Supporting Information

Polymer supported ascorbate functionalized task specific ionic liquid: an efficient reusable catalyst for 1,3-dipolar cycloaddition

Jayavant D. Patil, Supriya A. Patil and Dattaprasad M. Pore,*

*Department of Chemistry, Shivaji University, Kolhapur- 416004, India
*E-mail: p.dattaprasad@rediffmail.com

bDepartment of Chemistry, Hanyang University, Sungdong-Ku, Haengdang-dong 17, Seoul, 133-791, Republic of Korea.

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A) General Information

Alkynes (Aldrich/Alfa Aesar), sodium azide (Spectrochem, Mumbai) and copper sulphate pentahydrate (Spectrochem, Mumbai) were used as received. All reactions were carried out in air atmosphere in predried glassware. Infrared spectra were measured with an Agilent Cary (IR-630) spectrophotometer. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Brucker AC spectrometer (300 MHz for $^1$H NMR and 75 MHz for $^{13}$C.
NMR), using CDCl$_3$ as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are expressed in parts per million (ppm) and coupling constants are expressed in hertz (Hz). Mass spectra were recorded on a Shimadzu QP2010 GCMS. FESEM was performed using a HITACHI S-4800.

**B) Typical procedure for the preparation of Ascorbate functionalized polymer supported task specific ionic liquid catalyst (MR-IMZ-As)**

**Step-1 Preparation of imidazolium-loaded polymeric support (MR-IMZ-Cl)**

In 100 mL round bottom flask were added Merrifield peptide resin (2 % cross linked, 2-4 mmol Cl/g) 5 g, N-methyl imidazole (0.0609 mmol) in toluene (25 mL) and refluxed for 24 hours. On completion, the reaction mixture was cooled to room temperature. It was then filtered and the residue obtained was washed with toluene, 0.1M HCl, water and methanol sequentially followed by drying under reduced pressure to afford imidazolium-loaded polymeric support. The catalyst was further characterized by FTIR to check the attachment of the ionic liquid. A strong band centred at 1561 cm$^{-1}$ confirms the attachment of the imidazole on Merrifield resin.

**Step-2 Preparation of imidazolium-loaded polymeric support (MR-IMZ-OH)**

(MR-IMZ-Cl) (1.0 g) was suspended in 10 mL aqueous solution of KOH (0.448 g). The resulting mixture was stirred for 24 h at room temperature, afterward the polymer was filtered and washed with water, methanol and dried under vacuum to afford (MR-IMZ-OH). IR Shows absorption bands at 3386, 3029, 2923, 1572, 1451, 1332, 1159, 1113, 1020, 820 cm$^{-1}$

**Step-3 Preparation of polymer supported Ascorbate anionic ionic liquid catalyst (MR-IMZ-As)**

A mixture of the imidazolium loaded polymeric support (MR-IMZ-OH) (1.0 g) and Ascorbic acid (1.408 g, 8mmol) was suspended in water (20 mL). The mixture was then stirred at room temperature for 24 h. On completion, the reaction mixture was filtered and the polymeric support was washed vigorously with distilled water (10 mL × 5), MeOH (10mL × 5) and dried under reduced pressure to give (MR-IMZ-As).
C) General procedure for synthesis of 1, 4-disubstituted 1, 2, 3-triazole

In a 50 mL round bottom flask aryldiazonium tetrafluoroborate (1 mmol), sodium azide (1.2 mmol), alkyne (1.0 mmol), CuSO$_4$.5H$_2$O (10 mg, 0.04 mmol) and MR-IMZ-As (25 mg, 0.16 mmol) were mixed and stirred in 5 mL water. The reaction was allowed to proceed for 2 h at room temperature. Reactions were monitored by Thin Layer Chromatography (TLC) using aluminium backed silica gel 60 (F$_{254}$) plates. After completion of the reaction, the reaction mixture was filtered and quenched with water (10 mL) the organic products were separated from the reaction mixture by extraction with ethyl acetate (15 mL X 2). The organic layer was dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure then the product was purified by silica gel column chromatography.

