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Supporting Information

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The room-temperature stabilization of bicyclo[2.2.2]oct-1-ene and bicyclo[3.2.1]oct-1-ene.

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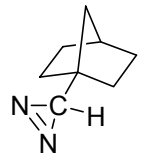
1. Photolysis and Thermolysis Experiments:

Photolysis were carried out in sealed Pyrex NMR tubes using the output of a 200 W Hg-Power-Max lamp (Oriel). The sample was immersed into a partially silvered Dewar filled with ice/water and was positioned in the focal point of the light beam. A 10 cm water filter and a WG320 cut-off filter were placed between light source and sample for the photolysis above 300 nm. For the photolysis above 335 nm, a 10 cm water filter, a NG-5 cut-off filter and a 1 cm acetone filter were placed in the light beam. Thermolysis were carried out in sealed pyrex NMR tubes (medium wall thickness). The whole sample tube was immersed in an iso-temperature bath for a given time. The temperature was measured with a calibrated thermocouple. For the photolysis or thermolysis under unaerobic conditions, samples were degassed by four freeze-pump-thaw cycles under vacuum. Product analysis was carried out by ^{1}H NMR spectroscopy from the integration of selected multiplets: **5⊙6**: δ -1.31 (s, 1H); **5⊙10**: δ -2.21 (s, 1H, C*H*N_2); **5⊙1**: δ -0.52 - -0.62 (m, 2H); **5⊙(*Z*)-2**: δ -1.41 (m, 1H); **5⊙11**: δ 4.92 (s, 1H); **4**:[1] δ 5.23 (d, J = 17.4 Hz, 1H).

2. Syntheses and compound characterizations:

2.1. 1-Bicyclo[2.2.1]heptyldiazirine 6:



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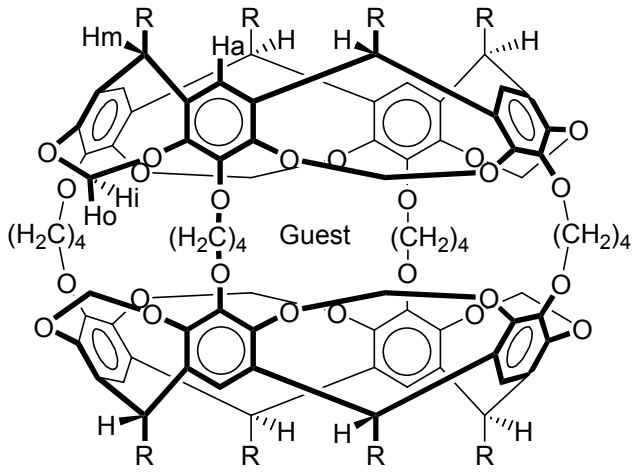
1-Bicyclo[2.2.1]heptyldiazirine was prepared via a general procedure for the preparation of diazirines from aldehydes or ketones.[2] Within 2-3 minutes, a 1 M solution of lithium bis(trimethylsilyl)amide (45 ml, 45 mmol) in THF was added drop-wise under Ar to a cooled (0 ^{o}C) solution of 1-bicyclo[2.2.1]heptylcarboxaldehyde **7** (2.5 g, 20 mmol) in dry THF (30 ml).[3] After 30 minutes at 0 ^{o}C, the reaction solution was cooled to – 30 ^{o}C and NH_2SO_3H (2.52 g, 26 mmol) dissolved in dry diglyme (20 ml) was added drop-wise. The suspension was stirred for one hour at 0 ^{o}C before a

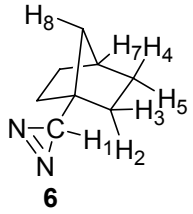
solution of freshly prepared *tert*-butyl hypochloride (2.2 ml) in *tert*-butanol (2.4 ml) was added drop-wise over 15 minutes. The reaction solution was stirred for one hour at 0 °C and poured onto 10 % sodium meta bisulfite in water (300 ml). Both phases were separated and the aqueous layer extracted with pentane (4 x 30 ml). The combined organic layers were dried over $MgSO_4$ and concentrated to about 5 ml. The residual crude product was purified by column chromatography (SiO_2, pentane). The combined product fractions were concentrated at a rotavaporator leaving 1-bicyclo[2.2.1]heptyldiazirine **6** as a colorless oil (540 mg, 24 % yield).

^{1}H NMR: ($CDCl_3$; 200 MHz; 23 °C): δ_H 2.18 (m, 1H, $H_{bridgehead}$), 1.66-1.4 (m, 2H), 1.4-1.06 (m, 8H), 0.95 (s, 1H, $(N_2)CH$). ^{13}C NMR ($CDCl_3$; 50.29 MHz; 23 °C): δ_C 47.3, 40.8, 37.0, 32.3, 30.0, 24.5. UV/Vis (CH_2Cl_2): λ_{max} 340 nm (ε = 100). FT-IR ($CDCl_3$): ν (cm^{-1}) 2957.2 (s), 2920.8 (m), 2871.4 (m), 1612.7 (w), 1583.6 (m), 1456.4 (w), 1334.7 (w), 1303.5 (w). DCI-MS (NH_3) : *m/z* 109 $[M\text{-}N_2 + H]^+$ (40 %), 126 $[2M\text{-}N_2\text{+}NH_4]^+$ (22%).

2.2. Hemicarceplex 5⊙6:



Guests:



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5⊙Guest R = $CH_2CH_2C_6H_5$

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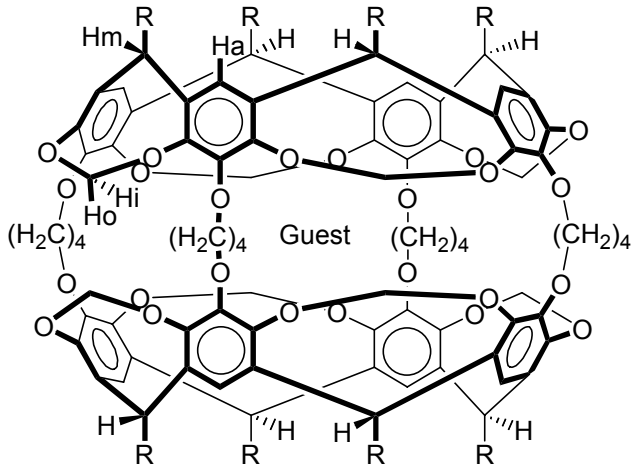
1-Bicyclo[2.2.1]heptyldiazirine **6** (0.2 ml) was added via syringe to a suspension of **8** (155 mg, 0.071 mmol),[4] 1,4-butanediol dimesylate (87 mg, 0.353 mmol), and Cs_2CO_3 (1g) in dry HMPA (8 ml). The suspension was stirred 4 days under argon in the dark at room temperature. The reaction was quenched by the addition of brine (40 ml). The precipitate was filtered off, washed with water (2 x 10 ml), methanol (2 x 2 ml), and was dried at high vacuum. The crude product was dissolved in the minimum amount of chloroform and purified by preparative TLC (silica gel, 2mm, $CHCl_3$) to give **5⊙6** (60 mg,

36% yield) as a white powder. ^{1}H NMR (400 MHz; $CDCl_3$; 23 °C): δ_H = 7.26-7.14 (m, 40H, Ph-*H*), 6.84 (s, 8H, H_a), 5.75 (d, ^3J(H,H)= 6.7 Hz, 8H, OCH_oHO), 4.83 (t, ^3J(H,H)= 7.8 Hz, 8H, CH_m), 4.32 (d, ^3J(H,H)= 6.7 Hz, 8H, OCH_iHO), 4.01 (sb, 16H, OCH_2CH$_2$), 2.72-2.67 (m, 16 H, CH$_2$CH_2Ph), 2.52-2.45 (m, 16H, CH_2CH$_2$Ph), 1.93 (sb, 16H, OCH$_2$CH_2), 0.17 (s, 2H, H_8, **6**), 0.044 (m, 1H, H_7, **6**), 0.01(t, 4H, **6**), -0.26 (m, 2H, **6**), -0.88 (m, 2H, **6**), -1.31 (s, 1H, H_1, **6**). ^{13}C NMR ($CDCl_3$; 50.29 MHz; 23 °C): δ_C 148.82, 144.39, 142.13, 139.02, 128.79, 128.67, 126.22, 114.58, 98.37, 71.73, 45.32 (G), 40.14 (G), 37.43, 34.92, 34.83 (G), 32.75, 31.64 (G) 29.03 (G), 28.44, 22.06 (G). LR FAB-MS (NBA-matrix): *m/z* 2385.3 (100) $[M+H]^+$, 2356.6 (95) $[M-N_2+H]^+$, 2249.8 (30) $[M-$**6**$+H]^+$; elemental analysis calcd (%) for $C_{152}H_{148}N_2O_{24}$: C, 76.49; H, 6.25; N, 1.17; found: C, 76.76; H, 6.10; N, 1.29.

2.3. Hemicarceplex 5⊙9:



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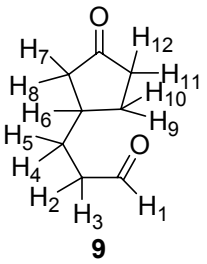

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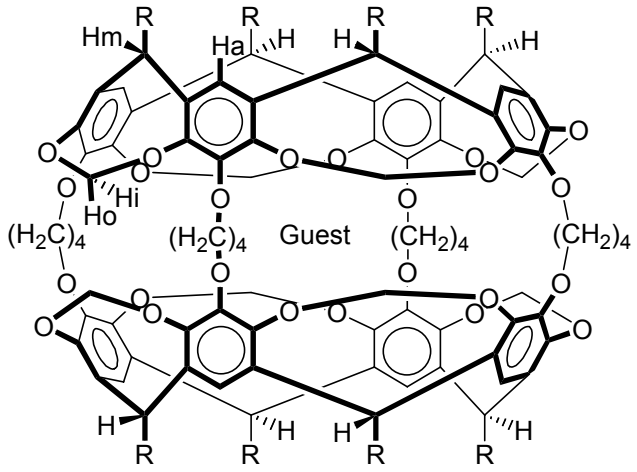
5⊙Guest R = $CH_2CH_2C_6H_5$

Hemicarceplex **5⊙9** was isolated by preparative TLC (SiO_2, $CHCl_3$) from the product mixture, which results if **5⊙6** is photolyzed in $CDCl_3$ (λ > 300 nm, 0 °C) and the photoproducts are heated as a solid for 2 days at 60 °C in the presence of oxygen. ^{1}H NMR (400 MHz; $CDCl_3$; 23 °C): δ_H = 7.25-7.14 (m, 40H, Ph-*H*), 6.85 (s, 8H, H_a), 5.81 (s, 1H, H_1, **9**), 5.79 (d, ^3J(H,H)= 7.4 Hz, 8H, OCH_oHO), 4.84 (t, ^3J(H,H)= 8 Hz, 8H, CH_m), 4.35 (d, ^3J(H,H)= 7.4 Hz, 8H, OCH_iHO), 4.10 (m, 8H, OCH*H*CH$_2$), 3.96 (m, 8H, OC*H*HCH$_2$), 2.70-2.65 (m, 16 H, CH$_2$CH_2Ph), 2.52-2.45 (m, 16H, CH_2CH$_2$Ph), 2.04-1.83 (m, 16H, OCH$_2$CH_2), 1.37 (m, 1H, H_6, **9**), 1.24 (dd, *J* = 17.4, 8.4, 1H, H_8, **9**), 0.54 (m, 1H, H_7, **9**), 0.51 (m, 1H, H_4, **9**), 0.51 (m, 1H, H_5, **9**), 0.48 (m, 1H, H_2, **9**), 0.43 (m, 1H, H_3, **9**), 0.15 (m, 1H, H_{12} **9**), -0.61 (dd, *J* = 11, 19.6 Hz, 1H, H_{11}, **9**), -0.78 (m, 1H, H_9, **9**), -0.90 (m, 1H, H_{10}, **9**). FT-IR ($CHCl_3$): ν (cm^{-1})

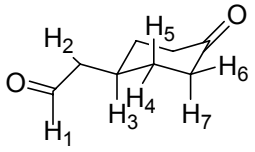
2948.7 (s), 2875.3 (m), 2821 (w), 2729.5 (w), 1742.4 (m), 1602.4 (m), 1576.6 (w), 1496.9 (m), 1474.2 (s), 1467.2 (s), 1440.8 (s), 1374.5 (m), 1316.7 (s). LR FAB-MS (NBA-matrix): *m/z* 2390.5 (45) $[M+H]^+$, 2250.4 (100) $[M\text{-}\mathbf{9}+H]^+$. Elemental analysis calcd (%) for $C_{152}H_{148}N_2O_{24}$: C, 76.36; H, 6.24; found: C, 76.33; H, 6.06.

2.4. Hemicarceplex 5⊙11:



5⊙Guest R = $CH_2CH_2C_6H_5$

Guests:



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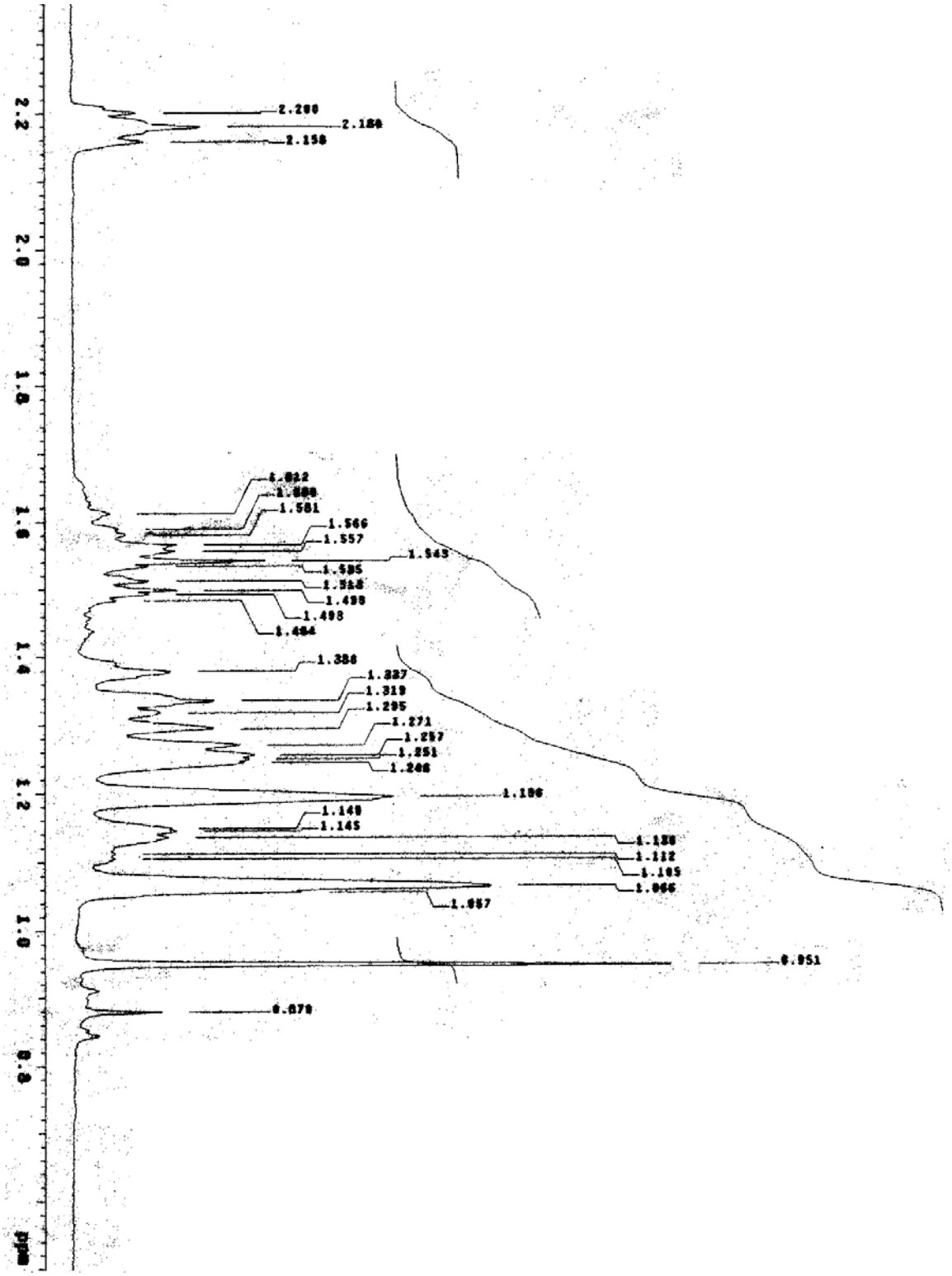
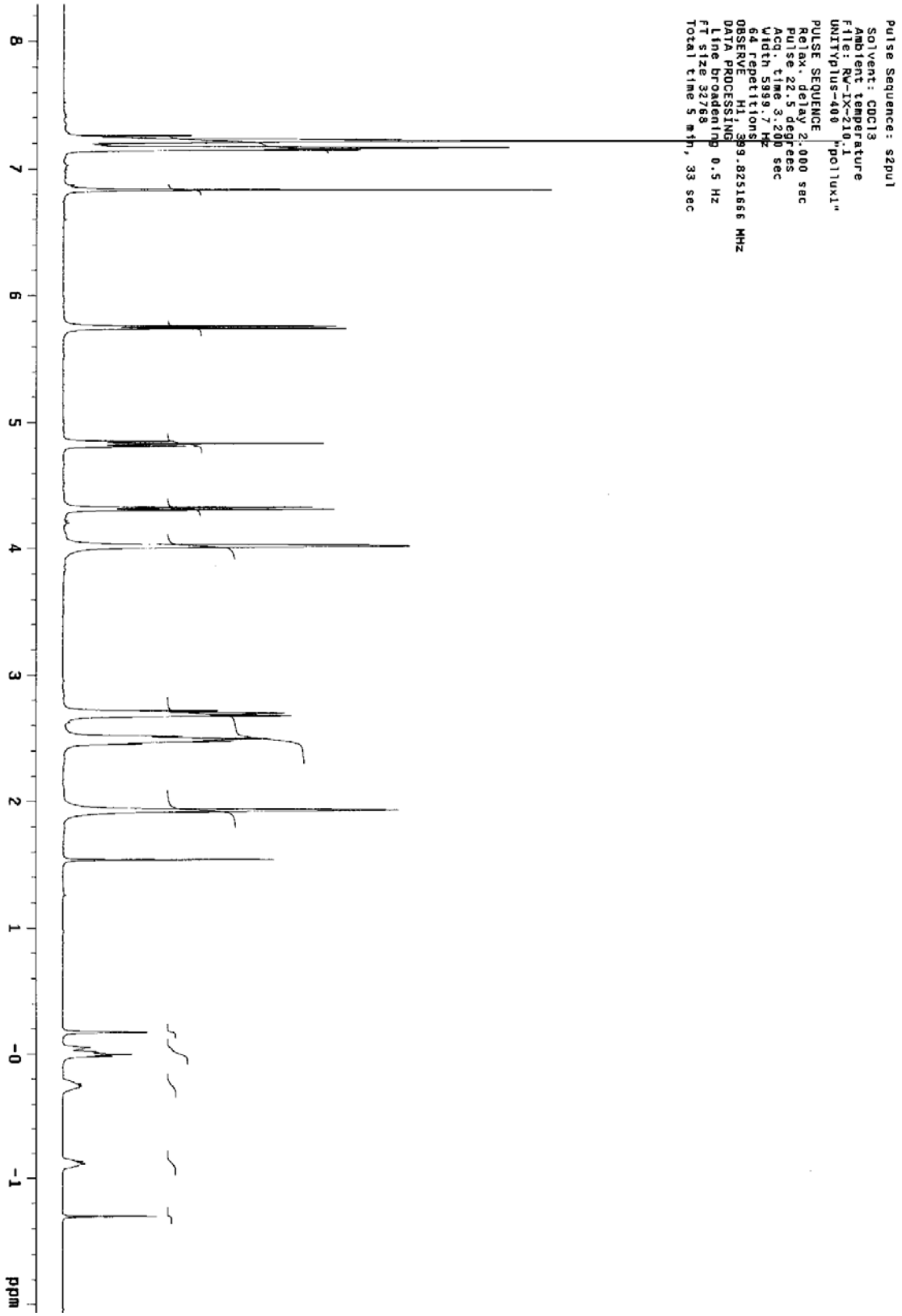
Hemicarceplex **5⊙11** was isolated by preparative TLC (SiO_2, $CHCl_3$) from the product mixture, which results if **5⊙6** is photolyzed (λ > 300 nm, 23 °C) in the presence of oxygen. ^{1}H NMR (400 MHz; $CDCl_3$; 23 °C): δ_H = 7.25-7.15 (m, 40H, Ph-*H*), 6.87 (s, 8H, H_a), 5.73 (d, ^3J(H,H)= 6.8 Hz, 8H, OCH_oHO), 4.92 (s, 1H, H_1, **11**), 4.83 (t, ^3J(H,H)= 7.88 Hz, 8H, CH_m), 4.21 (d, ^3J(H,H)= 6.8 Hz, 8H, OCH_iHO), 4.02 (s, 16H, OCH_2CH$_2$), 2.75-2.68 (m, 16 H, CH$_2$CH_2Ph), 2.56-2.47 (m, 16H, CH_2CH$_2$Ph), 1.90 (s, 16H, OCH$_2$CH_2), 1.06 (m, 1H, H_3, **11**), 0.97 (d, J = 6 Hz, 2H, H_2, **11**), 0.97 (m, 2H, H_5, **11**), 0.81 (ddd, ^3J(H,H)= 6, 13, 13 Hz, 2H, H_4, **11**), 0.69 (m, 2H, H_6, **11**), 0.66 (m, 2H, H_7, **11**). FT-IR ($CDCl_3$): ν (cm^{-1}) 3085.8 (w), 3064.0 (w), 3027.2 (m), 2994.9 (w), 2947.9 (s), 2875.7 (m), 2847.9 (w), 2731.9 (w), 1726.2 (m), 1721.0 (m), 1602.1 (m), 1577.1 (w), 1496.9 (m), 1474.2 (s), 1468.2 (s), 1453.1 (m), 1440.5 (s), 1373.4 (m), 1313.6 (s), 1157.4 (s), 1106.9 (s), 1065 (s), 1024 (s), 994.8 (s). LR FAB-MS (NBA-matrix): *m/z* 2389.9 (45) $[M+H]^+$. Elemental analysis calcd (%) for $C_{152}H_{148}N_2O_{24}$: C, 76.36; H, 6.24; found: C, 76.47; H, 6.11.

