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Lewis acid catalyzed acylation reactions: scope and limitations

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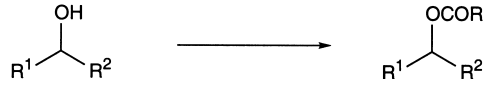
Abstract—Acylation of alcohols, thiols, and sugars were studied with a variety of Lewis acids, and it was found that Cu- and $Sn(OTf)_2$ are very efficient in catalyzing the reaction under mild conditions. Among these two catalysts, $Cu(OTf)_2$ was preferred because of its lower cost and relatively higher yield of the acylated product. The reaction was studied in several solvents, but CH_2Cl_2 was preferred. It was also observed that the present method is suitable for acylation of tertiary alcohols. Sugars were also acylated without any epimerization at the anomeric center. It is further shown here that this method is also suitable for selective acylation of primary or secondary alcohols over tertiary ones.

Acylation of alcohols is among the most frequently used processes in organic synthesis (Scheme 1).[1] Typically, it is performed with activated carboxylic acid derivatives such as acid anhydrides,[2a] acid chlorides,[2b] acyl imidazoles,[2c] or acyl ureas[2d] in the presence of amines such as Et_3N, pyridine, etc. 4-(dimethylamino)Pyridine (DMAP) and 4-pyrrolidinopyridine (PPY) are known to catalyze this reaction at enhanced rate.[3a,b] In 1993, Vedjes et al. reported tributylphosphine as a catalyst for the acylation of base sensitive alcohols by acetic or benzoic anhydride.[4] In addition to the above dual active (nucleophilic and basic) catalyst, protic acids such as *p*-toluene sulphonic acid[5] and Lewis acids such as $ZnCl_2$,[6a] $CoCl_2$,[6b] $TiCl_4/AgClO_4$,[6c] TMSCl,[6d] are also known to catalyze the acylation of alcohols with acid anhydrides, but these reagents preclude the presence of acid-sensitive groups. In 1996, Yamamoto and co-workers reported $Sc(OTf)_3$, a commercially available and moisture stable Lewis acid, as an extremely active catalyst for the acylation of alcohols with acid anhydrides.[7] In extension to the above work, the same group reported that $Sc(NTf_2)_3$ catalyst was superior to $Sc(OTf)_3$.[7c] Later, Barrett and Braddock used a variety of lanthanide triflates for acylation of alcohols, and found that $Sc(OTf)_3$ in AcOH was superior to other lanthanide catalysts. The advantage in this method was shown by recycling the catalyst and using AcOH as an inexpensive acylating agent.[8a] Recently Schreen et al. extended this method to selective acylation of 10-deacetylbaccatin using a catalytic amount of $La(OTf)_3$.[8b] Procopiou and co-workers successfully employed TMSOTf as an efficient catalyst for acylation of a variety of functionalized alcohols.[9] The drawback with this catalyst was intolerance of an acetonide group under the reaction condition. Recently, Greenwald and co-workers used a combination of $Sc(OTf)_3$ and DMAP as a dual catalyst for acylation of a variety of tertiary alcohols.[10] Vedjes and Daugulis reported $MgBr_2/Et_3N$ as a dual catalyst for benzoylation of hindered tertiary alcohols.[11] The reaction was also smooth with the hindered acylating reagents such as pivalic anhydrides. In contrast to $Sc(OTf)_3$ method, the present dual activation method facilitates the benzoylation over the pivalylation. Li and co-workers used montmorillonite K-10 and KSF as an efficient solid acid catalyst for acylation of alcohols, phenols, amines and thiols. In their method, primary and secondary alcohols were acylated smoothly, but tertiary alcohols failed to give considerable reaction.[12] More recently Ballini et al. reported the solvent free acylation reaction using HSZ-360 as a reusable solid acid catalyst.[13] In recent years, selective protection of diols has become important due to their synthetic utility. Breton used $NaHSO_4/SiO_2$ as a reagent for this purpose.[14] Similar kind of conversion has been reported by Otera et al. using Distannoxane as a catalyst.[15] Very recently, $KF–Al_2O_3$ has also been used as a catalyst for acylation reactions.[16] Some of the above catalysts have also been used in a chiral environment to impart asymmetric induction in non-enzymatic kinetic resolution of secondary alcohols.[17]



Scheme 1.

