Full Paper

CSIRO PUBLISHING

Aust. J. Chem. **2007**, *60*, 850–856

www.publish.csiro.au/journals/ajc

Silica Chloride-Catalyzed One-Pot Isomerization–Chlorination, Arylation, and Etherification of Baylis–Hillman Adducts

Ponnusamy Shanmugam,[A,B] *Baby Viswambharan*,[A] *and Vadivel Vaithiyanathan*[A]

[A]Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), Thiruvananthapuram-695 019, Kerala, India.

[B]Corresponding author. Email: shanmu196@rediffmail.com

A convenient and efficient one-pot isomerization–chlorination, arylation, and etherification of several Baylis–Hillman adducts with silica chloride, an eco-friendly heterogeneous catalyst, silica chloride–arenes, and silica chloride–saturated and unsaturated alcohols as reagent systems are reported. These reactions furnished highly functionalized isomerized Baylis–Hillman derivatives in good yield. The efficiency and necessity of silica chloride catalyst was compared with thionyl chloride. A plausible mechanism of the reaction is proposed.

Manuscript received: 25 April 2007.
Final version: 1 August 2007.

Introduction

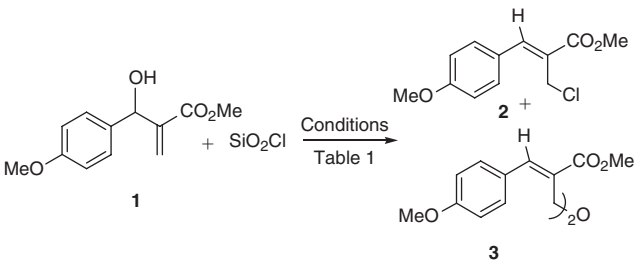
Silica chloride (SiO_2Cl) is an extensively used heterogeneous solid catalyst for a number of chemical transformations particularly in the area of novel synthetic methodologies.[1–16] The advantages of silica-modified silica chloride in organic synthesis are that the catalyst is stable, efficient, operationally simple, convenient in handling, inexpensive, solid, heterogeneous, and acidic in nature.[1–16] The Baylis–Hillman reaction is one of the important reactions for the construction of carbon–carbon bonds and leads to δ-methylene β-hydroxyalkanoates and alkane nitriles. The reaction generally affords densely functionalized molecules and the reaction is considered as atom-economic.[17] Stereoselective construction of (*E*)-trisubstituted alkenes appended with functional groups are one of the difficult tasks in organic synthesis and a few methods are known.[18–22] The isomerization of acetates of the Baylis–Hillman adducts catalyzed by trimethylsilyl trifluoromethanesulfonate,[20,21] trifluoroacetic acid,[23] benzyl trimethylammonium fluoride,[24] and Montmorillonite K10 clay–microwave[25] are known. The isomerization of non-activated Baylis–Hillman adducts to allyl bromides using bromodimethyl sulfonium bromide,[26] and isomerization–arylation using expensive metal catalysts with aryl boronic acid[27] have been reported. To the best of our knowledge, the synthesis of functionalized trisubstituted olefins appended with chlorine, aryl, and ether functional groups catalyzed by silica chloride, a heterogeneous catalyst, is unknown.

We have been working on the development of novel synthetic transformations using Baylis–Hillman adducts.[28–36] In continuation of our work on the synthetic applications of Baylis–Hillman adducts, herein we report the study of silica chloride-catalyzed one-pot isomerization–chlorination, etherification, and arylation of Baylis–Hillman adducts under neat and sealed tube conditions.

Results and Discussion

Optimization and Choice of Baylis–Hillman Adducts for the Silica Chloride-Catalyzed One-Pot Isomerization–Chlorination Reaction

The preliminary study on isomerization–chlorination reaction was carried out with Baylis–Hillman adduct **1** and SiO_2Cl (Scheme 1). Initially, the adduct **1** in dichloromethane was stirred with freshly prepared SiO_2Cl at room temperature for 12 h and the reaction furnished unchanged starting material. Repetition under refluxing CH_2Cl_2 for 12 h also provided starting material quantitatively. The reaction mixture without any solvent was heated at 140°C to afford only the dimerized compound **3** in 30% yield. However, the reaction mixture on irradiation in a microwave oven (750 PL) for 5 min afforded the isomerized–chlorinated compound **2** and dimerized compound **3** in 30 and



Scheme 1. Optimization of isomerization–chlorination of the Baylis–Hillman adduct.

10.1071/CH07123 0004-9425/07/110850

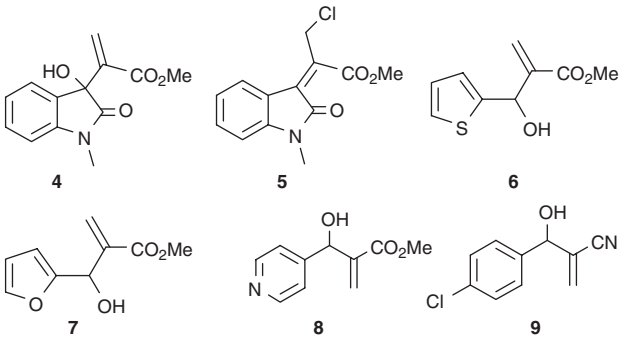


Fig. 1. Adducts tested for the isomerization using silica chloride.

