Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 664–666

Coordination and extraction properties of new bis- and tetrakis(diphenylphosphoryl)-substituted pyrazines towards *f*-block elements

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Analytical data (C, H, N content) were obtained with a Carlo Erba model 1106 microanalyzer. The phosphorus content was determined spectrophotometrically. Multinuclear ^{1}H and ^{13}C spectra were recorded with a Bruker Avance 400 spectrometer (^{1}H, 400.13 and ^{13}C, 100.61 MHz) and a Bruker Avance 600 spectrometer (^{1}H, 600.22 and ^{13}C, 150.93 MHz) using residual proton signals of deuterated solvent as an internal standard. ^{31}P NMR spectra were recorded with a Bruker Avance 300 spectrometer (121.49 MHz) using 85% H_3PO_4 as an external standard. The ^{13}C NMR spectra were registered using the JMODECHO mode; the signals for the C atom bearing odd and even numbers of protons have opposite polarities. IR spectra were recorded in KBr pellets on a Fourier-spectrometer "Magna-IR750" (Nicolet), resolution 2 cm^{-1}, 128 scans.

Starting polychloropyrazines **1a,b** were obtained from commercial 2-chloropyrazine [American Cyanamid Co., *FR Patent 1457963*, 1965] and 2,5-dioxopiperazine [S. Oda, T. Shimizu, T. Katayama, H. Yoshikawa and T. Hatakeyama, *Org. Lett.*, 2019, **21**, 1770], respectively.

2,3-Bis(diphenylphosphoryl)pyrazine **2a**.

Yield 57%, off-white powder, m.p. 169 °C.
^{31}P NMR (300 MHz, $CDCl_3$) δ: 20.05.
^{1}H NMR (400MHz, $CDCl_3$) δ: 7.36-7.41, 7.56-7.67 (both m, 8H+12H, C_6H_5), 9.53 (d, $^{4}J_{PH}$ = 4.0 Hz, 2H, pyrazine-C^{5,6}-H).
^{13}C NMR (400MHz, $CDCl_3$) δ: 128.57 (d, $^{3}J_{PC}$ = 12.9, *m*-C in C_6H_5), 130.63 (d, $^{1}J_{PC}$ = 106.0 Hz, *ipso*-C), 131.90 (d, $^{2}J_{PC}$ = 10.0 Hz, *o*-C in C_6H_5), 132.40 (*p*-C in C_6H_5), 149.15 (dd, $^{3}J_{PC}$ = 20.0 Hz, $^{4}J_{PC}$ = 3.0 Hz, C^5, C^6), 152.44 (dd, $^{1}J_{PC}$ = 122.0 Hz, $^{2}J_{PC}$ = 13.1 Hz, C^2, C^3).
Found (%): C 70.00; H 4.62; N 5.83; P 12.89. Calcd. for $C_{28}H_{22}N_2O_2P_2$ (%): C 69.94; H 4.62; N 5.77; P 12.79.
IR (KBr), ν, cm^{-1}: 526, 541, 556, 698, 725, 750, 1116, 1180, 1204 (P=O), 1439.

2,3,5,6-Tetrakis(diphenylphosphoryl)pyrazine **2b**.

Yield 74%, off-white powder, m.p. 320 °C.
^{31}P NMR (300 MHz, $CDCl_3$) δ: 24.77.
^{1}H NMR (400MHz, $CDCl_3$) δ: 7.33-7.36, 7.51-7.52 (both m, 32H+8H, C_6H_5).

^{13}C NMR (400MHz, $CDCl_3$) δ: 127.90 (d, $^3J_{PC}$ = 12.3, *m*-C in C_6H_5), 131.10 (d, $^1J_{PC}$ = 110.1 Hz, *ipso*-C), 131.61 (*p*-C in C_6H_5), 131.90 (d, $^2J_{PC}$ = 8.8 Hz, *o*-C in C_6H_5), 154.16 (dddd, $^1J_{PC}$ = 121.2 Hz, $^2J_{PC}$ = 13.0 Hz, $^3J_{PC}$ = 20.0 Hz, $^4J_{PC}$ = 4.2 Hz, C^2, C^3 C^5, C^6).
Found (%):C 70.67; H 4.43; N 3.08; P 13.86. Calcd. for $C_{52}H_{40}N_2O_4P_4$ (%): C 70.91; H 4.58; N 3.18; P 14.07.
IR (KBr), ν, cm^{-1}: 562, 564, 695, 724, 1119, 1207 (P=O), 1438.

