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TBAF-Mediated Reactions of 1,1-Dibromo-1-alkenes with Thiols and Amines and Regioselective Synthesis of 1,2-Heterodisubstituted Alkenes

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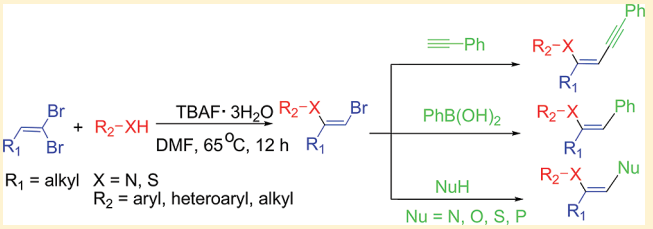
Supporting Information

ABSTRACT: An efficient synthesis of trisubstituted alkenes including 1,2-heterodisubstituted alkenes has been described. Reactions of thiols and amines with 1,1-dibromo-1-alkenes in the presence of TBAF·3H$_2$O afford (*Z*)-2-bromovinyl sulfides and (*Z*)-2-bromovinyl amines regio- and stereoselectively. The reaction proceeds under catalyst-free conditions with high efficiency. The coupling reactions of the obtained products bearing bromine atoms with phenylacetylene and phenylboronic acid gave trisubstituted alkenes in good to excellent yields. Cross-coupling with various N, O, S, and P nucleophiles selectively generated 1,2-N,O, 1,2-N,S, 1,2-S,P, 1,2-S,S, and 1,2-S,O heterodisubstituted alkenes.



INTRODUCTION

Vinyl sulfides and vinyl amines are important intermediates in the synthesis of biologically active compounds, medicines, and organic materials.[1,2] Thus the development of new synthetic methodologies for the construction of C(sp^2)−S/N bonds has been an important objective in organic synthesis. Metal-catalyzed hydrothiolation and hydroamination reactions of alkynes are the most attractive tools from the point of view of atom economy. Although sulfur compounds are often considered to be poisons to transition metal catalysts, hydrothiolation of alkynes has been reported to be catalyzed by Rh, Ni, Ir, Au, Pt, Pd, and organoactinide, organozirconium complexes.[3] Both Markovnikov and anti-Markovnikov adducts can be obtained depending on the metal catalyst and ligand selection. Hydroamination of alkynes is normally catalyzed by Ti, Zr, lanthanides, actinides, and late transition metal Pd, Ru, Rh, Ag, and Au catalysts.[4] Besides these metal catalysts, hydroamination of alkynes can also be promoted by a base. For example, tetrabutylammonium fluoride (TBAF) has been used to synthesize five- and six-membered heterocycles via 5-*exo-dig* and 6-*endo-dig* intramolecular hydroamination of alkynes.[5]

1,1-Dibromo-1-alkenes are easily available from aldehydes and may act as important building blocks for the synthesis of polysubstituted alkenes, 1,3-diynes, carboxamide, carbocycles, and heterocycles by metal-catalyzed C−C and C−X (X = N, O, S) coupling reactions.[6−10] 1,1-Dibromo-1-alkenes may also be used for synthesis of internal alkynes, (hetero)aryl alkynes, and ynamides as a convenient alternative of alkynyl bromides.[11−13] Very recently, we described the first aminothiolation of 1,1-dibromo-1-alkenes using inexpensive copper/*N*,*N*-dimethylethylenediamine catalyst leading to imidazol[2,1-*b*]thiazole and related *N*-fused heterocyles.[14] Here we report the hydrothiolation and hydroamination of alkynyl bromides, in situ generated from 1,1-dibromo-1-alkenes, and the regio- and stereoselective synthesis of trisubstituted alkenes including 1,2-N,O, 1,2-N,S, 1,2-S,P, 1,2-S,S, and 1,2-S,O heterodisubstituted alkenes from the resulting 2-bromovinyl sulfides and 2-bromovinyl amines.[15−18]

RESULTS AND DISCUSSION

It has been known that copper-catalyzed amination of 1,1-dibromo-1-alkenes with amide affords ynamides.[13] When we attempted the reaction of 1,1-dibromo-1-decene **1a** with 2-mercaptobenzimidazole **2a** under similar conditions, the aminothiolation took place to give an *N*-fused heterocylic product benzimidazol[2,1-*b*]thiazole. However, in the absence of a copper catalyst, the same reaction afforded selectively hydrothiolation product **3a** in an excellent yield (Scheme 1), and **3a** was characterized by X-ray diffraction analysis.[14] Vinyl sulfides are important intermediates in the synthesis of biologically active molecules and medicines. Furthermore, the sulfide bearing additional bromide offers opportunities for further functionalization to polysubstituted vinyl sulfides via various metal-catalyzed cross-coupling reactions.

To develop a general protocol for the preparation of 2-bromoalkenyl sulfides, metal salts including copper, palladium, and nickel salts, N- and P-donating ligands, solvents, and various inorganic and organic bases were screened with use of 1,1-dibromo-1-decene **1a** and 2-mercaptobenzimidazole **2a** as the model substrates. As listed in Table 1, the detailed studies showed

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that metal catalysts are not required, and the reaction could proceed in the presence of bases exclusively leading to (*Z*)-2-(1-bromooct-1-en-2-ylthio)-1*H*-benzimidazole **3a** (Table 1). No (*E*)-2-(1-bromooct-1-en-2-ylthio)-1*H*-benzimidazole and disulfide were observed. Although **2a** is an ambident nucleophile, no amination product **5** was observed when 1 equiv of **1a** was used. Bases are essential for the reaction and TBAF·3H_2O is the best among the bases examined. Tetrabutylammonium chloride (TBACl) and tetrabutylammonium bromide (TBAB) are totally ineffective (entries 15 and 16). In addition, DMF is more suitable than the other solvents (entries 14 and 17−20). Under the optimized conditions, **3a** was obtained in up to 81% yield (entry 14).

In the presence of 5 equiv of TBAF·3H_2O, a number of heteroaryl and aryl thiols could react with 1,1-dibromodecene providing 2-bromovinyl sulfides, and the results were summarized in Table 2. Heteroaryl thiols such as 2-mercaptoimidazole, 3-mercapto-1,2,4-triazole, and their derivatives gave high conversions and 75−98% isolated yields (Table 2, entries 1−5). Under the same reaction conditions, 2-mercaptobenzothiazole afforded the corresponding sulfide **3f** in moderate yield (entry 6). Likewise, 2-thioxo-2,3-dihydropyrimidin-4(1*H*)-one derivative gave quantitative conversions and excellent yield (entry 7). However, **3h** was isolated in only 60% yield in the case of 2-mercaptopyrimidin-4(1*H*)-one **2h** probably due to its large solubility in water (entry 8). 2-Mercaptopyridine gave high conversion and **3i** could be obtained in 91% isolated yields (entry 9). Imidazolidine-2-thione **2j** failed to react with 1,1-dibromodecene probably because it does not isomerize to its thiol form (entry 10). For thiophenol and their derivatives, 86−94% isolated yields of sulfides **3k**−**m** could be obtained (entries 11−13). Benzylthiol can also give the corresponding hydrothiolation product in relatively lower yield (46%) compared to aryl thiols together with 17% of alkyl sulfide (entry 14). With K_2CO_3 as the base, phenol reacted with 1,1-dibromodecene to give 2-bromovinyl phenyl ether **3o** at elevated temperature (entry 15). Compared to those thiols, the reaction of phenol is not clean and only ca. 25% of vinyl ether could be obtained. When 1,1-dibromo-1-alkenes bearing different alkyl substituents such as 1-hexyl, isopropyl, isobutyl, and cyclohexyl were heated with 4-toluenethiol at 65 °C in DMF in the presence of 5 equiv of

Scheme 1. Reactions of 1,1-Dibromo-1-alkene with Thiol

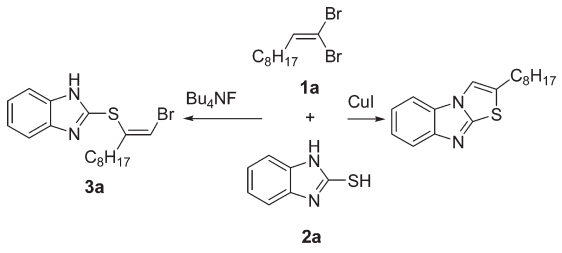
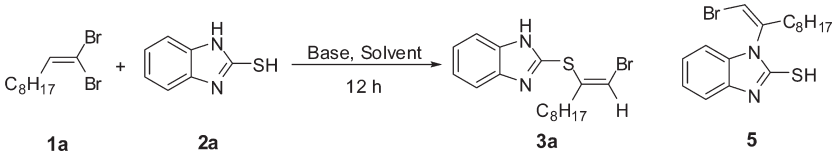


Table 1. Optimization of Reaction Conditions[a]



entry	metal/ligand[b]	solvent	base	*t* (°C)	yield (%)
1	CuI/DMEDA	DMF	Cs_2CO_3	110	0[d]
2	$Pd(OAc)_2$/dppf	DMF	Cs_2CO_3	110	49
3	$NiCl_2$/dmdi	DMF	Cs_2CO_3	110	57
4	CuI/DMEDA	DMF	TBAF·3H_2O	65	0[e]
5		DMF	Cs_2CO_3	110	52
6		DMF	K_3PO_3	65	45
7		DMF	K_2CO_3	65	69
8		DMF	Cs_2CO_3	65	55
9		DMF	Cs_2CO_3	rt	0
10		DMF	NEt_3	65	trace
11		DMF	KF	65	0
12		DMF		65	0
13		DMF	DBU[c]	65	78
14		DMF	TBAF·3H_2O	65	81
15		DMF	TBACl	65	0
16		DMF	TBAB	65	0
17		toluene	DBU	65	trace
19		dioxane	TBAF·3H_2O	65	80
20		THF	TBAF·3H_2O	65	79

[a] Reactions were carried out with **1a** (0.6 mmol), **2a** (0.5 mmol), base (2.5 mmol), and solvent (1.5 mL), 12 h, under N_2. [b] DMEDA = *N*,*N*′-dimethylethanediamine; dppf = 1,1′-bis(diphenyphosphino)ferrocene; dmdi = 1,1′-dimethyl-3,3′-methylenediimidazolium dibromide. [c] DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. [d] Benzimidazo[2,1-*b*]thiazole was obtained in 43% yields. [e] Benzimidazo[2,1-*b*]thiazole was obtained in 81% yields.

