o-Benzenedisulfonimide as a Reusable Brønsted Acid Catalyst for Hosomi–Sakurai Reactions

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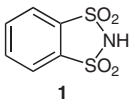
Abstract: Various acetals or alcohols react with allyl(trimethyl)silane or 1-phenyl-2-(trimethylsilyl)acetylene in the presence of a catalytic amount of the Brønsted acid *o*-benzenedisulfonimide under mild conditions to give good yields of the corresponding products. The catalyst can be easily recovered and purified for use in further reactions, which has economic and ecological advantages.

Key words: homogeneous catalysis, Brønsted acid, Hosomi–Sakurai reaction, acetals, alcohols

We have recently reported the use of *o*-benzenedisulfonimide (**1**, 1,3,2-benzodithiazole 1,1,3,3-tetraoxide; Figure 1) in catalytic amounts as a safe, nonvolatile, and noncorrosive Brønsted acid in some acid-catalyzed organic reactions, such as etherifications,[1] esterifications,[1,2] acetalizations,[1] Ritter reactions,[3] Nazarov electrocyclizations,[4] and disproportionations of dialkyl diarylmethyl ethers[5] under very mild and selective conditions. The catalyst can be easily recovered and purified for use in further reactions, which has economic and ecological advantages.



1

Figure 1 *o*-Benzenedisulfonimide (**1**)

The Hosomi–Sakurai reaction[6,7] generally involves the Lewis acid-promoted allylation of various electrophiles with allyl(trimethyl)silane; in rare instances, other silanes are used.[8] Surprisingly, the use of Brønsted acids in important reaction has only been reported in a few recent papers.[9] In the most significant of these,[9e] List describes the Hosomi–Sakurai allylation of both aromatic and aliphatic acetals in the presence of catalytic amount of six different Brønsted acids, the best results being obtained with 2,4-dinitrobenzenesulfonic acid.

We have found that the Hosomi–Sakurai reaction of two different classes of electrophiles, namely acetals or ketals **2** and alcohols **11**, with allyl(trimethyl)silane (**3**) or 1-phenyl-2-(trimethylsilyl)acetylene (**5**) takes place in the presence of **1** as a catalyst.

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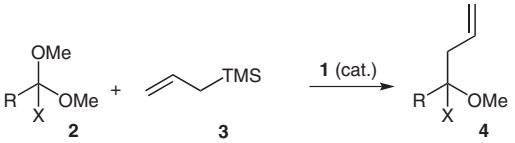
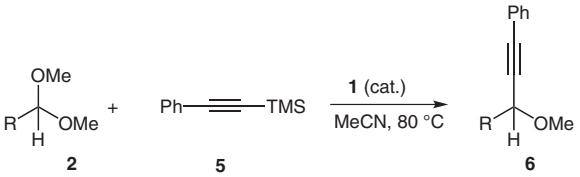
First, we studied the reactions between acetals **2a–g** or ketal **2h** with silane **3** (Scheme 1) in the presence of **1** (5 or 10 mol%); the results are listed in Table 1. We obtained the corresponding homoallylic ethers **4a–h** in good yields under simple and mild conditions. The products are useful as intermediates in organic synthesis,[10] or as precursors of molecules with biological activity.[11] Note also that the reactions were carried out under solvent-free conditions, which has economic and ecological benefits. Moreover, the reaction was chemoselective; in entry 5, only traces of diallylated product were detected. Furthermore, **1** could be recovered in good yield (85%) simply by evaporating the aqueous layer under reduced pressure and washing, as reported below.



2 3 4

Scheme 1 Hosomi–Sakurai reactions of acetals **2** with allyl(trimethyl)silane (**3**)

When the reaction was carried out with silane **5** (Scheme 1), the yields of products **6a–d** were fairly good (Table 2); however, it was necessary to use a larger amount of **1** (20 or 30 mol%) in acetonitrile as a solvent. Compounds **6** are interesting building blocks for use in natural product synthesis;[8a,c] furthermore, some diaryl-substituted propynyl compounds are useful in the treatment of disorders of cell differentiation, proliferation, and keratinization.[12]



2 5 6

Scheme 2 Hosomi–Sakurai reactions of acetals **2** with 1-phenyl-2-(trimethylsilyl)acetylene (**5**)

It was possible to reuse the recovered **1** in several consecutive runs without a significant loss of catalytic activity or a decrease in the yield of **4a** (Table 3).

