JOC The Journal of Organic Chemistry

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Cs_2CO_3-Promoted Carboxylation of *N*-Tosylhydrazones with Carbon Dioxide toward α-Arylacrylic Acids

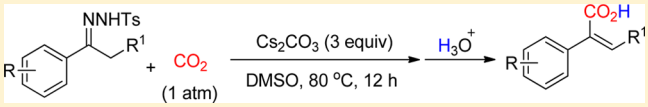
Song Sun,[†] Jin-Tao Yu,[†] Yan Jiang,[†] and Jiang Cheng*[,†,‡]

[†]School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Jiangsu Province Key Laboratory of Fine Petrochemical Engineering, Changzhou University, Changzhou 213164, P. R. China

[‡]State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P. R. China

Supporting Information

ABSTRACT: A Cs_2CO_3-promoted carboxylation of *N*-tosylhydrazones and CO_2 has been developed. The reaction proceeded efficiently at 80 °C under atmospheric CO_2, gave the corresponding α-arylacrylic acids in moderate to good yields. This method was featured with (1) the employment of Cs_2CO_3 rather than ^{n}BuLi as the base; (2) a reaction temperature of 80 °C rather than −78 °C.



α-Arylacrylic acids and their derivatives are important substructure motifs that widely exist in biologically active natural products and medicines (Figure 1). Moreover, they

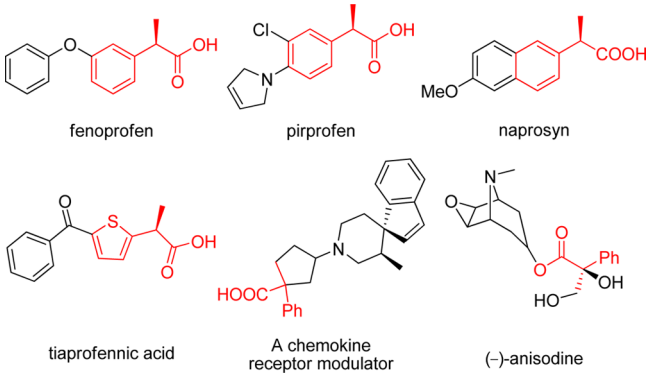
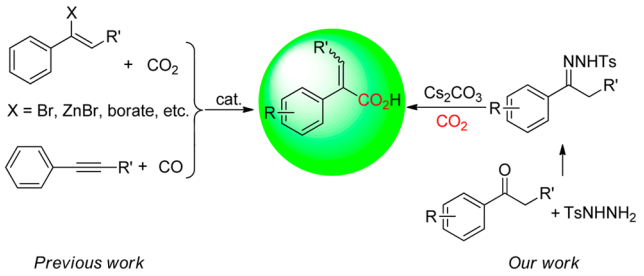


Figure 1. Some biologically active compounds derived from α-arylacrylic acids.

serve as key intermediates leading to a series of anti-inflammatory agents, such as naprosyn, pirprofen, and fenoprofen.[1,2] Therefore, except for the elegant one-step Pd-catalyzed carbonylation reaction of alkynes with CO toward α,β-unsaturated carboxylic acids,[3] considerable efforts have been paid to the carboxylation reactions of α-prefunctionalized aryl olefins (Scheme 1).[4] For instance, Nolan described Ni-catalyzed carboxylation of organoboronates to generate α-arylacrylic acids in moderate yield.[4a] Kondo reported LiCl-promoted transition-metal-free carboxylation of organozinc reagents.[4b] Yu reported ionic liquid-promoted hydroxycarbonylation of vinyl bromides to generate α,β-unsaturated carboxylic acids using CO as the carbonyl source.[4d] However, the α-prefunctionalization of aryl olefins is rather difficult and time-consuming. Thus, the development of more practical and efficient procedures using simple starting materials remains an area of synthetic interest.

Scheme 1. Some Pathways Leading to α-Arylacrylic Acids



On the other hand, the Shapiro reaction provides a powerful strategy for the synthesis of natural products[5] and polysubstituted alkenes,[6] many of which are not easily accessed by other means. Generally, a Shapiro reaction involves the treatment of the sulfonyl hydrazone with a base to provide the vinyl-lithium intermediate, followed by trapping of the vinyl anion with electrophiles to generate corresponding alkene-based products.[7] For example, the in situ generated vinyl-lithium intermediate could be trapped by CO_2 to give α-arylacrylic acids.[7h] However, the harsh reaction conditions such as the requirement of using strong bases such as ^{n}BuLi and an extremely low reaction temperature (−78 °C) dramatically decreases its practicality. Thus, the development of more practical and mild procedures is highly desirable. Herein, we wish to report our study on the Cs_2CO_3-promoted carboxylation of *N*-tosylhydrazones with atmospheric CO_2[8,9] toward α-arylacrylic acids. The procedure was featured with (1) the employment of Cs_2CO_3 rather than ^{n}BuLi as the base and (2) a reaction temperature of 80 °C rather than −78 °C.

