

## Water-initiated hydrocarboxylation of terminal alkynes with CO<sub>2</sub> and hydrosilane

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## Supplementary information

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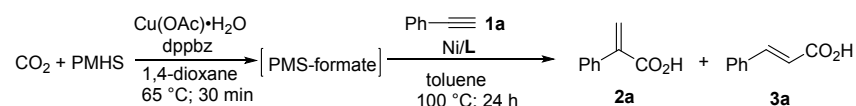
General: All the reagents and solvents were used as received unless otherwise specified. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub>/DMSO-*d*<sub>6</sub>/CD<sub>3</sub>OD on a Bruker Advance 400 NMR spectrometer. Chemical shifts are given in ppm with reference to TMS attributed to 0 ppm and spin-spin coupling constants, J, are given in Hz. Gas chromatographic (GC) analyses were carried out on an Agilent 7890B equipped with a flame-ionization detector and a TCD detector using a HP-5 column or TDX-01 column.

## (A) Experimental procedures

### 1. General Procedure for the Tandem Reaction in a One-pot Manner

A 25 mL Schlenk tube equipped with a magnetic stir bar was fitted with a balloon filled with CO<sub>2</sub>. The tube was charged with Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.01 mmol, 1.0 mol%), dppbz (0.015 mmol, 1.5 mol%), and a solution of PMHS (Acros, FW: ca. 1900, 0.165 g, Si-H, 2.5 mmol, 2.5 equiv.) in 1,4-dioxane (2 mL). The tube was then flushed with CO<sub>2</sub>. After that, the tube was tightly sealed at balloon pressure of CO<sub>2</sub>, and stirred at 65 °C for 30 min, resulting in a transparent light yellow solution. Once completed, the tube containing the silyl formate solution was removed from the oil bath. Then, THF (8 mL), phenylacetylene (1.0 mmol, 1.0 equiv.), Ni(acac)<sub>2</sub> (5 mol%), dppbz (10 mol%) were added sequentially under CO<sub>2</sub> atmosphere. After that, CO<sub>2</sub> balloon was removed, and the Schlenk tube was tightly sealed and stirred at 100 °C for 24 h. After the reaction mixture was cooled to room temperature, NaOH solution (1.0 M, 5 mL) was added, and the mixture was stirred at rt for 10 min. The obtained emulsion was filtered if necessary, and the filtrate was then extracted with EtOAc (3×15mL) with vigorous shaking. The aqueous layer was acidified with HCl (2.0 M, 5 mL), and extracted with EtOAc (3×15 mL). Finally, the obtained organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to afford the α, β-unsaturated acid products.

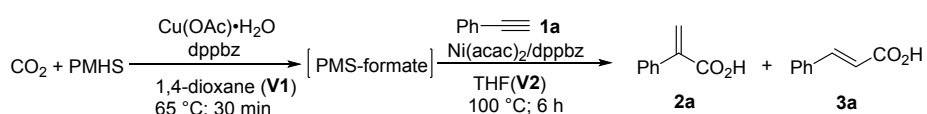
**Table S1 Optimization of the reaction conditions<sup>a</sup>**



Entry	Catalyst	Ligand	Yield(%)	2a/3a
1	Ni(acac) <sub>2</sub>	PPh <sub>3</sub>	N.D	/
2	Ni(acac) <sub>2</sub>	tchp	N.D	/
3	Ni(acac) <sub>2</sub>	dppp	trace	/
4	Ni(acac) <sub>2</sub>	dppf	trace	/
5	Ni(acac) <sub>2</sub>	Xantpho	trace	/
6	Ni(OAc) <sub>2</sub>	dppbz	trace	/
7	Ni(PPh <sub>3</sub> ) <sub>2</sub> Br <sub>2</sub>	dppbz	trace	/
8	Ni(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	dppbz	19	18.0:1

<sup>a</sup> Reaction conditions: Step 1: Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (1.0 mol%), dppbz (1.5 mol%), PMHS (0.165 g, Si-H, 2.5 mmol), CO<sub>2</sub> (balloon), 1,4-dioxane (2 mL), 65 °C, 30 min; Step 2: **1a** (1.0 mmol), [Ni] (5 mol%), for monophosphine ligands (20 mol%), for bisphosphine ligands (10 mol%), toluene (8 mL), 100 °C, 24 h. tchp = tricyclohexyl phosphine; dppp = 1,3-bis(diphenylphosphino)propane; dppf = 1,1'-bis(diphenylphosphino)ferrocene; Xantphos = dimethylbis(diphenylphosphino)xanthene. N.D. = not detected.