Table 1 Hosomi–Sakurai Reactions of Acetals **2a–g** or Ketal **2h** with Allyl(trimethyl)silane (**3**)

Entry	Acetal/ketal	R	X	Ratio **2/3**	Catalyst **1** (mol%)	Temp (°C)	Time (h)	Product	Yield[a] (%)
1	**2a**	Ph	H	1:1.2	5	45	2	**4a**	90
2	**2b**	4-$MeOC_6H_4$	H	1:1.2	5	45	2.5	**4b**	88
3	**2c**	4-$O_2NC_6H_4$	H	1:1.2	5	r.t.	3	**4c**	88
4	**2d**	$(CH_2)_4Me$	H	1:1.5	10	r.t.	2.5	**4d**	90
5	**2e**	(*E*)-CH_2CH=$CHMe$	H	1:1.5	10	r.t.	1	**4e**	72[b]
6	**2f**	Cy	H	1:1.5	10	r.t.	1.5	**4f**	81
7	**2g**	Bn	H	1:1.5	10	r.t.	8	**4g**	91[c]
8	**2h**	Ph	Me	1:1.5	10	r.t.	24	**4h**	79[c]

[a] Yield of pure product.
[b] **4e** was purified by flash chromatography (PE–Et_2O, 9.8:0.2). In the GC/MS analyses of the crude residue, weak traces of diallylated product, MS (EI, 70 eV): *m/z* 155 (8) [$M^+ - 41$], were detected.
[c] The products were purified by flash chromatography on a short column (PE–Et_2O, 9.8:0.2).

Table 2 Hosomi–Sakurai Reactions of Acetals **2a–d** with 1-Phenyl-2-(trimethylsilyl)acetylene (**5**)

Entry	Acetal	R	Ratio **2/5**	Catalyst **1** (mol%)	Time (h)	Product	Yield[a] (%)
1	**2a**	Ph	1:1.5	20	7	**6a**	65
2	**2b**	4-$MeOC_6H_4$	1:1.5	30	8	**6b**	65
3	**2c**	4-$O_2NC_6H_4$	1:1.5	30	8	**6c**	54
4	**2d**	$(CH_2)_4Me$	1:1.5	30	4.5	**6d**	55

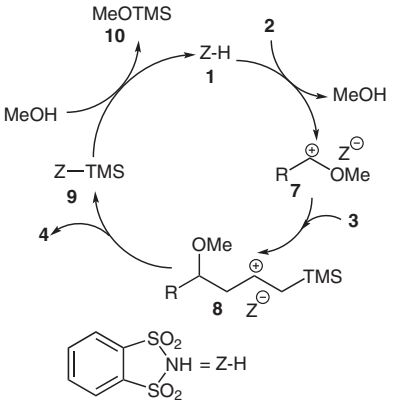
[a] Yield of pure product obtained by flash chromatography on a short column (PE–Et_2O, 9.8:0.2).

Table 3 Consecutive Reactions with Recycled Catalyst **1**

Entry	Yield[a] (%) of **4a**	Recovery of **1**
1	90[b]	85% (94 mg)[c]
2	85[d]	80% (75 mg)[e]
3	85[f]	75% (56 mg)

[a] Yields refer to the pure product; the reaction time was 2 hours for all the reactions.
[b] The reaction was performed with 10 mmol of **2a** (1.52 g) and 5 mol% of **1** (0.11 g, 0.5 mmol).
[c] The recovered **1** (94 mg) was reused in entry 2.
[d] The reaction was performed with 8.58 mmol of **2a** (1.30 g) and 5 mol% of **1** (94 mg, 0.429 mmol).
[e] The recovered **1** (75 mg) was reused in entry 3.
[f] The reaction was performed with 6.84 mmol of **2a** (1.04 g) and 5 mol% of **1** (75 mg, 0.342 mmol).

As reported by List,[9e] the reaction can be described by a catalytic cycle (Scheme 3), in which **1** is regenerated by the reaction of the intermediate **9** with methanol (or water in the case of the reactions shown below in Scheme 4). It must be stressed that no traces of **9** were detected; on the contrary, product **10** was identified by GC-MS analysis, but could not be isolated because of its volatility. In light of this, the silane **5** reacts less readily because, instead of the stable carbocation **8**, a less-stable vinylic carbocation is formed.



