An Easy Access to Carboxylic Acids via Pd-Catalyzed

Hydrocarboxylation of Olefins with HCOOLi as CO Surrogate

under Mild Conditions

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Supporting Information

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General Methods. All commercially available reagents were used without further purification unless otherwise noted. All solvents used for the reaction were purified with solvent purification system. Column chromatography was performed on silica gel (200-300 mesh). ¹H NMR spectra were recorded on a 400 MHz NMR spectrometer and ¹³C NMR spectra were recorded on a 100 MHz NMR spectrometer. IR spectra were recorded on a FT-IR spectrometer. Melting points were uncorrected.

Representative procedure for hydrocarboxylation (Table 2, entry 1). To a stirred mixture of Pd(OAc)₂ (0.0056 g, 0.025 mmol), Xantphos (0.0145 g, 0.025 mmol), HCOOLi·H₂O (0.070 g, 1.00 mmol), and DCE (0.30 mL) in a vial (1.5 mL) were added α -methylstyrene (**1a**) (0.0591 g, 0.50 mmol) and Ac₂O (0.0511 g, 0.50 mmol) successively via syringe. The vial was purged with Ar to remove the air and tightly sealed with a septum cap. The reaction mixture was stirred at 90 °C for 24 h, cooled to rt, diluted with CH₂Cl₂ (3.0 mL), and poured into 1N aqueous NaOH (40 mL) in a separatory funnel. Upon vigorous shaking, the mixture was washed with CH₂Cl₂ (3 x 40 mL). The aqueous layer was acidified with 2N HCl (40 mL), extracted with CH₂Cl₂ (3 x 30 mL), dried over Na₂SO₄, filtered, and concentrated to give carboxylic acid **2a** as a light yellow oil (0.0739 g, 90 % yield) [for Table 2, entries 16 and 17, saturated aqueous NaHCO₃ (40 mL) was used instead of 1N aqueous NaOH (40 mL)].

Procedures for gram scale hydrocarboxylation reaction (Scheme 4). To a stirred mixture of Pd(OAc)₂ (0.1123 g, 0.50 mmol), Xantphos (0.2893 g, 0.50 mmol), and DCE (6.0 mL) in a sealed tube (50.0 mL) were added α-methylstyrene (**1a**) (1.180 g, 10.0 mmol), HCOOLi·H₂O (1.40 g, 20.0 mmol), and Ac₂O (1.020 g, 10.0 mmol) successively via syringe. The tube was purged with Ar to remove the air and tightly sealed. The reaction mixture was stirred at 90 °C for 48 h, cooled to rt, diluted with CH₂Cl₂ (6.0 mL), and poured into 1N NaOH (80 mL) in a separatory funnel. Upon vigorous shaking, the mixture was washed with CH₂Cl₂ (3 x 100 mL). The aqueous layer was acidified with 2N HCl (80 mL), extracted with CH₂Cl₂ (3 x 100 mL), dried

over Na₂SO₄, filtered, and concentrated to give carboxylic acid **2a** as a light yellow oil (1.409 g, 86 % yield).

Table 2, entry 1



Light yellow oil; IR (film) 2966, 1707, 1452 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.25 (m, 2H), 7.25-7.15 (m, 3H), 3.33-3.19 (m, 1H), 2.66 (dd, J = 15.5, 6.8 Hz, 1H), 2.56 (dd, J = 15.5, 8.2 Hz, 1H), 1.31 (d, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.2, 145.6, 128.8, 126.9, 126.7, 42.8, 36.3, 22.0.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.
Wang, Y.; Ren, W.; Shi, Y. Org. Biomol. Chem. 2015, 13, 8416.

Table 2, entry 2



Light yellow oil; IR (film) 2964, 1708 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.23 (m, 2H), 7.23-7.11 (m, 3H), 3.04-2.91 (m, 1H), 2.65 (dd, J = 15.6, 7.2 Hz, 1H), 2.59 (dd, J = 15.6, 7.9 Hz, 1H), 1.79-1.66 (m, 1H), 1.66-1.52 (m, 1H), 0.77 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.3, 143.8, 128.6, 127.7, 126.7, 43.7, 41.4, 29.3, 12.0.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.

