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One-pot synthesis of *gem*-difluorostyrenes from benzyl bromide via olefination of phosphonium ylide with difluorocarbene

Xiao-Yun Deng, Jin-Hong Lin, Ji-Chang Xiao *

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

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ABSTRACT

A new approach for the synthesis of *gem*-difluorostyrenes from benzyl bromide is described. Quaternization of triphenylphosphine with benzyl bromide to give phosphonium salts, deprotonation of the corresponding phosphonium salts to produce phosphonium ylide, and the subsequent olefination of phosphonium ylide with difluorocarbene generated from difluoromethylene phosphobetaine ($Ph_3P^+CF_2CO_2^-$) by decarboxylation can occur smoothly in one-pot, furnishing the final *gem*-difluorostyrenes in good yields.

1. Introduction

As *gem*-difluoroolefins have proved to be important intermediates in organic synthesis and the *gem*-difluorovinyl moiety is a valuable functionality in medicinal and agricultural chemistry and materials science [1], intensive studies have been devoted to the exploration of efficient methods for the synthesis of *gem*-difluoroolefins. The traditional β-elimination or addition–elimination protocols require the tedious preparation of fluorinated precursors [2]. The use of building blocks such as *gem*-difluorovinylmetals is a promising approach, but suffers from the multistep synthesis of moisture-sensitive building blocks [3]. A straightforward alternative is the *gem*-difluoroolefination of carbonyl groups, including Wittig reaction [4], Julia reaction [5] and Horner–Wadsworth–Emmons reaction [6]. Interestingly, nucleophilic substitution of alkyl halides with in situ generated functionalized difluoromethyl anion species [XCF_2^-, X = $PhSO_2$, PhSO(NTBS)] followed by a base-mediated 1,2-elimination reaction can also lead to *gem*-difluoroolefins, but the nucleophilic substitution products need to be isolated first or the air-sensitive base must be used in the 1,2-elimination reaction [2g,2i,7]. Clearly, the attractive protocol is the convenient reactions starting from commercially available materials by employing easily accessible reagents. Our efforts have been aimed at the development of attractive methods for the synthesis of *gem*-difluoroolefins [4e,4f,8], not only from the perspective of synthetic interest, but also from the perspective of theoretical investigation. Herein we describe a one-pot synthesis of *gem*-difluorostyrenes from benzyl bromide via olefination of phosphonium ylide with difluorocarbene generated by decarboxylation.

The synthesis of *gem*-difluoroolefins via olefination of phosphonium ylide with difluorocarbene was once explored by Burton (Eq. (a), Scheme 1) [9]. They found that the phosphonium ylide can not only deprotonate HCF_2Cl to produce difluorocarbene, but also trap difluorocarbene to afford the final products. Although this approach is promising, it suffers from the need to prepare the pure phosphonium salts, the use of air-sensitive lithium reagent as the base, and the use of volatile ozone-depleting reagent. We found that the phosphonium ylide produced from benzyl bromide can further react with difluoromethylene phosphobetaine ($Ph_3P^+CF_2CO_2^-$, PDFA, **1**), which has been shown to be an efficient difluorocarbene reagent [10], to furnish the expected *gem*-difluorostyrenes in one-pot (Eq. (b), Scheme 1).

2. Results and discussion

4-Phenyl-benzyl bromide (**2a**) was selected as the substrate to screen the reaction conditions (Table 1). Due to our previous

* Corresponding author. Tel.: +86 21 5492 5340; fax: +86 21 6416 6128.
E-mail address: jchxiao@sioc.ac.cn (J.-C. Xiao).

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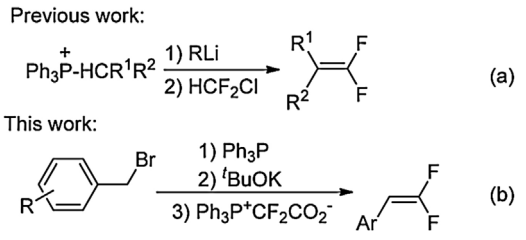


Scheme 1. Olefination of phosphonium ylide with difluorocarbene.

