RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2017, 7, 3534

Cp_2TiCl_2-catalyzed hydrocarboxylation of alkynes with CO_2: formation of α,β-unsaturated carboxylic acids†

Peng Shao,[a] Sheng Wang,[a] Gaixia Du*[a] and Chanjuan Xi*[ab]

Received 10th October 2016
Accepted 22nd November 2016

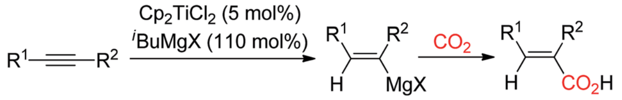
DOI: 10.1039/c6ra25003c

www.rsc.org/advances

Cp_2TiCl_2-catalyzed hydrocarboxylation of alkynes with CO_2 (atmospheric pressure) has been reported. A range of alkynes were transformed to the corresponding α,β-unsaturated carboxylic acids in high yields with high regioselectivity. The reaction proceeded with hydrotitanation, transmetalation, and subsequently carboxylation with CO_2.

Introduction

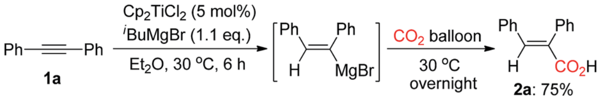
α,β-Unsaturated carboxylic acids are important chemicals,[1] and can be used as basic materials in the production of plastics, superabsorbent, polymers, and rubbers. Various synthetic methodologies for their synthesis have been developed, for example, oxidation of propene over heterogeneous catalysts at high temperature yielded the α,β-unsaturated carboxylic acids[2] and hydrocarboxylation of alkynes utilization of metal carbonyls complexes also formed the α,β-unsaturated carboxylic acids.[3] From the viewpoint of sustainable chemistry, the development of efficient routes with high atom and step-economy under mild conditions could be highly desirable. Carbon dioxide (CO_2) is an environmental friendly, low-toxic and abundant carbon source. Many reaction have been developed utilization of CO_2 as a C1 feedstock in organic synthesis.[4] The addition of CO_2 to alkynes could serve as a most powerful synthetic route for construction of the α,β-unsaturated carboxylic acids. Recently, Ma and co-workers reported a nickel-catalyzed hydrocarboxylation of alkynes with diethyl zinc and CO_2 to form the α,β-unsaturated carboxylic acids.[5] In the meantime, Tsuji and co-workers developed a copper-catalyzed hydrocarboxylation of alkynes with CO_2 by using hydrosilane as hydrogen source to afford the α,β-unsaturated carboxylic acids.[6] On the other hand, direct reaction of vinylmagnesium halides with CO_2 could also afford the α,β-unsaturated carboxylic acids, however, the vinylmagnesium reagents are required preparation in advanced and thus limitation their use.[7] It was reported that alkynes reacted with isobutylmagnesium bromide (^iBuMgBr) in the presence of a catalytic amount of Cp_2TiCl_2 to afford alkenylmagnesium halides,[8] in which isobutylmagnesium bromide is not only as a hydrogen source but also as a transmetallation reagent. Encouraged by this work and as part of our ongoing project on group IV metal complex in organic synthesis,[9] Herein we reported a Cp_2TiCl_2-catalyzed hydrocarboxylation of alkynes with CO_2 in the presence of isobutylmagnesium halide to afford the α,β-unsaturated carboxylic acids (Scheme 1).



Scheme 1 Cp_2TiCl_2-catalyzed hydrocarboxylation of alkynes with CO_2 in the presence of Grignard reagent.

Results and discussion

In initial study, we carried out the first trial in the utilization of diphenylacetylene **1a** as the substrate, 5 mol% of Cp_2TiCl_2 as a catalyst in the presence of isobutylmagnesium bromide in diethyl ether. The reaction mixture was stirred at 30 °C for 6 h. Subsequently, CO_2 balloon was connected to the reaction mixture and the mixture was stirred at 30 °C overnight under CO_2 atmosphere to obtain an α,β-unsaturated carboxylic acid **2a** in 75% yield (eqn (1)).



