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Rhodium-Catalyzed Regioselective Olefination Directed by a Carboxylic Group

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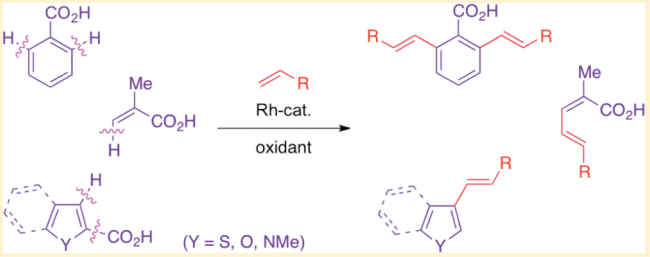
Supporting Information

ABSTRACT: The *ortho*-olefination of benzoic acids can be achieved effectively through rhodium-catalyzed oxidative coupling with alkenes. The carboxylic group is readily removable to allow *ortho*-olefination/decarboxylation in one pot. α,β-Unsaturated carboxylic acids such as methacrylic acid also undergo the olefination at the β-position. Under the rhodium catalysis, the *cine*-olefination of heteroarene carboxylic acids such as thiophene-2-carboxylic acid proceeds smoothly accompanied by decarboxylation to selectively produce the corresponding vinylheteroarene derivatives.



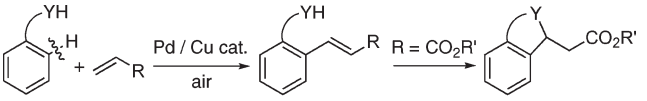
INTRODUCTION

Since vinylarene structures can be widely seen in various fine chemicals,[1] the development of methods for their effective construction has attracted considerable attention in organic synthesis. The conventional syntheses of such derivatives through transition-metal-catalyzed cross-coupling and Mizoroki−Heck reactions or Wittig-type reactions usually need complicated multisteps forming halogen- or phosphorus-containing byproducts.

On the other hand, direct olefination reactions on aromatic rings involving regioselective C−H bond cleavage have been developed to provide more simple synthetic routes for vinylarene derivatives.[2] As early examples, we reported that 2-phenylphenols (Scheme 1, YH = 2-HOC_6H_4),[3] *N*-(arylsulfonyl)-2-phenylanilines (YH = 2-($ArSO_2NH$)C_6H_4),[4] and benzoic acids (YH = CO_2H)[4] undergo regioselective olefination at the *ortho*-position of YH upon treatment with an alkene such as acrylate ester (R = CO_2R') and an appropriate oxidant under palladium/copper catalysis. In each case, subsequent nucleophilic cyclization takes place to afford the corresponding heterocyclic product. Later, aromatic amides,[5] benzylamines,[6] phenylacetic acids,[7] 1-phenylprazoles,[8] and 2-phenylethanols[9] have also been shown to undergo the direct *ortho*-olefination under palladium or rhodium catalysis.

Among these examples, the reaction of benzoic acids and related carboxylic acids is of particular interest because of their wide availability as building blocks. Furthermore, if the carboxylic group remains in the olefinated products without undergoing the subsequent cyclization, it can be readily removed and further transformed.[10] Therefore, the reaction sequence of *ortho*-olefination/decarboxylation seems to be applicable to constructing a wide range of vinylarenes. In the course of our study of the functionalization of carboxylic acids,[11] it has been revealed that *ortho*-olefinated benzoic acids can be obtained upon treatment of the parent acids with styrenes in place of acrylates under rhodium catalysis.[12] Expectedly, some of the products underwent decarboxylation during post-treatment in the same pot to produce stilbene derivatives. Besides a series of substituted benzoic acids, naphthoic acids, α,β-unsaturated acids, and heteroarene carboxylic acids also underwent the regioselective olefination. The details of these findings are described herein.

Scheme 1. Pd/Cu-Catalyzed *Ortho*-Olefination



YH = 2-HOC_6H_4, 2-($ArSO_2NH$)C_6H_4, CO_2H

RESULTS AND DISCUSSION

In an initial attempt, benzoic acid (**1a**) (0.5 mmol) was treated with styrene (**2a**) (1.5 mmol) under conditions similar to those employed for the reaction with acrylates.[4b] In the presence of [Cp*RhCl_2]$_2$ (0.005 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.025 mmol) in *o*-xylene (2.5 mL) at 120 °C under air for 10 h, a mixture of mono- and diolefinated products was formed, which were subsequently methylesterified for quantification to give **3a** and **4a**, respectively (entry 1 in Table 1, Cp* = pentamethylcyclopentadienyl). Under conditions using a stoichiometric amount of $Cu(OAc)_2 \cdot H_2O$ (2 mmol) in DMF under N_2, the yield of **4a** was improved to 71% (entry 3). Moreover, the use of AgOAc (2 mmol) as the oxidant significantly enhanced the reaction efficiency to produce **4a** in 96% yield (entry 4). The reaction was sluggish at 100 °C or in *o*-xylene (entries 5 and 6).

Under the conditions employed for entry 4 in Table 1, the couplings of **1a** with 4-methyl- (**2b**), methoxy- (**2c**), and

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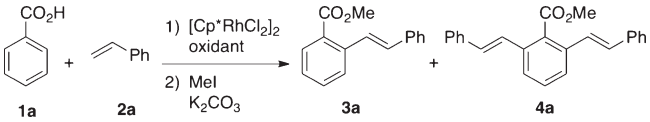
Table 1. Reaction of Benzoic Acid (1a) with Styrene (2a)[a]



entry	oxidant (mmol)	solvent	temp (°C)	yield[b] (%) 3a	4a
1[c]	$Cu(OAc)_2 \cdot H_2O$ (0.025)	*o*-xylene	120	19	10
2[c]	$Cu(OAc)_2 \cdot H_2O$ (0.025)	DMF	120	20	12
3	$Cu(OAc)_2 \cdot H_2O$ (2)	DMF	120	23	71
4	AgOAc (2)	DMF	120	4	96 (87)
5	AgOAc (2)	DMF	100	4	43
6	AgOAc (2)	*o*-xylene	120	14	8

[a] Reaction conditions: (1) **1a** (0.5 mmol), **2a** (1.5 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), solvent (2.5 mL) under N_2 for 10 h; (2) with the addition of MeI (3 mmol) and K_2CO_3 (1.5 mmol) at rt for 3 h. [b] GC yield based on the amount of **1a** used. Value in parentheses indicates yield after purification. [c] Under air.

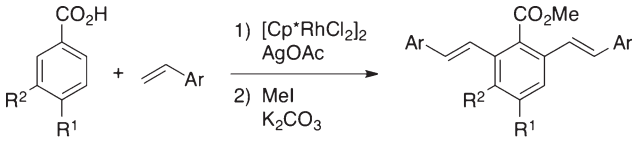
chloro-substituted (**2d**) styrenes proceeded smoothly to form the corresponding 2,6-distyrylbenzoates **4b**−**d** (Table 2, entries 1−3). The reaction of **1a** with 2-vinylnaphthalene (**2e**) occurred in a similar manner to give a diolefinated product **4e** in 84% yield (entry 4). A series of 4-substituted benzoic acids **1b**−**h** underwent the diolefination to form **4f**−**l** (entries 5−11). For the reactions of electron-deficient benzoic acids such as **1g** and **1h**, increased amounts of the Rh catalyst were needed (entries 10 and 11). The diolefination of 3-methoxy- (**1i**), chloro- (**1j**), and fluoro-substituted (**1k**) benzoic acids also took place to form **4m**−**o** (entries 12−14).

As expected, monoolefinated products **3b**−**i** were obtained upon treatment of 2-substituted or 2,4-disubstituted benzoic acids **1l**−**s** with styrene (**2a**) under standard conditions (Table 3, entries 1−8). Exceptionally, the reactions of **1p** and **1r** were conducted at 100 °C (entries 5 and 7). At 120 °C, the products **3f** and **3h** partly underwent decarboxylation. The reaction of 3-methylbenzoic acid (**1t**) also gave monoolefinated **3j** exclusively, in contrast to the cases with other 3-substituted benzoic acids **1i**−**k**, which were selectively transformed to diolefinated products (entries 12−14, Table 2). Naphthoic acids **1u** and **1v** underwent regioselective monoolefination to afford 2- and 3-styrylnaphthoates **3k** and **3l**, respectively (entries 10 and 11).

A plausible mechanism for the *ortho*-olefination of **1** with **2** is illustrated in Scheme 2, in which neutral ligands are omitted. Coordination of the carboxylate oxygen of **1** to $Cp^*Rh(III)X_2$ gives a rhodium(III) benzoate **A**. Subsequent *ortho*-rhodation to form a rhodacycle intermediate **B**,[13] styrene insertion, and β-hydrogen elimination occur to produce a monoolefinated product. After the release of the product, the resulting Cp*Rh(I) species may be oxidized in the presence of a silver(I) or copper(II) salt to regenerate $Cp^*Rh(III)X_2$. In the cases shown in Tables 1 and 2, the second olefination may proceed by the same mechanism.

For providing further mechanistic information, competitive reactions of d_0-benzoic acid (**1a**-d_0) and d_5-benzoic acid (**1a**-d_5) with **2a** were conducted under standard olefination conditions (Scheme 3). In the early stage of these reactions, significant primary isotopic effects of 2.7 and 9.0 were observed for the

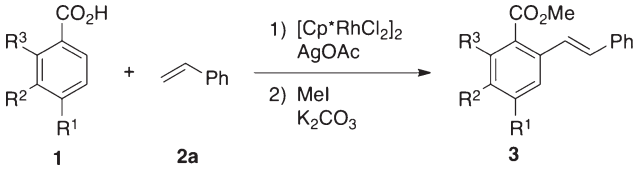
Table 2. Reaction of Benzoic Acids 1 with Styrenes 2[a]



entry	1	R^1	R^2	2	Ar	product, % yield[b]
1	**1a**	H	H	**2b**	4-Bu^{t}C$_6$H$_4$	**4b**, 69
2	**1a**	H	H	**2c**	4-MeOC$_6$H$_4$	**4c**, 66
3	**1a**	H	H	**2d**	4-ClC$_6$H$_4$	**4d**, 63
4	**1a**	H	H	**2e**	2-naphthyl	**4e**, 84
5	**1b**	Me	H	**2a**	Ph	**4f**, 73
6	**1c**	OMe	H	**2a**	Ph	**4g**, 65
7	**1d**	Cl	H	**2a**	Ph	**4h**, 75
8	**1e**	Br	H	**2a**	Ph	**4i**, 72
9	**1f**	Ph	H	**2a**	Ph	**4j**, 81
10[c]	**1g**	Ac	H	**2a**	Ph	**4k**, 74
11[c]	**1h**	CF_3	H	**2a**	Ph	**4l**, 69
12	**1i**	H	OMe	**2a**	Ph	**4m**, 60
13	**1j**	H	Cl	**2a**	Ph	**4n**, 66
14	**1k**	H	F	**2a**	Ph	**4o**, 65

[a] Reaction conditions: (1) **1** (0.5 mmol), **2** (1.5 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), AgOAc (2 mmol), DMF (2.5 mL) under N_2 at 120 °C for 8−10 h; (2) with the addition of MeI (3 mmol) and K_2CO_3 (1.5 mmol) at rt for 3 h. [b] Isolated yield. [c] With $[Cp^*RhCl_2]_2$ (0.01 mmol).

