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# Supporting information for:

# Anion binding and transport with *meso*-alkyl substituted two-armed calix[4]pyrroles bearing urea and hydroxyl groups

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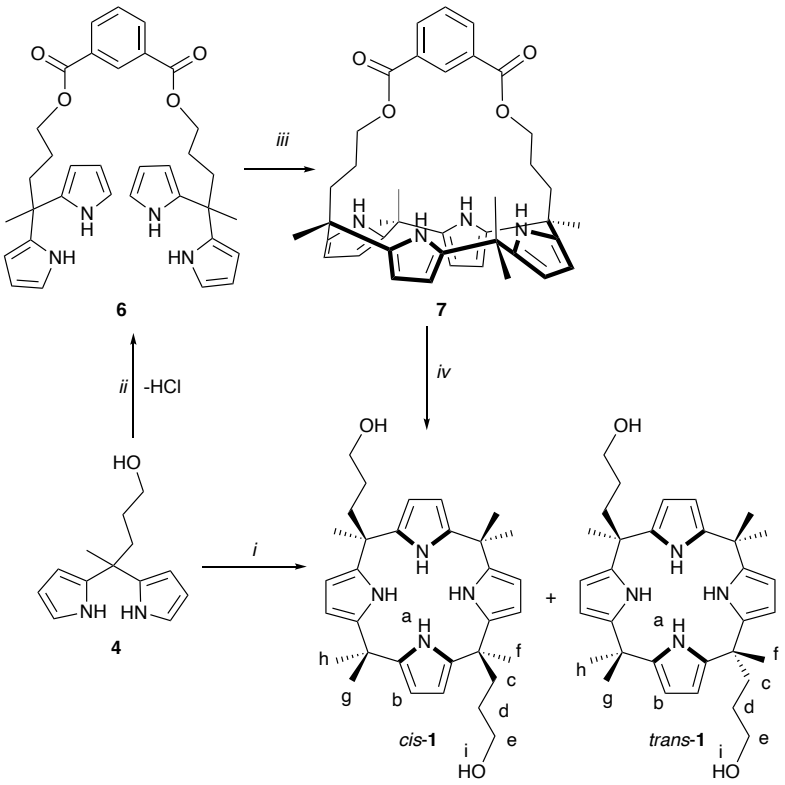
# 1. General

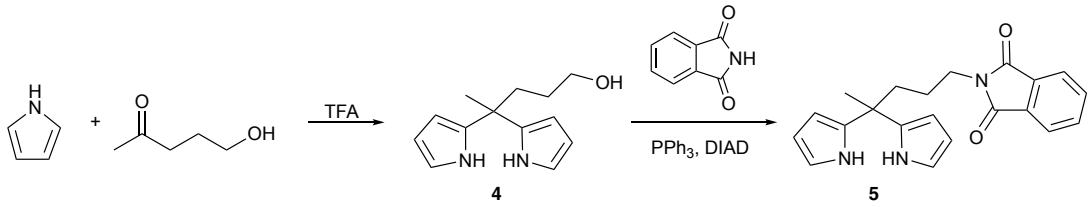
Chemicals were purchased from Sigma-Aldrich (Merck), VWR, Fischer Scientific and TCI Europe, and were used as received unless otherwise noted. Dry THF was obtained from MBraun SPS solvent purification system and acetone was dried using activated 4 Å molecular sieves. Dipyrromethanes **4** and **5** were prepared according to modified literature procedures.[1,2] NMR spectra were recorded with a Bruker Avance III 500 spectrometer equipped with a Prodigy cryoprobe (500 MHz for $^{1}$H NMR and 125 MHz for $^{13}$C NMR) or with Bruker Avance 400 (400 MHz for $^{1}$H NMR and 100 MHz for $^{13}$C NMR). Chemical shifts (δ, in ppm) were calibrated to the residual solvent signals and the coupling constants (*J*) are given in Hz.

# 2. Synthesis

In this work, *cis*-**1** and *trans*-**1** were synthesized by one step from **4**. Previously, *cis*-**1** has been previously synthesized via hydrolysis of the ester groups of a strapped calix[4]pyrrole **7** (Scheme S-1).[3]

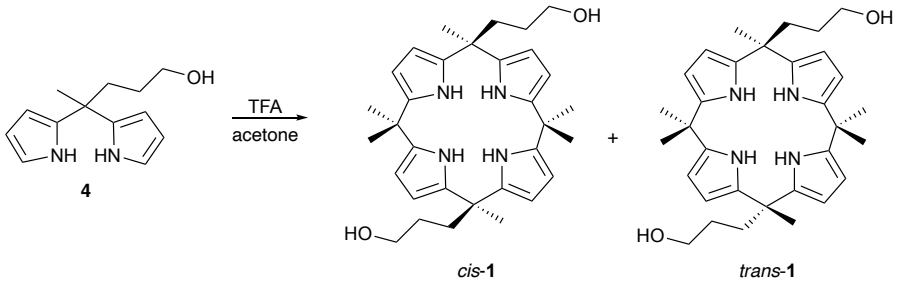



Scheme S-1 Alternative synthesis routes to calix[4]pyrrole *cis*-**1**. Conditions: *i*) trifluoroacetic acid in acetone, *ii*) isophthaloyl chloride and pyridine in dichloromethane; *iii*) $BF_3 \cdot Et_2O$ in acetone, *iv*) DIBAL-H in THF.




**4,4-di(1H-pyrrol-2-yl)pentan-1-ol (4)**. Freshly distilled pyrrole (15 ml) and 5-hydroxy-2-pentanone (1 ml, 9.86 mmol) were mixed for five minutes at room temperature. Trifluoroacetic acid (0.7 ml, 0.91 mmol) was added to the solution dropwise, and the mixture was stirred for 10 minutes at room temperature. Sodium hydroxide (25 ml, 0.1 M) was added to quench the reaction. The mixture was extracted with 4 x 20 ml of dichloromethane. The organic phase was dried with anhydrous $Na_2SO_4$ and filtrated through filtration paper. The solvent and excess pyrrole were removed under reduced pressure. Resulting brownish oil was purified by column chromatography using $SiO_x$ and 7:3 dichloromethane/ethyl acetate as an eluent ($R_f$ = 0.67). The collected fraction was concentrated under vacuum to provide yellow solid, which was recrystallized from dichloromethane/hexane. The off-white crystals were filtrated with suction, washed with hexane and dried in vacuum. Yield 57.2%, 1.23 g. **Melting point**: 97.9-98.8 °C. **$^1$H NMR** (500 MHz, $CDCl_3$): δ = 7.84 (s, br, 2H), 6.64-6.60 (m, 2H), 6.15-6.11 (m, 2H), 6.11-6.07 (m, 2H), 3.58 (m, 2H), 2.04 (m, 2H), 1.59 (s, 3H), 1.51-1.43 (m, 2H), 1.22 (t, *J* = 5.2 Hz, 1H) ppm. **$^{13}$C NMR** (100.6 MHz, $CDCl_3$): δ = 137.96 (2C), 117.14 (2C), 107.92 (2C), 104.76 (2C), 63.25, 39.06, 37.35, 28.01, 26.62 ppm.

**2-(4,4-di(1H-pyrrol-2-yl)pentyl)isoindoline-1,3-dione (5)**. The dipyrromethane **4** (1.00 g, 4.61 mmol), phthalimide (2.03 g, 13.82 mmol) and triphenylphospine (3.60 g, 13.73 mmol) were dissolved in 80 ml of dry tetrahydrofuran under argon. The solution was cooled in an ice bath and di-isopropyl azodicarboxylate (2.73 ml, 13.84 mmol) was added dropwise during 15 minutes to the solution. The rection mixture was strirred over night for 17 hours allowing the bath to warm to room temperature. The orange solution was quenched with 100 ml of water, and extracted with dichloromethane (4 x 30 ml). The organic extracts were dried with anhydrous $Na_2SO_4$ and concentrated in a rotary evaporator to produce 10 g of orange oil. The crude was passed through a column of silica (120 g) using 95:5 dichloromethane/ethyl acetate as an eluent ($R_f$ = 0.70). First, an orange fraction was collected, and recrystallized from 1:4 dichloromethane/hexane. An oily residue from the recrystallization experiment was combined with the second fraction (brown color) and both were subjected to silica column chromatography using 98:2 dichloromethane/*tert*-butyl methyl ether as an eluent. The combined fractions of the product were recrystallized from dichloromethane/hexane to yield yellow crystalline solid (1.18 g, 73 %). **Melting point**: 109.9-110.7 °C. ***R<sub>f</sub>***: 0.70 (DCM/EtOAc 19:1). **$^1$H NMR** (500 MHz, $CDCl_3$): δ = 7.84-7.80 (m, 2H), 7.77 (s, br, 2H), 7.72-7.68 (m, 2H), 6.62-6.57 (m, 2H), 6.11-6.08 (m, 2H), 6.07-6.04 (m, 2H), 3.61 (t, *J* = 7.3 Hz, 2H), 2.05-1.99 (m, 2H), 1.64-1.57 (m, 2H), 1.57 (s, 3H) ppm. **$^{13}$C NMR** (100.67.85 MHz, $CDCl_3$): δ = 168.55 (2C), 137.59 (2C), 134.03 (2C), 32.24 (2C), 123.33 (2C), 117.28 (2C), 107.94 (2C), 104.83 (2C), 38.95, 38.37, 38.31, 26.41, 24.02 ppm.

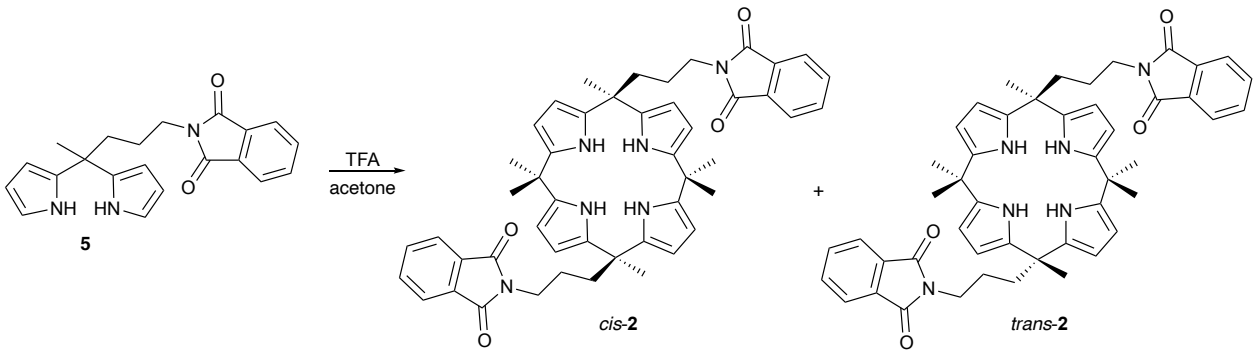



**Calix[4]pyrrole 1**. To a solution of dipyrromethane **4** (3.25 g, 14.89 mmol) in dry acetone (150 ml), trifluoroacetic acid (3.33 ml, 43.49 mmol) dissolved in 10 ml of dry acetone was added dropwise during 15 minutes. The mixture was stirred at room temperature under nitrogen for 15 hours. The dark purple reaction mixture was quenched by adding triethylamine (8.3 ml, 59.5 mmol) while cooling the sample in an ice-water bath. The solution was concentrated in a rotary evaporator to a volume of ca. 25 ml and left for crystallization for three days. The obtained crystalline precipitate was filtered and washed with cold acetone to obtain pure *trans*-isomer as white crystalline powder (0.395 g, 10.3 %). To the filtrate was added dichloromethane (120 ml) and water (120 ml). The water phase was separated and washed with dichloromethane (2 x 80 ml). The combined organic extracts were concentrated on a rotary evaporator, dissolved in acetone (30 ml) and adsorbed on silica (13.4 g). The product was purified with silica column chromatography using 90:10 to 50:50 dichloromethane/ethyl acetate gradient as an eluent. The fractions containing the *cis*-isomer were evaporated to dryness and dried in vacuum. Yield 0.471 g of pale-yellow powder (12.0 %).

Alternative method for separation of the *cis*-**1** and *trans*-**1** isomers by flash chromatography: Starting from 980 mg of dipyrromethane **4** in dry acetone (80 ml) the synthesis and workup were performed as above. After quenching with triethylamine, the crude was concentrated with a rotary evaporator and the residue was dissolved into dichloromethane (60 ml) and washed with water (3 x 60 ml). The water phases were combined and washed once with 40 ml of dichloromethane. The combined organic extracts were dried with $Na_2SO_4$ and filtered. The solution was concentrated with a rotary evaporator and the residue was dried in vacuum. The residue was dissolved into acetone (60 ml) and adsorbed on silica (5 g). The product was purified with flash column chromatography using 80 g Redisep silica column and 90:10 to 55:45 dichloromethane/ethyl acetate gradient as an eluent. The fractions containing the products were evaporated to dryness and dried in vacuum. Yield 82 mg of *trans*-**1** (7.1 %) and 216 mg of and *cis*-**1** (18.7 %).

*cis*-**1**: HR-MS (ESI-TOF): *m/z* calcd. for $[M+Na]^+$ $C_{32}H_{44}N_4O_2Na^+$ 539.3357; found 539.3342. **$^1$H NMR** (500 MHz, acetone-$d_6$): δ = 7.98 (s, 4H, NH), 5.75 (m, 8H, β-Py), 3.43 (m, 4H, OC$H_2$), 3.35 (t, *J* = 5.3, 2H, OH), 1.91 (m, 4H, CC$H_2$), 1.48 (s, 6H, $CH_3$), 1.45 (s, 6H, $CH_3$), 1.43 (s, 6H, $CH_3$), 1.34 (m, 4H, $OCH_2CH_2$) ppm. **$^{13}$C NMR** (126 MHz, acetone-$d_6$): δ = 139.25 (4C, α-Py), 138.41 (4C, α-Py), 104.03 (4C, β-Py), 103.17 (4C, β-Py), 62.91 (2C, O$CH_2$), 39.22 (2C, *meso*-C), 37.49 (2C, C$CH_2$), 35.82 (2C, *meso*-C), 29.84 (2C overlapping with acetone, $CH_3$) 28.97 (2C), 28.88 (2C), 25.96 (2C, $CH_3$) ppm.

*trans*-**1**: HR-MS (ESI-TOF): *m/z* calcd. for $[M+Na]^+$ $C_{32}H_{44}N_4O_2Na^+$ 539.3357; found 539.3342. **$^1$H NMR** (500 MHz, DMSO-$d_6$): δ = 9.23 (s, 4H, NH), 5.68 (m, 8H, β-Py), 4.31 (t, *J* = 5.1, 2H, OH), 3.27 (m overlapping with $H_2O$, 4H, OC$H_2$), 1.91 (m, 4H, CC$H_2$), 1.50 (s, 12H, $CH_3CCH_3$), 1.43 (s, 6H, $CH_3$), 1.21–1.11 (m, 4H, $OCH_2CH_2$) ppm. **$^{13}$C NMR** (126 MHz, DMSO-$d_6$): δ = 138.56 (4C, α-Py), 137.70 (4C, α-Py), 102.60 (4C, β-Py), 101.77 (4C, β-Py), 61.32 (2C, O$CH_2$), 37.86 (2C, *meso*-C), 36.09 (2C, C$CH_2$), 34.56 (2C, *meso*-C), 29.12 (4C, $CH_3CCH_3$), 27.84 (2C, $CH_2$), 25.65 (2C, $CH_3$) ppm.

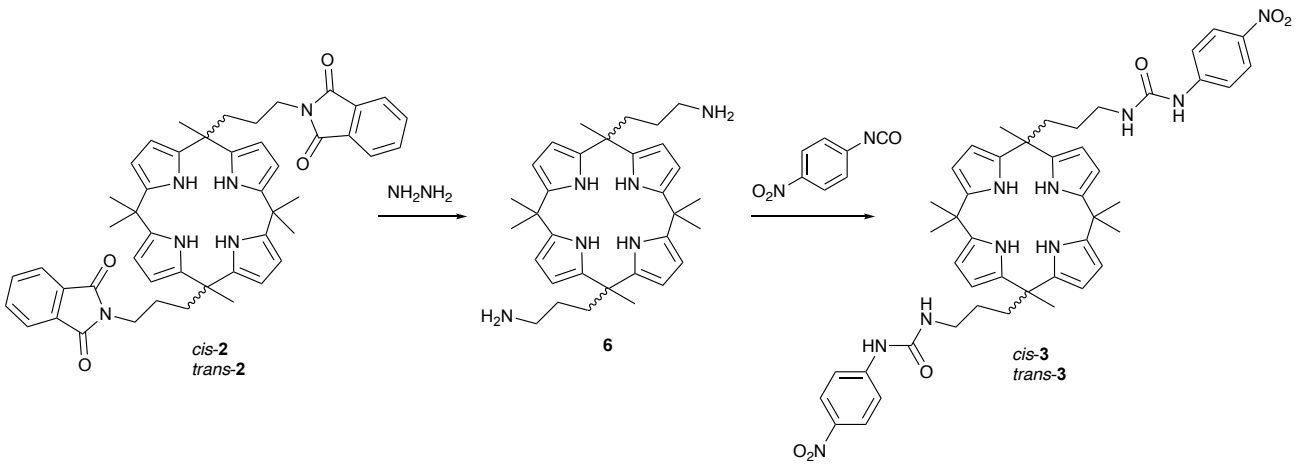



**Calix[4]pyrrole 2**. To a solution of dipyrromethane **5** (0.40 g, 1.15 mmol) in dry acetone (8 ml), trifluoroacetic acid (0.27 ml, 3.46 mmol) dissolved in 3.5 ml of dry acetone was added. The mixture was stirred at room temperature under argon for 17 hours. The reaction was quenched by adding triethylamine (800 μl) while cooling the sample in an ice bath. The solution was concentrated in a rotary evaporator and the resulting dark oil was dissolved in 40 ml of DCM. The solution was washed with water (3 x 15 ml), dried with $Na_2SO_4$ and evaporated to dryness to yield brown glue. The product was purified with silica column chromatography using 98:2 dichloromethane/ethyl acetate as an eluent. The product eluted with an Rf ~0.3. The combined fractions were evaporated to dryness and dried in vacuum. Yield 0.179 g 40 % (mixture of *cis*-**2** and *trans*-**2** isomers), light yellow solid. The isomers of **2** were separated on a milligram scale by repeated (2-3) washing with acetonitrile. The evaporated acetonitrile solution was enriched in *cis*-**2** and the precipitate that was not dissolved in acetonitrile was enriched in *trans*-**2** leading to 90 % pure isomers according to the $^1$H NMR spectra.

HR-MS (ESI-TOF): *m/z* calcd. for $[M+H]^+$ $C_{48}H_{51}N_6O_4^+$ 775.3966; found 775.3966.

*cis*-**2**: **$^1$H NMR** (400 MHz, acetone-$d_6$): δ = 7.89 (s, 4H, NH), 7.83 (s, 8H, Phth), 5.71-5.66 (m, 8H, β-Py), 3.58 (t, *J*=6.8 Hz, 4H, NC*H*$_2$), 1.94-1.88 (m, 4H, $CH_2$), 1.50-1.40 (m, 8H, $NCH_2CH_2$), 1.42 (s, 6H, $CH_3$), 1.39 (s, 6H, $CH_3$), 1.35 (s, 6H, CH3) ppm. **$^{13}$C NMR** (101 MHz, acetone-$d_6$): δ = 168.83 (4C), 139.42 (4C), 138.03 (4C), 134.85 (4C), 133.27 (4C), 123.64 (4C), 104.18 (4C, β-Py), 103.23 (4C, β-Py), 39.19 (2C), 38.70 (2C, N*C*H$_2$), 37.94 (2C, *C*H$_2$), 35.82 (2C), 29.45 (4C, *C*H$_3$ overlapping with acetone) 26.39 (2C, *C*H$_3$), 24.51 (2C, $NCH_2CH_2$) ppm.

*trans*-**2**: **$^1$H NMR** (400 MHz, acetone-$d_6$): δ = 7.98 (s, 4H, NH), 7.82 (s, 8H, Phth), 5.71-5.65 (m, 8H, β-Py), 3.57 (t, *J*=6.8 Hz, 4H, NC*H*$_2$), 1.96-1.87 (m, 4H, $CH_2$), 1.51-1.39 (m, 4H, $NCH_2CH_2$), 1.40 (s, 6H, $CH_3$), 1.39 (s, 12H, C*H*$_3$CC*H*$_3$) ppm. **$^{13}$C NMR** (101 MHz, acetone-$d_6$): δ = 168.86 (4C), 139.44 (4C), 138.02 (4C), 134.82 (4C), 133.28 (4C), 123.63 (4C), 104.16 (4C, β-Py), 103.19 (4C, β-Py), 39.16 (2C), 38.69 (2C, N*C*H$_2$), 38.12 (2C, $CH_2$), 35.81 (2C), 29.48 (4C, *C*H$_3$ overlapping with acetone), 26.15 (2C, *C*H$_3$), 24.57 (2C, $NCH_2CH_2$) ppm.




**Calix[4]pyrrole 3**. Calix[4]pyrrole **2** as a mixture of the *cis* and *trans* isomers (300 mg, 0.38 mmol) was dissolved in dichloromethane (8 ml) in a round-bottomed flask equipped with a magnetic stirrer bar, condenser and nitrogen balloon and ethanol (8 ml) was added. Hydrazine monohydrate (0.15 ml, 3.1 mmol) was added, and the solution was heated to reflux overnight (20 h). The evaporated dichloromethane was replenished, and the solution was allowed to cool to room temperature. White/creamy precipitate (side product) was filtered off and washed with ethanol (5 ml) and dichloromethane (2 x 5 ml). To the filtrate was added 0.1 M aqueous NaOH solution (30 ml), the water phase was separated and extracted with dichloromethane (3 x 15 ml). The combined organic extracts were dried with $Na_2SO_4$, filtered into 100 ml flask, and evaporated to dryness under vacuum to afford the intermediate **6** as a creamy solid. The product was used immediately in the next step.

Bis-amine **6** (197 mg, 0.38 mmol), previously dried under vacuum, was suspended in dry THF (30 ml) under nitrogen atmosphere. The suspension was cooled with an ice bath and a solution of *p*-nitrophenyl isocyanate (140 mg, 0.85 mmol) in THF (15 ml) was added via syringe with stirring. The obtained creamy-yellowish solution was allowed to warm to room temperature. The suspension turned to clear solution in 30 minutes. After 4 hours of stirring the solvent was evaporated on a rotary evaporator and the obtained orange-yellow residue was dried under vacuum. The crude was dissolved in ethyl acetate, adsorbed on silica (1.5 g) and subjected to flash chromatography using 80 g Redisep Gold silica column and dichloromethane/ethyl acetate 100:0 to 80:20 gradient as an eluent. The fractions containing the *trans*-**3** were combined and concentrated to yield 62.6 mg (19.4 %) of pure product. The fractions containing *cis*-**3** isomer gave 45 mg (13.9 %) of pure α,α-**3** after drying under vacuum.

*cis*-**3**: HR-MS (ESI-TOF): *m/z* calcd. for $[M+Na]^+$ $C_{46}H_{54}N_{10}O_6Na^+$ 865.4120; found 865.4062. **$^1$H NMR** (500 MHz, acetone-$d_6$): δ = 8.51 (s, 2H, ArN*H*), 8.13 (d, *J* = 9.2, 4H, Ar*H*), 7.99 (s, 4H, Py-N*H*), 7.71 (d, *J* = 9.2, 4H, Ar*H*), 6.04 (t, *J* = 5.3, 2H, $CH_2NH$), 5.75 (m, 8H, β-Py), 3.14 (m, 4H, NHC$H_2$), 1.92 (m, 4H, CC$H_2$), 1.47 (s, 6H, C$H_3$), 1.44 (s, 6H, C$H_3$), 1.43 (s, 6H, C$H_3$), 1.39–1.31 (m, 4H, $NCH_2CH_2$) ppm. **$^{13}$C NMR** (126 MHz, acetone-$d_6$): δ = 155.18 (2C, *C*=O), 148.15 (2C, Ar), 142.14 (2C, Ar), 139.37 (4C, α-Py), 138.21 (4C, α-Py), 125.70 (4C, ArH), 117.86 (4C, ArH), 104.09 (4C, β-Py), 103.23 (4C, β-Py), 40.86 (2C, N$CH_2$), 39.24 (2C, *meso*-C), 38.34 (2C, *C*$CH_2$), 35.82 (2C, *meso*-C), 29.84 (2C overlapping with acetone, *C*$H_3$), 28.97 (2C, *C*$H_3$), 26.10 (2C), 25.99 (2C) ppm.

*trans*-**3**: HR-MS (ESI-TOF): *m/z* calcd. for $[M+Na]^+$ $C_{46}H_{54}N_{10}O_6Na^+$ 865.4120; found 865.4065. **$^1$H NMR** (500 MHz, acetone-$d_6$): δ = 8.48 (s, 2H, ArN*H*), 8.13 (d, *J* = 9.2, 4H, Ar*H*), 7.99 (s, 4H, Py-N*H*), 7.70 (d, *J* = 9.2, 4H, Ar*H*), 6.02 (t, *J* = 5.3, 2H, $CH_2NH$), 5.75 (m, 8H, β-Py), 3.14 (m, 4H, NHC$H_2$), 1.93 (m, 4H, CC$H_2$), 1.45 (s, 12H, C$H_3$CC$H_3$), 1.43 (s, 6H, C$H_3$), 1.39–1.30 (m, 4H, $NCH_2CH_2$) ppm. **$^{13}$C NMR** (126 MHz, acetone-$d_6$): δ = 155.20 (2C, *C*=O), 148.16 15 (2C, Ar), 142.19 (2C, Ar), 139.42 (4C, α-Py), 138.25 (4C, α-Py), 125.69 (4C, ArH), 117.89 (4C, ArH), 104.15 (4C, β-Py), 103.28 (4C, β-Py), 40.89 (2C, N$CH_2$), 39.28 (2C, *meso*-C), 38.22 (2C, *C*$CH_2$), 35.85 (2C, *meso*-C), 29.6 (4C overlapping with acetone, *C*$H_3$), 26.21 (2C), 26.09 (2C) ppm.

## 3. NMR spectra

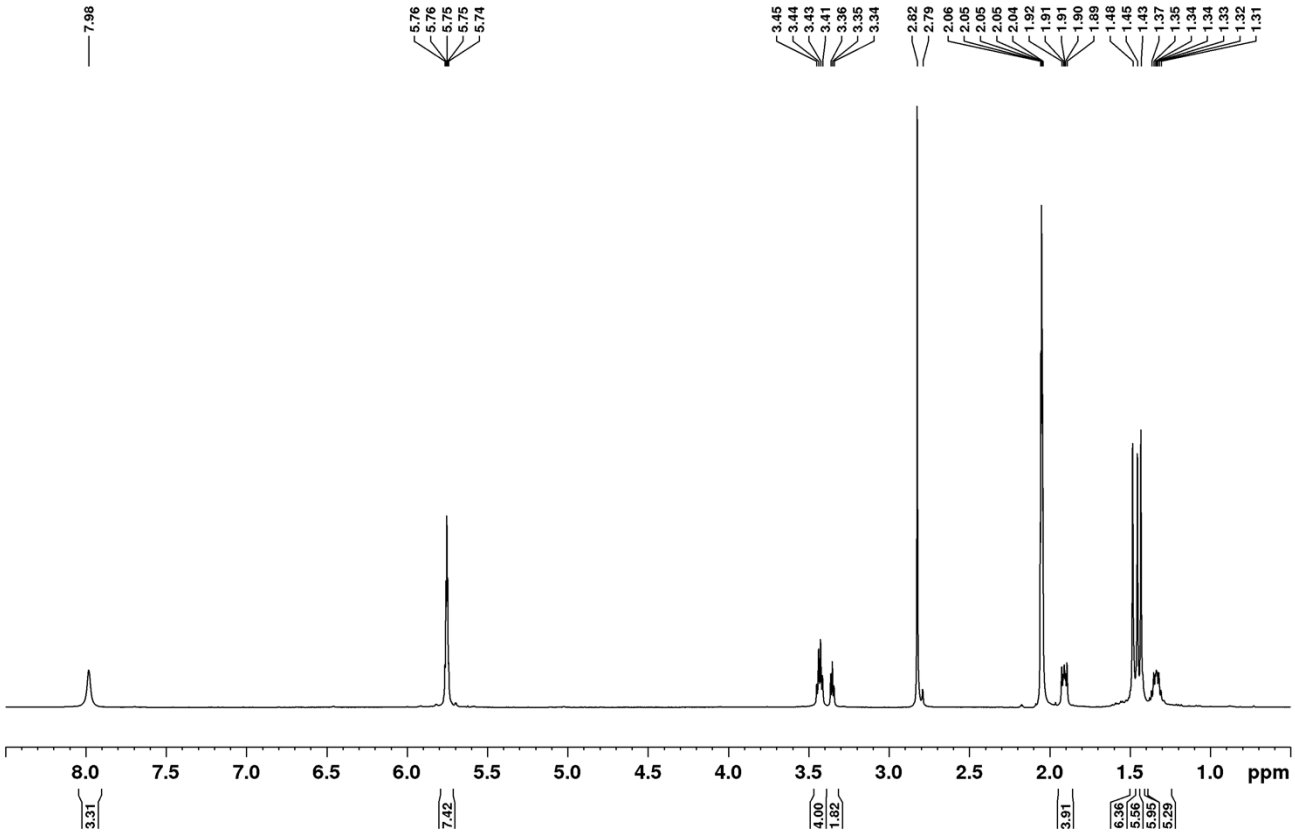



Fig. S-1 $^{1}$H NMR spectrum of *cis*-**1** in acetone-$d_6$ (at 30 °C, 500 MHz).

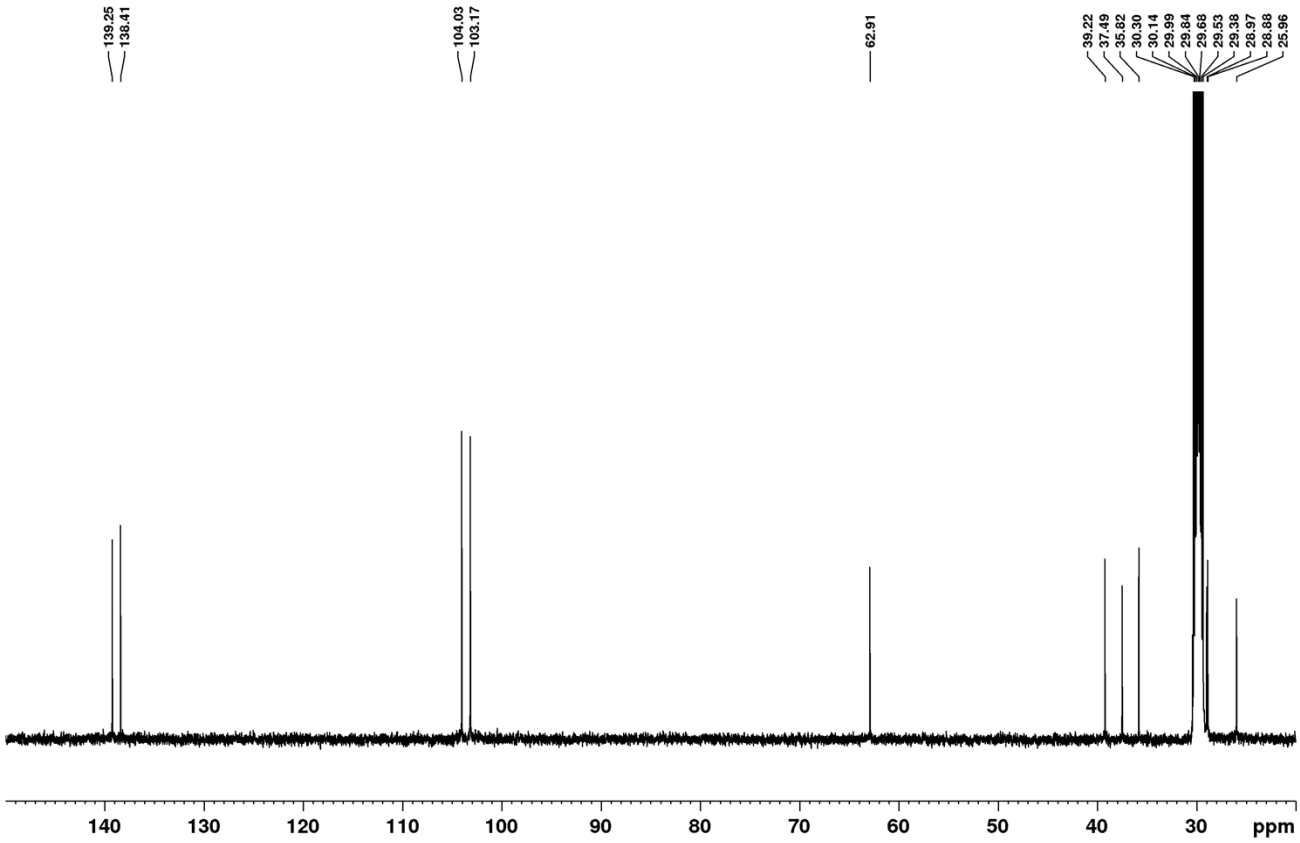


Fig. S-2 $^{13}$C NMR spectrum of *cis*-**1** in acetone-$d_6$ (at 30 °C, 126 MHz).

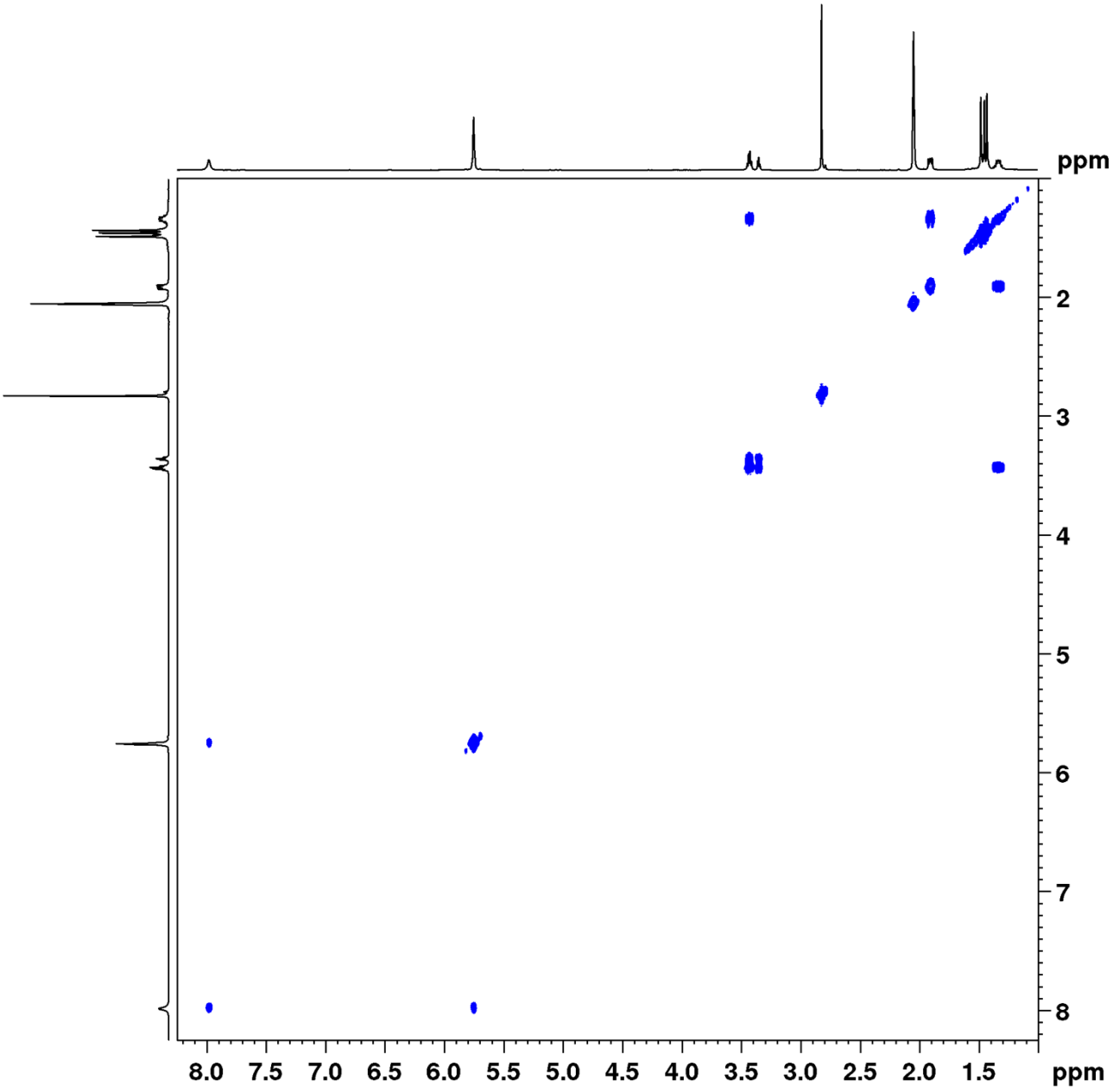



Fig. S-3 $^{1}$H-$^{1}$H COSY of *cis*-**1** in acetone-$d_6$ (at 30 °C, 500 MHz).

