Electronic Supplementary Information (ESI)

JandaJel as a polymeric supports to improve the catalytic efficiency of immobilized-1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) under solvent-free conditions.

Daniela Lanari,*a Roberto Ballini,b Simona Bonollo,a Alessandro Palmieri,b Ferdinando Pizzo,a and Luigi Vaccaro*a

a Laboratory of Green Synthetic Organic Chemistry, CEMIN - Dipartimento di Chimica, Università di Perugia Via Elce di Sotto, 8; Perugia, Italia.
Fax: +39 075 5855560; Tel: +39 075 5855541; E-mail: luigi@unipg.it
b "Green Chemistry Group" School of Science and Technology, Chemistry Division, Via S. Agostino 1, 62032 Camerino-Italy.

CONTENTS
page S2-S3 Experimental Section
page S4-S6 Representative experimental procedure for the synthesis of catalysts 1a-g and characterization (elemental analysis, FT-IR, SEM).
page S7 Representative experimental procedure for the Michael addition of thiols and the thiolysis of epoxides.
page S8-S10 Full characterization data (1H NMR, 13C NMR, GC-EIMS, mp, elemental analyses) for compounds 10, 11, 12, 18, 19, 20, 29.
page S11-S17 Copies of the 1H and 13C NMR for compounds 10, 11, 12, 18, 19, 20, 29.
Experimental section

All chemicals were purchased and used without any further purification.

GC analyses were performed by using Hewett-Packard HP 5890 series II equipped with a capillary column SPB-5 (30 m, 0.25 mm), a FID detector and hydrogen as gas carrier. GC-EIMS analyses were carried out by using a Hewett-Packard HP 6890 Series GC system/5973 Mass Selective Detector equipped with a electron impact ionizer at 70 eV. All $^1$H NMR and $^{13}$C NMR spectra were recorded at 200 MHz or 400 MHz, and at 50.3 or 100.6 MHz respectively, using a Bruker DRX-ADVANCE 200 MHz and a Bruker DRX-ADVANCE 400 MHz spectrometers. Deuterated solvents were used with the residual peak as internal standard, or TMS in the case of CDCl$_3$. Chemical shift was reported in ppm and coupling constants in Hertz. All melting points were measured with Buchi Melting Point 510 apparatus and are uncorrected. Microanalyses were realized by using a Carlo Erba Elemental analyzer mod. 1106. Thin Layer Chromatography analyses were performed on silica gel on aluminum plates and UV and/or KMnO$_4$ were used as revealing systems. Column chromatographies were performed by using silica gel 230-400 mesh and eluting as reported below. SEM pictures of gold coated polymers (instrument EMITECH K55OX SPUTTER COATER) were taken on a SEM XL30 PHILIPS. FTIR spectra were recorded on a Bruker ISF 28.

Compounds 4, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25 (α and β regioisomers), 26 (α and β regioisomers), 27 (α and β regioisomers), 28 (α$^{13}$ and β$^{14}$ regioisomers), 30, 31, 32, 33, 34, 35, 36, 37, 38 are known and their spectroscopic data are in agreement with those reported in literature.

Compounds 10, 11, 12, 18, 19, 20, 29 are new and their characterization data ($^1$H NMR, $^{13}$C NMR, GC-EIMS, mp and elemental analyses) are reported below.

References

Representative experimental procedure for the synthesis of JJ-TBD 1a

A two-necked round-bottomed flask (25 ml) equipped with a magnetic stirrer, reflux condenser, and inert gas in- and outlet was charged with 7 ml of anhydrous THF and TBD (0.134 g, 0.96 mmol). The stirred solution was cooled to -78°C, and n-BuLi in hexane (0.6 ml, 0.96 mmol) was added drop wise under nitrogen. After the addition was complete, the solution was stirred for additional 2 h and JandaJel-Cl (200-400 mesh, 2% cross-linked, 1.163 g, 0.55 mmol Cl/g, 0.64 mmol) was added to the solution. The mixture was allowed to warm slowly to room temperature and stirred for 48 h under nitrogen. Then 2 ml of methanol were added to the reaction mixture, the polymer beads were isolated by filtration and washed thoroughly with THF-MeOH (1:1), methanol, methanol-water (1:1), acetone, THF, and dichloromethane. The catalyst was subsequently dried under vacuum for 15 h at room temperature and 4 h at 50 °C furnishing JJ-TBD 1a as a yellow solid. Elemental analysis: C, 87.76; H, 7.69; N, 1.45; 0.34 mmol TBD/g.

Data for:
JJ-TBD 100-200 mesh, 2% cross-linked 1b: Yellow solid. Elemental analysis: C, 87.47; H, 7.71; N, 2.04; 0.48 mmol TBD/g.

JJ-TBD 50-100 mesh, 2% cross-linked 1c: Yellow solid. Elemental analysis: C, 89.17; H, 8.10, N, 2.07; 0.49 mmol TBD/g.

JJ-TBD 100-200 mesh, 1% cross-linked 1d: Yellow solid. Elemental analysis: C, 88.98; H, 7.87, N, 2.54; 0.60 mmol TBD/g.

