Supporting Information

Structure-Reactivity Relationships: Reactions of a 5-Substituted Aziadamantane in a Resorcin[4]arene-based Cavitand

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Instruments

Elemental analyses were performed at the Mikrolabor des Institutes für Physikalische Chemie der Universität Wien.

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance DRX 400 (at 400.13 and 100.62 MHz) and Bruker Avance DRX 600 (at 600.13 and 150.92 MHz) spectrometer at 298 K. NMR solvent peaks were used as internal standard. All shifts are given in ppm.
Abbreviations used: s (singlet), d (doublet), t (triplet), m (multiplet), b (broad).

GC/MS spectra were performed on a Hewlett Packard HP6890 Series instrument equipped with a HP5973 Mass Selective Detector (70 eV) using a HP-5 column. Helium was used as carrier gas.

Analytical HPLC spectra were recorded on a HP 1090 Series and Agilent Technologies 1200 Series instrument equipped with a G 1315D DAD UV detector on a Zorbax RX-Sil (5 μm) column.

Silica gel 60 (Merck, 230-400 mesh) was used for flash chromatography.

TLC aluminium foils (silica gel 60 F_{254}) for Tin Layer Chromatography were obtained from Merck.

Photolyses were performed using a Heraeus medium pressure Hg arc lamp (Heraeus TQ718-Z4, 700 W, doped with FeI_2). The lamp was placed in a water-cooled jacket made of borosilicate glass, which filtered out light below λ = 300 nm.

DSC measurements were performed on a METTLER TOLEDO DSC823e module with a heating rate of 5 °C/min. N_2 was used as protecting gas (flow: ca. 60 mL/min).

Melting points were measured on a Leica Galen III Kofler-type melting point microscope and are uncorrected.

Chemicals

All common solvents were destilled before use.

All chemicals were obtained either from Fluka or Sigma-Aldrich, and were used without further purification.

Gaseous ammonia was dried by passing through a drying tower filled with potassium hydroxide scraps.

MeOH was dried by heating to reflux over CaH_2 for ca. 2 h and subsequent fractional distillation in vacuum. Afterwards it was stored over molecular sieves under argon.

Procedures

*Cavitand **4***

Cavitand **4** was prepared according to *Chem. Eur. J.* **2003**, *9*, 130. Mp > 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46-2.54 (m, 8H), 2.57-2.62 (m, 8H), 4.53 (s, 4H), 4.83 (t, 4H, *J* = 8.0 Hz), 5.99 (s, 4H), 6.50 (d, 8H, *J* = 2.0 Hz), 6.61 (t, 4H, *J* = 2.2 Hz), 6.97 (t, 4H, *J* = 2.0 Hz), 7.08-7.11 (m, 8H), 7.17-7.22 (m, 24H), 7.56 (t, 4H, *J* = 8.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 32.8, 34.3, 36.6, 105.6, 107.6, 109.7, 115.3, 115.7, 120.6, 122.1, 126.2, 128.3, 128.6, 131.2, 136.7, 139.1, 141.3, 156.5, 156.6, 161.2.

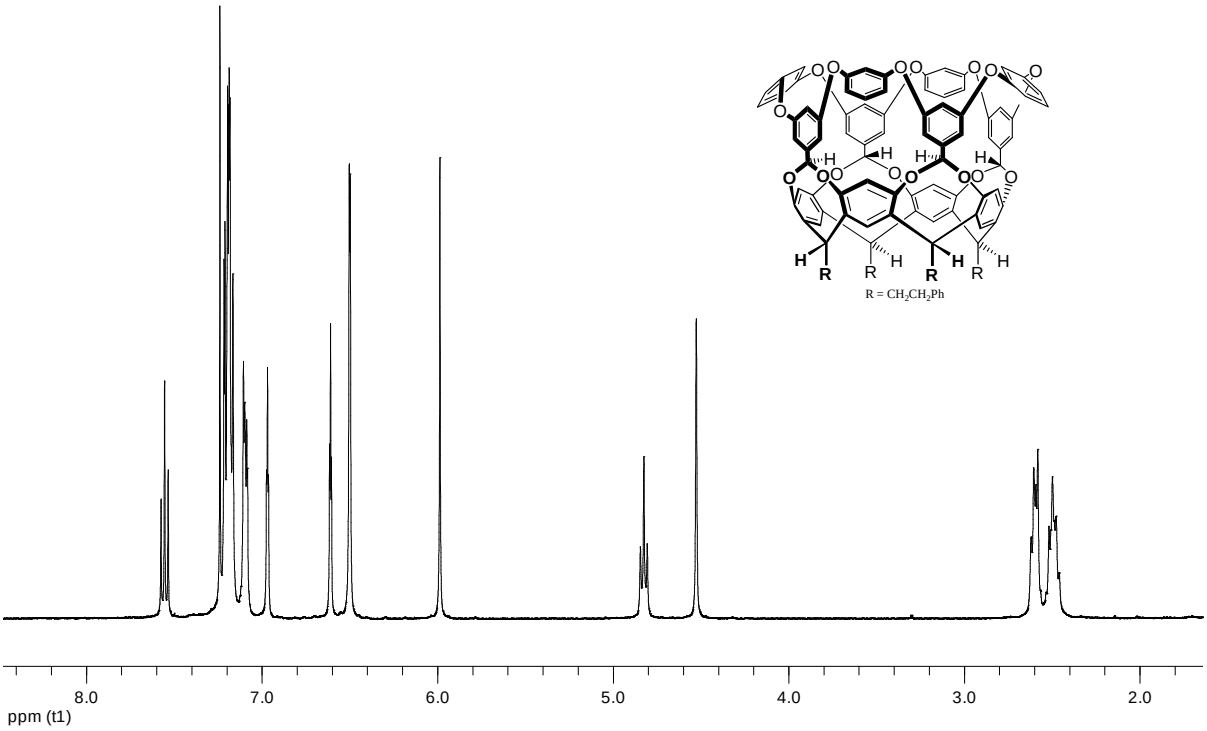

Figure S1. ^{1}H NMR spectrum of cavitand **4**.

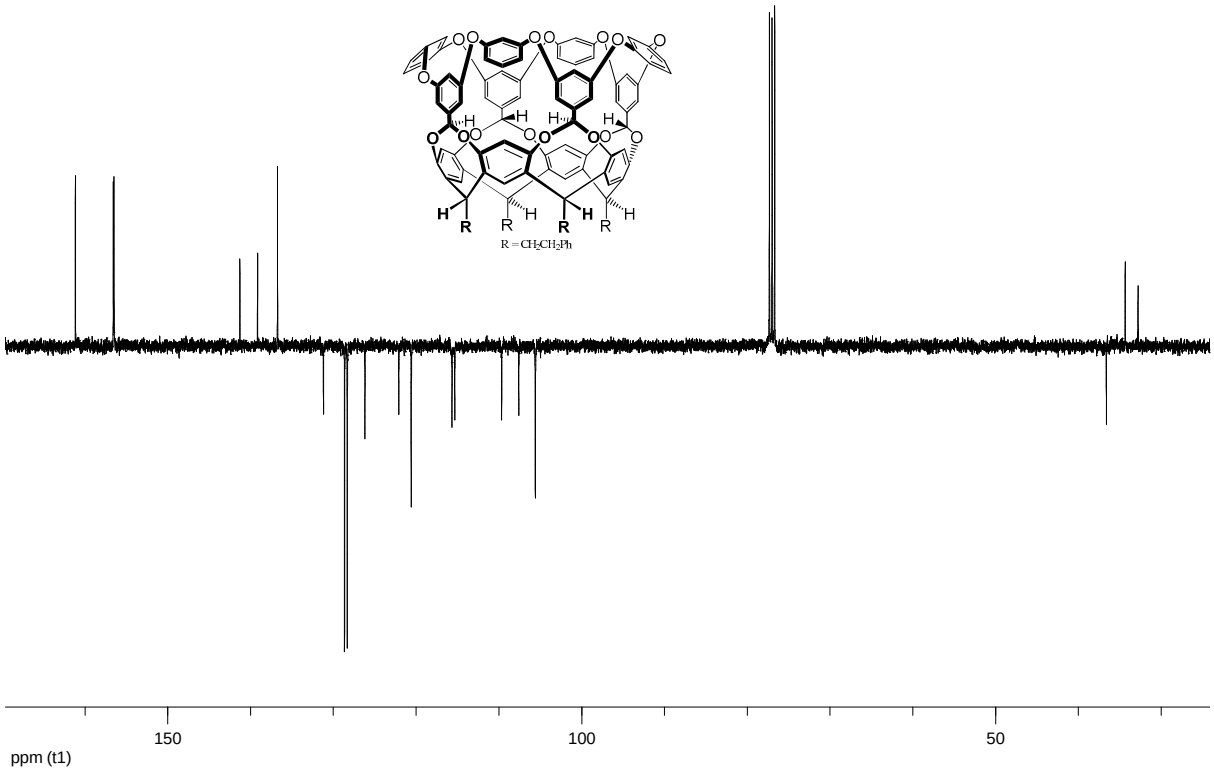

Figure S2. ^{13}C NMR spectrum of cavitand **4**.

*5-Bromo-2-adamantanone (**7**)*

1 g (6.02 mmol) of 5-hydroxy-2-adamantanone (**5**) were dissolved in 20 mL of 48% HBr solution and heated to reflux for ca. 16 h. After addition of 15 mL of water, the mixture was extracted three times with Et_2O. The organic phase was washed with brine and dried over anhydrous $MgSO_4$. The organic phase was removed *in vacuo* to yield 0.8 g (3.49 mmol, 58% yield) of 5-bromo-2-adamantanone (**7**). Mp: 150-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97-2.10 (m, 4H), 2.24 (bs, 1H), 2.49-2.63 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 31.3, 37.5, 47.8, 49.0, 49.1, 59.9, 214.3; HRMS (EI) calcd. for $C_{10}H_{13}BrO$ (M^+) 228.0150, found 228.0144; Anal. calcd. for $C_{10}H_{13}BrO$ C, 52.42 H, 5.72 Br, 34.88, found C, 52.06 H, 5.80 Br, 34.56.

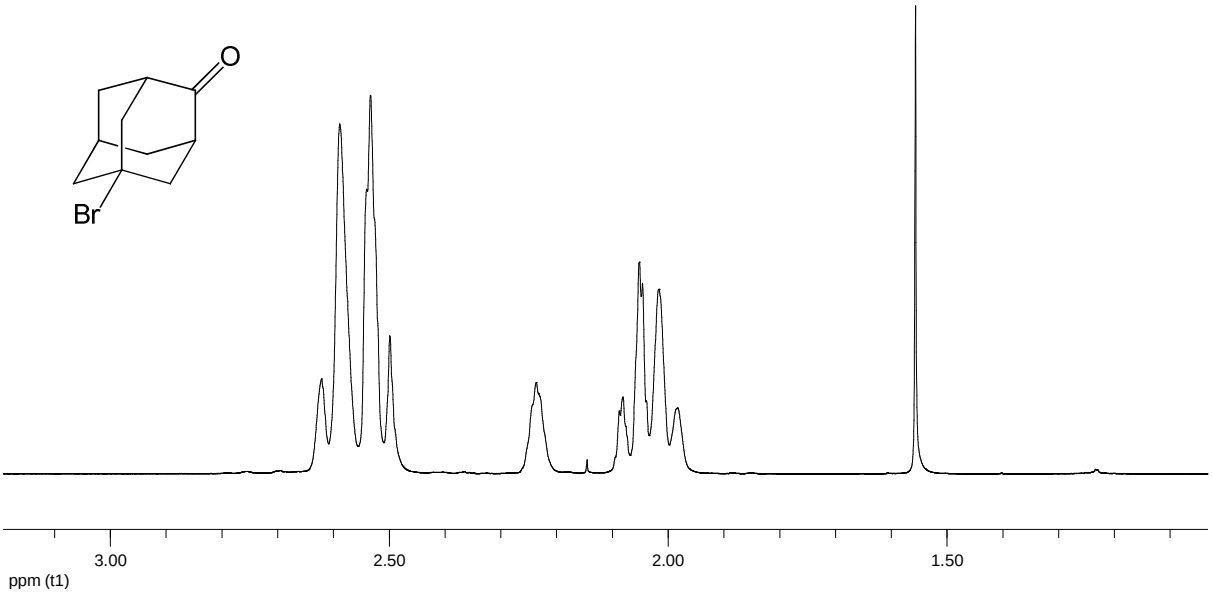

Figure S3. ^{1}H NMR spectrum of 5-bromo-2-adamantanone (**7**).