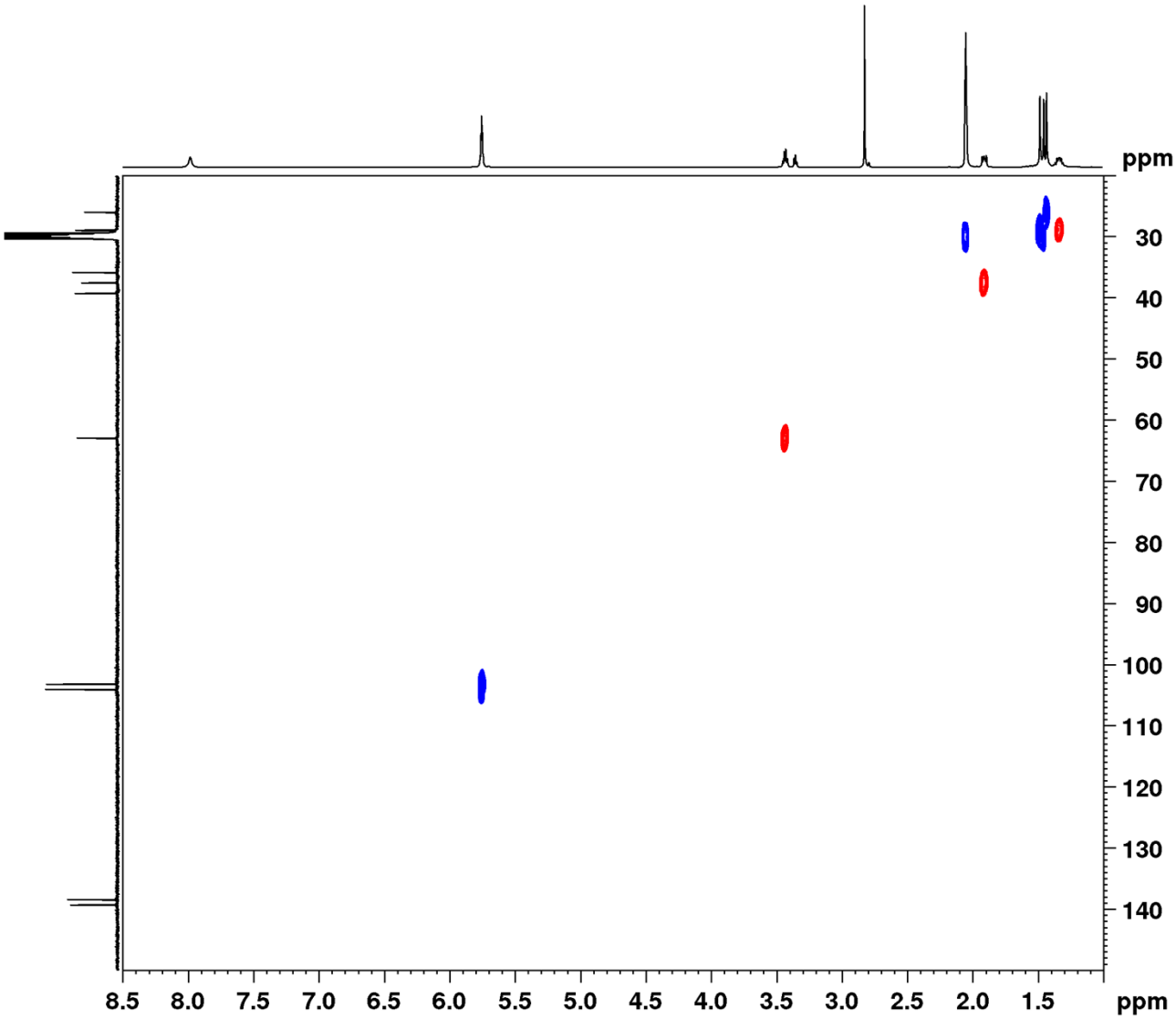



Fig. S-4 HSQC of *cis*-**1** in acetone-$d_6$ (at 30 °C, 500 MHz).

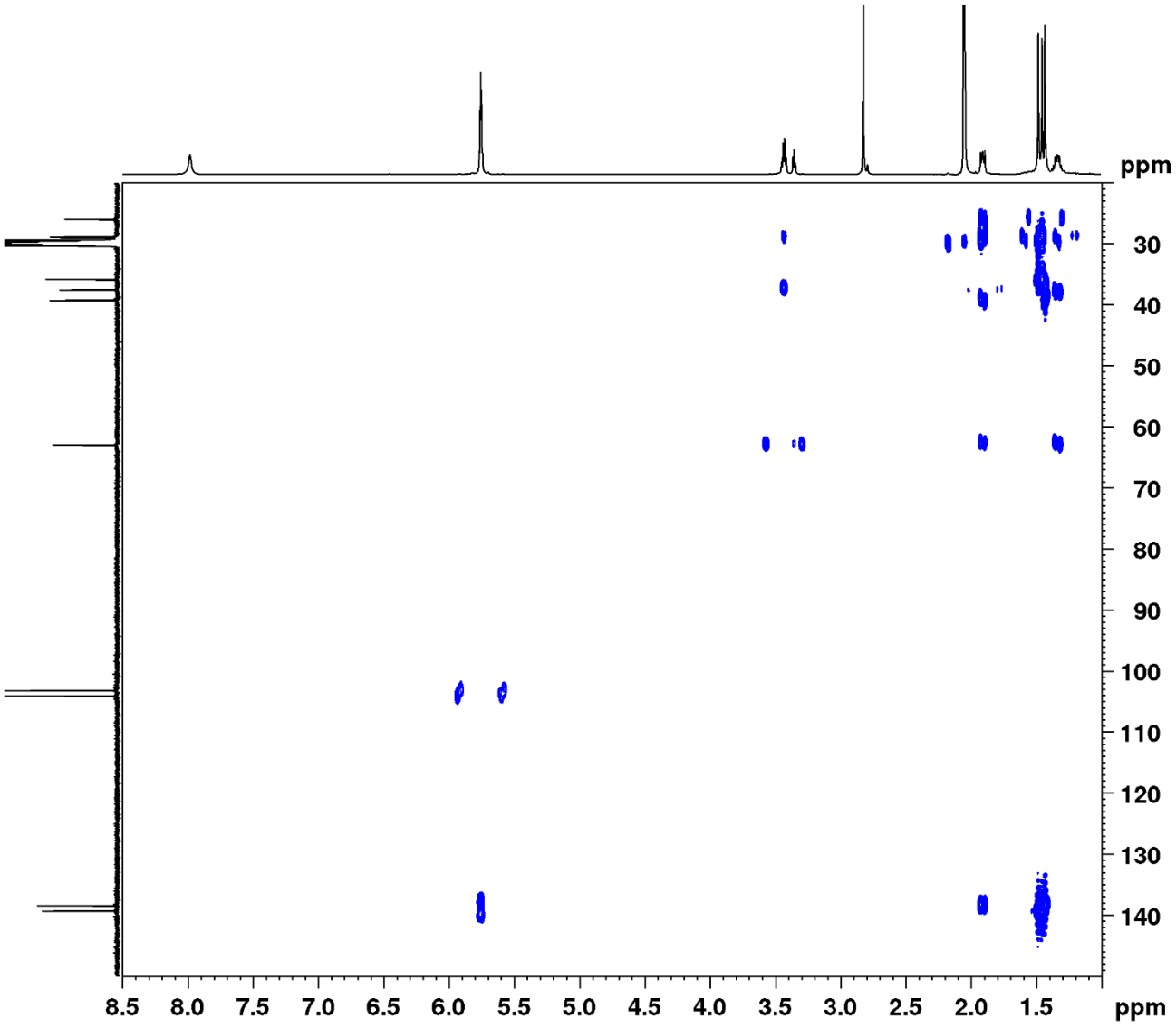



Fig. S-5 HMBC of *cis*-**1** in acetone-$d_6$ (at 30 °C, 500 MHz).

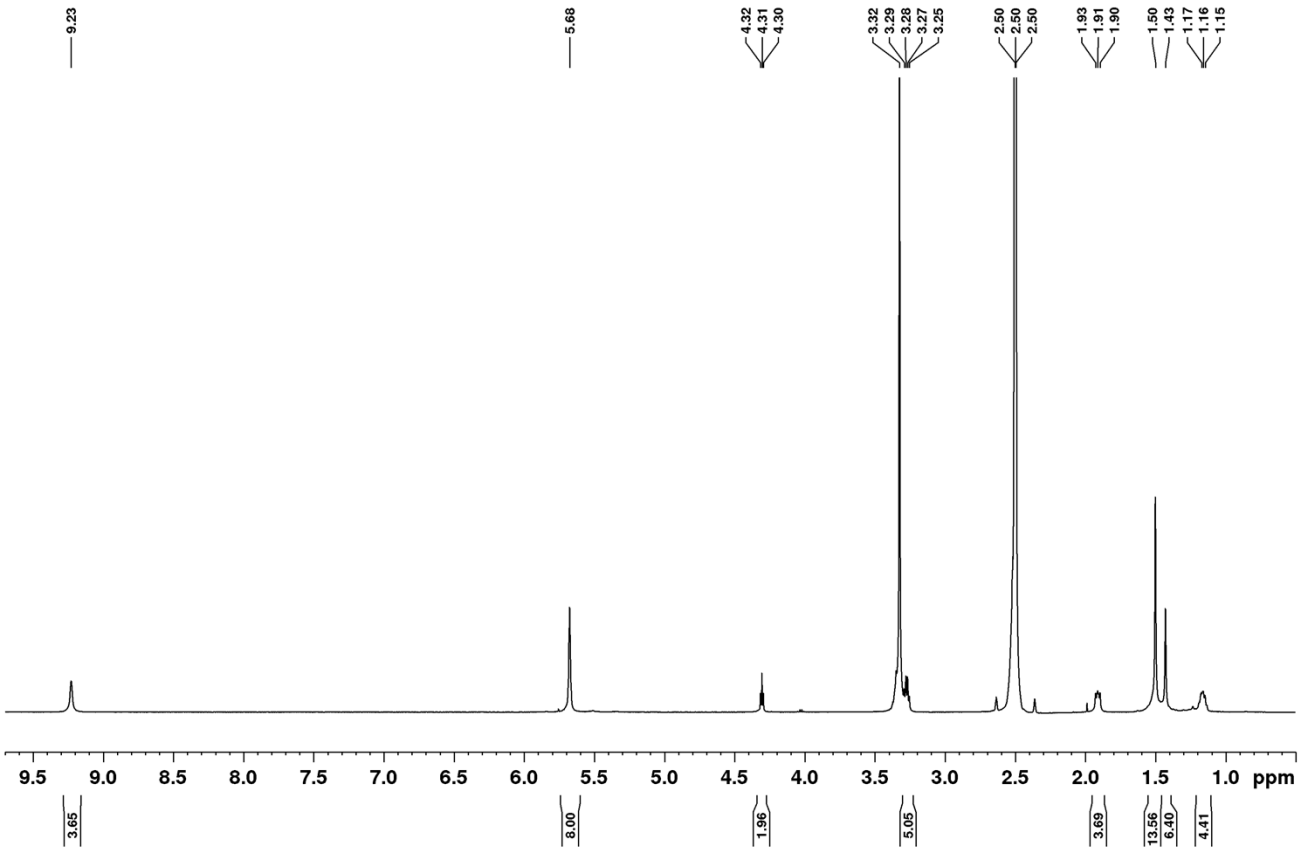



Fig. S-6 $^{1}$H NMR spectrum of *trans*-**1** in DMSO-$d_6$ (at 30 °C, 500 MHz).

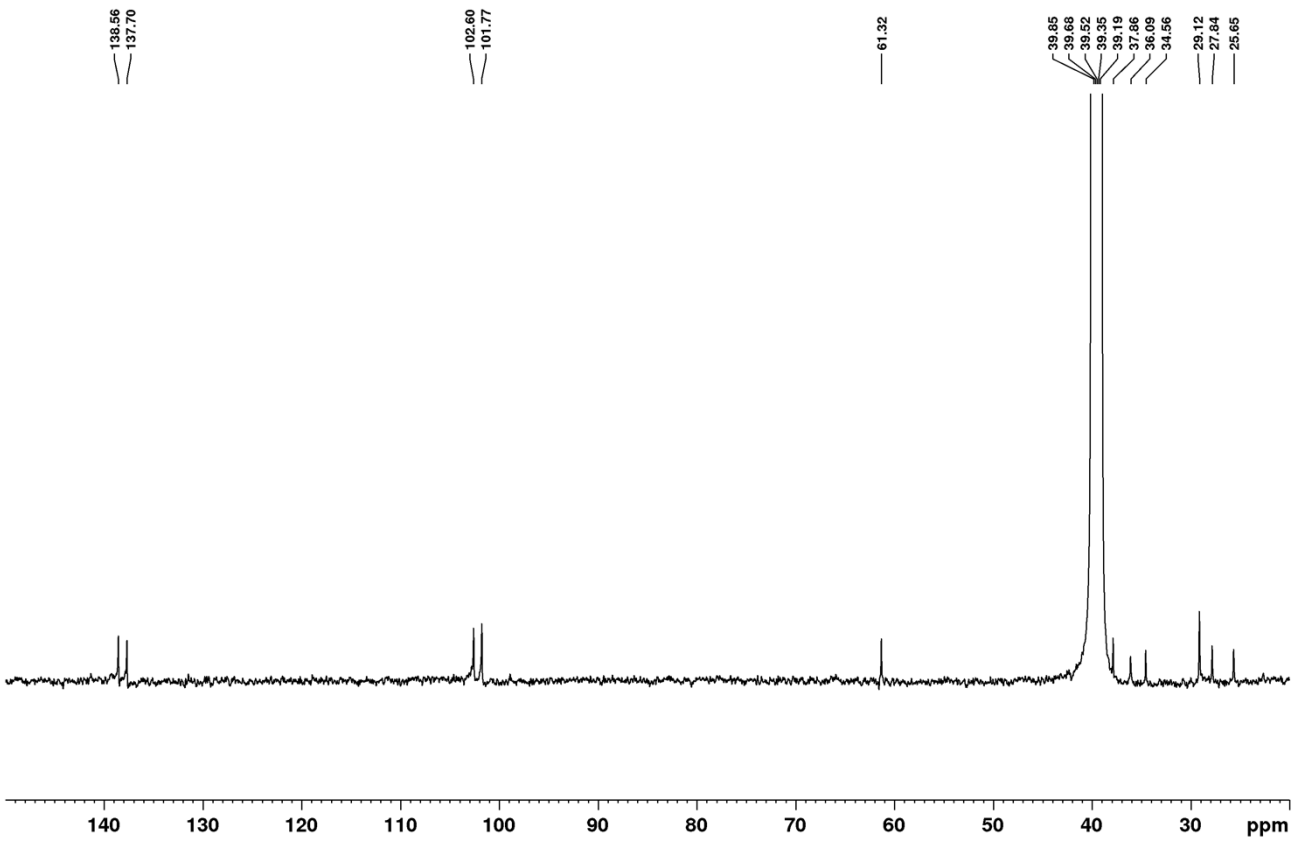



Fig. S-7 $^{13}$C NMR spectrum of *trans*-**1** in DMSO-$d_6$ (at 30 °C, 126 MHz).

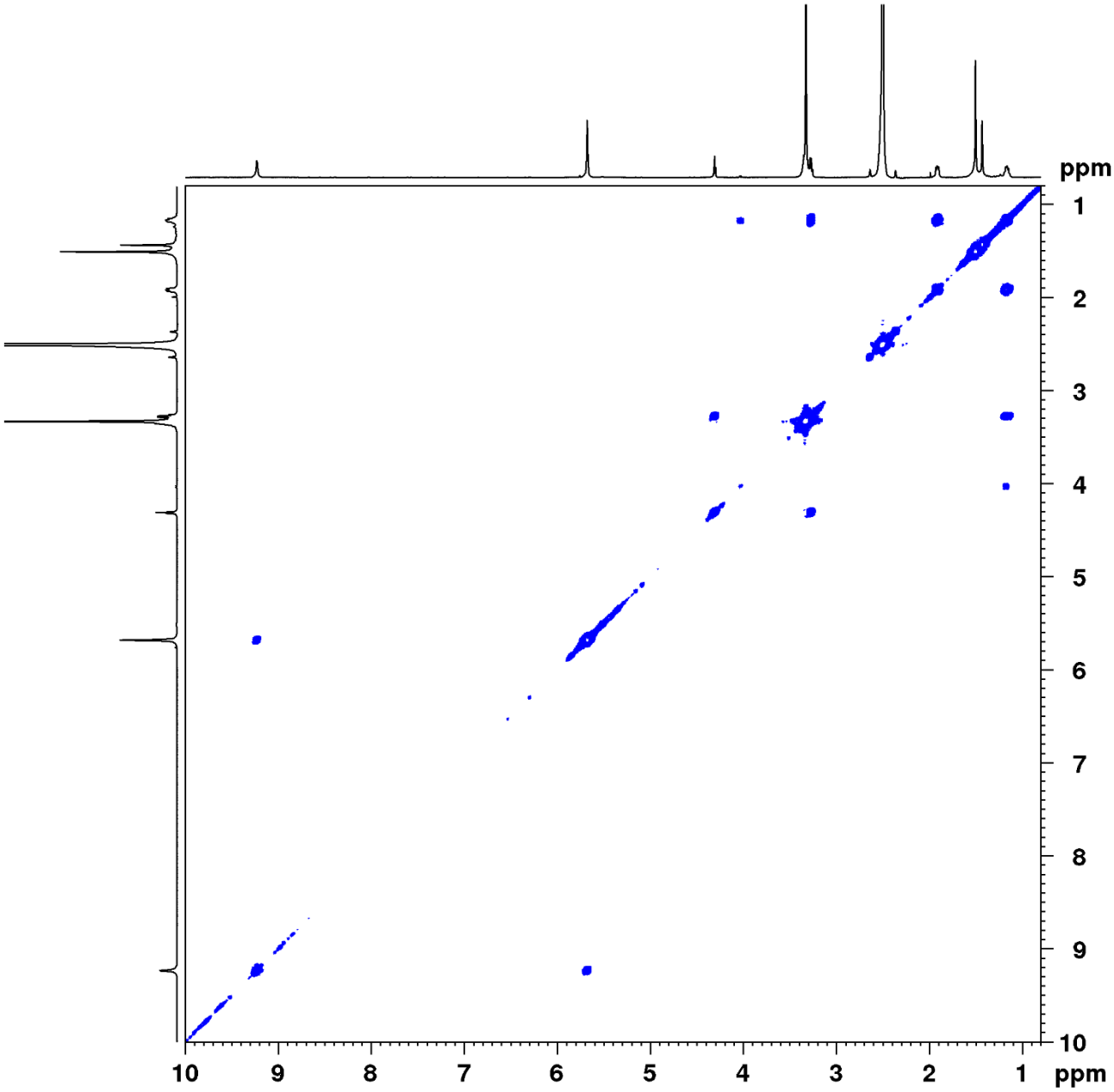



Fig. S-8 $^{1}$H-$^{1}$H COSY spectrum of *trans*-**1** in DMSO-$d_6$ (at 30 °C, 500 MHz).

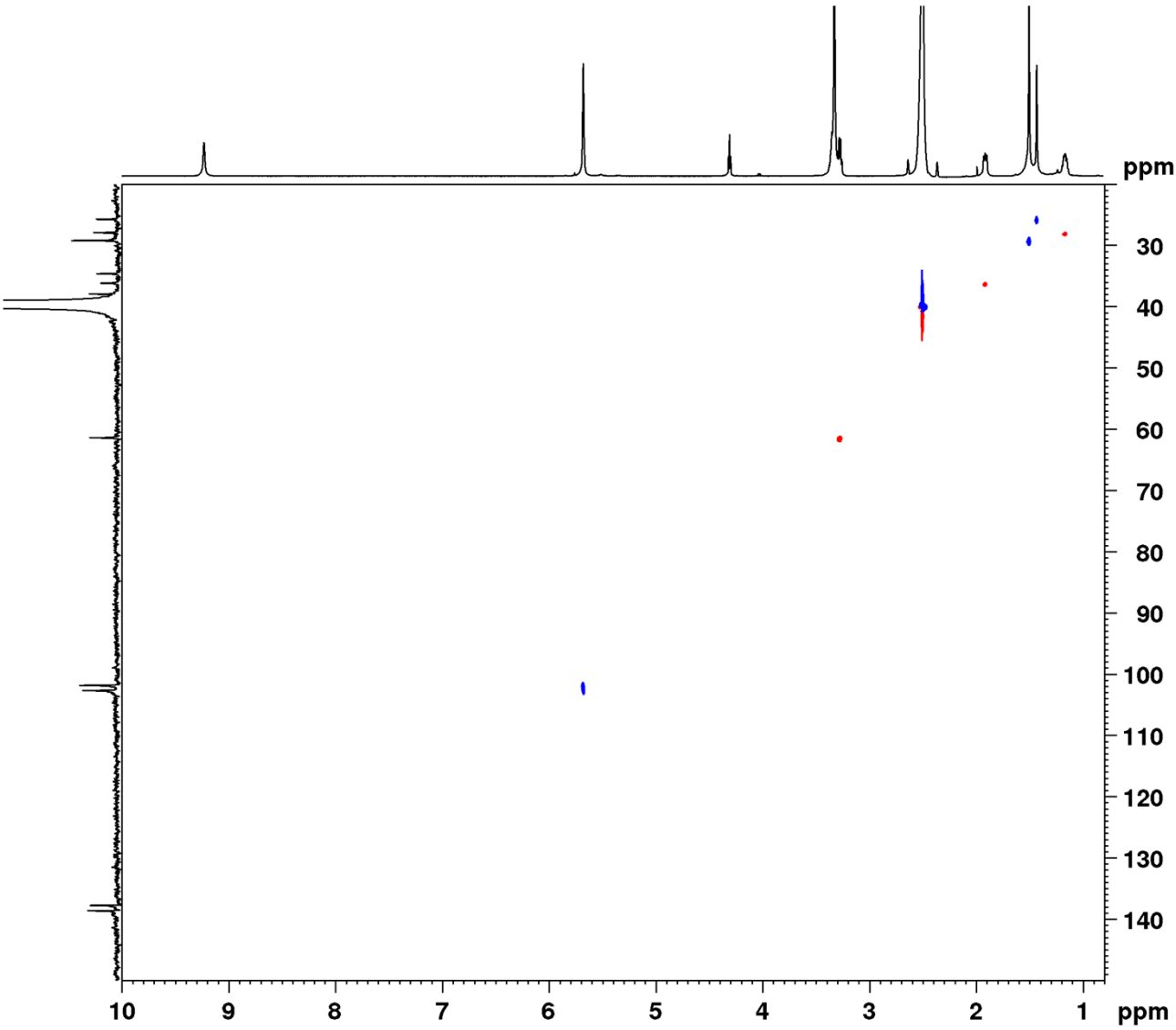



Fig. S-9 HSQC spectrum of *trans*-**1** in DMSO-$d_6$ (at 30 °C, 500 MHz).

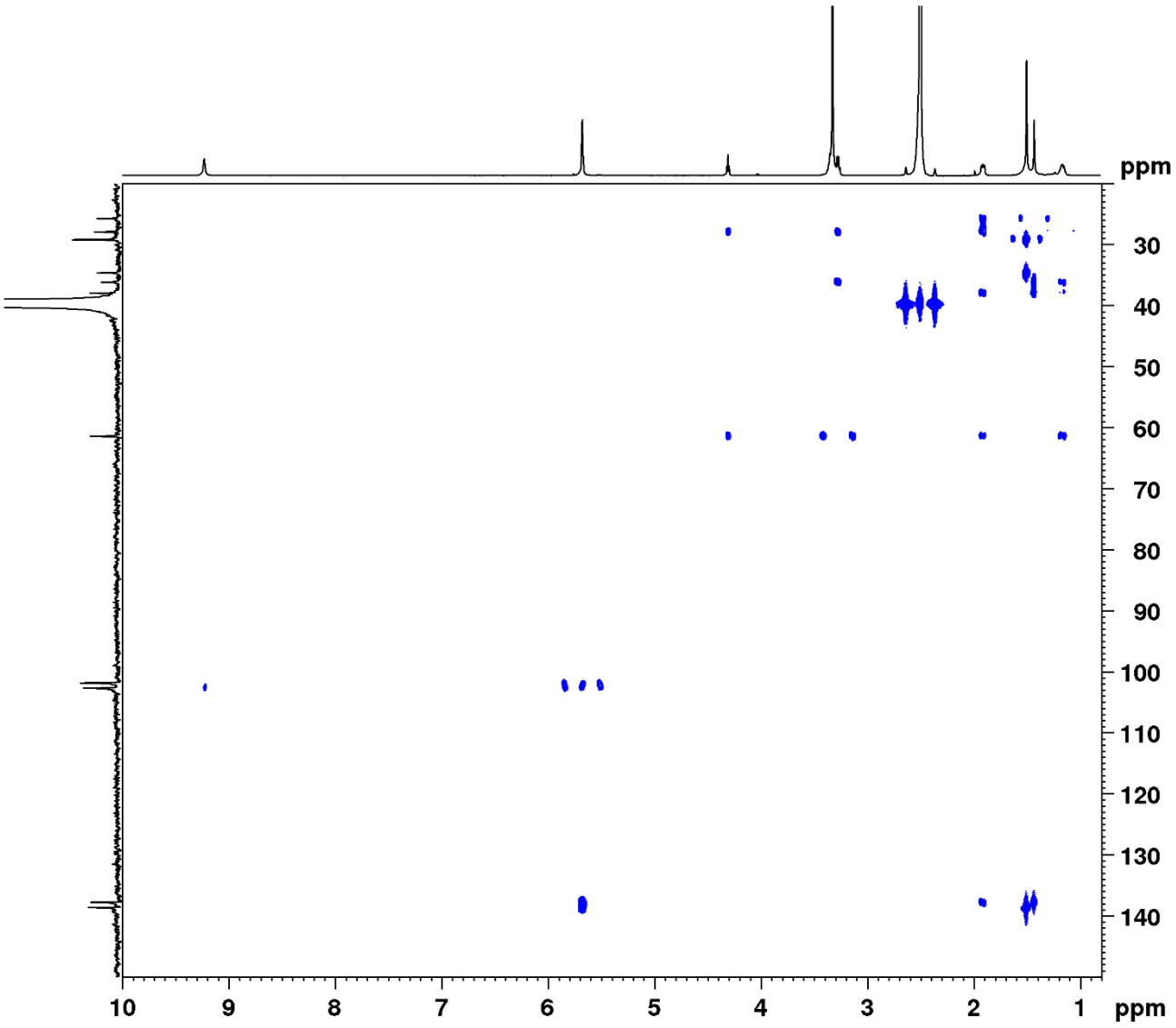



Fig. S-10 HMBC spectrum of *trans*-**1** in DMSO-$d_6$ (at 30 °C, 500 MHz).

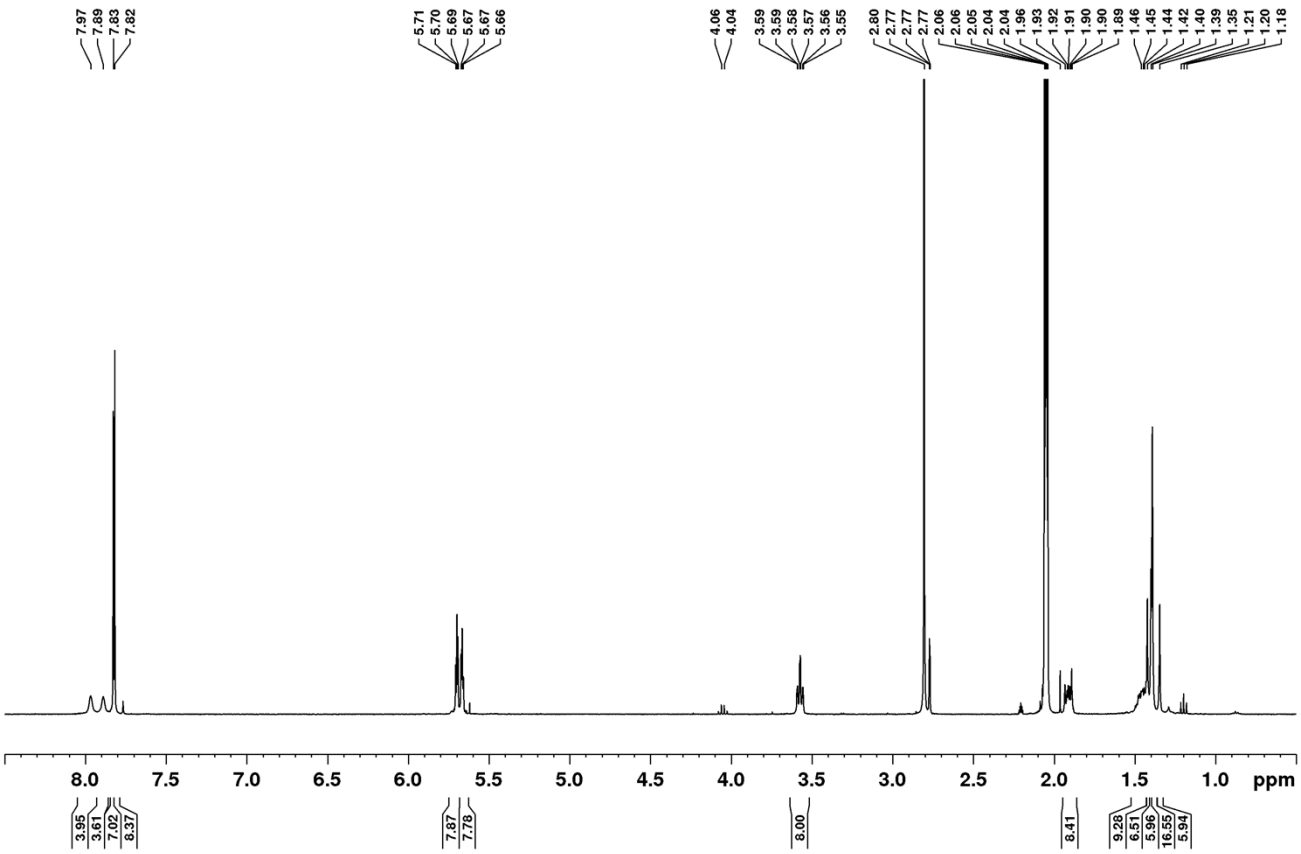



Fig. S-11 $^{1}$H NMR spectrum of **2** after column chromatography (mixture of *cis*- and *trans*-isomers) in acetone-$d_6$ (at 25 °C, 400 MHz).

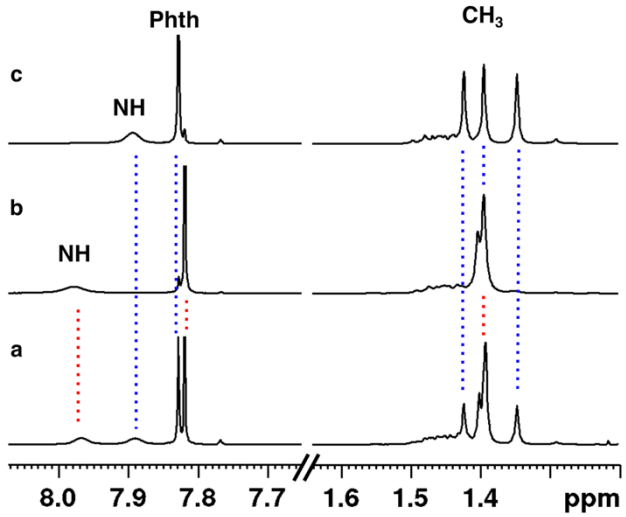



Fig. S-12 Aromatic region and *meso*-methyl groups of a) mixture of *cis*-**2** and *trans*-**2**, b) *trans*-**2** and c) *cis*-**2** in acetone-$d_6$ at 400 MHz.

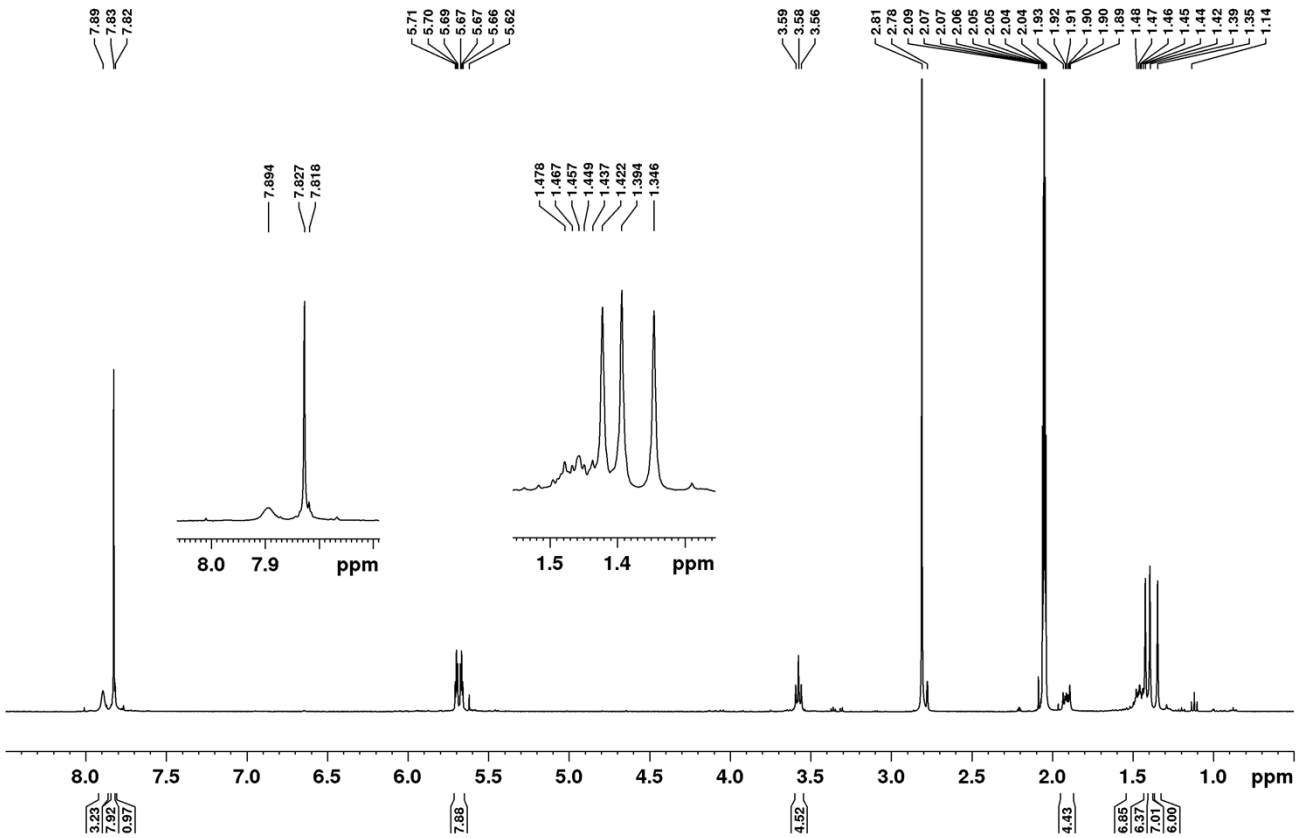



Fig. S-13 $^{1}$H NMR spectrum of *cis*-**2** in acetone-$d_6$ (at 25 °C, 400 MHz).

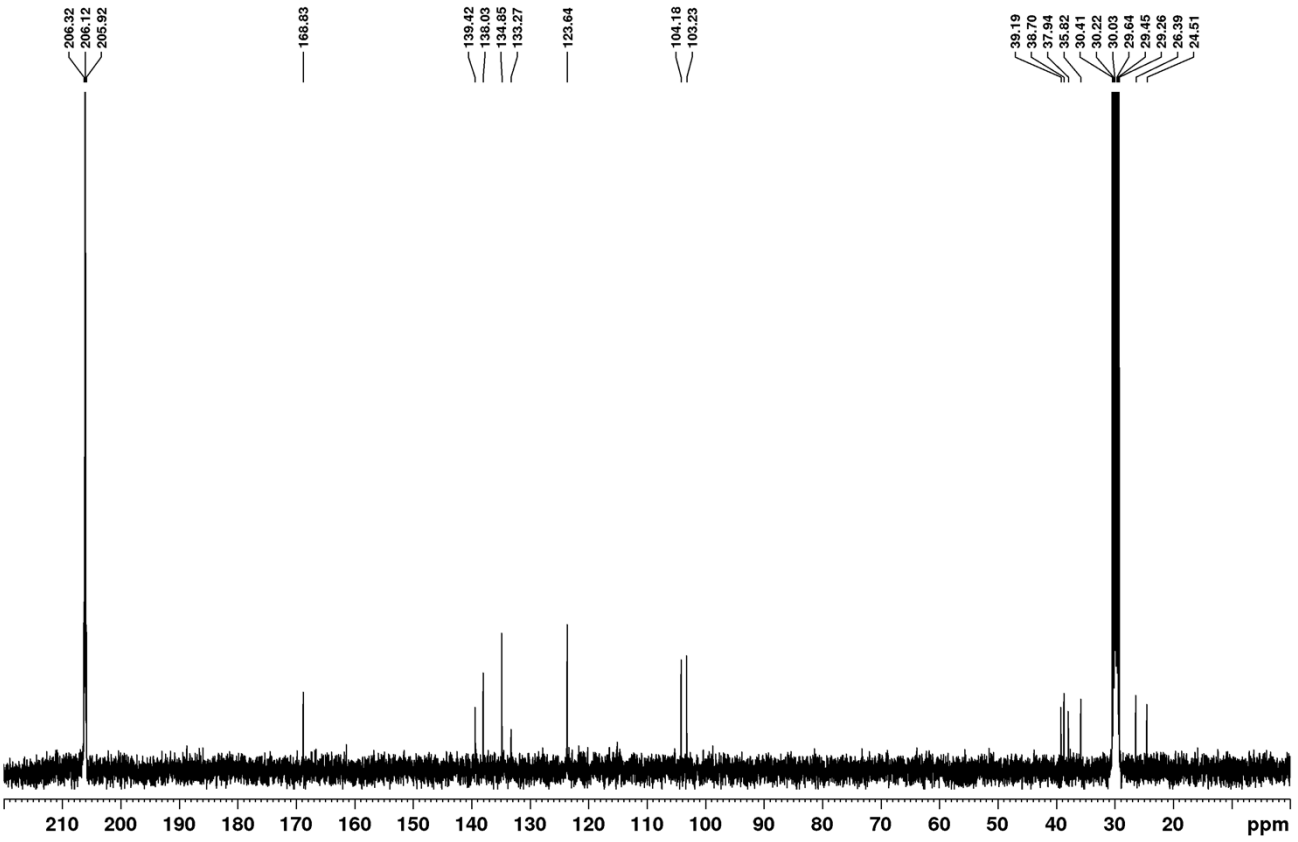



Fig. S-14 $^{13}$C NMR spectrum of *cis*-**2** in acetone-$d_6$ (at 25 °C, 100 MHz).

