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Methods for the Preparation of Allenes Employing Indium- and Zinc-Mediated Dehalogenation Reactions in Aqueous Solutions

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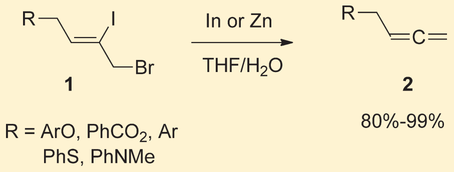
S *Supporting Information*

ABSTRACT: Simple and mild methods for the synthesis of allenes, employing indium- and zinc-mediated dehalogenation reactions of vicinal dihalides in an aqueous solvent, are described. By using these procedures, various allenylmethyl aryl ethers and monosubstituted allenes have been prepared in good to excellent yields.



Recently, allenes have become important and versatile intermediates in organic synthesis.[1] In addition, many natural products containing an allene functional group have been shown to possess pharmacological activities,[2] and some allenylmethyl aryl ethers are known to have antitumor activities.[3] Several approaches have been developed for the synthesis of allenes. For example, terminal allenes can be prepared either by reactions of terminal alkynes with paraformaldehyde in the presence of diisopropylamine and CuBr in dioxane[4] or through reactions of geminal dihalocyclopropanes with organolithium compounds.[5] Moreover, olefination reactions, including dehalogenation[6] and Peterson[7] and carbonyl allenations,[4c,8] have been used to generate these substances. Conditions for performing dehalogenation reactions of vicinal dihalides to form terminal allenes typically involve the use of zinc dust at high temperature in alcoholic solvents,[6a] chromous sulfate under a nitrogen atmosphere,[6b] or methyl lithium at low temperatures.[6c] However, the reported procedures[6] have limited scope when they are applied to the preparation of terminal allenes containing sensitive functional groups, such as aldehydes, esters, cyanides, and halides.

The general method most often utilized for the synthesis of allenylmethyl aryl ethers begins with an allenylmethyl bromide, prepared from 2-butyne-1,4-diol, as shown in Scheme 1.[3,9] However, several drawbacks are associated with this method, including difficult separation of the monochloro propargylic alcohol intermediate from the dichloroalkyne byproduct and the need to handle large quantities of lithium aluminum hydride. In recent studies,[10] we observed that allenes are produced as side products in metal-mediated 2-haloallylation reactions of formaldehyde. This finding stimulated an investigation aimed at the development of metal-mediated dehalogenation reactions of vicinal dihalides (**1**, Scheme 2) as a method to generate allenes. Here we describe the results of this effort that has led to the development of mild indium- and zinc-mediated dehalogenation processes for the synthesis of terminal allenes.

Our effort began with the exploration of various metal sources for the aqueous dehalogenation reaction of iodoallylic bromide **1**, which was prepared by using a similar procedure described earlier.[11] The conditions employed for these processes that generate allene **2a** are summarized in Table 1. The preliminary results showed that both zinc and to a lesser extent indium are ideal metals for the dehalogenation reaction (Table 1, entries 5 and 15). Complete conversion to product was observed to take place in 1 h when zinc dust (325 mesh) was employed, but 12 h is required to complete the process promoted by indium powder (325 mesh). Metal particle size was found to have a dramatic effect on the reaction rate where smaller particle sizes promote faster reactions (Table 1, entry 4 versus entry 5). In addition, the indium-mediated dehalogenation reaction is solvent dependent as reflected by the observations that the reaction (1) does not occur when either pure THF or water are employed as solvent (Table 1, entries 1 and 2), (2) takes place sluggishly in 1:1 aqueous THF (Table 1, entry 3), and (3) takes place optimally in 4:1 aqueous THF to afford allene **2a** in excellent yield (Table 1, entry 5). Although other metals, such as gallium, aluminum, tin, manganese, iron, and copper, and tin-containing Lewis acids do not promote the dehalogenation reaction of **1a** (Table 1, entries 6−11 and 16), the tin-mediated process does occur when HBr is present (Table 1, entry 18).[12]

The substrate scope of indium- and zinc-mediated dehalogenation reactions of **1a** was probed next (Table 2). As can be seen by viewing the results given in Table 2, halide, cyanide, carbonyl, ester, and amide groups all tolerate in the indium-mediated dehalogenation reaction condition.

The method described above is not limited to the synthesis of allenylmethyl aryl ethers. Thus, in addition to phenols, carboxylic acids, Grignard reagent, *N*-methylaniline, and thiophenol react with the iodoallylic iodide shown in Scheme 2 to furnish precursors of the corresponding iodoallylic bromides **1l**−**p** (Table 2, entries 12−16). In addition, it should be noted that allenes **2m**,**n** are volatile compounds, and consequently, the actual yields of indium- and zinc-mediated dehalogenation reactions of **1m**,**n** are likely higher than those of the isolated products.

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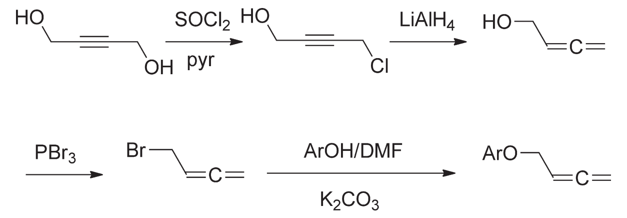
Scheme 1



Scheme 2

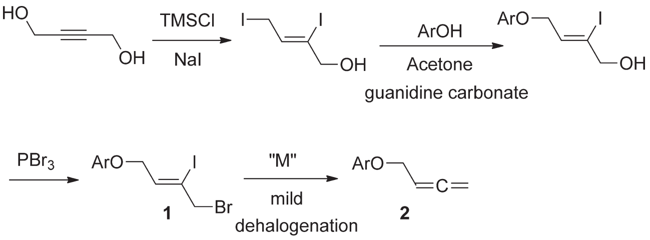
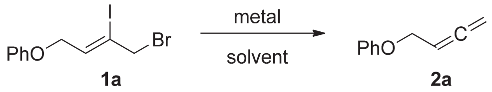


