Supporting Information

Contents

Reference 13c

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Experimental Part

General remarks

All commercially available chemicals were reagent grade and used without further purification. Solvents were purified and dried according to standard procedures. Mass spectra were recorded with a Waters Q-TOF Ultima (ESI), Varian 1200L triple-quadrupole GC/MS (electron-impact or chemical ionizations, reagent gas: NH_3), or Shimadzu Axima-CFR plus (MALDI-TOF) instruments. High-resolution mass spectra (ESI) were calibrated using phosphoric acid as the lock-mass correction channel with Waters MassLynx software. NMR spectra were measured on a Bruker Avance DPX-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) or Bruker DRX-600 (^{1}H: 600 MHz, ^{13}C: 150 MHz) spectrometers at 25 °C and referenced to poly(dimethylsiloxane) (δ_H = 0.07 ppm, δ_C = 1.04 ppm)[1] initially present in the commercial $CDCl_3$. Multiplicities of ^{13}C NMR signals were determined by means of DEPT135 or HSQC experiments. NMR solvents $CDCl_3$ and CD_2Cl_2 were purified by passing through a bed of basic Al_2O_3. Melting points were determined in open-end capillary tubes with a melting point instrument (Edmund Bühler Sp6) and have been corrected. Combustion analyses were performed with a Thermo Scientific Flash 2000 Organic Elemental Analyzer. Unless stated otherwise, the yields refer to the products containing only trace amounts of solvents or impurities, as judged by ^{1}H NMR spectroscopy. The syntheses and the characterization data of compounds **1–3**, **7a** and **7b** have been reported in a recent communication.[2] 1,1,1-Triphenylethane (**9**),[3,4] 1,1,1-triphenyl-2,2-dimethylpropane (**10**),[4] 1,3,5-triphenyladamantane (**15**)[5] and 1,3,5-tris(aminomethyl)-2,4,6-triethylbenzene (**23**)[6] were synthesized according to published procedures.

Synthesis of ligand 6

2-Benzyloxy-4-iodo-3-methoxymethoxypyridine (4): 2-Benzyloxy-3-methoxymethoxy-pyridine (**1**, 2.45 g, 10.0 mmol)[2] was degassed by stirring in vacuo, anhyd. THF (90 mL) was added, and the solution was cooled to −80 °C. *t*BuLi (1.7 M in hexanes, 11.8 mL, 20.0 mmol) was slowly added within 20 min, while the temperature was kept below −80 °C. The reaction mixture was stirred for another 30 min at −80 °C before a solution of iodine (5.08 g, 20.0 mmol) in anhyd. THF (20 mL) was added slowly within 30 min. The reaction mixture was stirred for 30 min at −80 °C, allowed to warm to room temperature, and stirred for 60 min. A saturated aqueous NH_4Cl solution (150 mL) and Et_2O (60 mL) were added; the phases were separated, and the aqueous phase was additionally extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with 10% aq. $Na_2S_2O_3$, water, and brine, and then dried over anhyd. Na_2SO_4. The solvents were removed in vacuo and the crude product was purified by column chromatography (SiO_2; eluent: CH_2Cl_2–cyclohexane 70:30 to 80:20), to give **4** as a colorless oil (2.41 g, 65%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.59 (s, 3H), 5.22 (s, 2H), 5.41 (s, 2H), 7.30 (d, 2H, ^3J = 5.3 Hz), 7.32–7.45 (m, 5H), 7.54 (d, 2H, ^3J = 5.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 58.6 (CH_3), 68.4 (CH_2), 98.5 (CH_2), 102.4 (C_q), 127.6 (CH), 128.1 (CH), 128.2 (CH), 128.6 (CH), 136.9 (C_q), 141.6 (CH), 141.7 (C_q), 156.0 (C_q); MS (ESI$^+$): *m*/*z* (%) = 410 (16) $[M + K]^+$, 394 (23) $[M + Na]^+$, 372 (63) $[M + H]^+$, 340 (27) $[M - OMe]^+$, 250 (100) $[M - OMe - OBn]^{\bullet+}$; HRMS (ESI$^+$): *m*/*z* = 372.0094 $[M + H]^+$; calcd. for $[C_{14}H_{14}NIO_3 + H]^+$: 372.0097.

2-Benzyloxy-4-(3-formylphenyl)-3-methoxymethoxypyridine (5): A mixture of **4** (1.36 g, 3.66 mmol), 3-formylphenylboronic acid (686 mg, 4.58 mmol), $Pd(PPh_3)_4$ (0.18 mmol, 211 mg), toluene (40 mL), EtOH (4.0 mL), and aq. K_2CO_3 solution (2M, 4.0 mL) was thoroughly degassed and then heated at reflux temperature, under nitrogen atmosphere, for 24 h. After cooling, the mixture was diluted with water and Et_2O (40 mL each), the phases were separated, and the aqueous phase was additionally extracted with Et_2O (40 mL). The combined organic phases were washed with water and brine, dried over anhyd. Na_2SO_4, evaporated, and the residue was purified by flash chromatography (SiO_2; eluent: CH_2Cl_2–cyclohexane 90:10 to 100:0), to give **5** (1.21 g, 95%) as a pale-yellow oil, which solidified upon cooling; m.p. < 25 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.92 (s, 3H), 4.97 (s, 2H), 5.49 (s, 2H), 6.94 (d, ^3J = 5.2 Hz, 1H), 7.32–7.40 (m, 3H), 7.47–7.49 (m, 2H), 7.62 (app t, ^3J = 7.7 Hz, 1H), 7.86–7.89 (m, 1H), 7.90–7.93 (m, 1H), 7.99 (d, ^3J = 5.2 Hz, 1H), 8.10 (m,

1H), 10.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 57.1 (CH_3), 68.3 (CH_2), 98.4 (CH_2), 118.5 (CH), 128.0 (CH), 128.1 (CH), 128.6 (CH), 129.1 (CH), 131.0 (CH), 135.5 (CH), 136.6 (C_q), 137.2 (C_q), 137.5 (C_q), 137.8 (C_q), 141.4 (CH), 142.3 (C_q), 157.6 (C_q), 192.1 (CH); HRMS (ESI$^+$): m/z = 350.1376 $[M + H]^+$; calcd. for $[C_{21}H_{19}NO_4 + H]^+$: 350.1392.

4-(3-Formylphenyl)-3-hydroxy-2(1H)-pyridone (6): A solution of **5** (1.20 g, 3.43 mmol) in a mixture of anhyd. CH_2Cl_2 (15 mL) and trifluoroacetic acid (15 mL) was stirred at room temperature under inert atmosphere for 18 h. The volatiles were removed in vacuo, and the residue was co-evaporated with toluene (3 × 10 mL), suspended in CH_2Cl_2 (15 mL), sonicated, and filtered. The solid was washed with CH_2Cl_2, Et_2O, and dried in vacuo, to give **6** (557 mg, 75%) as a white solid, decomp. without melting above 200 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 6.33 (d, ^3J = 6.9 Hz, 1H), 6.98 (d, ^3J = 6.9 Hz, 1H), 7.67 (app t, ^3J = 7.7 Hz, 1H), 7.89 (d, ^3J = 7.6 Hz, 1H), 7.97 (d, ^3J = 7.7 Hz, 1H), 8.19 (s, 1H), 9.24 (br s, 1H), 10.06 (s, 1H), 11.84 (br s, 1H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 106.4 (CH), 123.4 (CH), 125.0 (C_q), 128.6 (CH), 129.1 (CH), 129.7 (CH), 134.5 (CH), 136.1 (C_q), 136.8 (C_q), 143.7 (C_q), 158.6 (C_q), 190.2 (CH); HRMS (ESI$^+$): m/z = 216.0670 $[M + H]^+$; calcd. for $[C_{12}H_9NO_3 + H]^+$: 216.0661.

Synthesis of the metallamacrocyclic trialdehydes 7a–c, 8a and 8b

General procedure: A mixture of ligand **3** or **6** (1.00 mmol), [(arene)$RuCl_2]_2$ (0.50 mmol), and Cs_2CO_3 (652 mg, 2.00 mmol) in CH_2Cl_2 (25 mL) and MeOH (25 mL) was stirred at room temperature under inert atmosphere for 18 h. The solution was filtered, and the filtrate was concentrated at 50 °C under reduced pressure until onset of crystallization. The suspension was cooled at +4 °C overnight, and the crystallized product was collected, washed with cold methanol several times, and dried in vacuo. The characterization data of **7a** and **7b,** as well as the structure of the latter (from single-crystal X-ray diffraction data) have been reported elsewhere.[2]

Metallamacrocycle 7c: Yield 70%; orange microcrystalline solid; decomp. without melting at 235 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (d, ^3J = 6.9 Hz, 27H), 1.40 (d, ^3J = 6.9 Hz, 27H), 3.03 (sept, ^3J = 6.9 Hz, 9H), 4.90 (s, 9H), 5.91 (d, ^3J = 6.8 Hz, 3H), 6.41 (d, ^3J = 6.7 Hz, 3H), 10.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9 (CH_3), 23.4 (CH_3), 31.2 (CH), 68.1 (CH), 104.5 (CH), 110.3 (C_q), 121.6 (C_q), 131.5 (CH), 165.0 (C_q), 174.7 (C_q),

190.4 (CH); HRMS (ESI$^+$): m/z = 1329.3158 $[M + H]^+$; calcd. for $[C_{63}H_{81}N_3O_9Ru_3 + H]^+$: 1329.3224; anal. calcd. (%) for $C_{63}H_{81}N_3O_9Ru_3$ (1327.54): C 57.00, H 6.15, N 3.17; found: C 56.72, H 6.32, N 3.28; crystallographic data: see Table S1.

Metallamacrocycle 8a: Yield 79%; brown amorphous solid, decomp. without melting at 174–175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (d, ^3J = 6.9 Hz, 9H), 1.40 (d, ^3J = 6.9 Hz, 9H), 2.17 (s, 9H), 2.86 (sept, ^3J = 6.9 Hz, 3H), 5.12 (d, ^3J = 5.7 Hz, 3H), 5.34 (d, ^3J = 5.7 Hz, 3H), 5.45 (d, ^3J = 5.7 Hz, 3H), 5.72 (d, ^3J = 5.7 Hz, 3H), 5.95 (d, ^3J = 6.6 Hz, 3H), 6.71 (d, ^3J = 6.6 Hz, 3H), 7.43 (app t, ^3J = 7.7 Hz, 3H), 7.66 (d, ^3J = 7.6 Hz, 3H), 8.09 (d, ^3J = 7.9 Hz, 3H), 8.54 (s, 3H), 10.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8 (CH_3), 23.0 (CH_3), 23.2 (CH_3), 31.4 (CH), 77.3 (CH), 79.5 (CH), 82.3 (CH), 82.7 (CH), 97.1 (C_q), 98.2 (C_q), 109.8 (CH), 123.3 (C_q), 126.7 (CH), 128.4 (CH), 130.8 (CH), 131.7 (CH), 134.1 (CH), 136.1 (C_q), 139.6 (C_q), 155.2 (C_q), 171.9 (C_q), 193.3 (CH); HRMS (ESI$^+$): m/z = 1347.1791 $[M + H]^+$; calcd. for $[C_{66}H_{63}N_3O_9Ru_3 + H]^+$: 1347.1816; anal. calcd. (%) for $C_{66}H_{63}N_3O_9Ru_3$ (1345.43): C 58.92, H 4.72, N 3.12; found: C 58.66, H 4.83, N 3.25; crystallographic data: see Table S1.

Metallamacrocycle 8b: Yield 91%; red-brown microcrystalline solid, decomp. without melting above 210 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 27H), 4.81 (s, 9H), 5.95 (d, ^3J = 6.7 Hz, 3H), 6.72 (d, ^3J = 6.7 Hz, 3H), 7.40 (app t, ^3J = 7.7 Hz, 3H), 7.64 (d, ^3J = 7.6 Hz, 3H), 8.11 (d, ^3J = 8.0 Hz, 3H), 8.86 (s, 3H), 10.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1 (CH_3), 73.9 (CH), 101.4 (C_q), 108.9 (CH), 121.7 (C_q), 126.5 (CH), 128.2 (CH), 130.9 (CH), 132.4 (CH), 133.7 (CH), 136.0 (C_q), 139.5 (C_q), 156.2 (C_q), 172.1 (C_q), 193.4 (CH); HRMS (ESI$^+$): m/z = 1304.1292 $[M]^+$; calcd. for $[C_{63}H_{57}N_3O_9Ru_3]^+$: 1304.1267; anal. calcd. (%) for $C_{63}H_{57}N_3O_9Ru_3 \times CH_2Cl_2$ (1388.28): C 55.38, H 4.28, N 3.03; found: C 55.73, H 4.73, N 3.35; crystallographic data: see Table S1.

Synthesis of triamines 13, 14 and 17

General procedure for the synthesis of tris(4-nitrophenyl) derivatives 11, 12 and 16: To a nitrating mixture, prepared by dropwise addition of H_2SO_4 (96%, d = 1.84, 16 mL) to HNO_3 (65%, d = 1.41, 15 mL) at –5 °C, was added very finely ground hydrocarbon (**9**, **10** or **15**, 10.0 mmol) in portions at this temperature. The reaction mixture was vigorously stirred for 2 h while maintaining the temperature of the cooling bath between –5 and 0 °C; then warmed to room temperature and poured into ice-water (300 mL). The mixture was extracted with

CH_2Cl_2 (3 × 100 mL); the organic layers were combined, washed with water and brine, dried over anhyd. $MgSO_4$, and evaporated. The residue was purified by column chromatography and/or recrystallization from a suitable solvent (*vide infra*), to give the corresponding nitroarenes as white crystalline solids.

1,1,1-Tris(4-nitrophenyl)ethane[7] (11): yield 24% after purification by column chromatography (SiO_2; eluent: cyclohexane–CH_2Cl_2 50:50); m.p. (from PhMe) 201–203 °C (lit.[7b] 203–204 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 7.26 (d, ^3J = 9.0 Hz, 6H), 8.20 (d, ^3J = 9.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.5 (CH_3), 53.5 (C_q), 124.0 (CH), 129.5 (CH), 147.0 (C_q), 153.5 (C_q); MS (CI): *m*/*z* (%) = 393 (12) $[M + NH_4]^+$, 378 (100) $[M - Me]^{\bullet+}$; anal. calcd. (%) for $C_{20}H_{15}N_3O_6 \times 0.33\ H_2O$ (399.29): C 60.16, H 3.95, N 10.52; found: C 60.26, H 4.17, N 10.20.

2,2-Dimethyl-1,1,1-tris(4-nitrophenyl)propane (12): yield 36% after purification by column chromatography (SiO_2; eluent: CH_2Cl_2); m.p. (decomp.; from C_6H_6) 206–208 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (s, 9H), 7.40 (d, ^3J = 9.1 Hz, 6H), 8.17 (d, ^3J = 9.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.4 (CH_3), 40.5 (C_q), 65.0 (C_q), 123.0 (CH), 132.0 (CH), 146.7 (C_q), 152.1 (C_q); MS (CI): *m*/*z* (%) = 453 (38) $[M + NH_4]^+$, 434 (21) $[M - H]^+$, 420 (54) $[M - CH_3]^{\bullet+}$, 389 (66) $[M - NO_2]^{\bullet+}$, 380 (100) $[M - C_4H_7]^+$; anal. calcd. (%) for $C_{23}H_{21}N_3O_6 \times 0.33\ H_2O$ (441.37): C 62.59, H 4.95, N 9.52; found: C 62.66, H 5.24, N 9.29.

1,3,5-Tris(4-nitrophenyl)adamantane (16): yield 70% after recrystallization from chlorobenzene; m.p. 296–300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.09 (d, ^3J = 3.0 Hz, 6H), 2.13–2.20 (m, 6H), 2.69 (sept, ^3J = 3.0 Hz, 1H), 7.60 (d, ^3J = 9.0 Hz, 6H), 8.22 (d, ^3J = 9.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.70 (CH), 39.1 (C_q), 40.8 (CH_2), 47.3 (CH_2), 123.9 (CH), 126.1 (CH), 146.6 (C_q), 156.1 (C_q); MS (CI): *m*/*z* (%) = 517 (14) $[M + NH_4]^+$, 499 (59) $[M]^{\bullet+}$; anal. calcd. (%) for $C_{28}H_{25}N_3O_6$ (499.51): C 67.33, H 5.04, N 8.41; found: C 67.07, H 5.13, N 8.09.

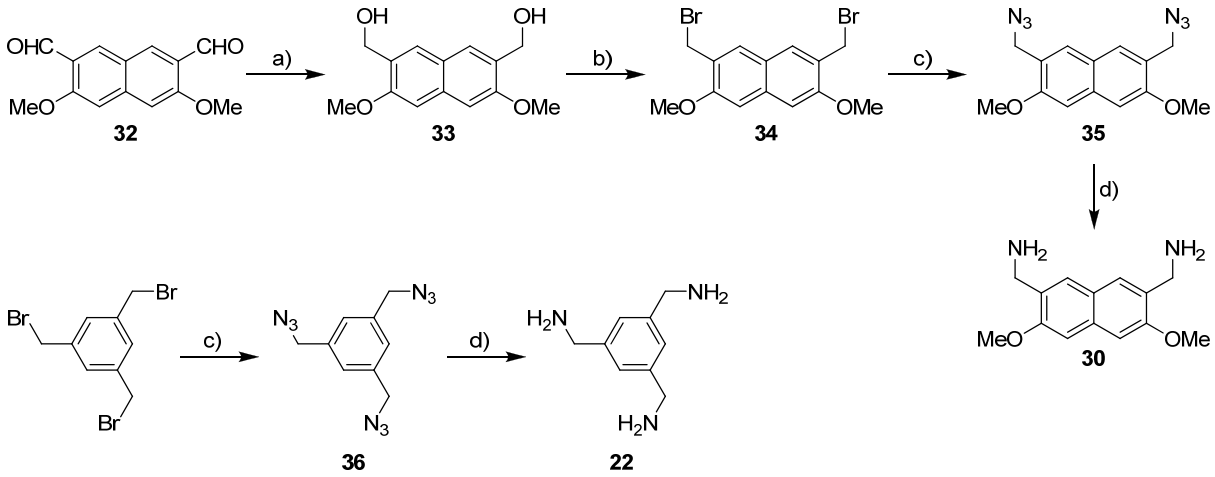
General procedure for the synthesis of triamines 13, 14 and 17: A suspension of nitroarene **11**, **12**, or **16** (500 μmol) in absolute EtOH (50 mL) was deoxygenated and then hydrogenated in the presence of reduced Pd/C (20%, 50 mg) under 1 atm of H_2 for a given time at the indicated temperature (*vide infra*); the reaction progress was monitored by TLC (SiO_2; eluent: CH_2Cl_2–MeOH 9:1). Cooling, filtration and evaporation of the solvent gave the corresponding triamines.

1,1,1-Tris(4-aminophenyl)ethane (13): obtained in 53% yield after hydrogenation for 2 h at 40 °C, followed by recrystallization from EtOH; pale-rose leaflets, m.p. 191–195 °C (lit.[7a] 191–192 °C); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.04$ (s, 3H), 3.56 (br s, 6H), 6.57 (d, $^{3}J = 8.6$ Hz, 6H), 6.87 (d, $^{3}J = 8.6$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 30.7$ (CH_3), 50.5 (C_q), 116.4 (CH), 129.7 (CH), 140.5 (C_q), 144.0 (C_q); HRMS (ESI$^+$): $m/z = 304.1812$ $[M + H]^+$; calcd. for $[C_{20}H_{21}N_3 + H]^+$: 304.1814.

2,2-Dimethyl-1,1,1-tris(4-aminophenyl)propane (14): obtained in 96% yield after hydrogenation for 4 h at 25 °C; off-white solid turning pinkish upon prolonged exposure to the air, m.p. (decomp.) 209–211 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.24$ (s, 9H), 3.50 (br s, 6H), 6.54 (d, $^{3}J = 8.7$ Hz, 6H), 7.02 (d, $^{3}J = 8.7$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 32.5$ (CH_3), 39.9 (C_q), 63.2 (C_q), 113.8 (CH), 132.4 (CH), 138.4 (C_q), 143.7 (C_q); MS (ESI$^+$): m/z (%) = 346.2 (100) $[M + H]^+$, 288.1 (9) $[M - t\text{Bu}]^{+\bullet}$; HRMS (ESI$^+$): $m/z = 346.2267$ $[M + H]^+$; calcd. for $[C_{23}H_{27}N_3 + H]^+$: 346.2283; anal. calcd. (%) for $C_{23}H_{27}N_3 \times H_2O$ (363.50): C 76.00, H 8.04, N 11.56; found: C 76.33, H 7.33, N 12.08.

1,3,5-Tris(4-aminophenyl)adamantane (17): obtained in 74% yield after hydrogenation for 4 h at 60 °C, followed by recrystallization from EtOH; white microcrystalline solid, m.p. 236–238 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.90$ (d, $^{3}J = 3.0$ Hz, 6H), 1.98 (br s, 6H), 2.45 (sept, $^{3}J = 3.0$ Hz, 1H), 3.56 (br s, 6H), 6.66 (d, $^{3}J = 8.6$ Hz, 6H), 7.21 (d, $^{3}J = 9.0$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 30.5$ (CH), 37.7 (C_q), 41.9 (CH_2), 48.7 (CH_2), 115.2 (CH), 126.0 (CH), 140.9 (C_q), 144.3 (C_q); HRMS (ESI$^+$): $m/z = 410.2651$ $[M + H]^+$; calcd. for $[C_{28}H_{31}N_3 + H]^+$: 410.2596; anal. calcd. (%) for $C_{28}H_{31}N_3$ (409.57): C 82.11, H 7.63, N 10.26; found: C 82.24, H 7.69, N 10.36.

Synthesis of amines 30 and 22



Scheme S1. Synthesis of amines **30** and **22**. Reagents and conditions: a) $NaBH_4$, EtOH, room temp., 83%; b) PBr_3, THF, 0 °C, 52%; c) NaN_3, DMF, room temp., **35**: 78%, **36**: 72%; d) H_2 (1 atm), Pd/C, EtOH, room temp., **30**: 94%, **22**: 94%.