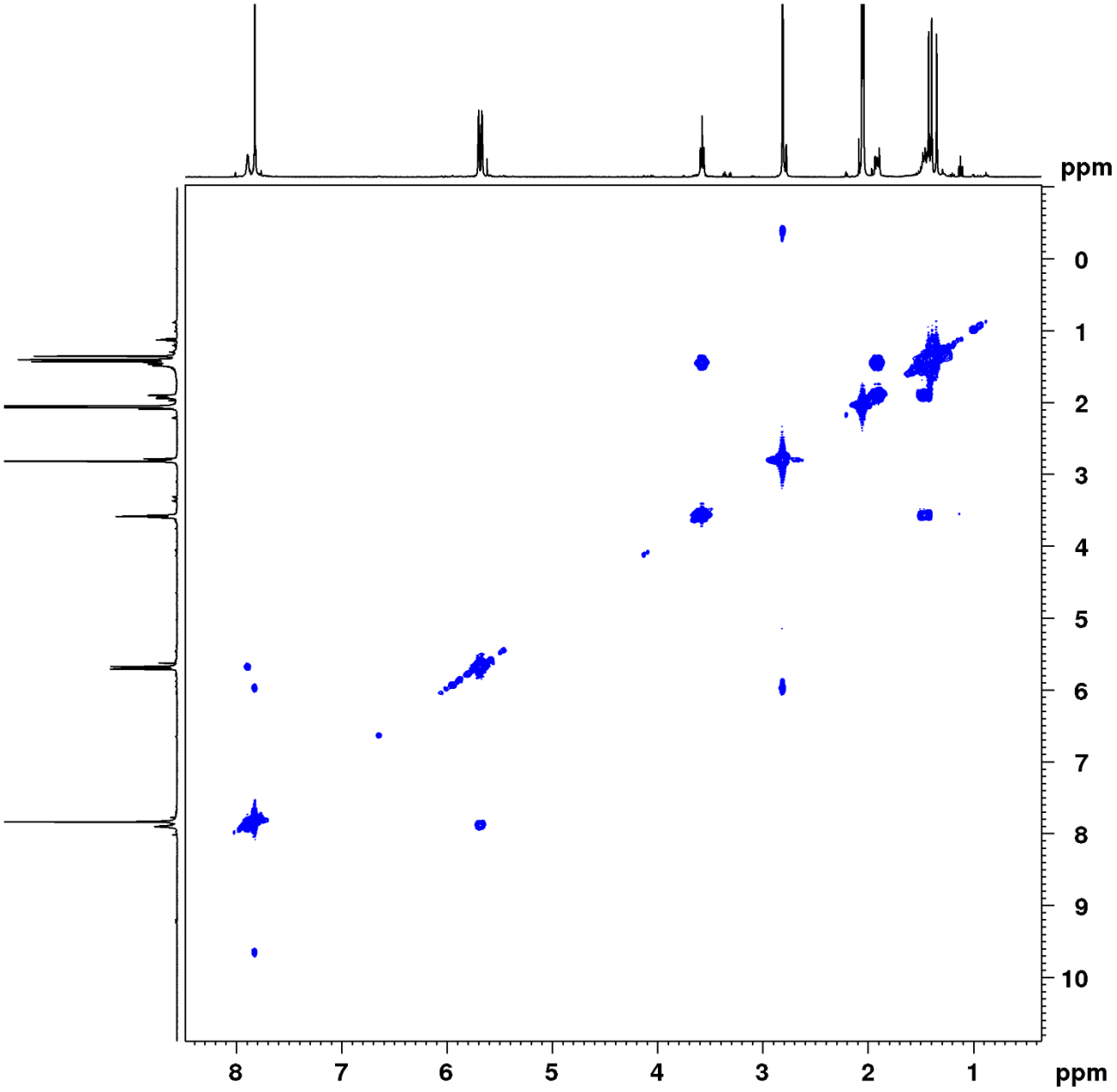



Fig. S-15 $^{1}$H-$^{1}$H COSY of *cis*-**2** in acetone-$d_6$ (at 25 °C, 400 MHz).

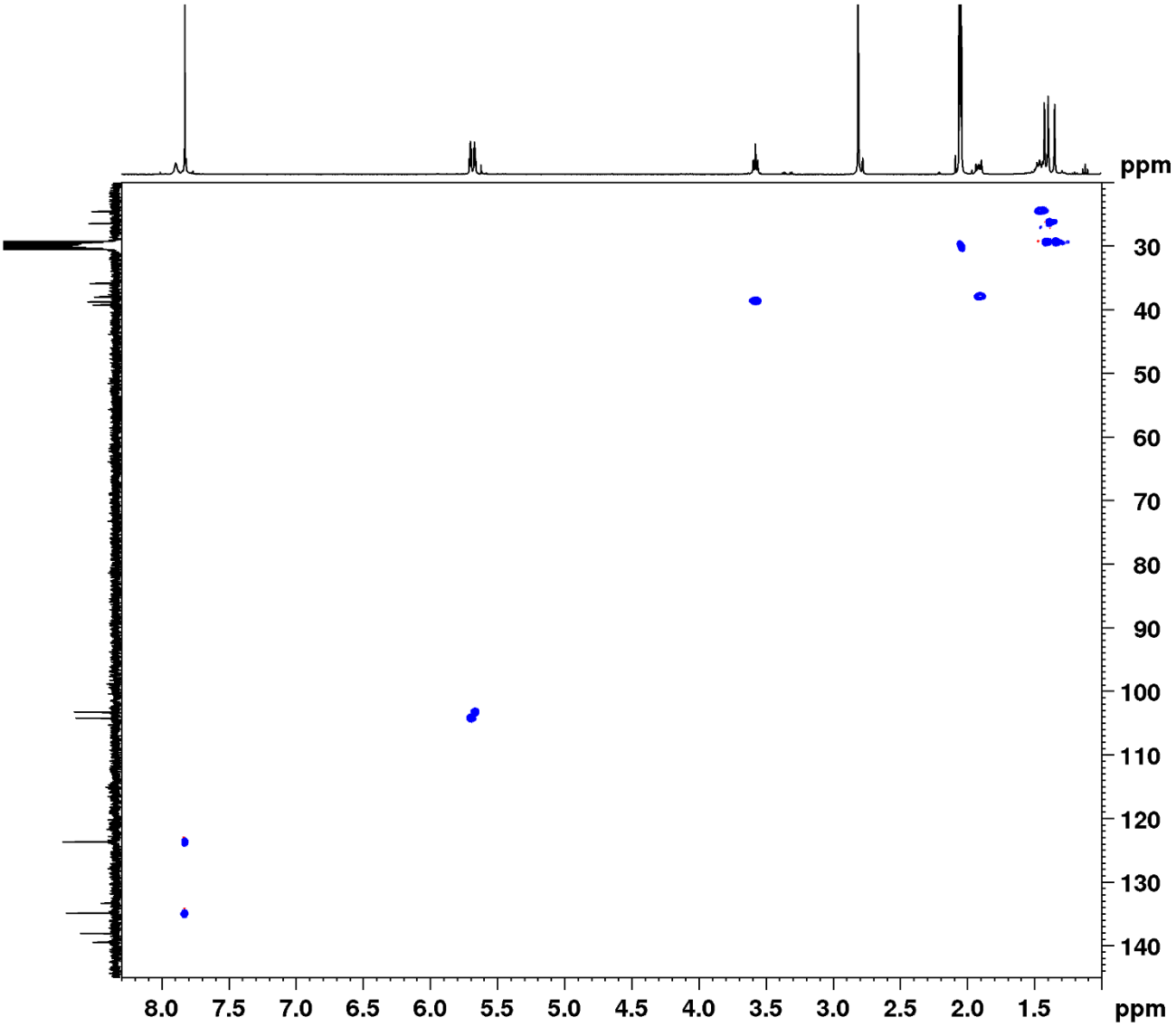



Fig. S-16 HSQC of *cis*-**2** in acetone-$d_6$ (at 25 °C, 400 MHz).

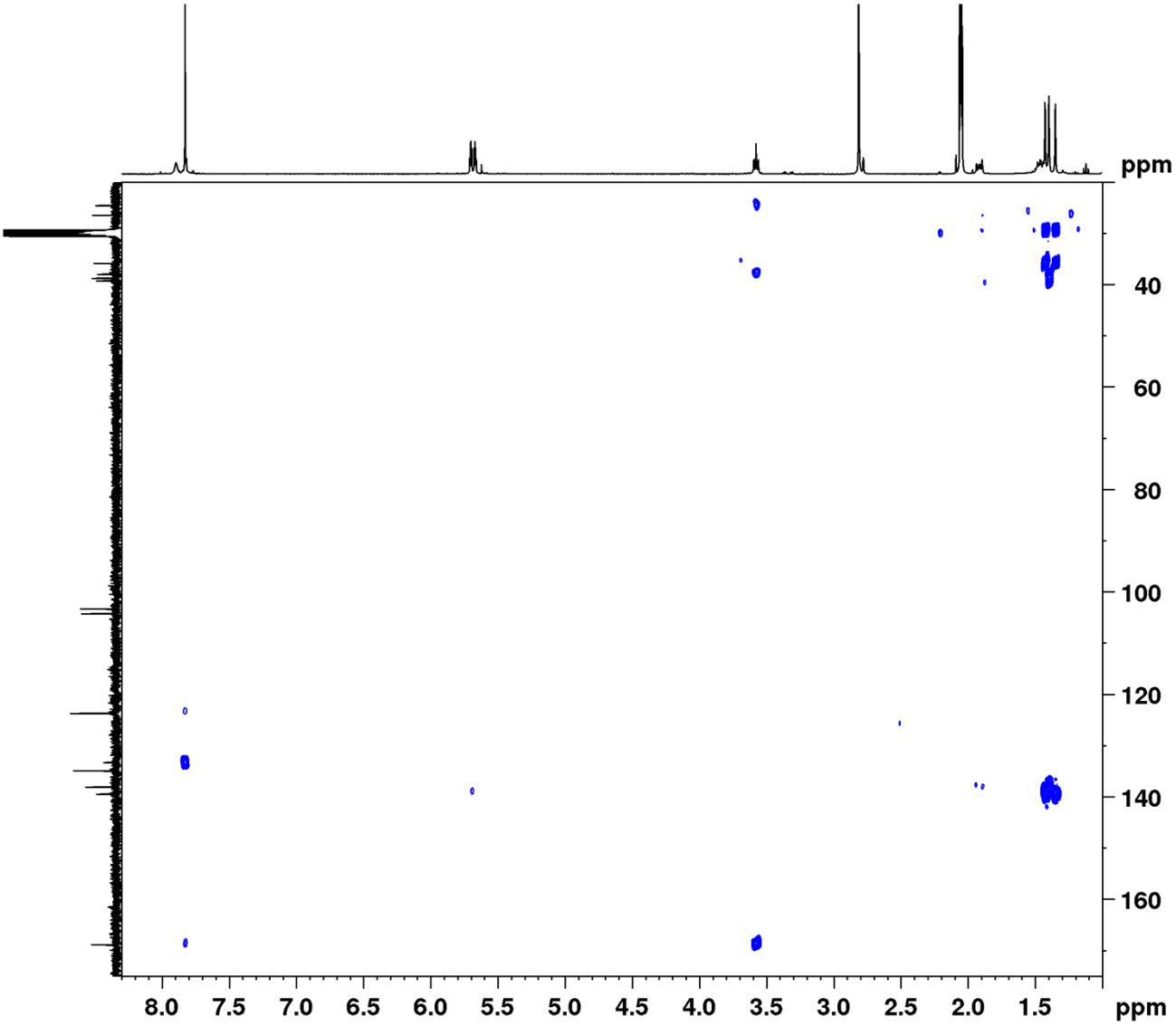



Fig. S-17 HMBC of *cis*-**2** in acetone-$d_6$ (at 25 °C, 400 MHz).

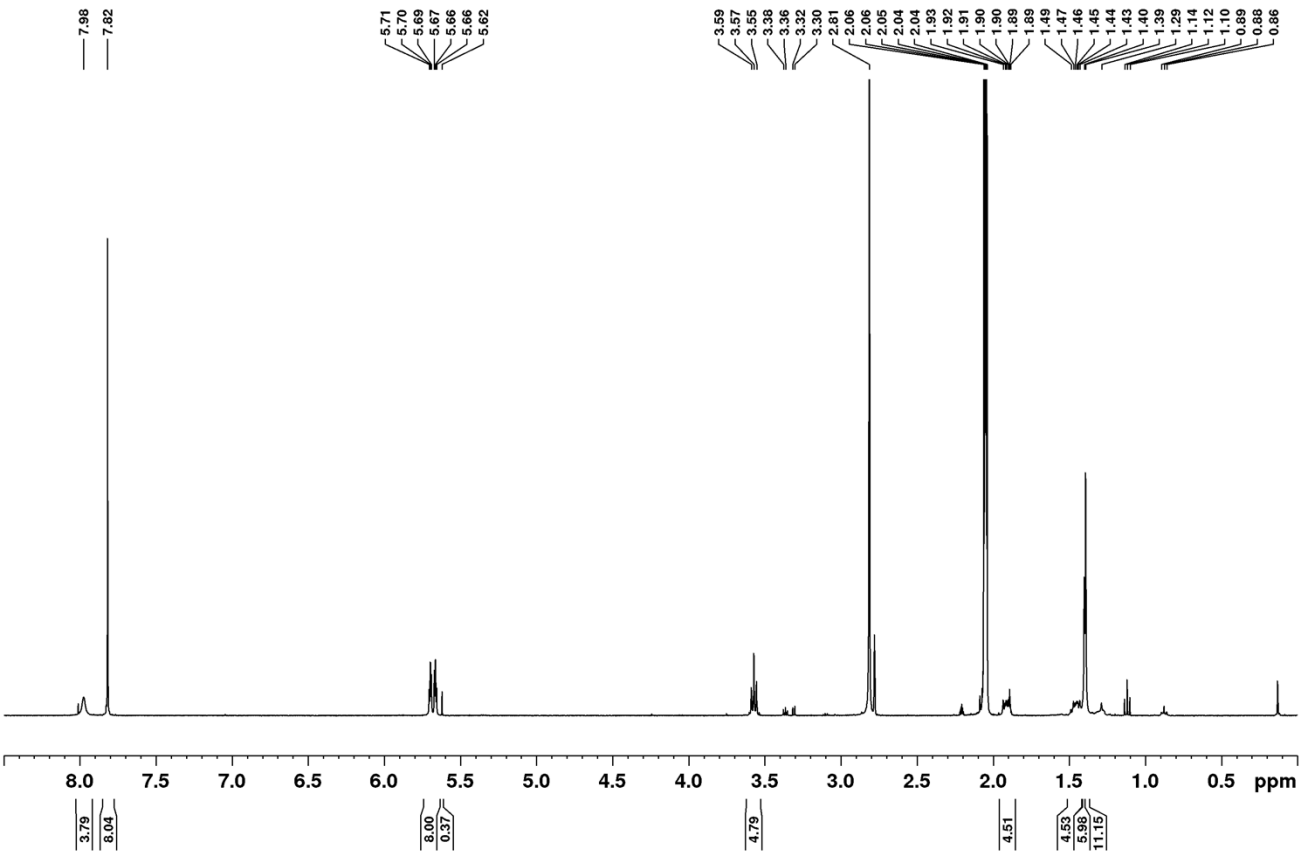



Fig. S-18 $^{1}$H NMR spectrum of *trans*-**2** in acetone-$d_6$ (at 25 °C, 400 MHz).

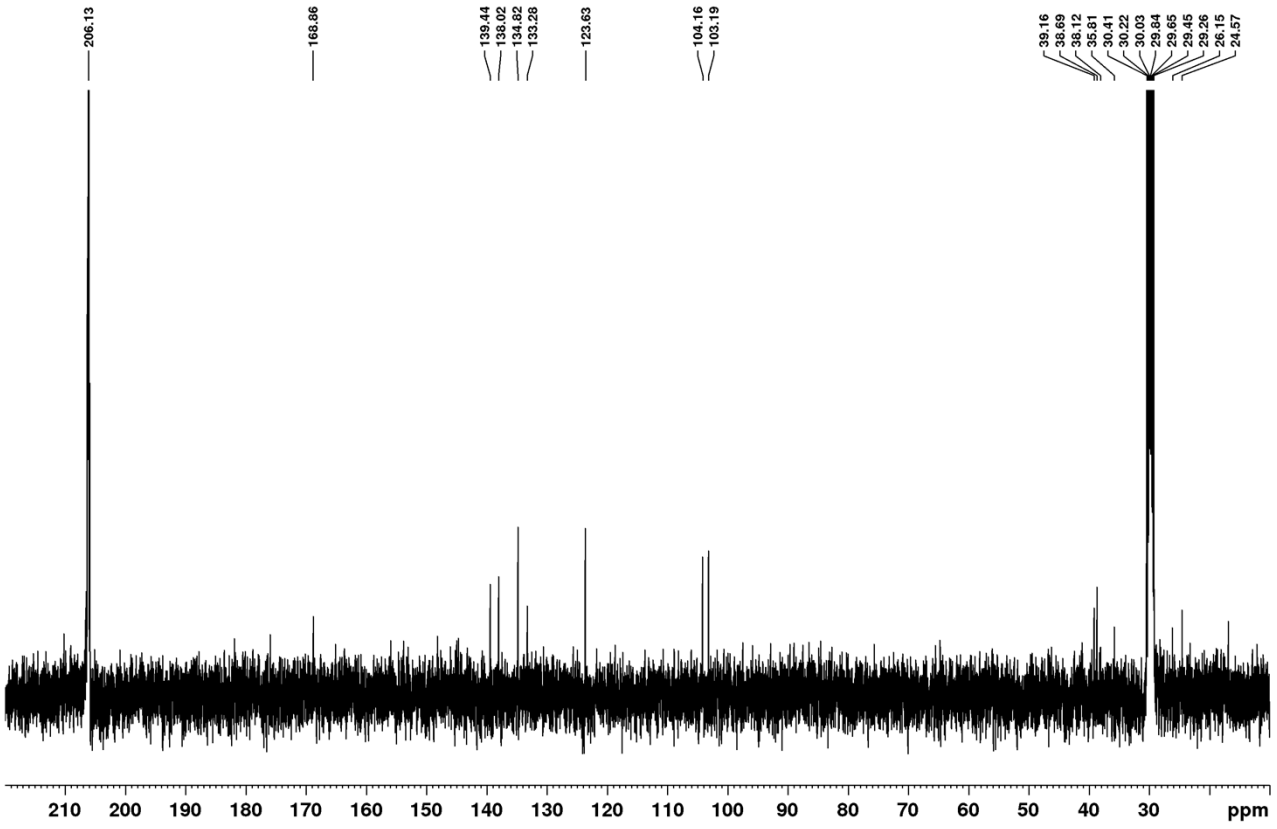



Fig. S-19 $^{13}$C NMR spectrum of *trans*-**2** in acetone-$d_6$ (at 25 °C, 100 MHz).

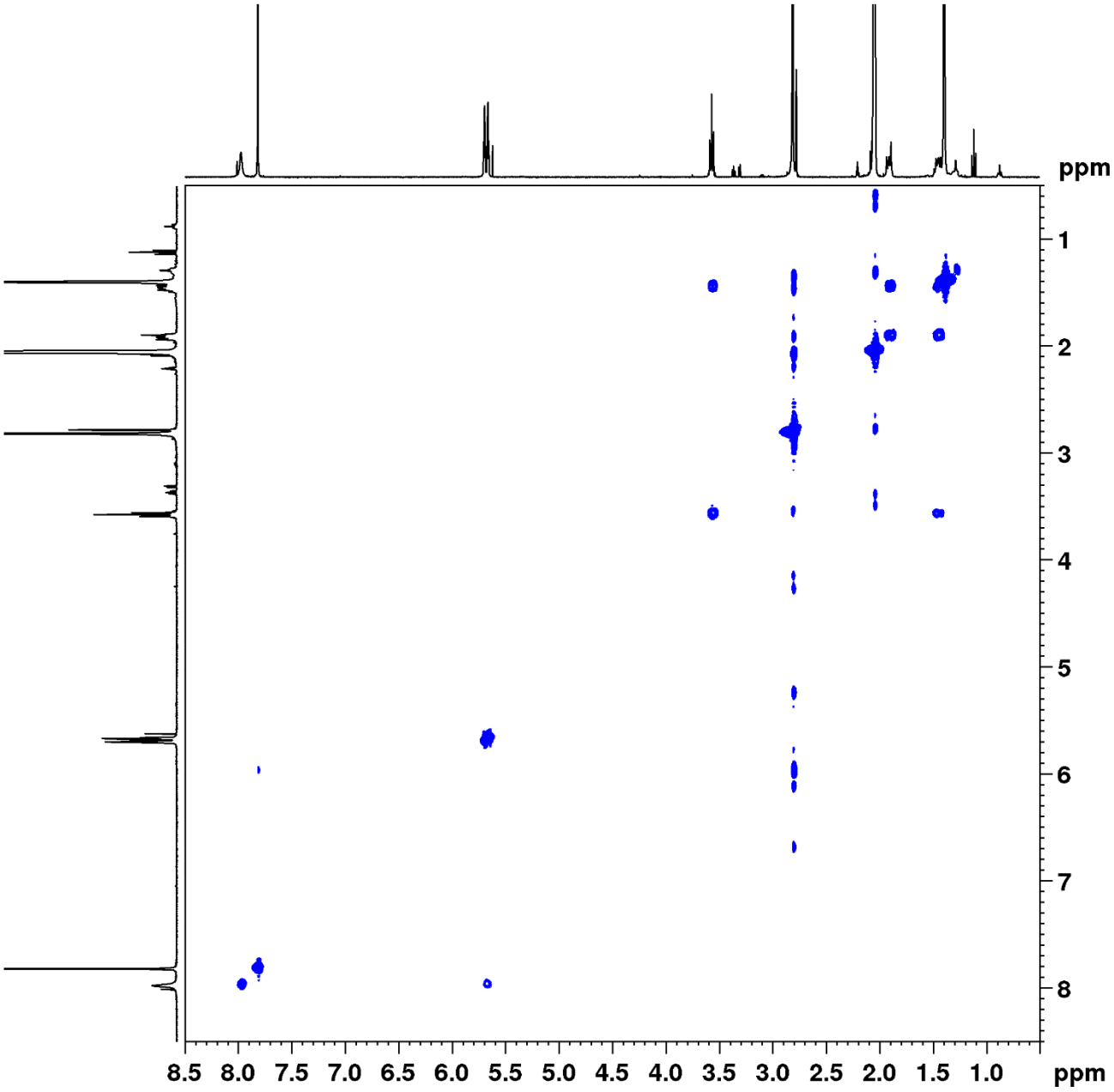



Fig. S-20 $^{1}$H-$^{1}$H COSY of *trans*-**2** in acetone-$d_6$ (at 25 °C, 400 MHz).

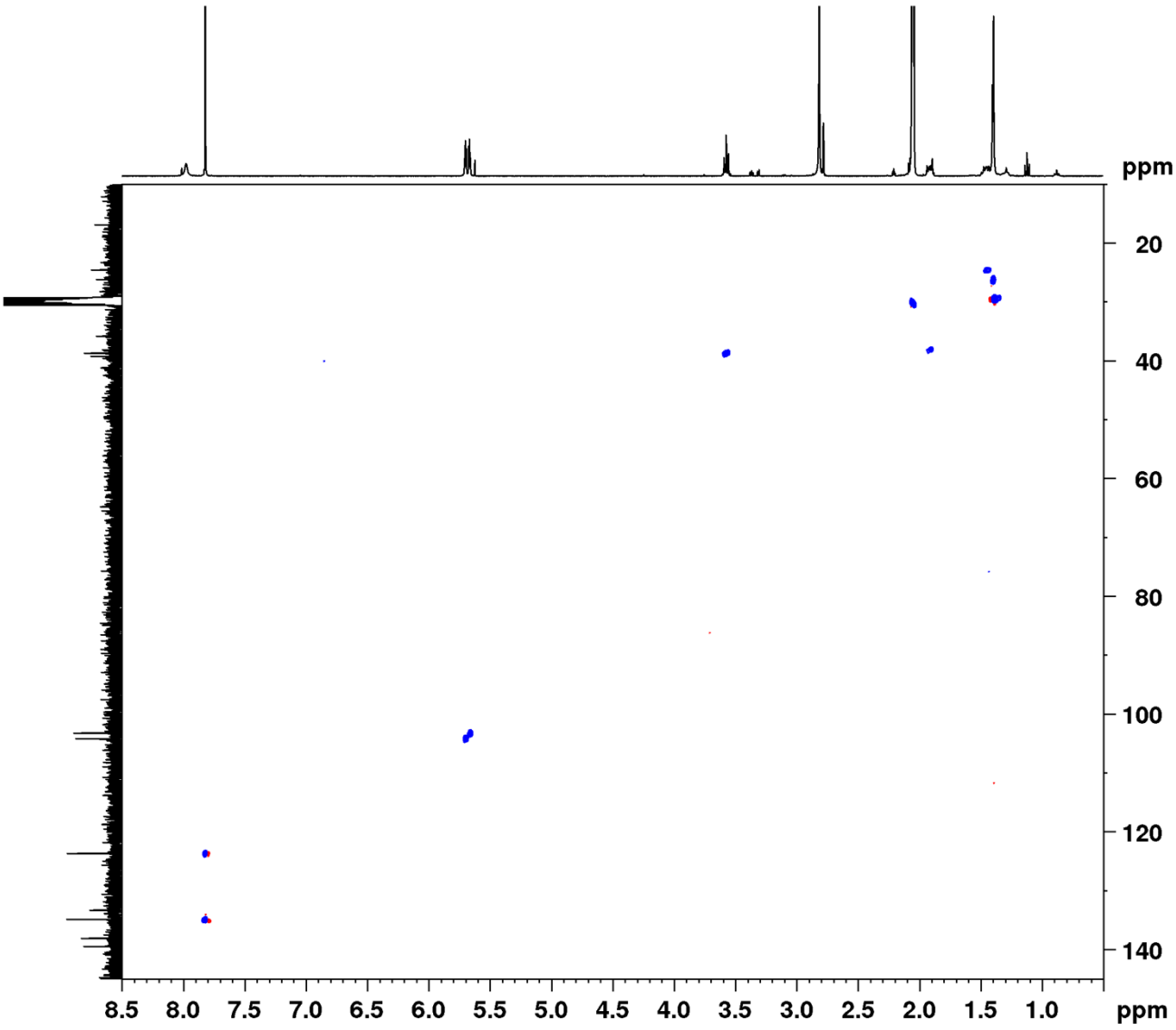



Fig. S-21 HSQC of *trans*-**2** in acetone-$d_6$ (at 25 °C, 400 MHz).

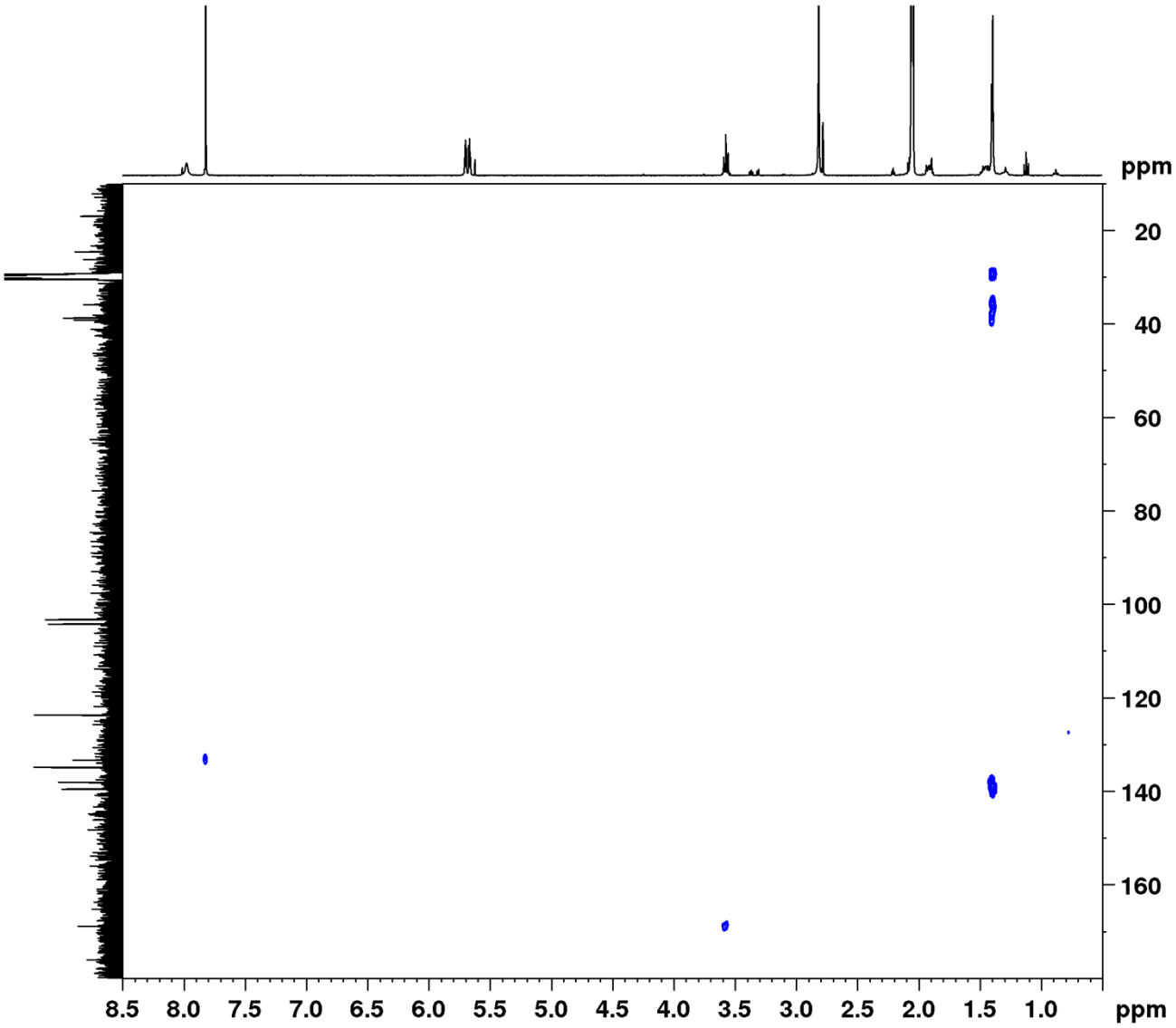



Fig. S-22 HMBC of *trans*-**2** in acetone-$d_6$ (at 25 °C, 400 MHz).

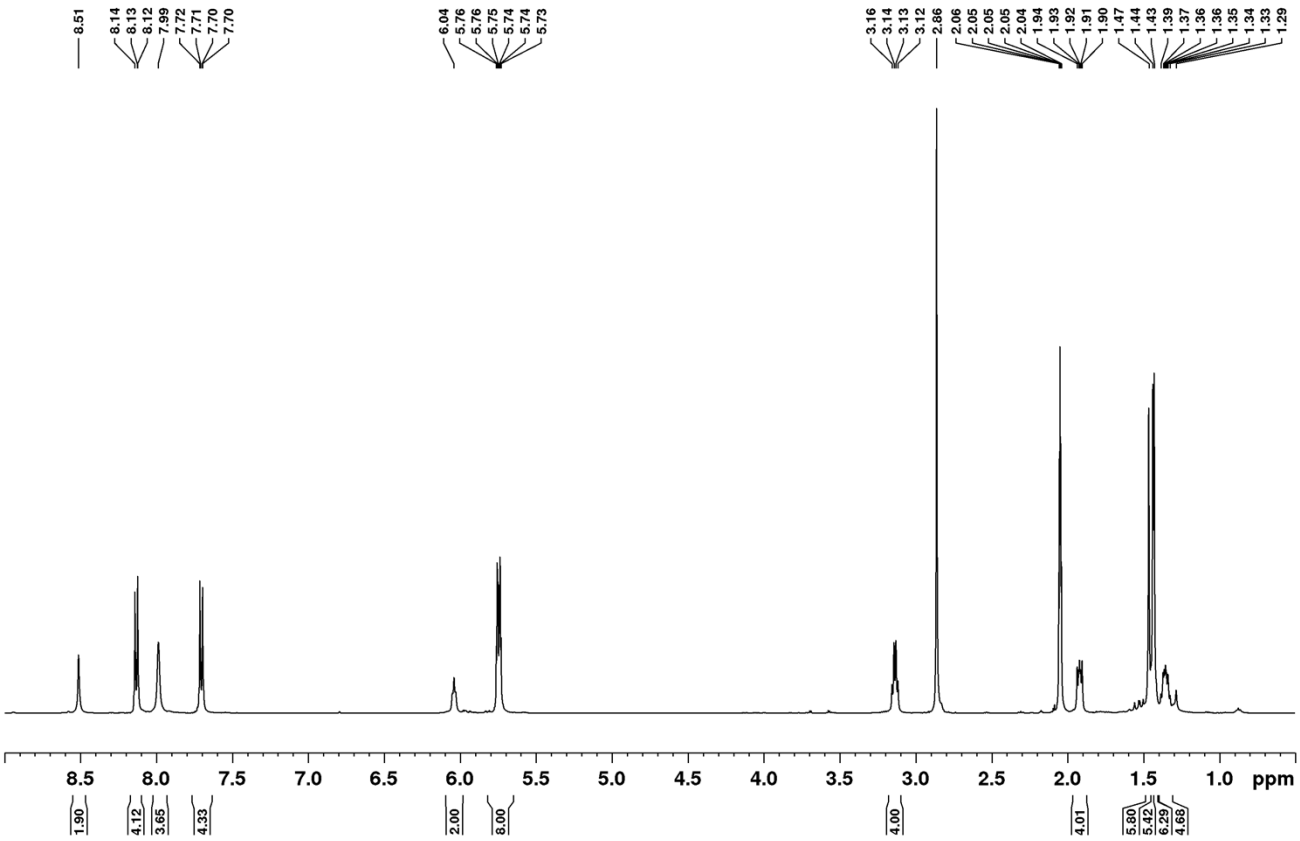



Fig. S-23 $^{1}$H NMR spectrum of *cis*-**3** in acetone-$d_6$ (at 30 °C, 500 MHz).

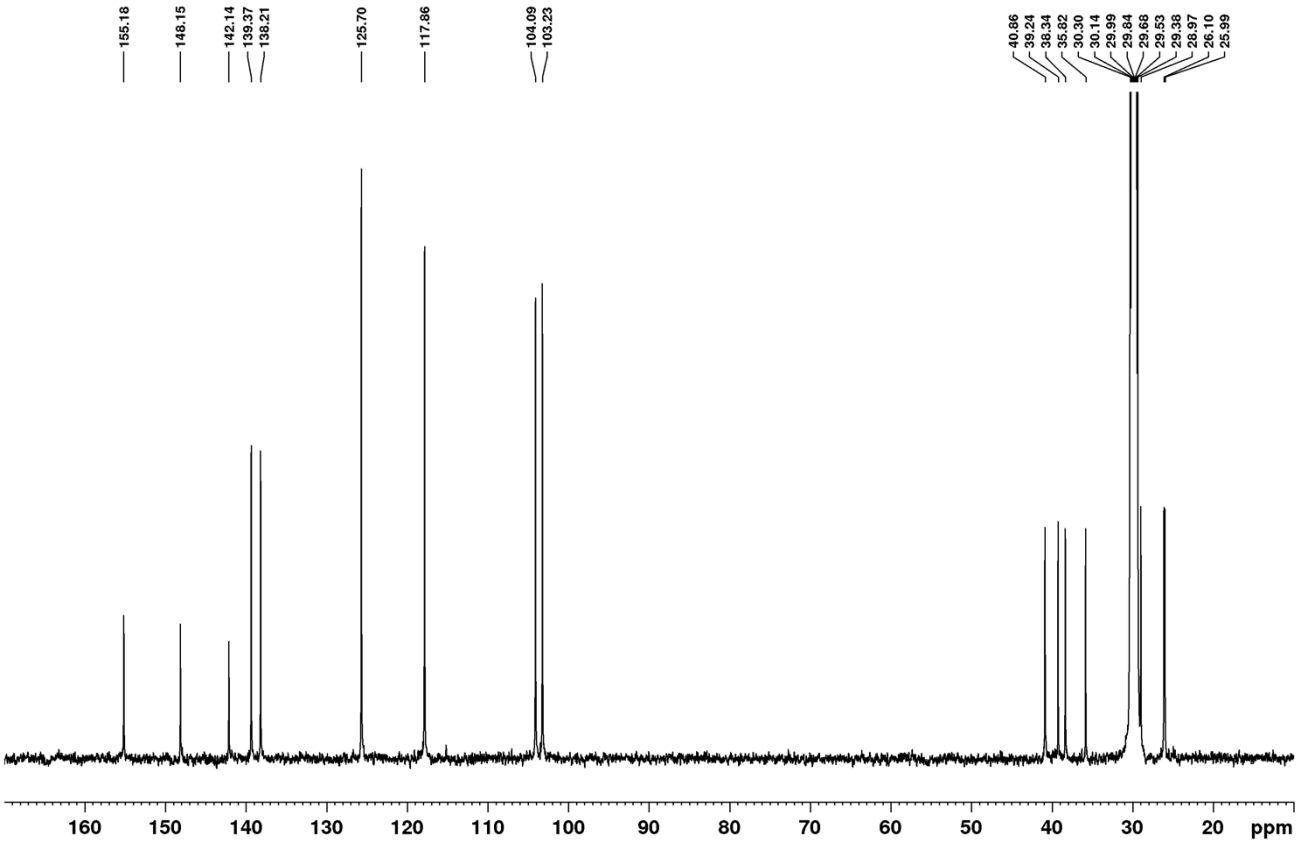



Fig. S-24 $^{13}$C NMR spectrum of *cis*-**3** in acetone-$d_6$ (at 30 °C, 126 MHz).

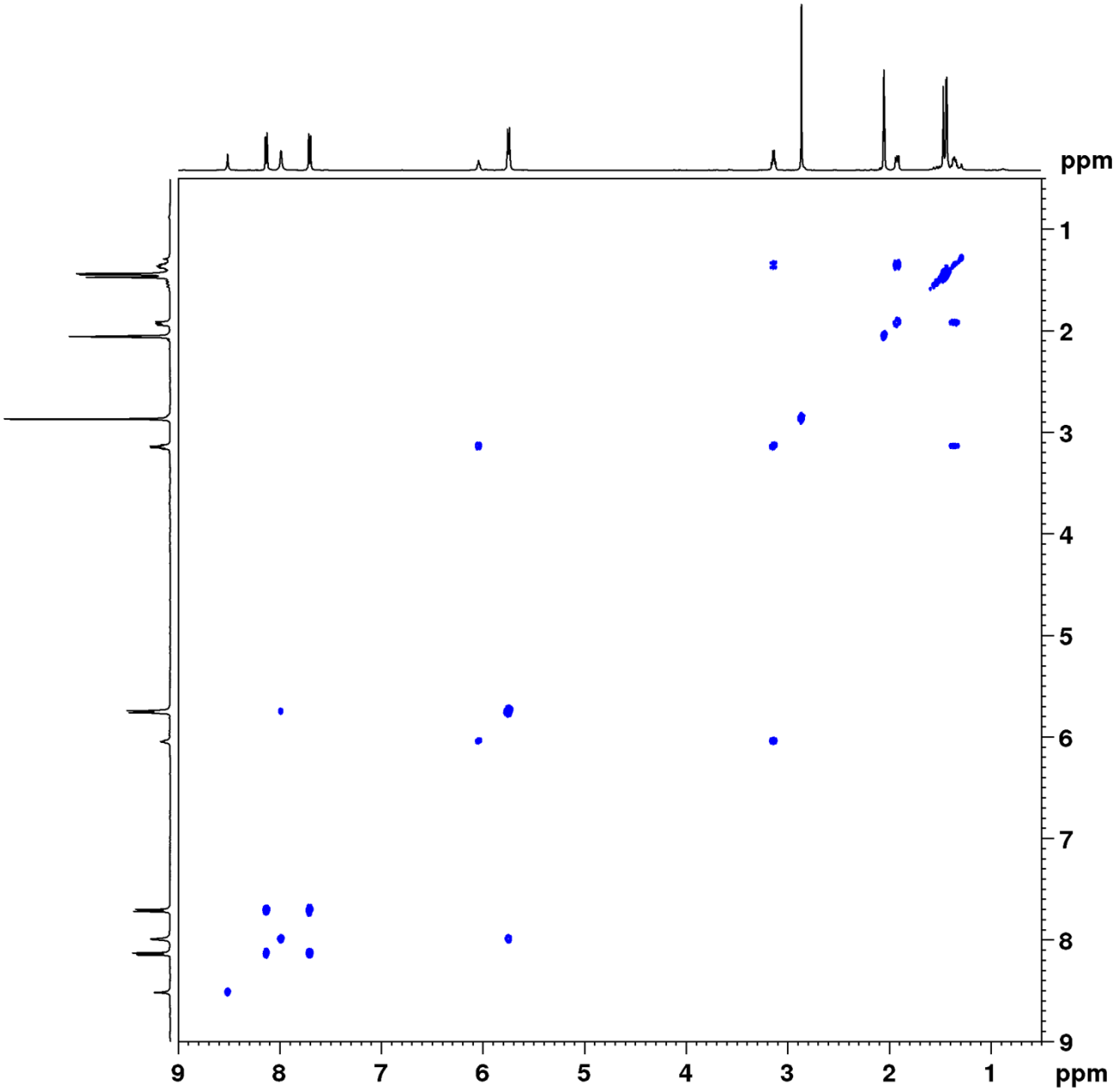



Fig. S-25 $^{1}$H-$^{1}$H COSY of *cis*-**3** in acetone-$d_6$ (at 30 °C, 500 MHz).