50% yields, respectively. To improve the yield of isomerized–chlorinated product **2,** optimized conditions were found to be the mixture of starting material and SiO_2Cl in a sealed tube and heating at 100°C for 12 h to afford the desired chlorinated compound **2** in 75% yield along with 10% of dimerized compound **3**. The compounds were separated by column chromatography and characterized by spectroscopic methods.

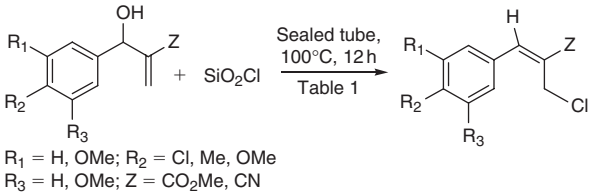
To find the reactivity and suitability of various Baylis–Hillman adducts for the reaction, adduct derived from isatin **4** (Fig. 1) furnished only a trace (~5%) of chlorinated compound **5**. Adducts derived from heteroaromatic aldehydes bearing thiophene, furan, and pyridine substituents (**6**, **7**, and **8**, respectively) yielded neither chlorinated nor dimerized compounds. However, the simple nitrile adduct **9** furnished chlorinated compound **10** and the corresponding dimerized compound in 50 and 8% yields, respectively. Thus, only simple aryl-derived Baylis–Hillman adducts are suitable for the isomerization–chlorination reaction with SiO_2Cl.

Silica Chloride-Catalyzed One-Pot Isomerization–Chlorination of Baylis–Hillman Adducts

As the preliminary experiments showed promising results on the isomerization–chlorination reaction, we were prompted to examine the reaction with several simple Baylis–Hillman adducts (Scheme 2). Thus, the adduct **11** under optimized conditions afforded the isomerized–chlorinated derivative **12** in 58% yield along with the corresponding dimerized product in 30% yield (Table 1, entry 3). Similarly, the other Baylis–Hillman adducts underwent the isomerization–chlorination reaction under optimized conditions to produce good yields of the desired products (Table 1, entries 1–6). It should be noted that adduct **19**, bearing an electron-withdrawing group at the aryl ring, and adduct **20**, with a nitrile group at the activated position, afforded neither desired isomerization–chlorination products nor the dimerized compounds (Table 1, entries 7 and 8). However, adduct **9**, bearing halogen substitutions on the aryl ring and a nitrile group at the activated alkene, afforded only moderate yields of isomerized–chlorinated and dimerized compounds, respectively (Table 1, entry 2). Longer reaction times and variation of temperature (80–120°C) did not minimize the formation of dimerized products.

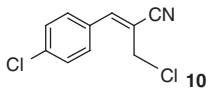
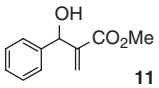
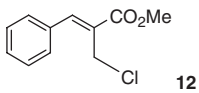
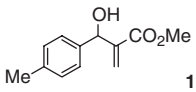
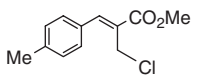
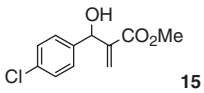
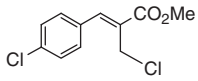
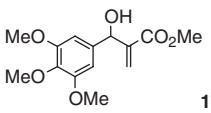
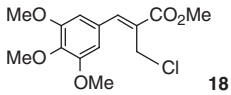
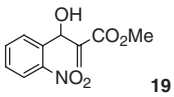
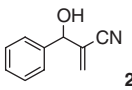
Silica Chloride-Catalyzed One-Pot Isomerization–Arylation of Baylis–Hillman Adducts

The successful isomerization–chlorination reaction of Baylis–Hillman adducts with silica chloride prompted us to further



Scheme 2. Isomerization–chlorination of Baylis–Hillman adducts.

Table 1. Isomerization–chlorination of Baylis–Hillman adducts

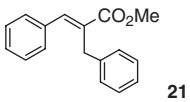
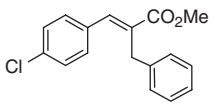
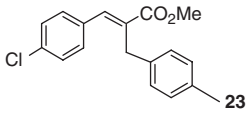
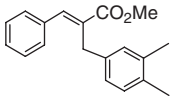
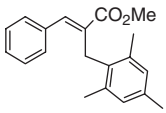
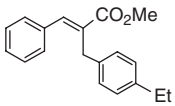
Entry	Substrate[A]	Products	Yield [%][B]
1	**1**	**2**	75[C]
2	**9**	 **10**	50
3	 **11**	 **12**	58
4	 **13**	 **14**	78
5	 **15**	 **16**	39
6	 **17**	 **18**	42[D]
7	 **19**	–	–
8	 **20**	–	–

[A] SiO_2Cl, sealed tube, 100°C, 12 h.
[B] Only *Z*-isomers were obtained.
[C] Based on isolation of starting material.
[D] SiO_2Cl, 1 h, sealed tube, 100°C.

explore the reaction in the presence of simple aromatic hydrocarbons to trap the reactive intermediate with aromatic hydrocarbons (Scheme 3). The Friedel–Crafts reaction afforded highly functionalized arylated trisubstituted alkenes in excellent yields. Thus, the adduct **11** with two equivalents of benzene afforded an excellent yield of isomerized phenylated compound **21** (Table 2, entry 1). It was observed that only the *E*-isomer **21** was formed as evidenced by ^1H NMR (chemical shifts of alkene proton; see Experimental). To show the general nature of the reaction, experiments with other aromatic hydrocarbons such as toluene, mesitylene, *o*-xylene, and ethyl benzene afforded the corresponding isomerized–arylated compounds in excellent yields (Table 2, entries 3–5 and 8). Gas chromatography–mass

Scheme 3. Isomerization–arylation of Baylis–Hillman adducts.

