SUPPORTING INFORMATION

Mesoionic bis(Py-*tz*NHC) Palladium(II) Complex Catalyses "Green" Sonogashira Reaction Through an Unprecedented Mechanism

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1. GENERAL INFORMATION

Starting materials were used as obtained from the commercial sources (Sigma, Aldrich, Fluka). Acetonitrile (MeCN) was freshly distilled from calcium hydride (CaH_2) under argon atmosphere.

Melting points were determined on a Kofler micro hot stage and are uncorrected.

NMR spectra were recorded with a Bruker Avance III 500 MHz instrument operating at 500 MHz (^{1}H), 126 MHz (^{13}C), 471 MHz (^{19}F) and 160 MHz (^{11}B) at 296 K. Proton spectra in $CDCl_3$ and DMSO-d_6 are referenced to $Si(CH_3)_4$ as the internal standard (δ = 0.00 ppm). Carbon chemical shifts are given against the central line of the solvent signal: $CDCl_3$ (δ = 77.0), DMSO-d_6 (δ = 39.5 ppm). ^{19}F NMR and ^{11}B NMR spectra were referenced to CCl_3F and 15% BF_3 etherate in $CDCl_3$, respectively, as external standards at δ 0. Chemical shifts are given on the δ scale (parts per million). Coupling constants (J) are given in Hertz. Multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), or br (broadened). Assignments of proton, carbon and nitrogen resonances were performed by standard 2D NMR techniques (^{1}H–^{1}H *gs*-COSY, ^{1}H–^{13}C *gs*-HSQC, ^{1}H–^{13}C *gs*-HMBC). Conversions were determined by qNMR assay (pulse program = zg; relaxation delay time = 60 s; number of scans = 32) by using internal standard as indicated below.
Optical rotations were measured at 22 °C with Perkin-Elmer 241 MC polarimeter (concentration in g/100 mL solvent).

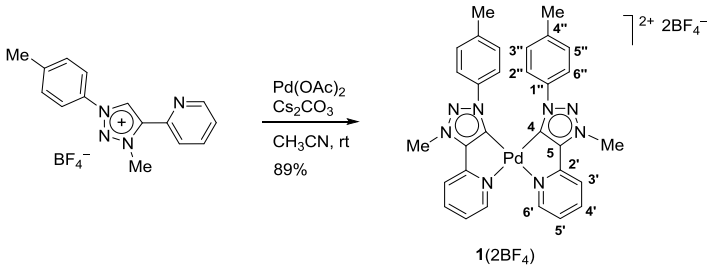
IR spectra were obtained with a Perkin-Elmer Spectrum 100, equipped with a Specac Golden Gate Diamond ATR as a solid sample support.

An Agilent 6224 time-of-flight (TOF) mass spectrometer equipped with a double orthogonal electrospray source at atmospheric pressure ionization (ESI) coupled to an Agilent 1260 HLPC was used for recording HRMS spectra. Mobile phase composed of two solvents: A was 0.1% formic acid in Milli-Q water, and B was 0.1% formic acid in acetonitrile mixed in the ratio of 1:1. Compounds were prepared by dissolving the samples in acetonitrile. 0.1–10 μL of each sample and injected into the LC-MS. Flow rate was 0.4 mL/min. Fragmentor voltage was 150 V. Capillary voltage 4000 V. Mass range 100–1700.

Analytical thin-layer chromatography (TLC) was carried out on Fluka Silica Gel TLC cards visualized with a UV lamp (254 nm).

2. EXPERIMENTAL

2.1. Synthesis of complex 1(2BF_4)



A mixture of 3-methyl-4-(pyridin-2-yl)-1-(*p*-tolyl)-1*H*-1,2,3-triazolium tetrafluoroborate[1] (68 mg, 0.2 mmol), palladium(II) acetate (45 mg, 0.2 mmol) and Cs_2CO_3 (65 mg, 0.2 mmol) in dry acetonitrile (6 mL) was stirred at room temperature for 5 days. The reaction mixture was filtered through a pad of Celite (CAS: 91053-39-3) and the solvent was removed *in vacuo* to give pure complex **1**(2BF_4) as a white solid (69 mg, 89%).

Mp 254–256 °C; IR: 1662, 1619, 1511, 1454, 1326, 1285, 1030, 824, 784, 749, 701, 680 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.42 (s, 3H, CH_3-Ar), 4.45 (s, 3H, CH_3-N3), 7.37 (d, J = 8.2 Hz, 2H, H-3"/H-5"), 7.49 (d, J = 7.6 Hz, 2H, H-2"/H-6"), 7.73 (dd, J_1 = 7.2 Hz, J_2 = 5.6 Hz, 1H, H-5'), 8.25 (dt, J_1 = 1.5 Hz, J_2 = 7.9 Hz, 1H, H-4'), 8.52 (d, J = 8.0 Hz, 1H, H-3'), 8.81 (d, J = 4.5 Hz, 1H, H-6'). ^{13}C NMR (126 MHz, DMSO-d_6): δ 19.6 (CH_3-Ar), 40.4 (CH_3-N3), 122.2 (C-3'), 123.0 (C-2"/C-6"), 124.5 (C-5'), 128.8 (C-3"/C-5"), 133.5 (C-1"), 138.8 (C-4'), 140.0 (C-4"), 143.5 (C-4), 143.6 (C-5), 144.7 (C-2'), 148.3 (C-6'). ^{19}F NMR (471 MHz, DMSO-d_6): δ –148.3 (d, J = 26 Hz, 4F, BF_4); ^{11}B NMR (160 MHz, DMSO-d_6): δ –1.3 (s, 1B, BF_4); ESI-HRMS: calcd for $C_{30}H_{28}N_8Pd^{2+}$ [**1**]$^{2+}$ *m/z* 303.0730; found: 303.0732.

[1] A. Bolje and J. Košmrlj, *Org. Lett.*, 2013, **15**, 5084.

2.1.1. Thermal stability of 1(2BF$_4$) in D$_2$O solution

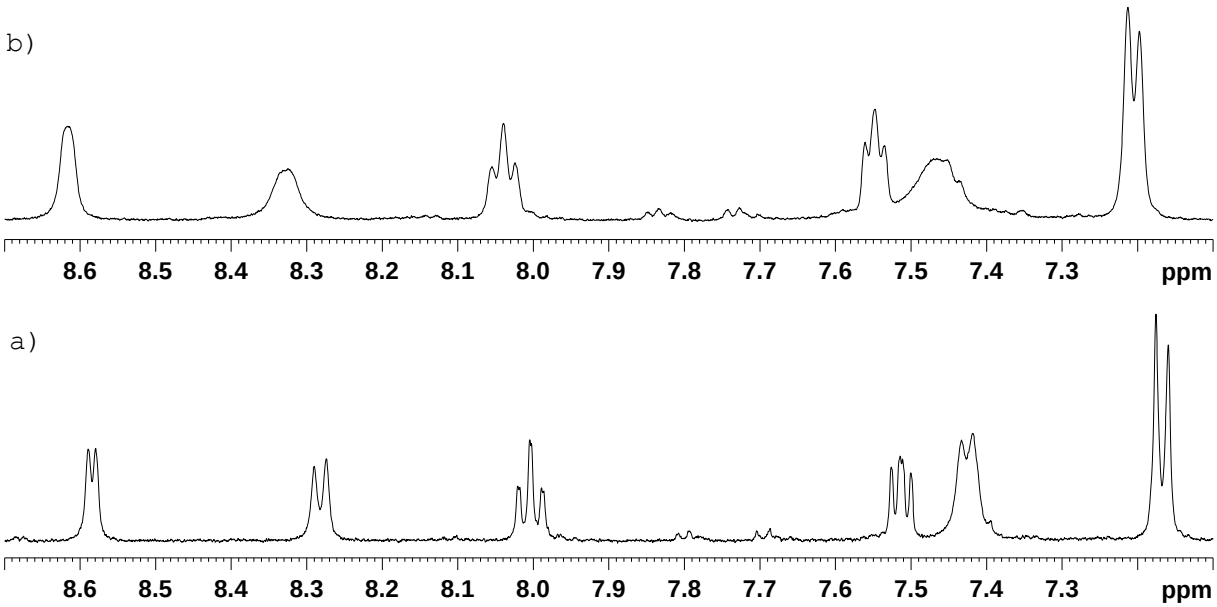
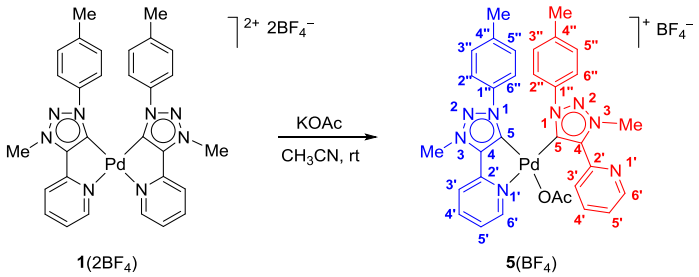


Figure S1. Aromatic part of ^{1}H NMR spectrum of complex **1**(2BF$_4$) (4.0 mg, 0.00513 mmol) recorded in D$_2$O at room temperature: a) before, and b) after heating for 1 h at 140 °C. Boc-glycine (2.5 eqiv., 2.25 mg, 0.01283 mmol) was used as internal standard for qNMR.

2.2. Synthesis of complex 5(BF$_4$)



A mixture of **1**(2BF$_4$) (156 mg, 0.2 mmol) and potassium acetate (98 mg, 1 mmol) in acetonitrile (5 mL) was stirred at room temperature for 1 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. Purification of crude product with flash column chromatography (dichloromethane/methanol = 1/1) afforded pure complex **5**(BF$_4$) as a white solid (127 mg, 84%).

Mp 166–170 °C; IR: 3448, 3369, 1666, 1615, 1586, 1511, 1450, 1378, 1325, 1049 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.36 (s, 3H, CH$_3$-Ar), 2.48 (s, 3H, CH$_3$-Ar), 4.31 (s, 3H, CH$_3$-N3), 4.49 (s, 3H, CH$_3$-N3), 6.79 (d, J = 8.1 Hz, 2H, H-2"/H-6"), 7.32 (d, J = 8.1 Hz, 2H, H-3"/H-5"), 7.42 (d, J = 8.4 Hz, 2H, H-3"/H-5"), 7.53–7.57 (m, 1H, H-5'), 7.83–7.88 (m, 1H, H-5'), 8.03 (dt, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1H, H-4'), 8.11 (d, J = 8.4 Hz, 2H, H-2"/H-6"), 8.19 (d, J = 8.0 Hz, 1H, H-3'), 8.36 (dt, J_1 = 8.0 Hz, J_2 = 1.4 Hz, 1H, H-4'), 8.84 (d, J = 4.3 Hz, 1H, H-6'), 9.04 (d, J = 7.9 Hz, 1H, H-3'), 9.35 (d, J = 4.9 Hz, 1H, H-6'); ^{13}C NMR (126 MHz, DMSO-d_6): δ 20.7 (CH$_3$-Ar), 20.8 (CH$_3$-Ar), 39.4 (CH$_3$-N3), 40.0

(CH_3-N3), 122.1 (C-3'), 123.8 (C-2"/C-6"), 124.5 (C-5'), 124.9 (C-2"/C-6"), 125.2 (C-3'), 126.1 (C-5'), 129.4 (C-3"/C-5"), 129.9 (C-3"/C-5"), 133.8 (C-1"), 135.9 (C-1"), 137.3 (C-4'), 140.4 (C-4"), 141.0 (C-4"), 141.3 (C-4'), 141.9 (C-4), 144.9 (C-5), 146.2 (C-2'), 146.4 (C-4), 147.0 (C-2'), 149.4 (C-6'), 150.5 (C-6'), 151.5 (C-5); ^{15}N NMR (51 MHz, DMSO-d_6): δ 235 (N3), 239 (N3), 241 (N1'), 256 (N1), 259 (N1), 311 (N1'), 347 (N2), 349 (N2).

