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ORIGINAL PAPER

Decarboxylative olefination of potassium benzoates via bimetallic catalysis strategy

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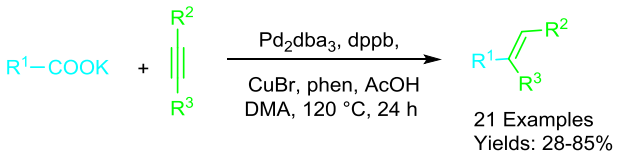
Abstract

A novel synthesis of styrene derivatives through decaroxylative olefination of potassium benzoates with alkynes using Pd_2dba_3/CuBr as catalyst system has been developed. The protocol proceeded smoothly and in most cases *Z*-alkene was the main product. Electron-rich potassium benzoates reacted more efficiently than those of electron-deficient substrates. Heteroaromatic and electron-deficient aryl alkynes were not consistent with this transformation.

Graphical abstract



Keywords Bimetallic catalysis · Decarboxylation · Hydrometalation · Benzoic acid · Alkyne

Introduction

The introduction of new and efficient routes for the synthesis of organic skeletons serves as one of the most interesting topics in organic chemistry [1–3]. In this context, metal-catalyzed cross-coupling reactions have profoundly changed the protocols for the construction of organic compounds and led to the formation of compounds from simpler starting materials. However, these catalytic reactions still suffer from the fundamental drawbacks [4–6]. Since the report of a palladium-catalyzed decarboxylative olefination of benzoic acids by Meyers [7], extensive studies have been conducted to form C–C bonds via this strategy [8–12]. Moreover, Gooßen and co-workers have developed an outstanding decarboxylation reaction to form biaryl structures using bimetallic strategy [13]. In 2010, Gooßen and co-workers reported a decarboxylative reaction for the synthesis of biaryl compounds with Ag/Pd catalyst system [14]. The same group described a modular, decarboxylative coupling of α-ketocarboxylates, amines, and aryl halides catalysis in copper/palladium [15]. Cahiez developed an efficient decarboxylation reaction for the synthesis of simple arenes [16]. Ge and co-workers reported a room temperature decarboxylative *ortho*-acylation of acetanilides with α-oxocarboxylic acids [17]. The use of cheap and readily available carboxylic acids as the source of active aryl instead of costly preformed reagents (e.g., aryl iodide) makes this procedure very attractive from economic and environmental points of view. However, using this strategy for direct olefination of aryl carboxylic acids is a challenging goal.

The introduction of alkenyl group into aromatic ring has long been a fundamental transformation within the field of

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organic chemistry. The seminal research of Fujiwara, Mizoroki, and Heck demonstrated that cross-coupling reactions can offer a general approach for substitution on sp^2-C atoms. In recent years, a variety of catalytic methods have been developed for the construction of styrene skeletons [18–23]. An alternative strategy to the synthesis of aryl-olefin bond involves hydroarylation of C–C multiple bonds using a low-valent transition metal catalyst [24–27].

Recently, Han and co-workers have reported an outstanding work on selective hydrogenation of alkynes with formic acid in the presence of palladium salts [28]. Tunge developed a polymer-supported rhodium(I) catalyst for the addition of boronic acid to internal alkyne [29]. Norton reported that the reaction between activated alkynes and benzene using $CpCr(CO)_3H$ affords styrene derivatives in good yields [30]. Based on this finding and in continuation of valuable researches that have been published in bimetallic catalysis [31–34], the efficacy of potassium benzoates and acetylenic esters for the synthesis of styrene derivatives was examined.