Table 2. Isomerization–arylation of Baylis–Hillman adducts

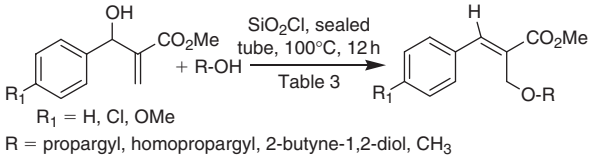
Entry	Substrate[A]	Ar–H	Product	Yield [%][B]
1	**11**	Benzene	 **21**	90
2	**15**	Benzene	 **22**	96
3	**15**	Toluene	 **23**	95[C]
4	**11**	*o*-Xylene	 **24**	90[C]
5	**11**	Mesitylene	 **25**	52
6	**11**	Indole	–	–
7	**11**	Naphthalene	–	–
8	**11**	Ethylbenzene	 **26**	70[C]

[A] SiO_2Cl, sealed tube, 100°C, 12 h.
[B] Only *E*-isomer was obtained.
[C] Mixture of *o*, *p*-derivatives (3:7) inseparable by column chromatography.

spectrometry coupled technique (GCMS) analysis of the toluene derivative **23** showed two peaks having the same mass with different retention times and we found these *o*- and *p*-isomers inseparable by column chromatography in the ratio of 3:7. Experiments with naphthalene and indole did not yield any characterized products (Table 2, entries 6 and 7). The results are collected in Table 2.

Silica Chloride-Catalyzed Isomerization–Etherification of Baylis–Hillman Adducts

The successful isomerization of Baylis–Hillman adducts with SiO_2Cl and SiO_2Cl–aromatic compounds prompted us further



Scheme 4. Isomerization–etherification of Baylis–Hillman adducts.

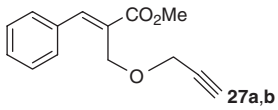
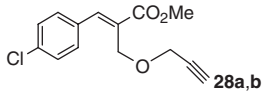
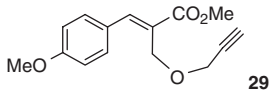
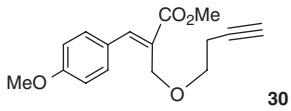
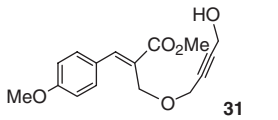
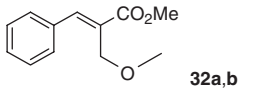
to explore the reaction in the presence of saturated and unsaturated alcohols to functionalize the adducts by trapping the intermediate with alcohols. The reaction was highly successful and afforded functionalized trisubstituted alkenyl ethers in excellent yields (Scheme 4). Thus, adduct **11** with silica chloride–propargyl alcohol afforded isomerized–etheriated *E*- and *Z*-isomers **27a** and **27b** in 75% combined yield (Table 3, entry 1). It should be noted that the *p*-methoxy-substituted adduct **1**, with propargyl and homopropargyl alcohol, furnished only the *Z*-isomer of isomerized–ether derivatives **29** and **30** as determined by ^{1}H NMR spectroscopy (Table 3, entries 3 and 4) and GCMS analysis. The adducts **11** and **15** furnished both *E*- and *Z*-isomers in the ratio of 2:1 as determined by ^{1}H NMR analysis. Adduct **11** with methanol produced both *E*- and *Z*-isomers **32a**,**b**, which were separated by column chromatography. The reaction of adduct **11** with but-2-yne-1,4-diol furnished the corresponding ether derivative **31** in 51% yield (Table 3, entry 5) as a single isomer. To our surprise, the reactions with allyl alcohol and benzyl alcohol did not yield any isomerized–ether products (Table 3, entries 6 and 8). A trace amount (<5%) of isomerized–chlorinated compounds was found in all reaction mixtures.

Reactivity and Efficiency of Silica Chloride Catalyst v. *Thionyl Chloride*

The efficiency and necessity of silica chloride (conditions B, Table 4) were compared with thionyl chloride (conditions A, Table 4) in the isomerization–chlorination, arylation, and etherification reactions. The reaction was compared and demonstrated with adduct **11**. As shown in Table 4, in the case of the isomerization–chlorination reaction, there was not much difference in the product formation (Table 4). However, in the cases of arylation and etherification reactions, it was found that the silica chloride catalyst is essential as the yields are significantly higher with silica chloride than thionyl chloride (Table 4). Further, unlike thionyl chloride, which is difficult to handle, the advantages of the silica chloride catalyst are that it is stable, efficient, and easy to handle. The reactivity of the SiO_2Cl of this reaction was also tested by variation in loading weight % of the catalyst and the reaction time. We have used 100% w/w of the catalyst and varying the catalyst by percentage loading did not alter the yields.

