JOC The Journal of Organic Chemistry
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Pd-Catalyzed Regio- and Stereoselective Addition of Boronic Acids to Silylacetylenes: A Stereodivergent Assembly of *β*,*β*-Disubstituted Alkenylsilanes and Alkenyl Halides

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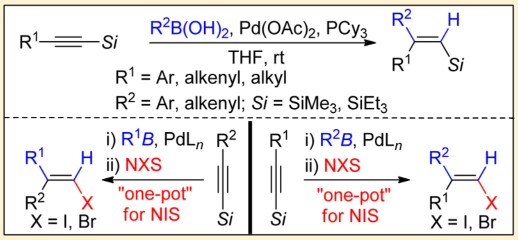
Ⓢ *Supporting Information*

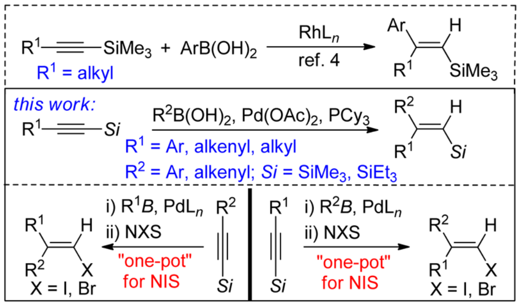
ABSTRACT: An efficient Pd-catalyzed addition of boronic acids to silylacetylenes is described, providing *β*,*β*-disubstituted (*E*)- or (*Z*)-alkenylsilanes in satisfactory yields with excellent regio- and stereoselectivity under mild reaction conditions. It represents the first highly regio- and stereoselective addition of boronic acids to aryl and alkenyl silylacetylenes. Moreover, the sequential Pd-catalyzed boron addition/*N*-halosuccinimide-mediated halodesilylation reaction results in a stereodivergent approach to *β*,*β*-disubstituted alkenyl halides, which can serve as versatile synthetic intermediates for the stereodivergent assembly of (*E*)- and (*Z*)-trisubstituted alkenes via transition-metal-catalyzed cross-coupling reactions.



INTRODUCTION

Since the pioneering work of Hayashi,[1] transition-metal-catalyzed addition of boronic acids to alkynes has emerged as a powerful tool for the elaboration of di- or trisubstituted alkenes, which are versatile structural units in organic chemistry.[2,3] In this respect, control of the regioselectivity is an essential issue for the design and development of synthetically useful alkyne hydroarylation reactions. To date, the utilization of strong electron-withdrawing or coordinating groups stands out as an effective strategy to achieve the regioselective boron addition reaction of unsymmetrical acetylenes. Alternatively, substitution of the C−C triple bonds with heteroatoms can sometimes solve the problem of regiocontrol in alkyne hydroarylation with organoboron reagents.[4−7] Studies by Michelet and Genêt indicated that a stereospecific hydroarylation of alkyl trimethylsilylacetylenes could be achieved with a Rh catalyst in a water/toluene biphasic system; however, a 1:1 mixture of two inseparable regioisomers was observed for aryl substrates under the same reaction conditions (Scheme 1).[4] Therefore, the stereospecific addition of organoboron compounds to aryl silylacetylenes constitutes an unmet goal. Recently, regio- and stereoselective hydroarylation of ynol ethers[5] and ynamides[6] has been realized in our group, furnishing stereodefined heteroatom-substituted olefins in good yields. As part of our ongoing studies in this field, we herein describe a Pd-catalyzed regio- and stereoselective addition of boronic acids to silylacetylenes that results in the stereodivergent formation of *β*,*β*-disubstituted alkenylsilanes[8] in good yields with excellent regio- and stereoselectivity. It constitutes the first regio- and stereoselective hydroarylation or hydroalkenylation of aryl and alkenyl silylacetylenes with boronic acids. Meanwhile, an operationally simple and stereodivergent method for the assembly of *β*,*β*-disubstituted (*Z*)- and (*E*)-alkenyl halides[9] via a sequential boron addition/*N*-halosuccinimide-mediated halodesilylation reaction has been developed, thus providing a stereodivergent and expeditous approach to stereodefined trisubstituted (*Z*)- and (*E*)-alkenes by the cross-coupling strategy.

Scheme 1. Summary of This Work



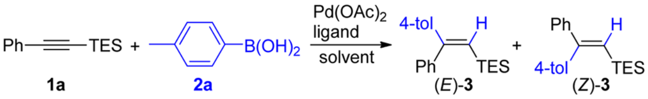
RESULTS AND DISCUSSION

We began our investigations by examining the reaction between 2-triethylsilyl-1-phenylacetylene (**1a**) and 4-tolylboronic acid (**2a**) utilizing $Pd(OAc)_2$ as the catalyst. As shown in Table 1, we found promising results when 5 mol % $Pd(OAc)_2$ and 10 mol % PCy_3 were used in dioxane at room temperature under a N_2 atmosphere for 11 h, which provided *β*,*β*-disubstituted alkenylsilane **3** in 68% yield with excellent stereoselectivity ($E/Z > 96{:}4$) (Table 1, entry 1). Encouraged by this result, we further examined other solvents for this reaction. Replacing dioxane with EtOH, DMF, toluene, or MeCN significantly

Received: April 26, 2014
Published: June 5, 2014

dx.doi.org/10.1021/jo500925p | J. Org. Chem. 2014, 79, 5799−5805

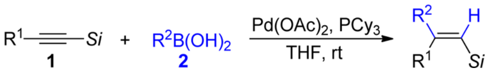
Table 1. Optimization of the Reaction Conditions[a]



