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Allylation and Vinylation of Aryl Radicals Generated from Diazonium Salts

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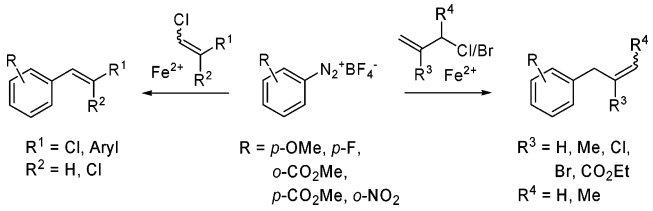

Allylation and vinylation of aryl radicals generated from aryl diazonium salts provides rapid and efficient access to chlorinated and brominated derivatives of styrene and allylbenzene. Allyl chlorides were found to be better substrates than bromides due to decreased halogen transfer. Donor- and acceptor-substituted diazonium salts are well tolerated. The products represent important precursors for numerous further transformations.

Introduction

Starting from the earliest report by Lewis and Winstein,[1] radical addition−fragmentation reactions have become widely used for the allylation and vinylation of carbon-centered radicals.[2] While major studies were based on trialkyltin-substituted olefinic substrates,[3,4] the role of several other allylic substituents or functional groups[5] such as sulfides,[6] sulfoxides,[7] sulfones,[8] cobaloximes,[9] silanes,[10] halides,[11] and phosphine oxides[12] has been investigated as well. Allylation reactions have been carried out with a wide variety of carbon-centered radicals, including all types of alkyl and acyl radicals.[13] Only reports on the behavior of aryl radicals, as depicted in Scheme 1 (path A), remained rare in the literature and thus appear to be more complicated.[14,15] A recent advance in this field was made by Frejd,[16] who achieved allylation of aryl radicals via diazotizative deamination of acceptor-substituted aromatic amines in the presence of allyl bromide. Literature precedence for the corre-

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(13) For overviews, see: (a) Curran, D. P.; Porter, N. A.; Giese, B., Eds. *Stereochemistry of Radical Reactions*: *Concepts*, *Guidelines*, *and Synthetic Applications*; VCH: Weinheim, Germany, 1996. (b) Giese, B. *Radicals in Organic Synthesis*: *Formation of Carbon−Carbon Bonds*; Pergamon Press: Oxford, UK, 1986.

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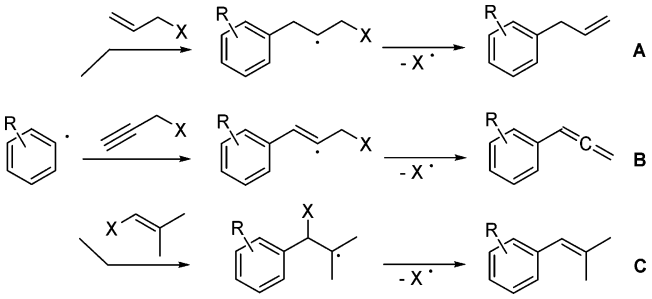
SCHEME 1. Allylation (A), Allenylation (B), and Vinylation (C) of Aryl Radicals via an Addition−Fragmentation Mechanism



sponding allenylation and vinylation reactions, which would be based on a similar radical addition−fragmentation sequence, is even more difficult to find (Scheme 1, paths B and C).[17]

In general, the addition of aryl radicals to olefins is well-known from the classical Meerwein arylation,[18] although this reaction type is mostly employed for a limited group of activated, electron-deficient olefins.[19,20] Nonactivated olefins, in contrast, were believed to be too unreactive giving rise to side reactions such as hydrogen abstraction or biaryl couplings.[21a] This uncertainty is somehow reflected by the wide range of rate constants published for the addition step.[21] Since our recent studies on radical functionalizations indicate that the large number of nonactivated olefins represents an equally suitable group of substrates for aryl radicals,[22] we got inspired to investigate reactions of aryl radicals with a variety of allylic, vinylic, and propargylic halides. Herein, we would like to report our results on allylation and vinylation.

Results and Discussion

The products obtained from the reactions of *p*-methoxy-, *p*-fluoro-, *o*-carbomethoxy-, *p*-carbomethoxy-, and *o*-nitro-substituted aryl diazonium tetrafluoroborates **1a**−**e** with various olefinic chlorides and bromides are summarized in Tables 1−3. Initial experiments identified several factors that were crucial to achieving good selectivity and high yields in these reactions. A key element to achieve selectivity in reactions of aryl radicals appears to be the use of water as a solvent or at least cosolvent.[21c,22] For the purpose of allylation and vinylation, it is crucial that the concentration of the aryl diazonium ions in the reaction mixture is kept at a low level at any time. If this is not the case, azo coupling reactions occur as undesired side processes, which are due to the fact that aryl diazonium salts can act as efficient nitrogen-centered radical scavengers.[14,22,23] To suppress these side processes, we adjusted our basic procedure such that the diazonium salt was added slowly to the reaction mixture. In our initial experiments, we were pleased to find that these alterations indeed had the desired effect and only traces of azo compounds were formed as byproducts. Another important issue of radical allylation and vinylation reactions is the nature of the leaving group.[24] Unlike most known radical functionalizations of this type, we chose to perform the reaction in a non-chain, self-terminating fashion. To facilitate broader application, we concentrated our efforts on the use of low-cost, commercially available chlorides and bromides as olefinic substrates. Since a bromine or chlorine radical would be formed in the final β-scission step, which possesses itself significant reactivity, this radical has to be reduced to the corresponding anion as fast as possible to minimize side reactions. Regarding the overall results of the allylation and vinylation experiments, iron(II) appears to be a suitable and efficient scavenger for the halogen radicals forming in this process.

Except for the attempts to achieve allenylation, all allylation and vinylation experiments furnished synthetically useful yields. A careful examination of the product mixtures revealed that the reaction, as described here, can be disturbed by hydrogen abstraction, halogen abstraction, double addition, and intramolecular cyclization. These four types of undesired side reactions will be discussed in the above-mentioned order. Hydrogen abstraction occurs when the addition step of the aryl radical to the substrate is too slow (e.g., sterically hindered olefins) or when easily abstractable hydrogen atoms are present in the target molecule. In general, acceptor-substituted aryl radicals more likely stabilize themselves by hydrogen abstraction than donor-substituted intermediates as can be seen from the three series of entries 5−6, 7−9−10, and 20−22.[25] The increased amount of reduced products found with 3-chloro-1-butene (**2d**) (entries 5 and 6) is most probably caused by the presence of a hydrogen atom on a chlorine-substituted *secondary* carbon atom. In all other substrates, the carbon atom bearing the allylic hydrogen is primary.[26]

In contrast to bromine abstraction by the aryl radical, the atom transfer of chlorine was not observed in our study. This circumstance, undoubtedly related to the increased strength of

(14) For the first report on allylations of aryl radicals, see: Al Adel, I.; Salami, B. A.; Levisalles, J.; Rudler, H. *Bull. Soc. Chim. Fr.* **1976**, 934−938.

