Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 325-327

Pyrano[3,4-*c*]pyrandiium dication

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^{1}H, ^{13}C NMR two-dimensional correlation spectra and general procedures of all obtained compounds

^{1}H, ^{13}C and two-dimensional correlation NMR spectra were acquired on a Bruker DPX-250 spectrometer (250 and 63 MHz, respectively). All resonances are reported relative to TMS. Spectra were calibrated relative to solvents residual proton and carbon chemical shifts. Elemental analysis was performed on an Elemental Vario Microcube CHNS analyzer. The content of halogens was determined separately by the Schöniger method. Melting points were determined in open capillaries on a Khimlaborpribor PTP apparatus. All commercially available compounds were used without further purification.

1-Ethoxy-3,8-diphenyl-5-methyl-1*H*-pyrano[3,4-*c*]pyran-7-ium perchlorate 1 was obtained by the procedure reported previously[S1].

1-Hydroxy-5-methyl-3,8-diphenyl-1*H*-pyrano[3,4-*c*]pyran-7-ium perchlorate 3

1-Ethoxy-3,8-diphenyl-5-methyl-1*H*-pyrano[3,4-*c*]pyran-7-ium perchlorate **1** (0.222 g, 0.5 mmol) was added to a mixture of propionic anhydride (3 ml, 23 mmol) and 70% $HClO_4$ (1 ml, 10 mmol). The reaction mixture was heated until complete dissolution of the initial salt. After cooling, the formed yellow crystalline precipitate was filtered off, washed with diethyl ether, and air-dried.

^{1}H NMR (250 MHz, formic acid-d) δ 8.78 (s, 1H), 8.13 – 7.39 (m, 10H, H-Ar), 7.21 (s, 1H), 6.95 (s, 1H), 2.50 (s, 3H, CH_3)

^{13}C NMR (63 MHz, formic acid-d) δ 173.68, 170.64, 160.94, 157.11, 138.11, 136.95, 134.34, 132.92 (2C), 132.81 (2C), 132.64 (2C), 131.69 (2C), 131.56, 128.36, 119.50, 100.05, 93.59, 15.56

Yield 0.162 g (78%), mp 187-188 °C
Yellow crystals
Calculated, %: C, 60.51; H, 4.11; Cl, 8.51
Found, %: C, 60.59; H, 4.19; Cl, 8.43

