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for

Photoelimination of Nitrogen from Adamantane and Pentacycloundecane (PCU) Diazirines: Spectroscopic Study and Supramolecular Control

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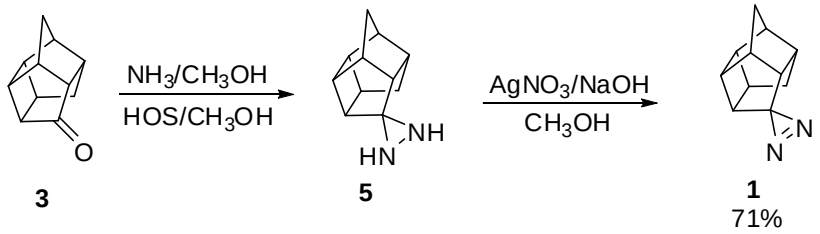
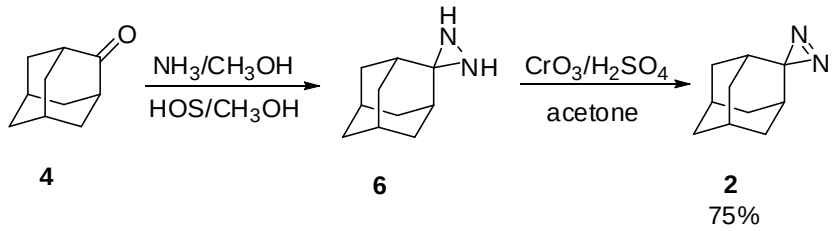


3 **5** **1** 71%

Scheme S1.



4 **6** **2** 75%

Scheme S2.

Preparation of Diaziridines, General procedure[1]

Ketone **3** or **4** (1 mmol) was dissolved in anhydrous MeOH (10 mL) and cooled to -78 °C. Anhydrous ammonia (~ 20 mL) was condensed from a cylinder to the solution stirred at -78 °C. After the ammonia addition, the stirring was continued for 45 min, and then, hydroxylamine-*O*-sulfonic acid (2 mmol) in anhydrous MeOH (5 mL) was added to the solution in two portions within 30 min at -78 °C. The resulting mixture was stirred at -78 °C for additional 2 h, allowed to reach rt, and stirred overnight. To the reaction mixture, water (20 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (3 × 25 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated on a rotational evaporator to afford the crude diaziridine **5** or **6** which was used in the next step without further purification.

PCU diaziridine 5[2]

Prepared according to the general procedure, PCU diaziridine was obtained from PCU ketone **3** (0.32 g, 2 mmol), giving the crude diaziridine **5** (0.34 g, ≈ 100%) in the form of colorless crystals.

Adamantane diaziridine 6[1]

Prepared according to the general procedure, adamantane diaziridine **6** was obtained from 2-adamantanone (**4**, 0.45 g, 3 mmol) giving the crude diaziridine **6** (0.49 g, ≈ 100%) in the form of colorless crystals.

Synthesis of PCU diazirine 1

To the solution of the crude diaziridine **5** (0.34 g, 2 mmol) in methanol (10 mL) an aqueous solution of $AgNO_3$ (1M, 4 mmol) was added, followed by the aqueous solution of NaOH (2.5 M, 4 mmol) added in small portions. The mixture was stirred for 15 min and hexane (50 mL) was added. The organic and the aqueous layers were separated and the aqueous layer was extracted with hexane (3 × 25 mL). The collected organic phases were dried over anhydrous $MgSO_4$. After filtration, the solvent was removed on a rotary evaporator. The crude residue was chromatographed on a column of silica gel using hexane as eluent to afford the pure product (0.25 g, 71%) in the form of colorless crystals.

Pentacyclo[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecan-8-diazirine (1)

^{1}H NMR (600 MHz, $CDCl_3$) δ/ppm: 2.78-2.86 (m, 2H), 2.62-2.64 (m, 2H), 2.49-2.53 (m, 1H), 2.38-2.43 (m, 2H), 1.68 (d, 1H, *J* = 10.6 Hz), 1.47-1.51 (m, 1H), 1.38 (dt, 1H, *J* = 4.1 Hz, *J* = 12.3 Hz), 1.33 (d, 1H, *J* = 10.6 Hz), 1.16-1.20 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ/ppm: 47.6 (d), 46.0 (d), 44.1 (d), 43.8 (d), 43.0 (d), 41.3 (d), 39.2 (d), 38.1 (s), 37.3 (d), 35.3 (t), 30.0 (t). The NMR spectroscopic data are in accord with those in the literature.[2]

Synthesis of adamantane diazirine 2

The crude adamantane diaziridine **6** (0.94 g, 5.7 mmol) was suspended in acetone (30 mL) and CrO_3 (0.85 g, 8.5 mmol) dissolved in H_2SO_4 (20%, 25 mL) was added dropwise within 90 min at 5-10 °C. The mixture was stirred for 1 h at rt and poured on 400 mL of ice. The aqueous phase was extracted with CH_2Cl_2 (5 × 25 mL) and the organic phase was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed on a rotary evaporator and the residue chromatographed

on silica gel using hexane as eluent. The pure product (0.69 g, 75%) was isolated in the form of colorless crystals.

^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 1.99-2.14 (m, 6H), 1.73-1.86 (m, 6H), 0.65 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 36.8 (t, 1C), 35.1 (t, 4C), 34.5 (d, 2C), 27.5 (d, 2C), one singlet was not observed. The NMR spectroscopic data are in accord with those in the literature.1

Photochemical experiments with diazirine 2

Photochemistry of 2 in cyclohexane According to the general procedure, the photolysis and GC analysis gave yields of the photoproducts that are reported in Table 2 in the manuscript.

To isolate photoproducts, according to a modification of the general procedure, **2** (15 mg) was dissolved in cyclohexane (22 mL). The solution was irradiated in the reactor with 8 lamps (350 nm, 1 lamp 8 W) 6 min. The chromatographic separation after photolysis gave traces of **11** (< 1%) detected only by GC, whereas starting compound **2** (4 mg, 27 %), 2-cyclohexyladamantane **9** (4.6 mg, 23%), alcohol **10** (0.5 mg, 4%), ketone **4** (1 mg, 7%), and a mixture of azines **12** (1.1 mg, 4%) were isolated. Photolysis was performed in triplicate and the average value is reported.

2-Cyclohexyladamantane (9) colorless crystals; ^{1}H NMR (600 MHz, $CDCl_3$, 20°C): δ = 1.91 (s, 2H), 1.76-1.78 (m, 8H), 1.61-1.76 (m, 7H), 1.44-1.51 (m, 3H), 1.10-1.24 (m, 4H), 0.69-0.79 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 20°C): δ = 49.6 (d), 39.4 (t), 38.3 (t), 36.5 (d), 31.9 (t), 30.7 (t), 28.5 (d), 28.1 (d), 27.8 (d), 26.8 (t), 26.6 (t) ppm. The NMR spectroscopic data are in accord with those in the literature.[3,4]

Adamantan-2-one (4) colorless crystals, ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ = 2.54 (s, 2H), 1.90-2.13 (m, 12 H) ppm. The NMR spectroscopic data are in accord with those in the literature.[5]

2-Hydroxyadamantane (10) colorless crystals; ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ = 3.87 (br. s, 1H), 2.02-2.11 (m, 2H), 1.60-1.99 (m, 11H), 1.52 (m, 2H) ppm. The NMR spectroscopic data are in accord with those in the literature.[6]

1,2-Bis(adamantane-2-ylidene)hydrazine (12) colorless crystals; ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ = 3.28 (s, 2H), 2.63 (s, 2H), 1.75-2.04 (m, 24H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 20°C): δ = 170.6 (s), 39.5 (d), 39.2 (t), 37.9 (t), 36.5 (t), 31.6 (d), 27.8 (d) ppm. The NMR spectroscopic data are in accord with those in the literature.3,[5]

Photochemistry of 2 in benzene According to the general procedure, the photolysis and GC analysis gave yields of the photoproducts that are reported in Table 2.

Alternatively, diazirine **2** (5.1 mg) was dissolved in benzene (7.5 mL), the solution was purged with Ar 30 min and irradiated in a Luzchem reactor with 8 lamps at 350 nm for 5 min. The irradiated mixture was analyzed by GC and ^{1}H NMR. According to GC and ^{1}H NMR the photolysis gave starting diazirine **2** (50%), traces of **11** (5%), ketone **4** (12%), alcohol **10** (20%) and azine **12** (10%).

Photochemistry of 2 in methanol According to the general procedure, the photolysis and GC analysis gave yields of the photoproducts that are reported in Table 2.

To isolate photoproducts, according to a modification of the general procedure **2** (30 mg) was dissolved in methanol (44 mL). The solution was irradiated in the reactor with 8 lamps (350 nm, 1 lamp 8 W) 5 min. The photolysis and chromatographic separation gave traces of **11** (2%) detected only by GC, whereas the starting compound **2** (2 mg, 7%), 2-methoxyadamantane **13** (9 mg, 30%), and ketone **4** (1 mg, 4%) were isolated. Photolysis was performed twice and the average value is reported.

2-Methoxyadamantane (13) colorless crystals; ^{1}H NMR (600 MHz, $CDCl_3$, 20°C): δ = 3.29-3.27 (m, 4H), 1.96-2.09 (m, 4H), 1.80-1.88 (m, 3H), 1.77 (br. s, 1H), 1.71 (s, 2H), 1.62-1.68 (m, 2H), 1.44-1.51 (m, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 20°C): δ = 83.2 (d), 55.2 (d), 37.5 (t), 36.4 (t), 31.3 (t), 31.2 (q), 27.4 (d), 27.3 (d) ppm. The NMR spectroscopic data are in accord with those in the literature.4

Photochemistry of 2 in H_2O-DMSO (9:1) According to the general procedure, the photolysis, extraction with hexane (see procedure for the irradiations in the inclusion complexes) and GC analysis gave yields of the photoproducts that are reported in Table 2 in the manuscript.

Photochemical experiments with the inclusion complexes Diazirine **2** (20 mg) was dissolved in DMSO (10 mL) and added to the solution of cyclodextrins (c = 1.32 × 10^{-2} M) or cucurbit[7]uril (c = 0.1 × 10^{-3} M) in H_2O. The solution was purged with Ar for 30 min and irradiated in a Rayonet reactor with 11 lamps (350 nm, 1 lamp 8 W) for 5 min. After the

irradiation, the photolyzed solution was extracted with hexane (3 × 50 mL), followed by CH_2Cl_2 (3 × 50 mL), and the organic extracts were dried over anhydrous $MgSO_4$. The solvent was evaporated on a rotary evaporator. The residue was analyzed by GC and ^1H NMR but only pentane solution contained products. The retention times of the photoproducts were compared to those of the synthesized molecules. Separation of photoproducts was accomplished by the chromatography on a column of silica gel using pentane as eluent.

Photochemistry of 2 in the presence of β-CD According to the general procedure, the photolysis, extraction with hexane and GC analysis gave the following yields of the photoproducts: dehydroadamantane **11** (3%), ketone **4** (2%), alcohol **10** (78%), and a mixture of azines **12** (13%) (Table 2 in the manuscript). Photolysis was performed twice and the average value is reported.

Photochemistry of 2 in the presence of γ-CD According to the general procedure, the photolysis, extraction with hexane and GC analysis gave the following yields of the photoproducts: dehydroadamantane **11** (1%), ketone **4** (1%), alcohol **10** (81%), and a mixture of azines **12** (13%) (Table 2 in the manuscript).

Photochemistry of 2 in the presence of CB[7] According to the general procedure, the photolysis, extraction with hexane and GC analysis gave the following yields of the photoproducts: dehydroadamantane **11** (1%), ketone **4** (15%), alcohol **10** (30%), and a mixture of azines **12** (54%) (Table 2 in the manuscript).

Characterization of known PCU photoproducts 3, 17, 18 and 21

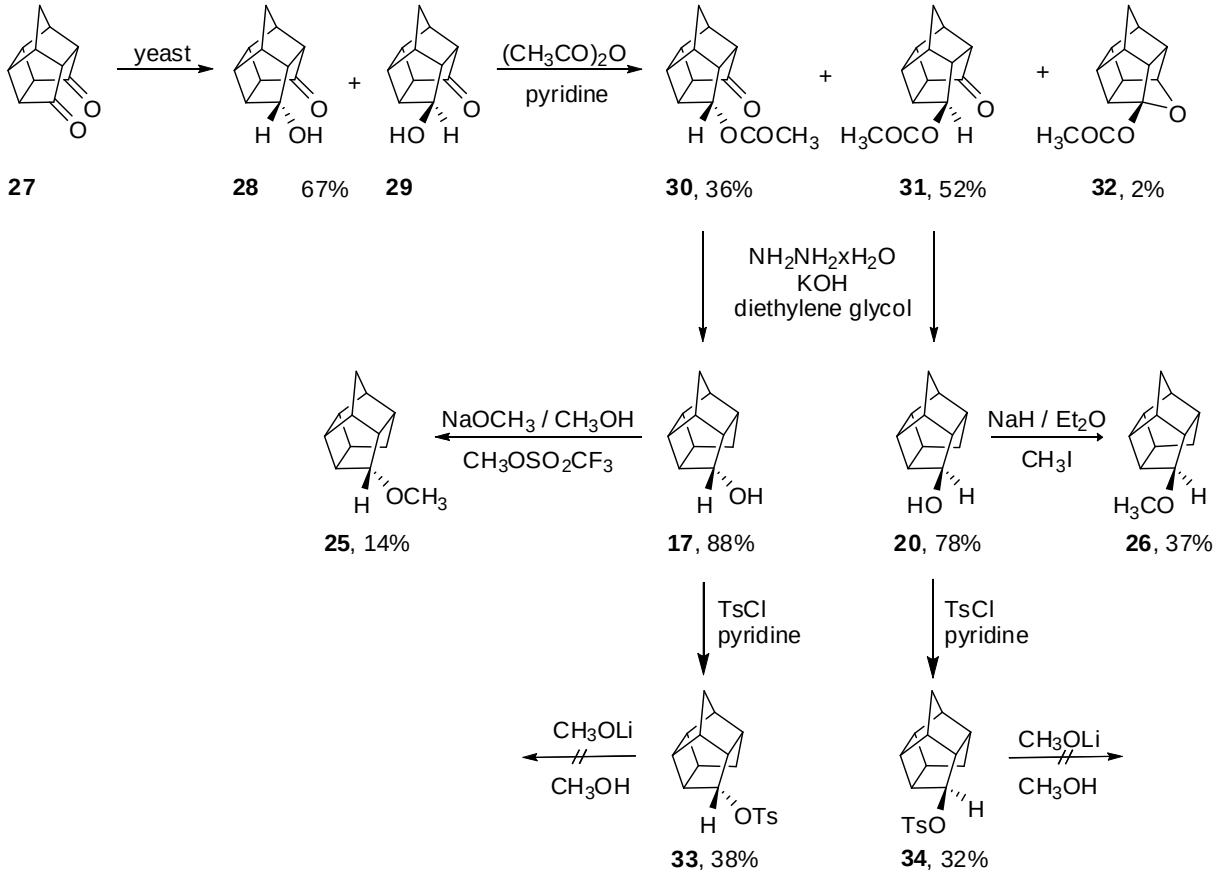
Pentacyclo[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecane-8-on (3). Colorless crystals; ^{1}H NMR (600 MHz, $CDCl_3$, 20°C): δ = 2.91-3.01 (m, 2H), 2.77-2.82 (m, 1H), 2.68-2.75 (m, 1H), 2.55-2.60 (m, 2H), 2.50-2.54 (m, 1H), 2.30-2.35 (m, 1H), 1.88 (d, *J* = 10.8 Hz, 1H), 1.55 (d, *J* = 10.8 Hz, 1H), 1.47-1.51 (m, 1H), 1.41-1.46 (m, 1H) ppm. The NMR spectroscopic data are in accord with those in the literature. [7]

***Endo*-pentacyclo[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecane-8-ol (17).**7 Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$, 20°C): δ = 3.93 (t, *J* = 3.9 Hz, 1H), 2.70-2.75 (m, 1H), 2.60-2.65 (m, 1H), 2.53-2.57 (m, 1H), 2.38-2.44 (m, 2H), 2.18-2.30 (m, 4H), 1.70 (d, *J* = 10.3 Hz, 1H), 1.47 (br. s, 1H), 1.17 (d, *J* = 10.2 Hz, 1H), 1.08 (dt, *J* = 3.8 Hz, *J* = 11.8 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 20°C): δ = 74.4 (d), 47.0 (d), 45.7 (d), 43.1 (d), 42.0 (d), 39.9 (d), 38.8 (d), 35.9 (d), 35.2 (t), 28.8 (t) ppm. The NMR spectroscopic data are in accord with those in the literature.[8]

1,2-Bis(pentacyclo[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecane-8-ylidene)hydrazine (18). Colorless crystals; mixture of isomers; ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ = 3.27-3.60 (m, 2H), 2.83-2.96 (m, 2H), 2.57-2.78 (m, 7H), 2.36-2.49 (m, 4H), 1.74-1.84 (m, 2H), 1.41 (d, *J* = 10.7 Hz, 2H), 1.25-1.34 (m, 5H) ppm. The NMR spectroscopic data are in accord with those in the literature.2

(*D*$_3$)-Trishomocuban-4-ol (21). Isolated from the photolysis mixture on a column chromatography on silica gel using CH_2Cl_2 as eluent. Colorless solid; IR (KBr): *ν* = 2956.6, 2362.6, 1718.4, 1654.8, 1508.2, 1097.4 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, 20°C): δ = 4.17 (br. s, 1H), 2.55-2.65 (m, 1H), 2.06-2.18 (m, 4H), 1.91-1.97 (m, 3H), 1.49 (d, *J* = 10.2 Hz, 1H), 1.28-1.38 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 20°C): δ = 77.4 (d), 53.6 (d), 52.3 (d), 47.5 (d), 47.2 (d), 44.2 (d), 43.2 (d), 41.3 (d), 40.7 (d), 33.7 (t), 33.0 (t) ppm. The NMR spectroscopic data are in accord with those in the literature.7

Synthesis of PCU ethers 25 and 26



Scheme S3. Synthesis of PCU ethers **25** and **26**.

Endo-alcohol **17** was prepared in a high yield by a $LiAlH_4$ reduction of PCU ketone **3**.[7] The alcohol was converted to *endo*-ether **25** in a low yield by use of methyl trifluoromethanesulfonate. However, it provided enough ether **25** for a complete spectroscopic characterization. For the preparation of *exo*-alcohol and the corresponding ether, we used a different approach starting from PCU diketone **27** (Scheme S3). The reduction by yeast gave a mixture of *endo*- and *exo*-ketoalcohols **28** and **29** that were used as a mixture in the acetylation step.[9] The reaction gave the reported acetyl derivatives **30** and **31** and a new cyclized product **32**, which were all separated and fully characterized by NMR. The acetylated ketoalcohols **30** and **31** were transformed into alcohols **17** and **20**, respectively, in one step under the Wolff-Kishner reduction conditions. The alcohols were tosylated in modest yields to transform the OH into a good leaving group but the attempts to perform S_N2 reactions on the tosylated derivatives **33** and

34 with CH_3OLi failed and only the starting material was recovered. *Exo*-methoxy ether **26** was therefore prepared from *exo*-alcohol **20** by treatment with NaH, followed by methyl iodide. Although the ethers were obtained in low yields, enough samples were obtained for a complete spectroscopic characterization and comparison with the photoproducts.

Synthesis of *endo*-pentacyclo[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecane-8-ol (17).[7,9] PCU ketone **3** (2.0 g, 12.5 mmol) was dissolved in dry ether (125 mL) and added dropwise to the suspension of $LiAlH_4$ (0.95 g, 25 mmol) in dry ether (65 mL). The reaction mixture was heated at reflux for 2 h. After cooling, the excess of $LiAlH_4$ was destroyed by a careful addition of water. The Et_2O solution was decanted, washed with brine and dried over $MgSO_4$. After filtration the solvent was removed on a rotary evaporator to furnish the product (1.9 g, 94%) in the form of colorless solid. (For the characterization of **17**, *vide supra*).

Synthesis of PCU ketoalcohols 28 and 29 (*endo*- and *exo*-11-hydroxy-pentacyclo[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecane-8-on).[10] The solution of yeast was prepared by dissolving sucrose (8 g) and Na_2HPO_4 (0.05 g) in lukewarm water (50 mL), and then dry yeast (3.5 g) was added. After 15 min at warm place, the yeast solution was ready to use. A flask (500 mL) was charged with PCU diketone **27** (0.50 g, 2.87 mmol) and the solution of yeast was added. The reaction mixture was stirred at 35 °C for 72 h. The reaction mixture was filtered through a short plug of celite. The filtrate was saturated with NaCl and extracted with ether (3 × 50 mL). The combined ether extracts were dried over anhydrous $MgSO_4$. After filtration and removal of the solvent on a rotary evaporator the crude mixture was purified by column chromatography on silica gel using 25% EtOAc/Et_2O as eluent to afford a mixture of ketoalcohols **28** and **29** (0.34 g, 67%) which was used in the next step.

Acetylation of PCU ketoalcohols 28 and 29.[10] A mixture of PCU ketoalcohols **28** and **29** (100 mg, 0.57 mmol), was dissolved in $CHCl_3$ (20 mL) and a mixture of acetanhydride in pyridine (1:1, 10 mL) was added. The reaction mixture was stirred at 90 °C for 1 h. The solvent was removed on a rotary evaporator to afford the crude product (128 mg) in the form of yellow oil.

Column chromatography on silica gel with Et_2O/hexane (1:1) as eluent gave three products: **30** (46 mg, 36%), **31** (67 mg, 52%), and **32** (2 mg, 2%).

***Endo*-11-acetoxy-pentacyclo[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecane-8-on (30).** Colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ = 4.90 (br. s, 1H), 2.98-3.07 (m, 1H), 2.86-2.94 (m, 2H), 2.72-2.82 (m, 2H), 2.63-2.68 (m, 1H), 2.53-2.60 (m, 1H), 2.34-2.42 (m, 1H), 1.99 (br. s, 3H), 1.89 (d, *J* = 10.7 Hz, 1H), 1.67 (d, *J* = 11.2 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 20°C): δ = 216.8 (s), 170.2 (s), 77.3 (d), 51.3 (d), 51.0 (d), 46.9 (d), 43.9 (d), 42.7 (d), 42.0 (d), 41.2 (d), 37.6 (t), 36.5 (d), 21.2 (q) ppm. The NMR spectroscopic data are in accord with those in the literature.[10]

***Exo*-11-acetoxy-pentacyclo[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecane-8-on (31).** Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$, 20°C): δ = 4.79 (t, *J* = 4.3 Hz, 1H), 3.12-3.16 (m, 1H), 2.94-2.97 (m, 1H), 2.83-2.92 (m, 2H), 2.66-2.68 (m, 1H), 2.58-2.62 (m, 1H), 2.52-2.55 (m 1H), 2.38-2.42 (m, 1H), 1.98 (br. s, 3H), 1.90 (d, *J* = 11.1 Hz, 1H), 1.53 (d, *J* = 11.1 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 20°C): δ = 216.2 (s), 170.6 (s), 73.5 (d), 50.6 (d), 50.1 (d), 44.4 (d), 42.0 (d), 40.9(d), 40.7 (d), 40.1 (d), 38.3 (t), 36.9 (d), 20.8 (q) ppm. The NMR spectroscopic data are in accord with those in the literature.8

1-Acetoxy-12-oxahexacyclo[7.2.0.0$^{2.9}$.0$^{3.7}$.0$^{4.11}$.0$^{6.10}$]dodecane (32). Colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ = 4.74 (t, *J* = 5.2 Hz, 1H), 2.82-2.85 (m, 2H), 2.70-2.73 (m, 2H), 2.56-2.64 (m, 1H), 2.42-2.44 (m, 1H), 2.10 (br. s, 3H), 1.88 (d, *J* = 10.5 Hz, 1H), 1.58 (d, *J* = 10.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 20°C): δ = 168.7 (s), 120.9 (s), 81.7 (d), 55.7 (d), 55.3 (d), 45.4 (d), 45.2 (d), 44.7 (d), 44.0 (d), 42.9 (t), 42.6 (d), 41.6 (d), 21.4 (q) ppm; HRMS (MALDI-TOF) calculated for $C_{13}H_{14}NO_6 + Na^+$ 241.0841, found 241.0831.

***Endo*-pentacyclo[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecane-8-ol (17).**7 PCU ketoacetate **30** (1.58 g, 7.86 mmol) and hydrazine hydrate (98%, 5 mL) in diethylene glycol (20 mL) was refluxed for 5 h and then stirred at rt overnight. In the reaction mixture, KOH (1 g) was added and excess of water and hydrazine hydrate was distilled off until the temperature of 190 °C was reached. The reaction mixture was heated at 190 °C for 3 h and then, the product was separated by steam water distillation. An extraction with CH_2Cl_2 (3 × 50 mL) was carried out and the extracts were dried over $MgSO_4$. After filtration and removal of the solvent on a rotary evaporator, the pure product

(1.04 g, 88%) was obtained in the form of colorless solid. The NMR spectroscopic data (*vide supra*) are in accord with those in the literature.[10]

***Exo*-pentacyclo[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecane-8-ol (20).**7 According to the above procedure for alcohol **17**, starting from PCU ketoacetate **31** (1.05 g, 0.522 mmol), the reaction furnished the product (0.68 g, 78%) in the form of colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$, 20°C): δ = 4.04 (br.s, 1H), 2.65-2.69 (m, 1H), 2.52-2.63 (m, 3H), 2.46-2.49 (m, 1H), 2.32-2.35 (m, 1H), 2.19-2.25 (m, 2H), 1.68 (d, *J* = 10.4 Hz, 1H), 1.34 (d, *J* = 10.4 Hz, 1H), 0.97 (dt, *J* = 3.7 Hz, *J* = 12.4 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 20°C): δ = 74.1 (d), 48.5 (d), 47.2 (d), 44.0 (d), 42.6 (d), 42.4 (d), 42.3 (d), 41.7 (d), 35.6 (d), 33.9 (t), 26.8 (t) ppm. The NMR spectroscopic data are in accord with those in the literature.7

Synthesis of *endo*-8-tosyloxypentacyclo[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecane (33). To a solution of tosyl chloride (286 mg, 1.5 mmol) in pyridine (10 mL), cooled by an ice/water bath, PCU alcohol **17** (162 mg, 1 mmol) was added in small portions during 4-5 h. The reaction mixture was stirred and cooled by the ice/water bath for additional 3 h, and then, left in a refrigerator for 72 h. The reaction mixture was poured on ice and extracted with hexane (5 × 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvent was removed on a rotary evaporator. The residue was chromatographed on a column of silica gel using CH_2Cl_2 as eluent to afford product 32 (120 mg, 38 %) and recover the unreacted PCU alcohol (85 mg 52%).

Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$, 20°C): δ = 7.75 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.46 (br. s, 1H), 2.58 (br. s, 3H), 2.45 (br. s, 3H), 2.28-2.40 (m, 3H), 2.23 (br. s, 1H), 2.16 (br. s, 1H), 2.04 (d, *J* = 12.1 Hz, 1H), 1.66 (d, *J* = 10.6 Hz, 1H), 1.15 (d, *J* = 10.6 Hz, 1H), 1.04 (d, *J* = 12.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 20°C): δ = 144.3 (s), 134.5 (s), 129.7 (d, 2C), 127.7 (d, 2C), 82.1 (d), 46.8 (d), 43.7 (d), 42.2 (d), 42.0 (d), 41.9 (d), 38.6 (d), 36.8 (d), 35.5 (d), 35.0 (t), 28.6 (t), 21.7 (q) ppm.

Synthesis of *exo*-8-tosyloxypentacyclo[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecane (34). According to the above procedure for tosylate **33**, starting from PCU alcohol **20** (162 g, 1.0 mmol), the reaction furnished product **34** (100 mg, 32%), and PCU alcohol (71 mg, 44%) was recovered.

Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$, 20°C): δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.76-4.78 (m, 1H), 2.65-2.69 (m, 1H), 2.56-2.61 (m, 3H), 2.51-2.54 (m, 1H), 2.45 (br. s, 3H), 2.31-2.38 (m, 2H), 2.22-2.25 (m, 1H), 1.64 (d, *J* = 10.8 Hz, 1H), 1.48 (d, *J* = 12.6 Hz, 1H), 1.31 (d, *J* = 10.6 Hz, 1H), 0.98-1.02 (m, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 20°C): δ = 144.2 (s), 135.0 (s), 125.7 (d, 2C), 122.5 (d, 2C), 87.5 (d), 47.2 (d), 46.8 (d), 44.7 (d), 42.8 (d), 42.6 (d), 41.7 (d), 40.4 (d), 36.0 (d), 33.8 (t), 26.8 (t), 21.6 (q) ppm.

Synthesis of *endo*-8-methoxypentacyclo[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecane (25). A solution of $NaOCH_3$ was prepared by reacting Na in CH_3OH (>10 eq.). PCU-alcohol **17** (162 mg, 1 eq) was dissolved in the solution of $NaOCH_3$ and stirred at rt for 10 min. The solvent was removed on a rotary evaporator and the crude residue dissolved in dry CH_3CN (5 mL). The reaction mixture was cooled with an ice/water bath and methyl triflate (1.1 mL, 10 mmol) was added dropwise. The reaction mixture was heated at reflux 2 h and then stirred at rt 72 h. To the reaction mixture water (50 mL) was added and an extraction with ether (3 × 50 mL) was conducted. The combined extracts were dried over anhydrous $MgSO_4$, filtered and the solvent was removed on a rotary evaporator. The residue was chromatographed on a column of silica gel using Et_2O/hexane (0→100%) as eluent to afford pure product **25** (25 mg, 14%). Unreacted PCU alcohol (82 mg, 51%) was recovered.

Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$, 20°C): δ = 3.44 (br. s, 1H), 3.29 (br. s, 3H), 2.72-2.75 (m, 2H), 2.58-2.64 (m, 1H), 2.42-2.46 (m, 1H), 2.35-2.38 (m, 2H), 2.23-2.27 (m, 2H), 2.17-2.20 (m, 1H), 1.70 (d, *J* = 10.2 Hz, 1H), 1.19 (d, *J* = 10.2 Hz, 1H), 1.00 (d, *J* = 11.4 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 20°C): δ = 82.8 (d), 56.8 (q), 47.1 (d), 42.9 (d), 42.8 (d), 42.4 (d), 42.3 (d), 39.4 (d), 36.14 (d), 36.07 (d), 35.2 (t), 28.6 (t) ppm. NMR spectroscopic data are in accord with those in the literature.[10]

Synthesis of *exo*-8-methoxypentacycl0[5.4.0.0$^{2.6}$.0$^{3.10}$.0$^{5.9}$]undecane (26). NaH (50% in mineral oil, 29 mg, 1.2 mmol) was washed with pentane (4 × 25 mL) and ether (5 mL) was

added under N_2. PCU alcohol **20** (50 mg, 0.3 mmol) dissolved in ether (5 mL) was added and the reaction mixture was stirred at rt for 30 min. Methyl iodide (85 mg, 0.6 mmol, 37 μL) was added and the reaction mixture was heated at reflux for 4 h. After cooling, excess of NaH was destroyed by a careful addition of water (~0.2 mL) and the reaction mixture was extracted with pentane (3 × 15 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and the solvent was removed on a rotary evaporator. The residue was chromatographed on a column of silica gel using CH_2Cl_2 as eluent to afford pure product **26** (20 mg, 37%).

Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$, 20°C): δ = 3.53 (s, 1H), 3.21 (br. s, 3H), 2.65-2.70 (m, 1H), 2.59-2.63 (m, 1H), 2.55-2.57 (m, 1H), 2.50-2.54 (m, 1H), 2.46-2.49 (m, 1H), 2.30-2.35 (m, 2H), 2.10-2.20 (m, 1H), 1.65 (d, *J* = 10.4 Hz, 1H), 1.55 (d, *J* = 12.4 Hz, 1H), 1.30 (d, *J* = 10.5 Hz, 1H), 0.94-0.99 (m, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$, 20°C): δ = 82.9 (d), 55.4 (q), 47.2 (d), 45.0 (d), 44.3 (d), 42.7 (d), 42.13 (d), 42.06 (d), 38.9(d), 35.5 (d), 33.8 (t), 26.7 (t) ppm.

2. Absorption and fluorescence spectra of 1 and 2

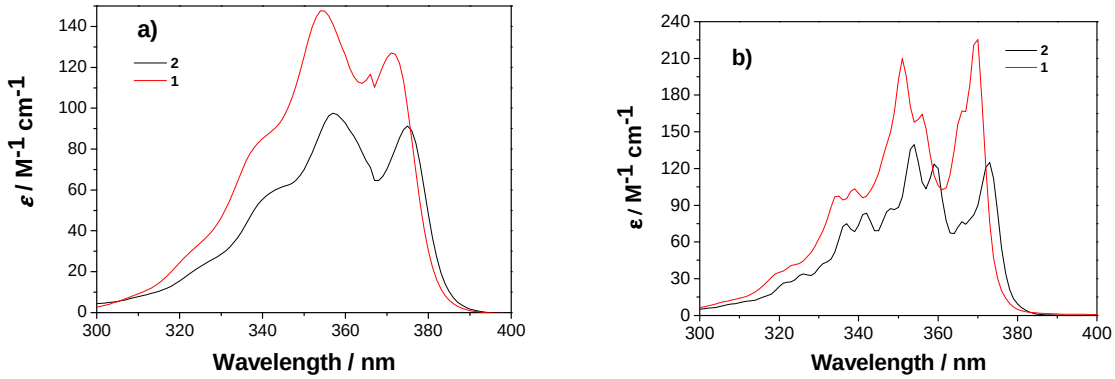


Figure S1. Absorption spectra of **1** and **2** in different solvents: a) CH_3OH and b) cyclohexane.

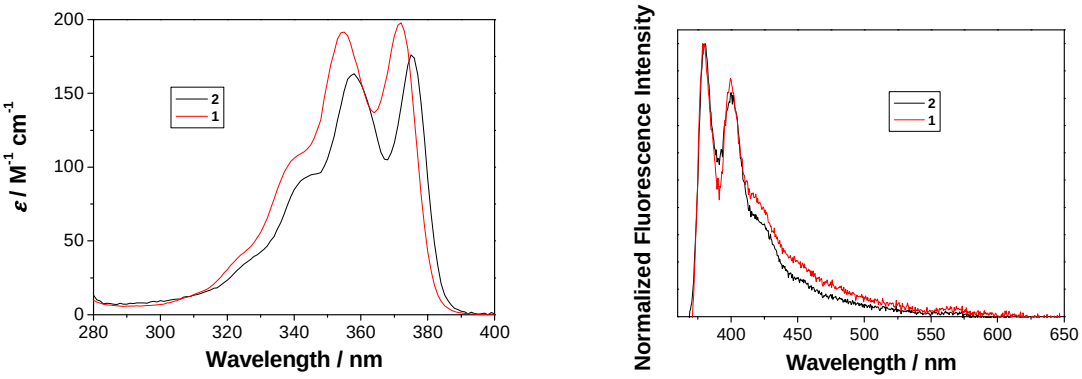


Figure S2. Absorption and normalized emission spectra (λ_{ex} = 350 nm) of **1** and **2** in benzene.

Quantum yield of fluorescence and time-resolved fluorescence

The following equation was used for the determination of fluorescence quantum yields:

$$\Phi = \Phi_R \frac{I}{I_R} \frac{A_R}{A} \left(\frac{n_D}{n_D^R}\right)^2 \quad \text{(S1)}$$

wherein

Φ - quantum yield of fluorescence

Φ_R - quantum yield of fluorescence of reference compound, quinine sulfate in aqueous 1.0 N H_2SO_4 (Φ = 0.55)[11]

I - intensity of fluorescence (integral of the corrected emission spectrum)

I_R - intensity of fluorescence (integral of the corrected emission spectrum) for the reference compound

A - absorbance of the solution at the excitation wavelength

A_R - absorbance of the solution of the reference compound at the excitation wavelength

n_D - refractive index of the solvent

n_D^R - refractive index of the solvent use to dissolve the reference compound (H_2O)

Fluorescence decays, were fit as sums of exponentials using Gaussian-weighted non-linear least-squares fitting based on Marquardt-Levenberg minimization implemented in the Fast software.

Fluorescence decays were fit to a sum of exponentials using the following expression:

$$F(t) = \alpha_1 \exp\left(-\frac{t}{\tau_1}\right) + \alpha_2 \exp\left(-\frac{t}{\tau_2}\right) + \alpha_3 \exp\left(-\frac{t}{\tau_3}\right) + \ldots \quad \text{(S2)}$$

3. Complexation of 1 and 2 with CB[7], β-CD and γ-CD: NMR study

I. NMR titration

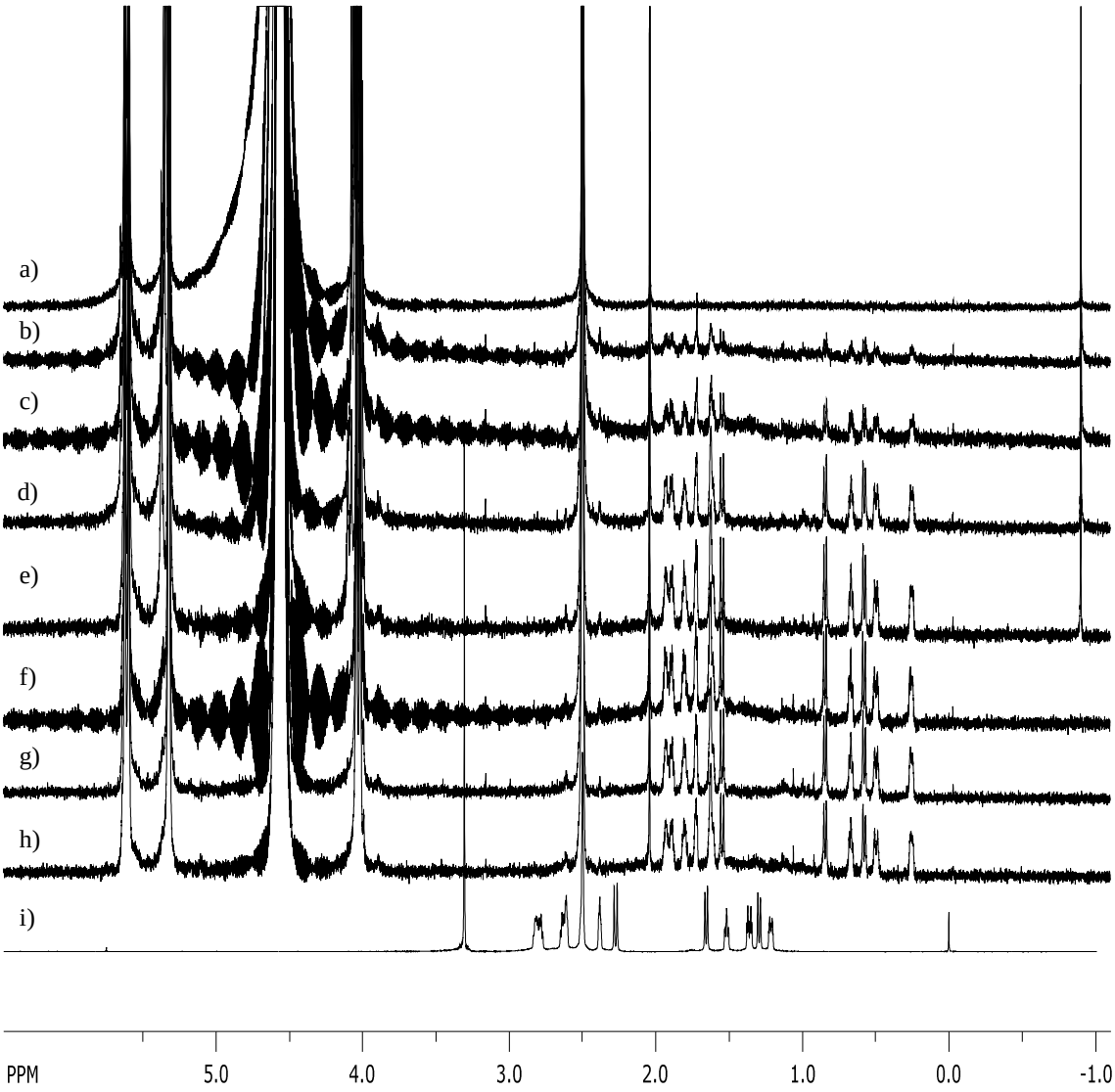


Figure S3. ^{1}H NMR spectra from titration of **1**: a) CB[7] (1 mM) in D_2O:DMSO-d_6 (9:1), b-h) CB[7] (1 mM) in D_2O:DMSO-d_6 (9:1) + 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 equivalent of **1**, respectively, i) **1** (60 mM) in DMSO-d_6.

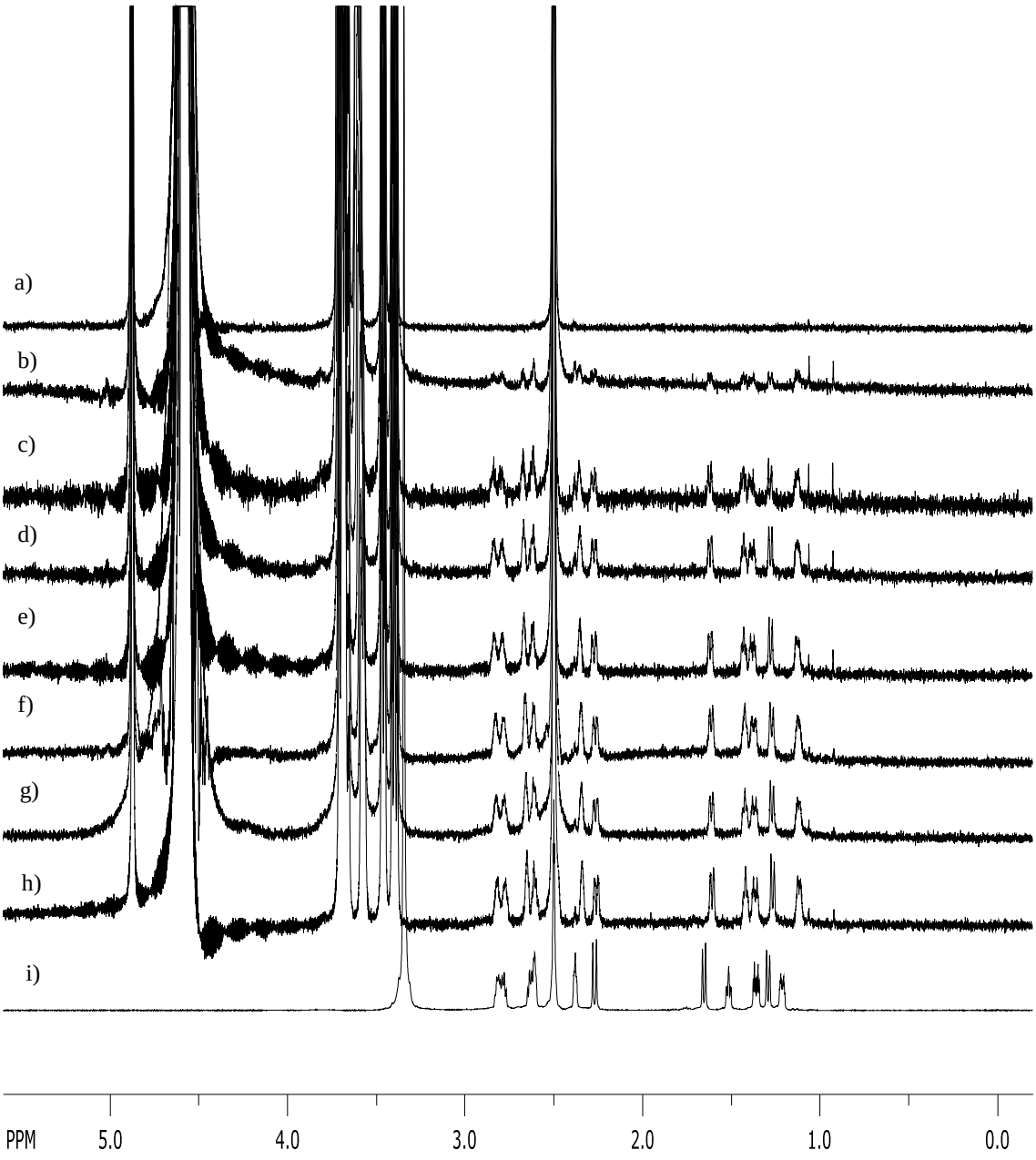


Figure S4. ^{1}H NMR spectra from titration of **1**: a) β-CD (1 mM) in D_2O:DMSO-d_6 (9:1), b-h) β-CD (1 mM) in D_2O:DMSO-d_6 (9:1) + 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 equivalent of **1**, respectively, i) **1** (63 mM) in DMSO-d_6.

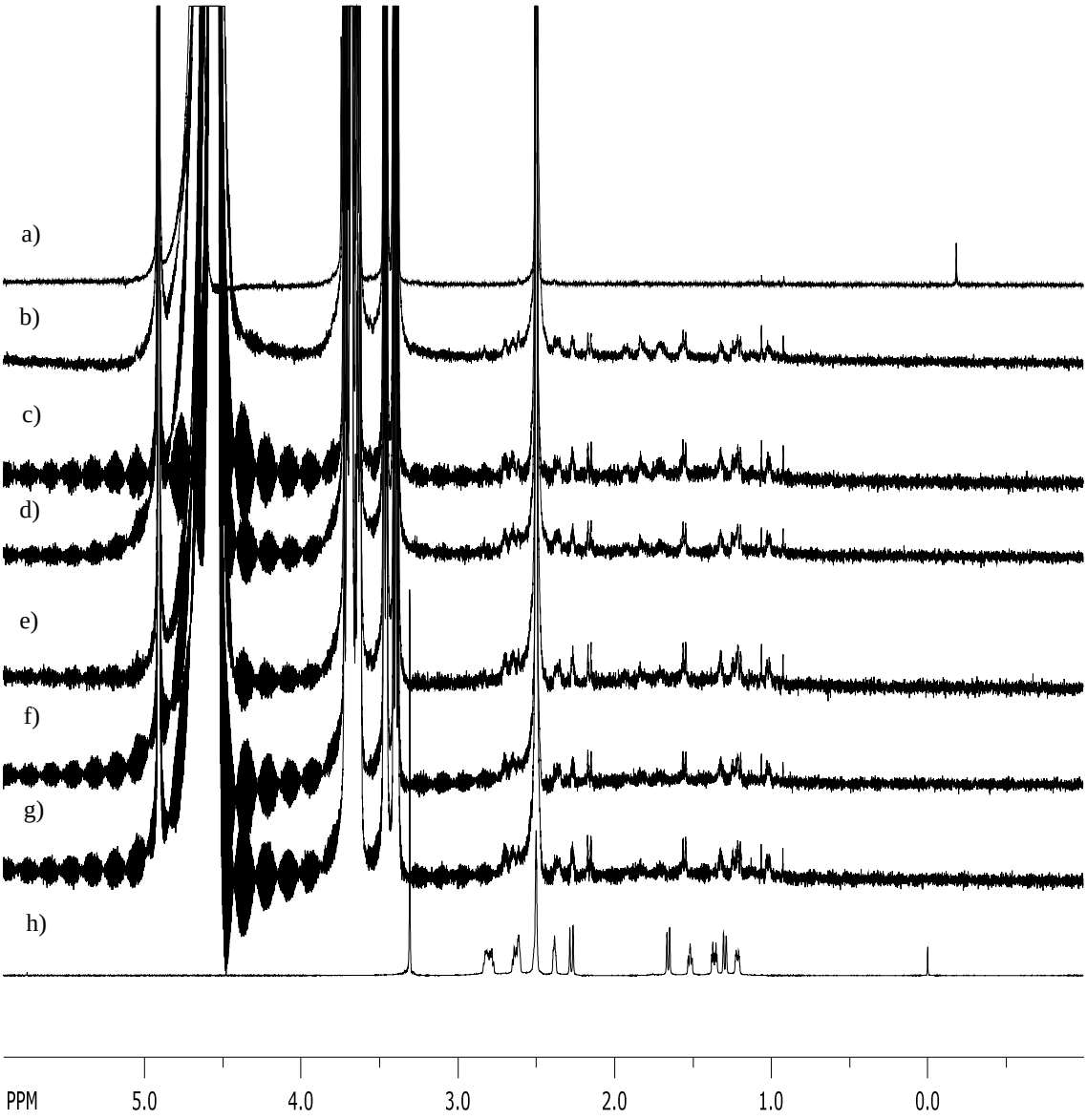


Figure S5. ^{1}H NMR spectra from titration of **1**: a) γ-CD (1 mM) in D_2O:DMSO-d_6 (9:1), b-g) γ-CD (1 mM) in D_2O:DMSO-d_6 (9:1) + 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 equivalent of **1**, respectively, h) **1** (63 mM) in DMSO-d_6.

