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Friedel-Crafts Alkylation of Arenes Catalyzed by Ion-Exchange Resin Nanoparticles: An Expedient Synthesis of Triarylmethanes

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Friedel-Crafts alkylation of electron-rich arenes with aldehydes has been achieved in the presence of an active and selective Amberlyst-15® catalyst at the reaction temperature of 60 °C in solvent-free conditions. The catalyst exhibits a very high activity and offers the corresponding triarylmethanes in excellent yields with a high selectivity. The use of highly reactive and selective Amberlyst-15® makes this procedure simple, convenient, cost-effective, practical and environmentally friendly. This method provides an easy access to triarylmethanes in a single step using a readily available acidic ionic resin, which is a stable and easy to separate from the reaction mixture by a simple filtration technique.

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1. INTRODUCTION

Multi-component reactions (MCRs) are highly important because of their wide range of applications in pharmaceutical chemistry for production of highly diversified structural scaffolds and combinatorial libraries for drug discovery.[1] MCRs are extremely convergent, producing a remarkably high molecular complexity in a single step. Triarylmethanes have attracted much attention in synthetic, medicinal, and industrial chemistry.[2] They are also used as photochromic materials[3] and dyes.[4] In particular, hydroxy substituted triarylmethanes are attractive as antioxidants and antitumor agents especially in medicinal chemistry.[5] The acid-catalyzed condensation of veratrole with formaldehyde leads to cyclotriveratralene which is an important building block in supramolecular chemistry to construct more complex cage-like cryptophane.[6]

The mostpopular $AlCl_3$-catalyzed alkylation of arenes with aldehydes has not received much attention until recently because of the formation of many side products such as diarylmethanes, triarylmethanes and anthracene derivatives.[7] For example, diarylmethanes are formed selectively in the reaction of arenes with formaldehyde in the presence of acid catalysts such as $CaCl_2$,[8] $Sc(OTf)_3$,[9] and $InCl_3$/TMSCl.[10] Subsequently, the preparation of triarylmethanes have been reported using various catalytic systems such as $AuCl_3$/AgOTf,[11] $Ir(COD)Cl_2/SnCl_4$,[12] $Yb(OTf)_3$,[13] and $SbCl_3$.[14] The silica supported $ZnBr_2$/AcBr has also been used for the synthesis of triarylmethanes.[15] However, the use of acetyl halides as activators, high temperatures, extended reaction times and harsh conditions and the necessity of several reaction steps in many cases limit their practical utility in large scale synthesis. Therefore, the development of a simple, convenient and efficient method for the preparation of triarylmethanes would certainly expand the scope of the Friedel-Crafts alkylation.

Recently, the use of solid acidic catalysts such as sulfated zirconia, heteropoly acids, acidic polymers, clays and zeolites has enhanced the replacement of liquid acid

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catalysts for organic transformations.[16] Due to their operational simplicity, environmental compatibility, non-toxic, reusability, low cost, and ease of isolation. In particular, ion exchange resins are the most widely used heterogeneous catalysts due to their advantages such as high activity and selectivity, reusability, non-hazardous nature and ease of removal from the reaction mixture *via* simple filtration.[17] However, there are no reports on the use of acidic ion-exchange resins for the direct alkylation of electron-rich arenes with aldehydes.

2. EXPERIMENTAL SECTION

IR spectra were recorded on FT-IR spectrometer and reported in reciprocal centimeters (cm^{-1}). ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR at 75 MHz. For ^{1}H NMR, tetramethylsilane (TMS) was used as internal standard ($\delta = 0$) and the values are reported as follows: chemical shift, integration, multiplicity ($s =$ singlet, $d =$ doublet, $t =$ triplet, $q =$ quartet, $m =$ multiplet, br = broad), and the coupling constants in Hz. For ^{13}C NMR, CDCl$_3$ ($\delta = 77.27$) was used as internal standard and spectra were obtained with complete proton decoupling. Low-resolution MS and HRMS data were obtained using *APCI* ionization. Melting points were measured on micro melting point apparatus.