Table 3. Reaction of Benzoic and Naphthoic Acids 1 with Styrene (2a)[a]



entry	1	R^1	R^2	R^3	product, % yield[b]
1	**1l**	H	H	Me	**3b**, 75
2	**1m**	H	H	OMe	**3c**, 62
3	**1n**	H	H	Cl	**3d**, 58
4	**1o**	Me	H	Me	**3e**, 79
5[c]	**1p**	OMe	H	OMe	**3f**, 73
6	**1q**	Cl	H	Me	**3g**, 82
7[c]	**1r**	H	H	F	**3h**, 85
8	**1s**	H	H	Ph	**3i**, 78
9	**1t**	H	Me	H	**3j**, 62
10	**1u**	H	−(CH)$_4$−		**3k**, 63
11	**1v**	−(CH)$_4$−		H	**3l**, 57

[a] Reaction conditions: (1) **1** (0.5 mmol), **2a** (1 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), AgOAc (1 mmol), DMF (2.5 mL) under N_2 at 120 °C for 8 h; (2) with the addition of MeI (3 mmol) and K_2CO_3 (1.5 mmol) at rt for 3 h. [b] Isolated yield. [c] At 100 °C.

mono- and diolefinated products, respectively, which suggests that the rate-determining step involves C−H(D) bond cleavage (from **A** to **B** in Scheme 2). It was confirmed that H incorporation was significantly slow (<10%) at the *ortho*-position(s) of starting **1a**-d_5 as well as **3a**-d_n.

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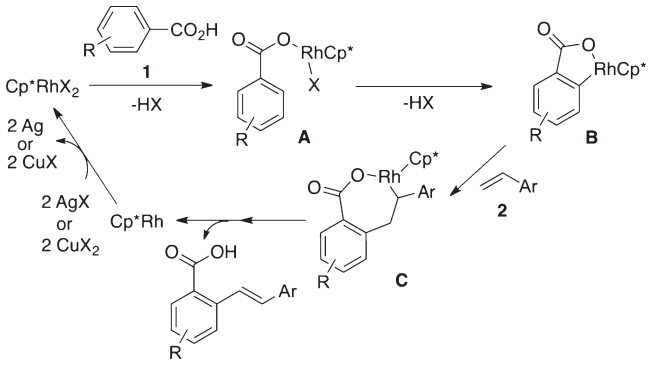
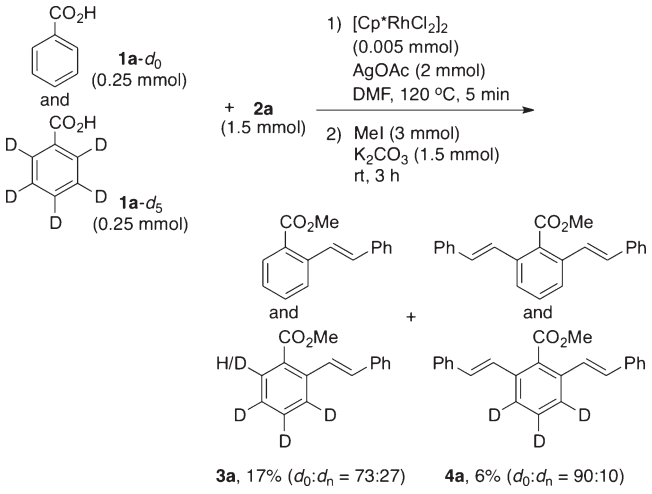
Scheme 2. Plausible Mechanism for the Reaction of 1 with 2



Scheme 3. Competitive Reaction of 1a-d_0 and 1a-d_5



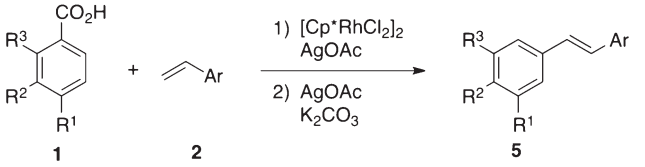
It was confirmed that the carboxylic group in 2-styrylbenzoic acids, produced in the monoolefination of 2-substituted benzoic acids **1m**,**p**,**r**,**s**,**w** and 1-naphthoic acid (**1u**), can be readily removed. Thus, after the olefination of **1p** (0.5 mmol) as in Table 3, AgOAc (1 mmol) and K_2CO_3 (1 mmol) were added into the same pot and the resulting mixture was heated at 160 °C for 4 h for decarboxylation.[14−16] As a result, an *ortho*-olefination/decarboxylation product, 3,5-dimethoxystilbene (**5a**) was obtained in 80% yield (Table 4, entry 1). Substituted styrenes **2b**−**d** also reacted with **1p** to give substituted stilbenes **5b**−**d** (entries 2−4). It should be noted that the obtained 3,5,4′-trimethoxystilbene (**5c**), an analogue of naturally occurring resveratrol,[17] is of particular interest for its biological activities including anticancer properties.[18] Under similar conditions, **1m**,**r**,**s**,**w** also underwent the decarboxylative olefination to afford the corresponding 3-substituted stilbenes **5e**−**h** (entries 5−8).[19] From **1u**, 2-styrylnaphthalene (**5i**) could be synthesized effectively (entry 9).

Unsubstituted benzoic acid (**1a**) also underwent the decarboxylative olefination upon treatment with **2a**. In this case, diolefination at the 2- and 6-positions and subsequent decarboxylation took place to form 1,3-distyrylbenzene (**6a**)[20] selectively (Scheme 4). The reaction of 4-methoxybenzoic acid (**1c**) with **2a** also proceeded in a similar manner to give distyrylbenzene **6b**.

The olefination of commercially available aromatic dicarboxylic acids were next examined. Treatment of isophthalic acid (**7**) with **2a** under standard olefination conditions and subsequent methyl esterification gave the corresponding monoolefinated product **8** (Scheme 5). Similar treatment of diphenic acid (**9**) afforded a mixture of mono- (**10**) and diolefinated products (**11**). Interestingly, a 1,4-distyrylbenzene derivative, which is of importance in organic material field,[21] could be obtained through the diolefination/decarboxylation of phthalic acid (**12**) with **2a**. In this case, a better result was obtained by using $Cu(OAc)_2 \cdot H_2O$ as an oxidant under mild conditions (100 °C).

Under the present Rh-catalysis, the regioselective olefination was found to take place not only on an aromatic but also vinylic sp^2-carbon at the neighboring site of a carboxylic group.[11e] Thus, treatment of methacrylic acid (**14a**) with **2a** in the presence of $[Cp^*RhCl_2]_2$ (0.005 mmol) and AgOAc (1 mmol) in DMF (2.5 mL) at 120 °C under N_2 for 10 h followed by methyl esterification gave (2*Z*,4*E*)-methyl 2-methyl-5-phenylpenta-2,4-dienoate (**15a**) as a regio- and stereoselective olefination product in 38% yield (Table 5, entry 1). The reaction efficiency was slightly improved by the use of $Cu(OAc)_2 \cdot H_2O$ as an oxidant (entry 2). With $[Cp^*RhCl_2]_2$ (0.01 mmol), the product yield increased to 60% (entry 3). The yield decreased at 100 or 140 °C (entries 4 and 5). Similarly, **14a** and tiglic acid (**14b**) reacted with 2-vinylnaphthalene (**2e**) to form the corresponding β-olefinated products **15b** and **15c**, respectively (entries 6 and 7).

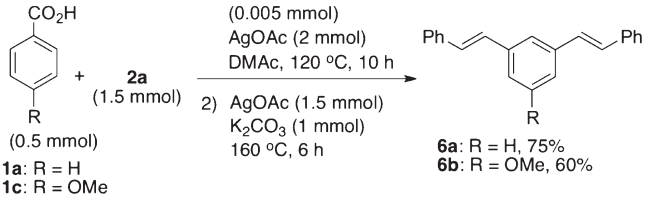
Table 4. Decarboxylative Olefination of Benzoic and Naphthoic Acids 1 with Styrenes 2[a]



entry	1	R^1	R^2	R^3	2	Ar	product, % yield[b]
1	**1p**	OMe	H	OMe	**2a**	Ph	**5a**, 80
2	**1p**	OMe	H	OMe	**2b**	4-Bu^{t}C$_6$H$_4$	**5b**, 67
3	**1p**	OMe	H	OMe	**2c**	4-MeOC$_6$H$_4$	**5c**, 73
4	**1p**	OMe	H	OMe	**2d**	4-ClC$_6$H$_4$	**5d**, 65
5	**1m**	H	H	OMe	**2a**	Ph	**5e**, 66
6	**1w**	H	H	NHAc	**2a**	Ph	**5f**, 66
7	**1r**	H	H	F	**2a**	Ph	**5g**, 66
8	**1s**	H	H	Ph	**2a**	Ph	**5h**, 54
9	**1u**	H	−(CH)$_4$−		**2a**	Ph	**5i**, 70

[a] Reaction conditions: (1) **1** (0.5 mmol), **2** (1 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), AgOAc (1−1.5 mmol), DMAc (2.5 mL) under N_2 at 120 °C for 8 h; (2) with the addition of AgOAc (1 mmol) and K_2CO_3 (1 mmol) at 160 °C for 4 h. [b] Isolated yield.

