

Generation of Diarylcarbenium Ion Pools via Electrochemical C–H Bond Dissociation

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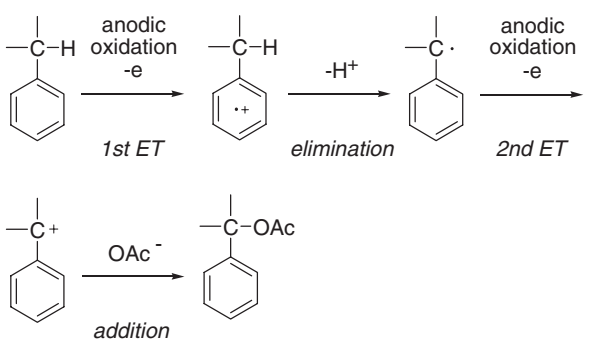
The "cation pools" of diarylcarbenium ions have been generated by the low-temperature electrochemical oxidation of diphenylmethane derivatives. In addition to diphenylmethanes having various substituents, 9,10-dihydroanthracene, dibenzosuberane, and xanthenes, which are annulated derivatives of diphenylmethane were also found to serve as a precursor of cation pools. The generation of the diarylcarbenium ion was confirmed by low-temperature NMR analysis and cold-spray mass analysis. Reactivity was also investigated by reactions with various carbon nucleophiles such as allyltrimethylsilane, 1,3,5-trimethylbenzene, and anisole.

Electron transfer (ET) activation[1] such as electrochemical oxidation[2,3] has emerged as a valuable method for selective transformation in organic synthesis. In pioneering work concerning anodic oxidation of aromatic compounds, Eberson and Nyberg reported side-chain anodic acetoxylation of alkylaromatic compounds.[4] Several groups including Eberson's proposed a mechanism involving two electron transfer processes (Scheme 1).[5] The one electron oxidation of alkylaromatic compounds (1st ET) results in the formation of the corresponding radical cation, which is highly reactive and undergoes fast subsequent reactions. The benzylic C–H bond cleavage (elimination) is typically observed for alkyl-substituted aromatic compounds having at least one hydrogen atom in the benzylic position. The thus-generated radicals are more easily oxidized than the corresponding neutral compounds, making possible the second electron transfer at the electrode (2nd ET). The cationic intermediates thus produced are finally converted to neutral products by nucleophilic attack of an acetate ion (addition). This reaction mechanism has been well accepted as an anodic behavior of alkylaromatics.

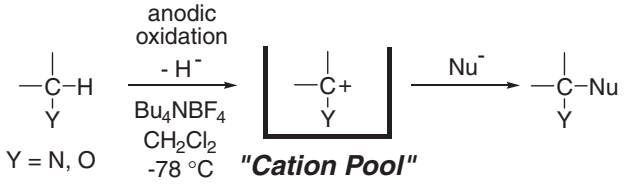
As depicted in Scheme 1, the benzylic C–H bond cleavage of radical cation is an essential step in the side-chain oxidation of alkylaromatics. Significant weakening of the benzylic C–H bond caused by the overlap of its σ orbital with the SOMO of the aromatic ring seems to be responsible for the success of this process. Indeed, the deprotonation rate of an aromatic radical cation is affected by the structural feature of substrates, especially the relative orientation of the scissile C–H bond and the aromatic π-system.



Scheme 1.

We have developed a cation pool method that involves electrochemical oxidative generation and accumulation of carbocations in the absence of nucleophiles at low temperature.[6] The reactions involve the oxidative cleavage of C–H, although the dissociation of C–Si and C–C bonds are also effective (Scheme 2). It is important to note that the accumulation of cationic species was confirmed by low-temperature NMR spectroscopy.

Thus, we envisioned that diarylcarbenium ions would be generated by the anodic oxidation of diarylmethanes derivatives via benzylic C–H bond dissociation. Some diarylcarbenium ions have received significant research interest from mechanistic[7] and synthetic view points,[8] although, to the best of our knowledge, the generation of diarylcarbenium ions by electrochemical methods had never been examined.[9] Recently, we reported the generation of diarylcarbenium ion pools via oxidative C–H bond cleavage of diarylmethanes.[6p] During the course of our study, we found that the efficiency of the cation generation process depends on the structures of diarylmethanes. In this paper we report the full details of the electrochemical generation of diarylcarbenium ion pools.



