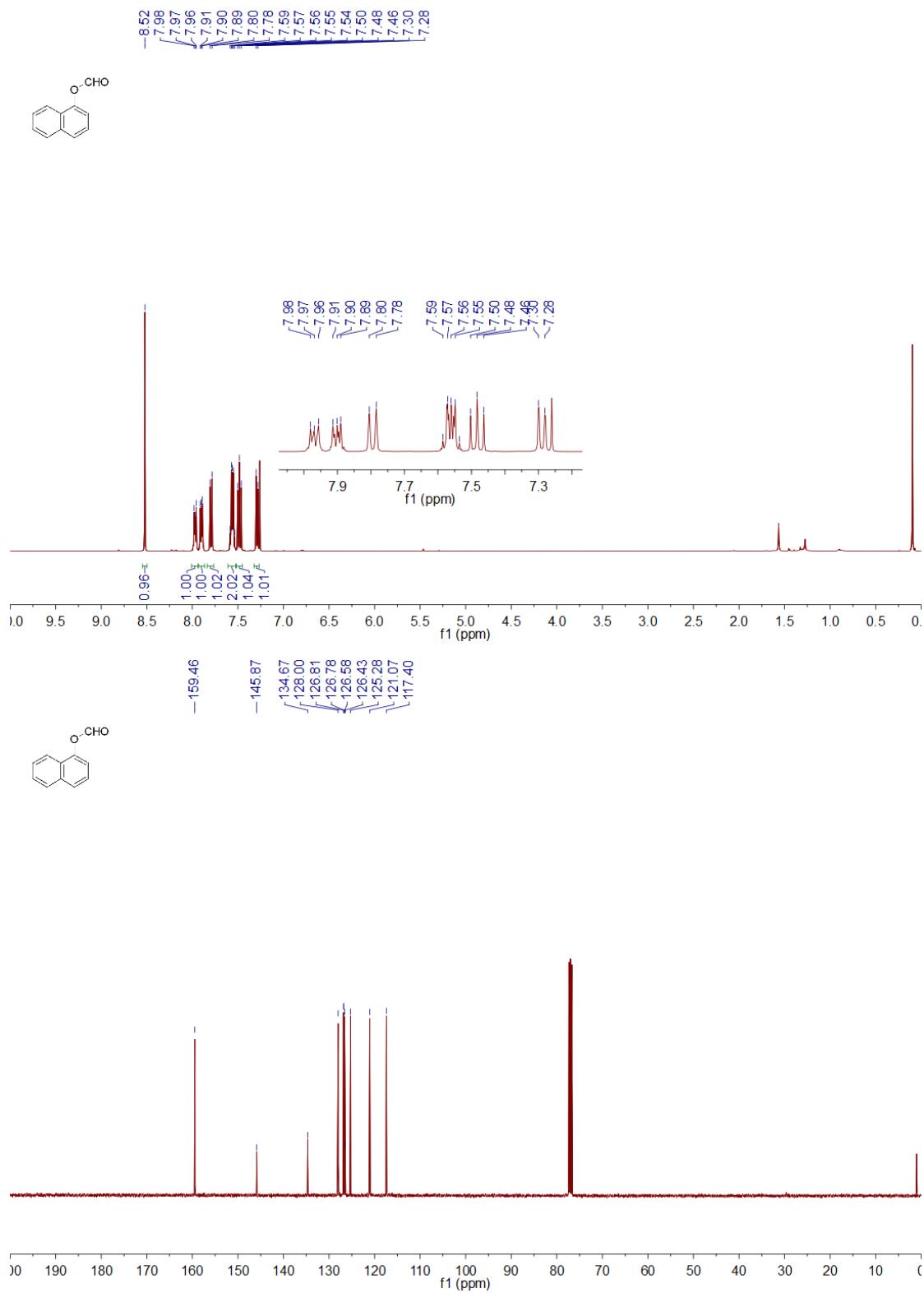
**[1,1'-biphenyl]-3-yl formate (3e.**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )



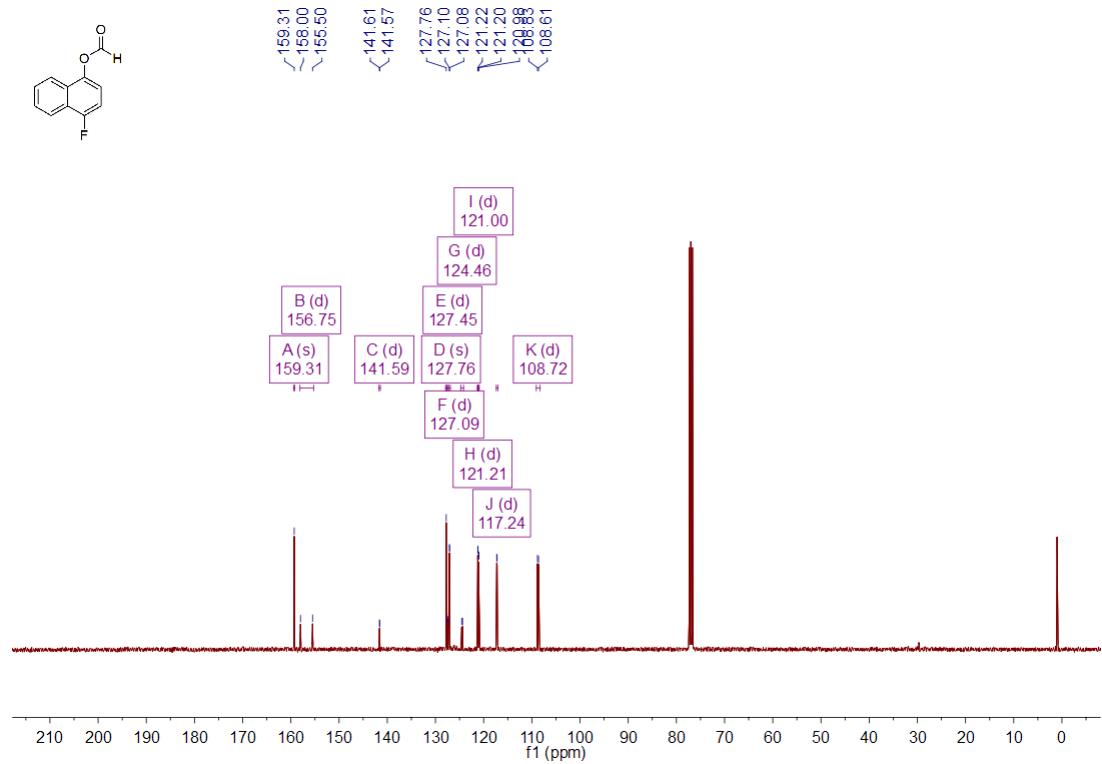
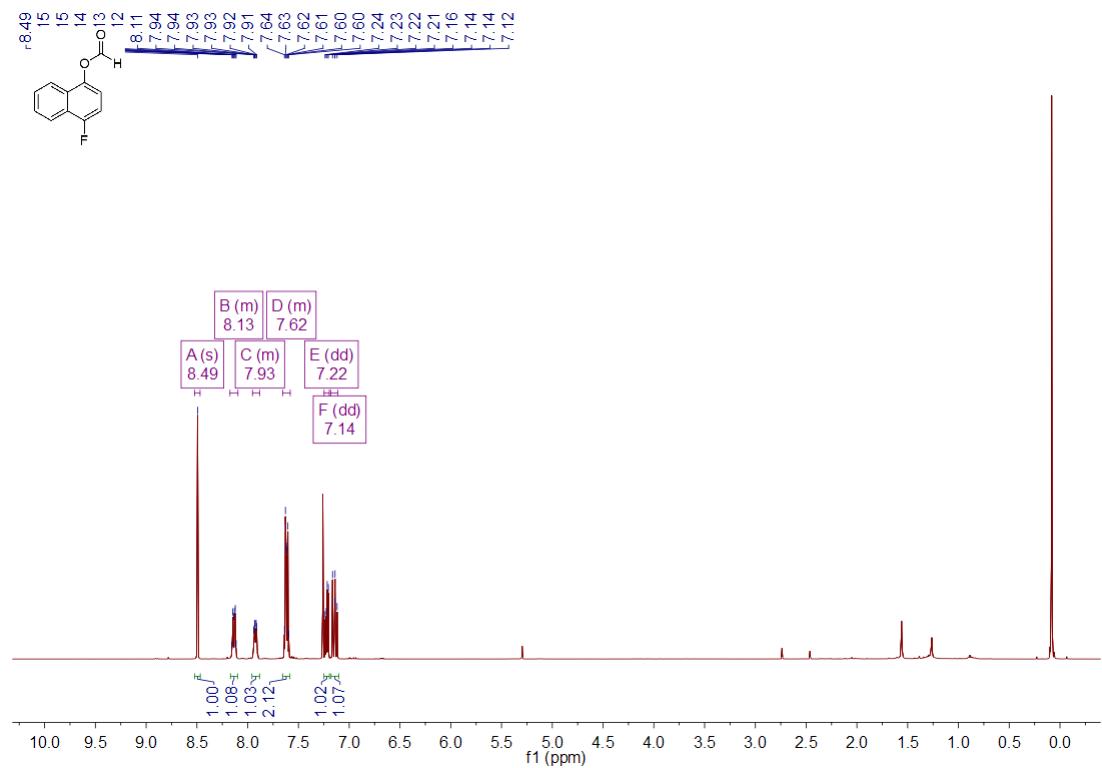
**2-benzylphenyl formate (3f.**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ ).

