JOC The Journal of Organic Chemistry

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Substrate-Dependent Mechanistic Divergence in Decarboxylative Heck Reaction at Room Temperature

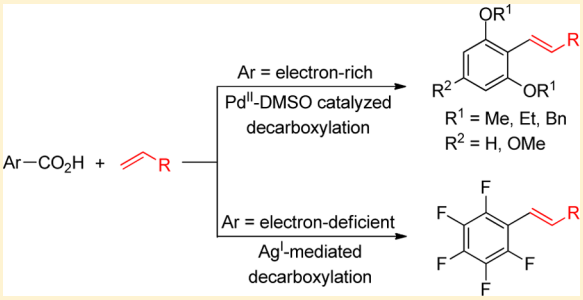
Asik Hossian,[†,‡] Samir Kumar Bhunia,[†,‡] and Ranjan Jana*[,†,‡]

[†]Organic and Medicinal Chemistry Division, CSIR-Indian Institute of Chemical Biology, 4 Raja S. C. Mullick Road, Jadavpur, Kolkata-700032, West Bengal, India

[‡]Academy of Scientific and Innovative Research, Kolkata-700032, West Bengal, India

Supporting Information

ABSTRACT: We report herein a Pd(II)-catalyzed Heck-type coupling between arene carboxylic acids and alkenes at room temperature. Mechanistically, the reaction proceeds in two distinct pathways where electron-rich substrates undergo a palladium(II)-catalyzed decarboxylation and electron-deficient substrates proceed through silver(I)-assisted decarboxylation. Dimethyl sulfoxide (DMSO) or sulfide ligands have positive and negative roles in the reaction outcome, respectively. The present protocol is combined for the peptide modification under mild reaction conditions.



INTRODUCTION

The decarboxylative cross-coupling of arene carboxylic acids with olefins and aryl electrophiles provides an attractive approach for the alkene functionalization and biaryl synthesis.[1] Inexpensive and readily available carboxylic acid as nucleophilic coupling partner is a user-friendly alternative to the air and moisture sensitive organometallic reagents. In a seminal report in 2002, Myers and co-workers reported a decarboxylative Heck-type olefination of arene carboxylic acids.[2] However, one of the major pitfalls in decarboxylative cross-coupling is the requirement of high reaction temperature (120−190 °C) which restricts its application in the synthesis of complex molecular frameworks. Because of the prevalence of stilbenes in numerous natural product, bioactive molecules and high tech materials (Figure 1),[3] we were particularly interested to the development of decarboxylative Heck-type coupling at room temperature.

Although, palladium-catalyzed decarboxylative coupling of nitroalkanes[4] and α-ketocarboxylic acids[5] at room temperature is known, there is no report of decarboxylative cross-coupling of arene carboxylates at room temperature. We report here for the first time a palladium-catalyzed decarboxylative Heck-type coupling at room temperature (Scheme 1). We also report the substrate-dependent mechanistic variation and distinct role of dimethyl sulfoxide/sulfide ligands in the present transformation.

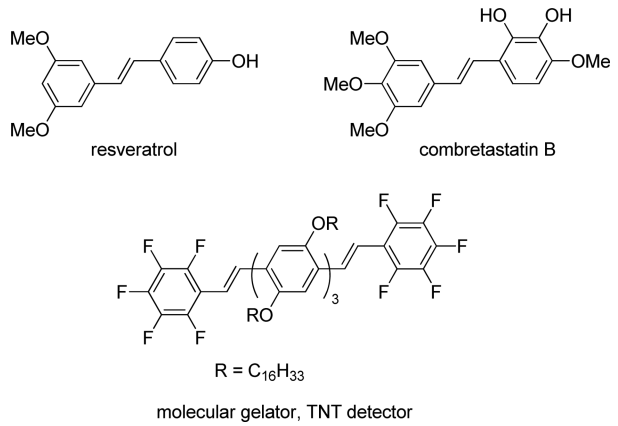


Figure 1. Representative example of some important stilbenes.

RESULTS AND DISCUSSION

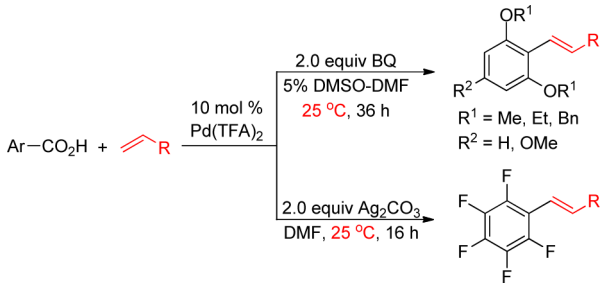
From literature it was evident that *o,o′*-disubstitution facilitates carbon dioxide extrusion.[6] In addition, from our previous experience with the decarboxylative allylation of *ortho*-nitrobenzoic acids, we realized that the incipient anion which is generated after decarboxylation needs to be stabilized for further cross-couplings.[7] Thus, we rationalized that either 2,6-dimethoxy benzoic acid or pentafluorobenzoic acid could be model substrates to study room temperature decarboxylative cross-coupling which will be a major advancement in this field.

Initially, we started screening for decarboxylative Heck reaction between 2,6-dimethoxybenzoic acid and styrene under the Myers's original conditions. But a trace amount of corresponding Heck product was isolated at room temperature. However, a good yield of the coupling product was isolated after 36 h stirring. In search for alternative oxidants to stoichiometric silver carbonate, 1,4-benzoquinone (BQ) was found to be suitable.[8] Finally, an excellent yield of the stilbene product was obtained after stirring the reaction mixture for 36 h

Received: January 15, 2016
Published: February 19, 2016

DOI: 10.1021/acs.joc.6b00100
J. Org. Chem. 2016, 81, 2521−2533

Scheme 1. Decarboxylative Heck-Arylation with Olefins

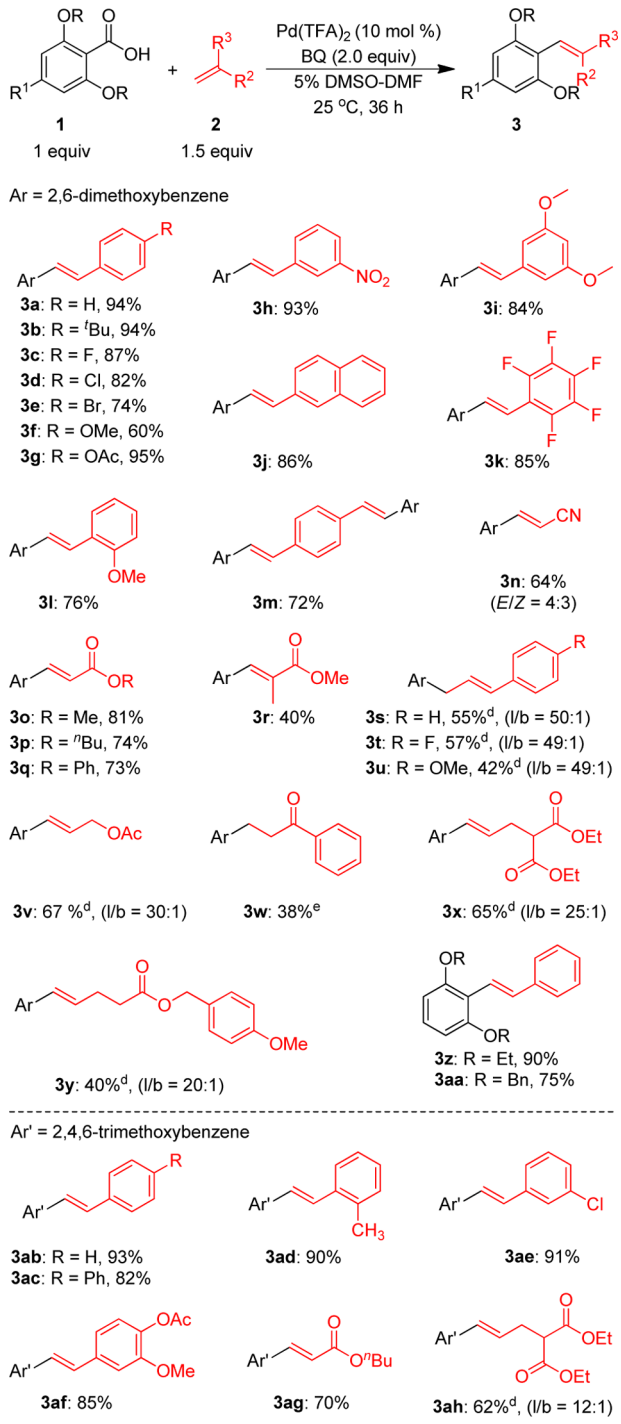


at room temperature with 10 mol % palladium catalyst and 2.0 equiv of 1,4-benzoquinone.

Being encouraged, several alkene partners were examined. A wide variety of styrenes having electron-withdrawing and electron-donating substituents underwent decarboxylative coupling providing high to excellent yields (Scheme 2). Fluoro-, chloro-, bromo-, (**3c**−**3e**, **3t**, **3ae**, Scheme 2) and remarkably acetoxy- (**3g**, **3af**, Scheme 2) groups were intact under the reaction conditions demonstrating the mild nature of this present protocol. Besides styrenes, activated alkenes such as acrylonitrile, (**3n**, Scheme 2) acrylates (**3o**−**3r**, **3ag**, Scheme 2) also provided the corresponding cross-coupling products. Interestingly, unactivated allylbenzenes (**3s**−**3u**, Scheme 2), allyl acetate (**3v**, Scheme 2), allyl malonate (**3x**, **3ah**, Scheme 2), and unactivated terminal alkene (**3y**, Scheme 2) also afforded the corresponding coupling products in good to moderate yields and good styrenyl selective products under slightly higher catalyst loading. The Heck coupling with an allyl alcohol (**3w**, Scheme 2) provided the corresponding ketone product via selective β-hydride elimination in moderate yield.[6b] Remarkably, 1,4-divinylbenzene provided the double cross-coupling product in one stroke (**3m**, Scheme 2). 2,6-Diethoxy- (**3z**, Scheme 2) and 2,6-dibenzyloxy (**3aa**, Scheme 2) benzoic acid also provided the corresponding coupling products in excellent yields. However, benzoic acid, mesitylenecarboxylic acid, 2-methoxy benzoic acid, and heteroaryl carboxylic acids such as pyridine-2-carboxylic acid, and benzofuran-2-carboxylic acid did not furnish any desired product. It was found that *o*,*o*-dialkoxy substitution is essential for decarboxylative coupling at room temperature presumably due to coordination between oxygen and arylpalladium species.

Next we turned our attention to the pentafluoroarenes as they exhibit distinct chemical and physical properties to their hydrocarbon counterpart.[9] Also an increasing use of perfluorinated compounds in material science, biomedical and bioanalytical research, defense, refrigeration, and domestic appliances has been observed.[10] Therefore, introduction of perfluorinated moiety into the organic backbone has become a fascinating field of research in the last years.[11] However, the metal-catalyzed cross-coupling reaction with this highly electron-deficient arenes poses a great challenge, due to poor coordination with the metal center and reluctance to undergo cross-coupling. A seminal work of palladium-catalyzed Heck coupling between pentafluorohalobenzene (X = I, Br) and styrenes was reported by the Espinet and Milstein groups.[12] Recently, an oxidative Heck coupling between pentafluorobenzene and styrenes were reported by the Zhang group,[13a] and a decarboxylative allylation of pentafluorobenzoates was reported by the Gooβen group at 120 and 110 °C

Scheme 2. Substrate Scope with Electron-Rich Carboxylic Acids[a,b,c]



[a]Conditions: The reaction was carried out in 0.2 mmol scale, 0.06 M. [b]Yield referred to here is the average of at least two experiments. [c]Unless otherwise stated *E*/*Z* ratio of the Heck products are >20:1 as determined by ^{1}H NMR. [d]20 mol % $Pd(TFA)_2$ and 3.0 equiv BQ were used. [e]Reaction time 48 h.

respectively.[13b] Direct oxidative cross-coupling with perfluoroarenes also an emerging field of research.[14]

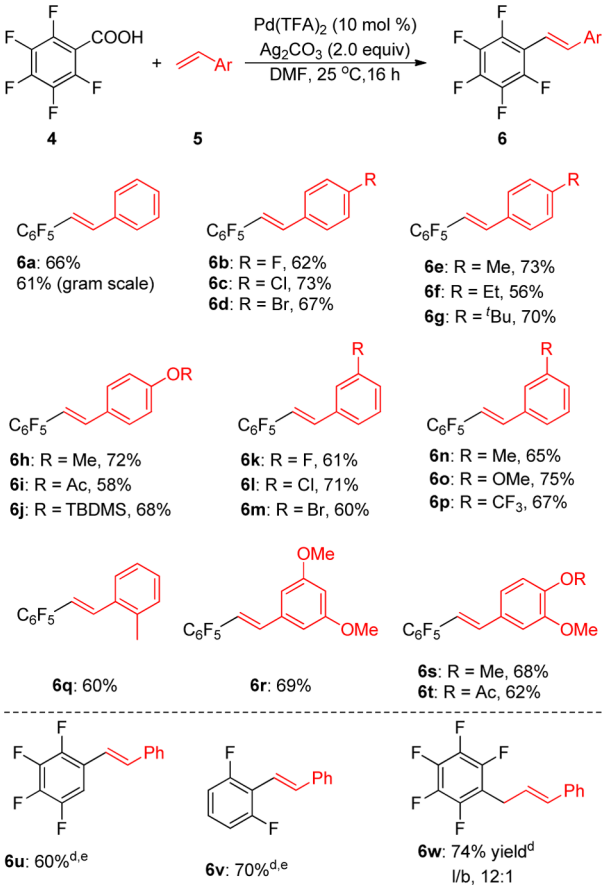
To examine decarboxylative Heck coupling with electron-deficient substrates, pentafluorobenzoic acid was employed under the optimized reaction conditions but no product was formed. Since Pd^{II}/Ag^{I} combination is essential for the

DOI: 10.1021/acs.joc.6b00100
J. Org. Chem. 2016, 81, 2521−2533

decarboxylative coupling of electron-deficient substrates,[15] benzoquinone was replaced by silver carbonate. Still no Heck product was isolated. Surprisingly, the reaction in pure DMF provided the Heck product at room temperature. This is in sharp contrast to the earlier reports where addition of 5% dimethyl sulfoxide (DMSO) in dimethylformamide (DMF) was found to improve the yield at elevated temperature. Finally, the desired Heck-products were obtained with 10 mol % $Pd(tfa)_2$ and 2.0 equiv of Ag_2CO_3 in good yields after 16 h stirring at room temperature.