Scheme 2.

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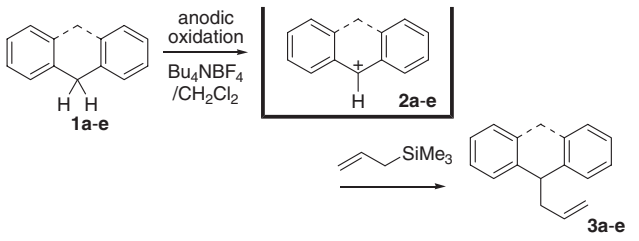
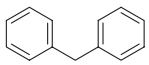
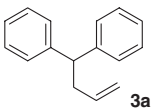
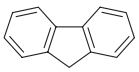
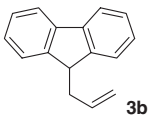
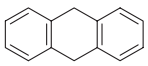
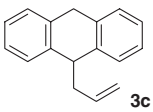
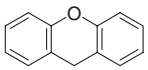
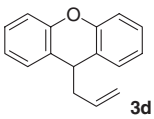
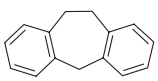
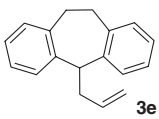
Table 1.

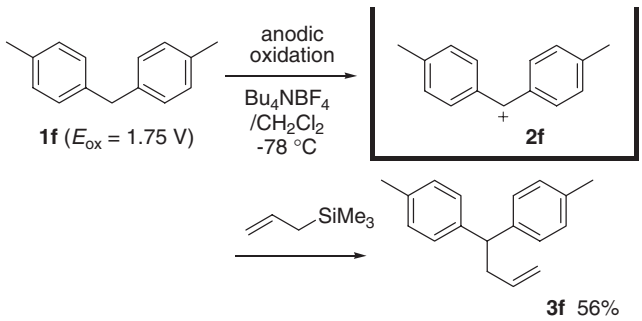


Entry	Substrate/E_{ox}	Temperature/°C	Product/yield
1	 **1a** E_{ox} = 1.91 V	−78	 **3a** 0%
2	 **1b** E_{ox} = 1.52 V	−78	 **3b** 0%
3	 **1c** E_{ox} = 1.44 V	−78	 **3c** 80%
4	 **1d** E_{ox} = 1.36 V	−48	 **3d** 70% (38%)[a]
5	 **1e** E_{ox} = 1.91 V	−48	 **3e** 71% (17%)[a]

a) Reactions were performed at −78 °C.

Results and Discussion

We initiated our study by measuring the oxidation potential of diphenylmethane derivatives. As shown in Table 1, oxidation potentials of diphenylmethane derivatives were lower than 2 V. These values indicated that all these molecules can be oxidized under conventional preparative electrochemical conditions. The low-temperature anodic oxidation of diphenylmethane derivatives was performed under the "cation pool" condition and thus-generated cations were treated with allyltrimethylsilane as a nucleophile (Table 1). Diphenylmethane (**1a**) did not give the corresponding allylated product **3a** and a significant amount (54%) of diphenylmethane (**1a**) was recovered unchanged (Entry 1). Although the conversion of diphenylmethane (**1a**) was slightly increased (73% conversion) at higher reaction temperature (−48 °C), the allylated product **3a** was not observed. The anodic oxidation of fluorene (**1b**) seems to be interesting because fluorenyl cation is antiaromatic. Though **1b** was consumed completely during the electrolysis, the allylated product **3b** was not obtained after treatment with allyltrimethylsilane (Entry 2). 9,10-Dihydroanthracene (**1c**) gave the allylated product **3c** in 80% yield at −78 °C (Entry 3). Xanthene (**1d**) and dibenzosuberane (=10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene) (**1e**) gave allylated products **3d** and **3e** in reasonable yields at higher temperature (−48 °C) (Entries 4 and 5). In both cases, yields of allylated products were moderate at −78 °C as shown in parentheses.