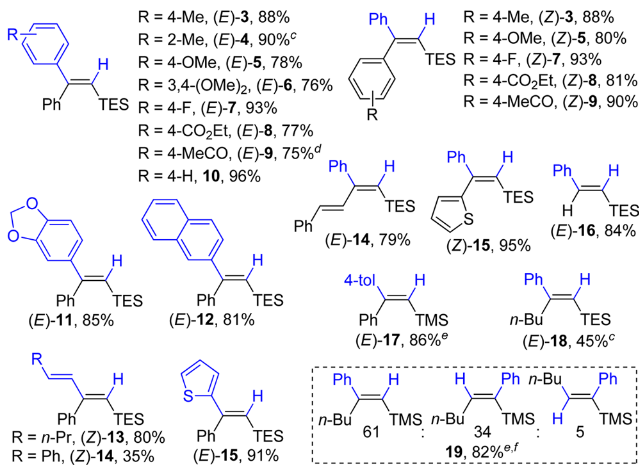
entry	ligand	solvent	E/Z[b]	yield (%)[c]
1	PCy_3	dioxane	>96:4	68
2	PCy_3	EtOH	>98:2	26
3	PCy_3	DMF	–	trace
4	PCy_3	toluene	–	trace
5	PCy_3	CH_3CN	–	trace
6	PCy_3	THF	>97:3	78
7[d]	PCy_3	THF	–	trace
8	PPh_3	THF	–	trace
9	$P(4\text{-tol})_3$	THF	>98:2	10
10	$P(3\text{-tol})_3$	THF	–	trace
11	$P(t\text{-Bu})_3$	THF	–	7
12	Xphos	THF	–	trace
13	dppe	THF	–	trace
14[e]	PCy_3	THF	>97:3	88
15[e,f]	PCy_3	THF	62:38	90

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.50 mmol), $Pd(OAc)_2$ (5 mol %), and ligand (10 mol %) under N_2 at rt for 11 h, unless otherwise specified. [b] Determined by GC. [c] Isolated yields. [d] Under an air atmosphere. [e] **2a** (0.75 mmol) was used. [f] 28 h.

Table 2. Scope of Addition of Boronic Acids to Silylacetylenes[a,b]



R^1/*Si* (**1**)	R^2 (**2**)
Ph/TES, **1a**	4-MeC_6H_4, **2a**
4-MeC_6H_4/TES, **1b**	2-MeC_6H_4, **2b**
4-OMeC_6H_4/TES, **1c**	4-OMeC_6H_4, **2c**
4-FC_6H_4/TES, **1d**	$3,4\text{-(OMe)}_2C_6H_3$, **2d**
$4\text{-CO}_2\text{EtC}_6H_4$/TES, **1e**	4-FC_6H_4, **2e**
4-MeCOC_6H_4/TES, **1f**	$4\text{-CO}_2\text{EtC}_6H_4$, **2f**
(*E*)-styryl/TES, **1g**	4-MeCOC_6H_4, **2g**
2-thienyl/TES, **1h**	Ph, **2h**
H/TES, **1i**	3,4-methylenedioxyphenyl, **2i**
Ph/TMS, **1j**	2-naphthyl, **2j**
n-Bu/TES, **1k**	*n*-Pr, **2k**
n-Bu/TMS, **1l**	(*E*)-styryl, **2l**
3,4-methylenedioxyphenyl/TES, **1m**	2-thienyl, **2m**



[a] Reaction conditions: **1** (0.25 mmol), **2** (0.75 mmol), $Pd(OAc)_2$ (5 mol %), and PCy_3 (10 mol %) under N_2 at 27 °C for 11 h, unless otherwise noted. Except where noted otherwise, the desired products were obtained with >95:5 stereoselectivity and no regioisomers were detected. [b] Isolated yields are shown. [c] 22 h. [d] 2 equiv of **2g** was used. [e] 6 h. [f] A mixture of three isomers (61:34:5) was obtained.

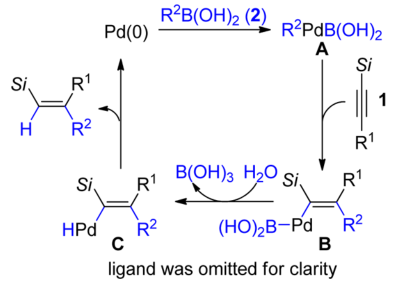
diminished the reaction yield, while using THF as the solvent led to a better result (Table 1, entries 2–6). It should be noted that running the reaction under an atmosphere of air resulted in almost no product formation (Table 1, entry 7), indicating that a Pd(0) species might be involved in this transformation. A brief scan over ligands demonstrated that PCy_3 served as the privileged ligand (Table 1, entries 8–13). The utilization of 3 equiv instead of 2 equiv of **2a** resulted in full conversion of **1a**, generating (*E*)-**3** in 88% isolated yield with >97% *E* selectivity (Table 1, entry 14). Interestingly, increasing the reaction time from 11 to 28 h dramatically decreased the stereoselectivity (Table 1, entry 15),[10] implying that (*E*)-**3** might be the kinetically controlled product.

Next, we carried out a substrate scope study on boronic acids (Table 2). In particular, the steric effect of the boronic acid had little influence on the hydroarylation reaction when there was substitution at the *ortho* position of the aryl ring of **2** [Table 2, (*E*)-**3** and (*E*)-**4**]. The reaction was insensitive to changes in the electronic nature of the boronic acid employed, delivering the desired *β*,*β*-disubstituted (*E*)-alkenylsilanes in satisfactory yields with excellent stereoselectivity [Table 2, (*E*)-**5** through (*E*)-**9**]. Pleasingly, the reaction also applied well to alkenylboronic acids, as demonstrated by the production of 1,3-dienylsilanes (*Z*)-**13** and (*Z*)-**14**. Heteroarylboronic acid **2m** also participated well in this transformation, giving (*E*)-**15** in 91% yield.

The scope of this reaction with regard to silylacetylenes was subsequently investigated. For example, the addition of $PhB(OH)_2$ (**2h**) to silylacetylenes **1b** and **1c** provided (*Z*)-**3** and (*Z*)-**5** in yields of 88 and 80%, respectively. Hence, it enables a stereodivergent protocol for the construction of *β*,*β*-disubstituted (*E*)- and (*Z*)-alkenylsilanes by a simple choice of different types of starting materials. A variety of functional groups such as F, CO_2Et, Ac, and alkenyl groups were perfectly tolerated under the optimized reaction conditions [Table 2, (*Z*)-**7** through (*Z*)-**9** and (*E*)-**14**]. The presence of sulfur-containing heterocycles did not interfere with the hydrophenylation reaction [Table 2, (*Z*)-**15**].[11] Furthermore, triethylsilylacetylene (**1i**) was also good for this reaction, giving (*E*)-**16**[12] in 84% yield. Treatment of 2-trimethylsilyl-1-phenylacetylene (**1j**) with **2a** under the standard conditions for 6 h furnished (*E*)-**17** in 86% yield. Interestingly, the hydrophenylation of 1-hexynyltriethylsilane (**1k**) formed the expected *β*,*β*-disubstituted alkenylsilane (*E*)-**18** with excellent regio- and stereoselectivity after 22 h, while the reaction of 1-hexynyltrimethylsilane (**1l**) enabled the formation of **19** as a mixture of three isomers under the reaction conditions for 6 h. These results indicated that the steric hindrance of silyl groups could improve the regioselectivity of carbopalladation of alkynes.[13] The regio- and stereochemistry of this Pd-catalyzed boron addition reaction was determined by NOE analysis (see the Supporting Information).