2.1. General Procedure

A mixture of aromatic aldehyde (1 mmol), aromatic ether (2 mmol) and Amberlyst-15 (100 mg) was stirred at 60 °C under solvent free condition. Upon completion as indicated by TLC, the catalyst was recovered by simple filtration with ethyl acetate. After evaporation of the solvent, the crude product was purified by silica gel column chromatography (100–200 mesh) using *n*-hexane-EtOAc (8:2) to afford the pure triarylmethane derivative. Spectral data for the selected products.

2.2. 4,4-(Phenyl Ethylene)Bis(1,2-Dimethoxybenzene) (3a)

White solid, m.p. 120–122 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.19–7.27 (m, 3 H), 7.09 (d, $J = 1.5$ Hz, 1 H), 7.05 (d, $J = 1.5$ Hz, 1 H), 6.74 (s, 1 H), 6.71 (s, 1 H), 6.60 (d, $J = 1.9$ Hz, 2 H), 6.54 (d, $J = 1.9$ Hz, 1 H), 6.52 (d, $J = 2.3$ Hz, 1 H), 5.39 (s, 1 H), 3.84 (s, 6 H), 3.75 (s, 6 H);^{13}C NMR (75 MHz, CDCl$_3$): δ 148.7, 147.4, 144.3, 136.7, 129.2, 128.2, 121.4, 112.7, 110.7, 58.79, 55.85; IR (KBr): $\nu_{\max}$ 3448, 1591, 1460, 1262, 1228, 1026, 743 cm^{-1}; ESI-MS: m/z 387 (M + Na); HRMS Calculated for $C_{23}H_{24}O_4Na$, 387.1572, Found: 387.1584.

2.3. Bis(4-Methoxyphenyl)(4-Chlorophenyl) Methane (3b)

white solid, m.p. 69–70 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.23 (d, $J = 8.4$ Hz, 2 H), 7.05–6.95 (m, 6 H), 6.82 (d, $J = 8.7$ Hz, 4 H), 5.41 (s, 1 H), 3.78 (s, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 158.3, 143.3, 136.0, 132.1, 130.8, 130.3, 128.5, 113.9, 55.3, 54.7; IR (KBr): $\nu_{\max}$ 3419, 2980, 2910, 2840, 1560, 1511, 1240, 1120, 1023, 810, 740 cm^{-1}; ESI-MS: m/z 361 (M + Na)$^{+}$.

2.4. 1,2-Dimethoxy-4-((3,4-Dimethoxyphenyl) (4-Methoxyphenyl)Methyl)Benzene (3c)

Red color semisolid; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.96 (d, $J = 7.55$ Hz, 2 H), 6.76 (d, $J = 7.55$ Hz, 2 H), 6.71 (d, $J = 8.30$ Hz, 2 H), 6.59 (s 2 H), 6.51 (d, $J = 8.30$ Hz, 2 H), 5.32 (s, 1 H), 3.82 (s, 6 H), 3.76 (s, 1 H), 3.74 (s, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 149.4, 148.7, 174.6, 145.3, 133.2, 128.7, 123.2, 120.0, 111.6, 110.8, 56.2, 55.4, 55.3, IR (KBr): $\nu_{\max}$ 3345, 2944, 2832, 1655, 1413, 1111, 1205, 752, 599 cm^{-1}; ESI-MS: m/z 412(M + NH$_4$)$^{+}$.

