Stereospecific synthesis of unsymmetrical (*E*)- and (*Z*)- 1,2-difluorostilbenes*

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Abstract:

The synthesis of 1,2-difluorostilbenes *via* a Suzuki reaction using a benzene/ethanol/water solvent mixture required long reaction times and generated significant quantities of a homo-coupled boronic acid product, which was difficult to separate. Therefore, we attempted 1,4-dioxane as a solvent for these reactions, which showed remarkable increased reaction rates and minimized the amount of homo-coupled products to aid in purification. Both (*E*)- and (*Z*)-1-chloro-1,2-difluorostyrenes stereospecifically gave the 1,2-difluorostilbenes in moderate to excellent yields. We investigated 4 protocols for the reaction. Protocols 2 and 3 were recommended for scale up, since the chlorostyrene starting material can be obtained in large quantities stereospecifically as described in previous reports. This work represents the first practical synthesis of unsymmetrical (*E*)- and (*Z*)-1,2-difluorostilbenes from readily available starting materials.

Keywords: Unsymmetrical (*E*)-1,2-difluorostilbenes, Unsymmetrical (*Z*)-1,2-difluorostilbenes, 1,4-dioxane was a superior solvent to the normal Suzuki reaction systems, Protocol for scaled up synthesis of unsymmetrical 1,2-difluorostilbenes.

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1. Introduction

Receiving little attention, unsymmetrical (*Z*)-1,2-difluorostilbenes were previously synthesized *via* photochemical isomerization of (*E*)-1,2-difluorostilbenes and separated by GLPC [1]. Additional attempts to improve separation *via* HPLC have been reported [2]. Nevertheless, obtaining significant quantities with these methods remains tedious and difficult. Symmetrical (*E*)-1,2-difluorostilbenes can be prepared in good yield through Stille-type coupling of (*E*)-(1,2-difluoro-1,2-ethenediyl)bis[tributylstannane] (Eq. 1) [3]. (*Z*)-1,2-difluorostilbenes can be prepared in several steps (Eq. 2) [2]. However, the reaction is tedious due to the number of steps, and does not contain a common intermediate similar to the preparation of (*E*)-1,2-difluorostilbene [3].

The synthesis for some unsymmetrical (*E*)-1,2-difluorostilbenes has been reported through the reaction of an alkyl lithium or Grignard reagent with trifluorostyrenes [4]. However, this route does not provide access to the (*Z*)-1,2-difluorostilbenes and contains no common intermediate for further derivatization.

2. Results and Discussion

Our objective for the synthesis of unsymmetrical (*E*)- and (*Z*)-1,2-difluorostilbenes was to start from an easily obtained and stereospecific starting material: such as (*E*)- or (*Z*)-2-chloro-1,2-difluoro-1-iodoethene [5], (*E*)- or (*Z*)-1-chloro-1,2-difluorostyrenes [6]. Initially, we carried out these reactions on a small scale to establish the stereospecificity of the final product and to assist in purification. We investigated several protocols to accomplish this objective and these protocols are discussed in detail below.

Protocol 1: Preparation of (*E*)- or (*Z*)-1,2-difluorostilbenes in benzene/ethanol/water.

Initially, sequential Suzuki couplings were attempted with varied boronic acids and (*E*)- or (*Z*)-2-chloro-1,2-difluoro-1-iodoethene. When a benzene/ethanol/water solvent mixture was used, the 2nd step of the reaction required a significant amount of time and heat while resulting in substantial amounts of a homo-coupled boronic acid byproduct [7]. Electron-withdrawing groups exacerbated the issue, requiring additional heat and time. Also, when the compound contained a methoxy group on the aryl ring, the product could not be effectively purified. In only one case were we able to obtain reasonable yield and purity of the final product (Eq. 3).

Protocol 2: Preparation of (*E*)-1,2-difluorostilbenes in 1,4-dioxane.

Since the benzene/ethanol/water solvent mixture did not meet our objective, we looked for a better solvent system to accomplish the preparation of unsymmetrical 1,2-difluorostilbenes more rapidly and to affect the purification of the final stilbene. Molander and Yun have described coupling reactions of primary alkylboronic acids in 1,4-dioxane [8]. Richards and coworkers have also described Suzuki reactions aided by the use of 1,4-dioxane as a solvent system [9]. To test the effectiveness of 1,4-dioxane as a reaction solvent, the reactions were monitored by ^{19}F -NMR spectroscopy. 1,4-Dioxane showed a remarkable rate increase, as compared to the benzene/ethanol/water mixture, for the Suzuki coupling of (*E*)-1-chloro-1,2-difluorostyrenes. The reaction was completed in less time and the amount of homocoupled product was decreased (7). Protocol 2 was successfully carried out for a series of unsymmetrical (*E*)-1,2-difluorostilbenes with both electron-withdrawing and electron-donating groups (Table 1).

Table 1. Preparation of unsymmetrical (*E*)-1,2-difluorostilbenes in 1,4-dioxane

Entry	X	Y	yield ^a	t (h)	°C
2	<i>m</i> -CH ₃	<i>p</i> -F	54%	1.5	100
3	<i>p</i> -OMe	<i>p</i> -F	67%	4	100
3	<i>p</i> -F	<i>p</i> -OMe	73%	2	100
4	2-thienyl	<i>p</i> -F	53%	1.5	100
5	<i>p</i> -NO ₂	<i>p</i> -F	65%	1.5	100

^a isolated yield

Protocol 3: Preparation of (*Z*)-1,2-difluorostilbenes in 1,4-dioxane.

As expected, coupling of the (*Z*)-1-chloro-1,2-difluorostyrenes was slightly slower, but gave reasonable yields and purity. Occasionally, the reaction was terminated early to minimize self-coupling of the boronic acid. A series of unsymmetrical (*Z*)-1,2-difluorostilbenes with both electron-withdrawing and electron-donating groups were successfully synthesized in moderate yields and high purity (Table 2).

Table 2. Preparation of unsymmetrical (Z)-1,2-difluorostilbenes in 1,4-dioxane

Entry	X	Y	yield ^a	t (h)	°C
6	<i>p</i> -Me	<i>p</i> -F	60%	6	100
7	<i>p</i> -OMe	<i>p</i> -F	72%	6	100
8	<i>o</i> -CF ₃	<i>p</i> -F	48%	9	100
9	<i>p</i> -OMe	<i>m</i> -CF ₃	65%	5	100

^a isolated yield

Protocol 4: One-pot preparation of unsymmetrical (Z)-1,2-difluorostilbenes.

