Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2012, **10**, 7347

www.rsc.org/obc

PAPER

Facile coupling of propargylic, allylic and benzylic alcohols with allylsilane and alkynylsilane, and their deoxygenation with Et_3SiH, catalyzed by $Bi(OTf)_3$ in [BMIM][BF_4] ionic liquid (IL), with recycling and reuse of the IL

G. G. K. S. Narayana Kumar and Kenneth K. Laali*

Received 30th May 2012, Accepted 12th July 2012
DOI: 10.1039/c2ob26046h

Allyltrimethylsilane (allyl-TMS) reacts with propargylic alcohols **1a–1d** in the presence of 10% $Bi(OTf)_3$ in [BMIM][BF_4] solvent to furnish the corresponding 1,5-enynes in respectable isolated yields (87–93%) at room temperature. The utility of $Bi(OTf)_3$ as a superior catalyst was demonstrated in a survey study on coupling of allyl-TMS with **1a** employing several metallic triflates (Bi, Ln, Al, Yb) as well as, $B(C_6F_5)_3$, $Zn(NTf_2)_2$ and $Bi(NO_3)_3{\cdot}5H_2O$. Coupling of cyclopropyl substituted propargylic alcohol **1e** with allyl-TMS gave the skeletally intact 1,5-enyne and a ring opened derivative as a mixture. Coupling of propargylic/allylic alcohol **1f** with allyl-TMS resulted in allylation at both benzylic (2 isomers) and propargylic positions, as major and minor products respectively. The scope of this methodology for allylation of a series of allylic and benzylic alcohols was explored. Chemoselective reduction of a host of propargylic, propagylic/allylic, bis-allylic, allylic, and benzylic alcohols with Et_3SiH was achieved in high yields with short reaction times. The same approach was successfully applied to couple representative propargylic and allylic alcohols with 1-phenyl-2-trimethylsilylacetylene. The recovery and reuse of the ionic liquid (IL) was gauged in a case study with minimal decrease in isolated yields after six cycles.

Introduction

Coupling of π-activated alcohols (propargylic, allylic, and benzylic) with silicon-based carbanion equivalents, in particular allylsilanes and alkynylsilanes, is an area of substantial current interest. Direct coupling of the propargylic alcohols is of particular interest since it enables the assembly of enynes and diynes in a one-pot approach. Early studies demonstrated the viability of these transformations by employing rhenium,[1] ruthenium,[2,3] and Au(III) catalysts,[4a,b] with mixtures of rhenium and gold catalysts reported to give higher yields.[2] The ruthenium catalyst was also employed in reduction of propargylic systems with silanes.[3] The utility of a heterobimetallic "Pd–Sn" catalyst system has also been recognized.[5] These reactions are typically carried out in $MeNO_2$, DCE, or DCM, and in the case of rhenium-oxo catalyst require a co-catalyst.[1] The reported BCl_3-mediated reaction of the alkoxides (*n*-BuLi/DCM) with allyl-TMS represents a different approach to the generation of propargylic cations for reaction with allylsilanes.[6]

Several other Lewis acid catalysts have also been used, namely $Cu(BF_4)_2$,[7] $Sc(OTf)_3$,[7] $FeCl_3$,[8] and iodine,[9] typically employing MeCN and DCM as solvent. The potential of early main group metals to bring about allylation and deoxygentation was shown by using $Ca(NTf_2)_2/Bu_4NBF_4$ system.[10,11]

In addition to these reports several studies on coupling of allylic and benzylic alcohols with allylsilanes have appeared, using various Lewis and Brønsted acids, namely $BiCl_3$,[12] $ZrCl_4$,[13] ion-exchanged montmorillonite,[14] phosphomolybdic acid,[15] $FeCl_3{\cdot}6H_2O$,[16] and $HN(SO_2F)_2$.[17]

Despite the availability of these earlier methods, development of high yielding approaches that employ readily available catalysts in combination with non-volatile solvents that can be recycled and reused is highly desirable.

In continuation of our work on electrophilic and onium ion chemistry in ionic liquids (ILs),[18] and in relation to recent studies from our laboratory focusing on generation and chemistry of propargylic cations in ILs,[19] we describe herein efficient allylation (with allyl-TMS), reduction (with Et_3SiH), and alkynylation (with alkynyl-TMS) methods for a wide range of propargylic, allylic, and benzylic alcohols.

Results and discussion

Activation of propargylic alcohols with metallic triflate/ionic liquid systems for arene propargylation and for the facile assembly of propargylic ethers was demonstrated in earlier works from this laboratory,[19a] and in other studies bismuth nitrate/IL system

Department of Chemistry, University of North Florida, 1 UNF Drive, Jacksonville, FL 32224, USA

proved efficient in propargylation of 1,3-diketones,[19b] as well as indoles, and carbazole.[19c] The finding that "tamed" propargylic cations can be generated selectively in the IL media under mild conditions for coupling to various nucleophiles provided the impetus for the present study to examine coupling of propargylic alcohols with allyl-TMS **2**, the alkynylsilane **3**, and their deoxygenation with Et_3SiH **4**. This project was then extended to include a host of allylic, and benzylic alcohols.

Using the coupling reaction of propargylic alcohol (±)-**1a** with allylsilane **2** as a standard reaction (Fig. 1), and with [BMIM][BF_4] as solvent, the efficiency of a series of metallic triflates (Ln, Bi, Al, Yb) as well as $B(C_6F_5)_3$, $Bi(NO_3)_3$, and Zn $(NTf_2)_2$ were explored. For comparison, the reaction was also carried out in the absence of Lewis acid in [BMIM][BF_4], [nitro-BMIM][NTf_2]$_2$,[19b] and in ethylammonium nitrate (EAN) (Table 1).

This comparative study indicated that whereas several catalytic systems were functional, $Bi(OTf)_3$ was superior to all of them. Based on the experiments performed without an added Lewis acid (runs 9–11), [nitro-BMIM][NTf_2] ionic liquid showed potential, but with the goal to perform these reaction at r.t. to avoid side reactions, it was not selected for further study. A control experiment performed in 1,2-DCE as solvent employing 10 mol% $Bi(OTf)_3$ (run 12) gave a lower isolated yield relative to run 5. Based on the results summarized in Table 1, 10 mol% of $Bi(OTf)_3$ dissolved in [BMIM][BF_4] solvent was selected as an optimum system for subsequent studies.

Reaction of propargylic alcohols **1b**, **1c**, and **1d** with allyl-TMS gave the corresponding 1,5-enynes (**6**, **7**, and **8**) in

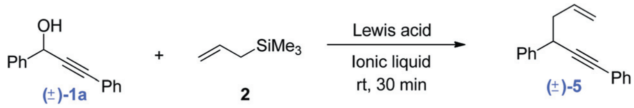
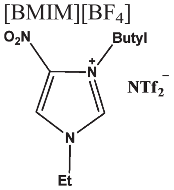


Fig. 1 Coupling reaction selected for the survey study.

Table 1 Screening of Lewis acid/IL systems as catalysts for the synthesis of (±)-**5**

Screen No	Lewis acid	IL and molecular solvent	Isolated yield (%)
1	$Ln(OTf)_3$	[BMIM][BF_4]	66
2	$Al(OTf)_3$	[BMIM][BF_4]	46
3	$Yb(OTf)_3$	[BMIM][BF_4]	66
4	$Bi(OTf)_3$[a]	[BMIM][BF_4]	80
5	$Bi(OTf)_3$	[BMIM][BF_4]	93
6	$Bi(NO_3)_3{\cdot}5H_2O$	[BMIM][BF_4]	39
7	$B(C_6F_5)_3$	[BMIM][BF_4]	63
8	$Zn(NTf_2)_2$	[BMIM][BF_4]	12
9	—[b]	[$C_2H_5NH_3$][NO_3]	Trace
10	—[b]	[BMIM][BF_4]	9
11	—[b]		26
12	$Bi(OTf)_3$	1,2-DCE	82

[a] 5 mol% of Lewis acid. All reactions were carried out on a 1 mmol scale with 10 mol% of Lewis acid in 3.5 mL of fresh ionic liquid at room temperature and monitored for 30 min. [b] Reaction carried out without Lewis acid.