We initiated our investigation on the model reaction of *N*-tosylhydrazones (**1a**) with CO_2 to optimize the critical reaction parameters (Table 1). To our delight, we found that in the

Received: December 23, 2014
Published: February 19, 2015

DOI: 10.1021/jo502908v
J. Org. Chem. 2015, 80, 2855−2860

Table 1. Selected Results for Screening the Optimized Reaction Conditions[a]

entry	base	solvent	temp. (°C)	yield (%)[b]
1	KO^{t}Bu	DMF	100	27
2	KO^{t}Bu	CH_3CN	100	8
3	KO^{t}Bu	dioxane	100	trace
4	KO^{t}Bu	toluene	100	trace
5	KO^{t}Bu	THF	100	<10
6	KO^{t}Bu	DMSO	100	38
7	LiO^{t}Bu	DMSO	100	trace
8	K_2CO_3	DMSO	100	56
9	AcONa	DMSO	100	trace
10	NaH	DMSO	100	<10
11	Cs_2CO_3	DMSO	100	65 (63)[c] (61)[d] (43)[e]
12	Cs_2CO_3	DMSO	80	68 (65)[f] (53)[g]
13	Cs_2CO_3	DMSO	60	41
14[h]	Cs_2CO_3	DMSO	80	0
15	-	DMSO	80	0
16[i]	Cs_2CO_3	DMSO	80	63

[a]Reaction conditions: **1a** (0.2 mmol), base (0.6 mmol), solvent (2.5 mL), under 1 atm of CO_2 for 12 h, in a sealed Schlenk tube, unless otherwise noted. [b]Isolated yield. [c]Cs_2CO_3 (1.0 mmol). [d]Cs_2CO_3 (0.4 mmol). [e]Cs_2CO_3 (0.2 mmol). [f]7 h. [g]3 h. [h]Under N_2. [i]CO_2 (1.0 MPa).

presence of a catalytic amount of $Pd(OAc)_2$ and 3 equiv of KO^{t}Bu the reaction of **1a** under atmospheric CO_2 could afford **2a** in 25% yield. Interestingly, the process could proceed even in the absence of a palladium catalyst (Table 1, entry 1). Encouraged by these initial results, other reaction conditions, such as solvent, base, and reaction temperature, were also screened. First, the solvent was found to have a profound effect: specifically, DMSO was superior to CH_3CN, DMF, or dioxane (Table 1, entries 1−6). Subsequently, other bases such as LiO^{t}Bu, AcONa, K_2CO_3, and Cs_2CO_3 were also tested. Cs_2CO_3 appeared to be the best, delivering the carboxylation product in 65% yield (Table 1, entries 7−11). Additionally, 80 °C was found to be more suitable for this reaction (Table 1, entries 11−13). Furthermore, controlled experiments revealed that the carbonyl group indeed came from CO_2 and the base was essential for this reaction (Table 1, entries 14−15). However, increasing the pressure of CO_2 did not have any positive effect for this transformation (Table 1, entry 16). After considerable experimentation, we found that the combination of 3 equiv of Cs_2CO_3 in DMSO at 80 °C under atmospheric CO_2 for 12 h served as the optimal conditions for this transformation (Table 1, entry 12).

With the optimized reaction conditions in hand, we then explored the scope and limitation of this transformation on the presence of a variety of functional groups of the *N*-tosylhydrazones. As shown in Figure 2, a variety of functional groups on the *N*-tosylhydrazones proceeded smoothly with CO_2 and generated the desired carboxylation products in moderate to good yields. Generally, the hindrance of the phenyl ring of *N*-tosylhydrazones had some effect on the efficiency. For example, the *ortho*-substituted substrates resulted in lower yields (**2a** vs **2c** and **2d**; Figure 2). Furthermore, the reaction efficiency was sensitive to the electronic property of the groups on the phenyl ring of *N*-tosylhydrazones. Substrates bearing

