Tetrahedron 67 (2011) 5621–5629

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Silicomolybdic acid supported on silica gel: an efficient catalyst for Hosomi–Sakurai reactions

Kaliyappan Murugan, Sankareswaran Srimurugan, Chinpiao Chen *

Department of Chemistry, National Dong Hwa University, Soufeng, Hualien 974, Taiwan, ROC

ARTICLE INFO

Article history:
Received 23 April 2011
Received in revised form 22 May 2011
Accepted 23 May 2011
Available online 30 May 2011

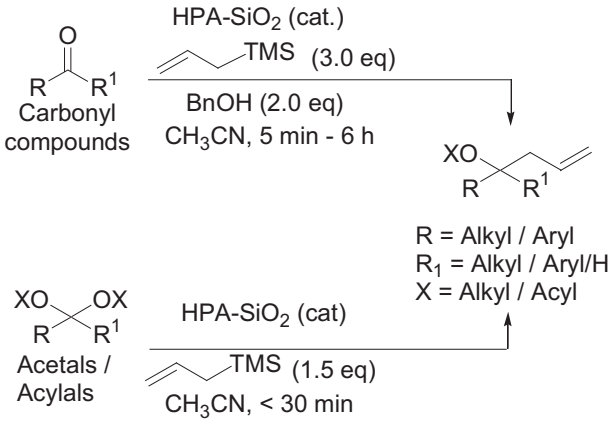
Keywords:
Silicomolybdic acid (SMA)
Hosomi–Sakurai reaction
Brønsted acids
Allylation
Homoallylic ether

ABSTRACT

Silicomolybdic acid that is supported on silica gel (50 wt %) efficiently catalyzes the high-yielding Hosomi–Sakurai allylation of carbonyl compounds by allyltrimethylsilane in the presence of benzyl alcohol. The reaction rates of inactive substrates and the yields were greatly increased when preformed acetals were used as substrates.

1. Introduction

The Hosomi–Sakurai allylation of carbonyl compounds and acetals by allyltrimethylsilane to form homoallyl alcohols or ethers is an extensively explored carbon–carbon bond-forming reaction.[1–6] The reaction is usually promoted using a stoichiometric or catalytic amount of Lewis acid,[7–29] Brønsted acid[30–40] or other material.[3,41] The direct allylation of carbonyl compounds using allyltrimethylsilane has limited applicability, because it involves high catalyst loadings, low yields, and long reaction times. However, the acetals of the corresponding carbonyl compounds greatly increase reaction rates and yields. The use of Brønsted acids in this conversion has been less studied than has the use of Lewis acids. In fact, sulfonamide[37,40] and sulfonic acid-bearing electron-withdrawing substituents[38,39] are the only classes of Brønsted acid catalysts that have been used. Other readily available sulfonic acids, such as *p*-TsOH and camphorsulfonic acid, have been shown to be less active as catalysts of the allylation reaction. The authors' continued interest in the asymmetric allylation of carbonyl compounds[42] and the replacement of conventional Brønsted acid and Lewis acid catalysts with more selective, highly acidic, and greener solid acid catalysts for various functional group transformations[43] have led us to study the use of heteropoly acids[44–47] as catalysts for the Hosomi–Sakurai allylation (Scheme 1). Various heteropoly acids are reportedly excellent catalysts of the synthesis of acetals, thioacetals, and acylals from carbonyl compounds.[48]



Scheme 1. Hosomi–Sakurai reaction of carbonyl compounds, acetals, and acylals with allyltrimethylsilane.

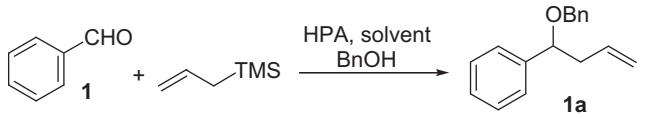
2. Results and discussion

The feasibility of the allylation was initially explored using benzaldehyde **1** (Table 1) as a model substrate and various heteropoly acids as catalysts. Initial attempts at the direct allylation of **1** to homoallyl alcohol by allyltrimethylsilane were either

* Corresponding author. Tel.: +886 3 863 3597; fax: +886 3 863 0475; e-mail address: chinpiao@mail.ndhu.edu.tw (C. Chen).

0040-4020/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2011.05.093

Table 1
Optimization of reaction conditions for Hosomi–Sakurai allylation of benzaldehyde catalyzed by heteropoly acids



Entry	HPA[a]	*x* (mol %)	Solvent	*T* (°C)	*t* (h)	Yield[b] (%)
1	PMA	5.0	CH_3CN	rt	2.0	75
2	PWA	5.0	CH_3CN	rt	0.25	92
3	SWA	5.0	CH_3CN	rt	2.0	85
4	SMA	5.0	CH_3CN	rt	0.25	99
5	SMA	3.0	CH_3CN	rt	0.25	97
6	SMA	2.0	CH_3CN	rt	0.25	97
7	SMA	1.0	CH_3CN	rt	2.0	86
8	SMA	1.0	CH_3CN	40	2.0	70
9	SMA/SiO_2 (10 wt %)	2.0	CH_3CN	rt	2.0	90
10	SMA/SiO_2 (20 wt %)	2.0	CH_3CN	rt	1.5	93
11	SMA/SiO_2 (30 wt %)	2.0	CH_3CN	rt	0.5	95
12	SMA/SiO_2 (30 wt %)	1.0	CH_3CN	40	3.0	85
13	SMA/SiO_2 (40 wt %)	2.0	CH_3CN	rt	0.5	95
14	SMA/SiO_2 (50 wt %)	2.0	CH_3CN	rt	0.08	99
15	SMA/SiO_2 (50 wt %)	2.0	THF	rt	2.0	5
16	SMA/SiO_2 (50 wt %)	2.0	CH_2Cl_2	rt	2.0	68
17	SMA/SiO_2 (50 wt %)	2.0	Toluene	rt	2.0	73
18	SMA/SiO_2 (50 wt %)	2.0	DMF	rt	2.0	—
19	SMA/SiO_2 (first cycle)	2.0	CH_3CN	rt	0.08	99
20	SMA/SiO_2 (second cycle)	2.0	CH_3CN	rt	1.0	90
21	SMA/SiO_2 (third cycle)	2.0	CH_3CN	rt	3.0	85

[a] HPA: PMA-Phosphomolybdic acid; PWA-Phosphotungstic acid; SMA-Silicomolybdic acid; SWA-Silicotungstic acid.
[b] Isolated yields.

unsuccessful or afforded only traces of the product under various reaction conditions. An alternative protocol for acetal formation prior to allylation was therefore attempted by reacting benzaldehyde, allylsilane, and benzyl alcohol in the presence of heteropoly acids. Many of the reported catalyst systems failed or were inefficient, and so more expensive benzyl trimethylsilyl ether was used.[20,39] The commonly used phosphomolybdic acid (PMA) gave the desired product **1a** in 75% yield at a catalyst loading of 5 mol % (Table 1, entry 1). The reaction did not proceed to completion, but halted after 30 min no product was formed after a reaction time of 2 h. Complete conversion required a minimum of 3.0 equiv of allyltrimethylsilane, and attempts to reduce the number of equivalents resulted in partial conversions and lower yields.

The more acidic phosphotungstic acid (PWA) yielded more product in a shorter reaction time. Similarly complete conversion was achieved using silicotungstic acid (SWA) after 2 h, the products obtained using both catalysts contained an impurity (Table 1, entries 2 and 3). Surprisingly, less silicomolybdic acid (SMA) was a more effective, forming homoallyl ether **1a** quantitatively in 15 min (Table 1, entry 4). The catalyst retained similar reactivity at a lower loading of 2 mol %, below which the reaction proceeded more slowly. Heating the reaction mixture to 40 °C reduced the yield, probably because of competitive hydrolysis of the acetal back to aldehyde (Table 1, entry 8). A more active and selective form of SMA catalyst, supported on silica gel, was prepared and screened for effectiveness in the allylation reaction. The loading of bulk supported catalyst (2 mol %) that was made from 10 to 50 wt % SMA on silica gel was investigated. The activity of the supported catalyst increased with the surface loading of the silica gel with SMA, and 50 wt % loading was found to be optimal (Table 1, entries 9–14). Reactions that were performed at higher temperature by reducing the catalyst loading or the surface loading again proceeded more slowly, owing to the hydrolysis of acetal. Dichloromethane and toluene afforded good yields that were exceeded only by those achieved when the reaction solvent was acetonitrile (Table 1, entries 15–18). The catalyst was recycled up to three times although each run considerably reduced catalytic activity (Table 1, entries 19–21).