Table 1. Metal-Mediated Dehalogenation of Vicinal Dihalides[a]



entry	metal/additive	solvent	time (h)	yield (%)
1	In (325 mesh)	H_2O	12	0
2	In (325 mesh)	THF	12	0
3	In (325 mesh)	THF/H_2O (1/1)	12	15[b]
4	In (100 mesh)	THF/H_2O (4/1)	62	85
5	In (325 mesh)	THF/H_2O (4/1)	12	91
6	Ga	THF/H_2O (4/1)	12	0
7	Al	THF/H_2O (4/1)	12	0
8	Sn	THF/H_2O (4/1)	12	0
9	Mn	THF/H_2O (4/1)	12	0
10	Fe	THF/H_2O (4/1)	12	0
11	Cu	THF/H_2O (4/1)	12	0
12	Zn (325 mesh)	H_2O	12	19[b]
13	Zn (325 mesh)	THF	12	74[b]
14	Zn (100 mesh)	THF/H_2O (4/1)	12	87
15	Zn (325 mesh)	THF/H_2O (4/1)	1	94
16	$SnCl_2$/KI	H_2O	12	0
17	$SnCl_2$/KI	THF/H_2O (4/1)	12	49[b]
18[c]	Sn/HBr	THF/H_2O	12	94

[a] Conditions: **1a** (1.5 mmol) and indicated metal (1.5 mmol) in 2.0 mL of solvent at rt. [b] The conversion was determined by ^{1}H NMR. [c] Conditions: **1a** (1.5 mmol), tin powder (1.5 mmol), and HBr (0.2 mL) in THF (1.0 mL)/water (0.8 mL) at rt.

The mechanistic pathway followed in the indium-mediated dehalogenation reactions of iodoallylic bromides **1** presumably involves the generation of the corresponding allylic radical and followed by β-elimination to produce the allene group.[13] To test this hypothesis, the *p*-nitrophenoxy-substituted iodoallylic bromide **1q** was subjected to the indium-mediated dehalogenation reaction conditions (eq 1, Scheme 3). The fact that **1q** remains unreacted under these conditions suggests that the nitrophenyl group acts in a typical way[14] to trap the radical intermediate.

Several examples for the indium-mediated dehalogenation of vicinal dibromides into alkenes have been reported.[15] To explore this process further, other vicinal dihalides such as iodoallylic chloride **1r** and bromoallylic bromide **1s** were examined. The indium- and zinc-mediated dehalogenation reactions of iodoallylic chloride **1r** failed to yield any desired product (eq 2, Scheme 3). The allene formation was observed in the indium- and zinc-mediated debromination reactions of bromoallylic bromide **1s** (eq 3, Scheme 3).[16]

As can be seen by comparing the results displayed in Table 2, zinc is more effective than indium in promoting dehalogenation reactions of the substrates that do not possess substituents or that contain a *p*-chloro group on the aromatic ring (Table 2, entries 1, 2, and 13). On the other hand, zinc-mediated dehalogenation reactions become less efficient when certain functional groups are present on the aromatic ring (Table 2, entries 3−11 and 16).

In summary, in this effort we have uncovered a new method for the preparation of allenes that employs dehalogenation reactions of vicinal dihalides in aqueous solutions. The processes, which occur in high yields, are both simple and mild.

EXPERIMENTAL SECTION

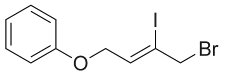
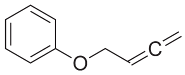
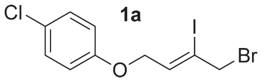
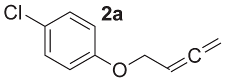
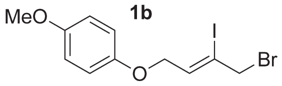
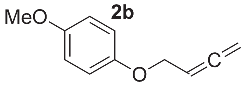
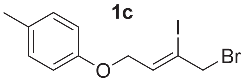
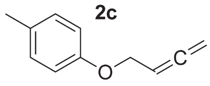
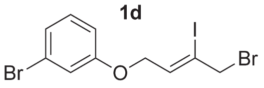
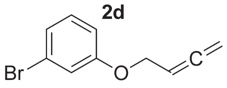
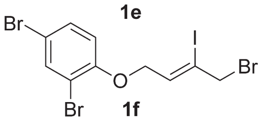
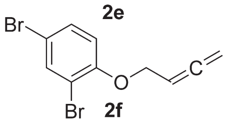
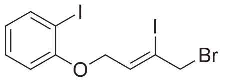
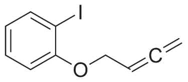
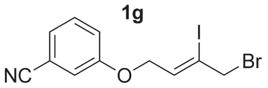
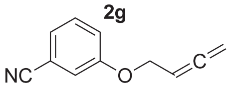
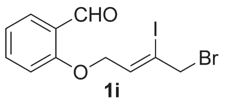
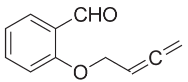
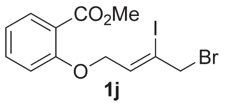
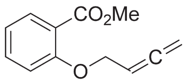
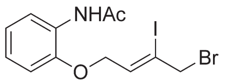
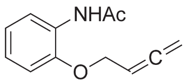
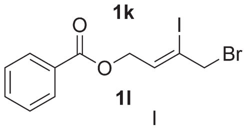
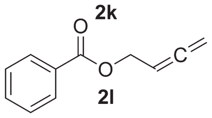
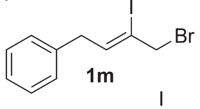
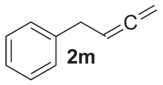
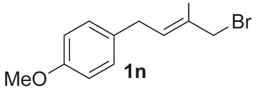
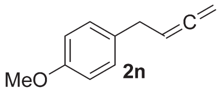
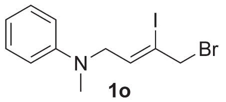
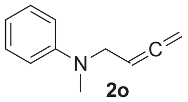
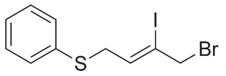
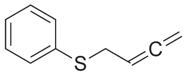
General Information and Materials. All commercially available chemicals were used without further purification. Iodoallylic bromides **1a**−**q**[11] and **1s**[17] were prepared from reported procedures followed by bromination using PBr_3 in ether, and iodoallylic chloride **1r** was prepared by chlorination of the precursor of **1a** using $POCl_3$ in DMF. TLC analyses were run on a glass plate (silica gel 60 F254) and were visualized using UV or a solution of phosphomolybdic acid in ethanol (5 wt %) or *p*-anisaldehyde stain. Flash chromatography was performed using silica gel (70−230 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts are reported relative to $CHCl_3$ [δ_H 7.24, δ_C (central line) 77.0]. Mass spectra and high-resolution mass spectra were recorded under electron spray interface (ESI) conditions.