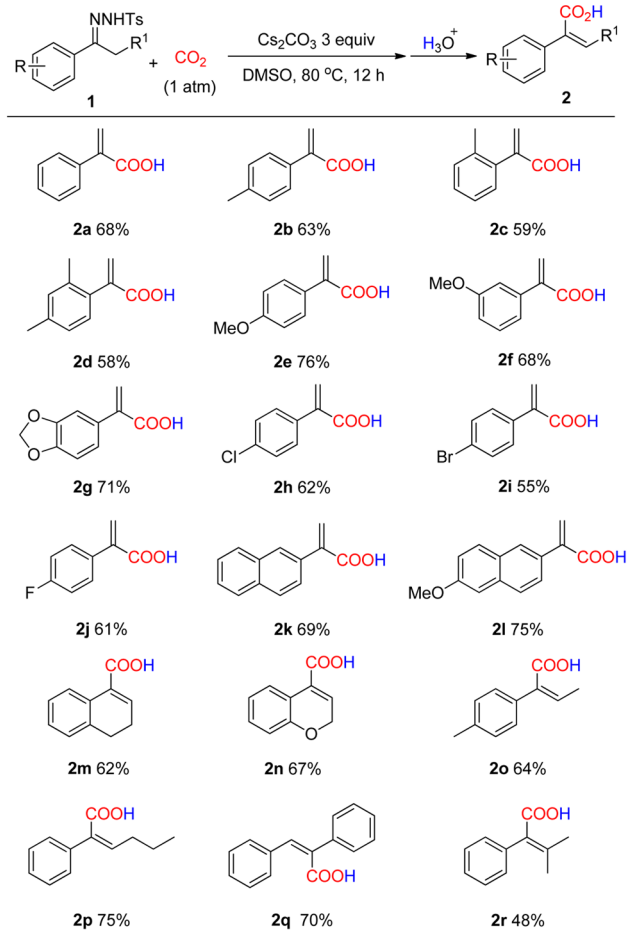
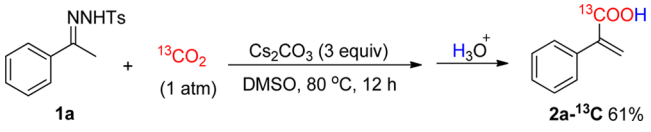


Figure 2. Scope of *N*-tosylhydrazones. **1** (0.2 mmol), Cs_2CO_3 (0.6 mmol), DMSO (2.5 mL), at 80 °C under 1 atm of CO_2, for 12 h, in a sealed Schlenk tube.

electron-donating groups gave a slightly higher yield than those analogues with electron-withdrawing groups (**2e**, **2f**, and **2g** vs **2h**, **2i**, and **2j**; **2k** vs **2l**, Figure 2). Unfortunately, strong electron-withdrawing groups such as CF_3, CN, and NO_2 inhibited the reaction. Notably, some reactive functional groups, such as chloro and bromo, which were suitable for potentially further functionalization, survived in these reactions. In comparison, strong bases such as ^{n}BuLi used in traditional Shapiro reactions were not tolerated well by bromo- and chloro-substituted derivatives.[7] Notably, *N*-tosylhydrazones with secondary or tertiary carbon in the *β*-position also worked well under the standard conditions with moderate to good yields (**2m**−**2r**). In particular, the procedure was applicable to cyclic substrates. For instance, **2m** and **2n** were isolated in 62% and 67% yields, respectively. Interestingly, only *Z*-configuration products were formed for products **2o**−**2q**[10] (for details, see Figures S1−S4, Supporting Information).

The carboxylation of **1a** with $^{13}CO_2$ was examined (Scheme 2) in order to confirm whether CO_2 participated in this

Scheme 2. ^{13}C-Labeling Study

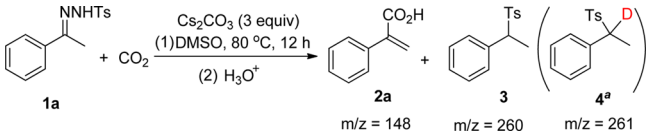


DOI: 10.1021/jo502908v
J. Org. Chem. 2015, 80, 2855−2860

reaction. α-Phenylacrylic acid **2a-^{13}C** with ^{13}C-carboxyl group was isolated in 61% yield. The incorporation of ^{13}C-carboxyl was confirmed by EI-MS (m/z [M$^+$]: 149, [M$^+$] − ^{13}COOH: = 103) and ^{13}C NMR (the strong signal at 172.0 ppm in $CDCl_3$), which was similar to the result reported by Baba[11] (Figures S5−S6, Supporting Information).

