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Studies on montmorillonite K10-microwave assisted isomerisation of Baylis–Hillman adduct. Synthesis of *E*-trisubstituted alkenes and synthetic application to lignan core structures by vinyl radical cyclization

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Abstract—The isomerisation of acetates from the Baylis–Hillman adducts with Mont.K10 clay-microwave combination furnished *E*-trisubstituted alkenes in high yield. The simple Baylis–Hillman adducts with trimethyl orthoformate and unsaturated alcohols under clay catalytic condition gave densely functionalised-isomerized products under solvent free condition. Application of the propargyl derivatives thus obtained from the isomerisation of the Baylis–Hillman adducts with propargyl alcohol has been demonstrated in the synthesis of lignan core structures by tri-*n*-butyltin hydride mediated vinyl radical cyclization.

1. Introduction

Synthetic methodologies based on green chemistry processes are increasingly of interest in organic synthesis.[1] Amongst the several green chemistry processes known, methodologies based on eco-friendly clay catalysts play an important role in the manufacture of industrial products and in organic synthesis.[2] The use of clays in the later and its application as a catalyst for a number of organic reactions are well documented.[3–5] The Montmorillonite K10 and its structurally modified clays such as ion-exchanged and pillared clays, are known to act as both Bronsted and Lewis acid catalysts for a variety of industrially important organic reactions.[2] The clay catalysts are known as eco-friendly acid catalysts which have potential for replacing the conventional mineral acids and are non-pollutants. The advantages of the clay-catalyzed reactions are that they are generally mild, solvent free and easy work-up. The Baylis–Hillman reaction is one of the important carbon–carbon bond forming reactions and has been used in organic synthesis for the preparation of a variety of compounds having diverse functional groups. These adducts have been used as the starting point for a number of synthetic organic transformations.[6–14] Stereoselective construction of (*E*)-trisubstituted alkene is one of the more difficult tasks in organic synthesis and only a few methods are known in the literature.[9,10,15] The isomerisation of acetates of the Baylis–Hillman adducts catalyzed by TMSOTf,[9,10] trifluoroacetic acid,[11] benzyl trimethylammonium fluoride[12] have appeared in the literature. Montmorillonite K10-microwave combination has been utilized for carrying out many organic transformations as a catalyst.[16–18]

In continuation of our research on clay catalysis[19–23] in organic synthesis, herein we give an account on the mont-K10-microwave assisted stereoselective isomerisation of acetates of Baylis–Hillman adducts, a one-pot protection-isomerisation with trimethyl orthoformate and unsaturated alcohols. A synthetic application of propargyl derivatives of the Baylis–Hillman adduct thus obtained, in the synthesis of lignan core structures through a vinyl radical cyclization, have also been explored.

2. Results and discussion

2.1. Isomerisation of acetates of the Baylis–Hillman adducts

The general isomerisation studies of the acetates of Baylis–Hillman adduct is depicted in Scheme 1. The Baylis–Hillman adducts **1a–o** and its acetate adducts **2a–p** were prepared according to the literature.[9] The preliminary study was initiated by stirring acetate **2a** with 50% w/w montmorillonite K10 clay in CH_2Cl_2 at room temperature

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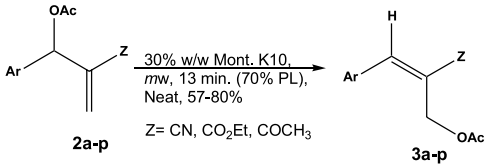


Scheme 1. Isomerization of acetates of Baylis–Hillman adducts catalysed by Mont. K10-microwave.

for 48 h afforded the starting material and the deacetylated product (20%). Heating the same reaction mixture at reflux temperature for 24 h furnished only the starting material. However, when a slurry of the acetate **2a** with 50% w/w mont-K10 clay without any solvent was irradiated in a microwave oven for 6 min, a clean isomerised product **3a** was obtained in 60% yield (~10% decomposition to aldehyde) as determined by ^{1}H NMR spectroscopy. Among the several variations tested to optimize the condition,[22] the condition involving acetate **2a** with 30% w/w of mont-K10 clay, 70% microwave power level (PL) and 13 min. irradiation time was found to be the best and yielded the clean isomerised product **3a** (in 9:1, *E*:*Z* isomer) in 74% after column purification. It should be noted that the microwave irradiation of acetate **2a** under similar conditions without any clay furnished the starting material quantitatively confirming the importance of clay catalyst for this reaction. The simple adduct **1** under similar conditions furnished only 20% of the isomerized product with remaining decomposed products. Hence, the acetate protection of the Baylis–Hillman adduct is essential for good yields.

In order to demonstrate the general nature of this reaction, we chose a variety of acetates of Baylis–Hillman adduct **2b–p**, which underwent a facile isomerisation with the mont-K10-microwave combination to give clean isomerised products **3b–p** in good yield. Yields of the adduct bearing nitrile and carbonyl groups were lower than that of the ester group and needed a longer irradiation time with higher power level (100% PL). The isomer ratios (*E*:*Z*) of the products were estimated by ^{1}H NMR spectroscopy and the results are summarized in Table 1.

The efficiency of commercial montmorillonite-K10 clay (2:1 layer type, available from Aldrich Co.)[2,3] in this reaction was compared with Fe^{3+}-mont-K10[24] (an ion exchanged clay) and an acid treated regional natural kaolinite clay.[25–26] The use of Fe^{3+}-mont-K10 was found to be as good as montmorillonite K10 clay, while with acid treated regional natural kaolinite (1:1 layer type) clay, the reaction was unsuccessful and starting material was recovered quantitatively. The reason for this observation with natural kaolinite clay[25,26] may be that the interlayer distance is <7 Å compared to Mont. K10 clay whose interlayer gap is 10 Å.[2,3] Hence, due to the small interlayer distance in the acid treated regional natural kaolinite clay,[26] the substrate molecules are presumably unable to enter the interlayer space where the reactions are believed to occur and hence the reaction found failed. It should be noted that we have tested the kaolinite clay catalyst only for the isomerisation of the acetates of the Baylis–Hillman adduct, which with Mont. K10 clay catalyst furnished desired products in good yield and we had not examined the smaller substrates for the comparative studies. The results are summarized in Table 2.

2.2. One-pot protection-isomerisation of Baylis–Hillman adducts with trimethyl orthoformate

Encouraged by the preliminary results, we were interested in the possibility of a one-pot protection-isomerisation of Baylis–Hillman adducts without acetate protection using a similar catalysts system with trimethyl orthoformate. The results are impressive and furnished a highly stereoselective

Table 1. Mont. K10 clay[a]-microwave assisted isomerisation of Baylis–Hillman acetate adducts **2a–p**

Entry	Substrate	Ar	Z	Condition[b]	Product (*E*/*Z*)[c]	Yield (%)[d]
1	**2a**	Ph	–CO_2Et	Clay, MW, 13 min	**3a**, 9:1	74
2	**2b**	Ph	–CN	Clay, MW, 15 min	**3b**, 9.5:0.5	68
3	**2c**	Naphth-1-yl	–CO_2Et	Clay, MW (80% PL), 13 min	**3c**, 9.4:0.6	70
4	**2d**	Naphth-1-yl	–CN	Clay, MW, 16 min	**3d**, 9.2:0.8	62
5	**2e**	4-Cl–Ph–	CO_2Et	Clay, MW, 13 min	**3e**, 9.3:0.7	60
6	**2f**	4-Cl–Ph–	CN	Clay, MW (80% PL), 16 min	**3f**, 9.5:0.5	57
7	**2g**	–Ph	$COCH_3$	Clay, MW, 13 min	**3g**, 9.6:0.4	59
8	**2h**	4-Me–Ph	CO_2Et	Clay, MW, 13 min	**3h**, 9:1	71
9	**2i**	4-Me–Ph	CN	Clay, MW (80% PL), 16 min	**3i**, 8:2	66
10	**2j**	2,4-Cl_2–Ph	CO_2Et	Clay, MW, 13 min	**3j**, 9.2:0.8	72
11	**2k**	2,4-Cl_2–Ph	CN	Clay, MW, 16 min	**3k**, 8.7:1.3	70
12	**2l**	4-MeO–Ph	CO_2Et	Clay, MW (80% PL), 13 min	**3l**, 9.6:0.4	80
13	**2m**	4-MeO–Ph	CN	Clay, MW, 16 min	**3m**, 9.2:0.8	76
14	**2n**	Naphth-2-yl	CO_2Et	Clay, MW, 13 min	**3n**, 9.1:0.9	68
15	**2o**	Naphth-2-yl	CN	Clay, MW (80% PL), 16 min	**3o**, 9.5:0.5	62
16	**2p**	4-Me–Ph	$COCH_3$	Clay, MW, 13 min	**3p**, 9.1:0.9	65

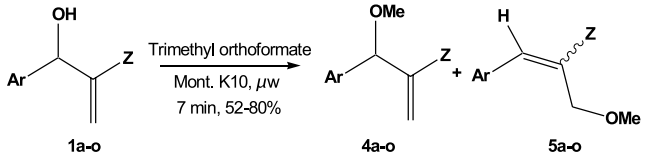
Microwave irradiation was carried out on a KenStar microwave oven with 70% PL.
[a] Montmorillonite K10 clay was dried at 85 °C for 2 h before each use.
[b] 30% w/w montmorillonite-K10 clay was used in each case.
[c] *E*/*Z*—ratio was assigned based on ^{1}H and ^{13}C NMR.
[d] After column purification.

Table 2. Comparison of mont-K10[a], Fe^{3+}-Mont.-K10[a] and acid treated regional natural kaolinite clay catalysts on isomerisation of acetate of the adduct **2a** into **3a**

Clay	Condition[b]	*E*/*Z*—ratio[c]	Yield (%)[d]
Montmorillonite-K10	30% w/w clay, MW, 13 min	9:1	74
Fe^{3+}-mont. K10	30% w/w clay, MW, 6 min	9:1	72
Natural kaolinite clay	30% w/w clay, MW, 8 min	—	No reaction

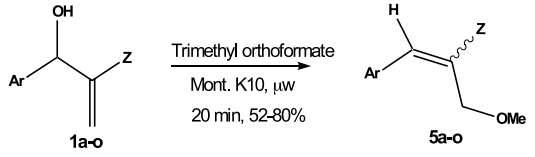
[a] All the clays were dried at 85 °C for 2 h before each use.
[b] Microwave irradiation was carried out on a KenStar microwave oven (70% PL).
[c] *E*/*Z*—ratio was estimated based on ^{1}H and ^{13}C NMR.
[d] After column purification.