Scheme 3 Catalytic cycle

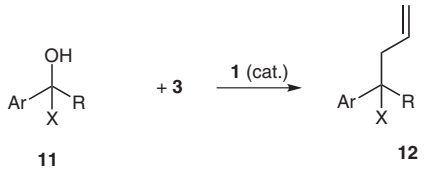
To further explore the synthetic usefulness of *o*-benzenedisulfonimide (**1**) in Hosomi–Sakurai reactions, we also studied the reactions between alcohols **11a–h** and silane **3**

Table 4 Hosomi–Sakurai Reactions of Alcohols **11**

Entry	Alcohol	Ar	X	R	Catalyst **1** (mol%)[a]	Time (h)	Temp (°C)	Product	Yield[b] (%)
1	**11a**	Ph	H	Me	30	24	70	**12a**	72[c]
2	**11b**	Ph	H	Ph	30	24	70	**12b**	75[d]
3	**11c**	Ph	H	2-HOC_6H_4	5	0.25	r.t.	**12c**	91
4	**11d**	4-$MeOC_6H_4$	H	Ph	5	0.25	r.t.	**12d**	93
5	**11e**	4-$MeOC_6H_4$	H	4-$MeOC_6H_4$	5	0.25	r.t.	**12e**	95
6	**11f**	4-$Me_2NC_6H_4$	H	4-$Me_2NC_6H_4$	5	1	r.t.	**12f**	92
7	**11g**	4-FC_6H_4	H	4-FC_6H_4	30	24	70	**12g**	74[e]
8	**11h**	Ph	Ph	Ph	5	0.25	r.t.	**12h**	95

[a] The reactants ratio was **11/3** = 1:1.5.
[b] Yield of pure product.
[c] **12a** was purified by flash chromatography (PE–Et_2O, 9.8:0.2). In the GC/MS analyses of the crude residue, weak traces of styrene, MS (EI, 70 eV): *m/z* = 104 (100) $[M]^+$ and bis(1-phenylethyl) ether, MS (EI, 70 eV): *m/z* = 226 (54) $[M]^+$, 105 (100), were detected.
[d] **12b** was purified by flash chromatography (PE–Et_2O, 9.8:0.2). In the GC/MS analyses of the crude residue, weak traces of bis(diphenylmethyl)ether, MS (EI, 70 eV): *m/z* = 350 (34) $[M]^+$, 167 (100) were detected.
[e] **12g** was purified by flash chromatography (PE–Et_2O, 9.8:0.2). In the GC/MS analyses of the crude residue, weak traces of bis[bis(4-fluorophenyl)methyl)] ether, MS (EI, 70 eV): *m/z* = 422 (4) $[M]^+$, 203 (100) were detected.

in the presence of **1** as a catalyst (Scheme 4). The results are reported in Table 4. We obtained excellent results with diarylmethanols **11c–f** (entries 3–6) bearing one or two electron-donating groups, and with triphenylmethanol (**11h**; entry 8); these reactions took place rapidly under solvent-free conditions, and it was necessary to use only 5 mol% of **1**. With **11a**, **11b**, and **11g**, (entries 1, 2, and 7, respectively), which do not contain strong electron-donating groups, we obtained lower yields of products **6**, and harsher reaction conditions were required. The greater stability of the cations arising from **11c–f** and **11h** facilitates the reaction significantly.



Scheme 4 Hosomi–Sakurai reactions of alcohols **11**

Several reactions between various alcohols and silyl compounds in the presence of Lewis acids[7i,l,m,8a,c,13] or the Brønsted acid bis(fluorosulfuryl)imide[9a] as catalysts are known. However, most of these reactions require the use of environmentally dangerous halogenated solvents or neurotoxic hexane.