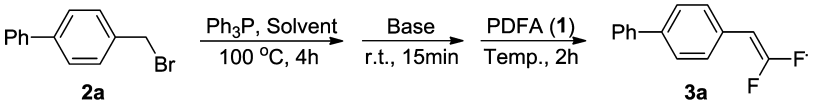
observation that the generation of difluorocarbene from PDFA occurred smoothly in *p*-xylene, it was firstly used as the reaction solvent. The quaternization of triphenylphosphine with substrate **2a** proceeded very well in *p*-xylene to give the corresponding phosphonium salt. To our delight, deprotonation of this salt by ^{t}BuOK and the subsequent olefination with PDFA at 70 °C occurred smoothly, albeit in low yield of the desired product (entry 1). But no desired product was observed with the use of other base to deprotonate the phosphonium salt (entries 2 and 3). The temperature was found to be crucial for olefination step (entries 4–6). Lowering the temperature to 40 °C resulted in an obvious decrease in the yield (entry 4). The yield was increased to 53% (entry 5) while elevating the temperature to 100 °C. But further increasing the temperature didn't improve the yield (entry 6). The reaction was influenced by the choice of solvent (entries 7–9). The reaction worked very well in 1,4-dioxane or toluene, giving the difluoroolefinated product in 47–48% yield (entries 7–8). But polar solvent such as DMF was not suitable for this conversion (entry 9). The molar ratio of **2a**:Ph_3P:^{t}BuOK:PDFA greatly influenced the reaction (entries 10–13). 1:1.2:1.8:2 of **2a**:Ph_3P:^{t}BuOK:PDFA was found to be the optimal choice (entry 13). The product was isolated in 70% yield under these conditions.

With the optimal reaction conditions in hand (entry 13, Table 1), we then explored the substrate scope of this reactions. As shown in Scheme 2, the reactions can tolerate a variety of functional groups and proceeded smoothly to give the desired products in good yields. Interestingly, small amount of (*Z*)-monofluorostyrene (<9%) was detected by ^{19}F NMR spectroscopy in each reaction system, which could be explained by the following proposed reaction mechanism. Although 3′-MeO-substituted substrate could be converted well into the expected product in moderate yield (**3b**), lower yield was obtained for the transformation of the 4′-MeO-substituted substrate (**3c**). The electron-deficient substrates seemed quite reactive under these conditions (**3d–3m**). The ketonic carbonyl group remains intact in this conversion (**3f**), meaning the side Wittig reaction of carbonyl group with PDFA was suppressed [4e]. Unactivated alkyl bromide such as 2-phenylethyl bromide cannot quaternize triphenylphosphorus to give phosphonium salt under these conditions. This phosphonium salt could be obtained with the use of 2-phenylethyl iodide instead of 2-phenylethyl bromide, but it could not be transformed into the corresponding *gem*-difluoroolefin. Some products are too volatile to be isolated (**3b–3c**, **3h**, **3j**, **3n**), so the corresponding yields were determined by ^{19}F NMR. It is noteworthy that the *gem*-difluorovinyl moiety does not further react with difluorocarbene to generate cyclopropanes.

The olefination of phosphonium ylide with PDFA should involve the difluorocarbene species. In order to support our hypothesis, further experimental evidence was collected. In the olefination step, tetramethylethylene ($Me_2C = CMe_2$, 2 equiv.), a difluorocarbene scavenger, was added into the reaction system. The yield of the desired *gem*-difluorostyrene **3a** was reduced dramatically (Scheme 3). The cyclopropanation product **5** was obtained in very low yield (8%), which might be due to its high volatility. The reaction was carried out at high temperature in Schlenk tube, meaning that it is difficult to keep the compound **5** in the solution. As a result, low yield of **5** was offered. The reaction proved that difluorocarbene is involved.

