Synthesis and Recognition Studies with a Ditopic, Photoswitchable Deep Cavitand †

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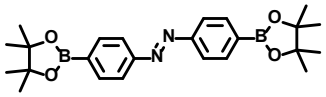
I. General methods

All reactions were carried out under an atmosphere of argon unless otherwise indicated. All reagents were purchased from Aldrich and were used as received without further purification. All deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. Analytical thin-layer chromatography (TLC) was performed on Silicycle 60 F254 glass-backed plates. Column chromatography was performed using Silicycle R10030B 60 Å 230-400 mesh silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded at 600 MHz and 150 MHz respectively, using a Bruker DRX-600 spectrometer equipped with a 5 mm QNP probe. Chemical shifts of ^{1}H NMR and ^{13}C NMR of characterized compounds are given in ppm by the using residual solvent peak as reference. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), br (broad), d (doublet), t (triplet), q (quartet), m (multiplet). MALDI-TOF spectra and high-resolution mass spectra (HRMS) were recorded respectively on an Applied Biosystems Voyager STR (2) apparatus and an Agilent ESI-TOF mass spectrometer. UV absorption spectra were recorded on a Varian Cary 50 UV-Visible spectrophotometer. Photoisomerization to the *cis* isomer was performed with a Blak-Ray Long Wave Ultraviolet Lamp, Model B-100 AP after filtering out all light above 400 nm with a filter obtained from Andover Corporation. For the reverse isomerization process a High Intensity Discharge – Quartz Metal Halide light was used (GE Multi-Vapor Quartz Metal Halide ED37). The irradiation of the solutions was conducted in the NMR tubes. Heating steps were also done in the NMR tubes using a heatgun. Molecular modeling (semi-empirical calculations) was carried out using the PM3 force field as implemented by Spartan.

II. Synthetic procedures

1. Synthesis of diboronic ester 3

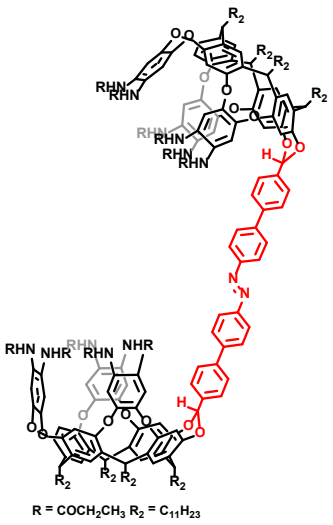


4,4'-dibromoazobenzene[1] (958 mg, 2.81 mmol, 1 eq.), bis(pinacolato)diboron (2.67 g, 10.63 mmol, 3.8 eq.) and potassium acetate (1.114 g, 11.35 mmol, 4 eq.) were dissolved in neat DMSO (15 mL). The mixture was degassed by N_2 bubbling (10 min) then $Pd(PPh_3)_4$ (500 mg, 0.43 mmol, 15% mol) was added. The mixture was warmed at 80°C and stirred for 28 hours. After cooling, dichloromethane (50 mL) and H_2O (50 mL) were added. After separation, the aqueous phase was extracted with dichloromethane (3 x 50 mL). Organic layers were combined, dried over Na_2SO_4 and concentrated. The crude was purified by flash chromatography on a silicagel column (Deposit was done with the minimum possible of hot AcOEt/Hexanes 10/90; elution gradient: 2/98 AcOEt/Hexanes, then 5/95) to afford the desired pure diboronic ester **3** (258 mg, 20 %) as an orange solid.

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ ppm 7.96 (d, 4H, ^3J = 8.0 Hz, H_{arom}), 7.90 (d, 4H, ^3J = 8.0 Hz, H_{arom}), 1.37 (s, 24 H, CH_3).

HRMS-ESI: $[MH]^+$; calculated for $C_{24}H_{33}B_2N_2O_4^+$: 435.2621 found: 435.2637.

2. Synthesis of receptor 1



In a vial (2 mL) equipped with a screw cap were introduced iodo-cetal cavitand **2**[2] (49 mg, 25 µmol, 2 eq.) and diboronic ester **3** (5.9 mg, 14 µmol, 1.1 eq.). Then a degassed solution (20 min bubbling N_2) of aqueous K_2CO_3 (200 µL; 2M), degassed THF (20 min bubbling N_2) (500 µL) and $PdCl_2(PPh_3)_2$ (1.7 mg, 2 µmol, 8% mol cavitand) were successively added. The vial was flushed with N_2, capped and stirred in an oil bath preheated at 70°C. After 24 hours at

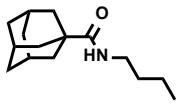
the same temperature, the crude was evaporated to dryness and purified by flash chromatography on a silicagel column (Ø1.5 cm x 20 cm; Elution gradient: CH_2Cl_2 pure, 5/95 AcOEt/CH_2Cl_2, 15/85, 25/75, 35/65 then 45/55) to give the pure receptor **1** (20 mg, 42 %) as an orange solid.

^{1}H NMR (600 MHz, $CDCl_3$, 300 K) (Trans isomer): δ ppm 9.60-9.45 (br s, 4H, NH), 9.341-9.25 (br s, 4H, NH), 8.12 (d, 4H, ^3J = 8.0 Hz, $H_{arom\ azo\ wall}$), 8.06 (d, 4H, ^3J = 8.0 Hz, $H_{arom\ azo\ wall}$), 8.04-7.92 (br s, 4H, NH), 7.84 (d, ^3J = 8.2 Hz, 4H, $H_{arom\ azo\ wall}$), 7.81 (d, ^3J = 8.2 Hz, 4H, $H_{arom\ azo\ wall}$), 7.60-7.45 (m, 8H, H_{arom}), 7.44-7.19 (m, 16H, H_{arom}), 7.01-6.91 (br s, 4H, H_{arom}), 5.81 (t, 2H, ^3J = 8.2 Hz, methine feet), 5.77 (t, 4H, ^3J = 8.1 Hz, methine feet), 5.42 (s, 2H, benzal hydrogen), 4.91 (t, 2H, ^3J = 8.0 Hz, methine feet), 2.54-2.17 (m, 40H, CH_2 feet & $COCH_2$), 1.53-1.12 (m, 180H, CH_3 amide & CH_2 feet), 0.93-0.84 (m, 24H, CH_3 feet).

^{13}C NMR (150 MHz, $CDCl_3$, 300 K) (Trans isomer): δ ppm 173.86, 173.56, 155.08, 154.68, 152.19, 150.12, 149.78, 143.54, 140.96, 139.18, 138.26, 135.96, 135.68, 128.29, 128.02, 127.72, 127.46, 124.50, 123.67, 121.89, 120.71, 116.42, 107.22, 99.74, 88.40, 36.50, 33.56, 32.60, 32.12, 30.89, 30.31, 29.99, 29.90, 29.58, 29.21, 28.18, 22.87, 14.29, 10.53, 9.95.

MALDI-TOF: $[MNa]^+$; calculated for $C_{242}H_{310}N_{14}O_{28}Na^+$: 3883 found: 3883.

3. Synthesis of guest G1



To a solution of 1-adamantanecarbonyl chloride (366 mg, 1.8 mmol, 1 eq.) in dry THF (10 mL) at 0°C was added dropwise n-butylamine (632 µL, 6.3 mmol, 3.5 eq.). After 1 hour of stirring at the same temperature, MR was warmed at RT and stirred for 15 hours. After evaporation, AcOEt (10 mL) and HCl aq. 1M (10 mL) were added. Organic phase was washed another time with HCl aq. 1M, dried over Na_2SO_4 and concentrated. The crude was purified by flash chromatography on a silicagel column (Elution gradient: 15/85 AcOET/Hexanes then 25/85) to yield **G1** (232 mg, 54%) as a white solid.

Rf 0.46 (20/80 AcOEt/Hexanes)

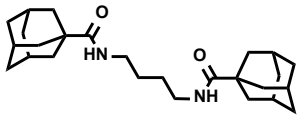
^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ ppm 5.54 (br, 1H, NH), 3.23 (m, 2H, CH_2N), 2.04 (m, 3H, Ad), 1.85 (m, 6H, Ad), 1.72 (m, 6H, Ad), 1.47 (m, 2H, CH_2CH_2N), 1.34 (m, 2H, CH_2CH_3), 0.92 (t, ^3J = 7.3 Hz, 3H, CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 300 K): δ ppm 177.97, 39.48, 39.30, 38.98, 36.54, 31.73, 28.16, 20.04, 13.75.

4. General synthetic procedure for homoditopic guests G2 – G6

To a solution of 1-adamantanecarbonyl chloride (2.1 eq.) and triethylamine (3 eq.) in dry THF (0.1 M) at 0°C was added by portions the diamine (1 eq.). After 1 hour of stirring at the same temperature, the mixture was warmed to RT and stirred for 17 hours. The crude was diluted with CH_2Cl_2. The organic phase was washed with HCl aq. 1M (x2) (if the crude was not enough diluted, a white solid, which is the desired compound, could be observed at the interface), dried over Na_2SO_4 and concentrated. The crude was purified by flash column chromatography on a silicagel column (dry loading; elution gradient: 20/80 AcOEt/Hexanes then 50/50 AcOEt/CH_2Cl_2) to yield the desired diadamantane derivatives **G2-G6** as white solids.

- Guest **G2**:



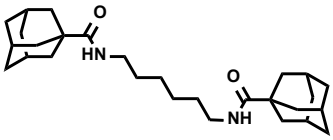
Yield: 61%

Rf: 0.58 (30/70 AcOEt/CH_2Cl_2)

^{1}H NMR (600 MHz, MeOD, 300 K): δ ppm 3.17 (m, 4H, CH_2 linker), 2.01 (m, 6H, CH Ad), 1.83 (m, 12H, CH_2 Ad), 1.73 (m, 12H, CH_2 Ad), 1.46 ppm (m, 4H, CH_2 linker).

^{13}C NMR (150 MHz, MeOD, 300 K): δ ppm 180.20, 41.28, 39.75, 39.42, 37.15, 29.06, 27.35.

- Guest **G3**:

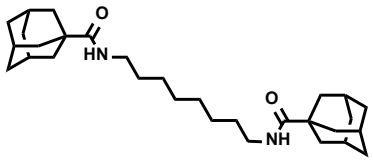


Yield: 54%

^{1}H NMR (600 MHz, MeOD, 300 K): δ ppm 3.22 (t, ^{3}J = 4.3 Hz, 4H, CH_2 linker), 2.53 (m, 6H, CH Ad), 2.43 (m, 12H, CH_2 Ad), 2.37 (m, 12H, CH_2 Ad), 2.22 (m, 4H, CH_2 linker), 2.12 ppm (m, 4H, CH_2 linker).

^{13}C NMR (150 MHz, MeOD, 300 K): δ ppm 180.44, 41.52, 39.98, 39.96, 37.38, 30.19, 29.35, 27.22.

- Guest **G4**:

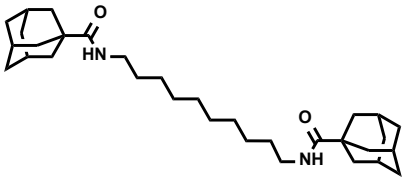


Yield : 56%

^{1}H NMR (600 MHz, MeOD, 300 K): δ ppm 6.81 (br, NH), 3.15 (m, 4H, CH_2 linker), 2.01 (m, 6H, CH Ad), 1.83 (m, 12H, CH_2 Ad), 1.73 (m, 12H, CH_2 Ad), 1.47 (m, 4H, CH_2 linker), 1.30 ppm (m, 8H, CH_2 linker).

^{13}C NMR (150 MHz, MeOD, 300 K): δ ppm 180.17, 41.35, 40.15, 39.83, 37.20, 30.08, 29.91, 29.13, 27.48.

- Guest **G5**:



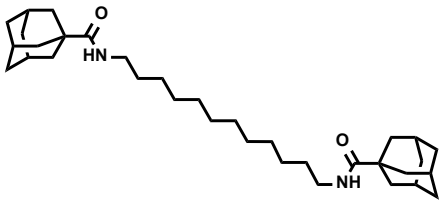
Yield : 59%

Rf: 0.44 (50/50 AcOEt/CH_2Cl_2)

^{1}H NMR (600 MHz, MeOD, 300 K): δ ppm 3.15 (m, 4H, CH_2 linker), 2.01 (m, 6H, CH Ad), 1.83 (m, 12H, CH_2 Ad), 1.72 (m, 12H, CH_2 Ad), 1.47 (m, 4H, CH_2 linker), 1.29 ppm (m, 12H, CH_2 linker).

^{13}C NMR (150 MHz, MeOD, 300 K): δ ppm 180.16, 41.36, 40.10, 39.84, 37.23, 30.19, 30.14, 30.03, 29.16, 27.58.

- Guest **G6**:



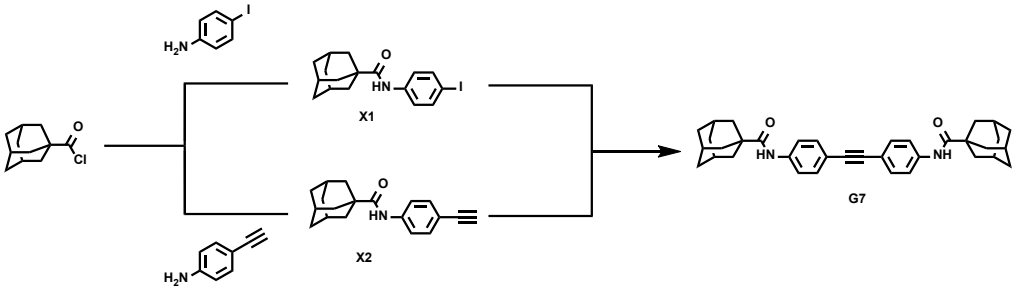
Yield : 53%

Rf: 0.5 (50/50 AcOEt/CH_2Cl_2)

^{1}H NMR (600 MHz, MeOD, 300 K): δ ppm 3.15 (t, ^{3}J = 7.1 Hz, 4H, CH_2 linker), 2.01 (m, 6H, CH Ad), 1.83 (m, 12H, CH_2 Ad), 1.74 (m, 12H, CH_2 Ad), 1.47 (m, 4H, CH_2 linker), 1.28 ppm (m, 12H, CH_2 linker).

