Supporting Information

Photocarboxylation of Benzylic C-H bonds

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1. General information

All NMR spectra were recorded at room temperature using a Bruker Avance 300 (300 MHz for $^1$H, 75 MHz for $^{13}$C, 282 MHz for $^{19}$F) or a Bruker Avance 400 (400 MHz for $^1$H, 100 MHz for $^{13}$C, 376 MHz for $^{19}$F) or a Bruker Avance 600 (600 MHz for $^1$H, 150 MHz for $^{13}$C). All chemical shifts are reported in δ-scale as parts per million [ppm] (multiplicity, coupling constant $J$, number of protons) relative to the solvent residual peaks as the internal standard. Coupling constants $J$ are given in Hertz [Hz]. Abbreviations used for signal multiplicity: $^1$H-NMR: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, and m = multiplet. High resolution mass spectra (HRMS) were obtained from the central analytic mass spectrometry facilities of the Faculty of Chemistry and Pharmacy, Regensburg University, and are reported according to the IUPAC recommendations 2013. All mass spectra were recorded on a Finnigan MAT 95, Thermo Quest Finnigan TSQ 7000, Finnigan MATSSQ 710 A or an Agilent Q-TOF 6540 UHD instrument. GC measurements were performed on a GC 7890 from Agilent Technologies. Data acquisition and evaluation was done with Agilent ChemStation Rev.C.01.04. Analytical TLC was performed on silica gel coated alumina plates (MN TLC sheets ALUGRAM® Xtra SIL G/UV254). Visualization was done by UV light (254 or 366 nm). If necessary, potassium permanganate was used for chemical staining. Purification by column chromatography was performed with silica gel 60 M (40-63 μm, 230-440 mesh, Merck) on a Biotage® Isolera TM Spektra One device. Gas chromatography (GC) measurements were performed on a GC 7890 from Agilent Technologies. Reactions about carboxylation of benzylic C-H bond were performed with 455 nm LEDs (OSRAM Oslon SSL 80 royal-blue LEDs (3.5 V, 700 mA; 2.7-3.5 V, 2 A). UV–Vis and fluorescence measurements were performed with a Varian Cary 100 UV/Vis spectrophotometer and FluoroMax-4 spectrofluorometer, respectively. Electrochemical studies were carried out under argon atmosphere. The measurements were performed in anhydrous DMF containing 0.1 M tetra-n-butylammonium tetrafluoroborate (TBA TF B) using ferrocene/ferrocinium (Fc/Fc$^+$) as an internal reference. A glassy carbon electrode (working electrode), platinum wire counter electrode, and Ag quasi-reference electrode were employed. Substrates ethylbenzene (1a), 2-ethyltoluene (1b), 3-ethyltoluene (1c), 4-ethyltoluene (1d), 2-ethylanisole (1e), 4-ethylanisole (1f), 1-ethyl-4-fluorobenzene (1g), 1-ethyl-4-chlorobenzene (1h), 1-phenylpropane (1i), 1-phenylbutane (1j), isopentylbenzene (1k), bibenzyl (1l), 9,10-dihydroanthracene (1s), acenaphthene (1t), 9,10-dihydrophenanthrene (1u), 2-ethylthiophene (1v), 2-ethylbenzofuran (1w) and 2,3-dihydrobenzofuran (1x) are commercially available and were used without further purification. Other substrates were synthesized according to the reported literatures, shown below. For all the thiol catalysts tried here are also commercially available. For the photosensitizers, 2,4,5,6-tetra(carbazol-9-yl)isophthalonitrile (4CzIPN), 2,4,6-tris(diphenylamino)-5-fluoroisophthalonitrile (3DPAFIPN), 2,4,6-tris(diphenylamino)-3,5-difluorobenzonitrile (3DPA2FBN), 2,3,4,5,6-penta(9H-carbazol-9-yl)benzonitrile (5CzBN), 2,3,5,6-tetra(9H-carbazol-9-yl)benzonitrile (4CzBN), Ir(ppy)$_3$, Ir(ppy)$_2$(dtBubpy)PF$_6$ and Ir(df-CF$_3$-ppy)$_2$(dtBubpy)PF$_6$ were synthesized according to the reported procedures.
2. Experimental procedures

General procedure A for the carboxylation of benzyl C-H bond with CO\textsubscript{2}

In a 9 mL snap vial with magnetic stirring bar, 4CzIPN (9.5 mg, 0.012 mmol) was dissolved in dry DMF (2 mL) and the resulting mixture was degassed under vacuum via a syringe needle for 2 times. Then it was bubbled with CO\textsubscript{2} for 5 min. After that, the starting materials (0.2 mmol, if solid, it should be added at the beginning) and triisopropylsilanethiol (7.6 mg, 0.04 mmol) were injected. The vial was cooled to be 0 ℃. 21 mL of CO\textsubscript{2} was injected and the vial was sealed with wax. Then the vial was irradiated with a 455 nm LEDs. After 24 h, the mixture was concentrated \textit{in vacuo}. 5 mL of 0.2 M HCl aqueous was added and this solution was extracted with EtOAc (3x5 mL). The combined organic layers were washed with brine and concentrated \textit{in vacuo}. The obtained crude material was re-dissolved in 4 mL of Et\textsubscript{2}O and extracted with 1 M NaOH (3 x 4 mL). Then the aqueous solution was washed with hexane (3x5 mL). Finally, the aqueous fractions were acidified (pH < 2) by addition of 5 M HCl and extracted with EtOAc (3 x 5 mL). The combined organic layers were dried with Na\textsubscript{2}SO\textsubscript{4}, filtered, and concentrated \textit{in vacuo} to give the final product.

General procedure B for the carboxylation of benzyl C-H bond with CO\textsubscript{2}

In a 9 mL snap vial with magnetic stirring bar, 4CzIPN (9.5 mg, 0.012 mmol) was dissolved in dry DMF (2 mL) and the resulting mixture was degassed under vacuum via a syringe needle for 2 times. Then it was bubbled with CO\textsubscript{2} for 5 min. After that, the starting material (0.2 mmol, if solid, it should be added at the beginning) and triisopropylsilanethiol (7.6 mg, 0.04 mmol) were injected. The vial was cooled to be 0 ℃. 21 mL of CO\textsubscript{2} was injected and the vial was sealed with wax. Then the vial was irradiated with a 455 nm LEDs. After 24 h, the mixture was concentrated \textit{in vacuo}. 5 mL of 0.2 M HCl aqueous was added and this solution was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine and concentrated \textit{in vacuo}. Then the residue was purified by silica gel chromatography using first petroleum ether/EtOAc (10/1, v/v), then petroleum ether/EtOAc (3/1, v/v), and finally EtOAc as an eluent.
3. Optimization details for carboxylation of ethyl benzene