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(16) Ek, F.; Axelsson, O.; Wistrand, L.-G.; Frejd, T. *J. Org. Chem.* **2002**, *67*, 6376−6381.

(17) (a) Cohen, S. G.; Wolosinski, H. T.; Scheuer, P. J. *J. Am. Chem. Soc.* **1950**, *72*, 3952−3953. (b) Reijnhart, A. F. A. *Recl. Trav. Chim. Pays-Bas* **1927**, *46*, 72−76.

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(20) For notable exceptions, see: (a) Raucher, S.; Koolpe, G. A. *J. Org. Chem.* **1983**, *48*, 2066−2069. (b) Gorbovoi, P. M.; Kudrik, E. Y.; Grishchuk, B. D. *Russ. J. Gen. Chem.* **1998**, *68*, 1132−1134. (c) Molinaro, C.; Mowat, J.; Gosselin, F.; O'Shea, P. D.; Marcoux, J.-F.; Angelaud, R.; Davies, I. W. *J. Org. Chem.* **2007**, *72*, 1856−1858. (d) Reference 16.

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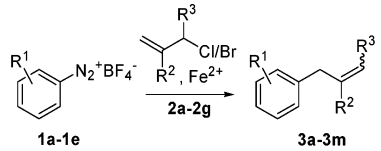
(23) Depending on whether the aryl radicals are trapped by the diazonium salts before or after reacting with the olefin (as alkyl radicals), biaryl azo compounds or carbodiazenylation products are obtained. See also ref 22.

(24) For relative rate constants of β-fragmentations, see: Wagner, P. J.; Sedon, J. H.; Lindstrom, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 2579−2580.

(25) A reliable determination of the degree of hydrogen abstraction by *p*-fluoroaryl radicals was not possible due to the volatility of fluorobenzene.

(26) The absolute rate constants determined for the addition of aryl radicals to double and triple bonds differ only by a factor of 2 ($k_{double} = 2.9 \times 10^7\ M^{-1}\ s^{-1}$ and $k_{triple} = 1.4 \times 10^7\ M^{-1}\ s^{-1}$), see ref 21c. For relative rates of aryl radical additions to various olefins, see: Bridger, R. F.; Russell, G. A. *J. Am. Chem. Soc.* **1963**, *85*, 3754−3765.

TABLE 1. Allylation of Arenes



1a-1e 3a-3m

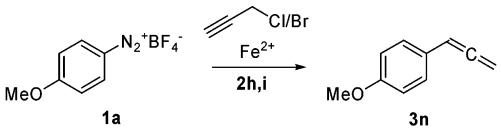
entry	diazonium salt **1**	olefin **2**	product **3**[a]	by-product
1	**1a**	**2a**	**3a** (69%)	**4a** (8%)[b]
2	**1b**	**2a**	**3b** (58%)	
3	**1a**	**2b**	**3a** (59%)	**4b** (24%)[b]
4	**1a**	**2c**	**3c** (75%)	**4a** (12%)[b]
5	**1a**	**2d**	**3d** (48%) (*E*):(*Z*) = 4:1	**4a** (25%)[b]
6	**1c**	**2d**	**3e** (42%) (*E*):(*Z*) = 3:1	**4c** (45%)[b]
7	**1a**	**2e**	**3f** (85%)	**4a** (3%)[b]
8	**1b**	**2e**	**3g** (76%)	
9	**1c**	**2e**	**3h** (67%)	**4c** (9%)[b]
10	**1d**	**2e**	**3i** (78%)	**4c** (10%)[b]
11	**1e**	**2e**	(0%)	**4d** (32%)
12	**1a**	**2f**	**3j** (68%)	**4b** (24%)[b]
13	**1c**	**2f**	**3k** (82%)	**4c** (2%)[b]
14	**1e**	**2f**	**3l** (63%)	**4f** (11%)[b]
15	**1a**	**2g**	**3m** (58%)	

[a] Reactions conducted according to the general procedure. [b] Structures and yields of products were determined by GC, ^{1}H NMR, and ^{13}C NMR analysis of the crude product mixture.

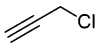
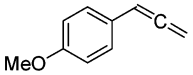
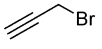
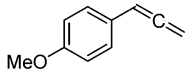
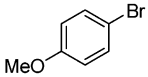
the carbon−chlorine bond, made chlorinated substrates become our preferred substrates. This became even more true since we saw no negative effect arising from the fragmentation step, although β-scission has been reported to proceed about 65 times faster when bromine is released instead of a chlorine radical,[24] and Migita[15b] observed a drop in yield from 63% to 8% when reacting phenyl radicals with allyl chloride instead of allyl bromide. Although troubled by halogen transfer, good results can be obtained from brominated compounds, given that the addition step to the double or triple bond occurs sufficiently fast. The competition of the desired addition−fragmentation pathway and bromine abstraction is reflected in the series of entries 17, 3, and 12. As the addition to the substrate becomes more and more effective, bromine transfer is more and more repressed.[21c,26] It is interesting to note that the experiment with allyl bromide (**2b**) (entry 3) leads to the same ratio of abstraction versus addition as previously reported,[16] despite the fact that the reaction conditions applied are totally different.

Double addition is observed when the product formed in the addition−fragmentation sequence represents a more reactive olefin than the original substrate itself. Notable examples are listed in entries 16, 18, and 19. The addition to propargyl chloride (**2h**) is not disturbed by halogen abstraction as seen from the corresponding bromide **2i**, nor does hydrogen abstraction occur. These two findings suggest that the aryl radicals effectively undergo addition reactions, with the simple but far-reaching limitation that those which are generated in a later stage of the reaction more likely attack allene **3n** than they would add to the alkyne **2h**. As a result, only a small amount of allene

TABLE 2. Attempted Allenylation of Arenes



1a 3n

entry	diazonium salt **1**	acetylene **2**	product **3**[a]	by-product
16	**1a**	 **2h**	 **3n** (10%)[b]	complex mixture
17	**1a**	 **2i**	 **3n** (8%)[b]	 **4b** (61%)

[a] Reactions conducted according to the general procedure. [b] Structures and yields of products were determined by GC, ^{1}H NMR, and ^{13}C NMR analysis of the crude product mixture.

3n was detected among a complex mixture of other products with higher molecular weight.

