

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.

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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 ^1H 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**,¹ **6**,² **7**,³ **8**,⁴ **9**,⁵ **13**,¹ **14**,⁶ **15**,⁴ **16**,⁷ **17**,⁸ **21**,¹ **22**,² **23**,¹ **24**,⁹ **25** (α and β regioisomers),¹⁰ **26** (α and β regioisomers),¹¹ **27** (α and β regioisomers),¹² **28** (α ¹³ and β ¹⁴ regioisomers), **30**,¹¹ **31**,¹⁴ **32**,¹⁵ **33**,¹⁶ **34**,¹¹ **35**,¹² **36**,¹⁷ 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 (^1H NMR, ^{13}C NMR, GC-EIMS, mp and elemental analyses) are reported below.

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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.

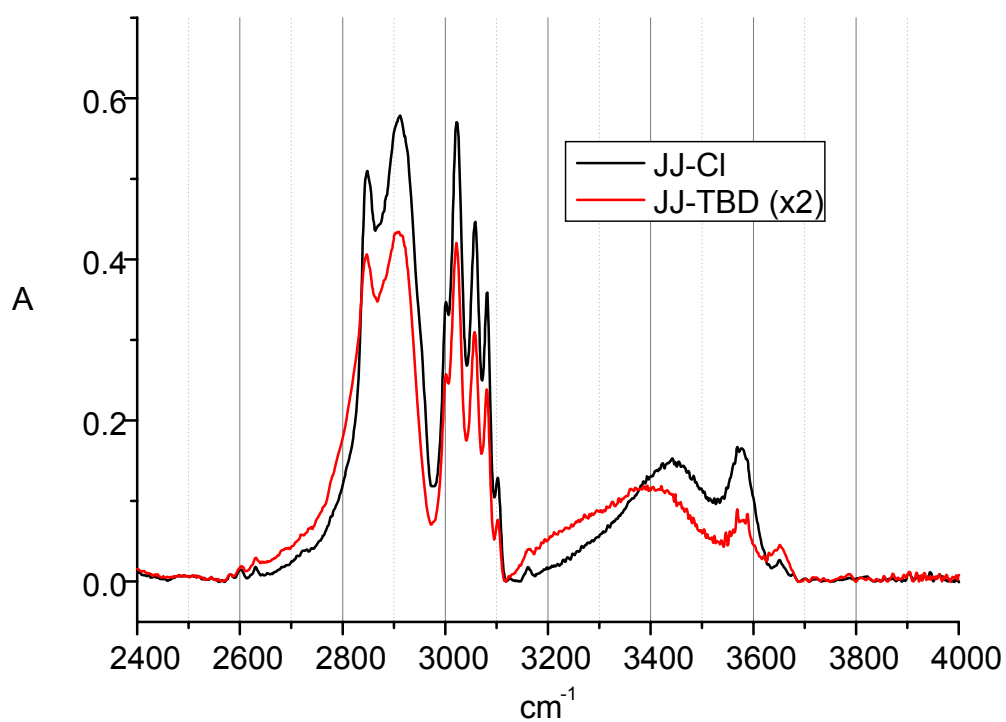
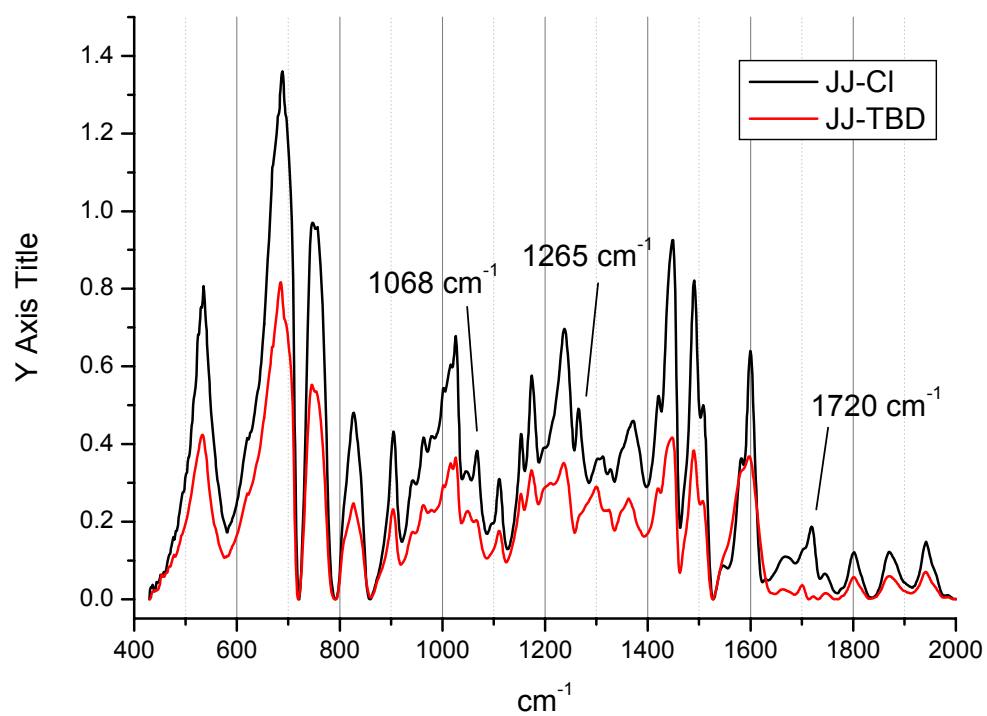
JJ-TBD 100-200 mesh, 1% cross-linked **1d**: Yellow solid. Elemental analysis: C, 88.98; H, 7.87, N, 2.54; 0.60 mmol TBD/g.

