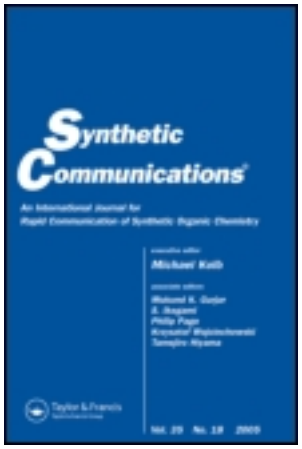

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Indium-Promoted Allylation of Alkynes with Allylic Alcohols: Highly Regioselective Synthesis of Halogen-Substituted 1,4-Dienes

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INDIUM-PROMOTED ALLYLATION OF ALKYNES WITH ALLYLIC ALCOHOLS: HIGHLY REGIOSELECTIVE SYNTHESIS OF HALOGEN-SUBSTITUTED 1,4-DIENES

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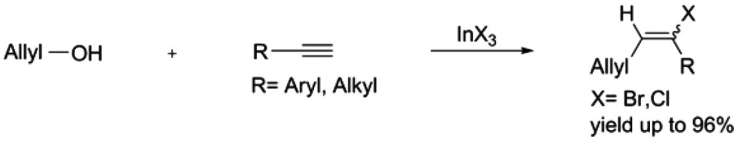
GRAPHICAL ABSTRACT



Abstract *Indium-promoted allylation of alkynes by direct use of allyl alcohols as the allylating agents has been developed under mild conditions, in which a wide range of allylic alcohols and alkynes (both aromatic and aliphatic alkynes) could be tolerated, and the corresponding halogen-substituted 1,4-dienes were obtained in moderate to excellent yields.*

Keywords Alkynes; allyl alcohols; allylation; halogen-substituted 1,4-dienes; indium(III) salt

INTRODUCTION

Allylation of carbon–carbon triple bonds is an important and useful method for the construction of 1,4-dienes, which widely exist in naturally occurring and biologically active compounds.[1] In general, allylmetal compounds such as allyl-Zn, allyl-In, allyl-Si, and allyl-Sn are employed as allylating agents for this transformation.[2] Nevertheless, the lack of facile and general methods for the preparation of these allylic organometallics has limited their extensive applications. Recently, alternative approaches for allylation of alkynes with metal and allylic halides to produce 1,4-dienes have been developed.[3] From the synthetic standpoint, the direct allylation of alkynes by using allylic alcohols instead of allylmetal reagents and allylic halides is an ideal process to access 1,4-dienes because of its advantages in terms of synthetic efficiency, atom economy, and environmental sustainability.

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Despite the tremendous advantages of using allylic alcohols as substrates, to date, the direct allylation of alkynes with allylic alcohols to form substituted 1,4-dienes has very rarely been investigated.[4–7] Huang et al. described a palladium-catalyzed allylation of alkynes with allylic alcohols in the presence of a stoichiometric amount of a $CuCl_2$/HOAc, leading to chloro-substituted 1,4-dienes.[4] Micalizio and Cha reported a Ti(O*i*-Pr)$_4$- or ClTi(O*i*-Pr)$_3$-mediated allylation of alkynes with allylic alcohols in the presence of an excess amount of C_5H_9MgCl to give substituted 1,4-dienes at $-78\,^{\circ}C$.[5,6] Biswas et al. reported a FeX_3-promoted coupling of (*E*)-1,3-diphenylprop-2-en-1-ol with phenylacetylene to form chloro/bromo-substituted 1,4-diene in moderate yield.[7] Obviously, these results are not satisfactory with regard to yield and/or reaction conditions. Therefore, the development of a mild, simple, convenient, and efficient method for the allylation of alkynes with allylic alcohols to construct substituted 1,4-dienes is still in high demand and is a challenging goal.

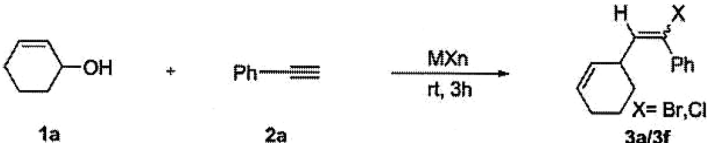
Herein, we describe a simple and efficient indium(III) halide–promoted allylation of unactivated alkynes with allyl alcohols to afford the halogen-substituted 1,4-dienes in moderate to excellent yields, in which indium halides not only accomplish the formation of chemical bonds but also serve as halide sources under mild conditions without any additives.