Recently, we communicated that a catalytic amount of $Cu(OTf)_2$ efficiently catalyzed the acylation reactions.[18] While extending the scope of this reaction for acylation of sensitive *tert*-alcohols such as linalool, we observed that the reaction was not reproducible even in our hands. The yield of acylated product varied from 2 to 60% and it depended upon conditions. This prompted us to disclose full details of

Keywords: acylation reactions; alcohols; thiols; phenols and sugars; copper triflate; tin triflate; acetic anhydride.

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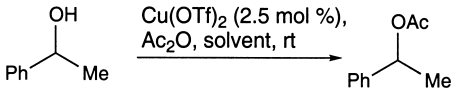
Table 1.



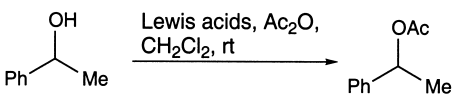
Entry	Solvent	Time	Yield (%)
1	CH_2Cl_2	1	92
2	Toluene	1.5	90
3	Ether	2	90
4	MeCN	20	90
5	$MeNO_2$	22	86
6	AcOH (no Ac_2O)	20	88[a]

[a] This reaction was carried out at 60°C.

the acylation reaction catalyzed by Lewis acids. At the outset, 1-phenyl ethanol was chosen as a model substrate for the acylation reaction. It was treated with 2 equiv. of acetic anhydride (Ac_2O) in the presence of 2.5 mol% of $Cu(OTf)_2$ in CH_2Cl_2 at room temperature (Method A). The reaction was complete in 1 h, and the acetylated product was isolated in more than 92% yield. Although the reaction was very clean (by tlc) in CH_2Cl_2, it was still studied in other solvents (Table 1). The reaction in non-polar solvents such as toluene and ether gave similar results, but it was very slow in polar solvents such as MeCN, and $MeNO_2$. When acetic acid, instead of Ac_2O, was used as acylating reagent and was taken in excess as a solvent, the reaction was almost negligible at room temperature. However, comparable results for acylation were obtained when the reaction was carried out with an excess of acetic acid at 60°C for a longer period of time (Method B).

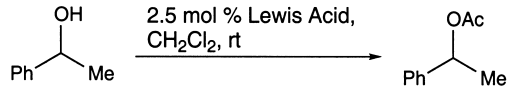
The acylation reaction was then studied in the presence other Lewis acids (Table 2). $Sn(OTf)_2$ and $BF_3{\cdot}OEt_2$ were equally effective in the acylation reaction. Other Lewis acids such as $ZnCl_2$, $SnCl_2$, $CuCl_2$, and $FeCl_3$ were not effective for the above reaction. Although $ZnCl_2$ was known[19] to catalyze acylation of alcohols, it was effective only when the reaction was performed at reflux temperature. It was observed that $ZnCl_2$ can give good yield of the acylated product when it was used in stoichiometric amount. Under identical experimental conditions, it was found that $Cu(OTf)_2$ is superior to basic reagents (pyridine or DMAP), which indicated that $Cu(OTf)_2$ was less prone to undergo deactivation by a carboxylic acid (AcOH), a by-product in the reaction. Surprisingly, $CuCl_2$ did not catalyze the reaction. The acylation reaction was also studied with other acid anhydrides such as propionic and benzoic anhydride (Table 3). Whereas propionic anhydride gave similar yield

Table 2.