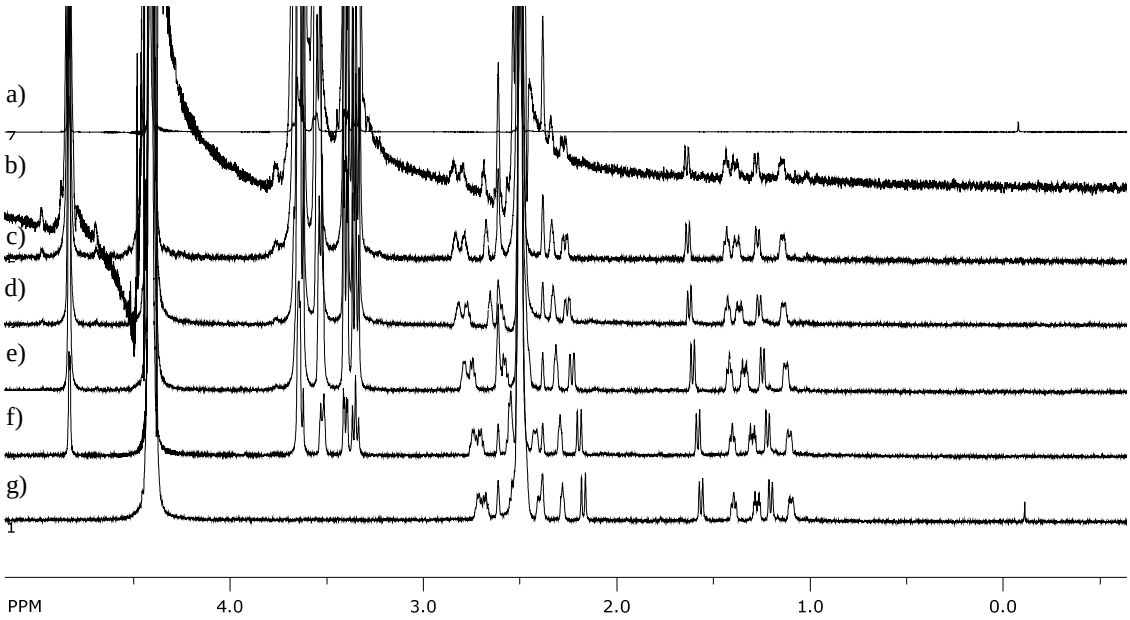


Figure S6. ^{1}H NMR spectra of a) β-CD (6 mM) in D_2O:DMSO-d_6 (1:1), b-f) β-CD (6 mM) and **1** (6 mM), both in D_2O:DMSO-d_6 (1:1) in various ratios of 9:1, 7:3, 1:1, 3:7, 1:9 of β-CD:**1**, respectively, g) **1** (6 mM) in D_2O:DMSO-d_6 (1:1).

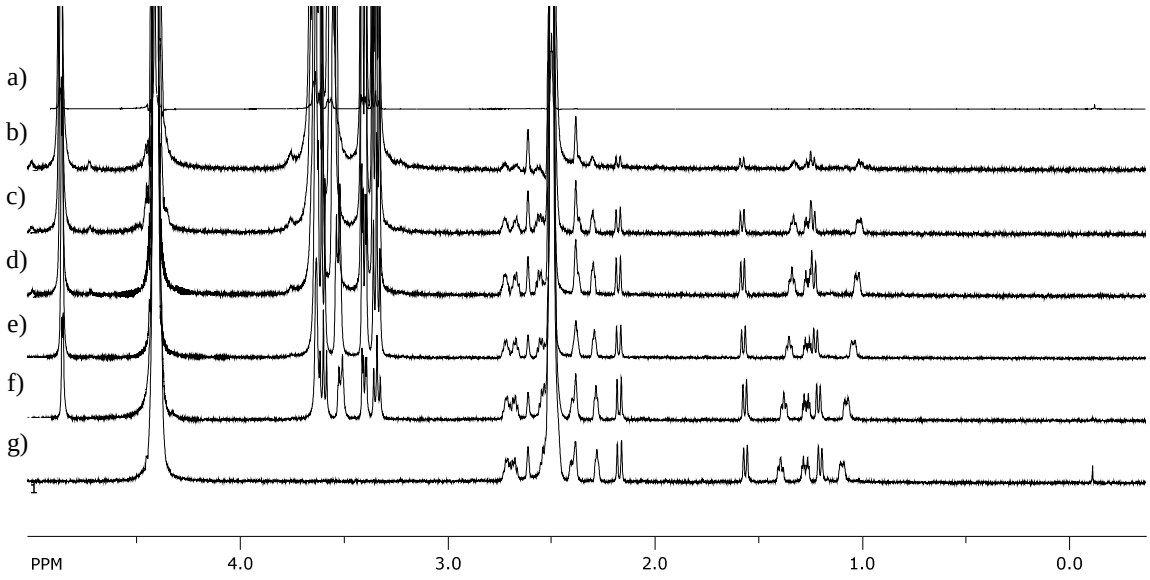


Figure S7. ^{1}H NMR spectra of a) γ-CD (6 mM) in D_2O:DMSO-d_6 (1:1), b-g) γ-CD (6 mM) and **1** (6 mM), both in D_2O:DMSO-d_6 (1:1) in various ratios of 9:1, 7:3, 1:1, 3:7, 1:9 of γ-CD:**1**, respectively, h) **1** (6 mM) in D_2O:DMSO-d_6 (1:1).

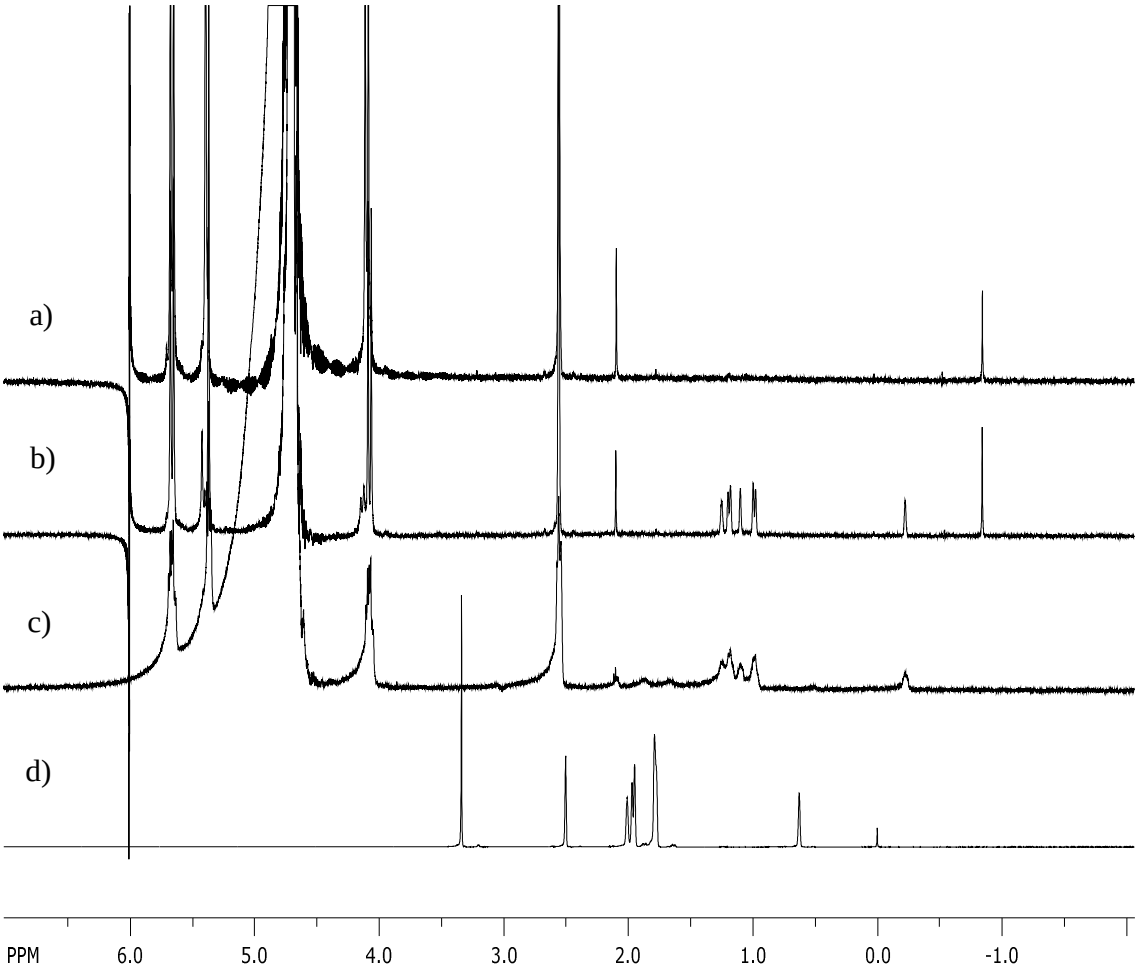


Figure S8. ^{1}H NMR spectra from titration of **2:** a) CB[7] (1mM) in D_2O:DMSO-d_6 (9:1), b-c) CB[7] (1 mM) in D_2O:DMSO-d_6 (9:1), + 0.3 or 1.0 equivalent of **2,** respectively, d) **2** (55 mM) in DMSO-d_6.

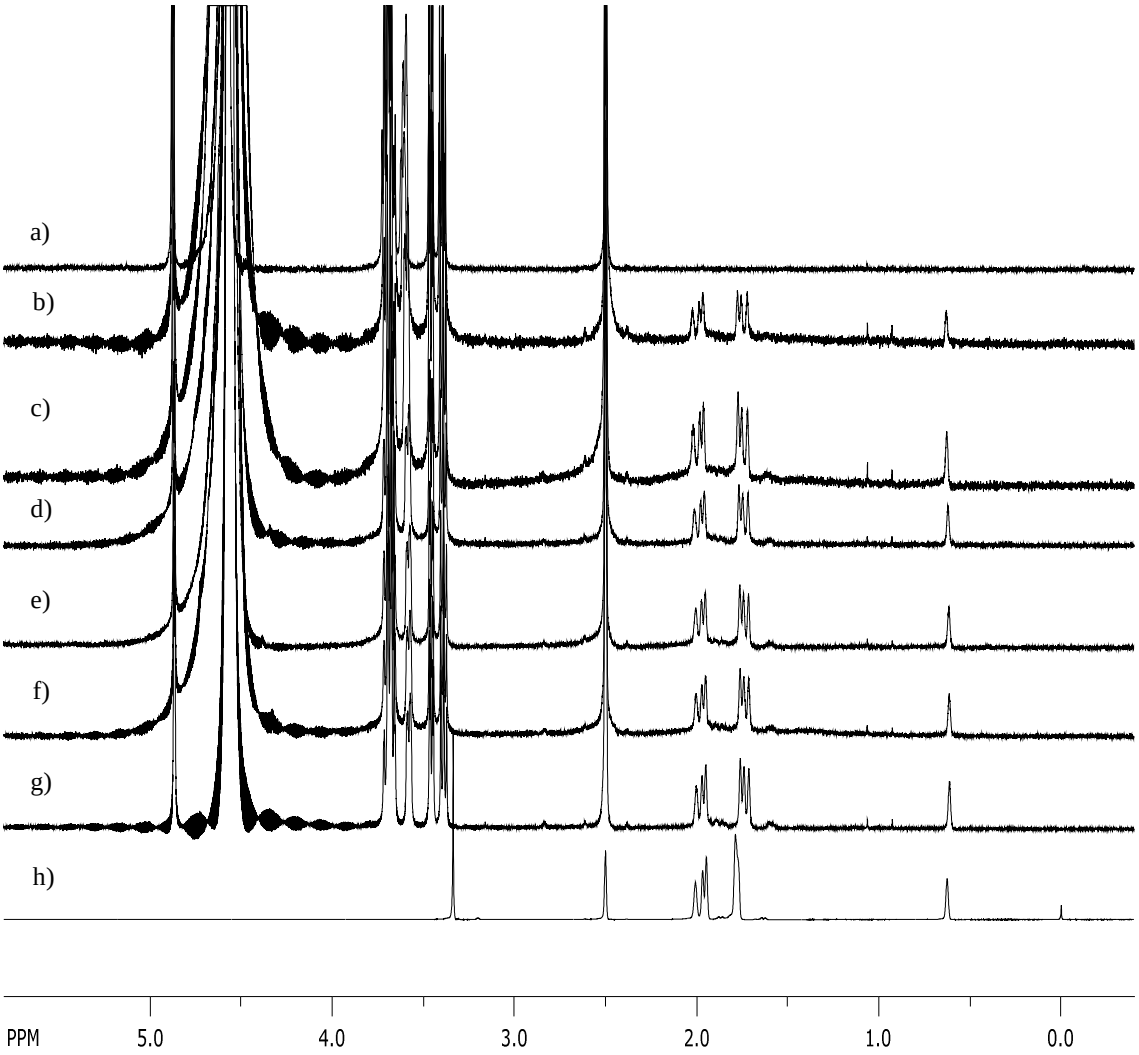


Figure S9. ^{1}H NMR spectra from titration of **2**: a) β-CD (1 mM) in D_2O:DMSO-d_6 (9:1), b-g) β-CD (1 mM) in D_2O:DMSO-d_6 (9:1) + 0.2, 0.4, 0.6, 0.8, 1.0 or 1.2 equivalent of **2**, respectively, h) **2** (55 mM) in DMSO-d_6.

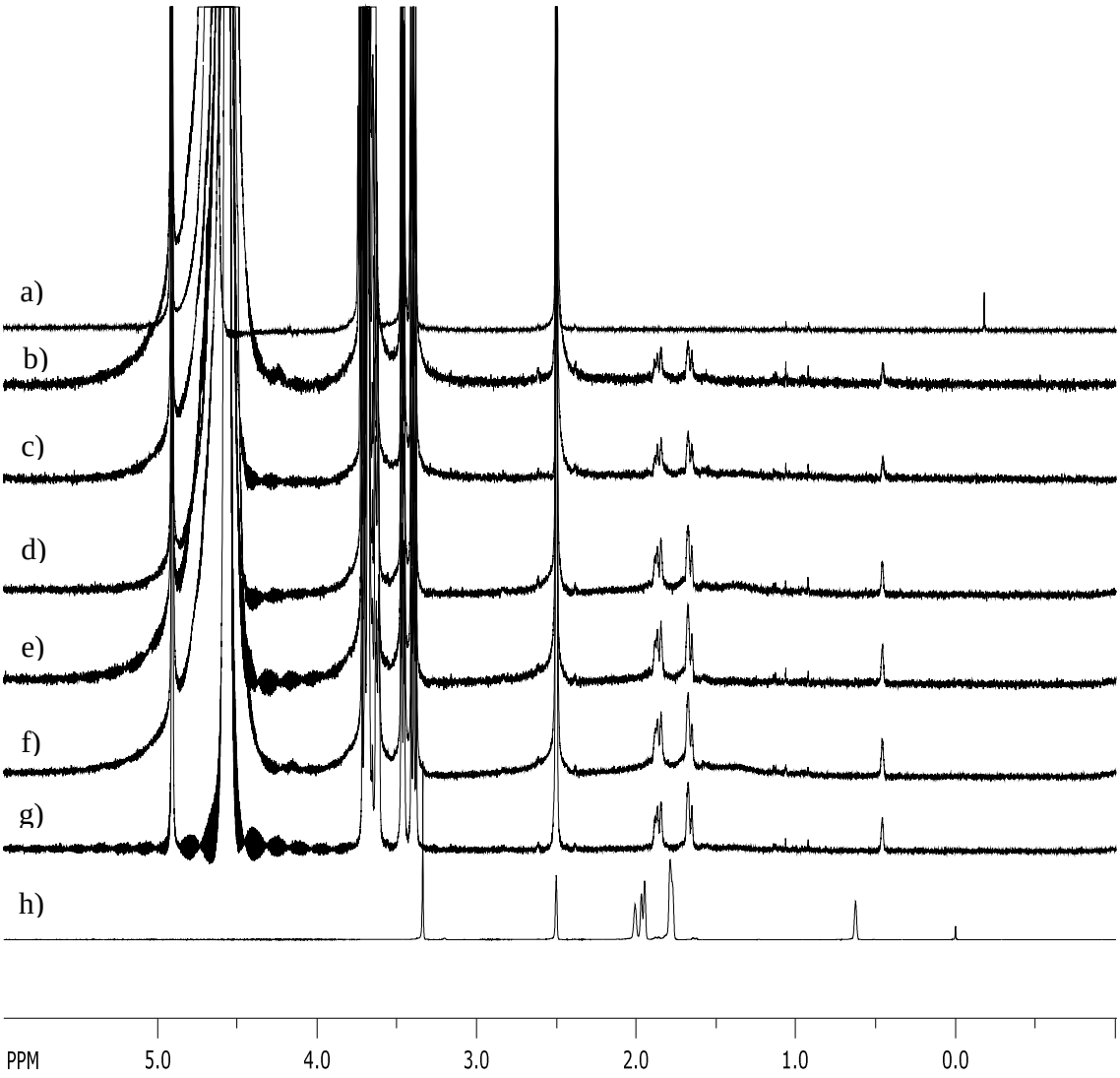


Figure S10. ^{1}H NMR spectra from titration of **2**: a) γ-CD (1 mM) in D_2O:DMSO-d_6 (9:1), b-g) γ-CD (1 mM) in D_2O:DMSO-d_6 (9:1) +0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 equivalent of **2**, respectively, h) **2** (55 mM) in DMSO-d_6.

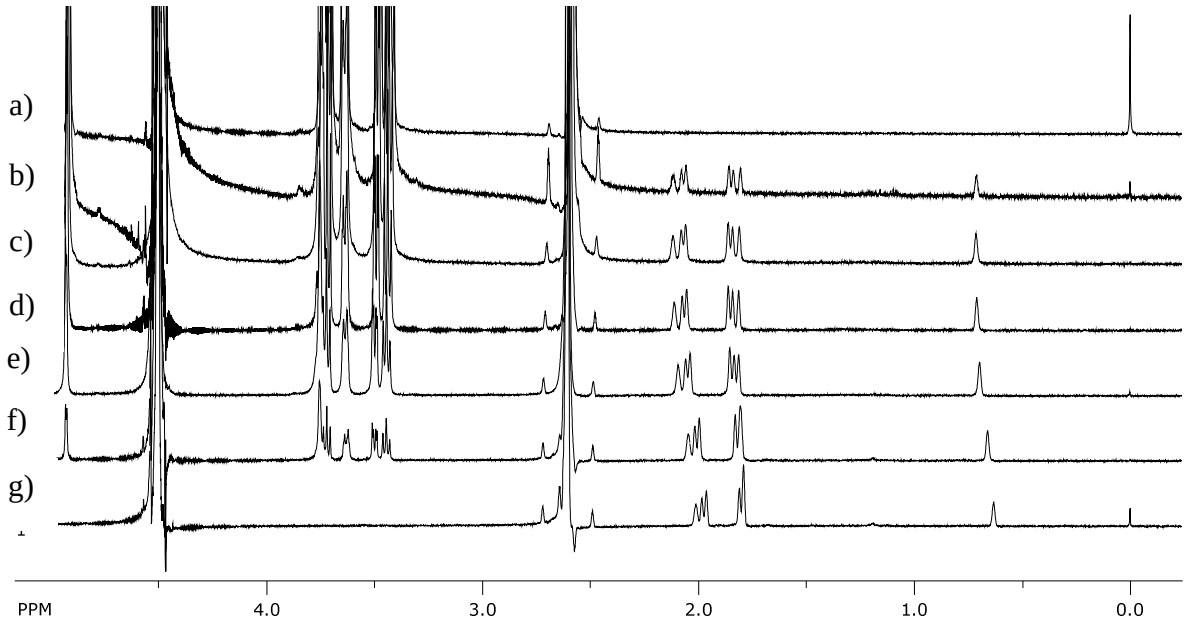


Figure S11. ^{1}H NMR spectra of a) β-CD (6 mM) in D_2O:DMSO-d_6 (1:1), b-f) β-CD (6 mM) and **2** (6 mM), both in D_2O:DMSO-d_6 (1:1) in various ratios of 9:1, 7:3, 1:1, 3:7, 1:9 of β-CD:**2**, respectively, g) **2** (6 mM) in D_2O:DMSO-d_6 (1:1).

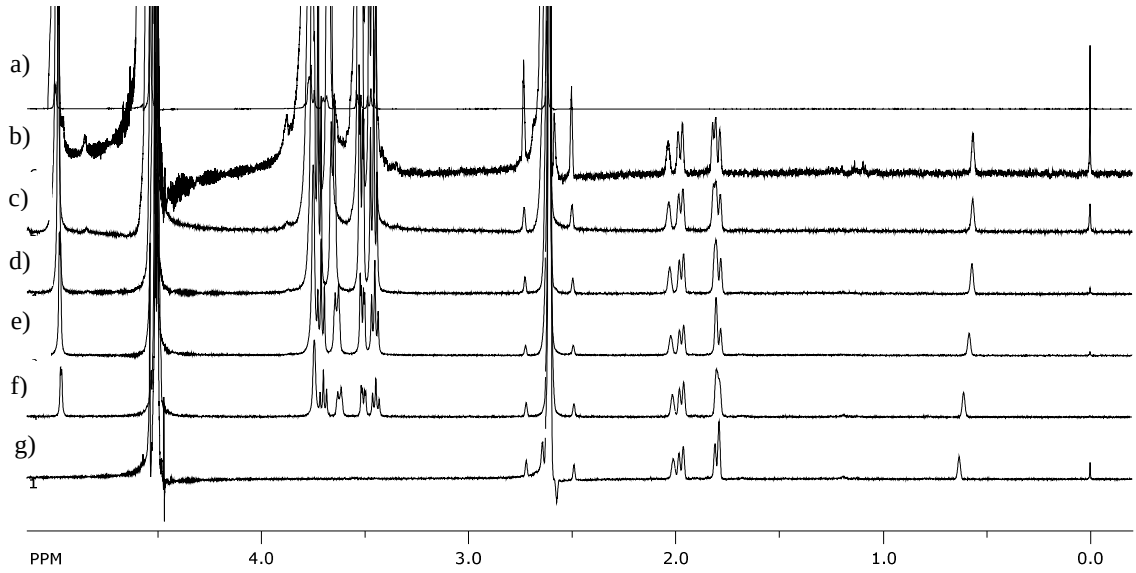


Figure S12. ^{1}H NMR spectra of a) γ -CD (6 mM) in D_2O:DMSO-d_6 (1:1), b-f) γ -CD (6 mM) and **2** (6 mM), both in D_2O:DMSO-d_6 (1:1) in various ratios of 9:1, 7:3, 1:1, 3:7, 1:9 of γ -CD:**2**, respectively, g) **2** (6 mM) in D_2O:DMSO-d_6 (1:1).

II. NOESY Spectra

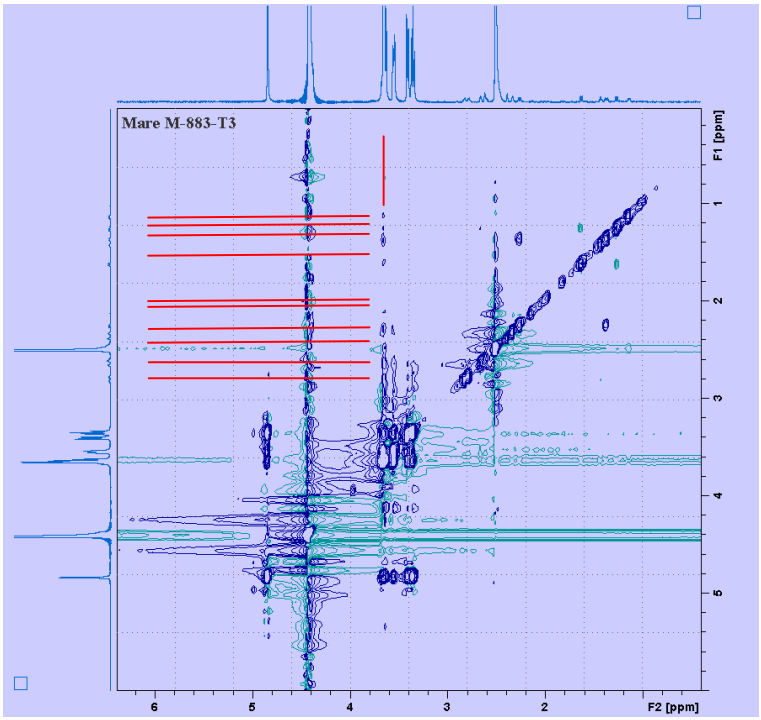


Figure S13. 2-D NOESY NMR spectrum of **1** (6 mM) + β-CD (6 mM) in D_2O:DMSO-d_6 (1:1).

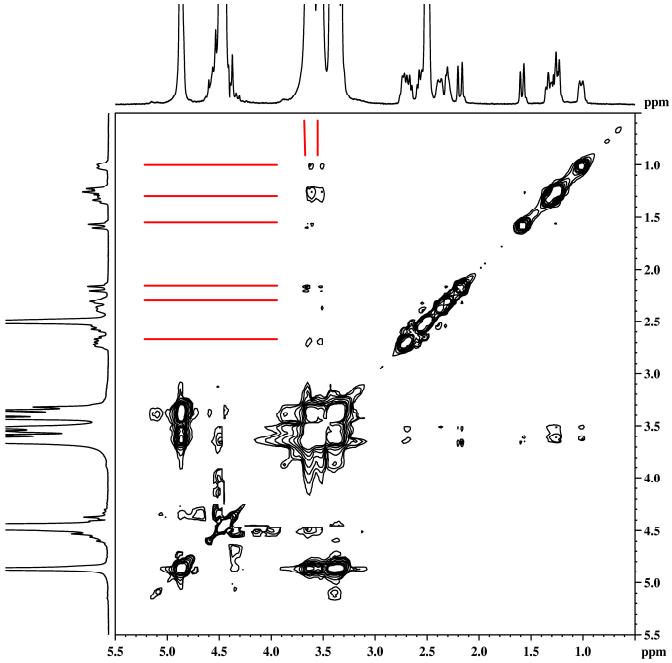


Figure S14. 2-D NOESY NMR spectrum of **1** (12 mM) + γ-CD (12 mM) in D_2O:DMSO-d_6 (1:1).

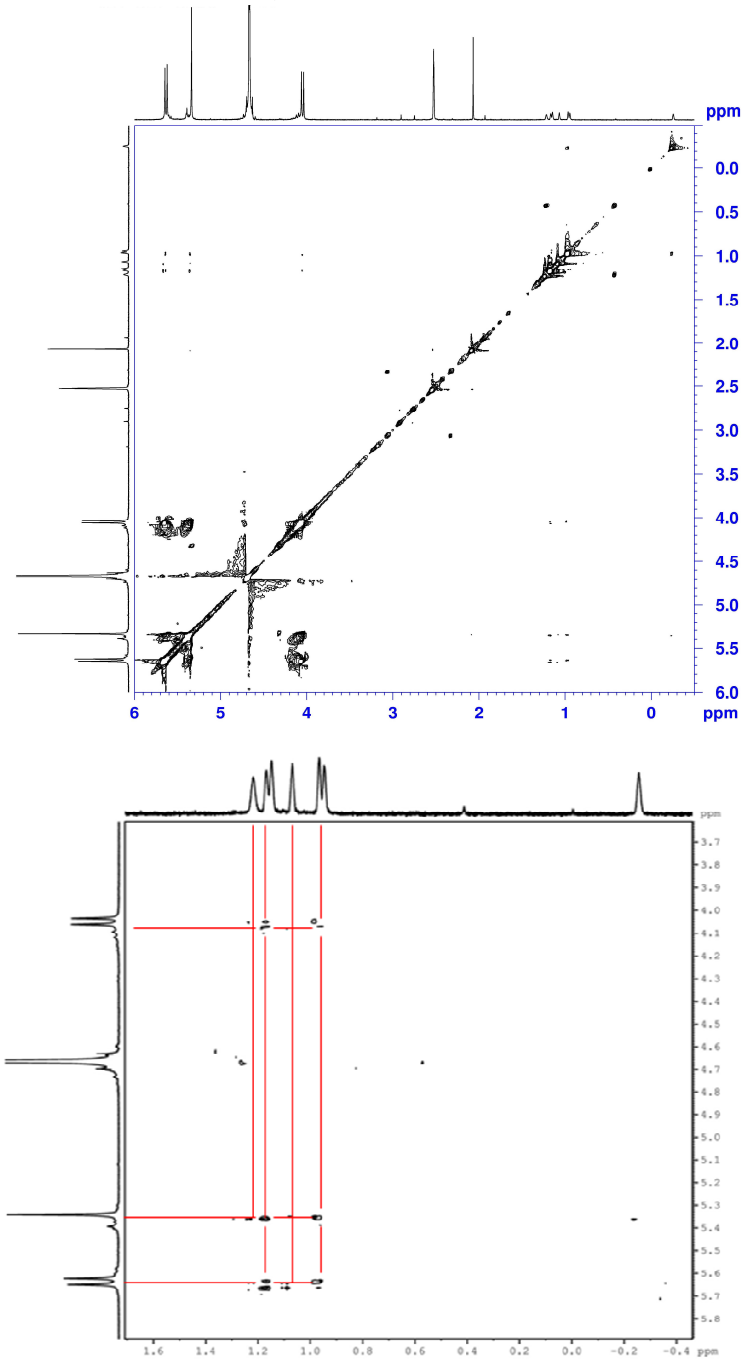


Figure S15. 2-D NOESY NMR spectra of **2** (1 mM) + CB[7] (1 mM) in D_2O:DMSO-d_6 (9:1).

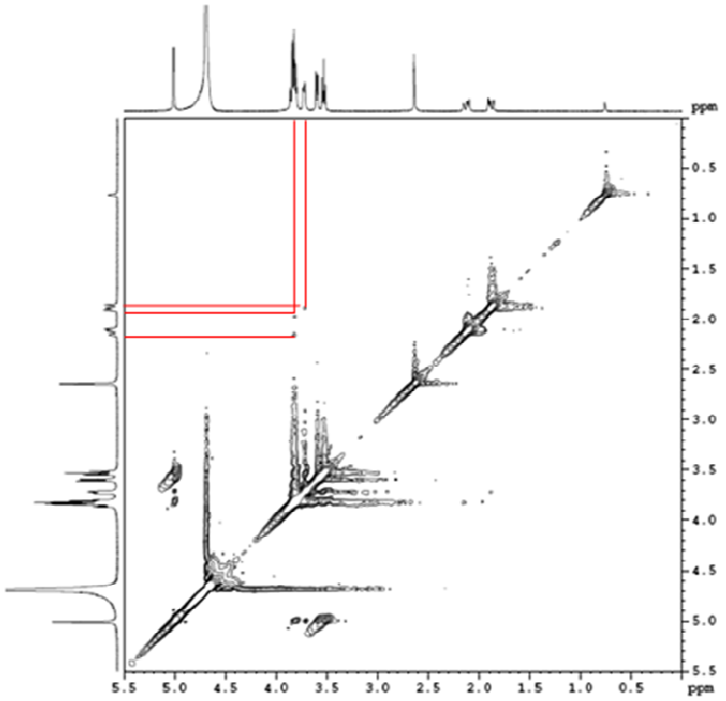


Figure S16. 2-D NOESY NMR spectrum of **2** (1mM) + β-CD (1 mM) in D_2O:DMSO-d_6 (9:1).

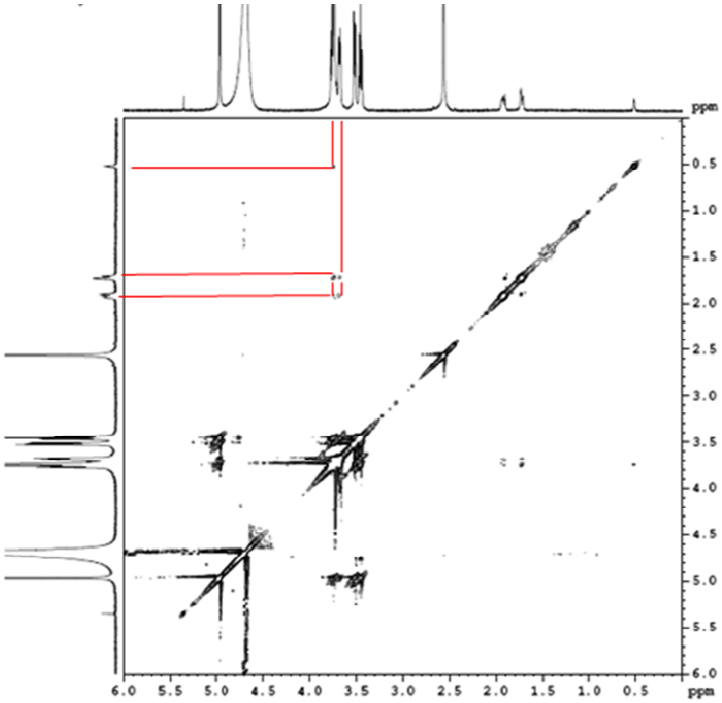


Figure S17. 2-D NOESY NMR spectrum of **2** (1 mM) + γ-CD (1 mM) in D_2O:DMSO-d_6 (9:1).

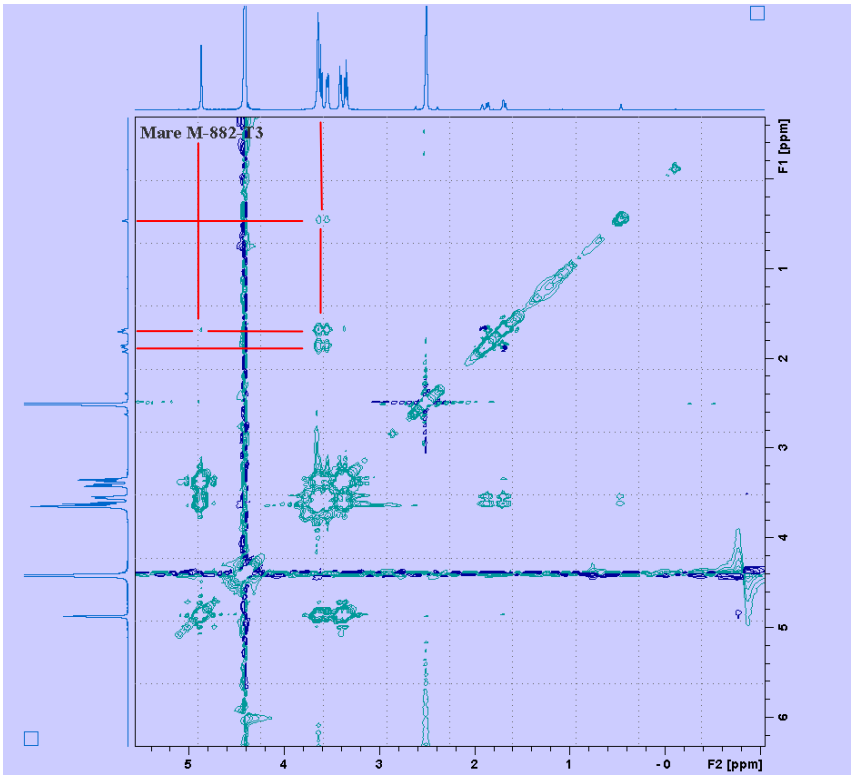


Figure S18. 2-D NOESY NMR spectrum of **2** (6 mM) + γ-CD (6 mM) in D_2O:DMSO-d_6 (1:1).

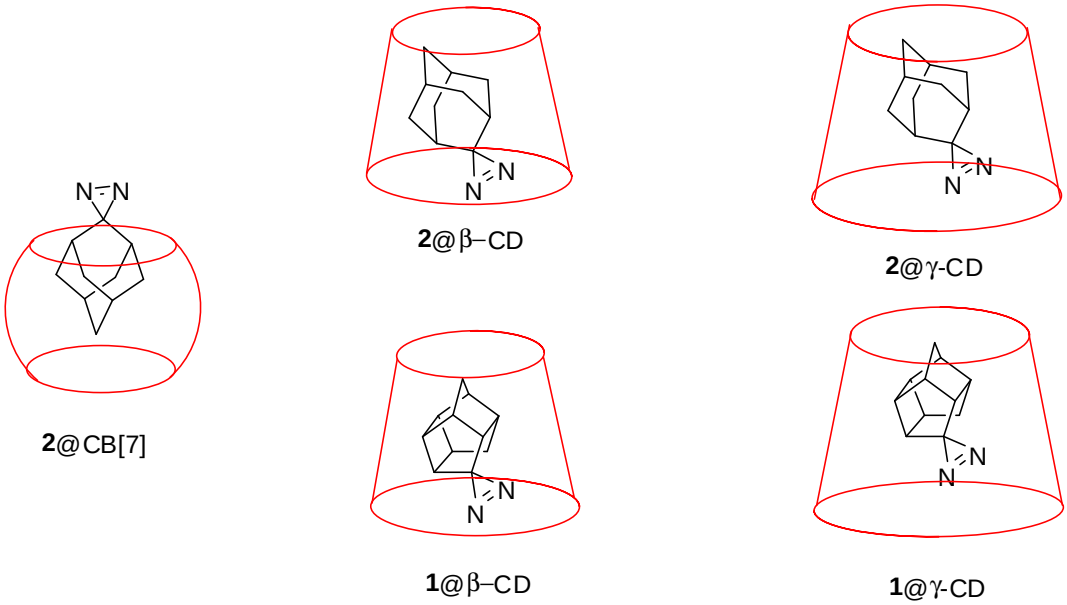


Figure S19. Structures of the inclusion complexes based on the NOESY spectra.

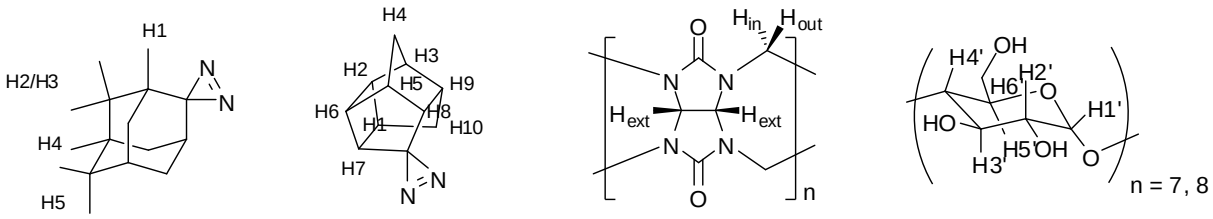


Figure S20. Signal assignment of H-atoms for the corresponding diazirine and supramolecular hosts.

Table S1. List of important NOE interactions between diazirines **1** or **2** and host H atoms. The spectra were recorded in D_2O- DMSO-d_6 9:1 or 1:1.

Compound / Solvent mixture	CB[7]	β-CD	γ-CD
1 in 1:1	Interactions were not observed	all PCU protons ⋯ H5' and H6'	all PCU protons ⋯ H3', H5' and H6'
2 in 9:1	H2/H3 ⋯ Hout H2/H3 ⋯ Hext H2/H3 ⋯ Hin H4 or H5 ⋯ Hext H4 or H5 ⋯ Hin	H2/H3 ⋯ H3' and H5' H4 or H5 ⋯ H6' H4 or H5 ⋯ H3' and H5	H1⋯ H3' and H5' H2/H3⋯ H3' and H5' H2/H3⋯H6' H4 or H5⋯H6' H4 or H5⋯ H3 and H5'
2 in 1:1	–[a]	–[a]	H1⋯ H3' and H5'(weak) H2/H3⋯H1' H2/H3⋯ H3' and H5' H2/H3⋯ H6' H4 or H5⋯ H3' and H5' H4 or H5⋯ H6'

[a] The spectrum was not recorded.

4. Complexation of 1 and 2 with CB[7], β-CD and γ-CD; ITC study

The titrations where performed on a MicroCal VP-ITC Isothermal titration calorimeter (ITC). Before titrations the samples where degassed at 23 °C, 0.4 atm, with stirring at 120 rpm for 10 min. The titrations where performed at 25 °C, with the CB[7] or β-CD in the cell and ligand **1** or **2** in syringe at 351 rpm. Ligands where added in 30 injections within the concentration range 1-0.8 mM. The concentration of the macromolecule in the cell was 0.05 mM.

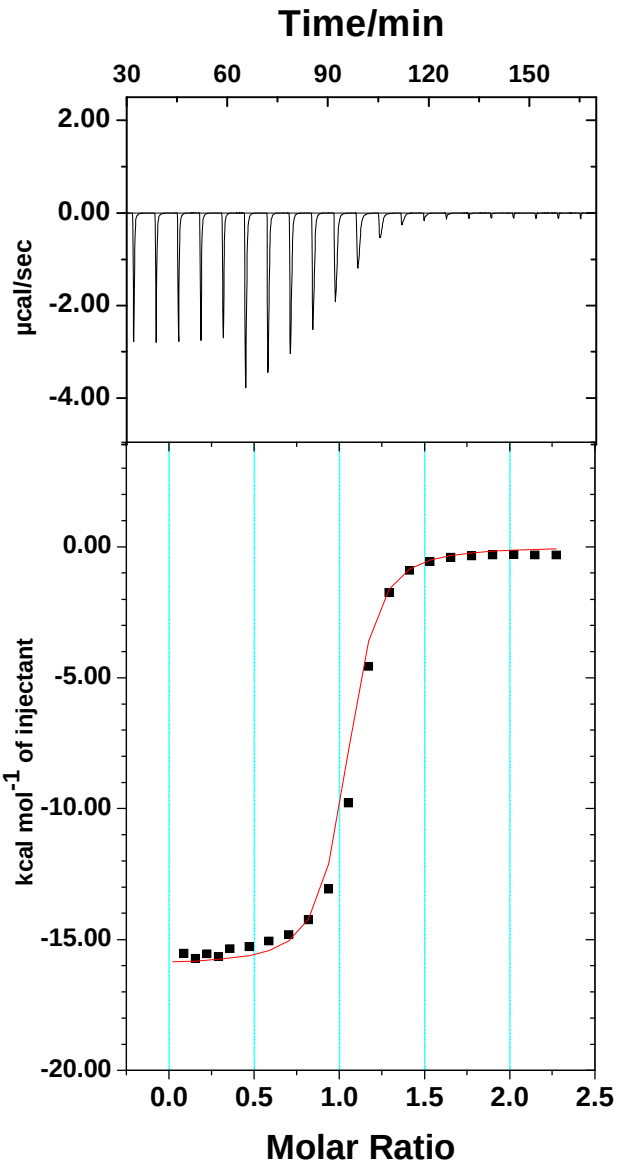


Figure S21. Calorimetric titration of CB[7] (*c* = 0.05 mM) with **2** (*c* = 1.0 mM) at 25 °C in DMSO-H_2O (1:1). Top: raw ITC data; Bottom: dependence of the successive enthalpy change per mol of titrant on **2**: CB[7] ratio.

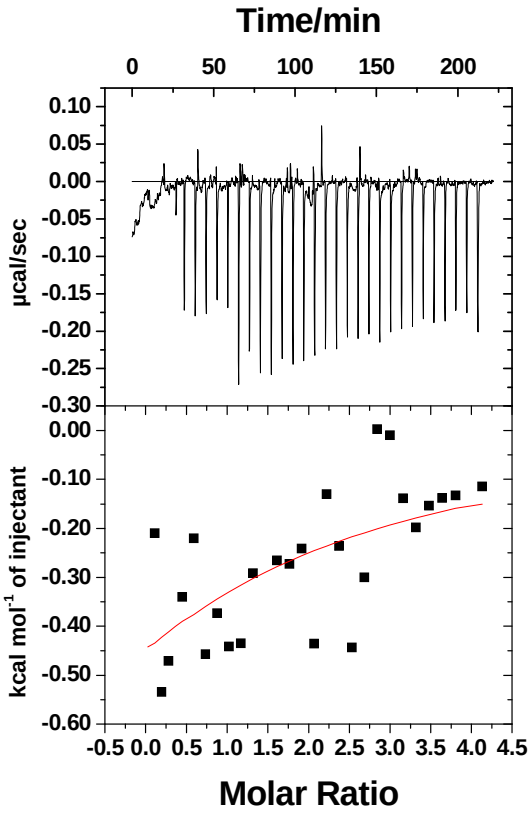


Figure S22. Calorimetric titration of β-CD (c = 0.05 mM) with **2** (c = 1.0 mM) at 25 °C in DMSO-H_2O (1:1). Top: raw ITC data; Bottom: dependence of the successive enthalpy change per mol of titrant on **2**: β-CD ratio.

Table S2. Thermodynamic parameters for the complexation of **1** and **2** with with CB[7] and **2** with β-CD [a]

Complex	log ($K_{1:1}$ / M^{-1})	ΔH / kcalmol^{-1}	ΔS / cal/mol/deg
1@CB[7]	5.9 ± 0.1	-1.60 ± 0.08	-26.6
2@CB[7]	6.4 ± 0.1	-16.0 ± 0.2	-24.2
2@β-CD	3.4 ± 0.3	-3.2 ± 1.2	5.5

[a]The measurement was performed in DMSO-H_2O (1:1).

5. Complexation of 1 and 2 with β-CD and γ-CD; circular dichroism study

Materials and Methods

The solution of **1** or **2** was prepared in DMSO (5 mM) one day prior to the titrations and kept at +4^{o}C. The β- or γ-CD solution (50 mM) in H_2O was prepared one day prior to the titrations. The solutions for the measurements where prepared according to Tables S2-S5, by mixing the solution of compound (**1** or **2**) with the solution of cyclodextrine (β- or γ-CD) under low light conditions. The solution volume was adjusted to total volume of 2 mL according to Table S3-S6. Using these concentrations (Table S3-S6), the ratio r = *c*(host)/*c*(guest) spans through values 0-12. Each solution was incubated at least 2 min prior to the measurement.

The circular dichroism spectra where taken on a JASCO-815 UV-Cd, using measuring parameters: band width 2 nm, response 1 sec, sensitivity standard, measurement range 420 - 300 nm, data pitch 0.1 nm, scanning speed 200 nm/min, accumulation 2, cell length 1 cm, solvent DMSO-H_2O (1:1), temperature 25 ºC. All the spectra where corrected by subtraction of baseline DMSO-H_2O (1:1).

Using these concentrations (Table S3-S6), the ratio r = c(host)/c(guest) spans through values 0-12. Each solution was incubated at least 2 min prior to the measurement.

The circular dichroism (Cd) spectra where taken on a JASCO-815 UV-Cd, using measuring parameters: band width 2 nm, response 1 sec, sensitivity standard, measurement range 420 - 300 nm, data pitch 0.1 nm, scanning speed 200 nm/min, accumulation 2, cell length 1 cm, solvent DMSO-H_2O (1:1), temperature 25 ºC. All the spectra where corrected by subtraction of baseline DMSO-H_2O (1:1).

The binding constants where calculated by the use of HypSpec2014 software[12] with the batch titration option. Since HypSpec2014 supports the data from absorbance (uv, visible or ir) or luminescence (fluorescence) measurements, before the calculation, Cd/mdeg units where converted to absorbance (*A*) units according to equation S3 taken from table from reference[13]

$$A = (\text{Cd/mdeg}) / 32980 \qquad \text{(S3)}$$

Table S3. Volumes of the stock solutions of **1** (c = 5 mM) and β-CD (c = 50 mM) mixed and adjusted to total volume of 2 mL and their corresponding concentrations.

Entry	V(**1**)/μL	c(**1**)×10^3/M	V(β -CD)/μL	c(β-CD)×10^3/M	V(DMSO)/μL	V(H_2O)/μL
1	80	0.20	16	0.40	920	984
2	56	0.14	38	0.95	944	962
3	120	0.30	48	1.20	880	952
4	140	0.35	95	2.36	860	905
5	280	0.70	189	4.73	720	811
6	400	1.0	280	7.0	600	720
7	400	1.0	400	10	600	600
8	400	1.0	480	12	600	520
9	120	0.30	0	0	880	1000
10	0	0	189	4.73	1000	811

CD spectra are shown in the manuscript in Fig. 2.

Table S4. Volumes of the stock solutions of **1** (c = 5 mM) and γ-CD (c = 50 mM) mixed and adjusted to total volume of 2 mL and their corresponding concentrations.

Entry	V(**1**)/μL	c(**1**)×10^3/M	V(γ-CD)/μL	c(γ-CD)×10^3/M	V(DMSO)/μL	V(H_2O)/μL
1	80	0.20	16	0.40	920	984
2	56	0.14	38	0.95	944	962
3	120	0.30	48	1.20	880	952
4	140	0.35	95	2.36	860	905
5	280	0.70	189	4.73	720	811
6	400	1.0	280	7.0	600	720
7	400	1.0	400	10	600	600
8	400	1.0	480	12	600	520
9	40	0.10	0	0	960	1000
10	0	0	189	4.73	1000	811

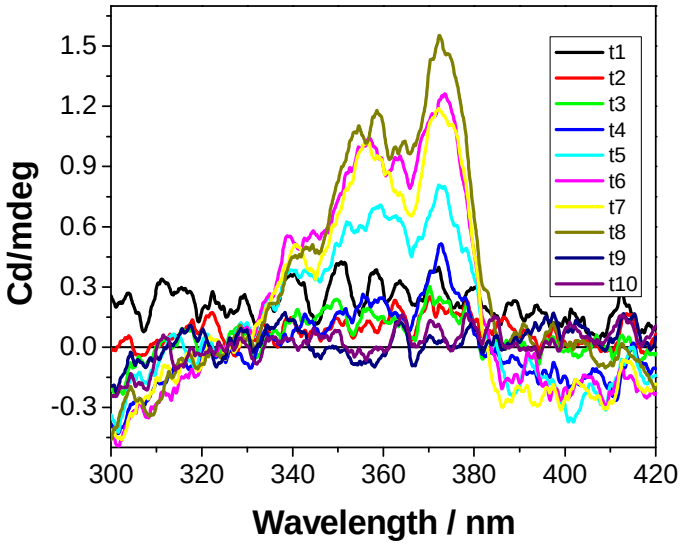


Figure S23. Circular dichroism spectra of the solutions containing **1** and γ-CD, according to Table S4.

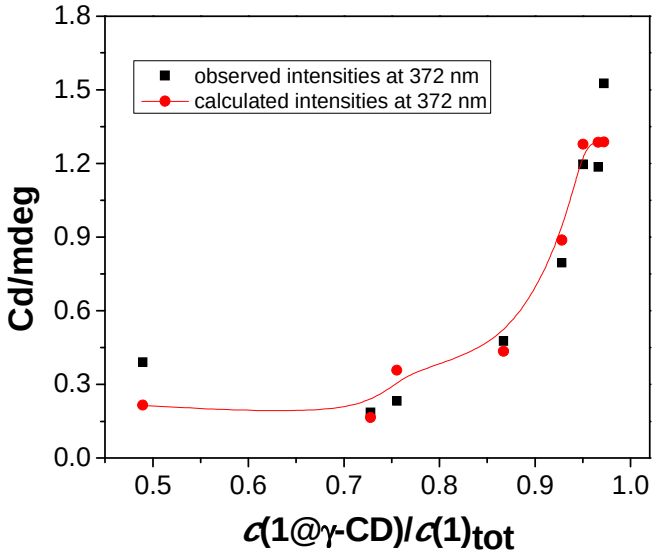


Figure S24. Dependence of the circular dichroism (Cd/mdeg, taken from S23) on the concentration of complex **1**@γ-CD expressed as c(**1**@γ-CD)/c(**1**)$_{tot}$. The red line only connects the calculated points and is not a fit.