Table 2, entry 3



Light yellow oil; IR (film) 2958, 1708 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.23 (m, 2H), 7.23-7.12 (m, 3H), 3.14-3.00 (m, 1H), 2.64 (dd, J = 15.6, 7.2 Hz, 1H), 2.58 (dd, J = 15.0, 7.3 Hz, 1H), 1.69-1.50 (m, 2H), 1.28-1.04 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.3, 144.0, 128.6, 127.6, 126.7, 41.8, 41.7, 38.6, 20.6, 14.1.

Estévez, M. C.; Galve, R.; Baeza, F. S.; Marco, M. P. Anal. Chem. 2005, 77, 5283.

Table 2, entry 4



White soild; mp. 44-46 °C; IR (film) 2969, 1708 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.21-7.04 (m, 4H), 3.60-3.45 (m, 1H), 2.66 (dd, *J* = 15.6, 6.3 Hz, 1H), 2.55 (dd, *J* = 15.6, 8.6 Hz, 1H), 2.36 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.4, 143.8, 135.5, 130.7, 126.6, 126.4, 125.1, 42.1, 31.3, 21.4, 19.6.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.
Wang, Y.; Ren, W.; Shi, Y. Org. Biomol. Chem. 2015, 13, 8416.

Table 2, entry 5



2e

Light yellow oil; IR (film) 2966, 1708 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.22-7.13 (m, 1H), 7.06-6.96 (m, 3H), 3.29-3.16 (m, 1H), 2.65 (dd, J = 15.5, 6.6 Hz, 1H), 2.55 (dd, J = 15.5, 8.4 Hz, 1H), 2.32 (s, 3H), 1.29 (d, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.3, 145.6, 138.3, 128.6, 127.7, 127.5, 123.9, 42.8, 36.2, 22.0, 21.6.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.
Wang, Y.; Ren, W.; Shi, Y. Org. Biomol. Chem. 2015, 13, 8416.

Table 2, entry 6

White soild; mp. 86-88 °C; IR (film) 2966, 1701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.12 (s, 4H), 3.31-3.18 (m, 1H), 2.66 (dd, J = 15.4, 6.8 Hz, 1H), 2.56 (dd, J = 15.5, 8.2 Hz, 1H), 2.32 (s, 3H), 1.30 (d, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.6, 142.6, 136.2, 129.5, 126.8, 42.8, 36.0, 22.2, 21.2.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.Wang, Y.; Ren, W.; Shi, Y. Org. Biomol. Chem. 2015, 13, 8416.

Table 2, entry 7



Light yellow oil; IR (film) 2963, 1708 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.17 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 3.32-3.19 (m, 1H), 2.65 (dd, J = 15.4, 7.0 Hz, 1H), 2.57 (dd, J = 15.4, 8.1 Hz, 1H), 1.32 (d, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.1, 158.3, 137.7, 127.8, 114.1, 55.4, 43.1, 35.5, 22.2.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.

Table 2, entry 8



White solid; mp. 89-90 °C; IR (film) 2963, 1702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 3.30-3.18 (m, 1H), 2.62

(dd, J = 15.6, 7.2 Hz, 1H), 2.56 (dd, J = 15.6, 7.8 Hz, 1H), 1.29 (d, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.9, 144.0, 132.4, 128.9, 128.3, 42.7, 35.8, 22.1.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.
Wang, Y.; Ren, W.; Shi, Y. Org. Biomol. Chem. 2015, 13, 8416.

Table 2, entry 9

White solid; mp. 63-67 °C; IR (film) 2973, 1702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.23-7.15 (m, 2H), 7.04-6.94 (m, 2H), 3.34-3.20 (m, 1H), 2.64 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.58 (dd, *J* = 15.6, 7.9 Hz, 1H), 1.31 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.1, 161.7 (d, *J* = 243 Hz), 141.2 (d, *J* = 3 Hz), 128.3 (d, *J* = 8 Hz), 115.5 (d, *J* = 21 Hz), 42.9, 35.7, 22.2.