3. NMR spectra

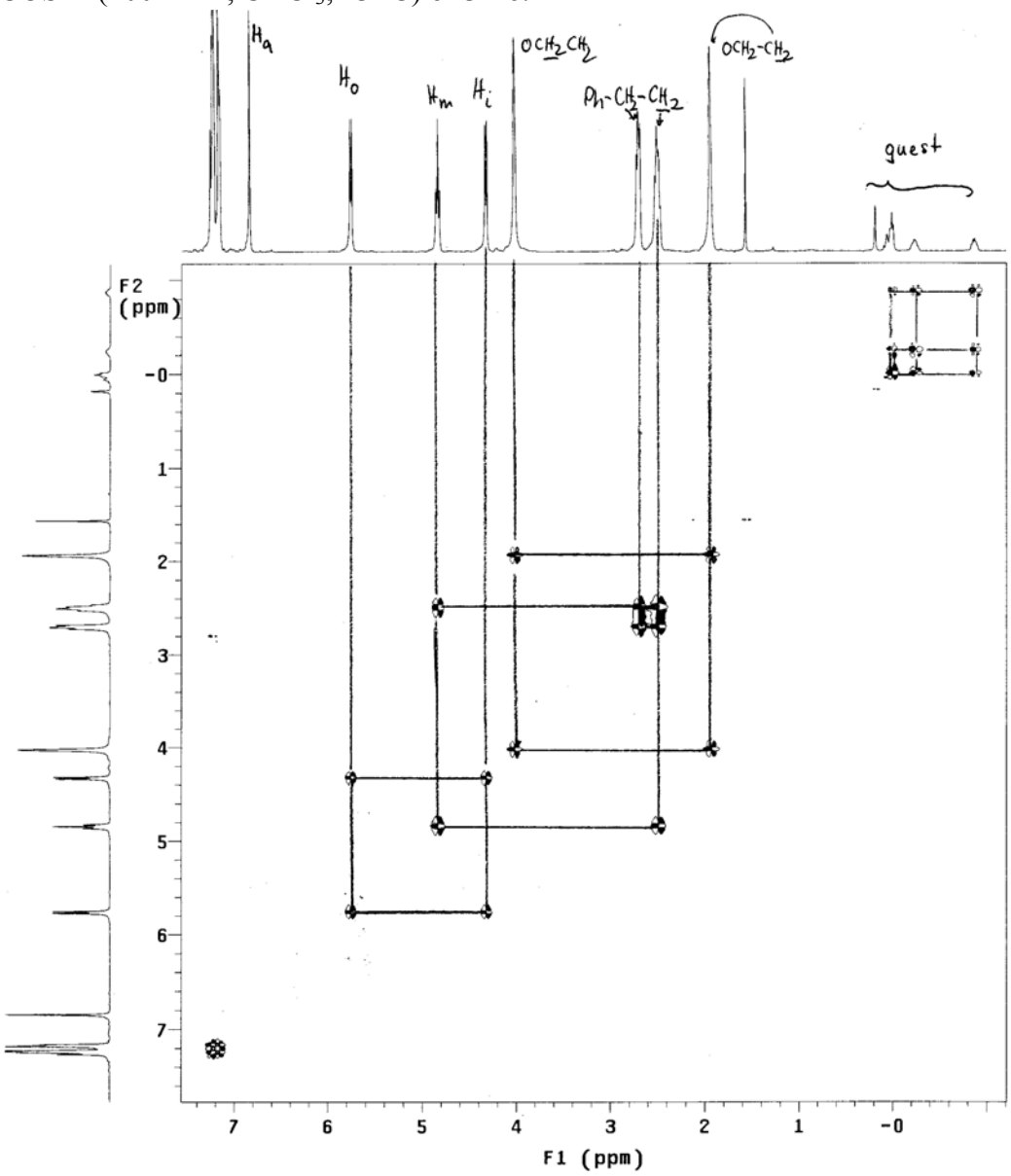
3.1. ^{1}H NMR spectrum (200 MHz; $CDCl_3$, 23 ^{o}C) of **6**.

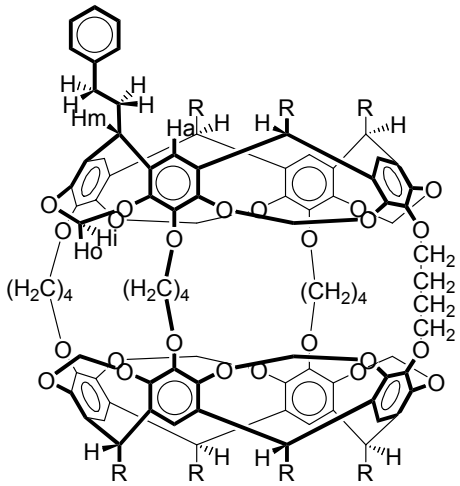


3.2. ^{1}H NMR spectrum (400 MHz; $CDCl_3$, 23 ^{o}C) of **5⊙6** (Full spectrum Figure 1a).

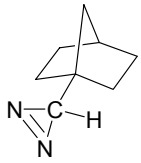


3.3. DQCOSY (400 MHz; $CDCl_3$, 23 °C) of **5⊙6**.





R = $CH_2CH_2C_6H_5$ **5⊙6**



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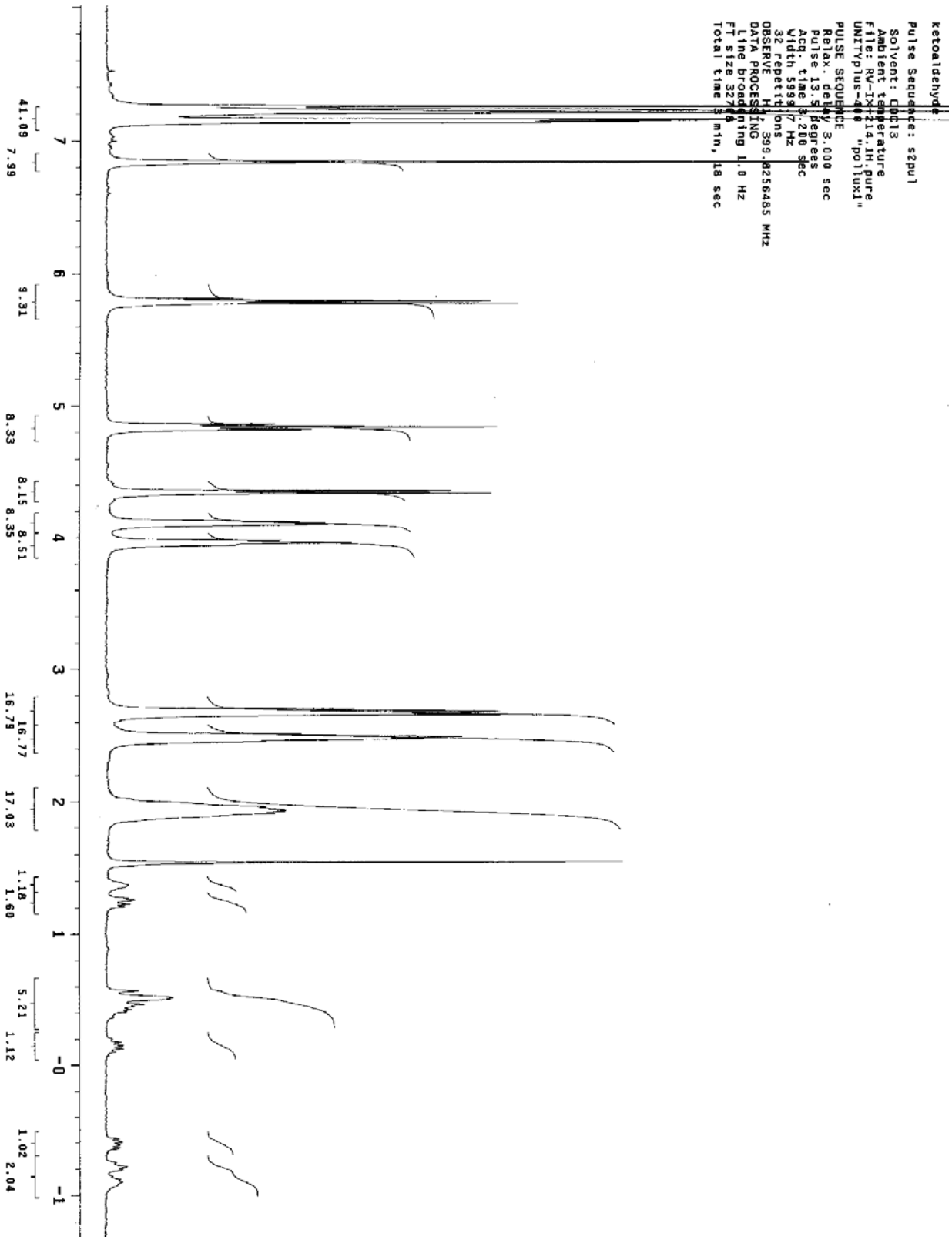
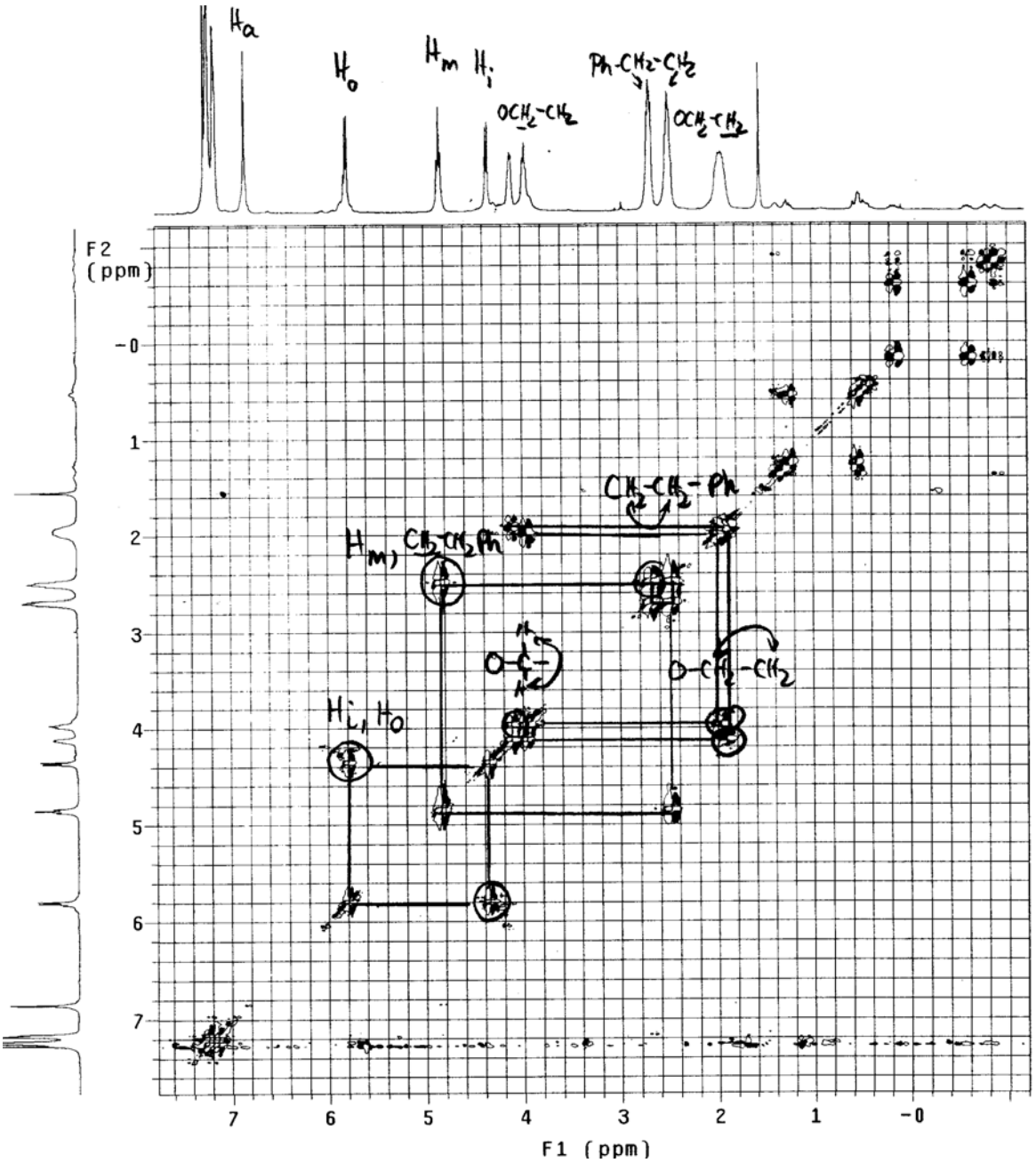
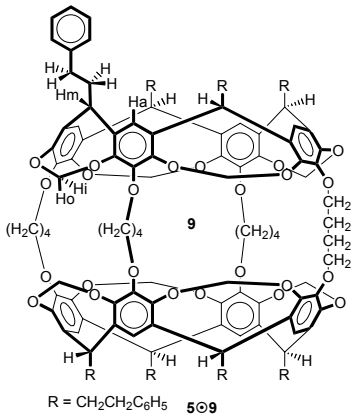
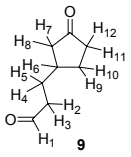
3.4. ^{1}H NMR spectrum (400 MHz; $CDCl_3$, 23 ^{o}C) of **5⊙9**.



3.5.1, DQCOSY (400 MHz; $CDCl_3$, 23 ^oC) of **5⊙9**.

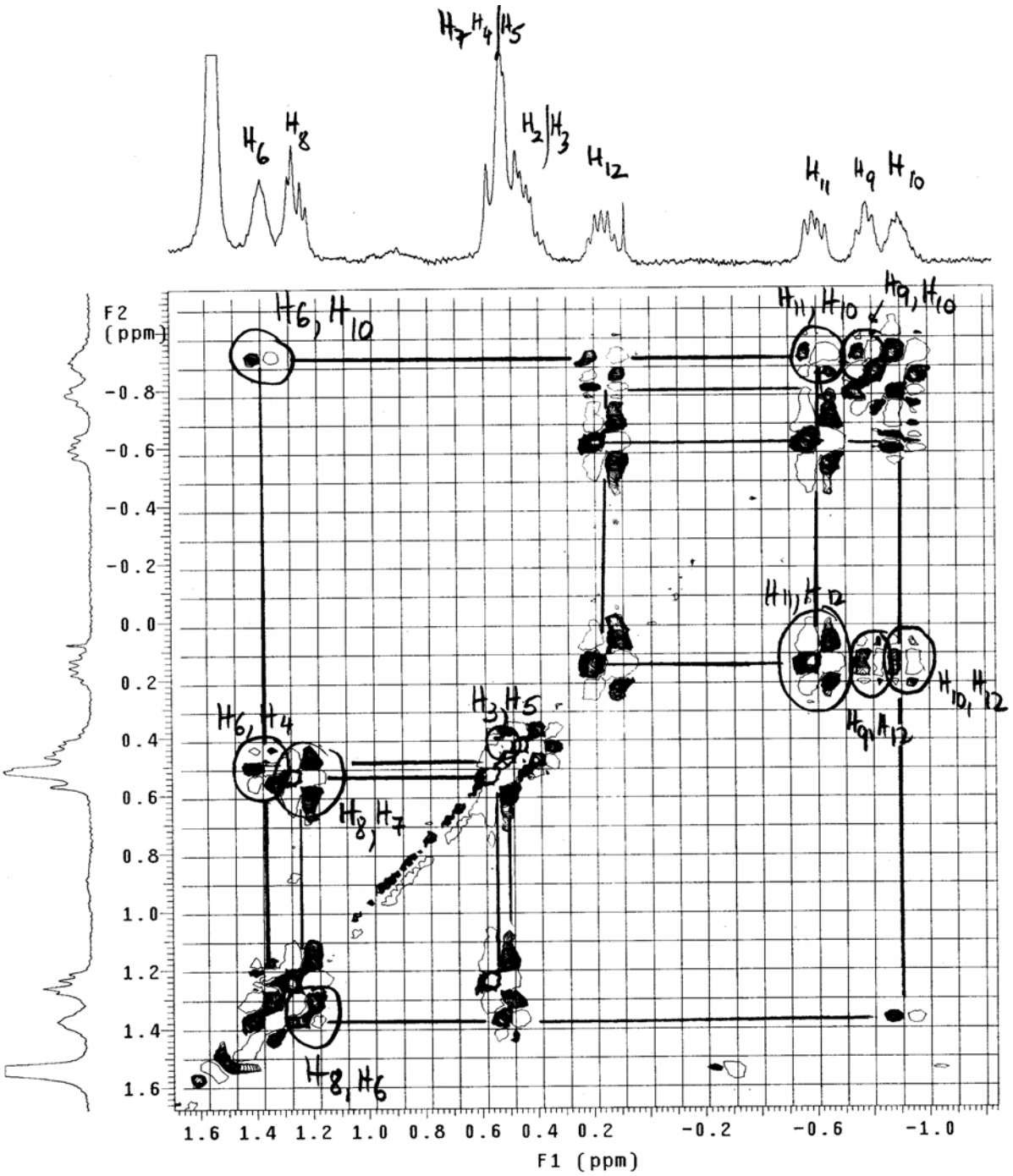


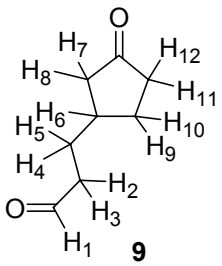




H1 = 4.92 ppm H7 = 1.24 ppm
H2 = 0.43 ppm H8 = 0.54 ppm
H3 = 0.48 ppm H9 = -0.78 ppm
H4 = 0.51 ppm H10 = -0.90 ppm
H5 = 0.51 ppm H11 = -0.61 ppm
H6 = 1.37 ppm H12 = 0.15 ppm

3.5.2, Partial DQCOSY (400 MHz; $CDCl_3$, 23 ^oC) of **5⊙9**.





