Iodine-Catalyzed Three-Component Reaction: A Rapid Synthesis of α-Alkoxy Azides and Homoallyl Ethers

Jhillu S. Yadav,* Basi V. Subba Reddy, Ganapuram Madhusudhan Reddy, Ravirala Narender

Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad 500 007, India
Fax +91(40)27160512; E-mail: yadavpub@iict.res.in

Received 13 November 2008; revised 15 November 2008

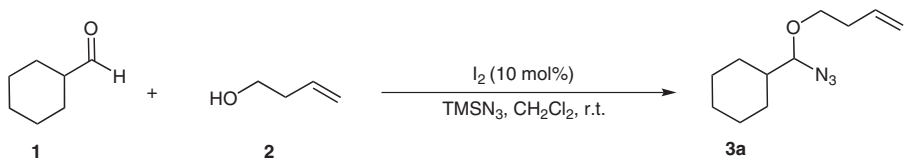
Abstract: Iodine is found to be an efficient catalyst for the three-component coupling of aldehydes, alcohols, and $TMSN_3$ under mild and neutral conditions to provide α-alkoxy azides in good yields and with high selectivity. Allyltrimethylsilane also reacts rapidly with aldehydes in the presence of alcohols to produce homoallyl ethers under similar conditions. The use of iodine makes this procedure simple, convenient and cost-effective.

Key words: three-component reaction, molecular iodine, α-alkoxy azides, homoallylic ethers

Multicomponent reactions have attracted considerable attention because of their wide range of applications in pharmaceutical chemistry for production of structural scaffolds and combinatorial libraries for drug discovery.[1] Organic azides are versatile building blocks for the synthesis of natural products and nitrogen containing heterocycles such as triazoles, tetrazoles, and isocyanates of pharmacological relevance.[2] Recently, they have been popularized due to their pivotal role in the emerging field of click chemistry.[3] Thus, the introduction of azido functionality in an organic molecule is a challenging task to the synthetic chemists. As a result, several methods have been reported for the introduction of the azide group.[2] Trimethylsilyl azide has been frequently employed for this purpose because of its handy property.[4] Consequently, there have been some reports on the reactivity of trimethylsilyl azide[5,6] or hydrazoic acid[7,8] toward carbonyl compounds using $ZnCl_2$, $FeCl_3$, $SnCl_2$, and $TiCl_4$. However, many of these methods are limited to aliphatic aldehydes. Furthermore, α-siloxy azides derived from aldehydes were found to be unstable and difficult to isolate in pure form.[5c] Subsequently, new catalytic systems are being continuously explored in search of improved efficiencies and cost effectiveness.[6] Since organic azides are useful and important in the field of click chemistry, the development of simple, convenient and one-pot procedures is desirable. Recently, molecular iodine has received considerable attention as an inexpensive, nontoxic, readily available catalyst for various organic transformations; affording the corresponding products with high selectivity in excellent yields.[9] The mild Lewis acidity associated with iodine enhanced its usage in organic synthesis to perform several organic transformations using stoichiometric to catalytic amounts. Owing to the advantages associated with this eco-friendly catalyst, molecular iodine has been explored as a powerful reagent for several organic transformations.[10]

In continuation of our interest on the catalytic application of molecular iodine for various organic transformations,[11] we herein report a direct and metal free approach for the one-pot preparation of a range of α-alkoxy azides and homoallyl ethers including benzyl, allyl, and propargyl ethers, which are the most important and popular protecting groups for the hydroxy function. While working on the termination of Prins cyclization with $TMSN_3$, surprisingly, we observed the formation of α-homoallyloxy azides. This provided incentive for an extensive study. First, we attempted a three-component coupling (3 CC) of cyclohexanecarboxaldehyde, $TMSN_3$, and homoallyl alcohol under the influence of 10 mol% of molecular iodine. The 3 CC reaction proceeded rapidly at 23 °C under neutral conditions and the desired product, [azido(but-3-enyloxy)methyl]cyclohexane (**3a**) was obtained in 79% yield (Scheme 1, Table 1, entry **a**). Similarly, various substrates such as primary and secondary alcohols participated in this reaction to provide a wide range of α-alkoxy azides (Table 1, entries **b**–**j**).