To expedite the synthetic procedure, we attempted sequential couplings to (Z)-2-chloro-1,2-difluoro-1-iodoethene (Eq. 4 and 5). Two synthetic procedures were attempted: first, the zinc reagent from (Z)-2-chloro-1,2-difluoro-1-iodoethene was generated *in situ* followed by a Negishi coupling [6] and then a boronic acid and Pd catalyst were added to affect the formation of the final unsymmetrical 1,2-difluorostilbene (Eq. 4). Second, a Suzuki reaction with (Z)-2-chloro-1,2-difluoro-1-iodoethene and an aryl boronic acid was carried out in 1,4-dioxane to generate the (Z)-1-chloro-1,2-difluorostyrenes *in situ*. Sequentially, a second boronic acid was added to achieve the formation of the final unsymmetrical (Z)-1,2-difluorostilbene (Eq. 5).

Further butadienyl derivatives

To illustrate that the reaction can be extended further, we developed a method for the preparation of a butadienyl silane (Eq. 6). By conventional methods, elaboration of the silane to a stannane followed by Stille-type coupling with an aromatic iodide would lead to an extended derivative [10]. Further coupling with methods described in this account could yield 1,4-bis(aryl)-1,2,3,4-tetrafluorobutadiene derivatives.

3. Comparisons and Conclusion

(*E*)- and (*Z*)-1,2-difluorostilbenes can be readily prepared by the protocols 2, 3, or 4, since the 1,4-dioxane solvent system showed an enhanced rate as compared to the benzene/ethanol/water solvent mixture described in protocol 1. However, protocols 2 and 3 are recommended for scale up as the 1-chloro-1,2-difluorostyrenes are readily prepared in good yields [6] and further derivatization from a common styrene could lead to a library of unsymmetrical (*E*)- and (*Z*)-1,2-difluorostilbenes. We feel this methodology provided the best stereospecific route to unsymmetrical (*E*)- or (*Z*)-1,2-difluorostilbenes. Both NMR and Mass spectra data support the assigned structures.

4. Experimental

Routine ^{19}F -NMR spectra were recorded on a JEOL FX90Q Spectrometer (83.81 MHz) and high-resolution data was obtained on a Bruker AC-300 Spectrometer (282.41 MHz). Chemical shifts have been reported in ppm relative to internal CFCl_3 . Spectra of reaction mixtures were obtained in the ^7Li external lock mode. Quantitative determinations were carried out by integration relative to internal benzotrifluoride. Routine ^1H -NMR (300.17 MHz) spectra and high-resolution data were generally obtained on a Bruker AC-300 Spectrometer. Unless noted otherwise, CDCl_3 was used as the NMR lock solvent. Chemical shifts have been reported in ppm relative to internal TMS. High resolution $\{^1\text{H}\}^{13}\text{C}$ NMR spectra were recorded on a Bruker AC-300 Spectrometer (75.48 MHz). Chemical shifts have been reported in ppm relative to internal TMS. High-resolution mass spectra were obtained by the University of Iowa High Resolution Mass Spectrometry Facility. Silica gel was purchased from EM Science (Silica Gel 60, particle sized 0.063-0.200 μm , 70-230 Mesh, ASTM). The aryl boronic acids were obtained commercially and used without further purification. The 1-chloro-1,2-difluorostyrenes [6] and 2-chloro-1,2-difluoro-1-iodoethene [5] were synthesized according to literature. $\text{Pd}(\text{PPh}_3)_4$ was prepared by Coulson's procedure [11]. Dry 1,4-dioxane was achieved by the addition of NaBH_4 . The solution was filtered and distilled under argon until about 60-70% of the 1,4-dioxane was distilled; the rest was destroyed with ice. It was used immediately. As with all protocols, the reaction was carried by bubbling Argon through the reaction mixture (Fig. 1).

Figure 1. Reaction apparatus.

Protocol 1: Preparation of (*E*)-1-(4-fluorophenyl)-2-(4-methylphenyl)-1,2-difluoroethene (1**) in benzene/ethanol/water.**

A 100 mL 3-necked round bottom, as described above, was charged with palladium *tetrakis*(triphenylphosphine) (0.09 g, 0.08 mmol) and 15 mL of benzene. Argon was bubbled through the above solution *via* a steel needle for 30 min. Then, (*E*)-1-chloro-2-iodo-1,2-difluoroethene (0.4 g, 1.8 mmol), 4-fluorophenylboronic acid (0.21 g, 1.5 mmol), Na₂CO₃ (0.48 g, 4.5 mmol), and 20 mL of ethanol/water (1:1) were added to the Pd(0) solution. The temperature of the reaction mixture was increased to the reflux temperature (65 °C) while Argon was bubbled through. After 12 h, ¹⁹F-NMR analysis showed competition of the Suzuki coupling reaction of 4-fluorophenylboronic acid and (*E*)-1-chloro-2-iodo-1,2-difluoroethene. Then, 4-tolylboronic acid (0.2 g, 1.5 mmol) was added and the reaction mixture was returned to reflux. After 48 h, ¹⁹F-NMR analysis showed 84% conversion. Volatiles were removed by rotary evaporation. Organic materials were extracted by diethyl ether (3 x 30 mL) and washed with water (20 mL). The combined organic layers were dried over MgSO₄ and concentrated by rotary evaporation. Silica gel column chromatography (*R*_f = 0.4 in hexane) gave **1** as white crystals (0.23 g, 0.93 mmol, 62% isolated yield, mp = 82-83 °C, purity = 99% by ¹H-NMR). ¹H-NMR (CDCl₃): 7.74 (ddt, ⁴*J*_{HF} = 5.3 Hz, ³*J*_{HH} = 9.2 Hz, ^{4,5}*J*_{HF} = 2.3 Hz, 2H), 7.64 (d, ³*J*_{HH} = 8.4 Hz, 2H), 7.26 (d, ³*J*_{HH} = 8.3 Hz, 2H), 7.14 (t, ³*J*_{HF} = ³*J*_{HH} = 8.8 Hz, 2H), 2.4 (s, 3H). ¹⁹F-NMR (CDCl₃): -152.9 (d, ³*J*_{FF} = 120.8 Hz, 1F), -152.4 (d, ³*J*_{FF} = 120.8 Hz, 1F), -112 (m, 1F). ¹³C-NMR (CDCl₃): 162.6 (dd, ¹*J*_{CF} = 250.0 Hz, ⁵*J*_{CF} = 1.5 Hz), 148.4 (dd, ¹*J*_{CF} = 186.9 Hz, ²*J*_{CF} = 2.1 Hz), 147.3 (dd, ¹*J*_{CF} = 171.8 Hz, ²*J*_{CF} = 13.9 Hz), 139.2 (d, ⁵*J*_{CF} = 1.6 Hz), 129.2 (d, ⁴*J*_{CF} = 1.4 Hz), 127.8 (q, ^{3,3',4}*J*_{CF} = 8.8 Hz), 127.2 (d, ²*J*_{CF} = 18.5 Hz), 126.6 (dd, ²*J*_{CF} = 19.2 Hz,

$^3J_{\text{CF}} = 3.9$ Hz), 125.7 (dd, $^3J_{\text{CF}} = 8.6$ Hz, $^4J_{\text{CF}} = 8.1$ Hz), 115.6 (dd, $^2J_{\text{CF}} = 22.0$ Hz, $^4J_{\text{CF}} = 1.6$ Hz), 21.4 (s). HRMS ($\text{C}_{15}\text{H}_{11}\text{F}_3$, calculated: 248.0813, observed: 248.0813). GC-MS 248 (M^+ , 100), 233 (29), 232 (26), 183 (18).

