JOC The Journal of Organic Chemistry

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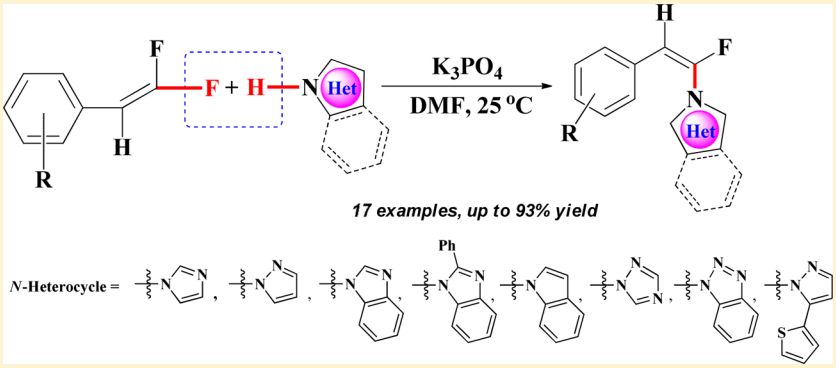
Synthesis of *N*-(α-Fluorovinyl)azoles by the Reaction of Difluoroalkenes with Azoles

Yang Xiong, Xuxue Zhang, Tao Huang, and Song Cao*

Shanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology, Shanghai 200237, China

Supporting Information



ABSTRACT: A mild and versatile method for the construction of C−N bonds by the reaction of (2,2-difluorovinyl)arenes with various N−H-containing heterocycles in the presence of K_3PO_4 has been developed. The reaction proceeded efficiently at room temperature (25 °C) affording the (*E*)-*N*-α-fluorovinyl derivatives of azoles **3** in good to excellent yields with relatively high stereoselectivity.

INTRODUCTION

The Cu-catalyzed Ullmann cross-coupling reaction of nitrogen-containing heterocycles with aryl halides is an important and widely used strategy for the synthesis of *N*-arylazoles.[1] *N*-Vinylazoles such as *N*-vinylimidazole and *N*-vinylpyrazole are useful building blocks and intermediates in organic syntheses.[2] Up to now, most of the research has been focused on the synthesis and application of *N*-arylazoles,[3] and only a few methods for the synthesis of *N*-vinylazoles have been reported. The most common and efficient tool for the construction of the *N*-vinylazole (for example *N*-vinylimidazole) framework is the Cu-catalyzed Ullmann-type coupling reaction of vinyl iodides, bromides, or chlorides with azoles at relatively high temperatures (e.g., 100−120 °C) or in the presence of complicated ligand.[4] However, the use of vinyl fluorides as reactants or coupling partners has rarely been reported.

The introduction of a α-fluorovinyl functionality into organic molecules has attracted much attention due to its specific properties and significant effects on their reactivity and biological activity.[5] Nowadays, vinyl fluorides have found many applications in pharmaceuticals,[6] agrochemicals,[7] especially in peptide chemistry,[8] but only a limited number of methods are available for the synthesis of substituted monofluoroalkenes.[9]

Terminal *gem*-difluoroalkenes exhibit unusual reactivity toward nucleophiles because of their high electron-deficient and strong polar nature of the double bond. They easily undergo vinylic nucleophilic substitution reaction (S_NV) to form α-substituted fluoroalkenes.[10] Ichikawa and co-workers have extensively investigated the reactivity and potential application of the difluoroalkene building blocks, and developed several methods to synthesize the ring-fluorinated heterocyclic compounds.[11]

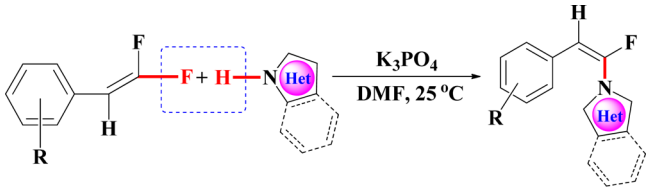
Based on the above-mentioned considerations, we envisioned that the direct nucleophilic attack of the polarized double bond of the difluoroalkenes by azoles might also take place easily. A literature survey revealed that there are only two examples involving the nucleophilic substitution reaction of difluoroalkene with azoles. In 2004, Yagupolski reported that the reaction of chlorotrifluoroethylene with azoles in the presence of potassium metal could afford a mixture of fluorine substitution and alkene addition products. However, the yields and ratios of two types of products were not satisfactory.[12] In 2000, Shi reported the reaction of ethyl 3,3-difluoro-2-[(trimethylsilyl)methyl]propenoate with indole via nucleophilic substitution of vinylic fluorine using *n*-BuLi as base at −78 °C (only one example). They proposed a possible C−F···Si-type coordinative interaction to explain the observed stereochemical outcome.[13] In this paper, we report an efficient and stereoselective synthesis of (*E*)-*N*-(α-fluorovinyl)azoles **3** by *N*-α-fluorovinylation of 1*H*-azoles **2a**−**i** with 1-aryl-2,2-

Received: March 12, 2014
Published: April 1, 2014

   dx.doi.org/10.1021/jo5005845 | J. Org. Chem. 2014, 79, 6395−6402

difluoroethenes **1a–i** in the presence of K_3PO_4 at room temperature without any additional metal catalyst (Scheme 1).

Scheme 1. *N*-α-Fluorovinylation of 1*H*-Azoles 2a–i with 1-Aryl-2,2-difluoroethenes 1a–i

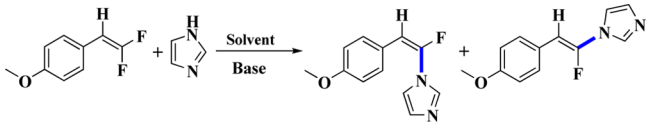


1a-i 2a-i 3

RESULTS AND DISCUSSION

More recently, Diness and Fairlie developed a novel and straightforward catalyst-free method for *N*-arylation of azole with halogenated fluorobenzenes at high temperatures, typically 120–190 °C with the assistance of microwave.[14] Therefore, in the beginning, we carried out the reaction of 1-(2,2-difluorovinyl)-4-methoxybenzene **1a** with 1*H*-imidazole **2a** at 120 °C in the presence of K_3PO_4 using DMF as a solvent (Table 1). We observed that the vinylation reaction took place

Table 1. Fluorovinylation of 2a with 1a under Different Reaction Conditions[a]



1a 2a (*E*)-3aa (*Z*)-3aa

entry	amt of **1a** (equiv)	temp (°C)	base (equiv)	solvent	yield of **3aa**[b] (%)	*E*/*Z*[b]
1	1.2	120	K_3PO_4(3)	DMF	>99	99:1
2	1.2	60	K_3PO_4(3)	DMF	>99	97:3
3	1.2	25	K_3PO_4(3)	DMF	>99	98:2
4	1.2	25	none	DMF	0	
5	1.2	25	Cs_2CO_3(3)	DMF	>99	97:3
6	1.2	25	DBU(3)	DMF	>99	96:4
7	1.2	25	NaO-*t*-Bu(3)	DMF	93	96:4
8	1.2	25	KO-*t*-Bu (3)	DMF	91	96:4
9	1.2	25	K_3PO_4(2)	DMF	>99	98:2
10	1.2	25	K_3PO_4(1)	DMF	80	96:4

[a]Reaction conditions: 1*H*-imidazole **2a** (1 mmol), solvent (2 mL), 12 h. DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). [b]The ratios of *E*/*Z* isomers in the crude reaction mixture were determined by ^{19}F NMR or GC. Yields determined by GC analysis and based on **2a**. The configuration of the *E*-isomer **3aa** (after purification) was determined by its $^3J_{H-F}$ coupling constant in the ^1H NMR spectrum.

smoothly to give the corresponding product **3aa** in almost quantitative yield with excellent stereoselectivity (*E*/*Z* = 99:1) (entry 1). We were pleased to find that the reaction also proceeded very efficiently at lower temperatures even if the temperature decreased to 25 °C (entries 2 and 3).