To gain further insight into the reaction mechanism, first, we tried to examine the main byproducts of the reaction. When the reaction of **1a** with CO_2 was conducted under the standard conditions (Scheme 3), apart from the main product of **2a**

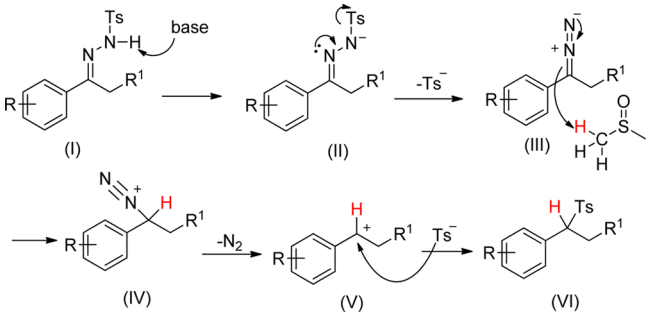
Scheme 3. Preliminary Mechanism Study[a]



[a]DMSO-d_6 was used instead of DMSO.

isolated in 68% yield, sulfone[12] **3** (m/z = 260) was also detected by GC-MS as the major byproduct (Figure S7, Supporting Information). However, when the reaction was conducted in DMSO-d_6, the deuterated product **4** (m/z = 261) (Figure S8, Supporting Information) rather than the non-deuterated **3** (m/z = 260) was detected. As shown in Scheme 4,

Scheme 4. Proposed Mechanism for the Byproduct

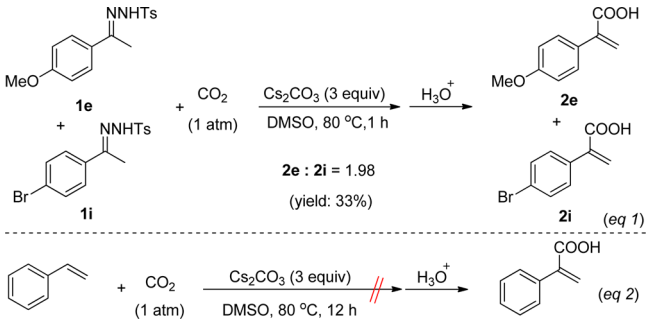


the pathway for the formation of the byproduct sulfone may involve Cs_2CO_3-promoted deprotonation of **I** to generate **II**, subsequent desulfonation to generate the diazo intermediate **III**. Then, the abstraction of the hydride of DMSO generated **IV**, followed by the extrusion of N_2, and the nucleophilic addition of Ts^- to **V** generates the final product **VI**.[13]

On the other hand, the competitive experiment of **1e** and **1i** under the standard conditions (Figure S9, Supporting Information) confirmed that the electron-donating group was beneficial for this transformation (Scheme 5, eq 1). On the other hand, styrene did not furnish the corresponding carboxylation product at all under the optimized reaction conditions (Scheme 5, eq 2).

Based on the preliminary experimental results, a plausible mechanism for the formation of the desired carboxylate product is outlined in Scheme 6. It may involve Cs_2CO_3-promoted deprotonation of **A** to generate **B**, which would tautomerize to intermediate **C**. Subsequently, **C** would be trapped by CO_2 to give **D**. Then, C−H cleavage assisted by base would proceed along with the desulfonation and the extrusion of N_2 leading to **F** (route *a*). Alternatively, desulfonation of **D** affords **E**, followed by C−H cleavage and the extrusion of N_2 to generate

Scheme 5



F (route *b*). Finally, protonation of **F** by acid provides the desired carboxylic acid **G**.

In conclusion, we have developed a mild and environmentally benign Cs_2CO_3-promoted carboxylation of *N*-tosylhydrazones with CO_2 leading to the α-arylacrylic acids in moderate to good yields. This method was different from the traditional Shapiro reaction, where the strong base ^{n}BuLi and extremely low reaction temperature (−78 °C) were not required. Thus, it represents an exceedingly attractive alternative to the traditional methods leading to α-arylacrylic acids.

EXPERIMENTAL SECTION

General Experimental Details. Chemicals were used as received without special purification unless stated otherwise. ^{1}H and ^{13}C NMR were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for ^{13}C NMR). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) or DMSO-d_6 (δ 2.50 or 39.5 ppm) as the internal standard. All new compounds were further characterized by HRMS. Column chromatography was performed on silica gel 300−400 mesh.