2,3-Bis(diphenylphosphoryl)quinoxaline **2c**.

Yield 83%, off-white powder, m.p. 267 °C (decomp).
^{31}P NMR (300 MHz, $CDCl_3$) δ: 25.31.
^{1}H NMR (600MHz, $CDCl_3$) δ: 7.37-7.41, 7.47-7.50, 7.78-7.81 (all m, 8H+4H+8H, C_6H_5), 7.83-7.86, 8.02-8.04 (both m, 2H+2H, quinoxaline-$C^{5,6,7,8}$-H).
^{13}C NMR (600MHz, $CDCl_3$) δ: 127.92 (d, $^3J_{PC}$ = 12.5 Hz, *m*-C in C_6H_5), 129.89 (C^5-C^8), 131.44 (*p*-C in C_6H_5), 132.33 (d, $^2J_{PC}$ = 9.0 Hz, *o*-C in C_6H_5), 132.86 (d, $^1J_{PC}$ = 108.4 Hz, *ipso*-C), 140.04 (dd, $^3J_{PC}$ = 18.3 Hz, $^4J_{PC}$ = 4.4 Hz, C^{4a}, C^{8a}), 155.66 (dd, $^1J_{PC}$ = 121.7 Hz, $^2J_{PC}$ = 22.6 Hz, C^2, C^3).
Found (%): C 72.34; H 4.73; N 5.25; P 11.52. Calcd. for $C_{32}H_{24}N_2O_2P_2$ (%): C 72.45; H 4.56; N 5.28; P 11.68.
IR (KBr), ν, cm^{-1}: 532, 554, 605, 696, 723, 789, 1118, 1186, 1208 (P=O), 1216, 1438.

[2,3-Bis(diphenylphosphoryl)pyirazine]uranyl dinitrate **3a**.

Yield 90%, yellow powder, m.p. 284 °C (decomp).
Found (%): C 38.95; H 2.62; N 7.61. Calcd. for (UO_2)**4**$(NO_3)_2 \cdot 1CH_3CN$ – $C_{30}H_{25}N_5O_{10}P_2U$ (%): C 39.36; H 2.75; N 7.65.
IR (KBr), ν, cm^{-1}: 537, 554, 690, 730, 747, 938 (UO_2), 1087, 1140 (P=O), 1280 (NO_2), 1385, 1438, 1486 (N=O), 1522.

[2,3,5,6-Tetrakis(diphenylphosphoryl)pyrazine]bis(uranyl dinitrate) **3b**.

Yield 91%, yellow crystals, m.p. >350 ºC (decomp.).
Found (%): C 36.30; H 2.73; N 6.42; P, 6.95. Calcd. for $[(UO_2)_2$**5**$(NO_3)_4] \cdot 2CH_3CN$ - $C_{56}H_{46}N_8O_{20}P_4U_2$ (%): C 38.41; H 2.65; N 6.40; P, 7.08.
IR (KBr), ν, cm^{-1}: 536, 565, 598, 689, 732, 747, 938 (UO_2), 1097, 1123, 1148, 1174 (P=O), 1282 (NO_2), 1385, 1439, 1485 (N=O), 1522, 1534.

[2,3-Bis(diphenylphosphoryl)quinoxaline]uranyl dinitrate **3c**.

Yield 93%, yellow crystals, m.p. 311 ºC (decomp.).
Found (%): C 41.67; H 2.78; N 6.19; P, 7.04. Calcd. for (UO_2)**6**$(NO_3)_2$ - $C_{32}H_{24}N_4O_{10}P_2U$ (%): C 41.57; H 2.62; N 6.06; P, 6.70.
IR (KBr), ν, cm^{-1}: 531, 543, 608, 689, 925, 941 (UO_2), 1094, 1138, 1154 (P=O), 1272, 1299 (NO_2), 1385, 1438, 1485 (N=O), 1521.