With this optimized reaction conditions we explored the substrate scope. A wide variety of substituted styrenes provided the Heck product in high yields. Besides alkyl substituents, halogens (**6b**−**6d**, **6k**−**6m**, Scheme 3), labile acetoxy (**6i**, **6t**, Scheme 3) and *tert*-butyldimethylsilyloxy (**6j**, Scheme 3) groups were compatible under these mild reaction conditions. The reaction was also reproduced in gram scale in comparable yield. However, 2,3,4,5-tetrafluoro and 2,6-difluoro benzoic acids provided the coupling product at 120 °C (**6u**, **6v**, Scheme 3). Interestingly, the reaction with allylbenzene at 120 °C provided the corresponding allylation product in high yield and selectivity (**6w**, Scheme 3). Activated alkenes such as methyl acrylate afforded only a trace amount of Heck product under the same reaction conditions.

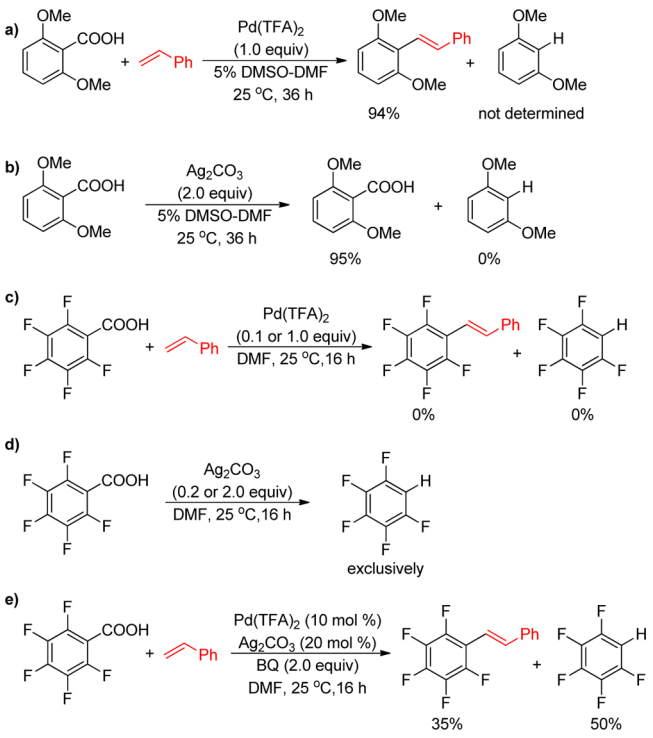
Scheme 3. Substrate Scope with Perfluorobenzoic Acids[a,b,c]



[a]Conditions: The reaction was carried out in 0.2 mmol scale, 0.06 M. [b]Yield referred to here is the average of at least two experiments. [c]*E*/*Z* ratio of the Heck products are >20:1 as determined by ^{1}H NMR. [d]120 °C was used. [e]20 mol % $Pd(TFA)_2$, 3.0 equiv Ag_2CO_3 and 5% DMSO−DMF were used, reaction time 4 h.

Reaction Mechanism. In their report, the Myers group applied a general reaction conditions for electron-rich and electron-deficient carboxylic acids. In addition, experimental and theoretical mechanistic investigation was performed exclusively based on the electron-rich substrates.[16] In their study with catalytic and stoichiometric palladium(II)-trifluoroacetate, it was observed that decarboxylation occurs by palladium salt where silver salt acts as an oxidant for catalytic turnover.[16b] However, the mechanism for electron-deficient substrate was illusive. In this present study, we have also observed that electron-rich 2,6-dimethoxybenzoic acid undergoes decarboxylative Heck reaction by a catalytic amount of palladium(II) trifluoroacetate where silver(I) carbonate was replaced by benzoquinone for practical applications. A stoichiometric palladium salt also reproduced the same result in the absence of benzoquinone (Scheme 4a). Additionally, a control experiment suggests that even a superstoichiometric amount of silver(I) carbonate (2 equiv) did not furnish decarboxylation of the 2,6-dimethoxybenzoic acid in the absence of palladium at room temperature (Scheme 4b). However, exclusive decarboxylative protonation product was observed by the Larrosa group with 10 mol % Silver(I) carbonate at 120 °C.[17] In sharp contrast, in the absence of silver salt the reaction with electron-deficient pentafluorobenzoic acid did not proceed even with stoichiometric amount of palladium-(II) trifluoroacetate (Scheme 4c). However, either stoichiometric (2 equiv) or a catalytic amount (20 mol %) of silver(I) carbonate resulted in decarboxylative protonation product exclusively (Scheme 4d). Additionally, a catalytic amount of silver(I) carbonate (20 mol %), palladium(II) trifluoroacetate (10 mol %), and benzoquinone (2.0 equiv) afforded the corresponding Heck product from the pentafluorobenzoic acid and styrene albeit in low yield (35%) (Scheme 4e). Therefore, electron-deficient substrates may follow a distinct pathway for

Scheme 4. Control Experiments



DOI: 10.1021/acs.joc.6b00100
J. Org. Chem. 2016, 81, 2521−2533

the decarboxylative Heck reaction from electron-rich substrates at room temperature. A similar observation was also observed by the Su group where 2,4-dimethoxybenzoic acid underwent decarboxylative protonation with stoichiometric palladium(II)-trifluoroacetate at 80 °C but 2-nitrobenzoic acid was unreactive. On the other hand, electron-deficient 2-nitrobenzoic acid afforded decarboxylative protonation exclusively with super-stoichiometric amount of silver(I) carbonate (3.0 equiv) only. Ultimately, a Pd/Ag bimetallic system was applied for the C-3 selective arylation of indoles with electron-deficient nitro-benzoic acids.[15,18]

Interestingly, in the earlier reports dimethyl sulfoxide (DMSO) or other sulfide ligands exhibited a prominent role in decarboxylative, direct alkenylation or allylic C−H activations where addition of 5% DMSO as a cosolvent was found to improve yields and catalytic efficiency.[2,16,19] From NMR and crystal structure studies, the Myers group has also shown that DMSO acts as a ligand on the arylpalladium species in decarboxylative Heck-type coupling.[16b] In sharp contrast, for the first time we have observed that DMSO or sulfide ligand exhibit a negative role in the decarboxylative alkenylation reaction between pentafluorobenzoic acid and styrene at room temperature. A careful study revealed that the yield of the alkenylation product was decreased successively with the increase of DMSO (Figure 2) with respect to the

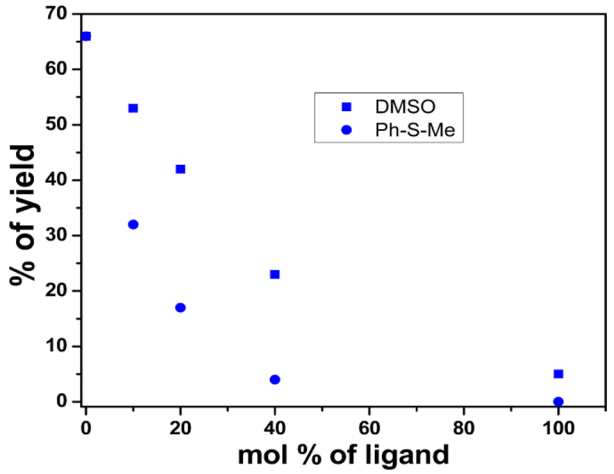
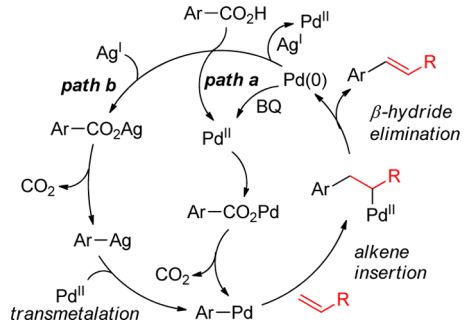


Figure 2. Negative role of sulfoxide or sulfide ligand in the heck reaction between pentafluorobenzoic acid and styrene at room temperature.

pentafluorobenzoic acid. In lieu of pure DMF (Scheme 4d), 5% DMSO−DMF also furnished the decarboxylative proto-nation product exclusively suggesting that DMSO has no role in siver-mediated decarboxylation. Therefore, DMSO may act as a ligand on the palladium and influence negatively for the subsequent cross-coupling processes with electron-deficient carboxylic acids. The same trend was also observed with phenyl methyl sulfide. Although, the exact reason for this negative effect of DMSO is not clear at this moment but this room temperature decarboxylation will leads to the development of new cross-coupling reactions under mild conditions.

On the basis of earlier reports and the present study it is speculated that depending of the electronic nature of the carboxylic acids a mechanistic divergence is observed in the decarboxylative Heck coupling reaction. The electron-rich substrates may follow a palladium-catalyzed decarboxylation where dimethyl sulfoxide acts as a ligand and benzoquinone plays as an oxidant for catalytic turnover as shown in *path a*, Scheme 5.[1h] Whereas, pentafluorobenzoic acid may undergo a

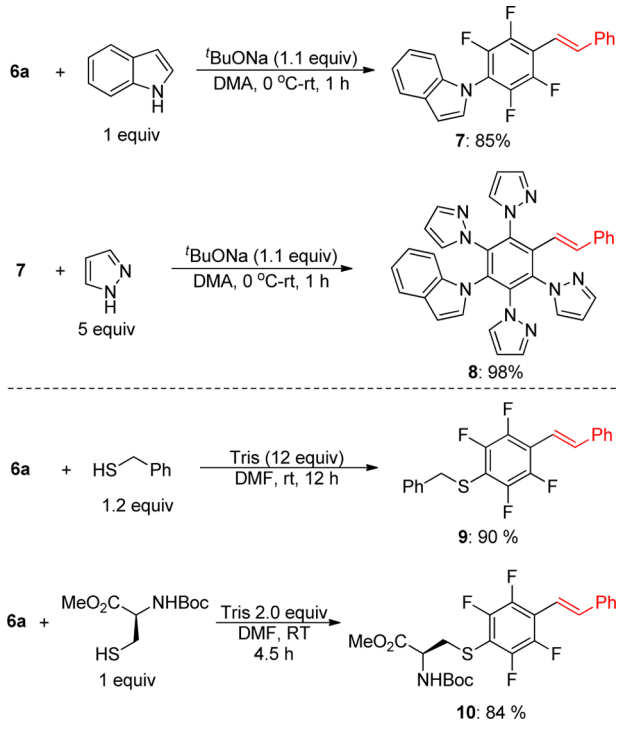
Scheme 5. Plausible Mechanism



silver-assisted decarboxylation which forms a arylpalladium species after transmetalation as depicted in *path b*, Scheme 5. Subsequently, the arylpalladium species undergoes migratory alkene insertion and *β*-hydride elimination to provide the Heck product and palladium(0). Finally, the palladium(0) is oxidized either by silver(I) salt or benzoquinone in *path a* and *path b* respectively to complete the catalytic cycle.

