Electronic supplementary materials *Mendeleev Commun.*, 2025, **35**, 39–41

9-[6-(Diphenylphosphino)pyridin-2-yl]-9*H*-carbazole: synthesis and coordination properties toward Cu^{I} and Pd^{II}

Andrey Yu. Baranov, Irina Yu. Bagryanskaya and Alexander V. Artem’ev

§1. Materials and Instrumentation

CuI (≥99%, Aldrich), Pd(COD)Cl$_2$ (99%, Aldrich) 2,6-dibromopiridine (98%, Aldrich), K_3PO_4 (≥98%, Aldrich), Carbazole (96%, Acros Organics), *n*-BuLi (2.5 M in hexanes, Aldrich), Ph$_2$PCl (98%, Dalchem) were used as purchased. Et$_2$O and THF were distilled from sodium-benzophenone ketyl prior to use.

9-(6-Bromopyridin-2-yl)-9*H*-carbazole was prepared according to the described procedure.[S1]

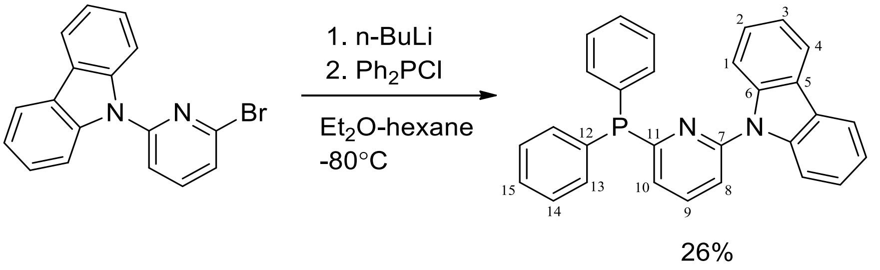
FT-IR spectra were recorded on a Bruker Vertex 80 spectrometer at ambient temperature. The microanalyses were performed on a MICRO cube analyzer.

^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were registered using a Bruker AV-500 spectrometer at 500.13, 125.76 and 202.46 MHz, respectively, with solvent peaks as reference (for ^{1}H and ^{13}C). The ^{31}P{^{1}H} NMR shifts are referenced to 85% H_3PO_4/D_2O as an external standard.

The CHN microanalyses were performed on a vario MICRO cube analyzer.

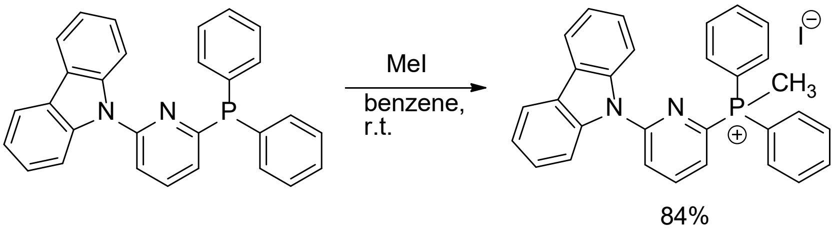
§2. Synthetic procedures and characterization data

Compound 1



An argon flushed two neck round bottom Schlenk flask (100 mL) equipped with a magnetic stirring bar and a dropping funnel was charged with *n*-BuLi (1.5 mL, 2.5 M solution in hexane). A solution of CbPyBr (1.18 g, 3.66 mmol) in Et$_2$O (27 mL) was syringed into the dropping funnel through a septum. The CbPyBr solution was added dropwise to *n*-BuLi at –80 ˚C. After addition, the mixture was stirred at –80 ˚C for 1.5 h. The dropping funnel was then charged with a solution of Ph$_2$PCl (808 mg, 3.66 mmol) in Et$_2$O (5 mL), and the solution was added dropwise to the reaction mixture at –80 ˚C for 30 min. The resulting mixture was stirred for 1 h at –80 ˚C and then at ambient temperature overnight. The solvent was then removed *in vacuo*, and the residue was diluted with H_2O (20 mL) and extracted with CHCl$_3$ (3×15 mL). The combined organic phase was dried over NaSO$_4$ and evaporated. After column chromatography on silica gel (benzene-hexane 3:1, v.v.), the crude product was recrystallized from the hexane-benzene mixture (1:1, v.v.) to give a white solid. Yield: 405 mg (26%). Anal. Calc. for $C_{29}H_{21}N_2P$ (428.46): C, 81.3; H, 4.9; N, 6.5%. Found: C, 81.6; H, 4.8; N, 6.8%. ^{31}P{^{1}H} NMR (202.46 MHz, CDCl$_3$, ppm): –2.91. ^{1}H NMR (500.13 MHz, CDCl$_3$, ppm), δ: 8.11–8.07 (m, 2H, H-4 in Cbz), 7.81 (td, J = 7.6 Hz, J = 2.3 Hz, 1H, H-9 in Py), 7.65–7.61 (m, 2H, H-1 in Cbz), 7.61–7.55 (m, 1H, H-8 in Py, and 4H, H-13 in Ph), 7.48–7.41 (m, 4H, H-14, and 2H, H-15 in Ph), 7.32–7.27 (m, 2H, H-2 and 2H, H-3 in Cbz), 7.25 (ddd, *J* = 0.8 Hz, *J* = 2.0 Hz, *J* = 7.6 Hz, 1H, H-10). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, ppm), *δ*: 164.39 (s, C-7), 152.18 (d, *J* = 10.8 Hz, C-11), 139.38 (s, C-6), 137.8 (d, *J* = 4.5 Hz, C-9), 135.9 (d, *J* = 10.0 Hz, C-12), 134.61 (d, *J* = 20.0 Hz, C-13), 129.24 (s, C-15), 128.70 (d, *J* = 7.4 Hz, C-14 in Ph), 126.07 (s, C-2), 125.17 (d, *J* = 22.1 Hz, C-10), 124.46 (s, C-5), 120.94 (s, C-3), 119.96 (s, C-4),116.88 (s, C-8), 111.74 (s, C-1).