RESULTS AND DISCUSSION

In an initial experiment, cyclohex-2-enol **1a** (0.25 mmol) was added to a mixture of phenylacetylene **2a** (0.38 mmol) and $BiBr_3$ (0.025 mmol) in 1,2-dibromoethane (DBE) at room temperature under air, and a poor yield (<5%) of bromo-substituted 1,4-diene **3a** was obtained (Table 1, entry 1). The addition of NaBr (0.25 mmol) or KBr (0.25 mmol) as sources of bromine ions did not improve this reaction (Table 1, entries 2 and 3). To our delight, 52% yield of **3a** was isolated when the loading of $BiBr_3$ was increased to 0.08 mmol (Table 1, entry 4). Subsequently, the reaction activity of other metal halides was further investigated in this reaction system (Table 1, entries 5–13). None of the desired product was detected in the presence of $TiBr_4$, $AlBr_3$, $ZnBr_2$, $CuBr_2$, and AgBr salts (Table 1, entries 5–9). Among $BiBr_3$, $PbBr_2$, $AuBr_3$, $SnBr_4$, and $InBr_3$, $InBr_3$ was proved to be the best choice (Table 1, entries 10–13). Further exploration using $InBr_3$ as promoter suggested that DBE was the optimal reaction medium. After an extensive screening of the reaction parameters (Table 1, entries 14–17), the best yield of **3a** (82%) was obtained by employing $InBr_3$ (0.125 mmol) at room temperature in DBE (entry 17). However, when $InCl_3$ was used as promoter, the corresponding chloro-substituted 1,4-diene **3f** was generated in very poor yield (<10%) under the optimal reaction conditions. Fortunately, good yield (80%) of **3f** could be obtained when the temperature was raised to 60 °C (entry 18).

With the optimized conditions in hand, the scope and limitation of this reaction were further investigated using various combinations of alkynes and allylic alcohols in the presence of InX_3 (X = Br or Cl). As shown in Table 2, a variety of Br- or Cl-substituted 1,4-dienes were obtained in moderate to excellent yields. In general, aryl alkynes with electron-rich groups gave better yields of the expected products than those bearing electron-deficient groups (**3a–3h**). Heteroaromatic alkynes such

Table 1. Optimization of the reaction conditions[a]



1a 2a 3a/3f

Entry	MX_n (mmol)	Solvent	Yield (%)[b]
1	$BiBr_3$ (0.025)	DBE	5<
2	$BiBr_3$ (0.025), NaBr (0.25)	DBE	5<
3	$BiBr_3$ (0.025), KBr (0.25)	DBE	5<
4	$BiBr_3$ (0.08)	DBE	52
5	$TiBr_4$ (0.06)	DBE	—
6	$AlBr_3$ (0.08)	DBE	—
7	$ZnBr_2$ (0.125)	DBE	—
8	$CuBr_2$ (0.125)	DBE	—
9	AgBr (0.25)	DBE	—
10	$PbBr_2$ (0.125)	DBE	5<
11	$AuBr_3$ (0.08)	DBE	36
12	$SnBr_4$ (0.06)	DBE	64
13	$InBr_3$ (0.08)	DBE	73
14	$InBr_3$ (0.08)	DCE	52
15	$InBr_3$ (0.08)	$CHCl_3$	33
16	$InBr_3$ (0.08)	CH_2Cl_2	54
17	$InBr_3$ (0.125)	DBE	82
18	$InCl_3$ (0.125)	DBE	80[c]

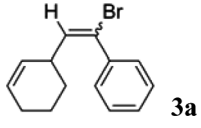
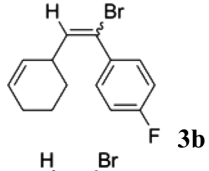
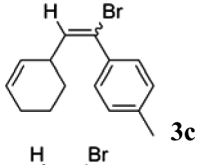
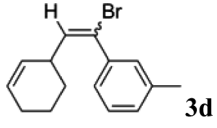
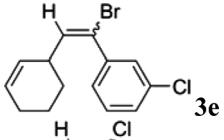
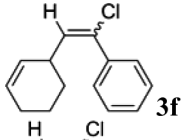
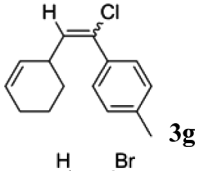
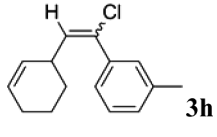
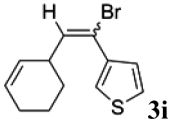
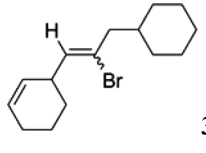
[a]Reaction conditions: cyclohex-2-enol **1a** (0.25 mmol), phenylacetylene **2a** (0.38 mmol), MX_n (0.06–0.25 mmol).
[b]Isolated yields based on alcohol **1a**.
[c]The reaction was carried out at 60 °C.

