**Tandem one-pot CO$_2$ reduction-silyloxy carbonylation of aryl/vinyl halides to access carboxylic acids**

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**Supplementary information**

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General: All the reagents and solvents were used as such received unless otherwise specified. $^1$H NMR and $^{13}$C NMR spectra were recorded in CDCl$_3$/DMSO-d$_6$ on a Bruker Avance 400 NMR spectrometer. Chemical shifts are given in ppm with reference to TMS attributed to 0 ppm and spin-spin coupling constants, $J$, are given in Hz. HRMS data were recorded on a Finnigan MAT 95 system.

I. Experimental Procedures:

1. General procedure for preparation of mono carboxylic acids

To a mixture of Cu(OAc)$_2$.H$_2$O (0.01 mmol, 1.0 mol%) and 1,2-bis(diphenylphosphanyl)benzene (0.015 mmol, 1.5 mol%) in an oven dried Schlenk tube connected to a CO$_2$ balloon, a solution of PMHS (2.5 mmol, 2.5 equiva.) in 1,4-dioxane (2.0 mL) was added, flushed the tube with CO$_2$ and heated the resulting blue solution to 65 °C while vigorously stirring for 20 minutes under balloon pressure CO$_2$ and the solution becomes light brown. This formate solution was removed from the heating bath and added toluene (8 ml), aryl/vinyl bromide (1.0 mmol, 1.0 equiv.), Pd(OAc)$_2$ (3 mol%, 0.03 equiva.), xantphos (6 mol%, 0.06 equiva.) and Et$_3$N (2.5 mmol, 2.5 equiva.) sequentially under CO$_2$ atmosphere. CO$_2$ was removed, the Schlenk tube was closed and heated to 100 °C for the time period until the disappearance of aryl bromide as shown by TLC. Then, the reaction mixture was cooled to ambient temperature and added 10 ml of 1N NaOH or NaHCO$_3$ and stirred for 10 min. The resulting emulsion was filtered and the filtrate was extracted with EtOAc (3*15 mL), organic fractions separated and discarded. Aqueous layer was acidified with 1.0 N HCl or citric acid and extracted with EtOAc (3*15 mL). The later organic fractions were dried over Na$_2$SO$_4$ and concentrated to get the pure acid compound.

2. General procedure for preparation of di/tri-carboxylic acids from dihaloaryls

To a mixture of Cu(OAc)$_2$.H$_2$O (0.02 mmol, 2 mol%) and 1,2-bis(diphenylphosphanyl)benzene L1 (0.03 mmol, 3 mol%) in an oven dried Schlenk tube connected to a CO$_2$ balloon, a solution of PMHS (4.0 mmol, 4.0 equiva.) in 1,4-dioxane (3.0 mL) was added, flushed the tube with CO$_2$, heated the resulting blue solution to 65 °C while vigorously stirring for 25 minutes under CO$_2$ balloon pressure and the solution becomes light brown. This formate solution was removed from the heating bath and added toluene (12 ml), aryl dihalide (1.0 mmol, 1.0 equiv.), Pd(OAc)$_2$ (5 mol%, 0.05 mmol), xantphos L2 (10 mol%, 0.1 mmol) and Et$_3$N (4.0 mmol, 4.0 equiva.) sequentially under CO$_2$ atmosphere. The
Schlenk tube was closed, CO$_2$ balloon was removed, and heated to 100 °C for the time 10 h – 20 h. Then, the reaction mixture was cooled to ambient temperature and added 20 ml of 1N NaOH and stirred for 10 min. The resulting emulsion was filtered and the filtrate was extracted with EtOAc (3*20 mL), aqueous portion separated was acidified with 1.0 N HCl or 1M citric acid, solid precipitated was filtered, suck dried to get the pure diacid. If no precipitation occurs, extracted with EtOAc (3*30 mL) and these organic fractions were dried over Na$_2$SO$_4$ and concentrated to get the pure diacid compound. (Note: For tricarboxylation: PMHS (5.0 equiva.), Pd(OAc)$_2$ (8 mol%), L2 (16 mol%) and Et$_3$N (5.0 equiva.)

