

**Dinuclear Complexes of a Pseudocalixarene Macrocyclic: Structural
Consequences of Intramolecular Hydrogen Bonding.**

Julia Barreira Fontecha, Sandrine Goetz and Vickie McKee*
Chemistry Department, Loughborough University, Loughborough LE11 3TU

Supplementary Data

Synthetic details (4 pages)

Superimposed structures (3 Figures)

Details of nmr assignments for complex 2

PDB files suitable for CHIME for each structure (separate files)

Synthesis

2,2'-dihydroxy-5,5'-di-*tert*-butyl-3,3'-methanediyl dibenzaldehyde (dhtmb). The precursor 2,2'-dihydroxy-5,5'-di-*tert*-butyl-3,3'-methanediyl dibenzyl alcohol was prepared from 4-*tert*-butylphenol as a white crystalline solid following the literature procedure¹⁹ with some minor modifications. The alcohol groups were oxidized to aldehyde by MnO₂ oxidation after the phenol groups had been protected using allyl bromide. The allyl groups were then removed using 10% Pd on charcoal to yield 2,2'-dihydroxy-5,5'-di-*tert*-butyl-3,3'-methanediyl dibenzaldehyde (dhtmb) in 40% yield for the three step process^{14, 20}. Found: C 74.51, H 7.86% Calc (for C₂₃H₂₈O₄): C 74.97, H 7.66%. IR (KBr, cm⁻¹): 1658($\nu_{C=O}$), 1270(ν_{Ar-OH}), 1216(s). ¹H NMR (CDCl₃, 400 MHz) ppm: 11.19 [s, 2H, Ar-OH], 9.86 [s, 2H, CHO], 7.64 [d, 2H, ArH], 7.87 [d, 2H, ArH], 4.03 [s, 2H, Ar-CH₂-Ar], 1.29 [s, 18H, C(CH₃)₃].

[Cu₂(H₄L)Cl]Cl·2MeOH (1): Anhydrous CuCl₂ (0.073 g 0.543 mmol) was dissolved in 40ml of hot dry ethanol and added to dhtmb (0.20 g 0.543 mmol) in 35 ml of hot dry ethanol. After 10 min. reflux a solution of 1,3-diaminopropan-2-ol (0.052 g, 0.58 mmol) in 20 ml of dry methanol was added. The green solution was refluxed for 2 h. The solution was cooled, filtered and the volume reduced, giving the product in 36% yield (0.12 g). Found: C 58.43, H 6.56, N 5.08%. Calc. for C₅₄H₇₄Cl₂Cu₂N₄O₈ (1): C 58.68, H 6.75, N 5.07%. IR (KBr, cm⁻¹): 3421(s,b); 2954(s); 1626(s, $\nu_{C=N}$); 1560(w, ν_{C-O}); 1474(m); 1363(m); 1221(m).

Emerald green crystals of the solvate [Cu₂(H₄L)Cl]Cl·1.6Et₂O·EtOH (**1a**) were obtained by diethylether diffusion into the filtrate.

[Zn₂(H₄L)Cl]Cl·H₂O (2): ZnCl₂ (0.074g, 0.543 mmol) and dhtmb (0.2 g, 0.543 mmol) were dissolved in hot dry ethanol (80 mL) and refluxed for 15 min before adding a solution of 1,3-diaminopropan-2-ol (0.052g, 0.58 mmol) in 10 mL of methanol. The yellow solution was refluxed for 2h, concentrated under vacuum and allowed to evaporate slowly. The yellow solid which precipitated was filtered off (yield 0.24g 78%). Found: C 58.76, H 6.52, N 5.26%. Calc. for C₅₂H₆₈Cl₂N₄O₇Zn₂ (2): C 58.76, H 6.45, N 5.27%. IR (KBr, cm⁻¹): 3422(s,b); 2963(s); 1638(s, $\nu_{C=N}$); 1553(w, ν_{C-O}); 1479(m); 1364(m); 1220(m). ¹H NMR (CDCl₃, 400 MHz) ppm: 8.10 [s, 4H, N=CH], 7.37 [d, 4H, ArH], 7.05 [d, 4H, ArH], 4.75 [d, 2H, Ar-CH₂-Ar], 4.51 [d, 4H, N-CH₂], 4.25 [s(br), 2H, CHOH], 3.75 [dd, 4H, N-CH₂], 3.55 [d, 2H, N-CH₂], 1.28 [s, 36H, C(CH₃)₃]. ¹³C NMR (CDCl₃, 400 MHz) ppm: 171.4 [C=N], 157.1 [Ar-

OH], 141.6 [Ar-^tBu] 132.3 [C(Ar)H], 132.1 [Ar-C=N], 129.7 [C(Ar)H], 119.2 [Ar-CH₂-Ar], 68.2 [N-CH₂], 67.9 [CH(OH)], 33.9 [Ar-CH₂-Ar], 31.3 [C(CH₃)₃], 31.0 [C(CH₃)₃].

The complex was crystallised from ethanol solution by slow diffusion of diethylether, yielding pale yellow crystals of [Zn₂(H₄L)Cl]Cl·Et₂O·0.5EtOH·0.55H₂O (**2a**) after a few days.

[Ni₂(H₄L)Cl]Cl·4H₂O (3) NiCl₂·6H₂O (0.13 g, 0.543 mmol) and dhtmb (0.2 g, 0.543 mmol) were dissolved in hot dry ethanol (100 mL) and refluxed for 15 min before adding a solution of 1,3-diaminopropan-2-ol (0.052 g, 0.58 mmol) in 10 mL of methanol dropwise. The pale green solution was refluxed for 2h, concentrated under vacuum and allowed to evaporate slowly. The green solid which precipitated was filtered off, washed and dried in air. (Yield 0.07 g 22%).

Found: C 56.57, H 6.50, N 4.70%. Calc. for C₅₂H₇₄Cl₂N₄O₁₀Ni₂ (**3**): C 56.60, H 6.76, N 5.08%. IR (KBr, cm⁻¹): 3383(s,b); 2956(s); 1634(s, ν_{C=N}); 1551(w, ν_{C-O}); 1476(m); 1364(m); 1223(m).

[Co₂(H₄L)(H₂O)₃](ClO₄)₂·2H₂O (4): Co(ClO₄)₂·6H₂O (0.40 g, 1.08 mmol) was dissolved in dry methanol (20 mL) and added to a hot solution of dhtmb (0.20 g, 0.543 mmol) in dry ethanol (60 mL). Nitrogen was bubbled through the mixture, which was refluxed for *ca.* 30 min. A solution containing 0.052 g (0.58 mmol) of 1,3-diaminopropan-2-ol in dry degassed methanol (10 mL) was added drop-wise to the reaction mixture. The solution turned slightly darker yellow/orange. The solution was left under reflux under nitrogen for 24 h. The resulting yellow/orange solution was concentrated *in vacuo* to *ca.* 5 mL and degassed diethylether (15 mL) added. A small amount of starting material was isolated by a quick filtration in air. The compound is not very air sensitive but the filtrate was degassed all the same, concentrated to 5 mL and degassed diethylether (15 mL) added. The pale yellow/orange solid was then quickly filtered in air and dried *in vacuo* (Yield 0.15 g, 45%). Found: C 50.01, H 5.63, N 4.29%; Calc. for C₅₂H₇₆Cl₂Co₂N₄O₁₉ (**4**): C 49.96, H 6.13, N 4.48%. IR (KBr, cm⁻¹): 3423(s,b); 2958(s); 1630(s, ν_{C=N}); 1560(w, ν_{C-O}); 1476(m); 1436(m); 1365(m); 1223(m); 1134(s, ν₃(ClO₄⁻)); 1117(s, ν₃(ClO₄⁻)); 1088(s, ν₃(ClO₄⁻)); 626(m, ν₄(ClO₄⁻))

Yellow crystals of [Co₂(H₄L)H₂O(EtOH)₂](ClO₄)₂·4EtOH (**4a**) were isolated by slow evaporation of an ethanol solution of the compound. As the product is air sensitive in solution over a period of time the complex was partially oxidised and found to be a mixture of

yellow crystals and brown powder, presumed to be a dicobalt(III) complex. Attempts to separate the two compounds were unsuccessful.

[Ni₂(H₄L)(H₂O)](ClO₄)₂·3H₂O (5): Ni(ClO₄)₂·6H₂O (0.20 g, 0.54 mmol) and dhtmb (0.20 g, 0.54 mmol) were dissolved in dry ethanol (80 mL) and refluxed for 30 min. A solution of 1,3-diaminopropan-2-ol (0.054 g, 0.60 mmol) in 10 mL of dry ethanol was then added drop-wise to the refluxing solution. The green solution reaction mixture refluxed for 5 h, cooled, filtered, and concentrated under vacuum. Pale green crystals of [Ni₂(H₄L)H₂O(EtOH)₂](ClO₄)₂·4EtOH (**5a**) suitable for X-ray crystallography separated after a few hours. The bulk of the material was filtered off, washed with diethylether and dried *in vacuo*. The colour changed from green to orange under vacuum but picked up water rapidly on exposure to the atmosphere (Yield 0.23 g, 47%).