2.5. 1(Bis(3,4Dimethoxyphenyl)Methyl) 2,4-Dichlorobenzene (3d)

White solid m.p. 110–112 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.87 (d, $J = 8.78$ Hz, 1 H), 6.72 (d, $J = 8.78$ Hz, 2 H), 6.55 (s 2 H), 6.44 (d, $J = 8.78$ Hz, 2 H), 5.70 (s, 1 H), 3.85 (s 6 H), 3.76 (s 6 H); ^{13}CNMR (75 MHz, CDCl$_3$): δ 148.8, 147.6, 140.6, 137.6, 131.6, 129.3, 126.7, 121.2, 112.5, 110.7, 55.9, 55.7, 52.0; IR (KBr): $\nu_{\max}$ 3419, 300, 2931, 2834, 1590, 1515, 1258, 1138, 1023, 812, 750 cm^{-1}; ESI-MS: m/z 455 (M + Na)$^{+}$; HRMS Calculated for $C_{23}H_{22}O_4Cl_2Na$ 455.0792, Found: 455.0782.

2.6. 2-(Bis(3,4-Dimethoxyphenyl)Methyl)-1,3-Dimethoxy Benzene (3e)

White solid, m.p. 131–134 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.76–6.63(m, 3 H), 6.54 (s, 2 H), 6.49 (d, $J = 8.3$ Hz, 2 H), 6.38 (d, $J = 2.8$ Hz, 1 H), 5.69 (s, 1 H), 3.84 (s, 6 H), 3.76 (s, 6 H), 3.66 (s, 3 H), 3.64 (s, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 153.3, 151.4, 148.5, 147.2, 136.2, 134.4, 121.1, 117.1, 112.6, 111.0, 110.8, 110.6, 56.3, 55.7, 55.5, 48.8; IR (KBr): $\nu_{\max}$ 3430, 2944, 1593, 1511, 1461, 1269, 1213, 1024, 815, 757 cm^{-1}; ESI-MS: m/z: 447 (M + Na); HRMS Calculated for $C_{25}H_{28}O_6Na$ 447.1783, Found: 447.1804.

2.7. 2-(Bis(3-Bromo-4-Methoxyphenyl)Methyl) Naphthalene (3f)

White solid, m.p. 145–146 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.82–7.72 (m, 4 H), 7.61 (s, 1 H), 7.53 (d, $J = 1.95$ Hz, 2 H), 7.44 (t, $J = 2.93$ Hz, 2 H), 7.35 (d, $J = 8.80$, Hz 1 H), 7.10 (d, $J = 8.80$ Hz, 2 H), 6.78 (d, $J = 8.8$ Hz, 2 H), 5.87 (s, 1 H), 3.88 (s, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 155.0, 143.4, 140.0, 132.6, 128.4, 128.1, 128.0, 127.4, 126.4, 126.3, 125.7, 111.7, 111.4, 111.1, 57, 56.2; IR (KBr): $\nu_{\max}$ 3450, 2922, 2851, 1599, 1493, 1257, 1054, 1020, 786, 679, 1257, 1054, 786, 679 cm^{-1}; ESI-MS: m/z 512 (M)$^{+}$.

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2.8. 1,2-Dimethoxy-4-((3,4-Dimethoxyphenyl)(4-Nitrophenyl)Methyl) Benzene (3g)

Light yellow color solid m.p. 151–154 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.12 (*d*, $J = 9.06$ Hz, 2 H), 7.25 (*d*, $J = 9.06$ Hz, 2 H), 6.75 (*d*, $J = 8.30$ Hz, 2 H), 6.57 (*d*, $J = 2.26$ Hz, 2 H), 6.50 (*d*, $J = 2.26$ Hz, 2 H), 6.48 (*d*, $J = 8.30$ Hz, 1 H), 5.47 (*s*, 1 H), 3.85 (*s*, 1 H), 3.76 (*s*, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 151.9, 148.7, 147.6, 146.1, 134.8, 129.8, 123.2, 121.0, 112.2, 110.8, 55.6, 55.4, IR (KBr): $\nu_{\max}$ 3405, 2945, 2257, 1592, 1540, 1455, 1268, 998, 698 cm^{-1}; ESI-MS: m/z 412 $(\mathrm{M+NH_4})^+$.