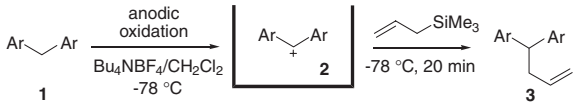
Scheme 3.

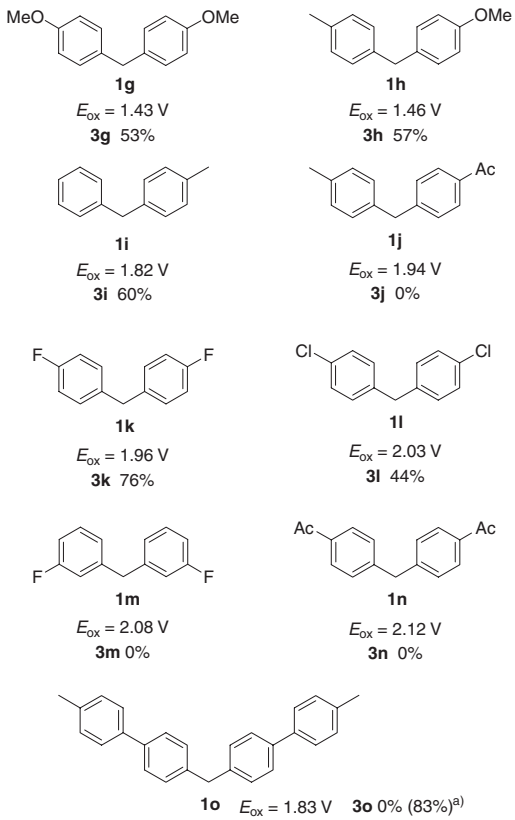
It is still uncertain why simple diphenylmethane (**1a**) did not give the corresponding allylated product at all. The introduction of electron-donating groups on both phenyl groups was examined because it should cause a decrease in the oxidation potential. Thus, we examined bis(*p*-methylphenyl)methane (**1f**) as a precursor of the "diarylcarbenium ion pool" as depicted in Scheme 3. In this case the allylated product **3f** was obtained in 56% yield.

The introduction of other substituents at para positions of diarylmethanes was found to be effective for accumulation of diarylcarbenium ions and the corresponding allylated diarylmethanes **3** were obtained in moderate to high yields (Table 2). It was surprising that not only electron-donating substituents (**1g** and **1h**), but also electron-withdrawing substituents such as halogen atoms (**1k** and **1l**) were effective. It is interesting that the introduction of a methyl group at the para position of one of the two benzene rings is effective for generation of diarylcarbenium ion (**1i**), although meta substitution is not effective (**1m**). On the other hand, the introduction of an acetyl group at least one of two benzene rings retards generation of diarylcarbenium ions (**1j** and **1n**). Successful reaction of diarylmethane **1o** at higher temperatures indicated that the cleavage reaction depends upon the bond dissociation energy of the benzylic C–H bond in the radical cation and that the cleavage can be thermally promoted. It seems to be reasonable to consider that the deprotonation of the initially formed radical cation requires higher temperature because of the charge delocalization through the extended π-system. Though the detailed mechanism has not been clarified yet, the substituent effect can be explained as follows. The introduction of an electron-donating group makes the electron transfer easier, but decreases the rate of deprotonation. On the other hand, the introduction of an electron-withdrawing group facilitates the C–H bond cleavage, although the initial electron transfer is less favorable.

The accumulation of diarylcarbenium ion was confirmed by low-temperature NMR spectroscopy (Figure 1). For example, a solution of a pool of **2k**, which was generated from **1k** exhibited a signal at 192.6 ppm due the carbenium carbon C_a. The HMQC spectrum shows a cross peak between this carbenium carbon C_a and the remaining benzylic hydrogen H_a (9.90 ppm). The chemical shift of C_a is very close to that (193.3 ppm) of **2k** generated in a super acid media (SO_2ClF).[10]

Table 2.





a) The reaction was performed at −10 °C.