Aromatic aldehydes are also effective for this conversion (Table 1, entries **b** and **c**). In the case of aliphatic aldehydes, the corresponding α-alkoxy azides were obtained in good yields in short reaction times. Next, we examined the reactivity of allyltrimethylsilane towards the in situ



Scheme 1

SYNTHESIS 2009, No. 6, pp 0963–0968
Advanced online publication: 11.02.2009
DOI: 10.1055/s-0028-1087802; Art ID: Z24608SS

formed acetals from aldehydes and alcohols. Interestingly, both aromatic and aliphatic aldehydes participated in this reaction (Table 1, entries **k**–**s**). Accordingly, treatment of 2-naphthaldehyde with allyltrimethylsilane in the presence of allyl alcohol under the influence of 10 mol% of molecular iodine afforded 2-[1-allyloxy)but-3-enyl]naphthalene (**3l**) in 75% yield (Scheme 2).

Table 1 Iodine-Catalyzed α-Alkoxy Azides and Homoallyl Ethers via Three-Component Reaction

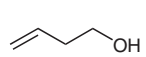
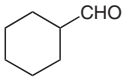
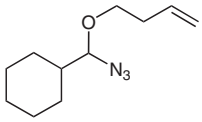
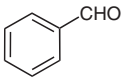
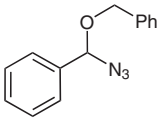
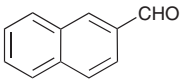
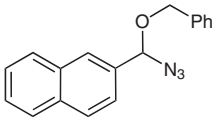
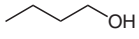
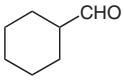
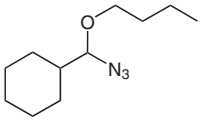
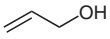
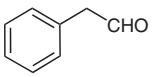
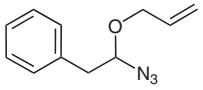
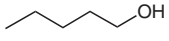
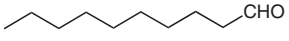
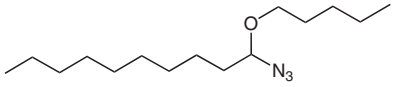
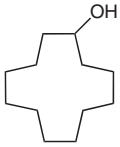
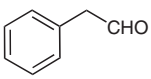
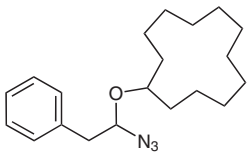
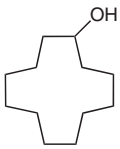
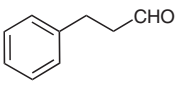
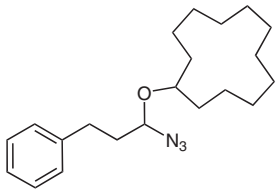
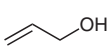
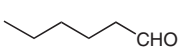
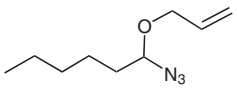
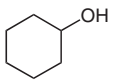
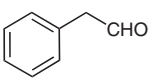
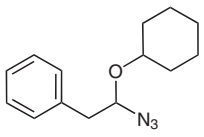
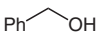
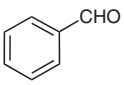
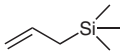
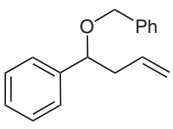
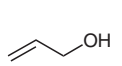
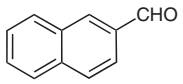
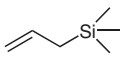
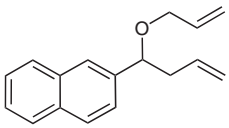
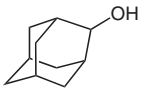
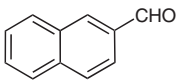
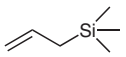
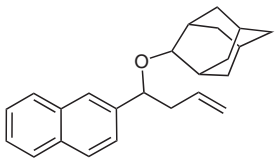
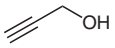
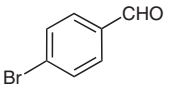
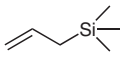
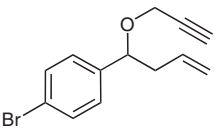
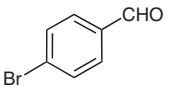
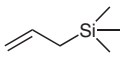
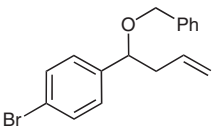
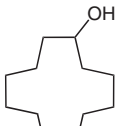
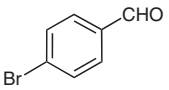
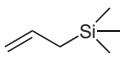
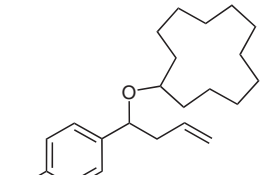
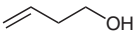
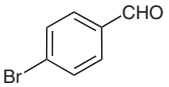
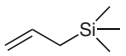
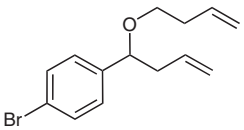
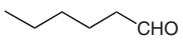
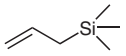
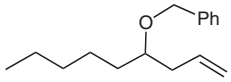
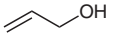
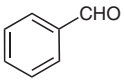
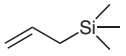
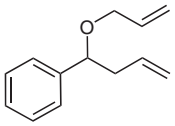
Entry	Alcohol	Aldehyde	Nucleophile	Product[a]	Time (min)	Yield (%)[b]
a			$TMSN_3$		15	79
b			$TMSN_3$		10	72
c			$TMSN_3$		10	70
d			$TMSN_3$		10	73
e			$TMSN_3$		15	75
f			$TMSN_3$		10	72
g			$TMSN_3$		15	70
h			$TMSN_3$		15	71
i			$TMSN_3$		20	74
j			$TMSN_3$		15	75
k					15	80