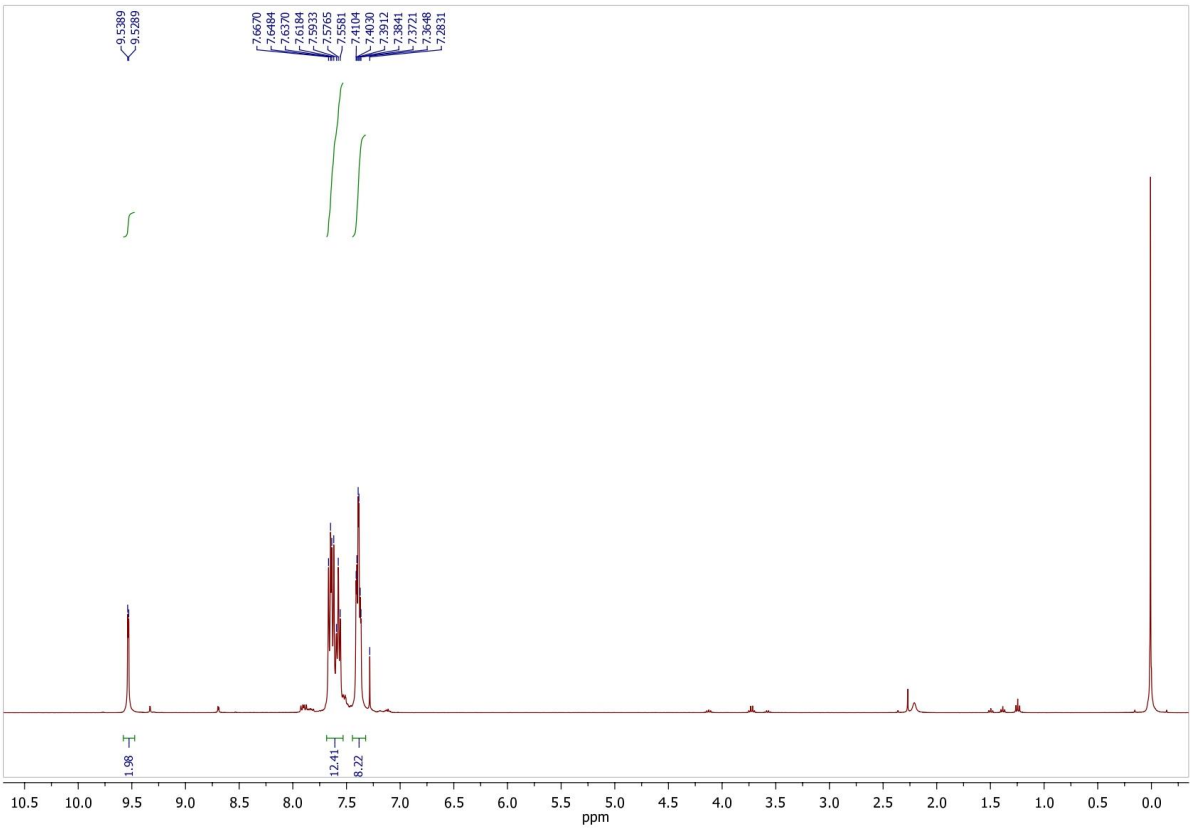

Figure S1 ^{1}H NMR for compound **2a**