(*Z*)-(4-Bromo-3-iodobut-2-enyloxy)benzene (1a): 91%; oil; TLC (EtOAc/hexanes (1:5)) R_f = 0.53; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.34 (s, 2 H), 4.60 (d, J = 5.1 Hz, 2 H), 6.41 (t, J = 5.1 Hz, 1 H), 6.86 (d, J = 7.8 Hz, 2 H), 6.97 (t, J = 7.8 Hz, 1 H), 7.29 (dd, J = 7.8, 2.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.9 (CH_2), 71.9 (CH_2), 101.8 (C), 114.6 (CH × 2), 121.3 (CH), 129.6 (CH × 2), 136.5 (CH), 158.0 (C); MS *m*/*z* (rel intensity) 352 (M^+, 0.5), 273 (22), 132 (15), 94 (100); HRMS $[M]^+$ for $C_{10}H_{10}BrIO$ 351.8960, found 351.8950.

(*Z*)-1-(4-Bromo-3-iodobut-2-enyloxy)-4-chlorobenzene (1b): 89%; oil; TLC (EtOAc/hexanes (1:5)) R_f = 0.58; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.33 (s, 2 H), 4.53 (d, J = 5.1 Hz, 2 H), 6.37 (t, J = 5.1 Hz, 1 H), 6.80 (d, J = 9.0 Hz, 2 H), 7.23 (d, J = 9.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.7 (CH_2), 72.0 (CH_2), 102.1 (C), 115.8 (CH × 2), 126.0 (C), 129.3 (CH × 2), 135.7 (CH), 156.4 (C); MS *m*/*z* (rel intensity) 386 (M^+, 4), 261 (21), 259 (20), 128 (100); HRMS $[M]^+$ for $C_{10}H_9BrClIO$ 385.8570, found 385.8572.

(*Z*)-1-(4-Bromo-3-iodobut-2-enyloxy)-4-methoxybenzene (1c): 94%; oil; TLC (EtOAc/hexanes (1:5)) R_f = 0.48; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 (s, 3 H), 4.32 (s, 2 H), 4.53 (d, J = 5.1 Hz, 2 H), 6.39 (t, J = 5.1 Hz, 1 H), 6.78−6.83 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.9 (CH_2), 55.5 (CH_3), 72.4 (CH_2), 101.6 (C), 114.5 (CH × 2), 115.5 (CH × 2), 136.5 (CH), 151.9 (C), 154.0 (C); MS *m*/*z*

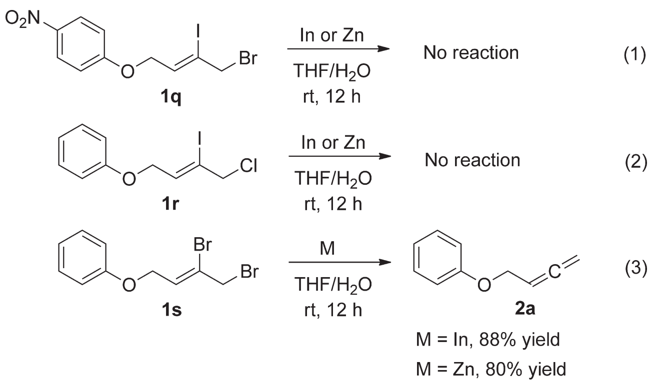
Table 2. Indium- and Zinc-Mediated Dehalogenation Reactions in Aqueous Solvent to Form Allenes

entry	substrate	product	time, yield from In	time, yield from Zn
1	 **1a**	 **2a**	12 h, 91%	1 h, 94%
2	 **1b**	 **2b**	12 h, 89%	4 h, 92%
3	 **1c**	 **2c**	12 h, 99%	12 h, 87%
4	 **1d**	 **2d**	12 h, 85%	12 h, 71%
5	 **1e**	 **2e**	12 h, 85%	12 h, 80%
6	 **1f**	 **2f**	12 h, 87%	12 h, 64%
7	 **1g**	 **2g**	12 h, 88%	12 h, 75%
8	 **1h**	 **2h**	12 h, 87%	12 h, 75%
9	 **1i**	 **2i**	12 h, 87%	12 h, 9%
10	 **1j**	 **2j**	12 h, 85%	12 h, 59%
11	 **1k**	 **2k**	12 h, 88%	12 h, 64%
12	 **1l**	 **2l**	12 h, 96%	1 h, 90%
13	 **1m**	 **2m**	12 h, 82%	2 h, 81%
14	 **1n**	 **2n**	12 h, 80%	-----
15	 **1o**	 **2o**	18 h, 82%	-----
16	 **1p**	 **2p**	12 h, 83%	24 h, 72%

(rel intensity) 382 (M^+, 5), 176 (5), 124 (64), 123 (100); HRMS $[M]^+$ for $C_{11}H_{12}BrIO_2$ 381.9065, found 381.9068.