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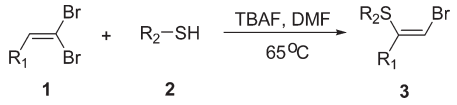
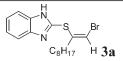
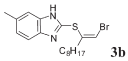
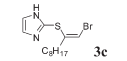
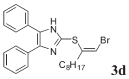
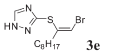
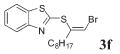
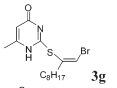
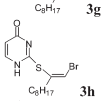
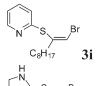
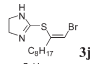
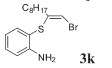
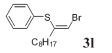
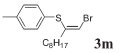
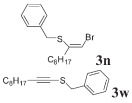
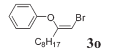
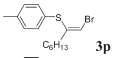
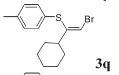
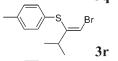
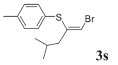
Table 2. Reactions of 1,1-Dibromo-1-alkenes with Various Thiols [a]



entry	1,1-dibromo-1-alkene	thiol	product	yield (%)
1	 **1a**	 **2a**	 **3a**	81
2	**1a**	 **2b**	 **3b**	75
3	**1a**	 **2c**	 **3c**	79
4	**1a**	 **2d**	 **3d**	98
5	**1a**	 **2e**	 **3e**	82
6	**1a**	 **2f**	 **3f**	64
7	**1a**	 **2g**	 **3g**	99
8	**1a**	 **2h**	 **3h**	60
9	**1a**	 **2i**	 **3i**	91
10	**1a**	 **2j**	 **3j**	-
11	**1a**	 **2k**	 **3k**	86
12	**1a**	 **2l**	 **3l**	93
13	**1a**	 **2m**	 **3m**	94
14	**1a**	 **2n**	 **3n** **3w**	46 (**3n**), 17 (**3w**) [b]
15	**1a**	 **2o**	 **3o**	25 [c]
16	 **1b**	**2m**	 **3p**	93
17	 **1c**	**2m**	 **3q**	93
18	 **1d**	**2m**	 **3r**	83
19	 **1e**	**2m**	 **3s**	95
20	**1f**	**2m**	**3t**	77
21	**1a**	**2a**	**3u**	83 [d]

[a] Reaction conditions: 1,1-dibromo-1-alkenes **1** (0.6 mmol), thiols **2** (0.5 mmol), TBAF·$3H_2O$ (2.5 mmol), and DMF (1.5 mL), 65 °C, 12 h, under N_2. [b] **3n** and **3w** could not be separated by column chromatography. [c] K_2CO_3 (1.0 mmol), 110 °C. [d] 5 equiv of **1a** was used.

Table 3. Reactions of 1,1-Dibromo-1-alkene with Various Amines [a]

entry	1,1-dibromo-1-alkene	amine	product	yield (%)
1	**1a**	**4a**	**5a**	85
2	**1a**	**4b**	**5b**	41
3	**1a**	**4c**	**5c**	77
4	**1a**	**4d**	**5d**	-
5	**1a**	**4e**	**5e**	48
6	**1b**	**4a**	**5f**	75
7	**1c**	**4a**	**5g**	83
8	**1d**	**4a**	**5h**	76
9	**1e**	**4a**	**5i**	75
10	**1a**	**4f**	**5j**	40 [b]
11	**1f**	**4f**	**5k**	53 [b]
12	**1g**	**4f**	**5l**	61 [b]
13	**1h**	**4f**	**5m**	74 [b]
14	**1i**	**4f**	**5n**	55 [b]
15	**1j**	**4f**	**5o**	68 [b]
16	**1k**	**4f**	**5p**	59 [b]

[a] Reaction conditions: 1,1-dibromo-1-alkenes **1** (0.6 mmol), amines **4** (0.5 mmol), TBAF·$3H_2O$ (2.5 mmol), and DMF (1.5 mL), 65 °C, 12 h. [b] Cs_2CO_3 (1.5 mmol), 110 °C, 24 h.

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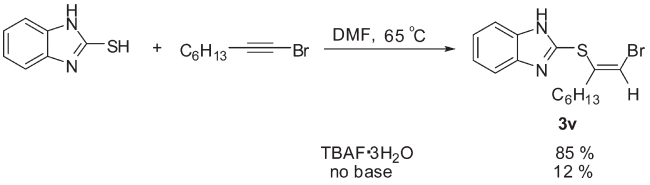
TBAF·3H_2O, the reactions occurred via hydrothiolation of alkynyl bromide regio- and stereoselectively affording 2-bromovinyl sulfides in excellent yields (entries 16−19). Unlike these aliphatic 1,1-dibromo-1-alkenes, the reaction with 1,1-dibromostyrene afforded phenylethynyl *p*-tolyl sulfide **3t** other than 2-bromovinyl sulfide (entry 20). It seems that nucleophilic substitution of alkynyl bromide is favored in the case of aromatic substrate, whereas nucleophilic addition reaction is facile in the case of aliphatic 1,1-dibromo-1-alkenes.

The above results show that the ambident nucleophiles containing SH and NH moieties did not yield *N*-substituted products when 1 equiv of 1,1-dibromo-1-alkene was used, illustrating that N−H bond is less reactive than the S−H bond. This is probably because thiols are more acidic than imidazoles. The generation of more nucleophilic thiolates is more facile than imidazolates, and thus nucleophilic addition of SH is favored. However, when 5 equiv of 1,1-dibromo-1-alkene was used, both N- and S-vinylation occurred giving the final product **3u** in 83% yield (entry 21). The result tells that the N−H group also reacted with 1,1-dibromo-1-alkene in the presence of TBAF·3H_2O. Actually, in copper-catalyzed coupling reactions of alkynyl bromides with imidazoles to alkynylimidazoles, the N−H addition to alkynyl bromide has been found to give *N*-bromovinylimidazole as a side product in 20% yield.[19] It was also reported that 1,1-dibromo-1-alkene is converted to ketene *N*,*N*-acetal via CuI/DMEDA-catalyzed double amidation.[13b] The reaction is thought to proceed through a regioselective C−N monocoupling followed by dehydrobromination and hydroamination. To examine the possibility of preparation of 2-bromovinylamine and bromovinylimines, a few NH containing compounds were subjected to reactions with 1,1-dibromo-1-alkene, and the results are summarized in Table 3.

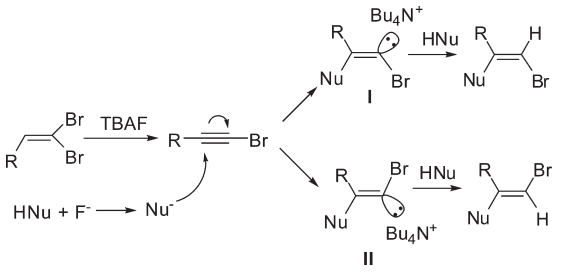
NH-containing heteroarenes such as imidazole, benzoimidazole, and triazole could react with 1,1-dibromo-1-alkenes giving (*Z*)-bromovinylheteroarenes **5a**−**c** (Table 3, entries 1−3). However, indole is not a suitable substrate, and the expected (*Z*)-1-(1-bromodec-1-en-2-yl)-1*H*-indole **5d** was not formed presumably due to the weaker acidity of NH (pK_a = 16.2) (entry 4). Sulfonamide **4e** reacted with **1a** affording 2-bromovinylamine **5e** in a low yield (entry 5). Similarly, 1,1-dibromo-1-alkenes (**1b**−**e**) bearing different substituents afforded *N*-(*Z*)-bromovinylbenzoimidazole derivatives **5f**−**i** selectively (entries 6−9). Recently, copper-catalyzed 1,2-double amination of alkynyl bromides or 1,1-dibromo-1-alkenes with *N*,*N*′-ethylenedi(toluenesulfonamide) **4f** to tetrahydropyrazines has been briefly described.[20] However, we found that in the absence of a copper catalyst, the reaction between **4f** and 1,1-dibromo-1-decene did not lead to cyclization but afforded double 2-bromovinylated product **5j** (entry 10). The structure of **5j** has been unambiguously determined by X-ray diffraction analysis.[21] However, the cyclization reaction of aromatic 1,1-dibromo-1-alkenes with **4f** could proceed yielding tetrahydropyrazine derivatives even without using a copper catalyst (entries 11−16). In the case of 1,1-dibromostyrene, the yield of the copper-free cyclization reaction is comparable to the reported value.[20] 2-(2,2-Dibromovinyl)thiophene and aromatic dibromoalkenes bearing halogen substituents at the phenyl rings are more reactive than 1,1-dibromostyrene. To confirm the structure of the cyclization product, the structure of **5l** was determined by X-ray diffraction analysis.[21] In the NOESY spectra of **3m** and **5a** (see the Supporting Information), the olefinic protons show NOE cross peaks to their corresponding methylene protons of the octyl groups illustrating their *Z*-configuration.