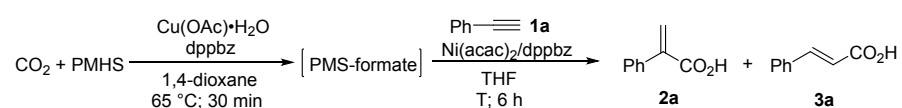
**Table S2 Effect of the ratio of two solvents on the hydrocarboxylation of phenylacetylene<sup>a</sup>**



Entry	1,4-dioxane / THF (V <sub>1</sub> /V <sub>2</sub> )(mL/mL)	Conversion <sup>b</sup> (%)	Yield of styrene <sup>c</sup>
1	2:2	8	3
2	2:4	20	13
3	2:8	94	13
4	1:4	45	9

<sup>a</sup>Reaction conditions: Step 1: Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (1.0 mol%), dppbz (1.5 mol%), PMHS (0.165 g, Si-H, 2.5 mmol), CO<sub>2</sub> (balloon), 1,4-dioxane (V<sub>1</sub> mL), 65 °C, 30 min; Step 2: **1a** (1.0 mmol), Ni(acac)<sub>2</sub> (5 mol%), dppbz (10 mol%), THF (V<sub>2</sub> mL), 100 °C /6 h. <sup>b</sup>Conversion of phenylacetylene, <sup>c</sup>yield of styrene was determined by GC analysis using anisole as internal standard. \*Apart from styrene, the phenylacetylene homo-coupling product is another by-product of the reaction, the yield of which is vanishingly small, so the conversion of phenylacetylene minus the yield of styrene can basically be used to evaluate the amount of product acids.

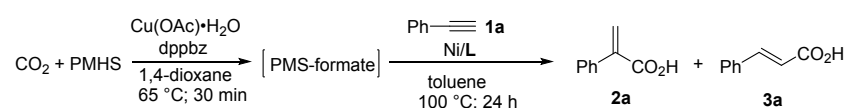
**Table S3 Effect of the temperature of step 2 on the hydrocarboxylation of phenylacetylene<sup>a</sup>**



Entry	T	Conversion <sup>b</sup> (%)	Yield of styrene <sup>c</sup>
1	80	63	5
2	100	94	13
3	120	100	23

<sup>a</sup>Reaction conditions: Step 1: the same as that in table S1; Step 2: **1a** (1.0 mmol), Ni (acac)<sub>2</sub> (5 mol%), dppbz (10 mol%), THF (8 ml), T, 6 h; <sup>b,c</sup>the same as that in table S2; \*the same as that in table S2.

**Table S4 Control reactions<sup>a</sup>**



Entr y	Condition	Yield <sup>b</sup> (%)
1	Standard	86
2	Without dppbz	N.D
3	Without Ni(acac) <sub>2</sub>	N.D
4	One-time addition <sup>c</sup>	N.D

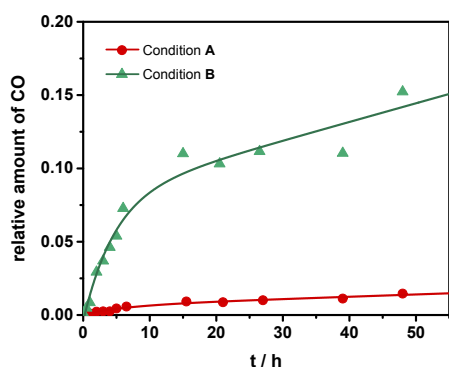
<sup>a</sup> Standard reaction conditions: Step 1: the same as that in table S1; Step 2: **1a** (1.0 mmol), Ni(acac)<sub>2</sub> (5 mol%), dppbz (10 mol%), THF (8 mL), 100 °C, 24 h; <sup>b</sup>Isolated yield; <sup>c</sup>One-time addition means Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, Ni(acac)<sub>2</sub>, dppbz, PMHS, CO<sub>2</sub> (balloon), **1a**, 1,4-dioxane, THF were added in one time.