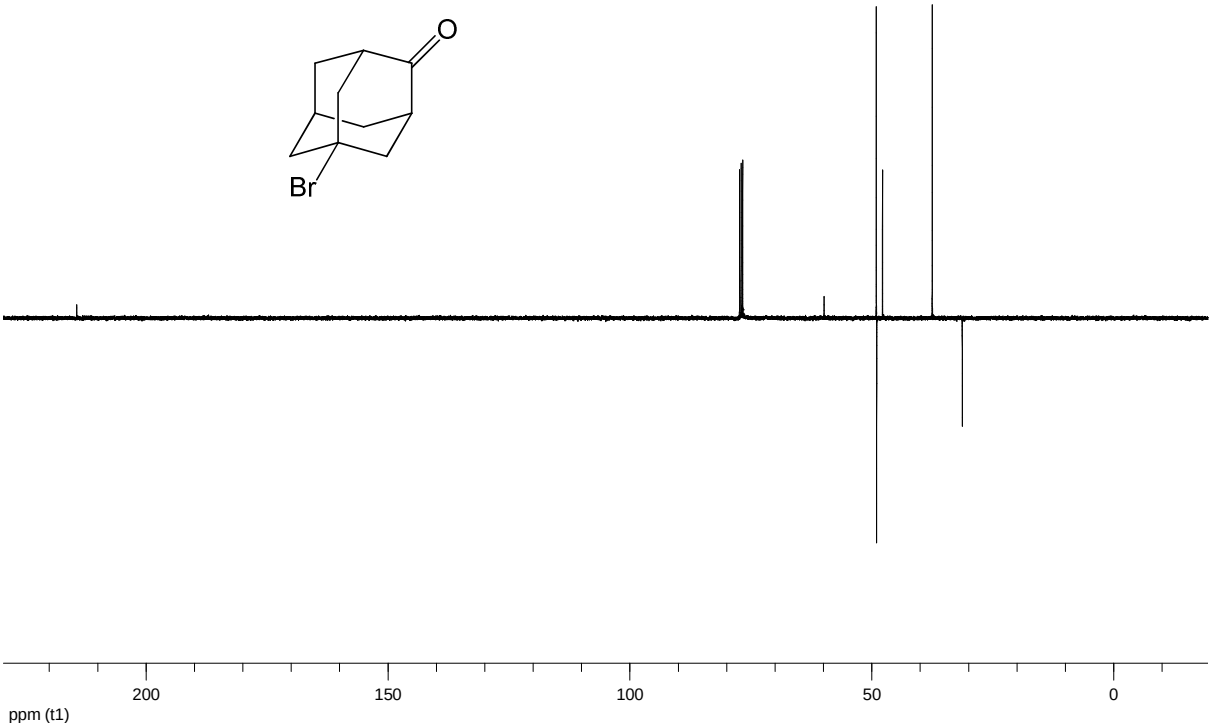

Figure S4. ^{13}C NMR spectrum of 5-bromo-2-adamantanone (**7**).

*5-Bromo-2-aziadamantane (**3**)*

1.9 g (8.29 mmol) of 5-bromo-2-adamantanone (**7**) were dissolved in ca. 30 mL of anhydrous MeOH and cooled to 0 °C. Anhydrous ammonia was passed slowly through the solution for 75 min. The temperature was held between 0 and ca. 10 °C during this process. Afterwards the solution was cooled to -12 °C and 1.13 g (9.99 mmol) of hydroxylamine-*O*-sulfonic acid were added in small portions under stirring within 2.5 h. The resulting mixture was kept in the refrigerator (+7 °C) overnight.

Afterwards MeOH and the NH_3 were removed in vacuum at ca. 40 °C. The solid residue was suspended in 50 mL of acetone and 1.25 g (12.50 mmol) of CrO_3 in 14 mL of 20% H_2SO_4 were added dropwise within 20 min at 0 °C. The mixture was stirred for 1 h at ambient temperature and, afterwards, poured onto 300 mL of ice. The water phase was extracted three times with CH_2Cl_2 and the organic phase was then dried over anhydrous $MgSO_4$. Removal of the solvent *in vacuo* and subsequent chromatography on silica gel with hexane as eluant gave 0.96 g (3.98 mmol, 48% yield) of 5-bromo-2-azidamantane (**3**). Mp: 85-90 °C; IR (KBr): 2934, 2858, 1577, 1451, 1079, 1014, 809, 789, 716 cm^{-1}; UV (cyclohexane) λ_{max} (ε): 344 (165), 349 (141), 362 (226); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (bs, 2H), 1.77 (dm, 2H), 2.07 (bd, 2H, *J* = 12.9 Hz), 2.24-2.27 (m, 1H), 2.33 (dm, 2H), 2.41 ("s", 2H), 2.68 (dm, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 31.6, 33.4, 37.9, 46.5, 48.5, 62.5; HRMS (ESI) calcd. for $C_{20}H_{27}Br_2N_2$ (corresponding azine) ($M+H^+$) 455.0521, found 455.0532; the diazirine dimerized to the corresponding azine; Anal. calcd. for $C_{10}H_{13}BrN_2$ C, 49.81 H, 5.43 N, 11.62, found C, 49.46 H, 5.11 N, 11.50.

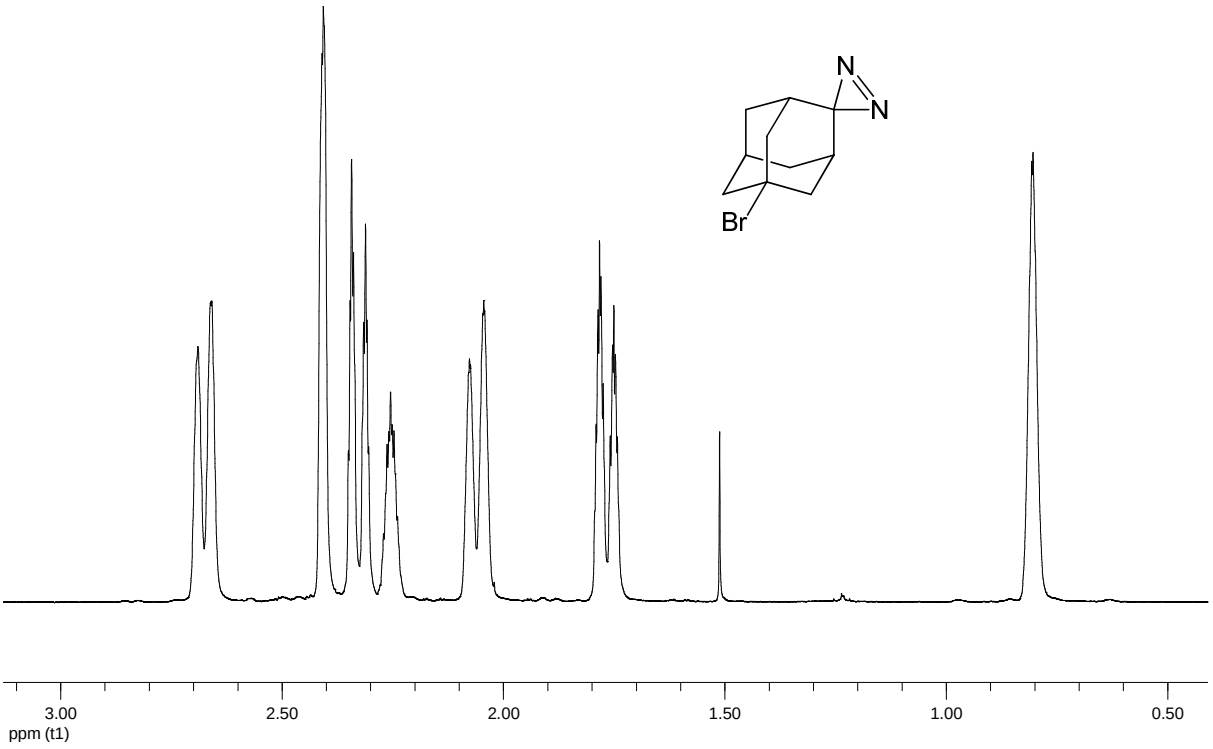

Figure S5. ^{1}H NMR spectrum of 5-bromo-2-aziadamantane (**3**).

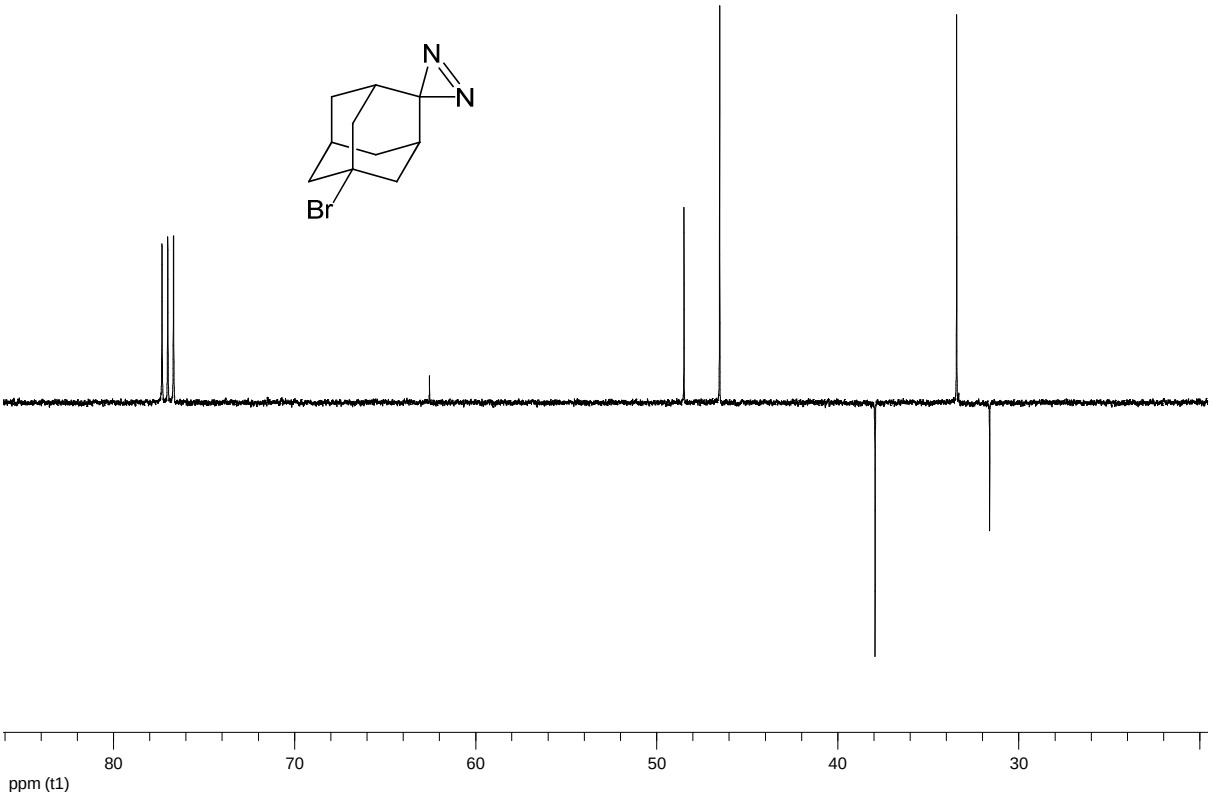

Figure S6. ^{13}C NMR spectrum of 5-bromo-2-aziadamantane (**3**).