It is known that 1,1-dibromo-1-alkene is easily converted to alkynyl bromide under basic conditions, and TBAF is the most effective base for dehydrobromination.[22] Thus the reaction is reasonably assumed

Scheme 2. TBAF·3H_2O-Promoted Hydrothiolation of Alkynyl Bromide



Scheme 3. Plausible Mechanism of Hydrothiolation/Hydroamination of 1,1-Dibromo-1-alkene



to take place via nucleophilic addition of the S−H bond to alkynyl bromide. Actually, 1-octynyl bromide reacted with 2-mercaptobenzimidazole giving the addition product **3v** in 85% yield in the presence TBAF·3H_2O in DMF (Scheme 2). Without TBAF·3H_2O, the reaction afforded the same product in much lower yield illustrating that the base also plays an important role in the nucleophilic addition reaction.

A proposed mechanism is shown in Scheme 3 based on the classical base-promoted hydrothiolation reactions of alkynes.[23] The reaction would take place via nucleophilic addition of 1-bromoalkyne, which is more electrophilic than normal alkynes. A nucleophile would attack the more electron-deficient carbon atom adjacent to the alkyl group. Anti addition leads to the energetically preferable alkenyl anion **I** other than **II**. The configuration of **I** is expected since the negative charge and the negatively charged thiolate group would tend to be as far apart as possible. In addition, the allylic strain between bromine and the allylic substituent also disfavors the generation of **II**. Subsequent hydrogen abstraction from HNu would regio- and stereoselectively give the (*Z*)-product.

These products bearing bromine atoms at their double bonds are potentially versatile building materials in organic synthesis which could offer opportunities for further functionaliztion through metal-catalyzed coupling reactions with various nucleuophiles. The utilization of 2-bromovinyl sulfides was illustrated by using **3m** as the model substrate, and the results were shown in Scheme 4. The coupling reactions afforded trisubstituted alkenes in good to excellent yields. As expected, under typical Sonogashira conditions (5 mol % of $Pd(PPh_3)_2Cl_2$ and 5 mol % of CuI), **3m** could couple with phenylacetylene affording the enyne product **6** in a nearly quantitative yield. Suzuki coupling of **3m** with phenylboronic acid gave **7** in 74% yield. More importantly, our methodology can also be used for the preparation of 1,2-heterodisubstituted (S,S; S,O; S,N; S,P; N,S; and N,O) olefins. When 10 mol % of CuI, 15 mol % of DMEDA, and 2 equiv of Cs_2CO_3 were used at 110 °C, the coupling of **3m** with imidazole or benzimidazole gave *N*-vinylimidazole

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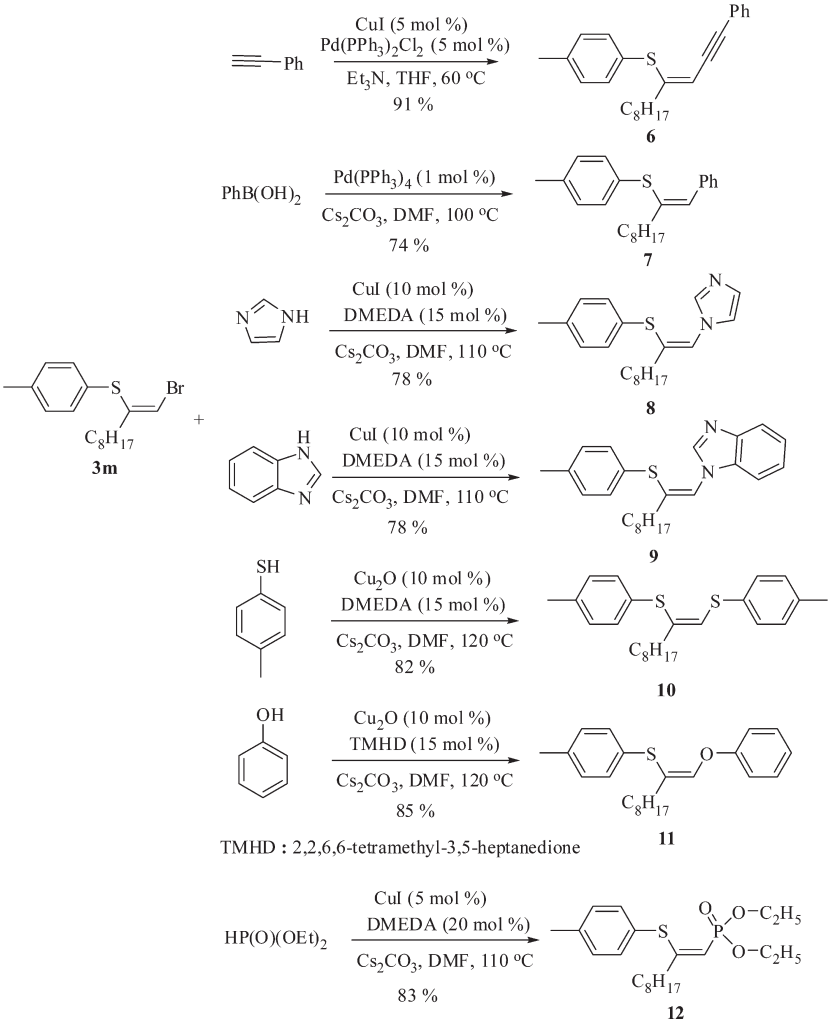
Scheme 4. Metal-Catalyzed Coupling Reactions of 3m



derivatives **8** and **9** in 78% yields. When phenol and thiophenol were used, copper-catalyzed C−O and C−S coupling reactions could be achieved to generate 1,2-diarylthio alkene **10** and 1-arylthio-2-alkoxyl alkene **11** in 82% and 85% yields, respectively. The NOESY spectrum of **10** shows NOE cross peak of the alkenic proton to the methylene protons of the octyl group, indicating that the *Z*-configuration maintains. Under similar reaction conditions, the C−P coupling reaction of diethyl phosphite with **3m** gave **12** in 83% yield.

We also attempted the coupling reactions of *N*-(2-bromovinyl)benzimidazole **5a** with different nucleophiles to synthesize trisubstituted alkenes, and the results are shown in Scheme 5. The trisubstituted alkenes **13**, **14** and 1,2-diheteroalkenes **15**, **16** could be successfully obtained in good yields.

1,2-Heterodisubstituted olefins are useful building blocks in organic synthesis and considerable effort has been made to develop efficient methods for preparation of them. However, most of the synthetic methods reported suffer many limitations, such as low yields, poor stereoselectivity, extreme reaction conditions, or requirement of precious metals. The procedures presented above provide a general and practical synthetic approach to 1,2-heterodisubstituted olefins via hydroelementation and subsequent copper-catalyzed C−X (X = N, O, S, P) coupling reactions.

CONCLUSIONS

In summary, TBAF·3H_2O-promoted reactions of thiols and amines with 1,1-dibromo-1-alkenes have been investigated leading to various 2-bromovinyl sulfides and 2-bromovinyl amines in good to excellent yields and selectivity. The reactions are assumed to proceed via nucleophilic addition of S−H or N−H to alkynyl bromide in situ generated from the dehydrobromination of 1,1-dibromo-1-alkenes in the presence of TBAF·3H_2O. These sequential thiolation (amination)/C−X coupling reactions offer an easy access to highly functionalized alkenes bearing various heteroatom substituents, which might be useful intermediates for the synthesis of organic compounds with interesting chemical and biological properties.