Next we turned our attention to utilize the decarboxylative Heck product for further useful transformations. Under basic conditions, the pentafluoroarene moiety, **6a** undergoes an activated aromatic nucleophilic substitution (S_NAr) with indole selectively at the *para*-position to afford (**7**, Scheme 6). The remaining fluorenes are further substituted by excess pyrazoles to provide (**8**, Scheme 6).[20] Development of novel synthetic methods for the postsynthetic modification of peptide is an attractive research field.[21] In this vein, we have applied the decarboxylative Heck product for the arylation with cysteine.

Scheme 6. Product Derivatization



DOI: 10.1021/acs.joc.6b00100
J. Org. Chem. 2016, 81, 2521−2533

To demonstrate with the sulfur nucleophiles, the Heck product **6a** was reacted with benzyl mercaptan to afford (**9**, Scheme 6) in excellent yield. Similarly, it also underwent activated aromatic nucleophilic substitution (S_NAr) with the protected cysteine selectively at the *para*-position to provide (**10**, Scheme 6).

CONCLUSION

In conclusion, we have developed a decarboxylative Heck-type coupling between arene carboxylic acids and alkenes at room temperature. A substrate-dependent mechanistic divergence was observed where electron-rich arene carboxylic acids undergo palladium-catalyzed decarboxylation and electron-deficient arene carboxylic acids undergo silver-assisted decarboxylation. Similarly, dimethyl sulfoxide or other sulfide ligands exhibit positive and negative roles respectively in the present transformation. The pentafluoroarene moiety obtained from the cross-coupling was further derivatized via activated aromatic nucleophilic substitution (S_NAr) with nitrogen and sulfur nucleophiles. Therefore, this room temperature reaction sequence is useful for peptide modification under mild reaction conditions.

EXPERIMENTAL SECTION

General Information. Melting points were determined in open end-capillary tubes and are uncorrected. TLC was performed on silica gel plates (Merck silica gel 60, f254), and the spots were visualized with UV light (254 and 365 nm) and $KMnO_4$ stain. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in $CDCl_3$ using TMS as the internal standard. The ^{19}F NMR spectra were recorded in $CDCl_3$ solvent using hexafluorobenzene as the internal standard. HRMS (m/z) were measured using EI (magnetic sector, positive ion) and ESI (Q-TOF, positive ion) techniques. Infrared (IR) spectra were recorded on Fourier transform infrared spectroscopy; only intense peaks were reported.

General Experimental Procedure for the Decarboxylative Heck Reaction between Electron-Rich Carboxylic Acids and Alkenes. To an oven-dried 15 mL sealed tube, a mixture of carboxylic acids (0.20 mmol, 1.0 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv) and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv) was taken. Then dry DMF (3.0 mL) and DMSO (0.15 mL) were added to it. After purging the reaction vessel with nitrogen, the corresponding alkene (0.30 mmol, 1.5 equiv) was added to the reaction mixture via microliter syringe and the vessel was sealed with a screw cap. The reaction mixture was allowed to stir for 36 h at room temperature. After completion (as detected by TLC), the reaction mixture was poured into water (20 mL) and extracted with ethyl acetate (30 mL). The organic layer was washed with aqueous NaOH solution (2 N, 10 mL), water (10 mL), and brine solution (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate/hexane as eluent to afford the desired product.

1-(2,6-Dimethoxystyryl)benzene, ***3a****, Scheme 2.*[22] The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), styrene (35 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a colorless oil, (45 mg, 94%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 6.8 Hz, 1H), 7.57 (d, J = 7.8 Hz, 2H), 7.49 (d, J = 16.5 Hz, 1H), 7.37 (t, J = 7.2 Hz, 2H), 7.24 (t, J = 7.5 Hz, 1H), 7.19 (t, J = 8.4 Hz, 1H), 6.62 (d, J = 8.4 Hz, 2H), 3.92 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 158.5, 139.2, 132.2, 128.4, 128.0, 126.8, 126.3, 119.8, 114.6, 103.9, 55.7; IR (neat) υ_{max} 2934, 1584, 1470, 1248, 1106, 976, 749 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{16}H_{16}O_2$ $[M]^+$ 240.1150, found 240.1157.

1-(2,6-Dimethoxystyryl)-4-tert-butylbenzene, ***3b****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 4-*tert*-butylstyrene (55 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a white solid, (56 mg, 94%), mp 98−100 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 16.8 Hz, 1H), 7.42−7.48 (m, 3H), 7.35 (d, J = 8.4 Hz, 2H), 7.14 (t, J = 8.4 Hz, 1H), 6.58 (d, J = 8.1 Hz, 2H), 3.87 (s, 6H), 1.33 (s, 9H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 158.6, 149.9, 136.6, 132.2, 127.8, 126.1, 125.4, 119.2, 115.1, 104.0, 55.8, 34.5, 31.3; IR (neat) υ_{max} 2958, 1581, 1470, 1252, 1108, 770 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{20}H_{24}O_2Na$ $[M + Na]^+$ 319.1674, found 319.1694.

1-(2,6-Dimethoxystyryl)-4-fluorobenzene, ***3c****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 4-fluorostyrene (36 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a colorless oil, (45 mg, 87%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, J = 16.8 Hz, 1H), 7.51−7.54 (m, 2H), 7.40 (d, J = 16.8 Hz, 1H), 7.20 (t, J = 8.4 Hz, 1H), 7.05 (t, J = 8.4 Hz, 2H), 6.62 (d, J = 8.4 Hz, 2H), 3.92 (s, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 162.0 (d, J = 244.5 Hz), 158.6, 135.4 (d, J = 3.0 Hz), 131.1, 128.1, 127.8 (d, J = 7.5 Hz), 119.6 (d, J = 1.5 Hz), 115.3 (d, J = 2.1 Hz), 114.6, 104.0, 55.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ −119.0 (s, 1F); IR (neat) υ_{max} 2935, 1590, 1506, 1470, 1246, 1106, 775 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{16}H_{15}FO_2Na$ $[M + Na]^+$ 281.0954, found 281.0929.

1-(2,6-Dimethoxystyryl)-4-chlorobenzene, ***3d****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 4-chlorostyrene (38 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a colorless oil, (45 mg, 82%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 16.8 Hz, 1H), 7.41−7.48 (m, 3H), 7.30 (d, J = 8.4 Hz, 2H), 7.18 (t, J = 8.1 Hz, 1H), 6.60 (d, J = 8.4 Hz, 2H), 3.90 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 158.6, 137.8, 132.4, 130.9, 128.6, 128.4, 127.6, 120.5, 114.4, 103.9, 55.8; IR (neat) υ_{max} 2935, 1585, 1484, 1249, 1109, 975, 774 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{16}H_{15}ClO_2Na$ $[M + Na]^+$ 297.0658, found 297.0681.

1-(2,6-Dimethoxystyryl)-4-bromobenzene, ***3e****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 4-bromostyrene (40 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a colorless oil, (47 mg, 74%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, J = 16.8 Hz, 1H), 7.46−7.48 (m, 3H), 7.42 (d, J = 8.4 Hz, 2H), 7.20 (t, J = 8.4 Hz, 1H), 6.61 (d, J = 8.4 Hz, 2H), 3.91 (s, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 158.6, 138.3, 131.5, 130.9, 128.4, 127.9, 120.6, 120.5, 114.4, 103.9, 55.8; IR (neat) υ_{max} 2935, 1584, 1475, 1249, 1106, 772 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{16}H_{15}BrO_2Na$ $[M + Na]^+$ 341.0153, found 341.0155.

2-(4-Methoxystyryl)-1,3-dimethoxybenzene, ***3f****, Scheme 2.*[23] The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 4-vinylanisole (40 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 95:5 hexane/ethyl acetate) afforded the desired product as a white solid, (32 mg, 60%), mp 71−73 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 16.5 Hz, 1H), 7.49 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 16.5 Hz, 1H), 7.16 (t, J = 8.4 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.60 (d, J = 8.4 Hz, 2H), 3.90 (s, 6H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 158.8, 158.4, 132.0, 131.8, 127.6, 127.5, 117.8, 114.9, 113.8, 103.9, 55.7, 55.2; IR (neat)

DOI: 10.1021/acs.joc.6b00100
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υ_{max} 2937, 1601, 1581, 1469, 1249, 1106, 1033, 773 cm^{-1}; HRMS (EI, *m*/*z*) calcd. for $C_{17}H_{18}O_3$ $[M]^+$ 270.1256, found 270.1257.

4-(2,6-Dimethoxystyryl)phenyl acetate, ***3g****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 4-acetoxystyrene (46 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 95:5 hexane/ethyl acetate) afforded the desired product as a colorless oil, (57 mg, 95%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.54−7.60 (m, 3H), 7.42 (d, *J* = 16.5 Hz, 1H), 7.19 (t, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 6H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 171.3, 160.1, 151.3, 138.9, 133.0, 129.9, 129.0, 123.3, 122.0, 116.3, 105.7, 57.5, 22.9; IR (neat) υ_{max} 2937, 1760, 1584, 1504, 1195, 1105, 772 cm^{-1}; HRMS (ESI, *m*/*z*) calcd. for $C_{18}H_{18}O_4Na$ $[M + Na]^+$ 321.1103, found 321.1115.

1-(2,6-Dimethoxystyryl)-3-nitrobenzene, ***3h****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 3-nitrostyrene (42 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 95:5 hexane/ethyl acetate) afforded the desired product as a yellow solid, (53 mg, 93%), mp 116−118 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.04−8.06 (m, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.59−7.66 (m, 2H), 7.49 (t, *J* = 8.4 Hz, 1H), 7.23 (t, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 2H), 3.93 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 158.8, 148.6, 141.2, 132.0, 129.6, 129.2, 129.1, 122.9, 121.3, 120.9, 113.7, 103.9, 55.8; IR (neat) υ_{max} 1527, 1473, 1343, 1107, 737 cm^{-1}; HRMS (EI, *m*/*z*) calcd. for $C_{16}H_{15}NO_4$ $[M]^+$ 285.1001, found 285.1013.

(E)-1-(2,6-Dimethoxyphenyl)-2-(3,5-dimethoxyphenyl)ethene, ***3i****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 3,5-dimethoxystyrene (49 mg, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (50 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a colorless oil, (45 mg, 84%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 16.8 Hz, 1H), 7.46 (d, *J* = 16.8 Hz, 1H), 7.19 (t, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 1.8 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 6.40 (t, *J* = 2.4 Hz, 1H), 3.91 (s, 6H), 3.86 (s, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 160.8, 158.6, 141.4, 132.3, 128.2, 120.4, 114.6, 104.5, 104.0, 99.4, 55.8, 55.3; IR (neat) υ_{max} 2937, 2838, 1587, 1472, 1153, 773 cm^{-1}; HRMS (ESI, *m*/*z*) calcd. for $C_{18}H_{20}O_4Na$ $[M + Na]^+$ 323.1259, found 323.1278.

2-(2,6-Dimethoxystyryl)naphthalene, ***3j****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 2-vinylnaphthalene (46 mg, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a white solid, (50 mg, 86%), mp 136−138 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.75−7.87 (m, 6H), 7.62 (d, *J* = 16.8 Hz, 1H), 7.40−7.49 (m, 2H), 7.20 (t, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 3.94 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 158.7, 136.9, 133.9, 132.9, 132.4, 128.2, 128.0, 127.96, 127.7, 126.2, 126.1, 125.4, 123.8, 120.4, 114.9, 104.1, 55.8; IR (neat) υ_{max} 1583, 1470, 1242, 1105, 772 cm^{-1}; HRMS (EI, *m*/*z*) calcd. for $C_{20}H_{18}O_2$ $[M]^+$ 290.1307, found 290.1310.

1-(2,6-Dimethoxystyryl)-2,3,4,5,6-pentafluorobenzene, ***3k****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), pentafluorostyrene (42 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a white solid, (56 mg, 85%), mp 146−148 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 17.4 Hz, 1H), 7.47 (d, *J* = 16.8 Hz, 1H), 7.24 (t, *J* = 8.4 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 158.9, 144.6 (dm, *J* = 249.0 Hz), 139.1, (dm, *J* = 250.5 Hz), 137.7 (dm, *J* = 247.5 Hz), 129.6, 128.6 (t, *J* = 9.0 Hz), 116.2, 114.2 (td, *J* = 13.5 Hz, 4.5 Hz), 113.8, 103.8, 55.8 (d, *J* = 3.0 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ −144.6 (dd, *J* = 26.8 Hz, 8.9 Hz, 2F), −159.5 (t, *J* = 26.3 Hz, 1F), −165.0 (td, *J* = 26.3 Hz, 8.9 Hz, 2F); IR (neat) υ_{max} 1585, 1496, 1245, 1108, 1000, 774 cm^{-1}; HRMS (EI, *m*/*z*) calcd. for $C_{16}H_{11}F_5O_2$ $[M]^+$ 330.0679, found 330.0665.