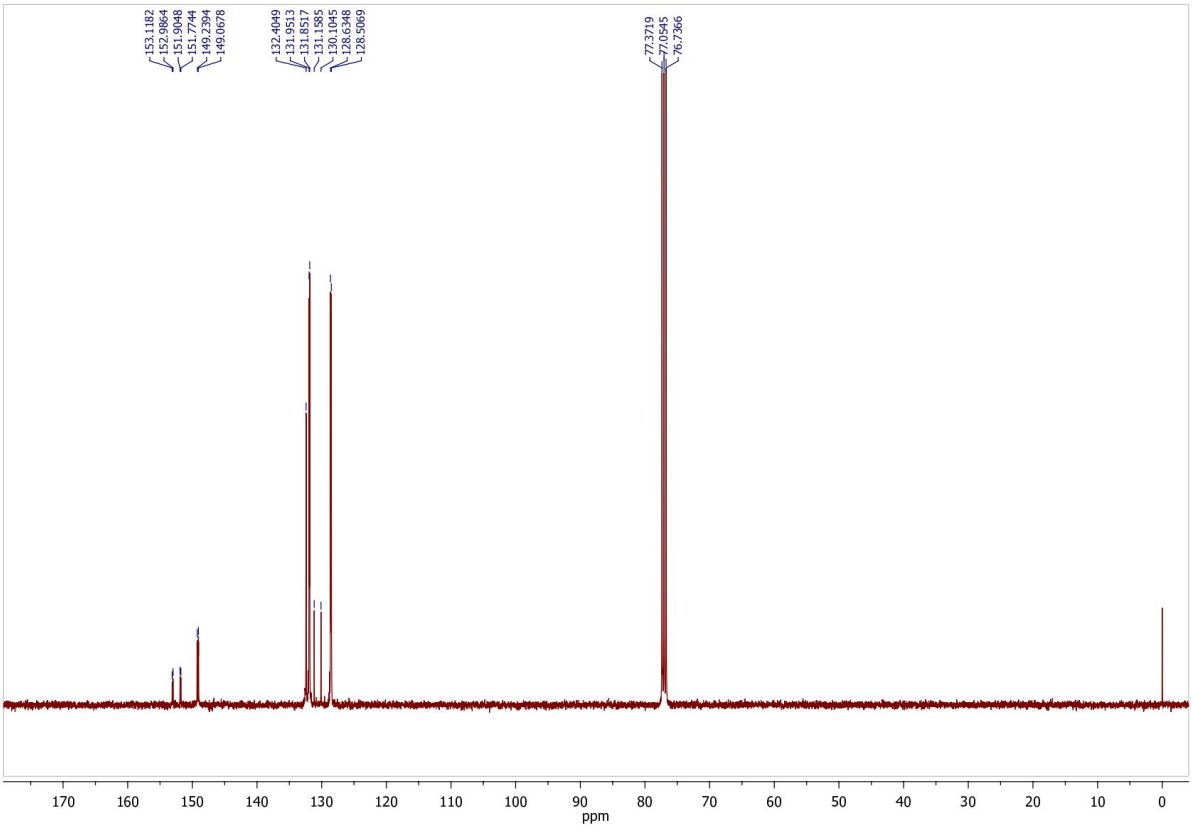

Figure S2 ^{13}C NMR for compound **2a**

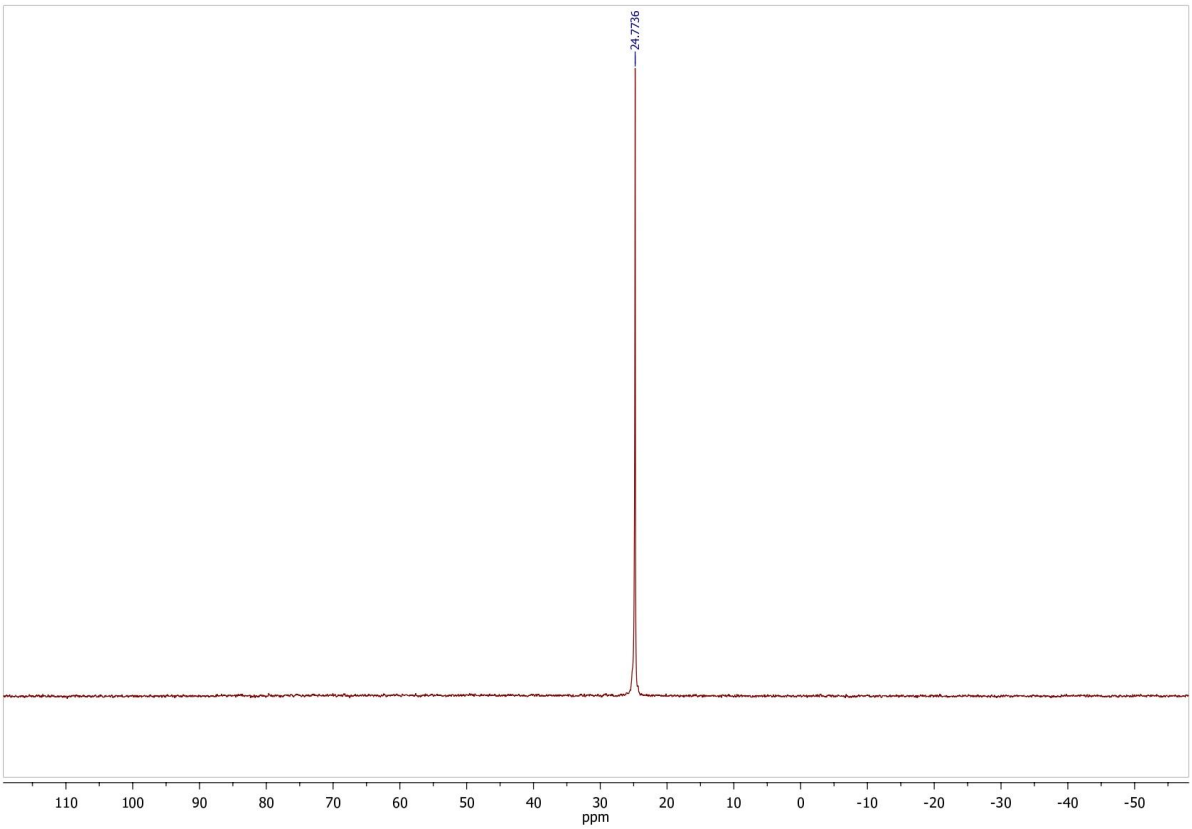