D) SEM, TEM-EDS analysis of polymer supported task specific ionic liquid:

![Fig.1 SEM analysis of polymer supported task specific ionic liquid (MR-IMZ-As) before (a) and after (b) use respectively](image)

Fig.1 SEM analysis of polymer supported task specific ionic liquid (MR-IMZ-As) before (a) and after (b) use respectively
Fig. 2 TEM-EDS analysis of polymer supported task specific ionic liquid after first cycle

Fig. 3 TEM-EDS analysis of polymer supported task specific ionic liquid after fifth cycle

a) IR spectra of imidazolium-loaded polymeric support (MR-IMZ-Cl)
b) IR spectra of imidazolium-loaded polymeric support (MR-IMZ-OH)
c) IR spectra of Ascorbate functionalized polymer supported task specific ionic liquid catalyst (MR-IMZ-As)

![IR Spectrum of Ascorbate Functionalized Polymer Supported Task Specific Ionic Liquid Catalyst](image)

- 3026.920 26.741
- 2924.735 104.593
- 1720.446 16.570
- 1626.114 -0.034
- 1019.873 29.516
- 1451.032 58.062
- 1602.326 16.837
- 1562.142 0.000
- 825.225 38.088
- 1158.900 157.374

d) IR spectra of copper incorporated ascorbate functionalized polymer supported task specific ionic liquid catalyst (MR-IMZ-As-Cu)

![IR Spectrum of Copper Incorporated Ascorbate Functionalized Polymer Supported Task Specific Ionic Liquid Catalyst](image)

- 2123.539 17.737
- 1493.128 12.503
- 818.705 39.5
- 754.808 1.240
- 1119.815 2343.5

S-6
E) Spectral data of synthesized 1,2,3-triazole compounds:

**Entry 1, Table 1:** 1-(2-methoxyphenyl)-4-phenyl-1\(H\)-1,2,3-triazole

![Chemical Structure](image_url)

IR (ZnSe): 3126, 2940, 2842, 2286, 1879, 1725, 1610, 1576, 1517, 1440, 1302, 1230, 1183, 1110, 1073, 918, 826, 800 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\) ) : \(\delta\) (ppm): 3.88 (s, 3H), 7.02-7.07 (dd, 2H, \(J = 3, 3\) Hz), 7.35-7.40 (t, 1H, \(J = 15\) Hz), 7.44-7.49 (t, 2H, \(J = 15\) Hz), 7.67-7.71 (dt, 2H, \(J = 3, 9\) Hz), 7.91-7.93 (d, 2H, \(J = 6\) Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\) ) : \(\delta\) (ppm): 55.65, 114.82, 117.94, 122.19, 125.87, 128.41, 128.92, 130.18, 130.46, 148.10, 159.91; MS (EI): 237 (M\(^+\)-14), 222, 207, 194, 179, 165, 152, 130, 115, 103, 91, 77, 51 m/z.

**Entry 2, Table 1:** 1-(3-methylphenyl)-4-phenyl-1\(H\)-1,2,3-triazole
IR (Znse): 3126, 2921, 2856, 2305, 2114, 1872, 1664, 1610, 1592, 1475, 1396, 1228, 1085, 1044, 971, 898, 832, 785, 765 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\) ) : \(\delta\) (ppm): 2.49 (s, 3H), 7.29 (s, 1H), 7.36-7.41 (m, 2H), 7.44- 7.51 (m, 2H), 7.57-7.60 (d, 1H, \(J= 9\) Hz), 7.65 (s, 1H), 7.91-7.95 (m, 2H), 8.20 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) (ppm): 21.44, 117.61, 117.67, 121.22, 125.86, 128.40, 129.55, 130.30, 137.02, 140.04, 148.30; MS (EI): 235, 207, 192, 179, 165, 152, 130, 116, 103, 91, 76, 65, 51 m/z.