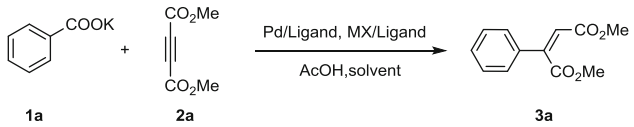
Results and discussion

We initially examined the reaction of potassium benzoate (**1a**) with dimethyl acetylenedicarboxylate (**2a**) as a model reaction to assess the reaction efficiency. When a mixture of **1a** (1.2 mmol) and **1b** (1.0 mmol) was stirred in dioxane in reflux condition for 24 h using $Pd(Ph_3P)_4$ (3 mol%), 1,4-bis(diphenylphosphino)butane (12 mol%), Cu_2O (10 mol%), 1,10-phenanthroline (5 mol%), and acetic acid (4.0 mmol), **3a** was obtained in 29% yield (Table 1, entry 1). Our studies were followed by attempting the reaction under different catalyst systems, solvents, and reaction temperatures (Table 1). Control experiments revealed that palladium and copper metallic source were necessary for this reaction, and the reaction was totally halted if either of them was absent (Table 1, entries 2 and 3). Among palladium precatalyst examined, the use of Pd_2dba_3 led to the formation of **3a** in a higher yield (Table 1, entries 1, 4, and 5). The choice of ligand also has great impact for the high productivity and stereoselectivity (Table 1, entries 5–8). We believed that bulky ligands exhibiting a large cone angle destabilize hydrometalated intermediate and disfavored subsequent transmetallation step. Screening of the catalysts for the decarboxylation path also revealed that CuBr was the best choice (Table 1, entries 9–12). However, catalyst screen indicated that Pd_2dba_3 and $AgBF_4$ also afforded the product (Table 1, entry 13). Although the reaction proceeded acceptably in dioxane, we felt that a better coordinative solvent may facilitate the decarboxylation step and hereby improve the overall yield (Table 1, entries 14–17). Reduction of the loading of ligand delivered a slightly lower yield and stereoselectivity (Table 1, entry 18). Lowering the reaction temperature proved to be detrimental, and the yield of the product decreased as the temperature was lowered (Table 1, entry 19). Upon shortening the reaction time, lower yield was obtained (Table 1, entry 20). Reaction conducted in the absence of 1,10-phenanthroline as a σ-donor ligand formed a lower yield of the product (Table 1, entry 21). Unfortunately, the reaction with cheaper benzoate salt like sodium benzoate resulted in formation of the desired product in lower yield (Table 1, entry 22).

With the optimized conditions in hand, we began to examine the scope of the reaction with various potassium benzoates (Table 2). Besides the model substrate, alkyl-substituted potassium benzoates like **2b**–**2d** were all competent substrates in the reaction, and they all gave the products in good yields (Table 2, entries 2–4). It should be emphasized that steric hindrance of substrates adversely affects the yield as potassium 2-methylbenzoate (**2e**) affords a moderate yield and potassium 2-(*tert*-butyl)benzoate (**2f**) only affords the product in traces amounts (Table 2, entries 5 and 6). In addition, potassium benzoates bearing chloride in the *ortho*- and *para*-positions were also reliable reaction partners with **2a** (Table 2, entries 7 and 8). Potassium 4-methoxybenzoate (**1i**) provided a lower yield of the product than **1a** (Table 2, entry 9). A possible reason is that the methoxy group might impede the reaction by binding to palladium or interfering in decarboxyation step. Additionally, electron-deficient substrates gave the corresponding products in low yields (Table 2, entries 10–12). Surprisingly, an excellent yield of the product was achieved when potassium furan-2-carboxylate (**1m**) was used as the substrate, an outcome we attribute to the facilitating the transmetallation step by coordination of heteroatom to the hydropalladiated intermediate (Table 2, entry 13). Potassium cinnamate (**1n**) was proven to be a good substrate in this reaction (Table 2, entry 14). In general, the reaction favored by lack of hindrance on substrates which is consistent with conditions promotes transmetallation step in bimetallic catalysis. It should be noted that aliphatic carboxylic salt such as potassium acetate (**1o**) did not participate in this transformation (Table 2, entry 15).

In addition, we examined the reaction with different alkynes (Table 3). The investigation disclosed that aliphatic terminal alkynes afforded the products in acceptable yields; however, the *Z*/*E* selectivities were not satisfactory (Table 3, entries 1 and 2). Phenyl acetylene (**2d**) afforded the product in good yield and selectivity (Table 3, entry 3). Other acetylenic esters also proved to be good substrates for the current transformation (Table 3, entries 4–6). Internal aryl alkyne was also successfully