Figure S3 ^{31}P NMR for compound **2b**

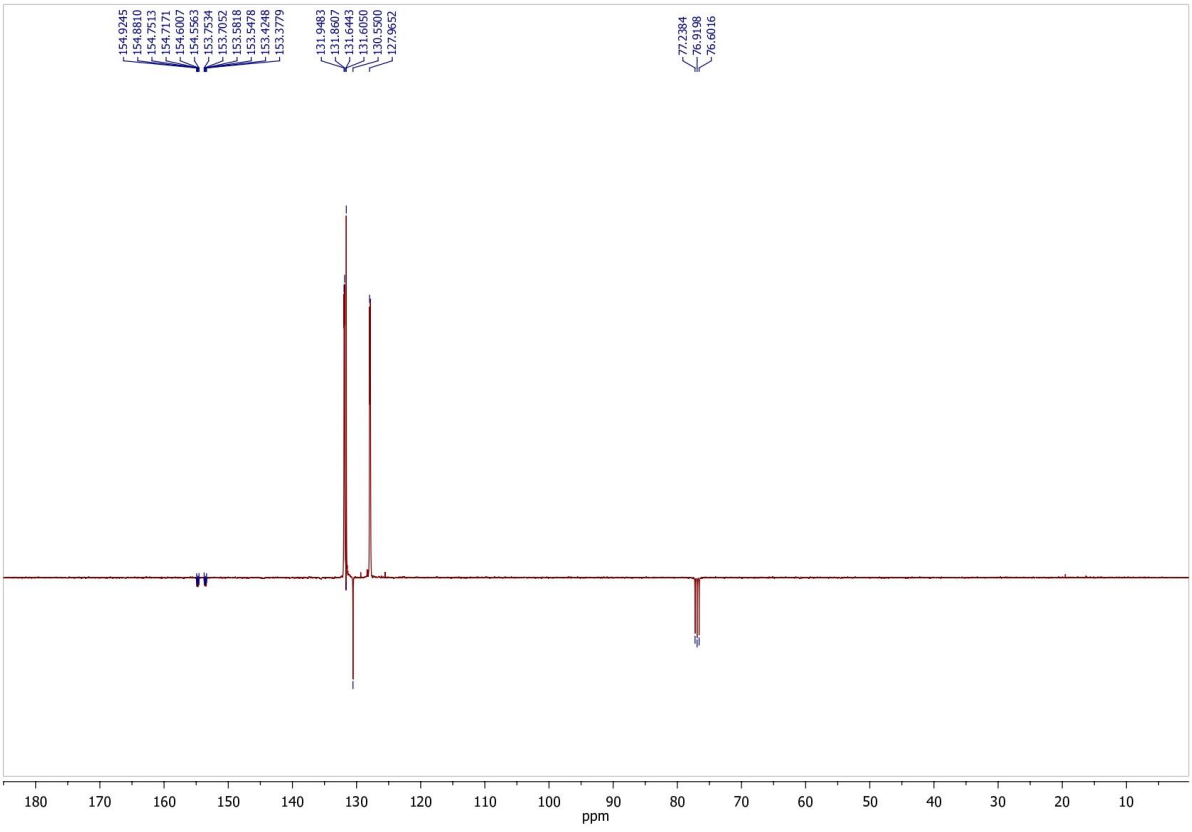