Unlike with propargyl chloride (**2h**), single and double addition to 1,2-dichloroethenes **2j** and **2k** led to simple mixtures containing chlorostyrene **3o** and stilbene **4e** as main products. Only the (*E*)-configured styrene **3o** was isolated from both attempts, and the final product distribution is somehow effected by the initial olefin configuration. To get a better insight, we repeated the experiment with increasing amounts of (*E*)-1,2-dichloroethene (**2k**) (entry 19, 10 and 20 equiv) and found that the double addition to give the stilbene **4e** can successfully be suppressed. The different ratios of styrene **3o** to stilbene **4e** obtained under standard conditions with 6 equiv of substrate **2k** can be explained in the following way. As the concentration of the initial chlorostyrene product **3o** increases over the course of the reaction, it competes with the starting 1,2-dichloroethene **2k** for addition of the aryl radical. Since the rate of addition to (*E*)-1,2-dichloroethene (**2k**) is probably faster than the rate for addition to (*Z*)-1,2-dichloroethene (**2j**), more stilbene **4e** is produced in the reaction with the less reactive (*Z*)-isomer (entry 18). Similar differences in olefin reactivity have been found by Giese,[27] who reported that the cyclohexyl radical adds faster to a series of (*E*)-olefins than to the corresponding (*Z*)-olefins. The effectiveness of the initially undesired aryl radical addition to chlorostyrene **3o** becomes apparent in an independent experiment, in which the diazonium salt **1a** and only 2 equiv of styrene **3o** furnished 61% of stilbene **4e** (entry 23). Due to the trisubstituted double bond present in the styrenes **3p**−**r** (entries 20−22), double addition does not occur in reactions with trichloroethene (**2l**),[21b,28] but it does again complicate the formation of the cinnamic ester **3s**. Vinylation experiments with the chloro- and bromoacrylates **2m** and **2n** as radical acceptors gave the cinnamate **3s** in poor yields together with several side products of higher molecular weight (entries 24 and 25).

Among the five diazonium salts **1a**−**e**, only the *o*-nitro-substituted derivative **1e** failed to yield allylation products in the reaction with 2,3-dichloropropene (**2e**) (entry 11). In this special case, the chloroalkyl radical arising from the addition step preferably attacks the nitro group rather than stabilizing itself by β-scission (Scheme 2).[29,30] Nitroketone (**4d**) is most likely formed by subsequent hydrolysis of an intermediate benzoxacine.[31] When 2,3-dibromopropene (**2f**) is used instead of the dichloro derivative **2e**, the release of bromine in the fragmentation step is sufficiently fast to overcome the cyclization on the nitro group.

In summary, we have shown that the intermolecular allylation and vinylation of aryl radicals is a simple, low-cost, and environmentally benign route to halogenated allylbenzenes and styrenes, which has so far only marginally been exploited. Especially the chlorinated and brominated products are important precursors for a wide range of further transfor-

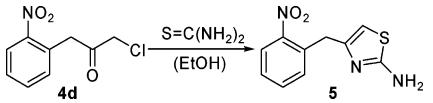
(27) Giese, B. *Angew. Chem., Int. Ed.* **1983**, *22*, 753−764.

(28) Attempts to achieve vinylation with tetrachloroethene and diazonium salt **1a** gave nearly quantitative yields of anisole and only traces of trichlorostyrene although additions of aryl radicals to this substrate have been reported. See ref 17.

(29) For intramolecular additions of alkyl radicals to nitrobenzenes, see: Beckwith, A. L. J.; Lawton, D. L. *J. Chem. Soc., Perkin Trans. 2* **1973**, 2134−2137.

(30) The allylation reported by Freyd does tolerate *o*-nitro substituents due to the use of allyl bromide, which undergoes faster fragmenation. See ref 16.

(31) The structure of nitro compound **4d** was confirmed by conversion to aminothiazole **5** according to the literature: Hardy, K. D.; Harrington, F. P.; Stachulski, A. V. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1227−1236.



4d 5

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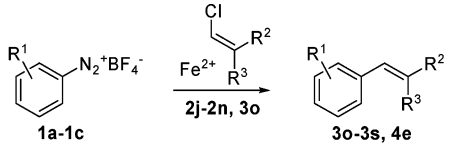
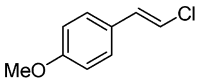
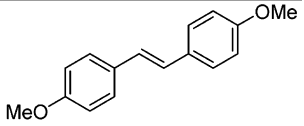
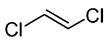
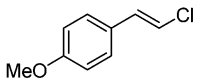
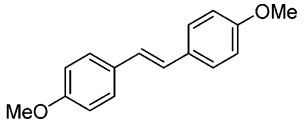
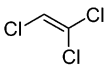
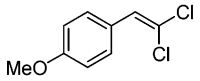
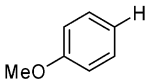
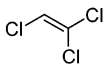
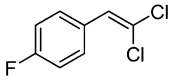
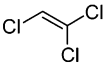
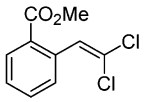
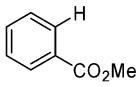
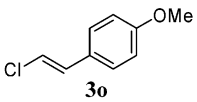
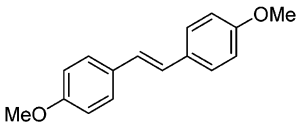
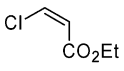
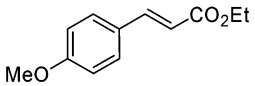
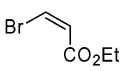
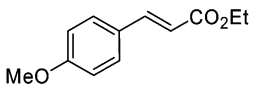
TABLE 3. Vinylation of Arenes

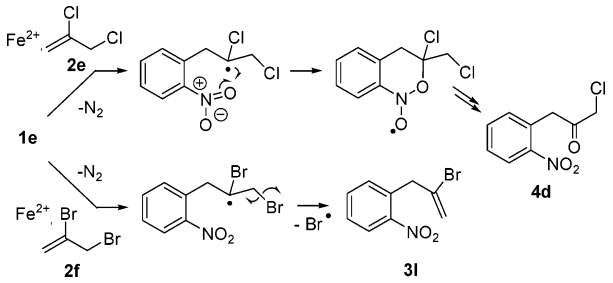


entry	salt **1**	olefin **2**	product **3**[a]	by-product
18	**1a**	 **2j**	 **3o** (32%)	 **4e** (28%)
19	**1a**	 **2k**	 **3o** (53%) (63%)[c] (72%)[d]	 **4e** (11%)[b] (5%)[b,c] (<2%)[b,d]
20	**1a**	 **2l**	 **3p** (61%)	 **4a** (<2%)[b]
21	**1b**	 **2l**	 **3q** (46%)	
22	**1c**	 **2l**	 **3r** (45%)	 **4c** (26%)[b]
23	**1a**	 **3o**	 **4e** (61%)[e]	
24	**1a**	 **2m**	 **3s** (19%)[b]	complex mixture
25	**1a**	 **2n**	 **3s** (15%)[b]	complex mixture