2,7-Bis(hydroxymethyl)-3,6-dimethoxynaphthalene (33): A suspension of 3,6-dimethoxy-naphthalene-2,7-dicarbaldehyde (**32**, 1.11 g, 4.55 mmol)[8] and $NaBH_4$ (690 mg, 18.2 mmol) in absolute EtOH (30 mL) was stirred at room temperature for 3 h, then poured into water (100 mL). The precipitate was collected, washed with water, and dried, to give **33** (1.02 g, 90%) as a white solid, m.p. (from EtOH) 191–192 °C; ^{1}H NMR (400 MHz, [D6]DMSO): δ = 3.87 (s, 6H), 4.59 (d, ^3J = 5.5 Hz, 4H), 5.07 (t, ^3J = 5.5 Hz, 2H), 7.19 (s, 2H), 7.72 (s, 2H); ^{13}C NMR (100 MHz, [D6]DMSO): δ = 55.1 (CH_3), 58.4 (CH_2), 104.0 (CH), 123.0 (C_q), 125.2 (CH), 129.3 (C_q), 133.5 (C_q), 155.1 (C_q); HRMS (MALDI, matrix: CHCA): m/z = 248.1061 $[M]^{\bullet+}$; calcd. for $C_{14}H_{16}O_4$: 248.1047; anal. calcd. (%) for $C_{14}H_{16}O_4 \times 0.5\ C_2H_5OH$ (271.31): C 66.40, H 7.06; found: C 66.76, H 7.16.

2,7-Bis(bromomethyl)-3,6-dimethoxynaphthalene (34): To a suspension of **33** (840 mg, 3.39 mmol) in anhyd. THF (18.0 mL), stirred at 0 °C under inert atmosphere, a solution of PBr_3 (640 µL, 1.84 g, 6.81 mmol) in anhyd. THF (2.0 mL) was added dropwise within 10 min, while the solid gradually dissolved. After stirring at 0 °C for 1 h and at room temperature for 2 h, the mixture was poured into water (50 mL) and extracted with Et_2O (3 × 20 mL). The combined organic phases were washed thrice with water, brine, dried over

anhyd. $MgSO_4$, evaporated, and the residue was purified by flash chromatography (SiO_2; eluent: cyclohexane–MTBE 80:20), to give **34** (1.00 g, 79%) as a white solid, m.p. (from cyclohexane–benzene) 132–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.99 (s, 6H), 4.68 (s, 4H), 7.03 (s, 2H), 7.70 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.6 (CH_2), 55.8 (CH_3), 105.1 (CH), 123.3 (C_q), 125.8 (C_q), 130.4 (CH), 136.8 (C_q), 156.7 (C_q); MS (EI): m/z = 374 (19) $[M]^{\bullet+}$, 293 (100) $[M - Br]^{\bullet+}$, 214 (10) $[M - 2Br]^{\bullet+}$, 184 (26) $[M - 2Br - OMe]^{\bullet+}$; anal. calcd. (%) for $C_{14}H_{14}Br_2O_2 \times 0.17\ C_6H_6$ (387.1): C 46.54, H 3.91; found: C 46.25, H 3.92.

2,7-Bis(azidomethyl)-3,6-dimethoxynaphthalene (35): A solution of **34** (328 mg, 0.88 mmol) and NaN_3 (65.0 mg, 2.82 mmol) in DMF (3.0 mL) was stirred at room temperature for 18 h, then poured into water (25 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with water, brine, dried over anhyd. $MgSO_4$, evaporated, and the residue was purified by column chromatography (SiO_2; eluent: cyclohexane–CH_2Cl_2 50:50), to give **35** (205 mg, 78%) as a pale-yellow oil, which solidified upon cooling; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.97 (s, 6H), 4.47 (s, 4H), 7.08 (s, 2H), 7.63 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.8 (CH_2), 55.6 (CH_3), 104.8 (CH), 123.2 (C_q), 123.6 (C_q), 129.4 (CH), 136.2 (C_q), 156.8 (C_q).

2,7-Bis(aminomethyl)-3,6-dimethoxynaphthalene (30): A solution of **35** (200 mg, 0.67 mmol) in absolute EtOH (25 mL) was deoxygenated and then hydrogenated in the presence of reduced Pd/C (20%, 13 mg) under 1 atm of H_2 for 3 h at room temperature; the reaction progress was monitored by TLC (SiO_2; eluent: CH_2Cl_2–7M NH_3 in MeOH, 9:1). After filtration and evaporation of the solvent, the diamine **30** (155 mg, 94%) was obtained as a white solid, m.p. 126–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 4H), 3.95 (s, 6H), 7.04 (s, 2H), 7.54 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.2 (CH_2), 55.4 (CH_3), 104.4 (CH), 123.8 (C_q), 126.8 (CH), 131.1 (C_q), 134.4 (C_q), 156.7 (C_q); MS (ESI^+): m/z = 247 (14) $[M + H]^+$, 230 (100) $[M - NH_2]^+$; HRMS (ESI^+): m/z = 247.1439 $[M + H]^+$; calcd. for $[C_{14}H_{18}N_2O_2 + H]^+$: 247.1447; anal. calcd. (%) for $C_{14}H_{18}N_2O_2$ (246.31): C 68.27, H 7.37, N 11.37; found: C 68.51, H 7.56, N 11.80.

1,3,5-Tris(aminomethyl)benzene[9] (22): A solution of 1,3,5-tris(azidomethyl)benzene (**36**, 685 mg, 2.82 mmol)[10] in absolute EtOH (150 mL) was deoxygenated and then hydrogenated in the presence of reduced Pd/C (20%, 90 mg) under 1 atm of H_2 for 3 h at room temperature;

the reaction progress was monitored by TLC (SiO_2; eluent: CH_2Cl_2–7M NH_3 in MeOH, 9:1). After filtration and evaporation of the solvent, the residue was purified by vacuum sublimation (100 °C, 0.02 mbar) to give **22** (437 mg, 94%) as a white, very hygroscopic solid which was handled under inert atmosphere, m.p. 51–53 °C (lit.[11] m.p. 44 - 46 °C)[a]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48 (br s, 6H), 3.88 (s, 6H), 7.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.4 (CH_2), 124.4 (CH), 143.9 (C_q); MS (ESI^+): not detected.

Synthesis of cages

General procedure for the synthesis of tetrahedral cages: A solution of the metallamacrocyclic trialdehyde **7a**, **7b**, or **7c** (50 μmol) in a mixture of MeOH (3.0 mL) and CH_2Cl_2 (7.0 mL) was added dropwise via a syringe (over 2–3 h) to a solution of triamine **13**, **14**, **17** or tris(2-aminoethyl)amine (50 μmol) in a mixture of MeOH (3.0 mL) and CH_2Cl_2 (3.5 mL), stirred under inert atmosphere at ambient temperature. The reaction mixture was left without stirring for 7–8 days (for the synthesis of **18a**, **18b**, **19a**, **19b**, **20a** and **20b**) or 24 h (for the synthesis of **21a–c**) and then (unless stated otherwise, *vide infra*) adiabatically concentrated in vacuo to approx. 20% of its initial volume. T he precipitated solid was collected by centrifugation, washed with MeOH and Et_2O (2 × 5 mL each), and dried in vacuo to give the cages as orange amorphous solids, which contained only trace amounts of solvents and impurities (according to ^{1}H NMR spectroscopy). Single crystals were grown by vapor diffusion of Et_2O into solutions of the products in $CHCl_3$ or $CHCl_3$–MeOH (95:5). In the case of reaction of **7b** with triamine **17**, the product **20b** crystallized from the reaction mixture after 3–5 days as long, soft, needle-like crystals suitable for the X-ray diffraction analysis.

Cage 18a: Yield 33%; ^{1}H NMR (400 MHz, $CDCl_3$–CD_3OD 90:10): δ = 1.32 (d, ^3J = 6.9 Hz, 36H), 1.39 (d, ^3J = 6.9 Hz, 36H), 1.94 (s, 36H), 2.15 (s, 12H), 2.85 (sept, ^3J = 6.9 Hz, 12H), 5.10 (d, ^3J = 5.8 Hz, 12H), 5.31 (d, ^3J = 5.8 Hz, 12H), 5.61 (d, ^3J = 5.7 Hz, 12H), 5.82 (d, ^3J = 5.8 Hz, 12H), 6.26 (d, ^3J = 6.7 Hz, 12H), 6.56 (d, ^3J = 6.7 Hz, 12H), 6.89 (d, ^3J = 8.6 Hz, 24H), 6.94 (d, ^3J = 8.6 Hz, 24H), 8.56 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$–CD_3OD 90:10): δ = 18.3 (CH_3), 22.2 (CH_3), 23.7 (CH_3), 29.8 (CH_3), 31.3 (CH), 51.6 (C_q), 76.6 (CH), 79.4 (CH), 82.5 (CH), 82.6 (CH), 97.3 (C_q), 99.3 (C_q), 107.6 (CH), 120.2 (CH), 123.3 (C_q), 129.2

[a] We believe the higher melting point is due to the higher purity of our sample obtained by sublimation.

(CH), 131.4 (CH), 146.0 (C_q), 150.9 (C_q), 157.2 (CH), 158.4 (C_q), 172.0 (C_q); HRMS (ESI^+): m/z = 1094.3918 $[M + 5H]^{5+}$; calcd. for $[C_{272}H_{264}N_{24}O_{24}Ru_{12} + 5H]^{5+}$: 1094.3856.

Cage 18b: Yield 45%; ^1H NMR (400 MHz, $CDCl_3$–MeOD 95:5): δ = 2.17 (br s, 120H), 4.74 (s, 36H), 6.21 (d, ^3J = 6.6 Hz, 12H), 6.55 (d, ^3J = 6.6 Hz, 12H), 6.83 (d, ^3J = 8.6 Hz, 24H), 6.94 (d, ^3J = 8.6 Hz, 24H), 8.56 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$–MeOD 95:5): δ = 18.7 (CH_3), 30.1 (CH_3), 51.6 (C_q), 73.8 (CH), 101.4 (C_q), 106.9 (CH), 120.3 (CH), 122.1 (C_q), 129.2 (CH), 131.7 (CH), 145.4 (C_q), 151.8 (C_q), 157.9 (CH), 160.5 (C_q), 172.4 (C_q); HRMS (ESI^+): m/z = 884.1241 $[M + 6H]^{6+}$; calcd. for $[C_{260}H_{240}N_{24}O_{24}Ru_{12} + 6H]^{6+}$: 884.1246.

Cage 19a: Yield 48%; ^1H NMR (600 MHz, $CDCl_3$–CD_3OD 95:5): δ = 1.30 (s, 36H), 1.33 (d, ^3J = 6.9 Hz, 36H), 1.40 (d, ^3J = 6.9 Hz, 36H), 1.95 (s, 36H), 2.87 (sept, ^3J = 6.9 Hz, 12H), 5.05 (d, ^3J = 5.7 Hz, 12H), 5.29 (d, ^3J = 5.7 Hz, 12H), 5.59 (d, ^3J = 5.7 Hz, 12H), 5.78 (d, ^3J = 5.7 Hz, 12H), 6.31 (d, ^3J = 6.6 Hz, 12H), 6.61 (d, ^3J = 6.6 Hz, 12H), 6.79 (d, ^3J = 8.7 Hz, 24H), 7.09 (d, ^3J = 8.7 Hz, 24H), 8.54 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$–CD_3OD 95:5): δ = 18.3 (CH_3), 22.2 (CH_3), 23.8 (CH_3), 31.4 (CH), 33.1 (CH_3), 40.2 (C_q), 76.6 (CH), 79.2 (CH), 82.7 (2CH), 97.4 (C_q), 99.1 (C_q), 107.9 (CH), 119.4 (CH), 123.5 (C_q), 131.2 (CH), 131.8 (CH), 143.9 (C_q), 151.4 (C_q), 157.3 (CH), 158.7 (C_q), 172.0 (C_q); HRMS (ESI^+): m/z = 940.1960 $[M + 6H]^{6+}$; calcd. for $[C_{284}H_{288}N_{24}O_{24}Ru_{12} + 6H]^{6+}$: 940.1874.

Cage 19b: Yield 50%; ^1H NMR (400 MHz, $CDCl_3$–CD_3OD 95:5): δ = 1.34 (s, 36H), 2.18 (s, 108H), 4.76 (s, 36H), 6.25 (d, ^3J = 6.6 Hz, 12H), 6.58 (d, ^3J = 6.6 Hz, 12H), 6.79 (d, ^3J = 8.6 Hz, 24H), 7.10 (d, ^3J = 8.6 Hz, 24H), 8.58 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$–CD_3OD 95:5): δ = 18.7 (CH_3), 33.3 (CH_3), 40.1 (C_q), 73.9 (CH), 101.3 (C_q), 107.0 (CH), 119.5 (CH), 122.2 (C_q), 131.7 (2CH),[b] 143.6 (C_q), 151.6 (C_q), 157.6 (CH), 160.5 (C_q), 172.3 (C_q); HRMS (ESI^+): m/z = 912.1549 $[M + 6H]^{6+}$; calcd. for $[C_{272}H_{264}N_{24}O_{24}Ru_{12} + 6H]^{6+}$: 912.1559.

Cage 20a: Yield 39%; ^1H NMR (400 MHz, $CDCl_3$–CD_3OD 95:5): δ = 1.33 (d, ^3J = 6.9 Hz, 36H), 1.41 (d, ^3J = 6.9 Hz, 36H), 1.96–2.17 (m, 84H), 2.56 (br s, 4H), 2.83 (sept, ^3J = 6.9 Hz, 12H), 5.18 (d, ^3J = 5.6 Hz, 12H), 5.27 (d, ^3J = 5.7 Hz, 12H), 5.48 (d, ^3J = 5.7 Hz, 12H), 5.62 (d, ^3J = 5.7 Hz, 12H), 6.32 (d, ^3J = 6.7 Hz, 12H), 6.49 (d, ^3J = 6.7 Hz, 12H), 7.06 (d, ^3J = 8.5 Hz, 24H), 7.37 (d, ^3J = 8.5 Hz, 24H), 8.66 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$–CD_3OD 95:5): δ = 18.3 (CH_3), 22.5 (CH_3), 23.3 (CH_3), 30.4 (CH), 31.2 (CH), 38.0 (C_q), 41.1 (CH_2), 48.7 (CH_2), 77.6 (CH), 80.1 (CH), 81.3 (CH), 81.8 (CH), 96.0 (C_q), 99.6 (C_q), 106.9

[b] detected via a ^1H–^{13}C HSQC experiment.

(CH), 120.8 (CH), 122.9 (C_q), 125.4 (CH), 130.9 (CH), 147.0 (C_q), 150.4 (C_q), 156.0 (CH), 158.7 (C_q), 172.3 (C_q); HRMS (ESI^+): m/z = 1179.2520 $[M + 5H]^{5+}$; calcd. for $[C_{304}H_{304}N_{24}O_{24}Ru_{12} + 5H]^{5+}$: 1179.2484.

Cage 20b: crystallized from the reaction mixture in 33% yield; ^1H NMR (400 MHz, [D5]pyridine): δ = 1.94 (m, 36H), 2.21 (s, 108H), 2.29–2.33 (m, 12H), 2.42 (br s, 4H), 4.94 (s, 36H), 6.94 (d, ^3J = 6.6 Hz, 12H), 7.00 (d, ^3J = 6.7 Hz, 12H), 7.24 (d, ^3J = 8.4 Hz, 24H), 7.46 (d, ^3J = 8.5 Hz, 24H), 9.25 (s, 12H); ^{13}C NMR (150 MHz, [D5]pyridine): δ = 19.1 (CH_3), 31.4 (CH),[b] 38.8 (C_q), 41.4 (CH_2), 50.0 (CH_2), 74.4 (CH), 102.1 (C_q), 107.1 (CH), 121.3 (CH), 122.6 (C_q), 126.6 (CH), 132.2 (CH), 147.3 (C_q), 153.0 (C_q), 156.6 (CH), 162.1 (C_q), 173.9 (C_q); HRMS (ESI^+): m/z = 954.8480 $[M + 6H]^{6+}$; calcd. for $[C_{292}H_{280}N_{24}O_{24}Ru_{12} + 6H]^{6+}$: 954.8480.

Cage 21a: Yield 58%; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 (d, ^3J = 6.9 Hz, 36H), 1.37 (d, ^3J = 6.9 Hz, 36H), 2.06 (s, 36H), 2.17 (dt, ^2J = 12.1 Hz, ^3J = 3.8 Hz, 12H), 2.77 (sept, ^3J = 6.9 Hz, 12H), 3.08 (dt, ^2J = 12.1 Hz, ^3J = 5.6 Hz, 12H), 3.48 (dt, ^2J = 11.5 Hz, ^3J = 3.8 Hz, 12H), 3.84 (dt, ^2J = 11.5 Hz, ^3J = 5.7 Hz, 12H), 5.24 (d, ^3J = 5.7 Hz, 12H), 5.27 (d, ^3J = 5.8 Hz, 12H), 5.45 (d, ^3J = 5.7 Hz, 12H), 5.73 (d, ^3J = 5.7 Hz, 12H), 6.16 (d, ^3J = 6.6 Hz, 12H), 6.50 (d, ^3J = 6.6 Hz, 12H), 8.50 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.5 (CH_3), 22.7 (CH_3), 23.3 (CH_3), 31.0 (CH), 57.9 (CH_2), 61.1 (CH_2), 77.4 (CH), 80.1 (CH), 81.6 (CH), 82.3 (CH), 96.5 (C_q), 99.2 (C_q), 107.8 (CH), 122.8 (C_q), 130.6 (CH), 157.8 (C_q), 158.3 (CH), 172.3 (C_q); HRMS (ESI^+): m/z = 1613.5997 $[M + 3H]^{3+}$; calcd. for $[C_{216}H_{252}N_{28}O_{24}Ru_{12} + 3H]^{3+}$: 1613.6095.

Cage 21b: Yield 65%; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.11–2.20 (m, 12H),[b] 2.20 (s, 108H), 3.06 (dt, ^2J = 12.3 Hz, ^3J = 6.0 Hz, 12H), 3.47 (dt, ^2J = 11.3 Hz, ^3J = 6.0 Hz, 12H), 3.87 (dt, ^2J = 11.3 Hz, ^3J = 3.7 Hz, 12H), 4.76 (s, 36H), 6.16 (d, ^3J = 6.6 Hz, 12H), 6.56 (d, ^3J = 6.6 Hz, 12H), 8.59 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.7 (CH_3), 58.2 (CH_2), 61.4 (CH_2), 74.2 (CH), 101.2 (C_q), 107.1 (CH), 122.0 (C_q), 131.9 (CH), 158.6 (CH), 158.8 (C_q), 172.1 (C_q); HRMS (ESI^+): m/z = 779.2759 $[M + 6H]^{6+}$; calcd. for $[C_{204}H_{228}N_{28}O_{24}Ru_{12} + 6H]^{6+}$: 779.2773.

Cage 21c: Yield 29%; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (d, ^3J = 6.8 Hz, 108H), 1.37 (d, ^3J = 6.8 Hz, 108H), 2.15 (dt, ^2J = 11.6 Hz, ^3J = 3.4 Hz, 12H), 3.08 (m, 48H), 3.43 (dt, ^2J = 11.2 Hz, ^3J = 3.3 Hz, 12H), 3.83 (dt, ^2J = 11.0 Hz, ^3J = 4.7 Hz, 12H), 4.84 (s, 36H), 5.98 (d, ^3J = 6.7 Hz, 12H), 6.50 (d, ^3J = 6.6 Hz, 12H), 8.47 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.0 (CH_3), 23.3 (CH_3), 30.8 (CH), 57.8 (CH_2), 61.1 (CH_2), 68.1 (CH), 106.3

(CH), 109.3 (C_q), 121.4 (C_q), 131.9 (CH), 158.4 (CH), 158.9 (C_q), 173.0 (C_q); HRMS (ESI^+): m/z = 1420.9339 $[M + 4H]^{4+}$; calcd. for $[C_{276}H_{372}N_{28}O_{24}Ru_{12} + 3H]^{3+}$: 1420.9445.

Synthesis of the tetrahedral cage 25 by rearrangement from 24: The cylindrical cage **24** (8.0 mg, 3 μmol) was dissolved in $CHCl_3$ (0.5 mL) and was left to stand at room temperature for 30 h. The precipitated solid was collected by centrifugation, washed with MeOH (2 × 0.5 mL), Et_2O (2 × 1 mL), and dried in vacuo to give cage **25** (3.1 mg, 41%) as an orange solid; ^{1}H NMR (400 MHz, $CDCl_3$–CD_3OD 95:5): δ = 1.32 (d, ^3J = 6.9 Hz, 36H), 1.40 (d, ^3J = 6.9 Hz, 36H), 2.07 (s, 36H), 2.84 (sept, ^3J = 4.7 Hz, 12H), 4.52 (d, ^2J = 14.9 Hz, 12H), 4.71 (d, ^2J = 13.4 Hz, 12H), 5.15 (d, ^3J = 5.7 Hz, 12H), 5.26 (d, ^3J = 5.7 Hz, 12H), 5.51 (d, ^3J = 5.7 Hz, 12H), 5.68 (d, ^3J = 5.7 Hz, 12H), 6.27 (d, ^3J = 6.3 Hz, 12H), 6.55 (d, ^3J = 6.3 Hz, 12H), 7.09 (s, 12H), 8.57 (s, 12H); ^{13}C NMR was not recorded due to poor solubility; HRMS (ESI^+): m/z = 983.7489 $[M + 5H]^{5+}$; calcd. for $[C_{228}H_{240}N_{24}O_{24}Ru_{12} + 5H]^{5+}$: 983.7477.

General procedure for the synthesis of the cylindrical cages 24, 28 and 29: A solution of the metallamacrocyclic trialdehyde **7a** (40 μmol) in a mixture of MeOH (3.0 mL) and CH_2Cl_2 (7.0 mL) was added dropwise via a syringe (over 2–3 h) to a solution of 1,3,5-tris(aminomethyl)benzene (**22**) (for the synthesis of **24**), ethylenediamine (for the synthesis of **28**) or 2,7-bis(aminomethyl)-3,6-dimethoxynaphthalene (**30**) (for the synthesis of **29**) (60 μmol) in a mixture of MeOH (3.0 mL) and CH_2Cl_2 (3.5 mL), stirred in a round-bottom flask with a rubber septum under inert atmosphere at ambient temperature. After 24 h, the reaction mixture was adiabatically concentrated in vacuo until onset of precipitation. The precipitated solid was collected by centrifugation, washed with MeOH and Et_2O (2 × 5 mL each), and dried in vacuo to give the cages as orange amorphous solids, which contained only trace amounts of solvents and impurities (according to ^{1}H NMR spectroscopy).