Figure S4 ^{13}C NMR for compound **2b**

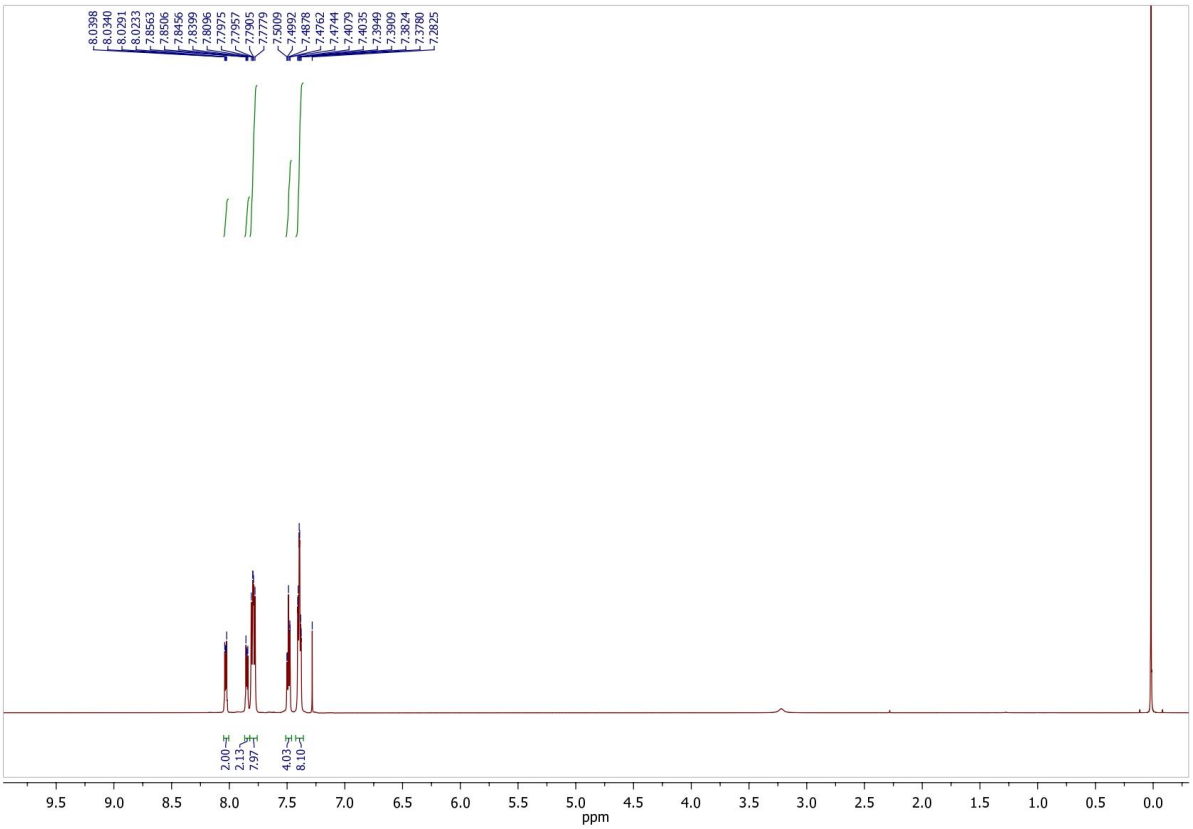

Figure S5 ^{1}H NMR for