On the basis of the above results and previous reports,[2] a plausible mechanism for this Pd-catalyzed regio- and stereoselective addition of boronic acids to silylacetylenes is proposed in Scheme 2. Palladium intermediate **A**, generated by the oxidative addition of Pd(0) species with the boronic acid (**2**),[5a] reacts with **1** to form species **B** regio- and stereoselectively, since the silyl group can stabilize the adjacent C–Pd bond in the carbopalladation step.[14] Then hydrolysis of the Pd–B bond of **B** and subsequent reductive elimination produces the *β*,*β*-

Scheme 2. A Possible Mechanism

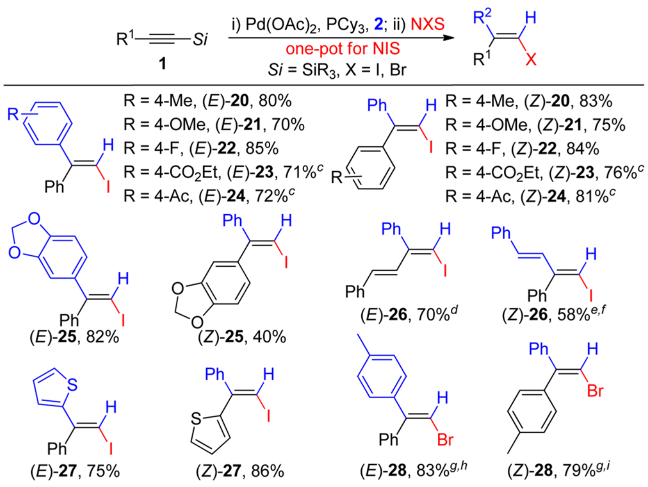


disubstituted alkenylsilane with regeneration of the Pd(0) species. Of course, the hydropalladation mechanism[2a] cannot be ruled out at the current stage.

On the other hand, stereodefined *β,β*-disubstituted alkenyl halides are versatile building blocks in organic synthesis that can act as convenient precursors for the preparation of stereodefined trisubstituted alkenes via transition-metal-catalyzed cross-coupling reactions. However, there are only a limited number of methods for the regio- and stereoselective construction of these motifs.[9] With the current boron addition reaction in hand, we decided to explore a mild as well as efficient protocol for the synthesis of *β,β*-disubstituted alkenyl halides.

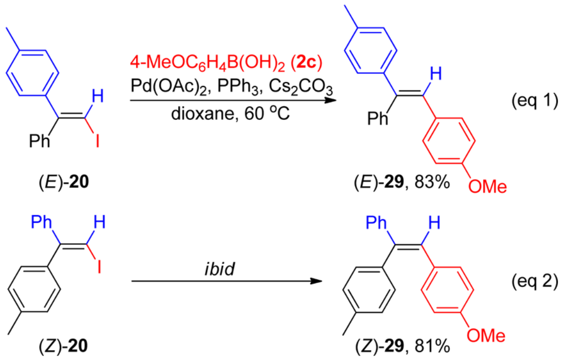
After some trials, we found that Pd-catalyzed coupling of **2a** and **1a** followed by stirring with 2 equiv of NIS[15] in MeCN at room temperature for 10 h generated *β,β*-diarylethenyl iodide (*E*)-**20** in 80% yield based on **1a**, whereas the sequential hydrophenylation/iododesilylation process from **1b** produced (*Z*)-**20** in 83% yield (Table 3). Thus, this approach offers a stereodivergent and one-pot route to *β,β*-disubstituted vinylic halides. The structure of (*E*)-**25** was determined by X-ray crystallography. Interestingly, subjecting **1g** to the one-pot procedure gave rise to 1,3-dienyl iodide (*E*)-**26** in 70% yield with excellent regio- and stereoselectivity, while hydroalkenylation of **1j** with **2l** and subsequent iododesilylation produced (*Z*)-**26** with moderate stereoselectivity (*Z*/*E* = 74:26), probably because of the reduced thermodynamic stability. In contrast, the one-pot process was not suitable for the formation of alkenyl bromides, but fortunately, a two-step procedure was found to be successful, leading to (*E*)- and (*Z*)-**28** in high yields with excellent stereoselectivity using NBS as the halogenation reagent.

Table 3. Stereodivergent Synthesis of *β,β*-Disubstituted Alkenyl Halides[a,b]



[a]Reaction conditions: (i) **1** (0.25 mmol), **2** (0.75 mmol), $Pd(OAc)_2$ (5 mol %), and PCy_3 (10 mol %) under N_2 at rt for 11 h; (ii) NIS (0.50 mmol), MeCN, rt, 10 h. *Si* = $SiEt_3$; NIS = *N*-iodosuccinimide; NBS = *N*-bromosuccinimide. [b]Isolated yields are shown. [c]NIS (1.0 mmol) and 36 h were used. [d]2 h was used for iododesilylation reaction. [e]**1j** was employed as the starting material and 1 h was used for iododesilylation reaction. [f]*Z*/*E* = 74:26. [g]A two-step procedure was used. [h]*E*/*Z* = 91:9. [i]*Z*/*E* = 91:9.

Finally, the synthetic usefulness of this reaction was further exemplified by the stereodivergent access to trisubstituted alkenes that it provides. For example, treatment of (*E*)-**20** with 1.2 equiv of **2c**, 5 mol % $Pd(OAc)_2$, 10 mol % PPh_3, and 1.5 equiv of Cs_2CO_3 in dioxane at 60 °C overnight gave (*E*)-**29**[16] in 83% yield upon isolation (eq 1), while the Suzuki–Miyaura coupling[17] of (*Z*)-**20** provided (*Z*)-**29**[16] in high yield (eq 2). Thus, both trisubstituted (*E*)- and (*Z*)-olefins can be synthesized by this protocol.