(*Z*)-1-(4-Bromo-3-iodobut-2-enyloxy)-4-methylbenzene (1d): 55%; white solid, mp 43–44 °C; TLC (EtOAc/hexanes (1:5))

Scheme 3



R_f = 0.53; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3 H), 4.33 (s, 2 H), 4.56 (d, J = 5.1 Hz, 2 H), 6.40 (t, J = 5.1 Hz, 1 H), 6.77 (d, J = 8.4 Hz, 2 H), 7.07 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5 (CH_3), 41.9 (CH_2), 72.0 (CH_2), 101.6 (C), 114.4 (CH × 2), 130.0 (CH × 2), 130.4 (C), 136.6 (CH), 155.8 (C); MS m/z (rel intensity) 366 (M^+, 2), 287 (15), 132 (12), 108 (100); HRMS $[M]^+$ for $C_{11}H_{12}BrIO$ 365.9116, found 365.9127.

(*Z*)-1-Bromo-3-(4-bromo-3-iodobut-2-enyloxy)benzene (1e): 55%; oil; TLC (EtOAc/hexanes (1:5)) R_f = 0.60; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.34 (s, 2 H), 4.57 (d, J = 5.1 Hz, 2 H), 6.38 (t, J = 5.1 Hz, 1 H), 6.78−6.82 (m, 1 H), 7.02−7.17 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.7 (CH_2), 72.2 (CH_2), 102.3 (C), 113.6 (CH), 118.1 (CH), 122.9 (C), 124.4 (CH), 130.7 (CH), 135.6 (CH), 158.8 (C); MS m/z (rel intensity) 432 (M^+, 1), 353 (79), 351 (81), 172 (100); HRMS $[M]^+$ for $C_{10}H_9Br_2IO$ 429.8065, found 429.8075.

(Z)-2,4-Dibromo-1-(4-bromo-3-iodobut-2-enyloxy)benzene (1f): 60%; white solid, mp 57−58 °C; TLC (EtOAc/hexanes (1:10)) R_f = 0.48; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.33 (s, 2 H), 4.61 (d, J = 5.1 Hz, 2 H), 6.42 (t, J = 5.1 Hz, 1 H), 6.70 (d, J = 8.7 Hz, 1 H), 7.34 (d, J = 8.7 Hz, 1 H), 7.65 (d, J = 4.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.6 (CH_2), 73.3 (CH_2), 102.5 (C), 113.1 (C), 113.8 (C), 114.8 (CH), 131.2 (CH), 135.3 (CH), 135.7 (CH), 153.7 (C); MS m/z (rel intensity) 510 (M^+, 3), 383 (7), 252 (100), 223 (16); HRMS $[M]^+$ for $C_{10}H_8Br_3IO$ 507.7170, found 507.7166.

(*Z*)-1-(4-Bromo-3-iodobut-2-enyloxy)-2-iodobenzene (1g): 85%; white solid, mp 59−60 °C; TLC (EtOAc/hexanes (1:10)) R_f = 0.45; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.34 (s, 2 H), 4.63 (d, J = 5.1 Hz, 2 H), 6.46 (t, J = 5.1 Hz, 1 H), 6.70−6.78 (m, 2 H), 7.29 (t, J = 7.5 Hz, 1 H), 7.76 (dd, J = 7.5, 1.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.9 (CH_2), 73.2 (CH_2), 86.5 (C), 102.0 (C), 112.6 (CH), 123.2 (CH), 129.5 (CH), 136.0 (CH), 139.7 (CH), 156.6 (C); MS m/z (rel intensity) 478 (M^+, 3), 399 (7), 259 (12), 220 (100); HRMS $[M]^+$ for $C_{10}H_9BrI_2O$ 477.7926, found 477.7929.

(*Z*)-3-(4-Bromo-3-iodobut-2-enyloxy)benzonitrile (1h): 70%; white solid; mp 51−52 °C; TLC (EtOAc/hexanes (1:5)) R_f = 0.30; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.33 (s, 2 H), 4.58 (d, J = 5.1 Hz, 2 H), 6.38 (t, J = 5.1 Hz, 1 H), 7.07−7.10 (m, 2 H), 7.22−7.26 (m, 1 H), 7.34−7.40 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.5 (CH_2), 72.2 (CH_2), 102.8 (C), 113.2 (C), 117.7 (CH), 118.4 (C), 119.7 (CH), 125.0 (CH), 130.4 (CH), 134.9 (CH), 158.0 (C); MS m/z (rel intensity) 377 (M^+, 0.1), 298 (55), 261 (98), 259 (100); HRMS $[M]^+$ for $C_{11}H_9BrINO$ 376.8912, found 376.8917.