Table S5. Volumes of the stock solutions of **2** (c = 5 mM) and β-CD (c = 50 mM) mixed and adjusted to total volume of 2 mL and their corresponding concentrations.

Entry	V(**2**)/μL	c(**2**)×10^3/M	V(β-CD)/μL	c(β-CD)×10^3/M	V(DMSO)/μL	V(H_2O)/μL
1	80	0.20	16	0.40	920	984
2	56	0.14	38	0.95	944	962
3	120	0.30	48	1.20	880	952
4	140	0.35	95	2.36	860	905
5	280	0.70	189	4.73	720	811
6	400	1.0	280	7.0	600	720
7	400	1.0	400	10	600	600
8	400	1.0	480	12	600	520
9	120	0.30	0	0	880	1000
10	0	0	189	4.73	1000	811

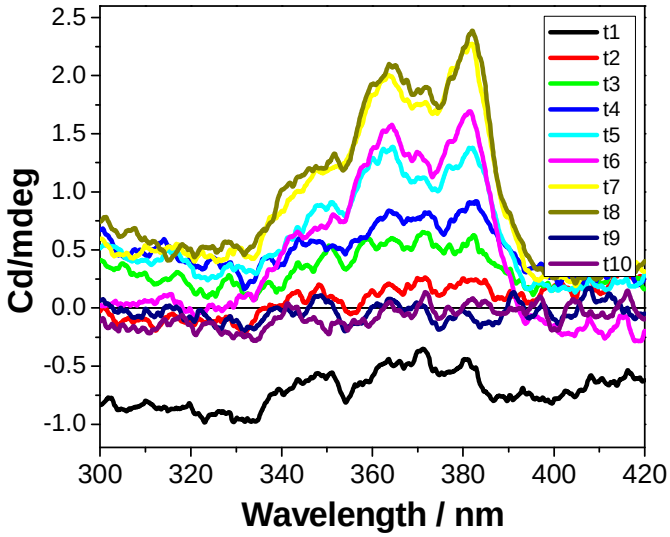


Figure S25. Circular dichroism spectra of the solutions containing **2** and β-CD, according to Table S5.

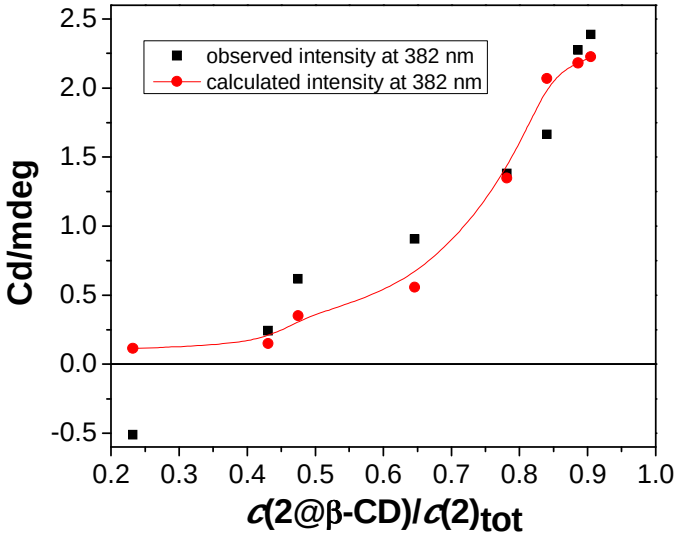


Figure S26. Dependence of the circular dichroism (Cd/mdeg, taken from S25) on the concentration of complex **2**@β-CD expressed as c(**2**@β-CD)/c(**2**)$_{tot}$). The red line only connects the calculated points and is not a fit.

Table S6. Volumes of the stock solutions of **2** (c = 5 mM) and γ-CD (c = 50 mM) mixed and adjusted to total volume of 2 mL and their corresponding concentrations.

Entry	V(**2**)/μL	c(**2**)×10^3/M	V(γ-CD)/μL	c(γ-CD)×10^3/M	V(DMSO)/μL	V(H_2O)/μL
1	80	0.20	16	0.40	920	984
2	56	0.14	38	0.95	944	962
3	120	0.30	48	1.20	880	952
4	140	0.35	95	2.36	860	905
5	280	0.70	189	4.73	720	811
6	400	1.0	280	7.00	600	720
7	400	1.0	400	10	600	600
8	400	1.0	480	12	600	520
9	28	0.07	0	0	972	1000
10	0	0	189	4.73	1000	811

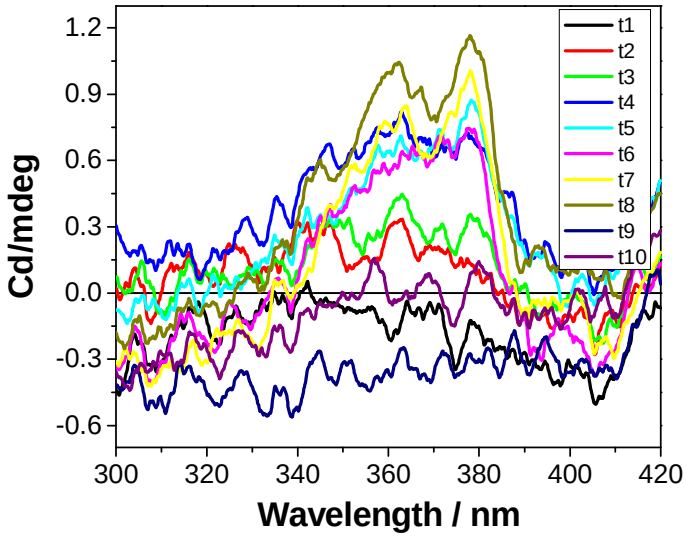


Figure 27. Circular dichroism spectra of the solutions containing **2** and γ-CD, according to Table S6.

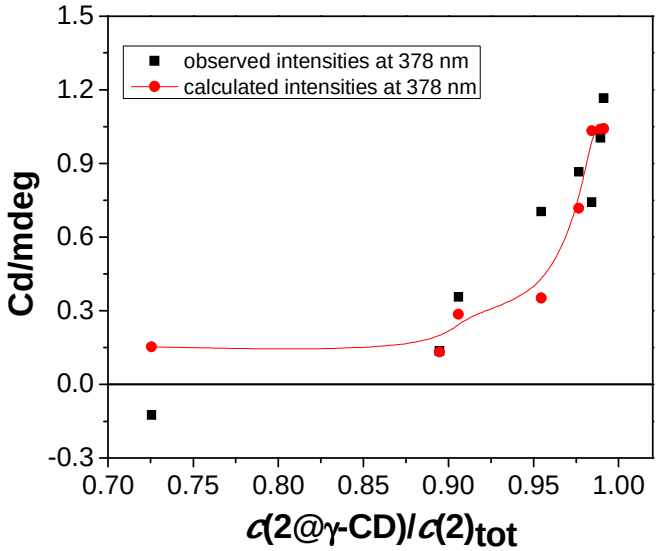


Figure 28. Dependence of the circular dichroism (Cd/mdeg, taken from S27) on the concentration of complex **2**@γ-CD expressed as c(**2**@γ-CD)/c(**2**)$_{tot}$. The red line only connects the calculated points and is not a fit.

6. Quantum yield of the reaction

The number of the absorbed photons for the ferrioxalate actinometer was calculated from:

$$n(\text{absorbed photons}) = \frac{\Delta A_{510} \times V_{irr}}{\varepsilon_{510} \times \ell \times \Phi_{\text{lit.}}} \times \frac{V_{\text{phen}}}{V_{irr}} \qquad \text{(S4)}$$

where:

ΔA_{510} ... absorbance difference at 510 nm for the irradiated and non-irradiated sample

V_{irr} ..... volume of the solution which was irradiated

V_{phen} ..... added volume of the phenanthroline solution

ε_{510} molar absorption coefficient for $[Fe(phen)_3]^{2+}$, that is 11100 M^{-1} cm^{-1}

l length of the optical path (1 cm in all experiments)

$\Phi_{\text{lit.}}$ quantum yield for the actinometer, $\Phi_{355} = 1.25$

The quantum yield of the photoelimination of nitrogen was calculated according to:

$$\Phi = \frac{A_{355} \cdot V_{\text{irr}} \cdot x(\text{photoproduct})}{\varepsilon_{355} \cdot \ell \cdot n(\text{total photons}) \cdot (1 - T_{355})} \qquad \text{(S5)}$$

For the absorbances in the range 0.4-0.8 the number of absorbed photons was calculated according to:

$$n(\text{absorbed photons}) = n(\text{total photons}) \times (1 - T) \qquad \text{(S6)}$$

7. Laser Flash Photolysis

Preparation of benzene solutions for the LFP measurements

Solutions of **1** and **2** for the LFP measurements were prepared by dissolving 4.4 mg or 4.6 mg, respectively, in 10 mL benzene (corresponding to the concentrations of or 2.56×10^{-3} M or 2.84×10^{-3} M). Absorbances at the excitation wavelength were 0.22-0.34. Measurements were performed in 7 × 7 mm cells, and the cell was changed after certain number of laser pulses to assure that sample was not contaminated with products. Absorption spectra were recorded before and after the measurement. Spectra are shown in the figs. bellow. The samples were excited with a Nd:YAG laser at 355 nm.

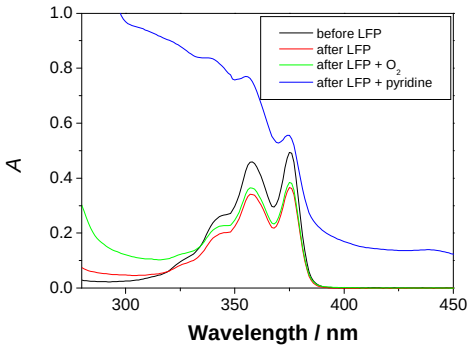


Figure S29. Absorption spectra of **2** in benzene before and after LFP.

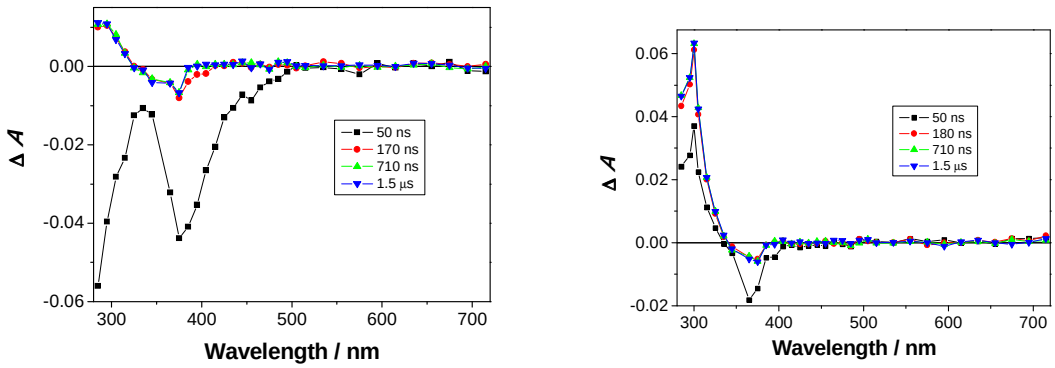


Figure S30. Transient absorption spectra of **2** in N_2 (left) and O_2 (right) purged benzene.

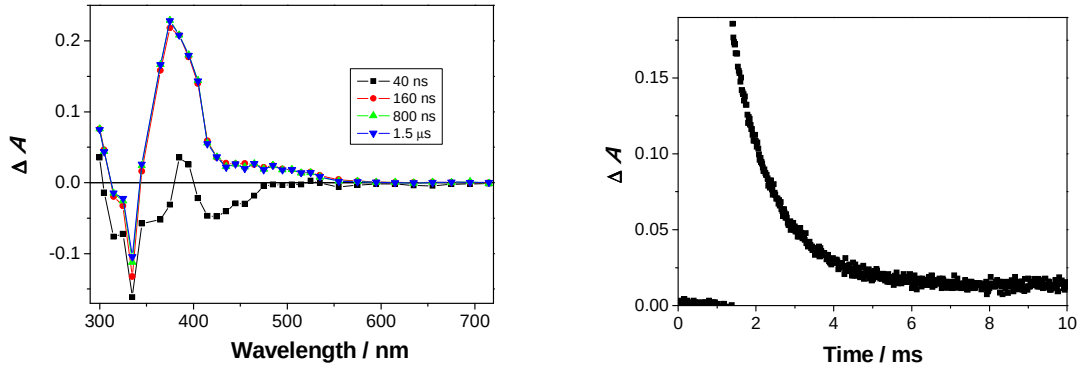


Figure S31. Transient absorption spectra of **2** (c = 2.84 × 10^{-3} M) in N_2-purged benzene in the presence of pyridine (c = 6.21 × 10^{-2} M)(left) and decay at 400 nm (right).

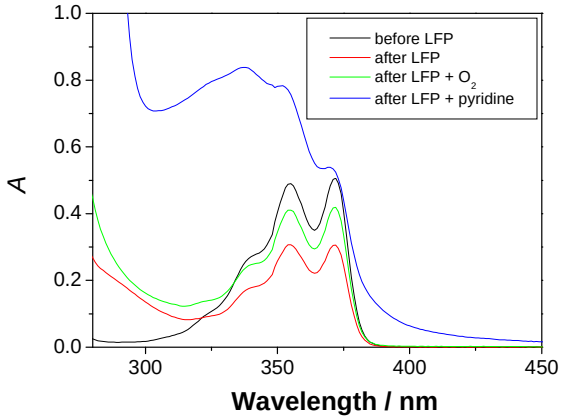


Figure S32. Absorption spectra of **1** in benzene, before and after LFP.

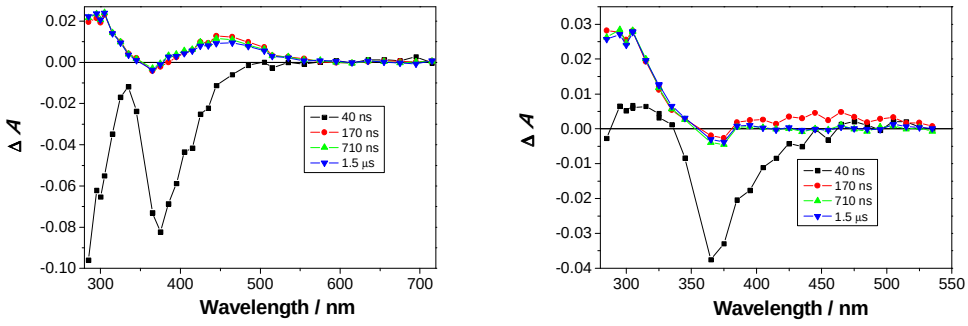


Figure S33. Transient absorption spectra of **1** in N_2 (left) and O_2 (right) purged benzene.

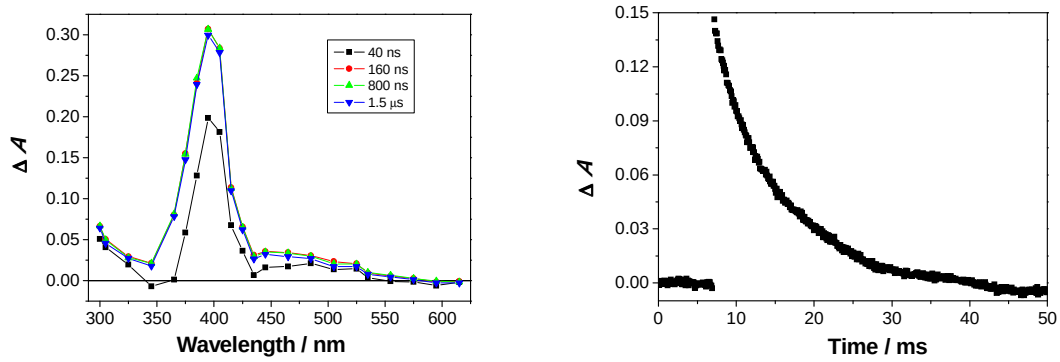


Figure S34. Transient absorption spectra of **1** (c = 2.56 × 10^{-3} M) in N_2-purged benzene in the presence of pyridine (c = 6.21 × 10^{-2} M)(left) and decay of transient absorbance at 410 nm (right).

Preparation of pentane solutions for the LFP measurements

The samples for the LFP measurements were prepared by dissolving 2.7 mg or 2.4 of compound in 5 mL of pentane. Prior to the measurements the solution was purged with N_2 for 30 min. The samples were excited at 355 nm with a Nd:YAG laser. The absorbances at the excitation wavelength were 0.24 and 0.39.

The spectra and decays are shown in the figs that follow:

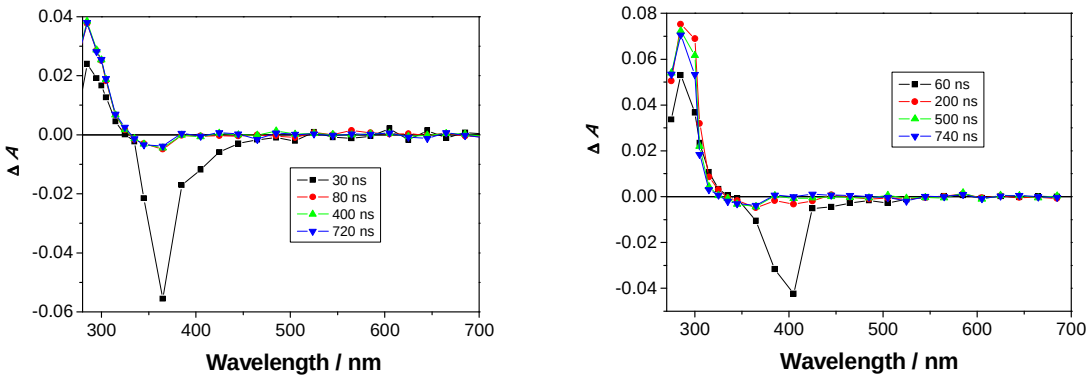


Figure S35. Transient absorption spectra of N_2-purged pentane solution of **2** at room temperature (left) and at ≈ -80 °C (right).

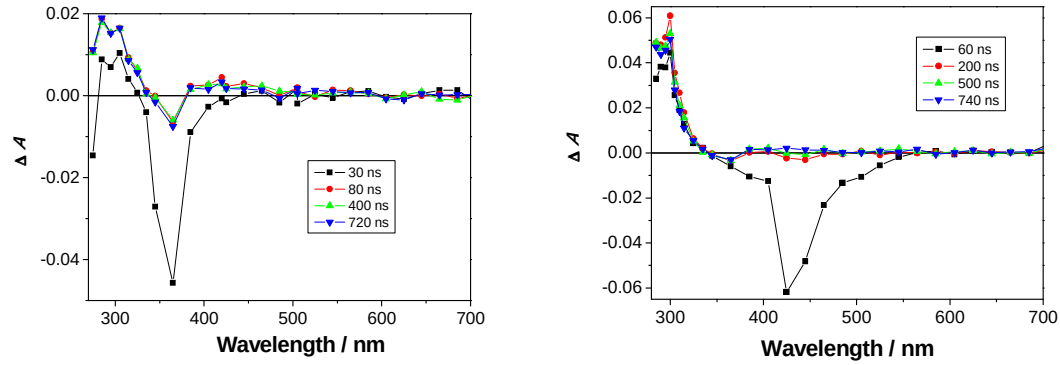


Figure S36. Transient absorption spectra of N_2-purged pentane solution of **1** at room temperature (left) and at ≈ -80 °C (right).

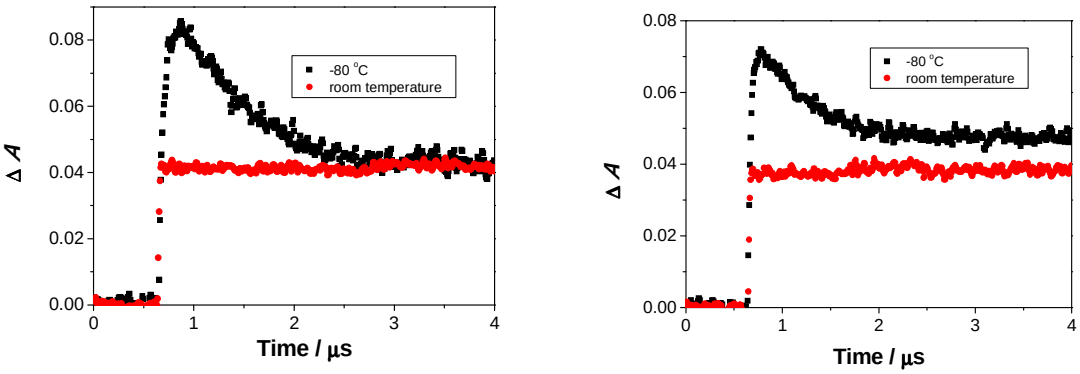


Figure S37. Decay of transient absorption at 300 nm for **2** (left) and **1** (right) in N_2-purged pentane solution at rt and at ≈ -90 °C.

The solution for LFP measurement was prepared by dissolving **1** (2.2 mg) in pentane (5mL). The concentrations were 2.56×10^{-3} M, corresponding to the absorbances at the excitation wavelength of $A_{355} = 0.37$. The samples were excited with a Nd:YAG at 355 nm. The results are shown in the following figures.

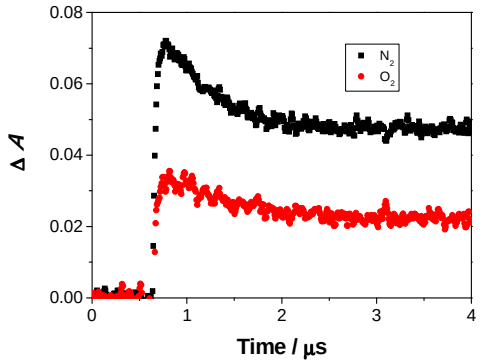


Figure S38. Decay of transient absorbance at 300 nm for the N_2-and O_2-purged solution of **1** in pentane at - 90 °C. The solutions were not optically matched A_{N2} = 0.56 and A_{O2} = 0.35. The measured lifetime in N_2-purged solution was 480 ns, and in O_2-purged it was 560 ns.

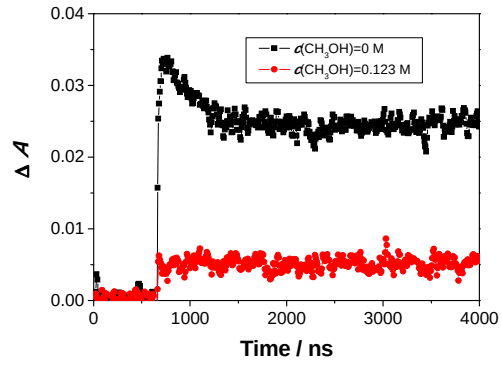


Figure S39. Decay of transient absorption at 300 nm for not purged pentane solution of **1** at -90 °C without and in the presence of CH_3OH.

In the quenching experiment, compound **1** (3.2 mg) was dissolved in benzene (10 mL). The absorbance at 355 nm was 0.25. The solution was purged with N_2 30 min prior to measurement. Pyridine was added by a Hamilton syringe (additions of 1 μL) to the solution (2 mL) and the decays were detected at 420 and 450 nm.

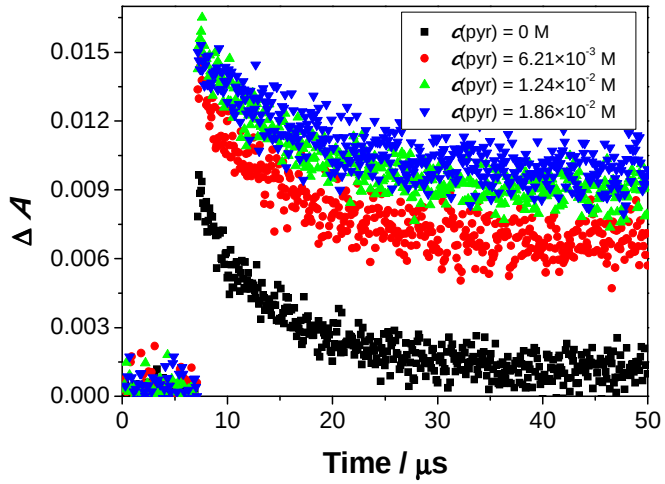


Figure S40. Decay of transient absorption at 450 nm for N_2-purged benzene solution of **1** (c = 1.86×10^{-3} M) in the presence of pyridine at different concentrations.

Quenching experiment with CH_3OH was also performed for the transient observed by LFP at 400-600 nm for benzene solution of **1** at rt. The decays were collected at 420 and 450 nm in the presence of different CH_3OH concentration.

The slope of the k_{obs} *vs.* CH_3OH concentration gave the k_q of $9 \pm 1 \times 10^6$ $M^{-1}s^{-1}$, which is close to the reported values for triplet carbenes reacting with CH_3OH.

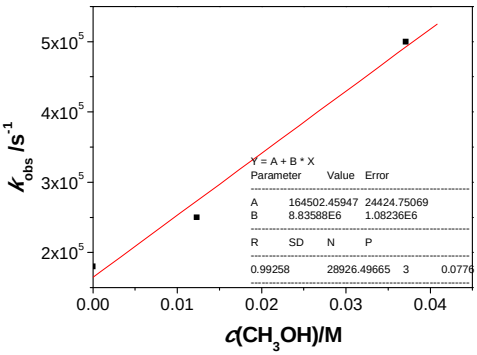


Figure S41. Quenching plot for the transient absorbing at 400-600 nm in N_2-purged benzene solution of **1**.

LFP experiment with **2** in the presence of β-CD and CB[7]

Stock solution of **2** in DMSO was prepared by dissolving 9.3 mg of compound in 5 mL of solvent (c = 1.15 × 10^{-2} M).

Stock solution of CB[7] was prepared by dissolving 281.7 mg of compound, and 146 mg NaCl in 25 mL of deionized water (c(CB[7]) = 9.70 × 10^{-3} M, c (NaCl) = 0.100 M). To determine real concentration, titration was performed.[14]

Stock solution of β-cyclodextrin (β-CD) was prepared by dissolving 1.5000 g of β-CD in 100 mL deionized water (c(β-CD) = 1.321 × 10^{-2} M).

The **2**@CB[7] solution for LFP measurement was prepared by taking 1 mL of DMSO stock, which was diluted to 10 mL with the stock of CB[7]. Since the sample was not dissolved, it was further diluted to 25 mL with DMSO-H_2O (1:9). The final concentrations were c (**2**) = 4.60 × 10^{-4} M (A_{355} = 0.113), c(CB[7]) = 3.88 × 10^{-4} M and c(NaCl) = 0.04 M. The spectra obtained by exciting sample with a Nd:YAG laser at 355 nm are shown below:

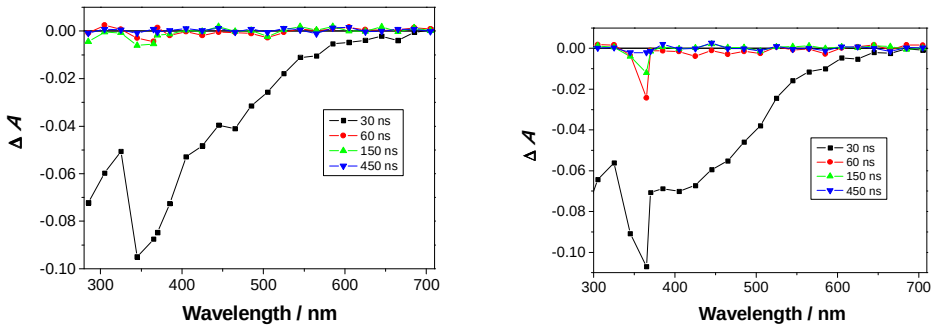


Figure S42. Transient absorption spectra of **2** (c = 4.60 × 10^{-4} M, A_{355} = 0.113) in DMSO-H_2O (1:9) in the presence of CB[7] (c = 3.88 × 10^{-4} M, not corrected after titration) and NaCl (c = 0.04 M), left: N_2-purged solution, right: O_2-purged solution.

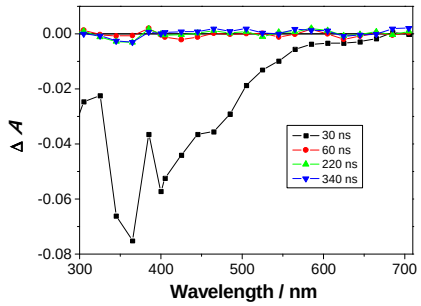


Figure S43. Transient absorption spectra of **2** (c = 4.60 × 10^{-4} M, A_{355} = 0.113) in N_2-purged DMSO-H_2O (1:9) solution in the presence of CB[7] (c = 3.88 × 10^{-4} M, not corrected after titration), NaCl (c = 0.04 M), and pyridine (c = 6.21 ×10^{-2} M).

The **2**@βCD solution for LFP measurement was prepared by taking 1 mL of DMSO stock, which was diluted to 10 mL with the stock of βCD. The resulting concentrations were c(**2**) = 1.15 × 10^{-3} M (A_{355} = 0.14), c(βCD) = 1.19 × 10^{-2} M. The spectra are shown below:

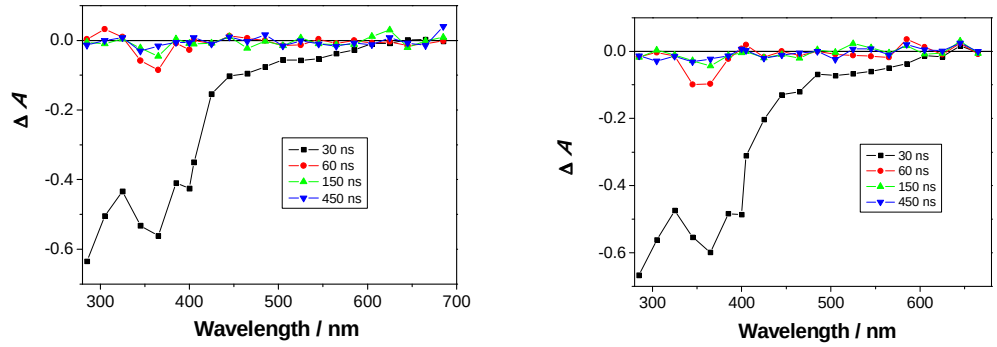


Figure S44. Transient absorption spectra of **2** (c = 1.15 × 10^{-3} M, A_{355} = 0.14) in DMSO-H_2O (1:9) in the presence of βCD (c = 1.19 × 10^{-2} M), left: N_2-purged solution, right: O_2-purged solution.

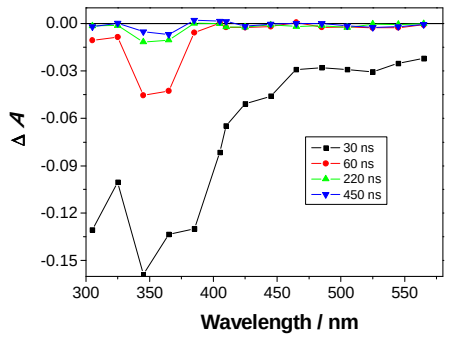


Figure S45. Transient absorption spectra of **2** (c = 1.15 × 10^{-3} M, A_{355} = 0.14) in N_2-purged solution in DMSO-H_2O (1:9) in the presence of βCD (c = 1.19 × 10^{-2} M), and pyridine (c = 6.21 × 10^{-2} M).

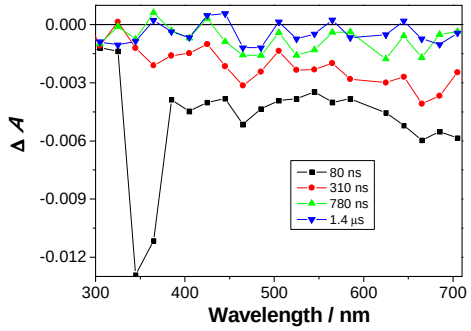
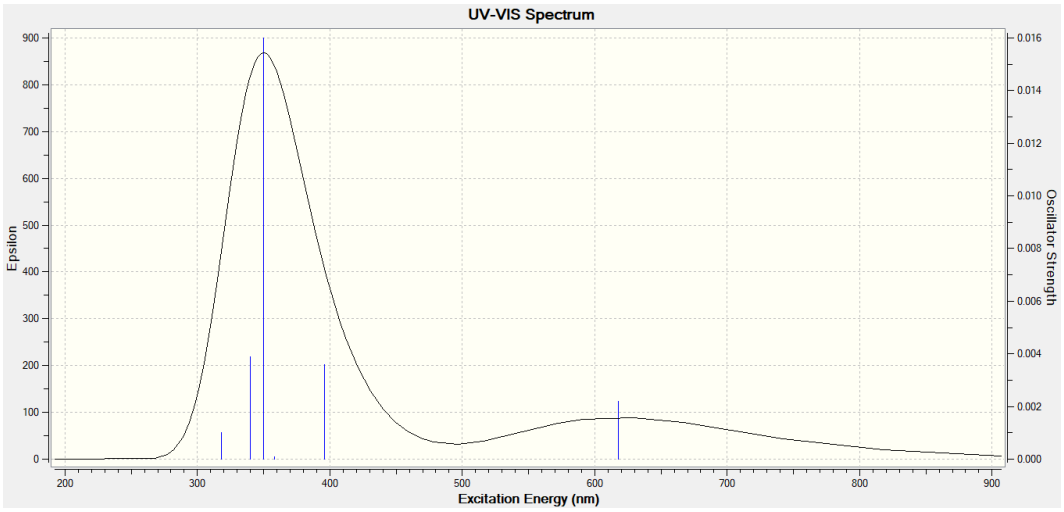
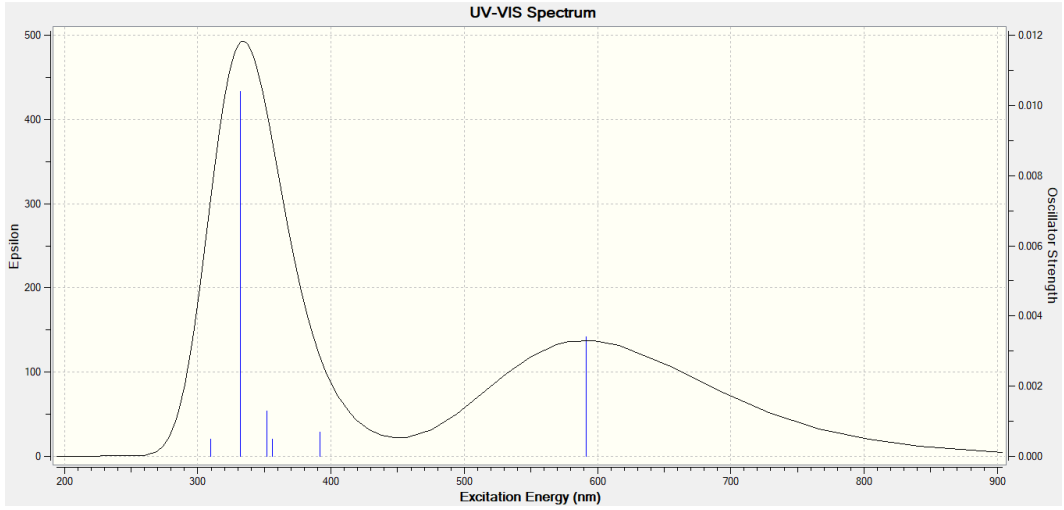


Figure S46. Transient absorption spectra of **2** (c = 1.15 × 10^{-3} M, A_{355} = 0.113) in N_2-purged DMSO-H_2O (1:9) solution in the presence of pyridine (c = 6.21 × 10^{-2} M).

8. Computations



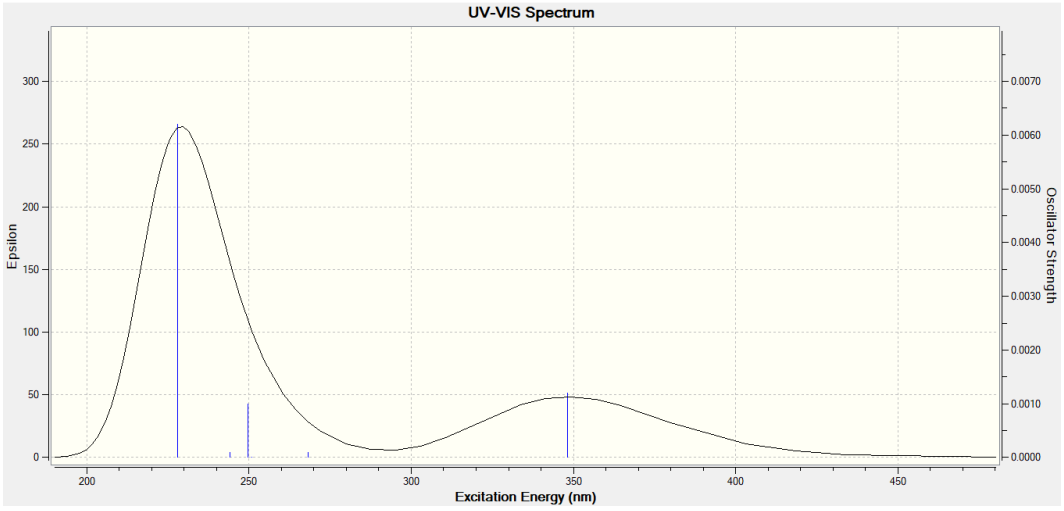
a)



b)

Figure S47. Simulated spectra of **8** (a) and **15** (b) computed at the CPCM(pentane)/TD-MN12-SX/6-311+G(d) level of theory.

a)



b)

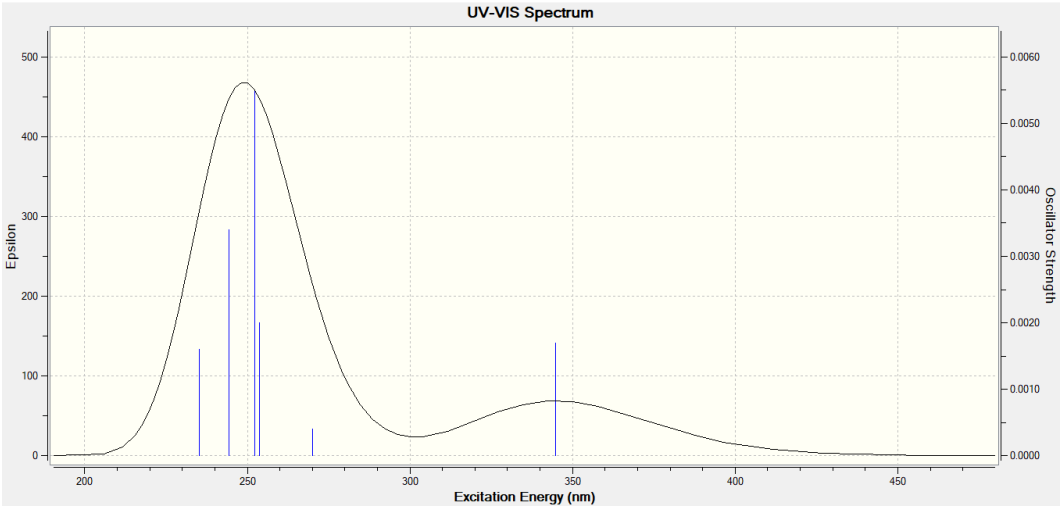
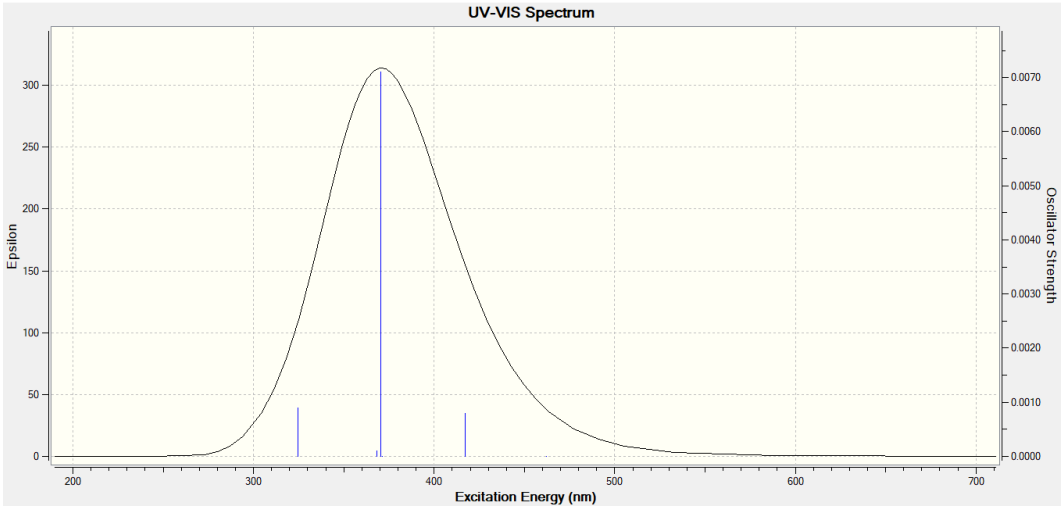


Figure S48. Simulated spectra of diazirine **2** (a) and diazirine **1** (b) computed at the CPCM(pentane)/TD-MN12-SX/6-311+G(d) level of theory.

a)



b)

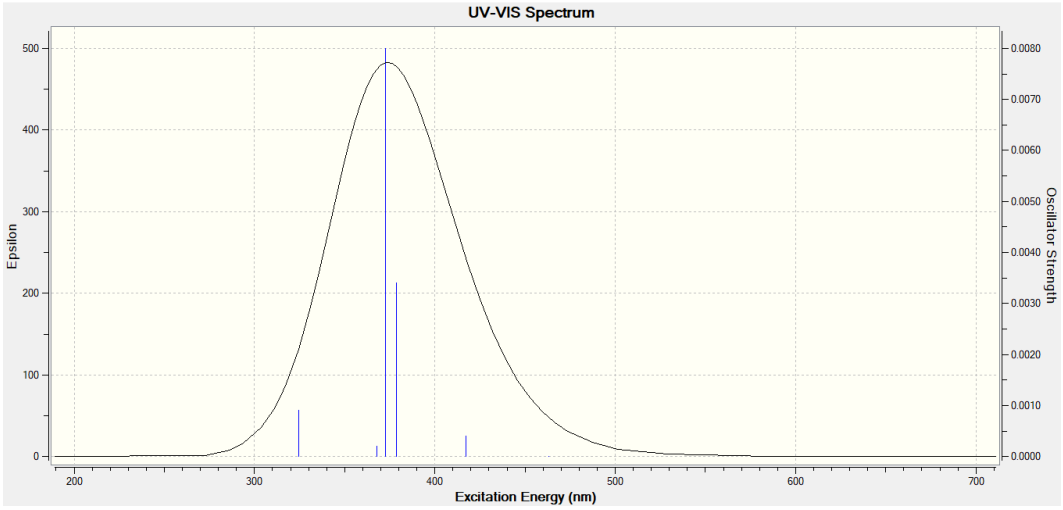


Figure S49. Simulated spectra of diazo **7** (a) and diazo **14** (b) computed at the CPCM(pentane)/TD-MN12-SX/6-311+G(d) level of theory.

Table S7. Vertical excitation of singlet **8**, **15**, **2**, **1**, **7**, and **14** computed at the CPCM(pentane)/TD-MN12-SX/6-311+G(d) level of theory.

8				
Excited State 1:	Singlet-A'	2.0061 eV	618.03 nm	f=0.0022 <S**2>=0.000
37 -> 38	0.60781			
37 -> 39	0.24558			
37 -> 41	0.22244			
37 -> 46	-0.10063			

Excited State	2:	Singlet-A'	3.1294 eV	396.19 nm	f=0.0036 <S**2>=0.000
37 -> 38	-0.27958				
37 -> 39	0.64652				
Excited State	3:	Singlet-A'	3.4619 eV	358.14 nm	f=0.0001 <S**2>=0.000
37 -> 38	-0.20417				
37 -> 39	-0.13783				
37 -> 41	0.65390				
Excited State	4:	Singlet-A"	3.5412 eV	350.12 nm	f=0.0160 <S**2>=0.000
37 -> 40	0.70498				
Excited State	5:	Singlet-A'	3.6459 eV	340.07 nm	f=0.0039 <S**2>=0.000
37 -> 42	0.69575				
Excited State	6:	Singlet-A"	3.8981 eV	318.07 nm	f=0.0010 <S**2>=0.000
37 -> 43	0.70271				

15

Excited State	1:	Singlet-A	2.0971 eV	591.21 nm	f=0.0034 <S**2>=0.000
39 -> 40	0.57360				
39 -> 41	0.30916				
39 -> 43	0.22977				
39 -> 48	0.10536				
Excited State	2:	Singlet-A	3.1669 eV	391.50 nm	f=0.0007 <S**2>=0.000
39 -> 40	-0.34245				
39 -> 41	0.61463				
Excited State	3:	Singlet-A	3.4801 eV	356.26 nm	f=0.0005 <S**2>=0.000
39 -> 42	0.70042				
Excited State	4:	Singlet-A	3.5258 eV	351.65 nm	f=0.0013 <S**2>=0.000
39 -> 40	-0.21379				
39 -> 41	-0.12613				
39 -> 43	0.64564				
Excited State	5:	Singlet-A	3.7352 eV	331.93 nm	f=0.0104 <S**2>=0.000
39 -> 43	0.10977				
39 -> 44	0.69241				
Excited State	6:	Singlet-A	4.0041 eV	309.65 nm	f=0.0005 <S**2>=0.000
39 -> 45	0.70268				

2

Excited State	1:	Singlet-A"	3.5608 eV	348.19 nm	f=0.0012 <S**2>=0.000
41 -> 46	0.12888				
44 -> 46	0.67105				
44 -> 52	-0.15196				
Excited State	2:	Singlet-A'	4.6225 eV	268.22 nm	f=0.0001 <S**2>=0.000
44 -> 45	0.70320				
Excited State	3:	Singlet-A"	4.9405 eV	250.95 nm	f=0.0000 <S**2>=0.000
44 -> 48	0.70442				
Excited State	4:	Singlet-A'	4.9677 eV	249.58 nm	f=0.0010 <S**2>=0.000

44 -> 47	0.70457				
Excited State	5: Singlet-A'	5.0777 eV	244.18 nm	f=0.0001	<S**2>=0.000
44 -> 49	0.70253				
Excited State	6: Singlet-A'	5.4359 eV	228.08 nm	f=0.0062	<S**2>=0.000
43 -> 46	0.68842				

1

Excited State	1: Singlet-A	3.5971 eV	344.68 nm	f=0.0017	<S**2>=0.000
46 -> 48	0.57584				
46 -> 49	0.16610				
46 -> 50	0.29227				
46 -> 54	-0.14802				
Excited State	2: Singlet-A	4.5898 eV	270.13 nm	f=0.0004	<S**2>=0.000
46 -> 47	0.70194				
Excited State	3: Singlet-A	4.8885 eV	253.63 nm	f=0.0020	<S**2>=0.000
46 -> 48	-0.32970				
46 -> 50	0.62076				
Excited State	4: Singlet-A	4.9133 eV	252.34 nm	f=0.0055	<S**2>=0.000
46 -> 48	-0.15011				
46 -> 49	0.68112				
46 -> 50	-0.10082				
Excited State	5: Singlet-A	5.0759 eV	244.26 nm	f=0.0034	<S**2>=0.000
46 -> 51	0.69916				
Excited State	6: Singlet-A	5.2684 eV	235.34 nm	f=0.0016	<S**2>=0.000
45 -> 47	0.51948				
45 -> 48	-0.40810				
45 -> 50	-0.21762				

7

Excited State	1: Singlet-A	2.6826 eV	462.18 nm	f=0.0000	<S**2>=0.000
44 -> 46	-0.28849				
44 -> 53	0.18935				
44 -> 54	0.59701				
44 -> 60	0.10096				
Excited State	2: Singlet-A	2.9705 eV	417.38 nm	f=0.0008	<S**2>=0.000
44 -> 45	0.69943				
Excited State	3: Singlet-A	3.3380 eV	371.43 nm	f=0.0000	<S**2>=0.000
44 -> 46	0.64159				
44 -> 54	0.29178				
Excited State	4: Singlet-A	3.3459 eV	370.56 nm	f=0.0071	<S**2>=0.000
44 -> 47	0.70585				
Excited State	5: Singlet-A	3.3663 eV	368.31 nm	f=0.0001	<S**2>=0.000
44 -> 48	0.69825				
Excited State	6: Singlet-A	3.8214 eV	324.45 nm	f=0.0009	<S**2>=0.000
44 -> 49	0.70563				

14					
Excited State	1: Singlet-A	2.6770 eV	463.15 nm	f=0.0000	<S**2>=0.000
46 -> 51	0.43497				
46 -> 55	0.50036				
Excited State	2: Singlet-A	2.9724 eV	417.12 nm	f=0.0004	<S**2>=0.000
46 -> 47	0.69597				
Excited State	3: Singlet-A	3.2750 eV	378.58 nm	f=0.0034	<S**2>=0.000
46 -> 48	0.57852				
46 -> 49	-0.39784				
Excited State	4: Singlet-A	3.3286 eV	372.48 nm	f=0.0080	<S**2>=0.000
46 -> 48	0.38774				
46 -> 49	0.56752				
46 -> 50	-0.14654				
Excited State	5: Singlet-A	3.3700 eV	367.90 nm	f=0.0002	<S**2>=0.000
46 -> 48	0.10579				
46 -> 49	0.11150				
46 -> 50	0.68030				
Excited State	6: Singlet-A	3.8216 eV	324.43 nm	f=0.0009	<S**2>=0.000
46 -> 51	-0.24029				
46 -> 52	0.64213				
46 -> 55	0.15567				

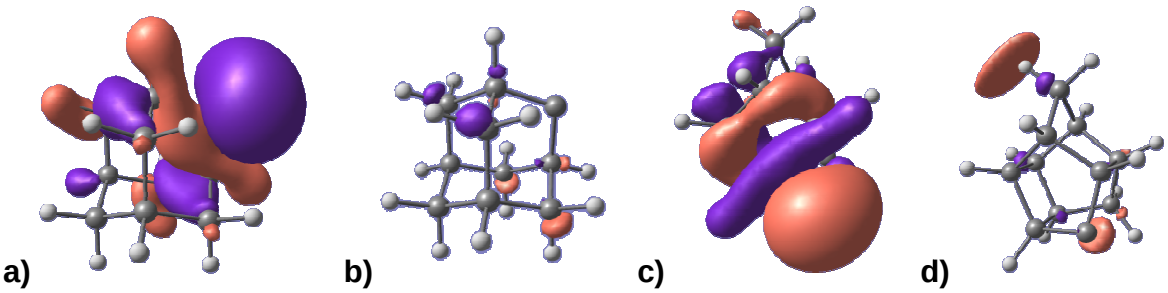


Figure S50. Molecular orbitals of **8** (a and b) and **15** (c and d) involved in the excitation to S_4 and S_5, respectively. a) MO37 (HOMO). b) MO40 (LUMO+2). c) MO39 (HOMO). d) MO44 (LUMO+4). Computations done at the CPCM(pentane)/TD-MN12-SX/6-311+G(d) level of theory.