3. General procedure for optimization studies:

![Reaction Diagram](https://via.placeholder.com/150)

To a mixture of Cu(OAc)$_2$.H$_2$O (0.01 mmol, 1.0 mol%) and 1,2-bis(diphenylphosphaneyl)benzene (0.015 mmol, 1.5 mol%) in an oven dried Schlenk tube connected to a CO$_2$ balloon, a solution of R$_3$SiH (2.5 equiva.) in 1,4-dioxane (2.0 mL) was added, flushed the tube with CO$_2$. Heated the resulting blue solution to 65 °C with vigorous stirring for 20 minutes under CO$_2$ balloon pressure and the solution becomes light brown. To silyloxycarbonylation take effect, this formate solution was lifted up the heating bath and added solvent B (8 mL), aryl bromide (1.0 mmol, 1.0 equiv.), Pd(II), L2 and Et$_3$N (2.5 equiva.) sequentially under CO$_2$ atmosphere. CO$_2$ was removed, the Schlenk tube was closed and heated to 100 °C for 3 h. Then, the reaction mixture was cooled to ambient temperature, added 0.5 ml of H$_2$O, concentrated to dryness under reduced pressure and determined the constituents by $^1$H NMR.
Table S1: Solvent screening for silyloxycarbonylation

\[
\text{PMHS (2.5 mmol)} + \text{CO}_2 \xrightarrow{\text{b, balloon}} \text{dioxane (2 mL)} \xrightarrow{65^\circ C, 20 \text{ min}} \text{Et}_3\text{N (2.5 mmol), toluene (8 mL)} \xrightarrow{100^\circ C, 3 \text{ h, closed \textit{vessel}}} \text{Pd(OAc)}_2 (3 \text{ mol%})/\text{L2 (6 mol%)} \xrightarrow{1a (1.0 mmol)} 2a
\]

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<thead>
<tr>
<th>entry</th>
<th>Solvent B</th>
<th>% conversion(^a)</th>
<th>2a(^a) %</th>
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<td>1</td>
<td>Dioxane</td>
<td>100</td>
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<tr>
<td>2</td>
<td>THF</td>
<td>50</td>
<td>45</td>
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<tr>
<td>3</td>
<td>ACN</td>
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<td>46</td>
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\(^a\) determined by \(^1\)H NMR

Table S2: Screening of hydrosilane\(^c\)

\[
\text{R}_3\text{SiH (2.5 mmol)} + \text{CO}_2 \xrightarrow{\text{b, balloon}} \text{dioxane (2 mL)} \xrightarrow{65^\circ C, 20 \text{ min}} \text{Et}_3\text{N (2.5 mmol), toluene (8 mL)} \xrightarrow{100^\circ C, 3 \text{ h, closed \textit{vessel}}} \text{Pd(OAc)}_2 (3 \text{ mol%})/\text{L2 (6 mol%)} \xrightarrow{1a (1.0 mmol)} 2a
\]

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<tr>
<th>entry</th>
<th>R(_3)SiH</th>
<th>% conversion(^a)</th>
<th>2a(^a) %</th>
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<tr>
<td>1</td>
<td>PMHS(^b)</td>
<td>90</td>
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<td>2</td>
<td>Et(_3)SiH</td>
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\(^a\) see table S1; \(^b\) 2.0 equiv.; \(^c\) 2.0 equiv.; \(^d\) not determined
Table S3: Catalyst screening for silyloxy carbonylation

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<th>2a^b %</th>
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<td>Pd(OAc)(_2) (3 mol%)/PPPh(_3) (6 mol%)</td>
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<tr>
<td>2</td>
<td>Pd(OAc)(_2) (3 mol%)/L1 (6 mol%)</td>
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<td>6</td>
<td>PdCl(_2) (3 mol%)/L2 (6 mol%)</td>
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<td>69</td>
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<tr>
<td>3</td>
<td>Pd(_2)(dba)(_3) (3 mol%)/L2 (6 mol%)</td>
<td>100</td>
<td>81</td>
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<tr>
<td>4</td>
<td>Pd(OAc)(_2) (3 mol%)/L2 (3 mol%)</td>
<td>95</td>
<td>45</td>
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<tr>
<td>5(^c)</td>
<td>Pd(OAc)(_2) (1 mol%)/L2 (2 mol%)</td>
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<td>90</td>
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<tr>
<td>6(^d)</td>
<td>Pd(OAc)(_2) (3 mol%)/L2 (3 mol%)</td>
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<td>60</td>
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^a see table S1; ^b isolated yield; ^c reaction time 6 h; ^d time 16 h.