Entry	Lewis acids (2.5 mol%)	Time (h)	Yield (%)
1	$Cu(OTf)_2$	1	92
2	$Sn(OTf)_2$	1	90
3	$BF_3{\cdot}OEt_2$	1	85
4	$ZnCl_2$	1	05
5	$SnCl_2{\cdot}2H_2O$	28	10
6	$CuCl_2$	8	Nil
7	$FeCl_3$	2	68

Table 3.

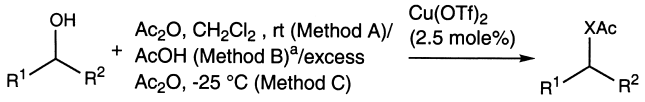


Entry	Lewis acid	Yields (%)		
		$(MeCO)_2O$	$(MeCH_2CO)_2O$	$(PhCO)_2O$
1	$Cu(OTf)_2$	92	90	Nil
2	$Sn(OTf)_2$	90	88	Nil
3	$BF_3{\cdot}OEt_2$	85	74	Nil

of acylated product using copper triflate, tin triflate, and boron trifluoride, benzoic anhydride failed to give any product even after several hours. Although it was clear from the above results that both the copper and tin triflates are efficient in catalyzing the acylation reaction, the former was preferred for further reactions because of its lower cost and higher stability.

In order to extend the scope of acylation reaction, it was carried out on a variety of substrates using 2.5 mol% of copper triflate in CH_2Cl_2 and results are described in Table 4. Most of the substrates could be acylated at rt with acetic anhydride in very short time (Method A). It was observed that the acylation reaction could also be carried out with acetic acid (Method B), but the reaction was very slow at rt. Although primary alcohols could be acylated in AcOH in the presence of 2.5 mol% of $Cu(OTf)_2$ at rt, secondary alcohols required higher temperature (60–65°C) for completion of the reaction. Phenols, thiols, and sugars could also be acylated at rt in high yields. In the case of methyl-α-D-glucopyranoside (entry 34) the methoxy group at the anomeric center remained intact and other hydroxyl groups were acetylated. This result was in a sharp contrast with that of some other Lewis acids, which acetylated the anomeric methoxy group as well.[20] It was noticed that in a few selected substrates only secondary alcohols could be acylated and hindered tertiary alcohols remained untouched (entries 25 and 26).[21] It was observed that sensitive alcohols such as allylic and tertiary alcohols could not be acylated in an efficient manner under Method A or B. Thus, by taking linalool (entry 22) as a model substrate for sensitive tertiary alcohols, we studied the reaction in detail. It was found that the reaction carried under Method A conditions gave mainly decomposed products. On doing the same reaction for 12 h at 0°C, instead of rt, gave more than 70% unreacted alcohol. When the reaction was set up at 0°C and it was allowed to warm to rt over 12 h, it gave mainly eliminated products. Other solvents such as toluene and ether gave similar results. Finally, the acylation of linalool (1 mmol) was tried without using solvent by taking 500 μL of Ac_2O in the presence of 1 mol% of $Cu(OTf)_2$ at −25°C. The reaction was virtually complete in 5 h at this temperature, and 83% yield of the acetylated product (ratio of linalool acetate and rearranged product=91.5:8.5) was obtained. It must be noted here that any deviation from the above reaction conditions failed to give a satisfactory yield in the acylation reaction of linalool. Then, a variety of sensitive tertiary and allylic alcohols were acylated in high yield (Table 4; entries 22–24) under the above conditions (Method C).

