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Controlled mono- and double-Heck reaction catalyzed by a dicarbene dipalladium complex

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ABSTRACT

The phosphine-free mono- and double-Heck reaction of terminal olefins with electron-deficient and electron-rich aryl halides (iodides and bromides) is described. These reactions are catalyzed by the di-carbene dipalladium complex **1** by controlling the stoichiometry of the aryl halide and the olefine, the loading of the palladium catalyst, as well as using different base, and with or without additive. The procedure of double-Heck reaction allows β,β-diarylation and β,β′-diarylation of terminal olefins and affords trisubstituted olefins in good to excellent yields.

1. Introduction

Palladium-catalyzed C–C cross-coupling reaction is one of the most important classes of organometallic reactions and finds widely applications in pharmaceuticals, fine chemicals, and natural products.[1] Among various coupling reactions, the Mizoroki–Heck reaction is one of the most powerful methods for C–C bond formation, and can be accomplished using a great amount of palladium catalyst precursors under various reaction conditions.[2] The classical intermolecular Heck reaction is mainly limited to the monoarylation of terminal alkenes, whereas the synthesis of trisubstituted alkenens by diarylation has been scarcely investigated and most synthetic protocols are only effective with aryl iodides or acrylates.[3] Therefore the development of an efficient process for diarylation of more general terminal alkenes with aryl halides (esp. cheap aryl bromides) would be desirable. Over the last years, the chemistry of palladium *N*-heterocyclic carbene (NHC) complexes has become an area of great interest and has been extensively studied.[4] We have been interested in the chemistry of bimetallic di-NHC complexes concentrated on *homo*dinuclear and *hetero*-dinuclear complexes,[5] with special emphasis on developing inexpensive, user-friendly, and highly efficient precatalyst for C–C cross-coupling reactions. The design and synthesis of binuclear palladium complexes with di-NHC are of considerable interest because the adjacent metals could function in a synergic manner in their interactions with substrate molecules. We report now that a di-NHC dipalladium complex is an appropriate precatalyst for the controlled mono and diarylation of terminal alkenes under phosphine-free conditions.

2. Results and discussion

The structure of di-NHC dipalladium complex **1** used in this study was shown in Chart 1. The synthesis of **1** was achieved by the reaction of $PdCl_2$ with bisimidazolium dichlorides in pyridine in the presence of K_2CO_3 in 65% yield.[6]

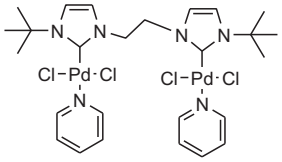

Chart 1. Palladium catalyst **1** used in this study.

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2.1. Monoarylation of terminal alkenes

From the previous result of screening the solvents, bases, catalyst loadings, and temperatures, the mono-arylation of styrene catalyzed by **1** can be effectively performed with 0.5 mol % of catalyst with K_3PO_4 as base (1.5 equiv) in the solvent of dimethyl acetamide (DMA) at 100 °C in 5 h.[6] To investigate the scope of the reaction, the application of **1** in the mono-arylation of styrene with a series of aryl halides was shown in Table 1. From the results we can see that deactivated electron-rich aryl iodides and bromides are coupled with styrene in good yields (Table 1, entries 2, 11, 13, 14). Sterically hindered aryl iodide with *ortho*-substitution worked well in the reaction, whereas, the yield decreased with *ortho*-substituted bromide (Table 1, entries 14 vs 11). A wide variety of functional groups were tolerated on the aromatic ring (Table 1, entries 2–10). Unfortunately, the catalyst was not effective for aryl chloride. Furthermore, the application of **1** in the coupling reaction of various aryl halides with ethyl acrylate was shown in Table 2. The complex **1** was also highly active for the coupling of electron-rich and electron-deficient aryl halides (iodides and bromides) with ethyl acrylate. Steric effect still only plays role in the reaction of aryl bromide (Table 2, entries 10 vs 13). A wide variety of functional groups were tolerated in the coupling reaction with aryl halides.

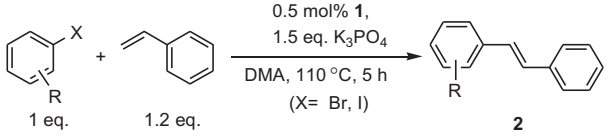
From these results, it can be summarized that the mono-arylation of terminal alkene with aryl iodides and bromides can be performed efficiently with 0.5 mol % of the di-NHC di-Pd complex **1** using K_3PO_4 as base in the solvent of DMA.

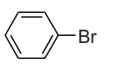
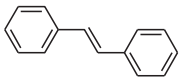
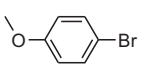
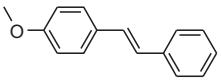
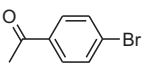
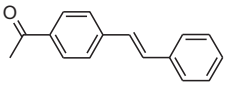
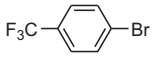
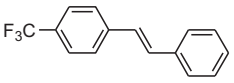
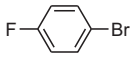
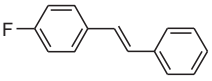
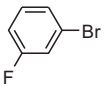
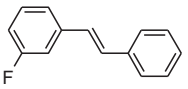
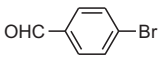
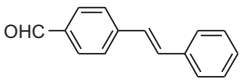
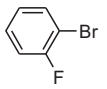
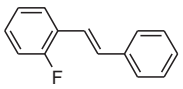
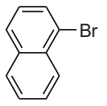
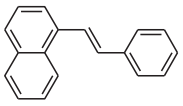
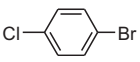
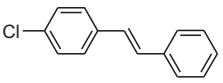
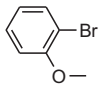
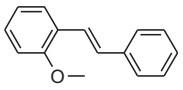
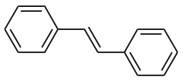
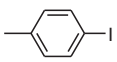
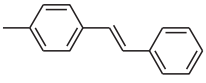
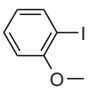
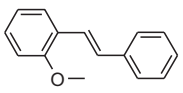
2.2. Diarylation of terminal alkene

To develop a general protocol for the diarylation of terminal olefins, we initially tested the reaction of ethyl acrylate (1 equiv) with bromobenzene (2.2 equiv) with tetra-*n*-butylammonium bromide (TBAB) as additive and higher loading of Pd catalyst (1 mol %) in DMA in presence of different bases (2.5 equiv) (Table 3). The diarylated product was obtained in 10% when K_3PO_4 was used as the base, and 18% of monoarylated product was observed at the meanwhile (Table 3, entry 1). Cs_2CO_3 did not work for both diarylation (5%) and monoarylation (8%). Moreover, NaOH failed in diarylation, whereas gave 65% of monoarylation product. However, when NaOAc or K_2CO_3 was employed, the yield of diarylation was dramatically increased to 88% or 82% and no monoarylated product was detected for NaOAc. TBAB is necessary for the successful diarylation, otherwise, only 76% of monoarylation product was obtained with NaOAc under the same conditions (Table 3, entry 4). To optimize the reaction conditions, a few other solvents including toluene, DMF, DMSO, and TBAB were screened. DMA is the best solvent tested for diarylation, and relatively low yield was observed in DMF, toluene, and TBAB. No diarylation product was found in DMSO used as solvent. Therefore, all diarylation reactions below were carried with 1 mol % of Pd, TBAB (2 equiv), NaOAc (2.5 equiv) in DMA at 120 °C for 18 h.