Table S4: Control reactions

Standard reaction

Deviations from standard reaction condition:

```
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<th>2a^a %</th>
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<td>1</td>
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<tr>
<td>2</td>
<td>Without Et(_3)N</td>
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<td>nd</td>
</tr>
<tr>
<td>3</td>
<td>Without Pd(OAc)(_2)/L2</td>
<td>0</td>
<td>nd</td>
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<tr>
<td>4</td>
<td>toluene instead of dioxane</td>
<td>100</td>
<td>62</td>
</tr>
<tr>
<td>5</td>
<td>Pd(OAc)(_2)/L2 instead of Cu(OAc)(_2).H(_2)O/L1</td>
<td>70</td>
<td>48</td>
</tr>
<tr>
<td>6</td>
<td>One-time addition</td>
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^a see table S1
Table S5: Hydrolysis role

Standard condition:

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<th>Yield (%)</th>
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</tr>
<tr>
<td>No 2</td>
<td>&lt; 10</td>
<td>0 trace</td>
</tr>
</tbody>
</table>

To a mixture of Cu(OAc)₂.H₂O (1.0 mol%) and 1,2-bis(diphenylphosphanylmethyl)benzene (1.5 mol%) in an oven dried Schlenk tube connected to a CO₂ balloon, a solution of PMHS (2.5 mmol) in 1,4-dioxane (2.0 mL) was added, flushed the tube with CO₂. Heated the resulting blue solution to 65 °C with vigorous stirring for 20 minutes under CO₂ balloon pressure and the solution becomes light brown. Removed CO₂, added H₂O (2.5 mmol) and stirred at 65 °C under Ar-atmosphere for 20 min. This solution was lifted up the heating bath and added toluene (8 mL), aryl bromide (1.0 mmol, 1.0 equiv.), Pd(II), L₂ and Et₃N (2.5 equiv.) sequentially under Ar-atmosphere. The Schlenk tube was closed and heated to 100 °C for 3 h. Then, the reaction mixture was cooled to ambient temperature, added 0.5 ml of H₂O, concentrated to dryness under reduced pressure and determined the constituents by ¹H NMR.

Table S6: Formic acid role

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<th>Conditions</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No 1</td>
<td>&gt; 95</td>
<td>0</td>
</tr>
<tr>
<td>No 2</td>
<td>&gt; 95</td>
<td>0</td>
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</tbody>
</table>
To a mixture of Cu(OAc)$_2$.H$_2$O (1.0 mol%) and 1,2-bis(diphenylphosphanyl)benzene (1.5 mol%) in an oven dried Schlenk tube, added toluene (8 mL), aryl bromide (1.0 mmol, 1.0 equiv.), Pd(OAc)$_2$ (3 mol%), L2 (6 mol%) and Et$_3$N (2.5 equiv.) sequentially under Ar-atmosphere. The Schlenk tube was closed, a solution of HCOOH (2.5 mmol) in 1,4-dioxane (2.0 mL) was added and heated to 100 °C for 3 h. Then, the reaction mixture was cooled to ambient temperature, added 0.5 ml of H$_2$O, concentrated to dryness under reduced pressure and determined the constituents by $^1$H NMR.

4. Procedure for silyl ester (2a’):