2.9. Bis(4-Methoxy-1-Naphthyl)Phenylmethane (3h)

White solid, m.p. 97–99 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.32 (*d*, $J = 8.1$ Hz, 2 H), 7.89 (*d*, $J = 8.1$ Hz, 2 H), 7.50–7.10 (*m*, 8 H), 6.79 (*d*, $J = 8.1$ Hz, 2 H), 6.73 (*s*, 1 H), 6.63 (*d*, $J = 8.1$ Hz, 2 H), 3.95 (*s*, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 154.6, 144.2, 132.8, 132.2, 130.0, 128.5, 127.9, 126.8, 126.4, 126.2, 124.9, 124.2, 122.6, 103.2, 55.5, 48.9; IR (KBr): $\nu_{\max}$ 3399, 2925, 2257, 1650, 1455, 998, 760 cm^{-1}; ESI-MS: m/z 423 $(\mathrm{M+Na})^+$.

2.10. Bis(4-Methoxyphenyl)(*p*-Tolyl)Methane (3i)

White solid, m.p. 55–56 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.11–6.97 (*m*, 8 H), 6.82 (*d*, $J = 8.4$ Hz, 4 H), 5.42 (*s*, 1 H), 3.78 (*s*, 6 H), 2.32 (*s*, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 158.0, 141.8, 136.8, 130.4, 129.3, 129.1, 113.7, 55.3, 54.9, 21.1; IR (KBr): $\nu_{\max}$ 3362, 2929, 1599, 1451, 1024, 693, 524 cm^{-1}; ESI-MS: m/z 419 $(\mathrm{M+H})^+$.

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2.11. Bis(4-Methoxyphenyl)Phenylmethane (3j)

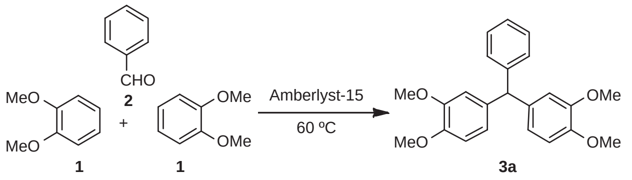
White solid, m.p. 99–101 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.31–7.14 (*m*, 3 H), 7.09 (*d*, $J = 7.2$ Hz, 2 H), 7.01 (*d*, $J = 8.7$ Hz, 4 H), 6.81 (*d*, $J = 8.7$ Hz, 4 H), 5.44 (*s*, 1 H), 3.77 (*s*, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 158.1, 144.7, 136.6, 130.4, 129.4, 128.4, 126.3, 113.8, 55.3; IR (KBr): $\nu_{\max}$ 3448, 1551, 1440, 1252, 1228, 1150, 1026, 743 cm^{-1}; ESI-MS: m/z 315 $(\mathrm{M+H})^+$.

2.12. 6,6((4-Bromophenyl)Methylene)Bis(2,3-Dihydrobenzo[b][1,4]Dioxane) (3k)

Liquid, ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.35 (*d*, $J = 8.5$ Hz, 2 H), 6.95 (*d*, $J = 8.3$ Hz, 2 H), 6.72 (*s*, 1 H), 6.69 (*s*, 3 H), 6.52–6.48 (*m*, 4 H), 5.22 (*s*, 1 H), 4.20 (*s*, 8 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 143.2, 142.0, 136.7, 131.7, 130.9, 122.1, 117.9, 117.0, 64.3, 54.7. IR (KBr): $\nu_{\max}$ 2923, 1588, 1502, 1286, 1066, 882, 779 cm^{-1}; ESI-MS: m/z 439 (M$^+$). HRMS calculated for $C_{23}H_{19}BrO_4$ 439.3152, Found: 439.3157.

2.13. Bis(4-Methoxyphenyl)(4-Nitrophenyl)Methane (3l)

White solid, m.p. 45–46 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.13 (*d*, $J = 8.7$ Hz, 2 H), 7.27 (*d*, $J = 8.4$ Hz, 2 H), 6.98 (*d*, $J = 8.4$ Hz, 4 H), 6.83 (*d*, $J = 8.7$ Hz, 4 H), 5.53 (*s*, 1 H), 3.79 (*s*, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 158.5, 152.5, 146.5, 134.9, 130.3,130.2, 123.6, 114.1, 55.4, 55.2; IR (KBr): $\nu_{\max}$ 3399, 2945, 2257, 1540, 1455, 1268, 998, 598 cm^{-1}; ESI-MS: m/z 350 $(\mathrm{M+H})^+$.