(*Z*)-2-(4-Bromo-3-iodobut-2-enyloxy)benzaldehyde (1i): 60%; pale yellow solid; mp 68−70 °C; TLC (EtOAc/hexanes (1:4)) R_f = 0.33; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.35 (s, 2 H), 4.70 (d, J = 5.1 Hz, 2 H), 6.45 (t, J = 5.1 Hz, 1 H), 6.92 (d, J = 7.5 Hz, 1 H), 7.04 (t, J = 7.5 Hz, 1 H), 7.50−7.56 (m, 1 H), 7.82 (dd, J = 7.5, 1.8 Hz, 1 H), 10.45 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.5 (CH_2), 72.3 (CH_2), 102.7 (C), 112.7 (C), 121.3 (CH), 125.0 (C), 128.7 (CH), 135.2 (CH), 135.9 (CH), 160.2 (C), 189.4 (CH); MS m/z (rel intensity) 380 (M^+, 0.1), 301 (89), 259 (30), 122 (100); HRMS $[M]^+$ for $C_{11}H_{10}BrIO_2$ 379.8909, found 379.8915.

(*Z*)-Methyl 2-(4-bromo-3-iodobut-2-enyloxy)benzoate (1j): 60%; white solid; mp 35−36 °C; TLC (EtOAc/hexanes (1:5)) R_f = 0.33; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.87 (s, 3 H), 4.33 (s, 2 H), 4.66 (d, J = 5.1 Hz, 2 H), 6.45 (t, J = 5.1 Hz, 1 H), 6.89 (d, J = 8.4 Hz, 1 H), 7.00 (t, J = 8.4 Hz, 1 H), 7.42−7.48 (m, 1 H), 7.78 (dd, J = 7.5, 1.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.8 (CH_3), 52.0 (CH_2), 73.2 (CH_2), 101.8 (C), 113.9 (CH), 120.8 (C), 121.0 (CH), 131.8 (CH), 133.5 (CH), 133.3 (CH), 157.5 (C), 166.4 (C); MS m/z (rel intensity) 410 (M^+, 0.06), 331 (87), 152 (75), 120 (100); HRMS $[M]^+$ for $C_{12}H_{12}BrIO_3$ 409.9014, found 409.9018.

(*Z*)-*N*-(2-(4-Bromo-3-iodobut-2-enyloxy)phenyl)acetamide (1k): 65%; white solid; mp 107−108 °C; TLC (EtOAc/hexanes (1:1)) R_f = 0.44; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 3 H), 4.29 (s, 2 H), 4.59 (d, J = 5.1 Hz, 2 H), 6.36 (t, J = 5.1 Hz, 1 H), 6.76 (dd, J = 7.5, 1.8 Hz, 1 H), 6.89−7.00 (m, 2 H), 7.79 (br s, 1 H), 8.29 (d, J = 7.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.7 (CH_3), 41.6 (CH_2), 72.1 (CH_2), 102.7 (C), 111.1 (CH), 120.1 (CH), 121.5 (CH), 123.5 (CH), 127.6 (C), 135.2 (CH), 146.0 (C), 168.0 (C); MS m/z (rel intensity) 409 (M^+, 8), 330 (34), 150 (40), 108 (100); HRMS $[M]^+$ for $C_{12}H_{13}BrINO_2$ 408.9174, found 408.9180.

(*Z*)-4-Bromo-3-iodobut-2-enyl benzoate (1l): 88%; white solid; mp 65−66 °C; TLC (EtOAc/hexanes (1:5)) R_f = 0.53; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.34 (s, 2 H), 4.86 (d, J = 5.1 Hz, 2 H), 6.39 (t, J = 5.1 Hz, 1 H), 7.43 (d, J = 7.5 Hz, 2 H), 7.56 (d, J = 7.5 Hz, 1 H), 8.03 (d, J = 7.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.7 (CH_2), 68.5 (CH_2), 103.1 (C), 128.4 (CH × 2), 129.5 (CH × 2), 129.7 (C), 133.2 (CH), 134.7 (CH), 166.1 (C); MS m/z (rel intensity) 380 (M^+, 0.0), 301 (94), 105 (100), 77 (50); HRMS $[M]^+$ for $C_{11}H_{10}BrIO_2$ 379.8909, found 379.8916.

(*Z*)-(4-Bromo-3-iodobut-2-enyl)benzene (1m): 75%; oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.53; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.51 (d, J = 6.9 Hz, 2 H), 4.36 (s, 2 H), 6.12 (t, J = 6.9 Hz, 1 H), 7.19−7.34 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.6 (CH_2), 43.1 (CH_2), 102.8 (C), 126.6 (CH), 128.4 (CH × 2), 128.6 (CH × 2), 137.8 (C), 139.4 (CH); MS m/z (rel intensity) 336 (M^+, 8), 257 (59), 130 (100), 115 (12); HRMS $[M]^+$ for $C_{10}H_{10}BrI$ 335.9011, found 335.9016.

(Z)-1-(4-Bromo-3-iodobut-2-enyl)-4-methoxybenzene (1n): 70%; oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.53; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.44 (d, J = 6.9 Hz, 2 H), 3.78 (s, 3 H), 4.35 (s, 2 H), 6.08 (t, J = 6.9 Hz, 1 H), 6.84 (d, J = 8.4 Hz, 2 H), 7.11 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.8 (CH_2), 43.2 (CH_2), 55.2 (CH_3), 102.3 (C), 114.0 (CH × 2), 129.4 (CH × 2), 129.8 (C), 139.8 (CH), 158.3 (C); MS m/z (rel intensity) 366 (M^+, 35), 287 (100), 160 (62), 121 (95); HRMS $[M]^+$ for $C_{11}H_{12}BrIO$ 365.9116, found 365.9125.

(*Z*)-*N*-(4-Bromo-3-iodobut-2-enyl)-*N*-methylaniline (1o): 80%; oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.53; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.95 (s, 3 H), 3.97 (d, J = 5.4 Hz, 2 H), 4.30 (s, 2 H), 6.07 (t, J = 5.4 Hz, 1 H), 6.67−6.77 (m, 3 H), 7.20−7.26 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.6 (CH_3), 42.5 (CH_2), 58.5 (CH_2), 102.7 (C), 112.8 (CH × 2), 117.1 (CH), 129.1 (CH × 2), 137.0 (CH), 148.7 (C); MS m/z (rel intensity) 365 (M^+, 10), 308 (32), 286 (100), 180 (26); HRMS $[M]^+$ for $C_{11}H_{13}BrIN$ 364.9276, found 364.9272.

