Preparation of tricationic tris(pyridylpalladium(II)) metallacyclophane as an anion receptor

Supporting Information

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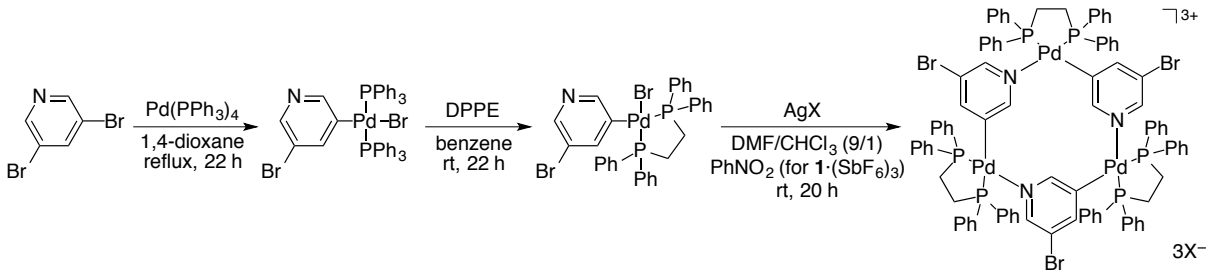
Table of Contents

General. All manipulations were carried out under nitrogen atmosphere. NMR spectra were recorded on a Agilent UNITY INOVA 500 (500 MHz for ^{1}H, 126 MHz for ^{13}C, and 202 MHz for ^{31}P) or a Agilent Mercury 300 (300 MHz for ^{1}H). Chemical shifts were reported in δ ppm referenced to an internal tetramethylsilane standard or residual DMSO-d_5 (δ 2.49 ppm) for ^{1}H NMR. $CDCl_3$ (δ 77.0 ppm) or DMSO-d_6 (δ 39.5 ppm) was used as internal reference for ^{13}C NMR. An external 85% H_3PO_4 standard was used for ^{31}P NMR. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 25 °C unless otherwise noted. IR spectra were recorded on a JASCO FT/IR-4200. Nominal (LRMS) and exact mass (HRMS) spectra were recorded on a JEOL JMS-T100LP.

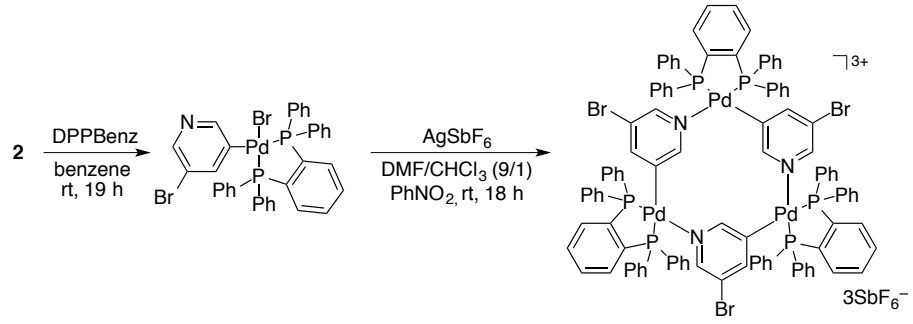
Materials. All reagents were obtained from commercial sources and used without further purification.



2: 90% yield

3: quant.

1·X_3, X = NO_3: 96% yield
X = BF_4: 96% yield
X = TsO: 99% yield
X = SbF_6: 65% yield



7: 98% yield

4·$(SbF_6)_3$: 92% yield

Preparation of 2

An oven-dried 200 mL 2-necked flask equipped with a condenser was charged with 3,5-dibromobenzene (711 mg, 3.00 mmol), $Pd(PPh_3)_4$ (3.47 g, 3.00 mmol), and 1,4-dioxane (90 mL) at nitrogen atmosphere, and the mixture was refluxed for 22 h. After allowed to room temperature, the mixture was evaporated, and the residue was washed with ethyl acetate for four times. The resulting precipitate was dried under reduced pressure to give **2** as a white solid (2.34 g, 90% yield); mp. > 258 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.93 (d, J = 2 Hz, 1H), 7.60–7.54 (m, 12H), 7.53 (d, J = 2 Hz, 1H), 7.40–7.35 (m, 6H), 7.34–7.28 (m, 12H), 6.65–6.62 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) 159.0 (t, J(C,P) = 5 Hz), 151.4 (t, J(C,P) = 4 Hz), 145.1 (t, J(C,P) = 4 Hz), 143.3, 134.5 (t, J(C,P) = 6 Hz), 130.39 (t, J(C,P) = 23 Hz), 130.35, 128.1 (t, J(C,P) = 5 Hz), 120.7; ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ (ppm) 23.9; IR (ATR) 3055, 3008, 1519, 1478, 1432, 1095, 999, 864, 741, 690, 521, 508 cm^{-1}; MS (ESI+) m/z 869 ([M+H]$^+$, 100), 825 ([M–Br+Cl+H]$^+$, 90), 630 ([M–PPh_3+Na+H]$^+$, 72), 789 ([M–Br]$^+$, 60), 1693 ([2M–Br+Cl+H]$^+$, 10), 1649 ([2M–2Br+2Cl+H]$^+$, 6), 1737 ([2M+H]$^+$, 4); HRMS (ESI+): m/z Calcd. for $C_{41}H_{34}Br_2NP_2Pd$ [M+H]$^+$: 865.95681. Found: 865.95976.

Preparation of 3: a Typical Procedure

An oven-dried 500 mL 2-necked flask was charged with **2** (2.33 g, 2.68 mmol), 1,2-bis(diphenylphosphino)ethane (1.05 g, 2.64 mmol), and benzene (230 mL) at nitrogen

atmosphere, and the suspension was stirred at room temperature for 22 h. The reaction mixture was then evaporated and the residue was dropped into vigorously stirred *n*-hexane (ca. 600 mL). The precipitate was filtered and dried under reduced pressure to give **3** as a white solid (1.95 g, quantitative yield); mp. > 255 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.25 (dd, J = 1 Hz, 3 Hz, 1H), 7.94 (dd, J = 1 Hz, 2 Hz, 1H), 7.93–7.87 (m, 4H), 7.54–7.46 (m, 8H), 7.45–7.37 (m, 8H), 7.20 and 7.19 (dd, J = 2 Hz, 3 Hz, 1H), 2.58–2.45 (m, 2H), 2.30–2.17 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) 157.0 (d, J(C,P) = 135 Hz), 156.4, 153.7, 145.8 (d, J(C,P) = 3 Hz), 144.6, 133.4 (d, J(C,P) = 12 Hz), 133.0 (d, J(C,P) = 11 Hz), 132.0 (d, J(C,P) = 4 Hz), 131.2 (d, J(C,P) = 2 Hz), 130.2 (d, J(C,P) = 37 Hz), 129.2 (d, J(C,P) = 9 Hz), 129.1 (d, J(C,P) = 8 Hz), 127.9 (d, J(C,P) = 53 Hz), 120.9 (d, J(C,P) = 10 Hz), 29.9 (dd, J(C,P) = 21 Hz, 33 Hz), 23.9 (dd, J(C,P) = 12 Hz, 27 Hz); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ (ppm) 55.4 (J(P,P) = 24 Hz), 37.3 (J(P,P) = 24 Hz); IR (ATR) 3046, 3020, 2944, 2909, 1520, 1480, 1434, 1308, 1184, 1102, 1009, 868, 818, 747, 693, 532, 520 cm^{-1}; MS (ESI+) *m/z* 743 ([M+H]$^+$, 100), 1404 ([2M–Br]$^+$, 77), 1326 ([2M–BrPy]$^+$, 52), 694 ([M–Br+CH_3OH]$^+$, 37), 698 ([M–Br+Cl+H]$^+$, 28), 1282 ([2M–BrPy–Br+Cl]$^+$, 24), 924 ([M–Br+PPh_3]$^+$, 24), 1359 ([2M–2Br+Cl]$^+$, 13), 1090 ([M–Br+DPPE+CH_3OH]$^+$, 13); HRMS (ESI+): *m/z* Calcd. for $C_{31}H_{28}Br_2NP_2Pd$ [M+H]$^+$: 739.90986. Found: 739.91377.

7: 98% yield as a colorless crystal; mp. > 242 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.16 (dd, J = 2 Hz, 4 Hz, 1H), 8.01 (dd, J = 1 Hz, 3 Hz, 1H), 7.72–7.64 (m, 6H), 7.63–7.54 (m, 2H), 7.53–7.42 (m, 8H), 7.38–7.29 (m, 8H), 7.25 and 7.23 (dd, J = 2 Hz, 4 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) 157.4 (d, J(C,P) = 136 Hz), 156.9, 153.7 (d, J(C,P) = 4 Hz), 146.0 (d, J(C,P) = 7 Hz), 144.8, 143.6 (dd, J(C,P) = 46 Hz, 52 Hz), 140.7 (dd, J(C,P) = 35 Hz, 42 Hz), 134.3 (d, J(C,P) = 16 Hz), 133.8 (d, J(C,P) = 12 Hz), 133.5 (d, J(C,P) = 17 Hz), 133.2 (d, J(C,P) = 11 Hz), 132.6–132.2 (m), 131.7 (d, J(C,P) = 2 Hz), 131.1, 130.4 (d, J(C,P) = 41 Hz), 129.0 (d, J(C,P) = 11 Hz), 128.9 (d, J(C,P) = 10 Hz), 128.5 (d, J(C,P) = 55 Hz), 120.8 (d, J(C,P) = 10 Hz); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ (ppm) 55.2 (J(P,P) = 24 Hz), 45.6 (J(P,P) = 24 Hz); IR (ATR) 3047, 3025, 2972, 1523, 1480, 1433, 1303, 1181, 1159, 1098, 1007, 867, 747, 690, 666, 546, 525 cm^{-1}; MS (ESI+) *m/z* 1499 ([2M–Br]$^+$, 100), 1185 ([M–Br+DPPBenz+CH_3OH]$^+$, 57), 1326 ([2M–BrPy]$^+$, 52), 742 ([M–Br+CH_3OH]$^+$, 41), 710 ([M–Br]$^+$, 18); HRMS (ESI+): *m/z* Calcd. for $C_{70}H_{54}Br_3N_2P_4Pd_2$ [2M–Br]$^+$: 1494.88572. Found: 1494.89538.

Preparation of 1·$(NO_3)_3$: a Typical Procedure

An oven-dried 100 mL 2-necked flask was charged with **3** (381 mg, 0.514 mmol), DMF (25 mL), and chloroform (13 mL) at nitrogen atmosphere, and the mixture was stirred at room temperature for 10 min. To the solution was added silver nitrate (87.4 mg, 0.514 mmol) at rt, and the suspension was stirred at intact temperature for 20 h. The mixture was then

concentrated to ca. 20 mL and filtered through Celite pad. The filtrate was concentrated under reduced pressure to give **1**·$(NO_3)_3$ as a white solid, which was further purified by crystallization from its DMF/chloroform (1:1) solution by vapor diffusion with diethyl ether (357 mg, 96% yield as a colorless crystal); mp. > 225 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 9.96 (s, 3H), 8.25 (dd, J = 8 Hz, 13 Hz, 6H), 7.94 (dd, J = 7 Hz, 12 Hz, 6H), 7.68 (dt, J = 3 Hz, 8 Hz, 6H), 7.47 (t, J = 7 Hz, 3H), 7.37–7.19 (m, 21H), 7.09 (dt, J = 3 Hz, 9 Hz, 6H), 7.05 (t, J = 2 Hz, 3H), 6.95 (t, J = 13 Hz, 6H), 6.93 (t, J = 13 Hz, 6H), 6.80 (d, J = 7 Hz, 3H), 3.53–3.38 (m, 3H), 3.23–3.07 (m, 3H), 2.62–2.42 (m, 3H), 2.00–1.82 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ (ppm) 161.5 (dd, J(C,P) = 4 Hz, 121 Hz), 153.1 (d, J(C,P) = 5 Hz), 148.6 (d, J(C,P) = 5 Hz), 145.9, 135.3 (d, J(C,P) = 12 Hz), 134.8 (d, J(C,P) = 13 Hz), 132.6, 132.1, 132.0 (d, J(C,P) = 10 Hz), 131.25 (d, J(C,P) = 10 Hz), 131.21, 130.8, 130.2 (d, J(C,P) = 11 Hz), 129.8 (d, J(C,P) = 11 Hz), 129.2 (d, J(C,P) = 10 Hz), 129.1 (d, J(C,P) = 41 Hz), 128.8 (d, J(C,P) = 11 Hz), 127.8 (d, J(C,P) = 46 Hz), 127.7 (d, J(C,P) = 56 Hz), 127.4 (d, J(C,P) = 61 Hz), 120.5 (d, J(C,P) = 9 Hz), 31.5 (dd, J(C,P) = 17 Hz, 35 Hz), 25.5 (dd, J(C,P) = 9 Hz, 29 Hz); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ (ppm) 56.6 (J(P,P) = 18 Hz), 46.3 (J(P,P) = 19 Hz); IR (ATR) 3050, 2954, 2922, 1655, 1520, 1435, 1332, 1107, 997, 876, 819, 748, 707, 692, 532 cm^{-1}; MS (ESI+) m/z 1024 ([M+NO_3]$^{2+}$, 100), 734 ([BrPy(dppe)+THF]$^+$, 18), 1386 ([M–BrPyPd(dppe)+NO_3]$^+$, 16), 662 ([BrPyPd(dppe)]$^+$, 13), 2110 ([M+2NO_3]$^+$, 3); HRMS (ESI+): m/z Calcd. for $C_{93}H_{81}Br_3N_4O_3P_6Pd_3$ [M+NO_3]$^{2+}$: 2041.93890. Found: 2041.93943.

1·$(BF_4)_3$: 96% yield as a colorless crystal; mp. > 237 °C (decomp.); ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 9.51 (s, 3H), 8.29 (dd, J = 8 Hz, 13 Hz, 6H), 7.90 (dd, J = 7 Hz, 12 Hz, 6H), 7.71 (dt, J = 2 Hz, 8 Hz, 6H), 7.62 (dt, J = 2 Hz, 8 Hz, 3H), 7.53 (t, J = 8 Hz, 3H), 7.49 (t, J = 8 Hz, 3H), 7.32–7.23 (m, 15H), 7.21 (t, J = 2 Hz, 3H), 7.11 (d, J = 7 Hz, 3H), 7.06 (dt, J = 2 Hz, 8 Hz, 6H), 6.91–6.82 (m, 12H), 3.45–3.12 (m, 6H), 2.80–2.60 (m, 3H), 1.83–1.66 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ (ppm) 162.6 (dd, J(C,P) = 3 Hz, 120 Hz), 152.3, 148.3, 145.2, 135.4 (d, J(C,P) = 13 Hz), 134.6 (d, J(C,P) = 14 Hz), 132.5, 131.75 (d, J(C,P) = 9 Hz), 131.72, 131.4 (d, J(C,P) = 11 Hz), 131.0, 130.5, 129.9 (d, J(C,P) = 9 Hz), 129.7 (d, J(C,P) = 41 Hz), 129.4 (d, J(C,P) = 10 Hz), 128.9 (d, J(C,P) = 40 Hz), 128.50 (d, J(C,P) = 56 Hz), 128.48 (d, J(C,P) = 10 Hz), 128.0 (d, J(C,P) = 11 Hz), 127.3 (d, J(C,P) = 54 Hz), 119.4 (d, J(C,P) = 9 Hz), 30.2 (dd, J(C,P) = 17 Hz, 35 Hz), 24.0 (dd, J(C,P) = 8 Hz, 30 Hz); ^{31}P{^{1}H} NMR (202 MHz, DMSO-d_6) δ (ppm) 57.5 (J(P,P) = 20 Hz), 45.7 (J(P,P) = 18 Hz); IR (ATR) 3054, 2970, 2930, 1739, 1520, 1435, 1050, 877, 818, 744, 690, 533, 520 cm^{-1}; MS (ESI+) m/z 1036 ([M+BF_4]$^{2+}$, 100), 1404 ([M–BrPyPd(dppe)+Br]$^+$, 42), 694 ([BrPy(dppe)+CH_3OH]$^+$, 29), 662 ([BrPyPd(dppe)]$^+$, 18), 1410 ([M–BrPyPd(dppe)+BF_4]$^+$, 8), 2159 ([M+2BF_4]$^+$, 6); HRMS (ESI+): m/z Calcd. for $C_{93}H_{81}Br_3F_4N_3P_6Pd_3$ [M+BF_4]$^{2+}$: 2066.95400. Found: 2066.94348.

1·$(OTs)_3$: 99% yield as a colorless crystal; mp. 230–233 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ

(ppm) 10.17 (s, 3H), 8.35 (ddd, *J* = 2 Hz, 8 Hz, 13 Hz, 6H), 8.07 (dd, *J* = 7 Hz, 12 Hz, 6H), 7.98 (br s, 6H), 7.37–7.02 (m, 42H), 6.98 (dt, *J* = 8 Hz, 11 Hz, 6H), 6.84 (t, *J* = 2 Hz, 3H), 6.60 (d, *J* = 7 Hz, 3H), 3.53–3.38 (m, 3H), 3.31–3.11 (m, 3H), 2.63–2.40 (m, 3H), 2.37 (br s, 9H), 2.01–1.87 (m, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ (ppm) 162.0 (dd, *J*(C,P) = 2 Hz, 109 Hz), 154.0 (d, *J*(C,P) = 5 Hz), 148.0 (d, *J*(C,P) = 3 Hz), 145.2, 145.0, 138.7, 135.6 (d, *J*(C,P) = 13 Hz), 135.2 (d, *J*(C,P) = 14 Hz), 132.15, 132.07 (d, *J*(C,P) = 9 Hz), 131.7, 131.4 (d, *J*(C,P) = 9 Hz), 131.1, 130.7, 129.7 (d, *J*(C,P) = 12 Hz), 129.5 (d, *J*(C,P) = 42 Hz), 129.32 (d, *J*(C,P) = 8 Hz), 129.25 (d, *J*(C,P) = 9 Hz), 128.7 (d, *J*(C,P) = 11 Hz), 128.5, 128.4 (d, *J*(C,P) = 41 Hz), 128.2 (d, *J*(C,P) = 55 Hz), 127.8 (d, *J*(C,P) = 55 Hz), 126.5, 120.1 (d, *J*(C,P) = 8 Hz), 31.5 (dd, *J*(C,P) = 17 Hz, 34 Hz), 25.4 (dd, *J*(C,P) = 9 Hz, 29 Hz); $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) δ (ppm) 55.5 (*J*(P,P) = 20 Hz), 45.4 (*J*(P,P) = 20 Hz); IR (ATR) 3050, 2916, 1739, 1633, 1519, 1484, 1434, 1199, 1105, 1033, 1011, 874, 815, 747, 693, 678, 563, 529 cm^{-1}; MS (ESI+) *m/z* 1078 ($[M+OTs]^{2+}$, 100), 662 ($[BrPyPd(dppe)]^{+}$, 35), 694 ($[BrPy(dppe)+CH_3OH]^{+}$, 33), 1359 ($[M–BrPyPd(dppe)+Cl]^{+}$, 29), 1495 ($[M–BrPyPd(dppe)+OTs]^{+}$, 4), 2328 ($[M+2OTs]^{+}$, 2); HRMS (ESI+): *m/z* Calcd. for $C_{100}H_{88}Br_3N_3O_3P_6Pd_3S$ $[M+OTs]^{2+}$: 2150.96267. Found: 2150.95244.

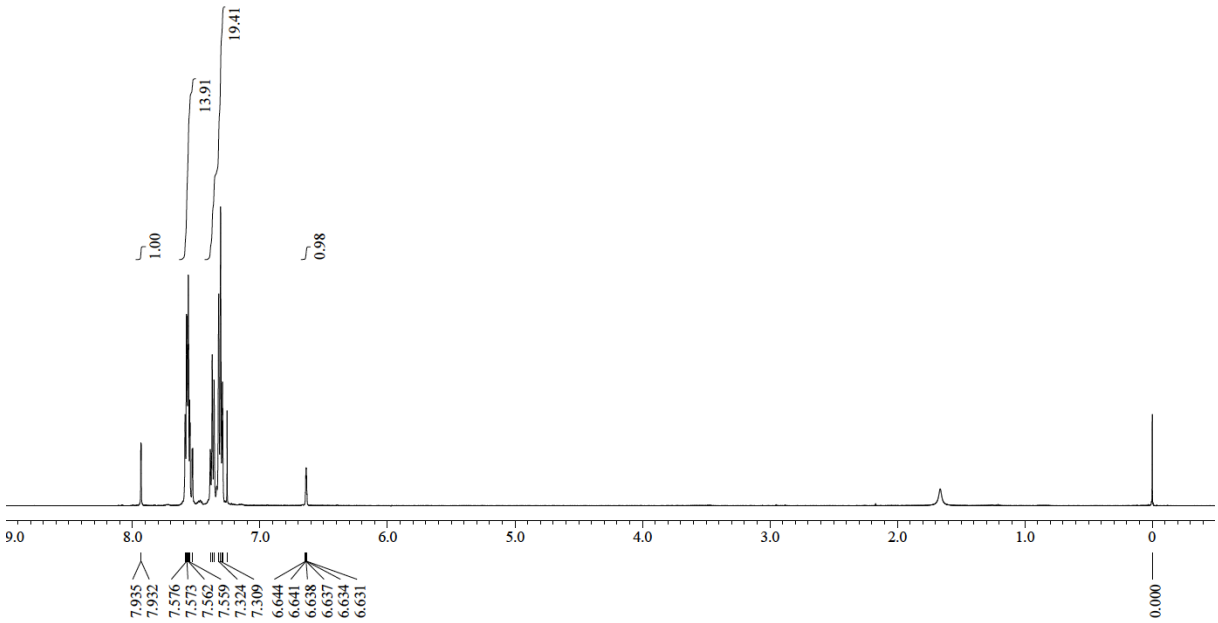
Preparation of 1·$(SbF_6)_3$: a Typical Procedure

An oven-dried 100 mL 2-necked flask was charged with **3** (1.95 g, 2.63 mmol), DMF (135 mL), and chloroform (68 mL) at nitrogen atmosphere, and the mixture was stirred at room temperature for 10 min. To the solution was added nitrobenzene (270 μL, 2.63 mmol) and silver hexafluoroantimonate (904 mg, 2.63 mmol) at rt, and the suspension was stirred at intact temperature for 20 h. The mixture was then concentrated to ca. 100 mL and filtered through Celite pad. The filtrate was concentrated under reduced pressure to give **3**·$(SbF_6)_3$ as a white solid, which was further purified by crystallization from its DMF/chloroform (1:1) solution by vapor diffusion with diethyl ether (1.54 g, 65% yield as a colorless crystal); mp. > 232 °C (decomp.); ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 9.19 (s, 3H), 7.94–7.87 (m, 6H), 7.71 (dd, *J* = 8 Hz, 12 Hz, 6H), 7.60 (s, 3H), 7.55 (t, *J* = 8 Hz, 6H), 7.50–7.40 (m, 12H), 7.38–7.24 (m, 18H), 7.09 (d, *J* = 7 Hz, 3H), 7.04 (dd, *J* = 9 Hz, 12 Hz, 6H), 6.98 (dd, *J* = 9 Hz, 11 Hz, 6H), 3.40–3.20 (m, 3H), 3.17–2.96 (m, 3H), 2.60–2.2.55 (m, 3H), 2.30–2.13 (m, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ (ppm) 161.5 (d, *J*(C,P) = 122 Hz), 152.3, 148.6, 145.7, 134.1 (d, *J*(C,P) = 12 Hz), 133.8 (d, *J*(C,P) = 12 Hz), 132.7, 132.253 (d, *J*(C,P) = 9 Hz), 132.250, 131.6, 131.5 (d, *J*(C,P) = 11 Hz), 131.0, 129.5 (d, *J*(C,P) = 12 Hz), 129.4 (d, *J*(C,P) = 40 Hz), 128.7 (d, *J*(C,P) = 10 Hz), 128.5 (d, *J*(C,P) = 11 Hz), 128.1 (d, *J*(C,P) = 40 Hz), 128.0 (d, *J*(C,P) = 54 Hz), 127.8 (d, *J*(C,P) = 55 Hz), 119.8 (d, *J*(C,P) = 9 Hz), 29.7 (dd, *J*(C,P) = 17 Hz, 36 Hz), 24.5 (dd, *J*(C,P) = 9 Hz, 31 Hz); $^{31}P\{^{1}H\}$ NMR (202 MHz, DMSO-d_6) δ (ppm) 55.7 (*J*(P,P) = 19 Hz), 46.0 (*J*(P,P) = 18 Hz); IR (ATR) 3059, 2921, 1666,

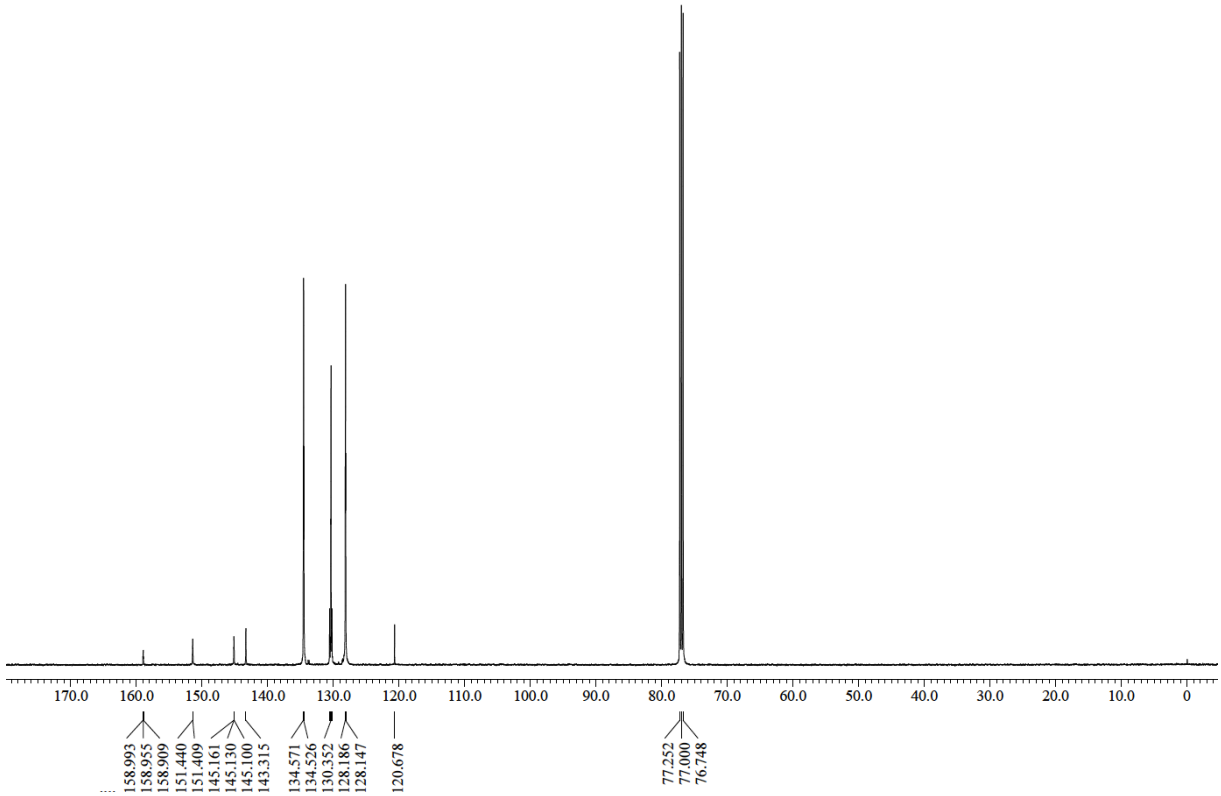
1521, 1484, 1436, 1386, 1308, 1106, 1070, 998, 870, 813, 749, 692, 654, 530 cm^{-1}; MS (ESI+) *m/z* 1049 ($[M+Br+CH_3OH]^{2+}$, 100), 662 ($[BrPyPd(dppe)]^{+}$, 79), 1010 ($[M+Cl]^{2+}$, 62), 694 ($[BrPy(dppe)+CH_3OH]^{+}$, 79), 1359 ($[M–BrPyPd(dppe)+Cl]^{+}$, 40), 1111 ($[M+SbF_6]^{2+}$, 20), 1436 ($[M–BrPyPd(dppe)+Br+CH_3OH]^{+}$, 19), 2333 ($[M+SbF_6+Br]^{+}$, 2), 2257 ($[M+SbF_6+Cl]^{+}$, 2), 2457 ($[M+2SbF_6]^{+}$, 1), 2209 ($[M+2Br+2CH_3OH]^{+}$, 1); HRMS (ESI+): *m/z* Calcd. for $C_{93}H_{81}Br_3F_{12}N_3P_6Pd_3Sb_2$ $[M+2SbF_6]^{+}$: 2449.73956. Found: 2449.74932.

4·(SbF$_6$)$_3$: 92% yield as a colorless crystal; mp. > 241 °C (decomp.); ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm) 8.93 (s, 3H), 7.92–7.74 (m, 12H), 7.73–7.65 (m, 9H), 7.63–7.56 (m, 12H), 7.54 (t, *J* = 8 Hz, 3H), 7.50 (t, *J* = 8 Hz, 3H), 7.45–7.37 (m, 12H), 7.35–7.27 (m, 12H), 7.17 (d, *J* = 8 Hz, 3H), 7.07 (dd, *J* = 9 Hz, 11 Hz, 12H); $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ (ppm) 160.9 (d, *J*(C,P) = 122 Hz), 151.7, 148.3, 145.8, 141.0 (dd, *J*(C,P) = 43 Hz, 57 Hz), 138.2 (dd, *J*(C,P) = 31 Hz, 49 Hz), 134.1 (d, *J*(C,P) = 18 Hz), 134.0–133.7 (m), 133.4 (d, *J*(C,P) = 13 Hz), 132.74 (d, *J*(C,P) = 11 Hz), 132.68, 132.4, 132.2 (d, *J*(C,P) = 11 Hz), 132.0, 131.6, 129.8 (d, *J*(C,P) = 12 Hz), 129.7 (d, *J*(C,P) = 13 Hz), 129.1 (d, *J*(C,P) = 11 Hz), 128.8 (d, *J*(C,P) = 11 Hz), 128.2 (d, *J*(C,P) = 42 Hz), 127.2 (d, *J*(C,P) = 56 Hz), 126.4 (d, *J*(C,P) = 59 Hz), 126.3 (d, *J*(C,P) = 46 Hz), 119.8 (d, *J*(C,P) = 10 Hz); $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) δ (ppm) 54.5 (*J*(P,P) = 22 Hz), 48.2 (*J*(P,P) = 22 Hz); IR (ATR) 3056, 2943, 1748, 1669, 1520, 1436, 1386, 1217, 1098, 998, 871, 748, 692, 654, 546, 527 cm^{-1}; MS (ESI+) *m/z* 742 ($[M–2BrPyPd(dppbenz)+CH_3OH]^{+}$, 100), 710 ($[M–2BrPyPd(dppbenz)]^{+}$, 79), 972 ($[M–2BrPyPd(dppbenz)+PPh_3]^{+}$, 42), 1532 ($[M–BrPyPd(dppe)+Br+CH_3OH]^{+}$, 9), 1655 ($[M–BrPyPd(dppe)+SbF_6]^{+}$, 2), 2601 ($[M+2SbF_6]^{+}$, 2), 2477 ($[M+SbF_6+Br+CH_3OH]^{+}$, 1); HRMS (ESI+): *m/z* Calcd. for $C_{105}H_{81}Br_3F_{12}N_3P_6Pd_3Sb_2$ $[M+2SbF_6]^{+}$: 2593.73956. Found: 2593.75442.

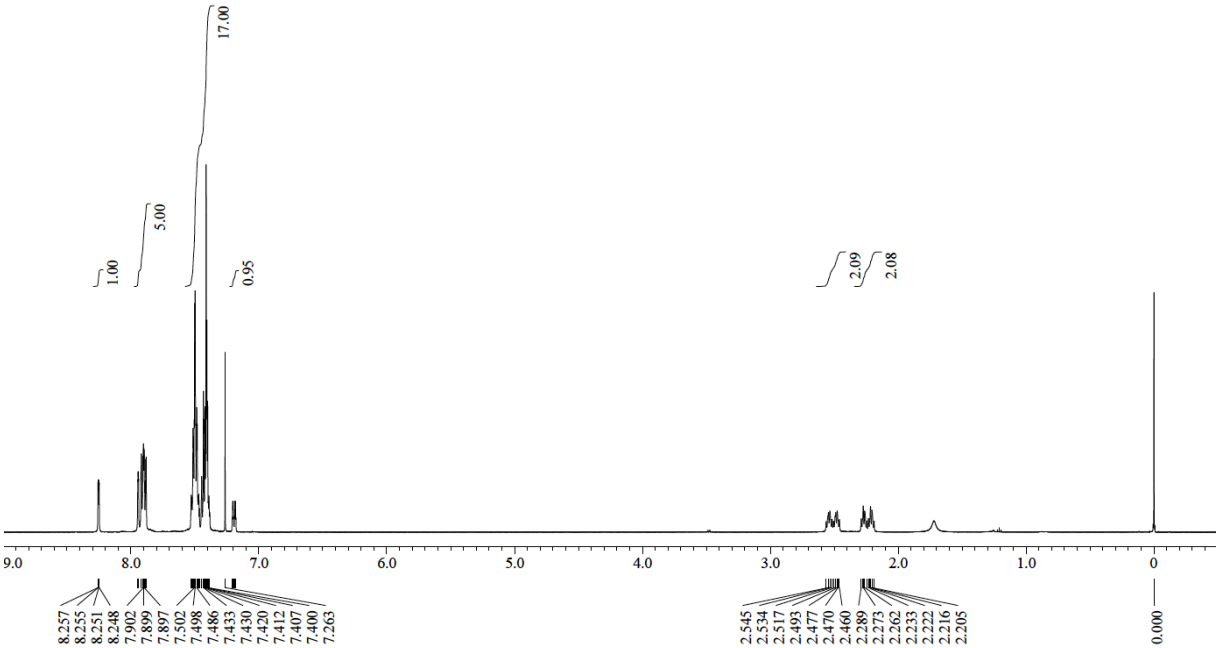
2, ^{1}H NMR (500 MHz, in $CDCl_3$, 25 °C)



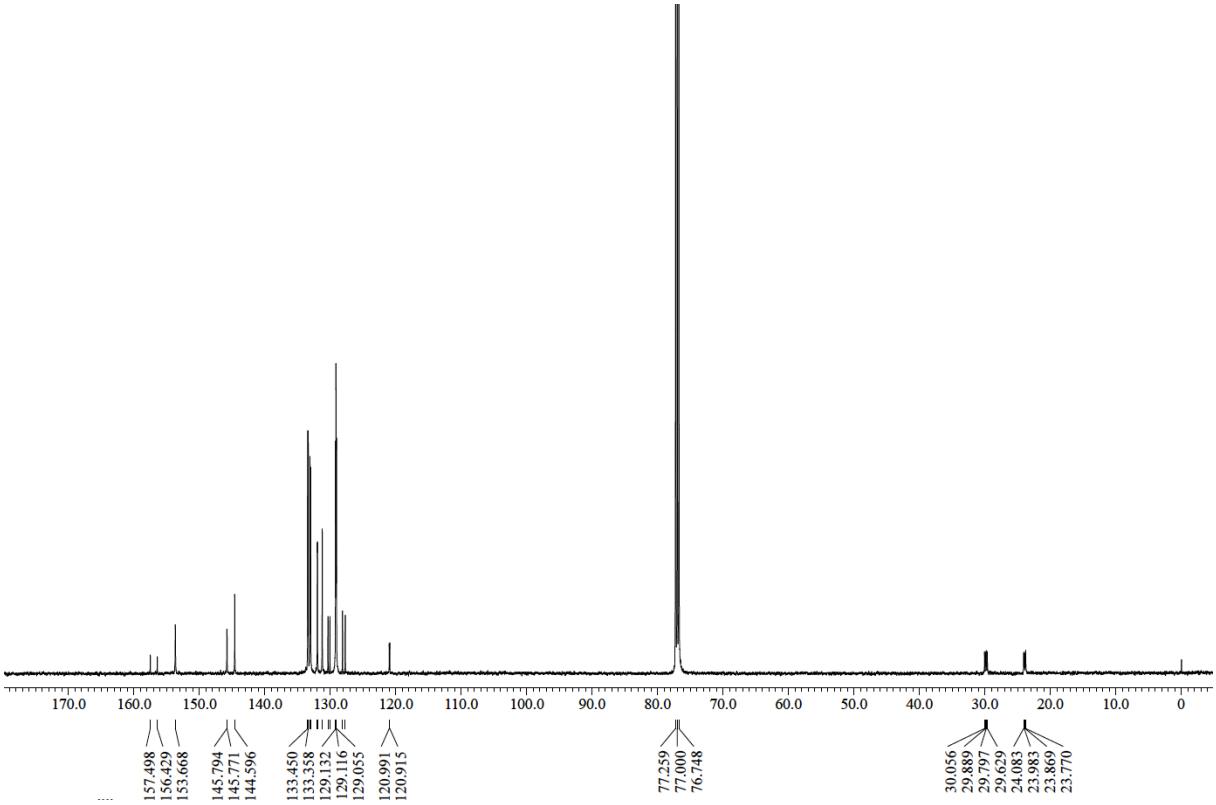
2, ^{13}C NMR (126 MHz, in $CDCl_3$, 25 °C)



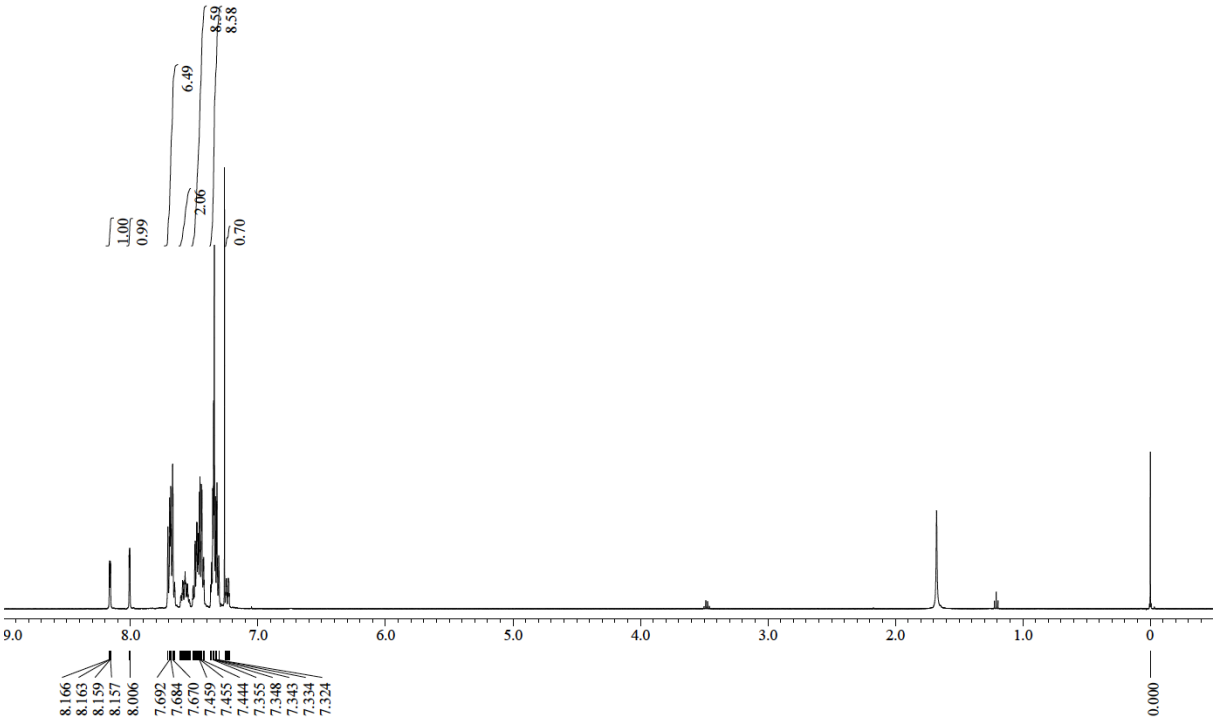
3, ^{1}H NMR (500 MHz, in $CDCl_3$, 25 °C)



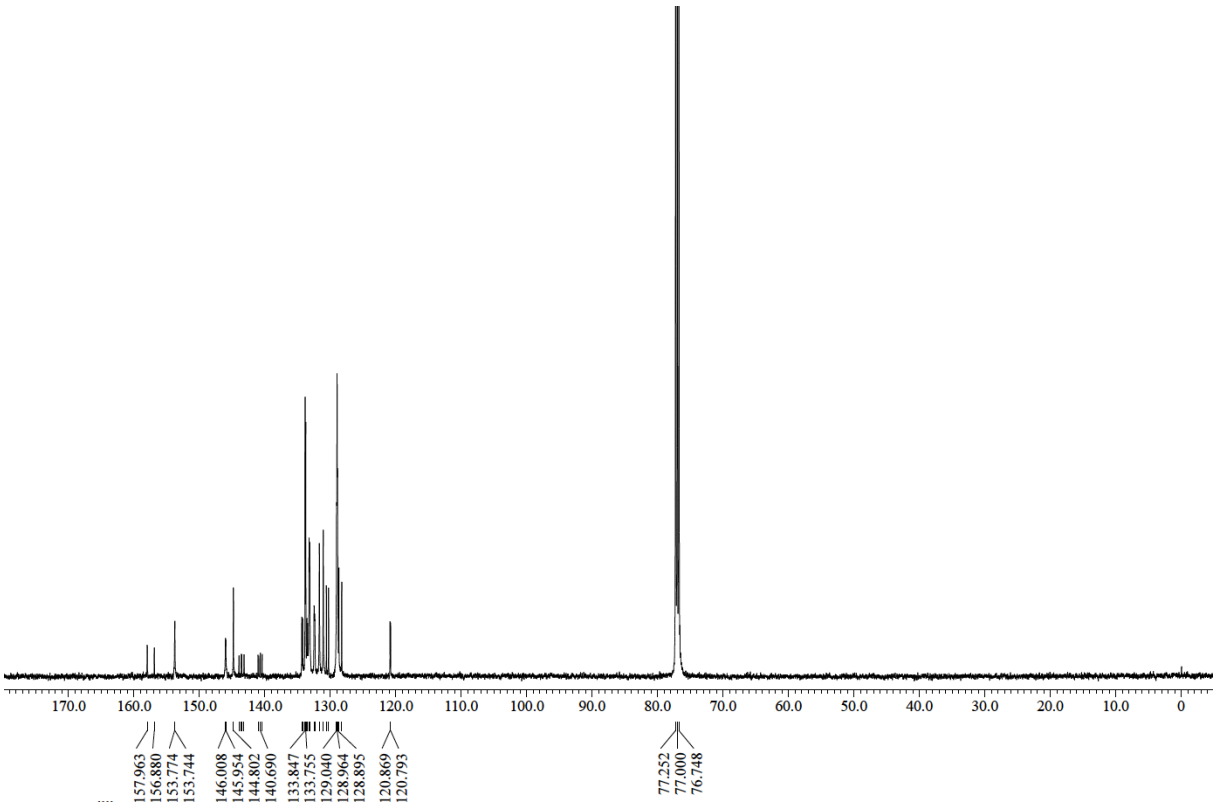
3, ^{13}C NMR (126 MHz, in $CDCl_3$, 25 °C)



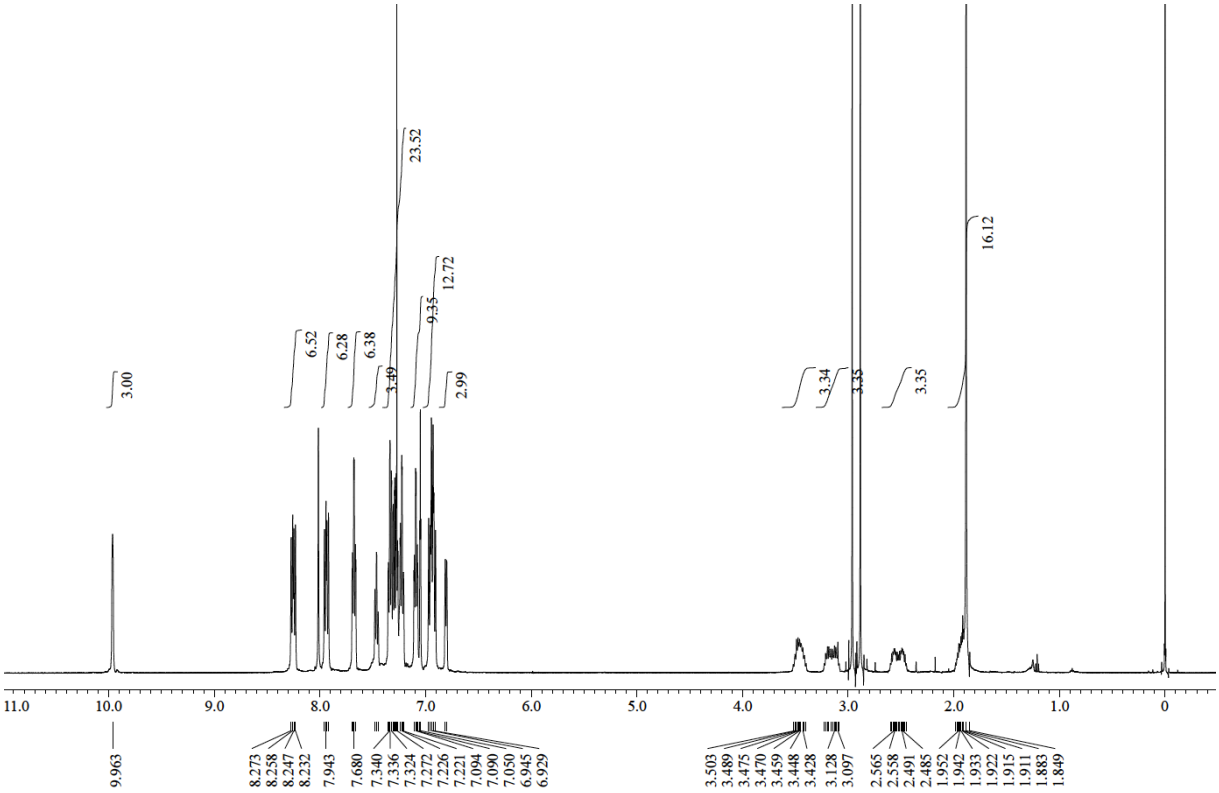
7, ^{1}H NMR (500 MHz, in $CDCl_3$, 25 °C)



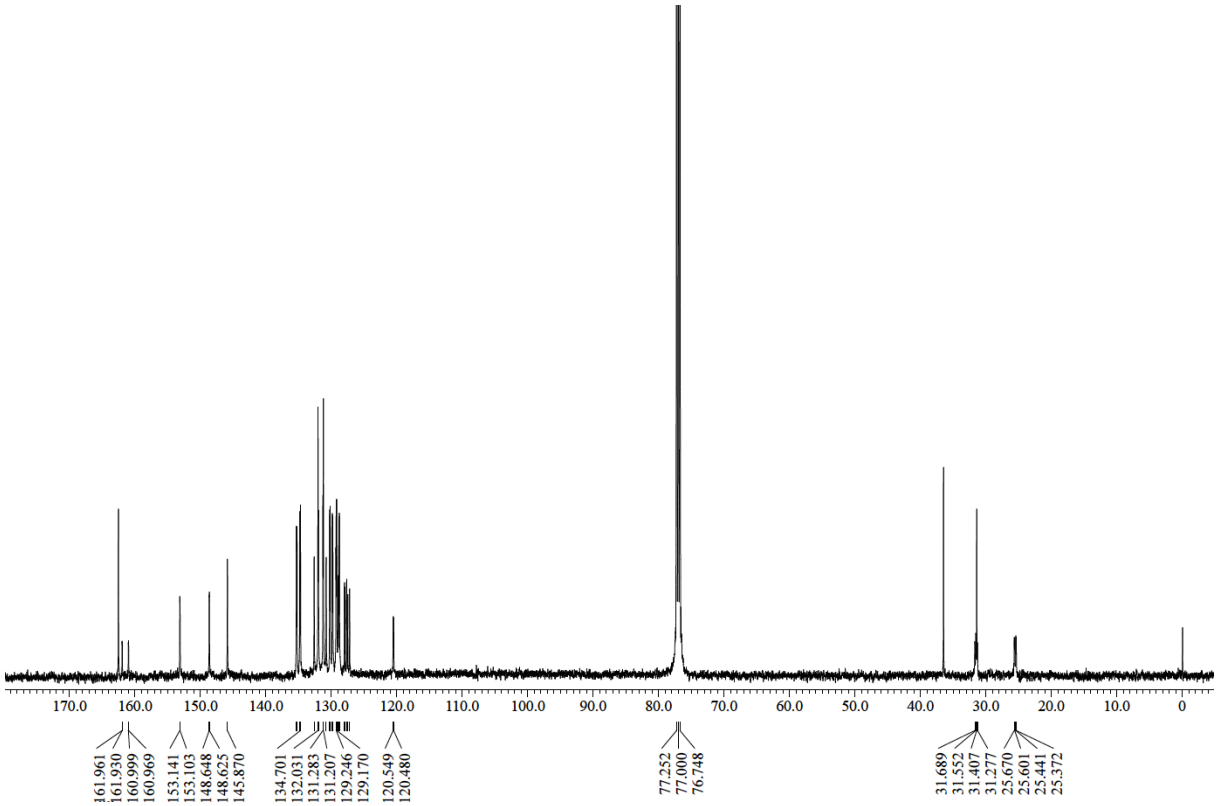
7, ^{13}C NMR (126 MHz, in $CDCl_3$, 25 °C)



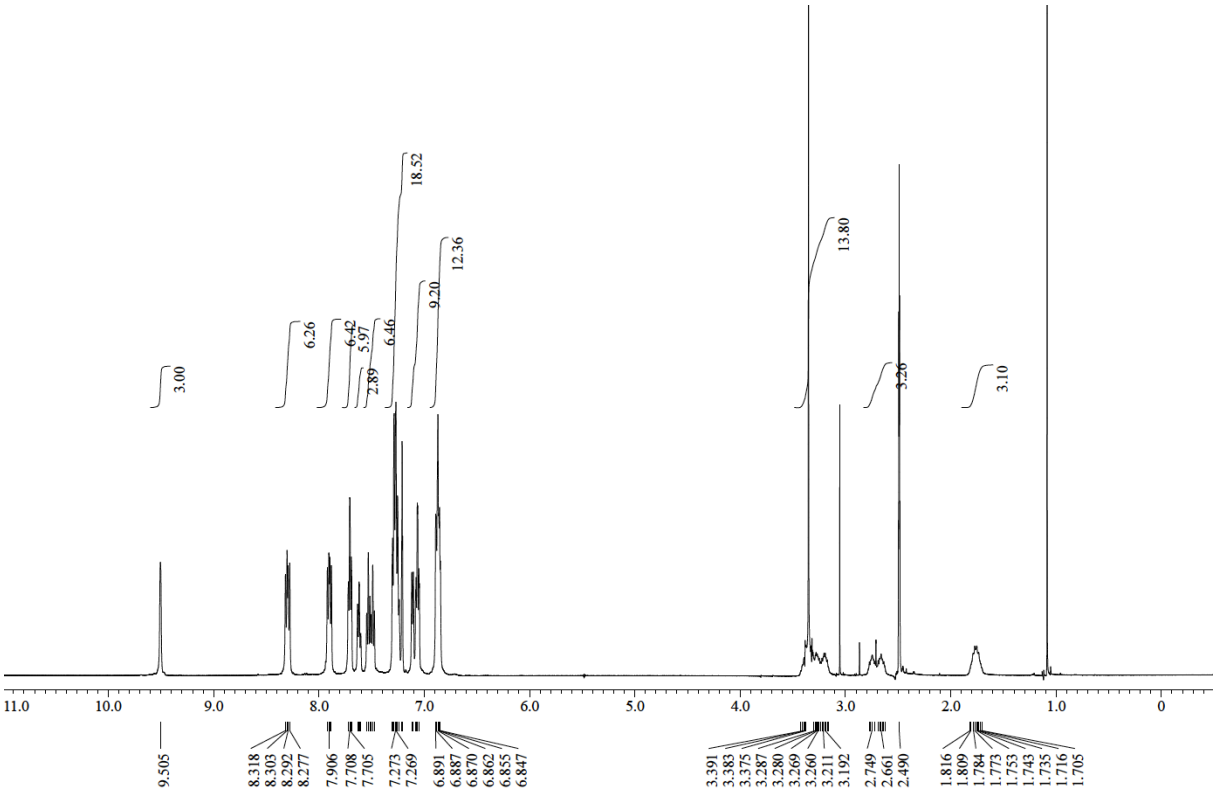
1·$(NO_3)_3$, ^{1}H NMR (500 MHz, in $CDCl_3$, 25 °C)



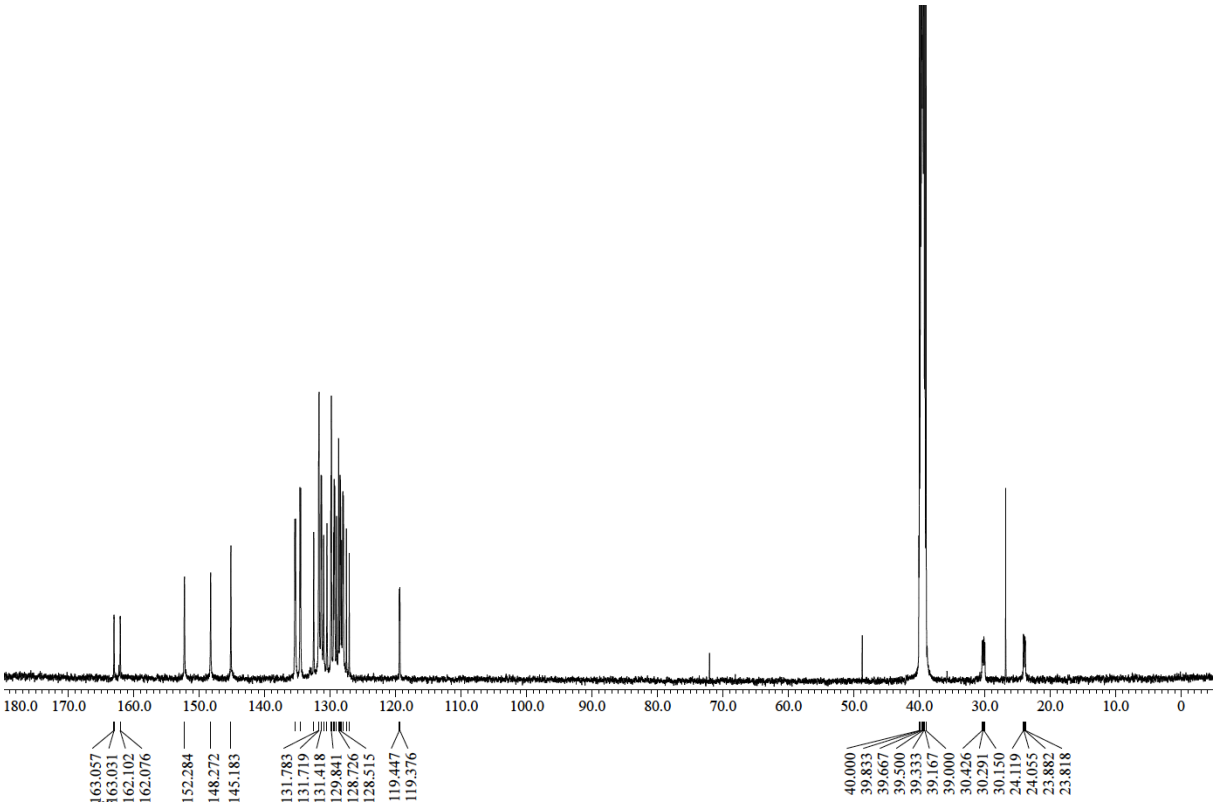
1·$(NO_3)_3$, ^{13}C NMR (126 MHz, in $CDCl_3$, 25 °C)



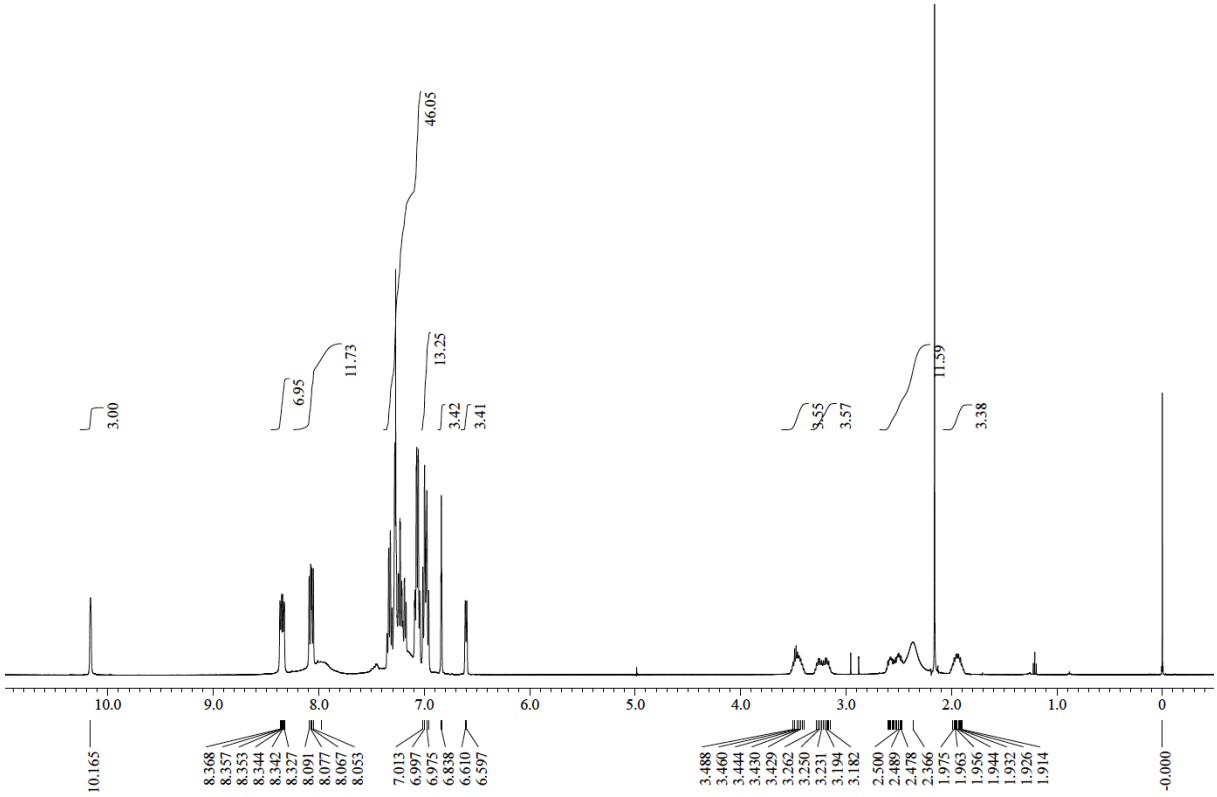
1·$(BF_4)_3$, ^{1}H NMR (500 MHz, in DMSO-d_6, 25 °C)



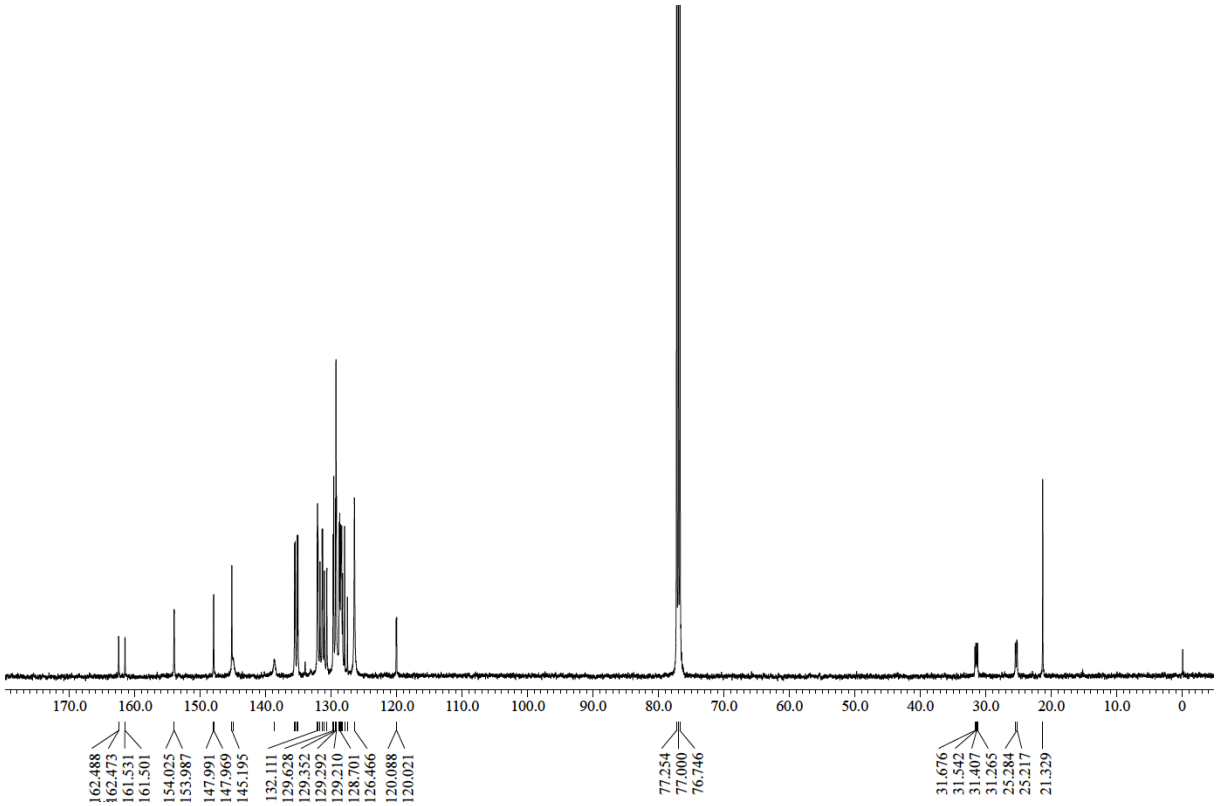
1·$(BF_4)_3$, ^{13}C NMR (126 MHz, in DMSO-d_6, 25 °C)



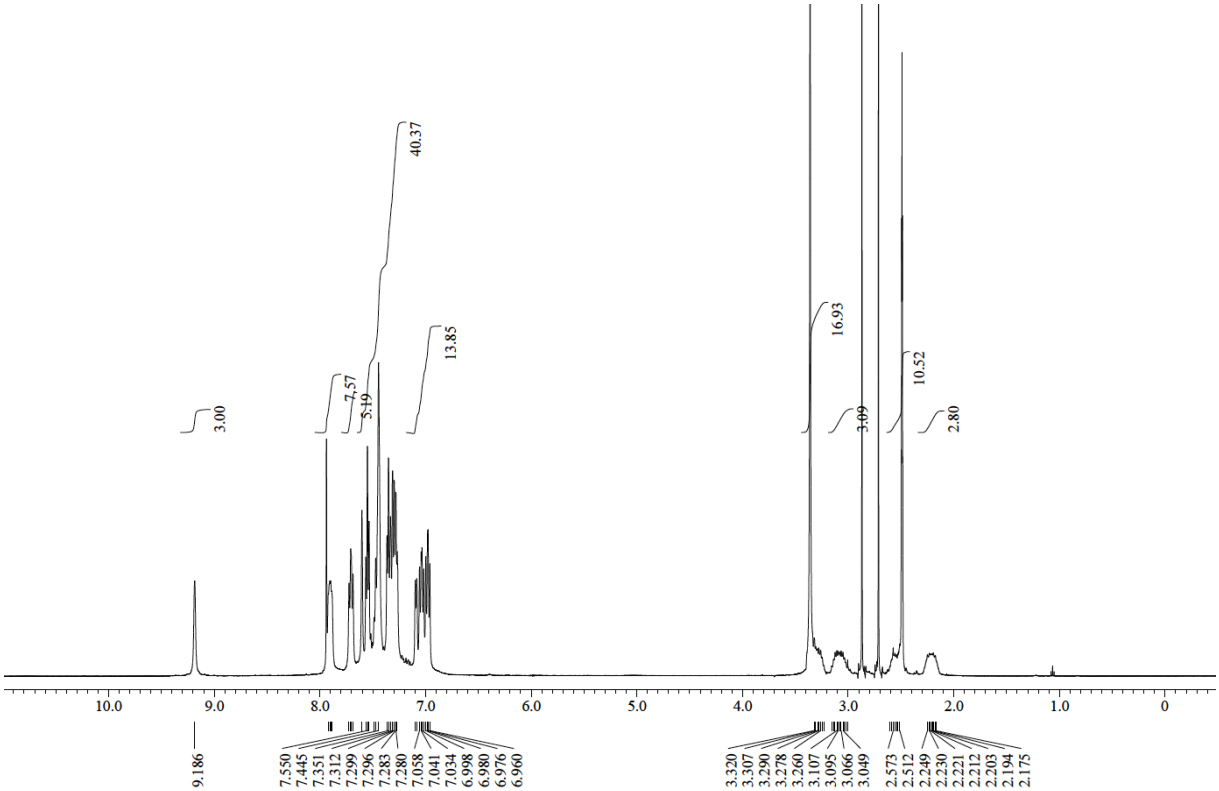
1·$(OTs)_3$, ^1H NMR (500 MHz, in $CDCl_3$, 25 °C)



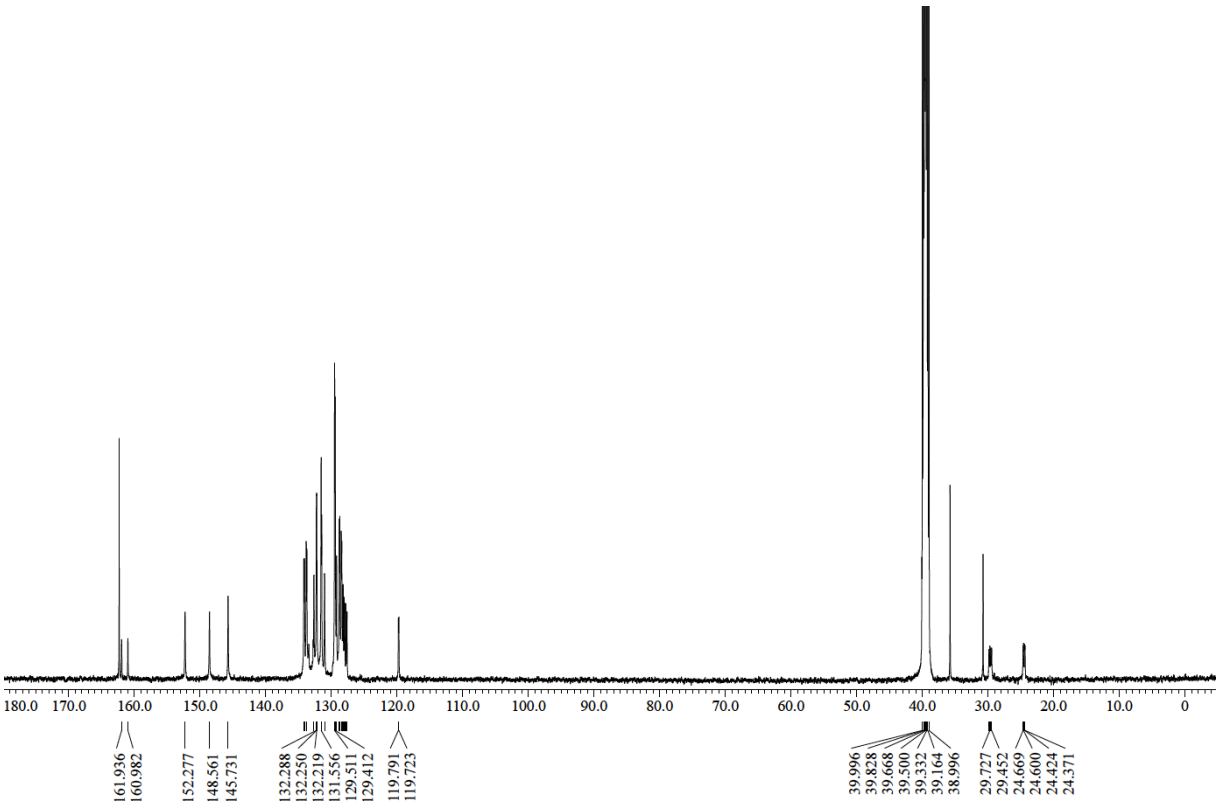
1·$(OTs)_3$, ^{13}C NMR (126 MHz, in $CDCl_3$, 25 °C)



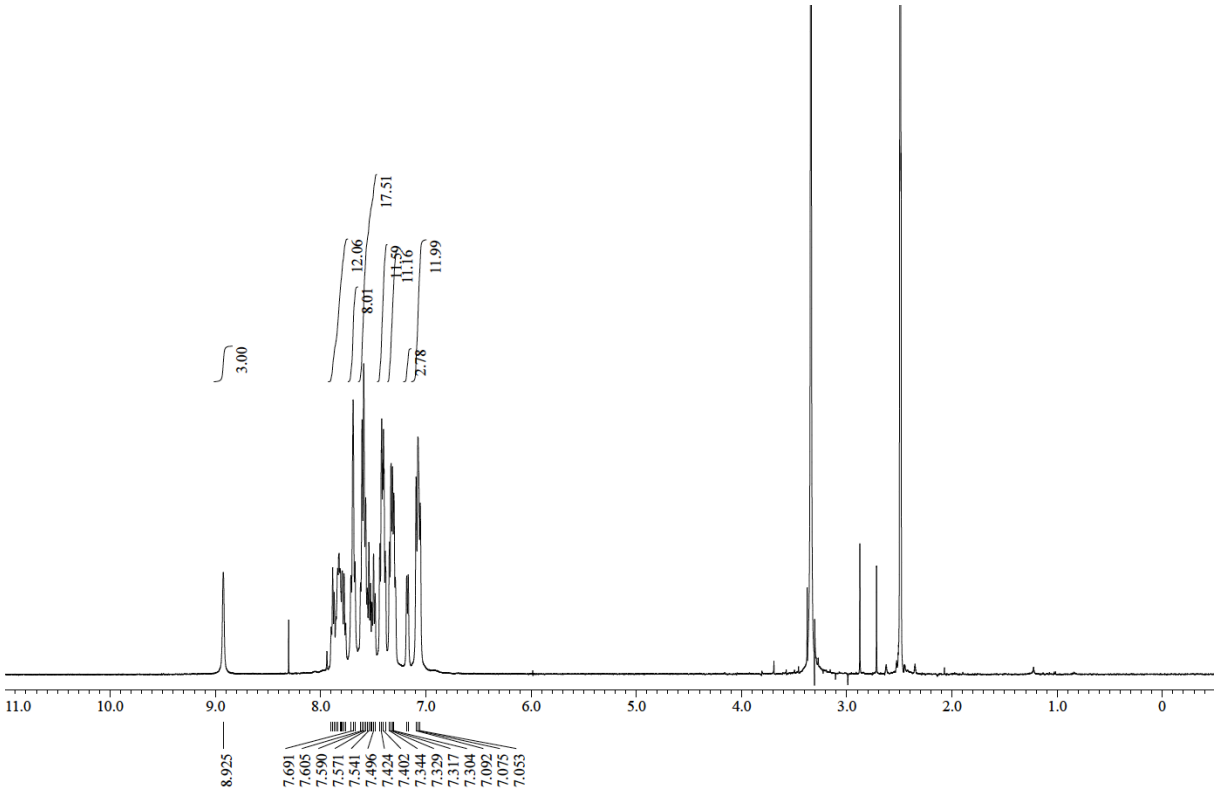
1·$(SbF_6)_3$, ^{1}H NMR (500 MHz, in DMSO-d_6, 25 °C)



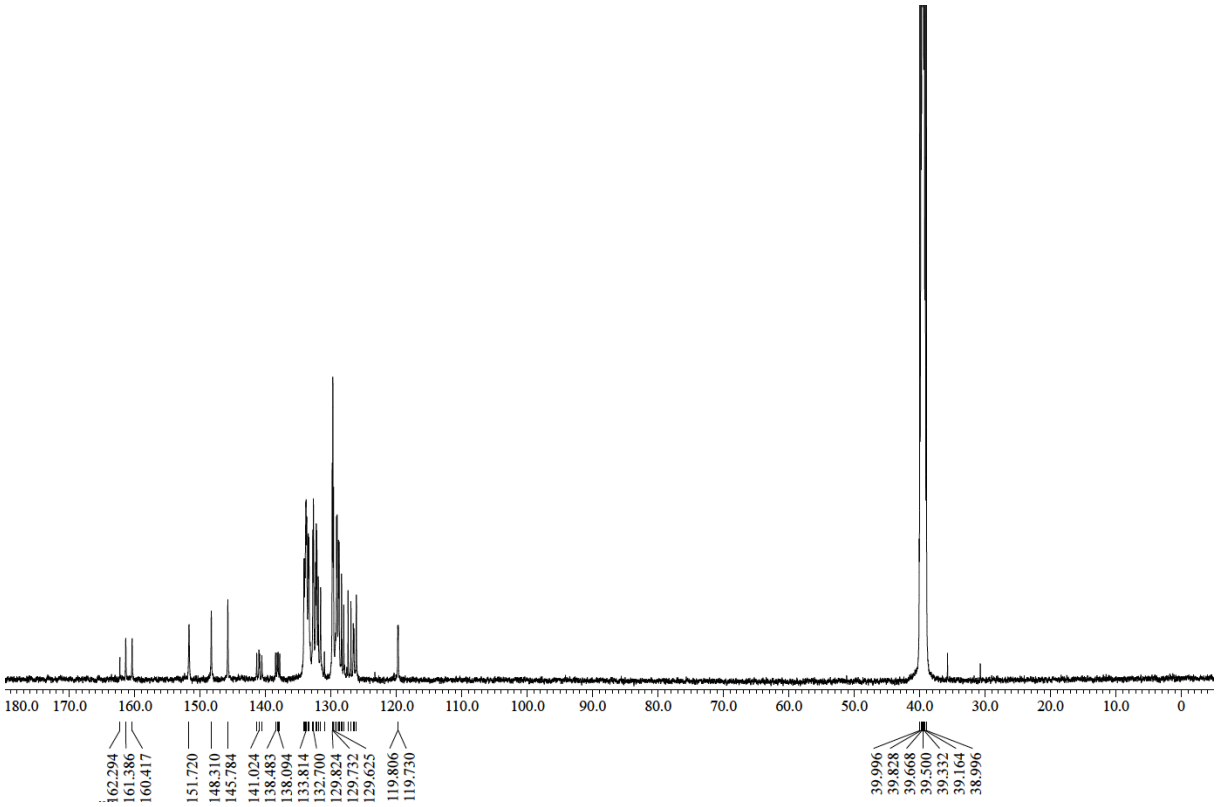
1·$(SbF_6)_3$, ^{13}C NMR (126 MHz, in DMSO-d_6, 25 °C)



4·$(SbF_6)_3$, ^1H NMR (500 MHz, in DMSO-d_6, 25 °C)



4·$(SbF_6)_3$, ^{13}C NMR (126 MHz, in DMSO-d_6, 25 °C)



^{1}H NMR experiment (Fig. 3)

NMR experiments were performed on a Agilent Mercury 300 (300 MHz) at 298 K. Each sample solution was prepared in a sample vial and transferred to a 5 mm quartz NMR tube with adjusting 50 mm of solution height.

Dye extraction experiment (Fig. 4)

The dye solution was prepared by dissolving **5**·Na (1.25 mg, 3.0 μmol, for (b)) or **6**·Na (0.98 mmg, 3.0 μmol, for (c)) in water (300 mL). The dye solution (10 mL) and chloroform (10 mL) was added to a sample vial, and the bilayer was shaken and left to stand (left). To this bilayer was then added **1**·$(SbF_6)_3$ (0.27 mg, 0.10 μmol) and the bilayer was again shaken and left to stand (right).

Single crystal X-ray diffraction experiment (Fig. 2, S1, S2, S3, S4, and S5)

A single crystal was immersed in Paratone-N oil and placed in the N_2 cold stream at 173 K. Data were collected using a diffractometer with Dectris PILATUS3R 200K-A detector (RIGAKU XtaLAB Pro, CuKα : λ = 1.54184 Å). Absorption correction was performed by an empirical method implemented in SCALE3 ABSPACK. Structure solution and refinement were performed by using SHELXT-2018/2[1] and SHELXL-2018/3[2]. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 137, 23, 33 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms.

1·$(NO_3)_3$: colourless prismatic crystal (0.500 × 0.300 × 0.200 mm^3), obtained from DMF/$CHCl_3$/*n*-hexane.

$C_{101}H_{97}Br_3Cl_6N_8O_{11}P_6Pd_3$, *M*r = 2556.31; triclinic, space group *P*-1, *Z* = 2, D_{calc} = 1.618 g·cm^{-3}, *a* = 16.3967(3), *b* = 16.6563(2), *c* = 23.2181(4) Å, α = 73.1360(10), β = 73.9560(10), γ = 61.181(2)°, *V* = 5245.82(17) Å^3, 63189 measured and 20004 independent [$I > 2\sigma(I)$] reflections, 1257 parameters, 6 restraints, final R_1 = 0.0478, wR_2 = 0.1309, *S* = 1.030 [$I > 2\sigma(I)$]. CCDC 2109899

Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms.

1·$(BF_4)_3$: colourless plate crystal (0.080 × 0.050 × 0.010 mm^3), obtained from DMF/$CHCl_3$/*n*-hexane.

$C_{101}H_{97}B_3Br_3Cl_6F_{12}N_5O_2P_6Pd_3$, *M*r = 2630.71; triclinic, space group *P*-1, *Z* = 2, D_{calc} = 1.629 g·cm^{-3}, *a* = 16.4427(3), *b* = 16.7626(3), *c* = 23.5756(4) Å, α = 72.5019(15), β = 74.1791(14), γ = 61.1214(19)°, *V* = 5363.12(19) Å^3, 57487 measured and 13963 independent [$I > 2\sigma(I)$] reflections, 1274 parameters, final R_1 = 0.1220, wR_2 = 0.3137, *S* = 1.204 [$I > 2\sigma(I)$]. CCDC

2109900

Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms.

1·(OTs)$_3$: colourless plate crystal (0.200 × 0.150 × 0.020 mm^3), obtained from DMF/Et_2O. $C_{117}H_{109.6}Br_3N_4O_{10.3}P_6Pd_3S_3$, *M*r = 2577.592; triclinic, space group *P*-1, Z = 2, D_{calc} = 1.572 g·cm^{-3}, a = 14.6590(2), b = 18.6024(2), c = 22.3327(3) Å, α = 76.0582(10), β = 86.6453(11), γ = 67.2209(12)°, V = 5445.46(13) Å^3, 62210 measured and 15252 independent [$I > 2\sigma(I)$] reflections, 1273 parameters, final R_1 = 0.0697, wR_2 = 0.1829, S = 1.079 [$I > 2\sigma(I)$]. CCDC 2109901

Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 137, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms.

In the final stage of structure refinement, The solvent mask in Olex2[3] was applied.

1·(SbF$_6$)$_3$: colourless prismatic crystal (0.200 × 0.200 × 0.100 mm^3), obtained from acetone/*tert*-butyl methyl ether.

$C_{108}H_{106}Br_3F_{18}N_4P_6Pd_3Sb_3$, *M*r = 3008.118; triclinic, space group *P*-1, Z = 2, D_{calc} = 1.825 g·cm^{-3}, a = 16.8469(4), b = 18.3312(3), c = 21.5816(3) Å, α = 71.4480(10), β = 69.156(2), γ = 63.581(2)°, V = 5475.5(2) Å^3, 68796 measured and 17352 independent [$I > 2\sigma(I)$] reflections, 1162 parameters, final R_1 = 0.0605, wR_2 = 0.1638, S = 0.996 [$I > 2\sigma(I)$]. CCDC 2109902

Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 23 and 43) with U_{iso} values constrained to 1.2 U_{eq} of their parent atoms.

In the final stage of structure refinement, The solvent mask in Olex2[3] was applied.

1·(OTs)(SbF$_6$)$_2$: colourless plate crystal (0.150 × 0.100 × 0.020 mm^3), obtained from DMF/CHCl$_3$/Et$_2$O.

$C_{115.45}H_{124.65}Br_3F_{12}N_{8.15}O_{8.45}P_6Pd_3SSb_2$, Mr = 3010.042; monoclinic, space group $P2_1/c$, Z = 4, D_{calc} = 1.637 g·cm^{-3}, a = 16.5257(3), b = 35.6560(4), c = 21.5547(3) Å, β = 105.892(2)°, V = 12215.5(3) Å^3, 74152 measured and 18794 independent [$I > 2\sigma(I)$] reflections, 1611 parameters, 608 restraints, final R_1 = 0.0615, wR_2 = 0.1552, S = 0.9917 [$I > 2\sigma(I)$]. CCDC 2109903

Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 137, 23, 33 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms.

In the final stage of structure refinement, The solvent mask in Olex2[3] was applied.

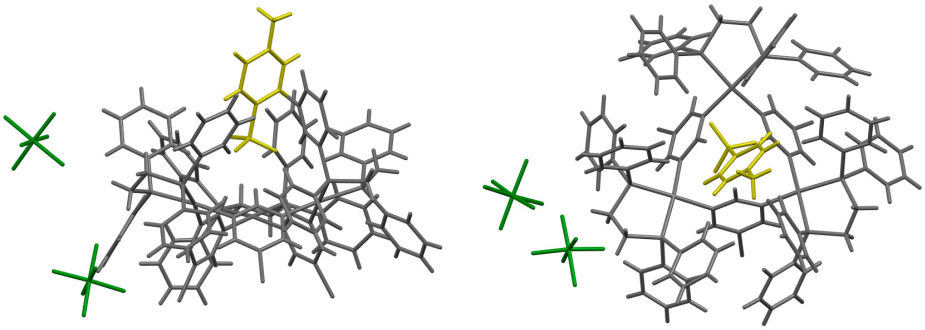


Fig. S1 Crystal structure of **1**·(OTs)(SbF$_6$)$_2$ obtained from a mixture of **1**·(SbF$_6$)$_3$ and TBAOTs drawn by the stick model. Front (left) and top (right) views. Metallacyclophane **1**$^{3+}$ is shown in gray, *p*-toluenesulfonate ion in yellow, and hexafluoroantimonate ion in green. Solvent molecules (DMF) are omitted for clarity.

2: colorless plate crystal (0.100 × 0.100 × 0.010 mm^3), obtained from $CHCl_3/Et_2O$.
$C_{41}H_{33}Br_2NP_2Pd$, *M*r = 867.84; monoclinic, space group *Pc*, *Z* = 4, D_{calc} = 1.611 $g{\cdot}cm^{-3}$, *a* = 12.33630(10), *b* = 11.97080(10), *c* = 24.3472(2) Å, *β* = 95.4730(10)°, *V* = 3579.09(5) $Å^3$, 21865 measured and 10039 independent [$I > 2\sigma(I)$] reflections, 891 parameters, 62 restraints, final $R_1 = 0.0484$, $wR_2 = 0.1264$, $S = 1.039$ [$I > 2\sigma(I)$]. CCDC 2109904
Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 43) with U_{iso} values constrained to 1.2 U_{eq} of their parent atoms.

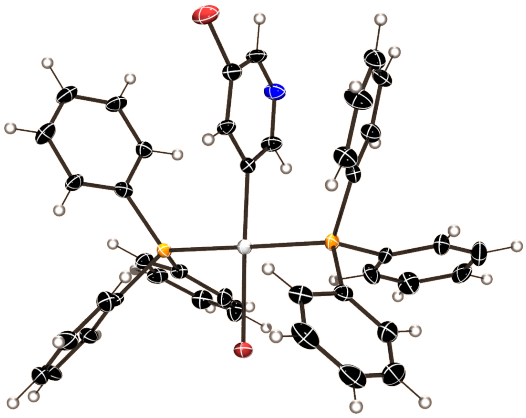


Fig. S2 An ORTEP drawing of the crystal structure of **2** (30% probability).

3: colourless plate crystal (0.350 × 0.200 × 0.200 mm^3), obtained from $CHCl_3/Et_2O$.
$C_{31}H_{27}Br_2NP_2Pd$, *M*r = 741.69; monoclinic, space group $P2_1/n$, $Z = 4$, $D_{calc} = 1.713$ g·cm^{-3}, a = 9.71886(11), b = 16.93137(16), c = 17.59126(16) Å, β = 96.4054(9)°, V = 2876.63(5) $Å^3$, 18017 measured and 5252 independent [$I > 2\sigma(I)$] reflections, 334 parameters, final R_1 = 0.0518, $wR_2 = 0.1385$, $S = 1.123$ [$I > 2\sigma(I)$]. CCDC 2109905
Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 23 and 43) with U_{iso} values constrained to 1.2 U_{eq} of their parent atoms.

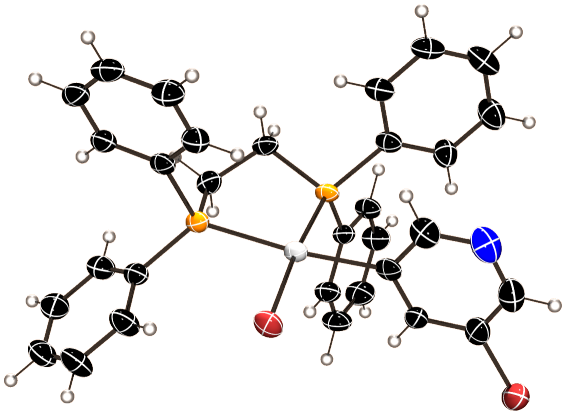


Fig. S3 An ORTEP drawing of the crystal structure of **3** (50% probability).

4·(SbF$_6$)$_3$: colourless block crystal (0.350 × 0.150 × 0.100 mm^3), obtained from acetone/*tert*-butyl methyl ether.

$C_{125.66}H_{122.32}Br_3F_{18}N_3O_{6.89}P_6Pd_3Sb_3$, *M*r = 3236.917; monoclinic, space group $P2_1/n$, $Z = 4$, $D_{calc} = 1.536$ g·cm^{-3}, $a = 13.51766(15)$, $b = 26.3003(2)$, $c = 36.6039(4)$ Å, $\beta = 94.7417(10)°$, $V = 12968.8(2)$ Å^3, 88803 measured and 22039 independent [$I > 2\sigma(I)$] reflections, 1448 parameters, 318 restraints, final $R_1 = 0.0856$, $wR_2 = 0.2223$, $S = 1.0268$ [$I > 2\sigma(I)$]. CCDC 2109906

Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 137, 33 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms.

In the final stage of structure refinement, The solvent mask in Olex2[3] was applied.

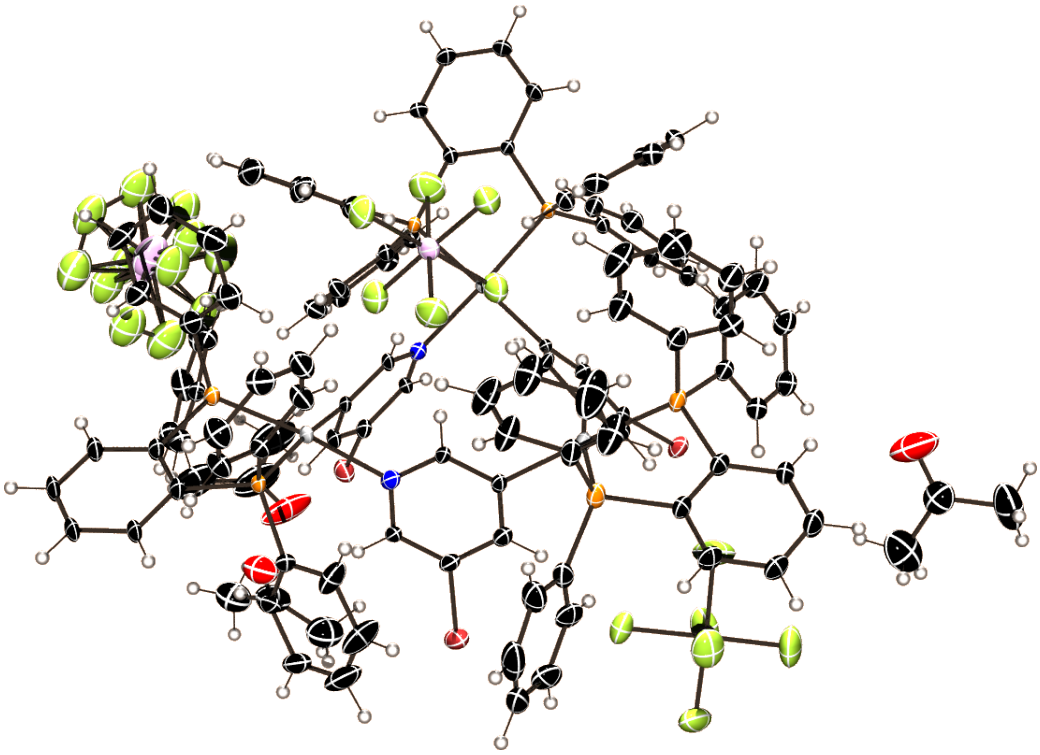


Fig. S4 An ORTEP drawing of the crystal structure of **4**·(SbF$_6$)$_3$ (30% probability).

7: low diffracting colourless plate crystal (0.800 × 0.150 × 0.070 mm^3), obtained from $CHCl_3/Et_2O$.

$C_{36}H_{28}Br_2Cl_3NP_2Pd$, Mr = 909.10; monoclinic, space group $P2_1/c$, Z = 4, D_{calc} = 1.696 $g{\cdot}cm^{-3}$, a = 11.88724(13), b = 19.9861(2), c = 15.1044(2) Å, β = 97.0850(12)°, V = 3561.11(8) $Å^3$, 19825 measured and 5382 independent [$I > 2\sigma(I)$] reflections, 383 parameters, 108 restraints, final R_1 = 0.1562, wR_2 = 0.4345, S = 1.906 [$I > 2\sigma(I)$]. CCDC 2109907

Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13 and 43) with U_{iso} values constrained to 1.2 U_{eq} of their parent atoms. SIMU/RIGU/EADP were applied in the refinement.

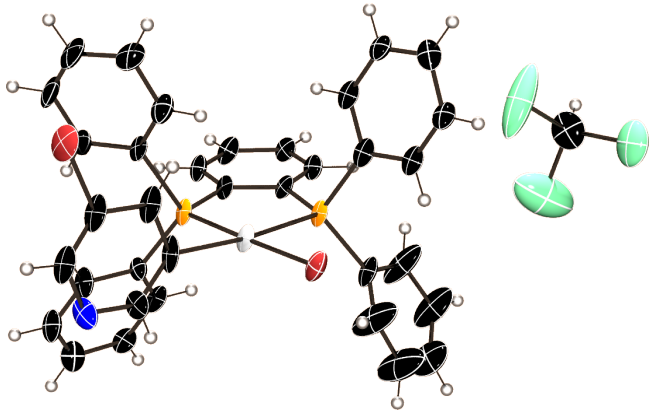


Fig. S5 An ORTEP drawing of the crystal structure of **7** (30% probability).

NMR titration experiment (binding studies, Fig. S6–S12)

NMR measurements were performed on a Agilent Mercury 300 (300 MHz) at 298 K. Each sample solution was prepared by mixing 500 μL of **1**·$(SbF_6)_3$ solution (8.0 or 10.0 mM in DMSO-d_6) and the appropriate amount (25–500 μL) of the solution of each TBA salt of guest anion (10.0 mM in DMSO-d_6) followed by adjusting the total amount of 1.0 mL with DMSO-d_6, and transferred to a 5 mm quartz NMR tube with adjusting 50 mm of solution height.

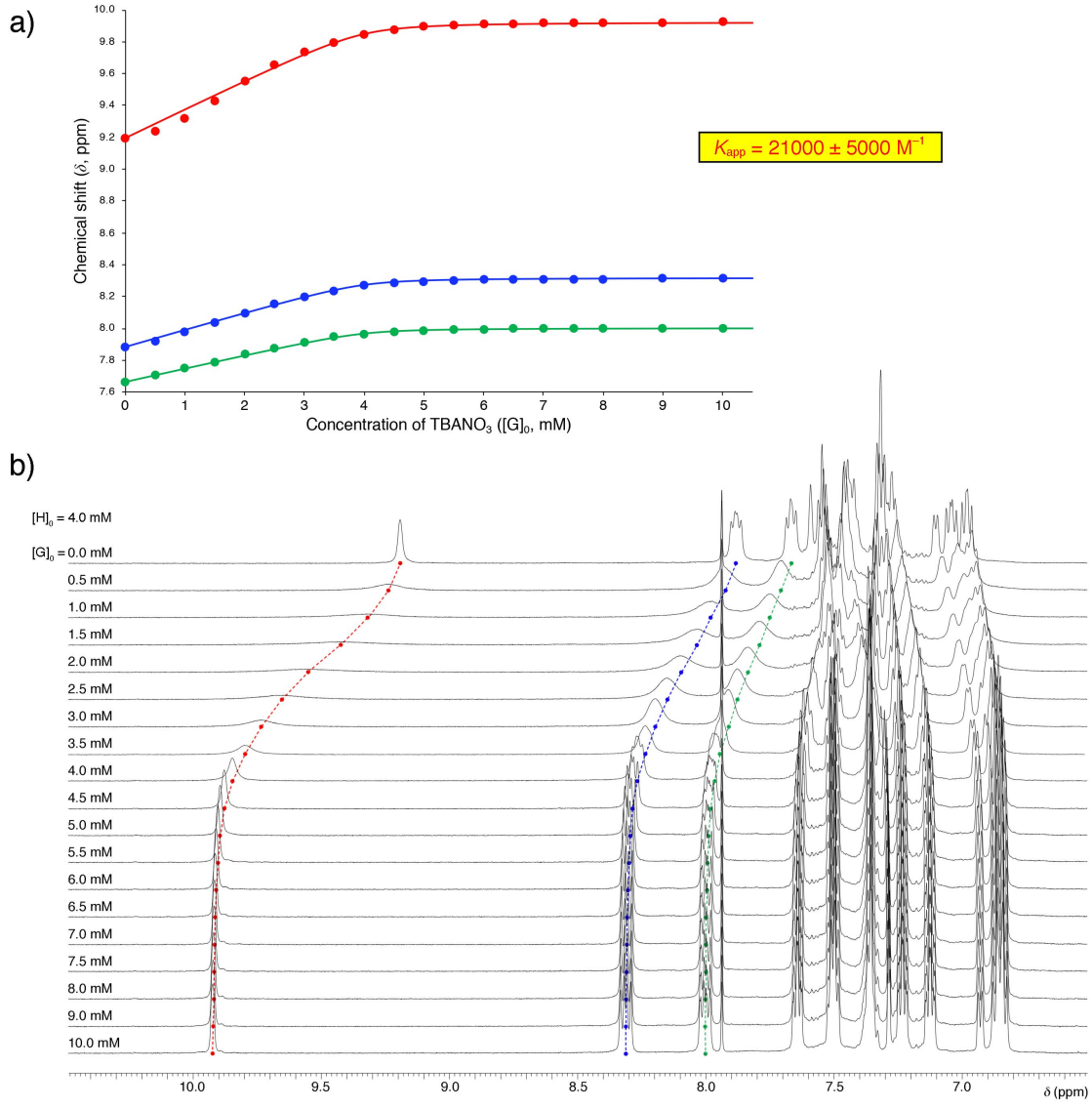


Fig. S6 (a) Binding curve for $\mathbf{1}^{3+}$ titrated with NO_3^- from ^{1}H NMR signal of $\mathbf{1}^{3+}$ in DMSO-d_6 at 25 °C. (b) Partial ^{1}H NMR spectra (300 MHz, 25 °C in DMSO-d_6) of mixtures of **1**·$(SbF_6)_4$ and $TBANO_3$ in various mole fraction ratio. The fitting curves in (a) were drawn according to the host:guest = 1:1 binding constant analysis using *supramolecular.org* program.[4]

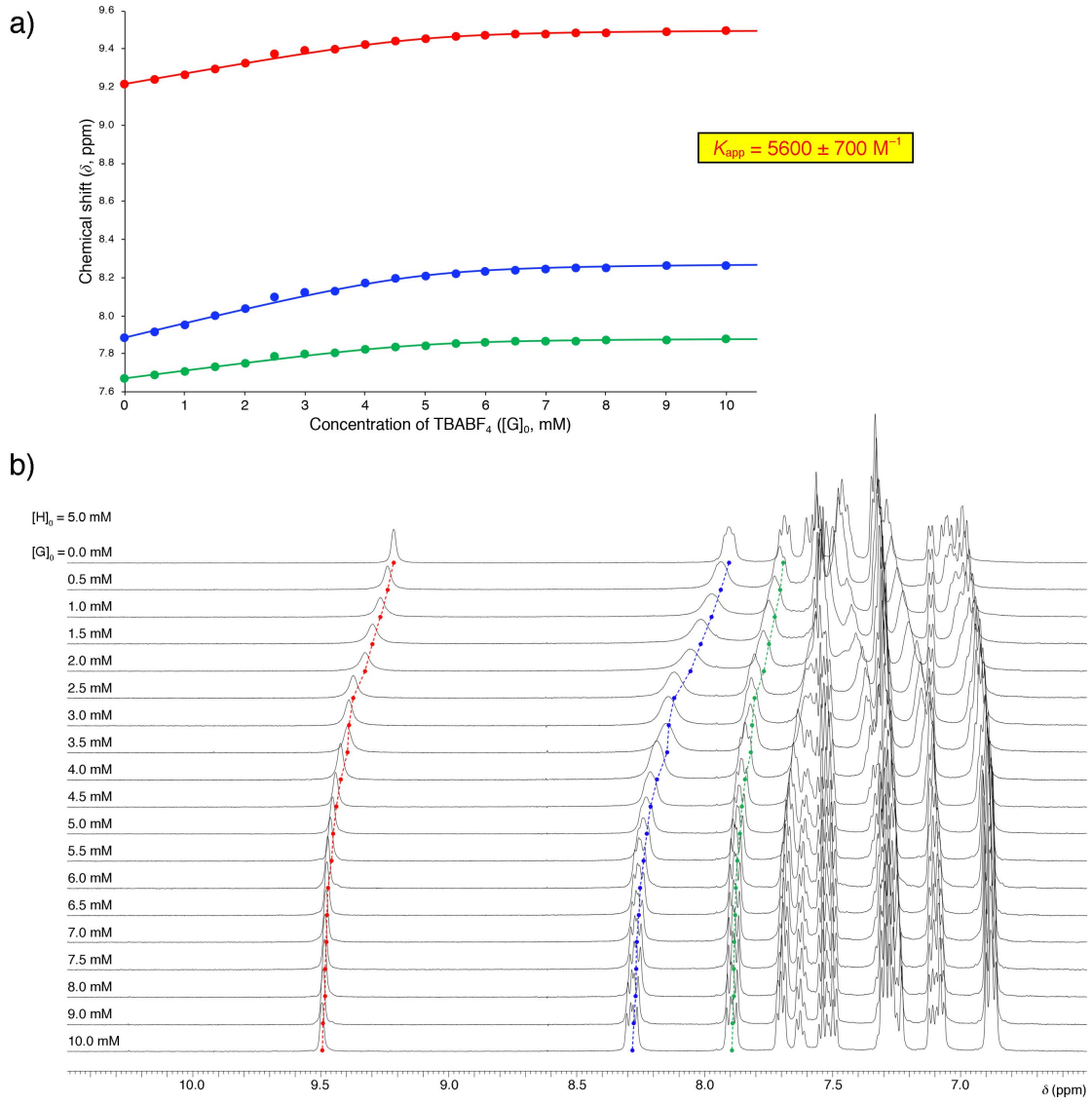


Fig. S7 (a) Binding curve for $\mathbf{1}^{3+}$ titrated with BF_4^- from ^{1}H NMR signal of $\mathbf{1}^{3+}$ in DMSO-d_6 at 25 °C. (b) Partial ^{1}H NMR spectra (300 MHz, 25 °C in DMSO-d_6) of mixtures of $\mathbf{1}\cdot(SbF_6)_4$ and $TBABF_4$ in various mole fraction ratio. The fitting curves in (a) were drawn according to the host:guest = 1:1 binding constant analysis using *supramolecular.org* program.[4]

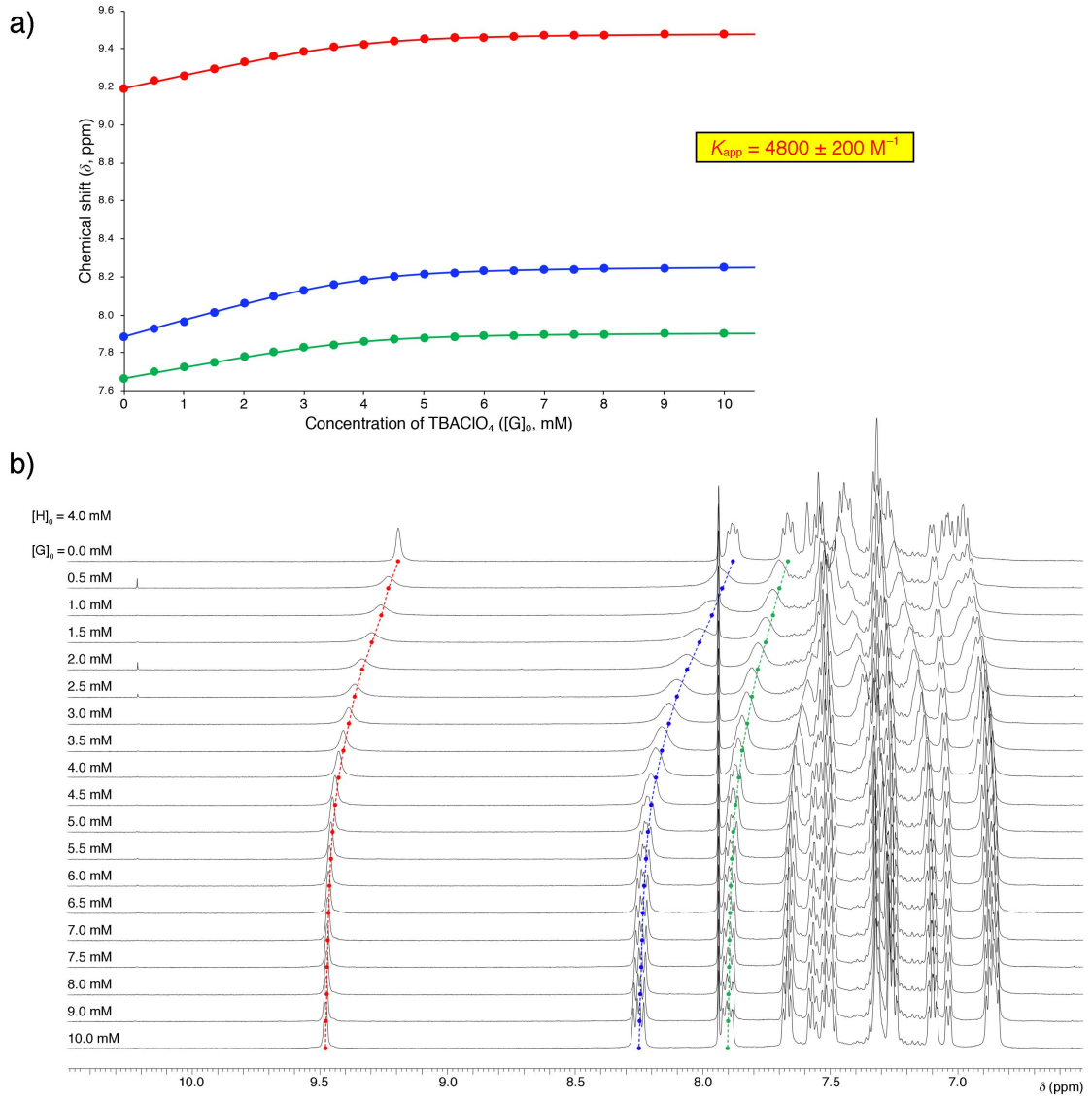


Fig. S8 (a) Binding curve for $\mathbf{1}^{3+}$ titrated with ClO_4^- from ^{1}H NMR signal of $\mathbf{1}^{3+}$ in DMSO-d_6 at 25 °C. (b) Partial ^{1}H NMR spectra (300 MHz, 25 °C in DMSO-d_6) of mixtures of $\mathbf{1}\cdot(SbF_6)_4$ and $TBAClO_4$ in various mole fraction ratio. The fitting curves in (a) were drawn according to the host:guest = 1:1 binding constant analysis using *supramolecular.org* program.[4]

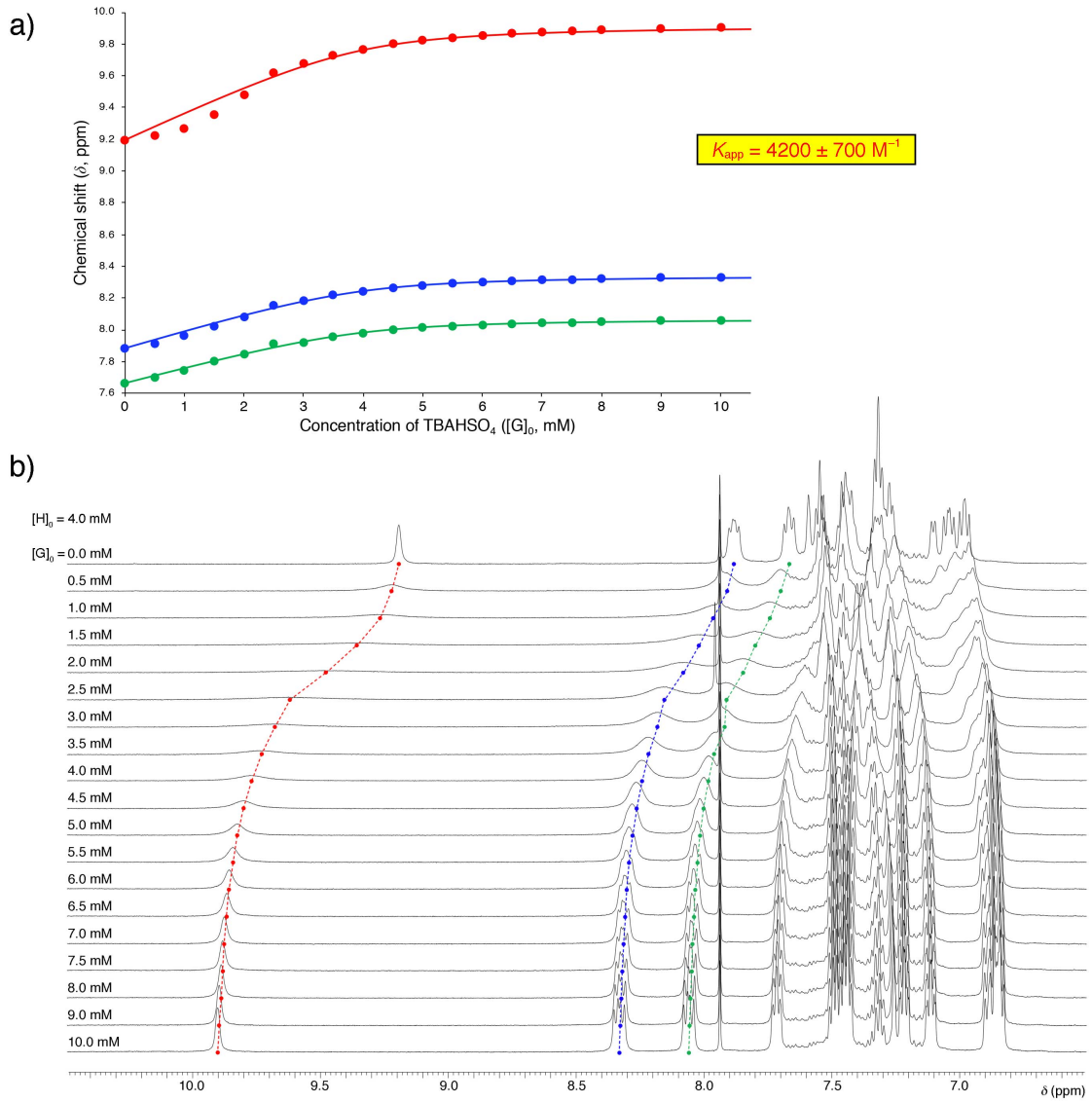


Fig. S9 (a) Binding curve for $\mathbf{1}^{3+}$ titrated with HSO_4^- from ^{1}H NMR signal of $\mathbf{1}^{3+}$ in DMSO-d_6 at 25 °C. (b) Partial ^{1}H NMR spectra (300 MHz, 25 °C in DMSO-d_6) of mixtures of $\mathbf{1}\cdot(SbF_6)_4$ and $TBAHSO_4$ in various mole fraction ratio. The fitting curves in (a) were drawn according to the host:guest = 1:1 binding constant analysis using *supramolecular.org* program.[4]

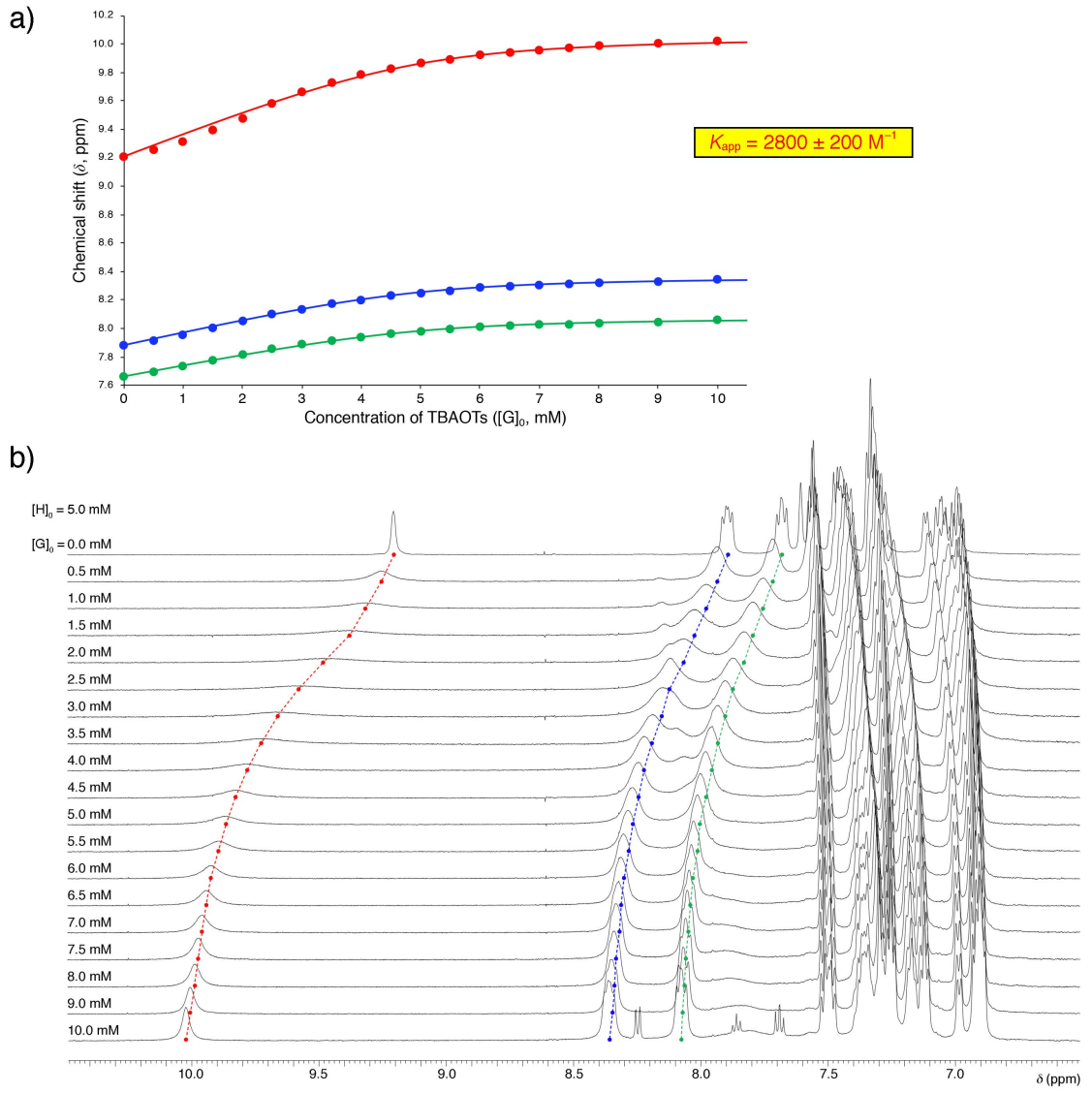


Fig. S10 (a) Binding curve for $\mathbf{1}^{3+}$ titrated with TsO^- from ^1H NMR signal of $\mathbf{1}^{3+}$ in DMSO-d_6 at 25 °C. (b) Partial ^1H NMR spectra (300 MHz, 25 °C in DMSO-d_6) of mixtures of $\mathbf{1}\cdot(SbF_6)_4$ and TBAOTs in various mole fraction ratio. The fitting curves in (a) were drawn according to the host:guest = 1:1 binding constant analysis using *supramolecular.org* program.[4]

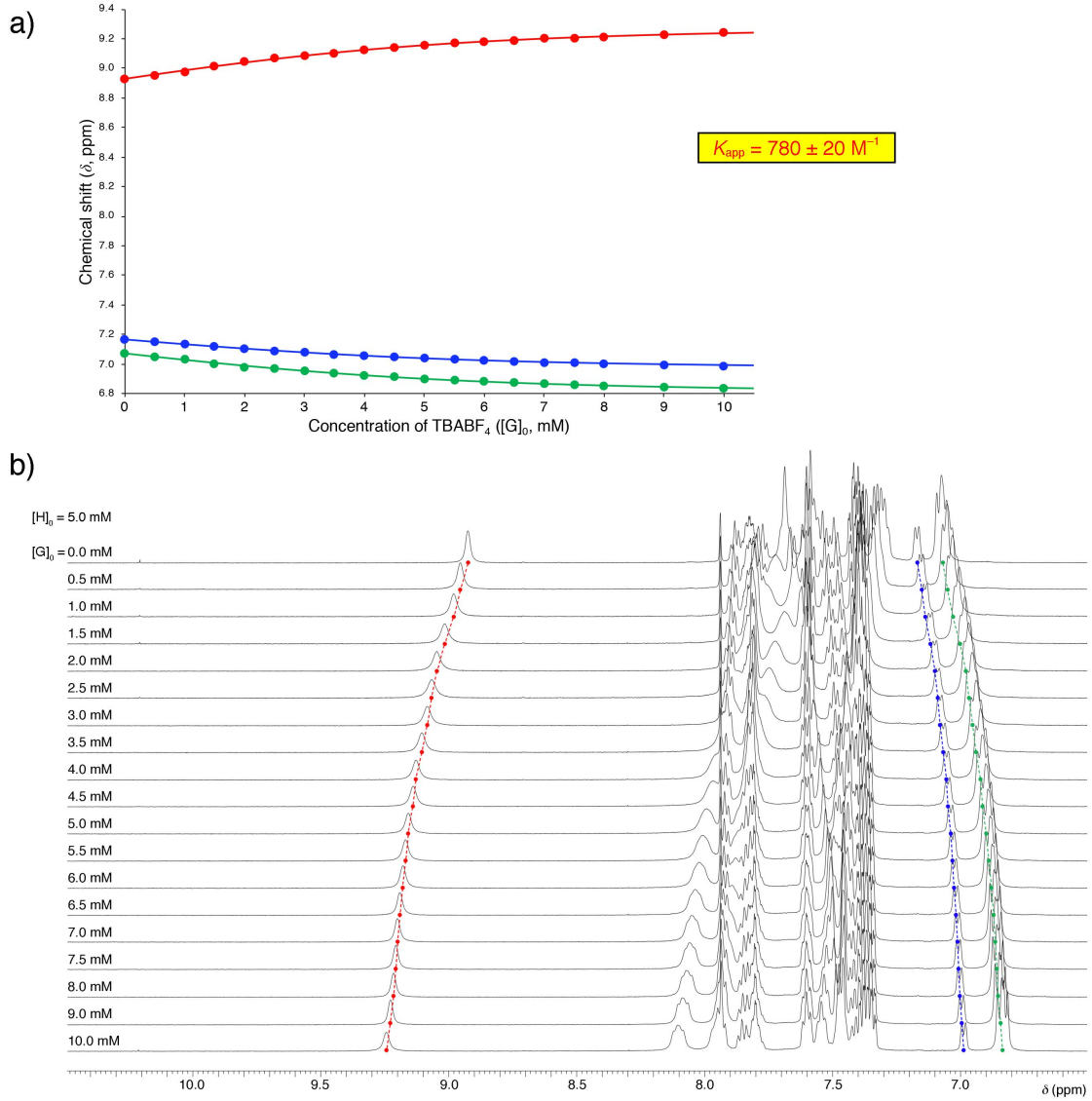


Fig. S11 (a) Binding curve for $\mathbf{4}^{3+}$ titrated with BF_4^- from ^{1}H NMR signal of $\mathbf{4}^{3+}$ in DMSO-d_6 at 25 °C. (b) Partial ^{1}H NMR spectra (300 MHz, 25 °C in DMSO-d_6) of mixtures of $\mathbf{4}\cdot(SbF_6)_4$ and $TBABF_4$ in various mole fraction ratio. The fitting curves in (a) were drawn according to the host:guest = 1:1 binding constant analysis using *supramolecular.org* program.[4]

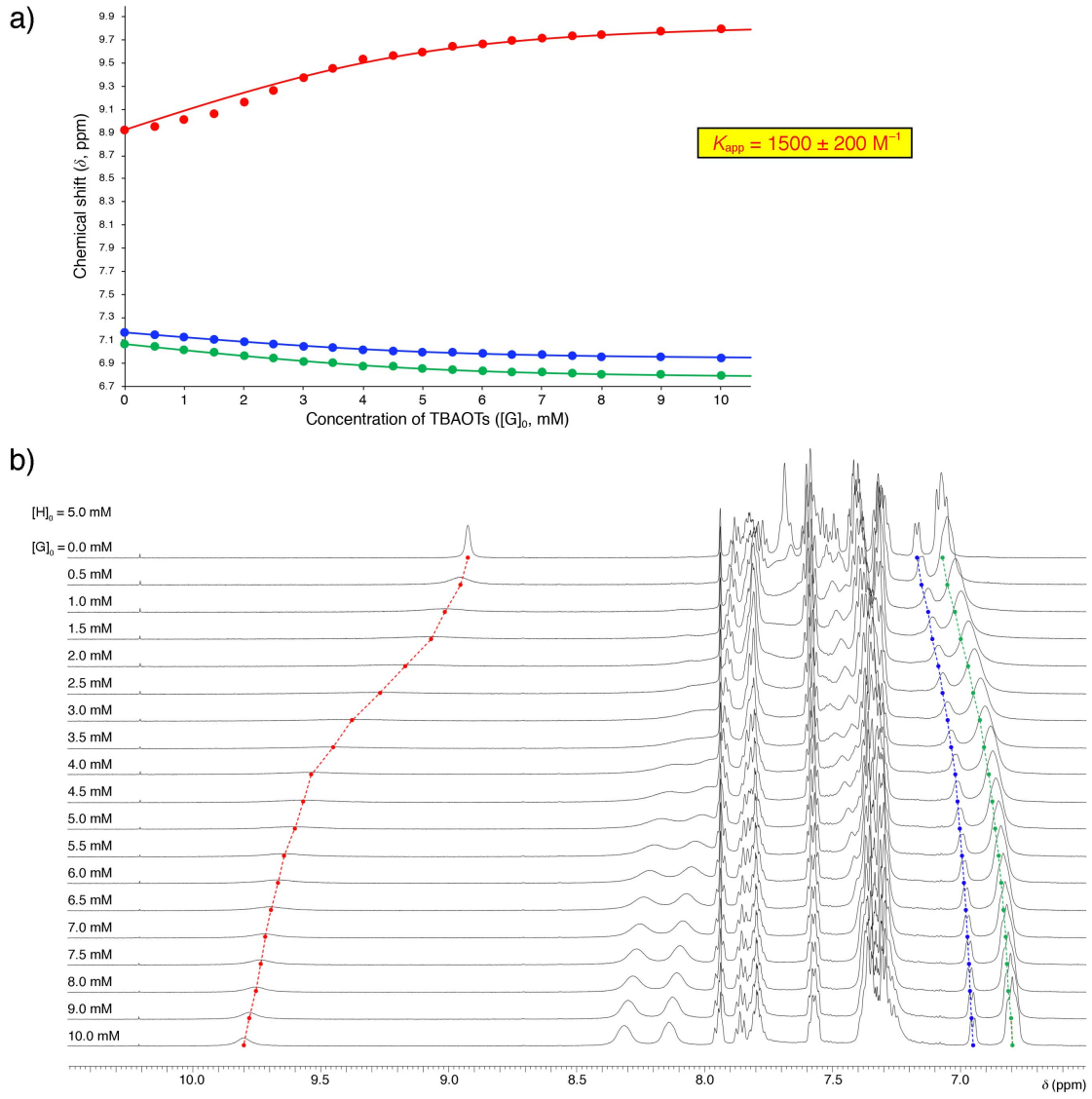


Fig. S12 (a) Binding curve for $\mathbf{4}^{3+}$ titrated with TsO^- from ^1H NMR signal of $\mathbf{4}^{3+}$ in DMSO-d_6 at 25 °C. (b) Partial ^1H NMR spectra (300 MHz, 25 °C in DMSO-d_6) of mixtures of $\mathbf{4}\cdot(SbF_6)_4$ and TBAOTs in various mole fraction ratio. The fitting curves in (a) were drawn according to the host:guest = 1:1 binding constant analysis using *supramolecular.org* program.[4]

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4 Supramolecular.org (online binding constant calculators), http://supramolecular.org, (accessed December 2021), which is cited in D. B. Hibbert and P. Thordarson, *Chem. Commun*., 2016, **52**, 12792–12805.