■ CONCLUSION

We have developed a simple catalytic system to achieve regio- and stereoselective boron addition of silylacetylenes with the readily available $Pd(OAc)_2$ catalyst under mild reaction conditions. Notably, it represents the first highly regio- and stereoselective addition of boronic acids to aryl and alkyl silylacetylenes. A variety of *β,β*-disubstituted (*E*)- or (*Z*)-alkenylsilanes can be successfully assembled in satisfactory yields with excellent regio- and stereoselectivity. Moreover, a stereodivergent approach to *β,β*-disubstituted alkenyl halides has been realized via the Pd-catalyzed boron addition and subsequent halodesilylation reaction with NIS or NBS. Ultimately, this provides an effective and stereodivergent route to trisubstituted (*E*)- and (*Z*)-alkenes via the Suzuki–Miyaura coupling of *β,β*-disubstituted alkenyl halides thus obtained, and therefore, we believe that it will be useful for the construction of complex molecules.

■ EXPERIMENTAL SECTION

General. Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. Toluene, THF, and dioxane were distilled from sodium prior to use. ^1H, ^{13}C, and ^{19}F NMR spectra were measured on a 600 MHz NMR spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shifts (*δ*) are given in parts per million relative to TMS, and the coupling constants are given in hertz. High-resolution mass spectrometry (HRMS) analyses were carried out using a TOF MS instrument with an ESI source. Column chromatography was performed using silica gel (300–400 mesh).

General Procedure for the Pd-Catalyzed Regio- and Stereoselective Addition of Boronic Acids to Silylacetylenes. To a mixture of **2a** (102 mg, 0.75 mmol), $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol), and PCy_3 (7.0 mg, 0.025 mmol) was added a solution of **1a** (54 mg, 0.25 mmol) in 1 mL of THF under a nitrogen atmosphere. After 11 h of stirring at 27 °C, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel using petroleum ether as the eluent gave 68 mg (88% yield) of (*E*)-**3** as a colorless oil. R_f = 0.74 (petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 7.30−7.35 (m, 3H), 7.15−7.22 (m, 4H), 7.05−7.10 (m, 2H), 6.20 (s, 1H), 2.32 (s, 3H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.34 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.8, 143.0, 140.8, 137.4, 129.5, 128.7, 127.7, 127.3, 127.1, 125.5, 21.1, 7.5, 4.4; HRMS (ESI) calcd for $C_{21}H_{29}Si$ $(M + H)^+$ 309.2039, found 309.2026.

*Compound (Z)-**3**.* 88% yield (68 mg); colorless oil; R_f = 0.72 (petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 7.21−7.30 (m, 5H), 7.07−7.14 (m, 4H), 6.20 (s, 1H), 2.37 (s, 3H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.37 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1, 143.9, 139.9, 137.0, 129.4, 128.4, 127.9, 127.5, 127.3, 126.3, 21.3, 7.6, 4.5; HRMS (ESI) calcd for $C_{21}H_{29}Si$ $(M + H)^+$ 309.2039, found 309.2017.

*Compound (E)-**4**.* 90% yield (69 mg); colorless oil; R_f = 0.73 (petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 7.23−7.27 (m, 3H), 7.20−7.22 (m, 2H), 7.10−7.18 (m, 4H), 5.74 (s, 1H), 2.14 (s, 3H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.47 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 146.0, 143.3, 135.0, 130.2, 129.7, 129.5, 128.6, 127.6, 127.4, 127.1, 125.4, 20.6, 7.6, 4.8; HRMS (ESI) calcd for $C_{21}H_{29}Si$ $(M + H)^+$ 309.2039, found 309.2036.

*Compound (E)-**5**.* 78% yield (63 mg); colorless oil; R_f = 0.60 (petroleum ether/EtOAc = 20:1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.30−7.35 (m, 3H), 7.16−7.24 (m, 4H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.13 (s, 1H), 3.79 (s, 3H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.34 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 157.4, 143.0, 136.3, 129.5, 128.4, 127.7, 127.3, 124.2, 113.3, 55.2, 7.5, 4.5; HRMS (ESI) calcd for $C_{21}H_{29}OSi$ $(M + H)^+$ 325.1988, found 325.1968.

*Compound (Z)-**5**.* 80% yield (65 mg); colorless oil; R_f = 0.61 (petroleum ether/EtOAc = 20:1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.22−7.30 (m, 5H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.17 (s, 1H), 3.84 (s, 3H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.39 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 157.8, 144.0, 135.3, 130.6, 127.9, 127.5, 127.3, 126.3, 113.0, 55.2, 7.6, 4.5; HRMS (ESI) calcd for $C_{21}H_{29}OSi$ $(M + H)^+$ 325.1988, found 325.1977.

*Compound (E)-**6**.* 76% yield (67 mg); colorless oil; R_f = 0.74 (petroleum ether/CH_2Cl_2 = 1:1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.31−7.37 (m, 3H), 7.19−7.23 (m, 2H), 6.87−6.89 (m, 1H), 6.74−6.78 (m, 2H), 6.14 (s, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.35 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 148.8, 148.3, 142.8, 136.5, 129.5, 127.7, 127.3, 124.5, 120.2, 110.3, 110.2, 55.9, 55.8, 7.6, 4.4; HRMS (ESI) calcd for $C_{22}H_{31}O_2Si$ $(M + H)^+$ 355.2093, found 355.2081.

*Compound (E)-**7**.* 93% yield (73 mg); colorless oil; R_f = 0.72 (petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 7.30−7.39 (m, 3H), 7.22−7.27 (m, 2H), 7.14−7.22 (m, 2H), 6.92−6.96 (m, 2H), 6.17 (s, 1H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.36 (q, *J* = 7.9 Hz, 6H); ^{19}F NMR ($CDCl_3$, 565 MHz) δ −115.1; ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5 (d, *J* = 245.6 Hz), 157.0, 142.7, 139.9 (d, *J* = 3.2 Hz), 129.5, 128.9 (d, *J* = 7.9 Hz), 127.9, 127.6, 126.5, 114.8 (d, *J* = 21.2 Hz), 7.6, 4.4; HRMS (ESI) calcd for $C_{20}H_{26}FSi$ $(M + H)^+$ 313.1788, found 313.1782.