[a] Reactions conducted according to the general procedure (6 equiv of olefinic substrate). [b] Structures and yields of products were determined by GC, ^{1}H NMR, and ^{13}C NMR analysis of the crude product mixture. [c] Experiment with 10 equiv of substrate **2k**. [d] Experiment with 20 equiv of substrate **2k**. [e] Experiment with 2 equiv of substrate **3o**, standard solvent mixture changed to DMSO−H_2O (5:1 v/v) due to the solubility of substrate **3o**.

mations. 2-Chloroallyl and 2-bromoallyl derivatives, for example, have successfully been employed as precursors for reactive organotitanium,[32a] organolithium,[32b,c] and organozirconium[32d] intermediates as well as in copper-[32e] and stannane-based[32f,g] cross-coupling reactions. 2-Chlorostyrenes have served as reactants in carbonylations[33a,b] and metal-mediated C−C bond-forming processes.[33c−e] 2,2-Dichlorostyrenes can be converted to acetylenes,[34a,b] chloroacetylenes,[34c] and allenes.[34d] Cross-couplings have been achieved via Grignard[34e] and Negishi[34f,g] protocols. In contrast to Friedel−Crafts alkylation and previously described radical allylations,[16] our access is not limited to either donor- or acceptor-substituted arenes. The

SCHEME 2. Cyclization versus Fragmentation in Allylations of *o*-Nitrophenyl Radicals



reaction also compares well with known organometallic methods[36,38] due to the simple conditions, easily available starting materials, and insensitivity toward cheap bulk materials of technical grade purity.

Experimental Section

General Details. All chemicals were used as commercially available without further purification. The solvent mixture DMSO−H_2O (5:2 v/v) and the olefins were degassed by a stream of argon prior to use.

General Procedure for the Preparation of the Aryl Diazonium Tetrafluoroborates 1a−e. To an ice−salt-cooled solution of the aniline (40.0 mmol) in HBF_4 (50%, 14 mL) and water (15 mL) was dropwise added a precooled solution of $NaNO_2$ (2.90 g, 42.0 mmol) in water (6.5 mL). During the addition, the temperature was carefully kept below 5 °C and the resulting mixture was left to stir at 0 °C for 30 min. The diazonium salt was collected by filtration, washed with Et_2O, and extensively dried in vacuo. (Yields: 80−95%). (**Caution:** Diazonium salts may decompose violently upon heating.)

4-Methoxybenzenediazonium tetrafluoroborate (1a):[35a] ^{1}H NMR (CD_3CN, 250 MHz) δ 4.05 (s, 3H), 7.34 (d, J = 9.5 Hz, 2 H), 8.42 (d, J = 9.5 Hz, 2 H); ^{13}C NMR (CD_3CN, 63 MHz) δ 58.4 (CH_3), 100.9 (C_q), 118.7 (2 × CH), 136.7 (2 × CH), 171.2 (C_q).

4-Fluorobenzenediazonium tetrafluoroborate (1b):[35a] ^{1}H NMR (CD_3CN, 250 MHz) δ 7.67 (dd, J_{HF} = 8.0 Hz, J = 9.1 Hz, 2 H), 8.59 (dd, J_{HF} = 4.3 Hz, J = 9.1 Hz, 2 H); ^{13}C NMR (CD_3CN, 63 MHz) δ 111.1 (C_q), 121.0 (d, J_{CF} = 25.4 Hz, 2 × CH), 137.6 (d, J_{CF} = 12.6 Hz, 2 × CH), 170.8 (d, J_{CF} = 270.5 Hz, C_q); ^{19}F NMR (CD_3CN, 235 MHz) δ −150.2.

2-Methoxycarbonylbenzenediazonium tetrafluoroborate (1c): ^{1}H NMR (CD_3CN, 250 MHz) δ 4.07 (s, 3 H), 8.17 (ddd, J = 1.6 Hz, J = 7.5 Hz, J = 8.3 Hz, 1 H), 8.33−8.46 (m, 2 H), 8.70 (dd, J = 1.1 Hz, J = 8.4 Hz, 1 H); ^{13}C NMR (CD_3CN, 63 MHz) δ 55.1 (CH_3), 115.4 (C_q), 132.2 (C_q), 134.1 (CH), 136.3 (CH), 136.4 (CH), 142.8 (CH), 162.5 (C_q).

4-Methoxycarbonylbenzenediazonium tetrafluoroborate (1d):[35b] ^{1}H NMR (CD_3CN, 250 MHz) δ 3.98 (s, 3 H), 8.41 (d, J = 9.1 Hz, 2 H), 8.60 (d, J = 9.1 Hz, 2 H); ^{13}C NMR (CD_3CN, 63 MHz) δ 54.2 (CH_3), 119.5 (C_q), 132.8 (2 × CH), 133.8 (2 × CH), 142.0 (C_q), 164.8 (C_q).

2-Nitrobenzenediazonium tetrafluoroborate (1e):[35c] ^{1}H NMR (CD_3CN, 250 MHz) δ 8.29−8.36 (m, 1 H), 8.48−8.56 (m, 1 H), 8.71 (dd, J = 1.2 Hz, J = 8.3 Hz, 1 H), 8.84 (dd, J = 1.2 Hz, J = 8.1 Hz, 1 H); ^{13}C NMR (CD_3CN, 63 MHz) δ 129.5 (CH), 137.8 (CH), 137.9 (CH), 144.2 (CH), two C_q signals not visible.

2-Chloromethylacrylic acid ethyl ester (**2g**) was prepared according to procedures described in refs 35d,e: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.32 (t, J = 7.1 Hz, 3 H), 4.26 (q, J = 7.1 Hz, 2 H), 4.29 (dd, J = 0.4 Hz, J = 1.2 Hz, 2 H), 5.96 (m, 1H), 6.38 (m, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 14.1 (CH_3), 42.6 (CH_2), 61.2 (CH_2), 128.4 (CH_2), 137.1 (C_q), 165.0 (C_q); GC-MS (EI) *m*/*z* (%) 150 (1) [^{37}Cl − M$^+$], 148 (4) [^{35}Cl − M$^+$], 122 (29), 120 (86), 113 (62), 105 (34), 103 (100), 95 (18), 85 (25), 75 (35).