E-alkene (99.9%) in good yield. The advantages of this methodology are **1**. Avoiding adducts bearing acetate protection (AcCl, Pyridine) **2**. The resulting isomer is highly *E*-selective (99.9%) and **3**. The procedure is one-pot and mild condition. The general one-pot protection-isomerisation studies are outlined in Scheme 2.



Scheme 2. Protection Isomerization of Baylis–Hillman adduct with trimethyl orthoformate under clay catalyst-microwave condition.

A slurry of the adduct **1a** with 30% w/w mont-K10 clay, trimethyl orthoformate without any solvent was irradiated in a microwave [100% PL] oven for 7 min, a mixture of products were obtained in 70% yield. The products were separated and identified as **4a** along with ~10% of the isomerised product **5a**. However, when the same was irradiated for 20 min with 100% PL yielded the only required isomerised product **5a** (in 99.8:0.2, *E*:*Z* isomer) in 74% yield after column purification (Scheme 3).



Scheme 3. Isomerization of Simple Baylis–Hillman adduct with trimethyl orthoformate.

As anticipated, the other Baylis–Hillman adducts **1b–o** underwent a facile isomerisation with mont-K10-microwave combination to give clean isomerised products **5b–o** in good yield. We observed that in all these cases, the yields of adduct with nitrile were lower than that of the ester functional group at the activated alkene and needed a longer irradiation time (22 min). The results are summarized in Table 3. Hence, the isomerisation reaction was very smooth without acetate protection with trimethyl orthoformate. Basavaiah et al.[10] have reported that the Baylis–Hillman adduct bearing CN substitution undergoes isomerisation in better in good yield (50–68%) under sulfuric acid conditions, while Kim et al.[11] have reported that the Baylis–Hillman adducts bearing CO_2Et substitution undergoes isomerisation better yield (51–72%) than that of substrates bearing CN substitution(27–40%) with trifluoroacetic acid conditions. It should be noted that the present clay catalyst condition holds good for both the cases furnished better yield and higher *E*-selectivity.

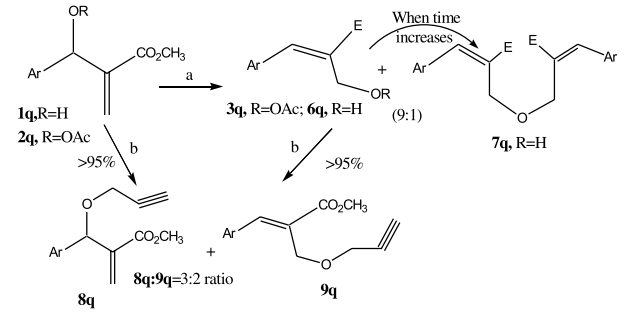
2.3. Isomerisation of the Baylis–Hillman adduct with unsaturated alcohols

We examined the behaviour of the Baylis–Hillman adduct with unsaturated alcohols under clay catalytic condition (Scheme 4). The results were good and yielded densely functionalised propargyl derivative of the Baylis–Hillman adduct.[23] Heating a slurry 75 °C, 1.5 h) made with the adduct **1q**, 2 equiv of propargyl alcohol and 60% w/w Mont. K10 without any solvent furnished ether **8q**[27] and its

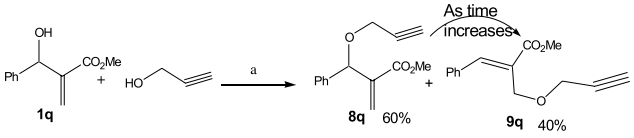
Table 3. Montmorillonite-K10[a]-Microwave assisted one-pot protection-isomerisation of the Baylis–Hillman adducts **1a–o** with trimethyl orthoformate

Entry	Reactant	R	Z	Condition[b,c]	Product[d]	Yield (%)[e]
1	**1a**	Ph	CO_2Et	Clay, MW, 20 min	**5a**	74
2	**1b**	Ph	CN	Clay, MW, 22 min	**5b**	70
3	**1c**	Naphth-1-yl	CO_2Et	Clay, MW, 21 min	**5c**	72
4	**1d**	Naphth-1-yl	CN	Clay, MW, 23 min	**5d**	60
5	**1e**	4-Cl–Ph–	CO_2Et	Clay, MW, 19 min	**5e**	62
6	**1f**	4-Cl–Ph–	CN	Clay, MW, 20 min	**5f**	52
7	**1h**	4-Me–Ph	CO_2Et	Clay, MW, 18 min	**5h**	70
8	**1i**	4-Me–Ph	CN	Clay, MW 21 min	**5i**	64
9	**1l**	4-MeO–Ph	CO_2Et	Clay, MW, 20 min	**5l**	80
10	**1m**	4-MeO–Ph	CN	Clay, MW 21 min	**5m**	77
11	**1n**	Naphth-2-yl	CO_2Et	Clay, MW, 21 min	**5n**	69
12	**1o**	Naphth-2-yl	CN	Clay, MW 22 min	**5o**	63

[a] Montmorillonite K10 clay was dried at 85 °C for 2 h before each use.
[b] Microwave irradiation was carried out on a KenStar microwave oven with 100% PL.
[c] 30% w/w montmorillonite-K10 clay was used in each case.
[d] *E*/*Z*—ratio was assigned based on ^{1}H and ^{13}C NMR.
[e] After column purification.



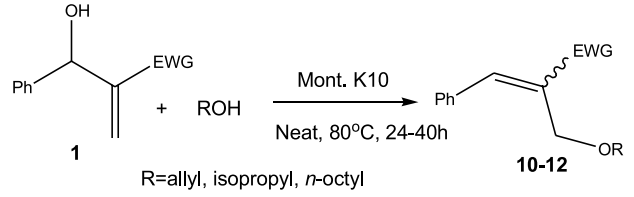
Scheme 4. Conditions: (a) 60% w/w Mont, K10, neat, 2 h 75 °C; (b) w/w% Mont.K10, propargyl alcohol, neat, 6 h, 75 °C.



Scheme 5. Conditions: (a) 60% w/w Mont, K10, neat, 2.5 equiv propargyl alcohol, neat, 75 °C, 2 h.

Table 4

Time (h)	8q (%)	9q (%)
6	42	58
15	25	75
22	<5	>95
24	<1	>99



Scheme 6.

isomerised product **9q** (99.9; *E*-selectivity)[28] in 90% combined yield and in 3:2 product ratio.[29] The reaction proceeded smoothly and furnished pure products as indicated. The compounds were separated by silica gel column chromatography and characterized by NMR spectroscopy.

The effect of the reactivity of the Baylis–Hillman adduct **1q**, its acetate protected adduct **2q** and their isomerised compounds **6q** and **3q** with propargyl alcohol under the reaction condition described above are compared and all the reactions furnished compounds **8q** and **9q**. All these reactions furnished the desired products almost in the same yield and product ratio (3:2).

Interestingly, the simple Baylis–Hillman adducts **1q** and **2q** underwent isomerisation and provided an excellent yield (95%) of compounds **8q** and **9q**. Compounds **6q** and **3q** with propargyl alcohol under similar conditions furnished **8q** and **9q** in excellent yield (>95%) and in a ratio of 3:2. The product ratio of compounds **8q** and **9q** was determined by proton NMR spectroscopy as integration of the protons at δ 5.51 and 7.92 respectively. Therefore, the nucleophilicity of the propargyl alcohol on the isomerised **6q** and **3q** and unisomerized Baylis–Hillman adducts (**1q** and **2q**) are identical since they afforded same products **8q** and **9q** in the same product ratio (3:2). Hence, the experiment reveals that the reaction of propargyl alcohol with simple unisomerized Baylis–Hillman adducts provide the required products in excellent yield. Hence, no protected/isomerised starting materials are necessary to effect this transformation. We also observed that the simple adduct **1q** with 60% w/w clay at 75 °C for 2 h under neat condition furnished the isomerised compound **6q** and ether **7q** in 60% combined yield and in a 9:1 ratio. As the reaction time increases, ether **7q** was found as sole product. The details are shown in Scheme 4. The formation of the only isomerised product **9q** with propargyl alcohol over **8q** under the conditions described above can be achieved by increasing the reaction time (Scheme 5). The complete conversion of **8q** into isomerised product **9q** was observed at a reaction time 24 h. The distribution of products with respect to reaction time is summarized in Table 4.

In order to demonstrate the general nature of this reaction, we have chosen three different alcohols and found that the reactions are clean and high yielding (**10**–**12**) under the optimized conditions described above (Scheme 6). However the reaction with higher boiling alcohols yielded only a complex reaction mixture and/or starting materials. The results are summarized in Table 5. The Mont. K10 clay recovered from the reaction mixture by filtration can be recycled three times without losing its activity by activating the clay at 100 °C for 3 h.

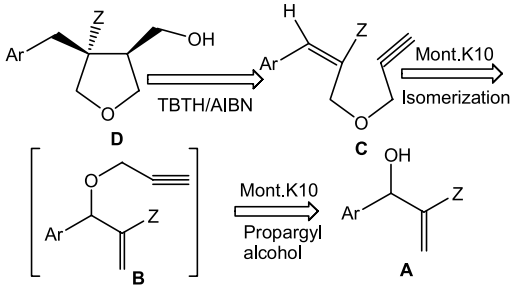
2.4. Synthetic application of the propargyl derivative of Baylis–Hillman adduct. Synthesis of lignan cores via vinyl radical cyclization

The lignans are common and structurally diverse group of

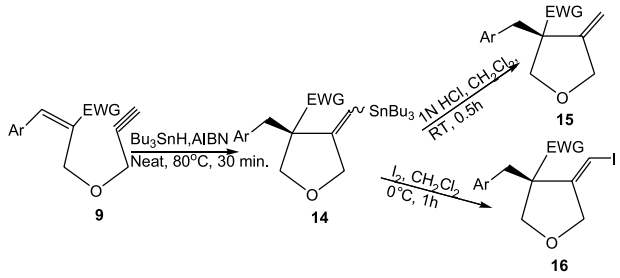
Table 5. Isomerisation of Baylis–Hillman adduct with alcohols[a,b,c]

Entry	Reactant	Alcohol	Z	Product	Yield (%)[d]
1	**1a**	Allyl	CO_2Et	**10a**	94
2	**1q**	Allyl	CO_2Me	**10q**	95
3	**1q**	Isopropyl	CO_2Me	**11q**	95
4	**1b**	*n*-Octyl	CN	**12b**	98
5	**1q**	*n*-Octyl	CO_2Me	**12q**	97

[a] Montmorillonite K10 clay was dried at 100 °C for 1 h before each use.
[b] 60% w/w Mont.-K10 clay was used in each case.
[c] Mont. K10, 75 °C, 24 h.
[d] After column purification.