*Compound (Z)-**7**.* 93% yield (73 mg); colorless oil; R_f = 0.70 (petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 7.22−7.28 (m, 5H), 7.15−7.19 (m, 2H), 7.00−7.05 (m, 2H), 6.25 (s, 1H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.37 (q, *J* = 7.9 Hz, 6H); ^{19}F NMR (565 MHz, $CDCl_3$) δ −114.8; ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3 (d, *J* = 246.1 Hz), 156.9, 143.4, 138.8 (d, *J* = 3.5 Hz), 131.1 (d, *J* = 7.9 Hz), 128.0, 127.7, 127.2, 127.2, 114.7 (d, *J* = 21.3 Hz), 7.5, 4.4; HRMS (ESI) calcd for $C_{20}H_{26}FSi$ $(M + H)^+$ 313.1788, found 313.1779.

*Compound (E)-**8**.* 77% yield (70 mg); colorless oil; R_f = 0.60 (petroleum ether/EtOAc = 20:1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.31−7.36 (m, 5H), 7.15−7.24 (m, 2H), 6.35 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.38 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4, 157.1, 147.7, 142.1, 129.5, 129.4, 129.4, 129.3, 127.9, 127.6, 127.1, 60.8, 14.3, 7.5, 4.3; HRMS (ESI) calcd for $C_{23}H_{31}O_2Si$ $(M + H)^+$ 367.2093, found 367.2083.

*Compound (Z)-**8**.* 81% yield (74 mg); colorless oil; R_f = 0.58 (petroleum ether/EtOAc = 20:1); ^1H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.21−7.32 (m, 7H), 6.31 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.37 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 157.0, 147.6, 142.9, 129.5, 129.4, 129.1, 128.1, 127.8, 127.7, 127.1, 61.0, 14.3, 7.5, 4.4; HRMS (ESI) calcd for $C_{23}H_{31}O_2Si$ $(M + H)^+$ 367.2093, found 367.2074.

*Compound (E)-**9**.* 75% yield (63 mg); colorless oil; R_f = 0.36 (petroleum ether/EtOAc = 20:1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.33−7.38 (m, 5H), 7.15−7.22 (m, 2H), 6.37 (s, 1H), 2.57 (s, 3H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.38 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 157.0, 148.0, 142.1, 135.9, 129.9, 129.5, 128.2, 128.0, 127.7, 127.4, 26.7, 7.6, 4.4; HRMS (ESI) calcd for $C_{22}H_{29}OSi$ $(M + H)^+$ 337.1988, found 337.1961.

*Compound (Z)-**9**.* 90% yield (76 mg); colorless oil; R_f = 0.36 (petroleum ether/EtOAc = 20:1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.22−7.29 (m, 5H), 6.31 (s, 1H), 2.65 (s, 3H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.37 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9, 156.8, 148.0, 142.9, 136.0, 129.8, 128.1, 127.9, 127.9, 127.8, 127.1, 26.7, 7.5, 4.4; HRMS (ESI) calcd for $C_{22}H_{29}OSi$ $(M + H)^+$ 337.1988, found 337.1961.

*Compound **10**.* 96% yield (71 mg); colorless oil; R_f = 0.69 (petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 7.30−7.40 (m, 3H), 7.15−7.30 (m, 7H), 6.24 (s, 1H), 0.86 (t, *J* = 7.9 Hz, 9H), 0.36 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 158.0, 143.6, 142.8, 129.5, 128.0, 127.7, 127.5, 127.4, 127.2, 126.7, 7.5, 4.4; HRMS (ESI) calcd for $C_{20}H_{27}Si$ $(M + H)^+$ 295.1882, found 295.1877.

*Compound (E)-**11**.* 85% yield (72 mg); colorless oil; R_f = 0.67 (petroleum ether/EtOAc = 20:1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.27−7.38 (m, 3H), 7.16−7.20 (m, 2H), 6.82−6.85 (m, 1H), 6.67−6.72 (m, 2H), 6.11 (s, 1H), 5.92 (s, 2H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.34 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4, 147.5, 147.2, 142.9, 138.3, 129.5, 127.7, 127.4, 125.0, 121.4, 107.6, 107.5, 101.0, 7.5, 4.4; HRMS (ESI) calcd for $C_{21}H_{27}O_2Si$ $(M + H)^+$ 339.1780, found 339.1771.

*Compound (E)-**12**.* 81% yield (70 mg); colorless oil; R_f = 0.72 (petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 7.69−7.79 (m, 3H), 7.55−7.58 (m, 2H), 7.30−7.46 (m, 5H), 7.24−7.28 (m, 2H), 6.39 (s, 1H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.40 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9, 142.8, 140.8, 133.1, 132.8, 129.6, 128.4, 127.8, 127.5, 127.5, 127.4, 127.4, 126.7, 126.0, 126.0, 125.2, 7.6, 4.5; HRMS (ESI) calcd for $C_{24}H_{29}Si$ $(M + H)^+$ 345.2039, found 345.2033.

*Compound (Z)-**13**.* 80% yield (57 mg); colorless oil; R_f = 0.70 (petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 7.26−7.35 (m, 3H), 7.11−7.14 (m, 2H), 6.33 (d, *J* = 15.5 Hz, 1H), 5.64 (s, 1H), 5.13−5.22 (m, 1H), 2.02 (q, *J* = 7.1 Hz, 2H), 1.31−1.38 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H), 0.80 (t, *J* = 7.9 Hz, 9H), 0.25 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.2, 141.4, 137.1, 134.4, 129.2, 127.8, 127.5, 126.9, 34.7, 22.3, 13.8, 7.5, 4.2; HRMS (ESI) calcd for $C_{19}H_{31}Si$ $(M + H)^+$ 287.2195, found 287.2182.