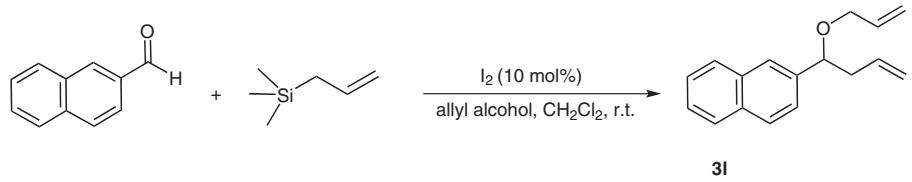
Table 1 Iodine-Catalyzed α-Alkoxy Azides and Homoallyl Ethers via Three-Component Reaction (continued)

Entry	Alcohol	Aldehyde	Nucleophile	Product[a]	Time (min)	Yield (%)[b]
l					20	75
m					20	70
n					15	72
o					15	80
p					15	75
q					15	78
r					10	70
s					20	76

[a] The products were characterized by ^{1}H, ^{13}C NMR, IR, and mass spectrometry.
[b] Yields refer to pure products after chromatography.

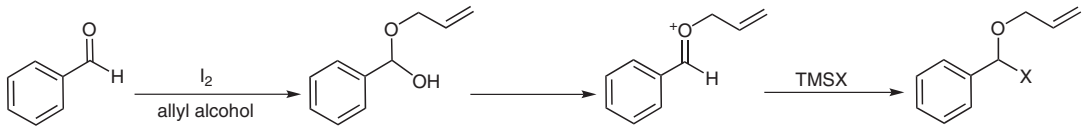
In the case of sterically hindered alcohols, the desired products were obtained in good yields (Table 1, entries **g**, **h**, **m**, and **p**) as well. However, no reaction was observed in the absence of iodine even after a long reaction time (12 h). Furthermore, the use of allyltributylstannane in place of allyltrimethylsilane did not yield the desired product under these reaction conditions, perhaps because iodine does not interact with allyltributyltin. Thus, the combination of allyltrimethylsilane and iodine could be the method of choice for this conversion. Interestingly, a catalytic amount of TMSI was also found to be an equally effective catalyst for this conversion. As solvent, dichloromethane appeared to give the best results. In all cases, the reactions proceeded rapidly at room temperature under mild conditions. The scope and generality of this process is illustrated in Table 1. A possible reaction mechanism is depicted in Scheme 3.

In summary, molecular iodine has proved to be a useful and novel catalyst for the one-pot synthesis of α-alkoxy azides and homoallyl ethers in good yields in short reaction times from aldehydes, alcohols, and $TMSN_3$/allyltrimethylsilane, respectively, under mild conditions. This method is simple, convenient and the reaction conditions are amenable to scale-up. It is a direct method for the conversion of aldehydes into the corresponding α-alkoxy



3l

Scheme 2



Scheme 3 A plausible reaction mechanism for the reported three-component reaction

azides and homoallyl ethers using a catalytic amount of iodine in a single step.

Melting points were recorded on a Büchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr optics. ^{1}H NMR and ^{13}C spectra were recorded on Gemini-200 spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. Column chromatography was performed using E. Merck 60–120 mesh silica gel.