Substituted aromatic aldehydes, such as 4-methylbenzaldehyde **2** and 4-*tert*-butylbenzaldehyde **3** gave the homoallyl ethers **2a** and **3a** in high yields under the optimal conditions (Table 2, entries

Table 2
Hosomi–Sakurai allylation of carbonyl compounds catalyzed by SMA/SiO_2[a]

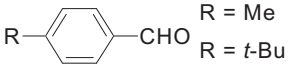
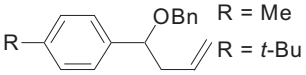
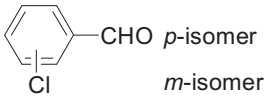
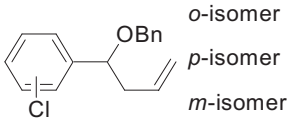
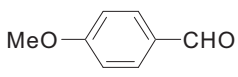
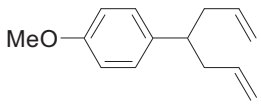
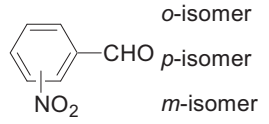
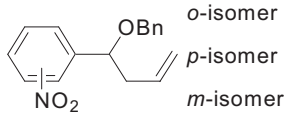
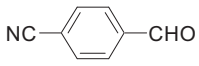
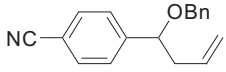
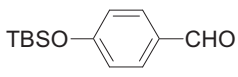
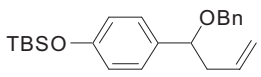
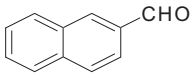
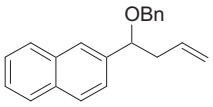
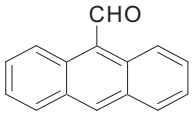
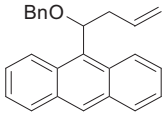
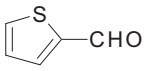
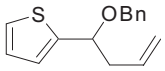
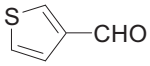
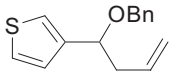
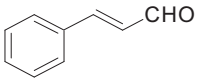
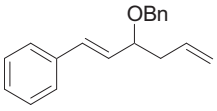
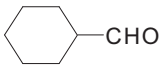
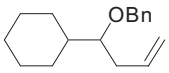
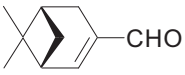
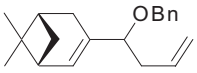
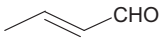
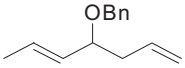
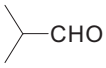
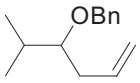
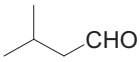
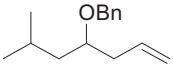
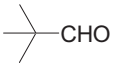
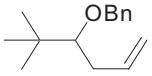
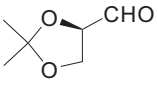
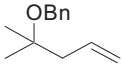
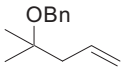
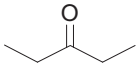
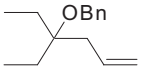
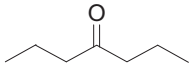
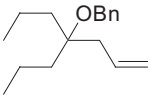
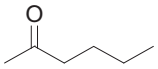
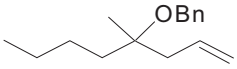
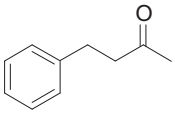
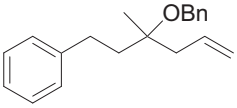
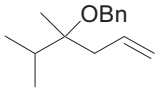
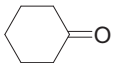
Entry	Substrate		*t* (h)	Product		Yield[b] (%)
1		**2**	0.5		**2a**	95
2		**3**	1.0		**3a**	82
3		**4**	0.75		**4a**	92
4		**5**	0.75		**5a**	99
5		**6**	0.5		**6a**	98
6		**7**	1.0		**7a**	40[c]
7		**8**	6.0		**8a**	61
8		**9**	3.0		**9a**	57
9		**10**	3.0		**10a**	50
10		**11**	1.5		**11a**	80
11		**12**	0.16		**12a**	70

Table 2 (*continued*)

Entry	Substrate		*t* (h)	Product		Yield[b] (%)
12		**13**	0.75		**13a**	95
13		**14**	1.0		**14a**	82
14		**15**	2.0		**15a**	30
15		**16**	1.0		**16a**	90
16		**17**	1.0		**17a**	82
17		**18**	3.0		**18a**	78
18		**19**	1.0		**19a**	40 (dr 3:2)
19		**20**	2.0		**20a**	61
20		**21**	3.0		**21a**	50
21		**22**	2.0		**22a**	80
22		**23**	1.5		**23a**	92
23		**24**	0.5		**25a**	85
24		**25**	0.16		**25a**	60
25		**26**	1.0		**26a**	55
26		**27**	2.0		**27a**	50

(*continued on next page*)

Table 2 (*continued*)

Entry	Substrate		*t* (h)	Product		Yield[b] (%)
27		**28**	2.0		**28a**	60
28		**29**	2.0		**29a**	60
29		**30**	2.0		**30a**	51
30		**31**	0.25		**31a**	90

[a] Catalyst loading (2.0 mol %) and 3.0 equiv allyltrimethylsilane, 2.0 equiv benzyl alcohol.
[b] Isolated yields.
[c] No homoallyl ether was observed.

1 and 2). The position of the substituents on the aryl ring did not affect the yield of the reaction, as observed when isomeric chlorobenzaldehydes **4**–**6** were used (Table 2, entries 3–5). *p*-Anisaldehyde **7**, with an electron-releasing methoxy group, reacted slowly to form the corresponding diallyl compound **7a** in 40% yield without any trace of the expected homoallyl ether (Table 2, entry 6). In contrast, the electron-withdrawing nitro group on the benzaldehyde **8**–**10** gave homoallyl ethers in moderate yields, irrespective of the position of the functional group (Table 2, entries 7–9).

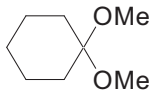
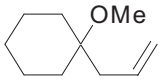
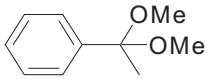
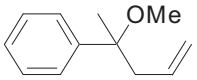
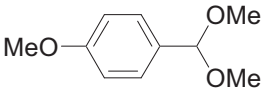
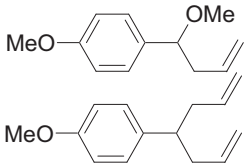
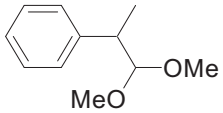
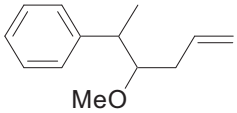
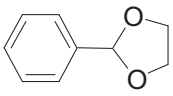
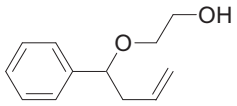
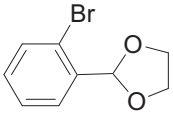
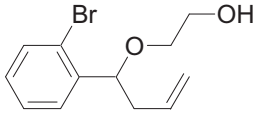
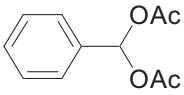
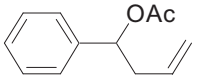
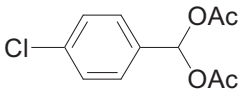
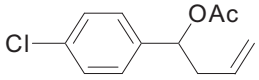
4-Cyanobenzaldehyde **11** formed the desired allylated product **11a** in good yield without any other product, because the nitrile groups underwent side reactions (hydrolysis and the Ritter reaction)[49] (Table 2, entry 10). The extreme stability of the TBS group under catalytic conditions resulted in a high yield of silylated homoallyl ether **12a** in a short reaction time. Polycyclic aromatic aldehydes, such as naphthaldehyde **13** and anthracenecarboxaldehyde **14**, reacted similarly to benzaldehyde (Table 2, entries 12 and 13), whereas heteroaromatic aldehydes reacted differently, depending on the position of the carbonyl group. Unreacted starting material thiophene-2-carboxaldehyde **15** was obtained along with the product (30%), but the reaction ran to completion when the corresponding 3-isomer **16** was instead (Table 2, entries 14 and 15). Cinnamaldehyde **17** underwent allylation selectively at the 1,2 position, forming the homoallyl ether in 82% yield.

The efficiency of the allylation of aliphatic and alicyclic aldehydes with SMA/SiO_2 was similar to that with aromatic aldehydes. The yields were a little lower in the former systems because incomplete conversions yielded homoallyl ethers as the only product, without any impurity. Monocyclic cyclohexanecarboxaldehyde **18** afforded higher yields than the chiral bicyclic myrtenal **19**, which reacted at the 1,2 position across the conjugated enone with a weak diastereoselectivity (3:2). Aliphatic aldehydes **20**–**23** exhibited similar tendencies to undergo allylation under the optimal conditions, affording homoallyl ethers in 50–92% yield.