PS-TBD 200-400 mesh, 2% cross-linked 1e: Pale yellow solid. Elemental analysis: C, 73.98; H, 8.90, N, 10.12; 2.41 mmol TBD/g.

PS-TBD 100-200 mesh, 2% cross-linked 1f: White solid. Elemental analysis: C, 74.12; H, 8.43, N, 9.98; 2.38 mmol TBD/g.

PS-TBD 50-100 mesh, 1% cross-linked 1g: Pale yellow solid. Elemental analysis: C, 75.02; H, 8.19, N, 10.27; 2.45 mmol TBD/g.
FTIR spectra of JandaJel-TBD catalyst 1a in comparison to those of the starting material JandaJel-Cl.
Representative SEM IMAGE for catalyst 1a. Size and pictures for all the other catalysts were identical.
Representative experimental procedure for the Michael addition of 1-butanethiol (3a) to (E)-benzylideneacetone (2a) catalyzed by polymer-supported-TBD 1a-h under solvent-free conditions.

In a screw-capped vial equipped with a magnetic stirrer JJ-TBD 1b (0.021 g, 0.48 mmol TBD/g, 0.01 mmol), (E)-benzylideneacetone (2a) (0.292 g, 2.0 mmol) and 1-butanethiol (3a) (0.215 ml, 2 mmol) were consecutively added and the resulting mixture was left under stirring at 30 °C. After 40 minutes, ethyl acetate was added, the catalyst recovered by filtration, and the organic solvent evaporated under vacuum to give ≥ 98% pure 4-(butylthio)-4-phenylbutan-2-one (4) as a yellowish oil (0.463 g, 98% yield).

Representative experimental procedure for the thiolysis of 2,3-epoxypropyl-phenylether (5a) by thiophenol (3b) catalyzed by polymer-supported-TBD 1a-h under solvent-free conditions.

In a screw-capped vial equipped with a magnetic stirrer JJ-TBD 1b (0.031 g, 0.48 mmol TBD/g, 0.015 mmol), 2,3-epoxypropyl-phenylether (5a) (0.410 ml, 3.03 mmol) and thiophenol (3b) (0.311 ml, 3.03 mmol) were consecutively added and the resulting mixture was left under stirring at 30 °C. After 100 minutes, ethyl acetate was added, the catalyst recovered by filtration, and the organic solvent evaporated under vacuum to give ≥ 98% pure 1-phenoxy-3-(phenylthio)propan-2-ol (6) as a colourless oil (0.764 g, 97% yield).
Characterization data for new compounds 10, 11, 12, 18, 19, 20, 29.

4-Butylsulfanyl-4-(4-chlorophenyl)-butan-2-one (10)

\[
\begin{align*}
\text{Cl} & \quad \text{SBu} \\
\text{O} & \\
\end{align*}
\]

Isolated in 99% yield. Colourless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = 0.84\) (t, 3H, \(J = 7.3\) Hz), 1.20-1.40 (m, 2H), 1.40-1.55 (m, 2H), 2.09 (s, 3H), 2.20-2.40 (m, 2H), 2.90-3.00 (m, 2H), 4.29 (t, 1H, \(J = 7.2\) Hz), 7.20-7.35 (m, 4H). \(^{13}\)C NMR (CDCl\(_3\), 100.6 MHz) \(\delta = 205.2, 140.7, 129.1, 128.6, 50.0, 43.3, 31.1, 31.0, 30.7, 21.9, 13.6\). Anal. calc. for C\(_{14}\)H\(_{19}\)ClOS (FW 271): C, 62.09; H, 7.07; S 11.84. Found: C, 61.81; H, 7.04; S, 11.89. GC-EIMS (m/z, %) 270 (M\(^+\), 63), 213 (46), 184 (27), 183 (27), 182 (84), 181 (54), 138 (61), 103 (42), 102 (24), 77 (23), 43 (100).

4-(4-Chlorophenyl)-4-phenylsulfanyl-butan-2-one (11)

\[
\begin{align*}
\text{Cl} & \quad \text{SPh} \\
\text{O} & \\
\end{align*}
\]

Isolated in 99% yield. White solid, m.p. = 101-103 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = 2.05\) (s, 3H), 3.00 (d, 2H, \(J = 7.3\) Hz), 4.66 (t, 1H, \(J = 7.2\) Hz), 7.10-7.30 (m, 9H). \(^{13}\)C NMR (CDCl\(_3\), 100.6 MHz) \(\delta = 205.0, 139.7, 133.4, 132.9, 129.0, 128.8, 128.5, 127.8, 49.1, 47.2, 30.5\). Anal. calc. for C\(_{16}\)H\(_{15}\)ClOS (FW 291): C, 66.08; H, 5.20; S 11.03. Found: C, 65.78; H, 5.18; S, 11.08. GC-EIMS (m/z, %) 291 (M\(^+\), 7), 290 (40), 181 (88), 180 (24), 103 (42), 43 (100).