The effect of base on the reaction of **1a** with **2a** was studied. In the absence of the base, the reaction hardly proceeded and no desired product **3aa** was observed (entry 4). When Cs_2CO_3, DBU, NaO-*t*-Bu, KO-*t*-Bu were employed, the yields and *E*/*Z* selectivity were nearly the same as that of K_3PO_4 (entries 5–8). Furthermore, addition of 2 equiv of K_3PO_4 was enough to make the reaction proceed readily (entry 9), whereas the decrease in the amount of K_3PO_4 (e.g., 1 equiv; entry 10) led to an obvious decrease in the yields. Thus, the optimized reaction conditions are as follows: 1*H*-imidazole **2a** (1 mmol), 1-(2,2-difluorovinyl)-4-methoxybenzene **1a** (1.2 equiv), K_3PO_4 (2 equiv), and DMF (2 mL), stirring for 12 h at 25 °C (entry 9).

The scope and limitations of this fluorovinylation were investigated by treatment of 1-(2,2-difluorovinyl)-4-methoxybenzene **1a** with various nitrogen-containing heterocycles under the aforementioned optimized reaction conditions (Table 2). The results indicated that the reactions of **1a** with imidazole (**2a**), pyrazole (**2b**), substituted 1*H*-benzo[*d*]-imidazole (**2c**), 1*H*-indole (**2d**), 1*H*-benzo[*d*][1,2,3]triazole (**2e**), and 1*H*-1,2,4-triazole (**2f**) proceeded well to afford the expected *N*-vinylazoles in good to excellent yields as the pure *E*-isomers. The vinylation of 5-(thiophene-2-yl)-1*H*-pyrazole (**2g**) also provided pure *E*-isomer with excellent regioselectivity (*N*-1 versus *N*-2) due to the presence of a bulky 3-thienyl group on the pyrazole ring, and no 2-regioisomer was observed.[14] The reaction of 1*H*-indazole (**2h**) with **1a** afforded two regioisomers, (*E*)-1-(1-fluoro-2-(4-methoxyphenyl)vinyl)-1*H*- indazole (**3ah**) and (*E*)-2-(1-fluoro-2-(4-methoxyphenyl)-vinyl)-2*H*-indazole (**3ah′**), in relatively lower yield and selectivity. We also employed 1*H*-benzo[*d*]imidazole (**2i**) as a nucleophilic substrate; it only gave a mixture of *E* and *Z* isomers **3ai** which could be separated by column chromatography (*E*/*Z* = 86:14).

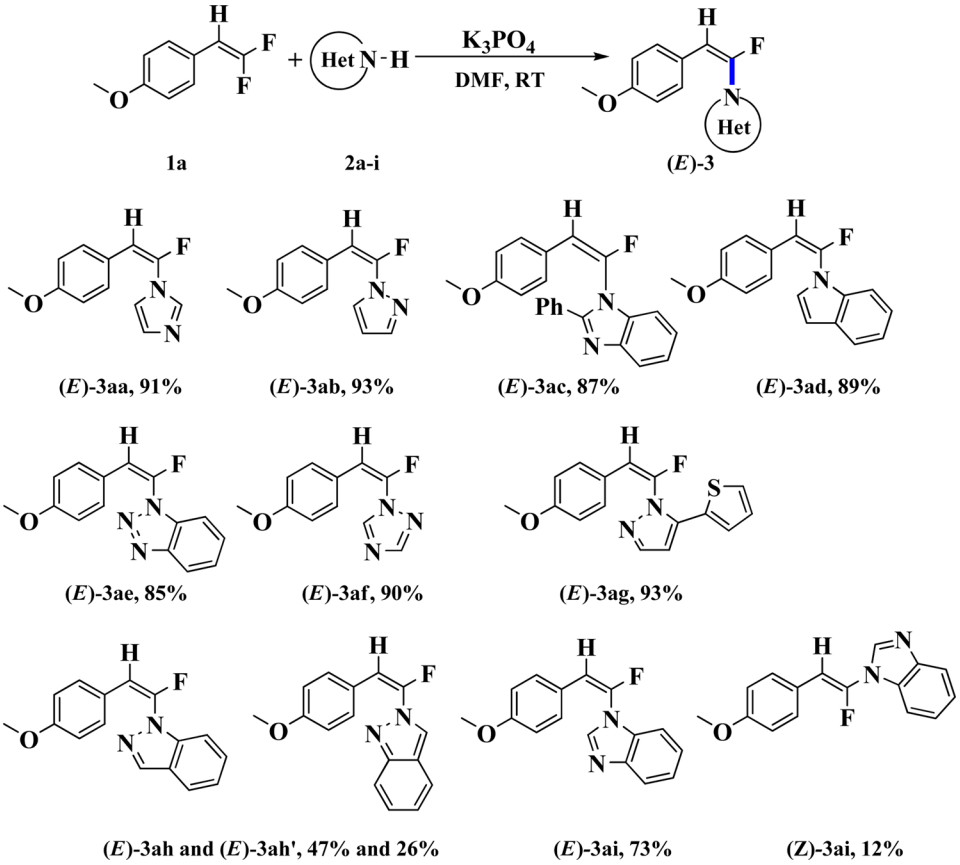
To examine the applicability of this novel vinylation reaction, the reactions of benzimidazole **2i** with various 1-aryl-2,2-difluoroethenes **1b–i** were carried out under the above-optimized conditions. The results were summarized in Table 3. It was found that for those difluoroethenes with electron-donating substituents such as CH_3 (**1b**) and OCH_2O (**1c**) on the aromatic ring could afford the corresponding products in high yields and moderate stereoselectivity. 1-Aryl-2,2-difluoroethenes having naphthyl group or halide (Cl, Br and I) atoms on the aryl ring have been converted into the corresponding *N*-vinylbenzimidazoles in excellent yields; however, the *E*/*Z* selectivity of the reaction decreased, furnishing a chromatographically separable mixture of two E and *Z* isomers. Furthermore, the stereoselectivity is also not satisfactory when 1*H*-imidazole **2a** was used as substrate to react with 1-aryl-2,2-difluoroethenes having halide atom (such as Br) on the aryl ring. Unfortunately, attempts to prepare difluoroethenes having a strong electron-withdrawing group such as NO_2 according to the method described in the literature failed.[15]

In addition, when symmetrical *gem*-difluoroalkenes were employed as the substrates, the reactions proceeded well and gave the desired products in excellent yields (Scheme 2).