Scheme 4. Decarboxylative Olefination of Benzoic Acids 1 with Styrene (2a)



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Scheme 5. Reaction of Aromatic Dicarboxylic Acids with 2a

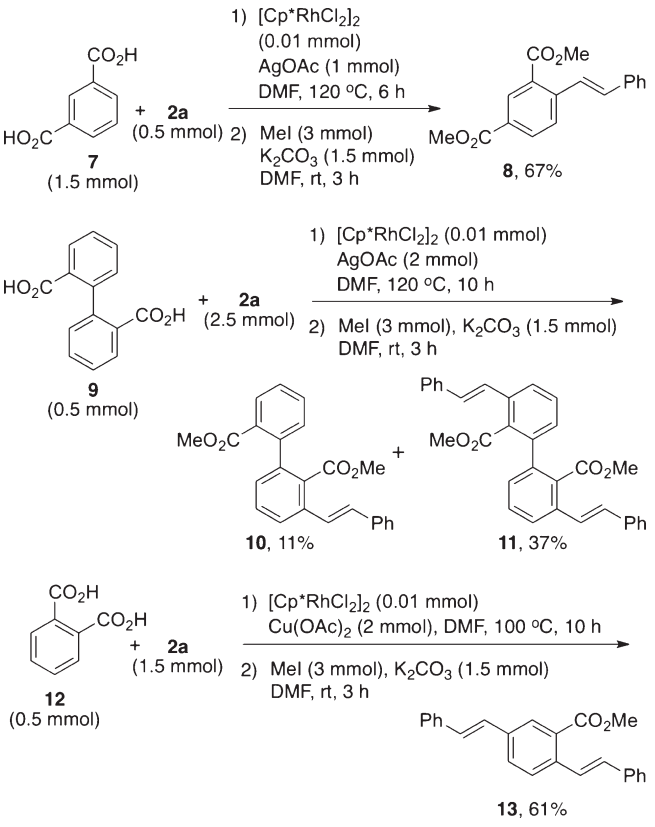
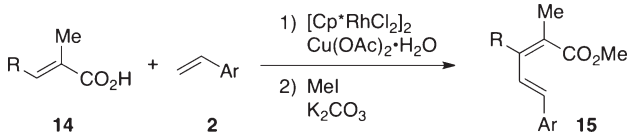


Table 5. Reaction of α,β-Unsaturated Carboxylic Acids 14 with Styrenes 2[a]

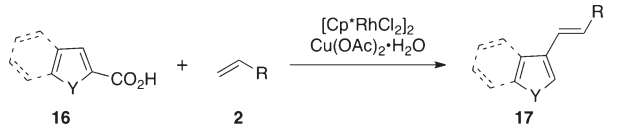


entry	14	R	2	Ar	temp (°C)	product, % yield[b]
1[c,d]	**14a**	H	**2a**	Ph	120	**15a**, 38
2[c]	**14a**	H	**2a**	Ph	120	**15a**, 48
3	**14a**	H	**2a**	Ph	120	**15a**, 60 (58)
4	**14a**	H	**2a**	Ph	100	**15a**, 50
5	**14a**	H	**2a**	Ph	140	**15a**, 24
6	**14a**	H	**2e**	2-naphthyl	120	**15b**, 70 (64)
7	**14b**	Me	**2e**	2-naphthyl	120	**15c**, 43 (40)

[a] Reaction conditions: (1) **14** (0.5 mmol), **2** (1 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $Cu(OAc)_2 \cdot H_2O$ (1 mmol), DMF (2.5 mL) under N_2 for 10 h; (2) with the addition of MeI (3 mmol) and K_2CO_3 (1.5 mmol) at rt for 3 h. [b] GC yield based on the amount of **14** used. Value in parentheses indicates yield after purification. [c] With $[Cp^*RhCl_2]_2$ (0.005 mmol). [d] AgOAc (1 mmol) was used in place of $Cu(OAc)_2 \cdot H_2O$.

In general, electron-rich, five-membered heteroarene carboxylic acids tend to undergo decarboxylation more readily than benzoic acids in the presence of an appropriate transition-metal catalyst.[11d,f,g,i,j] When thiophene-2-carboxylic acid (**16a**) (0.5 mmol) was treated with **2a** (1 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.01 mmol) and $Cu(OAc)_2 \cdot H_2O$ (1 mmol),

Table 6. Reaction of Heteroarene Carboxylic Acids 16 with Alkenes 2[a]



entry	16	2 (mmol)	product	% yield[b]
1[c]	**16a**	**2a** (1)	**17a**	23
2[c]		**2a** (2)		30
3		**2a** (2)		64
4[d]		**2a** (2)		56
5		**2a** (4)		70 (63)
6[e]	**16a**	**2f** (1)	**17b**	(84)
7[e]	**16b**	**2f** (1)	**17c**	(70)
8[e]	**16c**	**2f** (1)	**17d**	(70)
9[e]	**16d**	**2f** (1)	**17e**	(82)
10[e]	**16e**	**2f** (1)	**17f**	(74)

[a] Reaction conditions: **16** (0.5 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), $Cu(OAc)_2 \cdot H_2O$ (1 mmol), DMF (2.5 mL) under N_2 at 140 °C for 6−8 h. [b] GC yield based on the amount of **16** used. Value in parentheses indicates yield after purification. [c] At 120 °C. [d] With AgOAc (1 mmol) in place of $Cu(OAc)_2 \cdot H_2O$. [e] With $[Cp^*RhCl_2]_2$ (0.005 mmol).

3-styrylthiophene (**17a**) was formed through 3-olefination/decarboxylation even under mild conditions at 120 °C (Table 6, entry 1). A significant amount of normal 3-olefinated product possessing the carboxylic group intact was also detected by GC and GC−MS (ca. 20%) after methyl esterification. Increasing the amount of **2a** slightly improved the yield of **17a** (entry 2). At 140 °C, the reaction efficiency was significantly enhanced to selectively produce **17a** in 64% yield (entry 3). AgOAc was less effective as an oxidant than $Cu(OAc)_2 \cdot H_2O$ (entry 4). Finally, **17** was obtained in 70% yield by using 4 mmol of **2a** (entry 5).

Previously, we have reported that indole-, pyrrole-, and benzofuran-2-carboxylic acids undergo the carboxylic group directed 3-olefination/decarboxylation upon treatment with alkenes and an oxidant under palladium catalysis to produce

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2-vinylheteroarenes.[11j] However, the application of the palladium-based catalyst system to the reaction of thiophene and benzothiophene-2-carboxylic acids was problematic, in which mixtures of 2- and 3-olefinated products were formed. These acids underwent decarboxylation more reaily under the Pd-catalyzed conditions. Therefore, at least parts of the 2-olefinated products seem to arise from the sequence of the initial decarboxylation and subsequent nondirected olefination of the resulting thiophene and benzothiophene. Under the present rhodium catalysis, the carboxylic groups may be kept until completion of the olefination to avoid the 2-olefination.

The Rh-catalyst system could be applied to the reaction of various heteroarene carboxylic acids **16a**−**e** with butyl acrylate (**2f**) (entries 6−10). The reaction proceeded smoothly even with a reduced amount of rhodium catalyst (1 mol %). In all cases, the product yields became higher than those in the Pd-catalyzed reactions, and formation of regioisomers could not be detected.

CONCLUSIONS

In summary, we have demonstrated that the regioselective olefination of benzoic and naphthoic acids, α,β-unsaturated carboxylic acids, and heteroarene carboxylic acids with alkenes can be performed at the neighboring position(s) of their carboxylic group in the presence of a rhodium catalyst and a silver or copper salt oxidant. In most cases, the directing group can be readily removed during the olefination reaction or post-treatment.

EXPERIMENTAL SECTION

General Methods. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz for $CDCl_3$ or DMSO-d_6 solutions. MS data were obtained by EI. GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m). GC−MS analysis was carried out using a CBP-1 capillary column (i.d. 0.25 mm × 25 m). The structures of all products listed below were unambiguously determined by ^{1}H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

All starting materials and reagents were commercially available.

General Procedure for Diolefination of Benzoic Acids with Styrenes. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added benzoic acid **1** (0.5 mmol), styrene **2** (1.5 mmol), [(Cp*RhCl$_2$)$_2$] (0.005 mmol, 3 mg), AgOAc (2 mmol, 333 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMF (2.5 mL). The resulting mixture was stirred under nitrogen at 120 °C for 8−10 h. After the mixture was cooled, iodomethane (3 mmol, 423 mg) and K_2CO_3 (1.5 mmol, 207 mg) were added, and the resulting mixture was stirred under air at room temperature for 3 h. GC and GC−MS analyses of the mixtures confirmed formation of **4**. The reaction mixture was then extracted with ethyl acetate (100 mL). The organic layer was washed with water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvent under vacuum, product **4** was isolated by column chromatography on silica gel using hexane−ethyl acetate (95:5, v/v) as eluant.

Procedure for Competitive Reaction of 1a-d_0 and 1a-d_5. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added d_0-benzoic acid (**1a**-d_0) (0.25 mmol, 31 mg), d_5-benzoic acid (**1a**-d_5) (0.25 mmol, 32 mg), styrene (**2a**) (1.5 mmol, 156 mg), AgOAc (2 mmol, 333 mg), 1-methylnaphthalne (ca. 50 mg) as internal standard, and DMF (2.5 mL). The resulting mixture was stirred under N_2 at 120 °C for 5 min (Scheme 3). After the mixture was cooled, iodomethane (3 mmol, 423 mg) and K_2CO_3 (1.5 mmol, 207 mg) were added, and the resulting mixture was stirred under air at room temperature for 3 h. The reaction mixture was then extracted with ethyl acetate (100 mL). The organic layer was washed with water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvent under vacuum, the product was isolated by column chromatography on silica gel using hexane−ethyl acetate (95:5, v/v) as eluant. **3a** (20 mg, 17%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 7.01 (d, J = 16.5 Hz, 1H), 7.25−7.37 (m, 3.7H), 7.49−7.56 (m, 2.7H), 7.72 (d, J = 7.7 Hz, 0.73H), 7.92−7.94 (m, 0.76H), 7.99 (d, J = 16.5 Hz, 1H). Kinetic isotope effect determined by ^{1}H NMR: k_H/k_D = 0.73/0.27 = 2.7. **4a** (9.5 mg, 6%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, 3H), 7.06 (d, J = 16.1 Hz, 2H), 7.13 (d, J = 16.1 Hz, 2H), 7.25−7.30 (m, 2H), 7.34−7.38 (m, 4H), 0.7.42 (t, J = 7.7 Hz, 0.90H), 7.47−7.50 (m, 4H), 7.61 (d, J = 7.7 Hz, 1.8H). Kinetic isotope effect determined by ^{1}H NMR: k_H/k_D = 0.90/0.10=9.0.

General Procedure for Monoolefination/Decarboxylation of 2-Subtituted Benzoic Acids with Styrenes. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added 2-substituted benzoic acid **1** (0.5 mmol), styrene **2** (1 mmol), [(Cp*RhCl$_2$)$_2$] (0.005 mmol, 3 mg), AgOAc (1−1.5 mmol), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMAc (2.5 mL). Then, the resulting mixture was stirred under nitrogen at 120 °C for 8 h. After cooling, AgOAc (1 mmol, 166 mg) and K_2CO_3 (1 mmol, 138 mg) were added and the resulting mixture was stirred under nitrogen at 160 °C for 4 h. GC and GC−MS analyses of the mixtures confirmed formation of **5**. The reaction mixture was then extracted with ethyl acetate (100 mL). The organic layer was washed with water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvent under vacuum, product **5** was isolated by column chromatography on silica gel using hexane−ethyl acetate (95:5, v/v) as eluant.