Table 1 Optimization of the reaction conditions



1a **2a** **3a**

Entry	Pd system	Cu system	Solvent	Yield of **3a**/%, (*E*/*Z*)[a]
1	$Pd(Ph_3P)_4$/dppb	Cu_2O/phen	Dioxane	29 (64/36)
2	–	Cu_2O/phen	Dioxane	–
3	$Pd(Ph_3P)_4$/dppb	–	Dioxane	Traces
4	$Pd(OAc)_2$/dppb	Cu_2O/phen	Dioxane	16
5	Pd_2dba_3/dppb	Cu_2O/phen	Dioxane	51 (90/10)
6	Pd_2dba_3/dppp	Cu_2O/phen	Dioxane	44 (81/19)
7	Pd_2dba_3/P(2-Fur)$_3$	Cu_2O/phen	Dioxane	16
8	Pd_2dba_3/P^{t}Bu$_3$	Cu_2O/phen	Dioxane	Traces
9	Pd_2dba_3/dppb	CuCl/phen	Dioxane	36 (88/12)
10	Pd_2dba_3/dppb	CuBr/phen	Dioxane	64 (95/5)
11	Pd_2dba_3/dppb	$CuPF_6$/phen	Dioxane	51 (85/15)
12	Pd_2dba_3/dppb	$CuBF_4$/phen	Dioxane	27 (67/33)
13	Pd_2dba_3/dppb	$AgBF_4$	Dioxane	40[b] (68/32)
14	Pd_2dba_3/dppb	CuBr/phen	DMA	71 (99/1)
15	Pd_2dba_3/dppb	CuBr/phen	DMF	61 (97/3)
16	Pd_2dba_3/dppb	CuBr/phen	NMP	70 (97/3)
17	Pd_2dba_3/dppb	CuBr/phen	DMSO	56 (94/6)
18	Pd_2dba_3/dppb	CuBr/phen	DMA	57[c] (77/23)
19	Pd_2dba_3/dppb	CuBr/phen	DMA	28[d] (99/1)
20	Pd_2dba_3/dppb	CuBr/phen	DMA	60[e] (97/3)
21	Pd_2dba_3/dppb	CuBr	DMA	36 (95/5)
22	Pd_2dba_3/dppb	CuBr/phen	DMA	35 (95/5)

Reaction conditions: **1a** (1.2 mmol), **2a** (1.0 mmol), Pd precatalyst (3 mol%), ligand (12 mol%), Cu salt (10 mol%), ligand (5 mol%), acetic acid (4.0 mmol), and 3.0 cm^3 solvent were stirred at 120 °C for 24 h, under a N_2 atmosphere

Phen 1,10-phenanthroline, *dppp* 1,4-bis(diphenylphosphino)butane

[a]Determined by GC

[b]20 mol% of $AgBF_4$ was used

[c]6 mol% of dppb was used

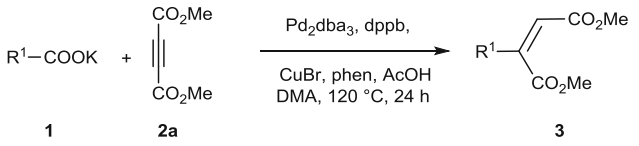
[d]The reaction conducted at 100 °C

[e]The mixture was stirred for 18 h

reduced to **3u** with excellent stereoselectivity (Table 3, entry 7). Heteroaromatic alkynes like 2-ethynylfuran (**2j**) and electron-deficient aryl alkynes like 1-ethynyl-4-nitrobenzene (**2k**) were completely inconsistent with this transformation (Table 3, entries 8 and 9). This represents one of the major limitations of this reaction, which should be improved in further studies.

The mechanism of the reaction is not clear. However, as suggested in previous reports [35, 36], the complexation of carboxylate **1** by salt metathesis with copper-bromide gives **4**, followed by generating an arylcopper intermediate **5** and carbon dioxide (Scheme 1). By considering this proposed mechanism, the role of a σ-donor ligand like 1,10-phenanthroline would be to favor the oxidative addition of the C–C bond. In a parallel path, hydrometalation proceeds via the reaction of an alkyne coordinated Pd(0) complex **6**, followed by generating intermediate **7** by the act of acetic acid. On the basis of Hou's findings [28], the current reduction of an alkyne to a *Z*-alkene with acetic acid can be clearly rationalized to take place via a catalytic cycle involving hydropalladation of the triple bond with acetic acid to produce alkenenylpalladium species **7**. Subsequent