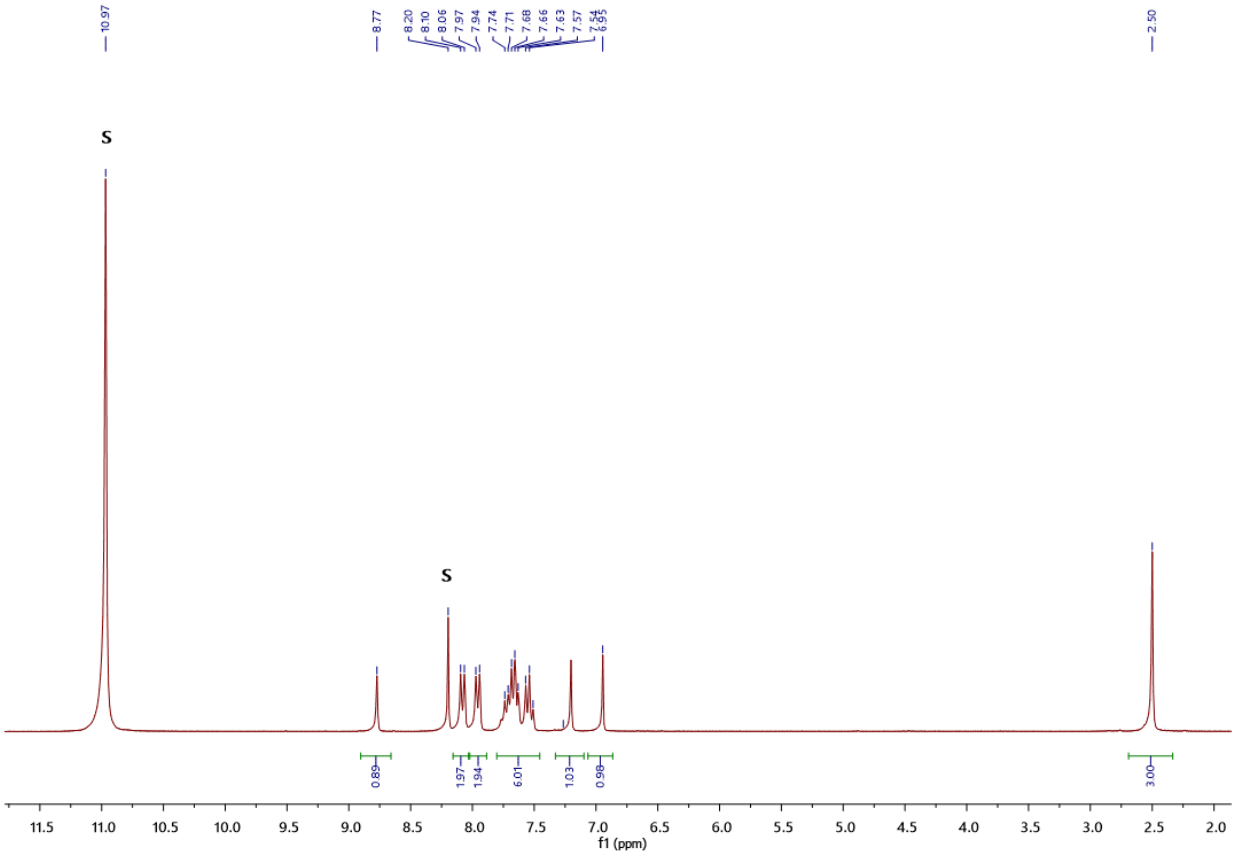

Figure S1 ^{1}H NMR spectrum of structure **3**.