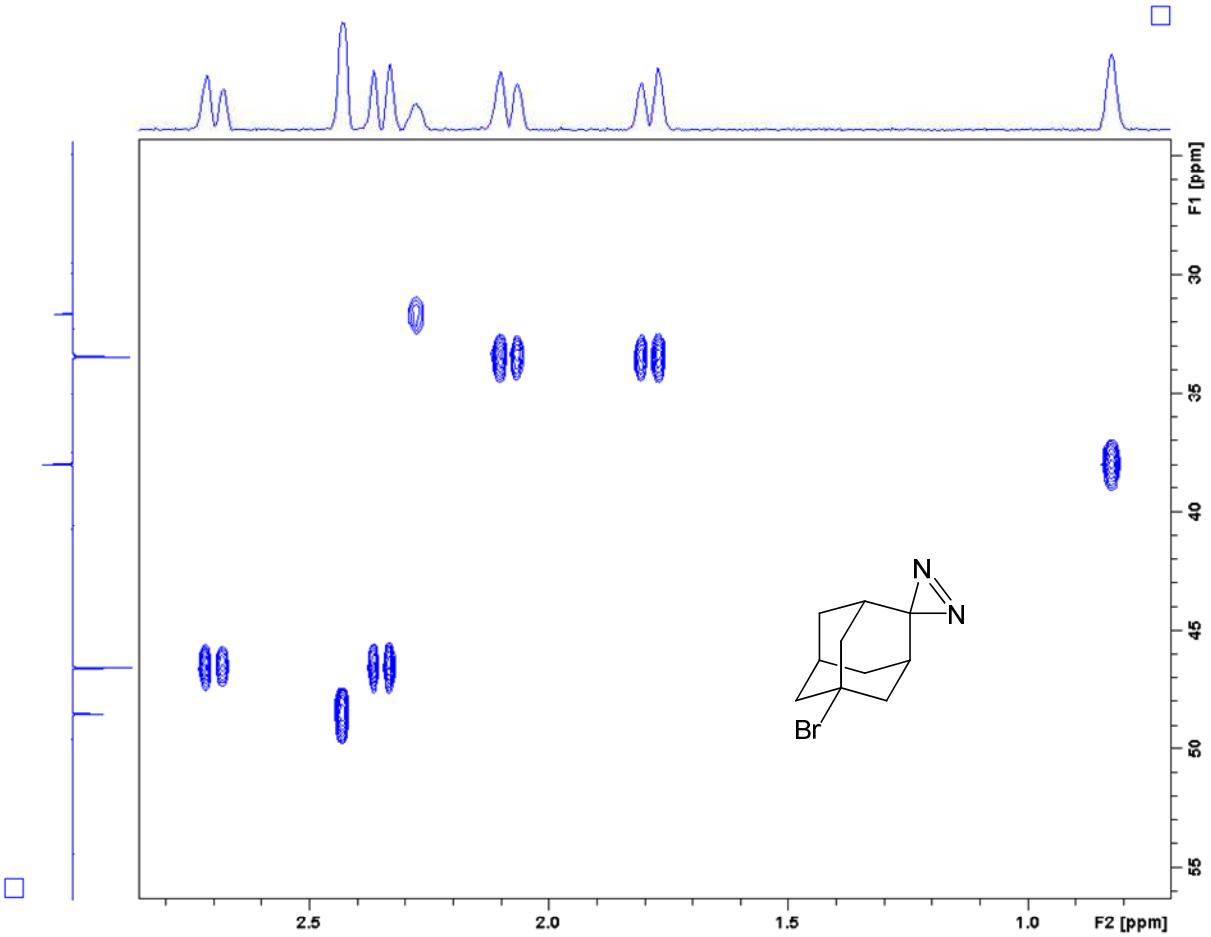

Figure S7. HSQC NMR spectrum of 5-bromo-2-aziadamantane (**3**).

*5-Chloro-2-adamantanone (**6**)*

38 mL (61.9 g, 0.52 mol) of thionyl chloride were added to 6.16 g (37.06 mmol) of 5-hydroxy-2-adamantanone (**5**) and refluxed for 2 h. Afterwards the thionyl chloride was removed *in vacuo* and the residue was dissolved in CH_2Cl_2. The organic was washed two times with 0.1 M NaOH solution, two times with 10% NaCl solution and dried over anhydrous Na_2SO_4. Removal of the solvent *in vacuo* and recrystallization in hexane afforded 4.2 g (22.74 mmol, 61% yield) of 5-chloro-2-adamantanone (**6**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92-2.04 (m, 4H), 2.27-2.31 (m, 2H), 2.32-2.35 ("s", 3H), 2.42 (d, 2H, J = 12.3 Hz), 2.61 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.6, 37.6, 46.4, 47.5, 48.0, 64.5, 214.6; HRMS (EI) calcd. for $C_{10}H_{13}ClO$ (M^+) 184.0655, found 184.0653.

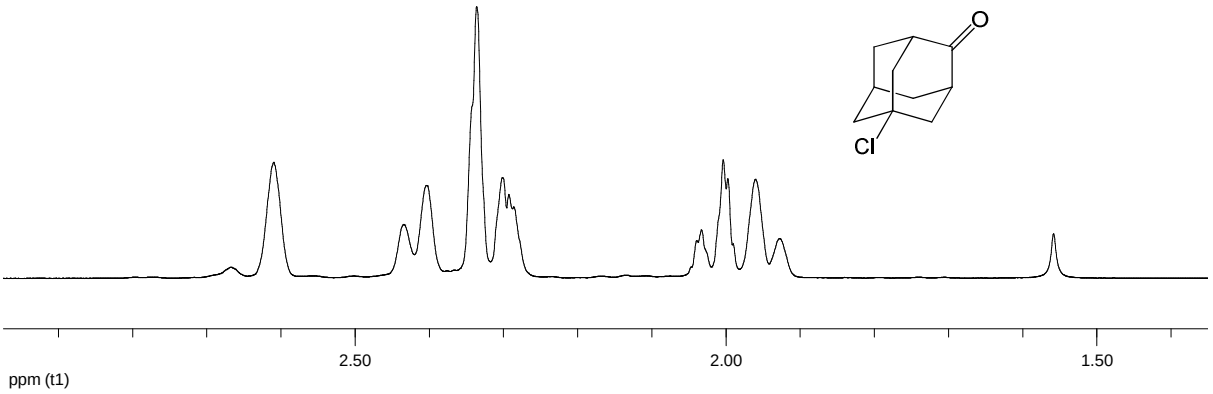

Figure S8. ^{1}H NMR spectrum of 5-chloro-2-adamantanone (**6**).

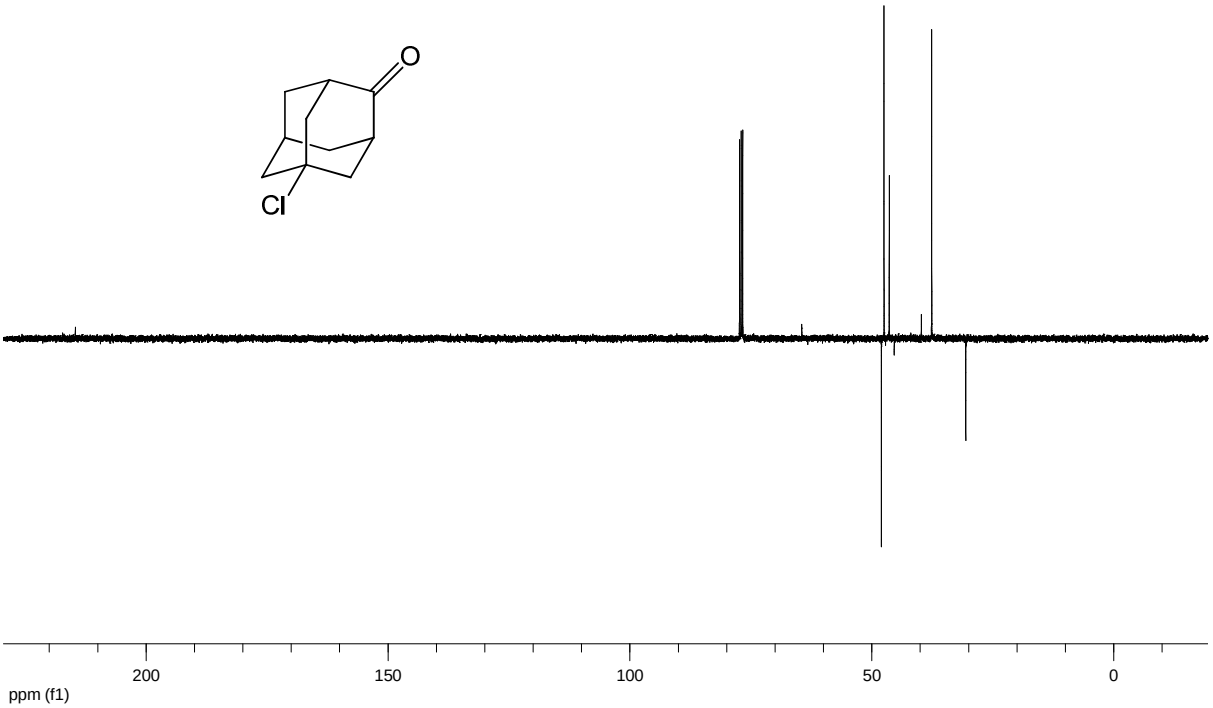

Figure S9. ^{13}C NMR spectrum of 5-chloro-2-adamantanone (**6**).

*2-Aziadamantane (**1**)*

1.8 g (11.98 mmol) of adamantan-2-one were dissolved in ca. 40 mL of anhydrous MeOH and cooled to 0 °C. Anhydrous ammonia was passed slowly through the solution for 1 h. The temperature was held between 0 and ca. 10 °C during this process. Afterwards the solution was cooled to -12 °C and 1.38 g (12.20 mmol) of hydroxylamine-*O*-sulfonic acid were added in small portions under stirring within 4 h. The resulting mixture was kept in the freezer (-24 °C) overnight.
Then MeOH and NH_3 were removed *in vacuo* at ca. 40 °C. The solid residue was suspended in ca. 70 mL of acetone and 1.82 g (18.20 mmol) of CrO_3 in 25 mL of 20% H_2SO_4 were added dropwise within 90 min at 5-10 °C. The mixture was stirred for 1 h at ambient temperature and, afterwards, poured onto 750 mL of ice. The water phase was extracted five times with CH_2Cl_2 and the organic phase was dried over anhydrous $MgSO_4$. Removal of the solvent *in vacuo* and subsequent chromatography on silica gel with hexane as eluant gave 0.97 g (5.98 mmol, 50% yield) of 2-azidamantane (**1**). Mp: decomposition > 200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.63 (s, 2H), 1.73-1.80 (m, 6H), 2.01-2.08 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 27.7, 34.6, 35.2, 36.9; Anal. calcd. for $C_{10}H_{14}N_2$ C, 74.03 H, 8.70 N, 17.27, found C, 73.99 H, 8.62 N, 17.38.

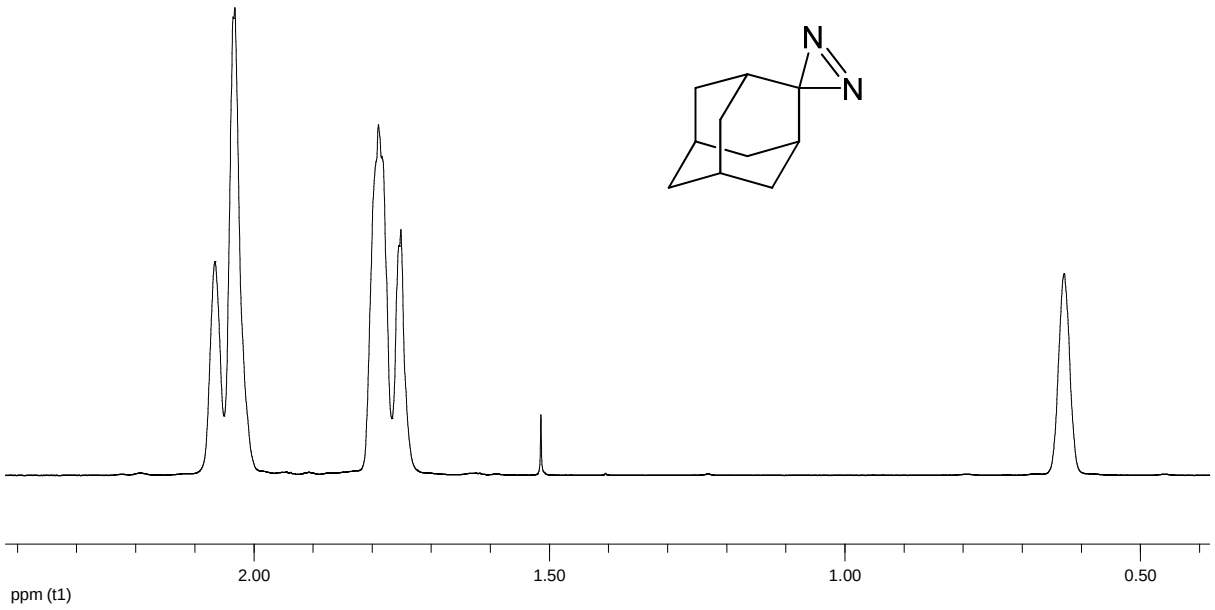

Figure S10. ^{1}H NMR spectrum of 2-aziadamantane (**1**).

