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Mizoroki–Heck cross-coupling reactions using palladium immobilized on DABCO-functionalized silica

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Abstract
A heterogeneous palladium catalyst supported on silica modified by DABCO has been prepared by post-synthetic modification of silica gel. This heterogeneous catalytic system exhibits high activity and stability in the Mizoroki–Heck cross-coupling reaction of various aryl halides with olefins. The reaction proceeds efficiently under efficiently under mild mild reaction conditions and high yield, with the formation of *E*-isomers selectively. Moreover, we successfully established a gram-scale synthesis, and the catalyst was reused for up to ten catalytic cycles.

Introduction

An important part of modern chemistry is based on the use of precious platinum group metal (PGM) catalysts [1–9]. In particular, Pd, which is an active metal with high demand, has been most widely used for the fabrication of carbon–carbon and carbon–heteroatom bonds for the production of intermediates of biologically active compounds, natural products and fine chemicals [10–13]. The Pd-catalyzed coupling of olefins with aryl or vinyl halides [14] to form a C–C bond is known as the Mizoroki–Heck cross-coupling reaction and has been widely used for the synthesis of important compounds like flavoring agents, pharmaceuticals, agrochemicals and UV absorbents [15, 16].

Though the Mizoroki–Heck cross-coupling reaction has been most widely applied with homogeneous catalysts [17–20], it suffers from various disadvantages such as tedious workup procedures, lack of reusability and contamination of residual metals in the desired product. These disadvantages can be overcome by using heterogeneous catalysts, via immobilization of Pd on various solid supports such as polymers [21], activated carbons [22], metal oxides [23], biopolymers and zeolites [24]. Recently, it has been found that Pd complexes with various ligands supported on silica have considerable utility in various cross-coupling reactions including Mizoroki–Heck cross-coupling reaction [25, 26], as silica displays many advantageous properties such as excellent chemical and thermal stability, good accessibility and porosity. In addition, the organic groups can be easily grafted on the silica surface by simple post-synthetic modifications [27].

As amines are less toxic, inexpensive, easy to handle and less air sensitive, catalytic systems based on DABCO might be ideal to carry out the Mizoroki–Heck cross-coupling reaction under phosphine-free conditions [28–31]. DABCO is a cage-like, small diazabicyclic molecule with medium steric hindrance and has received considerable attention as an organocatalyst for various organic transformations [32–35]. In 2014, Li et al. [36] reported the first use of DABCO as a ligand in Pd-catalyzed phosphine-free cross-coupling reactions, while our research group reported [37] Pd–DABCO supported on SiO_2 as an effective reusable catalyst system for Suzuki–Miyaura cross-coupling in aqueous ethanol using K_2CO_3 as a base at 80 °C. The results showed that the catalyst could be used to convert a variety of aryl bromides and boronic acids to the desired coupling products in good-to-excellent yields, which encouraged us to use this catalytic system for Mizoroki–Heck cross-coupling reactions. As a matter of fact, we succeeded in obtaining a very rapid and quantitative conversion of various aryl bromides with different olefins into a variety of coupling products in DMF using K_2CO_3 as a base at 100 °C temperature and with high selectivity.