(1)

Following the hydrocarboxylation of a variety of symmetrical internal alkynes was carried out in the presence of ^iBuMgBr as hydride source. The representative results are summarized in Table 1. The diaryl alkynes bearing methyl group at any position

---

[a] *Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology, Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China*

[b] *State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China. E-mail: cjxi@tsinghua.edu.cn*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra25003c

Table 1 Preparation of functionalized acrylic acids by Cp_2TiCl_2-catalyzed hydrocarboxylation of symmetrical alkynes with CO_2[a]

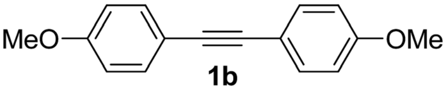
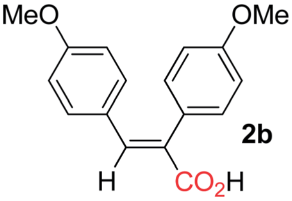
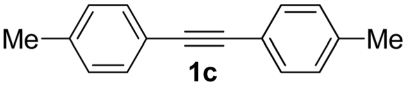
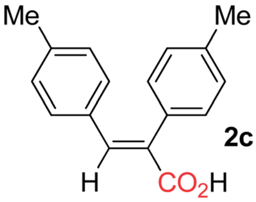
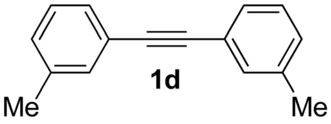
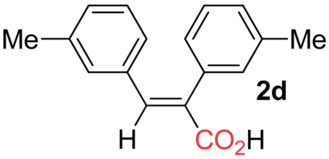
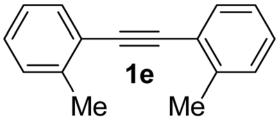
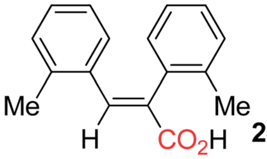
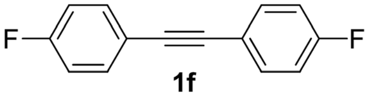
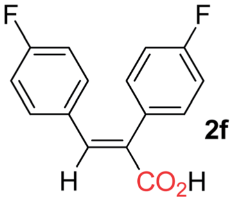
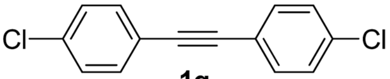
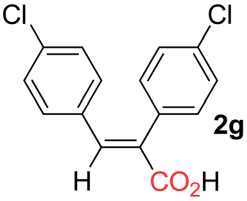
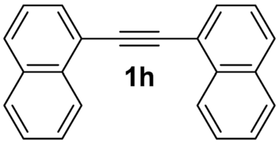
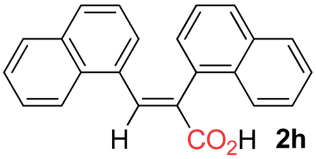
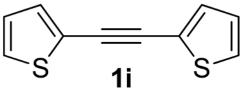
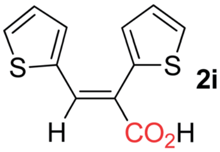
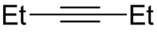
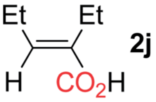
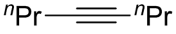
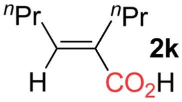
Entry	Alkyne	Product	Yield[b] (%)
1	 **1b**	 **2b**	80
2	 **1c**	 **2c**	77
3	 **1d**	 **2d**	66
4	 **1e**	 **2e**	43
5	 **1f**	 **2f**	62
6	 **1g**	 **2g**	41
7	 **1h**	 **2h**	43
8	 **1i**	 **2i**	53
9	 **1j**	 **2j**	65

Table 1 *(Contd.)*

Entry	Alkyne	Product	Yield[b] (%)
10	 **1k**	 **2k**	73

[a] Reaction conditions: (i) alkynes (1 mmol), Cp_2TiCl_2 (0.05 mmol), ^iBuMgBr (1.1 mmol), Et_2O (4 mL), 30 °C; (ii) CO_2 balloon, 30 °C, overnight. [b] Isolated yield.

of the phenyl ring could proceed smoothly and afforded the corresponding diaryl substituted α,β-unsaturated carboxylic acids (entries 2–4). When electron-withdrawing group such as F or Cl was tolerated on the phenyl ring, the hydrocarboxylative acids were obtained with a slightly reduced yield (entries 5 and 6). Notably, for more electron-deficient alkyne, such as di-(4-CF_3-phenyl) acetylene was used, no hydrocarboxylative product was obtained. When dinaphthyl or dithienyl substituted alkynes were employed as a substrate, the corresponding α,β-unsaturated carboxylic acids **2h** and **2i** could also be obtained in acceptable yields, respectively (entries 7 and 8). Moreover, internal alkynes possessing aliphatic substituents could also be applied in this system, giving the corresponding product **2j** and **2k** in good yield (entries 9 and 10).