Compound 2



A solution of **1** (50 mg, 0.1167 mmol) and MeI (20 mg, 0.1400 mmol) in benzene (2 mL) was stirred at ambient temperature for 15 h. The formed precipitate was centrifuged, washed with benzene (2 mL) and dried under reduced pressure. Yield: 56 mg (84%). Anal. Calc. for $C_{30}H_{24}IN_2P$ (570.40): C, 63.2; H, 4.2; N, 4.9%. Found: C, 63.6; H, 4.1; N, 4.7%. ^1H NMR (500.13 MHz, DMSO-d^6, ppm), *δ*: 8.49–8.44 (m, 1H), 8.27 (dd, *J* = 2.6 Hz, *J* = 8.3 Hz, 1H), 8.22 (m, 2H), 8.13 (m, 1H), 7.97–7.90 (m, 6H), 7.82-7.76 (m, 4H), 7.54–7.51 (m, 2H), 7.36–7.28 (m, 4H), 3.25 (d, $J_{H\text{-}C\text{-}P}$ = 14.7 Hz, Me). $^{31}P\{^1H\}$ NMR (202.46 MHz, DMSO-d^6, ppm): 20.75 (s).

Compound 3

To a stirring solution of **1** (28 mg, 0.0653 mmol) in CH_2Cl_2 (2 mL), Pd(COD)Cl_2 (9 mg, 0.0327 mmol) was added. The mixture was stirred for 5 h. The formed precipitate was collected by centrifugation, washed with Et_2O (3×2 mL) and then dried in vacuum. Yield: 31 mg (92%). Pale-yellow powder. X-ray quality single crystals were obtained by Et_2O vapors diffusion into DMF solution. Anal. Calc. for $C_{58}H_{42}Cl_2N_4P_2Pd$ (1034.25): C, 67.3; H, 4.1; N, 5.4%. Found: C, 66.9; H, 4.3; N, 5.1%. FT-IR (KBr, cm^{-1}): 426 (w), 476 (w), 513 (m), 534 (w), 561 (vw), 600 (vw), 640 (vw), 652 (w), 692 (m), 725 (m), 748 (m), 754 (m), 800 (w), 974 (vw), 991 (vw), 1028 (vw), 1096 (w), 1103 (w), 1152 (vw), 1190 (w), 1223 (m), 1308 (w), 1335 (m), 1360 (w), 1439 (vs), 1447 (vs), 1479 (w), 1489 (w), 1558 (w), 1574 (m).

Compound 4

A mixture of CuI (8 mg, 0.0389 mmol) and **1** (25 mg, 0.0583 mmol) in MeCN (2 mL) was stirred at ambient temperature for 5 h. The formed precipitate was centrifuged, washed with Et_2O (3 mL) and dried under reduced pressure. Yield: 29 mg (89%). White powder. X-ray quality single crystals were obtained by slow evaporation of the MeCN solution. Anal. Calc. for $C_{87}H_{63}Cu_2I_2N_6P_3$ (1666.29): C, 62.7; H, 3.8; N, 5.0%. Found: C, 63.0; H, 3.7; N, 5.5%. FT-IR (KBr, cm^{-1}): 420 (m), 465 (w), 473 (m), 494 (m), 509 (m), 523 (m), 561 (w), 600 (w) 615 (w), 638 (w) 700 (m), 723 (s), 750 (vs), 799 (m), 854 (vw), 912 (w), 935 (vw), 972 (w), 997 (w), 1030 (w), 1096 (w), 1152 (m), 1190 (m), 1221 (m), 1306 (m), 1333 (m), 1356 (w), 1437 (vs), 1449 (vs), 1479 (m), 1489 (m), 1558 (m), 1570 (m), 1597 (w), 3026 (vw), 3051 (vw).