as 3-ethynylthiophene could also be used in the reaction to give the desired product in 67% yield (**3i**). Notably, aliphalic alkynes were tolerated in this process, leading to the corresponding products **3j**–**3l** in moderate yields. However, none of the desired products were observed when internal alkynes such as 1,2-diphenylethyne, 1-phenyl-1-butyne, and 4-octyne were applied in this reaction. With respect to allylic alcohols, in addition to cyclohex-2-enol **1a**, a series of cyclic allylic alcohols including cyclopen-2-enol and substituted cyclohex-2-enols were all suitable substrates and generated the corresponding products in moderate to excellent yields (**3m–3q**). Acyclic allylic alcohol such as (*E*)-1,3-diphenylprop-2-en-1-ol was also compatible with this reaction, affording the desired product **3r** in 61% yield. Nevertheless, none of the desired products were detected when simple aliphatic allylic alcohols such as but-3-en-2-ol and penta-1,4-dien-3-ol were used as the substrates.

Based on these above results and previous studies,[8] a plausible pathway of this coupling reaction is proposed in Scheme 1. Initially, allylic alcohol **1** was activated by InX_3(X = Br or Cl) to generate the cationic intermediate **4**. Then, the intermolecular addition of **4** to terminal alkyne **2** activated by InX_3 would give alkenyl

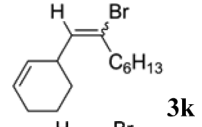
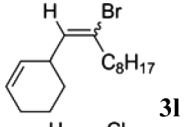
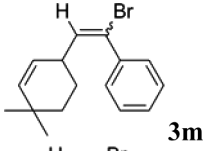
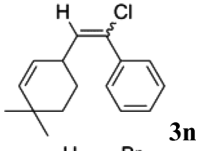
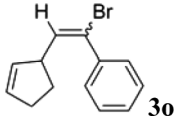
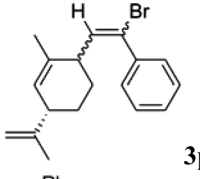
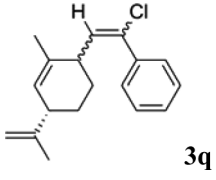
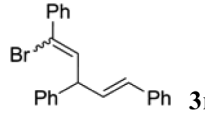
Table 2. Results for reactions of allylic alcohols, alkynes, and InX_3 [a,b,c]

1 2 3

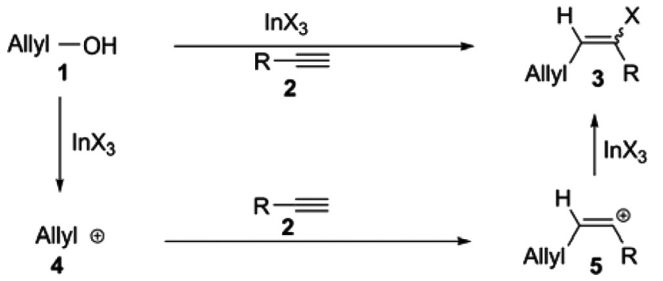
Entry	Product	Yield (%)[b]	Ratio (E/Z)[c]	Entry	Product	Yield (%)[b]	Ratio (E/Z)[c]
1	 **3a**	82	5.5:1	10	 **3b**	42	1:1
2	 **3c**	79	4.5:1	11	 **3d**	50	1:1.6
3	 **3e**	93	1.5:1	12	 **3f**	66	1:1
4	 **3g**	96	2.8:1	13	 **3h**	91	4.3:1
5	 **3i**	64	3:1	14 [d]	 **3j**	85	8.3:1

(*Continued*)

Table 2. Continued

Entry	Product	Yield (%)[b]	Ratio (E/Z)[c]	Entry	Product	Yield (%)[b]	Ratio (E/Z)[c]
6[d]	 **3k**	80	4:1	15	 **3l**	63	1:1.1
7[d]	 **3m**	83	4.6:1	16	 **3n**	61	1.9:1
8[d]	 **3o**	81	3.2:1	17 [d]	 **3p**	56	1.7:1
9	 **3q**	67	1:1.4	18	 **3r**	65	3:1

[a]Reaction conditions: allylic alcohols **1** (0.25 mmol), alkynes **2** (0.38 mmol), InX_3 (0.125 mmol), $BrCH_2CH_2Br$ (1 mL), room temperature.
[b]Isolated yields based on allylic alcohols **1**.
[c]The ratio of *E*/*Z* is determined by ^1H NMR analysis on the crude mixture.
[d]The reaction was carried out in the presence of $InCl_3$ at 60 °C.