In further to examine the scope of hydrocarboxylation of alkynes, unsymmetrical internal alkynes were selected as substrates, and the representative results are shown in Table 2. When 1-phenyl-1-propyne **1l** was used, the hydrocarboxylation worked well with good regioselectivity, affording desired products with the CO_2H group connected to the sp^2 carbon atom bearing the phenyl group as a major product in good yield (entry 1). Utilization of unsymmetrical internal alkynes with some other alkyl moieties, such as Et, ^{t}Bu, cyclopropyl or ether, also proceeded smoothly to afford the corresponding disubstituted acrylic acids with good regioselectivity (entries 2–4 and 6). It is noteworthy that the hydrocarboxylation of the alkyne with hydroxyl group took place regioselectively in moderate yield, albeit one more equivalent of ^{i}BuMgBr was necessary (entry 5). The large steric hindrance group TMS was also tolerated in this system with good regioselectivity (entry 7). Alkyne with phenyl and cyclohexenyl groups gave a mixture of two products in 7 : 1 ratio (entry 8). However, when 1-phenyl-2-thienyl acetylene **1t** and 1-(4-F-phenyl)-2-phenyl acetylene **1u** were used as substrates, the reaction could proceed, while the regioselectivity of products decreased (entries 9 and 10). When 1-(3,3-dimethylbut-1-yn-1-yl)-4-fluorobenzene **1v** was employed in the reaction, less amount of **2v** was observed and 3-methylbutanoic acid was obtained as a major product (entry 11). Utilization of 1-(3,3-dimethylbut-1-yn-1-yl)-4-methoxybenzene **1w** in this reaction and desired product was obtained in 46% yield (entry 12). When terminal alkynes, for example phenylacetylene and 1-octyne, were applied in this reaction, no hydrocarboxylative products were detected.

Based on the above results and literatures about hydromagnesiation of unsaturated hydrocarbons,[8] a possible reaction mechanism was proposed as shown in Scheme 2. First, reduction of Cp_2TiCl_2 by Grignard reagent gives species Cp_2Ti^iBu, which was followed by β-hydride elimination to give Cp_2TiH.[8] Then addition of alkyne affords an intermediate **A**, which undergoes transmetallation with the Grignard reagent to produce complex **B** and release hydromagnesiated product **C**. The hydromagnesiated **C** reacts with CO_2 and subsequent hydrolysis to afford the α,β-unsaturated carboxylic acids **2**. The β-hydride elimination of the complex **B** to regenerate species of Cp_2TiH.

Conclusion

We have developed Cp_2TiCl_2-catalyzed an efficient hydrocarboxylation of alkynes with CO_2, affording the corresponding carboxylic acids in good yields with high regioselectivity. This protocol provides a convenient pathway for the synthesis of the α,β-unsaturated carboxylic acids by use of CO_2 as a renewable source of carbon in organic synthesis.

Experimental section

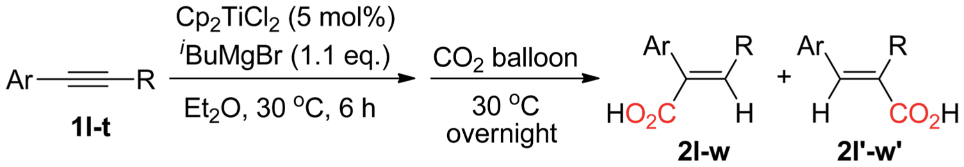
General information

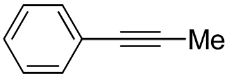
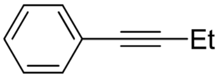
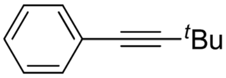
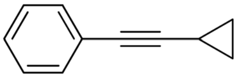
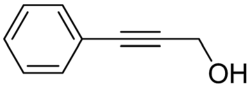
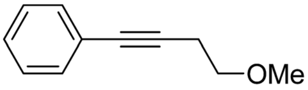
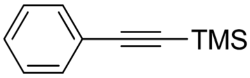
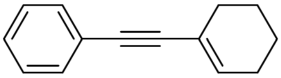
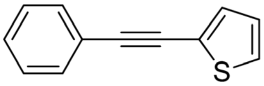
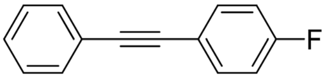
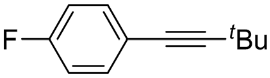
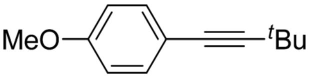
All the reactions were carried out in oven-dried Schleck tubes under N_2 atmosphere. Unless indicated, all materials were obtained from commercial sources and used as received. THF and diethyl ether were fresh distilled. Column chromatography was performed on silica gel (particle size 200–300 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on 400 MHz at ambient temperature with $CDCl_3$ or DMSO-d_6 as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (J) were given in hertz (Hz). The term m, d, s referred to multiplet, doublet, and singlet.