^{13}C NMR (150 MHz, MeOD, 300 K): δ ppm 180.24, 41.42, 40.14, 39.89, 37.28, 30.31, 30.32, 30.19, 30.10, 29.23, 27.63.

5. Synthetic procedures of guest G7



- Synthesis of intermediate **X1**

To a solution of 1-adamantanecarbonyl chloride (650 mg, 3.27 mmol, 1.3 eq.) and triethylamine (670 µL, 2 eq.) in dry THF (12 mL) at 0°C was added by portions p-iodoaniline (526 mg, 2.4 mmol, 1 eq.) followed by DMAP (0.1 eq.). After 1 hour of stirring at the same temperature, the mixture was warmed at RT and stirred for 24 hours. After evaporation, AcOEt (15 mL) and HCl aq. 1M (10 mL) were added. Organic phase was washed another time with HCl aq. 1M, dried over Na_2SO_4 and concentrated. The crude was purified by flash chromatography on a silicagel column (Dry loading ; Elution gradient: 10/90 AcOEt/Hexanes, 20/80 then 50/50) to yield **X1** (718 mg, 78%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ ppm 7.60 (d, ^{3}J = 8.7 Hz, 2H, H_{ar}), 7.33 (d, ^{3}J = 8.7 Hz, 2H, H_{ar}), 2.10 (s, 3H, CH Ad), 1.95 (s, 6H, CH_2 Ad), 1.78 (m, 3H, CH_2 Ad), 1.73 (m, 3H, CH_2 Ad).

- Synthesis of intermediate **X2**

To a solution of 1-adamantanecarbonyl chloride (881 mg, 4.43 mmol, 1.3 eq.) and triethylamine (920 µL, 3.5 eq.) in dry THF (15 mL) at 0°C was added by portions 4-ethynylaniline (400 mg, 3.41 mmol, 1 eq.) followed by DMAP (0.1 eq.). After 1 hour of stirring at the same temperature, the mixture was heated at reflux for 24 hours. After evaporation, AcOEt (15 mL) and HCl aq. 1M (10 mL) were added. Organic phase was washed another time with HCl aq. 1M, dried over Na_2SO_4 and concentrated. The crude was purified by flash chromatography on a silicagel column (Dry loading ; Elution gradient: 10/90 AcOEt/Hexanes, then 15/85) to yield **X2** (704 mg, 73%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ ppm 7.52 (d, ^{3}J = 8.6 Hz, H_{ar}), 7.44 (d, ^{3}J = 8.6 Hz, H_{ar}), 7.31 (s, NH), 3.03 (s, 1H, CH alkyne), 2.11 (s, 3H, CH Ad), 1.96 (m, 6H, CH_2 Ad), 1.79 (m, 3H, CH_2 Ad), 1.74 (m, 3H, CH_2 Ad).

- Synthesis of guest **G7**

To a mixture of **X1** (277 mg, 0.72 mmol, 1 eq.), **X2** (203 mg, 0.72 mmol, 1 eq.), copper iodine (14 mg, 0.1 eq.) and $Pd(PPh_3)_4$ (42 mg, 5% mol) were added successively degassed DMF (20 mL) and degassed diethylamine (3.3 mL) under argon. The mixture was warmed to 65°C for 29 hours. After cooling to RT, the solid in suspension was filtered, washed with DMF and dried to give the desired guest **G7** (181 mg, 47%).

^{1}H NMR (600 MHz, DMSO, 300 K): δ ppm 9.25 (br s, 2H, NHC), 7.73 (d, ^{3}J = 8.2 Hz, 4H, H_{ar}), 7.43 (d, *J* = 8.1 Hz, 4H, H_{ar}), 2.02 (m, 6H, CH Ad), 1.91 (m, 12H, CH_2 Ad), 1.71 (m, 12H, CH_2 Ad).

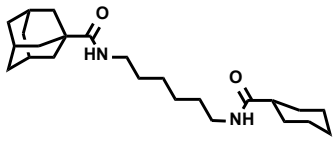
^{13}C NMR (151 MHz, DMSO, 300 K): δ ppm 131.07, 119.85, 88.36, 38.03, 35.75, 27.42.

6. General synthetic procedure for heteroditopic guests G8-G9

To a solution of diamine (1 eq.) in dry THF (0.1 M) and dry triethylamine (2 eq.), solutions of adamantane carbonyl chloride (1 eq.) and cyclohexanecarboxylic acid chloride (1 eq.) in THF (0.27 M) were added dropwise and simultaneously under argon. A few minutes after addition, a white triethylammonium chloride salt precipitates. The reaction is stirred at room temperature overnight. THF was evaporated under vacuum and the raw material was taken up in dichloromethane and washed successively with NaOH 1M, HCl 10% and $NaHCO_3$ aq.. Organic phase was dried over Na_2SO_4 and filtered through a Büchner filter (porosity 5). The filtrate was

evaporated and the crude material was purified by flash chromatography on a silicagel column with an eluent AcOEt/CH_2Cl_2 1:2. Compounds **G8-G9** were obtained as white solids.

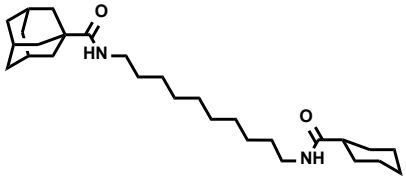
- Guest **G8**:



^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ ppm 5.68 (br s, 2H), 3.24-3.19 (m, 4H, CH_2N), 2.10-2.00 (m, 4H), 1.84 (s, 8H), 1.79-1.64 (m, 9H), 1.50-1.38 (m, 6H), 1.36-1.20 (m, 8H).

^{13}C NMR (150 MHz, $CDCl_3$, 300 K): δ ppm 178.17, 176.28, 45.76, 40.72, 39.46, 38.84, 36.69, 29.90, 29.72, 29.64, 28.30, 26.10, 26.07, 25.92.

- Guest **G9**:



Yield: 10%

^{1}H NMR (600 MHz, MeOD, 300 K): δ ppm 7.74 (br s, 1H, NHC), 7.37 (br, 1H, NHC), 3.14 (m, 4H, CH_2N), 2.02 (m, 3H, Ad), 1.86 & 1.85 (2*s, 6H, Ad), 1.73 (m, 12H, Ad, Cy), 1.47 (m, 4H, CH_2CH_2N), 1.42 (m, 2H), 1.31 (m, 15H).

^{13}C NMR (150 MHz, MeOD, 300 K): δ ppm 180.71, 179.12, 46.56, 41.78, 40.48, 40.36, 40.27, 40.26, 40.19, 37.65, 30.77, 30.56, 30.51, 30.45, 30.38, 30.36, 29.69, 27.93, 27.91, 26.91, 26.85.

HRMS-ESI: $[MH]^+$; calculated for $C_{28}H_{48}N_2O_2H^+$: 445.3788 found: 445.3787.

III. ^{1}H NMR spectra of receptor 1 in $CDCl_3$ before and after photoirradiation at 365 nm

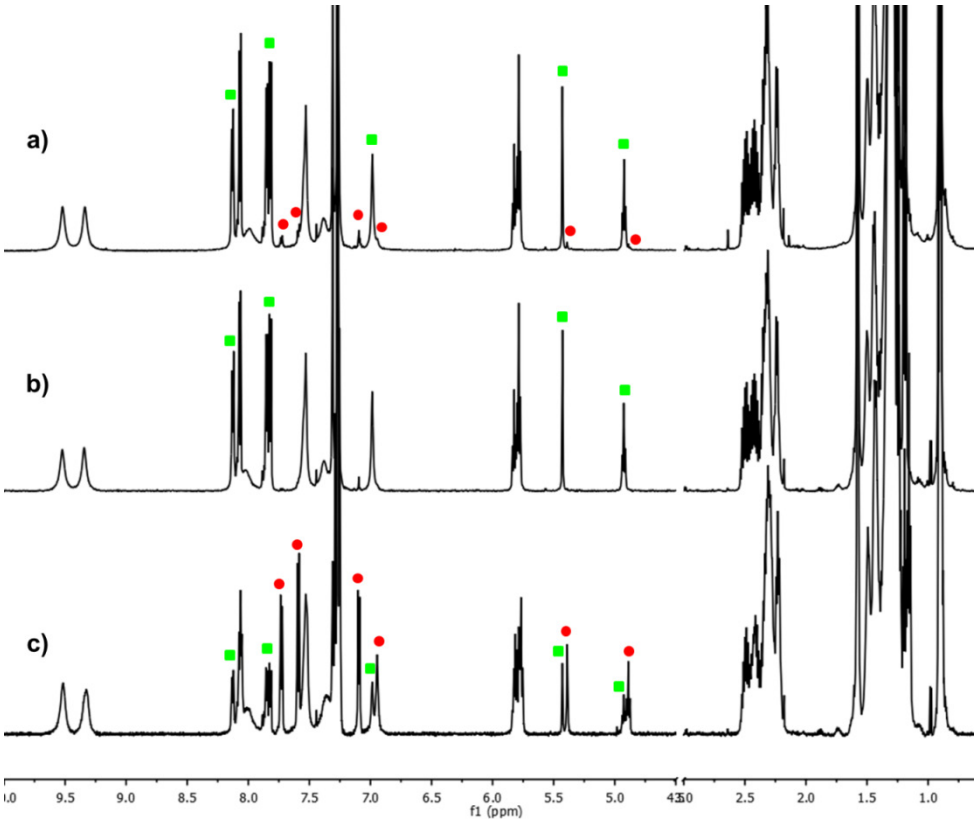


Figure S1: ^{1}H NMR spectra (300K) in deuterated chloroform of receptor **1**: (a) recorded just after the purification; (b) after a heating followed by a cooling in the dark; (c) after photoirradiation at 365 nm for 1h45. Green squares and red circles correspond to the specific signals respectively of the *trans* and *cis* isomer.

IV. Reproducibility of the switching process

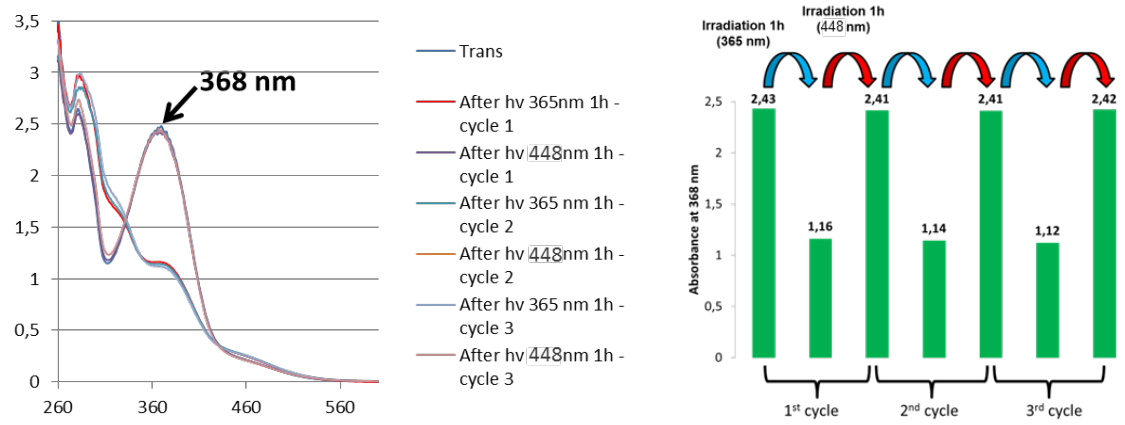


Figure S2. Reproducibility of the switching process of receptor **1** in chloroform monitored by UV-Vis after photoirradiations at 365 nm and 448 nm as switching stimuli. (characteristic π-π* absorption band of the *trans* isomer of the azobiphenyl moiety in $CHCl_3$ λ_{max} = 368 nm; ε = 27000 $L.mol^{-1}.cm^{-1}$)

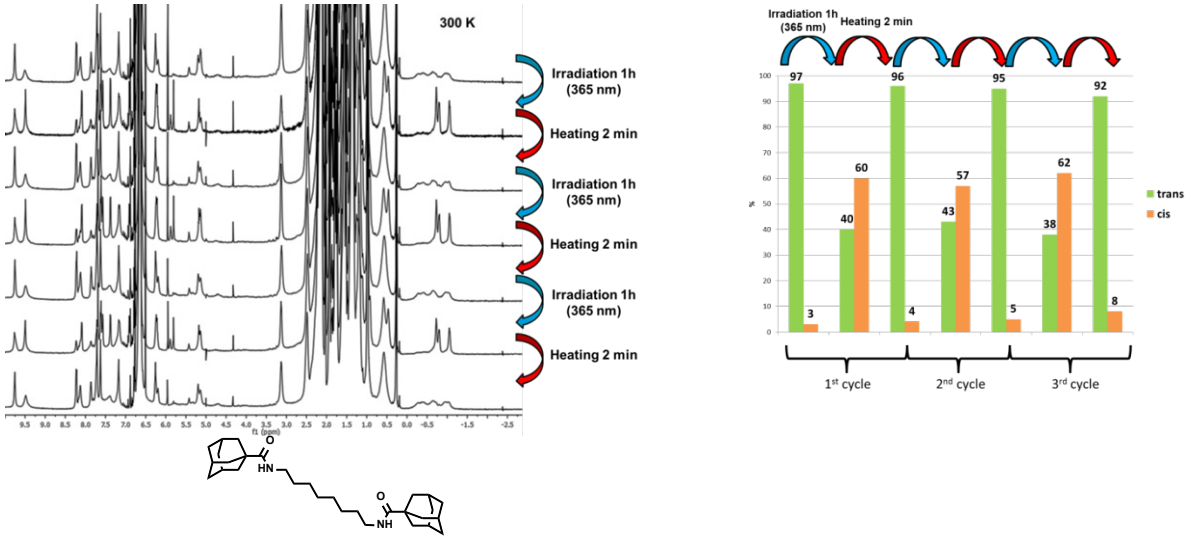


Figure S3. Reproducibility of the switching process monitored by ^1H NMR of receptor **1** in presence of homo-ditopic guest **G5** in deuterated mesitylene after photoirradiation at 365 nm and heating as switching stimuli.