Cage 24: Yield 32%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (d, ^3J = 6.8 Hz, 18H), 1.40 (d, ^3J = 6.8 Hz, 18H), 2.09 (s, 18H), 2.83 (sept, ^3J = 6.8 Hz, 6H), 3.17 (s, 6H), 4.45 (d, ^2J = 12.9 Hz, 6H), 4.73 (d, ^2J = 12.8 Hz, 6H), 5.19 (d, ^3J = 5.6 Hz, 6H), 5.30 (d, ^3J = 5.7 Hz, 6H), 5.46 (d, ^3J = 5.6 Hz, 6H), 5.70 (d, ^3J = 5.7 Hz, 6H), 6.25 (d, ^3J = 6.7 Hz, 6H), 6.52 (d, ^3J = 6.6 Hz, 6H), 6.67 (s, 6H), 7.02 (s, 3H), 8.66 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 18.5 (CH_3), 22.7 (CH_3), 23.4 (CH_3), 31.3 (CH), 45.7 (CH_2), 66.2 (CH_2), 77.5 (CH), 80.3 (CH), 81.5 (CH), 82.0 (CH), 96.2 (C_q), 99.3 (C_q), 106.7 (CH), 122.3 (C_q), 125.6 (CH), 127.0

(CH), 130.8 (CH), 139.5 (C_q), 143.6 (C_q), 158.6 (CH), 158.7 (C_q), 172.5 (C_q); HRMS (ESI^+): m/z = 875.1669 $[M + 3H]^{3+}$; calcd. for $[C_{123}H_{135}N_{15}O_{12}Ru_6 + 3H]^{3+}$: 875.1666.

Cage 28: Yield 56%; ^{1}H NMR (400 MHz, $CDCl_3$–CD_3OD 95:5): δ = 1.26 (d, ^3J = 6.9 Hz, 18H), 1.35 (d, ^3J = 6.9 Hz, 18H), 1.96 (s, 18H), 2.76 (sept, ^3J = 6.9 Hz, 6H), 3.95 (m, 12H), 5.07 (d, ^3J = 5.7 Hz, 6H), 5.22 (d, ^3J = 5.7 Hz, 6H), 5.45 (d, ^3J = 5.7 Hz, 6H), 5.69 (d, ^3J = 5.7 Hz, 6H), 6.00 (d, ^3J = 6.6 Hz, 6H), 6.35 (d, ^3J = 6.6 Hz, 6H), 8.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$–CD_3OD 95:5): δ = 18.3 (CH_3), 22.5 (CH_3), 23.3 (CH_3), 31.2 (CH), 62.3 (CH_2), 76.8 (CH), 79.4 (CH), 82.2 (CH), 82.7 (CH), 97.0 (C_q), 98.5 (C_q), 106.8 (CH), 122.1 (C_q), 130.7 (CH), 157.9 (C_q), 159.7 (CH), 172.1 (C_q); HRMS (ESI^+): m/z = 577.8423 $[M + 4H]^{4+}$; calcd. for $[C_{102}H_{114}N_{12}O_{12}Ru_6 + 4H]^{4+}$: 577.8333. Crystals were grown by vapor diffusion of pentane into solution of **28** in $CHCl_3$–MeOH (95:5).

Cage 29: Yield 46%; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.32 (d, ^3J = 6.9 Hz, 18H), 1.42 (d, ^3J = 6.9 Hz, 18H), 2.25 (s, 18H), 2.77 (sept, ^3J = 6.9 Hz, 6H), 3.75 (s, 18H), 4.65 (d, ^2J = 11.1 Hz, 6H), 4.71 (d, ^2J = 11.1 Hz, 6H), 5.19 (d, ^3J = 5.7 Hz, 6H), 5.25 (d, ^3J = 5.7 Hz, 6H), 5.32 (d, ^3J = 5.7 Hz, 6H), 5.58 (d, ^3J = 5.7 Hz, 6H), 6.11 (d, ^3J = 6.6 Hz, 6H), 6.45 (d, ^3J = 6.6 Hz, 6H), 6.81 (s, 6H), 7.60 (s, 6H), 8.94 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 18.8 (CH_3), 22.9 (CH_3), 23.2 (CH_3), 31.3 (CH), 55.4 (CH_3), 63.0 (CH_2), 78.0 (CH), 80.0 (CH), 81.4 (CH), 82.5 (CH), 96.1 (C_q), 98.4 (C_q), 104.9 (CH), 106.2 (CH), 122.1 (C_q), 123.4 (C_q), 126.0 (C_q), 129.0 (CH), 130.1 (CH), 135.0 (C_q), 157.4 (C_q), 159.2 (C_q), 160.9 (CH), 172.9 (C_q); HRMS (ESI^+): m/z = 1433.7681 $[M + 2H]^{2+}$; calcd. for $[C_{138}H_{144}N_{12}O_{18}Ru_6 + 2H]^{2+}$: 1433.7616.

Synthesis of the cylindrical cage D_3-26: To a solution of *p*-xylylenediamine (45 μmol) in a mixture of MeCN (3.0 mL) and CH_2Cl_2 (3.0 mL), stirred in a round-bottom flask with a rubber septum under inert atmosphere at ambient temperature, a solution of the metallamacrocyclic trialdehyde **7a** (30 μmol) in a mixture of MeCN (3.0 mL) and CH_2Cl_2 (3.0 mL) was added, followed by a catalytic amount of AcOH (2 μL). After stirring for 2 days, the precipitated solid was collected by centrifugation, washed with EtOH (3 × 1 mL), and dried in vacuo to give ***D*$_3$-26** as an orange amorphous solid, which contained only trace amounts of solvents and impurities (according to ^{1}H NMR spectroscopy). Yield 62%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (d, ^3J = 6.9 Hz, 18H), 1.38 (d, ^3J = 6.9 Hz, 18H), 1.98 (s, 18H), 2.82 (sept, ^3J = 6.9 Hz, 6H), 4.47 (d, ^2J = 15.5 Hz, 6H), 4.80 (d, ^2J = 15.5 Hz, ^4J = 1.5 Hz, 6H), 5.10 (d, ^3J = 5.7 Hz, 6H), 5.27 (d, ^3J = 5.8 Hz, 6H), 5.50 (d, ^3J = 5.7 Hz, 6H), 5.76 (d, ^3J = 5.8 Hz, 6H), 6.27 (d, ^3J = 6.6 Hz, 6H), 6.54 (d, ^3J = 6.6 Hz, 6H), 7.17 (s, 12

H), 8.71 (d, ^4J = 1.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.3 (CH_3), 22.4 (CH_3), 23.5 (CH_3), 31.2 (CH), 64.7 (CH_2), 76.5 (CH), 79.3 (CH), 82.5 (CH), 82.6 (CH), 97.2 (C_q), 98.5 (C_q), 107.8 (CH), 122.8 (C_q), 128.0 (CH), 130.8 (CH), 138.4 (C_q), 157.8 (C_q), 158.7 (CH), 172.0 (C_q); HRMS (ESI$^+$): m/z = 846.1400 $[M + 3H]^{3+}$; calcd. for $[C_{120}H_{126}N_{12}O_{12}Ru_6 + 3H]^{3+}$: 634.8570. Crystals were grown by vapor diffusion of pentane into solution of ***D*$_3$-26** in fluorobenzene.

General procedure for the synthesis of the cages 31a and 31b: A solution of the metallamacrocyclic trialdehyde **8a** or **8b** (100 μmol) in a mixture of MeOH (6.0 mL) and CH_2Cl_2 (14.0 mL) was added dropwise via a syringe (over 2–3 h) to a solution of triamine **23** (100 μmol) in a mixture of MeOH (6.0 mL) and CH_2Cl_2 (7.0 mL), stirred in a round-bottom flask with a rubber septum under inert atmosphere at ambient temperature. After stirring for 5–7 days, the reaction mixture was adiabatically concentrated in vacuo until onset of precipitation. The precipitated solid was collected by centrifugation, washed with MeOH and Et_2O (2 × 5 mL each), and dried in vacuo to give the cages as orange amorphous solids. Single crystals of **31a** and **31b** were grown by diffusion of pentane vapors or liquid cyclohexane, respectively, into solutions of the cages in fluorobenzene.

Cage 31a: Yield 28%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 7.5 Hz, 9H), 1.31 (d, ^3J = 6.9 Hz, 9H), 1.36 (d, ^3J = 6.9 Hz, 9H), 2.27 (s, 9H), 2.30–2.44 (m, 6H), 2.76 (sept, ^3J = 6.9 Hz, 3H), 4.99 (d, ^2J = 18.7 Hz, 6H), 5.04 (d, ^3J = 6.8 Hz, 3H), 5.11 (d, ^3J = 5.8 Hz, 3H), 5.18 (d, ^2J = 18.7 Hz, 3H), 5.30–5.33 (m, 6H), 5.62 (d, ^3J = 5.9 Hz, 3H), 6.04 (d, ^3J = 6.7 Hz, 3H), 6.48 (s, 3H), 7.36 (app t, ^3J = 7.8 Hz, 3H), 7.62 (s, 3H), 7.81 (d, ^3J = 7.8 Hz, 3H), 8.30 (d, ^3J = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 16.1 (CH_3), 18.9 (CH_3), 22.6 (CH_3), 23.1 (CH_3), 23.7 (CH_2), 31.1 (CH), 54.3 (CH_2), 77.4 (CH), 79.8 (CH), 81.3 (CH), 82.0 (CH), 96.1 (C_q), 97.6 (C_q), 108.6 (CH), 122.0 (CH), 124.3 (C_q), 127.6 (CH), 130.0 (CH), 131.0 (C_q), 131.8 (CH), 132.3 (CH), 135.6 (C_q), 139.2 (C_q), 144.4 (C_q), 154.8 (C_q), 159.6 (CH), 171.3 (C_q); HRMS (ESI$^+$): m/z = 1542.3706 $[M + H]^+$; calcd. for $[C_{81}H_{84}N_6O_6Ru_3 + H]^+$: 1542.3708.

Cage 31b: Yield 47%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 7.4 Hz, 9H), 2.23–2.48 (m, 6H), 2.28 (s, 27H), 4.77 (s, 9H), 4.97–5.02 (m, 6H), 5.19 (d, ^2J = 18.8 Hz, 3H), 6.12 (d, ^3J = 6.7 Hz, 3H), 6.47 (s, 3H), 7.35 (app t, ^3J = 7.8 Hz, 3H), 7.62 (s, 3H), 7.81 (d, ^3J = 7.8 Hz, 3H), 8.35 (d, ^3J = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 16.1 (CH_3), 19.0 (CH_3), 23.7 (CH_2), 54.2 (CH_2), 73.6 (CH), 100.8 (C_q), 108.3 (CH), 121.8 (CH), 123.6

(C_q), 127.4 (CH), 130.0 (CH), 131.0 (C_q), 131.9 (CH), 133.3 (CH), 135.6 (C_q), 139.4 (C_q), 144.3 (C_q), 155.0 (C_q), 159.6 (CH), 170.9 (C_q); HRMS (ESI^+): m/z = 750.6686 $[M + 2H]^{2+}$; calcd. for $[C_{78}H_{78}N_6O_6Ru_3 + 2H]^{2+}$: 750.6658.

General procedure for the one-pot synthesis of the cages 21a, 21b, 29 and 31a. A mixture of ligand **3** or **6** (90 μmol), $[(arene)RuCl_2]_2$ (45 μmol), the corresponding di- (45 μmol) or triamine (30 μmol), and Cs_2CO_3 (180 μmol) in a mixture of MeOH (4 mL) and CH_2Cl_2 (7 mL) was stirred at room temperature under a nitrogen atmosphere for 18 h. The reaction mixture was then adiabatically concentrated until onset of precipitation. The precipitated solid was collected by centrifugation, washed with MeOH (1 mL), Et_2O (2 × 1 mL), pentane (2 × 1 mL), and dried in vacuo to give the products whose characterization data were identical with the ones given above.

Procedure for the self-sorting reaction between 7a, ethylenediamine and tris(2-aminoethyl)amine. A mixture of **7a** (4.0 μmol), ethylenediamine (3.0 μmol) and tris(2-aminoethyl)amine (2.0 μmol) in a mixture of CD_2Cl_2 (0.63 mL) and CD_3OD (0.36 mL) was left without stirring at room temperature under a nitrogen atmosphere for 18h to give cages **28** and **21a**, which were not isolated.

Procedure for the amine exchange reaction between 21a and ethylenediamine. A mixture of **21a** (1.0 μmol) and ethylenediamine (60 μmol) in a mixture of CD_2Cl_2 (0.63 mL) and CD_3OD (0.36 mL) was left without stirring at room temperature under nitrogen atmosphere for 18h to give a mixture of the cage **28** and free tris(2-aminoethyl)amine. The cage was not isolated.

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Crystallographic studies

Selected structure refinement details can be found in Tables S1 to S4. Diffraction intensity data were collected using MoKα radiation on four-circle kappa goniometers equipped with either an Oxford Diffraction KM4 sapphire CCD or a Nonius-Bruker Apex II CCD, and with Oxford Cryostream cooling heads. Data were reduced by EvalCCD[12] or CrysAlis PRO 1.7.1.[13] Absorption corrections were applied to all data sets using a semi-empirical method.[14] All structures were solved using conventional heavy atom methods and refined using full-matrix least-squares on F^2. The hydrogen atoms were placed in calculated positions using the riding model with $U_{iso} = aU_{eq}$ (where a is 1.5 for methyl hydrogen atoms and 1.2 for others). Refinement and geometrical calculations were carried out on all structures with SHELXTL.[15] Cage structures **18b**, **20b**, **21a** and **21b** generally all scattered weakly due to large amounts of poorly ordered co-solvent in the lattice. This affected the resolution of the complex molecules to varying degrees but in all cases an extensive regime of restraints was applied in order to compensate for low data/parameter ratios and/or to retain chemically sensible geometry during refinement. Typically, all 1,2- and 1,3-distances were restrained (DFIX and/or SAME) to target values obtained from an analysis of analogous fragments in the CSD, whilst atoms making up cyclic aromatic group were restrained to be co-planar (FLAT). Where data was of sufficient quality to refine anisotropic displacement parameters (**20b**, **21a** and **21b**), displacement parameter restraints (SIMU and ISOR) were liberally applied to all light atoms. For **18b**, only the Ru atoms were refined with anisotropic displacement parameters due to a very low data/parameter ratio. For structures **8a**, **8b**, **18b**, **20b**, **21a**, **21b**, **26** and **31b** the scattering contributions from residual diffuse electron density (i.e. disordered solvent) were removed using the SQUEEZE routine in PLATON.[16] The number of solvates featuring in the molecular formulae for these structures are thus necessarily estimates and aim to reflect the likely content of solvate in the lattice. Crystals of **24** were non-merohedrally twinned by pseudo two-fold rotation about the crystallographic [1,1,0] direction. The structure was therefore refined against non-merged reflection data, and with the twin law 0 1 0, 1 0 0, 0.33 0.33 -1, until the twin fractional domain parameter (x parameter) converged to a value of 0.4.

Table S1. Crystallographic data and structure refinement details of metallamacrocyclic trialdehydes.

	7c	**8a**	**8b**
Empirical formula	$C_{63}H_{81}N_3O_9Ru_3$ $\cdot 0.35Et_2O \cdot 0.65CHCl_3$	$C_{66}H_{63}N_3O_9Ru_3$ $\cdot 1.6CHCl_3$	$C_{63}H_{57}N_3O_9Ru_3$ $\cdot CHCl_3$
Formula weight	1431.05	1536.39	1422.69
Temperature / K	100(2)	140(2)	140(2)
Wavelength / Å	0.71073	0.71073	0.71073
Space group	$P2_1/n$	P-1	P-1
Unit cell dimensions / Å	a = 11.1899(18)	a = 12.8074(10)	a = 11.7185(6)
	b = 39.912(7)	b = 17.1174(15)	b = 13.5985(8)
	c = 14.267(2)	c = 19.0333(13)	c = 21.1648(8)
	α = 90°	α = 104.466(7)°	α = 93.476(4)°
	β = 92.541(13)°	β = 92.224(6)°	β = 96.109(4)°
	γ = 90°	γ = 111.419(8)°	γ = 114.941(5)°
Volume / Å^3	6365.8(18)	3722.0(5)	3019.9(3)
Z	4	2	2
Calculated density / g cm^{-3}	1.493	1.371	1.565
Absorption coefficient / mm^{-1}	0.842	0.824	0.932
F(000)	2946	1554	1436
Crystal size / mm	0.88 × 0.29 × 0.22	0.36 × 0.34 × 0.25	0.40 × 0.26 × 0.17
Measured θ range	3.36 to 25.03°	2.91 to 25.68°	2.92 to 27.48°
Limiting indices	$-13 \le h \le 9$	$-15 \le h \le 15$	$-15 \le h \le 15$
	$-47 \le k \le 47$	$-20 \le k \le 20$	$-17 \le k \le 17$
	$-16 \le l \le 16$	$-23 \le l \le 22$	$-27 \le l \le 27$
Reflections collected / unique	100176 / 11042	27081 / 13965	26161 / 13645
R_{int}	0.0690	0.0567	0.0198
Data / restraints / parameters	11042 / 0 / 799	13965 / 66 / 820	13645 / 30 / 776
Goodness of fit on F^2	1.170	1.065	1.048
R indices [$I \ge 2\sigma(I)$]	R_1 = 0.0449 wR_2 = 0.0779	R_1 = 0.1015 wR_2 = 0.2896	R_1 = 0.0303 wR_2 = 0.0864
R indices (all data)	R_1 = 0.0581 wR_2 = 0.0825	R_1 = 0.1507 wR_2 = 0.3137	R_1 = 0.0339 wR_2 = 0.0885
Final Fourier residuals	0.618 and −0.751 e Å^{-3}	2.772 and −1.371 e Å^{-3}	0.988 and −0.619 e Å^{-3}

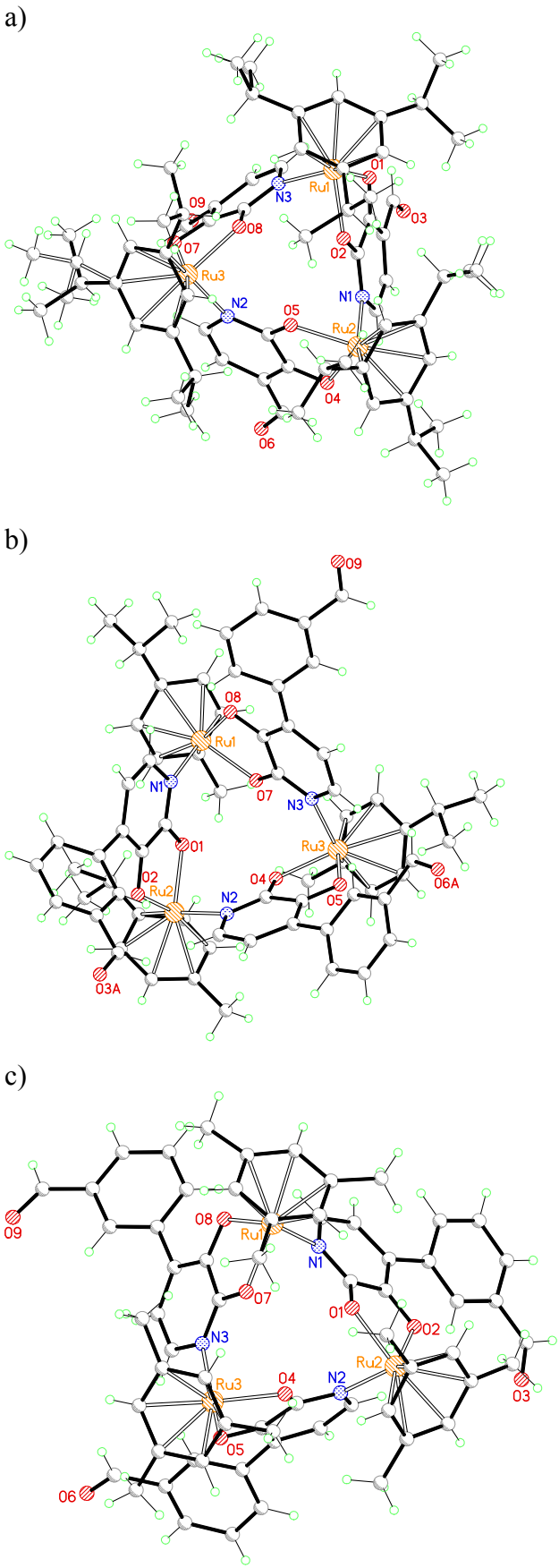


Figure S1. Structures of a) **7c**, b) **8a** and c) **8b** in the solid state. In each case, only one of the two stereoisomers is shown; solvent molecules are omitted for clarity.

Table S2. Crystallographic data and structure refinement details of tetrahedral cages.

	18b	**20b**	**21a**	**21b**
Empirical formula	$C_{260}H_{240}N_{24}O_{24}Ru_{12}$ ·10$CHCl_3$	$C_{292}H_{280}N_{24}O_{24}Ru_{12}$ ·10CH_3OH	$C_{216}H_{242}N_{28}O_{24}Ru_{12}$ ·10CH_3OH·2C_6H_5F	$C_{204}H_{228}N_{28}O_{24}Ru_{12}$ ·20$CHCl_3$
Formula weight	6491.28	6042.66	5339.84	7056.34
Temperature / K	100(2)	100(2)	100(2)	100(2)
Wavelength / Å	0.71073	0.71073	0.71073	0.71073
Space group	*C*2/*c*	*C*2/*c*	*P*2/*n*	*Pcca*
Unit cell dimensions / Å	*a* = 43.312(5)	*a* = 46.782(10)	*a* = 25.854(3)	*a* = 32.975(3)
	b = 20.595(2)	*b* = 21.660(7)	*b* = 18.338(3)	*b* = 43.449(9)
	c = 40.698(4)	*c* = 43.661(10)	*c* = 35.306(5)	*c* = 27.608(4)
	α = 90°	α = 90°	α = 90°	α = 90°
	β = 111.009(12)°	β = 113.095(12)°	β = 94.407(8)°	β = 90°
	γ = 90°	γ = 90°	γ = 90°	γ = 90°
Volume / $Å^3$	33890(6)	40697(18)	16689(4)	39554(10)
Z	4	4	2	4
Calculated density / g cm^{-3}	1.272	0.986	1.063	1.185
Absorption coefficient / mm^{-1}	0.809	0.481	0.579	0.894
F(000)	13072	12400	5468	14112
Crystal size / mm	0.31 × 0.29 × 0.22	0.50 × 0.22 × 0.15	0.46 × 0.24 × 0.12	0.51 × 0.48 × 0.32
Measured θ range	2.86 to 27.57	3.04 to 20.01°	3.00 to 22.00°	3.00 to 22.00°
Limiting indices	$-33 \le h \le 33$	$-44 \le h \le 44$	$-30 \le h \le 30$	$-30 \le h \le 31$
	$-15 \le k \le 15$	$-20 \le k \le 20$	$-21 \le k \le 21$	$-41 \le k \le 41$
	$-31 \le l \le 31$	$-42 \le l \le 42$	$-41 \le l \le 41$	$-26 \le l \le 26$
Reflections collected / unique	45982 / 8029	93370 / 18803	172853 / 28323	165876 / 17230
R_{int}	0.1749	0.0705	0.1274	0.0840
Data / restraints / parameters	8029 / 1058 / 671	18803 / 3888 / 1696	28323 / 1055 / 1293	17230 / 2334 / 1387
Goodness of fit on F^2	1.479	1.057	1.028	2.233
R indices [$I \ge 2\sigma(I)$]	R_1 = 0.1260	R_1 = 0.0800	R_1 = 0.1109	R_1 = 0.1557
	wR_2 = 0.2857	wR_2 = 0.2125	wR_2 = 0.2969	wR_2 = 0.3628
R indices (all data)	R_1 = 0.1857	R_1 = 0.1029	R_1 = 0.1872	R_1 = 0.1974
	wR_2 = 0.3008	wR_2 = 0.2273	wR_2 = 0.3457	wR_2 = 0.3772
Final Fourier residuals	0.676 and −0.475 e $Å^{-3}$	1.233 and −0.727 e $Å^{-3}$	1.724 and −0.888 e $Å^{-3}$	1.313 and −0.700 e $Å^{-3}$

Table S3. Crystallographic data and structure refinement details of cylindrical cages.