Table 4. $Cu(OTf)_2$ catalyzed acetylation reaction



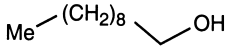
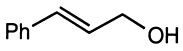
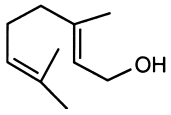
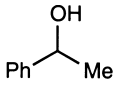
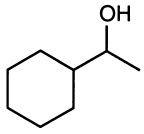
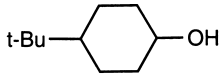
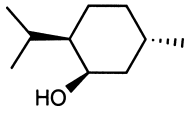
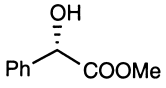
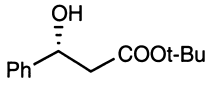
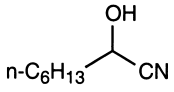
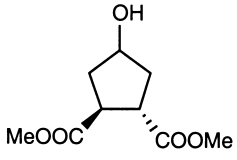
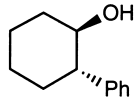
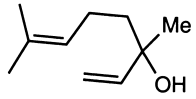
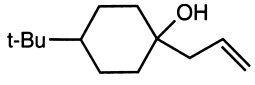
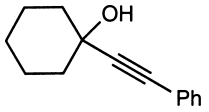
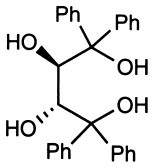
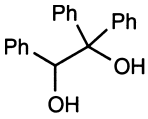
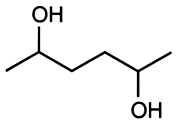
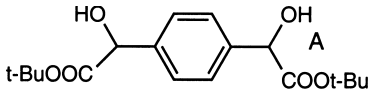
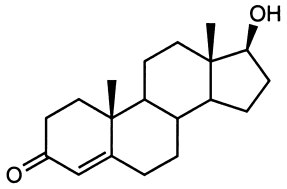
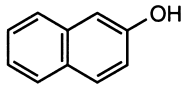
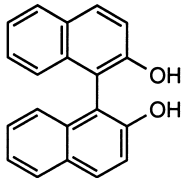
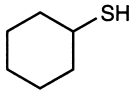
Entry	Substrates	Method	Time (h)	Yield (%)
1		A	1	99
2		B	6	96
3	$PhCH_2OH$	A	0.5	97
4	$PhCH_2OH$	B	8	94
5		C	7	90
6		C	7	90
7		A	1	92
8		B	14	94
9		A	1	96
10		B	10	89
11		A	1	98
12		B	10	96
13		A	0.5	98
14		B	12	96
15		A	1	97
16		B	12	96
17		A	3	92
18		A	1	99
19		A	2	90
20		A	1	99
21		B	10	97
22		C	5	83[b]
23		C	5	85

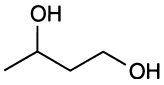
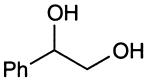
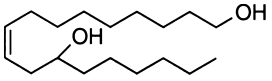
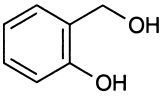
Table 4. (*continued*)

Entry	Substrates	Method	Time (h)	Yield (%)
24		C	1	70
25		A	8	86[c]
26		A	6	88[c]
27		A	2	99
28		A	2	88
29		A	3	92
30		A	2	96
31		A	2	87
32		A	5	84
33	D-(+)-Mannitol	A	6	91
34	Methyl-α-D-glucopyranoside	A	4	98

[a] For secondary alcohols, this method required 65°C. The reaction was done at rt unless stated otherwise.
[b] The ratio of the linalool acetate vs rearranged product is 91.5:8.5.
[c] Only secondary alcohols are acylated.

In order to increase the scope of the present method further, selective acylation of primary alcohols over secondary ones in unsymmetrical diols was studied. The acylation reaction was also compared with the literature method (pyridine and DMAP) and the results are summarized in Table 5. It is quite satisfying that the present method is selective in acylation of primary alcohols in the presence of secondary ones.

Table 5. Selective mono-acylation of unsymmetrical diols with acetic anhydride at rt in CH_2Cl_2

Entry	Diols	Reagents	Time (h)	Isolated yield (%)		Ratio
				1° acetate	Diacetate	
1		Pyridine, DMAP	12	49	40	55:45
2		$Cu(OTf)_2$ (cat.)	2	76	14	85:15
3		Pyridine, DMAP	12	64	31	67:33
4		$Cu(OTf)_2$ (cat.)	2	82	08	91:09
5		Pyridine, DMAP	12	31	58	35:65
6		$Cu(OTf)_2$ (cat.)	2	84	11	88:12
7		$Cu(OTf)_2$ (cat.)	2	40	48	46:54