It must be stressed that some compounds **12**, in particular **12c**,[14a–c] are important precursors of molecules that show interesting biological activities.[14]

In conclusion, the advantages of performing the Hosomi–Sakurai reactions in the presence of **1** as catalyst can be summarized as follows: 1) it is a safe, nonvolatile, and noncorrosive Brønsted acid; 2) it is readily recovered at the end of the reactions simply by evaporating the aqueous washings; 3) the target products **4**, **6**, and **12** are generally obtained in excellent yields under simple and mild reaction conditions; and 4) the reactions are usually carried out under solvent-free conditions, with consequent economic and ecological benefits.

All the reactions were conducted in open flasks. Analytical grade reagents and solvents were used and the reactions were monitored by TLC, GC, and GC-MS. Flash chromatography was carried out on silica gel (particle size 0.032–0.063 mm). Petroleum ether (PE) refers to the fraction boiling in the range 40–70 °C. ^1H NMR and ^{13}C NMR were recorded on a Bruker Avance 200 spectrometer at 200 and 50 MHz, respectively. Mass spectra were recorded on an HP 5989B mass-selective detector connected to an HP 5890 GC. The room temperature was 20–25 °C. *o*-Benzenedisulfonimide (**1**),[15] acetals **2c**, **2e**, **2f**,[16] and alcohols **11c** and **11f**[17] were prepared as reported in the literature; all the other reactants were purchased from Sigma-Aldrich. Yields of the pure (GC, GC-MS, TLC, ^1H NMR, ^{13}C NMR) isolated products **4**, **6**, and **12** are reported in Tables 1, 2, and 3 respectively. Structures and purity of the products **4a**,[18] **4b**,[18] **4f**,[19] **4g**,[20] **6a**,[21] **6b**,[22] **12a**,[13] **12b**,[13] **12d**,[23] **12e**,[13] **12g**[24], and **12h**[13] were confirmed by comparison of their physical and spectral data with those reported in the literature. Products **4c**,[9e] **4h**,[9e] **12c**,[14b] and **12f**[25] are known in the literature, but no physical and spectral data have been reported. Satisfactory microanalyses were obtained for the new compounds **4d**, **4e**, **6c**, and **6d**.

(1-Methoxybut-3-en-1-yl)benzene (4a); Typical Procedure

o-Benzenedisulfonimide (**1**; 0.11 g, 0.5 mmol; 5 mol%) was added to a mixture of acetal **2a** (1.52 g, 10 mmol) and allyl(trimethyl)silane (**3**, 1.37 g, 12 mmol), and the mixture was stirred at 45 °C. The reaction was monitored by TLC, GC, and GC-MS until **2a** completely disappeared (2 h). On GC-MS analysis, besides **4a** [MS (EI, 70 eV): *m/z* (%) = 162 (2) $[M^+]$, 121 (100)], methoxy(trimethyl)silane (**10**) [MS (EI, 70 eV): *m/z* (%) = 104 (2) $[M^+]$, 89 (100)], was

detected, but this could not be isolated owing to its volatility. The mixture was poured into Et_2O–H_2O (1:1; 100 mL), and the aqueous layer was separated and extracted with Et_2O (2 × 50 mL). The combined organic extracts were washed with H_2O (2 × 50 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The crude residue was the virtually pure (GC, GC-MS, TLC, ^{1}H NMR, ^{13}C NMR) **4a**, obtained as a yellow viscous oil; yield: 1.46 g (90%). The aqueous layer and aqueous washings were collected and evaporated under reduced pressure. After removal of the water, virtually pure (^{1}H NMR), *o*-benzenedisulfonimide (**1**) was recovered (94 mg, 85% yield). The recovered **1** was employed in other two catalytic cycles under the conditions described above.

Products **6** were synthesized in the same conditions as compounds **4**, the only difference being that of MeCN (5 mL) was added as a solvent.

1-Methoxy-4-(1-methoxybut-3-en-1-yl)benzene (4b)
Yellow viscous oil; yield: 1.69 g (88%) from **2b** (1.82 g, 10 mmol) and **3** (1.37 g, 12 mmol).

1-(1-Methoxybut-3-en-1-yl)-4-nitrobenzene (4c)
Yellow viscous oil; yield: 1.83 g (88%) from **2c** (1.97 g, 10 mmol) and **3** (1.37 g, 12 mmol).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.39–2.57 (m, 2 H), 3.33 (s, 3 H), 4.35–4.42 (m, 1 H), 4.97–5.06 (m, 2 H), 5.62–5.85 (m, 1 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 8.20 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.1, 64.5, 80.6, 117.3, 123.3, 127.1, 133.5, 147.0, 150.0.

