Supporting Information

A new method for the synthesis of diamantane by hydroisomerization of binor-S on treatment with sulfuric acid

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Experimental

General procedures and materials

$^1$H and $^{13}$C NMR spectra were measured on a Bruker Avance-III 400 Ascend instrument (400 MHz for $^1$H and 100 MHz for $^{13}$C in CDCl$_3$). Mass spectra were run on a Shimadzu GCMS-QP2010Plus mass spectrometer (SPB-5 capillary column, 30 m $\times$ 0.25 mm, helium as the carrier gas, temperature programming from 40 to 300°C at 8 °C/min, evaporation temperature of 280°C, ion source temperature of 200°C, and ionization energy of 70 eV). The elemental composition of the samples was determined on a Carlo Erba 1106 elemental analyzer. The course of the reaction and the purity of the products were monitored by gas liquid chromatography on a Shimadzu GC-9A, GC-2014 instrument [2 m $\times$ 3 mm column, SE-30 silicone (5%) on Chromaton N-AW-HMDS as the stationary phase, temperature programming from 50 to 270°C at 8 °C/min, helium as the carrier gas (47 mL/min)].

The sonication was carried out with an ultrasound generator IL10–0.63 (INLAB LTD) for 180 min at a frequency of 22 kHz with a submerged of 15 mm diameter titanium horn, with output power 150 W. The reactions were carried out in a 100 × 35 mm glass reactor equipped with a jacket to maintain the required temperature (20°C).

Preparation of diamantane.

Heptacyclo[8.4.0.0$^{2,12}$,0$^{3,8}$,0$^{4,6}$,0$^{5,9}$,0$^{11,13}$]tetradecane 2 (0.368 g, 2 mmol) and the solvent were charged into a glass reactor (V=100 mL). Then concentrated (98%) sulfuric acid (1.96 g, 20 mmol) was added in portions with vigorous stirring. When the whole amount of H$_2$SO$_4$ was added, the reaction mixture was stirred at 20°C for 15 h. After completion of the reaction, 10% NaOH was added to the reaction mixture, the organic phase was separated and filtered through a silica gel layer (with petroleum ether as the eluent). The solvent was distilled off and the residue was recrystallized from a 1:1 ethyl acetate : cyclohexane mixture.

**Diamantane 1.** White crystals, yield 65%, mp 244–245°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$=1.72–1.80 (m, 20H),$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$=25.95 (C,$^4$C$^9$), 37.64 (C,$^3$ C,$^5$ C,$^8$ C,$^{10}$ C,$^{13}$ C$^{14}$), 38.37 (C,$^1$ C,$^2$ C,$^6$ C,$^7$ C,$^{11}$ C$^{12}$). MS (EI, 70 eV): m/z (%)=188 [M$^+$] (100), 189 (15), 187 (18), 159 (10),145 (8), 131 (23), 130 (18), 117 (12), 105 (13), 93 (12), 92 (11), 91(28), 77 (15), 67 (8). Calcd for C$_{14}$H$_{20}$: C, 88.29; H, 11.71; found C, 88.75; H, 11.25.

Preparation of endo-endo-pentacyclo[7.3.1.1$^{5,8}$,0.0$^{3,7}$]tetradecane (tetrahydrobinor-S).

Heptacyclo[8.4.0.0$^{2,12}$,0$^{3,8}$,0$^{4,6}$,0$^{5,9}$,0$^{11,13}$]tetradecane 2 (0.368 g, 2 mmol) was charged into a glass reactor (V=100 mL) and dissolved in cyclohexane (10 mL). Then 75-80%
sulfuric acid (1.96 g, 20 mmol) was added in portions with vigorous stirring. When the whole amount of H$_2$SO$_4$ was added, the reaction mixture was stirred at 20°C for 7 h. After completion of the reaction, 10% NaOH was added to the reaction mixture, the organic part was separated and filtered through a silica gel layer (with petroleum ether as the eluent). The solvent was distilled off and the residue was recrystallized from a 1:1 ethyl acetate:cyclohexane mixture.

**Tetrahydrobinor-3c.** White crystals, 68% yield, mp 104-106°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$=0.95–0.98 (m, 4H), 1.38 (s, 8H), 1.66–1.71 (m, 4H), 1.99–2.01 (m, 2H), 2.12–2.16 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$=33.42 (C$_6$ C$_9$ C$_{13}$ C$_{14}$), 35.63 (C$_1$ C$_2$ C$_7$ C$_8$), 37.82 (C$_5$ C$_{10}$), 38.27 (C$_3$ C$_{12}$), 40.47 (C$_4$ C$_{11}$). MS (EI, 70 eV): m/z (%)=188 [M]$^+$ (100), 187 (35), 159 (24), 145 (23), 131 (38), 117 (25), 105 (39), 91 (82), 79 (57), 67 (29), 41 (47). Calc'd for C$_{14}$H$_{20}$: C, 89.29; H, 10.71; found C, 89.14; H, 10.86.

