## Supplementary Information

# Supramolecular Organogels Based on *N*-Benzyl, *N'*-Acylbispidinols

**Alexey V. Medved'ko [1], Alexander I. Dalinger [1], Vyacheslav N. Nuriev [1], Vera S. Semashko [1], Andrei V. Filatov [2], Alexander A. Ezhov [3,4], Andrei V. Churakov [5], Judith A. K. Howard [6], Andrey A. Shiryaev [7,8], Alexander E. Baranchikov [1,5], Vladimir K. Ivanov [5,9], and Sergey Z. Vatsadze [1,*]**

[1] Faculty of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia; lexeym@gmail.com (A.V.M.); dal1995@mail.ru (A.I.D.); nvn@org.chem.msu.ru (V.N.N.); vera-s@yandex.ru (V.S.S.); a.baranchikov@yandex.ru (A.E.B.)

[2] Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russia; filatov_andrey_@mail.ru

[3] Faculty of Physics, Lomonosov Moscow State University, 119991 Moscow, Russia; alexander-ezhov@yandex.ru

[4] Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991 Moscow, Russia

[5] Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 119991 Moscow, Russia; churakov@igic.ras.ru (A.V.C.); van@igic.ras.ru (V.K.I.)

[6] Department of Chemistry, University of Durham, Durham DH1 3LE, UK; j.a.k.howard@durham.ac.uk

[7] Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russia; a_shiryaev@mail.ru

[8] Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, 119017 Moscow, Russia

[9] Faculty of Material Science, Lomonosov Moscow State University, 119991 Moscow, Russia

* Correspondence: szv@org.chem.msu.ru; Tel.: +7-903-748-7892

Preparation of unsymmetrical bispidines. General method.

To a suspension of bispidine **3** in dry benzene was added a solution of acyl halide (1 eq) in dry benzene. Then the mixture was refluxed under vigorous stirring for 3.5 hours. To obtain the product as the hydrochloride, the resulting gelatinous mass (precipitate or colloidal solution) was centrifuged for 10-15 minutes (6000 rpm) or filtered on a Schott filter (por.40) and then was dried. The free base was isolated from the aqueous solution by treatment with sodium bicarbonate (3 eq.).

**Anti-1,5-dimethyl-3-benzoyl-7-benzyl-3,7-diazabicyclo[3.3.1]nonane-9-ol (4aa).**

140 mg (0.54 mmol) of bispidine **3a** and 75.6 mg (0.54 mmol) of benzoyl chloride in 10 ml of dry benzene give colloidal solution, from which 0.134 g of the free base was isolated. Yield 68%.

NMR $^1$H (DMSO-d$_6$, δ/ ppm, *J*/Hz): 0.65 (s, 3H, $CH_3$); 0.79 (s, 3H, $CH_3$); 2.13 (d, 1H, H6e/8e/6a/8a, *J* = 10.2 Hz); 2.24-2.32 (m, 2H, H6e/8e/6a/8a); 2.37 (d, 1H, H6e/8e/6a/8a, *J* = 11.3 Hz); 2.65 (d, 1H, H4a, *J* = 12,5 Hz); 3.04 (d, 1H, H2a, *J* = 12.5 Hz); 3.13-3.18 (m, 2H, $CH_2$Ph, H9); 3.42 (d, 1H, H2e, *J* = 12.9 Hz); 3.54 (d, 1H, $CH_2$Ph, *J* = 13.3 Hz); 4.47 (d, 1H, H4e, *J* = 13.2 Hz); 4,95 (d, 1H, OH, *J* = 4.7 Hz), 7.21-7.39 (m, 10H, H(Ar)).

NMR $^{13}$C (characteristic signals) (DMSO-d$_6$, δ/ ppm, *J*/Hz): 21.5 (s, $CH_3$); 21.8 (s, $CH_3$); 35.17 (br. s, C1, C5); 52.2 (s, C2); 57.3 (s, C4); 57.8 (s, C6); 58.1 (s, C8); 63.4 (s, $CH_2$Ph); 75.5 (s, C9); 126.2 (s, Ar), 128.3 (s, Ar), 129.0 (s, Ar), 130.16 (s, Ar), 130.45 (s, Ar), 130,56 (s, Ar), 133.15 (s, Ar); 168,5 (s, C=O).

Found (%): C, 75.80; H, 7.95; N, 7.46. Calculated for $C_{23}H_{28}N_2O_2$ (%): C, 75.79; H, 7.74; N, 7.69.

**Anti-1,5-dimethyl-3-benzoyl-7-(4-fluorobenzyl)-3,7-diazabicyclo[3.3.1]nonane-9-ol (4ca)**

70 mg (0.25 mmol) of bispidine **3c** and 35.4 mg (0.25 mmol) of benzoyl chloride in 5 ml of dry benzene give colloidal solution, from which 0.082 g of the free base was isolated. Yield 85%.

NMR $^1$H (DMSO-d$_6$, δ/ ppm, *J*/Hz): 0.65 (s, 3H, CH3), 0.79 (s, 3H, $CH_3$); 2.13 (d, 1H, H6e/8e/6a/8a, *J* = 10.2 Hz); 2.24-2.32 (m, 3H, H6e/8e/6a/8a); 2.65 (d, 1H, H4a, *J* = 12.9 Hz); 3.05 (d, 1H, H2a, *J* = 12.9 Hz); 3.13-3.17 (m, 2H, $CH_2$Ph, H9); 3.42 (d, 1H, H2e, *J* = 13.3 Hz); 3.52 (d, 1H, $CH_2$Ph, *J* = 12.9 Hz); 4.48 (d, 1H, H4e, *J* = 13.1 Hz); 4,95 (d, 1H, OH, *J* = 4.5 Hz); 7.08 (tr, 2H, CH(3,5) ($C_6H_4$F) *J* = 8,4 Hz); 7.29-7.41 (m, 6H, H(Ar)).

NMR $^{13}$C (characteristic signals) (DMSO-d$_6$, δ/ ppm, *J*/Hz): 21.4, 21.8 (both s, 2$CH_3$); 36.1, 36.6 (both s, C1, C5); 52.1, 57.1, 57.8, 58.1 (all s, C2, C4, C6, C8); 62.5 (s, $CH_2$Ph); 75.95 (s, C9); 127, 128.7, 129, 132.3, 130.85, 130.93, 134.9, 137.74 (all s, Ar); 168,5 (s, C=O).

Found (%):C, 72.57; H, 7.09; N, 7.12. Calculated for $C_{23}H_{27}FN_2O_2$ (%):C, 72.23; H, 7.12; N, 7.32.

**Anti-1,5-dimethyl-3-benzoyl-7-(4-chlorobenzyl)-3,7-diazabicyclo[3.3.1]nonane-9-ol (4ba)**

70 mg (0.24 mmol) of bispidine **3b** and 33.4 mg (0.24 mmol) of benzoyl chloride in 5 ml of dry benzene give colloidal solution, from which 0.084 g of the free base was isolated. Yield 88%.

NMR $^1$H (DMSO-d$_6$, δ/ ppm, *J*/Hz): 0.65, 0.79 (both s, 6H, 2$CH_3$); 2.13 (d, 1H, H6e/8e/6a/8a, *J* = 10.8 Hz); 2.23-2.36 (m, 3H, H6e/8e/6a/8a); 2.65 (d, 1H, H4a, *J* = 12.5 Hz); 3.05 (d, 1H, H2a, *J* = 13.9 Hz); 3.13-3.17 (m, 2H, $CH_2$Ph, H9); 3.44 (d, 1H, H2e, *J* = 14.0 Hz); 3.53 (d, 1H, $CH_2$Ph, *J* = 13.9 Hz); 4.49 (d, 1H, H4e, *J* = 12.9 Hz); 4,95 (d, 1H, OH, *J* = 5.28 Hz); 7.29-7.41 (m, 9H, CH(Ar)).

NMR $^{13}$C (characteristic signals) (DMSO-d$_6$, δ/ ppm, *J*/Hz): 21.4, 21.8 (both s, 2$CH_3$); 36.1, 36.6 (both s, C1, C5); 54.9, 55.7, 57.1, 58.1 (all s, C2, C4, C6, C8); 62.5 (s, $CH_2$Ph); 75.9 (s, C9); 127, 128.5, 128.74, 129.25, 132.3, 130.85, 130.93, 137.71(br.) (all s, Ar); 168,5 (s, C=O).

Found (%): C, 69.35; H, 6.95; N, 6.93. Calculated for $C_{23}H_{27}ClN_2O_2$ (%): C, 69.25; H, 6.82; N, 7.02.

**Anti-1,5-dimethyl-3-benzoyl-7-(4-bromobenzyl)-3,7-diazabicyclo[3.3.1]nonane-9-ol (4da)**

140 mg (0.4 mmol) of bispidine **3d** and 56.5 mg (0.4 mmol) of benzoyl chloride in 10 ml of dry benzene give gel, from which 0.14 g of the free base was isolated. Yield 79%.

NMR $^1$H (DMSO-d$_6$, δ/ ppm, *J*/Hz): 0.65, 0.79 (both s, 6H, 2$CH_3$); 2.15 (d, 1H, H6e/8e/6a/8a, *J* = 10.2 Hz); 2.23-2.36 (m, 3H, H6e/8e/6a/8a); 2.65 (d, 1H, H4a, *J* = 12.5 Hz); 3.05 (d, 1H, H2a, *J* = 13.3 Hz); 3.12-3.15 (m, 2H, $CH_2$Ph, H9); 3.42 (d, 1H, H2e, *J* = 13.7 Hz); 3.53 (d, 1H, $CH_2$Ph, *J* = 13.9 Hz); 4.48 (d 1H, H4e, *J* = 12.1 Hz); 4,95 (d, 1H, OH, *J* = 5.09 Hz); 7.29-7.31 (m, 4H, CH(Ar)); 7.40-7.41 (m, 3H, CH(Ar)); 7.44-7.46 (d, 2 H, CH(2,6)(Ar), *J* = 8.4 Hz).