(*Z*)-(4-Bromo-3-iodobut-2-enyl)(phenyl)sulfane (1p): 80%; oil; TLC (EtOAc/hexanes (1:5)) R_f = 0.48; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.59 (d, J = 7.2 Hz, 2 H), 4.28 (s, 2 H), 6.05 (t, J = 7.2 Hz, 1 H), 7.19−7.38 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.7 (CH_2), 42.5 (CH_2), 104.3 (C), 126.8 (CH), 128.9 (CH × 2), 130.8 (CH × 2), 134.3 (C), 136.3 (CH); MS *m*/*z* (rel intensity) 368 (M^+, 8), 289 (100), 162 (48), 109 (52); HRMS $[M]^+$ for $C_{10}H_{10}BrIS$ 367.8731, found 367.8740.

(*Z*)-1-(4-Bromo-3-iodobut-2-enyloxy)-4-nitrobenzene (1q): 55%; white solid, mp 88−89 °C; TLC (EtOAc/hexanes (1:5)) R_f = 0.30; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.34 (s, 2 H), 4.68 (d, *J* = 5.1 Hz, 2 H), 6.40 (t, *J* = 5.1 Hz, 1 H), 6.92 (d, *J* = 8.1 Hz, 2 H), 8.18 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.3 (CH_2), 72.6 (CH_2), 103.1 (C), 114.7 (CH × 2), 126.0 (CH × 2), 134.6 (CH), 141.9 (C), 162.9 (C); MS *m*/*z* (rel intensity) 397 (M^+, 0.3), 318 (35), 261 (92), 259 (100); HRMS $[M]^+$ for $C_{10}H_9BrINO_3$ 396.8810, found 396.8815.

(*Z*)-(4-Chloro-3-iodobut-2-enyloxy)benzene (1r): 73%; oil; TLC (Et_2O/hexanes (1:10)) R_f = 0.85; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.37 (s, 2 H), 4.63 (d, *J* = 5.1 Hz, 2 H), 6.45 (t, *J* = 5.1 Hz, 1 H), 6.91 (d, *J* = 8.1 Hz, 2 H), 6.99 (t, *J* = 8.1 Hz, 1 H), 7.32 (dd, *J* = 8.1, 2.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.4 (CH_2), 71.6 (CH_2), 101.3 (C), 114.6 (CH × 2), 121.2 (CH), 129.6 (CH × 2), 135.5 (CH), 158.0 (C); MS *m*/*z* (rel intensity) 308 (M^+, 7), 215 (8), 181 (9), 94 (100); HRMS $[M]^+$ for $C_{10}H_{10}ClIO$ 307.9465, found 307.9460.

(*Z*)-(3,4-Dibromobut-2-enyloxy)benzene (1s): 75%; oil; TLC (Et_2O/hexanes (1:10)) R_f = 0.65; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.24 (s, 2 H), 4.67 (d, *J* = 5.1 Hz, 2 H), 6.44 (t, *J* = 5.1 Hz, 1 H), 6.87 (d, *J* = 8.4 Hz, 2 H), 6.96 (t, *J* = 8.4 Hz, 1 H), 7.26−7.31 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.3 (CH_2), 67.3 (CH_2), 114.6 (CH × 2), 121.2 (CH), 123.5 (C), 129.6 (CH × 2), 130.5 (CH), 157.9 (C); MS *m*/*z* (rel intensity) 304 (M^+, 1), 259 (2), 225 (23), 94 (100); HRMS $[M]^+$ for $C_{10}H_{10}Br_2O$ 303.9098, found 303.9104.

General Procedure for Indium- or Zinc-Mediated Dehalogenation Reactions in an Aqueous Solvent to Form Allenes. A mixture of iodoallyl bromide substrate **1** (1.5 mmol), indium powder (325 mesh, 1.5 mmol), or zinc dust (325 mesh, 1.5 mmol) in THF (1.6 mL) and water (0.4 mL) was stirred at room temperature overnight. Water (2.0 mL) was added to the mixture, which was then extracted with Et_2O (3 × 5.0 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo, giving a residue which was subjected to silica gel chromatography to furnish the pure product **2** (hexanes).

(Buta-2,3-dienyloxy)benzene (2a): oil; TLC (EtOAc/hexanes (1:10)) R_f = 0.63; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.56 (dt, *J* = 6.9, 2.4 Hz, 2 H), 4.84 (dt, *J* = 6.9, 2.4 Hz, 2 H), 5.38 (quin, *J* = 6.9 Hz, 1 H), 6.89−6.97 (m, 3 H), 7.24−7.30 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 65.6 (CH_2), 76.4 (CH_2), 87.0 (CH), 114.7 (CH × 2), 120.8 (CH), 129.3 (CH × 2), 158.2 (C), 209.3 (C). These data are in agreement with those reported in the literature.[4b]

1-(Buta-2,3-dienyloxy)-4-chlorobenzene (2b): oil; TLC (EtOAc/hexanes (1:2)) R_f = 0.63; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.52 (dt, *J* = 6.9, 2.4 Hz, 2 H), 4.85 (dt, *J* = 6.9, 2.4 Hz, 2 H), 5.34 (quin, *J* = 6.9 Hz, 1 H), 6.79−6.85 (m, 2 H), 7.18−7.24 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 66.1 (CH_2), 76.6 (CH_2), 86.8 (CH), 116.2 (CH × 2), 125.8 (C), 129.3 (CH × 2), 156.9 (C), 209.4 (C). These data are in agreement with those reported in the literature.[18]