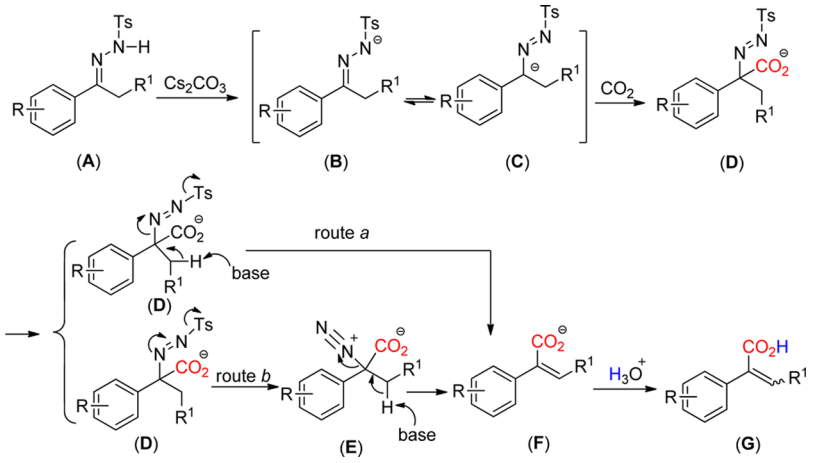
General Procedure. *N*-Tosylhydrazone (0.2 mmol), Cs_2CO_3 (0.6 mmol), and DMSO (2.5 mL) was added into a 10 mL Schlenk tube equipped with a stir bar. The reaction vessel was evacuated and backfilled with CO_2 (1 atm) (this sequence was repeated three times). Then, the sealed Schlenk tube was stirred at 80 °C for 12 h. After the reaction mixture was cooled to room temperature, 1 M HCl (1 mL) was added to terminate the reaction and convert the carboxylate into carboxylic acid. The reaction mixture was diluted with EtOAc and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel with petroleum ether−ethyl acetate as eluent to give the desired product.

*2-Phenylacrylic Acid (**2a**).*[3,14] Flash column chromatography on a silica gel (ethyl acetate-petroleum ether, 1:5) gave the product (20.1 mg, 68%) as a white solid. mp 97−100 °C (lit.[3] 101−103 °C). ^{1}H NMR ($CDCl_3$ 400 MHz): δ 11.06 (brs, 1H), 7.44−7.47 (m, 2H), 7.36−7.41 (m, 3H), 6.57 (s, 1H), 6.04 (s, 1H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 172.2, 140.6, 136.1, 129.5, 128.4, 128.3, 128.1.

*2-p-Tolylacrylic Acid (**2b**).* Flash column chromatography on a silica gel (ethyl acetate−petroleum ether, 1:5) gave the product (20.4 mg, 63%) as a white solid. mp 90−92 °C. ^{1}H NMR ($CDCl_3$ 400 MHz): δ 7.34 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 6.49 (s, 1H), 5.99 (s, 1H), 2.37 (s, 3H). ^{13}C

DOI: 10.1021/jo502908v
J. Org. Chem. 2015, 80, 2855−2860

Scheme 6. Proposed Mechanism for the Carboxylate Product



NMR ($CDCl_3$ 100 MHz): δ 172.1, 140.5, 138.2, 133.2, 128.8, 128.6, 128.3, 21.2. IR (KBr) ν 3438, 3067, 3028, 2993, 2920, 1682, 1606, 1515, 1434, 1336, 1280, 1089, 964 cm^{-1}. MS (EI): 162 (M^+); HRMS (ESI-TOF) m/z: calcd. for $C_{10}H_{10}NaO_2$ $[M + Na]^+$ 185.0573, found 185.0576.

2-o-Tolylacrylic Acid (**2c**). Flash column chromatography on a silica gel (ethyl acetate–petroleum ether, 1:5) gave the product (19.1 mg, 59%) as a white solid. mp 93–95 °C. ^1H NMR ($CDCl_3$ 400 MHz): δ 7.23–7.26 (m, 1H), 7.13–7.20 (m, 3H), 6.64 (dd, J = 1.4 Hz, 1H), 5.84 (dd, J = 1.4 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 171.2, 141.1, 136.5, 136.2, 130.8, 129.9, 129.5, 128.4, 125.7, 19.8. IR (KBr) ν 3435, 3066, 3022, 2957, 1726, 1686, 1614, 1577, 1512, 1485, 1379, 966 cm^{-1}. MS (EI): 162 (M^+); HRMS (ESI-TOF) m/z: calcd. for $C_{10}H_{10}NaO_2$ $[M + Na]^+$ 185.0573, found 185.0576.