Scheme 1. Preparation of triarylmethane **3a**.

3. RESULTS AND DISCUSSION

In continuation of our efforts to explore the synthetic utility of Amberlyst-15®[18], we herein report for the first time, a metal free approach for the synthesis of triarylmethanes *via* the Friedel–Crafts alkylation of electron-rich olefins with aromatic aldehydes using Amberlyst-15® as a novel solid acid catalyst. Accordingly, we first attempted the alkylation of 1,2-dimethoxybenzene (2 mmol, **1**) with benzaldehyde (1 mmol, **2**) in the presence of Amberlyst-15® (100 mg). Though the reaction proceeds at room temperature, the desired triarylmethane **3a** was obtained only in 20% yield after a long reaction time (6 h). Interestingly, the yield of **3a** was increased from 20 to 90% and the reaction time was drastically reduced from 6 h to 30 min when the reaction was performed at 60 °C (Scheme 1).

Next, we compared the catalytic efficiency of the Amberlyst-15® with other solid acids such as KSF clay and heteropoly acids including unsupported PMA and silica supported PMA and the results are presented in Table I. Among the catalysts studied, Amberlyst-15® was found to give the best results in terms of yields and selectivity.

After optimizing the reaction conditions, various aldehydes bearing both electron-donating and electron-withdrawing groups were investigated for the present protocol. It was found that the reactions proceeded well in both cases at 60 °C, affording the corresponding products in good yields (Table II). Notably, a sterically hindered 2-naphthaldehyde also gave the desired product in fairly good yield (entry f, Table II). Among the solvents such as benzene, toluene, THF and 1,4-dioxane studied for this transformation, solvent free condition gave the best results. Therefore, we decided to utilize solvent free condition

Table I. Efficiency of various acid catalysts in the synthesis of **3a**.

Entry	Catalyst	Catalyst Wt (mg)	Time (min)	Yield (%)[a]
a	KSF clay	100	20	60
b	PMA	100	20	40
c	5% PMA/SiO$_2$	100	20	58
d	Amberlyst-15	100	20	90

Note: [a]The reaction was carried out at 60 °C with 1 mmol of benzaldehyde and 2 mmol of 1,2-dimetoxybenzene.

Table II. Amberlsyt-15 promoted synthesis of triarylmethanes via the Friedel-Crafts alkylation.