## 2. General Procedure for the detection of CO gas under the reaction conditions with (condition A) or without phenylacetylene (condition B)

Two 25 mL oven dried Schlenk tubes equipped with magnetic stir bar were fitted with a balloon filled with CO<sub>2</sub> by tee. The tubes were charged with Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.01 mmol, 1.0 mol%), dppbz (0.015 mmol, 1.5 mol%), and a solution of PMHS

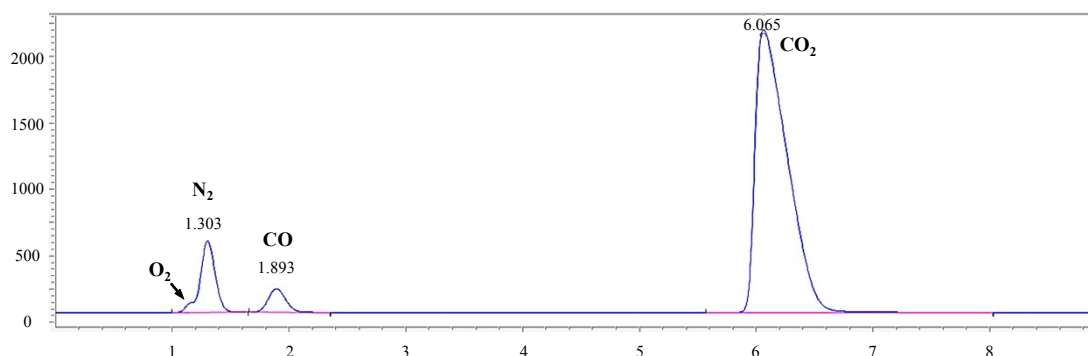
(0.165 g, Si-H, 2.5 mmol, 2.5 equiv.) in 1,4-dioxane (2 mL). The tubes were then flushed with CO<sub>2</sub>. After that, the tubes were tightly sealed at balloon pressure of CO<sub>2</sub>, and stirred at 65 °C for 30 min. Once completed, the tubes containing the silyl formate solution were removed from the oil bath. Then reaction A was added anisole (8 mL), phenylacetylene (1.0 mmol, 1.0 equiv.), Ni(acac)<sub>2</sub> (5 mol%), dppbz (10 mol%) sequentially under CO<sub>2</sub> atmosphere, reaction B was the same as reaction A except that phenylacetylene (1.0 mmol, 1.0 equiv.) was not added. After that, CO<sub>2</sub> balloon was removed, and the Schlenk tubes were tightly sealed. 1.0 mL of gas samples from the two Schlenk tubes were injected into GC 7890B, separately, to analyze the CO and CO<sub>2</sub>, which was recorded as A-0 h (condition A) or B-0 h (condition B). After sampling, two tubes stirred at 100 °C for a certain period of time. Then they were removed from the oil bath and cooled to room temperature for another gas samples testing, which was recorded as A-x h or B-x h. The following gas sample tests followed this pattern.

\*Compared with the amount of CO produced in the system, the amount of CO<sub>2</sub> originally present in the system is very large and basically unchanged. Therefore, CO<sub>2</sub> can be used as an internal standard to measure the change of CO amount. The trend of CO relative to CO<sub>2</sub> is consistent with the trend of CO itself. Therefore, the relative amount of CO was valued by the ratio of CO peak area /CO<sub>2</sub> peak area.



**Figure S1** The relative amount of CO gas existed on condition **A** or **B**

Reaction conditions: Condition **A**: Step 1: the same as that in Table S1; Step 2: **1a** (1.0 mmol); Ni(acac)<sub>2</sub> (5 mol%), dppbz (10 mol%), anisole (8 mL), 100 °C. Condition **B** was the same as that on condition **A**, except that **1a** was not added.