Table S1. Screening of solvents and photosensitizers

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Photosensitizer</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_3$CN</td>
<td>4CzIPN</td>
<td>22</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>DMF</td>
<td>4CzIPN</td>
<td>18</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>4CzIPN</td>
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</tr>
<tr>
<td>4</td>
<td>DMSO</td>
<td>4CzIPN</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>5$^d$</td>
<td>DMF</td>
<td>Ir(ppy)$_3$</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>6$^d$</td>
<td>DMF</td>
<td>Ir(ppy)$_2$(dtBuppy)PF$_6$</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>7$^d$</td>
<td>DMF</td>
<td>Ir(dF-CF$_3$-ppy)$_2$(dtBuppy)PF$_6$</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>8$^d$</td>
<td>DMF</td>
<td>5CzBN</td>
<td>12</td>
<td>7</td>
</tr>
<tr>
<td>9$^d$</td>
<td>DMF</td>
<td>3DPA2FBN</td>
<td>19</td>
<td>11</td>
</tr>
<tr>
<td>10$^d$</td>
<td>DMF</td>
<td>3DPAFIPN</td>
<td>34</td>
<td>14</td>
</tr>
<tr>
<td>11$^d$</td>
<td>DMF</td>
<td>4CzBN</td>
<td>28</td>
<td>23</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: Unless otherwise noted, all reactions were carried out with ethyl benzene (0.2 mmol), photosensitizer (0.002 mmol), iPr$_3$SiSH (HAT1, 0.02 mmol) in corresponding anhydrous solvent (2 mL), irradiation with blue LEDs at 25°C with a CO$_2$ balloon for 24 h. $^b$ Gas chromatography-flame ionization detector conversion using 1,3,5-trimethoxybenzene as an internal standard. $^c$ $^1$H nuclear magnetic resonance yield using 1,3,5-trimethoxybenzene as an internal standard. $^d$ 0.01 mmol of photosensitizer was used.
4. Unsuccessful examples for carboxylation

Table S2. Unsuccessful substrate scope

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-CHO</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>4-COCH₃</td>
<td>38</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>3-Br</td>
<td>27</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>4-I</td>
<td>12</td>
<td>3</td>
</tr>
</tbody>
</table>

* All reactions were carried out with corresponding ethylbenzene derivatives (0.2 mmol), iPr₃SiSH (0.04 mmol), 4CzIPN (0.012 mmol), and 4 atm of CO₂ in anhydrous DMF (2 mL), irradiation with blue LEDs at 0°C for 24 h.  
* Gas chromatography-flame ionization detector conversion using 1,3,5-trimethoxybenzene as an internal standard.  
* ¹H nuclear magnetic resonance yield using 1,3,5-trimethoxybenzene as an internal standard.
5. Radical inhibition experiments

Scheme S1. TEMPO and BHT were used as additives for the carboxylation of 1m.
6. Synthesis of 4CzPEBN

Following a reported procedure, a 9 mL crimp cap vial equipped with a magnetic stirring bar was loaded with 4CzIPN (23.7 mg, 0.03 mmol, 1 equiv.), Cs$_2$CO$_3$ (39.1 mg, 0.12 mmol, 4 equiv.), 2-phenylpropanoic acid (18 mg, 0.12 mmol, 4 equiv.) and DMF (2 mL). Then the resulting mixture was degassed under vacuum via a syringe needle for 2 times and subsequently stirred under light irradiation using a 455 nm (± 10 nm) LED for 3 h at 25 °C. Two reaction batches were combined and diluted with brine (10 mL), water (10 mL) and ethyl acetate (10 mL). The phases were separated and the water phase was extracted with ethyl acetate (10 mL). The combined organic phases were washed with brine/H$_2$O (1:1) (3 x 10 mL) and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure and the crude product was purified by automated flash column chromatography (PE/EtOAc, 10-20% EtOAc) to obtain the title compound as a yellow solid (30.2 mg, 58% yield). $^1$H NMR (600 MHz, DMF-d$_7$) δ (ppm) 8.33 – 8.26 (m, 2H), 8.23 – 8.09 (m, 3H), 8.02 – 7.95 (m, 3H), 7.90 – 7.81 (m, 3H), 7.81 – 7.74 (m, 1H), 7.74 – 7.64 (m, 2H), 7.45 – 7.37 (m, 4H), 7.30 (ddd, $J = 8.6, 7.4, 1.3$ Hz, 1H), 7.23 (ddd, $J = 8.5, 7.3, 1.3$ Hz, 1H), 7.19 – 7.07 (m, 5H), 7.07 – 7.00 (m, 2H), 6.97 (td, $J = 7.5, 1.1$ Hz, 1H), 6.88 (ddd, $J = 11.4, 8.3, 7.2, 1.3$ Hz, 2H), 6.78 (td, $J = 7.4, 2.7, 1.0$ Hz, 2H), 6.70 – 6.63 (m, 1H), 6.63 – 6.53 (m, 4H), 4.02 (q, $J = 7.4$ Hz, 1H), 1.50 (d, $J = 7.4$ Hz, 3H). $^{13}$C NMR (151 MHz, DMF-d$_7$) δ (ppm) 153.60, 144.42, 143.21, 142.93, 142.40, 141.75, 141.17, 140.67, 140.66, 140.41, 140.10, 139.80, 139.77, 127.69, 127.52, 126.53, 126.41, 126.01, 125.82, 125.66, 125.60, 125.43, 124.47, 124.40, 123.68, 123.66, 123.56, 123.45, 123.27, 123.25, 123.19, 121.40, 120.97, 120.93, 120.88, 120.80, 120.75, 120.69, 120.67, 120.12, 120.02, 119.99, 119.89, 119.29, 119.23, 113.08, 112.99, 112.92, 112.89, 112.74, 112.38, 112.04, 111.94, 111.78, 111.70, 111.50, 110.81, 110.11, 38.77, 18.63. LRMS (FD-MS) Calcd. for C$_{63}$H$_{41}$N$_5$ [M$^+$]: 867.3356. Found: 867.3357.
7. Cyclic voltammetry of 4CzPEBN

Figure S1. Cyclic voltammetry of 4CzPEBN in DMF. The reversible peak at 0.380 V refers to the added internal standard ferrocene. The measurement was conducted with TBATFB (0.1 M) as supporting electrolyte and a scan rate of 50 mV/s was used.
8. UV-vis and fluorescence of 4CzPEBN

Figure S2. UV-vis absorption (black) and emission (red) spectrum of 4CzPEBN in DMF. The intensity of absorption and emission spectra were normalized.

Using the ground state reduction potential of 4CzPEBN \( E_{1/2}(P/P^\bullet) = -1.69 \) V vs SCE, Figure S1), the excited state oxidation potential for 4CzPEBN was estimated from the crossing point of the normalized absorption and emission spectra (430 nm), \( E_{1/2}(P^*/P) = +1.19 \) V vs SCE was obtained.
9. Synthesis of substrates and characterization data

N-(4-ethylphenyl)acetamide (1i)

Following a reported procedure\(^5\) 4-ethylaniline (1.21 g, 10 mmol, 1 eq) was added to a round-bottom flask. Then the flask was purged with argon and dry DCM (40 mL) was added. Acetic anhydride (1.14 mL, 12 mmol, 1.2 eq) was added and the reaction was stirred at room temperature and monitored by TLC. Upon completion, the reaction mixture was washed with a saturated solution of sodium carbonate, the organic layers dried with MgSO\(_4\) and the solvent removed under reduced pressure. Purification by column chromatography (ethyl acetate/petroleum ether) afforded the product as a pale pink solid (1.52 g, 93% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.53 (s, 1H), 7.43 – 7.35 (m, 2H), 7.17 – 7.08 (m, 2H), 2.60 (q, \(J = 7.7\) Hz, 2H), 2.15 (s, 3H), 1.20 (t, \(J = 7.6\) Hz, 3H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm) 168.5, 140.5, 135.6, 128.4, 120.3, 28.4, 24.6, 15.8. HRMS (EI) Calcd. for C\(_{10}\)H\(_{13}\)N\(_2\)O \([M^+]: 163.0992\). Found: 163.0993.