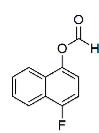


**Naphthalen-1-yl formate (3g.**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ ).

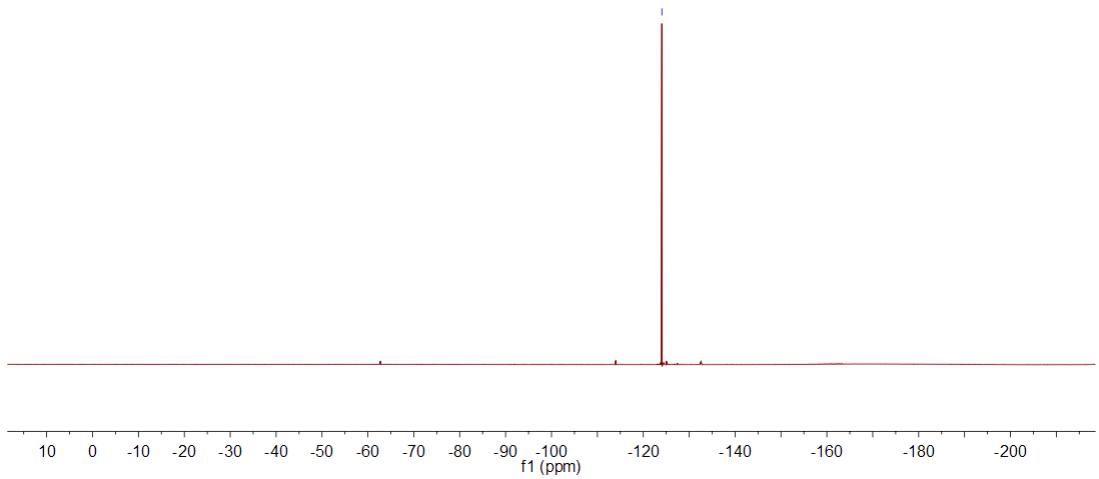


**4-fluoronaphthalen-1-yl formate (3h.**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ ;  $^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ )

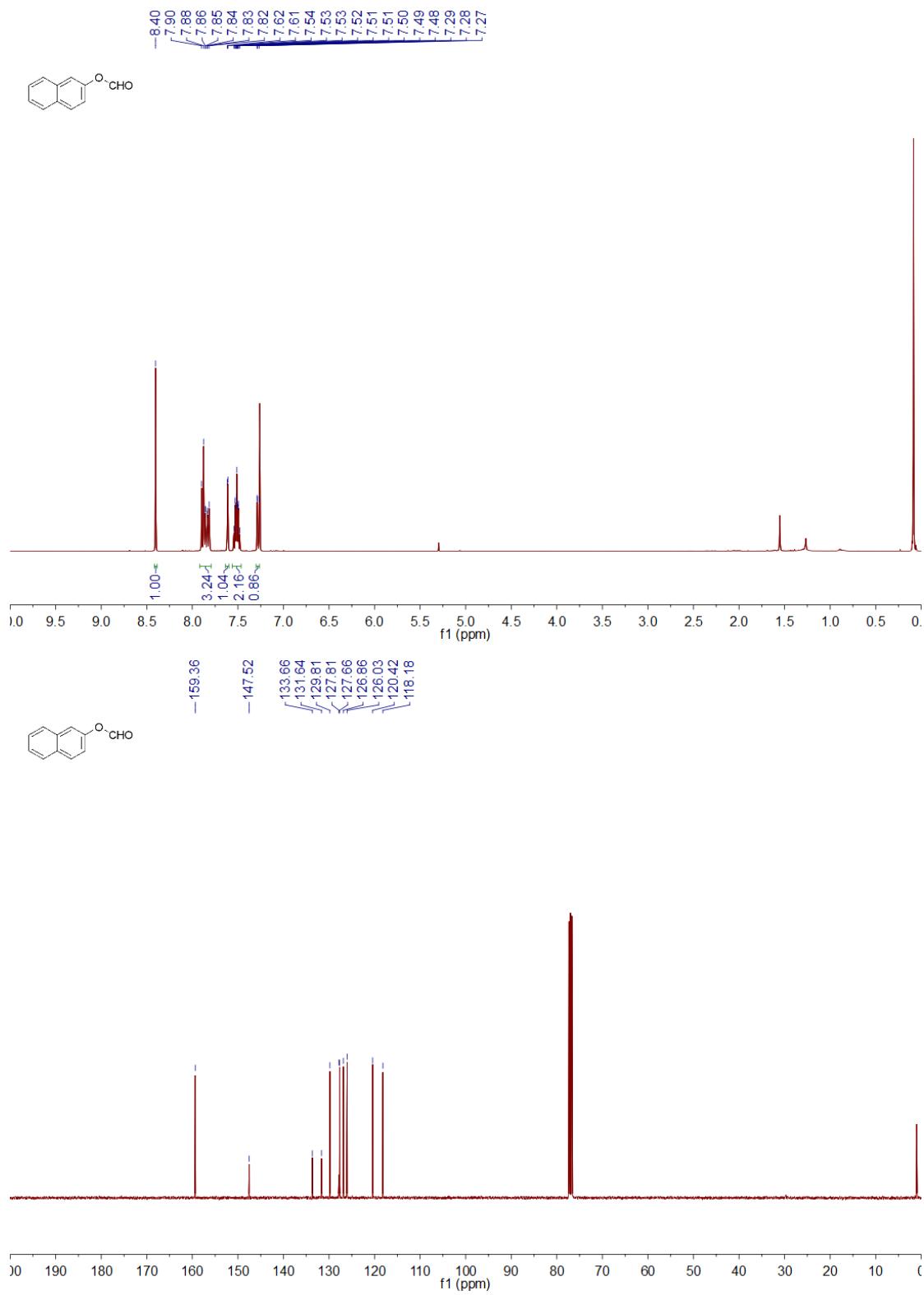




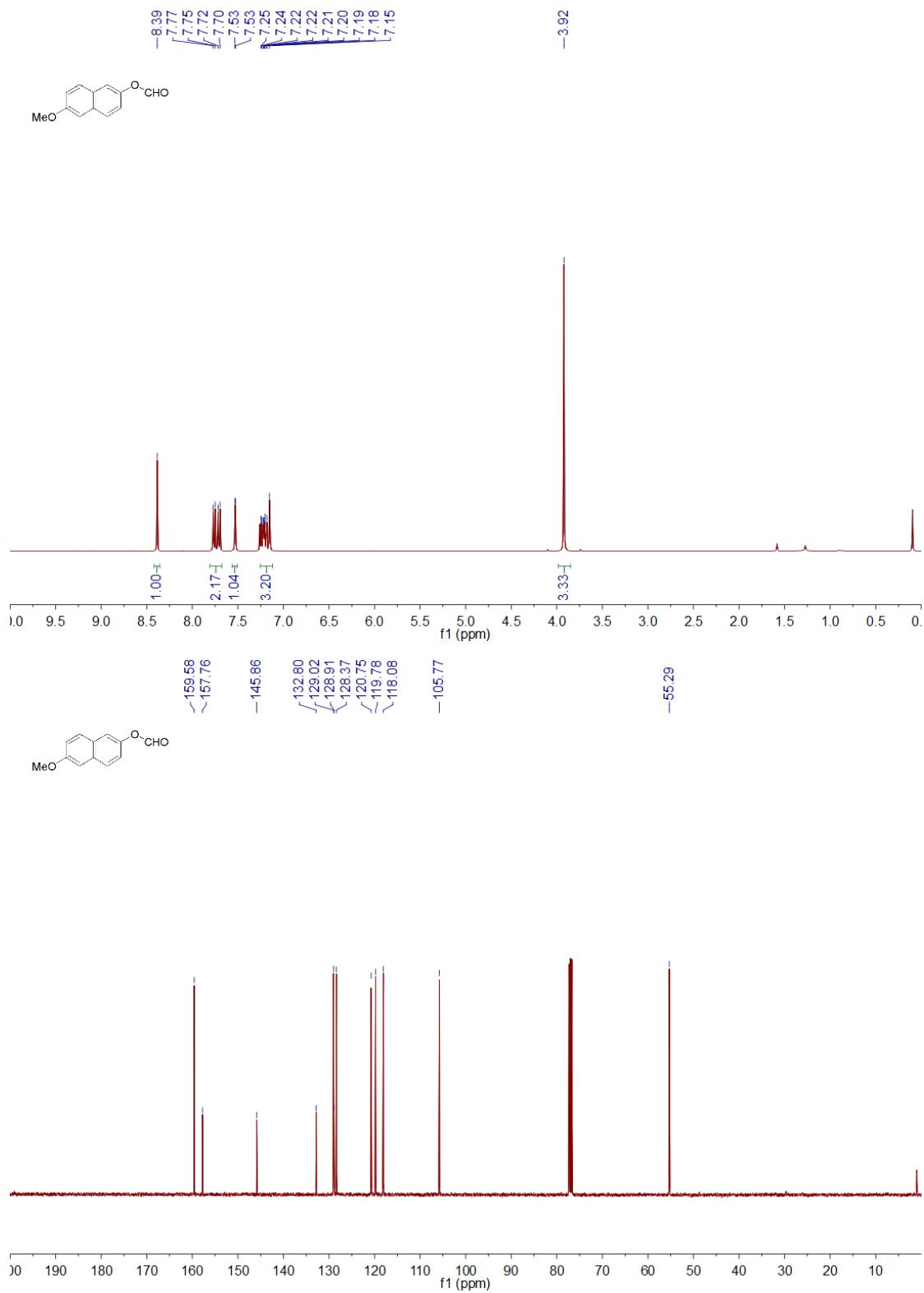
-124.05



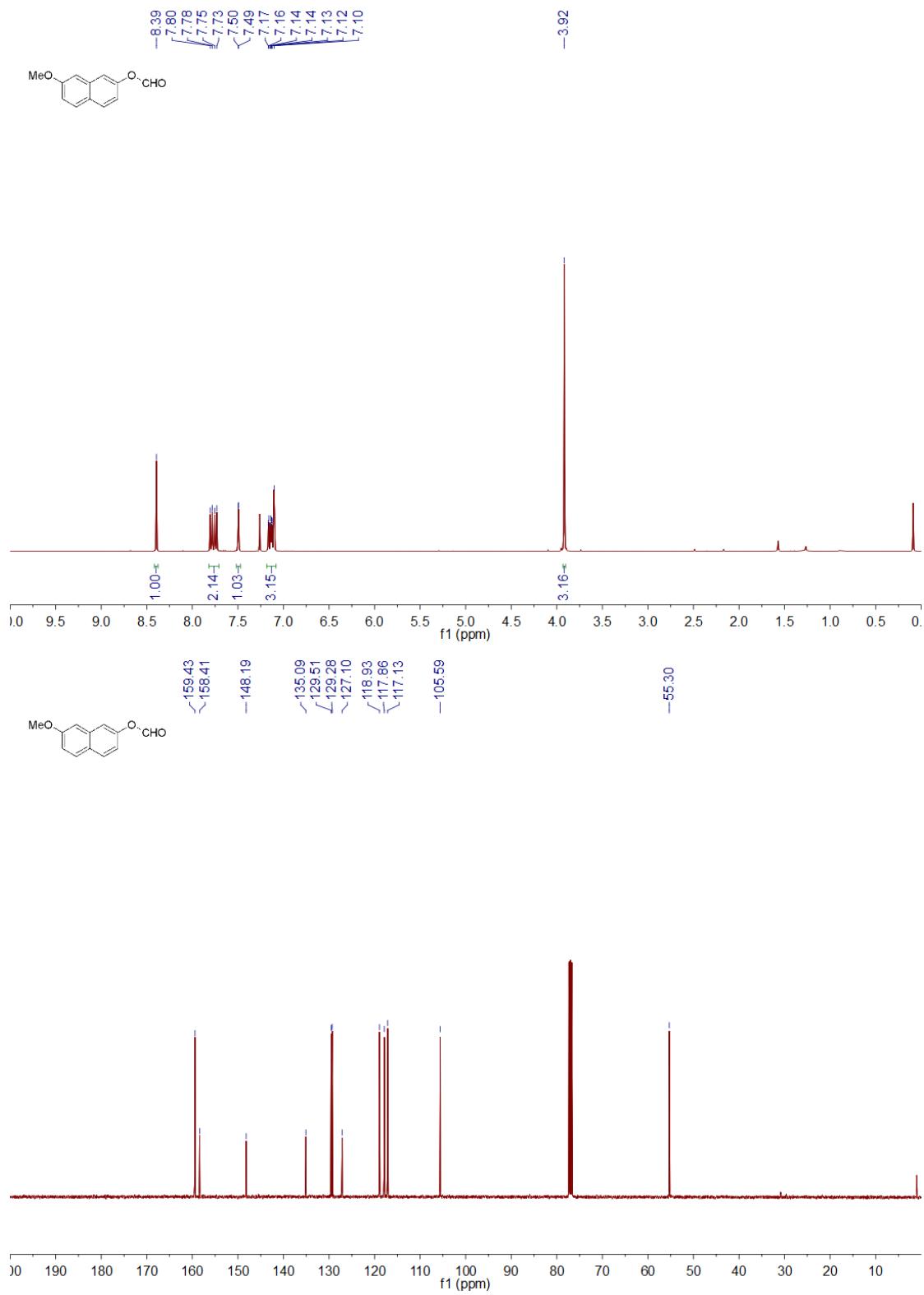
**Naphthalen-2-yl formate (3i).**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )



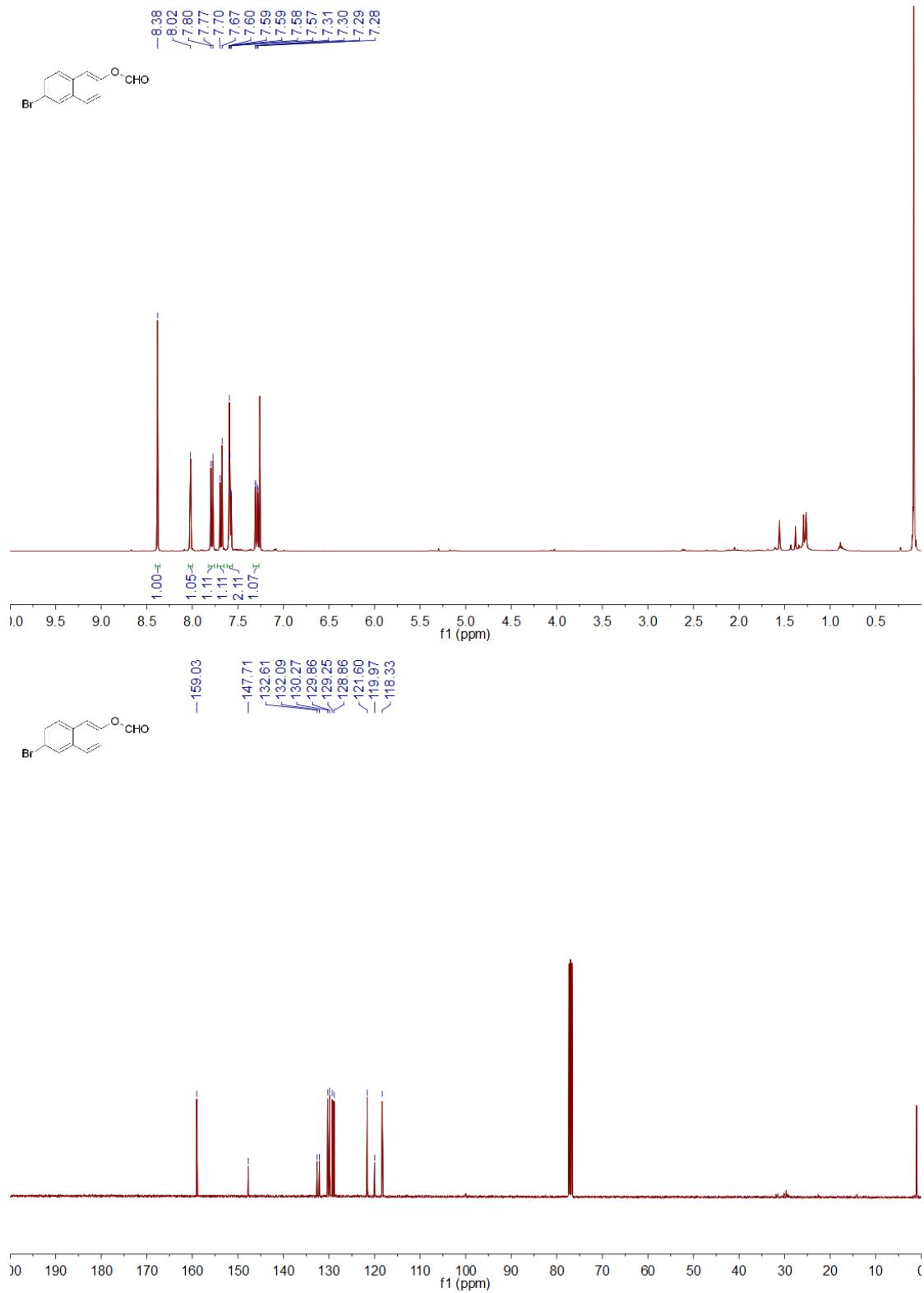
**6-Methoxynaphthalen-2-yl formate (3j).**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )



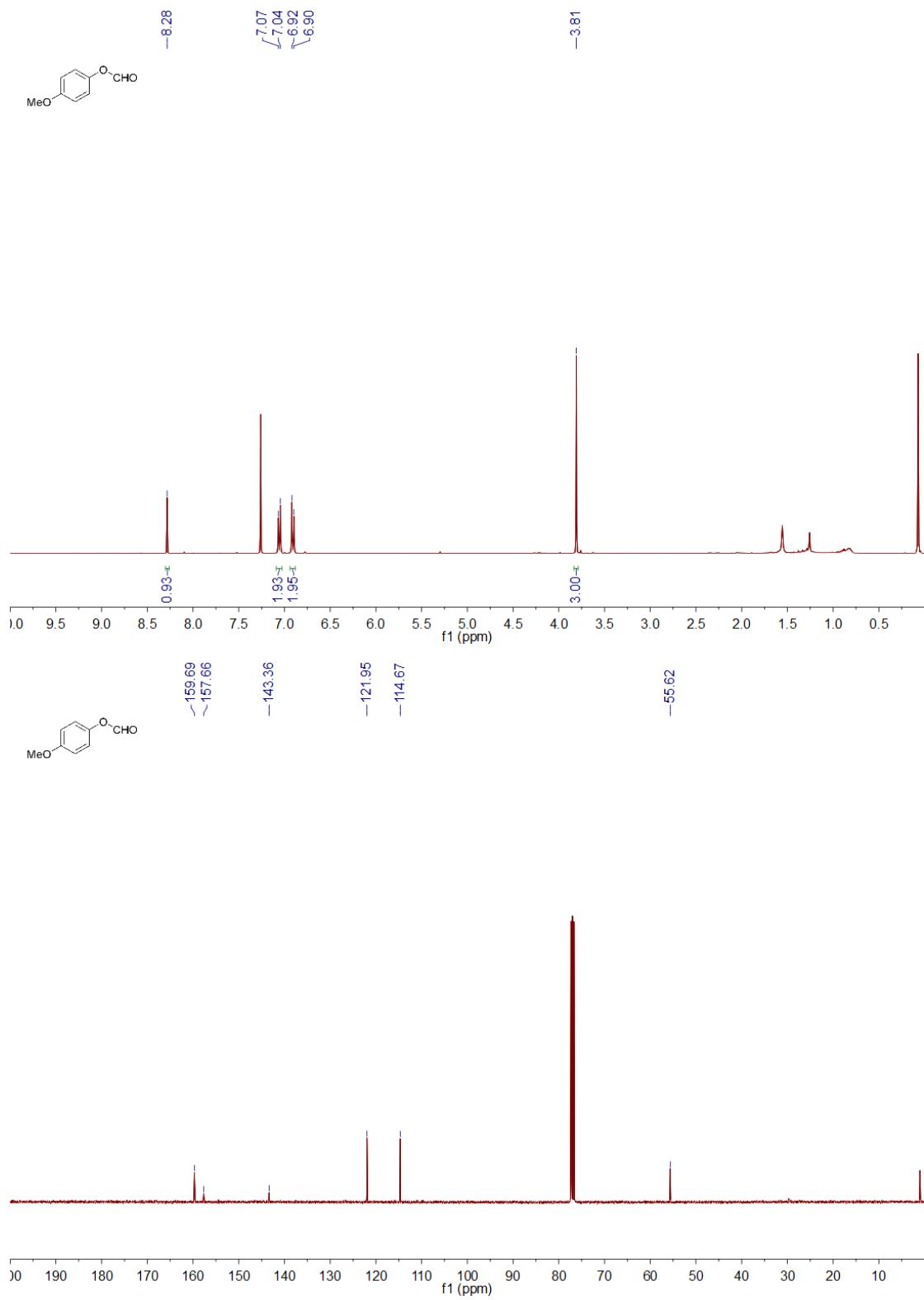
**7-Methoxynaphthalen-2-yl formate (3k).**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )



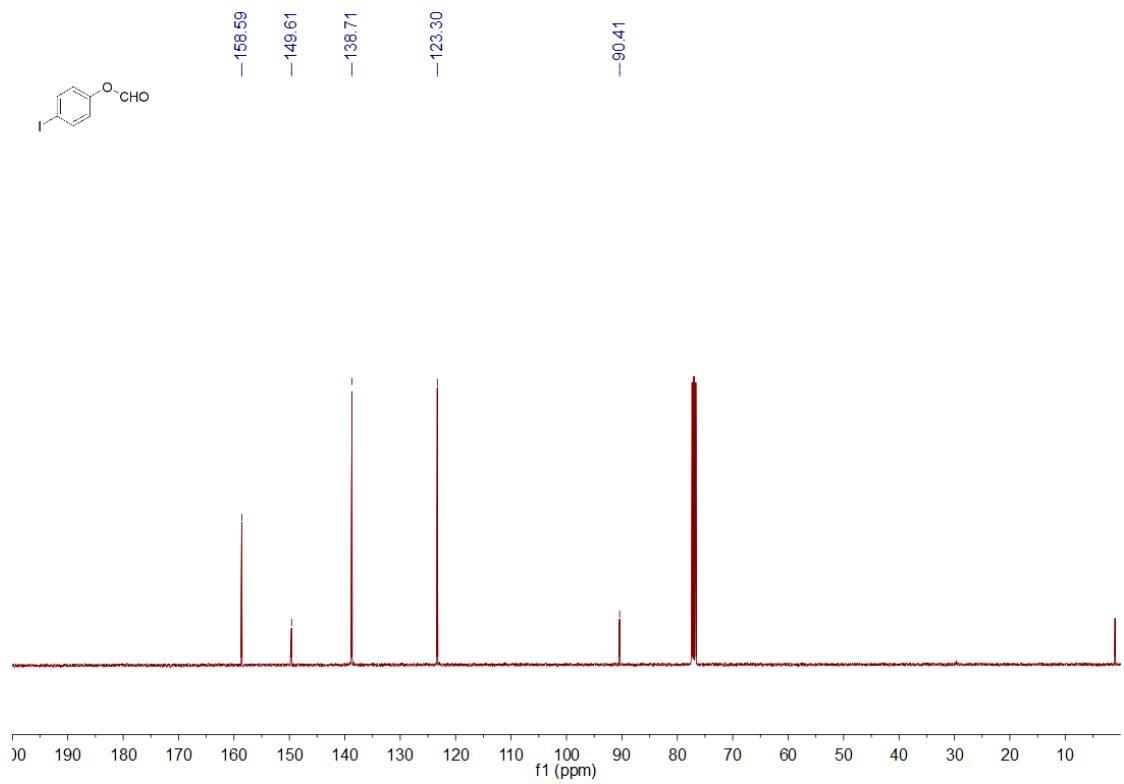
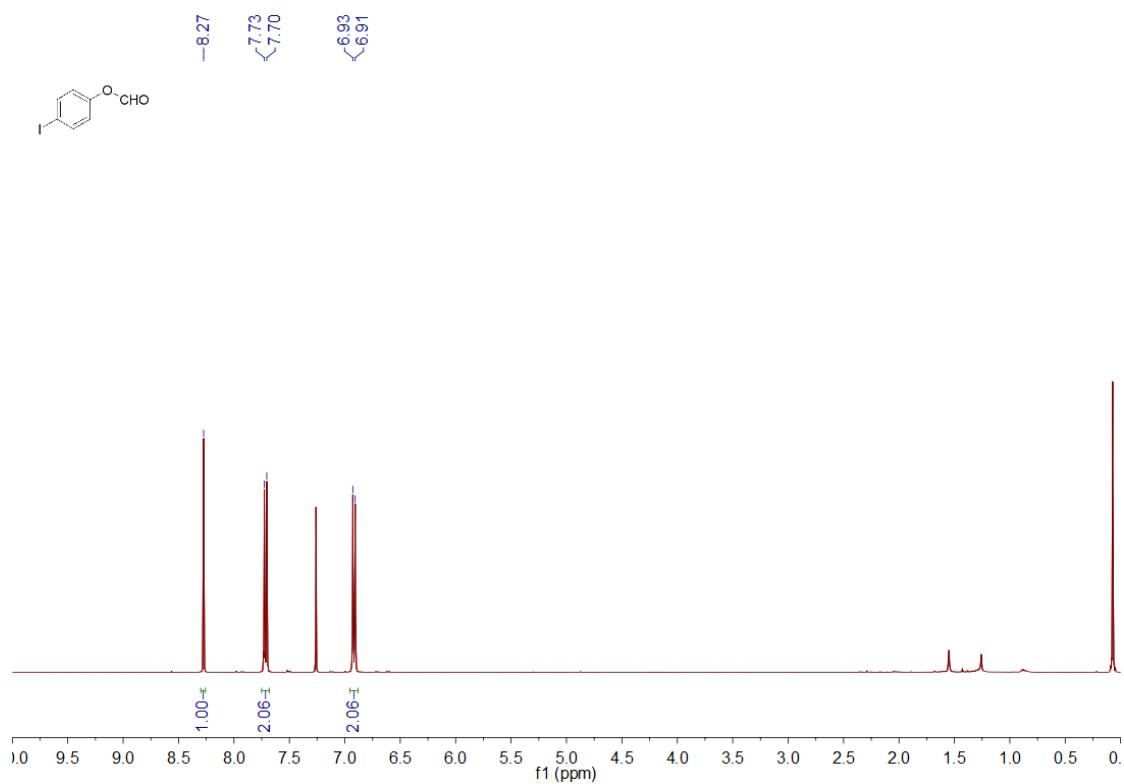
**6-Bromonaphthalen-2-yl formate (3l.**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )



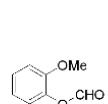
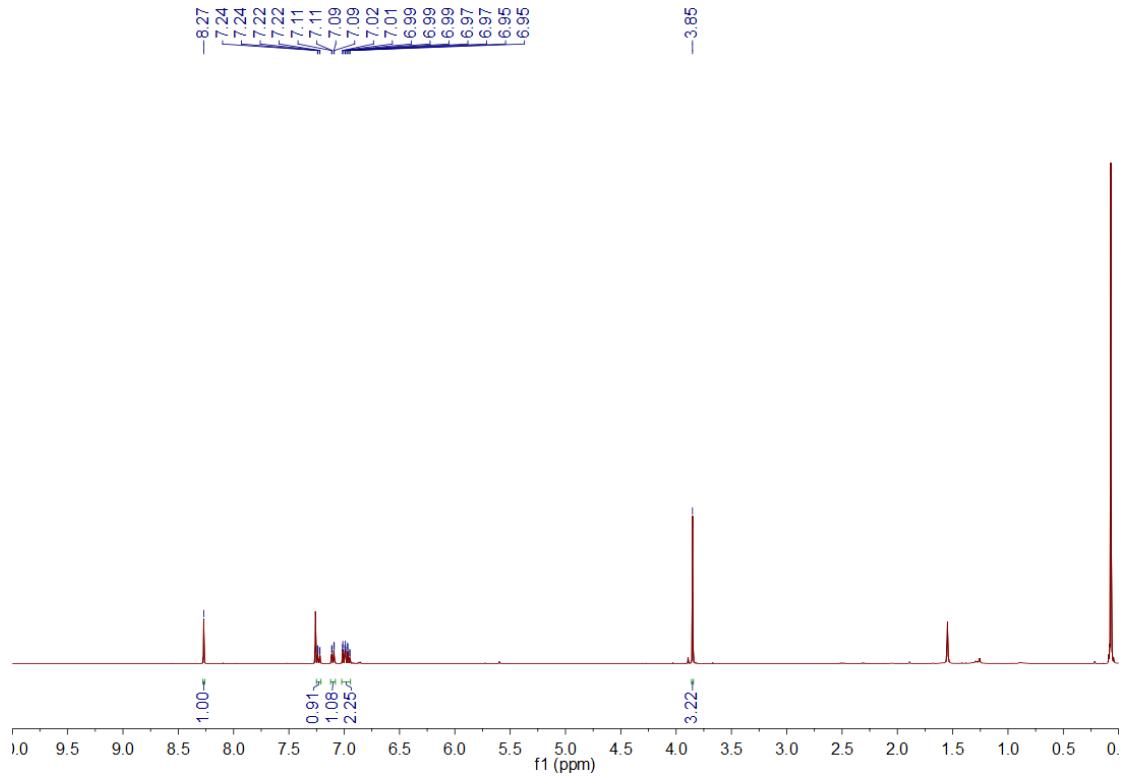
**4-Methoxyphenyl formate (3m).**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )



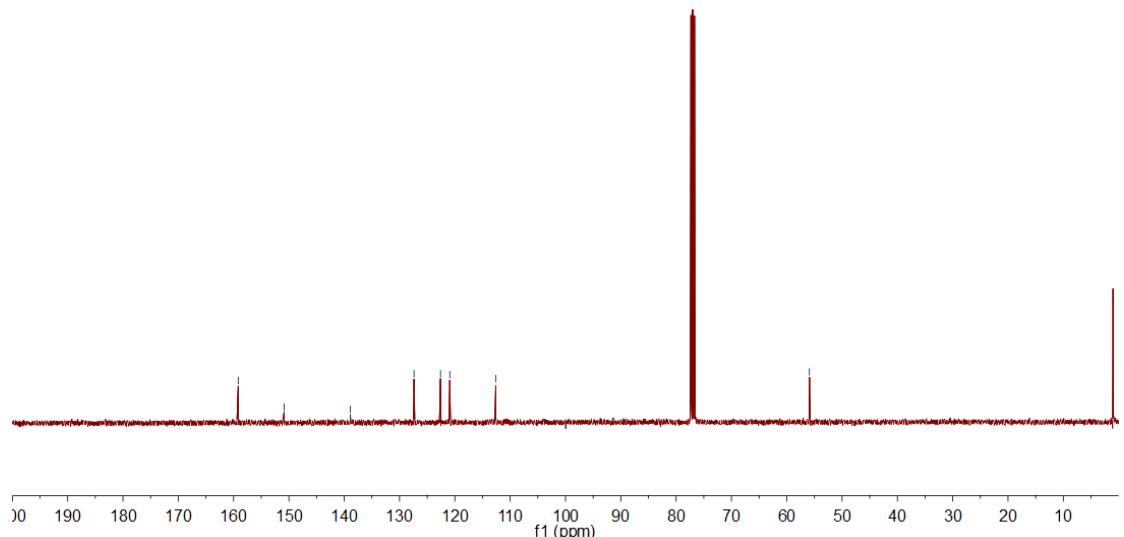
**4-Iodophenyl formate (3n).**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$



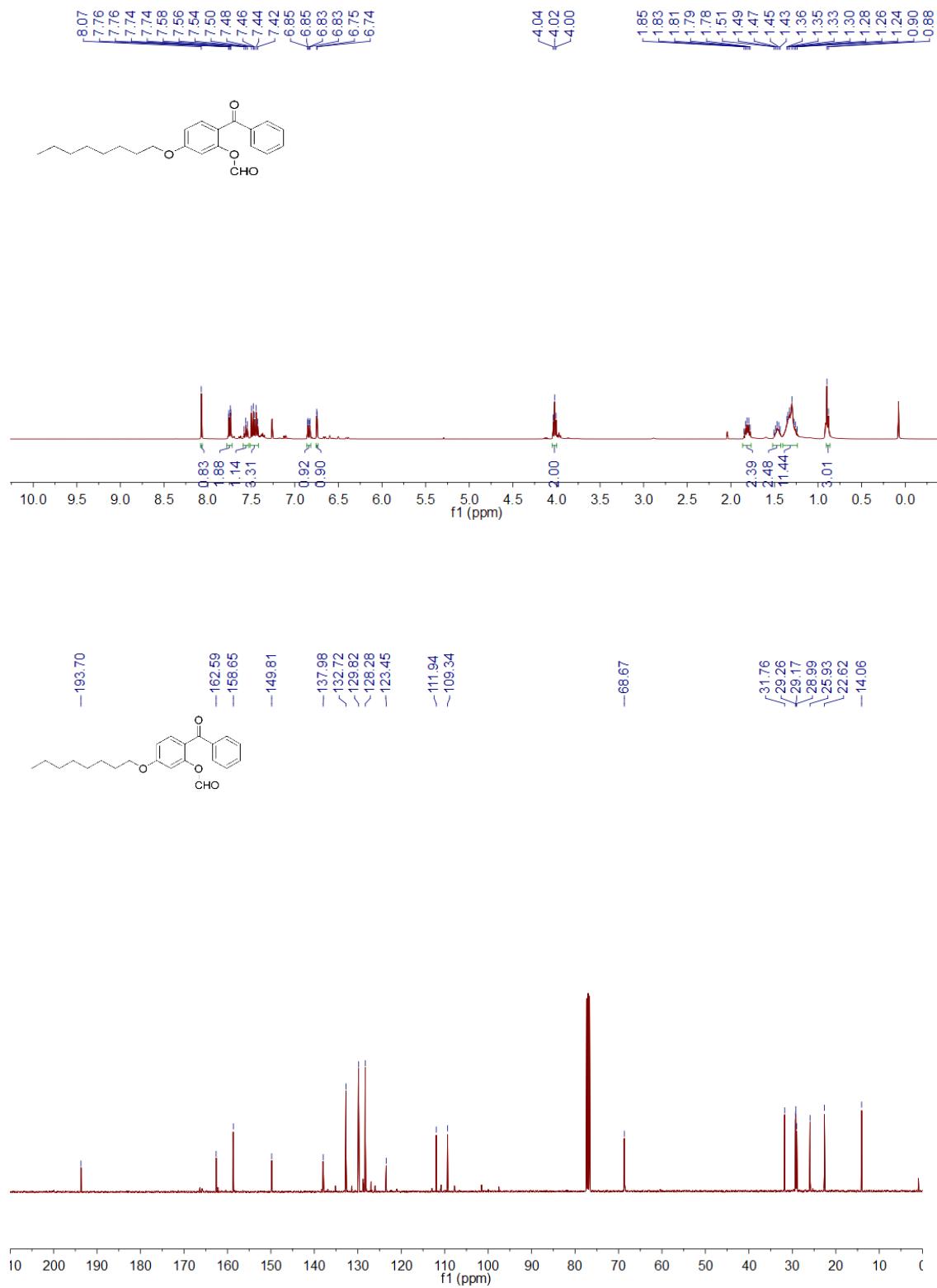
**2-Methoxyphenyl formate (3o;**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )



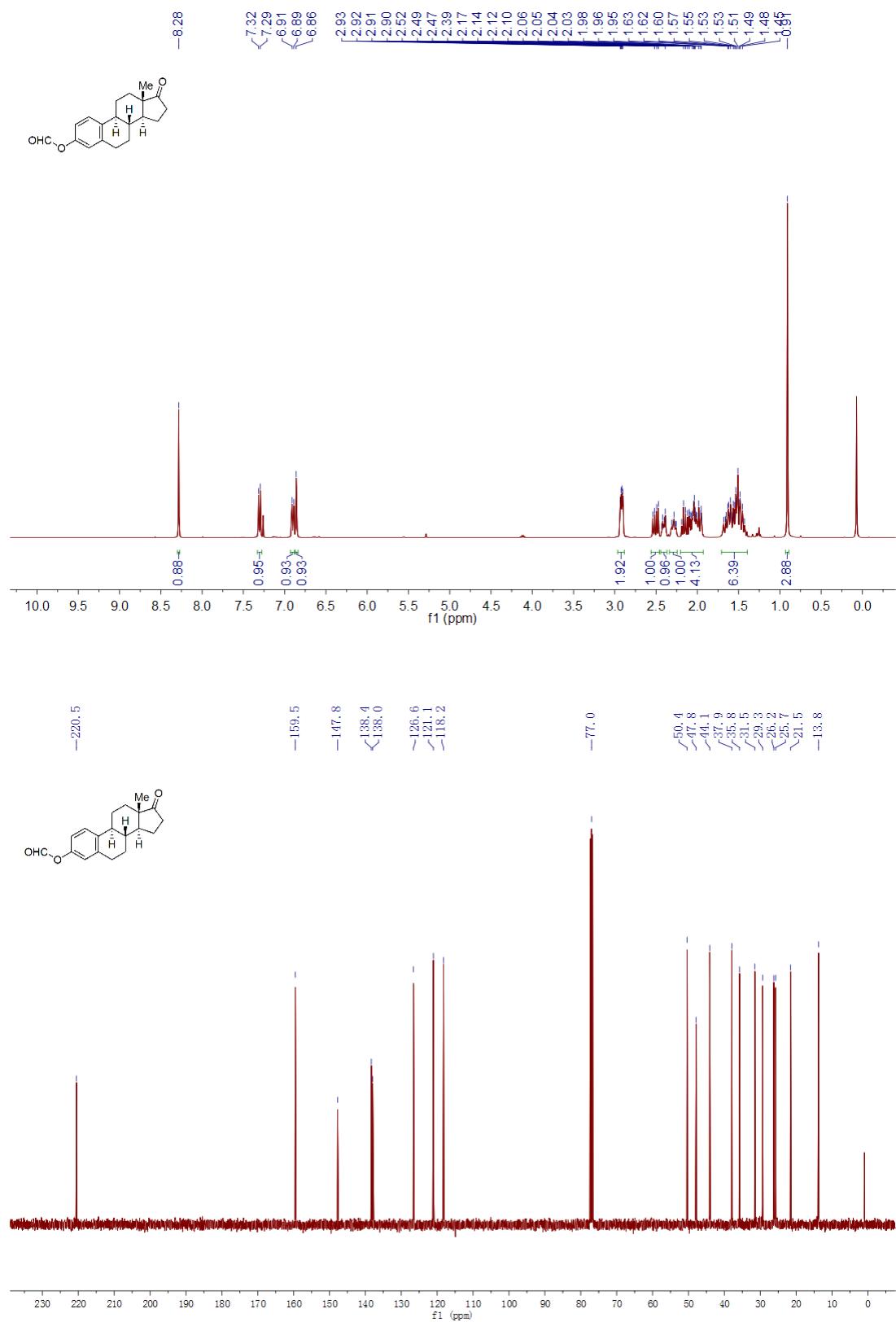
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-112.61  
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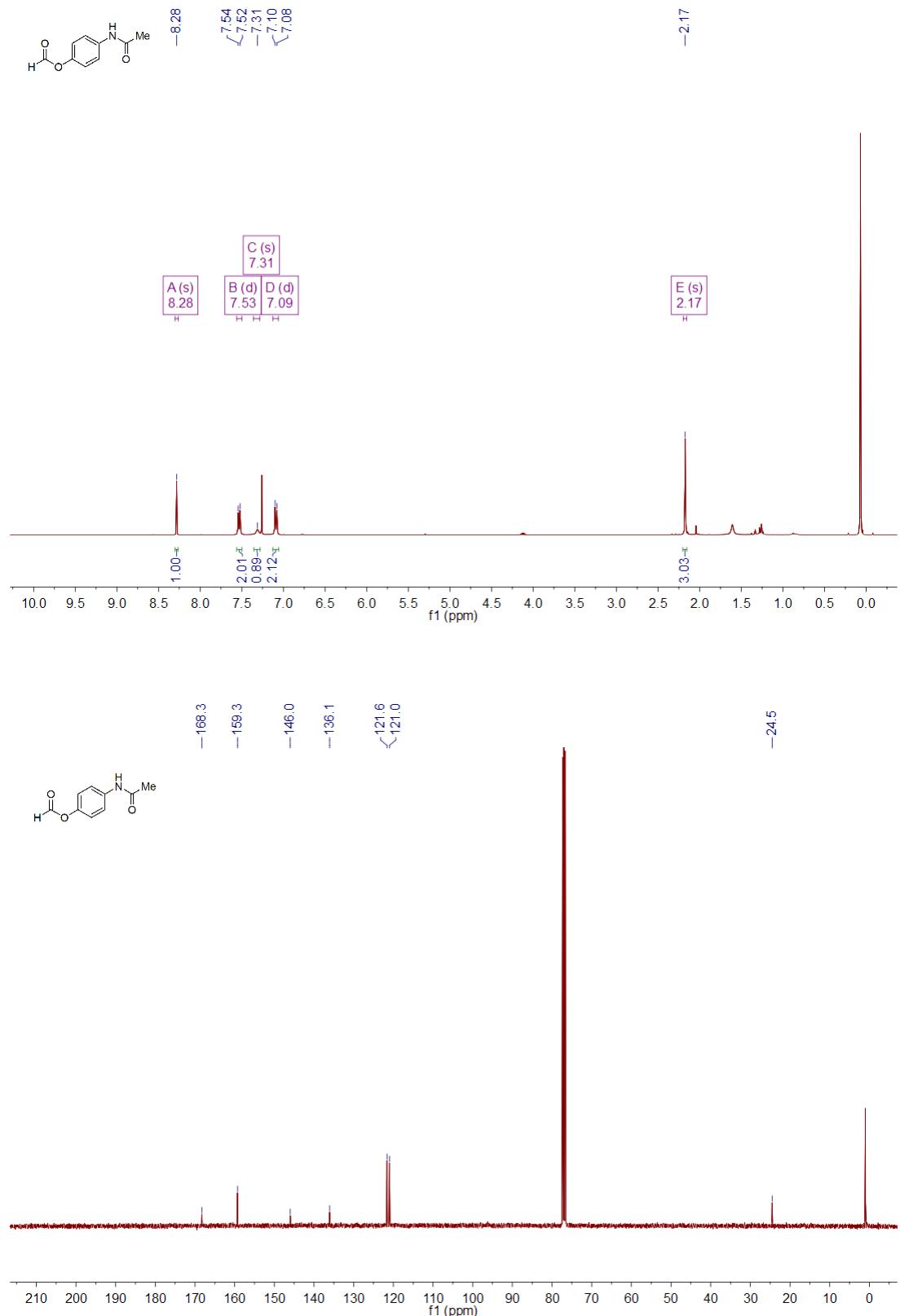
**2-Benzoyl-5-(octyloxy)phenyl formate (**4**;**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )



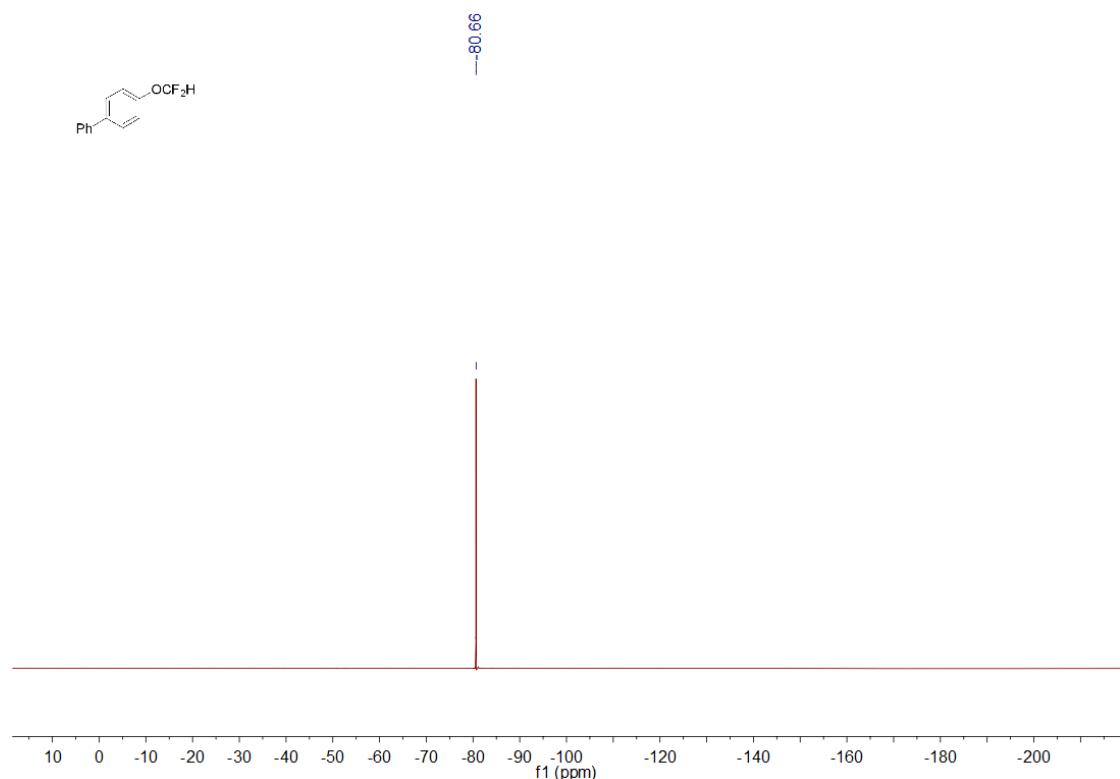
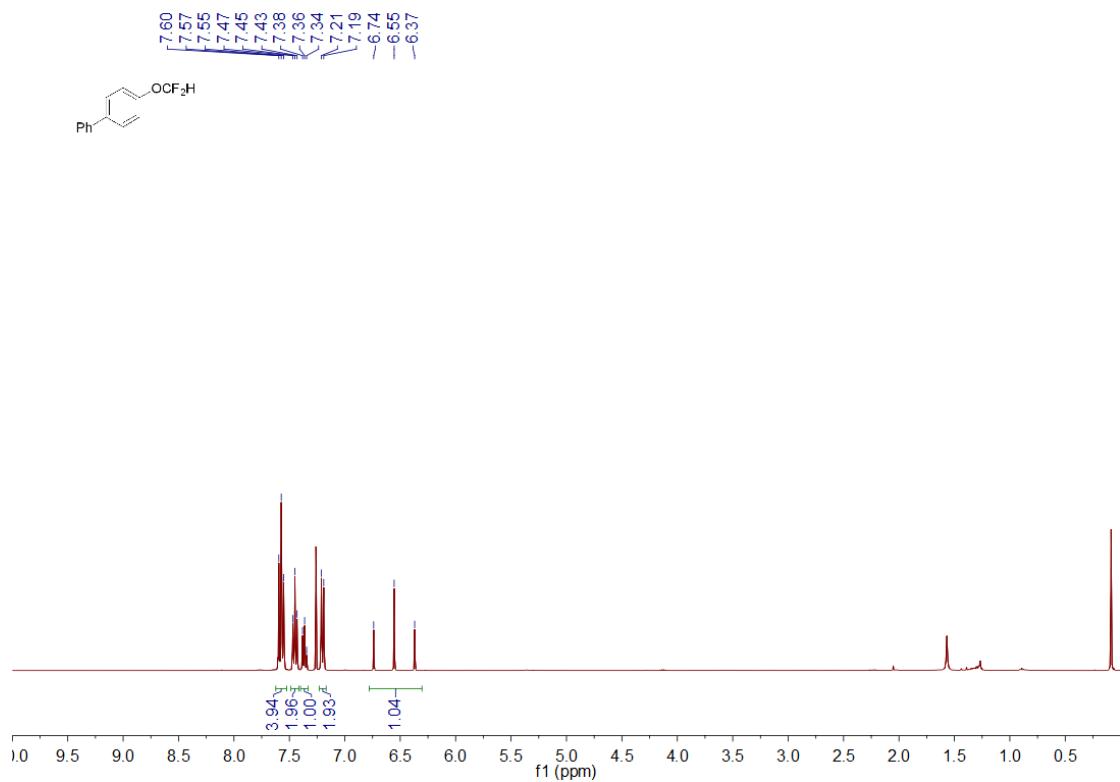
**Estrone formate (5;  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )**

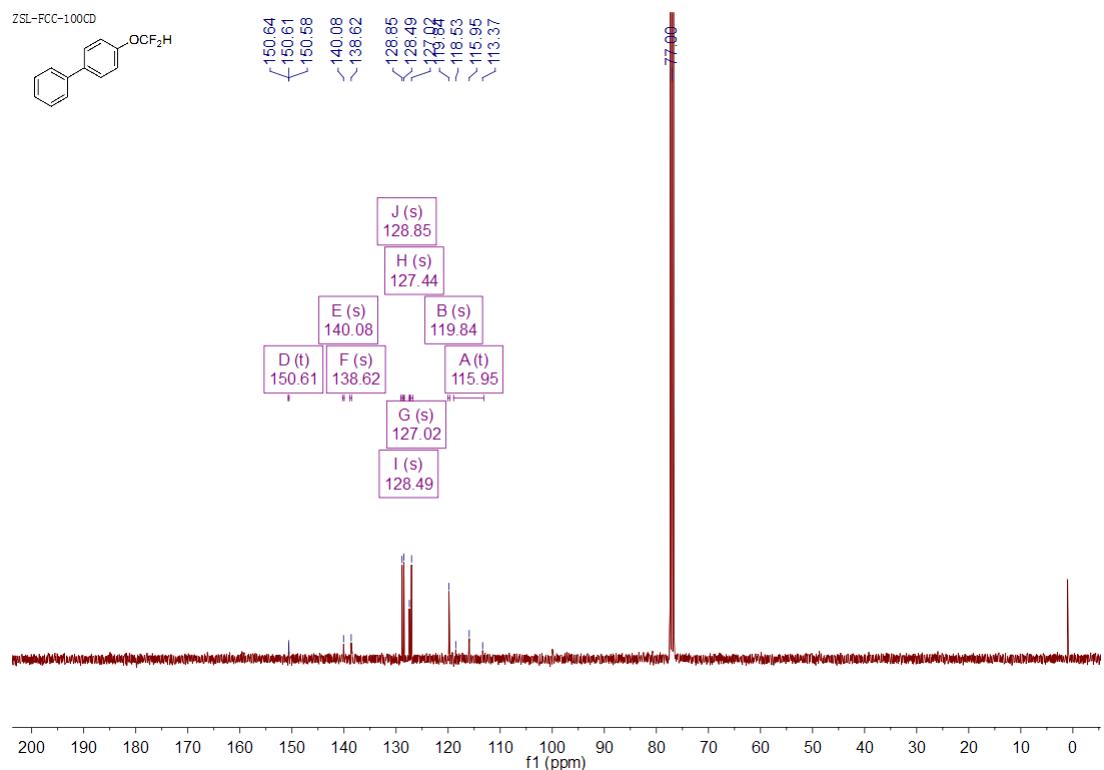


**4-Acetamidophenyl formate (6;**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )



**4-(Difluoromethoxy)-1,1'-biphenyl (7.**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ ;  $^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ )





**Tris([1,1'-biphenyl]-4-yloxy)methane (**8**).**  $^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ;  $^{13}\text{C}$  NMR 101 MHz,  $\text{CDCl}_3$ )