General procedure for synthesis of 2a–w

To an oven-dried Schleck tube was added Cp_2TiCl_2 (5 mol%), which was degassed and refilled with N_2 for 3 times. Dry diethyl ether (4 mL) was added *via* syringe, followed by the dropwise addition of ^{i}BuMgBr (1.1 mmol, 2 M in diethyl ether) at room temperature. Then, the alkynes **1a–t** (1 mmol) was added. The

Table 2 Preparation of functionalized acrylic acids by Cp_2TiCl_2-catalyzed hydrocarboxylation of unsymmetrical alkynes with CO_2[a]

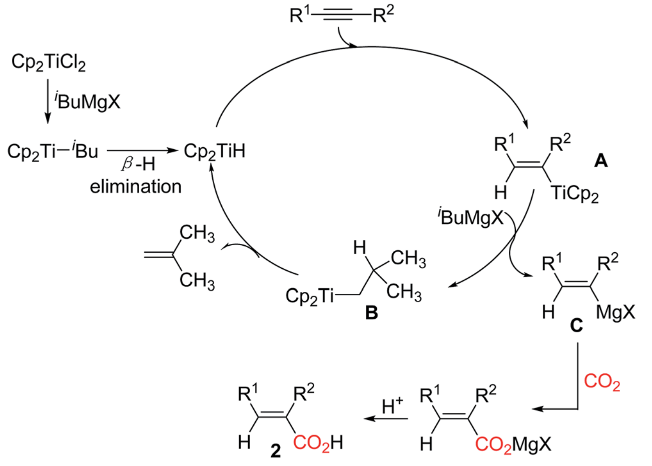


Entry	Alkyne	Yield[b] (%)	Ratio of product[c]
1		69	**2l** : **2l′** (97 : 3)
2		60	**2m** : **2m′** (96 : 4)
3		51	**2n** : **2n′** (96 : 4)
4		77	**2o** : **2o′** (95 : 5)
5[d]		60	**2p** : **2p′** (99 : 1)
6		41	**2q** : **2q′** (99 : 1)
7		49	**2r** : **2r′** (94 : 6)
8		63[e]	**2s** : **2s′** (7 : 1)
9		51[e]	**2t** : **2t′** (2 : 1)
10		54[e]	**2u** : **2u′** (2 : 1)
11[f]		Trace	**2v** : **2v′** (100 : —)
12		46	**2w** : **2w′** (92 : 8)

[a] Reaction conditions: alkyne (1 mmol), Cp_2TiCl_2 (0.05 mmol), ^iBuMgBr (1.1 mmol), Et_2O (4 mL). [b] Isolated yield of major product. [c] NMR ratio. [d] 2.1 equiv. ^iBuMgBr was used. [e] Combined yield. [f] 3-Methylbutanoic acid was obtained as major product.

resulting mixture was stirred at 30 °C for 6 h under N_2 atmosphere. Then the solution was stirred overnight under CO_2 balloon at room temperature. After that, the reaction was quenched with HCl solution (2 M) till pH = 3–4. Then the mixture was extracted with ethyl acetate (5 mL × 3) and the combined organic phase was dried over anhydrous Na_2SO_4, followed by filtration and concentration by rotary evaporator. The residue was purified by silica gel (petroleum ether/ethyl acetate = 5/1) to give the corresponding products **2a–w**.

(*E*)-2,3-Diphenylacrylic acid (2a). White solid, 168 mg, yield: 75%, mp 166–168 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.07 (d, J = 8 Hz, 2H), 7.16 (t, J = 8 Hz, 2H), 7.23–7.25 (m, 3H), 7.35–7.40 (m, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): 128.1, 128.4, 128.8, 129.6, 129.9, 131.0, 131.9, 134.4, 135.5, 142.5, 173.3; GC-MS *m*/*z*: 224.