3-ethylphenyl acetate (1j)

Following a reported procedure,\(^6\) 3-ethylphenol (10 mmol, 1.22 g) was added to a stirred solution of imidazole (0.8 mmol, 50 mg) and acetic anhydride (20 mmol, 1.88 mL) at ambient temperature. The progress of the resulting reaction was monitored by TLC. Upon completion of the reaction, the crude mixture was purified by column chromatography on silica gel using n-hexane/ethyl acetate (10/1) as the eluent to give 3-ethylphenyl acetate as a colorless liquid (1.36 g, 83% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.33 – 7.23 (m, 1H), 7.07 (ddt, \(J = 7.7, 1.8, 0.8\) Hz, 1H), 6.94 – 6.86 (m, 2H), 2.76 – 2.58 (m, 2H), 2.30 (s, 3H), 1.24 (t, \(J = 7.6\) Hz, 3H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm) 169.8, 150.8, 146.1, 129.3, 125.6, 121.0, 118.9, 28.8, 21.3, 15.4. HRMS (EI) Calcd. for C\(_{10}\)H\(_{12}\)O\(_2\) \([M^+]: 164.0832\). Found: 164.0834.

5-ethylbenzo[d][1,3]dioxole (1k)

Following a reported procedure,\(^7\) a 50 mL crimp vial was charged with 1-(benzo[d][1,3]dioxol-5-yl)ethan-1-one (821 mg, 5.00 mmol), palladium on charcoal (53.2 mg, 10 wt%, 50 \(\mu\)mol Pd, 1 mol %), 15 mL methanol and chlorobenzene (25.4 \(\mu\)L, 250 \(\mu\)mol, 5mol%). To the sealed vial, polymethylhydrosiloxane (1.5 mL, 25.0 mmol, 5 equiv.) was added via syringe pump over the course of one hour at room temperature. The mixture was stirred for another hour, filtered, using ethyl acetate to wash both vial and filter. The solvent was removed under reduced pressure and the crude product was submitted to automated column chromatography (50 g SiO\(_2\), pentane/ether = 100/0→95/5) to obtain the title compound as colourless oil (683 mg, 91% yield).
\[ ^1 \text{H NMR (300 MHz, CDCl}_3 \] \delta (ppm) 6.78 – 6.69 (m, 2H), 6.69 – 6.61 (m, 1H), 5.93 (s, 2H), 2.59 (q, \( J = 7.6 \text{ Hz, 2H} \)), 1.22 (t, \( J = 7.6 \text{ Hz, 3H} \)). \[^1 \text{C NMR (75 MHz, CDCl}_3 \] \delta (ppm) 147.6, 145.5, 138.3, 120.5, 108.5, 108.2, 100.8, 28.8, 16.1. HRMS (EI) Calcd. for C\(_9\)H\(_{10}\)O\(_2\) [M\(^+\)]: 150.0675. Found: 150.0673.

**2-ethyl-1,1'-biphenyl (II)**

Following a reported procedure, a mixture of phenyl boronic acid (914 mg, 7.5 mmol, 1.5 equiv.), 1-ethyl-2-iodobenzene (717 µL, 5.00 mmol, 1.0 equiv.), PdCl\(_2\)(Ph\(_3\))\(_2\) (70.2 mg, 100 µmol, 2mol%) and potassium carbonate (1.38 g, 10.0 mmol, 2.0 equiv.) in degassed DMF (20 mL) and water (4 mL) was stirred at 60 °C for 24 h. The reaction was diluted with water (100 mL) and extracted with ether (150 mL). The organic phase was washed with water (3 x 50 mL), dried over sodium sulfate, filtered, concentrated and submitted to automated column chromatography (25 g SiO\(_2\), pentane) to obtain the title compound as a white solid (589 mg, 65% yield). \[^1 \text{H NMR (300 MHz, CDCl}_3 \] \delta (ppm) 7.47 – 7.27 (m, 7H), 7.27 – 7.16 (m, 2H), 2.61 (q, \( J = 7.5 \text{ Hz, 2H} \)), 1.11 (t, \( J = 7.5 \text{ Hz, 3H} \)). \[^1 \text{C NMR (75 MHz, CDCl}_3 \] \delta (ppm) 142.1, 141.7, 130.1, 129.3, 128.7, 128.1, 127.6, 126.9, 125.7, 26.3, 15.8. HRMS (EI) Calcd. for C\(_{14}\)H\(_{14}\) [M\(^+\)]: 182.1090. Found: 182.1091.

**4-ethyl-1,1'-biphenyl (1m)**

A mixture of 4-ethynyl-1,1'-biphenyl (750 mg, 4.12 mmol) and palladium on charcoal (44.8 mg, 10 wt%, 42.1 µmol Pd, 1 mol%) in 20 mL methanol was stirred under hydrogen atmosphere for 5 h at room temperature, filtered, concentrated and submitted to automated column chromatography (25 g SiO\(_2\), pentane) to obtain the title compound as a white solid (625 mg, 81% yield). \[^1 \text{H NMR (400 MHz, CDCl}_3 \] \delta (ppm) 7.68 – 7.60 (m, 2H), 7.60 – 7.54 (m, 2H), 7.47 (t, \( J = 7.8 \text{ Hz, 2H} \)), 7.41 – 7.29 (m, 3H), 2.75 (q, \( J = 7.6 \text{ Hz, 2H} \)), 1.33 (t, \( J = 7.6 \text{ Hz, 3H} \)). \[^1 \text{C NMR (101 MHz, CDCl}_3 \] \delta (ppm) 143.5, 141.3, 138.8, 128.8, 128.4, 127.2, 127.14, 127.09, 28.7, 15.7. HRMS (EI) Calcd. for C\(_{14}\)H\(_{14}\) [M\(^+\)]: 182.1090. Found: 182.1094.

**1-(4-ethylphenyl)-1H-pyrazole (1n)**

Following a reported procedure, to an oven-dried flask was added Cu\(_2\)O (1.03 mmol), Cs\(_2\)CO\(_3\) (20.25 mmol) and pyrazole (10.00 mmol). Under a nitrogen atmosphere, 1-bromo-4-ethylbenzene (2.1 mL, 15.24 mmol) was added followed by anhydrous DMF (17 mL). The flask was heated up to 140 °C under an atmosphere of nitrogen. After 24 h, the reaction mixture was cooled to room temperature and diluted with dichloromethane. The resulting solution was filtered through a pad of silica gel and the solvent removed under reduced pressure. The residue was then diluted with...
EtOAc and washed with water (2 x 50 mL), the organic material was dried over MgSO₄, filtered and concentrated in vacuo. The crude residue was purified by silica flash column chromatography eluting with (EtOAc/ hexane) (1/9) to give a yellow solid (0.94 g, 54% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.92 – 7.85 (m, 1H), 7.72 (d, J = 1.9 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.32 – 7.22 (m, 2H), 6.48 – 6.40 (m, 1H), 2.69 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H).

13C NMR (101 MHz, CDCl₃) δ (ppm) 142.7, 140.8, 138.2, 128.8, 126.8, 119.4, 107.4, 28.4, 15.7. HRMS (EI) Calcd. for C₁₁H₁₂N₂ [M⁺]: 172.0995. Found: 172.0997.

chromane (1y)

Following a reported procedure, a 50 mL crimp vial was charged with chroman-4-one (740 mg, 5.00 mmol), palladium on charcoal (53.2 mg, 10 wt%, 50 µmol Pd, 1 mol%), 15 mL methanol and chlorobenzene (25.4 µL, 250 µmol, 5mol%). To the sealed vial, polymethylhydrosiloxane (1.5 mL, 25.0 mmol, 5 equiv.) was added via syringe pump over the course of one hour at room temperature. The mixture was stirred for another hour, filtered, using ethyl acetate to wash both vial and filter. The solvent was removed under reduced pressure and the crude product was submitted to automated column chromatography (50 g SiO₂, pentane/ether = 100/0 → 95/5) to obtain the title compound as colourless oil (616 mg, 92% yield).

¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.16 – 7.00 (m, 2H), 6.94 – 6.74 (m, 2H), 4.26 – 4.10 (m, 2H), 2.81 (t, J = 6.4 Hz, 2H), 2.12 – 1.93 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ (ppm) 155.0, 129.9, 127.3, 122.3, 120.2, 116.8, 66.5, 25.0, 22.5.


1-ethyl-3-phenoxybenzene (1aa)

Following a reported procedure, in a three-necked reaction vessel equipped with a magnetic stirring bar, CuBr (72 mg, 0.5 mmol, 0.1 equiv.), Cs₂CO₃ (3.42 g, 10.5 mmol, 2.1 equiv.) and ethyl 2-oxocyclohexanecarboxylate (170 mg, 1 mmol, 0.2 equiv.) were dissolved in DMSO (8 mL) under a N₂ atmosphere. Then iodobenzene (1.02 g, 5 mmol, 1 equiv.) and 3-ethylphenol (0.74 g, 6 mmol, 1.2 equiv.) were added, and the mixture was heated to 60 °C. After 20 h, the crude solution was filtered through a pad of silica gel. The filtrate was washed with brine, dried over MgSO₄ and concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel (PE/EtOAc-20:1) to afford the target compound as colorless oil (0.62 g, 63% yield). ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.40 – 7.29 (m, 2H), 7.30 – 7.21 (m, 1H), 7.15 – 7.07 (m, 1H), 7.07 – 7.00 (m, 2H), 6.97 (ddq, J = 7.5, 1.6, 0.7 Hz, 1H), 6.90 (ddd, J = 2.3, 1.8, 0.6 Hz, 1H), 6.87 – 6.80 (m, 1H), 2.78 – 2.53 (m, 2H), 1.25 (t, J = 7.6 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ (ppm) 157.5, 157.3, 146.5, 129.8, 129.6, 123.2, 123.0, 118.9, 118.6, 116.2, 28.9, 15.6. HRMS (EI) Calcd. for C₁₄H₁₄O [M⁺]: 198.1039. Found: 198.1038.

4-ethyl-2-fluoro-1,1'-biphenyl (1ab)

S-12
**Step 1:** A solution of 4-bromo-2-fluoro-1,1'-biphenyl (3.01 g, 12.0 mmol, 1.0 equiv.) in dry THF (24 mL) was cooled to −78 °C, treated with n-butyllithium (8.85 mL, 1.6 M in hexane, 14.2 mmol, 1.2 equiv.) and stirred for 30 min. A solution of acetaldehyde (1.21 mL, 21.6 mmol, 1.8 equiv.) in THF (5 mL) was added slowly over 30 min. The reaction was warmed to room temperature, quenched by the addition of methanol and concentrated under reduced pressure. The residue was taken up in ether (75 mL) and water (50 mL). After extraction of the aqueous phase with ether (3 x 75 mL), the combined organic phase was dried over sodium sulfate, filtered and concentrated under reduced pressure. Submission to automated column chromatography (50 g SiO₂, pentane/Et₂O = 90/10 → 70/30) furnished 1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethan-1-ol as a white solid (1.94 g, 8.97 mmol, 75% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.55 (dt, J = 8.1, 1.5 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.40 – 7.34 (m, 1H), 7.24 – 7.17 (m, 2H), 4.94 (qd, J = 6.5, 3.7 Hz, 1H), 1.88 (d, J = 3.8 Hz, 1H), 1.54 (d, J = 6.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 159.9 (d, J_CF = 248.2 Hz), 147.6 (d, J_CF = 6.9 Hz), 135.8, 130.9 (d, J_CF = 3.9 Hz), 129.1 (d, J_CF = 2.9 Hz), 128.6, 128.1 (d, J_CF = 13.6 Hz), 127.8, 121.4 (d, J_CF = 3.4 Hz), 113.2 (d, J_CF = 23.5 Hz), 69.8 (d, J_CF = 1.7 Hz), 25.4. ¹⁹F NMR (377 MHz, CDCl₃) δ (ppm) -118.2. HRMS (EI) Calcd. for C₁₄H₁₃OF [M⁺]: 216.0945. Found: 216.0946.

**Step 2:** Following a reported procedure, ⁷ a 50 mL crimp vial was charged with 1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethan-1-ol (1.50 g, 5.67 mmol), palladium on charcoal (63.6 mg, 10 wt%, 59.7 µmol Pd, 1 mol%), 18 mL methanol and chlorobenzene (30.3 µL, 298 µmol, 5 mol%). To the sealed vial, polymethylhydrosiloxane (29.9 mmol, 5 equiv.) in dr 50 mL crimp vial was charged with another hour, filtered, using ethyl acetate to wash both vial and filter. The solvent was removed under reduced pressure and the crude product was submitted to automated column chromatography (50 g SiO₂, pentane) to obtain the title compound as colourless oil (1.2 g, 93% yield). ¹H-NMR (300 MHz, CDCl₃) δ (ppm) 7.55 (dt, J = 8.2, 1.5 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.40 – 7.32 (m, 2H), 3.05 (ddd, J = 7.7, 1.6, 0.8 Hz, 1H), 7.01 (dd, J = 11.8, 1.7 Hz, 1H), 1.70 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 159.9 (d, J_CF = 247.5 Hz), 146.1 (d, J_CF = 7.6 Hz), 136.1, 130.6 (d, J_CF = 4.0 Hz), 129.1 (d, J_CF = 3.0 Hz), 128.5, 127.5, 126.3 (d, J_CF = 13.6 Hz), 124.0 (d, J_CF = 3.2 Hz), 115.5 (d, J_CF = 22.6 Hz), 28.5 (d, J_CF = 1.6 Hz), 154. ¹⁹F NMR (282 MHz, CDCl₃) δ (ppm) -119.3. HRMS (EI) Calcd. for C₁₄H₁₃OF [M⁺]: 200.0996. Found: 200.0999.

**1-ethyl-4-isobutylbenzene (1ac)**

**Step 1:** Following a reported procedure, ¹¹ a flame-dried round-bottom flask (100-mL) was charged with AlCl₃ (1.85 g, 14 mmol) and CH₂Cl₂ (18 mL). The mixture was cooled to 0 °C, and acetylchloride (1.0 mL, 14 mmol) and isobutylbenzene (2.0 mL, 12.8 mmol) were added
sequentially to the flask. The reaction was stirred at this temperature for 90 minutes. The mixture was poured into a mixture of ice water and CH₂Cl₂ (30 mL). The two layers were partitioned in a separatory funnel and the organic layer was washed with water (15 mL) and brine (10 mL). The organic layer was dried over MgSO₄, filtered and concentrated in vacuo. The crude residue was purified by flash column chromatography on silica gel (PE/EtOAc 20:1) to afford 1-(4-isobutylphenyl)ethanone as colorless oil (2.1 g, 93% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.91 – 7.83 (m, 2H), 7.25 – 7.16 (m, 2H), 2.58 (s, 3H), 2.53 (d, J = 7.2 Hz, 2H), 1.95 – 1.85 (m, 1H), 0.91 (d, J = 6.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 198.0, 147.7, 135.1, 129.4, 128.4, 45.5, 30.2, 26.7. HRMS (EI) Calcd. for C₁₇H₁₆O [M⁺]: 227.1196. Found: 227.1197.