Scheme 7. Retrosynthetic analysis.



Scheme 8.

plant natural products of phenyl propionoid origin, displaying physiological functions in planta, particularly in plant defence, in human nutrition and medicine, given their extensive health protective and curative properties.[30] A major sub-group of lignans such as lariciresinol, wikstromol, olivil and dihydrosesamine are comprised of di, tri and tetra substituted tetrahydrofurans.[30,31] Substituted tetrahydrofurans are the main constituents of many naturally occurring compounds including furanolignan and several methods are known for its synthesis.[32] A few reports are known using radical reactions for the construction of lignan cores[33,34] and other interesting routes[35] for the synthesis of lignan natural products as well.

The propargyl derivatives of the Baylis–Hillman adduct are suitable substrates for the construction of lignan core structures by a radical cyclization protocol. A key synthetic strategy is depicted in Scheme 7. The phenyl propionoid bearing furanolignan core **D** can be achieved by a 5-*exo*-trig vinyl radical cyclization of the alkenyl propargyl ether **C**. Compound **C** in turn can be synthesized from the compound **B** through a one-pot protection-isomerisation reaction of the Baylis–Hillman adduct **A** with propargyl alcohol catalyzed by Mont. K10 clay.[23]

The construction of spiroacetals from enyne ethers,[36a] α-methylene-γ-butyrolactone from allyl, crotyl propiolates,[36b] carbocycles and heterocyclics from dienes and enynes[36c] by a tin-mediated radical cyclization methods are known in the literature.

The synthetic study is represented in Scheme 8. The details of the preparation of enenyne ethers **9a–t** from adduct **1a–t** under clay catalytic condition is given in Table 6.

Radical cyclization of the alkenyl propargyl ether **9q** with 1.5 equiv of freshly distilled tri-*n*-butyltin hydride,[37] and a catalytic amount of azobisisobutyronitrile (AIBN) at 85 °C without any solvent under an inert atmosphere afforded crude vinylstannane **14a** through a 5-*exo*-trig cyclization process. The crude vinylstannane obtained was subjected to the protiodestannylation (without purification) with 1 N HCl in ether at room temperature for 4 h to give the cyclized product **15a** in 95% yield after column purification.

Table 6. Preparation of enyne ethers **9a–t** with propargyl alcohol

Entry	Reactant	Ar	Z	Product	Yield (%)
1	**1a**	C_6H_5	CO_2Et	**9a**	92
2	**1b**	C_6H_5	CN	**9b**	90
3	**1e**	4-Cl–C_6H_4	CO_2Et	**9e**	91
4	**1f**	4-Cl–C_6H_4	CN	**9f**	89
5	**1i**	4-Me–C_6H_4	CN	**9i**	86
6	**1m**	4-MeO–C_6H_4	CN	**9m**	72
7	**1q**	C_6H_5	CO_2Me	**9q**	95
8	**1r**	4-Cl–C_6H_4	CO_2Me	**9r**	90
9	**1s**	4-Me–C_6H_4	CO_2Me	**9s**	85
10	**1t**	4-MeO–C_6H_4	CO_2Me	**9t**	80

Table 7. Radical cyclization of enyne ethers **9a–t**

Entry	Reactant	Ar	Z	Product	Yield (%)
1	**9a**	C_6H_5	CO_2Et	**15a**	95
2	**9b**	C_6H_5	CN	**15b**	92
3	**9e**	4-Cl–C_6H_4	CO_2Et	**15e**	96
4	**9f**	4-Cl–C_6H_4	CN	**15f**	96
5	**9i**	4-Me–C_6H_4	CN	**15i**	94
6	**9m**	4-MeO–C_6H_4	CN	**15m**	94
7	**9q**	C_6H_5	CO_2Me	**15q**	95
8	**9r**	4-Cl–C_6H_4	CO_2Me	**15**r	97
9	**9s**	4-Me–C_6H_4	CO_2Me	**15s**	92
10	**9t**	4-MeO–C_6H_4	CO_2Me	**15t**	90

Table 8. Comparative NMR values of cyclized products

Cyclized products		Chemical shifts (δ) and coupling constants (J Hz)			
		C-2 protons(2H)	C-5 protons (2H)	Benzyl-H(2H)	Olefin-H
CO_2Me Substituted	Stannylated	d at δ 3.84 and 4.22 J=9.3 Hz	s δ 4.24	d at δ 2.78 & 3.33 J=13.7 Hz	s (1H), δ 6.1
	Destannylated **15a**	d at δ 4.0 and 4.24 J=9.3 Hz	d, δ 4.39 J=2.19 Hz	d at δ 2.89 & 3.34 J=13.7 Hz	s (1H), δ 5.13 t (1H), δ 5.35, J=2.4 Hz
	Iodo destannylated **16**	d at δ 4.05 and 4.25 J=9.3 Hz	dd at δ 4.31and 4.35 J=10.5, 2.6 Hz	d at δ 2.96 & 3.24 J=13.6 Hz	t (1H) δ 6.40 J=2.6 Hz
CN Substituted	Stannylated	d at δ 3.88 and 4.01, J=8.9 Hz	d ABq at δ 4.4 J=13.3, 2.4 Hz	s (2H), at δ 2.97	t (2H) δ 6.05, J=2.4 Hz
	Destannylated **15b**		d ABq at δ 4.4 J=13.3, 2.3 Hz		d at (2H) δ 5.2, J=2.3 Hz

Similarly, the corresponding nitrile substituted cyclized product **15b** was obtained in 92% yield from the enenyne ether **9b**. The ester group and or nitrile functional groups are available in the product for further manipulations on the tetrahydrofuran ring. To functionalize the vinylstannanes **14a**, treatment of the crude vinylstannane with iodine[38] in dichloromethane at 0 °C for 1 h afforded the iodo derivative **16** in quantitative yield as a solid. Similarly, following the same reaction sequence and experimental conditions other adducts **9e–t** bearing *p*-chlorophenyl, *p*-tolyl, *p*-anisyl aromatic moieties furnished the corresponding cyclized products **15e–t** in excellent yield (90–97%). The results are summarized in Table 7. All the new compounds were characterized by spectral and analytical data. The relative stereochemistry and structural determination of the cyclized products were assigned based on the detailed NMR analysis and in comparison with the literature report.[30,31] The benzyl proton of the compound **14a** showed two doublets at δ 2.78 and 3.33 due to geminal coupling while in the compound **14b** it appeared as a singlet at δ 2.97. The coupling constant of benzyl proton in the compound **14a** was found to be 13.7 Hz and is the same as that of literature known furanolignans.[30] The C-5 protons in **15a** and **15b** appeared as triplet and doublet of doublet at δ 4.39 and δ 4.3 and δ 4.4, respectively. Hence it is evident that in the compound **15b**, the allylic protons have considerable coupling with the vinylic protons in addition to geminal coupling. To confirm this observation, in the iodinated compound **16**, the allylic proton appeared as doublet of doublet while the same proton is appeared as triplet in the corresponding stannylated product (Table 8).

In conclusion, we have demonstrated the usefulness of montmorillonite K10 clay-microwave combination as an alternative, useful, speedy and efficient catalyst for the isomerisation of a variety of acetates of Baylis–Hillman adducts and with unsaturated alcohols which provides densely functionalised (*E*)-alkenes. We have also demonstrated the usefulness of same catalysts system for a one-pot protection isomerisation of a variety of Baylis–Hillman adducts with trimethyl orthoformate. Further, we showed the application of the propargyl derivative of the Baylis–Hillman adduct to the synthesis of furanolignan core structures by adopting tri-*n*-butyltin hydride mediated vinyl radical cyclization protocol as a key step. This methodology suggests that by incorporating suitably substituted propargyl alcohol at the isomerisation step, followed by radical cyclization would directly furnish the cores of furanolignan natural product. Studies on the total synthesis of lariciresinol and related natural products and use of clay catalytic conditions for other systems are being pursued in our laboratories.

3. Experimental

3.1. General consideration

All experiments were carried out in oven-dried glassware. Analytical thin layer chromatography was performed on silica gel TLC plates. Purification by gravity column chromatography was carried out using silica gel (100–200 mesh). Mixtures of ethyl acetate and hexane and pure ethyl acetate were used as eluent as required. Melting points were recorded on Aldrich Meltemp-II and are reported without corrections. IR spectra were run on a Nicolet (impact 400D FT-IR) spectrophotometer or Bomem MB-Series FT-IR spectrophotometer. NMR spectra were obtained using chloroform-d as solvent on Bruker DPX 300 MHz NMR spectrometer. Chemical shifts are given in δ scale with TMS as internal reference. HRMS were measured at the JMS 600 JEOL Mass Spectrometer. Micro analyses were performed at the Perkin–Elmer Series II 2400 analyser. Yields refer to quantities obtained after chromatography. Solvents used are reagent grade and were purified before use according to the literature procedure.

3.2. Typical experimental procedure for isomerisation of acetates of Baylis–Hillman adducts

A mixture of the acetates of Baylis–Hillman adducts (200 mg, 0.8 mmol) and montmorillonite K-10 (60 mg, 30% w/w of the adduct) was taken in a stoppered 25 mL conical flask and irradiated in the microwave oven (70% power mode) for 13 min. The mixture was cooled to room temperature and treated with CH_2Cl_2 (10 mL). Montmorillonite K-10 clay was recovered by filtration and washed with CH_2Cl_2 (2×5 mL). The solvent was removed in vacuo and the crude mixture was purified by silica gel column chromatography using petroleum ether–ethyl acetate (92:8) to give pure colourless isomerised products in 9:1 (*E*:*Z*) isomers as estimated by ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz).