V. Kinetic of thermal cis/trans isomerization of receptor 1

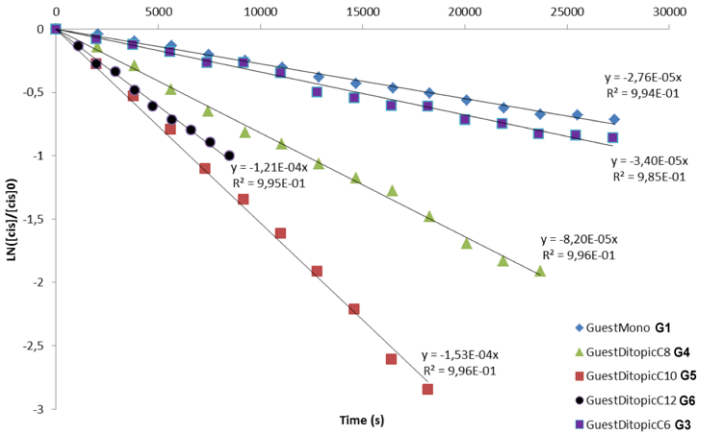
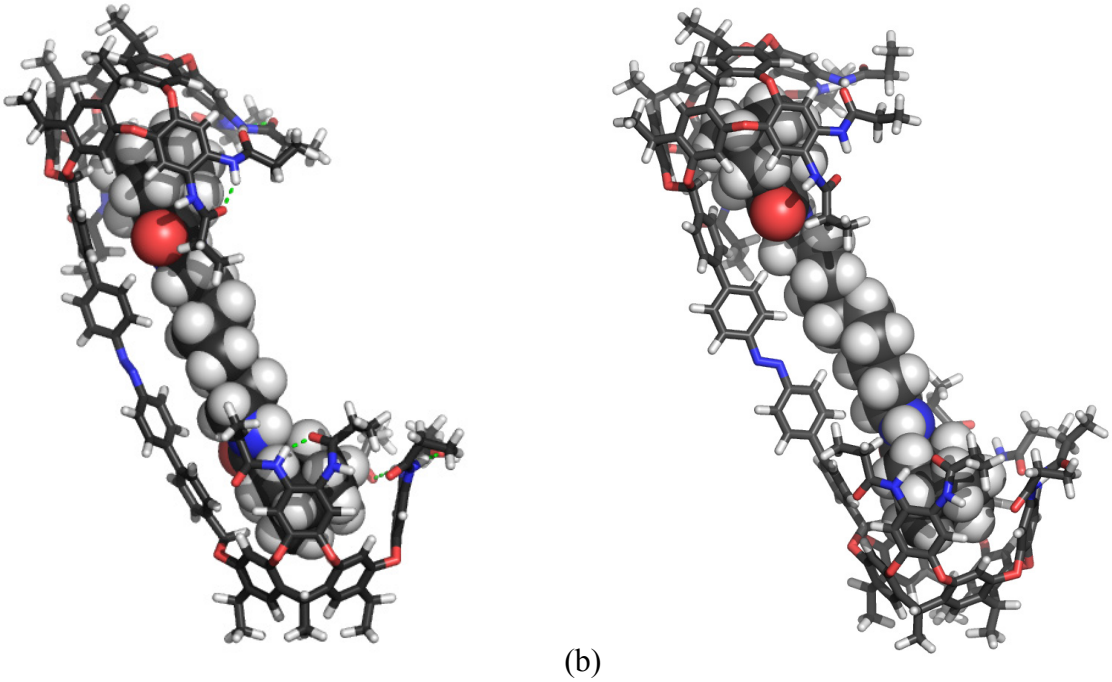


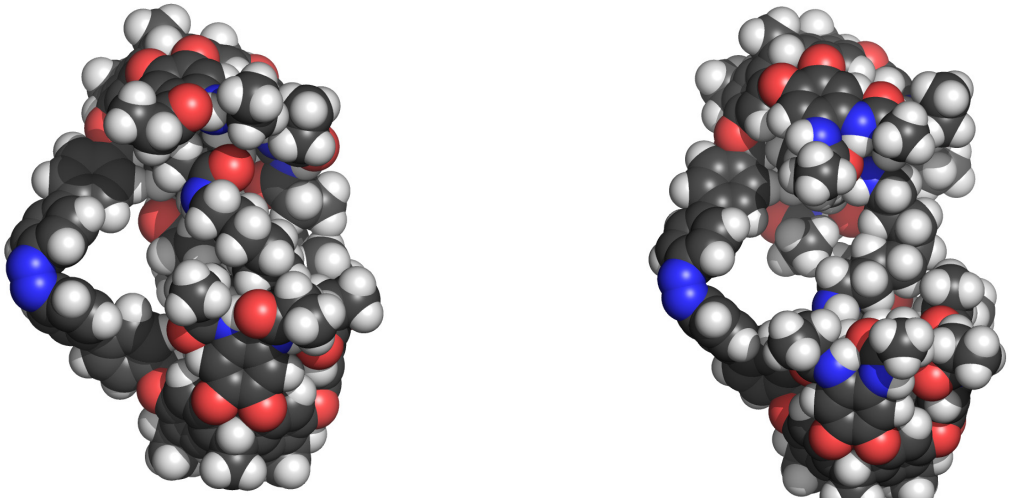
Figure S4. Thermal *cis*/*trans* isomerization kinetics followed by ^{1}H NMR in mesitylene-d_{12} at 300 K.

VI. Energy-minimized structures of receptor 1



(a) (b)

Figure S5. Energy-minimized structures of receptor **1** C-shaped *trans* isomer in presence of guest (a) **G4** and (b) **G5** (Spartan, PM3). R_2 alkyl chain feets are omitted for clarity.



(a) (b)

Figure S6. Energy-minimized structures of receptor **1** V-shaped *cis* isomer in presence of guests (a) **G3** and (b) **G4** (Spartan, PM3). R_2 alkyl chain feets are omitted for clarity.

VII. NMR spectra of receptor 1 with guests G1-G7 in mesitylene-d_{12}

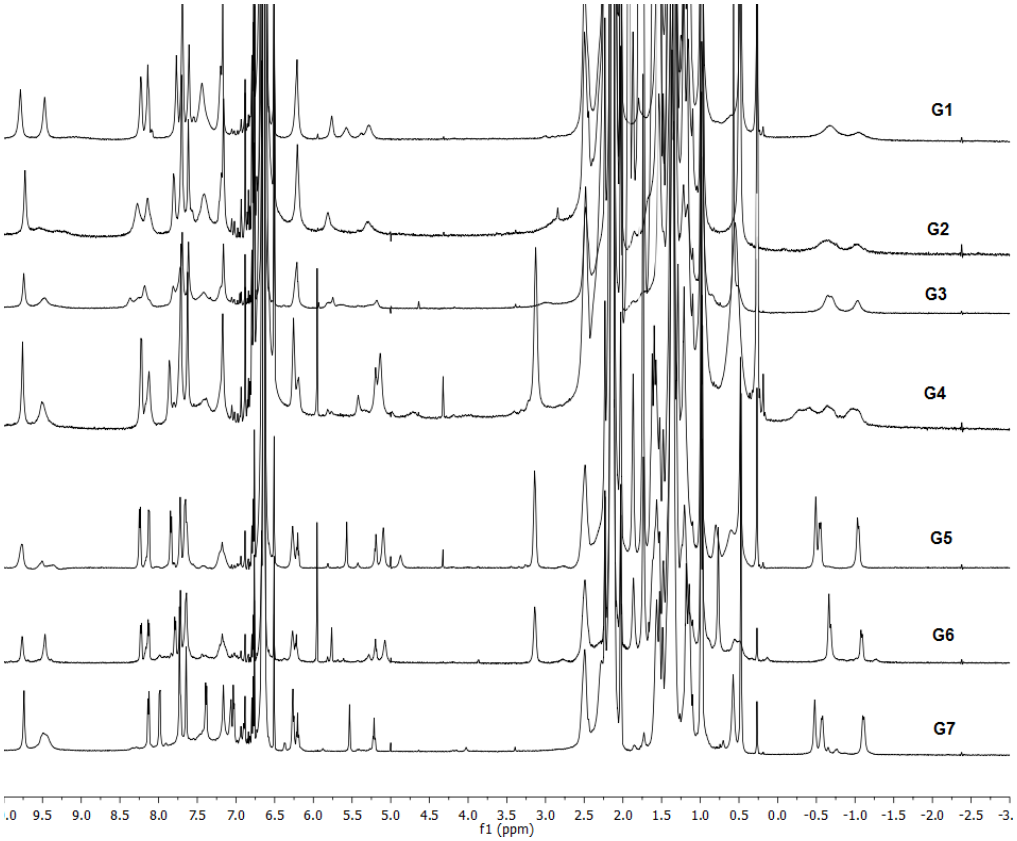


Figure S7. ^{1}H NMR spectra (mesitylene-d_{12}, 300 K) of *trans* isomer of receptor **1** (2 mM) with guests **G1-G7** (1 eq.).

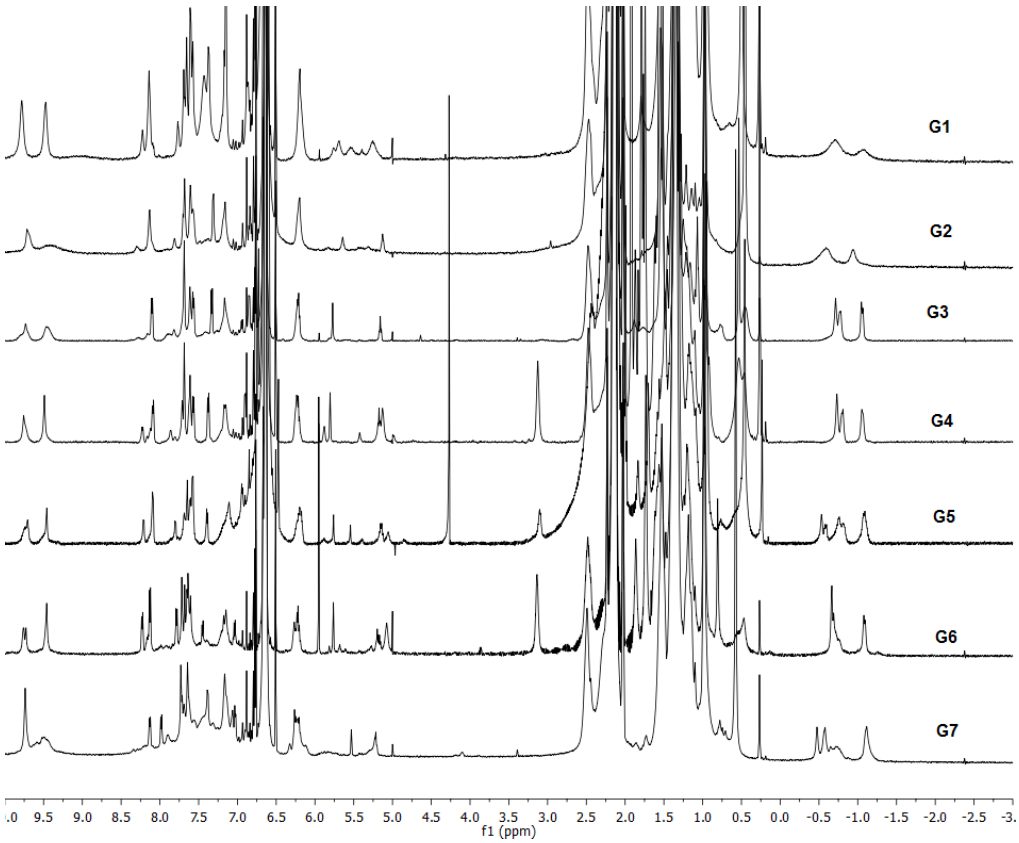


Figure S8. ^{1}H NMR spectra (mesitylene-d_{12}, 300 K) of receptor **1** (2 mM) with guests **G1-G7** (1 eq.) after photoirradiation at 365 nm (1-2h).

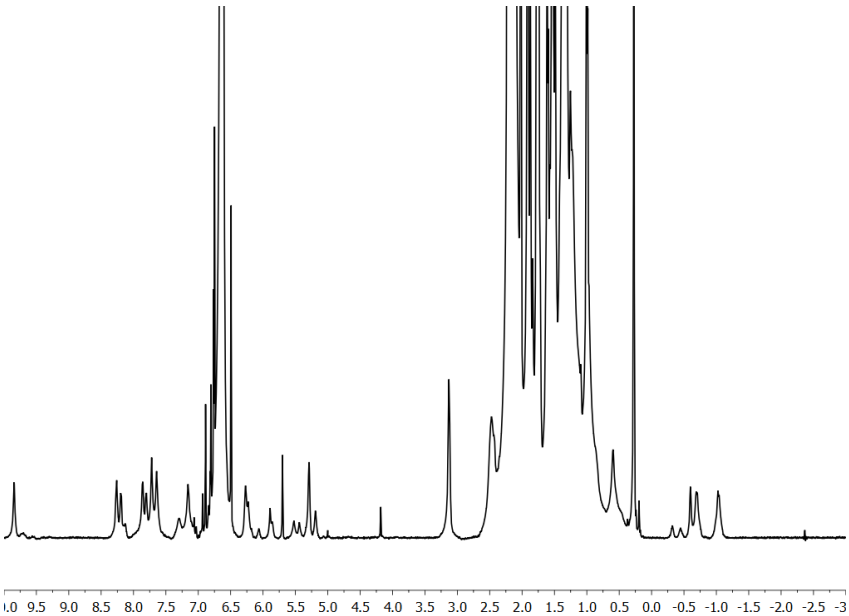


Figure S9. ^{1}H NMR spectrum (mesitylene-d_{12}, **270 K**) of receptor **1** trans (2 mM) in presence of guest **G4** (1 eq.).