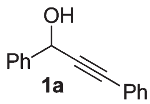
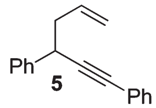
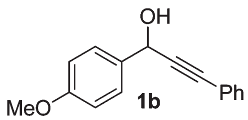
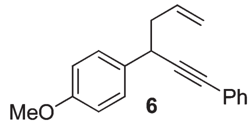
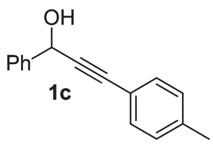
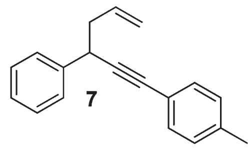
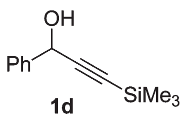
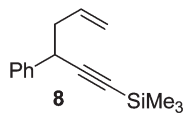
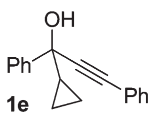
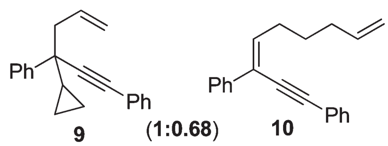
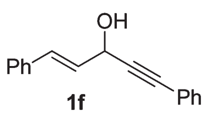
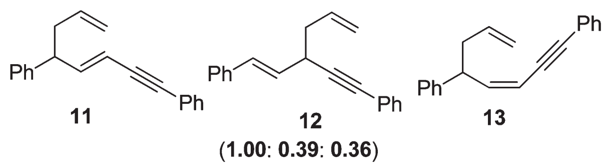
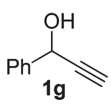
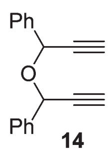
87–93% isolated yields (Table 2). Reaction of the cyclopropyl-substituted alcohol **1e** gave a mixture of skeletally intact 1,5-enyne **9** and the ring-opened derivative **10**, in 1.0 : 0.68 ratio by NMR. Coupling of propargylic/allylic alcohol **1f** with allyl-TMS resulted in allylation at both benzylic (**11** and **13**) and propargylic positions (**12**), as major and minor products respectively. The *trans* to *cis* isomeric ratio was measured as 1.0 to 0.36 by NMR. It is noteworthy that no allenyl-derived products, which were observed earlier in some transition metal catalyzed reactions,[1,11] and no bicyclic products derived from cycloisomerization of 1,5-enynes,[4b] were found in present study. The propargyl alcohol **1g** did not couple with allyl-TMS, instead the bis-propargylic ether **14** was isolated.[19a] Except for the runs 1, 5, and 6 reactions were performed in recycled IL, and judging from the isolated yields, this had only a minimal effect on the conversions (see Table 2).

At this point in the study it was necessary to establish the effect of recycling and re-use of the IL on the isolated yields over many cycles. The reaction shown in Fig. 1 was selected as benchmark for this purpose and the process was repeated for six cycles. The results, given in Table 3, show very small effects on the isolated yields and are therefore quite encouraging.

In the next phase of the study the scope of the method for coupling of allylic and benzylic alcohols with allyl-TMS was examined. The bis-allylic alcohol **1h** gave the skeletally intact coupling product **16** and the isomeric derivative **15**, in 0.42 : 1.0 ratio by NMR, providing strong indication for the formation of a doubly-allylic carbocation and its rearrangement to a benzylic/allylic carbocation. The allyl-derivatives **17** and **18** were formed in high yields from alcohols **1i** and **1j**, and the cyclopropyl derivative **1k** gave the skeletally intact allyl derivative **19**. Compound **20** obtained from alcohols **1l** is interesting as it shows that allylation is accompanied by efficient alkylation at C-5 by an α-thiophenyl-carbocation. By increasing the allyl-TMS to alcohol ratio the "normal" coupling product **21** was isolated as a minor product (see Table 4). The benzylic alcohols **1m** and **1n** gave the expected coupling products **22** and **23**. It is noteworthy that except for runs 1, 5, and 6 (Table 4) where fresh IL was employed other runs were performed in recycled IL.

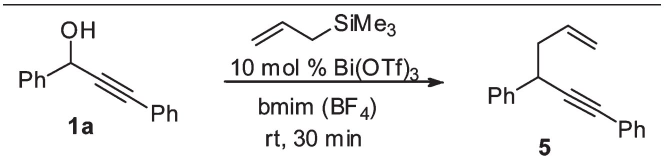
Attention was then focused on hydride transfer from Et_3SiH **4** to propagylic, allylic, and benzylic carbocations *via* alcohols with $Bi(OTf)_3$/[BMIM][BF_4], and the results are summarized in Table 5. Propargylic alcohols **1a** and **1b** gave the corresponding skeletally intact alkynes **24** and **25**. Whereas the predominant product of deoxygenation of the cyclopropyl-substituted alcohol **1e** was the intact hydrocarbon **26**, minor amounts of the ring opened product **27** was also detected by NMR. As was the case in coupling with allyl-TMS (Table 2), deoxygenation of the propargylic/allylic alcohols **1f** gave a mixture of three products, with predominant products arising from hydride transfer to the benzylic position to form skeletally rearranged isomeric hydrocarbons **28** and **29**, together with the skeletally intact hydrocarbon **30**. The product ratios were estimated by NMR as 2.0 : 0.29 : 0.12 respectively. A similar chemoselectivity was observed in deoxygenation of alcohol **1h**, forming an isomeric mixture of hydrocarbons **31** and **33**, along with the skeletally intact **32** as a minor component. Reaction of α-cyclopropyl-alcohol **1k** gave only the skeletally intact hydrocarbon **34**, and reaction of alcohols **1i**, and **1n** proceeded in high yields to furnish the corresponding hydrocarbons.

Table 2 Reaction of propargylic alcohols with allyltrimethylsilane (**2**) with $Bi(OTf)_3$ in (bmim) BF_4[a,b]

Entry	Alcohol	Products	Time (min)	Isolated yield (%)
1			30	93
2			20	90
3			30	89
4			25	87
5			60	76
6			30	86
7			30	89

[a] Fresh (bmim) BF_4 was used in runs 1, 5 and 6, whereas recycled IL was used in others. [b] The (bmim) BF_4 could be reused without purification for up to three runs, after which it was purified and reused.

Table 3 Recovery and reuse of (bmim) BF_4



No. of cycles	Isolated yield (%)
1	93
2	92
3	92
4	91
5	90
6	88

The last part of the study dealt with alkynylation of π-activated alcohols with 1-phenyl-2-trimethylacetylene **3** using $Bi(OTf)_3$/[BMIM][BF_4] to synthesize 1,5-diynes and 1,5-enynes. The feasibility was demonstrated in selected cases with propargyl alcohols **1a** and **1c** and allylic alcohol **1i**. The corresponding 1,5-diynes **37** and **38** and the 1,5-enyne **39** were obtained in very good isolated yields and short reaction times (Table 6).