On the basis of the above results and the reported literature [9], we propose the reaction mechanism as shown in Scheme 4. The quarternization and deprotonation afford the phosphonium ylide **A**. The ylide is trapped by difluorocarbene generated from PDFA by decarboxylation [10] to produce 1,3-dipolar species **B** and three-membered cyclic phosphorane **C**, between which an equilibrium is established. Both intermediates **B** and **C** can lead to the final product **3** via elimination of triphenylphosphine. Intermediate **C** can also undergo ring-cleavage to give benzyl anion species **D**, which is driven by the fact the carbanion is stabilized by both the inductive effect of the neighbouring groups and resonance effect of the phenyl ring. Elimination of triphenylphosphine from intermediate **D** also affords the desired product **3**. Another pathway for intermediate **D** is β-F elimination. Due to steric effect, β-F elimination prefers to the furnish phosphonium salt **E** with

Table 1
Optimization of reaction conditions.[a]



Entry	Solvent	Base	**2a**:Ph_3P:Base:**1**	Temp (°C)	Yield[a]
1	*p*-Xylene	^{t}BuOK	2.4:2:2:1	70	43
2	*p*-Xylene	NaH	2.4:2:2:1	70	0
3	*p*-Xylene	^{n}BuLi	2.4:2:2:1	70	0
4	*p*-Xylene	^{t}BuOK	2.4:2:2:1	40	26
5	*p*-Xylene	^{t}BuOK	2.4:2:2:1	100	53
6	*p*-xylene	^{t}BuOK	2.4:2:2:1	110	50
7	1,4-Dioxane	^{t}BuOK	2.4:2:2:1	100	48
8	Toluene	^{t}BuOK	2.4:2:2:1	100	47
9	DMF	^{t}BuOK	2.4:2:2:1	100	0
10	*p*-Xylene	^{t}BuOK	2.4:2:3:1	100	54
11	*p*-Xylene	^{t}BuOK	3.0:2:2:1	100	43
12	*p*-Xylene	^{t}BuOK	1:1:1.2:2	100	38
13[b]	*p*-Xylene	^{t}BuOK	1:1.2:1.8:2	100	70[c]

[a] Determined by ^{19}F NMR with trifluoromethylbenzene as an internal standard.
[b] The quaternization of triphenylphosphine with **2a** was carried out at 120 °C.
[c] Isolated yield.

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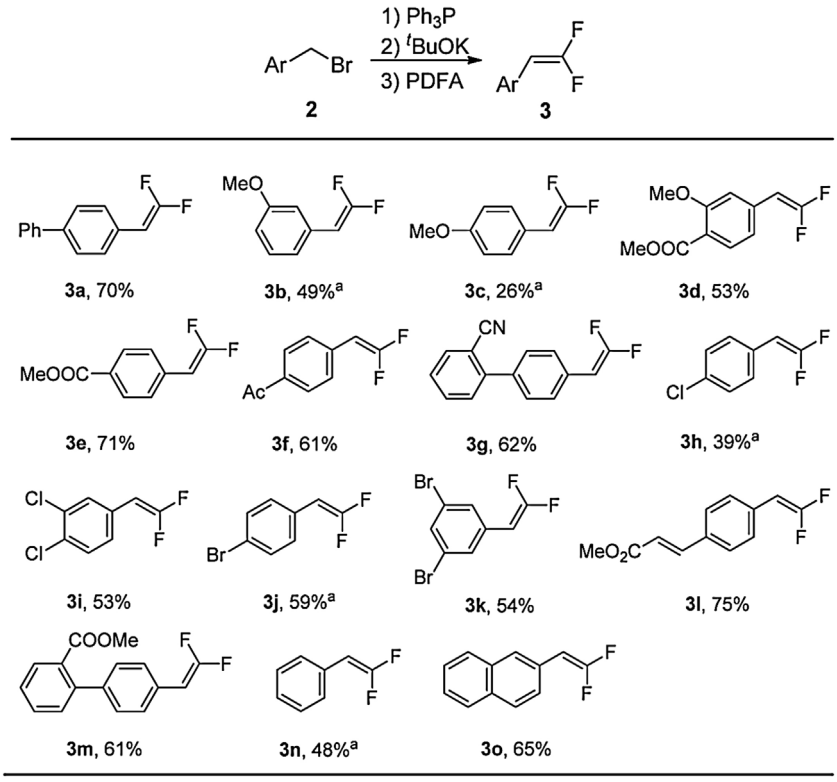
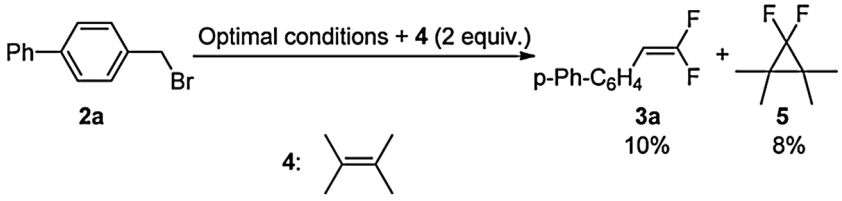
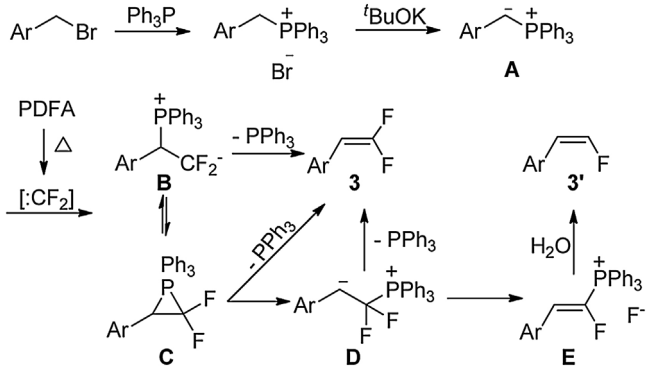


