

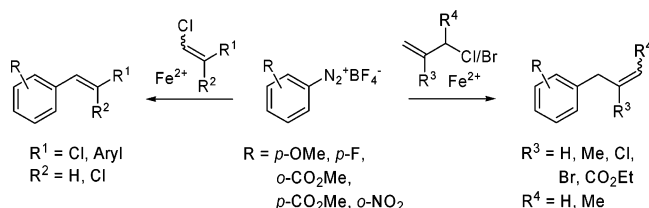
Allylation and Vinylation of Aryl Radicals Generated from Diazonium Salts

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Received August 8, 2007



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 groups⁵ such as sulfides,⁶ sulfoxides,⁷

sulfones,⁸ cobaloximes,⁹ silanes,¹⁰ halides,¹¹ and phosphine oxides¹² 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 diazotization of acceptor-substituted aromatic amines in the presence of allyl bromide. Literature precedence for the corre-

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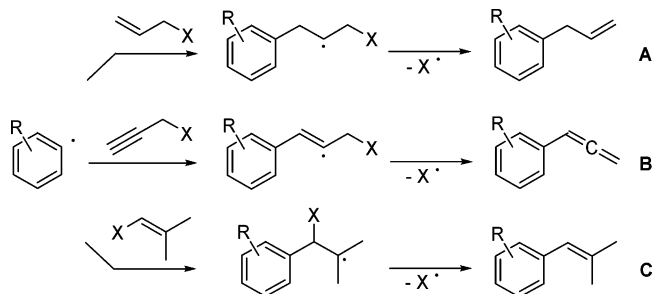
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SCHEME 1. Allylation (A), Allenylation (B), and Vinylation (C) of Aryl Radicals via an Addition–Fragmentation Mechanism



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

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TABLE 1. Allylation of Arenes

Reaction scheme: $\text{R}^1\text{-C}_6\text{H}_4\text{-N}_2^+\text{BF}_4^- + \text{R}^2\text{-C(R}^3\text{)=CH}_2 \xrightarrow{\text{Fe}^{2+}, \text{Cl}^-/\text{Br}^-} \text{R}^1\text{-C}_6\text{H}_4\text{-CH(R}^2\text{)-CH(R}^3\text{)}_2 + \text{by-product}$

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, ¹H NMR, and ¹³C 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

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, ¹H NMR, and ¹³C NMR analysis of the crude product mixture.

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

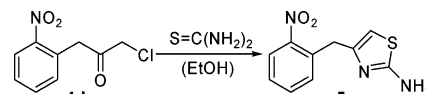
Unlike with propargyl chloride (**2h**), single and double addition to 1,2-dichloroethenes **2j** and **2k** led to simple mixtures containing chlorostyrene **3o** and stilbene **4e** as main products. Only the (*E*)-configured styrene **3o** was isolated from both attempts, and the final product distribution 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 benzoxazine.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-

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TABLE 3. Vinylation of Arenes

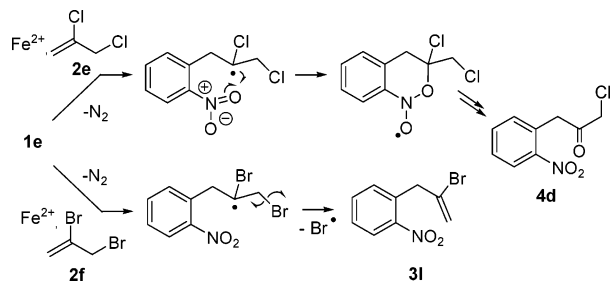
entry	salt 1	olefin 2	product 3 ^a	by-product
18	1a	 2j	 3o (32%)	 4e (28%)
19	1a	 2k	 3o (53%) (63%) ^c (72%) ^d	 4e (11%) ^b (5%) ^{b,c} (<2%) ^{b,d}
20	1a	 2l	 3p (61%)	 4a (<2%) ^b
21	1b	 2l	 3q (46%)	
22	1c	 2l	 3r (45%)	 4c (26%) ^b
23	1a	 3o	 4e (61%) ^c	
24	1a	 2m	 3s (19%) ^b	complex mixture
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, ¹H NMR, and ¹³C 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–H₂O (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–H₂O (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 HBF₄ (50%, 14 mL) and water (15 mL) was dropwise added a precooled solution of NaNO₂ (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 Et₂O, and extensively dried in vacuo. (Yields: 80–95%). (**Caution:** Diazonium salts may decompose violently upon heating.)