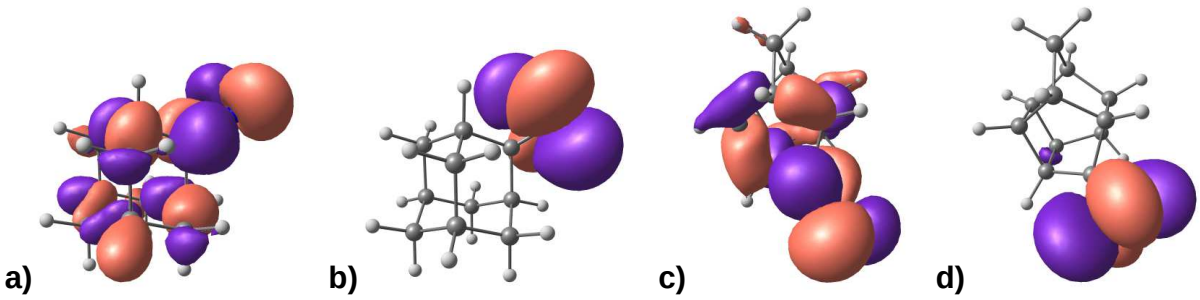


Figure S51. Molecular orbitals of **2** (a and b) and **1** (c and d) involved in the excitation to S_1. a) MO44 (HOMO). b) MO46 (LUMO+1). c) MO46 (HOMO). d) MO48 (LUMO+1). Computations done at the CPCM(pentane)/TD-MN12-SX/6-311+G(d) level of theory.

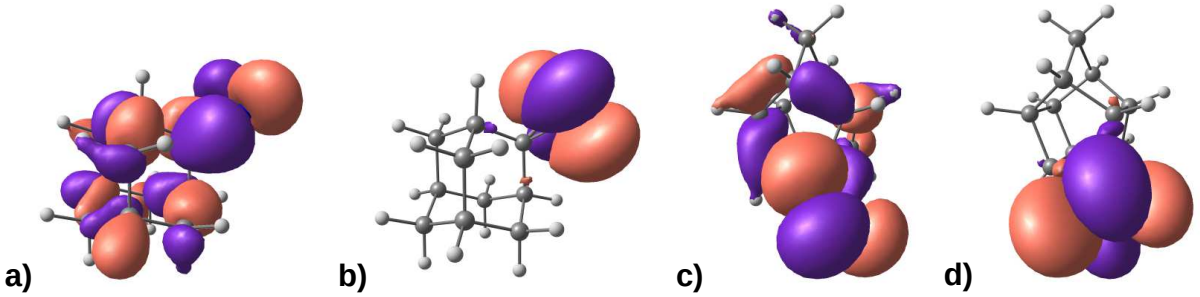


Figure S52. Molecular orbitals of **2** (a and b) and **1** (c and d) for the T_1 state. a) MO44A (SOMO1). b) MO45A (SOMO2). c) MO46A (SOMO1). d) MO47A (SOMO2). Computations done at the CPCM(pentane)/TD-MN12-SX/6-311+G(d) level of theory.

Table S8. Electronic energies, zero-point vibrational energies, enthalpies and Gibbs energies of singlet **8** in hartree computed at the CPCM(solvent)/MN12-SX/6-311+G(d) level of theory.

solvent	*E*	*ZPVE*	*H*	*G*
gas phase	-389.117151	0.217971	-388.890995	-388.930206
water	-389.124131	0.217790	-388.898158	-388.937359
DMSO	-389.124054	0.217792	-388.898080	-388.937281

benzene	-389.120718	0.217871	-388.894664	-388.933868
cyclohexane	-389.120325	0.217881	-388.894261	-388.933466
hexane	-389.120080	0.217888	-388.894008	-388.933214
pentane	-389.119991	0.217890	-388.893917	-388.933123

Table S9. Electronic energies, zero-point vibrational energies, enthalpies and Gibbs energies of triplet **8** in hartree computed at the CPCM(solvent)/MN12-SX/6-311+G(d) level of theory.

solvent	*E*	*ZPVE*	*H*	*G*
gas phase	-389.108805	0.218638	-388.882310	-388.921274
water	-389.110201	0.218198	-388.884130	-388.923117
DMSO	-389.110187	0.218202	-388.884111	-388.923097
benzene	-389.109528	0.218398	-388.883264	-388.922240
cyclohexane	-389.109450	0.218423	-388.883162	-388.922137
hexane	-389.109401	0.218439	-388.883097	-388.922072
pentane	-389.109383	0.218445	-388.883074	-388.922048

Table S10. Electronic energies, zero-point vibrational energies, enthalpies and Gibbs energies of singlet **15** in hartree computed at the CPCM(solvent)/MN12-SX/6-311+G(d) level of theory.

solvent	*E*	*ZPVE*	*H*	*G*
gas phase	-425.969791	0.200858	-425.761522	-425.799538
water	-425.976795	0.200604	-425.768749	-425.806816
DMSO	-425.976717	0.200607	-425.768669	-425.806735
benzene	-425.973349	0.200723	-425.765201	-425.803240
cyclohexane	-425.972955	0.200737	-425.764795	-425.802831
hexane	-425.972709	0.200746	-425.764541	-425.802575

pentane	-425.972620	0.200749	-425.764449	-425.802483

Table S11. Electronic energies, zero-point vibrational energies, enthalpies and Gibbs energies of triplet **15** in hartree computed at the CPCM(solvent)/MN12-SX/6-311+G(d) level of theory.

solvent	*E*	*ZPVE*	*H*	*G*
gas phase	-425.957126	0.201410	-425.748641	-425.787065
water	-425.958691	0.200980	-425.750610	-425.789071
DMSO	-425.958674	0.200984	-425.750589	-425.789050
benzene	-425.957929	0.201178	-425.749662	-425.788106
cyclohexane	-425.957841	0.201203	-425.749551	-425.787993
hexane	-425.957786	0.201218	-425.749482	-425.787922
pentane	-425.957766	0.201223	-425.749457	-425.787896

Table S12. Electronic energies, zero-point vibrational energies, enthalpies and Gibbs energies of singlet **2** in hartree computed at the CPCM(solvent)/MN12-SX/6-311+G(d) level of theory.

solvent	*E*	*ZPVE*	*H*	*G*
gas phase	-498.622238	0.230377	-498.382438	-498.424848
water	-498.625712	0.230035	-498.386244	-498.428653
DMSO	-498.625676	0.230038	-498.386205	-498.428614
benzene	-498.624070	0.230192	-498.384449	-498.426858
cyclohexane	-498.623874	0.230211	-498.384235	-498.426643
hexane	-498.623741	0.230302	-498.384017	-498.426424
pentane	-498.623706	0.230228	-498.384051	-498.426459

Table S13. Electronic energies, zero-point vibrational energies, enthalpies and Gibbs energies of singlet **1** in hartree computed at the CPCM(solvent)/MN12-SX/6-311+G(d) level of theory.

solvent	*E*	*ZPVE*	*H*	*G*
gas phase	-535.470891	0.213120	-535.249137	-535.290188
water	-535.474284	0.212770	-535.252862	-535.293932
DMSO	-535.474250	0.212774	-535.252824	-535.293894
benzene	-535.472680	0.212931	-535.251105	-535.292166
cyclohexane	-535.472489	0.212951	-535.250895	-535.291955
hexane	-535.472368	0.212964	-535.250763	-535.291822
pentane	-535.472324	0.212968	-535.250715	-535.291774

Table S14. Electronic energies, zero-point vibrational energies, enthalpies and Gibbs energies of singlet **7** in hartree computed at the CPCM(solvent)/MN12-SX/6-311+G(d) level of theory.

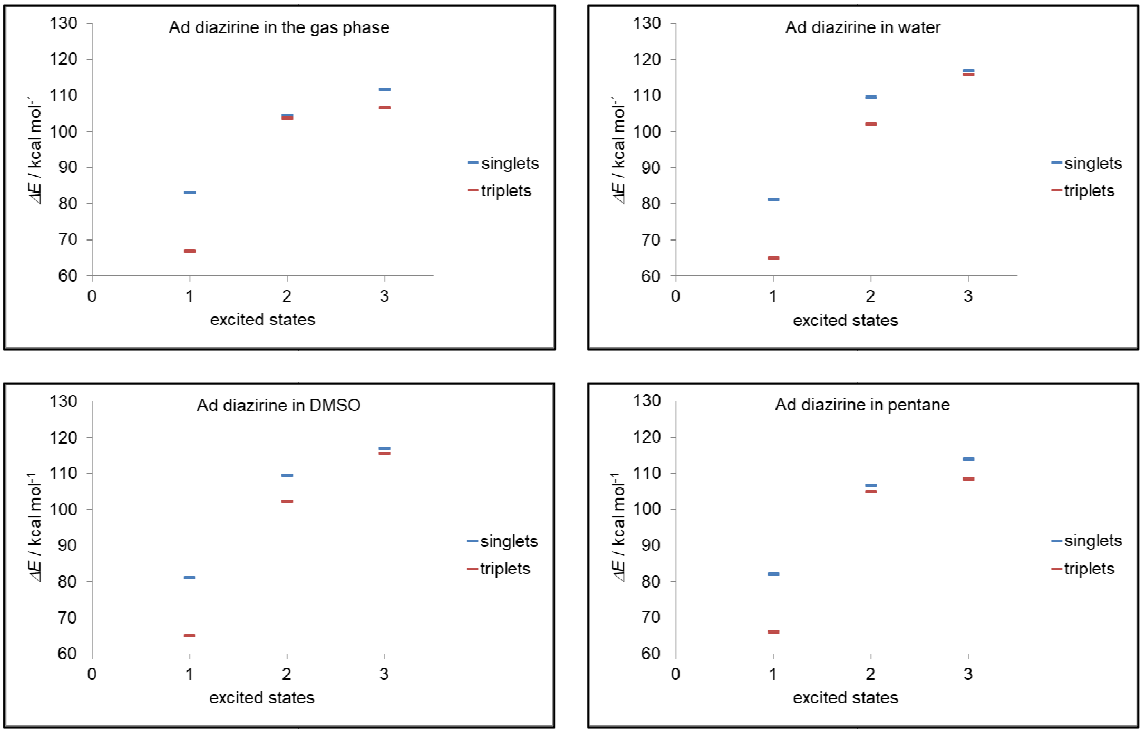
solvent	*E*	*ZPVE*	*H*	*G*
gas phase	-498.631173	0.230422	-498.390968	-498.434853
water	-498.635287	0.230085	-498.395425	-498.439155
DMSO	-498.635241	0.230088	-498.395375	-498.439108
benzene	-498.633251	0.230234	-498.393236	-498.437047
cyclohexane	-498.633020	0.230253	-498.392986	-498.436806
hexane	-498.632876	0.230265	-498.392829	-498.436654
pentane	-498.632824	0.230269	-498.392772	-498.436600

Table S15. Electronic energies, zero-point vibrational energies, enthalpies and Gibbs energies of singlet **14** in hartree computed at the CPCM(solvent)/MN12-SX/6-311+G(d) level of theory.

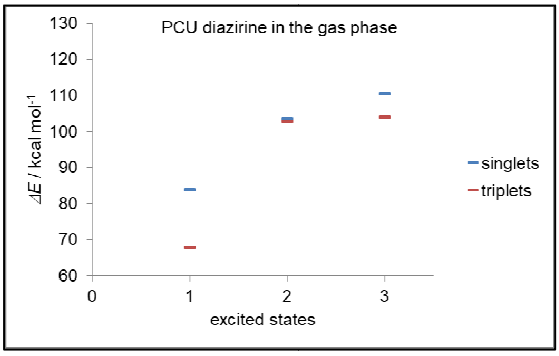
solvent	*E*	*ZPVE*	*H*	*G*

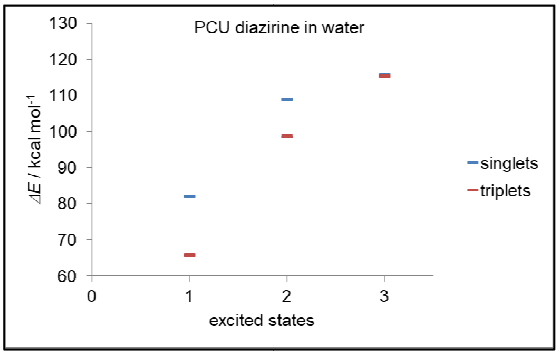
gas phase	-535.481934	0.212904	-535.260010	-535.302475
water	-535.485879	0.212537	-535.264302	-535.306793
DMSO	-535.485835	0.212540	-535.264254	-535.306746
benzene	-535.483930	0.212699	-535.262198	-535.304687
cyclohexane	-535.483709	0.212720	-535.261957	-535.304444
hexane	-535.483570	0.212733	-535.261806	-535.304291
pentane	-535.483520	0.212738	-535.261752	-535.304236

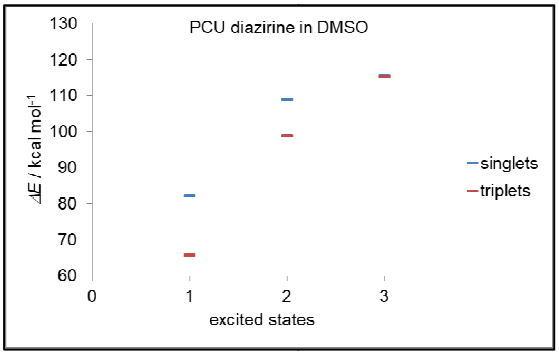
a)

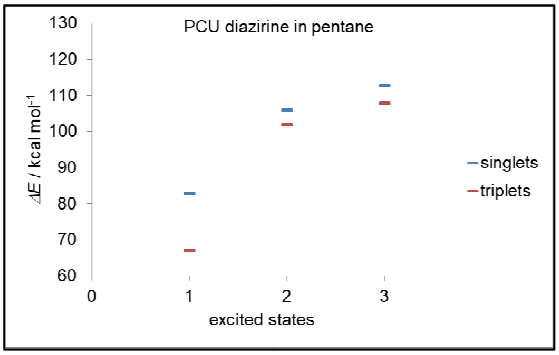


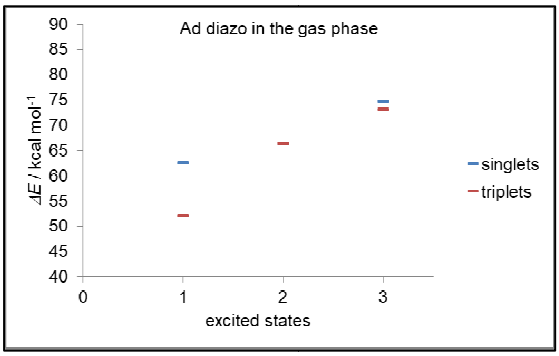
b)

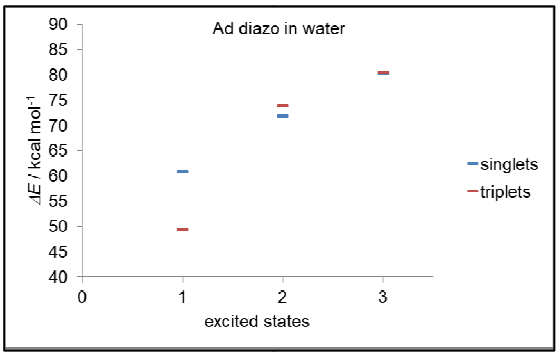

PCU diazirine in the gas phase
ΔE / kcal mol-1
excited states
singlets
triplets


PCU diazirine in water
ΔE / kcal mol-1
excited states
singlets
triplets

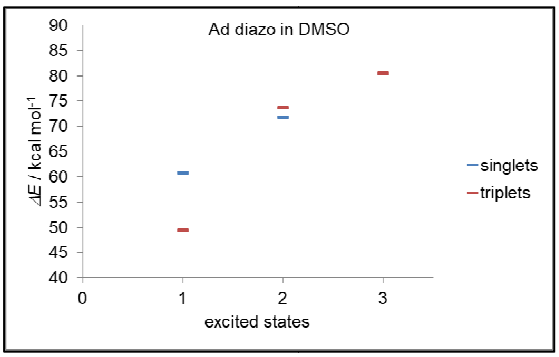

PCU diazirine in DMSO
ΔE / kcal mol-1
excited states
singlets
triplets

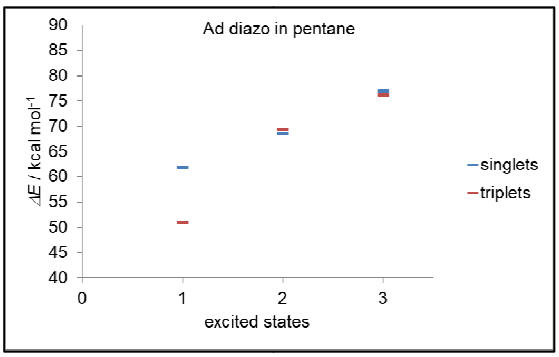

PCU diazirine in pentane
ΔE / kcal mol-1
excited states
singlets
triplets

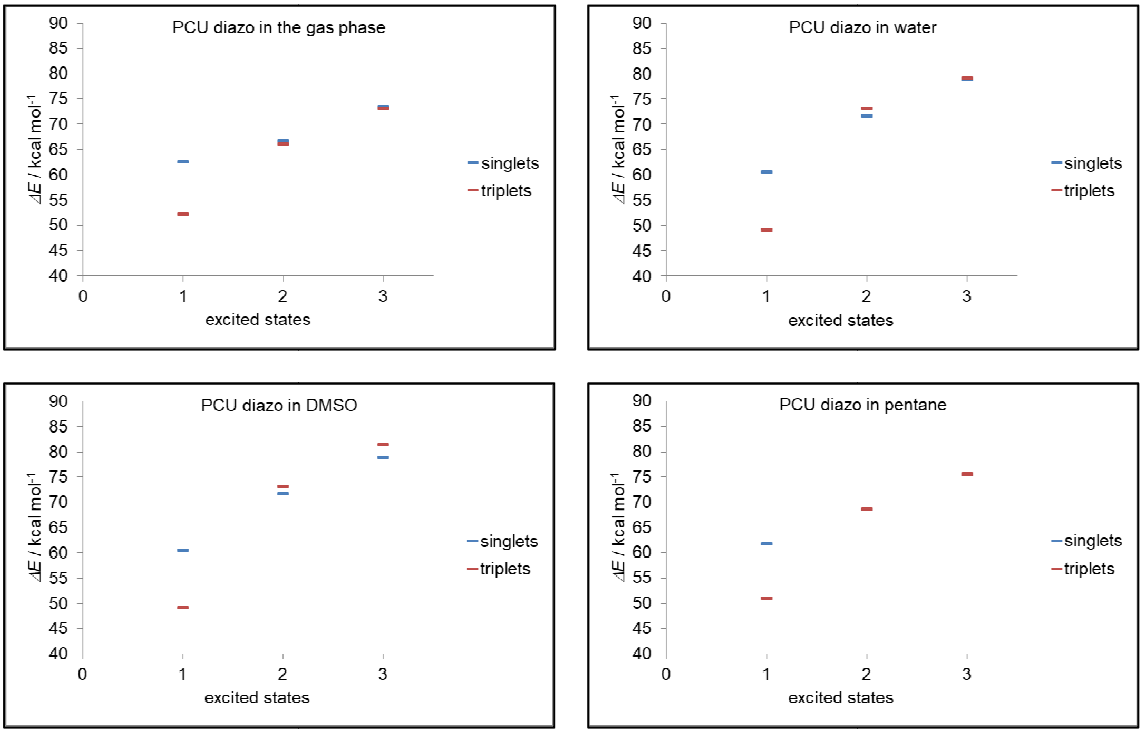

Ad diazo in the gas phase
ΔE / kcal mol-1
excited states
singlets
triplets


Ad diazo in water
ΔE / kcal mol-1
excited states
singlets
triplets

c)


Ad diazo in DMSO
ΔE / kcal mol-1
excited states
singlets
triplets


Ad diazo in pentane
ΔE / kcal mol-1
excited states
singlets
triplets



d)

Figure S53. Energy levels for the first three singlet and triplet excited states of diazirines **2** (a) and **1** (b) and diazo compounds **7** (c) and **14** (d) computed at the TD-MN12-SX/6-311+G(d) level of theory with a CPCM solvation model used. Ground state S_0 taken as a reference point.

Table S16. Energy difference between singlet S_1 state and triplet states (T_1-T_3) for diazirines **2** and **1** and diazo compounds **7** and **14** computed at the TD-MN12-SX/6-311+G(d) level of theory with a CPCM solvation model used.

difference of states	$\Delta E(S_1\text{-}T_n)$ / kcal mol^{-1}			
	gas phase	water	DMSO	pentane
2 (S_1-T_1)	16.0	16.3	16.2	15.9
2 (S_1-T_2)	-20.8	-20.9	-21.0	-22.7
2 (S_1-T_3)	-23.7	-34.5	-34.4	-26.4
1 (S_1-T_1)	15.9	16.4	16.3	15.9
1 (S_1-T_2)	-19.0	-16.6	-16.7	-18.9
1 (S_1-T_3)	-20.1	-33.3	-33.2	-24.8
7 (S_1-T_1)	10.4	11.5	11.5	10.8
7 (S_1-T_2)	-3.8	-13.0	-12.9	-7.5

7 (S_1-T_3)	-10.6	-19.7	-19.6	-14.2
14 (S_1-T_1)	10.3	11.4	11.4	10.7
14 (S_1-T_2)	-3.6	-12.6	-12.5	-7.0
14 (S_1-T_3)	-10.6	-18.5	-20.9	-13.8

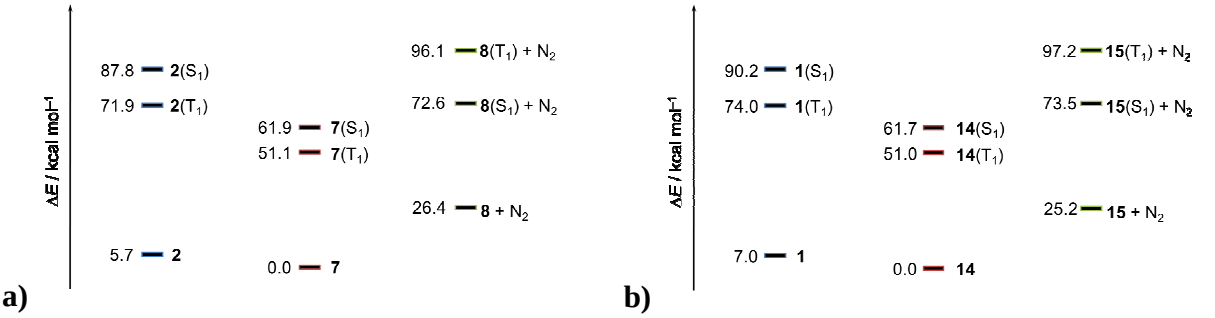


Figure S54. Energy levels for adamantane (a) and PCU (b) derivatives computed at the CPCM(pentane)/(TD-)MN12-SX/6-311+G(d) level of theory.

Table S17. Vertical excitation energies of **2** in hartree computed at the CPCM(solvent)/TD-MN12-SX/6-311+G(d) level of theory.

singlet **2** in the gas phase		triplet **2** in the gas phase	
S1	-498.490046	T1	-498.456908
S2	-498.455863	T2	-498.452353
S3	-498.444122	T3	-498.443033
S4	-498.442755	T4	-498.443033
S5	-498.438591	T5	-498.442177
S6	-498.425280	T6	-498.435180

singlet **2** in water		triplet **2** in water	
S1	-498.496274	T1	-498.522237
S2	-498.451163	T2	-498.462972
S3	-498.439495	T3	-498.441359
S4	-498.439018	T4	-498.428688
S5	-498.435244	T5	-498.427185
S6	-498.431796	T6	-498.423866

singlet **2** in DMSO		triplet **2** in DMSO	
S1	-498.496281	T1	-498.522164
S2	-498.451216	T2	-498.462878
S3	-498.439541	T3	-498.441532

S4	-498.439063	T4	-498.428853
S5	-498.435285	T5	-498.427354
S6	-498.431706	T6	-498.423969

singlet **2** in pentane		triplet **2** in pentane	
S1	-498.492848	T1	-498.518243
S2	-498.453832	T2	-498.456666
S3	-498.442146	T3	-498.450716
S4	-498.441146	T4	-498.437358
S5	-498.437104	T5	-498.436226
S6	-498.423940	T6	-498.430251

Table S18. Vertical excitation energies of **1** in hartree computed at the CPCM(solvent)/TD-MN12-SX/6-311+G(d) level of theory.

singlet **1** in the gas phase		triplet **1** in the gas phase	
S1	-535.382293	T1	-535.398713
S2	-535.375795	T2	-535.376627
S3	-535.364910	T3	-535.365392
S4	-535.362503	T4	-535.362647
S5	-535.360514	T5	-535.356653
S6	-535.344675	T6	-535.344849

singlet **1** in water		triplet **1** in water	
S1	-535.389327	T1	-535.407559
S2	-535.371666	T2	-535.369211
S3	-535.360167	T3	-535.359800
S4	-535.358830	T4	-535.355945
S5	-535.357771	T5	-535.352028
S6	-535.340099	T6	-535.341253

singlet **1** in DMSO		triplet **1** in DMSO	
S1	-535.389294	T1	-535.407459
S2	-535.371728	T2	-535.369310
S3	-535.360237	T3	-535.356061
S4	-535.358899	T4	-535.352118
S5	-535.357830	T5	-535.341321
S6	-535.340164	T6	-535.336558

singlet **1** in pentane		triplet **1** in pentane	
S1	-535.385142	T1	-535.402205
S2	-535.374287	T2	-535.373998
S3	-535.363166	T3	-535.363074
S4	-535.361196	T4	-535.361002

S5	-535.359675	T5	-535.355408
S6	-535.343079	T6	-535.343847

Table S19. Vertical excitation energies of **7** in hartree computed at the CPCM(solvent)/TD-MN12-SX/6-311+G(d) level of theory.

singlet **7** in the gas phase		triplet **7** in the gas phase	
S1	-498.531414	T1	-498.548008
S2	-498.525335	T2	-498.525334
S3	-498.511914	T3	-498.514485
S4	-498.511219	T4	-498.507727
S5	-498.510462	T5	-498.505823
S6	-498.494193	T6	-498.493894

singlet **7** in water		triplet **7** in water	
S1	-498.538301	T1	-498.556646
S2	-498.520762	T2	-498.517655
S3	-498.507139	T3	-498.506924
S4	-498.506970	T4	-498.500342
S5	-498.506463	T5	-498.498008
S6	-498.489036	T6	-498.485620

singlet **7** in DMSO		triplet **7** in DMSO	
S1	-498.538272	T1	-498.556548
S2	-498.520833	T2	-498.517750
S3	-498.507221	T3	-498.507013
S4	-498.507038	T4	-498.500439
S5	-498.506534	T5	-498.498124
S6	-498.489104	T6	-498.485721

singlet **7** in pentane		triplet **7** in pentane	
S1	-498.534240	T1	-498.551448
S2	-498.523660	T2	-498.522337
S3	-498.510154	T3	-498.511571
S4	-498.509864	T4	-498.505011
S5	-498.509114	T5	-498.503148
S6	-498.492390	T6	-498.490815

Table S20. Vertical excitation energies of **14** in hartree computed at the CPCM(solvent)/TD-MN12-SX/6-311+G(d) level of theory.

singlet **14** in the gas phase		triplet **14** in the gas phase	
S1	-535.382293	T1	-535.398713
S2	-535.375795	T2	-535.376627

S3	-535.364910	T3	-535.365392
S4	-535.362503	T4	-535.362647
S5	-535.360514	T5	-535.356653
S6	-535.344675	T6	-535.344849

singlet **14** in water		triplet **14** in water	
S1	-535.389327	T1	-535.407559
S2	-535.371666	T2	-535.369211
S3	-535.360167	T3	-535.359800
S4	-535.358830	T4	-535.355945
S5	-535.357771	T5	-535.352028
S6	-535.340099	T6	-535.341253

singlet **14** in DMSO		triplet **14** in DMSO	
S1	-535.389294	T1	-535.407459
S2	-535.371728	T2	-535.369310
S3	-535.360237	T3	-535.356061
S4	-535.358899	T4	-535.352118
S5	-535.357830	T5	-535.341321
S6	-535.340164	T6	-535.336558

singlet **14** in pentane		triplet **14** in pentane	
S1	-535.385142	T1	-535.402205
S2	-535.374287	T2	-535.373998
S3	-535.363166	T3	-535.363074
S4	-535.361196	T4	-535.361002
S5	-535.359675	T5	-535.355408
S6	-535.343079	T6	-535.343847

Table S21. Geometries of **8** in Cartesian coordinates in Å optimized at the CPCM(solvent)/MN12-SX/6-311+G(d).

singlet **8** in the gas phase			
6	0.570225000	-0.000001000	-1.704641000
6	-1.232881000	1.234271000	-0.323516000
6	0.166382000	-1.222249000	-0.958673000
6	0.166384000	1.222249000	-0.958673000
6	-1.232883000	-1.234269000	-0.323516000
6	-1.413426000	0.000001000	0.555737000
1	0.321291000	-2.125871000	-1.568280000
1	-2.001241000	-1.257483000	-1.110630000
1	-1.360471000	-2.159614000	0.261384000
1	-2.421160000	0.000002000	0.998728000
1	-1.360467000	2.159616000	0.261384000
1	-2.001239000	1.257487000	-1.110630000

1	0.321295000	2.125871000	-1.568280000
6	1.233329000	-1.234302000	0.184490000
1	1.096195000	-2.167143000	0.752326000
1	2.248210000	-1.256993000	-0.236164000
6	1.233331000	1.234300000	0.184490000
6	-0.363578000	0.000000000	1.668767000
1	-0.494701000	0.883488000	2.312571000
1	-0.494702000	-0.883487000	2.312571000
6	1.041076000	-0.000001000	1.061350000
1	1.794821000	-0.000002000	1.863971000
1	2.248212000	1.256989000	-0.236164000
1	1.096198000	2.167141000	0.752326000

triplet **8** in the gas phase

6	0.000000000	0.000000000	1.725981000
6	1.259265000	1.260081000	0.068884000
6	0.000000000	-1.266450000	0.964721000
6	0.000000000	1.266450000	0.964721000
6	1.259265000	-1.260081000	0.068884000
6	1.253760000	0.000000000	-0.805616000
1	0.000000000	-2.148766000	1.622326000
1	2.161321000	-1.287489000	0.697234000
1	1.275050000	-2.161130000	-0.565730000
1	2.150953000	0.000000000	-1.443971000
1	1.275050000	2.161130000	-0.565730000
1	2.161321000	1.287489000	0.697234000
1	0.000000000	2.148766000	1.622326000
6	-1.259265000	-1.260081000	0.068884000
1	-1.275050000	-2.161130000	-0.565730000
1	-2.161321000	-1.287489000	0.697234000
6	-1.259265000	1.260081000	0.068884000
6	0.000000000	0.000000000	-1.685868000
1	0.000000000	0.883697000	-2.342937000
1	0.000000000	-0.883697000	-2.342937000
6	-1.253760000	0.000000000	-0.805616000
1	-2.150953000	0.000000000	-1.443971000
1	-2.161321000	1.287489000	0.697234000
1	-1.275050000	2.161130000	-0.565730000

singlet **8** in water

6	0.537706000	0.000000000	-1.710887000
6	-1.236685000	1.234230000	-0.307490000
6	0.153961000	-1.222952000	-0.962354000
6	0.153960000	1.222952000	-0.962354000
6	-1.236685000	-1.234230000	-0.307490000

6	-1.405010000	0.000000000	0.573399000
1	0.300710000	-2.128743000	-1.570352000
1	-2.014887000	-1.258554000	-1.084455000
1	-1.349960000	-2.159160000	0.279619000
1	-2.407440000	0.000000000	1.027397000
1	-1.349960000	2.159160000	0.279619000
1	-2.014887000	1.258554000	-1.084455000
1	0.300710000	2.128743000	-1.570352000
6	1.237966000	-1.233439000	0.169544000
1	1.103939000	-2.167789000	0.734525000
1	2.249642000	-1.256783000	-0.259129000
6	1.237966000	1.233439000	0.169544000
6	-0.341772000	0.000000000	1.673393000
1	-0.463694000	0.884296000	2.317182000
1	-0.463694000	-0.884296000	2.317182000
6	1.054662000	0.000000000	1.047806000
1	1.819527000	0.000000000	1.839145000
1	2.249642000	1.256783000	-0.259129000
1	1.103939000	2.167789000	0.734525000

triplet **8** in water			
6	0.000000000	0.000000000	1.725171000
6	1.259663000	1.260035000	0.068790000
6	0.000000000	-1.267490000	0.965131000
6	0.000000000	1.267490000	0.965131000
6	1.259663000	-1.260035000	0.068790000
6	1.253746000	0.000000000	-0.805358000
1	0.000000000	-2.151749000	1.620208000
1	2.162671000	-1.288304000	0.696027000
1	1.272286000	-2.161194000	-0.565162000
1	2.151037000	0.000000000	-1.443244000
1	1.272286000	2.161194000	-0.565162000
1	2.162671000	1.288304000	0.696027000
1	0.000000000	2.151749000	1.620208000
6	-1.259663000	-1.260035000	0.068790000
1	-1.272286000	-2.161194000	-0.565162000
1	-2.162671000	-1.288304000	0.696027000
6	-1.259663000	1.260035000	0.068790000
6	0.000000000	0.000000000	-1.685631000
1	0.000000000	0.884442000	-2.341435000
1	0.000000000	-0.884442000	-2.341435000
6	-1.253746000	0.000000000	-0.805358000
1	-2.151037000	0.000000000	-1.443244000
1	-2.162671000	1.288304000	0.696027000
1	-1.272286000	2.161194000	-0.565162000

singlet **8** in DMSO			
6	0.538064000	0.000000000	-1.710823000
6	-1.236644000	1.234229000	-0.307668000
6	0.154098000	-1.222946000	-0.962309000
6	0.154098000	1.222946000	-0.962309000
6	-1.236644000	-1.234229000	-0.307668000
6	-1.405105000	0.000000000	0.573206000
1	0.300933000	-2.128709000	-1.570331000
1	-2.014733000	-1.258535000	-1.084751000
1	-1.350079000	-2.159165000	0.279418000
1	-2.407595000	0.000000000	1.027085000
1	-1.350079000	2.159165000	0.279418000
1	-2.014733000	1.258535000	-1.084751000
1	0.300933000	2.128709000	-1.570331000
6	1.237915000	-1.233449000	0.169707000
1	1.103857000	-2.167782000	0.734724000
1	2.249624000	-1.256783000	-0.258880000
6	1.237915000	1.233449000	0.169707000
6	-0.342012000	0.000000000	1.673345000
1	-0.464037000	0.884289000	2.317134000
1	-0.464037000	-0.884289000	2.317134000
6	1.054515000	0.000000000	1.047957000
1	1.819260000	0.000000000	1.839420000
1	2.249624000	1.256782000	-0.258880000
1	1.103857000	2.167782000	0.734724000

triplet **8** in DMSO			
6	0.000000000	0.000000000	1.725178000
6	1.259659000	1.260036000	0.068792000
6	0.000000000	-1.267480000	0.965126000
6	0.000000000	1.267480000	0.965126000
6	1.259659000	-1.260036000	0.068792000
6	1.253747000	0.000000000	-0.805361000
1	0.000000000	-2.151714000	1.620234000
1	2.162655000	-1.288293000	0.696042000
1	1.272315000	-2.161193000	-0.565170000
1	2.151037000	0.000000000	-1.443251000
1	1.272315000	2.161193000	-0.565170000
1	2.162655000	1.288293000	0.696042000
1	0.000000000	2.151714000	1.620234000
6	-1.259659000	-1.260036000	0.068792000
1	-1.272315000	-2.161193000	-0.565170000
1	-2.162655000	-1.288293000	0.696042000
6	-1.259659000	1.260036000	0.068792000

6	0.000000000	0.000000000	-1.685634000
1	0.000000000	0.884435000	-2.341451000
1	0.000000000	-0.884435000	-2.341451000
6	-1.253747000	0.000000000	-0.805361000
1	-2.151037000	0.000000000	-1.443251000
1	-2.162655000	1.288293000	0.696042000
1	-1.272315000	2.161193000	-0.565170000

singlet **8** in benzene			
6	0.553672000	0.000000000	-1.707914000
6	-1.234835000	1.234224000	-0.315399000
6	0.160080000	-1.222647000	-0.960470000
6	0.160080000	1.222647000	-0.960470000
6	-1.234835000	-1.234224000	-0.315399000
6	-1.409202000	0.000000000	0.564766000
1	0.310747000	-2.127280000	-1.569370000
1	-2.008085000	-1.257869000	-1.097482000
1	-1.355191000	-2.159376000	0.270683000
1	-2.414276000	0.000000000	1.013399000
1	-1.355191000	2.159377000	0.270683000
1	-2.008085000	1.257869000	-1.097482000
1	0.310747000	2.127280000	-1.569370000
6	1.235690000	-1.233882000	0.176848000
1	1.100212000	-2.167464000	0.743324000
1	2.248899000	-1.256831000	-0.247942000
6	1.235690000	1.233882000	0.176848000
6	-0.352472000	0.000000000	1.671172000
1	-0.478939000	0.883936000	2.314988000
1	-0.478939000	-0.883936000	2.314988000
6	1.048049000	0.000000000	1.054490000
1	1.807505000	0.000000000	1.851372000
1	2.248899000	1.256830000	-0.247942000
1	1.100212000	2.167464000	0.743324000

triplet **8** in benzene			
6	0.000000000	0.000000000	1.725521000
6	1.259465000	1.260061000	0.068846000
6	0.000000000	-1.267002000	0.964926000
6	0.000000000	1.267002000	0.964926000
6	1.259465000	-1.260061000	0.068846000
6	1.253761000	0.000000000	-0.805488000
1	0.000000000	-2.150235000	1.621314000
1	2.161983000	-1.287873000	0.696648000
1	1.273610000	-2.161160000	-0.565468000
1	2.151026000	0.000000000	-1.443594000

1	1.273610000	2.161160000	-0.565468000
1	2.161983000	1.287873000	0.696648000
1	0.000000000	2.150235000	1.621314000
6	-1.259465000	-1.260061000	0.068846000
1	-1.273610000	-2.161160000	-0.565468000
1	-2.161983000	-1.287873000	0.696648000
6	-1.259465000	1.260061000	0.068846000
6	0.000000000	0.000000000	-1.685754000
1	0.000000000	0.884111000	-2.342161000
1	0.000000000	-0.884111000	-2.342161000
6	-1.253761000	0.000000000	-0.805488000
1	-2.151026000	0.000000000	-1.443594000
1	-2.161983000	1.287873000	0.696648000
1	-1.273610000	2.161160000	-0.565468000

singlet **8** in cyclohexane

6	0.555503000	0.000000000	-1.707560000
6	-1.234621000	1.234227000	-0.316301000
6	0.160779000	-1.222607000	-0.960264000
6	0.160779000	1.222607000	-0.960264000
6	-1.234621000	-1.234227000	-0.316301000
6	-1.409676000	0.000000000	0.563771000
1	0.311908000	-2.127119000	-1.569254000
1	-2.007317000	-1.257810000	-1.098956000
1	-1.355782000	-2.159402000	0.269657000
1	-2.415047000	0.000000000	1.011785000
1	-1.355783000	2.159402000	0.269657000
1	-2.007317000	1.257810000	-1.098956000
1	0.311908000	2.127119000	-1.569254000
6	1.235429000	-1.233930000	0.177690000
1	1.099775000	-2.167427000	0.744326000
1	2.248820000	-1.256843000	-0.246648000
6	1.235429000	1.233931000	0.177690000
6	-0.353701000	0.000000000	1.670911000
1	-0.480686000	0.883890000	2.314727000
1	-0.480686000	-0.883890000	2.314727000
6	1.047283000	0.000000000	1.055252000
1	1.806112000	0.000000000	1.852771000
1	2.248820000	1.256843000	-0.246648000
1	1.099775000	2.167428000	0.744326000

triplet **8** in cyclohexane

6	0.000000000	0.000000000	1.725567000
6	1.259443000	1.260064000	0.068851000
6	0.000000000	-1.266943000	0.964904000

6	0.000000000	1.266943000	0.964904000
6	1.259443000	-1.260064000	0.068851000
6	1.253762000	0.000000000	-0.805503000
1	0.000000000	-2.150067000	1.621433000
1	2.161908000	-1.287827000	0.696716000
1	1.273766000	-2.161157000	-0.565500000
1	2.151021000	0.000000000	-1.443635000
1	1.273766000	2.161157000	-0.565500000
1	2.161908000	1.287827000	0.696716000
1	0.000000000	2.150067000	1.621433000
6	-1.259443000	-1.260064000	0.068851000
1	-1.273766000	-2.161157000	-0.565500000
1	-2.161908000	-1.287827000	0.696716000
6	-1.259443000	1.260064000	0.068851000
6	0.000000000	0.000000000	-1.685767000
1	0.000000000	0.884069000	-2.342246000
1	0.000000000	-0.884069000	-2.342246000
6	-1.253762000	0.000000000	-0.805503000
1	-2.151021000	0.000000000	-1.443635000
1	-2.161908000	1.287827000	0.696716000
1	-1.273766000	2.161157000	-0.565500000

singlet **8** in hexane			
6	-0.556636000	0.000000000	-1.707344000
6	1.234487000	-1.234229000	-0.316860000
6	-0.161214000	1.222583000	-0.960135000
6	-0.161215000	-1.222583000	-0.960135000
6	1.234488000	1.234228000	-0.316860000
6	1.409968000	-0.000001000	0.563153000
1	-0.312628000	2.127019000	-1.569181000
1	2.006840000	1.257774000	-1.099868000
1	1.356151000	2.159418000	0.269019000
1	2.415524000	-0.000001000	1.010782000
1	1.356150000	-2.159419000	0.269019000
1	2.006839000	-1.257775000	-1.099868000
1	-0.312629000	-2.127019000	-1.569182000
6	-1.235266000	1.233961000	0.178213000
1	-1.099504000	2.167406000	0.744949000
1	-2.248768000	1.256852000	-0.245846000
6	-1.235267000	-1.233960000	0.178213000
6	0.354462000	0.000000000	1.670749000
1	0.481769000	-0.883861000	2.314566000
1	0.481769000	0.883861000	2.314566000
6	-1.046807000	0.000000000	1.055725000
1	-1.805246000	0.000001000	1.853638000

1	-2.248769000	-1.256850000	-0.245846000
1	-1.099505000	-2.167405000	0.744949000

triplet **8** in hexane			
6	0.000000000	0.000000000	1.725593000
6	1.259429000	1.260066000	0.068854000
6	0.000000000	-1.266905000	0.964889000
6	0.000000000	1.266905000	0.964889000
6	1.259429000	-1.260066000	0.068854000
6	1.253763000	0.000000000	-0.805511000
1	0.000000000	-2.149962000	1.621507000
1	2.161862000	-1.287800000	0.696758000
1	1.273865000	-2.161154000	-0.565519000
1	2.151017000	0.000000000	-1.443662000
1	1.273865000	2.161154000	-0.565519000
1	2.161862000	1.287800000	0.696758000
1	0.000000000	2.149962000	1.621507000
6	-1.259429000	-1.260066000	0.068854000
1	-1.273865000	-2.161154000	-0.565519000
1	-2.161862000	-1.287800000	0.696758000
6	-1.259429000	1.260066000	0.068854000
6	0.000000000	0.000000000	-1.685774000
1	0.000000000	0.884041000	-2.342300000
1	0.000000000	-0.884041000	-2.342300000
6	-1.253763000	0.000000000	-0.805511000
1	-2.151017000	0.000000000	-1.443662000
1	-2.161862000	1.287800000	0.696758000
1	-1.273865000	2.161154000	-0.565519000

singlet **8** in pentane			
6	0.557063000	0.000000000	-1.707256000
6	-1.234439000	1.234229000	-0.317069000
6	0.161374000	-1.222573000	-0.960090000
6	0.161374000	1.222573000	-0.960090000
6	-1.234439000	-1.234229000	-0.317069000
6	-1.410078000	0.000000000	0.562923000
1	0.312898000	-2.126982000	-1.569155000
1	-2.006664000	-1.257763000	-1.100207000
1	-1.356285000	-2.159424000	0.268782000
1	-2.415702000	0.000000000	1.010408000
1	-1.356285000	2.159424000	0.268782000
1	-2.006664000	1.257763000	-1.100207000
1	0.312898000	2.126982000	-1.569155000
6	1.235207000	-1.233971000	0.178408000
1	1.099401000	-2.167397000	0.745179000

1	2.248752000	-1.256855000	-0.245545000
6	1.235207000	1.233971000	0.178408000
6	-0.354747000	0.000000000	1.670687000
1	-0.482173000	0.883850000	2.314504000
1	-0.482173000	-0.883850000	2.314504000
6	1.046630000	0.000000000	1.055901000
1	1.804923000	0.000000000	1.853961000
1	2.248752000	1.256855000	-0.245545000
1	1.099401000	2.167397000	0.745178000

triplet **8** in pentane			
6	0.000000000	0.000000000	1.725607000
6	1.259424000	1.260066000	0.068855000
6	0.000000000	-1.266893000	0.964884000
6	0.000000000	1.266893000	0.964884000
6	1.259424000	-1.260066000	0.068855000
6	1.253763000	0.000000000	-0.805515000
1	0.000000000	-2.149925000	1.621534000
1	2.161844000	-1.287789000	0.696773000
1	1.273899000	-2.161153000	-0.565527000
1	2.151016000	0.000000000	-1.443670000
1	1.273899000	2.161153000	-0.565527000
1	2.161844000	1.287789000	0.696773000
1	0.000000000	2.149925000	1.621534000
6	-1.259424000	-1.260066000	0.068855000
1	-1.273899000	-2.161153000	-0.565527000
1	-2.161844000	-1.287789000	0.696773000
6	-1.259424000	1.260066000	0.068855000
6	0.000000000	0.000000000	-1.685778000
1	0.000000000	0.884032000	-2.342318000
1	0.000000000	-0.884032000	-2.342318000
6	-1.253763000	0.000000000	-0.805515000
1	-2.151016000	0.000000000	-1.443670000
1	-2.161844000	1.287789000	0.696773000
1	-1.273899000	2.161153000	-0.565527000

Table S22. Geometries of **15** in Cartesian coordinates in Å optimized at the CPCM(solvent)/MN12-SX/6-311+G(d).

singlet **15** in the gas phase			
6	-0.836878000	1.159791000	-0.443374000
6	-0.318793000	-1.178508000	-0.840796000
6	1.431315000	0.178292000	-0.789142000
6	-1.267236000	-0.905656000	0.338102000