2.3. Comparison of ^{1}H NMR spectra of 1(2BF$_4$), 5(BF$_4$) and D(X)

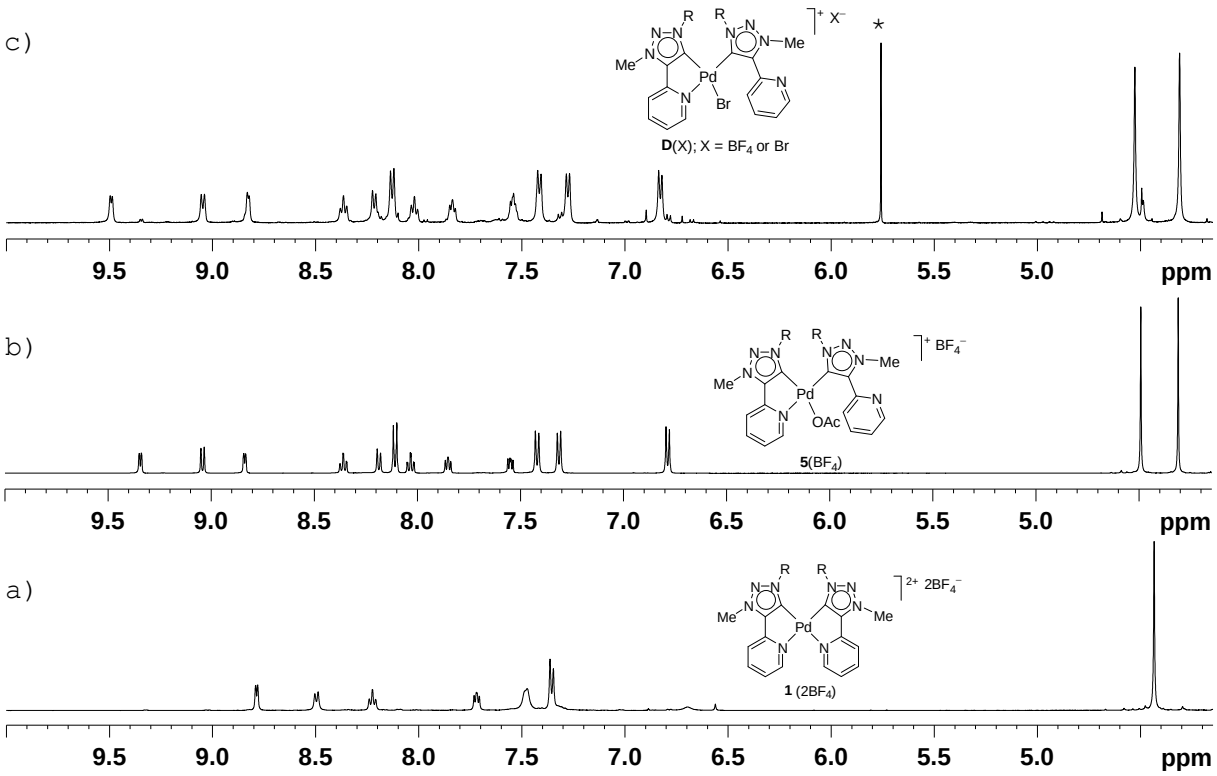
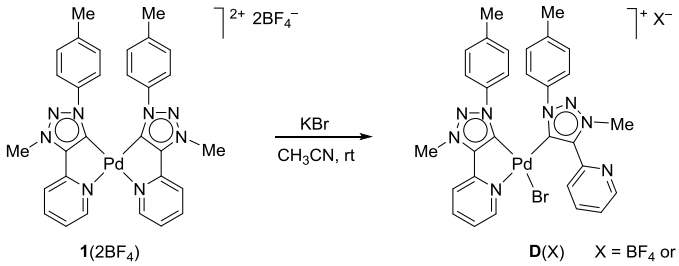


Figure S2. Selected parts of ^{1}H NMR spectra (DMSO-d_6) of: a) complex **1**(2BF$_4$), b) complex **5**(BF$_4$), and c) complex **D**(X) (X = BF$_4$ or Br) (asterisk denotes unidentified impurity). R = 4-Me-C$_6$H$_4$-.

*Preparation of **D**(X):*



Pd complex **D**(X) (X = BF$_4$ or Br) was prepared by treating **1**(2BF$_4$) (7.8 mg, 0.01 mmol) with potassium bromide (24 mg, 0.2 mmol) in acetonitrile (1 mL). The mixture was filtered and the solvent

was removed under reduced pressure. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.36 (s, 3H), 2.46 (s, 3H), 4.31 (s, 3H), 4.53 (s, 3H), 6.83 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.50–7.57 (m, 1H), 7.81–7.86 (m, 1H), 8.02 (dt, J_1 = 7.5 Hz, J_2 = 1.7 Hz, 1H), 8.13 (d, J = 8.3 Hz, 2H), 8.22 (d, J = 7.9 Hz, 1H), 8.36 (t, J = 7.7 Hz, 1H), 8.83 (d, J = 4.1 Hz, 1H), 9.05 (d, J = 7.9 Hz, 1H), 9.49 (d, J = 5.1 Hz, 1H); ESI-HMRS calcd for $C_{30}H_{28}{}^{79}BrN_8Pd^+$ $[M]^+$: 685.0650; found: 685.0643.

2.4. Crystallographic study

*Preparation of complex **1'**(4PF$_6$) and crystallization of **1'**(4PF$_6$) and **5**(BF$_4$) for X-ray structural analysis:*

Crystals suitable for X-ray diffraction analysis were obtained from **1**(2BF$_4$) after anion metathesis and subsequent crystallization, as follows.

To a mixture of **1**(2BF$_4$) (39 mg, 0.05 mmol) in methanol (7 mL), KPF$_6$ (150 mg, 0.82 mmol) was added. After stirring for 5 min at room temperature, water (2 mL) was added and the precipitated **1'**(4PF$_6$) (27 mg, 59%) was collected by filtration.

Crystals of compound **1'**(4PF$_6$), suitable for X-ray crystallography, were prepared by crystallization from a mixture of hexane and acetone at low temperature (4 °C). Crystals of compound **5**(BF$_4$), suitable for X-ray crystallography, were prepared by crystallization from a mixture of hexane and dichloromethane at low temperature (4 °C).

The structures of complex cation $[C_{60}H_{56}N_{16}Pd_2]^{4+}$ (**1'**) and $[C_{32}H_{31}N_8O_2Pd]^+$ (**5**) are shown in Figures S3 and S4, respectively. The crystallographic data and refinement details are given in Table S1. Selected bond lengths and angles are listed in Tables S2 and S3, respectively. Diffraction data were collected at 150 K with Agilent SuperNova dual source using an Atlas detector and equipped with mirror-monochromated MoKα radiation (λ = 0.71073 Å). The data were processed by using CrysAlis PRO.[2] The structure was solved by direct methods using SHELXS-97[3] and refined against F^2 on all data by a full-matrix least-square procedure with SHELXL-97.[3] All non–hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The hexane molecule in **1'**(4PF$_6$) lies on inversion centre in the structure and was poorly refined without hydrogen atoms attached to the carbons. The BF_4^- cation is disordered over 2-fold rotation axis in the structure of **5**(BF$_4$). The peaks higher than 1 e Å^{-3} observed in the last stages of refinement process were unrefineable and likely to belong an additional molecule of solvent. The figures were produced using DIAMOND.[4]

[2] Oxford Diffraction, CrysAlis PRO, Oxford Diffraction Ltd., Yarnton, England, 2009.
[3] G. M. Sheldrick, *Acta. Cryst. (A)*, 2008, **64**, 112.
[4] K. Brandenburg, DIAMOND, Crystal and Molecular Structure Visualization Version 3.2, Crystal Impact GbR, Bonn, Germany.

*Description of the crystal structures **1'**(4PF_6) and **5**(BF_4):*

Structure of compound **1'**(4PF_6) crystallizes as colourless crystals in monoclinic crystal system (space group $P2_1/n$). The asymmetric unit of **1'**(4PF_6) consists of dinuclear Pd(II) complex cation $[C_{60}H_{56}N_{16}Pd_2]^{4+}$ (Figure S3) and four PF_6^- counter-anions. The acetone and hexane were also found as solvent molecules in the crystal structure. Two palladium cations are connected by two bridging pyridyl-triazolium ligand. Each palladium ion is also bidentately coordinated by pyridyl-triazolium ligand. Short Pd–Pd intermetallic distance of 3.0232 Å was found in **1'**. Complex cation is further stabilized by π–π stacking interaction of 3.396 Å between pyridine rings of bidentately coordinated pyridyl-triazolium ligands.

Structure of compound **5**(BF_4) crystallizes as colourless crystals in orthorhombic crystal system (space group *Ibca*). The asymmetric unit of **5**(BF_4) consists of mononuclear Pd(II) complex cation $[C_{32}H_{31}N_8O_2Pd]^+$ (Figure S4) and two half of BF_4^- anion lying on crystallographic 2-fold rotation axis. Palladium ion is bidentately coordinated by pyridyl-triazolium ligand through pyridinium nitrogen and triazolium carbon atom and monodentately coordinated by triazolium carbon atom of other pyridyl-triazolium ligand. Monodentately coordinated acetate ligand completes a square-planar coordination geometry around Pd(II). Palladium ion is 0.0703(25) Å out of the best plane that contained the coordination sphere. The sum of the Pd containing angles equals 360°.

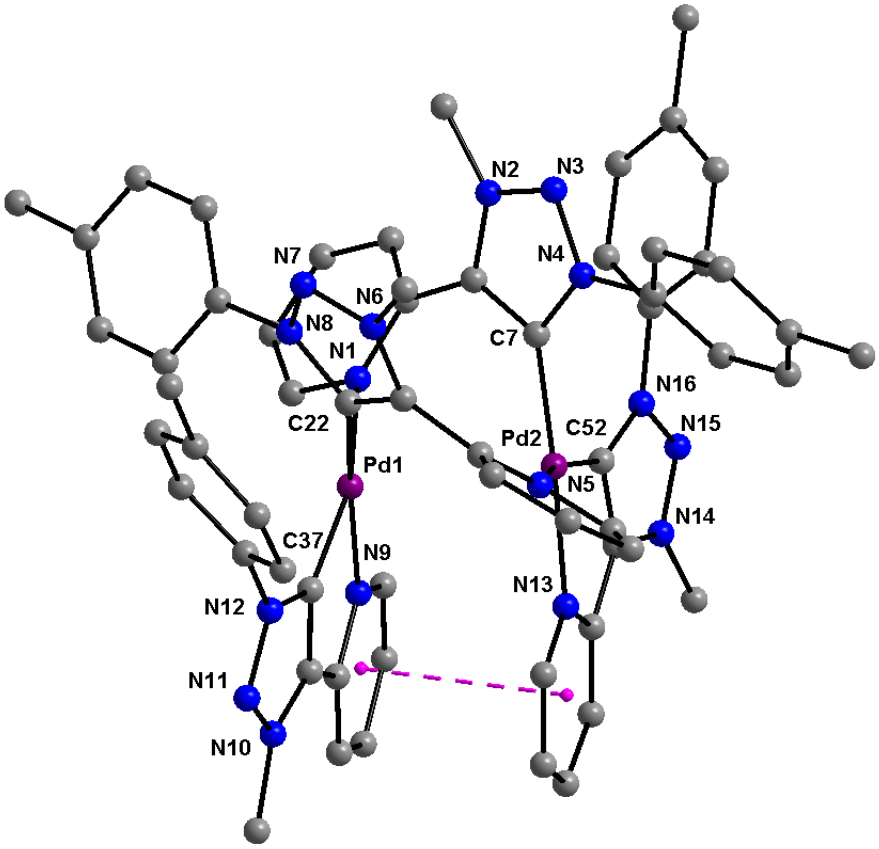


Figure S3. Structural representation of **1'**(4PF_6). The hydrogen atoms, PF_6^- anions, acetone and hexane solvent molecules were omitted for clarity. Centroid-to-centroid distance: 3.396(3) Å.

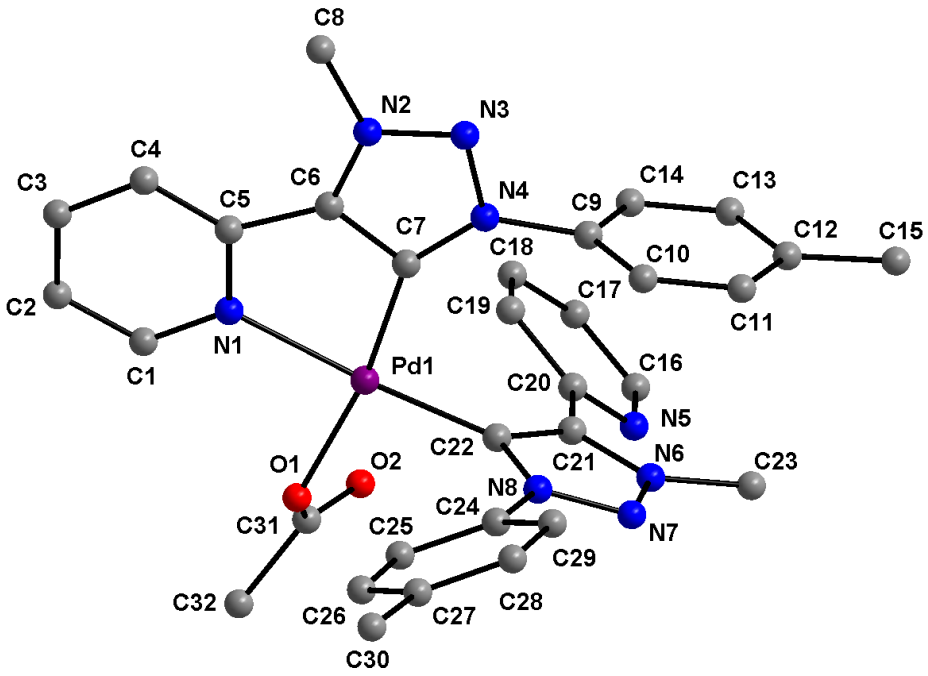


Figure S4. Structural representation of **5**(BF_4). The hydrogen atoms and BF_4^- anions were omitted for clarity.

Table S1. Crystallographic information for the compounds **1'**($4PF_6$) and **5**(BF_4).

	1'($4PF_6$)	**5**(BF_4)
Chemical formula	$C_{69}H_{75}F_{24}N_{16}O_2P_4Pd_2$	$C_{32}H_{31}BF_4N_8O_2Pd$
M_r	1953.13	752.86
Crystal system, Space group	Monoclinic, $P2_1/n$	Orthorhombic, Ibca
a, b, c (Å)	15.8294(4), 31.0399(8), 16.1007(4)	16.4014(6), 19.0245(7), 41.5572(15)
α, β, γ (°)	90, 92.257(2), 90	90, 90, 90
V (Å^3)	7904.8(3)	12967.0(8)
Z	4	16
Densitiy (g cm^{-3})	1.641	1.543
F(000)	3940	6112
Radiation Type	MoK_α	MoK_α
μ (mm^{-1})	0.648	0.639
Crystal size (mm)	0.20 × 0.10 × 0.03	0.20 × 0.10 × 0.10
Meas. Refl.	66462	22392
Indep. Refl.	18107	7441
Obsvd. [I > 2σ(I)] refl.	11243	3574
R_{int}	0.0750	0.1178
R [$F^2 > 2\sigma(F^2)$], wR(F^2), S	0.0583, 0.1277, 1.046	0.0653, 0.1341, 0.963
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.330, –0.620	1.103, –0.797
CCDC	1405057	1430207

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n/p)\}^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

Table S2. Selected bond lengths (Å) and angles (°) of compound **1'**($4PF_6$).