*Compound (E)-**14**.* 79% yield (63 mg); colorless oil; R_f = 0.71 (petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 7.29−7.38 (m, 9H), 7.20−7.25 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.70 (s, 1H), 1.03 (t, *J* = 7.9 Hz, 9H), 0.78 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.5, 143.6, 137.4, 133.1, 131.9, 130.0, 128.7, 128.5, 128.0, 127.7, 127.2, 126.5, 7.7, 5.1; HRMS (ESI) calcd for $C_{22}H_{29}Si$ $(M + H)^+$ 321.2039, found 321.2030.

*Compound (Z)-**14**.* 35% yield (28 mg); colorless oil; R_f = 0.70 (petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 7.32−7.38 (m, 5H), 7.24−7.29 (m, 2H), 7.17−7.22 (m, 3H), 7.07 (d, *J* = 15.9 Hz, 1H), 6.02 (d, *J* = 16.0 Hz, 1H), 5.94 (s, 1H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.29 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.9, 140.7, 137.2, 135.5, 132.0, 131.5, 129.3, 128.5, 127.7, 127.5, 127.2, 126.6, 7.5, 4.2; HRMS (ESI) calcd for $C_{22}H_{29}Si$ $(M + H)^+$ 321.2039, found 321.2051.

*Compound (E)-**15**.* 91% yield (68 mg); colorless oil; R_f = 0.69 (petroleum ether); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.31−7.37 (m, 3H), 7.26−7.29 (m, 2H), 7.17−7.19 (m, 1H), 6.86−6.89 (m, 1H), 6.55−6.57 (m, 1H), 6.22 (s, 1H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.32 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 151.0, 149.1, 141.7, 129.2, 127.7, 127.7, 127.5, 126.0, 125.4, 124.9, 7.5, 4.2; HRMS (ESI) calcd for $C_{18}H_{24}SSi$ $(M + H)^+$ 301.1446, found 301.1438.

*Compound (Z)-**15**.* 95% yield (71 mg); colorless oil; R_f = 0.71 (petroleum ether); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.26−7.36 (m, 6H), 6.95−7.03 (m, 2H), 6.26 (s, 1H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.49 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 150.5, 144.1, 143.8, 130.5, 128.0, 127.9, 127.7, 127.2, 126.4, 125.7, 7.7, 4.4; HRMS (ESI) calcd for $C_{18}H_{24}SSi$ $(M + H)^+$ 301.1446, found 301.1424.

*Compound (E)-**16**.*[12] 84% yield (46 mg); colorless oil; R_f = 0.70 (petroleum ether); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.41−7.47 (m, 2H), 7.30−7.34 (m, 2H), 7.22−7.26 (m, 1H), 6.89 (d, *J* = 19.3 Hz, 1H), 6.43 (d, *J* = 19.3 Hz, 1H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.66 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 144.8, 138.5, 128.5, 127.9, 126.3, 125.9, 7.4, 3.5.

*Compound (E)-**17**.* 86% yield (57 mg); colorless oil; R_f = 0.72 (petroleum ether); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.53−7.58 (m, 3H), 7.38−7.44 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.48 (s, 1H), 2.54 (s, 3H), 0.10 (s, 9H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 156.9, 142.7, 140.4, 137.4, 129.6, 128.7, 128.5, 127.8, 127.2, 127.1, 21.1, 0.0; HRMS (ESI) calcd for $C_{18}H_{23}Si$ $(M + H)^+$ 267.1569, found 267.1557.

*Compound (E)-**18**.* 45% yield (31 mg); colorless oil; R_f = 0.76 (petroleum ether); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.36−7.39 (m, 2H), 7.28−7.33 (m, 2H), 7.22−7.26 (m, 1H), 5.63 (s, 1H), 2.52−2.63 (m, 2H), 1.26−1.34 (m, 4H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.86 (t, *J* = 6.8 Hz, 3H), 0.68 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 158.9, 144.2, 128.1, 127.0, 126.2, 124.6, 35.3, 31.5, 23.0, 14.0, 7.7, 4.8; HRMS (ESI) calcd for $C_{18}H_{31}Si$ $(M + H)^+$ 275.2195, found 275.2186.

*Compound **19**.* 82% yield (48 mg); colorless oil; R_f = 0.75 (petroleum ether); ^{1}H NMR (600 MHz, CDCl$_3$) data for the major isomer[18] δ 7.03−7.21 (m, 5H), 5.54 (s, 1H), 2.38−2.44 (m, 2H), 1.11−1.15 (m, 4H), 0.66−0.70 (m, 3H), 0.00 (s, 9H).

*Compound (E)-**20**.* 80% yield (64 mg); white solid, mp 49−51 °C; R_f = 0.51 (petroleum ether); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.34−7.44 (m, 3H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.05−7.13 (m, 4H), 6.87 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 152.5, 142.0, 138.4, 138.1, 129.4, 129.0, 128.3, 127.9, 127.4, 77.9, 21.2; HRMS (ESI) calcd for $C_{15}H_{14}I$ $(M + H)^+$ 321.0140, found 321.0131.

*Compound (Z)-**20**.* 83% yield (66 mg); white solid, mp 34−36 °C; R_f = 0.53 (petroleum ether); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.25−7.29 (m, 3H), 7.19−7.23 (m, 4H), 7.14−7.18 (m, 2H), 6.88 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 152.6, 141.4, 138.8, 137.8, 129.3, 129.0, 128.3, 128.0, 127.6, 78.5, 21.4; HRMS (ESI) calcd for $C_{15}H_{14}I$ $(M + H)^+$ 321.0140, found 321.0115.

*Compound (E)-**21**.* 70% yield (59 mg); white solid, mp 69−71 °C; R_f = 0.61 (petroleum ether/EtOAc = 20:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.33−7.44 (m, 3H), 7.25 (d, *J* = 6.7 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.77−6.81 (m, 3H), 3.78 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 159.5, 152.1, 142.1, 133.9, 129.4, 128.8, 128.3, 127.9, 113.7, 76.6, 55.3; HRMS (ESI) calcd for $C_{15}H_{14}IO$ $(M + H)^+$ 337.0089, found 337.0076.

*Compound (Z)-**21**.*[19] 75% yield (63 mg); colorless oil; R_f = 0.63 (petroleum ether/EtOAc = 20:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.26−7.30 (m, 3H), 7.18−7.24 (m, 4H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.84 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 159.2, 152.2, 141.6, 133.9, 130.8, 128.3, 128.0, 127.7, 113.5, 78.2, 55.2.