**Step 2:** Following a reported procedure, a 50 mL crimp vial was charged with 1-(4-isobutylphenyl)ethanone (880 mg, 5.00 mmol), palladium on charcoal (53.2 mg, 10 wt%, 50 µmol Pd, 1 mol%), 15 mL methanol and chlorobenzene (25.4 µL, 250 µmol, 5 mol%). To the sealed vial, polymethylhydrosiloxane (1.5 mL, 25.0 mmol, 5 equiv.) was added via syringe pump over the course of one hour at room temperature. The mixture was stirred for another hour, filtered, using ethyl acetate to wash both vial and filter. The solvent was removed under reduced pressure and the crude product was submitted to automated column chromatography (50 g SiO₂, pentane) to obtain the title compound as colourless oil (697 mg, 86% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.19 – 6.98 (m, 4H), 2.65 (q, J = 7.6 Hz, 2H), 2.47 (d, J = 7.2 Hz, 2H), 1.93 – 1.82 (m, 1H), 1.26 (t, J = 7.6 Hz, 3H), 0.93 (d, J = 6.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 141.6, 139.0, 129.2, 127.7, 45.2, 30.4, 28.6, 22.6, 15.8. HRMS (EI) Calcd. for C₁₂H₁₈ [M⁺]: 162.1403. Found: 162.1405.

2-ethyl-6-methoxynaphthalene (1ad)

Following a reported procedure, a 50 mL crimp vial was charged with 1-(6-methoxynaphthalen-2-yl)ethan-1-one (1.00 g, 5.00 mmol), palladium on charcoal (53.2 mg, 10 wt%, 50 µmol Pd, 1 mol%), 15 mL methanol and chlorobenzene (25.4 µL, 250 µmol, 5 mol%). To the sealed vial, polymethylhydrosiloxane (1.5 mL, 25.0 mmol, 5 equiv.) was added via syringe pump over the course of one hour at room temperature. The mixture was stirred for another hour, filtered, using ethyl acetate to wash both vial and filter. The solvent was removed under reduced pressure and the crude product was submitted to automated column chromatography (50 g SiO₂, pentane) to obtain the title compound (848 mg, 4.55 mmol, 91% yield) as white solid. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.72 (dq, J = 8.4, 1.0 Hz, 2H), 7.60 (dt, J = 1.6, 0.8 Hz, 1H), 7.36 (dd, J = 8.4, 1.9 Hz, 1H), 7.17 (d, J = 8.3 Hz, 2H), 3.94 (s, 3H), 2.82 (q, J = 7.5 Hz, 2H), 1.36 (t, J = 7.6 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 157.2, 139.6, 133.0, 129.3, 129.0, 127.7, 126.8, 125.5, 118.7, 105.7, 55.4, 29.0, 15.8. HRMS (EI) Calcd. for C₁₃H₁₄O [M⁺]: 186.1039. Found: 186.1044.

4-(ethyl-1-d₁)-1,1'-biphenyl (1m-d₁)
**Step 1:** Following a reported procedure,\(^{12}\) a round bottom flask (50 mL) was added 1-\((1,1'\text{-biphenyl})\text{-4-yl})\)ethanone (5 mmol, 1.0 equiv.) and methanol (20 mL). The mixture was cooled to 0 °C in an ice bath. Then NaBD\(_4\) (20 mmol, 2.0 equiv.) was added in one portion and the reaction mixture was allowed to warm to room temperature while stirring. After TLC analysis showed completion, the reaction was quenched with saturated aqueous solution of NH\(_4\)Cl (5 mL). pH was adjusted to 3 and methanol was removed on the rotary evaporator. The mixture was extracted with dichloromethane (3 x 10 mL), the organic phases were collected, dried over Na\(_2\)SO\(_4\) and filtered. After evaporation of the solvent the desired alcohol were obtained directly for the next step.

**Step 2:** Following a reported procedure,\(^{13}\) anhydrous FeCl\(_3\) (24 mg, 0.15 mmol) was carefully weighed and stirred in 1,2-dichloroethane (20 mL) for 5 min. PMHS (0.5 mL, 9 mmol, 3.0 equiv) was then added to the prepared catalyst solution, followed by the above obtained alcohol (3 mmol, 1.0 equiv) and stirred at room temperature. The residual crude product was concentrated in vacuo and purified by flash chromatography (hexane/EtOAc-30:1) to afford the desired product as a white solid (516 mg, 94% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta \) (ppm) 7.65 – 7.51 (m, 4H), 7.50 – 7.40 (m, 2H), 7.40 – 7.27 (m, 3H), 2.78 – 2.63 (m, 1H), 1.30 (dt, \(J_{C-D} = 7.7, 1.1 \)Hz, 3H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta \) (ppm) 143.5, 141.3, 138.7, 128.8, 128.4, 127.2, 127.1, 28.3 (t, \(J_{C-D} = 19.4 \)Hz, 15.7.

HRMS (EI) Calcd. for C\(_{14}\)H\(_{13}\)D\(_2\) [M\(^+\)]: 183.1153. Found: 183.1149.

4-(ethyl-1,1-d\(_2\))-1,1'\text{-biphenyl} (1m-d\(_2\))

\begin{center}
\[ \text{Ph} \]
\end{center}

Following a reported procedure,\(^{10}\) a flame-dried vial was charged with water free AlCl\(_3\) (472 mg, 3.54 mmol, 1.77 equiv.) and lithium aluminum deuteride (84.0 mg, 2.00 mmol, 1.0 equiv.) under nitrogen atmosphere. The mixture was carefully suspended in dry ether (8 mL). 4-Acetylbiphenyl (392 mg, 2.0 mmol, 1.0 equiv.) was carefully added as solid (violent reaction) to the suspension. The mixture was stirred for 1 h at room temperature, diluted with ether (20 mL) and quenched by the addition of aqueous HCl (1 M). The phases where separated, and the aqueous phase was extracted with ether (3 x 10 mL). The organic phase was dried over sodium sulfate, filtered, and concentrated. After automated column chromatography (10 g SiO\(_2\), pentane) the title compound was obtained as a white solid (268 mg, 1.45 mmol, 73% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) (ppm) 7.63 – 7.56 (m, 2H), 7.57 – 7.49 (m, 2H), 7.47 – 7.39 (m, 2H), 7.38 – 7.31 (m, 1H), 7.31 – 7.27 (m, 2H), 1.28 (p, \(J = 1.1 \)Hz, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta \) (ppm) 143.4, 141.3, 138.8, 128.8, 128.4, 127.2, 127.1, 28.0 (p, \(J_{C-D} = 19.4 \)Hz), 15.6. HRMS (EI) Calcd. for C\(_{14}\)H\(_{12}\)D\(_2\) [M\(^+\)]: 184.1216. Found: 184.1214.
10. Characterization data for all products

2-phenylpropanoic acid (2a)

Using the general procedure A for carboxylation resulted in 16.5 mg (55% yield) of the title product, obtained as colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.31 – 7.16 (m, 5H), 3.68 (q, \(J = 7.2\) Hz, 1H), 1.45 (d, \(J = 7.2\) Hz, 3H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) (ppm) 181.0, 139.9, 128.8, 127.7, 127.5, 45.5, 18.2. HRMS (ESI) Calcd. for C\(_9\)H\(_{11}\)O\(_2\) [M+H\(^+\)]: 151.0754. Found: 151.0753.

2-(o-tolyl)propanoic acid (2b)

Using the general procedure A for carboxylation resulted in 23.6 mg (72% yield) of the title product, obtained as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.30 (dt, \(J = 7.2, 1.5\) Hz, 1H), 7.24 – 7.15 (m, 3H), 3.99 (q, \(J = 7.2\) Hz, 1H), 2.39 (s, 3H), 1.50 (d, \(J = 7.2\) Hz, 3H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) (ppm) 181.0, 138.4, 136.1, 130.7, 127.4, 126.7, 126.6, 41.2, 19.8, 17.7. HRMS (ESI) Calcd. for C\(_{10}\)H\(_{13}\)O\(_2\) [M+H\(^+\)]: 165.0913. Found: 165.0909.