§3. NMR Spectra

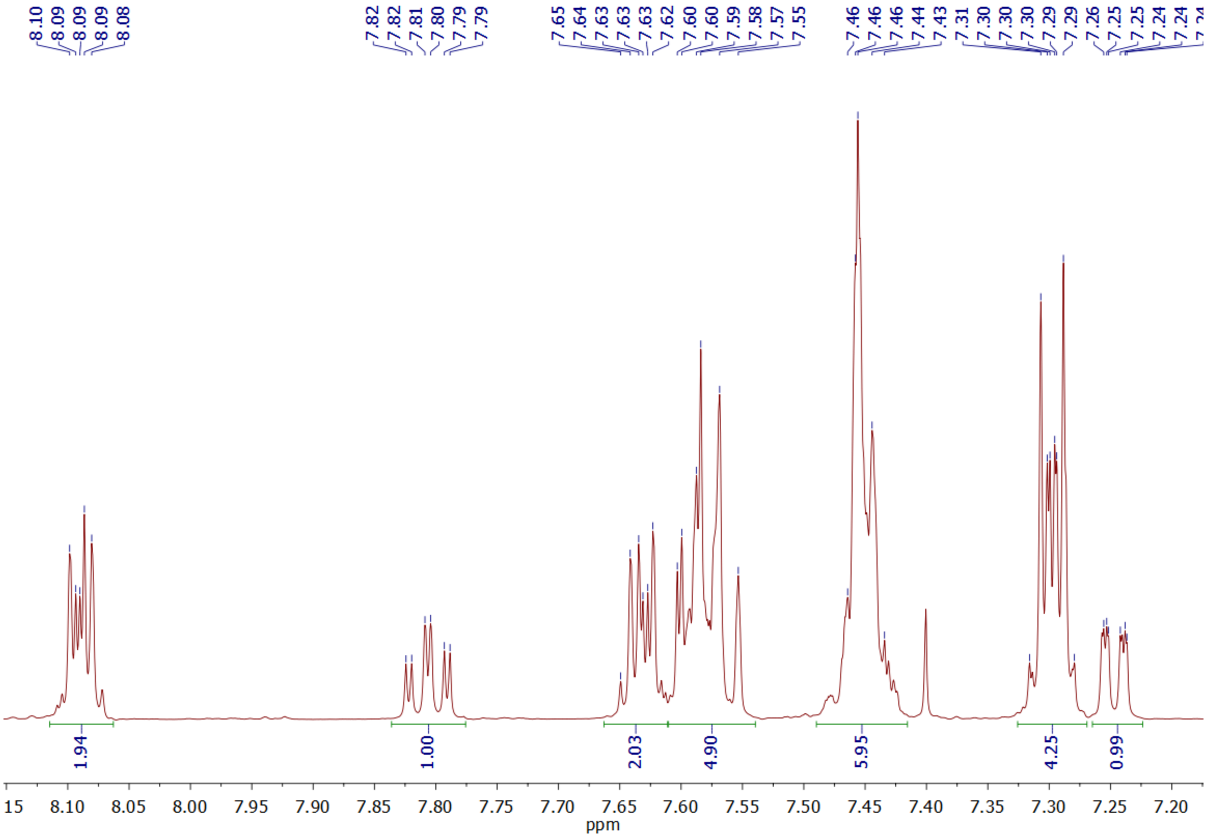


Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

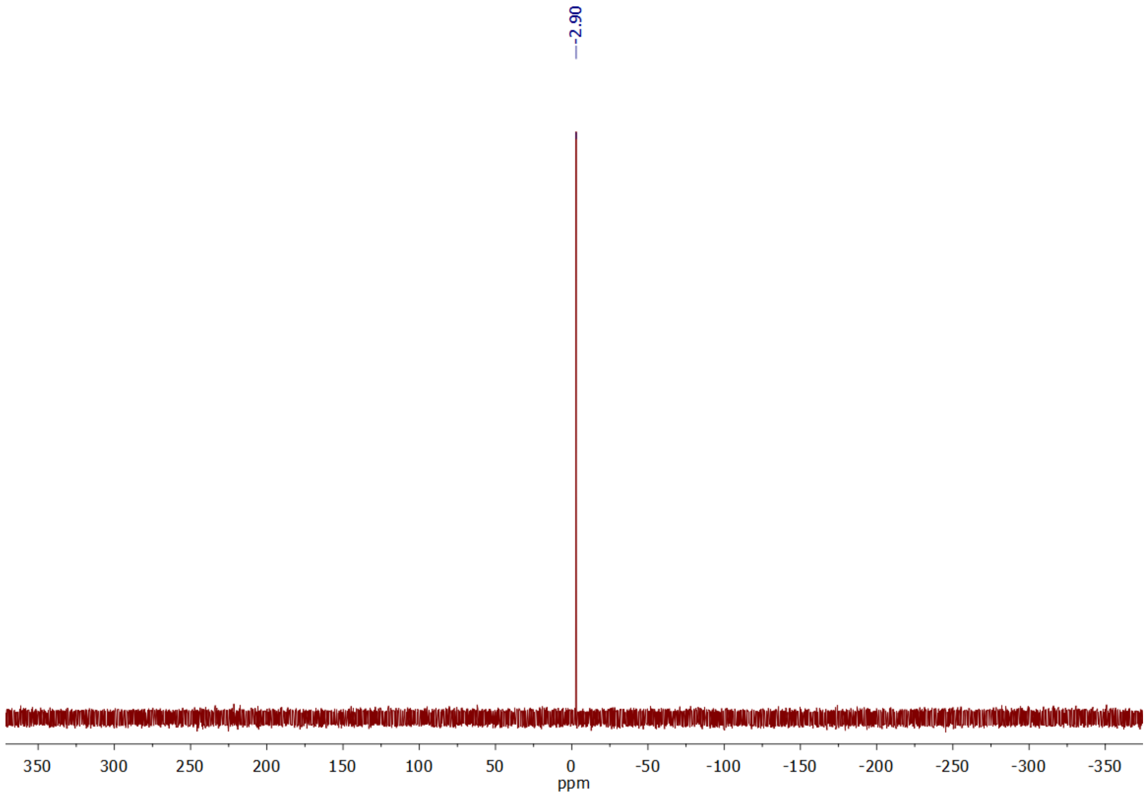