2-(2,4-Dimethylphenyl)acrylic Acid (**2d**). Flash column chromatography on a silica gel (ethyl acetate-petroleum ether, 1:5) gave the product (20.4 mg, 58%) as a white solid. mp 89–91 °C. ^1H NMR ($CDCl_3$ 400 MHz): δ 7.00–7.06 (m, 3H), 6.62 (d, J = 1.6 Hz, 1H), 5.82 (d, J = 7.7 Hz, 1H), 2.34 (s, 3H), 2.21 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 171.9, 141.0, 138.1, 136.0, 133.6, 130.8, 130.6, 129.5, 126.4, 21.1, 19.8. IR (KBr) ν 3432, 3075, 2952, 2921, 1683, 1616, 1577, 1498, 1429, 1305, 1238, 1218 cm^{-1}. MS (EI): 176 (M^+); HRMS (ESI-TOF) m/z: calcd. for $C_{11}H_{12}NaO_2$ $[M + Na]^+$ 199.0730, found 199.0733.

2-(4-Methoxyphenyl)acrylic Acid (**2e**). Flash column chromatography on a silica gel (ethyl acetate–petroleum ether, 1:3) gave the product (27.1 mg, 76%) as a white solid. mp 110–112 °C. ^1H NMR ($CDCl_3$ 400 MHz): δ 7.41 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.47 (s, 1H), 5.97 (s, 1H), 3.84 (s, 3H). ^{13}C NMR ($CDCl_3$ 75 MHz): δ 172.3, 159.7, 139.9, 129.7, 128.5, 128.0, 113.5, 55.3. IR (KBr) ν 3446, 3087, 3041, 2954, 1697, 1683, 1608, 1512, 1490, 1436, 1334, 1251, 1029 cm^{-1} MS (EI): 178 (M^+); HRMS (ESI-TOF) m/z: calcd. for $C_{10}H_{10}NaO_3$ $[M + Na]^+$ 201.0522, found 201.0528.

2-(3-Methoxyphenyl)acrylic Acid (**2f**). Flash column chromatography on a silica gel (ethyl acetate–petroleum ether, 1:3) gave the product (24.2 mg, 68%) as a colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.25–7.30 (m, 1H), 6.98–7.03 (m, 2H), 6.88–6.91 (m, 1H), 3.82 (s, 3H). ^{13}C NMR ($CDCl_3$ 75 MHz): δ 172.0, 159.3, 140.5, 137.5, 129.6, 129.2, 121.0, 114.3, 113.9, 55.3. IR (KBr) ν 3430, 3076, 2960, 2837, 1699, 1600, 1577, 1489, 1458, 1286, 1253, 1045 cm^{-1} MS (EI): 178 (M^+); HRMS (ESI-TOF) m/z: calcd. for $C_{10}H_9O_3$ $[M - H]^+$ 177.0552, found 177.0548.

2-(Benzo[d][1,3]dioxol-5-yl)acrylic Acid (**2g**). Flash column chromatography on a silica gel (ethyl acetate–petroleum ether, 1:5) gave the product (27.3 mg, 71%) as a white solid. mp 161–163 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.91–6.94 (m, 2H), 6.79–6.81 (m, 1H), 6.46 (d, J = 1.0 Hz, 1H), 5.98 (s, 2H), 5.96 (d, J = 1.0 Hz, 1H). ^{13}C NMR (DMSO-d_6 100 MHz): δ 167.9, 147.1, 147.0, 140.9, 130.6, 124.8, 121.9, 108.5, 107.8, 101.1. IR (KBr) ν 3446, 3078, 3035, 2904, 1683, 1608, 1502, 1491, 1436, 1245, 1043 cm^{-1}. MS (EI): 192 (M^+); HRMS (ESI-TOF) m/z calcd. for $C_{10}H_7O_4$ $[M - H]^+$ 191.0338, found 191.0344.

2-(4-Chlorophenyl)acrylic Acid (**2h**). Flash column chromatography on a silica gel (ethyl acetate–petroleum ether, 1:5) gave the product (22.6 mg, 62%) as a white solid. mp 89–91 °C. ^1H NMR ($CDCl_3$ 400 MHz): δ 7.33–7.40 (m, 4H), 6.57 (s, 1H), 6.04 (s, 1H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 171.8, 139.4, 134.5, 134.4, 130.0, 129.8, 128.3. IR (KBr) ν 3432, 3082, 3034, 2923, 1701, 1678, 1612, 1596, 1560, 1490, 1396, 1317, 1218, 1093, 1014, 970 cm^{-1}. MS (EI): 182 (M^+); HRMS (ESI-TOF) m/z calcd. for $C_9H_6ClO_2$ $[M - H]^+$ 181.0056, found 181.0054.