3.2.1. Ethyl (2*E*)-2-acetoxymethyl-3-phenylprop-2-enoate (3a). Colourless oil; yield: 74%; IR(neat) ν_{max}: 1744, 1726, 1633 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 1.35 (t, 3H, J=7.1 Hz), 2.10 (s, 3H), 4.31 (q, 2H, J=

7.1 Hz), 4.95 (s, 2H), 7.39 (s, 5H), 7.98 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 14.25, 20.86, 59.22, 61.03, 126.77, 128.64, 129.37, 129.47, 134.23, 144.98, 166.57, 170.37. Mass spectra *m/z*: 248 (M^+). Elemental analysis: Calcd for $C_{14}H_{16}O_4$: C, 67.73%, H, 6.50%. Found: C, 67.60%, H, 6.42%.

3.2.2. (2*E*)-2-Acetoxymethyl-3-phenyl prop-2-enenitrile (3b). Colourless oil; yield: 68%; IR(neat) ν_{max}: 2213, 1748, 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 2.16 (s, 3H), 4.82 (s, 2H), 7.23 (s, 1H), 7.45 (m, 3H), 7.79 (m, 2H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 20.51, 65.02, 105.88, 117.04, 128.58, 128.86, 130.75, 132.16, 146.90, 169.76. Mass spectra *m/z*: 201 (M^+). Elemental analysis: Calcd for $C_{12}H_{11}NO_2$: C, 71.63%, H, 5.51%, N, 6.96%. Found: C, 71.60%, H, 5.44%, N, 6.90%.

3.2.3. Ethyl (2*E*)-2-acetoxymethyl-3-naphth-1-ylprop-2-enoate (3c). Colourless oil; yield: 70%; IR(neat) ν_{max}: 1744, 1728, 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 1.36 (t, 3H, J=7.1 Hz), 2.09 (s, 3H), 4.31 (q, 2H, J=7.1cHz), 4.82 (s, 2H), 7.31–7.98 (m, 7H), 8.31 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 13.96, 20.55, 59.32, 60.92, 124.39, 125.25, 126.21, 126.61, 127.27, 128.54, 129.49, 131.60, 132.82, 133.36, 142.82, 166.13, 170.15. Mass spectra *m/z*: 298 (M^+). Elemental analysis: Calcd for $C_{18}H_{18}O_4$: C, 72.47%, H, 6.08%. Found: C, 72.40%, H, 6.01%.

3.2.4. (2*E*)-2-Acetoxymethyl-3-naphth-1-ylprop-2-enenitrile (3d). Colourless oil; yield: 62%; IR(neat) ν_{max}: 2214, 1745, 1618 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 2.16 (s, 3H), 4.79 (s, 2H), 7.51–8.2 (m, 8H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 20.52, 65.02, 105.85, 117.04, 124.52, 125.01, 126.43, 126.93, 128.61, 129.10, 129.83, 131.33, 131.62, 133.24, 146.15, 170.15. Mass spectra *m/z*: 251 (M^+). Elemental analysis: Calcd for $C_{16}H_{13}NO_2$: C, 76.48%, H, 5.21%, N, 5.57%. Found: C, 76.43%, H, 5.15%, N, 5.51%.

3.2.5. Ethyl (2*E*)-2-acetoxymethyl-3-(4-chlorophenyl)-prop-2-enoate (3e). Colourless oil; yield: 60%; IR(neat) ν_{max}: 1742, 1720, 1638 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 1.35 (t, 3H, J=7.1 Hz), 2.10 (s, 3H), 4.31 (q, 2H, J=7.1 Hz), 4.92 (s, 2H), 7.25–7.46 (m, 4H), 7.88 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 14.25, 20.82, 59.22, 61.00, 127.32, 129.01, 130.73, 132.62, 135.71, 143.89, 167.02, 170.51. Mass spectra *m/z*: 283 (M^+). HRMS: Calcd for $C_{14}H_{15}ClO_4$: 282.0659. Found: 282.0647.

3.2.6. (2*E*)-2-Acetoxymethyl-3-(4-chlorophenyl) prop-2-enenitrile (3f). Colourless oil; yield: 57%; IR(neat) ν_{max}: 2212, 1743, 1624 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 2.15 (s, 3H), 4.80 (s, 2H), 7.17 (s, 1H), 7.42 (d, 2H, J=8.8 Hz), 7.72 (d, 2H, J=8.8 Hz); ^{13}C NMR($CDCl_3$/TMS, 75.3 MHz): δ 20.51, 65.04, 106.75, 116.93, 129.34, 130.45, 131.10, 137.23, 145.72, 170.20. Mass spectra *m/z*: 235 (M^+). HRMS: Calcd for $C_{12}H_{10}ClNO_2$: 235.0400. Found: 235.0380.

3.2.7. (3*E*)-3-Acetoxymethyl-4-phenyl but-3-en-2-one (3g). Colourless oil; yield: 59%; IR(neat) ν_{max}: 1744, 1670, 1625 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 2.50 (s, 3H), 4.90 (s, 2H), 7.43–7.65 (m, 5H), 7.70 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 20.86, 25.65, 60.72, 128.73, 129.61, 129.71, 134.28, 137.41, 142.68, 167.45, 197.07. Mass spectra *m/z*: 218 (M^+). Elemental analysis: Calcd for $C_{13}H_{14}O_3$: C, 71.54%, H, 6.47%. Found: C, 71.50%, H, 6.42%.

3.2.8. Ethyl (2*E*)-2-acetoxymethyl-3-(4-methylphenyl)-prop-2-enoate (3h). Colourless oil; yield: 71%; IR(neat) ν_{max}: 1742, 1722, 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 1.35 (t, 3H, J=7.1 Hz), 2.10 (s, 3H), 2.39 (s, 3H), 4.32 (q, 2H, J=7.1 Hz), 4.96 (s, 2H), 7.20 (d, 2H, J=8.0 Hz), 7.30 (d, 2H, J=8.0 Hz), 7.92 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 14.25, 20.86, 21.22, 59.28, 60.95, 125.74, 129.37, 129.50, 131.33, 139.87, 145.37, 167.31, 170.49. Mass spectra *m/z*: 262 (M^+). Elemental analysis: Calcd for $C_{15}H_{18}O_4$: C, 68.68%, H, 6.92%. Found: C, 68.60%, H, 6.90%.

3.2.9. (2*E*)-2-Acetoxymethyl-3-(4-methyl phenyl)prop-2-enenitrile (3i). Colourless oil; yield: 66%; IR(neat) ν_{max}: 2214, 1745, 1626 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 2.14 (s, 3H), 2.39 (s, 3H), 4.78 (s, 2H), 7.18 (s, 1H), 7.24 (d, 2H, J=8.2 Hz), 7.69 (d, 2H, J=8.2 Hz); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 20.72, 21.56, 65.40, 104.50, 117.30, 129.24, 129.65, 129.84, 141.68, 147.32, 170.05. Mass spectra *m/z*: 215 (M^+). Elemental analysis: Calcd for $C_{13}H_{13}NO_2$: C, 72.54%, H, 6.09%, N, 6.51%. Found: C, 72.50%, H, 6.00%, N, 6.42%.

3.2.10. Ethyl (2*E*)-2-acetoxymethyl-3-(2,4-dichlorophenyl)prop-2-enoate (3j). Colourless oil; yield: 72%; IR(neat) ν_{max}: 1740, 1721, 1638 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 1.35 (t, 3H, J=7.1 Hz), 2.11 (s, 3H), 4.32 (q, 2H, J=7.1 Hz), 4.94 (s, 2H), 7.27 (m, 2H), 7.57 (s, 1H), 7.92 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 14.25, 20.85, 59.20, 61.10, 128.32, 129.21, 130.00, 131.41, 132.01, 134.95, 136.83, 144.71, 167.00, 170.55. Mass spectra *m/z*: 317 (M^+). HRMS: Calcd for $C_{14}H_{14}Cl_2O_4$:317.0260. Found: 317.0260.

3.2.11. (2*E*)-2-Acetoxymethyl-3-(2,4-dichlorophenyl)-prop-2-enenitrile (3k). Colourless oil; yield: 70%; IR(neat) ν_{max}: 2214, 1742, 1625 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 2.15 (s, 3H), 4.82 (s, 2H), 7.15 (s, 1H), 7.45 (d, 2H, J=8.9 Hz), 7.73 (d, 2H, J=8.9 Hz), 7.85 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 20.71, 65.08, 106.80, 117.00, 129.40, 130.90, 131.10, 131.90, 135.23, 137.60, 145.90, 170.20. Mass spectra *m/z*: 270 (M^+). HRMS: Calcd for $C_{12}H_9Cl_2NO_2$: 269.0010. Found: 269.0008.

3.2.12. Ethyl (2*E*)-2-acetoxymethyl-3-(4-methoxyphenyl)prop-2-enoate (3l). Colourless oil; yield: 80%; IR(neat) ν_{max}: 1740, 1718, 1628 cm^{-1}; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 1.35 (t, 3H, J=7.1 Hz), 2.10 (s, 3H), 3.80 (s, 3H), 4.31 (q, 2H, J=7.1 Hz), 4.95 (s, 2H), 7.20 (d, 2H, J=8.8 Hz), 7.70 (d, 2H, J=8.8 Hz), 7.90 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 14.25, 20.84, 55.34, 59.26, 60.95, 116.34, 125.82, 131.93, 144.45, 161.51, 167.31, 170.40. Mass spectra *m/z*: 278 (M^+). Elemental analysis: $C_{15}H_{18}O_5$: Cacld C, 64.74%, H, 6.52%. Found: C, 64.70%, H, 6.50%.

3.2.13. (2*E*)-2-Acetoxymethyl-3-(4-methoxyphenyl)prop-2-enenitrile (3m). Colourless oil; yield: 76%; IR(neat) ν_{max}:

2210, 1742, 1622 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 2.10 (s, 3H), 3.80 (s, 3H), 4.85 (s, 2H), 7.00 (d, 2H, J=8.8 Hz), 7.15 (s, 1H), 7.78 (d, 2H, J=8.8 Hz); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 20.84, 55.34, 60.30, 104.95, 115.34, 118.14, 125.82, 130.01, 144.39, 160.51, 170.70. Mass spectra *m/z*: 231 (M^+). Elemental analysis: Calcd for $C_{13}H_{13}NO_3$: C, 67.52%, H, 5.67%, N, 6.06%. Found: C, 67.48%, H, 5.62%, N, 6.02%.