To expand the application of this method, we further examined the reactivity of the second C–F bond in alkenes toward nitrogen-containing heterocycles (Scheme 3). First, the model substrate **1a** (1.2 mmol) was allowed to react with imidazole **2a** (2 equiv, 2.4 mmol) for 12 h at 25 °C. However, the reaction could not proceed to completion, and a mixture of monoamination and diamination product was observed. We were delighted to find that the reaction proceeded smoothly at elevated temperature (80 °C) and resulted in the formation of diamination product **4** in nearly quantitative yield, no trace of the monoamination product was detected. This might be due to the fact that the cleavage of the second C–F bond in difluoroalkenes is more difficult.

dx.doi.org/10.1021/jo5005845 | J. Org. Chem. 2014, 79, 6395–6402

Table 2. Reactions of 1a with Various Azoles[a,b]



[a]Reaction conditions: azoles **2a**–**i** (1 mmol), **1a** (1.2 mmol), K_3PO_4 (2 mmol), DMF (2 mL), 12 h, 25 °C. [b]The configurations of the *E*- and *Z*-isomers **3** were determined by their $^3J_{H-F}$ coupling constants in the ^1H NMR spectra.

Encouraged by this result, we also used **1a** (1.2 mmol) as a representative reactant to react sequentially with imidazole **2a** and pyrazole **2b**, respectively, and two α,α′-dihetaryl-substituted alkenes, (*E*)-**5** and (*Z*)-**5**, could be obtained in excellent yields by changing the addition sequence of **2a** and **2b** (Scheme 3). It is very interesting that the configuration of α,α′-dihetaryl substituted alkenes (*E* or *Z*) could be also controlled by the selection of different azoles. In order to get satisfactory results, the amination of *N*-(α-fluorovinyl)azoles, (*E*)-**3aa** and (*E*)-**3ab** was performed at a higher temperature (80 °C). It is noteworthy to mention here that the monoamination products such as (*E*)-**3aa** and (*E*)-**3ab** should be isolated and then reacted with another azole to yield diamination products. However, attempts to synthesize diamination products, (*E*)-**5** and (*Z*)-**5**, using the one-pot sequence without isolation of (*E*)-**3aa** and (*E*)-**3ab** were unsuccessful, and a mixture of Z and *E* diamination products was obtained. The configuration of the compound (*E*)-**5** was confirmed by X-ray crystallographic analysis (see the Supporting Information, Figure 1 and the CIF).

In summary, we have described a facile and straightforward method for the stereoselective synthesis of (*E*)-*N*-(α-fluorovinyl)azoles by the reaction of (2,2-difluorovinyl)arenes with various N–H-containing heterocycles in the absence of metal catalyst under very mild reaction conditions via vinylic nucleophilic substitution reaction (S_NV). Notably, the α-hetaryl-substituted monofluoroalkenes could further react with another π-electron-rich nitrogen heterocycle, affording the *N*,*N*′-α,α′-dihetaryl-substituted alkenes in excellent yields and tunable stereoselectivities. This method can be considered as a valuable strategy for direct access to various N-functionalized fluoroolefins and polysubstituted olefins.

EXPERIMENTAL SECTION

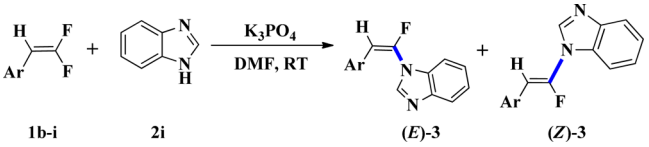
General Comments. All reagents were of analytical grade, obtained from commercial suppliers, and used without further purification. All solvents were dried by standard methods prior to use. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a 400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C) using TMS as internal standard. The ^{19}F NMR spectra were obtained using a 400 spectrometer (376 MHz). $CDCl_3$ was used as the NMR solvent in all cases. The GC and GC–MS were calibrated by authentic standards. High-resolution mass spectra (HRMS) were acquired in the electron-impact mode (EI) using a TOF mass analyzer.

Preparation of 1,1-Difluoroalkenes 1a–i and Symmetrical *gem*-Difluoroalkenes (1j,k). The 1,1-difluoroalkenes (**1a**–**i**) were prepared according to the reported procedure.[15] The symmetrical *gem*-difluoroalkenes (**1j**,**k**) were prepared according to Hu's reported procedure.[16]

Synthesis of Compounds 3. A solution of azole **2** (1.0 mmol) in DMF (1 mL) was added dropwise to a mixture of **1** (1.2 mmol) and K_3PO_4 (424.0 mg, 2 mmol) in DMF (1 mL) via syring and then stirred at room temperature for 12 h (monitored by TLC). After completion of the reaction, the mixture was quenched with H_2O (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$ and filtered, and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel using a hexane/dichloromethane (10:1) mixture as eluent to afford the pure target compound **3**.

dx.doi.org/10.1021/jo5005845 | J. Org. Chem. 2014, 79, 6395–6402

Table 3. *N*-Vinylation of Benzimidazole 2i with 1-Aryl-2,2-difluoroethenes 1b−i[a]

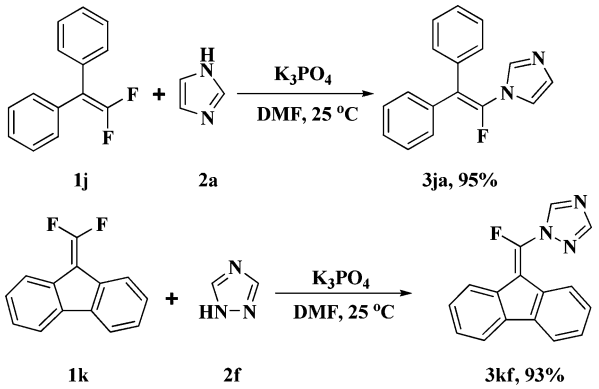


1b-i 2i (*E*)-3 (*Z*)-3

entry	Ar	product 3[b]	yield (%)
1	4-Me-C_6H_4 (**1b**)	(*E*)-**3bi**	86
		(*Z*)-**3bi**	0
2	3,4-OCH_2O-C_6H_3 (**1c**)	(*E*)-**3ci**	94
		(*Z*)- **3ci**	0
3	1-naphthyl (**1d**)	(*E*)-**3di**	81
		(*Z*)-**3di**	11
4	2-Br-C_6H_4 (**1e**)	(*E*)-**3ei**	55
		(*Z*)-**3ei**	38
5	3-Br-C_6H_4 (**1f**)	(*E*)-**3fi**	47
		(*Z*)-**3fi**	40
6	4-Br-C_6H_4 (**1g**)	(*E*)-**3gi**	69
		(*Z*)-**3gi**	23
7	3-Cl-C_6H_4 (**1h**)	(*E*)-**3hi**	57
		(*Z*)-**3hi**	33
8	3-I-C_6H_4 (**1i**)	(*E*)-**3ii**	60
		(*Z*)-**3ii**	39

[a]Reaction conditions: benzimidazole **2i** (1 mmol), **1b−i** (1.2 mmol), K_3PO_4 (2 mmol), DMF (2 mL), 12 h, 25 °C. [b]The configurations of the *E*- and Z-isomers were determined by their $^3J_{H-F}$ coupling constants in the ^1H NMR spectra (ca. 32.0 Hz for *Z*-isomers and 8.0 Hz for *E*-isomers).

Scheme 2. *N*-Vinylation of Azoles with Symmetrical *gem*-Difluoroalkenes[a]



[a]Reaction conditions: azoles **2a** and **2f** (1 mmol), **1j** and **1k** (1.2 mmol), K_3PO_4 (2 mmol), DMF (2 mL), 12 h, 25 °C.