	24	**26**	**28**
Empirical formula	$C_{123}H_{135}N_{15}O_{12}Ru_6$	$C_{120}H_{126}N_{12}O_{12}Ru_6$ ·4$CHCl_3$·2H_2O	$C_{102}H_{114}N_{12}O_{14}Ru_6$ ·7$CHCl_3$·2H_2O
Formula weight	2621.88	3048.25	3178.08
Temperature / K	100(2)	100(2)	100(2)
Wavelength / Å	0.71073	0.71073	0.71073
Space group	*P*-1	*R*-3*c*	*R*-3*c*
Unit cell dimensions / Å	a = 18.703(4)	a = 20.034(3)	a = 20.279(4)
	b = 18.732(4)	b = 20.034(3)	b = 20.279(4)
	c = 91.23.369(5)	c = 91.487(18)	c = 62.756(5)
	α = 89.61(3)	α = 90°	α = 90°
	β = 72.09(3)	β = 90°	β = 90°
	γ = 77.26(3)	γ = 120°	γ = 120°
Volume / $Å^3$	7583(3)	31801(9)	22351(7)
Z	2	6	6
Calculated density / g cm^{-3}	1.148	0.955	1.417
Absorption coefficient / mm^{-1}	0.634	0.607	1.023
F(000)	2676	9252	9576
Crystal size / mm	0.48 × 0.29× 0.25	0.59 × 0.38 × 0.30	0.38 × 0.24 × 0.22
Measured θ range	3.01 to 20.08°	3.11 to 18.90°	3.09 to 23.10°
Limiting indices	$-18 \le h \le 18$	$-15 \le h \le 0$	$-18 \le h \le 22$
	$-18 \le k \le 18$	$0 \le k \le 18$	$-22 \le k \le 22$
	$-22 \le l \le 22$	$0 \le l \le 82$	$-62 \le l \le 67$
Reflections collected / unique	13643	2788 / 2788	24753 / 3482
R_{int}	-	-	0.0779
Data / restraints / parameters	13643 / 1746 / 1389	2788 / 108 / 253	3482 / 30 / 278
Goodness of fit on F^2	1.308	1.278	1.118
R indices [$I \ge 2\sigma(I)$]	R_1 = 0.1310, wR_1 = 0.3399	R_1 = 0.1375, wR_1 = 0.3449	R_1 = 0.0617, wR_1 = 0.1605
R indices (all data)	R_1 = 0.1527, wR_1 = 0.3635	R_1 = 0.1870, wR_1 = 0.3832	R_1 = 0.0996, wR_1 = 0.1949
Final Fourier residuals	3.572 and −2.520 e $Å^{-3}$	1.437 and −0.589 e $Å^{-3}$	1.127 and −0.702 e $Å^{-3}$

Table S4. Crystallographic data and structure refinement details of small cages.

	31a	**31b**
Empirical formula	$C_{81}H_{84}N_6O_6Ru_3$ $\cdot 0.5C_6H_5F \cdot H_2O$	$C_{78}H_{78}N_6O_6Ru_3$ $\cdot C_6H_5F$
Formula weight	1606.82	1594.77
Temperature / K	100(2)	140(2)
Wavelength / Å	0.71073	0.71073
Space group	*R*-3	$P2_13$
Unit cell dimensions / Å	a = 16.332(2)	a = 20.5269(3)
	b = 16.332(2)	b = 20.5269(3)
	c = 47.642(10)	c = 20.5269(3)
	α = 90°	α = 90°
	β = 90°	β = 90°
	γ = 120°	γ = 90°
Volume / Å^3	11005(3)	8649.1(2)
Z	6	4
Calculated density / g cm^{-3}	1.455	1.225
Absorption coefficient / mm^{-1}	0.671	0.569
F(000)	4962	3272
Crystal size / mm	0.35 × 0.30 × 0.25	0.34 × 0.28 × 0.22
Measured θ range	3.00 to 25.02°	2.98 to 26.36°
Limiting indices	$-19 \le h \le 19$	$-17 \le h \le 25$
	$-19 \le k \le 19$	$-25 \le k \le 25$
	$-56 \le l \le 56$	$-17 \le l \le 25$
Reflections collected / unique	50070 / 4318	5890 / 5890
R_{int}	0.1641	-
Data / restraints / parameters	4318 / 13 / 317	5890 / 0 / 311
Goodness of fit on F^2	1.059	0.996
R indices [$I \ge 2\sigma(I)$]	R_1 = 0.0467, wR_1 = 0.1052	R_1 = 0.0637 wR_2 = 0.1438
R indices (all data)	R_1 = 0.0725, wR_1 = 0.1190	R_1 = 0.0987 wR_2 = 0.1558
Final Fourier residuals	1.200 and −0.707 e Å^{-3}	0.675 and −0.375 e Å^{-3}

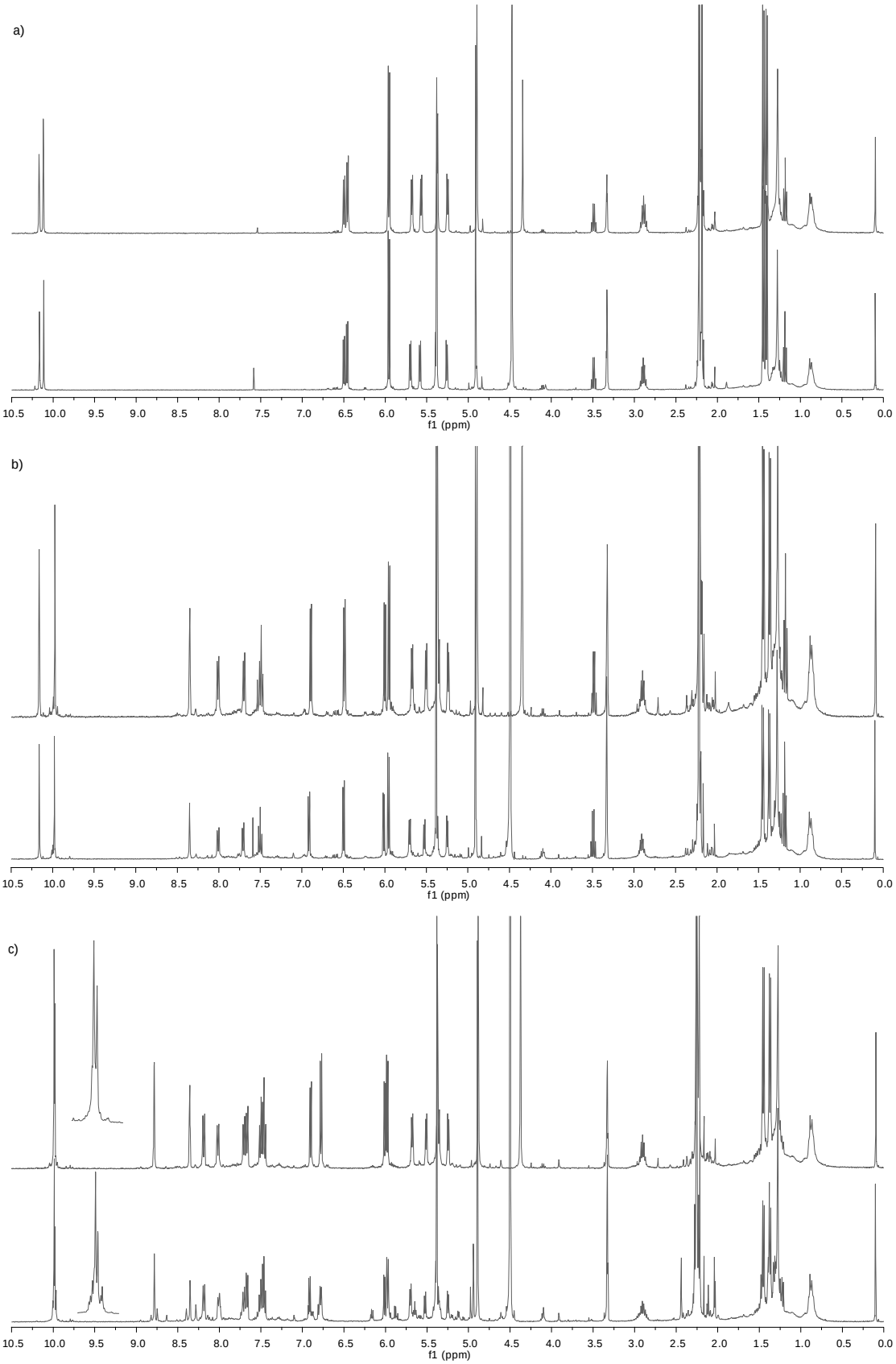


Figure S2. ^{1}H NMR (400 MHz) spectra of equimolar mixtures of a) **7a** and **7b**; b) **7a** and **8b**; c) **8a** and **8b**. Upper spectra: freshly prepared samples; lower spectra: samples equilibrated for 7 days at room temperature.

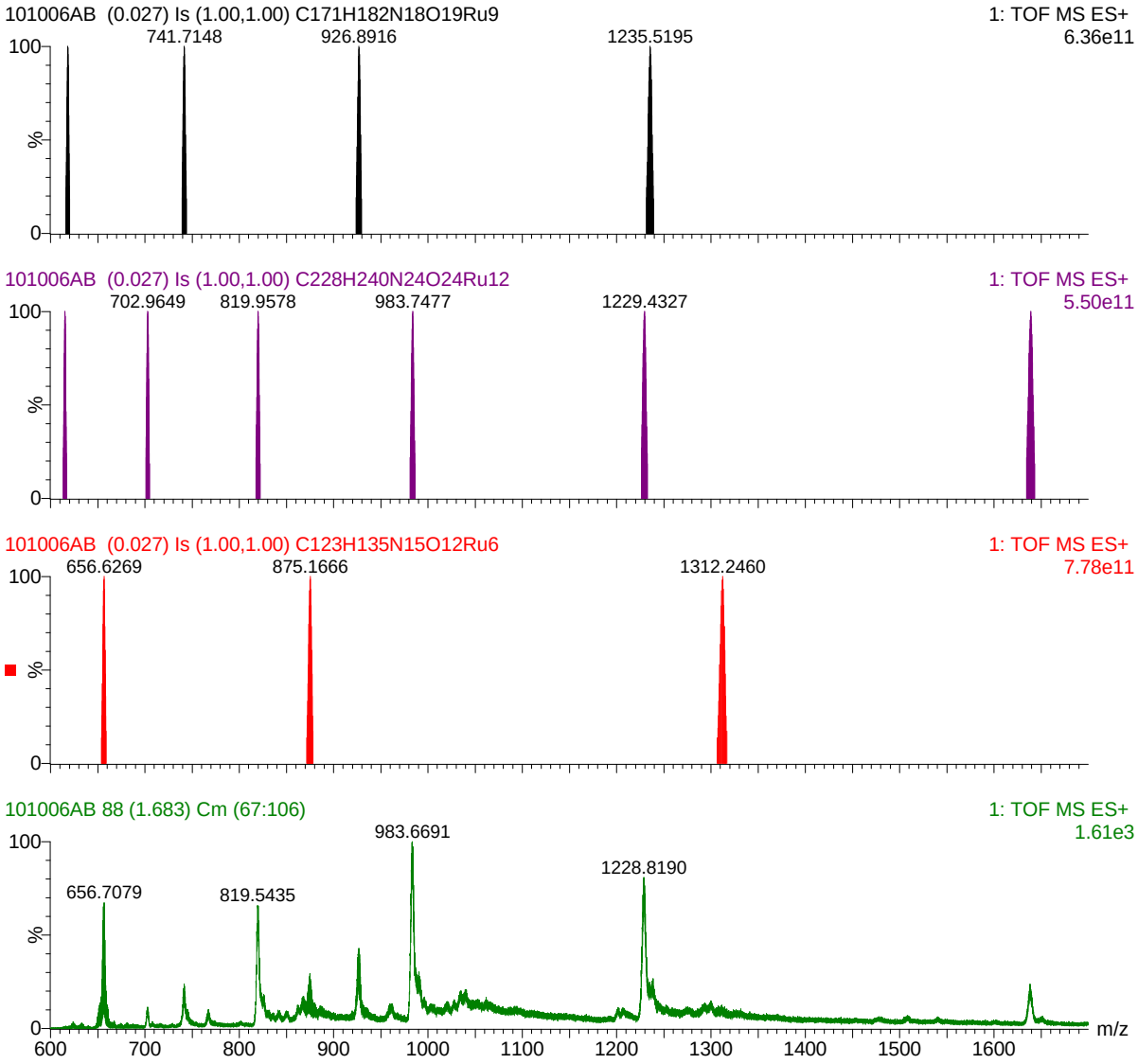


Figure S3. Mass spectrum (ESI^+) of the reaction mixture of equimolar amounts of **7a** and **22** after 18 h reaction time. Lower panel: experimental spectra, top panels: calculated charged series for the products of [3 + 3] (black), [4 + 4] (**25**: violet) and [2 + 3] (**24**: red) condensations.

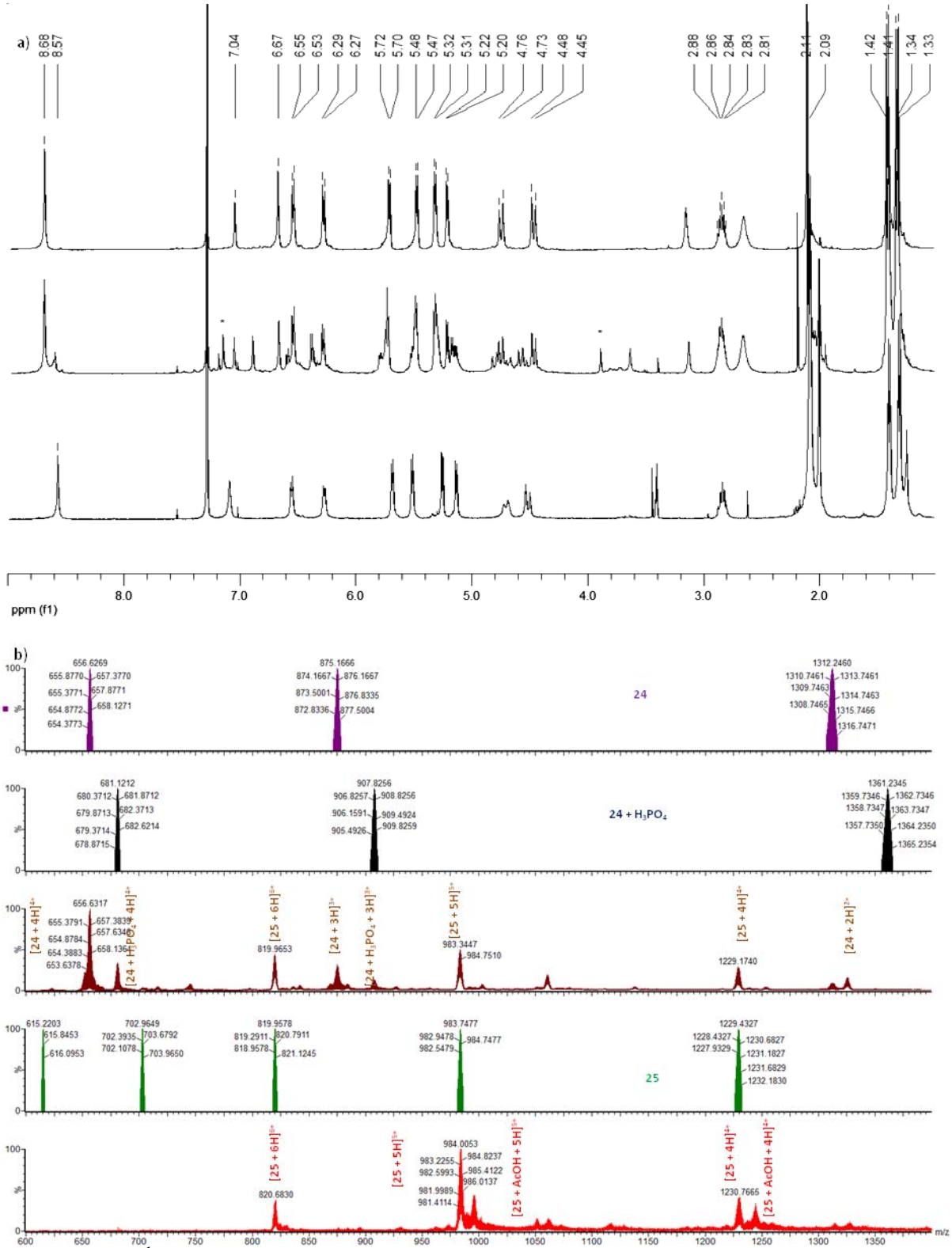
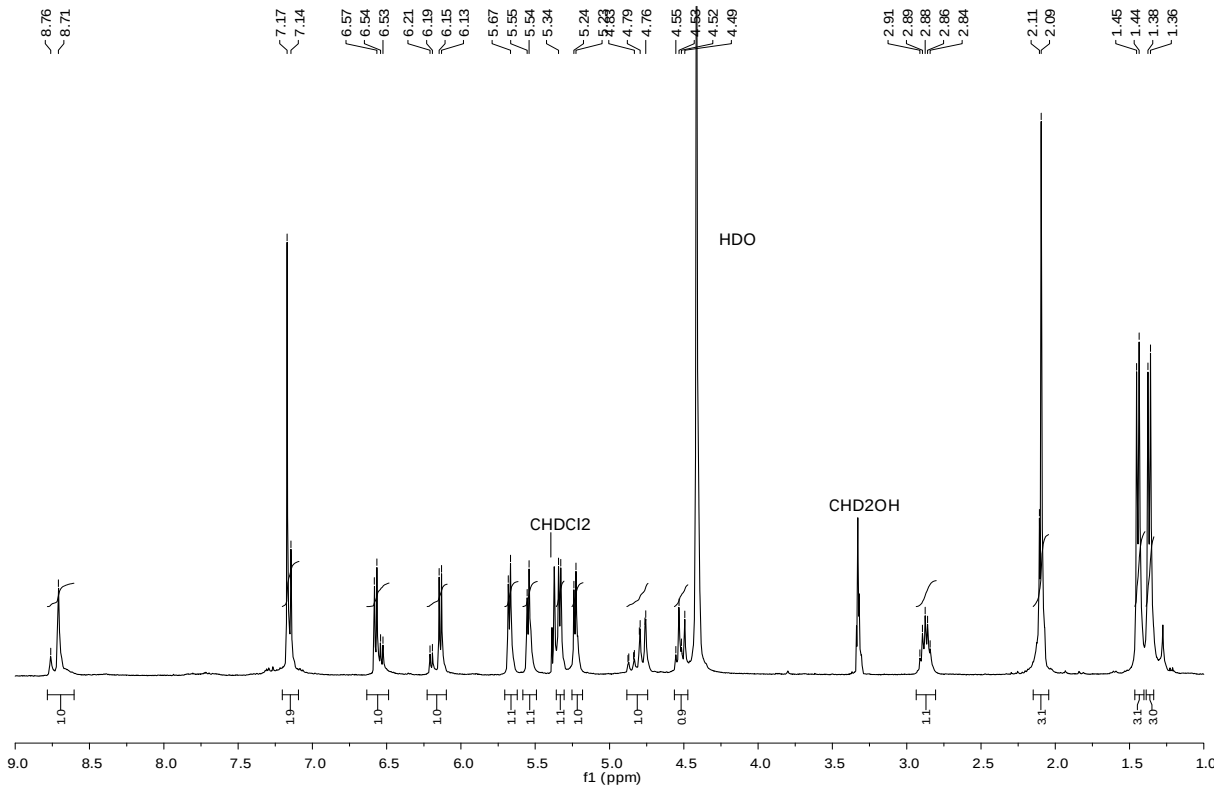


Figure S4. a) ^{1}H NMR spectra (400 MHz, $CDCl_3$) of fresh sample of **24** (top), of the sample after 30 h at room temperature (middle) and of **25** (bottom); the peaks labeled (*) correspond to free 1,3,5-tris(aminomethyl)benzene **22**; b) mass spectrum (ESI^+, brown) of the sample of **24** in $CDCl_3$ after 30 h at room temperature, calculated charged series for **24** (purple), **24** + H_3PO_4 (black) and **25** (green) and mass spectrum (ESI^+, red) of **25** in $CDCl_3$.

a)



b) c)

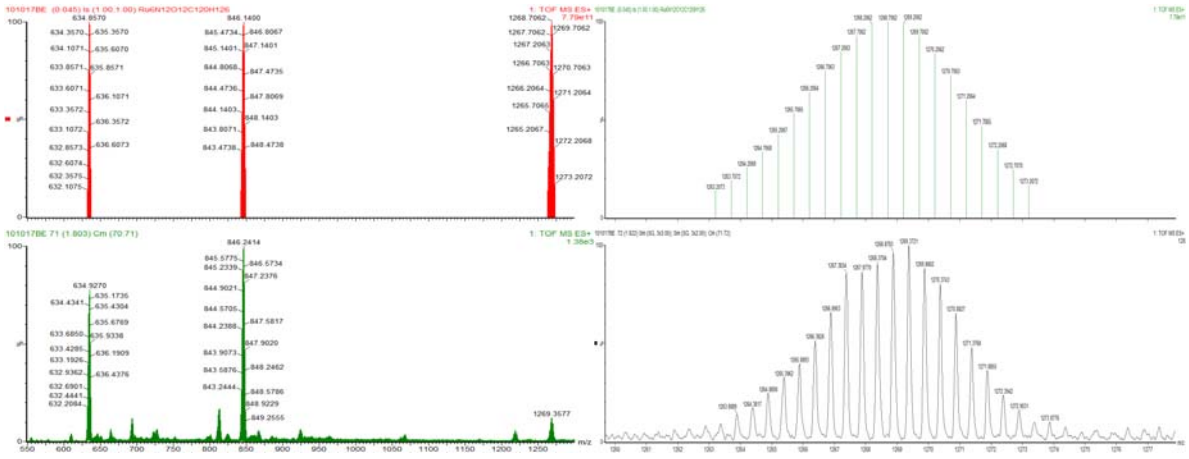


Figure S5. a) ^{1}H NMR ($CDCl_3$–CD_3OD 95:5 v/v, 400 MHz); b) low-resolution and c) high-resolution (ESI^+) mass spectra (lower panels: experimental spectra, top panels: calculated isotopic distribution of charged series) of the inseparable products of reaction of **7a** with *p*-xylylenediamine (mixture of *meso*-**26** and *P,P*/*M,M*-**26**: $C_{120}H_{126}N_{12}O_{12}Ru_6$).