Procedure for Diolefination/decarboxylation of Phthalic Acid with Styrene. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added phthalic acid (**12**) (0.5 mmol, 83 mg), styrene (**2a**) (1.5 mmol, 156 mg), [(Cp*RhCl$_2$)$_2$] (0.01 mmol, 6 mg), Cu(OAc)$_2$·H$_2$O (2 mmol, 400 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMF (2.5 mL). Then, the resulting mixture was stirred under nitrogen at 100 °C for 10 h. After cooling, iodomethane (3 mmol, 423 mg) and K_2CO_3 (1.5 mmol, 207 mg) were added, and the resulting mixture was stirred under air at room temperature for 3 h. GC and GC−MS analyses of the mixtures confirmed formation of **13** (104 mg, 61%). Then, the reaction mixture was extracted with ethyl acetate (100 mL). The organic layer was washed with water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvent under vacuum, product **13** (75 mg, 44%) was isolated by column chromatography on silica gel using hexane−ethyl acetate (95:5, v/v) as eluant.

General Procedure for Monoolefination/decarboxylation of Heteroarene-2-carboxylic Acids with Butyl Acrylate. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added heteroarene-2-carboxylic acid **16** (0.5 mmol), butyl acrylate **2f** (1 mmol, 128 mg), [(Cp*RhCl$_2$)$_2$] (0.005 mmol, 3 mg), Cu(OAc)$_2$·H$_2$O (1 mmol, 200 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMF (2.5 mL). Then, the resulting mixture was stirred under nitrogen at 140 °C for 6 h. GC and GC−MS analyses of the mixtures confirmed formation of **19**. Then, the reaction mixture was extracted with ethyl acetate (100 mL). The organic layer was washed with water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvent under vacuum, product **19** was isolated by column chromatography on silica gel using hexane−ethyl acetate (85:15, v/v) as eluant.

(*E*)-Methyl 2-styrylbenzoate (3a):[22]. oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 6.91 (d, J = 16.5 Hz, 1H), 7.24−7.38 (m, 4H), 7.49−7.56 (m, 3H), 7.71 (d, J = 7.7 Hz, 1H), 7.92 (d, J = 7.7 Hz, 1H), 7.99 (d, J = 16.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.1, 126.8, 127.0, 127.1, 127.4, 127.8, 128.5, 128.6, 130.7, 131.4, 132.1, 137.4, 139.2, 167.9; HRMS m/z calcd for $C_{16}H_{14}O_2$ (M^+) 238.0994, found 238.0992.

(*E*)-Methyl 2-methyl-6-styrylbenzoate (3b): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 3.83 (s, 3H), 6.93 (d, J = 16.0 Hz, 1H), 6.99−7.05 (m, 2H), 7.13−7.18 (m, 2H), 7.19−7.25 (m, 2H), 7.36 (d, J = 7.4 Hz, 2H), 7.40 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 52.0, 123.0, 125.6, 126.6, 127.9, 128.6, 129.2, 129.5, 131.3, 132.8, 134.9, 135.2, 137.0, 170.1; HRMS m/z calcd for $C_{17}H_{16}O_2$ (M^+) 252.1150, found 252.1150.

(*E*)-Methyl 2-methoxy-6-styrylbenzoate (3c): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 3.95 (s, 3H), 6.83 (d, J = 7.8 Hz, 1H), 7.03 (d, J = 16.0 Hz, 1H), 7.09 (d, J = 16.0 Hz, 1H), 7.24−7.29 (m, 2H), 7.32−7.36 (m, 3H), 7.46 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 55.9, 109.8, 117.6, 122.7, 124.8, 126.7, 128.0, 128.6, 130.5, 131.8, 136.1, 136.9, 156.5, 168.6; HRMS m/z calcd for $C_{17}H_{16}O_3$ (M^+) 268.1099, found 268.1096.

(*E*)-Methyl 2-chloro-6-styrylbenzoate (3d): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, 3H), 7.01 (d, J = 16.5 Hz, 1H), 7.08 (d, J = 16.5 Hz, 1H), 7.24−7.37 (m, 5H), 7.46 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.7, 123.7, 124.1, 126.8, 128.1, 128.4, 128.7, 130.4, 131.1, 132.5, 132.8, 136.4, 136.7, 167.6; HRMS m/z calcd for $C_{16}H_{13}ClO_2$ (M^+) 272.0604, found 272.0610.

(*E*)-Methyl 2,4-dimethyl-6-styrylbenzoate (3e): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.34 (s, 3H), 3.92 (s, 3H), 6.93 (s, 1H), 7.02 (d, J = 16.0 Hz, 1H), 7.14 (d, J = 16.0 Hz, 1H), 7.23−7.27 (m, 1H), 7.32−7.36 (m, 3H), 7.46 (d, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 21.2, 52.0, 123.6, 125.8, 126.6, 127.8, 128.6, 130.1, 130.2, 130.9, 135.0, 135.3, 137.1, 139.4, 170.3; HRMS m/z calcd for $C_{18}H_{18}O_2$ (M^+) 266.1307, found 266.1308.

(*E*)-Methyl 2,4-dimethoxy-6-styrylbenzoate (3f):[12]**.** oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.85 (s, 3H), 3.91 (s, 3H), 6.40 (s, 1H), 6.76 (s, 1H), 7.04 (d, J = 16.0 Hz, 1H), 7.10 (d, J = 16.0 Hz, 1H), 7.26 (t, J = 7.3 Hz, 1H), 7.34 (t, J = 7.3 Hz, 2H), 7.46 (d, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 55.4, 55.9, 97.9, 101.4, 115.8, 125.3, 126.7, 128.0, 128.6, 131.6, 136.7, 137.4, 158.1, 161.4, 168.4; HRMS m/z calcd for $C_{18}H_{18}O_4$ (M^+) 298.1205, found 298.1209.

(*E*)-Methyl 4-chloro-2-methyl-6-styrylbenzoate (3g): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.92 (s, 3H), 6.98−7.07 (m, 2H), 7.09 (s, 1H), 7.25−7.29 (m, 1H), 7.34 (t, J = 7.8 Hz, 2H), 7.45 (d, J = 7.8 Hz, 2H), 7.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 52.2, 122.9, 124.3, 126.8, 128.2, 128.7, 128.9, 131.2, 132.5, 135.4, 136.5, 136.9, 137.4, 169.3; HRMS m/z calcd for $C_{17}H_{15}ClO_2$ (M^+) 286.0761, found 286.0757.

(*E*)-Methyl 2-fluoro-6-styrylbenzoate (3h): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 6.91 (t, J = 8.7 Hz, 1H), 6.98 (d, J = 16.5 Hz, 1H), 7.15−7.21 (m, 2H), 7.25−7.28 (m, 3H), 7.37−7.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 114.5 (d, J = 22 Hz), 120.3 (d, J = 17 Hz), 121.3 (d, J = 2.9 Hz), 124.4 (d, J = 2.9 Hz), 126.8, 128.3, 128.7, 131.4 (d, J = 8.6 Hz), 132.7, 136.6, 138.2 (d, J = 2.9 Hz), 160.1 (d, J = 250 Hz), 165.9; HRMS m/z calcd for $C_{16}H_{13}FO_2$ (M^+) 256.0900, found 256.0902.

(*E*)-Methyl 3-styrylbiphenyl-2-carboxylate (3i): mp 106−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (s, 3H), 7.10 (d, J = 16.1 Hz, 1H), 7.23−7.28 (m, 3H), 7.32−7.39 (m, 7H), 7.43 (t, J = 7.7 Hz, 1H), 7.48 (d, J = 7.3 Hz, 2H), 7.68 (d, J = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.0, 124.3, 125.2, 126.7, 127.4, 128.0, 128.1, 128.3, 128.6, 128.8, 129.6, 132.0, 132.2, 135.3, 136.9, 140.5, 140.6, 169.8; HRMS m/z calcd for $C_{22}H_{18}O_2$ (M^+) 314.1307, found 314.1305.

(*E*)-Methyl 5-methyl-2-styrylbenzoate (3j): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.92 (s, 3H), 6.97 (d, J = 16.5 Hz, 1H), 7.23−7.36 (m, 4H), 7.54 (d, J = 7.8 Hz, 2H), 7.60−7.63 (m, 1H), 7.73 (s, 1H), 7.95 (d, J = 16.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 52.0, 126.7, 126.8, 127.2, 127.6, 128.3, 128.6, 130.5, 131.0, 133.0, 136.3, 137.0, 137.5, 168.0; HRMS m/z calcd for $C_{17}H_{16}O_2$ (M^+) 252.1150, found 252.1152.

(*E*)-Methyl 2-styryl-1-naphthoate (3k): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.06 (s, 3H), 7.20 (d, J = 16.5 Hz, 1H), 7.27−7.29 (m, 2H), 7.33−7.37 (m, 2H), 7.44−7.52 (m, 4H), 7.77−7.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 122.6, 125.0, 125.4, 126.2, 126.7, 127.3, 128.0, 128.1, 128.7, 129.8, 129.9, 130.0, 131.9, 132.4, 132.5, 136.9, 169.9; HRMS m/z calcd for $C_{20}H_{16}O_2$ (M^+) 288.1150, found 288.1148.

(*E*)-Methyl 3-styryl-2-naphthoate (3l): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3H), 7.06 (d, J = 16.0 Hz, 1H), 7.23−7.28 (m, 1H), 7.35−7.38 (m, 2H), 7.45−7.59 (m, 4H), 7.84−7.87 (m, 2H), 8.03 (d, J = 16.0 Hz, 1H), 8.08 (s, 1H), 8.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 126.0, 126.5, 126.8, 126.9, 127.7 (overlapped), 127.9, 128.4, 128.6, 128.7, 130.9, 131.6, 132.0, 134.9, 135.5, 137.6, 167.8; HRMS m/z calcd for $C_{20}H_{16}O_2$ (M^+) 288.1150, found 288.1144.

(*E*,*E*)-Methyl 2,6-distyrylbenzoate (4a):[12]**.** mp 116−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3H) 7.05 (d, J = 16.1 Hz, 2H), 7.13 (d, J = 16.1 Hz, 2H), 7.26−7.28 (m, 2H), 7.33−7.41 (m, 5H), 7.47 (d, J = 8.0 Hz, 4H), 7.58 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.3, 124.6, 125.3, 126.7, 128.0, 128.7, 129.7, 131.8, 131.9, 135.3, 136.9, 169.9; MS m/z 340. Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.46; H, 5.77.