Figure S2. $^{31}P\{^1H\}$ NMR spectrum of **1** in $CDCl_3$.

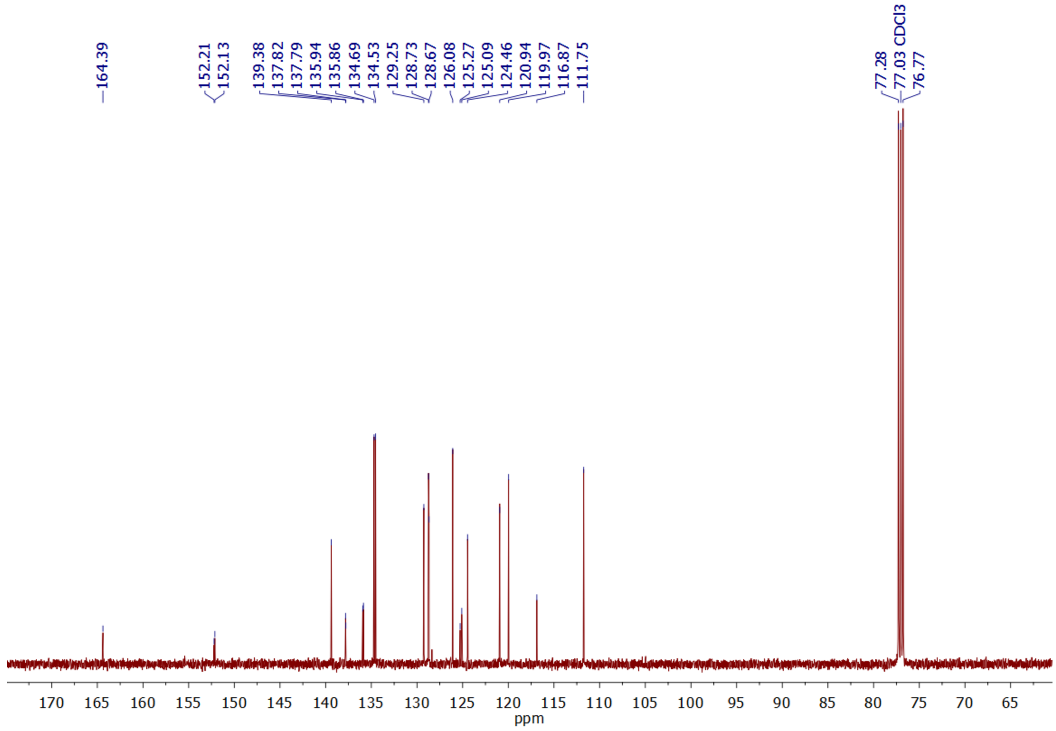


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$.