2-((m-tolyl)propanoic acid (2c)

Using the general procedure A for carboxylation resulted in 20.0 mg (61% yield) of the title product, obtained as colorless oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.25 – 7.19 (m, 1H), 7.17 – 7.05 (m, 3H), 3.71 (q, \(J = 7.2\) Hz, 1H), 2.35 (s, 3H), 1.50 (d, \(J = 7.1\) Hz, 3H). \(^1^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm) 180.8, 139.8, 138.5, 128.7, 128.4, 128.3, 124.7, 45.4, 21.6, 18.2. HRMS (ESI) Calcd. for C\(_{10}\)H\(_{11}\)O\(_2\) [M-H\(^-\)]: 163.0765. Found: 163.0773.

2-(p-tolyl)propanoic acid (2d)

Using the general procedure A for carboxylation with 3DPAFIPN instead of 4CzIPN, resulted in 12.5 mg (38% yield) of the title product, obtained as brown oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.22 (d, \(J = 8.3\) Hz, 2H), 7.14 (d, \(J = 7.9\) Hz, 2H), 3.71 (q, \(J = 7.2\) Hz, 1H), 2.33 (s, 3H), 1.50 (d, \(J = 7.2\) Hz, 1H), 2.13 (s, 3H), 1.50 (d, \(J = 7.2\) Hz, 1H).
7.1 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) 180.9, 137.2, 136.9, 129.5, 127.6, 45.0, 21.2, 18.2. HRMS (EI) Calcd. for C$_{10}$H$_{12}$O$_2$ [M$^+$]: 164.0832. Found: 164.0827.

2-(2-methoxyphenyl)propanoic acid (2e)

Using the general procedure A for carboxylation resulted in 27.4 mg (76% yield) of the title product, obtained as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.29 – 7.22 (m, 2H), 7.00 – 6.85 (m, 2H), 4.09 (q, $J$ = 7.2 Hz, 1H), 3.83 (s, 3H), 1.49 (d, $J$ = 7.3 Hz, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 181.1, 156.8, 128.8, 128.5, 128.1, 120.9, 110.9, 55.6, 44.6, 17.0. HRMS (ESI) Calcd. for C$_{10}$H$_{13}$O$_3$ [M+H$^+$]: 181.0859. Found: 181.0860.

2-(4-methoxyphenyl)propanoic acid (2f)

Using the general procedure A for carboxylation with 3DPA2FBN instead of 4CzIPN, resulted in 18.7 mg (52% yield) of the title product, obtained as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.29 – 7.19 (m, 2H), 6.91 – 6.82 (m, 2H), 3.79 (s, 3H), 3.69 (q, $J$ = 7.2 Hz, 1H), 1.49 (d, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) 180.8, 159.0, 135.0, 134.8, 129.5, 114.2, 110.9, 55.4, 44.6, 18.3. HRMS (EI) Calcd. for C$_{10}$H$_{12}$O$_3$ [M$^+$]: 180.0781. Found: 180.0776.

2-(4-fluorophenyl)propanoic acid (2g)

Using the general procedure A for carboxylation resulted in 17.1 mg (51% yield) of the title product, obtained as colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.31 – 7.25 (m, 2H), 7.06 – 6.96 (m, 2H), 3.73 (q, $J$ = 7.3 Hz, 1H), 1.50 (d, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 180.7, 162.2 (d, $J_{C,F}$ = 244.3 Hz), 135.5 (d, $J_{C,F}$ = 3.3 Hz), 129.3 (d, $J_{C,F}$ = 8.1 Hz), 115.7 (d, $J_{C,F}$ = 21.2 Hz), 44.7, 18.4. $^{19}$F NMR (376 MHz, CDCl$_3$) δ (ppm) -115.7. HRMS (ESI) Calcd. for C$_{9}$H$_{10}$FO$_2$ [M+H$^+$]: 169.0659. Found: 169.0659.

2-(4-chlorophenyl)propanoic acid (2h)
Using the general procedure A for carboxylation resulted in 18.0 mg (49% yield) of the title product, obtained as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.30 – 7.16 (m, 4H), 3.67 (q, $J = 7.2$ Hz, 1H), 1.45 (d, $J = 7.3$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 180.4, 138.2, 133.5, 129.1, 129.0, 44.9, 18.2. HRMS (ESI) Calcd. for C$_9$H$_{10}$ClO$_2$ [M+H$^+$]: 185.0364. Found: 185.0363.

2-(4-acetamidophenyl)propanoic acid (2i)

Using the general procedure A for carboxylation resulted in 19.0 mg (46% yield) of the title product, obtained as yellow oil. $^1$H NMR (400 MHz, CD$_3$OD) δ (ppm) 7.49 (d, $J = 8.7$ Hz, 2H), 7.25 (d, $J = 8.6$ Hz, 2H), 3.68 (q, $J = 7.2$ Hz, 1H), 2.11 (s, 3H), 1.43 (d, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CD$_3$OD) δ (ppm) 178.2, 171.6, 138.8, 138.2, 128.9, 121.3, 46.1, 23.8, 19.0. HRMS (ESI) Calcd. for C$_{11}$H$_{14}$N$_2$O$_3$ [M+H$^+$]: 208.0968. Found: 208.0968.

2-(3-acetoxyphenyl)propanoic acid (2j)

Using the general procedure B for carboxylation resulted in 23.3 mg (56% yield) of the title product, obtained as yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.34 (t, $J = 7.9$ Hz, 1H), 7.19 (dt, $J = 7.8$, 1.6 Hz, 1H), 7.06 (t, $J = 2.1$ Hz, 1H), 7.03 – 7.00 (m, 1H), 3.74 (q, $J = 7.2$ Hz, 1H), 2.29 (s, 3H), 1.52 (d, $J = 7.2$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) 179.7, 169.5, 151.0, 141.4, 129.7, 125.3, 121.0, 120.8, 45.1, 21.3, 18.2. HRMS (ESI) Calcd. for C$_{11}$H$_{13}$NO$_4$ [M+H$^+$]: 209.0808. Found: 209.0810.

2-(benzo[d][1,3]dioxol-5-yl)propanoic acid (2k)

Using the general procedure A for carboxylation with 3DPA2FBN instead of 4CzIPN, resulted in 19.0 mg (49% yield) of the title product, obtained as a green solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 6.83 (d, $J = 1.2$ Hz, 1H), 6.76 (d, $J = 1.0$ Hz, 2H), 5.94 (s, 2H), 3.66 (q, $J = 7.2$ Hz, 1H), 1.47 (d, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 180.9, 148.0, 147.0, 133.6, 121.0, 108.5, 108.1, 101.2, 45.1, 18.4. HRMS (EI) Calcd. for C$_{10}$H$_{11}$O$_4$ [M$^+$]: 194.0574. Found: 194.0578.

2-[(1,1'-biphenyl)-2-yl]propanoic acid (2l)
Using the general procedure A for carboxylation resulted in 28.9 mg (64% yield) of the title product, obtained as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.48 – 7.33 (m, 7H), 7.33 – 7.23 (m, 2H), 3.94 (q, $J = 7.1$ Hz, 1H), 1.39 (d, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 181.2, 142.0, 141.1, 138.1, 130.4, 129.6, 128.4, 128.0, 127.3, 127.09, 127.05, 41.2, 19.1. HRMS (EI) Calcd. for C$_{15}$H$_{14}$O$_2$ [M$^+$]: 226.0988. Found: 226.0992.