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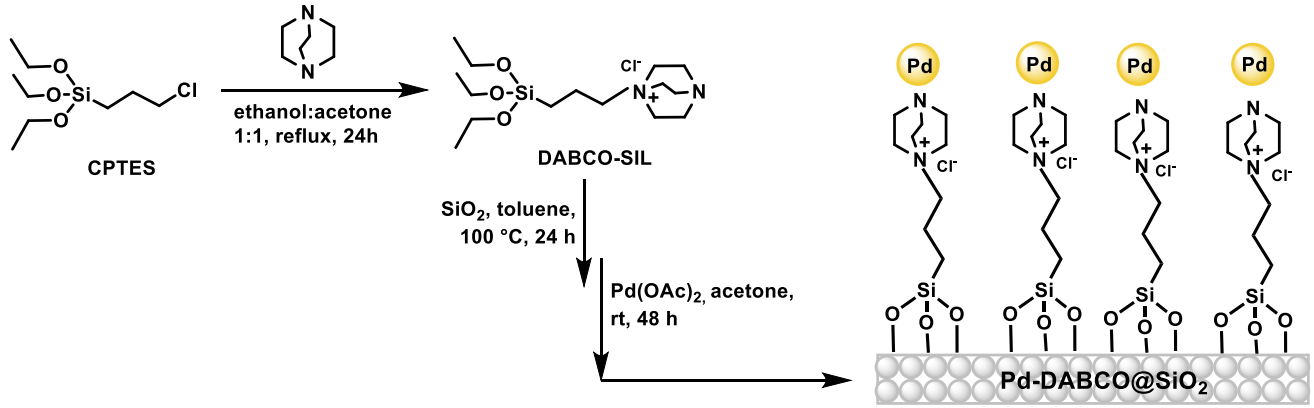
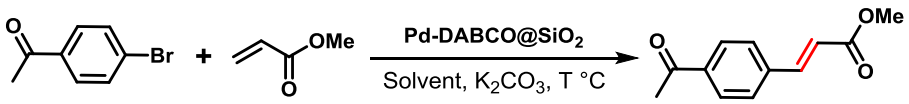


Scheme 1 Preparation of Pd–DABCO@SiO_2 catalyst

Table 1 Optimization studies for Mizoroki–Heck coupling reaction[a]



Entry	Solvent	Time (h)	*T* °C	Yield (%)[b]
1	CH_3CN	12	80	10
2	DMC	12	60	30
3	THF	12	66	20
4	Toluene	12	100	40
5	DMF	06	100	94
6	EtOH	12	80	05
7	H_2O	12	100	Trace
8	H_2O/DMF (50:50)	12	100	10
9	H_2O/DMF (20:80)	12	100	20

[a]Reaction conditions: 4-bromoacetophenone (1.0 mmol), methyl acrylate (1 mmol), Pd–DABCO@SiO_2 (1 mol%), K_2CO_3 (2.0 mmol), solvent (5 mL) in an open vessel. [b]Isolated yields based on the aryl halide used

Results and discussion

The preparation and characterization of the Pd–DABCO@SiO_2 catalyst were performed following the literature procedure as described in our previous report [37], as schematically represented in Scheme 1. The amount of Pd in the catalyst as determined by ICP–AES was found to be 0.075 mmol g^{-1} of solid support.

The catalytic activity of Pd–DABCO@SiO_2 catalyst was studied for the coupling of 4-bromoacetophenone with methyl acrylate as a model reaction using various bases, solvents and at different temperatures. Out of various protic and aprotic solvents used [38, 39], DMF worked well at 100 °C temperature using K_2CO_3 as a base (Table 1, entry 5). The catalyst was inactive in an aqueous medium and gave only trace amounts of coupling product with prolonged reaction time (Table 1, entry 7). When the reaction was carried out in H_2O/DMF mixture, only 10–20% yield was observed (Table 1, entries 8, 9).

The selection of the proper base is crucial for a success in Pd-catalyzed cross-coupling reactions [40]. The influence of the choice of base was investigated by performing the model reaction with varying organic and inorganic bases in DMF at 100 °C. We obtained very low yields with organic bases such as Et_3N and DBU (Table 2, entries 3 and 4). It was observed that 94% yield was obtained in the presence of K_2CO_3 as a base (Table 2, entry 5).