Silica chloride has been used as a multipurpose catalyst for the one-pot transformation of isomerization–chlorination, arylation, and ether formation of activated and non-activated Morita–Baylis–Hillman adducts without the use of solvent. It should be noted that the arylation reaction afforded excellent yields of the products. The advantages of silica chloride in organic synthesis are that the catalyst is stable, efficient, operationally simple, and the fact that it is convenient in handling, inexpensive, solid, heterogeneous, and acidic in nature have been exploited. Of particular note is the advantage that all three synthetic transformations as reported in the manuscript are performed with silica chloride alone; different reagent and

Table 3. Isomerization–etherification of Baylis–Hillman adducts

Entry	Substrate[A]	Alcohol	Ether products	Yield [%]
1	**11**	Propargyl alcohol	 **27a**,**b**	75
2	**15**	Propargyl alcohol	 **28a**,**b**	85
3	**1**	Propargyl alcohol	 **29**	64
4	**1**	Homopropargyl alcohol	 **30**	68
5	**11**	But-2-yne-1,4-diol	 **31**	51
6	**11**	Allyl alcohol	–	–
7	**11**	Methanol	 **32a**,**b**	60[B]
8	**17**	Benzyl alcohol	–	–

[A] SiO_2Cl, sealed tube, 100°C, 12 h.
[B] Combined yield of *E* to *Z* (2:1) isomers separable by column chromatography.

Table 4. Comparison of silica chloride catalyst *v.* thionyl chloride

No.	Substrate	Conditions		Product		Yield [%]	
		A	B	A	B	A	B
1	**11**	$SOCl_2$, neat, room temp.	SiO_2Cl, sealed tube, 100°C, 12 h	**12**	**12**	77	73
2	**11**	Benzene, 12 h, $SOCl_2$, sealed tube, 100°C	Benzene, SiO_2Cl, sealed tube, 100°C, 2 h	**21**	**21**	0	90
3	**11**	Propargyl alcohol, 12 h, $SOCl_2$, 100°C	Propargyl alcohol, 12 h, SiO_2Cl, sealed tube, 100°C	**27**	**27**	10	75

conditions are required to carry out the reactions as reported in the literature.[1–27]

Mechanistic Considerations

A plausible mechanism for the reaction of isomerization–chlorination, arylation, and etherification is postulated and shown in Fig. 2. The Si–Cl bond is weak and can give rise to Lewis acid-centred intermediates. The chloride ion in silica chloride could be displaced by the hydroxyl group of the Baylis–Hillman adduct to form tight ion pairs that upon nucleophilic attack with chloride or aryl or alkoxy nucleophiles in an

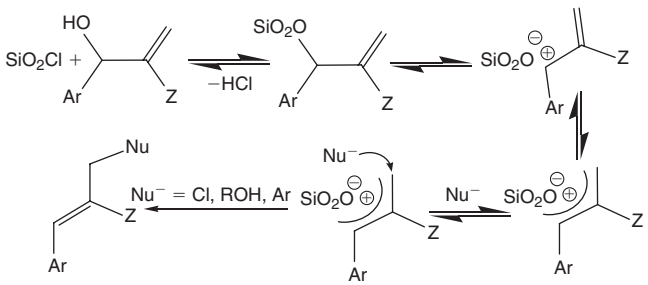


Fig. 2. Plausible mechanism for the reaction.

S_N^1 fashion form isomerized derivatives of the Baylis–Hillman adducts.

Conclusions

We have demonstrated a simple method for a one-pot isomerization–chlorination, arylation, and etherification of Baylis–Hillman adducts derived from simple aryl aldehydes with silica chloride, an eco-friendly heterogeneous catalyst, by using a simple experimental procedure. As the products obtained here are highly functionalized, they can be manipulated for further synthetic transformations. Further work on the use of the SiO_2Cl catalyst for novel synthetic methodologies is in progress in our laboratory.

Experimental

General

All experiments were carried out in oven-dried glassware. Analytical TLC was performed on silica gel TLC plates. Purification by gravity column chromatography was carried out with silica gel (100–200 mesh). Mixtures of ethyl acetate and hexane and pure hexane were used as eluent as required. Infrared (IR) spectra were run on a Nicolet (impact 400D FT-IR) spectrophotometer. NMR spectra were obtained using $CDCl_3$ as solvent on a Bruker DPX 300 MHz NMR spectrometer. Chemical shifts are given in the δ scale with tetramethylsilane (TMS) as internal reference. High resolution mass spectroscopy were measured on a JMS 600 JEOL mass spectrometer. Yields refer to quantities obtained after column chromatography. Solvents used are reagent grade and were purified before use according to the literature procedure.[37]

General Experimental Procedure

A mixture of Baylis–Hillman adduct (1 mmol), freshly prepared silica chloride (100% w/w), and alcohol (2 equiv.) or benzene (as reagent, 2 equiv.) were taken in an oven-dried sealed tube and heated in an oil bath at 100°C for 12 h. The crude mixture was diluted with dichloromethane (2 × 10 mL) and filtered through a pad of Celite. The organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum. The mixture was purified by silica gel (100–200 mesh) column chromatography, with hexane and a gradient mixture of hexane/ethyl acetate as eluent.

Preparation of SiO_2Cl Catalyst

Silica gel (10 g) was oven-dried (120°C under vacuum) in a round-bottomed flask (250 mL) equipped with a condenser and a drying tube, and thionyl chloride (40 mL) was added. The mixture was refluxed for 40 h. The unreacted thionyl chloride was distilled off under vacuum. The resulting white greyish powder was flame-dried and stored in a tightly capped bottle. This silica chloride can be used for a month without losing its activity.

