Carboxylic Acid Anhydrides via Pd-Catalyzed Carbyonylation of Aryl Halides at Atmospheric CO Pressure

Yang Li, Dong Xue*, Zhao-Tie Liu, Chao Wang and Jian-Liang Xiao

a Key Laboratory of Applied Surface and Colloid Chemistry (Shaanxi Normal University), Ministry of Education and School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi’an, 710062, China

b Department of Chemistry, Liverpool Centre for Materials and Catalysis, University of Liverpool, Liverpool, L69 7ZD, UK

E-mail: xuedong_welcome@snnu.edu.cn; j.xiao@liverpool.ac.uk

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1. General information
Flash chromatography was performed with freshly distilled solvents. $^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) spectra were recorded using CDCl$_3$ as solvent. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). The amount of water was determined with an 831 KF Coulometer (Metrohm, Switzerland). Solvents were purified using the following method. DMF, DMSO and DMAc were dried over CaH$_2$ for 24 h and distilled under reduced pressure. Toluene and dioxane were dried over sodium for 4 h, and distilled under N$_2$ atmosphere.

2. The effect of water on carbonylation of 4-iodoanisole
The concentration of water in DMF was determined to be 25 ppm after refluxing over CaH$_2$ for 24 h. From the background reaction, we found that water also came from the reaction system, including the CO gas and autoclave.

The actual amount of water in the reaction was determined in a blank experiment that mimicked the carbonylation reactions via the following procedure: an autoclave containing a 10 mL Teflon reaction tube was charged with a magnetic stir bar, which was then capped with a stopper and flushed with argon. 4-Iodoanisole (1 mmol), NEt$_3$ (2.5 mmol), DMF (2 mL) were added to the tube with a syringe. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with CO, then pressurized to 1 atm at room temperature and heated in an oil bath at 115 °C for 6 h. The autoclave was then cooled to room temperature and vented to discharge the CO. The amount of water in the DMF solution was determined by an 831 KF Coulometer; 4.9 mg (0.27 mmol) water was found, and this was assumed to be the background water. The effect of different amount of additionally-added water is shown in Table S1.
Table S1 The effect of added water on the reaction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Water added (mg)</th>
<th>Water concentration (mol%)</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>27</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
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<td>61</td>
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<tr>
<td>5</td>
<td>8</td>
<td>72</td>
<td>49</td>
</tr>
<tr>
<td>6</td>
<td>18</td>
<td>127</td>
<td>0</td>
</tr>
</tbody>
</table>

3. Optimization of reaction conditions for carbonylation of 4-iodoanisole

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. Pd(OAc)$_2$ (0.01 mmol), ligand (0.02 mmol) and a magnetic stir bar were placed in the tube, which was then capped with a stopper and flushed with argon. Then, 4-iodoanisole (1 mmol), base (2.5 mmol), solvent (2 mL, a certain amount of water added; see Table S2) were added to the tube with a syringe. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with CO, then pressurized to 1 atm at room temperature and heated in an oil bath at 115 °C for 6 h. The autoclave was then cooled to room temperature and vented to discharge the excess CO. Water (10 mL) was added, and the product was extracted with DCM (3×3 mL). The organic layers were washed with brine, dried over Na$_2$SO$_4$, and evaporated. The crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether as eluent to give 4-methoxy-benzoic anhydride. The isolated yields are given in Table S2. Structures of ligands are shown in Scheme S1.
Table S2 Optimization of carbonylation of 4-iodoanisole with water at 1 atm CO₂

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Base</th>
<th>Water contents (mol%)</th>
<th>Solvent</th>
<th>Isolated Yield (%)</th>
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<tbody>
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<td>DPPP</td>
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<td>DMF</td>
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<tr>
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<td>DMF</td>
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<tr>
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<td>Et₃N</td>
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<td>DMF</td>
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<td>DMF</td>
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<td>50%</td>
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<td>Et₃N</td>
<td>50%</td>
<td>Toluene</td>
<td>56</td>
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4. General procedure for carbonylation of aryl iodides

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. Pd(OAc)$_2$ (0.01 mmol), dppp (0.02 mmol) and a magnetic stir bar were placed in the tube which was then capped with a stopper and flushed with argon. Then, an aryl iodide (1 mmol), NEt$_3$ (2.5 mmol), DMF (2 mL, 0.22 mmol additional water added) were added to the tube with a syringe. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with CO, then pressurized to 1 atm at room temperature and heated in an oil bath at 115 °C for 6 h. The autoclave was then cooled to room temperature and vented to discharge CO. Water (10 mL) was added, and the product was extracted with DCM (3×3 mL). The organic layers were washed with brine, dried over Na$_2$SO$_4$, and evaporated. The crude product was purified by column chromatography on
silica gel using a mixture of ethyl acetate and petroleum ether as eluent to give the following compounds.