2-(4-Bromophenyl)acrylic Acid (**2i**). Flash column chromatography on a silica gel (ethyl acetate–petroleum ether, 1:5) gave the product (25.0 mg, 55%) as a white solid. mp 97–99 °C. ^1H NMR ($CDCl_3$ 400 MHz): δ 7.50 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.57 (s, 1H), 6.04 (s, 1H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 171.5, 139.4, 134.9, 131.3, 130.1, 122.7. IR (KBr) ν 3432, 3082, 3033, 2997, 1679, 1612, 1579, 1487, 1313, 1220, 1087, 1010, 831 cm^{-1}. MS (EI): 226 (M^+); HRMS (ESI-TOF) m/z: calcd. for $C_9H_6BrO_2$ $[M - H]^+$ 224.9551, found 224.9545.

2-(4-Fluorophenyl)acrylic Acid (**2j**). Flash column chromatography on a silica gel (ethyl acetate–petroleum ether, 1:5) gave the product (20.2 mg, 61%) as a white solid. mp 107–109 °C. ^1H NMR ($CDCl_3$ 400 MHz): δ 7.40–7.44 (m, 2H), 7.03–7.08 (m, 2H), 6.54 (s, 1H), 6.01 (s, 1H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 171.9, 163.2 (d, J = 246.0 Hz), 139.6, 132.1, 130.2 (d, J = 18.9 Hz), 129.5, 115.1 (d, J = 21.4 Hz). IR (KBr) ν 3432, 3082, 1701, 1612, 1512, 1436, 1313, 1228, 1163, 962 cm^{-1}. MS (EI): 166 (M^+); HRMS (ESI-TOF) m/z: calcd. for $C_9H_6FO_2$ $[M - H]^+$ 165.0352, found 165.0340.

2-(Naphthalen-2-yl)acrylic Acid (**2k**). Flash column chromatography on a silica gel (ethyl acetate–petroleum ether, 1:3)

DOI: 10.1021/jo502908v
J. Org. Chem. 2015, 80, 2855–2860

gave the product (27.3 mg, 69%) as a white solid. mp 116−118 °C. ^{1}H NMR ($CDCl_3$ 400 MHz): δ 7.94 (s, 1H), 7.83−7.87 (m, 3H), 7.56 (m, 1H), 7.50 (m, 2H), 6.64 (s, 1H), 6.15 (s, 1H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 172.0, 140.6, 133.6, 133.1, 133.0, 129.7, 128.3, 127.8, 127.7, 127.6, 126.5, 126.3, 126.2. IR (KBr) ν 3445, 3055, 3018, 1697, 1685, 1606, 1506, 1429, 1326, 1253, 1193 cm^{-1}. MS (EI): 198 (M^+); HRMS (ESI-TOF) m/z: calcd. for $C_{13}H_9O_2$ $[M - H]^+$ 197.0603, found 197.0599.

*2-(6-Methoxynaphthalen-2-yl)acrylic Acid (**2l**).*[15] Flash column chromatography on a silica gel (ethyl acetate−petroleum ether, 1:3) gave the product (34.2 mg, 75%) as a white solid. mp 169−172 °C (lit.[15] 172−174 °C) ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.78−7.91 (m, 3H), 7.52−7.55 (m, 1H), 7.32 (s, 1H), 7.16−7.18 (m, 1H), 6.26 (s, 1H), 6.06 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 168.5, 158.1, 142.0, 134.3, 132.3, 130.2, 128.5, 127.3, 127.0, 126.7, 125.9, 119.3, 106.2, 55.7.

*3,4-Dihydronaphthalene-1-carboxylic Acid (**2m**).*[16] Flash column chromatography on a silica gel (ethyl acetate−petroleum ether, 1:3) gave the product (21.6 mg, 62%) as a white solid. mp 120−122 °C. ^{1}H NMR ($CDCl_3$ 400 MHz): δ 7.94 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 4.8 Hz, 1H), 7.19−7.30 (m, 3H), 2.82 (t, J = 7.8 Hz, 2H), 2.45−2.50 (m, 2H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 172.0, 143.0, 136.2, 130.4, 129.9, 127.7, 127.5, 126.6, 126.2, 27.4, 23.7.