3.2.14. Ethyl (2*E*)-2-acetoxymethyl-3-naphth-2-yl prop-2-enoate (3n). Colourless oil; yield: 68%; IR(neat) ν_{max}: 1743, 1726, 1630 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 1.35 (t, 3H, J=7.1 Hz), 2.07 (s, 3H), 4.31 (q, 2H, J=7.1 Hz), 4.82 (s, 2H), 7.40–7.50 (m, 4H), 7.81–7.86 (m, 3H), 8.45 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 13.96, 20.54, 59.32, 60.92, 124.14, 124.92, 126.06, 126.38, 126.46, 128.28, 128.96, 129.37, 131.07, 131.23, 133.05, 143.12, 166.16, 170.05. Mass spectra *m/z*: 298 (M^+). Elemental analysis: Calcd for $C_{18}H_{18}O_4$: C, 72.47%, H, 6.08%. Found: C, 72.43%, H, 6.02%.

3.2.15. (2*E*)-2-Acetoxymethyl-3-naphth-1-yl prop-2-enenitrile (3o). Colourless oil; yield: 62%; IR(neat) ν_{max}: 2212, 1745, 1620 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 2.16 (s, 3H), 4.79 (s, 2H), 7.52–7.60 (m, 4H), 7.81–7.89 (m, 3H), 78.25 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 20.52, 65.02, 105.85, 117.04, 124.52, 125.00, 126.43, 126.93, 128.50, 129.05, 129.85, 131.31, 131.62, 133.21, 148.15, 170.15. Mass spectra *m/z*: 251 (M^+). Elemental analysis: Calcd for $C_{16}H_{13}$ N O_2: C, 76.48%, H, 5.21%, N, 5.57. Found: C, 76.42%, H, 5.18%, N, 5.50%.

3.2.16. (2*E*)-2-Acetoxymethyl-4-(4-methylphenyl)but-3-en-2-one (3p). Colourless oil; yield: 65%; IR(neat) ν_{max}: 1742, 1665, 1620 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 2.10 (s, 3H), 2.39 (s, 3H), 4.90 (s, 2H), 7.20 (d, 2H, J=8.0 Hz), 7.30 (d, 2H, J=8.0 Hz), 7.85 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 20.86, 21.22, 25.65, 60.72, 125.74, 129.37, 129.50, 131.33, 137.87, 144.63, 170.49, 197.07. Mass spectra *m/z*: 232 (M^+). Elemental analysis: Calcd for $C_{14}H_{16}O_3$: C, 72.39%, H, 6.94%. Found: C, 72.32%, H, 6.90%.

3.3. Typical experimental procedure for one-pot protection-isomerisation reaction

A mixture of the Baylis–Hillman adducts (200 mg, 0.8 mmol) and montmorillonite K-10 (60 mg, 30% w/w of the adduct) and trimethyl orthoformate (125 mg, 1.15 mol) was taken in a stoppered 25 mL conical flask and irradiated in the microwave oven (100% power mode) for 20 min. The mixture was cooled to room temperature and treated with CH_2Cl_2 (10 mL). Montmorillonite K-10 clay was recovered by filtration and washed with CH_2Cl_2 (2×5 mL). The solvent was removed in vacuum and the crude mixture was purified by silica gel column chromatography using petroleum ether–ethyl acetate (99.8:0.2) to give pure colourless isomerised products in 99.1:0.9 (*E*:*Z*) isomers as estimated by ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz). By reducing irradiation time (7 min 100% PL) the –OMe protected compounds are obtained.

3.3.1. Ethyl (2*E*)-2-methoxymethyl-3-phenyl prop-2-enoate (5a). Colourless oil; yield: 74%; IR(neat) ν_{max}: 1718, 1635 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 1.36 (t, 3H J=7.1 Hz), 3.43 (s, 3H), 4.22 (s, 2H), 4.28 (q, 2H J=7.1 Hz), 7.35–7.52 (m, 5H), 7.9 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 14.36, 58.27, 60.94, 66.50, 128.51, 129.07, 129.29, 129.85, 134.87, 144.33, 167.45. Mass spectra *m/z*: 220 (M^+). Elemental analysis: Calcd for $C_{13}H_{16}O_3$: C, 70.89%, H, 7.32%. Found: C, 70.85%, H, 7.32%.

3.3.2. (2*E*)-2-Methoxymethyl-3-phenyl prop-2-enenitrile (5b). Colourless oil; yield: 70%; IR(neat) ν_{max}: 2208, 1626 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 3.43 (s, 3H), 4.16 (s, 2H), 7.14 (s, 1H), 7.14–7.42 (m, 3H), 7.75–7.78 (m, 2H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 58.25, 73.46, 108.04, 117.41, 128.83, 128.93, 130.53, 132.95, 144.45. Mass spectra *m/z*: 173 (M^+). Elemental analysis: Calcd for $C_{11}H_{11}NO$: C, 76.28%, H, 6.40%, N, 8.09%. Found: C, 76.23%, H, 6.33%, N, 8.05%.

3.3.3. Ethyl (2*E*)-2-methoxymethyl-3-naphth-1-yl prop-2-enoate (5c). Colourless oil; yield: 72%; IR(neat) ν_{max}: 1720, 1630 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 1.36 (t, 3H J=7.1 Hz), 3.43 (s, 3H), 4.22 (s, 2H), 4.30 (q, 2H J=7.1 Hz), 7.44–7.60 (m, 4H), 7.81–7.98 (m, 3H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 14.36, 58.27, 60.94, 66.55, 124.39, 125.24, 126.20, 126.62, 127.27, 128.54, 129.48, 131.40, 131.60, 132.82, 133.86, 142.83, 167.45. Mass spectra *m/z*: 270 (M^+). Elemental analysis: Calcd for $C_{17}H_{18}O_3$: C, 75.53%, H, 6.71%. Found: C, 75.50%, H, 6.22%.

3.3.4. (2*E*)-2-Methoxymethyl-3-naphth-1-yl prop-2-enenitrile (5d). Colourless oil; yield: 60%; IR(neat) ν_{max}: 2214, 1618 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): 3.43 (s, 3H), 4.16 (s, 2H), 7.51–7.59 (m, 4H), 7.80–7.89 (m, 3H), 8.00 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 58.25, 73.46, 108.04, 117.41, 124.52, 125.01, 126.43, 126.93, 128.61, 129.00, 129.83, 131.33, 131.63, 133.22, 146.15. Mass spectra *m/z*: 223 (M^+). Elemental analysis: Calcd for $C_{15}H_{13}NO$: C, 80.69%, H, 5.87%. Found: C, 80.66%, H, 5.86%, N, 6.22%.

3.3.5. Ethyl (2*E*)-2-methoxymethyl-3-(4-chlorophenyl)-prop-2-enoate (5e). Colourless oil; yield: 62%; IR(neat) ν_{max}: 1715, 1638 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 1.35 (t, 3H J=7.1 Hz), 3.42 (s, 3H), 4.18 (s, 2H), 4.29 (q, 2H J=7.1 Hz), 7.37 (d, 5H J=8.5 Hz), 7.47 (d, 2H J=8.5 Hz), 7.9 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 14.21, 58.29, 61.17, 66.30, 128.50, 129.42, 131.12, 133.17, 135.41, 143.05, 167.32. Mass spectra *m/z*: 254 (M^+). HRMS: Calcd for $C_{13}H_{15}ClO_3$: 254.0710. Found: 254.0701.

3.3.6. (2*E*)-2-Methoxymethyl-3-(4-chlorophenyl)prop-2-enenitrile (5f). Colourless oil; yield: 52%; IR(neat) ν_{max}: 2210, 1634 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 3.44 (s, 3H), 4.15 (s, 2H), 7.10 (s, 1H), 7.50 (d, 2H J=8.4 Hz), 7.80 (d, 2H J=8.4 Hz); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 58.31, 73.16, 108.52, 117.15, 128.98, 130.00, 131.22, 136.36, 142.96. Mass spectra *m/z*: 208 (M^+).

HRMS: Calcd for $C_{11}H_{10}ClNO$: 207.0451. Found: 207.0444.

3.3.7. Ethyl (2*E*)-2-methoxymethyl-3-(4-methylphenyl)-prop-2-enoate (5h). Colourless oil; yield: 70%; IR(neat) ν_{max}: 1720, 1638 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 1.35 (t, 3H J=7.1 Hz), 2.39 (s, 3H), 3.43 (s, 3H), 4.21 (s, 2H), 4.32 (q, 2H J=7.1 Hz), 7.20 (d, 5H J=8.0 Hz), 7.30 (d, 2H J=8.0 Hz), 7.9 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 14.36, 21.22, 58.27, 60.95, 66.56, 125.74, 129.37, 129.52, 131.34, 139.87, 144.37, 167.45. Mass spectra *m*/*z*: 234 (M^+). Elemental analysis: Calcd for $C_{14}H_{18}O_3$: C, 71.77%, H, 7.74%. Found: C, 71.72%, H, 7.70%.

3.3.8. (2*E*)-2-Methoxymethyl-3-(4-methylphenyl)prop-2-enenitrile (5i). Colourless oil; yield: 64%; IR(neat) ν_{max}: 2212, 1624 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 3.43 (s, 3H), 4.16 (s, 2H), 7.10 (s, 1H), 7.24 (d, 2H J=8.2 Hz), 7.69 (d, 2H J=8.2 Hz); ^{13}C NMR($CDCl_3$/TMS, 75.3 MHz): δ 58.24, 73.45, 104.04, 117.41, 129.22, 129.64, 129.92, 141.76, 146.35, 170.20. Mass spectra *m*/*z*: 187 (M^+). Elemental analysis: Calcd for $C_{12}H_{13}NO$: C, 76.98%, H, 7.00%, N, 7.48%. Found: C, 76.90%, H, 6.92%, N, 7.41%.

3.3.9. Ethyl (2*E*)-2-methoxymethyl-3-(4-methoxyphenyl)prop-2-enoate (5l). Colourless oil; yield: 80%; IR(neat) ν_{max}: 1728, 1635 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 1.35 (t, 3H, J=7.1 Hz), 3.43 (s, 3H), 3.85 (s, 3H), 4.22 (s, 2H), 4.32 (q, 2H, J=7.1 Hz), 7.00 (d, 2H, J=8.8 Hz), 7.60 (d, 2H J=8.8 Hz), 7.90 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 14.36, 55.34, 58.28, 60.95, 66.55, 114.34, 118.34, 125.82, 131.93, 144.45, 160.50, 167.31. Mass spectra *m*/*z*: 250 (M^+). Elemental analysis: Calcd for $C_{14}H_{18}O_4$: C, 67.18%, H, 7.25%. Found: C, 67.10%, H, 7.20%.