NMR $^{13}$C (characteristic signals) (DMSO-d$_6$, δ/ ppm, *J*/Hz): 21.4, 21.8 (both s, 2$CH_3$); 36.1, 36.6 (both s, C1, C5); 54.6, 57.1, 58.1 (all s, C2, C4, C6, C8); 75.90 (s, C9); 127, 128.7, 131.3, 131.41 (all s, Ar).

Found (%): C, 62.32; H, 6.14; N, 6.10. Calculated for $C_{23}H_{27}BrN_2O_2$ (%): C, 62.31; H, 6.14; N, 6.32.

**Anti-1,5-dimethyl-3-(4-chlorobenzoyl)-7-benzyl-3,7-diazabicyclo[3.3.1]nonane-9-ol (4ab)**

70 mg (0.27 mmol) of bispidine **3a** and 47.1 mg (0.27 mmol) of 4-chlorobenzoyl chloride in 5 ml of dry benzene give gel, from which 0.093 g of the free base was isolated. Yield 78%.

NMR $^1$H (DMSO-d$_6$, δ/ ppm, *J*/Hz): 0.66, 0.79 (both s, 6H, 2$CH_3$); 2.13 (d, 1H, H6e/8e/6a/8a, *J* = 10.9 Hz); 2.25-2.32 (m, 2H, H6e/8e/6a/8a); 2.37 (d, 1H, H6e/8e/6a/8a, *J* = 10.6 Hz); 2.65 (d, 1H, H4a, *J* = 12.9 Hz); 3.06 (d, 1H, H2a, *J* = 13.3 Hz); 3.12-3.18 (m, 2H, $CH_2$Ph, H9); 3.37 (d, 1H, H2e, *J* = 13.5 Hz); 3.52 (d, 1H, $CH_2$Ph, *J* = 13.3 Hz); 4.45 (d, 1H, H4e, *J* = 12.9 Hz); 4,95 (d, 1H, OH, *J* = 4.9 Hz); 7.29-7.31 (m, 4H, CH(Ar)); 7.22-7.34 (m, 7H, CH(Ar)); 7.44-7.46 (d, 2 H, CH(2,6)(Ar), *J* = 8.2 Hz).

NMR $^{13}$C (characteristic signals) (DMSO-d$_6$, δ/ ppm, *J*/Hz): 21.4, 21.8 (both s, 2$CH_3$); 36.1, 36.6 (s, C1, C5); 52.2, 57.3, 57.8, 58.1 (all s, C2, C4, C6, C8); 63.4 (s, $CH_2$Ph); 75.9 (s, C9); 127.2, 128.6, 128.9, 129.0, 133.8, 136.5, 138,77 (all s, Ar); 167,5 (s, C=O).

Found (%): C, 69.48; H, 6.93; N, 6.93. Calculated for $C_{23}H_{27}ClN_2O_2$ (%): C, 69.25; H, 6.82; N, 7.02.

**Anti-1,5-dimethyl-3-(4-chlorobenzoyl)-7-(4-fluorobenzyl)-3,7-diazabicyclo[3.3.1]nonane-9-ol (4cb)**

70 mg (0.25 mmol) of bispidine **3c** and 44.1 mg (0.25 mmol) of 4-chlorobenzoyl chloride in 5 ml of dry benzene give gel, from which 0.089 g of the free base was isolated. Yield 92%.

NMR $^1$H (DMSO-d$_6$, δ/ ppm, *J*/Hz): 0.66, 0.78 (both, 6H, 2CH3); 2.13 (d, 1H, H6e/8e/6a/8a, *J* = 11.49 Hz); 2.23-2.36 (m, 3H, H6e/8e/6a/8a); 2.68 (d, 1H, H4a, *J* = 13.45 Hz); 3.06-3.15 (m, 3H, H2a, CH2Ph, H9); 3.41 (d, 1H, H2e, *J* = 13.33 Hz); 3.54 (d, 1H, $CH_2$Ph, *J* = 13.57 Hz); 4.48 (d, 1H, H4e, *J* = 14.18 Hz); 4,98 (d, 1H, OH, *J* = 5.14 Hz); 7.09 (tr, 2H, CH(3,5) ($C_6H_4$F) *J* = 8,86 Hz); 7.31-7.37 (m, 4H, H(Ar)); 7.49 (d, 2H, H(Ar), *J*=8.44 Hz).

NMR $^{13}$C (characteristic signals) (DMSO-d$_6$, δ/ ppm, *J*/Hz): 21.4, 21.8 (both s, 2$CH_3$); 36.1, 36.6 (s, C1, C5); 52.2, 57.0, 57.8, 58.0 (all s, C2, C4, C6, C8); 62.5 (s, $CH_2$Ph); 75.9 (s, C9); 128.9, 129.0, 133.9, 136.5 (all s, Ar); 167,5 (s, C=O).

Found (%): C, 66.37; H, 6.35; N, 6.61. Calculated for $C_{23}H_{26}ClFN_2O_2$ (%): C, 66.26; H, 6.29; N, 6.72.

**Anti-1,5-dimethyl-3-(4-chlorobenzoyl)-7-(4-chlorobenzyl)-3,7-diazabicyclo[3.3.1]nonane-9-ol (4bb)**

70 mg (0.24 mmol) of bispidine **3b** and 41.7 mg (0.24 mmol) of 4-chlorobenzoyl chloride in 5 ml of dry benzene give gel, from which 0.072 g of the free base was isolated. Yield 69%.

NMR $^1$H (DMSO-d$_6$, δ/ ppm, *J*/Hz): 0.66, 0.79 (both s, 6H, 2$CH_3$); 2.14 (d, 1H, H6e/8e/6a/8a, *J* = 11.49 Hz); 2.24-2.35 (m, 3H, H6e/8e/6a/8a); 2.68 (d, 1H, H4a, *J* = 13.45 Hz); 3.09 (*д*, 1H, H2a, *J* = 13.45 Hz); 3.12-3.16 (m, 2H, $CH_2$Ph, H9); 3.41 (d, 1H, H2e, *J* = 12.69 Hz); 3.55 (d, 1H, $CH_2$Ph, *J* = 13.45 Hz);

4.48 (d, 1H, H4e, *J* = 13.45 Hz); 4,98 (d, 1H, OH, *J* = 5.01 Hz); 7.31-7.37 (m, 6H, CH(Ar)), 7.47(d, 2H, H(2,6)(ArC=O), *J* = 8.19 Hz).

NMR $^{13}$C (characteristic signals) (DMSO-d$_6$, δ/ ppm, *J*/Hz): 21.4, 21.7 (both s, 2$CH_3$); 36.6 (br. s, C1, C5); 52.1, 53.9, 57.1, 58.0 (all s, C2, C4, C6, C8); 62.45 (s, $CH_2$Ph); 75.8 (s, C9); 128.5, 128.9, 130.9, 137.8 (all s, Ar); 167,5 (s, C=O).

Found (%): C, 63.70; H, 6.25; N, 6.34. Calculated for $C_{23}H_{26}Cl_2N_2O_2$ (%): C, 63.74; H, 6.05; N, 6.46.

**Anti-1,5-dimethyl-3-(4-chlorobenzoyl)-7-(4-bromobenzyl)-3,7-diazabicyclo[3.3.1]nonane-9-ol (4db)**

140 mg (0.4 mmol) of bispidine **3d** and 72.2 mg (0.4 mmol) of 4-chlorobenzoyl chloride in 5 ml of dry benzene give gel, from which 0.149 g of the free base was isolated. Yield 79%.

NMR $^1$H (DMSO-d$_6$, δ/ ppm, *J*/Hz): 0.66, 0.79 (both s, 6H, 2CH3); 2.12 (d, 1H, 6a/6e/8a/8e, *J* = 9.78 Hz); 2.23-2.35 (m, 3H, 6a/6e/8a/8e); 2.65 (d, 1H, H4a, *J* = 13.30 Hz); 3.06-3.15 (m, 3H, H2a, H9, -$CH_2$-Ar); 3.38 (d, 1H, ,H2e, *J* = 13.5 Hz); 3.49 (d, 1H, -$CH_2$-Ar, *J* = 13.30 Hz); 4.45 (d, 1H, 4He, *J* = 13,69 Hz); 4.96 (d, 1H, -OH, *J* = 5.09 Hz); 7.26-7.32 (m, 4H, Ar-Br); 7.45-7.48 (m, 4H, Ar-Cl).

NMR $^{13}$C (characteristic signals) (DMSO-d$_6$, δ/ ppm, *J*/Hz): 21.2, 21.7 (both s, 2$CH_3$); 36.1 (br. s, C1, C5); 128.9, 129.0, 131.4, 131.6 (all s, Ar); 171,9 (s, C=O).

Found (%): C, 57.69; H, 5.51; N, 5.85. Calculated for $C_{23}H_{26}BrClN_2O_2$ (%): C, 57.81; H, 5.48; N, 5.86.

**Anti-1,5-dimethyl-3-(2-thiophenecarbonyl)-7-benzyl-3,7-diazabicyclo[3.3.1]nonane-9-ol (4ae)**

70 mg (0.27 mmol) of bispidine **3a** and 39.3 mg (0.27 mmol) of 2-thiophenecarbonyl chloride in 5 ml of dry benzene give gel, from which 0.081 g of the free base was isolated. Yield 81%.