6	1.103365000	-1.288235000	-0.222735000
6	0.034476000	1.126691000	0.827384000
6	-0.256258000	-0.350557000	1.377988000
6	-0.007483000	0.244707000	-1.374289000
6	1.454870000	1.263510000	0.280082000
6	-2.061242000	0.318265000	-0.105757000
1	-1.843014000	-1.772207000	0.684862000
1	-0.236936000	1.875366000	1.581043000
1	-1.018054000	2.174592000	-0.818915000
1	-0.643268000	-1.940476000	-1.557822000
1	2.273878000	0.181184000	-1.488270000
1	-0.120158000	0.434810000	-2.447117000
1	2.249731000	1.162288000	1.025851000
1	-2.675564000	0.756138000	0.693102000
1	1.562652000	2.244890000	-0.207390000
1	-2.708187000	0.123798000	-0.972684000
6	1.057438000	-1.048269000	1.232573000
1	-0.637909000	-0.301932000	2.405066000
1	1.795386000	-2.058637000	-0.577947000

triplet **15** in the gas phase

6	-0.833096000	1.175035000	-0.432295000
6	-0.246561000	-1.133648000	-0.887463000
6	1.470509000	0.258159000	-0.747594000
6	-1.256284000	-0.924496000	0.266200000
6	1.191661000	-1.220608000	-0.257185000
6	-0.019464000	1.099057000	0.877929000
6	-0.313288000	-0.380125000	1.381476000
6	0.046167000	0.315300000	-1.366389000
6	1.431023000	1.237619000	0.417887000
6	-2.054402000	0.295827000	-0.178622000
1	-1.815708000	-1.819077000	0.561722000
1	-0.322919000	1.842414000	1.626480000
1	-1.022845000	2.197306000	-0.782525000
1	-0.531601000	-1.885291000	-1.631894000
1	2.325923000	0.367166000	-1.424173000
1	-0.050200000	0.530475000	-2.436344000
1	2.160780000	0.995911000	1.203442000
1	-2.717765000	0.689005000	0.604194000
1	1.627455000	2.264009000	0.074827000
1	-2.652400000	0.115391000	-1.082968000
6	0.895645000	-1.207793000	1.181591000
1	-0.750479000	-0.396794000	2.386552000
1	1.878304000	-1.986482000	-0.632516000

singlet **15** in water			
6	-0.833477000	1.162289000	-0.442715000
6	-0.313086000	-1.173487000	-0.846437000
6	1.436353000	0.184017000	-0.780581000
6	-1.267596000	-0.906308000	0.329229000
6	1.103681000	-1.292431000	-0.221771000
6	0.031130000	1.126800000	0.832129000
6	-0.263020000	-0.355797000	1.376993000
6	0.001203000	0.250948000	-1.372693000
6	1.452380000	1.266170000	0.290287000
6	-2.058830000	0.319434000	-0.113434000
1	-1.843378000	-1.775185000	0.669538000
1	-0.246647000	1.869637000	1.588599000
1	-1.012047000	2.178549000	-0.814197000
1	-0.631819000	-1.933862000	-1.566926000
1	2.283138000	0.181639000	-1.473864000
1	-0.103406000	0.444351000	-2.445183000
1	2.247640000	1.172971000	1.037297000
1	-2.676339000	0.754578000	0.684107000
1	1.557992000	2.247020000	-0.197507000
1	-2.699904000	0.125239000	-0.984504000
6	1.040884000	-1.065169000	1.230000000
1	-0.651538000	-0.307413000	2.401274000
1	1.798576000	-2.056317000	-0.584666000

triplet **15** in water			
6	-0.829802000	1.173806000	-0.438968000
6	-0.246310000	-1.137840000	-0.882844000
6	1.473363000	0.253165000	-0.745003000
6	-1.258543000	-0.922034000	0.267665000
6	1.191455000	-1.224069000	-0.250099000
6	-0.019728000	1.103363000	0.873645000
6	-0.318268000	-0.373218000	1.383420000
6	0.050356000	0.308321000	-1.367014000
6	1.431309000	1.238871000	0.414847000
6	-2.053259000	0.297940000	-0.184143000
1	-1.821225000	-1.813908000	0.565781000
1	-0.325136000	1.849117000	1.618597000
1	-1.016226000	2.194919000	-0.793783000
1	-0.529425000	-1.892444000	-1.624741000
1	2.330454000	0.355827000	-1.420140000
1	-0.042402000	0.517494000	-2.438257000
1	2.161432000	1.004404000	1.202814000
1	-2.716814000	0.695443000	0.596133000
1	1.626918000	2.263069000	0.065250000

1	-2.648272000	0.113381000	-1.089570000
6	0.889800000	-1.203968000	1.187746000
1	-0.759437000	-0.382604000	2.386785000
1	1.877888000	-1.990720000	-0.624389000

singlet **15** in DMSO			
6	-0.833512000	1.162267000	-0.442711000
6	-0.313148000	-1.173533000	-0.846387000
6	1.436301000	0.183956000	-0.780676000
6	-1.267593000	-0.906304000	0.329315000
6	1.103681000	-1.292367000	-0.221799000
6	0.031169000	1.126784000	0.832090000
6	-0.262954000	-0.355751000	1.377000000
6	0.001109000	0.250895000	-1.372712000
6	1.452411000	1.266131000	0.290189000
6	-2.058858000	0.319424000	-0.113351000
1	-1.843370000	-1.775160000	0.669690000
1	-0.246530000	1.869677000	1.588540000
1	-1.012106000	2.178519000	-0.814224000
1	-0.631941000	-1.933923000	-1.566842000
1	2.283042000	0.181655000	-1.474022000
1	-0.103596000	0.444275000	-2.445206000
1	2.247663000	1.172826000	1.037186000
1	-2.676332000	0.754589000	0.684212000
1	1.558053000	2.246996000	-0.197580000
1	-2.699998000	0.125238000	-0.984379000
6	1.041059000	-1.064999000	1.230028000
1	-0.651401000	-0.307380000	2.401310000
1	1.798536000	-2.056336000	-0.584602000

triplet **15** in DMSO			
6	-0.829840000	1.173820000	-0.438895000
6	-0.246311000	-1.137794000	-0.882895000
6	1.473331000	0.253220000	-0.745033000
6	-1.258516000	-0.922062000	0.267650000
6	1.191458000	-1.224030000	-0.250177000
6	-0.019725000	1.103315000	0.873692000
6	-0.318212000	-0.373294000	1.383399000
6	0.050309000	0.308398000	-1.367009000
6	1.431305000	1.238858000	0.414880000
6	-2.053273000	0.297915000	-0.184081000
1	-1.821159000	-1.813967000	0.565738000
1	-0.325111000	1.849042000	1.618685000
1	-1.016301000	2.194946000	-0.793659000
1	-0.529448000	-1.892368000	-1.624818000

1	2.330405000	0.355951000	-1.420184000
1	-0.042491000	0.517639000	-2.438239000
1	2.161423000	1.004308000	1.202820000
1	-2.716824000	0.695369000	0.596226000
1	1.626924000	2.263080000	0.065356000
1	-2.648321000	0.113401000	-1.089496000
6	0.889866000	-1.204008000	1.187678000
1	-0.759335000	-0.382762000	2.386784000
1	1.877895000	-1.990673000	-0.624474000

singlet **15** in benzene

6	-0.835110000	1.161189000	-0.442790000
6	-0.315854000	-1.175739000	-0.843931000
6	1.433951000	0.181275000	-0.784797000
6	-1.267430000	-0.906056000	0.333344000
6	1.103607000	-1.290003000	-0.222616000
6	0.032800000	1.126426000	0.830086000
6	-0.259878000	-0.353490000	1.377400000
6	-0.003048000	0.248240000	-1.373513000
6	1.453670000	1.264657000	0.285602000
6	-2.060047000	0.318910000	-0.109682000
1	-1.843079000	-1.773912000	0.676709000
1	-0.241685000	1.871958000	1.585407000
1	-1.014875000	2.176884000	-0.815999000
1	-0.637341000	-1.936870000	-1.562817000
1	2.278710000	0.181882000	-1.480904000
1	-0.111759000	0.440310000	-2.446157000
1	2.248660000	1.167179000	1.031996000
1	-2.676000000	0.755175000	0.688646000
1	1.560457000	2.245985000	-0.201605000
1	-2.704031000	0.124820000	-0.978805000
6	1.048858000	-1.057210000	1.231246000
1	-0.645100000	-0.305307000	2.403014000
1	1.796931000	-2.057300000	-0.581581000

triplet **15** in benzene

6	-0.831454000	1.174417000	-0.435693000
6	-0.246412000	-1.135784000	-0.885124000
6	1.471948000	0.255616000	-0.746299000
6	-1.257398000	-0.923265000	0.266964000
6	1.191571000	-1.222357000	-0.253596000
6	-0.019610000	1.101239000	0.875747000
6	-0.315813000	-0.376597000	1.382479000
6	0.048269000	0.311768000	-1.366744000
6	1.431167000	1.238260000	0.416337000

6	-2.053845000	0.296867000	-0.181408000
1	-1.818404000	-1.816505000	0.563835000
1	-0.324030000	1.845794000	1.622508000
1	-1.019520000	2.196125000	-0.788256000
1	-0.530483000	-1.888986000	-1.628221000
1	2.328260000	0.361372000	-1.422110000
1	-0.046322000	0.523922000	-2.437373000
1	2.161080000	1.000179000	1.203120000
1	-2.717277000	0.692213000	0.600177000
1	1.627188000	2.263560000	0.069967000
1	-2.650366000	0.114321000	-1.086301000
6	0.892691000	-1.205790000	1.184707000
1	-0.754963000	-0.389604000	2.386705000
1	1.878144000	-1.988633000	-0.628280000

singlet **15** in cyclohexane			
6	-0.835304000	1.161045000	-0.442830000
6	-0.316175000	-1.176026000	-0.843610000
6	1.433666000	0.180954000	-0.785280000
6	-1.267408000	-0.906020000	0.333849000
6	1.103590000	-1.289772000	-0.222666000
6	0.032986000	1.126425000	0.829814000
6	-0.259493000	-0.353191000	1.377458000
6	-0.003539000	0.247884000	-1.373602000
6	1.453807000	1.264513000	0.285022000
6	-2.060183000	0.318840000	-0.109248000
1	-1.843056000	-1.773745000	0.677580000
1	-0.241142000	1.872289000	1.584974000
1	-1.015219000	2.176656000	-0.816273000
1	-0.637987000	-1.937246000	-1.562300000
1	2.278187000	0.181852000	-1.481715000
1	-0.112703000	0.439763000	-2.446266000
1	2.248777000	1.166589000	1.031345000
1	-2.675958000	0.755262000	0.689152000
1	1.560713000	2.245867000	-0.202175000
1	-2.704497000	0.124731000	-0.978137000
6	1.049795000	-1.056252000	1.231390000
1	-0.644324000	-0.304992000	2.403230000
1	1.796756000	-2.057431000	-0.581201000

triplet **15** in cyclohexane			
6	-0.831639000	1.174486000	-0.435317000
6	-0.246426000	-1.135548000	-0.885384000
6	1.471788000	0.255897000	-0.746445000
6	-1.257271000	-0.923404000	0.266882000

6	1.191582000	-1.222162000	-0.253995000
6	-0.019594000	1.100997000	0.875989000
6	-0.315532000	-0.376987000	1.382370000
6	0.048034000	0.312161000	-1.366709000
6	1.431151000	1.238190000	0.416509000
6	-2.053909000	0.296749000	-0.181097000
1	-1.818094000	-1.816795000	0.563606000
1	-0.323905000	1.845416000	1.622952000
1	-1.019892000	2.196259000	-0.787622000
1	-0.530607000	-1.888583000	-1.628625000
1	2.328004000	0.362011000	-1.422337000
1	-0.046760000	0.524654000	-2.437265000
1	2.161044000	0.999701000	1.203156000
1	-2.717330000	0.691852000	0.600630000
1	1.627217000	2.263613000	0.070506000
1	-2.650598000	0.114435000	-1.085930000
6	0.893019000	-1.206006000	1.184360000
1	-0.754458000	-0.390404000	2.386691000
1	1.878167000	-1.988394000	-0.628739000

singlet **15** in hexane

6	-0.835430000	1.160952000	-0.442859000
6	-0.316373000	-1.176207000	-0.843405000
6	1.433485000	0.180756000	-0.785581000
6	-1.267390000	-0.905999000	0.334168000
6	1.103581000	-1.289630000	-0.222694000
6	0.033099000	1.126429000	0.829641000
6	-0.259246000	-0.352999000	1.377494000
6	-0.003848000	0.247658000	-1.373658000
6	1.453888000	1.264428000	0.284656000
6	-2.060269000	0.318791000	-0.108976000
1	-1.843036000	-1.773642000	0.678130000
1	-0.240812000	1.872501000	1.584697000
1	-1.015444000	2.176507000	-0.816449000
1	-0.638388000	-1.937484000	-1.561972000
1	2.277857000	0.181834000	-1.482224000
1	-0.113293000	0.439412000	-2.446334000
1	2.248846000	1.166230000	1.030936000
1	-2.675932000	0.755312000	0.689468000
1	1.560869000	2.245797000	-0.202538000
1	-2.704789000	0.124663000	-0.977716000
6	1.050386000	-1.055651000	1.231479000
1	-0.643831000	-0.304789000	2.403368000
1	1.796652000	-2.057511000	-0.580964000

triplet **15** in hexane			
6	-0.831720000	1.174457000	-0.435341000
6	-0.246367000	-1.135546000	-0.885380000
6	1.471746000	0.255951000	-0.746462000
6	-1.257213000	-0.923447000	0.266882000
6	1.191609000	-1.222083000	-0.253948000
6	-0.019654000	1.100991000	0.875957000
6	-0.315465000	-0.377002000	1.382338000
6	0.047994000	0.312180000	-1.366734000
6	1.431109000	1.238213000	0.416525000
6	-2.053935000	0.296646000	-0.181113000
1	-1.817946000	-1.816884000	0.563619000
1	-0.323955000	1.845449000	1.622900000
1	-1.020063000	2.196212000	-0.787669000
1	-0.530554000	-1.888599000	-1.628608000
1	2.327956000	0.362175000	-1.422356000
1	-0.046842000	0.524708000	-2.437287000
1	2.160927000	0.999597000	1.203184000
1	-2.717409000	0.691726000	0.600588000
1	1.627233000	2.263657000	0.070602000
1	-2.650660000	0.114329000	-1.085922000
6	0.893132000	-1.205946000	1.184412000
1	-0.754331000	-0.390508000	2.386688000
1	1.878230000	-1.988347000	-0.628554000

singlet **15** in pentane			
6	-0.835470000	1.160921000	-0.442870000
6	-0.316449000	-1.176274000	-0.843331000
6	1.433421000	0.180680000	-0.785690000
6	-1.267389000	-0.905987000	0.334283000
6	1.103573000	-1.289583000	-0.222700000
6	0.033145000	1.126431000	0.829578000
6	-0.259161000	-0.352931000	1.377508000
6	-0.003957000	0.247573000	-1.373678000
6	1.453923000	1.264394000	0.284522000
6	-2.060298000	0.318780000	-0.108879000
1	-1.843039000	-1.773598000	0.678328000
1	-0.240684000	1.872580000	1.584596000
1	-1.015515000	2.176456000	-0.816517000
1	-0.638539000	-1.937571000	-1.561852000
1	2.277739000	0.181816000	-1.482407000
1	-0.113504000	0.439284000	-2.446358000
1	2.248877000	1.166098000	1.030785000
1	-2.675920000	0.755340000	0.689580000
1	1.560928000	2.245766000	-0.202674000

1	-2.704893000	0.124650000	-0.977566000
6	1.050596000	-1.055431000	1.231513000
1	-0.643658000	-0.304711000	2.403417000
1	1.796608000	-2.057547000	-0.580872000

triplet **15** in pentane			
6	-0.831796000	1.174545000	-0.434996000
6	-0.246439000	-1.135347000	-0.885606000
6	1.471651000	0.256137000	-0.746569000
6	-1.257164000	-0.923521000	0.266811000
6	1.191592000	-1.221997000	-0.254335000
6	-0.019581000	1.100790000	0.876195000
6	-0.315294000	-0.377319000	1.382276000
6	0.047834000	0.312495000	-1.366678000
6	1.431137000	1.238130000	0.416655000
6	-2.053964000	0.296649000	-0.180833000
1	-1.817832000	-1.817042000	0.563410000
1	-0.323799000	1.845096000	1.623330000
1	-1.020208000	2.196373000	-0.787081000
1	-0.530712000	-1.888238000	-1.628969000
1	2.327786000	0.362556000	-1.422531000
1	-0.047132000	0.525275000	-2.437171000
1	2.161015000	0.999295000	1.203186000
1	-2.717376000	0.691546000	0.601014000
1	1.627243000	2.263657000	0.070965000
1	-2.650793000	0.114534000	-1.085614000
6	0.893299000	-1.206192000	1.184065000
1	-0.754030000	-0.391084000	2.386680000
1	1.878185000	-1.988191000	-0.629132000

Table S23. Geometries of singlet **2** in Cartesian coordinates in Å optimized at the CPCM(solvent)/MN12-SX/6-311+G(d).

2 in the gas phase			
6	-1.052603000	0.740545000	0.000000000
6	-0.373909000	-1.271540000	1.252427000
6	-0.373909000	0.263047000	-1.261561000
6	-0.373909000	0.263047000	1.261561000
6	-0.373909000	-1.271540000	-1.252427000
6	0.349850000	-1.778588000	0.000000000
1	-0.915787000	0.644262000	-2.139729000
1	-1.407575000	-1.648312000	-1.274918000
1	0.125290000	-1.649152000	-2.157904000
1	0.352077000	-2.879215000	0.000000000

1	0.125290000	-1.649152000	2.157904000
1	-1.407575000	-1.648312000	1.274918000
1	-0.915787000	0.644262000	2.139729000
6	1.070449000	0.781485000	-1.252441000
1	1.594497000	0.439210000	-2.157920000
1	1.075848000	1.881666000	-1.274932000
6	1.070449000	0.781485000	1.252441000
6	1.791240000	-1.260217000	0.000000000
1	2.328668000	-1.638319000	0.883508000
1	2.328668000	-1.638319000	-0.883508000
6	1.792211000	0.271574000	0.000000000
1	2.828883000	0.641299000	0.000000000
1	1.075848000	1.881666000	1.274932000
1	1.594497000	0.439210000	2.157920000
7	-2.491998000	1.002049000	0.000000000
7	-1.784946000	2.007011000	0.000000000

2 in water			
6	1.051038000	0.739514000	0.000000000
6	-1.070336000	0.781742000	1.252240000
6	0.374312000	0.263366000	-1.262697000
6	0.374312000	0.263366000	1.262697000
6	-1.070336000	0.781742000	-1.252240000
6	-1.791870000	0.271600000	0.000000000
1	0.915732000	0.644312000	-2.141107000
1	-1.077115000	1.882090000	-1.274859000
1	-1.591792000	0.438028000	-2.158156000
1	-2.828079000	0.641829000	0.000000000
1	-1.591792000	0.438028000	2.158156000
1	-1.077115000	1.882090000	1.274859000
1	0.915732000	0.644312000	2.141107000
6	0.374312000	-1.271468000	-1.252240000
1	-0.125320000	-1.646198000	-2.158156000
1	1.407714000	-1.649481000	-1.274856000
6	0.374312000	-1.271468000	1.252240000
6	-1.790943000	-1.260115000	0.000000000
1	-2.327184000	-1.637416000	0.884352000
1	-2.327184000	-1.637416000	-0.884352000
6	-0.349546000	-1.778309000	0.000000000
1	-0.351043000	-2.878671000	0.000000000
1	1.407714000	-1.649481000	1.274856000
1	-0.125320000	-1.646198000	2.158156000
7	1.783534000	2.006809000	0.000000000
7	2.491257000	1.000956000	0.000000000

2 in DMSO			
6	1.051058000	0.739536000	0.000000000
6	-1.070336000	0.781723000	1.252240000
6	0.374315000	0.263362000	-1.262683000
6	0.374315000	0.263362000	1.262683000
6	-1.070336000	0.781723000	-1.252240000
6	-1.791873000	0.271577000	0.000000000
1	0.915737000	0.644312000	-2.141089000
1	-1.077109000	1.882069000	-1.274855000
1	-1.591814000	0.438021000	-2.158155000
1	-2.828088000	0.641800000	0.000000000
1	-1.591814000	0.438021000	2.158155000
1	-1.077109000	1.882069000	1.274855000
1	0.915737000	0.644312000	2.141089000
6	0.374315000	-1.271470000	-1.252239000
1	-0.125312000	-1.646229000	-2.158154000
1	1.407720000	-1.649467000	-1.274858000
6	0.374315000	-1.271470000	1.252239000
6	-1.790945000	-1.260138000	0.000000000
1	-2.327195000	-1.637448000	0.884345000
1	-2.327195000	-1.637448000	-0.884345000
6	-0.349542000	-1.778321000	0.000000000
1	-0.351031000	-2.878686000	0.000000000
1	1.407720000	-1.649467000	1.274858000
1	-0.125312000	-1.646229000	2.158154000
7	1.783506000	2.006845000	0.000000000
7	2.491257000	1.001023000	0.000000000

2 in benzene			
6	1.051814000	0.740054000	0.000000000
6	-1.070366000	0.781581000	1.252334000
6	0.374149000	0.263223000	-1.262151000
6	0.374149000	0.263223000	1.262151000
6	-1.070366000	0.781581000	-1.252334000
6	-1.792042000	0.271542000	0.000000000
1	0.915804000	0.644307000	-2.140402000
1	-1.076498000	1.881840000	-1.274899000
1	-1.593072000	0.438496000	-2.158036000
1	-2.828486000	0.641536000	0.000000000
1	-1.593072000	0.438496000	2.158036000
1	-1.076498000	1.881840000	1.274899000
1	0.915804000	0.644307000	2.140402000
6	0.374149000	-1.271484000	-1.252313000
1	-0.125311000	-1.647588000	-2.158028000
1	1.407670000	-1.648889000	-1.274855000

6	0.374149000	-1.271484000	1.252313000
6	-1.791095000	-1.260226000	0.000000000
1	-2.327904000	-1.637913000	0.883966000
1	-2.327904000	-1.637913000	-0.883966000
6	-0.349684000	-1.778466000	0.000000000
1	-0.351495000	-2.878970000	0.000000000
1	1.407670000	-1.648889000	1.274855000
1	-0.125311000	-1.647588000	2.158028000
7	1.784095000	2.006938000	0.000000000
7	2.491543000	1.001585000	0.000000000

2 in cyclohexane			
6	-1.051895000	0.740064000	0.000000000
6	-0.374097000	-1.271499000	1.252345000
6	-0.374097000	0.263197000	-1.262107000
6	-0.374097000	0.263197000	1.262107000
6	-0.374097000	-1.271499000	-1.252345000
6	0.349701000	-1.778462000	0.000000000
1	-0.915770000	0.644294000	-2.140354000
1	-1.407627000	-1.648850000	-1.274887000
1	0.125357000	-1.647757000	-2.158024000
1	0.351573000	-2.878981000	0.000000000
1	0.125357000	-1.647757000	2.158024000
1	-1.407627000	-1.648850000	1.274887000
1	-0.915770000	0.644294000	2.140354000
6	1.070386000	0.781623000	-1.252345000
1	1.593241000	0.438633000	-2.158025000
1	1.076424000	1.881869000	-1.274882000
6	1.070386000	0.781623000	1.252345000
6	1.791096000	-1.260134000	0.000000000
1	2.327982000	-1.637863000	0.883926000
1	2.327982000	-1.637863000	-0.883926000
6	1.792046000	0.271623000	0.000000000
1	2.828506000	0.641619000	0.000000000
1	1.076424000	1.881869000	1.274882000
1	1.593241000	0.438633000	2.158025000
7	-2.491615000	1.001483000	0.000000000
7	-1.784281000	2.006848000	0.000000000

2 in hexane			
6	-1.286214000	-0.000001000	0.000000000
6	0.425686000	-1.255169000	1.252353000
6	-0.457388000	0.000000000	-1.262067000
6	-0.457388000	0.000000000	1.262067000
6	0.425686000	-1.255169000	-1.252353000

6	1.309366000	-1.253320000	0.000000000
1	-1.119709000	0.000000000	-2.140306000
1	-0.202503000	-2.158464000	-1.274889000
1	1.050720000	-1.275599000	-2.158016000
1	1.944174000	-2.152311000	0.000000000
1	1.050720000	-1.275599000	2.158016000
1	-0.202503000	-2.158464000	1.274889000
1	-1.119709000	0.000000000	2.140306000
6	0.425686000	1.255169000	-1.252352000
1	1.050718000	1.275601000	-2.158016000
1	-0.202504000	2.158464000	-1.274887000
6	0.425686000	1.255169000	1.252352000
6	2.189977000	0.000001000	0.000000000
1	2.846477000	0.000002000	0.883896000
1	2.846477000	0.000002000	-0.883896000
6	1.309366000	1.253322000	0.000000000
1	1.944174000	2.152313000	0.000000000
1	-0.202504000	2.158464000	1.274887000
1	1.050718000	1.275601000	2.158016000
7	-2.614108000	-0.614613000	0.000000000
7	-2.614110000	0.614608000	0.000000000

2 in pentane

6	1.051970000	0.740112000	0.000000000
6	-1.070390000	0.781613000	1.252355000
6	0.374077000	0.263180000	-1.262053000
6	0.374077000	0.263180000	1.262053000
6	-1.070390000	0.781613000	-1.252355000
6	-1.792061000	0.271626000	0.000000000
1	0.915772000	0.644289000	-2.140289000
1	-1.076362000	1.881851000	-1.274887000
1	-1.593373000	0.438693000	-2.158013000
1	-2.828542000	0.641599000	0.000000000
1	-1.593373000	0.438693000	2.158013000
1	-1.076362000	1.881851000	1.274887000
1	0.915772000	0.644289000	2.140289000
6	0.374077000	-1.271505000	-1.252355000
1	-0.125356000	-1.647901000	-2.158013000
1	1.407618000	-1.648797000	-1.274891000
6	0.374077000	-1.271505000	1.252355000
6	-1.791109000	-1.260134000	0.000000000
1	-2.328054000	-1.637900000	0.883885000
1	-2.328054000	-1.637900000	-0.883885000
6	-0.349717000	-1.778474000	0.000000000
1	-0.351626000	-2.879005000	0.000000000

1	1.407618000	-1.648797000	1.274891000
1	-0.125356000	-1.647901000	2.158013000
7	1.784353000	2.006855000	0.000000000
7	2.491651000	1.001532000	0.000000000

Table S24. Geometries of singlet **1** in Cartesian coordinates in Å optimized at the CPCM(solvent)/MN12-SX/6-311+G(d).

1 in the gas phase			
6	1.899041000	0.176629000	-0.489224000
6	0.508525000	-0.509671000	1.373808000
6	0.189414000	1.562028000	0.697348000
6	0.562056000	-1.503490000	0.188902000
6	-0.743008000	0.397672000	1.177390000
6	0.615018000	0.413888000	-1.315592000
6	-0.318450000	-0.765520000	-0.847489000
6	1.433582000	0.649458000	0.903589000
6	0.102019000	1.763421000	-0.810993000
6	1.981788000	-1.339861000	-0.343486000
1	0.222371000	-2.519057000	0.422396000
1	0.784098000	0.381860000	-2.399186000
1	2.785033000	0.688511000	-0.883697000
1	0.683089000	-0.951236000	2.360593000
1	0.128580000	2.478735000	1.294047000
1	2.228102000	0.984742000	1.578959000
1	-0.906955000	2.014113000	-1.162057000
1	2.151450000	-1.860289000	-1.296146000
1	0.777800000	2.568639000	-1.133598000
1	2.749460000	-1.664771000	0.372330000
6	-1.436370000	-0.229809000	0.005418000
1	-0.658284000	-1.392364000	-1.680694000
1	-1.383036000	0.605308000	2.041492000
7	-2.741887000	0.175649000	-0.500250000
7	-2.732885000	-0.893170000	0.107041000

1 in water			
6	1.898954000	0.173383000	-0.487456000
6	0.504942000	-0.508991000	1.374407000
6	0.190984000	1.563129000	0.696192000
6	0.557798000	-1.503843000	0.190125000
6	-0.744364000	0.401513000	1.176811000
6	0.617006000	0.412513000	-1.316228000
6	-0.318886000	-0.765325000	-0.849467000
6	1.432807000	0.647862000	0.904504000

6	0.107895000	1.763825000	-0.812501000
6	1.978383000	-1.343188000	-0.341026000
1	0.216659000	-2.519027000	0.423593000
1	0.786971000	0.377652000	-2.399270000
1	2.785571000	0.684008000	-0.881647000
1	0.676638000	-0.949481000	2.361933000
1	0.130075000	2.479155000	1.293534000
1	2.226487000	0.981880000	1.581133000
1	-0.898971000	2.020014000	-1.166888000
1	2.146909000	-1.864068000	-1.293515000
1	0.788049000	2.565798000	-1.133390000
1	2.743314000	-1.668908000	0.377296000
6	-1.434430000	-0.226605000	0.003799000
1	-0.658987000	-1.391110000	-1.682970000
1	-1.385647000	0.611750000	2.039101000
7	-2.741507000	0.176360000	-0.501371000
7	-2.730436000	-0.892546000	0.107961000

1 in DMSO			
6	1.898957000	0.173412000	-0.487472000
6	0.504974000	-0.508998000	1.374401000
6	0.190970000	1.563118000	0.696204000
6	0.557836000	-1.503839000	0.190111000
6	-0.744350000	0.401477000	1.176815000
6	0.616989000	0.412527000	-1.316220000
6	-0.318883000	-0.765324000	-0.849449000
6	1.432816000	0.647876000	0.904497000
6	0.107840000	1.763822000	-0.812485000
6	1.978415000	-1.343159000	-0.341049000
1	0.216707000	-2.519025000	0.423579000
1	0.786944000	0.377697000	-2.399269000
1	2.785570000	0.684048000	-0.881665000
1	0.676697000	-0.949503000	2.361919000
1	0.130062000	2.479152000	1.293538000
1	2.226506000	0.981904000	1.581114000
1	-0.899046000	2.019956000	-1.166839000
1	2.146951000	-1.864035000	-1.293540000
1	0.787950000	2.565828000	-1.133392000
1	2.743373000	-1.668874000	0.377247000
6	-1.434452000	-0.226633000	0.003813000
1	-0.658984000	-1.391116000	-1.682948000
1	-1.385624000	0.611689000	2.039120000
7	-2.741512000	0.176351000	-0.501359000
7	-2.730457000	-0.892552000	0.107952000

1 in benzene			
6	1.899041000	0.174820000	-0.488249000
6	0.506542000	-0.509329000	1.374116000
6	0.190315000	1.562619000	0.696739000
6	0.559680000	-1.503672000	0.189512000
6	-0.743731000	0.399781000	1.177036000
6	0.616133000	0.413178000	-1.315908000
6	-0.318704000	-0.765329000	-0.848581000
6	1.433204000	0.648543000	0.904119000
6	0.105248000	1.763679000	-0.811785000
6	1.979916000	-1.341736000	-0.342148000
1	0.219088000	-2.518990000	0.422978000
1	0.785675000	0.379696000	-2.399221000
1	2.785436000	0.685991000	-0.882532000
1	0.679512000	-0.950419000	2.361279000
1	0.129436000	2.478994000	1.293749000
1	2.227328000	0.983082000	1.580176000
1	-0.902588000	2.017292000	-1.164600000
1	2.148962000	-1.862416000	-1.294728000
1	0.783375000	2.567179000	-1.133477000
1	2.746116000	-1.667170000	0.375001000
6	-1.435399000	-0.227999000	0.004494000
1	-0.658757000	-1.391552000	-1.681937000
1	-1.384499000	0.608819000	2.040099000
7	-2.741734000	0.175993000	-0.500819000
7	-2.731489000	-0.892827000	0.107554000

1 in cyclohexane			
6	1.899046000	0.175004000	-0.488349000
6	0.506745000	-0.509368000	1.374082000
6	0.190227000	1.562557000	0.696805000
6	0.559921000	-1.503652000	0.189443000
6	-0.743654000	0.399564000	1.177068000
6	0.616020000	0.413255000	-1.315872000
6	-0.318680000	-0.765340000	-0.848469000
6	1.433248000	0.648633000	0.904067000
6	0.104916000	1.763656000	-0.811700000
6	1.980108000	-1.341548000	-0.342287000
1	0.219411000	-2.518992000	0.422910000
1	0.785514000	0.379935000	-2.399217000
1	2.785406000	0.686245000	-0.882647000
1	0.679877000	-0.950519000	2.361203000
1	0.129353000	2.478970000	1.293779000
1	2.227420000	0.983243000	1.580053000
1	-0.903039000	2.016959000	-1.164327000

1	2.149219000	-1.862202000	-1.294877000
1	0.782797000	2.567340000	-1.133487000
1	2.746463000	-1.666935000	0.374721000
6	-1.435509000	-0.228180000	0.004586000
1	-0.658718000	-1.391622000	-1.681808000
1	-1.384352000	0.608454000	2.040234000
7	-2.741756000	0.175953000	-0.500756000
7	-2.731628000	-0.892862000	0.107501000

1 in hexane			
6	1.899049000	0.175121000	-0.488412000
6	0.506873000	-0.509392000	1.374061000
6	0.190170000	1.562517000	0.696846000
6	0.560074000	-1.503640000	0.189400000
6	-0.743606000	0.399426000	1.177090000
6	0.615949000	0.413304000	-1.315850000
6	-0.318664000	-0.765348000	-0.848398000
6	1.433275000	0.648690000	0.904034000
6	0.104706000	1.763642000	-0.811646000
6	1.980230000	-1.341428000	-0.342375000
1	0.219617000	-2.518994000	0.422868000
1	0.785411000	0.380084000	-2.399214000
1	2.785385000	0.686407000	-0.882721000
1	0.680110000	-0.950580000	2.361156000
1	0.129300000	2.478955000	1.293798000
1	2.227476000	0.983347000	1.579975000
1	-0.903325000	2.016749000	-1.164155000
1	2.149382000	-1.862066000	-1.294971000
1	0.782430000	2.567440000	-1.133494000
1	2.746683000	-1.666785000	0.374543000
6	-1.435577000	-0.228296000	0.004644000
1	-0.658693000	-1.391669000	-1.681727000
1	-1.384259000	0.608223000	2.040321000
7	-2.741769000	0.175928000	-0.500716000
7	-2.731717000	-0.892884000	0.107468000

1 in pentane			
6	1.899050000	0.175163000	-0.488436000
6	0.506920000	-0.509401000	1.374053000
6	0.190150000	1.562503000	0.696861000
6	0.560130000	-1.503636000	0.189384000
6	-0.743588000	0.399376000	1.177098000
6	0.615923000	0.413322000	-1.315841000
6	-0.318658000	-0.765351000	-0.848372000
6	1.433285000	0.648711000	0.904021000

6	0.104629000	1.763636000	-0.811627000
6	1.980275000	-1.341385000	-0.342407000
1	0.219693000	-2.518995000	0.422853000
1	0.785374000	0.380138000	-2.399213000
1	2.785377000	0.686466000	-0.882748000
1	0.680194000	-0.950602000	2.361139000
1	0.129280000	2.478949000	1.293805000
1	2.227496000	0.983385000	1.579946000
1	-0.903429000	2.016673000	-1.164093000
1	2.149441000	-1.862016000	-1.295005000
1	0.782297000	2.567476000	-1.133497000
1	2.746763000	-1.666730000	0.374479000
6	-1.435602000	-0.228338000	0.004666000
1	-0.658683000	-1.391686000	-1.681697000
1	-1.384225000	0.608139000	2.040353000
7	-2.741773000	0.175920000	-0.500702000
7	-2.731749000	-0.892892000	0.107456000

Table S25. Geometries of singlet **7** in Cartesian coordinates in Å optimized at the CPCM(solvent)/MN12-SX/6-311+G(d).

7 in the gas phase

6	1.193441000	0.000000000	0.000001000
6	-0.508845000	-1.258953000	1.253167000
6	0.381419000	1.270033000	0.000000000
6	0.381419000	-1.270033000	0.000000000
6	-0.508845000	1.258953000	1.253167000
6	-1.384925000	0.000000000	1.252373000
1	1.041161000	2.148910000	0.000001000
1	0.116558000	1.291691000	2.157159000
1	-1.146678000	2.156801000	1.265989000
1	-2.019785000	0.000000000	2.151565000
1	-1.146679000	-2.156800000	1.265989000
1	0.116557000	-1.291691000	2.157159000
1	1.041159000	-2.148910000	0.000001000
6	-0.508843000	1.258953000	-1.253167000
1	-1.146677000	2.156801000	-1.265989000
1	0.116560000	1.291691000	-2.157158000
6	-0.508844000	-1.258953000	-1.253167000
6	-2.267209000	0.000000000	-0.000001000
1	-2.924132000	-0.883644000	-0.000001000
1	-2.924132000	0.883645000	-0.000001000
6	-1.384924000	0.000000000	-1.252374000

1	-2.019783000	0.000000000	-2.151566000
1	0.116559000	-1.291691000	-2.157158000
1	-1.146678000	-2.156800000	-1.265989000
7	2.471702000	-0.000001000	0.000000000
7	3.617287000	0.000000000	0.000000000

7 in water			
6	1.192762000	0.000000000	0.000001000
6	-0.507828000	-1.258037000	1.253767000
6	0.381085000	1.272121000	0.000000000
6	0.381085000	-1.272121000	0.000000000
6	-0.507827000	1.258037000	1.253767000
6	-1.384566000	0.000000000	1.252378000
1	1.041607000	2.149838000	0.000001000
1	0.117725000	1.290125000	2.157838000
1	-1.143216000	2.157097000	1.264566000
1	-2.018745000	0.000000000	2.151743000
1	-1.143217000	-2.157096000	1.264566000
1	0.117724000	-1.290126000	2.157838000
1	1.041607000	-2.149839000	0.000001000
6	-0.507826000	1.258037000	-1.253767000
1	-1.143215000	2.157097000	-1.264566000
1	0.117726000	1.290125000	-2.157837000
6	-0.507827000	-1.258037000	-1.253767000
6	-2.266760000	0.000000000	-0.000001000
1	-2.922304000	-0.884473000	-0.000001000
1	-2.922304000	0.884474000	-0.000001000
6	-1.384565000	0.000000000	-1.252379000
1	-2.018744000	0.000000000	-2.151744000
1	0.117726000	-1.290126000	-2.157837000
1	-1.143216000	-2.157096000	-1.264566000
7	2.465968000	0.000000000	0.000000000
7	3.616096000	0.000000000	0.000000000

7 in DMSO			
6	1.192770000	0.000000000	0.000001000
6	-0.507839000	-1.258048000	1.253758000
6	0.381092000	1.272097000	0.000000000
6	0.381091000	-1.272097000	0.000000000
6	-0.507839000	1.258048000	1.253758000
6	-1.384570000	0.000000000	1.252378000
1	1.041607000	2.149825000	0.000001000
1	0.117711000	1.290145000	2.157829000
1	-1.143259000	2.157093000	1.264579000
1	-2.018757000	0.000000000	2.151742000

1	-1.143260000	-2.157093000	1.264579000
1	0.117711000	-1.290145000	2.157829000
1	1.041607000	-2.149825000	0.000001000
6	-0.507838000	1.258048000	-1.253758000
1	-1.143258000	2.157093000	-1.264580000
1	0.117713000	1.290145000	-2.157828000
6	-0.507838000	-1.258048000	-1.253758000
6	-2.266765000	0.000000000	-0.000001000
1	-2.922324000	-0.884465000	-0.000001000
1	-2.922324000	0.884466000	-0.000001000
6	-1.384569000	0.000000000	-1.252379000
1	-2.018756000	0.000000000	-2.151743000
1	0.117712000	-1.290145000	-2.157828000
1	-1.143259000	-2.157093000	-1.264580000
7	2.466034000	0.000000000	0.000000000
7	3.616104000	0.000000000	0.000000000

7 in benzene

6	1.193103000	0.000000000	0.000000000
6	-0.508335000	-1.258519000	1.253430000
6	0.381312000	1.271074000	0.000000000
6	0.381311000	-1.271074000	0.000000000
6	-0.508334000	1.258519000	1.253430000
6	-1.384737000	0.000000000	1.252384000
1	1.041503000	2.149297000	0.000000000
1	0.117129000	1.290955000	2.157476000
1	-1.145035000	2.156934000	1.265202000
1	-2.019269000	0.000000000	2.151674000
1	-1.145036000	-2.156934000	1.265202000
1	0.117128000	-1.290955000	2.157476000
1	1.041502000	-2.149298000	0.000000000
6	-0.508334000	1.258519000	-1.253430000
1	-1.145034000	2.156934000	-1.265202000
1	0.117130000	1.290955000	-2.157475000
6	-0.508334000	-1.258519000	-1.253430000
6	-2.266982000	0.000000000	-0.000001000
1	-2.923198000	-0.884094000	-0.000001000
1	-2.923198000	0.884095000	-0.000001000
6	-1.384736000	0.000000000	-1.252385000
1	-2.019267000	0.000000000	-2.151674000
1	0.117129000	-1.290955000	-2.157475000
1	-1.145035000	-2.156934000	-1.265202000
7	2.468853000	-0.000001000	0.000000000
7	3.616568000	0.000000000	0.000000000

7 in cyclohexane			
6	1.193141000	0.000000000	0.000001000
6	-0.508392000	-1.258570000	1.253397000
6	0.381330000	1.270957000	0.000000000
6	0.381330000	-1.270957000	0.000000000
6	-0.508392000	1.258570000	1.253397000
6	-1.384757000	0.000000000	1.252384000
1	1.041478000	2.149245000	0.000001000
1	0.117062000	1.291043000	2.157438000
1	-1.145229000	2.156917000	1.265282000
1	-2.019327000	0.000000000	2.151663000
1	-1.145230000	-2.156917000	1.265282000
1	0.117062000	-1.291043000	2.157438000
1	1.041477000	-2.149246000	0.000000000
6	-0.508391000	1.258570000	-1.253397000
1	-1.145229000	2.156917000	-1.265282000
1	0.117064000	1.291043000	-2.157438000
6	-0.508392000	-1.258570000	-1.253397000
6	-2.267008000	0.000000000	-0.000001000
1	-2.923301000	-0.884047000	-0.000001000
1	-2.923301000	0.884048000	-0.000001000
6	-1.384756000	0.000000000	-1.252384000
1	-2.019326000	0.000000000	-2.151664000
1	0.117063000	-1.291043000	-2.157438000
1	-1.145229000	-2.156917000	-1.265282000
7	2.469176000	-0.000001000	0.000000000
7	3.616637000	0.000000000	0.000000000

7 in hexane			
6	1.193165000	0.000000000	0.000001000
6	-0.508428000	-1.258602000	1.253377000
6	0.381341000	1.270884000	0.000000000
6	0.381340000	-1.270884000	0.000000000
6	-0.508428000	1.258602000	1.253377000
6	-1.384770000	0.000000000	1.252383000
1	1.041460000	2.149214000	0.000000000
1	0.117021000	1.291098000	2.157415000
1	-1.145350000	2.156907000	1.265333000
1	-2.019364000	0.000000000	2.151657000
1	-1.145350000	-2.156907000	1.265333000
1	0.117021000	-1.291098000	2.157415000
1	1.041460000	-2.149215000	0.000001000
6	-0.508427000	1.258602000	-1.253377000
1	-1.145349000	2.156907000	-1.265333000
1	0.117022000	1.291098000	-2.157415000

6	-0.508428000	-1.258602000	-1.253377000
6	-2.267024000	0.000000000	-0.000001000
1	-2.923365000	-0.884018000	-0.000001000
1	-2.923365000	0.884019000	-0.000001000
6	-1.384769000	0.000000000	-1.252384000
1	-2.019362000	0.000000000	-2.151658000
1	0.117022000	-1.291098000	-2.157415000
1	-1.145350000	-2.156907000	-1.265333000
7	2.469377000	-0.000001000	0.000000000
7	3.616682000	0.000000000	0.000000000

7 in pentane			
6	1.193174000	0.000000000	0.000001000
6	-0.508441000	-1.258613000	1.253369000
6	0.381344000	1.270858000	0.000000000
6	0.381344000	-1.270858000	0.000000000
6	-0.508441000	1.258613000	1.253369000
6	-1.384775000	0.000000000	1.252383000
1	1.041454000	2.149203000	0.000001000
1	0.117006000	1.291117000	2.157407000
1	-1.145393000	2.156903000	1.265351000
1	-2.019377000	0.000000000	2.151654000
1	-1.145394000	-2.156903000	1.265351000
1	0.117006000	-1.291117000	2.157407000
1	1.041453000	-2.149204000	0.000000000
6	-0.508440000	1.258613000	-1.253369000
1	-1.145392000	2.156903000	-1.265352000
1	0.117008000	1.291117000	-2.157407000
6	-0.508440000	-1.258613000	-1.253369000
6	-2.267029000	0.000000000	-0.000001000
1	-2.923389000	-0.884007000	-0.000001000
1	-2.923388000	0.884008000	-0.000001000
6	-1.384774000	0.000000000	-1.252384000
1	-2.019375000	0.000000000	-2.151655000
1	0.117007000	-1.291117000	-2.157407000
1	-1.145393000	-2.156903000	-1.265352000
7	2.469449000	-0.000001000	0.000000000
7	3.616699000	0.000000000	0.000000000

Table S26. Geometries of singlet **14** in Cartesian coordinates in Å optimized at the CPCM(solvent)/MN12-SX/6-311+G(d).