Protocol 2: General preparation of (*E*)-1-(aryl)-2-(aryl')-1,2-difluoroethene (2-5) from (*E*)-1-chloro-1,2-difluorostyrenes.

A 50 mL 3-necked round bottom, as described above, was charged with palladium *tetrakis*(triphenylphosphine), dry 1,4-dioxane, (*E*)-1-chloro-2-aryl-1,2-difluoroethene, aryl-boronic acid, and K_3PO_4 . The temperature of the reaction mixture was increased to the reflux temperature (100 °C) while Argon was bubbled through. After ^{19}F -NMR analysis indicated 100% conversion, the reaction was stopped (1.5-4 h, Table 2) by the addition of 10 mL of water. Organic materials were extracted by hexane (3 x 15 mL) was washed with water (10 mL). The combined organic layers were dried over MgSO_4 and concentrated by rotary evaporation. Silica gel column chromatography gave the corresponding unsymmetrical (*E*)-1,2-difluorostilbene.

(*E*)-1-(4-fluorophenyl)-2-(3-methylphenyl)-1,2-difluoroethene (2).

Palladium *tetrakis*(triphenylphosphine) (0.06 g, 0.05 mmol), 8 mL dry 1,4-dioxane, (*E*)-1-chloro-2-(3-tolyl)-1,2-difluoroethene (0.2 g, 1.06 mmol), 4-fluorophenylboronic acid (0.2 g, 1.2 mmol), and K_3PO_4 (0.68 g, 3.2 mmol) gave **2** as white crystals (0.14 g, 0.57 mmol, 54% isolated yield, mp = 52-53 °C, purity = 95% by ^1H -NMR, $R_f = 0.3$ in hexane). ^1H -NMR (CDCl_3): 7.74 (dd, $^4J_{\text{HF}} = 5.3$ Hz, $J_{\text{HF}} = 3.6$ Hz, 2H), 7.56 (bs, 2H), 7.34 (t, $^3,^3J_{\text{HF}} = 7.9$ Hz, 1H), 7.25 ~ 7.11 (m, 3H), 2.41 (s, 3H). ^{19}F -NMR (CDCl_3): -151.8 (d, $^3J_{\text{FF}} = 121.4$ Hz, 1F), -152.4 (d, $^3J_{\text{FF}} = 121.6$ Hz, 1F), -111.8 (m, 1F). ^{13}C -NMR (CDCl_3): 162.7 (dd, $^1J_{\text{CF}} = 249.9$ Hz, $^5J_{\text{CF}} = 2.7$ Hz), 148.3 (dd, $^1J_{\text{CF}} = 206.1$ Hz, $^2J_{\text{CF}} = 18.4$ Hz), 147.6 (dd, $^1J_{\text{CF}} = 193.7$ Hz, $^2J_{\text{CF}} = 9.1$ Hz), 138.2 (d, $^4J_{\text{CF}} = 1.9$ Hz), 130.1 (dd, $^2J_{\text{CF}} = 21.6$ Hz, $^3J_{\text{CF}} = 3.5$ Hz), 129.9 (d, $^5J_{\text{CF}} = 1.9$ Hz), 128.4 (d, $^4J_{\text{CF}} = 1.9$ Hz), 127.9 (dt, $^3J_{\text{CF}} = 9.4$ Hz, $^3,^4J_{\text{CF}} = 8.1$ Hz), 126.6 (dt, $^2J_{\text{CF}} = 22.4$ Hz, $^3,^4J_{\text{CF}} = 3.4$ Hz), 126.3 (dd, $^3J_{\text{CF}} = 8.6$ Hz, $^4J_{\text{CF}} = 7.9$ Hz), 123.0 (dd, $^3J_{\text{CF}} = 9.4$ Hz, $^4J_{\text{CF}} = 8.0$ Hz), 115.6 (dd, $^2J_{\text{CF}} = 21.9$ Hz, $^4J_{\text{CF}} = 1.8$ Hz), 21.6 (s). HRMS ($\text{C}_{15}\text{H}_{11}\text{F}_3$, calculated: 248.0813, observed: 248.0813). GC-MS 248 (M^+ , 93), 233 (49), 232 (39), 228 (49), 227 (46), 225 (21), 229 (23), 214 (E5), 207 (32), 206 (18), 201 (41), 197 (20), 196 (18), 193 (17), 188 (17), 183 (93), 181 (24), 175 (24), 170 (15), 169 (52), 162 (22), 151 (60), 137 (17), 132 (33), 125 (40), 120 (15), 107 (13), 107 (21), 105 (19), 101 (19), 99 (18), 98 (22), 96 (19), 95 (20), 91 (18), 90 (20), 89 (19), 87 (24), 86 (16), 81 (43), 77 (45), 75 (56), 74 (44), 69 (21), 68 (17), 66 (31), 65 (30), 63 (42), 62 (89), 57 (23), 56 (44), 52 (99), 51 (74), 50 (100), 41 (30).

(*E*)-1-(4-fluorophenyl)-2-(4-methoxyphenyl)-1,2-difluoroethene (3).