5. Experimental data for products

(2a) 4-Methoxybenzoic anhydride

\[
\text{R}_f = 0.3 \text{ (petroleum ether/ethyl acetate 12:1), White solid; m.p. = 88-93 °C; } ^1\text{H NMR (300 MHz, CDCl}_3\text{)} \delta \text{ (ppm): } 8.10 \text{ (d, } J = 7.4 \text{ Hz, 4H), 6.98 (d, } J = 7.4 \text{ Hz, 4H), 3.90 (s, 6H); } ^{13}\text{C NMR (75 MHz, CDCl}_3\text{)} \delta \text{ (ppm): } 164.9, 162.3, 132.8, 121.3, 114.2, 55.6; \text{ IR (KBr): 3010, 1790, 1720, 1620, 1300, 1220, 1180 cm}^{-1}; \text{ HRMS (ESI) calc. for } (M + Na^+) 309.0739; \text{ found 309.0733.}
\]

(2b) Benzoic anhydride

\[
\text{R}_f = 0.3 \text{ (petroleum ether/ethyl acetate 15:1), White solid. m.p = 42-44°C, } ^1\text{H NMR (300 MHz, CDCl}_3\text{)} \delta \text{ (ppm): } 8.16 \text{ (d, } J = 7.5 \text{ Hz, 4H), 7.68 (d, } J = 7.5 \text{ Hz, 2H), 7.49-7.44 (m, 4H); } ^{13}\text{C NMR (75 MHz, CDCl}_3\text{)} \delta \text{ (ppm): } 162.4, 134.5, 128.8; \text{ IR (KBr) 3064, 1788, 1713, 1609, 1212,1167, 1000 cm}^{-1}; \text{ HRMS (ESI) calc. for } (M + Na^+) 249.0522 \text{ found 249.0520.}
\]

(2c) 4-Methylbenzoic anhydride

\[
\text{R}_f = 0.2 \text{ (petroleum ether/ethyl acetate 14:1), White solid. m.p = 78-80°C, } ^1\text{H NMR (300 MHz, CDCl}_3\text{)} \delta \text{ (ppm): } 8.04 \text{ (dd, } J = 7.8 \text{ Hz, } J = 5.1 \text{ Hz, 4H), 7.32 (d, } J = 7.8 \text{ Hz, 4H), 2.46 (s, 6H); } ^{13}\text{C NMR (75 MHz, CDCl}_3\text{)} \delta \text{ (ppm): } 162.6, 145.5, 130.6, 129.6, 126.3, 21.8; \text{ IR (KBr) 3010, 1775, 1717, 1616, 1229, 1175, 1043, 1000 cm}^{-1}; \text{ HRMS(ESI) calc. for } (M + Na^+) 277.0835 \text{ found 277.0836.}
\]
(2d) 4-chlorobenzoic anhydride (2d)

\[
\begin{align*}
\text{R}_f &= 0.3 \text{ (petroleum ether/ethyl acetate 9:1), White solid. m.p} = 184-185^\circ C, \quad \text{H NMR (300 MHz, CD}_2\text{OD)} \\
\delta (\text{ppm}): 7.51 \text{ (d, } J = 8.4 \text{ Hz 4H), } 8.07 \text{ (d, } J = 8.4 \text{ Hz 4H)}; \quad ^{13}\text{C NMR (75 MHz, CD}_2\text{OD)} \delta (\text{ppm}): 167.4, 138.8, 130.9, 128.3; \quad \text{IR (KBr) 3010, 1800, 1720,1600, 1220, 1180, 1060, 1000 cm}^{-1}; \quad \text{HRMS(ESI) calc. for (M + Na\textsuperscript{+}) 316.9748 found 316.9745.}
\end{align*}
\]