Three-Component Coupling of Aldehydes, Alcohols, and $TMSN_3$/Allyltrimethylsilane; General Procedure

A mixture of aldehyde (1 mmol), alcohol (1 mmol), $TMSN_3$ or allyltrimethylsilane (1.2 mmol) and I_2 (10 mol%) in CH_2Cl_2 (5 mL) was stirred at 23 °C for the specified amount of time (Table 1). After completion of the reaction as indicated by TLC, the mixture was quenched with H_2O (10 mL) and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with aq $Na_2S_2O_3$ (10 mL), brine (10 mL), and dried (Na_2SO_4). Removal of the solvent followed by purification on silica gel (EtOAc–hexane, 0.5:9.5) gave the pure α-alkoxy azide or homoallyl ether. The products thus obtained were characterized by IR, NMR, and mass spectroscopy. The spectral data of homoallyl ethers were found to be consistent with authentic samples.[12] The spectral data for new products are listed below.

[Azido(butoxy)methyl]cyclohexane (3d)

Liquid.

IR (neat): 2930, 2857, 2103, 1629, 1451, 1344, 1238, 1110, 969, 864, 756 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.97 (d, *J* = 6.7 Hz, 1 H), 3.30–3.78 (m, 2 H), 0.98–1.83 (m, 15 H), 0.85–0.92 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 97.0, 69.5, 42.8, 31.6, 31.4, 28.1, 26.2, 25.7, 25.6, 19.2, 13.7.

LCMS: *m*/*z* = 184 ([M + H – N_2]$^+$).

1-[2-(Allyloxy)-2-azidoethyl]benzene (3e)

Liquid.

IR (neat): 3447, 3029, 2924, 2855, 2107, 1635, 1494, 1455, 1380, 1221, 1083, 1020, 764, 699, 545 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19–7.33 (m, 5 H), 5.70–5.89 (m, 1 H), 5.13–5.27 (m, 2 H), 4.51 (t, *J* = 5.8 Hz, 1 H), 4.19–4.30 (m, 1 H), 3.95–4.07 (m, 1 H), 2.92–3.12 (m, 2 H).

LCMS: *m*/*z* = 176 ([M + H – N_2]$^+$.

1-Azido-1-(pentyloxy)decane (3f)

Liquid.

IR (neat): 3446, 2955, 2926, 2857, 2104, 1463, 1369, 1219, 1099, 862, 755 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.25 (t, *J* = 6.0 Hz, 1 H), 3.75–3.83 (m, 1 H), 3.39–3.47 (m, 1 H), 1.64–1.78 (m, 2 H), 1.25–1.52 (m, 20 H), 0.87–0.95 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 92.9, 67.7, 38.2, 34.6, 31.8, 29.4, 29.3, 29.2, 29.1, 24.7, 22.6, 22.5, 14.1, 14.0.

LCMS: *m*/*z* = 242 ([M + H – N_2]$^+$).

(1-Azido-2-phenylethoxy)cyclododecane (3g)

Liquid.

IR (neat): 3451, 3029, 2932, 2857, 2104, 1603, 1494, 1468, 1447, 1345, 1222, 1090, 996, 962, 873, 745, 697, 573 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16–7.30 (m, 5 H), 4.46 (t, *J* = 5.8 Hz, 1 H), 3.62–3.73 (m, 1 H), 2.98 (d, *J* = 5.0 Hz, 2 H), 1.15–1.71 (m, 22 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.0, 129.5, 128.3, 126.8, 91.2, 76.5, 41.6, 29.7, 29.6, 28.6, 24.3, 23.9, 23.5, 23.4, 22.9, 22.7, 21.0, 20.1.

LCMS: *m*/*z* = 302 ([M + H – N_2])$^+$.

(1-Azido-3-phenylpropoxy)cyclododecane (3h)

Liquid.

IR (neat): 2932, 2857, 2102, 1602, 1516, 1448, 1384, 1216, 1096, 1018, 877, 810, 745, 697, 669 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.12–7.27 (m, 5 H), 4.31 (t, *J* = 6.0 Hz, 1 H), 3.70–3.78 (m, 1 H), 2.61–2.79 (m, 2 H), 1.99–2.07 (m, 2 H), 1.25–1.73 (m, 22 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.8, 128.5, 128.3, 126.0, 89.9, 76.1, 36.4, 31.0, 29.7, 28.9, 24.4, 24.3, 23.9, 23.6, 23.5, 22.8, 22.7, 21.1, 20.4.

