Copper(II)-Catalyzed Esterification of Arenecarboxylic Acids with Aryl- and Vinyl-Substituted Trimethoxysilanes

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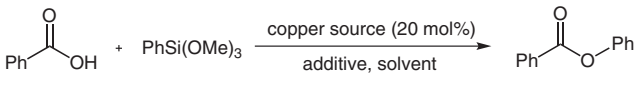
Abstract: In this paper, the copper(II)-catalyzed esterification reaction of arenecarboxylic acids with aryl- or vinyl-substituted trimethoxysilanes is described. A series of aryltrimethoxysilanes and arenecarboxylic acids worked well under this procedure, affording aryl benzoate derivatives in moderate to good yields. Notably, trimethoxy(vinyl)silanes also worked well under this procedure giving a facile and versatile method to access vinyl benzoate derivatives.

Key words: copper(II) catalyzed, trimethoxysilanes, carboxylic acids, esters, silver(I) fluoride

Benzoate derivatives are important building blocks in the synthesis of natural and pharmacological compounds.[1] The direct esterification of benzoic acid and phenol[2] as well as transesterification reactions[3] are often conducted under strongly acidic or basic conditions, which might limit the scope of functional groups and cause side reactions, such as carbonization, oxidation, etc.[4] The Baeyer–Villiger oxidation[5] reaction may suffer from low regioselectivity. In the past few years, the synthesis of alkyl benzoate derivatives starting from aldehydes and ketones has been developed.[6,7] However, less attention has been paid to the synthesis of aryl benzoate derivatives. Thus, from a synthetic point of view, it is a highly desirable goal to develop a versatile approach for the synthesis of aryl benzoate derivatives in a simple way.

The Chan–Lam coupling reaction, which allows aryl carbon–heteroatom bond formation via the oxidative coupling of arylboronic acids, stannanes, or siloxanes with N–H[8,9f] or O–H[9] containing compounds, has been widely studied in the last few years. Trialkoxy(aryl)silanes have been widely used as the transmetalation reagent in C–C,[10] C–N,[11] and C–S[12] bond formation, because of their low cost, easy availability, nontoxic byproducts, and stability under many reaction conditions. However, to the best of our knowledge, the scope of Chan–Lam reaction for the formation of C–O bonds was limited to phenol and alcohols, and the application of both carboxylic acids, as heteroatom nucleophiles, and siloxanes in the Chan–Lam reaction for the formation of the C–O bond was less widely reported.[9,13] In 2006, trimethoxy(phenyl)silane was used for the oxidative esterification of aldehydes.[14] We

Table 1 Effects of Copper Sources, Solvents, and Fluoride Sources on Formation of Phenyl Benzoate (**3aa**)



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

Entry	Cu source	F source	Solvent	Yield[a] (%)
1	$Cu(OAc)_2$	TBAF·3 H_2O	toluene	10
2	$Cu(OAc)_2$	KF	toluene	<5
3	$Cu(OAc)_2$	CsF	toluene	<5
4	$Cu(OAc)_2$	FeF_3	toluene	<5
5	$Cu(OAc)_2$	CuF_2	toluene	30
6	$Cu(OAc)_2$	AgF	toluene	65
7	$Cu(OAc)_2$	AgF	DMF	<5
8	$Cu(OAc)_2$	AgF	DMSO	<5
9	$Cu(OAc)_2$	AgF	NMP	<5
10	$Cu(OAc)_2$	AgF	DCE	30[b]
11	$Cu(OAc)_2$	AgF	MeCN	31[b]
12	CuF_2	AgF	toluene	72 (80)[c]
13	$CuSO_4$	AgF	toluene	50
14	$CuBr_2$	AgF	toluene	30
15	$Cu(OTf)_2$	AgF	toluene	32
16	$Cu(acac)_2$	AgF	toluene	<5
17	Cu_2O	AgF	toluene	33
18	CuI	AgF	toluene	30
19	CuBr	AgF	toluene	<5
20	CuF_2	–	toluene	12
21	–	AgF	toluene	0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Cu source (20 mol%), additive (2 equiv), anhyd solvent (2 mL), 130 °C, under air, 24 h. Isolated yield.
[b] 90 °C.
[c] AgF (3 equiv).