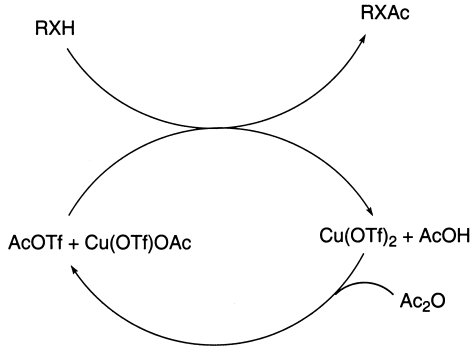


Figure 1. Proposed mechanism for acylation reactions.

In order to obtain mechanistic information on the acylation reaction, we carefully monitored the reaction by 400 MHz NMR spectroscopy. In a set of controlled experiments, $Cu(OTf)_2$ (2 mol%) in CD_2Cl_2 was mixed with acetic anhydride (1 mmol) at room temperature and the ^{13}C NMR spectrum was recorded. In addition to a signal at δ 166 ppm for the anhydride carbonyls, a smaller signal was seen at δ 177.7 ppm (AcOTf). Further, we treated this mixture with an alcohol (benzyl alcohol, 1 mmol) and monitored the reaction. It was found that a small peak at δ 11.89 was observed in the ^1H NMR spectrum, which indicated the formation of AcOH in the reaction. On the basis of these results, we propose that Ac_2O reacts with $Cu(OTf)_2$ to generate the acyl triflate which is attacked by RXH to give the acylated product and triflic acid. The triflate ion/triflic acid then reacts with Cu(OTf)OAc to generate $Cu(OTf)_2$ and acetic acid. The same catalytic cycle can also be used for Method B where acetic acid reacts with $Cu(OTf)_2$ to give Cu(OTf)OAc and AcOTf. The slow formation of these species, in this case, is perhaps responsible for the slower reaction when using Method B (Fig. 1).

In summary, we have shown that $Cu(OTf)_2$ is an efficient and versatile catalyst for acylation of alcohols, phenols, sugars, and thiols. On the basis of NMR studies we have proposed the catalytic cycle for the acylation reaction.

1. Experimental

^1H NMR spectra were recorded on Jeol and Brucker, as mentioned in the experimental, using TMS as internal standard. Chemical shifts are reported in ppm, and coupling constants are reported in Hz. IR spectra were recorded on Perkin–Elmer 580 and 1320 spectrometers.

Routine monitoring of reactions was performed using silica gel-G obtained from Acme. All the chromatographic separations were done by using silica gel (Acme's, 100–200 mesh). Petroleum ether used was of boiling range 60–80°C. Reactions, which needed anhydrous conditions, were run under an atmosphere of dry nitrogen or argon using flame-dried glasswares. The organic layer was washed with brine and stored over *anhydrous* Na_2SO_4 for 30 min before use. Evaporation of solvents was performed at reduced pressure, using a Büchi rotary evaporator.

Several compounds such as 1-decanyl acetate[13] (entries 1 and 2), benzyl acetate[7] (entries 3 and 4), cinnamyl acetate[6b] (entry 5), geranyl acetate[9] (entry 6), (−)-(1*R*)-menthyl acetate[7] (entries 13 and 14), linalyl acetate[7] (entry 22), 17β-acetyl testosterone (entry 29), and β-naphthyl acetate (entry 30) are commercially available. All the spectroscopic data of the above compounds matched with those of authentic samples. Similarly, the data for 2-phenyl ethylacetate (entries 7 and 8),[22] 2-cyclohexyl ethylacetate (entries 9 and 10),[23] and 2,5-diacyloxy hexane (entry 27)[23] matched well with the literature data.