2-(2-Methoxystyryl)-1,3-dimethoxybenzene, ***3l****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 2-vinylanisole (40 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a white solid, (41 mg, 76%), mp 66−68 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 16.8 Hz, 1H), 7.64 (dd, *J* = 7.5 Hz, 0.9 Hz, 1H), 7.39 (d, *J* = 16.8 Hz, 1H), 7.11−7.25 (m, 2H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 6H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 158.6, 156.7, 128.6, 128.0, 127.8, 127.2, 126.2, 120.7, 120.4, 115.4, 110.8, 104.0, 55.8, 55.6; IR (neat) υ_{max} 2935, 2837, 1586, 1468, 1243, 1106, 746 cm^{-1}; HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{18}O_3Na$ $[M + Na]^+$ 293.1154, found 293.1147.

1,4-Bis(2,6-dimethoxystyryl)benzene, ***3m****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 1,4-divinylbenzene (22 μL, 0.15 mmol, 0.75 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a yellow solid, (29 mg, 72%), mp 180−182 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 16.2 Hz, 2H), 7.54 (s, 4H), 7.50 (d, *J* = 16.8 Hz, 2H), 7.18 (t, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 4H), 3.93 (s, 12H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 158.6, 138.0, 132.2, 127.9, 126.5, 119.3, 115.0, 104.0, 55.8; IR (neat) υ_{max} 1582, 1472, 1251, 1105, 770 cm^{-1}; HRMS (EI, *m*/*z*) calcd. for $C_{26}H_{26}O_4$ $[M]^+$ 402.1831, found 402.1833.

(E)-3-(2,6-Dimethoxyphenyl)acrylonitrile, ***3n****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), acrylonitrile (20 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a colorless oil, (24 mg, 64%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 16.8 Hz, 1H), 7.28−7.34 (m, 2H), 7.22 (d, *J* = 12.0 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 16.8 Hz, 1H), 5.58 (d, *J* = 12.0 Hz, 1H), 3.89 (s, 12H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 158.8, 158.2, 141.4, 141.0, 132.0, 131.6, 120.2, 117.3, 111.9, 111.6, 103.7, 103.6, 99.9, 98.4, 55.8, 55.4; IR (neat) υ_{max} 2936, 2210, 1696, 1601, 1475, 1249, 1112, 777 cm^{-1}; HRMS (ESI, *m*/*z*) calcd. for $C_{11}H_{11}NO_2Na$ $[M + Na]^+$ 212.0687, found 212.0691.

(E)-Methyl 3-(2,6-dimethoxyphenyl)acrylate, ***3o****, Scheme 2.*[1h] The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), methyl acrylate (27 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (36 mg, 81%), mp 70−72 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 16.2 Hz, 1H), 7.26 (t, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 16.2 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 6H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 169.0, 160.0, 135.6, 131.2, 120.2, 112.1, 103.6, 55.7, 51.4; IR (neat) υ_{max} 2942, 1703, 1618, 1255, 1161, 1104, 748 cm^{-1}; HRMS (EI, *m*/*z*) calcd. for $C_{12}H_{14}O_4$ $[M]^+$ 222.0892, found 222.0902.

(E)-Butyl 3-(2,6-dimethoxyphenyl)acrylate, ***3p****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), butyl acrylate (43 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a colorless oil, (39 mg, 74%). ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 16.2 Hz, 1H), 7.26 (t, *J* = 8.4 Hz, 1H),

DOI: 10.1021/acs.joc.6b00100
J. Org. Chem. 2016, 81, 2521−2533

6.88 (d, J = 16.5 Hz, 1H), 6.55 (d, J = 8.4 Hz, 2H), 4.20 (t, J = 6.6 Hz, 2H), 3.88 (s, 6H), 1.64−1.74 (m, 2H), 1.38−1.50 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 168.6, 159.8, 135.2, 131.0, 120.5, 112.1, 103.5, 63.9, 55.6, 30.8, 19.1, 13.7; IR (neat) υ_{max} 2959, 1706, 1623, 1587, 1474, 1255, 1109, 744 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{15}H_{20}O_4$ $[M]^+$ 264.1362, found 264.1346.

(E)-Phenyl 3-(2,6-dimethoxyphenyl)acrylate, ***3q****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), phenyl acrylate (45 mg, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (41.5 mg, 73%), mp 106−108 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, J = 16.2 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.33 (t, J = 8.4 Hz, 1H), 7.26 (d, J = 8.1 Hz, 1H), 7.20 (d, J = 7.5 Hz, 2H), 7.11 (d, J = 16.2 Hz, 1H), 6.61 (d, J = 8.4 Hz, 2H), 3.93 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 167.0, 160.2, 151.2, 137.4, 131.8, 129.4, 125.5, 121.9, 119.6, 112.1, 103.7, 55.8; IR (neat) υ_{max} 1735, 1619, 1478, 1254, 1131, 738 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{17}H_{16}O_4Na$ $[M + Na]^+$ 307.0946, found 307.0957.

(E)-Methyl 3-(2,6-dimethoxyphenyl)-2-methyl acrylate, ***3r****, Scheme 2.*[24] The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), methyl methacrylate (32 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a colorless oil, (19 mg, 40%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.28 (t, J = 8.4 Hz, 1H), 6.59 (d, J = 8.4 Hz, 2H), 3.83 (s, 6H), 3.81 (s, 3H), 1.79 (d, J = 1.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 168.7, 157.7, 131.9, 130.9, 129.7, 113.4, 103.5, 55.6, 51.8, 15.2; IR (neat) υ_{max} 2950, 2840, 1710, 1587, 1470, 1253, 1105, 745 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_{16}O_4Na$ $[M + Na]^+$ 259.0946, found 259.0934.

1-((E)-3-(2,6-Dimethoxyphenyl)prop-1-enyl)benzene, ***3s****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), allylbenzene (40 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (13.4 mg, 0.04 mmol, 0.1 equiv), and 1,4-benzoquinone (65 mg, 0.4 mmol, 3.0 equiv). Column chromatography (SiO_2, eluting with 95:5 hexane/ethyl acetate) afforded the desired product as a colorless oil, (28 mg, 55%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, J = 7.2 Hz, 2H), 7.25−7.28 (m, 2H), 7.13−7.20 (m, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.32−6.41 (m, 2H), 3.85 (s, 6H), 3.58 (d, J = 6.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 158.2, 138.1, 129.4, 129.0, 128.3, 127.1, 126.5, 126.0, 116.5, 103.8, 55.8, 26.4; IR (neat) υ_{max} 2927, 1728, 1593, 1469, 1254, 1110, 729 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{17}H_{18}O_2Na$ $[M + Na]^+$ 277.1204, found 277.1179.

1-Fluoro-4-((E)-3-(2,6-dimethoxyphenyl)prop-1-enyl)benzene, ***3t****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 4-fluoroallylbenzene (41 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (13.4 mg, 0.04 mmol, 0.1 equiv), and 1,4-benzoquinone (65 mg, 0.4 mmol, 3.0 equiv). Column chromatography (SiO_2, eluting with 95:5 hexane/ethyl acetate) afforded the desired product as a white solid, (31 mg, 57%), mp 68−70 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.28−7.31 (m, 2H), 7.19 (t, J = 8.4 Hz, 1H), 6.96 (t, J = 8.4 Hz, 2H), 6.60 (d, J = 8.4 Hz, 2H), 6.36 (d, J = 15.6 Hz, 1H), 6.25−6.30 (m, 1H), 3.86 (s, 6H), 3.58 (d, J = 6.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 161.7 (d, J = 243.0 Hz), 158.2, 134.2 (d, J = 3.0 Hz), 128.7 (d, J = 3.0 Hz), 128.3, 127.3 (d, J = 7.5 Hz), 127.2, 116.4, 115.1 (d, J = 21.0 Hz), 103.8, 55.8, 26.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ −119.6 (s, 1F); IR (neat) υ_{max} 2929, 1592, 1470, 1255, 1107, 839 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{17}H_{17}FO_2$ $[M]^+$ 272.1213, found 272.1208.

2-(4-Methoxycinnamyl)-1,3-dimethoxybenzene, ***3u****, Scheme 2.*[8] The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 4-methoxyallylbenzene (46 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (13.4 mg, 0.04 mmol, 0.1 equiv), and 1,4-benzoquinone (65 mg, 0.4 mmol, 3.0 equiv). Column chromatography (SiO_2, eluting with 95:5 hexane/ethyl acetate) afforded the desired product as a white solid, (24 mg, 42%), mp 70−72 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, J = 9.0 Hz, 2H), 7.17 (t, J = 8.4 Hz, 1H), 6.81 (d, J = 8.4 Hz, 2H), 6.58 (d, J = 8.4 Hz, 2H), 6.34 (d, J = 15.6 Hz, 1H), 6.18−6.23 (m, 1H), 3.85 (s, 6H), 3.79 (s, 3H), 3.55 (d, J = 6.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 158.4, 158.2, 131.1, 128.8, 127.05, 127.02, 126.8, 116.8, 113.7, 103.8, 55.8, 55.2, 26.4; IR (neat) υ_{max} 2930, 1597, 1510, 1469, 1250, 1111, 833 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{18}H_{20}O_3$ $[M]^+$ 284.1412, found 284.1408.

2,6-Dimethoxycinnamyl acetate, ***3v****, Scheme 2.*[8] The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), allylacetate (33 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (13.4 mg, 0.04 mmol, 0.1 equiv), and 1,4-benzoquinone (65 mg, 0.6 mmol, 3.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a colorless oil, (32 mg, 67%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.18 (t, J = 8.4 Hz, 1H), 6.99 (d, J = 16.2 Hz, 1H), 6.71−6.76 (m, 1H), 6.56 (d, J = 8.4 Hz, 2H), 4.75 (dd, J = 6.6 Hz, 0.6 Hz, 2H), 3.86 (s, 6H), 2.11 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 171.0, 158.6, 128.6, 126.8, 125.0, 113.3, 103.8, 67.1, 55.7, 21.1; IR (neat) υ_{max} 2938, 1737, 1587, 1472, 1247, 772 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_{16}O_4Na$ $[M + Na]^+$ 259.0946, found 259.0923.

3-(2,6-Dimethoxyphenyl)-1-phenylpropan-1-one, ***3w****, Scheme 2.*[6b] The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 1-phenylprop-2-en-1-ol (40 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv) except the reaction was run for 48 h. Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (20.5 mg, 38%), mp 88−90 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.4 Hz, 1.2 Hz, 2H), 7.54−7.57 (m, 1H), 7.45−7.47 (m, 2H), 7.18 (t, J = 8.4 Hz, 1H), 6.57 (d, J = 8.4 Hz, 2H), 3.81 (s, 6H), 3.14−3.17 (m, 2H), 3.08−3.11 (m, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 200.6, 158.2, 137.0, 132.7, 128.4, 128.2, 127.1, 117.4, 103.5, 55.6, 38.3, 18.5; IR (neat) υ_{max} 2937, 1682, 1593, 1471, 1254, 1107, 778, 693 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{17}H_{18}O_3Na$ $[M + Na]^+$ 293.1154, found 293.1130.

Diethyl 2-(2,6-dimethoxycinnamyl)malonate, ***3x****, Scheme 2.*[8] The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), diethyl 2-allylmalonate (60 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (13.4 mg, 0.04 mmol, 0.1 equiv), and 1,4-benzoquinone (65 mg, 0.6 mmol, 3.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a colorless oil, (44 mg, 65%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.12 (t, J = 8.4 Hz, 1H), 6.74 (t, J = 16.2 Hz, 1H), 6.51−6.58 (m, 3H), 4.19−4.26 (m, 4H), 3.82 (s, 6H), 3.51 (t, J = 7.8 Hz, 1H), 2.83 (td, J = 7.8 Hz, 1.2 Hz, 2H), 1.28 (t, J = 6.6 Hz, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 169.1, 158.2, 129.7, 127.7, 123.0, 114.4, 103.9, 61.3, 55.6, 52.5, 34.0, 14.0; IR (neat) υ_{max} 2981, 1732, 1585, 1472, 1251, 1113, 772 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{18}H_{24}O_6Na$ $[M + Na]^+$ 359.1471, found 359.1468.

(E)-4-Methoxybenzyl 5-(2,6-dimethoxyphenyl)pent-4-enoate, ***3y****, Scheme 2.* The same general procedure was followed by using 2,6-dimethoxybenzoic acid (36.5 mg, 0.2 mmol, 1.0 equiv), 4-methoxybenzyl pent-4-enoate (66 mg, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (13.4 mg, 0.04 mmol, 0.1 equiv), and 1,4-benzoquinone (65 mg, 0.6 mmol, 3.0 equiv). Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as colorless oil, (28.5 mg, 40%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, J = 8.4 Hz, 2H), 7.13 (t, J = 8.4 Hz, 1H), 6.88 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 16.2 Hz, 1H), 6.57−6.62 (m, 1H), 6.56 (d, J = 8.4 Hz, 2H), 5.08 (s, 2H), 3.83 (s, 6H), 3.82 (s, 3H), 2.58−2.61 (m, 2H), 2.53−2.56 (m, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 173.2, 159.5, 158.2, 132.7, 130.0, 128.2, 127.5, 121.2, 114.6, 113.9, 103.9, 65.9, 55.7, 55.2, 34.5, 30.0; IR (neat) υ_{max} 2928, 1732, 1586, 1514, 1469, 1248, 1111, 823 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{21}H_{24}O_5Na$ $[M + Na]^+$ 379.1521, found 379.1530.