EXPERIMENTAL SECTION

Representative Procedure for Thiolation of 1,1-Dibromo-1-alkenes:

Synthesis of (*Z*)-2-(1-Bromodec-1-en-2-ylthio)-1*H*-benzimidazole (3a).[14] To a stirred solution of 2-mercaptobenzimidazole (75 mg, 0.5 mmol) and TBAF·3H_2O (788 mg, 2.5 mmol) in DMF (1.0 mL) was added 1,1-dibromo-1-decene (179 mg, 0.6 mmol) in 0.5 mL of DMF under nitrogen. The resulting mixture was stirred at

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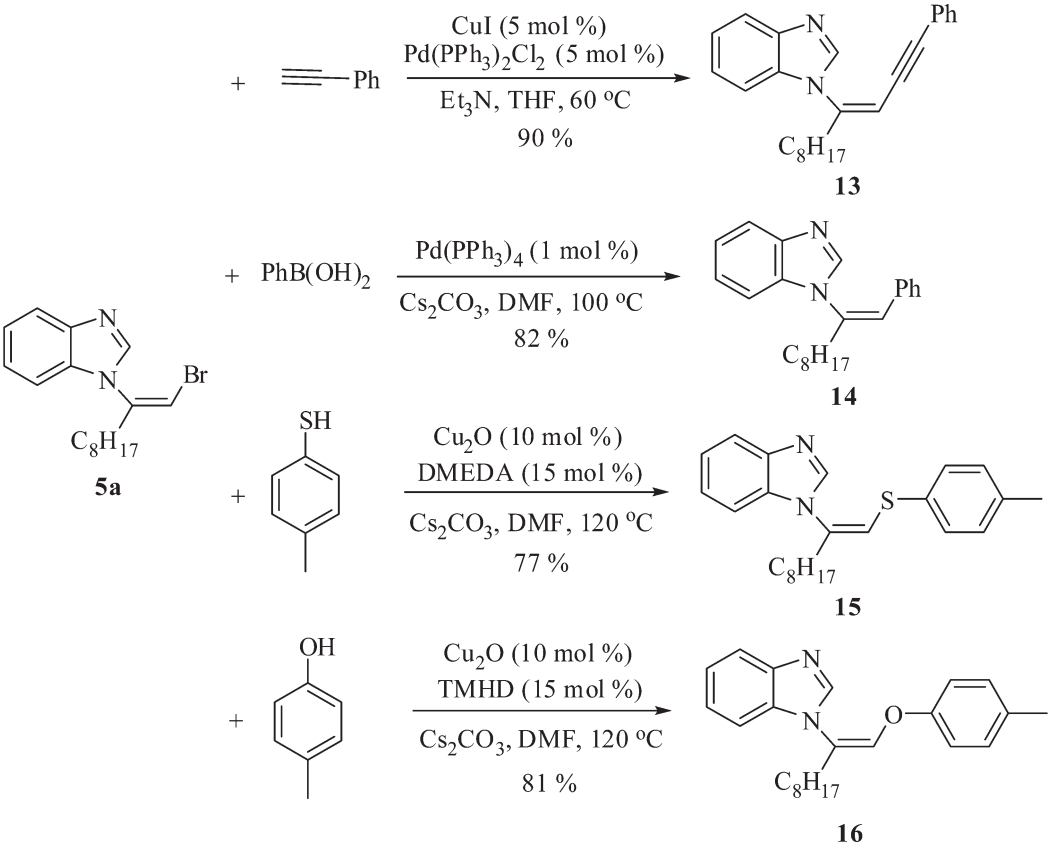
Scheme 5. Metal-Catalyzed Coupling Reactions of 5a



65 °C for 12 h. After being cooled to room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was further purified by flash column chromatography, using petroleum ether (PE) and ethyl acetate (EA) as the eluent (PE/EA = 3/1). White solid (149 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (br, 1H), 7.76 (br, 1H), 7.43 (br, 1H), 7.28−7.26 (m, 2H), 6.46 (s, 1H), 2.32 (t, J = 7.4 Hz, 2H), 1.48−1.45 (m, 2H), 1.24−1.14 (m, 10H), 0.84 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 139.5, 122.9, 106.9, 37.0, 31.7, 29.1, 29.0, 28.7, 28.1, 22.6, 14.1.

(*Z*)-2-(1-Bromodec-1-en-2-ylthio)-6-methyl-1*H*-benzimidazole (3b): white solid (143 mg, 75%); mp 163−164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.28 (br, 1H), 7.53−7.42 (m, 2H), 7.10 (d, J = 8.8 Hz, 1H), 6.34 (s, 1H), 2.47 (s, 3H), 2.30 (t, J = 7.4 Hz, 2H), 1.45−1.40 (m, 2H), 1.23−1.12 (m, 10H), 0.83 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 139.9, 132.9, 124.5, 105.8, 36.9, 31.7, 29.1, 28.8, 28.1, 22.6, 21.7, 14.1; IR (KBr) 3068, 2924, 2852, 2607, 1741, 1625, 1588, 1454, 1401, 1343, 1237, 987, 943, 804, 731, 631 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{18}H_{25}BrN_2S$ 380.0922, found 380.0912.

(*Z*)-2-(1-Bromodec-1-en-2-ylthio)-1*H*-imidazole (3c): white solid (125 mg, 79%); mp 85−86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.79 (br, 1H), 7.25 (s, 2H), 6.14 (s, 1H), 2.04 (t, J = 7.6 Hz, 2H), 1.40−1.36 (m, 2H), 1.27−1.12 (m, 10H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 134.5, 125.1, 100.9, 36.0, 31.7, 29.1, 29.0, 28.8, 28.0, 22.6, 14.0; IR (KBr) 3446, 3065, 2997, 2924, 2751, 2633, 1844, 1616, 1580, 1416, 1326, 1099, 963, 767 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{13}H_{21}BrN_2S$ 316.0609, found 316.0619.

(*Z*)-2-(1-Bromodec-1-en-2-ylthio)-4,5-diphenyl-1*H*-imidazole (3d):[14] white solid (230 mg, 98%); NMR (400 MHz, $CDCl_3$) δ 10.85 (br, 1H), 7.46−7.28 (m, 10H), 6.10 (s, 1H), 2.09 (t, J = 7.6 Hz, 2H), 1.46−1.40 (m, 2H), 1.26−1.15 (m, 10H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 134.8, 128.4, 127.9, 127.5, 101.5, 36.2, 31.8, 29.2, 29.1, 28.9, 28.1, 22.6, 14.1.

(*Z*)-3-(1-Bromodec-1-en-2-ylthio)-1*H*-1,2,4-triazole (3e): light yellow oil (130 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.78 (br, 1H), 8.38 (s, 1H), 6.33 (s, 1H), 2.20 (t, J = 7.4 Hz, 2H), 1.42−1.39 (m, 2H), 1.24−1.14 (m, 10H), 0.81 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 146.5, 139.5, 105.8, 36.5, 31.7, 29.09, 29.07, 28.6, 27.8, 22.5, 14.0; IR (neat) 2969, 2921, 1583, 1458, 1403, 1239, 1073, 868, 721 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{12}H_{20}BrN_3S$ 317.0561, found 317.0573.

(*Z*)-2-(1-Bromodec-1-en-2-ylthio)benzo[*d*]thiazole (3f): light yellow oil (123 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 6.73 (s, 1H), 2.53 (t, J = 7.4 Hz, 2H), 1.57−1.52 (m, 2H), 1.27−1.21 (m, 10H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 153.6, 139.2, 136.1, 126.2, 124.9, 122.4, 121.0, 112.8, 37.7, 31.7, 29.1, 29.0, 28.7, 28.2, 22.6, 14.1; IR (neat) 2969, 2923, 2853, 1582, 1458, 1423, 1238, 1074, 988, 802, 755, 725, 675 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{17}H_{22}BrNS_2$ 383.0377, found 383.0378.

(*Z*)-2-(1-Bromodec-1-en-2-ylthio)-6-methylpyrimidin-4(1*H*)-one (3g): white solid (178 mg, 99%); mp 67−68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.76 (br, 1H), 6.85 (s, 1H), 6.09 (s, 1H), 2.53 (t, J = 7.4 Hz, 2H), 2.26 (s, 3H), 1.56−1.53 (m, 2H), 1.29−1.26 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.1, 157.7, 136.1, 115.4, 109.0, 37.9, 31.7, 29.2, 29.1, 28.8, 27.9, 24.0, 22.6, 14.0; IR (KBr) 3447, 2923, 2853, 1663, 1580, 1549,1397, 1237, 1174,

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959, 841, 561 cm^{-1}; HRMS (TOF MS EI^+) m/z calcd for $C_{15}H_{23}BrN_2OS$ 358.0714, found 358.0703.

(*Z*)-2-(1-Bromodec-1-en-2-ylthio)pyrimidin-4(1*H*)-one (3h): white solid (104 mg, 60%); mp 81−82 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 12.45 (br, 1H), 7.88 (d, J = 6.4 Hz, 1H), 6.89 (s, 1H), 6.29 (d, J = 6.8 Hz, 1H), 2.55 (t, J = 7.6 Hz, 2H), 1.58−1.54 (m, 2H), 1.32−1.27 (br, 10H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 159.4, 155.3, 135.9, 116.5, 111.7, 38.1, 31.7, 29.2, 29.1, 28.8, 28.0, 22.6, 14.0; IR (KBr) 3447, 3085, 3038, 2926, 2854, 1685, 1626, 1567, 1537, 1450, 1272, 1777, 1073, 982, 917, 847 cm^{-1}; HRMS (TOF MS EI^+) m/z calcd for $C_{14}H_{21}BrN_2OS$: 344.0558, found 344.0550.

(*Z*)-2-(1-Bromodec-1-en-2-ylthio)pyridine (3i): light yellow oil (149 mg, 91%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 4.8 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.07−7.04 (m, 1H), 6.61 (s, 1H), 2.40 (t, J = 7.4 Hz, 2H), 1.49−1.44 (m, 2H), 1.26−1.18 (m, 10H), 0.84 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 150.0, 139.9, 136.7, 123.8, 120.7, 110.7, 37.4, 31.7, 29.1, 29.0, 28.7, 28.1, 22.6, 14.0; IR (neat) 2978, 2921, 1573, 1450, 1412, 1249, 1052, 893, 758, 722 cm^{-1}; HRMS (TOF MS EI^+) m/z calcd for $C_{15}H_{22}BrNS$ 327.0656, found 327.0666.