Spectroscopic Data for Chlorinated Compounds

(E)-Methyl 2-(Chloromethyl)-3-(4-methoxyphenyl) Acrylate **2**

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 1712, 1604, 1259, 1026, 837. δ_H ($CDCl_3$/TMS, 300.1 MHz) 3.87 (s, 6H, 2OMe), 4.52 (s, 2H), 6.97 (d, *J* 8.7, 2H), 7.56 (d, *J* 8.7, 2H), 7.83 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 39.5, 52.3, 55.3, 113.5, 114.3 (2C), 125.8, 126.6, 131.8 (2C), 143.7, 160.9. Calc. for $C_{12}H_{13}ClO_3$: 240.0553. Found: 240.0564.

(E)-2-(Chloromethyl)-3-(4-chlorophenyl)acrylonitrile **10**

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 2219, 1618, 823. δ_H ($CDCl_3$/TMS, 300.1 MHz) 4.31 (s, 2H), 7.18 (s, 1H), 7.43 (d, *J* 8.7, 2H), 7.73 (d, *J* 8.7, 2H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 45.6, 108.1, 117.8, 129.3 (2C), 130.4 (2C), 137.4, 145.1, 146.5. Calc. for $C_{10}H_7Cl_2N$: 210.9956. Found: 210.9968.

(E)-Methyl 2-(Chloromethyl)-3-phenyl Acrylate **12**

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 1714, 1626, 761. δ_H ($CDCl_3$/TMS, 300.1 MHz) 3.85 (s, 3H), 4.24 (s, 2H), 7.38–7.53 (m, 5H), 7.93 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 52.2, 58.3, 114.4, 128.5 (2C), 128.6, 129.8 (2C), 134.7, 144.7, 168.1. Calc. for $C_{11}H_{11}ClO_2$: 210.0448. Found: 210.0454.

(E)-Methyl 2-(Chloromethyl)-3-p-tolyl Acrylate **14**

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 1714, 1629, 812. δ_H ($CDCl_3$/TMS, 300.1 MHz) 2.40 (s, 3H), 3.87 (s, 3H), 4.49 (s, 2H), 7.26 (d, *J* 8.1, 2H), 7.46 (d, *J* 8.1, 2H), 7.85 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 21.4, 39.1, 52.3, 123.0, 126.0, 127.7, 129.7 (2C), 141.2, 143.9 (2C), 166.0. Calc. for $C_{12}H_{13}ClO_2$: 224.0604. Found: 224.0615.

(E)-Methyl 2-(Chloromethyl)-3-(4-chlorophenyl) Acrylate **16**

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 1716, 1632, 836. δ_H ($CDCl_3$/TMS, 300.1 MHz) 3.88 (s, 3H), 4.43 (s, 2H), 7.42 (d, *J* 8.4, 2H), 7.49 (d, *J* 8.4, 2H), 7.81 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 38.5, 52.7, 123.5, 129.4 (2C), 131.1 (2C), 141.3, 142.5, 146.5, 166.6. Calc. for $C_{11}H_{10}Cl_2O_2$: 244.0058. Found: 244.0072.

(E)-Methyl 2-(Chloromethyl)-3-(3,4,5-trimethoxy Phenyl) Acrylate **18**

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 1714, 1622, 1259, 1042, 779. δ_H ($CDCl_3$/TMS, 300.1 MHz) 3.88 (s, 3H), 3.90 (s, 9H), 4.52 (s, 2H), 6.86 (s, 2H), 7.83 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 39.6, 52.4, 56.1 (2C), 60.8, 106.9, 127.4, 129.4 (2C), 141.0, 144.1, 153.3 (2C), 166.6. Calc. for $C_{14}H_{17}ClO_5$: 300.0765. Found: 300.0775.

Spectroscopic Data for Arylated Compounds

Methyl-2-benzyl-3-phenyl Acrylate **21**

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 3060, 1714, 1633.79, 1592.50, 1493. δ_H ($CDCl_3$/TMS, 300.1 MHz) 3.74 (s, 3H), 3.95 (s, 2H), 7.34–7.19 (m, 10H), 7.93 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 33.1, 51.5, 109.5, 126.8, 128.5, 128.5, 128.7, 128.8, 128.9, 129.1, 129.5, 129.6, 130.7, 139.3, 168.6. Calc. for $C_{17}H_{16}O_2$: 252.1168. Found: 252.1158.

Methyl-2-benzyl-3-(4-chlorophenyl) Acrylate **22**

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 3060, 1714, 1633, 1592, 1493. δ_H ($CDCl_3$/TMS, 300.1 MHz) 3.73 (s, 3H), 3.97 (s, 2H), 7.83–7.15 (m, 9H), 7.86 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 33.0, 52.1, 128.5, 128.5, 128.7 (2C), 128.9 (2C), 129.1, 129.4 (2C), 130.4 (2C), 130.8, 133.6, 139.5, 168.3. Calc. for $C_{17}H_{15}ClO_2$: 286.0761. Found: 286.0755.

Methyl-2-(4-methylbenzyl)-3-(4-chlorophenyl) Acrylate **23**; Mixture of Inseparable o- and p-Isomers **23**

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 3060, 1714, 1633, 1592, 1493. δ_H ($CDCl_3$/TMS, 300.1 MHz) 2.20 (s, 3H), 2.22 (s, 3H),

3.64 (s, 3H), 3.65 (s, 3H), 3.78 (s, 2H), 3.79 (s, 2H), 6.8–7.3 (m, 18H), 7.75 (s, 1H), 7.82 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 19.2, 20.8, 30.8, 32.5, 38.6, 51.5, 126.1, 126.6, 128.6, 130.4 (3C), 133.4 (3C), 139.3, 139.8, 168.2. Calc. for $C_{18}H_{17}ClO_2$: 300.0917. Found: 300.0915.