The effect of amount of catalyst on the percentage conversion of the model reaction was studied. Thus, among the different catalyst loadings, 1 mol% proved to be the best affording the desired product in 6 h with 94% yield in DMF at 100 °C (Table 2 entry 5). To study the effect of temperature

Table 2 Screening of various reaction conditions for Mizoroki–Heck reaction[a]

Entry	Base	Catalyst (mol%)	*T* °C	Time (h)	Yield (%)[b]
1	K_3PO_4	1.0	100	12	56
2	NaOH	1.0	100	12	60
3	Et_3N	1.0	100	12	70
4	DBU	1.0	100	12	65
5	K_2CO_3	1.0	100	06	94
6	K_2CO_3	0.5	100	12	48
7	K_2CO_3	1.5	100	06	94
8	K_2CO_3	1.0	90	12	80
9	K_2CO_3	1.0	80	12	61
10	K_2CO_3	1.0	70	12	32

[a]Reaction conditions: 4-bromoacetophenone (1.0 mmol), methyl acrylate (1 mmol), Pd–DABCO@SiO_2 (0.5–1.5 mol%), base (2.0 mmol), DMF (5 mL) in an open vessel. [b]Isolated yields based on the aryl halide used

on catalytic activity, the model reaction was carried out at different temperatures. As the temperature was reduced from 100 to 70 °C, the reaction time was prolonged 12 h with low yields (Table 2, entries 8–10). These results indicated that the temperature of reaction is crucial for the catalytic efficiency.

In the optimization study, the effect of the reaction time on the yield of the final product was confirmed for the current model reaction, and the results are presented in Fig. 1. For this study, the model reaction was carried out in the time range of 1–6 h. It was observed that the percentage yield of desired product increased with the increase in the reaction time giving 94% yield in 6 h.