DOI: 10.1021/acs.joc.6b00100
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1-(2,6-Diethoxystyryl)benzene, ***3z****, Scheme 2.* The same general procedure was followed by using 2,6-diethoxybenzoic acid (42 mg, 0.2 mmol, 1.0 equiv), styrene (35 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 95:5 hexane/ethyl acetate) afforded the desired product as a white solid, (48 mg, 90%), mp 55−57 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 16.5 Hz, 1H), 7.50−7.56 (m, 3H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.21−7.26 (m, 1H), 7.13 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.12 (q, *J* = 6.9 Hz, 4H), 1.51 (t, *J* = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 158.1, 139.5, 132.1, 128.4, 128.0, 126.8, 126.3, 120.2, 114.8, 104.9, 64.2, 14.9; IR (neat) υ_{max} 2978, 1582, 1458, 1247, 1116, 1083, 748 cm^{-1}; HRMS (ESI, *m*/*z*) calcd. for $C_{18}H_{20}O_2Na$ [M + Na]$^+$ 291.1361, found 291.1352.

1-((3-(Benzyloxy)-2-styrylphenoxy)methyl)benzene, ***3aa****, Scheme 2.* The same general procedure was followed by using 2,6-dibenzyloxybenzoic acid (67 mg, 0.2 mmol, 1.0 equiv), styrene (35 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 95:5 hexane/ethyl acetate) afforded the desired product as a white solid, (59 mg, 75%), mp 88−90 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.8 Hz, 1H), 7.62 (d, *J* = 16.8 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 4H), 7.41−7.43 (m, 6H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 2H), 5.19 (s, 4H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 157.8, 139.2, 137.1, 132.7, 128.5, 128.4, 127.9, 127.8, 127.2, 126.9, 126.3, 119.7, 115.8, 105.9, 70.8; IR (neat) υ_{max} 2926, 1728, 1582, 1452, 1254, 1104, 741 cm^{-1}; HRMS (ESI, *m*/*z*) calcd. for $C_{28}H_{24}O_2Na$ [M + Na]$^+$ 415.1674, found 415.1674.

1,3,5-Trimethoxy-2-styrylbenzene, ***3ab****, Scheme 2.*[25] The same general procedure was followed by using 2,4,6-trimethoxybenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), styrene (35 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a colorless oil, (50 mg, 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 16.2 Hz, 1H), 7.44 (d, *J* = 16.2 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.20 (s, 2H), 3.91 (s, 6H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 160.2, 159.5, 139.7, 129.9, 128.4, 126.5, 126.1, 119.8, 108.1, 90.8, 55.8, 55.3; IR (neat) υ_{max} 2938, 1597, 1461, 1328, 1210, 1119, 813 cm^{-1}; HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{18}O_3Na$ [M + Na]$^+$ 293.1154, found 293.1140.

2-(4-Phenylstyryl)-1,3,5-trimethoxybenzene, ***3ac****, Scheme 2.* The same general procedure was followed by using 2,4,6-trimethoxybenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 4-vinylbiphenyl (54 mg, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (57 mg, 82%), mp 150−152 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64−7.66 (m, 2H), 7.59−7.62 (m, 4H), 7.53 (d, *J* = 16.8 Hz, 1H), 7.45−7.49 (m, 3H), 7.35 (t, *J* = 7.2 Hz, 1H), 6.21 (s, 2H), 3.92 (s, 6H), 3.87 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 160.3, 159.6, 141.0, 139.1, 138.8, 129.3, 128.7, 127.1, 127.0, 126.8, 126.6, 120.0, 108.2, 90.8, 55.8, 55.3; IR (neat) υ_{max} 1592, 1458, 1326, 1218, 1153, 1119, 766 cm^{-1}; HRMS (ESI, *m*/*z*) calcd. for $C_{23}H_{22}O_3Na$ [M + Na]$^+$ 369.1467, found 369.1467.

2-(2-Methylstyryl)-1,3,5-trimethoxybenzene, ***3ad****, Scheme 2.*[26] The same general procedure was followed by using 2,4,6-trimethoxybenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 2-methylstyrene (39 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (51 mg, 90%), mp 86−88 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62−7.69 (m, 2H), 7.24 (d, *J* = 16.5 Hz, 1H), 7.08−7.19 (m, 3H), 6.17 (s, 2H), 3.87 (s, 6H), 3.84 (s, 3H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 160.2, 159.4, 138.7, 135.3, 130.1, 128.0, 126.5, 126.0, 124.9, 120.8, 108.6, 90.8, 55.8, 55.3, 20.0; IR (neat) υ_{max} 2936, 1586, 1460, 1198, 1118, 809 cm^{-1}; HRMS (ESI, *m*/*z*) calcd. for $C_{18}H_{20}O_3Na$ [M + Na]$^+$ 307.1310, found 307.1308.

2-(3-Chlorostyryl)-1,3,5-trimethoxybenzene, ***3ae****, Scheme 2.*[26] The same general procedure was followed by using 2,4,6-trimethoxybenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 3-chlorostyrene (38 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (55 mg, 91%), mp 80−82 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (t, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 1.8 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.15−7.17 (m, 1H), 6.19 (s, 2H), 3.90 (s, 6H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 160.5, 159.6, 141.7, 134.3, 129.5, 128.2, 126.2, 125.9, 124.3, 121.2, 107.6, 90.7, 55.7, 55.3; IR (neat) υ_{max} 2961, 1586, 1462, 1326, 1220, 1117, 962, 796 cm^{-1}; HRMS (ESI, *m*/*z*) calcd. for $C_{17}H_{17}ClO_3Na$ [M + Na]$^+$ 327.0764, found 327.0783.

4-(2,4,6-Trimethoxystyryl)-2-methoxyphenyl acetate, ***3af****, Scheme 2.* The same general procedure was followed by using 2,4,6-trimethoxybenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 4-acetoxy-3-methoxystyrene (57 mg, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (61 mg, 85%), mp 105−107 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 16.8 Hz, 1H), 7.33 (d, *J* = 16.2 Hz, 1H), 7.10−7.11 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.19 (s, 2H), 3.898 (s, 3H), 3.896 (s, 6H), 3.86 (s, 3H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 169.2, 160.3, 159.5, 150.9, 138.9, 138.4, 129.3, 122.6, 120.2, 118.6, 110.0, 107.9, 90.8, 55.9, 55.8, 55.3, 20.7; IR (neat) υ_{max} 2933, 1761, 1598, 1460, 1118, 817 cm^{-1}; HRMS (ESI, *m*/*z*) calcd. for $C_{20}H_{22}O_6Na$ [M + Na]$^+$ 381.1314, found 381.1336.

(E)-Butyl 3-(2,4,6-trimethoxyphenyl)acrylate, ***3ag****, Scheme 2.*[27] The same general procedure was followed by using 2,4,6-trimethoxybenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), butyl acrylate (43 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and 1,4-benzoquinone (43 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (41 mg, 70%), mp 79−81 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 16.2 Hz, 1H), 6.75 (d, *J* = 16.2 Hz, 1H), 6.11 (s, 2H), 4.19 (t, *J* = 6.6 Hz, 2H), 3.87 (s, 6H), 3.84 (s, 3H), 1.64−1.73 (m, 2H), 1.37−1.50 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 169.1, 162.6, 161.1, 135.4, 117.4, 105.7, 90.3, 63.8, 55.6, 55.3, 30.9, 19.2, 13.8; IR (neat) υ_{max} 2939, 1699, 1602, 1461, 1156, 1119, 815 cm^{-1}; HRMS (ESI, *m*/*z*) calcd. for $C_{16}H_{22}O_5Na$ [M + Na]$^+$ 317.1365, found 317.1360.

Diethyl 2-(2,4,6-trimethoxycinnamyl)malonate, ***3ah****, Scheme 2.* The same general procedure was followed by using 2,4,6-trimethoxybenzoic acid (42.5 mg, 0.2 mmol), diethyl 2-allylmalonate (60 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (13.4 mg, 0.04 mmol, 0.1 equiv), and 1,4-benzoquinone (65 mg, 0.6 mmol, 3.0 equiv). Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a colorless oil, (45 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.66 (d, *J* = 16.2 Hz, 1H), 6.38−6.43 (m, 1H), 6.12 (s, 2H), 4.18−4.23 (m, 4H), 3.81 (s, 3H), 3.80 (s, 6H), 3.48 (t, *J* = 7.8 Hz, 1H), 2.80 (t, *J* = 7.8 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 169.2, 159.8, 159.0, 127.2, 122.8, 107.7, 90.6, 61.2, 55.6, 55.2, 52.6, 34.0, 14.0; IR (neat) υ_{max} 2939, 1729, 1604, 1462, 1124, 1036, 814 cm^{-1}; HRMS (ESI, *m*/*z*) calcd. for $C_{19}H_{26}O_7Na$ [M + Na]$^+$ 389.1576, found 389.1563.

General Experimental Procedure for the Decarboxylative Heck Reaction between Electron-Deficient Carboxylic Acids and Vinyl Arenes. To an oven-dried 15 mL sealed tube, a mixture of pentafluorobenzoic acid (0.20−0.24 mmol, 1.0−1.2 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv) was taken then dry DMF (3.0 mL) was added to it. After purging with nitrogen, the corresponding styrenes (0.20−0.30 mmol, 1.0−1.5 equiv) were added via microliter syringe and the vessel was sealed with a screw

DOI: 10.1021/acs.joc.6b00100
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cap. The reaction mixture was allowed to stir for 16 h at room temperature. After completion (as detected by TLC), the reaction mixture was poured into water (20 mL) and extracted with ethyl acetate (30 mL). The organic layer was washed with water (10 mL × 2) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate/hexane as eluent to afford the desired product.

1,2,3,4,5-Pentafluoro-6-styrylbenzene, ***6a****, Scheme 3.*[19] The same general procedure was followed by using pentafluorobenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), styrene (35 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as a white solid, (36 mg, 66%), mp 132−134 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 7.5 Hz, 2H), 7.31−7.47 (m, 4H), 6.98 (d, J = 16.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 144.8 (dm, J = 248.8 Hz), 139.7 (dm, J = 252.8 Hz), 137.7 (dm, J = 248.2 Hz), 137.1 (td, J = 8.2 Hz, 2.6 Hz), 136.4, 128.9, 128.8, 126.8 112.6 (d, J = 2.4 Hz), 112.4 (td, J = 13.6 Hz, 4.2 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ −146.0 (dd, J = 21.6 Hz, 7.0 Hz, 2F), −159.8 (t, J = 20.7 Hz, 1F), −166.2 (td, J = 20.7 Hz, 7.0 Hz, 2F); IR (neat) υ_{max} 1523, 1493, 1000, 959, 754 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{14}H_7F_5$ $[M]^+$ 270.0468, found 270.0448.

1-(4-Fluorostyryl)-2,3,4,5,6-pentafluorobenzene, ***6b****, Scheme 3.*[19] The same general procedure was followed by using pentafluorobenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 4-fluorostyrene (36 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as a white solid, (36 mg, 62%), mp 110−112 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (dd, J = 8.4 Hz, 5.4 Hz, 2H), 7.39 (d, J = 16.8 Hz, 1H), 7.09 (t, J = 8.4 Hz, 2H), 6.89 (d, J = 16.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 163.1 (d, J = 248.0 Hz), 144.8 (dm, J = 249.0 Hz), 139.7 (dm, J = 253.5 Hz), 137.7 (dm, J = 249.0 Hz), 135.9 (td, J = 9.0 Hz, 1.5 Hz), 132.6 (d, J = 3.0 Hz), 128.5 (d, J = 7.5 Hz), 115.9 (d, J = 22.5 Hz), 112.4, 112.2 (td, J = 13.5 Hz, 4.5 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ −115.2 (s, 1F), −146.1 (dd, J = 21.2 Hz, 7.5 Hz, 2F), −159.6 (t, J = 20.7 Hz, 1F), −166.1 (td, J = 21.2 Hz, 7.5 Hz, 2F); IR (neat) υ_{max} 1519, 1492, 1240, 1003, 958 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{14}H_6F_6$ $[M]^+$ 288.0374, found 288.0365.