Found: C 51.09, H 6.39, N 4.26%; Calc. for C₅₂H₇₂Cl₂N₄Ni₂O₁₇ (**5**): C 50.71, H 6.06, N 4.55%. IR (KBr, cm⁻¹): 3421(s,b); 2959(s); 1635(s, ν_{C=N}); 1561(w, ν_{C-O}); 1476(m); 1439(m); 1365(m); 1226(m); 1107(s, ν₃(ClO₄⁻)); 624(m, ν₄(ClO₄⁻)).

[Ni₂(H₄L)(NO₃)(H₂O)₂]NO₃·H₂O (6): Ni(NO₃)₂·6H₂O (0.16 g, 0.54 mmol) and dhtmb (0.20 g, 0.54 mmol) were dissolved in hot dry ethanol (75 mL). The solution was refluxed for 10-15 min. after which time a solution of 1,3-diaminopropan-2-ol (0.058 g) in 10 mL of dry methanol was added drop-wise to the refluxing solution. The solution turned slightly darker green. The reaction mixture was left under reflux for 6-7 h, cooled, filtered, and evaporated to dryness. The residue was washed with dichloromethane and the pale yellow/green powder was filtered and washed with water (Yield 0.16 g 52%). Found: C 55.10, H 6.20, N 7.12%; Calc. for C₅₂H₇₆N₆Ni₂O₁₅ (**6**): C 54.86, H 6.37, N 7.38. IR (KBr, cm⁻¹): 3418(m,s); 2958(s); 1634(s, ν_{C=N}); 1560(w, ν_{C-O}); 1475(m); 1384(s, ν₃(NO₃⁻)); 1223(m).

Green crystals of [Ni₂(H₄L)(NO₃)(dmf)₂]NO₃·2dmf·H₂O (**6a**) were obtained by slow evaporation of a dmf solution of Ni₂(H₄L)(NO₃)₂(H₂O)₃: dmf molecules replaced the coordinated water molecules.

[Zn₂(H₄L)(NO₃)(H₂O)₂]NO₃·3H₂O (7): Zn(NO₃)₂·6H₂O (0.162g, 0.543 mmol) and dhtmb (0.2g, 0.543 mmol) were dissolved in dry ethanol (90 mL) and refluxed for 15 min. A solution of 1,3-diaminopropan-2-ol (0.052 g, 0.58 mmol) in 10 mL of methanol was added drop-wise to the refluxing mixture. The yellow solution was refluxed for 2.5 h, and concentrated under

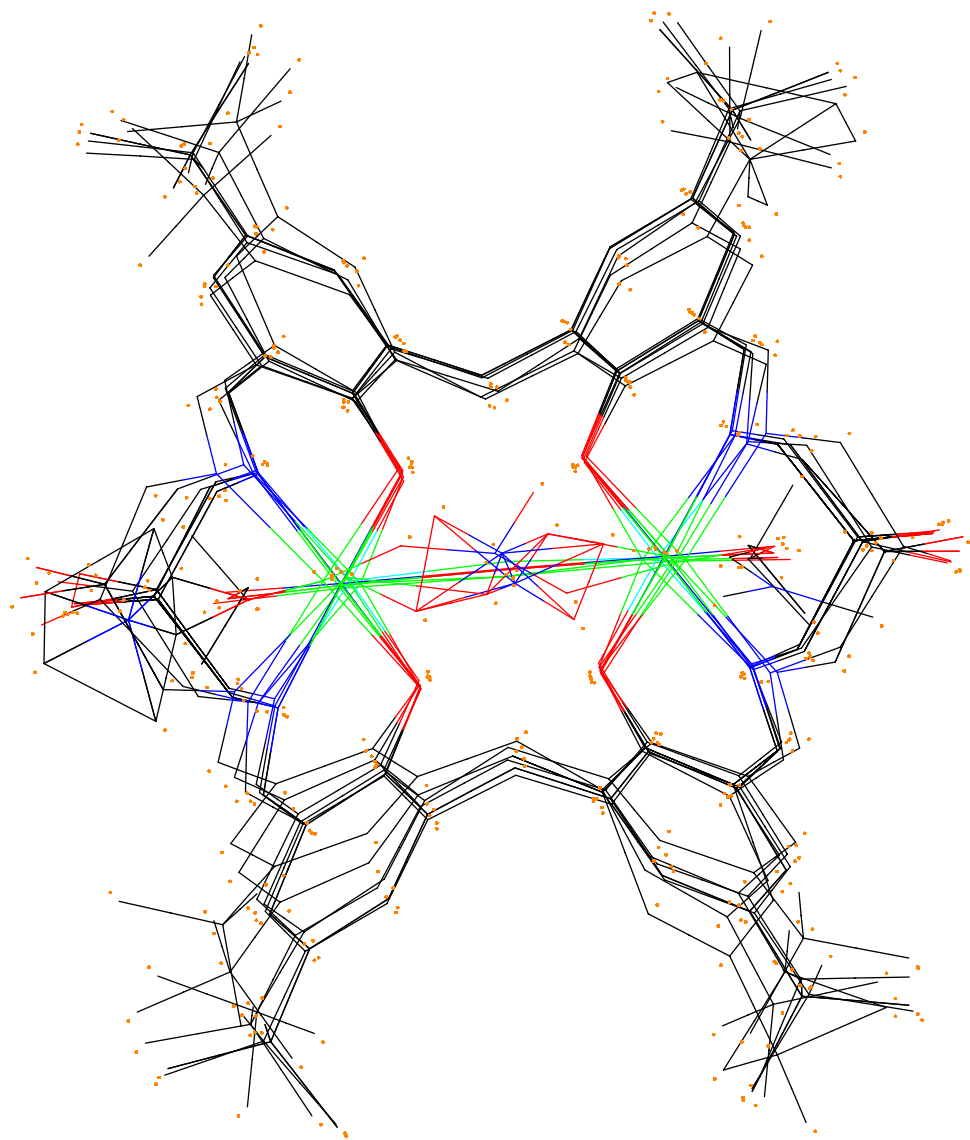
vacuum and allowed to crystallise in a closed container; complex **7** was isolated after two days (Yield 0.18 g, 24%). Found: C 54.01, H 6.19, N 7.87%; Calc. for $C_{52}H_{72}N_6Zn_2O_{15}$ (**7**): C 54.21, H 6.30, N 7.29%. IR (KBr, cm^{-1}): 3426(m,s); 2957(s); 1637(s, $\nu_{C=N}$); 1559(w, ν_{C-O}); 1475(m); 1384(s, $\nu_3(NO_3^-)$); 1221(m).

Pale yellow crystals of $[Zn_2(H_4L)(NO_3)(EtOH)]NO_3$ (**7a**) suitable for X-ray crystallography were obtained after a week.