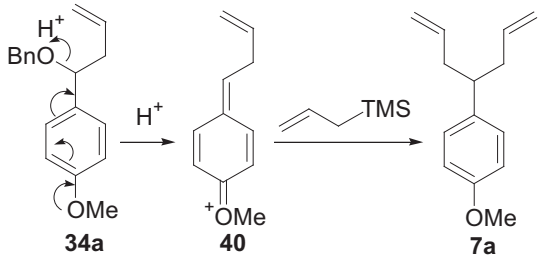
The stability of the acetonide group was examined using Garner aldehyde **24** as the substrate. A rapid reaction occurred but no desired product was obtained. Allylation occurred at the acetonide moiety, unlike at the aldehyde group, forming **25a** in 85% yield. The rapid formation of **25a** motivated the screening of acetone and other ketones for allylation under the optimal reaction conditions. Homoallyl ethers were obtained in a moderate to good yield in a short reaction time using various aliphatic ketones **25**–**30** (Table 2, entries 24–29). A variety of aromatic ketones (substituted acetophenones, benzophenones, and acetonaphthone) and heteroaromatic ketones reacted very slowly with 5–10% conversion under variously modified experimental conditions. Cyclohexanone **31** reacted similarly to aliphatic ketones with a 90% yield of allylated ether **31a** within 15 min.

Preformed ketals of unreactive ketones underwent allylation in a very short time. The amount of allylsilane that was used with these substrates was reduced greatly (1.5 equiv) without any drop in yield of the product (Table 3). The reaction was quantitative yield in the case of cyclohexanone dimethyl acetal **32** but a slight loss of yield was observed when acetophenone dimethyl acetal **33** was used. Similarly slow-reacting aldehydes afforded the product in quantitative yield in a very short reaction time with the preformed acetals, as demonstrated using anisaldehyde dimethyl acetal **34** and 2-phenylpropanal dimethyl acetal **35**. The reaction of anisaldehyde dimethyl acetal **34** formed a considerable amount of diallylated product **7a** under the typical conditions, as observed using free aldehyde **7**. Compound **7a** was obtained perhaps because the desired product **34a** was converted to an intermediate (**40**) and then reacted with allyltrimethylsilane to yield the product (**7a**) that was ultimately obtained (Scheme 2). However, reducing the number of equivalents of allylsilane to 1.0 equiv inhibited the formation of diallyl product **7a**, affording the desired homoallyl ether **34a** in 92% yield. Cyclic acetals **36** and **37** were shown to be useful substrates in the transformation, forming homoallyl ethers **36a** and **37a** in moderate yields in a very short reaction time. This result represents the first example of the ring-opening allylation of cyclic acetal under truly catalytic and ambient conditions.[50] Further reaction of the initially formed desired product (**36a** and **37a**) under the typical experimental conditions produced symmetric ether in near-quantitative yield in less than 10 min from **36** and **37**.[50] Many modifications were made in attempts to freeze the reaction at the desired product and resulted in reducing the loading of the mild catalyst (10 wt % SMA on silica) as a suitable reagent system. To facilitate further manipulation of the homoallyl product, the ether functional group of the substrate was replaced with ester moieties. Acylals **38** and **39** were used to investigate the feasibility of the reaction. Homoallyl esters **38a** and **39a** were successfully isolated from both of these substrates in 30–40% yield and the hydrolysis of acylal was found to be the dominating reaction. Optimization studies demonstrated that replacing acetonitrile with dichloromethane as the solvent suppressed the hydrolysis and improved the yields to over 80%.

Table 3
Hosomi–Sakurai allylation of ketals, acetals, and acylals catalyzed by SMA/SiO_2[a]

Entry	Substrate		t (h)	Product		Yield[b] (%)
1		**32**	0.16		**32a**	99
2		**33**	0.16		**33a**	82
3		**34**	0.16		**34a** **7a**	**34a**:**7a** 92:5[c] (74:19)[d]
4		**35**	0.16		**35a**	97 (dr 1:2.5)
5		**36**	0.32[e]		**36a**	55[50]
6		**37**	0.5[e]		**37a**	45[50]
7		**38**	0.16		**38a**	85[f]
8		**39**	0.25		**39a**	80[f]

[a] Catalyst loading (2.0 mol %) and 1.5 equiv allyltrimethylsilane.
[b] Isolated yields.
[c] Allyltrimethylsilane (1.0 equiv).
[d] Allyltrimethylsilane (1.5 equiv).
[e] SMA/SiO_2 (10 wt %) and 0.5 mol % catalyst loading.
[f] Solvent: DCM and 0.5 mol % catalyst loading.



Scheme 2. The proposed mechanism of formation of **7a**.

3. Conclusion

In summary, SMA that is supported on silica gel efficiently catalyzes the allylation of carbonyl compounds, acetals, ketals, and acylals in moderate to high yields in a short reaction time. This method represents the first example of the direct allylation of aldehydes and ketones in the presence of cheap and readily available benzyl alcohols. The difference between the reactivities of protected and free carbonyl compounds may be able to be exploited in the selective allylation of multi carbonyl compounds even higher yields.

4. Experimental section

4.1. Activation of silicomolybdic acid

Silicomolybdic acid hydrate (20%) was purchased from Aldrich (Milwaukee, WI, USA). SMA was placed in a single neck round-bottom flask, which was heated to 110 °C under reduced pressure for 6 h, yielding a fine yellow solid, which was used in a Hosomi–Sakurai reaction.

4.2. Preparation of SMA/SiO_2 (50% w/w) catalyst

To a solution of $H_4SiO_4Mo_{12}O_{36}\cdot xH_2O$ (500 mg, 0.5 equiv by wt) in MeOH (5 mL) was slowly added silica gel (500 mg, 0.5 equiv by wt, 70–230 mesh). The mixture was stirred at room temperature for 6 h. The evaporation of MeOH under reduced pressure gave a dry yellowish powder, which contained 50% w/w of SMA.

4.3. Allylation of carbonyl compounds

To a solution of benzaldehyde **1** (100 mg, 0.942 mmol) in acetonitrile (2 mL) was added 50 wt % SMA/SiO_2 (68 mg, 0.018 mmol). Then benzyl alcohol (195 μL, 1.88 mmol) and allyltrimethylsilane (0.449 mL, 2.82 mmol) were added dropwise at ambient temperature. The reactants were stirred for a further 5 min. After the completion of reaction (TLC), brine (10 mL) was added and the reaction mixture was extracted with ether (2×10 mL). The combined ether layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude product by column chromatography afforded pure homoallylic benzyl ether **1a** as a colorless oil (222 mg, 99%).

*4.3.1. Compound **1a**. 1-((1-Phenylbut-3-enyloxy)methyl)benzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28–7.38 (m, 10H), 5.75–5.85 (m, 1H), 5.01–5.07 (m, 2H), 4.48 (d, 1H, J=11.8 Hz), 4.36–4.39 (m, 1H), 4.28 (d, 1H, J=11.8 Hz), 2.61–2.68 (m, 1H), 2.41–2.48 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 141.8, 138.5, 134.9, 128.4, 128.3, 127.7, 127.4, 126.9, 116.8, 81.1, 70.3, 42.6; IR ν: 3064, 2862, 1950, 1810, 1640, 1494, 1454, 1354, 1203, 1091, 914, 735 cm^{-1}; EI-MS m/z: 237 (M^+, 1), 197 (18), 129 (6), 115 (4), 91 (100), 77 (5); HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{18}O$, 238.1358; found, 238.1352.

*4.3.2. Compound **2a**. 1-(1-(Benzyloxy)but-3-enyl)-4-methylbenzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.7.37 (m, 7H), 7.20 (d, 2H, J=8 Hz), 5.78–5.85 (m, 1H), 5.02–5.09 (m, 2H), 4.48–4.51 (d, 1H, J=11.9 Hz), 4.34–4.38 (m, 1H), 4.28 (d, 1H, J=11.9 Hz), 2.62–2.69 (m, 1H), 2.42–2.49 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 138.8, 138.6, 137.3, 135.0, 129.1, 128.3, 127.7, 127.4, 126.8, 116.7, 81.0, 70.2, 42.6, 21.1; IR ν: 3028, 2923, 2861, 1948, 1904, 1806, 1640, 1513, 1454, 1347, 1305, 1204, 1091, 914, 816, 734, 697 cm^{-1}; FABMS m/z: 253 (M^++1, 5), 237 (41), 237 (2), 213 (68), 167 (10), 147 (99), 121 (45), 107 (70), 93 (100); HRMS-FAB (m/z): $[M]^+$ calcd for $C_{18}H_{20}O$, 252.1514; found, 253.1583.

*4.3.3. Compound **3a**. 1-(1-(Benzyloxy)but-3-enyl)-4-tert-butylbenzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29–7.42 (m, 9H), 5.82–5.89 (m, 1H), 5.03–5.12 (m, 2H), 4.51 (d, 1H, J=11.9 Hz), 4.37–4.40 (m, 1H), 4.30 (d, 1H, J=11.8 Hz), 2.63–2.68 (m, 1H), 2.45–2.50 (m, 1H), 1.37 (s, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 150.5, 138.8, 138.7, 135.2, 128.3, 127.7, 127.4, 126.5, 125.3, 116.6, 81.0, 70.3, 42.7, 34.5, 31.4; IR ν: 3064, 3029, 2952, 2866, 1949, 1806, 1641, 1454, 1363, 1268, 1204, 1092, 1069, 1027, 914, 832, 734, 697 cm^{-1}; EI-MS m/z: 294 (M^+, 5), 253 (10), 161 (6) 147 (4), 91 (100), 57 (4); HRMS-EI (m/z): $[M]^+$ calcd for $C_{21}H_{26}O$, 294.1984; found, 294.1987.