To a mixture of Cu(OAc)$_2$.H$_2$O (0.01 mmol, 1.0 mol%) and 1,2-bis(diphenylphosphanyl)benzene (0.015 mmol, 1.5 mol%) in an oven dried Schlenk tube connected to a CO$_2$ balloon, a solution of (EtO)$_3$SiH (2.5 equiv.) in 1,4-dioxane (2.0 mL) was added, flushed the tube with CO$_2$. Heated the resulting blue solution to 65 °C with vigorous stirring for 20 minutes under CO$_2$ balloon pressure and the solution becomes light brown. To silyloxycarbonylation take effect, this formate solution lifted up the heating bath and added toluene (8 mL), aryl bromide (1.0 mmol, 1.0 equiv.), Pd(OAc) (3 mol%), L2 (6 mol%) and dry Et$_3$N (2.5 equiv.) sequentially under CO$_2$ atmosphere. CO$_2$ was removed, the Schlenk tube was closed and heated to 100 °C for 3 h. The Schlenk tube was cooled to ambient temperature, 1 mL of the reaction mass was taken under argon environment and concentrated to dryness. The sample was dissolved in deuterated solvent, added di-tert-butyl oxalate as internal standard, and recorded the NMR spectra.

2-Naphthoic (triethyl silicic) anhydride (2a’): $^1$H NMR (400 MHz, Chloroform-$_d$) $\delta$ 8.65 (d, $J = 1.8$ Hz, 1H), 8.10 – 8.05 (m, 1H), 7.90 (dd, $J = 8.1$, 5.8 Hz, 3H), 7.64 – 7.51 (m, 2H), 4.07 (dq, $J = 9.4$, 7.0 Hz, 6H), 1.32 (t, $J = 7.0$ Hz, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.3, 165.1, 135.7, 132.5, 132.2, 131.8, 129.5, 128.5, 128.2, 127.8, 126.7, 125.8, 60.1, 18.0; $^{29}$Si NMR (139 MHz, DMSO-$d_6$) $\delta$ -92.5.
Figure S1: $^1$H NMR of compound 2a' and 2a (in situ)

Figure S2: expansion region; (A) $^1$H NMR of compound 2a, (B) $^1$H NMR of compound 2a+$2a'$ (in situ)
Figure S3: $^{13}$C NMR of compound $2a + 2a'$ (in situ); {$\#$} (CO$_2$Bu)$_2$

Figure S4: expansion region; (A) $^{13}$C spectra of $2a + 2a'$ (in situ); (B) $^{13}$C spectra of $2a$; {$\#$} (CO$_2$Bu)$_2$
Figure S5: $^{29}$Si NMR in DMSO-d$_6$ of compound 2a' (in situ)$^{25}$

II. Spectral data:

2-Naphthoic acid (2a)$^1$: white solid; yield 98%; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.77 – 8.70 (m, 1H), 8.14 (dd, $J$ = 8.6, 1.7 Hz, 1H), 8.03 – 7.97 (m, 1H), 7.96 – 7.88 (m, 2H), 7.61 (dddd, $J$ = 22.1, 8.1, 6.9, 1.4 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.0, 136.0, 132.5, 132.2, 129.6, 128.7, 128.3, 127.8, 126.8, 126.5, 125.4.

4-(Methoxycarbonyl)benzoic acid (2c)$^1$: white solid; yield 94%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.34 (s, 1H), 8.05 (s, 4H), 3.88 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 167.1, 166.1, 135.3, 133.7, 130.1, 129.9, 53.0.

4-Acetylbenzoic acid (2d)$^1$: half-white solid, yield 72%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.04 (d, $J$ = 1.6 Hz, 4H), 2.62 (d, $J$ = 1.6 Hz,
3H); $^{13}$C NMR (101 MHz, DMSO) δ 198.2, 167.1, 140.3, 135.0, 130.0, 128.8, 27.5.

4-Formylbenzoic acid (2e): half-white solid, yield 97%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 13.31 (s, 1H), 10.10 (s, 1H), 8.17 – 8.07 (m, 2H), 8.05 – 7.97 (m, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 193.5, 167.0, 139.4, 136.1, 130.4, 130.0.

4-Nitrobenzoic acid (2f): pale yellow solid; yield 96%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 13.42 (s, 1H), 8.41 – 8.25 (m, 2H), 8.23 – 8.06 (m, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 166.3, 150.5, 136.9, 131.2, 124.2.