Scheme 2 Possible reaction mechanism.

Data were in accordance with those previously reported in the literature.[5]

(*E*)-2,3-Bis(4-methoxyphenyl)acrylic acid (2b). Yellow solid, 227 mg, yield: 80%, mp 206–208 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.82 (s, 3H), 3.83 (s, 3H), 6.87–6.95 (m, 5H), 7.40–7.43 (m, 4H); ^{13}C NMR (CDCl$_3$, 101 MHz): 55.4, 55.5, 114.1, 114.2, 128.2, 128.2, 129.9, 130.1, 131.6, 132.2, 159.7, 159.9, 174.9; GC-MS *m*/*z*: 284. Data were in accordance with those previously reported in the literature.[5]

(*E*)-2,3-Di-*p*-tolylacrylic acid (2c). White solid, 194 mg, yield: 77%, mp 184–186 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.27 (s, 3H), 2.38 (s, 3H), 6.98 (s, 4H), 7.12 (d, J = 8 Hz, 2H), 7.18 (d, J = 8 Hz, 2H), 7.89 (s, 1H); ^{13}C NMR (CDCl$_3$, 101 MHz): 21.5, 129.1, 129.6, 129.7, 130.7, 131.0, 131.8, 132.6, 137.8, 139.9, 142.4, 173.7; GC-MS *m*/*z*: 252. Data were in accordance with those previously reported in the literature.[5]

(*E*)-2,3-Di-*m*-tolylacrylic acid (2d). White solid, 167 mg, yield: 66%, mp 153–155 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.19 (s, 3H), 2.33 (s, 3H), 6.82–6.84 (s, 1H), 6.92 (s, 1H), 7.01–7.06 (m, 4H), 7.17 (d, J = 8 Hz, 1H), 7.25 (d, J = 8 Hz, 1H), 7.89 (s, 1H); ^{13}C NMR (CDCl$_3$, 101 MHz): 21.3, 21.5, 126.8, 127.9, 128.2, 128.7, 128.9, 130.3, 130.4, 131.6, 132.1, 134.4, 135.4, 137.9, 138.4, 142.5, 173.4; GC-MS *m*/*z*: 252. Data were in accordance with those previously reported in the literature.[5]

(*E*)-2,3-Di-*o*-tolylacrylic acid (2e). White solid, 108 mg, yield: 43%, mp 165–167 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.14 (s, 3H), 2.43 (s, 3H), 6.66 (d, J = 8 Hz, 1H), 6.81 (t, J = 8 Hz, 1H), 7.04 (d, J = 8 Hz, 1H), 7.08–7.25 (m, 5H), 8.21 (s, 1H); ^{13}C NMR (CDCl$_3$, 101 MHz): 19.7, 20.2, 125.6, 126.1, 128.2, 129.0, 129.3, 130.1, 130.3, 130.3, 131.7, 133.5, 134.8, 136.8, 138.2, 140.9, 172.8; GC-MS *m*/*z*: 252. Data were in accordance with those previously reported in the literature.[5]

(*E*)-2,3-Bis(4-fluorophenyl)acrylic acid (2f). White solid, 161 mg, yield: 62%, mp 171–173 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.77 (d, J = 8 Hz, 3H), 7.18–7.20 (m, 2H), 7.24–7.39 (m, 4H); ^{13}C NMR (CDCl$_3$, 101 MHz): 115.7 (d, $J_{\mathrm{C-F}}$ = 21.6 Hz), 116.1 (d, $J_{\mathrm{C-F}}$ = 21.4 Hz), 130.3 (d, $J_{\mathrm{C-F}}$ = 3.7 Hz), 130.9 (d, $J_{\mathrm{C-F}}$ = 3.4 Hz), 131.7 (d, $J_{\mathrm{C-F}}$ = 8.0 Hz), 132.9 (d, $J_{\mathrm{C-F}}$ = 8.5 Hz), 141.9, 162.7 (d, $J_{\mathrm{C-F}}$ = 249.1 Hz), 163.3 (d, $J_{\mathrm{C-F}}$ = 253.4 Hz), 173.3; HRMS (ESI$^-$) calcd for $C_{15}H_9F_2O_2^-$ 259.0576; found: 259.0572.