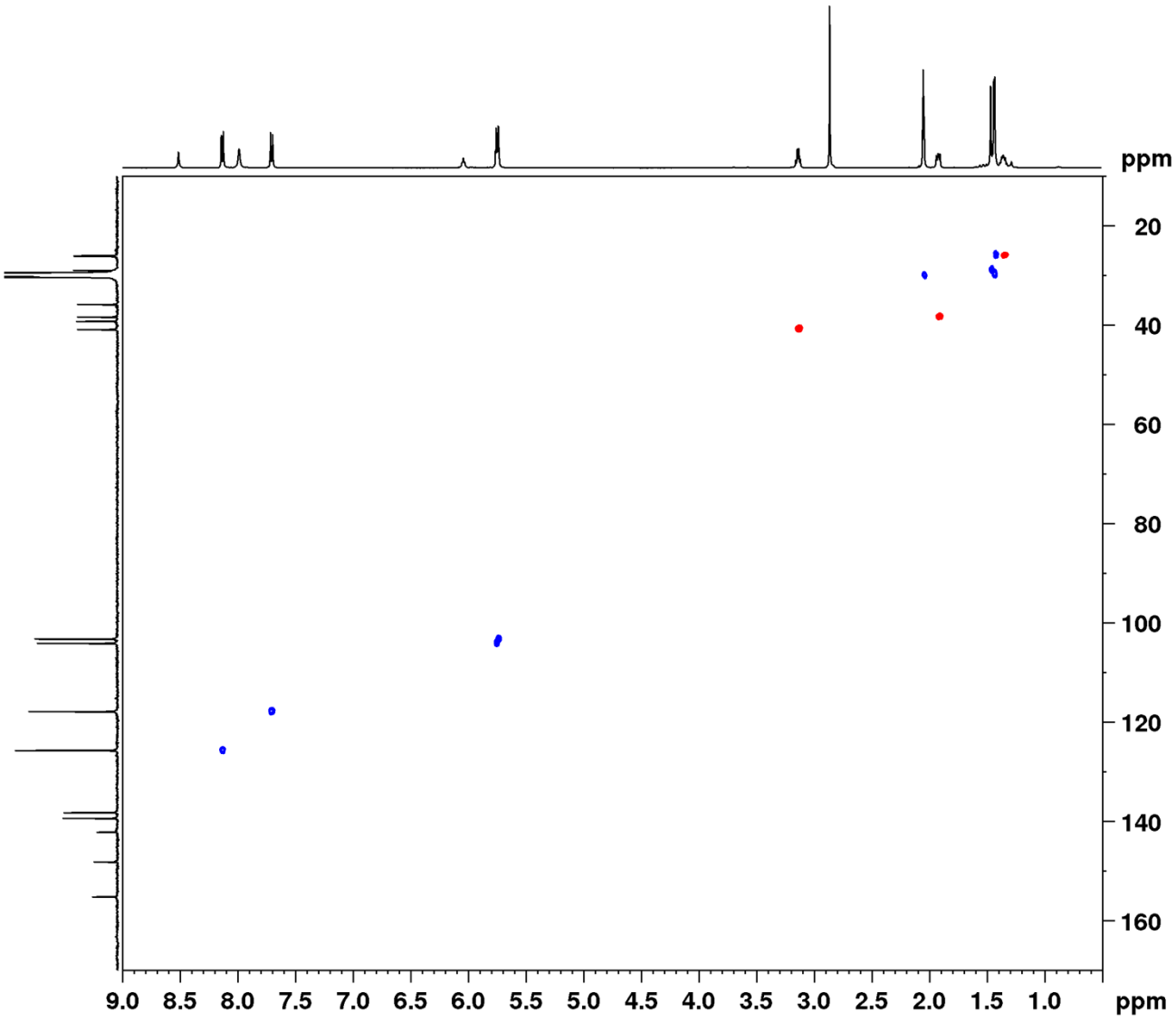



Fig. S-26 HSQC of *cis*-**3** in acetone-$d_6$ (at 30 °C, 500 MHz).

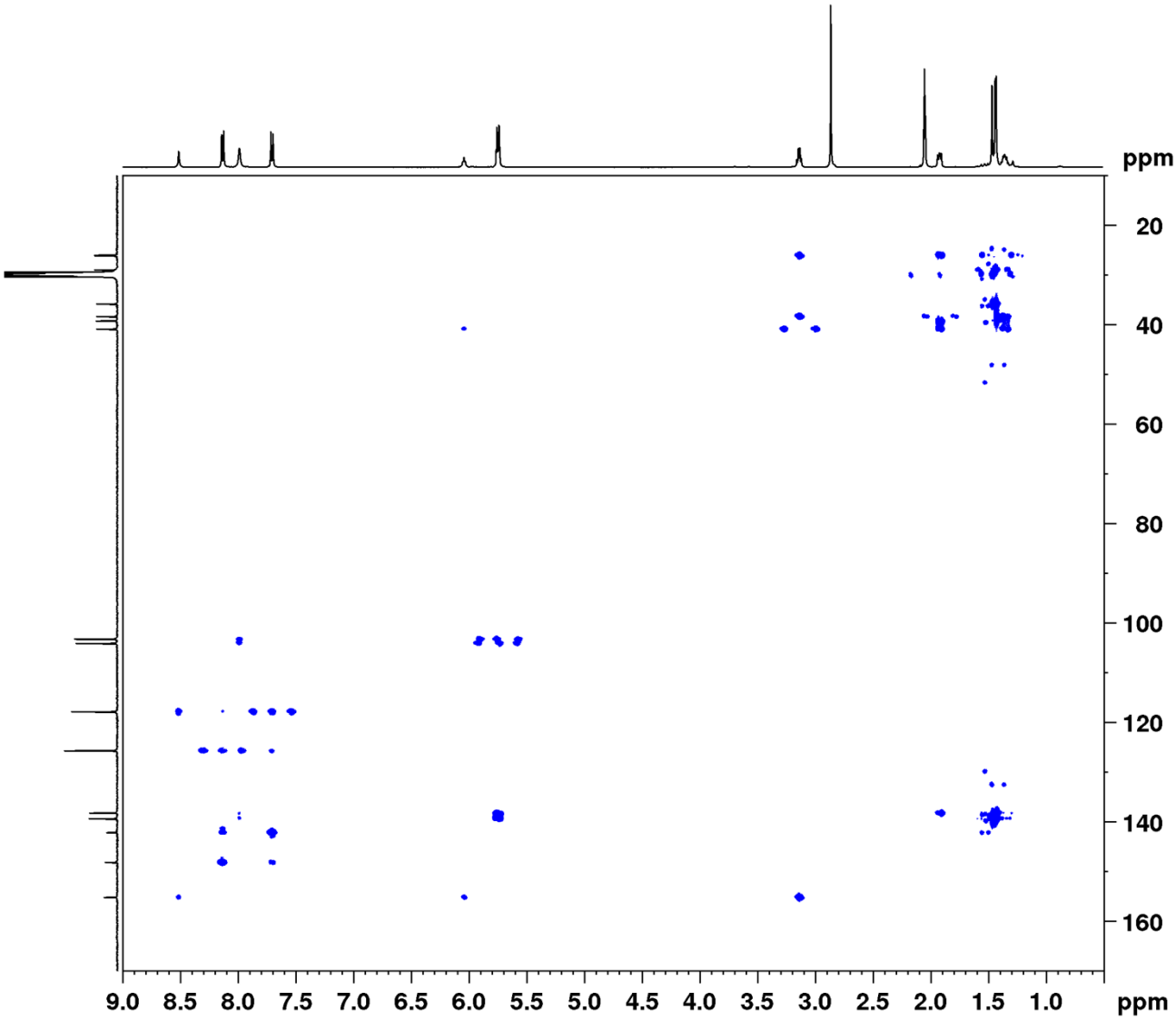



Fig. S-27 HMBC of *cis*-**3** in acetone-$d_6$ (at 30 °C, 500 MHz).

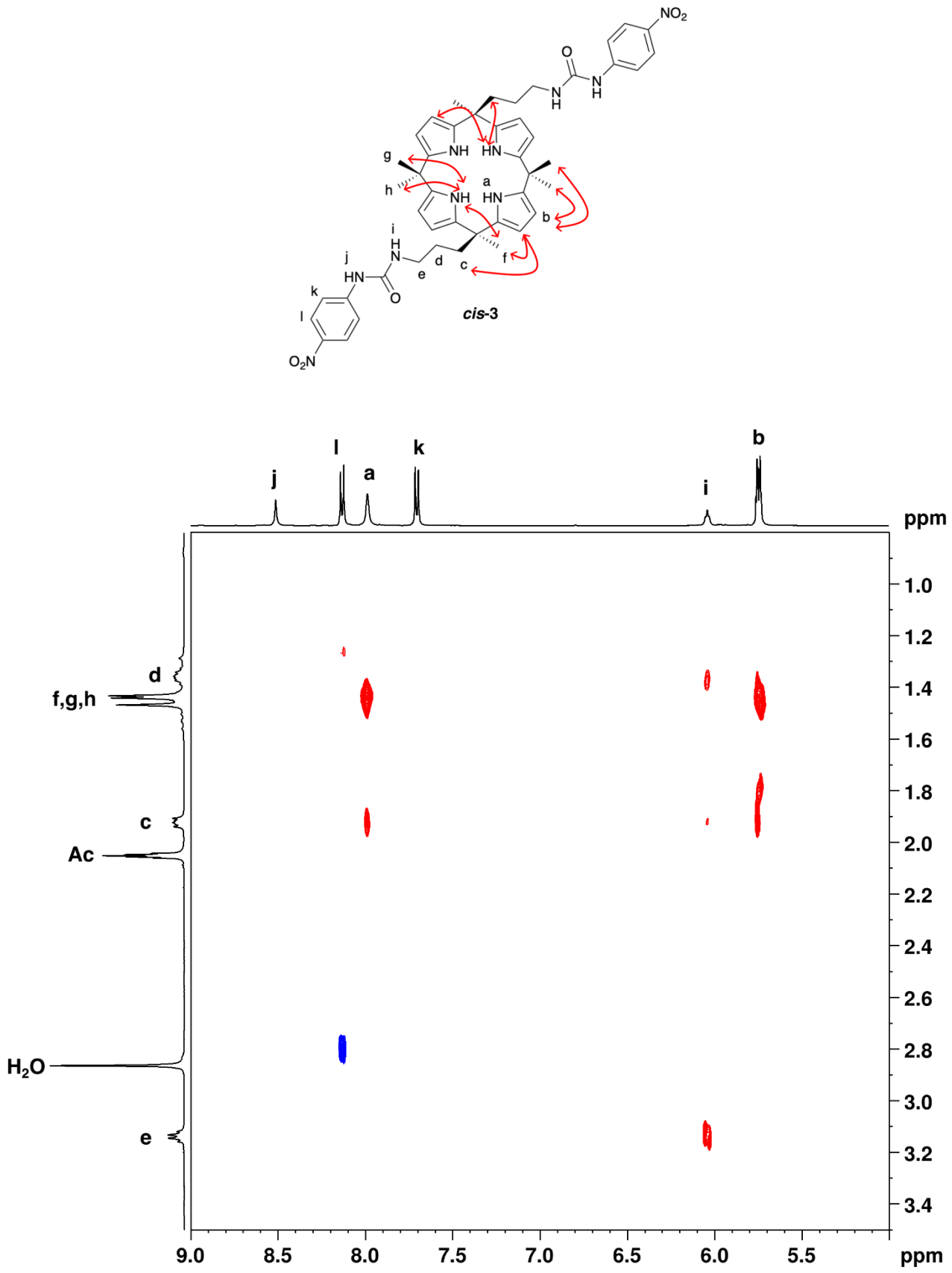



Fig. S-28 $^{1}$H,$^{1}$H-ROESY of *cis*-**3** in acetone-$d_6$ (at 30 °C, 500 MHz) showing ROE cross-peaks in red.

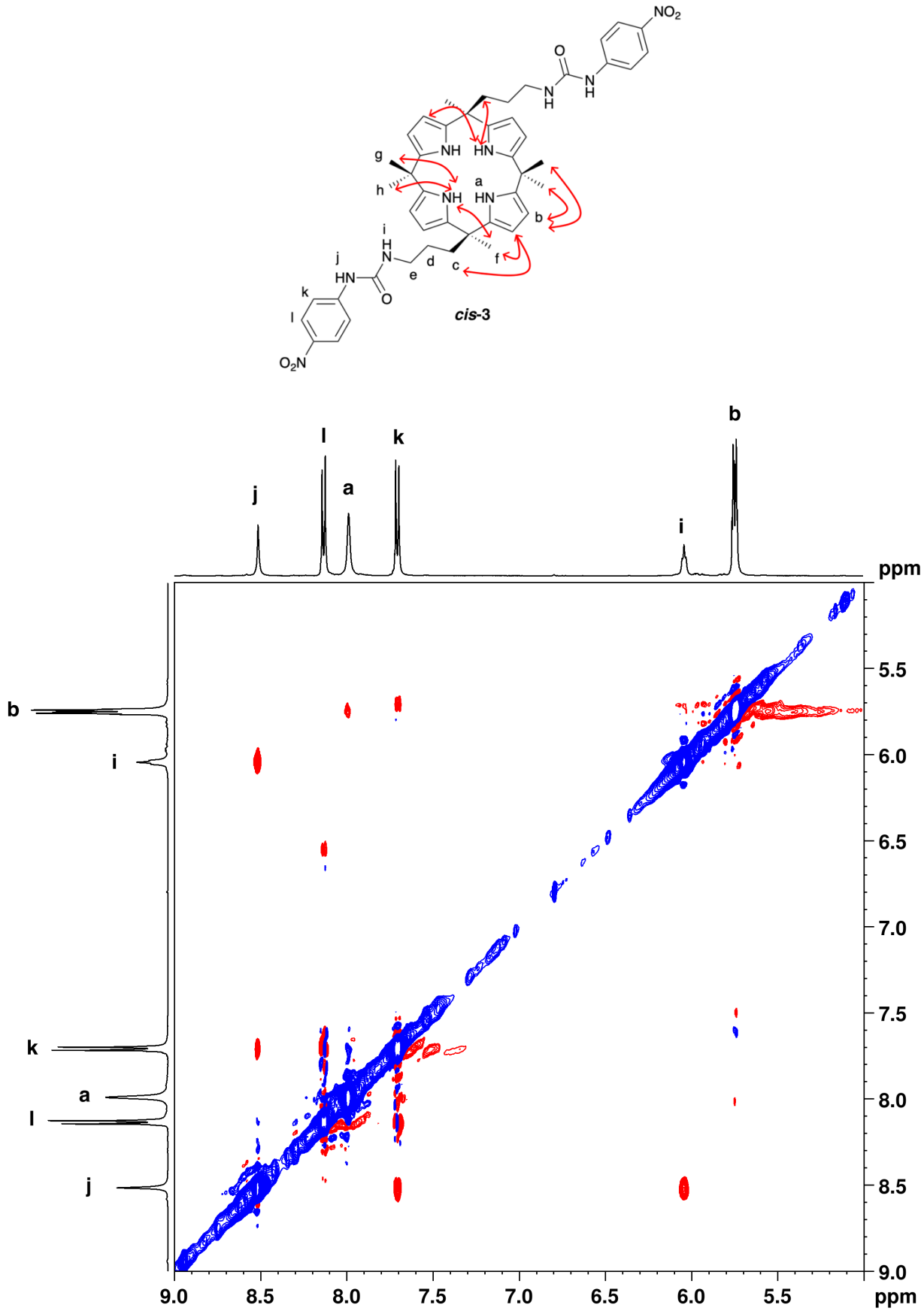



Fig. S-29 Aromatic region of $^{1}$H,$^{1}$H-ROESY of *cis*-**3** in acetone-$d_6$ (at 30 °C, 500 MHz) showing ROE cross-peaks in red.

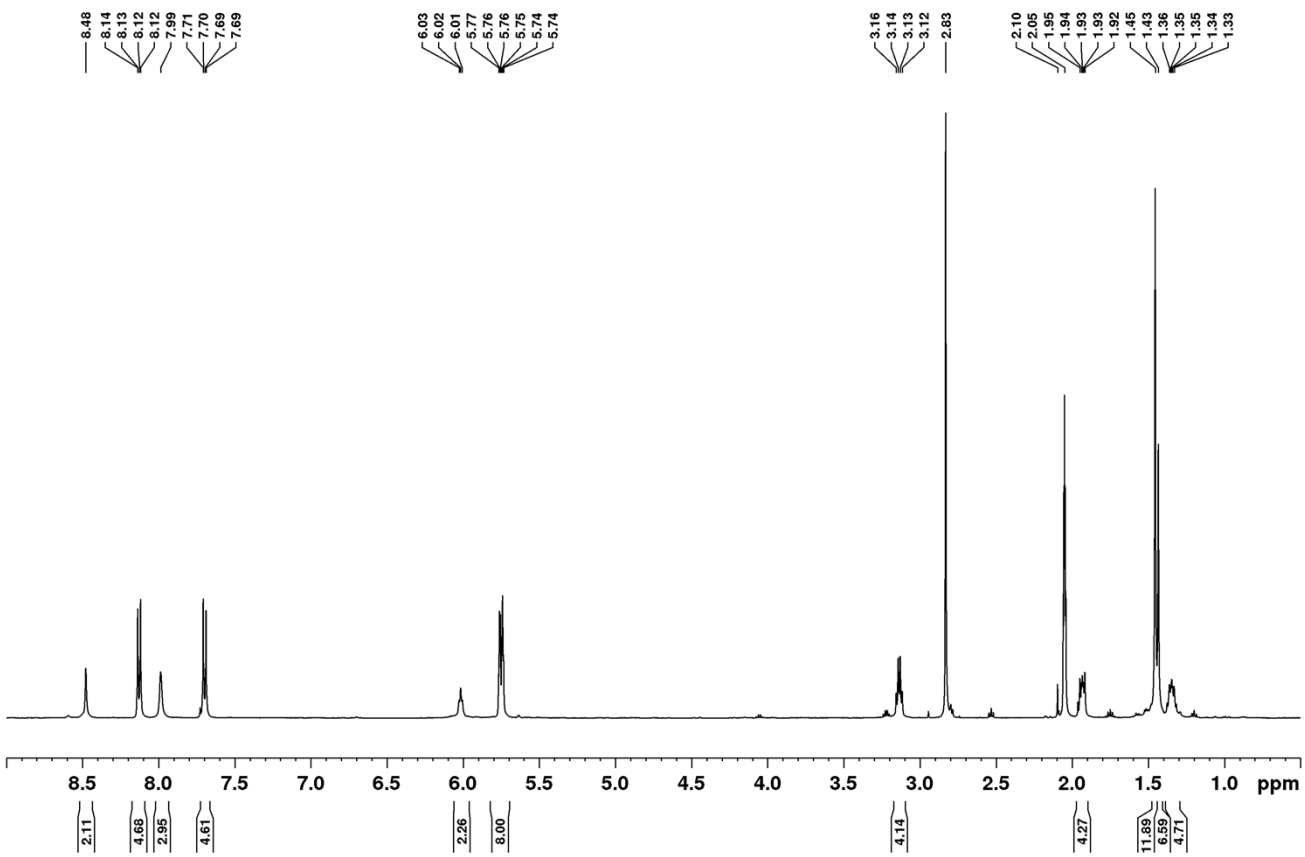



Fig. S-30 $^{1}$H NMR spectrum of *trans*-**3** in acetone-$d_6$ (at 30 °C, 500 MHz).

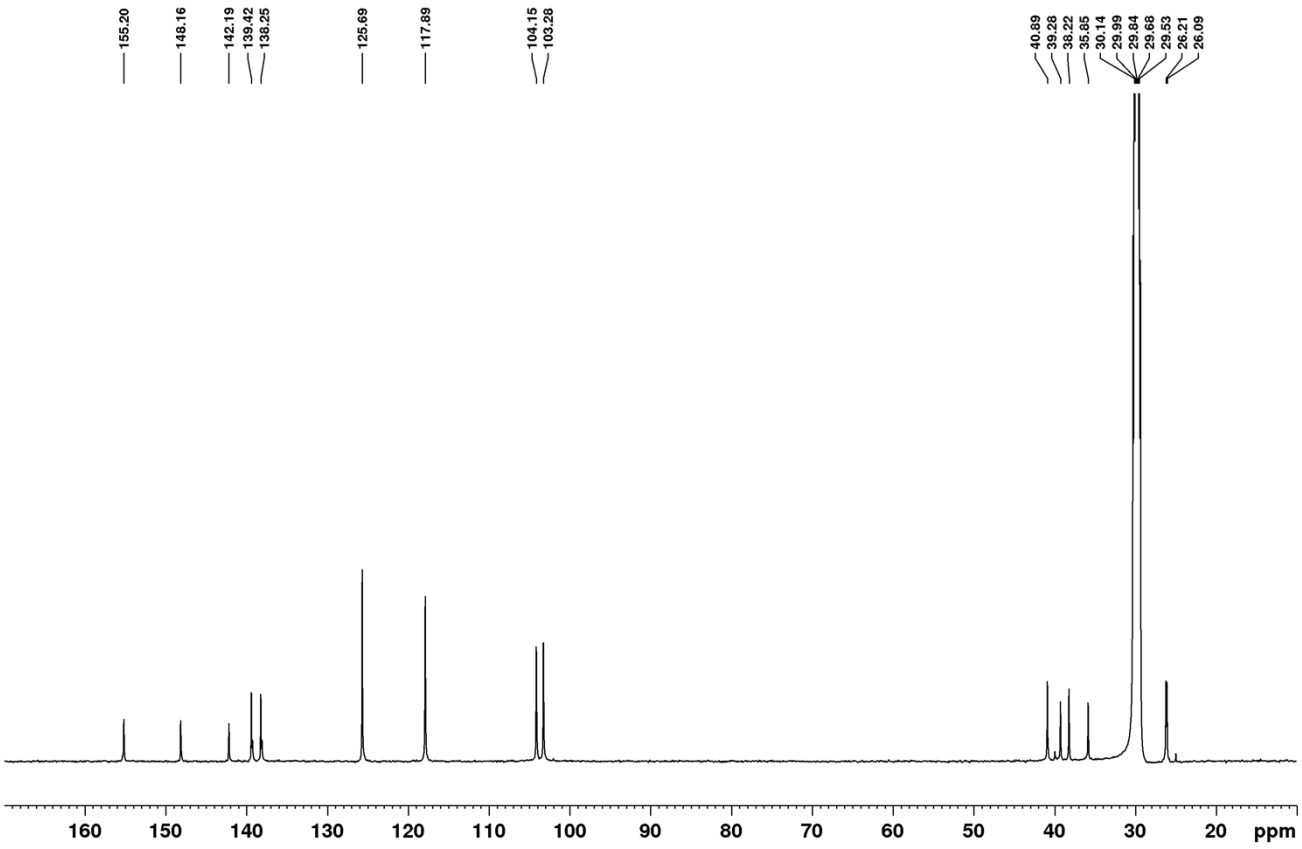



Fig. S-31 $^{13}$C NMR spectrum of *trans*-**3** in acetone-$d_6$ (at 30 °C, 126 MHz).

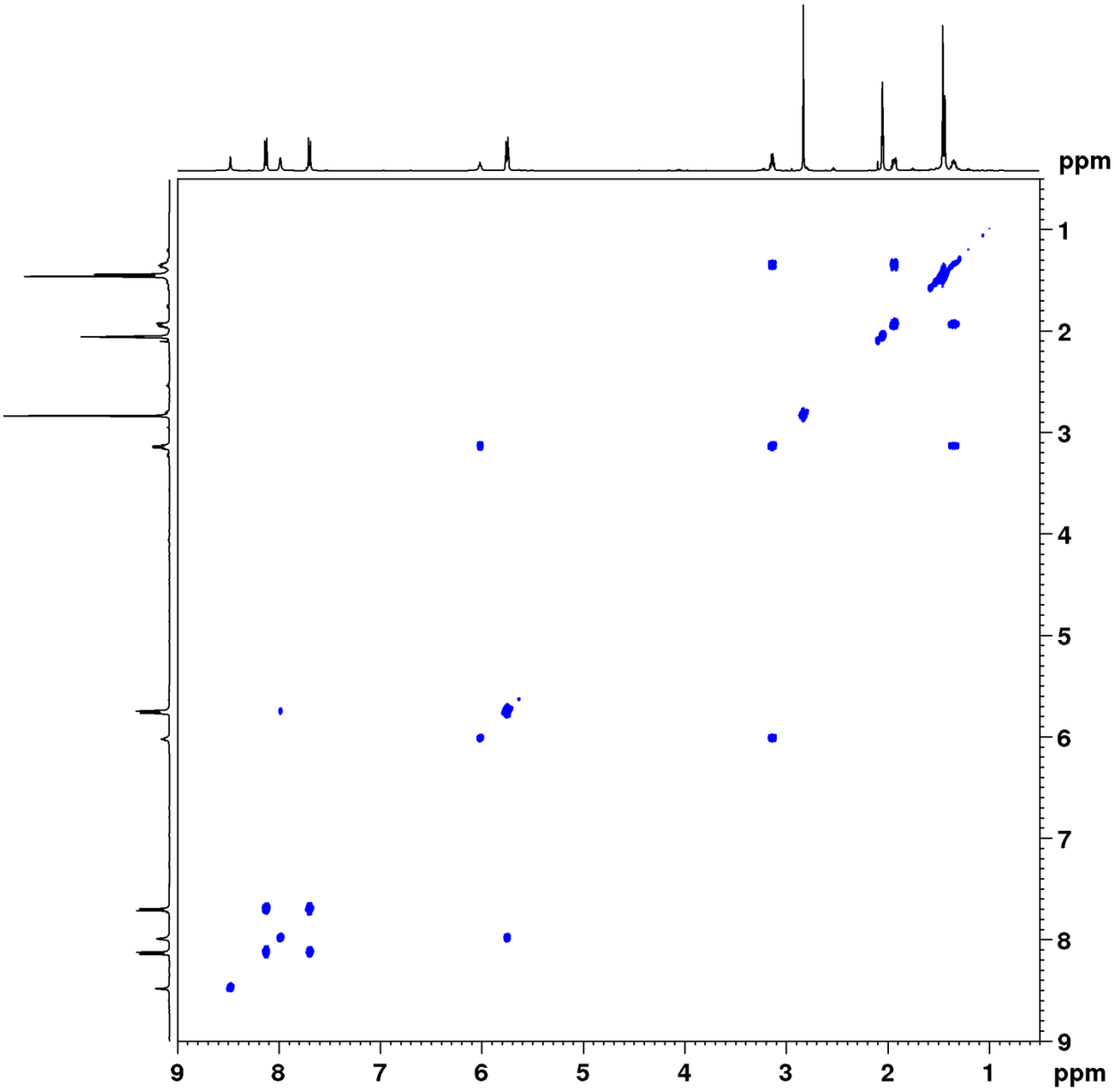



Fig. S-32 $^{1}$H-$^{1}$H COSY of *trans*-**3** in acetone-$d_6$ (at 30 °C, 500 MHz).

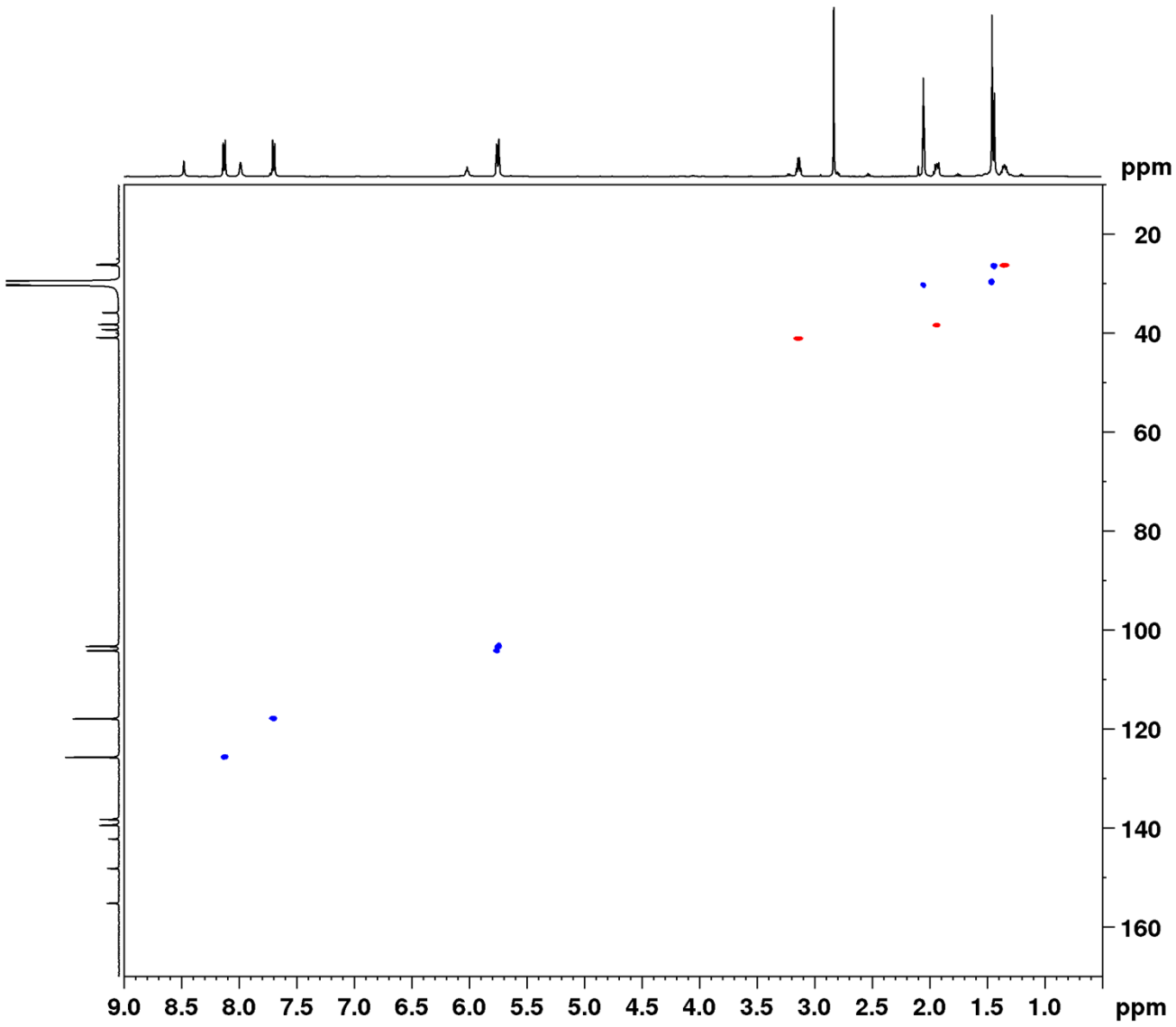



Fig. S-33 HSQC of *trans*-**3** in acetone-$d_6$ (at 30 °C, 500 MHz).

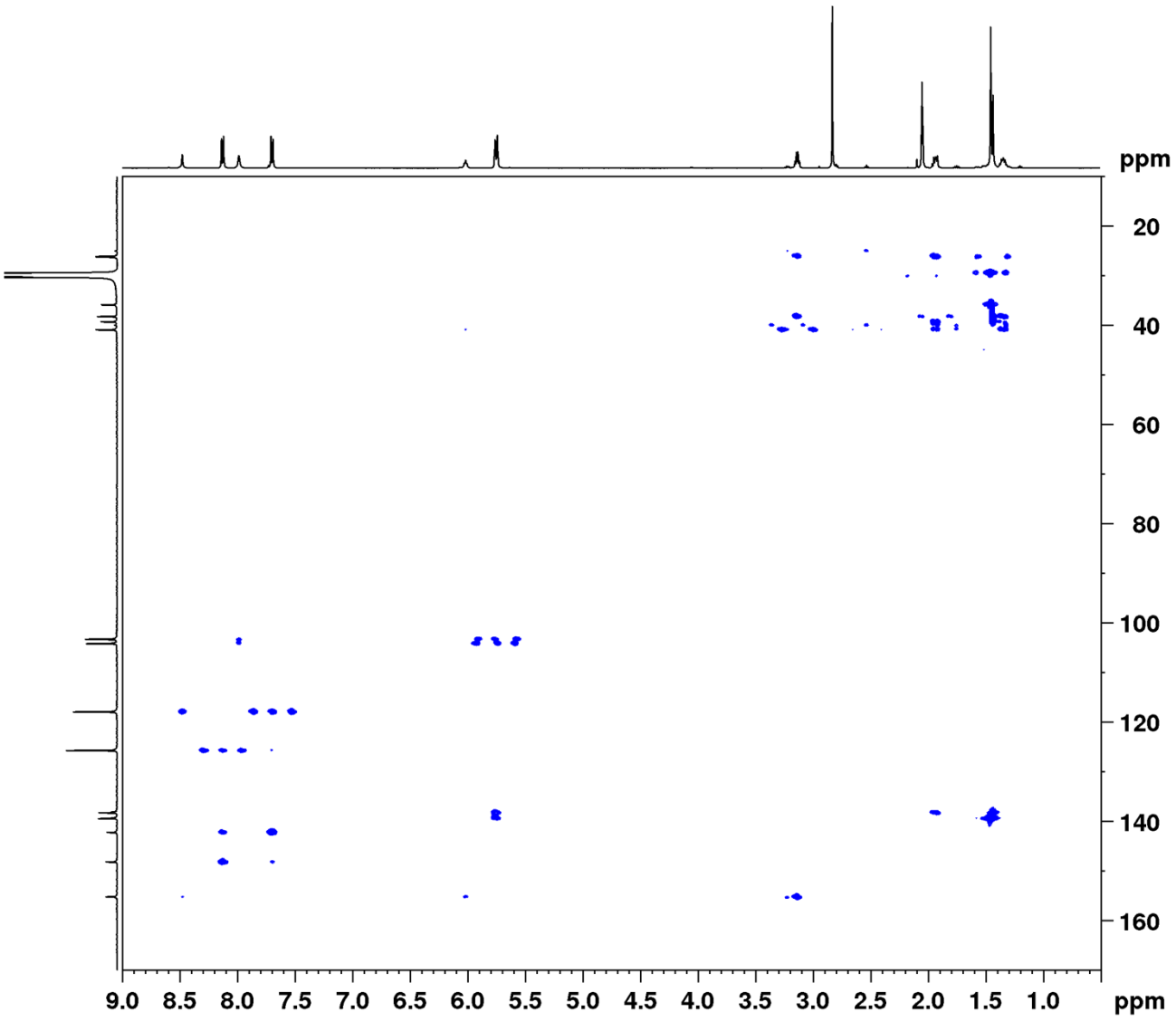



Fig. S-34 HMBC of *trans*-**3** in acetone-$d_6$ (at 30 °C, 500 MHz).

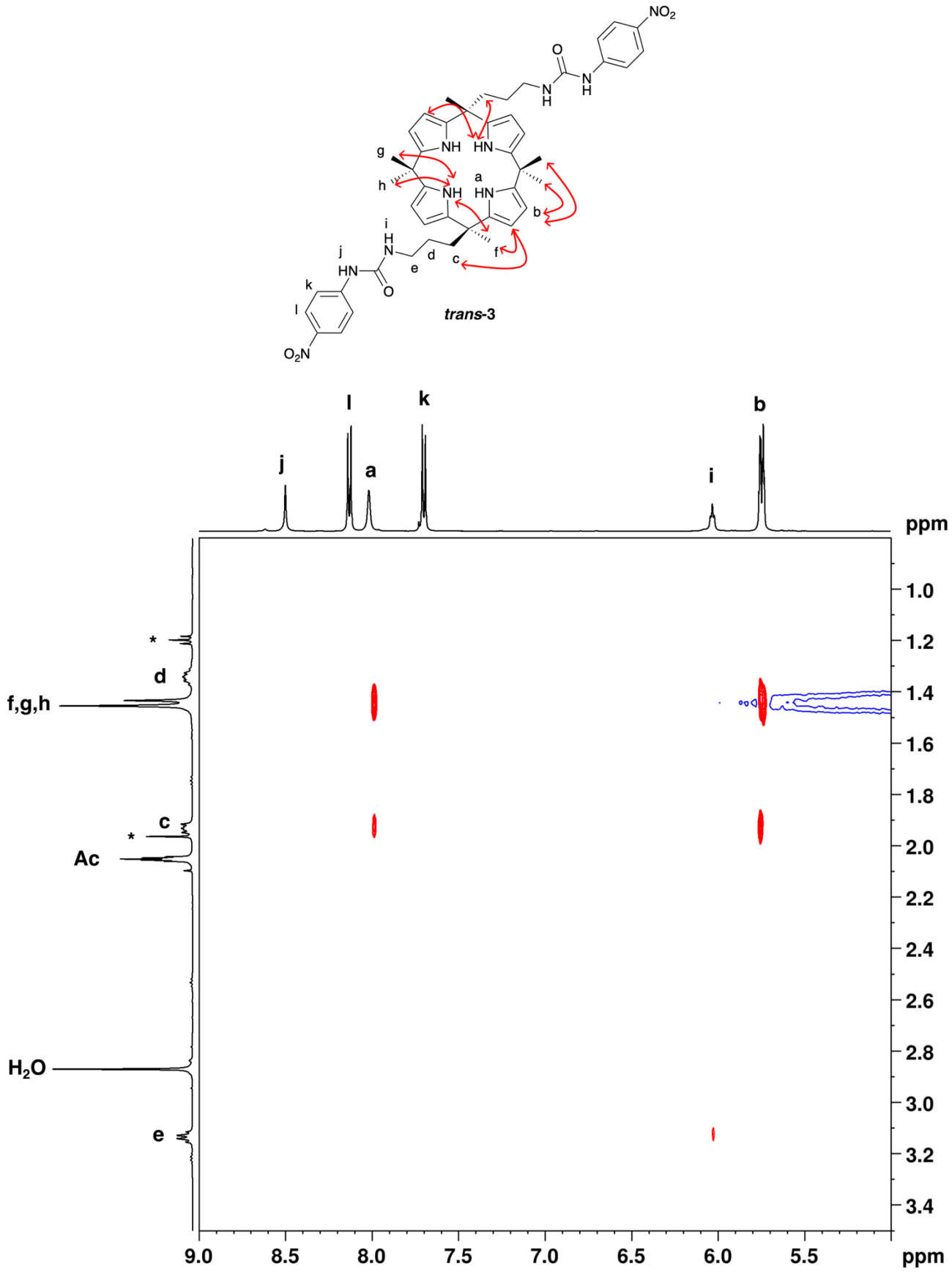



Fig. S-35 $^{1}$H,$^{1}$H-ROESY of *trans*-**3** in acetone-$d_6$ (at 30 °C, 500 MHz) showing ROE cross-peaks in red.