1-(Buta-2,3-dienyloxy)-4-methoxybenzene (2c): white solid; mp 43−44 °C (hexanes); TLC (EtOAc/hexanes (1:10)) R_f = 0.58; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 (s, 3 H), 4.50 (dt, *J* = 6.6, 2.7 Hz, 2 H), 4.84 (dt, *J* = 6.6, 2.7 Hz, 2 H), 5.37 (quin, *J* = 6.6 Hz, 1 H), 6.80−6.88 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.6 (CH_3), 66.5 (CH_2), 76.3 (CH_2), 87.3 (CH), 114.6 (CH × 2), 115.9 (CH × 2), 152.4 (C), 154.0 (C), 209.3 (C). These data are in agreement with those reported in the literature.[18]

1-(Buta-2,3-dienyloxy)-4-methylbenzene (2d): oil; TLC (EtOAc/hexanes (1:10)) R_f = 0.56; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3 H), 4.51−4.55 (m, 2 H), 4.82−4.86 (m, 2 H), 5.33−5.42 (m, 1 H), 6.79−6.83 (m, 2 H), 7.05−7.24 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5 (CH_3), 65.9 (CH_2), 76.4 (CH_2), 87.2 (CH), 114.7 (CH × 2), 129.9 (CH × 2), 130.2 (C), 156.2 (C), 209.4 (C). These data are in agreement with those reported in the literature.[18]

1-Bromo-3-(buta-2,3-dienyloxy)benzene (2e): oil; TLC (EtOAc/hexanes (1:10)) R_f = 0.67; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.53 (dt, *J* = 6.6, 2.4 Hz, 2 H), 4.88 (dt, *J* = 6.6, 2.4 Hz, 2 H), 5.36 (quin, *J* = 6.6 Hz, 1 H), 6.82−6.86 (m, 1 H), 7.06−7.15 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 65.9 (CH_2), 76.7 (CH_2), 86.6 (CH), 113.8 (CH), 118.1 (CH), 122.7 (C), 123.9 (CH), 130.4 (CH), 159.0 (C), 209.5 (C); MS *m*/*z* (rel intensity) 224 (M^+, 8), 226 (7), 174 (100), 145 (76); HRMS $[M]^+$ for $C_{10}H_9BrO$ 223.9837, found 223.9830.

2,4-Dibromo-1-(buta-2,3-dienyloxy)benzene (2f): oil; TLC (EtOAc/hexanes (1:10)) R_f = 0.60; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.60 (dt, *J* = 6.6, 2.4 Hz, 2 H), 4.85 (dt, *J* = 6.6, 2.4 Hz, 2 H), 5.36 (quin, *J* = 6.6 Hz, 1 H), 6.76 (d, *J* = 8.7 Hz, 1 H), 7.33 (dd, *J* = 8.7, 2.4 Hz, 1 H), 7.64 (d, *J* = 2.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 67.1 (CH_2), 76.9 (CH_2), 86.4 (CH), 113.2 (C × 2), 115.0 (CH), 131.0 (CH), 135.4 (CH), 154.0 (C), 209.4 (C); MS *m*/*z* (rel intensity) 302 (M^+, 1), 304 (2), 252 (100), 250 (50); HRMS $[M]^+$ for $C_{10}H_8Br_2O$ 301.8942, found 301.8948.

1-(Buta-2,3-dienyloxy)-2-iodobenzene (2g): oil; TLC (EtOAc/hexanes (1:10)) R_f = 0.55; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.60−4.64 (m, 2 H), 4.84−4.88 (m, 2 H), 5.40 (quin, *J* = 6.6 Hz, 1 H), 6.67−6.72 (m, 1 H), 6.82 (dd, *J* = 8.1, 1.2 Hz, 1 H), 7.23−7.29 (m, 1 H), 7.75 (dd, *J* = 7.8, 1.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 66.6 (CH_2), 76.6 (CH_2), 86.6 (CH), 86.7 (C), 112.5 (CH), 122.5 (CH), 129.0 (CH), 139.2 (CH), 156.5 (C), 208.9 (C). These data are in agreement with those reported in the literature.[19]

3-(Buta-2,3-dienyloxy)benzonitrile (2h): oil; TLC (Et_2O/hexanes (1:10)) R_f = 0.38; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.55−4.59 (m, 2 H), 4.86−4.90 (m, 2 H), 5.29−5.38 (m, 1 H), 7.10−7.14 (m, 2 H), 7.21−7.24 (m, 1 H), 7.32−7.37 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 66.0 (CH_2), 76.9 (CH_2), 86.3 (CH), 113.0 (C), 117.9 (CH), 118.6 (C), 120.1 (CH), 124.6 (CH), 130.2 (CH), 158.3 (C), 209.5 (C); MS *m*/*z* (rel intensity) 171 (M^+, 8), 156 (15), 119 (100), 91 (9); HRMS $[M]^+$ for $C_{11}H_9NO$ 171.0684, found 171.0689.