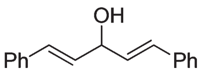
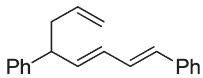
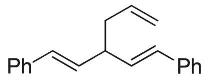
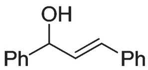
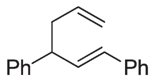
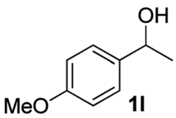
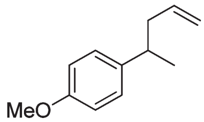
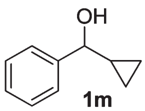
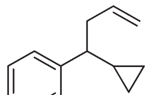
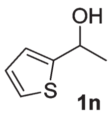
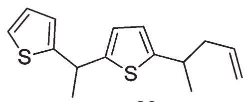
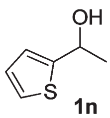
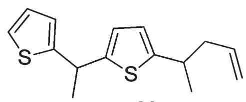
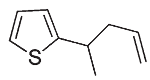
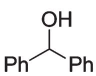
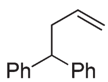
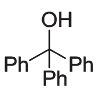
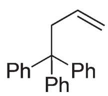
In summary, we have shown that $Bi(OTf)_3$ in [BMIM][BF_4] solvent is an efficient catalytic system for allylation, alkynylation and deoxygenation of propagylic, allylic and benzylic alcohols. Reactions are performed at room temperature and generally give very good isolated yields, typically in less than an hour. These attributes coupled to the added advantage of recycling and reuse of the IL make this a superior method for the synthesis of 1,5-enynes, 1,5-diynes and a host of other functional building blocks.

Experimental

General

The metallic triflates, bismuth nitrate and tris(pentafluorophenyl)-borane were high purity commercially available samples and

Table 4 Reaction of allylic and benzylic alcohols with allyltrimethylsilane (**2**) with $Bi(OTf)_3$ in (bmim) BF_4[a,b]

Entry	Alcohol	Products	Time (min)	Isolated yield (%)
1	 **1h**	 **15**  **16** (**1:0.42**)	20	85
2	 **1i**	 **17**	20	94
3	 **1l**	 **18**	25	94
4	 **1m**	 **19**	55	91
5	 **1n**	 **20**	30	84
6[c]	 **1n**	 **20**  **21**	30	76 : 16
7	 **1j**	 **22**	20	92
8	 **1k**	 **23**	60	86

[a] Fresh (bmim) BF_4 was used in runs 1, 5 and 6, whereas recycled IL was used in others. [b] The (bmim) BF_4 could be reused without purification for up to three runs, after which it was purified and reused. [c] 2.2 equi. of allyltrimethylsilane.

were used as received. Ethylammonium nitrate (EAN)[18e] and the nitro-IL [3-butyl-1-ethyl-4-nitroimidazolium bis(trifluoromethylsulfonyl)imide][19b] were prepared as previously reported. The propargylic alcohols (**1a**, **1d** & **1g**), benzylic alcohols (**1i**, **1m** & **1n**), allyltrimethyl silane **2**, triethylsilane **3**, and 1-phenyl-2-trimethylsilylacetylene **4** were purchased from ACROS, ALDRICH and ALFA-AESAR and were used without further purification. The other propargylic alcohols and benzylic alcohols were prepared as previously reported.[20] Reactions were carried out in oven-dried small Schlenk tubes under nitrogen. Column chromatography separations were performed on silica gel (200–400 mesh). In some cases preparative TLC was employed to isolate the products.

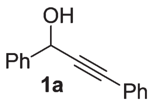
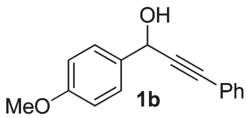
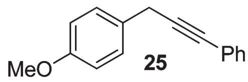
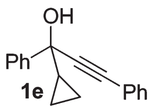
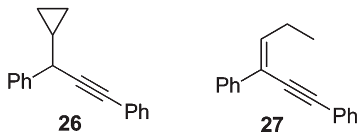
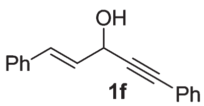
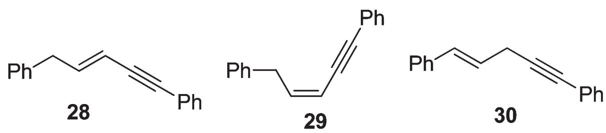
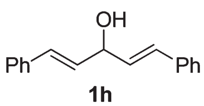
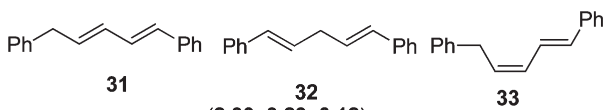
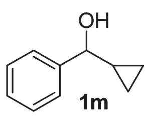
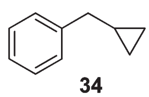
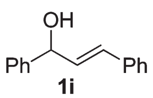
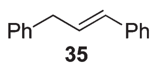
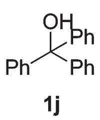
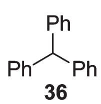
Melting points were recorded with a MEL-TEMP apparatus and are uncorrected.

NMR spectra were recorded in $CDCl_3$ (^1H at 500 MHz; ^{13}C at 125 MHz) on a Varian 500 NMR instrument (chemical shifts were referenced to internal solvent signals: for $CDCl_3$ – ^1H at 7.26 ppm/^{13}C at 77.16 ppm). IR spectra (solution in $CHCl_3$, cm^{-1}) were recorded on a SHIMADZU FT-IR spectrophotometer. GC analysis were performed on a Hewlett-Packard (HP) gas chromatograph model 5890 series II equipped with a split/splitless injector and a capillary RTX-5 column. GC-MS analyses were performed on HP 5890 series II GC/HP 5972 series mass spectrometer.

General procedure

The ionic liquid (for liquid reactants: 3.5 mL; 18.7 mmol; *IL mole fraction = 0.8904* – for solid reactants: 4.0 mL; 21.4 mmol; *IL mole fraction = 0.9029*) was charged into an oven-dried Schlenk tube under a nitrogen atmosphere and $Bi(OTf)_3$ (10 mol%) was added and upon sonication (for about 15 min) was dissolved in the IL. The respective alcohol (1.0 mmol) was then introduced into the Schlenk tube under a nitrogen atmosphere followed by the desired silyl nucleophile (1.2 mmol). The reaction mixture was magnetically stirred, until completion (as monitored by

Table 5 Reaction of alcohols with triethylsilane (**3**) with $Bi(OTf)_3$ in (bmim) BF_4[a,b]

Entry	Alcohol	Products	Time (min)	Isolated yield (%)
1	 **1a**	 **24**	15	95
2	 **1b**	 **25**	20	90
3	 **1e**	 **26**, **27** (**1:0.06**)	50	80
4	 **1f**	 **28**, **29**, **30** (**2.00**: **1.11**: **0.42**)	20	92
5	 **1h**	 **31**, **32**, **33** (**2.00**: **0.29**: **0.12**)	30	96
6	 **1m**	 **34**	60	83
7	 **1i**	 **35**	15	93
8	 **1j**	 **36**	40	91

[a] Fresh (bmim) BF_4 was used in runs 3 and 4, whereas recycled IL was used in others. [b] The (bmim) BF_4 could be reused without purification for up to three runs, after which it was purified and reused.

TLC). Once the reaction was over, the reaction mixture was extracted with dry diethyl ether, until the final extraction did not show a spot corresponding to the starting material or to the product. The combined organic extracts were washed with DI water, dried with $MgSO_4$ and concentrated to give the crude product, which upon purification through column chromatography furnished the desired products.

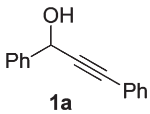
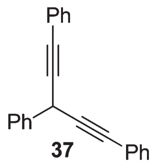
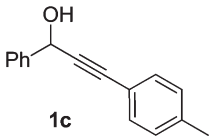
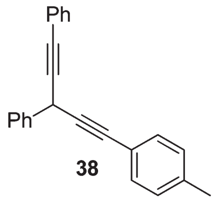
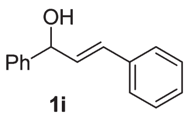
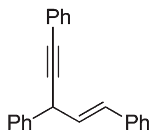
Re-use and recycling of IL

After extraction, the ionic liquid was dried under high-vacuum at 60–70 °C for about 6 hours and re-used in successive runs.