(*Z*)-2-(1-Bromodec-1-en-2-ylthio)aniline (3k): light yellow oil (147 mg, 86%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.6 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 6.72 (d, J = 7.6 Hz, 1H), 6.70 (t, J = 7.2 Hz, 1H), 6.21 (s, 1H), 4.20 (s, 2H), 1.98 (t, J = 7.6 Hz, 2H), 1.41−1.12 (m, 12H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 142.7, 137.2, 131.0, 118.3, 115.0, 113.1, 101.2, 35.2, 31.8, 29.1, 28.7, 28.1, 22.6, 14.1; IR (neat) 3472, 3372, 2923, 1731, 1608, 1479, 1448, 1246, 1072, 746 cm^{-1}; HRMS (TOF MS EI^+) m/z calcd for $C_{16}H_{24}BrNS$ 341.0813, found 341.0818.

(*Z*)-(1-Bromodec-1-en-2-yl)(phenyl)sulfane (3l): light yellow oil (152 mg, 93%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.2 Hz, 2H), 7.33−7.29 (m, 3H), 6.31 (s, 1H), 2.14 (t, J = 7.6 Hz, 2H), 1.44−1.39 (m, 2H), 1.28−1.15 (m, 10H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 133.3, 132.3, 129.2, 128.2, 104.3, 36.4, 32.0, 29.4, 29.3, 28.9, 28.4, 22.9, 14.3; IR (neat) 2966, 2924, 2853, 1581, 1473, 1438, 1211, 1023, 741, 691, 652 cm^{-1}; HRMS (TOF MS EI^+) m/z calcd for $C_{16}H_{23}BrS$ 326.0704, found 326.0705.

(*Z*)-(1-Bromodec-1-en-2-yl)(*p*-tolyl)sulfane (3m): light yellow oil (160 mg, 94%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.23 (s, 1H), 2.36 (s, 3H), 2.10 (t, J = 7.4 Hz, 2H), 1.42−1.37 (m, 2H), 1.29−1.13 (m, 10H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 138.2, 133.7, 129.8, 128.2, 102.4, 35.9, 31.8, 29.1, 29.0, 28.6, 28.2, 22.6, 21.2, 14.1; IR (neat) 2923, 2853, 1578, 1490, 1459, 1245, 1073, 1019, 808, 725 cm^{-1}; HRMS (TOF MS EI^+) m/z calcd for $C_{17}H_{25}BrS$ 340.0860, found 340.0859.

(*Z*)-Benzyl(1-bromodec-1-en-2-yl)sulfane (3n) and benzyl(dec-1-ynyl)sulfane (3w): obtained as a mixture, which could not be separated by column chromatography. **3n** (79 mg, 46%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.32 (m, 5H), 6.17 (s, 1H), 4.01 (s, 2H), 2.27 (t, J = 8.0 Hz, 2H), 1.56−1.46 (m, 2H), 1.28 (br, 10H), 0.91 (t, J = 6.8 Hz, 3H). **3w** (23 mg, 17%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.30−7.24 (m, 5H), 3.89 (s, 1H), 2.27 (t, J = 8.0 Hz, 2H), 1.56−1.46 (m, 2H), 1.28 (br, 10H), 0.91 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 137.2, 137.0, 128.9, 128.8, 128.5, 128.4, 127.5, 127.2, 103.3, 96.0, 67.9, 40.2, 36.6, 35.6, 31.8, 31.7, 29.2, 29.1, 29.0, 28.9, 28.8, 28.7, 28.2, 22.6, 20.1, 14.0; IR (neat) 2924, 2853, 1576, 1494, 1455, 1236, 1070, 762, 698 cm^{-1}; HRMS (TOF MS EI^+): **3n** m/z calcd for $C_{17}H_{25}BrS$ 340.0860, found 340.0872; **3w** m/z calcd for $C_{17}H_{24}S$ 260.1599, found 260.1595.

(*Z*)-(1-Bromodec-1-en-2-yloxy)benzene (3o): light yellow oil (39 mg, 25%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, J = 8.2 Hz, 2H), 7.07 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 5.76 (s, 1H), 2.24 (t, J = 7.4 Hz, 2H), 1.50−1.45 (m, 2H), 1.30−1.26 (m, 10H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 155.0, 129.5, 122.6, 116.8, 91.3, 32.1, 31.8, 29.2, 29.1, 28.8, 26.3, 22.6, 14.0; IR (neat) 2925, 2854, 1645, 1592, 1489, 1215, 1163, 920, 749, 690 cm^{-1}; HRMS (TOF MS EI^+) m/z calcd for $C_{16}H_{23}BrO$ 310.0932, found 310.0934.

(*Z*)-(1-Bromooct-1-en-2-yl)(*p*-tolyl)sulfane (3p): light yellow oil (146 mg, 93%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.6 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H), 6.19 (s, 1H), 2.32 (s, 3H), 2.07 (t, J = 7.6 Hz, 2H), 1.37−1.33 (m, 2H), 1.20−1.10 (m, 6H), 0.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 138.2, 133.7, 129.8, 128.1, 102.4, 35.9, 31.4, 28.3, 28.1, 22.4, 21.2, 14.0; IR (neat) 2966, 2923, 1576, 1491, 1455, 1401, 1234, 1068, 891, 808, 728 cm^{-1}; HRMS (TOF MS EI^+) m/z calcd for $C_{15}H_{21}BrS$ 312.0547, found 312.0543.

(*Z*)-(2-Bromo-1-cyclohexylvinyl)(*p*-tolyl)sulfane (3q): light yellow oil (145 mg, 93%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.41 (s, 1H), 2.34 (s, 3H), 2.02 (t, J = 11.8 Hz, 1H), 1.88 (d, J = 12.8 Hz, 2H), 1.70 (d, J = 11.2 Hz, 2H), 1.60 (m, 1H), 1.27−1.18 (m, 2H), 1.14−1.01 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 137.3, 131.7, 129.8, 129.5, 106.6, 44.9, 32.8, 26.4, 26.0, 21.1; IR (neat) 2979, 2923, 1565, 1489, 1447, 1402, 1247, 1053, 892, 805, 647 cm^{-1}; HRMS (TOF MS EI^+) m/z calcd for $C_{15}H_{19}BrS$ 310.0391, found 310.0388.

(*Z*)-(1-Bromo-3-methylbut-1-en-2-yl)(*p*-tolyl)sulfane (3r): light yellow oil (112 mg, 83%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31−7.28 (m, 2H), 7.14 (d, J = 7.6 Hz, 2H), 6.43 (d, J = 0.8 Hz, 1H), 2.46−2.39 (m, 1H), 2.36 (s, 3H), 1.11 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 137.7, 132.3, 130.1, 129.6, 106.0, 35.0, 22.3, 21.4; IR (neat) 2964, 2925, 1573, 1490, 1459, 1232, 1108, 997, 806, 758 cm^{-1}; HRMS (TOF MS EI^+) m/z calcd for $C_{12}H_{15}BrS$ 270.0078, found 270.0077.

(*Z*)-(1-Bromo-4-methylpent-1-en-2-yl)(*p*-tolyl)sulfane (3s): light yellow oil (135 mg, 95%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.6 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.21 (s, 1H), 2.36 (s, 3H), 1.97 (d, J = 6.8 Hz, 2H), 1.80−1.74 (m, 1H), 0.77 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 138.2, 133.7, 129.7, 128.1, 103.1, 45.0, 26.4, 21.8, 21.2; IR (neat) 2985, 2922, 1576, 1491, 1459, 1385, 1254, 1212, 1068, 892, 808, 745 cm^{-1}; HRMS (TOF MS EI^+) m/z calcd for $C_{13}H_{17}BrS$ 284.0234, found 284.0245.

(2-*p*-Tolylsulfanylethynyl)benzene (3t):[24] white solid (86 mg, 77%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.52−7.50 (m, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.37−7.33 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 131.9, 130.3, 129.5, 128.8, 128.6, 126.9, 123.3, 97.5, 76.4, 21.3.

1-((*Z*)-1-Bromodec-1-en-2-yl)-2-((*Z*)-1-bromodec-1-en-2-ylthio)-1*H*-benzimidazole (3u): light yellow oil (242 mg, 83%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80−7.77 (m, 1H), 7.31−7.27 (m, 1H), 7.19−7.16 (m, 1H), 6.64 (s, 1H), 6.52 (s, 1H), 2.67−2.56 (m, 2H), 2.49−2.41 (m, 2H), 1.54−1.51 (m, 2H), 1.46−1.38 (m, 2H), 1.33−1.20 (m, 20H), 0.88−0.83 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.4, 140.3, 138.9, 134.9, 123.4, 122.7, 119.6, 110.3, 108.5, 107.5, 36.9, 36.4, 31.74, 31.71, 29.2, 29.12, 29.10, 29.08, 29.03, 28.7, 28.1, 26.8, 22.6, 14.0; IR (neat) 2923, 2853, 1585, 1428, 1365, 1263, 798, 739 cm^{-1}; HRMS (TOF MS EI^+) m/z calcd for $C_{27}H_{40}Br_2N_2S$ 582.1279, found 582.1273.