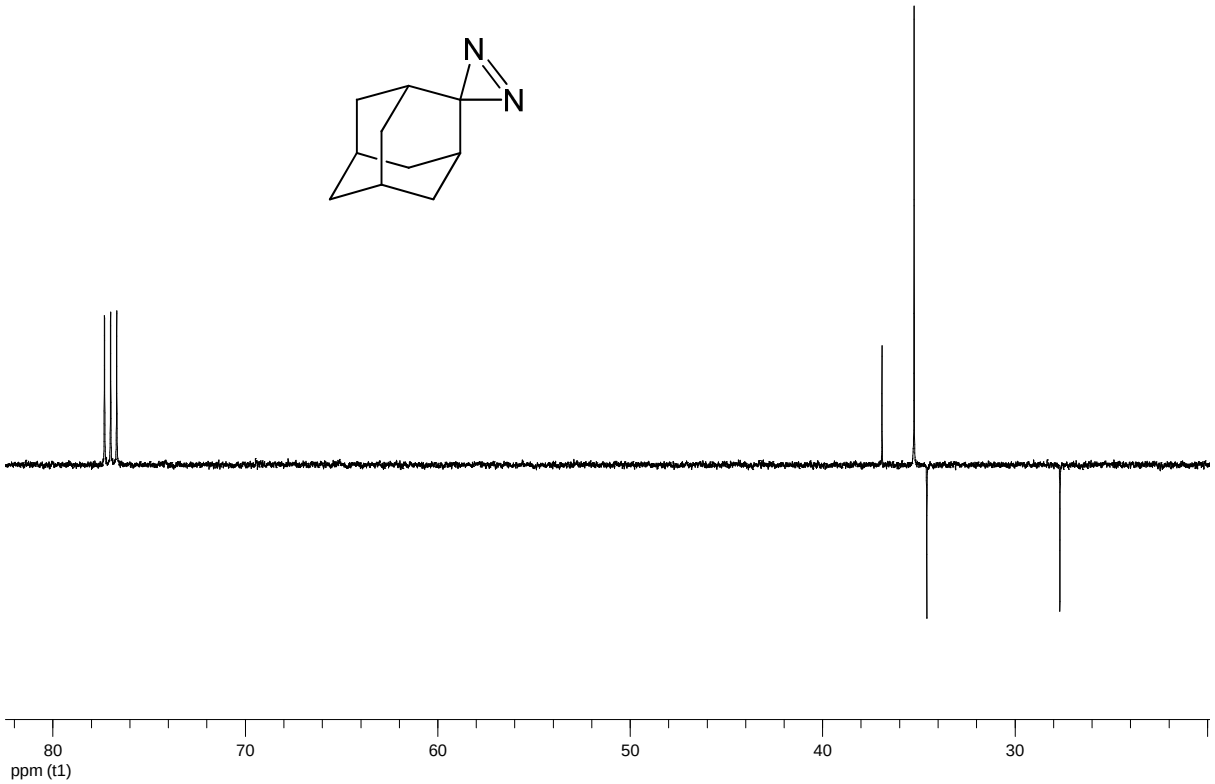

Figure S11. ^{13}C NMR spectrum of 2-aziadamantane (**1**).

*5-Chloro-2-aziadamantane (**2**)*

4 g (21.66 mmol) of 5-chloro-2-adamantanone (**6**) were dissolved in ca. 70 mL of anhydrous MeOH and cooled down to 0 °C. Anhydrous ammonia was passed slowly through the solution for 75 min. The temperature was held between 0 and ca. 10 °C during this process. Afterwards the solution was cooled to -12 °C and 2.96 g (26.17 mmol) of hydroxylamine-*O*-sulfonic acid were added in small portions under stirring within 3.5 h. The resulting mixture was kept in the freezer (-24 °C) overnight.
Then MeOH and NH_3 were removed *in vacuo* at ca. 40 °C. The solid residue was suspended in ca. 130 mL of acetone and 3.2 g (32.00 mmol) of CrO_3 in 36 mL of 20% H_2SO_4 were added dropwise within 20 min at 0 °C. The mixture was stirred for 1 h at ambient temperature and, afterwards, poured onto 700 mL of ice. The water phase was extracted three times with CH_2Cl_2 and the organic phase was then dried over anhydrous $MgSO_4$. Removal of the solvent *in vacuo* and subsequent chromatography on silica gel with hexane as eluant gave 1.15 g (5.85 mmol, 27% yield) of 5-chloro-2-azidamantane (**2**). Mp: decomposition starts at ca. 80-90 °C; IR (KBr): 2934, 2859, 1577, 1453, 1079, 1020, 828, 587 cm^{-1}; UV (pentane) λ_{max} (ε): 348 (134), 353 (114), 367 (207); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (bs, 2H), 1.73 (dm, 2H), 2.01 (d, 2H, *J* = 12.9 Hz), 2.11 (dm, 2H), 2.20 (bs, 2H), 2.28-2.32 (m, 1H), 2.48 (d, 2H, *J* = 11.3 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.9, 33.5, 37.1, 45.0, 47.0, 66.4; HRMS (ESI) calcd. for $C_{20}H_{27}Cl_2N_2$ (corresponding azine) ($M+H^+$) 365.1551, found 365.1558; the diazirine dimerized to the corresponding azine; Anal. calcd. for $C_{10}H_{13}ClN_2$ C, 61.07 H, 6.66 Cl, 18.03 N, 14.24, found C, 61.07 H, 6.47 Cl, 18.17 N, 14.13.

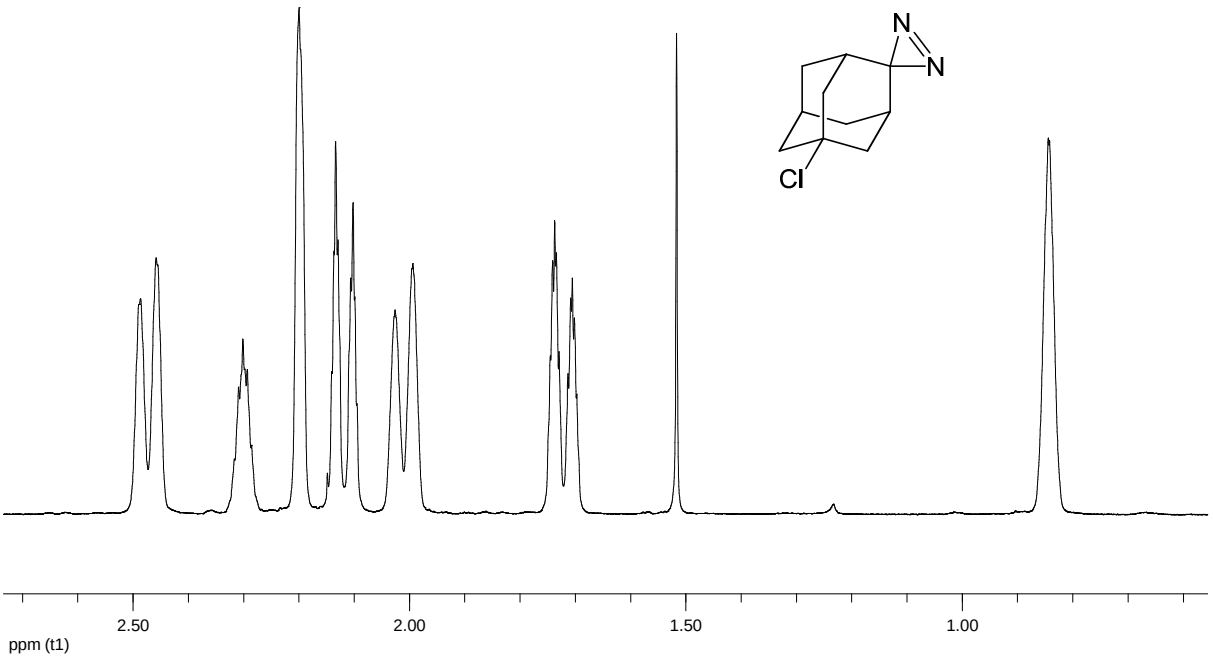

Figure S12. ^{1}H NMR spectrum of 5-chloro-2-aziadamantane (**2**).

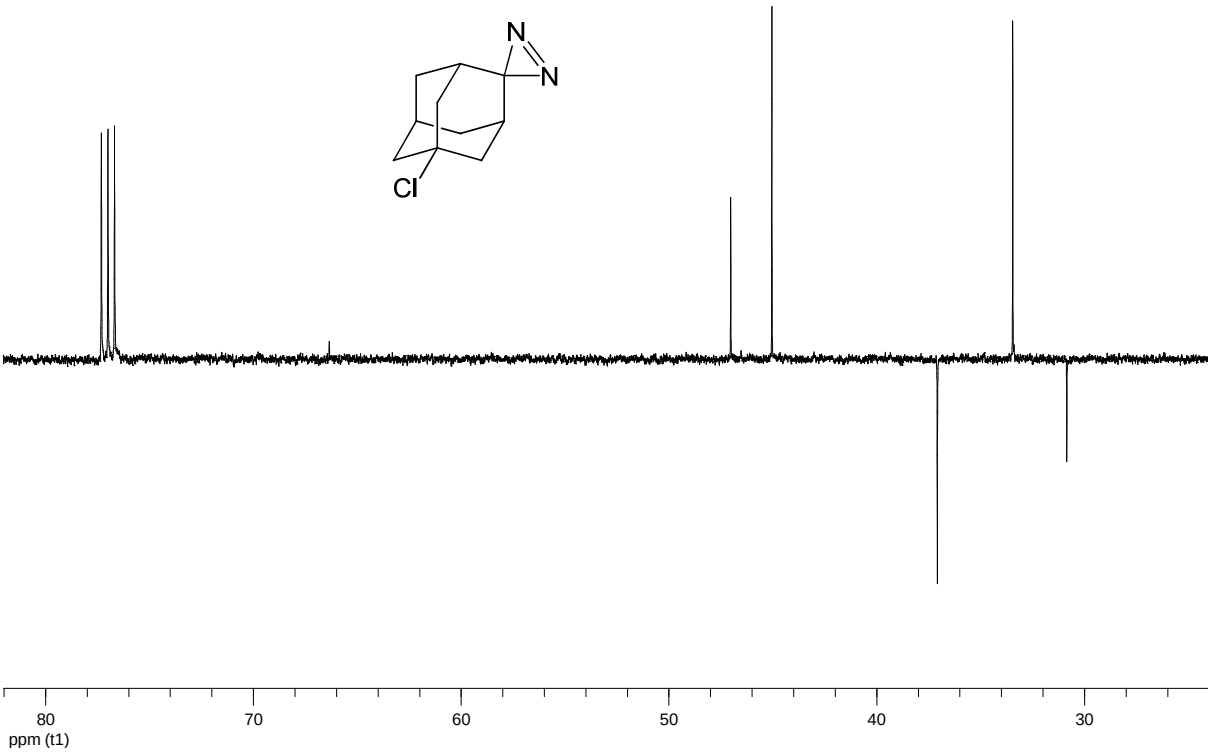

Figure S13. ^{13}C NMR spectrum of 5-chloro-2-aziadamantane (**2**).

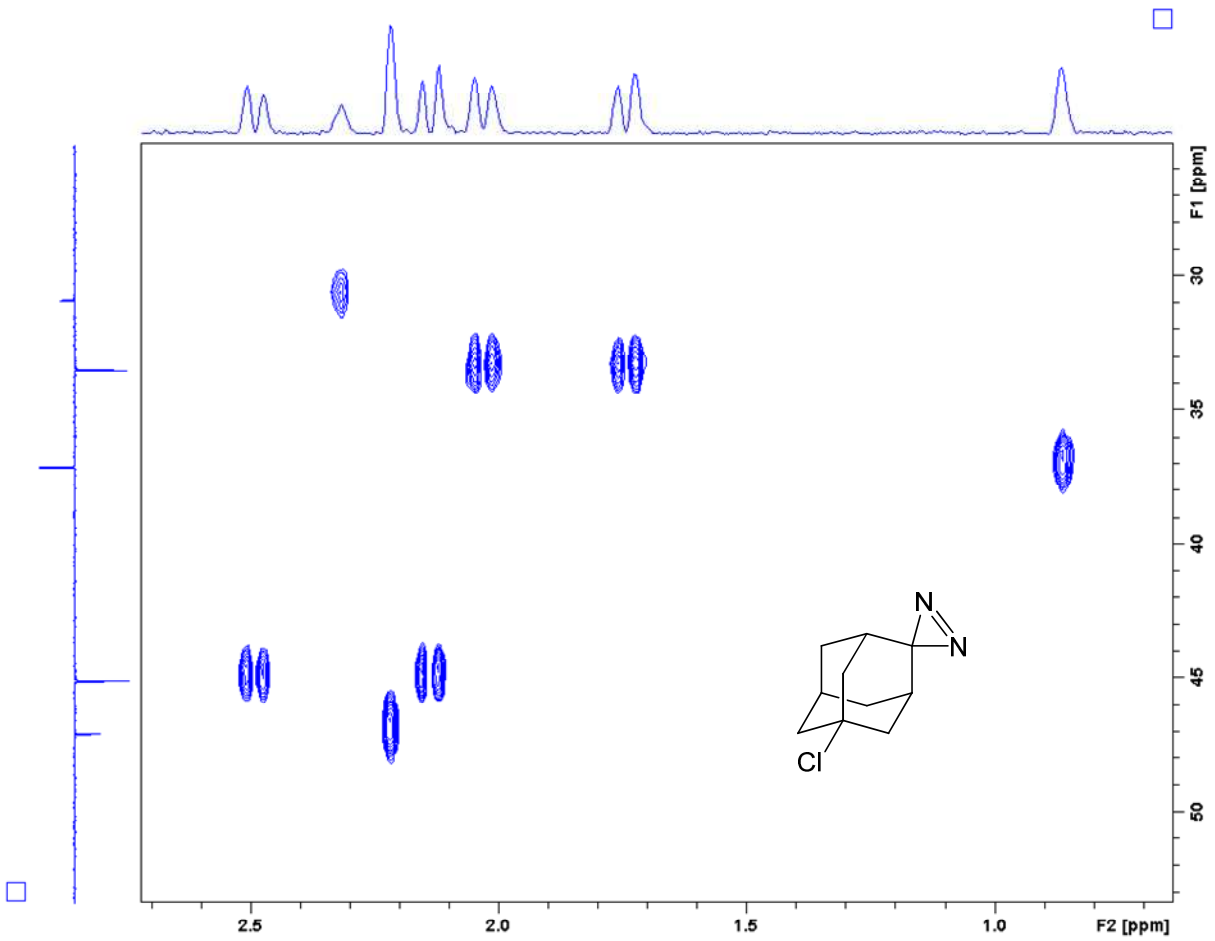

Figure S14. HSQC NMR spectrum of 5-chloro-2-aziadamantane (**2**).