(*E*,*E*)-Methyl 2,6-bis(4-*tert*-butylstyryl)benzoate (4b): mp 120−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32−1.33 (m, 18H), 3.95 (s, 3H), 7.04 (d, J = 16.0 Hz, 2H), 7.10 (d, J = 16.0 Hz, 2H), 7.36−7.43 (m, 9H), 7.56 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.2, 34.6, 52.3, 124.3, 124.5, 125.6, 126.5, 129.7, 131.5, 131.7, 134.2, 135.4, 151.2, 170.0; MS m/z 452. Anal. Calcd for $C_{32}H_{36}O_2$: C, 84.91; H, 8.02. Found: C, 84.70; H, 8.00.

(*E*,*E*)-Methyl 2,6-bis(4-methoxystyryl)benzoate (4c): mp 156−157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 6H), 3.96 (s, 3H), 6.88 (d, J = 8.7 Hz, 4H), 6.96 (d, J = 16.0 Hz, 2H), 7.02 (d, J = 16.0 Hz, 2H), 7.34−7.42 (m, 5H), 7.53 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.3, 55.2, 114.1, 123.1, 124.0, 127.9, 129.6, 129.8, 131.1, 131.4, 135.5, 159.5, 170.1; HRMS m/z calcd for $C_{26}H_{24}O_4$ (M^+) 400.1675, found 400.1673.

(*E*,*E*)-Methyl 2,6-bis(4-chlorostyryl)benzoate (4d): mp 178−180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 7.00 (d, J = 16.0 Hz, 2H), 7.09 (d, J = 16.0 Hz, 2H), 7.32 (d, J = 7.8 Hz, 4H), 7.38−7.43 (m, 5H), 7.58 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.5, 124.9, 125.8, 127.9, 128.9, 129.9, 130.6, 131.9, 133.7, 135.2, 135.4, 169.8; HRMS m/z calcd for $C_{24}H_{18}Cl_2O_2$ (M^+) 408.0684, found 408.0681.

Methyl 2,6-bis((*E*)-2-(naphthalen-2-yl)vinyl)benzoate (4e): mp 207−208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03 (s, 3H) 7.23 (d, J = 16.0 Hz, 2H), 7.28 (d, J = 16.0 Hz, 2H), 7.43−7.50 (m, 5H), 7.65−7.71 (m, 4H), 7.80−7.84 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.5, 123.5, 124.7, 125.6, 126.1, 126.4, 127.2, 127.7, 128.1, 128.4, 129.9, 131.91, 131.93, 133.2, 133.6, 134.4, 135.5, 170.0; HRMS m/z calcd for $C_{32}H_{24}O_2$ (M^+) 440.1776, found 440.1775.

(*E*,*E*)-Methyl 4-methyl-2,6-distyrylbenzoate (4f): mp 142−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.95 (s, 3H), 7.03 (d, J = 16.5 Hz, 2H), 7.14 (d, J = 16.5 Hz, 2H), 7.24−7.27 (m, 2H), 7.34 (t, J = 7.8 Hz, 4H), 7.40 (s, 2H), 7.47 (d, J = 7.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 52.2, 125.4, 125.5, 126.7, 127.9, 128.6, 129.3, 131.4, 135.4, 137.0, 139.6, 170.0; HRMS m/z calcd for $C_{25}H_{22}O_2$ (M^+) 354.1620, found 354. 1622.

(*E*,*E*)-Methyl 4-methoxy-2,6-distyrylbenzoate (4g): mp 142−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.83 (s, 3H), 6.91 (d, J = 16.0 Hz, 2H), 6.99 (s, 2H), 7.08 (d, J = 16.0 Hz, 2H), 7.14−7.18 (m, 2H), 7.22−7.25 (m, 4H), 7.37 (d, J = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 55.3, 110.2, 124.8, 125.6, 126.7, 128.0, 128.6, 131.7, 136.8, 137.5, 160.4, 169.7; HRMS m/z calcd for $C_{25}H_{22}O_3$ (M^+) 370.1569, found 370.1558.

(*E*,*E*)-Methyl 4-chloro-2,6-distyrylbenzoate (4h): mp 151−152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, 3H), 7.03−7.10 (m, 4H), 7.28−7.32 (m, 2H), 7.35−7.39 (m, 4H), 7.48

(d, J = 7.4 Hz, 4H), 7.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 124.1, 124.3, 126.9, 128.4, 128.8, 130.1, 132.9, 136.0, 136.5, 137.3, 169.2; MS m/z 374, 376. Anal. Calcd for $C_{24}H_{19}ClO_2$: C, 76.90; H, 5.11; Cl, 9.46. Found: C, 76.62; H, 4.94; Cl, 9.28.

(*E*,*E*)-Methyl 4-bromo-2,6-distyrylbenzoate (4i): mp 166−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3H), 7.00−7.04 (m, 4H), 7.26−7.30 (m, 2H), 7.33−7.37 (m, 4H), 7.45 (d, J = 7.3 Hz, 4H), 7.69 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.5, 123.9, 124.3, 126.9, 127.2, 128.4, 128.7, 130.5, 132.9, 136.4, 137.4, 169.2; MS m/z 418, 420. Anal. Calcd for $C_{24}H_{19}BrO_2$: C, 68.75; H, 4.57; Br, 19.06. Found: C, 68.49; H, 4.42; Br, 19.03.

(*E*,*E*)-Methyl 3,5-distyrylbiphenyl-4-carboxylate (4j): mp 137−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 3H), 7.10 (d, J = 16.0 Hz, 2H), 7.20 (d, J = 16.0 Hz, 2H), 7.24−7.28 (m, 2H), 7.32−7.41 (m, 5H), 7.45−7.50 (m, 6H), 7.65 (d, J = 7.8 Hz, 2H), 7.76 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 123.6, 125.4, 126.7, 127.3, 127.9, 128.1, 128.7, 128.8, 130.6, 132.0, 136.0, 136.9, 140.3, 142.8, 169.8; MS m/z 416. Anal. Calcd for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81. Found: C, 86.12; H, 5.71.

(*E*,*E*)-Methyl 4-acetyl-2,6-distyrylbenzoate (4k): mp 155−156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69 (s, 3H), 4.00 (s, 3H), 7.09 (d, J = 16.0 Hz, 2H), 7.16 (d, J = 16.0 Hz, 2H), 7.28−7.31 (m, 2H), 7.35−7.39 (m, 4H), 7.49 (d, J = 7.4 Hz, 4H), 8.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8, 52.6, 124.1, 124.3, 126.8, 128.4, 128.7, 132.9, 135.3, 135.9, 136.5, 137.8, 169.2, 197.5; MS m/z 382. Anal. Calcd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80 Found: C, 81.55; H, 5.65.

(*E*,*E*)-Methyl 2,6-distyryl-4-(trifluoromethyl)benzoate (4l): mp 186−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (s, 3H), 7.08 (d, J = 16.0 Hz, 2H), 7.14 (d, J = 16.0 Hz, 2H), 7.30−7.33 (m, 2H), 7.36−7.40 (m, 4H), 7.50 (d, J = 7.3 Hz, 4H), 7.81 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.7, 121.1 (q, J = 3.8 Hz), 123.7 (q, J = 272 Hz), 123.9, 126.9, 128.6, 128.8, 132.0 (q, J = 32 Hz), 133.5, 134.5, 136.4 (overlapped), 169.0; MS m/z 408. Anal. Calcd for $C_{25}H_{19}F_3O_2$: C, 73.52; H, 4.69; F, 13.96. Found: C, 73.25; H, 4.51; F, 13.98.

(*E*,*E*)-Methyl 3-methoxy-2,6-distyrylbenzoate (4m): mp 95−96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 3.86 (s, 3H), 6.91−6.98 (m, 2H), 7.02−7.09 (m, 2H), 7.17 (d, J = 16.5 Hz, 1H), 7.20−7.26 (m, 2H), 7.31−7.35 (m, 4H), 7.44−7.48 (m, 4H), 7.57 (d, J = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 55.7, 111.9, 122.6, 124.2, 124.8, 125.5, 126.49, 126.53, 127.4, 127.6, 127.7, 128.5, 128.6, 129.8, 133.3, 133.7, 137.2, 137.6, 156.9, 170.0; HRMS m/z calcd for $C_{25}H_{22}O_3$ (M^+) 370.1569, found 370.1575.

(*E*,*E*)-Methyl 3-chloro-2,6-distyrylbenzoate (4n). mp 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.80 (d, J = 16.5 Hz, 1H), 7.03−7.12 (m, 2H), 7.22 (d, J = 16.5 Hz, 1H), 7.28−7.38 (m, 6H), 7.42 (d, J = 8.7 Hz, 1H), 7.46−7.50 (m, 4H), 7.54 (d, J = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 124.0, 124.2, 125.2, 126.7, 126.8, 128.2, 128.3, 128.68, 128.71, 130.5, 132.3, 132.9, 133.4, 133.9, 134.3, 135.0, 136.6 (overlapped), 169.2; HRMS m/z calcd for $C_{24}H_{19}ClO_2$ (M^+) 374.1074, found 374.1065.

(*E*,*E*)-Methyl 3-fluoro-2,6-distyrylbenzoate (4o): mp 82−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 6.94−7.01 (m, 2H), 7.06 (d, J = 16.0 Hz, 1H), 7.11−7.19 (m, 2H), 7.25−7.30 (m, 2H), 7.33−7.37 (m, 4H), 7.45−7.48 (m, 4H), 7.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 117.3 (d. J = 24 Hz), 119.5, 123.1 (d, J = 14 Hz), 124.2, 125.7 (d, J = 8.6 Hz), 126.7 (overlapped), 128.1, 128.3, 128.7 (overlapped), 131.3 (d, J = 3.8 Hz), 131.6 (overlapped), 133.6 (d, J = 3.8 Hz), 135.8 (d, J = 9.5 Hz), 136.9 (d, J = 24 Hz), 159.7 (d, J = 250 Hz), 169.0 (d, J = 2.9 Hz); MS m/z 358. Anal. Calcd for $C_{24}H_{19}FO_2$: C, 80.43; H, 5.34; F, 5.30. Found: C, 80.15; H, 5.27; F, 5.27.