Table 2 Reaction scope for potassium carboxylate



Entry	1	R^1	Yield of 3/%, (*Z*/*E*)[a]
1	**1a**	Ph	**3a**, 71 (99/1)
2	**1b**	4-Me-C_6H_4	**3b**, 82 (99/1)
3	**1c**	3-Me-C_6H_4	**3c**, 76 (98/2)
4	**1d**	3,5-Me-C_6H_4	**3d**, 85 (99/1)
5	**1e**	2-Me-C_6H_4	**3e**, 47 (95/5)
6	**1f**	2-*t*-Bu-C_6H_4	**3f**, traces
7	**1g**	2-Cl-C_6H_4	**3g**, 56 (95/5)
8	**1h**	4-Cl-C_6H_4	**3h**, 80 (98/23)
9	**1i**	4-MeO-C_6H_4	**3i**, 59 (78/22)
10	**1j**	4-CH_3OCO-C_6H_4	**3j**, 53 (89/11)
11	**1k**	4-NO_2-C_6H_4	**3k**, 28 (99/1)
12	**1l**	3-CF_3-C_6H_4	**3l**, 61 (97/3)
13	**1m**	2-Furyl	**3m**, 81 (99/1)
14	**1n**	PhCHCH	**3n**, 68 (92/8)
15	**1o**	Me	–

Reaction conditions: **1** (1.2 mmol), **2a** (1.0 mmol), Pd_2dba_3 (3 mol%), dppb (12 mol%), CuBr (10 mol%), phen (5 mol%), acetic acid (4.0 mmol), and 3.0 cm^3 DMA were stirred at 120 °C for 24 h, under a N_2 atmosphere

[a]Determined by GC

transmetallation of **7** with intermediated **5** affords intermediate **8** and regenerates LCuBr. Finally, a reductive elimination of intermediate **8** gives the *Z*-products **3** and regenerates the palladium active catalyst (Scheme 1). No styrene derivative was obtained when the reaction repeated with benzene instead of potassium benzoate. It could be deduced that benzene intermediate did not involve in this transformation (see Supplementary Material, Scheme 1). It is worth mentioning that the reaction conducted in the absence of acetic acid resulted in formation of biphenyl in 91% yield (see Supplementary Material, Scheme 2). As such, the path involved the nucleophilic attack of carboxylate ion on complex **6** to form styrene derivatives could be overstated. Moreover, the reaction conducted with benzoic acid instead of benzoate salt afforded vinyl benzoate and dimeric alkene in low yields (see Supplementary Material, Scheme 3).

In summary, we have developed a catalytic reaction for the olefination of potassium carboxylate with acceptable catalyst and additive loading. Aryl and heteroaryl potassium carboxylate and a decent range of alkynes were competent substrates in the reaction, but heteroaromatic and electron-deficient aryl-substituted terminal alkynes and alkyl carboxylic salts were incompatible with the reaction conditions. A possible mechanism was proposed and distinctive transmetallation of hydropalladated intermediate with decarboxylated intermediate was proposed to be involved.

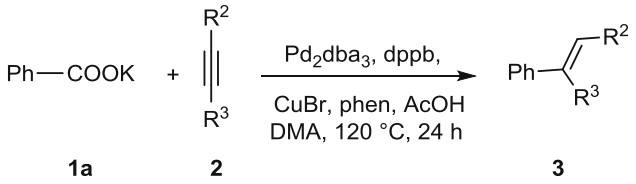
Experimental

Regents, compounds, catalyst, and solvents were obtained from commercial sources and were used without further purification. All reactions were carried out in oven-dried Schlenk tubes under N_2 atmosphere. Dry solvents were obtained by purification according to the standard methods. Reagents were used as received unless otherwise noted. Column chromatography was performed using Silica gel 60 (particle size 63–200 μm) (Merck, item number 7734-3). TLC was performed using Silica gel 60 (Merck, item number 116835). Melting points: Electrothermal-9100 apparatus. IR Spectra: Shimadzu IR-460 spectrometer. ^1H and ^{13}C NMR spectra: Bruker DRX-500 AVANCE instrument; in $CDCl_3$ at 500.1 and 125.7 MHz, resp; δ in ppm, *J* in Hz. EI-MS (70 eV): Finnigan-MAT-8430 mass spectrometer. Elemental analyses (C, H, N) were performed with a Heraeus CHN-O-Rapid analyzer. The results agreed favorably with the calculated values. Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2010 Series GC System equipped with a flame-ionization detector. GC–MS analysis was performed on Shimadzu GCMS-QP2010 Plus Gas Chromatograph/Mass Spectrometer.