Synthesis of Compound 4. A solution of imidazole **2a** (163.2 mg, 2.4 mmol) in DMF (2 mL) was added dropwise to a mixture of **1a** (204.0 mg, 1.2 mmol) and K_3PO_4 (1017.6 mg, 4.8 mmol) in DMF (2 mL) via syringe. The mixture was heated to 80 °C and stirred for 20 h (monitored by TLC). The reaction mixture was allowed to cool to room temperature and quenched with H_2O (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$ and filtered, and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel using a hexane/dichloromethane (5:1) mixture as eluent to afford **4**.

Synthesis of Compound (*E*)-5. A solution of pyrazole **2b** (63.2 mg, 0.93 mmol) in DMF (1 mL) was added dropwise to a mixture of (*E*)-**3aa** (202.7 mg, 0.93 mmol) and K_3PO_4 (281.6 mg, 1.8 mmol) in DMF (1 mL) via syringe. The mixture was heated to 80 °C and stirred for 12 h (monitored by TLC). The reaction mixture was allowed to cool to room temperature and quenched with H_2O (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$ and filtered, and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel using a hexane/dichloromethane (5:1) mixture as eluent to afford (*E*)-**5**.

Synthesis of Compound (*Z*)-5. A solution of imidazole **2a** (62.6 mg, 0.92 mmol) in DMF (1 mL) was added dropwise to a mixture of (*E*)-**3ab** (200.6 mg, 0.92 mmol) and K_3PO_4 (381.6 mg, 1.8 mmol) in DMF (1 mL) via syringe. The mixture was heated to 80 °C and stirred for 12 h (monitored by TLC). The reaction mixture was allowed to cool to room temperature and quenched with H_2O (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$ and filtered, and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel using a hexane/dichloromethane (5:1) mixture as eluent to afford (*Z*)-**5**.

(E)-1-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-1H-imidazole ***((E)-3aa)****:* yield 91% (198.4 mg), white solid; mp 93.5−94.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.08 (s, 1H), 6.96 (s, 1H), 6.67 (s, 4H), 6.16 (d, J = 10.0 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (d, $^4J_{CF}$ = 1.4 Hz), 143.9 (d, $^1J_{CF}$ = 259.3 Hz), 136.8, 130.4, 129.1 (d, $^3J_{CF}$ = 3.4 Hz), 122.5 (d, $^3J_{CF}$ = 7.1 Hz), 118.2 (d, $^3J_{CF}$ = 2.8 Hz), 114.4, 103.6 (d, $^2J_{CF}$ = 33.7 Hz), 55.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −86.8 (d, J = 10.0 Hz); HRMS (EI) calcd for $C_{12}H_{11}FN_2O$ $[M]^+$ 218.0855, found 218.0840.

(E)-1-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-1H-pyrazole ***((E)-3ab)****:* yield 93% (202.7 mg), white solid; mp 95.0−96.0 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 1.6 Hz, 1H), 7.47 (d, J = 2.5 Hz, 1H), 6.70 (s, 4H), 6.38−6.37 (m, 1H), 6.28 (d, J = 8.0 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 146.2 (d, $^1J_{CF}$ = 260.5 Hz), 142.6, 131.4 (d, $^4J_{CF}$ = 1.7 Hz), 129.3 (d, $^3J_{CF}$ = 3.4 Hz), 123.0 (d, $^3J_{CF}$ = 6.6 Hz), 114.1, 107.9, 104.6 (d, $^2J_{CF}$ = 34.8 Hz), 55.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −88.2 (d, J = 8.9 Hz); HRMS (EI) calcd for $C_{12}H_{11}FN_2O$ $[M]^+$ 218.0855, found 218.0856.

(E)-1-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-2-phenyl-1H-benzo-[d]imidazole ***((E)-3ac)****:* yield 87% (299.3 mg), white solid; mp 128.1−129.1 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89−7.87 (m, 3H), 7.41−7.34 (m, 6H), 6.59 (s, 4H), 6.52 (d, J = 8.0 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5 (d, $^4J_{CF}$ = 1.8 Hz), 152.0 (d, $^4J_{CF}$ = 2.9 Hz), 143.3 (d, $^1J_{CF}$ = 262.6 Hz), 143.2, 134.6 (d, $^3J_{CF}$ = 4.2 Hz), 130.4, 129.1, 128.9 (d, $^3J_{CF}$ = 3.5 Hz), 128.6, 128.4, 124.4, 124.0, 122.4 (d, $^3J_{CF}$ = 6.6 Hz), 120.3, 114.3, 110.8, 108.9 (d, $^2J_{CF}$ = 36.4 Hz), 55.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −83.9 (d, J = 8.3 Hz); HRMS (EI) calcd for $C_{22}H_{17}FN_2O$ $[M]^+$ 344.1325, found 344.1319.

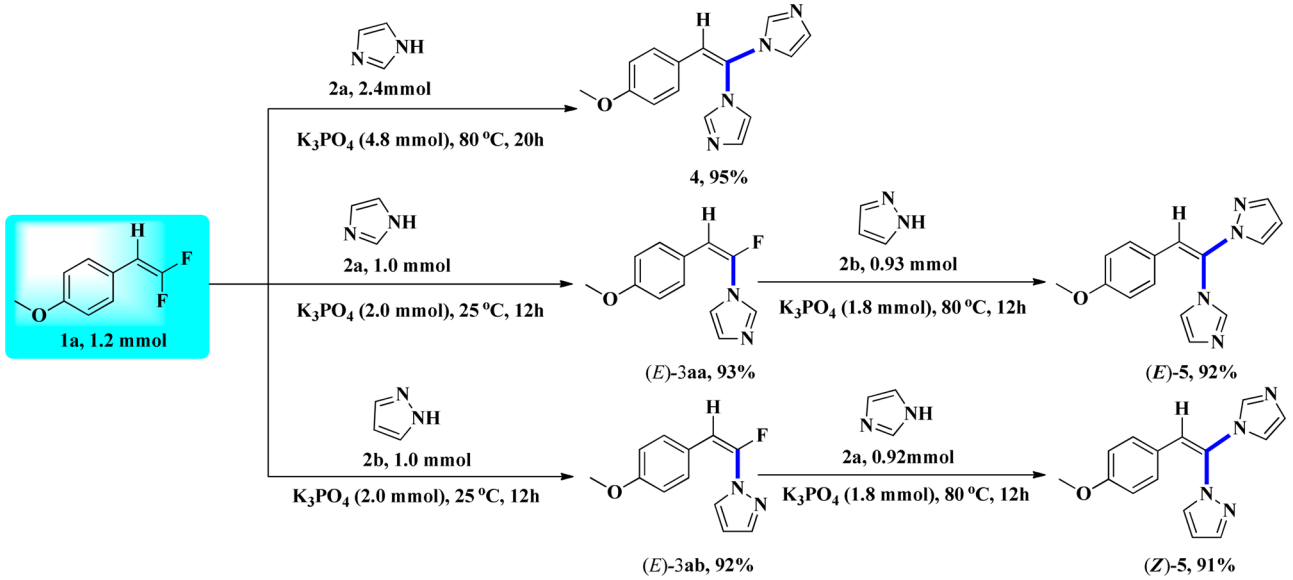
(E)-1-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-1H-indole ***((E)-3ad)****:* yield 89% (237.6 mg), white solid; mp 124.5−125.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72−7.70 (m, 1H), 7.41−7.39 (m, 1H), 7.28−7.26 (m, 2H), 7.14−7.13 (m, 1H), 6.77−6.70 (m, 5H), 6.40 (d, J = 8.0 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 146.2 (d, $^1J_{CF}$ = 261.2 Hz), 135.1 (d, $^3J_{CF}$ = 3.9 Hz), 129.1 (d, $^3J_{CF}$ = 3.4 Hz), 129.0, 126.7 (d, $^4J_{CF}$ = 3.2 Hz), 123.6 (d, $^3J_{CF}$ = 7.2 Hz), 123.4, 121.6, 121.1, 114.1, 111.5, 106.1, 103.8 (d, $^2J_{CF}$ = 39.0 Hz), 55.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −84.0 (d, J = 8.5 Hz); HRMS (EI) calcd for $C_{17}H_{14}FNO$ $[M]^+$ 267.1059, found 267.1058.