Hex-5-en-1-yne-1,3-diyldibenzene (5).[1] Pale yellow liquid, Yield: 93%. ^{1}H NMR (500 MHz; $CDCl_3$): δ_H 2.57–2.60 (m, 2H), 3.91 (t, J = 7.0 Hz, 1H), 5.06–5.12 (m, 2H), 5.87–5.95 (m, 1H), 7.23–7.35 (m, 6H), 7.41–7.45 (m, 4H) ppm; ^{13}C NMR (125 MHz; $CDCl_3$): δ_C 38.70, 42.92, 83.94, 91.08, 117.22, 123.84, 126.97, 127.71, 127.94, 128.34, 128.62, 131.81, 135.60, 141.53 ppm; IR (cm^{-1}, $CHCl_3$): ν 3078, 3062, 3030, 2980, 2931, 2912, 1641, 1597, 1489, 1452, 1442, 1344, 1070, 1029, 995, 914 cm^{-1}; GC-MS: m/z 232 (M^+), 191 [$(M - 41)^+$, 100%].

1-Methoxy-4-(1-phenylhex-5-en-1-yn-3-yl)benzene (6).[21] Brown liquid, Yield: 90%. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 2.55–2.58 (m, 2H), 3.80 (s, 3H), 3.86 (t, J = 7.0 Hz, 1H), 5.05–5.12 (m, 2H), 5.86–5.94 (m, 1H), 6.87 (d, J = 9.0 Hz, 2H), 7.25–7.29 (m, 3H), 7.33 (d, J = 9.0 Hz, 2H), 7.42–7.44 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 37.71, 42.88, 55.29, 83.60, 91.28, 113.86, 117.02, 123.74, 127.76, 128.19, 128.54, 131.65, 133.51, 135.55, 158.46 ppm; IR (cm^{-1}, $CHCl_3$): ν 3076, 3062, 3003, 2954, 2933, 2910, 1600, 1585, 1512, 1442, 1303, 1247, 1174, 1111, 1033, 995, 916, 831, 758 cm^{-1}; GC-MS: m/z 262 $(M)^+$.

Table 6 Reaction of alcohols with 1-phenyl-2-trimethylsilylacetylene (**4**) with $Bi(OTf)_3$ in (bmim) BF_4[a]

Entry	Alcohol	Products	Time (min)	Isolated yield (%)
1	 **1a**	 **37**	50	87
2	 **1c**	 **38**	40	91
3	 **1i**	 **39**	50	89

[a] Fresh (bmim) BF_4 was used.

1-Methyl-4-(3-phenylhex-5-en-1-ynyl)benzene (7). Yellow liquid, Yield: 89%. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 2.32 (s, 3H), 2.57 (t, J = 7.0 Hz, 2H), 3.89 (t, J = 7.0 Hz, 1H), 5.05–5.11 (m, 2H), 5.88–5.94 (m, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.22–7.25 (m, 1H), 7.31–7.34 (m, 4H), 7.41 (d, J = 8.0 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.56, 38.69, 42.98, 83.96, 90.25, 117.16, 120.72, 126.91, 127.71, 128.57, 129.08, 131.66, 135.66, 137.93, 141.64 ppm; IR (cm^{-1}, $CHCl_3$): ν 3078, 3028, 2920, 2862, 1722, 1683, 1674, 1604, 1510, 1448, 1315, 1286, 1278, 1219, 1178, 1107, 1074, 1029, 997, 916, 817 cm^{-1}; GC-MS: m/z 246 [(M)$^+$, 100%], 220 (M − 41)$^+$.

Trimethyl(3-phenylhex-5-en-1-ynyl)silane (8).[4a] Colorless oil, Yield 87%. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.18 (s, 9H), 2.52 (tt, J = 7.5, 1.5 Hz, 2H), 3.70 (t, J = 7.5 Hz, 1H), 5.02–5.06 (m, 2H), 5.79–5.87 (m, 1H), 7.21–7.35 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 0.30, 39.05, 42.98, 87.94, 107.81, 117.13, 126.89, 127.68, 128.54, 135.44, 141.20 ppm; IR (cm^{-1}, $CHCl_3$): ν 3080, 3064, 3030, 2958, 2935, 2899, 2173, 1641, 1600, 1494, 1452, 1440, 1415, 1340, 1328, 1301, 1247, 1076, 1055, 1031, 995, 981, 916, 879, 818, 756 cm^{-1}; GC-MS: m/z 228 (M)$^+$, 191 [(M − 41)$^+$, 100%].

(3-Cyclopropylhex-5-en-1-yne-1,3-diyl)dibenzene (9) and (*Z*)-nona-3,8-dien-1-yne-1,3-diyldibenzene (10)

Pale yellow liquid, Yield: 76% [pair of isomers in 1.0 : 0.68 ratio (**9** : **10**) by NMR]:

(3-Cyclopropylhex-5-en-1-yne-1,3-diyl)dibenzene (9). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.37–0.42 (m, 1H), 0.46–0.51 (m, 1H), 0.54–0.60 (m, 1H), 0.75–0.80 (m, 1H), 1.25–1.32 (m, 1H), 2.80 (d, J = 7.0 Hz, 2H), 4.97–5.07 (m, 2H), 5.77–5.90 (m, 1H), 7.22–7.66 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 1.95, 3.52, 20.44, 47.16, 47.92, 85.80, 90.24, 117.53, 123.72, 126.14, 126.94, 128.25, 128.36, 128.51, 131.83, 134.86, 138.70 ppm; IR (cm^{-1}, $CHCl_3$) (inseparable mixtures): ν 3078, 3028, 2920, 2862, 1722, 1683, 1674, 1604, 1510, 1448, 1315, 1286, 1278, 1219, 1178, 1107, 1074, 1029, 997, 916, 817 cm^{-1}; GC-MS (isomeric mixture): m/z 272 (M)$^+$.

(*Z*)-Nona-3,8-dien-1-yne-1,3-diyldibenzene (10). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.65 (pentet, J = 7.5 Hz, 2H), 2.14–2.19 (m, 2H), 2.60 (q, J = 7.5 Hz, 2H), 4.97–5.07 (m, 2H), 5.77–5.90 (m, 1H), 6.46 (t, J = 7.5 Hz, 1H), 7.22–7.66 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 28.52, 30.98, 33.59, 86.99, 95.33, 114.93, 123.93, 126.65, 127.63, 127.99, 128.32, 128.49, 131.65, 134.86, 138.39, 138.54, 144.76 ppm; IR (cm^{-1}, $CHCl_3$) (inseparable mixtures): ν 3078, 3028, 2920, 2862, 1722, 1683, 1674, 1604, 1510, 1448, 1315, 1286, 1278, 1219, 1178, 1107, 1074, 1029, 997, 916, 817 cm^{-1}; GC-MS (isomeric mixtures): m/z 272 (M)$^+$.

(*E*)-Octa-3,7-dien-1-yne-1,5-diyldibenzene (11), (*E*)-(3-allylpent-1-en-4-yne-1,5-diyl)dibenzene(12) and (*Z*)-octa-3,7-dien-1-yne-1,5-diyldibenzene (13)

Yellow liquid, Yield: 86% [in 1.00 : 0.39 : 0.36 ratio (**11** : **12** : **13**) by NMR]:

(*E*)-Octa-3,7-dien-1-yne-1,5-diyldibenzene (11). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 2.54 (t, J = 7.5 Hz, 2H), 3.47 (q, J = 7.0 Hz, 1H), 5.00–5.07 (m, 2H), 5.67 (d, J = 15.5 Hz, 1H), 5.70–5.82 (m, 1H), 6.39 (dd, J = 7.5, 15.5 Hz, 1H), 7.19–7.46 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 39.78, 49.25, 88.12, 89.21, 110.03, 116.84, 123.59, 126.75, 127.90, 128.12, 128.39, 128.74, 131.56, 136.11, 142.74, 147.04 ppm; IR (cm^{-1}, $CHCl_3$) (inseparable mixture): ν 3078, 3061, 3026, 3003, 2978, 2918, 1639, 1597, 1489, 1452, 1440, 1070, 1029, 993, 956, 912, 786, 754; GC-MS (isomeric mixture): *m/z* 217 $(M - 41)^+$.