*2H-Chromene-4-carboxylic Acid (**2n**).* Flash column chromatography on a silica gel (ethyl acetate−petroleum ether, 1:3) gave the product (23.6 mg, 67%) as a white solid. mp 134−136 °C. ^{1}H NMR ($CDCl_3$ 400 MHz): δ 7.97 (dd, J = 7.9 Hz, 1H), 7.18−7.22 (m, 1H), 7.05 (s, 1H), 6.98 (t, J = 7.7 Hz, 1H), 6.87 (dd, J = 8.1 Hz, 1H), 4.86 (m, 2H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 169.3, 154.1, 134.4, 130.0, 126.4, 121.8, 119.2, 116.3, 64.6. IR (KBr) ν 3434, 3067, 3031, 2981, 2813, 1691, 1625, 1604, 1569, 1487, 1454, 1375, 1226, 1004 cm^{-1}. MS (EI): 176 (M^+); HRMS (ESI-TOF) m/z: calcd. for $C_{10}H_7O_3$ $[M - H]^+$ 175.0395, found 175.0389.

*(Z)-2-(p-Tolyl)but-2-enoic Acid (**2o**).* Flash column chromatography on a silica gel (ethyl acetate−petroleum ether, 1:5) gave the product (22.5 mg, 64%) as a white solid. mp 108−110 °C. ^{1}H NMR ($CDCl_3$ 400 MHz): δ 7.23 (d, J = 7.9 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.41 (dd, J = 7.3 Hz, 1H), 2.34 (s, 3H), 2.14 (d, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 173.5, 139.9, 137.4, 135.4, 134.2, 128.9, 127.8, 21.1, 16.4. IR (KBr) ν 3436, 3075, 3034, 2958, 2923, 2852, 1733, 1685, 1616, 1577, 1512, 1458, 1288, 1076 cm^{-1}. MS (EI): 176 (M^+); HRMS (ESI-TOF) m/z: calcd. for $C_{11}H_{12}NaO_2$ $[M + Na]^+$ 199.0730, found 199.0727.

*(Z)-2-Phenylhex-2-enoic Acid (**2p**).* Flash column chromatography on a silica gel (ethyl acetate−petroleum ether, 1:5) gave the product (28.5 mg, 75%) as a colorless oil. ^{1}H NMR ($CDCl_3$ 400 MHz): δ 7.28−7.39 (m, 5H), 6.35 (t, J = 7.5 Hz, 1H), 2.59 (q, J = 7.4 Hz, 2H), 1.56 (m, 2H), 1.00 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 173.4, 145.9, 138.2, 133.4, 128.1, 128.0, 127.6, 32.2, 22.5, 13.8. IR (KBr) ν 3461, 3078, 3035, 2960, 2931, 2871, 1689, 1608, 1502, 1490, 1419, 1284, 1245, 1236 cm^{-1}. MS (EI): 190 (M^+); HRMS (ESI-TOF) m/z: calcd. for $C_{12}H_{14}NaO_2$ $[M + Na]^+$ 213.0886, found 213.0885.

*(Z)-2,3-Diphenylacrylic Acid (**2q**).* Flash column chromatography on a silica gel (ethyl acetate−petroleum ether, 1:4) gave the product (31.4 mg, 70%) as a white solid. mp 135−137 °C. The E configured counterpart is known.[10a] ^{1}H NMR ($CDCl_3$ 400 MHz): δ 7.49−7.55 (m, 4H), 7.35−7.45 (m, 6H), 7.12 (s, 1H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 174.9, 136.8, 135.4, 134.1, 133.8, 128.8, 128.7, 128.6, 128.5, 128.4, 126.9. IR (KBr) ν 3432, 3056, 3024, 2925, 1710, 1676, 1635, 1618, 1604, 1569, 1490, 1436, 1373 cm^{-1}. MS (EI): 224 (M^+); HRMS (ESI-TOF) m/z: calcd. for $C_{15}H_{12}NaO_2$ $[M + Na]^+$ 247.0730, found 247.0725.

*3-Methyl-2-phenylbut-2-enoic Acid (**2r**).*[17] Flash column chromatography on a silica gel (ethyl acetate−petroleum ether, 1:5) gave the product (16.9 mg, 48%) as a white solid. mp 150−152 °C (lit.[17] 149−150 °C) ^{1}H NMR ($CDCl_3$ 400 MHz): δ 7.33−7.37 (m, 2H), 7.29−7.30 (m, 1H), 7.16−7.18 (m, 2H), 2.24 (s, 3H), 1.71 (s, 3H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 173.2, 151.2, 138.2, 129.6, 128.9, 128.2, 127.1, 24.6, 22.9.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all the products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jiangcheng@cczu.edu.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (nos. 21272028 and 21202013), State Key Laboratory of Coordination Chemistry of Nanjing University, Jiangsu Key Laboratory of Advanced Catalytic Materials &Technology, Jiangsu Province Key Laboratory of Fine Petrochemical Engineering, and the Priority Academic Program Development of Jiangsu Higher Education Institutions for financial support.

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