(*E*)-3,5-Dimethoxystilbene (5a):[12]. mp 53−55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 6H), 6.40 (s, 1H), 6.67 (s, 2H), 7.03 (d, J = 16.5 Hz, 1H), 7.08 (d, J = 16.5 Hz, 1H), 7.24−7.27 (m, 1H), 7.35 (t, J = 7.7 Hz, 2H), 7.50 (d, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 100.0, 104.6, 126.6, 127.7, 128.7 (overlapped), 129.2, 137.1, 139.3, 161.0; HRMS m/z calcd for $C_{16}H_{16}O_2$ (M^+) 240.1150, found 240.1145.

(*E*)-4′-*tert*-Butyl-3,5-dimethoxystilbene (5b):[12]. oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 3.80 (s, 6H), 6.37 (t, J = 2.3 Hz, 1H), 6.66 (d, J = 2.3 Hz, 2H), 6.98 (d, J = 16.0 Hz, 1H), 7.06 (d, J = 16.0 Hz, 1H), 7.36 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.2, 34.6, 55.3, 99.8, 104.4, 125.6, 126.3, 127.8, 128.9, 134.3, 139.5, 150.8, 160.9; HRMS m/z calcd for $C_{20}H_{24}O_2$ (M^+) 296.1776, found 296.1779.

(*E*)-3,5,4′-Trimethoxystilbene (5c):[12]. mp 52−54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.805 (s, 3H), 3.810 (s, 6H), 6.37 (t, J = 2.3 Hz, 1H), 6.64 (d, J = 2.3 Hz, 2H), 6.87−6.91 (m, 3H), 7.03 (d, J = 16.0 Hz, 1H), 7.43 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 55.3, 99.5, 104.3, 114.1, 126.5, 127.8, 128.7, 129.9, 139.6, 159.3, 160.9; HRMS m/z Calcd for $C_{17}H_{18}O_3$ (M^+) 270.1256, found 270.1252.

(*E*)-4′-Chloro-3,5-dimethoxystilbene (5d):[12]. mp 72−73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 6H), 6.39−6.40 (t, J = 2.2 Hz, 1H), 6.63 (d, J = 2.2 Hz, 2H), 6.95 (d, J = 16.5 Hz, 1H), 7.00 (d, J = 16.5 Hz, 1H), 7.29 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 100.1, 104.6, 127.7, 127.8, 128.7, 129.2, 133.2, 135.6, 138.9, 160.9; HRMS m/z calcd for $C_{16}H_{15}ClO_2$ (M^+) 274.0761, found 274.0756.

(*E*)-3-Methoxystilbene (5e):[12]. oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (s, 3H), 6.79−6.81 (m, 1H), 7.03−7.09 (m, 4H), 7.21−7.27 (m, 2H), 7.33 (t, J = 7.7 Hz, 2H), 7.48 (d, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.1, 111.7, 113.2, 119.2, 126.5, 127.6, 128.5, 128.6, 128.9, 129.6, 137.2, 138.7, 159.8; HRMS m/z Calcd for $C_{15}H_{14}O$ (M^+) 210.1045, found 210.1039.

(*E*)-*N*-(3-Styrylphenyl)acetamide (5f):[12]. mp 188−190 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.08 (s, 3H), 7.16 (d, J = 16.5 Hz, 1H), 7.24 (d, J = 16.5 Hz, 1H), 7.27−7.32 (m, 3H), 7.39 (t, J = 7.8 Hz, 2H), 7.47−7.50 (m, 1H), 7.63 (d, J = 7.8 Hz, 2H), 7.84 (s, 1H), 10.0 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 24.1, 117.1, 118.6, 121.3, 126.6, 127.7, 128.50, 128.52, 128.7, 129.0, 136.9, 137.4, 139.7, 168.4; HRMS m/z calcd for $C_{16}H_{15}NO$ (M^+) 237.1154, found 237.1152.

(*E*)-3-Fluorostilbene (5g):[12]. mp 70−71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91−6.95 (m, 1H), 7.02 (d, J = 16.5 Hz, 1H), 7.08 (d, J = 16.5 Hz, 1H), 7.17−7.30 (m, 4H), 7.34 (t, J = 7.8 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.7 (d, J = 21.9 Hz), 114.3 (d, J = 21.0 Hz), 122.4 (d, J = 2.86 Hz), 126.6, 127.4 (d, J = 2.86 Hz), 128.0, 128.7, 129.96, 130.0 (d, J = 8.58 Hz), 136.8, 139.6 (d, J = 7.63 Hz), 163.1 (d, J = 244 Hz); HRMS m/z calcd for $C_{14}H_{11}F$ (M^+) 198.0845, found 198.0840.

(*E*)-3-Styrylbiphenyl (5h):[12]. mp 91−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−7.20 (m, 2H), 7.24−7.27 (m, 1H), 7.34−7.53 (m, 10H), 7.62 (d, J = 7.8 Hz, 2H), 7.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.35, 125.40, 126.50, 126.54, 127.2, 127.4, 127.7, 128.6, 128.7, 128.8, 129.0, 129.1, 137.2, 137.8, 141.1, 141.7; HRMS m/z calcd for $C_{20}H_{16}$ (M^+) 256.1252, found 256.1251.

(*E*)-2-Styrylnaphthalene (5i):[12]. mp 144−146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07−7.17 (m, 3H), 7.24−7.37 (m, 4H), 7.44 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.2 Hz, 1H), 7.67−7.71 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.5, 125.9, 126.3, 126.5, 126.6, 127.6, 127.7, 128.0, 128.3, 128.68, 128.71, 129.0, 133.0, 133.7, 134.8, 137.3; HRMS m/z calcd for $C_{18}H_{14}$ (M^+) 230.1096, found 230.1098.

(*E*,*E*)-1,3-Distyrylbenzene (6a):[12]. mp 162−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04−7.12 (m, 4H), 7.17−7.23 (m, 2H), 7.29−7.37 (m, 7H), 7.47 (d, J = 7.8 Hz, 4H), 7.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.7, 125.7, 126.5, 127.7, 128.5, 128.7, 129.0 (overlapped), 137.2, 137.7; HRMS m/z calcd for $C_{22}H_{18}$ (M^+) 282.1409, found 282.1404.

(*E*,*E*)-1,3-Distyryl-5-methoxybenzene (6b): mp 128−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.96 (s, 2H), 7.06

(d, J = 16.0 Hz, 2H), 7.12 (d, J = 16.0 Hz, 2H), 7.24−7.28 (m, 3H), 7.34−7.37 (m, 4H), 7.50 (d, J = 7.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 111.1, 118.0, 126.5, 127.7, 128.4, 128.7, 129.2, 137.1, 138.9, 160.1; HRMS m/z calcd for $C_{23}H_{20}O$ (M^+) 312.1514, found 312.1510.

(*E*)-Dimethyl 4-styrylisophthalate (8): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 3.95 (s, 3H), 7.11 (d, J = 16.5 Hz, 1H), 7.28−7.31 (m, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.56 (d, J = 7.8 Hz, 2H), 7.79 (d, J = 8.2 Hz, 1H), 8.04 (d, J = 16.5 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 8.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 52.3, 126.2, 126.9, 127.1, 128.36, 128.41, 128.6, 128.7, 132.2, 132.7, 133.6, 136.8, 143.4, 166.1, 167.0; HRMS m/z calcd for $C_{18}H_{16}O_4$ (M^+) 296.1049, found 296.1048.

(*E*)-Dimethyl 3-styrylbiphenyl-2,2′-dicarboxylate (10): mp 88−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (s, 3H), 3.65 (s, 3H), 7.10 (d, J = 16.1 Hz, 1H), 7.17 (d, J = 7.7 Hz, 1H), 7.22−7.29 (m, 3H), 7.35 (t, J = 7.3 Hz, 2H), 7.40−7.54 (m, 5H), 7.71 (d, J = 7.7 Hz, 1H), 7.97 (d, J = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.8, 51.9, 124.5, 125.7, 126.8, 127.6, 127.9, 128.4, 128.7, 129.2, 130.1, 130.2, 130.8, 131.4, 131.6, 131.7, 135.1, 137.1, 140.6, 141.3, 167.5, 169.1; HRMS m/z calcd for $C_{24}H_{20}O_4$ (M^+) 372.1362, found 372.1365.

Dimethyl 3,3′-distyrylbiphenyl-2,2′-dicarboxylate (11): mp 209−212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (s, 6H), 7.11 (d, J = 16.1 Hz, 2H), 7.20 (d, J = 7.7 Hz, 2H), 7.26−7.30 (m, 4H), 7.35 (t, J = 7.7 Hz, 4H), 7.42 (t, J = 7.7 Hz, 2H), 7.49 (d, J = 7.7 Hz, 4H), 7.71 (d, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.9, 124.9, 125.6, 126.8, 128.0, 128.67, 128.71, 129.2, 131.9, 132.2, 135.6, 137.0, 139.2, 169.0; HRMS m/z calcd for $C_{32}H_{26}O_4$ (M^+) 474.1831, found 474.1828.

(*E,E*)-Methyl 2,5-distyrylbenzoate (13):[12] mp 142−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H) 7.01−7.10 (m, 2H), 7.15 (d, J = 16.5 Hz, 1H), 7.22−7.28 (m, 2H), 7.33−7.37 (m, 4H), 7.50−7.55 (m, 4H), 7.61 (dd, J = 8.2, 1.8 Hz, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 16.0 Hz, 1H), 8.03 (d, J = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 126.6, 126.8 (overlapped), 127.1, 127.2, 127.8, 127.9, 128.6, 128.7, 128.8, 128.9, 129.5, 129.6, 131.2, 136.3, 136.9, 137.4, 138.0, 167.8; HRMS m/z calcd for $C_{24}H_{20}O_2$ (M^+) 340.1463, found 340.1456.

(2*Z*,4*E*)-Methyl 2-methyl-5-phenylpenta-2,4-dienoate (15a):[23] oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.02 (s, 3H), 3.79 (s, 3H), 6.59 (d, J = 11.7 Hz, 1H), 6.68 (d, J = 16.1 Hz, 1H), 7.24−7.33 (m, 3H), 7.47 (d, J = 7.7 Hz, 2H), 7.90 (dd, J = 11.7, 16.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 51.4, 125.9, 126.0, 127.1, 128.3, 128.6, 136.8, 138.2, 140.8, 167.9; HRMS m/z (M^+) calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0990.

(2*Z*,4*E*)-Methyl 2-methyl-5-(naphthalen-2-yl)penta-2,4-dienoate (15b): mp 80−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 3.82 (s, 3H), 6.64 (d, J = 11.5 Hz, 1H), 6.84 (d, J = 15.6 Hz, 1H), 7.43−7.47 (m, 2H), 7.68−7.70 (m, 1H), 7.77−7.80 (m, 4H), 8.04 (dd, J = 11.5, 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 51.5, 123.8, 126.0, 126.21, 126.24, 126.3, 127.5, 127.7, 128.1, 128.3, 133.4, 133.5, 134.4, 138.4, 141.0, 168.0; HRMS m/z (M^+) calcd for $C_{17}H_{16}O_2$ 252.1150, found 252.1151.