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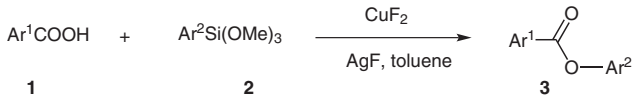
have devoted our efforts to the application of trialkoxy(aryl)silanes in many reactions.[10c,i–k,11a,b] Herein, we report the copper(II)-catalyzed esterification reaction of arenecarboxylic acids with aryl- or vinyl-substituted trimethoxysilanes under an air atmosphere, affording aryl or vinyl benzoate derivatives in moderate to good yields.

Initial studies were performed using benzoic acid (**1a**) with trimethoxy(phenyl)silane (**2a**) as model substrates, employing copper(II) acetate as the catalyst at 130 °C in a sealed tube (Table 1). Considering that C–Si bonds generally needs a fluoride source to activate it, we first focused screening for the fluoride source (2 equiv) and found that silver(I) fluoride showed good activity (Table 1, entry 6). The copper source used had a dramatic effect. Among the copper sources used, copper(II) fluoride exhibited the highest catalytic reactivity and **3aa** was isolated in 72% yield (Table 1, entry 12). The yield of **3aa** improved to 80% using three equivalents of silver fluoride (Table 1, entry 12). A profound solvent effect was also observed and toluene was found to be superior. In addition, **3aa** was formed in only 12% yield in the absence of silver(I) fluoride (Table 1, entry 20) and no desired product was detected without a copper source (Table 1, entry 21). Biphenyl, which is often detected in transition-metal-catalyzed coupling reactions, was formed as a byproduct.

With the optimized conditions in hand (Table 1, entry 12), we then explored the scope of this method. As expected, a series of aryltrimethoxysilanes **2a–e** worked well under these reaction conditions. Electron-donating as well as electron-neutral aryltrimethoxysilanes **2a–e** coupled effciently with benzoic acid (**1a**), and good yields of the products **3aa–ae** were obtained (Table 2, entries 1–5). Steric hindrance on the aryltrimethoxysilane or the acid has no obvious effect on the reaction (Table 2, entries 2, 3, 6–8). For example, **3ab**, **3ca**, **3fa**, and **3ha** were isolated in 83%, 90%, 84%, and 81% yields, respectively. This procedure tolerated a series of functional groups, such as OMe, Cl, Br, and NO_2 groups. Particularly, halogen-substituted carboxylic acids **1g–i** worked well with trimethoxy(phenyl)silane (**2a**) (Table 2, entries 11–14) and

Table 2 Copper(II)-Catalyzed Esterification Reaction of Arenecarboxylic Acids with Aryltrimethoxysilanes[a]



Entry	Substrate **1**	Ar^1	Substrate **2**	Ar^2	Product	Yield[b] (%)
1	**1a**	Ph	**2a**	Ph	**3aa**	80 (73)[c] (62)[d]
2	**1a**	Ph	**2b**	4-MeC_6H_4	**3ab**	83
3	**1a**	Ph	**2c**	2-MeC_6H_4	**3ac**	81
4	**1a**	Ph	**2d**	3,5-$Me_2C_6H_3$	**3ad**	65
5	**1a**	Ph	**2e**	1-naphthyl	**3ae**	70
6	**1b**	4-MeC_6H_4	**2a**	Ph	**3ba**	82
7	**1c**	2-MeC_6H_4	**2a**	Ph	**3ca**	90
8	**1d**	3-MeC_6H_4	**2a**	Ph	**3da**	81
9	**1e**	4-$MeOC_6H_4$	**2a**	Ph	**3ea**	83
10	**1f**	2-$MeOC_6H_4$	**2a**	Ph	**3fa**	84
11	**1g**	4-ClC_6H_4	**2a**	Ph	**3ga**	79
12	**1h**	2-ClC_6H_4	**2a**	Ph	**3ha**	81
13	**1i**	3-ClC_6H_4	**2a**	Ph	**3ia**	76
14	**1j**	4-BrC_6H_4	**2a**	Ph	**3ja**	60
15	**1k**	3-$O_2NC_6H_4$	**2a**	Ph	**3ka**	70
16	**1l**	CH=CHPh	**2a**	Ph	**3la**	45
17	**1m**	Bn	**2e**	1-naphthyl	**3me**	36

[a] Reaction conditions: Ar^1CO_2H **1** (0.2 mmol), $Ar^2Si(OMe)_3$ **2** (0.3 mmol), CuF_2 (20 mol%), AgF (3 equiv), anhyd toluene (2 mL), 130 °C, 24 h.
[b] Isolated yield.
[c] Scale increased to 0.5 mmol.
[d] Scale increased to 1.0 mmol.