NMR $^1$H (DMSO-d$_6$, δ/ ppm, *J*/Hz): 0.72, 0.80 (both s, 6H, 2$CH_3$); 2.16 (d, 1H, H6e/8e/6a/8a, *J* = 13.69 Hz); 2.24-2.30 (m, 2H, H6e/8e/6a/8a ); 2.35 (d, 2H, H6e/8e/6a/8a, *J* = 12.32 Hz); 2.67 (d, 1H, H4a, *J* = 13.3 Hz); 3.16 (d, 1H, H9, *J* = 5.09 Hz); 3.19-3.24 (m, 2H, H2a, $CH_2$Ph); 3.37 (H2e, under $H_2O$ signal); 3.90 (d, 1H, $CH_2$Ph, *J* = 13.3 Hz); 4.49 (d, 1H, H4e, *J* = 12.9 Hz); 4,96 (d, 1H, OH, *J* = 5.28 Hz); 7.07-7.09 (dd, 1H, CH(4)($C_4H_3S$), $J_1$ = 5.0 Hz, $J_2$ = 3.81 Hz), 7.16-7.28 (m, 6H, CH(Ph), CH(3)($C_4H_3S$)), 7.70 (d, 1H, CH(5)($C_4H_3S$), *J*=4.9 Hz).

NMR $^{13}$C (characteristic signals) (DMSO-d$_6$, δ/ ppm, *J*/Hz): 21.5, 21.7 (both s, 2$CH_3$); 36.2, 36.7 (s, C1, C5); 52.8, 57.6, 57.9 (br.) (all s, C2, C4, C6, C8); 63.4 (s, $CH_2$Ph); 75.9 (s, C9); 127.0, 127.2, 128.5, 128.7, 128.9, 129.0, 138.9 (all s, Ar); 162,2 (s, C=O)

Found (%): C, 68.43; H, 7.10; N, 7.35; S, 8.60. Calculated for $C_{21}H_{26}N_2O_2S$ (%): C, 68.08; H, 7.07; N, 7.56; S, 8.65.

**Anti-1,5-dimethyl-3-(2-thiophenecarbonyl)-7-(4-fluorobenzyl)-3,7-diazabicyclo[3.3.1]nonane-9-ol (4ce)**

70 mg (0.25 mmol) of bispidine **3c** and 36.8 mg (0.25 mmol) of 2-thiophenecarbonyl chloride in 5 ml of dry benzene give gel, from which 0.085 g of the free base was isolated. Yield 88%.

NMR $^1$H (DMSO-d$_6$, δ/ ppm, *J*/Hz): 1.49, 1.56 (both s, 6H, 2CH3); 2.93 (d, 1H, H6e/8e/6a/8a, *J* = 8.19 Hz); 3.02 (m, 2H, H6e/8e/6a/8a), 3.12 (d, 1H, H6e/8e/6a/8a, *J* = 10.76 Hz), 3.43 (d, 1H, H4a, *J* = 12.84 Hz); 3.93-4.01 (m, 3H, H2a, $CH_2$Ph, H9); 4.11 (H2e, under $H_2O$ signal); 4.70 (d, 1H, $CH_2$Ph, *J* = 13.69 Hz); 5.26 (d, 1H, H4e, *J* = 13.2 Hz); 5.75 (d, 1H, OH, *J* = 4.77 Hz); 7.77 (tr, 2H, CH(3,5) ($C_6H_4F$) *J* = 8,56 Hz); 7.84-7.87 (m, 1H, CH(4)($C_4H_3S$)), 8.03-8.06 (m, 3H, CH(2,6), ($C_6H_4F$), CH(3)($C_4H_3S$)), 8.48 (d, 1H, CH(5)($C_4H_3S$), *J* =4.52 Hz)

NMR $^{13}C$ (characteristic signals) (DMSO-$d_6$, δ/ ppm, *J*/Hz): 21.5, 21.7 (both s, $2CH_3$); 36.2, 36.7 (s, C1, C5); 52.7, 57.8 (br.) (all s, C2, C4, C6, C8); 62.4 (s, $CH_2Ph$); 75.9 (s, C9); 127.3, 128.4, 128.9, 129.0, 130.9, 131.6, 138.0 (all s, Ar); 162,3 (s, C=O).

Found (%): C, 64.89; H, 6.41; N, 6.99. Calculated for $C_{21}H_{25}FN_2O_2S$ (%): C, 64.92; H, 6.49; N, 7.21.

**Anti-1,5-dimethyl-3-(2-thiophenecarbonyl)-7-(4-chlorobenzyl)-3,7-diazabicyclo[3.3.1]nonane-9-ol (4be)**

70 mg (0.24 mmol) of bispidine **3b** and 34.8 mg (0.24 mmol) of 2-thiophenecarbonyl chloride in 10 ml of dry benzene give gel, from which 0.87 g of the free base was isolated. Yield 90%.

NMR $^{1}H$ (DMSO-$d_6$, δ/ ppm, *J*/Hz): 0.72, 0.79 (both s, 6H, 2CH3); 2.19 (d, 1H, H6e/8e/6a/8a, *J* = 10.39 Hz); 2.24-2.35 (m, 3H, H6e/8e/6a/8a); 2.68 (d, 1H, H4a, *J* = 13.45 Hz); 3.09 (d, 1H, H2a, *J* = 13.45 Hz); 3.12-3.16 (m, 2H, $CH_2Ph$, H9); 3.41 (d, 1H, H2e, *J* = 12.69 Hz); 3.55 (d, 1H, $CH_2Ph$, *J* = 13.45 Hz); 4.48 (d, 1H, H4e, *J* = 13.45 Hz); 4,98 (d, 1H, OH, *J* = 5.01 Hz); 7.31-7.31 (m, 6H, CH(Ar)), 7.49(d, 2H, H(2,6)(ArC=O), *J* = 8.19 Hz).

NMR $^{13}C$ (characteristic signals) (DMSO-$d_6$, δ/ ppm, *J*/Hz): 21.5, 21.7 (both s, $2CH_3$); 36.2, 36.7 (s, C1, C5); 52.7, 57.5, 57.8 (br.) (all s, C2, C4, C6, C8); 62.4 (s, $CH_2Ph$); 75.8 (s, C9); 127.3, 128.4, 128.9, 129.0, 130.9, 131.6, 138.0 (all s, Ar); 162,2 (s, C=O).

Found (%): C, 62.21; H, 6.15; N, 6.81. Calculated for $C_{21}H_{25}ClN_2O_2S$ (%): C, 62.28; H, 6.22; N, 6.92.

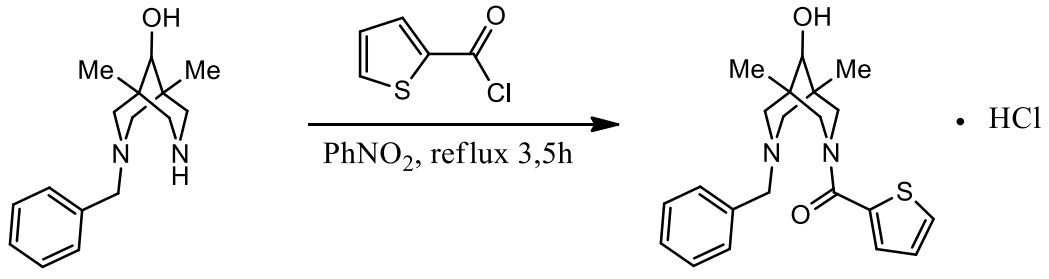
**Anti-1,5-dimethyl-3-(2-thiophenecarbonyl)-7-(4-bromobenzyl)-3,7-diazabicyclo[3.3.1]nonane-9-ol (4de)**

140 mg (0.4 mmol) of bispidine **3d** and 60 mg (0.4 mmol) of 2-thiophenecarbonyl chloride in 10 ml of dry benzene give gel, from which 0.149 g of the free base was isolated. Yield 83%.

NMR $^{1}H$ (DMSO-$d_6$, δ/ ppm, *J*/Hz): 0.72, 0.79 (both s, 6H, $2CH_3$); 2.16-2.34 (m, 4H, H6e/8e/6a/8a); 2.66 (d, 1H, H4a, *J* = 12.7 Hz); 3.09 (m, 3H, H2a, $CH_2Ph$, H9); 3.49 (H2e, under $H_2O$ signal); 3.91 (d, 1H, $CH_2Ph$, *J* = 12.72 Hz); 4.45 (d, 1H, H4e, *J* = 13.5 Hz), 4,98 (d, 1H, OH, *J* = 4.89 Hz); 7.31-7.31 (m, 6H, CH(Ar)), 7.49(d, 2H, CH(Ar), *J* = 8.19 Hz).

Found (%): C, 56.09; H, 5.77; N, 6.03. Calculated for $C_{21}H_{25}BrN_2O_2$ (%): C, 56.12; H, 5.61; N, 6.23.

**4ae*HCl in nitrobenzene**

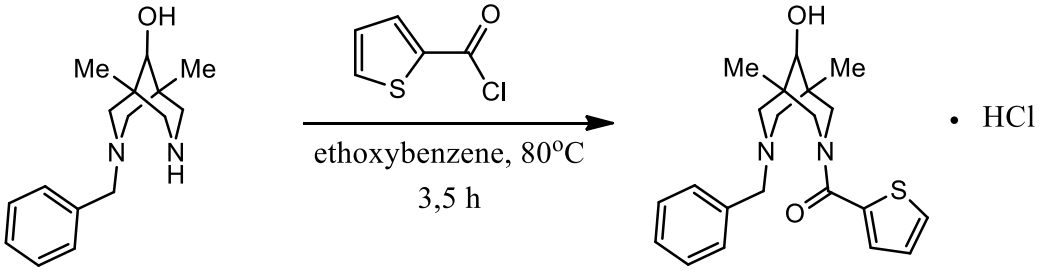



**4ae**

To a suspension of 70 mg (0.27 mmol) of bispidine **3a** in 2.5 ml of nitrobenzene was added dropwise a solution of 39 mg (0.27 mmol) of 2-thiophenecarbonyl chloride in 2.5 mL of nitrobenzene. Then the mixture was refluxed (210 °C) under vigorous stirring for 3.5 hours. Highly viscous and dense amber gel was formed after 2 days at room temperature.