**Figure S2** A example of GC chromatogram for gas sample B-4h.

**3. General Procedure for the anhydrous experiment with different amount of external H<sub>2</sub>O to measure the effect of water on the reaction**

An oven dried Schlenk tube (25 mL) equipped with a magnetic stir bar was fitted with a balloon filled with CO<sub>2</sub>. The tube was charged with Cu(OAc)<sub>2</sub> (0.01 mmol, 1.0 mol%), dppbz (0.015 mmol, 1.5 mol%), and a solution of PMHS (0.165 g, Si-H, 2.5 mmol, 2.5 equiv.) in dry 1,4-dioxane(superdry, stabilized with 250 ppm BHT) (2 mL). The tube was then flushed with CO<sub>2</sub>. After that, the tube was tightly sealed at balloon pressure of CO<sub>2</sub>, and stirred at 65 °C for 30 min, resulting in a transparent light yellow solution. Once completed, the tube containing the silyl formate solution was removed from the oil bath and dry anisole (8 mL) (superdry, stabilized with 250 ppm BHT), different amount of H<sub>2</sub>O(0 mol%、2.5mol%、5mol%、10mol%、

15mol%、20mol%、50mol%、100mol%), phenylacetylene (1.0 mmol, 1.0 equiv.), Ni(acac)<sub>2</sub> (5 mol%), dppbz (10 mol%) were added sequentially under CO<sub>2</sub> atmosphere. Then CO<sub>2</sub> balloon was removed, and the schlenk tube was tightly sealed and stirred at 100 °C for 24 h. After the reaction mixture cooled to room temperature, 1.0 M NaOH (5mL) was added, and the mixture was stirred at room temperature for 10min. The obtained emulsion was filtered if necessary, and the filtrate was then extracted with EtOAc (3×15mL) with vigorous shaking. The internal standard n-octane was added into the organic layer to measure the conversion of phenylacetylene and the yield of styrene by GC. The aqueous layer was acidified with HCl (2.0 M, 5mL), and extracted with EtOAc (3×15 mL). Finally, the obtained organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to afford α, β-unsaturated acid products.

#### **4. General Procedure for the anhydrous experiment with different amount of external formic acid to measure the effect of formic acid on the reaction**

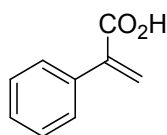
An oven dried Schlenk tube (25 mL) equipped with a magnetic stir bar was fitted with a balloon filled with CO<sub>2</sub>. The tube was charged with Cu(OAc)<sub>2</sub> (0.01 mmol, 1.0 mol%)、dppbz (0.015 mmol, 1.5 mol%)、and a solution of PMHS (0.165 g, Si-H, 2.5 mmol, 2.5 equiv.) in dry 1,4-dioxane(superdry, stabilized with 250 ppm BHT) (2 mL). The tube was then flushed with CO<sub>2</sub>. After that, the tube was tightly sealed at balloon pressure of CO<sub>2</sub>, and stirred at 65°C for 30 min, resulting in a transparent light yellow solution. Once completed, the tube containing the silyl formate solution was removed from the oil bath and dry anisole (8 mL) (superdry, stabilized with 250



ppm BHT), different amount of formic acid (0 mol%、2.5mol%、5mol%、10mol%、20mol%、50mol%、100mol%), phenylacetylene (1.0 mmol, 1.0 equiv.), Ni(acac)<sub>2</sub> (5 mol%), dppbz (10 mol%) were added sequentially under CO<sub>2</sub> atmosphere. Then CO<sub>2</sub> balloon was removed, and the schlenk tube was tightly sealed and stirred at 100 °C for 24 h. After the reaction mixture cooled to rt, 1.0 M NaOH (5 mL) was added, and the mixture was stirred at room temperature for 10min. The obtained emulsion was filtered if necessary, and the filtrate was then extracted with EtOAc (3×15mL) with vigorous shaking. The internal standard n-octane was added into the organic layer to measure the conversion of phenylacetylene and the yield of styrene by GC. The aqueous layer was acidified with HCl (2.0 M, 5 mL), and extracted with EtOAc (3×15 mL). Finally, the obtained organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to afford the α, β-unsaturated acid products.