Methyl-2-(3,4-dimethylbenzyl)-3-phenyl Acrylate ***24***

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 3060, 1714, 1633, 1592, 1493. δ_H ($CDCl_3$/TMS, 300.1 MHz) 2.26 (s, 6H), 3.65 (s, 3H), 3.92 (s, 2H), 6.8–7.3 (m, 8H, ArH), 7.82 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 19.2, 19.5, 20.87, 30.8, 32.5, 38.6, 51.5, 126.1, 126.6, 128.6, 130.4 (3C), 133.4 (3C), 139.3, 139.8, 168.6. Calc. for $C_{19}H_{20}O_2$: 280.1463. Found: 280.1455.

Methyl-2-(2,4,6-trimethylbenzyl)-3-phenyl Acrylate ***25***

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 3060, 1714, 1633, 1592, 1493. δ_H ($CDCl_3$/TMS, 300.1 MHz) 2.20 (s, 9H), 3.62 (s, 3H), 3.92 (s, 2H), 6.81–7.32 (m, 7H, ArH), 7.62 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 19.2, 19.5, 20.1, 20.8, 30.8, 32.5, 38.6, 51.5, 126.1, 126.6, 128.6, 130.4 (3C), 133.4 (3C), 139.3, 139.8, 168.4. Calc. for $C_{20}H_{22}O_2$: 294.1625. Found: 294.1620.

Methyl-2(4-ethylbenzyl)-3-phenylacrylate ***26***

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2): 3062, 1711, 1630, 1592, 1493. δ_H ($CDCl_3$/TMS, 300.1 MHz) 1.31 (t, 3H, CH_3), 2.26 (q, 2H, CH_2), 3.65 (s, 3H), 3.92 (s, 2H), 6.8–7.3 (m, 9H, ArH), 7.92 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 19.2, 19.5, 20.8, 30.8, 32.5, 38.6, 51.5, 126.1, 126.6, 128.6, 130.4 (3C), 133.4 (3C), 139.3, 139.8, 168.6. Calc. for $C_{19}H_{20}O_2$: 280.1463. Found: 280.1456.

Spectral Data for Ether Derivatives

(Z)-Methyl-3-phenyl-2-((prop-2-ynyloxy)methyl) Acrylate (Minor Isomer) ***27a***

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 3291, 2116, 1714, 1633, 1076. δ_H ($CDCl_3$/TMS, 300.1 MHz) 2.53–2.51 (t, *J* 2.4, 1H), 3.83 (s, 3H), 4.40 (s, 2H), 4.84–4.83 (d, *J* 2.4, 2H), 7.40–7.30 (m, 3H), 7.58–7.54 (m, 2H), 7.99 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 52.5, 58.0, 64.0, 74.9, 79.5, 127.3, 128.5, 129.7, 130.0, 134.2, 146.0, 166.5. Calc. for $C_{14}H_{14}O_3$: 230.0943. Found: 230.0935.

(E)-Methyl-3-phenyl-2-((prop-2-ynyloxy)methyl) Acrylate (Major Isomer) ***27b***

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 3291, 2116, 1714, 1633, 1076. δ_H ($CDCl_3$/TMS, 300.1 MHz) 2.48–2.47 (t, *J* 2.1, 1H), 3.83 (s, 3H), 4.28–4.27 (d, *J* 2.1, 2H), 4.41 (s, 2H), 7.40–7.30 (m, 3H), 7.58–7.54 (m, 2H), 7.94 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 52.1, 57.9, 64.1, 74.6, 79.5, 127.9, 128.4, 129.3, 129.9, 134.4, 145.1, 167.8. Calc. for $C_{14}H_{14}O_3$: 230.0943. Found: 230.0929.

(E)-Methyl 3-(4-Chlorophenyl)-2-(prop-2-ynyloxy) Methylacrylate (Minor Isomer) ***28a***

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 3297, 2951, 2116, 1714, 1633, 1077. δ_H ($CDCl_3$/TMS, 300.1 MHz) 2.51–2.50 (t, *J* 2.1, 1H), 3.84 (s, 3H), 4.28–4.27 (d, *J* 2.2.1, 2H), 4.37 (s, 2H), 7.39–7.35 (m, 2H), 7.87 (s, 1H), 7.87–7.51 (m, 2H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 52.5, 58.0, 63.8, 74.8, 79.4, 128.3, 128.6, 131.2, 132.7, 135.5, 143.7, 167.5. Calc. for $C_{14}H_{13}ClO_3$: 264.0553. Found: 264.0534.

(Z)-Methyl 3-(4-Chlorophenyl)-2-(prop-2-ynyloxy) Methylacrylate (Major Isomer) ***28b***

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 3297, 2951, 2116, 1714, 1633, 1077. δ_H ($CDCl_3$/TMS, 300.1 MHz) 2.54–2.52 (t, *J* 2.4, 1H), 3.83 (s, 3H), 4.39 (s, 2H), 4.85–4.84 (d, *J* 2.4, 2H), 7.39–7.35 (m, 2H), 7.87–7.51 (m, 2H), 7.92 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 52.5, 58.0, 63.8, 74.9, 79.3, 128.74, 129.7, 131.3, 132.5, 135.8, 144.6, 166.2. Calc. for $C_{14}H_{13}ClO_3$: 264.0553. Found: 264.0530.