**Figure S1.** Photo of **4ae*HCl** in nitrobenzene.

**4ae*HCl in ethoxybenzene**

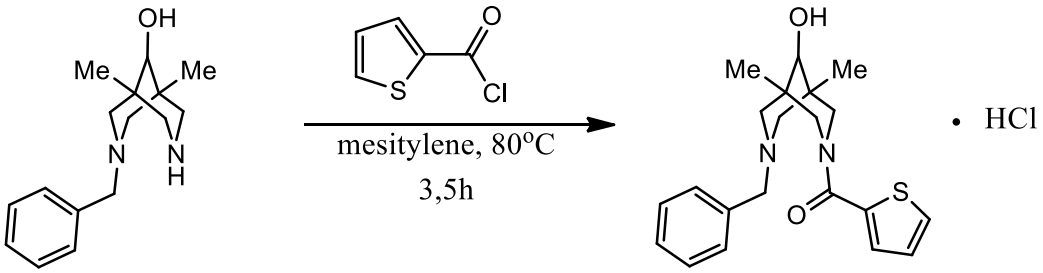



**4ae**

To a suspension of 70 mg (0.27 mmol) of bispidine **3a** in 2.5 mL of ethoxybenzene was added dropwise a solution of 39 mg (0.27 mmol) of 2-thiophenecarbonyl chloride in 2.5 mL of ethoxybenzene. Then the mixture was stirred at 80 °C for 3.5 hours. Highly viscous and dense colourless gel was formed after 1 hour at room temperature.

**Figure S2.** Photo of **4ae*HCl** in ethoxybenzene.

**4ae*HCl in mesitylene**

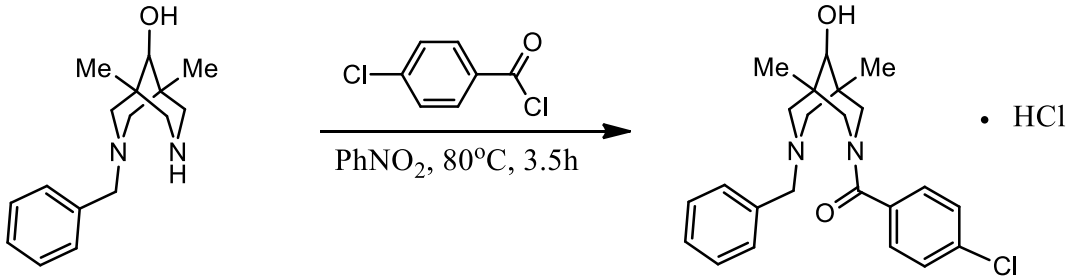



**4ae**

To a suspension of 70 mg (0.27 mmol) of bispidine **3a** in 2.5 mL of mesitylene was added dropwise a solution of 39 mg (0.27 mmol) of 2-thiophenecarbonyl chloride in 2.5 mL of mesitylene. Then the mixture was stirred at 80 °C for 3.5 hours. Loose colourless gel was formed after 1 hour at room temperature.

**Figure S3.** Photo of **4ae*HCl** in mesitylene.

**4ab*HCl in nitrobenzene.**

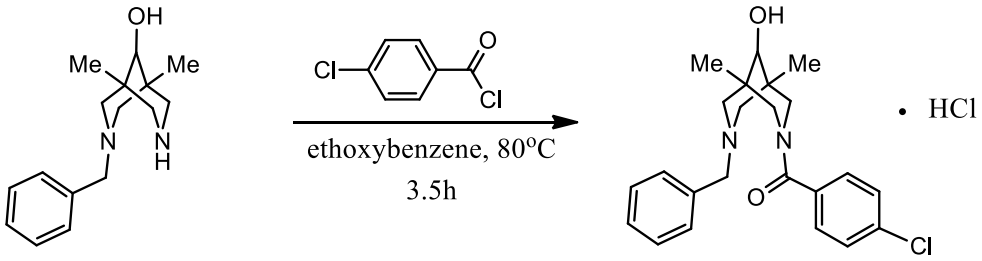



**4ab**

To a suspension of 70 mg (0.27 mmol) of bispidine **3a** in 2.5 mL of nitrobenzene was added dropwise a solution of 47.1 mg (0.27 mmol) of 4-chlorobenzoyl chloride in 2.5 mL of nitrobenzene. Then the mixture was stirred at 80 °C for 3.5 hours. A precipitate was formed.

**Figure S4.** Photo of **4ab*HCl** in nitrobenzene.

**4ab*HCl in ethoxybenzene**

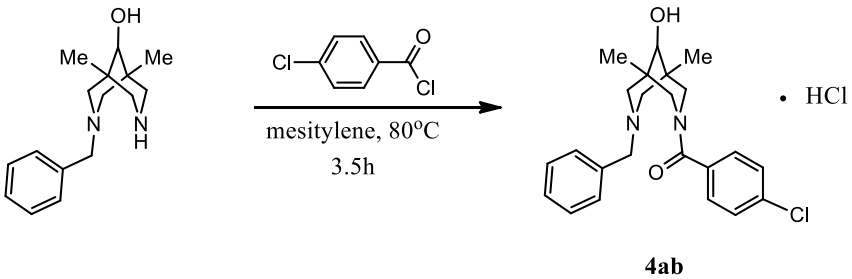



**4ab**

To a suspension of 70 mg (0.27 mmol) of bispidine **3a** in 2.5 mL of ethoxybenzene was added dropwise a solution of 47.1 mg (0.27 mmol) of 4-chlorobenzoyl chloride in 2.5 mL of ethoxybenzene. Then the mixture was stirred at 80 °C for 3.5 hours. Loose colourless gel was formed after 1 hour at room temperature.

**Figure S5.** Photo of **4ab*HCl** in ethoxybenzene.

**4ab*HCl in mesitylene.**




**4ab**

To a suspension of 70 mg (0.27 mmol) of bispidine **3a** in 2.5 mL of mesitylene was added dropwise a solution of 47.1 mg (0.27 mmol) of 4-chlorobenzoyl chloride in 2.5 mL of mesitylene. Then the mixture was stirred at 80 °C for 3.5 hours. Loose colourless gel was formed after 1 hour at room temperature.