*4.3.4. Compound **4a**. 1-(1-(Benzyloxy)but-3-enyl)-2-chlorobenzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, 1H, J=1.6 Hz), 7.29–7.58 (m, 7H), 7.21–7.26 (m, 1H), 5.87–5.91 (m, 1H), 5.05–5.11 (m, 2H), 4.93–4.97 (m, 1H), 4.49 (d, 1H, J=11.7 Hz), 4.35 (d, 1H, J=11.7 Hz), 2.52–2.55 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 139.5, 138.3, 134.5, 132.9, 129.4, 128.5, 128.3, 127.7, 127.5, 127.1, 117.0, 78.0, 71.0, 41.1; IR ν: 3067, 3031, 2863, 1950, 1810, 1640, 1439, 1394, 1351, 1206, 1092, 1035, 915, 755, 696 cm^{-1}; EI-MS m/z: 233 (4), 231 (12), 139 (3), 91 (100) 65 (5); HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{17}ClO$, 272.0968; found, 272.0977.

*4.3.5. Compound **5a**. 1-(1-(Benzyloxy)but-3-enyl)-4-chlorobenzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27–7.36 (m, 9H), 5.75–5.80 (m, 1H), 5.01–5.06 (m, 2H), 4.46 (d, 1H, J=11.8 Hz), 4.34–4.37 (m, 1H), 4.28 (d, 1H, J=11.8 Hz), 2.58–2.64 (m, 1H), 2.39–2.46 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 140.4, 138.2, 134.3, 133.3, 128.6, 128.3, 128.2, 127.6, 127.5, 117.2, 80.4, 70.5, 42.5; IR ν: 3066, 2903, 2861, 1901, 1641, 1597, 1492, 1454, 1342, 1296, 1205, 1088, 1014, 916, 827, 735 cm^{-1}; EI-MS m/z: 233 (4), 231 (12), 139 (3), 91 (100) 65 (5); HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{17}ClO$, 272.0968; found, 272.0961.

*4.3.6. Compound **6a**. 1-(1-(Benzyloxy)but-3-enyl)-3-chlorobenzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21–7.35 (m, 9H), 5.73–5.82 (m, 1H), 5.03–5.08 (m, 2H), 4.49 (d, 1H, J=11.8 Hz), 4.34–4.37 (m, 1H), 4.30 (d, 1H, J=11.8 Hz), 2.59–2.64 (m, 1H), 2.40–2.45 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 144.2, 138.2, 134.4, 134.3, 129.7, 128.3, 127.8127.7, 127.6, 126.9, 125.0, 117.3, 80.6, 70.6, 42.5; IR ν: 3066, 3030, 2863, 1948, 1872, 1641, 1596, 1575, 1430, 1391, 1341, 1195, 1096, 1074, 997, 916, 787, 735, 699 cm^{-1}; EI-MS m/z: 233 (4), 231 (13), 139 (3), 91 (100), 77 (2), 65 (5); HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{17}ClO$, 272.0968; found, 272.0964.

*4.3.7. Compound **7a**. 1-(Hepta-1,6-dien-4-yl)-4-methoxybenzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08 (d, 2H, J=8.5 Hz), 6.85 (d, 2H, J=8.6 Hz), 5.62–5.73 (m, 2H), 4.93–5.00 (m, 4H), 3.79 (s, 3H), 2.55–2.76 (m, 1H), 2.29–2.44 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 157.8, 136.9, 136.7, 128.5, 115.9, 113.6, 55.1, 44.7, 40.5; IR ν: 3075, 2911, 2835, 1830, 1742, 1639, 1611, 1508, 1441, 1301, 1248, 1177, 1038, 912, 827 cm^{-1}; EI-MS m/z: 202 (M^+, 5), 162 (11), 161 (100), 129 (8), 121 (6), 91 (11), 77 (4); HRMS-EI (m/z): $[M]^+$ calcd for $C_{14}H_{18}O$, 202.1358; found, 202.1362.

*4.3.8. Compound **8a**. 1-(1-(Benzyloxy)but-3-enyl)-2-nitrobenzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, 1H, J=8.1 Hz), 7.84 (d, 1H, J=7.8 Hz), 7.65 (t, 1H, J=7.5 Hz), 7.41–7.45 (m, 1H), 7.28–7.35 (m, 5H), 5.89–5.96 (m, 1H), 5.07–5.12 (m, 2H), 4.42 (d, 1H, J=11.6 Hz), 4.34 (d, 1H, J=11.6 Hz), 2.56–2.61 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.8, 138.0, 137.8, 134.1, 133.3, 128.4, 128.3, 128.1, 127.7, 127.7, 124.2, 117.5, 76.4, 71.5, 42.0; IR ν: 3073, 2923, 2863, 1951, 1835, 1641, 1524, 1395, 1353, 1298, 1092, 1027, 917, 856, 745 cm^{-1}; EI-MS m/z: 242 (8), 128 (1), 91 (100), 77 (3), 65 (6); HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{17}NO_3$, 283.1208; found, 283.1202.

*4.3.9. Compound **9a**. 1-(1-(Benzyloxy)but-3-enyl)-4-nitrobenzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, 2H, J=8.6 Hz), 7.50 (d, 2H, J=8.4 Hz), 7.29–7.36 (m, 5H), 5.71–5.81 (m, 1H), 5.00–5.06 (m, 2H), 4.36–4.52 (m, 2H), 4.34 (d, 1H, J=11.8 Hz), 2.59–2.66 (m, 1H), 2.42–2.49 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 149.5, 147.5, 137.7, 133.5, 128.4, 127.8, 127.6, 127.5, 123.7, 117.9, 80.2, 71.0, 42.2; IR ν: 3076, 2863, 2452, 1949, 1808, 1641, 1606, 1520, 1454, 1345, 1206, 1090, 918, 855, 699 cm^{-1}; EI-MS m/z: 242 (6), 128 (2), 91 (100), 77 (3), 65 (6); HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{17}NO_3$, 283.1208; found, 283.1212.

*4.3.10. Compound **10a**. 1-(1-(Benzyloxy)but-3-enyl)-3-nitrobenzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (s, 1H), 8.16 (d, 1H, J=7.8 Hz), 7.69 (d, 1H, J=7.7 Hz), 7.54 (t, 1H, J=7.8 Hz), 7.28–7.37 (m, 5H), 5.75–5.84 (m, 1H), 5.02–5.07 (m, 2H), 4.49–4.54 (m, 2H), 4.36 (d, 1H, J=11.8 Hz), 2.63–2.70 (m, 1H), 2.45–2.52 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.5, 144.3, 137.8, 133.5, 132.8, 129.4, 128.4, 127.8, 127.7, 122.6, 121.8, 117.9, 80.2, 71.0, 42.3; IR ν: 3069, 2865, 1959, 1740, 1641, 1530, 1345, 1205, 1092, 1028, 918, 809, 738, 697 cm^{-1}; EI-MS m/z: 242 (6), 128 (2), 92 (8), 91 (100), 77 (2), 65 (5); HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{17}NO_3$, 283.1208; found, 283.1205.

*4.3.11. Compound **11a**. 4-(1-(Benzyloxy)but-3-enyl)benzonitrile.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56–7.62 (m, 3H), 7.45–7.56 (m, 1H), 7.28–7.36 (m, 5H), 5.70–5.77 (m, 1H), 4.99–5.05 (m, 2H), 4.47 (d, 1H, J=11.8 Hz), 4.39–4.43 (m, 1H), 4.31 (d, 1H, J=11.8 Hz), 2.57–2.63 (m, 1H), 2.41–2.46 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 143.6, 137.8, 133.6, 131.3, 131.2, 130.4, 129.2, 128.4, 127.7, 127.6, 118.7, 117.8,

112.6, 80.2, 70.9, 42.3; IR ν: 3066, 3031, 2863, 2229, 1958, 1826, 1736, 1641, 1584, 1454, 1433, 1344, 1206, 1088, 1073, 918, 801, 737, 693 cm^{-1}; EI-MS m/z: 223 (2), 222 (15), 130 (3), 116 (2), 102 (2), 92 (7), 91 (100), 77 (3), 64 (7); HRMS-EI (m/z): $[M]^+$ calcd for $C_{18}H_{17}NO$, 263.1310; found, 263.1305.