(*E*)-(3-Allylpent-1-en-4-yne-1,5-diyl)dibenzene (12). ^1H NMR (500 MHz, $CDCl_3$): δ_H 2.49 (t, *J* = 7.0 Hz, 2H), 3.52 (q, *J* = 7.0 Hz, 1H), 5.06–5.19 (m, 2H), 5.92–6.01 (m, 1H), 6.21 (dd, *J* = 7.0, 15.5 Hz, 1H), 6.71 (d, *J* = 15.5 Hz, 1H), 7.19–7.46 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 35.56, 40.33, 84.26, 90.14, 117.33, 123.78, 126.53, 127.52, 128.28, 128.66, 128.71, 129.25, 130.93, 131.81, 135.43, 137.21 ppm; IR (cm^{-1}, $CHCl_3$) (isomeric mixture): *ν* 3078, 3061, 3026, 3003, 2978, 2918, 1639, 1597, 1489, 1452, 1440, 1070, 1029, 993, 956, 912, 786, 754; GC-MS (isomeric mixture): *m/z* 217 $(M - 41)^+$.

(*Z*)-Octa-3,7-dien-1-yne-1,5-diyldibenzene (13). ^1H NMR (500 MHz, $CDCl_3$): δ_H 2.58 (t, *J* = 7.0 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 1H), 5.06–5.19 (m, 2H), 5.73 (d, *J* = 10.0 Hz, 1H), 5.70–5.82 (m, 1H), 6.06 (t, *J* = 10.0 Hz, 1H), 7.19–7.46 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 40.05, 46.36, 86.48, 94.12, 109.17, 116.51, 123.68, 126.55, 127.62, 127.96, 128.35, 128.47, 131.60, 136.24, 143.52, 146.34 ppm; IR (cm^{-1}, $CHCl_3$) (isomeric mixture): *ν* 3078, 3061, 3026, 3003, 2978, 2918, 1639, 1597, 1489, 1452, 1440, 1070, 1029, 993, 956, 912, 786, 754; GC-MS (isomeric mixture): *m/z* 217 $(M - 41)^+$.

Bis(1-phenyl-2-propynyl)-ether (14).[19b] Colorless oil, Yield: 89%. NMR shows the presence of two geometrical isomers in 1 : 0.76 ratio. ^1H NMR (500 MHz, $CDCl_3$): δ_H 2.67 (d, *J* = 2.2 Hz, 2H), 2.72 (d, *J* = 2.0 Hz, 2H), 5.27 (d, *J* = 2.2 Hz, 2H), 5.67 (d, *J* = 2.0 Hz, 2H), 7.33–7.42 (m, 12H), 7.51–7.59 (m, 8H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 68.98, 69.49, 76.10, 76.44, 81.13, 81.54, 127.67, 127.88, 128.58, 128.66, 128.77, 128.94, 137.60, 137.83 ppm; IR (cm^{-1}, $CHCl_3$): *ν* 3286, 3064, 3032, 2875, 2115, 1494, 1452, 1344, 1301, 1267, 1193, 1080, 1001, 958, 912, 842, 823 cm^{-1}; GC-MS: *m/z* 131 $(PhCHO–C{\equiv}CH)^+$, 115 $[(PhCH–C{\equiv}CH)^+$, 100%].

(1*E*,3*E*)-Octa-1,3,7-triene-1,5-diyldibenzene (15) and (1*E*,4*E*)-3-allylpenta-1,4-diene-1,5-diyl)dibenzene (16)

Pale yellow liquid, Yield: 85% [in 1.00 : 0.42 (**15** : **16**) ratio by NMR]:

(1*E*,3*E*)-Octa-1,3,7-triene-1,5-diyldibenzene (15). ^1H NMR (500 MHz, $CDCl_3$): δ_H 2.56 (t, *J* = 7.0 Hz, 2H), 3.46 (q, *J* = 7.0 Hz, 1H), 5.00–5.08 (m, 2H), 5.69–5.80 (m, 1H), 5.99 (dd, *J* = 7.0, 16.0 Hz, 1H), 6.22 (dd, *J* = 10.5, 16.0 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.78 (dd, *J* = 10.5, 16.0 Hz, 1H), 7.12–7.37 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 40.30, 48.94, 116.46, 126.32, 126.49, 127.38, 127.86, 128.64, 128.73, 129.20, 130.54, 131.29, 136.64, 137.64, 138.12, 143.92 ppm; IR (cm^{-1}, $CHCl_3$) (isomeric mixture): *ν* 3061, 3026, 2954, 2920, 2848, 1641, 1600, 1494, 1448, 1219, 1072, 1029, 987, 966, 912; GC-MS (isomeric mixture): *m/z* 260 $(M)^+$, 217 $[(M - 41)^+$, 100%].

(1*E*,4*E*)-3-Allylpenta-1,4-diene-1,5-diyl)dibenzene (16). ^1H NMR (500 MHz, $CDCl_3$): δ_H 2.49 (t, *J* = 7.0 Hz, 2H), 3.14 (pentet, *J* = 7.0 Hz, 1H), 5.06–5.14 (m, 2H), 5.84–5.92 (m, 1H), 6.23 (dd, *J* = 7.0, 15.0 Hz, 2H), 6.46 (d, *J* = 15.0 Hz, 2H), 7.12–7.37 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 39.75, 46.13, 116.62, 126.29, 127.28, 128.68, 130.24, 132.49, 136.39, 137.59 ppm; IR (cm^{-1}, $CHCl_3$): *ν* 3061, 3026, 2954, 2920, 2848, 1641, 1600, 1494, 1448, 1219, 1072, 1029, 987, 966, 912; GC-MS: *m/z* 260 $(M)^+$, 217 $[(M - 41)^+, 100\%]^+$.

(*E*)-Hexa-1,5-diene-1,3-diyldibenzene (17).[10] Colorless oil, Yield: 94%. ^1H NMR (500 MHz, $CDCl_3$): δ_H 2.54–2.58 (m, 2H), 3.55 (dd, *J* = 13.5, 7.0 Hz, 1H), 4.95–5.05 (m, 2H), 5.70–5.78 (m, 1H), 6.30–6.38 (m, 2H), 7.12–7.31 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 40.29, 49.02, 116.46, 126.30, 126.47, 127.23, 127.85, 128.57, 128.62, 129.88, 133.56, 136.61, 137.56, 143.92; IR (cm^{-1}, $CHCl_3$): *ν* 3080, 3061, 3026, 2924, 1598, 1492, 1448, 1072, 1029, 964, 912, 758 cm^{-1}; GC-MS: *m/z* 193 $[(M - 41)^+$, 100%].

4-(4-Methoxyphenyl)-1-pentene (18).[12] Colorless oil, Yield: 94%. ^1H NMR (500 MHz, $CDCl_3$): δ_H 1.22 (d, *J* = 7.0 Hz, 3H), 2.22–2.35 (m, 2H), 2.72–2.76 (m, 1H), 4.93–5.00 (m, 2H), 5.66–5.73 (m, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 21.8, 39.06, 43.02, 55.36, 113.82, 115.92, 127.97, 137.44, 139.33, 157.90; IR (cm^{-1}, $CHCl_3$): *ν* 3074, 2997, 2958, 2926, 2908, 2835, 1639, 1612, 1583, 1512, 1456, 1440, 1300, 1240, 1176, 1035, 993, 912, 827, 806 cm^{-1}; GC-MS: *m/z* 176 $(M)^+$, 135 $[(M - 41)^+$, 100%].