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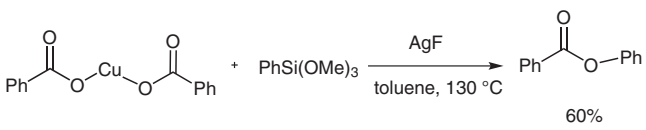
the remaining halogen atom could be valuable for further manipulation. It is worth noting that cinnamic acid (**1l**) was subjected to the standard procedure and phenyl cinnamate (**3la**) was obtained in moderate yield (Table 2, entry 16). Under the optimized reaction conditions, the reaction conducted on 0.5-mmol and 1-mmol scales formed the product **3aa** in 73% and 62% yields, respectively (Table 2, entry 1). Disappointingly, aliphatic acids did not react efficiently with aryltrimethoxysilanes. For example, **1l** and **1m** provided the product **3la** and **3me** in only 45% and 36% yields, respectively, and only a trace of the desired product was detected using acetic acid as the substrate. Importantly, the method obviated the use of an acyl chloride and phenol in the synthesis of benzoate derivatives. Thus, it represents an exceedingly practical and alternative method to access aryl benzoate derivatives.

Having demonstrated the utility of the optimized conditions on aryltrimethoxysilanes, we chose trimethoxy(vinyl)silane (**2f**) as the reaction partner. Fortunately, it ran smoothly and vinyl esters were obtained in moderate yields (Table 3). The direct addition of carboxylic acids to terminal alkynes catalyzed by Hg,[15] Ru,[16] or Ir[17] is a straightforward and atom-economical process for the synthesis of enol esters. However, the use of toxic mercury salts or expensive catalysts greatly diminished the scope of the aforementioned procedure. Thus, our procedure represents a practically alternative method to access vinyl esters.

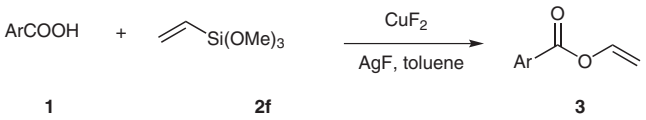
The stoichiometric reaction of trimethoxy(phenyl)silane (**2a**) with copper(II) benzoate was conducted and phenyl benzoate (**3aa**) was isolated in 60% yield (Scheme 1). A working mechanism was proposed as outlined in Scheme 2. In step (i), the reaction of copper(II) acetate with benzoic acid forms copper(II) benzoate **A**. In step (ii), phenyl is transferred to the Cu(II) center from $[RSiF(OMe)_3]^-$ **B**, which derives from the coordination of aryltrimethoxysilane **2** with F^-, producing intermediate **C**.[18] Finally, reductive elimination of intermediate **C** takes place to afford the target product **3** and generate the Cu(0) species, which is oxidized to a Cu(II) species by Ag(I).[19] It should be noted that a mechanism involving Cu(III) could not be completely excluded.[20]



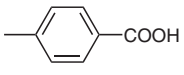
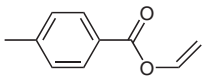
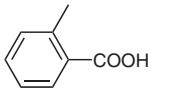
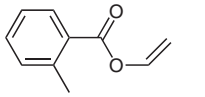
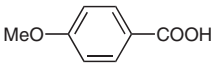
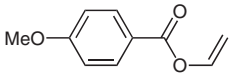
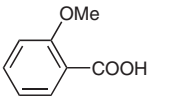
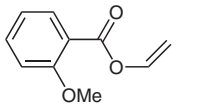
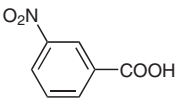
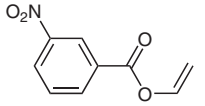
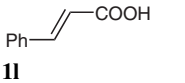
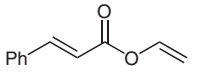
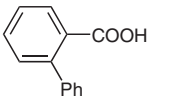
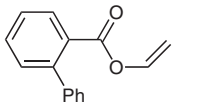
Scheme 1 Stoichiometric reactions of copper(II) benzoate with trimethoxy(phenyl)silane

In conclusion, we have developed a novel esterification reaction of carboxylic acids with the facile prepared aryl- and vinyl-substituted trimethoxysilanes. The procedure obviates the use of acyl chloride and phenol, which represents a practically alternative method for the synthesis of aryl and vinyl benzoate derivatives.