14 in the gas phase			
6	1.916689000	0.195488000	-0.625794000

6	0.724409000	-0.345685000	1.412041000
6	0.214613000	1.610889000	0.532163000
6	0.757436000	-1.469122000	0.353102000
6	-0.601753000	0.454962000	1.222783000
6	0.560957000	0.253654000	-1.363896000
6	-0.255231000	-0.920218000	-0.683672000
6	1.527628000	0.803247000	0.737728000
6	-0.009515000	1.616560000	-0.974435000
6	2.115623000	-1.285226000	-0.315542000
1	0.506455000	-2.467070000	0.729038000
1	0.647543000	0.101617000	-2.447504000
1	2.733124000	0.708809000	-1.147992000
1	0.999367000	-0.652966000	2.426689000
1	0.134766000	2.589287000	1.019625000
1	2.346996000	1.261984000	1.301539000
1	-1.064566000	1.745973000	-1.252614000
1	2.245441000	-1.905079000	-1.213476000
1	0.563597000	2.422778000	-1.454201000
1	2.958376000	-1.475821000	0.363005000
6	-1.326860000	-0.355320000	0.199930000
1	-0.606296000	-1.662328000	-1.410204000
1	-1.177483000	0.732584000	2.111878000
7	-2.580927000	-0.329989000	-0.047808000
7	-3.709259000	-0.349318000	-0.236796000

14 in water			
6	1.927567000	0.167571000	-0.609264000
6	0.700855000	-0.351100000	1.413860000
6	0.240277000	1.615822000	0.529232000
6	0.723634000	-1.474291000	0.354326000
6	-0.605979000	0.477735000	1.210291000
6	0.582744000	0.253358000	-1.364200000
6	-0.262954000	-0.905331000	-0.697123000
6	1.534641000	0.781998000	0.750053000
6	0.036160000	1.627532000	-0.980197000
6	2.093118000	-1.317143000	-0.298325000
1	0.449401000	-2.467906000	0.725976000
1	0.678412000	0.098326000	-2.446205000
1	2.759063000	0.665502000	-1.122114000
1	0.956672000	-0.663525000	2.431695000
1	0.171773000	2.593840000	1.018531000
1	2.355322000	1.223980000	1.324828000
1	-1.012079000	1.780579000	-1.272731000
1	2.219951000	-1.938431000	-1.195520000
1	0.634567000	2.420789000	-1.450265000

1	2.922402000	-1.524836000	0.391660000
6	-1.333096000	-0.313014000	0.171786000
1	-0.622315000	-1.638222000	-1.428071000
1	-1.190435000	0.765525000	2.089829000
7	-2.585701000	-0.317144000	-0.051736000
7	-3.720660000	-0.353491000	-0.226871000

14 in DMSO			
6	1.927430000	0.167932000	-0.609483000
6	0.701165000	-0.351021000	1.413842000
6	0.239943000	1.615765000	0.529257000
6	0.724077000	-1.474225000	0.354323000
6	-0.605926000	0.477449000	1.210454000
6	0.582459000	0.253354000	-1.364200000
6	-0.262856000	-0.905533000	-0.696943000
6	1.534555000	0.782282000	0.749886000
6	0.035563000	1.627388000	-0.980137000
6	2.093418000	-1.316733000	-0.298539000
1	0.450152000	-2.467900000	0.726038000
1	0.678005000	0.098350000	-2.446225000
1	2.758730000	0.666062000	-1.122462000
1	0.957237000	-0.663374000	2.431640000
1	0.171288000	2.593792000	1.018527000
1	2.355225000	1.224485000	1.324514000
1	-1.012771000	1.780122000	-1.272482000
1	2.220284000	-1.938009000	-1.195740000
1	0.633644000	2.420813000	-1.450340000
1	2.922881000	-1.524200000	0.391301000
6	-1.333019000	-0.313552000	0.172149000
1	-0.622117000	-1.638545000	-1.427827000
1	-1.190277000	0.765115000	2.090109000
7	-2.585644000	-0.317315000	-0.051678000
7	-3.720518000	-0.353448000	-0.226994000

14 in benzene			
6	1.921589000	0.182984000	-0.618516000
6	0.713985000	-0.347867000	1.412998000
6	0.225991000	1.613246000	0.530522000
6	0.742424000	-1.471433000	0.353990000
6	-0.603668000	0.465399000	1.217257000
6	0.570604000	0.253290000	-1.364119000
6	-0.258678000	-0.913819000	-0.689561000
6	1.530837000	0.793964000	0.743045000
6	0.010744000	1.621357000	-0.977379000
6	2.105732000	-1.299545000	-0.307617000

1	0.481260000	-2.467515000	0.728243000
1	0.661151000	0.099615000	-2.446973000
1	2.744716000	0.689450000	-1.136729000
1	0.980533000	-0.657267000	2.429146000
1	0.151071000	2.591539000	1.018681000
1	2.350875000	1.245329000	1.311655000
1	-1.041379000	1.761222000	-1.261946000
1	2.234090000	-1.920209000	-1.205131000
1	0.595261000	2.421750000	-1.453000000
1	2.942534000	-1.497619000	0.376141000
6	-1.329686000	-0.336150000	0.187275000
1	-0.613654000	-1.651842000	-1.417895000
1	-1.183531000	0.747759000	2.101861000
7	-2.583034000	-0.324379000	-0.049407000
7	-3.714419000	-0.351445000	-0.232224000

14 in cyclohexane			
6	1.920956000	0.184593000	-0.619467000
6	0.715339000	-0.347552000	1.412892000
6	0.224507000	1.612958000	0.530692000
6	0.744370000	-1.471132000	0.353919000
6	-0.603423000	0.464089000	1.217979000
6	0.569347000	0.253304000	-1.364101000
6	-0.258228000	-0.914680000	-0.688789000
6	1.530425000	0.795188000	0.742336000
6	0.008112000	1.620720000	-0.977046000
6	2.107023000	-1.297702000	-0.308609000
1	0.484549000	-2.467462000	0.728418000
1	0.659371000	0.099797000	-2.447046000
1	2.743211000	0.691946000	-1.138219000
1	0.982986000	-0.656652000	2.428856000
1	0.148929000	2.591271000	1.018747000
1	2.350383000	1.247520000	1.310315000
1	-1.044399000	1.759228000	-1.260791000
1	2.235553000	-1.918283000	-1.206166000
1	0.591175000	2.421855000	-1.453220000
1	2.944595000	-1.494788000	0.374492000
6	-1.329321000	-0.338588000	0.188894000
1	-0.612725000	-1.653233000	-1.416868000
1	-1.182786000	0.745861000	2.103131000
7	-2.582743000	-0.325119000	-0.049182000
7	-3.713753000	-0.351202000	-0.232797000

14 in hexane			
6	1.920569000	0.185575000	-0.620046000

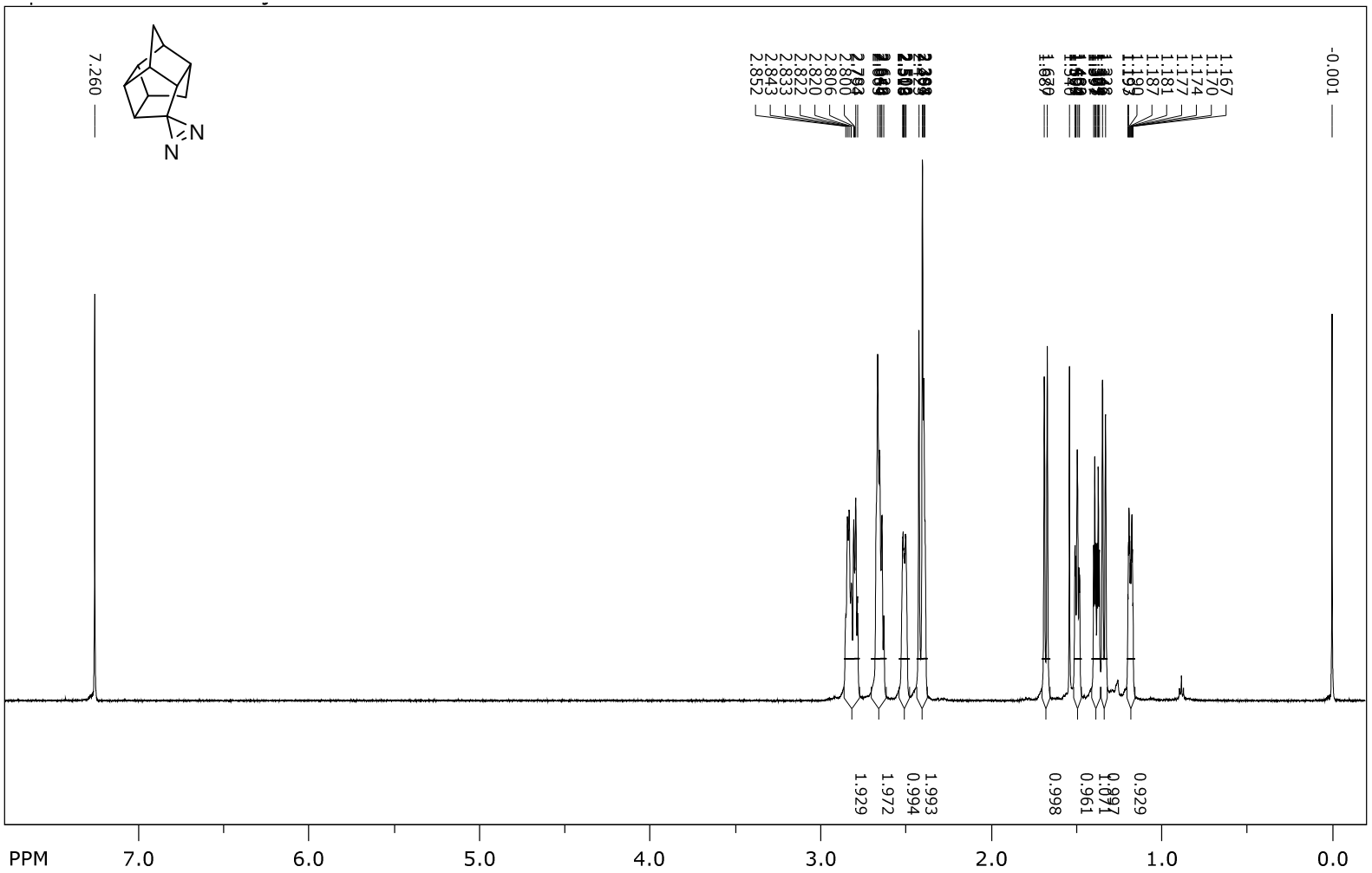
6	0.716163000	-0.347364000	1.412826000
6	0.223603000	1.612781000	0.530800000
6	0.745555000	-1.470949000	0.353871000
6	-0.603273000	0.463286000	1.218419000
6	0.568581000	0.253316000	-1.364089000
6	-0.257953000	-0.915202000	-0.688320000
6	1.530173000	0.795933000	0.741906000
6	0.006508000	1.620333000	-0.976837000
6	2.107808000	-1.296577000	-0.309218000
1	0.486551000	-2.467428000	0.728517000
1	0.658288000	0.099916000	-2.447090000
1	2.742292000	0.693469000	-1.139123000
1	0.984480000	-0.656282000	2.428676000
1	0.147626000	2.591104000	1.018794000
1	2.350080000	1.248853000	1.309502000
1	-1.046238000	1.758014000	-1.260081000
1	2.236445000	-1.917104000	-1.206802000
1	0.588682000	2.421921000	-1.453347000
1	2.945850000	-1.493062000	0.373481000
6	-1.329098000	-0.340079000	0.189883000
1	-0.612156000	-1.654078000	-1.416245000
1	-1.182328000	0.744697000	2.103908000
7	-2.582567000	-0.325569000	-0.049046000
7	-3.713346000	-0.351051000	-0.233149000

14 in pentane			
6	1.920431000	0.185925000	-0.620251000
6	0.716457000	-0.347297000	1.412802000
6	0.223281000	1.612718000	0.530840000
6	0.745977000	-1.470884000	0.353853000
6	-0.603220000	0.462999000	1.218575000
6	0.568309000	0.253321000	-1.364084000
6	-0.257855000	-0.915387000	-0.688153000
6	1.530083000	0.796197000	0.741753000
6	0.005937000	1.620195000	-0.976762000
6	2.108087000	-1.296176000	-0.309435000
1	0.487263000	-2.467416000	0.728551000
1	0.657902000	0.099960000	-2.447105000
1	2.741965000	0.694012000	-1.139445000
1	0.985011000	-0.656152000	2.428612000
1	0.147163000	2.591044000	1.018812000
1	2.349972000	1.249327000	1.309213000
1	-1.046892000	1.757582000	-1.259827000
1	2.236763000	-1.916684000	-1.207029000
1	0.587794000	2.421945000	-1.453391000

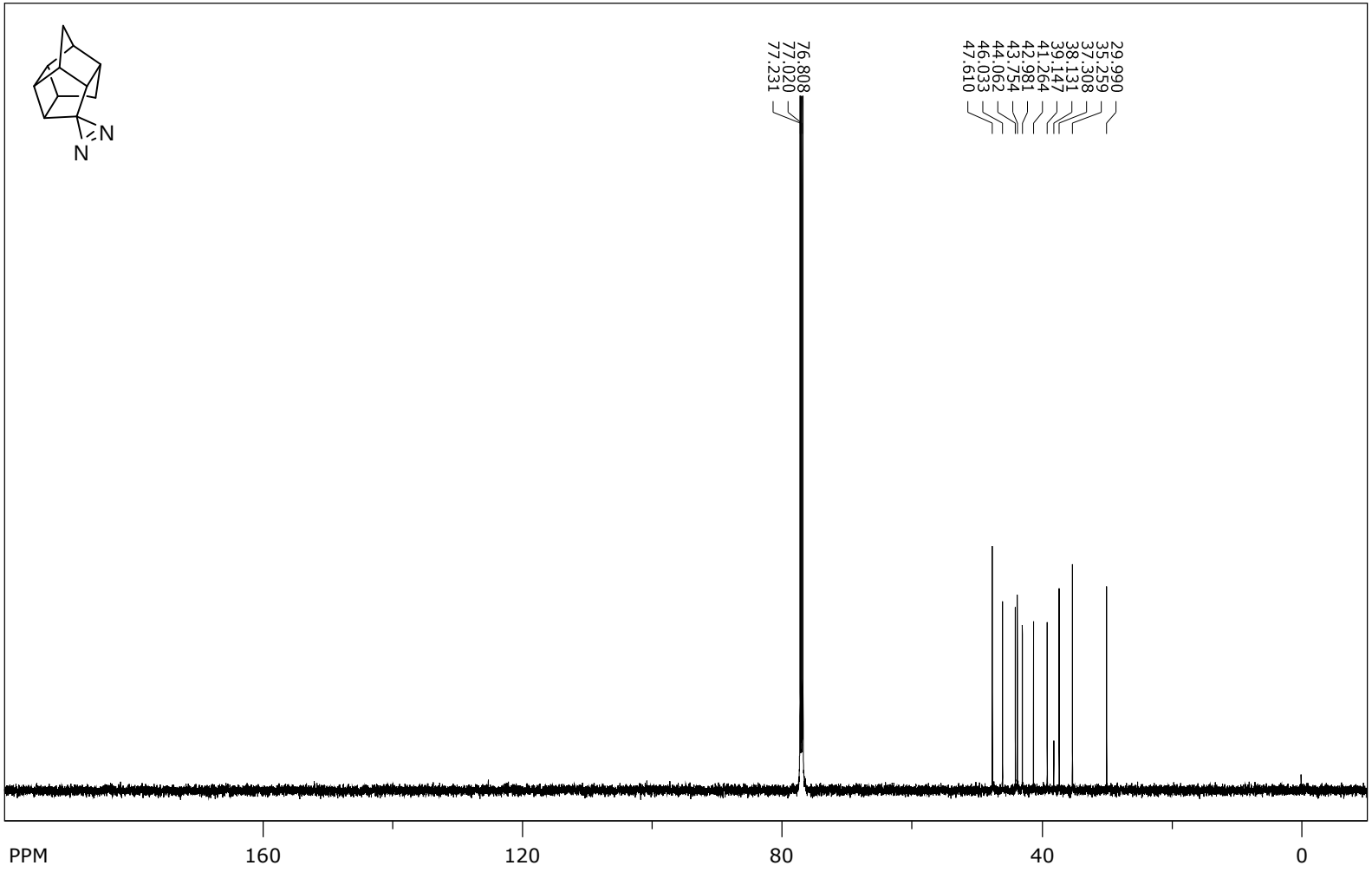
1	2.946297000	-1.492448000	0.373120000
6	-1.329019000	-0.340611000	0.190236000
1	-0.611953000	-1.654378000	-1.416024000
1	-1.182164000	0.744281000	2.104185000
7	-2.582504000	-0.325729000	-0.048998000
7	-3.713201000	-0.350996000	-0.233274000

9. NMR spectra

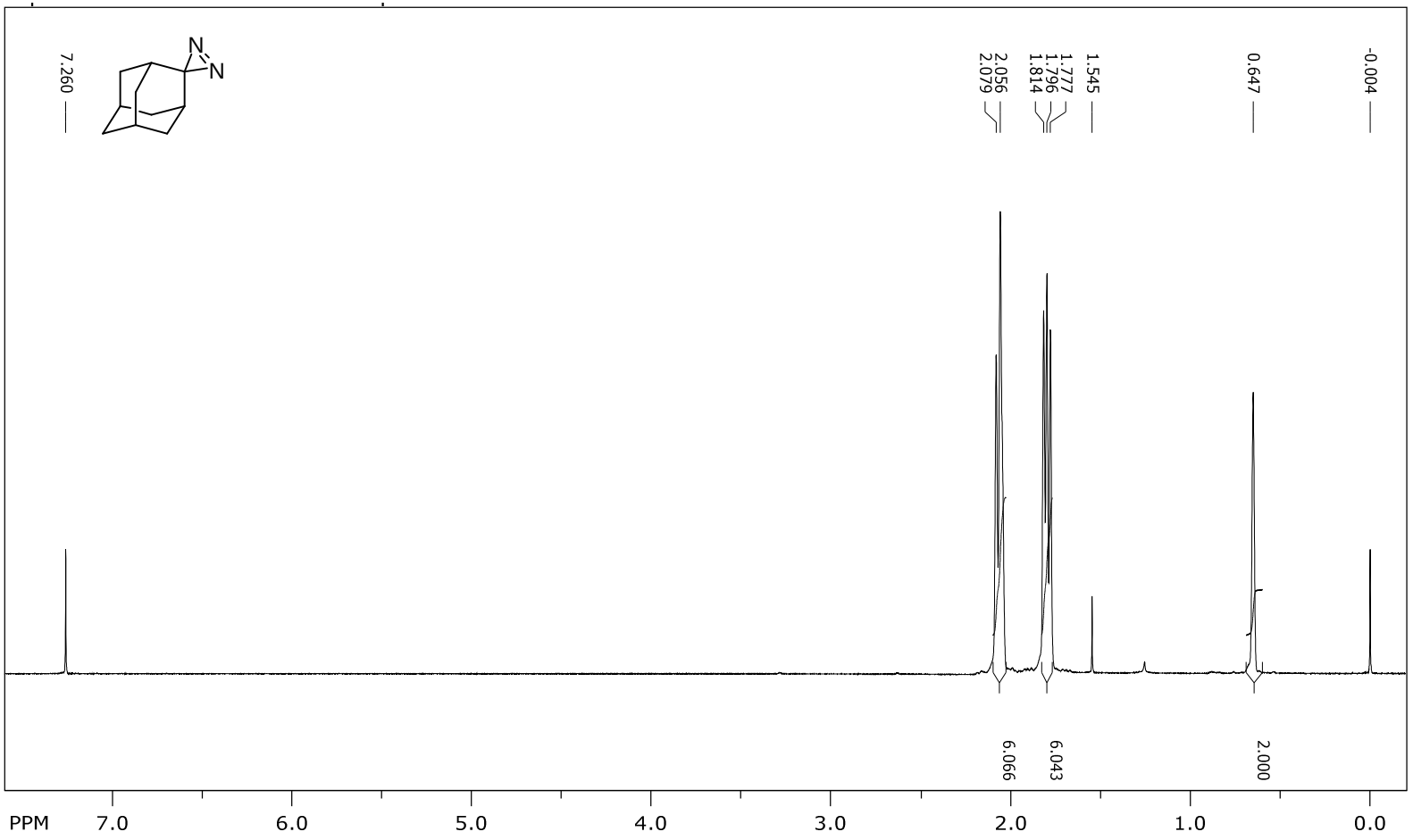
^{1}H NMR (600 MHz, $CDCl_3$) of **1**



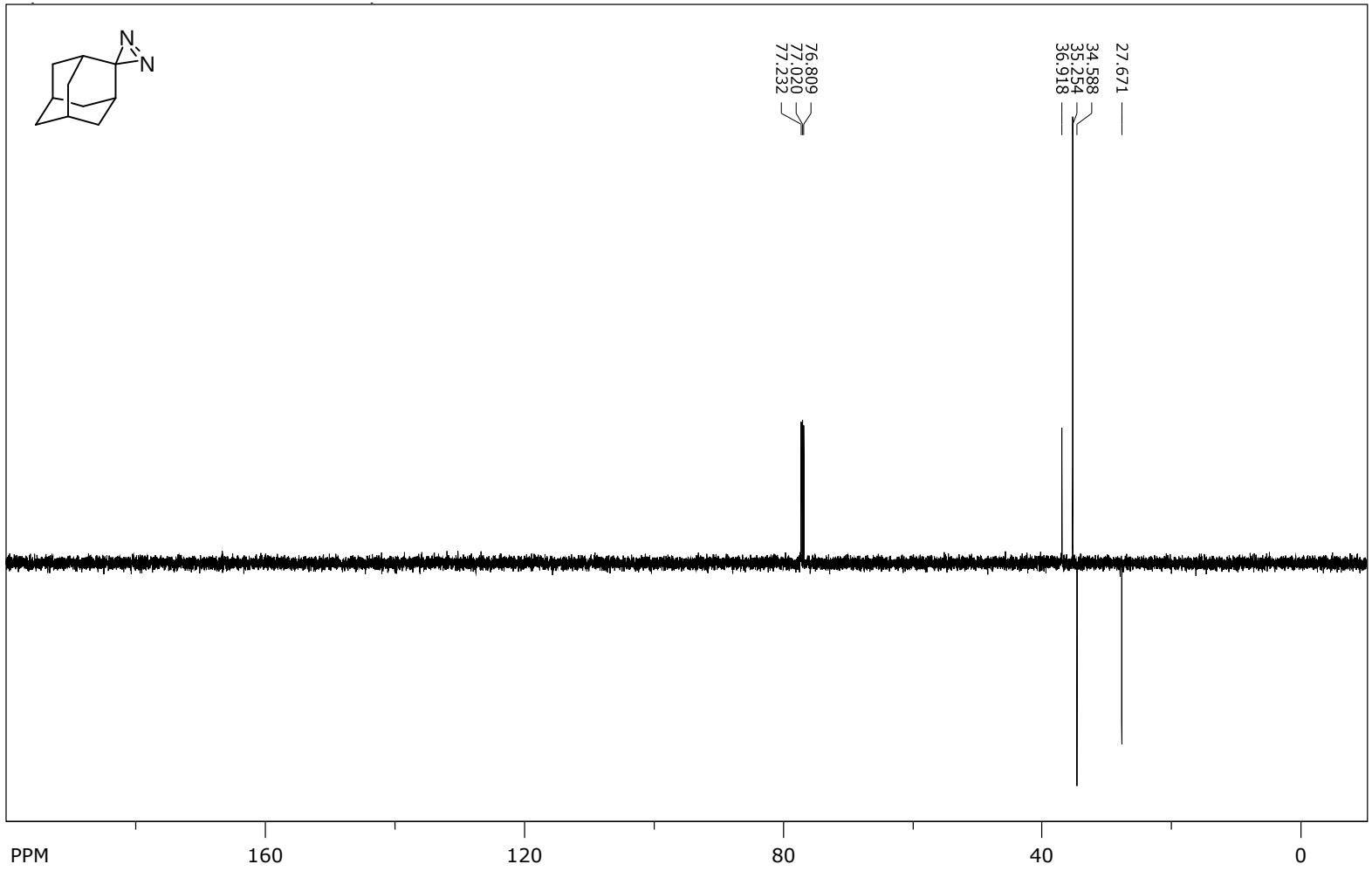
^{13} C NMR (150 MHz, $CDCl_3$) of **1**



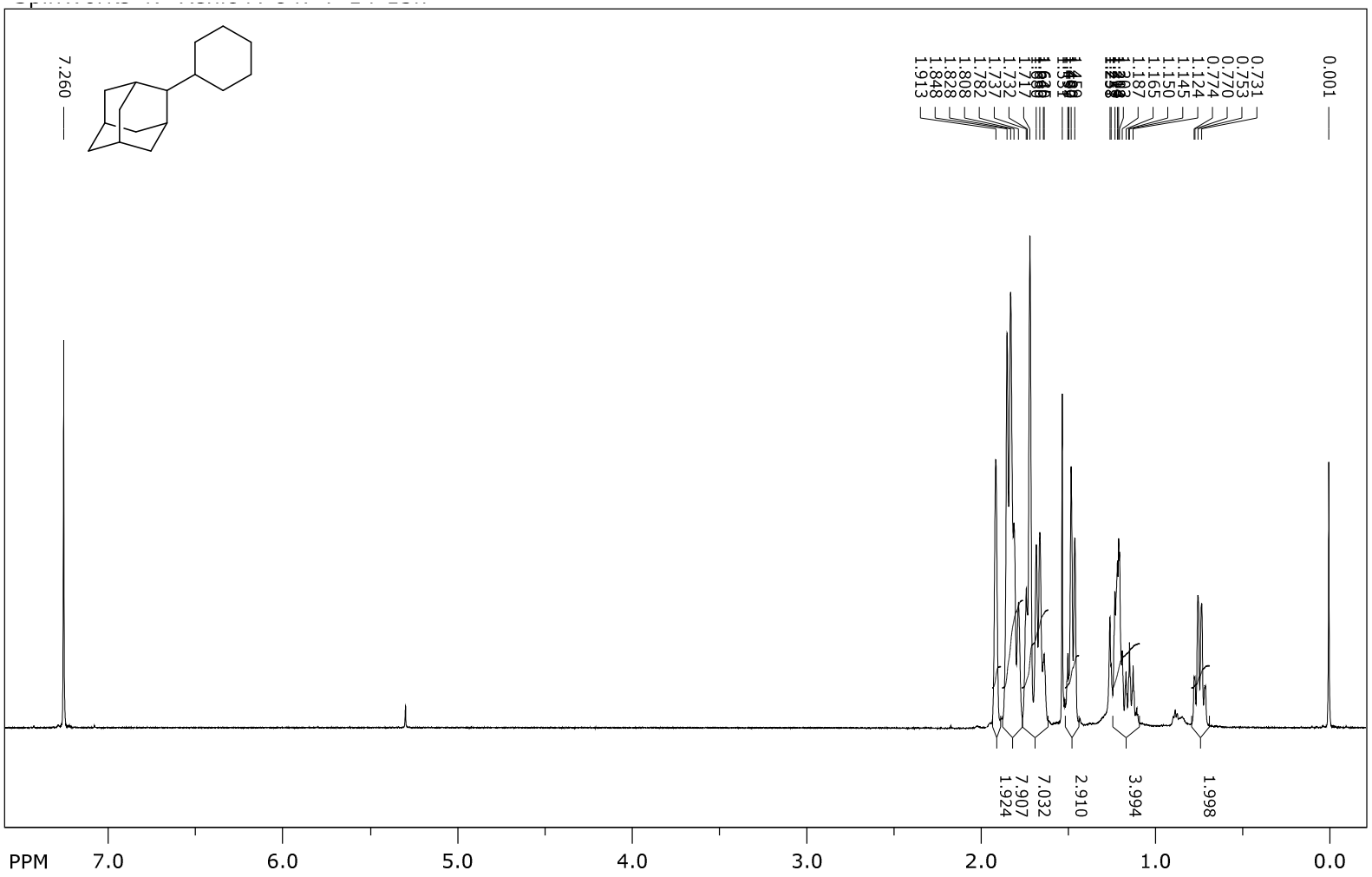
^{1}H NMR (300 MHz, $CDCl_3$) of **2**



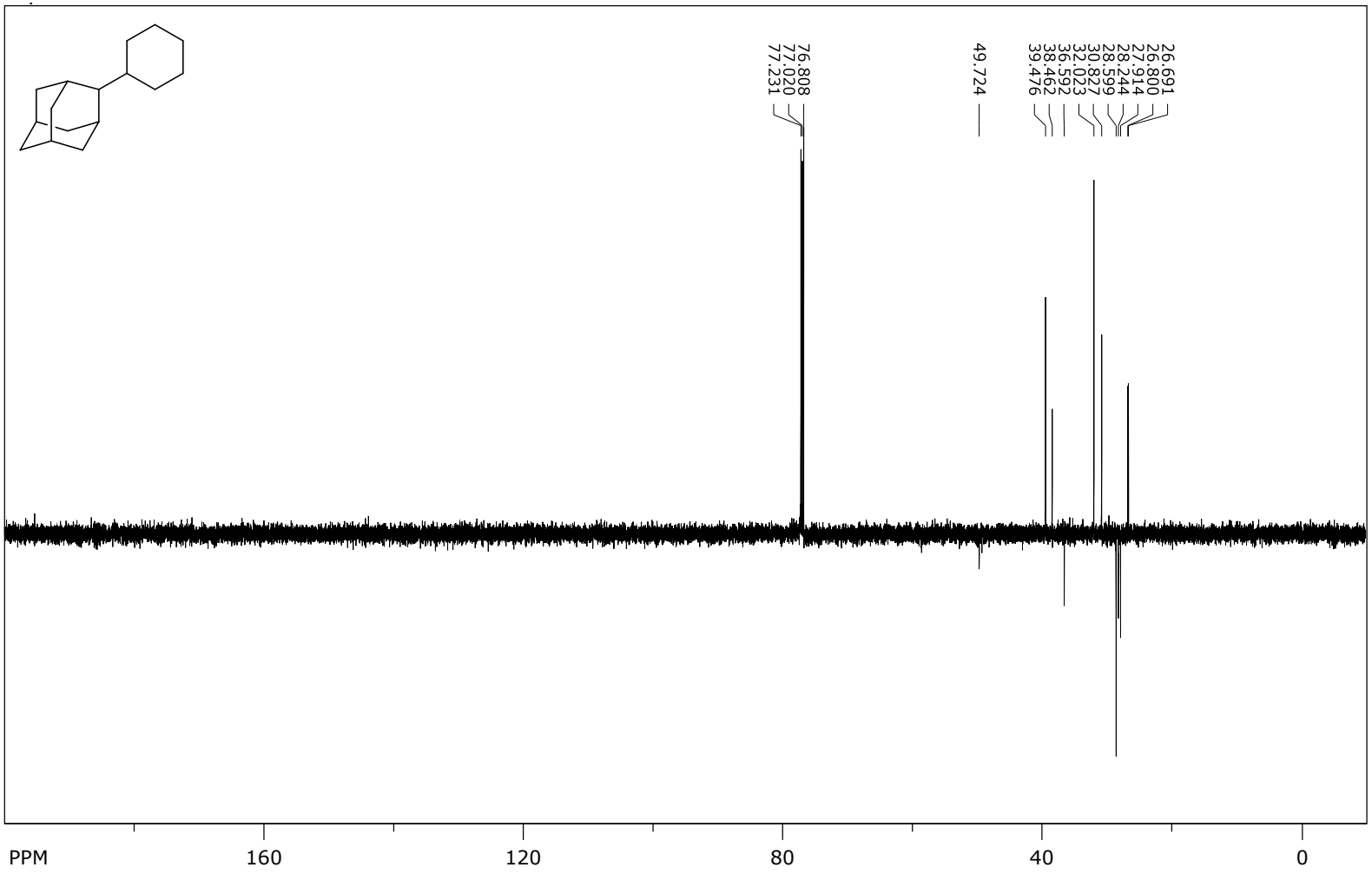
^{13}C NMR (75 MHz, CDCl3) of **2**



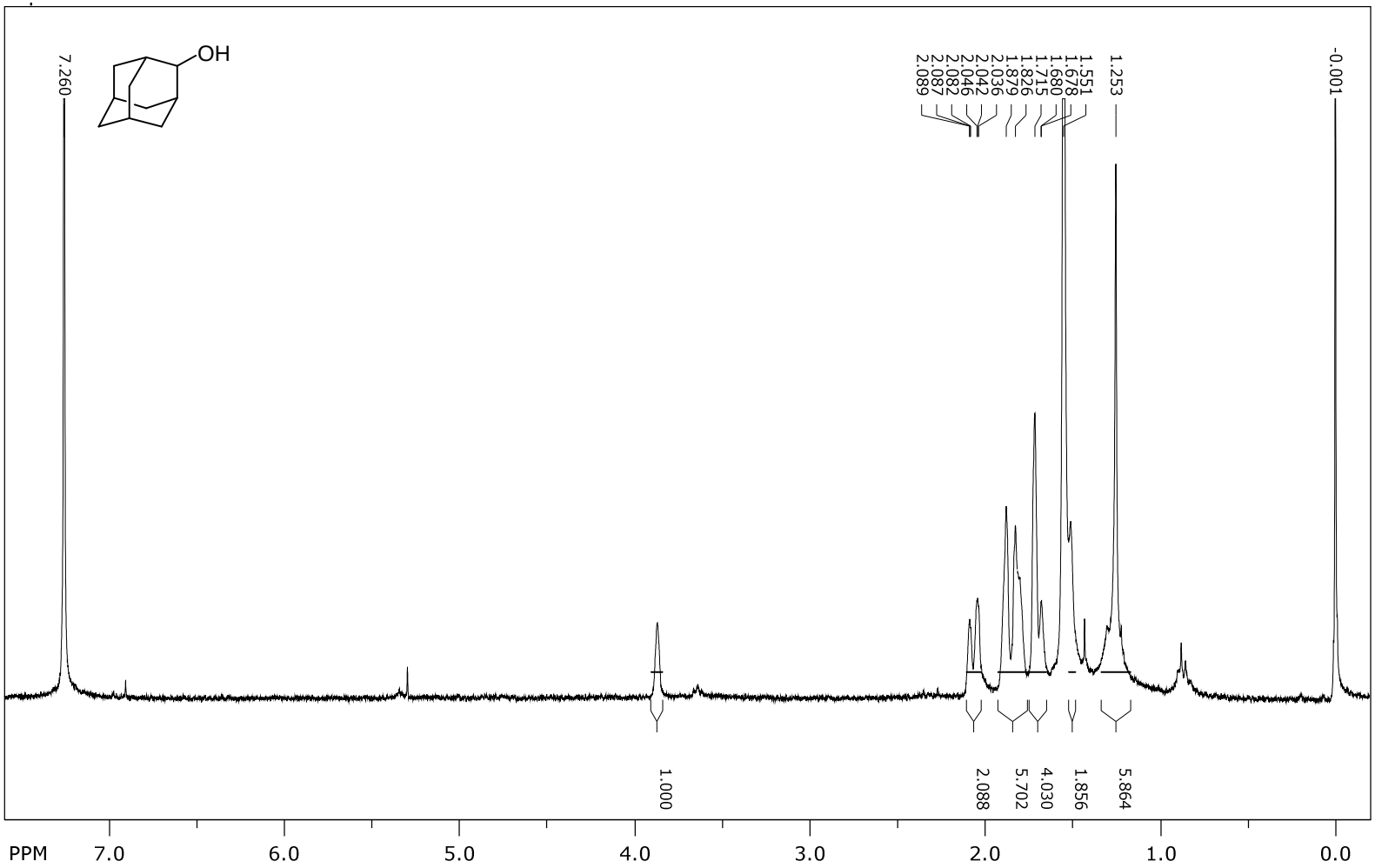
^{1}H NMR (600 MHz, $CDCl_3$) of **9**



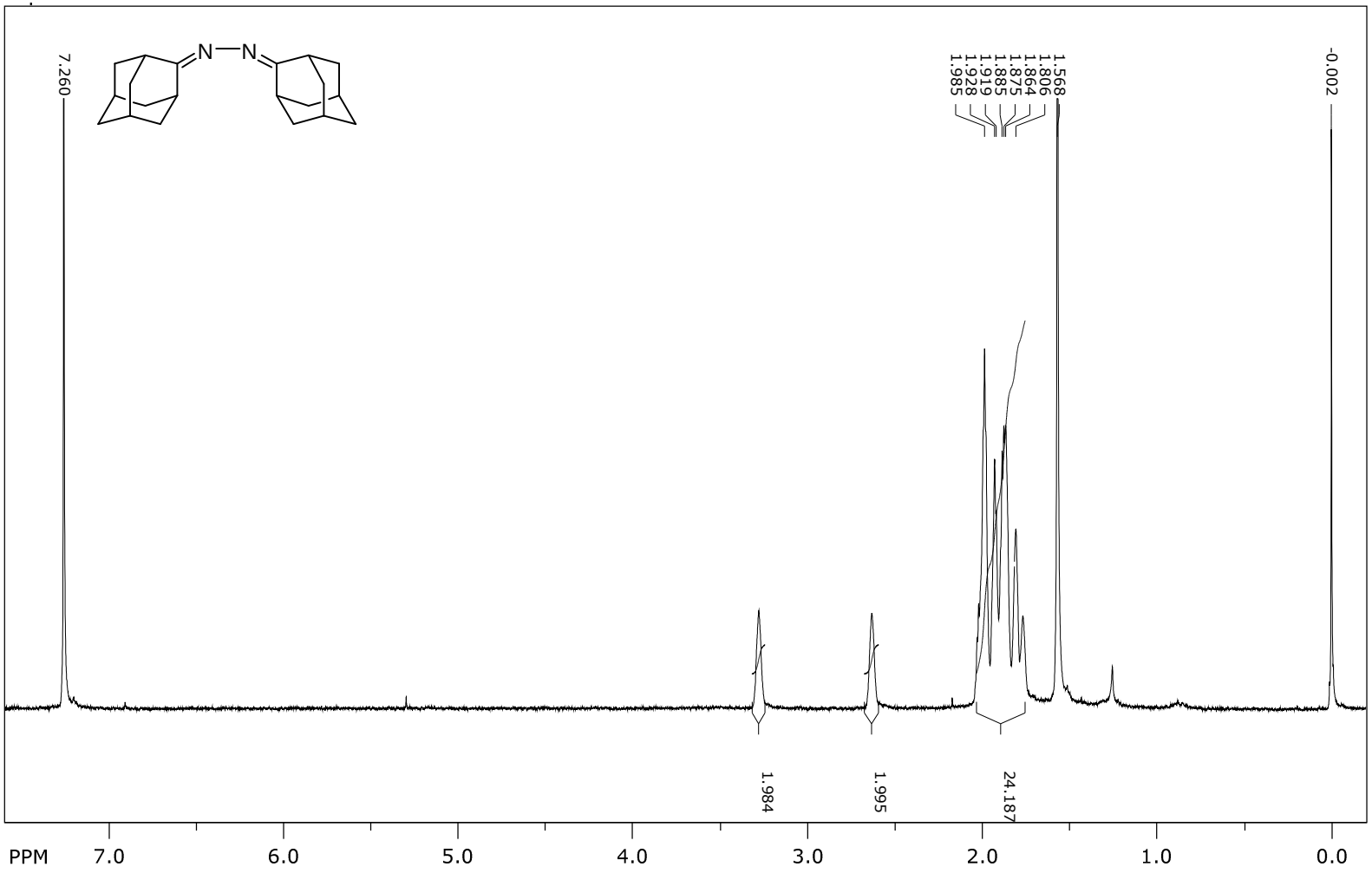
^{13}C NMR (150 MHz, $CDCl_3$) of **9**



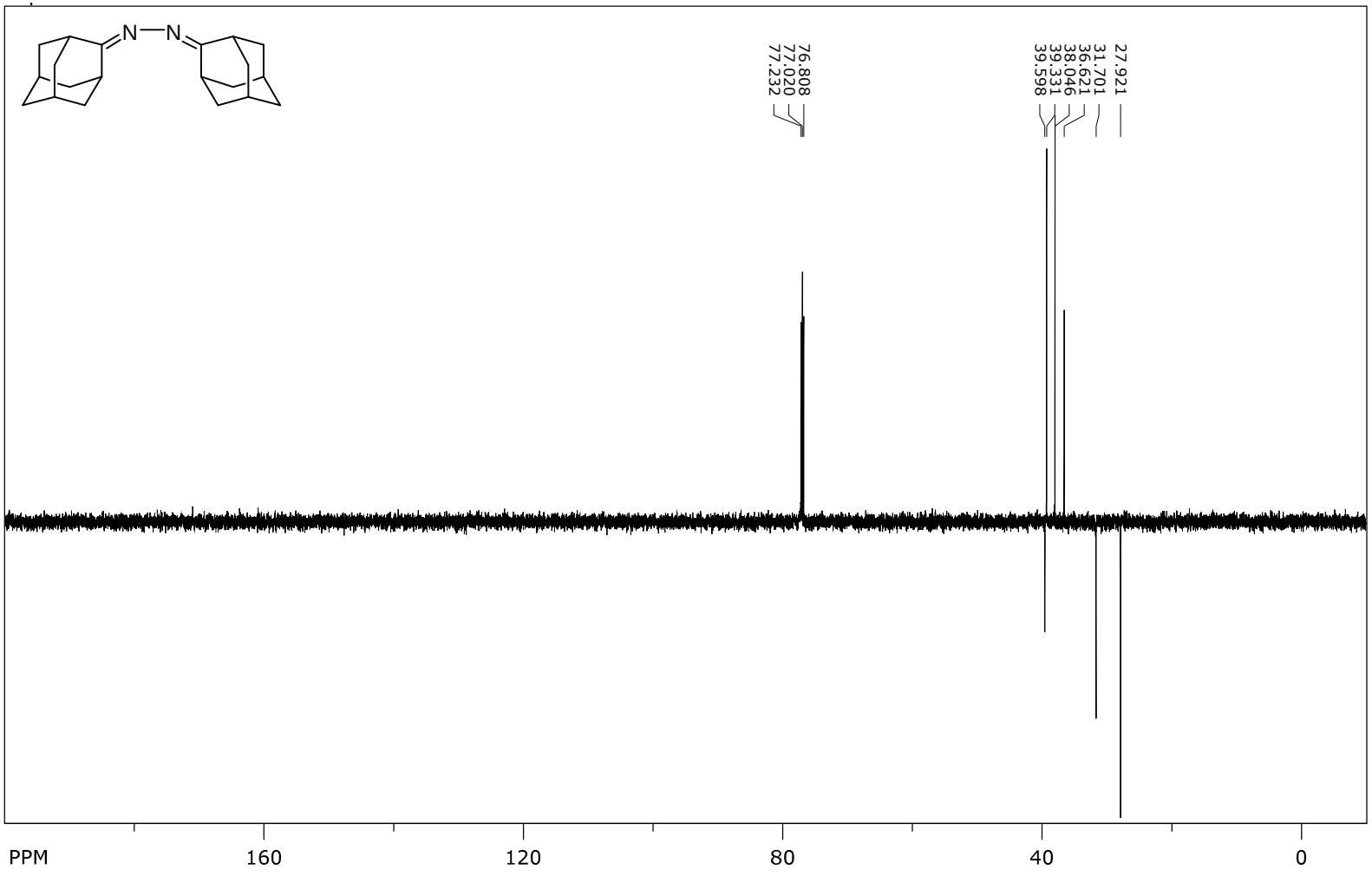
^{1}H NMR (600 MHz, $CDCl_3$) of **10**



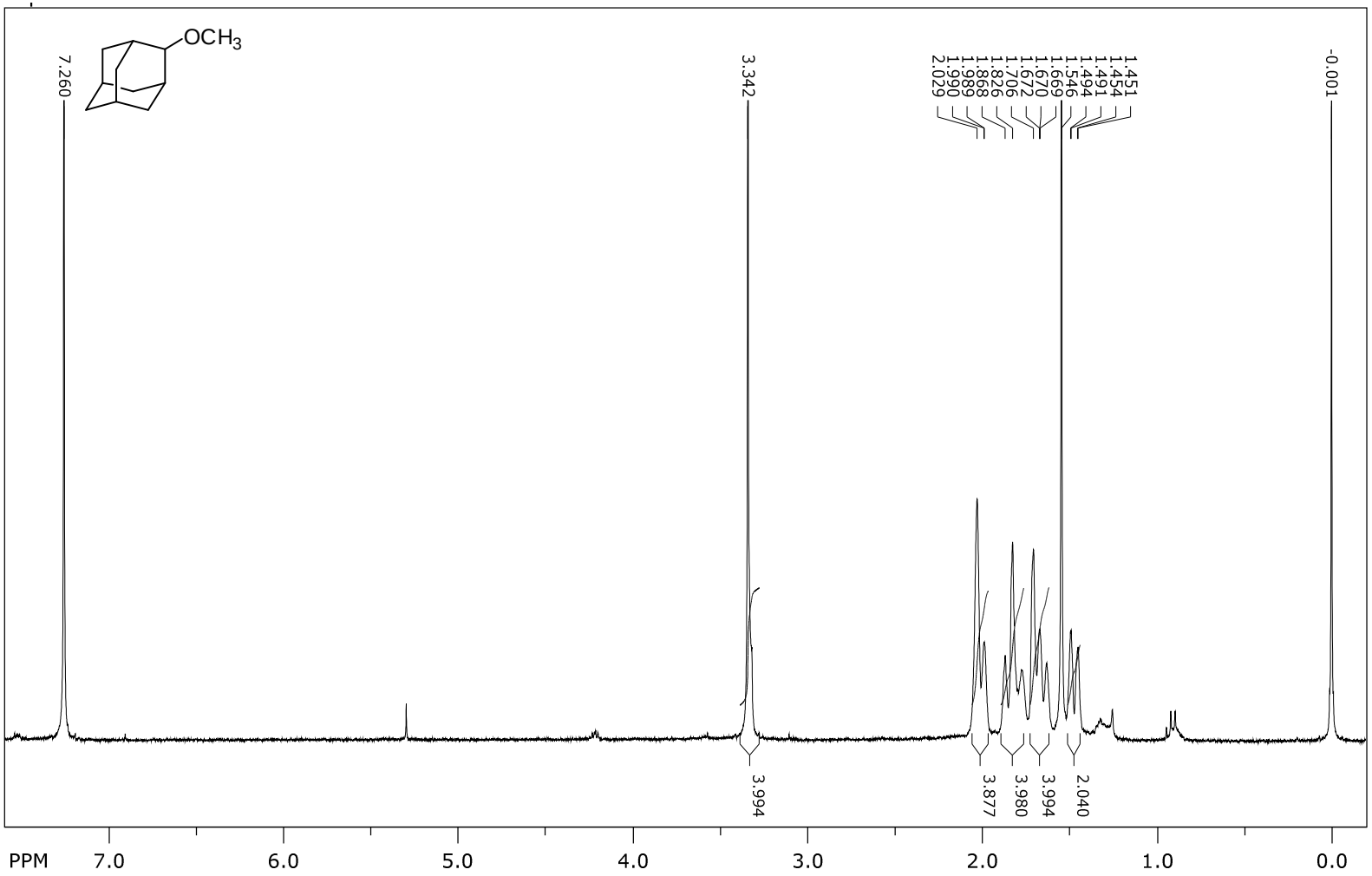
^{1}H NMR (300 MHz, $CDCl_3$) of **12**



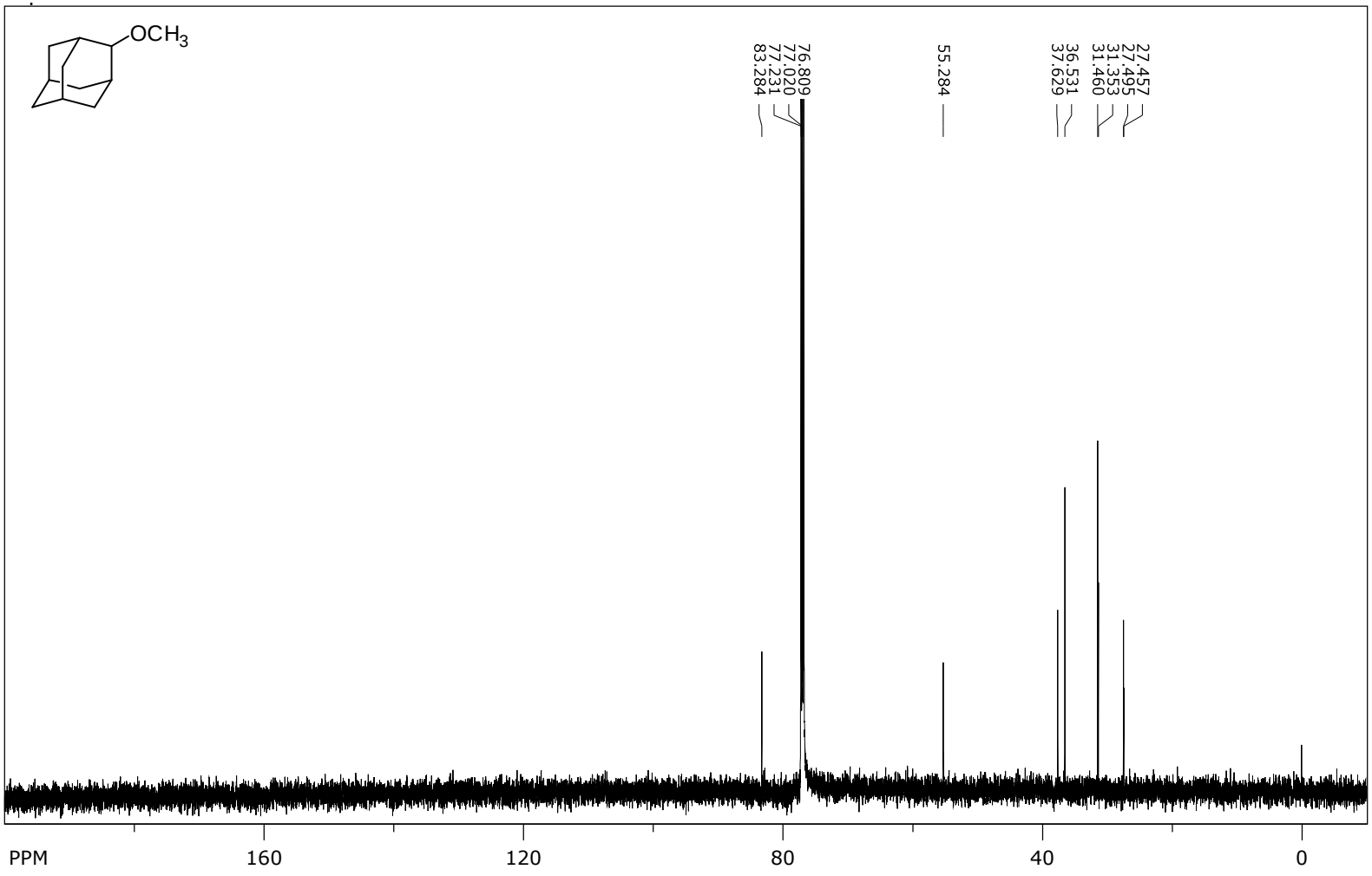
^{13}C NMR (150 MHz, $CDCl_3$) of **12**



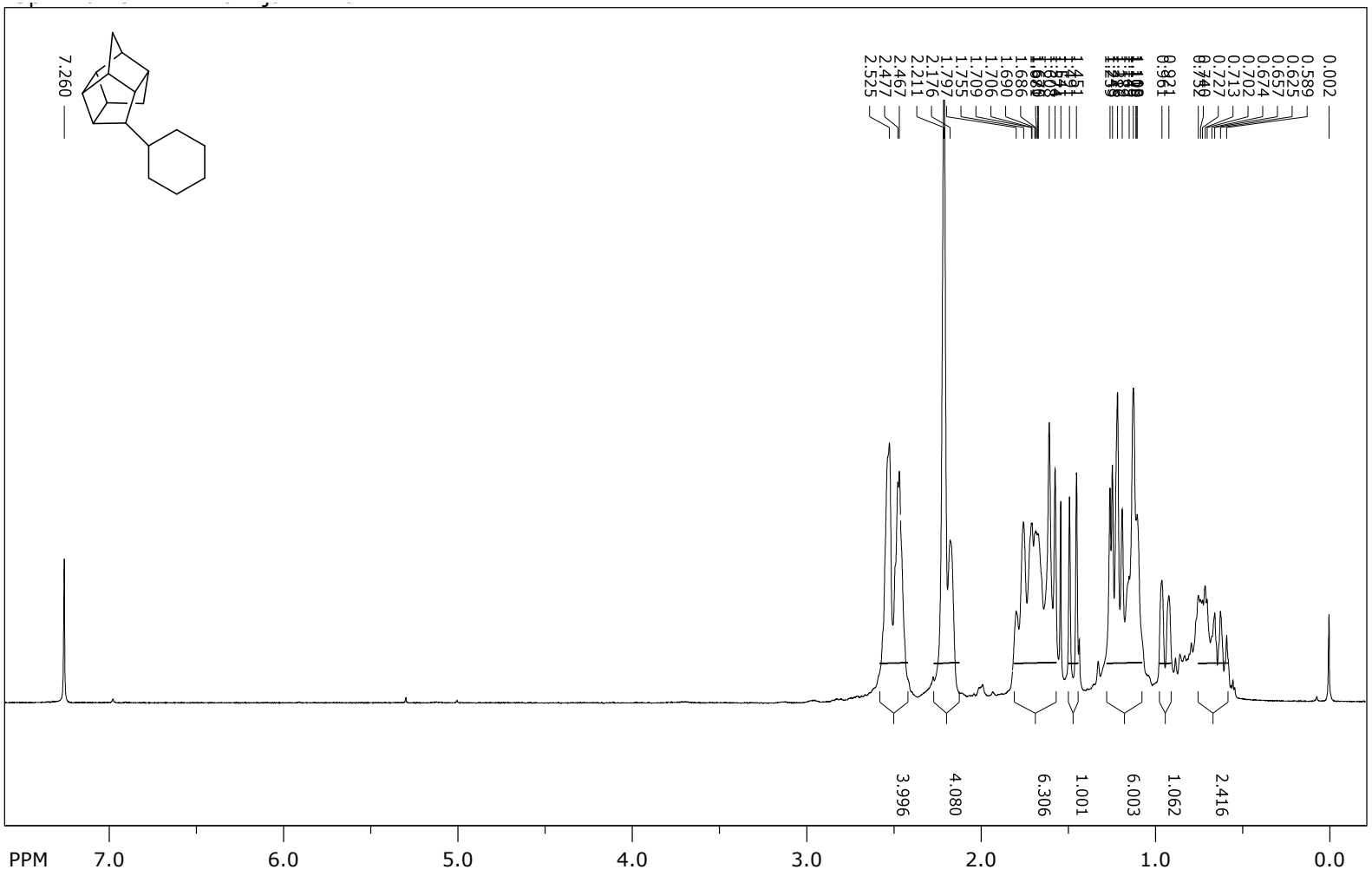
^{1}H NMR (300 MHz, $CDCl_3$) of **13**



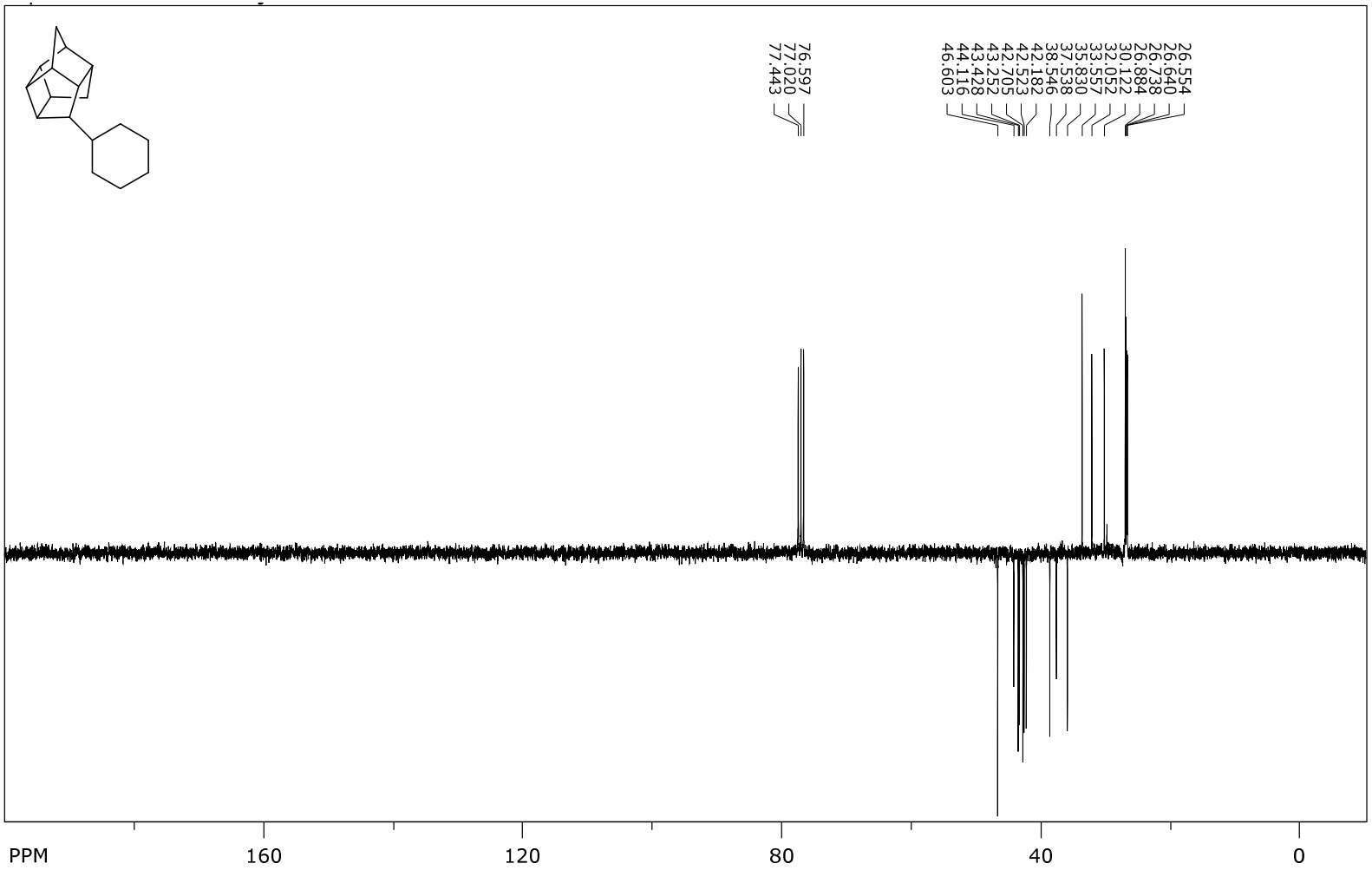
^{13}C NMR (150 MHz, $CDCl_3$) of **13**