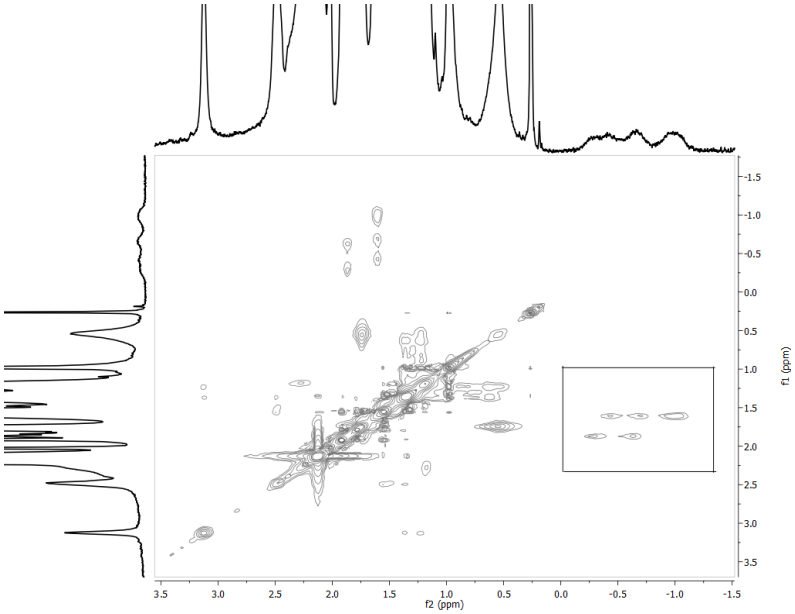


Figure S10. ROESY NMR spectrum (mesitylene-d_{12}, 300 K) of receptor **1** trans (2 mM) in presence of guest **G4** (1 eq.). Two host-guest complexes are observed.

VIII. NMR spectra of receptor 1 with guests G1-G5, G7 in toluene-d_8

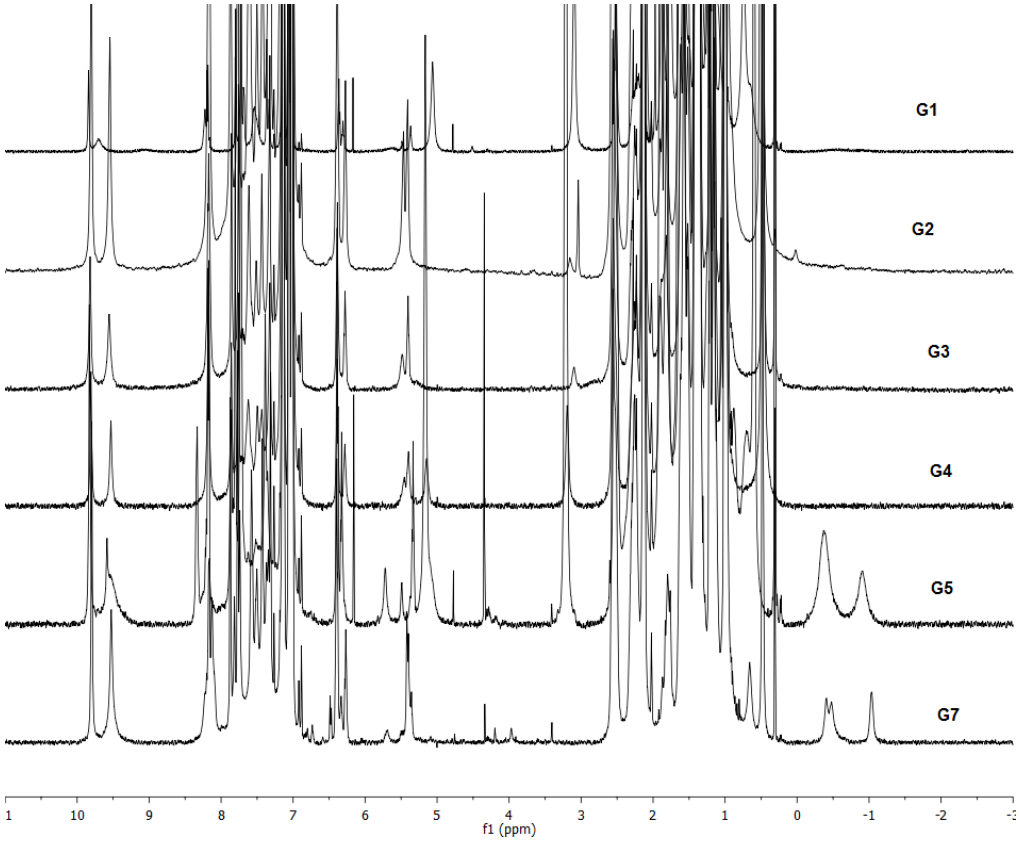


Figure S11. ^{1}H NMR spectra (toluene-d_8, 300 K) of *trans* isomer of receptor **1** (2 mM) with guests **G1-G5, G7** (1 eq.).

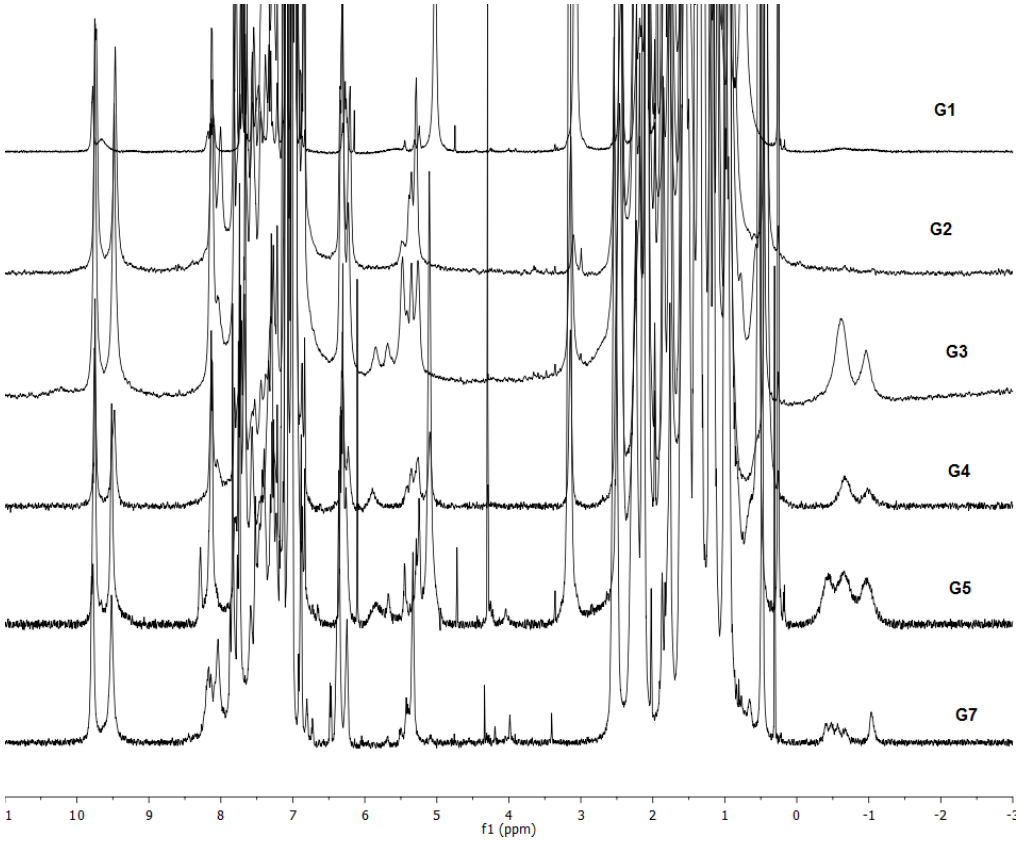


Figure S12. ^{1}H NMR spectra (toluene-d_8, 300 K) of receptor **1** (2 mM) with guests **G1-G5, G7** (1 eq.) after photoirradiation at 365 nm (1-2h).

IX. NMR spectra of receptor 1 with guests G8-G9 in toluene-d_8

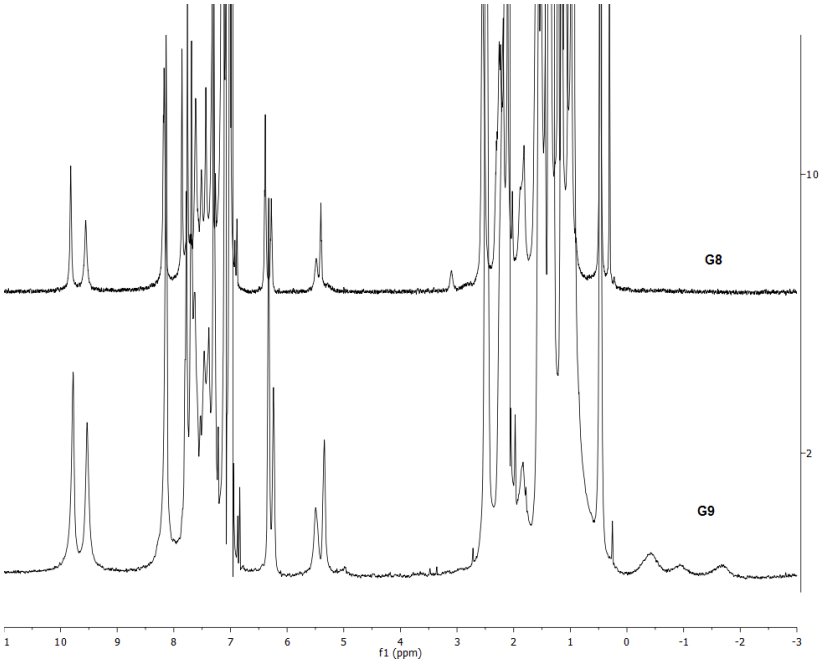


Figure S13. ^{1}H NMR spectra (toluene-d_8, 300 K) of *trans* isomer of receptor **1** (2 mM) with guests **G8-G9** (1 eq.).

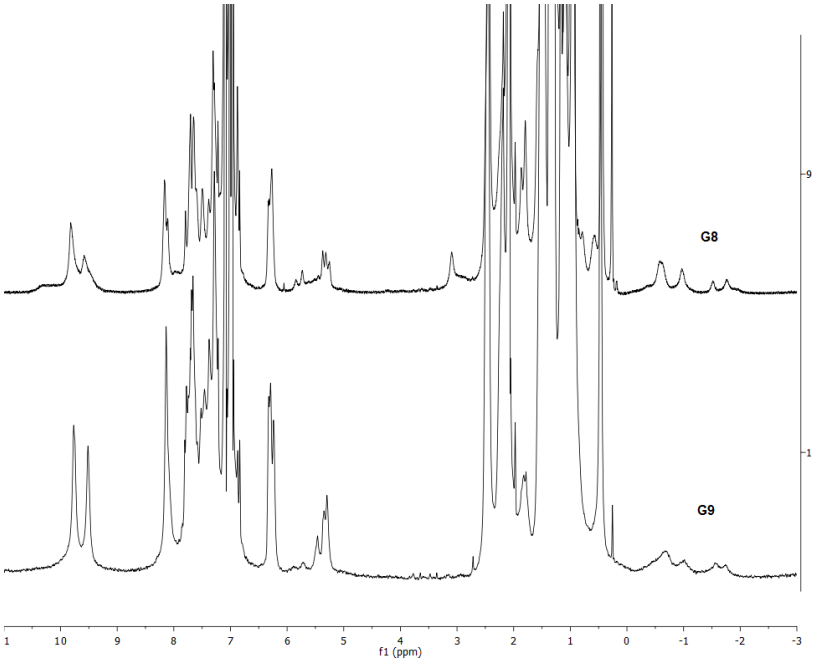
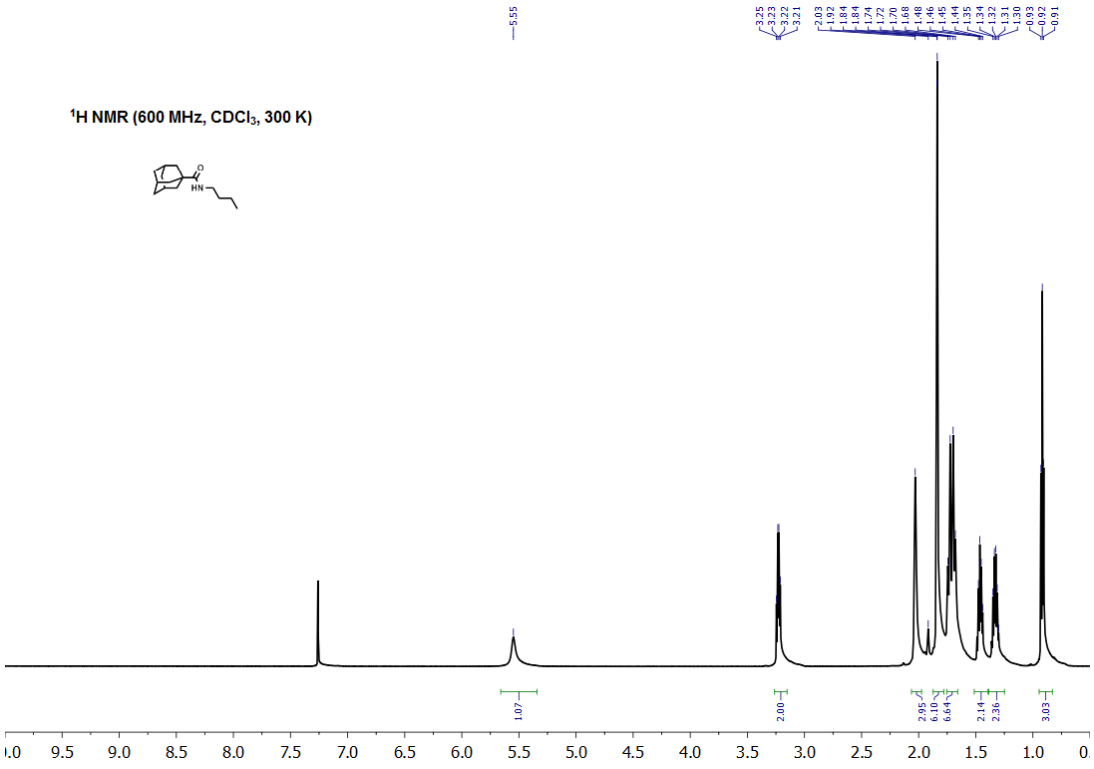