3.3.10. (2*E*)-2-Methoxymethyl-3-(4-methoxyphenyl)-prop-2-enenitrile (5m). Colourless oil; yield: 77%; IR(neat) ν_{max}: 2214, 1622 cm^{-1}. ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 3.43 (s, 3H), 3.85, 4.15 (s, 2H), 6.95 (d, 2H J=8.8 Hz), 7.06 (s, 1H), 7.75 (d, 2H, J=8.8 Hz); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 55.34, 58.23, 73.86, 104.95, 114.34, 118.14, 125.82, 130.93, 144.48, 161.51. Mass spectra *m*/*z*: 203 (M^+). Elemental analysis: Calcd for $C_{12}H_{13}NO_2$: C, 70.92%, H, 6.45%, N, 6.89. Found: C, 70.90%, H, 6.40%, N, 6.80%.

3.3.11. Ethyl (2*E*)-2-Methoxymethyl-3-naphth-2-yl prop-2-enoate (5n). Colourless oil; yield: 69%; IR(neat) ν_{max}: 1726, 1630 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 1.35 (t, 3H J=7.1 Hz), 3.43 (s, 3H), 3.85 (s, 3H), 4.32 (q, 2H J=7.1 Hz), 7.41–7.56 (m, 4H), 7.81–7.84 (m, 3H), 8.2 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 14.36, 58.20, 60.72, 73.45, 124.14, 124.92, 126.06, 126.38, 126.96, 128.29, 128.96, 129.31, 131.01, 131.23, 133.05, 143.12, 166.16. Mass spectra *m*/*z*: 270 (M^+). Elemental analysis: Calcd for $C_{17}H_{18}O_3$: C, 75.53%, H, 6.71%. Found: C, 75.50%, H, 6.68%.

3.3.12. (2*E*)-2-Methoxymethyl-3-naphth-2-yl prop-2-enenitrile (5o). Colourless oil; yield: 63%; IR(neat) ν_{max}: 2212, 1620 cm^{-1}; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 3.43 (s, 3H), 4.16 (s, 2H), 7.52–7.6 (m, 4H), 7. 81–7.92 (m, 4H); ^{13}C NMR ($CDCl_3$/TMS, 75.3 MHz): δ 58.24, 73.43, 105.85, 117.80, 124.52, 125.01, 126.43, 126.93, 128.50, 129.05, 129.85, 131.31, 131.62, 133.21, 146.15. Mass spectra *m*/*z*: 223 (M^+). Elemental analysis: Calcd for $C_{15}H_{13}NO$: C, 80.69%, H, 5.87%, N, 6.27%. Found: C, 80.65%, H, 6.21%, N, 5.82%

3.4. Typical experimental procedure for the reaction of Baylis–Hillman adducts with various alcohol

A slurry made of the adduct **1q** (150 mg, 0.78 mmol), propargyl alcohol (109 mg, 2.5 equiv, 1.95 mmol) and montmorillonite K10 clay (60% w/w) was taken in a 50 mL RB flask and was tightly closed and kept in an oil bath (85 °C) for 24 h. Then the flask was cooled to room temperature and 20 mL of CH_2Cl_2 was added and filtered through a celite pad. The clay was repeatedly washed with (3×10 mL) CH_2Cl_2 and the combined solvent was removed under vacuum. The crude mixture was purified through a column of silica gel using 98:2 mixture of hexane/ethyl acetate afforded 95% isomerised compound **9q** with 99.9% *E*-selectivity.

3.4.1. Methyl (2*E*)-2-[(allyloxy)methyl]-3-phenylacrylate (10q). Colourless oil; yield: 95%; IR(neat) ν_{max}: 1605, 1615, 1710 cm^{-1}; ^1H NMR: δ 3.83 (s, 3H), 4.09 (d, 2H, J=5.67 Hz), 4.27 (s, 2H), 5.16 (d, 1H, J=10.41 Hz), 5.28 (ABq, 1H, H=1.55 and 17.19 Hz), 5.97 (m, 1H), 7.38 (m, 3H), 7.53 (m, 2H), 7.89 (s, 1H); ^{13}CNMR: δ 51.94, 64.07, 71.60, 117.11, 128.36, 128.77, 129.18, 129.76, 134.67, 134.71, 144.44, 167.72. Mass spectra *m*/*z*: 232 (M^+). Elemental analysis: Calcd for $C_{14}H_{16}O_3$: C, 72.39%, H, 6.94%. Found: C, 72.35%, H, 6.98%.

3.4.2. Ethyl (2*E*)-2-[(allyloxy)methyl]-3-phenylacrylate (10a). Colourless oil; yield: 94%; IR(neat) ν_{max}: 1604, 1617, 1712 cm^{-1}; ^1H NMR: δ 1.36 (t, 3H, J=7.11 Hz), 4.15 (d, 2H, J=5.67), 4.27 (s, 2H), 4.30 (q, 2H, J=7.11 Hz), 5.2 (dd, 2H, J=17.19 and 10.23 Hz), 5.98 (m, 1H), 7.33 (m, 3H), 7.52 (m, 2H), 7.89 (s, 1H); ^{13}C NMR: δ 14.29, 61.09, 64.07, 71.60, 117.11, 128.36, 128.77, 129.18, 129.76, 134.67, 134.71, 144.4, 167.72. Mass spectra *m*/*z*: 246 (M^+). Elemental analysis: Calcd for $C_{15}H_{18}O_3$: C, 73.15%, H, 7.37%. Found: C, 73.10%, H, 7.32%.

3.4.3. Methyl (2*E*)-2-(isopropoxymethyl)-3-phenylacrylate (11q). Colourless oil; yield: 95%; IR(neat) ν_{max}: 1600, 1620, 1716 cm^{-1}; ^1H NMR: δ 1.24 (d, 6H, J=6.12 Hz), 3.72 (sextet, 1H, J=6.12 Hz), 3.83 (s, 3H), 4.27 (s, 2H), 7.38 (m, 3H), 7.58 (m, 2H), 7.9 (s, 1H); ^{13}C NMR: δ 21.04, 21.51, 51.08, 61.42, 70.81, 127.41, 128.13, 128.25, 128.86, 133.87, 143.28, 167.23. Mass spectra *m*/*z*: 234 (M^+). Elemental analysis: Calcd for $C_{14}H_{18}O_3$: C, 71.77%, H, 7.74%. Found: C, 71.85%, H, 7.70%.

3.4.4. (2*E*)-2-[(Octyloxy)methyl]-3-phenylacrylonitrile (12b). Colourless oil; yield: 98%; IR(neat) ν_{max}: 1600, 1622, 2214 cm^{-1}; ^1H NMR: δ 0.98 (t, 3H, J=6.9 Hz), 1.3 (m, 10H), 1.7 (m, 2H), 3.62 (t, 2H, J=6.52 Hz), 4.3 (s, 2H), 7.24 (s, 1H), 7.47 (m, 3H), 7.85 (m, 2H); ^{13}C NMR: δ 14.09, 22.62, 26.10, 29.21, 29.36, 29.58, 31.78, 71.03, 71.73,

106.03, 126.89, 128.65, 128.78, 128.91, 130.38, 143.83. Mass spectra *m/z*: 271 (M^+). Elemental analysis: Calcd for $C_{18}H_{25}NO$: C, 79.60%, H, 9.28%, N, 5.16%. Found: C, 79.63%, H, 9.23% N, 5.13%.

3.4.5. Methyl (2*E*)-2-[(octyloxy)methyl]-3-phenylacrylate (12q). Colourless oil; yield: 97%; IR(neat) ν_{max}: 1601, 1622, 2214 cm^{-1}; ^1H NMR: δ 0.88 (t, 3H, $J=6.93$ Hz), 1.25 (m, 10H), 1.63 (m, 2H), 3.54 (t, 2H, $J=6.54$ Hz), 3.83 (s, 3H), 4.26 (s, 2H), 7.39 (m, 3H), 7.53 (m, 2H), 7.9 (s, 1H); ^{13}C NMR: δ 14.14, 26.33, 27.71, 29.17, 29.35, 29.47, 29.77, 51.90, 64.81, 70.91, 128.29, 128.52, 129.36, 129.96, 134.88, 144.58, 167.42. Mass spectra *m/z*: 304 (M^+). Elemental analysis: Calcd for $C_{19}H_{28}O_3$: C, 74.96%, H, 9.27%. Found: C, 74.89%, H, 9.32%.

3.4.6. Ethyl (2*E*)-3-phenyl-2-[(prop-2-ynyloxy)methyl] acrylate (9a). Colourless oil; yield: 92%; IR(neat) ν_{max}: 1600, 1622, 1720, 2150, 3300 cm^{-1}; ^1H NMR: δ 1.36 (t, 3H, $J=7.11$ Hz), 2.4 (t, 1H, $J=2.34$ Hz), 4.26 (d, 2H, $J=2.34$ Hz), 4.30 (q, 2H, $J=7.11$ Hz), 4.37 (s, 2H), 7.38 (m, 3H), 7.55 (m., 2H), 7.89 (s, 1H); ^{13}C NMR: δ 14.29, 58.05, 61.09, 64.21, 74.64, 79.69, 128.30, 128.50, 129.44, 129.95, 134.58, 144.90, 167.45. Mass spectra *m/z*: 244 (M^+). Elemental analysis: Calcd for $C_{15}H_{16}O_3$: C, 73.75%, H, 6.60%. Found: C, 73.80%, H, 6.63%.

3.4.7. (2*E*)-3-Phenyl-2-[(prop-2-ynyloxy)methyl]acrylonitrile (9b). Colourless oil; yield: 90%; IR(neat) ν_{max}: 1600, 1620, 2200, 3300 cm^{-1}; ^1H NMR: δ 2.48 (s, 1H), 4.25 (s, 2H), 4.32 (s, 2H), 7.18 (s, 1H), 7.41 (m, 3H), 4.77 (m, 2H); ^{13}C NMR: δ 57.47, 70.35, 75.67, 79.10, 108.17, 117.01, 128.93, 129.10, 130.53, 132.95, 144.45. Mass spectra *m/z*: 197 (M^+). Elemental analysis: Calcd for $C_{13}H_{11}NO$: C, 79.16%, H, 5.62, N, 7.10%. Found: C, 79.15%, H, 5.60% N, 7.13%.