4.3.12. Compound ***12a****. (4-(1-(Benzyloxy)but-3-enyl)phenoxy)(tert-butyl)dimethylsilane.* ^1H NMR (400 MHz, $CDCl_3$) δ: 7.26–7.36 (m, 5H), 7.18 (m, 2H), 6.84 (q, 2H, J=1.8, 6.5 Hz), 5.75–5.81 (m, 1H), 4.99–5.06 (m, 5H), 5.70–5.77 (m, 2H), 4.45 (d, 1H, J=11.9 Hz), 4.27–4.32 (m, 1H), 4.24 (d, 1H, J=11.9 Hz), 2.60–2.65 (m, 1H), 2.40–2.45 (m, 1H), 1.00 (s, 9H), 0.22 (m, 6H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 155.1, 138.6, 135.0, 134.4, 128.3, 128.0, 127.7, 127.4, 119.8, 116.7, 82.1, 70.1, 42.6, 25.7, 18.2, −4.3; IR ν: 3449, 2930, 2858, 1607, 1509, 1259, 1092, 915, 839 cm^{-1}; HRMS-EI (m/z): $[M]^+$ calcd for $C_{23}H_{32}O_2Si$, 368.2172; found, 368.2168.

4.3.13. Compound ***13a****. 2-(1-(Benzyloxy)but-3-enyl)naphthalene.* ^1H NMR (400 MHz, $CDCl_3$) δ: 7.88–7.93 (m, 3H), 7.81 (s, H), 7.52–7.81 (m, 3H), 7.32–7.39 (m, 5H), 5.83–5.91 (m, 1H), 5.06–5.14 (m, 2H), 4.54–4.61 (m, 2H), 4.37 (d, 1H, J=11.9 Hz), 2.75–2.83 (m, 1H), 2.56–2.63 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 139.3, 138.5, 134.8, 133.3, 133.2, 128.4, 127.9, 127.8, 127.7, 127.5, 126.1, 125.9, 124.6, 117.1, 81.4, 70.5, 42.5; IR ν: 3030, 3059, 2860, 1949, 1807, 1640, 1496, 1454, 1365, 1320, 1270, 1090, 1072, 914, 857, 744 cm^{-1}; EI-MS m/z: 288 (M^+, 1), 248 (4), 247 (22), 171 (13), 155 (7), 127 (6), 91 (100), 77 (2), 65 (4); HRMS-EI (m/z): $[M]^+$ calcd for $C_{20}H_{21}O$, 288.1514; found, 288.1511.

4.3.14. Compound ***14a****. 10-(1-(Benzyloxy)but-3-enyl)anthracene.* ^1H NMR (400 MHz, $CDCl_3$) δ: 9.25 (br s, 1H) 8.46 (s, 1H), 8.18 (br s, 1H), 8.03–8.06 (m, 2H), 7.48–7.50 (m, 4H), 7.23–7.31 (m, 5H), 5.91–5.93 (m, 1H), 5.87–5.91 (m, 1H), 5.11 (dd, 1H J=17.1, 1.6 Hz), 5.02 (td, 1H, J=10.1, 1.5, 0.7 Hz), 4.42 (d, 1H, J=11.8 Hz), 4.28 (d, 1H, J=11.7 Hz), 3.23–3.31 (m, 1H), 2.84–2.91 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 138.5, 135.4, 132.0, 129.3, 128.2, 128.0, 127.4, 126.7, 125.9, 125.3, 124.8, 122.9, 116.7, 77.5, 70.7, 41.3; IR ν: 3051, 2920, 1946, 1810, 1724, 1674, 1640, 1495, 1370, 1206, 1158, 1072, 917, 888, 730, 697 cm^{-1}; EI-MS m/z: 338 (M^+, 4), 298 (7), 297 (23), 269 (16), 215 (5), 208 (16), 193 (10), 152 (16), 91 (100), 77 (12); HRMS-EI (m/z): $[M]^+$ calcd for $C_{25}H_{22}O$, 338.1671; found, 338.1680.

4.3.15. Compound ***15a****. 2-(1-(Benzyloxy)but-3-enyl)thiophene.* ^1H NMR (400 MHz, $CDCl_3$) δ: 7.29–7.39 (m, 10H), 7.00–7.01 (m, 2H), 5.77–5.86 (m, 1H), 5.08–5.13 (m, 2H), 4.66 (t, 1H, J=6.8 Hz), 4.57 (d, 1H, J=11.7 Hz), 4.37 (d, 1H, J=11.8 Hz), 2.72–2.78 (m, 1H), 2.56–2.61 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 145.8, 138.3, 134.3, 128.3, 127.8, 127.5, 126.3, 125.4, 125.1, 117.3, 76.5, 70.2, 42.8; IR ν: 3067, 2861, 1950, 1726, 1641, 1454, 1315, 1087, 1071, 916, 702 cm^{-1}; EI-MS m/z: 244 (M^+, 0.1), 203 (22), 197 (2), 111 (3), 92 (8), 91 (100), 77 (2), 65 (6); HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{16}OS$, 244.0922; found, 244.0917.

4.3.16. Compound ***16a****. 3-(1-(Benzyloxy)but-3-enyl)thiophene.* ^1H NMR (400 MHz, $CDCl_3$) δ: 7.29–7.38 (m, 6H), 7.19 (q, 1H, J=0.9 Hz), 7.13 (q, 1H, J=1.1 Hz), 5.79–5.85 (m, 1H), 5.04–5.11 (m, 2H), 4.50–4.54 (m, 2H), 4.34 (d, 1H, J=11.8 Hz), 2.66–2.73 (m, 1H), 2.48–2.55 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 143.3, 138.5, 134.7, 128.3, 127.7, 127.5, 126.1, 126.0, 122.1, 117.0, 77.4, 70.3, 41.7; IR ν: 3075, 2904, 2863, 1949, 1829, 1750, 1640, 1496, 1454, 1418, 1327, 1089, 1027, 993, 916, 786, 736,697 cm^{-1}; EI-MS m/z: 244 (M^+, 0.3), 203 (20), 135 (1), 111 (3), 92 (7), 91 (100), 77 (2), 65 (3); HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{16}OS$, 244.0922; found, 244.0917.

4.3.17. Compound ***17a****. (E)-1-((1-Phenylhexa-1,5-dien-3-yloxy)methyl)benzene.* ^1H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.43 (m, 10H), 6.58 (d, 1H, J=15.9 Hz), 6.17 (q, 1H, J=7.9 Hz), 5.89–5.93 (m, 1H), 5.01–5.07 (m, 2H), 4.48 (d, 1H, J=11.8 Hz), 4.36–4.39 (m, 1H), 5.08–5.16 (m, 2H), 4.66 (d, 1H, J=12.0 Hz), 4.46 (d, 1H, J=12.0 Hz), 4.00 (q, 1H, J=6.6, 14.0 Hz), 2.51–2.58 (m, 1H), 2.40–2.47 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 138.7, 136.6, 134.5, 132.5, 129.9, 128.6, 128.3, 127.7, 127.4, 126.5117.1, 79.7, 701., 40.4; IR ν: 3062, 3027, 2859, 1948, 1808, 1727, 1640, 1494, 1452, 1356, 1090, 1069, 968, 914, 748, 696 cm^{-1}; FABMS m/z: 264 (M^+, 0.6), 223 (8), 181 (3), 157 (12), 131 (12), 115 (22), 105 (30), 91 (100), 83 (22), 77 (16), 57 (43), 65 (6); HRMS-EI (m/z): $[M]^+$ calcd for $C_{19}H_{21}O$, 264.1514; found, 264.1586.

4.3.18. Compound ***18a****. 1-((1-Cyclohexylbut-3-enyloxy)methyl)benzene.* ^1H NMR (400 MHz, $CDCl_3$) δ: 7.26–7.36 (m, 5H), 5.75–5.90 (m, 1H), 5.03–5.12 (m, 2H), 4.57 (d, 1H, J=11.5 Hz), 4.47 (d, 1H, J=11.5 Hz), 3.18–4.3.21 (m, 1H), 2.30–2.36 (m, 2H), 1.86 (br d, 1H), 1.65–1.76 (m, 4H), 1.53–1.55 (m, 1H), 1.02–1.26 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 139.1, 135.6, 128.2, 127.7, 127.3, 116.4, 83.3, 71.8, 41.1, 35.3, 29.0, 28.6, 26.6, 26.4, 26.3; IR ν: 3064, 3030, 2852, 1946, 1809, 1734, 1639, 1496, 1346, 1207, 1069, 1026, 911, 733, 696 cm^{-1}; FABMS m/z: 243 (M^+, 4), 221 (4), 203 (35), 181 (21), 147 (13), 137(45), 111 (46), 95 (82), 91 (100), 83 (72), 77 (27), 57 (43), 69 (58), 55 (80); HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{24}O$, 244.1827; found, 244.1915.