4-Methoxybenzenediazonium tetrafluoroborate (1a):^{35a} ¹H NMR (CD₃CN, 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); ¹³C NMR (CD₃CN, 63 MHz) δ 58.4 (CH₃), 100.9 (C_q), 118.7 (2 × CH), 136.7 (2 × CH), 171.2 (C_q).

4-Fluorobenzenediazonium tetrafluoroborate (1b):^{35a} ¹H NMR (CD₃CN, 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); ¹³C NMR (CD₃CN, 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); ¹⁹F NMR (CD₃CN, 235 MHz) δ –150.2.

2-Methoxycarbonylbenzenediazonium tetrafluoroborate (1c): ¹H NMR (CD₃CN, 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); ¹³C NMR (CD₃CN, 63 MHz) δ 55.1 (CH₃), 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} ¹H NMR (CD₃CN, 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); ¹³C NMR (CD₃CN, 63 MHz) δ 54.2 (CH₃), 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} ¹H NMR (CD₃CN, 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); ¹³C NMR (CD₃CN, 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: ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 63 MHz) δ 14.1 (CH₃), 42.6 (CH₂), 61.2 (CH₂), 128.4 (CH₂), 137.1 (C_q), 165.0 (C_q); GC-MS (EI) *m/z* (%) 150 (1) [³⁷Cl – M⁺], 148 (4) [³⁵Cl – 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: ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 63 MHz) δ 14.1 (CH₃), 60.6 (CH₂), 121.4 (CH), 132.3 (CH), 163.4 (C_q); GC-MS (EI) *m/z* (%) 134 (1) [³⁵Cl – 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: ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 63 MHz) δ 14.1 (CH₃), 60.7 (CH₂), 121.1 (CH), 124.5 (CH), 163.9 (C_q); GC-MS (EI) *m/z* (%) 180 (1) [⁸¹Br – M⁺], 178 (1) [⁷⁹Br – 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–H₂O (3 mL, 5:2 v/v) under argon was dropwise added a solution of the diazonium salt (1 mmol) in DMSO–H₂O (1.5 mL, 5:2 v/v) over a period of 10 min. The resulting mixture was stirred for 10 min, diluted with H₂O (50 mL), and extracted with Et₂O (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% Et₂O); ¹H NMR (CDCl₃, 360 MHz) δ 3.31 (d, ³*J* = 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); ¹³C NMR (CDCl₃, 90 MHz) δ 39.3 (CH₂), 55.2 (CH₃), 113.8 (2 × CH), 115.3 (CH₂), 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); ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 63 MHz) δ 39.3 (CH₂), 114.1 (d, *J*_{CF} = 21.2 Hz, 2 × CH), 115.9 (CH₂), 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); ¹⁹F NMR (CDCl₃, 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% CH₂Cl₂); ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 63 MHz) δ 22.0 (CH₃), 43.7 (CH₂), 55.2 (CH₃), 111.5 (CH₂), 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/Et₂O = 2:1); ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 63 MHz) δ 17.8 (CH₃), 38.1 (CH₂), 55.2 (CH₃), 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/Et₂O = 1:2); ¹H NMR (CDCl₃, 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

(38) (a) Barluenga, J.; Moriel, P.; Aznar, F.; Valdés, C. *Adv. Synth. Catal.* **2006**, 348, 347–353. (b) Braverman, S.; Zafrani, Y. *Tetrahedron* **1998**, 54, 1901–1912. (c) Mun, S.; Lee, J.-E.; Yun, J. *Org. Lett.* **2006**, 8, 4887–4889.