compound **2c**

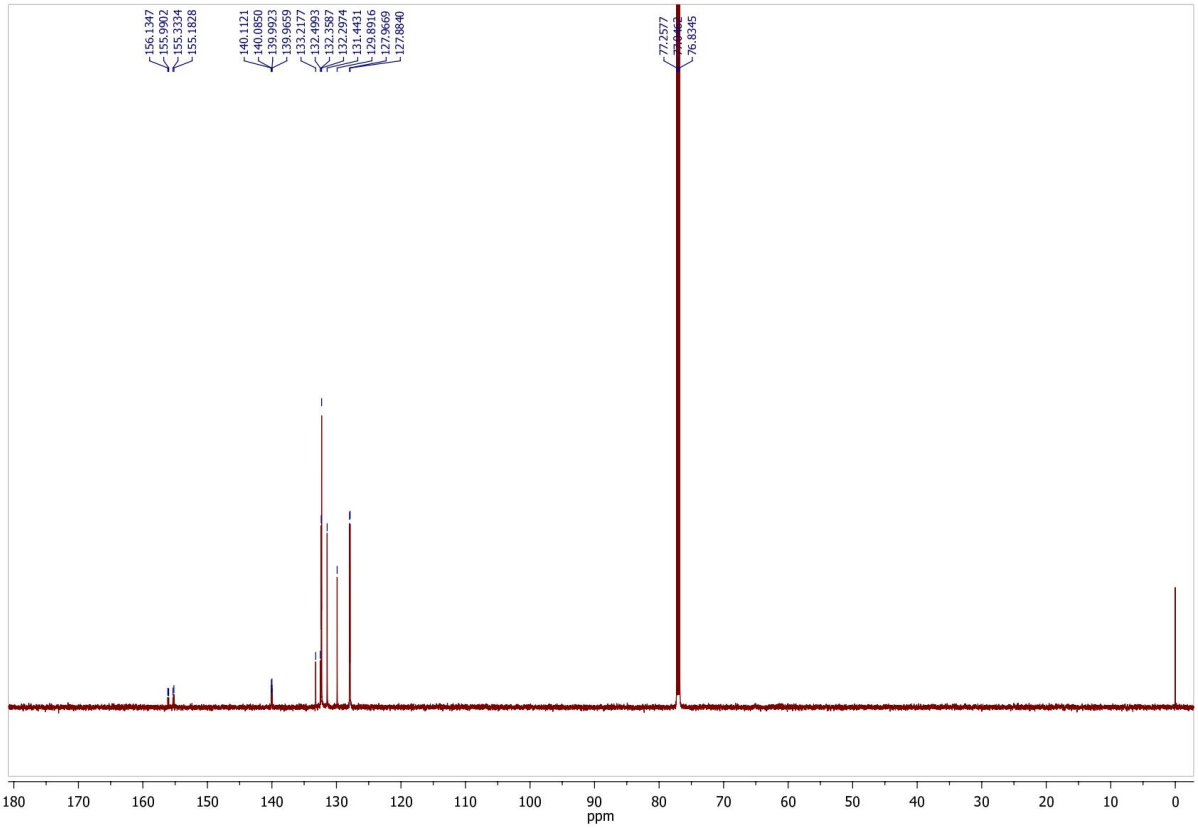

Figure S6 ^{13}C NMR for compound **2c**