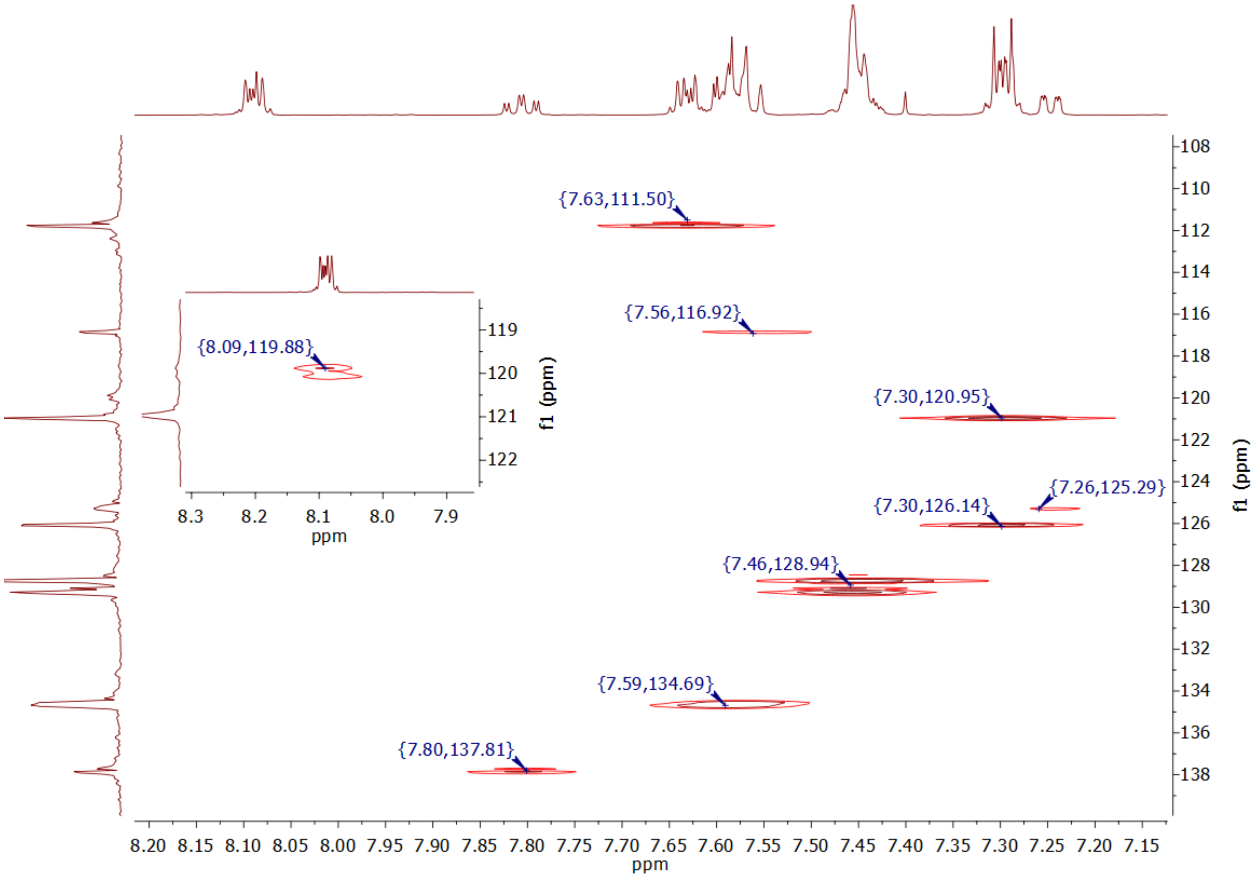


Figure S4. ^{1}H-^{13}C HSQC spectrum of **1** in $CDCl_3$.