Methyl 3-(4-Methoxyphenyl)-2-((prop-2-ynyloxy)methyl) Acrylate ***29***

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 3289, 2113, 1714, 1605, 1178. δ_H ($CDCl_3$/TMS, 300.1 MHz) 2.50–2.49 (t, *J* 3, 1H), 3.82 (s, 3H), 3.83 (s, 3H), 4.29–4.28 (d, *J* 3, 2H), 4.43 (s, 2H), 6.94–6.91 (d, *J* 8.7, 2H), 7.57–7.55 (d, *J* 8.7, 2H), 7.90 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 52.0, 53.6, 55.2, 57.8, 64.3, 74.6, 79.6, 98.8, 113.9, 125.4, 127.0, 132.0, 145.1, 160.8, 168.1. Calc. for $C_{15}H_{16}O_4$: 260.1049. Found: 260.1072.

Methyl 2-((But-3-ynyloxy)methyl)-3-(4-methoxyphenyl) Acrylate ***30***

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 3295.5, 2119.62, 1715.43, 1605.53, 1121. δ_H ($CDCl_3$/TMS, 300.1 MHz) 2.03–2.01 (t, *J* 2.7, 1H), 2.57–2.51 (dt, *J* 2.7, 6.9, 2H), 3.72–3.70 (t, *J* 6.6, 2H), 3.82 (s, 3H), 3.83 (s, 3H), 4.36 (s, 2H), 6.95–6.90 (m, 2H), 7.59–7.55 (m, 2H), 7.90 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 19.7, 51.9, 55.2, 64.9, 68.4, 69.1, 81.4, 113.9, 125.7, 127.1, 131.9, 144.9, 160.7, 168.2. Calc. for $C_{16}H_{18}O_4$: 274.1205. Found: 274.1210.

Methyl 2-((4-Hydroxybut-2-ynyloxy)methyl)-3-phenyl Acrylate ***31***

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 3445.5, 2319.72, 1745, 1632.38, 1436, 1119.31, 1069. δ_H ($CDCl_3$/TMS, 300.1 MHz) 2.20 (br s, 1H), 3.76 (s, 3H), 4.23 (s, 4H), 4.32 (s, 2H), 7.48–7.30 (m, 5H), 7.86 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 50.8, 52.21, 58.1, 63.9, 81.3, 85.0, 129.9, 134.3, 136.7, 145.1, 168.0. Calc. for $C_{15}H_{16}O_4$: 260.1049. Found: 260.1035.

(Z)-Methyl-2-(methoxymethyl)-3-phenylacrylate ***32a***

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 1715, 1633, 1237. δ_H ($CDCl_3$/TMS, 300.1 MHz) 3.44 (s, 3H), 3.846 (s, 3H), 4.24 (s, 2H), 7.53–7.37 (m, 5H), 7.94 (s, 1H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 52.1, 58.2, 66.4, 128.4, 128.6, 129.3, 129.7, 134.6, 144.7, 168.0. Calc. for $C_{12}H_{14}O_3$: 206.0943. Found: 206.0942.

(E)-Methyl-2-(methoxymethyl)-3-phenylacrylate ***32b***

Colourless oil. ν_{max}/cm^{-1} (CH_2Cl_2) 1715, 1633, 1237. δ_H ($CDCl_3$/TMS, 300.1 MHz) 3.412 (s, 3H), 3.68 (s, 3H), 4.25 (s, 2H), 6.90 (s, 1H), 7.35–7.28 (m, 5H). δ_C ($CDCl_3$/TMS, 75.3 MHz) 51.8, 58.2, 74.2, 124.8, 127.7, 128.4, 130.7, 135.2, 135.8, 168.6. Calc. for $C_{12}H_{14}O_3$: 206.0943. Found: 206.0943.

Acknowledgements

P.S. thanks Professor Dr T. K. Chandrashekar, Director-NIST, for infrastructure facilities. Financial support (SR/S1/OC-38/2005) from the DST (New Delhi) is gratefully acknowledged. B.V. and V.V. thank CSIR (New Delhi) for the award of a Senior Research Fellowship. Constructive suggestions for the improvement of the manuscript from the referees are greatly acknowledged.

References

[1] G. Lai, J. Peng, J. Li, H. Qiu, J. Jiang, K. Jiang, Y. Shen, *Tetrahedron Lett.* **2006**, *47*, 6951. doi:10.1016/J.TETLET.2006.07.122

[2] A. R. Gholap, N. S. Choker, T. Daniel, R. J. Lahothi, K. V. Srinivasan, *J. Mol. Catal. Chem.* **2006**, *245*, 37. doi:10.1016/J.MOLCATA.2005.09.021

[3] B. Das, V. S. Reddy, M. R. Reddy, *Tetrahedron Lett.* **2004**, *45*, 6717. doi:10.1016/J.TETLET.2004.07.076

[4] M. Sathe, M. P. Kaushik, *Catal. Commun.* **2006**, *7*, 644. doi:10.1016/J.CATCOM.2006.02.007

[5] H. Firouzabadi, N. Iranpoor, H. Hazarkhani, B. Karimi, *Synth. Commun.* **2003**, *33*, 3653. doi:10.1081/SCC-120025173

[6] H. Firouzabadi, N. Iranpoor, H. Hazarkhani, B. Karimi, *J. Org. Chem.* **2002**, *67*, 2572. doi:10.1021/JO016343C

[7] F. Shirini, M. A. Zolfingol, M. Khaleghi, *Bull. Korean Chem. Soc.* **2003**, *24*, 1021.