Scheme 1. Possible pathway.

cation **5**. Finally, the halide ion of the indium complex reacted with alkenyl cation **5**, leading to the desired product **3**.

CONCLUSIONS

In summary, we have developed an efficient In(III) halide–promoted allylation of alkynes by direct use of allylic alcohols as allylating agents. This mild and simple reaction system provides an attractive approach to a large number of halogen-substituted 1,4-dienes derivatives in moderate to excellent yields. Further investigations of reaction scope, precise mechanism, and synthetic applications are ongoing.

EXPERIMENTAL

All commercially available reagent-grade chemicals were purchased from Aldrich, Acros, and Alfa Aesar chemical companies. All reagents and solvents were used as received without further purification unless otherwise stated. NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 600 spectrometer with tetramethylsilane (TMS) as internal standard (600 MHz ^1H, 150 MHz ^{13}C) at room temperature, the chemical shifts (δ) are expressed in parts per million (ppm), and J values are given in hertz (Hz). The following abbreviations are used to indicate the multiplicity: s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). Mass analyses and higher-resoultion mass spectra (HRMS) were obtained on an Agilent 5973 N MSD mass spectrometer and a Waters Micromass GCT Premier mass spectrometer by the electron impact (EI) method, respectively. Column chromatography was performed on silica gel (200–300 mesh).

General Procedure for Allylation of Alkynes with Allylic Alcohols

The allylic alcohols (0.25 mmol) were added to a stirred mixture of alkynes (0.38 mmol) and InX_3 (0.125 mmol) in $BrCH_2CH_2Br$. The mixture was stirred for about 3–6 h at room temperature. Upon completion of the reaction, the mixture was filtered through silica gel and washed with EtOAc (10 mL) to give a brown solution. After filtration, the solvent was removed by vacuum evaporation. The residue was purified by silica-gel flash column chromatography using hexane/EtOAc as the

eluent. The desired product was isolated as colorless oil, which was suitable for analytical purposes.

Spectral Data for All the Compounds

1-Bromo-2-(cyclohex-2-enyl)vinyl)benzene (Table 2, 3a). E/Z (5.5:1); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3a**: δ = 7.54–7.27 (m, 5H), 6.06 (d, J = 10.8 Hz, 1H), 5.76–5.72 (m, 1H), 5.47–5.45 (m, 1H), 2.87–2.83 (m, 1H), 2.05–1.41 (m, 6H); (*Z*)**3a**: δ = 7.54–7.27 (m, 5H), 6.08 (d, J = 8.7 Hz, 1H), 5.80–5.79 (m, 1H), 5.62–5.60 (m, 1H), 3.40 (m, 1H), 2.05–1.41 (m, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ = 140.0, 138.9, 138.1, 135.2, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 127.6, 120.2, 39.2, 37.4, 29.0, 28.0, 24.8, 24.7, 20.9, 20.6; HRMS (EI): calcd. for $C_{14}H_{15}Br$, 262.0357; found, 262.0360.

1-(1-Bromo-2-(cyclohex-2-enyl)vinyl)-4-fluorobenzene (Table 2, 3b). E/Z (4.5:1); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3b**: δ = 7.50–6.99 (m, 4H), 6.06 (d, J = 10.6 Hz, 1H), 5.76–5.73 (m, 1H), 5.45–5.43 (m, 1H), 2.83–2.79 (m, 1H), 2.03–1.41 (m, 6H); (*Z*)**3b**: δ = 7.50–6.99 (m, 4H), 6.01 (d, J = 8.8 Hz, 1H), 5.81–5.79 (m, 1H), 5.60–5.58 (m, 1H), 3.38–3.37 (m, 1H), 2.03–1.41 (m, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ = 163.3, 161.6, 138.5, 136.2, 135.2, 134.9, 130.7, 130.67, 129.4, 129.3, 129.0, 128.8, 128.4, 128.2, 128.0, 127.6, 123.1, 118.9, 115.4, 115.2, 115.1, 115.0, 39.2, 37.4, 29.0, 28.0 24.8, 24.7, 20.8, 20.6; HRMS (EI): calcd. for $C_{14}H_{14}BrF$, 280.0263; found, 280.0268.

