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$InCl_3$ catalyzed carbene insertion into O–H bonds: efficient synthesis of ethers

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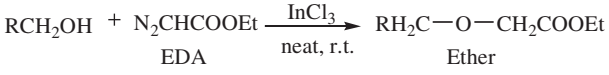
ABSTRACT

An efficient $InCl_3$ mediated insertion of the carbene fragment (:$CHCO_2Et$), generated in situ from ethyl diazoacetate into O–H bond of a series of saturated and unsaturated alcohols under mild conditions has been developed to afford the corresponding ethers as exclusive products in good to high yields (70–95%) and in shorter reaction times. In the case of unsaturated alcohols, the reaction proceeded with unprecedented selectivity resulting in ethers as the only products and in high yields.

Transition metal assisted transfer of carbene units through the decomposition of diazo compounds[1] in the presence of hydroxylic compounds (water, alcohols, phenols or carboxylic acids) to result in the formation of a new C–O bond, by a formal insertion of the carbene into the O–H bond, has a great synthetic bearing.[2] Thus, the synthesis of several natural products as well as of cyclic ethers have been achieved using this methodology at a certain stage of the synthetic pathway.[3] Several metals have been employed to mediate this transformation such as Rh,[4] Ru,[5] Cu,[6] Ni,[7] Sc[8] and Au.[9] Some of these metal complex catalysts are not readily available and need to be prepared through complicated procedure. Although Lewis acids like $Rh_2(OAc)_4$[4] and $Cu(OTf)_2$[4,6] reportedly catalyzed the insertion reaction, both were nonselective towards the saturated and unsaturated substrates and furnished mixture of products. Similarly, $BF_3{\cdot}Et_2O$[10] mediated transformation required low temperatures and the substrates with acid sensitive functional groups failed to survive such strong acidic conditions. Thus far the reports suggest that either the reaction failed completely in some cases[11] or resulted in moderate yield[12] in other cases or was nonselective[4,6] or required esoteric catalytic systems.[6] Alternatively, the same transformation could be effected by quenching the base induced oxyanion with ethyl haloacetate under convention conditions.[13] Nevertheless, it is plagued by harsh conditions. Bearing in mind the above limitations as well as given the importance of this reaction, a simple catalyst, that is, highly selective for the O–H etherization is warranted. Therefore, we turned our attention to find a catalyst system that is, mild, offers operationally simple reaction conditions, yet possibly display reasonable functional group compatibility over an array of substrates. In recent years, indium(III) chloride[14] emerged as a mild Lewis acid for effecting a variety of chemical transformations in chemo-, regio-, and stereo-selective fashion. Recently we reported facile $InCl_3$ catalyzed C–C coupling of aryl alcohols and TosMIC followed by the ready access of β-keto-(*E*)-enamino esters from 1,3-dicarbonyl



Scheme 1. $InCl_3$ catalyzed carbene insertion into O–H bond.

Table 1
Optimization of reaction conditions[a]

Entry	Lewis acid	Solvent	Time (h)	Yield[b] (%)
1	$InCl_3$	CH_2Cl_2	0.5	80
2	$InCl_3$	CH_2Cl_2	1	92
3	$InCl_3$	CH_3CN	2	70
4	$InCl_3$	THF	4	40
5	$InCl_3$	Neat	0.5	90
6	$InCl_3$	Neat	1	94
7	$ZrCl_4$	CH_2Cl_2	6	—[c]
8	$FeCl_3$	CH_2Cl_2	3	70

[a] Reaction conditions: benzyl alcohol (1.5 mmol), ethyl diazoacetate (1 mmol) and catalyst (0.2 mmol) stirred at rt for 0.5–6 h in solvents or as neat to give product in 40–94% yield.
[b] Isolated yields after purification by column chromatography.
[c] No conversion.

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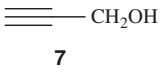
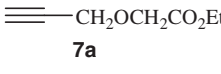
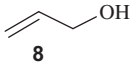
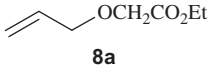
Table 2
$InCl_3$ catalyzed insertion of EDA into various alcohols[a]

Entry	Substrate	Product	Time (h)	Yield[b] (%)
1	$PhCH_2OH$ 1	$PhCH_2OCH_2CO_2Et$ 1a	1	94
2	$PhCH_2CH_2OH$ 2	$PhCH_2CH_2OCH_2CO_2Et$ 2a	0.5	95
3	CH_3OH 3	$CH_3OCH_2CO_2Et$ 3a	1.5	92
4	C_2H_5OH 4	$C_2H_5OCH_2CO_2Et$ 4a	1	91
5	C_4H_9OH 5	$C_4H_9OCH_2CO_2Et$ 5a	1.5	90
6	$CH_3(CH_2)_8CH_2OH$ 6	$CH_3(CH_2)_8CH_2OCH_2CO_2Et$ 6a	1.5	80
7	 7	 7a	0.5	95
8	 8	 8a	0.5	95
9	*p*-$NO_2C_6H_4CH_2OH$ 9	*p*-$NO_2C_6H_4CH_2OCH_2CO_2Et$ 9a	1	82
10	$(C_6H_5)_2CHOH$ 10	$(C_6H_5)_2CHOCH_2CO_2Et$ 10a	2	80