Wang, Y.; Ren, W.; Shi, Y. Org. Biomol. Chem. 2015, 13, 8416.

Table 2, entry 10



White solid; mp. 106-108 °C; IR (film) 2973, 1696 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.87-7.78 (m, 3H), 7.70 (s, 1H), 7.54-7.43 (m, 2H), 7.43-7.38 (m, 1H), 3.55-3.41 (m, 1H), 2.81 (dd, *J* = 15.6, 6.8 Hz, 1H), 2.70 (dd, *J* = 15.6, 8.1 Hz, 1H), 1.43 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.1, 143.0, 133.7, 132.5, 128.5, 127.9, 127.8, 126.2, 125.7, 125.6, 125.1, 42.7, 36.4, 22.1.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.
Wang, Y.; Ren, W.; Shi, Y. Org. Biomol. Chem. 2015, 13, 8416.

Table 2, entry 11

СООН 2k

Light yellow oil; IR (film) 2961, 1707 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.23 (m, 2H), 7.23-7.11 (m, 3H), 2.63 (dd, J = 13.4, 6.8 Hz, 1H), 2.51 (dd, J = 13.4, 7.4 Hz, 1H), 2.37 (dd, J = 14.8, 5.5 Hz, 1H), 2.33-2.21 (m, 1H), 2.16 (dd, J = 14.8, 7.9 Hz, 1H), 0.97 (d, J = 6.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 180.1, 140.2, 129.4, 128.5, 126.3, 43.1, 41.0, 32.3, 19.8.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.
Wang, Y.; Ren, W.; Shi, Y. Org. Biomol. Chem. 2015, 13, 8416.

Table 2, entry 12

Light yellow oil; IR (film) 2964, 1709 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.55 (dd, J = 14.9, 3.2 Hz, 1H), 1.99 (dd, J = 14.9, 10.8 Hz, 1H), 1.85-1.74 (m, 1H), 0.92 (d, J = 6.8 Hz, 3H), 0.88 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 181.4, 40.0, 37.6, 32.9, 27.3, 15.2.

Wang, Y.; Ren, W.; Shi, Y. Org. Biomol. Chem. 2015, 13, 8416.

Table 2, entry 13

____соон 2т

Light yellow oil; IR (film) 2964, 1709 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.36 (dd, J = 15.0, 6.0 Hz, 1H), 2.14 (dd, J = 15.0, 8.2 Hz, 1H), 1.96-1.81 (m, 1H), 1.46-1.32 (m, 1H), 1.32-1.16 (m, 1H), 0.96 (d, J = 6.7 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H); ¹³C

NMR (100 MHz, CDCl₃) δ 180.5, 41.5, 31.9, 29.5, 19.4, 11.5. HRMS (ESI) Calcd for C₆H₁₁O₂ (M-H): 115.0764; Found: 115.0765.

Troyanskii, E. I.; Svitan, I. V.; Nikishin, G. I. Organic Chemistry 1985, 125.

Table 2, entry 14

COOH 2n

Light yellow oil; IR (film) 2959, 1709 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.35 (dd, J = 15.0, 6.0 Hz, 1H), 2.14 (dd, J = 14.9, 8.2 Hz, 1H), 2.02-1.87 (m, 1H), 1.40-1.14 (m, 6H), 0.96 (d, J = 6.6 Hz, 3H), 0.89 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 180.4, 41.9, 36.6, 30.3, 29.3, 23.0, 19.9, 14.3. HRMS (ESI) Calcd for C₈H₁₅O₂ (M-H): 143.1077; Found: 143.1076.

Burger, B. V.; Petersen, W. G. B. Journal of Chemical Ecology 2002, 28, 501.

Table 2, entry 15

Light yellow oil; IR (film) 2964, 1708 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.28 (d, J = 7.0 Hz, 2H), 1.82-1.68 (m, 1H), 1.47-1.24 (m, 4H), 0.88 (t, J = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 180.8, 38.5, 37.9, 26.0, 11.0. HRMS (ESI) Calcd for C₇H₁₃O₂ (M-H): 129.0921; Found: 129.0922.