(*E*)-2,3-Bis(4-chlorophenyl)acrylic acid (2g). White solid, 120 mg, yield: 41%, mp 178–180 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.00 (d, J = 8 Hz, 2H), 7.15–7.19 (m, 4H), 7.36 (d, J = 8 Hz, 2H), 7.90 (s, 1H); ^{13}C NMR (CDCl$_3$, 101 MHz): 128.8, 129.2, 131.0, 131.3, 132.0, 132.5, 133.3, 134.5, 135.9, 141.7, 172.2; GC-MS *m*/*z*: 292. Data were in accordance with those previously reported in the literature.[6]

(*E*)-2,3-Di(naphthalen-2-yl)acrylic acid (2h). Yellow solid, 139 mg, yield: 43%, mp 237–239 °C; ^{1}H NMR (d$_6$-DMSO, 400 MHz): δ 6.82 (d, J = 8 Hz, 1H), 7.00 (t, J = 8 Hz, 1H), 7.20 (d, J = 8 Hz, 1H), 7.35 (t, J = 8 Hz, 1H), 7.42–7.49 (m, 2H), 7.55 (t, J = 8 Hz, 1H), 7.63 (t, J = 8 Hz, 1H), 7.70 (d, J = 8 Hz, 1H), 7.81 (t, J = 8 Hz, 2H), 7.86–7.91 (m, 2H), 8.20 (d, J = 8 Hz, 1H), 8.68 (s, 1H); ^{13}C NMR (d$_6$-DMSO, 101 MHz): 124.3, 125.4, 125.4, 126.0, 126.4, 126.8, 126.9, 127.4, 128.0, 128.3, 128.9, 129.1, 129.4, 131.7, 132.2, 132.4, 133.4, 133.5, 134.5, 135.1, 139.2, 168.8; HRMS (ESI$^-$) calcd for $C_{23}H_{15}O_2^-$ 323.1072; found: 323.1070.

(*Z*)-2,3-Di(thiophen-2-yl)acrylic acid (2i). Yellow solid, 125 mg, yield: 53%, mp 239–241 °C; ^{1}H NMR (d$_6$-DMSO, 400 MHz): δ 7.00 (d, J = 4 Hz, 3H), 7.04–7.07 (m, 1H), 7.14–7.16 (m, 1H), 7.49 (d, J = 4 Hz, 1H), 7.63 (d, J = 4 Hz, 1H), 7.73 (d, J = 8 Hz, 1H), 8.12 (s, 1H); ^{13}C NMR (d$_6$-DMSO, 101 MHz): 127.4, 128.2, 128.9, 129.3, 133.0, 135.7, 136.8, 167.5; GC-MS *m*/*z*: 236. Data were in accordance with those previously reported in the literature.[6]

(*E*)-2-Ethylpent-2-enoic acid (2j). Yellow oil, 83 mg, yield: 65%; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.03 (t, J = 8 Hz, 3H), 1.07 (t, J = 8 Hz, 3H), 2.19–2.27 (m, 2H), 2.28–2.34 (m, 2H), 6.88 (t, J = 8 Hz, 1H); ^{13}C NMR (CDCl$_3$, 101 MHz): 13.4, 14.0, 19.7, 22.0, 132.9, 146.5, 173.9; HRMS (ESI$^-$) calcd for $C_7H_{11}O_2^-$ 127.0759; found: 127.0763.

(*E*)-2-Propylhex-2-enoic acid (2k). Yellow oil, 114 mg, yield: 73%; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.90–0.97 (m, 6H), 1.40–1.53 (m, 4H), 2.16–2.22 (m, 2H), 2.27 (t, J = 8 Hz, 2H), 6.92 (t, J = 8 Hz, 1H); ^{13}C NMR (CDCl$_3$, 101 MHz): 14.0, 14.1, 22.1, 22.5, 28.5, 30.9, 131.8, 145.6, 173.9; GC-MS *m*/*z*: 156. Data were in accordance with those previously reported in the literature.[5]

(*E*)-2-Phenylbut-2-enoic acid (2l). White solid, 112 mg, yield: 69%, mp 115–117 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.77 (d, J = 8 Hz, 3H), 7.18–7.20 (m, 2H), 7.24–7.39 (m, 4H); ^{13}C NMR (CDCl$_3$, 101 MHz): 15.9, 127.7, 128.2, 129.9, 134.3, 134.5, 142.9, 172.7; GC-MS *m*/*z*: 162. Data were in accordance with those previously reported in the literature.[6]