Scheme 2. Substrate scope. Reaction conditions: **2** (0.2 mmol), Ph_3P (0.24 mmol), ^tBuOK (0.36 mmol), PDFA (0.4 mmol) in *p*-xylene. [a]The yields were determined by ^{19}F NMR with trifluoromethylbenzene as an internal standard.



Scheme 3. Trap of difluorocarbene. Compound **4** was added in the olefination step. The yields were determined by ^{19}F NMR and calculated on the basis of **2a**.



Scheme 4. Proposed mechanism.

E-stereoselectivity. Hydrolysis of intermediate **E** gives the byproduct (*Z*)-monofluorostyrene **3′**.

3. Conclusion

In summary, we have described a one-pot synthesis of *gem*-difluorostyrenes from benzyl bromide. The sequential reaction including quaternization of triphenylphosphine, deprotonation of phosphonium salts, and the olefination of phosphonium ylide with difluorocarbene generated from PDFA via decarboxylation proceeded smoothly to give the difluoroolefinated product in good yields. This mild procedure using commercially available substrates and easily accessible reagent PDFA would make this reaction become a convenient and practical method for the synthesis of difluoroolefins.

4. Experimental

Typical procedure for the synthesis of *gem*-difluorostyrenes

A dried Schlenk tube was charged with **2** (0.2 mmol), Ph_3P (63 mg, 0.24 mmol) and *p*-xylene (2 mL) under N_2. The resulting mixture was stirred at 120 °C for 6 h. After being cooled to room temperature, ^tBuOK (40 mg, 0.36 mmol) and *p*-xylene (0.5 mL) were added into the mixture under N_2 and stirred at room temperature for 15 min. PDFA (143 mg, 0.4 mmol) and *p*-xylene (0.5 mL) were added into the solution under N_2 and stirred at 100 °C for another 1 h. After being cooled to room temperature, the mixture was subjected to flash column chromatography to afford the pure product.

4-(2,2-Difluorovinyl)-1,1′-biphenyl (**3a**): 70%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61–7.56 (m, 4H), 7.47–7.32 (m, 5H), 5.32 (dd, J = 26.4, 3.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −81.91 (dd,

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J = 30.7, 26.4 Hz, 1F), −83.84 (dd, J = 30.7, 3.5 Hz, 1F). GC–MS(EI) calcd. for $C_{14}H_{10}F_2$ $[M]^+$ 216.1. Found 216.1.