(E)-1-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-1H-benzo[d][1,2,3]-triazole ***((E)-3ae)****:* yield 85% (228.6 mg), white solid; mp 126.6−127.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.14−8.12 (m, 1H), 7.48−7.36 (m, 3H), 6.72−6.69 (m, 3H), 6.62 (d, J = 8.8 Hz, 2H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (d, $^4J_{CF}$ = 1.6 Hz), 145.4, 142.3 (d, $^1J_{CF}$ = 263.6 Hz), 132.2 (d, $^4J_{CF}$ = 2.8 Hz), 129.4 (d, $^3J_{CF}$ = 3.4 Hz), 129.3, 125.0, 121.9 (d, $^3J_{CF}$ = 6.2 Hz), 120.3, 114.2, 110.0, 108.7 (d, $^2J_{CF}$ = 33.3 Hz), 55.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −89.7 (d, J = 8.8 Hz); HRMS (EI) calcd for $C_{15}H_{12}FN_3O$ $[M]^+$ 269.0964, found 269.0965.

(E)-1-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-1H-1,2,4-triazole ***((E)-3af)****:* yield 90% (197.1 mg), white solid; mp 96.0−97.1 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.0 Hz, 2H), 6.69 (s, 4H), 6.41 (d, J = 8.0 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8,

dx.doi.org/10.1021/jo5005845 | J. Org. Chem. 2014, 79, 6395−6402

Scheme 3. Influence of the Amount and the Order of Addition of 1*H*-Azoles on the Formation of Dihetaryl-Substituted Ethylene[a]



[a]Reaction conditions: 1.2 mmol of **1a**, 0.92 mmol of (*E*)-**3ab**, 0.93 mmol of (*E*)-**3aa**, indicated amount of 1*H*-imidazole **2a**, 1*H*-pyrazole **2b**, and K_3PO_4.

153.5, 145.1, 142.9 (d, $^1J_{CF}$ = 262.3 Hz), 129.3 (d, $^3J_{CF}$ = 3.3 Hz), 121.9 (d, $^3J_{CF}$ = 6.1 Hz), 114.5, 107.2 (d, $^2J_{CF}$ = 31.3 Hz), 55.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −91.4 (d, *J* = 9.1 Hz); HRMS (EI) calcd for $C_{11}H_{10}FN_3O$ $[M]^+$ 219.0791, found 219.0791.

(E)-1-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-5-(thiophene-2-yl)-1H-pyrazole (***(E)-3ag***): yield 93% (279.0 mg), white solid; mp 100.3−101.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.44 (m, 2H), 7.33−7.31 (m, 1H), 7.10−7.08 (m, 1H), 6.87−6.74 (m, 4H), 6.60 (d, *J* = 4.0 Hz, 1H), 6.31 (d, *J* = 8.0 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (d, $^4J_{CF}$ = 1.4 Hz), 149.8, 146.0 (d, $^1J_{CF}$ = 261.1 Hz), 135.3, 133.0 (d, $^4J_{CF}$ = 1.7 Hz), 129.5 (d, $^3J_{CF}$ = 3.3 Hz), 127.6, 125.8, 125.2, 123.0 (d, $^3J_{CF}$ = 6.4 Hz), 114.2, 105.3 (d, $^4J_{CF}$ = 0.9 Hz), 104.6 (d, $^2J_{CF}$ = 34.7 Hz), 55.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −88.9 (d, *J* = 8.9 Hz); HRMS (EI) calcd for $C_{16}H_{13}FN_2OS$ $[M]^+$ 300.0733, found 300.0735.

(E)-1-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-1H-indazole (***(E)-3ah***) *and (E)-2-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-2H-indazole* (***(E)-3ah′***). Major product: yield 47% (126.2 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 0.6 Hz, 1H), 7.71−7.69 (m, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.29−7.25 (m, 1H), 7.06−7.03 (m, 1H), 6.64−6.58 (m, 4H), 6.38 (d, *J* = 8.0 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 150.3, 146.6 (d, $^1J_{CF}$ = 261.1 Hz), 129.5 (d, $^3J_{CF}$ = 3.3 Hz), 127.9, 125.2, 123.2, 122.6 (d, $^3J_{CF}$ = 6.5 Hz), 121.9, 120.8, 118.6, 114.2, 105.2 (d, $^2J_{CF}$ = 32.4 Hz), 55.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −88.8 (d, *J* = 9.7 Hz); HRMS (EI) calcd for $C_{16}H_{13}FN_2O$ $[M]^+$ 268.1012, found 268.1013. Minor product: yield 26% (69.9 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 1.0 Hz, 1H), 7.70−7.67 (m, 1H), 7.28−7.24 (m, 1H), 7.17−7.14 (m, 2H), 6.64−6.62 (m, 2H), 6.55−6.53 (m, 2H), 6.43 (d, *J* = 8.0 Hz, 1H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 145.2 (d, $^1J_{CF}$ = 262.8 Hz), 139.4 (d, $^4J_{CF}$ = 3.1 Hz), 138.1, 129.3 (d, $^3J_{CF}$ = 3.4 Hz), 128.0, 124.5, 123.2 (d, $^3J_{CF}$ = 6.6 Hz), 122.5, 121.2, 114.1 (d, $^3J_{CF}$ = 21.5 Hz), 110.4, 106.2 (d, $^2J_{CF}$ = 37.3 Hz), 55.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −87.8 (d, *J* = 8.0 Hz); HRMS (EI) calcd for $C_{16}H_{13}FN_2O$ $[M]^+$ 268.1012, found 268.1011.

(E)-1-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-1H-benzo[d]imidazole (***(E)-3ai***): yield 73% (195.6 mg), white solid; mp 121.7−122.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.76 (m, 2H), 7.29−7.24 (m, 3H), 6.64−6.56 (m, 4H), 6.38 (d, *J* = 8.0 Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5 (d, $^4J_{CF}$ = 1.5 Hz), 143.3, 143.1 (d, $^1J_{CF}$ = 264.6 Hz), 141.9, 132.1 (d, $^3J_{CF}$ = 3.9 Hz), 129.1 (d, $^3J_{CF}$ = 3.4 Hz), 124.7, 123.8, 122.4 (d, $^3J_{CF}$ = 6.8 Hz), 120.7, 114.4, 111.2 (d, $^4J_{CF}$ = 1.2 Hz), 105.8 (d, $^2J_{CF}$ = 35.1 Hz), 55.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −87.8 (dd, *J* = 9.0, 2.9 Hz); HRMS (EI) calcd for $C_{16}H_{13}FN_2O$ $[M]^+$ 268.1012, found 268.1013.