2-((1,1'-biphenyl)-4-yl)propanoic acid (2m)

Using the general procedure A for carboxylation resulted in 40.2 mg (89% yield) of the title product, obtained as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.65 – 7.53 (m, 4H), 7.51 – 7.28 (m, 5H), 3.82 (q, $J = 7.2$ Hz, 1H), 1.58 (d, $J = 7.3$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 181.0, 140.8, 140.5, 138.8, 128.9, 128.2, 127.6, 127.4, 127.2, 45.2, 18.2. HRMS (EI) Calcd. for C$_{15}$H$_{14}$O$_2$ [M$^+$]: 226.0988. Found: 226.0987.

2-((4-(1H-pyrazol-1-yl)phenyl)propanoic acid (2n)

Using the general procedure A for carboxylation resulted in 33.7 mg (78% yield) of the title product, obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.87 (dd, $J = 2.5$, 0.6 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.67 – 7.58 (m, 2H), 7.46 – 7.35 (m, 2H), 6.45 (dd, $J = 2.5$, 1.9 Hz, 1H), 3.77 (q, $J = 7.2$ Hz, 1H), 1.53 (d, $J = 7.2$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) 179.5, 141.2, 139.2, 138.6, 128.8, 127.2, 119.8, 107.8, 45.0, 18.3. HRMS (EI) Calcd. for C$_{12}$H$_{12}$N$_2$O$_2$ [M$^+$]: 216.0893. Found: 216.0890.

2-phenylbutanoic acid (2o)

Using the general procedure A for carboxylation resulted in 18.0 mg (55% yield) of the title product, obtained as colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.37 – 7.26 (m, 5H), 3.47 (t, $J = 7.7$ Hz, 1H), 2.19 – 2.04 (m, 1H), 1.89 – 1.75 (m, 1H), 0.92 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (75 MHz,
CDCl$_3$ δ (ppm) 180.4, 138.5, 128.8, 128.2, 127.6, 53.4, 26.4, 12.2. HRMS (EI) Calcd. for C$_{10}$H$_{12}$O$_2$ [M$^+$]: 164.0832. Found: 164.0831.

2-phenylpentanoic acid (2p)

Using the general procedure A for carboxylation resulted in 18.9 mg (53% yield) of the title product, obtained as colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.36 – 7.24 (m, 5H), 3.57 (t, $J$ = 7.7 Hz, 1H), 2.12 – 2.00 (m, 1H), 1.83 – 1.71 (m, 1H), 1.40 – 1.20 (m, 2H), 0.92 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 180.5, 138.7, 128.8, 128.2, 127.6, 53.4, 26.4, 12.2.

HRMS (EI) Calcd. for C$_{11}$H$_{14}$O$_2$ [M$^+$]: 178.0988. Found: 178.0985.

4-methyl-2-phenylpentanoic acid (2q)

Using the general procedure A for carboxylation resulted in 23.0 mg (60% yield) of the title product, obtained as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.37 – 7.23 (m, 5H), 3.67 (t, $J$ = 7.8 Hz, 1H), 1.96 (dt, $J$ = 13.6, 7.7 Hz, 1H), 1.78 – 1.65 (m, 1H), 1.56 – 1.43 (m, 1H), 0.91 (d, $J$ = 6.6 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) 180.7, 138.7, 128.8, 128.2, 127.5, 49.6, 42.1, 25.9, 22.7, 22.3. HRMS (EI) Calcd. for C$_{12}$H$_{16}$O$_2$ [M$^+$]: 192.1145. Found: 192.1150.

2,3-diphenylpropanoic acid (2r)

Using the general procedure A for carboxylation resulted in 30.3 mg (67% yield) of the title product, obtained as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.37 – 7.27 (m, 5H), 7.27 – 7.17 (m, 3H), 7.17 – 7.09 (m, 2H), 3.88 (dd, $J$ = 8.4, 7.0 Hz, 1H), 3.43 (dd, $J$ = 13.7, 8.4 Hz, 1H), 3.06 (dd, $J$ = 13.8, 7.1 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) 179.7, 138.8, 138.0, 129.0, 128.8, 128.5, 128.2, 127.8, 126.6, 53.6, 39.4. HRMS (EI) Calcd. for C$_{15}$H$_{14}$O$_2$ [M$^+$]: 226.0988. Found: 226.0983.

9,10-dihydroanthracene-9-carboxylic acid (2s)
Using the general procedure A for carboxylation resulted in 34.5 mg (77% yield) of the title product, obtained as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.40 – 7.28 (m, 5H), 7.27 (d, J = 1.8 Hz, 1H), 7.26 – 7.22 (m, 2H), 4.94 (s, 1H), 4.27 (d, J = 18.2 Hz, 1H), 3.88 (d, J = 18.3 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 178.2, 136.8, 133.1, 128.5, 128.2, 127.9, 126.6, 52.7, 35.7. HRMS (EI) Calcd. for C$_{15}$H$_{12}$O$_2$ [M$^+$]: 224.0832. Found: 224.0834.

1,2-dihydroacenaphthylene-1-carboxylic acid (2t)

Using the general procedure A for carboxylation resulted in 17.0 mg (43% yield) of the title product, obtained as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.73 – 7.67 (m, 1H), 7.67 – 7.62 (m, 1H), 7.57 (dt, J = 7.1, 1.1 Hz, 1H), 7.50 (ddd, J = 8.3, 7.0, 5.5 Hz, 2H), 7.37 – 7.31 (m, 1H), 4.62 (ddt, J = 8.7, 4.0, 1.3 Hz, 1H), 3.92 – 3.81 (m, 1H), 3.70 – 3.57 (m, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 179.3, 143.0, 141.5, 138.2, 131.7, 128.3, 128.0, 124.3, 122.9, 120.7, 119.8, 48.3, 34.1. HRMS (EI) Calcd. for C$_{13}$H$_{10}$O$_2$ [M$^+$]: 198.0675. Found: 198.0680.

9,10-dihydrophenanthrene-9-carboxylic acid (2u)

Using the general procedure A for carboxylation resulted in 19.3 mg (43% yield) of the title product, obtained as a yellow solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.82 – 7.72 (m, 2H), 7.39 (ddd, J = 7.7, 5.8, 3.0 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.26 – 7.21 (m, 2H), 3.87 (dd, J = 6.0, 4.7 Hz, 1H), 3.29 (dd, J = 15.4, 4.7 Hz, 1H), 3.14 (dd, J = 15.2, 6.0 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 179.5, 134.2, 134.2, 133.6, 133.0, 129.1, 128.7, 128.6, 128.0, 127.8, 127.5, 124.2, 123.8, 44.5, 31.4. HRMS (EI) Calcd. for C$_{15}$H$_{12}$O$_2$ [M$^+$]: 224.0832. Found: 224.0830.

2-(thiophen-2-yl)propanoic acid (2v)

Using the general procedure A for carboxylation with 3DPAFIPN instead of 4CzIPN, resulted in 12.1 mg (42% yield) of the title product, obtained as yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.22 (dd, J = 4.9, 1.4 Hz, 1H), 7.02 – 6.94 (m, 2H), 4.04 (q, J = 7.2 Hz, 1H), 1.61 (d, J = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) 179.0, 142.1, 126.9, 125.3, 124.7, 40.7, 19.2. HRMS (EI) Calcd. for C$_7$H$_8$O$_2$S [M$^+$]: 156.0240. Found: 156.0240.