(2e) 4-fluorobenzoic anhydride

\[
\begin{align*}
\text{R}_f &= 0.2 \text{ (petroleum ether/ethyl acetate 20:1), White solid. m. p} = 112-114^\circ C, \quad \text{H NMR (300 MHz, CDCl}_3\text{)} \delta (\text{ppm}): 8.19-8.16 \text{ (m, 4H), 7.23-7.19 (m, 4H)}; \quad ^{13}\text{C NMR (75 MHz, CDCl}_3\text{)} \delta (\text{ppm}): 167.8, 165.3, 161.2, 133.4, 133.3, 125.1, 116.4, 116.2; \quad \text{IR (KBr) 2967, 1885, 1857, 1784, 1585, 1286, 1239, 1177, 1029 cm}^{-1}; \quad \text{HRMS(ESI) calc. for (M + Na\textsuperscript{+}) 285.0339 found 285.0334.}
\end{align*}
\]

(2f) 4-tert-butylbenzoic anhydride

\[
\begin{align*}
\text{R}_f &= 0.3 \text{ (petroleum ether/ethyl acetate 15:1), colorless oil. H NMR (300 MHz, CDCl}_3\text{)} \delta (\text{ppm}): 8.08 \text{ (d, } J = 8.4 \text{ Hz, 4H), 7.53 \text{ (d, } J = 8.4 \text{ Hz, 4H), 1.36 (s, 18H); } ^{13}\text{C NMR (75 MHz, CDCl}_3\text{)} \delta (\text{ppm): 162.5, 158.5, 130.5, 126.2, 125.9, 35.3, 31.0; \quad IR (KBr) 2966, 1783, 1722, 1607, 1409, 1224, 1042, 999 cm}^{-1}; \quad \text{HRMS(ESI) calc. for (M + Na\textsuperscript{+}) 361.1780 found 361.1778.}
\end{align*}
\]

(2g) 4-(trifluoromethoxy)benzoic anhydride

\[
\begin{align*}
\text{R}_f = 0.3 \text{ (petroleum ether/ethyl acetate 11:1), White solid. m.p} = 68-69^\circ C, \quad \text{H NMR (300 MHz, CDCl}_3\text{)} \delta (\text{ppm): 8.19 \text{ (d, } J = 8.4 \text{ Hz, 4H), 7.36 \text{ (d, } J = 8.1 \text{ Hz, 4H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta (\text{ppm): 160.9, 153.9, 132.7, 126.8, 121.3, 120.6, 119.2; \quad IR (KBr) 3010, 1791, 1725, 1609, 1508, 1225, 1171 cm}^{-1}; \quad \text{HRMS(ESI) calc. for (M + Na\textsuperscript{+}) 361.1780 found 361.1778.}
\end{align*}
\]
HRMS (ESI) calc. for (M + Na\(^+\)) 417.0174 found 417.0172.

(2h) 2-chlorobenzoic anhydride

\[
\begin{array}{c}
\text{Cl} & \text{O} & \text{O} & \text{Cl} \\
\text{Cl} & \text{O} & \text{O} & \text{Cl} \\
\end{array}
\]

\(R_f = 0.3\) (petroleum ether/ethyl acetate 15:1), White solid.

\(m.p = 63-68^\circ C\), \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 8.03 (d, \(J = 7.5\) Hz, 2H), 7.54-7.49 (m, 4H), 7.42-7.36 (m, 2H);

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 160.4, 135.1, 134.1, 132.6, 131.6, 126.9; IR (KBr): 3010, 1783, 1721, 1593, 1442, 1209, 1074, 1008 cm\(^{-1}\); HRMS (ESI) calc. for (M + Na\(^+\)) 316.9748 found 316.9745.

(2i) 2-methylbenzoic anhydride

\[
\begin{array}{c}
\text{O} & \text{O} & \text{O} \\
\text{O} & \text{O} & \text{O} \\
\end{array}
\]

\(R_f = 0.3\) (petroleum ether/ethyl acetate 15:1), White solid.

\(m.p = 87-89^\circ C\), \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.96 (d, \(J = 7.7\) Hz, 2H), 7.40-7.45 (m, 2H), 7.24 (d, \(J = 8.8\) Hz, 4H),

\(2.62\) (s, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 162.9, 142.5, 133.6, 132.3, 131.4, 127.8, 126.1, 21.9; IR (KBr): 2973, 1787, 1729, 1601, 1460, 1193, 1055, 980 cm\(^{-1}\); HRMS (ESI) calc. for (M + Na\(^+\)) 277.0841 found 277.0839.