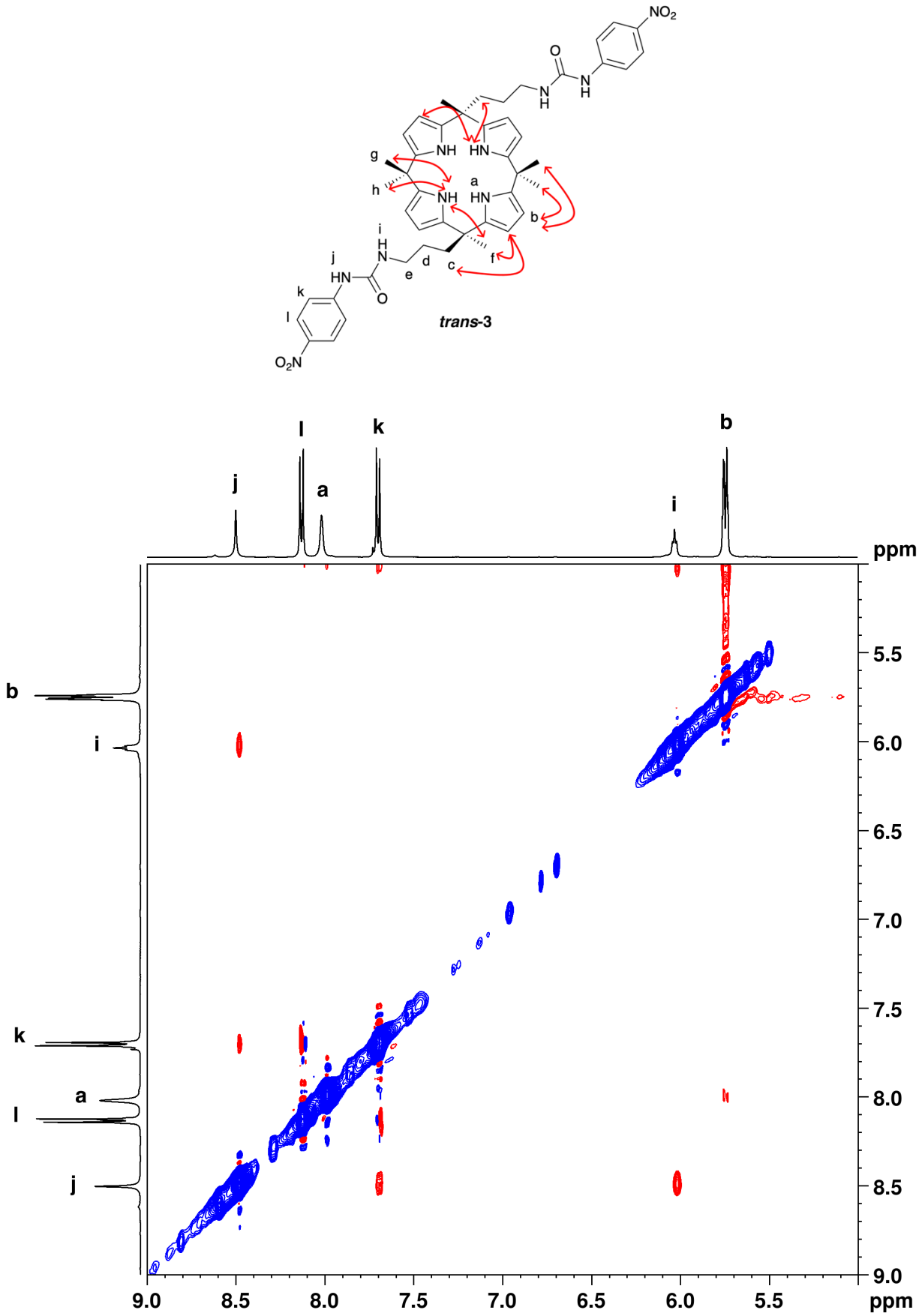



Fig. S-36 Aromatic region of $^{1}$H,$^{1}$H-ROESY of *trans*-**3** in acetone-$d_6$ (at 30 °C, 500 MHz) showing ROE cross-peaks in red.

## 4. NMR titrations

The binding studies were performed by preparing a solution of host (1 mM) in DMSO-$d_6$ or in acetone-$d_6$. After that, 600 µl of prepared solution was transferred to the NMR tube. The remaining host solution was used to prepare stock guest solutions (TBACl and $TBAH_2PO_4$) at approximately 60 mM concentration so that the host concentration remained constant during the titration. Additionally, diluted guest solutions were prepared to provide more convenient volumes for adding small amounts of guest. The aliquots of the guest solution were added to the NMR tube containing the host solution and the tube was carefully mixed before each measurement. $^1$H NMR spectrum was recorded after each addition. Binding constant was calculated by fitting the obtained NMR data to a theoretical 1:1 or 1:2 binding isotherm using HypNMR2008 software.[4]

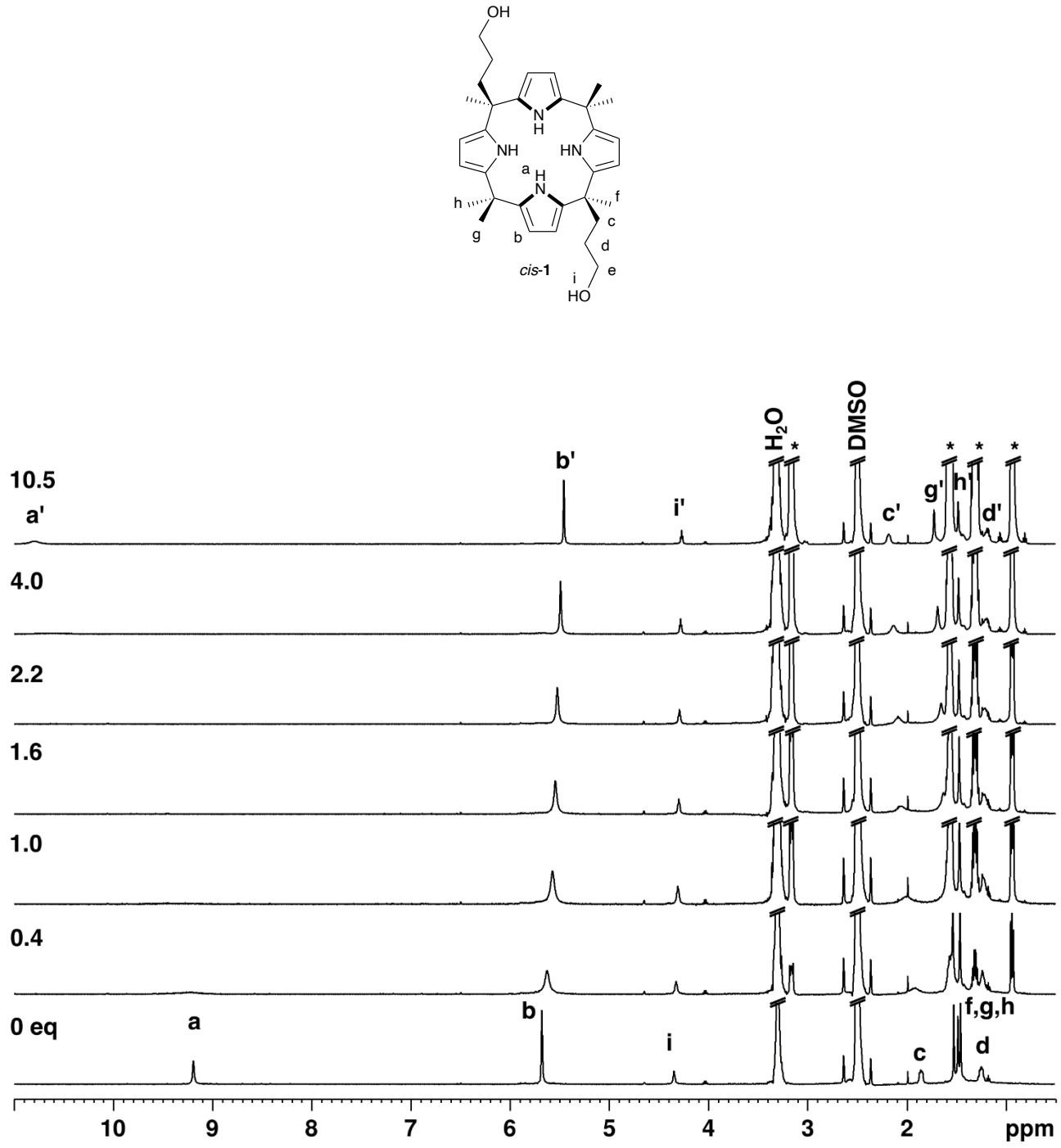



Fig. S-37 NMR titration of *cis*-**1** (1 mM) with incremental amount of TBACl (DMSO-$d_6$, 30 °C). Labels indicate molar equivalents of the added guest. The signals belonging to the bound host are marked with primed letters. TBA signals are indicated with (*).

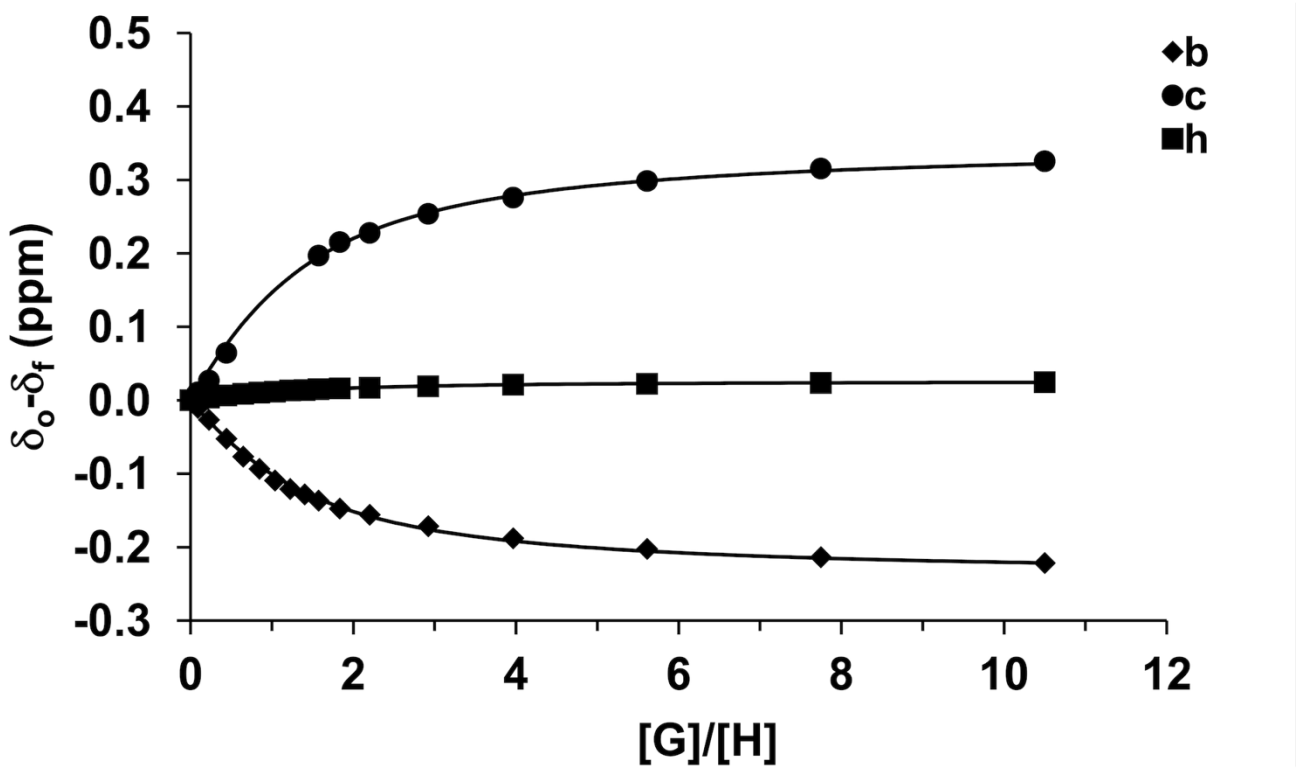



Fig. S-38 NMR titration data of *cis*-**1** with TBACl (markers) fitted to a theoretical 1:1 binding isotherm (lines) using HypNMR2008.

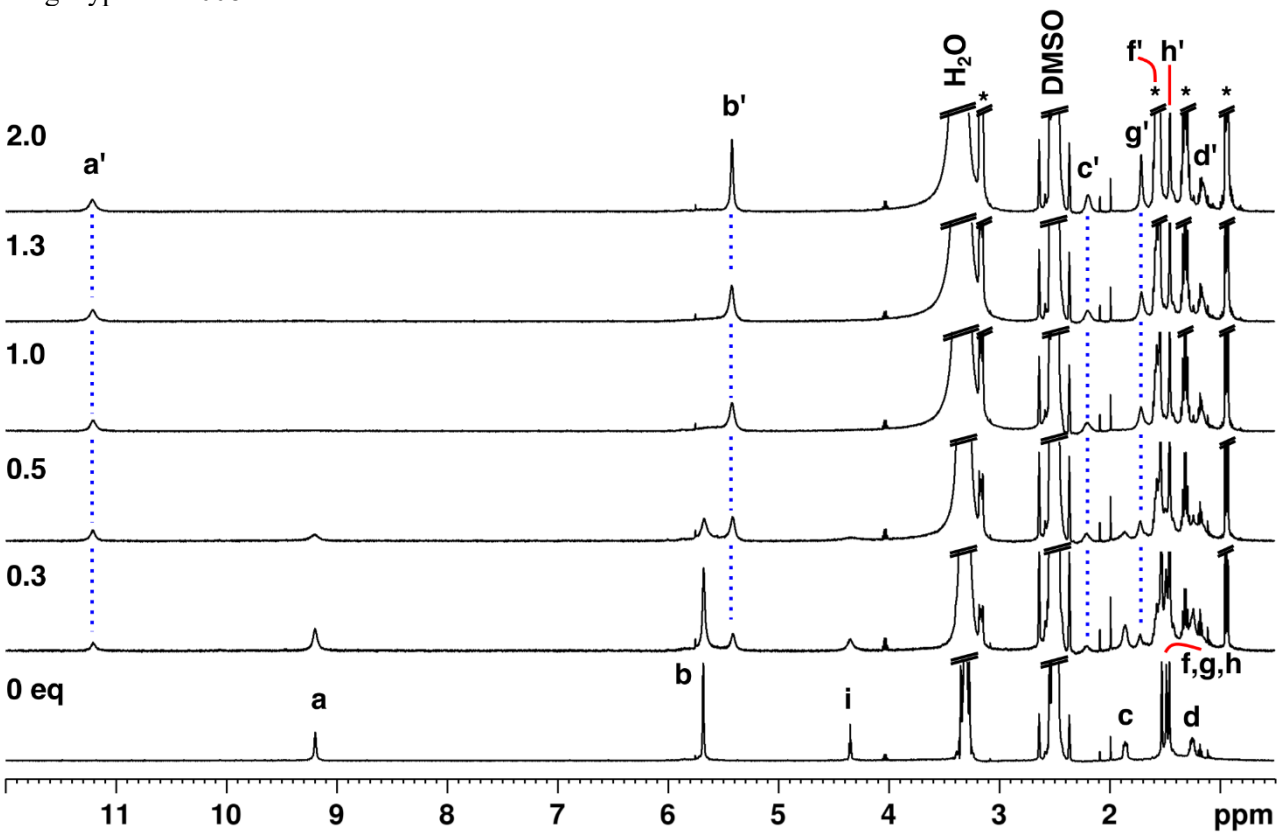



Fig. S-39 NMR titration of *cis*-**1** (1 mM) with incremental amount of $TBAH_2PO_4$ (DMSO-$d_6$, 30 °C). Labels indicate molar equivalents of the added guest. The signals belonging to the bound host are marked with primed letters. TBA signals are indicated with (*).

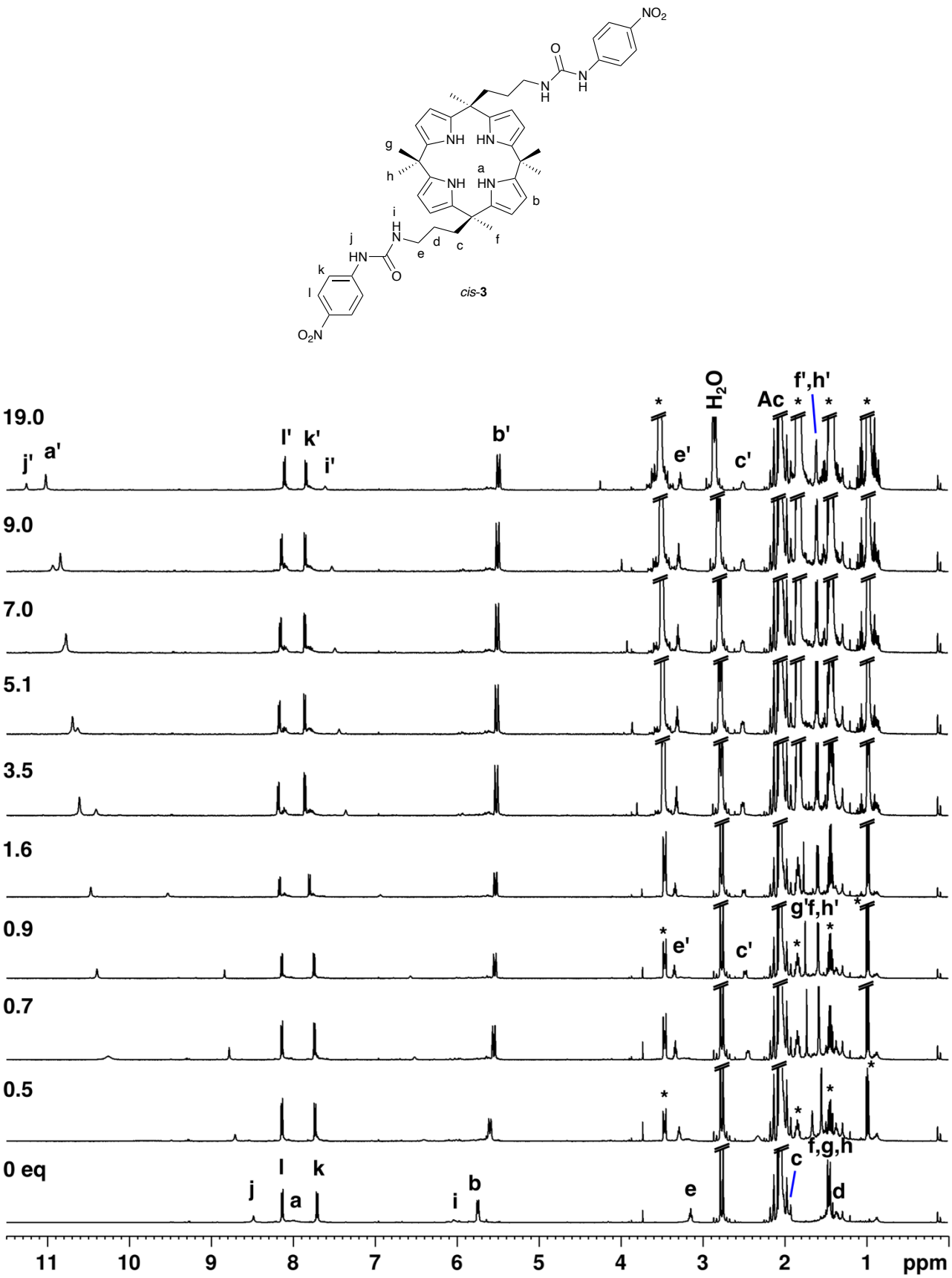



Fig. S-40 NMR titration of *cis*-**3** (1 mM) with incremental amount of TBACl (acetone-$d_6$, 30 °C). Labels indicate molar equivalents of the added guest. The signals belonging to the bound host are marked with primed letters. TBA signals are indicated with (*).

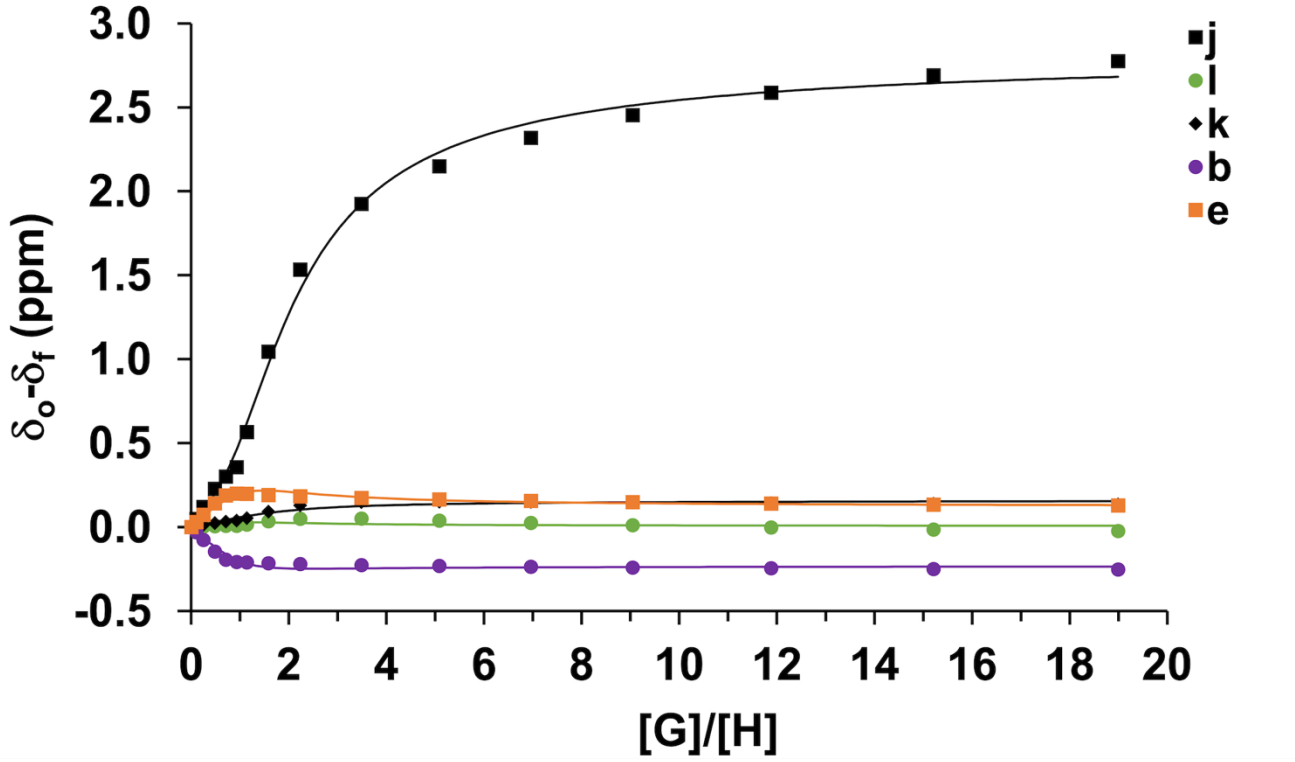



Fig. S-41 NMR titration data of *cis*-**3** with TBACl in acetone-$d_6$ (markers) fitted to a theoretical 1:2 binding isotherm (lines) using HypNMR2008.

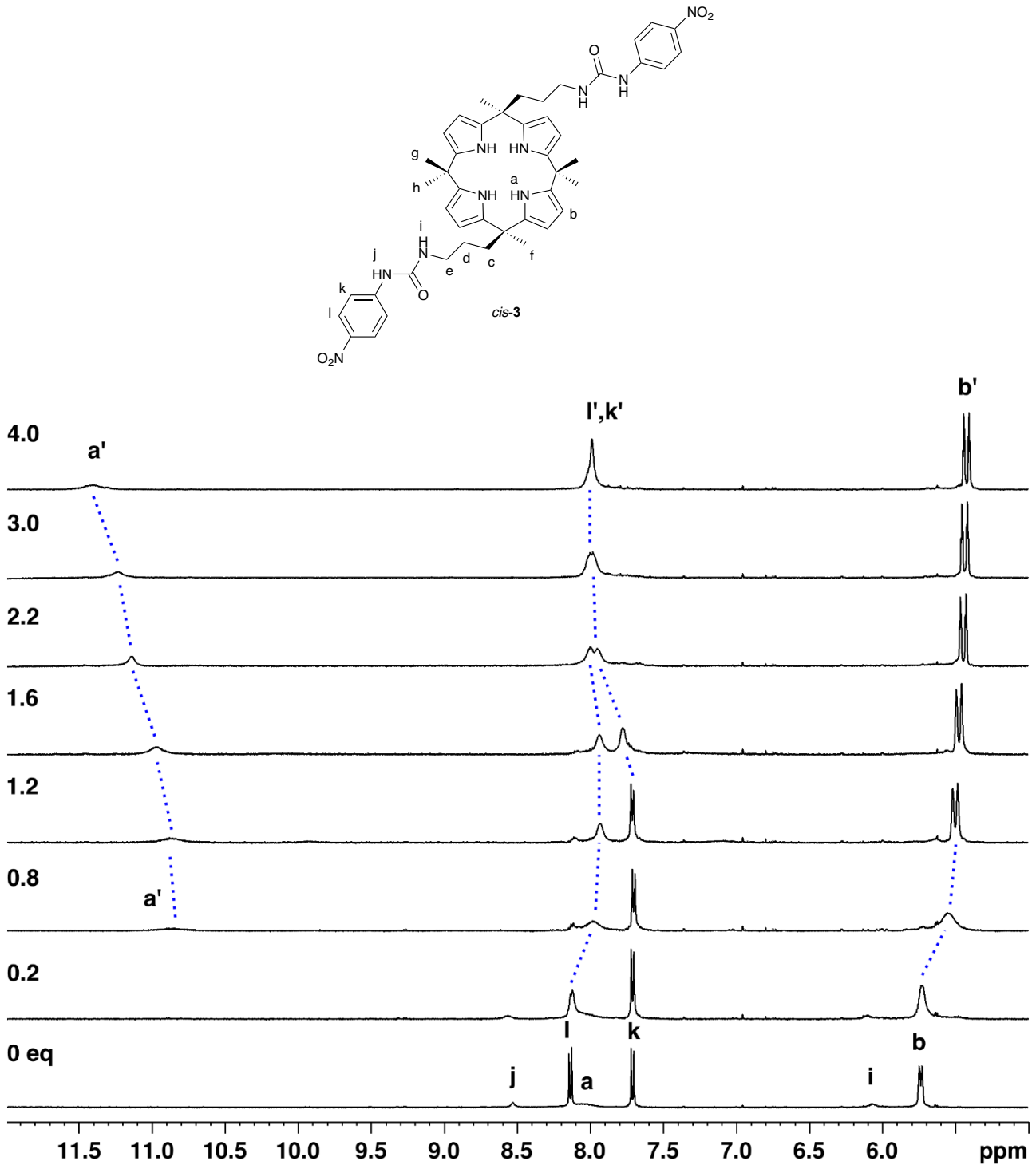



Fig. S-42 Aromatic region of the NMR titration of *cis*-**3** (1 mM) with incremental amount of $TBAH_2PO_4$ (acetone-$d_6$, 30 °C). Labels indicate molar equivalents of the added guest. The signals belonging to the bound host are marked with primed letters.

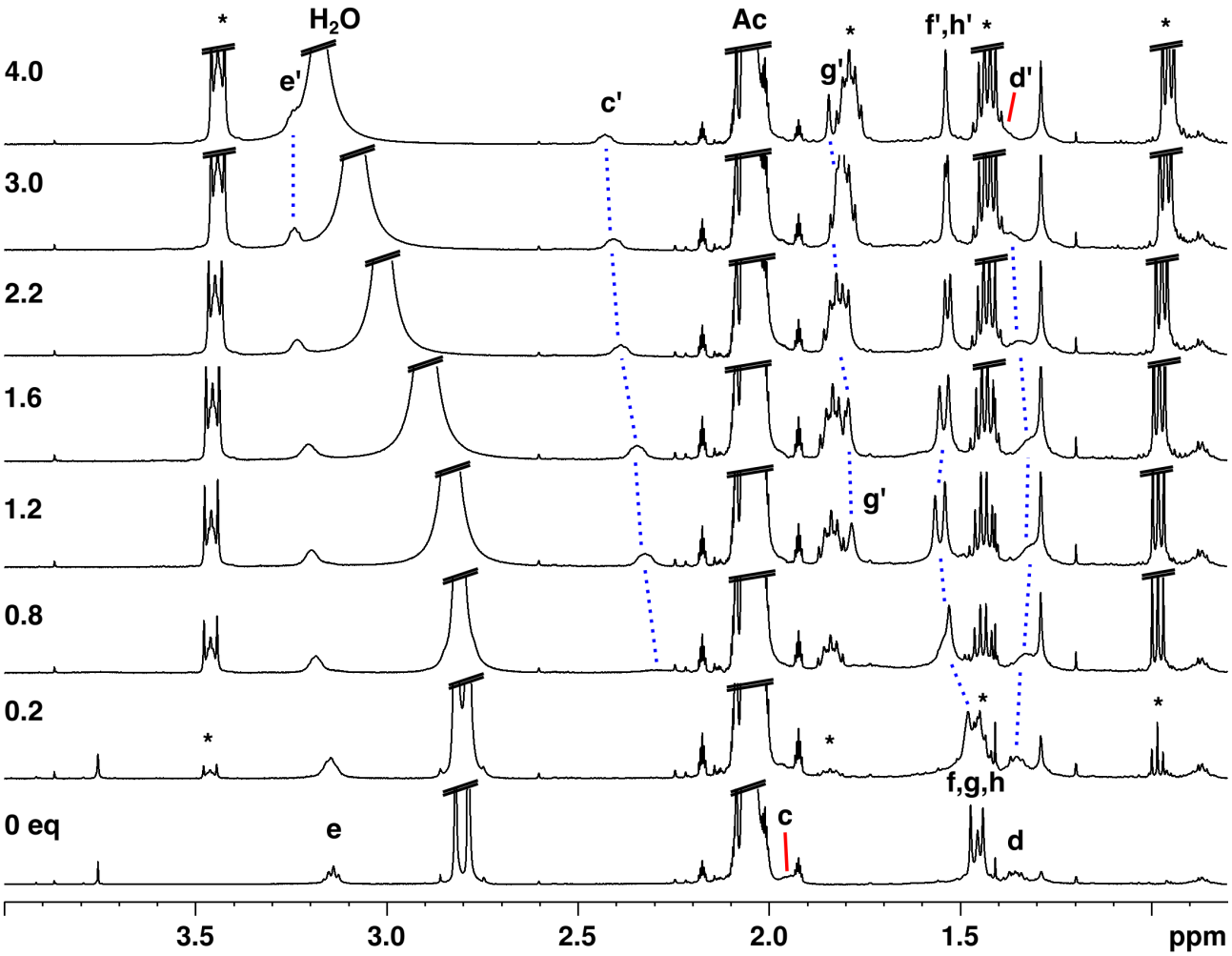



Fig. S-43 Aliphatic region of the NMR titration of *cis*-**3** (1 mM) with incremental amount of $TBAH_2PO_4$ (acetone-$d_6$, 30 °C). Labels indicate molar equivalents of the added guest. The signals belonging to the bound host are marked with primed letters. TBA signals are indicated with (*).

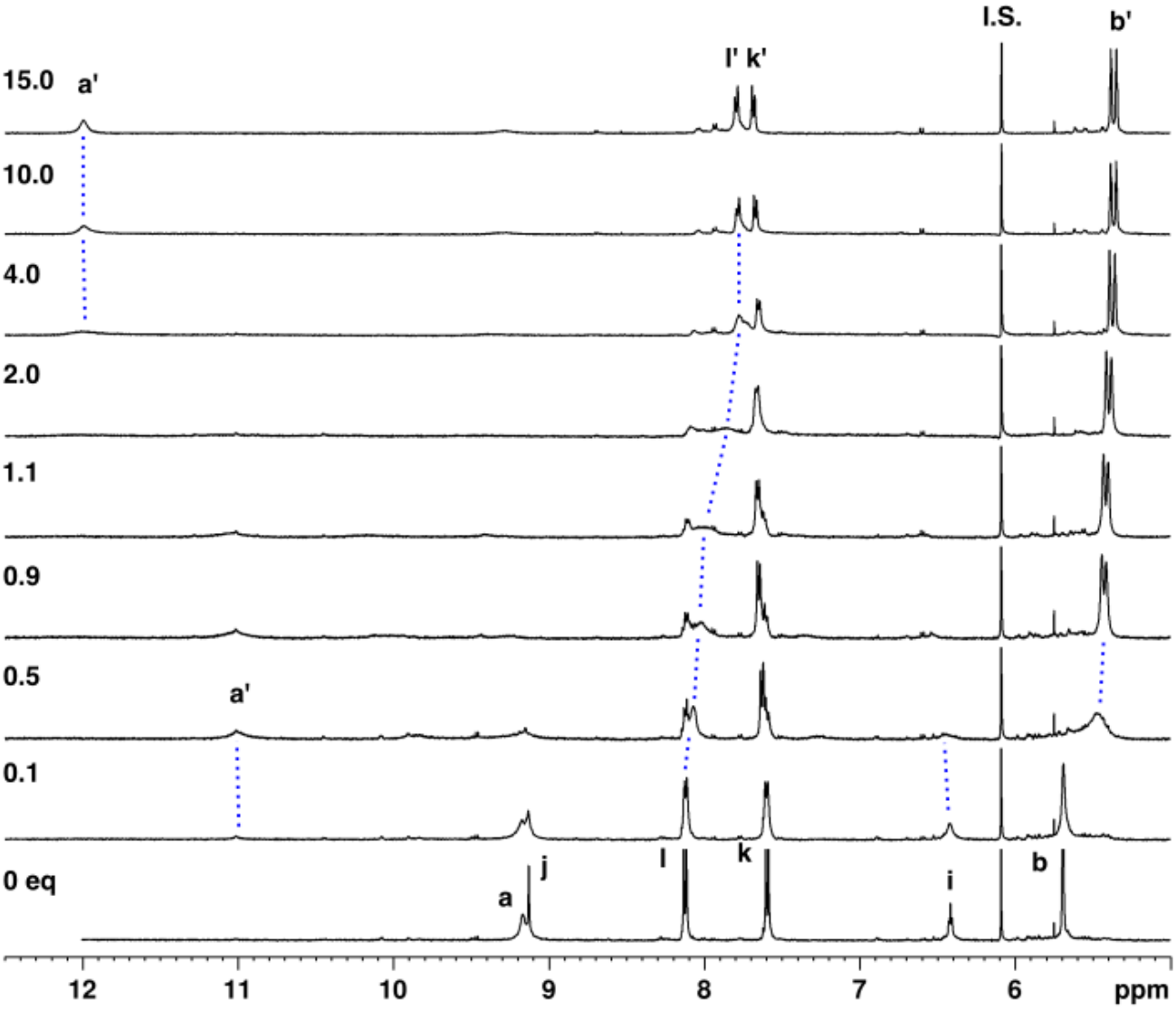



Fig. S-44 Aromatic region of the NMR titration of *cis*-**3** (1 mM) with incremental amount of $TBAH_2PO_4$ (DMSO-$d_6$, 30 °C). Labels indicate molar equivalents of the added guest. The signals belonging to the bound host are marked with primed letters. I.S. = 1,3,5-trimethoxybenzene.