[a] Reaction conditions: Alcohol (1.5 mmol), ethyl diazoacetate(1 mmol) and $InCl_3$ (0.2 mmol) were stirred at room temperature under neat conditions.
[b] Isolated yields after purification by column chromatography.

compounds and TosMIC.[15] Both these transformations inspired us to initiate a systematic study of $InCl_3$ catalyzed carbene insertion reaction. Herein, we report for the first time, the $InCl_3$ catalyzed insertion of :$CHCO_2Et$ into hydroxyl bonds to afford the corresponding ethers as exclusive products in high yields (Scheme 1).

Accordingly, first we performed the $InCl_3$ catalyzed test reaction with benzyl alcohol **1** and ethyl diazoacetate (EDA) as the carbene source in CH_2Cl_2 and pleased to find the insertion product **1a** in 92% yield in 1 h reaction time. Gratifyingly, carbene dimeric or oligomeric products like diethyl fumarate and maleate were not observed in the above transformation.[4] In the presence of $InCl_3$, generation of carbene takes place via the decomposition of ethyl diazoacetate, which on subsequent transfer to alcohols[16] afforded ethers as products.

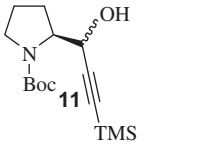
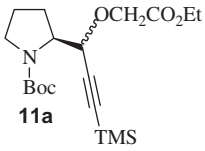
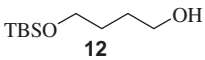
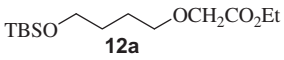
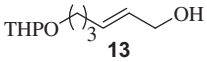
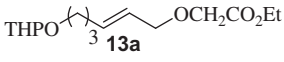
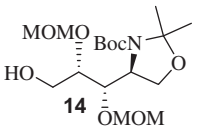
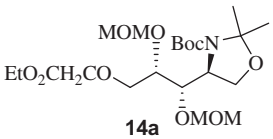
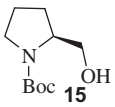
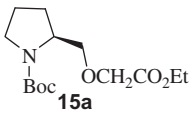
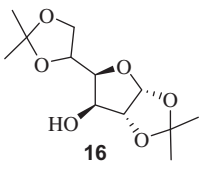
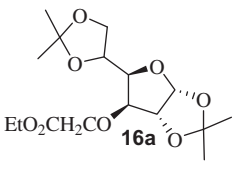
Next, the reaction optimization studies were performed between **1** and EDA using different solvents and Lewis acids (Table 1). After screening, $InCl_3$ was found to furnish the optimum product under solvent-free conditions. The reaction stoichiometry was checked using different equivalents of $InCl_3$ and the optimum product yield was obtained with 0.2 equiv of the catalyst.

In order to test the generality of this reaction, a series of saturated and unsaturated alcohols were studied towards the etherification reaction under the standardized reaction conditions (Table 2). Expectedly, all the alcohols **2**–**10** resulted in complete conversion to afford the corresponding ethers **2a**–**10a** in high yields.[17,18] In all the cases, no amount of residual EDA was detected after completion of the reaction. It is noteworthy to mention that the O–H insertion of unsaturated alcohols (Table 2, entries 7 and 8) proceeded with unprecedented selectivity resulting in exclusive ethers as products, that is, olefin cyclopropanation did not occur.

Earlier, Reed and Katzenellenbogen[11] attempted the O–H insertion on the propargylic alcohol **11** using the carbene precursor ethyl α-diazoisovalerate with three different Lewis acid catalysts (rhodium tetraacetate, copper(I) triflate, and boron trifluoride etherate) but failed to obtain the expected product. The starting material decomposed under those conditions. Interestingly, the same substrate underwent a facile O–H insertion to furnish the corresponding product **11a** in 80% yield under the present reaction conditions.

The next task was to study the functional group tolerance under these reaction conditions. Accordingly, various substrates having

Table 3
$InCl_3$ catalyzed insertion of EDA into substrates posessing acid sensitive protecting groups

Entry	Substrate	Product	Time (h)	Yield (%)
1	 11	 11a	2	80
2	 12	 12a	2	75
3	 13	 13a	3	80
4	 14	 14a	4	70
5	 15	 15a	2	70
6	 16	 16a	4	72

different functional groups were tested for $InCl_3$ catalyzed O–H insertion reaction (Table 3). To our delight, all the alcohols **11**–**16** are efficiently converted into their respective ethers **11a**–**16a**[17,18] in good yields and in shorter reaction time. In most of the cases, the $BF_3{\cdot}OEt_2$ failed to catalyze the reaction, excepting the prolinol derivative **15**. Acid sensitive groups like Boc, C-TMS, *O*-Silyl, MOM–ethers, acetonide groups remained unscathed during this transformation.

In summary, we have demonstrated a facile $InCl_3$ catalyzed insertion of $:CHCO_2Et$ fragment (from EDA) into the O–H bond under solvent-free conditions with remarkable chemoselectivity (high yielding ethers) and in case of unsaturated alcohols high regioselectivity (only insertion products were obtained) to afford the corresponding ethers. Furthermore, this methodology proved better than the reported ones, was general, and displayed good functional group tolerance and versatility. Overall, a facile synthesis of ethers from alcohols has been accomplished that may find varied applications in synthetic organic chemistry.[3]