We also observed the peaks assigned to the ortho and meta carbons (C_c and C_d), which split into two separate peaks, indicating a high rotation barrier for each *p*-fluorophenyl group because of the effective overlap of the π-system with the carbenium ion center as Olah and Watkins reported.[11] CSI-MS analysis[12] (spray temperature: −20 °C) also supported the formation of **2k** ($m/z = 203$).

In order to demonstrate the synthetic utility of diarylcarbenium ion pools, reactions with various nucleophiles have been examined. As shown in Table 3, the diarylcarbenium ion **2k** reacted with a ketene silyl acetal (Entry 1). The reaction with various organometallic reagents such as Grignard reagents and alkyllithiums were unsuccessful, but the reaction with diethylzinc gave the adduct **5** in moderate yield (Entry 2). On the other hand, Friedel–Crafts type reactions gave the corresponding products in moderate to high yields (Entries 3–7). It is noteworthy that 1,3-dimethoxybenzene gave the mono-substituted compound **9** as a single regioisomer, probably because both methoxy groups work as strong ortho–para directors (Entry 6). The reaction with anisole also proceeded regioselectively to give the para-substituted product **10** in moderate yield (Entry 7). Although thiophene was found to be

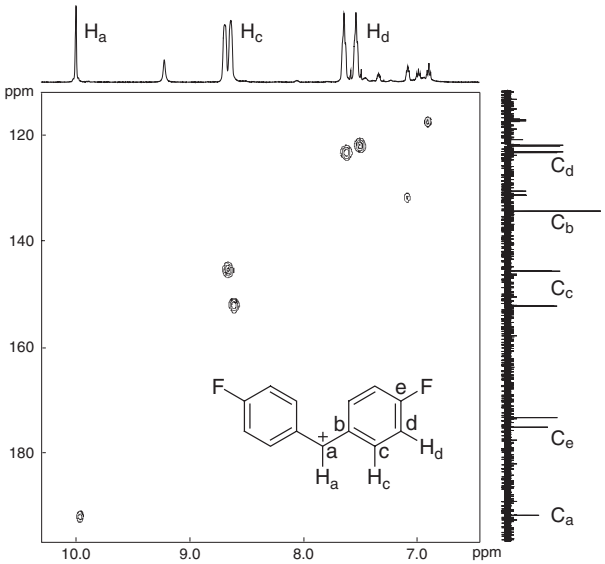


Figure 1. HMQC spectrum of diarylcarbenium ion **2k**. NMR measurement was performed at −78 °C in CD_2Cl_2 with CH_2Cl_2 as an internal standard (^{1}H NMR: 600 MHz, ^{13}C NMR: 150 MHz).

a good nucleophile for diarylcarbenium ions,[6p] it is difficult to obtain mono-substituted product **11** selectively (Entry 8). We observed a significant amount of 2,5-di-substituted product (40%) even in the reaction with a large excess amount of thiophene, because mono-substituted thiophene **10** is more nucleophilic than thiophene itself. Thus, a special mixing technique like ultra-high speed mixing using a micro mixer might be necessary for selective preparation of the mono-substituted product in this case.[6h,6m,13]