4-Chlorobenzoic acid (2g): white solid; yield 77%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 13.16 (s, 1H), 7.93 (d, $J$ = 8.1 Hz, 2H), 7.56 (d, $J$ = 8.1 Hz, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 166.9, 138.2, 131.6, 130.1, 129.2.

4-Methoxybenzoic acid (2h): white solid; yield 90%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.59 (s, 1H), 7.92 – 7.85 (m, 2H), 7.05 – 6.96 (m, 2H), 3.81 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 167.5, 163.4, 131.9, 123.5, 114.3, 56.0.

Benzo[d][1,3]dioxole-5-carboxylic acid (2i): white solid, yield 96%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.74 (s, 1H), 7.54 (dd, $J$ = 8.1, 1.7 Hz, 1H), 7.35 (d, $J$ = 1.7 Hz, 1H), 6.99 (d, $J$ = 8.1 Hz, 1H), 6.11 (s, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 167.1, 151.6, 148.0, 125.4, 125.2, 109.3, 108.5, 102.4.

3-Nitrobenzoic acid (2j): pale yellow solid, yield 77%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.60 (t, $J$ = 2.0 Hz, 1H), 8.45 (dd, $J$ = 8.3, 2.4 Hz, 1H), 8.33 (d, $J$ = 7.9 Hz, 1H), 7.80 (t, $J$ = 8.0 Hz, 1H); $^{13}$C NMR (101 MHz, DMSO) δ 166.0, 148.4, 135.89, 133.0, 131.0, 127.8, 124.2.

2-Fluorobenzoic acid (2k): White solid, yield 45%; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 13.18 (s, 1H), 7.87 (td, $J$ = 7.6, 1.7 Hz, 1H), 7.64 (dddd, $J$ = 7.9, 6.9, 5.0, 1.9 Hz, 1H), 7.36 – 7.26 (m, 2H); $^{13}$C NMR
3-Fluoro-4-methylbenzoic acid (2l): white solid, yield 84%; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.81 (dd, $J = 7.8$, 1.6 Hz, 1H), 7.74 (dd, $J = 10.0$, 1.6 Hz, 1H), 7.30 (t, $J = 7.7$ Hz, 1H), 2.37 (d, $J = 2.0$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.2, 162.2, 159.8, 131.6, 128.8, 125.8, 116.8, 116.5.

Thiophene-3-carboxylic acid (2m): half-white solid; yield 94%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.66 (s, 1H), 8.24 (dd, $J = 3.0$, 1.2 Hz, 1H), 7.59 (dd, $J = 5.0$, 3.0 Hz, 1H), 7.42 (dd, $J = 5.1$, 1.1 Hz, 1H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 164.0, 134.8, 133.7, 128.2, 127.7.

5-(Methoxycarbonyl)furan-2-carboxylic acid (2n): white solid; yield 75%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.45 (s, 1H), 7.40 (d, $J = 3.6$ Hz, 1H), 7.33 (d, $J = 3.6$ Hz, 1H), 3.86 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 159.2, 158.4, 147.8, 146.1, 119.4, 118.8, 52.7.

1-(tert-Butoxycarbonyl)-1H-indole-5-carboxylic acid (2o): half-white solid, yield 54%; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.40 (s, 1H), 8.23 (d, $J = 8.8$ Hz, 1H), 8.10 (dd, $J = 8.8$, 1.8 Hz, 1H), 7.68 (d, $J = 3.7$ Hz, 1H), 6.68 (d, $J = 3.8$ Hz, 1H), 1.70 (d, $J = 1.4$ Hz, 9H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 167.8, 144.6, 125.7, 122.6, 121.4, 119.4, 119.0, 110.3, 103.1, 79.8, 23.4; HRMS: calcd for C$_{14}$H$_{16}$NO$_4$ (M+H$^+$): 262.1074, Found: 262.1072.

Quinoline-3-carboxylic acid (2p): half-white solid, yield 92%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.36 (s, 1H), 9.31 (d, $J = 2.1$ Hz, 1H), 8.96 (d, $J = 2.1$ Hz, 1H), 8.18 (d, $J = 8.1$ Hz, 1H), 8.09 (d, $J = 8.4$ Hz, 1H), 7.98 – 7.83 (m, 1H), 7.70 (t, $J = 7.5$ Hz, 1H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 166.8, 150.3, 149.6, 139.0, 132.4, 130.0, 129.3, 127.9, 127.1, 124.1.