LCMS: *m*/*z* = 316 ([M + H – N_2]$^+$).

1-(Allyloxy)-1-azidohexane (3i)

Liquid.

IR (neat): 3423, 2954, 2930, 2864, 2106, 1631, 1526, 1462, 1378, 1239, 1146, 1024, 908, 729, 686 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.81–5.94 (m, 1 H), 5.19–5.34 (m, 2 H), 4.32 (t, *J* = 6.0 Hz, 1 H), 4.22–4.28 (m, 1 H), 3.98–4.05 (m, 1 H), 1.68–1.78 (m, 2 H), 1.28–1.43 (m, 6 H), 0.91 (t, *J* = 6.8 Hz, 3 H).

LCMS: *m*/*z* = 156 ([M + H – N_2]$^+$).

1-[2-Azido-2-(cyclohexyloxy)ethyl]benzene (3j)
Liquid.

IR (neat): 3446, 3029, 2931, 2856, 2105, 1451, 1354, 1223, 1093, 965, 873, 747, 698 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.21–7.32 (m, 5 H), 4.53 (t, *J* = 5.3 Hz, 1 H), 3.49–3.58 (m, 1 H), 2.95–3.07 (m, 2 H), 1.15–1.96 (m, 10 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.1, 129.6, 128.3, 126.8, 90.9, 76.9, 41.8, 33.1, 31.3, 25.5, 23.9, 23.6.

LCMS: *m*/*z* (%): 232 ($[M + H - N]^+$).

2-[1-(Allyloxy)but-3-enyl]naphthalene (3l)
Liquid.

IR (neat): 3450, 3058, 3014, 2924, 2854, 1640, 1508, 1425, 1366, 1322, 1271, 1125, 1080, 994, 917, 856, 819, 747, 663, 572, 478 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.82 (m, 3 H), 7.66 (s, 1 H), 7.40–7.48 (m, 3 H), 5.66–5.97 (m, 2 H), 4.95–5.27 (m, 4 H), 4.45 (t, *J* = 6.6 Hz, 1 H), 3.71–3.99 (m, 2 H), 2.38–2.73 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.2, 139.3, 134.9, 134.7, 133.2, 133.1, 128.2, 127.8, 127.7, 126.1, 125.9, 124.6, 117.0, 116.8, 81.3, 69.5, 42.6.

LCMS: *m*/*z* = 239 ($[M + H]^+$).

2-[1-(Adamantanyloxy)but-3-enyl]naphthalene (3m)
Liquid.

IR (neat): 3069, 2903, 2851, 2665, 1639, 1600, 1505, 1448, 1319, 1100, 1079, 1022, 913, 818, 745 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.38–7.87 (m, 7 H), 5.73–5.98 (m, 1 H), 4.96–5.12 (m, 2 H), 4.48–4.58 (m, 1 H), 3.31–3.36 (m, 1 H), 2.32–2.67 (m, 2 H), 0.84–2.20 (m, 14 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.8, 135.6, 132.9, 128.0, 127.8, 127.6, 125.8, 125.5, 125.4, 124.7, 116.5, 78.7, 78.3, 43.3, 37.6, 36.6, 36.3, 33.4, 31.8, 31.6, 30.4, 27.5, 27.4.

LCMS: *m*/*z* = 333 ($[M + H]^+$).

1-Bromo-4-[1-(prop-2-ynyloxy)but-3-enyl]benzene (3n)
Liquid.

IR (neat): 3433, 3298, 3076, 2923, 2854, 1639, 1590, 1484, 1441, 1407, 1343, 1297, 1078, 1009, 918, 823, 777, 670, 633, 538 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.6 Hz, 2 H), 7.16 (d, *J* = 8.6 Hz, 2 H), 5.59–5.81 (m, 1 H), 4.96–5.08 (m, 2 H), 4.49 (t, *J* = 6.2 Hz, 1 H), 4.09 (dd, *J* = 2.3, 13.3 Hz, 1 H), 3.80 (dd, *J* = 2.3, 13.3 Hz, 1 H), 2.35–2.64 (m, 2 H), 2.32 (t, *J* = 2.3 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.6, 133.9, 131.6, 128.7, 121.7, 113.4, 79.7, 79.5, 74.4, 55.6, 41.9.