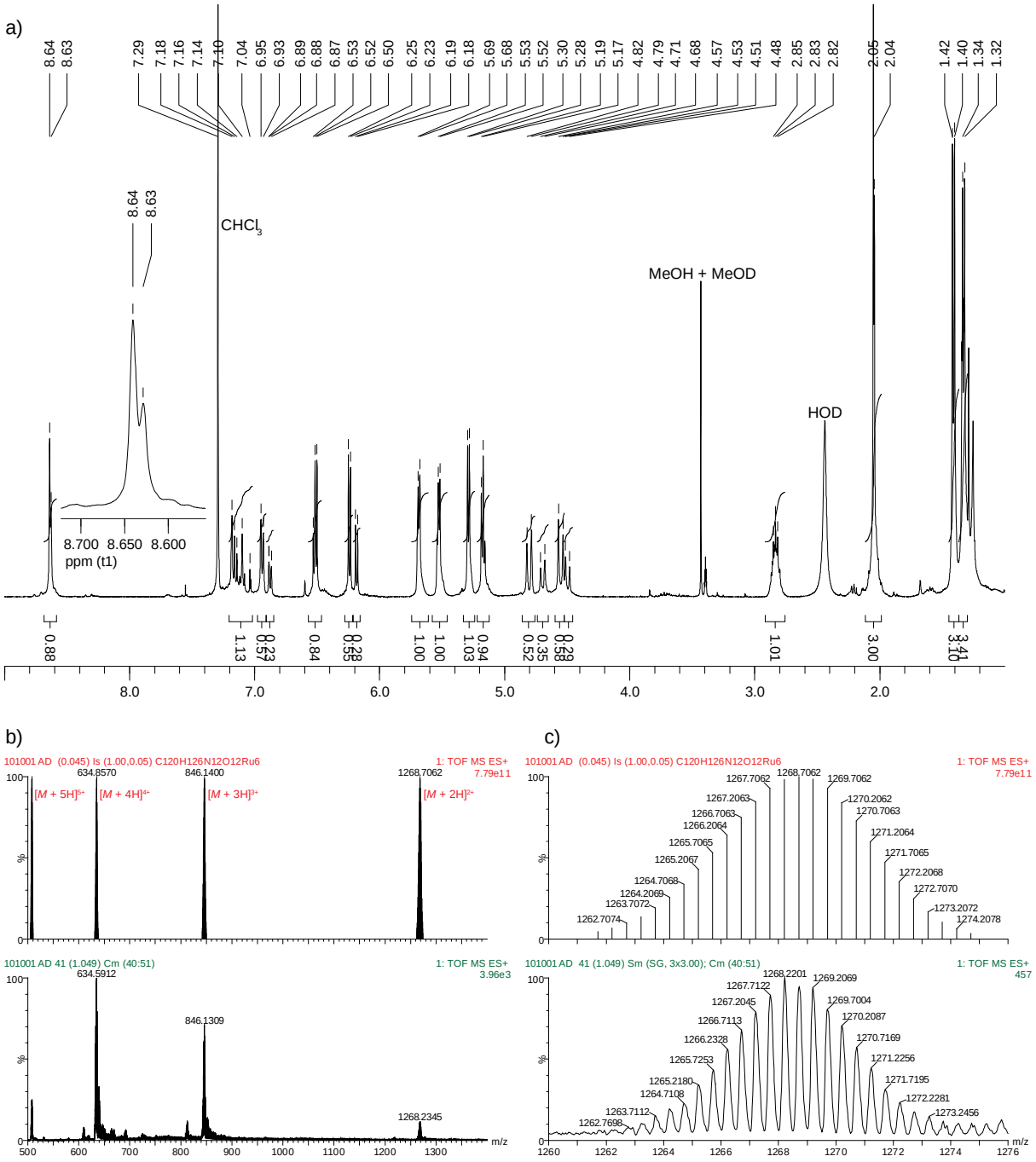
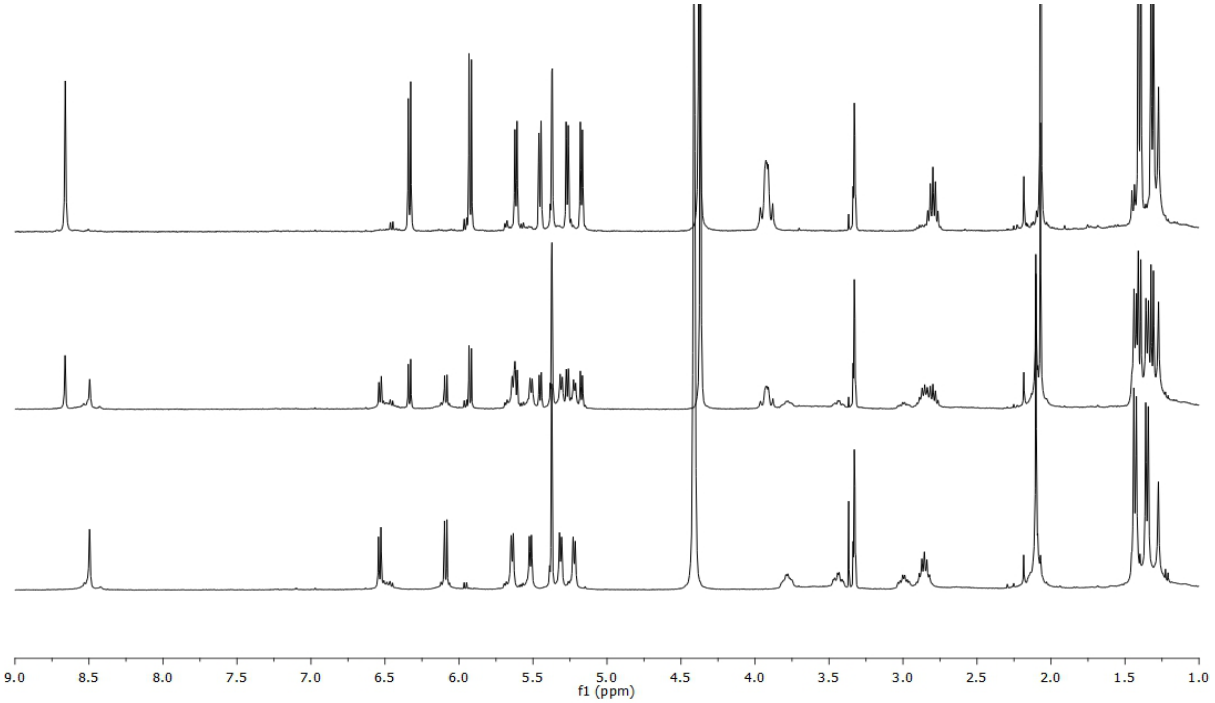


Figure S6. a) ^{1}H NMR ($CDCl_3$–CD_3OD 95:5 v/v, 400 MHz); b) low-resolution and c) high-resolution (ESI^+) mass spectra (lower panels: experimental spectra, top panels: calculated isotopic distribution of charged series) of the inseparable products of reaction of **7a** with *m*-xylylenediamine (mixture of *meso*-**27** and *P*,*P*/*M*,*M*-**27**: $C_{120}H_{126}N_{12}O_{12}Ru_6$).

a)



b)

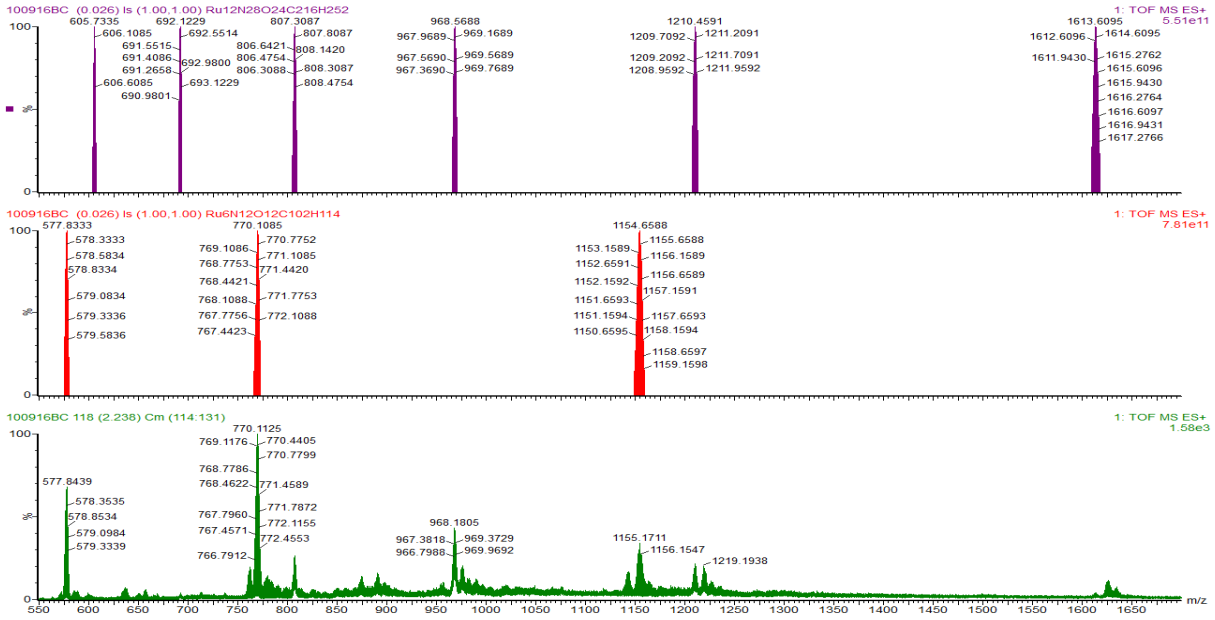
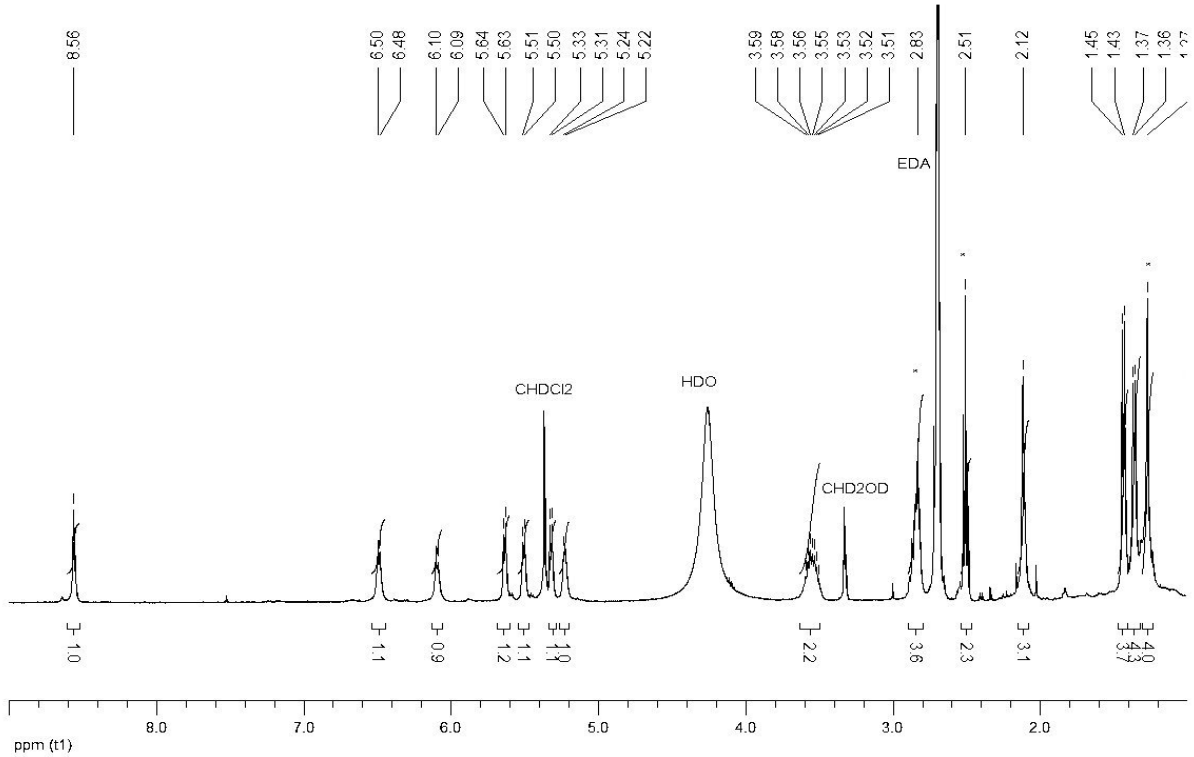


Figure S7. a) ^{1}H NMR spectra (CD_2Cl_2-MeOD 1.75-1 v/v, 400 MHz) of **28** (top), of the self-sorting reaction between the macrocycle **7a**, ethylenediamine and TREN (middle) and of **21a** (bottom); b) low-resolution (ESI^+) experimental mass-spectrum of the self-sorting reaction mixture (bottom) and calculated isotopic distribution of charged series for **21a** (middle) and **28** (top).

a)



b) c)

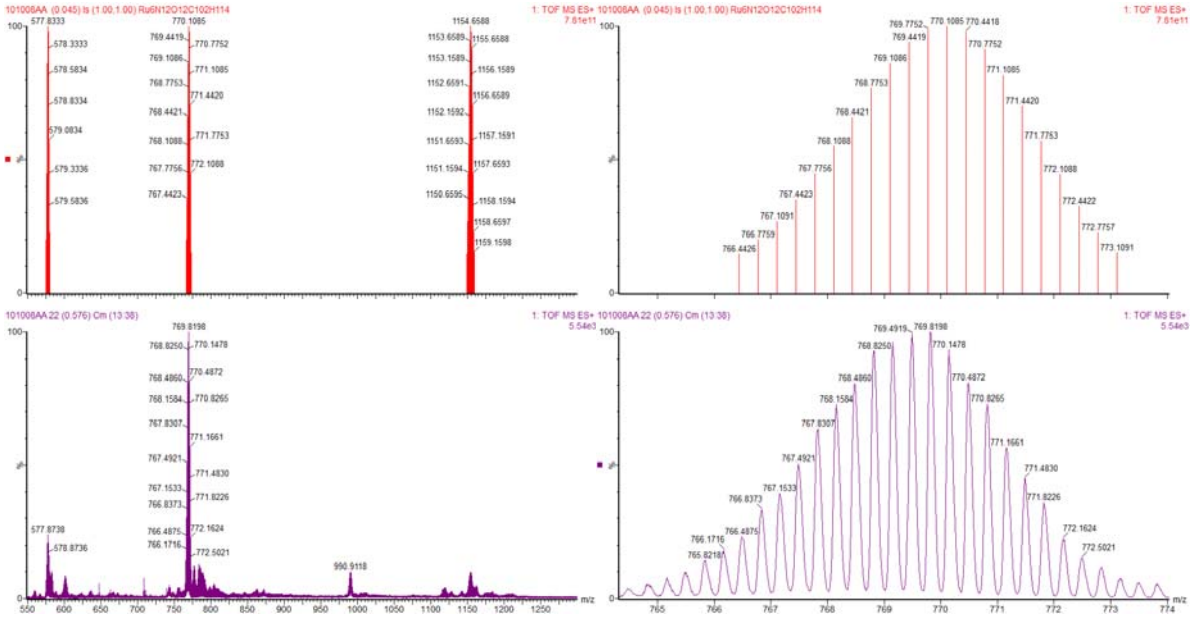


Figure S8. a) ^{1}H NMR ($CDCl_3$–CD_3OD 95:5 v/v, 400 MHz) of the reaction mixture of **21a** plus 10 equivalents of ethylenediamine (EDA) to give **28** (the peaks labeled with "*" correspond to free tris(2-aminoethyl)amine), and b) low-resolution and c) high-resolution (ESI^+) mass spectra (lower panels: experimental spectra, top panels: calculated isotopic distribution of charged series).

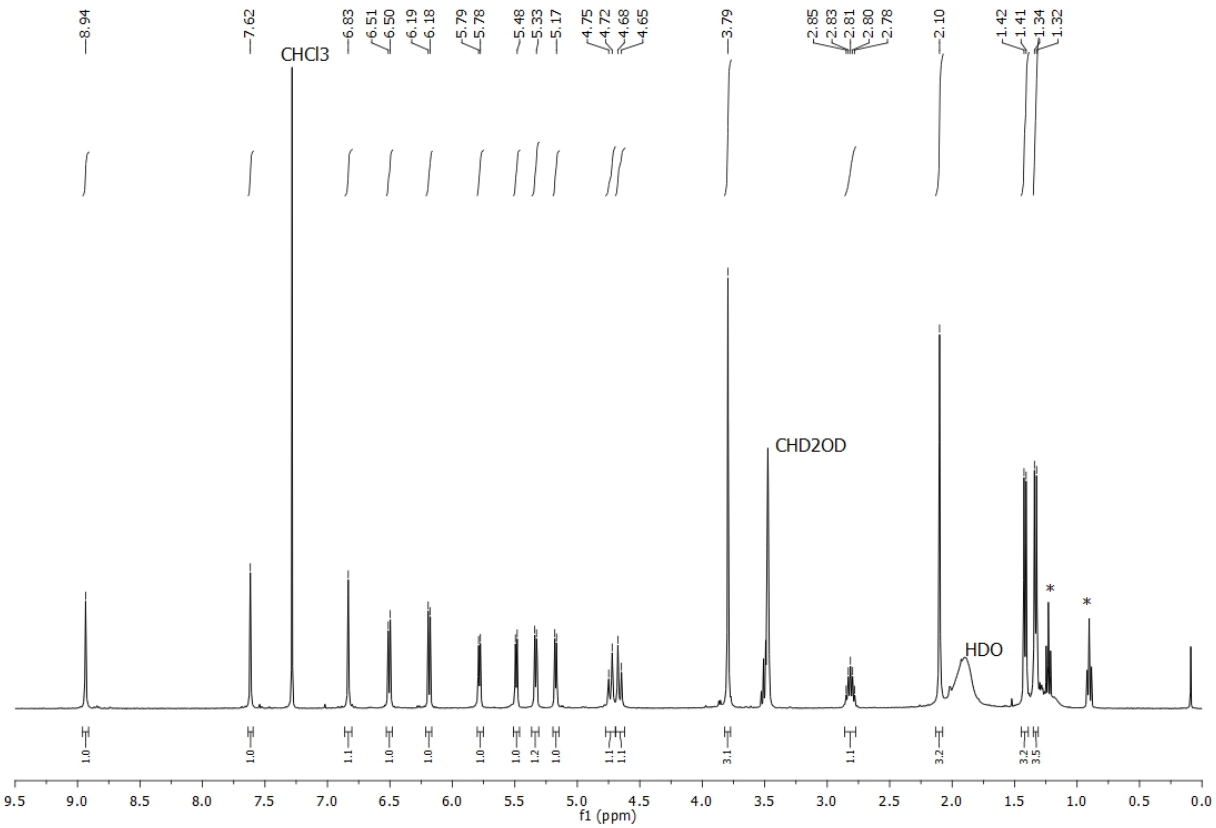


Figure S9. One-pot synthesis of **29**: ^{1}H NMR spectrum (400 MHz, $CDCl_3$–CD_3OD 95:5 v/v) of crude **29** synthesized using one-pot procedure (from $[(cymene)RuCl_2]_2$, **3**, and **30**) The peaks marked (*) correspond to the long-chain linear aliphatic hydrocarbon impurity.

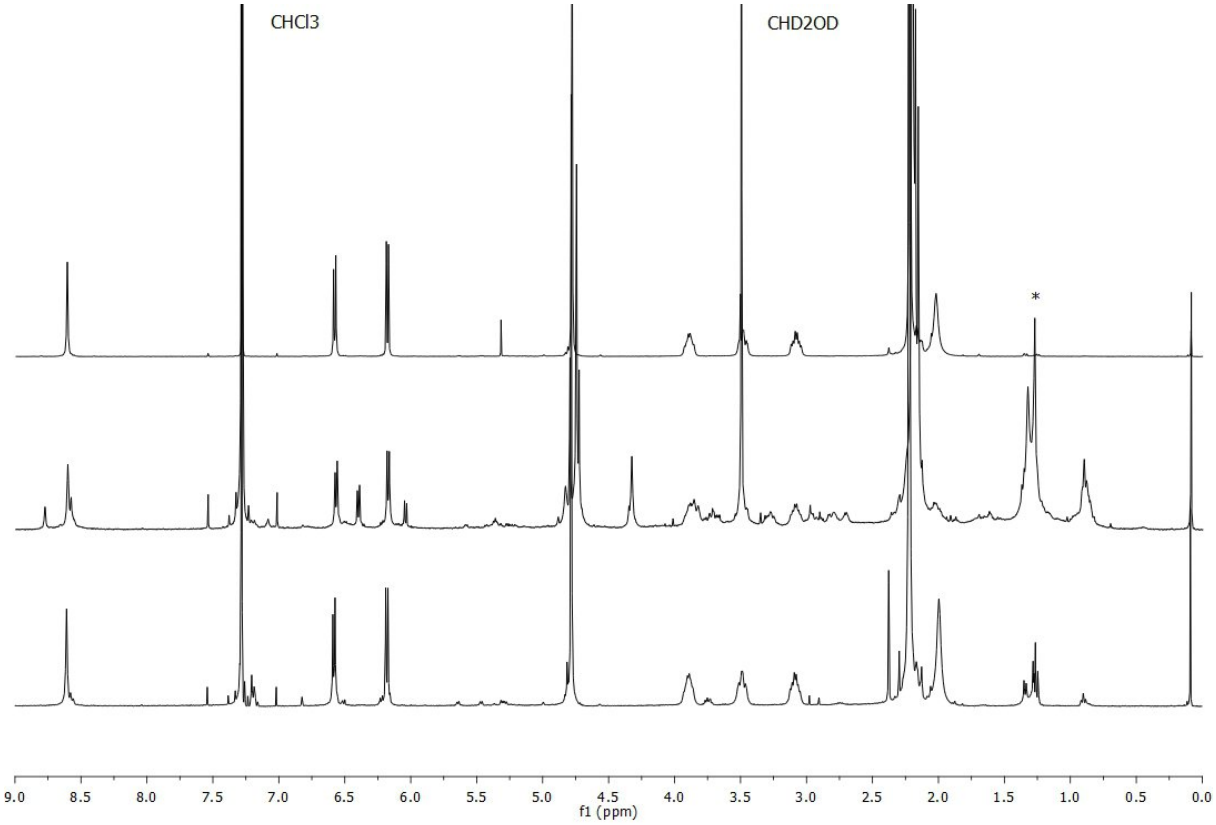


Figure S10. One-pot synthesis of **21b**. Top: ^{1}H NMR spectrum (400 MHz, $CDCl_3$–CD_3OD 95:5 v/v) of **21b** synthesized from **7b** and tris(2-aminoethyl)amine; middle: spectrum of crude **21b** synthesized using one-pot procedure (from $[(mesitylene)RuCl_2]_2$, **3**, and tris(2-amino-ethyl)amine); bottom: spectrum of **21b** precipitated from the one-pot reaction mixture after evaporation of dichloromethane. The peaks marked (*) correspond to the long-chain linear aliphatic hydrocarbon impurity.