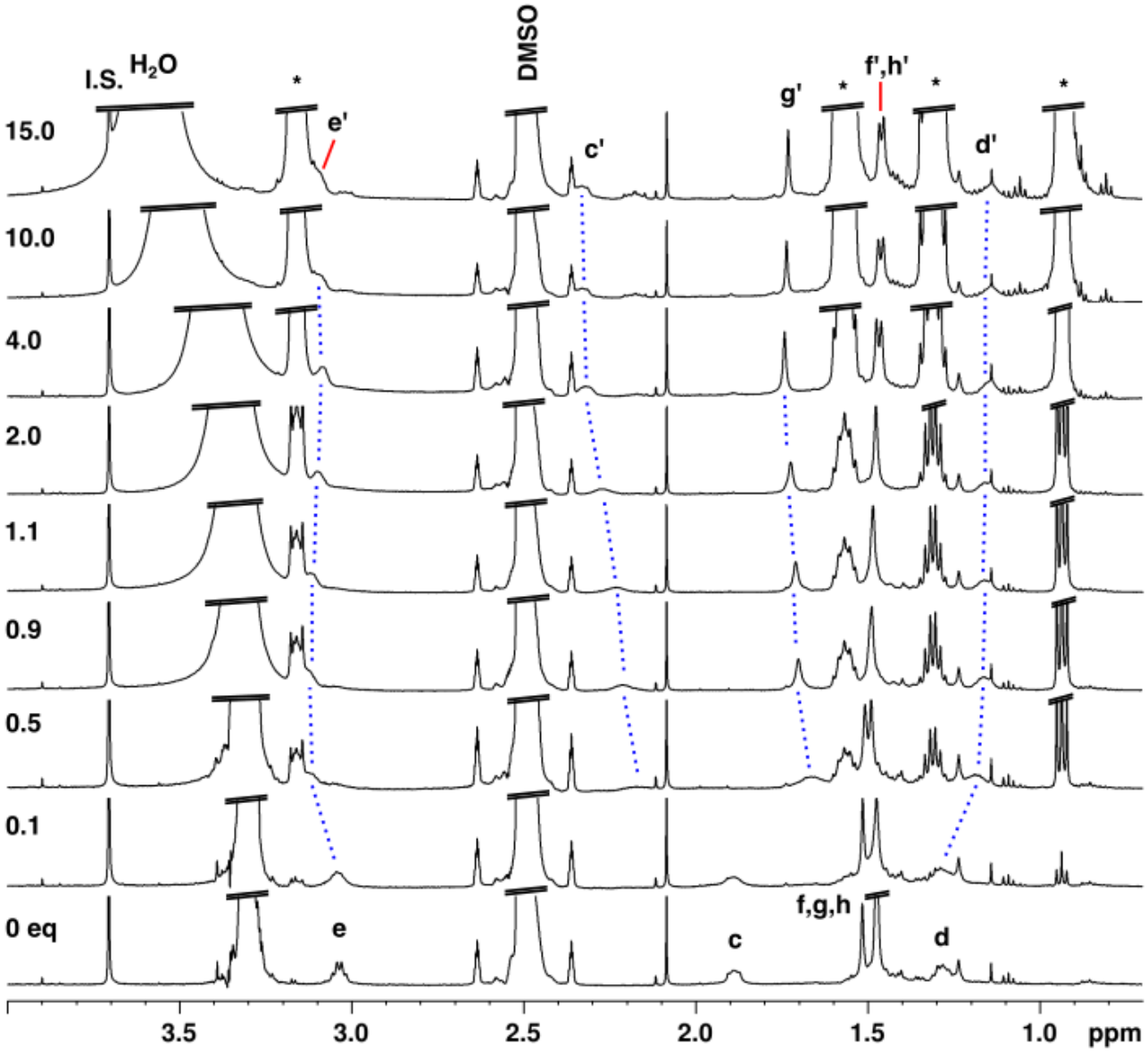



Fig. S-45 Aliphatic region of the NMR titration of *cis*-**3** (1 mM) with incremental amount of $TBAH_2PO_4$ (DMSO-$d_6$, 30 °C). Labels indicate molar equivalents of the added guest. The signals belonging to the bound host are marked with primed letters. TBA signals are indicated with (*). I.S. = 1,3,5-trimethoxybenzene.

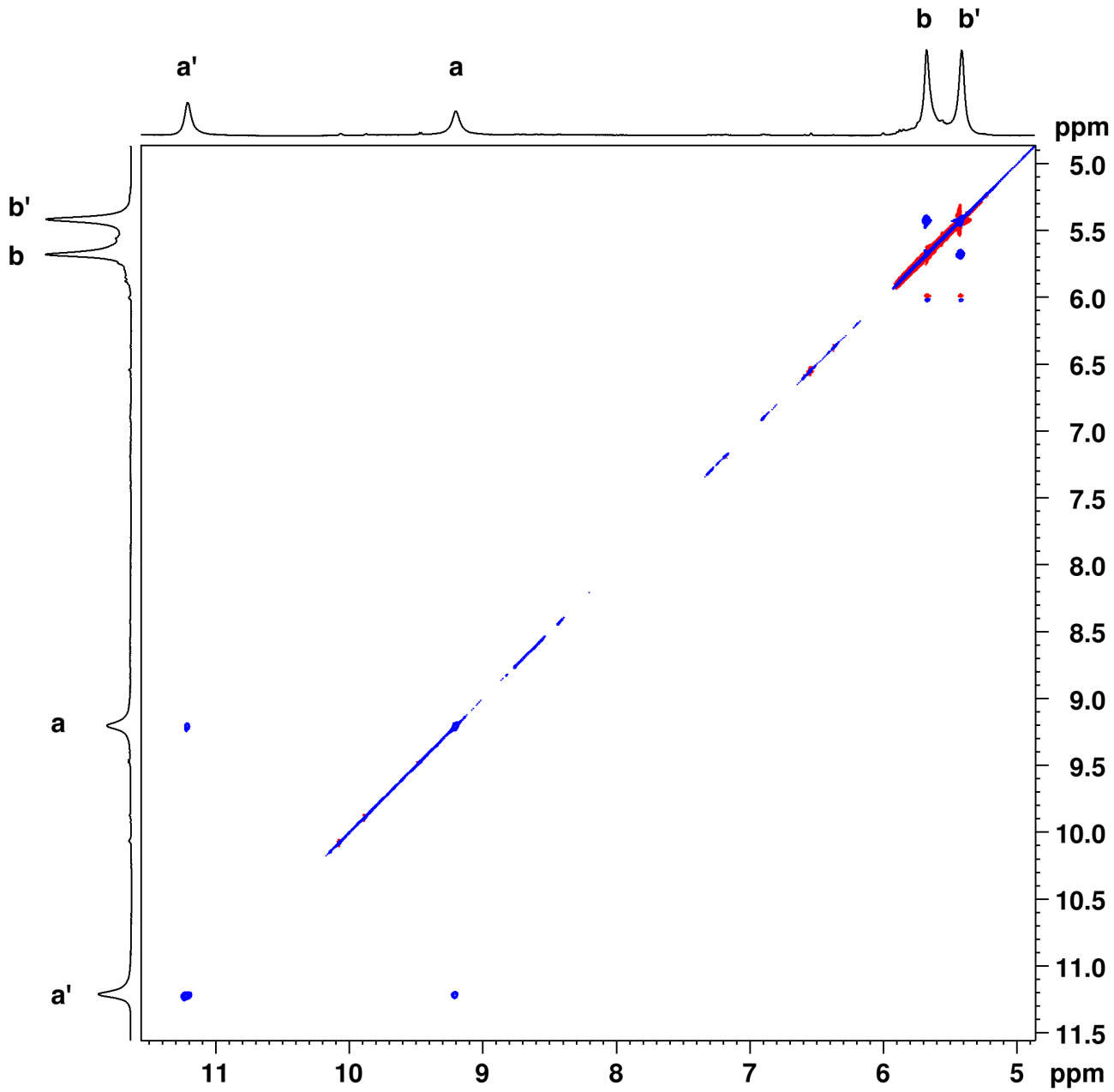



Fig. S-46 Aromatic region of $^{1}$H,$^{1}$H-ROESY of *cis*-**1** with $TBAH_2PO_4$ (0.5 eq) in DMSO-$d_6$ showing cross-peaks for chemical exchange in blue.

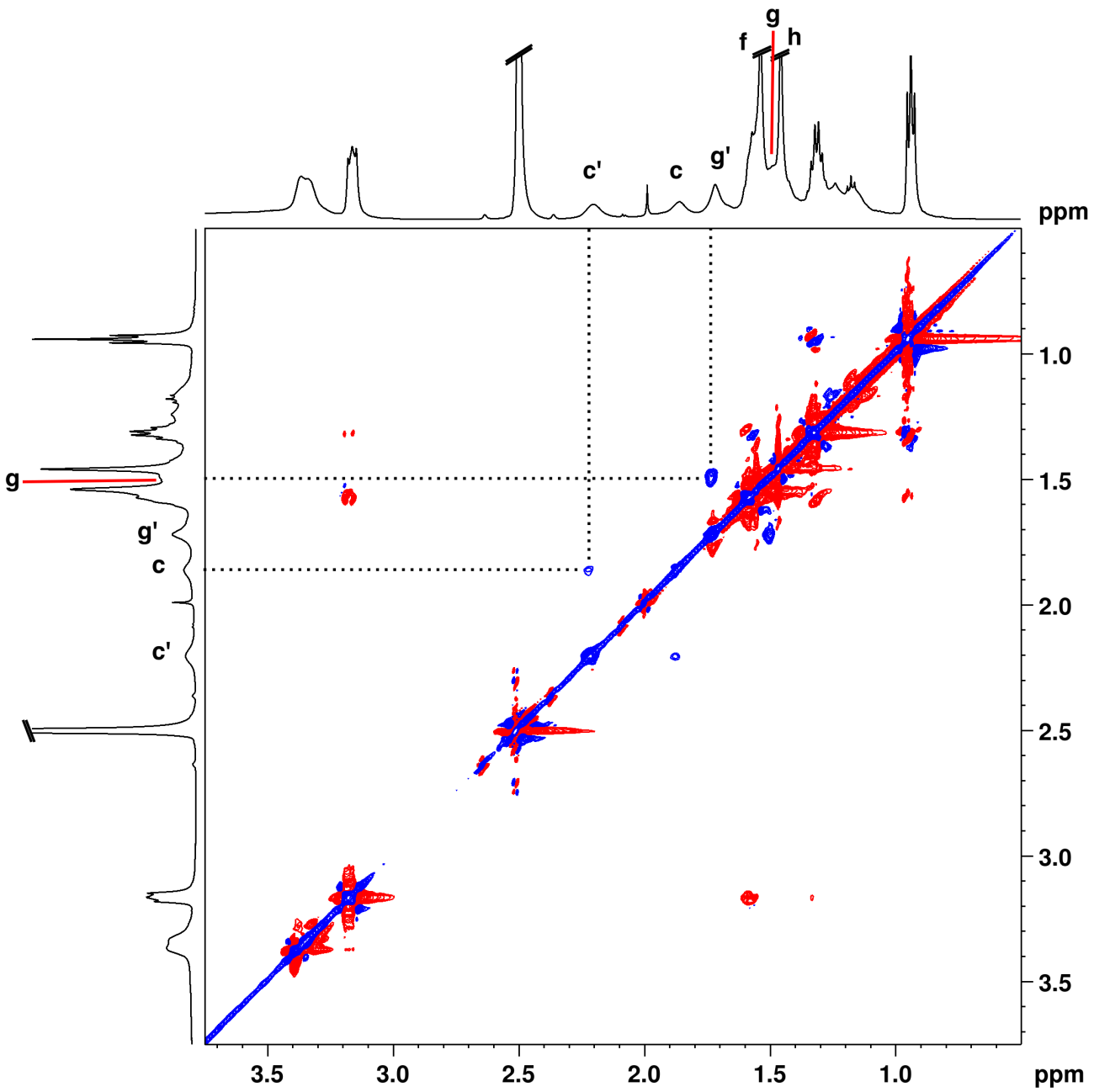



Fig. S-47 Aliphatic region of $^{1}$H,$^{1}$H-ROESY of *cis*-**1** with $TBAH_2PO_4$ (0.5 eq) in DMSO-$d_6$ showing cross-peaks for chemical exchange in blue.

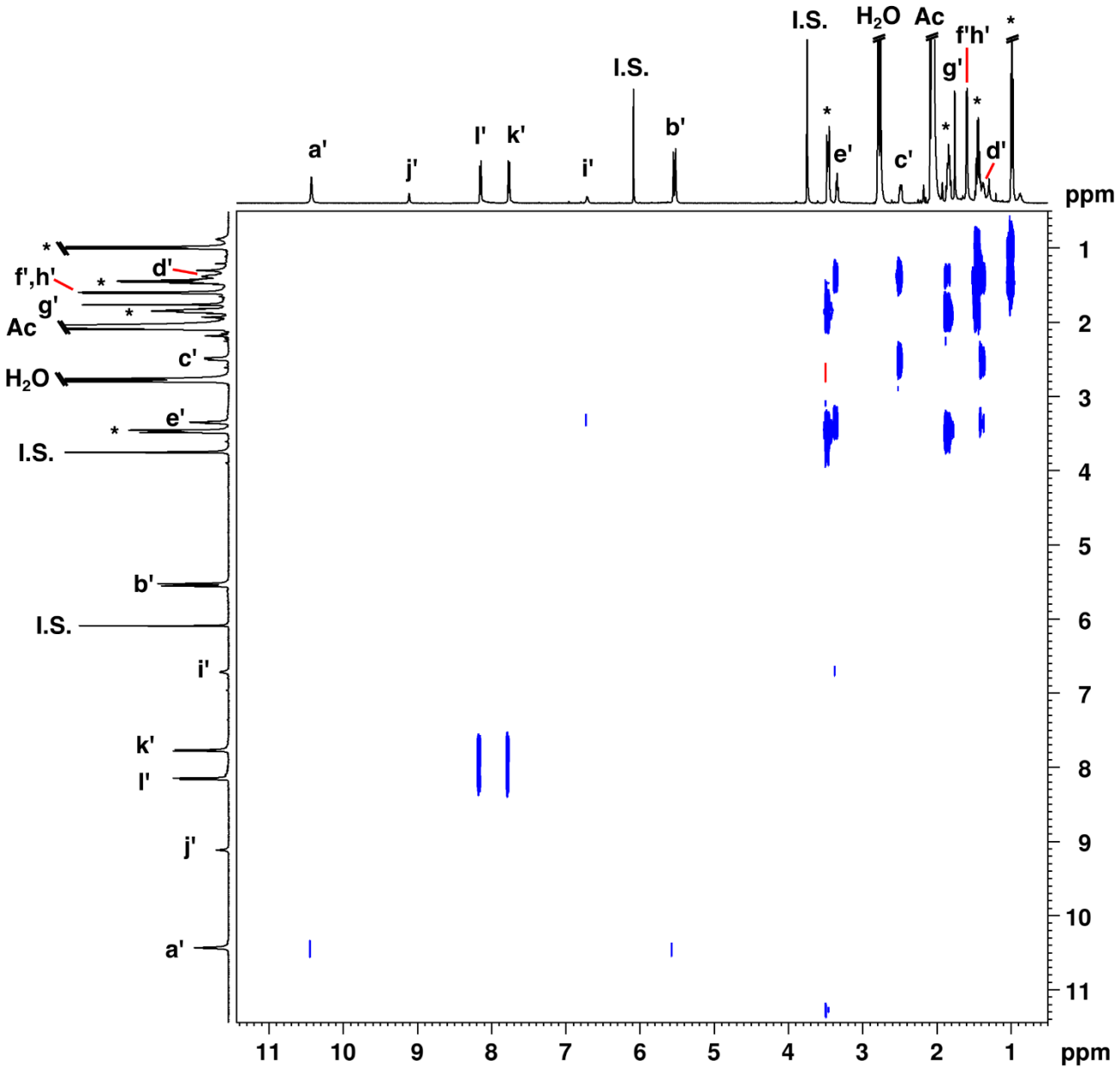



Fig. S-48 $^{1}$H,$^{1}$H-COSY of *cis*-**3** with TBACl (1 eq) in acetone-$d_6$. TBA signals are indicated with (*). I.S. = 1,3,5-trimethoxybenzene.

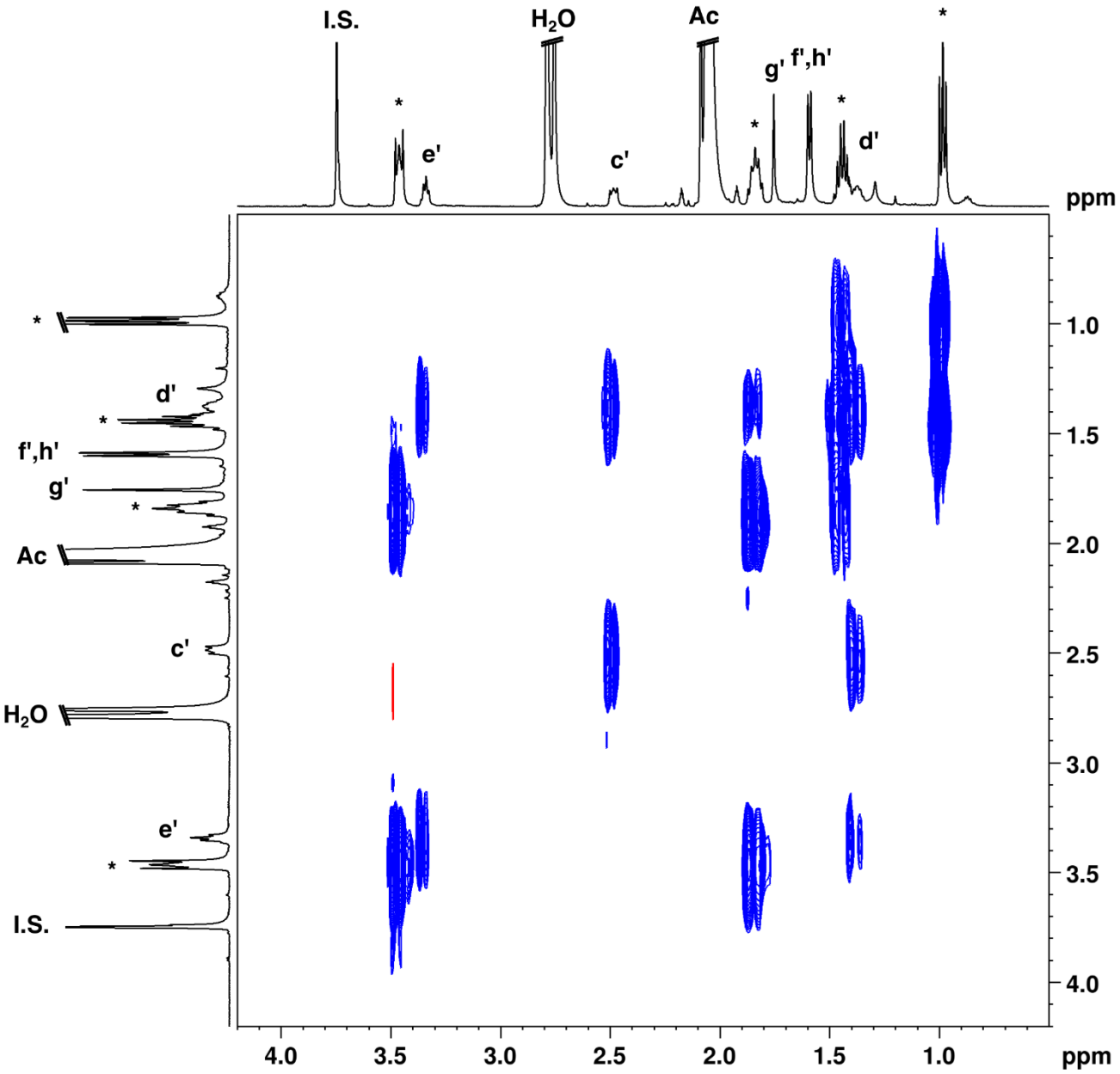



Fig. S-49 Aliphatic region of $^{1}$H,$^{1}$H-COSY of *cis*-**3** with TBACl (1 eq) in acetone-$d_6$. TBA signals are indicated with (*). I.S. = 1,3,5-trimethoxybenzene.

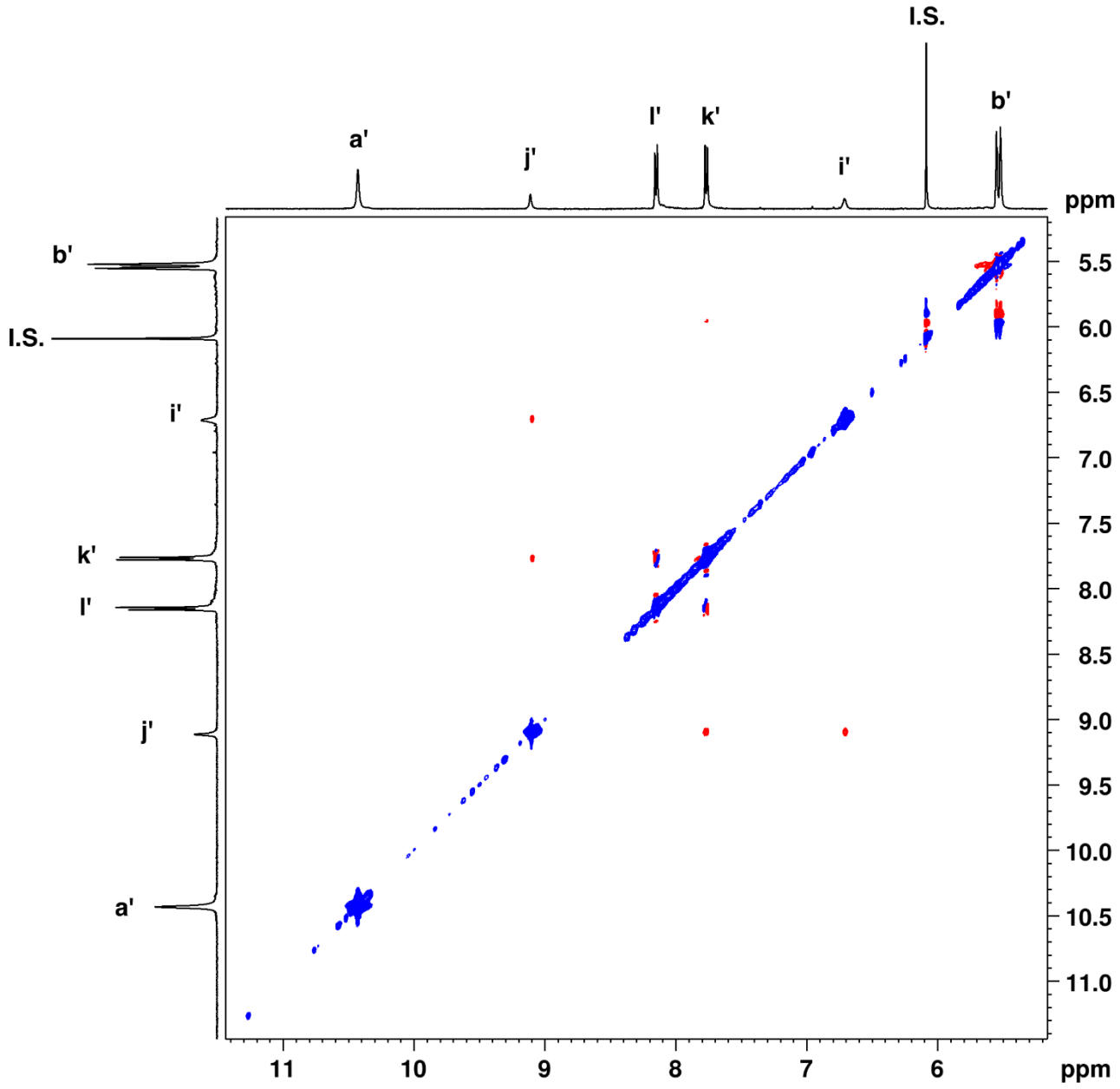



Fig. S-50 Aromatic region of $^{1}$H,$^{1}$H-ROESY of *cis*-**3** with TBACl (1 eq) in acetone-$d_6$ showing ROE cross-peaks in red. I.S. = 1,3,5-trimethoxybenzene.

## 5. ITC

The ITC measurements were performed using a MicroCal PEAQ-ITC microcalorimeter at 25 °C in a mixture of acetonitrile and DMSO (3 %) due to low solubility of the host in pure acetonitrile. The solvent mixture was dried with 3 Å molecular sieves. The titrations were carried out by injection of 400 μM TBACl solution to solution of 20 μM of host. Each titration was repeated three times. The data was fitted by fixing set of sites N = 1 and letting c (cell) vary.

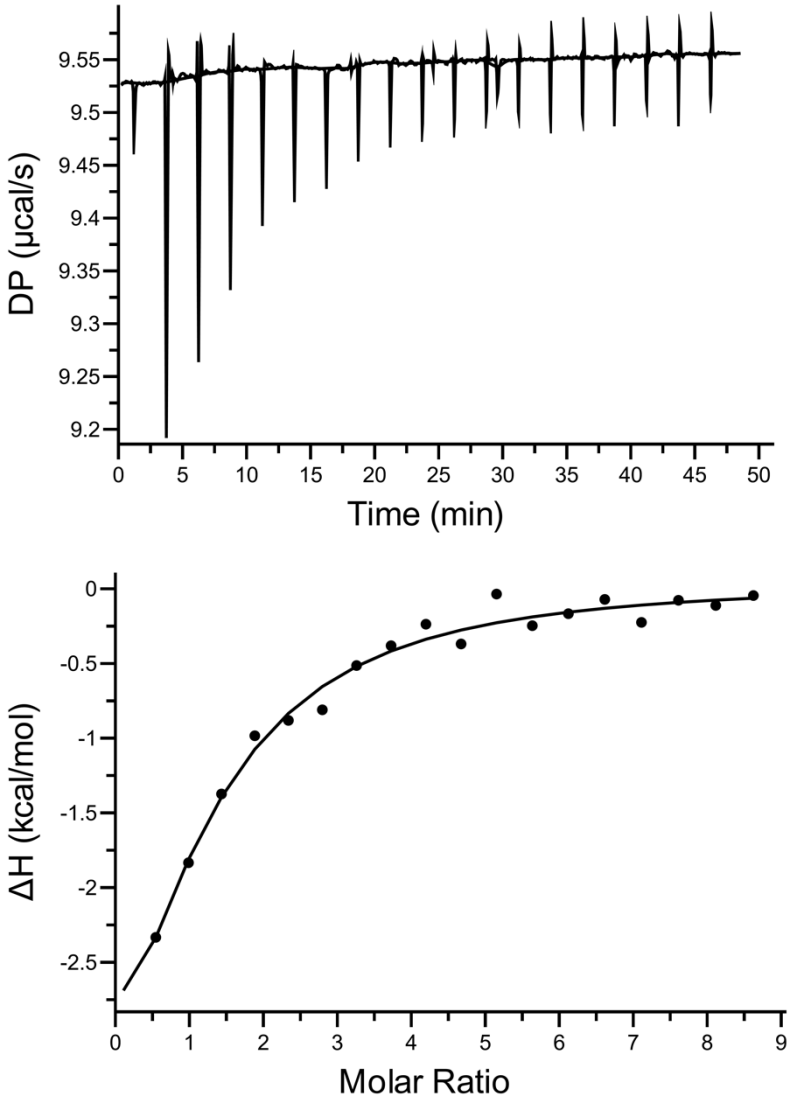



Fig. S-51 An ITC titration curve of *cis*-**1** with TBACl in acetonitrile with 3 % DMSO at 25 °C.

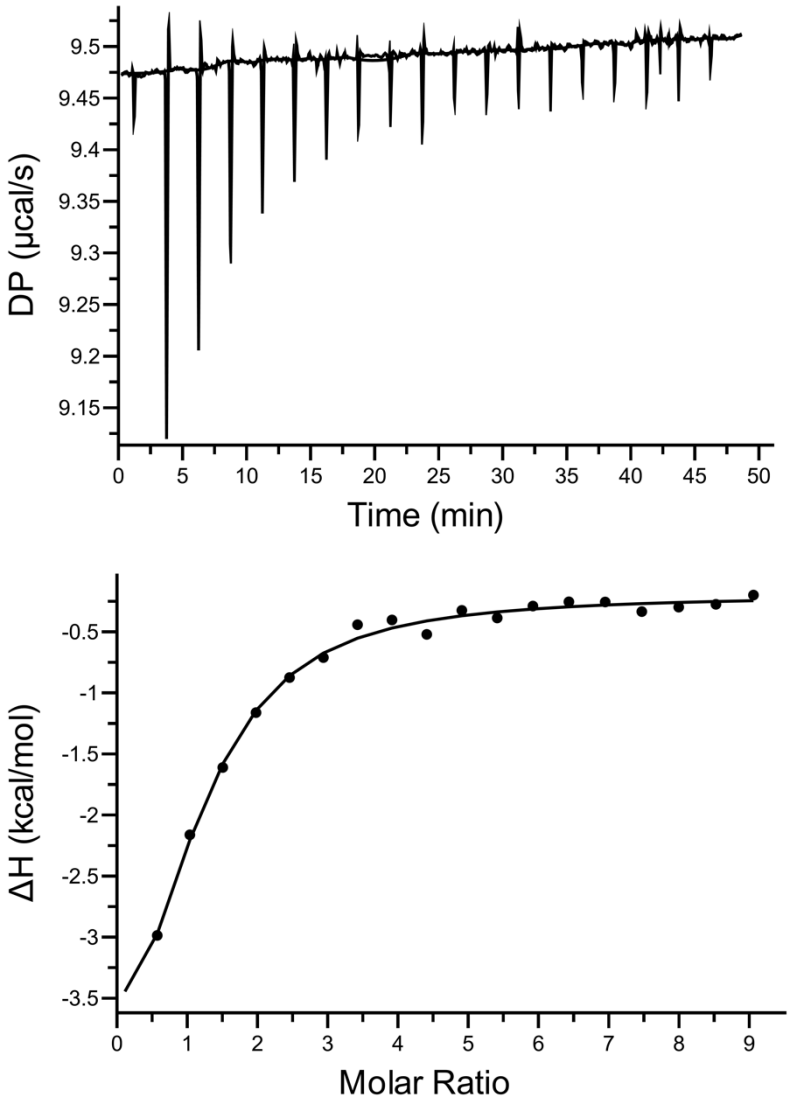



Fig. S-52 An ITC titration curve of *cis*-**3** with TBACl in acetonitrile with 3 % DMSO at 25 °C.

# 6. Anion transport studies

## 6.1. Preparation of the vesicles

1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) and cholesterol solutions (15-30 mM) in deacidified chloroform were combined in a 5 mL round bottom flask. The volumes of the aliquots were calculated from the concentrations of the lipid solutions to obtain a POPC to cholesterol ratio of 7:3 (for instance by combining 7 µmol POPC and 3 µmol cholesterol). The solvents were evaporated under a flow of nitrogen and the resulting lipid film was dried under high vacuum for at least 1 h.

The lipid film was then hydrated with 500 µL of an aqueous solution of *N,N'*-Dimethyl-9,9′-biacridinium dinitrate (Lucigenin, 0.8 mM) in the desired salt solution (225 mM $NaNO_3$ or 112.5 mM $Na_2SO_4$). The resulting mixture was sonicated for 30 s and stirred for 1 h to give heterogeneous vesicles. Multilamellar vesicles were disrupted by 10 freeze-thaw cycles. The mixture was diluted to 1 mL (by adding 0.5 mL of salt solution) and extruded 29 times through a polycarbonate membrane with 200 nm pores in a mini-extruder (Avanti Polar Lipids). The external dye was removed by passing the liposomes through a pre-packed size exclusion column (containing 8.3 mL Sephadex G-25 medium), eluted with salt solution. The collected large unilamellar vesicles (LUVs) were further diluted with salt solution to obtain total lipid concentration of 0.4 mM (25-35 mL) and used for transport measurements the same day.

| | | | Size (d.nm): | % Intensity: | St Dev (d.nm): |
|---|---|---|---|---|---|
| Z-Average (d.nm): | 167.6 | Peak 1: | 179.3 | 100.0 | 47.79 |
| PdI: | 0.057 | Peak 2: | 0.000 | 0.0 | 0.000 |
| Intercept: | 0.959 | Peak 3: | 0.000 | 0.0 | 0.000 |
| Result quality : | Good | | | | |

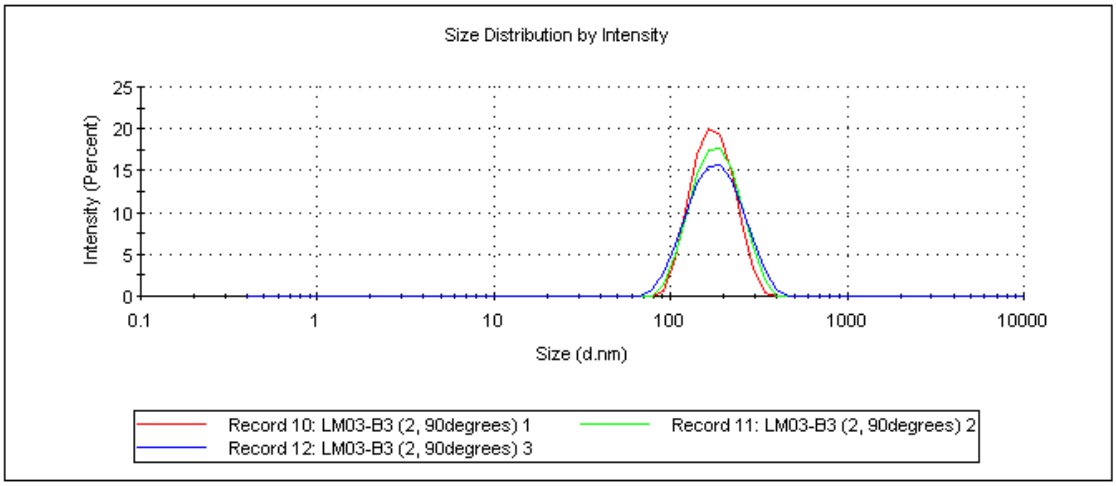



Fig. S-53 DLS data of LUVs with lucigenin encapsulated and suspended in 225 mM $NaNO_3$ for three consecutive measurements (using a refractive index of 1.45 for the liposomes and a refractive index of 1.33 and viscosity of 0.88 mPa·s for the aqueous solution). These curves are indicative of a monodisperse suspension of vesicles with a mean diameter (z-average) of 168 nm.

## 6.2. Chloride transport measurements

3.00 mL of the freshly prepared liposomes solution were placed in a quartz cuvette with a small stir bar, and the cuvette was placed inside the sample compartment of a Varian Cary Eclipse Fluorescence Spectrometer. The transporter was added to the liposomes as 12 µL of a stock solution (2-0.02 mM) in an organic solvent (methanol for compound *cis*-**1** and acetone for compounds *cis*-**3** and *trans*-**3**; transporter:lipid molar ratio 1:50). These

additions were performed using a Hamilton syringe and placing the end of the tip close to the magnetic bar on the bottom of the cuvette, while stirring. For blank curves, 12 µL of acetone were added. The temperature was allowed to stabilize by stirring at 25 ˚C for 3-5 minutes (these conditions were maintained during the whole transport experiment), and after equilibration the transport measurement was started. During transport measurements the fluorescence intensity at 505 nm (10 nm slits) was monitored over time (15 minutes, 0.2 s interval) with excitation at 430 nm (20 nm slits).

For transport measurements 75 µL of NaCl (1 M, in 225 mM $NaNO_3$) were added to the liposomes 30 s after the start of the fluorescence recording, to create a $Cl^-$ concentration gradient of 25 mM. The fluorescence intensity was measured for another 10 minutes, followed by lysing of the liposomes by addition of 50 µL of Triton X-100 (5% $^{w}/_{w}$ in water), to prove that all samples reached similar fluorescence intensity levels after lysis.

To normalize the curves, the initial 30-40 seconds were deleted to get rid of the fluorescence intensity in absence of NaCl (first 30 s) and the initial drop in fluorescence intensity after addition of NaCl (provoked by extravesicular lucigenin), and all the values were divided by the initial value of the resulting curve ($F/F_0$). The transport curves show the first 500 seconds of transport (lysis levels are omitted for clarity).

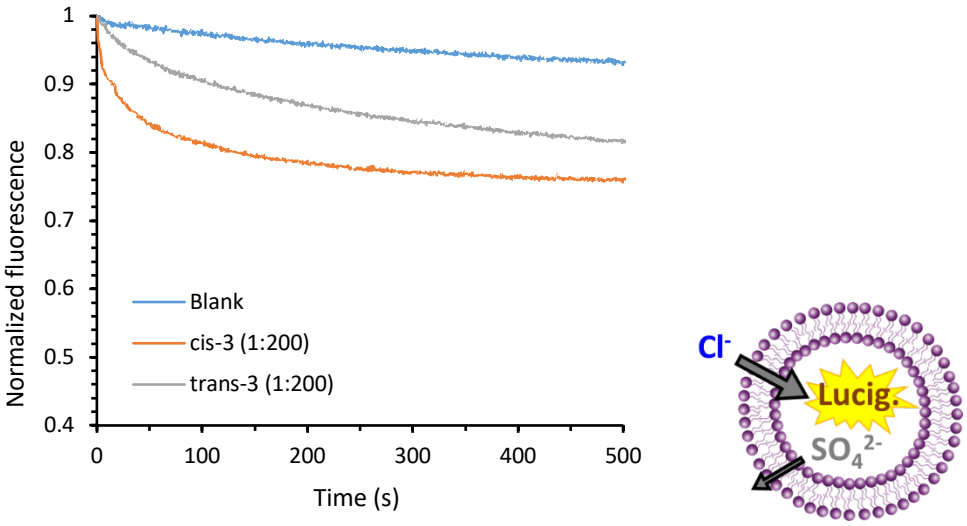



Fig. S-54 Chloride transport by calix[4]pyrroles *cis*-**3** and *trans*-**3** (at 1:200 transporter:lipid ratio) into LUVs of POPC:cholesterol (70:30) suspended in 112.5 mM $Na_2SO_4$ solution (interior and exterior), monitored by the quenching of the fluorescence of encapsulated lucigenin (0.8 mM) upon addition of 25 mM NaCl. The blank curve was recorded in absence of transporter.

### 6.3. **Quantification of chloride transport activity of *cis*-3 at different concentrations**

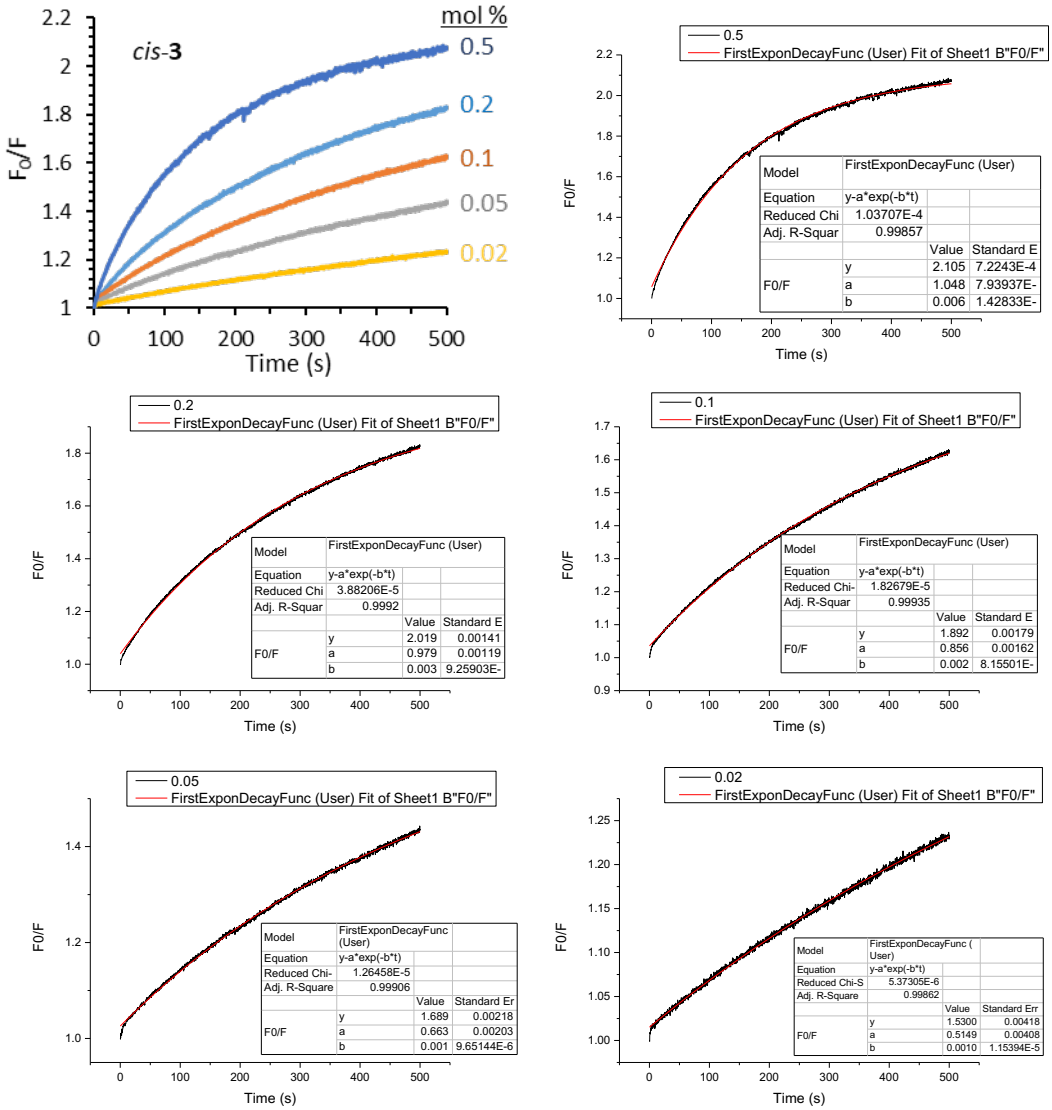
To quantify the transport of chloride by compound *cis*-**3**, the inverted transport curves ($F_0/F$ vs time) were fitted to a single exponential decay function:

$$F_0/F = y - a \cdot e^{-b \cdot t} \qquad (1)$$

According to the Stern-Volmer equation, $F_0/F$ is directly proportional to the concentration of quencher (chloride). Thus, plots of $F_0/F$ are directly related to the increase in the concentration of chloride inside the vesicles, and the derivatives of these plots give the transport rates. Therefore, the initial rates ($I$) were calculated from equation *(2)* that results from differentiation of equation *(1)* for t = 0.