4-Phenyl-4-cyclopropylbuta-1,2-ene (19).[15] Colorless oil, Yield: 90%. ^1H NMR (500 MHz, $CDCl_3$): δ_H 0.05–0.10 (m, 1H), 0.20–0.25 (m, 1H), 0.35–0.41 (m, 1H), 0.56–0.62 (m, 1H), 0.97–1.02 (m, 1H), 1.86–1.90 (m, 1H), 2.46–2.58 (m, 2H), 4.88–4.99 (m, 2H), 5.68–5.76 (m, 1H), 7.17–7.20 (m, 3H), 7.27–7.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 3.89, 5.77, 17.17, 41.26, 51.12, 115.74, 126.15, 127.77, 128.30, 137.24, 145.35; IR (cm^{-1}, $CHCl_3$): *ν* 3076, 3062, 3026, 3001, 2978, 2920, 2904, 2877, 1639, 1492, 1452, 1440, 1016, 995, 910, 852, 842, 819, 765 cm^{-1}; GC-MS: *m/z* 172 $(M)^+$, 131 $[(M - 41)^+$, 100%].

2-(Pent-4-en-2-yl)-5-(1-(thiophen-2-yl)ethyl)thiophene (20). Colorless liquid, ^1H NMR (500 MHz, $CDCl_3$): δ_H 1.29 (d, *J* = 6.5 Hz, 3H), 1.75 (d, *J* = 7.0 Hz, 3H), 2.24–2.30 (m, 1H), 2.40–2.46 (m, 1H), 3.02 (sextet, *J* = 7.0 Hz, 1H), 4.57 (q, *J* = 7.0 Hz, 1H), 4.99–5.05 (m, 2H), 5.72–5.80 (m, 1H), 6.61 (d, *J* = 3.5 Hz, 1H), 6.66 (dd, *J* = 1.0, 3.5 Hz, 1H), 6.88 (d, *J* = 3.5 Hz, 1H), 6.93 (dd, *J* = 3.5, 5.0 Hz, 1H), 7.16 (dd, *J* = 1.5, 5.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 22.16, 24.61/24.63, 35.41, 36.47, 43.49, 116.55, 122.01, 123.03, 123.66, 123.76, 126.63, 136.68, 147.16, 149.72, 150.36 ppm; IR (cm^{-1}, $CHCl_3$): *ν* 3072, 2968, 2924, 2870, 1639, 1452, 1436, 1375, 1284, 1234, 993, 914, 850, 827, 800, 748 cm^{-1}; GC-MS: *m/z* 262 $(M)^+$, 221 $[(M - 41)^+$, 100%].

4-(2-Thienyl)-1-pentene (21).[22] Colorless liquid, ^1H NMR (500 MHz, $CDCl_3$): δ_H 1.33 (d, *J* = 7.0 Hz, 3H), 2.29–2.35 (m, 1H), 2.42–2.48 (m, 1H), 3.08–3.15 (m, 1H), 4.99–5.06 (m, 2H), 5.72–5.80 (m, 1H), 6.80 (m, 1H), 6.92 (dd, *J* = 3.5, 5.5 Hz, 1H), 7.12 (dd, *J* = 1.0, 4.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 22.44, 35.27, 43.65, 116.63, 122.66, 122.74, 126.57, 136.61, 151.40 ppm; IR (cm^{-1}, $CHCl_3$): *ν* 3074, 2958, 2924, 2914, 1456, 1247, 991, 914, 862, 831, 773 cm^{-1}; GC-MS: *m/z* 152 $(M)^+$, 111 $[(M - 41)^+$, 100%].

4,4-Diphenyl-1-butene (22).[23] Colorless oil, Yield: 91%. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 2.81 (t, J = 7.0 Hz, 2H), 4.00 (t, J = 7.0 Hz, 1H), 4.93–5.04 (m, 2H), 5.67–5.74 (m, 1H), 7.15–7.28 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 40.09, 51.39, 116.42, 126.32, 128.09, 128.54, 136.98, 144.64; IR (cm^{-1}, $CHCl_3$): ν 3062, 3026, 2924, 1494, 1450, 1219, 1031, 993, 912. 771, 754 cm^{-1}; GC-MS: m/z 208 (M)$^+$, 167 [(M − 41)$^+$, 100%].

4-(4,4,4-Triphenyl)-1-butane (23).[15] White solid, m.p. 57–59 °C, Yield: 86%. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.49 (dt, J = 1.5, 7.0 Hz, 2H), 4.91–5.04 (m, 2H), 5.60–5.69 (m, 1H), 7.16–7.28 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 45.68, 56.44, 117.37, 126.10, 127.89, 129.56, 136.12, 147.43; IR (cm^{-1}, $CHCl_3$): ν 3057, 3032, 2929, 2916, 1492, 1446, 1087, 1035, 1001, 974, 914, 759 cm^{-1}; GC-MS: m/z 243 [(M − 41)$^+$, 100%].

1,3-Diphenylpropyne (24).[4b] Colorless liquid, Yield: 95%. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.82 (s, 2H), 7.22–7.45 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 25.89, 82.82, 87.67, 123.86, 126.77, 127.94, 128.11, 128.37, 128.68, 131.79, 136.92 ppm; IR (cm^{-1}, $CHCl_3$): ν 3062, 3030, 2918, 2889, 1950, 1693, 1670, 1597, 1452, 1427, 1417, 1336, 1317, 1292, 1070, 1028, 914 cm^{-1}; GC-MS: m/z 192 (M)$^+$.

1-Methoxy-4-(3-phenylprop-2-ynyl)benzene (25).[4b] Yellow liquid, Yield: 90%. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.76 (s, 2H), 3.79 (s, 3H), 6.87 (d, J = 8.5 Hz, 2H), 7.27–7.28 (m, 3H), 7.32 (d, J = 8.5 Hz, 2H), 7.43 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 25.01, 55.44, 82.54, 88.12, 114.11, 123.87, 127.89, 128.34, 128.93, 129.06, 131.76, 158.53 ppm; IR (cm^{-1}, $CHCl_3$): ν 3061, 3003, 2954, 2908, 2835, 1693, 1597, 1508, 1421, 1290, 1247, 1174, 1161, 1033, 831, 812, 756 cm^{-1}; GC-MS: m/z 222 [(M)$^+$, 100%], 207(M-Methyl)$^+$.

(3-Cyclopropylprop-1-yne-1,3-diyl)dibenzene (26) and (*Z*)-hex-3-en-1-yne-1,3-diylbenzene (27)

Pale yellow liquid, Yield: 80% [in 1 : 0.06 (**26** : **27**) ratio by NMR]:

(3-Cyclopropylprop-1-yne-1,3-diyl)dibenzene (26). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.51–0.59 (m, 4H), 1.13–1.25 (m, 1H), 3.68 (d, J = 7.0 Hz, 1H), 7.23–7.30 (m, 4H), 7.33–7.36 (m, 2H), 7.41–7.44 (m, 2H), 7.47–7.48 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 3.26, 4.21, 17.63, 41.44, 83.40, 89.74, 123.80, 126.97, 127.66, 127.91, 128.32, 128.60, 131.82, 142.16 ppm; IR (cm^{-1}, $CHCl_3$): ν 3080, 3062, 3028, 3003, 1689, 1670, 1598, 1489, 1452, 1442, 1276, 1070, 1020, 914 cm^{-1}; GC-MS (isomeric mixture): m/z 232 (M)$^+$.

(*Z*)-Hex-3-en-1-yne-1,3-diylbenzene (27). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.15 (t, J = 7.5 Hz, 3H), 2.58 (pentet, J = 7.5 Hz, 2H), 6.45 (t, J = 7.5 Hz, 1H), 7.23–7.66 (m, 10H) ppm; GC-MS: m/z 232 (M)$^+$.