(2*Z*,4*E*)-Methyl 2,3-dimethyl-5-(naphthalen-2-yl)penta-2,4-dienoate (15c): mp 78−79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 2.07 (s, 3H), 3.83 (s, 3H), 6.92 (d, J = 16.0 Hz, 1H), 7.41−7.45 (m, 2H), 7.66−7.69 (m, 1H), 7.76−7.81 (m, 4H), 7.92 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 16.9, 51.7, 123.7, 125.9, 126.2, 126.3, 127.1, 127.6, 128.0, 128.2, 128.6, 131.5, 133.1, 133.6, 134.9, 140.9, 169.8; HRMS m/z (M^+) calcd for $C_{18}H_{18}O_2$ 266.1307, found 266.1303.

(*E*)-3-Styrylthiophene (17a):[24] mp 118−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, J = 16.5 Hz, 1H), 7.10 (d, J = 16.5 Hz, 1H), 7.20−7.35 (m, 6H), 7.46 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.3, 122.8, 124.9, 126.1, 126.3, 127.4, 128.6 (overlapped), 137.3, 140.1; HRMS m/z (M^+) calcd for $C_{12}H_{10}S$ 186.0503, found 186.0500.

Butyl (*E*)-3-(thien-3-yl)-2-propenoate (17b):[11j] oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, J = 7.3 Hz, 3H), 1.40−1.46 (m, 2H), 1.64−1.71 (m, 2H), 4.20 (t, J = 6.4 Hz, 2H), 6.26 (d, J = 16.0 Hz, 1H), 7.28−7.33 (m, 2H), 7.47−7.48 (m, 1H), 7.66 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 19.1, 30.7, 64.2, 117.9, 125.1, 126.8, 127.9, 137.5, 137.9, 167.2; HRMS m/z (M^+) calcd for $C_{11}H_{14}O_2S$ 210.0715, found 210.0713.

Butyl (*E*)-3-(benzo[*b*]thien-3-yl)-2-propenoate (17c):[11j] oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, J = 7.3 Hz, 3H), 1.44−1.49 (m, 2H), 1.70−1.74 (m, 2H), 4.25 (t, J = 6.9 Hz, 2H), 6.54 (d, J = 16.0 Hz, 1H), 7.40−7.48 (m, 2H), 7.74 (s, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.96 (d, J = 16.0 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 30.7, 64.4, 118.7, 122.0, 122.9, 124.9, 125.0, 127.9, 131.6, 136.2, 137.1, 140.4, 167.2; HRMS m/z (M^+) calcd for $C_{15}H_{16}O_2S$ 260.0871, found 260.0870.

Butyl (*E*)-3-(benzo[*b*]furan-3-yl)-2-propenoate (17d):[11j] oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 3H), 1.34−1.40 (m, 2H), 1.59−1.64 (m, 2H), 4.15 (t, J = 6.9 Hz, 2H), 6.48 (d, J = 16.0 Hz, 1H), 7.25−7.29 (m, 2H), 7.43−7.45 (m, 1H), 7.70 (d, J = 16.0 Hz, 1H), 7.76−7.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 30.8, 64.4, 111.9, 117.8, 118.4, 121.0, 123.7, 124.7, 125.3, 134.3, 147.7, 156.1, 167.2; HRMS m/z (M^+) calcd for $C_{15}H_{16}O_3$ 244.1099, found 244.1094.

Butyl (*E*)-3-(1-methylpyrrol-3-yl)-2-propenoate (17e):[11j] oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 3H), 1.39−1.45 (m, 2H), 1.62−1.70 (m, 2H), 3.62 (s, 3H), 4.16 (t, J = 6.6 Hz, 2H), 6.07 (d, J = 15.8 Hz, 1H), 6.35−6.36 (m, 1H), 6.56−6.57 (m, 1H), 6.80−6.81 (m, 1H), 7.58 (d, J = 15.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 19.1, 30.8, 36.2, 63.7, 106.8, 112.6, 120.6, 123.7, 124.8, 138.7, 168.1; HRMS m/z (M^+) calcd for $C_{12}H_{17}NO_2$ 207.1259, found 207.1259.

Butyl (*E*)-3-(1-methylindol-3-yl)-2-propenoate (17f):[11j] oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95−0.99 (m, 3H), 1.42−1.48 (m, 2H), 1.66−1.71 (m, 2Hz), 3.72 (s, 3H), 4.18−4.22 (m, 2H), 6.40 (d, J = 16.0 Hz, 1H), 7.21−7.30 (m, 4H), 7.84−7.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 30.9, 33.0, 63.9, 109.8, 111.9, 112.5, 120.5, 121.1, 122.8, 125.9, 133.0, 137.9, 138.0, 168.4; HRMS m/z (M^+) calcd for $C_{16}H_{19}NO_2$ 257.1416, found 257.1410.

■ ASSOCIATED CONTENT

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

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■ REFERENCES

(1) For recent examples, see: (a) Hua, X.; Fu, Y.-J.; Zu, Y.-G.; Wu, N.; Kong, Y.; Li, J.; Peng, X.; Efferth, T. *J. Pharm. Biomed. Anal.* **2010**, *52*, 273. (b) Kong, Y.; Fu, Y.-J.; Zu, Y.-G.; Liu, W.; Wang, W.; Hua, X.; Yang, M. *Food Chem.* **2010**, *117*, 152. (c) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897.

(d) Vitrac, X.; Bornet, A.; Vanderlinde, R.; Valls, J.; Richard, T.; Delaunay, J.-C.; Mérillon, J.-M.; Teissédre, P.-L. *J. Agric. Food Chem.* **2005**, *53*, 5664. (e) Syah, Y. M.; Aminah, N. S.; Hakim, E. H.; Aimi, N.; Kitajima, M.; Takayama, H.; Achmad, S. A. *Phytochemistry* **2003**, *63*, 913. (f) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (g) Marder, S. R.; Kippelen, B.; Jen, A. K.-Y.; Peyghambarian, N. *Nature* **1997**, *388*, 845.

(2) For selected reviews concerning C−H bond functionalization, see: (a) Hirano, K.; Miura, M. *Synlett* **2011**, 294. (b) Satoh, T.; Miura, M. *Chem.—Eur. J.* **2010**, *16*, 11212. (c) Satoh, T.; Miura, M. *Synthesis* **2010**, 3395. (d) Karimi, B.; Behzadnia, H.; Elhamifar, D.; Akhavan, P. F.; Esfahani, F. K. *Synthesis* **2010**, 1399. (e) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (f) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Commun.* **2010**, *46*, 677. (g) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792. (h) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094. (i) Daugulis, O.; Do, H.-Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074. (j) McGlacken, G. P.; Bateman, L. M. *Chem. Soc. Rev.* **2009**, *38*, 2447. (k) Kakiuchi, F.; Kochi, T. *Synthesis* **2008**, 3013. (l) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2008**, *41*, 1013. (m) Ferreira, E. M.; Zhang, H.; Stoltz, B. M. *Tetrahedron* **2008**, *64*, 5987. (n) Park, Y. J.; Park, J.-W.; Jun, C.-H. *Acc. Chem. Res.* **2008**, *41*, 222. (o) Beccalli, E. M.; Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, *107*, 5318. (p) Herrerias, C. I.; Yao, X.; Li, Z.; Li, C.-J. *Chem. Rev.* **2007**, *107*, 2546. (q) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (r) Godula, K.; Sames, D. *Science* **2006**, *312*, 67. (s) Conley, B. L.; Tenn, W. J., III; Young, K. J. H.; Ganesh, S. K.; Meier, S. K.; Ziatdinov, V. R.; Mironov, O.; Oxgaard, J; Gonzales, J.; Goddard, W. A., III; Periana, R. A. *J. Mol. Catal. A* **2006**, *251*, 8. (t) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal.* **2003**, *345*, 1077. (u) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731. (v) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826. (w) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1698. (x) Kakiuchi, F.; Murai, S. *Top. Organomet. Chem.* **1999**, *3*, 47. (y) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

(3) Miura, M.; Tsuda, T.; Satoh, T.; Nomura, M. *Chem. Lett.* **1997**, 1103.

(4) (a) Miura, M.; Tsuda, T.; Satoh, T.; Nomura, M. *J. Org. Chem.* **1998**, *63*, 5211. For the Rh-catalyzed version, see: (b) Ueura, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2007**, *72*, 5362.

(5) (a) Rakshit, S.; Grohmann, C.; Besset, T.; Glorius, F. *J. Am. Chem. Soc.* **2011**, *133*, 2350. (b) Zhu, C.; Falck, J. R. *Org. Lett.* **2011**, *13*, 1214. (c) Patureau, F. W.; Besset, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 1064. (d) Wang, F.; Song, G.; Li, X. *Org. Lett.* **2010**, *12*, 5430. (e) Chen, J.; Song, G.; Pan, C.-L.; Li, X. *Org. Lett.* **2010**, *12*, 5426. (f) Kim, B. S.; Jang, C.; Lee, D. J.; Youn, S. W. *Chem. Asian J.* **2010**, *5*, 2336. (g) Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9982. (h) Nishikata, T.; Lipshutz, B. H *Org. Lett.* **2010**, *12*, 1972. (i) Rauf, W.; Thompson, A. L.; Brown, J. M. *Chem. Commun.* **2009**, 3874. (j) Houlden, C. E.; Bailey, C. D.; Ford, J. G.; Gagné, M. R.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. *J. Am. Chem. Soc.* **2008**, *130*, 10066. (k) Wang, J.-R.; Yang, C.-T.; Liu, L.; Guo, Q.-X. *Tetrahedron Lett.* **2007**, *48*, 5449. (l) Amatore, C.; Cammoun, C.; Jutand, A. *Adv. Synth. Catal.* **2007**, *349*, 292. (m) Lee, G. T.; Jiang, X.; Prasad, K.; Repič, O.; Blacklock, T. J. *Adv. Synth. Catal.* **2005**, *347*, 1921. (n) Boele, M. D. K.; van Strijdonck, G. P. F.; de Vries, A. H. M.; Kamer, P. C. J.; de Vries, J. G.; van Leeuwen., P. W. N. M. *J. Am. Chem. Soc.* **2002**, *124*, 1586.

(6) Cai, G.; Fu, Y.; Li, Y.; Wan, X.; Shi., Z. *J. Am. Chem. Soc.* **2007**, *129*, 7666.