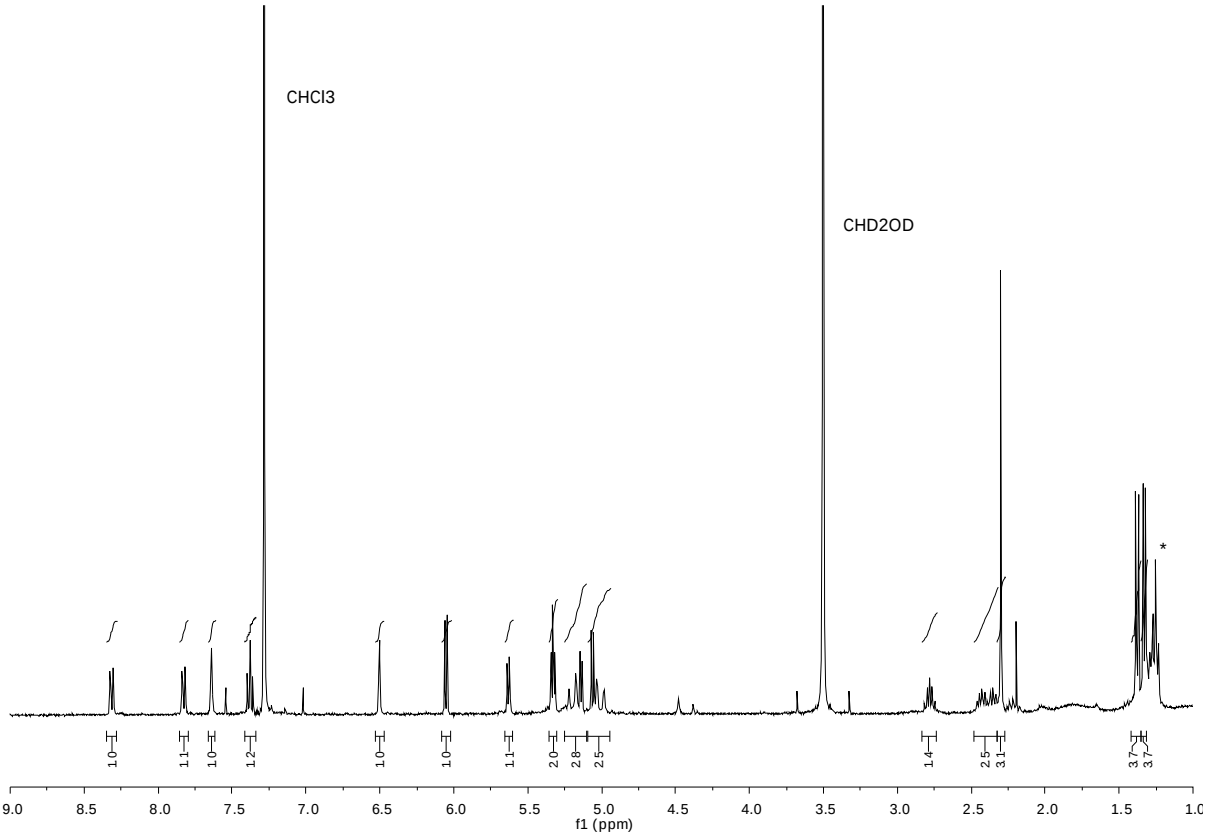


Figure S11. One-pot synthesis of **31a**: ^{1}H NMR spectrum (400 MHz, $CDCl_3$–CD_3OD 95:5 v/v) of crude **31a** synthesized using one-pot procedure (from $[(cymene)RuCl_2]_2$, **3**, and **23**). The peaks marked (*) correspond to the long-chain linear aliphatic hydrocarbon impurity.

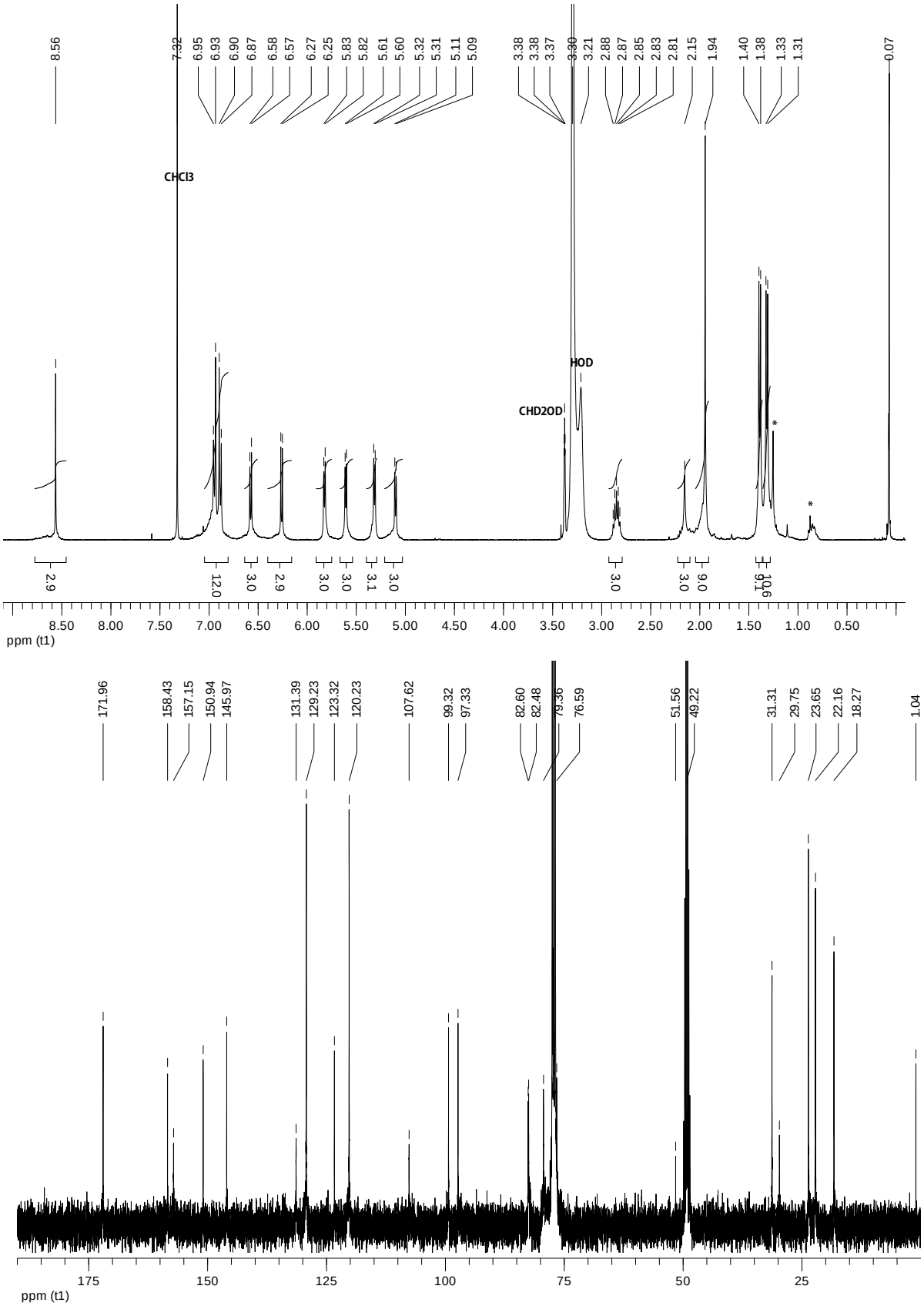


Figure S12. ^{1}H (top panel, 400 MHz) and ^{13}C (bottom panel, 100 MHz) NMR spectra of cage **18a** in $CDCl_3$–CD_3OD (90:10). The peaks marked (*) correspond to the long-chain linear aliphatic hydrocarbon impurity.

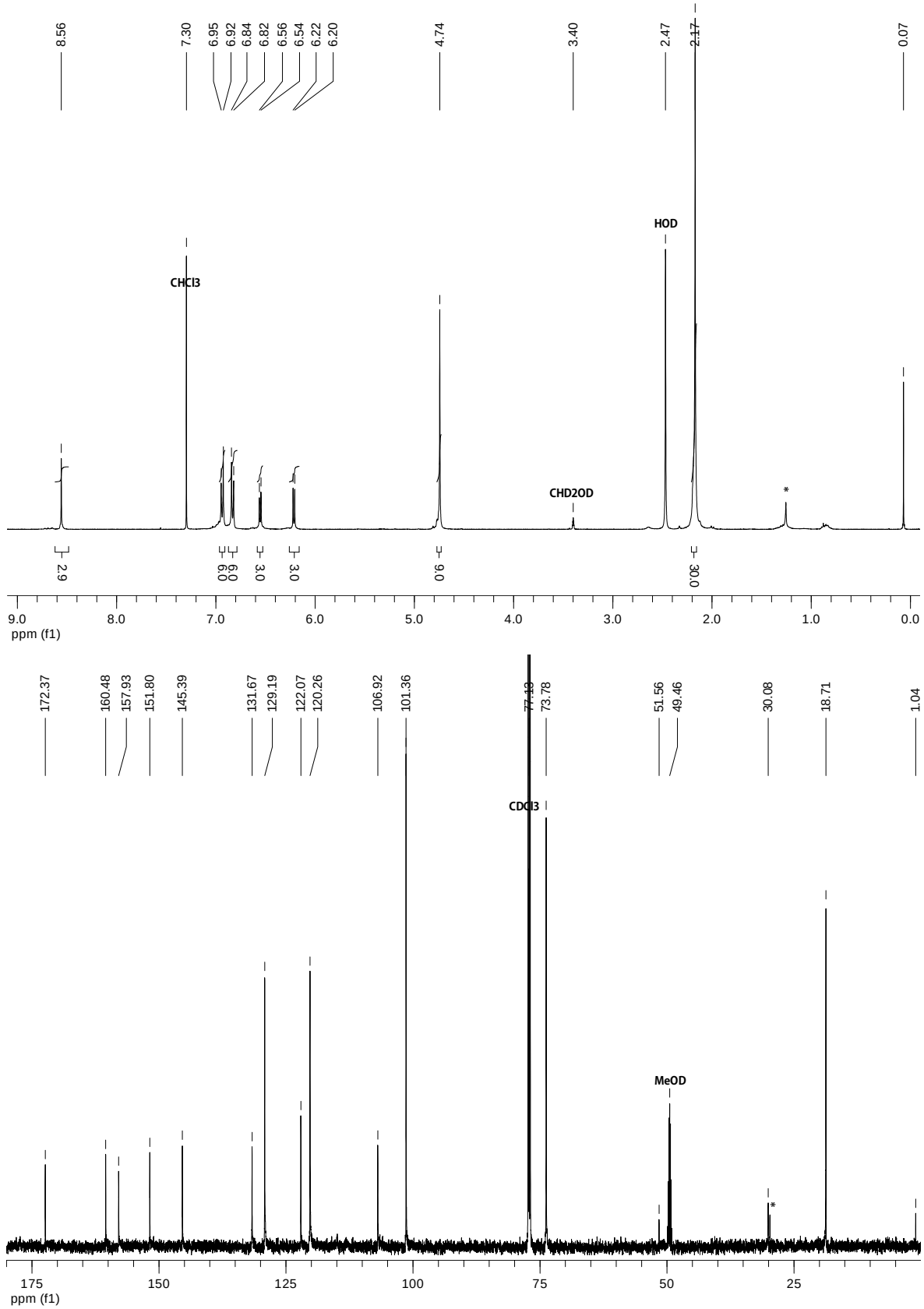


Figure S13. ^{1}H (top panel, 400 MHz) and ^{13}C (bottom panel, 150 MHz) NMR spectra of cage **18b** in $CDCl_3$–CD_3OD (95:5). The peaks marked (*) correspond to the long-chain linear aliphatic hydrocarbon impurity.

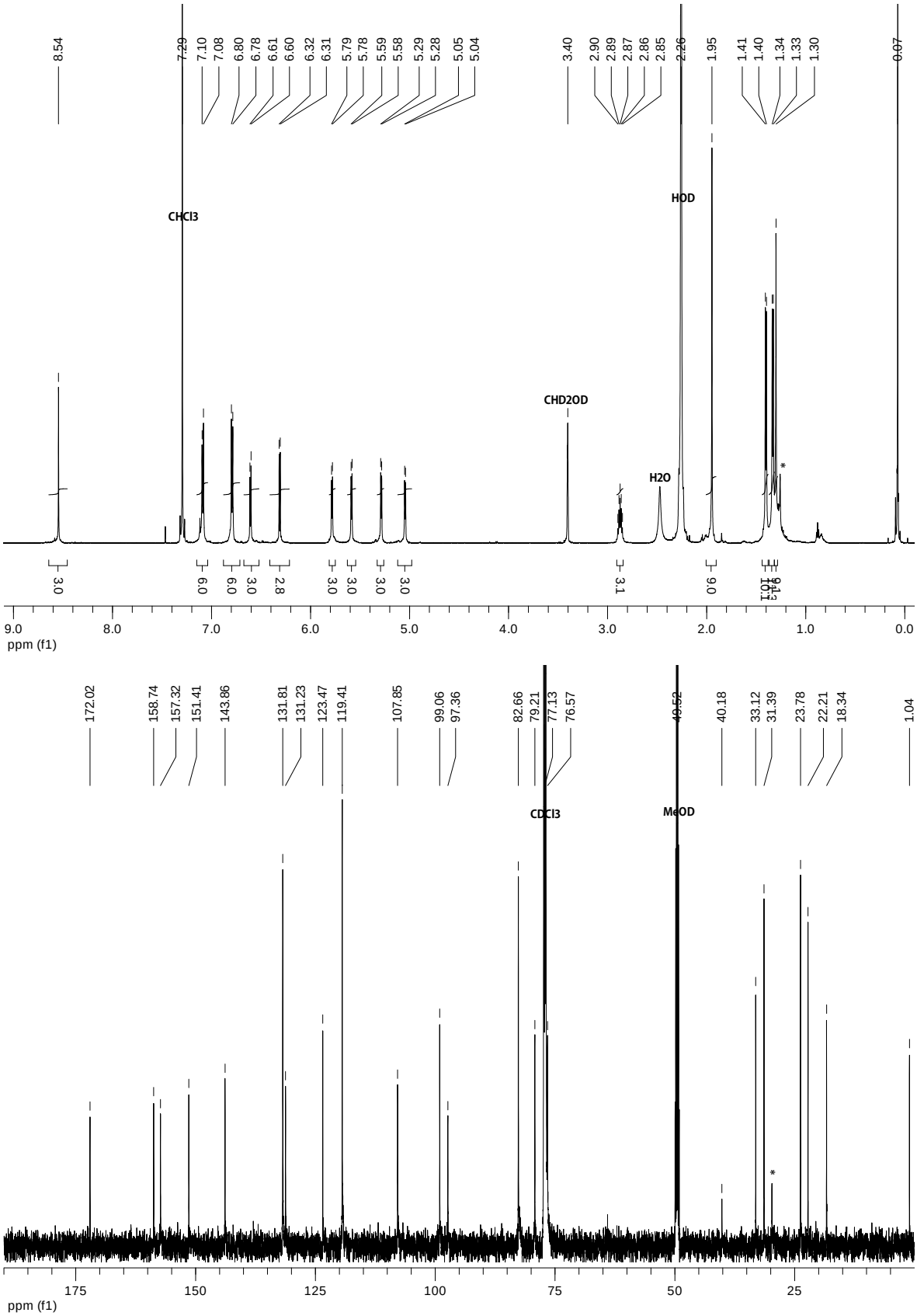


Figure S14. ^{1}H (top panel, 600 MHz) and ^{13}C (bottom panel, 150 MHz) NMR spectra of cage **19a** in $CDCl_3$–CD_3OD (95:5). The peaks marked (*) correspond to the long-chain linear aliphatic hydrocarbon impurity.

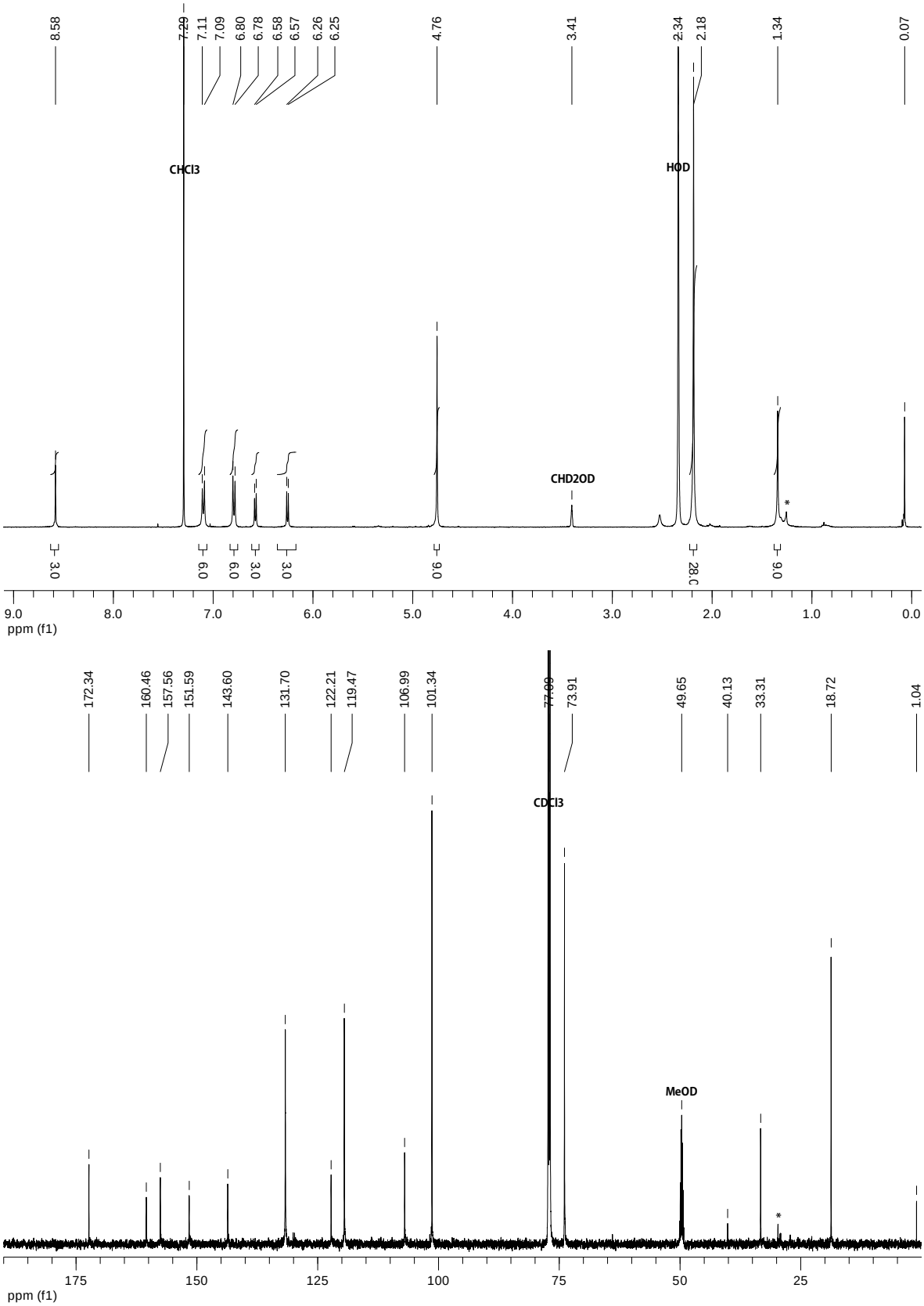


Figure S15. ^{1}H (top panel, 400 MHz) and ^{13}C (bottom panel, 150 MHz) NMR spectra of cage **19b** in $CDCl_3$–CD_3OD (95:5). The peaks marked (*) correspond to the long-chain linear aliphatic hydrocarbon impurity.