*Compound (E)-**22**.* 85% yield (69 mg); colorless oil; R_f = 0.60 (petroleum ether); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.32−7.45 (m, 3H), 7.23−7.27 (m, 2H), 7.16−7.23 (m, 2H), 6.93−6.98 (m, 2H), 6.88 (s, 1H); ^{19}F NMR (565 MHz, CDCl$_3$) δ −113.6; ^{13}C NMR (151 MHz, CDCl$_3$) δ 162.6 (d, *J* = 248.5 Hz), 151.7, 141.7, 137.4 (d, *J* = 3.3 Hz), 129.4, 129.2 (d, *J* = 8.2 Hz), 128.4, 128.1, 115.3 (d, *J* = 21.5 Hz), 78.5; HRMS (ESI) calcd for $C_{14}H_{11}FI$ $(M + H)^+$ 324.9889, found 324.9882.

*Compound (Z)-**22**.* 84% yield (68 mg); colorless oil; R_f = 0.62 (petroleum ether); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.18−7.30 (m, 7H), 7.07−7.12 (m, 2H), 6.92 (s, 1H); ^{19}F NMR (565 MHz, CDCl$_3$) δ −113.3; ^{13}C NMR (151 MHz, CDCl$_3$) δ 162.3 (d, *J* = 247.5 Hz), 151.7, 141.0, 137.6 (d, *J* = 3.6 Hz), 131.3 (d, *J* = 8.2 Hz), 128.4, 128.2, 127.5, 115.3 (d, *J* = 21.6 Hz), 79.3; HRMS (ESI) calcd for $C_{14}H_{11}FI$ $(M + H)^+$ 324.9889, found 324.9880.

*Compound (E)-**23**.* 71% yield (67 mg); colorless oil; R_f = 0.50 (petroleum ether/EtOAc = 20:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.33−7.47 (m, 3H), 7.22−7.30 (m, 4H), 7.09 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 166.2, 151.9, 145.1, 141.2, 129.8, 129.6, 129.3, 128.5, 128.2, 127.4, 81.4, 61.0, 14.3; HRMS (ESI) calcd for $C_{17}H_{16}IO_2$ $(M + H)^+$ 379.0195, found 379.0180.

*Compound (Z)-**23**.* 76% yield (72 mg); white solid, mp 37−39 °C; R_f = 0.49 (petroleum ether/EtOAc = 20:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.10 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.25−7.31 (m, 3H), 7.16−7.20 (m, 2H), 7.00 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 166.2, 151.9, 146.3, 140.5, 130.0, 129.6, 129.5, 128.5, 128.3, 127.4, 79.6, 61.0, 14.3; HRMS (ESI) calcd for $C_{17}H_{16}IO_2$ $(M + H)^+$ 379.0195, found 379.0198.

*Compound (E)-**24**.* 72% yield (62.5 mg); white solid, mp 87−89 °C; R_f = 0.30 (petroleum ether/EtOAc = 20:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.38−7.46 (m, 3H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 6.9 Hz, 2H), 7.11 (s, 1H), 2.57 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 197.4, 151.7, 145.2, 141.1, 136.2, 129.3, 128.5, 128.4, 128.2, 127.6, 81.8, 26.6; HRMS (ESI) calcd for $C_{16}H_{14}IO$ $(M + H)^+$ 349.0089, found 349.0102.

*Compound (Z)-**24**.* 81% yield (70.5 mg); white solid, mp 80−82 °C; R_f = 0.30 (petroleum ether/EtOAc = 20:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.26−7.32 (m, 3H), 7.17−7.20 (m, 2H), 7.00 (s, 1H), 2.64 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 197.6, 151.8, 146.6, 140.4, 136.4, 129.7, 128.5, 128.4, 128.3, 127.4, 79.8, 26.6; HRMS (ESI) calcd for $C_{16}H_{14}IO$ $(M + H)^+$ 349.0089, found 349.0097.

*Compound (E)-**25**.* 82% yield (72 mg); white solid, mp 79−81 °C; R_f = 0.56 (petroleum ether/EtOAc = 20:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.34−7.43 (m, 3H), 7.24 (d, *J* = 7.0 Hz, 2H), 6.80 (s, 1H), 6.66−6.73 (m, 3H), 5.93 (s, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 152.1, 147.6, 147.6, 141.9, 135.5, 129.4, 128.3, 128.0, 121.8, 108.0, 107.9, 101.2, 77.3; HRMS (ESI) calcd for $C_{15}H_{12}IO_2$ $(M + H)^+$ 350.9882, found 350.9878.

Crystal data for (*E*)-**25** ($C_{15}H_{11}IO_2$, 350.14): monoclinic, space group $P2_1$, a = 9.8867(5) Å, b = 5.6677(3) Å, c = 11.9084(6) Å, U = 660.06(6) Å^3, Z = 2, T = 293(2) K, absorption coefficient 2.416 mm^{-1}, reflections collected 3006, independent reflections 2300 (R_{int} = 0.0290), refinement by full-matrix least-squares on F^2, data/restraints/parameters 2300/1/163, goodness of fit on F^2 = 1.005, final R indices [$I > 2\sigma(I)$] R_1 = 0.0409, wR_2 = 0.0776, R indices (all data) R_1 = 0.0513, wR_2 = 0.0851, largest diff. peak and hole 0.696 and −0.478 e·Å^{-3}. Crystallographic data for the structure of (*E*)-**25** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 997720.

*Compound (Z)-**25**.* 40% yield (35 mg); colorless oil; R_f = 0.55 (petroleum ether/EtOAc = 20:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.21−7.29 (m, 5H), 6.72−6.77 (m, 2H), 6.71−6.79 (m, 2H), 6.00 (s, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 152.2, 147.5, 147.2, 141.3, 135.5, 128.3, 128.1, 127.6, 123.3, 110.0, 108.2, 101.2, 78.7; HRMS (ESI) calcd for $C_{15}H_{12}IO_2$ $(M + H)^+$ 350.9882, found 350.9866.