(2j) 2-ethylbenzoic anhydride

\[
\begin{array}{c}
\text{O} & \text{O} & \text{O} \\
\text{O} & \text{O} & \text{O} \\
\end{array}
\]

\(R_f = 0.3\) (petroleum ether/ethyl acetate 10:1), Colorless oil.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 8.02 (d, \(J = 8.1\) Hz, 2H),

7.56-7.51 (m, 2H), 7.37-7.25 (m, 4H), 3.0 (q, \(J = 7.2\)Hz, 4H),

1.29 (t, \(J = 7.2\)Hz, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 162.8, 148.4, 133.7, 131.4, 130.7, 127.4, 126.0, 27.6, 15.6; IR (KBr): 2964, 1782, 1723, 1604, 1465, 1229, 1052, 993 cm\(^{-1}\); HRMS (ESI) calc. for (M + Na\(^+\)) 305.1154 found 305.1157.

(2k) 2-methoxybenzoic anhydride

\[
\begin{array}{c}
\text{O} & \text{O} & \text{O} \\
\text{O} & \text{O} & \text{O} \\
\end{array}
\]

\(R_f = 0.3\) (petroleum ether/ethyl acetate 3:1), White solid.

\(m.p = 72-74^\circ C\), \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 8.00 (d, \(J = 6.9\)Hz, 2H),

7.55 (d, \(J = 6.7\)Hz, 2H), 7.06-6.92 (m, 4H),

3.84 (s, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 161.9, 160.1, 135.3, 133.0, 120.3,
118.1, 112.1, 55.8; IR (KBr); 2950, 1773, 1710, 1604, 1279, 1171, 1013 cm\(^{-1}\);
HRMS (ESI) calc. for (M + Na\(^{+}\)) 309.0739 found 309.0733.

(2l) 2-(trifluoromethoxy)benzoic anhydride

\[ \text{RF} = 0.3 \text{ (petroleum ether/ethyl acetate 10:1), white solid.} \]

m.p = 96-98°C, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm):
8.1 (d, \(J = 6.6 \text{ Hz}, 2\text{H})
7.71-7.64 (m, 4H, 2H)
7.48-7.26 (m, 4H);
\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 159.2, 148.4, 135.3, 134.3, 132.9, 127.2, 127.0, 122.8, 122.6, 122.4, 121.9, 118.5; IR(KBr) : 2976, 1690, 1601, 1496, 1457, 1413, 1260, 1154 cm\(^{-1}\);
HRMS (ESI) calc. for (M + Na\(^{+}\)) 417.0174 found 417.0171.

(2m) 3-methoxybenzoic anhydride

\[ \text{RF} = 0.3 \text{ (petroleum ether/ethyl acetate 8:1), White solid.} \]
m.p = 65-66 °C, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm):
7.73 (d, \(J = 7.8 \text{ Hz}, 2\text{H})
7.67 (s, 2H)
7.4 (t, \(J = 7.8 \text{ Hz}, 2\text{H})
7.21 (d, \(J = 7.8 \text{ Hz}, 2\text{H})
3.87 (s, 6H);
\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 162.3, 159.8, 130.1, 122.9, 120.9, 115.1, 55.6; IR (KBr): 3008, 1771, 1725, 1609, 1225, 1171, 1035, 1004 cm\(^{-1}\); HRMS (ESI) calc. for (M + Na\(^{+}\)) 309.0739 found 309.0736.

(2n) 3-methylbenzoic anhydride

\[ \text{RF} = 0.3 \text{ (petroleum ether/ethyl acetate 10:1), White solid.} \]
m.p = 64-66°C, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.8 (s, 4H)
7.39-7.32 (m, 6H)
2.36 (s, 6H);
\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 162.7, 138.8, 135.3, 131.1, 128.8, 127.7, 21.3;
IR (KBr): 3010, 1791, 1717, 1589, 1256, 1175, 1039 cm\(^{-1}\); HRMS (ESI) calc. for (M + Na\(^{+}\)) 277.0841 found 277.0839.