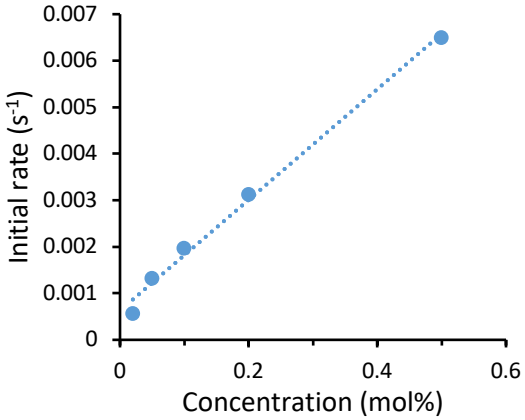
$$I = a \cdot b \qquad (2)$$

a)




b)

| Conc. (mol%) | a | b | Initial rate (*I*) |
|---|---|---|---|
| 0.5 | 1.0483 | 0.0062 | 0.0065 |
| 0.2 | 0.9799 | 0.0032 | 0.0032 |
| 0.1 | 0.8568 | 0.0023 | 0.0020 |
| 0.05 | 0.6638 | 0.002 | 0.0013 |
| 0.02 | 0.515 | 0.0011 | 0.0006 |



c)

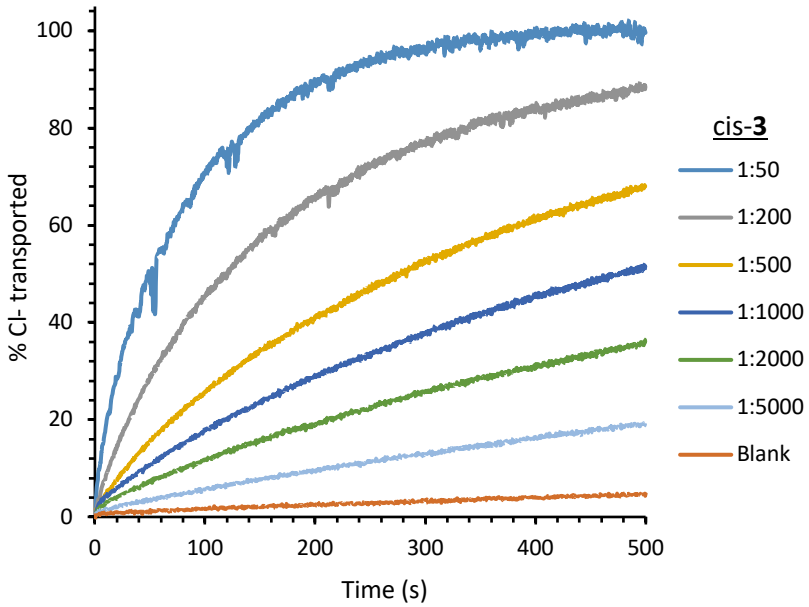



Fig. S-55 a) Chloride transport plots and single exponential fits of $F_0/F$ by calix[4]pyrrole *cis*-**3** at different concentrations. b) Plot of initial rate (*I*) vs concentration of *cis*-**3**. Concentrations are expressed in % molar ratio, referred to the lipids. c) Transport of chloride by compound *cis*-**3** at different concentrations represented as the % of this anion internalized inside the vesicles over time. The 100 % of chloride transported was established as the equilibration level of response from a curve with a high concentration of transporter (1:50).

# 7. ESI-MS and IM-MS experiments

Mass spectrometry experiments were carried out with Agilent 6560 ESI-IM-QTOF mass spectrometer equipped with AJS ESI ion source. Samples were injected using direct infusion from a syringe pump with a 5 µl/min flow rate. $N_2$ was used as dry- sheath and nebulizer gas from nitrogen generator. A dry-gas temperature of 225 °C, drying gas flow rate of 5 l/min, nebulizer pressure of 10 psi, sheath gas temperature of 200 °C and sheath gas flow of 10 l/min were used. Capillary voltage of 2000 V and fragmentor voltage of 350 V were set as source parameters. The mass spectrometer was calibrated with an ES tuning mix from Agilent Technologies. Data was acquired with MassHunter Acquisition B09.00 and analyzed using MassHunter Qualitative Analysis B.08.00 as software packages from Agilent Technologies, USA.

In IM-MS experiments $N_2$ from nitrogen cylinder (5.0) was used as a drift gas. In the single-field IM-MS experiments the high-pressure funnel was set to 3.80 Torr. The drift tube entrance and exit voltages were set as -1574 V and -250V, respectively. A trap filling time of 10 000 µs and a trap release time of 150 µs were used. Collision cross section ($^{DT}CCS_{N2}$) values were determined using multi-field measurements and the drift tube entrance voltage was varied from 1074 V to 1674 V with 100 V increments. ES tuning mix was measured after samples as a quality control sample for the CCS values.[5,6]

The solution of *cis*-**1** was prepared as 1mM in methanol, and *cis*-**3** 1 mM in acetone. The stock solutions of TBA salts were prepared as 2 or 5 mM in methanol or acetonitrile. Samples were prepared with 10 µM host concentration and 1:5 host:guest ratio in acetonitrile.

Theoretical CCS values were calculated with IMoSSuite 1.10[7] by using experimental parameters (gas, temperature and pressure). Coordinates for the calculations were obtained from DFT calculated structures (See section 9). Several theoretical approaches were tested (project approximation PA, trajectory method with Lennard-Jones parameters (TMLJ), diatomic trajectory method (DTM) and exact hard sphere scattering (EHSS/DHSS). The best comparison to experimental data was obtained using TMLJ method in IMoSSuite 1.10.

Table S1. Observed ions, their *m/z* values, mass accuracies, drift times and $^{DT}CCS_{N2}$ values. Theoretical $^{TMLJ}CCS_{N2}$ values were calculated for following ions: [**1**-H]$^-$ 229.31 Å$^2$ (accuracy -3.4 %), [**1**+Cl]$^-$ 237.10 Å$^2$ (accuracy -3.0 %), [**3**-H]$^-$ 308.99 Å$^2$ (accuracy -7.5 %) and for [**3**+Cl]$^-$ 316.30 Å$^2$ (accuracy -6.9 %).

| Ion | *m/z* theoretical | *m/z* experimental | mass accuracy (mDa) | Drift time (ms) | $^{DT}CCS_{N2}$ (Å$^2$) |
|---|---|---|---|---|---|
| [**1**-H]$^-$ | 515.3386 | 515.3389 | -0.3 | 29.60 | 221.8 |
| [**1**+Cl]$^-$ | 551.3158 | 551.3155 | 0.3 | 30.79 | 224.7 |
| [**1**+Br]$^-$ | 595.2653 | 595.1637 | 1.6 | 30.91 | 230.3 |
| [**1**+$H_2PO_4$]$^-$ | 613.3160 | 613.3148 | 1.2 | 31.46 | 234.2 |
| [**3**-H]$^-$ | 841.4155 | 841.4154 | 0.1 | 38.67 | 287.5 |
| [**3**+Cl]$^-$ | 877.3922 | 877.3922 | 0 | 39.96 | 295.8 |
| [**3**+SCN]$^-$ | 900.3985 | 900.3985 | 0 | 40.15 | 297 |
| [**3**+$NO_3$]$^-$ | 904.4111 | 904.4112 | -0.1 | 40.25 | 299 |
| [**3**+Br]$^-$ | 921.3417 | 921.3419 | -0.2 | 40.24 | 296.1 |
| [**3**+$ClO_4$]$^-$ | 941.3718 | 941.3731 | -1.3 | 40.33 | 298 |
| [**3**+I]$^-$ | 969.3278 | 969.3287 | -0.9 | 40.12 | 296.5 |
| [**3**+$PF_6$]$^-$ | 987.3875 | 987.3890 | -1.5 | 40.51 | 299.2 |
| [**3**+OTf]$^-$ | 991.3753 | 991.3770 | -1.7 | 41.19 | 304.9 |

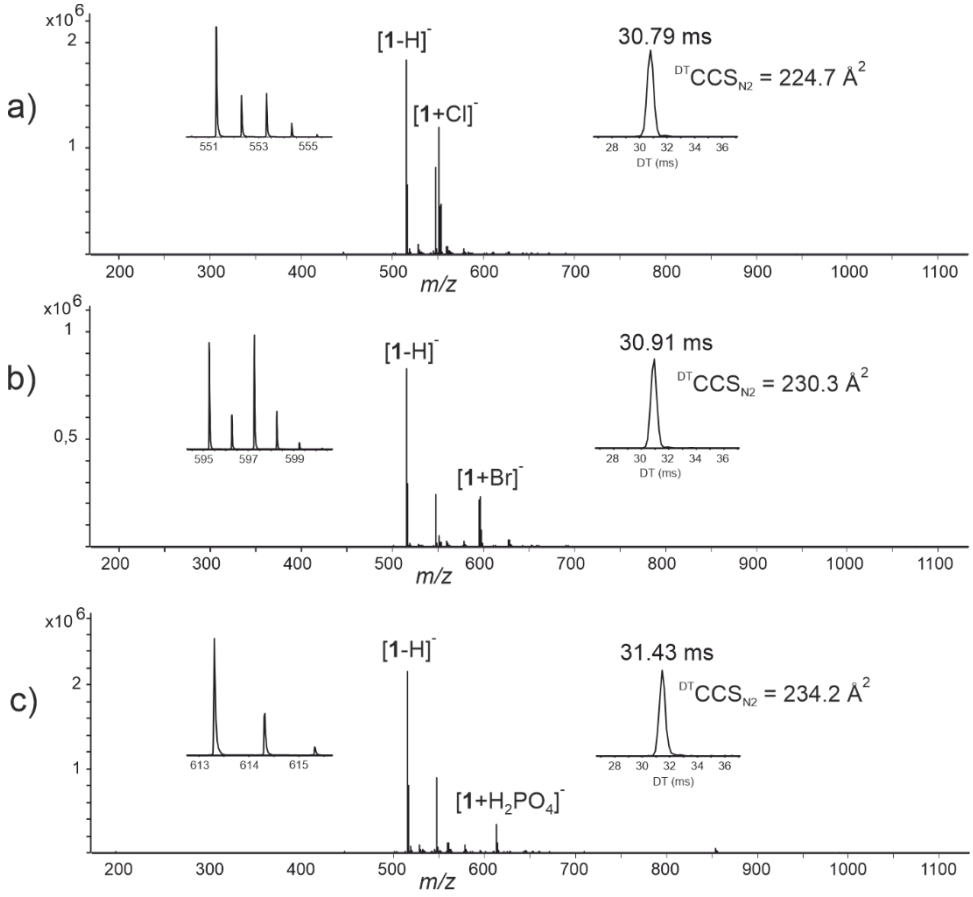
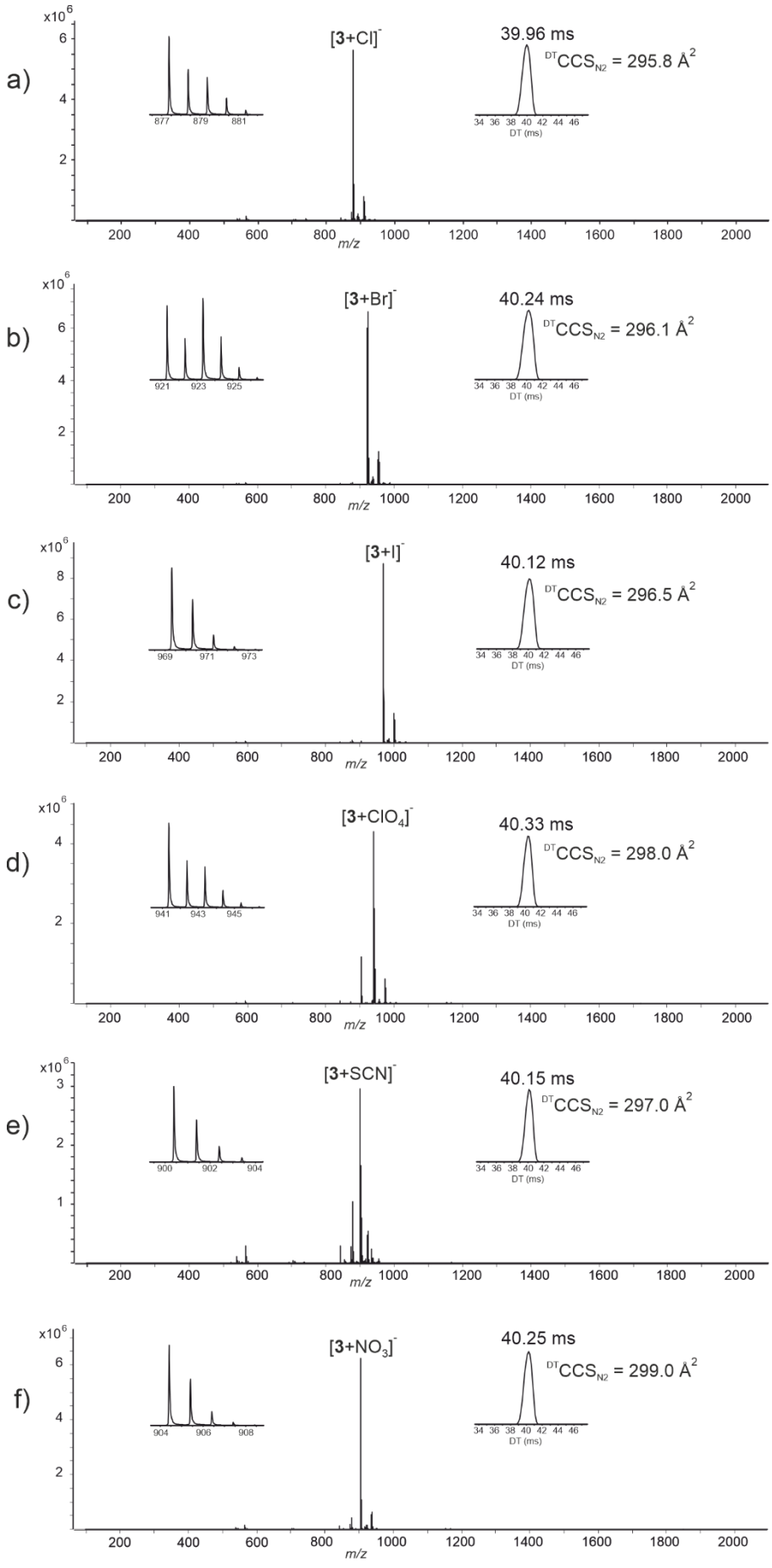



Fig. S-56 (–)ESI-MS spectra of *cis*-**1** with a) TBACl, b) TBABr and c) $TBAH_2PO_4$. Insets on the left are showing the isotopic distribution of the corresponding anion complexes and insets on the right the arrival time distributions for the same ions. The peak at *m/z* 547 corresponds to oxidized form of **1**, as $[\mathbf{1}\text{-}H+O_2]^-$ ion.


a)
[3+Cl]-
39.96 ms
DTCCSN2 = 295.8 Å2
b)
[3+Br]-
40.24 ms
DTCCSN2 = 296.1 Å2
c)
[3+I]-
40.12 ms
DTCCSN2 = 296.5 Å2
d)
[3+ClO4]-
40.33 ms
DTCCSN2 = 298.0 Å2
e)
[3+SCN]-
40.15 ms
DTCCSN2 = 297.0 Å2
f)
[3+NO3]-
40.25 ms
DTCCSN2 = 299.0 Å2
m/z
DT (ms)

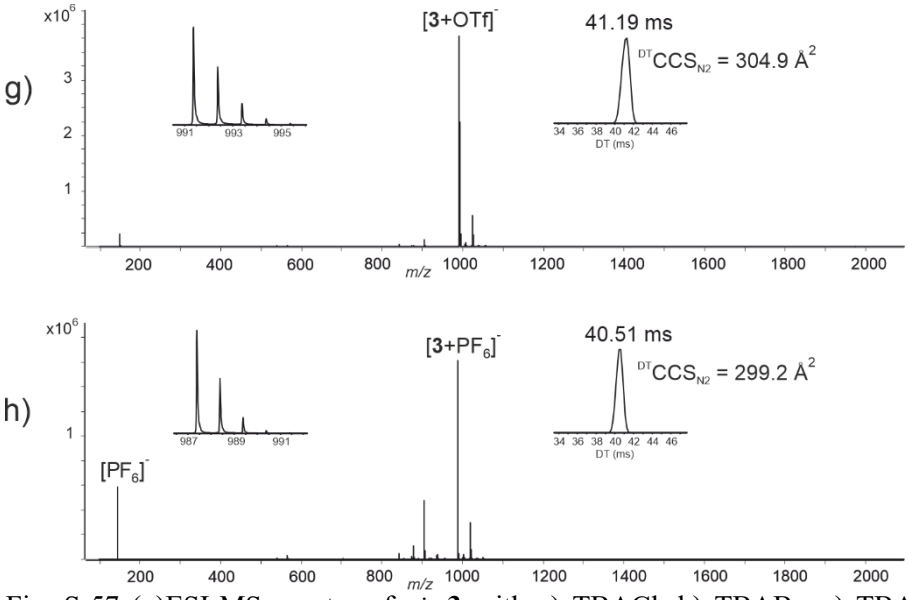



Fig. S-57 (–)ESI-MS spectra of *cis*-**3** with a) TBACl, b) TBABr, c) TBAI, d) $TBAClO_4$, e) TBASCN, f) $TBANO_3$, g) TBAOTf and h) $TBAPF_6$. Insets on the left are showing the isotopic distribution of the corresponding anion complexes and insets on the right the arrival time distributions for the same ions.

# 8. XRD

Diffraction data for structures *cis*-**1** · 0.25 THF, *trans*-**1**, and *cis*-**1** · TMACl · 0.5 EtOH were collected on an Rigaku Oxford Diffraction Supernova dual source diffractometer using an Atlas CCD detector with $CuK_\alpha$ irradiation (λ=1.54184 Å). The obtained data were processed, and absorption correction (gaussian or analytical) was applied using CrysAlisPro program (CrysAlisPro 1.171.40.67a, Rigaku Oxford Diffraction, 2019). The structures were solved using OLEX2 program[8] using Superflip[9] (charge flipping method) program and refined using SHELXL[10] full-matrix least-squares methods on $F^2$ with anisotropic displacement parameters for the non-hydrogen atoms.

Single crystal X-ray data for structures **5** and *trans*-**2** were recorded on a Bruker Apex DUO diffractometer equipped with an APEX 2 4K CCD area detector, and a Microfocus Source E025 IuS using MoKα (λ = 0.71073 Å) radiation monochromatized with Quazar MX Multilayer Optics. The data were processed with Bruker APEX2 v2014.9-0 and empirical absorption correction was made with SADABS-2014/4. The structure was solved with SHELXT[11] using direct and dual space methods and refined with ShelXLe[12] using ShelXL refinement package with least squares minimization.

Single crystal X-ray data for structure *cis*-**2** were recorded on a Rigaku MicroMax-007HF diffractometer with PILATUS 200K detector and Microfocus rotating anode X-ray tube with $MoK_\alpha$ (λ = 0.71073 Å) radiation. The data were processed and empirical absorption correction was made with CrysAlisPro. The structure was solved with sir2019 and refined with SHELXL in ShelXLe graphical interface.

The CH hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times the $U_{eq}$ of parent atom). The treatment of NH and OH hydrogens is described below for each structure. CCDC 2248771–2248776 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

**5** (Fig. S-58): Crystals suitable for single crystal X-ray diffraction were obtained by crystallization from dichloromethane/hexane. NH hydrogen atoms were calculated in idealized positions and refined as riding atoms with constrained parameters.

*cis*-**1** · 0.25 THF (Fig. 1c): Single crystals were grown by vapour diffusion of acetone into THF solution of *cis*-**1**. The NH and OH hydrogen atoms were located from the difference Fourier map and refined isotropically. The disordered THF molecule was modelled using restraints and its presence in 4:1 ratio was supported by $^1$H NMR spectrum of the crystals (Fig. S-59).

*trans*-**1** (Fig. 1a): Single crystals were grown from by vapour diffusion of acetone into THF solution of *trans*-**1**. The NH and OH hydrogen atoms were located from the difference Fourier map and refined isotropically.

*cis*-**2** · 3 $CH_3CN$ (Fig. S-62): Mixture of *cis*-**2** and *trans*-**2** (45 mg) was treated with acetonitrile (600 µl) and centrifuged. Precipitate and supernatant were separated, and the crystals grew in the supernatant. NH hydrogen atoms were calculated in idealized positions and refined as riding atoms with constrained parameters.

*trans*-**2** (Fig. S-61): A precipitate remaining after Soxhlet extraction of **2** with acetonitrile was recrystallized from dichloromethane. The NH hydrogen atoms were located from the difference Fourier map and refined isotropically.

*cis*-**1** · TMACl · 0.5 EtOH (Fig. 2a): Single crystals of *cis*-**1** · TMACl complex were obtained by the slow evaporation of ethanol mixture of *cis*-**1** (4.56 mg) and 5 eq of TMACl (5.22 mg). The NH hydrogen atoms were positioned from electron density maps and constrained to ride on their parent atoms. There is a disorder of molecule of ethanol (over symmetry element), C26, and the hydrogen bonding network. All disordered atoms were refined with occupancies fixed to 0.5 as dictated by the ethanol molecule.

Table S2. Crystallographic data

| | **5** | *cis*-**1** · 0.25 THF | *trans*-**1** | *cis*-**2** · 3 $CH_3CN$ | *trans*-**2** | *cis*-**1** · TMACl · 0.5 EtOH |
|---|---|---|---|---|---|---|
| CCDC number | 2248773 | 2248776 | 2248771 | 2248775 | 2248774 | 2248772 |
| Empirical formula | C21H21N3O2 | C33H46N4O2.25 | C32H44N4O2 | C54H59N9O4 | C48H50N6O4 | C74H118Cl2N10O5 |
| Formula weight | 347.41 | 534.74 | 516.71 | 898.1 | 774.94 | 1298.68 |
| Temperature/K | 100(2) | 120.01(10) | 120.01 | 293(2) | 100(2) | 120.01(10) |
| Crystal system | monoclinic | tetragonal | triclinic | monoclinic | monoclinic | monoclinic |
| Space group | P21/n | I41/a | P-1 | P21/n | C2/c | I2/a |
| a/Å | 8.9833(6) | 34.4880(3) | 10.4551(8) | 10.3501(3) | 16.5102(9) | 18.0787(9) |
| b/Å | 8.8691(5) | 34.4880(3) | 10.5908(7) | 14.2207(3) | 12.6105(6) | 18.1527(5) |
| c/Å | 22.8632(13) | 10.29560(10) | 14.0367(9) | 33.7063(11) | 20.3179(11) | 22.8772(12) |
| α/° | 90 | 90 | 97.348(5) | 90 | 90 | 90 |
| β/° | 95.4001(18) | 90 | 110.905(7) | 98.456(3) | 102.4282(19) | 108.690(5) |
| γ/° | 90 | 90 | 92.790(6) | 90 | 90 | 90 |
| Volume/$Å^3$ | 1813.51(19) | 12245.8(2) | 1432.54(18) | 4907.2(2) | 4131.1(4) | 7111.9(6) |
| Z | 4 | 16 | 2 | 4 | 4 | 4 |
| $\rho_{calc}$ g/$cm^3$ | 1.272 | 1.16 | 1.198 | 1.216 | 1.246 | 1.213 |
| μ/$mm^{-1}$ | 0.083 | 0.571 | 0.587 | 0.079 | 0.08 | 1.263 |
| F(000) | 736 | 4640 | 560 | 1912 | 1648 | 2824 |
| Radiation | MoKα (λ = 0.71073) | CuKα (λ = 1.54184) | CuKα (λ = 1.54184) | MoKα (λ = 0.71075) | MoKα (λ = 0.71073) | CuKα (λ = 1.54184) |
| Reflections collected | 33726 | 9771 | 8838 | 52031 | 13641 | 18056 |
| Independent reflections | 7532 | 5356 | 5395 | 9711 | 5358 | 7343 |
| $R_{int}$ | 0.0387 | 0.0190 | 0.0463 | 0.0469 | 0.0424 | 0.0318 |
| Data/restraints/parameters | 7532/0/236 | 5356/32/390 | 5395/0/373 | 9711/0/613 | 5358/0/267 | 7343/0/454 |
| Goodness-of-fit on F2 | 1.048 | 1.032 | 1.046 | 1.147 | 1.031 | 1.144 |
| R1[a] ($I \geq 2\sigma$) | 0.0490 | 0.0559 | 0.0523 | 0.0829 | 0.0503 | 0.0954 |
| wR2[b] ($I \geq 2\sigma$) | 0.1255 | 0.1681 | 0.1109 | 0.2049 | 0.1125 | 0.2272 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S3. Hydrogen bond angles and distances

| | D | H | A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° | Symmetry operations |
|---|---|---|---|---|---|---|---|---|
| **5** | N2 | H2 | O2[1] | 0.88 | 2.06 | 2.8604(11) | 150.6 | [1]1-X,1-Y,-Z |
| *cis*-**1** · 0.25 THF | N2 | H2 | O1[2] | 0.95(3) | 2.09(3) | 3.011(2) | 164(2) | [1]-1/4+Y,3/4-X,-1/4+Z; [2]-1/4+Y,5/4-X,5/4-Z |
| | N3 | H3 | O2[1] | 0.96(3) | 2.13(3) | 3.062(2) | 164(2) | |
| | N4 | H4 | O1[2] | 0.91(3) | 2.48(3) | 3.346(2) | 160(2) | |
| *trans*-**1** | N1 | H1 | O2[1] | 0.89(3) | 2.11(3) | 2.981(3) | 165(3) | [1]1-X,2-Y,1-Z; [2]-X,1-Y,-Z |
| | N2 | H2 | O1[2] | 0.91(3) | 2.27(3) | 3.169(2) | 169(2) | |
| | N3 | H3 | O2[1] | 0.91(3) | 2.26(3) | 3.145(3) | 164(2) | |
| | N4 | H4 | O1[2] | 0.92(3) | 2.08(3) | 2.977(2) | 164(3) | |
| *cis*-**2** · 3 $CH_3CN$ | N1 | H1 | N1A | 0.86 | 2.5 | 3.351(4) | 172.7 | [1]1-X,1-Y,1-Z |
| | N4 | H4 | N3A[1] | 0.86 | 2.55 | 3.397(4) | 168.5 | |
| *trans*-**2** | N2 | H2 | O2[1] | 0.88 | 2.17 | 2.9869(19) | 153.6 | [1]1-X,1-Y,-Z |
| *cis*-**1** · TMACl · 0.5 EtOH | O1 | H1B | Cl1 | 0.84 | 2.62 | 3.407(4) | 156.4 | [1]1/2-X,1/2-Y,3/2-Z |
| | O1 | H1A | O2[1] | 0.84 | 2.02 | 2.795(5) | 152.9 | |
| | O2 | H2B | O1[1] | 0.84 | 2.01 | 2.795(5) | 155 | |
| | O2 | H2A | O1S | 0.84 | 1.89 | 2.720(4) | 168.6 | |
| | N1 | H1 | Cl1 | 0.79(5) | 2.54(5) | 3.326(3) | 176(5) | |
| | N2 | H2 | Cl1 | 0.89(5) | 2.44(5) | 3.334(3) | 177(4) | |
| | N3 | H3 | Cl1 | 0.86(5) | 2.53(5) | 3.380(3) | 170(5) | |
| | N4 | H4 | Cl1 | 0.93(5) | 2.39(5) | 3.317(3) | 175(4) | |

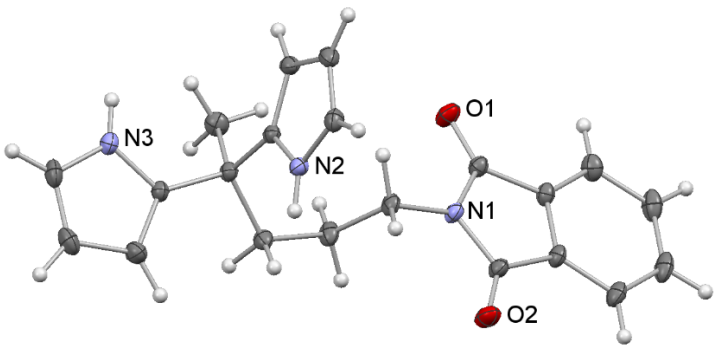



Fig. S-58 Crystal structure of **5** (anisotropic displacement parameters are drawn at 50% probability level).

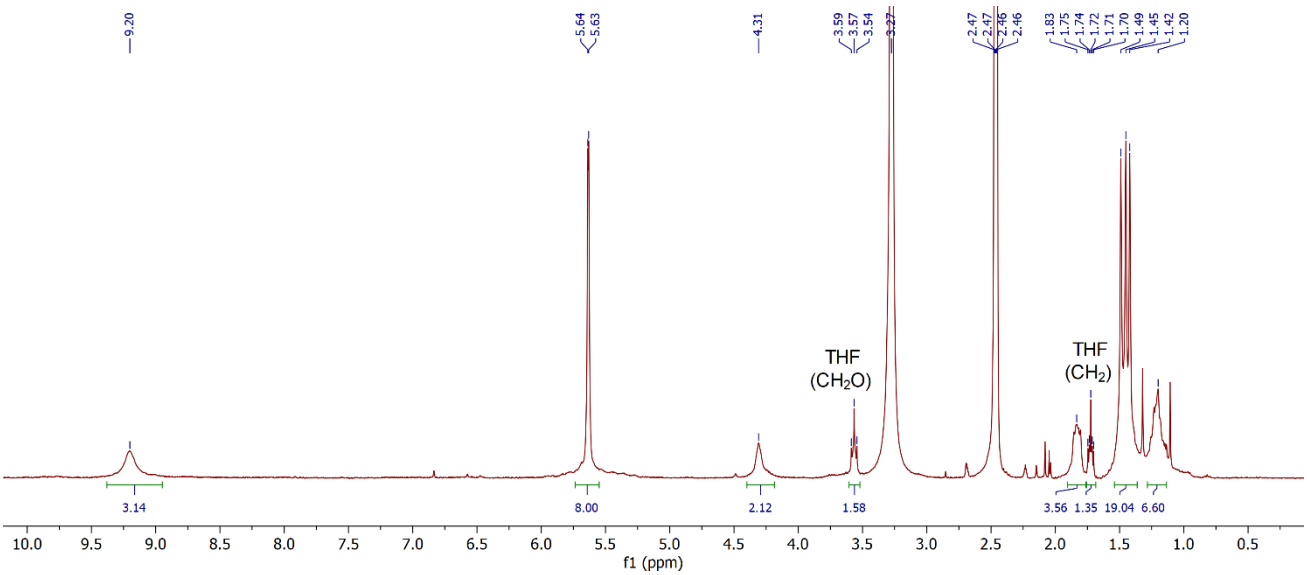



Fig. S-59 $^{1}$H NMR spectrum (300 MHz, 30 °C) of crystals *cis*-**1** · 0.25 THF disolved in DMSO-$d_6$.

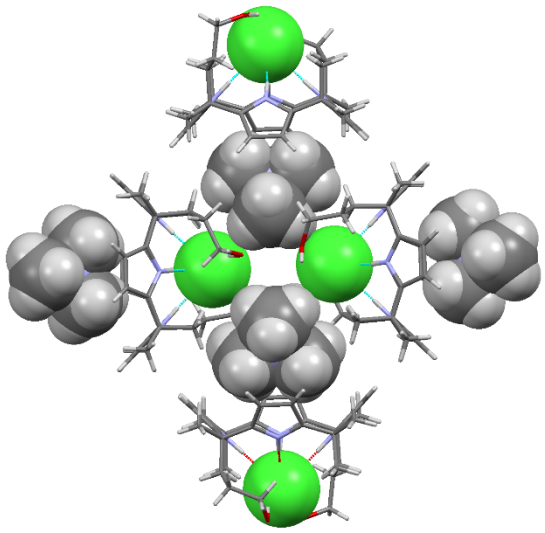


Fig. S-60 Arrangement of TBA cations in the crystal structure of *cis*-**1** · TMACl · 0.5 EtOH.

### 8.1. **Crystal structure description for *cis*-2 and *trans*-2**

Despite being unable to separate *trans*- and *cis*-isomers of **2** on the preparative scale, we could grow the single crystals of *trans*-**2** and *cis*-**2** from mixtures enriched with the corresponding isomer. Solvent-free form of *trans*-**2** was crystallized, whereas *cis*-**2** was crystallized as an acetonitrile solvate *cis*-**2** · 3 $CH_3CN$. In these crystal structures, the hosts adopt 1,3-alternate conformation of the calix[4]pyrrole macrocycles and equatorial orientation of the phthalimide propyl arms. In both structures the phthalimide groups are involved in intermolecular π-stacking interactions, and either host-to-host hydrogen bonded chains (N-H···O=C) or solvent mediated hydrogen bonded chains are formed in *trans*-**2** and *cis*-**2**, respectively.

In the crystal structure of *trans*-**2** the host molecule forms hydrogen bonds with two neighbours via phthalimide C=O group and one calix[4]pyrrole NH group (O···N distance 2.99 Å) on each side to form hydrogen bonded chains in one dimension (Fig. S-61 b), and interacts with another pair of neighbours via π-stacking of phthalimide fragments on each side (phthalimide centroid-centroid distance 3.58 Å) to form chains in the other dimension (Fig. S-61 c).

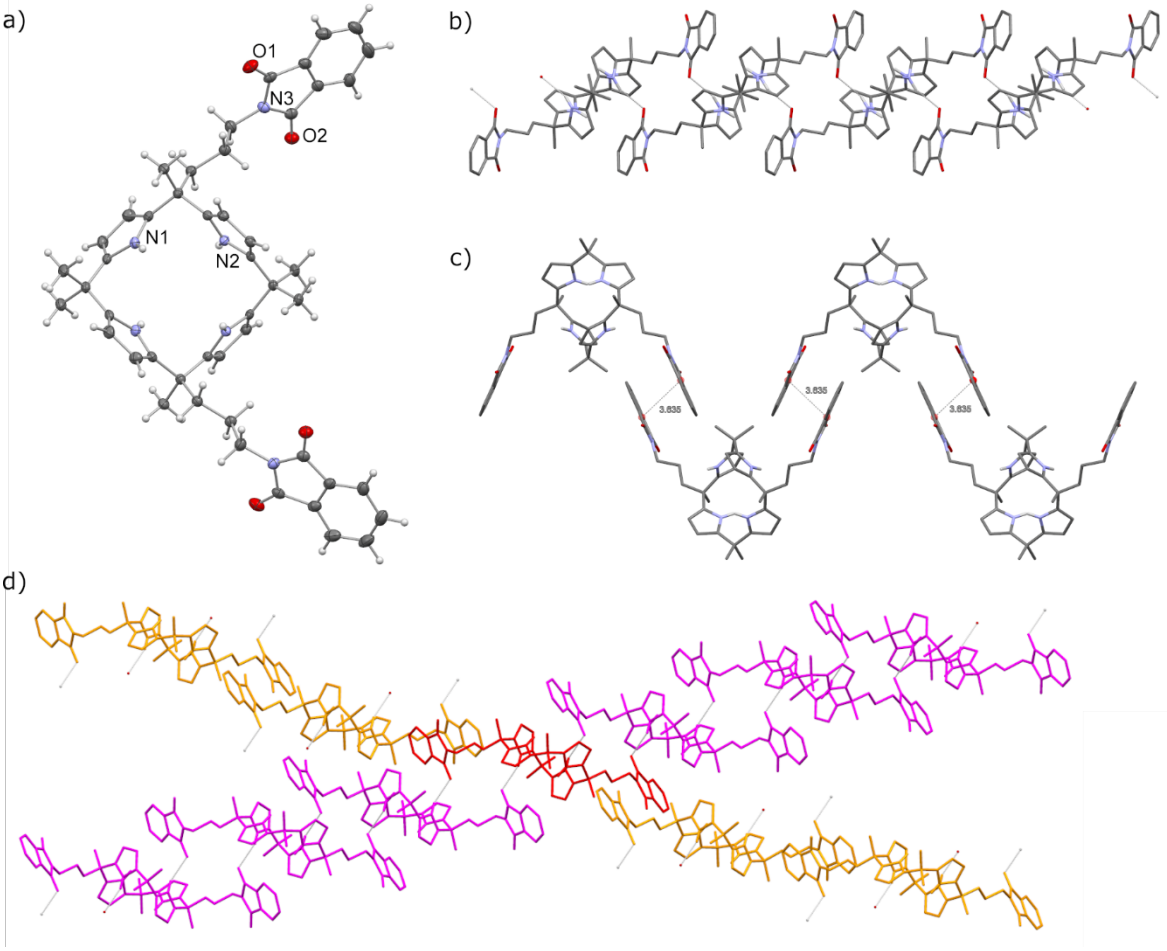



Fig. S-61 a) Crystal structure of *trans*-**2** (anisotropic displacement parameters are drawn at 50% probability level), b) hydrogen-bonded chain in the crystal structure of *trans*-**2** viewed along the b-axis, c) π-stacked chain in the crystal structure of *trans*-**2** viewed along the a-axis, d) 2D sheets in the crystal structure of *trans*-**2** formed by interlinked hydrogen bonded (colored in magenta) and π-stacked (colored in yellow) chains originating from the same molecule of *trans*-**2** (colored in red, non-NH hydrogen atoms are removed for clarity).