Ethyl (*Z*)-3-chloropropenoate (**2m**) was prepared according to the procedure described in ref 35f: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.30 (t, J = 7.1 Hz, 3 H), 4.23 (q, J = 7.1 Hz, 2 H), 6.18 (d, J = 8.2 Hz, 1 H), 6.69 (d, J = 8.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 14.1 (CH_3), 60.6 (CH_2), 121.4 (CH), 132.3 (CH), 163.4 (C_q); GC-MS (EI) *m*/*z* (%) 134 (1) [^{35}Cl − M$^+$], 121 (1), 119 (3), 108 (5), 106 (15), 99 (79), 91 (52), 89 (100).

Ethyl (*Z*)-3-bromopropenoate (**2n**) was prepared according to the procedure described in ref 35f: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.31 (t, J = 7.1 Hz, 3 H), 4.23 (q, J = 7.1 Hz, 2 H), 6.60 (d, J = 8.3 Hz, 1 H), 6.98 (d, J = 8.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 14.1 (CH_3), 60.7 (CH_2), 121.1 (CH), 124.5 (CH), 163.9 (C_q); GC-MS (EI) *m*/*z* (%) 180 (1) [^{81}Br − M$^+$], 178 (1) [^{79}Br − M$^+$], 152 (20), 150 (20), 135 (98), 133 (100), 107 (21), 105 (22), 99 (63).

General Procedure for Allylation and Vinylation. To a mixture of olefin (6 mmol) and iron(II)-sulfate heptahydrate (2.50 g, 9 mmol) in DMSO−H_2O (3 mL, 5:2 v/v) under argon was dropwise added a solution of the diazonium salt (1 mmol) in DMSO−H_2O (1.5 mL, 5:2 v/v) over a period of 10 min. The resulting mixture was stirred for 10 min, diluted with H_2O (50 mL), and extracted with Et_2O (3 × 30 mL). The combined extracts were washed with brine and dried over sodium sulfate. After careful evaporation of the solvents (volatility) the crude products were purified by silica gel column chromatography.

1-Allyl-4-methoxybenzene (3a):[36a] colorless oil; R_f 0.75 (100% Et_2O); ^{1}H NMR ($CDCl_3$, 360 MHz) δ 3.31 (d, ^3J = 6.8 Hz, 2 H), 3.76 (s, 3 H), 5.00−5.02 (m, 1 H), 5.03−5.07 (m, 1 H), 5.93 (ddd, J = 6.8 Hz, J = 10.2 Hz, J = 16.9 Hz, 1 H), 6.82 (d, J = 8.6 Hz, 2 H), 7.08 (d, J = 8.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 39.3 (CH_2), 55.2 (CH_3), 113.8 (2 × CH), 115.3 (CH_2), 129.4 (2 × CH), 132.0 (C_q), 137.8 (CH), 157.9 (C_q); GC-MS (EI) *m*/*z* (%) 148 (100) [M$^+$], 147 (62), 133 (20), 121 (32), 117 (30), 105 (18), 91 (20), 77 (21).

1-Allyl-4-fluorobenzene (3b):[36b] colorless oil; R_f 0.85 (P/EtOAc = 20:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.37 (d, J = 6.7 Hz, 2 H), 5.03−5.08 (m, 1 H), 5.10−5.12 (m, 1 H), 5.96 (tdd, J = 6.8 Hz, J = 13.3 Hz, J = 15.9 Hz, 1 H), 6.99 (dd, J = 8.8 Hz, J_{HF} = 8.8 Hz, 2 H), 7.15 (dd, J_{HF} = 5.5 Hz, J = 8.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 39.3 (CH_2), 114.1 (d, J_{CF} = 21.2 Hz, 2 × CH), 115.9 (CH_2), 129.9 (d, J_{CF} = 7.7 Hz, 2 × CH), 135.6 (d, J_{CF} = 3.1 Hz, C_q), 137.3 (CH), 161.4 (d, J_{CF} = 243.6 Hz, C_q); ^{19}F NMR ($CDCl_3$, 235 MHz) δ −118.0; GC-MS (EI) *m*/*z* (%) 136 (88) [M$^+$], 135 (100), 133 (26), 115 (23), 109 (51), 83 (12).

1-Methoxy-4-(2-methylallyl)benzene (3c):[36c] colorless oil; R_f 0.90 (100% CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.68 (s, 3 H), 3.27 (s, 2 H), 3.80 (s, 3 H), 4.72 (s, 1 H), 4.80 (s, 1 H), 6.86 (d, J = 8.6 Hz, 2 H), 7.11 (d, J = 8.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 22.0 (CH_3), 43.7 (CH_2), 55.2 (CH_3), 111.5 (CH_2), 113.7 (2 × CH), 129.8 (2 × CH), 131.8 (C_q), 145.5 (C_q), 158.0 (C_q); GC-MS (EI) *m*/*z* (%) 162 (95) [M$^+$], 147 (100), 131 (23), 121 (79), 115 (16), 91 (34), 77 (16).

1-((*E*)-But-2-enyl)-4-methoxybenzene (3d):[36c] colorless oil; R_f 0.85 (P/Et_2O = 2:1); ^{1}H NMR ($CDCl_3$, 250 MHz: δ 1.68 (d, J = 6.0 Hz, 3 H), 3.26 (d, J = 6.0 Hz, 2 H), 3.79 (s, 3 H), 5.44−5.64 (m, 2 H), 6.83 (d, J = 8.8 Hz, 2 H), 7.10 (d, J = 8.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 17.8 (CH_3), 38.1 (CH_2), 55.2 (CH_3), 113.7 (2 × CH), 125.9 (CH), 129.3 (2 × CH), 130.4 (CH), 133.1 (C_q), 157.8 (C_q); GC-MS (EI) *m*/*z* (%) 162 (94) [M$^+$], 147 (100), 131 (8), 131 (15), 121 (24), 117 (9), 115 (17), 91 (30), 77 (15).

2-((*E*)-But-2-enyl)benzoic acid methyl ester (3e): colorless oil; R_f 0.90 (P/Et_2O = 1:2); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.66 (dd, J = 1.3 Hz, J = 6.1 Hz, 3 H), 3.67 (d, J = 6.3 Hz, 2 H), 3.88 (s, 3 H), 5.41−5.68 (m, 2 H), 7.21−7.31 (m, 2 H), 7.42 ("t", J = 7.6

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Hz, 1 H), 7.85 (dd, $J = 1.2$ Hz, $J = 7.6$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 17.9 (CH_3), 37.2 (CH_2), 51.9 (CH_3), 125.9 (CH), 126.3 (CH), 129.6 (C_q), 129.8 (CH), 130.4 (CH), 130.7 (CH), 131.9 (CH), 142.5 (C_q), 168.2 (C_q); GC-MS (EI) *m*/*z* (%) 190 (28) [M^+], 161 (75), 159 (26), 158 (100), 157 (25), 148 (14), 133 (26), 131 (35), 130 (25), 129 (62), 128 (29), 115 (51), 91 (31), 77 (11); HRMS (EI) calcd for $C_{12}H_{14}O_2$ [M^+] 190.0988, found 190.0995.