Under the optimized conditions, the β,β-diarylation of alkyl acrylates was suitable to various aryl iodides and even less reactive aryl bromides, however, electron-rich trimethoxy(vinyl)silane does not couple at all (Table 4). Generally, the reactions of alkyl acrylates with unactivated aryl iodides containing electron-donating substituents gave good yields of trisubstituted olefine (Table 4, entries 8–10), whilst, the reactions with aryl bromides gave diarylation product in moderate to good yields (Table 4, entries 1–6). To further determine the scope of this catalytic system with other kinds of terminal olefins, different styrene substrates were chosen to react with aryl bromides or iodides under identical conditions. These reactions were afforded the desired product in good yield (Table 4, entries 13–17).

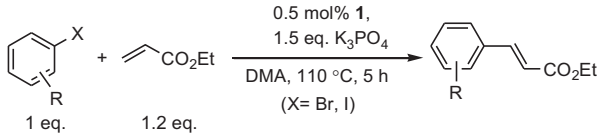
Table 1
Mizoroki–Heck cross-coupling reactions of styrene with aryl halides

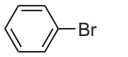
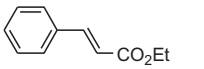
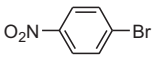
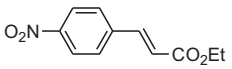
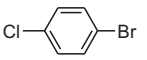
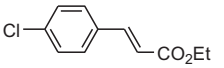
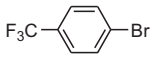
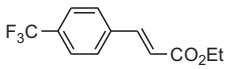
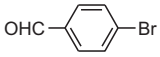
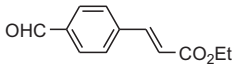
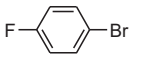
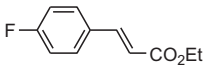
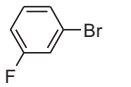
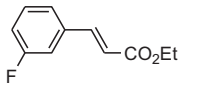
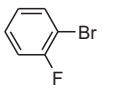
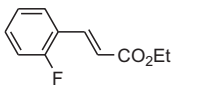
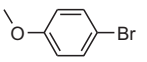
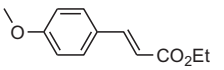
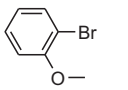
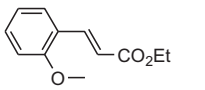
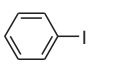
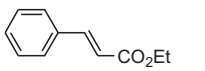
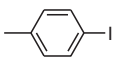
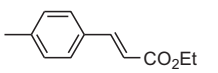
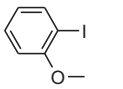
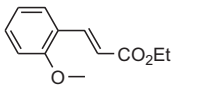
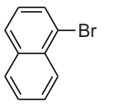
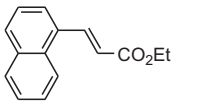


Entry[a]	Aryl halide	Product	**2** Yield (%)[b]
1			84 (**2a**)
2			95 (**2b**)
3			82 (**2c**)
4			80 (**2d**)
5			86 (**2e**)
6			80 (**2f**)
7			68 (**2g**)
8			83 (**2h**)
9			97 (**2i**)
10			93 (**2j**)
11			47 (**2k**)
12			83 (**2a**)
13			82 (**2l**)
14			88 (**2k**)

[a] Reaction conditions: 0.005 mmol of **1**, 1 mmol of aryl halides, 1.2 mmol of styrene, and 1.5 mmol of K_3PO_4 in 2 mL of DMA.
[b] Isolated yield.

Table 2
Mizoroki–Heck cross-coupling reactions of ethyl acrylate with aryl halides

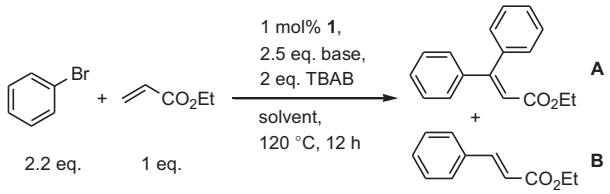


Entry[a]	Aryl halide	Product	**3** Yield (%)[b]
1			77 (**3a**)
2			79 (**3b**)
3			74 (**3c**)
4			90 (**3d**)
5			75 (**3e**)
6			70 (**3f**)
7			67 (**3g**)
8			68 (**3h**)
9			86 (**3i**)
10			52 (**3j**)
11			86 (**3a**)
12			84 (**3k**)
13			78 (**3j**)
14			82 (**3l**)

[a] Reaction conditions: 0.005 mmol of **1**, 1 mmol of aryl halides, 1.2 mmol of ethyl acrylate, and 1.5 mmol of K_3PO_4 in 2 mL of DMA.
[b] Isolated yield.

This methodology has also been extended to the synthesis of unsymmetrical diarylated alkenes, which represent an even more challenging task. Initially, ethyl acrylate was used as the starting material employing a one-pot strategy to introduce two different

Table 3
Diarylation of ethyl acrylate under different reactions



Entry[a]	Solvent	Base	Additive	Product **A** (**B**) yield[b]
1	DMA	K_3PO_4	TBAB	10 (18)
2	DMA	K_2CO_3	TBAB	82 (8)
3	DMA	NaOAc	TBAB	88 (0)
4	DMA	NaOAc	None	0 (76)
5	DMA	Cs_2CO_3	TBAB	5 (8)
6	DMA	NaOH	TBAB	0 (65)
7	DMA	Na_2CO_3	TBAB	64 (10)
8	Toluene	NaOAc	TBAB	24 (7)
9	DMF	NaOAc	TBAB	73 (5)
10	DMSO	NaOAc	TBAB	0 (8)
11	TBAB	NaOAc	None	15 (10)

[a] Reaction conditions: 0.005 mmol of **1**, 1.1 mmol of aryl halide, 0.5 mmol of ethyl acrylate, 1 mmol of TBAB, and 1.25 mmol of base in 2 mL of solvent.
[b] Isolated yield.

aromatic groups. The catalytic reaction was first performed with 1.0 equiv of *p*-tolyl iodide and ethyl acrylate at 120 °C. As expected, only the monoarylation took place, affording (*E*)-ethyl 3-*p*-tolylacrylate within 4 h. After cooling to room temperature, the second aryl halide was directly added to the crude mixture without isolation and heated to 150 °C again. Under these conditions, the unsymmetrical triarylated acrylates were obtained in up to 70% isolated yields (Table 5, entries 1–6). Furthermore, this one-pot strategy can be applied to prepare unsymmetrical triarylated ethylenes when styrene was used as the starting material instead of ethyl acrylate (Table 5, entries 7–11). In each run a mixture of *E*/*Z* isomers was obtained, and the *E*/*Z* ratios of these products were determined by GC–MS.