MS (EI, 70 eV): *m/z* (%) = 207 (2) [M$^+$], 166 (100).

4-Methoxynon-1-ene (4d)
Yellow viscous oil; yield: 1.40 g (90%) from **2d** (1.46 g, 10 mmol) and **3** (1.71 g, 15 mmol).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.6 Hz, 3 H), 1.29–1.45 (m, 8 H), 2.20–2.27 (m, 2 H) 3.15–3.21 (m, 1 H), 3.31 (s, 3 H), 5.00–5.11 (m, 2 H), 5.75–5.86 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8, 22.4, 24.7, 31.8, 33.1, 37.6, 56.3, 80.3, 116.5, 134.8.

MS (EI, 70 eV): *m/z* (%) = 115 (80) [M$^+$ – 41], 83 (100).

Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.82; H, 12.88.

(7*E*)-4-Methoxynona-1,7-diene (4e)
Yellow viscous oil; yield: 1.11 g (72%) from **2e** (1.44 g, 10 mmol) and **3** (1.71 g, 15 mmol).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 3 H), 1.44–1.50 (m, 2 H), 1.98–2.08 (m, 2 H), 2.20–2.27 (m, 2 H), 3.28–3.36 (m, 1 H), 3.51 (s, 3 H), 5.00–5.11 (m, 2 H), 5.28–5.35 (m, 1 H), 5.52–5.58 (m, 1 H), 5.75–5.88 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.6, 26.8, 35.9, 38.8, 56.2, 81.5, 114.7, 124.1, 131.5, 136.5.

MS (EI, 70 eV): *m/z* (%) = 113 (55) [M$^+$ – 41], 57 (100).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.83; H, 11.81.

(1-Methoxybut-3-en-1-yl)cyclohexane (4f)
Yellow viscous oil; yield: 1.36 g (81%) from **2f** (1.58 g, 10 mmol) and **3** (1.71 g, 15 mmol).

(2-Methoxypent-4-en-1-yl)benzene (4g)
Yellow viscous oil; yield: 1.61 g (91%) from **2g** (1.66 g, 10 mmol) and **3** (1.71 g, 15 mmol).

(2-Methoxypent-4-en-2-yl)benzene (4h)
Yellow viscous oil; yield: 1.39 g (79%) from **2h** (1.66 g, 10 mmol) and **3** (1.71 g, 15 mmol).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.55 (s, 3 H), 2.56 (d, *J* = 1.4 Hz, 2 H), 3.11 (s, 3 H), 5.00–5.08 (m, 2 H), 5.58–5.78 (m, 1 H), 7.27–7.40 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.6, 47.1, 50.2, 78.5, 117.4, 126.1, 126.7, 127.9, 133.9, 146.1.

MS (EI, 70 eV): *m/z* (%) = 161 (2) [M$^+$ – 15], 135 (100).

1,1′-(3-Methoxyprop-1-yne-1,3-diyl)dibenzene (6a)
Yellow viscous oil; yield: 1.45 g (65%) from **2a** (1.52 g, 10 mmol) and **5** (2.61 g, 15 mmol).

1-Methoxy-4-(1-methoxy-3-phenylprop-2-yn-1-yl)benzene (6b)
Yellow viscous oil; yield: 1.65 g (65%) from **2b** (1.82 g, 10 mmol) and **5** (2.61 g, 15 mmol).

1-(1-Methoxy-3-phenylprop-2-yn-1-yl)-4-nitrobenzene (6c)
Yellow viscous oil; yield: 1.44 g (54%) from **2c** (1.97 g, 10 mmol) and **5** (2.61 g, 15 mmol).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.56 (s, 3 H), 5.40 (s, 1 H), 7.33–7.37 (m, 3 H), 7.47–7.52 (m, 2 H), 7.76 (d, *J* = 8.8 Hz, 2 H), 8.26 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 54.4, 73.1, 86.2, 88.8, 122.4, 123.2, 128.4, 128.6, 132.6, 145.3, 148.2.

MS (EI, 70 eV): *m/z* (%) = 267 (25) [M$^+$], 236 (100).