(*E*)-Pent-3-en-1-yne-1,5-diyldibenzene (28), (*Z*)-pent-3-en-1-yne-1,5-diyldibenzene (29) and (*E*)-pent-1-en-4-yne-1,5-diyldibenzene (30)[16]

Yellow liquid, Yield: 92% [in 2.00 : 1.11 : 0.42 (**28** : **29** : **30**) ratio by NMR]:

(*E*)-Pent-3-en-1-yne-1,5-diyldibenzene (28). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.50 (d, J = 7.0 Hz, 2H), 5.73 (d, J = 16.0 Hz, 1H), 6.38 (dt, J = 7.0, 16.0 Hz, 1H), 7.19–7.47 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 39.53, 88.10, 88.86, 111.04, 123.58, 126.55, 128.29, 128.40, 128.71, 128.84, 131.57, 138.99, 143.04 ppm; IR (cm^{-1}, $CHCl_3$) (inseparable mixture): ν 3082, 3061, 3026, 2897, 1595, 1494, 1489, 1452, 1440, 1429, 1267, 1070, 1029, 956, 914, 829; GC-MS (isomeric mixture): m/z 218 (M)$^+$.

(*Z*)-Pent-3-en-1-yne-1,5-diyldibenzene(29). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.75 (d, J = 7.5 Hz, 2H), 5.80 (d, J = 10.5 Hz, 1H), 6.12 (dt, J = 7.5, 10.5 Hz, 1H), 7.19–7.47 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 36.82, 86.34, 93.87, 110.04, 123.59, 126.37, 128.12, 128.29, 128.46, 128.69, 131.57, 139.84, 141.98 ppm; IR (cm^{-1}, $CHCl_3$) (inseparable mixture): ν 3082, 3061, 3026, 2897, 1595, 1494, 1489, 1452, 1440, 1429, 1267, 1070, 1029, 956, 914, 829; GC-MS (isomeric mixture): m/z 218 (M)$^+$.

(*E*)-Pent-1-en-4-yne-1,5-diyldibenzene (30).[24] ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.36 (d, J = 5.5 Hz, 2H), 6.25 (dt, J = 5.5, 15.5 Hz, 1H), 6.71 (d, J = 15.5 Hz, 1H), 7.19–7.47 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.14, 83.01, 86.89, 123.79, 124.38, 126.41, 127.47, 127.95, 128.29, 128.66, 131.62, 131.77, 137.23 ppm; IR (cm^{-1}, $CHCl_3$) (inseparable mixture): ν 3082, 3061, 3026, 2897, 1595, 1494, 1489, 1452, 1440, 1429, 1267, 1070, 1029, 956, 914, 829; GC-MS (isomeric mixture): m/z 218 (M)$^+$.

(1*E*,3*E*)Penta-1,3-diene-1,5-diyldibenzene (31), (1*E*,4*E*)-1,5-diphenylpenta-1,4-diene (32) and (1*E*,3*Z*)-penta-1,3-diene-1,5-diyldibenzene (33)

Yellow Liquid, Yield: 96% [in 2.00 : 0.29 : 0.12 (**31** : **32** : **33**) ratio by NMR]:

(1*E*,3*E*)-Penta-1,3-diene-1,5-diyldibenzene (31).[25] ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.49 (d, J = 6.5 Hz, 2H), 5.97 (dt, J = 6.5, 15.0 Hz, 1H), 6.26 (dd, J = 10.5, 15.0 Hz, 1H), 6.48 (d, J = 15.5 Hz, 1H), 6.78 (dd, J = 10.5, 15.0 Hz, 1H), 7.18–7.38 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 39.34, 126.31, 126.35, 127.40, 128.63, 128.66, 128.71, 128.78, 129.11, 131.13, 131.84, 137.62, 140.27 ppm; IR (cm^{-1}, $CHCl_3$) (inseparable mixture): ν 3082, 3061, 3024, 2918, 1724, 1674, 1597, 1554, 1494, 1448, 1429, 1122, 1072, 1028, 989, 968, 910, 842, 779, 744; GC-MS: m/z 220 (M)$^+$, 129 [(M-benzyl)$^+$, 100%].

(1*E*,4*E*)-1,5-Diphenylpenta-1,4-diene (32).[26] ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.12 (t, J = 6.5 Hz, 2H), 6.30 (dt, J = 6.5, 16.0 Hz, 2H), 6.47 (d, J = 16.0 Hz, 2H), 7.18–7.38 (m, 10H) ppm; IR (cm^{-1}, $CHCl_3$) (inseparable mixture): ν 3082, 3061, 3024, 2918, 1724, 1674, 1597, 1554, 1494, 1448, 1429, 1122, 1072, 1028, 989, 968, 910, 842, 779, 744; GC-MS: m/z 220 (M)$^+$.

(1*E*,3*Z*)-Penta-1,3-diene-1,5-diyldibenzene (33).[27] ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.65 (d, J = 8.0 Hz, 2H), 5.69 (dd, J = 8.0, 11.2 Hz, 1H), 6.30 (merged with other isomer, 1H), 6.61 (d, J = 15.5 Hz, 1H), 7.18–7.38 (m, 10H) ppm; IR (cm^{-1}, $CHCl_3$) (inseparable mixture): ν 3082, 3061, 3024, 2918, 1724, 1674, 1597, 1554, 1494, 1448, 1429, 1122, 1072, 1028, 989, 968, 910, 842, 779, 744; GC-MS: m/z 220 $(M)^+$.

(Cyclopropylmethyl)benzene (34).[28] Colorless oil, Yield: 83%; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.19–0.22 (m, 2H), 0.50–0.53 (m, 2H), 0.91–1.00 (m, 1H), 2.55 (d, J = 6.5 Hz, 1H), 7.18–7.30 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 4.79, 11.98, 40.49, 125.95, 128.37, 128.49, 142.31; IR (cm^{-1}, $CHCl_3$): ν 3076, 3064, 3026, 3003, 2912, 2846, 1494, 1452, 1070, 1016, 769 cm^{-1}; GC-MS: m/z 132 $(M)^+$.

(*E*)-Pent-1-en-4-yne-1,5-diyldibenzene (35).[16] Colorless oil, Yield: 93%; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.50 (d, J = 7.0 Hz, 2H), 6.30 (dt, J = 7.0, 15.5 Hz, 1H), 6.42 (d, J = 15.5 Hz, 1H), 7.15–7.32 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 39.44, 126.24, 126.29, 127.20, 128.60, 128.77, 129.31, 131.19, 137.58, 140.25; IR (cm^{-1}, CH_2Cl_2): ν 3082, 3061, 3026, 2897, 1600, 1494, 1452, 1429, 1074, 1029, 964, 790 cm^{-1}; GC-MS: m/z 194 $(M)^+$.

Triphenylmethane (36).[29] White solid, m.p. 93–95 °C, Yield: 91%; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 5.54 (s, 1H), 7.10–7.12 (m, 6H), 7.18–7.23 (m, 3H), 7.26–7.29 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 56.99, 126.44, 128.44, 129.60, 144.05; IR (cm^{-1}, CH_2Cl_2): ν 3084, 3062, 3022, 1597, 1581, 1492, 1444, 1080, 1029, 920, 754 cm^{-1}; GC-MS: m/z 244 $(M)^+$.

Penta-1,4-diyne-1,3,5-triyltribenzene (37).[30] Pale yellow oil, Yield: 87%; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 5.21 (s, 1H), 7.26–7.33 (m, 7H), 7.39–7.42 (m, 2H), 7.47–7.49 (m, 4H), 7.67–7.69 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 30.08, 82.80, 86.58, 122.97, 127.32, 127.53, 128.21, 128.25, 128.73, 131.82, 137.97 ppm; IR (cm^{-1}, CH_2Cl_2): ν 3082, 3062, 3032, 2920, 2850, 1597, 1558, 1489, 1452, 1442, 1294, 1070, 1028, 914 cm^{-1}.