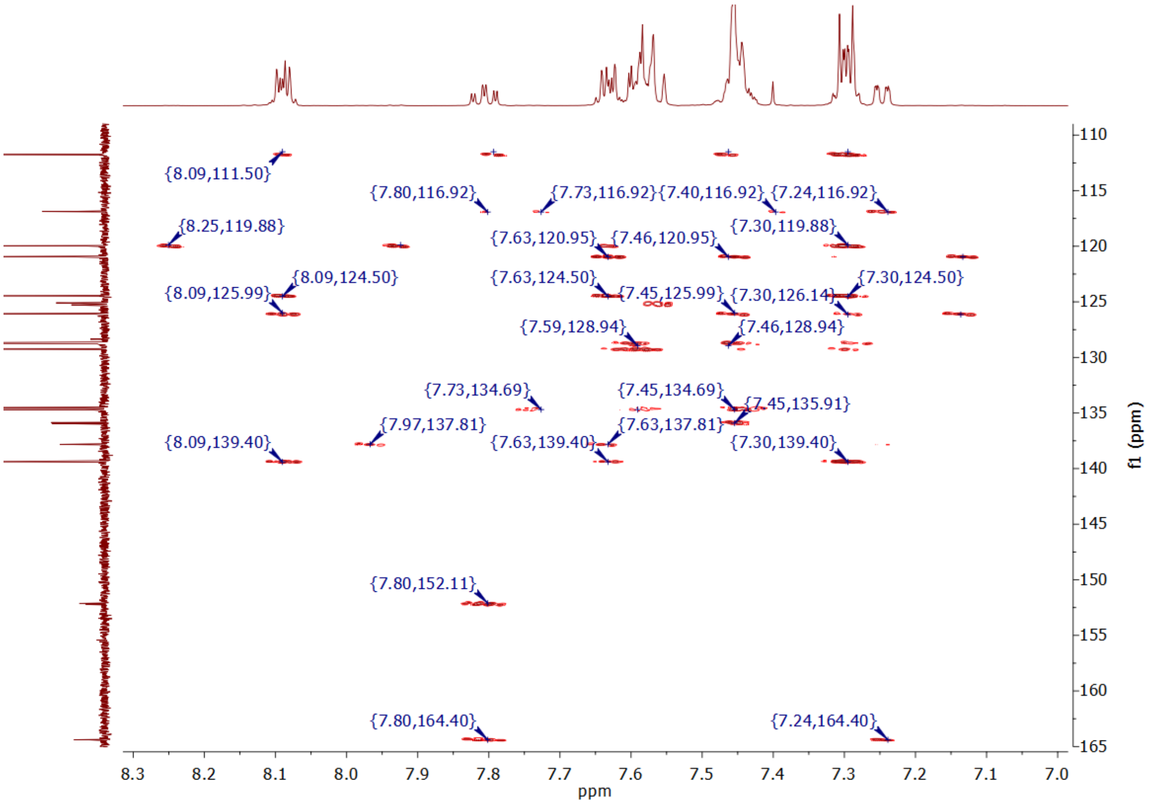


Figure S5. ^{1}H-^{13}C HMBC spectrum of **1** in CDCl$_3$.

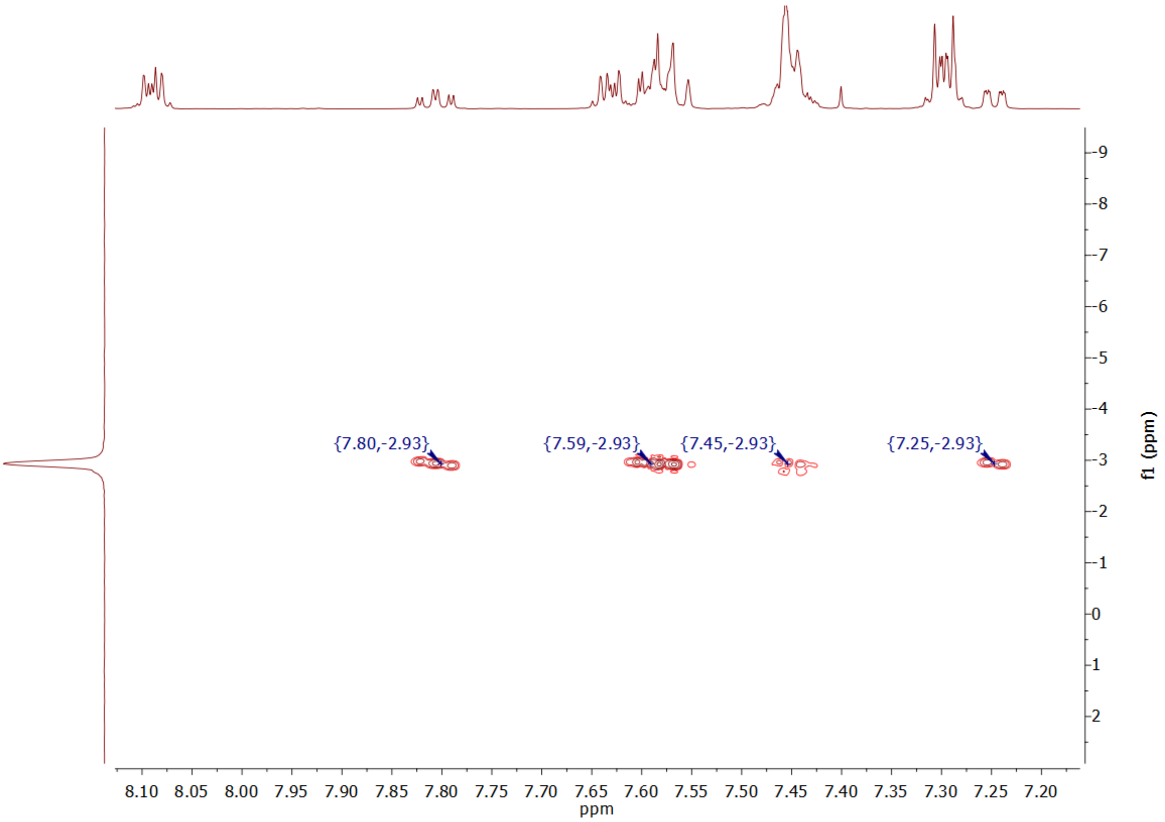


Figure S6. ^{1}H-^{31}P HMBC spectrum of **1** in CDCl$_3$.