LCMS: *m*/*z* = 266 ($[M + H]^+$).

1-Bromo-4-[1-(benzyloxy)but-3-enyl]benzene (3o)
Liquid.

IR (neat): 3069, 3029, 2860, 1641, 1590, 1486, 1453, 1389, 1339, 1071, 1008, 916, 822, 737, 696 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.16–7.49 (m, 9 H), 5.62–5.83 (m, 1 H), 4.96–5.04 (m, 2 H), 4.19–4.46 (m, 3 H), 2.29–2.64 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.7, 138.0, 134.1, 131.4, 128.4, 128.2, 127.5, 127.4, 121.2, 117.1, 80.3, 70.3, 42.3.

LCMS: *m*/*z* = 318 ($[M + H]^+$).

1-[1-(4-Bromophenyl)but-3-enyloxy]cyclododecane (3p)
Liquid.

IR (neat): 3075, 2934, 2859, 1641, 1590, 1470, 1444, 1407, 1339, 1296, 1073, 1008, 914, 822, 778, 719, 641, 541 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.7 Hz, 2 H), 7.16 (d, *J* = 8.7 Hz, 2 H), 5.60–5.81 (m, 1 H), 4.93–5.02 (m, 2 H), 4.26 (m, *J* = 6.5 Hz, 1 H), 3.20–3.32 (m, 1 H), 2.20–2.54 (m, 2 H), 1.04–1.62 (m, 22 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.8, 131.2, 131.0, 128.6, 116.9, 78.5, 74.3, 73.4, 42.7, 29.7, 29.0, 28.1, 24.6, 24.4, 24.1, 23.5, 23.4, 23.1, 22.8, 20.1.

LCMS: *m*/*z* = 394 ($[M + H^+]$).

1-Bromo-4-[1-(but-3-enyloxy)but-3-enyl]benzene (3q)
Liquid.

IR (neat): 3434, 3076, 2978, 2907, 2858, 1640, 1591, 1484, 1432, 1408, 1338, 1296, 1095, 1007, 991, 915, 821, 778, 630, 545, 407 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.3 Hz, 2 H), 7.14 (d, *J* = 8.3 Hz, 2 H), 5.64–5.83 (m, 2 H), 4.96–5.04 (m, 4 H), 4.15–4.20 (t, *J* = 7.5 Hz, 1 H), 3.24–3.38 (m, 2 H), 2.46–2.56 (m, 1 H), 2.26–2.36 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.3, 135.2, 134.4, 131.4, 128.4, 121.2, 117.1, 116.3, 81.5, 68.3, 42.5, 34.3.

LCMS: *m*/*z* = 282 ($[M + H]^+$).

4-(Benzyloxy)non-1-ene (3r)
Liquid.

IR (neat): 3445, 3068, 2956, 2928, 2859, 1739, 1644, 1499, 1458, 1378, 1250, 1214, 1147, 1091, 1024, 994, 912, 759, 697 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.20–7.31 (m, 5 H), 5.74–5.88 (m, 1 H), 5.00–5.09 (m, 2 H), 4.44–4.56 (m, 2 H), 3.35–3.43 (m, 1 H), 2.26–2.33 (m, 2 H), 0.87–1.55 (m, 11 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.9, 135.1, 128.4, 128.2, 127.8, 127.6, 123.4, 116.7, 78.5, 70.8, 38.3, 33.8, 31.9, 25.0, 22.6, 14.0.

LCMS: *m*/*z* = 233 ($[M + H^+]$).

Acknowledgment

G.M.R. thanks CSIR New Delhi for the award of a fellowship.

References

(1) Zhu, J.; Bienayme, H. *Multicomponent Reactions*; Wiley: Weinheim, **2005**.
(2) Scriven, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, *88*, 297.
(3) (a) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2001**, *40*, 2004. (b) Kolb, H. C.; Sharpless, K. B. *Drug Discovery Today* **2003**, *8*, 1128. (c) Breinbauer, R.; Kohn, M. *ChemBioChem* **2003**, *4*, 1147. (d) Bock, V. D.; Hiemstra, H.; van Maarseveen, J. H. *Eur. J. Org. Chem.* **2006**, 51.
(4) Groutas, W. C.; Felker, D. *Synthesis* **1980**, 861.
(5) (a) Birkofer, L.; Muller, F.; Kaiser, W. *Tetrahedron Lett.* **1967**, 2781. (b) Evans, D. A.; Truesdale, L. K. *Tetrahedron Lett.* **1973**, 4929. (c) Nishiyama, K.; Yamaguchi, T. *Synthesis* **1988**, 106.
(6) Omura, M.; Iwanami, K.; Oriyama, T. *Chem. Lett.* **2007**, *36*, 532.
(7) Kim, S.; Park, J. H.; Lee, S. *Tetrahedron Lett.* **1989**, *30*, 6697.
(8) Hassner, A.; Fibiger, R.; Amarasekara, A. S. *J. Org. Chem.* **1988**, *53*, 22.
(9) Togo, H.; Iida, S. *Synlett* **2006**, 2159.