1-(1-Bromo-2-(cyclohex-2-enyl)vinyl)-4-methylbenzene (Table 2, 3c). E/Z (1.5:1); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3c**: δ = 7.42–7.11 (m, 4H), 6.04 (d, J = 10.8 Hz, 1H), 5.74–5.72 (m, 1H), 5.47–5.45 (m, 1H), 2.87–2.85 (m, 1H), 2.36 (s, 3H), 2.03–1.42 (m, 6H); (*Z*)**3c**: δ = 7.42–7.11 (m, 4H), 6.03 (d, J = 8.3 Hz, 1H), 5.80–5.78 (m, 1H), 5.62–5.60 (m, 1H), 3.39–3.38 (m, 1H), 2.35 (s, 3H), 2.03–1.42 (m, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ = 138.4, 138.3, 137.8, 137.2, 136.0, 134.4, 128.9, 128.85, 128.7, 128.6, 128.5, 128.3, 128.2, 127.5, 124.5, 120.4, 39.2, 37.4, 29.0, 28.1, 24.8, 24.7, 21.3, 21.1, 20.9, 20.6; HRMS (EI): calcd. for $C_{15}H_{17}Br$, 276.0514; found, 276.0518.

1-(1-Bromo-2-(cyclohex-2-enyl)vinyl)-3-methylbenzene (Table 2, 3d). E/Z (2.8:1); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3d**: δ = 7.33–7.09 (m, 4H), 6.04 (d, J = 10.6 Hz, 1H), 5.75–5.73 (m, 1H), 5.48–5.46 (m, 1H), 2.86–2.84 (m, 1H), 2.36 (s, 3H), 2.03–1.41 (m, 6H); (*Z*)**3d**: δ = 7.33–7.09 (m, 4H), 6.05 (d, J = 8.6 Hz, 1H), 5.80–5.78 (m, 1H), 5.62–5.60 (m, 1H), 3.39 (m, 1H), 2.36 (s, 3H), 2.03–1.41 (m, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ = 139.9, 138.8, 138.0, 137.9, 135.0, 129.4, 129.2, 129.1, 128.6, 128.5, 128.3, 128.2, 128.1, 125.8, 124.8, 120.4, 39.2, 37.4, 29.0, 28.0, 24.8, 24.7, 21.4, 21.3, 20.9, 20.6; HRMS (EI): calcd. for $C_{15}H_{17}Br$, 276.0514; found, 276.0516.

1-(1-Bromo-2-(cyclohex-2-enyl)vinyl)-3-chlorobenzene (Table 2, 3e). E/Z (3:1); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3e**: δ = 7.52–7.20 (m, 4H), 6.08 (d, J = 11.0 Hz, 1H), 5.77–5.75 (m, 1H), 5.45–5.43 (m, 1H), 2.82 (m, 1H), 2.04–1.40 (m, 6H); (*Z*)**3e**: δ = 7.52–7.20 (m, 4H), 6.10 (d, J = 10.6 Hz, 1H), 5.82–5.80 (m, 1H), 5.59–5.58 (m, 1H), 3.39 (m, 1H), 2.04–1.40 (m, 6H); ^{13}C NMR

($CDCl_3$, 150 MHz, ppm): δ = 140.5, 139.1, 136.5, 134.1, 129.5, 129.4, 128.9, 128.88, 128.6, 128.56, 128.3, 128.0, 127.74, 127.70, 126.99, 125.8, 122.6, 118.1, 39.2, 37.4, 28.9, 27.9, 24.8, 24.7, 20.8, 20.5; HRMS (EI): calcd. for $C_{14}H_{14}BrCl$, 295.9967; found, 295.9963.

(1-Chloro-2-(cyclohex-2-enyl)vinyl)benzene (Table 2, 3f). *E*/*Z* (4:1); ^1H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3f**: δ = 7.58–7.28 (m, 5H), 5.82 (d, *J* = 11.0 Hz, 1H), 5.76–5.74 (m, 1H), 5.49–5.47 (m, 1H), 2.93–2.91(m, 1H), 2.04–1.41 (m, 6H); (*Z*)**3f**: δ = 7.58–7.28 (m, 5H), 6.02 (d, *J* = 8.8 Hz, 1H), 5.80–5.78 (m, 1H), 5.61–5.59 (m, 1H), 3.47 (m, 1H), 2.04–1.41 (m, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ = 138.2, 137.4, 133.9, 132.0, 131.5, 130.4, 128.7, 128.66, 128.5, 128.4, 128.3, 128.2, 126.4, 36.4, 36.2, 29.3, 28.2, 24.8, 24.7, 20.9, 20.6; HRMS (EI): calcd. for $C_{14}H_{15}Cl$, 218.0862; found, 218.0863.