(7) (a) Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 14137. (b) Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2010**, *49*, 6169. (c) Shi, B.-F.; Zhang, Y.-H.; Lam, J. K.; Wang, D.-H.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 460. (d) Wang, D.-H.; Engle, K. M.; Shi, B.-F.; Yu, J.-Q. *Science* **2010**, *327*, 315.

(8) Umeda, N.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2009**, *74*, 7094.

(9) Lu, Y.; Wang, D.-H.; Engle, K. M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 5916.

(10) For reviews, see ref 2b as well as the following: (a) Goossen, L. J.; Rodriguez, N.; Goossen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3100. (b) Baudoin, O. *Angew. Chem., Int. Ed.* **2007**, *46*, 1373.

(11) (a) Ueyama, T.; Mochida, S.; Fukutani, T.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2011**, *13*, 706. (b) Yamashita, M.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2010**, *12*, 592. (c) Yamashita, M.; Hirano, K.; Satoh, T.; Miura, M. *Chem. Lett.* **2010**, *39*, 68. (d) Yamashita, M.; Horiguchi, H.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2009**, *74*, 7481. (e) Mochida, S.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2009**, *74*, 6295. (f) Yamashita, M.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2009**, *11*, 2337. (g) Miyasaka, M.; Fukushima, A.; Satoh, T.; Hirano, K.; Miura, M. *Chem.—Eur. J.* **2009**, *15*, 3674. (h) Shimizu, M.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2009**, *74*, 3478. (i) Nakano, M.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett.* **2008**, *10*, 1851. (j) Maehara, A.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett.* **2008**, *10*, 1159.

(12) Preliminary communication: Mochida, S.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2010**, *12*, 5776.

(13) For stoichiometric *ortho*-rhodation of a Cp*Rh benzoate, see: Kisenyi, J. M.; Sunley, G. J.; Cabeza, J. A.; Smith, A. J.; Adams, H.; Salt, N. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, 2459.

(14) For Pd-catalyzed decarboxylative *ipso*-vinylation of *ortho*-substituted benzoic acids, see: (a) Hu, P.; Kan, J.; Su, W.; Hong, M. *Org. Lett.* **2009**, *11*, 2341. (b) Tanaka, D.; Romeril, S. P.; Myers, A. G. *J. Am. Chem. Soc.* **2005**, *127*, 10323. (c) Tanaka, D.; Myers, A. G. *Org. Lett.* **2004**, *6*, 433. (d) Myers, A. G.; Tanaka, D.; Mannion, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 11250.

(15) For Pd-catalyzed decarboxylative *ipso*-arylation of activated benzoic acids, see: (a) Goossen, L. J.; Lange, P. P.; Rodriguez, N.; Linder, C. *Chem.—Eur. J.* **2010**, *16*, 3906. (b) Goossen, L. J.; Rodriguez, N.; Lange, P. P.; Linder, C. *Angew. Chem., Int. Ed.* **2010**, *49*, 1111. (c) Goossen, L. J.; Linder, C.; Rodriguez, N.; Lange, P. P. *Chem.—Eur. J.* **2009**, *15*, 9336. (d) Shang, R.; Fu, Y.; Wang, Y.; Xu, Q.; Yu, H.-Z.; Liu, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 9350. (e) Goossen, L. J.; Rodriguez, N.; Linder, C. *J. Am. Chem. Soc.* **2008**, *130*, 15248. (f) Goossen, L. J.; Zimmermann, B.; Knauber, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 7103. (g) Voutchkova, A.; Coplin, A.; Leadbeater, N. E.; Crabtree, R. H. *Chem. Commun.* **2008**, 6312. (h) Becht, J.-M.; Le Drian, C. *Org. Lett.* **2008**, *10*, 3161. (i) Becht, J.-M.; Catala, C.; Le Drian, C.; Wagner, A. *Org. Lett.* **2007**, *9*, 1781. (j) Goossen, L. J.; Rodríguez, N.; Melzer, B.; Linder, C.; Deng, G.; Levy, L. M. *J. Am. Chem. Soc.* **2007**, *129*, 4824. (k) Goossen, L. J.; Deng, G.; Levy, L. M. *Science* **2006**, *313*, 662.

(16) For protodecarboxylation of benzoic acids, see: (a) Cornella, J.; Sanchez, C.; Banawa, D.; Larrosa, I. *Chem. Commun* **2009**, 7176. (b) Goossen, L. J.; Linder, C.; Rodríguez, N.; Lange, P. P.; Fromm, A. *Chem. Commun* **2009**, 7173. (c) Goossen, L. J.; Thiel, W. R.; Rodríguez, N.; Linder, C.; Melzer, B. *Adv. Synth. Catal.* **2007**, *349*, 2241. (d) Dickstein, J. S.; Mulrooney, C. A.; O'Brien, E. M.; Morgan, B. J.; Kozlowski, M. C. *Org. Lett.* **2007**, *9*, 2441.

(17) (a) Iriti, M.; Faoro, F. *Med. Hypotheses* **2006**, *67*, 833. (b) Heynekamp, J. J.; Weber, W. M.; Hunsaker, L. A.; Gonzales, A. M.; Orland, R. A.; Deck, L. M.; Vander Jagt, D. L. *J. Med. Chem.* **2006**, *49*, 7182. (c) Vessières, A.; Top, S.; Pigeon, P.; Hillard, E.; Boubeker, L.; Spera, D.; Jaouen, G. *J. Med. Chem.* **2005**, *48*, 3937. (d) Jang, M.; Cai, L.; Udeani, G. O.; Slowing, K. V.; Thomas, C. F.; Beecher, C. W. W.; Fong, H. H. S.; Farnsworth, N. R.; Kinghorn, A. D.; Mehta, R. G.; Moon, R. C.; Pezzuto, J. M. *Science* **1997**, *275*, 218.

(18) For recent example, see: (a) Mazué, F.; Colin, D.; Gobbo, J.; Wegner, M.; Rescifina, A.; Spatafora, C.; Fasseur, D.; Delmas, D.; Meunier, P.; Tringali, C.; Latruffe, N. *Eur. J. Med. Chem.* **2010**, *45*, 2972. (b) Wang, T. T. Y.; Schoene, N. W.; Kim, Y. S.; Mizuno, C. S.; Rimando, A. M. *Mol. Nutr. Food Res.* **2010**, *54*, 335. (c) Weng, C.-J.; Wu, C.-F.; Huang, H.-W.; Wu, C.-H.; Ho, C.-T.; Yen, G.-C. *J. Agric. Food Chem.* **2010**, *58*, 2886. (d) Sarpietro, M. G.; Ottimo, S.; Giuffrida, M. C.; Spatafora, C.; Tringali, C.; Castelli, F. *Int. J. Pharm.* **2010**, *388*, 144.

(19) For *meta*-olefination of arenes possessing an electron-withdrawing group, see: Zhang, Y.-H.; Shi, B.-F.; Yu, J.-Q. *J. Am. Chem. Soc.* **2009**, *131*, 5072.

(20) For example, see: (a) Ginocchietti, G.; Mazzucato, U.; Spalletti, A. *J. Photochem. Photobiol. A* **2008**, *196*, 233. (b) Tang, Y.; Wang, Y.; Wang, X.; Xun, S.; Mei, C.; Wang, L.; Yan, D. *J. Phys. Chem. B* **2005**, *109*, 8813. (c) Marri, E.; Galiazzo, G.; Mazzucato, U.; Spalletti, A. *Chem. Phys.* **2008**, *312*, 205. (d) Tang, Y.; Wang, Y.; Wang, G.; Wang, H.; Wang, L.; Yan, D. *J. Phys. Chem. B* **2004**, *108*, 12921. (e) Konstandakopoulou, F. D.; Iconomopoulou, S. M.; Gravalos, K. G.; Kallitsis, J. K. *Chem. Mater.* **2000**, *12*, 2957. (f) Lane, P. A.; Mellor, H.; Martin, S. J.; Hagler, T. W.; Bleyer, A.; Bradley, D. D. C. *Chem. Phys.* **2000**, *257*, 41.(g) Hidaka, T.; Nakatani, H.; Yamanaka, K. Jpn. Kokai Tokkyo Koho JP 03056449 1991. (h) Pavia, M. R.; Moos, W. H.; Hershenson, F. M. *J. Org. Chem.* **1990**, *55*, 560. (i) Noller, K.; Kosteyn, F.; Meier, H. *Chem. Ber* **1988**, *121*, 1609.(j) Colle, R.; Gozzo, F.; Camaggi, G.; Siddi, G. Jpn. Kokai Tokkyo Koho JP 53127425, 1978.

(21) For example, see: (a) Wang, Y.; Liu, D.; Ikeda, S.; Kumashiro, R.; Nouch, R.; Xu, Y.; Shang, H.; Ma, Y.; Tanigaki, K. *Appl. Phys. Lett.* **2010**, *97*, 033305. (b) Shimizu, M.; Hiyama, T. *Chem. Asian J.* **2010**, *5*, 1516. (c) Nielsen, C. B.; Arnbjerg, J.; Johnsen, M.; Jørgensen, M.; Ogilby, P. R. *J. Org. Chem.* **2009**, *74*, 9094. (d) Xie, Z.; Xie, W.; Li, F.; Liu, L.; Wang, H.; Ma, Y. *J. Phys. Chem. C* **2008**, *112*, 9066. (e) Xie, W.; Li, F.; Wang, H.; Xie, Z.; Shen, F.; Ma, Y.; Lu, W.; Zhang, D.; Ma, D. *Appl. Opt.* **2007**, *46*, 4431. (f) Xie, Z.; Yang, B.; Li, F.; Cheng, G.; Liu, L.; Yang, G.; Xu, H.; Ye, L.; Hanif, M.; Liu, S.; Ma, D.; Ma, Y. *J. Am. Chem. Soc.* **2005**, *127*, 14152. (g) Koch, F.; Heitz, W. *Macromol. Chem. Phys.* **1997**, *198*, 1531. (h) Oberski, J.; Bolle, B.; Schaper, A.; Greiner, A. *Polym. Adv. Technol.* **1993**, *5*, 105. (i) Vestweber, H.; Oberski, J.; Greiner, A.; Heitz, W.; Mahrt, R. F.; Bässler, H. *Adv. Mater. Opt. Electr* **1993**, *2*, 197.

(22) Shahzad, A. S.; Vivant, C.; Wirth, T. *Org. Lett.* **2010**, *12*, 1364.

(23) Mitsudo, T.; Takagi, M.; Zhang, S.-W.; Watanabe, Y. *J. Organomet. Chem.* **1992**, *423*, 405.

(24) Mu, B.; Li, T.; Xu, W.; Zeng, G.; Liu, P.; Wu, Y. *Tetrahedron* **2007**, *63*, 11475.