1-(4-Chlorostyryl)-2,3,4,5,6-pentafluorobenzene, ***6c****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 4-chlorostyrene (38 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as a white solid, (44 mg, 73%), mp 98−100 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.37−7.41 (m, 3H), 6.96 (d, J = 16.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 144.8 (dm, J = 249.2 Hz), 139.8 (dm, J = 253.5 Hz), 137.8 (dm, J = 249.2 Hz), 135.7 (td, J = 9.0 Hz, 3.0 Hz), 134.9, 134.7, 129.0, 128.0, 113.2 (d, J = 1.5 Hz), 112.0 (td, J = 13.5 Hz, 4.5 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ −142.6 (dd, J = 22.1 Hz, 7.0 Hz, 2F), −156.0 (t, J = 20.7 Hz, 1F), −162.8 (td, J = 20.7 Hz, 6.6 Hz, 2F) ; IR (neat) υ_{max} 1520, 1490, 1004, 958, 811 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{14}H_6ClF_5$ $[M]^+$ 304.0078, found 304.0061.

1-(4-Bromostyryl)-2,3,4,5,6-pentafluorobenzene, ***6d****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 4-bromostyrene (39 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as a white solid, (47 mg, 67%), mp 99−101 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52 (d, J = 8.1 Hz, 2H), 7.34−7.41 (m, 3H), 6.97 (d, J = 16.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 144.7 (dm, J = 248.9 Hz), 139.8 (dm, J = 252.8 Hz), 137.7 (dm, J = 249.8 Hz), 135.8 (td, J = 9.0 Hz, 1.5 Hz), 135.3, 132.0, 128.2, 122.9, 113.3 (d, J = 3.0 Hz), 112.0 (td, J = 13.5 Hz, 4.5 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ −142.6 (dd, J = 21.2 Hz, 6.6 Hz, 2F), −155.9 (t, J = 21.6 Hz, 1F), −162.7 (td, J = 21.6 Hz, 7.0 Hz, 2F); IR (neat) υ_{max} 1519, 1492, 1002, 961, 810 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{14}H_6BrF_5$ $[M]^+$ 347.9573, 349.9553, found 347.9570, 349.9529.

1-(4-Methylstyryl)-2,3,4,5,6-pentafluorobenzene, ***6e****, Scheme 3.*[13a] The same general procedure was followed by using pentafluorobenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 4-methylstyrene (40 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 97:3 hexane/ethyl acetate) afforded the desired product as a white solid, (41 mg, 73%), mp 142−144 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.44 (m, 3H), 7.20 (d, J = 8.1 Hz, 2H), 6.93 (d, J = 16.8 Hz, 1H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 144.7 (dm, J = 248.3 Hz), 139.5 (dm, J = 252.8 Hz), 139.1, 137.7 (dm, J = 250.5 Hz), 137.1 (td, J = 8.2 Hz, 2.2 Hz), 133.7, 129.5, 126.8, 112.6 (td, J = 13.5 Hz, 4.5 Hz), 111.6 (d, J = 2.2 Hz), 21.3; ^{19}F NMR (470 MHz, $CDCl_3$) −143.0 (dd, J = 22.6 Hz, 6.1 Hz, 2F), −157.1 (t, J = 20.7 Hz, 1F), −163.2 (td, J = 20.7 Hz, 6.1 Hz, 2F); IR (neat) υ_{max} 2924, 1519, 1492, 1001, 958, 804 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{15}H_9F_5$ $[M]^+$ 284.0624, found 284.0615.

1-(4-Ethylstyryl)-2,3,4,5,6-pentafluorobenzene, ***6f****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 4-ethylstyrene (44 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 97:3 hexane/ethyl acetate) afforded the desired product as a white solid, (33 mg, 56%), mp 134−136 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39−7.47 (m, 3H), 7.32 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 16.5 Hz, 1H), 2.67 (q, J = 7.5 Hz, 2H), 1.26 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 144.7 (dm, J = 248.4 Hz), 145.5, 139.5 (dm, J = 252.0 Hz), 137.8 (dm, J = 249.2 Hz), 137.1 (t, J = 8.2 Hz), 134.0, 128.4, 126.9, 112.6 (td, J = 13.5 Hz, 3.8 Hz), 111.7 (d, J = 1.5 Hz), 28.7, 15.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ −143.0 (dd, J = 20.2 Hz, 5.2 Hz, 2F), −157.1 (t, J = 20.7 Hz, 1F), −163.2 (td, J = 20.7 Hz, 5.6 Hz, 2F); IR (neat) υ_{max} 2925, 1522, 1491, 1001, 959, 819 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{16}H_{11}F_5$ $[M]^+$ 298.0781, found 298.0784.

1-(4-tert-Butylstyryl)-2,3,4,5,6-pentafluorobenzene, ***6g****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (51 mg, 0.24 mmol, 1.2 equiv), 4-*tert*-butylstyrene (37 μL, 0.2 mmol, 1.0 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as a white solid, (46 mg, 70%), mp 100−102 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.49 (m, 5H), 6.94 (d, J = 16.8 Hz, 1H), 1.34 (s, 9H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 152.4, 144.7 (dm, J = 248.2 Hz), 139.5 (dm, J = 252.0 Hz), 137.8 (dm, J = 249.0 Hz), 137.0 (t, J = 8.2 Hz), 133.7, 126.6, 125.8, 122.6 (td, J = 13.5 Hz, 3.8 Hz), 111.8, 34.8, 31.2; ^{19}F NMR (470 MHz, $CDCl_3$) −142.9 (dd, J = 21.6 Hz, 6.6 Hz, 2F), −157.0 (t, J = 20.7 Hz, 1F), −163.2 (td, J = 21.2 Hz, 6.6 Hz, 2F); IR (neat) υ_{max} 2971, 1520, 1498, 1003, 960, 822 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{18}H_{15}F_5$ $[M]^+$ 326.1094, found 326.1081.

1-(4-Methoxystyryl)-2,3,4,5,6-pentafluorobenzene, ***6h****, Scheme 3.*[19] The same general procedure was followed by using pentafluorobenzoic acid (51 mg, 0.24 mmol, 1.2 equiv), 4-vinylanisole (27 μL, 0.2 mmol, 1.0 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 97:3 hexane/ethyl acetate) afforded the desired product as a white solid, (43 mg, 72%), mp 128−130 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 9.0 Hz, 2H), 7.38 (d, J = 16.8 Hz, 1H), 6.92 (d, J = 9.0, 2H), 6.83 (d, J = 16.8 Hz, 1H), 3.85 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 160.3, 144.6 (dm, J = 247.5 Hz), 139.3 (dm, J = 252.0 Hz), 137.8 (dm, J = 247.5 Hz), 136.6 (td, J = 9.0 Hz, 1.5 Hz), 129.2, 128.2, 114.2, 112.7 (td, J = 13.5 Hz, 4.5 Hz), 110.3 (d, J = 3.0 Hz), 55.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ −143.2 (dd, J = 21.2 Hz, 5.2 Hz, 2F), −157.5 (t, J = 20.7 Hz, 1F), −163.3 (td, J = 20.7 Hz, 5.6 Hz, 2F); IR (neat) υ_{max}

DOI: 10.1021/acs.joc.6b00100
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2926, 1603, 1519, 1492, 1255, 1001, 956, 816 cm^{-1}; HRMS (EI, *m/z*) calcd. for $C_{15}H_9OF_5$ $[M]^+$ 300.0574, found 300.0561.

4-(Perfluorostyryl)phenyl acetate, ***6i****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (51 mg, 0.24 mmol, 1.2 equiv), 4-acetoxystyrene (30 μL, 0.2 mmol, 1.0 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). In this case little bit unreacted styrene was there with the same polarity desired products. To purify the desired products high pressure vacuum pump was used to remove the unreacted styrene. Column chromatography (SiO_2, eluting with 97:3 hexane/ethyl acetate) afforded the desired product as a white solid, (38 mg, 58%), mp 130−132 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.41, (d, *J* = 16.8 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 16.8 Hz, 1H), 2.3 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 169.3, 151.0, 144.8 (dm, *J* = 249.0 Hz), 139.7 (dm, *J* = 252.0 Hz), 137.7 (dm, *J* = 250.5 Hz), 136.0 (td, *J* = 9.0 Hz, 3.0 Hz), 134.2, 127.9, 122.0, 112.8 (d, *J* = 1.5 Hz), 112.2 (td, *J* = 13.5 Hz, 3.0 Hz), 21.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ −142.7 (dd, *J* = 21.6 Hz, 6.1 Hz, 2F), −156.4 (t, *J* = 20.7 Hz, 1F), −162.9 (td, *J* = 20.2 Hz, 5.6 Hz, 2F); IR (neat) υ_{max} 2925, 1761, 1518, 1497, 1197, 1007, 957 cm^{-1}; HRMS (EI, *m/z*) calcd. for $C_{16}H_9O_2F_5$ $[M]^+$ 328.0523, found 328.0525.

(4-(Perfluorostyryl)phenoxy)(tert-butyl)dimethylsilane, ***6j****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (51 mg, 0.24 mmol, 1.2 equiv), 4-(*tert*-butyldimethylsiloxy)styrene (47 μL, 0.2 mmol, 1.0 equiv), palladium-(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Here little bit unreacted styrene was there with the same polarity desired products. To purify the desired products high pressure vacuum pump was used to remove the unreacted styrene. Column chromatography (SiO_2, eluting with 97:3 hexane/ethyl acetate) afforded the desired product as a white solid, (54 mg, 68%), mp 116−118 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 16.8 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 16.8 Hz, 1H), 1.01 (s, 9H), 0.24 (s, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 156.6, 144.6 (dm, *J* = 248.1 Hz), 139.3 (dm, *J* = 252.0 Hz), 137.7 (dm, *J* = 248.7 Hz), 136.8 (td, *J* = 9.0 Hz, 1.5 Hz), 129.8, 128.2, 120.5, 112.7 (td, *J* = 13.5 Hz, 4.5 Hz), 110.5 (d, *J* = 1.5 Hz), 25.6, 18.2, −4.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ −143.2 (dd, *J* = 22.6 Hz, 6.1 Hz, 2F), −157.5 (t, *J* = 20.7 Hz, 1F), −163.3 (td, *J* = 20.7 Hz, 6.6 Hz, 2F); IR (neat) υ_{max} 2858, 1600, 1521, 1492, 1276, 1003, 960, 916 cm^{-1}; HRMS (EI, *m/z*) calcd. for $C_{20}H_{21}OSiF_5$ $[M]^+$ 400.1282, found 400.1278.

1-(3-Fluorostyryl)-2,3,4,5,6-pentafluorobenzene, ***6k****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 3-fluorostyrene (36 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as a white solid, (35 mg, 61%), mp 82−84 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 16.2 Hz, 1H), 7.34−7.37 (m, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.22−7.24 (m, 1H), 7.04 (td, *J* = 8.4 Hz, 1.8 Hz, 1H), 6.98 (d, *J* = 16.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 163.1 (d, *J* = 246.0 Hz), 144.8 (dm, *J* = 249.0 Hz), 139.9 (dm, *J* = 253.5 Hz), 138.7 (d, *J* = 7.5 Hz), 137.8 (dm, *J* = 247.5 Hz), 135.8 (t, *J* = 7.5 Hz), 130.3 (d, *J* = 9.0 Hz), 122.8 (d, *J* = 3.0 Hz), 115.8 (d, *J* = 21.0 Hz), 114.0 (d, *J* = 3.0 Hz), 113.2 (d, *J* = 22.5 Hz), 111.9 (td, *J* = 13.5 Hz, 3.0 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ −112.8 (s, 1F), −142.4 (dd, *J* = 20.7 Hz, 5.2 Hz, 2F), −155.7 (t, *J* = 20.7 Hz, 1F), −162.7 (m, 2F); IR (neat) υ_{max} 1521, 1494, 1004, 955, 680 cm^{-1}; HRMS (EI, *m/z*) calcd. for $C_{14}H_6F_6$ $[M]^+$ 288.0374, found 288.0365.

1-(3-Chlorostyryl)-2,3,4,5,6-pentafluorobenzene, ***6l****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 3-chlorostyrene (38 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as a white solid, (43 mg, 71%), mp 74−76 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.31−7.42 (m, 4H), 6.98 (d, *J* = 16.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 144.9 (dm, *J* = 246.8 Hz), 140.0 (dm, *J* = 256.5 Hz), 138.3, 137.8 (dm, *J* = 251.2 Hz), 135.6 (t, *J* = 8.2 Hz), 134.9, 130.0, 128.8, 126.7, 125.1, 114.1, 111.9 (td, *J* = 13.5 Hz, 4.5 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ −142.4 (dd, *J* = 21.2 Hz, 5.6 Hz, 2F), −155.6 (t, *J* = 20.7 Hz, 1F), 162.6 (td, *J* = 21.6 Hz, 7.0 Hz, 2F); IR (neat) υ_{max} 1519, 1497, 1003, 964, 782 cm^{-1}; HRMS (EI, *m/z*) calcd. for $C_{14}H_6ClF_5$ $[M]^+$ 304.0078, found 304.0075.