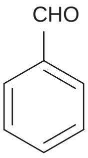
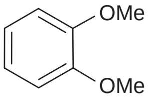
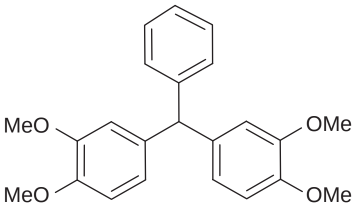
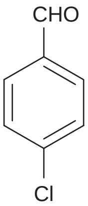
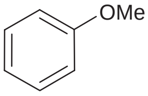
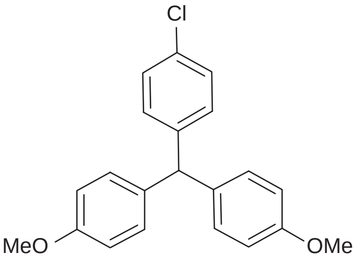
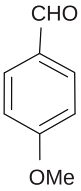
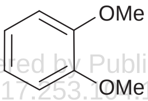
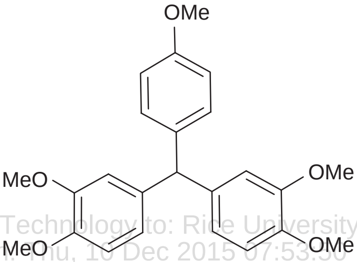
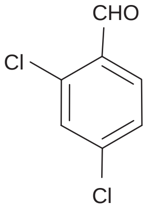
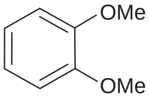
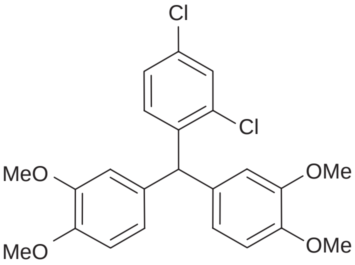
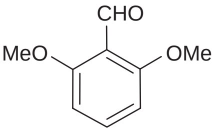
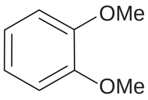
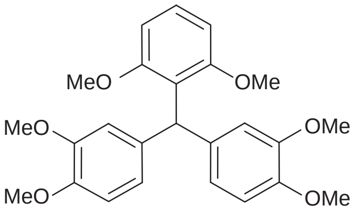
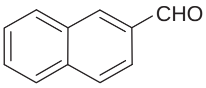
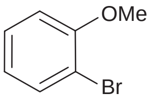
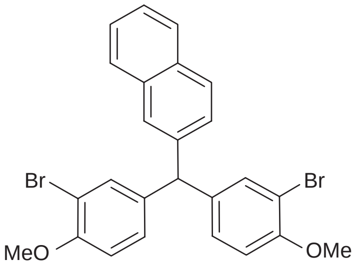
Entry	Aldehyde	Arene	Product	Time (min)	Yield (%)
a				30	90
b				40	82
c				25	85
d				35	86
e				25	80
f				35	70

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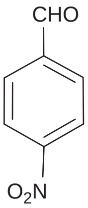
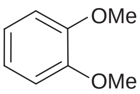
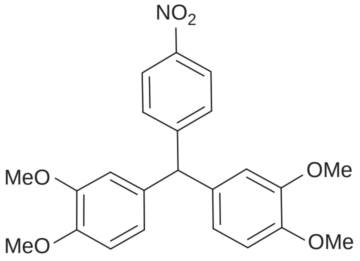
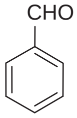
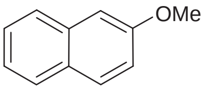
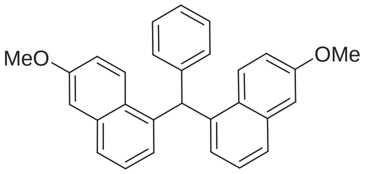
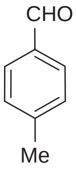
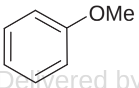
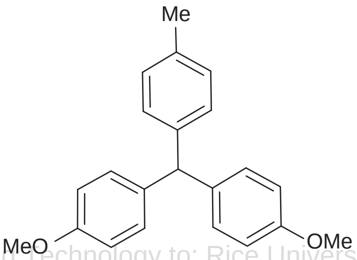
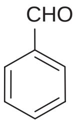
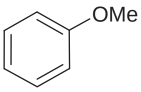
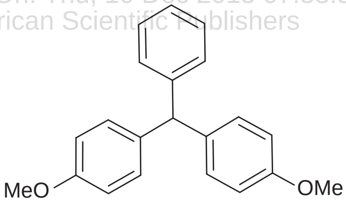
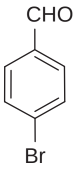
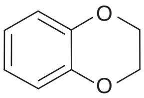
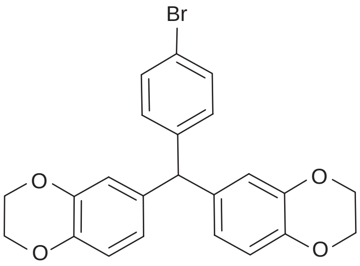
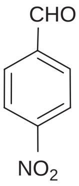
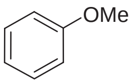
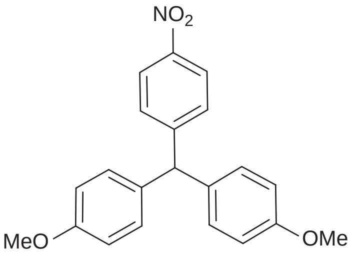
Table II. Continued.