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 $\text{C}_{12}\text{H}_{14}\text{O}_2$ [M^+] 190.0988, found 190.0995.

2-((Z)-But-2-enyl)benzoic acid methyl ester (3e): colorless oil; R_f 0.90 (P/Et₂O = 1:2); ^1H 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); ^1H 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 $\times$ CH), 128.8 (C_q), 130.0 (2 $\times$ CH), 142.1 (C_q), 158.5 (C_q); GC-MS (EI) m/z (%) 184 (29) [$^{37}\text{Cl} - \text{M}^+$], 182 (95) [$^{35}\text{Cl} - \text{M}^+$], 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); ^1H 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, $J_{\text{HF}} = 8.8$ Hz, 2 H), 7.21 (dd, $J_{\text{HF}} = 5.6$ 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, $J_{\text{CF}} = 21.4$ Hz, 2 $\times$ CH), 130.5 (d, $J_{\text{CF}} = 7.6$ Hz, 2 $\times$ CH), 132.5 (d, $J_{\text{CF}} = 3.3$ Hz, C_q), 141.4 (C_q), 161.9 (d, $J_{\text{CF}} = 245.1$ Hz, C_q); ^{19}F NMR (CDCl_3 , 235 MHz) δ -116.4; MS (EI) m/z (%) 172 (6) [$^{37}\text{Cl} - \text{M}^+$], 170 (18) [$^{35}\text{Cl} - \text{M}^+$], 135 (38), 133 (22), 110 (11), 109 (100), 83 (10); HRMS (EI) calcd for $\text{C}_9\text{H}_8^{35}\text{ClF}$ [$^{35}\text{Cl} - \text{M}^+$] 170.0299, found 170.0300.

2-(2-Chloroallyl)benzoic acid methyl ester (3h): colorless oil; R_f 0.80 (P/Et₂O = 1:1); ^1H 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) [$\text{M}^+ - \text{Cl}$], 143 (35), 116 (11), 115 (32), 91 (9), 89 (8); HRMS (EI) calcd for $\text{C}_{11}\text{H}_{11}\text{O}_2$ [$\text{M}^+ - \text{Cl}$] 175.0759, found 175.0759; MS (APCI) m/z (%) 211 [$^{35}\text{Cl} - \text{M}^+ + \text{H}$]; HRMS (APCI) calcd for $\text{C}_{11}\text{H}_{12}^{35}\text{ClO}_2$ [$^{35}\text{Cl} - \text{M}^+ + \text{H}$] 211.0521, found 211.0519.

4-(2-Chloroallyl)benzoic acid methyl ester (3i): colorless oil; R_f 0.70 (P/EtOAc = 4:1); ^1H 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 $\times$ CH), 129.8 (2 $\times$ CH), 140.5 (C_q), 142.0 (C_q), 166.8 (C_q); MS (EI) m/z (%) 212 (7) [$^{37}\text{Cl} - \text{M}^+$], 210 (29) [$^{35}\text{Cl} - \text{M}^+$], 181 (29), 179 (89), 175 (100), 151 (34), 147 (14), 131 (22), 116 (40), 115 (85), 91 (15), 89 (15); HRMS (EI) calcd for $\text{C}_{11}\text{H}_{11}^{35}\text{ClO}_2$ [$^{35}\text{Cl} - \text{M}^+$] 210.0448, found 210.0446.