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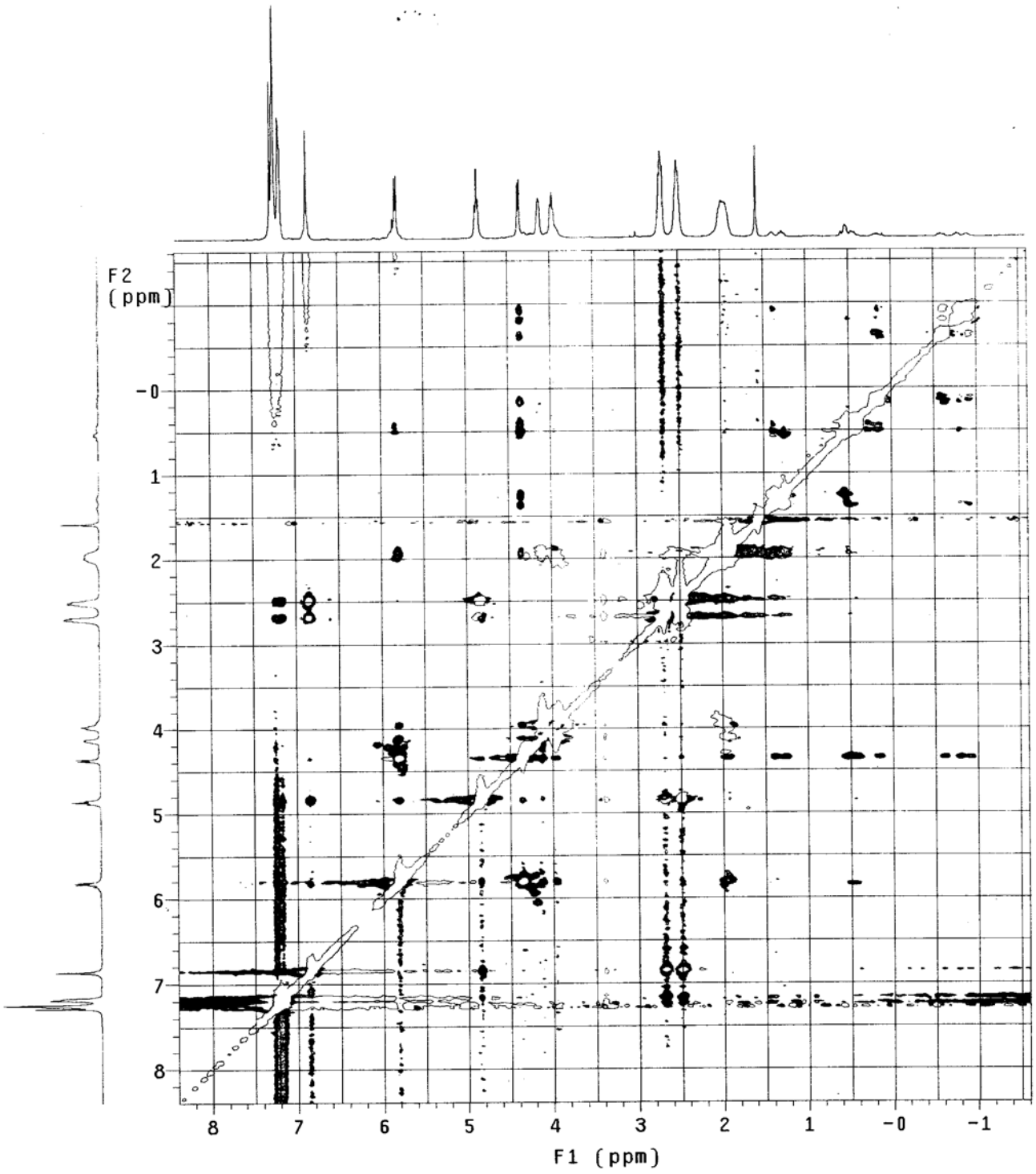
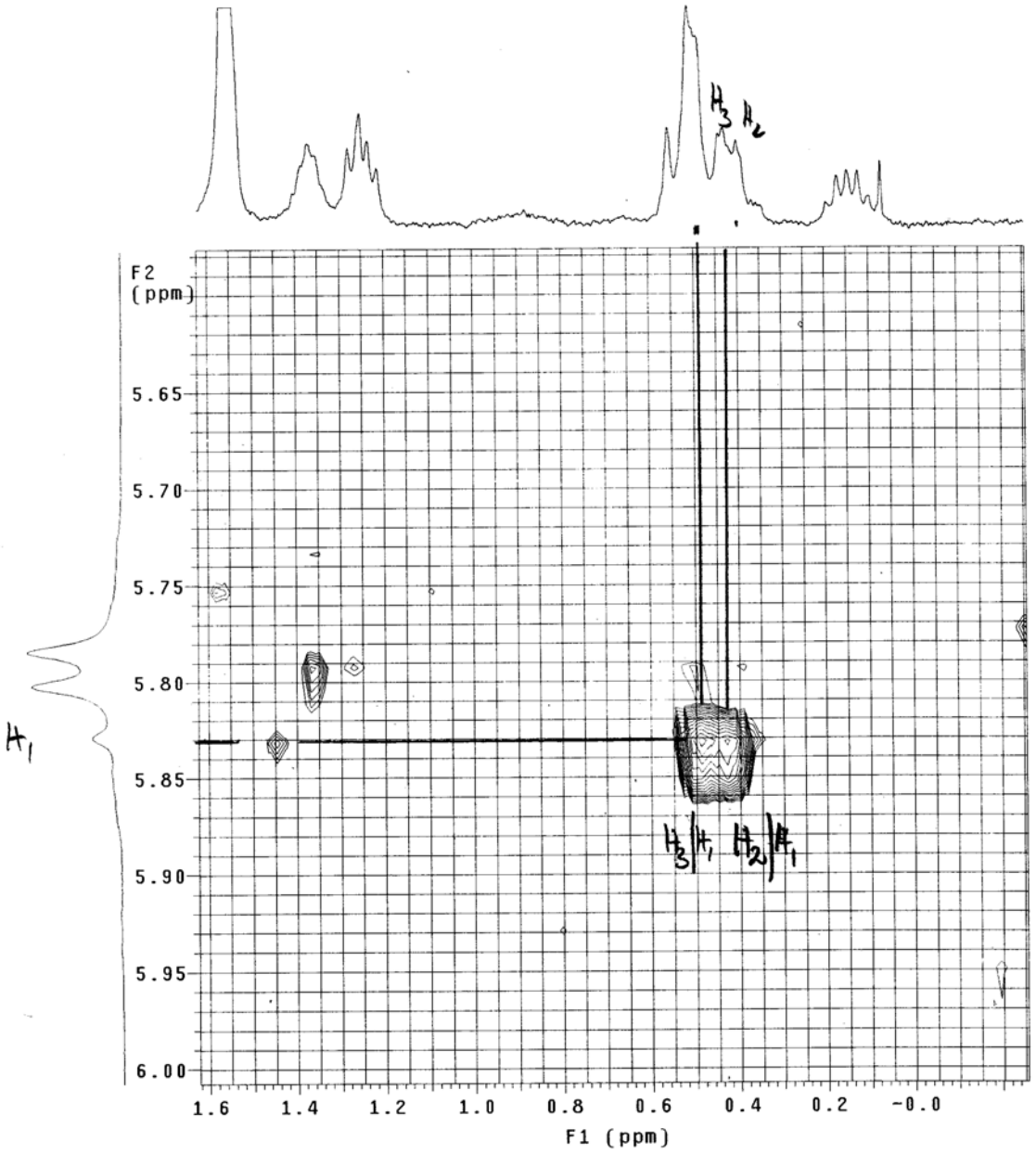
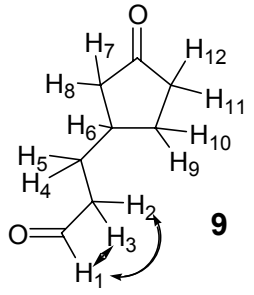
3.6.1. ROESY (400 MHz; $CDCl_3$, 15 ^oC, t_{mix} = 60 msec) of **5⊙9**.



3.6.2. Partial ROESY (400 MHz; $CDCl_3$, 15 ^oC, t_{mix} = 60 msec) of **5⊙9**.



observed NOEs:



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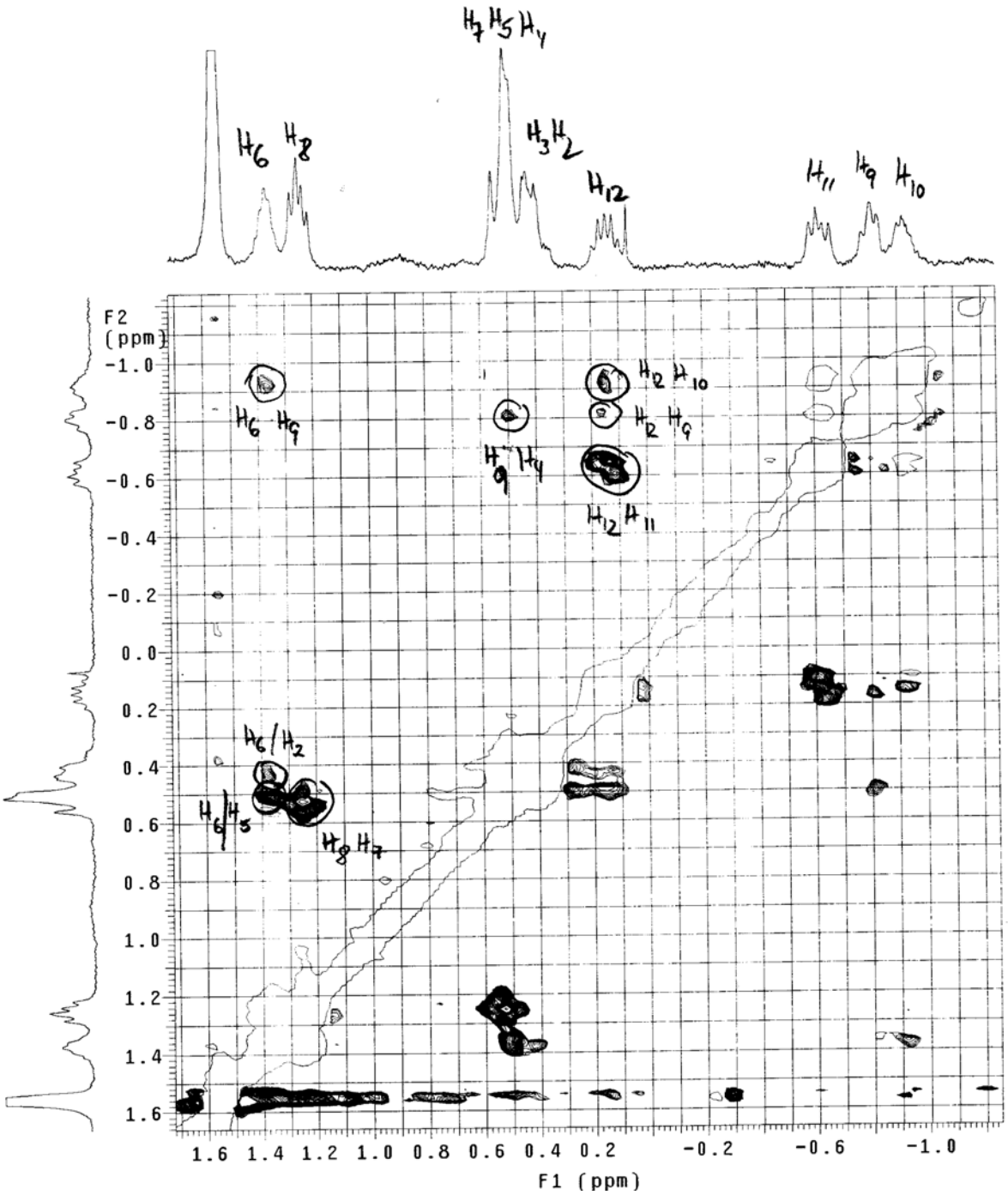
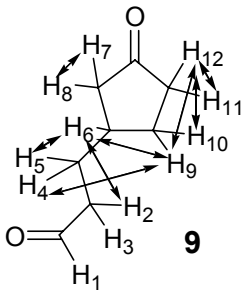
3.6.3. Partial ROESY (400 MHz; $CDCl_3$, 15 ^oC, t_{mix} = 60 msec) of **5⊙9**.



observed NOEs:



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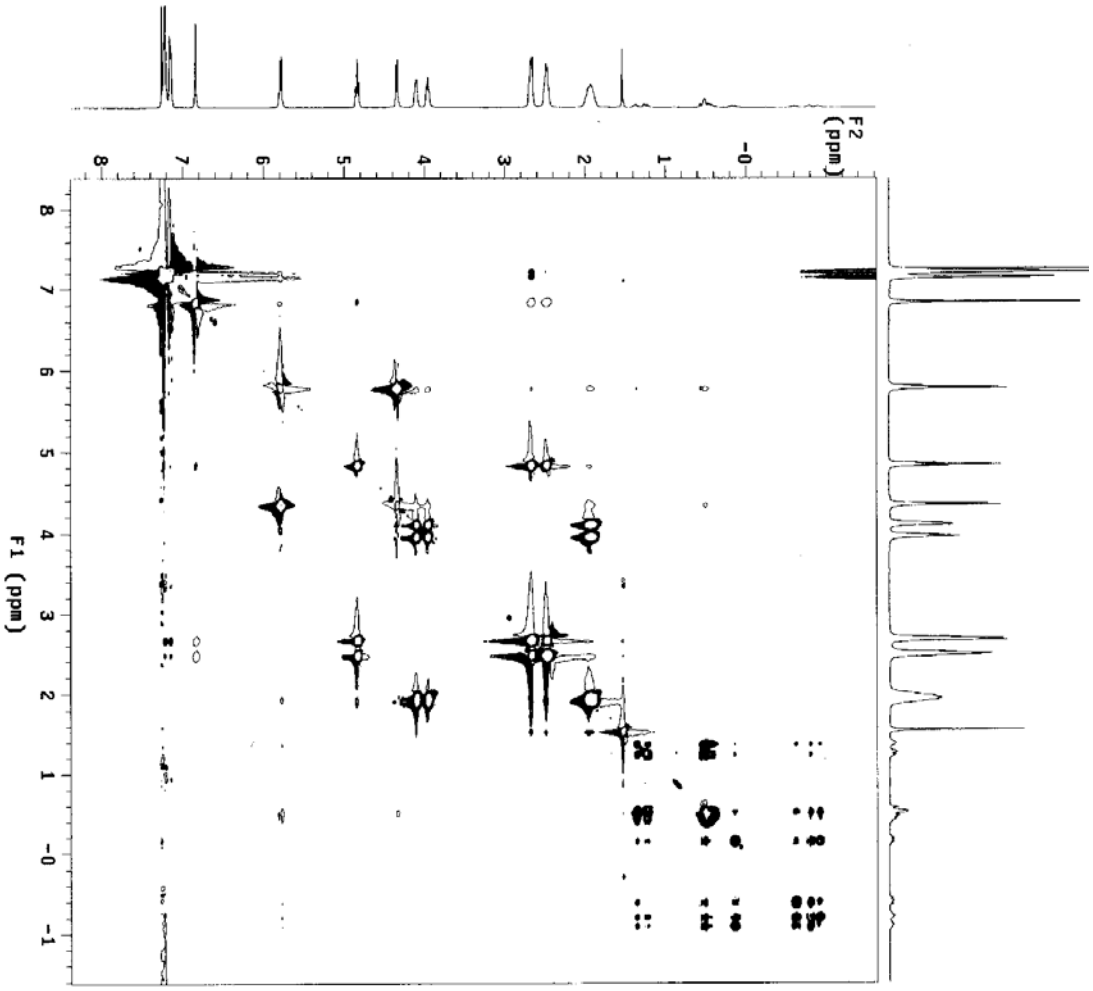
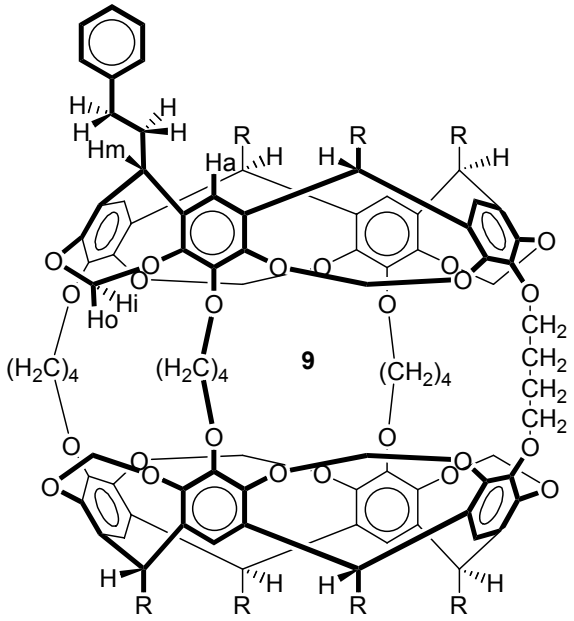
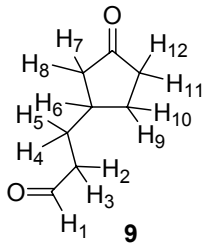
3.7.1. TOCSY (400 MHz; $CDCl_3$, 23 ^oC, t_{mix} = 100 msec) of **5⊙9**.



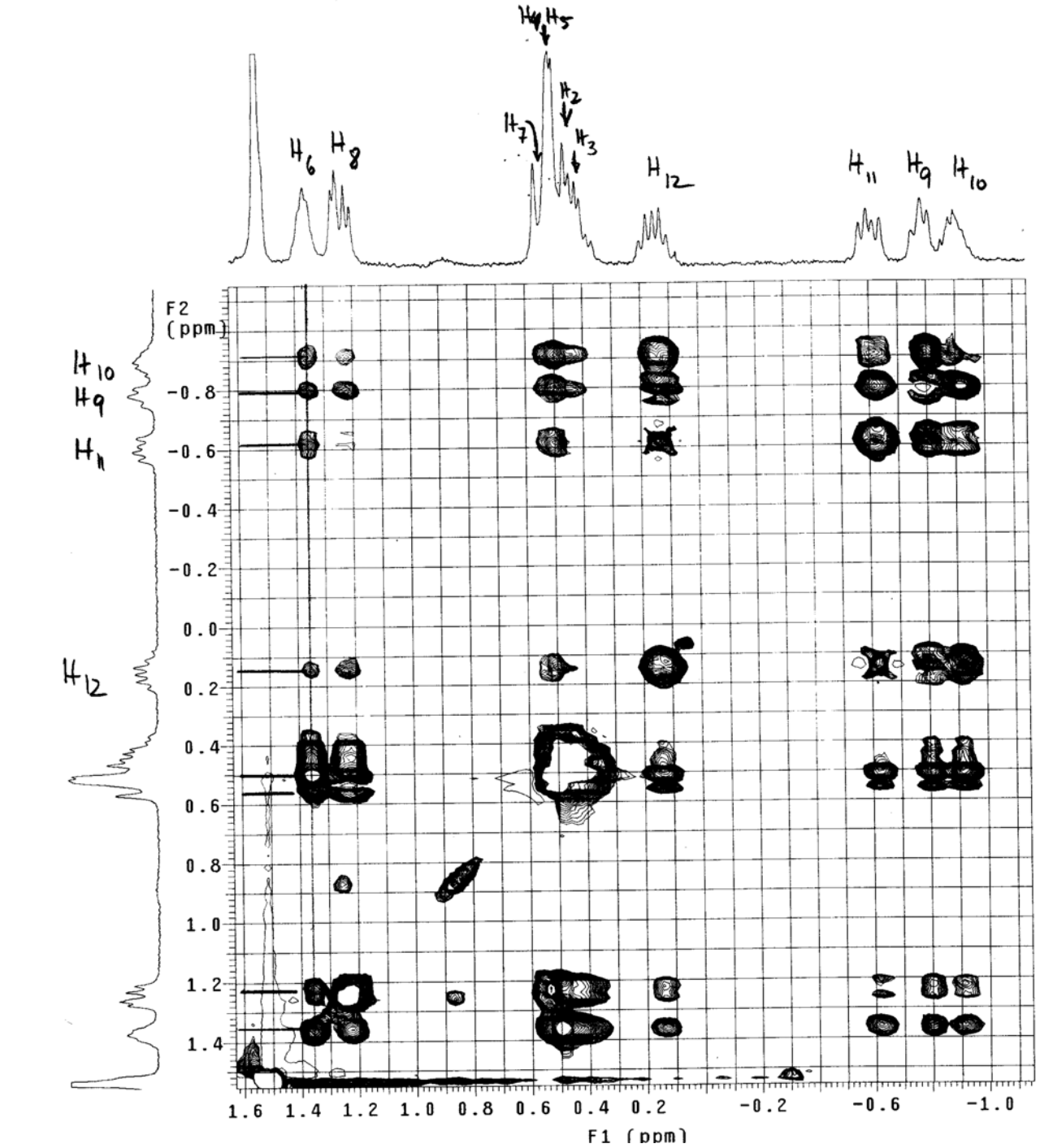


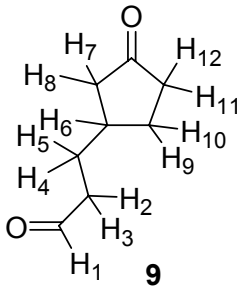
R = $CH_2CH_2C_6H_5$ **5⊙9**



H1 = 4.92 ppm H7 = 1.24 ppm
H2 = 0.43 ppm H8 = 0.54 ppm
H3 = 0.48 ppm H9 = -0.78 ppm
H4 = 0.51 ppm H10 = -0.90 ppm
H5 = 0.51 ppm H11 = -0.61 ppm
H6 = 1.37 ppm H12 = 0.15 ppm

3.7.2. Partial TOCSY (400 MHz; $CDCl_3$, 23 ^oC, t_{mix} = 100 msec) of **5⊙9**.





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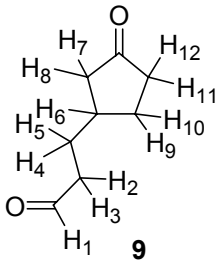
3.7.3. Partial TOCSY (400 MHz; $CDCl_3$, 23 ^oC, t_{mix} = 100 msec) of **5⊙9**.