Palladium *tetrakis*(triphenylphosphine) (0.03 g, 0.026 mmol), 4 mL dry 1,4-dioxane, (*E*)-1-chloro-2-(4-methoxyphenyl)-1,2-difluoroethene (0.14 g, 0.68 mmol), 4-fluorophenylboronic acid (0.12 g, 0.86 mmol), and K_3PO_4 (0.43 g 2.03 mmol) gave **3** as white crystals (0.12 g, 0.46 mmol, 67% isolated yield, mp = 87-88 °C, purity = 95% by ^1H -NMR, eluent 30:1 hexane/ethyl acetate). ^1H -NMR (CDCl_3): 7.74-7.67 (m,

4H), 7.13 (t, $^3J_{\text{HH}} = ^3J_{\text{HF}} = 8.6$ Hz, 2H), 6.97 (d, $^4J_{\text{HH}} = 8.6$ Hz, 2H), 3.86 (s, 3H). ^{19}F -NMR (CDCl_3): -154.2 (d, $^3J_{\text{FF}} = 120.6$ Hz, 1F), -151.8 (d, $^3J_{\text{FF}} = 120.6$ Hz, 1F), -112.1 (m, 1F). ^{13}C -NMR (CDCl_3): 162.5 (dd, $^1J_{\text{CF}} = 248.0$ Hz, $^5J_{\text{CF}} = 3.0$ Hz), 160.1 (d, $^5J_{\text{CF}} = 2.5$ Hz), 148.3 (ddd, $^1J_{\text{CF}} = 232.3$ Hz, $^2J_{\text{CF}} = 47.1$ Hz, $^6J_{\text{CF}} = 2.3$ Hz), 146.7 (dd, $^1J_{\text{CF}} = 229.8$ Hz, $^2J_{\text{CF}} = 48.0$ Hz), 127.6 (dd, $^2J_{\text{CF}} = 15.8$ Hz, $^3J_{\text{CF}} = 9.5$ Hz), 127.59 (d, $^3J_{\text{CF}} = 9.5$ Hz), 127.4 (dd, $^3J_{\text{CF}} = 9.1$ Hz, $^3J_{\text{CF}} = 7.8$ Hz), 122.6 (dd, $^2J_{\text{CF}} = 24.6$ Hz, $^3J_{\text{CF}} = 6.0$ Hz), 115.6 (dd, $^2J_{\text{CF}} = 21.7$ Hz, $^4J_{\text{CF}} = 2.0$ Hz), 114.0 (d, $^4J_{\text{CF}} = 2.0$ Hz), 55.3 (s). HRMS ($\text{C}_{15}\text{H}_{11}\text{F}_3\text{O}$, calculated: 264.0762, observed: 264.0763).

(E)-1-(4-fluorophenyl)-2-(4-methoxyphenyl)-1,2-difluoroethene (3).

Palladium *tetrakis*(triphenylphosphine) (0.02 g, 0.017 mmol), 4 mL dry 1,4-dioxane, (*E*)-1-chloro-2-(4-fluorophenyl)-1,2-difluoroethene (0.12 g, 0.62 mmol), 4-methoxyphenylboronic acid (0.11 g, 0.72 mmol), and K_3PO_4 (0.39 g 1.84 mmol) gave **3** as white crystals (0.12 g, 0.46 mmol, 73% isolated yield, mp = 87-88 °C, eluent 30:1 hexane/ethyl acetate).

(E)-1-(4-fluorophenyl)-2-(2-thienyl)-1,2-difluoroethene (4).

Palladium *tetrakis*(triphenylphosphine) (0.03 g, 0.026 mmol), 3 mL dry 1,4-dioxane, (*E*)-1-chloro-2-(4-fluoro)-1,2-difluoroethene (0.10 g, 0.55 mmol), 2-thienylboronic acid (0.09 g, 0.64 mmol), and K_3PO_4 (0.35 g 1.65 mmol) gave **4** as white solid (0.07 g, 0.29 mmol, 53% isolated yield, mp = 71-72 °C, eluent hexane). ^1H -NMR (CDCl_3): 7.74-7.69 (m, 2H), 7.46-7.41 (m, 2H), 7.16-7.11 (m, 3H). ^{19}F -NMR (CDCl_3): -149.3 (d, $^3J_{\text{FF}} = 117.9$ Hz, 1F), -148.8 (d, $^3J_{\text{FF}} = 118.0$ Hz, 1F), -111.7 (m, 1F). ^{13}C -NMR (CDCl_3): 162.7 (dd, $^1J_{\text{CF}} = 248.7$ Hz, $^5J_{\text{CF}} = 2.8$ Hz), 145.9 (ddd, $^1J_{\text{CF}} = 189.0$ Hz, $^2J_{\text{CF}} = 12.9$ Hz, $^6J_{\text{CF}} = 1.7$ Hz), 145.8 (dd, $^1J_{\text{CF}} = 192.9$ Hz, $^2J_{\text{CF}} = 11.9$ Hz), 131.6 (dd, $^2J_{\text{CF}} = 24.1$ Hz, $^3J_{\text{CF}} = 3.7$ Hz), 128.7 (dd, $^2J_{\text{CF}} = 29.6$ Hz, $^3J_{\text{CF}} = 2.2$ Hz), 127.4 (t, $^3J_{\text{CF}} = ^4J_{\text{CF}} = 12.7$ Hz), 127.37 (d, $^4J_{\text{CF}} = 9.0$ Hz), 127.3 (s), 125.6 (t, $^3J_{\text{CF}} = ^4J_{\text{CF}} = 5.4$ Hz), 115.8 (dd, $^2J_{\text{CF}} = 21.8$ Hz, $^4J_{\text{CF}} = 1.9$ Hz). HRMS ($\text{C}_{12}\text{H}_7\text{F}_3\text{S}$, calculated: 240.0221, observed: 240.0226).

(E)-1-(4-fluorophenyl)-2-(4-nitrophenyl)-1,2-difluoroethene (5).