(5-*p*-Tolylpenta-1,4-diyne-1,3-diyl)dibenzene (38). Pale yellow oil, Yield: 91%; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 2.34 (s, 3H), 5.20 (s, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.29–7.31 (m, 4H), 7.37–7.40 (m, 4H), 7.47–7.48 (m, 2H), 7.67 (d, J = 8.0 Hz, 2H), ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 21.61, 30.23, 82.86, 83.06, 85.94, 86.89, 120.04, 123.17, 127.47, 127.63, 128.34, 128.36, 128.85, 129.11, 131.83, 131.96, 138.24, 138.47 ppm; IR (cm^{-1}, CH_2Cl_2): ν 3082, 3061, 3028, 2951, 2922, 2852, 2196, 1510, 1490, 1452, 1442, 1292, 1180, 1029, 914, 815, 756 cm^{-1}.

(*E*)-Pent-1-en-4-yne-1,3,5-triyltribenzene (39).[10] Colorless oil, Yield: 89%; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 4.75 (d, J = 6.5 Hz, 1H), 6.34 (dd, J = 15.5, 6.5 Hz, 1H), 6.78 (d, J = 15.5 Hz, 1H), 7.22–7.40 (m, 12H), 7.49–7.50 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 41.37, 85.55, 88.96, 123.60, 126.67, 127.24, 127.68, 127.89, 128.17, 128.40, 128.67, 128.86, 129.77, 130.60, 131.85; IR (cm^{-1}, $CHCl_3$): ν 3082, 3061, 3028, 2956, 2926, 2856, 1724, 1598, 1490, 1448, 1274, 1070, 964, 756 cm^{-1}; GC-MS: m/z 294 $(M)^+$.

Acknowledgements

We thank University of North Florida for support and Dr Nelson Zhao of this department for NMR assistance.

References

1 M. R. Luzung and F. D. Toste, *J. Am. Chem. Soc.*, 2003, **125**, 15760–15761.
2 Y. Nishibayashi, A. Shinoda, Y. Miyake, H. Matsuzawa and M. Sato, *Angew. Chem., Int. Ed.*, 2006, **45**, 4835–4839.
3 Y. Kuninobu, E. Ishii and K. Takai, *Angew. Chem., Int. Ed.*, 2007, **46**, 3296–3299.
4 (*a*) M. Georgy, V. Boucard and J. M. Campagne, *J. Am. Chem. Soc.*, 2005, **127**, 14180–14181; (*b*) M. Georgy, V. Boucard, O. Debleds, C. D. Zotto and J.-M. Campagne, *Tetrahedron*, 2009, **65**, 1758–1766.
5 D. Das, S. Pratihar, U. K. Roy, D. Mal and S. Roy, *Org. Biomol. Chem.*, 2012, **10**, 4537–4542.
6 G. W. Kabalka, M. L. Yao and S. Borella, *J. Am. Chem. Soc.*, 2006, **128**, 11320–11321.
7 J. S. Yadav, B. V. S. Reddy, T. S. Rao and K. V. R. Rao, *Tetrahedron Lett.*, 2008, **49**, 614–618.
8 (*a*) Z. P. Zhan, J. L. Yu, H. J. Liu, Y. Y. Cui, R. F. Yang, W. Z. Yang and J. P. Li, *J. Org. Chem.*, 2006, **71**, 8298–8301; (*b*) Z. P. Zhan, W. Z. Yang, R. F. Yang, J. L. Yu, J. P. Li and H. J. Liu, *Chem. Commun.*, 2006, 3352–3354.
9 J. S. Yadav, B. V. S. Reddy, N. Thrimurtulu, N. M. Reddy and A. R. Prasad, *Tetrahedron Lett.*, 2008, **49**, 614–618.
10 V. J. Meyer and M. Niggemann, *Eur. J. Org. Chem.*, 2011, 3671–3674.
11 V. J. Meyer and M. Niggemann, *Chem.–Eur. J.*, 2012, **18**, 4687–4691.
12 S. K. De and R. A. Gibbs, *Tetrahedron Lett.*, 2005, **46**, 8345–8350.
13 G. V. M. Sharma, K. L. Reddy, P. S. Lakshmi, R. Ravi and A. C. Kunwar, *J. Org. Chem.*, 2006, **71**, 3967–3969.
14 J. Wang, Y. Masui and M. Onaka, *Tetrahedron Lett.*, 2010, **51**, 3300–3303.
15 S. T. Kadam, H. Lee and S. S. Kim, *Appl. Organomet. Chem.*, 2010, **24**, 67–70.
16 J. Wang, W. Huang, Z. Zhang, X. Xiang, R. Liu and X. Zhou, *J. Org. Chem.*, 2009, **74**, 3299–3304.
17 T. G. Kaur, M. Kaushik and S. Trehan, *Tetrahedron Lett.*, 1997, **38**, 2521–2524.
18 (*a*) J. Pavlinac, M. Zupan, K. K. Laali and S. Stavber, *Tetrahedron*, 2009, **65**, 5625–5662; (*b*) R. G. Kalkhambkar, S. N. Waters and K. K. Laali, *Tetrahedron Lett.*, 2011, **52**, 867–871; (*c*) R. G. Kalkhambkar and K. K. Laali, *Tetrahedron Lett.*, 2011, **52**, 1733–1737; (*d*) R. G. Kalkhambkar and K. K. Laali, *Tetrahedron Lett.*, 2011, **52**, 5525–5529; (*e*) G. Aridoss and K. K. Laali, *Eur. J. Org. Chem.*, 2011, 2827–2835; (*f*) G. Aridoss and K. K. Laali, *Eur. J. Org. Chem.*, 2011, 6343–6355; (*g*) G. Aridoss and K. K. Laali, *J. Org. Chem.*, 2011, **76**, 8088–8094.
19 (*a*) G. Aridoss, V. D. Sarca, Jr., J. F. Ponder, J. Crowe and K. K. Laali, *Org. Biomol. Chem.*, 2011, **9**, 2518–2529; (*b*) G. Aridoss and K. K. Laali, *Tetrahedron Lett.*, 2011, **52**, 6859–6864; (*c*) G. G. K. S. N. Kumar, G. Aridoss and K. K. Laali, *Tetrahedron Lett.*, 2012, **53**, 3066–3069.
20 (*a*) B. Jiang and G.-Y. Si, *Tetrahedron Lett.*, 2002, **43**, 8323–8325; (*b*) W. Rao, X. Zhang, E. M. L. Sze and P. W. H. Chan, *J. Org. Chem.*, 2009, 1740–1743.
21 J. S. Yadav, B. V. Subba Reddy, D. Chandrakanth and B. Prasanth, *Chem. Lett.*, 2008, **37**, 954–955.
22 H. T. Dao, U. Schneider and S. Kobayashi, *Chem. Commun.*, 2011, **47**, 692–694.
23 M. Yasuda, T. Saito, M. Ueba and A. Baba, *Angew. Chem., Int. Ed.*, 2004, **43**, 1414–1416.
24 D. K. Rayabarapu and J. A. Tunge, *J. Am. Chem. Soc.*, 2005, **127**, 13510–13511.
25 J. Barluenga, F. Rodriguez, L. Alvarez-Rodrigo and F. J. Fananas, *Chem.–Eur. J.*, 2004, **10**, 101–108.
26 E. Alacid and C. Najera, *J. Org. Chem.*, 2009, **74**, 2321–2327.
27 T. L. Underiner and H. L. Goering, *J. Org. Chem.*, 1991, **56**, 2563–2572.
28 J. Terao, H. Todo, S. A. Begum, H. Kuniyasu and N. Kambe, *Angew. Chem., Int. Ed.*, 2007, **46**, 2086–2089.
29 H. R. Dieguez, A. Lopez, V. Domingo, J. F. Arteaga, J. A. Dobado, M. M. Herrador, J. F. Q. Moral and A. F. Barrero, *J. Am. Chem. Soc.*, 2010, **132**, 254–259.
30 T. Wang, X. Chen, L. Chen and Z. Zhan, *Org. Lett.*, 2011, **13**, 3324–3327.