**Figure S6.** Photo of **4ab*HCl** in mesitylene.

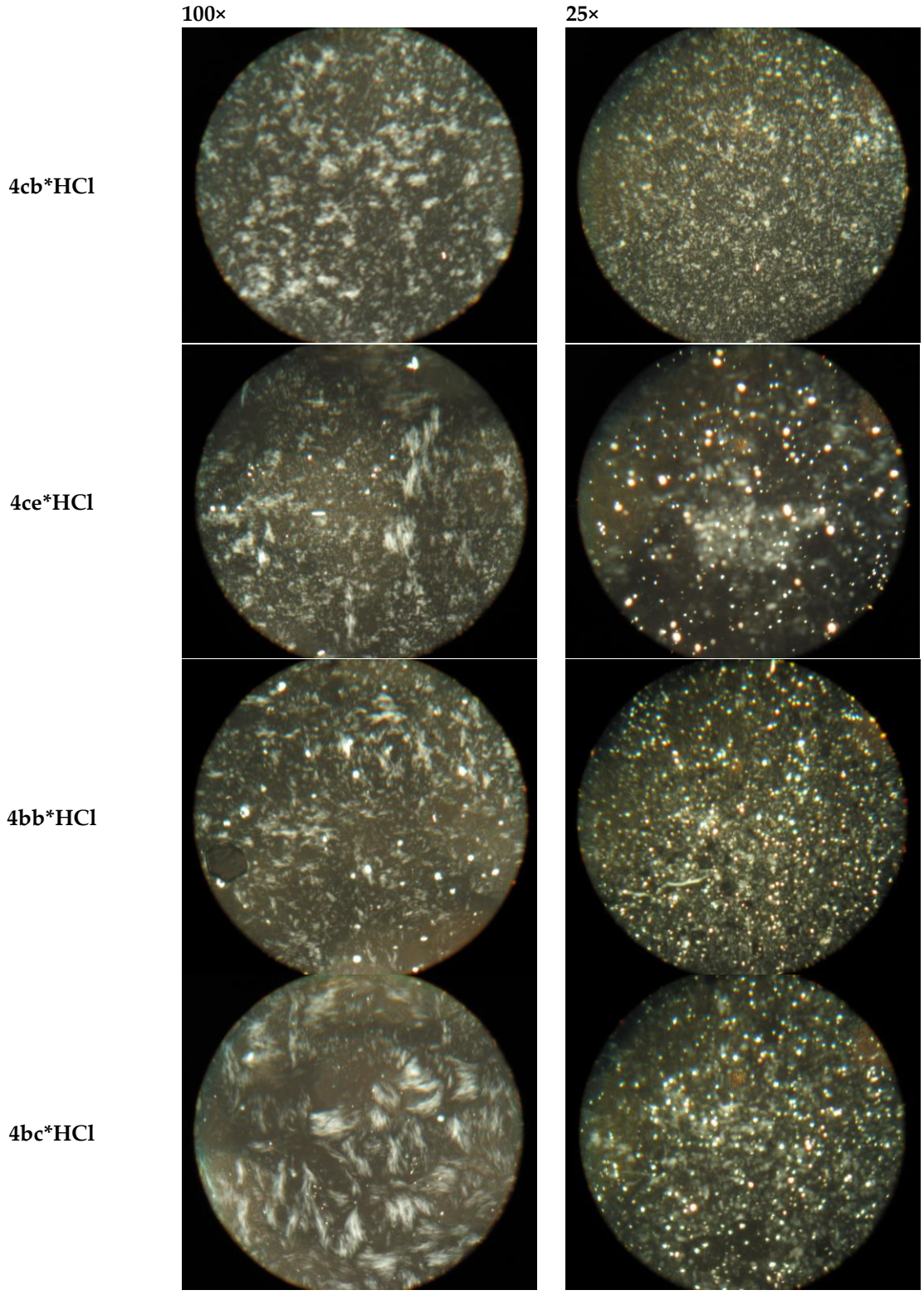



**Figure S7.** POM photomicrography of benzenogels obtained by Carl Zeiss microscope.

**Table S1.** Dependence of shear rate on viscosity **benzene@4ce*HCl.**

| Shear Rate, Pa | Viscosity, Pa*s |
|---|---|
| 100 | 0,0975 |
| 63,1 | 0,124 |
| 39,8 | 0,174 |
| 25,1 | 0,246 |
| 15,9 | 0,39 |
| 10 | 0,546 |
| 6,31 | 0,824 |
| 3,98 | 1,46 |
| 2,51 | 1,71 |
| 1,59 | 2,36 |
| 1 | 3,54 |
| 0,631 | 5,81 |
| 0,398 | 9,27 |
| 0,251 | 15 |
| 0,158 | 24,5 |
| 0,1 | 39,1 |
| 0,0631 | 62,2 |
| 0,0398 | 98,6 |
| 0,0251 | 158 |
| 0,0158 | 248 |
| 0,01 | 390 |
| 0,00631 | 613 |
| 0,00398 | 972 |
| 0,00251 | 1520 |
| 0,00158 | 2340 |
| 0,001 | 3680 |

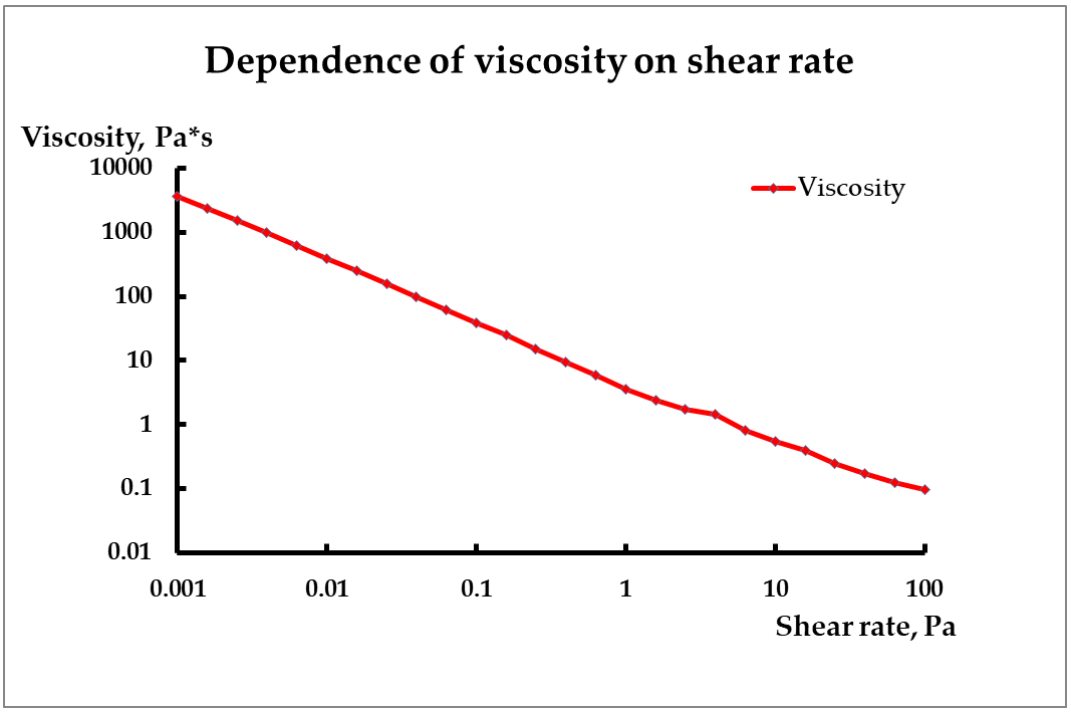



**Figure S8.** Dependence of viscosity of **benzene@4ce*HCl** on shear rate.

**Table S2.** Dependence of the loss and storage moduli on angular frequency **benzene@4ce*HCl**.

| Angular frequency (ω),Rad/s | Moduli | |
|---|---|---|
| | Loss (G″), Pa | Storage (G´), Pa |
| 0,996 | 56,9 | 70,1 |
| 1,58 | 119 | 155 |
| 2,5 | 168 | 219 |
| 3,96 | 204 | 278 |
| 6,28 | 246 | 343 |
| 9,96 | 292 | 421 |
| 15,8 | 357 | 516 |
| 25 | 427 | 599 |
| 39,6 | 535 | 702 |
| 62,8 | 689 | 746 |
| 99,6 | 904 | 851 |
| 158 | 945 | 934 |
| 250 | 1150 | 1130 |
| 396 | 1160 | 1110 |

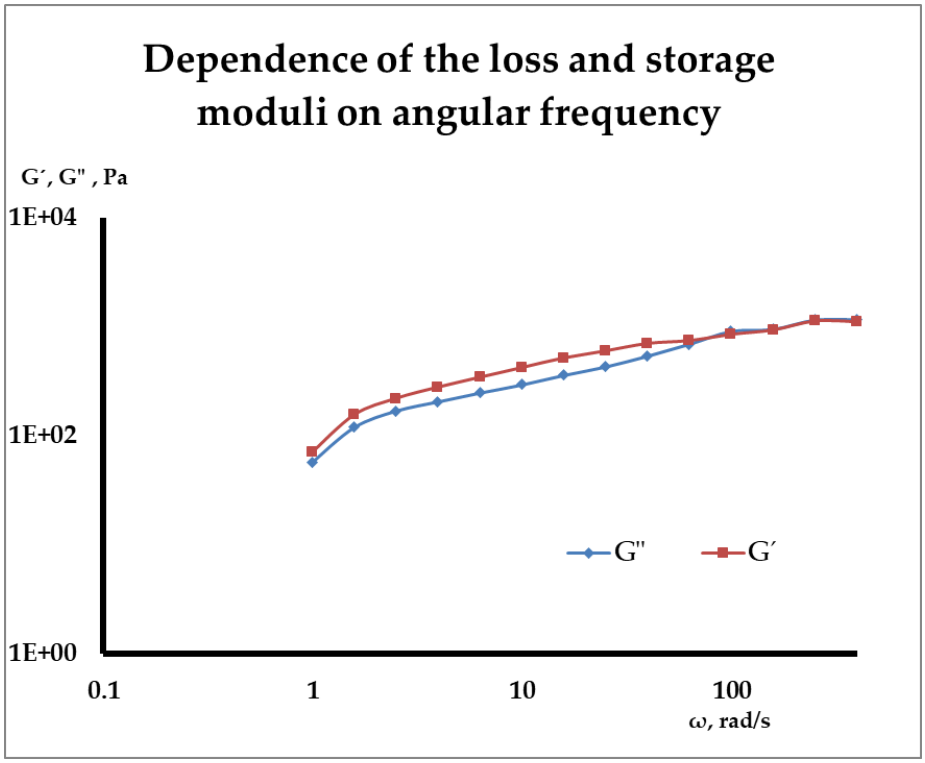



**Figure S9.** Dependence of the loss and accumulation modules on angular frequency **benzene@4ce*HCl.**

**Table S3.** Crystal data, data collection, structure solution and refinement parameters for **4cb**, **2c**, **3a**, **3c**, **1b**, **5,7-dimethyl-1,3-diazaadamantan-6-one** and **4da*HCl.**