**Entry 6, Table 1**: 1-[1-(3-methylphenyl)-1H-1,2,3-triazol-4-yl]cyclohexanol

IR (Znse): 3236, 3111, 3066, 2936, 2855, 2108, 2088, 1726, 1610, 1594, 1491, 1446, 1259, 1234, 1170, 1057, 1022, 967, 898, 869, 848, 780 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) (ppm): 1.27-1.42 (m, 2H), 1.64-1.82 (m, 3H), 1.93-2.12 (m, 6H), 2.46 (s, 3H), 7.26-7.28 (d, 1H, \(J= 6\) Hz), 7.37-7.43 (t, 1H, \(J= 9\) Hz ), 7.50-7.53 (d, 1H, \(J= 9\) Hz), 7.57 (s, 1H), 7.90 (s,1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) (ppm): 21.40, 21.98, 25.34, 38.14, 117.67, 121.28, 129.47, 129.50, 139.97; MS (EI): 256, 239,210, 196, 182, 168, 167, 144, 131, 118, 91, 79, 65, 51, 41, 40 m/z.

**Entry 7, Table 1**: 1-[1-(2-methoxyphenyl)-1H-1,2,3-triazol-4-yl]cyclohexanol

IR (Znse): 3229, 3107, 3063, 2934, 2855, 1872, 1726, 1613, 1595, 1516, 1438, 1413, 1364, 1305, 1255, 1225, 1155, 1106, 1080, 1058, 1036, 968, 895, 876, 826 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) (ppm): 1.26-1.41 (m, 2H), 1.64 (s, 2H), 1.77-1.82 (t, 2H, \(J= 6\) Hz ), 1.92-1.97 (m, 2H), 2.03-2.07 (m, 2H), 2.32 (s, 1H, -OH), 3.87 (s, 3H), 7.00-7.03 (d, 2H, \(J= 9\) Hz), 7.61-7.64 (d, 2H, \(J= 9\) Hz ), 7.83 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)):
δ (ppm): 21.99, 25.35, 38.12, 55.63, 69.67, 114.74, 122.22; MS (EI): 244 (M⁺-29), 227, 212, 198, 184, 160, 147, 132, 115, 103, 92, 77, 64, 51, 41, 40 m/z.

**Entry 8, Table 1:** 1-(1-phenyl-1H-1,2,3-triazol-4-yl)cyclohexanol

![Chemical Structure](image)

¹H NMR (300 MHz, CDCl₃): δ (ppm): 1.01-1.38 (m, 2H), 1.43-1.66 (m, 3H), 1.79 (s, 2H), 1.98-2.06 (m, 3H), 2.30 (s, 1H, -OH), 7.53 (s, 3H), 7.75 (s, 2H), 7.92 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 21.98, 25.34, 38.12, 69.71, 117.98, 120.57, 128.68, 129.73, 137.15; MS (EI): 243, 215, 196, 182, 168, 154, 141, 130, 117, 104, 91, 77, 66, 51, 41, 40 m/z.

**Entry 9, Table 1:** 1-[1-(4-methoxyphenyl)-1H-1,2,3-triazol-4-yl]cyclohexanol

![Chemical Structure](image)

¹H NMR (300 MHz, CDCl₃): δ (ppm): 1.26-1.46 (m, 2H), 1.59-1.64 (s, 2H), 1.81-1.82 (d, 2H, J= 3 Hz), 1.93-2.10 (m, 4H), 2.67 (s, 1H, -OH), 3.88 (s, 3H), 7.00-7.03 (d, 2H, J= 9 Hz), 7.61-7.64 (d, 2H, J= 9 Hz), 7.85 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 21.98, 22.17, 22.46, 25.35, 26.42, 38.14, 55.63, 69.64, 114.76, 122.08, 122.22, 125.85, 130.62, 159.81; MS (EI): 244 (M⁺-29), 227, 212, 198, 184, 160, 147, 132, 115, 103, 92, 77, 64, 51, 41, 40 m/z.