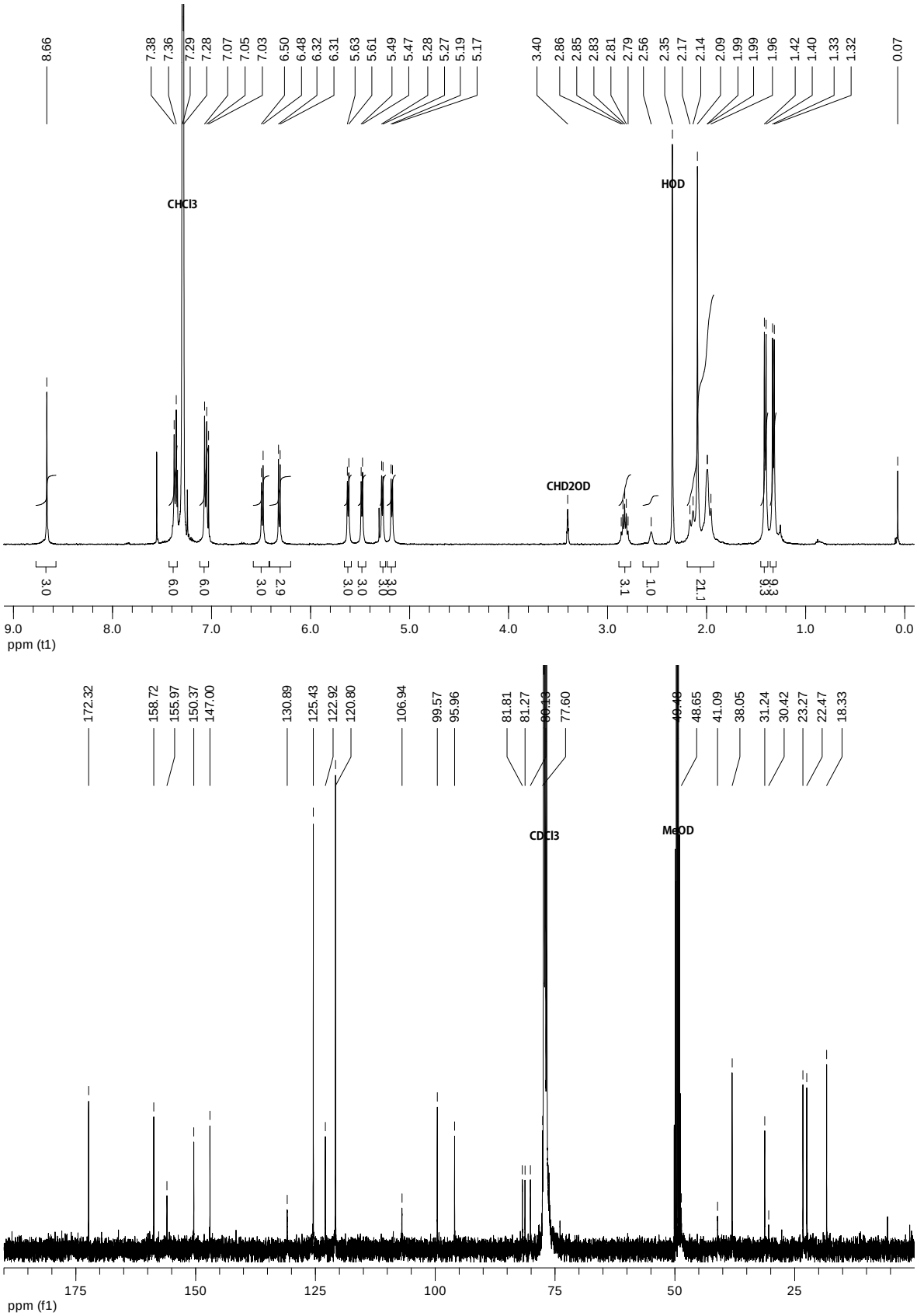


Figure S16. ^{1}H (top panel, 400 MHz) and ^{13}C (bottom panel, 100 MHz) NMR spectra of cage **20a** in $CDCl_3$–CD_3OD (95:5).

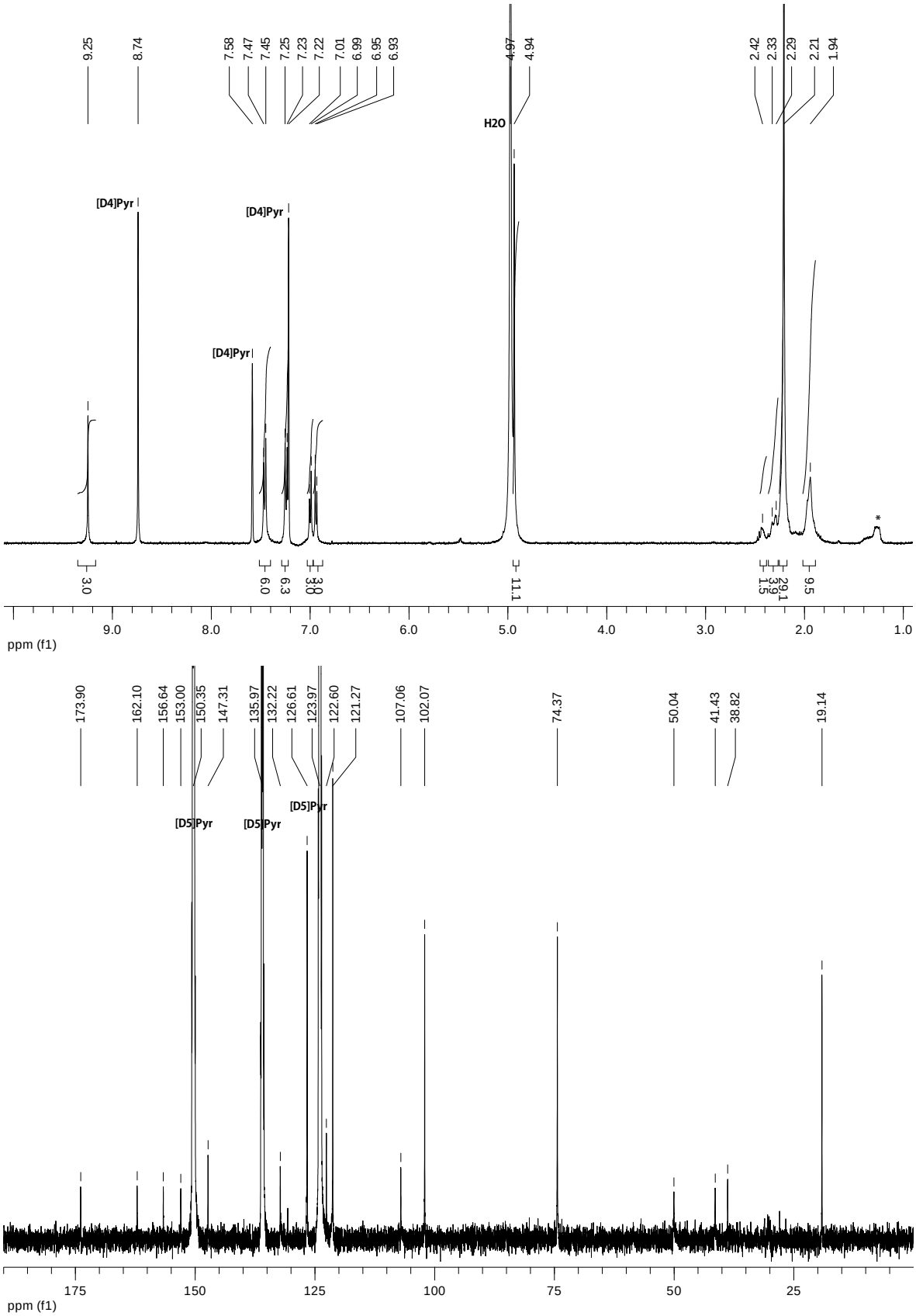


Figure S17. ^{1}H (top panel, 400 MHz) and ^{13}C (bottom panel, 150 MHz) NMR spectra of cage **20b** in [D5]pyridine. The peaks marked (*) correspond to the long-chain linear aliphatic hydrocarbon impurity.

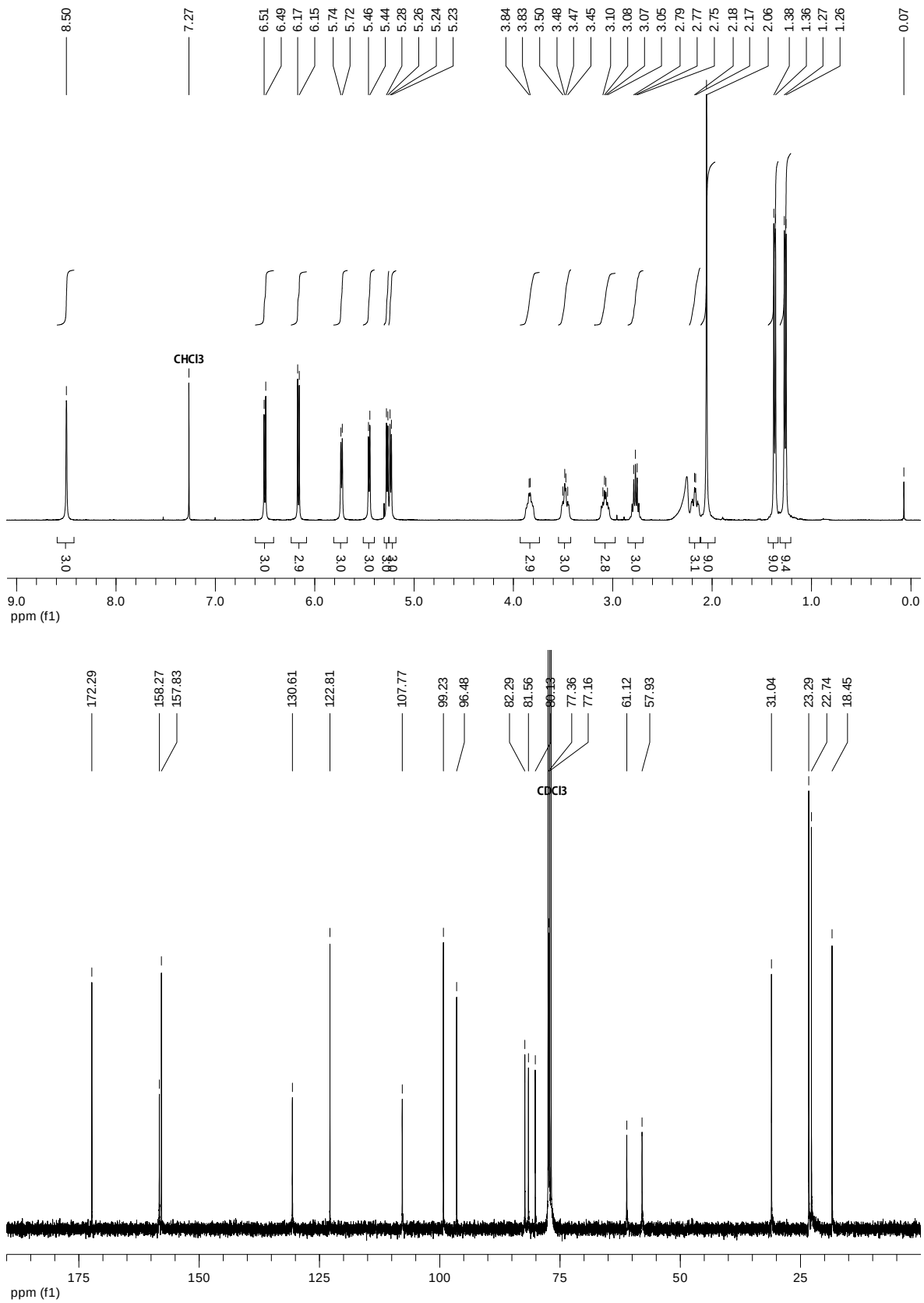


Figure S18. ^{1}H (top panel, 400 MHz) and ^{13}C (bottom panel, 100 MHz) NMR spectra of cage **21a** in $CDCl_3$.

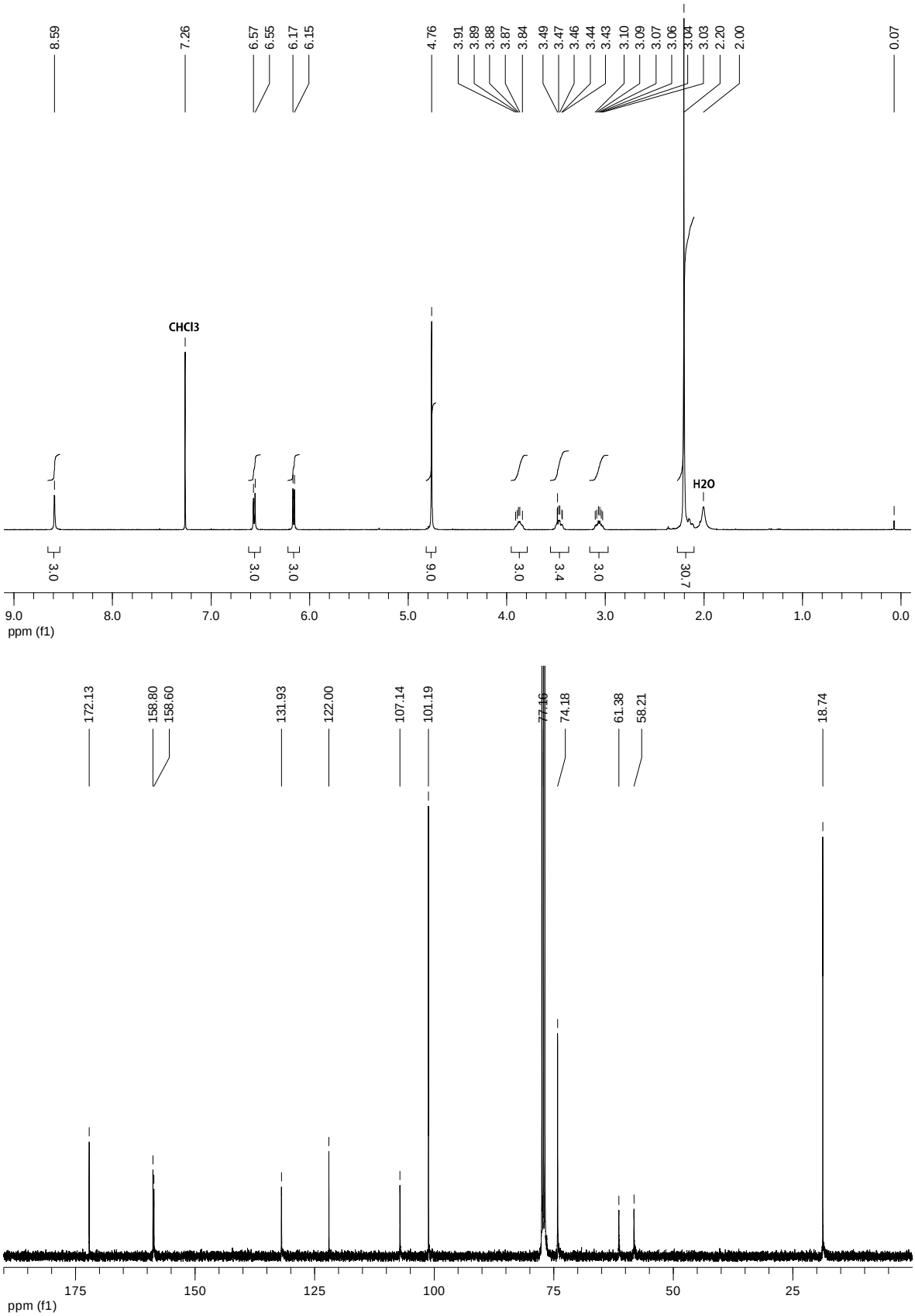


Figure S19. ^{1}H (top panel, 400 MHz) and ^{13}C (bottom panel, 100 MHz) NMR spectra of cage **21b** in $CDCl_3$.

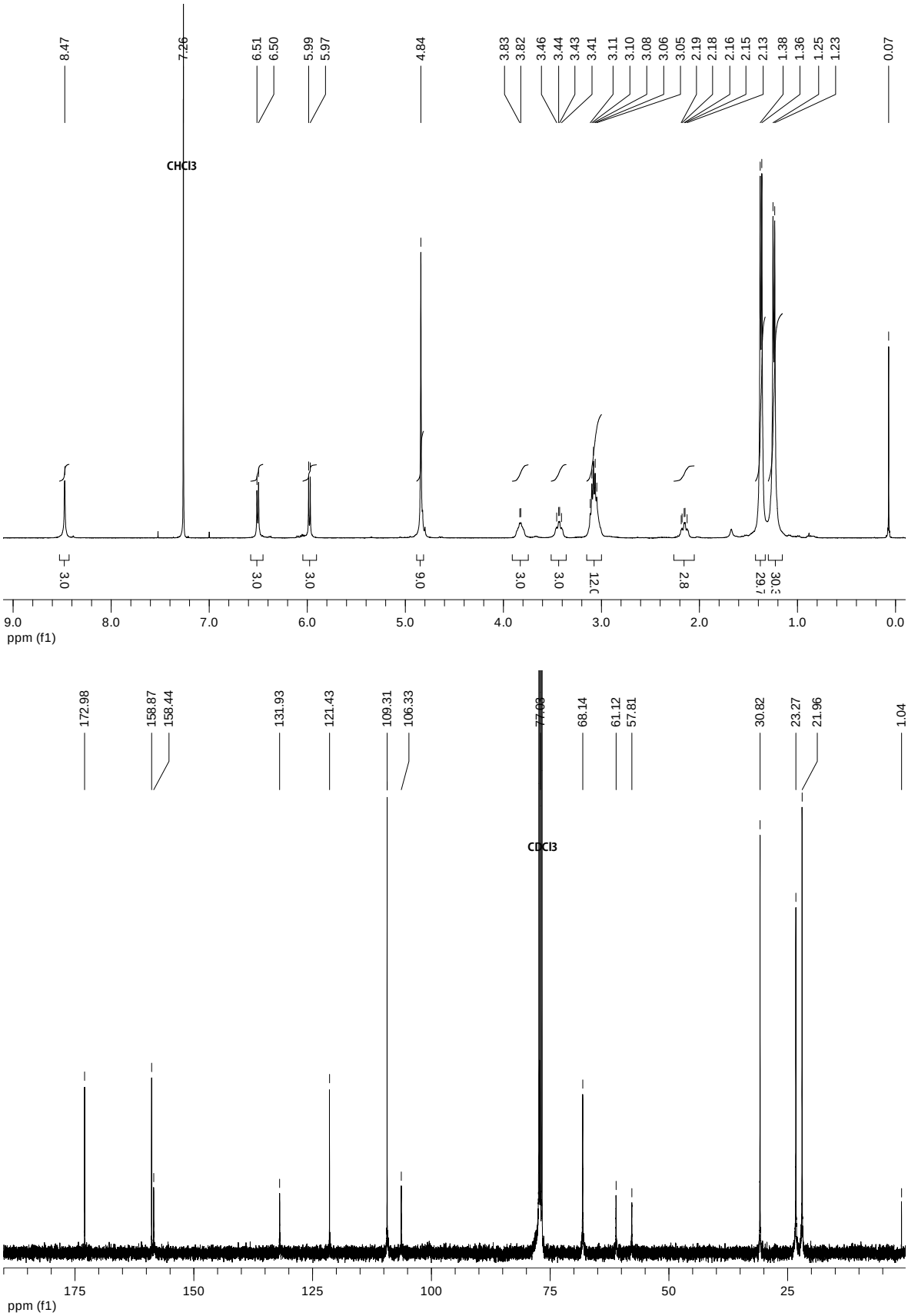


Figure S20. ^{1}H (top panel, 400 MHz) and ^{13}C (bottom panel, 100 MHz) NMR spectra of cage **21c** in $CDCl_3$.

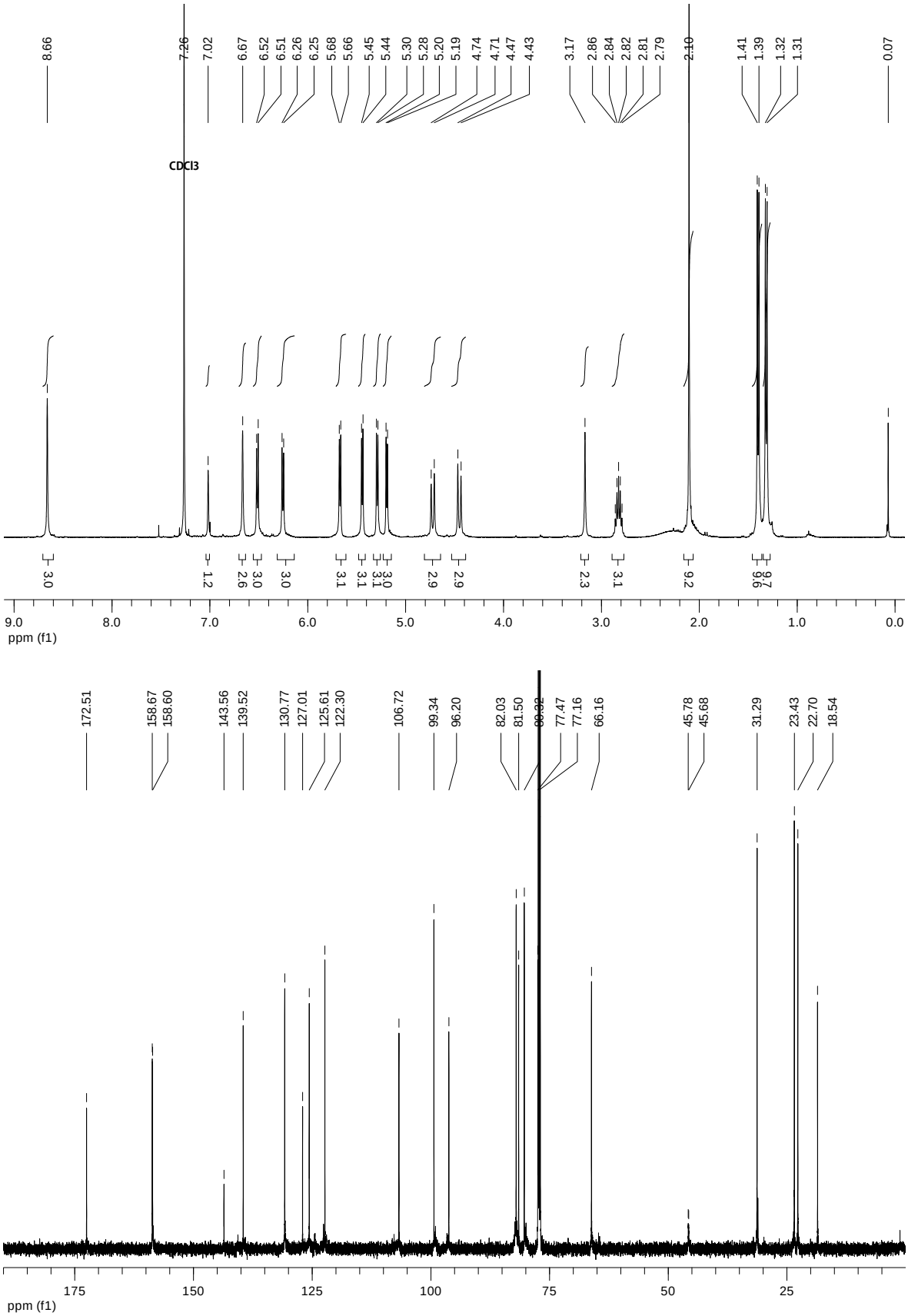


Figure S21. ^{1}H (top panel, 600 MHz) and ^{13}C (bottom panel, 150 MHz) NMR spectra of cage **24** in $CDCl_3$.