4.3.19. Compound ***19a****. (1R,5S)-2-(1-(Benzyloxy)but-3-enyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene.* ^1H NMR (400 MHz, $CDCl_3$) δ: diastereomeric ratio is 3:2; major diastereomers: 7.26–7.33 (m, 5H), 5.85–5.96 (m, 1H), 5.47 (s, 1H), 5.01–5.08 (m, 2H), 4.51–4.58 (m, 1H), 4.28–4.33 (m, 1H), 3.73–3.76 (m, 1H), 2.12–2.45 (m, 7H), 1.31 (s, 3H), 1.20 (d, 1H, J=8.5 Hz), 0.85 (s, 3H); minor diastereomers: 7.26–7.33 (m, 5H), 5.85–5.96 (m, 1H), 5.47 (s, 1H), 5.01–5.08 (m, 2H), 4.51–4.58 (m, 1H), 4.28–4.33 (m, 1H), 3.73–3.76 (m, 1H), 2.12–2.45 (m, 7H), 1.31 (s, 3H), 1.15 (d, 1H, J=8.5 Hz), 0.93 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 147.9, 147.5, 139.0, 135.6, 135.4, 128.2, 127.6, 127.2, 120.8, 120.4, 116.3, 116.1, 81.8, 70.1, 70.0, 53.4, 41.5, 41.2, 41.1, 41.0, 38.3, 38.2, 37.9, 37.8, 31.9, 31.8, 31.3, 26.2, 21.6; IR ν: 3066, 3029, 2984, 2936, 1944, 1730, 1641, 1496, 1454, 1364, 1331, 1203, 1090, 1070, 911, 733, 696 cm^{-1}; EI-MS m/z: 282 (M^+, 0.3), 241 (5), 149 (3), 131 (5), 105 (12), 91 (100), 77 (7), 65 (4); HRMS-EI (m/z): $[M]^+$ calcd for $C_{20}H_{26}O$, 282.1984; found, 282.1979.

4.3.20. Compound ***20a****. 1-((Hepta-1,5-dien-4-yloxy)methyl)benzene.* ^1H NMR (400 MHz, $CDCl_3$) δ: 7.26–7.35 (m, 5H), 5.79–5.87 (m, 1H), 5.62–5.71 (m, 1H), 5.38–5.44 (m, 1H), 5.04–5.10 (m, 2H), 4.59 (d, 1H, J=12.0 Hz), 4.37 (d, 1H, J=12.0 Hz), 3.77 (q, 1H, J=6.7 Hz), 2.41–2.45 (m, 1H), 2.28–2.34 (m, 1H), 1.76 (q, 3H, J=1.1 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 138.9, 134.9, 131.5, 129.0, 128.2, 127.6, 127.3, 116.5, 79.6, 69.7, 40.3, 17.6; IR ν: 3030, 2978, 2917, 2857, 1946, 1673, 1641, 1496, 1454, 1355, 1247, 1205, 1091, 1068, 968, 913, 734, 696 cm^{-1}; EI-MS m/z: 202 (M^+, 0.1), 161 (11), 135 (1), 105 (2), 63 (7), 91 (100), 77 (2), 65 (6); HRMS-EI (m/z): $[M]^+$ calcd for $C_{14}H_{18}O$, 202.1358; found, 202.1351.

4.3.21. Compound ***21a****. 1-((2-Methylhex-5-en-3-yloxy)methyl)benzene.* ^1H NMR (400 MHz, $CDCl_3$) δ: 7.26–7.37 (m, 5H), 5.86–5.93 (m, 1H), 5.04–5.13 (m, 2H), 4.58 (d, 1H, J=11.5 Hz), 4.51 (d, 1H, J=11.5 Hz), 3.19–3.23 (m, 1H), 2.31–1.92 (m, 1H), 1.87–1.92 (m, 1H), 0.91–0.99 (m, 6H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 141.8, 138.5, 134.9, 128.4, 128.3, 127.7, 127.4, 126.9, 116.8, 81.1, 70.3, 42.6; IR ν: 3066, 3030, 2960, 2872, 1946, 1640, 1454, 1348, 1206, 1094, 1068, 1028, 911, 734, 696 cm^{-1}; EI-MS m/z: 203 (M^+, 0.3), 203 (20), 163 (7), 162 (10), 105 (2), 98 (10), 91 (100), 83 (9), 77 (2), 65 (7); HRMS-EI (m/z): $[M]^+$ calcd for $C_{14}H_{20}O$, 204.1514; found, 204.1505.

4.3.22. Compound ***22a****. 1-((6-Methylhept-1-en-4-yloxy)methyl)benzene.* ^1H NMR (400 MHz, $CDCl_3$) δ: 7.27–7.36 (m, 5H), 5.81–5.88 (m, 1H), 5.05–5.12 (m, 2H), 4.60 (d, 1H, J=11.5 Hz), 4.46 (1H, J=11.5 Hz),

3.49–3.52 (m, 1H), 2.32–2.35 (m, 2H), 1.75–1.83 (m, 1H), 1.50–1.57 (m, 1H), 1.23–1.29 (m, 1H), 0.90 (d, 3H, J=6.7 Hz), 0.85 (d, 3H, J=6.6 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 138.9, 135.0, 128.3, 127.8, 127.4, 116.9, 70.8, 43.5, 38.5, 24.5, 23.3, 22.2; IR ν: 3066, 3030, 2957, 2927, 2868, 1952, 1739, 1640, 1454, 1349, 1095, 1069, 912, 733, 696 cm^{-1}; EI-MS m/z: 218 (M^+, 0.6), 177 (5), 161 (2), 115 (2), 92 (7), 91 (100), 77 (2), 65 (4); HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{22}O$, 218.1671; found, 218.1662.

4.3.23. Compound ***23a****. 1-((2,2-Dimethylhex-5-en-3-yloxy)methyl) benzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27–7.40 (m, 5H), 5.15 (dd, 1H, J=17.1, 1.5 Hz), 5.06 (d, 1H, J=10.1 Hz), 4.69 (d, 1H, J=11.2 Hz), 4.53 (d, 1H, J=11.2 Hz), 3.11 (dd, 1H, J=8.4, 3.3 Hz), 2.42–2.44 (m, 1H), 2.29–2.34 (m, 1H), 0.99 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 139.2, 137.4, 128.2, 127.5, 127.3, 116.0, 87.8, 74.3, 36.1, 35.8, 26.4; IR ν: 3067, 3031, 2952, 2868, 1946, 1823, 1639, 1454, 1389, 1362, 1218, 1097, 986, 910, 733, 696 cm^{-1}; EI-MS m/z: 218 (M^+, 0.1), 177 (6), 161 (5), 105 (2), 92 (10), 91 (100), 77 (2), 65 (6); HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{22}O$, 218.1671; found, 218.1663.

4.3.24. Compound ***25a****. 1-((2-Methylpent-4-en-2-yloxy)methyl)benzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29–7.43 (m, 5H), 5.96–6.04 (m, 1H), 5.14–5.18 (m, 2H), 4.53 (s, 2H), 2.42 (d, 2H, J=7.2 Hz), 1.33 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 139.8, 134.8, 128.3, 127.4, 127.2, 117.4, 75.1, 63.8, 45.2, 25.5; IR ν: 3066, 2975, 1947, 2418, 1639, 1454, 1382, 1228, 1148, 1092, 913, 732 cm^{-1}; HRMS-EI (m/z): $[M]^+$ calcd for $C_{13}H_{18}O$, 190.1358; found, 190.1350.

4.3.25. Compound ***26a****. 1-((3-Ethylhex-5-en-3-yloxy)methyl)benzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24–7.38 (m, 5H), 5.80–5.91 (m, 1H), 5.07–5.13 (m, 2H), 4.39 (s, 2H), 2.34 (d, 2H, J=7.1 Hz), 1.55–1.62 (m, 4H), 0.90 (t, 3H, J=7.5 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 139.6, 134.3, 128.2, 127.3, 127.1, 117.1, 79.0, 62.6, 38.7, 26.9, 7.5; IR ν: 3027, 2933, 1946, 1869, 1806, 1639, 1496, 1453, 1381, 1065, 913, 734 cm^{-1}; HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{22}O$, 218.1671; found, 218.1675.

4.3.26. Compound ***27a****. 1-((4-Propylhept-1-en-4-yloxy)methyl)benzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23–7.36 (m, 5H), 5.80–5.90 (m, 1H), 5.06–5.08 (m, 2H), 4.38 (s, 2H), 2.33 (d, 2H, J=7.2 Hz), 1.49–1.55 (m, 4H), 1.32–1.40 (m, 4H), 0.95 (t, 3H, J=7.1 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 139.6, 134.4, 128.2, 127.3, 127.1, 117.1, 78.7, 62.26, 39.8, 37.5, 16.3, 14.6; IR ν: 3030, 2872, 1944, 1825, 1740, 1639, 1454, 1378, 1154, 1060, 912, 732 cm^{-1}; HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{24}O$, 246.1984; found, 246.1990.

4.3.27. Compound ***28a****. 1-((4-Methyloct-1-en-4-yloxy)methyl)benzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26–7.39 (m, 5H), 5.88–5.95 (m, 1H), 5.10–5.14 (m, 2H), 4.45 (s, 2H), 2.36–2.40 (m, 2H), 1.56–1.61 (m, 2H), 1.32–1.42 (m, 4H), 1.24 (s, 3H), 0.95 (t, 3H, J=7.1 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 139.77, 134.67, 128.3, 127.3, 127.1, 117.2, 76.9, 63.2, 42.9, 37.7, 25.6, 23.4, 23.3, 14.2; IR ν: 3030, 2872, 1944, 1825, 1740, 1639, 1454, 1378, 1154, 1060, 912, 732 cm^{-1}; HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{24}O$, 232.1827; found, 232.1817.