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.

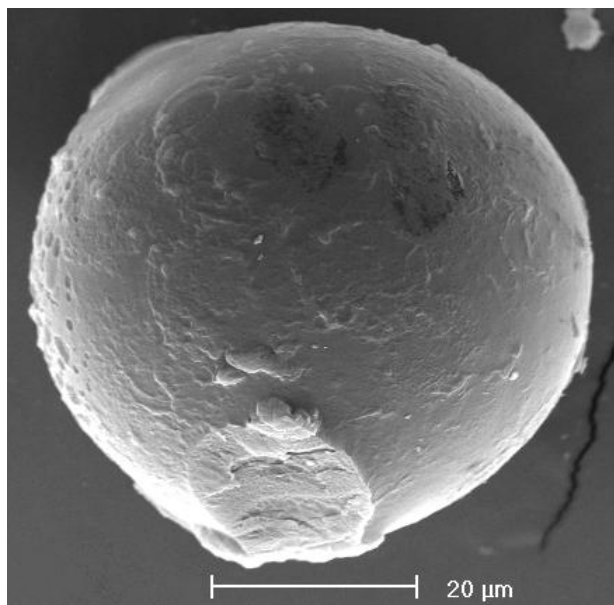
PS-TBD 100-200 mesh, 2% cross-linked **1f**: White solid. Elemental analysis: C, 74.12; H, 8.43, N, 9.98; 2.38 mmol TBD/g.

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.

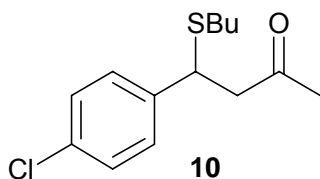
In a screw-capped vial equipped with a magnetic stirrer JJ-TBD **1b** (0.021 g, 0.48 mmol TBD/g, 0.01 mmol), (*E*)-benzylideneacetone (**2a**) (0.292 g, 2.0 mmol) and 1-butanethiol (**3a**) (0.215 ml, 2 mmol) were consecutively added and the resulting mixture was left under stirring at 30 °C. After 40 minutes, ethyl acetate was added, the catalyst recovered by filtration, and the organic solvent evaporated under vacuum to give $\geq 98\%$ 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 $\geq 98\%$ pure 1-phenoxy-3-(phenylthio)propan-2-ol (**6**) as a colourless oil (0.764 g, 97% yield).