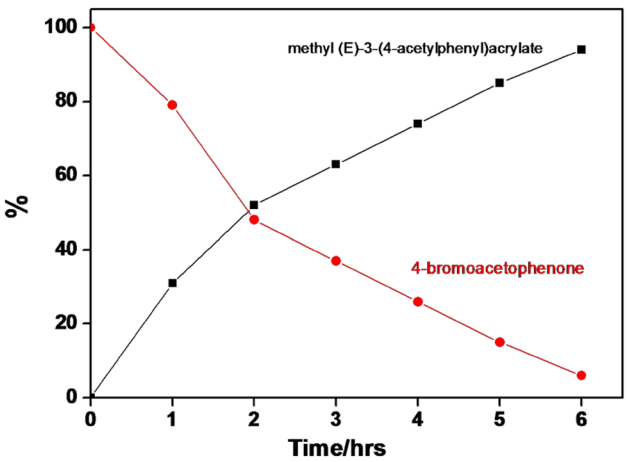


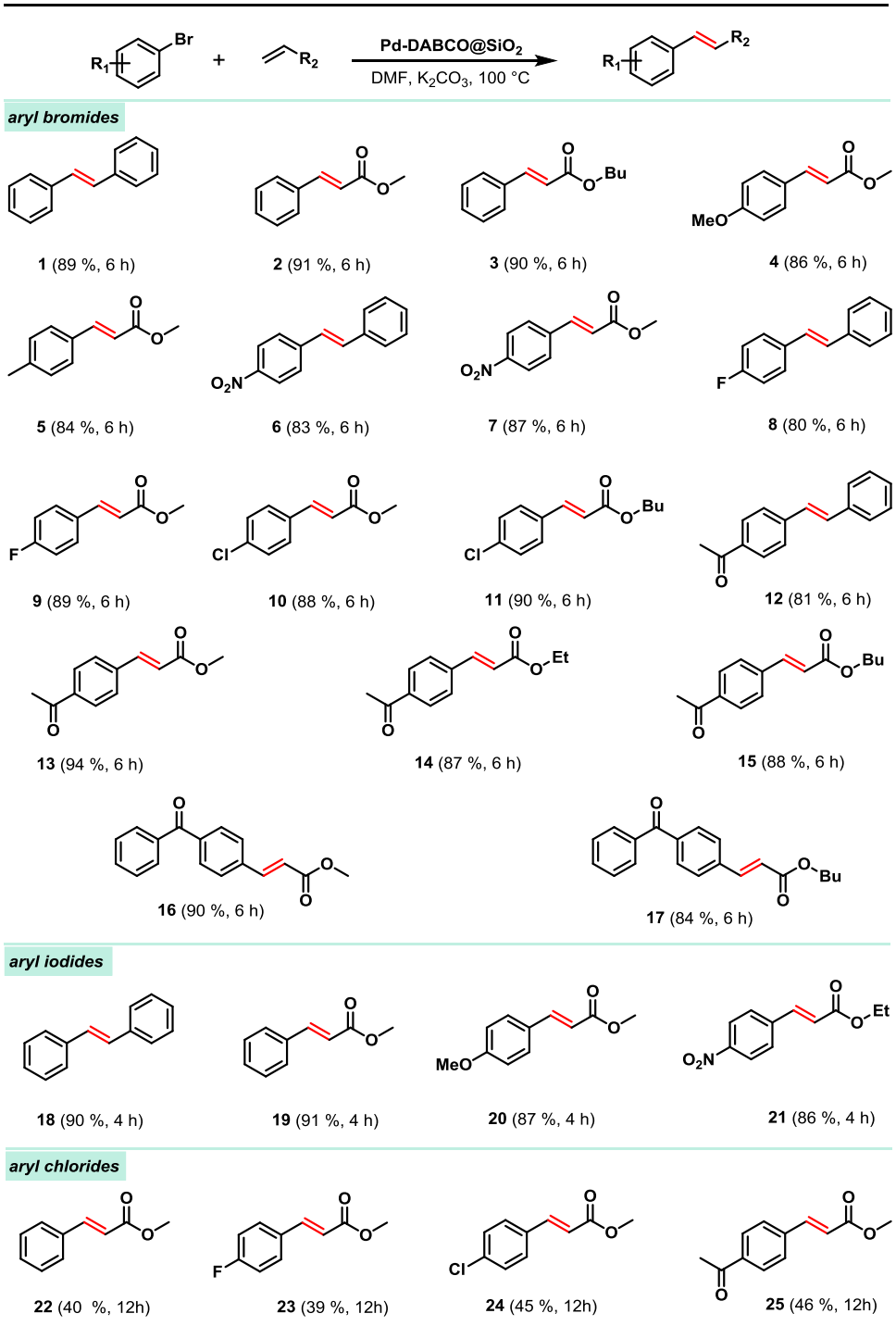
Fig. 1 Effect of reaction time on the yield of the desired product

To extend the scope of our work, a range of aryl halides and olefin compounds were examined using 1 mol% Pd–DABCO@SiO_2 in DMF at 100 °C using K_2CO_3 as a base. Various aryl bromides and olefins reacted smoothly to afford the desired coupling products in good-to-excellent yields, with the formation of only *E*-isomers (Table 3, entries 1–17). From a practical point of view, the utilization of the easily available, inactive and inexpensive aryl chlorides is highly desirable, and the catalyst showed moderate activity giving 39–46% yield of the desired product in 12 h (Table 3, entries 22–25). Active aryl iodides and olefins reacted smoothly as compared with aryl bromides and aryl chlorides to afford the desired coupling products in good-to-excellent yields in 4 h (Table 3, entries 18–21).

Gram-scale synthesis: As a part of our ongoing research in organic synthesis, we report a scalable synthetic approach for Mizoroki–Heck cross-coupling reactions by using optimized reaction conditions (Scheme 2). Treatment of 10 mmol of butyl acrylate with various aryl bromides gave good-to-excellent yields of the corresponding products. These results demonstrated the reproducibility and practical method for industrial applications.

Catalyst recyclability: The recyclability of Pd–DABCO@SiO_2 was investigated with consecutive coupling reactions of 4-bromoacetophenone with methyl acrylate (Fig. 2). After the first cycle, the catalyst was separated by centrifugation and washed with water, acetone and dichloromethane. The catalyst was then dried under vacuum before performing the reusability test and charging with fresh substrate. In this way, the catalyst was reused for ten consecutive cycles. As shown in Fig. 2, the catalyst could be used up to five times without significant loss of catalytic performance as well as

Table 3 Mizoroki-Heck reaction of various aryl halides and olefins over Pd–DABCO@SiO_2