3. Conclusion

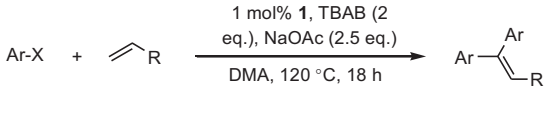
We can conclude that the di-NHC dipalladium complex **1** are efficient precatalyst for the phosphine-free monoarylation of terminal alkenes using K_3PO_4 as base in DMA at 110 °C. Both electron-rich and electron-deficient aryl iodides and bromides could be coupled with styrene or ethyl acrylate in good yield. A wide variety of functional groups were tolerated in the coupling reaction. The phosphine-free diarylation reaction of terminal alkenes can be performed in the presence of TBAB as additive and NaOAc as base with higher catalyst loading (1 mol %) in DMA at 120 °C. The double arylation of terminal olefins afforded trisubstituted olefins in good to excellent yields. The protocol is applicable to the coupling of both aryl iodides and bromides leading to symmetrical and unsymmetrical β,β-diarylated and β,β′-diarylated alkenes.

4. Experimental section

4.1. General information

All reactions have been carried out under argon atmosphere. The palladium complex was prepared according to our previous procedure.[6] DMA and DMF were distilled from anhydrous magnesium sulfate, and DMSO was distilled from calcium hydride. Toluene was distilled from sodium benzophenone ketyl prior to use. All other reagents were commercially available and were used without further purification. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer at room temperature and referenced to the

Table 4
β,β-Diarylation of olefines with aryl halides



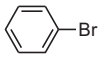
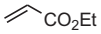
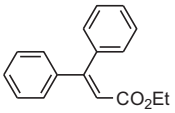
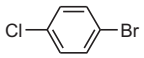
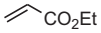
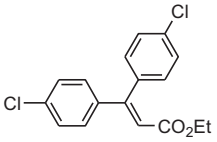
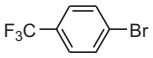
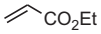
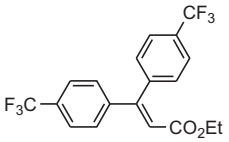
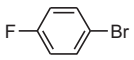
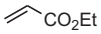
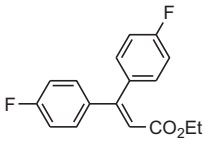
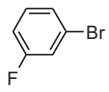
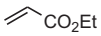
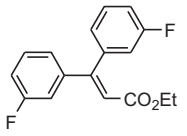
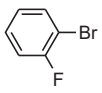
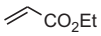
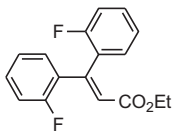
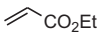
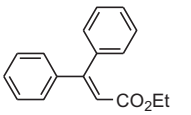
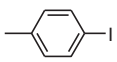
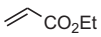
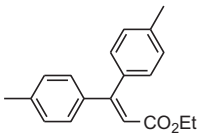
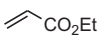
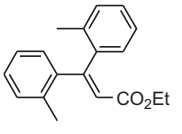
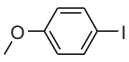
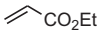
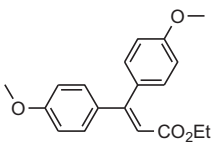
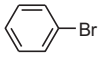
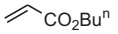
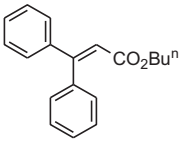
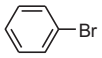
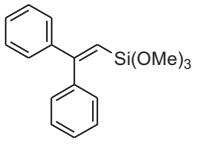
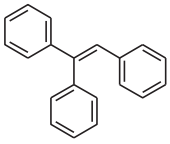
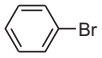
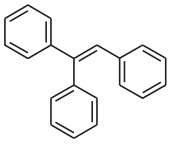
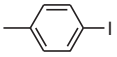
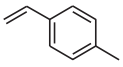
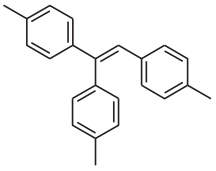
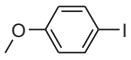
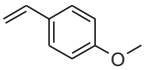
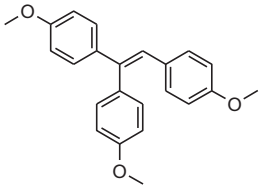
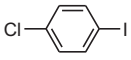
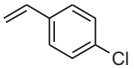
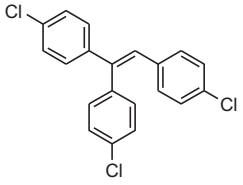
Entry[a]	Ar-X	Olefins	Product	**4** Yield (%)[b]
1				88 (**4a**)
2				69 (**4b**)
3[c]				72 (**4c**)
4				89 (**4d**)
5				82 (**4e**)
6				40 (**4f**)
7				95 (**4a**)
8				90 (**4g**)
9				75 (**4h**)
10				84 (**4i**)

Table 4 (*continued*)

Entry[a]	Ar-X	Olefins	Product	**4** Yield (%)[b]
11				86 (**4j**)
12				0
13				71 (**4k**)
14				87 (**4k**)
15				82 (**4l**)
16				79 (**4m**)
17				76 (**4n**)

[a] Reaction conditions: 0.005 mmol of **1**, 0.5 mmol of olefin, 1 mmol of TBAB, 1.1 mmol of aryl halide, and 1.25 mmol of NaOAc in 2 mL of DMA.
[b] Isolated yield.
[c] The reaction was carried out for 24 h.

residual signals of the solvent. GC–MS was performed on an Agilent 6890-5973N system with electron ionization (EI) mass spectrometry. HRMS was recorded on a Fisher LTQ-Orbitrap XL combined-type mass spectrometry.