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.95; H, 4.84; N, 5.31.

(3-Methoxyoct-1-yn-1-yl)benzene (6d)
Yellow viscous oil; yield: 1.18 g (55%) from **2d** (1.46 g, 10 mmol) and **5** (2.61 g, 15 mmol).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 6.6 Hz, 3 H), 1.27–138 (m, 6 H), 1.79–1.86 (m, 2 H), 3.45 (s, 3 H), 4.18 (t, *J* = 6.2 Hz, 1 H), 7.30–7.34 (m, 3 H), 7.44–7.46 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8, 22.4, 24.8, 32.4, 35.5, 56.3, 71.6, 86.1, 88.0, 122.5, 128.0, 128.2, 131.5.

MS (EI, 70 eV): *m/z* (%) = 216 (2) [M$^+$], 145 (100).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.32; H, 9.38.

1,1′-But-1-ene-4,4-diylbis(4-methoxybenzene) (12e); Typical Procedure
o-Benzenedisulfonimide (**1**; 0.11 g, 0.5 mmol; 5 mol%) was added to a mixture of alcoho **11e** (2.44 g, 10 mmol) and allyl(trimethyl)silane (**3**, 1.71 g, 15 mmol), and the mixture was stirred at r.t. for 15 min. The crude residue consisted of virtually pure (GC, GC-MS, TLC, ^{1}H NMR, ^{13}C NMR) compound **12e**, waxy solid; yield: 2.55 g (95%). *o*-Benzenedisulfonimide (**1**) was also recovered (98 mg, 89% yield).

Pent-4-en-2-ylbenzene (12a)
Yellow viscous oil; yield: 1.05 g (72%) from **11a** (1.22 g, 10 mmol) and **3** (1.71 g, 15 mmol).

1,1′-But-1-ene-4,4-diyldibenzene (12b)
Yellow viscous oil; yield: 1.55 g (75%) from **11b** (1.84 g, 10 mmol) and **3** (1.71 g, 15 mmol).

2-(1-Phenylbut-3-en-1-yl)phenol (12c)
Yellow viscous oil; yield: 1.05 g (91%) from **11c** (2.04 g, 10 mmol) and **3** (1.71 g, 15 mmol).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.75–2.87 (m, 2 H), 4.07–4.13 (t, *J* = 6.2 Hz, 1 H), 5.05–5.20 (m, 2 H), 5.78–5.96 (m, 1 H), 6.73–6.85 (m, 2 H), 7.02–7.30 (m, 7 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 41.5, 53.3, 114.0, 116.7, 122.3, 126.5, 127.8, 128.4, 129.1, 129.5, 133.5, 135.6, 144.3, 154.1.

MS (EI, 70 eV): *m/z* (%) = 224 (2) [M$^+$], 183 (100).

1-Methoxy-4-(1-phenylbut-3-en-1-yl)benzene (12d)
Yield: 2.21 g (93%) from **11d** (2.14 g, 10 mmol) and **3** (1.71 g, 15 mmol); mp 44–45 °C (MeOH).

4,4′-But-1-ene-4,4-diylbis(*N*,*N*-dimethylaniline) (12f)
Yellow viscous oil; yield: 2.71 g (92%) from **11f** (2.70 g, 10 mmol) and **3** (1.71 g, 15 mmol).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.85 (s, 6 H), 2.90–2.97 (m, 2 H), 4.08–4.15 (t, *J* = 6.2 Hz, 1 H), 5.07–5.22 (m, 2 H), 5.75–6.00 (m, 1 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 6.94 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 39.9, 40.1, 50.3, 113.8, 116.2, 129.1, 132.8, 136.6, 146.2.

MS (EI, 70 eV): *m/z* (%) = 294 (2) [M$^+$], 253 (100).

1,1′-But-1-ene-4,4-diylbis(4-fluorobenzene) (12g)
Yellow viscous oil; yield: 1.80 g (74%) from **11g** (2.20 g, 10 mmol) and **3** (1.71 g, 15 mmol).

1,1′,1″-But-1-ene-4,4,4-triyltribenzene (12h)
Yield: 2.69 g (95%) from **11h** (2.60 g, 10 mmol) and **3** (1.71 g, 15 mmol); mp 70–71 °C (MeOH).

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