2-(Buta-2,3-dienyloxy)benzaldehyde (2i): oil; TLC (EtOAc/hexanes (1:11)) R_f = 0.30; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.65 (dt, *J* = 6.6, 2.7 Hz, 2 H), 4.87 (dt, *J* = 6.6, 2.7 Hz, 2 H), 5.38 (quin, *J* = 6.6 Hz, 1 H), 6.95−7.02 (m, 2 H), 7.47−7.53 (m, 1 H), 7.80 (dd, *J* = 7.8, 1.5 Hz, 1 H), 10.47 (d, *J* = 0.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 66.1 (CH_2), 77.0 (CH_2), 86.5 (CH), 112.9 (CH), 120.9 (CH), 125.1 (C), 128.3 (CH), 135.7 (CH), 160.7 (C), 189.8 (CH), 209.4 (C). These data are in agreement with those reported in the literature.[20]

Methyl 2-(buta-2,3-dienyloxy)benzoate (2j): oil; TLC (EtOAc/hexanes (1:10)) R_f = 0.25; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 3 H), 4.63−4.67 (m, 2 H), 4.82−4.86 (m, 2 H), 5.35−5.44 (m, 1 H), 6.94−6.99 (m, 2 H), 7.39−7.42 (m, 1 H), 7.72−7.80 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.8 (CH_3), 66.8 (CH_2), 76.5 (CH_2), 86.9 (CH), 114.0 (CH), 120.4 (CH), 120.8 (C), 131.5 (CH), 133.1 (CH), 157.7 (C), 166.6 (C), 209.2 (C); MS *m*/*z* (rel intensity) 204 (M^+, 2), 152 (31), 120 (100), 92 (26); HRMS $[M]^+$ for $C_{12}H_{12}O_3$ 204.0786, found 204.0781.

***N*-(2-(Buta-2,3-dienyloxy)phenyl)acetamide (2k):** white solid; mp 58−59 °C (hexanes); TLC (EtOAc/hexanes (1:10)) R_f = 0.25; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 3 H), 4.55−4.59 (m, 2 H), 4.86−4.90 (m, 2 H), 5.34−5.39 (m, 1 H), 6.82−6.98 (m, 3 H), 7.80 (br s, 1 H), 8.32 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.9 (CH_3), 66.0 (CH_2), 76.9 (CH_2), 86.9 (CH), 111.4 (CH), 120.0 (CH), 121.4 (CH), 123.4 (CH), 128.1 (C), 146.4 (C), 168.1 (C), 209.4 (C); MS *m*/*z* (rel intensity) 203 (M^+, 8), 161 (15), 134 (19), 109 (100); HRMS $[M]^+$ for $C_{12}H_{13}NO_2$ 203.0946, found 203.0949.

Buta-2,3-dienyl benzoate (2l): oil; TLC (EtOAc/hexanes (1:10)) R_f = 0.53; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.79−4.88 (m, 4 H), 5.40 (quin, *J* = 6.6 Hz, 1 H), 7.39−7.44 (m, 2 H), 7.51−7.57

(m, 1 H), 8.02−8.05 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 62.3 (CH_2), 76.7 (CH_2), 86.4 (CH), 128.3 (CH × 2), 129.6 (CH × 2), 130.1 (C), 133.0 (CH), 166.3 (C), 209.8 (C). These data are in agreement with those reported in the literature.[21]

Buta-2,3-dienylbenzene (2m): oil; TLC (EtOAc/hexanes (1:10)) R_f = 0.55; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.37 (dt, *J* = 6.6, 2.7 Hz, 2 H), 4.73 (dt, *J* = 6.6, 2.7 Hz, 2 H), 5.29 (quin, *J* = 6.6 Hz, 1 H), 7.20−7.34 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.0 (CH_2), 75.1 (CH_2), 89.5 (CH), 126.2 (CH), 128.4 (CH × 4), 140.2 (C), 209.0 (C). These data are in agreement with those reported in the literature.[22]

1-(Buta-2,3-dienyl)-4-methoxybenzene (2n): oil; TLC (EtOAc/hexanes (1:10)) R_f = 0.60; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.28 (dt, *J* = 6.6, 3.0 Hz, 2 H), 3.78 (s, 3 H), 4.70 (dt, *J* = 6.6, 3.0 Hz, 2 H), 5.24 (quin, *J* = 6.6 Hz, 1 H), 6.81−6.86 (m, 2 H), 7.12−7.16 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.2 (CH_2), 55.2 (CH_3), 75.0 (CH_2), 90.0 (CH), 113.7 (CH × 2), 129.3 (CH × 2), 132.3 (C), 158.0 (CH), 209.0 (C); MS *m*/*z* (rel intensity) 160 (M^+, 35), 159 (16), 145 (9), 121 (100); HRMS $[M]^+$ for $C_{11}H_{12}O$ 160.0888, found 160.0882.

***N*-(Buta-2,3-dienyl)-*N*-methylaniline (2o):** oil; TLC (EtOAc/hexanes (1:10)) R_f = 0.63; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.94 (s, 3 H), 3.95−3.99 (m, 2 H), 4.72−4.76 (m, 2 H), 5.14 (td, *J* = 6.6, 6.3 Hz, 1 H), 6.70−6.77 (m, 3 H), 7.20−7.27 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.0 (CH_3), 51.5 (CH_2), 75.8 (CH_2), 86.0 (CH), 112.9 (CH × 2), 116.7 (CH), 129.1 (CH × 2), 149.0 (C), 209.1 (C). These data are in agreement with those reported in the literature.[23]

Buta-2,3-dienyl(phenyl)sulfane (2p): oil; TLC (EtOAc/hexanes (1:10)) R_f = 0.47; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.52−3.56 (m, 2 H), 4.70−4.74 (m, 2 H), 5.23 (quin, *J* = 7.5 Hz, 1 H), 7.18−7.40 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.1 (CH_2), 76.1 (CH_2), 87.3 (CH), 126.2 (CH), 128.7 (CH × 2), 130.0 (CH × 2), 135.6 (C), 209.4 (C); MS *m*/*z* (rel intensity) 162 (M^+, 75), 147 (55), 129 (82), 110 (100); HRMS $[M]^+$ for $C_{10}H_{10}S$ 162.0503, found 162.0501.

ASSOCIATED CONTENT

Supporting Information. Copies of ^{1}H and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org).

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