**Entry 10, Table 1:** 1-(2-methoxyphenyl)-4-(4-methylphenyl)-1H-1,2,3-triazole

![Chemical Structure](image)

IR (Znse): 3159, 3017, 2925, 2856, 2111, 2086, 1913, 1725, 1603, 1590, 1516, 1493, 1475, 1289, 1256, 1227, 1179, 1126, 1088, 1020, 932 809, 749, 715 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ (ppm): 2.41 (s, 3H), 3.92 (s, 3H), 7.10-7.15 (t, 2H, J= 9 Hz), 7.26- 7.29 (d, 1H, J= 9 Hz), 7.44 (t, 1H), 7.81-7.85 (dd, 3H, J= 6, 3 Hz), 8.30 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 21.30, 56.06, 112.36, 121.17, 121.51, 125.49, 125.78, 126.40,
127.75, 130.11, 137.99, 147.22, 151.18; MS (EI): 265, 238, 237, 222, 207, 194, 179, 165, 152, 130, 115, 103, 91, 77, 51 m/z.

Entry 13, Table 1: 1-(naphthalen-1-yl)-4-phenyl-1H-1,2,3-triazole

\[
\text{N} \quad \text{N} \quad \text{N}
\]

\[1^1\text{H NMR (300 MHz, CDCl}_3\text{): } \delta \text{ (ppm): 7.28-7.30 (d, 2H, } J= 6 \text{ Hz ), 7.46- 7.59 (m, 5H), 7.57-7.59 (d, 2H, } J= 6 \text{ Hz), 7.66- 7.68 (d, 2H, } J= 6 \text{ Hz), 7.84- 7.87 (m, 1H), 8.13-8.16 (m, 1H); } \text{ } ^{13}\text{C NMR (75 MHz, CDCl}_3\text{): } \delta \text{ (ppm): 113.95, 122.61, 124.73, 125.70, 126.18, 126.45, 126.93, 127.78, 134.39, 136.54.}\]

Entry 14, Table 1: 1-(4-methylphenyl)-4-phenyl-1H-1,2,3-triazole

\[
\text{N} \quad \text{N} \quad \text{N}
\]

\[1^1\text{H NMR (300 MHz, CDCl}_3\text{): } \delta \text{ (ppm): 2.40 (s, 3H), 7.23-7.26 (m, 6H), 7.34- 7.35 (m, 3H), 7.85 (s, 1H); } ^{13}\text{C NMR (75 MHz, CDCl}_3\text{): } \delta \text{ (ppm): 21.18, 124.99, 126.86, 128.54, 129.10, 129.89, 133.28, 134.12, 137.61, 139.33.}\]

Entry 15, Table 1: 4-(4-chlorophenyl)-1-(4-methylphenyl)-1H-1,2,3-triazole

\[
\text{N} \quad \text{N} \quad \text{N}
\]

\[1^1\text{H NMR (300 MHz, CDCl}_3\text{): } \delta \text{ (ppm): 2.41 (s, 3H), 7.15-7.17 (d, 2H, } J= 6 \text{ Hz), 7.23-7.26 (m, 4H), 7.31-7.33 (d, 2H, } J= 6 \text{ Hz), 7.85 (s, 1H); } ^{13}\text{C NMR (75 MHz, CDCl}_3\text{): } \delta \text{ (ppm): 21.17, 125.29, 129.12, 129.74, 130.02, 133.27, 133.82, 135.31, 136.54, 139.61.}\]

Entry 16, Table 1: 4-(4-chlorophenyl)-1-(naphthalen-1-yl)-1H-1,2,3-triazole

\[
\text{N} \quad \text{N} \quad \text{N}
\]

\[1^1\text{H NMR (300 MHz, CDCl}_3\text{): } \delta \text{ (ppm): 7.30 (s, 1H ), 7.47- 7.60 (m, 6H), 7.60-7.66 (d, 1H).}\]
$^{1}H, J = 12 \text{ Hz}$, 7.85-7.88 (dd, 2H, $J = 6, 3 \text{ Hz}$), 8.14-8.18 (t, 2H, $J = 6 \text{ Hz}$); $^{13}C$ NMR (75 MHz, CDCl$_3$): $\delta$ (ppm): 113.93, 122.57, 124.71, 125.68, 126.16, 126.43, 126.90, 127.75, 134.36, 136.53.

Entry 1, table 1:
Entry 2, table 1:
Entry 6, table 1:
Entry 9 table 1:
Entry 10, table 1:
Entry 13, table 1:
Entry 14, table 1:
Entry 15, table 1:
Entry 16, table 1: