Benzyne/benzyne/RNC or CO triple sequential insertion into the Pd–C bond: synthesis of ten-membered N-heterocycles through stable ten- and eleven-membered palladacycles

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Experimental Section

General Procedures. Melting points were determined on a Reicher apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. Exact masses were recorded on an AUTOSPEC 5000 VG mass spectrometer. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets. NMR spectra were recorded on a Brucker Avance 300 or 400 spectrometer, at room temperature. Chemical shifts were referenced to TMS (^{1}H, ^{13}C{^{1}H}). NMR assignments were performed with the help of APT, HMQC and HMBC techniques.

The palladacycle $[Pd\{C,N\text{-}C_6H_2CH_2CH_2NH_2\text{-}2,(MeO)_2\text{-}4,5\}(\mu\text{-}Br)]_2$ (**A**) was prepared as previously reported.[1] 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate, CsF, XyNC (Aldrich), ^{t}BuNC (Alfa Aesar), 4-picoline (Fluka) and CO (Air Products) were used as received. TlOTf was prepared by reaction of Tl_2CO_3 and HO_3SCF_3 (1:2) in water, and recrystallized from acetone/Et_2O. Chart 1 shows the numbering scheme used for NMR assignments.

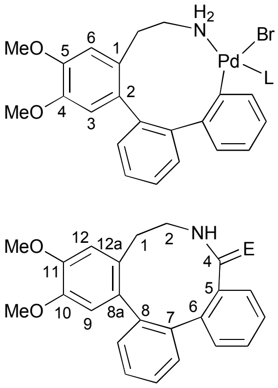

Chart 1. Numbering Scheme

Synthesis of [Pd(*C*,*N*-$(C_6H_4)_2(C_6H_2CH_2CH_2NH_2$-2,$(OMe)_2$-4,5}(*μ*-Br)]$_2$ (1). A solution of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (598 µL, 2.445 mmol) in dry MeCN (10 mL) was added dropwise to a suspension of palladacycle **A** (300 mg, 0.409 mmol) and CsF (373 mg, 2.455 mmol) in dry MeCN (15 mL) under N_2 atmosphere, and the mixture was stirred for 24 h. The solvent was removed, CH_2Cl_2 (30 mL) was added, and the suspension was filtered through a plug or $MgSO_4$. The filtrate was concentrated to ca. 2 mL, and Et_2O (30 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to afford a first crop of crude complex **1** as an orange solid (175 mg). The filtrate was concentrated to ca. 2 mL, and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to afford a second crop of crude complex **1** as an orange solid (70 mg). Yield: 245 mg, 0.236 mmol, 58%. Crude complex **1** was purified by chromatography on silica gel, rinsing the column with *n*-hexane first, and then using a 1:3 EtOAc/$CHCl_3$ mixture as eluent. The collected orange fraction was concentrated to ca. 1 mL, and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was washed with n-pentane (2 x 3 mL) and air-dried to give an spectroscopically pure sample of **1** as an orange solid (195 mg, 0.188 mmol; recrystallization yield: 80%). This solid was dried in a vacuum oven at 60 ºC for 12 h to obtain an analytically pure sample. Anal. Calcd for $C_{44}H_{44}Br_2N_2O_4Pd_2$ (1037.454): C, 50.94; H, 4.20; N, 2.70. Found: C, 51.00; H, 4.42; N, 3.03. Mp: 147 °C. ESI-HRMS: calcd for $C_{22}H_{21}NO_2Pd$ 438.0631 [$(M - HBr)^+$], found 438.0694. IR (cm^{-1}): *ν*(NH) 3306 w, 3249 m. ^1H NMR (600 MHz, DMSO-*d*$_6$): δ 1.65 (m, 1 H, NH_2), 2.49–2.63 (m, partially obscured by the dmso-*d*$_6$ signal, 1 H, CH_2Ar), 2.64–2.69 (m, 2 H, CH_2Ar + CH_2N), 3.30–3.33 (m, partially obscured by the DMSO-*d*$_6$, 1 H, CH_2N), 3.61 (s, 3 H, MeO), 3.66 (s, 3 H, MeO), 4.65 (br d, 1 H, NH_2, $^2J_{HH}$ = 9.0 Hz), 6.65 (s, 1

H, H6), 6.74 (s, 1 H, H3), 6.78–6.84 (m, 2 H, C_6H_4), 7.07–7.16 (m, 3 H, C_6H_4), 7.42–7.47 (m, 3 H, C_6H_4). $^{13}C\{^1H\}$ NMR (75.45 MHz, DMSO-d_6): δ 31.6 (s, CH_2Ar), 44.8 (s, CH_2N), 55.2 (s, MeO), 55.4 (s, MeO), 110.5 (s, CH, C6), 114.7 (s, CH, C3), 122.9 (s, CH, C_6H_4), 126.0 (s, CH, C_6H_4), 126.8 (s, CH, C_6H_4), 127.1 (s, C1), 130.2 (s, CH, C_6H_4), 130.3 (s, CH, C_6H_4), 130.4 (s, CH, C_6H_4), 132.3 (s, CH, C_6H_4), 134.4 (s, C2), 140.0 (s, C, C_6H_4), 144.7 (s, C, C_6H_4), 144.8 (s, C, C_6H_4), 145.8 (s, C4), 145.8 (s, C5), 151.9 (s, C, C_6H_4).

Synthesis of [Pd{*C*,*N*-$(C_6H_4)_2(C_6H_2CH_2CH_2NH_2$-2,$(OMe)_2$-4,5}Br($NC_5H_4Me$-4)] (2a). 4-Picoline (0.015 mL, 0.154 mmol) was added to a solution of complex **1** (80 mg, 0.077 mmol) in CH_2Cl_2 (20 mL), and the resulting solution was stirred for 30 min. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and Et_2O (30 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to afford a first crop of complex **2a** as a yellow solid (25 mg). The filtrate was concentrated to ca. 2 mL, and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to afford a second crop of complex **2a** as a yellow solid (33 mg). Yield: 58 mg, 0.095 mmol, 62%. Mp: 157 °C. Anal. Calcd for $C_{28}H_{29}BrN_2O_2Pd$ (611.875): C, 54.96; H, 4.77; N, 4.58. Found: C, 55.04; H, 5.10; N, 4.46. IR (cm^{-1}): ν(NH) 3466 br w, 3301 m, 3239 w, 3201 w. ^1H NMR (400.91 MHz): δ 1.91 (m, 1 H, NH_2), 2.29 (br s, 4 H, 3 H of Me + 1 H of NH_2), 2.84–2.68 (m, 3 H, 1 H of CH_2Ar + 2 H of CH_2N), 3.60–3.68 (m, partially obscured by the MeO signal, 1 H, CH_2Ar), 3.66 (s, 3 H, MeO), 3.81 (s, 3 H, MeO), 5.96 (d, 1 H, C_6H_4, $^3J_{HH}$ = 7.6 Hz), 6.43 (s, 1 H, H3), 6.61 (s, 1 H, H6), 6.93–7.10 (m, 5 H, 2 H of m-H pic + 3 H of C_6H_4), 7.18–7.35 (m, 4 H, C_6H_4), 8.05 (br s, 2 H, *o*-H, pic). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 21.0 (s, Me), 32.3 (s, CH_2Ar), 44.6 (s, CH_2N), 55.6 (s, MeO), 55.8 (s, MeO), 109.4 (s, CH, C6), 115.0 (s, CH, C3), 123.1 (s, CH, C_6H_4), 124.6 (s, CH, C_6H_4), 126.2 (s, CH, C_6H_4), 126.3 (s, *m*-CH, pic), 126.7 (s, CH, C_6H_4), 128.4 (s, CH, C_6H_4), 129.4 (s, CH, C_6H_4), 130.6 (s, CH, C_6H_4), 132.8 (s, CH, C_6H_4), 135.6 (s, C2), 140.9 (s, C1), 144.9 (s, C, C_6H_4), 146.2 (s, C4), 147.4 (s, C, C_6H_4), 148.1 (s, C5), 149.6 (s, *p*-C, pic), 152.7 (s, *o*-CH, pic). Two of the ^{13}C NMR resonances corresponding to the *C*-C_6H_4 groups were not observed. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **2a** in $CHCl_3$.

Synthesis of [Pd{*C*,*N*-(C_6H_4)$_2$($C_6H_2CH_2CH_2NH_2$-2,(OMe)$_2$-4,5}Br(CN^{t}Bu)] (2b). ^{t}BuNC (0.017 mL, 0.154 mmol) was added to a solution of complex **1** (80 mg, 0.077 mmol) in $CHCl_3$ (25 mL), and the resulting mixture was heated at 65 ºC for 6 h. The suspension was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and Et_2O (30 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to afford complex **2a** as a pale yellow solid. Yield: 45 mg, 0.075 mmol, 48%. Mp: 138 °C. Anal. Calcd for $C_{27}H_{31}BrN_2O_2Pd$ (608.915): C, 53.88; H, 5.19; N, 4.65. Found: C, 53.74; H, 5.29; N, 5.10. IR (cm^{-1}): ν(NH) 3362 w, 3291 w; 3177 w; ν(CN) 2199 s. ^{1}H NMR (200.1 MHz): δ 1.44 (s, 9 H, Me, ^{t}Bu), 1.62–1.74 (m, partially obscured by the H_2O signal, 1 H, NH_2), 2.36–2.41 (m, 2 H, 1 H of CH_2Ar + 1 H of NH_2), 2.66–2.87 (m, 2 H, 1 H of CH_2Ar + 1 H of CH_2N), 3.10–3.18 (m, 1 H, CH_2N), 3.74 (s, 3 H, MeO), 3.81 (s, 3 H, MeO), 6.58 (s, 1 H, H6), 6.60 (s, 1 H, H3), 6.86–6.90 (m, 2 H, C_6H_4), 7.06–7.25 (m, 4 H, C_6H_4), 7.36–7.40 (m, 4 H, C_6H_4). ^{13}C{^{1}H} NMR (75.45 MHz): δ 30.0 (s. Me), 32.0 (s, CH_2Ar), 45.0 (s, CH_2N), 55.8 (s, MeO), 55.8 (s, MeO), 109.5 (s, C6), 111.2 (s, *C*-CN), 111.8 (s, CN), 114.9 (s, CH, C3), 115.8 (s, C, C_6H_4), 123.2 (s, CH, C_6H_4), 126.3 (s, CH, C_6H_4), 126.6 (s, CH, C_6H_4), 126.8 (s, CH, C_6H_4), 129.5 (s, CH, C_6H_4), 130.2 (s, CH, C_6H_4), 130.6 (s, CH,

C_6H_4), 134.5 (s, CH, C_6H_4), 135.4 (s, C2), 140.2 (s, C1), 145.6 (s, C, C_6H_4), 145.9 (s, C, C_6H_4), 146.3 (s, C4), 147.5 (s, C, C_6H_4), 148.2 (s, C5).

Synthesis of [Pd{*C*,*N*-$(C_6H_4)_2C(=NXy)(C_6H_2CH_2CH_2NH_2$-2,$(OMe)_2$-4,5}Br(CNXy)] (3). XyNC (51 mg, 0.384 mmol) was added to a solution of complex **1** (100 mg, 0.096 mmol) in CH_2Cl_2 (20 mL), and the resulting solution was stirred for 1 h. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and Et_2O (30 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to afford a first crop of complex **3** as a yellow solid (55 mg). The filtrate was concentrated to ca. 2 mL, and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to afford a second crop of complex **3** as a yellow solid (25 mg). Yield: 80 mg, 0.102 mmol, 53%. Mp: 122 °C. Anal. Calcd for $C_{40}H_{40}BrN_3O_2Pd$ (781.001): C, 61.51; H, 5.16; N, 5.38. Found: C, 61.36; H, 4.76; N, 5.70. IR (cm^{-1}): ν(NH) 3433 w, 3376 w, 3286 w, 3229 w; ν(CN) 2170 s. ^1H NMR (400.91 MHz): δ 1.25–1.34 (m, 1 H, CH_2N), 1.84–1.87 (m, 1 H, NH_2), 2.11 (s, 3 H, inserted Xy), 2.16 (s, 6 H, coordinated Xy), 2.40 (s, 3 H, inserted Xy), 2.69–2.75 (m, 1 H, CH_2N), 2.82–2.90 (m, 1 H, CH_2Ar), 3.19–3.21 (m, 1 H, NH_2), 3.57–3.67 (m, 1 H, CH_2Ar), 3.85 (s, 3 H, MeO), 3.87 (s, 3 H, MeO), 6.51 (s, 1 H, H6), 6.66 (d, 1 H, C_6H_4, $^3J_{HH} = 7.2$ Hz), 6.75 (t, 1 H, *p*-H, inserted Xy, $^3J_{HH} = 7.6$ Hz), 6.90 (s, 1 H, H3), 6.93–7.25 (m, 7 H, 2 H of *m*-CH, inserted Xy + 2 H of *m*-CH, coordinated Xy + 1 H of *p*-CH coordinated Xy + 2 H of C_6H_4), 7.31–7.40 (m, 3 H, C_6H_4), 7.52 (br d, 1 H, C_6H_4, $^3J_{HH} = 7.2$ Hz), 7.68 (br d, 1 H, C_6H_4, $^3J_{HH} = 7.2$ Hz). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 19.2 (s, Me, coordinated Xy), 19.5 (s, Me, inserted Xy), 19.9 (s, Me, inserted Xy), 36.6 (s, CH_2Ar), 42.7 (s, CH_2N), 55.8 (s, MeO), 55.9 (s, MeO), 111.5 (s, CH, C6), 114.9 (s, CH, C3), 123.3 (s, *m*-CH, inserted Xy), 126.3 (s, C_6H_4), 126.4 (s, *m*-CH, inserted Xy), 127.1 (s, *o*-C, inserted Xy), 127.2 (s, *p*-CH, inserted Xy + CH, C_6H_4), 127.6 (s, CH, C_6H_4), 127.6 (s, CH, C_6H_4), 127.6 (s, *m*-CH + *o*-CH, coordinated Xy), 128.2 (s, CH, C_6H_4), 128.3 (s, CH, C_6H_4), 128.5 (s, C1), 129.2 (s, CH, C_6H_4), 131.9 (s, CH, C_6H_4), 132.9 (s, CH, C_6H_4), 133.3 (s, C2), 133.5 (s, CH, C_6H_4), 135.4 (s, *o*-C, coordinated Xy), 135.7 (s, CN, coordinated Xy), 137.9 (s, C, C_6H_4), 139.3 (s, C, C_6H_4), 140.2 (s, C, C_6H_4), 142.4 (s, C, C_6H_4), 147.0 (s, C4), 148.1 (s, C5), 150.3 (s, *o*-C, inserted Xy), 177.8 (s, CN, inserted Xy). The ^{13}C resonances corresponding to the *i*-C of the Xy groups were not observed.

Synthesis of 4·H_2O. TlOTf (45 mg, 0.128 mmol) was added to a suspension of complex **3** (100 mg, 0.128 mmol) in acetone (20 mL), and the resulting suspension was stirred for 30 min. The mixture was filtered through a plug of Celite, the solvent was removed from the filtrate, and toluene (10 mL) was added. The mixture was heated at 110 ºC for 16 h. Decomposition to metallic palladium was observed. The suspension was filtered through a plug of Celite, the solvent was removed from the filtrate, and the residue was vigorously stirred in Et_2O (30 mL). The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to afford **4**·H_2O as an orange solid Yield: 38 mg, 0.060 mmol, 47%. Mp: 114 °C. Compound **4**·H_2O was dried in a vacuum oven, at 40 ºC for 12 h. Even though, one molecule of water was observed in the ^{1}H NMR spectrum. Anal. Calcd for $C_{32}H_{31}F_3N_2O_5S\cdot H_2O$ (630.682): C, 60.94; H, 5.27; N, 4.44; S, 5.08. Found: C, 60.32; H, 5.29; N, 4.92; S, 4.73. EI-HRMS: exact mass calcd for $C_{31}H_{31}N_2O_2$ 463.2386 [$(M–OTf)^+$]; found 463.2383. Λ_M (Ω^{-1} cm^2 mol^{-1}) = 106 (1.6 x 10^{-4} M). IR (cm^{-1}): ν(NH) 3187 br m; ν(CN) 1634 s. ^{1}H NMR (300.1 MHz): δ 1.61 (br s, 2 H, H_2O), 1.99 (s, 3 H, Me, Xy), 2.34 (s, 3 H, Me, Xy), 2.49–2.58 (m, 2 H, CH_2Ar + CH_2N), 2.81 (m, 1 H, CH_2Ar), 3.62–3.70 (m, 1 H, CH_2N), 3.77 (s, 3 H, MeO), 3.89 (s, 3 H, MeO), 6.33 (s, 1 H, H12), 6.84 (s, 1 H, H9), 7.01–7.31 (m, 5 H, 2 H of C_6H_4 + 1 H of *p*-H, Xy + 2 H of *m*-H, Xy), 7.37–7.48 (m, 5 H, C_6H_4), 7.62–7.67 (m, 1

H, C_6H_4), 8.42 (br s, 1 H, CH_2NH), 10.67 (s, 1 H, XyNH). $^{13}C\{^1H\}$ NMR (100.81 MHz): δ 18.0 (s, Me, Xy), 18.5 (s, Me, Xy), 33.9 (s, CH_2Ar), 46.1 (s, CH_2N), 55.8 (s, MeO), 56.2 (s, MeO), 111.4 (s, CH, C12), 113.2 (s, CH, C9), 126.6 (s, C, C_6H_4), 127.8 (s, CH, C_6H_4), 127.9 (s, CH, C_6H_4), 128.1 (s, CH, C_6H_4), 128.4 (s, CH, C_6H_4), 129.7 (s, *p*-CH, Xy + CH, C_6H_4), 129.8 (s, C, C_6H_4), 130.1 (s, *m*-CH + *m*-CH, Xy), 130.9 (s, C12a), 131.4 (s, CH, C_6H_4), 131.5 (s, CH, C_6H_4), 131.9 (s, 8a), 132.1 (s, CH, C_6H_4), 135.0 (s, *o*-C, Xy), 136.0 (s, *o*-C, Xy), 138.5 (s, *i*-C, Xy), 140.7 (s, C, C_6H_4), 140.8 (s, C, C_6H_4), 146.9 (s, C10), 148.6 (s, C11), 165.0 (s, CN). Single crystals of **4**·CH_2Cl_2 suitable for an X-ray diffraction study were obtained by slow diffusion of *n*-pentane into a solution of **4**·H_2O in CH_2Cl_2.

Synthesis of 5·H₂O. CO was bubbled through a solution of complex **1** (100 mg, 0.096 mmol) in CH_2Cl_2 (25 mL) and the resulting mixture was stirred for 16 h under a CO atmosphere (1 atm). Decomposition to metallic palladium was observed. The mixture was filtered through a plug of Celite, the filtrate was concentrated to ca. 2 mL, and Et_2O (30 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (2 x 5 mL) and air-dried to afford a first crop of compound **5**·H_2O as a pale yellow solid (18 mg). The filtrate was concentrated to ca. 2 mL, and *n*-pentane (20 mL) was added. The suspension was filtered, and the solid was washed with *n*-pentane (2 x 5 mL) and air-dried to afford a second crop of compound **5**·H_2O as a pale yellow solid (25 mg). Yield: 43 mg, 0.114 mmol, 59%. Mp: 92 °C. The second crop of complex **5**·H_2O was dried in a vacuum oven, at 40 ºC for 12 h. Even though, one molecule of water was observed in the ^1H NMR spectrum. Anal. Calcd for $C_{23}H_{21}NO_3{\cdot}H_2O$ (377.433): C, 73.19; H, 6.14; N, 3.71. Found: C, 72.60; H, 5.84; N, 3.99. EI-HRMS: exact mass calcd for $C_{23}H_{22}NO_3$ 360.1600 $[(M+H)^+]$; found 360.1603. IR (cm^{-1}): ν(NH) 3352 br s; ν(CO) 1700 s. ^1H NMR (300.1 MHz): δ 1.62 (br s, 2 H, H_2O), 2.53–2.59 (m, 1 H,

CH_2Ar), 2.92–3.17 (m, 3 H, 1 H of CH_2Ar + 2 H of CH_2N), 3.41 (s, 3 H, MeO), 3.88 (s, 3 H, MeO), 5.22 (br d, 1 H, NH, $^2J_{HH}$ = 11.4 Hz), 6.16 (s, 1 H, H9), 6.81 (s, 1 H, H12), 7.18 (br d, 1 H, C_6H_4, $^3J_{HH}$ = 7.5 Hz), 7.27–7.34 (m, 6 H, C_6H_4), 7.69 (br d, 1 H, C_6H_4, $^3J_{HH}$ = 7.5 Hz). $^{13}C\{^1H\}$ NMR (75.45 MHz): δ 32.4 (s, CH_2Ar), 42.9 (s, CH_2N), 55.6 (s, MeO), 55.7 (s, MeO), 112.7 (s, CH, C9), 113.4 (s, CH, C12), 127.7 (s, CH, C_6H_4), 128.1 (s, CH + CH, C_6H_4), 129.2 (s, C12a), 130.0 (s, CH, C_6H_4), 130.8 (s, CH, C_6H_4), 131.8 (s, CH + CH, C_6H_4), 132.0 (s, CH, C_6H_4), 133.4 (s, C8a), 133.5 (s, C, C_6H_4), 138.8 (s, C, C_6H_4), 139.8 (s, C, C_6H_4), 141.3 (s, C, C_6H_4), 147.0 (s, C10), 148.9 (s, C11), 148.5 (s, C9), 168.4 (s, CO).

Relevant crystallographic data and details of the refinements for the structures of compounds 2a and 4·CH_2Cl_2. *Data Collection*. Crystals suitable for X-ray diffraction were mounted in a loop fiber and transferred to a SuperNova, Dual, Cu at zero, Atlas (**2a**) or a Bruker D8 QUEST (**4**·CH_2Cl_2) diffractometers. Data were recorded at 100(2) K, using mirror-monochromated Cu-Kα radiation (λ = 1.54184 Å; **2a**) or multilayer-monochromated Mo-Kα radiation (λ = 0.71073 Å; **4**·CH_2Cl_2), and ω-scan (**2a**) or ω- and ϕ-scan (**4**·CH_2Cl_2) modes. Analytical numeric absorption correction using a multifaceted crystal model based on expresion derived by Clark and Reid[2] was applied for complex **2a**. Multi-scan absorption correction was applied for compound **4**·CH_2Cl_2. *Structure Solution and Refinements*. Crystal structures were solved by iterative (**2a**) or direct (**4**·CH_2Cl_2) methods and all non hydrogen atoms refined anisotropically on F^2 using the program SHELXL-97.[3] Hydrogen atoms were refined as follows: Complex **2a**: NH_2, free with SADI; methyl, rigid group; all others, riding. Compound **4**·CH_2Cl_2: NH, free; ordered methyl, rigid group; all others, riding. *Special features*: Compound **4**·CH_2Cl_2: absolute structure (Flack) parameter[4] –0.12(7). One Me group is disordered over two positions with a ca. 71:29 occupancy distribution; the triflate anion is disordered over two positions with a ca. 56:44 occupancy distribution; the CH_2Cl_2 is disordered over two positions with a ca. 75:25 occupancy distribution.

*Crystallographic data for **2a***: $C_{28}H_{29}BrN_2O_2Pd$, formula weight = 611.84, crystal dimensions: 0.14 x 0.10 x 0.03 mm^3, crystal system: monoclinic, space group: *C*2/*c*, a = 29.001(2) Å, b = 9.2274(7) Å, c = 19.9745(16) Å, α = 90°, β = 102.373(7)°, γ = 90°, V = 5221.1(7) Å^3, Z = 8, ρ_{calcd} = 1.557 g cm^{-3}, μ = 7.736 mm^{-1}, mirror-monochromated Cu-Kα radiation (λ = 1.54184 Å), T = 100(2) K, $2\theta_{max}$ = 149.6, no. of measured reflections: 9964, no. of independient reflections: 5145, R_{int} = 0.0419, R = 0.0479, wR = 0.1370, largest diff. peak and hole: 1.616 and –1.495. CCDC 928375.

*Crystallographic data for **4**·CH$_2$Cl$_2$*: $C_{33}H_{33}Cl_2F_3N_2O_5S$, formula weight = 697.57, crystal dimensions: 0.20 x 0.11 x 0.01 mm^3, crystal system: orthorhombic, space group: *Pna*2$_1$, a = 17.0215(8) Å, b = 12.1750(5), c = 5.8959(7) Å, α = 90°, β = 90°, γ = 90°, V = 3294.2(3) Å^3, Z = 4, ρ_{calcd} = 1.407 g cm^{-3}, μ = 0.321 mm^{-1}, multilayer-monochromated Mo-Kα radiation (λ = 0.71073 Å), T = 100(2) K, $2\theta_{max}$ = 56.7, no. of measured reflections: 84 946, no. of independent reflections: 8153, R_{int} = 0.0356, R = 0.0548, wR = 0.1515, largest diff. peak and hole: 0.763 and –0.484. CCDC 928374. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Hydrogen bonds for compound **2b** (Å and deg).

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(1)–H(01A)···Br(1)#1	0.84(4)	2.54(4)	3.364(4)	167(5)
C(24)–H(24)···Br(1)#2	0.95	2.82	3.692(5)	153.1

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2

#2 x,y+1,z

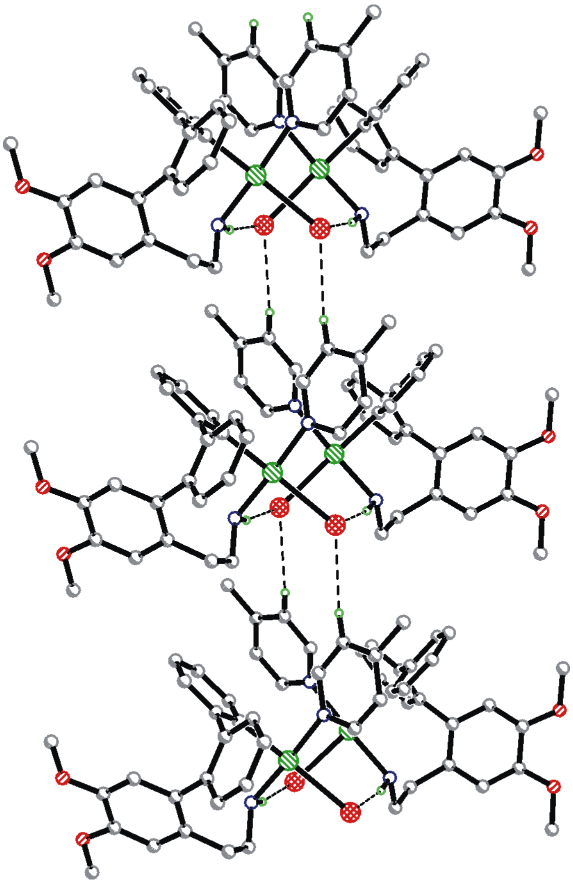

Figure 1. X-ray packing view of complex **2a** (50% probability) showing the double chain along the *b* axis formed through hydrogen bond interactions.

Hydrogen bonds for compound **4**·CH_2Cl_2 (Å and deg).

D–H···A	d(D–H)	d(H···A)	d(D···A)	< (DHA)
N(1)–H(01)···O(2)#1	0.84(3)	2.12(4)	2.927(3)	160(3)

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,-y+1/2,z

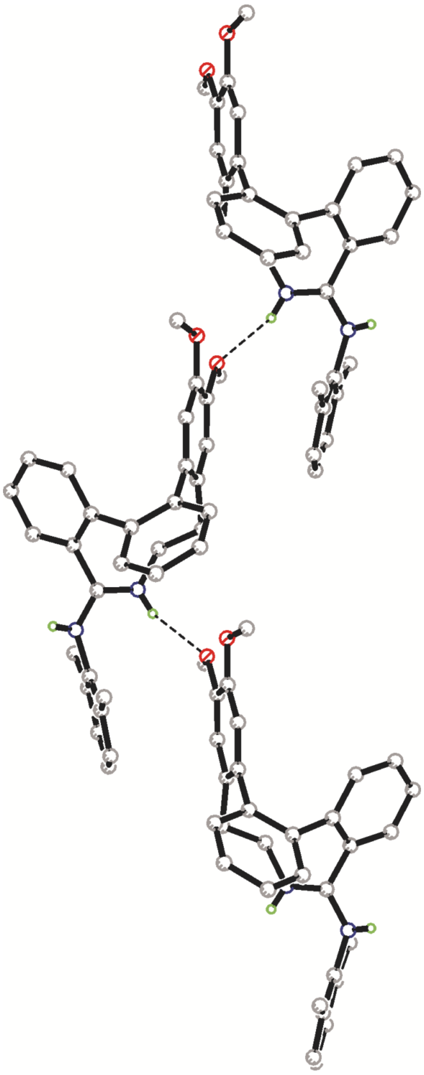

Figure 2. X-ray packing view of compound **4**·CH_2Cl_2 showing the chain along the *a* axis formed through hydrogen bond interactions.

References

1. M.-J. Oliva-Madrid, J.-A. García-López, I. Saura-Llamas, D. Bautista and J. Vicente, *Organometallics*, 2012, **31**, 3647.
2. R. C. Clark and J. S. Reid, *Acta Crystallogr., Sect. A*, 1995, **51**, 887.
3. Sheldrick, G. M. SHELX-97; University of Göttingen, Göttingen, Germany, 1997.
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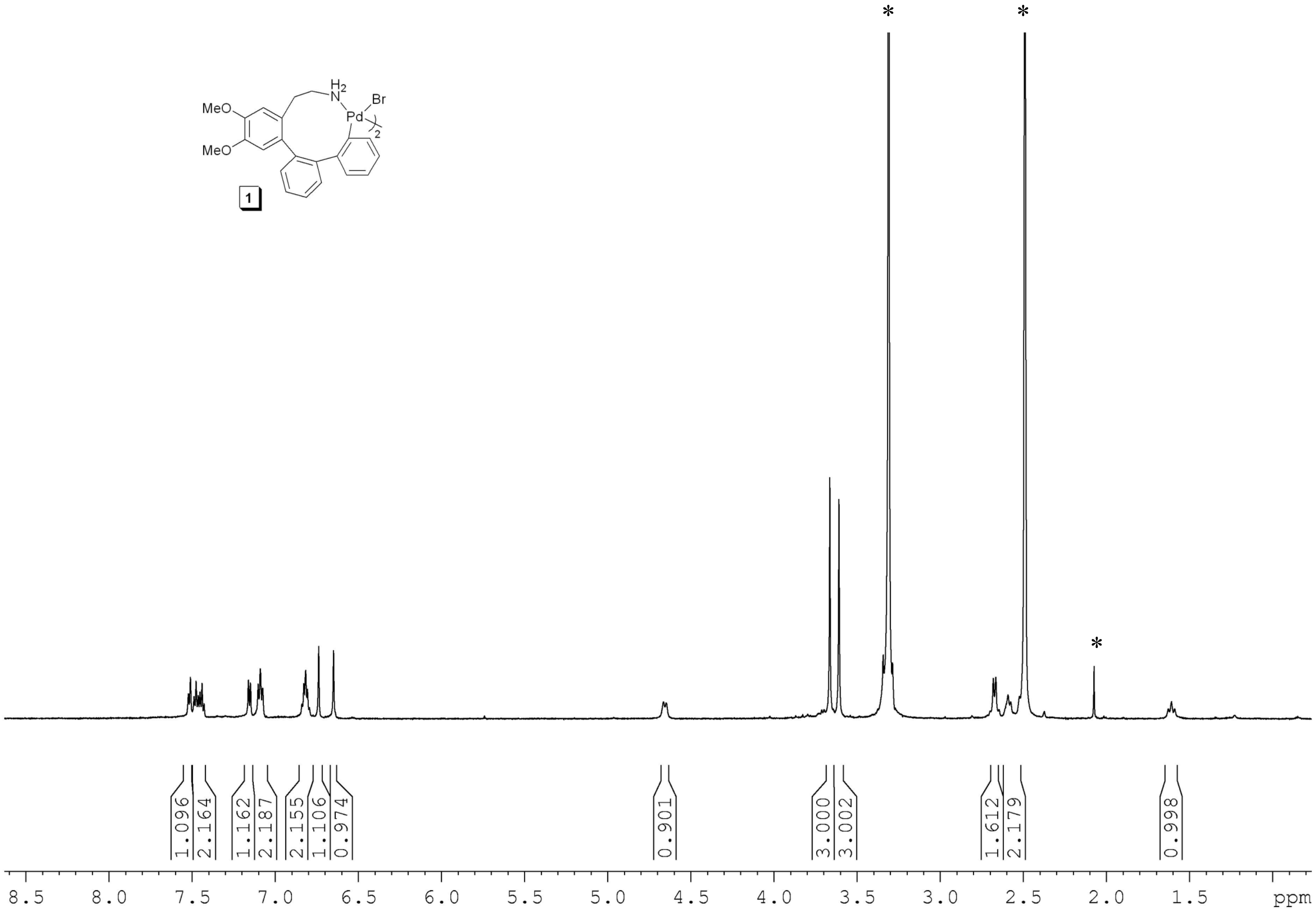
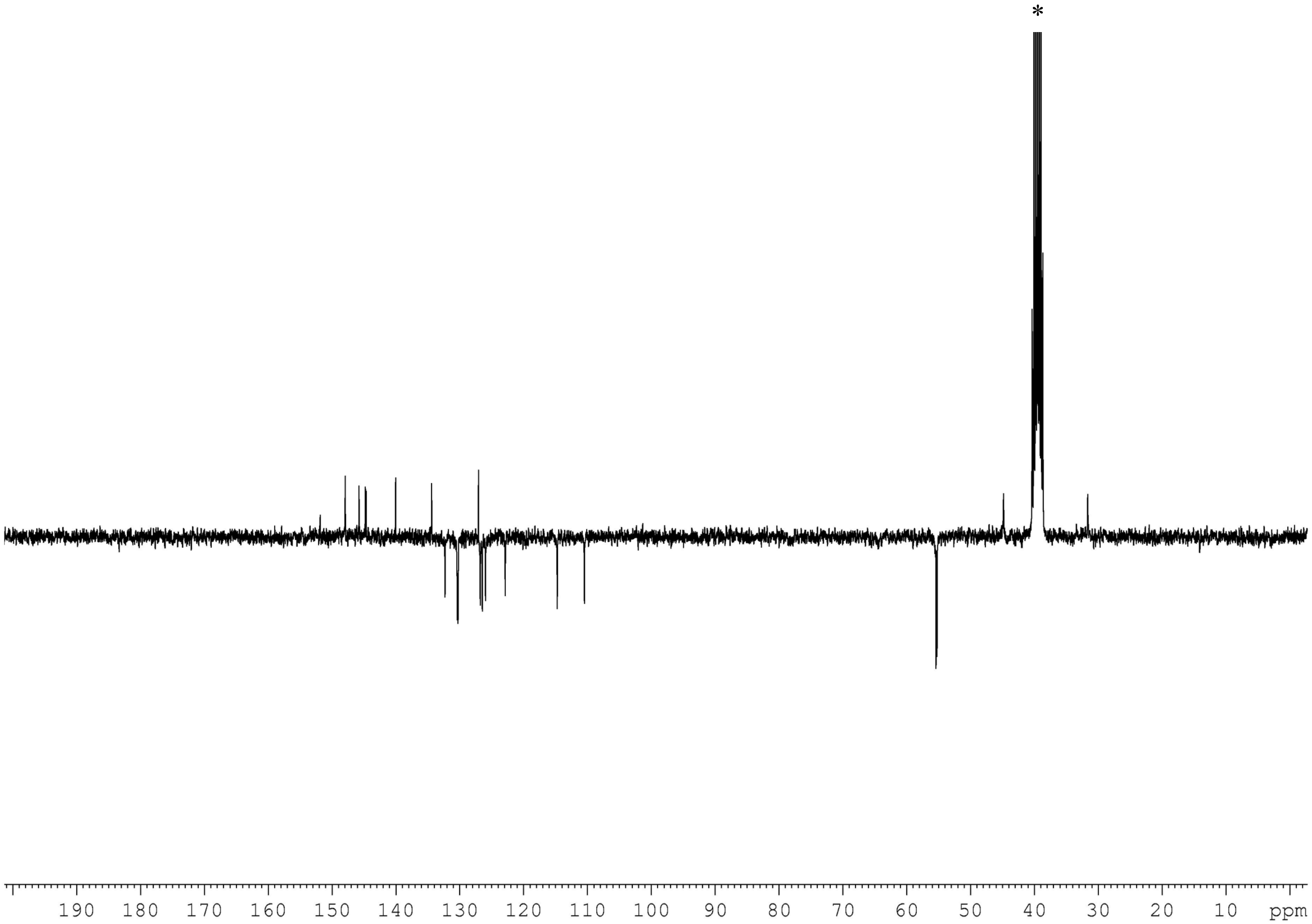
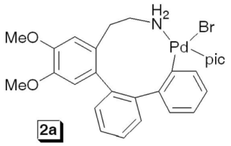


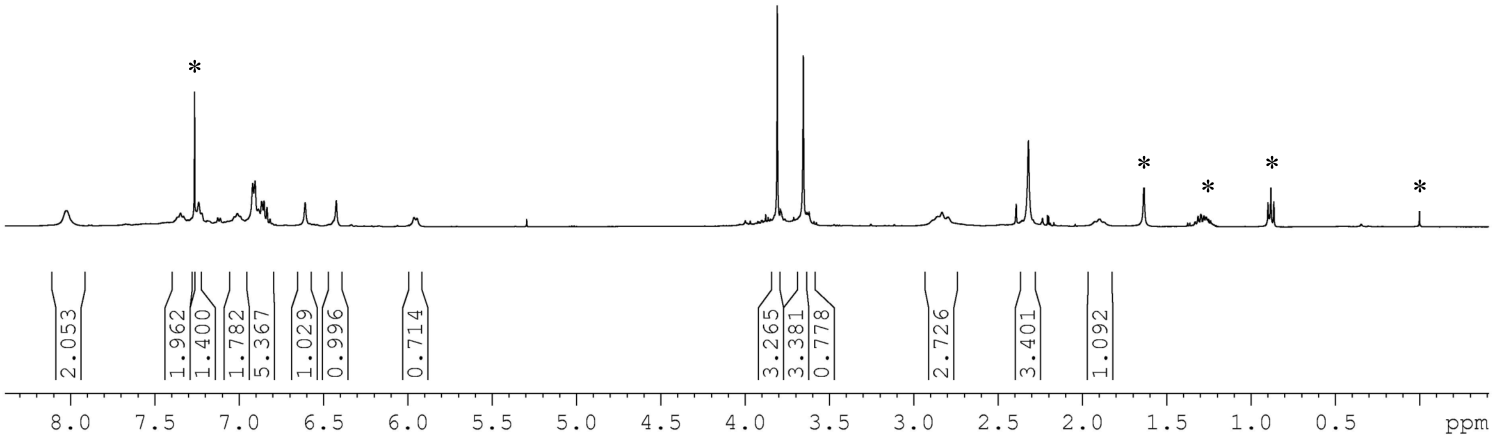
^{1}H NMR spectrum of **1** (DMSO-d_6, 25 ºC).
(From left to right, the asteriks indicate the signals corresponding to H_2O, DMSO-d_5, and acetone)



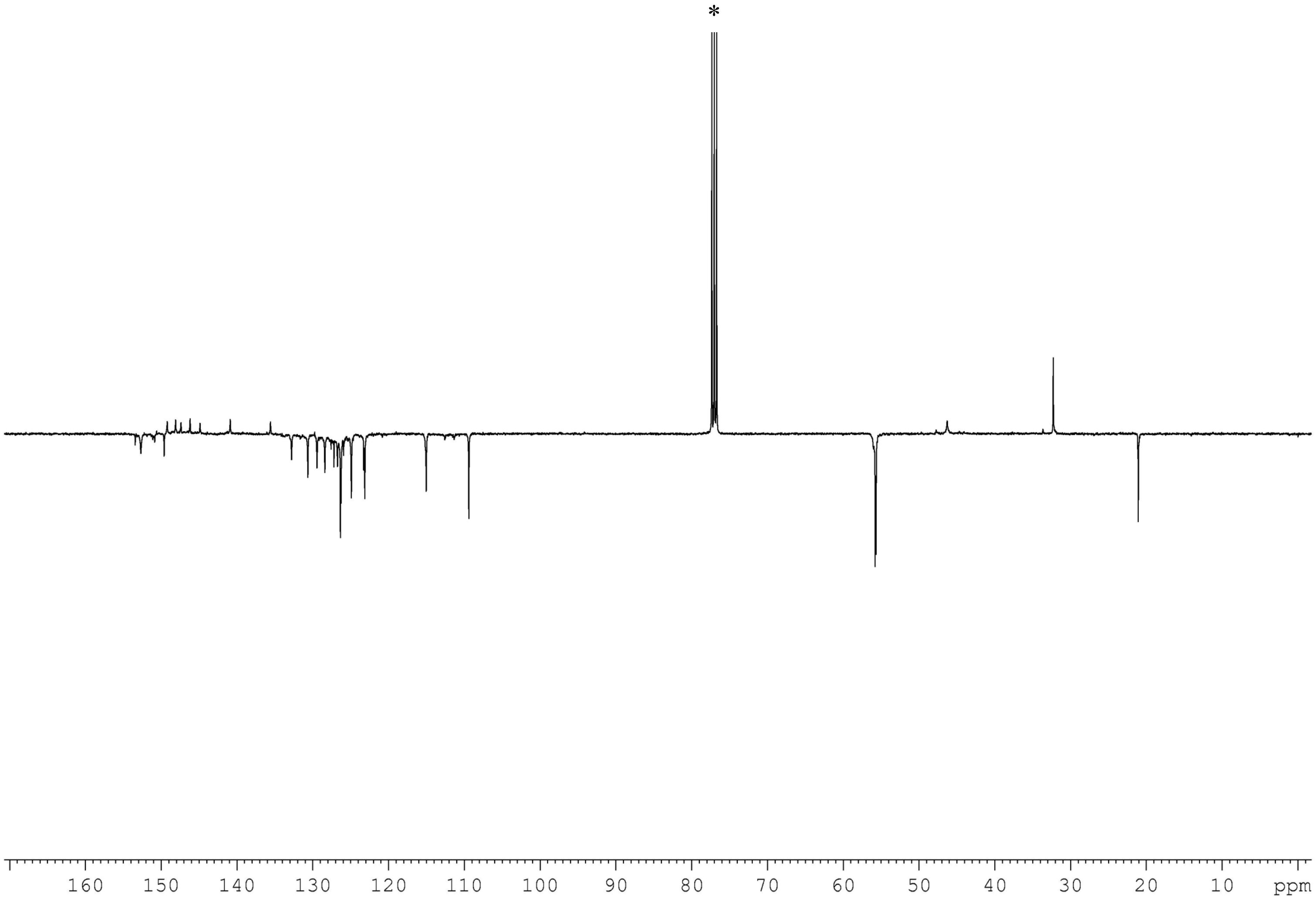
APT spectrum of **1** (DMSO-d_6, 25 ºC)
(The asterik indicates the signal corresponding to DMSO-d_6)



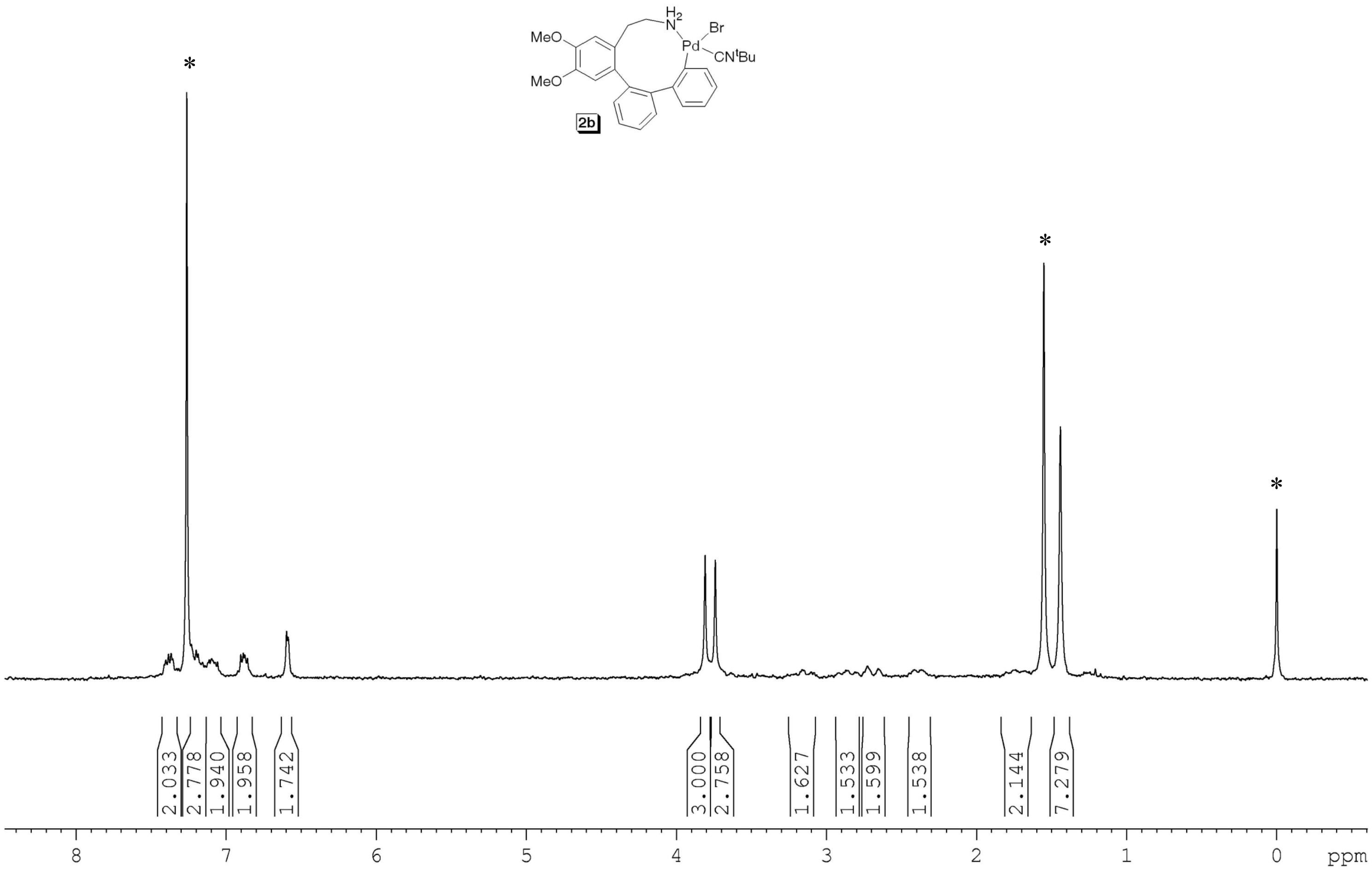
2a



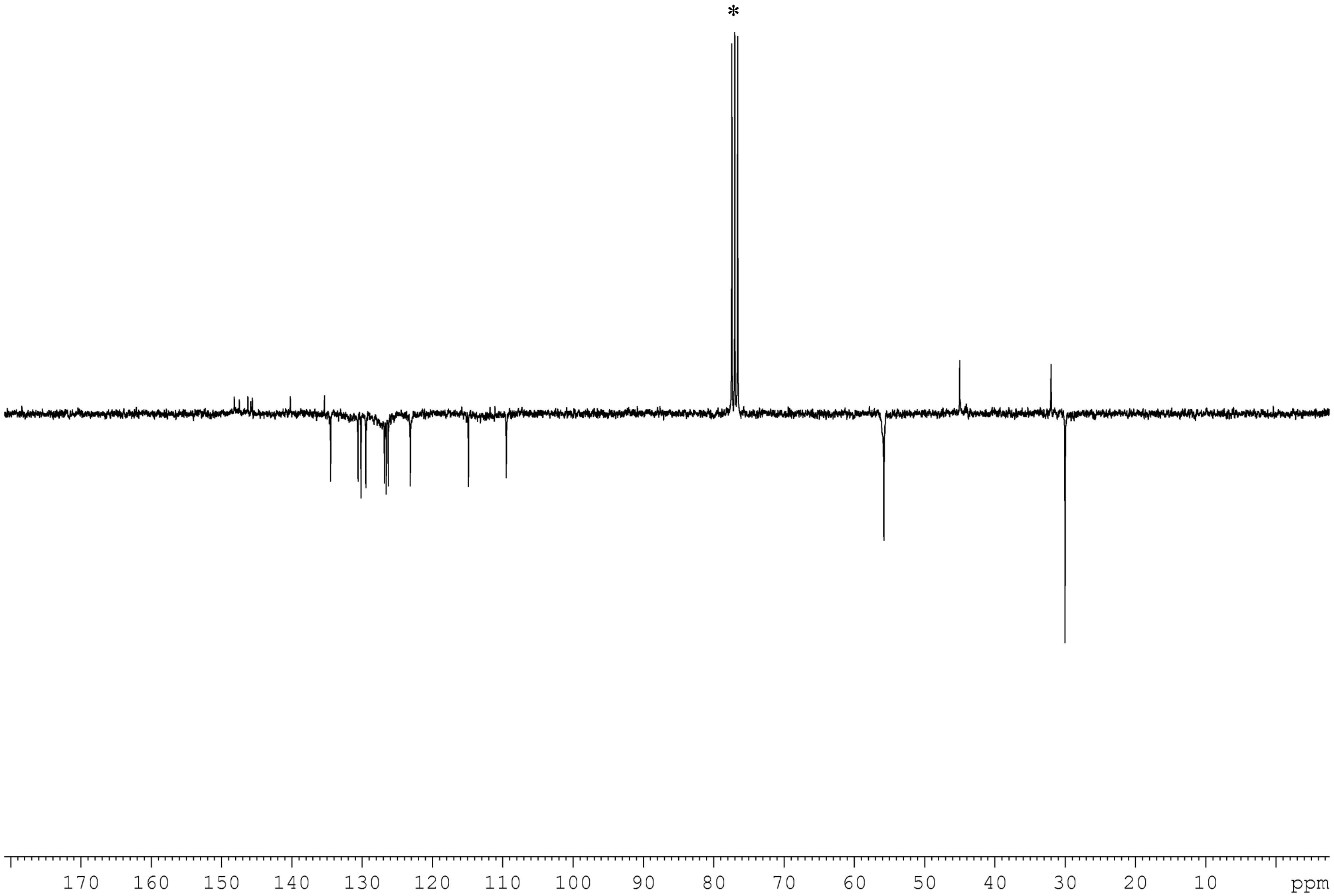
^{1}H NMR spectrum of **2a** ($CDCl_3$ + TMS, 25 ºC)
(From left to right, the asteriks indicate the signals corresponding to $CHCl_3$, H_2O, *n*-pentane and TMS)



APT spectrum of **2a** ($CDCl_3$ + TMS, 25 ºC)
(The asterik indicates the signal corresponding to $CDCl_3$)



^{1}H NMR spectrum of **2b** ($CDCl_3$ + TMS, 25 ºC)
(From left to right, the asteriks indicate the signals corresponding to $CHCl_3$, H_2O, and TMS)



APT spectrum of **2b** ($CDCl_3$ + TMS, 25 ºC)
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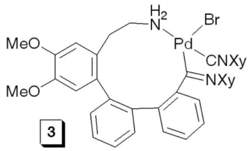
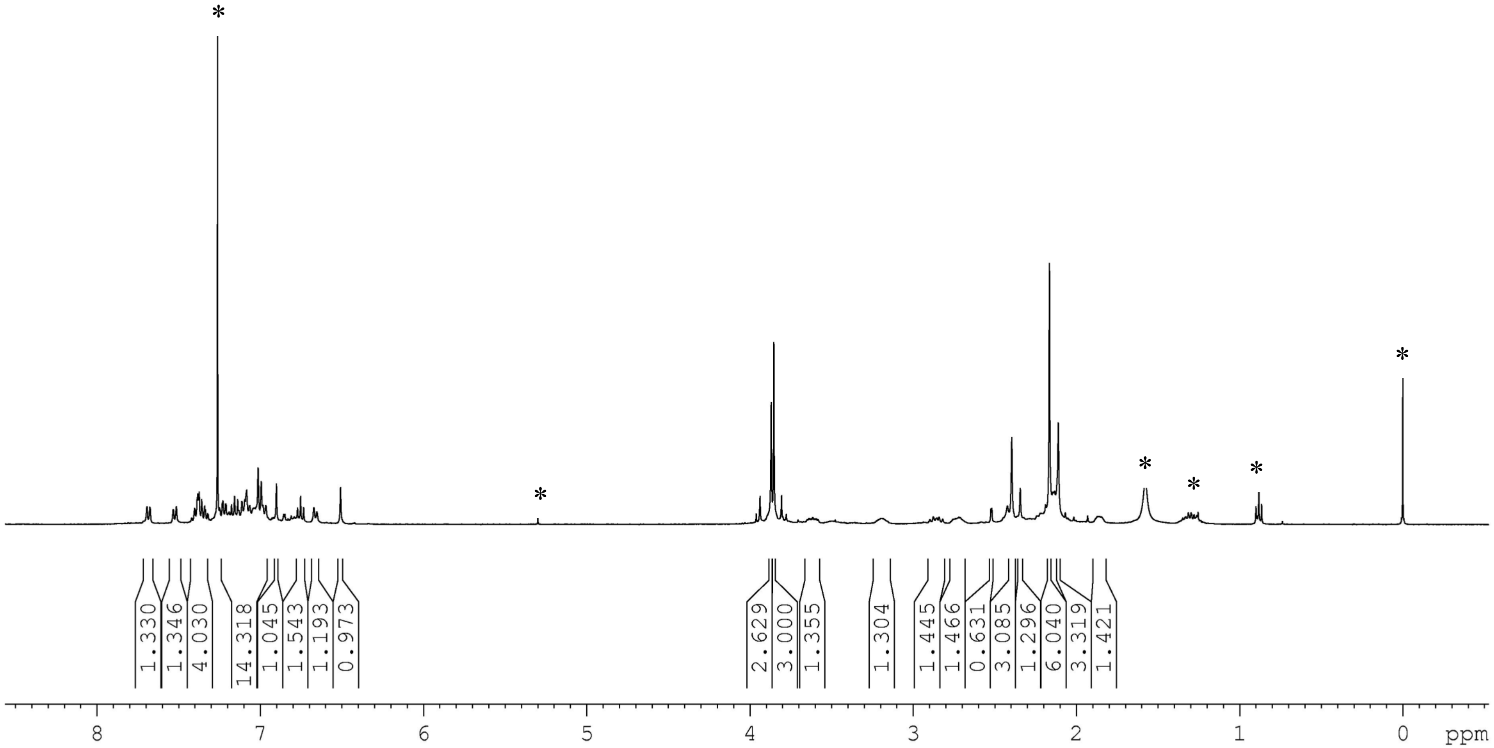
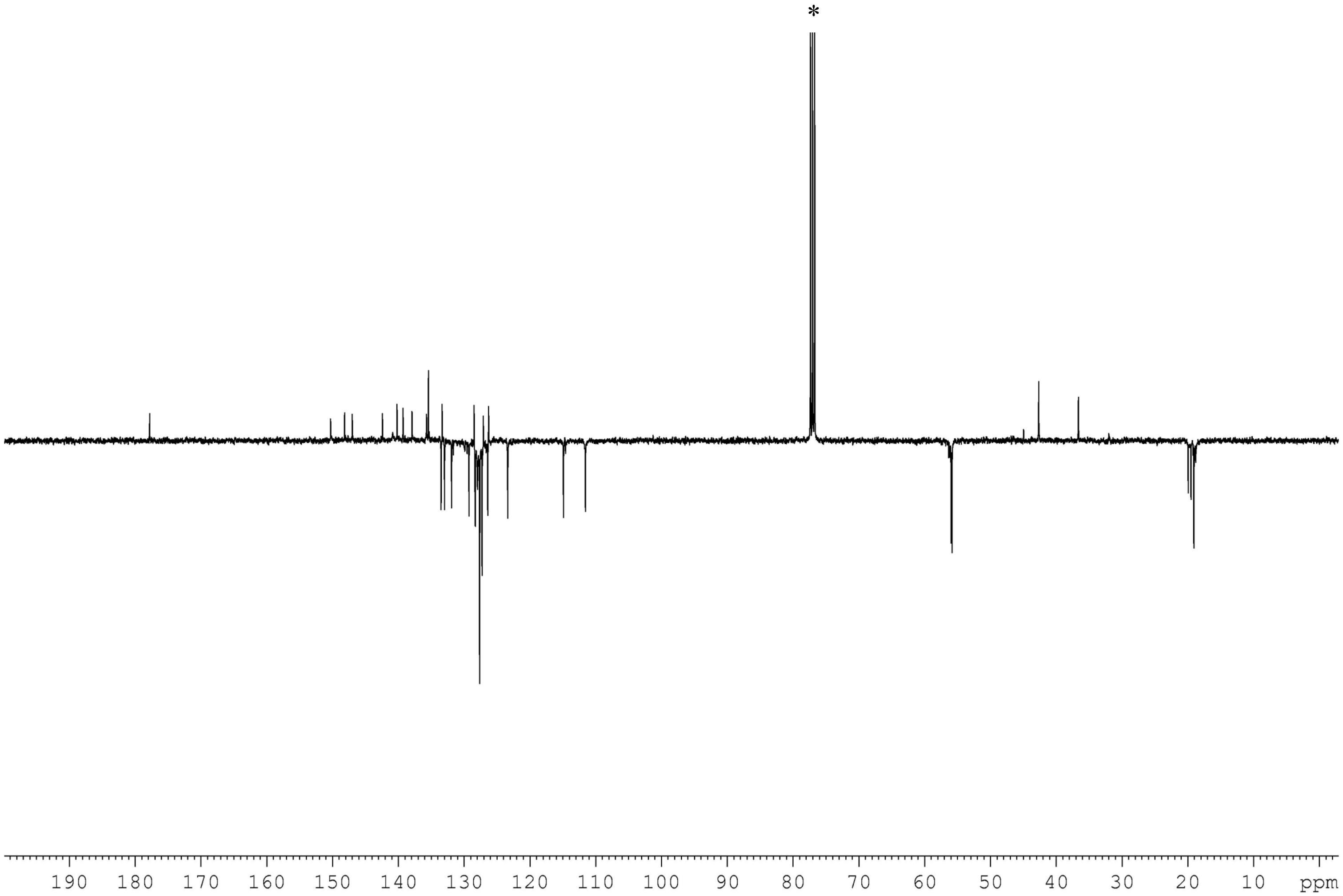


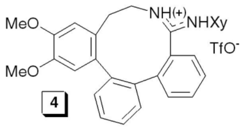
3



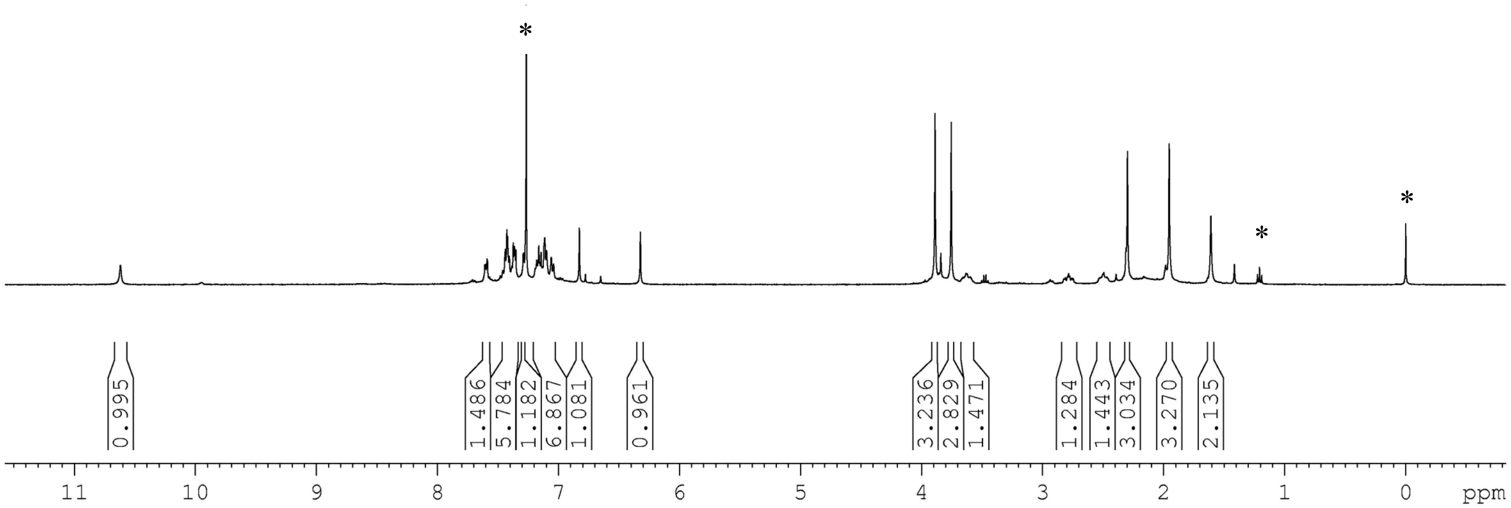
^{1}H NMR spectrum of **3** ($CDCl_3$ + TMS, 25 ºC)
(From left to right, the asteriks indicate the signals corresponding to $CHCl_3$, CH_2Cl_2, H_2O, *n*-pentane, and TMS)



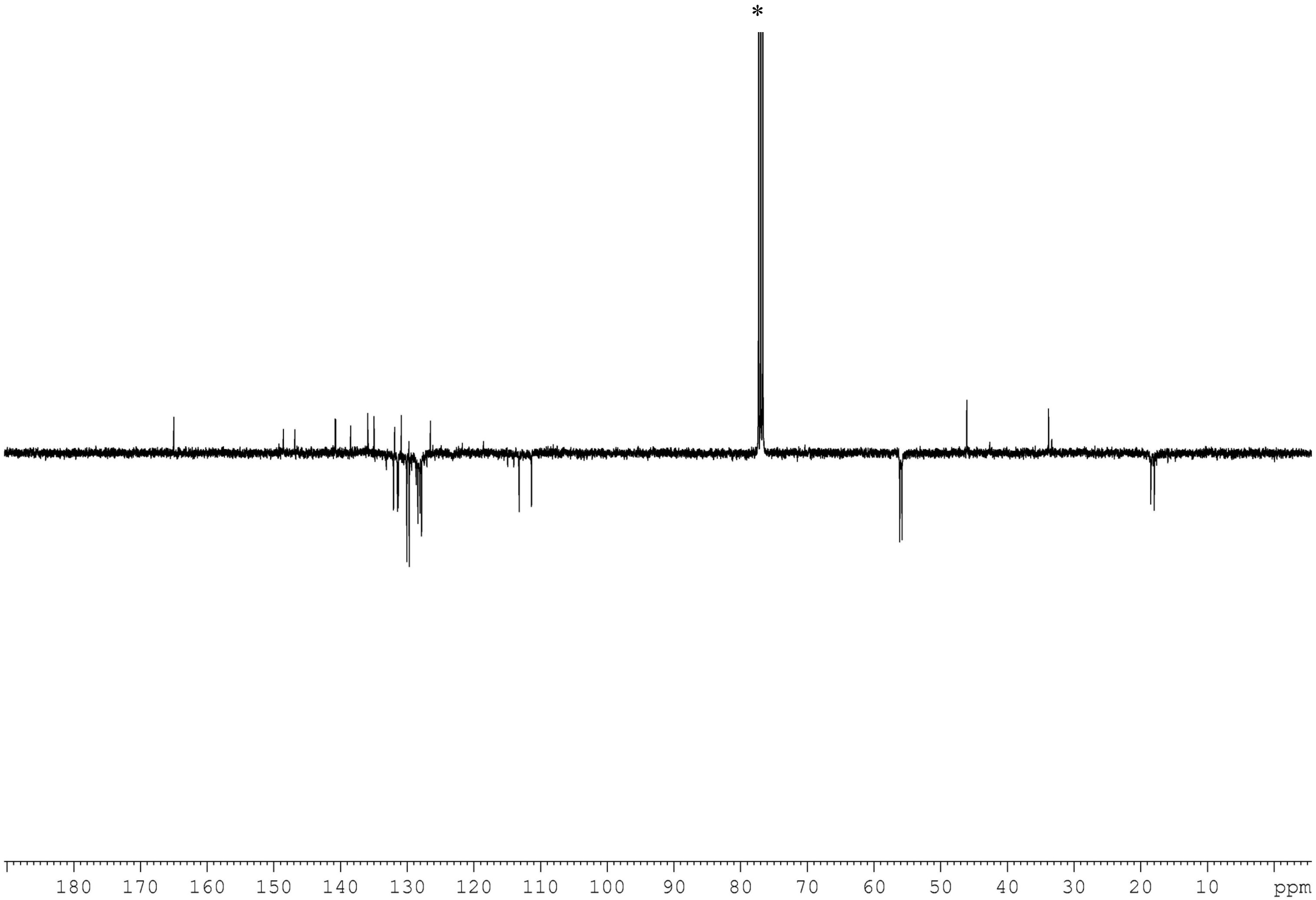
APT spectrum of **3** ($CDCl_3$ + TMS, 25 ºC)
(The asterik indicates the signal corresponding to $CDCl_3$)