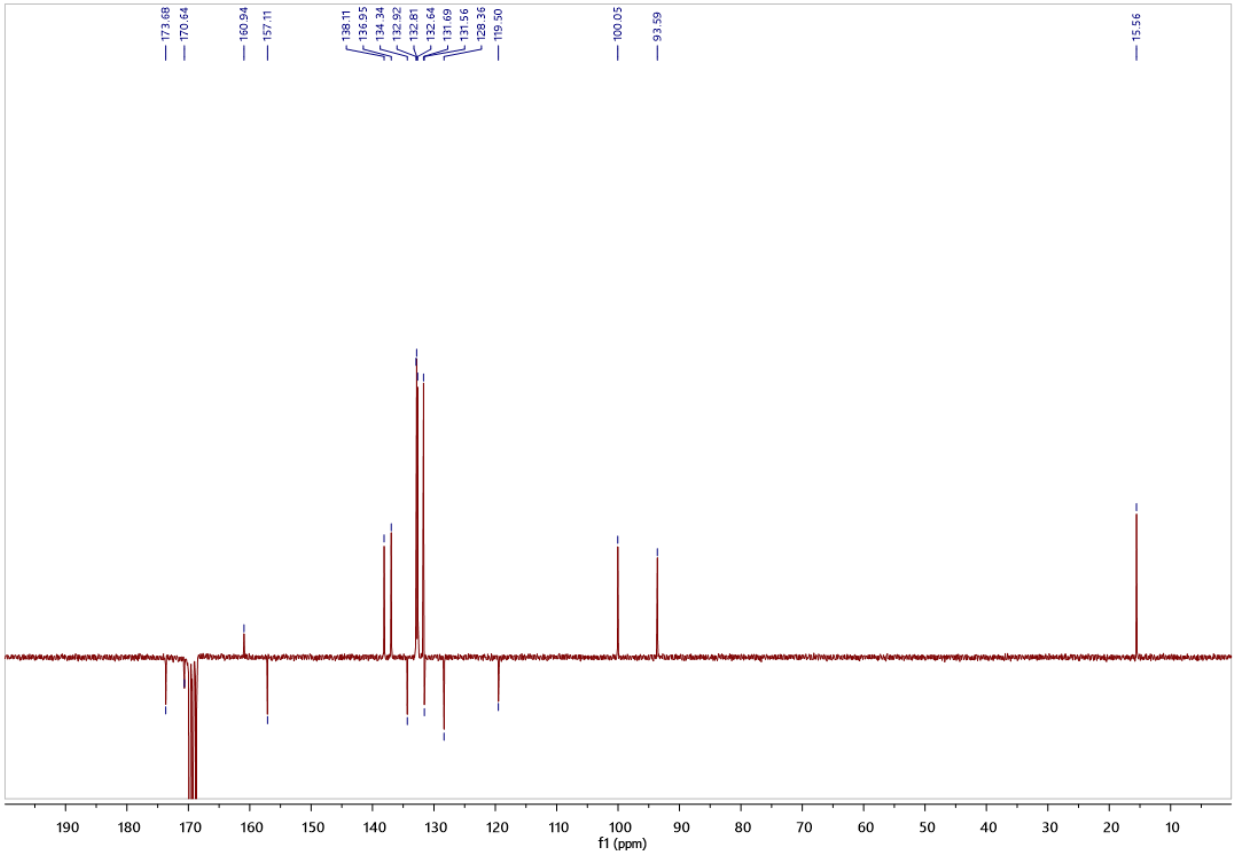

Figure S2 ^{13}C NMR spectrum of structure **3**.

1,1'-Oxybis(5-methyl-3,8-diphenyl-1*H*-pyrano[3,4-*c*]pyrandiium) bis[hexachloroantimonate$^{(1-)}$] 4

1-Ethoxy-3,8-diphenyl-5-methyl-1*H*-pyrano[3,4-*c*]pyrandiium perchlorate **1** (0.222 g, 0.5 mmol) was added to a solution of antimony pentachloride (1 ml, 7.8 mmol) in absolute 1,2-dichloroethane (3 ml, 38 mmol). The reaction mixture was kept at room temperature until crystals formed (2 months). The orange crystals formed were filtered off, washed with absolute 1,2-dichloroethane, and air-dried.

Yield 0.358 g (56%), mp above 350 °C.

Orange crystals

Calculated, %: C, 74.73; H, 5.71

Found, %: C, 74.70; H, 5.75

4-Methyl-1,6-diphenylpyrano[3,4-*c*]pyrandiium bis(deuterium sulfate) 2b

1-Hydroxy-5-methyl-3,8-diphenyl-1*H*-pyrano[3,4-*c*]pyrandiium perchlorate **3** (0.01 g, 0.024 mmol) was dissolved in deuterosulfuric acid 0.6 ml in an ampoule to record NMR spectra.

^{1}H NMR (250 MHz, D_2SO_4) δ 10.67 (s, 1H, H-8), 9.13 (s, 1H, H-3), 9.11 (s, 1H, H-5), 8.83 – 8.46 (m, 5H, H-Ar), 8.36 – 7.97 (m, 5H, H-Ar), 3.06 (s, 1H, CH_3)

^{13}C NMR (63 MHz, $CDCl_3$) δ 188.85, 179.75, 175.58, 157.22, 153.00, 152.93, 144.59, 141.45, 136.49 (2C), 132.73 (2C), 131.75 (2C), 131.71 (2C), 127.65, 127.24, 126.38, 118.26, 12.51