2-((*Z*)-But-2-enyl)benzoic acid methyl ester (3e′): colorless oil; R_f 0.90 (P/Et_2O = 1:2); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.73 (dd, $J = 0.8$ Hz, $J = 5.1$ Hz, 3 H), 3.76 (d, $J = 5.4$ Hz, 2 H), 3.89 (s, 3 H), 5.41−5.68 (m, 2 H), 7.21−7.31 (m, 2 H), 7.42 ("t", $J = 7.6$ Hz, 1 H), 7.85 (dd, $J = 1.2$ Hz, $J = 7.6$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 12.9 (CH_3), 31.6 (CH_2), 51.9 (CH_3), 124.9 (CH), 125.8 (CH), 128.9 (CH), 129.7 (C_q), 130.4 (CH), 130.5 (CH), 131.9 (CH), 142.6 (C_q), 169.2 (C_q).

1-(2-Chloroallyl)-4-methoxybenzene (3f):[36d] colorless oil; R_f 0.75 (P/EtOAc = 20:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.55 (s, 2 H), 3.76 (s, 3 H), 5.09 (dt, $J = 1.3$ Hz, $J = 1.3$ Hz, 1 H), 5.21 (m, 1 H), 6.85 (d, $J = 8.8$ Hz, 2 H), 7.13 (d, $J = 8.8$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 44.5 (CH_2), 55.1 (CH_3), 113.1 (CH_2), 113.8 (2 × CH), 128.8 (C_q), 130.0 (2 × CH), 142.1 (C_q), 158.5 (C_q); GC-MS (EI) *m*/*z* (%) 184 (29) [^{37}Cl − M^+], 182 (95) [^{35}Cl − M^+], 167 (12), 147 (60), 131 (14), 121 (100), 115 (23), 103 (22), 91 (15), 77 (22).

1-(2-Chloroallyl)-4-fluorobenzene (3g): colorless oil; R_f 0.85 (P/EtOAc = 20:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.61 (s, 2 H), 5.15 (dt, $J = 1.3$ Hz, $J = 1.3$ Hz, 1 H), 5.27 (m, 1 H), 7.02 (dd, $J = 8.8$ Hz, $J_{HF} = 8.8$ Hz, 2 H), 7.21 (dd, $J_{HF} = 5.6$ Hz, $J = 8.8$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 44.6 (CH_2), 113.6 (CH_2), 115.3 (d, $J_{CF} = 21.4$ Hz, 2 × CH), 130.5 (d, $J_{CF} = 7.6$ Hz, 2 × CH), 132.5 (d, $J_{CF} = 3.3$ Hz, C_q), 141.4 (C_q), 161.9 (d, $J_{CF} = 245.1$ Hz, C_q); ^{19}F NMR ($CDCl_3$, 235 MHz) δ −116.4; MS (EI) *m*/*z* (%) 172 (6) [^{37}Cl − M^+], 170 (18) [^{35}Cl − M^+], 135 (38), 133 (22), 110 (11), 109 (100), 83 (10); HRMS (EI) calcd for $C_9H_8{}^{35}ClF$ [^{35}Cl − M^+] 170.0299, found 170.0300.

2-(2-Chloroallyl)benzoic acid methyl ester (3h): colorless oil; R_f 0.80 (P/Et_2O = 1:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.88 (s, 3 H), 4.08 (s, 2 H), 4.97 (dt, $J = 1.3$ Hz, $J = 1.3$ Hz, 1 H), 5.23 (m, 1 H), 7.31−7.37 (m, 2 H), 7.45−7.51 (m, 1 H), 7.94 (dd, $J = 1.5$ Hz, $J = 8.0$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 43.1 (CH_2), 52.0 (CH_3), 113.4 (CH_2), 127.0 (CH), 129.8 (C_q), 130.8 (CH), 131.4 (CH), 132.0 (CH), 138.1 (C_q), 141.3 (C_q), 167.5 (C_q); MS (EI) *m*/*z* (%) 175 (100) [M^+ − Cl], 143 (35), 116 (11), 115 (32), 91 (9), 89 (8); HRMS (EI) calcd for $C_{11}H_{11}O_2$ [M^+ − Cl] 175.0759, found 175.0759; MS (APCI) *m*/*z* (%) 211 [^{35}Cl − M^+ + H]; HRMS (APCI) calcd for $C_{11}H_{12}{}^{35}ClO_2$ [^{35}Cl − M^+ + H] 211.0521, found 211.0519.

4-(2-Chloroallyl)benzoic acid methyl ester (3i): colorless oil; R_f 0.70 (P/EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.68 (s, 2 H), 3.90 (s, 3 H), 5.17 (dt, $J = 1.3$ Hz, $J = 1.3$ Hz, 1 H), 5.29 (m, 1 H), 7.31 (d, $J = 8.2$ Hz, 2 H), 8.00 (d, $J = 8.2$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 45.3 (CH_2), 52.0 (CH_3), 114.2 (CH_2), 128.9 (C_q), 129.0 (2 × CH), 129.8 (2 × CH), 140.5 (C_q), 142.0 (C_q), 166.8 (C_q); MS (EI) *m*/*z* (%) 212 (7) [^{37}Cl − M^+], 210 (29) [^{35}Cl − M^+], 181 (29), 179 (89), 175 (100), 151 (34), 147 (14), 131 (22), 116 (40), 115 (85), 91 (15), 89 (15); HRMS (EI) calcd for $C_{11}H_{11}{}^{35}ClO_2$ [^{35}Cl − M^+] 210.0448, found 210.0446.

1-(2-Bromoallyl)-4-methoxybenzene (3j): colorless oil; R_f 0.90 (P/Et_2O = 10:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.68 (s, 2 H), 3.81 (s, 3 H), 5.49 (m, 1 H), 5.55 (dt, $J = 1.5$ Hz, $J = 1.5$ Hz, 1 H), 6.87 (d, $J = 8.8$ Hz, 2 H), 7.15 (d, $J = 8.8$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 46.9 (CH_2), 55.2 (CH_3), 113.9 (2 × CH), 117.6 (CH_2), 129.3 (C_q), 130.0 (2 × CH), 133.4 (C_q), 158.6 (C_q); MS (EI) *m*/*z* (%) 228 (82) [^{81}Br − M^+], 226 (84) [^{79}Br − M^+], 188 (18), 186 (16), 147 (100), 121 (95), 115 (23), 103 (16), 91 (26), 78 (16), 77 (25); HRMS (EI) calcd for $C_{11}H_{11}{}^{79}BrO$ [^{79}Br − M^+] 225.9993, found 225.9991.