3.4.8. Ethyl (2*E*)-3-(4-chlorophenyl)-2-[(prop-2-ynyloxy)methyl]acrylate (9e). Colourless oil; yield: 91%; IR(neat) ν_{max}: 1600, 1622, 1712, 2150, 3305 cm^{-1}; ^1H NMR: δ 1.36 (t, 3H, $J=7.11$ Hz), 2.4 (t, 1H, $J=2.34$ Hz), 4.25–4.32 (m, 4H), 4.35 (s, 2H), 7.35 (d, 2H, $J=8.4$ Hz), 7.5 (d, 2H, $J=8.4$ Hz), 7.83 (s, 1H); ^{13}C NMR: δ 14.29, 58.10, 61.12, 64.25, 74.61, 79.64, 128.77, 128.40, 130.98, 13.20, 135.45, 143.12, 167.42. Mass spectra *m/z*: 278 (M^+). HRMS: Calcd for $C_{15}H_{15}ClO_3$: 278.0710. Found: 278.0701.

3.4.9. (2*E*)-3-(4-Chlorophenyl)-2-[(prop-2-ynyloxy)-methyl]acrylonitrile (9f). Colourless oil; yield: 89%; IR(neat) ν_{max}: 1605, 2140, 3302 cm^{-1}; ^1H NMR: δ 2.47 (t, 1H, $J=2.34$ Hz), 4.28 (s, 2H), 4.30 (s, 2H), 7.19 (s, 1H), 7.38 (d, 2H, $J=8.4$ Hz), 7.5 (d, 2H, $J=8.4$ Hz); ^{13}C NMR: δ 57.45, 70.32, 75.66, 79.10, 108.52, 117.12, 128.98, 130.02, 131.23, 136.36, 143.06. Mass spectra *m/z*: 231 (M^+). HRMS: Calcd for $C_{13}H_{10}ClO_3$: 231.0451. Found: 231.0450.

3.4.10. (2*E*)-3-(4-Methylphenyl)-2-[(prop-2-ynyloxy)-methyl]acrylonitrile (9i). Colourless oil; yield: 86%; IR(neat) ν_{max}: 1600, 2145, 3300 cm^{-1}; ^1H NMR: δ 2.34 (s, 3H), 2.42 (t, 1H, $J=2.3$ Hz), 4.25 (s, 2H), 4.32 (s, 2H), 7.18 (s, 1H), 7.12 (d, 2H, $J=7.8$ Hz), 7.22 (d, 2H, $J=7.8$ Hz); ^{13}C NMR: δ 42.10, 57.45, 70.40, 75.62, 79.13, 108.18, 117.04, 127.58, 129.00, 135.12, 138.00, 144.39. Mass spectra *m/z*: 211 (M^+). Elemental analysis: $C_{14}H_{13}NO$, Calcd C, 79.59%, H, 6.20%, N, 6.63%. Found: C, 79.55%, H, 6.21%, N, 6.60%.

3.4.11. (2*E*)-3-(4-Methoxyphenyl)-2-[(prop-2-ynyloxy)-methyl]acrylonitrile (9m). Colourless oil; yield: 72%; IR(neat) ν_{max}: 1600, 2100, 3300 cm^{-1}; ^1H NMR: δ 2.48 (s, 1H), 3.83 (s, 3H), 4.25 (s, 2H), 4.32 (s, 2H), 7.00 (d, 2H, $J=8.8$ Hz), 7.09 (s, 1H), 7.74 (d, 2H, $J=8.8$ Hz); ^{13}C NMR: δ 55.34, 57.45, 70.35, 75.66, 79.15, 105.01, 114.34, 118.12, 125.82, 130.94, 144.50, 161.52. Mass spectra *m/z*: 227 (M^+). Elemental analysis: $C_{14}H_{13}NO_2$: Calcd C, 73.99%, H, 5.77%, N, 6.16%. Found: C, 73.95%, H, 5.79%, N, 6.10%;.

3.4.12. Methyl (2*E*)-3-phenyl-2-[(prop-2-ynyloxy)-methyl]acrylate (9q). Colourless oil; yield: 95%; IR(neat) ν_{max}: 1600, 1715, 2100, 3300 cm^{-1}; ^1H NMR: δ 2.42 (t, 1H, $J=2.34$ Hz), 3.84 (s, 3H), 4.26 (d, 2H, $J=2.34$ Hz), 4.39 (s, 2H), 7.32 (m, 3H), 7.53 (m, 2H), 7.92 (s, 1H); ^{13}C NMR: δ 52.26, 58.08, 64.25, 74.70, 79.63, 128.51, 18.54, 129.55, 129.99, 134.51, 145.27, 167.98. Mass spectra *m/z*: 230 (M^+). Elemental analysis: $C_{14}H_{14}O_3$: Calcd C, 73.03%, H, 6.13%. Found: C, 73.00%, H, 6.12%.

3.4.13. Methyl (2*E*)-3-(4-chlorophenyl)-2-[(prop-2-ynyloxy)methyl]acrylate (9r). Colourless oil; yield: 90%; IR(neat) ν_{max}: 1600, 1710, 2100, 3300 cm^{-1}; ^1H NMR: δ 2.42 (t, 1H, $J=2.3$ Hz), 3.85 (s, 3H), 4.28 (d, 2H, $J=2.34$ Hz), 4.4 (s, 2H), 7.35 (d, 2H, $J=8.4$ Hz), 7.5 (d, 2H, $J=8.4$ Hz), 7.84 (s, 1H); ^{13}C NMR: δ 52.08, 58.10, 64.20, 74.68, 79.64, 128.75, 129.42, 131.12, 133.17, 135.41, 143.03, 167.96. Mass spectra *m/z*: 264 (M^+). HRMS: Calcd for $C_{14}H_{13}ClO_3$: 264.0553. Found: 264.0550.

3.4.14. Methyl (2*E*)-3-(4-methylphenyl)-2-[(prop-2-ynyloxy)methyl]acrylate (9s). Colourless oil; yield: 85%; IR(neat) ν_{max}: 1600, 1710, 2100, 3300 cm^{-1}; ^1H NMR: δ 2.32 (s, 3H), 2.42 (t, 1H, $J=2.3$ Hz), 3.83 (s, 3H), 4.25 (d, 2H, $J=2.3$ Hz), 4.39 (s, 2H), 7.14 (d, 2H, $J=7.8$ Hz), 7.26 (d, 2H, $J=7.8$ Hz), 7.9 (s, 1H); ^{13}C NMR: δ 42.08, 52.24, 58.10, 64.26, 74.68, 79.60, 127.80, 129.04, 134.54, 135.20, 138.10, 145.22, 167.89. Mass spectra *m/z*: 244 (M^+). Elemental analysis: $C_{15}H_{16}O_3$: Calcd C, 73.75%, H, 6.60%. Found: C, 73.70%, H, 6.57%.

3.4.15. Methyl (2*E*)-3-(4-methoxyphenyl)-2-[(prop-2-ynyloxy)methyl]acrylate (9t). Colourless oil; yield: 80%; IR(neat) ν_{max}: 1600, 1705, 2100, 3300 cm^{-1}; ^1H NMR: δ 2.41 (t, 1H, $J=2.3$ Hz), 3.78 (s, 3H), 3.83 (s, 3H), 4.24 (d, 2H, $J=2.3$ Hz), 4.38 (s, 2H), 6.94 (d, 2H, $J=8.78$ Hz), 7.75 (d, 2H, $J=8.78$ Hz), 7.86 (s, 1H); ^{13}C NMR: δ 52.30, 55.43, 58.06, 64.20, 74.68, 79.62, 114.34, 125.82, 130.93, 134.40, 145.20, 161.51, 166.24. Mass spectra *m/z*: 260 (M^+). Elemental analysis: $C_{15}H_{16}O_4$: Calcd C, 69.22%, H, 6.20%. Found: C, 69.20%, H, 6.15%.

3.5. Typical experimental procedure for radical cyclization and protiodestannylation

A mixture of alkenyl propargyl ether **6a** (200 mg, 0.86 mmol), 1.5 equiv of freshly prepared tri-*n*-butyltin

hydride(1.3 mmol, 379 mg) and 5 mg of AIBN were taken in a 25 mL RB-Flask under inert atmosphere. The above mixture was stirred well and immersed into a preheated oil bath at 85 °C. The reaction was continued to stir until complete disappearance of starting material (TLC) and formation of the cyclized product. The crude cyclized stannylated product thus obtained was dissolved in diethyl ether (10 mL) and Con. HCl was added (5 drops) and the mixture was stirred for 2 h at RT. After the disappearance of stannylated compound (TLC), it was diluted with ether (50 mL) and washed with brine (15 mL×2). The organic layer was separated and dried (Na_2SO_4) and concentrated. The crude was purified by a silica gel column chromatography using gradient elution with hexane and hexane and EtOAc solvent system afforded pure cyclized product **15a** in 97% yield.

Iododestannylation. The stannylated product was taken in CH_2Cl_2 (15 mL) and iodine in CH_2Cl_2 was added until purple colour persists at 0 °C. The reaction was allowed to stir for 1 h. Saturated sodium disulphide ($Na_2S_2O_5$) was added drop wise till the purple colour disappears. The mixture was diluted with CH_2Cl_2 (15 mL) and washed with brine solution, separated and dried over anhyd.Na_2SO_4. The solvent was removed under vacuum. The crude compound was purified through a column of silica gel using hexane–ethyl acetate as eluent affording the iodinated compound **16** as a solid in 99% yield.

3.5.1. Ethyl 3-benzyl-4-methylenetetrahydrofuran-3-carboxylate (15a). Yield: 95%; IR(neat) ν_{max}: 1600, 1650, 1720 cm^{-1}; ^1H NMR: δ 1.21 (t, 3H, J=7.13 Hz), 2.88 (d, 1H, J=13.7 Hz), 3.32 (d, 1H, J=3.71 Hz), 3.86 (d, 1H, J=9.27 Hz), 4.13 (m, 3H), 4.36 (d, 2H, J=2 Hz), 5.1 (s, 1H), 5.32 (t, 1H, J=2.3 Hz), 7.12–7.27 (m, 5H); ^{13}C NMR: δ 14.32, 42.30, 57.75, 58.00, 71.89, 73.55, 106.68, 126,.69, 128.22, 128.35, 129.53, 129.69, 136.85, 149.90, 172.34. Mass spectra *m/z*: 246 (M^+). HRMS: Calcd for $C_{15}H_{18}O_3$: 246.1256. Found: 246.1252.

3.5.2. 3-Benzyl-4-methylenetetrahydrofuran-3-carbonitrile (15b). Yield: 92%; IR(neat) ν_{max}: 1595, 1647, 2200 cm^{-1}; ^1H NMR: δ 2.97 (s, 2H), 3.86 (d, 1H, J=8.9 Hz), 4.02 (d, 1H, J=8.9 Hz), 4.42 and 4.50 (dABq, 2H, J=13.5, 2.2 Hz), 5.2 (s, 2H), 7.28–7.36 (m, 5H); ^{13}C NMR: δ 42.34, 47.51, 70.85, 75.0, 108.91, 120.00, 127.74, 128.57, 128.64, 130.20, 134.87, 147.47. Mass spectra *m/z*: 199 (M^+). HRMS: Calcd for $C_{13}H_{13}NO$: 199.0997. Found: 199.0993.

3.5.3. Ethyl 3-(4-chlorobenzyl)-4-methylenetetrahydrofuran-3-carboxylate (15e). Yield: 96%; IR(neat) ν_{max}: 1600, 1650, 1719 cm^{-1}; ^1H NMR: δ 1.23 (t, 3H, J=7.13 Hz), 2.85 (d, 1H, J=13.75 Hz), 3.25 (d, 1H, 13.75 Hz), 3.84 (d, 1H, J=9.3 Hz), 4.13 (m, 3H), 4.36 (s, 2H), 5.09 (s, 1H), 5.27 (t, 1H, J=2.2 Hz), 7.08 (d, 2H, J=8.32 Hz), 7.20 (d, 2H, J=8.34 Hz); ^{13}C NMR: δ 14.30, 42.25, 58.05, 57.80, 72.01, 73.65, 107.53, 127.32, 129.61, 132.41, 135.90, 142.83, 170.82. Mass spectra *m/z*: 280 (M^+). HRMS: Calcd for $C_{15}H_{17}ClO_3$: 280.0866. Found: 280.0864.

3.5.4. 3-(4-Chlorobenzyl)-4-methylenetetrahydrofuran-3-carbonitrile (15f). Yield: 96%; IR(neat) ν_{max}: 1600, 1650, 2200 cm^{-1}; ^1H NMR: δ 2.95 (s, 2H), 3.84 (d, 1H, J=8.9 Hz), 4.02 (d, 1H, J=8.9 Hz), 4.40 and 4.48 (d ABq, 2H, J=13.5 and 2.2 Hz), 5.32 (s, 2H), 7.08 (d, 2H, J=8.32 Hz), 7.18 (d, 2H, J=8.32 Hz); ^{13}C NMR: δ 43.01, 48.00, 71.00, 75.61, 69.00, 121.01, 127.50, 129.00, 131.32, 134.74, 142.21. Mass spectra *m/z*: 233 (M^+). HRMS: Calcd for $C_{13}H_{12}NO$: 233.0607. Found: 233.0600.

3.5.5. 3-(4-Methylbenzyl)-4-methylenetetrahydrofuran-3-carbonitrile (15i). Yield: 94%; IR(neat) ν_{max}: 1600, 1652, 2205 cm^{-1}; ^1H NMR: δ 2.34 (s, 3H), 2.95 (s, 2H), 3.89 (d, 1H, J=8.9 Hz), 4.05 (d, 1H, J=8.9 Hz), 4.40 and 4.50 (dABq, 2H, J=13.5 and 2.2 Hz), 5.4 (s, 2H), 7.12 (d, 2H, J=7.8 Hz), 7.26 (d, 2H, J=7.8 Hz); ^{13}C NMR: δ 20.89, 42.06, 47.49, 70.86, 75.21, 108.88, 120.12, 127.75, 128.55, 134.18, 137.83, 147.56. Mass spectra *m/z*: 213 (M^+). HRMS: Calcd for $C_{14}H_{15}NO$: 213.1154. Found: 213.1150.

3.5.6. 3-(4-Methoxybenzyl)-4-methylenetetrahydrofuran-3-carbonitrile (15m). Yield: 94%; IR(neat) ν_{max}: 1600, 1650, 2200 cm^{-1}; ^1H NMR: δ 3.12, 3.78 (s, 3H), 3.9 (d, 1H, J=8.9 Hz), 4.08 (d, 1H, J=8.9 Hz), 4.4 and 4.5 (dABq, 2H, J=13.5, 2.2 Hz), 5.2 (s, 2H), 7.04 (d, 2H, J=8.6 Hz), 7.25 (d, 2H, J=8.6 Hz); ^{13}C NMR: δ 42.81, 55.42, 47.22, 70.90, 75.00, 108.88, 120.04, 114.51, 126.10, 130.85, 148.85, 158.72. Mass spectra *m/z*:229 (M^+). HRMS: Calcd for $C_{14}H_{15}NO_2$: 229.1103. Found: 229.1100.

3.5.7. Methyl 3-benzyl-4-methylenetetrahydrofuran-3-carboxylate (15q). Yield: 95%; IR(neat) ν_{max}: 1600, 1650, 1718 cm^{-1}; ^1H NMR: δ 2.88 (d, 1H, J=13.71 Hz), 3.35 (d, 1H, J=13.7 Hz), 3.7 (s, 3H), 3.88 (d, 1H, J=9.3 Hz), 4.20 (d, 1H, J=9.3 Hz), 4.39 (t, 2H, J=2.2 Hz), 5.13 (s, 1H), 5.34 (t, 1H, J=2.4 Hz, 7.13–7.21 (m, 2H), 7.24–7.39 (m, 3H); ^{13}C NMR: δ 42.38, 52.16, 57.77, 71.55, 73.73, 106.68, 126.76, 128.24, 128.33, 129.53, 129.75, 137.01, 149.84, 172.64. Mass spectra *m/z*: 232 (M^+). HRMS: Calcd for $C_{14}H_{16}O_2$: 232.1099. Found: 232.1097.

3.5.8. Methyl 3-(4-chlorobenzyl)-4-methylenetetrahydrofuran-3-carboxylate (15r). Yield: 97%; IR(neat) ν_{max}: 1600, 1650, 1720 cm^{-1}; ^1H NMR: δ 2.82 (d, 1H, J=13.75 Hz), 3.23 (d, 1H, 13.75 Hz), 3.68 (s, 3H), 3.80 (d, 1H, J=9.3 Hz), 4.1 (d, 1H, J=9.3 Hz), 4.39 (s, 2H), 5.11 (s, 1H), 5.24 (t, 1H, J=2.2 Hz), 7.10 (d, 2H, J=8.3 Hz), 7.2 (d, 2H, J=8.3 Hz); ^{13}C NMR: δ 42.35, 52.25, 57.80, 71.50, 73.70, 107.00, 127.60, 129.40, 132.40, 135.05, 142.10, 170.51. Mass spectra *m/z*: 266 (M^+). HRMS: Calcd for $C_{14}H_{15}ClO_3$: 266.0710. Found: 266.0708.

3.5.9. Methyl 3-(4-methylbenzyl)-4-methylenetetrahydrofuran-3-carboxylate (15s). Yield: 92%; IR(neat) ν_{max}: 1600, 1650, 1720 cm^{-1}; ^1H NMR: δ 2.32 (s, 3H), 2.85 (d, 1H, J=13.71 Hz), 3.32 (d, 1H, J=13.71 Hz), 3.7 (s, 3H), 3.85 (d, 1H, J=9.3 Hz), 4.22 (d, 1H, J=9.3 Hz), 4.36 (t, 2H, J=2.2 Hz), 5.1 (s, 1H), 5.34 (t, 1H, J=2.4 Hz), 7.15 (d, 2H, J=7.8 Hz), 7.28 (d, 2H, J=7.8 Hz); ^{13}C NMR: δ 20.98, 42.35, 52.15, 57.80, 71.50, 74.00, 107.01, 127.78, 129.00, 135.21, 138.02, 148.96, 172.32. Mass spectra *m/z*: 246 (M^+). HRMS: Calcd for $C_{15}H_{18}O_3$: 246.1256. Found: 246.1253.

3.5.10. Methyl 3-(4-methoxybenzyl)-4-methylene

tetrahydrofuran-3-carboxylate (15t). Yield: 90%; IR(neat) ν_{max}: 1600, 1650, 1720 cm^{-1}; ^1H NMR: δ 2.85 (d, 1H, $J=13.71$ Hz), 3.4 (d, 1H, $J=13.71$ Hz), 3.69 (s, 3H), 3.80 (s, 3H), 3.9 (d, 1H, $J=9.3$ Hz), 4.22 (d, 1H, $J=9.3$ Hz), 4.35 (t, 2H, $J=2.2$ Hz), 5.18 (s, 1H), 5.39 (t, 1H, $J=2.2$ Hz), 7.0 (d, 2H, $J=8.6$ Hz), 7.28 (d, 2H, $J=8.6$ Hz); ^{13}C NMR: δ 44.25, 52.18, 55.41, 58.20, 71.43, 73.65, 106.77, 114.32, 125.82, 130.95, 150.00, 160.59, 172.52. Mass spectra *m/z*: 262 (M^+). HRMS: Calcd for $C_{15}H_{18}O_4$: 254.0710. Found: 254.0701.

3.5.11. Iodo compound 16. Yield: 99%; IR(neat) ν_{max}: 1600, 1620, 1720 cm^{-1}; ^1H NMR (300.1 MHz): δ 2.96 (d, 1H, $J=13.6$ Hz, benzylic), 3.25 (d, 1H, $J=13.6$ Hz, benzylic), 3.69 (s, 3H, CO_2Me), 4.05 (d, 1H, $J=9.3$ Hz, C2), 4.25 (d, 1H, $J=9.3$ Hz, C2), 4.31 & 4.35 (dd, 2H, $J=10.5$, 2.6 Hz), 6.40 (t, H, $J=2.6$ Hz), 7.(m, 2H, Ar), 7.27 (m, 3H, Ar); ^{13}C NMR: δ 42.91, 52.10, 60.70, 71.76, 4.87, 78.61, 127.22, 127.88, 128.12, 128.64, 129.81, 136.34, 151.69, 171.15. HRMS: Calcd for $C_{14}H_{15}IO_3$: 358.0086. Found 358.0084.

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