4.3.28. Compound ***29a****. 1-((3-Methyl-1-phenylhex-5-en-3-yloxy) methyl)benzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35–7.49 (m, 8H), 7.26–7.29 (m, 2H), 5.97–6.04 (m, 1H), 5.20–5.25 (m, 2H), 4.57 (s, 2H), 2.79–2.83 (m, 2H), 2.52 (t, 2H, J=6.8 Hz), 1.93–2.00 (m, 2H), 1.39 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 142.9, 139.6, 134.4, 128.5, 128.4, 127.4, 127.3, 125.8, 117.7, 76.7, 63.4, 43.1, 40.1, 30.0, 23.4; IR ν: 3067, 2969, 1945, 1806, 1742, 1639, 1453, 1384, 1257, 1088, 911, 732 cm^{-1}; HRMS-EI (m/z): $[M]^+$ calcd for $C_{20}H_{24}O$, 280.1827; found, 280.1820.

4.3.29. Compound ***30a****. 1-((2,3-Dimethylhex-5-en-3-yloxy)methyl) benzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.38 (m, 5H), 5.92–5.98 (m, 1H), 5.08–5.13 (m, 2H), 4.44 (s, 2H), 2.36–2.40 (m, 2H), 2.00–2.04 (m, 1H), 1.14 (s, 3H), 0.98 (d, 3H, J=6.8 Hz), 0.93 (d, 3H, J=6.8 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 139.9, 134.7, 128.2, 127.2, 127.0, 116.9, 79.1, 62.9, 39.9, 34.0, 19.1, 17.5, 17.1; IR ν: 2929, 1945, 1806, 1741, 1639, 1454, 1380, 1261, 1148, 1090, 1064, 912, 732 cm^{-1}; HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{22}O$, 218.1671; found, 218.1675.

4.3.30. Compound ***31a****. 1-((1-Allylcyclohexyloxy)methyl)benzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26–7.44 (m, 5H), 5.91–5.98 (m, 1H), 5.12 (d, 2H, J=13.0 Hz), 4.45 (s, 2H), 2.39 (d, 2H, J=7.1 Hz), 1.87–1.90 (m, 2H), 1.61–1.71 (m, 3H), 1.48–1.54 (m, 2H), 1.31–1.44 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 139.7, 134.2, 128.3, 127.4, 127.1, 117.2, 75.4, 62.4, 41.9, 34.4, 25.9, 21.9; IR ν: 3030, 2935, 2856, 1944, 1741, 1638, 1496, 1449, 1089, 1063, 911, 732 cm^{-1}; HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{22}O$, 230.1671; found, 230.1665.

4.4. Allylation of acetals, ketals, and acylals

To a solution of cyclohexanone dimethyl ketal **32** (100 mg, 0.693 mmol) in acetonitrile (2 mL) was added 50 wt % SMA–SiO_2 (50 mg, 0.013 mmol); then, allyltrimethylsilane (165 μL, 0.104 mmol) was added dropwise at ambient temperature. The reactants were stirred for a further 10 min. After the reaction had run to completion (TLC), brine (10 mL) was added and the reaction mixture was extracted with diethyl ether (2×10 mL). The combined ether layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude product by column chromatography afforded pure homoallyl ether **32a** as a colorless oil (106 mg, 99%).

4.4.1. Compound ***32a****. 1-Allyl-1-methoxycyclohexane.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.77–5.84 (m, 1H), 5.01–5.06 (m, 2H), 3.16 (s, 3H), 2.20 (d, 2H, J=7.2 Hz), 1.68 (d, 2H, J=13.3 Hz), 1.48–1.57 (m, 3H), 1.38–1.43 (m, 2H), 1.20–1.30 (m, 4H), 0.83–0.89 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 134.0, 117.0, 74.8, 48.0, 40.9, 33.8, 25.8, 21.7; IR ν: 2924, 2851, 1739, 1454, 1359, 1082, 990, 900, 808, 792 cm^{-1}; EI-MS m/z: 155 (M^++1, 2), 154 (M^+, 1), 149 (8), 141 (3), 129 (3), 113 (100), 111 (11), 91 (13), 81 (51), 79 (14), 57 (22); HRMS-EI (m/z): $[M]^+$ calcd for $C_{10}H_{18}O$, 154.1358; found, 154.1360.

4.4.2. Compound ***32a****. 1-(2-Methoxypent-4-en-2-yl)benzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.41 (m, 4H), 7.25–7.29 (m, 1H), 5.62–5.73 (m, 1H), 5.01–5.05 (m, 2H), 3.10 (s, 3H), 2.49 (m, 2H), 1.54 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 144.7, 134.1, 128.1, 126.9, 126.2, 117.6, 78.7, 50.4, 47.2, 22.8; IR ν: 3075, 2979, 2934, 2824, 1950, 1811, 1737, 1639, 1493, 1446, 1371, 1287, 1221, 1161, 1071, 997, 915, 838, 764 cm^{-1}; EI-MS m/z: 176 (M^+, 0.3), 161 (1), 155 (1), 145 (5), 136 (8), 135 (100), 129 (8), 105 (9), 91 (12), 77 (11), 65 (2); HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{16}O$, 176.1201; found, 176.1204.

4.4.3. Compound ***34a****. 1-Methoxy-4-(1-methoxybut-3-enyl)benzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (d, 2H, J=8.5 Hz), 6.89 (d, 2H, J=8.5 Hz), 5.71–5.81 (m, 1H), 5.00–5.07 (m, 2H), 4.12 (t, 1H, J=6.8 Hz), 3.8 (s, 3H), 3.2 (s, 3H), 2.54–2.61 (m, 1H), 2.36–2.42 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 159.1, 134.9, 133.6, 127.9, 116.7, 113.7, 83.1, 56.3, 55.2, 42.4; IR ν: 3075, 2979, 2934, 2820, 2060, 1611, 1512, 1463, 1354, 1302, 1247, 1173, 1096, 1036, 915, 831 cm^{-1}; EI-MS m/z: 192 (M^+, 0.1), 161 (9), 152 (8), 151 (100), 135 (13), 121 (3), 108 (4), 91 (5), 77 (4), 65 (2); HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{16}O_2$, 192.1150; found, 192.1144.

4.4.4. Compound ***35a****. 1-(3-Methoxyhex-5-en-2-yl)benzene.* ^{1}H NMR (400 MHz, $CDCl_3$) δ: diastereomeric ratio is 1:2.5; major diastereomers: 7.20–7.33 (m, 5H), 5.80–5.87 (m, 1H), 4.99–5.09 (m, 2H), 3.38 (s, 3H), 3.31–3.35 (m, 1H), 2.89–2.92 (m, 1H), 2.21–2.22 (m, 2H), 1.34 (d, 3H, J=7.0 Hz); minor diastereomers: 7.20–7.33 (m, 5H), 5.80–5.87 (m, 1H), 4.99–5.09 (m, 2H), 3.33 (s, 3H), 3.31–3.35 (m, 1H), 2.96–3.03 (m, 1H), 2.02–2.10 (m, 2H), 1.30 (d, 3H, J=7.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 144.8, 143.9, 135.4, 134.9, 128.3, 128.2, 128.1, 127.9, 126.2, 126.1, 116.8, 85.6, 85.4, 58.1, 57.9, 43.3, 42.5, 35.8, 35.3, 17.1,

16.6; IR ν: 3077, 2976, 2931, 2823, 1944, 1810, 1640, 1602, 1494, 1453, 1376, 1224, 1096, 997, 912, 760, 700 cm^{-1}; EI-MS m/z: 190 (M^+, 0.1), 150 (4), 149 (37), 117 (14), 105 (14), 91 (10), 85 (100), 77 (7), 54 (17); HRMS-EI (m/z): $[M]^+$ calcd for $C_{13}H_{18}O$, 190.1358; found, 190.1350.

4.4.5. Compound ***36a****. 2-(1-Phenylbut-3-enyloxy)ethanol.* ^1H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.36 (m, 5H), 5.75–5.82 (m, 1H), 5.02–5.09 (m, 2H), 4.30 (q, 1H, J=5.6, 7.7 Hz), 3.68 (br s, 2H), 3.37–3.47 (m, 2H), 2.42–2.60 (m, 2H), 2.13 (br s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 141.7, 134.7, 128.4, 127.7, 126.6, 117.2, 82.3, 69.9, 61.9, 42.5; IR ν: 3412, 3076, 2929, 1952, 1641, 1453, 1353, 1107, 915, 758, 701 cm^{-1}; HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{16}O_2$, 192.1150; found, 192.1152.