1-(3-Bromostyryl)-2,3,4,5,6-pentafluorobenzene, ***6m****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 3-bromostyrene (39 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Here little bit unreacted styrene was there with the same polarity desired products. To purify the desired products high pressure vacuum pump was used to remove the unreacted styrene. Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as a white solid, (42 mg, 60%), mp 76−78 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.67−7.68 (m, 1H), 7.43−7.48 (m, 2H), 7.36 (d, *J* = 16.8 Hz, 1H), 7.24−7.29 (m, 1H), 6.97 (d, *J* = 16.8 Hz, 1H); $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$) δ 144.9 (dm, *J* = 249.4 Hz), 140.0 (dm, *J* = 253.6 Hz), 138.6, 137.8 (dm, *J* = 250.5 Hz), 135.5 (t, *J* = 8.2 Hz), 131.8, 130.3, 129.6, 125.5, 123.0, 114.1, 111.9 (td, *J* = 13.5 Hz, 3.8 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ −145.6 (dd, *J* = 20.7 Hz, 7.0 Hz, 2F), −158.8 (t, *J* = 20.7 Hz, 1F), −165.9 (td, *J* = 20.7 Hz, 7.0 Hz, 2F); IR (neat) υ_{max} 1521, 1496, 1002, 964, 780 cm^{-1}; HRMS (EI, *m/z*) calcd. for $C_{14}H_6BrF_5$ $[M]^+$ 347.9573, 349.9553, found 347.9573, 349.9541.

1-(3-Methylstyryl)-2,3,4,5,6-pentafluorobenzene, ***6n****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 3-methylstyrene (32 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as a white solid, (37 mg, 65%), mp 104−106 °C. ^1H NMR (600 MHz $CDCl_3$) δ 7.40 (d, *J* = 16.8 Hz, 1H), 7.33−7.34 (m, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 16.8 Hz, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 144.8 (dm, *J* = 249.0 Hz), 139.6 (dm, *J* = 253.5 Hz), 138.5, 137.7 (dm, *J* = 249.0 Hz), 137.3 (td, *J* = 9.0 Hz, 3.0 Hz), 136.4, 129.8, 128.7, 127.5, 124.0, 112.43 (td, *J* = 13.5 Hz, 3.0 Hz), 112.40 (d, *J* = 3.0 Hz), 21.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ −142.8 (dd, *J* = 21.6 Hz, 7.0 Hz, 2F), −156.8 (t, *J* = 20.7 Hz, 1F), −163.1 (m, 2F); IR (neat) υ_{max} 2924, 1521, 1493, 1000, 962, 783 cm^{-1}; HRMS (EI, *m/z*) calcd. for $C_{15}H_9F_5$ $[M]^+$ 284.0624, found 284.0598.

1-(3-Methoxystyryl)-2,3,4,5,6-pentafluorobenzene, ***6o****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (51 mg, 0.24 mmol, 1.2 equiv), 3-vinylanisole (28 μL, 0.2 mmol, 1.0 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 97:3 hexane/ethyl acetate) afforded the desired product as a white solid, (45 mg, 75%), mp 140−142 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 16.8 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 1.8 Hz, 1H), 6.97 (d, *J* = 16.8 Hz, 1H), 6.90 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 159.9, 144.8 (dm, *J* = 249.0 Hz), 139.7 (dm, *J* = 252.0 Hz), 137.8, 137.7 (dm, *J* = 247.5 Hz), 137.0 (td, *J* = 9.0 Hz, 3.0 Hz), 129.8, 119.5, 114.6, 113.0 (d, *J* = 3.0 Hz), 112.3 (td, *J* = 13.5 Hz, 3.0 Hz), 112.1, 55.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ −142.7 (dd, *J* = 22.1 Hz, 6.1 Hz, 2F), −156.5 (t, *J* = 20.7 Hz, 1F), −163.0 (td, *J* = 21.2 Hz, 6.1 Hz, 2F); IR (neat) υ_{max} 1578, 1522, 1495, 1268, 1045, 1002, 965, 778 cm^{-1}; HRMS (EI, *m/z*) calcd. for $C_{15}H_9OF_5$ $[M]^+$ 300.0574, found 300.0564.

1-(3-(Trifluoromethyl)styryl)-2,3,4,5,6-pentafluorobenzene, ***6p****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 3-trifluoromethylstyrene (45 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as

DOI: 10.1021/acs.joc.6b00100
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a white solid, (45 mg, 67%), mp 76−78 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 7.46 (d, J = 16.2 Hz, 1H), 7.05 (d, J = 16.8 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 144.9 (dm, J = 249.0 Hz), 140.1 (dm, J = 255.0 Hz), 137.2, 137.8 (dm, J = 251.7 Hz), 135.5 (td, J = 9.0 Hz, 1.5 Hz), 131.4 (q, J = 33.0 Hz), 129.8, 129.3, 123.9 (q, J = 271.5 Hz), 125.4 (q, J = 4.5 Hz), 123.6 (q, J = 3.0 Hz), 114.6 (d, J = 3.0 Hz), 111.7 (td, J = 13.5 Hz, 4.5 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ −66.1 (s, 1F), −145.6 (dd, J = 21.2 Hz, 7.5 Hz, 2F), −158.6 (t, J = 20.7 Hz, 1F), −165.8 (td, J = 21.2 Hz, 7.5 Hz, 2F); IR (neat) υ_{max} 2924, 1520, 1497, 1331, 1128, 1004, 961, 695 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{15}H_6F_8$ [M]$^+$ 338.0342, found 338.0343.

1-(2-Methylstyryl)-2,3,4,5,6-pentafluorobenzene, ***6q****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), 2-methylstyrene (31 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as a white solid, (34 mg, 60%), mp 112−114 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 16.8 Hz, 1H), 7.57−7.61 (m, 1H), 7.19−7.28 (m, 3H), 6.86 (d, J = 16.5 Hz, 1H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 144.8 (dm, J = 248.2 Hz), 139.7 (dm, J = 252.8 Hz), 137.8 (dm, J = 249.8 Hz), 136.4, 135.7, 135.2 (td, J = 8.2 Hz, 3.0 Hz), 130.6, 128.8, 126.4, 125.3, 113.8 (d, J = 3.0 Hz), 112.6 (td, J = 13.5 Hz, 4.5 Hz), 19.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ −143.0 (dd, J = 20.2 Hz, 7.5 Hz, 2F), −156.7 (t, J = 20.7 Hz, 1F), −163.0 (td, J = 21.2 Hz, 7.0 Hz, 2F); IR (neat) υ_{max} 2924, 1522, 1494, 1000, 962, 754 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{15}H_9F_5$ [M]$^+$ 284.0624, found 284.0620.

1,3-Dimethoxy-5-(perfluorostyryl)benzene, ***6r****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (51 mg, 0.24 mmol, 1.2 equiv), 3,5-dimethoxystyrene (33 μL, 0.2 mmol, 1.0 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 97:3 hexane/ethyl acetate) afforded the desired product as a white solid, (46 mg, 69%), mp 103−105 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, J = 16.5 Hz, 1H), 6.95 (d, J = 16.8 Hz, 1H), 6.67 (d, J = 2.1 Hz, 2H), 6.46 (t, J = 2.1 Hz, 1H), 3.84 (s, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 161.1, 144.8 (dm, J = 249.2 Hz), 139.7 (dm, J = 253.0 Hz), 137.7 (dm, J = 249.8 Hz), 138.4, 137.1 (td, J = 8.2 Hz, 1.5 Hz), 113.1 (d, J = 2.2 Hz), 112.2 (td, J = 13.5 Hz, 4.5 Hz), 104.9, 101.1, 55.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ −142.6 (dd, J = 20.7 Hz, 5.6 Hz, 2F), −156.4 (t, J = 20.7 Hz, 1F), −163.0 (m, 2F); IR (neat) υ_{max} 1593, 1522, 1494, 1296, 1155, 1061, 1005 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{16}H_{11}O_2F_5$ [M]$^+$ 330.0679, found 330.0678.

1-(3,4-Dimethoxystyryl)-2,3,4,5,6-pentafluorobenzene, ***6s****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (51 mg, 0.24 mmol, 1.2 equiv), 3,4-dimethoxystyrene (30 μL, 0.2 mmol, 1.0 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Here little bit unreacted styrene was there with the same polarity desired products. To purify the desired products high pressure vacuum pump was used to remove the unreacted styrene. Column chromatography (SiO_2, eluting with 97:3 hexane/ethyl acetate) afforded the desired product as a white solid, (45 mg, 68%), mp 131−133 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, J = 16.2 Hz, 1H), 7.08 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.04 (d, J = 1.8 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.82 (d, J = 16.8 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.6, 149.2, 144.6 (dm, J = 247.5 Hz), 139.4 (dm, J = 247.5 Hz), 137.7 (dm, J = 247.5 Hz), 136.9 (td, J = 9.0 Hz, 1.5 Hz), 120.6, 112.6 (td, J = 13.5 Hz, 4.5 Hz), 111.1, 110.5 (d, J = 3.0 Hz), 108.8, 55.92, 55.90; ^{19}F NMR (470 MHz, $CDCl_3$) δ −143.2 (dd, J = 20.7 Hz, 5.2 Hz, 2F), −157.3 (t, J = 20.7 Hz, 1F), −163.2 (td, J = 20.7 Hz, 5.2 Hz, 2F); IR (neat) υ_{max} 1520, 1494, 1262, 1022, 961 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{16}H_{11}O_2F_5Na$ [M + Na]$^+$ 353.0577, found 353.0577.

2-Methoxy-4-(perfluorostyryl)phenyl acetate, ***6t****, Scheme 3.* The same general procedure was followed by using pentafluorobenzoic acid (51 mg, 0.24 mmol, 1.2 equiv), 4-acetoxy-3-methoxystyrene (38 μL, 0.2 mmol, 1.0 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 97:3 hexane/ethyl acetate) afforded the desired product as a white solid, (44 mg, 62%), mp 149−151 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 16.8 Hz, 1H), 7.12 (dd, J = 8.4 Hz, 1.8 Hz, 1H), 7.09 (s, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.91 (d, J = 16.8 Hz, 1H), 3.90 (s, 3H), 2.53 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 168.9, 151.3, 144.8 (dm, J = 249.0 Hz), 140.3, 139.7 (dm, J = 252.6 Hz), 137.7 (dm, J = 250.5 Hz), 136.4 (td, J = 9.0 Hz, 1.5 Hz), 135.4, 123.1, 119.6, 112.9 (d, J = 1.5 Hz), 112.2 (td, J = 13.5 Hz, 3.0 Hz), 110.4, 55.9, 20.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ −142.7 (dd, J = 20.7 Hz, 5.6 Hz, 2F), −156.3 (t, J = 20.7 Hz, 1F), −162.9 (m, 2F); IR (neat) υ_{max} 1764, 1517, 1496, 1204, 1004, 968 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{17}H_{11}O_3F_5Na$ [M + Na]$^+$ 381.0526, found 381.0534.

1,2,3,4-Tetrafluoro-5-styrylbenzene, ***6u****, Scheme 3.*[13a] The same general procedure was followed by using 1,2,3,4-tetrafluorobenzoic acid (39 mg, 0.2 mmol, 1.0 equiv), styrene (35 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (13.4 mg, 0.04 mmol, 0.2 equiv), and silver carbonate (165 mg, 0.6 mmol, 3.0 equiv). 5% DMSO was used as a co solvent and the reaction was run for 4 h at 120 °C. Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as a white solid, (30 mg, 60%), mp 86−88 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.33 (t, J = 7.8 Hz, 1H), 7.18−7.22 (m, 1H), 7.08−7.15 (m, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 147.3 (dm, J = 244.8 Hz), 145.3 (dm, J = 248.4 Hz), 141.0 (dm, J = 250.0 Hz), 139.6 (dm, J = 252.9 Hz), 136.1, 132.9 (t, J = 3.0 Hz), 128.8, 128.7, 126.8, 121.7 (m), 117.9 (t, J = 3.0 Hz), 107.4 (dt, J = 21.0 Hz, 3.0 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ −139.8 (dd, J = 21.2 Hz, 11.3 Hz, 1F), −144.1 (dd, J = 20.7 Hz, 10.8 Hz, 1F) −156.0 (t, J = 19.3 Hz, 1F), −157.0 (t, J = 20.7 Hz, 1F); IR (neat) υ_{max} 1527, 1477, 1039, 942, 756, 693 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{14}H_8F_4$ [M]$^+$ 252.0562, found 252.0556.