*Preparation of complex **3**@**4** in the solid state*

44 mg (0.18 mmol) of 5-bromo-2-aziadamantane (**3**) were dissolved in 1.1 mL of CH_2Cl_2 at ambient temperature. 100 mg (0.059 mmol) of cavitand **4** were added to this mixture and dissolved by low heating of the probe. After scratching with a spatula to initiate the crystallization process, the suspension was stored in the dark for further crystallization for 1 h at room temperature. The volume of the solution was then reduced *in vacuo* to ca. 0.6 mL and, afterwards, the probe was stored in the dark for further crystallization for 1 h. Then the solution was further reduced *in vacuo* to 0.3 mL and, again, stored for crystalliazation for an additional 1 h. The finely granulated crystals were filtered using a frit, washed four times with 0.5 mL hexane and air was sucked through for ca. 1.5 h to facilitate drying. Drying *in vacuo* (0.1 Torr) for ca. 17 h at ambient temperature afforded 85 mg (74% yield) of complex **3**@**4** in a 1:1 ratio.

*Photolysis of complex **3**@**4** in the solid state*

131 mg of **3**@**4** (1:1) were grinded and placed in a 250 mL round-bottom flask and alternately evacuated and purged with argon three times. The flask was partially immersed in a cooled water bath (ca. +10 °C) and slowly rotated for the whole irradiation period. After photolysis for 5 h the formed crude product mixture was submitted to NMR, GC/MS and HPLC

(conversion: 100%; nitrobenzene as internal standard) analysis, respectively, to afford 5-bromo-2-hydroxyadamantanes **18** and **19** (74% combined yield), didehydroadamantanes **13** and **15** (25% combined yield) and traces of 5-bromo-2-adamantanone **7** (ca. 1%).
Chromatography on silica gel (gradient elution starting with $CHCl_3$/pentane (2:3) and then changing to pure $CHCl_3$) furnished 5-bromo-2-hydroxyadamantanes **18** and **19** (63% combined yield) and didehydroadamantanes **13** and **15** (25% combined yield). The yields of **18** and **19** have been partly calculated from NMR spectra of the mixtures with cavitand **4**, since a complete isolation of both alcohols was not possible due to the strong complexation of host **4** with **18** and **19** with the eluants used.

*5-Bromo-2-hydroxyadamantanes (**18** and **19**)*

18.3 mg (0.48 mmol) of $NaBH_4$ were dissolved in 2 mL of EtOH and added dropwise to a solution of 100 mg (0.44 mmol) of 5-bromo-2-adamantanone (**7**) in 5 mL of EtOH and stirred for ca. 1 h at ambient temperature. After this time, the mixture was poured onto 10 mL of ice with 1 mL of 36% HCl. The water phase was extracted three times with CH_2Cl_2 and the organic layer was dried over anhydrous $MgSO_4$. Removal of the solvent *in vacuo* gave 78 mg (0.34 mmol, 77% yield) of 5-bromo-2-hydroxyadamantanes **18** and **19**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46-1.52 (m, 2H), 1.62-1.69 (m, 1H), 1.77-1.84 (m, 1H), 1.97-2.13 (m, 5H), 2.29-2.37 (m, 4H), 2.67-2.73 (m, 1H), 3.79-3.83 (bs, 0.42H, (*Z*)-OH; **18**), 3.92-3.96 (bs, 0.58H, (*E*)-OH; **19**); ^{13}C NMR (150 MHz, $CDCl_3$) (*E*)-OH **19** δ 29.1, 31.8, 38.2, 47.6, 49.20, 63.8, 72.5; ^{13}C NMR (150 MHz, $CDCl_3$) (*Z*)-OH **18** δ 31.2, 34.4, 38.8, 42.6, 49.12, 64.8, 71.9; Anal. calcd. for $C_{10}H_{15}BrO$ C, 51.97 H, 6.54 Br, 34.57, found C, 52.11 H, 6.81 Br, 34.19.

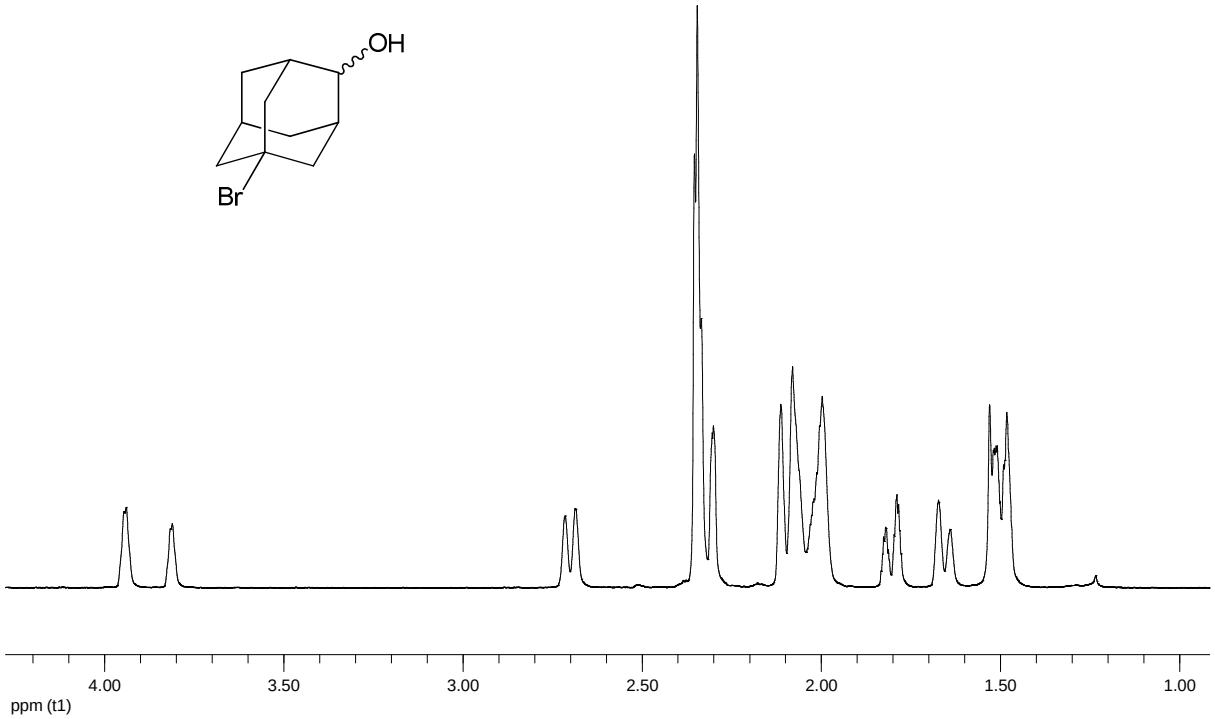

Figure S15. ^{1}H NMR spectrum of 5-bromo-2-hydroxyadamantanes (**18** and **19**).

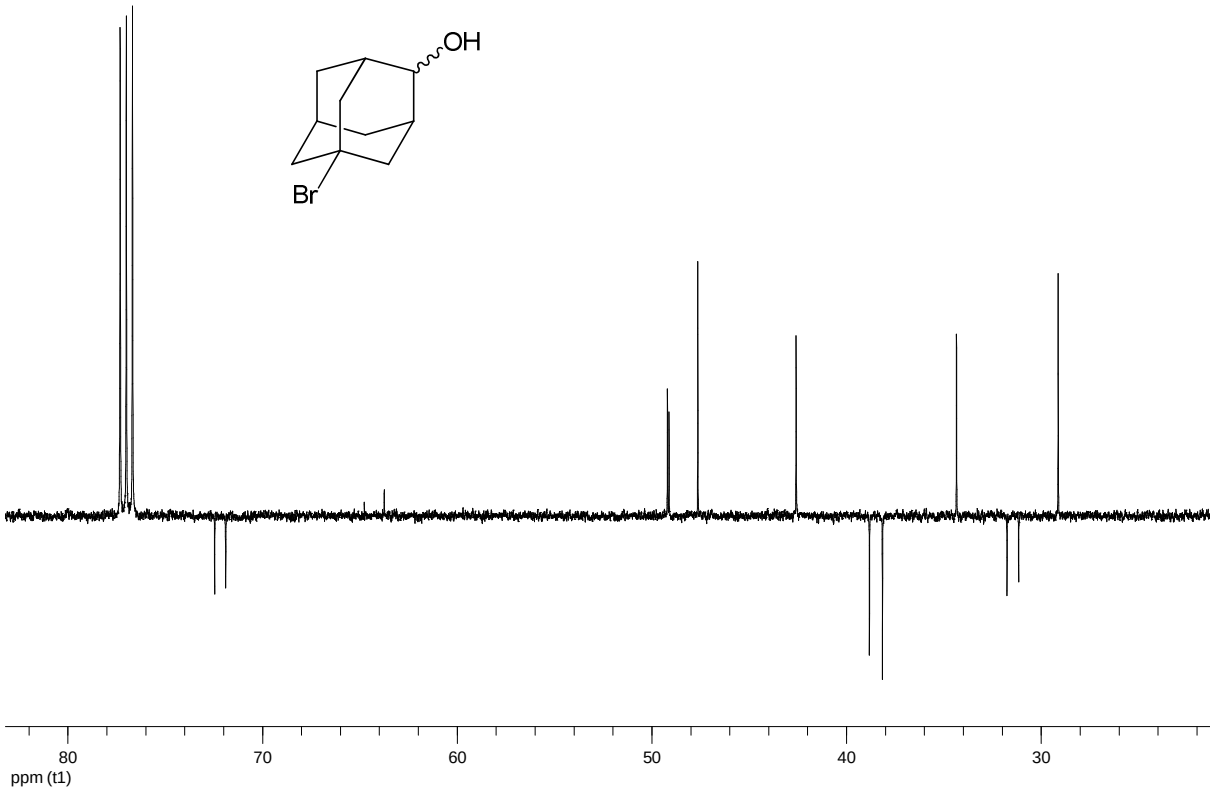

Figure S16. ^{13}C NMR spectrum of 5-bromo-2-hydroxyadamantanes (**18** and **19**).

*Preparative Vacuum Pyrolysis of 5-Bromo-2-aziadamantane (**3**)*

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*7-Bromo-2,4-didehydroadamantane (**13**)*

A two-necked round bottom flask, equipped with a trap immersed in liquefied nitrogen and a bent small flask, was evacuated to 0.5-1.0 Torr. 86 mg (0.36 mmol) of 5-bromo-2-aziadamantane (**3**) were placed in the bent flask and the two-necked round bottom flask was heated to 230-270 °C. The diazirine was knocked slowly in portions into the two-necked flask. After reaching the hot surface, the volatile products sublimed and were collected in the cooling trap. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45-1.55 (m, 4H), 2.00 (bs, 4H), 2.11-2.17 (m, 1H), 2.41 (bs, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.5, 26.7, 36.6, 40.2, 45.0, 51.3, 65.8; HRMS (EI) calcd. for $C_{10}H_{13}Br$ (M^+) 212.0201, found 212.0194.