1-(1-Chloro-2-(cyclohex-2-enyl)vinyl)-4-methylbenzene (Table 2, 3g). *E*/*Z* (4.6:1); ^1H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3g**: δ = 7.46–7.13 (m, 4H), 5.78 (d, *J* = 11.0 Hz, 1H), 5.75–5.73 (m, 1H), 5.48–5.47 (m, 1H), 2.93–2.91 (m, 1H), 2.36 (S, 3H), 2.03–1.40 (m, 6H); (*Z*)**3g**: δ = 7.46–7.13 (m, 4H), 5.96 (d, *J* = 9.2 Hz, 1H), 5.77 (m, 1H), 5.61–5.59 (m, 1H), 3.45 (m, 1H), 2.35 (S, 3H), 2.03–1.40 (m, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ = 138.5, 138.2, 135.5, 134.5, 133.5, 132.0, 130.6, 130.56, 128.9, 128.87, 128.6, 128.4, 128.1, 126.3, 36.2, 29.3, 28.3, 24.9, 24.7, 21.3, 21.1, 20.9, 20.7; HRMS (EI): calcd. for $C_{15}H_{17}Cl$, 232.1019; found, 232.1020.

1-(1-Chloro-2-(cyclohex-2-enyl)vinyl)-3-methylbenzene (Table 2, 3h). *E*/*Z* (3.2:1); ^1H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3h**: δ = 7.38–7.10 (m, 4H), 5.80 (d, *J* = 10.6 Hz, 1H), 5.76–5.74 (m, 1H), 5.49–5.47 (m, 1H), 2.93–2.90 (m, 1H), 2.38 (s, 3H), 2.04–1.41 (m, 6H); (*Z*)**3h**: δ = 7.38–7.10 (m, 4H), 5.99 (d, *J* = 8.8 Hz, 1H), 5.78 (m, 1H), 5.61–5.59 (m, 1H), 3.46 (m, 1H), 2.36 (s, 3H), 2.04–1.41 (m, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ = 138.3, 138.0, 137.9, 137.3, 133.7, 131.3, 130.6, 129.3, 129.26, 129.1, 128.8, 128.5, 128.4, 128.1, 127.1, 125.7, 123.6, 36.3, 36.2, 29.2, 28.2, 24.8, 24.7, 21.4, 20.9, 20.6; HRMS (EI): calcd. for $C_{15}H_{17}Cl$, 232.1019; found, 232.1021.

3-(1-Bromo-2-(cyclohex-2-enyl)vinyl)thiophene (Table 2, 3i). *E*/*Z* (1:1.4), ^1H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3i**: δ = 7.43–7.14 (m, 3H), 6.04 (d, *J* = 10.6 Hz, 1H), 5.80–5,76 (m, 1H), 5.49–5.47 (m, 1H), 3.04 (m, 1H), 2.03–1.43 (m, 6H); (*Z*)**3i**: δ = 7.43–7.14 (m, 3H), 6.14 (d, *J* = 8.8 Hz, 1H), 5.80–5,76 (m, 1H), 5.59–5.58 (m, 1H), 3.38 (m, 1H), 2.03–1.43 (m, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ = 141.1, 138.8, 138.6, 133.7, 128.7, 128.4, 128.35, 128.3, 128.2, 125.9, 125.5, 125.3, 124.7, 123.9, 118.6, 114.5, 38.8, 37.5, 29.1, 28.1, 24.8, 24.7, 20.9, 20.6; HRMS (EI): calcd. for $C_{12}H_{13}BrS$, 267.9921; found, 267.9910.

(*Z*)-3-(2-Bromo-3-cyclohexylprop-1-enyl)cyclohex-1-ene (Table 2, 3j). The *Z* isomer of compound **3j** could be isolated by silica-gel column chromatography): ^1H NMR ($CDCl_3$, 600 MHz, ppm): δ = 5.74–5.71 (m, 1H), 5.51–5.50 (m, 1H), 5.46 (d, *J* = 8.8 Hz, 1H), 3.19 (m, 1H), 2.26 (d, *J* = 7.0 Hz, 2H), 1.98 (m, 2H), 1.87–1.82 (m, 1H), 1.70–1.55 (m, 8H), 1.40–1.34 (m, 2H), 1.28–1.22 (m, 2H), 1.16–1.10 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ = 133.4, 128.9, 127,7,

126.0, 49.2, 38.2, 35.6, 32.5, 28.3, 26.5, 26.2, 24.8, 20.9; HRMS (EI): calcd. for $C_{15}H_{23}Br$, 282.0983; found, 282.0981.