1-(2,6-Difluorostyryl)benzene, ***6v****, Scheme 3.*[13a] The same general procedure was followed by using 2,6-difluorobenzoic acid (32 mg, 0.2 mmol, 1.0 equiv), styrene (35 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (13.4 mg, 0.04 mmol, 0.2 equiv), and silver carbonate (165 mg, 0.4 mmol, 3.0 equiv). 5% DMSO was used as a co solvent and the reaction was run for 4 h at 120 °C. Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as a white solid, (30 mg, 70%), mp 65−67 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 7.2 Hz, 2H), 7.25−7.42 (m, 4H), 7.11−7.18 (m, 2H), 6.91 (t, J = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 161.0 (dm, J = 249.8 Hz), 137.4, 135.1 (t, J = 8.1 Hz), 128.7, 128.2, 127.8 (t, J = 10.5 Hz), 126.7, 115.2, 114.8 (t, J = 15.0 Hz), 111.5 (m); ^{19}F NMR (470 MHz, $CDCl_3$) δ −113.0 (s, 2F); IR (neat) υ_{max} 1565, 1463, 1210, 993, 748 cm^{-1}.

1-Cinnamyl-2,3,4,5,6-pentafluorobenzene, ***6w****, Scheme 3.*[28] The same general procedure was followed by using pentafluorobenzoic acid (42.5 mg, 0.2 mmol, 1.0 equiv), allylbenzene (40 μL, 0.3 mmol, 1.5 equiv), palladium(II) trifluoroacetate (6.7 mg, 0.02 mmol, 0.1 equiv), and silver carbonate (110 mg, 0.4 mmol, 2.0 equiv) except the reaction was run at 120 °C. Column chromatography (SiO_2, eluting with 98:2 hexane/ethyl acetate) afforded the desired product as a colorless liquid, (42 mg, 74%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23−7.36 (m, 5H), 6.50 (d, J = 15.6 Hz, 1H), 6.21−6.26 (m, 1H), 3.62 (dd, J = 6.6 Hz, 0.6 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 145.0 (dm, J = 244.5 Hz), 139.8 (dm, J = 250.5 Hz), 137.5 (dm, J = 249.0 Hz), 136.5, 132.4, 128.6, 127.6, 126.2, 124.2, 113.2 (td, J = 19.5 Hz, 4.5 Hz), 25.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ −143.9 (dd, J = 21.6 Hz, 7.0 Hz, 2F), −157.3 (t, J = 20.7 Hz, 1F), −162.5 (td, J = 20.7 Hz, 7.0 Hz, 2F); IR (neat) υ_{max} 1498, 1118, 990, 963, 911, 754, 694 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{15}H_9F_5$ [M]$^+$ 284.0624, found 284.0608.

Gram Scale Reaction: (Synthesis of 1,2,3,4,5-Pentafluoro-6-styrylbenzene, Scheme 3, ***6a****).* To an oven-dried 250 mL round-bottom flask, a mixture of pentafluorobenzoic acid (1.0 g, 4.7 mmol, 1.0 equiv), palladium(II) trifluoroacetate (156 mg, 0.47 mmol, 0.1 equiv), and silver carbonate (2.6 g, 9.4 mmol, 2.0 equiv) was taken then dry DMF (80 mL) was added to it under nitrogen atmosphere.

DOI: 10.1021/acs.joc.6b00100
J. Org. Chem. 2016, 81, 2521−2533

To this reaction mixture styrene (0.8 mL, 7.05 mmol,) was added via syringe. The reaction mixture was allowed to stir for 16 h at room temperature under nitrogen atmosphere. After completion (as detected by TLC), the reaction mixture was poured into water (60 mL) and extracted with ethyl acetate (80 mL). The organic layer was washed with water (30 mL) and brine (20 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The pure 1,2,3,4,5-pentafluoro-6-styrylbenzene (**6a**) was obtained as a white solid in 61% (775 mg) yield after column chromatography of the crude reaction mixture using ethyl acetate/hexane (98:2) as eluent.

Experimental Procedure for the Preparation of 1-(2,3,5,6-Tetrafluoro-4-styrylphenyl)-1H-indole, ***7****, Scheme 6 from 1,2,3,4,5-Pentafluoro-6-styrylbenzene (****6a****).* Sodium *tert*-butoxide (53 mg, 0.55 mmol, 1.1 equiv) was added to a glass vial containing indole (59 mg, 0.5 mmol, 1.0 equiv) in dry DMA (3.0 mL). The mixture was stirred at room temperature for 1.0 min. The mixture was cooled and added to a cooled solution of 1,2,3,4,5-pentafluoro-6-styrylbenzene (162 mg, 0.6 mmol,1.2 equiv) in dry DMA (3.0 mL) under stirring in a 10 mL round-bottom flask. After 15 min the cooling bath was removed and the reaction mixture was allowed to stir for 1 h at room temperature under nitrogen atmosphere. After completion (as detected by TLC), the reaction mixture was mixed with sat. NH_4Cl (aq.) (5.0 mL) and water (10 mL) then extracted with ethyl acetate (20 mL) The organic layer was washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography eluting with hexane/ethyl acetate (8:2) afforded the desired product as a white solid, (156 mg, 85%), mp 130−132 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.8 Hz, 1H), 7.61−7.64 (m, 3H), 7.46 (t, J = 7.8 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H), 7.33 (td, J = 8.4 Hz, 1.2 Hz, 1H), 7.28 (td, J = 7.8 Hz, 1.2 Hz, 1H), 7.23−7.26 (m, 2H), 7.18 (d, J = 16.8 Hz, 1H), 6.83 (d, J = 3.6 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 145.0 (dm, J = 249.2 Hz), 142.8 (dm, J = 250.0 Hz), 138.0 (t, J = 9.0 Hz), 136.4, 136.3, 129.2, 128.9, 128.7, 128.3, 127.1, 123.1, 121.2 (d, J = 3.0 Hz), 116.6 (m), 116.2 (t, J = 13.5 Hz), 113.2, 110.6, 105.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ −145.6 (m, 2F), −150.7 (m, 2F); IR (neat) υ_{max} 1519, 1487, 1204, 971, 748, 693 cm^{-1}; HRMS (FAB, m/z) calcd. for $C_{22}H_{14}NF_4$ $[M + H]^+$ 368.1062, found 368.1062.

Experimental Procedure for the Preparation of 1-(2,3,5,6-Tetra(1H-pyrazol-1-yl)-4-styrylphenyl)-1H-indole, ***8****, Scheme 6 from 1-(2,3,5,6-Tetrafluoro-4-styrylphenyl)-1H-indole (****7****).* Sodium *tert*-butoxide (48 mg, 0.5 mmol, 5.0 equiv) was added to a glass vial containing pyrazole (34 mg, 0.5 mmol, 5.0 equiv) in dry DMA (1.0 mL). The mixture was stirred at room temperature for 1.0 min. The mixture was cooled and added to a cooled solution of 1-(2,3,5,6-tetrafluoro-4-styrylphenyl)-1*H*-indole (37 mg, 0.1 mmol, 1.0 equiv) in dry DMA (1.0 mL) under stirring in a 10 mL round-bottom flask. After 15 min the cooling bath was removed and the reaction mixture was allowed to stir for 1 h at room temperature under nitrogen atmosphere. After completion (as detected by TLC), the reaction mixture was quenched with sat. NH_4Cl (aq.) (1.0 mL) then extracted with ethyl acetate (20 mL) and water (10 mL). The organic layer was washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography eluting with hexane/ethyl acetate (7:3) afforded the desired product as a white solid, (55 mg, 98%), mp 280−282 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, J = 1.8 Hz, 2H), 7.53 (d, J = 2.4 Hz, 2H), 7.42−7.43 (m, 1H), 7.27−7.28 (m, 2H), 7.23−7.24 (m, 3H), 7.00−7.05 (m, 7H), 6.84 (d, J = 3.0 Hz, 1H), 6.41 (d, J = 3.0 Hz, 1H), 6.38 (d, J = 16.8 Hz, 1H), 6.35 (t, J = 1.8 Hz, 2H), 5.90 (t, J = 1.8 Hz, 2H), 5.86 (d, J = 16.8 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 141.12, 141.10, 138.4, 137.17, 137.16, 136.9, 136.33, 136.28, 132.7, 132.5, 131.3, 128.8, 128.6, 128.3, 127.9, 126.8, 122.4, 120.5, 117.7, 109.6, 107.2, 106.8, 104.8; IR (neat) υ_{max} 2923, 1519, 1480, 1389, 1037, 950, 756 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{34}H_{25}N_9$ $[M]^+$ 559.2233, found 559.2235.

Experimental Procedure for the Preparation of Benzyl(2,3,5,6-tetrafluoro-4-styrylphenyl)sulfane, ***9****, Scheme 6 from 1,2,3,4,5-Pentafluoro-6-styrylbenzene (****6a****).* A mixture of 1,2,3,4,5-pentafluoro-6-styrylbenzene (27 mg, 0.1 mmol, 1.0 equiv), phenylmethanethiol (14 μL, 0.12 mmol, 1.2 equiv) and TRIS (145 mg, 1.2 mmol, 12 equiv) in dry DMF (2.0 mL) was stirred for 12 h at room temperature under argon atmosphere in a 10 mL round-bottom flask. After completion (as detected by TLC), the reaction mixture was poured into water (10 mL) and extracted with ethyl acetate (20 mL). The organic layer was washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography eluting with hexane/ethyl acetate (8:2) to afford the desired product as a white solid, (34 mg, 90%), mp 108−110 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, J = 7.8 Hz, 2H), 7.50 (d, J = 16.8 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 7.36 (t, J = 7.8 Hz, 1H), 7.25−7.31 (m, 5H), 7.06 (d, J = 16.8 Hz, 1H), 4.16 (s, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 147.1 (dm, J = 242.8 Hz), 144.4 (dm, J = 250.2 Hz), 137.6 (t, J = 9.0 Hz), 136.5 (d, J = 1.5 Hz), 129.0, 128.83, 128.78, 128.6, 127.7, 127.0, 117.0 (t, J = 13.5 Hz), 113.7, 111.4 (t, J = 21.0 Hz), 39.0 (t, J = 3.0 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ −138.4 (dd, J = 22.6 Hz, 11.3 Hz, 2F), −146.2 (dd, J = 22.6 Hz, 11.3 Hz, 2F); IR (neat) υ_{max} 1468, 1064, 959, 752, 693 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{21}H_{14}SF_4$ $[M]^+$ 374.0752, found 374.0734.

Experimental Procedure for the Preparation of tert-Butyl (S)-1-(methoxycarbonyl)-2-(2,3,5,6-tetrafluoro-4-styrylphenylthio)-ethylcarbamate, ***10****, Scheme 6 from 1,2,3,4,5-Pentafluoro-6-styrylbenzene (****6a****).* A mixture of 1,2,3,4,5-pentafluoro-6-styrylbenzene, **6a** (27 mg, 0.1 mmol, 1.0 equiv), *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester (21 μL, 0.1 mmol, 1.0 equiv) and TRIS (25 mg, 0.2 mmol, 2.0 equiv) in dry DMF (2.0 mL) was stirred for 4.5 h at room temperature under argon atmosphere in a 10 mL round-bottom flask. After completion (as detected by TLC), the reaction mixture was poured into water (10 mL) and extracted with ethyl acetate (20 mL). The organic layer was washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography eluting with hexane/ethyl acetate (7:3) to afford the desired product as a white solid, (41 mg, 84%), mp 90−92 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, J = 7.2 Hz, 2H), 7.52 (d, J = 16.2 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 16.8 Hz, 1H), 5.39 (d, J = 6.6 Hz, 1H), 4.58−4.60 (m, 1H), 3.70 (s, 3H), 3.47 (dd, J = 14.4 Hz, 4.2 Hz, 1H), 3.38 (dd, J = 14.4 Hz, 4.2 Hz, 1H), 1.41 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 170.4, 154.7, 147.1(dm, J = 243.0 Hz), 144.4 (dm, J = 250.5 Hz), 138.0 (t, J = 9.0 Hz), 136.4, 129.1, 128.8, 127.0, 117.5 (t, J = 13.5 Hz), 113.5, 111.0 (t, J = 21.0 Hz), 80.3, 53.7, 52.6, 36.6, 28.1; ^{19}F NMR (470 MHz, $CDCl_3$) δ −134.5 (m, 2F), −142.6 (m, 2F); IR (neat) υ_{max} 1739, 1706, 1472, 1342, 1160, 1063, 1015, 963, 754 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{23}H_{23}NO_4SF_4$ $[M]^+$ 485.1284, found 485.1287.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00100.

^{1}H, ^{13}C and ^{19}F NMR spectra. (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Fax: (+91) 33 2473 5197. E-mail: rjana@iicb.res.in.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

RJ thanks SERB, Govt. of India for Ramanujan fellowship; award no. SR/S2/RJN-97/2012 for financial support. AH and SKB thank CSIR, and UGC respectively for their fellowships.

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