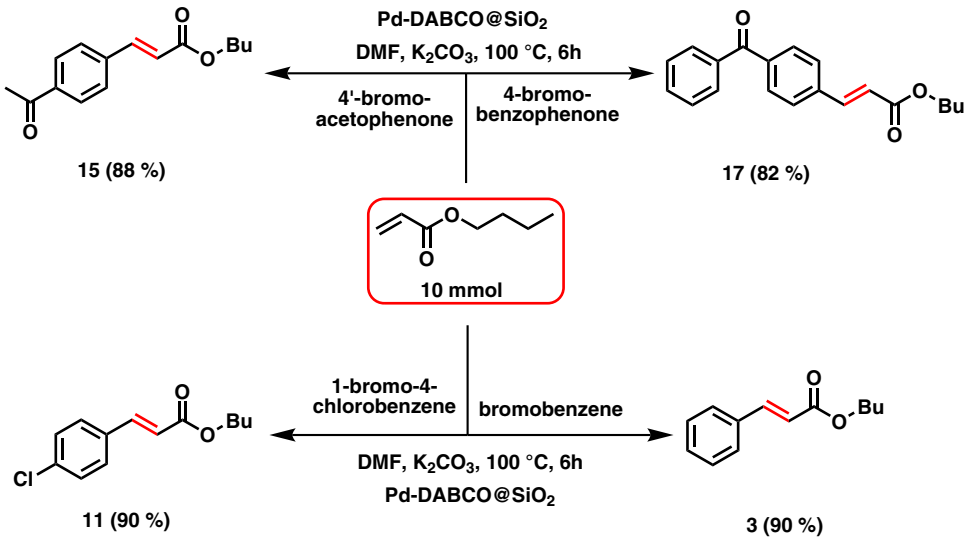
Reaction conditions: aryl halides (1 mmol), olefins (1 mmol), Pd–DABCO@SiO_2 (1 mol%), K_2CO_3 (2 mmol), DMF (5 mL, 100 °C), under air. Isolated yields after column chromatography

selectivity. The drop-off in reactivity of catalyst after the seventh catalytic cycle may be due to the deactivation of palladium metal.

Conclusion

In conclusion, Pd–DABCO@SiO_2 catalyst has been successfully synthesized followed by known grafting chemistry involving quaternization of DABCO. The resulting material was used as a heterogeneous catalyst for Mizoroki–Heck

Scheme 2 Gram-scale synthesis of acrylate derivatives



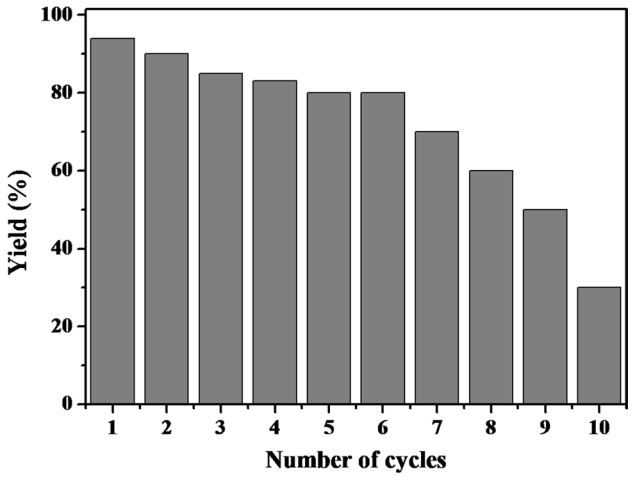


Fig. 2 Recycling of Pd–DABCO@SiO_2 catalyst for Mizoroki–Heck reaction

coupling reactions of various aryl halides with olefins to give the *E*-isomer selectively in good-to-excellent yields. The catalyst showed interesting features such as high efficiency, economy and simple reaction processing. Moreover, easy recovery with recyclability is one of the additional advantages of this catalyst. In addition, the protocol could be applied for gram-scale synthesis of acrylates.