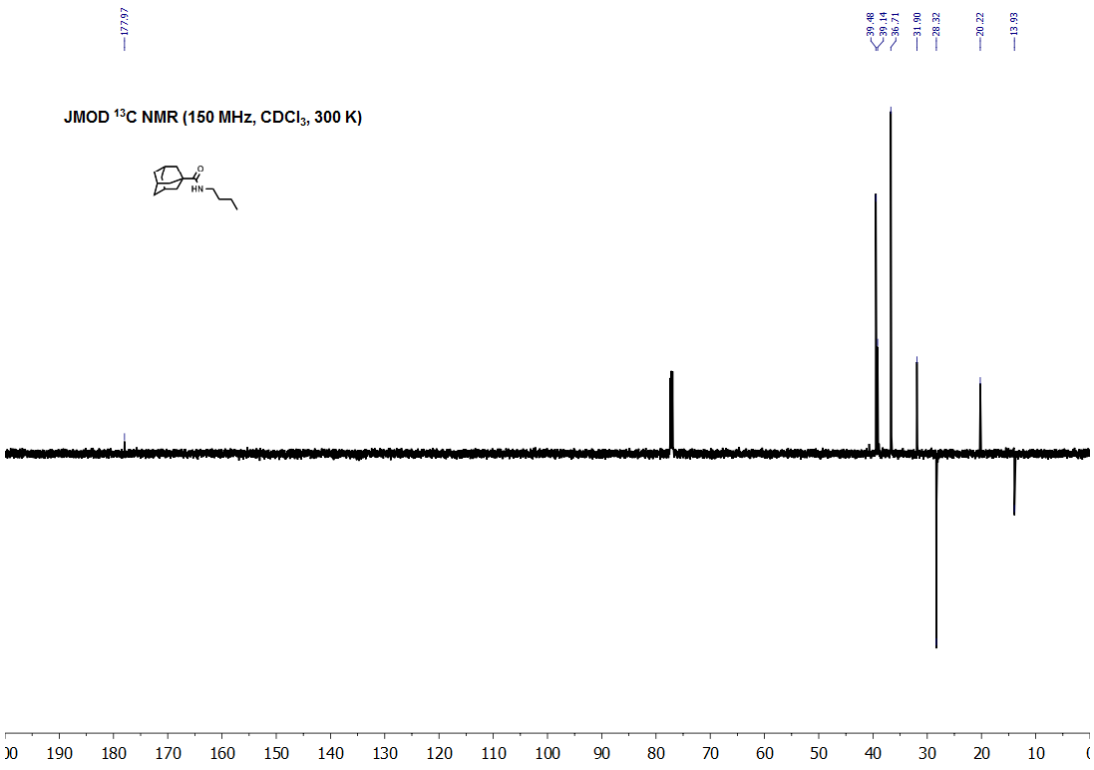
Figure S14. ^{1}H NMR spectra (toluene-d_8, 300 K) of receptor **1** (2 mM) with guests **G8-G9** (1 eq.) after photoirradiation at 365 nm (1-2h)..

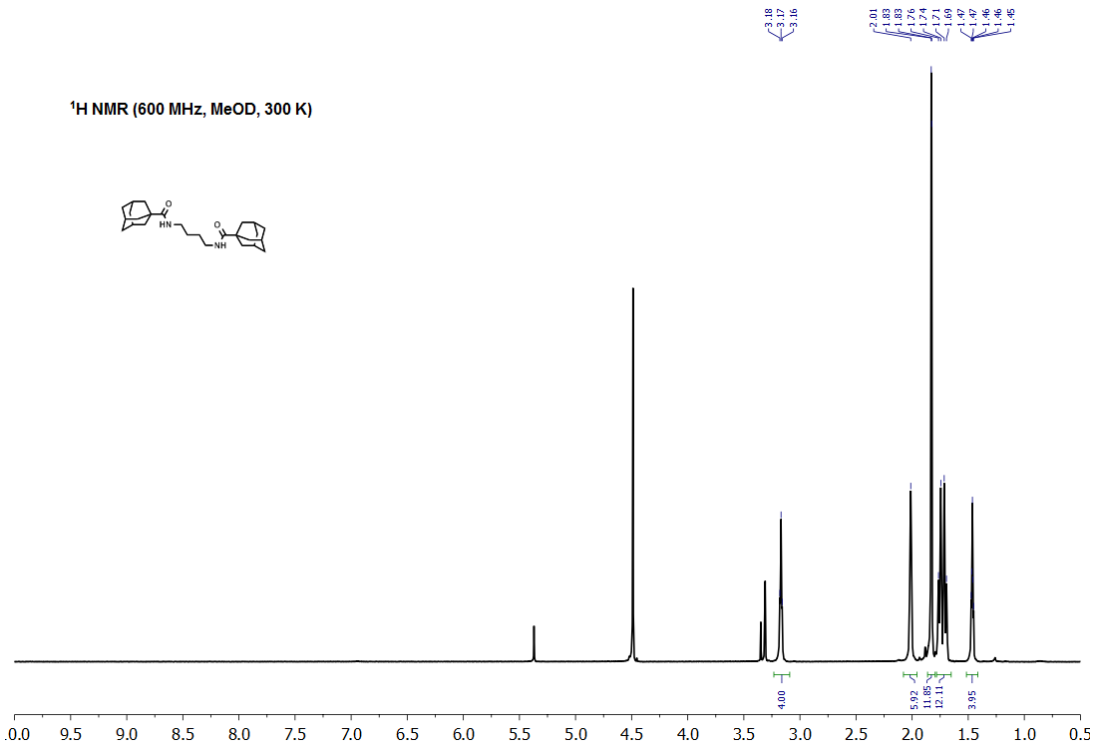
X. References

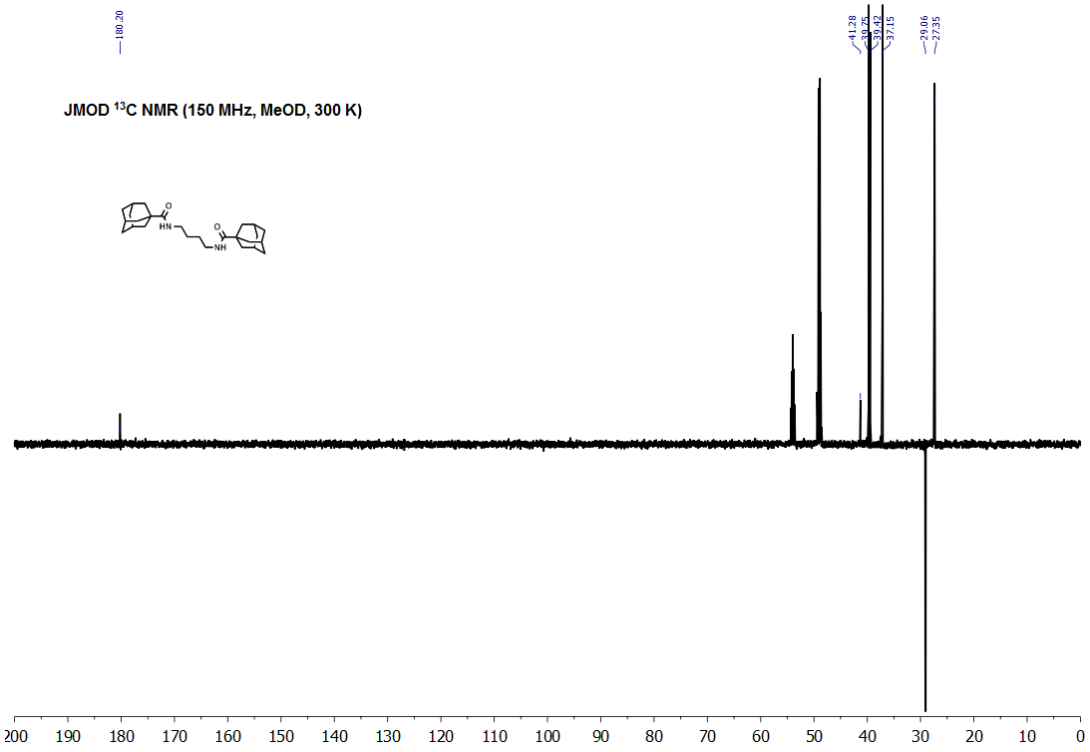
1. T. Yamamoto, I. Nishiyama and H. Yokoyama, *Chem. Lett.*, 2007, **36**, 1108.
2. M. Degardin, E. Busseron, D.-A. Kim, D. Ajami and J. Rebek, *Chem. Commun.*, 2012, **48**, 11850.

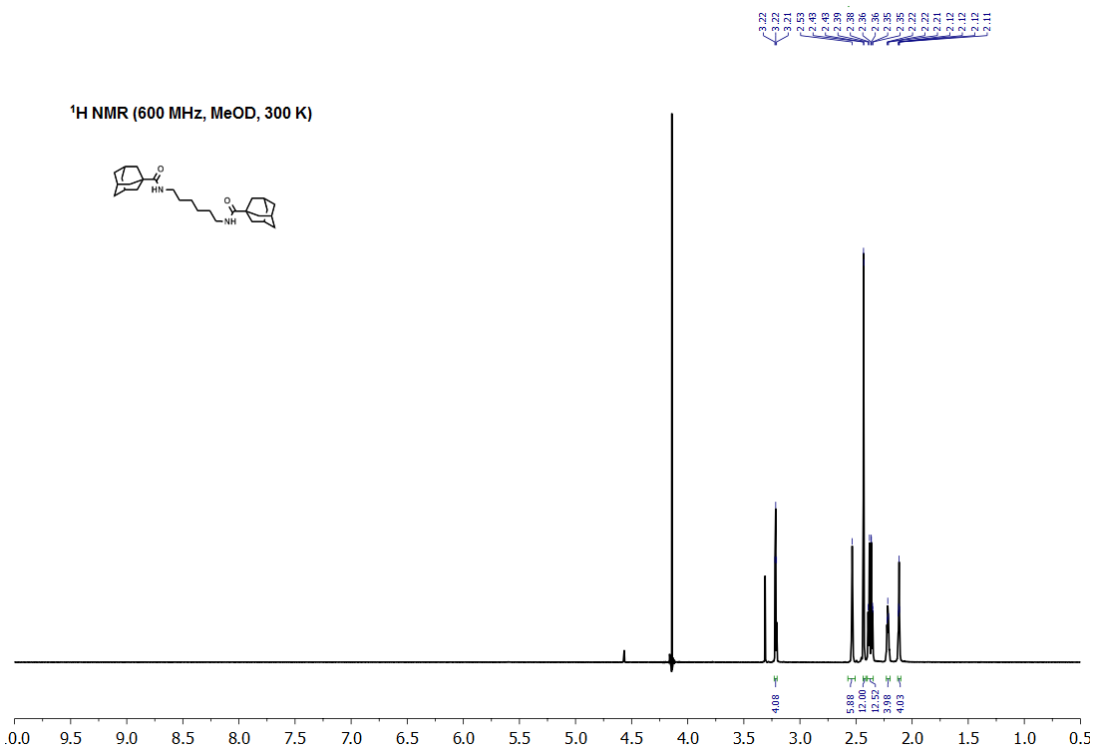
XI. NMR spectra of synthesized compounds