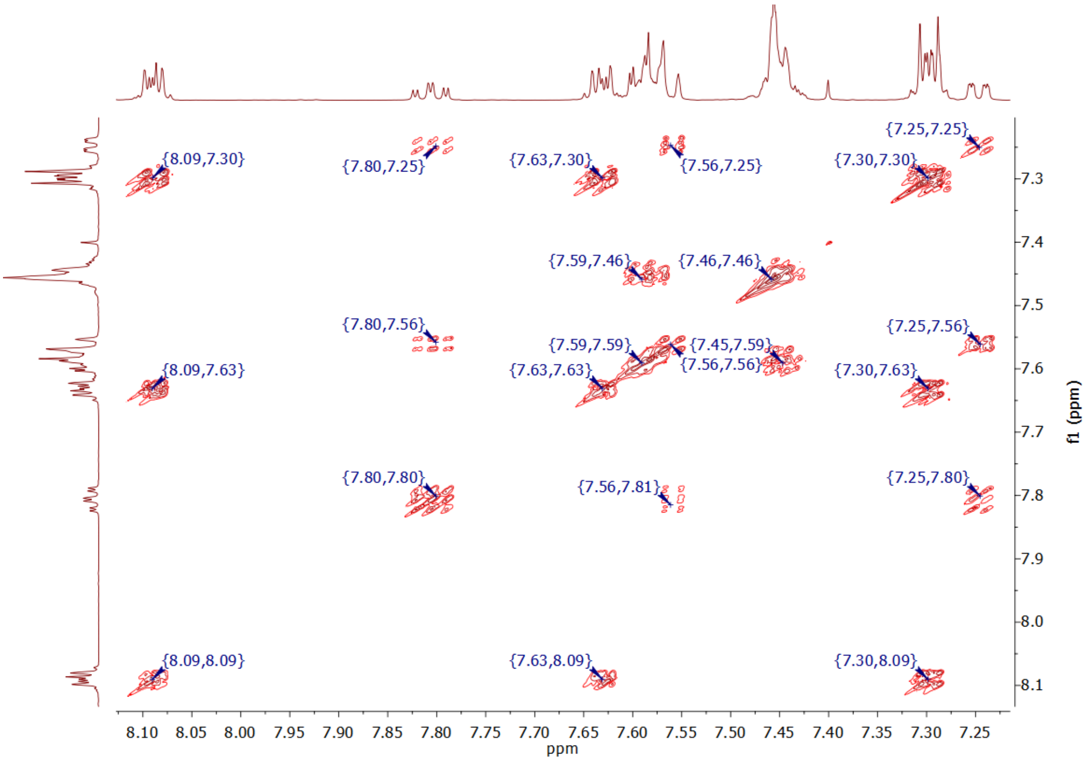


Figure S7. ^{1}H-^{1}H COSY spectrum of **1** in CDCl$_3$.

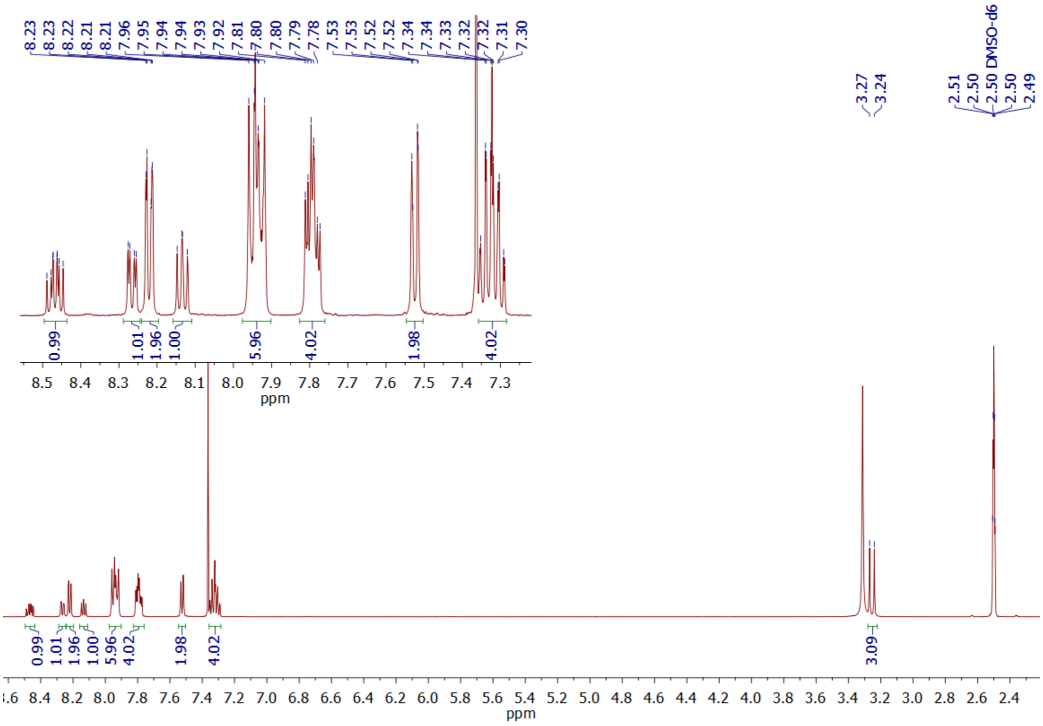


Figure S8. ^{1}H NMR spectrum of **2** in DMSO-d$_6$.