Entry	Aldehyde	Arene	Product[a]	Time (min)	Yield (%)
g				30	83
h				40	75
i				45	85
j				35	80
k				40	85
l				55	78

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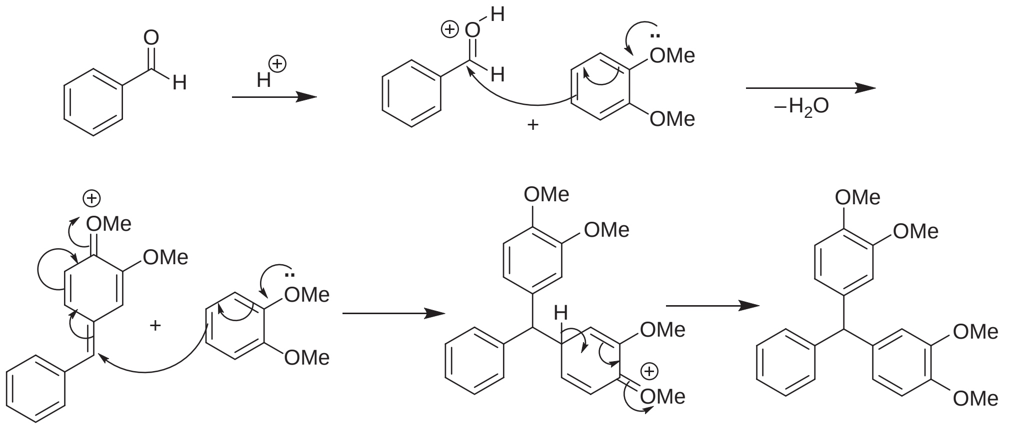
Notes. [a] All products were characterized by 1 H NMR, 1R and mass spectroscopy. [b] Yield refers to pure products after chromatography.



Scheme 2. A plausible reaction pathway.

to perform the Friedel–Crafts reaction of aldehydes with other aromatic ethers. Among various aromatic ethers, disubstituted benzene derivatives such as 1,4-benzodioxane, and 1,2-dimethoxybenzene are much more active than mono-substituted aromatic ethers (Table II).

As seen in Table II, the condensation of aromatic aldehydes with electron-rich arenes allows the preparation of a wide range of triarylmethane derivatives in a single step process. All the products were characterized and confirmed by ^{1}H NMR, ^{13}C NMR, IR and mass spectroscopy. Finally, recycling experiments were conducted to find out the efficiency of the catalyst after the reaction. After three repeated cycles using the recovered catalyst, the reaction of 1,2-dimethoxybenzene with benzaldehyde gave 90, 87 and 85% yields respectively. These results reveal that the catalyst Amberlyst-15® can be recycled several times without losing much activity. In addition, the catalyst is highly active, selective, easy to handle, eco-friendly, thermally robust, non-volatile, and non-explosive for this conversion. The above results confirm that Amberlyst-15® works efficiently for this transformation. The scope and generality of this process is illustrated with respect to various aromatic ethers and aryl aldehydes and the results are presented in Table II.[19]

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Mechanistically, we assume that arene initially attacks on activated aldehyde by acidic resin followed by dehydration to give the quinone intermediate, which subsequently reacts with another equivalent of arene to give the desired triarylmethane derivative (Scheme 2).

4. CONCLUSION

In summary, Amberlyst-15® has proved to be an efficient and reusable solid acid catalyst for the synthesis of triarylmethanes in high yields with high selectivity. This method offers significant advantages such as operational simplicity, low cost and reusability of the catalyst which make this procedure an attractive strategy for the synthesis of triarylmethanes.

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