### (B) <sup>1</sup>H and <sup>13</sup>C NMR spectra data of the products

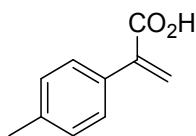
Following the general procedure using **1a** to afford mixture of **2a** and **3a** (**2a/3a** = 4.7:1) as a white solid (86% yield). The spectroscopic data correspond to those previously reported in the literature.<sup>1</sup>



**2a**

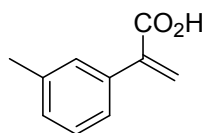
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28-7.24(m, 2H), 7.24-7.18(m, 3H), 6.36(s, 1H), 5.85(d, *J* = 1.1 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.6, 140.6, 136.1, 129.4, 128.5, 128.4, 128.2.

Following the general procedure using **1b** to afford mixture of **2b** and **3b** (**2b/3b** = 8.8:1) as a white solid (93% yield). The spectroscopic data correspond to those previously reported in the literature.<sup>1</sup>



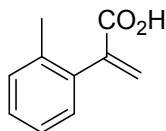
**2b** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32-7.24 (m, 2H), 7.15-7.08 (m, 2H), 6.43 (d, *J* = 1.1 Hz, 1H), 5.93 (d, *J* = 1.1 Hz, 1H), 2.30 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.4, 140.5, 138.3, 133.3, 128.9, 128.7, 128.4, 21.2.

Following the general procedure using **1c** to afford mixture of **2c** and **3c** (**2c/3c** = 16.7:1) as a white solid (80% yield). The spectroscopic data correspond to those previously reported in the literature.<sup>1</sup>



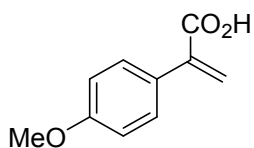
**2c** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.65 (s, 1H), 7.28-7.17 (m, 3H), 7.17-7.11 (m, 1H), 6.20 (d, *J* = 1.1 Hz, 1H), 5.92 (d, *J* = 1.2 Hz, 1H), 2.31 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 168.3, 142.1, 137.5, 137.1, 129.1, 129.0, 128.4, 126.1, 125.7, 21.4.

Following the general procedure using **1d** to afford mixture of **2d** and **3d** (**2d/3d** = 25.0:1) as a white solid (71% yield). The spectroscopic data correspond to those previously reported in the literature.<sup>1</sup>



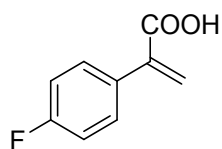
**2d**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22-7.16 (m, 1H), 7.16-7.05 (m, 3H), 6.58 (d,  $J = 1.5$  Hz, 1H), 5.78 (d,  $J = 1.5$  Hz, 1H), 2.17 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.4, 141.1, 136.5, 136.2, 130.9, 130.0, 129.6, 128.4, 125.7, 19.9.

Following the general procedure using **1e** to afford mixture of **2e** and **3e** (**2e/3e** = 9.2:1) as a white solid (90% yield). The spectroscopic data correspond to those previously reported in the literature.<sup>1</sup>



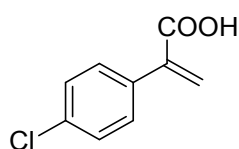
**2e**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.38 (m, 2H), 6.91-6.89 (m, 2H), 6.45 (d,  $J = 1.1$  Hz, 1H), 5.96 (d,  $J = 1.1$  Hz, 1H), 3.83 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.1, 159.8, 139.9, 129.7, 128.6, 128.0, 113.6, 55.3.

Following the general procedure using **1f** to afford mixture of **2f** and **3f** (**2f/3f** = 4.1:1) as a yellow solid (66% yield).



**2f**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.29 (m, 2H), 7.06-6.96 (m, 2H), 6.46 (d,  $J = 0.8$  Hz, 1H), 5.93 (d,  $J = 0.9$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.8, 162.8 (d,  $J = 247.9$  Hz), 139.6, 132.1, 130.3, 129.6, 115.2.

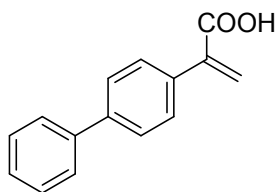
Following the general procedure using **1g** to afford mixture of **2g** and **3g** (**2g/3g** = 9.3:1) as a yellow solid (74% yield). The spectroscopic data correspond to those previously reported in the literature.<sup>1</sup>



**2g**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33-7.25 (m, 4H), 6.48 (d, *J* = 0.8 Hz, 1H), 5.96 (d, *J* = 0.9 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>OD) δ 172.1, 144.7, 139.6, 137.6, 133.6, 131.7, 130.3.