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17. *General experimental procedure*: To a mixture of alcohol (1.5 mmol) and EDA (1.0 mmol), $InCl_3$ (0.2 mmol) was added and stirred under neat at ambient temperature until the completion of the reaction as indicated by TLC. To the reaction mixture, water (5.0 mL) was added and the product was extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed with brine (10 mL), dried (Na_2SO_4) and purified by column chromatography (Silica gel, 60–120 mesh, EtOAc:*n*-hexane, 1:9–2:8) to afford products.
18. *Analytical and spectral data of selected compounds:* Compound **2a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28–7.14 (m, 5H, Ar–H), 4.17 (q, 2H, J = 6.86 Hz, O–CH_2), 4.00 (s, 2H, O–CH_2), 3.72 (t, 2H, J = 6.86 Hz, O–CH_2), 2.91 (t, 2H, J = 6.86 Hz, CH_2), 1.27 (t, 3H, J = 7.84 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 138.2, 128.8, 128.2, 126.1, 72.4, 68.3, 60.9, 36.0, 13.9. IR (neat): 3440, 2930, 1750, 1260, 1157, 1055, 810, 775 cm^{-1}. ESI–MS: 231 [M+Na]$^+$. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21, H, 7.74. Found: 69.19, H, 7.70. Compound **6a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.21 (q, 2H, J = 7.18 Hz, O–CH_2), 3.99 (s, 2H, O–CH_2), 3.48 (t, 2H, J = 6.61 Hz, O–CH_2), 1.35–1.26 (m, 19H), 0.88 (t, 3H, J = 6.42 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 71.9, 68.3, 64.9, 31.9, 29.5, 29.4, 29.3, 29.2, 28.5, 25.9,25.8, 22.6, 14.1. IR (neat): 3440, 2930, 1690, 1510, 1257, 1036 cm^{-1}. ESI–MS: 267 [M+Na]$^+$. Anal. Calcd for $C_{14}H_{28}O_3$: C, 68.81, H, 11.55. Found: 68.84, H, 11.51. Compound **9a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, 2H, J = 7.18 Hz, Ar–H), 7.51 (d, 2H, J = 8.31 Hz, Ar–H), 4.71 (s, 2H, O–CH_2), 4.21 (q, 2H, J = 7.55 Hz, O–CH_2), 4.13 (s, 2H, CH_2), 1.31 (t, 3H, J = 7.55 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 147.3, 144.8, 127.8, 123.4, 71.8, 67.7, 60.9, 14.0. IR (neat): 3450, 2830, 1690, 1410, 1257, 1036, 850, 770 cm^{-1}. ESI–MS: 262 [M+Na]$^+$. Anal. Calcd for $C_{11}H_{13}NO_5$: C, 55.23, H, 5.48, N, 5.86. Found: 55.21, H, 5.52, N, 5.83. Compound **10a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34–7.15 (m, 10H, Ar–H), 5.54 (s, 1H, CH), 4.18 (q, 2H, J = 6.80 Hz, O–CH_2), 4.04 (s, 2H, O–CH_2), 1.28 (t, 3H, J = 7.55 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 141.0, 128.3, 127.7, 127.2, 83.4, 65.9, 60.7, 14.1. IR (neat): 3450, 2830, 1695, 1250, 1157, 1050, 834, 776 cm^{-1}. ESI–MS: 293 [M+Na]$^+$. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53, H, 6.71. Found: 75.55, H, 6.75. Compound **11a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.70 (d, 1H, J = 2.26 Hz, O–CH), 4.28–4.11 (m, 4H, 2 × O–CH_2), 3.54–3.24 (m, 3H), 2.26–1.65 (m, 4H, 2 × CH_2), 1.45 (s, 9H, 3 × CH_3), 1.28 (t, 3H, J = 6.79 Hz, CH_3), δ = 0.16 (s, 9H, 3 × CH_3). ^{13}C NMR (75MHz, $CDCl_3$): δ 169.5, 168.6, 102.3, 96.2, 79.1, 70.8, 65.9, 60.5, 60.4, 47.0, 28.2, 26.0, 24.5, 14.4, −0.26. IR (neat): 3451, 2856, 1739, 1254, 1040, 700 cm^{-1}. ESI–MS: m/z 407 [M+Na]$^+$. Anal. Calcd for $C_{19}H_{34}NO_5Si$: C, 59.34, H, 8.91, N, 3.64. Found: C, 59.36, H, 8.94, N, 3.66. Compound **12a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.15 (q, 2H, J = 7.18 Hz, O–CH_2), 3.98 (s, 2H, O–CH_2), 3.59 (t, 2H, J = 6.04 Hz, O–CH_2), 3.49 (t, 2H, J = 6.23 Hz, O–CH_2), 1.29–1.16 (m, 4H, 2 × CH_2), 1.26 (t, 3H, J = 7.17 Hz), 0.85 (s, 9H, 3 × CH_3), 0.00 (s, 6H, 2 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 96.2, 71.6, 68.3, 62.8, 29.8, 29.4, 26.1, 22.9, 14.3, −5.1. IR (neat): 3078, 2932, 2858, 1711, 1433, 1254, 1090, 834 cm^{-1}. ESI–MS: m/z 313 [M+Na]$^+$. Anal. Calcd for $C_{14}H_{30}O_4Si$: C, 57.89, H, 10.41. Found: 57.92, H, 10.44. Compound **13a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.79–5.49 (m, 2H, olefinic), 4.54 (s, 1H, O–CH), 4.18 (m, 2H, O–CH_2), 3.99–3.97 (m, 4H, 2 × O–CH_2), 3.82–3.64 (m, 2H, O–CH_2), 3.47–3.27 (m, 2H, O–CH_2), 2.17 (t, 2H, J = 6.04 Hz, CH_2), 1.82–1.39 (m, 8H, 4 × CH_2), 1.31–1.25 (m, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 135.1, 125.5, 98.6, 71.8, 66.6, 66.5, 62.0, 60.5, 30.5, 28.8, 28.7, 25.2, 19.4, 13.9. IR (neat): 3050, 2952, 1720, 1455, 1260, 1065 cm^{-1}. ESI–MS: m/z 309 [M+Na]$^+$. Anal. Calcd for $C_{15}H_{26}O_5$: C, 62.91, H, 9.15. Found: 62.93, H, 9.19. Compound **14a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.80–4.56 (m, 6H, 3 × O–CH_2), 4.24–4.05 (m, 3H), 4.01 (s, 2H, O–CH_2), 3.87 (t, 1H, J = 7.93 Hz), 3.78–3.55 (m, 3H), 3.33 (s, 3H, O–CH_3), 3.33 (s, 3H, O–CH_3), 1.41 (d, 15H, J = 8.9 Hz, 5 × CH_3), 1.24 (t, 3H, J = 6.94 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.4, 151.6, 98.2, 95.9, 93.0, 79.6, 71.5, 70.9, 68.3, 63.2, 60.2, 58.5, 57.8, 55.9, 55.3, 28.2, 14.0. IR (neat): 3120, 2965, 2870, 1730, 1460, 1250, 1050, cm^{-1}. ESI–MS: m/z 481 [M+H]$^+$, 503 [M+Na]$^+$. Anal. Calcd for $C_{22}H_{42}NO_{10}$: C, 54.98, H, 8.81, N, 2.91. Found: C, 54.96, H, 8.78, N, 2.94. Compound **15a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.62 (s, 1H), 4.28–4.15 (m, 4H, 2 × O–CH_2), 4.03 (br. s, 1H), 3.62 (d, J = 6.9 Hz, 1H) 3.31 (br. s, 2H), 2.15–1.82 (m, 4H, 2 × CH_2), 1.45 (s, 9H), 1.29 (t, 3H, J = 6.9 Hz, O–CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 153.8, 78.5, 71.4, 67.9, 63.2, 60.0, 56.0, 46.5, 28.2, 23.5, 13.9. ESI–MS: m/z 288 [M+H]$^+$, 310 [M+Na]$^+$. Anal. Calcd for $C_{14}H_{25}NO_5$: C,58.52, H, 8.77, N, 4.87. Found: C, 58.54, H, 8.75, N, 4.89.