3-(2-Bromooct-1-enyl)cyclohex-1-ene (Table 2, 3k). E/Z (1:1.6); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3k**: $\delta = 5.74$ (d, $J = 10.3$ Hz, 1H), 5.73–5.71 (m, 1H), 5.43–5.42 (m, 1H), 2.98 (m, 1H), 2.46–0.87 (m, 19H); (*Z*)**3k**: $\delta = 5.73$–5.71 (m, 1H), 5.51–5.50 (m, 1H), 5.49 (d, $J = 8.4$ Hz, 1H), 3.19 (m, 1H), 2.46–0.87 (m, 19H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): $\delta = 136.1$, 132.1, 128.9, 128.2, 127.7, 127.6, 126.1, 41.5, 38.1, 36.6, 35.7, 31.6, 31.5, 29.1, 28.3, 28.24, 28.21, 28.1, 28.0, 24.8, 24.7, 22.6, 20.9, 20.8, 14.0; HRMS (EI): calcd. for $C_{14}H_{23}Br$, 270.0983; found, 270.0989.

3-(2-Bromodec-1-enyl)cyclohex-1-ene (Table 2, 3l). E/Z (1:1); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3l**: $\delta = 5.73$ (d, $J = 9.9$ Hz, 1H), 5.73–5.72 (m, 1H), 5.43–5.42 (m, 1H), 2.97 (m, 1H), 2.45–0.87 (m, 23H); (*Z*)**3l**: $\delta = 5.73$–5.72 (m, 1H), 5.51–5.50 (m, 1H), 5.49 (d, $J = 8.8$ Hz, 1H), 3.19 (m, 1H), 2.45–0.87 (m, 23H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): $\delta = 136.0$, 132.1, 128.9, 128.2, 127.7, 127.6, 126.1, 41.5, 38.2, 36.5, 35.7, 31.9, 29.4, 29.3, 29.2, 29.1, 28.6, 28.3, 28.27, 28.21, 28.1, 24.8, 24.7, 22.6, 20.9, 20.8, 14.1; HRMS (EI): calcd. for $C_{16}H_{27}Br$, 298.1296; found, 298.1296.

(1-Bromo-2-(4,4-dimethylcyclohex-2-enyl)vinyl)benzene (Table 2, 3m). E/Z (4.3:1); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3m**: $\delta = 7.53$–7.27 (m, 5H), 6.04 (d, $J = 10.7$ Hz, 1H), 5.48–5.46 (m, 1H), 5.33–5.31 (m, 1H), 2.80–2.79 (m, 1H), 1.70–0.78 (m, 10H); (*Z*)**3m**: $\delta = 7.53$–7.27 (m, 5H), 6.05 (d, $J = 8.8$ Hz, 1H), 5.51 (m, 1H), 5.40 (m, 1H), 3.34 (m, 1H), 1.70–0.78 (m, 10H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): $\delta = 140.0$, 139.0, 138.8, 137.9, 135.4, 135.1, 128.9, 128.85, 128.4, 128.3, 128.2, 127.6, 127.2, 125.9, 125.6, 124.6, 120.3, 39.4, 37.5, 35.6, 35.3, 31.4, 31.3, 30.1, 29.3, 29.1, 28.1, 26.1, 25.2; HRMS (EI): calcd. for $C_{16}H_{19}Br$, 290.0670; found, 290.0664.

(1-Chloro-2-(4,4-dimethylcyclohex-2-enyl)vinyl)benzene (Table 2, 3n). E/Z (8.3:1); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3n**: $\delta = 7.58$–7.29 (m, 5H), 5.80 (d, $J = 10.7$ Hz, 1H), 5.49–5.47 (m, 1H), 5.35–5.32 (m, 1H), 2.86–2.82 (m, 1H), 1.74–0.78 (m, 10H); (*Z*)**3n**: $\delta = 7.58$–7.29 (m, 5H), 5.81 (d, $J = 8.9$ Hz, 1H), 5.51 (m, 1H), 5.42 (m, 1H), 3.42 (m, 1H), 1.74–0.78 (m, 10H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): $\delta = 139.0$, 138.7, 137.7, 137.4, 133.8, 131.4, 131.2, 130.5, 128.8, 128.7, 128.5, 128.4, 128.3, 127.9, 127.1, 126.4, 126.1, 125.8, 36.5, 36.4, 35.7, 35.4, 32.1, 31.3, 30.1, 29.3, 29.1, 28.2, 26.4, 25.4; HRMS (EI): calcd. for $C_{16}H_{19}Cl$, 246.1175; found, 246.1177.