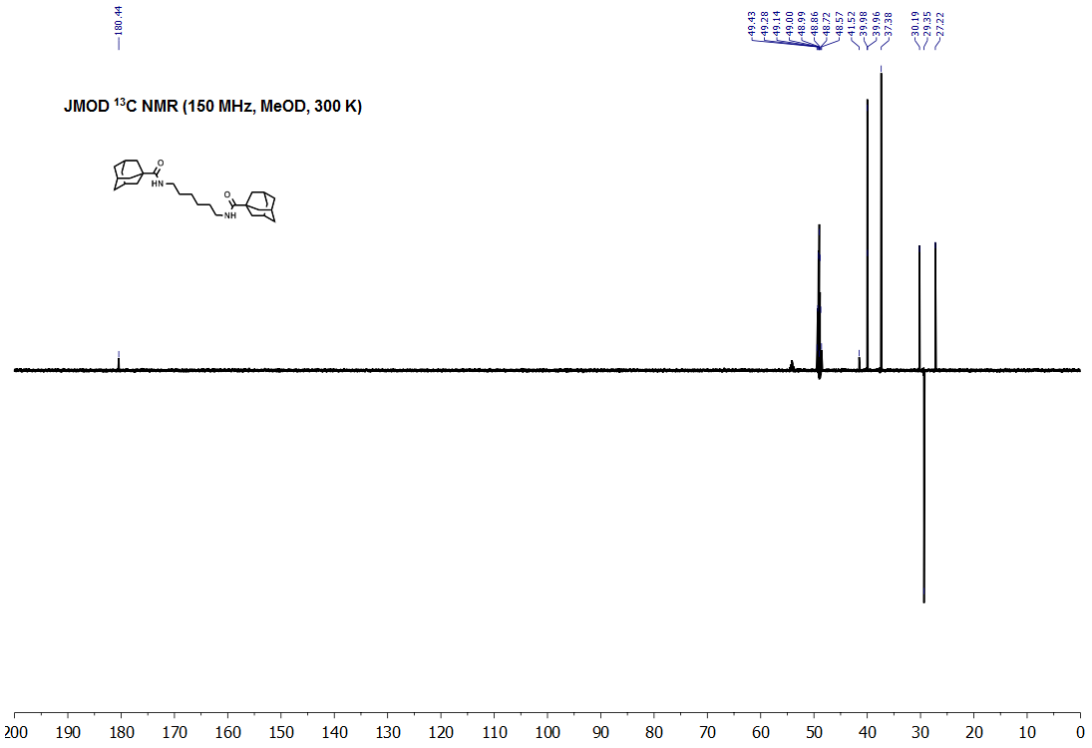


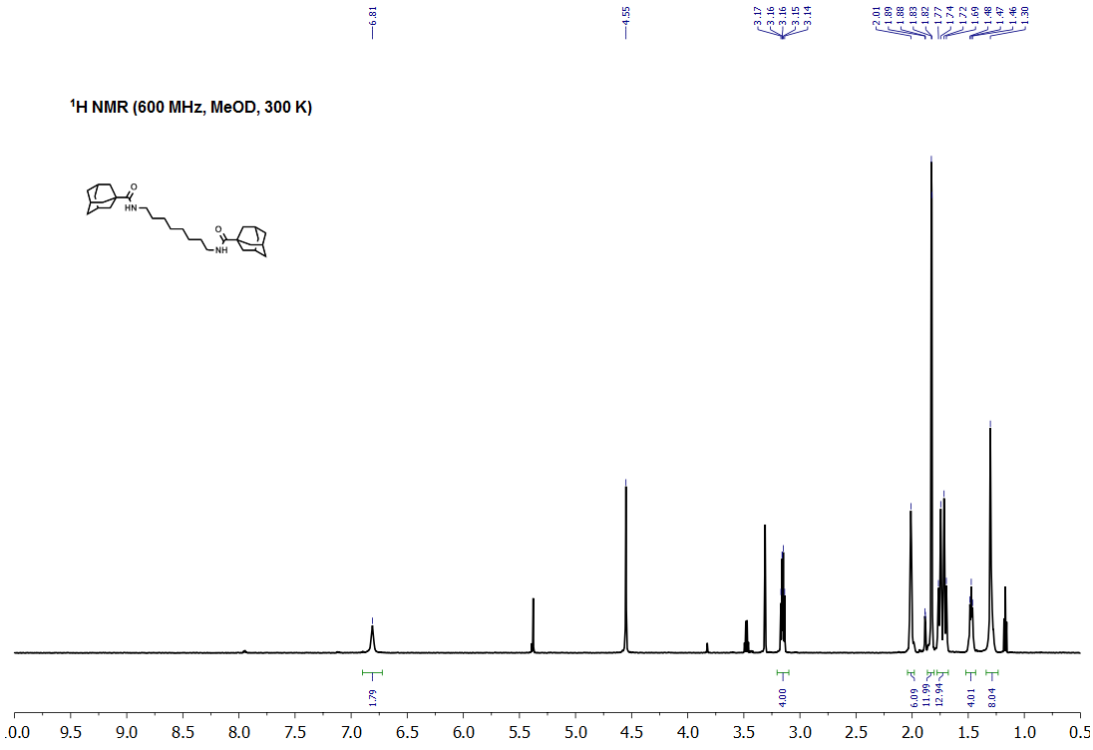

JMOD ^{13}C NMR (150 MHz, $CDCl_3$, 300 K)
177.97
39.48
39.14
36.71
31.90
28.32
20.22
13.93

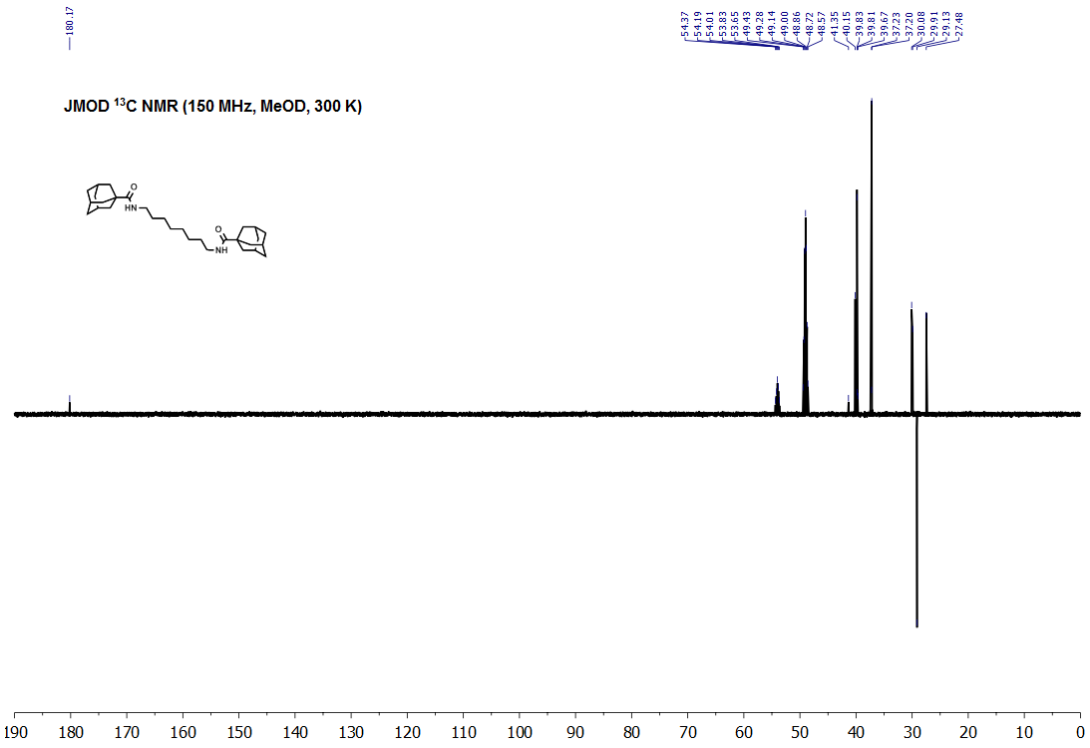

^{1}H NMR (600 MHz, MeOD, 300 K)
3.18
3.17
3.16
2.01
1.83
1.83
1.76
1.74
1.71
1.69
1.47
1.46
1.46
1.45
4.00
5.92
11.85
12.11
3.95

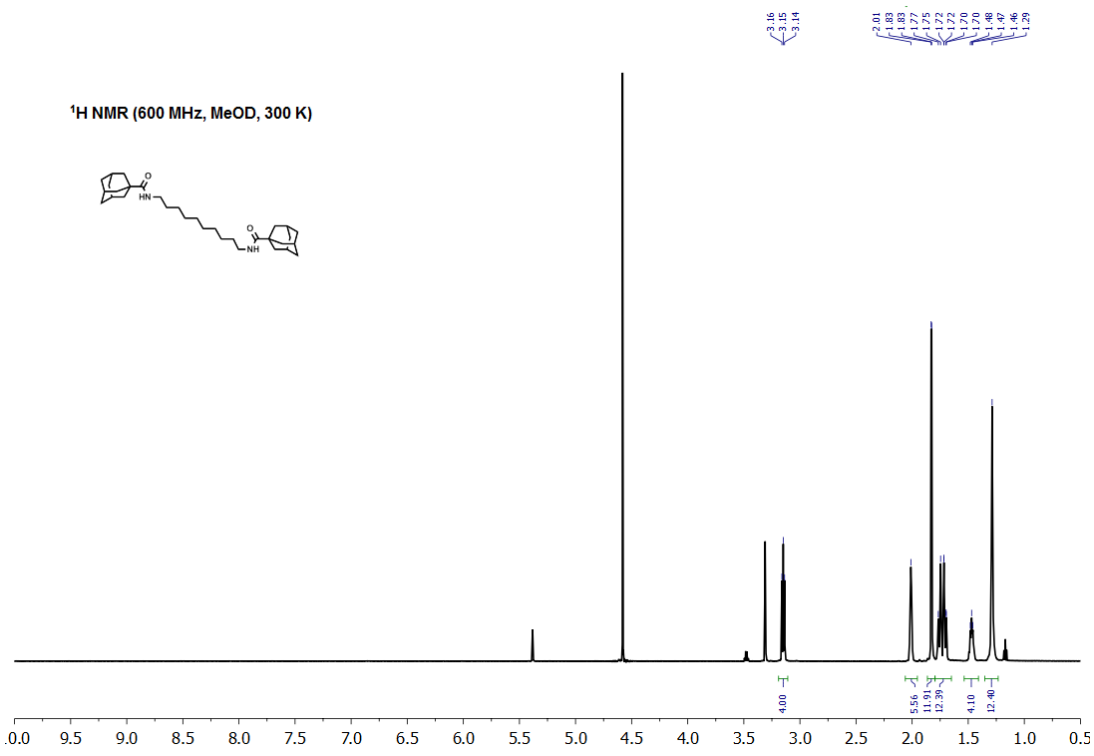

JMOD ^{13}C NMR (150 MHz, MeOD, 300 K)
180.20
41.28
39.35
39.42
37.15
29.06
27.35
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

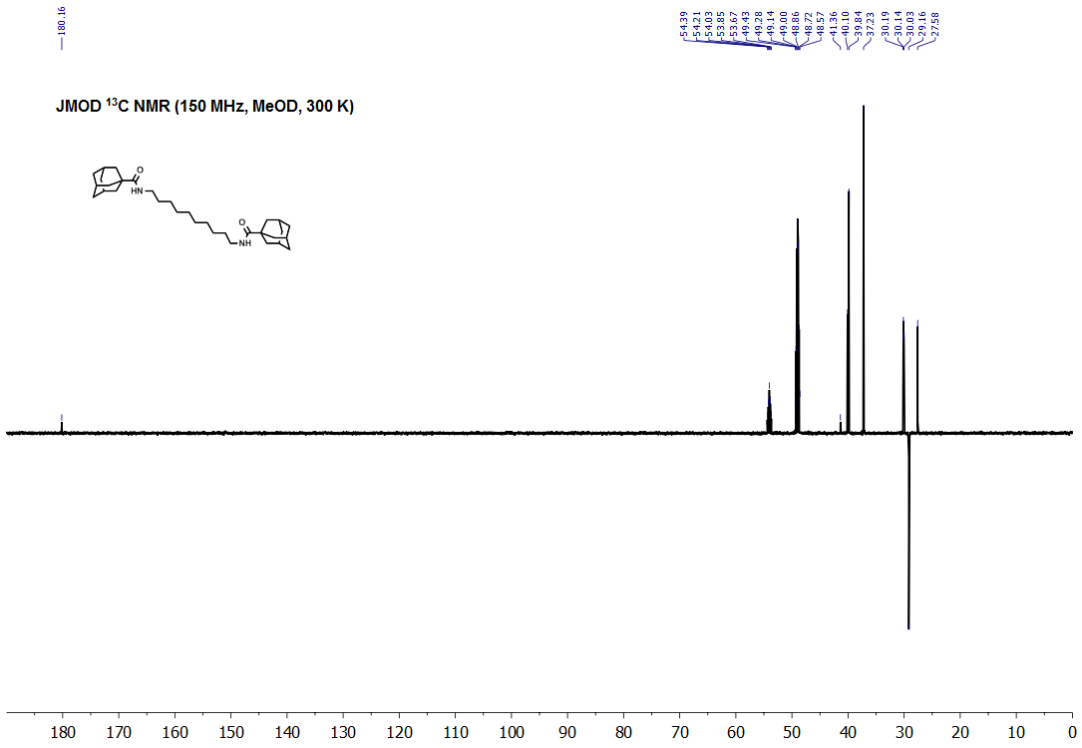

^{1}H NMR (600 MHz, MeOD, 300 K)
3.22
3.22
3.21
2.53
2.48
2.48
2.39
2.38
2.36
2.36
2.35
2.35
2.22
2.22
2.21
2.12
2.12
2.12
2.12
2.11
4.08
5.88
12.00
12.52
3.98
4.03
.0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

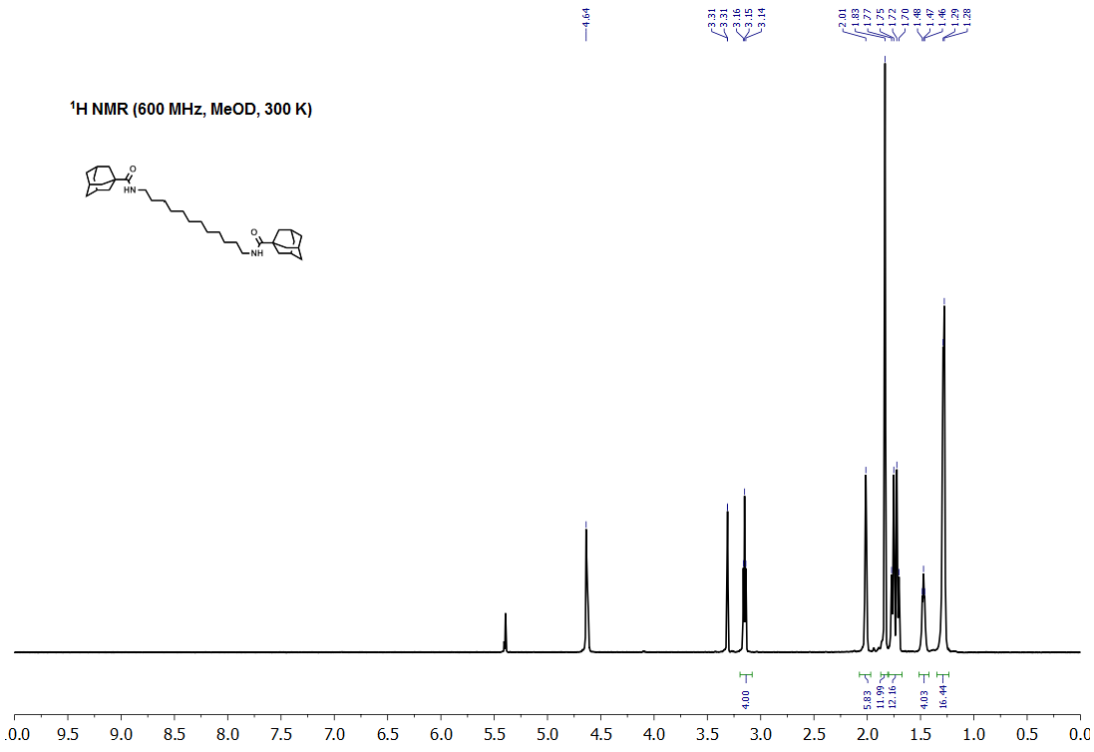

JMOD ^{13}C NMR (150 MHz, MeOD, 300 K)
180.44
49.43
49.28
49.14
49.00
48.86
48.72
48.57
48.42
39.98
39.96
37.38
30.19
29.35
27.22
HN
NH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