1-(2-Bromoallyl)-4-methoxybenzene (3j): colorless oil; R_f 0.90 (P/Et₂O = 10:1); ^1H 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 $\times$ CH), 117.6 (CH_2), 129.3 (C_q), 130.0 (2 $\times$ CH), 133.4 (C_q), 158.6 (C_q); MS (EI) m/z (%) 228 (82) [$^{81}\text{Br} - \text{M}^+$], 226 (84) [$^{79}\text{Br} - \text{M}^+$], 188 (18), 186 (16), 147 (100), 121 (95), 115 (23), 103 (16), 91 (26), 78 (16), 77 (25); HRMS (EI) calcd for $\text{C}_{11}\text{H}_{11}^{79}\text{BrO}$ [$^{79}\text{Br} - \text{M}^+$] 225.9993, found 225.9991.

2-(2-Bromoallyl)benzoic acid methyl ester (3k): colorless oil; R_f 0.85 (P/EtOAc = 1:1); ^1H 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) [$^{81}\text{Br} - \text{M}^+ - \text{OCH}_3$], 233 (3) [$^{79}\text{Br} - \text{M}^+ - \text{OCH}_3$], 176 (12), 175 (100) [$\text{M}^+ - \text{Br}$], 160 (6), 143 (28), 131 (6), 116 (23), 115 (38); MS (APCI) m/z (%) 255 [$^{79}\text{Br} - \text{M}^+ + \text{H}$]; HRMS (APCI) calcd for $\text{C}_{11}\text{H}_{12}^{79}\text{BrO}_2$ [$^{79}\text{Br} - \text{M}^+ + \text{H}$] 255.0015, found 225.0001.

1-(2-Bromoallyl)-2-nitrobenzene (3l): light yellow oil; R_f 0.70 (P/EtOAc = 4:1); ^1H 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) [$^{81}\text{Br} - \text{M}^+ - \text{OH}$], 224 (9) [$^{79}\text{Br} - \text{M}^+ - \text{OH}$], 162 (100) [$\text{M}^+ - \text{Br}$], 145 (28), 134 (48), 130 (28), 117 (54), 116 (35), 115 (97), 104 (22), 91 (32), 89 (49), 77 (31); HRMS (EI) calcd for $\text{C}_9\text{H}_7^{81}\text{BrNO}$ [$^{81}\text{Br} - \text{M}^+ - \text{OH}$] 225.9691, found 225.9692.

2-(4-Methoxybenzyl)acrylic acid ethyl ester (3m):^{36g} colorless oil; R_f 0.50 (P/EtOAc = 4:1); ^1H 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 $\times$ CH), 125.6 (CH_2), 130.0 (2 $\times$ 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 ^1H 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 $\times$ CH), 126.0 (C_q), 127.7 (2 $\times$ 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/Et₂O = 20:1); ^1H 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 $\times$ CH), 116.3 (CH), 127.3 (2 $\times$ CH), 127.6 (C_q), 132.6 (CH), 159.5 (C_q); GC-MS (EI) m/z (%) 170 (34) [$^{37}\text{Cl} - \text{M}^+$], 168 (100) [$^{35}\text{Cl} - \text{M}^+$], 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); ^1H 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 $\times$ CH), 118.7 (C_q), 125.9 (C_q), 128.0 (CH), 130.0 (2 $\times$ CH), 159.5 (C_q); GC-MS (EI) m/z (%) 206 (11) [$^{37}\text{Cl}_2 - \text{M}^+$], 204 (63) [$^{37}\text{Cl}^{35}\text{Cl} - \text{M}^+$], 202 (100) [$^{35}\text{Cl}_2 - \text{M}^+$], 191 (6), 189 (39), 187 (60), 161 (20), 159 (32), 132 (9), 123 (14), 89 (15); HRMS (EI) calcd for $\text{C}_9\text{H}_8^{35}\text{Cl}_2\text{O}$ [$^{35}\text{Cl}_2 - \text{M}^+$] 201.9952, found 201.9948.