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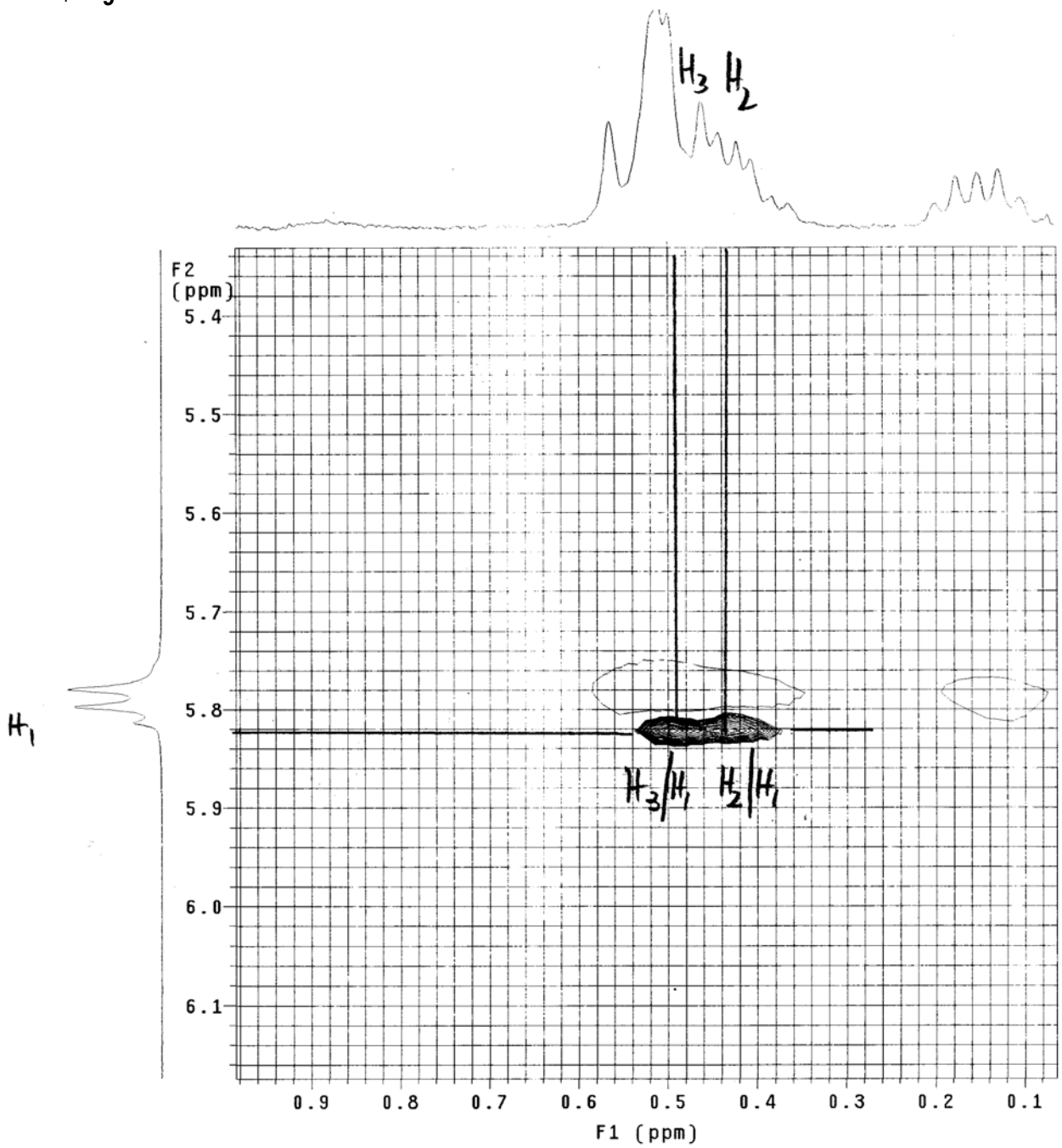
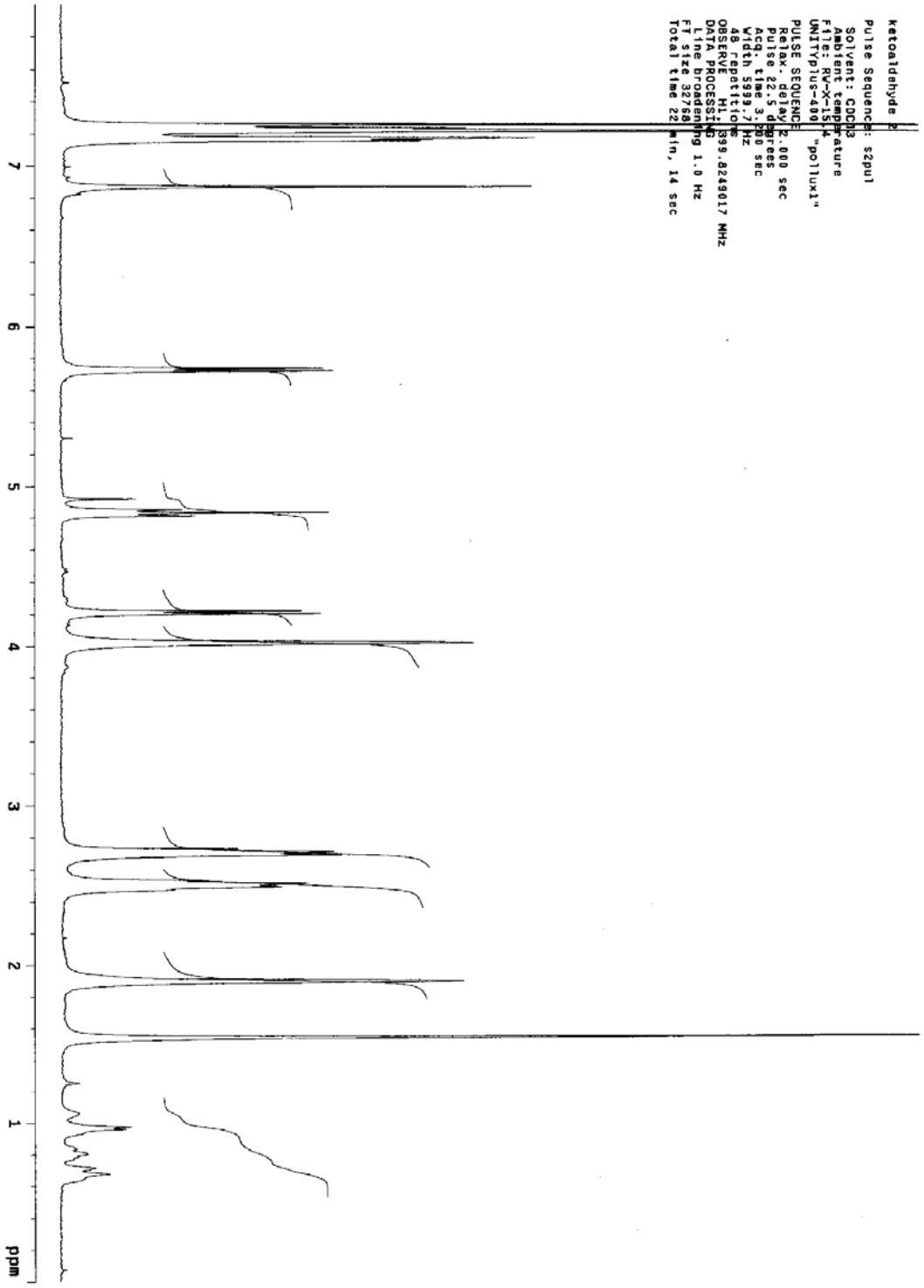
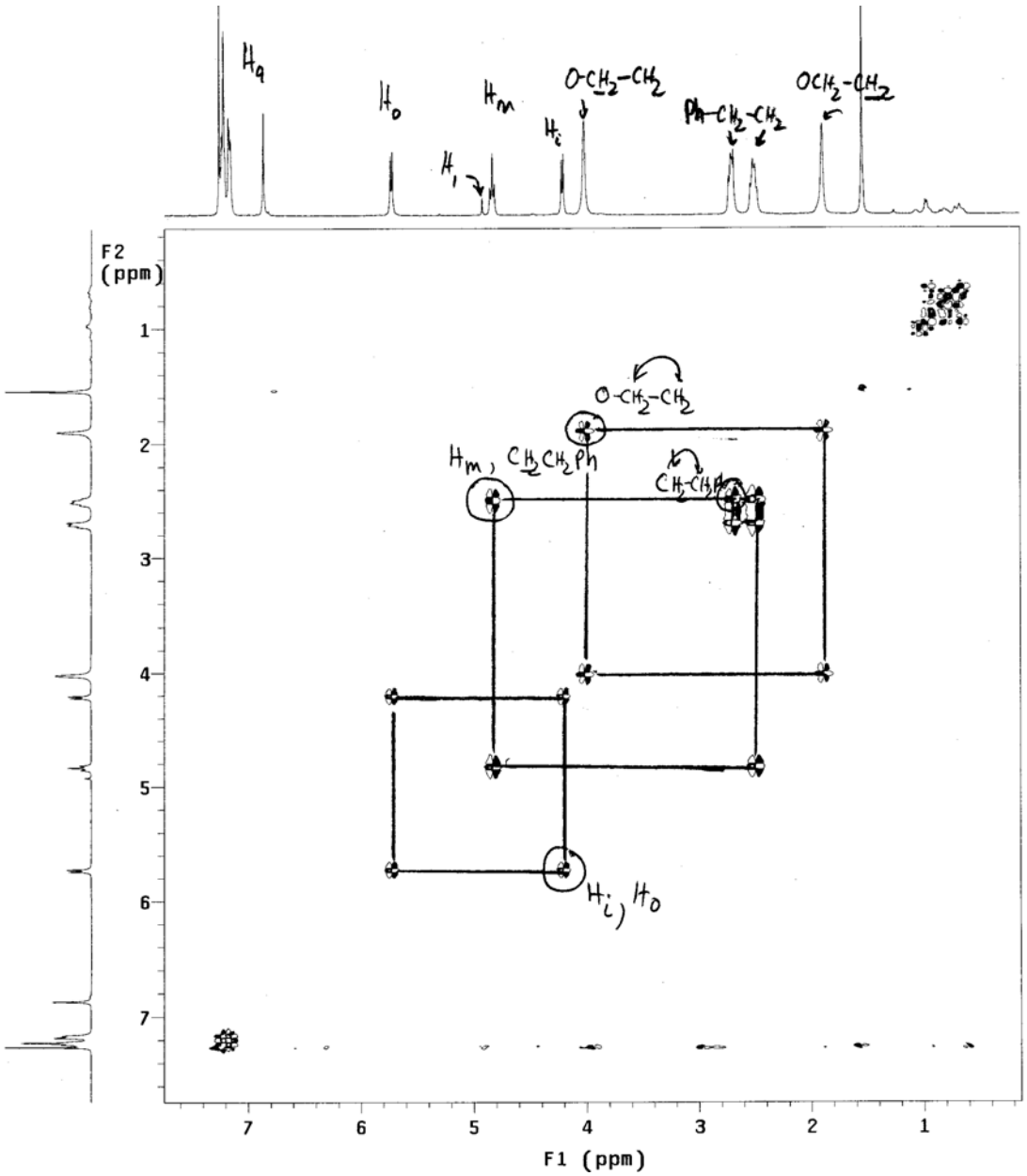
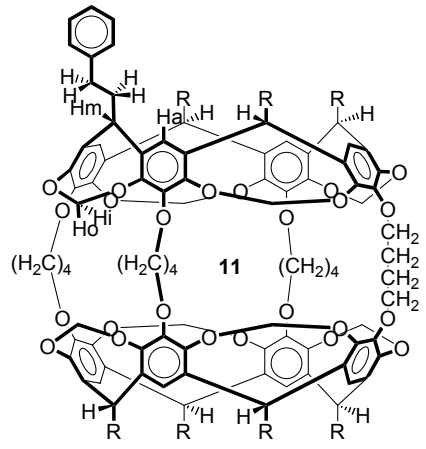


3.8. ^{1}H NMR spectrum (400 MHz; $CDCl_3$, 23 ^{o}C) of **5⊙11**.

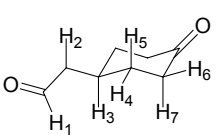


3.9.1. DQCOSY (400 MHz; $CDCl_3$, 23 ^oC) of **5⊙11**.





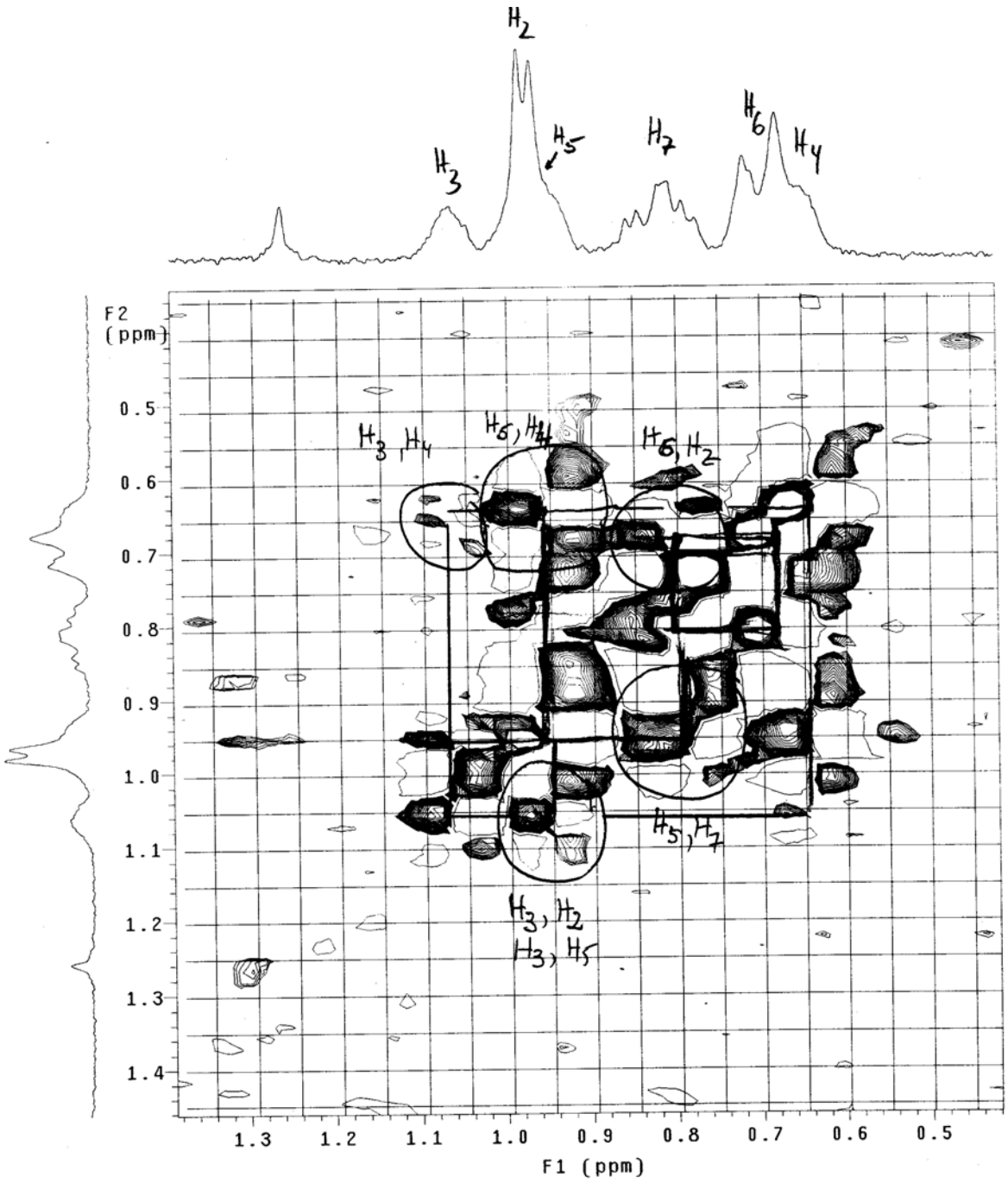
R = $CH_2CH_2C_6H_5$ **5⊙11**

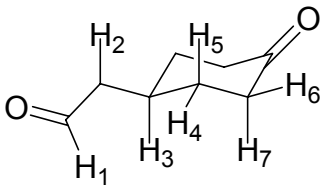


11

H1 = 4.92 ppm
H2 = 0.97 ppm
H3 = 1.06 ppm
H4 = 0.65 ppm
H5 = 0.97 ppm
H6 = 0.69 ppm
H7 = 0.81 ppm

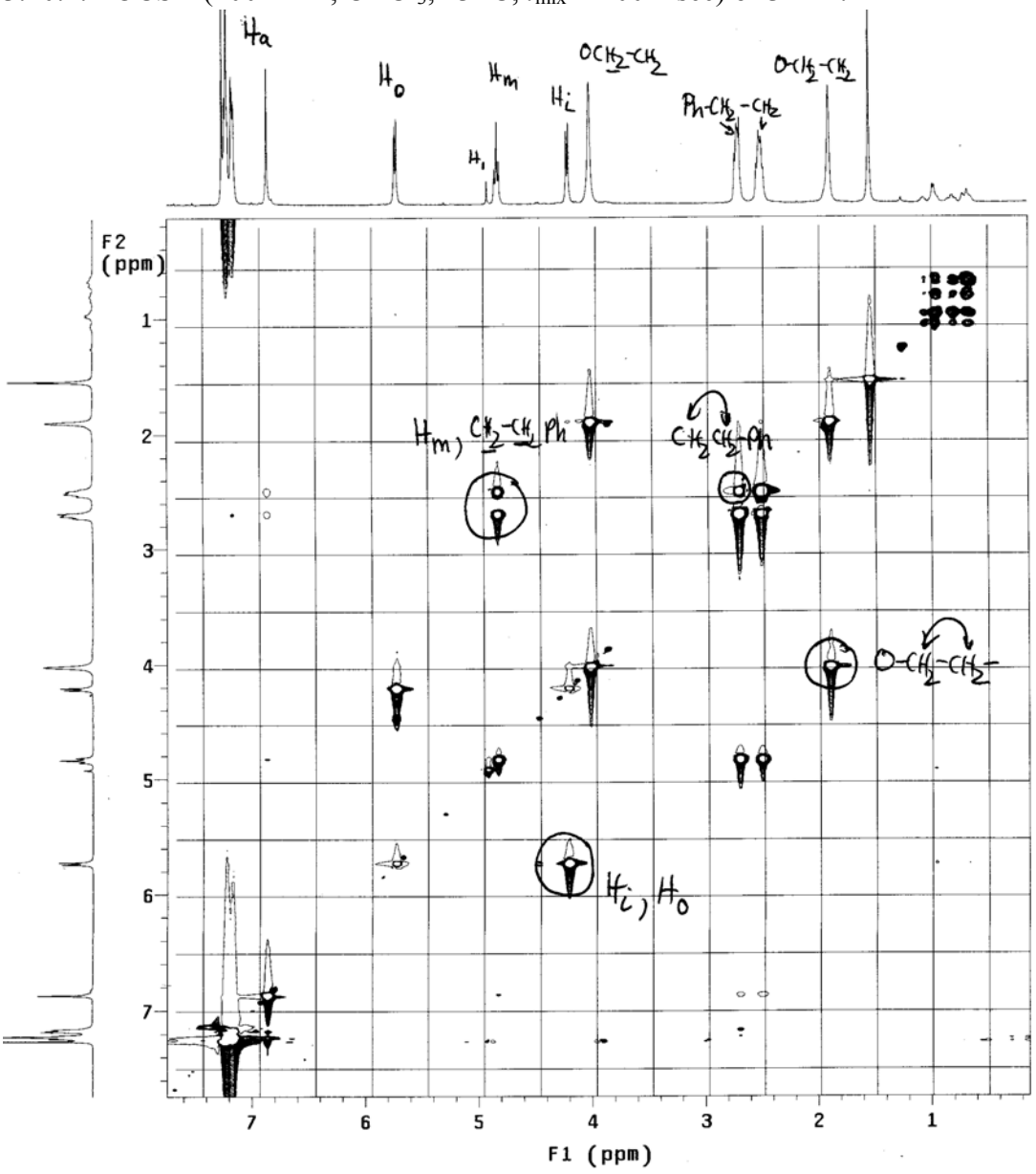
3.9.2. Partial DQCOSY (400 MHz; $CDCl_3$, 23 ^oC) of **5⊙11**.

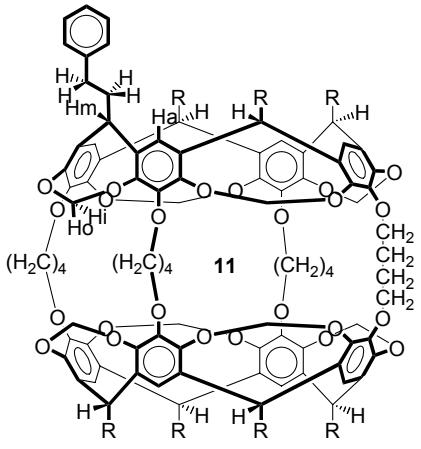




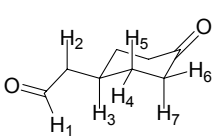
11

3.10.1. TOCSY (400 MHz; $CDCl_3$, 23 °C, t_{mix} = 100 msec) of **5⊙11**.





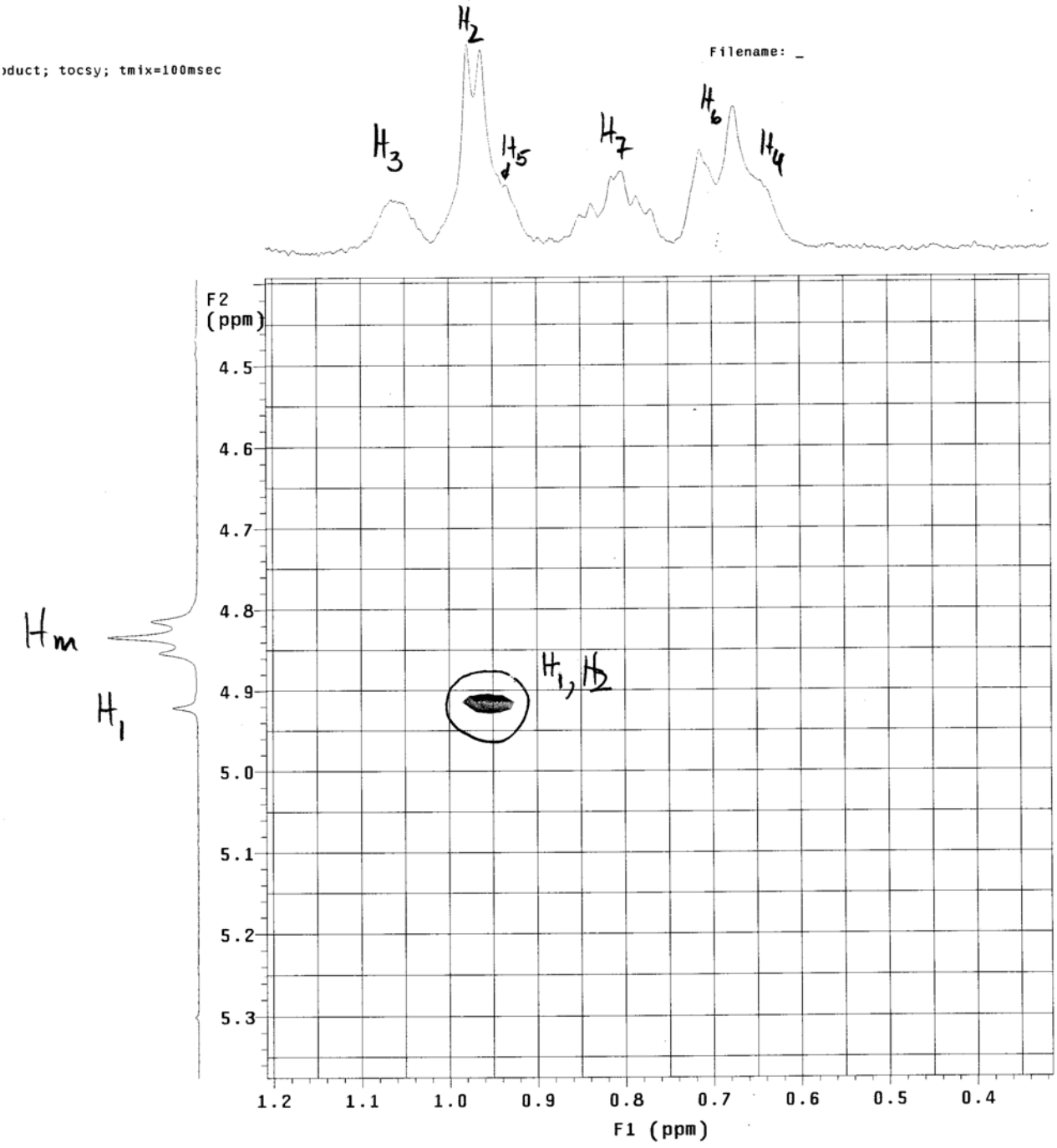
R = $CH_2CH_2C_6H_5$ **5⊙11**

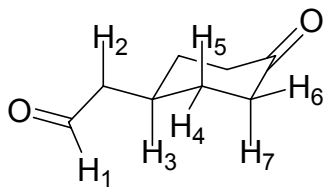


11

H1 = 4.92 ppm
H2 = 0.97 ppm
H3 = 1.06 ppm
H4 = 0.65 ppm
H5 = 0.97 ppm
H6 = 0.69 ppm
H7 = 0.81 ppm