2-(2-Bromoallyl)benzoic acid methyl ester (3k): colorless oil; R_f 0.85 (P/EtOAc = 1:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.89 (s, 3 H), 4.18 (s, 2 H), 5.39 (dt, $J = 1.5$ Hz, $J = 1.5$ Hz, 1 H), 5.48 (m, 1 H), 7.31−7.38 (m, 2 H), 7.45−7.52 (m, 1 H), 7.92−7.96 (dd, $J = 1.3$ Hz, $J = 8.3$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 45.4 (CH_2), 52.0 (CH_3), 117.8 (CH_2), 127.1 (CH), 129.9 (C_q), 130.9 (CH), 131.5 (CH), 132.1 (CH), 132.2 (C_q), 138.4 (C_q), 167.5 (C_q); GC-MS (EI) *m*/*z* (%) 235 (3) [^{81}Br − M^+ − OCH_3], 233 (3) [^{79}Br − M^+ − OCH_3], 176 (12), 175 (100) [M^+ − Br], 160 (6), 143 (28), 131 (6), 116 (23), 115 (38); MS (APCI) *m*/*z* (%) 255 [^{79}Br − M^+ + H]; HRMS (APCI) calcd for $C_{11}H_{12}{}^{79}BrO_2$ [^{79}Br − M^+ + H] 255.0015, found 225.0001.

1-(2-Bromoallyl)-2-nitrobenzene (3l): light yellow oil; R_f 0.70 (P/EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 4.12 (s, 2 H), 5.53−5.58 (m, 2 H), 7.42−7.48 (m, 2 H), 7.56−7.63 (m, 1 H), 7.96 (d, $J = 8.7$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 44.1 (CH_2), 119.5 (CH_2), 124.9 (CH), 128.3 (CH), 129.5 (C_q), 131.8 (C_q), 132.3 (CH), 133.1 (CH), 149.1 (C_q); GC-MS (EI) *m*/*z* (%) 226 (9) [^{81}Br − M^+ − OH], 224 (9) [^{79}Br − M^+ − OH], 162 (100) [M^+ − Br], 145 (28), 134 (48), 130 (28), 117 (54), 116 (35), 115 (97), 104 (22), 91 (32), 89 (49), 77 (31); HRMS (EI) calcd for $C_9H_7{}^{81}BrNO$ [^{81}Br − M^+ − OH] 225.9691, found 225.9692.

2-(4-Methoxybenzyl)acrylic acid ethyl ester (3m):[36g] colorless oil; R_f 0.50 (P/EtOAc = 4:1); ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.27 (t, $J = 7.1$ Hz, 3 H), 3.57 (s, 2 H), 3.79 (s, 3 H), 4.18 (q, $J = 7.1$ Hz, 2 H), 5.43 (dt, $J = 1.5$ Hz, $J = 1.5$ Hz, 1 H), 6.20 (m, 1 H), 6.83 (d, $J = 8.7$ Hz, 2 H), 7.11 (d, $J = 8.7$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 91 MHz) δ 14.2 (CH_3), 37.2 (CH_2), 55.2 (CH_3), 60.7 (CH_2), 113.8 (2 × CH), 125.6 (CH_2), 130.0 (2 × CH), 130.8 (C_q), 140.8 (C_q), 158.1 (C_q), 167.0 (C_q); GC-MS (EI) *m*/*z* (%) 221 (11), 220 (83) [M^+], 191 (8), 175 (23), 147 (25), 146 (100), 145 (28), 131 (19), 121 (25), 115 (17), 103 (16), 91 (11).

1-Methoxy-4-propa-1,2-dienylbenzene (3n):[37] ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 3.78 (s, 3 H), 5.12 (d, $J = 6.8$ Hz, 2 H), 6.13 (t, $J = 6.8$ Hz, 1 H), 6.86 (d, $J = 8.8$ Hz, 2 H), 7.23 (d, $J = 8.8$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 55.2 (CH_3), 78.7 (CH_2), 93.3 (CH), 114.1 (2 × CH), 126.0 (C_q), 127.7 (2 × CH), 158.7 (C_q), 209.3 (C_q); GC-MS (EI) *m*/*z* (%) 146 (100) [M^+], 131 (27), 115 (14), 103 (55), 102 (16), 77 (20).

1-((*E*)-2-Chlorovinyl)-4-methoxybenzene (3o):[38a] colorless oil; R_f 0.50 (P/Et_2O = 20:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.80 (s, 3 H), 6.49 (d, $J = 13.8$ Hz, 1 H), 6.77 (d, $J = 13.8$ Hz, 1 H), 6.85 (d, $J = 8.8$ Hz, 2 H), 7.22 (d, $J = 8.8$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 55.2 (CH_3), 114.2 (2 × CH), 116.3 (CH), 127.3 (2 × CH), 127.6 (C_q), 132.6 (CH), 159.5 (C_q); GC-MS (EI) *m*/*z* (%) 170 (34) [^{37}Cl − M^+], 168 (100) [^{35}Cl − M^+] 155 (17), 153 (49), 133 (8), 125 (29), 89 (18).

1-(2,2-Dichlorovinyl)-4-methoxybenzene (3p):[38b] colorless oil; R_f 0.90 (100% CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.83 (s, 3 H), 6.79 (s, 1 H), 6.90 (d, $J = 8.8$ Hz, 2 H), 7.51 (d, $J = 8.8$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 55.2 (CH_3), 113.8 (2 × CH), 118.7 (C_q), 125.9 (C_q), 128.0 (CH), 130.0 (2 × CH), 159.5 (C_q); GC-MS (EI) *m*/*z* (%) 206 (11) [$^{37}Cl_2$ − M^+], 204 (63) [^{37}Cl^{35}Cl − M^+], 202 (100) [$^{35}Cl_2$ − M^+], 191 (6), 189 (39), 187 (60), 161 (20), 159 (32), 132 (9), 123 (14), 89 (15); HRMS (EI) calcd for $C_9H_8{}^{35}Cl_2O$ [$^{35}Cl_2$ − M^+] 201.9952, found 201.9948.