(*Z*)-2-(1-Bromooct-1-en-2-ylthio)-1*H*-benzimidazole (3v): white solid (144 mg, 85%); mp 123−125 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 10.48 (br, 1H), 7.66−7.62 (m, 2H), 7.28−7.25 (m, 2H), 6.33 (s, 1H), 2.35 (t, J = 7.6 Hz, 2H), 1.48−1.41 (m, 2H), 1.18−1.04 (m, 6H), 0.77 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 139.8, 139.7, 123.2, 115.3, 107.1, 37.3, 31.6, 28.6, 28.3, 22.7, 14.2; IR (KBr) 3447, 3072, 2954, 2926, 2606, 1584, 1407, 1351, 1267, 1230, 975, 834, 745 cm^{-1}; HRMS (TOF MS EI^+) m/z calcd for $C_{15}H_{19}BrN_2S$ 338.0452, found 338.0456.

Representative Procedure for Amination of 1,1-Dibromo-1-alkenes:

Synthesis of (*Z*)-1-(1-Bromodec-1-en-2-yl)-1*H*-benzimidazole (5a) To a stirred solution of benzoimidazole (59 mg, 0.5 mmol) and TBAF·$3H_2O$ (788 mg, 2.5 mmol) in DMF (1.0 mL) was added

1,1-dibromo-1-decene (179 mg, 0.6 mmol) in 0.5 mL of DMF. The resulting mixture was stirred at 65 °C for 12 h. After being cooled to room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was further purified by flash column chromatography, using petroleum ether (PE) and ethyl acetate (EA) as the eluent (PE/EA = 3/1). Light yellow oil (142 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.83−7.81 (m, 1H), 7.30−7.27 (m, 3H), 6.47 (s, 1H), 2.54 (t, J = 6.6 Hz, 2H), 1.24−1.16 (m, 12H), 0.82 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 141.8, 140.2, 132.4, 123.5, 122.6, 120.5, 110.8, 104.1, 36.1, 31.6, 29.0, 28.6, 26.7, 22.5, 14.0; IR (neat) 2924, 2855, 1637, 1611, 1486, 1454, 1215, 1051, 739 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{17}H_{23}BrN_2$ 334.1045, found 334.1029.

(*Z*)-1-(1-Bromodec-1-en-2-yl)-1*H*-imidazole (5b): light yellow oil (58 mg, 41%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.13 (s, 1H), 6.99 (s, 1H), 6.19 (s, 1H), 2.44 (t, J = 7.0 Hz, 2H), 1.32−1.21 (m, 12H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 136.8, 129.5, 118.3, 100.1, 37.2, 32.0, 29.3, 29.2, 28.9, 26.8, 22.8, 14.3; IR (neat) 2971, 2923, 1640, 1484, 1378, 1250, 1061, 900, 813, 729, 665 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{13}H_{21}BrN_2$ 284.0888, found 284.0886.

(*Z*)-1-(1-Bromodec-1-en-2-yl)-1*H*-1,2,4-triazole (5c): light yellow oil (110 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.01 (s, 1H), 6.22 (s, 1H), 2.61 (t, J = 7.0 Hz, 2H), 1.29−1.19 (m, 12H), 0.82 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 144.3, 141.2, 98.4, 35.5, 31.6, 29.0, 28.9, 28.6, 26.5, 22.5, 14.0; IR (neat) 2969, 2923, 1643, 1501, 1457, 1413, 1257, 1138, 1054, 952, 878, 667 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{12}H_{20}BrN_3$ 285.0841, found 285.0840.

(*E*)-*N*-Benzyl-*N*-(1-bromodec-1-en-2-yl)benzenesulfonamide (5e): light yellow oil (111 mg, 48%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.4 Hz, 2H), 7.27−7.24 (m, 5H), 6.02 (s, 1H), 4.61 (s, 2H), 2.03 (br, 2H), 1.27−1.06 (m, 12H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 140.4, 135.6, 132.7, 129.4, 129.0, 128.3, 128.1, 127.7, 106.0, 51.8, 37.5, 31.7, 29.1, 29.0, 28.9, 26.7, 22.6, 14.1; IR (neat) 2968, 2923, 1610, 1449, 1348, 1253, 1161, 1054,879, 752, 723, 691 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{23}H_{30}BrNO_2S$ 463.1181, found 463.1164.

(*Z*)-1-(1-Bromooct-1-en-2-yl)-1*H*-benzimidazole (5f): light yellow oil (115 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.81−7.79 (m, 1H), 7.28−7.23 (m, 3H), 6.46 (s, 1H), 2.53 (t, J = 6.6 Hz, 2H), 1.24−1.15 (m, 8H), 0.78 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 141.8, 140.2, 132.4, 123.5, 122.6, 120.5, 110.8, 104.1, 36.1, 31.2, 28.3, 26.7, 22.3, 13.9; IR (neat) 3077, 2968, 2926, 2856, 1637, 1612, 1488, 1454, 1285, 1215, 887, 739, 626 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{15}H_{19}BrN_2$ 306.0732, found 306.0736.

(*Z*)-1-(2-Bromo-1-cyclohexylvinyl)-1*H*-benzimidazole (5g): light yellow oil (127 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.84 (m, 1H), 7.82 (s, 1H), 7.31−7.25 (m, 3H), 6.55 (s, 1H), 2.46 (t, J = 9.2 Hz, 1H), 1.86−1.70 (m, 4H), 1.65 (d, J = 12.8 Hz, 1H), 1.28−1.03 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.1, 141.8, 133.0, 123.4, 122.4, 120.4, 110.8, 105.7, 45.1, 30.9, 25.8, 25.6; IR (neat) 3077, 2927, 2852, 1612, 1484, 1451, 1371, 1284, 1215, 1006, 891, 741, 665, 629 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{15}H_{17}BrN_2$ 304.0575, found 304.0563.

(*Z*)-1-(1-Bromo-3-methylbut-1-en-2-yl)-1*H*-benzimidazole (5h): light yellow oil (101 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.84 (m, 1H), 7.83 (s, 1H), 7.33−7.25 (m, 3H), 6.59 (s, 1H), 2.90−2.83 (m, 1H), 1.12 (t, J = 1.0 Hz, 3H), 1.11 (t, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 143.1, 141.8, 132.9, 123.5, 122.5, 120.4, 110.8, 105.4, 35.6, 20.4; IR (neat) 3078, 2969, 2921, 1611, 1484, 1454, 1285, 1216, 1074, 889, 741, 667, 631 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{12}H_{13}BrN_2$ 264.0262, found 264.0252.

(*Z*)-1-(1-Bromo-4-methylpent-1-en-2-yl)-1*H*-benzimidazole (5i): light yellow oil (105 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.86−7.83 (m, 1H), 7.33−7.30 (m, 3H), 6.48 (s, 1H), 2.48 (d, J = 7.2 Hz, 2H), 1.47−1.40 (m, 1H), 0.89 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 141.8, 139.3, 132.3, 123.5, 122.6, 120.5, 111.0, 104.3, 45.2, 25.6, 21.9; IR (neat) 3078, 2957, 1633, 1611, 1488, 1454, 1370, 1289, 1211, 1098, 888, 739, 659, 625 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{13}H_{15}BrN_2$ 278.0419, found 278.0422.

Representative Procedure for Amination of 1,1-Dibromo-1-alkenes with *N*,*N*′-Bis(*p*-toluenesulfonyl)ethylenediamine 4f:

Synthesis of 5-Phenyl-1,4-di(*p*-toluenesulfonyl)-1,2,3,4-tetrahydropyrazine (5k).[20] To a mixture of *N*,*N*′-di(*p*-toluenesulfonyl)ethylenediamine (184 mg, 0.5 mmol) and powdered Cs_2CO_3 (489 mg, 1.5 mmol) was added 1,1-dibromostyrene (157 mg, 0.6 mmol) in 1.5 mL of DMF. The mixture was stirred at 110 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was further purified by flash column chromatography, using petroleum ether (PE) and ethyl acetate (EA) as the eluent (PE/EA = 3/1). White solid (124 mg, 53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 2H), 7.44−7.40 (m, 4H), 7.36−7.29 (m, 5H), 7.16 (d, J = 8.0 Hz, 2H), 6.70 (s, 1H), 3.43 (t, J = 4.8 Hz, 2H), 3.03 (t, J = 5.0 Hz, 2H), 2.47 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 144.1, 137.0, 134.7, 134.1, 129.9, 129.6, 128.0, 127.7, 127.5, 126.9, 126.7, 121.8, 115.9, 43.4, 41.3, 21.6, 21.5.

***N*,*N*′-(Ethane-1,2-diyl)bis(*N*-((*Z*)-1-bromodec-1-en-2-yl)-4-methylbenzenesulfonamide) (5j):** white solid (161 mg, 40%); mp 66−67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 4H), 7.28 (d, J = 8.0 Hz, 4H), 6.12 (s, 2H), 3.60 (s, 4H), 2.42 (s, 6H), 2.32 (t, J = 7.4 Hz, 4H), 1.46−1.44 (m, 4H), 1.31−1.26 (m, 20H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 143.5, 136.2, 129.3, 127.6, 105.9, 49.1, 36.4, 31.5, 29.1, 28.9, 28.8, 27.2, 22.3, 21.3, 13.8; IR (KBr) 3078, 2925, 2855, 1595, 1462, 1352, 1304, 1166, 1067, 961, 818, 780, 706, 624, 572, 546 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{36}H_{54}Br_2N_2O_4S_2$ 800.1892, found 800.1887.