Pd1–N1	2.149(4)	N1–Pd1–N9	94.91(14)
Pd1–N9	2.138(4)	N1–Pd1–C22	93.61(17)
Pd1–C22	1.965(5)	N9–Pd1–C37	79.74(16)
Pd1–C37	1.975(4)	C22–Pd1–C37	92.75(18)
Pd2–N5	2.136(4)	N5–Pd2–N13	93.88(14)
Pd2–N13	2.117(4)	N5–Pd2–C7	93.90(16)
Pd2–C7	1.966(4)	N13–Pd2–C52	80.31(16)
Pd2–C52	1.967(4)	C7–Pd2–C52	93.11(17)
Pd1···Pd2	3.0232(4)		

Table S3. Selected bond lengths (Å) and angles (°) of compound **5**(BF_4).

Pd1–N1	2.109(4)	N1–Pd1–O1	90.34(17)
Pd1–O1	2.048(4)	N1–Pd1–C7	79.97(19)
Pd1–C7	1.965(5)	N1–Pd1–C22	173.56(19)
Pd1–C22	1.979(5)	C7–Pd1–C22	94.2(2)

2.5. ESI-HRMS mechanistic study

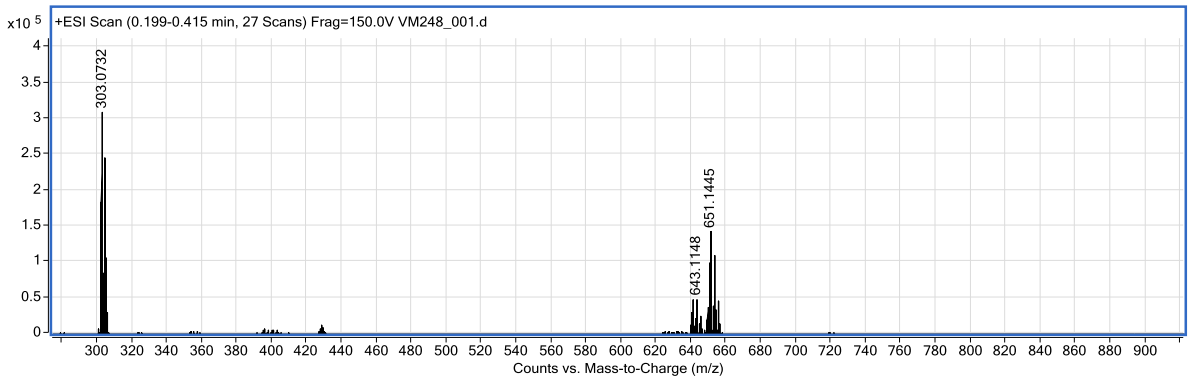


Figure S5. Positive-ion ESI-HRMS spectrum of **1**($2BF_4$): *m/z* 303.0732 (calcd for $C_{30}H_{28}N_8Pd^{2+}$ $[\mathbf{1}]^{2+}$ 303.0736), *m/z* 643.1148 (calcd for $C_{30}H_{28}ClN_8Pd^{+}$ [**1** + Cl]$^{+}$ 643.1159), *m/z* 651.1445 (calcd for $C_{31}H_{29}N_8O_2Pd^{+}$ [**1** + HCO_2]$^{+}$ 651.1454).

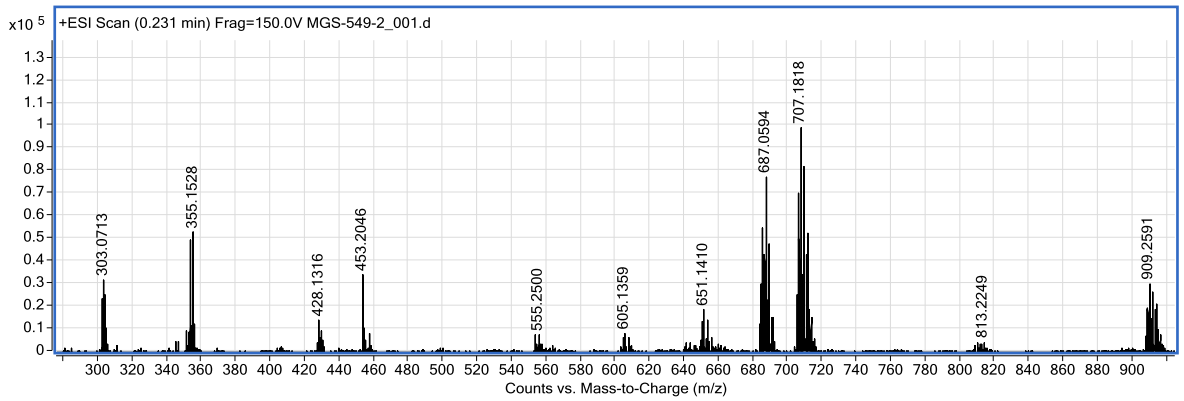


Figure S6. Positive-ion ESI-HRMS of **1**($2BF_4$) (5.0 mg, 0.0064 mmol, 1 equiv.) + 4-bromobenzaldehyde (**2b**, 2.0 mg, 0.011 mmol, 2 equiv.) + phenylacetylene (**3a**, 2.0 mg, 0.020 mmol, 4 equiv.) + Cs_2CO_3 (3.3 mg, 0.011 mmol, 2 equiv.), aged in DMF (0.5 mL) at 100 °C for 20 minutes.

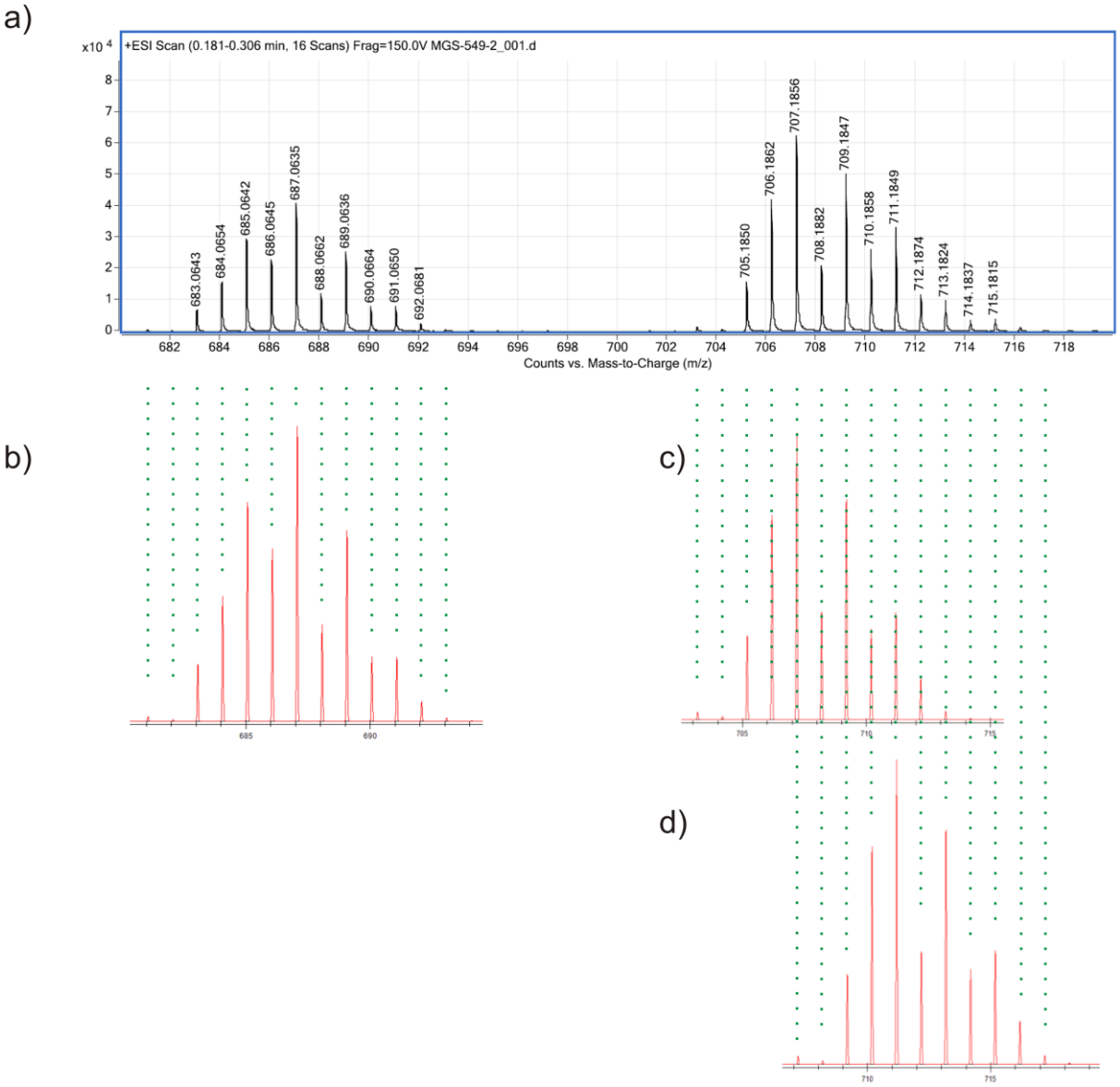


Figure S7. a) Inset from the positive-ion ESI-HRMS shown in Figure S6 with the calculated isotope pattern for: b) L_2PdBr^+: $C_{30}H_{28}BrN_8Pd^+$; *m/z* 685.0650 (for ^{106}Pd and ^{79}Br), c) $L_2Pd(C{\equiv}CPh)^+$: $C_{38}H_{33}N_8Pd^+$; *m/z* 707.1858, d) $L_2Pd(C_6H_4CHO)^+$: $C_{37}H_{33}N_8OPd^+$; *m/z* 711.1807.

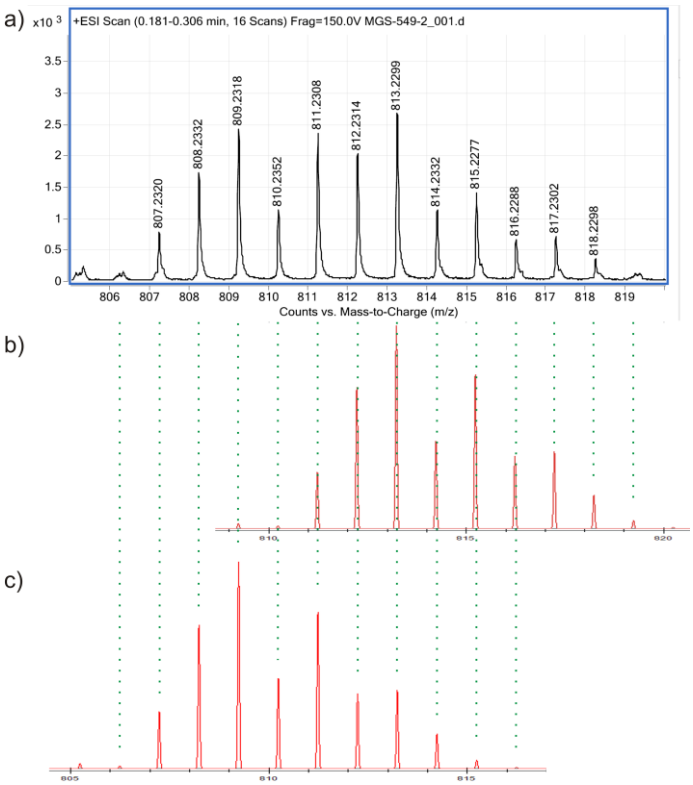
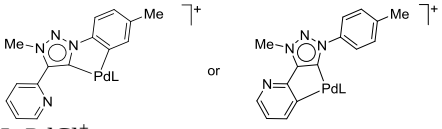
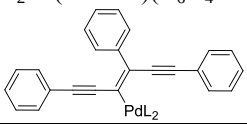


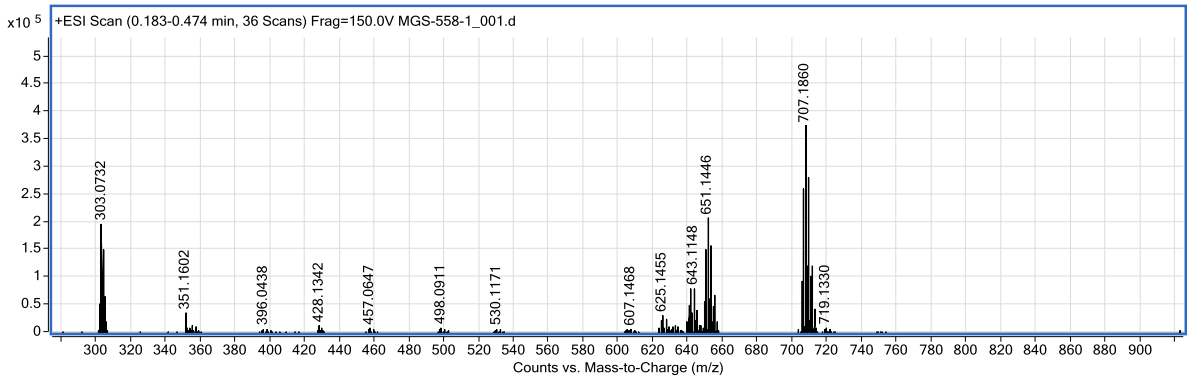
Figure S8. a) Inset from the positive-ion ESI-HRMS shown in Figure S6 with the calculated isotope pattern for: b) ($L_2Pd(C{\equiv}CPh)_2 + H^+$): $C_{45}H_{39}N_8OPd^+$; *m/z* 809.2327, c) ($L_2Pd(C{\equiv}CPh)(C_6H_4CHO) + H^+$): $C_{46}H_{39}N_8Pd^+$; *m/z* 813.2276.

Table S4. Comparison of the results of accurate mass determination and the masses calculated for the proposed ion structures (see Scheme 3).[a]

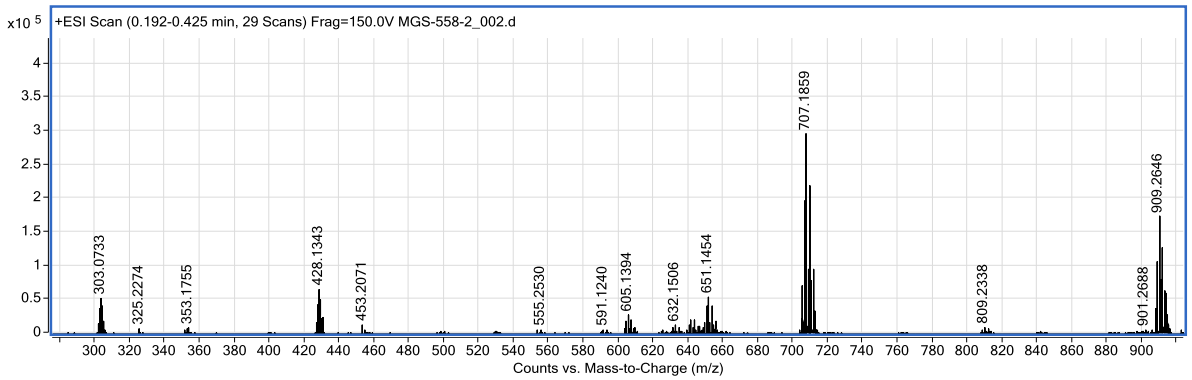
Species	Ion elemental composition	Measured *m/z*	Calculated *m/z*	Relative error (ppm)
L_2Pd^{2+}; $[\mathbf{1}]^{2+}$	$C_{30}H_{28}N_8Pd^{2+}$	303.0731	303.0730	–0.3
	$C_{30}H_{27}N_8Pd^+$	605.1391	605.1399	1.3
L_2PdCl^+	$C_{30}H_{28}{}^{37}ClN_8Pd^+$	643.1148	643.1159	1.7
$L_2Pd(HCO_2)^+$	$C_{31}H_{29}N_8O_2Pd^+$	651.1445	651.1454	1.4
L_2PdBr^+; $[\mathbf{D}]^+$	$C_{30}H_{28}{}^{79}BrN_8Pd^+$	685.0642	685.0650	1.2
$L_2Pd(C{\equiv}CPh)^+$; $[\mathbf{C}]^+$	$C_{38}H_{33}N_8Pd^+$	707.1856	707.1858	0.2
$L_2Pd(C_6H_4CHO)^+$; $[\mathbf{A} - Br]^+$ [b]	$C_{37}H_{33}N_8OPd^+$	711.1849	711.1807	5.9
$L_2Pd(C{\equiv}CPh)_2 + H^+$	$C_{46}H_{39}N_8Pd^+$	809.2318	809.2327	1.1
$L_2Pd(C{\equiv}CPh)(C_6H_4CHO) + H^+$; $[\mathbf{B} + H]^+$	$C_{45}H_{39}N_8OPd^+$	813.2299	813.2276	2.8
	$C_{54}H_{43}N_8Pd^+$	909.2643	909.2640	0.3

[a] L = Py-*tz*NHC. The values are reported for ^{106}Pd complexes. [b] Interpreted as in-source collision-induced dissociation (CID) of a bromide ion $[\mathbf{A} - Br]^+$ from the intermediate **A**.

a)



b)



c)

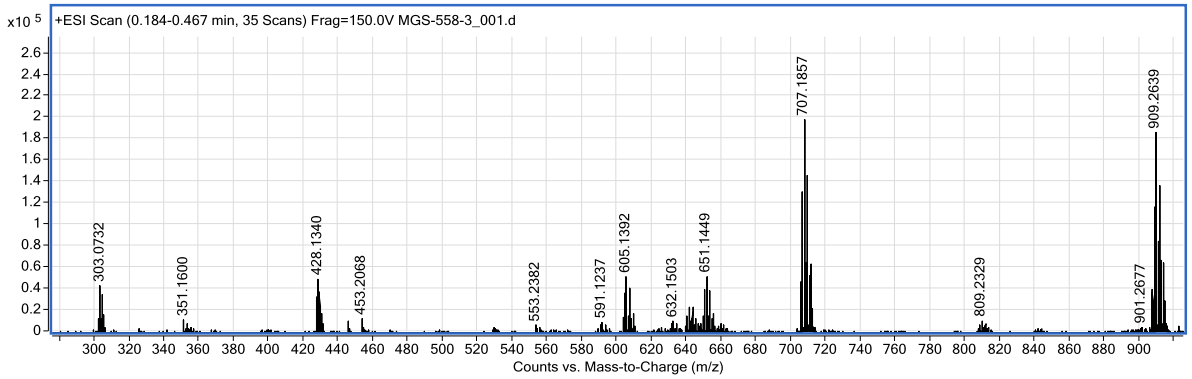
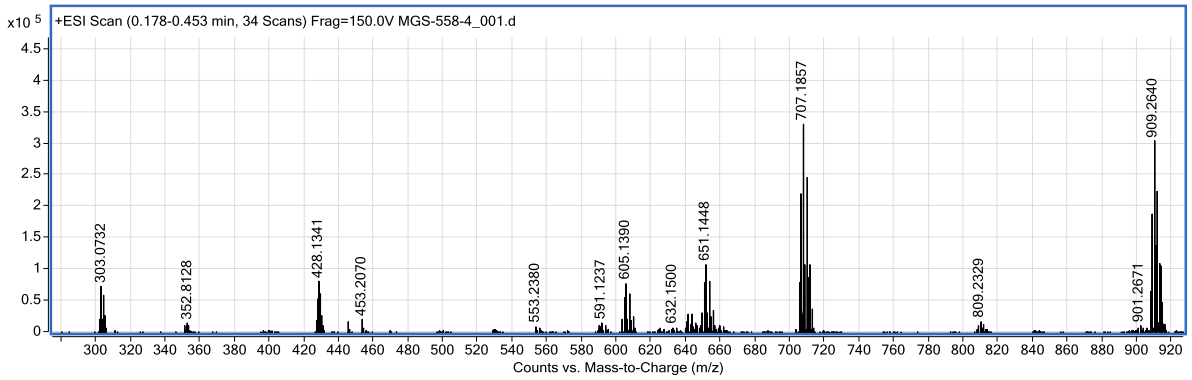


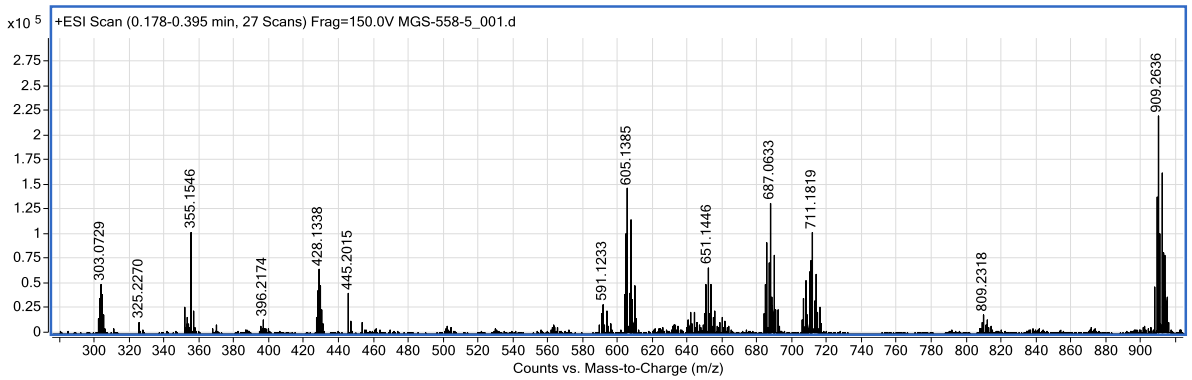
Figure S9. Positive-ion ESI-HRMS of **1**($2BF_4$) (4.5 mg, 0.0058 mmol) + phenylacetylene (**3a**, 2.0 mg, 0.020 mmol) + Cs_2CO_3 (2 mg, 0.0061 mmol): a) immediately after dissolution in DMF (0.5 mL) at room temperature, b) after heating at 100 °C for 15 min, c) after heating at 100 °C for 30 min.

NOTE: Similar ESI-HRMS spectra were obtained when the reaction was conducted under identical conditions as above by using complex **D**(X) in place of **1**($2BF_4$).

a)



b)



c)

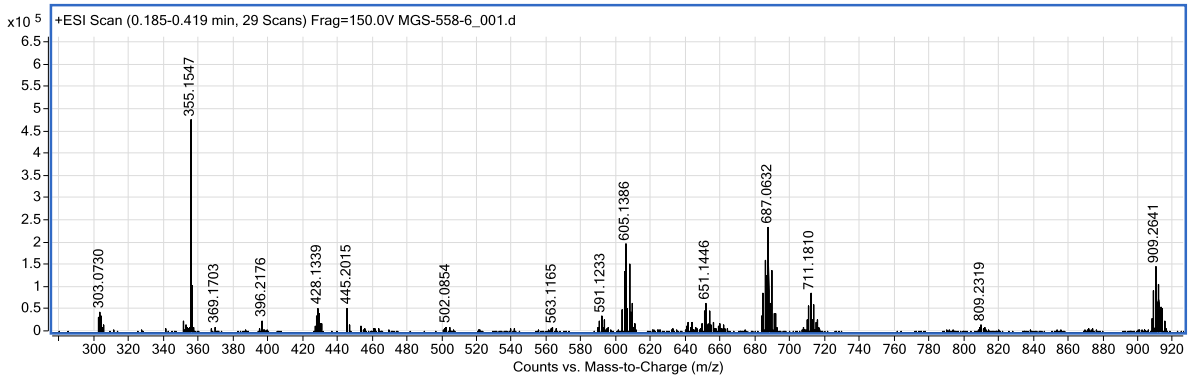


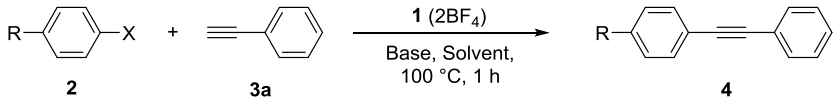
Figure S10. Positive-ion ESI-HRMS of the reaction mixture obtained as described in Figure S9; a) 15 min after cooling down to room temerature and addition of excess of 4-bromobenzaldehyde (**2b**, 5.5 mg, 0.030 mmol), b) after heating at 100 °C for 15 min, c) after heating at 100 °C for 30 min.

2.6. General procedure for the Sonogashira cross-coupling

A mixture of selected bromide **2** (0.25 mmol), acetylene **3** (0.5 mmol), base (0.5 mmol), solvent (2 mL) and the appropriate amount of complex **1**($2BF_4$) was stirred in an ACE pressure tube. For details about the reaction temperature, time and additive, see Table 1, Table S5 and the discussion. The reaction mixture was cooled down to room temperature and extracted with ethyl acetate or diethyl ether (4 × 15 mL). The combined organic layers were dried over Na_2SO_4 and evaporated to dryness. The conversions were determined by integrations of ^{1}H NMR spectra of crude products. The results reported are from two consecutive runs. Conversions were determined by qNMR assay using 1,3,5-trimethoxybenzene as internal standard.

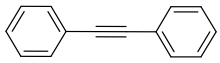
2.7. Initial screening of complex 1($2BF_4$) in Sonogashira cross-coupling: aryl halogenides, solvents, base; mercury poisoning experiments and performance of 1($2BF_4$) in DMF/DABCO

Table S5. Initial screening of complex **1**($2BF_4$) in Sonogashira cross-coupling: aryl halogenides, solvents, base and mercury poisoning experiment.[a]



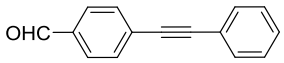
Entry	**2**	R	X	mol% of **1**	Solvent	Base	**4** (%)[b]
1	**2k**	H	I	0.5	H_2O/DMF, 1:2	Cs_2CO_3	**4n**, 100
2	**2a**	CHO	Br	0.5	H_2O/DMF, 1:2	Cs_2CO_3	**4a**, 96
3	**2l**	CHO	Cl	0.5	H_2O/DMF, 1:2	Cs_2CO_3	**4a**, 0
4	**2a**	CHO	Br	1.0	H_2O	Cs_2CO_3	**4a**, 46
5	**2a**	CHO	Br	1.0	H_2O[c]	Cs_2CO_3	**4a**, 40
6	**2a**	CHO	Br	1.0	H_2O	K_2CO_3	**4a**, 44
7	**2a**	CHO	Br	1.0	H_2O	Na_2HPO_4	**4a**, 20
8	**2a**	CHO	Br	1.0	H_2O	NaOH	**4a**, 50
9	**2a**	CHO	Br	1.0	H_2O	KOAc	**4a**, 22
10	**2a**	CHO	Br	1.0	H_2O	Et_3N	**4a**, 19
11	**2a**	CHO	Br	1.0	H_2O	DABCO	**4a**, 64

[a] Reaction conditions: aryl halide **2** (0.25 mmol), phenylacetylene **3a** (0.5 mmol), base (0.5 mmol), solvent (2.0 mL), complex **1**($2BF_4$), 100 °C in ACE tube, 1 h. [b] As determined by ^{1}H NMR (qNMR) spectroscopy. [c] Addition of Hg (320 equiv.) at the onset of the reaction.



4-Diphenylethyne (**4n**; Table S4, Entry 1)

By following the general procedure for the Sonogashira cross-coupling, a mixture of iodobenzene **2k** (51 mg, 0.25 mmol), phenylacetylene **3a** (51 mg, 0.5 mmol), Cs_2CO_3 (163 mg, 0.5 mmol), and complex **1**($2BF_4$) (1 mg, 0.00125 mmol, 0.5 mol%) in DMF/H_2O (2:1, 2 mL) was stirred in ACE pressure tube for 1 h at 100 °C. Then, the reaction mixture was cooled to room temperature and extracted with diethyl ether (4 × 15 mL). The combined organic layers were dried over Na_2SO_4 and evaporated to dryness. The conversion was determined by ^{1}H NMR (100%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33–7.45 (m, 6H), 7.51–7.69 (m, 4H). The data are in agreement with those from the literature.[5]



4-(phenylethynyl)benzaldehyde (**4a**; Table S4, entries 2, 4–11)

Following general procedure for the Sonogashira cross-coupling, using 4-bromobenzaldehyde (**2a**) (46 mg, 0.25 mmol) and phenylacetylene (**3a**) (51 mg, 0.5 mmol), base (0.5 mmol) and solvent (2 mL). For details see Table S5. The conversion was determined by ^{1}H NMR. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–7.40 (m, 3H), 7.54–7.58 (m, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 10.02 (s, 1H). The data are in agreement with those from the literature.[6]

Mercury poisoning experiments

General procedure: A mixture of **2a** (46 mg, 0.25 mmol), **3a** (51 mg, 0.5 mmol), caesium carbonate (163 mg, 0.5 mmol), water (2.0 mL), **1**($2BF_4$) (2 mg, 0.0025 mmol, 1 mol%) was heated at 100 °C for 0.5 h. Then Hg(0) (200 mg, 1 mmol, 400 equiv.) was added and the reaction mixture was under vigorous stirring heated at 100 °C for the time indicated in Table S6. The results are collected in Table S6 and shown in Figure S11. Each conversion was determined by qNMR spectroscopy of an independent run (seven runs).

Table S6. Mercury poisoning experiment at 100 °C [a]

Entry	Time (h)	Hg-free experiment (test run): conversion (%)	Experiment with Hg(0) added after 0.5 h: conversion (%)
1	0.5	31	–
2	1	42	38
3	2	53	51
4	4	59	55

[a] Conversion determined by ^{1}H NMR (qNMR) spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

[5] V. Sashuk, J. Ignatowska and K. Grela, *J. Org. Chem.*, 2004, **69**, 7748.
[6] S. R. Halper and S. M. Cohen, *Chem. – Eur. J.*, 2003, **9**, 4661.

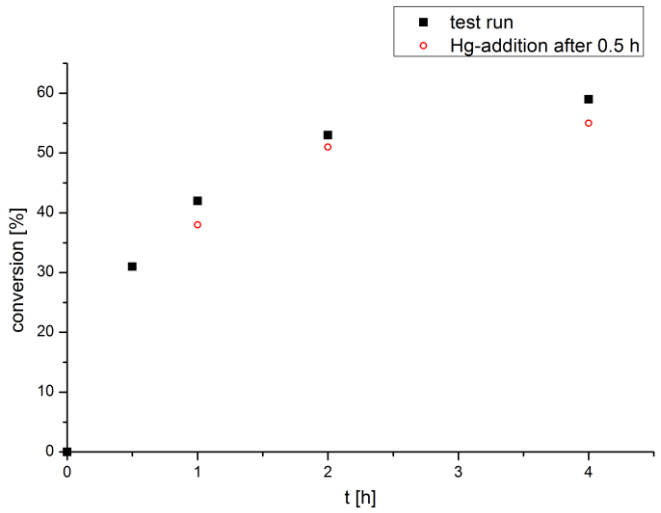


Figure S11. Graphical representation of the data from Table S6.

The above mercury poisoning experiment was repeated under identical reaction conditions as above at 140 °C. The results are shown in Table S7 and Figure S12.

Table S7. Mercury poisoning experiment at 140 °C [a]

Entry	Time (h)	Hg-free experiment (test run): conversion (%)	Experiment with Hg(0) added after 0.5 h: conversion (%)
1	0.5	36	–
2	2	60	66
3	4	75	76

[a] Conversion determined by ^{1}H NMR (qNMR) spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

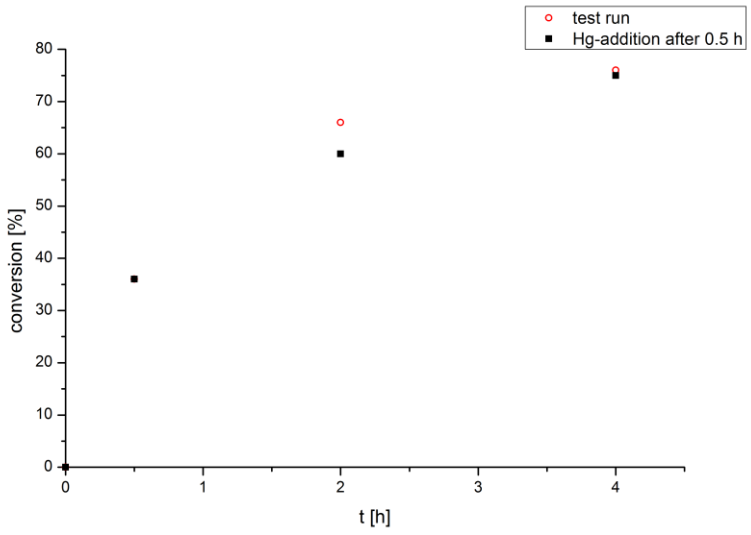
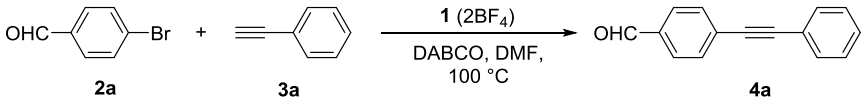


Figure S12. Graphical representation of the data from Table S7.

Table S8: Performance of **1**($2BF_4$) in DMF/DABCO.[a]



2a **3a** **4a**

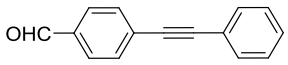
Entry	mol% of **1**($2BF_4$)	t (h)	Conversion[b] (Yield)[c]
1	0.1	1	100 (96)
2	0.01	1	37
3	0.01	4	82
4	0.01	8	98 (94)

[a] Reaction conditions: **2a** (1 eqiv.), **3a** (2 eqiv.), DABCO (2 equiv.), DMF (1 mL/mmol of **2a**), **1**($2BF_4$), 100 °C; [b] As determined by ^{1}H NMR (qNMR) spectroscopy (1,3,5-trimethoxybenzene as internal standard); [c] Percent yield of the isolated pure product.

2.8. Synthesis and characterization of products from Table 1

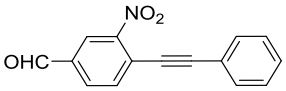
Conditions A: A mixture of selected (hetero)aryl bromide **2** (0.25 mmol), acetylene **3** (0.5 mmol), Cs_2CO_3 (163 mg, 0.5 mmol), complex **1**($2BF_4$) (2 mg, 0.0025 mmol, 1 mol%), and water (2 mL) was stirred in an ACE pressure tube for 1 h at 100 °C. The reaction mixture was cooled down to room temperature and extracted with diethyl ether (4 × 15 mL). The combined organic layers were dried over Na_2SO_4 and evaporated to dryness.

Conditions B: A mixture of selected (hetero)aryl bromide **2** (0.25 mmol), acetylene **3** (0.5 mmol), K_2CO_3 (69 mg, 0.5 mmol), complex **1**($2BF_4$) (2 mg, 0.0025 mmol, 1 mol%), and water (2 mL) was stirred in an ACE pressure tube for 4 h at 140 °C. The reaction mixture was cooled down to room temperature and extracted with ethyl acetate (4 × 15 mL). The combined organic layers were dried over Na_2SO_4 and evaporated to dryness.



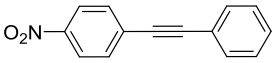
4-(phenylethynyl)benzaldehyde (**4a**; Table 1, Entry 2)

Following the procedure for Conditions B, using 4-bromobenzaldehyde (**2a**, 46 mg, 0.25 mmol) and phenylacetylene (**3a**, 51 mg, 0.5 mmol). The title product **4a** (39 mg, 75%) was obtained after flash column chromatography (hexanes/ethyl acetate = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–7.40 (m, 3H), 7.54–7.58 (m, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 10.02 (s, 1H). The data are in agreement with those from the literature.[6]



3-Nitro-4-(phenylethynyl)benzaldehyde (**4b**; Table 1, Entry 4)

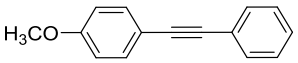
Following the procedure for Conditions B, using 4-bromo-3-nitrobenzaldehyde (**2b**, 58 mg, 0.25 mmol) and phenylacetylene (**3a**, 51 mg, 0.5 mmol). The title product **4b** (58 mg, 92%) was obtained after flash column chromatography (hexanes/ethyl acetate = 7/1). Yellow solid; mp 61–63 °C; IR 3062, 2208, 1699, 1610, 1529, 1491, 1445, 1382, 1278 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.38–7.48 (m, 3H), 7.60–7.66 (m, 2H), 7.89 (d, J = 8.1 Hz, 1H), 8.11 (dd, J_1 = 8.1 Hz, J_2 = 1.4 Hz, 1H), 8.57 (d, J = 1.4 Hz, 1H), 10.08 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 84.6, 101.9, 121.7, 124.2, 126.1, 128.6, 130.1, 132.2, 132.4, 135.46, 135.51, 149.9, 189.1; HMRS calcd for $C_{15}H_{10}NO_3$ $[M + H]^+$: 252.0655; found: 252.0657.



1-Nitro-4-(phenylethynyl)benzene (**4c**; Table 1, entries 5 and 6)

Following the procedure for Conditions B, using 1-bromo-4-nitrobenzene (**2c**, 51 mg, 0.25 mmol) and phenylacetylene (**3a**, 51 mg, 0.5 mmol). The title product **4c** (36 mg, 65%) was obtained after flash column chromatography (hexanes/ethyl acetate = 5/1).

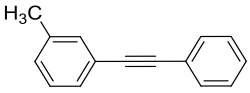
Following the procedure for Conditions A, using 1-bromo-4-nitrobenzene (**2c**, 51 mg, 0.25 mmol), phenylacetylene (**3a**, 51 mg, 0.5 mmol) and DMF/water (2:1, 2 mL) as a solvent. The title product **4c** (51 mg, 91%) was obtained after flash column chromatography (hexanes/ethyl acetate = 5/1). ^1H NMR (500 MHz, $CDCl_3$): δ 7.38–7.43 (m, 3H), 7.55–7.59 (m, 2H), 7.67 (d, J = 8.9 Hz, 2H), 8.23 (d, J = 8.9 Hz, 2H). The data are in agreement with those from the literature.[7]



1-Methoxy-4-(phenylethynyl)benzene (**4d**; Table 1, Entry 7)

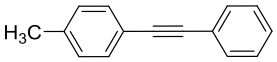
Following the procedure for Conditions B, using 4-bromoanisole (**2d**, 47 mg, 0.25 mmol), phenylacetylene (**3a**, 51 mg, 0.5 mmol) and DMF/water (2:1, 2 mL) as a solvent. The conversion into title product **4d** (36%) was determined by ^1H NMR. ^1H NMR (500 MHz, $CDCl_3$): δ 3.80 (s, 3H), 6.85 (d, J = 8.8 Hz, 2H), 7.28–7.39 (m, 3H), 7.42–7.50 (m, 4H). The data are in agreement with those from the literature.[7]

[7] S. B. Park and H. Alper, *Chem. Commun.*, 2004, 1306.



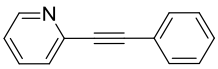
1-Methyl-3-(phenylethynyl)benzene (**4e**; Table 1, Entry 8)

Following the procedure for Conditions B, using 3-bromotoluene (**2e**, 43 mg, 0.25 mmol) and phenylacetylene (**3a**, 51 mg, 0.5 mmol). The title product **4e** (46 mg, 95%) was obtained after flash column chromatography (hexanes/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.33 (s, 3H), 7.08–7.16 (m, 2H), 7.27–7.37 (m, 5H), 7.50 (dd, J_1 = 7.9, J_2 =1.6 Hz, 2H). The data are in agreement with those from the literature.[8]



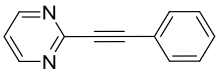
1-Methyl-4-(phenylethynyl)benzene (**4f**; Table 1, Entry 10)

Following the procedure for Conditions A, using 4-bromotoluene (**2f**, 43 mg, 0.25 mmol) and phenylacetylene (**3a**, 51 mg, 0.5 mmol) and DMF/water (2:1, 2 mL) as a solvent. The title product **4f** (42 mg, 86%) was obtained after flash column chromatography (hexanes/ethyl acetate 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.37 (s, 3H) 7.14 (d, J = 7.8 Hz, 2H), 7.30–7.38 (m, 3H), 7.42 (d, J = 7.8 Hz, 2H), 7.50–7.54 (m, 2H). The data are in agreement with those from the literature.[9]



2-(Phenylethynyl)pyridine (**4g**; Table 1, Entry 11)

Following the procedure for Conditions B, using 2-bromopyridine (**2g**, 40 mg, 0.25 mmol) and phenylacetylene (**3a**, 51 mg, 0.5 mmol). The title product **4g** (43 mg, 97%) was obtained after flash column chromatography (hexanes/ethyl acetate = 6/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20–7.35 (m, 4H) 7.53 (d, J = 7.8 Hz, 1H), 7.59–7.62 (m, 2H), 7.68 (dt, J_1 = 7.8, J_2 = 1.8 Hz, 1H), 8.61–8.65 (m, 1H). The data are in agreement with those from the literature.[10]

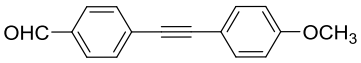


2-(Phenylethynyl)pyrimidine (**4h**, Table 1, Entry 12)

Following the procedure for Conditions B, using 2-bromopyrimidine (**2h**, 40 mg, 0.25 mmol) and phenylacetylene (**3a**, 51 mg, 0.5 mmol). The conversion into title product **4h** (66%) was determined

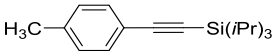
[8] T. Suzuka, Y. Okada, K. Ooshiro and Y. Uozumi, *Tetrahedron*, 2010, **66**, 1064.
[9] N. Kakusawa, K. Yamaguchi and J. Kurita, *J. Organomet. Chem.*, 2005, **690**, 2956.
[10] F. Roschangar, J. Liu, E. Estanove, M. Dufour, S. Rodríguez, V. Farina, E. Hickey, A. Hossain, P.-J. Jones, H. Lee, B. Z. Lu, R. Varsolona, J. Schröder, P. Beaulieu, J. Gillard and C. H. Senanayake, *Tetrahedron Lett.*, 2008, **49**, 363.

by ^{1}H NMR. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23–7.26 (m, 1H), 7.31–7.35 (m, 3H), 7.65–7.70 (m, 2H), 8.77 (d, J = 4.9 Hz, 2H). The data are in agreement with those from the literature.[11]



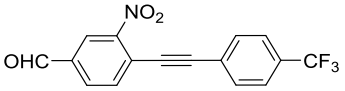
4-((4-Methoxyphenyl)ethynyl)benzaldehyde (**4i**; Table 1, Entry 13)

Following the procedure for Conditions B, using 4-bromobenzaldehyde (**2a**, 46 mg, 0.25 mmol) and 4-ethynylanisole (**3b**, 66 mg, 0.5 mmol). The title product **4i** (54 mg, 91%) was obtained after flash column chromatography (hexanes/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.85 (s, 3H), 6.91 (d, J = 8.9 Hz, 2H), 7.50 (d, J = 8.9 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H), 7.86 (d, J = 8.3 Hz, 2H), 10.01 (s, 1H). The data are in agreement with those from the literature.[12]



Triisopropyl(*p*-tolylethynyl)silane (**4j**; Table 1, Entry 14)

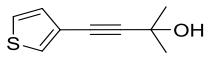
Following the procedure for Conditions B, using 4-bromotoluene (**2f**, 43 mg, 0.25 mmol) and (triisopropylsilyl)acetylene (**3c**, 91 mg, 0.5 mmol). The title product **4j** (65 mg, 95%) was obtained after flash column chromatography (hexanes/ethyl acetate = 8/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.11–1.14 (m, 21H), 2.34 (s, 3H), 7.10 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H). The data are in agreement with those from the literature.[13]



3-Nitro-4-((4-trifluoromethyl)phenyl)ethynyl)benzaldehyde (**4k**, Table 1, Entry 15)

Following the procedure for Conditions B, using 4-bromo-3-nitrobenzaldehyde (**2b**, 58 mg, 0.25 mmol) and 4-ethynyl-α,α,α-trifluorotoluene (**3d**, 85 mg, 0.5 mmol). The title product **4k** (71 mg, 89%) was obtained as yellow solid after flash column chromatography (hexanes/ethyl acetate = 6/1). R_f 0.33 (hexanes/ethyl acetate = 3/1); mp 71–73 °C; IR 2962, 2219, 1701, 1613, 1558, 1532, 1406, 1318 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.91 (d, J = 8.0 Hz, 1H), 8.14 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 8.60 (d, J = 1.5 Hz, 1H), 10.10 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 86.3, 99.5, 123.3, 123.7 (q, J = 272.9 Hz), 125.4 (q, J = 1.5 Hz), 125.5 (q, J = 3.7 Hz), 126.0, 131.5 (q, J = 32.8 Hz), 132.3, 132.4, 135.6, 136.0, 150.1, 188.9; ^{19}F NMR (471 MHz, $CDCl_3$): δ –63.0; ESI-HMRS calcd for $C_{16}H_8F_3NO_3$ $[M + H]^+$: 320.0529; found: 320.0531.

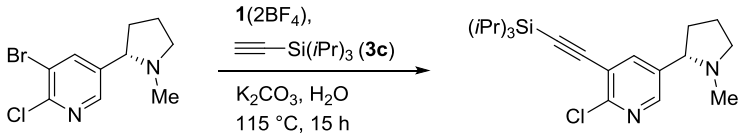
[11] U. S. Sørensen and E. Pombo-Villar, *Tetrahedron*, 2005, **61**, 2697.
[12] I. Katsuyama, P. V. Chouthaiwale, H.-L. Cui, Y. Io, A. Sando, H. Tokiwa and F. Tanaka, *Tetrahedron*, 2013, **69**, 4098.
[13] D. Castagnolo and M. Botta, *Eur. J. Org. Chem.*, 2010, 3224.



2-Methyl-4-(thiophen-3-yl)but-3-yn-2-ol (**4l**, Table 1, Entry 16)

Following the procedure for Conditions A, using 3-bromotiophene (**2i**, 41 mg, 0.25 mmol), 2-methyl-3-butyn-2-ol (**3e**, 42 mg, 0.5 mmol). The title product **4l** (36 mg, 87%) was obtained after flash column chromatography (hexanes/ethyl acetate = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.54 (s, 6H), 1.93 (br s, 1H), 7.02 (dd, J_1 = 5.0 Hz, J_2 = 1.1 Hz, 1H), 7.18 (dd, J_1 = 5.0 Hz, J_2 = 3.0 Hz, 1H), 7.35 (dd, J_1 = 3.0 Hz, J_2 = 1.1 Hz, 1H). The data are in agreement with those from the literature.[14]

2.9. Synthesis of Altinicline (SIB-1508Y) intermediate (*S*)-5-[(triisopropylsilyl)ethynyl]nicotine (4m)

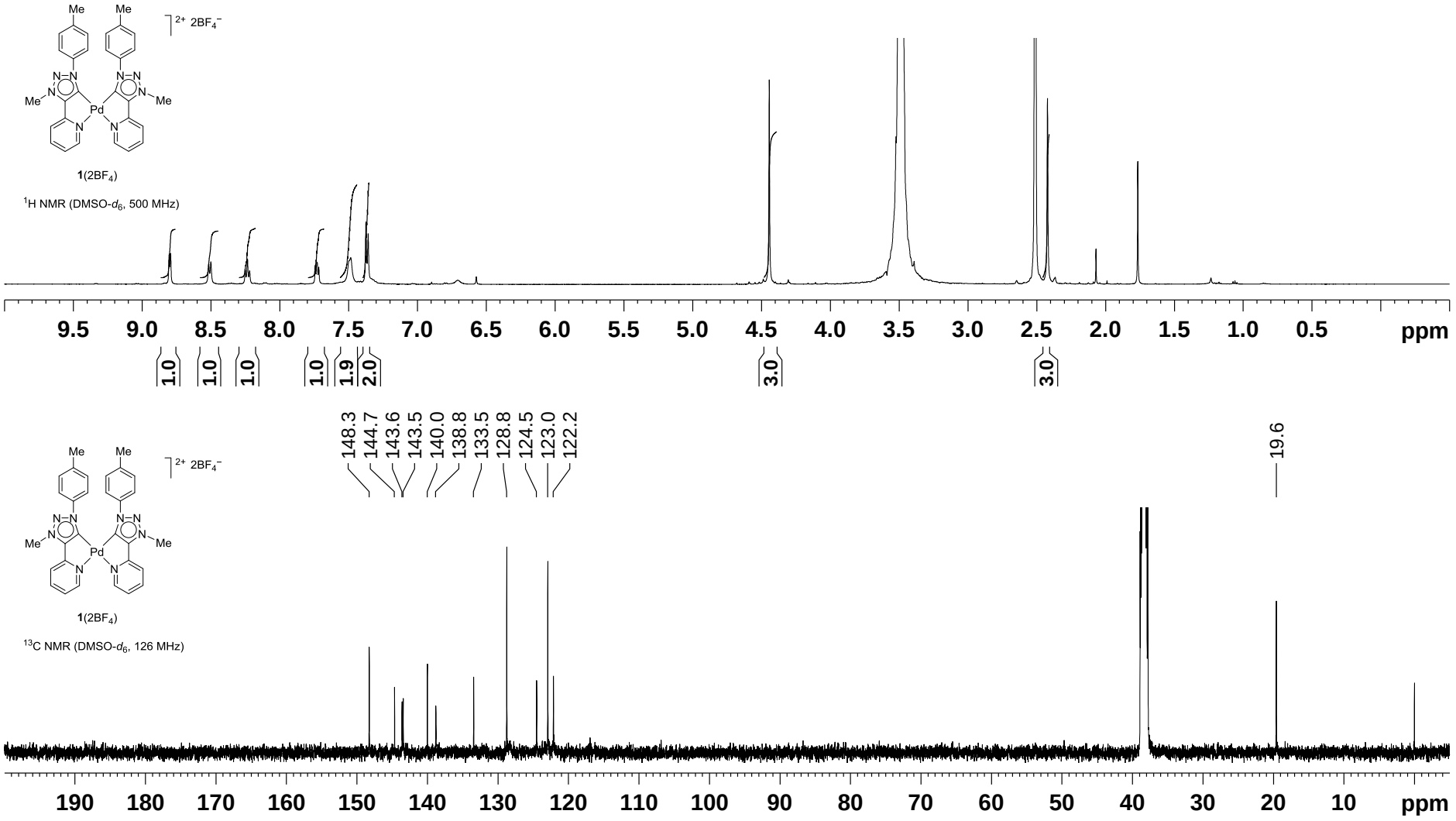


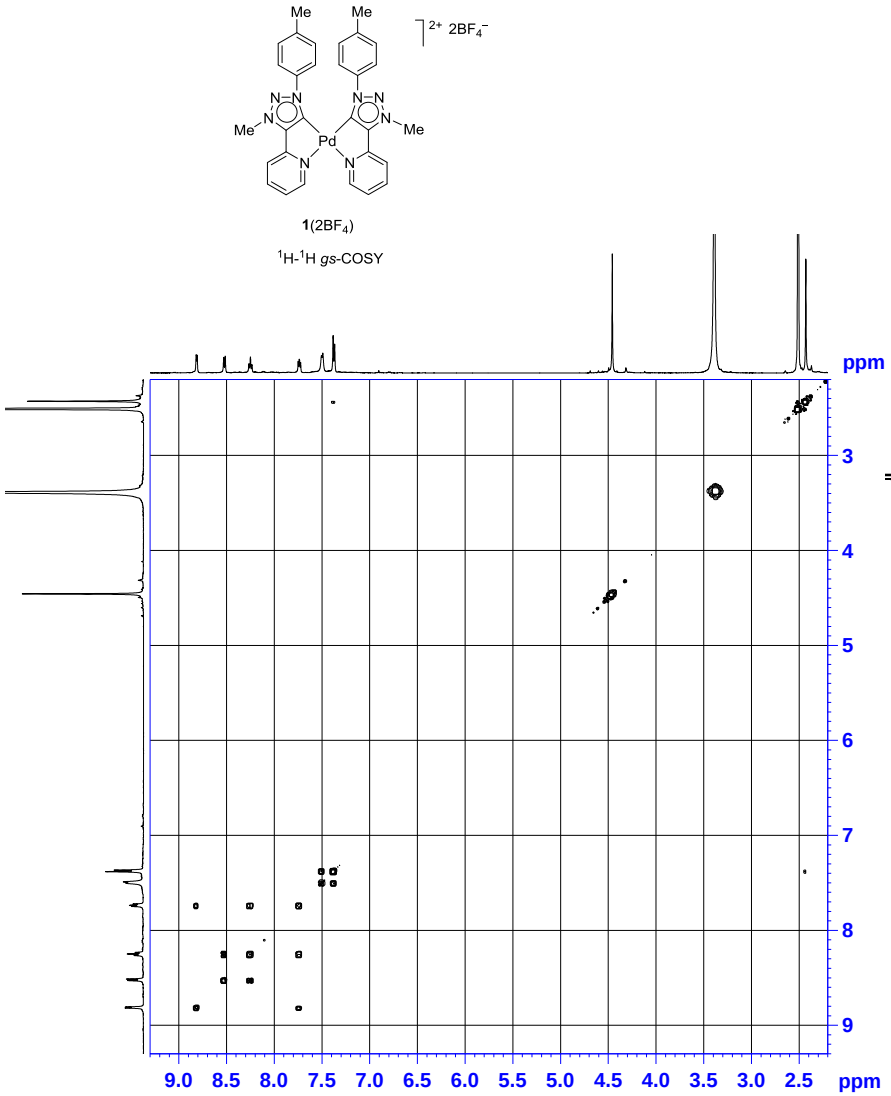
2j **4m**

A mixture of (*S*)-5-bromo-6-chloronicotine[15] (**2j**, 36 mg, 0.13 mmol), (triisopropylsilyl)acetylene (**3c**, 102 mg, 0.56 mmol), K_2CO_3 (43 mg, 0.31 mmol), complex **1**($2BF_4$) (1.0 mg, 0.0013 mmol, 1 mol%) and water (2 mL) was stirred in an ACE pressure tube for 14 h at 115 °C. The reaction mixture was cooled down to room temperature and extracted with ethyl acetate (4 × 10 mL). The combined organic layers were dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by column chromatography (hexanes/ethyl acetate = 8/1 and 1% Et_3N) to afford title product (*S*)-5-[(tiriisopropylsilyl)ethynyl]nicotine (**4m**, 40 mg, 82%) as yellow oil. R_f 0.55 (hexanes/ethyl acetate = 4/1 and 1% Et_3N); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13–1.18 (m, 21H), 1.65–1.73 (m, 1H), 1.77–1.86 (m, 1H), 1.90–2.01 (m, 1H), 2.18 (s, 3H), 2.19–2.24 (m, 1H), 2.27–2.35 (m, 1H), 3.08 (t, J = 8.3 Hz, 1H), 3.21–3.27 (m, 1H), 7.81 (d, J = 2.3 Hz, 1H), 8.22 (d, J = 2.3 Hz, 1H). The data are in agreement with those from the literature.[16] Optical rotation: $[\alpha]_D^{22}$ –141 (c 0.59, CH_2Cl_2) is in agreement with the literature report:[16] $[\alpha]_D^{31}$ –109 (c 0.35, CH_2Cl_2).

[14] C. Torborg, J. Huang, T. Schulz, B. Schäffner, A. Zapf, A. Spannenberg, A. Börner and M. Beller, *Chem. – Eur. J.*, 2009, **15**, 1329.
[15] F. F. Wagner and D. L. Comins, *Eur. J. Org. Chem.*, 2006, 3562.
[16] F. F. Wagner and D. L. Comins, *J. Org. Chem.*, 2006, **71**, 8673.

3. COPIES OF NMR SPECTRA

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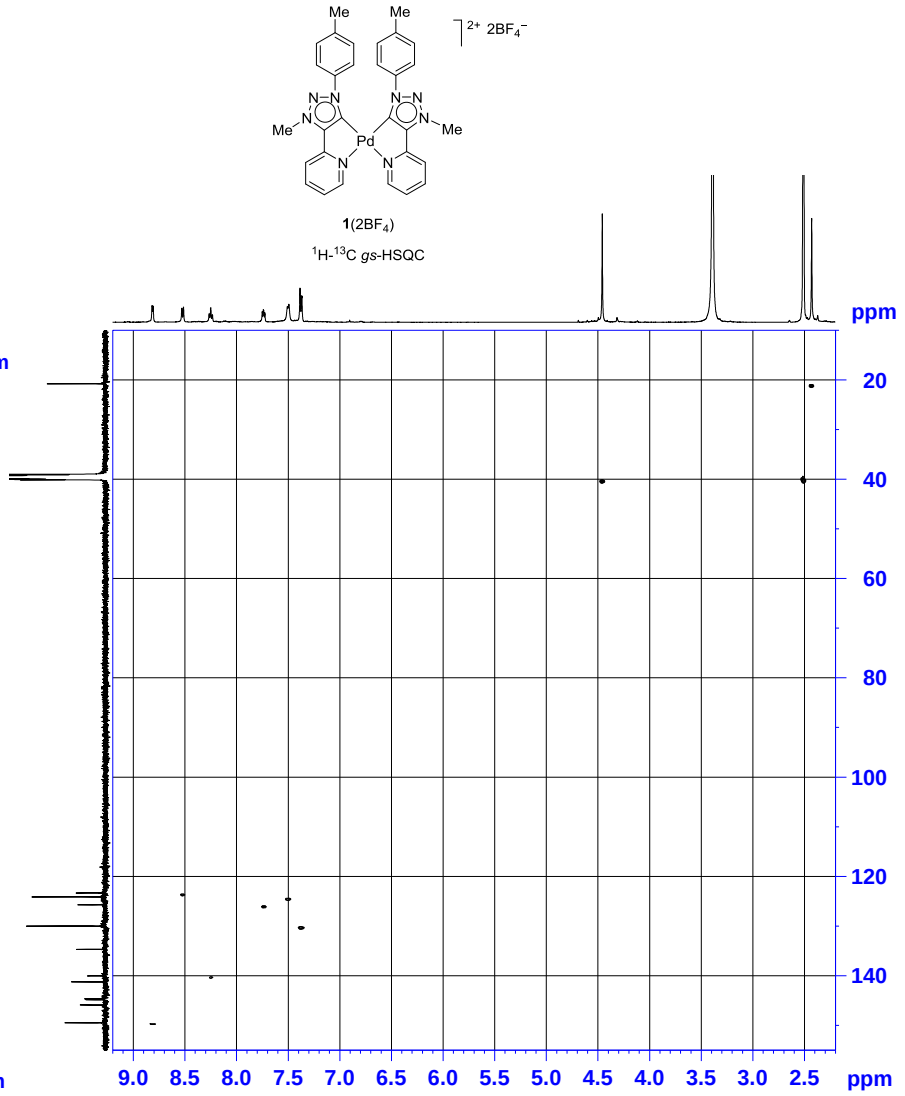
Me
Pd
Me
1(2BF4)
1H-1H gs-COSY
ppm
3
4
5
6
7
8
9
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm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Pd
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140
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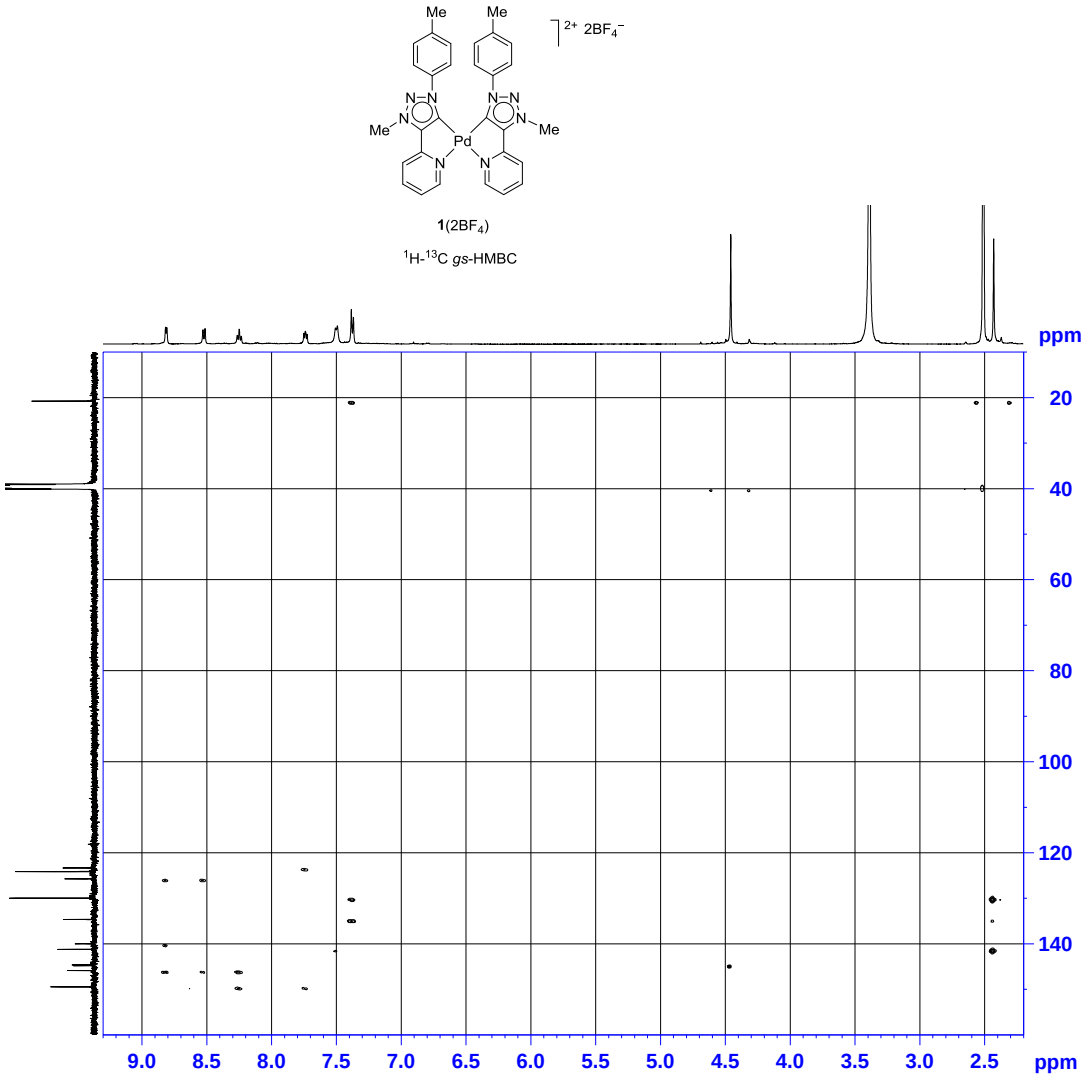
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Pd
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60
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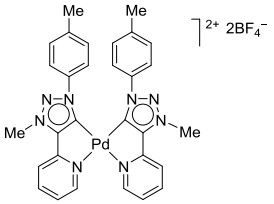
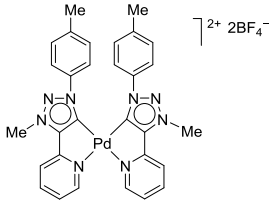
100
120
140
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm



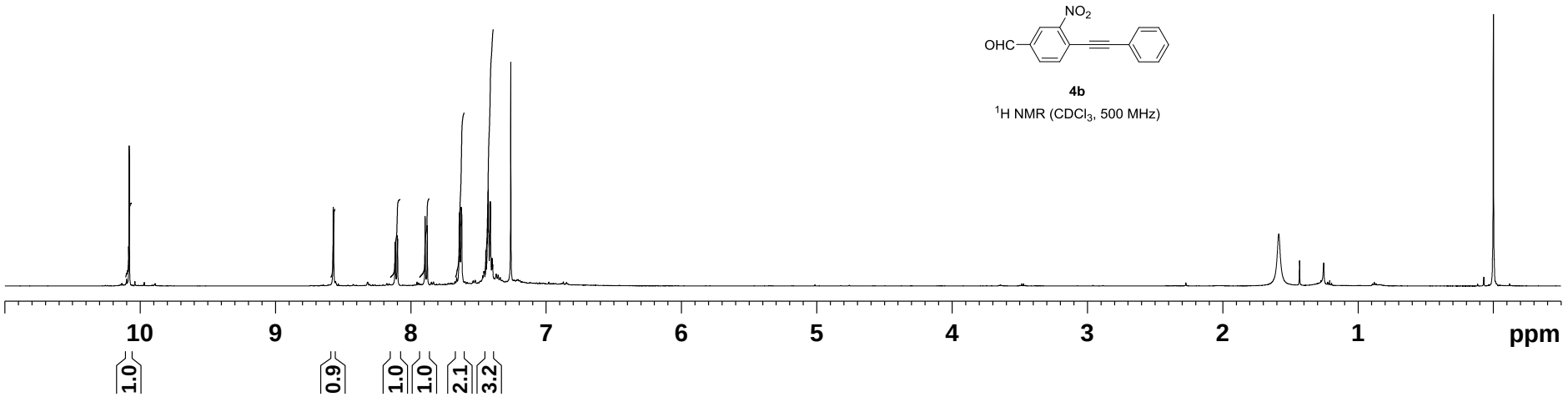
1($2BF_4$)

^{19}F NMR (DMSO-d_6, 471 MHz)



1($2BF_4$)

^{11}B NMR (DMSO-d_6, 160 MHz)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OHC
4b
1H NMR (CDCl3, 500 MHz)
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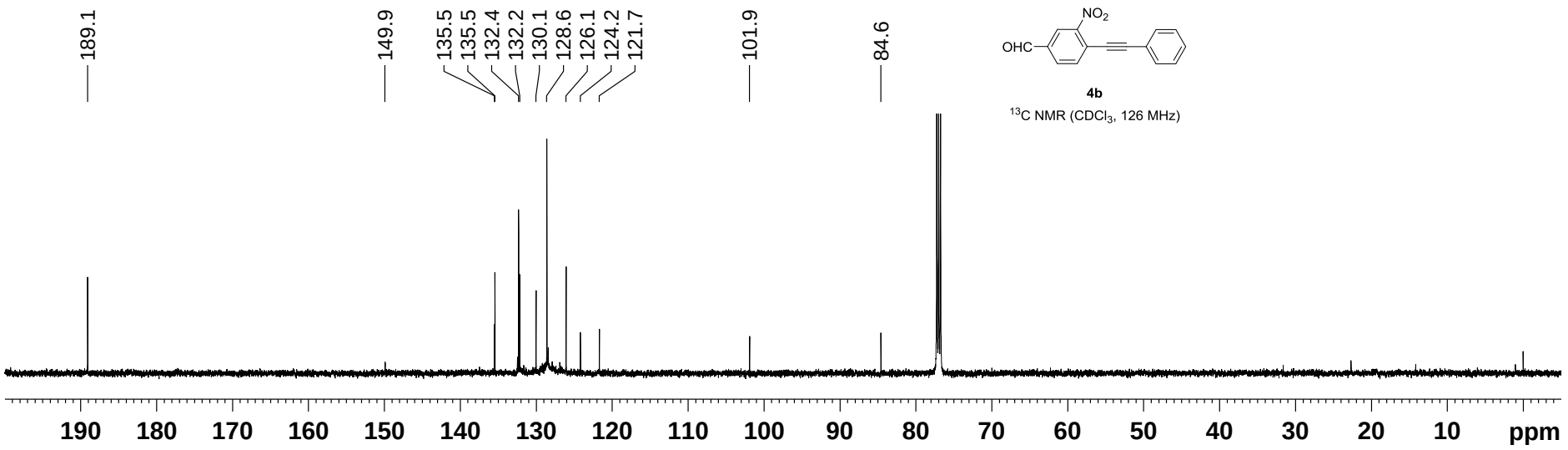
9
8
7
6
5
4
3
2
1
ppm
1.0
0.9
1.0
1.0
2.1
3.2