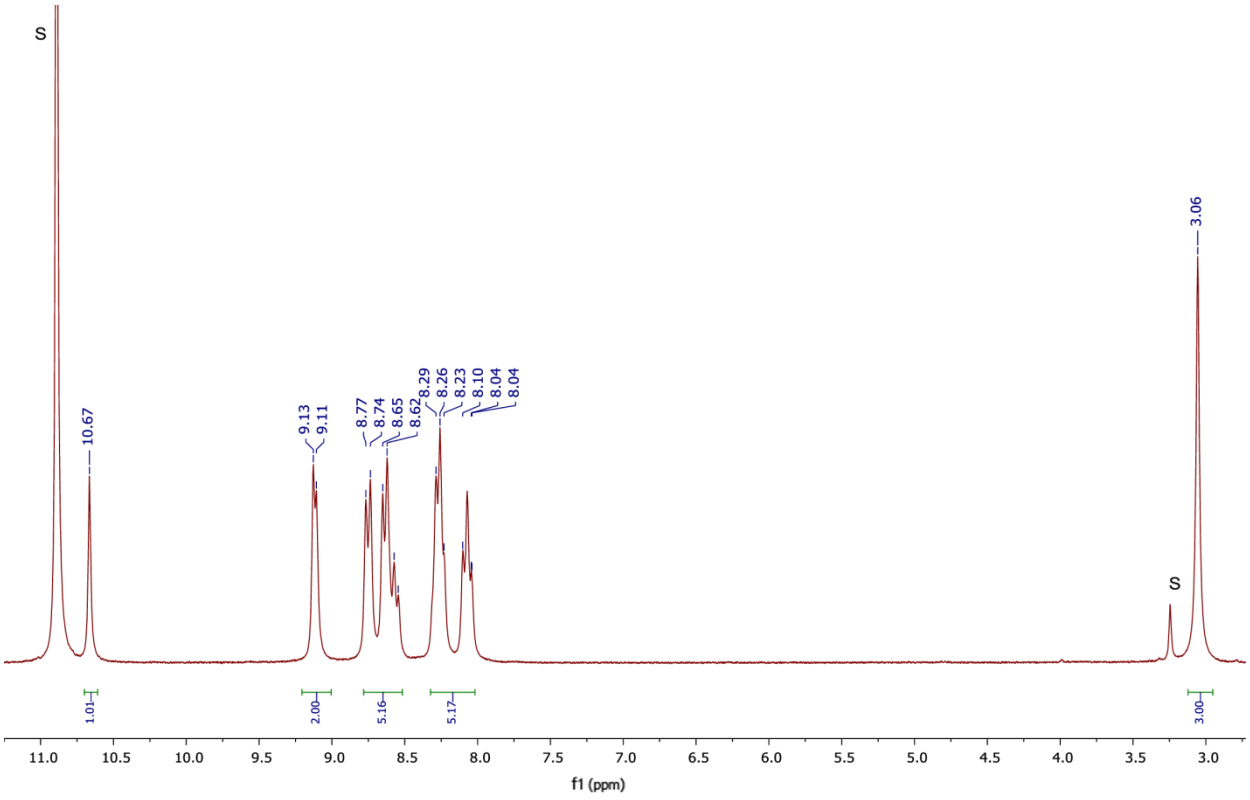

Figure S3 ^{1}H NMR spectrum of structure **2b**.