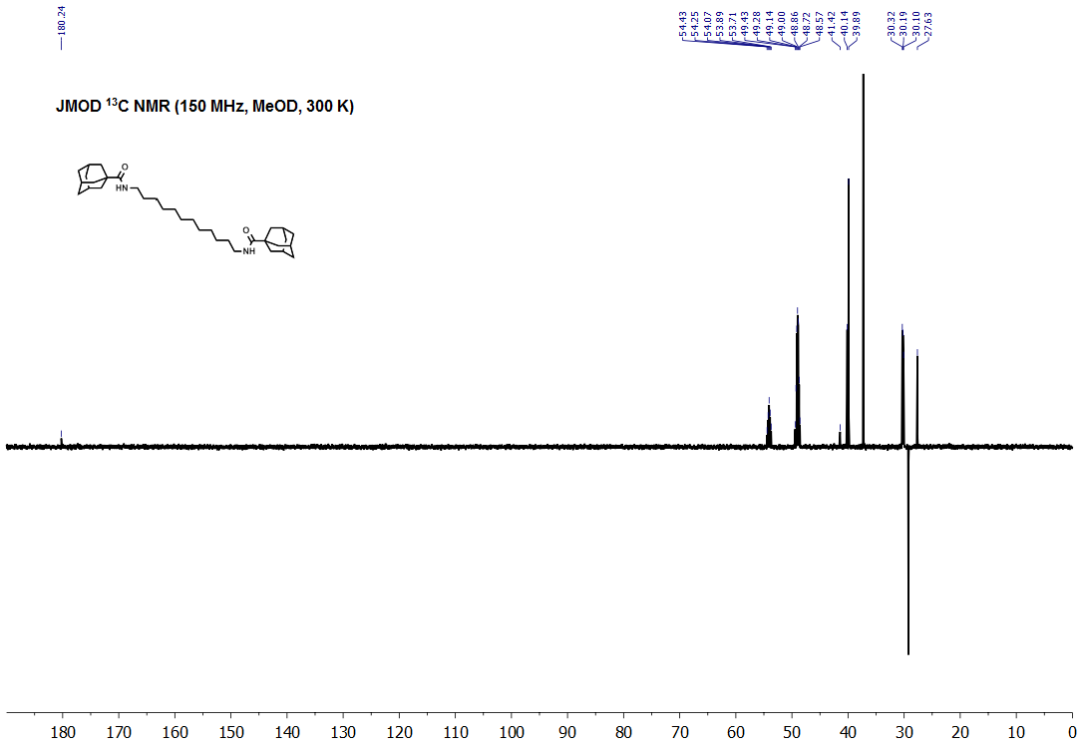

^{1}H NMR (600 MHz, MeOD, 300 K)
6.81
4.55
3.17
3.16
3.16
3.15
3.14
2.01
1.89
1.88
1.83
1.82
1.77
1.74
1.72
1.69
1.48
1.47
1.46
1.30
HN
NH
1.79
4.00
6.09
11.99
12.94
4.01
8.04
.0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

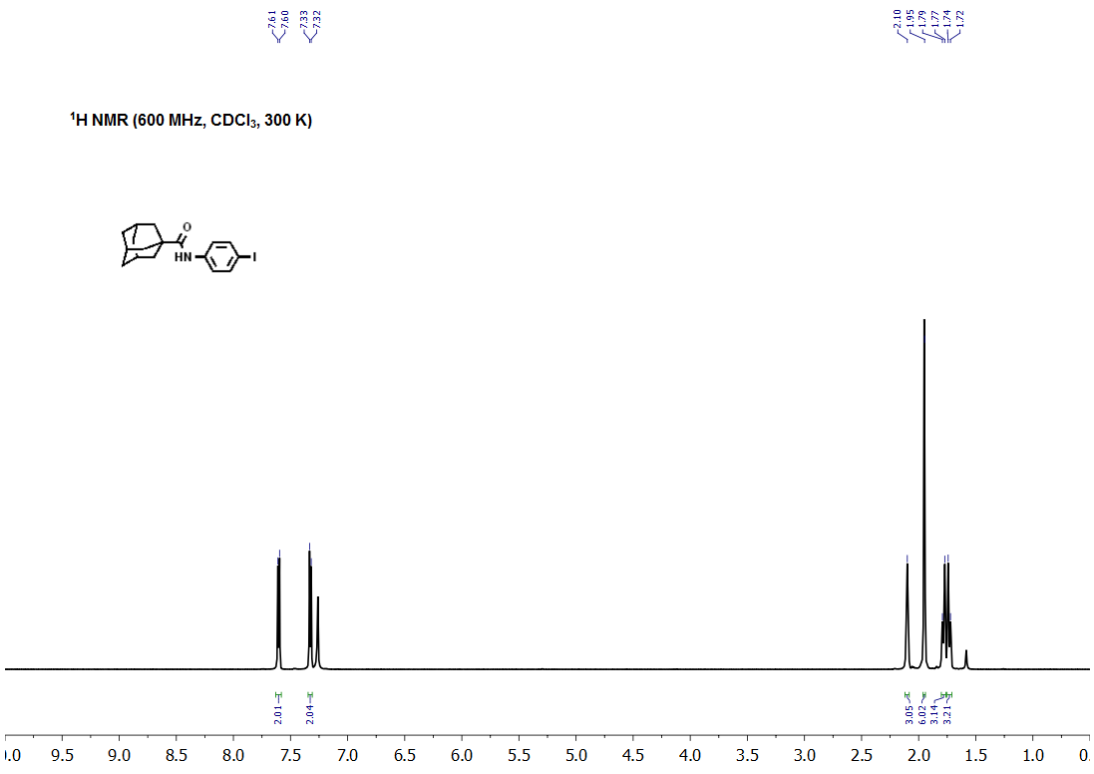

JMOD ^{13}C NMR (150 MHz, MeOD, 300 K)
180.17
54.37
54.19
54.01
53.83
53.65
49.43
49.28
49.14
49.00
48.86
48.72
48.57
41.35
40.15
39.83
39.81
39.67
37.23
37.20
30.08
30.01
29.13
27.48
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

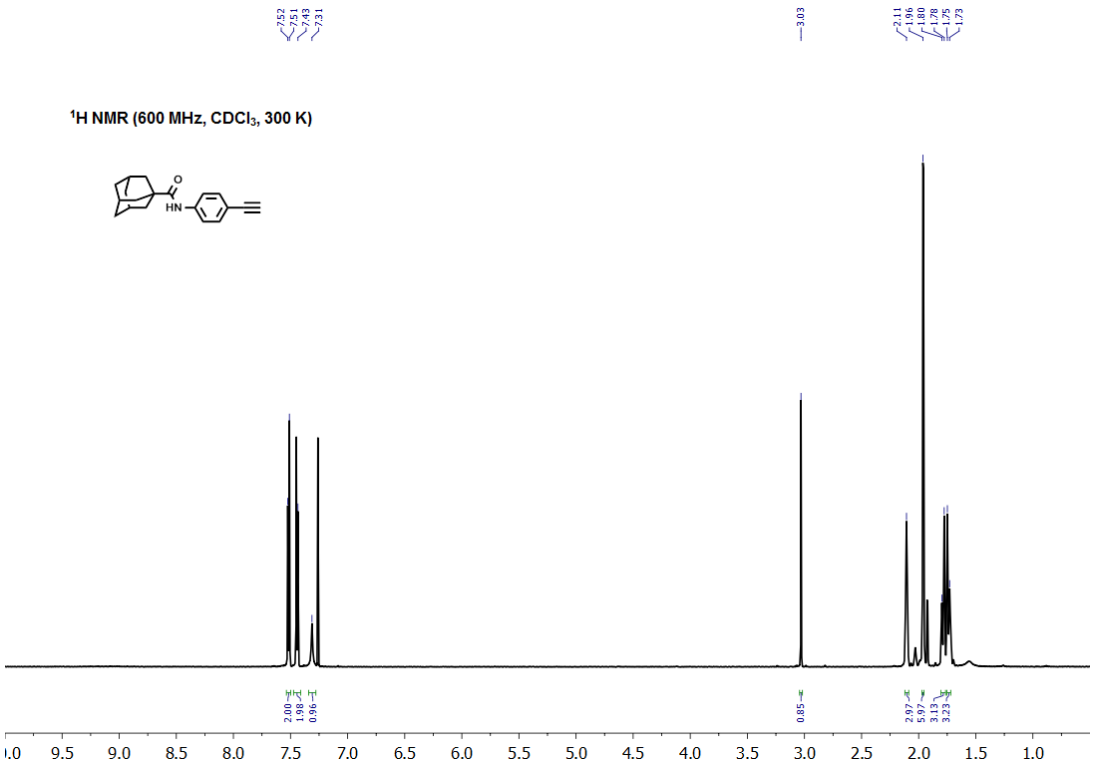

^{1}H NMR (600 MHz, MeOD, 300 K)
3.16
3.15
3.14
2.01
1.83
1.83
1.77
1.75
1.72
1.72
1.70
1.70
1.48
1.47
1.46
1.29
4.00
5.56
11.91
12.39
4.10
12.40
.0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


JMOD ^{13}C NMR (150 MHz, MeOD, 300 K)
180.16
54.39
54.21
54.03
53.85
53.67
49.43
49.28
49.14
49.00
48.86
48.72
48.57
41.36
40.10
39.84
37.23
30.19
30.14
30.03
29.16
27.58
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

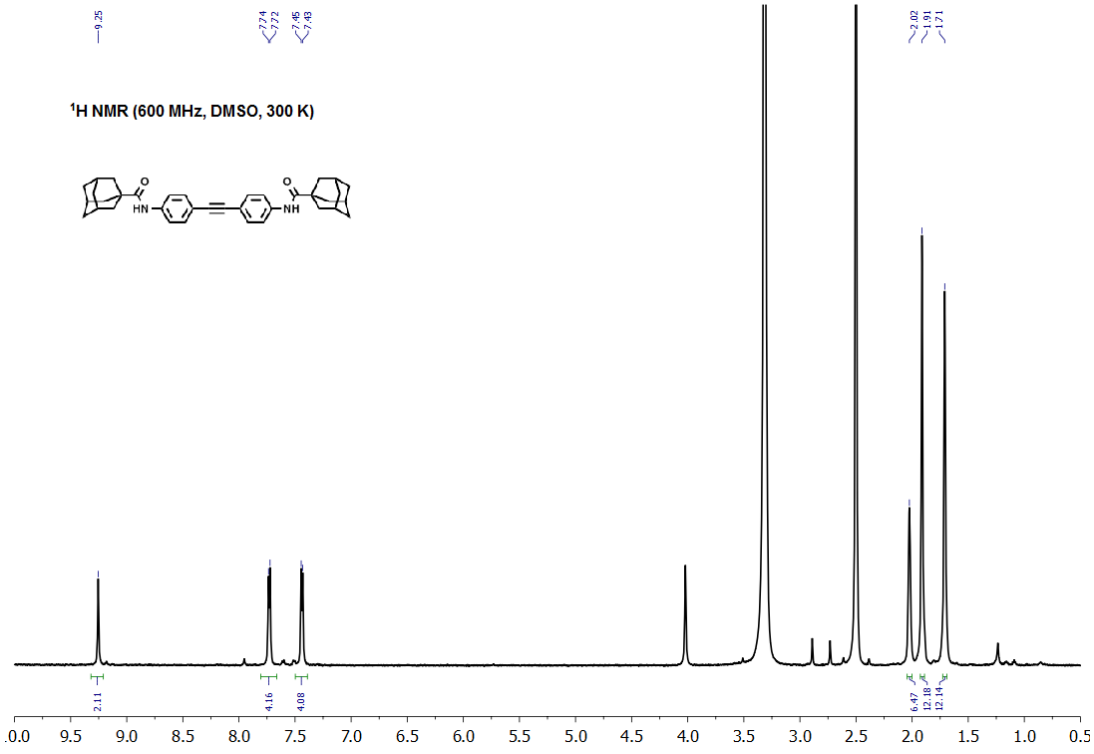

^{1}H NMR (600 MHz, MeOD, 300 K)
4.64
3.31
3.31
3.16
3.15
3.14
2.01
1.83
1.77
1.75
1.72
1.70
1.48
1.47
1.46
1.29
1.28
4.00
5.83
11.99
12.16
4.03
16.44
.0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


JMOD ^{13}C NMR (150 MHz, MeOD, 300 K)
180.24
54.43
54.25
54.07
53.89
53.71
49.43
49.28
49.14
49.00
48.86
48.72
48.57
41.42
40.14
39.89
30.32
30.19
30.10
27.63
HN
NH
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