Table 3 Copper(II)-Catalyzed Esterification Reaction of Arenecarboxylic Acids with Trimethoxy(vinyl)silane[a]



1 2f 3

Entry	Substrate **1**	Product **3**	Yield[b] (%)
1	 **1b**	 **3bf**	70
2	 **1c**	 **3cf**	62
3	 **1e**	 **3ef**	64
4	 **1f**	 **3ff**	63
5	 **1k**	 **3kf**	67
6	 **1l**	 **3lf**	40
7	 **1m**	 **3mf**	68

[a] Reaction conditions: $ArCO_2H$ **1** (0.2 mmol), trimethoxy(vinyl)silane (**2f**, 0.3 mmol), CuF_2 (20 mol%), AgF (3 equiv), anhyd toluene (2 mL), 130 °C, 24 h.
[b] Isolated yield.

^1H and ^{13}C NMR spectra were measured on a 300 or 500 MHz Bruker spectrometer (^1H 300 MHz, ^{13}C 75 or 125 MHz), in $CDCl_3$ with TMS as the internal standard at r.t. Column chromatography was performed using EM Silica gel 60 (300–400 mesh).

Arenecarboxylic Acid Esters 3; General Procedure

Under air, a sealed tube was charged with carboxylic acid **1** (0.2, 0.5, or 1.0 mmol), trimethoxysilane **2** (1.5 equiv), CuF_2 (20 mol%), AgF (3 equiv), and anhyd toluene (2, 3, or 5 mL). The mixture was stirred at 130 °C. The mixture was refluxed for 24 h, the solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography (silica gel) to give the product.

Phenyl Benzoate (3aa)[21]

^1H NMR (300 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 7.2 Hz, 2 H), 7.67–7.62 (m, 1 H), 7.54–7.41 (m, 4 H), 7.31–7.21 (m, 3 H).

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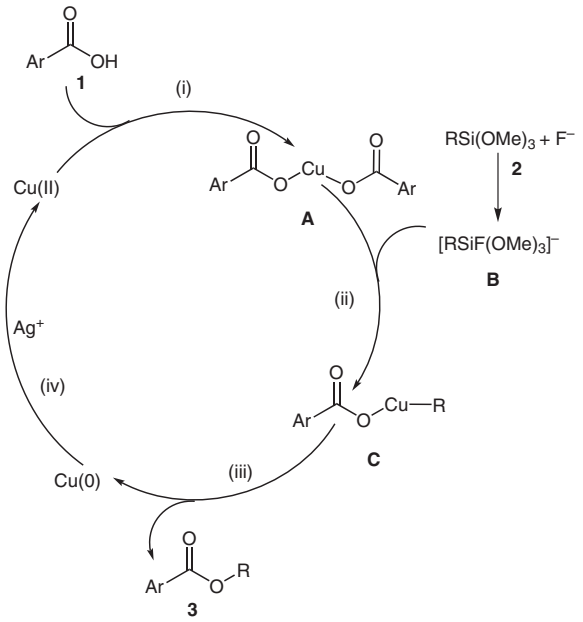

Scheme 2 Possible mechanism

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 150.9, 133.6, 130.1, 129.6, 129.5, 128.5, 125.8, 121.7.

o-Tolyl Benzoate (3ab)[22]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 7.8 Hz, 2 H), 7.65–7.63 (m, 1 H), 7.55–7.50 (m, 2 H), 7.30–7.25 (m, 2 H), 7.22–7.14 (m, 2 H), 2.25 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.8, 149.5, 133.5, 131.1, 130.3, 130.1, 129.5, 128.6, 126.9, 126.0, 121.9, 16.2.

m-Tolyl Benzoate (3ac)[23]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 7.2 Hz, 2 H), 7.67–7.62 (m, 1 H), 7.54–7.49 (m, 2 H), 7.34–7.29 (m, 1 H), 7.10–7.01 (m, 3 H), 2.40 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3, 150.9, 139.6, 133.5, 130.1, 129.7, 129.2, 128.5, 126.6, 122.3, 118.6, 21.3.