(*E*)-2-Phenylpent-2-enoic acid (2m). Colorless oil, 106 mg, yield: 60%; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.02 (t, J = 8 Hz, 3H), 2.12 (m, 2H), 7.16–7.20 (m, 3H), 7.29–7.38 (m, 3H); ^{13}C NMR (CDCl$_3$, 101 MHz): 13.3, 23.3, 127.7, 128.1, 129.8, 132.8, 134.8, 149.3, 172.8; GC-MS *m*/*z*: 176. Data were in accordance with those previously reported in the literature.[6]

(*E*)-4,4-Dimethyl-2-phenylpent-2-enoic acid (2n). White solid, 104 mg, yield: 51%, mp 138–140 °C; ^{1}H NMR (d$_6$-DMSO, 400 MHz): δ 0.92 (s, 9H), 7.12–7.16 (m, 3H), 7.29–7.31 (m, 3H); ^{13}C NMR (d$_6$-DMSO, 101 MHz): 30.3, 34.5, 127.6, 127.7, 130.2, 130.8, 135.7, 155.8, 173.8; GC-MS *m*/*z*: 204. Data were in accordance with those previously reported in the literature.[6]

(*E*)-3-Cyclopropyl-2-phenylacrylic acid (2o). White solid, 145 mg, yield: 55%, mp 93–95 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.70–0.74 (m, 2H), 0.89–0.94 (m, 2H), 1.49–1.55 (m, 1H), 6.54 (d, $J = 8$ Hz, 1H), 7.24–7.39 (m, 5H); ^{13}C NMR (CDCl$_3$, 101 MHz): 9.56, 13.0, 127.6, 128.1, 130.3, 130.5, 135.0, 153.2, 172.5; GC-MS *m*/*z*: 188. Data were in accordance with those previously reported in the literature.[10]

(*E*)-4-Hydroxy-2-phenylbut-2-enoic acid (2p). Light-yellow solid, 107 mg, yield: 60%, mp > 300 °C; ^{1}H NMR (d$_6$-DMSO, 400 MHz): δ 3.97 (d, $J = 8$ Hz, 2H), 4.98 (s, 1H), 6.91–6.94 (m, 1H), 7.15 (d, $J = 8$ Hz, 2H), 7.31–7.38 (m, 3H), 12.6 (s, 1H); ^{13}C NMR (d$_6$-DMSO, 101 MHz): 59.0, 128.0, 128.3, 130.0, 133.5, 135.5, 144.1, 168.2; HRMS (ESI$^-$) calcd for $C_{10}H_9O_3^-$ 177.0552; found: 177.0556.

(*E*)-5-Methoxy-2-phenylpent-2-enoic acid (2q). Yellow oil, 85 mg, yield: 41%; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.36–2.41 (m, 2H), 3.30 (s, 3H), 3.44 (t, $J = 8$ Hz, 2H), 7.18–7.24 (m, 3H), 7.31–7.37 (m, 3H); ^{13}C NMR (CDCl$_3$, 101 MHz): 30.4, 58.7, 71.0, 127.8, 128.2, 129.8, 134.6, 134.8, 144.0, 172.2; HRMS (ESI$^-$) calcd for $C_{12}H_{13}O_3^-$ 205.0865; found: 205.0868.

(*E*)-2-Phenyl-3-trimethylsilylacrylic acid (2r). Light-yellow solid, 108 mg, yield: 49%; mp 110–112 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.09 (s, 9H), 7.39–7.42 (m, 2H), 7.52–7.54 (m, 3H); ^{13}C NMR (CDCl$_3$, 101 MHz): 0.73, 127.8, 128.1, 129.5, 137.7, 146.9, 148.5, 172.0; HRMS (ESI$^-$) calcd for $C_{12}H_{15}O_2Si^-$ 219.0841; found: 219.0837.

(*E*)-2-(4-Methoxyphenyl)-4,4-dimethylpent-2-enoic acid (2w). White solid, 108 mg, yield: 46%; mp 176–178 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.94 (s, 9H), 3.81 (s, 3H), 6.85–6.87 (d, 2H), 7.05–7.07 (d, 2H), 7.16 (s, 1H); ^{13}C NMR (CDCl$_3$, 101 MHz): 30.4, 34.5, 55.3, 113.2, 131.3, 156.1, 159.0, 174.2. HRMS (ESI$^-$) calcd for $C_{14}H_{17}O_3^-$ 233.1183; found: 233.1183.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21472106 and 21272132) and the National Key Basic Research Program of China (973 program) (2012CB933402). We also thank Dr Chao Chen in Tsinghua University for his kind discussion.