*Compound (E)-**26**.* 70% yield (58 mg); colorless oil; R_f = 0.64 (petroleum ether); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.42−7.45 (m, 2H), 7.35−7.39 (m, 3H), 7.24−7.33 (m, 6H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.36 (s, 1H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 149.2, 139.9, 136.6, 136.5, 130.3, 128.8, 128.7, 128.3, 128.3, 128.0, 126.9, 82.1; HRMS (ESI) calcd for $C_{16}H_{14}I$ $(M + H)^+$ 333.0140, found 333.0132.

*Compound (Z)-**26**.* 58% yield (48 mg); colorless oil; *Z*/*E* = 74:26; R_f = 0.66 (petroleum ether); ^{1}H NMR (600 MHz, CDCl$_3$) data for the major isomer δ 7.48–7.18 (m, 10H), 7.06 (d, J = 15.8 Hz, 1H), 6.76 (s, 1H), 6.15 (d, J = 15.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) data for the major isomer δ 152.2, 139.8, 136.6, 132.7, 130.2, 129.1, 128.6, 128.5, 128.0, 127.9, 126.6, 84.2; HRMS (ESI) calcd for $C_{16}H_{14}I$ $(M + H)^+$ 333.0140, found 333.0149.

*Compound (E)-**27**.* 75% yield (59 mg); colorless oil; R_f = 0.66 (petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40–7.45 (m, 3H), 7.27–7.30 (m, 2H), 7.22–7.25 (m, 1H), 6.97 (s, 1H), 6.90 (m, 1H), 6.66–6.70 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.2, 144.6, 141.2, 129.1, 128.4, 128.3, 127.4, 126.5, 125.9, 77.5; HRMS (ESI) calcd for $C_{12}H_{10}IS$ $(M + H)^+$ 312.9548, found 312.9533.

*Compound (Z)-**27**.* 86% yield (67 mg); colorless oil; R_f = 0.68 (petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, J = 5.0 Hz, 1H), 7.27–7.35 (m, 5H), 7.14–7.18 (m, 1H), 7.04–7.10 (m, 1H), 6.76 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 142.3, 142.2, 129.7, 128.3, 128.3, 128.0, 126.6, 126.6, 78.2; HRMS (ESI) calcd for $C_{12}H_{10}IS$ $(M + H)^+$ 312.9548, found 312.9546.

*Compound (E)-**28**.*[20] 83% yield (57 mg); colorless oil; E/Z = 91:9; R_f = 0.58 (petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27–7.42 (m, 5H), 7.08–7.10 (m, 4H), 6.72 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.6, 139.2, 138.0, 137.9, 129.6, 129.1, 128.2, 127.9, 127.5, 104.3, 21.1.

*Compound (Z)-**28**.* 79% yield (54 mg); colorless oil; Z/E = 91:9; R_f = 0.56 (petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26–7.30 (m, 3H), 7.18–7.23 (m, 6H), 6.72 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.7, 140.9, 137.8, 136.0, 129.6, 128.9, 128.4, 128.0, 127.7, 104.8, 21.4; HRMS (ESI) calcd for $C_{15}H_{14}Br$ $(M + H)^+$ 273.0279, found 273.0281.

General Procedure for the Stereodivergent Synthesis of Trisubstituted Alkenes via Suzuki–Miyaura Coupling. To a mixture of **2c** (46 mg, 0.3 mmol), $Pd(OAc)_2$ (2.8 mg, 0.0125 mmol), PPh_3 (6.6 mg, 0.025 mmol), and Cs_2CO_3 (122 mg, 0.375 mmol) was added a solution of (*E*)-**20** (80 mg, 0.25 mmol) in 1 mL of dioxane under a nitrogen atmosphere. After stirring at 60 °C overnight, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography (petroleum ether/EtOAc = 50:1) on silica gel generated 62 mg (83% yield) of (*E*)-**29**[16] as a colorless oil. R_f = 0.36 (petroleum ether/EtOAc = 50:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28–7.35 (m, 3H), 7.16–7.23 (m, 4H), 7.09 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 6.88 (s, 1H), 6.65 (d, J = 8.8 Hz, 2H), 3.72 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2, 140.7, 140.7, 140.4, 137.0, 130.7, 130.4, 130.1, 128.8, 128.6, 127.25, 127.16, 126.8, 113.3, 55.1, 21.1.

*Compound (Z)-**29**.*[16] 81% yield (56 mg); colorless oil; R_f = 0.65 (petroleum ether/EtOAc = 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22–7.32 (m, 5H), 7.07–7.16 (m, 4H), 6.98 (d, J = 8.6 Hz, 2H), 6.87 (s, 1H), 6.67 (d, J = 8.7 Hz, 2H), 3.73 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.2, 143.8, 140.5, 137.5, 136.9, 130.7, 130.2, 130.1, 129.4, 128.1, 127.4, 127.4, 127.1, 113.3, 55.1, 21.3.

1-(4-Methylphenyl)-1-phenylethene.[21] To 1 mL of HOAc was added **3** (66.5 mg, 0.25 mmol, E/Z = 58:42). After 10 h of stirring at 90 °C, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over Na_2SO_4, and concentrated. Column chromatography on silica gel using petroleum ether as the eluent gave 42 mg (87% yield) of the title compound as a colorless oil. R_f = 0.62 (petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28–7.36 (m, 5H), 7.23 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 5.43 (s, 1H), 5.40 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.8, 141.6, 138.6, 137.5, 128.8, 128.3, 128.12, 128.09, 127.6, 113.6, 21.2.

ASSOCIATED CONTENT

Supporting Information

Spectroscopic data for products **3**–**29** and 1-(4-methylphenyl)-1-phenylethene and X-ray data for (*E*)-**25** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful for the financial support from the Natural Science Foundation of Zhejiang Province (LR12B02001), the National Natural Science Foundation of China (21172199), and the Open Research Fund of the Key Laboratory of the Ministry of Education for Advanced Catalysis Materials (ZJHX201310).

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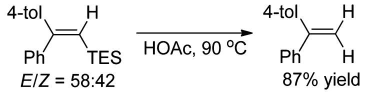

(11) It should be noted that decomposition of (Z)-**15** was observed upon purification by silica gel chromatography, and therefore, crude NMR spectra were used for (Z)-**15** in the Supporting Information.

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