Methyl 4-(2,2-difluorovinyl)-2-methoxybenzoate (**3d**): 53%; Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 1H), 6.96–6.91 (m, 2H), 5.30 (dd, J = 25.1, 3.6 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −79.00 (t, J = 25.1, 1F), −81.12 (dd, J = 25.1, 3.6 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.17 (s), 159.42 (s), 156.78 (dd, J = 300.2, 290.7 Hz), 135.94 (dd, J = 7.3, 6.4 Hz), 132.16 (s), 119.51 (dd, J = 6.5, 3.5 Hz), 118.46 (s), 111.05 (dd, J = 7.0, 3.5 Hz), 82.16 (dd, J = 29.8, 12.9 Hz), 55.99 (s), 51.97 (s). IR (neat) ν = 2953, 1725, 1611, 1566, 1508, 1465, 1435, 1413, 1354, 1300, 1261, 1220, 1185, 1165, 1089, 1037, 982, 923, 894, 859, 817, 779, 754 cm^{-1}. HRMS (EI): calcd. for $C_{11}H_{10}F_2O_3$: 228.0598. Found: 228.0595.

Methyl 4-(2,2-difluorovinyl)benzoate (**3e**): 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 5.31 (dd, J = 25.8, 3.6 Hz, 1H), 3.89 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −79.16 (dd, J = 25.8, 23.8 Hz, 1F), −81.11 (dd, J = 23.8, 3.6 Hz, 1F). GC–MS(EI) calcd. for $C_{10}H_8F_2O_2$ $[M]^+$ 198.1. Found 198.1.

1-(4-(2,2-Difluorovinyl)phenyl)ethanone (**3f**): 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 5.34 (dd, J = 25.9, 3.5 Hz, 1H), 2.59 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −79.01 (dd, J = 25.9, 23.1 Hz, 1F), −80.83 (dd, J = 23.1, 3.5 Hz, 1F). GC–MS(EI) calcd. for $C_{10}H_8F_2O$ $[M]^+$ 182.1. Found 182.1.

4′-(2,2-Difluorovinyl)-[1,1′-biphenyl]-2-carbonitrile (**3g**): 62%; A white solid. M.p. 91–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.57–7.41 (m, 6H), δ 5.34 (dd, J = 27.2, 3.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.93 (t, J = 27.2 Hz, 1F), −82.77 (dd, J = 27.2, 3.2 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.51 (dd, J = 299.1, 289.4 Hz), 144.80 (s), 136.66 (t, J = 2.0 Hz), 133.80 (s), 132.88 (s), 130.93 (t, J = 6.6 Hz), 129.90 (s), 129.05 (s), 127.88 (dd, J = 6.5, 3.6 Hz), 127.64 (s), 118.68 (s), 111.10 (s), 81.85 (dd, J = 29.5, 13.4 Hz). IR (neat) ν = 3854, 3079, 3033, 2221, 1728, 1685, 1654, 1612, 1596, 1477, 1445, 1415, 1366, 1324, 1289, 1254, 1198, 1179, 1168, 1006, 958, 941, 879, 857, 820, 763, 723, 708, 593, 582, 575, 562, 544, 512, 486 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_9F_2N$: 241.0703. Found: 241.0701.

1,2-Dichloro-4-(2,2-difluorovinyl)benzene (**3i**): 53%; Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.37 (m, 2H), 7.15 (dd, J = 8.4, 2.1 Hz, 1H), 5.22 (dd, J = 25.9, 3.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −79.98 (t, J = 25.9 Hz, 1F), −81.81 (dd, J = 25.9, 3.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.54 (dd, J = 299.3, 290.4 Hz), 132.82 (s), 130.93 (t, J = 2.6 Hz), 130.58 (s), 130.41 (dd, J = 7.3, 6.1 Hz), 129.22 (dd, J = 6.9, 3.7 Hz), 126.77 (dd, J = 6.6, 3.5 Hz), 80.87 (dd, J = 30.7, 13.5 Hz). IR (neat) ν = 3853, 3042, 1728, 1594, 1556, 1474, 1396, 1351, 1275, 1240, 1175, 1136, 1095, 1033, 956, 882, 866, 826, 747, 723, 697, 680, 671, 598, 566, 516, 506, 440 cm^{-1}. HRMS (EI): calcd. for $C_8H_4Cl_2F_2$: 207.9658. Found: 207.9662.