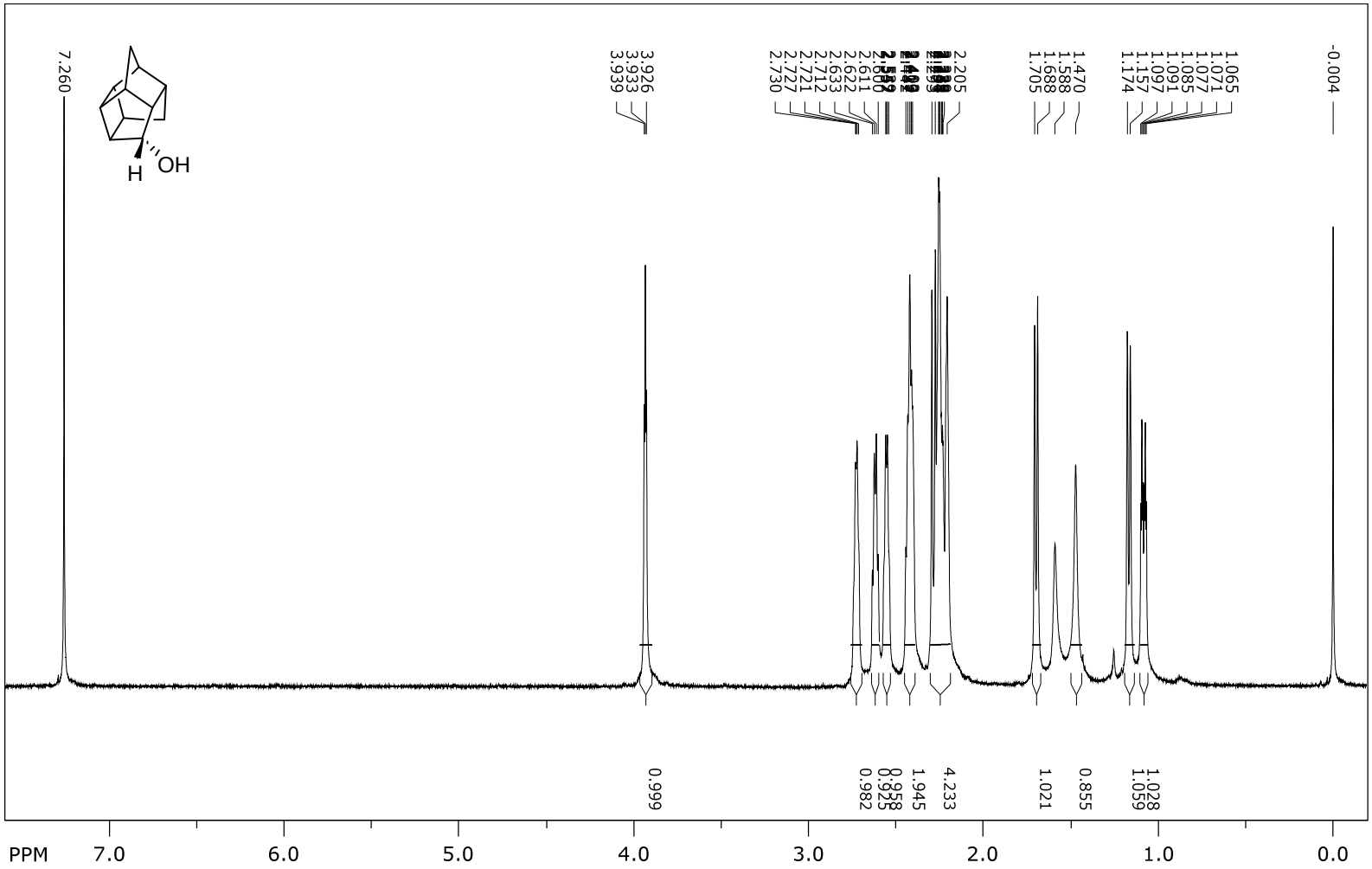
^{1}H NMR (300 MHz, $CDCl_3$) of **16**



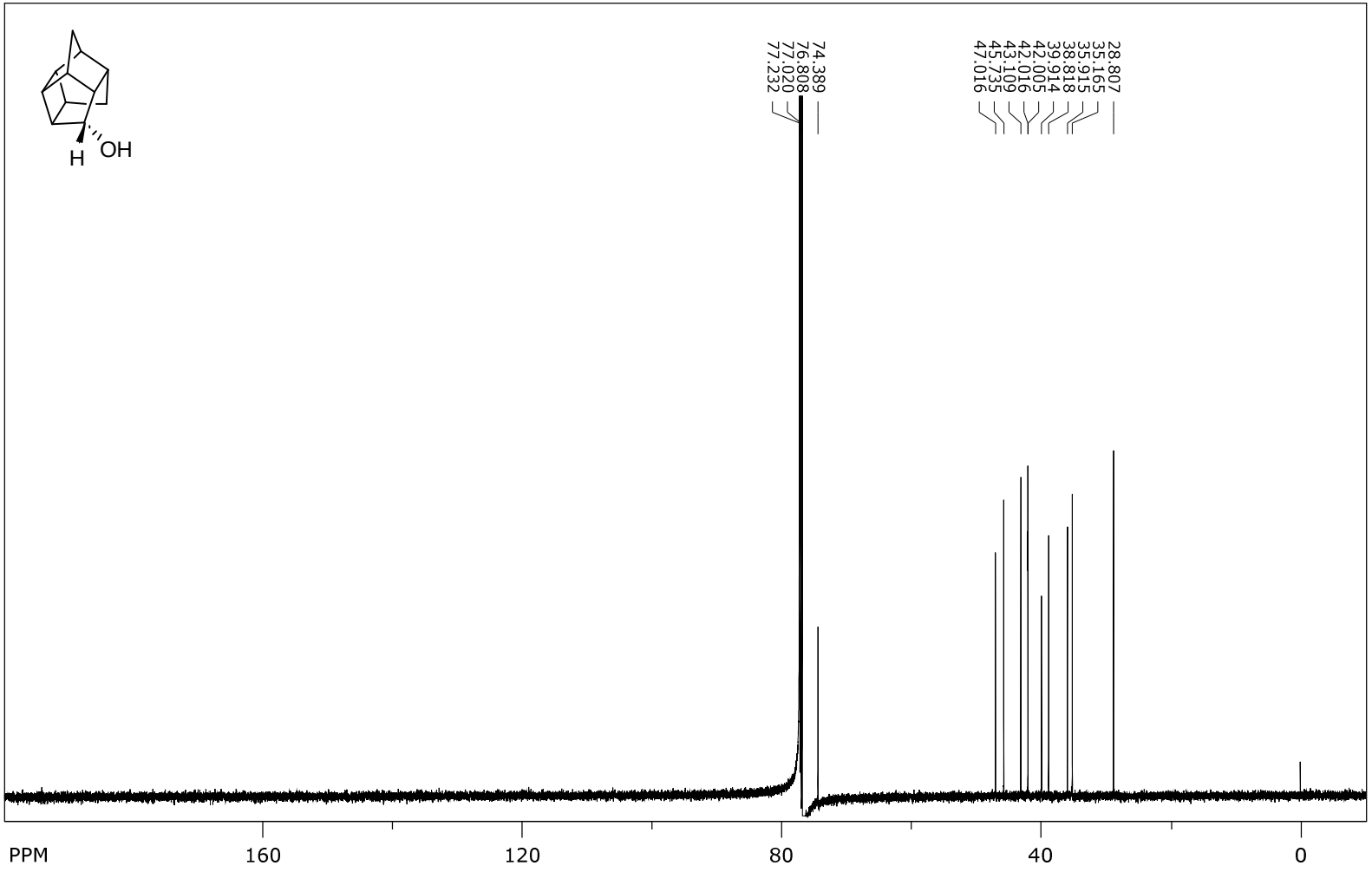
^{13}C NMR (75 MHz, $CDCl_3$) of **16**



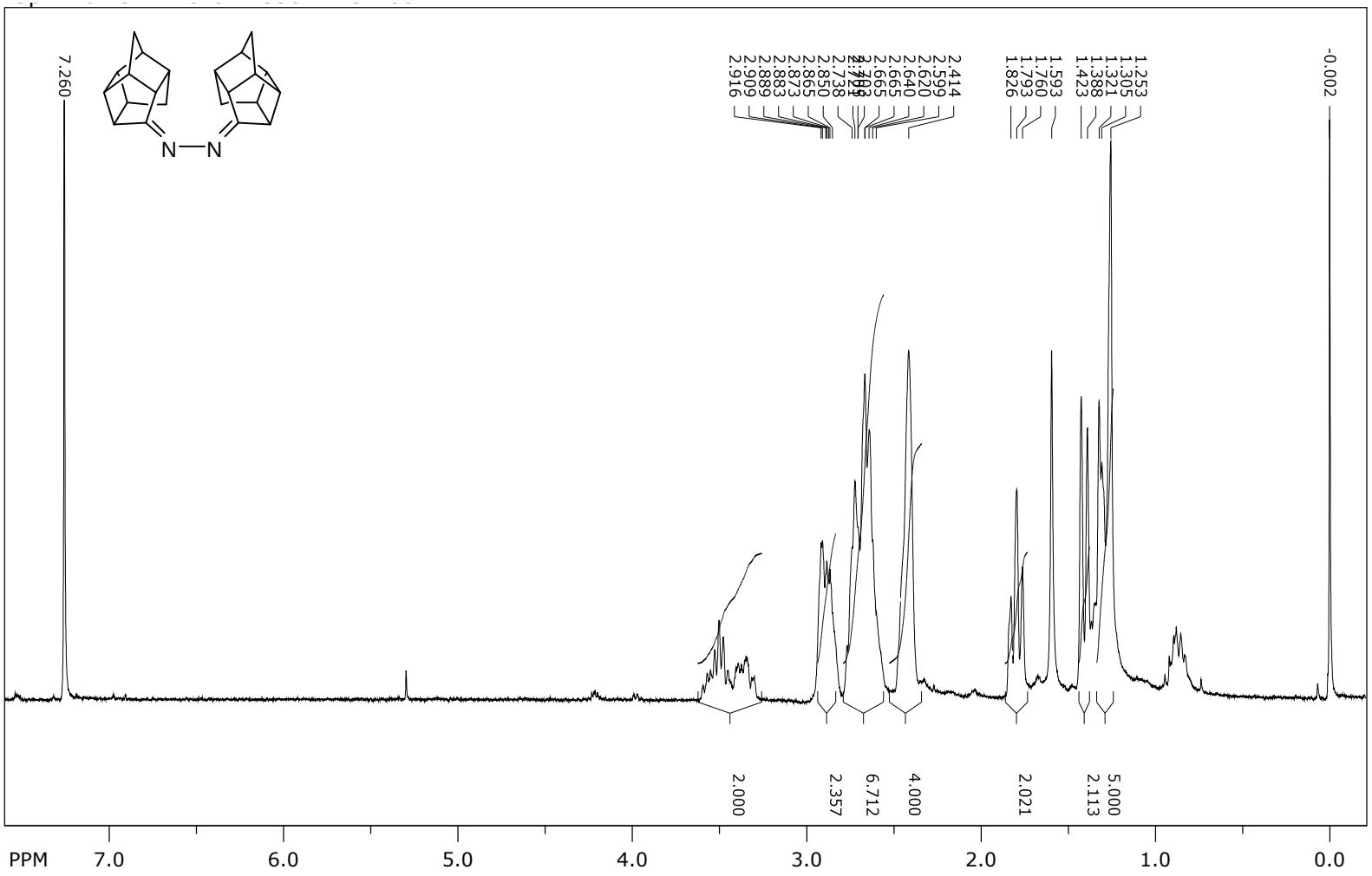
^{1}H NMR (600 MHz, $CDCl_3$) of **17**



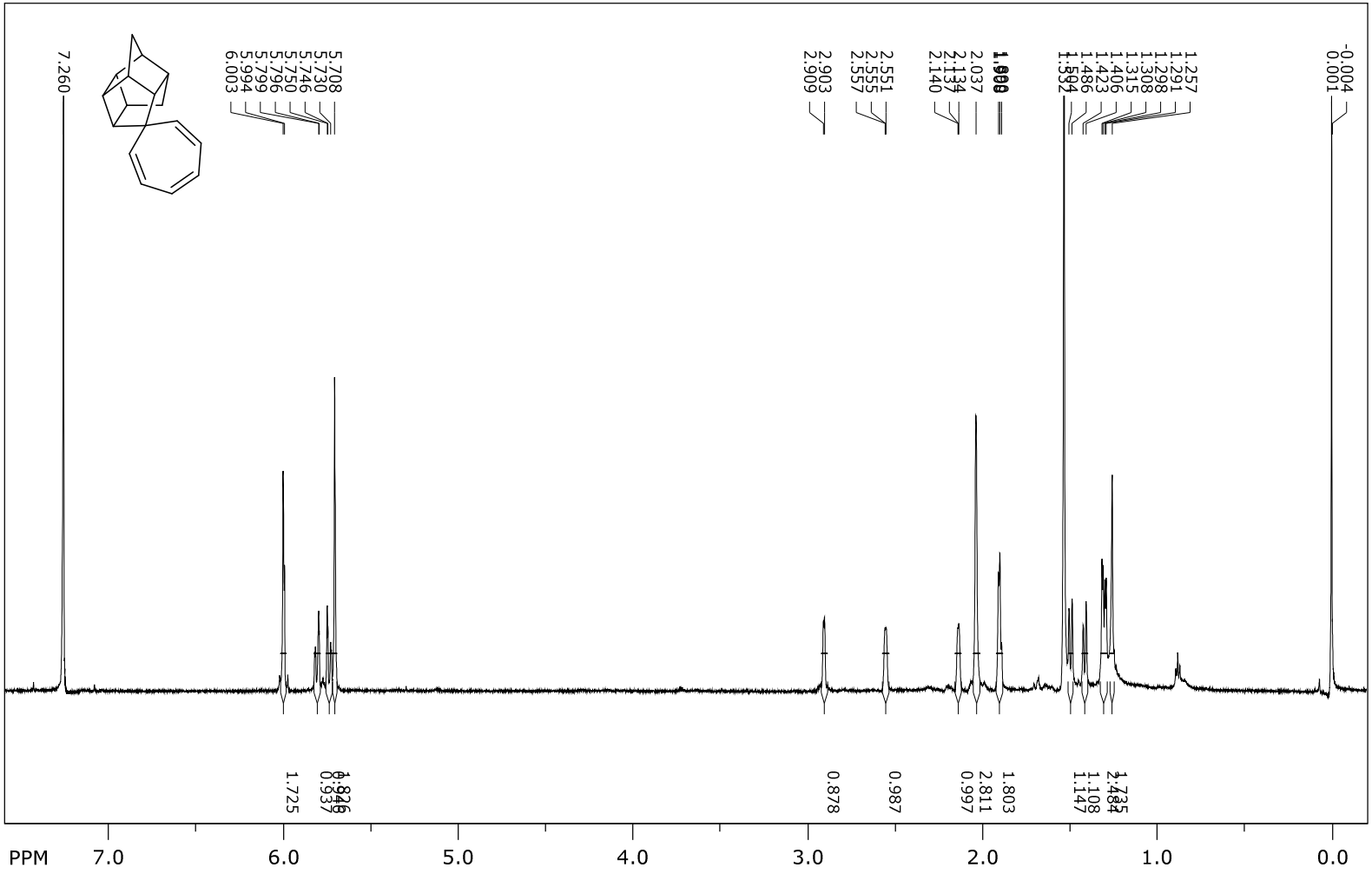
^{13}C NMR (150 MHz, $CDCl_3$) of **17**



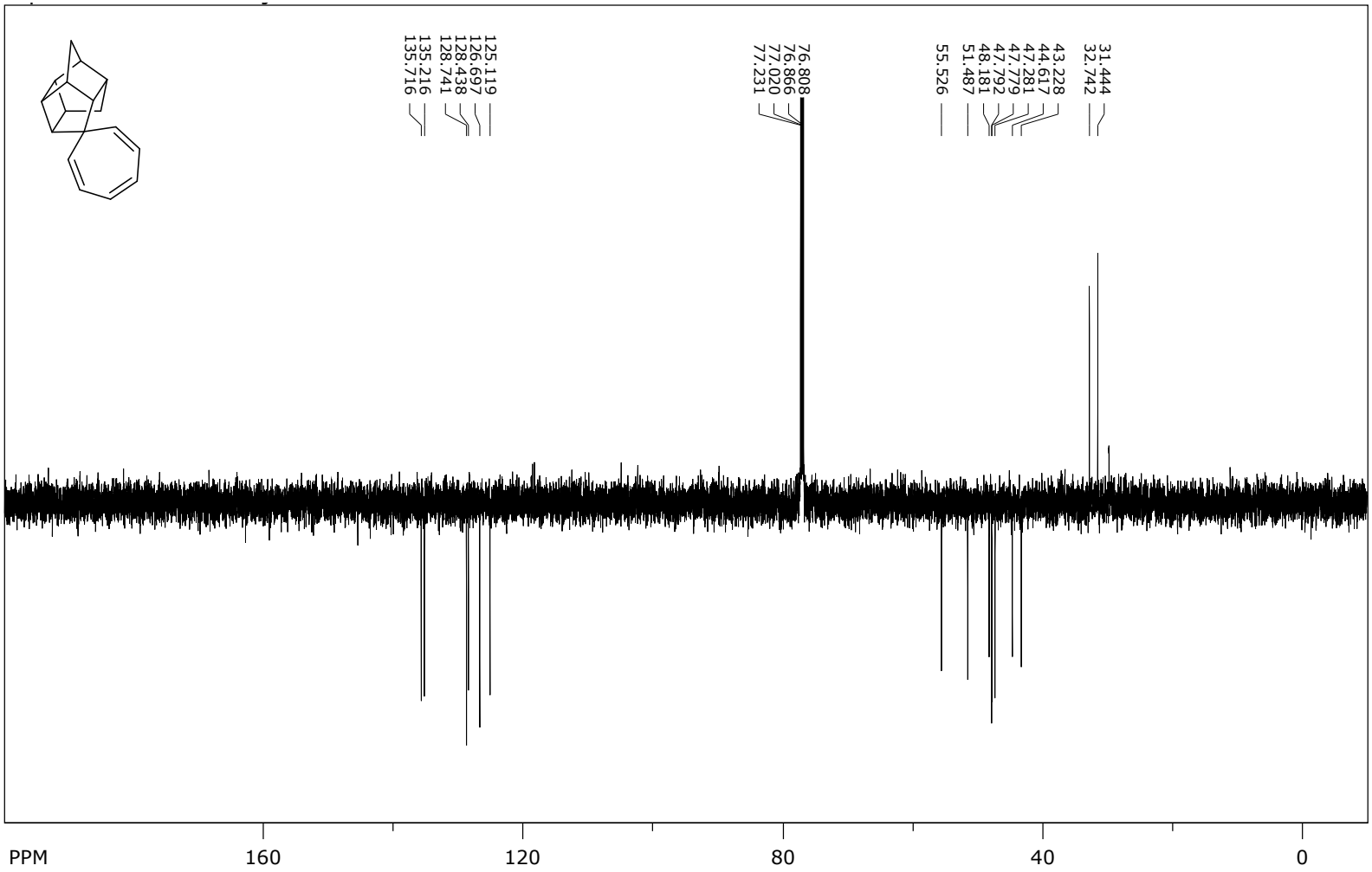
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of **18**



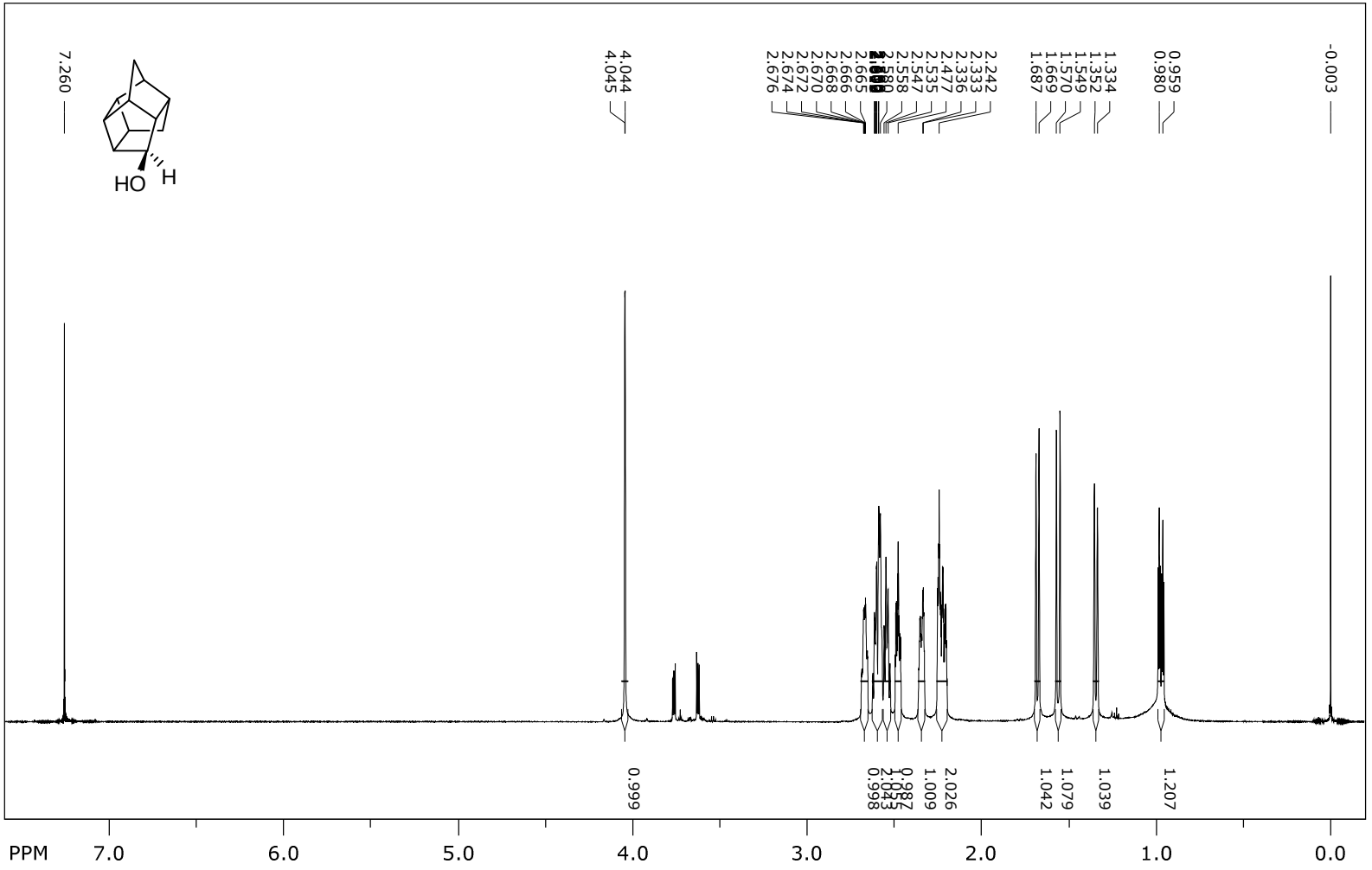
^{1}H NMR (600 MHz, $CDCl_3$) of **19**



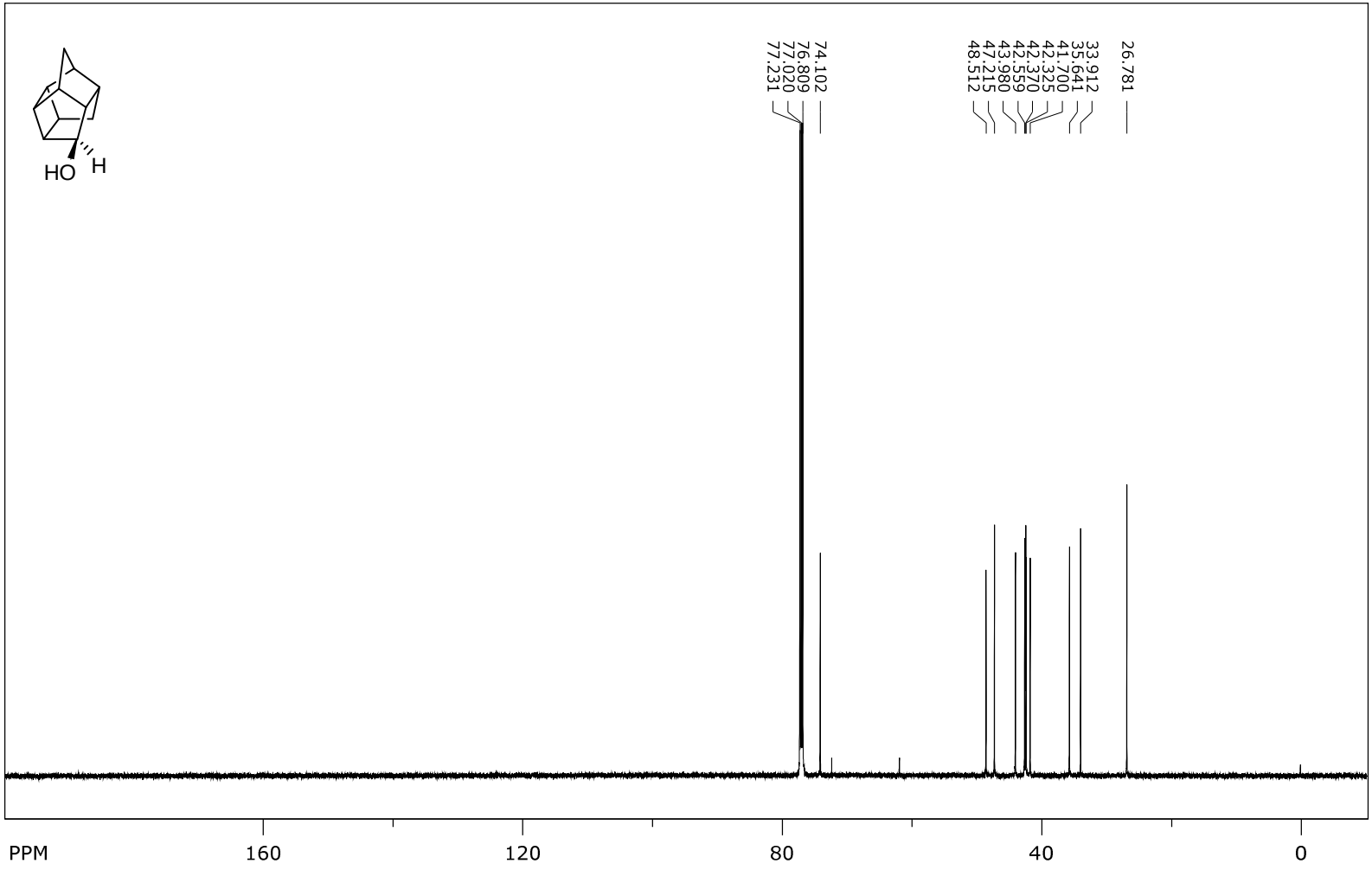
^{13}C NMR (150 MHz, $CDCl_3$) of **19**



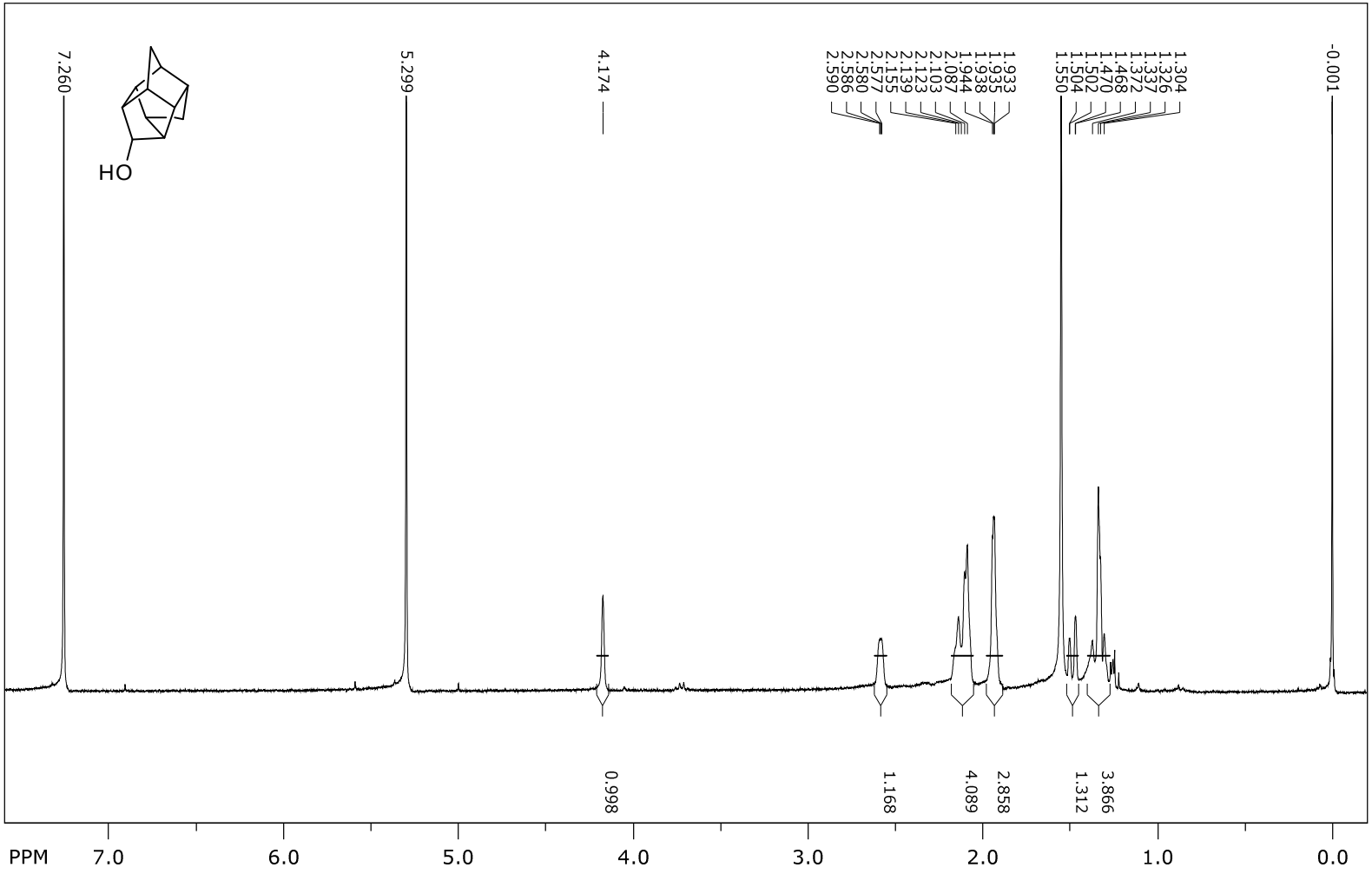
^{1}H NMR (600 MHz, $CDCl_3$) of **20**



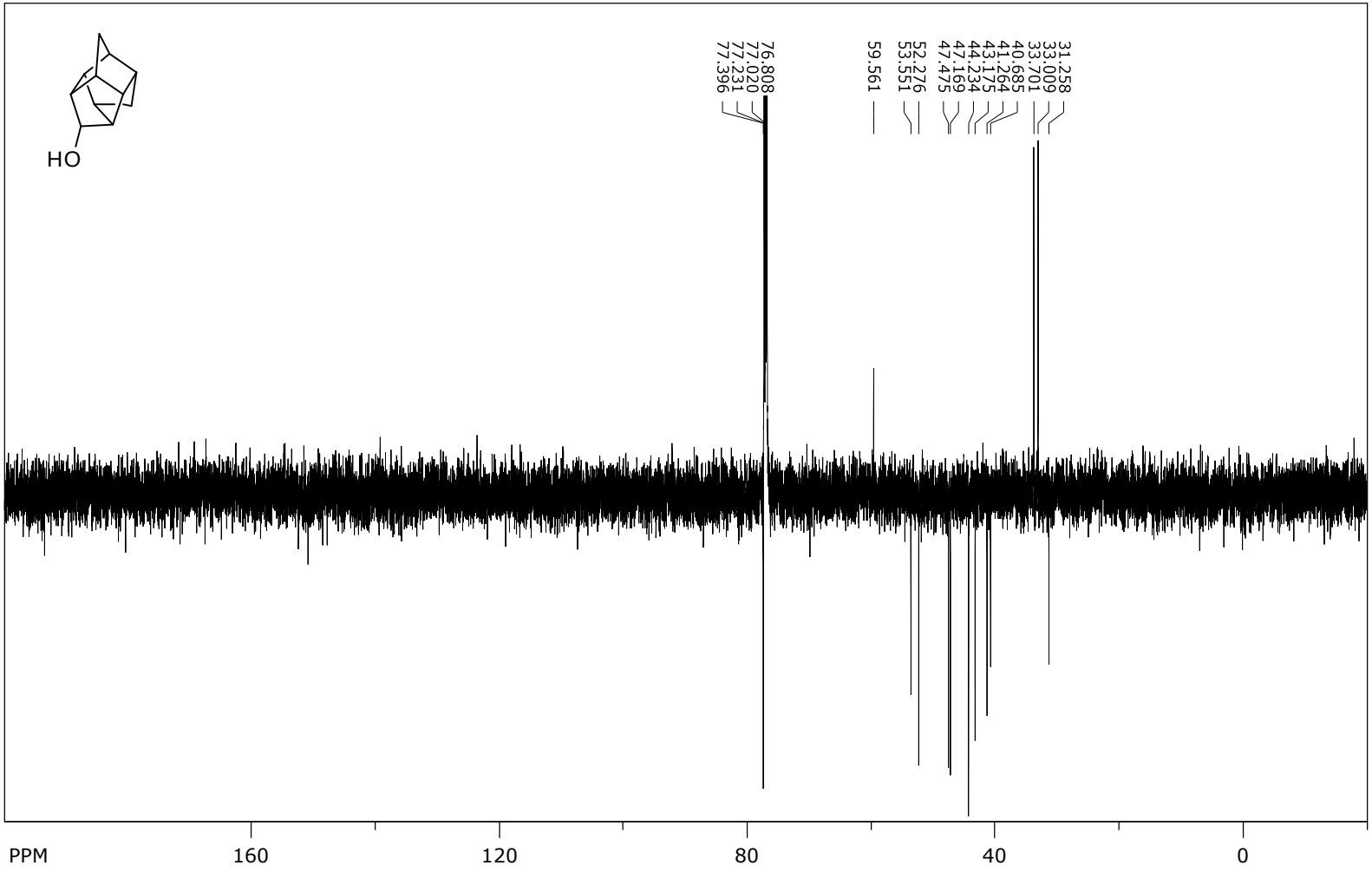
^{13}C NMR (150 MHz, $CDCl_3$) of **20**



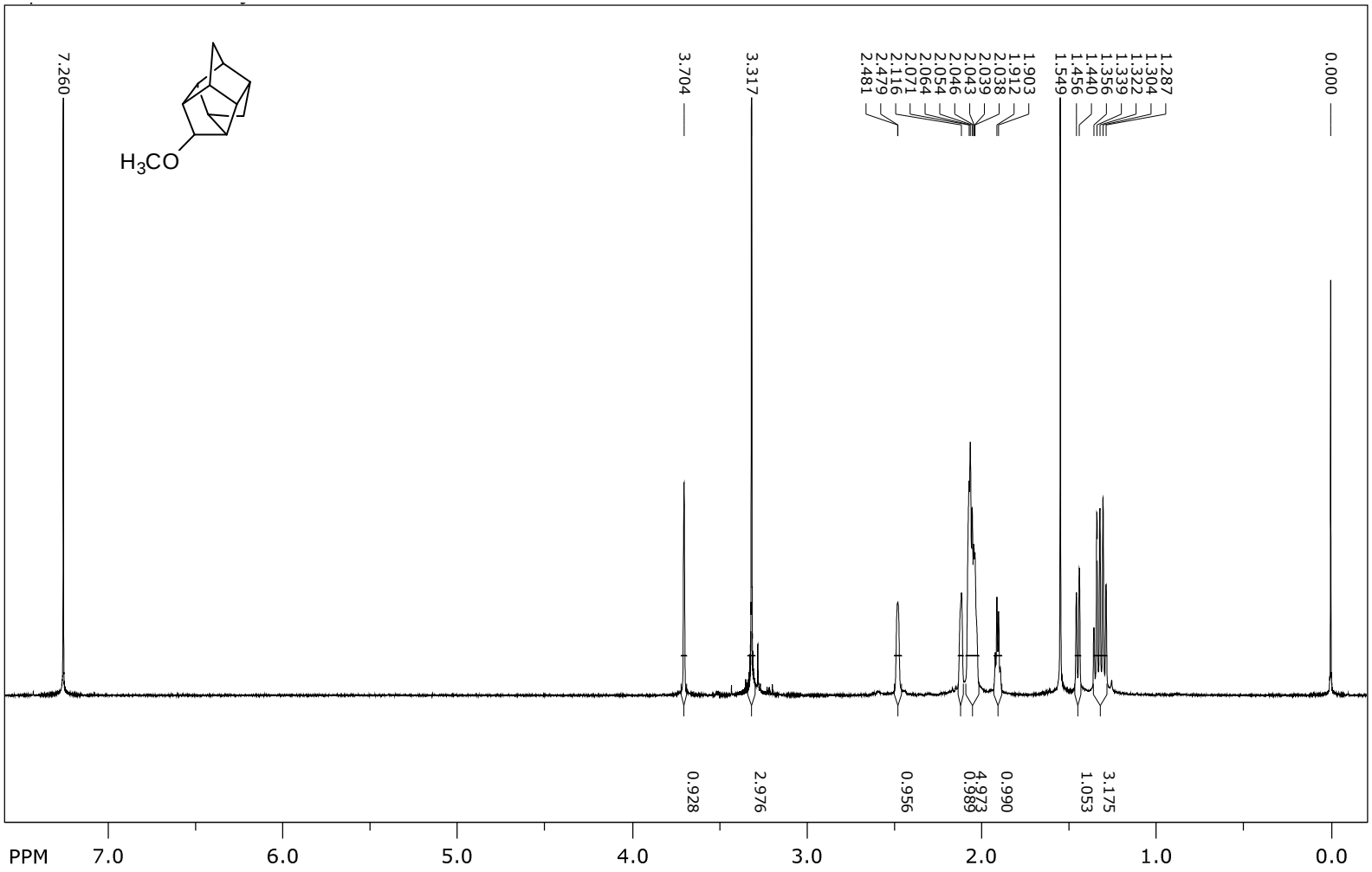
^{1}H NMR (600 MHz, $CDCl_3$) of **21**



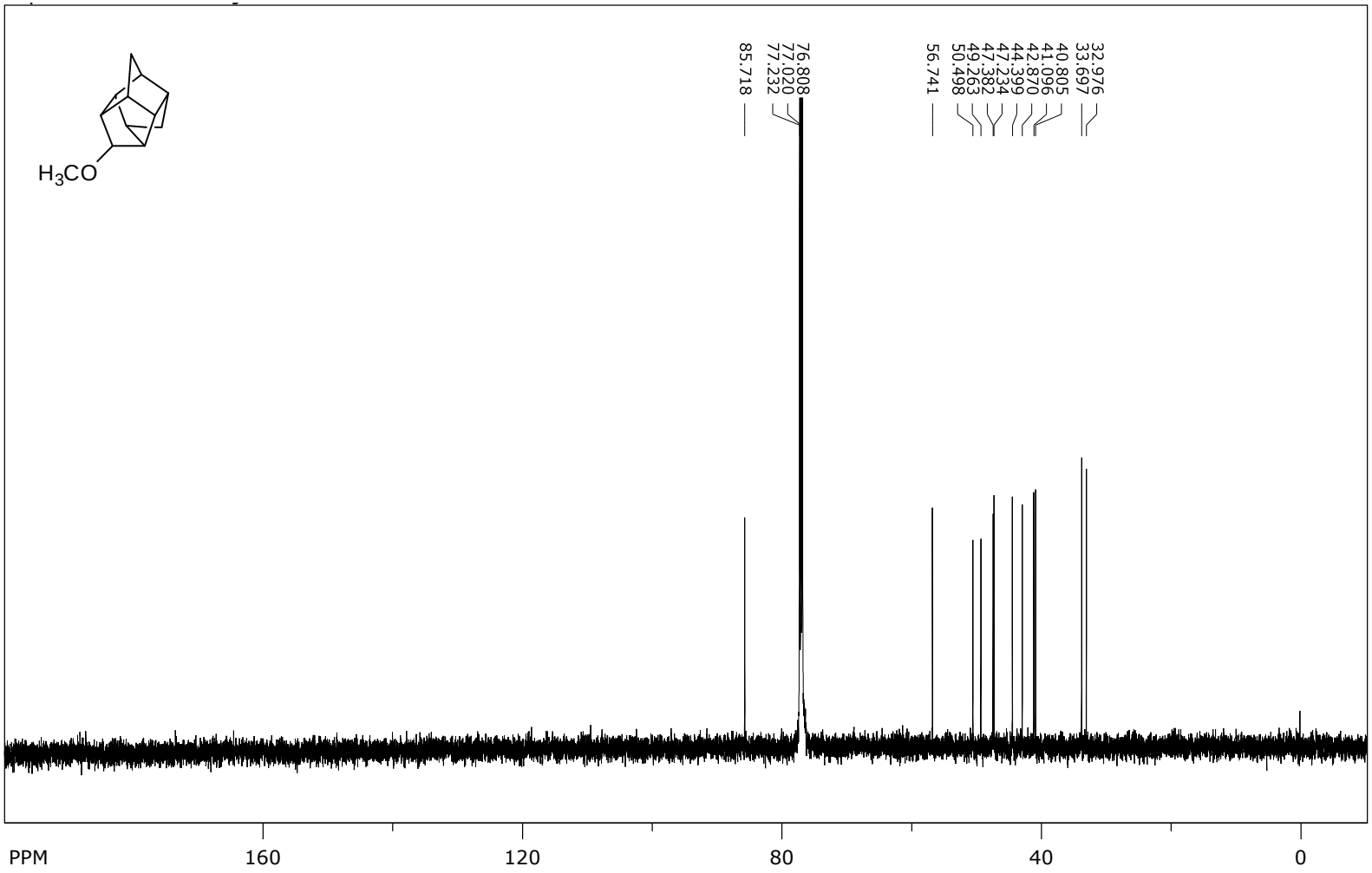
^{13} C NMR (150 MHz, $CDCl_3$) of **21**



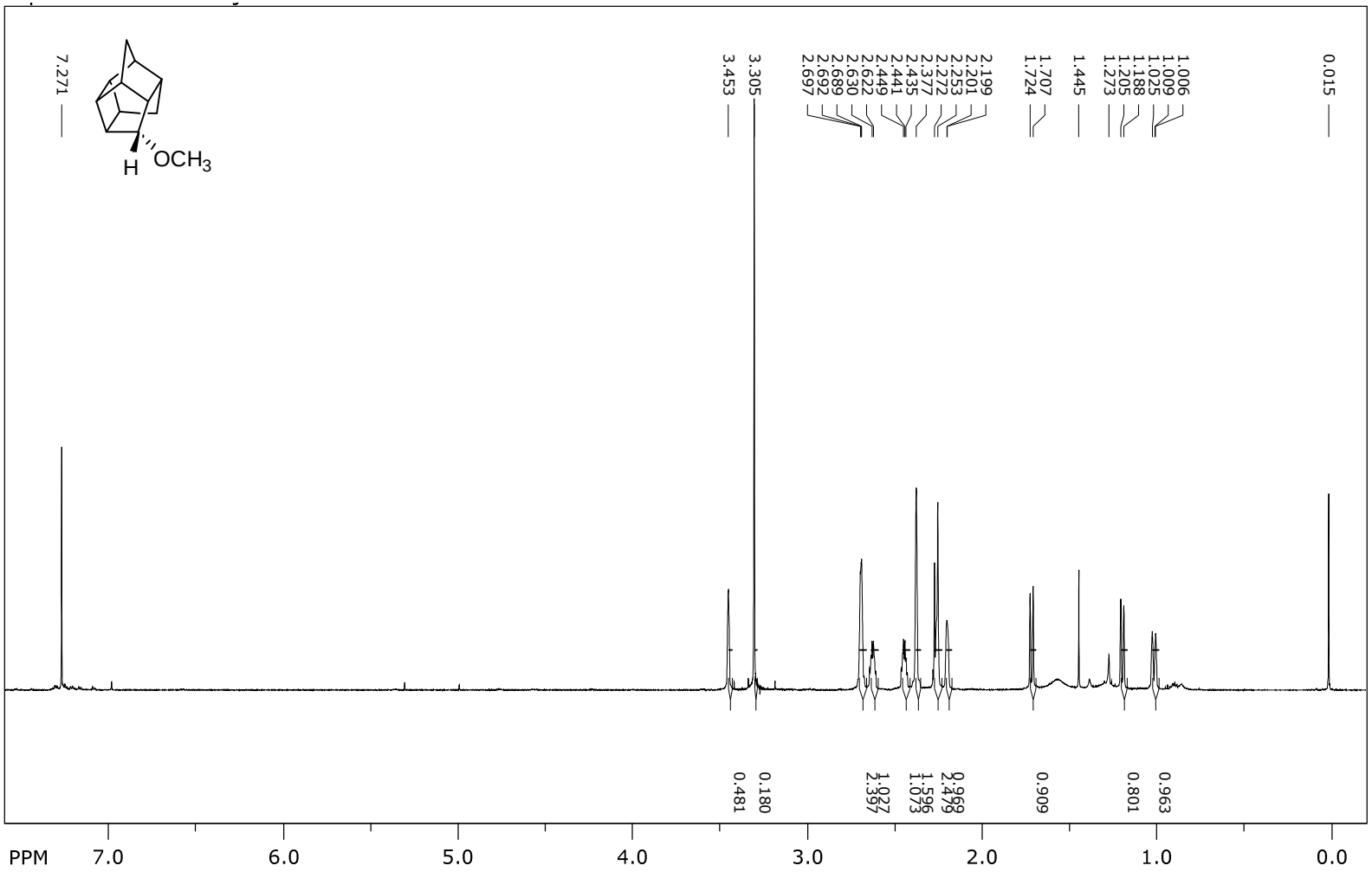
^{1}H NMR (600 MHz, $CDCl_3$) of **24**



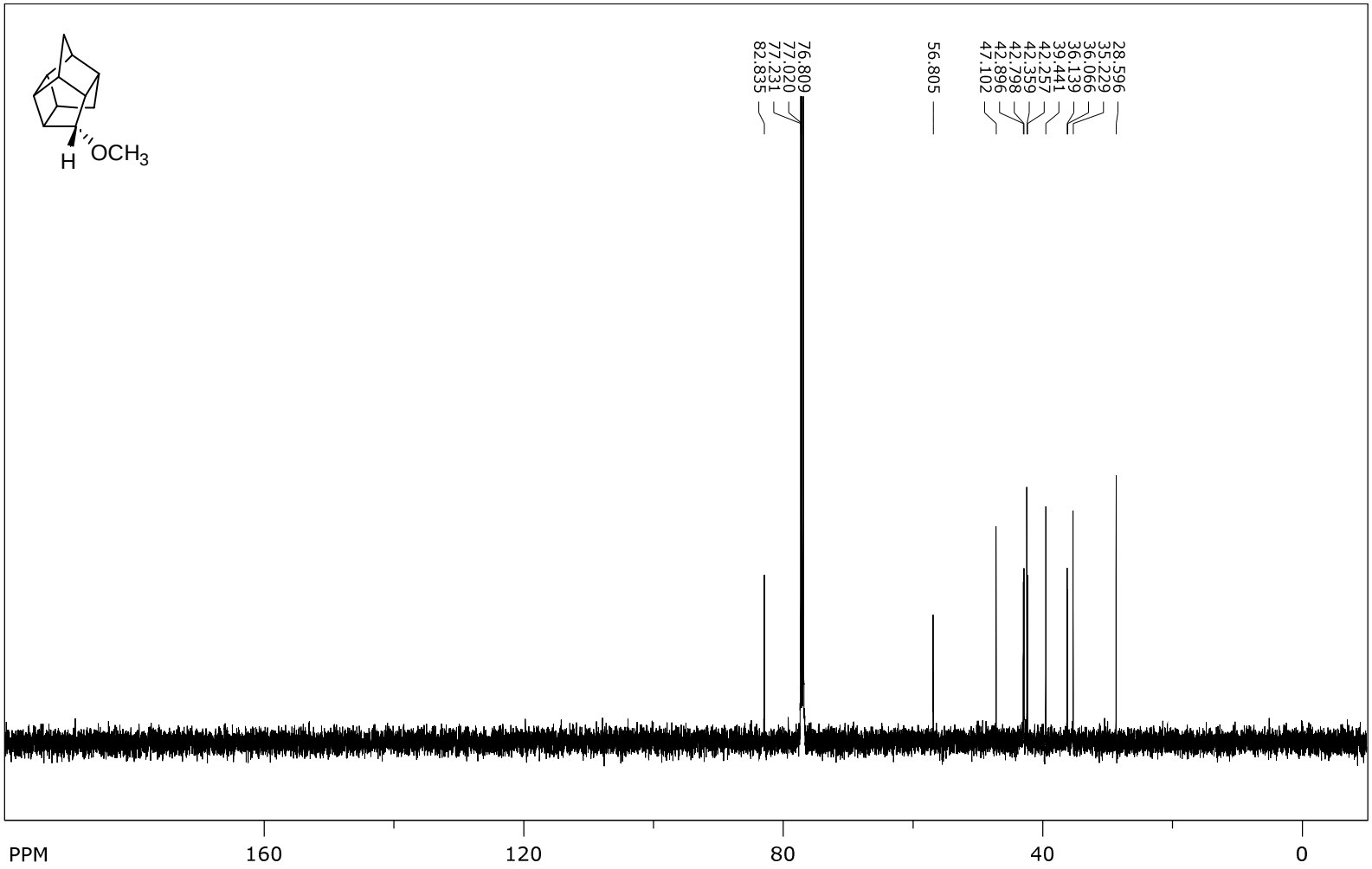
^{13}C NMR (150 MHz, $CDCl_3$) of **24**