Table 2, entry 16

Light yellow oil; IR (film) 2964, 1739, 1710 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.20-4.00 (m, 2H), 2.36 (dd, J = 15.2, 6.0 Hz, 1H), 2.20 (dd, J = 15.3, 7.8 Hz, 1H),

2.15-2.05 (m, 1H), 2.02 (s, 3H), 1.77-1.63 (m, 1H), 1.60-1.45 (m, 1H), 0.99 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.1, 171.5, 62.6, 41.4, 35.1, 27.3, 21.1, 19.7.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.

Table 2, entry 17

Light yellow oil; IR (film) 2960, 1709 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.51-3.35 (m, 4H), 2.39 (dd, J = 14.8, 5.7 Hz, 1H), 2.19 (dd, J = 14.8, 7.9 Hz, 1H), 2.15-2.00 (m, 1H), 1.72-1.60 (m, 1H), 1.60-1.42 (m, 3H), 1.42-1.27 (m, 2H), 0.98 (d, J = 6.6 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.2, 71.0, 68.9, 41.7, 36.3, 31.9, 27.8, 20.1, 19.5, 14.1;

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.

Table 2, entry 18

Light yellow oil; IR (film) 2925, 1707 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.21 (d, J = 6.8 Hz, 2H), 1.87-1.56 (m, 6H), 1.36-1.20 (m, 2H), 1.20-1.06 (m, 1H), 1.06-0.84 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 180.2, 42.2, 34.8, 33.2, 26.3, 26.2. HRMS (ESI) Calcd for C₈H₁₃O₂ (M-H): 141.0921; Found: 141.0921.

Bonaparte, A. C.; Betush, M. P.; Panseri, B. M.; Mastarone, D. J.; Murphy, R. K.; Murphree, S. S. *Org. Lett.* **2011**, *13*, 1447.

Table 2, entry 19



Light yellow oil; IR (film) 2920, 1709 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.35 (t, J = 7.2 Hz, 2H), 1.73-1.35 (m, 15H), 1.35-1.19 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 181.2, 37.0, 32.9, 32.5, 32.1, 27.4, 26.4, 25.5. HRMS (ESI) Calcd for C₁₁H₁₉O₂ (M-H): 183.1390; Found: 183.1390.

Table 2, entry 20

соон 2t

Light yellow oil; IR (film) 2961, 1704 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.82-2.69 (m, 1H), 1.99-1.77 (m, 4H), 1.77-1.65 (m, 2H), 1.65-1.52 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 183.8, 43.9, 30.2, 26.0.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.
Wang, Y.; Ren, W.; Shi, Y. Org. Biomol. Chem. 2015, 13, 8416.

Table 2, entry 21

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Light yellow oil; IR (film) 2934, 1704 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.32 (tt, J = 11.2, 3.6 Hz, 1H), 1.99-1.86 (m, 2H), 1.82-1.69 (m, 2H), 1.69-1.58 (m, 1H), 1.52-1.36 (m, 2H), 1.36-1.14 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 183.1, 43.2, 29.0, 25.9, 25.5.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.
Wang, Y.; Ren, W.; Shi, Y. Org. Biomol. Chem. 2015, 13, 8416.

Table 2, entry 22



Light yellow oil; IR (film) 2928, 1703 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.56-2.45 (m, 1H), 2.02-1.89 (m, 2H), 1.79-1.62 (m, 4H), 1.62-1.39 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 184.0, 45.0, 30.8, 28.5, 26.4.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. Org. Lett. 2014, 16, 5960.

Wang, Y.; Ren, W.; Shi, Y. Org. Biomol. Chem. 2015, 13, 8416.



S-12







, COOH





Table 2, Entry 3, 2c

соон











СООН



















































Table 2, Entry 17, 2q

"BuO СООН





S-46







COOH









}−соон

S-50







соон







S-54