Experimental

General remarks

^{1}H-NMR and ^{13}C-NMR spectra of the pure compounds were recorded on a Bruker Avon 200 MHz, 400 MHz or 500 MHz spectrometer. Chemical shifts for ^{1}H NMR are referred to internal TMS (0 ppm), and chemical shifts for ^{13}C NMR are referred to the carbon resonance of the solvent ($CDCl_3$: δ 77.0 ppm). Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. Mass spectra were recorded on a Shimadzu QP2010 GCMS with an ion source temperature of 280 °C. All the chemicals were obtained from Aldrich and were used without further purification.

General procedure for Mizoroki–Heck coupling reactions

In a Schlenk flask, equipped with a magnetic stir bar, septum and a condenser were placed the aryl halide (1.0 mmol), olefin compound (1 mmol), K_2CO_3 (2 mmol), catalyst (1 mol%) and DMF (5 mL). The flask was immersed in an oil bath and a reaction mixture stirred at 100 °C. Upon complete consumption of starting materials as determined by TLC analysis (petroleum ether/ethyl acetate, 8:2), the catalyst was separated by filtration and water (20 mL) was added. The filtrate was extracted with diethyl ether (3 × 10 mL). The combined organic layer was collected, dried over anhydrous Na_2SO_4 and concentrated in vacuum, and the resulting compound was purified by column chromatography.

Procedure for preparation of the Pd–DABCO@SiO_2 catalyst [37]

Synthesis of DABCO@SiO_2

Activated mesoporous amorphous silica gel (average particle size 60–120 mesh) (10 g) was heated at 100 °C with

DABCO-SIL (3.52 g, 10 mmol) in dry toluene for 24 h. The resulting reaction mixture was filtered off and washed with hot toluene for 12 h in a continuous extraction apparatus (Soxhlet) and then dried at 100 °C for overnight to give (12.9 g) silica-supported DABCO-SIL.

Synthesis of Pd–DABCO@SiO_2

To a solution of silica-supported DABCO-SIL (2 g) in dry acetone, $Pd(OAc)_2$ (0.044 g, 0.19 mmol) was added and the resulting mixture was stirred at room temperature for 24 h. The solid product was filtered off, washed with acetone, distilled water and acetone successively and dried under vacuum at 60 °C for 4 h to give the yellow product Pd–DABCO@SiO_2 (2.03 g) which was characterized by characterized by analytical methods.

Spectroscopic analysis

(*E*)-methyl cinnamate (Table 3, entry 2) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz); δ 3.71 (s, 3H), 6.44 (d, 1H, J = 15.9 Hz), 7.33 (*t*, 3H, J = 3.3 Hz), 7.50–7.55 (m, 2H), 7.75 (d, 1H, J = 15.9 Hz). ^{13}CNMR (75 MHz, $CDCl_3$) δ 52.1, 112.3, 126.8, 128.01, 136.2, 144.5, 165.6. GCMS $C_{10}H_{10}O_2$: m/z 162.

Methyl(*E*)-3-(4-methoxyphenyl)acrylate (Table 3, entry 4) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63 (d, 1H, J = 16.0 Hz), 7.42 (d, 2H, J = 8.1 Hz), 6.89 (d, 2H, J = 8.03 Hz), 6.33 (d, 1H, J = 16.01 Hz), 3.86 (s, 3 H), 3.78 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.6, 162.3, 145.2, 130.6, 126.2, 117.1, 112.2, 54.2, 50.7 ppm. MS (ESI) $C_{11}H_{12}O_3$: m/z 192.

Methyl(*E*)-3-(p-tolyl)acrylate (Table 3, entry 5) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, 1H, J = 16.0 Hz), 7.40 (d, 2H, J = 8.2 Hz), 7.19 (d, 2H, J = 8.1 Hz), 6.41 (d, 1H, J = 16.1 Hz), 3.82 (s, 3 H), 2.34 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 145.2, 141.7, 135.2, 131.3, 129.1, 115.4, 52.8, 22.3 ppm. MS (ESI) $C_{11}H_{12}O_2$: m/z 176.