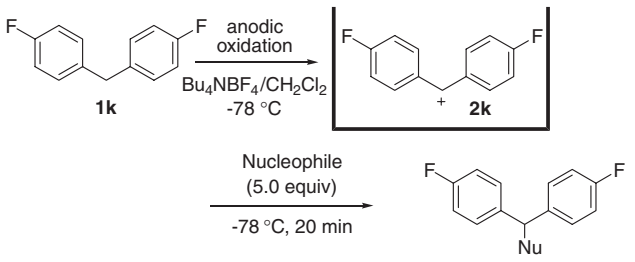
Conclusion

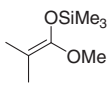
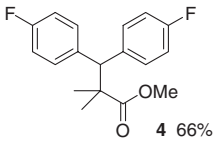
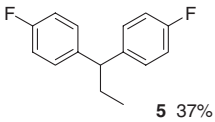
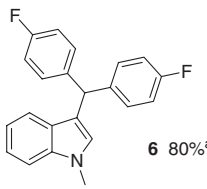
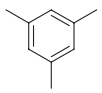
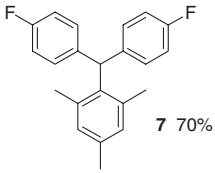
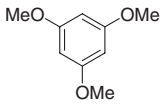
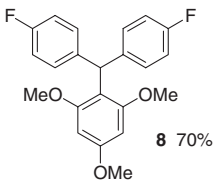
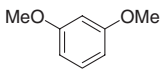
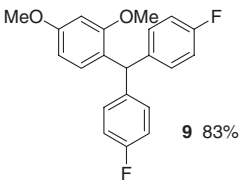
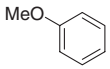
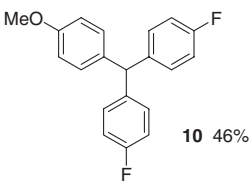
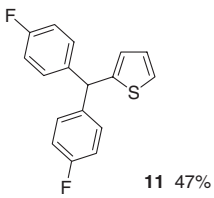
The "cation pool" method was found to be effective for the generation of diarylcarbenium ions, although the efficiency depends on the nature of the starting diarylmethanes. The present method serves as a powerful method for the construction of organic compounds having diarylmethane structures, and it is hoped that various substituted diarylmethanes will be synthesized using the present method.

Experimental

General. ^{1}H and ^{13}C NMR spectra were recorded on Varian MERCURY plus-400 (^{1}H 400 MHz, ^{13}C 100 MHz) and JEOL ECA-600P (^{1}H 600 MHz, ^{13}C 150 MHz) instruments. EI mass spectra were recorded on a JMS-SX102A spectrometer. FAB mass spectra were recorded on a JMS-HX110A spectrometer. CSI mass spectra were recorded on a JMS-T100CSK spectrometer. Starting materials **1g**,[14] **1h**,[15] **1i**,[15] **1j**,[15] **1m**,[15] and **1o**[16] were prepared according to reported procedures. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Dichloromethane was washed with water, distilled from P_2O_5, redistilled from dried K_2CO_3 to remove a trace amount of acid, and stored over molecular sieves 4A. Unless otherwise noted, all oxidation potential were measured as follows. Rotating-disk electrode voltammetry was carried out using BAS 100B and Nikko Keisoku RRDE-1 rotating disk electrodes with a Nikko Keisoku SC-5 controller. Measurements

Table 3.



Entry	Nucleophile	Product (yields)
1		 **4** 66%
2	Et_2Zn	 **5** 37%
3		 **6** 80%[a]
4		 **7** 70%
5		 **8** 70%
6		 **9** 83%
7		 **10** 46%
8		 **11** 47%

a) NMR yields (1,1′,2,2′-tetrachloroethane as an internal standard).

were carried out in 0.1 M $LiClO_4/CH_3CN$ using a glassy carbon disk working electrode, a platinum wire counter electrode, and an SCE reference electrode with sweep rate of 10 mV s^{-1} at 5000 rpm.

Spectral Analysis of Electrochemically Generated Diarylcarbenium Ion. NMR Analysis of Diarylcarbenium Ion 2k: The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 160 mg, dried at 250 °C/1 mmHg for 2.5 h before use) and a platinum plate cathode (10 mm × 10 mm). In the anodic chamber were placed **1k** (21.7 mg, 0.106 mmol) and 0.3 M Bu_4NBF_4 in CH_2Cl_2/CD_2Cl_2 (10:1) (4.0 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (38.2 mg, 0.254 mmol) and 0.3 M Bu_4NBF_4 in CH_2Cl_2/CD_2Cl_2 (10:1) (4.0 mL). The constant current electrolysis (5.0 mA) was carried out at −78 °C with magnetic stirring. After 2.5 F mol^{-1} of electricity was consumed, the reaction mixture of the anodic chamber was transferred to a 5 mm ϕ NMR tube with a septum cap under Ar atmosphere at −78 °C. The NMR measurement was carried out at −80 °C. Chemical shifts are reported using the methylene signal of CH_2Cl_2 at δ 53.49 (^{13}C NMR) as an internal standard. The huge signal coming from CH_2Cl_2 is reduced by usual pulse techniques: ^{13}C NMR (150 MHz, CH_2Cl_2/CD_2Cl_2 (10:1)): δ 119.3 (d, $J = 21.0$ Hz), 120.6 (d, $J = 22.5$ Hz), 132.3, 144.2 (d, $J = 15.0$ Hz), 151.1 (d, $J = 13.5$ Hz), 174.2 (d, $J = 283.5$ Hz), 192.6. Selected peaks for ^1H NMR (600 MHz, CH_2Cl_2/CD_2Cl_2 (10:1)): δ 7.59 (dm, $J = 60.3$ Hz, 4H), 8.62 (d, $J = 28.7$ Hz, 4H), 9.90 (s, 1H).