1-(2,2-Dichlorovinyl)-4-fluorobenzene (3q): colorless oil; R_f 0.90 (100% CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.82 (s, 1 H), 7.06 (dd, $J = 8.8$ Hz, $J_{HF} = 8.8$ Hz, 2 H), 7.52 (dd, $J_{HF} = 5.4$ Hz, $J = 8.8$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 91 MHz) δ 115.5 (d, J_{CF} = 21.7 Hz, 2 × CH), 120.9 (C_q), 127.4 (CH), 129.5 (d, $J_{CF} = 3.4$ Hz, C_q), 130.5 (d, $J_{CF} = 8.2$ Hz, 2 × CH), 162.4 (d, $J_{CF} = 249.6$ Hz, C_q); ^{19}F NMR ($CDCl_3$, 235 MHz) δ −112.4; GC-MS (EI) *m*/*z* (%) 194 (8) [$^{37}Cl_2$ − M^+], 192 (62) [^{37}Cl^{35}Cl − M^+], 190 [$^{35}Cl_2$ − M^+], 157 (8), 155 (31), 135 (6), 120 (58); HRMS (EI) calcd for $C_8H_5{}^{35}Cl_2F$ [$^{35}Cl_2$ − M^+] 189.9747, found 189.9744.

2-(2,2-Dichlorovinyl)benzoic acid methyl ester (3r): colorless oil; R_f 0.90 (100% CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.90 (s, 3 H), 7.36−7.42 (m, 1 H), 7.43 (s, 1 H), 7.50−7.59 (m, 2 H), 8.01 (d, $J = 8.3$ Hz, 1 H); ^{13}C NMR ($CDCl_3$,91 MHz) δ 52.2 (CH_3), 121.7 (C_q), 128.2 (CH), 128.6 (C_q), 128.7 (CH), 130.4 (CH), 130.6

(CH), 132.1 (CH), 135.0 (C_q), 166.7 (C_q); GC-MS (EI) *m*/*z* (%) 197 (35) [$^{37}Cl - M^+ - Cl$], 195 (100) [$^{35}Cl - M^+ - Cl$], 152 (15), 153 (49), 136 (12); HRMS (EI) calcd for $C_{10}H_8{}^{35}ClO_2$ [$^{35}Cl - M^+ - Cl$] 195.0207, found 195.020.

Ethyl (*E*)-3-(4-methoxyphenyl)-2-propenoate (3s):[38c] ^1H NMR ($CDCl_3$, 250 MHz) δ 1.32 (t, $J = 7.0$ Hz, 3 H), 4.25 (q, $J = 7.0$ Hz, 2 H), 6.30 (d, $J = 16.0$ Hz, 1 H), 6.89 (d, $J = 8.9$ Hz, 2 H), 7.47 (d, $J = 8.9$ Hz, 2 H), 7.64 (d, $J = 16.0$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 14.3 (CH_3), 55.3 (CH_3), 60.6 (CH_2), 114.3 (2 × CH), 115.8 (CH), 127.3 (CH), 129.6 (2 × CH), 144.4 (C_q), 161.5 (C_q), 167.4 (C_q); GC-MS (EI) *m*/*z* (%) 206 (73) [M^+], 178 (11), 161 (100), 134 (45), 133 (27).

1-Bromo-4-methoxybenzene (4b):[39a] colorless oil; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.78 (s, 3 H), 6.79 (d, $J = 9.0$ Hz, 2 H), 7.38 (d, $J = 9.0$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 55.4 (CH_3), 112.8 (C_q), 115.7 (2 × CH), 132.2 (2 × CH), 158.6 (C_q); GC-MS (EI) *m*/*z* (%) 188 (96) [$^{81}Br - M^+$], 186 (100) [$^{79}Br - M^+$] 173 (45), 171 (46), 145 (37), 143 (38).

1-Chloro-3-(2-nitrophenyl)propan-2-one (4d):[39b] orange solid; mp 85−88 °C; R_f 0.75 (CH_2Cl_2/MeOH = 50:1); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.28 (s, 2 × 2 H), 7.33 (d, $J = 7.5$ Hz, 1 H), 7.50 ("t", $J = 7.5$ Hz, 1 H), 7.63 ("t", $J = 7.5$ Hz, 1 H), 8.16 (d, $J = 7.5$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, 91 MHz) δ 45.1 (CH_2), 48.2 (CH_2), 125.5 (CH), 128.8 (CH), 129.5 (C_q), 133.8 (CH), 133.9 (CH), 148.2 (C_q), 198.5 (C_q); GC-MS (EI) *m*/*z* (%) 167 (3) [$^{35}Cl - M^+ - NO_2$], 164 (98) [$M^+ - CH_2Cl$], 137 (19), 136 (100) [$M^+ - COCH_2Cl$], 120 (73), 92 (42), 89 (42), 78 (79), 77 (47); MS (ESI) *m*/*z* (%) 212 [$M^+ - H$]; HRMS (ESI) calcd for $C_9H_7O_3N_1{}^{35}Cl$ [$M^+ - H$] 212.0115, found 212.0131.

(*E*)-4,4′-Dimethoxystilbene (4e):[39c] colorless solid; R_f 0.55 (P/EtOAc = 10:1); ^1H NMR ($CDCl_3$, 360 MHz) δ 3.83 (s, 6 H), 6.89 (d, $J = 8.6$ Hz, 4 H), 6.93 (s, 2 H), 7.43 (d, $J = 8.6$ Hz, 4 H); ^{13}C NMR ($CDCl_3$, 91 MHz) δ 55.3 (2 × CH_3), 114.1 (4 × CH), 126.2 (2 × CH), 127.4 (4 × CH), 130.5 (2 × C_q), 159.0 (2 × C_q); GC-MS (EI) *m*/*z* (%) 240 (100) [M^+], 225 (53), 165 (19), 153 (14).

4-(2-Nitrobenzyl)thiazol-2-ylamine (5): dark brown oil; R_f 0.40 (CH_2Cl_2/MeOH = 20:1); ^1H NMR ($CDCl_3$, 360 MHz) δ 4.21 (s, 2 H), 6.09 (s, 1 H), 7.34−7.39 (m, 2 H), 7.49−7.54 (m, 1 H), 7.92 (dd, $J = 1.1$ Hz, $J = 8.6$ Hz, 1 H); ^{13}C NMR ($CDCl_3$, 91 MHz) δ 34.7 (CH_2), 104.8 (CH), 124.8 (CH), 127.6 (CH), 132.3 (CH), 133.0 (CH), 133.9 (C_q), 149.0 (C_q), 167.8 (C_q), one C_q signal missing due to overlap; MS (ESI) *m*/*z* (%) 236 [$M^+ + H$]; HRMS (ESI) calcd for $C_{10}H_{10}O_2N_3{}^{32}S$ [$M^+ + H$] 236.0488, found 236.0485.

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Supporting Information Available: ^1H NMR and ^{13}C NMR spectra for all new compounds and ^{13}C NMR for **3a**−**m**, **3o**−**r**, **4d**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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