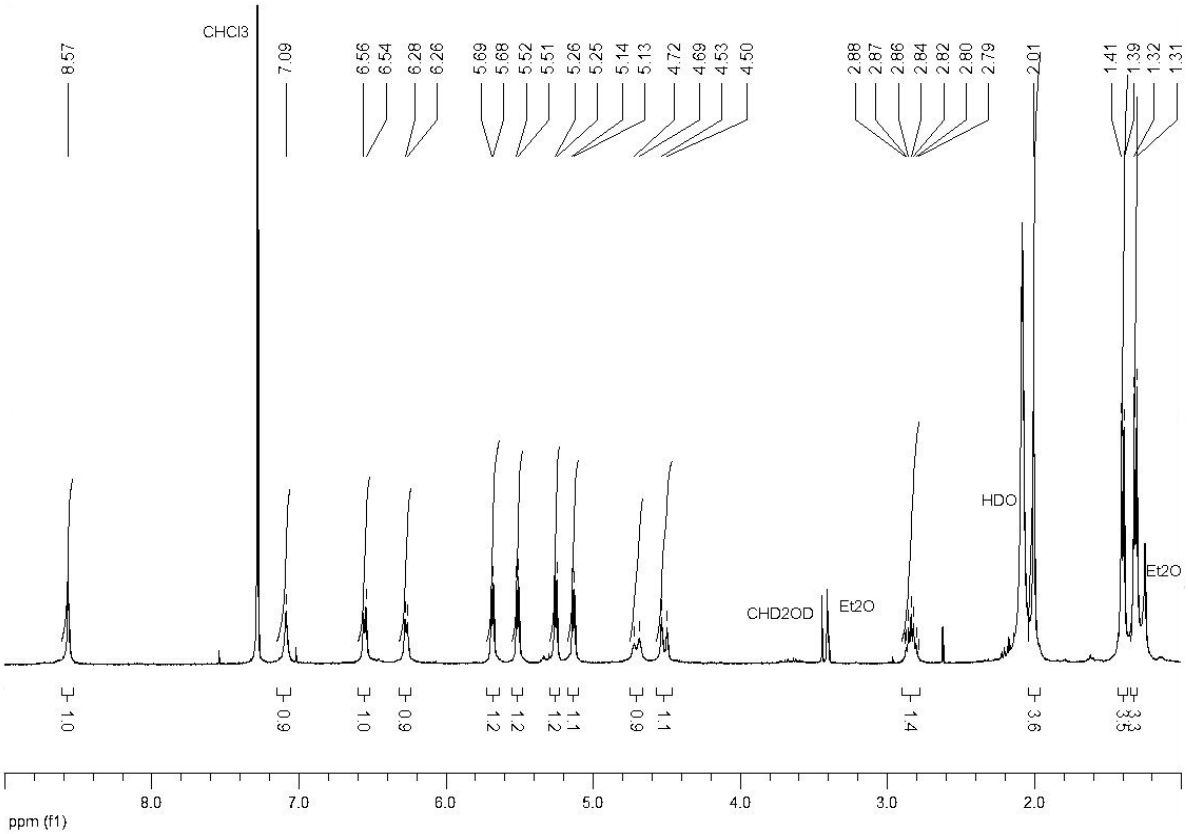


Figure S22. ^{1}H (400 MHz) NMR spectrum of cage **25** in $CDCl_3$ –CD_3OD (95:5).

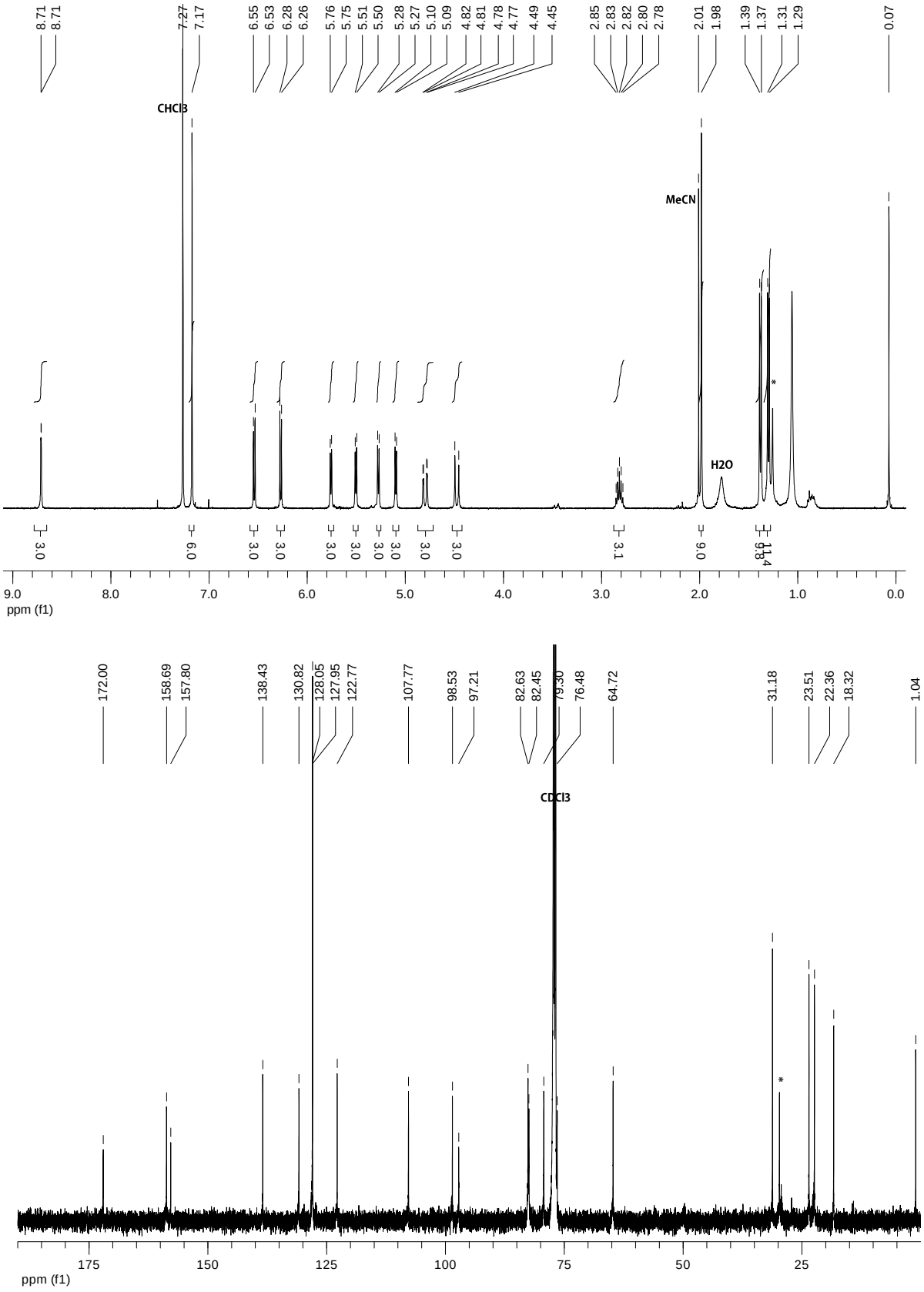


Figure S23. ^{1}H (top panel, 400 MHz) and ^{13}C (bottom panel, 100 MHz) NMR spectra of cage D_3-**26** in $CDCl_3$. The peaks marked (*) correspond to the long-chain linear aliphatic hydrocarbon impurity.

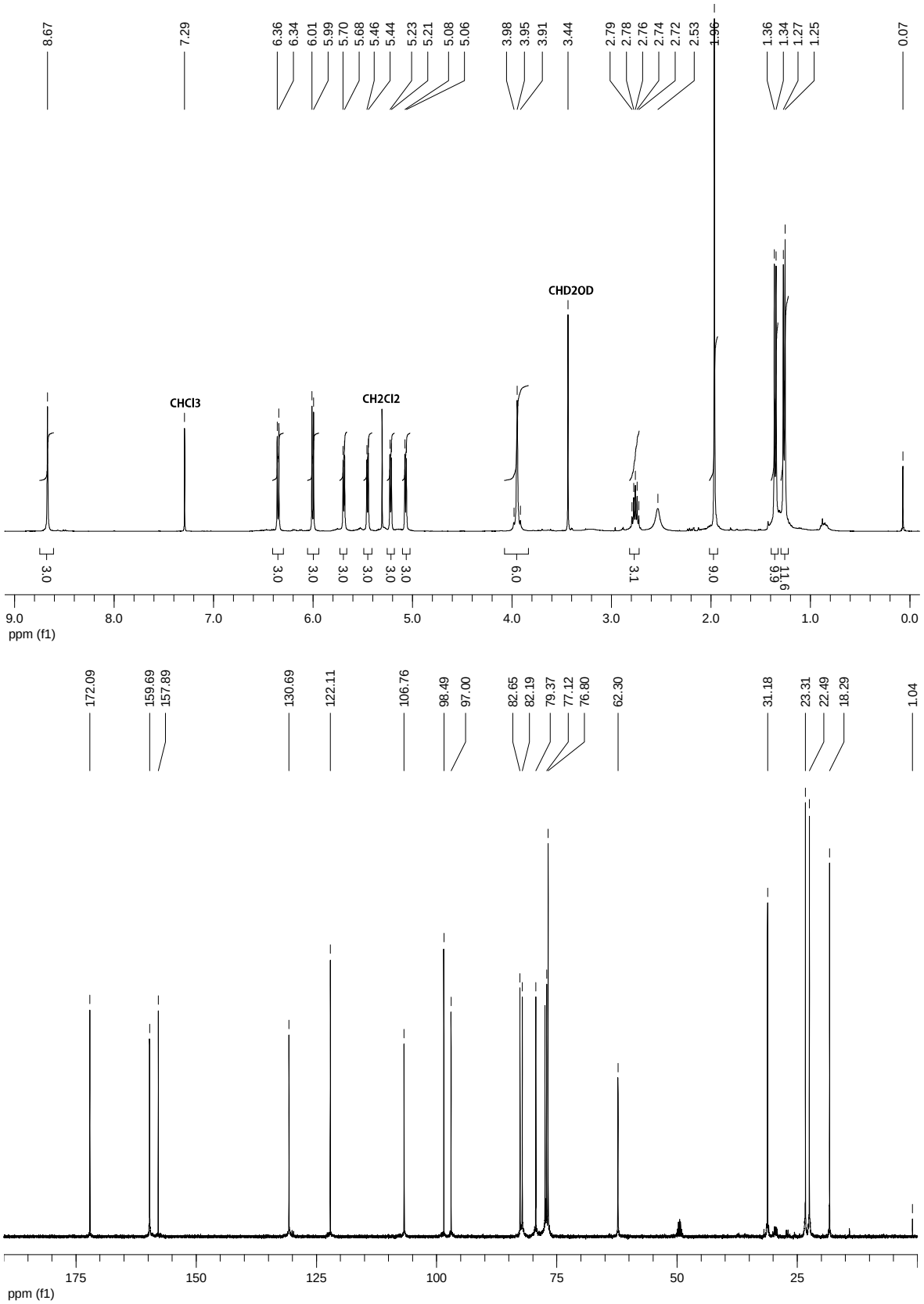


Figure S24. ^{1}H (top panel, 400 MHz) and ^{13}C (bottom panel, 100 MHz) NMR spectra of cage **28** in $CDCl_3$–MeOD (95:5).

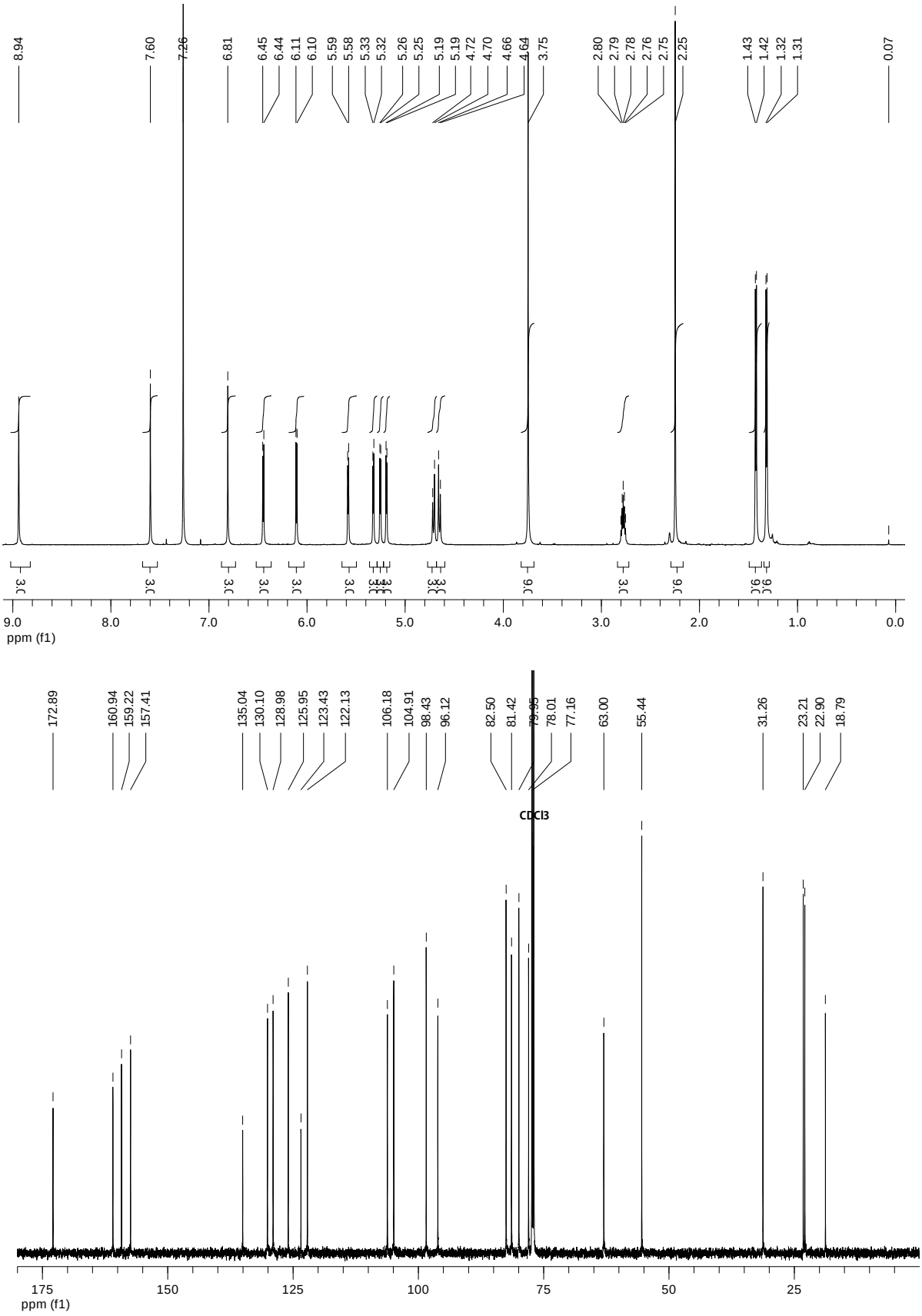


Figure S25. ^{1}H (top panel, 600 MHz) and ^{13}C (bottom panel, 150 MHz) NMR spectra of cage **29** in $CDCl_3$.

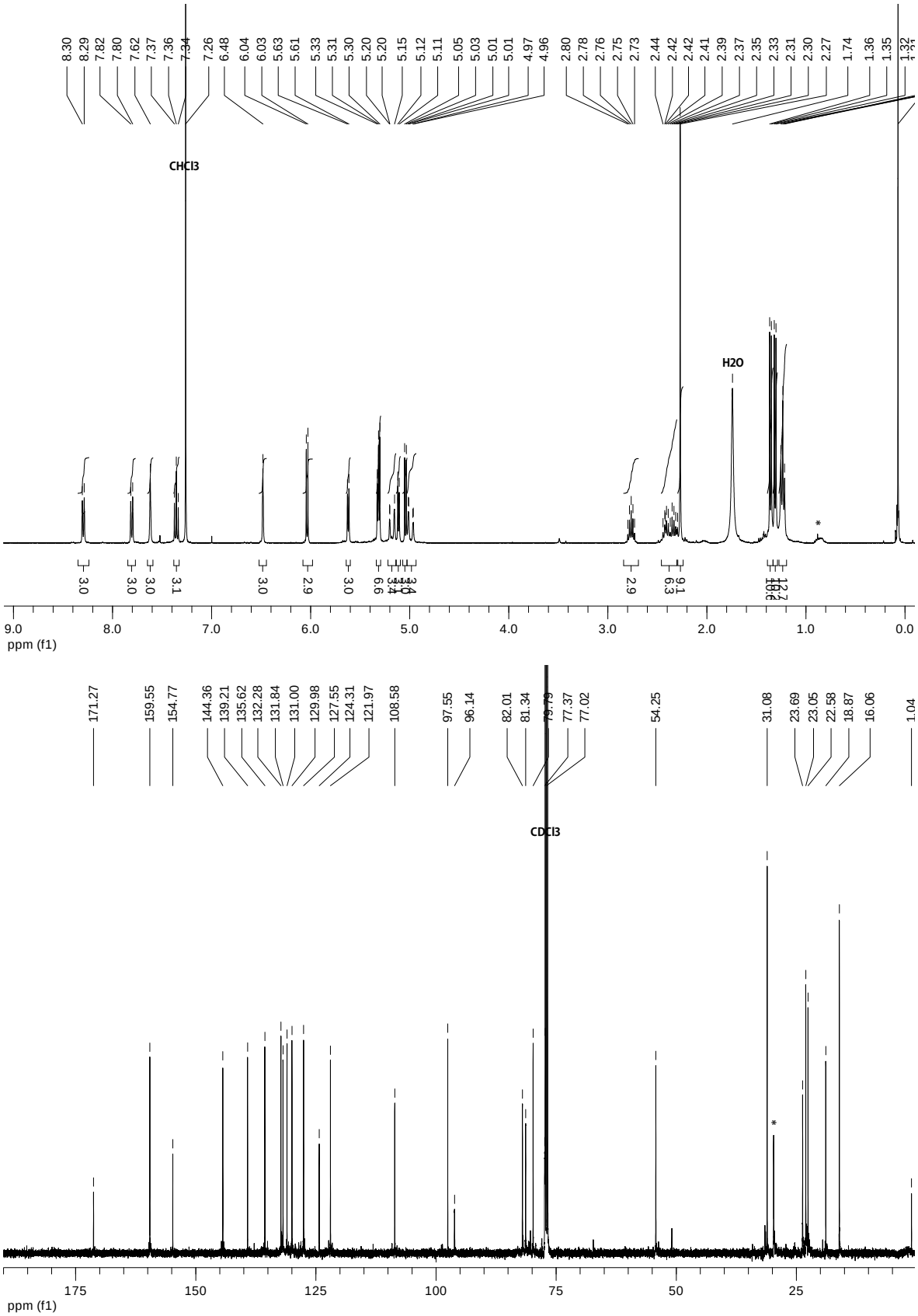


Figure S26. ^{1}H (top panel, 400 MHz) and ^{13}C (bottom panel, 150 MHz) NMR spectra of cage **31a** in $CDCl_3$.The peaks marked (*) correspond to the long-chain linear aliphatic hydrocarbon impurity.

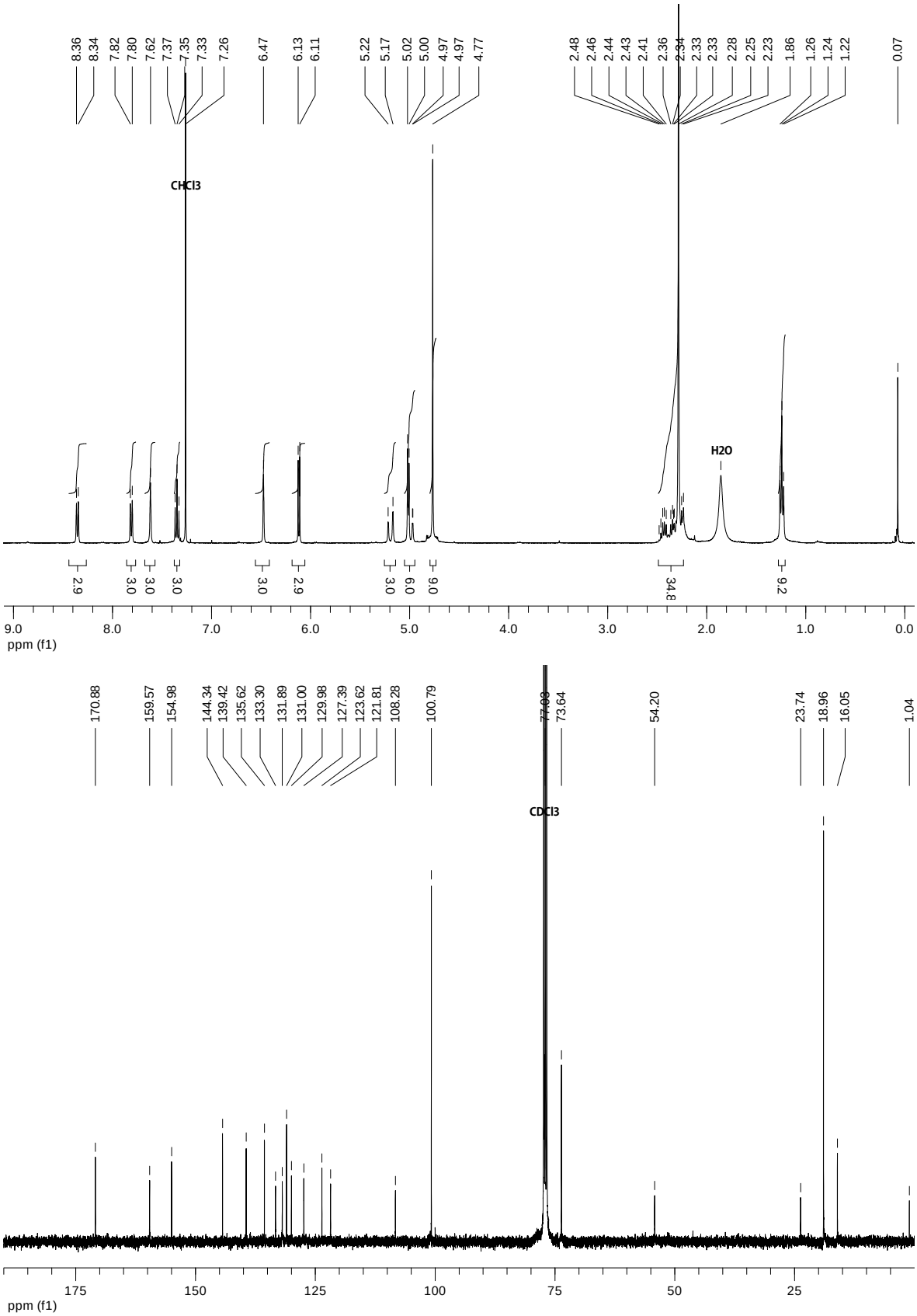


Figure S27. ^{1}H (top panel, 400 MHz) and ^{13}C (bottom panel, 150 MHz) NMR spectra of cage **31b** in $CDCl_3$.

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