Quinoline-6-carboxylic acid (2q): white solid, yield 78%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.23 (s, 1H), 9.00 (dd, $J = 4.2$, 1.7 Hz, 1H), 8.66 (d, $J = 1.9$ Hz, 1H), 8.55 (dd, $J = 8.5$, 1.7 Hz, 1H), 8.21 (dd, $J = 8.8$, 1.9 Hz, 1H), 8.08 (d, $J = 8.8$ Hz, 1H), 7.61 (dd, $J = 8.3$, 4.2 Hz, 1H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 167.5, 153.1, 149.8, 138.0, 131.4, 129.8, 129.3, 129.2, 127.7, 122.7.

3-Bromobenzoic acid (2r): light grey solid; yield 52%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.05 (bs, 1H); 8.03 (t, $J = 1.8$ Hz, 1H), 7.92 (dt, $J = 7.5$, 1.3 Hz, 1H), 7.82 (dd, $J = 8.1$, 2.0 Hz, 1H), 7.47 (t, $J = 7.9$ Hz, 1H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 166.4, 136.0, 133.5, 132.2, 131.4, 128.7, 122.2.

Methyl 3-acetylbenzoate (2s): white solid; yield 76%; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.57 (dt, $J = 1.8$, 1.1 Hz, 1H), 8.21 (dt, $J = 7.7$, 1.5 Hz, 1H), 8.14 (ddd, $J = 7.8$, 1.8, 1.3 Hz, 1H), 7.54 (td, $J = 7.8$, 0.6 Hz, 1H), 3.94 (s, 3H), 2.64 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.2, 166.3, 137.3, 133.9, 132.3, 130.7, 129.5, 128.8, 52.4, 26.7.

3-(Methoxycarbonyl)benzoic acid (2t): white solid, yield 20%; $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.77 (d, $J = 1.7$ Hz, 1H), 8.30 (dt, $J = 7.8$, 1.9 Hz, 2H), 7.59 (t, $J = 7.8$ Hz, 1H), 3.97 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.4, 166.1, 134.7, 134.3, 131.4, 130.8, 129.6, 128.8, 52.5.

6-Chloropicolinic acid (2u): half-white solid; yield 45%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.40 (s, 1H), 8.07 – 8.00 (m, 2H), 7.74 (dd, $J = 6.1$, 2.8 Hz, 1H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 165.3, 150.6, 149.3, 141.6, 128.4, 124.5.

Quinoline-2-carboxylic acid (2v): made salt with AcOH after extraction with EtOAc and concentrated to obtain half-white solid. yield 45%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.65 (s, 1H), 8.55 (d, $J = 8.5$ Hz, 1H), 8.22 – 8.02 (m, 3H), 7.87 (t, $J = 7.7$ Hz, 1H), 7.74 (t, $J = 7.7$ Hz, 1H), 7.60 – 7.25 (m, 5H), 6.94 (s, 1H), 6.86 (d, $J = 8.2$ Hz, 1H), 6.70 (d, $J = 8.2$ Hz, 1H), 3.94 (s, 3H), 2.64 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.8, 166.3, 137.3, 133.9, 132.3, 130.7, 129.5, 128.8, 52.4, 26.7.
= 7.5 Hz, 1H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 166.8, 149.2, 147.3, 138.1, 131.0, 130.2, 129.3, 129.0, 128.5, 121.2.

Terephthalic acid (3a)$^{15}$: half-white solid; yield 93%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.19 (s, 2H), 8.03 (s, 4H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 167.2, 135.0, 129.9.

Isophthalic acid (3b)$^{16}$: light grey solid, yield 62%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.15 (s, 2H), 8.47 (d, $J = 1.8$ Hz, 1H), 8.16 (dd, $J = 7.8$, 1.7 Hz, 2H), 7.63 (t, $J = 7.8$ Hz, 1H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 167.1, 133.9, 131.7, 130.5, 129.6.