(*E*)-5-Styryl-1,4-di(*p*-toluenesulfonyl)-1,2,3,4-tetrahydropyrazine (5l): white solid (151 mg, 61%); mp 197−198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.44 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 16.0 Hz, 1H), 6.83 (s, 1H), 6.70 (d, J = 16.4 Hz, 1H), 3.26 (t, J = 4.6 Hz, 2H), 2.93 (t, J = 4.8 Hz, 2H), 2.43 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 144.2, 136.8, 134.9, 133.9, 130.0, 129.8, 128.6, 127.6, 127.4, 127.1, 126.9, 126.6, 125.2, 121.1, 113.3, 42.9, 41.4, 21.6, 21.5; IR (KBr) 3038, 2924, 1596, 1494, 1452, 1353, 1166, 1088, 1027, 996, 816, 751, 671, 618, 550 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{26}H_{26}N_2O_4S_2$ 494.1334, found 494.1342.

5-(Thiophen-2-yl)-1,4-di(*p*-toluenesulfonyl)-1,2,3,4-tetrahydropyrazine (5m): pale yellow solid (176 mg, 74%); mp 63−65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.24−7.22 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.07−7.06 (m, 1H), 6.97−6.94 (m, 1H), 6.81 (s, 1H), 3.42 (t, J = 5.2 Hz, 2H), 3.08 (t, J = 4.6 Hz, 2H), 2.45 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 144.2, 139.9, 134.8, 134.0, 130.0, 129.7, 127.6, 127.0, 126.7, 125.0, 124.9, 115.9, 115.7, 43.6, 41.5, 21.6, 21.5; IR (KBr) 2982, 2903, 1734, 1356, 1247, 1164, 1051, 963, 811, 679, 661 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{22}H_{22}N_2O_4S_3$ 474.0742, found 474.0744.

5-(4-Fluorophenyl)-1,4-di(*p*-toluenesulfonyl)-1,2,3,4-tetrahydropyrazine (5n): white solid (134 mg, 55%); mp 200−201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.37−7.33 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.01 (t, J = 8.4 Hz, 2H), 6.63 (s, 1H), 3.42 (t, J = 5.0 Hz, 2H), 3.01

(t, J = 4.6 Hz, 2H), 2.46 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F} = 246 Hz), 144.3, 144.2, 134.6, 134.1, 133.0 (d, J_{C-F} = 4 Hz), 129.9, 129.7, 128.4 (d, J_{C-F} = 8 Hz), 127.5, 126.9, 120.9, 115.7, 115.0 (d, J_{C-F} = 22 Hz), 43.4, 41.3, 21.6, 21.5; IR (KBr) 3093, 2929, 2885, 1634, 1597, 1505, 1490, 1352, 1250, 1166, 1094, 985, 827, 763, 690, 660, 612, 564 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{24}H_{23}FN_2O_4S_2$ 486.1083, found 486.1088.

5-(4-Chlorophenyl)-1,4-di(*p*-toluenesulfonyl)-1,2,3,4-tetrahydropyrazine (5o): white solid (171 mg, 68%); mp 170−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.35−7.27 (m, 6H), 7.15 (d, J = 8.0 Hz, 2H), 6.68 (s, 1H), 3.41 (t, J = 4.8 Hz, 2H), 3.00 (t, J = 4.6 Hz, 2H), 2.45 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 144.3, 135.6, 134.5, 134.0, 133.4, 130.0, 129.7, 128.2, 127.9, 127.5, 126.9, 120.6, 116.2, 43.3, 41.2, 21.6, 21.5; IR (KBr) 3090, 2925, 1633, 1596, 1490, 1355, 1248, 1168, 1092, 983, 815, 713, 682, 619, 552 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{24}H_{23}ClN_2O_4S_2$ 502.0788, found 502.0781.

5-(4-Bromophenyl)-1,4-di(*p*-toluenesulfonyl)-1,2,3,4-tetrahydropyrazine (5p): white solid (161 mg, 59%); mp 187−188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.69 (s, 1H), 3.40 (t, J = 5.0 Hz, 2H), 3.00 (t, J = 5.0 Hz, 2H), 2.45 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 144.3, 136.1, 134.5, 134.0, 131.2, 130.0, 129.7, 128.2, 127.5, 126.9, 121.5, 120.6, 116.3, 43.3, 41.2, 21.6, 21.5; IR (KBr) 3089, 2924, 1634, 1595, 1488, 1356, 1247, 1168, 1068, 983, 816, 704, 687, 618, 553 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{24}H_{23}BrN_2O_4S_2$ 546.0283, found 546.0289.

Representative Procedure for Sonogashira Cross-Coupling Reaction:

Synthesis of (*Z*)-(1-Phenyldodec-3-en-1-yn-4-yl)(*p*-tolyl)sulfane (6) Ethynylbenzene (61 mg, 0.6 mmol) was added to a stirred solution of (*Z*)-(1-bromodec-1- en-2-yl)(*p*-tolyl)sulfane (171 mg, 0.5 mmol), Et_3N (101 mg, 1.0 mmol), $Pd(PPh_3)_2Cl_2$ (18 mg, 0.025 mmol), and CuI (5 mg, 0.025 mmol) in 1.0 mL of THF under nitrogen. The resulting mixture was stirred at 60 °C for 12 h. After being cooled to room temperature, the reaction mixture was purified by flash column chromatography, using petroleum ether as the eluent. Light yellow oil (165 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.51 (m, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.38−7.31 (m, 3H), 7.20 (d, J = 8.0, 2H), 5.86 (s, 1H), 2.40 (s, 3H), 2.23 (t, J = 7.4 Hz, 2H), 1.51−1.46 (m, 2H), 1.37−1.23 (m, 10 H), 0.96 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 138.1, 133.9, 131.4, 129.7, 128.7, 128.2, 127.9, 123.7, 106.0, 95.9, 86.8, 35.9, 31.8, 29.2, 29.1, 28.8, 28.6, 22.7, 21.2, 14.1; IR (neat) 3019, 2924, 2853, 1611, 1569, 1488, 1316, 809, 753, 689 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{25}H_{30}S$ 362.2068, found 362.2079.

(*Z*)-1-(1-Phenyldodec-3-en-1-yn-4-yl)-1*H*-benzo[*d*]imidazole (13): light yellow oil (161 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.89−7.87 (m, 1H), 7.49−7.46 (m, 1H), 7.33−7.31 (m, 2H), 7.21−7.15 (m, 3H), 7.06−7.03 (m, 2H), 5.93 (s, 1H), 2.71 (t, J = 6.8 Hz, 2H), 1.39−1.22 (m, 12H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 142.3, 131.3, 128.5, 128.4, 128.1, 123.3, 122.5, 122.4, 120.4, 111.8, 105.2, 95.7, 84.2, 35.5, 31.7, 29.1, 29.0, 28.8, 27.1, 22.5, 14.0; IR (neat) 3013, 2924, 1736, 1610, 1488, 1453, 1391, 1221, 1066, 754, 689 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{25}H_{28}N_2$ 356.2252, found 356.2249.

Representative Procedure for Suzuki−Miyaura Cross-Coupling Reaction:

Synthesis of (*Z*)-(1-Phenyldec-1-en-2-yl)(*p*-tolyl)sulfane (7) (*Z*)-(1-Bromodec-1-en-2-yl)(*p*-tolyl)sulfane (171 mg, 0.5 mmol) was added to a stirred solution of phenylboronic acid (122 mg, 1.0 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), and Cs_2CO_3 (326 mg, 1.0 mmol) in 2.0 mL of DMF under nitrogen. The resulting mixture was stirred at 100 °C for 12 h. After being cooled to room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was further purified by flash column chromatography, using petroleum ether as the eluent. Light yellow oil (125 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.2 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 7.26 (t, J = 7.4 Hz, 1H), 7.20 (d, J = 8.4 Hz, 2H), 6.76 (s, 1H), 2.35 (s, 3H), 2.28 (t, J = 7.4 Hz, 2H), 1.59−1.57 (m, 2H), 1.34−1.26 (m, 10H), 0.91 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 132.2, 131.7, 130.7, 130.4, 130.0, 129.8, 129.6, 129.2, 129.0, 127.9, 126.9, 38.0, 31.9, 29.3, 29.2, 28.9, 28.8, 22.6, 21.1, 14.1; IR (neat) 3022, 2923, 2853, 1601, 1491, 1457, 1086, 1018, 806, 748, 692 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{23}H_{30}S$ 338.2068, found 338.2064.

(*Z*)-1-(1-Phenyldec-1-en-2-yl)-1*H*-benzo[*d*]imidazole (14): light yellow oil (136 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.2 Hz, 1H), 7.74 (s, 1H), 7.29−7.22 (m, 3H), 7.08−7.02 (m, 3H), 6.72−6.69 (m, 2H), 6.63 (s, 1H), 2.64 (t, J = 6.8 Hz, 2H), 1.39−1.23 (m, 12 H), 0.86 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 142.2, 134.6, 133.8, 132.9, 128.6, 128.0, 127.9, 126.5, 123.5, 122.5, 120.4, 111.0, 37.1, 31.8, 29.3, 29.2, 28.9, 27.1, 22.7, 14.2; IR (neat) 2924, 2854, 1656, 1611, 1484, 1454, 1221, 741, 694 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{23}H_{28}N_2$ 332.2252, found 332.2253.