1,3-Dibromo-5-(2,2-difluorovinyl)benzene (**3k**): 54%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (t, J = 1.6 Hz, 1H), 7.40 (d, J = 1.6 Hz, 2H), 5.19 (dd, J = 24.4, 3.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −78.62 (t, J = 24.4, 1F), −80.61 (dd, J = 24.4, 3.3 Hz, 1F). GC–MS(EI) calcd. for $C_8H_4Br_2F_2$ $[M]^+$ 297.9. Found 298.0.

(*E*)-Methyl 3-(4-(2,2-difluorovinyl)phenyl)acrylate (**3l**): 75%; A yellow solid. M.p. 56–57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 16.0 Hz, 1H), 7.49 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 6.43 (d, J = 16.0 Hz, 1H), 5.30 (dd, J = 26.1, 3.3 Hz, 1H), 3.81 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.06 (t, J = 26.1 Hz, 1F), −82.12 (dd, J = 26.1, 3.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.42 (s), 156.58 (dd, J = 299.9, 290.1 Hz), 144.11 (s), 133.01 (t, J = 2.2 Hz), 132.50 (t, J = 6.6 Hz), 128.40 (s), 127.98 (dd, J = 6.7, 3.6 Hz), 117.72 (s), 82.06 (dd, J = 29.7, 13.3 Hz), 51.75 (s). IR (neat) ν = 3406, 3034, 2955, 1716, 1636, 1606, 1559, 1513, 1435, 1421, 1320, 1252, 1213, 1169, 1072, 1003, 981, 941, 850, 836, 819, 724, 710, 688, 521, 508 cm^{-1}. HRMS (EI): calcd. for $C_{12}H_{10}F_2O_2$: 224.0649. Found: 224.0646.

Methyl 4′-(2,2-difluorovinyl)-[1,1′-biphenyl]-2-carboxylate (**3m**): 61%; Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.7 Hz, 1H), 7.53 (t, J = 7.1 Hz, 1H), 7.45–7.33 (m, 4H), 7.30–7.20 (m, 2H), 5.31 (dd, J = 26.4, 3.7 Hz, 1H), 3.66 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −81.80 (dd, J = 30.6, 26.4 Hz, 1F), −83.86 (dd, J = 30.6, 3.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.95 (s), 156.33 (dd, J = 298.6, 288.5 Hz), 141.94 (s), 140.00 (t, J = 2.1 Hz), 131.37 (s), 130.65 (s), 129.91 (s), 129.34 (dd, J = 7.0, 5.9 Hz), 128.81 (s), 128.66 (s), 128.18 (s), 127.28 (dd, J = 6.3, 3.7 Hz), 82.00 (dd, J = 29.3, 13.6 Hz), 52.01 (s). IR (neat) ν = 3032, 2952, 2664, 1728, 1599, 1575, 1519, 1482, 1448, 1433, 1410, 1351, 1290, 1248, 1191, 1168, 1127, 1089, 1048, 1006, 940, 853, 795, 764, 735, 714, 668, 578, 565, 527, 447 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{12}F_2O_2$: 204.0805. Found: 204.0801.

2-(2,2-Difluorovinyl)naphthalene (**3o**): 65%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.73 (m, 4H), 7.51–7.43 (m, 3H), 5.43 (dd, J = 26.3, 3.9 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −81.90 (dd, J = 30.8, 26.3 Hz, 1F), −83.64 (dd, J = 30.8, 3.9 Hz, 1F). GC–MS(EI) calcd. for $C_{12}H_8F_2$ $[M]^+$ 190.1. Found 190.1.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2015.06.009.

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