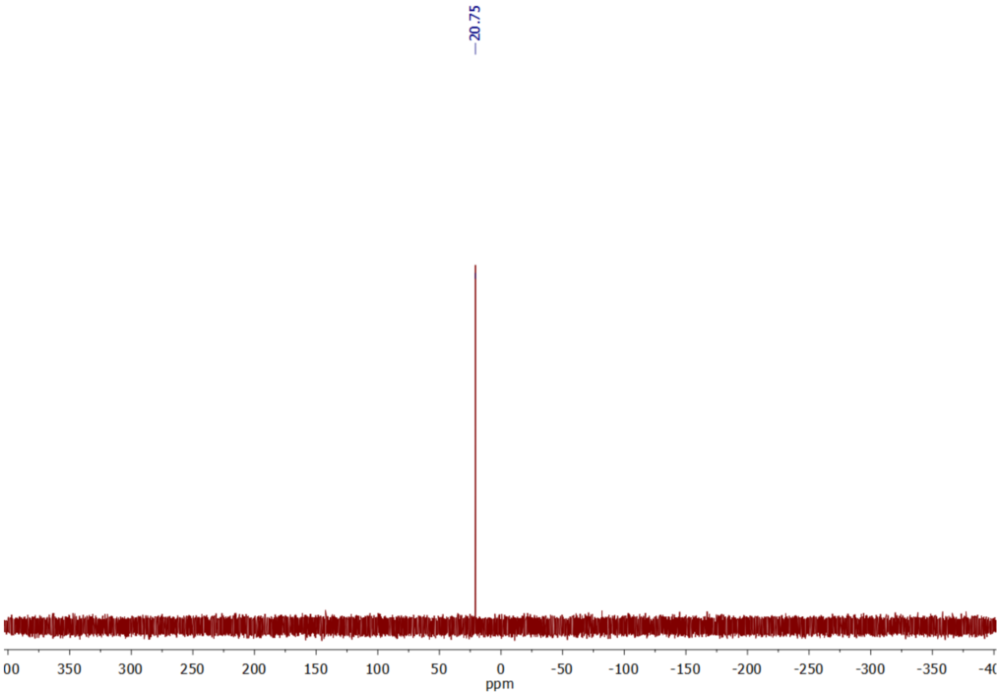


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in DMSO-d$_6$.

§4. FT-IR spectra

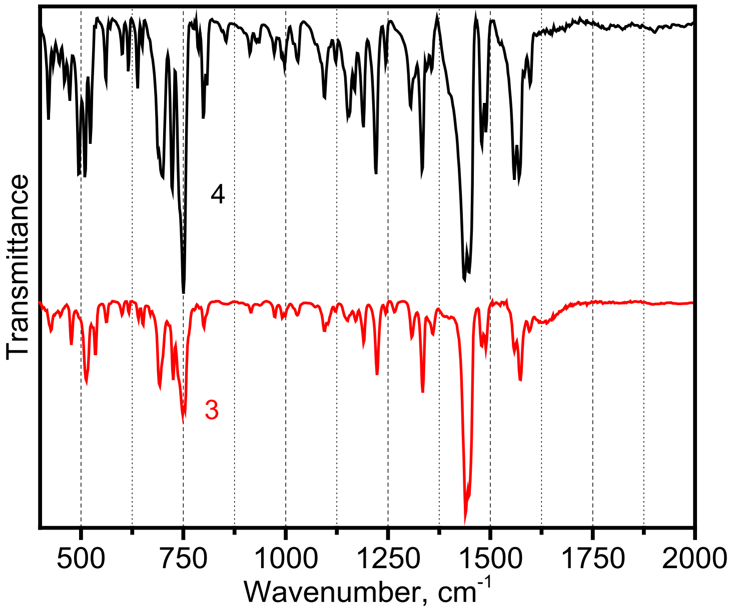


Figure S10. FT-IR spectra for the complexes **3** and **4** in the 400–2000 cm^{-1} region.

§5. References

[S1] S.-G. Ihn, N. Lee, S. O. Jeon, M. Sim, H. Kang, Y. Jung, D. H. Huh, Y. M. Son, S. Y. Lee, M. Numata, H. Miyazaki, R. Gómez-Bombarelli, J. Aguilera-Iparraguirre, T. Hirzel, A. Aspuru-Guzik, S. Kim and S. Lee, *Adv. Sci.*, 2017, **4**, 1600502; https://doi.org/10.1002/advs.201600502.