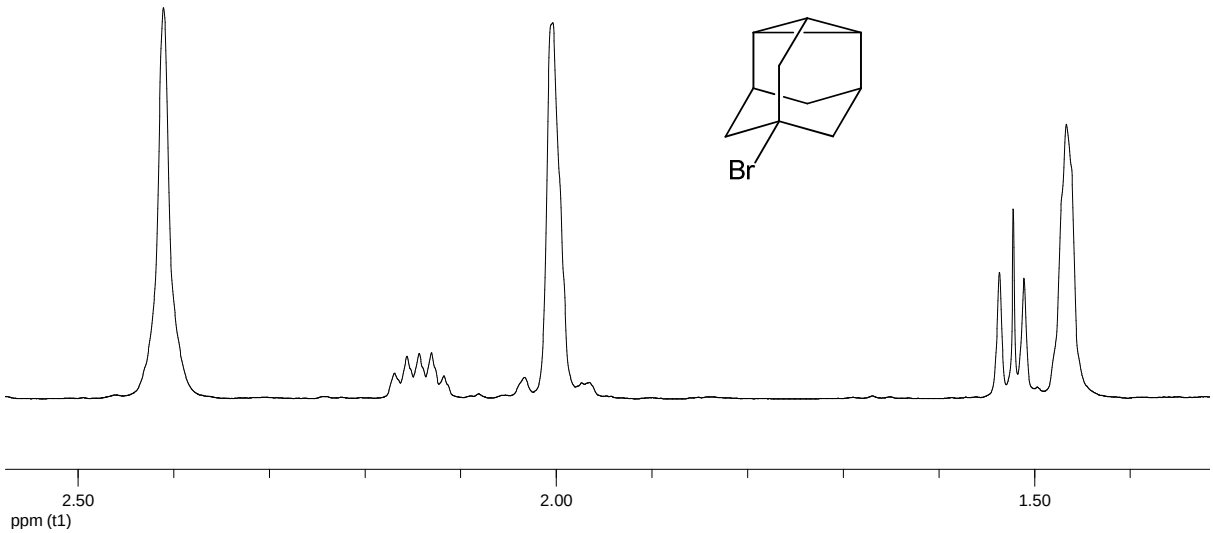

Figure S17. ^{1}H NMR spectrum of 7-bromo-2,4-didehydroadamantane (**13**).

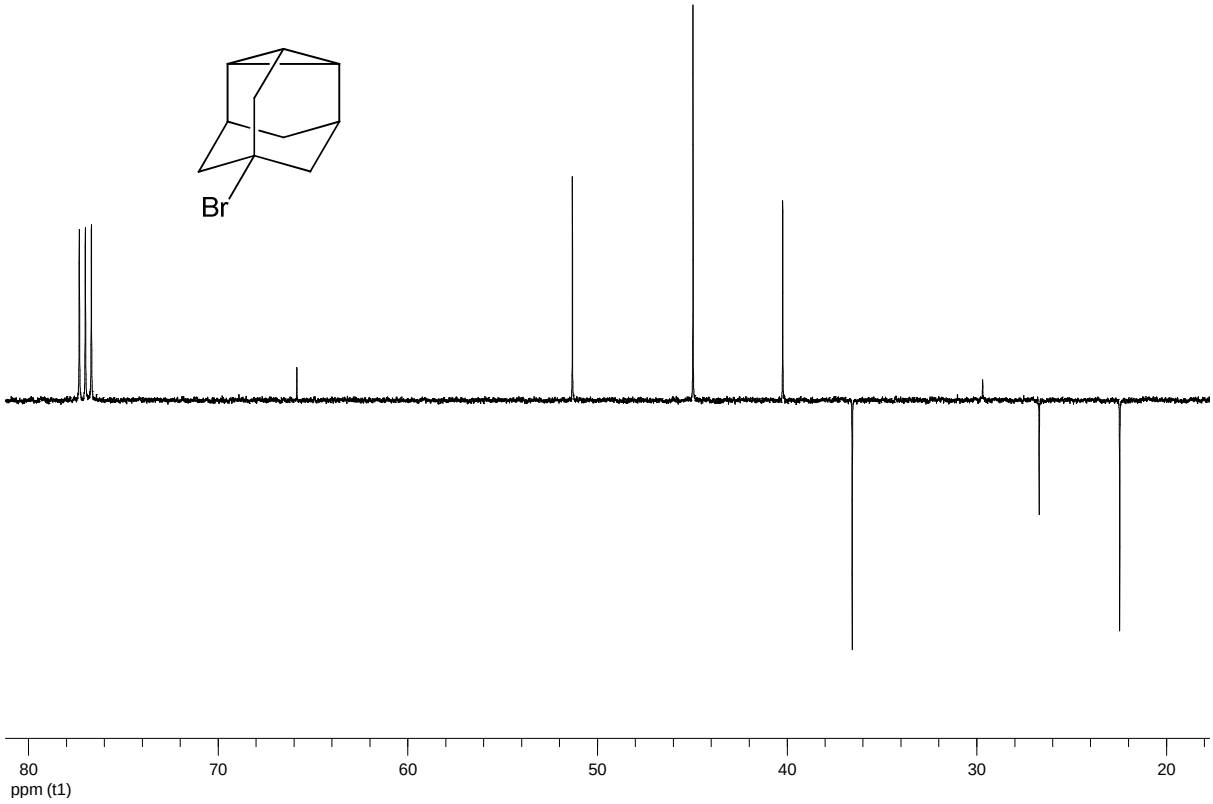

Figure S18. ^{13}C NMR spectrum of 7-bromo-2,4-didehydroadamantane (**13**).

*Preparative Vacuum Pyrolysis of 5-Chloro-2-aziadamantane (**2**)*

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*7-Chloro-2,4-didehydroadamantane (**12**)*

A two-necked round bottom flask, equipped with a trap immersed in liquefied nitrogen and a bent small flask, was evacuated to 0.05-0.1 Torr. 100 mg (0.51 mmol) of 5-chloro-2-aziadamantane (**2**) were placed in the bent flask and the two-necked round bottom flask was heated to 230-270 °C. The diazirine is knocked slowly in portions into the two-necked flask.

After reaching the hot surface, the volatile products sublimed and were collected in the cooling trap. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43-1.57 (m, 4H), 1.74-1.84 (m, 4H), 2.06-2.13 (m, 1H), 2.17-2.21 (m, 2H), 2.48 (bs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.6, 26.7, 36.1, 38.9, 43.6, 51.2, 69.0; HRMS (EI) calcd. for $C_{10}H_{13}Cl$ (M^+) 168.0706, found 168.0707.

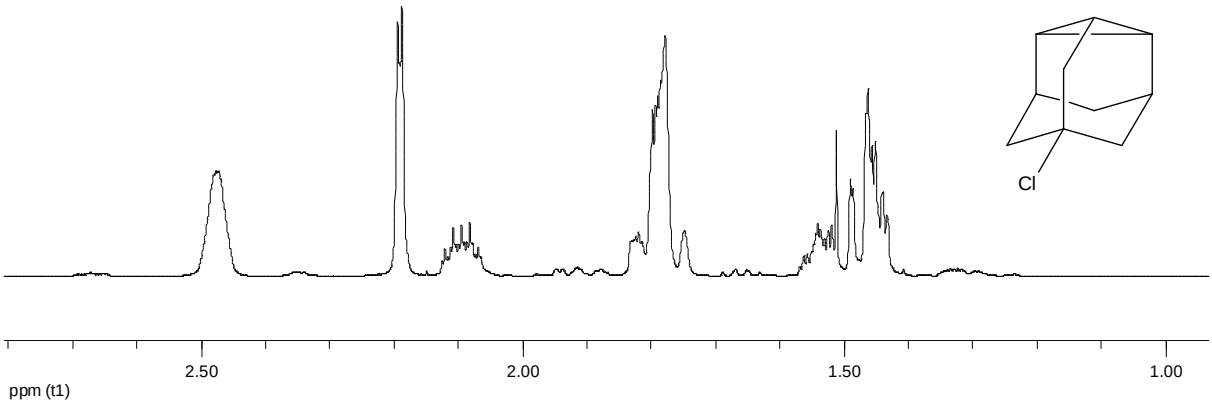

Figure S19. ^{1}H NMR spectrum of 7-chloro-2,4-didehydroadamantane (**12**).

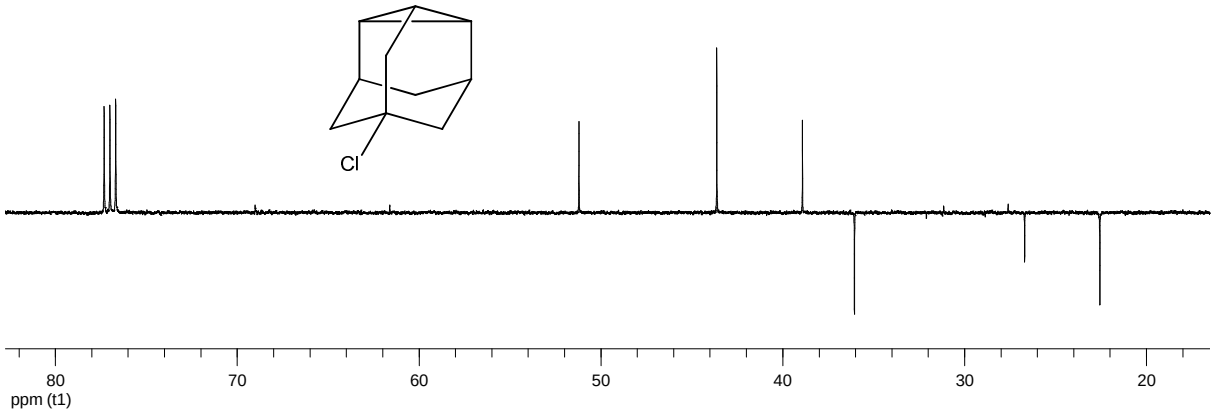

Figure S20. ^{13}C NMR spectrum of 7-chloro-2,4-didehydroadamantane (**12**).[1]

*Photolysis of 5-Bromo-2-aziadamantane (**3**)*

↓

*5-Bromo-2-adamantanone Azine (**17**)*

25 mg (0.10 mmol) of 5-bromo-2-aziadamantane (**3**) were placed in a 250 mL round-bottom flask and alternately evacuated and purged with argon three times. The flask was partially immersed into a cooled water bath (ca. +10 °C) and slowly rotated for the whole irradiation period. After photolysis for 4.5 h, the crude product mixture was washed with hot hexane to give 16 mg (0.035 mmol, 70% yield) of 5-bromo-2-adamantanone azine (**17**). Mp: 175-179 °C; IR (neat): 2931, 2855, 1646, 1445, 1077, 1017, 809, 648; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74-180 (m, 2H), 1.86-1.93 (m, 4H), 1.95-2.01 (m, 2H), 2.20 (bs, 2H), 2.32-2.51 (m, 12H), 2.74 (bs, 2H), 3.47 (bs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 31.9, 34.8, 36.26, 36.31, 37.50,

(1) The small peaks not included in the peak list correspond to minor isomer **14**.

37.52, 42.5, 48.1, 48.6, 49.8, 62.2, 62.3; HRMS (ESI) calcd. for $C_{20}H_{27}Br_2N_2$ ($M+H^+$) 455.0521, found 455.0526.