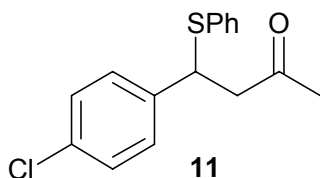
Characterization data for new compounds 10, 11, 12, 18, 19, 20, 29.

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



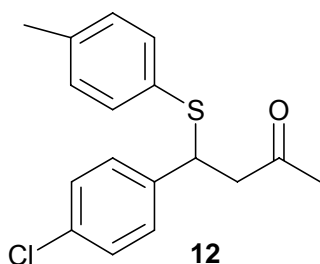
Isolated in 99% yield. Colourless oil. ^1H NMR (CDCl_3 , 400 MHz) δ = 0.84 (t, 3H, J = 7.3 Hz), 1.20-1.40 (m, 2H), 1.40-1.55 (m, 2H), 2.09 (s, 3H), 2.20-2.40 (m, 2H), 2.90-3.00 (m, 2H), 4.29 (t, 1H, J = 7.2 Hz), 7.20-7.35 (m, 4H). ^{13}C NMR (CDCl_3 , 100.6 MHz) δ = 205.2, 140.7, 132.8, 129.1, 128.6, 50.0, 43.3, 31.1, 31.0, 30.7, 21.9, 13.6. Anal. calc. for $\text{C}_{14}\text{H}_{19}\text{ClOS}$ (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)



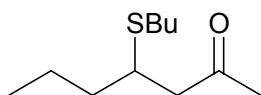
Isolated in 99% yield. White solid, m.p. = 101-103 °C. ^1H NMR (CDCl_3 , 400 MHz) δ = 2.05 (s, 3H), 3.00 (d, 2H, J = 7.3 Hz), 4.66 (t, 1H, J = 7.2 Hz), 7.10-7.30 (m, 9H). ^{13}C NMR (CDCl_3 , 100.6 MHz) δ = 205.0, 139.7, 133.4, 132.9, 132.9, 129.0, 128.8, 128.5, 127.8, 49.1, 47.2, 30.5. Anal. calc. for $\text{C}_{16}\text{H}_{15}\text{ClOS}$ (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), 43 (100).

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



Isolated in 96% yield. White solid, m.p. = 89-91 °C. ^1H NMR (CDCl_3 , 400 MHz) δ = 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) δ = 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 $\text{C}_{17}\text{H}_{17}\text{ClOS}$ (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).

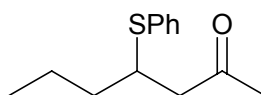
4-Butylsulfanyl-heptan-2-one (18)



18

Isolated in 88% yield. Colourless oil. ^1H NMR (CDCl_3 , 400 MHz) δ = 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) δ = 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 $\text{C}_{11}\text{H}_{22}\text{OS}$ (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).

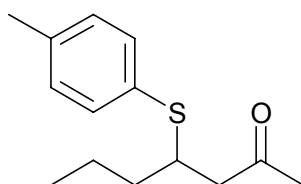
4-Phenylsulfanyl-heptan-2-one (19)



19

Isolated in 98% yield. Colourless oil. ^1H NMR (CDCl_3 , 400 MHz) δ = 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) δ = 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 $\text{C}_{13}\text{H}_{18}\text{OS}$ (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 , %) (M^+ , 60), 110 (96), 109 (28), 43 (100).

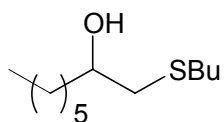
4-*p*-Tolylsulfanyl-heptan-2-one (20)



20

Isolated in 97% yield. Colourless oil. ^1H NMR (CDCl_3 , 400 MHz) δ = 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) δ = 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 $\text{C}_{14}\text{H}_{20}\text{OS}$ (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 , %) (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)



29

Isolated in 90% yield. Colourless oil. ^1H NMR (CDCl_3 , 400 MHz) δ = 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) δ = 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 $\text{C}_{12}\text{H}_{26}\text{OS}$ (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).

¹H and ¹³C-NMR Spectra