1.1. Typical experimental procedure for the acetylation of alcohols

Method A. To a mixture of an alcohol (1 mmol) and $Cu(OTf)_2$ (10 mg, 2.5 mol%) in dry DCM (5 mL) was added acetic anhydride (190 μL, 2 mmol) at rt. After being stirred for 2h the solution was quenched with saturated bicarbonate solution, and the product was extracted with DCM (three times). The combined organic extracts were washed with water, and brine. The organic layer was dried over sodium sulfate and condensed in vacuo. The resulting crude product was purified by column

chromatography on silica gel using ethyl acetate–petroleum ether as eluent to give the pure product.

Method B. To a solution of $Cu(OTf)_2$ (10 mg, 2.5 mol%) in acetic acid (2 mL) was added an alcohol (1 mmol) at rt. The reaction mixture was stirred at 65°C, and monitored by tlc. After completion, the solution was poured on water, diluted with CH_2Cl_2 (15 mL), and stirred for few minutes. The resulting organic layer was separated and washed with water, brine, and dried over sodium sulfate. Solvent removal and purification over silica gel column using EtOAc–petroleum ether as eluent gave the pure product.

Method C. A mixture of Ac_2O (3 mmol) and $Cu(OTf)_2$ (3.6 mg, 1 mol%) was stirred at rt for 10 min. The flask was cooled to −25°C and an alcohol was added drop by drop. The reaction mixture was stirred at the same temperature till completion of the reaction (by tlc). The reaction mixture was quenched at the same temperature by the addition of aq. $NaHCO_3$. It was diluted with CH_2Cl_2 and organic layer was separated. It was washed with water, brined, and dried. The resulting crude product was purified by column chromatography on silica gel using ethyl acetate–petroleum ether as eluent to give the pure product.

1.1.1. 4-*tert*-Butyl cyclohexylacetate (entries 11 and 12). Yield 98% as a viscous liquid; R_f 0.90 (10% EtOAc in petroleum ether); IR (neat) 1720, 1250 cm^{-1}; ^1H NMR (CCl_4, 400 MHz) δ 0.85 (s, 9H), 0.95–1.34 (m, 5H), 1.81 (m, 2H), 1.99 (m, 2H), 2.02 (s, 3H), 4.62 (tt, J=11.2, 4.4 Hz, 1H). Anal. calcd for $C_{12}H_{22}O_2$: C, 72.73; H, 11.11. Found: C, 72.86; H, 11.20.

1.1.2. (−)-(1*R*)-Methyl acetate (entries 13 and 14). Yield 97% as a colorless liquid; R_f 0.90 (10% EtOAc in petroleum ether); $[\alpha]_D^{25}$=−117.7 (*c* 1.0, $CHCl_3$) {lit.[7b] $[\alpha]_D^{20}$=−80.5° (*c* 8.0, benzene)}.

1.1.3. (+) Methyl (*S*)-α-acetoxy phenylacetate (entries 15 and 16). Yield 97% as a colorless liquid; R_f 0.85 (20% EtOAc in petroleum ether); $[\alpha]_D^{25}$=+134.2 (*c* 2.4, $CHCl_3$); IR (neat) 2960, 1735, 1250, 830, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.18 (s, 3H), 3.69 (s, 3H), 5.95 (s, 1H), 7.33–7.46 (m, 5H). Anal. calcd for $C_{15}H_{20}O_4$: C, 68.18; H, 7.57. Found: C, 68.66; H, 7.42.

1.1.4. *tert*-Butyl (*S*)-3-acetoxy-3-phenyl propanoate (entry 17). Yield 92% as a colorless liquid; R_f 0.50 (10% EtOAc in petroleum ether); IR (neat) 1720, 1640, 1250, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.39 (s, 9H), 2.03 (s, 3H), 2.65–2.70 (dd, J=15, 6 Hz, 1H), 2.84–2.90 (dd, J=15, 8 Hz, 1H), 6.11–6.15 (dd, J=9, 5 Hz, 1H), 7.27–7.37 (m, 5H). Anal. calcd for $C_{15}H_{20}O_4$: C, 68.18; H, 7.57. Found: C, 68.26; H, 7.62.