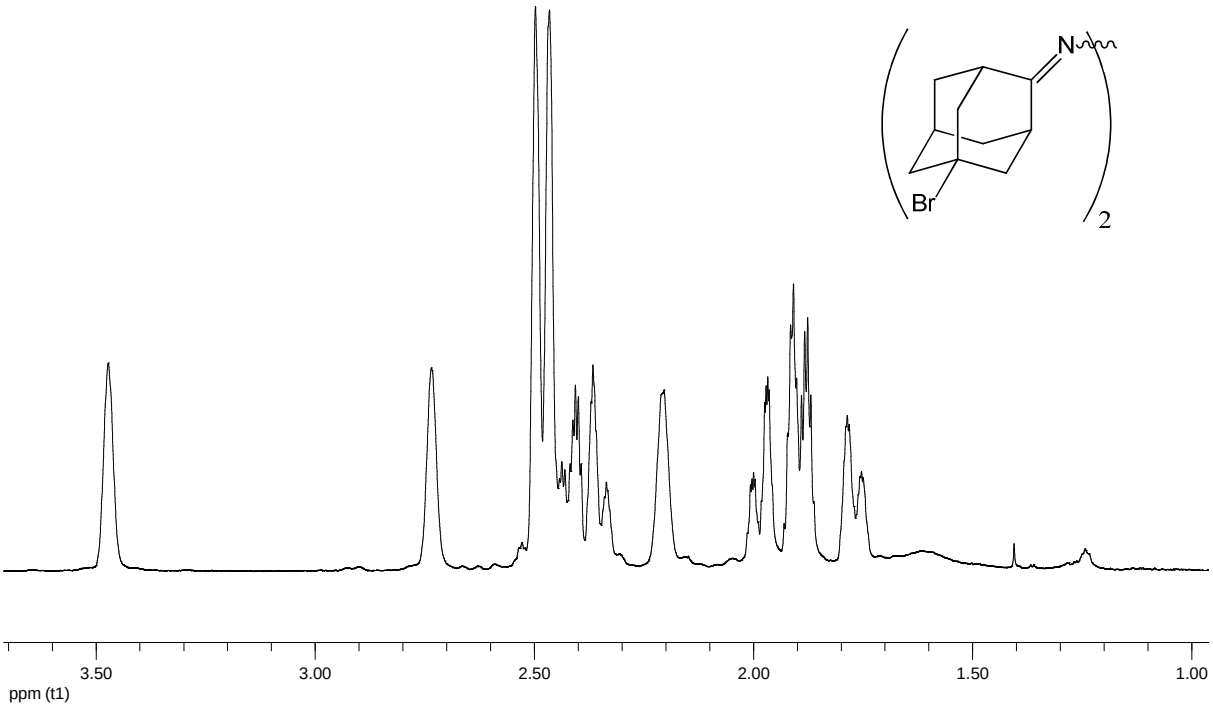

Figure S21. [1]H NMR spectrum of 5-bromo-2-adamantanone azine (**17**).[2]

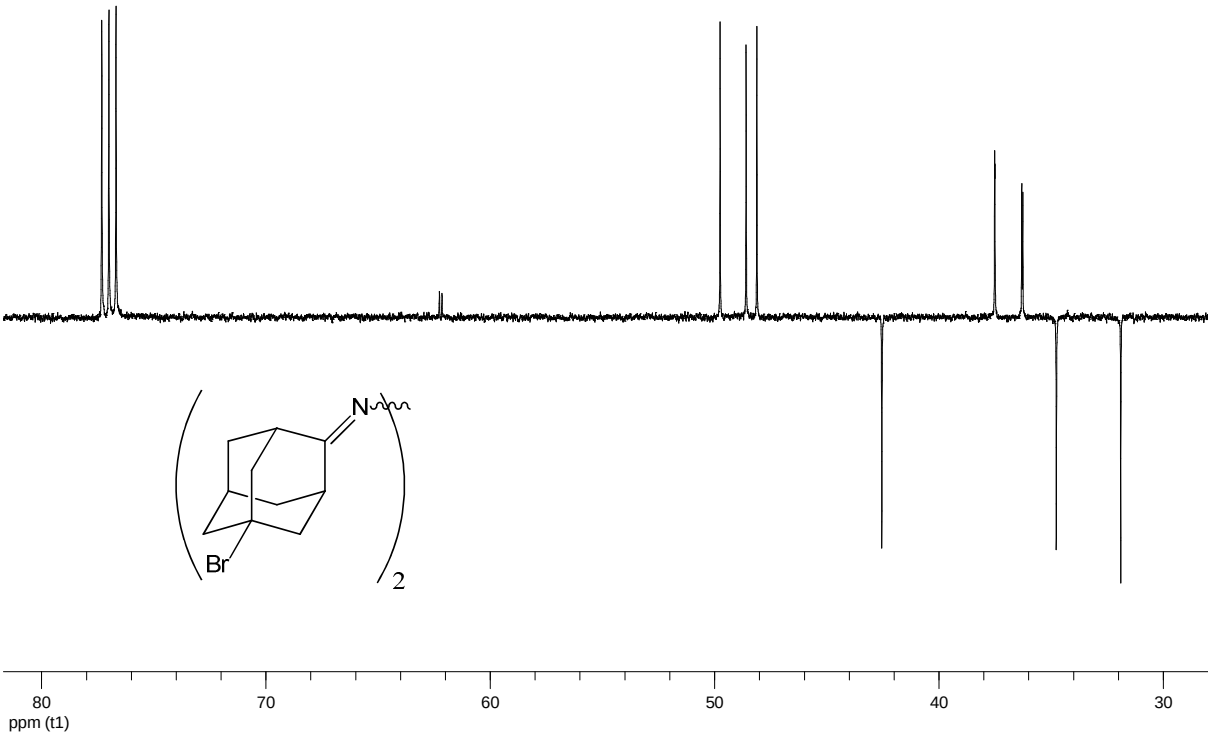

Figure S22. [13]C NMR spectrum of 5-bromo-2-adamantanone azine (**17**).[2]

(2) The spectra include two azine isomers.

*Photolysis of 5-Chloro-2-aziadamantane (**2**)*

↓

*5-Chloro-2-adamantanone Azine (**16**)*

50 mg (0.25 mmol) of 5-chloro-2-aziadamantane (**2**) were placed in a 250 mL round-bottom flask and alternately evacuated and purged with argon three times. The flask was partially immersed into a cooled water bath (ca. +10 °C) and slowly rotated for the whole irradiation period. After photolysis for 4.3 h, the crude product mixture was recrystallized in hexane to give 29 mg (0.08 mmol, 63% yield) of 5-chloro-2-adamantanone azine (**16**). Mp: 177-179 °C; IR (neat): 2925, 2855, 1648, 1448, 1077, 1023, 827, 666; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67-1.75 (m, 2H), 1.80-1.88 (m, 4H), 1.90-1.97 (m, 2H), 2.12-2.30 (m, 14H), 2.76 (bs, 2H), 3.49 (bs, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 31.1, 33.8, 36.32, 36.36, 37.56, 37.58, 41.6, 46.7, 47.0, 48.1, 66.02, 66.09, 169.44, 169.49; HRMS (ESI) calcd. for $C_{20}H_{27}Cl_2N_2$ ($M+H^+$) 365.1551, found 365.1557.

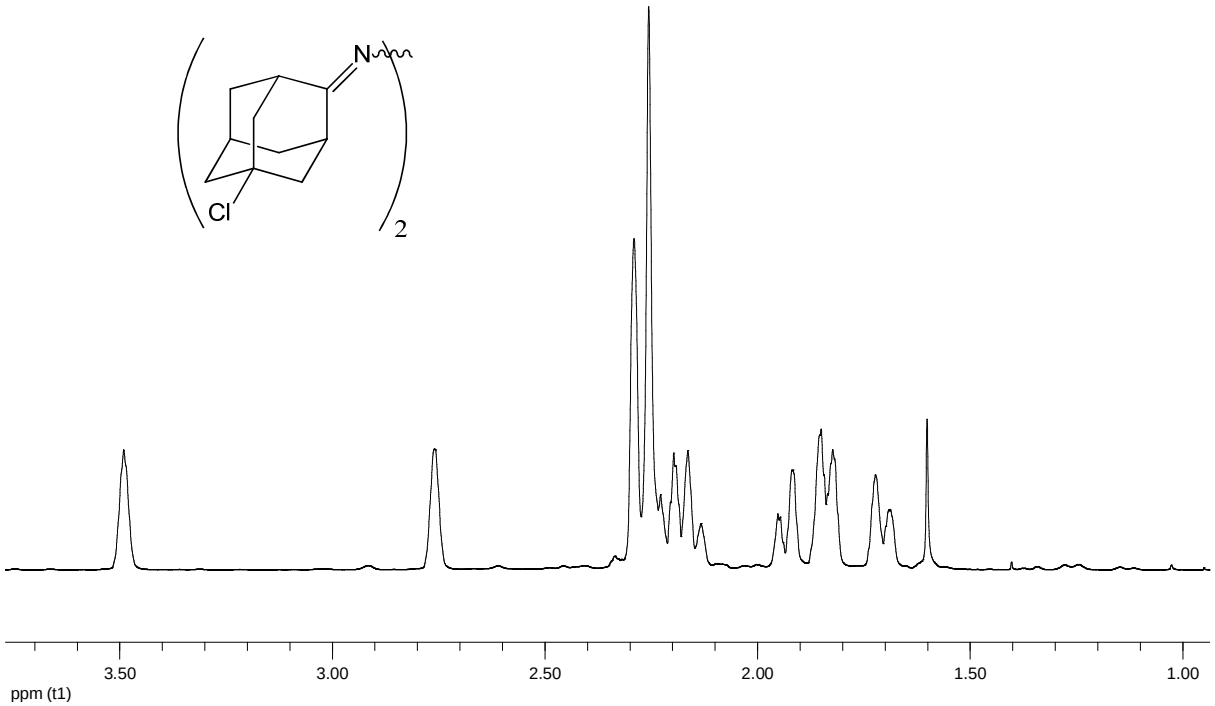

Figure S23. ^{1}H NMR spectrum of 5-chloro-2-adamantanone azine (**16**).[3]

(3) The spectra include two azine isomers.

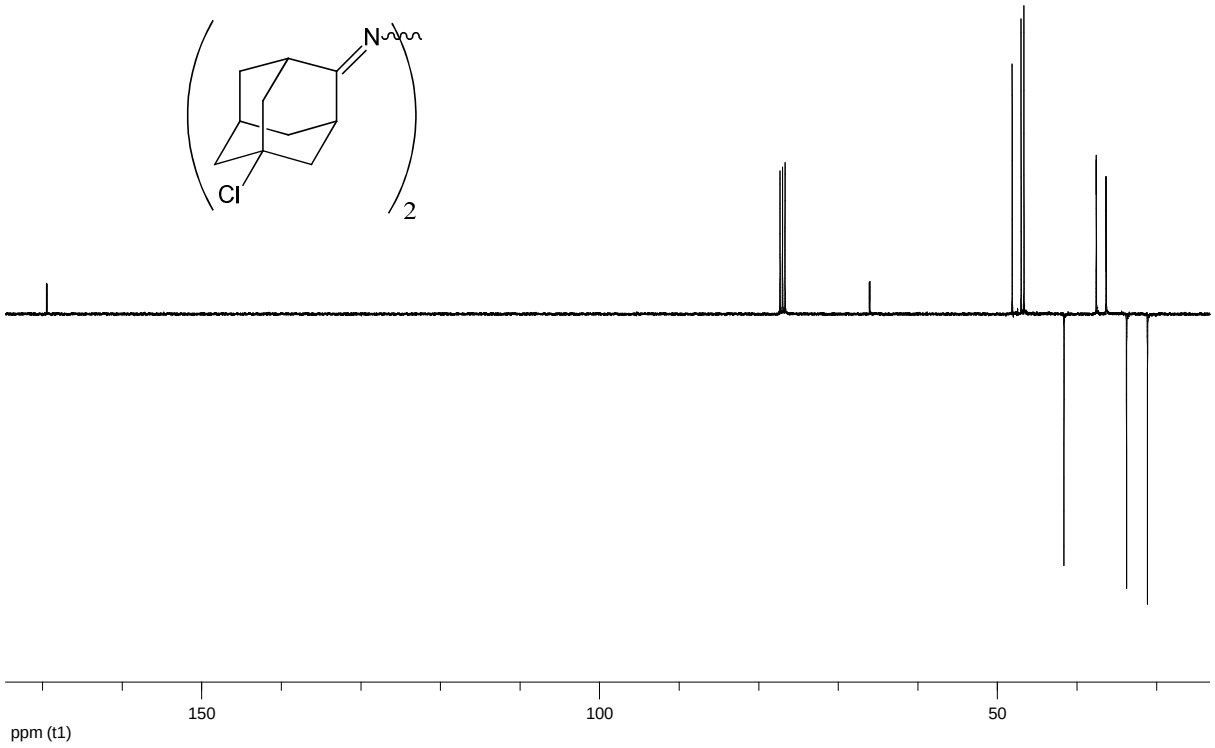

Figure S24. ^{13}C NMR spectrum of 5-chloro-2-adamantanone azine (**16**).[3]

Binding experiments

Cavitand **4** forms slow binding 1:1 complexes on the NMR time scale (400 MHz) with all adamantanediazirines investigated in DMSO-d_6. The integrations of the signals for H_a from the host in free and complexed form were used to obtain the equilibrium concentrations for the calculation of the association constants K_a.

$$H + G \rightleftharpoons HG \qquad [H] = [H]_0\text{-}[HG] \qquad [G] = [G]_0\text{-}[HG]$$

$$K_a = \frac{[HG]}{[H][G]}$$

A representative ^{1}H NMR spectrum is shown in Figure S25 for the **3**@**4** complex.