(10) (a) Lin, X.-F.; Cui, S.-L.; Wang, Y.-G. *Tetrahedron Lett.* **2006**, *47*, 4509. (b) Chen, W.-Y.; Lu, J. *Synlett* **2005**, 1337. (c) Royer, L.; De S, K.; Gibbs, R. A. *Tetrahedron Lett.* **2005**, *46*, 4595. (d) Banik, B. K.; Fernandez, M.; Alvarez, C. *Tetrahedron Lett.* **2005**, *46*, 2479. (e) Wang, S.-Y. *Synlett* **2004**, 2642. (f) Ko, S.; Sastry, M. N. V.; Lin, C.; Yao, C.-F. *Tetrahedron Lett.* **2005**, *46*, 5771.

(11) (a) Yadav, J. S.; Reddy, B. V. S.; Hashim, S. R. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3082. (b) Yadav, J. S.; Reddy, B. V. S.; Premalatha, K.; Swamy, T. *Tetrahedron Lett.* **2005**, *46*, 2687. (c) Yadav, J. S.; Reddy, B. V. S.; Rao, C. V.; Chand, P. K.; Prasad, A. R. *Synlett* **2001**, 1638. (d) Yadav, J. S.; Reddy, B. V. S.; Sabitha, G.; Reddy, G. S. K. K. *Synthesis* **2000**, 1532. (e) Yadav, J. S.; Reddy, B. V. S.; Reddy, M. S.; Prasad, A. R. *Tetrahedron Lett.* **2002**, *43*, 9703. (f) Yadav, J. S.; Chand, P. K.; Anjaneyulu, S. *Tetrahedron Lett.* **2002**, *43*, 3783.

(12) (a) Tietze, L. F.; Wulff, C.; Wegner, C.; Schuffenhauer, A.; Schiemann, K. *J. Am. Chem. Soc.* **1998**, *120*, 4276. (b) Tietze, L. F.; Schiemann, K.; Wegner, C.; Wulff, C. *Chem. Eur. J.* **1998**, *4*, 1862. (c) Tietze, L. F.; Schiemann, K.; Wegner, C.; Wulff, C. *Chem. Eur. J.* **1996**, *2*, 1164. (d) Tietze, L. F.; Dölle, A.; Schiemann, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1372. (e) Tietze, L. F.; Schiemann, K.; Wegner, C. *J. Am. Chem. Soc.* **1995**, *117*, 5851. (f) Mukaiyama, T.; Ohshima, M.; Miyoshi, N. *Chem. Lett.* **1987**, 1121. (g) Hosomi, A.; Endo, M.; Sakurai, H. *Chem. Lett.* **1976**, 941. (h) Hosomi, A.; Endo, M.; Sakurai, H. *Chem. Lett.* **1978**, 499. (i) Hosomi, A.; Ando, M.; Sakurai, H. *Chem. Lett.* **1986**, 365. (j) Mukaiyama, T.; Nagaoka, H.; Murakami, M.; Ohsima, M. *Chem. Lett.* **1985**, 977. (k) Sakurai, H.; Sasaki, K.; Hosomi, A. *Tetrahedron Lett.* **1981**, *22*, 745. (l) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 71. (m) Ishii, A.; Kotera, O.; Saeki, T.; Mikami, K. *Synlett* **1997**, 1145. (n) Wieland, L. C.; Zerth, H. M.; Mohan, R. S. *Tetrahedron Lett.* **2002**, *43*, 4597. (o) Mekhalfia, A.; Markó, I. E. *Tetrahedron Lett.* **1991**, *32*, 4779. (p) Wang, M. W.; Chen, Y. J.; Wang, D. *Synlett* **2000**, 385.