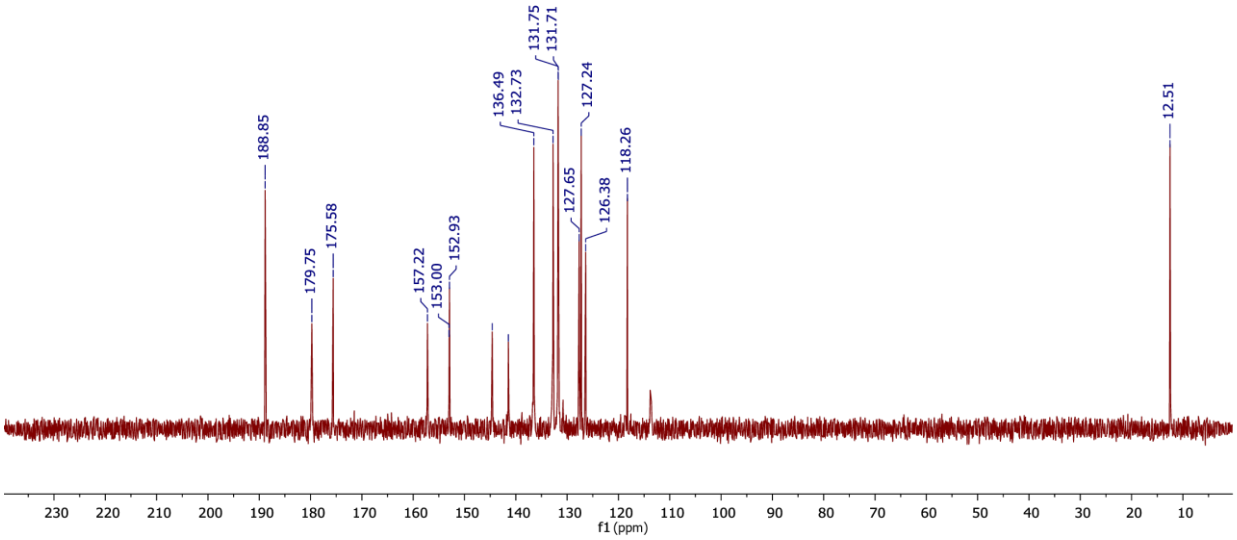

Figure S4 ^{13}C NMR spectrum of structure **2b**.

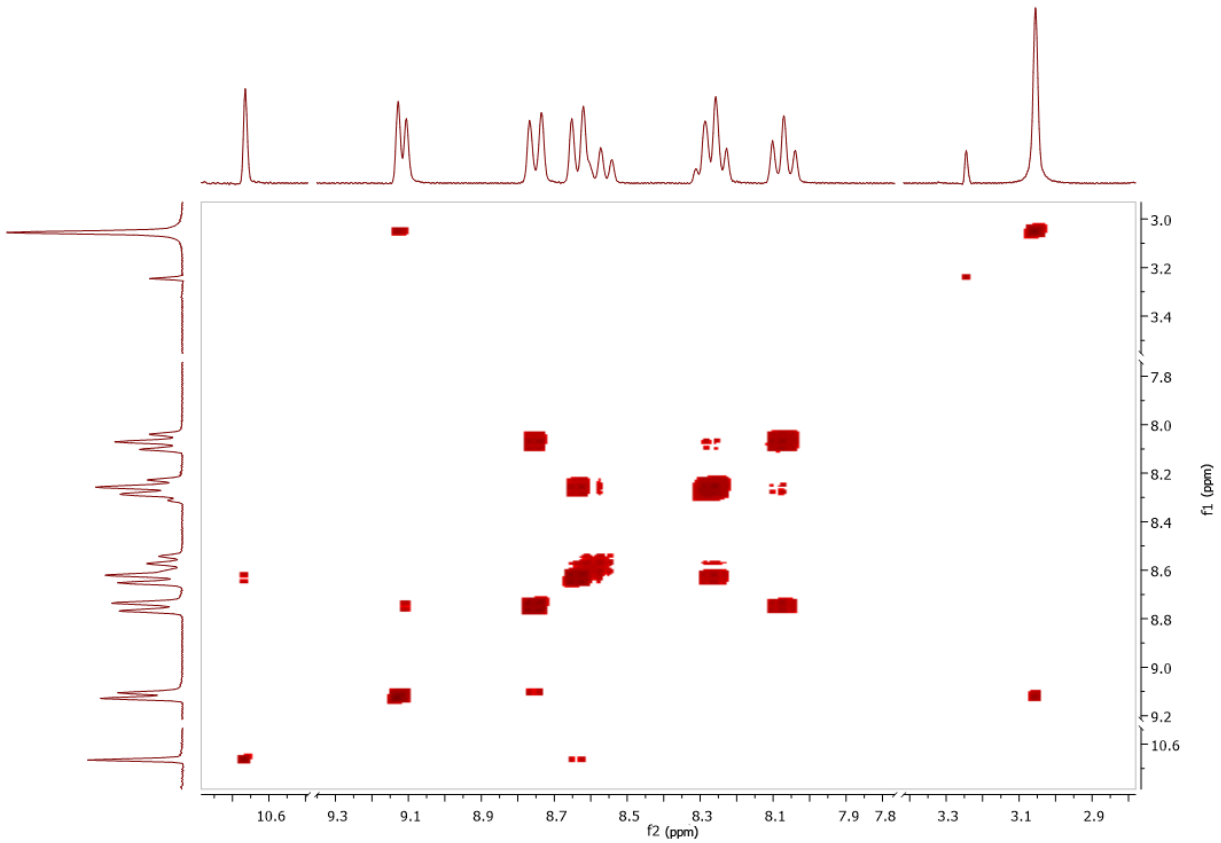

Figure S5 NOESY spectrum of structure **2b**.