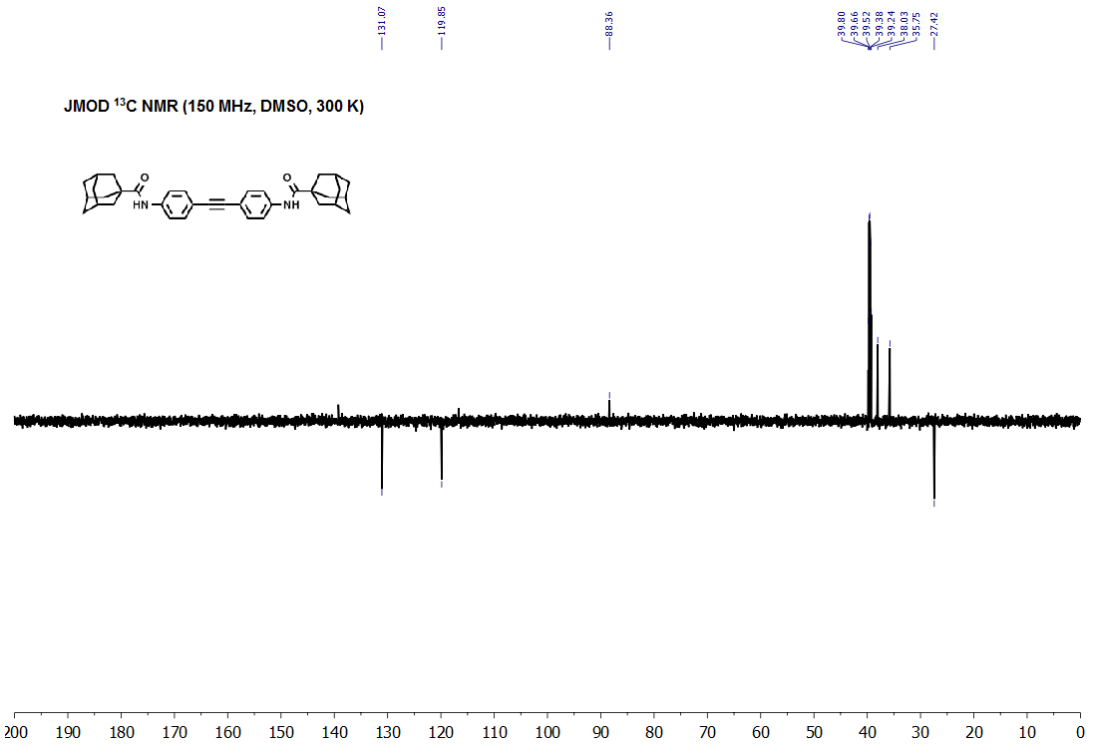

^{1}H NMR (600 MHz, CDCl$_3$, 300 K)
7.61
7.60
7.33
7.32
2.10
1.95
1.79
1.77
1.74
1.22
HN
I
2.01
2.04
3.05
6.02
3.14
3.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0

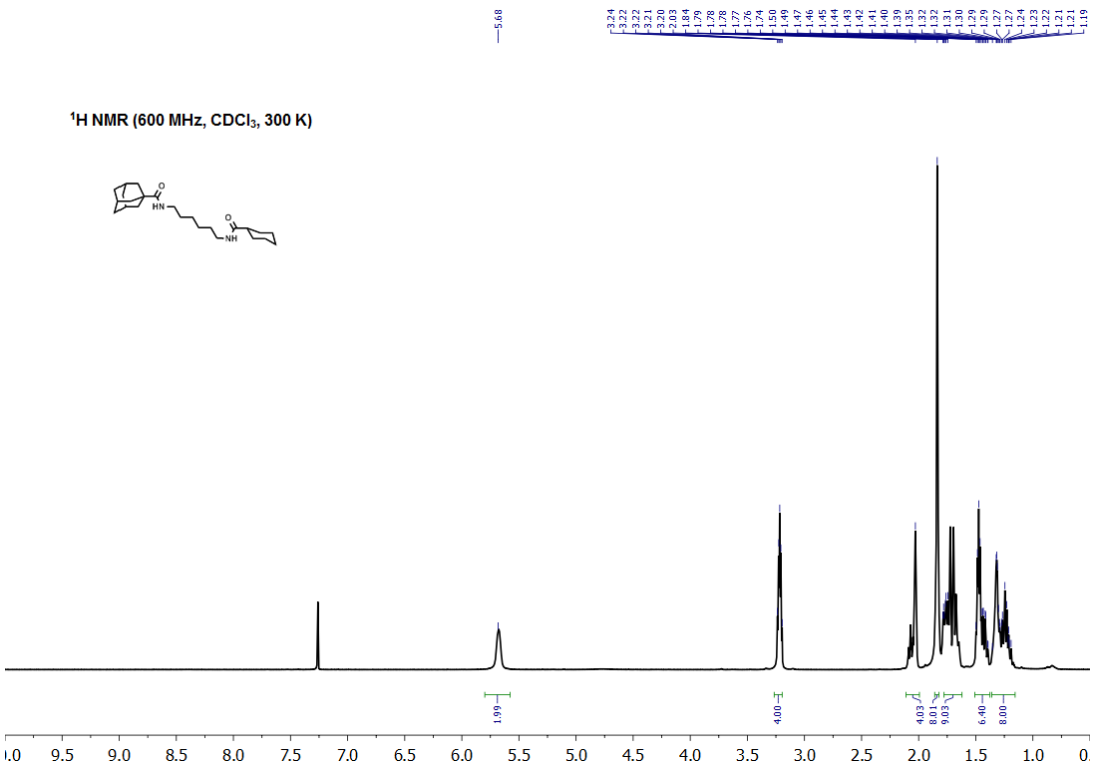


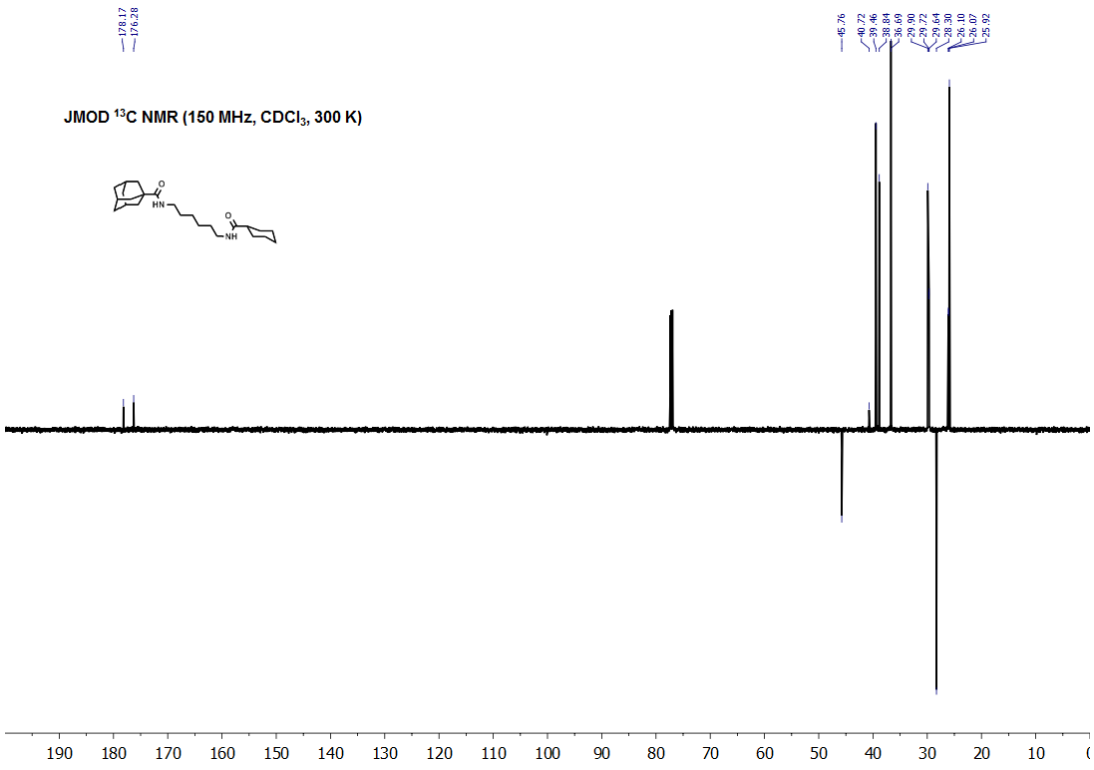
^{1}H NMR (600 MHz, $CDCl_3$, 300 K)

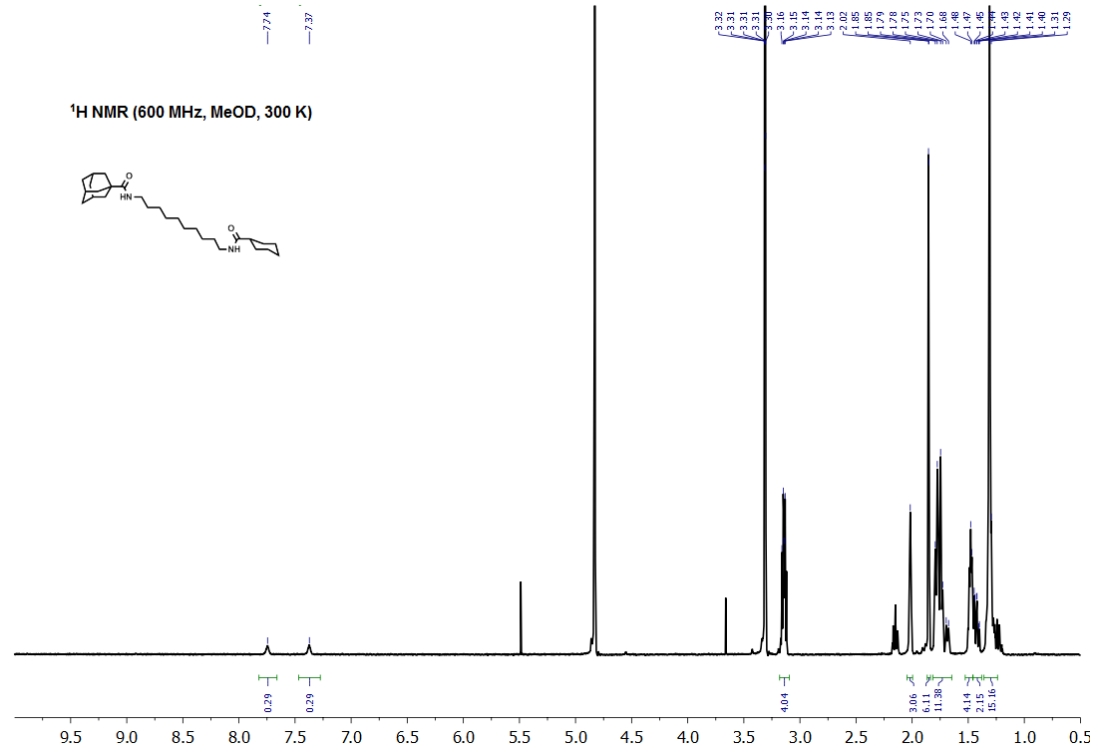


^{1}H NMR (600 MHz, DMSO, 300 K)


131.07
119.85
88.36
39.80
39.66
39.52
39.38
39.24
38.03
35.75
27.42
JMOD ^{13}C NMR (150 MHz, DMSO, 300 K)
HN
NH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


5.68
3.24
3.22
3.21
3.20
2.03
1.84
1.79
1.78
1.77
1.76
1.74
1.50
1.49
1.47
1.46
1.45
1.44
1.43
1.42
1.41
1.40
1.39
1.35
1.32
1.31
1.30
1.29
1.27
1.24
1.23
1.22
1.21
1.19
^{1}H NMR (600 MHz, CDCl$_3$, 300 K)
HN
NH
1.99
4.00
4.03
8.01
9.03
6.40
8.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0


JMOD ^{13}C NMR (150 MHz, $CDCl_3$, 300 K)
178.17
176.28
46.76
40.72
39.46
38.84
36.69
29.90
29.72
29.64
28.80
26.10
26.07
25.92
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


^{1}H NMR (600 MHz, MeOD, 300 K)
7.74
7.37
3.32
3.31
3.31
3.31
3.16
3.15
3.14
3.14
3.13
2.02
1.85
1.79
1.78
1.75
1.73
1.70
1.68
1.48
1.47
1.46
1.45
1.42
1.41
1.40
1.31
1.29
0.29
0.29
4.04
3.06
6.11
11.38
4.14
2.15
15.16
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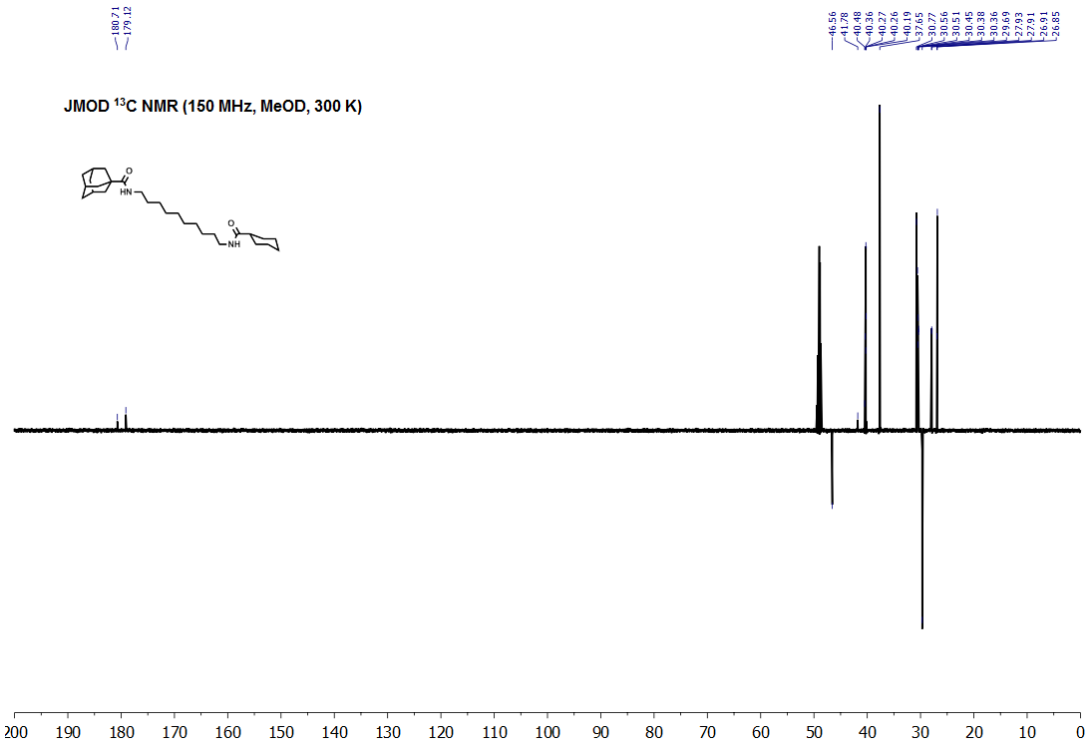
180.71
179.12
46.56
41.78
40.48
40.36
40.27
40.26
40.19
37.65
30.77
30.56
30.51
30.45
30.38
30.36
29.69
27.93
27.91
26.91
26.85
JMOD 13C NMR (150 MHz, MeOD, 300 K)
HN
NH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0