2-(benzofuran-2-yl)propanoic acid (2w)
Using the general procedure A for carboxylation resulted in 32.3 mg (85% yield) of the title product, obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.37 – 7.31 (m, 1H), 7.30 – 7.23 (m, 1H), 7.10 – 6.97 (m, 2H), 6.44 (s, 1H), 3.81 (q, J = 7.2 Hz, 1H), 1.47 (d, J = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) 178.5, 155.5, 154.9, 128.4, 124.2, 122.9, 121.0, 111.3, 103.7, 39.9, 15.7. HRMS (EI) Calcd. for C$_{11}$H$_{10}$O$_3$ [M$^+$]: 190.0625. Found: 190.0624.

**2,3-dihydrobenzofuran-3-carboxylic acid (2x)**

Using the general procedure A for carboxylation resulted in 12.8 mg (39% yield) of the title product, obtained as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.45 – 7.38 (m, 1H), 7.24 – 7.18 (m, 1H), 6.91 (td, J = 7.5, 1.0 Hz, 1H), 6.87 – 6.79 (m, 1H), 4.92 (dd, J = 9.3, 6.3 Hz, 1H), 4.67 (t, J = 9.5 Hz, 1H), 4.43 – 4.28 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 177.5, 159.9, 129.9, 125.6, 123.5, 121.0, 110.2, 72.3, 47.1. HRMS (EI) Calcd. for C$_9$H$_8$O$_3$ [M$^+$]: 164.0468. Found: 164.0467.

**Chroman-4-carboxylic acid (2y)**

Using the general procedure A for carboxylation resulted in 21.7 mg (61% yield) of the title product, obtained as colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.32 – 7.26 (m, 1H), 7.22 – 7.16 (m, 1H), 6.95 – 6.82 (m, 2H), 4.31 – 4.22 (m, 2H), 3.83 (dd, J = 6.2, 3.6 Hz, 1H), 2.42 – 2.27 (m, 1H), 2.16 (dtt, J = 14.0, 8.1, 6.1 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 180.0, 154.7, 130.6, 129.1, 120.6, 117.7, 117.5, 63.5, 39.6, 24.7. HRMS (EI) Calcd. for C$_{10}$H$_{10}$O$_3$ [M$^+$]: 178.0625. Found: 178.0627.

**2-(3-Phenoxyphenyl)propanoic acid (2aa)**

Using the general procedure A for carboxylation resulted in 25.7 mg (53% yield) of the title product, obtained as yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 7.40 – 7.26 (m, 3H), 7.17 – 6.96 (m, 5H), 6.90 (dd, J = 8.1, 2.5, 1.0 Hz, 1H), 3.73 (q, J = 7.2 Hz, 1H), 1.52 (d, J = 7.3 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 180.7, 157.6, 157.0, 141.8, 130.0, 129.9, 123.5, 122.5, 119.1, 118.4, 117.6, 45.3, 18.2. HRMS (EI) Calcd. for C$_{15}$H$_{14}$O$_3$ [M$^+$]: 242.0938. Found: 242.0940.
2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid (2ab)

Using the general procedure A for carboxylation resulted in 37.1 mg (76% yield) of the title product, obtained as a white solid. \( ^1 \)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) (ppm) 7.55 (dt, \( J = 8.2, 1.6 \) Hz, 2H), 7.50 – 7.32 (m, 4H), 7.23 – 7.12 (m, 2H), 3.80 (q, \( J = 7.1 \) Hz, 1H), 1.57 (d, \( J = 7.1 \) Hz, 3H). \( ^{13} \)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) (ppm) 180.4, 159.8 (d, \( J_{CF} = 24.68 \) Hz), 141.0 (d, \( J_{CF} = 7.7 \) Hz), 135.5, 131.0 (d, \( J_{CF} = 3.7 \) Hz), 129.1 (d, \( J_{CF} = 2.9 \) Hz), 128.6, 128.3 (d, \( J_{CF} = 13.2 \) Hz), 127.8, 123.8 (d, \( J_{CF} = 3.3 \) Hz), 115.5 (d, \( J_{CF} = 23.4 \) Hz), 45.0, 18.1. \(^{19} \)F NMR (282 MHz, CDCl\(_3\)) \( \delta \) -117.9. HRMS (EI) Calcd. for C\(_{15}\)H\(_{13}\)O\(_2\)F [M\(^+\)]: 244.0894. Found: 244.0897.

2-(4-isobutylphenyl)propanoic acid (2ac-1) and 2-(4-ethylphenyl)-3-methylbutanoic acid (2ac-2)

Using the general procedure A for carboxylation resulted in 14.8 mg (36% yield) of the title products, obtained as green oil. The ratio between 2ac-1 and 2ac-2 is 8:1 determined by \(^1\)H NMR. Characterization data for 2ac-1 is given. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm) 7.23 (d, \( J = 8.2 \) Hz, 2H), 7.11 (d, \( J = 8.3 \) Hz, 2H), 3.71 (q, \( J = 7.2 \) Hz, 1H), 2.45 (d, \( J = 7.2 \) Hz, 2H), 1.90 – 1.80 (m, 1H), 1.50 (d, \( J = 7.2 \) Hz, 3H), 0.90 (d, \( J = 6.6 \) Hz, 6H). \(^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) (ppm) 181.0, 141.0, 137.1, 129.5, 127.4, 45.2, 45.1, 30.3, 22.5, 18.2. HRMS (El) Calcd. for C\(_{13}\)H\(_{18}\)O\(_2\) [M\(^+\)]: 206.1301. Found: 206.1297.

2-(6-methoxynaphthalen-2-yl)propanoic acid (2ad)

Using the general procedure A for carboxylation with 3DPAFIPN instead of 4CzIPN, resulted in 17.5 mg (38% yield) of the title product, obtained as a yellow solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) (ppm) 7.75 – 7.64 (m, 3H), 7.43 (dd, \( J = 8.5, 1.9 \) Hz, 1H), 7.19 – 7.08 (m, 2H), 3.91 (s, 3H), 3.87 (q, \( J = 7.1 \) Hz, 1H), 1.60 (d, \( J = 7.2 \) Hz, 3H). \(^{13} \)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) (ppm) 181.1, 157.8, 135.0, 133.9, 129.4, 129.0, 127.4, 126.3, 119.2, 105.7, 55.4, 45.4, 18.3. HRMS (El) Calcd. for C\(_{14}\)H\(_{14}\)O\(_3\) [M\(^+\)]: 230.0938. Found: 230.0934.

2-[(1,1'-biphenyl)-4-yl]propanoic acid (2m) and 2-d1-2-[(1,1'-biphenyl)-4-yl]propanoic acid (2m-d1)
Using the general procedure A for carboxylation resulted in 26.3 mg (58% yield) of the title products, obtained as a white solid. The ratio between $2m$ and $2m$-d$_1$ is 1:4.9 determined by $^1$H NMR. Characterization data for $2m$-d$_1$ is given. $^1$H NMR (600 MHz, CDCl$_3$) δ (ppm) 7.58 (dd, $J = 8.1, 5.9$ Hz, 4H), 7.48 – 7.39 (m, 4H), 7.35 (t, $J = 7.4$ Hz, 1H), 1.56 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 180.6, 140.9, 140.6, 138.8, 128.9, 128.2, 127.6, 127.4, 127.2, 44.8 (t, $J_{C,D} = 19.0$ Hz), 18.2. HRMS (EI) Calcd. for C$_{15}$H$_{13}$D$_2$O$_2$ [M$^+$]: 227.1051. Found: 227.1047.
11. $^1$H and $^{13}$C NMR spectra
1m-d1
2a

S-42
2k

Chemical shifts and other spectral data are shown below.
2m
2o
12. References