4.2. General procedure for the mono-arylation

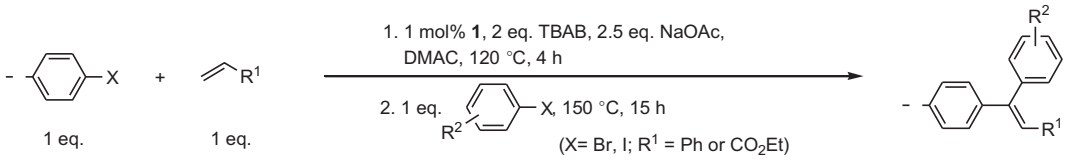
In a typical run, a 5 mL of vial equipped with a magnetic bar was charged with a mixture of aryl halide (1 mmol), olefins (1.2 mmol), Pd catalyst (0.005 mmol, 4 mg), K_3PO_4 (1.5 mmol, 318 mg), and 2 mL of DMA in argon. The reaction was heated at 110 °C for 5 h, then brine was added into it. The resulting mixture was extracted with ethyl acetate for three times, and the crude was obtained by removing volatile. The product was purified by flash column chromatography on silica gel (eluent: dichloromethane/petroleum ether).

*4.2.1. (E)-1,2-Diphenylethene (**2a**).*[7a] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J=7.6, 4H), 7.37 (t, J=7.6, 4H), 7.28 (d, J=7.6, 2H), 7.1 (s, 2H).

*4.2.2. (E)-1-Methoxy-4-styrylbenzene (**2b**).*[7a] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.45 (m, 4H), 7.35 (t, J=7.6 Hz, 2H), 7.22 (d, J=7.2 Hz, 1H), 7.09–6.96 (m, 2H), 6.90 (d, J=8.8 Hz, 2H), 3.83 (s, 3H).

*4.2.3. (E)-1-(4-Styrylphenyl)ethanone (**2c**).*[7a] Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J=8.0 Hz, 2H), 7.60–7.53 (m, 4H), 7.38

Table 5
β,β′-Diarylation of ethyl acrylate or styrene with aryl halides



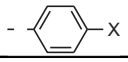
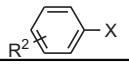
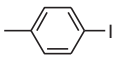
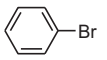
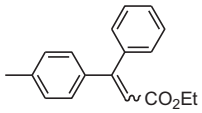
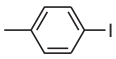
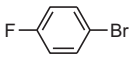
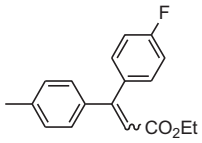
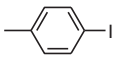
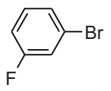
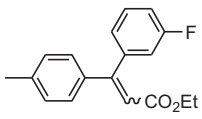
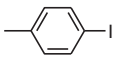
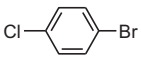
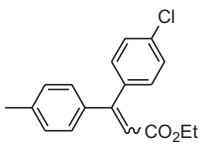
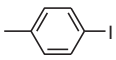
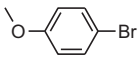
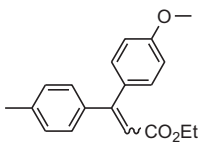
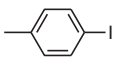
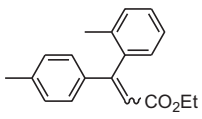
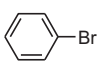
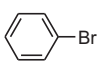
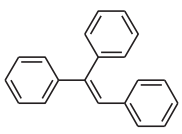
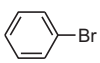
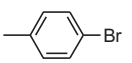
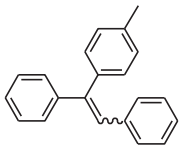
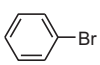
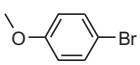
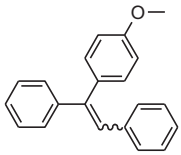
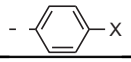
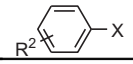
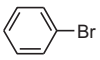
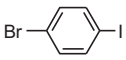
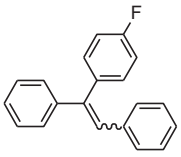
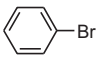
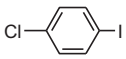
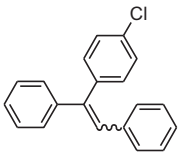
Entry[a]		R^1		Product	**5** Yield (%)[b]	*E*/*Z* ratio[d]
1[c]		CO_2Et			88 (**5a**)	63:36
2[c]		CO_2Et			85 (**5b**)	81:19
3[c]		CO_2Et			79 (**5c**)	61:39
4[c]		CO_2Et			75 (**5d**)	52:48
5[c]		CO_2Et			86 (**5e**)	71:29
6[c]		CO_2Et			70 (**5f**)	51:49
7		Ph			87 (**4j**)	—
8		Ph			79 (**5g**)	80:20
9		Ph			89 (**5h**)	83:17

Table 5 (*continued*)

Entry[a]		R^1		Product	**5** Yield (%)[b]	*E*/*Z* ratio[d]
10		Ph			85 (**5i**)	90:10
11		Ph			81 (**5j**)	63:37

[a] Reaction conditions: 0.005 mmol of **1**, 0.5 mmol of olefin, 1 mmol of TBAB, 0.5 mmol of the first aryl halide, 0.5 mmol of the second aryl halide, and 1.25 mmol of NaOAc in 2 mL of DMA.
[b] Isolated yield.
[c] The reaction time of second step is 18 h.
[d] The *E*/*Z* ratio was determined by GC–MS.

(t, *J*=7.2 Hz, 2H), 7.31 (d, *J*=7.2 Hz, 1H), 7.21–7.11 (m, 2H), 2.61 (s, 3H).

*4.2.4. (E)-1-Styryl-4-(trifluoromethyl)benzene (**2d**).*[7b] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 4H), 7.54 (d, *J*=7.6 Hz, 2H), 7.38 (t, *J*=7.6 Hz, 2H), 7.31 (d, *J*=7.6, 1H), 7.22–7.10 (m, 2H).

*4.2.5. (E)-1-Fluoro-4-styrylbenzene (**2e**).*[7a] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.46 (m, 4H), 7.37 (d, *J*=7.2 Hz, 2H), 7.28 (d, *J*=7.2 Hz, 1H), 7.10–7.00 (m, 4H).

*4.2.6. (E)-1-Fluoro-3-styrylbenzene (**2f**).*[7c] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J*=7.6 Hz, 2H), 7.38 (t, *J*=7.6 Hz, 2H), 7.33–7.21 (m, 4H), 7.14–7.02 (m, 2H), 6.96 (t, *J*=8.0 Hz, 1H).