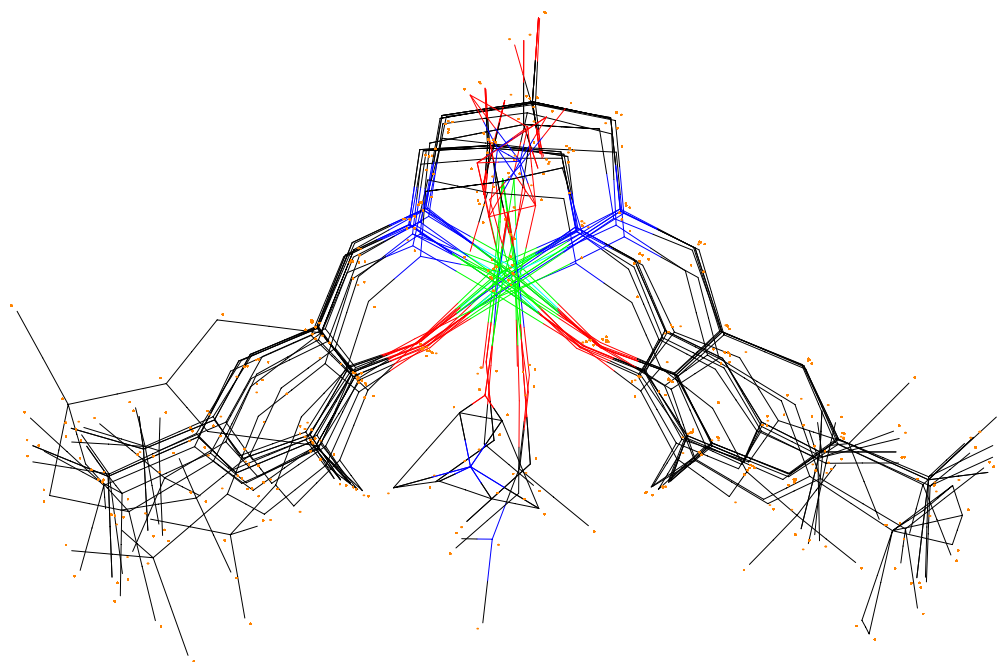
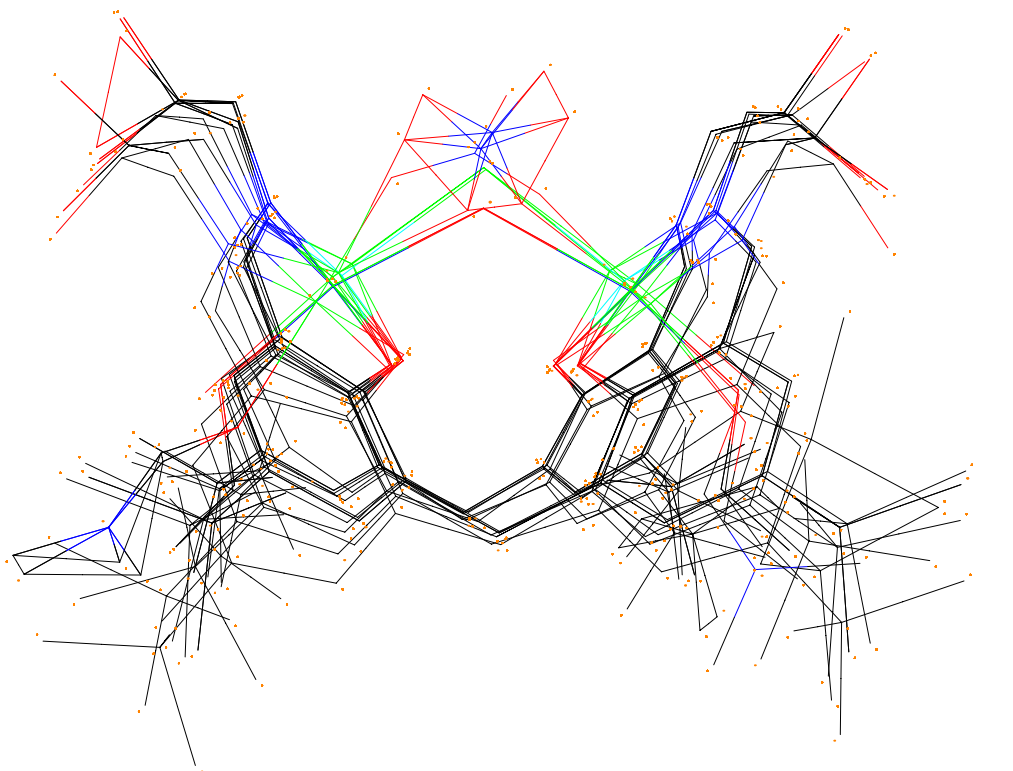
$[Mn_2(H_2L)(Cl)_2(EtOH)_2] \cdot 6H_2O$ (8**)**: $MnCl_2 \cdot 4H_2O$ (0.107 g, 0.543 mmol) and dhtmb (0.2 g, 0.543 mmol) were dissolved in 100 mL of hot dry ethanol and the solution refluxed for 10-15 min. before 1,3-diaminopropan-2-ol (0.052g, 0.58 mmol) in 10 mL of dry ethanol was added drop-wise. Reflux was continued for 2 h during which the colour changed from yellow to dark brown, then cooled. The orange solid product precipitated when the volume of the solution was reduced. (Yield 0.172 g, 52%). Found: C 54.99, H 7.39, N 4.94%; Calc. for $C_{56}H_{88}Cl_2Mn_2N_4O_{14}$ (**8**): C 55.03, H 7.26, N 4.59%. IR (KBr, cm^{-1}): 3422 (b, s); 2958 (m); 1618 (s, $\nu_{C=N}$); 1550 (m, ν_{C-O}); 1439(m); 1363(w); 1309 (w); 1267(m).

Dark brown crystals of $[Mn_2(H_2L)(Cl)_2(dmf)(dmsO)] \cdot 1.5dmf \cdot 0.3Et_2O$ (**8a**) were obtained by slow diffusion of diethylether into a solution of **8** in dmf/dmsO.