(*E*)-p-nitromethyl cinnamate (Table 3, entry 7) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 3.80 (s, 3H), 6.55 (d, 1H, J = 16.2 Hz), 7.67–7.70 (m, 2H, J = 9 Hz), 7.76 (d, 1H, J = 16.2 Hz), 8.28–8.25 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) 52.2, 122.3, 124.5, 128.4, 140.8, 142.0, 149.5, 165.9. GCMS $C_{10}H_9NO_4$: m/z 207.

Methyl(*E*)-3-(4-fluorophenyl)acrylate (Table 3, entry 9) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 16.0 Hz, 1H), 7.44–7.38 (m, 2 H), 7.05–6.98 (m, 2H), 6.32 (d, J = 16.0, 1 H), 3.86 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 162.1, 142.3, 129.1, 127.9, 115.4, 114.3, 113.5, 53.2 ppm. MS (ESI) $C_{10}H_9FO_2$: m/z 180.

Methyl(*E*)-3-(4-chlorophenyl)acrylate (Table 3, entry 10) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, 1H, J = 16.0 Hz), 7.55–7.40 (m, 4 H), 6.44 (d, 1H, J = 15.9 Hz), 3.80 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 142.1, 137.2, 133.2, 128.7, 126.1, 119.3, 52.7 ppm. MS (ESI) $C_{10}H_9ClO_2$: m/z 196.

Butyl(*E*)-3-(4-chlorophenyl)acrylate (Table 3, entry 11) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, 1H, J = 16.0 Hz), 7.32 (d, 2H, J = 8.4 Hz), 7.26 (d, 2H, J = 8.3 Hz), 6.28 (d, 1H, J = 15.9 Hz), 4.16 (*t*, 2H, J = 6.3 Hz), 1.67–1.53 (m, 2 H), 1.42–1.35 (m, 2 H), 0.93 (*t*, 3H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 142.0, 137.2, 132.01, 128.3, 126.8, 126.2, 116.8, 62.2, 32.8, 18.1, 14.5 ppm. MS (ESI) $C_{13}H_{15}ClO_2$: m/z 238.

(*E*)-1-(4-styrylphenyl)ethanone (Table 3, entry 12) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a white solid. ^{1}H NMR ($CDCl_3$ 300 MHz) δ (ppm) 2.60 (s, 3H), 7.25 (d, 1H, J = 16.2 Hz), 7.35–7.44 (m, 3H), 7.54–7.59 (m, 2H), 7.62 (d, 2H, J = 8.4 Hz), 7.93 (d, 1H, J = 15.9 Hz), 7.96 (d, 2H, J = 8.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.1, 125.5, 126.3, 128.4, 130.3, 131.8, 131.5, 132.1, 136.9, 137.7, 143.0, 196.4. MS (ESI) $C_{16}H_{14}O$: m/z 222.

(*E*)-methyl-3-(4-acetophenonyl)acrylate (Table 3, entry 13) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a white solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 2.62 (s, 3H), 3.88 (s, 3H), 6.55 (d, 1H, J = 15.9 Hz), 7.62 (d, 2H, J = 8.1 Hz), 7.72 (d, 1H, J = 16.2 Hz), 7.97 (d, 2H, J = 8.4 Hz). ^{13}CNMR (75 MHz, $CDCl_3$): δ (ppm), 28.6, 52.8, 121.3, 128.5, 128.9, 130.5, 139.7, 144.2, 165.8, 196.1. MS (ESI) $C_{12}H_{12}O_3$: m/z 204.

Ethyl(*E*)-3-(4-acetylphenyl)acrylate (Table 3, entry 14) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, 2H, J = 8.1 Hz), 7.54 (d, 1H, J = 16.0 Hz), 7.47 (d, 2H, J = 8.0 Hz), 6.45 (d, 1H, J = 15.9 Hz), 4.19 (q, 2H, J = 7.2 Hz), 2.48 (s, 3 H), 1.28 (*t*, 3H, J = 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.3, 165.4, 140.7, 136.6, 136.4, 127.2, 127.2, 117.8, 61.6, 24.6, 14.5 ppm; MS (ESI) $C_{13}H_{14}O_3$: m/z 218.