**Preparation of hexacyclo[8.4.0.0$^{2,7}$,0$^{3,14}$,0$^{4,8}$,0$^{9,13}$]tetradec-5-ene and hexacyclo[6.6.0.0$^{2,6}$,0$^{5,14}$,0$^{7,12}$,0$^{9,13}$]tetradec-3-ene**

Heptacyclo[8.4.0.0$^{2,12}$,0$^{3,8}$,0$^{4,6}$,0$^{5,9}$,0$^{11,13}$]tetradecane 2 (0.368 g, 2 mmol) was charged into a glass reactor (V=100 mL) and dissolved in cyclohexane, then [Et$_3$NH]$^+$[HSO$_4$]- (1.99 g, 10 mmol) was added, and the reaction mixture was stirred at 40°C for 8 h. Then the reactor was cooled down to room temperature, and the reaction mixture was extracted with petroleum ether and filtered through a silica gel layer (with petroleum ether as the eluent).

Hexacyclo[8.4.0.0$^{2,7}$,0$^{3,14}$,0$^{4,8}$,0$^{9,13}$]tetradecene-5 4a and hexacyclo[6.6.0.0$^{2,6}$,0$^{5,14}$,0$^{7,12}$,0$^{9,13}$]tetradecene-3 4b (45:55)

Colorless oil, 78% yield; 4a: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.04 (d, J = 7.2 Hz, 2H), 1.41 (d, J = 7.6 Hz, 2H), 1.95 (s, 2H), 2.09 (d, J = 7.2 Hz, 4H), 2.21 (d, J = 7.2 Hz, 2H), 5.87 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$=26.27 (C$_1$ C$_{12}$), 34.62 (C$_{10}$ C$_{13}$), 36.34 (C$_{1}$ C$_{14}$), 37.27 (C$_2$ C$_3$), 40.68 (C$_4$ C$_7$), 44.68 (C$_8$), 52.88 (C$_9$), 134.82 (C$_5$ C$_6$). MS (EI, 70 eV): m/z (%)=184 [M]$^+$ (44), 169 (14), 155 (16), 142 (34), 117 (100), 115 (37), 105 (22), 91 (73), 80 (38), 65 (17), 41 (21). 4b: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.09–1.24 (m, 1H), 1.31–1.36 (m, 1H), 1.48 (s, 1H), 1.56–1.59 (m, 2H), 1.71 (t, J = 6 Hz, 1H), 2.03–2.06 (m, 3H), 2.15–2.17 (m, 2H), 2.22 (s, 1H), 2.52 (s, 2H), 5.86–5.98 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$=24.08 (C$_9$), 27.16 (C$_{11}$), 40.52 (C$_1$), 40.93 (C$_{12}$), 42.30 (C$_{14}$), 45.66 (C$_9$), 47.38 (C$_2$), 47.94 (C$_{13}$), 48.61 (C$_7$), 50.20 (C$_8$), 54.09 (C$_5$), 60.05 (C$_6$), 133.69 (C$_4$), 133.75 (C$_3$). MS (EI, 70 eV): m/z (%)=184 [M]$^+$ (40), 169 (21), 155 (45), 141 (45), 129 (51), 117 (100), 115 (53), 91 (88), 78 (43), 65 (21), 41 (20).
Figure S1. Mass spectrum of diamantane 1

Figure S2. Mass spectrum of tetrahydrobinor-S 3c

Figure S3. Mass spectrum of hexacyclo[8.4.0.0\^{\text{2}}\text{7}.0\text{3}.\text{14}.0\text{4}.\text{9}.\text{0}.\text{9}.\text{13}]tetradec-5-ene 4a

Figure S4. Mass spectrum of hexacyclo[6.6.0.0\^{\text{2}}\text{6}.0\text{5}.\text{14}.0\text{7}.\text{12}.0\text{9}.\text{13}]tetradec-3-ene 4b
Figure S5. $^1$H NMR spectrum of diamantane 1 in CDCl$_3$
Figure S6. $^{13}$C NMR spectrum of diamantane 1 in CDCl$_3$
Figure S7. $^1$H NMR spectrum of tetrahydrobinor-S 3c in CDCl₃
Figure S8. $^{13}$C NMR spectrum of tetrahydrobinor-S 3c in CDCl$_3$
Figure S9. $^1$H NMR spectrum of mixture hexacyclo[8.4.0.0$^{2,7,10,14,0^{4,8,0^{9,13}}}$]tetradec-5-ene 4a and hexacyclo[6.6.0.0$^{2,6,0^{5,14,0^{7,12,0^{9,13}}}}$]tetradec-3-ene 4b in CDCl$_3$. 

Figure S9.
Figure S10. $^{13}$C NMR spectrum of mixture hexacyclo[8.4.0.0$^2$.7.0$^3$.14.0$^4$.8.0$^9$.13]tetrade-5-ene 4a and hexacyclo[6.6.0.0$^2$.6.0$^5$.14.0$^7$.12.0$^9$.13]tetrade-3-ene 4b in CDCl$_3$. 