Typical Procedure for the Generation of a Diarylcarbenium Ion Pool and Reactions with a Nucleophile. The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 160 mg, dried at 250 °C/1 mmHg for 2.5 h before use) and a platinum plate cathode (10 mm × 10 mm). In the anodic chamber were placed a solution of dihydroanthracene (**1c**) (72.1 mg, 0.400 mmol) and 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (90 μL) and 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL). The constant current electrolysis (10.0 mA) was carried out at −78 °C with magnetic stirring until 2.5 F mol^{-1} of electricity was consumed. Then allyltrimethylsilane (133.2 mg, 1.17 mmol) was added to the anodic chamber at −78 °C and the mixture was stirred for 30 min. The resulting mixture was treated with triethylamine (0.5 mL) at −78 °C. After stirring at room temperature for 10 min, the solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2 × 3 cm) of silica gel to remove Bu_4NBF_4 by using Et_2O as an eluent. Removal of the solvent of the combined filtrate under reduced pressure and purification of the crude product by flash chromatography gave 9-(2-propenyl)-9,10-dihydroanthracene (**3c**).[17]

9-(2-Propenyl)-9,10-dihydroanthracene (3c): 80% yield from dihydroanthracene (**1c**) and allyltrimethylsilane. ^1H NMR (400 MHz, $CDCl_3$): δ 2.42 (dt, $J = 1.2$, 7.2 Hz) and 2.55 (dt, $J = 0.67$, 7.0 Hz) (total 2H), 3.88–4.18 (m, 3H), 4.86–5.08 (m, 2H), 5.68–5.98 (m, 1H), 7.16–7.32 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.3, 36.2, 42.2, 46.7, 46.8, 47.7, 116.5, 125.8, 125.90, 125.93, 127.2, 127.6, 127.9, 128.8, 135.9, 136.0, 136.5, 136.8, 138.8, 139.6. HRMS (EI) m/z calcd for $C_{17}H_{15}$ ($M^+ - H$): 219.1174, found 219.1173.

9-(2-Propenyl)xanthene (3d): 70% yield from xanthene (**1d**) and allyltrimethylsilane at −48 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.50 (t, $J = 6.8$ Hz, 2H), 4.79–4.95 (m, 2H), 5.59–5.70 (m, 1H), 7.04–7.09 (m, 4H), 7.19–7.26 (m, 4H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 39.4, 45.3, 116.2, 117.5, 122.9, 124.6, 127.4, 128.6, 134.4, 152.0. HRMS (CI) calcd for $C_{16}H_{15}O$ (MH^+) 223.1123, found 223.1122.

5-(2-Propenyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (3e): 71% yield from dibenzosuberane (**1e**) and allyltrimethylsilane. The reaction was performed at −48 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.85 (t, $J = 7.4$ Hz, 2H), 3.02–3.11 (m, 2H), 3.28–3.36 (m, 2H), 4.10 (t, $J = 8.0$ Hz, 1H), 4.90–5.00 (m, 2H), 5.62–5.75 (m, 1H), 7.08–7.16 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.3, 41.5, 52.7, 115.8, 125.8, 126.2, 126.3, 129.3, 130.1, 136.9, 139.2, 141.1. HRMS (CI) m/z calcd for $C_{18}H_{19}$ (MH^+): 235.1487, found 235.1487.