The following 3 figures show the cores of structures 1,2,4,5,6 and 7 superimposed by fitting the phenolic oxygen atoms.



Supplementary Material for Dalton Transactions



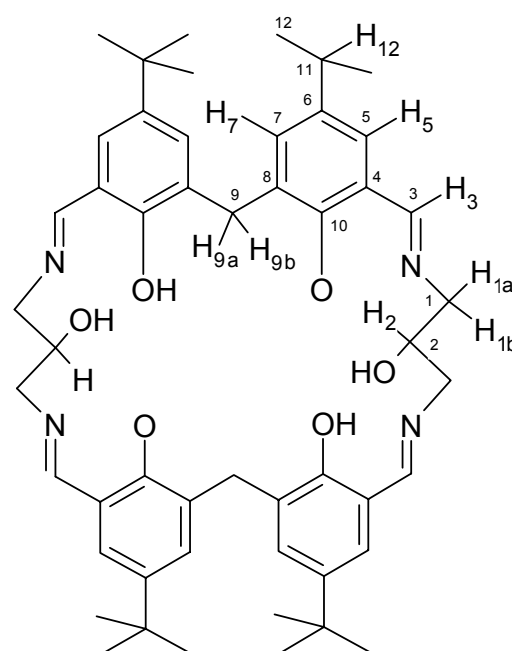
NMR spectroscopy studies of the complex [Zn₂(H₄L1)Cl]·Cl·H₂O (JBZn3)

¹H NMR (CDCl₃, 400 MHz): δ 1.28 (s, 36, C(CH₃)₃); 3.58 (d, 2, Ar-CH_aH_b-Ar); 3.75 (dd, 4, CH_aH_b); 4.24 (s, 2, CHOH), 4.56 (d, 4, CH_aH_b); 4.80 (d, 2, Ar-CH_aH_b-Ar); 7.05 (d, 4, Ar-H); 7.38 (d, 4, Ar-H); 8.09 (s, 4, CHN).

¹³C NMR (CDCl₃, 400 MHz): δ 30.97 (C(CH₃)₃); 31.27 (C(CH₃)₃); 33.88 (Ar-CH₂-Ar); 67.95 (CHOH), 68.17 (CH₂); 119.23 (Ar); 129.73 (Ar); 132.11 (Ar); 132.30 (Ar); 141.62 (Ar); 157.14 (Ar); 171.37 (CHN).

H	δ	analysis
H _{1a}	4.56	¹ H NMR, DQF-COSY
H _{1b}	3.75	¹ H NMR, DQF-COSY
H ₂	4.24	¹ H NMR, DQF-COSY
H ₃	8.09	¹ H NMR, DQF-COSY
H ₅	7.05	¹ H NMR, DQF-COSY, nOe
H ₇	7.38	¹ H NMR, DQF-COSY, nOe
H _{9a}	4.80	¹ H NMR, DQF-COSY
H _{9b}	3.57	¹ H NMR, DQF-COSY
H ₁₂	1.28	¹ H NMR, DQF-COSY

C	δ	Analysis
C ₁	67.95	¹³ C NMR, DEPT, DQF-COSY
C ₂	68.17	¹³ C NMR, DEPT, DQF-COSY
C ₃	171.37	¹³ C NMR, DEPT, DQF-COSY
C ₄	132.11	¹³ C NMR, DEPT, DQF-COSY
C ₅	129.73	¹³ C NMR, DEPT, DQF-COSY
C ₆	141.62	¹³ C NMR, DEPT, DQF-COSY, HMBC
C ₇	132.30	¹³ C NMR, DEPT, DQF-COSY
C ₈	119.23	¹³ C NMR, DEPT, DQF-COSY
C ₉	33.88	¹³ C NMR, DEPT, DQF-COSY
C ₁₀	157.14	¹³ C NMR, DEPT, DQF-COSY, HMBC
C ₁₁	30.97	¹³ C NMR, DEPT, DQF-COSY
C ₁₂	31.27	¹³ C NMR, DEPT, DQF-COSY



¹H NMR: proton NMR spectrum

¹³C NMR: carbon NMR spectrum

DEPT: Distortionless Enhancement by Polarization Transfer (assign C, CH, CH₂ and CH₃)

DQF-COSY: Double Quantum Filtered COrelated SpectroscopY (coupling between signals)

HMBC: Heteronuclear Multiple Bond Correlation (useful for verifying assignment of carbon signals, particularly quaternary carbons)

nOe: nuclear Overhauser enhancement