[8] K. V. N. S. Srinivas, I. Mahender, B. Das, *Chem. Lett. (Jpn.)* **2003**, *32*, 738. doi:10.1246/CL.2003.738

[9] M. Sathe, R. Ghorpade, M. P. Kaushik, *Chem. Lett. (Jpn.)* **2006**, *35*, 1004. doi:10.1246/CL.2006.1004

[10] H. Firouzabadi, N. Iranpoor, H. Hazarkhani, *Tetrahedron Lett.* **2002**, *43*, 7139. doi:10.1016/S0040-4039(02)01706-9

[11] M. A. Zolfigol, M. Torabi, S. E. Mallakpour, *Tetrahedron* **2001**, *57*, 8381. doi:10.1016/S0040-4020(01)00832-8

[12] K. V. N. N. S. Srinivas, I. Mahender, B. Das, *Synthesis* **2003**, *16*, 2479.

[13] M. A. Zolfigol, M. Bagherzadeh, S. Mallakpour, A. G. Chehardoli, E. Kolvari, A. G. Choghamarani, N. Koukabi, *Catal. Commun.* **2007**, *8*, 256. doi:10.1016/J.CATCOM.2006.04.006

[14] M. Sathe, A. K. Guptha, M. P. Kaushik, *Tetrahedron Lett.* **2006**, *47*, 3107. doi:10.1016/J.TETLET.2006.02.159

[15] V. K. Rajput, B. Roy, B. Mukhopadhyay, *Tetrahedron Lett.* **2006**, *47*, 6987. doi:10.1016/J.TETLET.2006.07.125

[16] H. Firouzabadi, N. Iranpoor, B. Karimi, H. Hazarkhani, *Synlett* **2000**, 263. doi:10.1055/S-2000-6483

[17] D. Basavaiah, A. J. Rao, T. Satyanarayana, *Chem. Rev.* **2003**, *103*, 811. doi:10.1021/CR010043D

[18] S. E. Drewes, G. H. P. Roos, *Tetrahedron* **1988**, *44*, 4653. doi:10.1016/S0040-4020(01)86168-8

[19] K. Y. Lee, S. Gowrisankar, J. N. Kim, *Bull. Korean Chem. Soc.* **2005**, *26*, 1481.

[20] D. Basavaiah, K. Muthukumaran, B. Sreenivasulu, *Synthesis* **2000**, 545. doi:10.1055/S-2000-6372

[21] D. Basavaiah, K. Padmaja, T. Satyanarayana, *Synthesis* **2000**, 1662, and references cited therein. doi:10.1055/S-2000-8213

[22] S. E. Kelly, in *Comprehensive Organic Synthesis* (Eds B. M. Trost, I. Fleming) **1991**, Vol. 1, pp. 797 (Pergamon Press: New York, NY).

[23] H. S. Kim, T. Y. Kim, K. Y. Ley, Y. M. Cheng, H. J. Lee, J. N. Kim, *Tetrahedron Lett.* **2000**, *41*, 2613. doi:10.1016/S0040-4039(00)00229-X

[24] A. Foucaud, F. E1. Guemmount, *Bull. Soc. Chem. Fr.* **1989**, 403.

[25] P. Shanmugam, P. Rajasingh, *Synlett* **2001**, 1314. doi:10.1055/S-2001-16040

[26] B. Das, K. Venkadeswarlu, M. Krishnaiah, H. Holla, A. Majhi, *Helv. Chim. Acta* **2006**, *89*, 1417. doi:10.1002/HLCA.200690141

[27] L. Navarre, S. Darses, J. P. Genet, *Chem. Commun.* **2004**, 1108. doi:10.1039/B402928C

[28] P. Shanmugam, P. Rajasingh, *Chem. Lett. (Jpn.)* **2002**, *31*, 1212. doi:10.1246/CL.2002.1212

[29] P. Shanmugam, P. Rajasingh, *Tetrahedron* **2004**, *60*, 9283. doi:10.1016/J.TET.2004.07.067

[30] P. Shanmugam, P. Rajasingh, *Synlett* **2005**, 0939. doi:10.1055/S-2005-864815

[31] P. Shanmugam, P. Rajasingh, *Tetrahedron Lett.* **2005**, *46*, 3369. doi:10.1016/J.TETLET.2005.03.086

[32] P. Shanmugam, P. Rajasingh, *Chem. Lett. (Jpn.)* **2005**, *34*, 1494. doi:10.1246/CL.2005.1494

[33] P. Shanmugam, V. Vaithiyanathan, B. Viswambharan, *Tetrahedron* **2006**, *62*, 4342. doi:10.1016/J.TET.2006.02.072

[34] P. Shanmugam, V. Vaithiyanathan, B. Viswambharan, *Tetrahedron Lett.* **2006**, *47*, 6851. doi:10.1016/J.TETLET.2006.07.070

[35] P. Shanmugam, V. Vaithiyanathan, B. Viswambharan, *Aust. J. Chem.* **2007**, *60*, 296. doi:10.1071/CH07020

[36] P. Shanmugam, V. Vaithiyanathan, B. Viswambharan, M. Suchithra, *Tetrahedron Lett.* **2007**, *48*, in press.

[37] D. D. Perrin, W. F. L. Armearego, *Purification of Laboratory Chemicals, 3rd edn* **1988** (Pergamon Press: New York, NY).