2-Methyl terephthalic acid (3c)$^{17}$: pale yellow solid, yield 72%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.17 (bs, 2H), 7.93 – 7.77 (m, 3H), 2.54 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 168.7, 167.2, 139.4, 135.1, 133.6, 132.6, 130.6, 127.1, 21.4; HRMS: calcd for C$_9$H$_7$O$_4$ (M-H$^+$) 179.0350, Found 179.0358.

Naphthalene-2,6-dicarboxylic acid (3d)$^{18}$: half white solid, yield 93%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.23 (s, 2H), 8.65 (s, 2H), 8.19 (d, $J = 8.6$ Hz, 2H), 8.04 (d, $J = 8.6$ Hz, 2H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 167.7, 134.7, 130.7, 130.2, 126.4.

[1,1'-biphenyl]-4,4'-dicarboxylic acid (3e)$^{19}$: white solid, yield 91%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.96 (s, 2H), 8.08 – 8.01 (m, 4H), 7.89 – 7.82 (m, 4H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 167.5, 143.6, 130.9, 130.5, 127.6.

[2,2'-bipyridine]-4,4'-dicarboxylic acid (3f)$^{20}$: milky white solid; yield 84%; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.82 (s, 2H), 8.92 (d, $J = 4.9$ Hz, 2H), 8.87 – 8.84 (m, 2H), 7.92 (dd, $J = 5.0$, 1.6 Hz, 2H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 166.5, 155.9, 151.1, 140.1, 123.9, 120.0.
Benzene-1,3,5-tricarboxylic acid (4)\(^\text{21}\): white solid; yield 97%; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 13.34 (s, 3H), 8.63 (s, 3H); \(^13\)C NMR (101 MHz, DMSO) \(\delta\) 166.4, 134.1, 132.4.

\textbf{trans-Cinnamic acid (8a)}\(^\text{22}\): white solid; yield 91%; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.41 (s, 1H), 7.71 – 7.64 (m, 2H), 7.59 (dd, \(J = 16.0, 1.7\) Hz, 1H), 7.40 (q, \(J = 2.6\) Hz, 3H), 6.53 (dd, \(J = 16.0, 1.8\) Hz, 1H); \(^13\)C NMR (101 MHz, DMSO) \(\delta\) 168.1, 144.3, 134.6, 130.6, 129.3, 128.6, 119.6.

\textbf{2-Phenylacrylic acid (8b)}\(^\text{23}\): white solid, yield 89%; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.82 (s, 1H), 7.46 – 7.40 (m, 2H), 7.40 – 7.32 (m, 3H), 6.23 (d, \(J = 1.2\) Hz, 1H), 5.96 (d, \(J = 1.2\) Hz, 1H); \(^13\)C NMR (101 MHz, DMSO) \(\delta\) 168.1, 141.9, 137.1, 128.5, 128.4, 128.3, 126.4.

\textbf{1H-indene-2-carboxylic acid (8c)}\(^\text{24}\): white solid, yield 93%; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.51 (s, 1H), 7.68 (d, \(J = 2.1\) Hz, 1H), 7.62 – 7.50 (m, 2H), 7.33 (dt, \(J = 5.2, 2.1\) Hz, 2H), 3.62 (s, 2H); \(^13\)C NMR (101 MHz, DMSO) \(\delta\) 166.2, 145.2, 143.1, 140.7, 139.0, 127.8, 127.3, 124.9, 123.8, 38.6.

### III. References

1. Compounds 2a, 2b, 2c, 2d, 2e, 2h, 2i, 2j, 2n, 2s, 8a: X. Zhang, W.-Z. Zhang, L.-L Shi, C.-X. Guo, L.-L. Zhang and X.-B. Lu, 

2. Compounds 2b, 2c, 2g, 2j, 2v: M. Yoshida, Y. Katagiri, W.-B. Zhu, K. Shishido, 

3. Compound 2f: W. Wang, G. Zhang, R. Lang, C. Xia and F. Li, 
   \textit{Green Chem.} 2013, 15, 635.


5. Compound 2l: C. J. Mallia, G. C. Walter and I. R. Baxendale, 

6. Compound 2m: W. Han, F. Jin and Q. Zhou, 
   \textit{Synthesis (Stuttg).} 2015, 47, 1861.

7. Compound 2n: C. Schmuck and U. Machon, 
8. Compound 2o: new compound
IV. Copies of $^1$H NMR and $^{13}$C NMR
HNMR-20180326-UMMAR-045-31a.10.fid
PROTON DMSO (D:\NMR400\503) nmr 20

HNMR-20180326-UMMAR-045-31a.11.fid
C12CPD DMSO (D:\NMR400\503) nmr 20