| **Compound** | | **4cb** | **2c** | **3a** | **3c** | **1b** | **5,7-dimethyl-1,3-diazaadamantan-6-one** | **4da*HCl*($C_6H_6$)$_2$** |
|---|---|---|---|---|---|---|---|---|
| Empirical formula | | C23H26Cl1F1N2O2 | C17H23F1N2O2 | C16H24N2O1 | C16H23F1N2O1 | C34H50Cl2F2N4O5 | C10H16N2O1 | C29H34Br1Cl1N2O2 |
| Formula weight | | 416.91 | 306.37 | 260.37 | 278.36 | 703.68 | 180.25 | 557.94 |
| Colour, habit | | Colourless block | Colourless block | Colourless block | Colourless prism | Colourless block | Colourless prism | Colourless plate |
| Crystal size/mm | | 0.35×0.18×0.08 | 0.35×0.35×0.20 | 0.40×0.20×0.10 | 0.40×0.30×0.20 | 0.20×0.15×0.06 | 0.40×0.20×0.10 | 0.25×0.08×0.01 |
| Crystal system | | orthorhombic | orthorhombic | orthorhombic | monoclinic | monoclinic | orthorhombic | monoclinic |
| Space group | | Pna21 | Pbcn | Pbca | P21/n | P21 | Fdd2 | C2/c |
| Unit cell dimensions: | a/Å | 14.4619(10) | 19.3091(11) | 12.1577(4) | 7.8747(5) | 7.623(6) | 14.7493(16) | 27.43(8) |
| | b/Å | 17.2081(12) | 8.4233(5) | 14.6409(5) | 16.6186(10) | 14.139(11) | 44.868(5) | 10.69(3) |
| | c/Å | 8.3953(6) | 19.6775(12) | 16.6996(6) | 12.0211(8) | 15.983(13) | 5.7913(6) | 19.81(5) |
| | /° | 90 | 90 | 90 | 107.649(1) | 95.175(13) | 90 | 112.93(4) |
| Volume/Å3 | | 2089.3(3) | 3200.5(3) | 2972.52(18) | 1499.11(16) | 1716(2) | 3832.5(7) | 5349(26) |
| Z | | 4 | 8 | 8 | 4 | 2 | 16 | 8 |
| Density (calculated)/g·cm-3 | | 1.325 | 1.272 | 1.164 | 1.233 | 1.362 | 1.250 | 1.386 |
| Abs. coefficient/mm-1 | | 0.213 | 0.091 | 0.073 | 0.086 | 0.247 | 0.082 | 1.666 |
| F(000) | | 880 | 1312 | 1136 | 600 | 748 | 1568 | 2320 |
| Temperature/K | | 120.0(2) | 120.0(2) | 160(2) | 160(2) | 150(2) | 150(2) | 160(2) |
| range/° | | 1.84 to 26.00 | 2.07 to 25.05 | 2.44 to 28.00 | 2.16 to 28.00 | 1.28 to 25.25 | 1.82 to 30.00 | 2.07 to 25.25 |
| Index ranges | | -15 h 17<br>-9 k 21<br>-10 l 10 | -22 h 23<br>-9 k 10<br>-23 l 13 | -15 h 16<br>-19 k 19<br>-22 l 22 | -10 h 10<br>-21 k 21<br>-15 l 15 | -9 h 9<br>-16 k 16<br>-19 l 19 | -20 h 20<br>-62 k 62<br>-6 l 8 | -32 h 32<br>-12 k 12<br>-23 l 16 |
| Reflections collected | | 11202 | 16298 | 28966 | 15258 | 11580 | 9106 | 13547 |
| Unique reflections [Rint] | | 3955 [Rint=0.0440] | 2829 [Rint=0.0437] | 3579 [Rint=0.0315] | 3617 [Rint=0.0236] | 6117 [Rint=0.0903] | 1517 [Rint=0.0376] | 4817 [Rint=0.235] |
| Data / restraints / params | | 3955 / 1 / 269 | 2829 / 0 / 225 | 3579 / 0 / 182 | 3617 / 0 / 273 | 6117 / 1 / 429 | 1517 / 1 / 183 | 4817 / 39 / 295 |
| Reflections with I>2σ(I) | | 3377 | 2117 | 2862 | 3017 | 3711 | 1367 | 2030 |
| Goodness-of-fit on F2 | | 1.024 | 1.040 | 1.085 | 1.064 | 0.972 | 1.074 | 0.985 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Final R indices [I>2σ(I)] | R1 = 0.0418<br>wR2 = 0.0811 | R1 = 0.0581<br>wR2 = 0.1198 | R1 = 0.0414<br>wR2 = 0.1120 | R1 = 0.0399<br>wR2 = 0.1047 | R1 = 0.0783<br>wR2 = 0.1699 | R1 = 0.0339<br>wR2 = 0.0874 | R1 = 0.1159<br>wR2 = 0.2769 |
| R indices (all data) | R1 = 0.0540<br>wR2 = 0.0848 | R1 = 0.0810<br>wR2 = 0.1306 | R1 = 0.0543<br>wR2 = 0.1188 | R1 = 0.0489<br>wR2 = 0.1098 | R1 = 0.1320<br>wR2 = 0.1943 | R1 = 0.0388<br>wR2 = 0.0904 | R1 = 0.2320<br>wR2 = 0.3363 |
| Abs. structure parameter | 0.21(7) | — | — | — | 0.24(12) | — | — |
| Largest diff. peak/hole (e·Å-3) | 0.170 / -0.180 | 0.242 / -0.265 | 0.347 / -0.173 | 0.360 / -0.200 | 0.607 / -0.391 | 0.243 / -0.163 | 1.413 / -0.682 |
| CCDC deposition number | 1838470 | 1838469 | 1838468 | 1838467 | 1838471 | 1838466 | 1838465 |

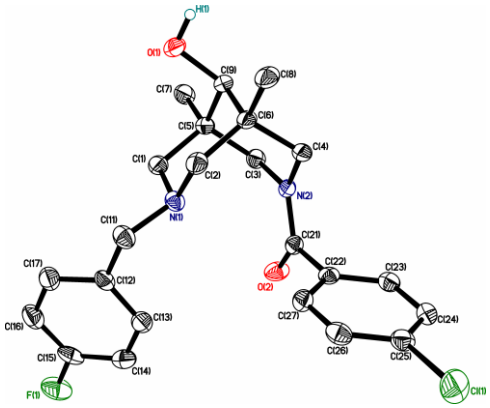



**Figure S10.** Molecular structure of **4cb**. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

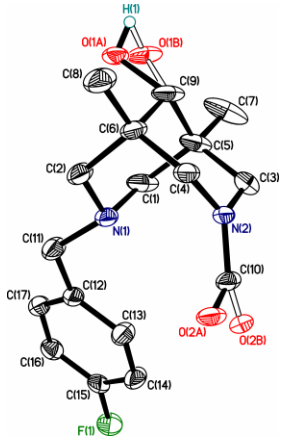



**Figure S11.** Molecular structure of **2c**. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Minor components of disorder are drawn as open lines.

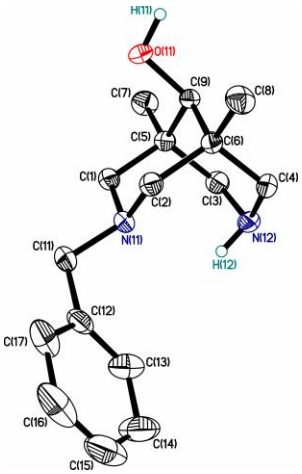



**Figure S12.** Molecular structure of **3a**. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

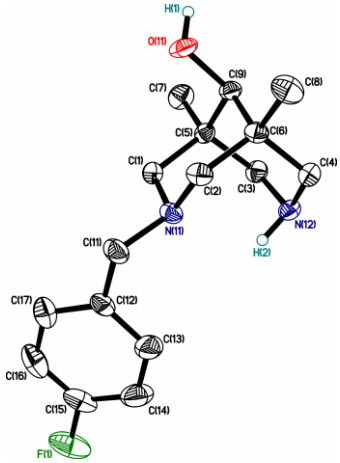



**Figure S13.** Molecular structure of **3c**. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

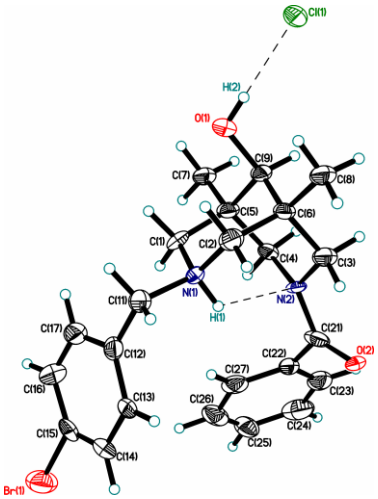



**Figure S14.** Molecular structure of **4da*HCl*(C$_6$H$_6$)$_2$.** Displacement ellipsoids are shown at 50% probability level. Solvent benzen molecules are not shown for cleraty.

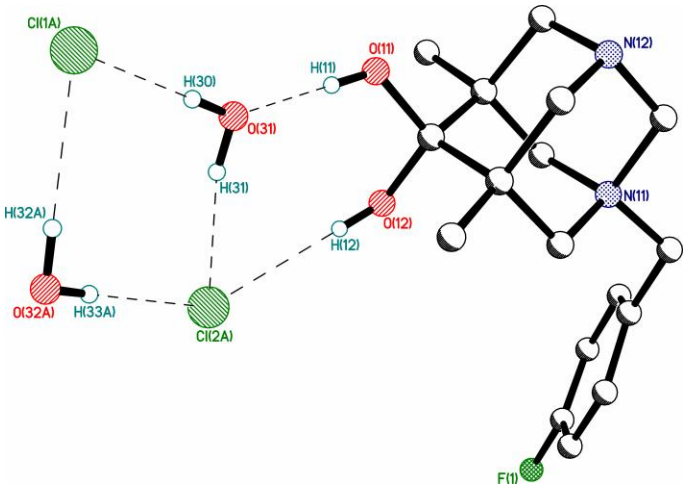



**Figure S15.** Hydrogen-bonded finite motif in the structure **1c+H2O**.

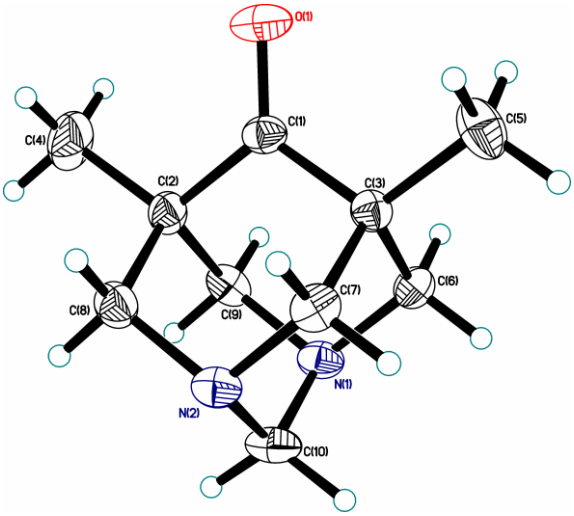



**Figure S16.** Molecular structure of 5,7-dimethyl-1,3-diazaadamantan-6-one. Displacement ellipsoids are shown at 50% probability level.