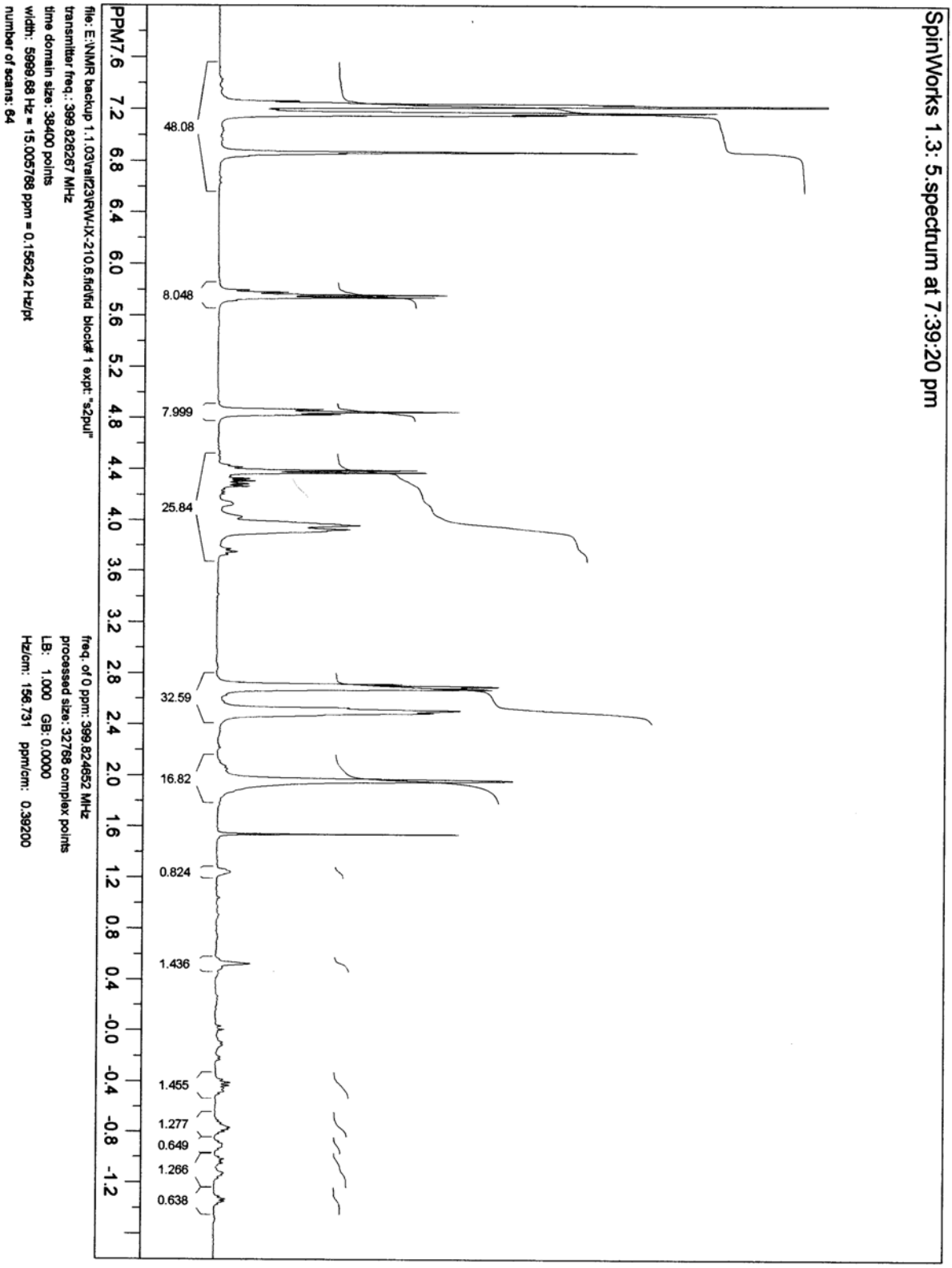
3.10.1. Partial TOCSY (400 MHz; $CDCl_3$, 23 ^oC, t_{mix} = 100 msec) of **5⊙11**.



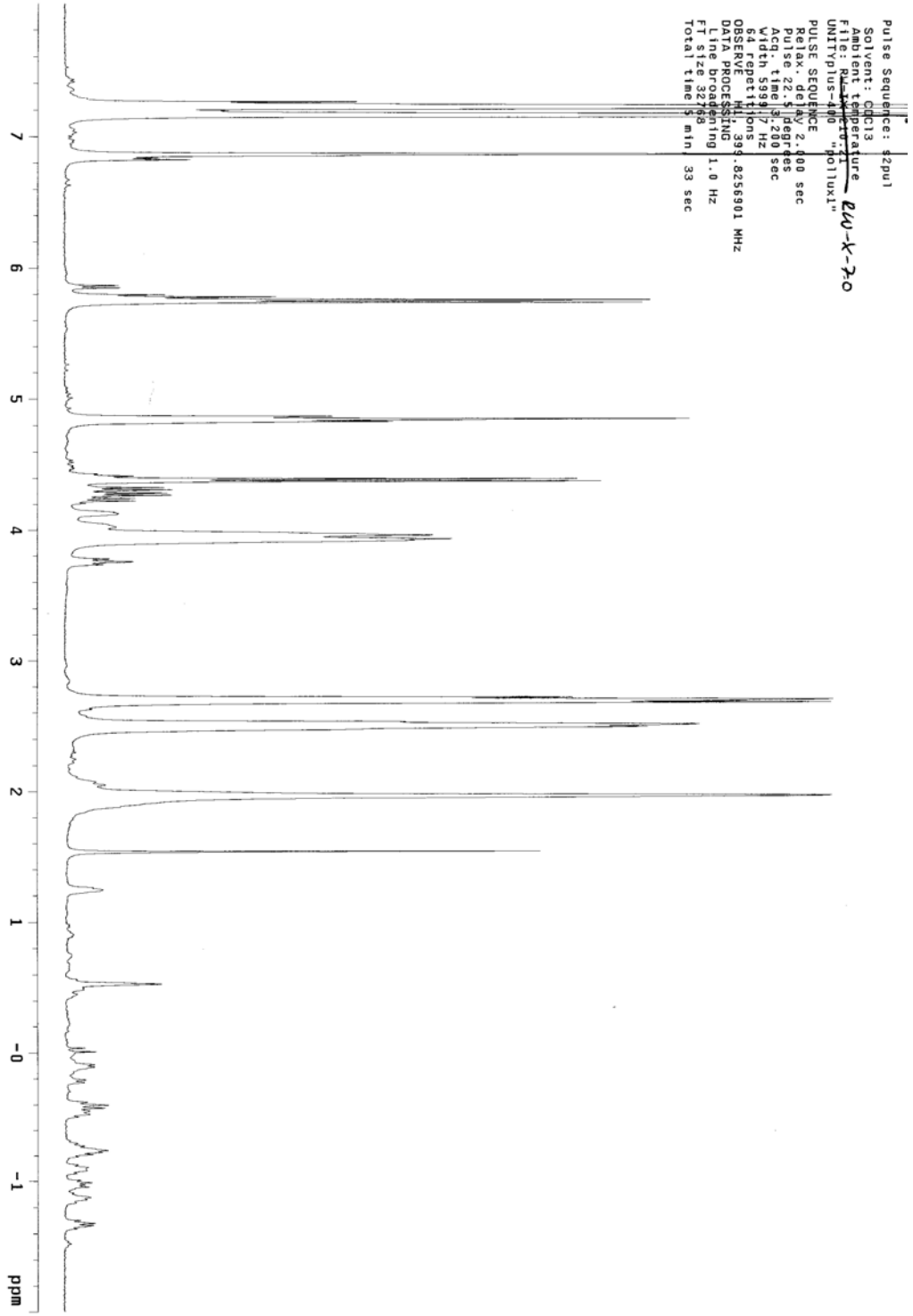


11

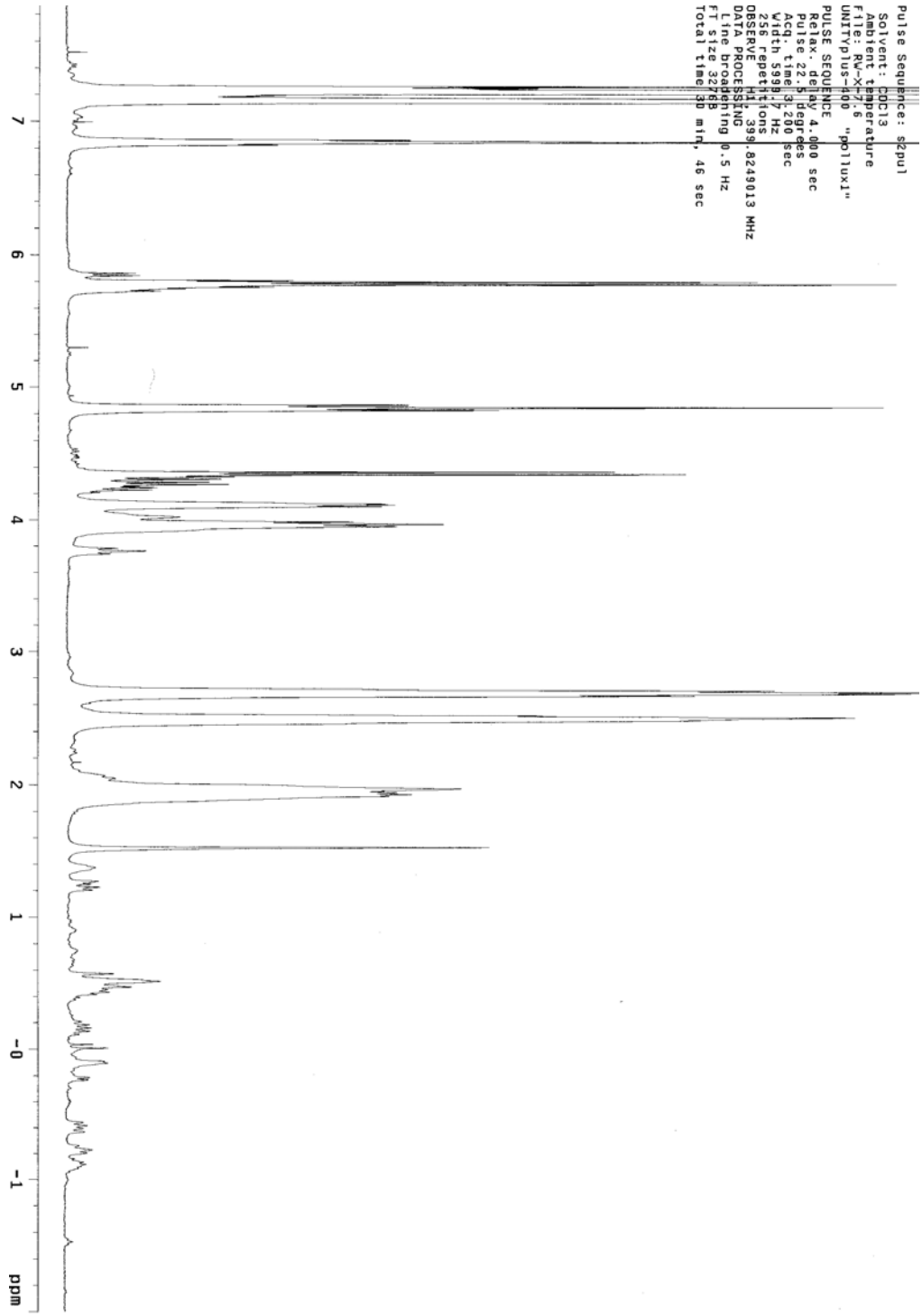
3.11. ^{1}H NMR spectrum (400 MHz; $CDCl_3$, 23 ^{o}C) of a solution containing 64 % **5**⊙(*Z*)-**2** (Full spectrum Figure 1b).



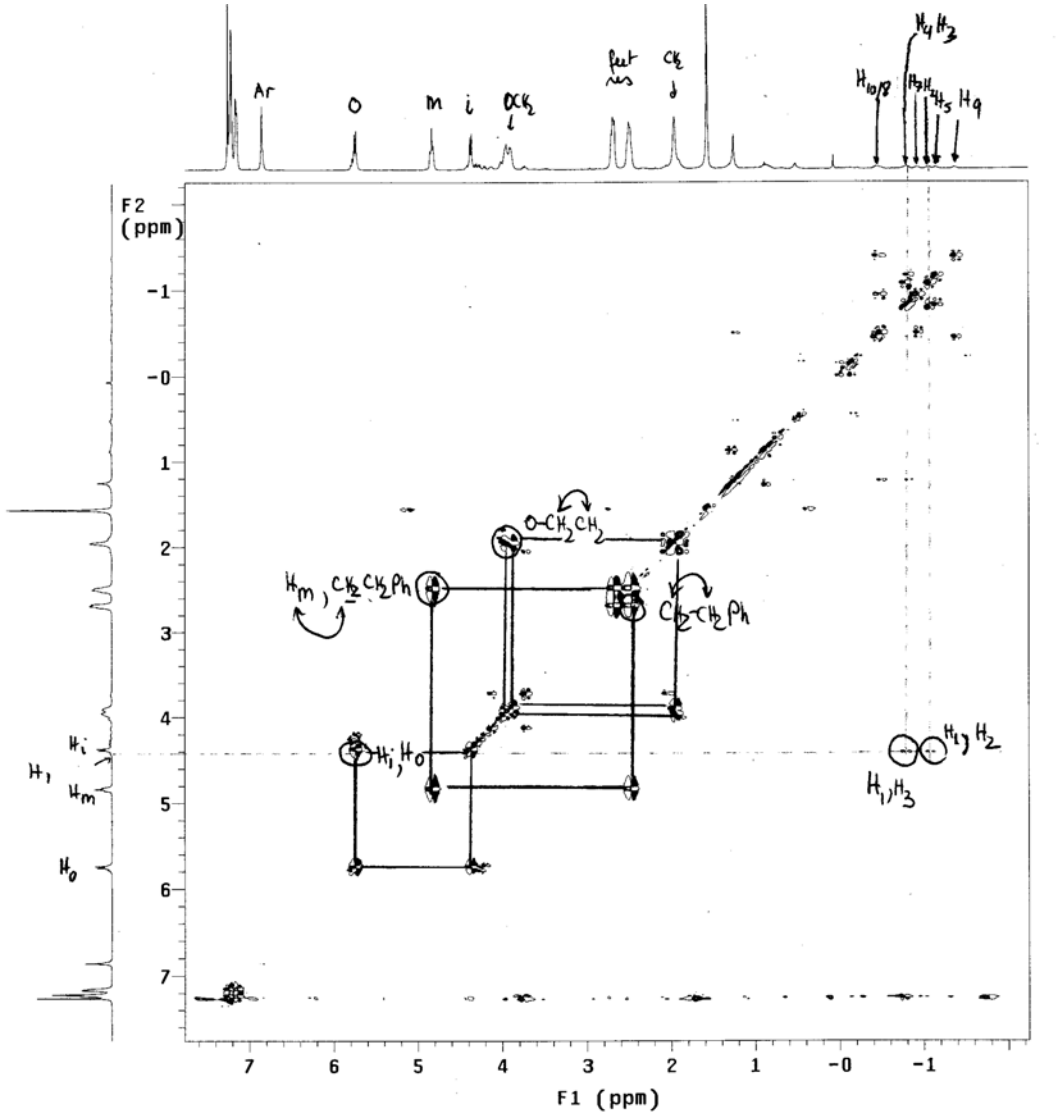
3.12. Full spectrum Figure 1c.

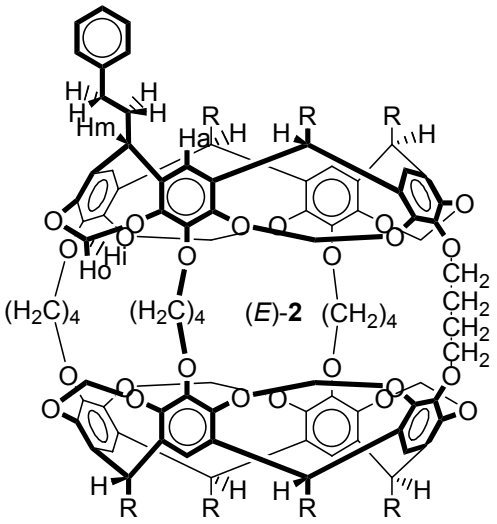


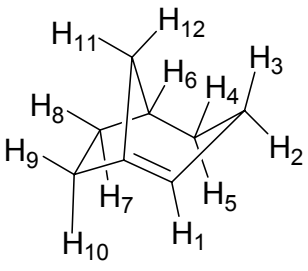
3.13. Full spectrum Figure 1d.



3.14.1. DQCOSY (400 MHz; $CDCl_3$, 15 ^oC) of a solution containing 64 % **5**⊙(*Z*)-**2**.

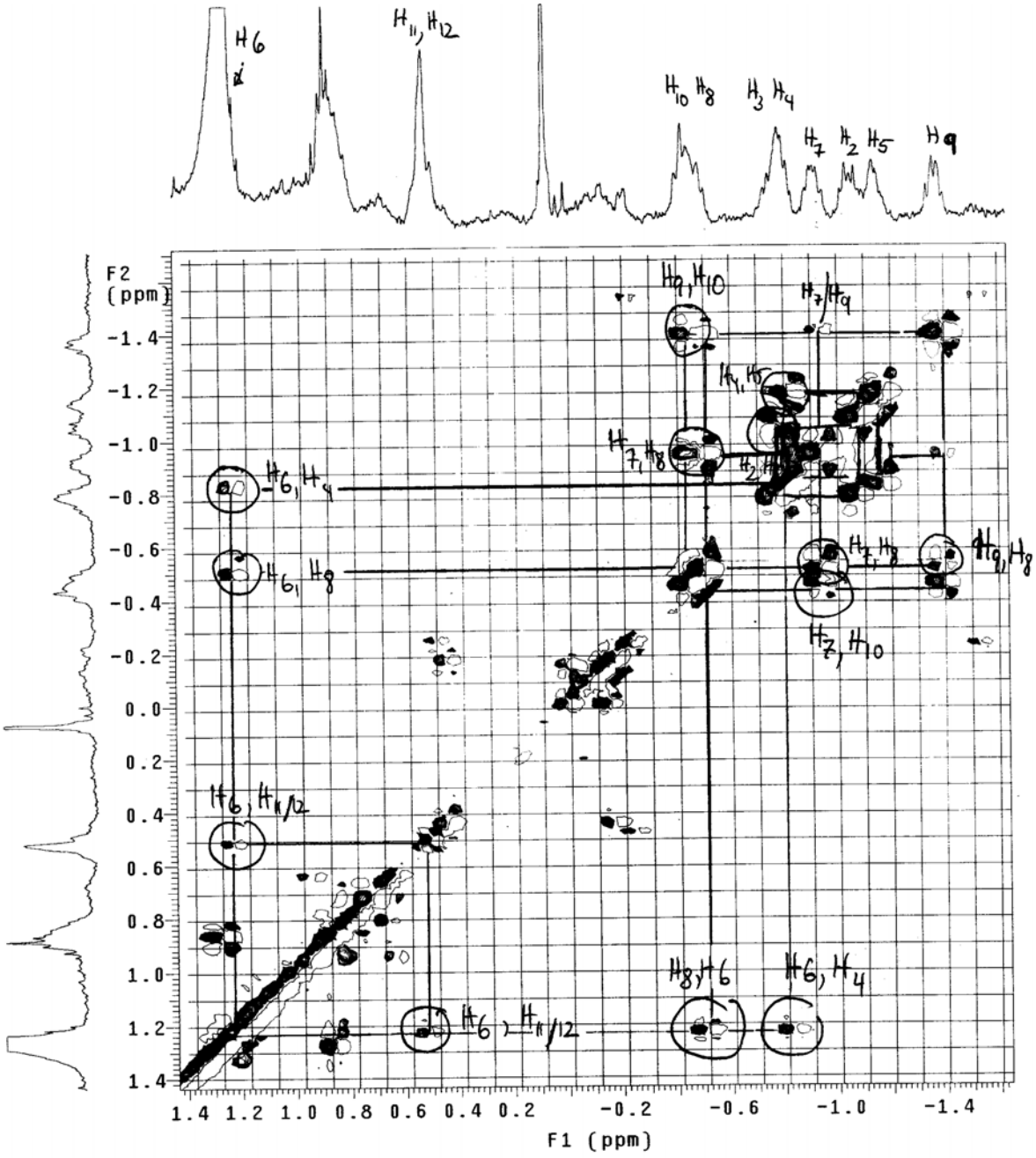


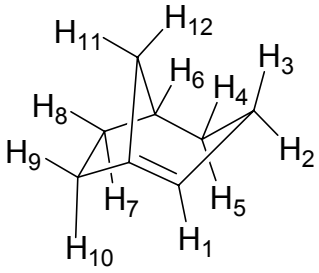




H1 = 4.41 ppm H7 = -0.91ppm
H2 = -1.03 ppm H8 = -0.47 ppm
H3 = -0.74 ppm H9 = -1.34 ppm
H4 = -0.79 ppm H10 = -0.41 ppm
H5 = -1.14 ppm H11 = 0.52 ppm
H6 = 1.24 ppm H12 = 0.52 ppm