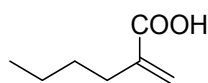
Following the general procedure using **1h** to afford mixture of **2h** and **3h** (**2h/3h** = 8.2:1) as a yellow solid (50% yield).



**2h**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74-7.70 (m, 4H), 7.58-7.45 (m, 5H), 6.25 (d, *J* = 0.6 Hz, 1H), 6.03 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.0, 146.3, 144.9, 144.9, 141.0, 134.2, 133.9, 132.8, 131.8, 131.5, 131.1.

Following the general procedure using **1i** to afford mixture of **2i** and **3i** (**2i/3i** = 12.5:1) as a colorless oil (52% yield). The spectroscopic data correspond to those previously reported in the literature.<sup>1</sup>



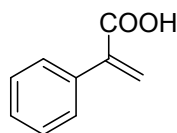
**2i**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.21 (s, 1H), 5.57 (d, *J* = 1.3 Hz, 1H), 2.28-

2.20 (m, 2H), 1.45-1.36 (m, 2H), 1.28 (dq,  $J = 14.3, 7.1$  Hz, 2H), 0.85 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 140.3, 126.9, 31.2, 30.5, 22.3, 13.9.

Following the general procedure using **1j** as substrate, the TMS group was removed during the reaction, leaving a mixture of **2a** and **3a** (**2a/3a** = 6.8:1) as product (white solid, 62% yield). The spectroscopic data correspond to those previously reported in the literature.<sup>1</sup>

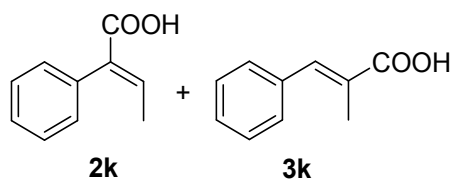


**2a**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.33 (m, 2H), 7.33-7.24 (m, 3H), 6.47

(d,  $J = 1.1$  Hz, 1H), 5.95 (d,  $J = 1.1$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.9, 140.6, 136.1, 129.5, 128.5, 128.4, 128.2.

Following the general procedure using **1k** to afford mixture of **2k** and **3k** (**2k/3k** = 0.8:1) as a white solid (22% yield). The spectroscopic data correspond to those previously reported in the literature.<sup>1</sup>



**2k**

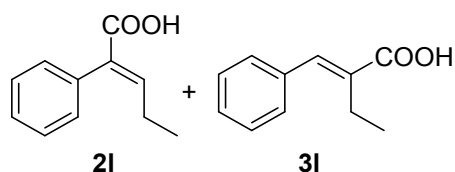
**3k**

**3k**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 1.3$  Hz, 1H), 7.48-7.38 (m, 5H), 2.15 (d,  $J = 1.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 141.1, 135.6, 129.8, 128.4, 128.1, 127.6, 13.7.

**2k**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.28(m, 5H), 7.21 (dd,  $J = 8.2, 1.4$  Hz, 1H), 1.79

(d,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 142.8, 134.4, 134.2, 129.8, 128.7, 127.7, 15.8.

Following the general procedure using **1I** to afford mixture of **2I** and **3I** (**2I/3I** = 1.8:1) as a yellow solid (26% yield). The spectroscopic data correspond to those previously reported in the literature.<sup>2</sup>



**2I**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (s, 1H), 7.14-7.10 (m, 5H), 2.05 (p,  $J = 7.6$  Hz, 1H), 0.96 (t,  $J = 7.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.5, 149.3, 134.7, 132.7, 129.7, 128.7, 128.1, 23.2, 13.2.

**3I**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (s, 1H), 7.37-7.22 (m, 5H), 2.48 (q,  $J = 7.4$  Hz, 2H), 1.13 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 140.8, 135.5, 133.8, 129.4, 128.5, 127.6, 20.6, 13.8.

## (C) References

1. J. Hou, J.-H. Xie and Q.-L. Zhou, *Angew. Chem. Int. Ed.*, 2015, **54**, 6302.
2. M.-C. Fu, R. Shang, W.-M. Cheng and Y. Fu, *ACS Catal.*, 2016, **6**, 2501.