4.4.6. Compound ***37a****. 2-(1-(2-Bromophenyl)but-3-enyloxy)ethanol.* ^1H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.53 (m, 2H), 7.32–7.35 (m, 1H), 7.11–7.15 (m, 1H), 5.85–5.90 (m, 1H), 5.06–5.13 (m, 2H), 4.78 (q, 1H, J=4.4, 8.1 Hz), 3.71 (br s, 2H), 3.39–3.52 (m, 2H), 2.38–2.54 (m, 2H), 2.15 (br s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 140.8, 134.5, 132.7, 128.9, 127.7, 127.6, 122.8, 117.4, 80.4, 70.3, 61.8, 41.1; IR ν: 3400, 3073, 2926, 1927, 1838, 1640, 1437, 1346, 1110, 915 cm^{-1}; EI-MS m/z: 271(M^++1, 0.4), 270 (M^+, 0.2), 231 (38), 229 (40), 209 (43), 199 (22), 185 (19), 130 (100), 129 (55), 91 (11), 77 (12), 65 (2); HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{15}BrO_2$, 270.0255; found, 270.0250.

4.4.7. Compound ***38a****. 1-Phenylbut-3-enyl acetate.* ^1H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.35 (m, 5H), 5.82 (q, 1H, J=6.1 Hz), 5.67–5.74 (m, 1H), 5.04–5.11 (m, 2H), 2.07–2.68 (m, 2H), 2.07 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 170.1, 140.1, 133.3, 128.4, 127.9, 126.5, 118.0, 75.1, 40.7, 21.2; IR ν: 3078, 2939, 1740, 1643, 1495, 1433, 1372, 1233, 1022, 920, 760, 699 cm^{-1}; EI-MS m/z: 190 (M^+, 0.2), 150 (6), 149 (64), 145, 129 (10), 115 (7), 107 (100), 105 (8), 91 (7), 79 (15), 77 (14); HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{14}O_2$, 190.0994; found, 190.0992.

4.4.8. Compound ***39a****. 1-(4-Chlorophenyl)but-3-enyl acetate.* ^1H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.32 (m, 4H), 5.74–5.77 (m, 1H), 5.04–5.08 (m, 1H), 2.59–2.66 (m, 1H), 2.49–2.55 (m, 1H), 2.06 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 170.1, 138.5, 133.7, 132.8, 128.6, 127.9, 118.3, 74.4, 40.5, 21.1; IR ν: 3079, 2928, 1738, 1643, 1494, 1372, 1234, 1091, 1014, 920, 824 cm^{-1}; EI-MS m/z: 224 (M^+, 0.5), 185 (14), 183 (41), 156 (26), 143 (24), 141 (100), 139 (83), 129 (15), 111 (31), 77 (22); HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{13}ClO_2$, 224.0604; found, 224.0595.

Acknowledgements

The authors thank Ms. L.M. Hsu at the Instruments Center, National Chung Hsing University, for her help in obtaining HRMS, and the National Science Council of the Republic of China, Taiwan, for financially supporting this research under Contract NSC 97-2113-M-259-002-MY3. Ted Knoy is appreciated for his editorial assistance.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.05.093.

References and notes

1. Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, *17*, 1295–1298.
2. Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1–22.
3. Sakurai, H.; Sasaki, K.; Hayashi, J.; Hosomi, A. *J. Org. Chem.* **1984**, *49*, 2808–2809.
4. Sakurai, H. *Pure Appl. Chem.* **1985**, *57*, 1759–1770.
5. Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200–206.
6. Hosomi, A.; Miura, K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 835–851.
7. Hosomi, A.; Endo, M.; Sakurai, H. *Chem. Lett.* **1976**, 941–942.
8. Hosomi, A.; Endo, M.; Sakurai, H. *Chem. Lett.* **1978**, 499–500.
9. Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 71–74.
10. Sakurai, H.; Sasaki, K.; Hosomi, A. *Tetrahedron Lett.* **1981**, *22*, 745–748.
11. Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron* **1981**, *37*, 3899–3910.
12. Hathaway, S. J.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 3351–3353.
13. Trehan, A.; Vij, A.; Walia, M.; Kaur, G.; Verma, R. D.; Trehan, S. *Tetrahedron Lett.* **1993**, *34*, 7335–7338.
14. Hollis, T. K.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Tetrahedron Lett.* **1993**, *34*, 4309–4312.
15. Mayr, H.; Gorath, G.; Bauer, B. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 788–789.
16. Komatsu, N.; Uda, M.; Suzuki, H.; Takahashi, T.; Domae, T.; Wada, M. *Tetrahedron Lett.* **1997**, *38*, 7215–7218.
17. Ishii, A.; Kotera, O.; Saeki, T.; Mikami, K. *Synlett* **1997**, 1145–1146.
18. Yadav, J. S.; Subba Reddy, B. V.; Srihari, P. *Synlett* **2001**, 673–675.
19. Wieland, L. C.; Zerth, H. M.; Mohan, R. S. *Tetrahedron Lett.* **2002**, *43*, 4597–4600.
20. Watahiki, T.; Akabane, Y.; Mori, S.; Oriyama, T. *Org. Lett.* **2003**, *5*, 3045–3048.
21. Zerth, H. M.; Leonard, N. M.; Mohan, R. S. *Org. Lett.* **2003**, *5*, 55–57.
22. Jung, M. E.; Maderna, A. *J. Org. Chem.* **2004**, *69*, 7755–7757.
23. Jung, M. E.; Maderna, A. *Tetrahedron Lett.* **2004**, *45*, 5301–5304.
24. Wadamoto, M.; Yamamoto, Y. *J. Am. Chem. Soc.* **2005**, *127*, 14556–14557.
25. Anazalone, P. W.; Baru, A. R.; Danielson, E. M.; Hayes, P. D.; Nguten, M. P.; Panico, A. F.; Smith, R. C.; Mohan, R. S. *J. Org. Chem.* **2005**, *70*, 2091–2096.
26. Arai, S.; Sudo, Y.; Nishida, A. *Tetrahedron* **2005**, *61*, 4639–4642.
27. Lucero, C. G.; Woerpel, K. A. *J. Org. Chem.* **2006**, *71*, 2641–2647.
28. Reddy, U. C.; Bondalapati, S.; Saikia, A. K. *Eur. J. Org. Chem.* **2009**, 1625–1629.
29. Kumar, R. S. C.; Reddy, G. V.; Babu, K. S.; Rao, J. M. *Chem. Lett.* **2009**, *38*, 564–565.
30. Denmark, S. E.; Wilson, T. M. *J. Am. Chem. Soc.* **1989**, *111*, 3475–3476.
31. Kaur, G.; Manju, K.; Trehan, S. *Chem. Commun.* **1996**, 581–582.
32. Kaur, G.; Kaushik, M.; Trehan, S. *Tetrahedron Lett.* **1997**, *38*, 2521–2524.
33. Kuhnert, N.; Peverley, J.; Robertson, J. *Tetrahedron Lett.* **1998**, *39*, 3215–3216.
34. Ishihara, K.; Hasegawa, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4077–4079.
35. Ishihara, K.; Hiraiwa, Y.; Yamamoto, H. *Synlett* **2001**, 1851–1854.
36. Ishihara, K.; Hasegawa, A.; Yamamoto, H. *Synlett* **2002**, 1299–1301.
37. Cossy, J.; Lutz, F.; Alauze, V.; Meyer, C. *Synlett* **2002**, 45–48.
38. Kampen, D.; List, B. *Synlett* **2006**, 2589–2592.
39. Kampen, D.; Ladépêche, A.; Claβen, G.; List, B. *Adv. Synth. Catal.* **2008**, *350*, 962–966.
40. Barbero, M.; Bazzi, S.; Cadamuro, S.; Dughera, S.; Piccinini, C. *Synthesis* **2010**, 315–319.
41. Kataki, D.; Phukan, P. *Tetrahedron Lett.* **2009**, *50*, 1958–1960.
42. Huang, X. R.; Chen, C.; Lee, G. H.; Peng, S. M. *Adv. Synth. Catal.* **2009**, *351*, 3089–3095.
43. Murugan, K.; Srimurugan, S.; Chen, C. *Chem. Commun.* **2010**, 1127–1129.
44. Nagaraju, P.; Pasha, N.; Saiprasad, P. S.; Lingaiah, N. *Green Chem.* **2007**, *9*, 1126–1129.
45. Rafiee, E.; Joshaghani, M.; Eavani, S.; Rashidzadeh, S. *Green Chem.* **2008**, *10*, 982–989.
46. Xu, L.; Wang, Y.; Yang, X.; Yu, X.; Guo, Y.; Clark, J. H. *Green Chem.* **2008**, *10*, 746–755.
47. Geboers, J.; Vyver, S. V. D.; Carpentier, K.; Blochouse, K. D. *Chem. Commun.* **2010**, 3577–3579.
48. Firouzabadi, H.; Jafari, A. A. *J. Iran. Chem. Soc.* **2005**, *2*, 85–114 and references cited therein.
49. Yadav, J. S.; Subba Reddy, B. V.; Pandurangam, T.; Jayasudan Reddy, Y.; Gupta, M. K. *Catal. Commun.* **2008**, *9*, 1297–1301.
50. Motokura, K.; Yoneda, H.; Miyaji, A.; Baba, T. *Green Chem.* **2010**, *12*, 1373–1375.