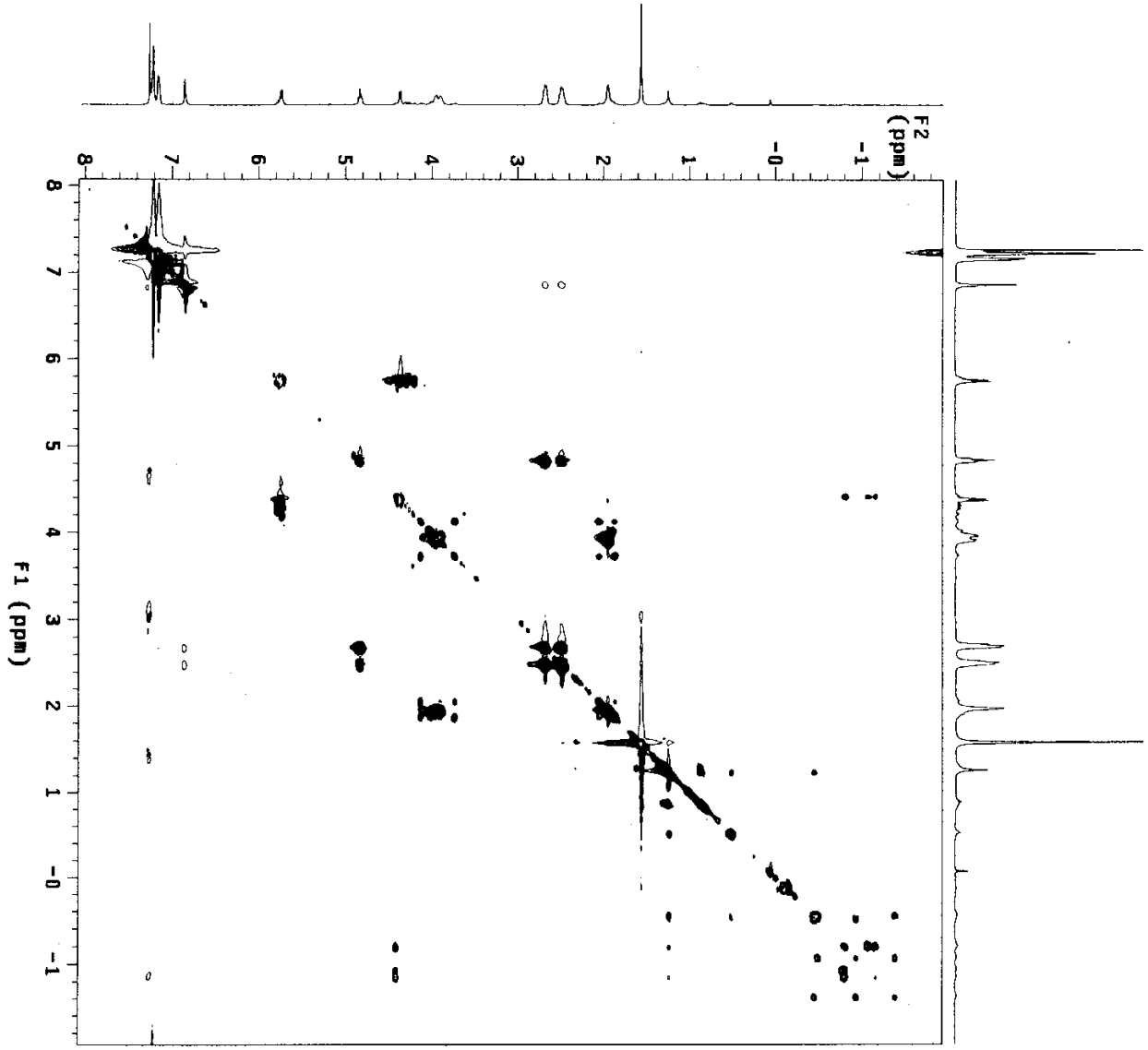
3.14.2. Partial DQCOSY (400 MHz; $CDCl_3$, 15 °C) of a solution containing 64 % **5**⊙(*Z*)-**2**.

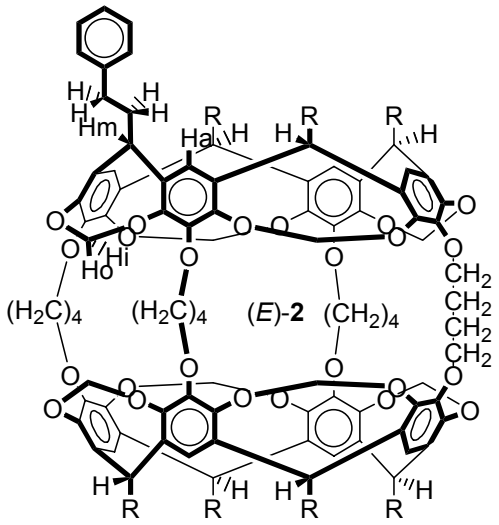


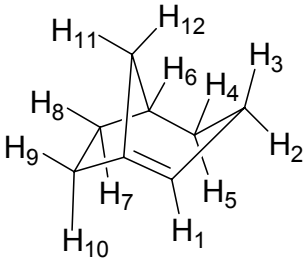


(*E*)-**2**

3.15.1. TOCSY (400 MHz; $CDCl_3$, 15 °C, t_{mix} = 60 msec) of a solution containing 64 % **5**⊙(*Z*)-**2**.

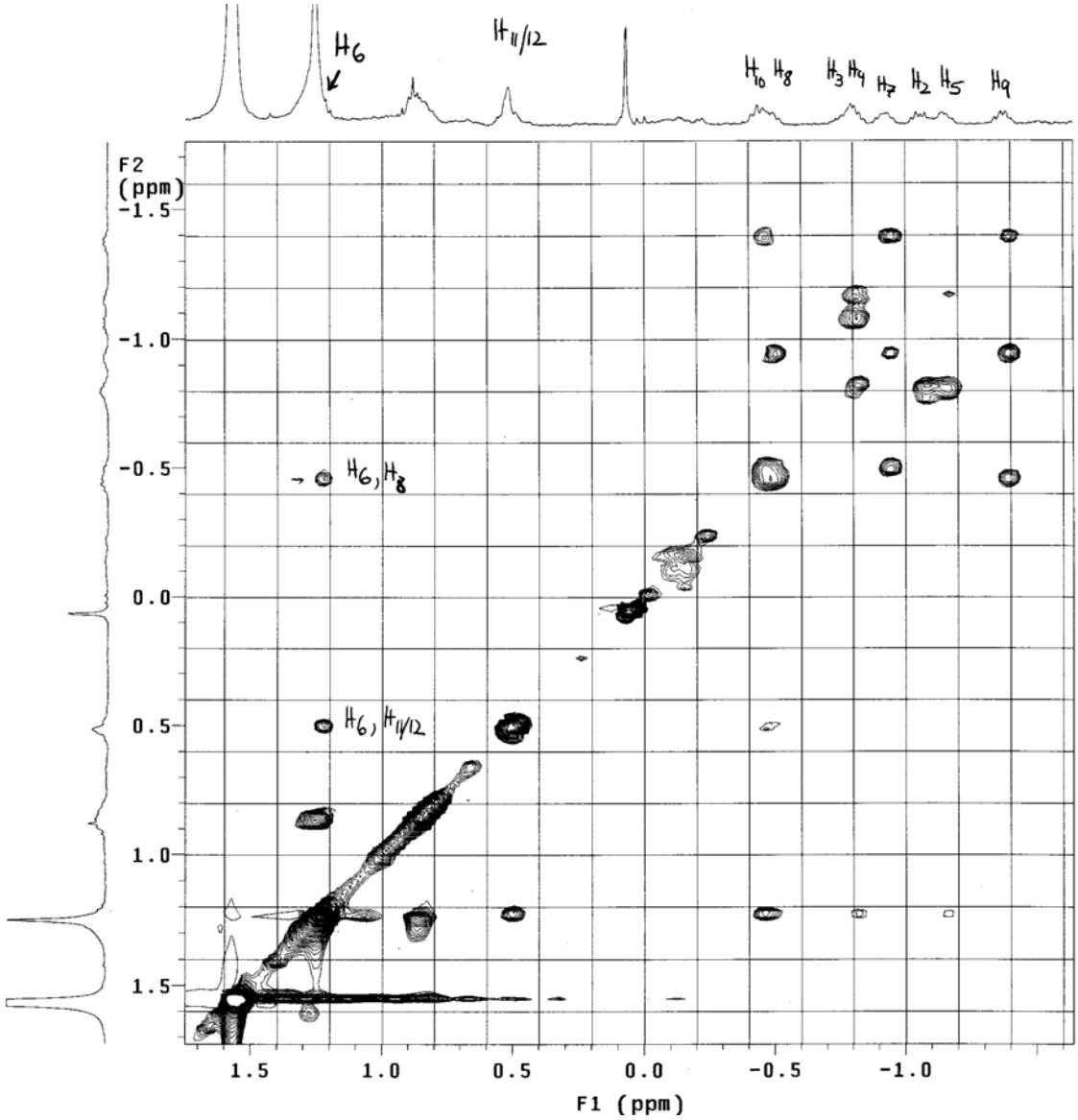


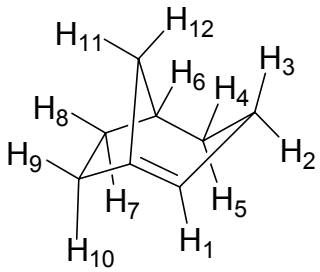




H1 = 4.41 ppm	H7 = -0.91ppm
H2 = -1.03 ppm	H8 = -0.47 ppm
H3 = -0.74 ppm	H9 = -1.34 ppm
H4 = -0.79 ppm	H10 = -0.41 ppm
H5 = -1.14 ppm	H11 = 0.52 ppm
H6 = 1.24 ppm	H12 = 0.52 ppm

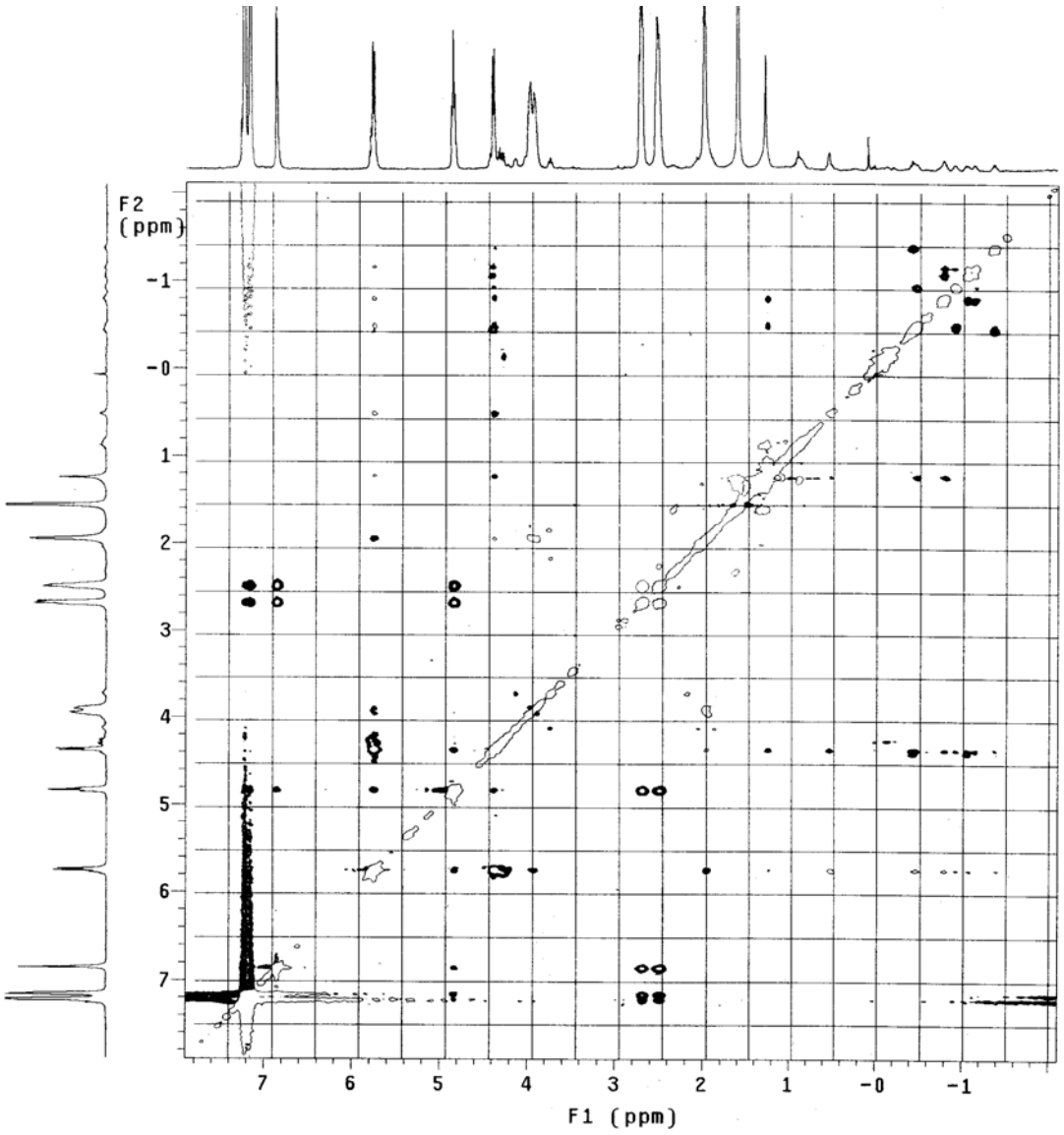
3.15.2. Partial TOCSY (400MHz; $CDCl_3$, 15°C, t_{mix} = 60 msec) of a solution containing 64% **5**⊙(*Z*)-**2**.

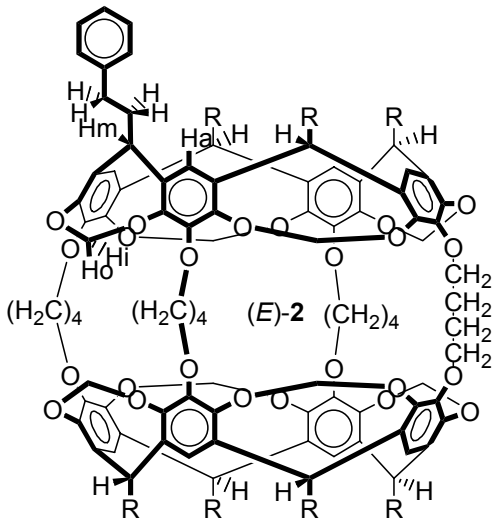




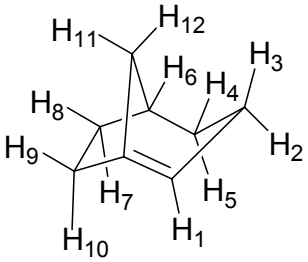
(*E*)-**2**

3.16.1. ROESY (400 MHz; $CDCl_3$, 15 °C, t_{mix} = 600 msec) of a solution containing 64 % **5**⊙(*Z*)-**2**.



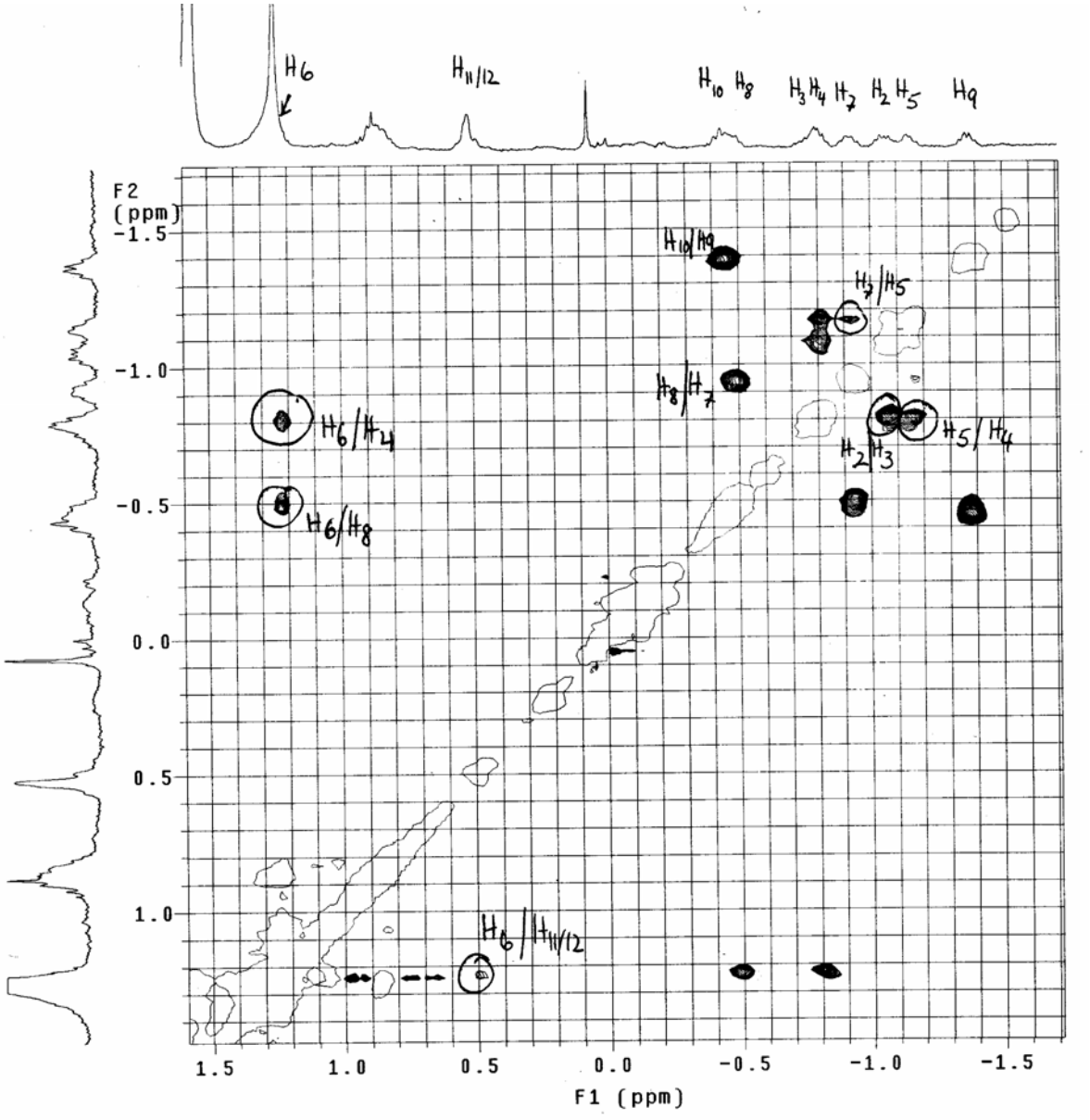


R = $CH_2CH_2C_6H_5$ **5**⊙(*E*)-**2**

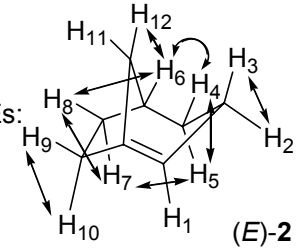


H1 = 4.41 ppm	H7 = -0.91ppm
H2 = -1.03 ppm	H8 = -0.47 ppm
H3 = -0.74 ppm	H9 = -1.34 ppm
H4 = -0.79 ppm	H10 = -0.41 ppm
H5 = -1.14 ppm	H11 = 0.52 ppm
H6 = 1.24 ppm	H12 = 0.52 ppm