(Z)-1-(1-Fluoro-2-(4-methoxyphenyl)vinyl)-1H-benzo[d]imidazole (***(Z)-3ai***): yield 12% (32.2 mg), white solid; mp 134.0−135.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.32−7.25 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 5.84 (d, *J* = 32.0 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 143.7 (d, $^1J_{CF}$ = 270.7 Hz), 143.4, 141.3, 132.7 (d, $^3J_{CF}$ = 3.0 Hz), 130.0 (d, $^3J_{CF}$ = 7.4 Hz), 129.8, 124.6, 123.7, 120.8, 114.3, 111.2 (d, $^4J_{CF}$ = 2.4 Hz), 102.0 (d, $^2J_{CF}$ = 15.6 Hz), 55.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −95.4 (dd, *J* = 31.1, 2.7 Hz); HRMS (EI) calcd for $C_{16}H_{13}FN_2O$ $[M]^+$ 268.1012, found 268.1010.

(E)-1-(1-Fluoro-2-p-tolylvinyl)-1H-benzo[d]imidazole (***(E)-3bi***): yield 86% (216.7 mg), white solid; mp 122.4−123.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.88 (m, 2H), 7.44−7.35 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 2H), 6.51 (d, *J* = 8.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9 (d, $^1J_{CF}$ = 263.6 Hz), 143.3, 141.8 (d, $^4J_{CF}$ = 2.6 Hz), 138.3 (d, $^4J_{CF}$ = 1.6 Hz), 132.1 (d, $^3J_{CF}$ = 3.9 Hz), 129.6, 127.7 (d, $^3J_{CF}$ = 3.4 Hz), 127.3 (d, $^3J_{CF}$ = 6.9 Hz), 124.7, 123.8, 120.7, 111.2 (d, $^4J_{CF}$ = 1.4 Hz), 105.9 (d, $^2J_{CF}$ = 34.6 Hz), 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −86.8 (d, *J* = 9.1 Hz); HRMS (EI) calcd for $C_{16}H_{13}FN_2$ $[M]^+$ 252.1063, found 252.1064.

(E)-1-(2-(Benzo[d][1,3]dioxol-5-yl)-1-fluorovinyl)-1H-benzo[d]-imidazole (***(E)-3ci***): yield 94% (265.1 mg), white solid; mp 126.5−127.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.88−7.85 (m, 1H), 7.37 (m, 3H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 6.41−6.39 (m, 1H), 6.18 (d, *J* = 1.7 Hz, 1H), 5.84 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 147.6 (d, $^4J_{CF}$ = 1.6 Hz), 143.5 (d, $^1J_{CF}$ = 262.6 Hz), 143.3, 141.8 (d, $^4J_{CF}$ = 2.6 Hz), 132.1 (d, $^3J_{CF}$ = 4.0 Hz), 124.7, 124.0 (d, $^3J_{CF}$ = 7.0 Hz), 123.8, 122.4 (d, $^3J_{CF}$ = 4.0 Hz), 120.8, 111.1 (d, $^4J_{CF}$ = 1.3 Hz), 108.7, 107.4 (d, $^4J_{CF}$ = 3.0 Hz), 105.9 (d, $^2J_{CF}$ = 35.8 Hz), 101.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −87.4 (d, *J* = 9.1 Hz); HRMS (EI) calcd for $C_{16}H_{11}FN_2O_2$ $[M]^+$ 282.0805, found 282.0806.

(E)-1-(1-Fluoro-2-(naphthalen-1-yl)vinyl)-1H-benzo[d]imidazole (***(E)-3di***): yield 81% (233.3 mg), white solid; mp 120.7−122.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.66−7.62 (m, 2H), 7.53−7.50 (m, 2H), 7.36−7.32 (m, 2H), 7.26−7.24 (m, 1H), 7.16−7.07 (m, 2H), 6.96−6.92 (m, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2 (d, $^1J_{CF}$ =

dx.doi.org/10.1021/jo5005845 | J. Org. Chem. 2014, 79, 6395−6402

262.3 Hz), 143.1, 141.7 (d, $^4J_{CF}$ = 1.6 Hz), 133.6, 132.3 (d, $^3J_{CF}$ = 3.7 Hz), 131.6 (d, $^3J_{CF}$ = 3.6 Hz), 128.9, 127.5, 127.4, 126.9, 126.4, 125.9 (d, $^4J_{CF}$ = 1.9 Hz), 125.6, 124.6, 123.7, 123.6, 120.7, 111.4 (d, $^3J_{CF}$ = 2.5 Hz), 101.6 (d, J = 33.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −87.4 (d, J = 8.6 Hz); HRMS (EI) calcd for $C_{19}H_{13}FN_2$ $[M]^+$ 288.1063, found 288.1062.

*(Z)-1-(1-Fluoro-2-(naphthalen-1-yl)vinyl)-1H-benzo[d]imidazole **((Z)-3di)**:* yield 11% (31.7 mg), white solid; mp 136.0−137.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.91−7.85 (m, 4H), 7.70 (d, J = 8.0 Hz, 1H), 7.56−7.53 (m, 3H), 7.43−7.39 (m, 2H), 6.63 (d, J = 32.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8 (d, $^1J_{CF}$ = 269.7 Hz), 143.6, 141.0, 133.7, 132.4, 131.3, 128.9, 128.8 (d, $^4J_{CF}$ = 0.8 Hz), 127.3 (d, $^3J_{CF}$ = 8.6 Hz), 127.2 (d, $^3J_{CF}$ = 4.8 Hz), 126.7, 126.1, 125.5, 124.8, 123.9, 123.5, 121.0, 111.4 (d, $^3J_{CF}$ = 2.6 Hz), 97.8 (d, $^2J_{CF}$ = 16.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −95.4 (d, J = 29.1 Hz); HRMS (EI) calcd for $C_{19}H_{13}FN_2$ $[M]^+$ 288.1063, found 288.1064.

*(E)-1-(2-(2-Bromophenyl)-1-fluorovinyl)-1H-benzo[d]imidazole **((E)-3ei)**:* Yield 55% (173.8 mg), white solid; mp 119.8−121.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82−7.80 (m, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.37−7.32 (m, 3H), 7.07−7.03 (m, 1H), 6.97−6.93 (m, 1H), 6.65 (d, J = 8.0 Hz, 1H), 6.60−6.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9 (d, $^1J_{CF}$ = 263.9 Hz), 143.1, 141.4 (d, $^4J_{CF}$ = 2.0 Hz), 133.0, 132.0 (d, $^3J_{CF}$ = 3.5 Hz), 129.7, 128.9, 128.8, 127.8, 124.8, 124.3 (d, $^3J_{CF}$ = 5.0 Hz), 123.8, 120.7, 111.3 (d, $^4J_{CF}$ = 2.1 Hz), 104.0 (d, $^2J_{CF}$ = 36.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −86.4 (d, J = 8.4 Hz); HRMS (EI) calcd for $C_{15}H_{10}BrFN_2$ $[M]^+$ 316.0011, found 316.0010.

*(Z)-1-(2-(2-Bromophenyl)-1-fluorovinyl)-1H-benzo[d]imidazole **((Z)-3ei)**:* yield 38% (120.1 mg), white solid; mp 134.2−135.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.77−7.73 (m, 2H), 7.61−7.59 (m, 1H), 7.54−7.52 (m, 1H), 7.32−7.27 (m, 3H), 7.07−7.06 (m, 1H), 6.29 (d, J = 32.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9 (d, $^1J_{CF}$ = 271.5 Hz), 143.7, 140.6, 133.0, 132.0, 131.1 (d, $^3J_{CF}$ = 5.9 Hz), 130.0 (d, $^3J_{CF}$ = 11.0 Hz), 129.4 (d, $^4J_{CF}$ = 1.3 Hz), 127.7, 124.9, 124.0, 123.9 (d, $^4J_{CF}$ = 1.8 Hz), 121.0, 111.4 (d, $^4J_{CF}$ = 2.5 Hz), 99.0 (d, $^2J_{CF}$ = 13.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −95.1 (d, J = 31.0 Hz); HRMS (EI) calcd for $C_{15}H_{10}BrFN_2$ $[M]^+$ 316.0011, found 316.0010.