Palladium *tetrakis*(triphenylphosphine) (0.03 g, 0.026 mmol), 4 mL dry 1,4-dioxane, (*E*)-1-chloro-2-(4-nitrophenyl)-1,2-difluoroethene (0.12 g, 0.55 mmol), 2-thienylboronic acid (0.09 g, 0.64 mmol), and K_3PO_4 (0.35 g 1.65 mmol) gave **5** as white solid (0.10 g, 0.36 mmol, 65% isolated yield, mp = 117-118 °C, eluent 20:1 hexane/ethyl acetate). ^1H -NMR (CDCl_3): 8.31 (d, $^3J_{\text{HH}} = 8.6$ Hz, 2H), 7.80 (dd, $^3J_{\text{HH}} = 9.1$ Hz, $^4J_{\text{HF}} = 5.3$ Hz, 2H), 7.92 (d, $^3J_{\text{HH}} = 9.2$ Hz, 2H), 7.19 (t, $^3J_{\text{HH}} = ^3J_{\text{HF}} = 8.5$ Hz, 2H). ^{19}F -NMR (CDCl_3): -154.1 (d, $^3J_{\text{FF}} = 119.8$ Hz, 1F), -145.2 (d, $^3J_{\text{FF}} = 119.9$ Hz, 1F), -109.4 (m, 1F). ^{13}C -NMR (CDCl_3): 163.4 (dd, $^1J_{\text{CF}} = 250.6$ Hz, $^6J_{\text{CF}} = 3.1$ Hz), 150.1 (dd, $^1J_{\text{CF}} = 241.5$ Hz, $^2J_{\text{CF}} = 46.4$ Hz), 147.4 (d, $^5J_{\text{CF}} = 3.0$ Hz), 146.3 (ddd, $^1J_{\text{CF}} = 233.7$ Hz, $^2J_{\text{CF}} = 47.0$ Hz, $^6J_{\text{CF}} = 2.1$ Hz), 136.1 (dd, $^2J_{\text{CF}} = 24.2$ Hz, $^3J_{\text{CF}} = 6.7$ Hz), 128.52 (dd, $^2J_{\text{CF}} = 16.5$ Hz, $^3J_{\text{CF}} = 9.6$ Hz), 128.51 (d, $^3J_{\text{CF}} = 9.6$ Hz), 126.3 (dd, $^3J_{\text{CF}} = 10.8$ Hz, $^3J_{\text{CF}} = 8.1$ Hz), 123.9 (d, $^4J_{\text{CF}} = 2.4$ Hz), 116.0 (dd, $^2J_{\text{CF}} = 21.9$ Hz, $^4J_{\text{CF}} = 2.0$ Hz). HRMS ($\text{C}_{14}\text{H}_8\text{F}_3\text{NO}_2$, calculated: 279.0507, observed: 279.0503).

Protocol 3: General preparation of (Z)-1-(aryl)-2-(aryl')-1,2-difluoroethene (6-9) from (Z)-1-chloro-1,2-difluorostyrenes.

A 50 mL 3-necked round bottom, as described above, was charged with palladium *tetrakis*(triphenylphosphine), dry 1,4-dioxane, (*Z*)-1-chloro-2-aryl-1,2-difluoroethene, aryl-boronic acid, and K₃PO₄. The temperature of the reaction mixture was increased to the reflux temperature (100 °C) while Argon was bubbled through. After ¹⁹F-NMR analysis indicated 100% conversion, the reaction was stopped (5-9 h, Table 3) by the addition of 10 mL of water. Organic materials were extracted by hexane (3 x 15 mL) was washed with water (10 mL). The combined organic layers were dried over MgSO₄ and concentrated by rotary evaporation. Silica gel column chromatography gave the corresponding unsymmetrical (*Z*)-1,2-difluorostilbene.

(*Z*)-1-(4-fluorophenyl)-2-(4-methylphenyl)-1,2-difluoroethene (6).

Palladium *tetrakis*(triphenylphosphine) (0.03 g, 0.03 mmol), 6 mL dry 1,4-dioxane, (*Z*)-1-chloro-2-(4-tolyl)-1,2-difluoroethene (0.1 g, 0.53 mmol), 4-fluorophenylboronic acid (0.08 g, 0.6 mmol), and K₃PO₄ (0.34 g, 1.59 mmol) gave **6** as colorless liquid (0.08 g, 0.32 mmol, 60% isolated yield, purity = 99% by ¹H-NMR, R_f = 0.3 in hexane). ¹H-NMR (CDCl₃): 7.37 (ddm, ⁴J_{HF} = 5.4 Hz, ³J_{HH} = 8.2 Hz, 2H), 7.27 (d, ³J_{HH} = 8.1 Hz, 2H), 7.17 (d, ³J_{HH} = 8.2 Hz, 2H), 7.04 (t, ³J_{HF} = ³J_{HH} = 8.5 Hz, 2H), 2.40 (s, 3H). ¹⁹F-NMR (CDCl₃): -129.4 (d, ³J_{FF} = 13.6 Hz, 1F), -127.4 (d, ³J_{FF} = 13.7 Hz, 1F), -111.2 (m, 1F). ¹³C-NMR (CDCl₃): 163.1 (d, ¹J_{CF} = 250.0 Hz), 145.5 (dd, ¹J_{CF} = 247.1 Hz, ²J_{CF} = 21.6 Hz), 144.3 (dd, ¹J_{CF} = 245.2 Hz, ²J_{CF} = 21.6 Hz), 140.0 (s), 130.0 (dt, ³J_{CF} = 8.0 Hz, ^{3,4}J_{CF} = 4.1 Hz), 129.3 (s), 128.0 (t, ^{3,4}J_{CF} = 3.6 Hz), 126.9 (d, ²J_{CF} = 24.5 Hz), 126.4 (dd, ²J_{CF} = 24.8 Hz, ³J_{CF} = 2.5 Hz), 115.7 (d, ²J_{CF} = 21.9 Hz), 21.4 (s). HRMS (C₁₅H₁₁F₃, calculated: 248.0813, observed: 248.0814). GC-MS 249 (18), 248 (M⁺, 97), 233 (100), 228 (20), 227 (38), 225 (16), 201 (19), 196 (19), 183 (59), 151 (17), 109 (16), 98 (21).

(*Z*)-1-(4-fluorophenyl)-2-(4-methoxyphenyl)-1,2-difluoroethene (7).

Palladium *tetrakis*(triphenylphosphine) (0.06 g, 0.06 mmol), 12 mL dry 1,4-dioxane, (*Z*)-1-chloro-2-(4-methoxyphenyl)-1,2-difluoroethene (0.2 g, 1.0 mmol), 4-fluorophenylboronic acid (0.16 g, 1.2 mmol), and K₃PO₄ (0.68 g, 3.18 mmol) gave **7** as colorless liquid (0.19 g, 0.72 mmol, 72% isolated yield, purity = 99% by ¹H-NMR, R_f = 0.05 in hexane). ¹H-NMR (CDCl₃): 7.29 (dd, ³J_{HH} = 8.9 Hz, ⁴J_{HF} = 5.3 Hz, 2H), 7.25 (d, ³J_{HH} = 9.0 Hz, 2H), 6.96 (t, ³J_{HH} = ³J_{HF} = 8.7 Hz, 2H), 6.82 (d, ³J_{HH} = 8.9 Hz, 2H), 3.79 (s, 3H). ¹⁹F-NMR (CDCl₃): -130.8 (d, ³J_{FF} = 14.9 Hz, 1F), -126.2 (d, ³J_{FF} = 14.9 Hz, 1F), -111.3 (bs, 1F). ¹³C-NMR (CDCl₃): 163.0 (d, ¹J_{CF} = 250.1 Hz), 160.6 (s), 145.4 (dd, ¹J_{CF} = 247.4 Hz, ²J_{CF} = 20.8 Hz), 143.9 (dd, ¹J_{CF} = 244.8 Hz, ²J_{CF} = 22.0 Hz), 129.9 (dt, ³J_{CF} = 13.4 Hz, ^{3,4}J_{CF} = 3.9 Hz), 129.8 (t, ^{3,4}J_{CF} = 3.5 Hz), 126.5 (dd, ²J_{CF} = 25.0 Hz, ³J_{CF} = 3.5), 122.1 (d, ²J_{CF} = 24.8 Hz), 115.6 (d, ²J_{CF} = 22.0 Hz), 114.1 (s), 55.3 (s). HRMS (C₁₅H₁₁OF₃, calculated: 264.0762, observed: 248.0758). GC-MS 264- (M⁺, 55), 249 (32), 201 (100), 57 (19), 51 (18), 50 (20).