3.16.2. Partial ROESY (400 MHz; $CDCl_3$, 15 °C, t_{mix} = 600 msec) of a solution containing 64 % **5**⊙(*Z*)-**2**.

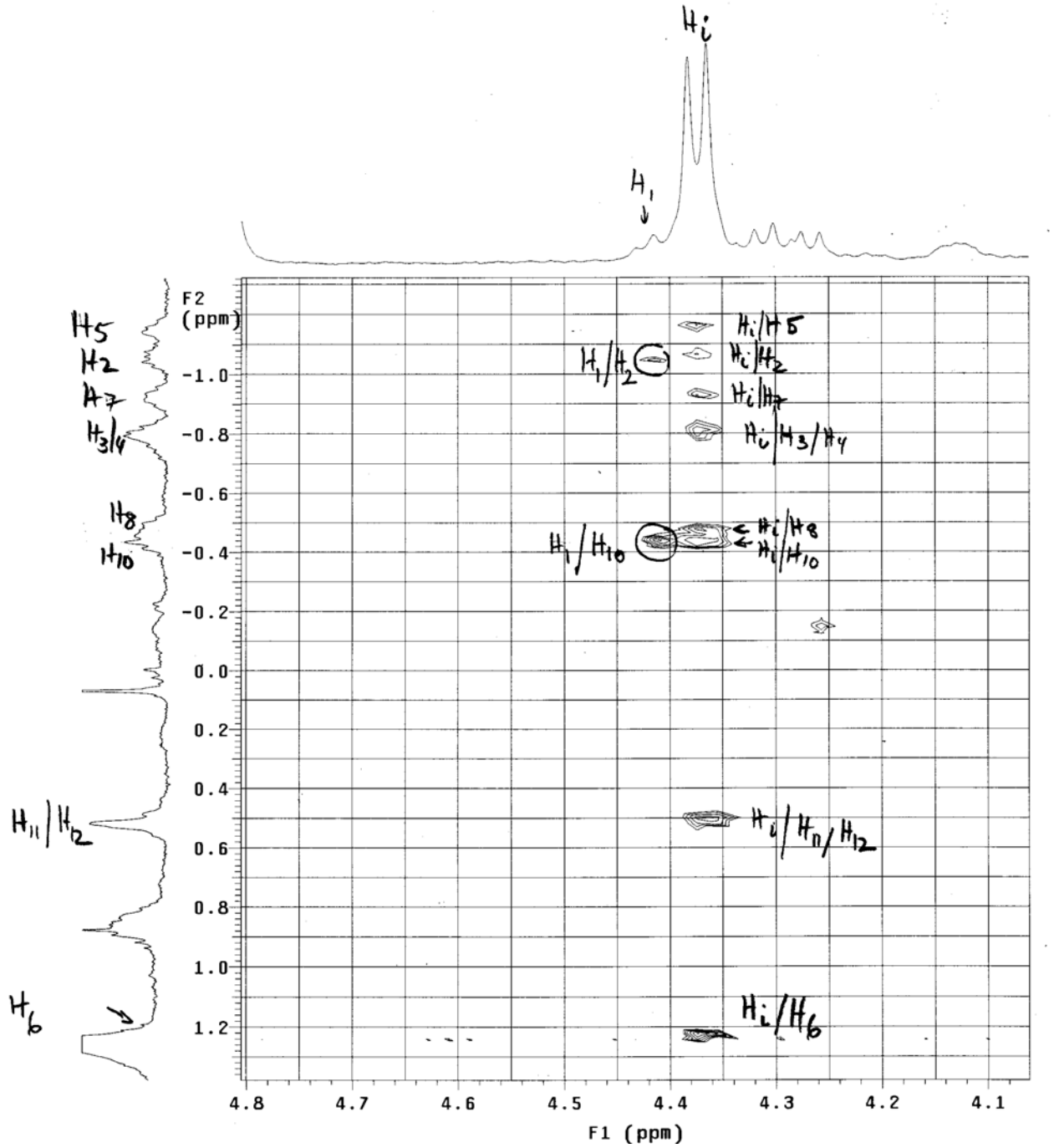


observed NOEs:

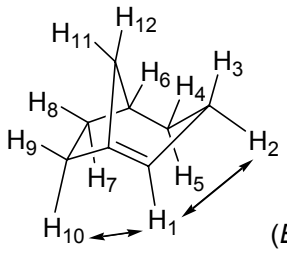


(*E*)-**2**

3.16.2. Partial ROESY (400 MHz; $CDCl_3$, 15 °C, t_{mix} = 600 msec) of a solution containing 64 % **5**⊙(*Z*)-**2**.

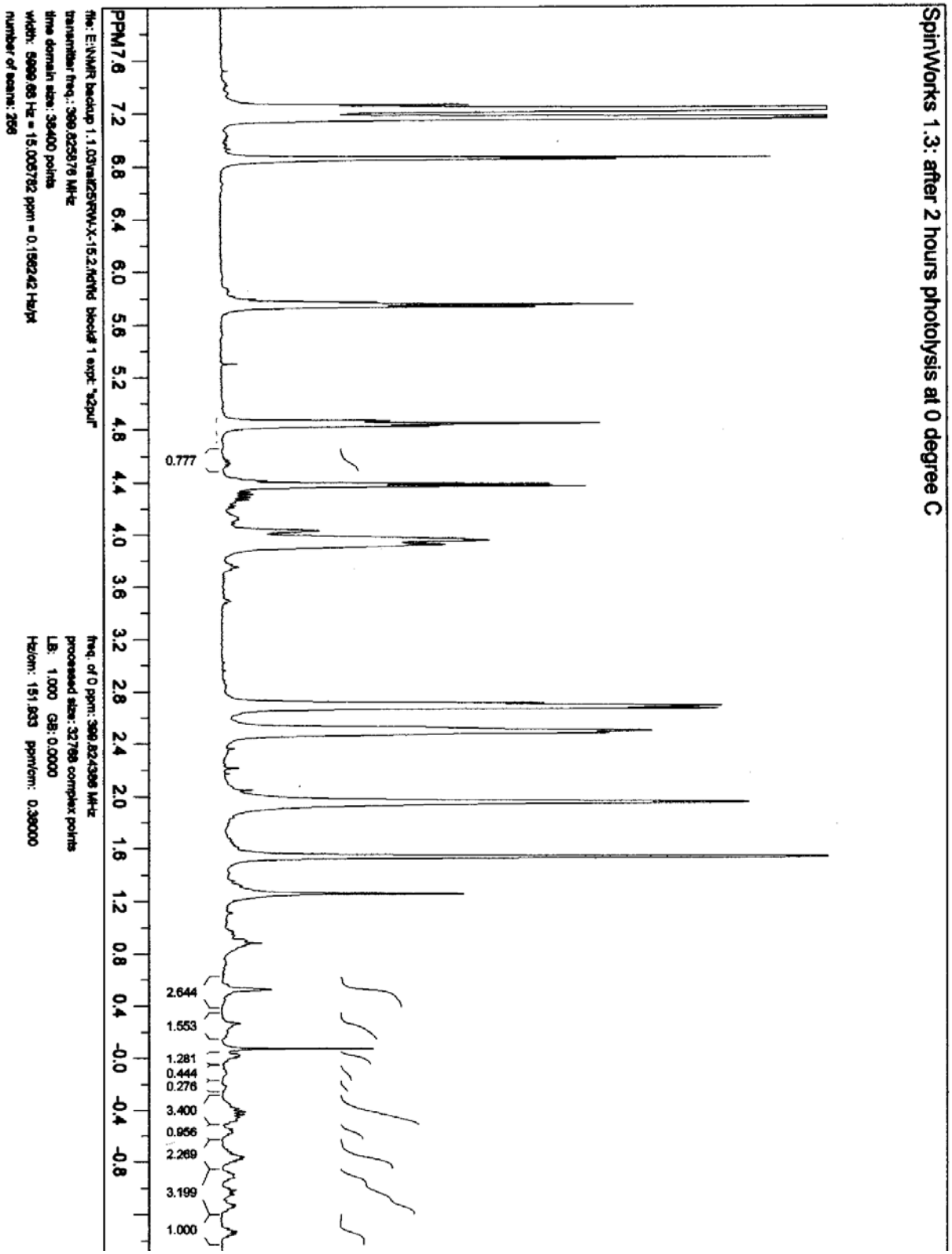


observed NOEs:

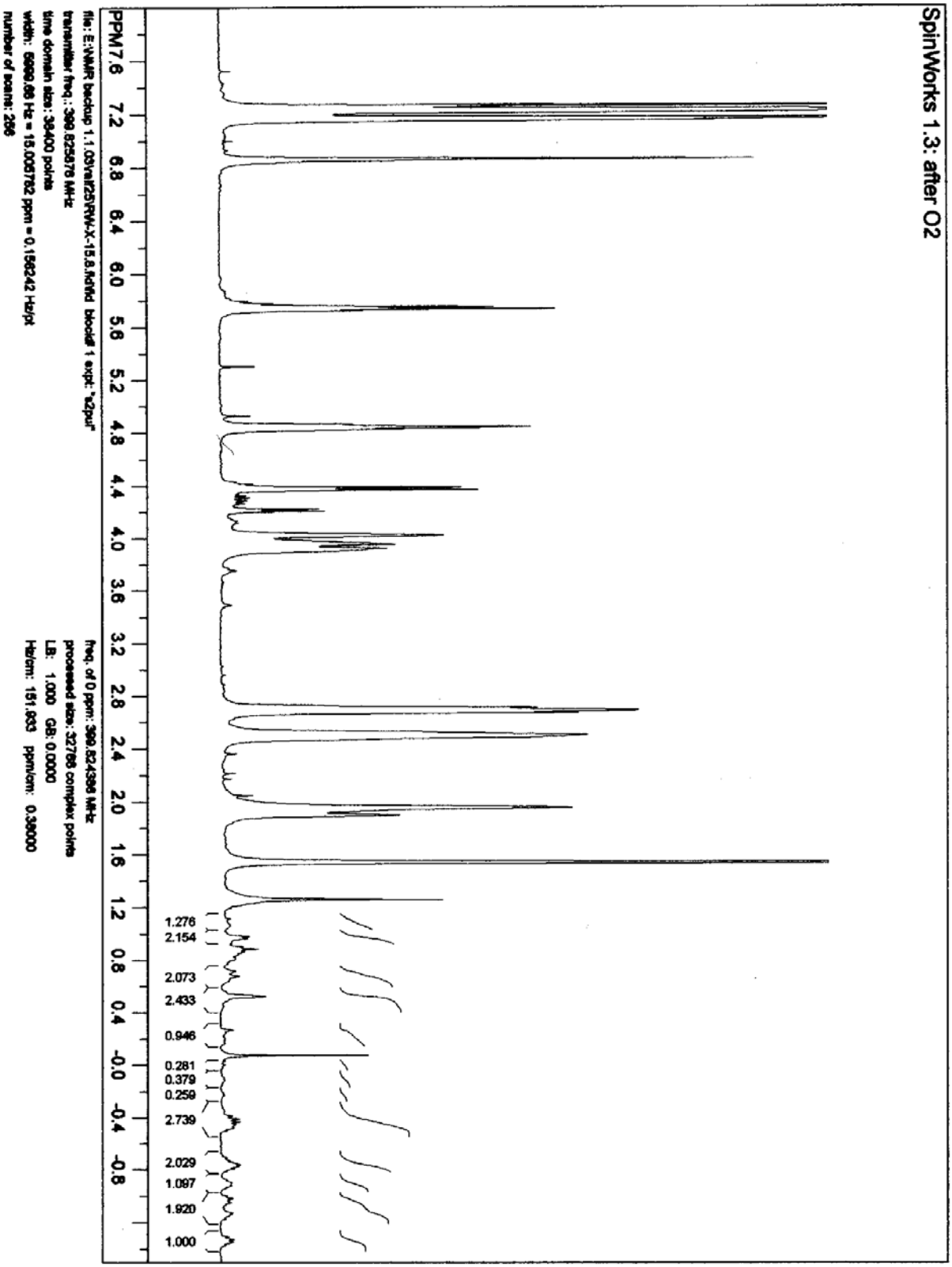


(*E*)-**2**

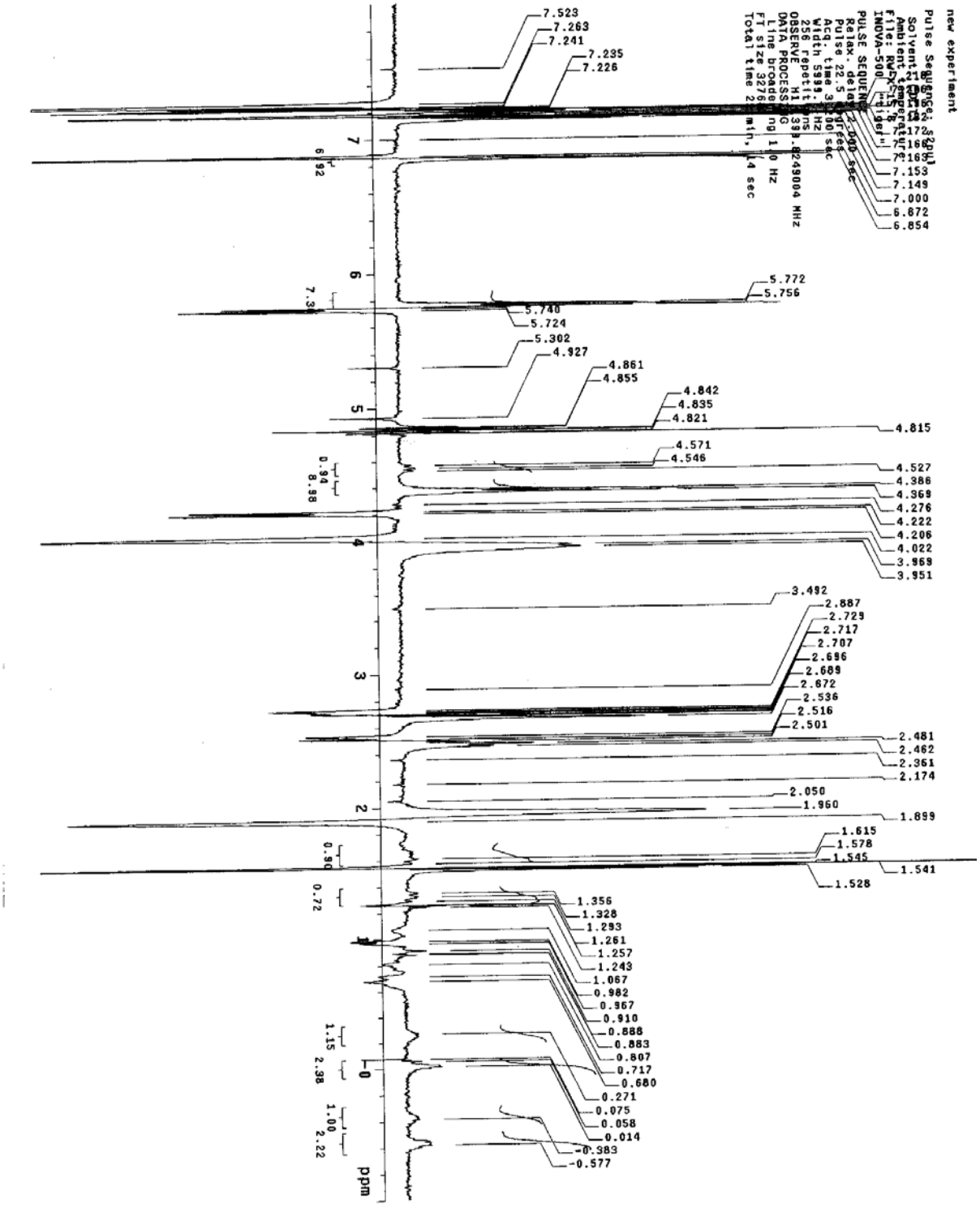
3.17. ^{1}H NMR spectrum (400 MHz; $CDCl_3$, 23 ^{o}C) of a solution containing **5⊙1** (23 %), **5⊙**(*Z*)-**2** (54 %), and **5⊙10** (15 %) (Full spectrum Figure 1a).



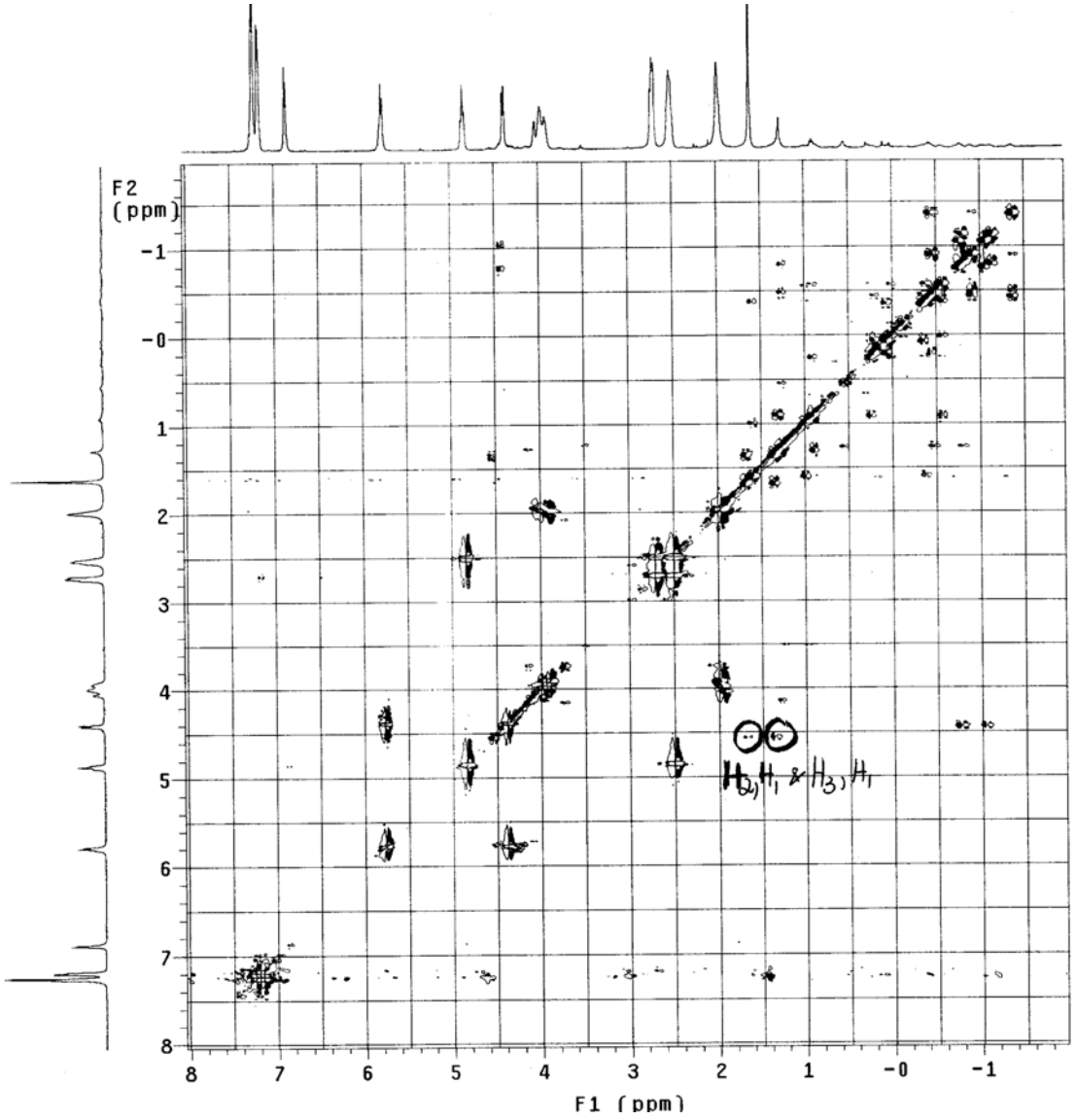
3.18. Full spectrum Figure 1b.

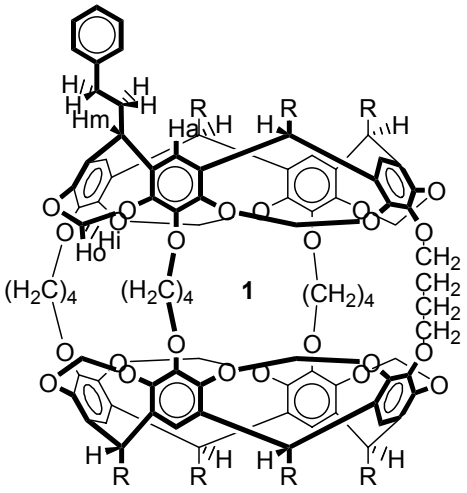


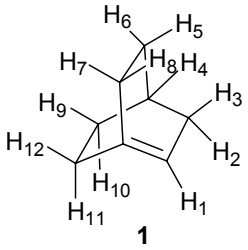
3.19. Difference spectrum between spectra 3.17. and 3.18. (Full spectrum Figure 1c). Signals pointing up or down are assigned to hemicarceplexes **5⊙1** or **5⊙11**, respectively.



3.20.1. DQCOSY (400 MHz; $CDCl_3$, 12 °C) of a solution containing **5⊙1** (23 %), **5⊙**(*Z*)-**2** (54 %), and **5⊙10** (15 %).