*4.2.7. (E)-4-Styrylbenzaldehyde (**2g**).*[7b] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J*=7.6 Hz, 2H), 7.38 (t, *J*=7.6 Hz, 2H), 7.33–7.21 (m, 4H), 7.14–7.02 (m, 2H), 6.96 (t, *J*=8.0 Hz, 1H).

*4.2.8. (E)-1-Fluoro-2-styrylbenzene (**2h**).*[7d] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (t, *J*=7.6 Hz, 1H), 7.53 (d, *J*=7.2 Hz, 2H), 7.36 (t, *J*=7.6 Hz, 2H), 7.29–7.19 (m, 4H), 7.15–7.05 (m, 2H).

*4.2.9. (E)-1-Styrylnaphthalene (**2i**).*[7a] Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J*=8.4 Hz, 1H), 7.93–7.88 (m, 2H), 7.82 (d, *J*=8.0 Hz, 1H), 7.77 (d, *J*=6.8 Hz, 1H), 7.63 (d, *J*=7.6 Hz, 2H), 7.58–7.49 (m, 3H), 7.43 (t, *J*=7.2 Hz, 2H), 7.34–7.30 (m, 1H), 7.17 (d, *J*=16.0 Hz, 1H).

*4.2.10. (E)-1-Chloro-4-styrylbenzene (**2j**).*[7a] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J*=7.6 Hz, 2H), 7.44 (d, *J*=8.8 Hz, 2H), 7.36 (t, *J*=7.6 Hz, 2H), 7.33–7.27 (m, 3H), 7.11–7.02 (m, 2H).

*4.2.11. (E)-1-Methoxy-2-styrylbenzene (**2k**).*[7e] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J*=7.6 Hz, 1H), 7.55–7.47 (m, 3H), 7.35 (t, *J*=7.6 Hz, 2H), 7.24 (d, *J*=6.8 Hz, 2H), 7.11 (d, *J*=16.4 Hz, 1H), 6.97 (t, *J*=7.6 Hz, 1H), 6.90 (d, *J*=8.0 Hz, 1H), 3.88 (s, 3H).

*4.2.12. (E)-1-Methyl-4-styrylbenzene (**2l**).*[7a] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J*=7.2 Hz, 2H), 7.41 (d, *J*=8.0 Hz, 2H), 7.35 (t, *J*=7.2 Hz, 2H), 7.25 (t, *J*=4.0 Hz, 1H), 7.16 (d, *J*=8.0 Hz, 2H), 7.11–7.02 (m, 2H).

*4.2.13. Ethyl cinnamate (**3a**).*[8a] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J*=16.0 Hz, 1H), 7.52 (s, 2H), 7.37 (s, 3H), 6.44 (d, *J*=16.0 Hz, 1H), 4.29–4.23 (m, 2H), 1.33 (t, *J*=7.2 Hz, 3H).

*4.2.14. (E)-Ethyl 3-(4-nitrophenyl)acrylate (**3b**).*[8a] Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J*=8.8 Hz, 2H), 7.72–7.66 (m, 3H), 6.55 (d, *J*=16.0 Hz, 1H), 4.32–4.26 (m, 2H), 1.35 (t, *J*=7.2 Hz, 3H).

*4.2.15. (E)-Ethyl 3-(4-chlorophenyl)acrylate (**3c**).*[8a] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J*=16.0 Hz, 1H), 7.34 (d, *J*=8.4 Hz, 2H), 7.25 (d, *J*=8.0 Hz, 2H), 6.30 (d, *J*=16.0 Hz, 1H), 4.19–4.14 (m, 2H), 1.24 (t, *J*=7.2 Hz, 3H).

*4.2.16. (E)-Ethyl 3-(4-(trifluoromethyl)phenyl)acrylate (**3d**).*[8b] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.62 (m, 5H), 6.50 (d, *J*=16.0 Hz, 1H), 4.30–4.25 (m, 2H), 1.34 (t, *J*=7.2 Hz, 3H).

*4.2.17. (E)-Ethyl 3-(4-formylphenyl)acrylate (**3e**).*[7b] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 7.89 (d, *J*=8.0 Hz, 2H), 7.72–7.66 (m, 3H), 6.54 (d, *J*=16.0 Hz, 1H), 4.31–4.25 (m, 2H), 1.34 (t, *J*=7.2 Hz, 3H).

*4.2.18. (E)-Ethyl 3-(4-fluorophenyl)acrylate (**3f**).*[8a] Yellow oil; ^{1}H NMR (400 MHz, DMSO): δ 7.64 (d, *J*=16.0 Hz, 1H), 7.52–7.49 (m, 2H), 7.09–7.04 (m, 2H), 6.35 (d, *J*=16.0 Hz, 1H), 4.28–4.23 (m, 2H), 1.33 (t, *J*=7.2 Hz, 3H).

*4.2.19. (E)-Ethyl 3-(3-fluorophenyl)acrylate (**3g**).*[8c] Yellow oil; ^{1}H NMR (400 MHz, DMSO): δ 7.64 (d, *J*=16.0 Hz, 1H), 7.52–7.49 (m, 2H), 7.09–7.04 (m, 2H), 6.35 (d, *J*=16.0 Hz, 1H), 4.28–4.23 (m, 2H), 1.33 (t, *J*=7.2 Hz, 3H).

*4.2.20. (E)-Ethyl-3-(2-fluorophenyl) acrylate (**3h**).*[8d] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J*=16.0 Hz, 1H), 7.45 (t, *J*=7.2 Hz, 1H), 7.26 (s, 1H), 7.09–6.99 (m, 2H), 6.45 (d, *J*=16.0 Hz, 1H), 4.22–4.16 (m, 2H), 1.26 (t, *J*=7.2 Hz, 3H).

*4.2.21. (E)-Ethyl 3-(4-methoxyphenyl)acrylate (**3i**).*[8e] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J*=16.2 Hz, 1H), 7.49 (d,

J=7.5 Hz, 1H), 7.33 (t, *J*=7.7 Hz, 1H), 7.01–6.83 (m, 2H), 6.52 (d, *J*=16.2 Hz, 1H), 4.26 (m, 2H), 3.87 (s, 3H), 1.35 (s, 3H).

*4.2.22. (E)-Ethyl 3-(p-tolyl)acrylate (**3j**).*[8e] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J*=16.0 Hz, 1H), 7.47 (d, *J*=8.4 Hz, 2H), 6.89 (d, *J*=8.4 Hz, 2H), 6.30 (d, *J*=16.0 Hz, 1H), 4.27–4.22 (m, 2H), 2.83 (s, 3H), 1.32 (t, *J*=7.2 Hz, 3H).