General procedure for synthesis of compound 3

An oven-dried and nitrogen-flushed Schlenk tube equipped with a mechanical stirrer was charged with potassium carboxylate (1.2 mmol), copper(I) bromide (10 mol%), Phen (5 mol%), and 3.0 cm^3 DMA. The resulting mixture was stirred at 120 °C for 2 h. Afterwards, the mixture was charged with $Pd_2(dba)_3$ (3 mol%), dppb (12 mol%), and alkynes (1.0 mmol). The Schlenk tube was sealed and then evacuated and backfilled with Ar (3 cycles). After stirring the mixture at room temperature for 15 min, AcOH (4.0 mmol) was injected and the reaction was heated to 120 °C for 22 h. The mixture was cooled to room temperature and filtered through Celite. The solid was rinsed with 50 cm^3 ethyl acetate and the resulting filtrate was concentrated under vacuum. The residues were purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, gradient 20:1 to 5:1) furnishing **3**.

Table 3 Reaction scope for alkynes



1a **2** **3**

Entry	2	R^2	R^3	Yield of **3**/%, (*Z*/*E*)[a]
1	**2b**	*n*-Bu	H	**3o**, 62 (75/25)
2	**2c**	*n*-Pr	H	**3p**, 60 (78/22)
3	**2d**	Ph	H	**3q**, 73 (89/11)
4	**2e**	CO_2Et	CO_2Et	**3r**, 79 (99/1)
5	**2f**	Ph	CO_2Et	**3s**, 65 (98/2)
6	**2g**	CO_2Et	H	**3t**, 83 (99/1)
7	**2h**	Ph	Ph	**3u**, 84 (99/1)
8	**2j**	2-Furyl	H	–
9	**2k**	4-NO_2-C_6H_4	H	–

Reaction conditions: **1a** (1.2 mmol), **2** (1.0 mmol), Pd_2dba_3 (3 mol%), dppb (12 mol%), CuBr (10 mol%), phen (5 mol%), acetic acid (4.0 mmol), and 3.0 cm^3 DMA were stirred at 120 °C for 24 h, under a N_2 atmosphere

[a]Determined by GC

Dimethyl 2-phenylmaleate (3a) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 4/1, R_f = 0.32) affording 0.16 g (73%) of **3a**. Spectroscopic data were consistent with that reported in Ref. [30].

Dimethyl 2-(*p*-tolyl)maleate (3b) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 4/1, R_f = 0.35) affording 0.19 g (82%) of **3b**. Spectroscopic data were consistent with that reported in Ref. [37].

Dimethyl 2-(*m*-tolyl)maleate (3c) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 4/1, R_f = 0.46) affording 0.18 g (76%) of **3c**. Spectroscopic data were consistent with that reported in Ref. [37].

Dimethyl 2-(3,5-dimethylphenyl)maleate (3d, $C_{14}H_{16}O_4$) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 5/1, R_f = 0.42) affording 0.21 g (85%) of **3d**. IR (KBr): $\bar{\nu}$ = 3028, 2965, 1738, 1727, 1644, 1451, 1316, 1102 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.35 (6H, s, 2 CH_3), 3.56 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 6.60 (1H, s, CH), 7.17 (2H, s, 2 CH), 7.25 (1H, s, CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 25.6 (2 CH_3), 53.5 (OCH_3), 56.6 (OCH_3), 107.2 (CH), 126.9 (2 CH), 131.4 (CH), 134.8 (C), 139.6 (2 C), 149.5 (C), 165.3 (C=O), 167.0 (C=O) ppm; EI-MS (70 eV): *m*/*z* (%) = 248 (M^+, 2), 217 (16), 189 (32), 187 (46), 142 (56), 105 (100), 81 (79).