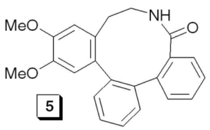
4



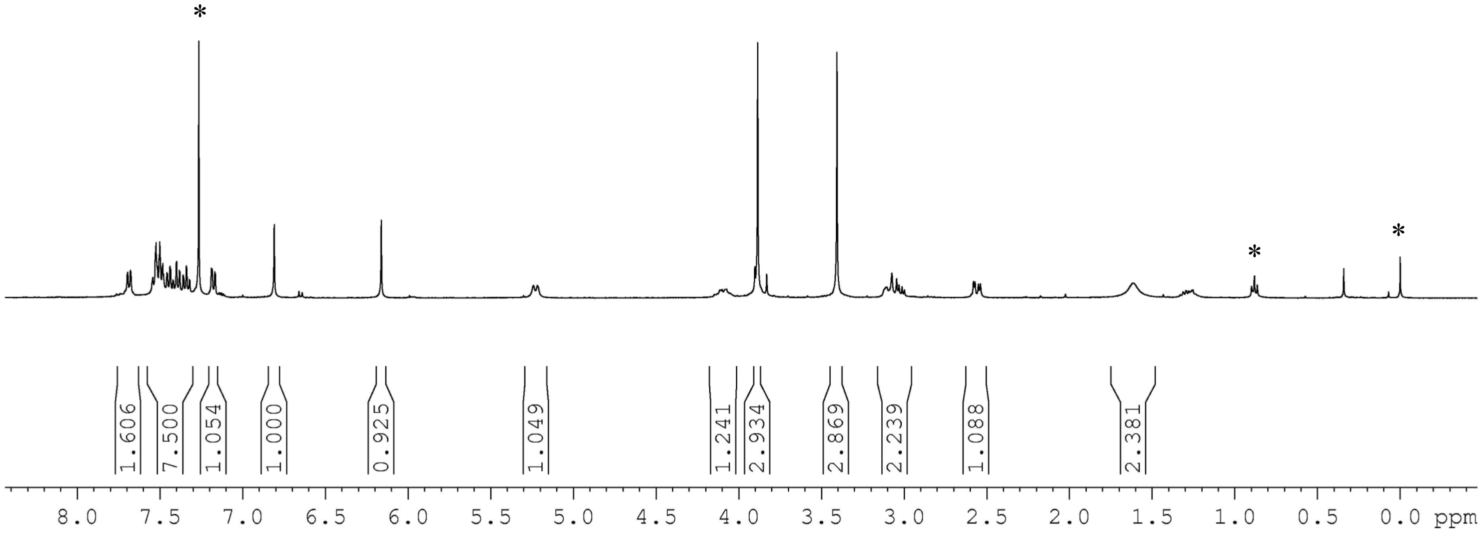
^{1}H NMR spectrum of **4**·H_2O ($CDCl_3$ + TMS, 25 ºC)
(From left to right, the asteriks indicate the signals corresponding to $CHCl_3$, traces of pentane, and TMS)



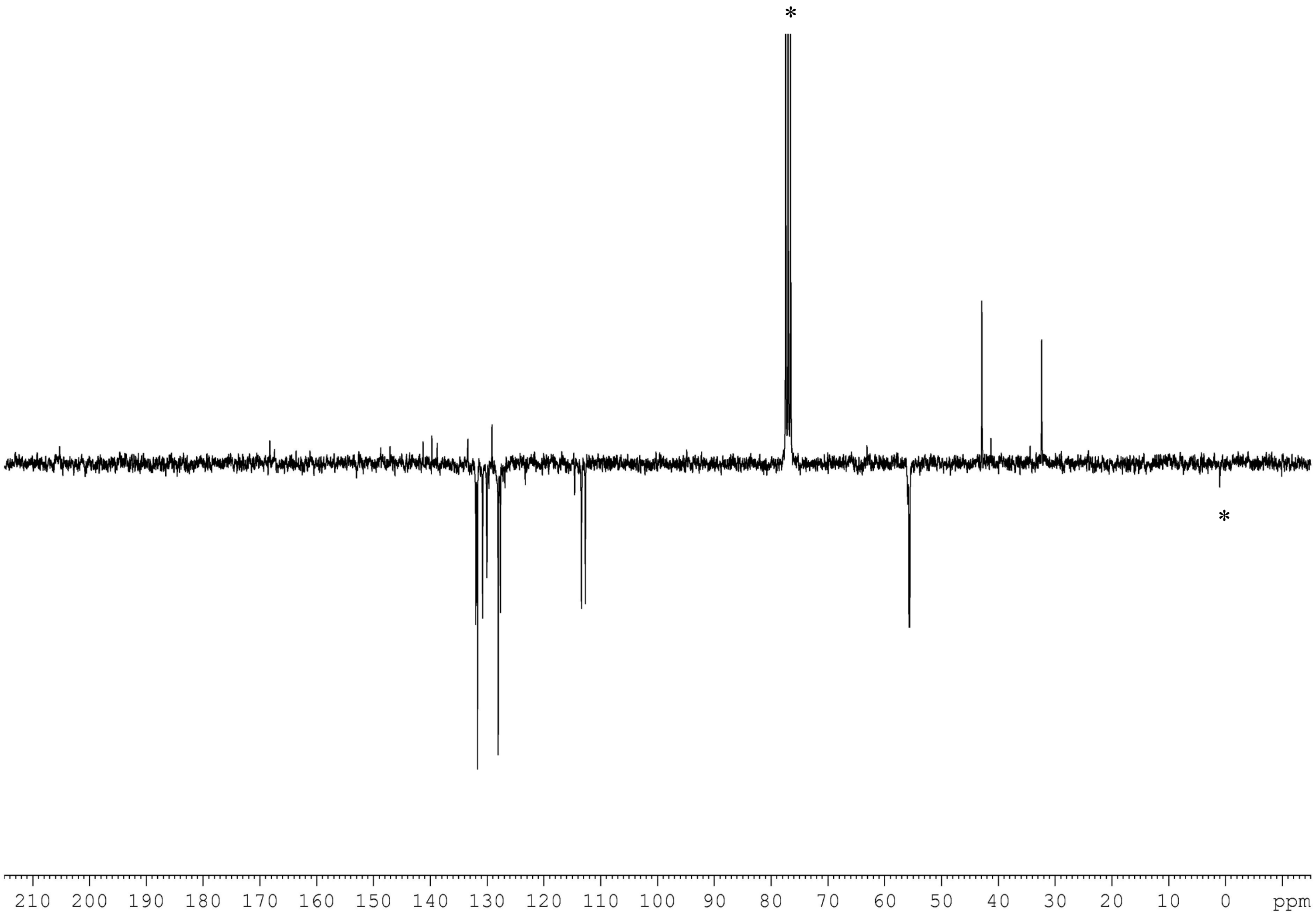
APT spectrum of **4** ($CDCl_3$ + TMS, 25 ºC)
(The asterik indicates the signal corresponding to $CDCl_3$)



5



^{1}H NMR spectrum of **5**·H_2O ($CDCl_3$ + TMS, 25 ºC)
(From left to right, the asteriks indicate the signals corresponding to $CHCl_3$, traces of pentane, and TMS)



APT spectrum of **5** ($CDCl_3$ + TMS, 25 ºC)
(From left to right, the asteriks indicate the signals corresponding to $CDCl_3$ and TMS)