(*Z*)-1-(4-fluorophenyl)-2-(2-trifluoromethylphenyl)-1,2-difluoroethene (8).

Palladium *tetrakis*(triphenylphosphine) (0.03 g, 0.026 mmol), 3 mL dry 1,4-dioxane, (*Z*)-1-chloro-2-(2-trifluoromethylphenyl)-1,2-difluoroethene (0.1 g, 0.41 mmol), 4-

fluorophenylboronic acid (0.07 g, 0.50 mmol), and K₃PO₄ (0.26 g, 1.23 mmol) gave **8** as colorless oil (0.06 g, 0.2 mmol, 48% isolated yield, eluent hexane). ¹H-NMR (CDCl₃): 7.81 (d, ³J_{HH} = 7.6 Hz, 1H), 7.59 (td, ³J_{HH} = ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 0.6 Hz, 1H), 7.51 (t, ³J_{HH} = ³J_{HH} = 7.5 Hz, 1H), 7.37 (d, ³J_{HH} = 7.6 Hz, 1H), 7.10 (dd, ³J_{HH} = 8.9 Hz, ⁴J_{HF} = 5.3 Hz, 2H), 6.90 (t, ³J_{HH} = ³J_{HF} = 8.5 Hz, 2H). ¹⁹F-NMR (CDCl₃): -130.7 (d, ³J_{FF} = 15.5 Hz, 1F), -117.6 (m, 1F), -111.1 (m, 1F), -61.3 (d, ⁴J_{FF} = 10.4 Hz, 3F). ¹³C-NMR (CDCl₃): 162.9 (d, ¹J_{CF} = 249.0 Hz), 145.5 (dd, ¹J_{CF} = 246.5 Hz, ²J_{CF} = 20.6 Hz), 142.6 (dd, ¹J_{CF} = 250.2 Hz, ²J_{CF} = 22.9 Hz), 133.4 (t, ³J_{CF} = ⁴J_{CF} = 2.3 Hz), 132.4 (s), 130.9 (d, ⁴J_{CF} = 2.6 Hz), 130.8 (qd, ²J_{CF} = 25.2 Hz, ³J_{CF} = 2.5 Hz), 129.1 (ddd, ³J_{CF} = 8.4 Hz, ³J_{CF} = 5.0 Hz, ⁴J_{CF} = 3.4 Hz), 127.9 (dt, ²J_{CF} = 23.1 Hz, ³J_{CF} = ⁴J_{CF} = 2.0 Hz), 127.3 (qd, ³J_{CF} = 4.9 Hz, ⁴J_{CF} = 2.1 Hz), 125.5 (dd, ²J_{CF} = 24.6 Hz, ³J_{CF} = 3.5 Hz), 123.4 (q, ¹J_{CF} = 272.3 Hz), 115.6 (d, ²J_{CF} = 21.9 Hz). HRMS (C₁₅H₈F₆, calculated: 302.0530, observed: 302.0531).

(Z)-1-(4-methoxyphenyl)-2-(3-trifluoromethylphenyl)-1,2-difluoroethene (9).

Palladium *tetrakis*(triphenylphosphine) (0.03 g, 0.026 mmol), 4 mL dry 1,4-dioxane, (Z)-1-chloro-2-(4-methoxyphenyl)-1,2-difluoroethene (0.14 g, 0.68 mmol), 3-trifluoromethylphenylboronic acid (0.16 g, 0.84 mmol), and K₃PO₄ (0.43 g, 2.00 mmol) gave **9** as yellow oil (0.14 g, 0.45 mmol, 65% isolated yield, eluent 40:1 hexane/ethyl acetate). ¹H-NMR (CDCl₃): 7.60 (s, 1H), 7.54 (d, ³J_{HH} = 7.6 Hz, 1H), 7.44 (d, ³J_{HH} = 7.6 Hz, 1H), 7.37 (t, ³J_{HH} = ³J_{HH} = 7.9 Hz, 1H), 7.29 (dd, ³J_{HH} = 9.0 Hz, ⁴J_{HH} = 1.0 Hz, 2H), 6.86 (d, ³J_{HH} = 8.3 Hz, 2H). ¹⁹F-NMR (CDCl₃): -121.8 (d, ³J_{FF} = 14.2 Hz, 1F), -134.2 (d, ³J_{FF} = 14.2 Hz, 1F), -63.4 (s, 3F). ¹³C-NMR (CDCl₃): 161.6 (d, ⁵J_{CF} = 1.2 Hz), 146.6 (dd, ¹J_{CF} = 249.3 Hz, ²J_{CF} = 20.1 Hz), 143.4 (dd, ¹J_{CF} = 242.8 Hz, ²J_{CF} = 22.3 Hz), 131.4 (dd, ²J_{CF} = 24.7 Hz, ³J_{CF} = 1.4 Hz), 131.0 (q, ²J_{CF} = 32.5 Hz), 130.6 (m), 130.1 (t, ³J_{CF} = ⁴J_{CF} = 3.3 Hz), 128.9 (s), 125.6 (q, ³J_{CF} = 3.7 Hz), 124.3 (dd, ³J_{CF} = 8.7 Hz, ⁴J_{CF} = 3.9 Hz), 123.7 (q, ¹J_{CF} = 270.8 Hz), 121.6 (d, ²J_{CF} = 24.5 Hz), 114.3 (s), 55.4 (s). HRMS (C₁₆H₁₁OF₅, calculated: 314.0730, observed: 314.0728).

Protocol 4a: Preparation of (Z)-1-(4-fluorophenyl)-2-(phenyl)-1,2-difluoroethene (10).