*4.2.23. (E)-Ethyl 3-(2-methoxyphenyl)acrylate (**3k**).*[8f] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J*=16.0 Hz, 1H), 7.49 (d, *J*=8.0 Hz, 1H), 7.33 (t, *J*=6.8 Hz, 1H), 6.96–6.88 (m, 2H), 6.52 (d, *J*=16.0 Hz, 1H), 4.28–4.22 (m, 2H), 3.86 (s, 3H), 1.33 (t, *J*=6.8 Hz, 3H).

*4.2.24. (E)-Ethyl 3-(naphthalen-1-yl)acrylate (**3l**).*[8g] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J*=16.0 Hz, 1H), 8.20 (d, *J*=8.0 Hz, 1H), 7.88 (t, *J*=7.6 Hz, 2H), 7.75 (d, *J*=7.2 Hz, 1H), 7.60–7.46 (m, 3H), 6.54 (d, *J*=16.0 Hz, 1H), 4.36–4.30 (m, 2H), 1.39 (t, *J*=7.2 Hz, 3H).

4.3. Representative procedure for β,β-diarylation of terminal olefins

To a stirred solution of TBAB (1 mmol, 322 mg), sodium acetate (102 mg, 1.25 mmol), and catalyst (4 mg, 0.005 mmol) in DMA (2 mL) was added aryl halide (1.1 mmol) and olefin (0.5 mmol). The mixture was stirred at 120 °C for 18 h under argon. The solids were removed by filtration, and rinsed with 10 mL of ethyl acetate. The filtrate was concentrated under vacuum. The crude product was purified by flash column chromatography using petroleum ether (PE) and ethyl acetate (EA) as the eluent (PE/EA 30/1).

*4.3.1. Ethyl 3,3-diphenylacrylate (**4a**).*[3b] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (t, *J*=3.2 Hz, 4H), 7.35–7.31 (m, 4H), 7.23–7.21 (m, 2H), 6.37 (s, 1H), 4.08–4.03 (m, 2H), 1.12 (t, *J*=7.2 Hz, 4H).

*4.3.2. Ethyl 3,3-bis(4-chlorophenyl)acrylate (**4b**).*[3b] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J*=8.0 Hz, 2H), 7.30 (d, *J*=8.0 Hz, 2H), 7.20 (d, *J*=8.0 Hz, 2H), 7.13 (d, *J*=8.0 Hz, 2H), 6.33 (s, 1H), 4.09–4.04 (m, 2H), 1.15 (t, *J*=7.2 Hz, 3H).

*4.3.3. Ethyl 3,3-bis(4-(trifluoromethyl)phenyl)acrylate (**4c**).*[9] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.59 (m, 4H), 7.39–7.32 (m, 4H), 6.47 (s, 1H), 4.10–4.05 (m, 2H), 1.13 (t, *J*=7.2 Hz, 3H).

*4.3.4. Ethyl 3,3-bis(4-fluorophenyl)acrylate (**4d**).*[3b] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.24 (m, 2H), 7.19–7.16 (m, 2H), 7.10–6.99 (m, 4H), 6.30 (s, 1H), 4.09–4.04 (m, 2H), 1.15 (t, *J*=7.2 Hz, 3H).

*4.3.5. Ethyl 3,3-bis(3-fluorophenyl)acrylate (**4e**).*[3b] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.27 (m, 2H), 7.12–7.04 (m, 3H), 7.00–6.90 (m, 3H), 6.38 (s, 1H), 4.09–4.04 (m, 2H), 1.15 (t, *J*=7.2 Hz, 3H).

*4.3.6. Ethyl 3,3-bis(2-fluorophenyl)acrylate (**4f**).*[3b] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.30 (m, 2H), 7.13–7.06 (m, 6H), 6.47 (s, 1H), 4.12–4.06 (m, 2H), 1.14 (t, *J*=6.8 Hz, 3H).

*4.3.7. Ethyl 3,3-di-p-tolylacrylate (**4g**).*[3b] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.19 (m, 4H), 7.12 (t, *J*=8.0 Hz, 4H), 6.32 (s, 1H), 4.10–4.05 (m, 2H), 2.40 (s, 3H), 2.36 (s, 3H), 1.16 (t, *J*=7.2 Hz, 3H).

*4.3.8. Ethyl 3,3-di-o-tolylacrylate (**4h**).*[3b] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.19 (m, 5H), 7.13 (s, 3H), 6.16 (s, 1H), 4.11–4.05 (m, 2H), 2.37 (s, 3H), 2.19 (s, 3H), 1.13 (t, *J*=6.8 Hz, 3H).

*4.3.9. Ethyl 3,3-bis(4-methoxyphenyl)acrylate (**4i**).*[3b] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J*=10.0 Hz, 2H), 7.15 (d, *J*=8.8 Hz, 3H), 6.90 (d, *J*=8.8 Hz, 2H), 6.84 (d, *J*=9.2 Hz, 2H), 6.22 (s, 1H), 4.10–4.04 (m, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 1.16 (t, *J*=7.2 Hz, 3H).

*4.3.10. Butyl 3,3-diphenylacrylate (**4j**).*[3b] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.29 (m, 6H), 7.26–7.24 (m, 2H), 7.14–7.12 (m, 2H), 6.32 (s, 1H), 3.92 (t, *J*=6.4 Hz, 2H), 1.39 (m, 2H), 1.17 (m, 2H), 0.81 (t, *J*=7.4 Hz, 3H).

*4.3.11. Ethene-1,1,2-triyltribenzene (**4k**).*[3b] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J*=7.6 Hz, 2H), 7.36–7.18 (m, 9H), 7.13–7.06 (m, 3H), 7.02–6.95 (m, 2H).

*4.3.12. 4,4′,4″-(Ethene-1,1,2-triyl)tris(methylbenzene) (**4l**).*[3b] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J*=8.4 Hz, 2H), 7.15–7.08 (m, 6H), 6.94 (s, 4H), 6.87 (s, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 2.27 (s, 3H).

*4.3.13. 4,4′,4″-(Ethene-1,1,2-triyl)tris(methoxybenzene) (**4m**).*[3b] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J*=9.2 Hz, 2H), 7.15 (d, *J*=8.4 Hz, 2H), 7.00 (d, *J*=8.4 Hz, 2H), 6.88 (d, *J*=8.8 Hz, 2H), 6.82 (d, *J*=8.8 Hz, 2H), 6.80 (s, 1H), 6.70 (d, *J*=8.8 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 3.76 (s, 3H).