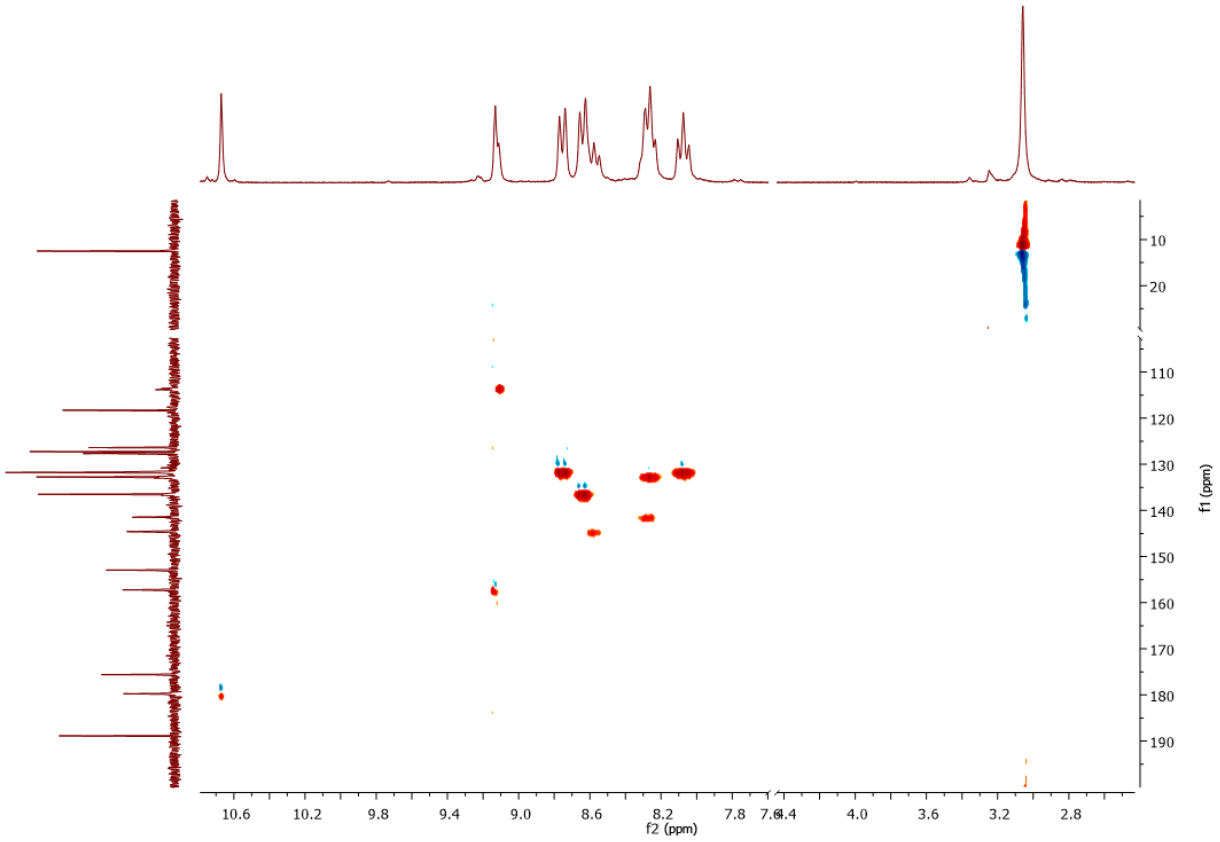

Figure S6 HMQC spectrum of structure **2b**.

References

S1 K.F. Suzdalev, A.V. Krachkovskaya, M.E. Kletskii, O.N. Burov, A.V. Tatarov and S.V. Kurbatov, *Chem. Heterocycl. Compd.*, 2017, **53**, 156.