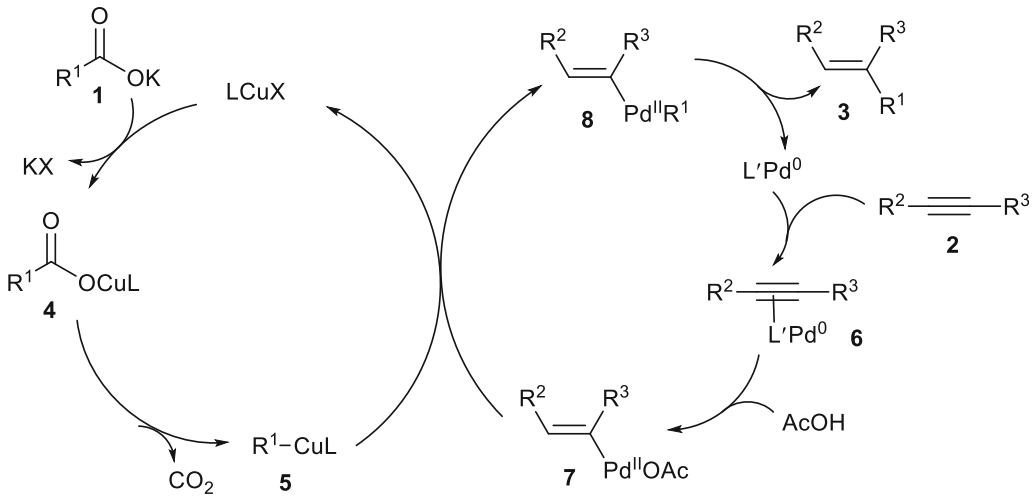
Dimethyl 2-(*o*-tolyl)maleate (3e) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 3/1, R_f = 0.46) affording 0.11 g (47%) of **3e**. Spectroscopic data were consistent with that reported in Ref. [38].

Dimethyl 2-(2-chlorophenyl)maleate (3g, $C_{12}H_{11}ClO_4$) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 3/1, R_f = 0.34) affording 0.14 g (56%) of **3 g**. IR (KBr): $\bar{\nu}$ = 3046, 2981, 1728, 1718, 1634, 1466, 1357, 1087 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 3.58 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 6.65 (1H, s, CH), 7.15 (1H, t, ^3J = 6.9 Hz, CH), 7.30-7.38 (2H, m, 2 CH), 7.65 (1H, d, ^3J = 6.9 Hz, CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 54.1 (OCH_3), 56.8 (OCH_3), 102.6 (CH), 128.7 (CH), 129.3 (CH), 131.2 (CH), 131.7 (CH), 134.2 (C), 137.1 (C), 149.4 (C), 165.7 (C=O), 168.1 (C=O) ppm; EI-MS (70 eV): *m*/*z* (%) = 256 ($[M + 2]^+$, 12), 254 (M^+, 4), 223 (16), 195 (41), 193 (51), 136 (62), 111 (100), 85 (49).

Dimethyl 2-(4-chlorophenyl)maleate (3h) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 4/1, R_f = 0.21) affording 0.20 g (80%) of **3h**. Spectroscopic data were consistent with that reported in Ref. [41].

Dimethyl 2-(4-methoxyphenyl)maleate (3i) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 3/1, R_f = 0.38) affording 0.15 g (59%) of

Scheme 1



3i. Spectroscopic data were consistent with that reported in Ref. [37].

Dimethyl 2-[4-(methoxycarbonyl)phenyl]maleate (3j, $C_{14}H_{14}O_6$) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 3/1, $R_f = 0.56$) affording 0.15 g (53%) of **3j**. IR (KBr): $\bar{\nu}$ = 3018, 2960, 1736, 1725, 1710, 1638, 1466, 1314, 1094 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.69 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 6.92 (1H, s, CH), 7.52 (2H, d, ^3J = 7.0 Hz, 2 CH), 7.80 (2H, d, ^3J = 7.0 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 53.1 (OCH_3), 55.0 (OCH_3), 56.2 (OCH_3), 111.6 (CH), 130.1 (2 CH), 133.5 (C), 134.6 (2 CH), 138.2 (C), 153.1 (C), 165.7 (C=O), 165.9 (C=O), 167.1 (C=O) ppm; EI-MS (70 eV): *m/z* (%) = 278 (M^+, 6), 247 (13), 219 (34), 217 (30), 160 (48), 129 (69), 105 (100).

Dimethyl 2-(4-nitrophenyl)maleate (3k, $C_{20}H_{24}N_2O_6$) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 2/1, $R_f = 0.21$) affording 0.08 g (28%) of **3 k**. IR (KBr): $\bar{\nu}$ = 3042, 2952, 1736, 1721, 1655, 1537, 1448, 1373, 1322, 1101 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.72 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 7.23 (1H, s, CH), 7.58 (2H, d, ^3J = 6.8 Hz, 2 CH), 8.29 (2H, d, ^3J = 6.8 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 54.7 (OCH_3), 56.8 (OCH_3), 116.1 (CH), 127.4 (2 CH), 134.9 (2 CH), 140.1 (C), 148.2 (C), 152.5 (C), 166.9 (C=O), 169.7 (C=O) ppm; EI-MS (70 eV): *m/z* (%) = 265 (M^+, 1), 234 (11), 204 (39), 142 (100), 122 (51), 54 (63).

Dimethyl 2-[3-(trifluoromethyl)phenyl]maleate (3l, $C_{13}H_{11}F_3O_4$) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 3/1, $R_f = 0.26$) affording 0.18 g (61%) of **3 l**. IR (KBr): $\bar{\nu}$ = 3043, 2978, 1729, 1718, 1671, 1453, 1361, 1182 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.55 (3H, s, OCH_3), 3.76 (3H, s, OCH_3), 7.02 (1H, s, CH), 7.19-7.30 (2H, m, 2 CH), 7.44 (1H, d, ^3J = 6.9 Hz, CH), 7.59 (1H, s, CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 54.1 (OCH_3), 57.9 (OCH_3), 114.4 (CH), 125.1 (CH, q, ^3J = 3.9 Hz), 126.2 (CH, q, ^3J = 3.9 Hz), 128.7 (CF_3, q, ^1J = 273.1 Hz), 129.5 (CH), 131.2 (C, q, ^2J = 31.9 Hz), 133.2 (CH), 135.8 (C), 151.1 (C), 166.1 (C=O), 169.2 (C=O) ppm; EI-MS (70 eV): *m/z* (%) = 288 (M^+, 11), 268 (12), 171 (38), 120 (58), 105 (100), 77 (60).

Dimethyl 2-(furan-2-yl)maleate (3m, $C_{10}H_{10}O_5$) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 4/1, $R_f = 0.47$) affording 0.17 g (81%) of **3m**. IR (KBr): $\bar{\nu}$ = 3058, 2982, 1739, 1728, 1654, 1461, 1440, 1337, 1106 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 3.61 (3H, s, OCH_3), 3.72 (3H, s, OCH_3), 6.85-6.91 (2H, m, 2 CH), 7.31 (1H, d, ^3J = 6.1 Hz, CH), 8.38 (1H, d, ^3J = 6.2 Hz, CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 53.9 (OCH_3), 56.2 (OCH_3), 113.3 (CH), 115.8 (CH), 116.2 (CH), 149.1 (CH), 150.3 (C), 150.8 (C), 166.3 (C=O), 168.0 (C=O) ppm; EI-MS (70 eV): *m/z* (%) = 210 (M^+, 12), 179 (18), 151 (53), 149 (35), 92 (61), 67 (100).

Dimethyl 2-[(*E*)-styryl]maleate (3n) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 5/1, $R_f = 0.21$) affording 0.17 g (68%) of **3n**. Spectroscopic data were consistent with that reported in Ref. [30].

Hex-1-en-1-ylbenzene (3o) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 7/1,

R_f = 0.52) affording 0.10 g (62%) of **3o**. Spectroscopic data were consistent with that reported in Ref. [38].

Pent-1-en-1-ylbenzene (3p) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 7/1, R_f = 0.47) affording 0.09 g (60%) of **3p**. Spectroscopic data were consistent with that reported in Ref. [39].

Ethene-1,1-diyldibenzene (3q) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 6/1, R_f = 0.24) affording 0.13 g (73%) of **3q**. Spectroscopic data were consistent with that reported in Ref. [43].

Diethyl 2-phenylmaleate (3r) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 4/1, R_f = 0.38) affording 0.20 g (79%) of **3r**. Spectroscopic data were consistent with that reported in Ref. [40].

Ethyl (*Z*)-2,3-diphenylacrylate (3s) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 5/1, R_f = 0.21) affording 0.16 g (65%) of **3s**. Spectroscopic data were consistent with that reported in Ref. [41].

Ethyl 2-phenylacrylate (3t) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 3/1, R_f = 0.29) affording 0.15 g (83%) of **3t**. Spectroscopic data were consistent with that reported in Ref. [42].

Ethene-1,1,2-triyltribenzene (3u) The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 4/1, R_f = 0.36) affording 0.21 g (84%) of **3u**. Spectroscopic data were consistent with that reported in Ref. [30].