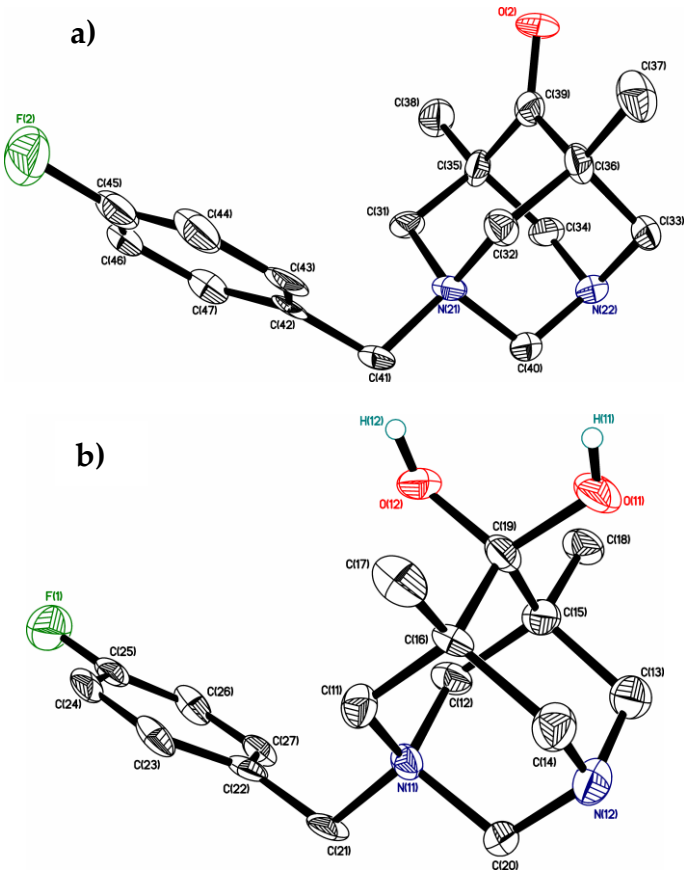



**Figure S17.** The structures **a)** and **b)** of ketone and its diol form in the crystal **1c**. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