4-(4-Chlorophenyl)-4-\(p\)-tolylsulfanyl-butan-2-one (12)

\[
\begin{align*}
\text{Cl} & \quad \text{S} \\
\text{O} & \\
\end{align*}
\]

Isolated in 96% yield. White solid, m.p. = 89-91 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = 2.05\) (s, 3H), 2.28 (s, 3H), 2.99 (d, 2H, \(J = 7.4\) Hz), 4.59 (t, 1H, \(J = 7.2\) Hz), 7.03 (d, 2H, \(J = 7.8\) Hz), 7.10-7.23 (m, 6H). \(^{13}\)C NMR (CDCl\(_3\), 100.6 MHz) \(\delta = 205.0, 139.7, 138.0, 133.5, 132.8, 129.6, 128.9, 128.4, 49.0, 47.6, 30.5, 21.0\). Anal. calc. for C\(_{17}\)H\(_{17}\)ClOS (FW 305): C, 66.98; H, 5.62; S 10.52. Found: C, 67.30; H, 5.59; S, 10.55. GC-EIMS (m/z, %) (M\(^+\), 34), 181 (45), 124 (81), 91 (22), 43 (100).
4-Butylsulfanyl-heptan-2-one (18)

Isolated in 88% yield. Colourless oil. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 0.85-1.05$ (m, 6H), 1.30-1.65 (m, 8H), 2.15 (s, 3H), 2.48 (t, $2H, J = 7.4$ Hz), 2.61 (dd, 1H, $J = 6.7, 16.7$ Hz), 2.69 (dd, 1H, $J = 7.1, 16.7$ Hz), 3.00-3.15 (m, 1H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta =$ 207.1, 49.7, 40.3, 37.5, 31.8, 30.7, 30.5, 22.0, 19.9, 13.8, 13.6. Anal. calc. for C$_{11}$H$_{22}$OS (FW 202): C, 65.29; H, 10.96; S 15.85. Found: C, 65.58; H, 11.00; S, 15.79. GC-EIMS (m/z, %) (M+, 48), 145 (32), 117 (22), 55 (20), 43 (100).

4-Phenylsulfanyl-heptan-2-one (19)

Isolated in 98% yield. Colourless oil. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 0.90$ (t, 3H, $J = 6.9$ Hz), 1.40-1.65 (m, 4H), 2.12 (s, 3H), 2.63 (dd, 1H, $J = 7.3, 17.1$ Hz), 2.72 (dd, 1H, $J = 6.2, 17.1$ Hz), 3.55-3.65 (m, 1H), 7.20-7.35 (m, 3H), 7.35-7.45 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta =$ 206.8, 134.4, 132.2, 128.9, 127.0, 49.0, 43.4, 36.9, 30.6, 20.0, 13.7. Anal. calc. for C$_{13}$H$_{18}$OS (FW 222): C, 70.22; H, 8.16; S 14.42. Found: C, 70.54; H, 8.18; S, 14.35. GC-EIMS (m/z, %) 222 (M+, 60), 110 (96), 109 (28), 43 (100).

4-4p-Tolylsulfanyl-heptan-2-one (20)

Isolated in 97% yield. Colourless oil. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 0.90$ (t, 3H, $J = 6.4$ Hz), 1.40-1.60 (m, 4H), 2.12 (s, 3H), 2.33 (s, 3H), 2.59 (dd, 1H, $J = 7.3, 17.0$ Hz), 2.69 (dd, 1H, $J = 6.3, 17.0$ Hz), 3.45-3.55 (m, 1H), 7.10 (d, 2H, $J = 7.9$ Hz), 7.31 (d, 2H, $J = 8.0$ Hz). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta =$ 206.9, 137.4, 133.1, 130.4, 129.6, 49.0, 43.8, 36.8, 30.6, 21.0, 20.0, 13.8. Anal. calc. for C$_{14}$H$_{20}$OS (FW 236): C, 71.14; H, 8.53; S 13.57. Found: C, 70.80; H, 8.49; S, 13.52. GC-EIMS (m/z, %) 236 (M+, 100), 151 (26), 137 (44), 124 (100), 123 (85), 113 (30), 91 (100), 79 (39), 77 (40), 45 (29), 43 (100).

1-Butylsulfanyl-octan-2-ol (29)
Isolated in 90\% yield. Colourless oil. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ = 0.85-1.00 (m, 6H), 1.25-1.65 (m, 15H), 2.43 (dd, 1H, $J$ = 9.1, 13.6 Hz), 2.52 (t, 2H, $J$ = 7.4 Hz), 2.74 (dd, 1H, $J$ = 3.2, 13.6 Hz), 3.55-3.65 (m, 1H). $^{13}$C NMR (CDCl$_3$, 100.6 MHz) $\delta$ = 69.1, 40.3, 36.3, 31.9, 31.8, 29.3, 25.8, 22.6, 22.0, 14.1, 13.7. Anal. calc. for C$_{12}$H$_{26}$OS (FW 218): C, 65.99; H, 12.00; S 14.68. Found: C, 66.72; H, 11.96; S, 14.73. GC-EIMS (m/z, %) 218 ($M^+$, 12), 104 (75), 56 (100), 43 (23).
$^1$H and $^{13}$C-NMR Spectra