3,5-Dimethylphenyl Benzoate (3ad)[24]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.1 Hz, 2 H), 7.63–7.61 (m, 1 H), 7.53–7.48 (m, 2 H), 6.91 (s, 1 H), 6.84 (s, 2 H), 2.35 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3, 150.8, 139.3, 133.4, 130.1, 129.7, 128.5, 127.6, 119.2, 21.2.

Naphthalen-1-yl Benzoate (3ae)[25]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 7.8 Hz, 2 H), 7.94–7.90 (m, 2 H), 7.82–7.68 (m, 2 H), 7.61–7.50 (m, 5 H), 7.39 (d, *J* = 7.7 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 146.8, 134.7, 133.8, 130.3, 129.4, 128.7, 128.0, 126.9, 126.49, 126.46, 126.1, 125.5, 121.2, 118.2.

Phenyl 4-Methylbenzoate (3ba)[6a]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.2 Hz, 2 H), 7.46–7.41 (m, 2 H), 7.33–7.20 (m, 5 H), 2.46 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 151.0, 144.4, 130.2, 129.4, 129.3, 126.8, 125.8, 121.8, 21.7.

Phenyl 2-Methylbenzoate (3ca)[26]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 7.9 Hz, 1 H), 7.52–7.42 (m, 3 H), 7.36–7.28 (m, 3 H), 7.24–7.21 (m, 2 H), 2.69 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.8, 150.9, 141.3, 132.7, 131.9, 131.1, 129.5, 128.6, 125.9, 125.8, 121.8, 21.9.

Phenyl 3-Methylbenzoate (3da)[27]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.2 Hz, 2 H), 7.47–7.38 (m, 4 H), 7.30–7.20 (m, 3 H), 2.45 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3, 150.9, 138.4, 134.3, 130.6, 129.4, 128.4, 128.2, 127.3, 125.8, 121.7, 21.3.

Phenyl 4-Methoxybenzoate (3ea)[6a]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.8 Hz, 2 H), 7.45–7.40 (m, 2 H), 7.29–7.19 (m, 3 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 3.89 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.9, 163.9, 151.1, 132.3, 129.4, 125.7, 121.9, 121.8, 113.8, 55.5.

Phenyl 2-Methoxybenzoate (3fa)[28]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 7.6 Hz, 1 H), 7.58–7.53 (m, 1 H), 7.45–7.40 (m, 2 H), 7.28–7.22 (m, 3 H), 7.08–7.03 (m, 2 H), 3.94 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.4, 159.9, 150.9, 134.3, 132.2, 129.3, 125.7, 121.8, 120.2, 119.1, 112.2, 56.0.

Phenyl 4-Chlorobenzoate (3ga)[29]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.6 Hz, 2 H), 7.51–7.41 (m, 4 H), 7.31–7.20 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3, 150.7, 140.1, 131.5, 129.5, 128.9, 128.0, 126.0, 121.6.

Phenyl 2-Chlorobenzoate (3ha)[30]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.8 Hz, 1 H), 7.52–7.42 (m, 5 H), 7.29–7.24 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.1, 150.7, 134.3, 133.1, 131.8, 131.3, 129.5, 129.3, 126.7, 126.0, 121.6.

Phenyl 3-Chlorobenzoate (3ia)[27]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.19 (s, 1 H), 8.10 (d, *J* = 7.8 Hz, 1 H), 7.63–7.60 (m, 1 H), 7.49–7.42 (m, 3 H), 7.32–7.20 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.9, 150.7, 134.7, 133.6, 131.3, 130.1, 129.9, 129.5, 128.2, 126.0, 121.5.

Phenyl 4-Bromobenzoate (3ja)[31]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.5 Hz, 2 H), 7.65 (d, *J* = 8.5 Hz, 2 H), 7.46–7.41 (m, 2 H), 7.31–7.19 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.5, 150.7, 131.9, 131.6, 129.5, 128.8, 128.4, 126.0, 121.6.

Phenyl 3-Nitrobenzoate (3ka)[32]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.04 (s, 1 H), 8.54–8.48 (m, 2 H), 7.74 (m, 2 H), 7.46 (m, 2 H), 7.34–7.23 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.0, 150.4, 135.7, 131.3, 129.8, 139.63, 129.61, 127.9, 126.3, 125.0, 121.4.

Phenyl Cinnamate (3la)[27]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 16.0 Hz, 1 H), 7.61–7.58 (m, 2 H), 7.44–7.39 (m, 5 H), 7.28–7.23 (m, 1 H), 7.17 (d, *J* = 7.9 Hz, 2 H), 6.64 (d, *J* = 16.0 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.4, 150.8, 146.5, 134.2, 130.6, 129.4, 128.9, 128.3, 125.7, 121.6, 117.3.

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Vinyl Cinnamate (3lf)[33]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 16.0 Hz, 1 H), 7.56–7.54 (m, 2 H), 7.46–7.40 (m, 4 H), 6.46 (d, *J* = 16.0 Hz, 1 H), 4.98 (d, *J* = 13.9 Hz, 1 H), 4.64 (d, *J* = 6.2 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.9, 146.6, 141.2, 134.0, 130.7, 128.9, 128.2, 116.6, 97.7.

Naphthalen-1-yl 2-Phenylacetate (3me)[34]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.0 Hz, 1 H), 7.73 (d, *J* = 8.2 Hz, 1 H), 7.60–7.39 (m, 9 H), 7.26–7.22 (m, 1 H), 4.03 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.9, 146.5, 134.6, 133.5, 129.4, 128.8, 127.9, 127.5, 126.7, 126.43, 126.41, 126.0, 125.3, 121.0, 118.0, 41.6.

Vinyl 4-Methylbenzoate (3bf)[35]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.2 Hz, 2 H), 7.51 (dd, J_1 = 14.0, J_2 = 6.3 Hz, 1 H), 7.28–7.26 (m, 2 H), 5.06 (dd, J_1 = 14.0, J_2 = 1.5 Hz, 1 H), 4.69 (dd, J_1 = 6.3, J_2 = 1.5 Hz, 1 H), 3.88 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.7, 144.4, 141.5, 130.0, 129.2, 97.9, 21.6.

Vinyl 2-Methylbenzoate (3cf)[36]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.6 Hz, 1 H), 7.50 (dd, J_1 = 13.9, J_2 = 6.2 Hz, 1 H), 7.46–7.42 (m, 1 H), 7.30–7.26 (m, 2 H), 5.04 (dd, J_1 = 13.9, J_2 = 1.5 Hz, 1 H), 4.69 (dd, J_1 = 6.2, J_2 = 1.5 Hz, 1 H), 2.63 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.2, 141.3, 141.1, 132.6, 131.8, 130.9, 128.1, 125.8, 97.9, 21.7.

Vinyl 4-Methoxybenzoate (3ef)[37]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.3 Hz, 2 H), 7.52 (dd, J_1 = 14.0, J_2 = 6.3 Hz, 1 H), 6.95 (d, *J* = 8.3 Hz, 2 H), 5.03 (dd, J_1 = 14.0, J_2 = 1.6 Hz, 1 H), 4.67 (dd, J_1 = 6.3, J_2 = 1.6 Hz, 1 H), 3.88 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.9, 163.3, 141.5, 132.1, 121.1, 113.8, 97.6, 55.4.

Vinyl 2-Methoxybenzoate (3ff)[36]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 7.9 Hz, 1 H), 7.51 (dd, J_1 = 14.0, J_2 = 6.3 Hz, 1 H), 7.51–7.48 (m, 1 H), 7.02–7.6.98 (m, 2 H), 5.01 (dd, J_1 = 14.0, J_2 = 1.5 Hz, 1 H), 4.66 (dd, J_1 = 6.3, J_2 = 1.5 Hz, 1 H), 3.92 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.7, 159.9, 141.5, 134.3, 132.0, 120.2, 118.5, 112.2, 97.8, 56.0.

Vinyl 3-Nitrobenzoate (3kf)[38]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.93–8.92 (m, 1 H), 8.48–8.42 (m, 2 H), 7.73–7.67 (m, 1 H), 7.51 (dd, J_1 = 13.9, J_2 = 6.2 Hz, 1 H), 5.17 (dd, J_1 = 13.9, J_2 = 1.9 Hz, 1 H), 4.80 (dd, J_1 = 6.2, J_2 = 1.9 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.6, 148.4, 141.1, 135.5, 130.8, 129.8, 127.9, 124.9, 99.4.

Vinyl Biphenyl-2-carboxylate (3mf)[39]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99–7.96 (m, 1 H), 7.59–7.26 (m, 9 H), 4.59–4.49 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 143.4, 141.3, 141.0, 131.9, 131.0, 130.4, 129.2, 128.4, 128.0, 127.2, 98.1.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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