A 50 mL 3-necked round bottom, as described above, was charged with acid washed zinc powder (0.39 g, 6.0 mmol) and 7 mL of THF. Then, (Z)-1-chloro-2-iodo-1,2-difluoroethene (1.12 g, 5.0 mmol) was transferred to the above solution *via* syringe. The reaction mixture was stirred for 1 hour at reflux temperature. ¹⁹F-NMR confirmed the generation of the corresponding zinc reagent (99 % NMR yield). Another 50 mL 3-necked round bottom, as described above, was charged with 1-fluoro-4-iodobenzene (0.85 g, 3.85 mmol), and palladium *tetrakis*(triphenylphosphine) (0.22 g, 0.19 mmol). The pregenerated zinc reagent was added dropwise to the Pd(0) solution *via* a syringe. The reaction mixture was stirred for 2 hours at the reflux temperature, and ¹⁹F-NMR analysis showed the formation of (Z)-1-chloro-2-(4-fluorophenyl)-1,2-difluoroethene (98 % NMR yield). Without isolation of the product, the reaction mixture was mixed with phenylboronic acid (0.56 g, 4.6 mmol), KOH (0.85 g, 15.2 mmol), palladium *tetrakis*(triphenylphosphine) (0.22 g, 0.19 mmol), and 15 mL of water. The reaction mixture was stirred for 24 hours at reflux temperature, and the completion of the reaction was confirmed by ¹⁹F-NMR analysis. After removal of volatiles by rotary

evaporation, the organic material was extracted by diethyl ether (3 x 10 mL) and washed with water (15 mL). The combined organic layers were dried over MgSO_4 , and concentrated by rotary evaporation. Silica gel column chromatography (R_f = 0.45 in hexane) gave **10** as white crystals (0.60 g, 2.6 mmol, 68 % isolated yield, mp = 51-53 °C, purity = 99 % by ^1H -NMR). ^1H -NMR (CDCl_3): 7.34-7.28 (m, 7H), 6.98 (t, $^3J_{\text{HF}}$ = 8.5 Hz, 2H). ^{19}F -NMR (CDCl_3): -128.0 (d, $^3J_{\text{FF}}$ = 13.8 Hz, 1F), -128.6 (d, $^3J_{\text{FF}}$ = 13.9 Hz, 1F), -110.8 (m, 1F). ^{13}C -NMR (CDCl_3): 163.2 (d, $^1J_{\text{CF}}$ = 250.9 Hz), 145.4 (dd, $^1J_{\text{CF}}$ = 247.3 Hz, $^2J_{\text{CF}}$ = 21.1 Hz), 144.7 (dd, $^1J_{\text{CF}}$ = 246.2 Hz, $^2J_{\text{CF}}$ = 20.8 Hz), 130.2 (dt, $^3J_{\text{CF}}$ = 8.2 Hz, $^3,4J_{\text{CF}}$ = 3.7 Hz), 130.0 (d, $^2J_{\text{CF}}$ = 24.1 Hz), 129.6 (s), 128.6 (s), 128.0 (t, $^3,4J_{\text{CF}}$ = 4.2 Hz), 126.2 (dd, $^2J_{\text{CF}}$ = 24.6 Hz, $^3J_{\text{CF}}$ = 3.3 Hz), 115.7 (d, $^2J_{\text{CF}}$ = 22.1 Hz). HRMS ($\text{C}_{14}\text{H}_9\text{F}_3$, calculated: 234.0656, observed: 234.0658). GC-MS 234 (M^+ , 75), 233 (28), 232 (17), 219 (17), 214 (100), 183 (66), 81 (28), 75 (20), 74 (25), 63 (22), 62 (25), 57 (43), 51 (79), 50 (73).

Protocol 4b: Preparation of (Z)-1-(3-nitrophenyl)-2-(phenyl)-1,2-difluoroethene (11).

A 50 mL 3-necked round bottom, as described above, was charged with palladium *tetrakis*(triphenylphosphine) (0.03 g, 0.03 mmol), (Z)-1-chloro-2-iodo-1,2-difluoroethene (0.22 g, 1 mmol) and 12 mL of dry dioxane. Argon was bubbled through above Pd(0) solution by a syringe needle for 30 min. Then, phenylboronic acid (0.13 g, 1.1 mmol) and K_3PO_4 (0.64 g, 3 mmol) were added to the above solution. The temperature of the reaction mixture was increased to the reflux (100 °C) while argon was bubbled through the reaction mixture. ^{19}F -NMR analysis indicated 100% conversion after reflux for 2 hours. To the above reaction mixture, (3-nitrophenyl)boronic acid (0.17 g, 1.1 mmol), palladium *tetrakis*(triphenylphosphine) (0.01 g, 0.01 mmol), and K_3PO_4 (0.42 g, 2 mmol) were added. The temperature of the reaction mixture was increased again to the reflux (100 °C). After ^{19}F -NMR analysis indicated 100% conversion, the reaction was stopped (6 h). Water (10 mL) was added to the reaction mixture. Organic materials were extracted by hexane (3 x 20 mL) and washed with water (20 mL). The organic layer was dried over anhydrous MgSO_4 , and concentrated by rotary evaporation. Silica gel column chromatography (R_f = 0.05 in hexane) gave **11** as yellow crystals (0.18 g, 0.69 mmol, 69 % isolated yield, mp = 38-39 °C, purity = 98 % by ^1H -NMR). ^1H -NMR (CDCl_3): 8.19 (bt, $^4,5J_{\text{HF}}$ = 1.9 Hz, 1H), 8.16 (bd, $^3J_{\text{HH}}$ = 8.2 Hz, 1H), 7.58 (bd, $^3J_{\text{HH}}$ = 8.2 Hz, 1H), 7.45-7.36 (m, 6H). ^{19}F -NMR (CDCl_3): -133.0 (d, $^3J_{\text{FF}}$ = 12.5 Hz, 1F), -121.3 (d, $^3J_{\text{FF}}$ = 12.4 Hz, 1F). ^{13}C -NMR (CDCl_3): 148.3 (s), 147.1 (dd, $^1J_{\text{CF}}$ = 252.5 Hz, $^2J_{\text{CF}}$ = 20.2 Hz), 143.3 (dd, $^1J_{\text{CF}}$ = 246.2 Hz, $^2J_{\text{CF}}$ = 22.4 Hz), 133.2 (dd, $^3J_{\text{CF}}$ = 4.4 Hz, $^4J_{\text{CF}}$ = 2.9 Hz), 132.0 (dd, $^2J_{\text{CF}}$ = 25.2 Hz, $^3J_{\text{CF}}$ = 1.5 Hz), 130.6 (d, $^4J_{\text{CF}}$ = 1.8 Hz), 129.5 (s), 129.2 (bd, $^2J_{\text{CF}}$ = 23.4 Hz), 129.0 (s), 128.5 (t, $^3,4J_{\text{CF}}$ = 3.0 Hz), 123.9 (s), 122.5 (dd, $^3J_{\text{CF}}$ = 5.1 Hz, $^4J_{\text{CF}}$ = 3.8 Hz). HRMS ($\text{C}_{14}\text{H}_9\text{F}_2\text{O}_2\text{N}$, calculated: 261.0601, observed: 261.0597). GC-MS 261 (M^+ , 100), 215 (18), 214 (90), 194 (16), 165 (26), 164 (15), 50 (17).