*(E)-1-(2-(3-Bromophenyl)-1-fluorovinyl)-1H-benzo[d]imidazole **((E)-3fi)**:* yield 47% (148.5 mg), white solid; mp 115.4−116.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.86 (m, 2H), 7.37−7.28 (m, 4H), 7.12−7.11 (m, 1H), 6.97−6.93 (m, 1H), 6.61 (d, J = 8.0 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2 (d, $^1J_{CF}$ = 265.0 Hz), 143.3, 141.4 (d, $^4J_{CF}$ = 2.4 Hz), 132.5 (d, $^3J_{CF}$ = 7.6 Hz), 131.8 (d, $^3J_{CF}$ = 3.8 Hz), 131.3 (d, $^3J_{CF}$ = 3.9 Hz), 131.2 (d, $^4J_{CF}$ = 1.2 Hz), 130.4, 125.7 (d, $^4J_{CF}$ = 2.9 Hz), 124.9, 124.0, 122.9, 120.9, 111.2 (d, $^4J_{CF}$ = 1.5 Hz), 104.2 (d, $^2J_{CF}$ = 35.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −83.9 (d, J = 8.6 Hz); HRMS (EI) calcd for $C_{15}H_{10}BrFN_2$ $[M]^+$ 316.0011, found 316.0010.

*(Z)-1-(2-(3-Bromophenyl)-1-fluorovinyl)-1H-benzo[d]imidazole **((Z)-3fi)**:* yield 40% (126.4 mg), white solid; mp 138.2−139.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.80−7.78 (m, 1H), 7.69−7.68 (m, 1H), 7.57−7.55 (m, 1H), 7.45−7.43 (m, 1H), 7.39−7.35 (m, 1H), 7.34−7.31 (m, 2H), 7.23 (d, J = 8.0 Hz, 1H), 5.87 (d, J = 32.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1 (d, $^1J_{CF}$ = 263.2 Hz), 143.6, 140.8, 133.3 (d, $^3J_{CF}$ = 6.1 Hz), 132.2, 131.4 (d, $^3J_{CF}$ = 8.0 Hz), 131.1 (d, $^4J_{CF}$ = 2.1 Hz), 130.4, 127.1 (d, $^3J_{CF}$ = 7.2 Hz), 124.8, 124.0, 123.0, 121.0, 111.3 (d, $^4J_{CF}$ = 2.8 Hz), 99.8 (d, $^2J_{CF}$ = 14.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −92.1 (d, J = 30.6 Hz); HRMS (EI) calcd for $C_{15}H_{10}BrFN_2$ $[M]^+$ 316.0011, found 316.0012.

*(E)-1-(2-(4-Bromophenyl)-1-fluorovinyl)-1H-benzo[d]imidazole **((E)-3gi)**:* yield 69% (218.0 mg), white solid; mp 118.3−119.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.87 (m, 2H), 7.38−7.30 (m, 5H), 6.70 (d, J = 8.0 Hz, 2H), 6.47 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7 (d, $^1J_{CF}$ = 264.5 Hz), 143.3, 141.4 (d, $^3J_{CF}$ = 2.5 Hz), 132.2, 131.8 (d, $^3J_{CF}$ = 3.9 Hz), 129.4, 129.3, 124.9, 124.0, 122.3 (d, $^4J_{CF}$ = 1.6 Hz), 120.9, 111.2, 104.8 (d, $^2J_{CF}$ = 35.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −84.4 (d, J = 8.7 Hz); HRMS (EI) calcd for $C_{15}H_{10}BrFN_2$ $[M]^+$ 316.0011, found 316.0013.

*(Z)-1-(2-(4-Bromophenyl)-1-fluorovinyl)-1H-benzo[d]imidazole **((Z)-3gi)**:* yield 23% (72.7 mg), white solid; mp 138.7−139.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.79−7.77 (m, 1H), 7.55−7.54 (m, 1H), 7.48−7.46 (m, 2H), 7.39−7.37 (m, 2H), 7.34−7.30 (m, 2H), 5.87 (d, J = 32.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4 (d, $^1J_{CF}$ = 271.6 Hz), 143.5, 140.8, 132.3 (d, $^4J_{CF}$ = 2.8 Hz), 132.1, 130.2 (d, $^3J_{CF}$ = 6.1 Hz), 130.1 (d, $^3J_{CF}$ = 7.5 Hz), 124.8, 123.9, 122.1 (d, $^3J_{CF}$ = 3.4 Hz), 121.0, 111.3 (d, $^4J_{CF}$ = 2.7 Hz), 100.4 (d, $^2J_{CF}$ = 14.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −92.8 (d, J = 30.8 Hz); HRMS (EI) calcd for $C_{15}H_{10}BrFN_2$ $[M]^+$ 316.0011, found 316.0012.

*(E)-1-(2-(3-Chlorophenyl)-1-fluorovinyl)-1H-benzo[d]imidazole **((E)-3hi)**:* yield 57% (155.0 mg), white solid; mp 107.4−108.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.75 (m, 2H), 7.26−7.21 (m, 3H), 7.02 (d, J = 8.0 Hz, 1H), 6.92−6.88 (m, 1H), 6.82 (s, 1H), 6.47 (d, J = 8.0 Hz, 1H), 6.32 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2 (d, $^1J_{CF}$ = 264.9 Hz), 143.4, 141.5, 134.8, 132.2 (d, $^3J_{CF}$ = 7.6 Hz), 130.1, 128.4, 128.3, 128.2, 125.4 (d, $^3J_{CF}$ = 2.9 Hz), 124.9, 124.0, 120.9, 111.2 (d, $^4J_{CF}$ = 1.2 Hz), 104.3 (d, $^2J_{CF}$ = 35.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −84.0 (d, J = 8.7 Hz); HRMS (EI) calcd for $C_{15}H_{10}ClFN_2$ $[M]^+$ 272.0517, found 272.0512.

*(Z)-1-(2-(3-Chlorophenyl)-1-fluorovinyl)-1H-benzo[d]imidazole **((Z)-3hi)**:* yield 33% (89.8 mg), white solid; mp 125.8−126.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.85−7.83 (m, 1H), 7.61−7.57 (m, 2H), 7.44−7.29 (m, 5H), 5.90 (d, J = 32.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8 (d, $^1J_{CF}$ = 272.1 Hz), 143.5, 140.8, 134.7, 133.0 (d, $^3J_{CF}$ = 6.0 Hz), 132.2 (d, $^4J_{CF}$ = 2.6 Hz), 130.1, 128.4 (d, $^3J_{CF}$ = 8.0 Hz), 128.1 (d, $^4J_{CF}$ = 2.0 Hz), 126.7 (d, $^3J_{CF}$ = 7.2 Hz), 124.8, 123.9, 120.9, 111.3 (d, $^4J_{CF}$ = 2.9 Hz), 99.7 (d, $^2J_{CF}$ = 14.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −92.4 (d, J = 30.8 Hz); HRMS (EI) calcd for $C_{15}H_{10}ClFN_2$ $[M]^+$ 272.0517, found 272.0515.