In the case of *cis*-**2**, the direct hydrogen bonding between the molecules is absent; instead, the calix[4]pyrrole macrocycle forms hydrogen bonds with the acetonitrile molecules of crystallization on both sides to form hydrogen bonded chains. The π-stacking of phthalimide fragments also takes place on each side of the molecule with centroid-centroid distances of 3.77 and 4.28 Å, resulting in combination with the hydrogen bonding in formation of 2D sheets, containing discrete π-stacked columns of four phthalimide units (Fig. S-62 b).

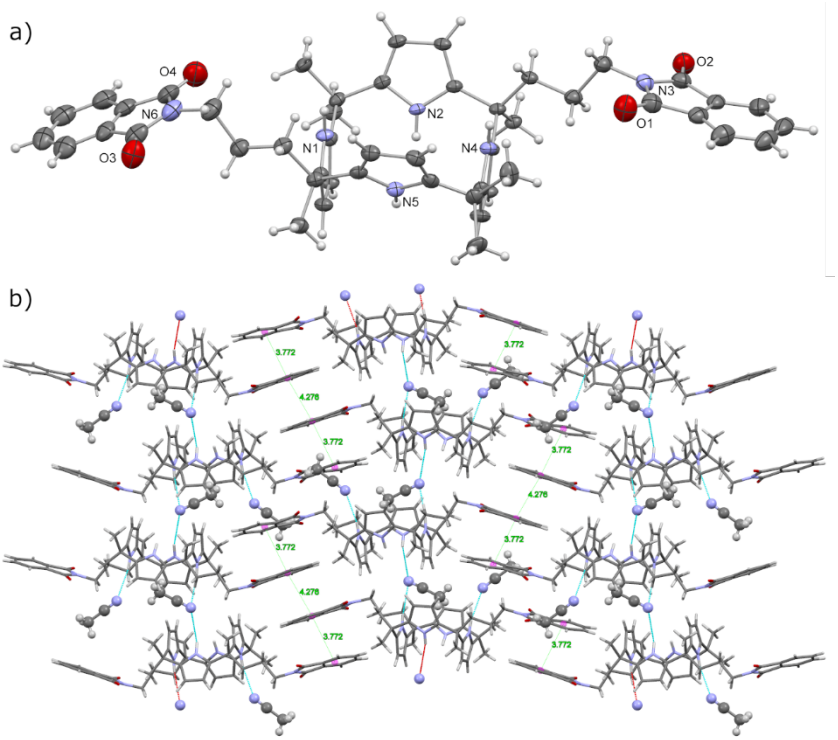



Fig. S-62 Crystal structure of *cis*-**2** (anisotropic displacement parameters are drawn at 50% probability level), b) 2D sheet in the crystal structure of *cis*-**2**, formed by π-stacking and hydrogen bonding (marked by green and turquoise lines accordingly), viewed along the a-axis (the acetonitrile molecules not participating in the hydrogen bond network are omitted for clarity).

## 9. DFT

The geometry optimizations were performed with Gaussian 09 program[13] using density functional theory (DFT) at B3LYP/6-311++G(d,p) level[14–19] with dispersion correction[20] in gas phase. Additionally, frequency calculations were performed to confirm that the optimized structures are at their minimum. The initial coordinates of the calix[4]pyrrole-Cl complexes were obtained from the crystal structure *cis*-**1** · TMACl or from a related crystal structure, and the structure of the host was modified accordingly with Maestro program (Maestro Version 12.6.144, Schrödinger, LLC, NY, 2020). Each structure was minimized after modifications using the OPLS3e force field incorporated in the Maestro interface before launching the DFT geometry optimization. Optimization of the free hosts *cis*-**1** and *cis*-**3** were performed with the neutral receptors (Fig. S-63). The atomic coordinates for the energy minimized structures are shown in Table S4-S8.

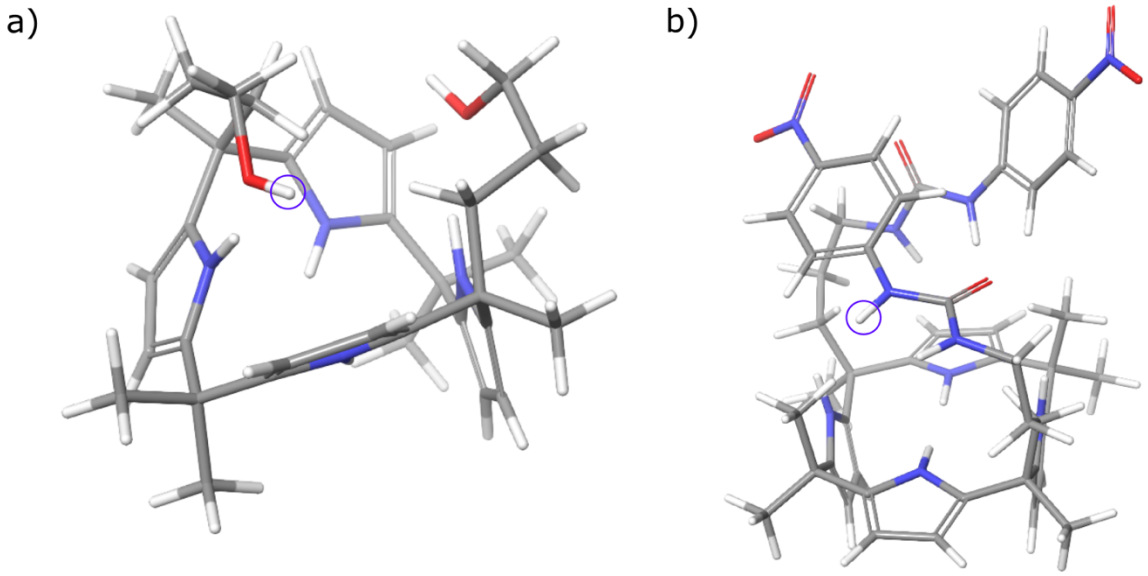



Fig. S-63 DFT optimized geometries for the free receptors a) *cis*-**1** and b) *cis*-**3** in gas phase. For $^{DT}CCS_{N2}$ calculations, the encircled acidic protons were removed from the list of coordinates.

Table S4. DFT coordinates of *cis*-**1** in gas phase.

| | | | |
|---|---|---|---|
| O | -2.535614 | 0.166287 | 2.125250 |
| H | -2.584805 | -0.771749 | 2.343999 |
| O | 2.535788 | -0.166496 | 2.124995 |
| N | -1.779862 | 1.317360 | -0.344435 |
| H | -1.937206 | 0.763954 | 0.496150 |
| N | 1.496781 | 1.604694 | -0.680060 |
| H | 0.758505 | 1.188751 | -1.226465 |
| N | 1.779809 | -1.317308 | -0.344741 |
| H | 1.937220 | -0.763973 | 0.495878 |
| N | -1.496846 | -1.604614 | -0.680068 |
| H | -0.758624 | -1.188604 | -1.226494 |
| C | -2.397686 | 1.045086 | -1.541912 |
| C | -2.092545 | 2.089544 | -2.397775 |
| H | -2.413085 | 2.184746 | -3.423420 |
| C | -1.281381 | 3.013935 | -1.678290 |

| | | | |
|---|---|---|---|
| H | -0.831261 | 3.912437 | -2.071771 |
| C | -1.100349 | 2.515164 | -0.399709 |
| C | -0.130825 | 2.953892 | 0.689529 |
| C | 1.283534 | 2.581126 | 0.259224 |
| C | 2.526969 | 2.914464 | 0.769823 |
| H | 2.722505 | 3.662757 | 1.523159 |
| C | 3.498835 | 2.098588 | 0.109478 |
| H | 4.562589 | 2.101732 | 0.286894 |
| C | 2.830916 | 1.282607 | -0.781818 |
| C | 3.294426 | 0.175187 | -1.708478 |
| C | 2.397536 | -1.044930 | -1.542245 |
| C | 2.092342 | -2.089324 | -2.398167 |
| H | 2.412803 | -2.184439 | -3.423846 |
| C | 1.281250 | -3.013785 | -1.678693 |
| H | 0.831114 | -3.912263 | -2.072209 |
| C | 1.100314 | -2.515120 | -0.400057 |
| C | 0.130891 | -2.953957 | 0.689227 |
| C | -1.283507 | -2.581139 | 0.259099 |
| C | -2.526894 | -2.914533 | 0.769781 |
| H | -2.722357 | -3.662903 | 1.523059 |
| C | -3.498824 | -2.098596 | 0.109609 |
| H | -4.562561 | -2.101762 | 0.287125 |
| C | -2.830993 | -1.282523 | -0.781668 |
| C | -3.294600 | -0.175010 | -1.708169 |
| C | -3.239922 | -0.662298 | -3.175547 |
| H | -2.223409 | -0.944888 | -3.458465 |
| H | -3.579130 | 0.120311 | -3.859346 |
| H | -3.887505 | -1.533123 | -3.300621 |
| C | -4.749668 | 0.209951 | -1.356025 |
| H | -5.420660 | -0.644371 | -1.484499 |
| H | -5.086456 | 1.014974 | -2.012195 |
| H | -4.818065 | 0.554123 | -0.321921 |
| C | -0.236364 | 4.473855 | 0.921329 |
| H | 0.494794 | 4.799023 | 1.666345 |
| H | -1.234857 | 4.739934 | 1.275327 |
| H | -0.043234 | 5.022520 | -0.001702 |
| C | -0.382576 | 2.188864 | 2.025785 |
| H | -0.189408 | 1.129822 | 1.834971 |
| H | 0.392519 | 2.508165 | 2.727970 |
| C | -1.770809 | 2.341165 | 2.684192 |
| H | -1.742993 | 3.085956 | 3.484432 |
| H | -2.509859 | 2.691369 | 1.957159 |
| C | 3.239585 | 0.662621 | -3.175802 |
| H | 3.578718 | -0.119919 | -3.859716 |
| H | 3.887153 | 1.533460 | -3.300861 |
| H | 2.223040 | 0.945237 | -3.458578 |
| C | 4.749534 | -0.209802 | -1.356530 |
| H | 4.818043 | -0.554079 | -0.322469 |
| H | 5.420507 | 0.644537 | -1.484987 |
| H | 5.086257 | -1.014755 | -2.012819 |
| C | 0.236443 | -4.473948 | 0.920849 |
| H | 0.043212 | -5.022511 | -0.002220 |
| H | -0.494639 | -4.799191 | 1.665907 |
| H | 1.234971 | -4.740072 | 1.274713 |
| C | 0.382778 | -2.189083 | 2.025544 |
| H | 0.189582 | -1.130019 | 1.834876 |

| | | | |
|---|---|---|---|
| H | -0.392239 | -2.508472 | 2.727775 |
| C | 1.771086 | -2.341449 | 2.683779 |
| H | 1.743364 | -3.086328 | 3.483941 |
| H | 2.510055 | -2.691569 | 1.956624 |
| C | 2.271712 | -1.014060 | 3.248678 |
| H | 1.513551 | -0.563581 | 3.903813 |
| H | 3.188577 | -1.159149 | 3.832562 |
| C | -2.271380 | 1.013716 | 3.248999 |
| H | -3.188167 | 1.158746 | 3.833020 |
| H | -1.513139 | 0.563149 | 3.903981 |
| H | 2.585045 | 0.771510 | 2.343859 |

Table S5. DFT coordinates of *cis*-**3** in gas phase.

| | | | |
|---|---|---|---|
| N | -2.009523 | 1.858958 | 2.046944 |
| H | -1.156136 | 2.216961 | 1.652692 |
| N | -3.692290 | 1.133343 | -0.878649 |
| H | -3.174585 | 0.585457 | -0.208895 |
| N | -2.678842 | -2.345564 | -0.860423 |
| H | -1.851027 | -2.339304 | -1.431666 |
| N | -1.322640 | -1.646173 | 2.218289 |
| H | -2.026864 | -1.157044 | 1.685378 |
| C | -2.067703 | 0.967116 | 3.098614 |
| C | -3.406430 | 0.797051 | 3.393874 |
| C | -4.159552 | 1.621413 | 2.511169 |
| C | -3.273481 | 2.286250 | 1.687295 |
| C | -3.520711 | 3.216414 | 0.506001 |
| C | -4.140439 | 2.410282 | -0.619868 |
| C | -5.084916 | 2.702556 | -1.580901 |
| C | -5.225446 | 1.550824 | -2.419441 |
| C | -4.363749 | 0.583503 | -1.948761 |
| C | -4.045444 | -0.826944 | -2.406019 |
| C | -3.864544 | -1.712463 | -1.182504 |
| C | -4.758847 | -2.015198 | -0.176495 |
| C | -4.100135 | -2.862233 | 0.755894 |
| C | -2.808330 | -3.067767 | 0.311834 |
| C | -1.659140 | -3.824116 | 0.960988 |
| C | -1.122249 | -3.008871 | 2.131441 |
| C | -0.354423 | -3.361098 | 3.227069 |
| C | -0.107943 | -2.180349 | 3.990511 |
| C | -0.740874 | -1.130496 | 3.356977 |
| C | -0.826207 | 0.345618 | 3.714574 |
| C | -4.461714 | 4.359803 | 0.930318 |
| C | -2.156727 | 3.788650 | 0.020649 |
| C | -5.193763 | -1.374882 | -3.278801 |
| H | -4.961326 | -2.389988 | -3.608426 |
| H | -5.340247 | -0.749291 | -4.163559 |
| H | -6.128410 | -1.401674 | -2.717271 |
| C | -2.750408 | -0.789372 | -3.250826 |
| C | -2.192690 | -5.180896 | 1.474941 |
| C | -0.526647 | -4.071662 | -0.090259 |
| C | -0.887906 | 0.501300 | 5.251212 |
| H | -1.760744 | -0.009900 | 5.659246 |
| H | -0.949293 | 1.558853 | 5.517327 |
| H | 0.004660 | 0.079363 | 5.719663 |
| H | -1.921249 | -0.377786 | -2.670291 |

| | | | |
|---|---|---|---|
| H | -2.904461 | -0.149777 | -4.122810 |
| H | -2.475403 | -1.787089 | -3.609404 |
| H | -2.576836 | -5.772238 | 0.640395 |
| H | -2.998535 | -5.031827 | 2.194446 |
| H | -3.994575 | 4.953278 | 1.719574 |
| H | -5.405584 | 3.965375 | 1.309106 |
| C | 0.447949 | 1.057117 | 3.201618 |
| H | 1.334875 | 0.593310 | 3.635462 |
| H | 0.530705 | 0.979795 | 2.113912 |
| H | 0.452487 | 2.117857 | 3.469543 |
| C | 0.698978 | -4.869451 | 0.414143 |
| H | -0.172381 | -3.099971 | -0.449583 |
| H | -0.974289 | -4.588586 | -0.945127 |
| C | 2.035636 | -4.156547 | 0.205210 |
| H | 0.755768 | -5.834855 | -0.094063 |
| H | 0.597251 | -5.097018 | 1.475686 |
| N | 2.017319 | -2.833349 | 0.830594 |
| H | 2.245988 | -4.026775 | -0.859001 |
| H | 2.851888 | -4.762912 | 0.611783 |
| C | 3.086430 | -2.001098 | 0.665628 |
| H | 1.384983 | -2.687883 | 1.609322 |
| N | 2.885856 | -0.722747 | 1.209149 |
| O | 4.097942 | -2.315188 | 0.060661 |
| H | 1.924345 | -0.465090 | 1.374319 |
| C | 5.519409 | 2.508249 | 0.954176 |
| C | 6.040947 | 1.222318 | 1.088512 |
| C | 5.181473 | 0.137810 | 1.170749 |
| C | 3.791588 | 0.338209 | 1.111679 |
| C | 3.287904 | 1.641388 | 0.961865 |
| C | 4.145336 | 2.725948 | 0.887517 |
| H | 7.112446 | 1.083914 | 1.131504 |
| H | 5.576179 | -0.862637 | 1.261761 |
| H | 2.225588 | 1.804845 | 0.838839 |
| H | 3.763302 | 3.728172 | 0.753295 |
| N | 6.433028 | 3.654282 | 0.866185 |
| O | 5.940389 | 4.774433 | 0.755620 |
| O | 7.639550 | 3.433065 | 0.908805 |
| H | -1.409060 | -5.753571 | 1.973273 |
| C | -2.204907 | 4.745375 | -1.173854 |
| H | -1.525645 | 2.941828 | -0.256694 |
| H | -1.661908 | 4.295282 | 0.857550 |
| C | -0.860483 | 4.782265 | -1.912736 |
| H | -2.456339 | 5.759892 | -0.849293 |
| H | -2.984150 | 4.432180 | -1.875718 |
| N | -0.565283 | 3.528983 | -2.607016 |
| H | -0.037402 | 4.967021 | -1.220844 |
| H | -0.854019 | 5.584633 | -2.655299 |
| C | 0.266904 | 2.567406 | -2.106964 |
| N | 0.320922 | 1.415648 | -2.896336 |
| H | -1.064292 | 3.350648 | -3.464743 |
| O | 0.901488 | 2.693495 | -1.067562 |
| H | -0.409742 | 1.290445 | -3.580480 |
| C | 3.102971 | -1.700946 | -2.851123 |
| C | 1.848731 | -1.897144 | -3.417564 |
| C | 0.938849 | -0.851076 | -3.413810 |
| C | 1.267139 | 0.381981 | -2.824788 |

| | | | |
|---|---|---|---|
| C | 2.533733 | 0.551239 | -2.243596 |
| C | 3.454004 | -0.486509 | -2.272255 |
| H | 1.603418 | -2.853363 | -3.859417 |
| H | -0.028910 | -0.986942 | -3.881387 |
| H | 2.792780 | 1.487173 | -1.774473 |
| H | 4.432048 | -0.375966 | -1.826354 |
| N | 4.076220 | -2.800856 | -2.876686 |
| O | 5.259483 | -2.519253 | -2.781281 |
| O | 3.632095 | -3.941288 | -3.006783 |
| H | -4.685447 | 5.019191 | 0.088809 |
| H | 0.455728 | -2.122726 | 4.908229 |
| H | -0.019438 | -4.354531 | 3.478650 |
| H | -3.801223 | 0.146636 | 4.158864 |
| H | -5.234538 | 1.702299 | 2.468031 |
| H | -5.772163 | -1.650189 | -0.113048 |
| H | -4.522282 | -3.263184 | 1.663717 |
| H | -5.625816 | 3.630967 | -1.676097 |
| H | -5.894097 | 1.451155 | -3.259838 |

Table S6. DFT coordinates of $Cl^{-}\subset$*cis*-**1** in gas phase.

| | | | |
|---|---|---|---|
| Cl | -0.000082 | -0.000132 | 2.067595 |
| O | -3.014913 | -0.804720 | 3.406974 |
| H | -2.167983 | -0.443106 | 3.102450 |
| O | 3.014643 | 0.804257 | 3.407344 |
| N | -2.186575 | -0.920149 | -0.367693 |
| H | -1.589124 | -0.692685 | 0.419072 |
| N | -0.900997 | 2.213918 | -0.357861 |
| H | -0.619370 | 1.588713 | 0.389574 |
| N | 2.186605 | 0.920200 | -0.367406 |
| H | 1.589095 | 0.692638 | 0.419286 |
| N | 0.901024 | -2.213868 | -0.358071 |
| H | 0.619338 | -1.588762 | 0.389425 |
| C | -2.235362 | -2.153243 | -0.982122 |
| C | -3.192063 | -2.065311 | -1.973761 |
| H | -3.480276 | -2.857172 | -2.646776 |
| C | -3.733951 | -0.746955 | -1.941821 |
| H | -4.508399 | -0.359005 | -2.584376 |
| C | -3.095764 | -0.052774 | -0.934359 |
| C | -3.295365 | 1.364775 | -0.421515 |
| C | -2.170874 | 2.274059 | -0.892958 |
| C | -2.150764 | 3.264083 | -1.854831 |
| H | -2.984209 | 3.568001 | -2.468080 |
| C | -0.833929 | 3.809979 | -1.891449 |
| H | -0.490050 | 4.604065 | -2.534979 |
| C | -0.074172 | 3.143476 | -0.951046 |
| C | 1.375603 | 3.323392 | -0.531094 |
| C | 2.235439 | 2.153372 | -0.981675 |
| C | 3.192219 | 2.065565 | -1.973250 |
| H | 3.480484 | 2.857511 | -2.646142 |
| C | 3.734104 | 0.747205 | -1.941434 |
| H | 4.508601 | 0.359334 | -2.583977 |
| C | 3.095837 | 0.052897 | -0.934110 |
| C | 3.295397 | -1.364717 | -0.421428 |

| | | | |
|---|---|---|---|
| C | 2.170944 | -2.273941 | -0.893074 |
| C | 2.150910 | -3.263845 | -1.855073 |
| H | 2.984404 | -3.567686 | -2.468294 |
| C | 0.834078 | -3.809737 | -1.891863 |
| H | 0.490251 | -4.603742 | -2.535521 |
| C | 0.074246 | -3.143352 | -0.951437 |
| C | -1.375561 | -3.323320 | -0.531621 |
| C | -1.921917 | -4.614574 | -1.169385 |
| H | -1.888769 | -4.569256 | -2.259933 |
| H | -2.959330 | -4.769897 | -0.865073 |
| H | -1.326832 | -5.471394 | -0.845322 |
| C | -1.462299 | -3.475647 | 1.009959 |
| H | -0.877919 | -4.343658 | 1.328794 |
| H | -2.502354 | -3.611479 | 1.317203 |
| H | -1.078632 | -2.603893 | 1.541800 |
| C | -4.632997 | 1.907233 | -0.959302 |
| H | -4.806974 | 2.915870 | -0.576831 |
| H | -5.457118 | 1.262304 | -0.650908 |
| H | -4.632379 | 1.952611 | -2.049911 |
| C | -3.328982 | 1.372010 | 1.137298 |
| H | -2.346898 | 1.079111 | 1.510606 |
| H | -3.468186 | 2.408218 | 1.466123 |
| C | -4.386079 | 0.471455 | 1.790074 |
| H | -5.371795 | 0.950470 | 1.747398 |
| H | -4.465072 | -0.475810 | 1.247836 |
| C | 1.922006 | 4.614726 | -1.168655 |
| H | 2.959395 | 4.770014 | -0.864244 |
| H | 1.326894 | 5.471504 | -0.844531 |
| H | 1.888941 | 4.569543 | -2.259211 |
| C | 1.462222 | 3.475524 | 1.010511 |
| H | 1.078511 | 2.603704 | 1.542213 |
| H | 0.877822 | 4.343498 | 1.329411 |
| H | 2.502254 | 3.611312 | 1.317853 |
| C | 4.633071 | -1.907108 | -0.959179 |
| H | 4.632540 | -1.952344 | -2.049795 |
| H | 4.807014 | -2.915796 | -0.576828 |
| H | 5.457170 | -1.262222 | -0.650637 |
| C | 3.328892 | -1.372148 | 1.137385 |
| H | 2.346779 | -1.079293 | 1.510653 |
| H | 3.468065 | -2.408398 | 1.466092 |
| C | 4.385938 | -0.471680 | 1.790363 |
| H | 5.371658 | -0.950685 | 1.747693 |
| H | 4.464966 | 0.475662 | 1.248265 |
| C | 4.056724 | -0.152418 | 3.252524 |
| H | 3.819360 | -1.080842 | 3.796075 |
| H | 4.930568 | 0.293217 | 3.737816 |
| C | -4.056976 | 0.151984 | 3.252213 |
| H | -4.930859 | -0.293714 | 3.737377 |
| H | -3.819646 | 1.080329 | 3.795914 |
| H | 2.167740 | 0.442687 | 3.102696 |

Table S7. DFT coordinates of $Cl^{-}$⊂*cis*-**3** in gas phase.

| | | | |
|---|---|---|---|
| N | -2.778340 | 1.441218 | 1.984810 |
| H | -2.022338 | 1.068612 | 1.427534 |
| N | -3.179606 | 1.898433 | -1.321604 |

| | | | |
|---|---|---|---|
| H | -2.467279 | 1.285626 | -0.949120 |
| N | -3.215407 | -1.437951 | -1.845236 |
| H | -2.351135 | -1.081107 | -1.461681 |
| N | -2.936095 | -1.886313 | 1.472193 |
| H | -2.309097 | -1.286790 | 0.954106 |
| C | -3.299691 | 0.820936 | 3.101980 |
| C | -4.283828 | 1.653922 | 3.592712 |
| C | -4.346300 | 2.802213 | 2.751011 |
| C | -3.399817 | 2.653998 | 1.758222 |
| C | -3.026789 | 3.563079 | 0.595488 |
| C | -3.622628 | 3.052267 | -0.706251 |
| C | -4.590978 | 3.591861 | -1.526029 |
| C | -4.730662 | 2.738224 | -2.659563 |
| C | -3.842470 | 1.692802 | -2.515492 |
| C | -3.528212 | 0.524454 | -3.436591 |
| C | -3.949741 | -0.803835 | -2.826988 |
| C | -5.029070 | -1.618232 | -3.100891 |
| H | -5.802615 | -1.420005 | -3.825190 |
| C | -4.934121 | -2.768340 | -2.265363 |
| H | -5.626804 | -3.594130 | -2.240192 |
| C | -3.798502 | -2.640535 | -1.492581 |
| C | -3.218166 | -3.555829 | -0.423562 |
| C | -3.525110 | -3.028483 | 0.968517 |
| C | -4.304439 | -3.550598 | 1.979027 |
| C | -4.176439 | -2.699011 | 3.115838 |
| C | -3.318132 | -1.672548 | 2.781593 |
| C | -2.782077 | -0.515670 | 3.608590 |
| C | -3.577020 | 4.974184 | 0.877000 |
| C | -1.470418 | 3.634900 | 0.486997 |
| C | -4.284854 | 0.721463 | -4.764315 |
| H | -4.063517 | -0.103672 | -5.444276 |
| H | -3.977558 | 1.657859 | -5.234910 |
| H | -5.364665 | 0.756741 | -4.608861 |
| C | -2.009429 | 0.507261 | -3.754527 |
| C | -3.843696 | -4.955179 | -0.577848 |
| C | -1.672678 | -3.664916 | -0.620909 |
| C | -3.230195 | -0.698568 | 5.071286 |
| H | -4.318208 | -0.709898 | 5.159002 |
| H | -2.846403 | 0.120504 | 5.682840 |
| H | -2.847170 | -1.642301 | 5.465687 |
| Cl | -0.582059 | -0.010064 | -0.203212 |
| H | -1.396931 | 0.385259 | -2.859747 |
| H | -1.718256 | 1.449422 | -4.226112 |
| H | -1.777381 | -0.316686 | -4.435083 |
| H | -3.621836 | -5.353720 | -1.570055 |
| H | -4.927766 | -4.918497 | -0.458553 |
| H | -3.148601 | 5.362832 | 1.803288 |
| H | -4.662936 | 4.959680 | 0.982927 |
| C | -1.230703 | -0.533373 | 3.581022 |
| H | -0.861183 | -1.483403 | 3.974727 |
| H | -0.832945 | -0.422853 | 2.571427 |
| H | -0.833160 | 0.283230 | 4.189704 |
| C | -0.923589 | -4.474003 | 0.450925 |
| H | -1.260982 | -2.655149 | -0.655738 |
| H | -1.483163 | -4.090062 | -1.612858 |
| C | 0.589382 | -4.233325 | 0.438631 |

| | | | |
|---|---|---|---|
| H | -1.098282 | -5.543755 | 0.303023 |
| H | -1.311763 | -4.222768 | 1.442489 |
| N | 0.892165 | -2.855515 | 0.808202 |
| H | 1.005846 | -4.464472 | -0.552055 |
| H | 1.090933 | -4.888943 | 1.152486 |
| C | 2.142865 | -2.461791 | 1.187527 |
| H | 0.244247 | -2.136634 | 0.513085 |
| N | 2.217657 | -1.074822 | 1.384763 |
| O | 3.079476 | -3.228373 | 1.354985 |
| H | 1.366244 | -0.561046 | 1.184300 |
| C | 5.521841 | 1.445137 | 1.707395 |
| C | 5.731189 | 0.066673 | 1.733603 |
| C | 4.655293 | -0.801529 | 1.650517 |
| C | 3.350666 | -0.287614 | 1.526393 |
| C | 3.161427 | 1.110598 | 1.512173 |
| C | 4.235321 | 1.973924 | 1.594996 |
| H | 6.740210 | -0.315074 | 1.806926 |
| H | 4.805142 | -1.869343 | 1.655678 |
| H | 2.159695 | 1.510549 | 1.399562 |
| H | 4.096103 | 3.044495 | 1.547910 |
| N | 6.664098 | 2.350765 | 1.789546 |
| O | 6.444774 | 3.561594 | 1.819946 |
| O | 7.792924 | 1.860990 | 1.824309 |
| H | -3.449148 | -5.639033 | 0.174952 |
| C | -0.919112 | 4.422168 | -0.711026 |
| H | -1.079100 | 2.617352 | 0.446384 |
| H | -1.084765 | 4.059765 | 1.420568 |
| C | 0.587915 | 4.231635 | -0.905263 |
| H | -1.108701 | 5.491201 | -0.579890 |
| H | -1.439495 | 4.119964 | -1.625094 |
| N | 0.887735 | 2.848748 | -1.266009 |
| H | 1.131006 | 4.508502 | 0.008066 |
| H | 0.957417 | 4.884523 | -1.699575 |
| C | 2.167082 | 2.442750 | -1.516899 |
| N | 2.259677 | 1.054276 | -1.687341 |
| H | 0.205885 | 2.140492 | -1.027793 |
| O | 3.115306 | 3.209059 | -1.599815 |
| H | 1.399904 | 0.538453 | -1.531749 |
| C | 5.587221 | -1.453198 | -1.815512 |
| C | 4.298332 | -1.986746 | -1.777609 |
| C | 3.218463 | -1.127069 | -1.758455 |
| C | 3.402716 | 0.271840 | -1.761993 |
| C | 4.710700 | 0.790411 | -1.811620 |
| C | 5.792630 | -0.074129 | -1.831620 |
| H | 4.160688 | -3.057794 | -1.737275 |
| H | 2.213366 | -1.530603 | -1.704454 |
| H | 4.857350 | 1.858601 | -1.807662 |
| H | 6.802798 | 0.311271 | -1.846647 |
| N | 6.735662 | -2.354573 | -1.829530 |
| O | 7.862561 | -1.860803 | -1.789919 |
| O | 6.523045 | -3.565874 | -1.879984 |
| H | -3.331695 | 5.654408 | 0.060155 |
| H | -5.012834 | 3.641457 | 2.869310 |
| H | -4.891514 | 1.470296 | 4.464350 |
| H | -4.656809 | -2.835567 | 4.071346 |
| H | -4.894954 | -4.450828 | 1.921229 |

| | | | |
|---|---|---|---|
| H | -5.405294 | 2.885487 | -3.487427 |
| H | -5.138151 | 4.502961 | -1.344423 |

Table S8. DFT coordinates of $Cl^{-}\subset$*trans*-**3** in gas phase.

| | | | |
|---|---|---|---|
| Cl | 3.714122 | -0.821382 | 0.916175 |
| N | 5.629609 | -0.152670 | -1.732652 |
| H | 5.287610 | -0.598648 | -0.886658 |
| N | 1.809517 | -1.174328 | -1.898857 |
| H | 2.472154 | -0.937283 | -1.163450 |
| N | 2.537566 | -3.833781 | 0.013023 |
| H | 2.831908 | -2.896785 | 0.275754 |
| N | 1.171109 | -2.186277 | 2.600325 |
| H | 2.008004 | -1.710973 | 2.265996 |
| N | 0.344248 | 0.266613 | 0.616095 |
| H | 0.063806 | -0.671484 | 0.371306 |
| C | 0.728469 | -0.383977 | -2.236310 |
| C | -0.005094 | -1.083957 | -3.173773 |
| H | -0.900461 | -0.736674 | -3.664831 |
| C | 0.661555 | -2.319012 | -3.412462 |
| H | 0.347076 | -3.092675 | -4.094429 |
| C | 1.785428 | -2.356207 | -2.612063 |
| C | 2.843098 | -3.440087 | -2.469302 |
| C | 2.520996 | -4.322476 | -1.275889 |
| C | 2.149279 | -5.649409 | -1.197976 |
| H | 2.031456 | -6.324908 | -2.030425 |
| C | 1.939896 | -5.961463 | 0.178244 |
| H | 1.636652 | -6.916420 | 0.577049 |
| C | 2.188676 | -4.818077 | 0.910609 |
| C | 2.118018 | -4.550472 | 2.402921 |
| C | 1.011476 | -3.552120 | 2.709992 |
| C | -0.293001 | -3.772616 | 3.107399 |
| H | -0.748178 | -4.735199 | 3.276142 |
| C | -0.927840 | -2.506922 | 3.245142 |
| H | -1.943278 | -2.337979 | 3.567812 |
| C | -0.000144 | -1.532880 | 2.928851 |
| C | -0.045973 | -0.027697 | 3.105233 |
| C | 0.509697 | 0.716267 | 1.908989 |
| C | 1.059010 | 1.979317 | 1.824785 |
| H | 1.308361 | 2.617402 | 2.657824 |
| C | 1.238841 | 2.285484 | 0.446320 |
| H | 1.655433 | 3.194093 | 0.044894 |
| C | 0.796268 | 1.204883 | -0.286522 |
| C | 0.613687 | 1.054481 | -1.781433 |
| C | -0.787635 | 1.600005 | -2.154944 |
| H | -1.571611 | 1.008460 | -1.673795 |
| H | -0.946493 | 1.571871 | -3.236728 |
| H | -0.876373 | 2.634535 | -1.817457 |
| C | 1.683329 | 1.896398 | -2.521572 |
| H | 1.599332 | 2.955496 | -2.264448 |
| H | 1.552608 | 1.791280 | -3.600861 |
| H | 2.689017 | 1.566190 | -2.261709 |
| C | 2.852493 | -4.302519 | -3.745625 |
| H | 3.634810 | -5.062267 | -3.676110 |
| H | 3.037019 | -3.682720 | -4.624066 |
| H | 1.898323 | -4.812634 | -3.887377 |

| | | | |
|---|---|---|---|
| C | 4.253600 | -2.812759 | -2.261993 |
| H | 4.261290 | -2.316096 | -1.290709 |
| H | 4.972828 | -3.635226 | -2.176197 |
| C | 4.721127 | -1.822641 | -3.338691 |
| H | 4.993478 | -2.356301 | -4.255796 |
| H | 3.911469 | -1.134779 | -3.598467 |
| C | 1.813583 | -5.871695 | 3.135684 |
| H | 1.746559 | -5.694358 | 4.211127 |
| H | 2.610539 | -6.594626 | 2.946471 |
| H | 0.872248 | -6.311477 | 2.801239 |
| C | 3.482647 | -4.022900 | 2.914710 |
| H | 3.786293 | -3.098012 | 2.422849 |
| H | 4.257218 | -4.770188 | 2.722029 |
| H | 3.433324 | -3.835249 | 3.991444 |
| C | -1.514695 | 0.441352 | 3.343591 |
| C | 0.779275 | 0.332699 | 4.366447 |
| H | 1.822114 | 0.038620 | 4.237805 |
| H | 0.747468 | 1.407507 | 4.564613 |
| C | 5.932805 | -0.997068 | -2.879404 |
| H | 6.276686 | -0.340395 | -3.678869 |
| H | 6.762483 | -1.663478 | -2.614652 |
| C | 5.471682 | 1.199044 | -1.835468 |
| N | 4.926823 | 1.747640 | -0.667061 |
| O | 5.778439 | 1.859124 | -2.820896 |
| H | 4.559557 | 1.075250 | 0.011195 |
| C | 4.469067 | 5.709363 | 0.545734 |
| C | 4.143630 | 4.654885 | 1.405012 |
| C | 4.308480 | 3.355572 | 0.973666 |
| C | 4.800065 | 3.077006 | -0.322715 |
| C | 5.121080 | 4.153474 | -1.176634 |
| C | 4.955233 | 5.456594 | -0.738060 |
| H | 3.762628 | 4.869580 | 2.393794 |
| H | 4.037512 | 2.529854 | 1.620746 |
| H | 5.487504 | 3.946472 | -2.169647 |
| H | 5.195565 | 6.288729 | -1.385546 |
| N | 4.297233 | 7.082850 | 0.995642 |
| O | 4.585975 | 7.994383 | 0.217273 |
| O | 3.869088 | 7.274792 | 2.135728 |
| C | -2.425880 | 0.338304 | 2.118111 |
| H | -1.473328 | 1.486490 | 3.666657 |
| H | -1.936667 | -0.130960 | 4.177440 |
| C | -3.873619 | 0.701268 | 2.431222 |
| H | -2.389438 | -0.674569 | 1.707006 |
| H | -2.045975 | 1.011832 | 1.342489 |
| N | -4.664265 | 0.663956 | 1.199580 |
| H | -3.934554 | 1.696914 | 2.887184 |
| H | -4.317260 | -0.003494 | 3.137623 |
| C | -6.026274 | 0.658068 | 1.216485 |
| H | -4.167718 | 0.834812 | 0.338115 |
| N | -6.591624 | 0.643322 | -0.073496 |
| O | -6.690909 | 0.647933 | 2.238600 |
| H | -5.950099 | 0.529153 | -0.844159 |
| C | -10.579681 | 0.740639 | -1.308471 |
| C | -9.552434 | 0.611001 | -2.242943 |
| C | -8.243348 | 0.578529 | -1.801969 |
| C | -7.935131 | 0.673617 | -0.428515 |

| | | | |
|---|---|---|---|
| C | -8.986932 | 0.803568 | 0.498944 |
| C | -10.298862 | 0.835906 | 0.053308 |
| H | -9.790542 | 0.537326 | -3.294914 |
| H | -7.441447 | 0.477653 | -2.526163 |
| H | -8.761060 | 0.869464 | 1.551100 |
| H | -11.114103 | 0.934251 | 0.756915 |
| N | -11.968752 | 0.774907 | -1.767422 |
| O | -12.854210 | 0.890450 | -0.922933 |
| O | -12.179727 | 0.686779 | -2.975919 |
| H | 0.372996 | -0.191818 | 5.234790 |

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