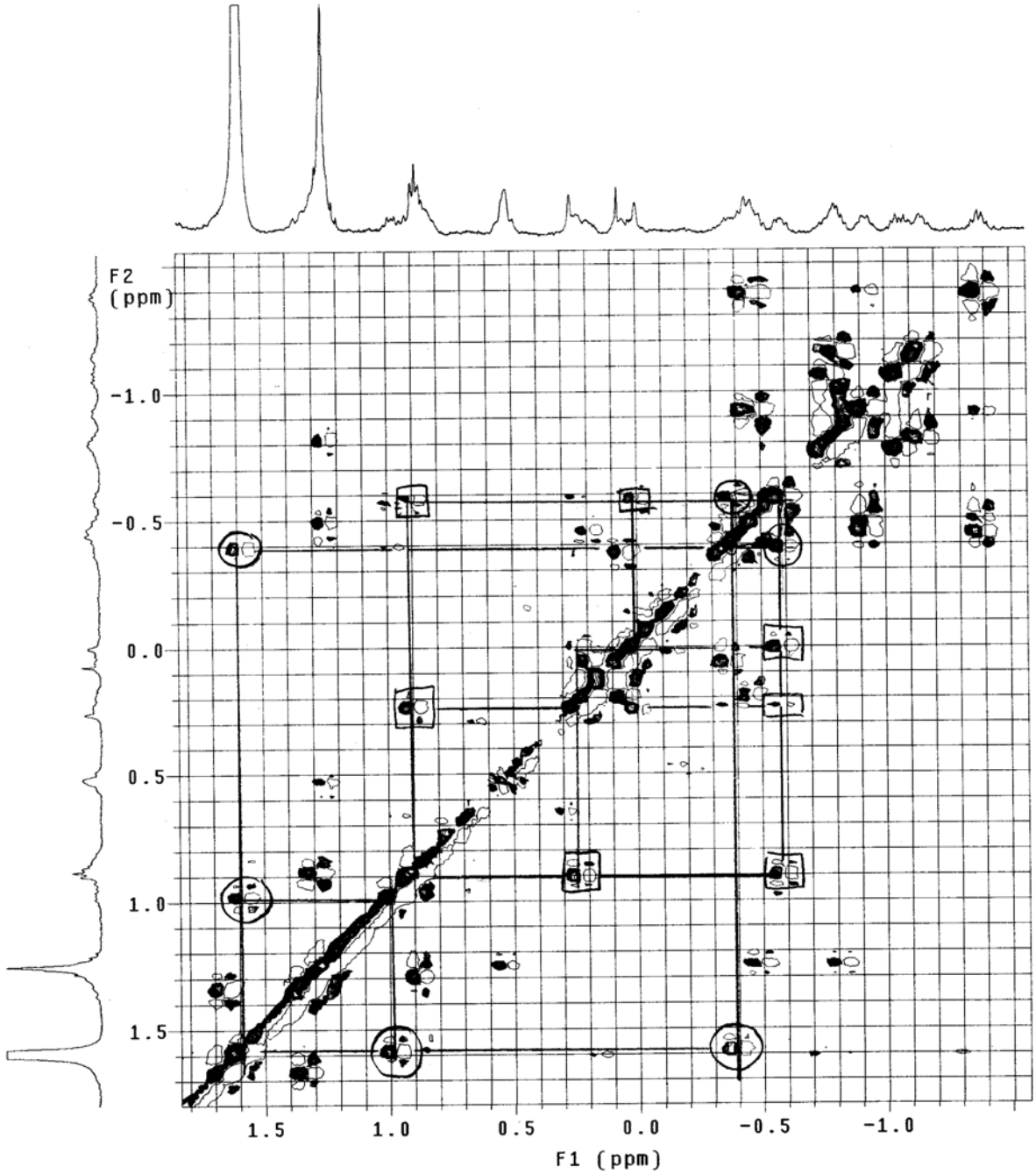


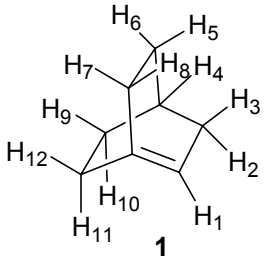




H1 = 4.55 ppm
H2, H3 = 1.33, 1.65 ppm
H4 = 0.01 ppm
H5, H6, H9, H10 = 1.58, 0.97, 0.01. -0.57 ppm
H7, H8, H11, H12 = 0.27, 0.91, -0.38. -0.59 ppm

3.20.2. Partial DQCOSY (400 MHz; $CDCl_3$, 12 ^oC) of a solution containing **5⊙1** (23 %), **5⊙(*Z*)-2** (54 %), and **5⊙10** (15 %).

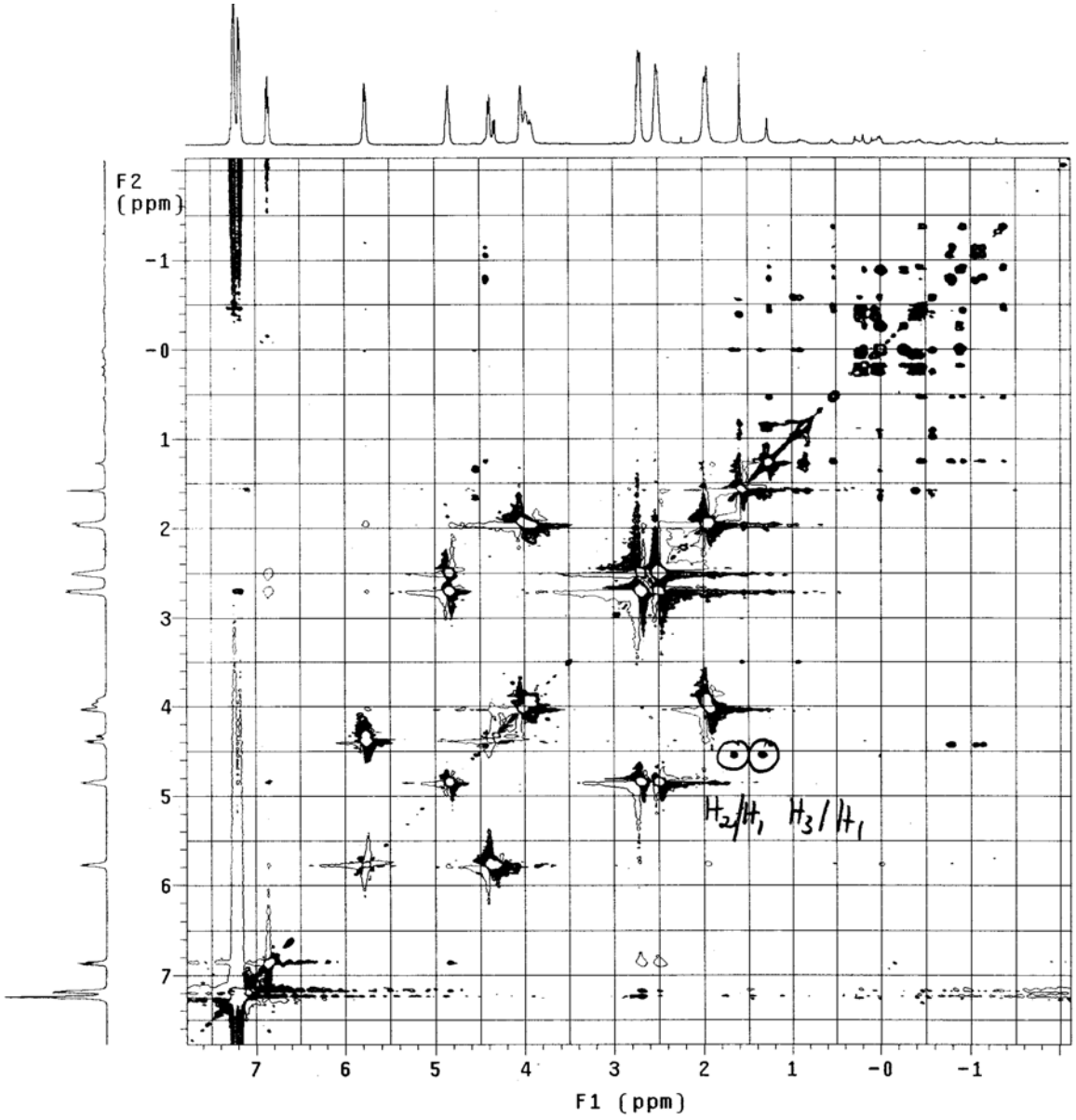


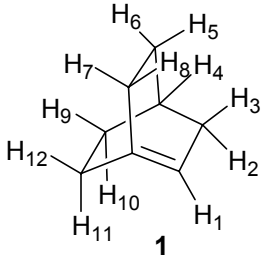


1

H1 = 4.55 ppm
H2, H3 = 1.33, 1.65 ppm
H4 = 0.01 ppm
H5, H6, H9, H10 = 1.58, 0.97, 0.01. -0.57 ppm
H7, H8, H11, H12 = 0.27, 0.91, -0.38. -0.59 ppm

3.21.1.TOCSY (400 MHz; $CDCl_3$, 15 ^oC, t_{mix} = 100 msec) of a solution containing **5⊙1** (18 %), **5⊙**(*Z*)-**2** (29 %), **5⊙10** (23 %) and **5⊙10** (23 %).

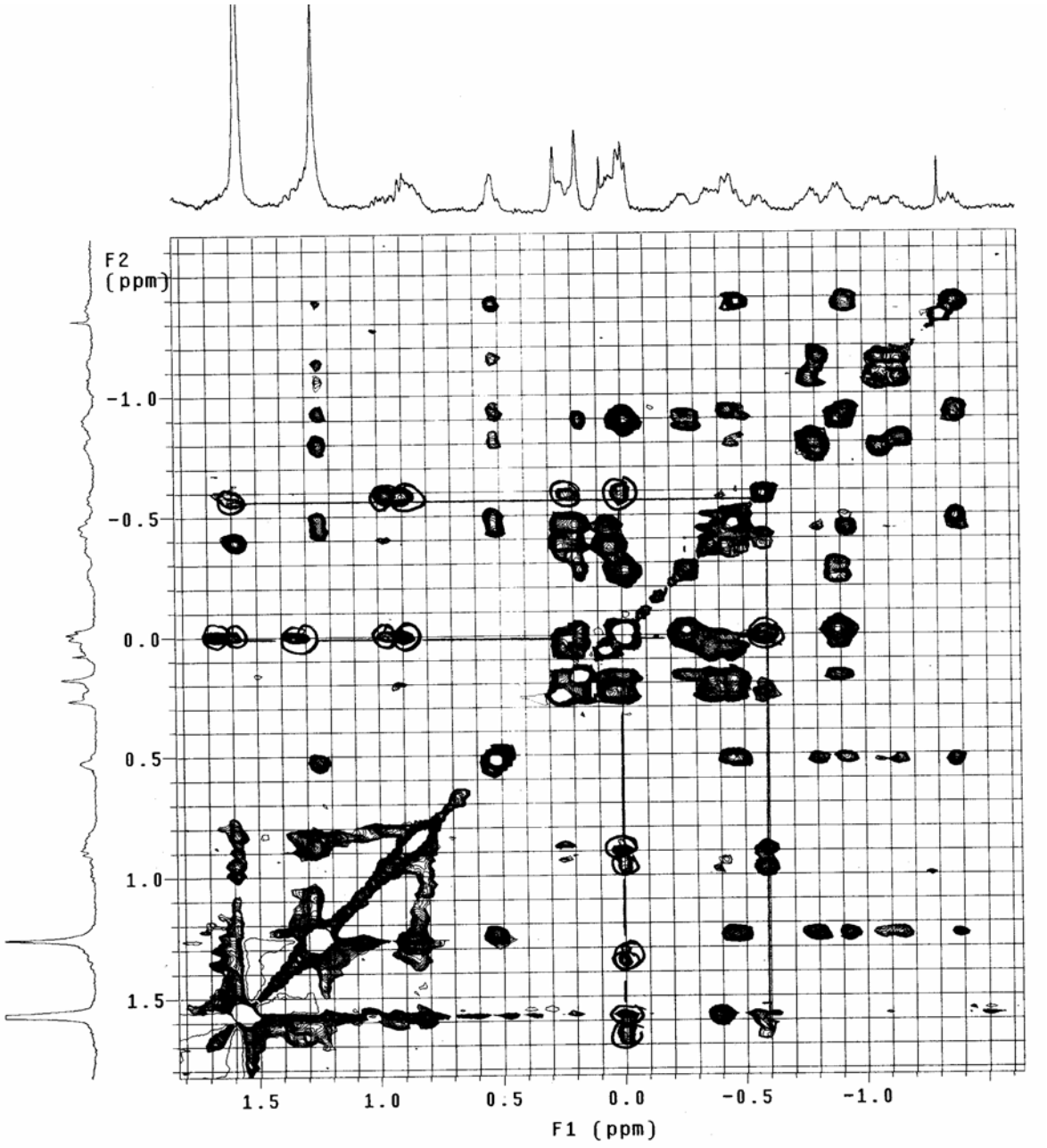


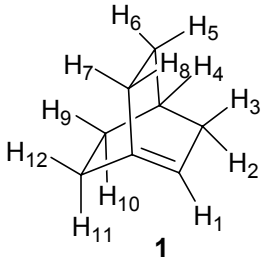


1

H1 = 4.55 ppm
H2, H3 = 1.33, 1.65 ppm
H4 = 0.01 ppm
H5, H6, H9, H10 = 1.58, 0.97, 0.01. -0.57 ppm
H7, H8, H11, H12 = 0.27, 0.91, -0.38. -0.59 ppm

3.21.2.Partial TOCSY (400 MHz; $CDCl_3$, 15 ^oC, t_{mix} = 100 msec) of a solution containing **5⊙1** (18 %), **5⊙**(*Z*)-**2** (29 %), **5⊙10** (23 %) and **5⊙10** (23 %).

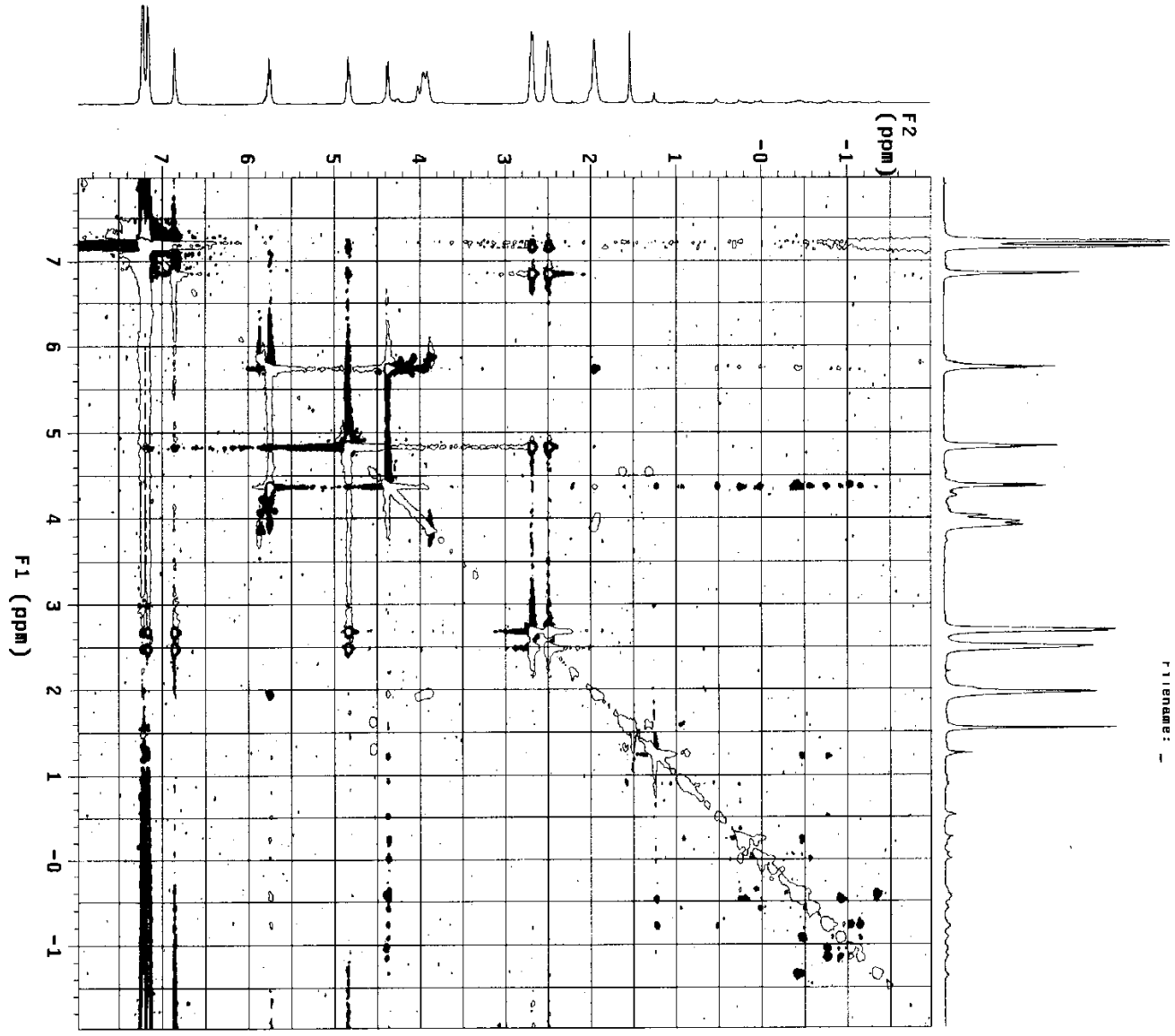


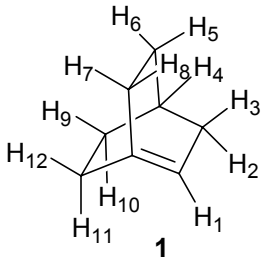


1

H1 = 4.55 ppm
H2, H3 = 1.33, 1.65 ppm
H4 = 0.01 ppm
H5, H6, H9, H10 = 1.58, 0.97, 0.01. -0.57 ppm
H7, H8, H11, H12 = 0.27, 0.91, -0.38. -0.59 ppm

3.22.1. ROESY (400 MHz; $CDCl_3$, 12 °C, t_{mix} = 600 msec) of a solution containing **5⊙1** (23 %), **5⊙**(*Z*)-**2** (54 %), and **5⊙10** (15 %).

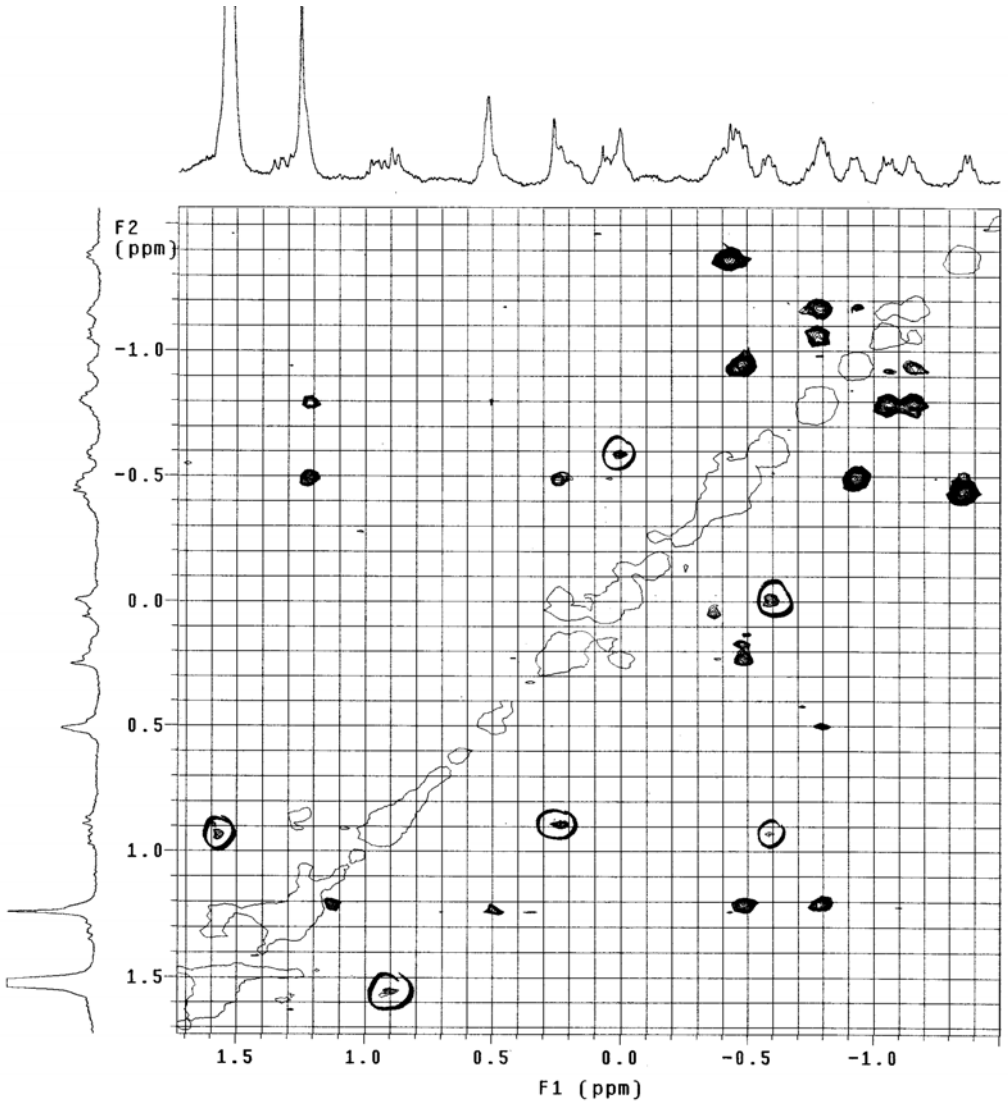


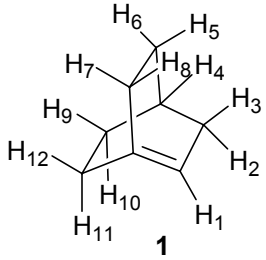


1

H1 = 4.55 ppm
H2, H3 = 1.33, 1.65 ppm
H4 = 0.01 ppm
H5, H6, H9, H10 = 1.58, 0.97, 0.01. -0.57 ppm
H7, H8, H11, H12 = 0.27, 0.91, -0.38. -0.59 ppm

3.22.2. Partial ROESY (400 MHz; $CDCl_3$, 12 °C, t_{mix} = 600 msec) of a solution containing **5⊙1** (23 %), **5⊙**(*Z*)-**2** (54 %), and **5⊙10** (15 %).





1

H1 = 4.55 ppm
H2, H3 = 1.33, 1.65 ppm
H4 = 0.01 ppm
H5, H6, H9, H10 = 1.58, 0.97, 0.01. -0.57 ppm
H7, H8, H11, H12 = 0.27, 0.91, -0.38. -0.59 ppm

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