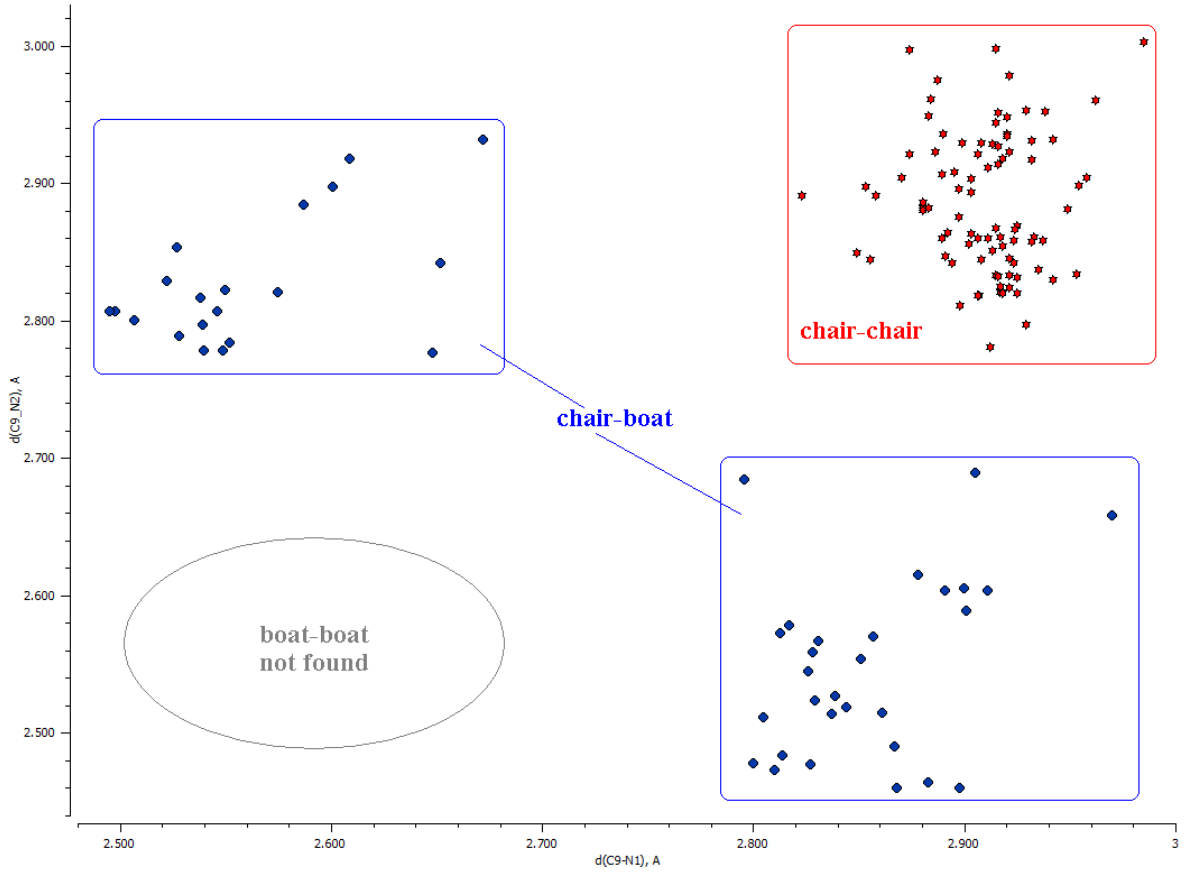



**Figure S18.** Scatterplot of C9…N separations in structures of neutral organic flexible bispidines.

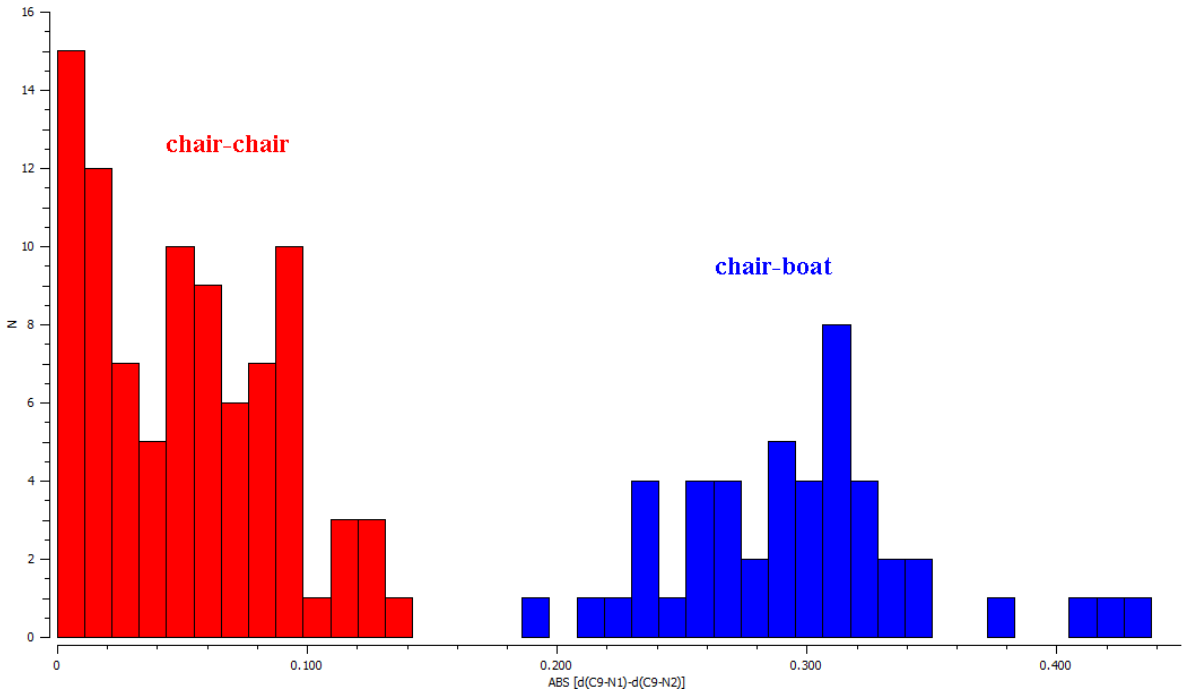



**Figure S19.** Histogram of absolute differences between C9…N separations.

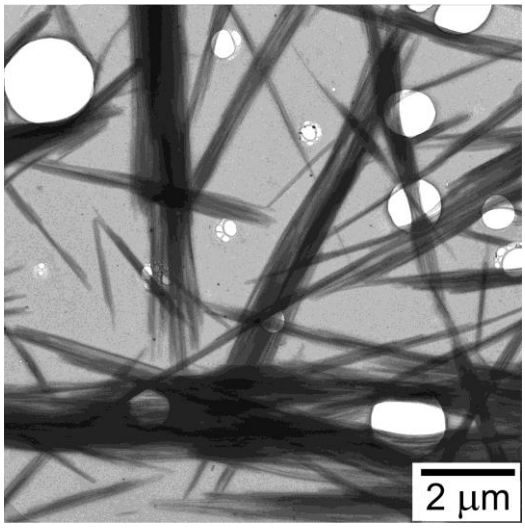



**Figure S20.** TEM micrograph of **4bc*HCl**.

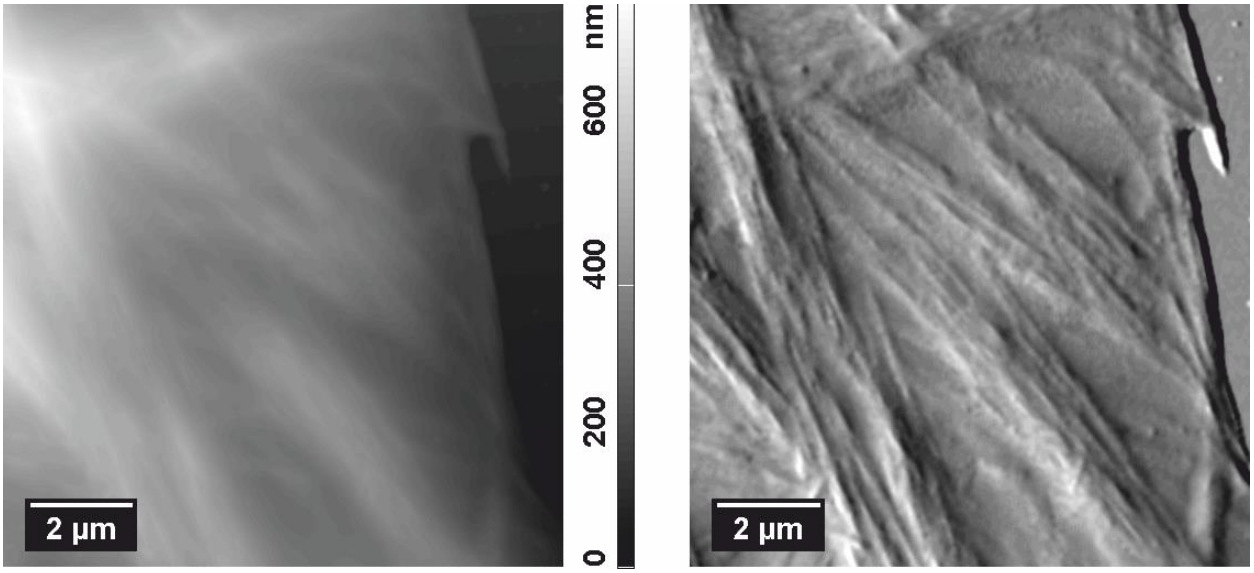



**Figure S21.** AFM micrograph of **4bc*HCl** (the left picture is topography and the right picture is error signal).

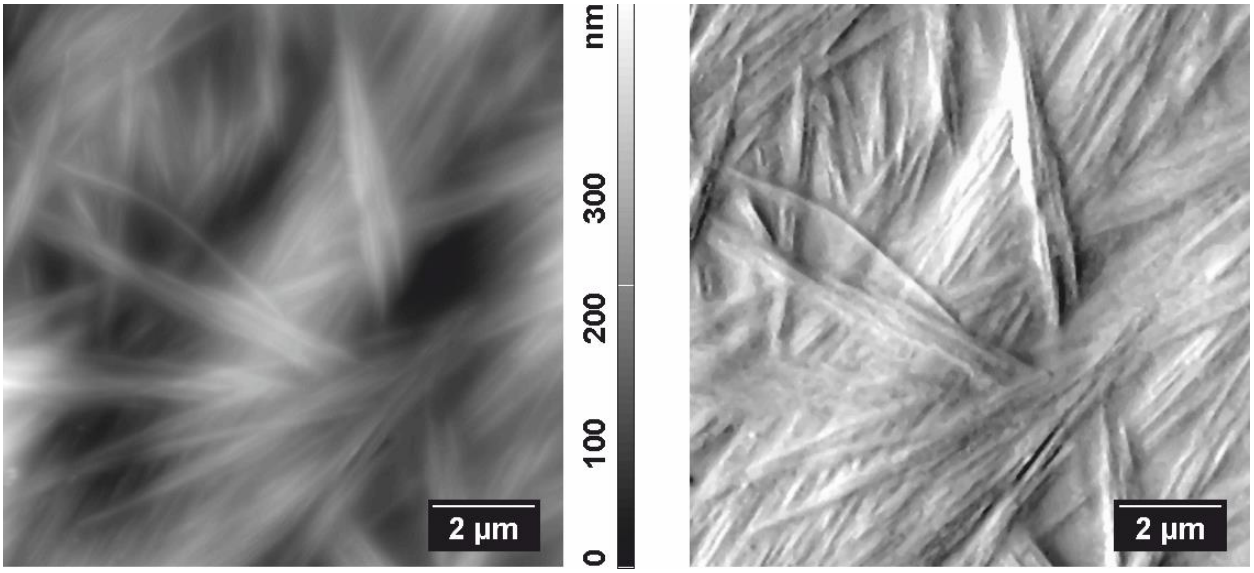



**Figure S22.** AFM micrograph of **4bc*HCl** (the left picture is topography and the right picture is error signal).

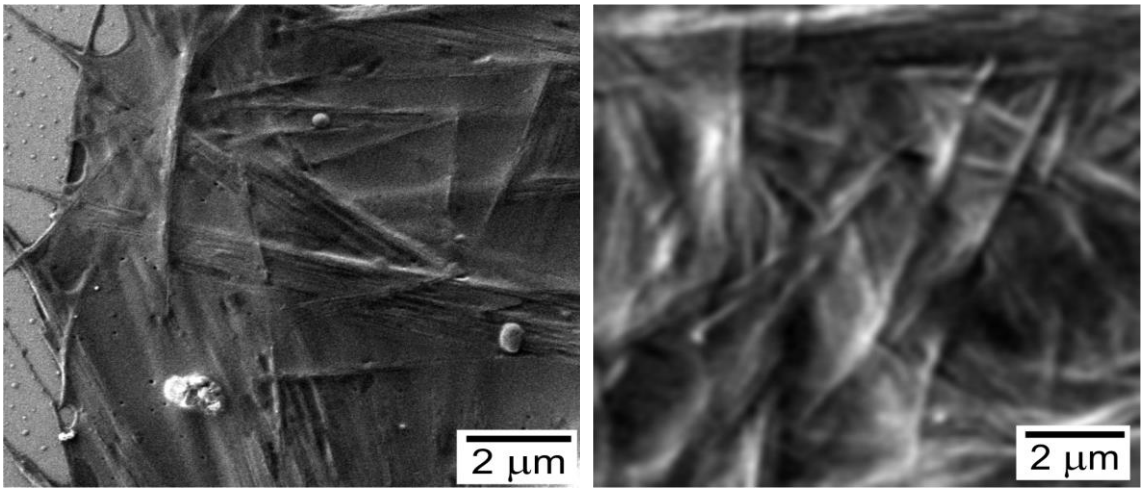



**Figure S23.** AFM micrograph of **4bc*HCl** (15 K×).

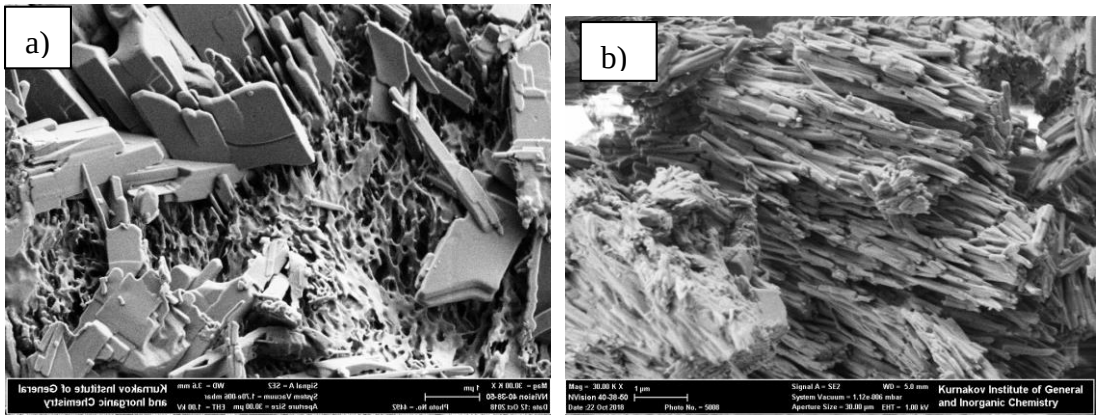



**Figure S24.** SEM micrographs of dry gel samples made by different methods of solvent removal from **ethoxybenzene@4ae*HCl:** under reduced pressure (**a**), sc-CO2 drying (**b**). Scale bar is 1 µm.

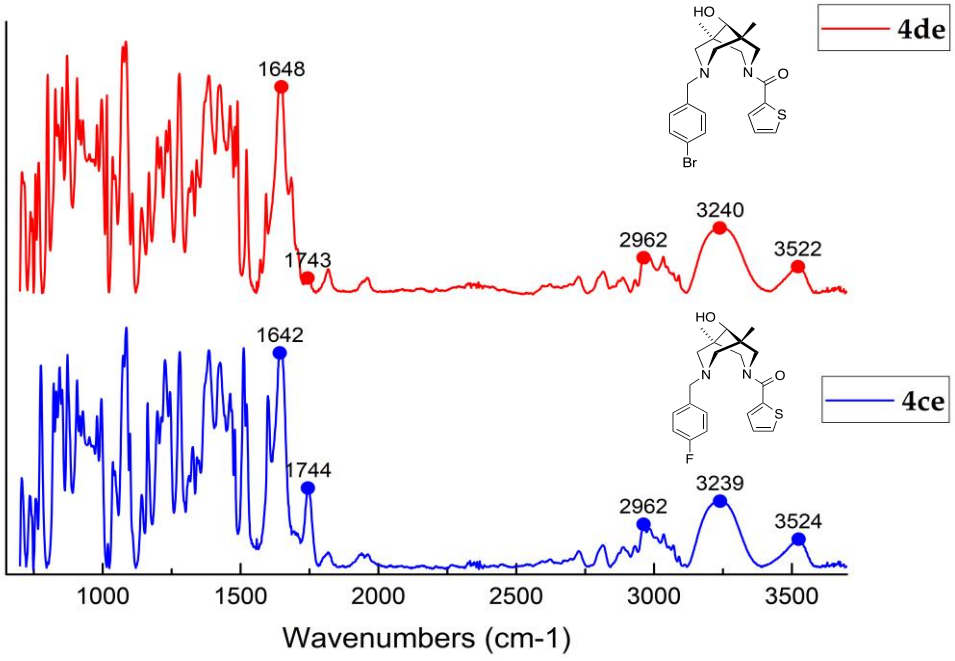



**Figure S25.** FT IR spectra of the native gels benzene@4de*HCl and benzene@4ce*HCl.