1.1.5. 1-Cyano heptanyl-1-acetate (entry 18). Yield 99% as a viscous liquid; R_f 0.40 (5% EtOAc in petroleum ether); IR (neat) 2250, 1730, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.89 (t, J=6.5 Hz, 3H), 1.30 (m, 6H), 1.49 (m, 2H), 1.88 (m, 2H), 2.13 (s, 3H), 5.31 (t, J=7.5 Hz, 1H); MS (EI, *m/z*): 182 (M^+). Anal. calcd for $C_{10}H_{17}NO_2$: C, 65.57; H, 9.28; N, 7.65. Found: C, 65.38; H, 9.32; N, 7.74.

1.1.6. 3,4-Dicarbomethoxy cyclopentenyl-1-acetate (entry 19). Yield 90% as a viscous liquid; R_f 0.60 (25% EtOAc in petroleum ether); IR (neat) 1735, 1710, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.09 (s, 3H), 2.16–2.21 (m, 4H), 3.74 (s, 6H), 4.16 (m, 2H), 5.19 (m, 1H). Anal. calcd for $C_{11}H_{16}O_6$: C, 54.09; H, 6.56. Found: C, 54.56; H, 6.46.

1.1.7. 1-Acetoxy-2-phenyl cyclohexane (entries 20 and 21).[24] Yield 99% as a liquid; R_f 0.45 (5% EtOAc in petroleum ether); IR (neat) 3010, 2960, 1730, 1250, 830, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.25–2.12 (bm, 8H), 1.75 (s, 3H), 2.65 (ddd, J=12.2, 11.0, 3.9 Hz, 1H), 4.97 (ddd, J=10.5, 4.4 Hz, 1H), 7.24 (m, 5H, aromatics); MS (EI, *m/z*): 218 (M^+), 175, 158 (base peak).

1.1.8. Linalyl acetate (entry 22).[7] Yield 83% (based on recovered linalool) as a colorless liquid; R_f 0.60 (5% EtOAc in petroleum ether); IR (neat) 3010, 1720, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.54 (s, 3H), 1.59 (s, 3H), 1.64 (s, 3H), 1.76 (m, 2H), 1.86 (m, 2H), 2.00 (s, 3H), 4.58 (m, 0.085H, 8.5%, rearranged isomer), 5.13 (m, 3H), 5.96 (dd, J=11, 5.6 Hz, 0.915H, 91.5%).

1.1.9. 1-Allyl-4-*tert*-butyl-1-cyclohexyl acetate (entry 23). Yield 85% as a liquid; R_f 0.60 (5% EtOAc in petroleum ether); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.85 (s, 9H), 0.99 (m, 2H), 1.2 (m, 3H), 1.56 (m, 2H), 1.99 (s, 3H), 2.38 (m, 2H), 2.62 (d, J=7.6 Hz, 2H), 5.03 (d, J=3.4 Hz, 1H), 5.06 (s, 1H), 5.76 (m, 1H). Anal. calcd for $C_{15}H_{26}O_2$: C, 75.63; H, 10.92. Found: C, 75.46; H, 11.02.

1.1.10. 1-Phenyl ethynyl-1-cyclohexyl acetate (entry 24). Yield 70% as a liquid; R_f 0.60 (5% EtOAc in petroleum ether); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.28 (m, 1H), 1.67 (m, 7H), 2.02 (s, 3H), 2.47 (d, J=11 Hz, 2H), 7.3 (m, 5H), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.0, 25.2, 36.1, 82.3, 124.4, 126.8, 128.1, 145.5, 169.4. Anal. calcd for $C_{16}H_{18}O_2$: C, 79.34; H, 7.44. Found: C, 79.26; H, 7.52.

1.1.11. TADDOL diacetate (entry 25). Yield 86% as a white solid; mp 172–175°C, $[\alpha]_D^{25}$=−105.1 (*c* 1.0, $CHCl_3$); R_f 0.80 (20% EtOAc in petroleum ether); IR (KBr) 3020, 2950, 1735, 1710, 1210, 830, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.62 (s, 6H), 6.31 (s, 2H), 7.12–7.34 (m, 16H), 7.59 (d, J=8 Hz, 4H). Anal. calcd for $C_{32}H_{30}O_6$: C, 75.29; H, 5.88. Found: C, 75.46; H, 5.90.

1.1.12. 2-Hydroxy-1,2,2-triphenylethylacetate (entry 26). Yield 88%; white solid, mp 70–72°C; R_f 0.70 (20% EtOAc in petroleum ether); IR (KBr) 1730 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.97 (s, 3H), 7.06 (m, 1H), 7.12–7.4 (m, 15H). MS (EI, *m/z*): 308 (M^+). Anal. calcd for $C_{22}H_{20}O_3$: C, 79.51; H, 6.02. Found: C, 79.66; H, 6.12.

1.1.13. 1,4 Bis (*S*,*S*)-(*t*-butyl 1-propanoyl-1-acetoxy)-xylene (entry 28). Yield 88% as a white solid; mp 133–135°C; R_f 0.50 (20% EtOAc in petroleum ether); $[\alpha]_D^{25}$=+17.9 (*c* 1.0, $CHCl_3$); IR (KBr) 3010, 2980, 1735, 1710, 1670, 830, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.39 (s, 18H), 2.17 (s, 6H), 2.62–2.67 (dd, J=15, 6 Hz, 2H), 2.81–2.87 (dd, J=15, 9 Hz, 2H), 6.09–6.12 (m, 2H), 7.34 (s, 4H, aromatics); ^{13}C NMR ($CDCl_3$,

100 MHz) δ 21.04, 27.92, 42.57, 72.01, 81.17, 126.85, 139.40, 168.81, 169.72. Anal. calcd for $C_{24}H_{34}O_8$: C, 64.0; H, 7.55. Found: C, 64.12; H, 7.43.

1.1.14. 2,2′-Binaphthol diacetate (entry 31).[13] Yield 87% as a white crystalline material; mp 101–103°C; R_f 0.60 (20% EtOAc in petroleum ether); IR (KBr) 1735, 1210, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.88 (s, 6H), 7.16–7.46 (m, 8H), 7.91–8.02 (dd, J=15, 9 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.54, 121.80, 123.30, 125.60, 126.10, 126.60, 127.92, 129.43, 131.40, 133.21, 146.60, 169.32; MS (EI, *m/z*): 370 (M^+), 328, 285 (base peak).

1.1.15. Cyclohexyl thioacetate (entry 32). Yield 84% as a colorless liquid; R_f 0.80 (2% EtOAc in petroleum ether); IR (neat) 1730 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.50 (m, 10H), 2.25 (s, 3H), 3.38 (m, 1H). Anal. calcd for $C_8H_{14}SO$: C, 60.75; H, 8.86; S, 20.25. Found: C, 60.53; H, 8.92; S, 20.08.

1.1.16. 1,2,3,4,5,6-Hexa-*O*-acetyl-D-mannitol (entry 33). Yield 91% as a white crystalline solid; mp 80–83°C {lit.[20b] mp 123–124°C}; $[\alpha]_D^{25}$=+34.4 (*c* 1.2, $CHCl_3$) {lit.[20b] $[\alpha]_D^{25}$=+27 (*c* 1.0, $CHCl_3$).

1.1.17. 2,3,4,6-Tetra-*O*-acetyl-α-D-methylglucopyranose (entry 34). Yield 97% as a white solid; mp 102–104°C {lit.[20b] mp 100–101°C}; $[\alpha]_D^{25}$=+117.1 (*c* 9.1, $CHCl_3$) {lit.[20b] $[\alpha]_D^{25}$=+130 (*c* 1.0, $CHCl_3$).

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