Representative Procedure for C−N Cross-Coupling Reaction:

Synthesis of (*Z*)-1-(2-(*p*-Tolylthio)dec-1-enyl)-1*H*-imidazole (8) (*Z*)-(1-Bromodec-1-en-2-yl)(*p*-tolyl)sulfane (171 mg, 0.5 mmol) was added to a stirred solution of imidazole (68 mg, 1.0 mmol), CuI (10 mg, 0.05 mmol), DMEDA (8 μL, 0.075 mmol), and Cs_2CO_3 (326 mg, 1.0 mmol) in 2.0 mL of DMF under nitrogen. The resulting mixture was stirred at 110 °C for 48 h. After being cooled to room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was further purified by flash column chromatography, using petroleum ether (PE) and ethyl acetate (EA) as the eluent (PE/EA = 3/1). Light yellow oil (128 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.34 (s, 1H), 7.22 (d, J = 7.6 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.06 (s, 1H), 6.86 (s, 1H), 2.32 (s, 3H), 2.16 (t, J = 7.4 Hz, 2H), 1.52−1.49 (m, 2H), 1.28−1.21 (m, 10H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 132.3, 131.3, 130.1, 129.2, 128.5, 122.7, 119.6, 35.1, 32.0, 29.4, 29.3, 29.0, 28.6, 22.8, 21.3, 14.3; IR (neat) 3113, 2924, 2853, 1643, 1488, 1292, 1231, 1077, 1019, 807, 729, 656 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{20}H_{28}N_2S$ 328.1973, found 328.1970.

(*Z*)-1-(2-(*p*-Tolylthio)dec-1-enyl)-1*H*-benzimidazole (9): light yellow oil (148 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.82−7.80 (m, 1H), 7.41−7.39 (m, 1H), 7.35−7.29 (m, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.92 (s, 1H), 2.30 (t, J = 7.2 Hz, 2H), 2.29 (s, 3H), 1.62−1.57 (m, 2H), 1.34−1.28 (m, 10H), 0.91 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.4, 136.2, 133.9, 132.7, 130.1, 128.0, 123.5, 122.9, 120.6, 119.9, 110.2, 34.9, 32.1, 29.5, 29.4, 29.0, 28.8, 22.9, 21.3, 14.4; IR (neat) 3114, 2924, 2853, 1635, 1487, 1456, 1280, 1223, 807, 739 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{24}H_{30}N_2S$ 378.2130, found 378.2125.

Representative Procedure for C−S Cross-Coupling Reaction:

(*Z*)-Dec-1-ene-1,2-diylbis(*p*-tolylsulfane) (10) (*Z*)-(1-Bromodec-1-en-2-yl)(*p*-tolyl)sulfane (171 mg, 0.5 mmol) was added to a stirred solution of 4-methylbenzenethiol (124 mg, 1.0 mmol), Cu_2O (7 mg, 0.05 mmol), DMEDA (8 μL, 0.075 mmol), and Cs_2CO_3 (326 mg, 1.0 mmol) in 2.0 mL of DMF under nitrogen. The resulting mixture was stirred at 120 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was further purified by flash column

chromatography, using petroleum ether (PE) and ethyl acetate (EA) as the eluent (PE/EA = 20/1). Light yellow oil (157 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.27 (m, 4H), 7.13−7.08 (m, 4H), 6.45 (s, 1H), 2.32 (s, 3H), 2.31 (s, 3H), 2.20 (t, J = 7.2 Hz, 2H), 1.49−1.46 (m, 2H), 1.29−1.20 (m, 10H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.12, 137.11, 134.7, 132.8, 131.5, 130.4, 130.3, 130.1, 130.0, 128.8, 37.2, 32.1, 29.6, 29.5, 29.1, 28.8, 22.9, 21.4, 21.3, 14.4; IR (neat) 3021, 2923, 2853, 1611, 1491, 1458, 1089, 1017, 803 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{24}H_{32}S_2$ 384.1945, found 384.1949.

(*Z*)-1-(1-(*p*-Tolylthio)dec-1-en-2-yl)-1*H*-benzo[*d*]imidazole (15): light yellow oil (145 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.84−7.82 (m, 1H), 7.36−7.34 (m, 1H), 7.32−7.28 (m, 2H), 7.23−7.21 (m, 2H), 7.09−7.07 (m, 2H), 6.45 (s, 1H), 2.55 (t, J = 6.8 Hz, 2H), 2.29 (s, 3H), 1.31−1.18 (m, 12H), 0.84 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.3, 137.6, 133.6, 132.9, 130.7, 130.4, 130.1, 124.1, 123.3, 122.5, 120.5, 111.0, 36.4, 31.8, 29.2, 29.1, 28.9, 27.3, 22.7, 21.1, 14.2; IR (neat) 2924, 2854, 1611, 1487, 1453, 1214, 804, 739 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{24}H_{30}N_2S$ 378.2130, found 378.2127.

Representative Procedure for C−O Cross-Coupling Reaction:

Synthesis of (*Z*)-(1-Phenoxydec-1-en-2-yl)(*p*-tolyl)sulfane (11) (*Z*)-(1-Bromodec-1-en-2-yl)(*p*-tolyl)sulfane (171 mg, 0.5 mmol) was added to a stirred solution of phenol (94 mg, 1.0 mmol), Cu_2O (7.0 mg, 0.05 mmol), TMHD (17 μL, 0.075 mmol), and Cs_2CO_3 (326 mg, 1.0 mmol) in 2.0 mL of DMF under nitrogen. The resulting mixture was stirred at 120 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was further purified by flash column chromatography, using petroleum ether (PE) and ethyl acetate (EA) as the eluent (PE/EA = 20/1). Light yellow oil (150 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.26 (m, 4H), 7.07−6.99 (m, 5 H), 6.71 (s, 1H), 2.29 (s, 3H), 2.10 (t, J = 7.4 Hz, 2H), 1.50−1.46 (m, 2H), 1.29−1.22 (m, 10H), 0.86 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 141.9, 136.7, 131.3, 130.8, 129.84, 129.81, 123.3, 118.0, 116.9, 32.3, 32.1, 29.6, 29.5, 29.1, 28.6, 22.9, 21.3, 14.4; IR (neat) 2924, 2853, 1642, 1592, 1489, 1225, 1166, 806, 753, 689 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{23}H_{30}OS$ 354.2017, found 354.2019.

(*Z*)-1-(1-(*p*-Tolyloxy)dec-1-en-2-yl)-1*H*-benzo[*d*]imidazole (16): light yellow oil (147 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.84−7.82 (m, 1H), 7.39−7.37 (m, 1H), 7.30−7.27 (m, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 6.70 (s, 1H), 2.53 (br, 2H), 2.29 (s, 3H), 1.31−1.22 (m, 12H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 143.4, 142.9, 137.2, 133.7, 133.1, 130.2, 123.2, 122.2, 120.2, 118.9, 116.2, 111.2, 31.8, 31.4, 29.2, 28.8, 27.2, 22.7, 20.6, 14.1; IR (neat) 2967, 2923, 1688, 1609, 1505, 1487, 1454, 1223, 1051, 816, 740 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{24}H_{30}N_2O$ 362.2358, found 362.2353.

(*Z*)-Diethyl-2-(*p*-tolylthio)dec-1-enylphosphonate (12). (*Z*)-(1-Bromodec-1-en-2-yl)(*p*-tolyl)sulfane (171 mg, 0.5 mmol) was added to a stirred solution of diethyl phosphite (138 mg, 1.0 mmol), CuI (5 mg, 0.025 mmol), DMEDA (23 μL, 0.1 mmol), and Cs_2CO_3 (326 mg, 1.0 mmol) in 1.0 mL of anhydrous toluene under nitrogen. The reaction mixture was stirred at 110 °C for 18 h. Then the reaction mixture was filtered and washed with ethyl acetate. The filtrate was concentrated and the residue was purified by flash column chromatography, using petroleum ether (PE) and ethyl acetate (EA) as the eluent (PE/EA = 2/1). Light yellow oil (165 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 5.66 (d, J = 14.8 Hz, 1H), 4.22−4.15 (m, 4H), 2.36 (s, 3H), 2.12 (t, J = 7.6 Hz, 2H), 1.42−1.36 (m, 2H), 1.38 (t, J = 7.0 Hz, 6H), 1.27−1.24 (m, 2H), 1.18 (br, 4H), 1.12 (br, 4H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, J = 1.8 Hz), 138.9, 134.6, 129.8, 127.6, 112.1 (d, J = 193.7 Hz), 61.7 (d, J = 6.4 Hz), 37.8 (d, J = 19.3 Hz), 31.7, 29.0 (d, J = 5 Hz), 28.6, 28.4 (d, J = 1.4 Hz), 22.5, 21.2, 16.4 (d, J = 6.6 Hz), 14.0; IR (neat) 2980, 2924, 1567, 1390, 1224, 1051, 1025, 955, 809, 627 cm^{-1}; HRMS (TOF MS EI$^+$) m/z calcd for $C_{21}H_{35}O_3PS$ 398.2045, found 398.2045.

■ ASSOCIATED CONTENT

Supporting Information. Original ^{1}H and ^{13}C NMR spectra and crystallograhic infromation (cif) of compounds **5j** and **5l**. This material is available free of charge via the Internet at http://pubs.acs.org.

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