(2o) 2,4-dimethoxybenzoic anhydride
R_f = 0.3 (petroleum ether/ethyl acetate 1.5:1), White solid. m.p = 104-106 °C, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 8.0 ( d, \(J= 8.7\)Hz, 2H), 6.65-46 (m, 4H), 3.89 (s, 6H), 3.82 (s, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 165.5, 162.3, 161.6, 135.2, 111.0, 105.2, 98.8, 55.8, 55.5; IR (KBr): 3009, 1775, 1713, 1609, 1225, 1167, 1039, 1000 cm\(^{-1}\); HRMS (ESI) calc. for (M + Na\(^+\)) 369.0950 found 309.0945.

(2p) 3,5-dimethylbenzoic anhydride

R_f = 0.3 (petroleum ether/ethyl acetate 15:1), White solid. m.p = 173-176 °C, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.68 (s, 4H), 7.24 (s, 2H), 2.33 (s, 12H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 163.0, 138.6, 136.2, 128.8, 128.3, 21.2, 21.1; IR (KBr): 3010, 1779, 1717, 1609, 1225, 1171, 1043, 1000 cm\(^{-1}\); HRMS (ESI) calc. for (M + Na\(^+\)) 305.1154 found 305.1153.

(2q) 3,4-dimethylbenzoic anhydride

R_f = 0.3 (petroleum ether/ethyl acetate 15:1), White solid. m.p =120-121 °C, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.8 (m, 4H), 7.2 ( s, 2H), 2.3 ( s, 12H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 162.9, 144.2, 137.3, 131.5, 130.1, 128.1, 126.5, 20.2, 19.7; IR (KBr): 3010, 1771, 1713, 1612, 1244, 1206, 1120, 1051 cm\(^{-1}\); HRMS (ESI) calc. for (M + Na\(^+\)) 305.1154 found 305.1150.

(2r) 2,4,6-trimethylbenzoic anhydride

R_f = 0.3 (petroleum ether/ethyl acetate 20:1), White solid. m.p = 102-104 °C, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 6.87 ( s, 4H) 2.39 ( s, 12 H) 2.28 ( s, 6 H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 166.3, 140.7, 136.3, 128.8, 21.1, 20.1; IR (KBr): 3010, 1779, 1713, 1609, 1221, 1171, 1039, 1004 cm\(^{-1}\); HRMS (ESI) calc. for (M + Na\(^+\)) 333.1467 found 333.1462.
1-Naphthoic Anhydride (2s)

R_f = 0.3 (petro ether/ethyl acetate 6:1), white solid. m.p = 142-144 °C, 1H NMR (400 MHz, CDCl_3) δ (ppm): 9.1 (d, J = 8.6Hz, 2 H), 8.4 (d, J = 4.5Hz, 2 H), 8.1 (d, J = 8.1Hz, 2 H), 7.9 (d, J = 7.9Hz, 2 H), 7.5–7.7 (m, 6 H); 13C NMR (100MHz, CDCl_3) δ (ppm): 162.9, 135.5, 134.0, 132.1, 128.8, 129.3, 127.2, 126.8, 126.2, 125.2, 124.9; IR (KBr): 3054, 1771, 1705, 1593, 1225, 1171, 1054, 958 cm⁻¹; HRMS (ESI) calc. for (M + Na⁺) 349.0841 found 349.0838.

4-Phenylbenzoic anhydride (2t)

R_f = 0.3 (petroleum ether/ethyl acetate 5:1), white solid. m.p = 137-139 °C, 1H NMR (400 MHz, CDCl_3) δ (ppm): 8.2 (d, J = 7.4 Hz, 4H), 7.7(d, J = 7.9Hz, 4H), 7.6 (d, J = 7.2Hz, 4H), 7.4 (m, J = 7.3Hz, 6H); 13C NMR (100 MHz, CDCl_3) δ (ppm): 162.4, 147.4, 139.6, 131.2, 129.1, 128.6, 127.7, 127.6, 127.4; IR (KBr): 3010, 1770, 1730, 1600, 1244, 1175, 1050, 961 cm⁻¹; HRMS (ESI) calc. for (M + Na⁺) 401.1154 found 401.1152.

6. References available for known products

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NA: Not available;

NO: No reference was found via SCIfinder.

**References:**


7. Traces of the $^1$H NMR and $^{13}$C NMR spectra of products

![NMR Spectra](image)
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