*(E)-1-(1-Fluoro-2-(3-iodophenyl)vinyl)-1H-benzo[d]imidazole **((E)-3ii)**:* yield 60% (218.4 mg), white solid; mp 96.1−97.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.83 (m, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.35−7.30 (m, 4H), 6.80−6.77 (m, 1H), 6.60 (d, J = 8.0 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0 (d, $^1J_{CF}$ = 265.0 Hz), 143.2, 141.3 (d, $^4J_{CF}$ = 2.4 Hz), 137.2 (d, $^3J_{CF}$ = 3.9 Hz), 137.1 (d, $^4J_{CF}$ = 1.3 Hz), 132.5 (d, $^3J_{CF}$ = 7.4 Hz), 131.7 (d, $^3J_{CF}$ = 3.8 Hz), 130.5, 126.2 (d, $^4J_{CF}$ = 2.8 Hz), 124.9, 124.0, 120.9, 111.2 (d, $^4J_{CF}$ = 1.5 Hz), 104.0 (d, $^2J_{CF}$ = 35.8 Hz), 94.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −84.0 (d, J = 8.7 Hz); HRMS (EI) calcd for $C_{15}H_{10}FIN_2$ $[M]^+$ 363.9873, found 363.9872.

*(Z)-1-(1-Fluoro-2-(3-iodophenyl)vinyl)-1H-benzo[d]imidazole **((Z)-3ii)**:* yield 29% (105.6 mg), white solid; mp 110.2−111.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.92−7.91 (m, 1H), 7.85−7.83 (m, 1H), 7.65−7.62 (m, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.39−7.36 (m, 2H), 7.15−7.11 (m, 1H), 5.87 (d, J = 32.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7 (d, $^1J_{CF}$ = 272.1 Hz), 143.5, 140.8, 137.2 (d, $^3J_{CF}$ = 7.8 Hz), 137.0 (d, $^4J_{CF}$ = 2.2 Hz), 133.4 (d, $^3J_{CF}$ = 6.1 Hz), 132.2 (d, $^4J_{CF}$ = 2.6 Hz), 130.5, 127.7 (d, $^3J_{CF}$ = 7.5 Hz), 124.8, 124.0, 121.0, 111.3 (d, $^4J_{CF}$ = 2.8 Hz), 99.6 (d, $^2J_{CF}$ = 14.6 Hz), 94.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −92.4 (d, J = 30.5 Hz); HRMS (EI) calcd for $C_{15}H_{10}FIN_2$ $[M]^+$ 363.9873, found 363.9872.

*1-(1-Fluoro-2,2-diphenylvinyl)-1H-imidazole (**3ja**):* yield 90% (237.8 mg), white solid; mp 102.2−103.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.40−7.37 (m, 5H), 7.29−7.27 (m, 3H), 7.06−7.03 (m, 3H), 6.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6 (d, $^1J_{CF}$ = 265.6 Hz), 137.3, 135.8 (d, $^3J_{CF}$ = 3.9 Hz), 135.6 (d, $^3J_{CF}$ = 3.4 Hz), 129.7, 129.6, 129.6, 129.5, 128.9, 128.4, 128.2 (d, $^3J_{CF}$ = 6.0 Hz), 118.6, 115.7 (d, $^2J_{CF}$ = 20.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −93.2 (s); HRMS (EI) calcd for $C_{17}H_{13}FN_2$ $[M]^+$ 264.1063, found 264.1064.

*1-((9H-Fluoren-9-ylidene)fluoromethyl)-1H-1,2,4-triazole (**3kf**):* yield 91% (240.3 mg), white solid; mp 104.1−105.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.32 (s, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.67 (dd, J = 12.0, 8.0 Hz, 2H), 7.45−7.29 (m, 3H), 7.06−7.03 (m, 1H), 6.15 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 145.9, 141.1 (d, $^1J_{CF}$ = 280.8 Hz), 140.7 (d, $^4J_{CF}$ = 5.0 Hz), 140.1, 134.2 (d, $^3J_{CF}$ = 6.7 Hz), 133.2 (d, $^3J_{CF}$ = 5.2 Hz), 129.9 (d, $^4J_{CF}$ = 2.4 Hz), 129.6 (d, $^4J_{CF}$ = 2.3 Hz), 128.0, 127.6, 126.1 (d, $^3J_{CF}$ = 13.5 Hz), 122.6 (d, $^4J_{CF}$ = 2.5 Hz), 120.4, 120.1, 117.9 (d, $^2J_{CF}$ = 22.4 Hz);

dx.doi.org/10.1021/jo5005845 | J. Org. Chem. 2014, 79, 6395−6402

^{19}F NMR (376 MHz, $CDCl_3$) δ −80.2 (s); HRMS (EI) calcd for $C_{16}H_{10}FN_3$ $[M]^+$ 263.0860, found 263.0860.

1,1′-(2-(4-Methoxyphenyl)ethene-1,1-diyl)bis(1H-imidazole) (4): yield 94% (250.0 mg), white solid; mp 86.8−87.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.55 (s, 1H), 7.24 (s, 1H), 7.12 (s, 1H), 6.96 (s, 2H), 6.76 (s, 4H), 6.59 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 137.4, 135.8, 131.2, 130.7, 129.8, 125.1, 123.7, 118.7, 117.5, 116.4, 114.5, 55.3; HRMS (EI) calcd for $C_{15}H_{14}N_4O$ $[M]^+$ 266.1168, found 266.1169.

(E)-1-(1-(1H-Imidazol-1-yl)-2-(4-methoxyphenyl)vinyl)-1H-pyrazole ((E)-5): yield 86% (228.8 mg), white solid; mp 87.0−88.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.58 (d, J = 1.3 Hz, 1H), 7.42 (d, J = 2.4 Hz, 1H), 7.11 (s, 1H), 7.01 (d, J = 2.4 Hz, 1H), 6.65−6.60 (m, 4H), 6.38−6.37 (m, 1H), 6.24−6.23 (m, 1H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 142.4, 141.6, 132.4, 131.1, 130.0, 127.9, 124.8, 115.4, 114.1, 108.0, 107.2, 55.2; HRMS (EI) calcd for $C_{15}H_{14}N_4O$ $[M]^+$ 266.1168, found 266.1170.

(Z)-1-(1-(1H-Imidazol-1-yl)-2-(4-methoxyphenyl)vinyl)-1H-pyrazole ((Z)-5): yield 85% (226.1 mg), white solid; mp 86.6−87.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.49 (s, 1H), 7.18 (s, 1H), 7.06 (s, 1H), 6.90 (s, 2H), 6.70 (s, 4H), 6.54 (s, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 137.4, 135.8, 131.2, 130.7, 129.8, 125.1, 123.7, 118.7, 117.5, 116.4, 114.5, 55.3; HRMS (EI) calcd for $C_{15}H_{14}N_4O$ $[M]^+$ 266.1168, found 266.1169.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C, and ^{19}F NMR spectra and HRMS (EI) spectra of compounds **3**; ^{1}H, ^{13}C NMR spectra and HRMS (EI) spectra of compounds **4**, (*E*)-**5**, (*Z*)-**5**; X-ray analysis data of (*E*)-**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: scao@ecust.edu.cn. Tel: +86-21-64253452.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support from the National Natural Science Foundation of China (Grant Nos. 21272070, 21072057), the National Basic Research Program of China (973 Program, 2010CB126101), and the Twelfth Five-year Plan of China (2011BAE06B01-15).

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