*4.3.14. 4,4′,4″-(Ethene-1,1,2-triyl)tris(chlorobenzene) (**4n**).*[3b] White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J*=8.4 Hz, 2H), 7.29 (d, *J*=8.8 Hz, 2H), 7.20 (d, *J*=8.4 Hz, 2H), 7.13 (d, *J*=8.8 Hz, 2H), 7.10 (d, *J*=8.4 Hz, 2H), 6.94 (d, *J*=8.4 Hz, 2H), 6.87 (s, 1H).

4.4. Representative procedure for β,β′-diarylation of terminal olefins

In a typical run, a 5 mL of vial equipped with a magnetic bar was charged with a mixture of the first aryl halide (0.5 mmol), olefine (0.5 mmol), Pd catalyst (4 mg, 0.005 mmol), TBAB (322 mg, 1 mmol), NaOAc (102 mg, 1.25 mmol), and 2 mL of DMA in argon. The reaction was heated at 120 °C for 4 h. After cooling to room temperature, the second aryl halide (0.5 mmol) was directly added to the crude mixture without isolation. The reaction was heated at 150 °C for 15 or 18 h again. The resulting mixture was extracted with ethyl acetate for three times, and the crude was obtained by removing volatile. The product was purified by flash column chromatography on silica gel.

*4.4.1. (E)- and (Z)-Ethyl 3-phenyl-3-(p-tolyl)acrylate (**5a**).*[10a] This product was isolated as a yellow oily mixture of the two *E*/*Z* stereoisomers, yield 88%, *E*/*Z*: 63:36.

4.4.1.1. (E)-Ethyl 3-phenyl-3-(p-tolyl)acrylate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.26 (m, 2H), 7.20–7.15 (m, 3H), 7.10–7.07 (m, 2H), 7.05–6.98 (m, 2H), 6.27 (s, 1H), 4.10–4.05 (m, 2H), 2.40 (s, 3H), 1.15 (t, *J*=7.2 Hz, 3H).

4.4.1.2. (Z)-Ethyl 3-phenyl-3-(p-tolyl)acrylate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.26 (m, 2H), 7.20–7.15 (m, 3H), 7.10–7.07 (m, 2H), 7.05–6.98 (m, 2H), 6.34 (s, 1H), 4.10–4.04 (m, 2H), 2.36 (s, 3H), 0.97 (t, *J*=7.2 Hz, 3H).

*4.4.2. (E)- and (Z)-Ethyl 3-(4-fluorophenyl)-3-(p-tolyl)acrylate (**5b**).* This product was isolated as a yellow oily mixture of the two *E*/*Z* stereoisomers, yield 85%, *E*/*Z*: 81:19, HRMS (ESI): *m*/*z* calcd for: $C_{18}H_{17}FO_2$, 307.1110, found: 307.1074.

4.4.2.1. (E)-Ethyl 3-(4-fluorophenyl)-3-(p-tolyl)acrylate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.26 (m, 2H), 7.19 (d, *J*=8.0 Hz, 2H), 7.08 (d, *J*=8.0 Hz, 2H), 7.00 (t, *J*=8.8 Hz, 2H), 6.26 (s, 1H), 4.09–4.04 (m,

2H), 2.39 (s, 3H), 1.14 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 166.1, 164.8, 162.3, 155.8, 138.3, 137.3, 135.8, 130.3, 128.8, 117.0, 115.5, 60.1, 21.5, 14.1.

4.4.2.2. (Z)-Ethyl 3-(4-fluorophenyl)-3-(p-tolyl)acrylate. ^{1}H NMR (400 MHz, $CDCl_3$): 7.29–7.26 (m, 2H), 7.19 (d, *J*=8.0 Hz, 2H), 7.08 (d, *J*=8.0 Hz, 2H), 7.00 (t, *J*=8.8 Hz, 2H), 6.26 (s, 1H), 4.09–4.04 (m, 2H), 2.39 (s, 3H), 1.14 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 166.1, 164.8, 162.3, 155.8, 138.3, 137.3, 135.8, 130.3, 129.2, 117.0, 115.3, 60.1, 21.5, 14.1.

*4.4.3. (E)- and (Z)-Ethyl 3-(3-fluorophenyl)-3-(p-tolyl)acrylate (**5c**).* This product was isolated as a yellow oily mixture of the two *E*/*Z* stereoisomers, yield 79%, *E*/*Z*: 61:39, HRMS (ESI): *m*/*z* calcd for: $C_{18}H_{17}FO_2$, 307.1110, found: 307.1088.

4.4.3.1. (E)-Ethyl 3-(3-fluorophenyl)-3-(p-tolyl)acrylate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.26 (m, 1H), 7.21–7.17 (m, 2H), 7.15–6.97 (m, 5H), 6.32 (s, 1H), 4.11–4.05 (m, 2H), 2.40 (s, 1H), 1.15 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 166.0, 163.9, 161.5, 155.4, 143.5, 135.4, 129.8, 129.2, 128.8, 124.1, 118.1, 116.1, 115.5, 60.2, 21.5, 14.1.

4.4.3.2. (Z)-Ethyl 3-(3-fluorophenyl)-3-(p-tolyl)acrylate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.26 (m, 1H), 7.21–7.17 (m, 2H), 7.15–6.97 (m, 5H), 6.37 (s, 1H), 4.11–4.05 (m, 2H), 2.36 (s, 1H), 1.15 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 166.0, 163.9, 161.5, 155.4, 143.4, 138.4, 129.9, 129.3, 128.2, 124.1, 117.1, 116.3, 115.3, 60.2, 21.3, 14.1.

*4.4.4. (E)- and (Z)-Ethyl 3-(4-chlorophenyl)-3-(p-tolyl)acrylate (**5d**).* This product was isolated as a yellow oily mixture of the two *E*/*Z* stereoisomers, yield 75%, *E*/*Z*: 52:48, HRMS (ESI): *m*/*z* calcd for: $C_{18}H_{17}ClO_2$, 323.0815, found: 323.0828.

4.4.4.1. (E)-Ethyl 3-(4-chlorophenyl)-3-(p-tolyl)acrylate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.26 (m, 2H), 7.24–7.18 (m, 4H), 7.13–7.07 (m, 2H), 6.29 (s, 1H), 4.10–4.04 (m, 2H), 2.39 (s, 3H), 1.15 (t, *J*=6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 166.0, 155.5, 139.7, 138.4, 136.1, 135.54, 135.52, 129.7, 129.2, 128.8, 128.6, 117.5, 60.2, 21.5, 14.1.

4.4.4.2. (Z)-Ethyl 3-(4-chlorophenyl)-3-(p-tolyl)acrylate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.26 (m, 2H), 7.24–7.16 (m, 4H), 7.13–7.07 (m, 2H), 6.29 (s, 1H), 4.10–4.04 (m, 2H), 2.36 (s, 3H), 1.15 (t, *J*=6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 166.0, 155.5, 139.7, 138.4, 135.54, 135.52, 129.7, 129.2, 128.8, 128.6, 117.5, 60.2, 21.5, 14.1.