References

1 (*a*) B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, 1989, **89**, 863; (*b*) S. E. Kelly, in *Comprehensive Organic Synthesis*, Pergamon, Oxford, 1991, vol. 1, pp. 729–817; (*c*) W. Bauer Jr, in *Kirk-Othmer Encyclopedia of Chemical Technology*, ed. A. Seidel, Wiley, Hoboken, 2004, vol. 1, pp. 342–369.

2 M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kuhn, *Angew. Chem., Int. Ed.*, 2011, **50**, 8510.

3 M. Beesu and M. Periasamy, *J. Organomet. Chem.*, 2012, **705**, 30.

4 For selected reviews, see: (*a*) P. Braunstein, D. Matt and D. Nobel, *Chem. Rev.*, 1988, **88**, 747; (*b*) X. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27; (*c*) M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975; (*d*) A. Correa and R. Martín, *Angew. Chem., Int. Ed.*, 2009, **48**, 6201; (*e*) R. Martín and A. W. Kleij, *ChemSusChem*, 2011, **4**, 1259; (*f*) Y. Tsuji and T. Fujihara, *Chem. Commun.*, 2012, **48**, 9956; (*g*) B. Yu, Z. F. Diao, C. X. Guo and L. N. He, *J. CO$_2$ Util.*, 2013, **1**, 60; (*h*) L. Zhang and Z. Hou, *Chem. Sci.*, 2013, **4**, 3395; (*i*) K. Huang, C. Sun and Z. Shi, *Chem. Soc. Rev.*, 2011, **40**, 2435; (*j*) Q. Liu, L. Wu, R. Jackstell and M. Beller, *Nat. Commun.*, 2015, **6**, 1.

5 S. Li, W. Yuan and S. Ma, *Angew. Chem., Int. Ed.*, 2011, **50**, 2578.

6 T. Fujihara, T. Xu, K. Semba, J. Terao and Y. Tsuji, *Angew. Chem., Int. Ed.*, 2011, **50**, 523.

7 (*a*) I. Mutule and E. Suna, *Tetrahedron*, 2005, **61**, 11168; (*b*) L. N. Mander and S. P. Sethi, *Tetrahedron Lett.*, 1983, **24**, 5425.

8 (*a*) H. L. Finkbeiner and G. D. Cooper, *J. Org. Chem.*, 1961, **26**, 4779; (*b*) G. D. Cooper and H. L. Finkbeiner, *J. Org. Chem.*, 1962, **27**, 1493; (*c*) H. L. Finkbeiner and G. D. Cooper, *J. Org. Chem.*, 1962, **27**, 3395; (*d*) E. C. Ashby and R. D. Ainslie, *J. Organomet. Chem.*, 1983, **250**, 1; (*e*) F. Sato, H. Ishikawa and M. Sato, *Tetrahedron Lett.*, 1981, **22**, 85; (*f*) F. Sato, *J. Organomet. Chem.*, 1985, **285**, 53.

9 For selected reviews, see: (*a*) X. Yan and C. Xi, *Acc. Chem. Res.*, 2015, **48**, 935; (*b*) X. Yan and C. Xi, *Coord. Chem. Rev.*, 2016, **308**, 22; (*c*) C. Chen and C. Xi, *Chin. Sci. Bull.*, 2010, **55**, 3235; (*d*) P. Shao, S. Wang, C. Chen and C. Xi, *Chem. Commun.*, 2015, **51**, 6640; (*e*) Y. Zhou, C. Chen, X. Yan and C. Xi, *Organometallics*, 2014, **33**, 844; (*f*) C. Xi, X. Yan, W. You and T. Takahashi, *Angew. Chem., Int. Ed.*, 2009, **48**, 8120; (*g*) C. Chen, C. Xi, Y. Jiang and X. Hong, *J. Am. Chem. Soc.*, 2005, **127**, 8024; (*i*) P. Shao, S. Wang, C. Chen and C. Xi, *Org. Lett.*, 2016, **18**, 2050; (*j*) S. Wang, P. Shao, C. Chen and C. Xi, *Org. Lett.*, 2015, **17**, 5112.

10 X. Wang, M. Nakajima and R. Martin, *J. Am. Chem. Soc.*, 2015, **137**, 8924.