1-(2,2-Dichlorovinyl)-4-fluorobenzene (3q): colorless oil; R_f 0.90 (100% CH_2Cl_2); ^1H NMR (CDCl_3 , 250 MHz) δ 6.82 (s, 1 H), 7.06 (dd, $J = 8.8$ Hz, $J_{\text{HF}} = 8.8$ Hz, 2 H), 7.52 (dd, $J_{\text{HF}} = 5.4$ Hz, $J = 8.8$ Hz, 2 H); ^{13}C NMR (CDCl_3 , 91 MHz) δ 115.5 (d, $J_{\text{CF}} = 21.7$ Hz, 2 $\times$ CH), 120.9 (C_q), 127.4 (CH), 129.5 (d, $J_{\text{CF}} = 3.4$ Hz, C_q), 130.5 (d, $J_{\text{CF}} = 8.2$ Hz, 2 $\times$ CH), 162.4 (d, $J_{\text{CF}} = 249.6$ Hz, C_q); ^{19}F NMR (CDCl_3 , 235 MHz) δ -112.4; GC-MS (EI) m/z (%) 194 (8) [$^{37}\text{Cl}_2 - \text{M}^+$], 192 (62) [$^{37}\text{Cl}^{35}\text{Cl} - \text{M}^+$], 190 [$^{35}\text{Cl}_2 - \text{M}^+$], 157 (8), 155 (31), 135 (6), 120 (58); HRMS (EI) calcd for $\text{C}_8\text{H}_5^{35}\text{Cl}_2\text{F}$ [$^{35}\text{Cl}_2 - \text{M}^+$] 189.9747, found 189.9744.

2-(2,2-Dichlorovinyl)benzoic acid methyl ester (3r): colorless oil; R_f 0.90 (100% CH_2Cl_2); ^1H 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) [³⁷Cl – M⁺ – Cl], 195 (100) [³⁵Cl – M⁺ – Cl], 152 (15), 153 (49), 136 (12); HRMS (EI) calcd for C₁₀H₈³⁵ClO₂ [³⁵Cl – M⁺ – Cl] 195.0207, found 195.020.

Ethyl (E)-3-(4-methoxyphenyl)-2-propenoate (3s):^{38c} ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 63 MHz) δ 14.3 (CH₃), 55.3 (CH₃), 60.6 (CH₂), 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 (CDCl₃, 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); ¹³C NMR (CDCl₃, 63 MHz) δ 55.4 (CH₃), 112.8 (C_q), 115.7 (2 × CH), 132.2 (2 × CH), 158.6 (C_q); GC-MS (EI) *m/z* (%) 188 (96) [⁸¹Br – M⁺], 186 (100) [⁷⁹Br – 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 (CH₂Cl₂/MeOH = 50:1); ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 91 MHz) δ 45.1 (CH₂), 48.2 (CH₂), 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) [³⁵Cl – M⁺ – NO₂],

164 (98) [M⁺ – CH₂Cl], 137 (19), 136 (100) [M⁺ – COCH₂Cl], 120 (73), 92 (42), 89 (42), 78 (79), 77 (47); MS (ESI) *m/z* (%) 212 [M⁺ – H]; HRMS (ESI) calcd for C₉H₇O₃N₁³⁵Cl [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 (CDCl₃, 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); ¹³C NMR (CDCl₃, 91 MHz) δ 55.3 (2 × CH₃), 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 (CH₂Cl₂/MeOH = 20:1); ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 91 MHz) δ 34.7 (CH₂), 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 C₁₀H₁₀O₂N₃³²S [M⁺ + H] 236.0488, found 236.0485.

Acknowledgment. This project was financed by the Fonds der Chemischen Industrie (Liebig fellowship) and the Deutsche Forschungsgemeinschaft. We are grateful to the Präsidialfonds (M.K.) and the Ausbildungszentrum (D.U.) of the Technische Universität München. The generous help and support of Prof. Dr. Thorsten Bach and his group is gratefully acknowledged.

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

JO701717K

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