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References

1. Liao K, Negretti S, Musaev DG, Bacsa J, Davies HML (2016) Nature 533:230
2. Chen W, Ma L, Paul A, Seidel D (2018) Nat Chem 10:165
3. Jones WD (2002) Science 295:289
4. Seechurn CCCJ, Sperger T, Scrase TG, Schoenebeck F, Colacot TJ (2017) J Am Chem Soc 139:5194
5. Takise R, Muto K, Yamaguchi J (2017) Chem Soc Rev 46:5864
6. Shi S, Szostak M (2017) Chem Commun 53:10584
7. Myers AG, Tanaka D, Mannion MR (2002) J Am Chem Soc 124:11250
8. Hu G, Gao Y, Zhao Y (2014) Org Lett 16:4464
9. Kan J, Huang S, Lin J, Zhang M, Su W (2015) Angew Chem Int Ed 54:2199
10. Sun F, Gu Z (2015) Org Lett 17:2222
11. Zhu Y, Li X, Wang X, Huang X, Shen T, Zhang Y, Sun X, Zou M, Song S, Jiao N (2015) Org Lett 17:4702
12. Tan H, Li H, Ji W, Wang (2015) Angew Chem Int Ed 54:8374
13. Gooßen LJ, Deng G, Levy LM (2006) Science 313:662
14. Gooßen LJ, Lange PP, Rodríguez N, Linder C (2010) Chem Eur J 16:3906
15. Rudolphi F, Song B, Gooßen LJ (2011) Adv Synth Catal 353:337
16. Cahiez G, Moyeux A, Gager A, Poizat M (2013) Adv Synth Catal 355:790
17. Fang P, Li M, Ge H (2010) J Am Chem Soc 132:11898
18. Wen H, Zhang L, Zhu S, Liu G, Huang Z (2017) ACS Catal 7:6419
19. Traficante CI, Fagundez C, Serra GL, Mata EG, Delpiccolo CML (2016) ACS Comb Sci 18:225
20. Kong W, Che C, Wu J, Ma L, Zhu G (2014) J Org Chem 79:5799
21. Gordillo A, Ortuño MA, López-Mardomingo C, Lledós A, Ujaque G, de Jesús E (2013) J Am Chem Soc 135:13749
22. Ackermann L, Gunnoe TB, Habgood LG (2018) Catalytic hydroarylation of carbon-carbon multiple bonds. Wiley-VCH, Weinheim
23. Jia C, Piao D, Oyamada J, Lu W, Kitamura T, Fujiwara Y (2000) Science 287:1992
24. Huang L, Biafora A, Zhang G, Bragoni V, Gooßen LJ (2016) Angew Chem Int Ed 55:6933
25. Zhang X, Li Y, Shi H, Zhang L, Zhang S, Xu X, Liu Q (2014) Chem Commun 50:7306
26. Manikandan R, Jeganmohan M (2015) Org Biomol Chem 13:10420
27. Yamamoto Y (2014) Chem Soc Rev 43:1575
28. Shen R, Chen T, Zhao Y, Qiu R, Zhou Y, Yin S, Wang X, Goto M, Han LB (2011) J Am Chem Soc 133:17037
29. Jana R, Tunge JA (2011) J Org Chem 76:8376
30. Estes DP, Norton JR, Jockusch S, Sattler W (2012) J Am Chem Soc 134:15512
31. Pye DR, Mankad NP (2017) Chem Sci 81:705
32. Mankad NP (2016) Chem Eur J 22:5822
33. Vercruysse S, Cornelissen L, Nahra F, Collard L, Riant O (2014) Chem Eur J 20:1834
34. Rudolphi F, Song B, Gooßen LJ (2011) Adv Synth Catal 353:337
35. Cohen T, Berninger RW, Wood JT (1978) J Org Chem 43:837
36. Cahiez G, Moyeux A, Gager O, Poizat M (2013) Adv Synth Catal 355:790
37. Gadge ST, Bhanage BM (2013) Synlett 24:981
38. Giannerini M, Fañanás-Mastral M, Feringa BL (2013) Nat Chem 5:667
39. Pérez M, Fañanás-Mastral M, Bos PH, Rudolph A, Harutyunyan SR, Feringa BL (2011) Nat Chem 3:377
40. Kondolff I, Doucet H, Santelli M (2003) Tetrahedron Lett 44:8487
41. Tsuji J, Nogi T (1966) J Am Chem Soc 88:1289
42. Fructos MR, Díaz-Requejo MM, Pérez PJ (2009) Chem Commun 14:5153
43. Li J, Liu Q, Shen H, Huang R, Zhang X, Xiong Y, Chen C (2015) RSC Adv 5:85291