*4.4.5. (E)- and (Z)-Ethyl 3-(4-methoxyphenyl)-3-(p-tolyl)acrylate (**5e**).*[10a] This product was isolated as a yellow oily mixture of the two *E*/*Z* stereoisomers, yield 86%, *E*/*Z*: 71:29.

4.4.5.1. (E)-Ethyl 3-(4-methoxyphenyl)-3-(p-tolyl)acrylate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J*=8.8 Hz, 2H), 7.14 (d, *J*=7.6 Hz, 2H), 7.04 (d, *J*=8.0 Hz, 2H), 6.78 (d, *J*=8.0 Hz, 2H), 6.22 (s, 1H), 4.03–3.98 (m, 2H), 3.76 (s, 3H), 2.34 (s, 3H), 1.09 (t, *J*=7.2 Hz, 3H).

4.4.5.2. (Z)-Ethyl 3-(4-methoxyphenyl)-3-(p-tolyl)acrylate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J*=8.8 Hz, 2H), 7.14 (d, *J*=7.6 Hz, 2H), 7.04 (d, *J*=8.0 Hz, 2H), 6.78 (d, *J*=8.0 Hz, 2H), 6.22 (s, 1H), 4.10–4.04 (m, 2H), 3.76 (s, 3H), 2.34 (s, 3H), 1.09 (t, *J*=7.2 Hz, 3H).

*4.4.6. (E)- and (Z)-Ethyl 3-(o-tolyl)-3-(p-tolyl)acrylate (**5f**).* This product was isolated as a yellow oily mixture of the two *E*/*Z* stereoisomers, yield 70%, *E*/*Z*: 51:49, HRMS (ESI): *m*/*z* calcd for: $C_{19}H_{20}O_2$, 303.1361, found: 303.1356.

4.4.6.1. (E)-Ethyl 3-(o-tolyl)-3-(p-tolyl)acrylate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.19 (m, 4H), 7.15–7.04 (m, 4H), 5.96 (s, 1H), 4.16–4.11 (m, 2H), 2.34 (s, 3H), 2.05 (s, 3H), 1.20 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 166.4, 157.1, 142.2, 138.5, 136.1, 135.7, 130.6, 129.6, 129.2, 128.4, 127.4, 125.7, 119.4, 60.2, 21.4, 20.4, 14.2.

4.4.6.2. (Z)-Ethyl 3-(o-tolyl)-3-(p-tolyl)acrylate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.19 (m, 4H), 7.15–7.04 (m, 4H), 6.50 (s, 1H), 4.03–3.98 (m, 2H), 2.34 (s, 3H), 2.08 (s, 3H), 1.07 (t, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 166.0, 155.9, 139.8, 138.9, 136.4, 135.4, 130.6, 129.8, 129.4, 128.4, 127.7, 125.4, 116.6, 59.9, 21.3, 19.6, 14.0.

*4.4.7. (E)- and (Z)-(1-(p-Tolyl)ethene-1,2-diyl)dibenzene (**5g**).*[10b,c] This product was isolated as a light yellow oily mixture of the two *E*/*Z* stereoisomers, yield 79%, *E*/*Z*: 80:20.

4.4.7.1. (E)-(1-(p-Tolyl)ethene-1,2-diyl)dibenzene.[10b] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.33 (m, 4H), 7.25–7.21 (m, 2H), 7.15–7.10 (m, 6H), 7.04–7.02 (m, 2H), 6.95 (s, 1H), 2.37 (s, 3H).

4.4.7.2. (Z)-(1-(p-Tolyl)ethene-1,2-diyl)dibenzene.[10c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.33 (m, 4H), 7.25–7.21 (m, 2H), 7.15–7.10 (m, 6H), 7.04–7.02 (m, 2H), 6.95 (s, 1H), 2.39 (s, 3H).

*4.4.8. (E)- and (Z)-(1-(4-Methoxyphenyl)ethene-1,2-diyl)dibenzene (**5h**).*[10b,c] This product was isolated as a light yellow oily mixture of the two *E*/*Z* stereoisomers, yield 89%, *E*/*Z*: 83:17.

4.4.8.1. (E)-(1-(4-Methoxyphenyl)ethene-1,2-diyl) dibenzene.[10b] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.31 (m, 3H), 7.25–7.20 (m, 3H), 7.14–7.10 (m, 3H), 7.06–7.02 (m, 2H), 6.98 (s, 1H), 6.92–6.80 (m, 3H), 3.77 (s, 3H).

4.4.8.2. (Z)-(1-(4-Methoxyphenyl)ethene-1,2-diyl) dibenzene.[10c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.31 (m, 3H), 7.25–7.20 (m, 3H), 7.14–7.10 (m, 3H), 7.06–7.02 (m, 2H), 6.96 (s, 1H), 6.92–6.80 (m, 2H), 6.75 (s, 1H), 3.77 (s, 3H).

*4.4.9. (E)- and (Z)-(1-(4-Fluorophenyl)ethene-1,2-diyl)dibenzene (**5i**).*[10d,e] This product was isolated as a light yellow oily mixture of the two *E*/*Z* stereoisomers, yield 85%, *E*/*Z*: 90:10.

4.4.9.1. (E)-(1-(4-Fluorophenyl)ethene-1,2-diyl)dibenzene.[10d] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.25 (m, 5H), 7.20–7.09 (m, 5H), 7.03–6.95 (m, 4H), 6.89 (s, 1H).

4.4.9.2. (Z)-(1-(4-Fluorophenyl)ethene-1,2-diyl)dibenzene.[10e] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.25 (m, 5H), 7.20–7.09 (m, 5H), 7.03–6.95 (m, 5H).

*4.4.10. (E)- and (Z)-(1-(4-Chlorophenyl)ethene-1,2-diyl)dibenzene (**5j**).*[10b,c] This product was isolated as a light yellow oily mixture of the two *E*/*Z* stereoisomers, yield 81%, *E*/*Z*: 63:37.

4.4.10.1. (E)-(1-(4-Chlorophenyl)ethene-1,2-diyl)dibenzene.[10b] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.18 (m, 7H), 7.15–7.07 (m, 5H), 7.01–6.96 (m, 2H), 6.93 (s, 1H).

4.4.10.2. (Z)-(1-(4-Chlorophenyl)ethene-1,2-diyl) dibenzene.[10c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.18 (m, 7H), 7.15–7.07 (m, 5H), 7.01–6.96 (m, 2H), 6.96 (s, 1H).

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