4,4-Bis(4-methylphenyl)-1-butene (3f):[6p] 56% yield from **1f** and allyltrimethylsilane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 6H), 2.73–2.78 (m, 2H), 3.90 (t, $J = 8.0$ Hz, 1H), 4.87–4.92 (m, 1H), 4.95–5.01 (m, 1H), 5.61–5.72 (m, 1H), 6.70–7.07 (m, 8H).

4,4-Bis(4-methoxyphenyl)-1-butene (3g):[6p] 53% yield from **1g** and allyltrimethylsilane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.74 (dd, $J = 7.6$, 7.6 Hz, 2H), 3.75 (s, 6H), 3.91 (t, $J = 7.6$ Hz, 1H), 4.91–4.94 (m, 1H), 4.98–5.03 (m, 1H), 5.65–5.75 (m, 1H), 6.80 (d, $J = 8.0$ Hz, 4H), 7.11 (d, $J = 8.0$ Hz, 4H).

4-(4-Methoxyphenyl)-4-(4-methylphenyl)-1-butene (3h):[6p] 57% yield from **1h** and allyltrimethylsilane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 2.74–2.78 (m, 2H), 3.75 (s, 3H), 3.92 (t, $J = 8.0$ Hz, 1H), 4.91–4.95 (m, 1H), 4.98–5.04 (m, 1H), 5.65–5.75 (m, 1H), 6.78–6.82 (m, 2H), 7.05–7.14 (m, 6H).

4-(4-Methylphenyl)-4-phenyl-1-butene (3i):[6p] 60% yield from **1i** and allyltrimethylsilane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H), 2.75–2.79 (m, 2H), 3.94 (t, $J = 7.6$ Hz, 1H), 4.88–4.91 (m, 1H), 4.96–5.00 (m, 1H), 5.61–5.72 (m, 1H), 7.01–7.11 (m, 5H), 7.15–7.22 (m, 4H).

4,4-Bis(4-fluorophenyl)-1-butene (3k):[6p] 76% yield from **1k** and allyltrimethylsilane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.74–2.79 (m, 2H), 3.99 (t, $J = 7.8$ Hz, 1H), 4.95–5.05 (m, 2H), 5.63–5.73 (m, 1H), 6.94–7.00 (m, 4H), 7.13–7.18 (m, 4H).

4,4-Bis(4-chlorophenyl)-1-butene (3l):[6p] 44% yield from **1l** and allyltrimethylsilane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.70–2.74 (m, 2H), 3.92 (t, $J = 7.6$ Hz, 1H), 4.90–5.00 (m, 2H), 5.56–5.66 (m, 1H), 7.04–7.07 (m, 4H), 7.16–7.20 (m, 4H).

4,4-Bis[4-(4-methylphenyl)phenyl]-1-butene (3o):[6p] 83% yield from **1o** and allyltrimethylsilane. The reaction was performed at −10 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 6H), 2.85–2.89 (m, 2H), 4.07 (t, $J = 8.0$ Hz, 1H), 4.96–5.10 (m, 2H), 5.72–5.82 (m, 1H), 7.19–7.21 (m, 4H), 7.29–7.32 (m, 8H), 7.43–7.47 (m, 4H).

3,3-Bis(4-fluorophenyl)-2,2-dimethylpropionic Acid Methyl Ester (4):[6p] 66% yield from **1k** and dimethylketene methyl trimethylsilyl acetal. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 6H), 3.52 (s, 3H), 4.37 (s, 1H), 6.91–6.97 (m, 4H), 7.19–7.25 (m, 4H).

1,1-Bis(4-fluorophenyl)propane (5):[6p] 37% yield from **1k** and diethylzinc. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, $J = 7.6$ Hz, 3H), 2.00 (dq, $J = 7.6$, 7.6 Hz, 2H), 3.75 (t, $J = 7.6$ Hz, 1H), 6.92–6.98 (m, 4H), 7.11–7.16 (m, 4H).