(1-Bromo-2-(cyclopent-2-enyl)vinyl)benzene (Table 2, 3o). E/Z (1:1.1); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3o**: $\delta = 7.53$–7.27 (m, 5H), 6.04 (d, $J = 10.3$ Hz, 1H), 5.80–5.79 (m, 1H), 5.55–5.54 (m, 1H), 3.37–3.35 (m, 1H), 2.45–1.63 (m, 4H); (*Z*)**3o**: $\delta = 7.53$–7.27 (m, 5H), 6.08 (d, $J = 8.4$ Hz, 1H), 5.87–5.86 (m, 1H), 5.70–5.68 (m, 1H), 3.89–3.88 (m, 1H), 2.45–1.63 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): $\delta = 139.9$, 138.8, 137.9, 135.4, 132.5, 132.3, 132.2, 129.1, 128.4, 128.3, 128.2, 127.6, 124.1, 119.6, 48.8, 46.9, 32.3, 32.1, 30.7, 30.1; HRMS (EI): calcd. for $C_{13}H_{13}Br$, 248.0201; found, 248.0205.

(S)-(1-Bromo-2-(2-methyl-4-(prop-1-en-2-yl)cyclohex-2-enyl)vinyl)benzene (Table 2, 3p). E/Z (1.9:1); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3p**: δ = 7.54–7.28 (m, 5H), 6.23 (d, J = 11.3 Hz, 1H), 5.44 (m, 1H), 4.73–4.71 (m, 2H), 2.76-2.74 (m, 1H), 2.32–1.60 (m, 11H); (*Z*)**3p**: δ = 7.54–7.28 (m, 5H), 6.20 (d, J = 9.5 Hz, 1H), 5.52 (m, 1H), 4.73–4.71 (m, 2H), 3.35 (m, 1H), 2.32–1.60 (m, 11H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ = 149.5, 149.4, 140.1, 139.0, 137.5, 137.4, 137.1, 134.8, 134.6, 134.0, 128.9, 128.8, 128.4, 128.2, 127.8, 127.6, 125.1, 122.8, 120.6, 108.9, 42.8, 40.8, 37.1, 36.4, 33.7, 33.1, 30.8, 22.2, 22.1, 20.8, 20.7; HRMS (EI): calcd. for $C_{18}H_{21}Br$, 316.0827; found, 316.0823.

(S)-(1-Chloro-2-(2-methyl-4-(prop-1-en-2-yl)cyclohex-2-enyl)vinyl)benzene (Table 2, 3q). E/Z (1.7:1); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3q**: δ = 7.59–7.29 (m, 5H), 5.99 (d, J = 11.0 Hz, 1H), 5.44 (m, 1H), 4.73–4.71 (m, 2H), 2.83–2.80 (m, 1H), 2.33–1.62 (m, 11H); (*Z*)**3q**: δ = 7.59–7.29 (m, 5H), 6.14 (d, J = 9.5 Hz, 1H), 5.52 (m, 1H), 4.73–4.71 (m, 2H), 3.41 (m, 1H), 2.33–1.62 (m, 11H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ = 149.4, 138.3, 137.5, 134.8, 134.3, 133.3, 132.6, 131.1, 131.0, 128.7, 128.65, 128.5, 128.4, 128.3, 126.6, 122.4, 108.9, 108.8, 40.0, 39.7, 37.0, 36.4, 34.0, 33.1, 30.8, 22.2, 22.1, 20.8, 20.7; HRMS (EI): calcd. for $C_{18}H_{21}Cl$, 272.1332; found, 272.1336.

((1*Z*,4*E*)-1-Bromopenta-1,4-diene-1,3,5-triyl)tribenzene (Table 2, 3r). E/Z (3:1); ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): (*E*)**3r**: δ = 7.60–7.21 (m, 15H), 6.61–6.32 (m, 3H), 4.28 (dd, J = 10.4 Hz, J = 6.5 Hz, 1H); (*Z*)**3r**: δ = 7.60–7.21 (m, 15H), 6.61–6.32 (m, 3H), 4.91 (dd, J = 9.3 Hz, J = 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ = 142.0, 139.7, 138.4, 137.1, 137.0, 134.5, 132.1, 131.0, 130.9, 130.8, 130.0, 128.8, 128.79, 128.72, 128.6, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 126.9, 126.3, 126.1, 122.3, 51.4, 49.5; HRMS (EI): calcd. for $C_{23}H_{19}Br$, 374.0670; found, 374.0666.

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