Preparation of (1E,3Z)-1-chloro-1,2,3,4-difluoro-4-trimethylsilylbutadiene (12).

A 50 mL 3-necked round bottom, as described above, was charged with acid washed zinc powder (0.39 g, 6.0 mmol) and 7 mL of THF. Then, (*Z*)-1-chloro-2-iodo-1,2-difluoroethene (1.12 g, 5.0 mmol) was transferred to the above solution *via* syringe. The reaction mixture was stirred for 1 hour at reflux temperature, and ^{19}F -NMR analysis confirmed generation of the corresponding zinc reagent (98 % NMR yield). The stirring of the reaction mixture was stopped to settle down unreacted zinc metal for over 1 hour. The concentration of the THF solution of the zinc reagent was estimated to be 0.88 M by ^{19}F -NMR analysis using an internal standard (trifluorotoluene). Another 50 mL 3-necked round bottom, as described above, was charged with (*E*)-1-iodo-2-trimethylsilyl-1,2-difluoroethene (3.0 g, 11.3 mmol) and palladium *tetrakis*(triphenylphosphine) (0.69 g, 0.7 mmol). The pregenerated zinc reagent was added dropwise to the Pd(0) solution via syringe. The reaction mixture was stirred for 8 hours at the reflux. ^{19}F -NMR analysis showed the formation of (1*E*,3*Z*)-1-chloro-1,2,3,4-tetrafluoro-4-trimethylsilylbutadiene (96% NMR yield). Volatiles including the product were flash distilled and collected by a liquid nitrogen trap. Simple distillation (bp = 122-124 °C) of the distillates under atmospheric pressure gave **12** (1.96 g, 8.44 mmol, 75% isolated yield, purity = 93% by ^1H -NMR). ^1H -NMR (CDCl_3): 0.29 (dd, $^4J_{\text{HF}} = 1.3$ Hz, $^5J_{\text{HF}} = 0.8$ Hz, 9H). ^{19}F -NMR (CDCl_3): -157.6 (bdd, $^3J_{\text{FF}} = 137.3$ Hz, $^3J_{\text{FF}} = 34.4$ Hz, 1F), -148.2 (ddd, $^3J_{\text{FF}} = 139.1$ Hz, $^4J_{\text{FF}} = 11.1$ Hz, $^5J_{\text{FF}} = 11.1$ Hz, 1F), -141.0 (ddd, $^3J_{\text{FF}} = 35.1$ Hz, $^4J_{\text{FF}} = 12.0$ Hz, $^3J_{\text{FF}} = 8.7$ Hz, 1F), -96.2 (ddd, $^3J_{\text{FF}} = 10.1$ Hz, $^5J_{\text{FF}} = 10.1$ Hz, $^3J_{\text{FF}} = 4.5$ Hz, 1F). ^{13}C -NMR (CDCl_3): 163.1 (ddt, $^1J_{\text{CF}} = 284.1$ Hz, $^2J_{\text{CF}} = 71.7$ Hz, $^3,^4J_{\text{CF}} = 2.5$ Hz), 149.7 (dddd, $^1J_{\text{CF}} = 226.9$ Hz, $^2J_{\text{CF}} = 38.5$ Hz, $^2J_{\text{CF}} = 23.7$ Hz, $^3J_{\text{CF}} = 2.1$ Hz), 141.2 (dddd, $^1J_{\text{CF}} = 307.0$ Hz, $^2J_{\text{CF}} = 32.2$ Hz, $^3J_{\text{CF}} = 7.4$ Hz, $^4J_{\text{CF}} = 4.2$ Hz), 133.1 (dddd, $^1J_{\text{CF}} = 250.1$ Hz, $^2J_{\text{CF}} = 32.2$ Hz, $^2J_{\text{CF}} = 23.1$ Hz, $^3J_{\text{CF}} = 2.3$ Hz), -2.9 (bt, $^4,^5J_{\text{CF}} = 2.0$ Hz). HRMS ($\text{C}_7\text{H}_9\text{F}_4^{35}\text{Cl}^{28}\text{Si}$, calculated: 232.0098, observed: 232.0096). GC-MS 234 ($\text{M}^+ + 2$, 0.04), 232 (M^+ , 0.08), 142 (17), 140 (50), 109 (24), 101 (30), 93 (15), 90 (31), 81.4 (34), 80.5 (40), 77.4 (87), 76.6 (100), 73 (30), 63 (18), 62 (24), 49.3 (35), 48.6 (51), 47 (35), 46 (52), 45 (16), 43 (89).

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6. References

- [1] For a typical example: J. Guo-Zhen, C. Guo-Fei, W. Zong-Mei and J. Xi-Kui, *Acta Chim. Sinica*, 5 (1987), 273-279.
- [2] D.J. Burton, C.A. Wesolowski, Q. Liu, C.R. Davis, *J. Fluorine Chem.* 131 (2010) 989-995.

- [3] a) Q. Liu, D.J. Burton, J. Fluorine Chem. 131 (2010) 1082-1085 b) Q. Liu, D.J. Burton, Org. Lett. 2002, 4, 1483-1485.
- [4] J. Irisawa, O. Yokokoji, T. Shimizu, Y. Ishida, H. Ko, K. Oike, K. Machida, Asahi Glass Co Ltd, Japan; Seimi Chem Kk. "Difluorostilbene compounds, liquid-crystal compositions thereof, and liquid-crystal display devices", Patent, 1994.
- [5] C. Lim, C.A. Wesolowski, D.J. Burton, J. Fluorine Chem. 159 (2014) 21-28.
- [6] C. Lim, D.J. Burton, J. Fluorine Chem. 167 (2014) 61-73.
- [7] Unpublished results: C. Lim, Ph.D. Thesis, University of Iowa, 2004 pp. 181
- [8] G.A. Molander, C. Yun, Tetrahedron 58 (2002) 1465-1470
- [9] T.E. Pickett, F.X. Roca, C.J. Richards J. Org. Chem. 2003 68 2592-2599.
- [10] S. Lukaszewski-Rose, D.J. Burton, J. Fluorine Chem. 179 (2015) 23-32.
- [11] D.R. Coulson, Inorg. Synth. 13 (1972) 121-124.