Butyl(*E*)-3-(4-acetylphenyl)acrylate (Table 3, entry 15) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, 2H, J = 8.2 Hz), 7.65 (d, 1H, J = 16.1 Hz), 7.54 (d, 2H, J = 8.2 Hz), 6.42 (d, 1H, J = 15.9 Hz), 4.12 (*t*, 2H, J = 6.4 Hz), 2.50 (s, 3 H), 1.68–1.52 (m, 2 H), 1.48–1.34 (m, 2 H), 0.86 (*t*, 3H, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.3, 166.8, 142.1, 137.3, 136.2, 126.2, 125.1, 121.7, 62.6, 30.2, 24.5, 20.1, 14.6 ppm; MS (ESI) $C_{15}H_{18}O_3$: m/z 246.

Methyl(*E*)-3-(4-benzoylphenyl)acrylate (Table 3, entry 16) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83–7.75 (m, 4H), 7.74–7.61 (m, 4 H), 7.66–7.54 (m, 2 H), 6.52 (d, 1H, J = 15.9 Hz), 3.82 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 163.9, 142.2, 137.5, 136.2, 135.3, 131.6, 129.5, 129.0, 127.4, 127.1, 18.7 ppm; MS (ESI) $C_{17}H_{14}O_3$: m/z 266.

Butyl(*E*)-3-(4-benzoylphenyl)acrylate (Table 3, entry 17) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82–7.74 (m, 4 H), 7.67–7.55 (m, 4 H), 7.52–7.44 (m, 2 H), 6.52 (d, 1H, J = 16.1 Hz), 4.22 (*t*, 2H, J = 4.3 Hz), 1.71–1.61 (m, 2 H), 1.58–1.40 (m, 2H), 0.93 (*t*, 3H, J = 4.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9, 166.5, 142.2, 137.4, 137.2, 131.6, 130.3, 129.0, 127.8, 127.4, 119.7, 62.7, 32.3, 18.2, 14.7 ppm; MS (ESI) $C_{20}H_{20}O_3$: m/z 308.

Methyl(*E*)-3-(4-methoxyphenyl)acrylate (Table 3, entry 20) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a white solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.60 (d, 1H, J = 16.0 Hz), 7.44 (d, 2H, J = 8.2 Hz), 6.92 (d, 2H, J = 8.2 Hz), 6.32 (d, 1H, J = 15.9 Hz), 3.80 (s, 3 H), 3.76 (s, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 166.5, 160.3, 143.4, 128.6, 126.2, 116.3, 113.2, 56.2, 52.4 ppm. MS (ESI) $C_{11}H_{12}O_3$: m/z 192.

Ethyl(*E*)-3-(4-nitrophenyl)acrylate (Table 3, entry 21) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.32 (d, 2H, J = 8.4 Hz), 7.84–7.75 (m, 3 H), 6.58 (d, 1H, J = 15.9 Hz), 4.34 (q, 2H, J = 7.4 Hz), 1.38 (*t*, 3H, J = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.2, 147.3, 140.5, 138.6, 130.6, 126.3, 124.5, 60.2, 13.9 ppm. MS (ESI) $C_{11}H_{11}NO_4$: m/z 221.

Methyl(*E*)-3-(4-chlorophenyl)acrylate (Table 3, entry 24) The product was purified by column chromatography on silica gel 60–120 mesh (hexane/ethyl acetate = 9:1) as a yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.76 (d, 1H, J = 16.0 Hz), 7.58–7.44 (m, 4 H), 6.46 (d, 1H, J = 15.9 Hz), 3.84 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.2, 142.8, 135.3, 134.5, 128.4, 127.2, 116.3, 52.6 ppm. MS (ESI) $C_{10}H_9ClO_2$: m/z 196.

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Compliance with ethical standards

Conflicts of interest The authors declare that they have no conflict of interest.

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