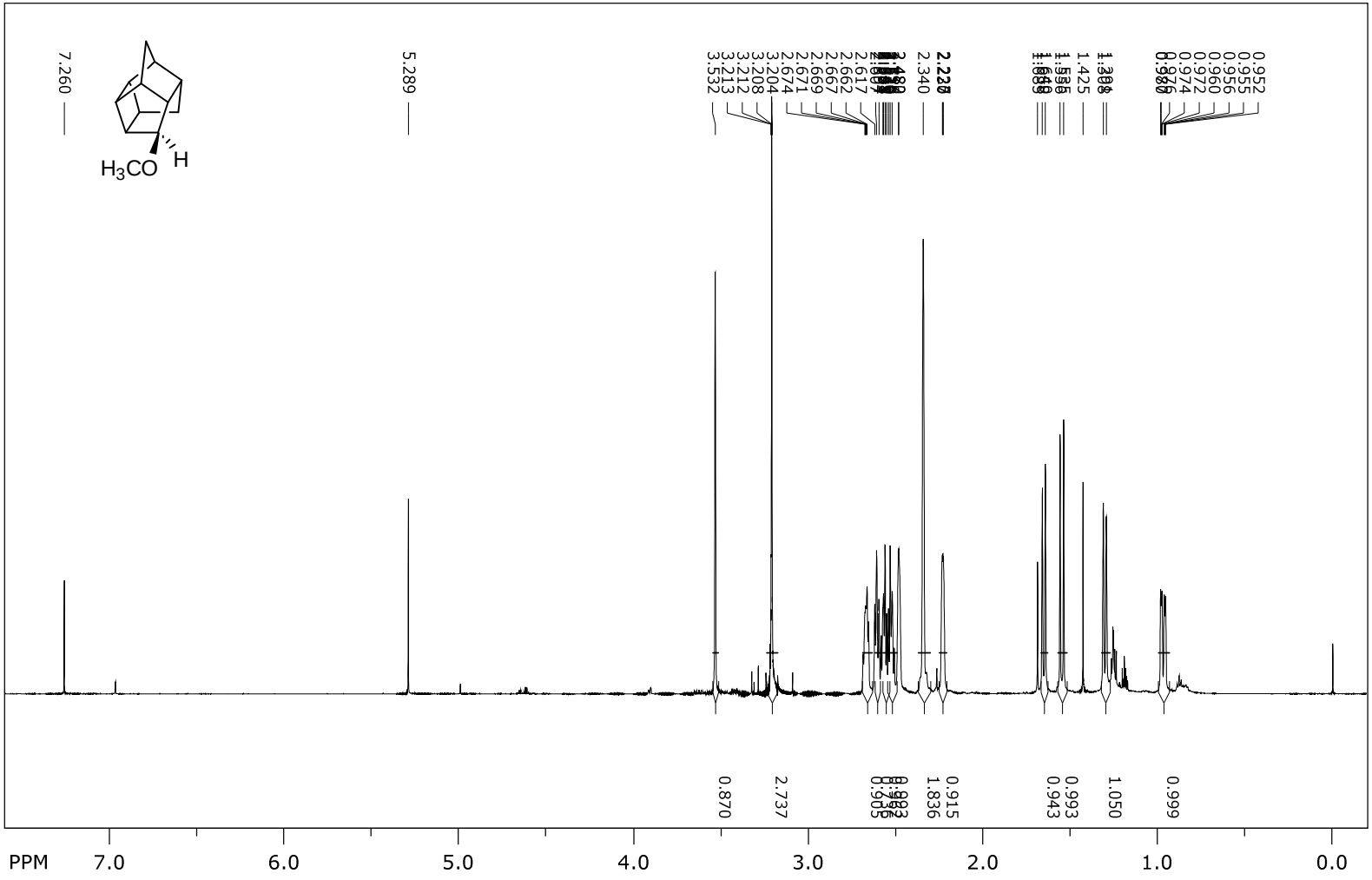
^{1}H NMR (600 MHz, $CDCl_3$) of **25**



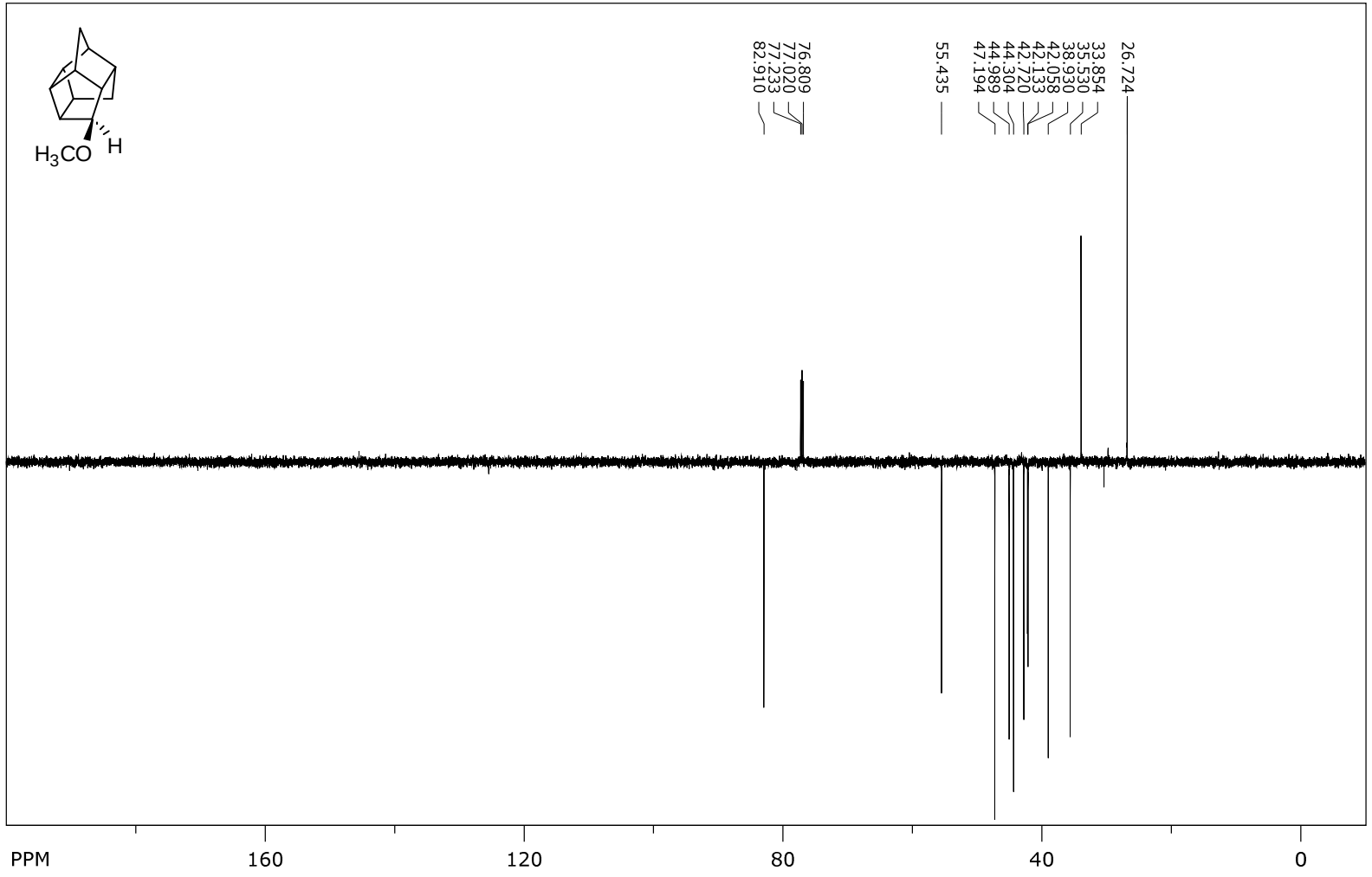
^{13} C NMR (150 MHz, $CDCl_3$) of **25**



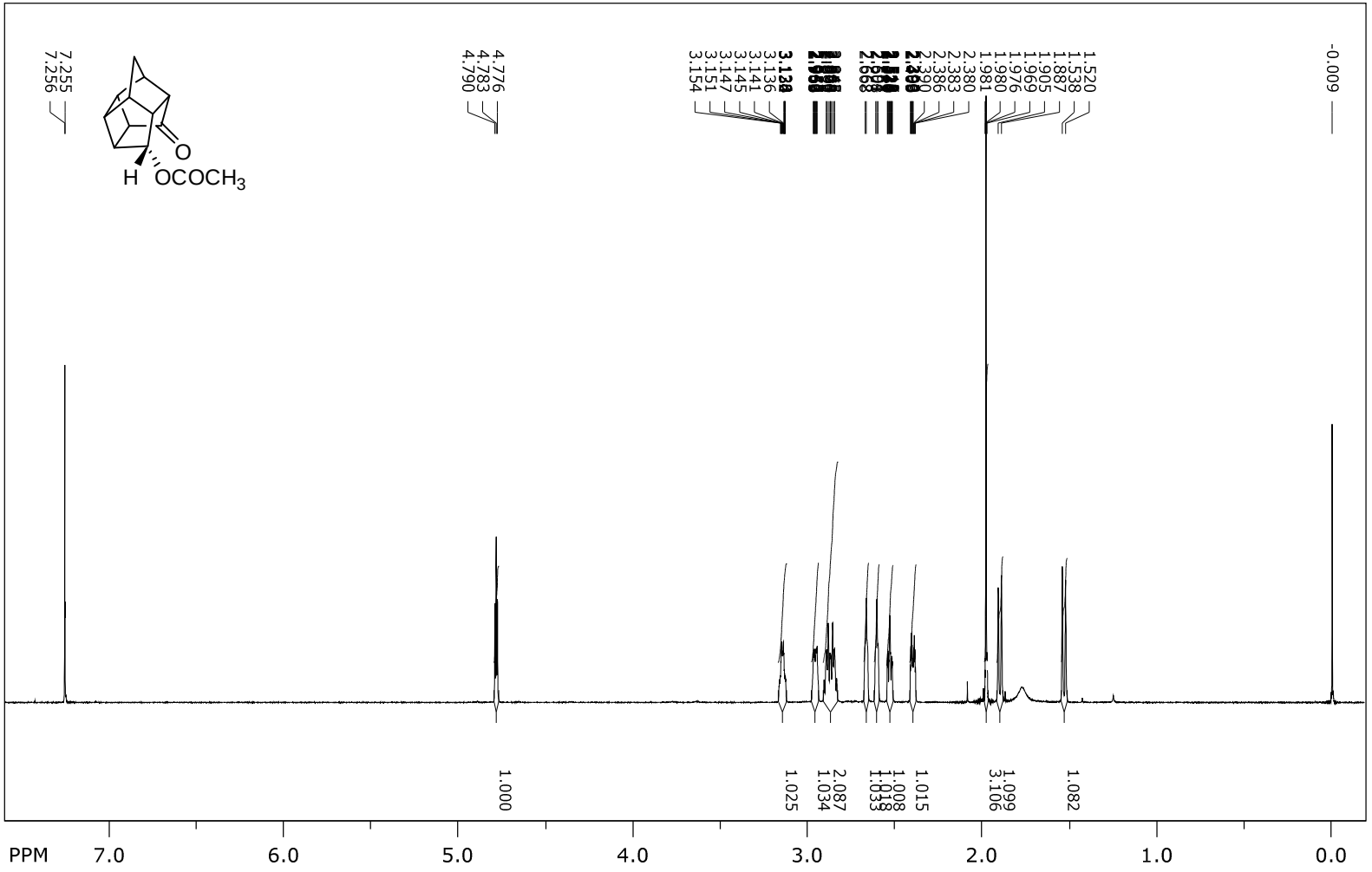
^{1}H NMR (600 MHz, $CDCl_3$) of **26**



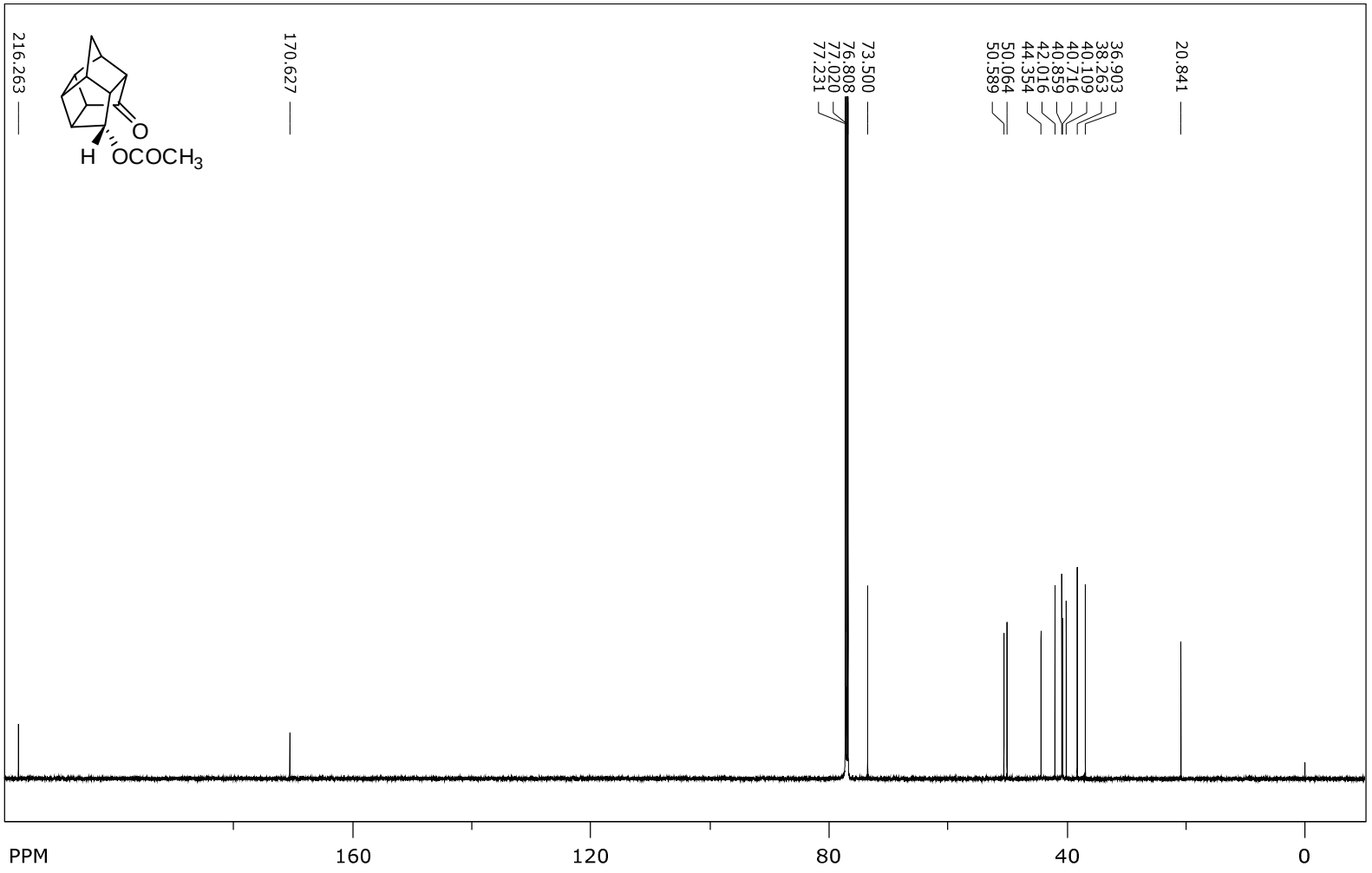
^{13}C NMR (150 MHz, $CDCl_3$) of **26**



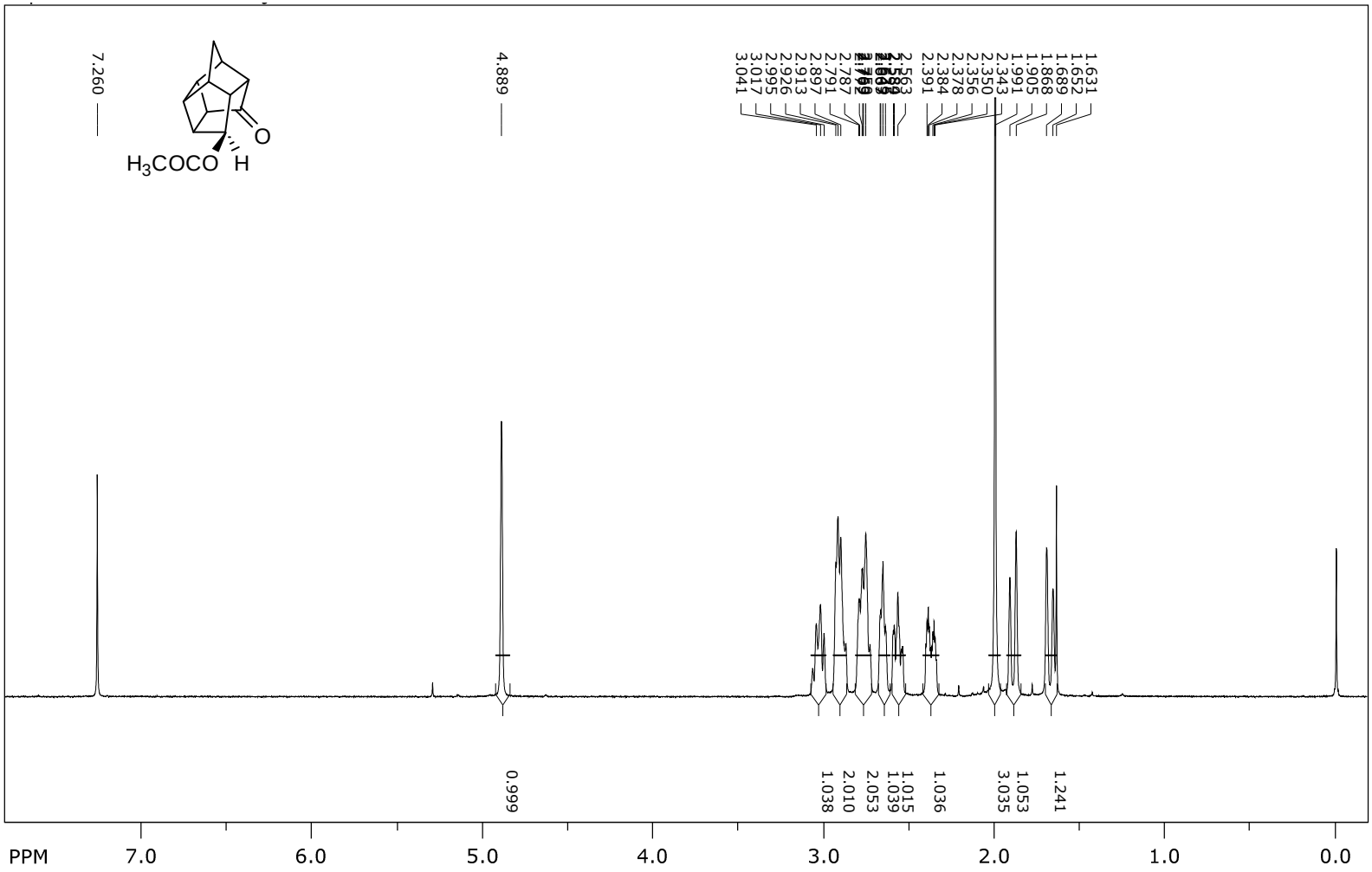
^{1}H NMR (300 MHz, $CDCl_3$) of **30**



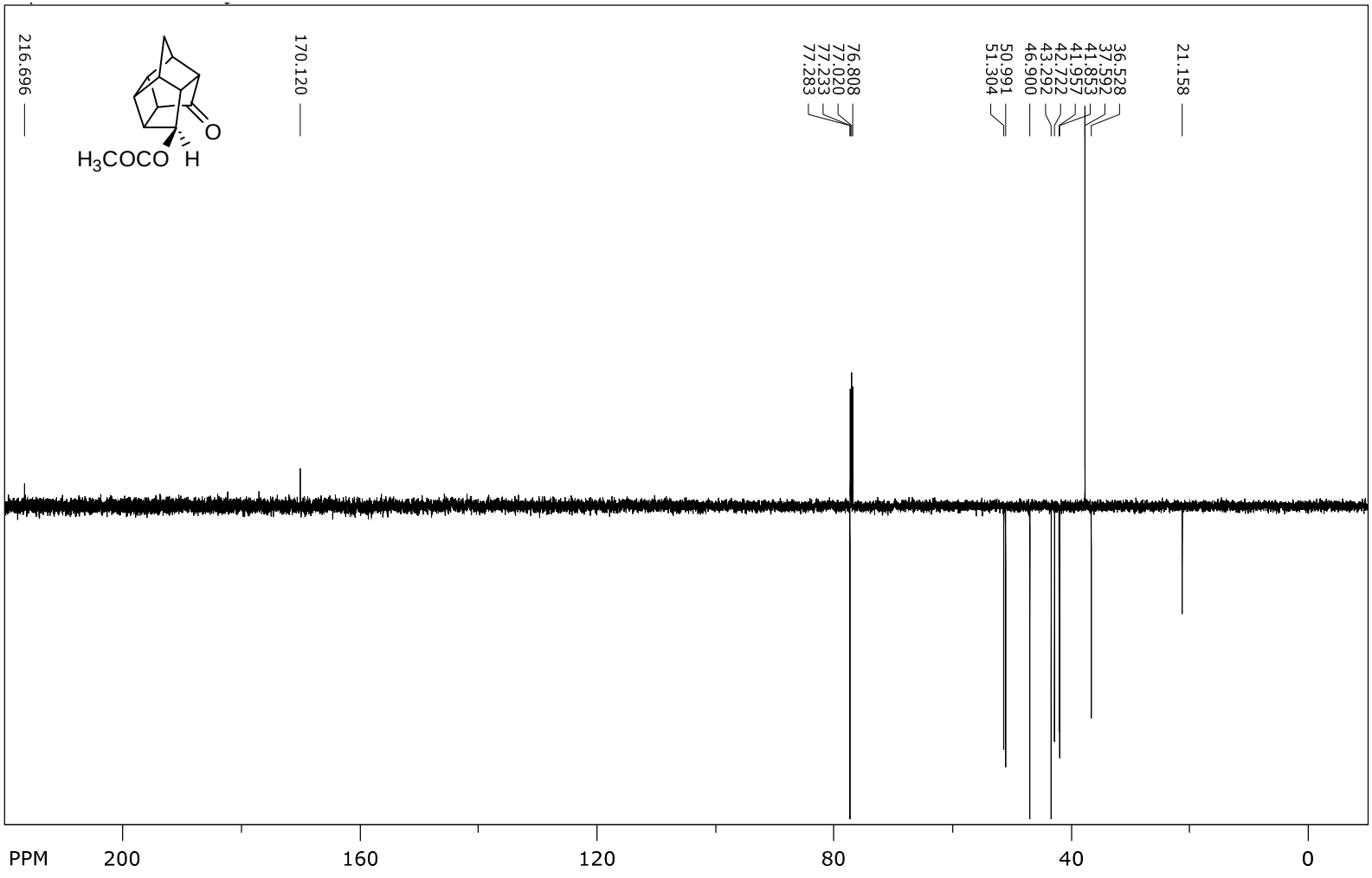
^{13}C NMR (75 MHz, $CDCl_3$) of **30**



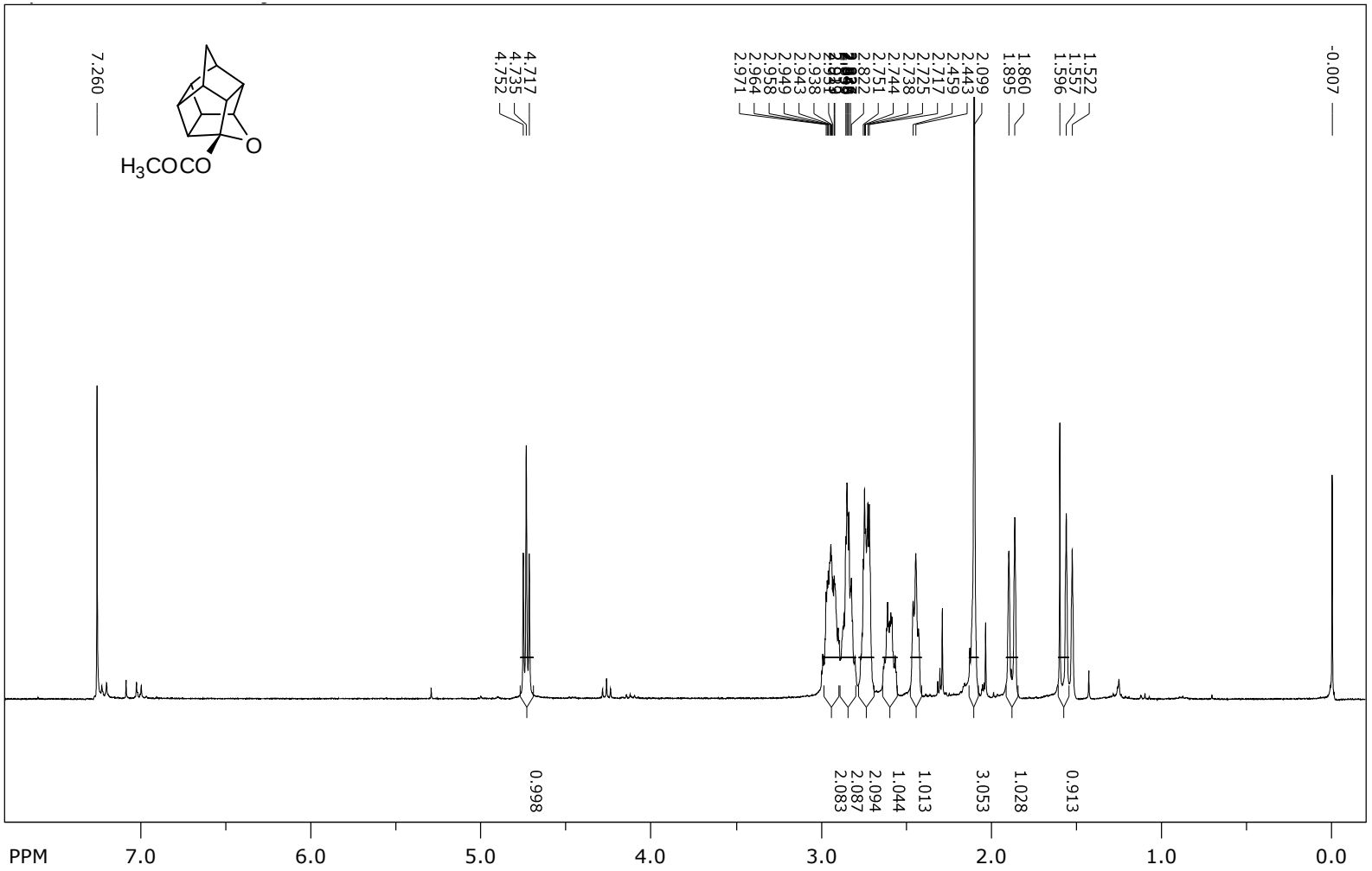
^{1}H NMR (300 MHz, $CDCl_3$) of **31**



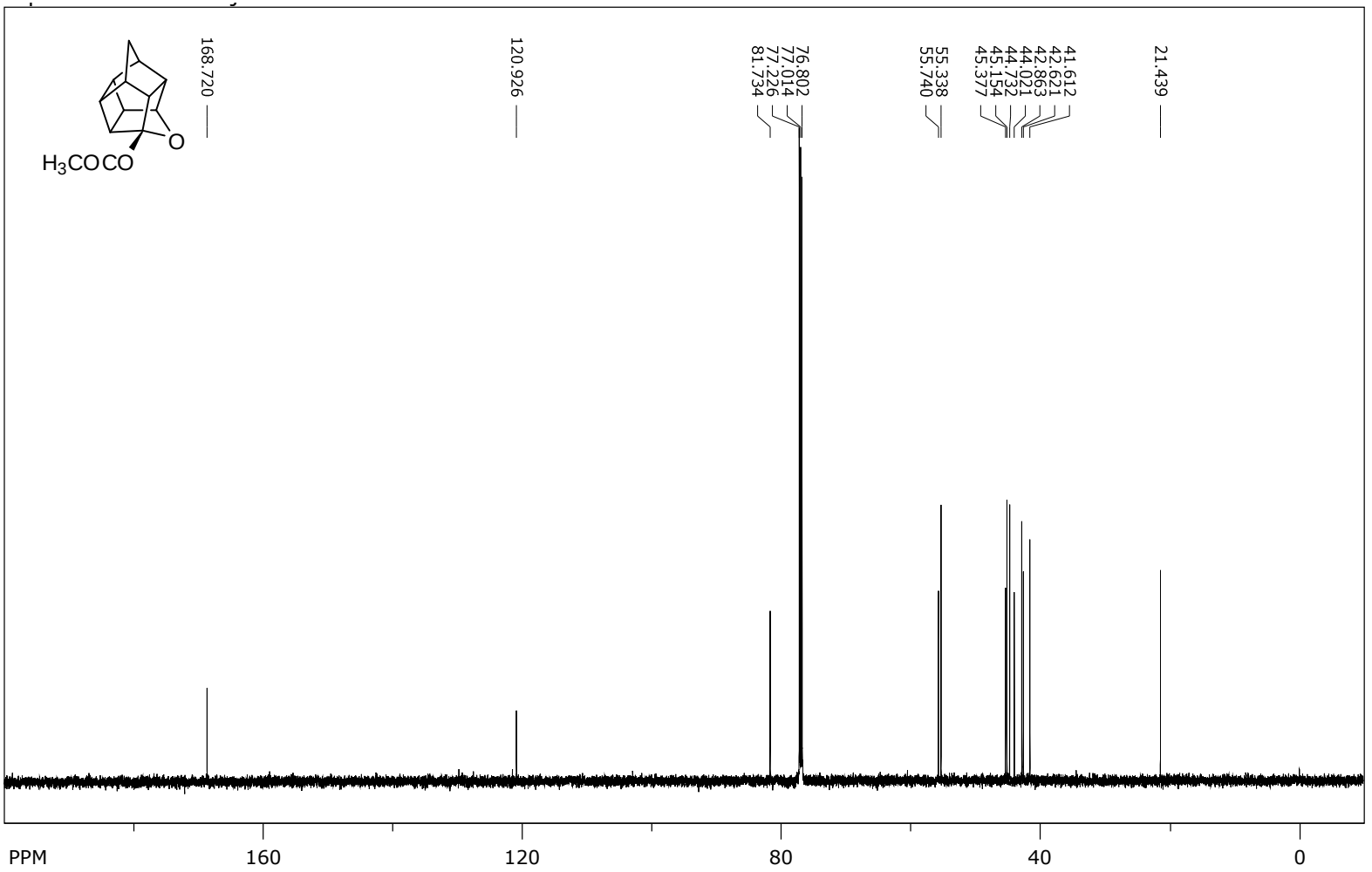
^{13}C NMR (75 MHz, $CDCl_3$) of **31**



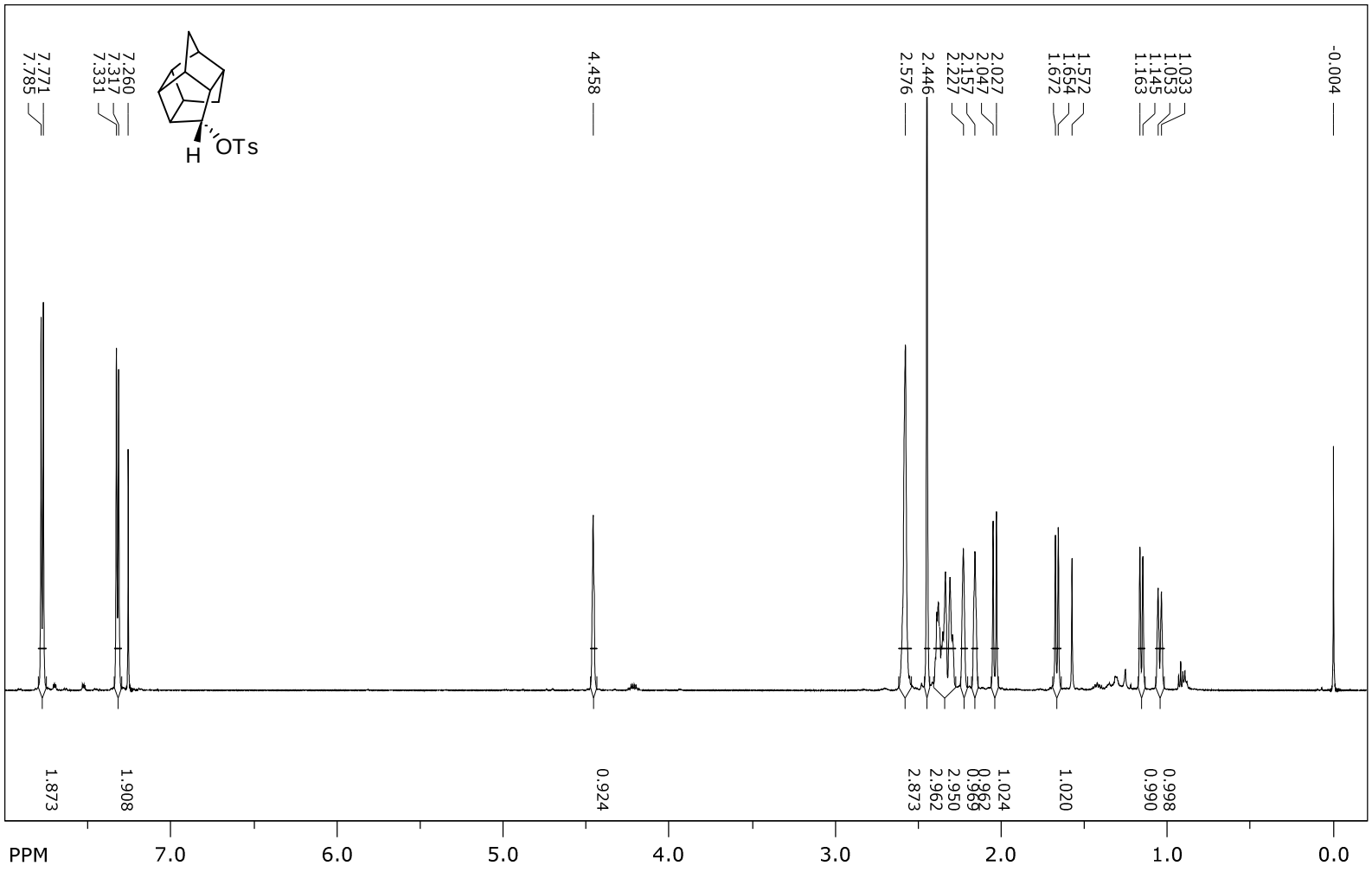
^{1}H NMR (300 MHz, $CDCl_3$) of **32**



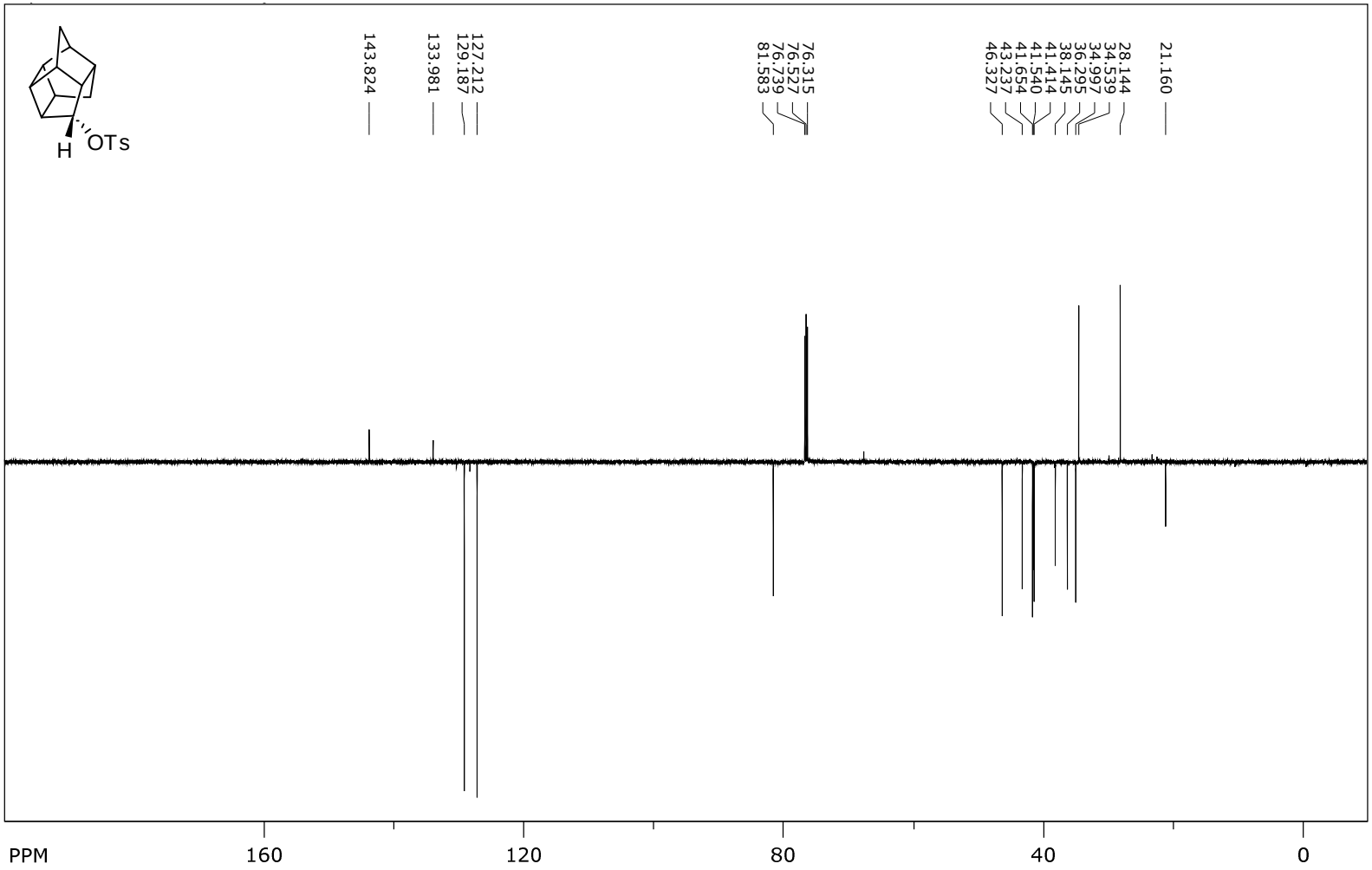
^{13}C NMR (75 MHz, $CDCl_3$) of **32**



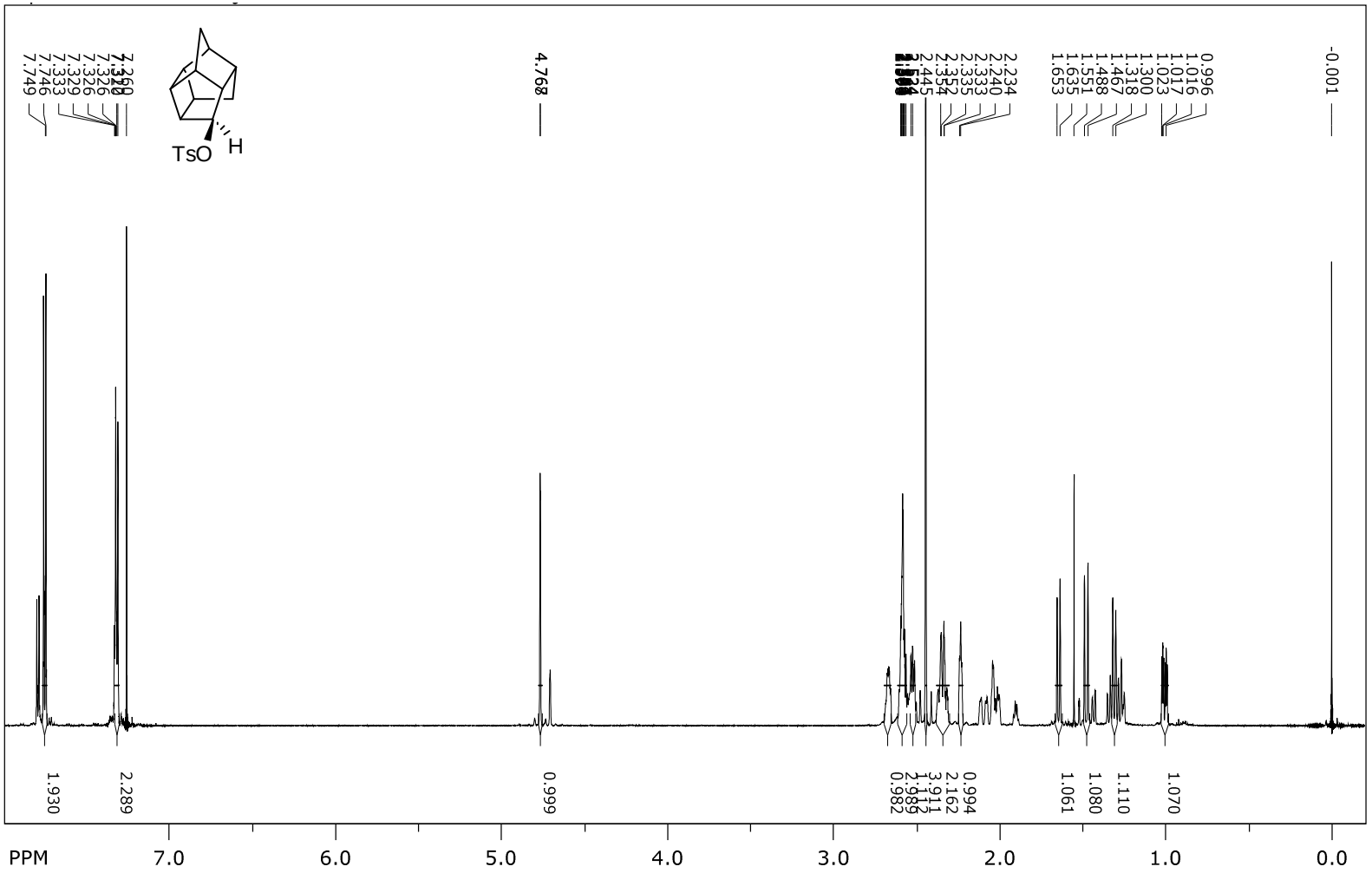
^{1}H NMR (600 MHz, $CDCl_3$) of **33**



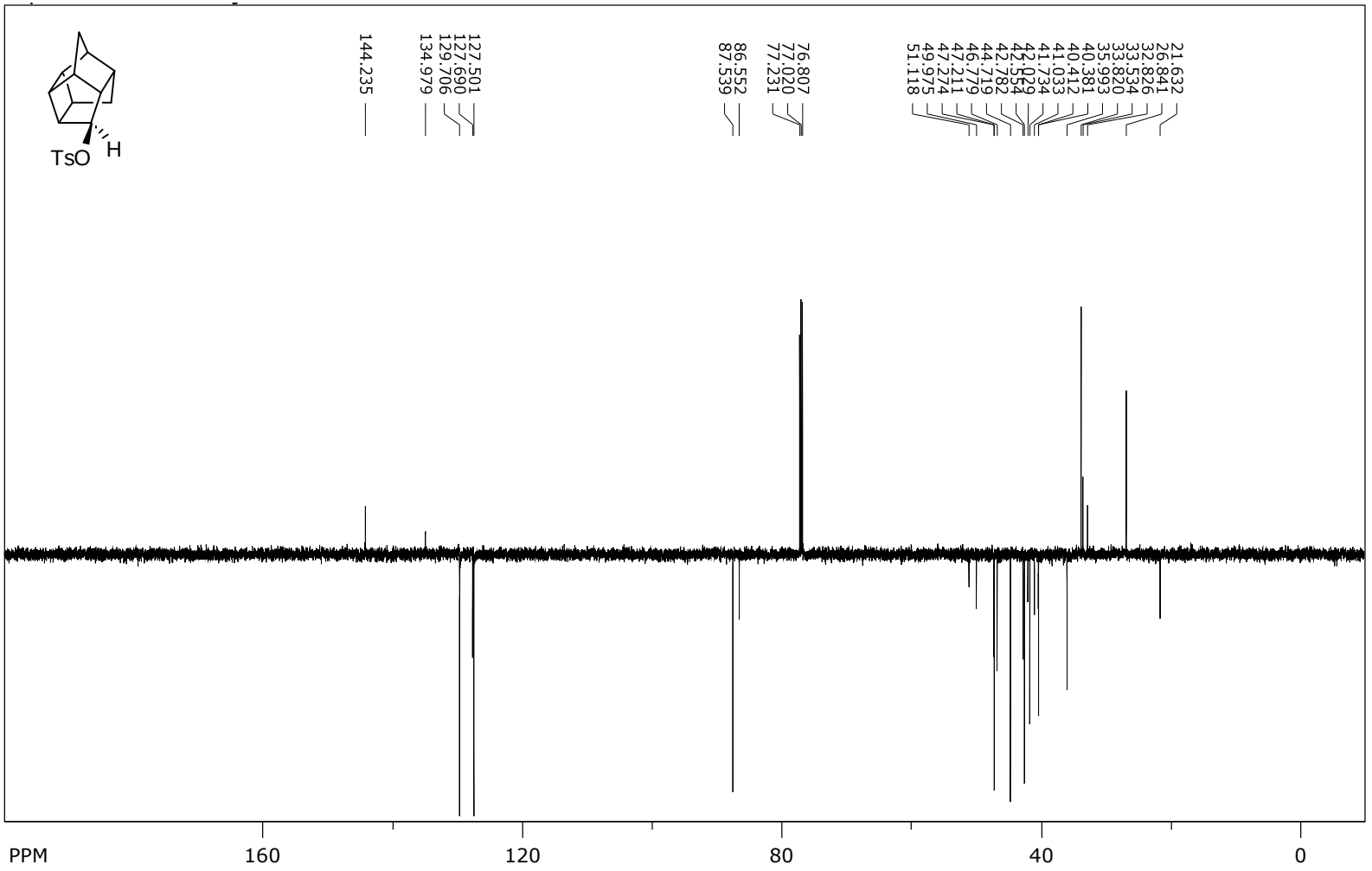
^{13} C NMR (150 MHz, $CDCl_3$) of **33**



^{1}H NMR (600 MHz, $CDCl_3$) of **34**



^{13} C NMR (150 MHz, $CDCl_3$) of **34**



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