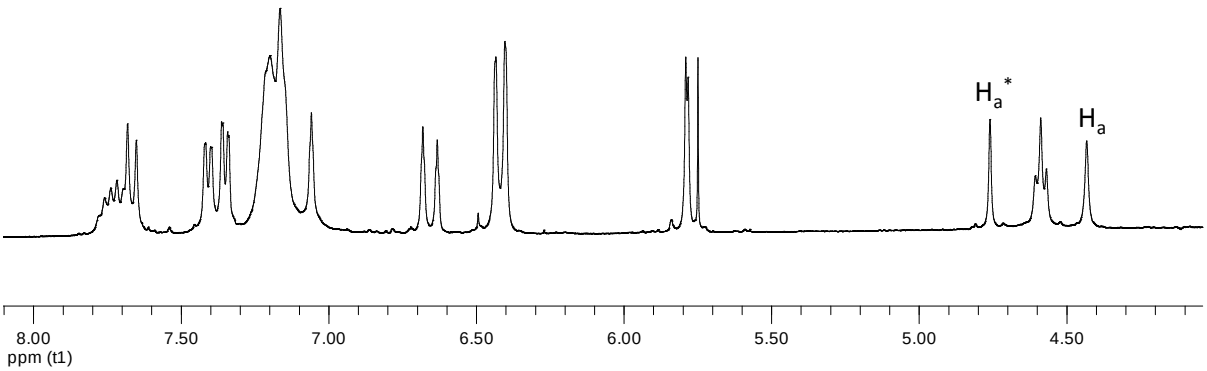

Figure S25. Part of the ^{1}H NMR spectrum of complex **3@4** in DMSO-d_6 (* corresponds to complexed state).

Guest orientation

ROESY NMR was used to determine the orientation of slow binding 5-bromo-2-aziadamantane (**3**) within the cavity of cavitand **4** in DMSO-d_6. The peak assignments are shown in Figure S26.

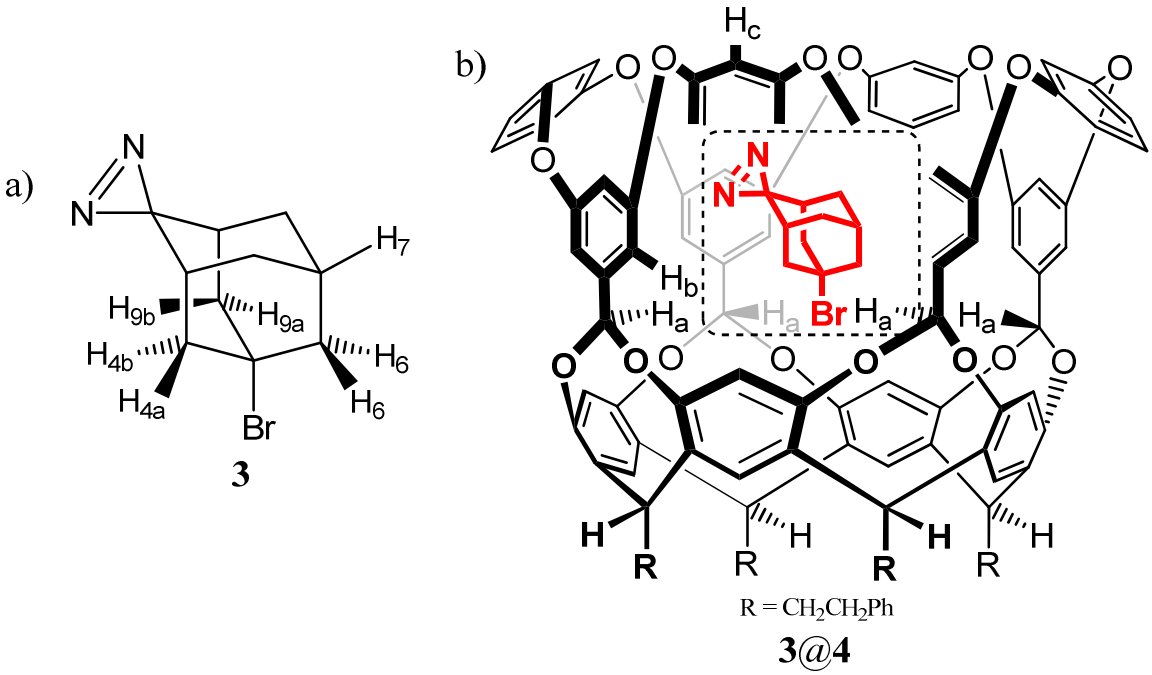

Figure S26. Signal assignments of a) 5-bromo-2-aziadamantane (**3**) and b) complex **3@4** for ROESY NMR analysis (Figure S27).

NOE cross peaks (Figure S27) occur between H_a^* from the host and H_6^*/H_{4a}^* from diazirine **3**.[4] Additionally, NOE signals between H_b^* and H_6^*/H_{4a}^* and between H_c^* and H_7^* are observed, indicating that 5-bromo-2-aziadamantane (**3**) is positioned in a bromine-down orientation within cavitand **4** (Figure S26b).

(4) H_{4a} and H_{9a} are identical.

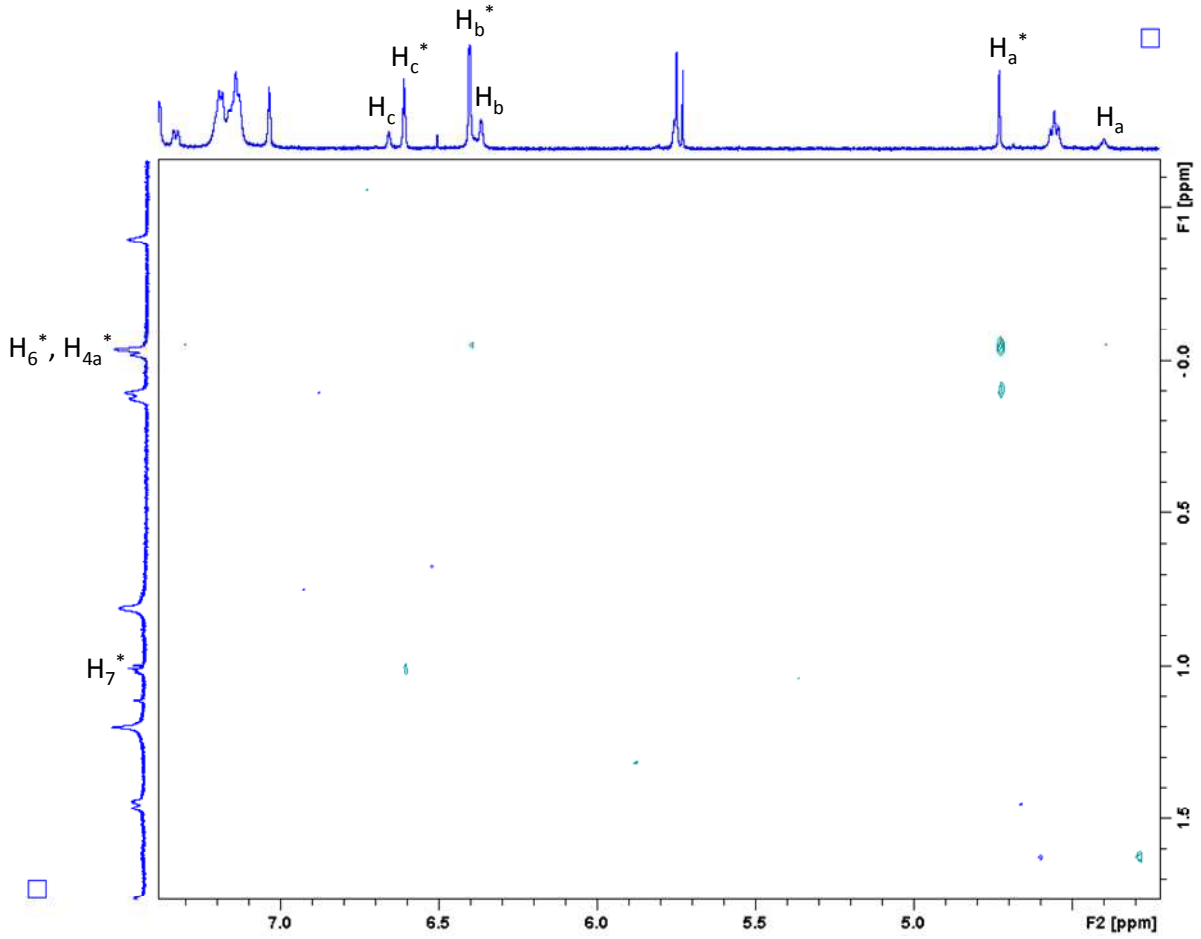

Figure S27. ROESY NMR of complex **3@4** in DMSO-d_6.

Severely Disordered X-ray structure of 3@4

The crystals for X-ray diffraction were grown from a solution of cavitand **4** and 5-bromo-2-aziadamantane (**3**) in $CHCl_3$. The quality of the X-ray data is too low for publication, due to severe disorder. Nevertheless, it is deemed to be assured that the bromine atom of **3** is pointing inward the cavity of cavitand **4** (Figure S28).

Crystallographic data: Space group: P-1
Cell Parameters:
Cell lengths: **a** 13.350(3) **b** 18.348(5) **c** 24.948(7)
Cell angles: **α** 75.032(7) **β** 82.770(7) **γ** 76.203(7)

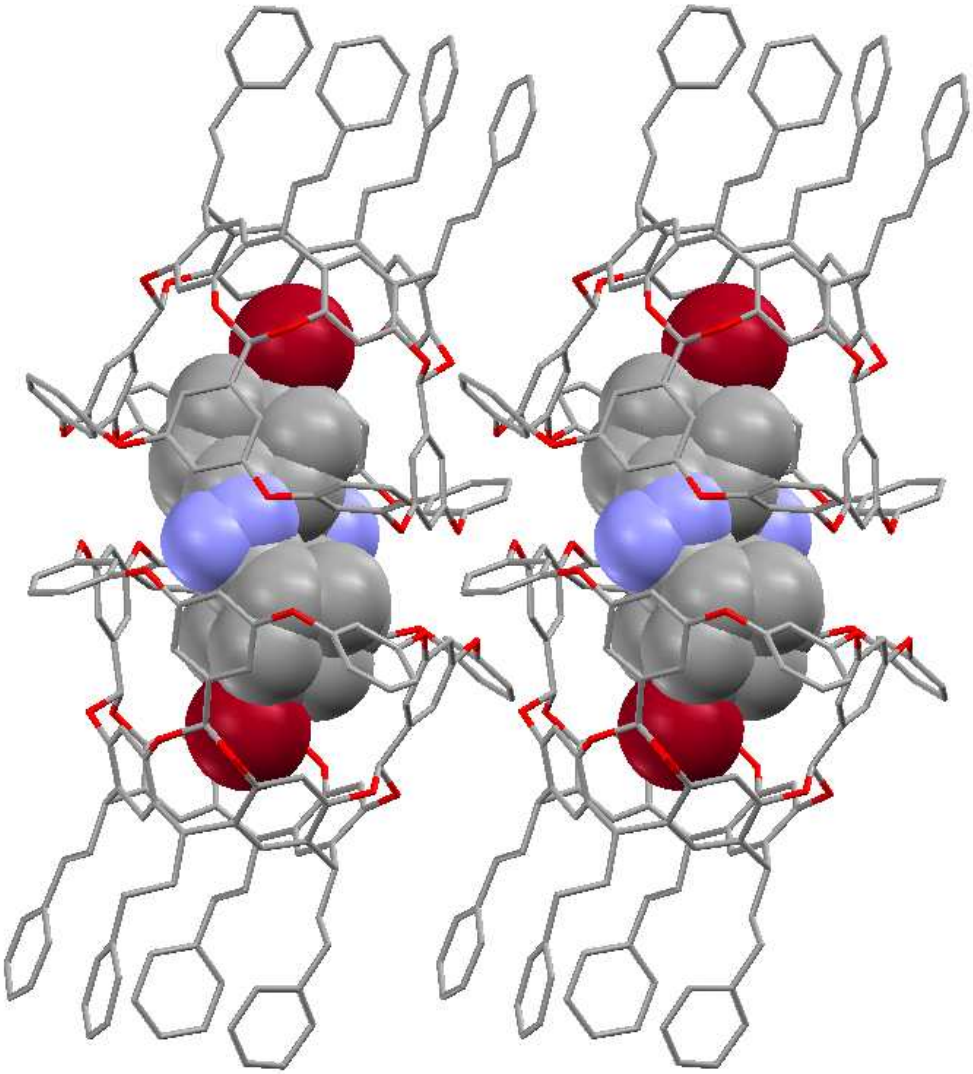

Figure S28. Detail of the crystal lattice of **3@4** showing the bromine group in a down orientation of disordered 5-bromo-2-aziadamantane (**3**) inside the cavity of cavitand **4**.