(1-Methyl-1*H*-indol-3-yl)bis(4-fluorophenyl)methane (6):[18] 80% NMR yield from **1k** and 1-methylindole. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 (s, 3H), 5.64 (s, 1H), 6.38 (d, $J = 0.8$ Hz, 1H), 6.96–7.02 (m, 5H), 7.15–7.19 (m, 5H), 7.22 (ddd, $J = 8.4$, 6.8, 1.2 Hz, 1H), 7.31 (dd, $J = 7.6$, 0.8 Hz, 1H).

2-Bis(4-fluorophenyl)methyl-1,3,5-trimethylbenzene (7): 70% yield from **1k** and 1,3,5-trimethylbenzene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 6H), 2.31 (s, 3H), 5.95 (s, 1H), 6.89 (s, 2H), 6.95–7.01 (m, 4H), 7.03–7.09 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8, 21.9, 49.6, 115.0 (d, $J = 21.0$ Hz), 130.3, 130.6 (d, $J = 7.5$ Hz), 136.3, 136.6, 137.3, 138.0 (d, $J = 3.2$ Hz), 161.2 (d, $J = 243.2$ Hz). HRMS (EI) m/z calcd for $C_{22}H_{20}F_2$: 322.1533, found 322.1534.

2-Bis(4-fluorophenyl)methyl-1,3,5-trimethoxybenzene (8):[6p] 70% yield from **1k** and 1,3,5-trimethoxybenzene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.59 (s, 6H), 3.80 (s, 3H), 5.96 (s, 1H), 6.14 (s, 2H), 6.87–6.92 (m, 4H), 7.09–7.13 (m, 4H).

4-Bis(4-fluorophenyl)methyl-1,3-dimethoxybenzene (9): 83% yield from **1k** and 1,3-dimethoxybenzene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.69 (s, 3H), 3.79 (s, 3H), 5.75 (s, 1H), 6.39 (dd, $J = 8.4$, 2.4 Hz, 1H), 6.46 (d, $J = 2.4$ Hz, 1H), 6.66 (d, $J = 8.4$ Hz, 1H), 6.92–7.02 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.7, 55.3, 55.5, 98.7, 103.8, 114.9 (d, $J = 21.0$ Hz), 124.8, 130.4, 130.6 (d, $J = 7.5$ Hz), 139.7 (d, $J = 3.2$ Hz), 157.8, 159.6, 161.2 (d, $J = 242.8$ Hz). HRMS (EI) m/z calcd for $C_{21}H_{18}O_2F_2$: 340.1275, found 340.1273.

4-Bis(4-fluorophenyl)methyl-1-methoxybenzene (10): 46% yield from **1k** and anisole. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 3H), 5.46 (s, 1H), 6.83–6.87 (m, 2H), 6.95–7.02 (m, 6H), 7.03–7.08 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.4, 55.2, 113.8, 115.1 (d, $J = 21.0$ Hz), 130.1, 130.6 (d, $J = 8.0$ Hz), 135.7, 139.8 (d, $J = 3.2$ Hz), 158.1, 161.4 (d, $J = 243.2$ Hz). HRMS (EI) m/z calcd for $C_{20}H_{16}OF_2$: 310.1169, found 310.1176.

2-Bis(4-fluorophenyl)methylthiophene (11): 47% NMR yield from **1k** and thiophene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.67 (s, 1H), 6.67 (ddd, $J = 3.6$, 1.5, 1.2 Hz, 1H), 6.95 (dd, $J = 5.2$, 3.6 Hz, 1H), 6.98–7.04 (m, 4H), 7.14–7.19 (m, 4H), 7.23 (dd, $J = 5.2$, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.5, 115.3 (d, $J = 21.4$ Hz), 124.8, 126.4, 126.7, 130.2 (d, $J = 7.9$ Hz), 139.3 (d, $J = 3.1$ Hz), 147.5, 161.7 (d, $J = 244.0$ Hz). HRMS (EI) m/z calcd for $C_{17}H_{12}SF_2$: 286.0629, found 286.0632.

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