189.1
149.9
135.5
135.5
132.4
132.2
130.1
128.6
126.1
124.2
121.7
101.9
84.6
NO2
OHC
4b
13C NMR (CDCl3, 126 MHz)
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150
140
130
120
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80
70
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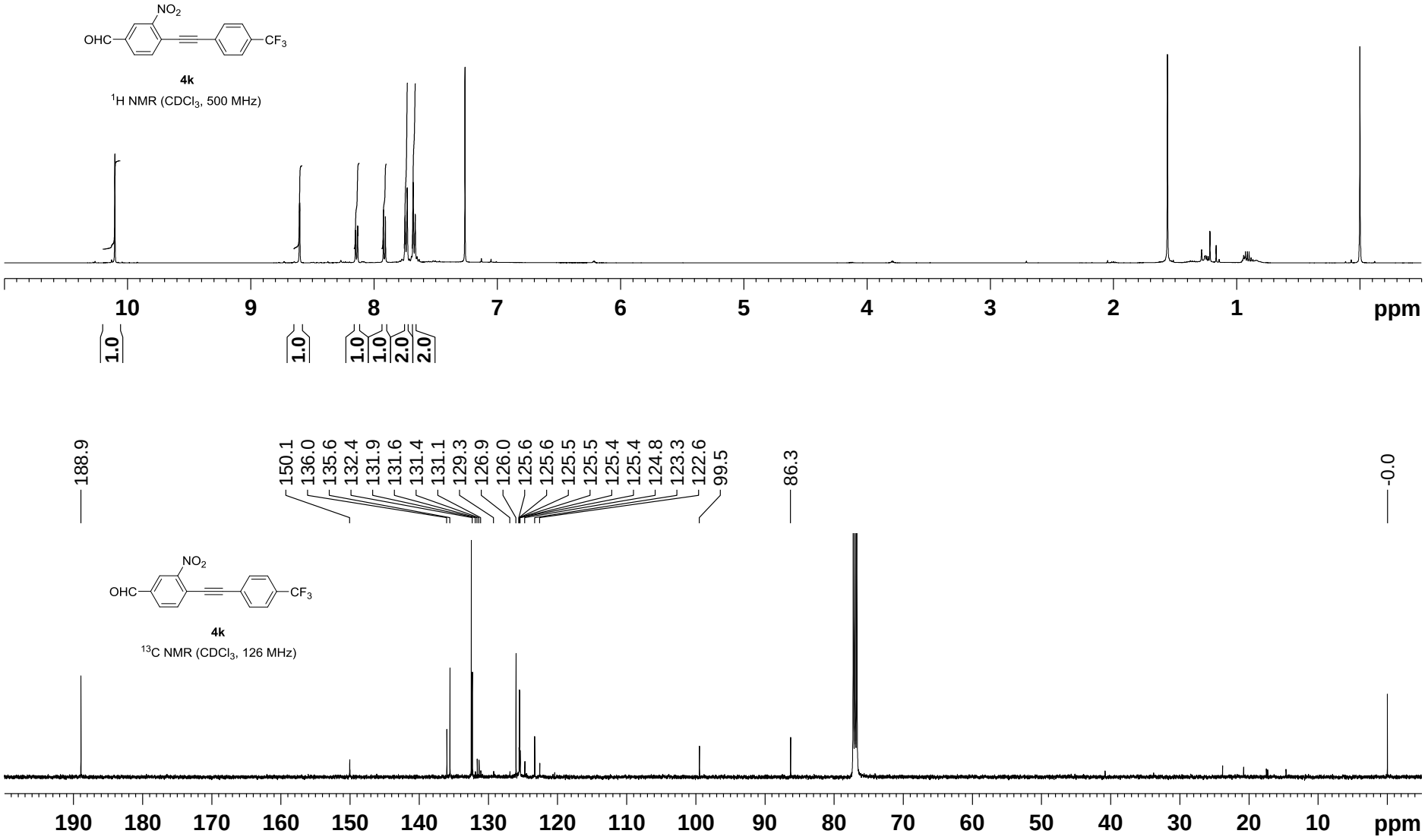
30
20
10
ppm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OHC
CF3
4k
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1.0
1.0
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2.0
2.0
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125.4
125.4
124.8
123.3
122.6
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NO2
OHC
CF3
4k
13C NMR (CDCl3, 126 MHz)
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140
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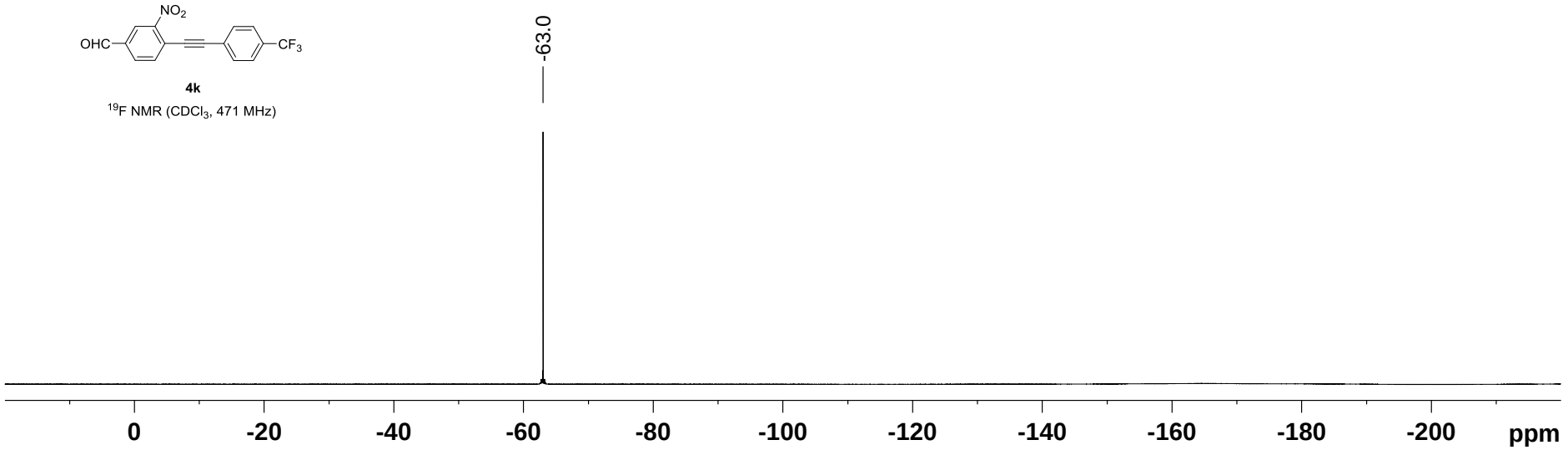
80
70
60
50
40
30
20
10
ppm


NO2
OHC
CF3
4k
19F NMR (CDCl3, 471 MHz)
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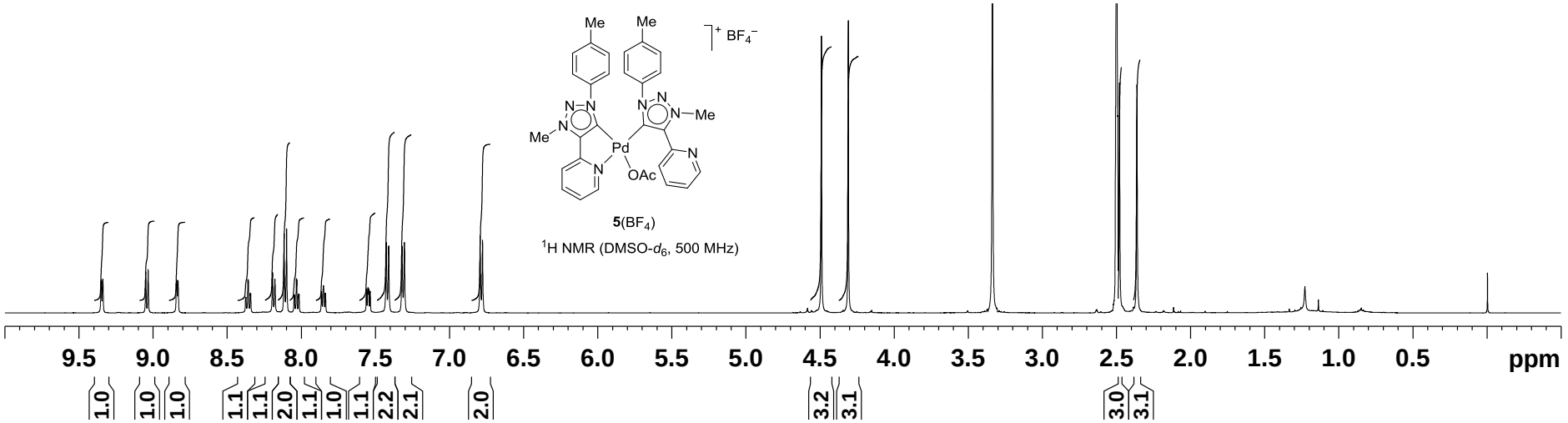
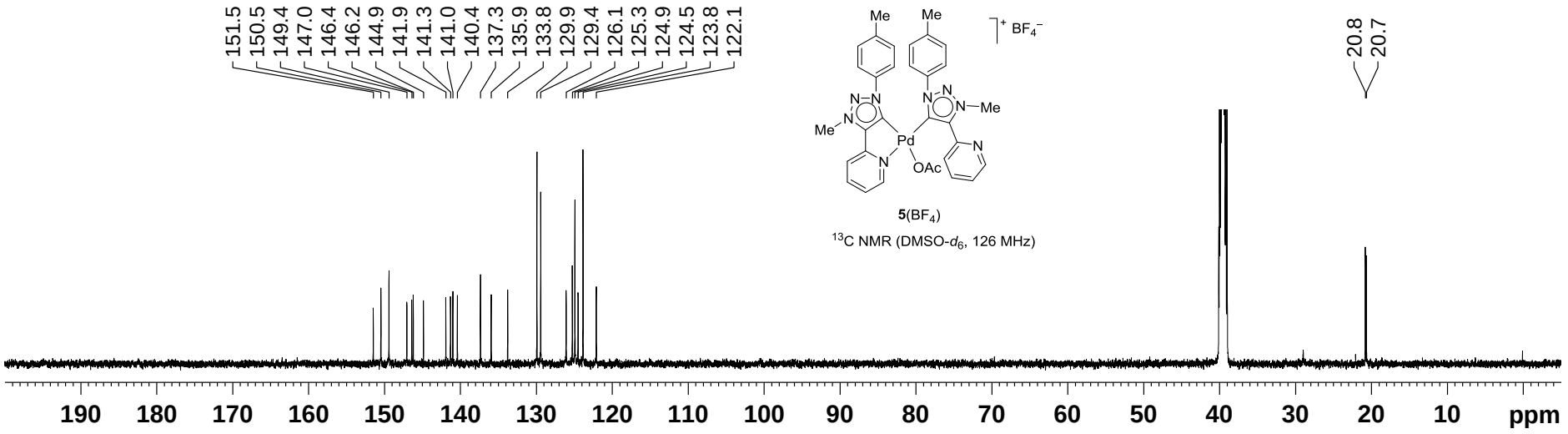
ppm



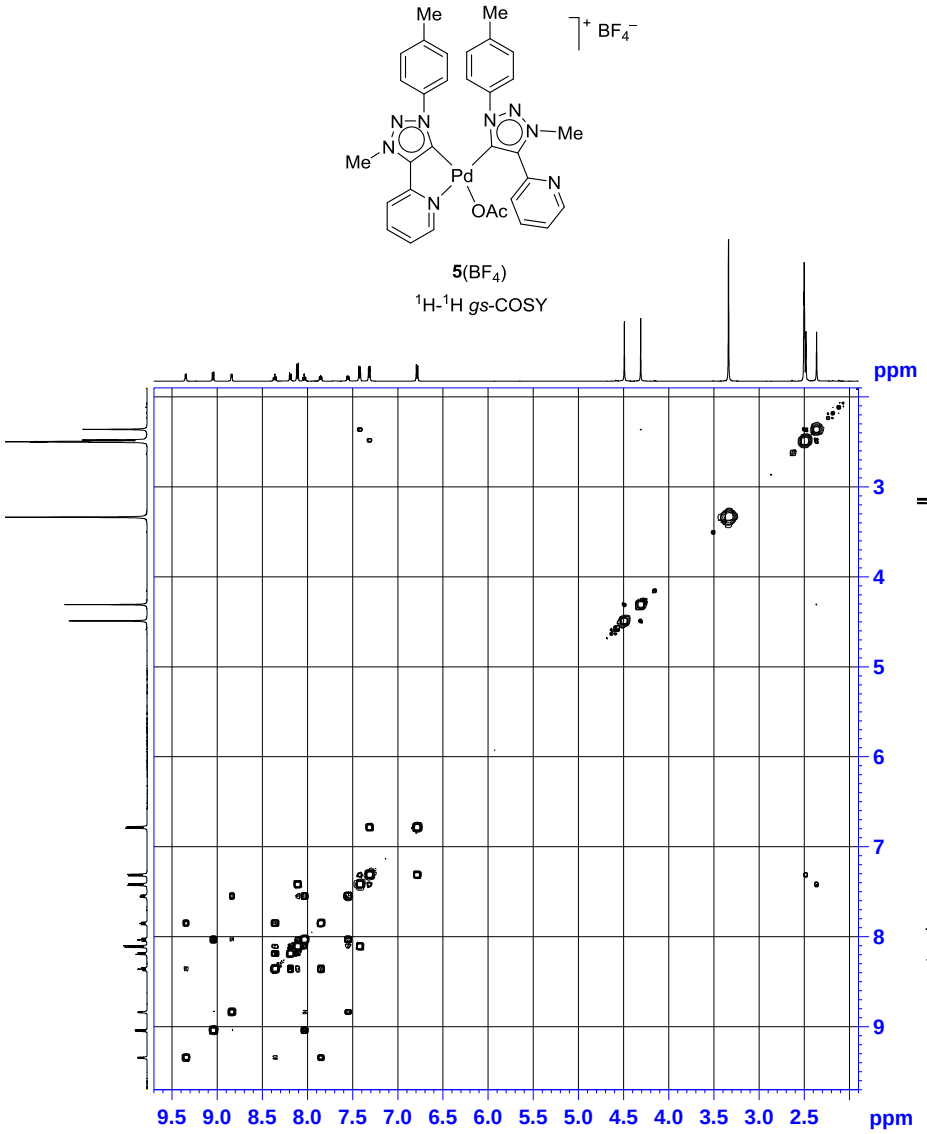
5(BF_4)

^{1}H NMR (DMSO-d_6, 500 MHz)



5(BF_4)

^{13}C NMR (DMSO-d_6, 126 MHz)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OAc
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1H-1H gs-COSY
ppm
3
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5
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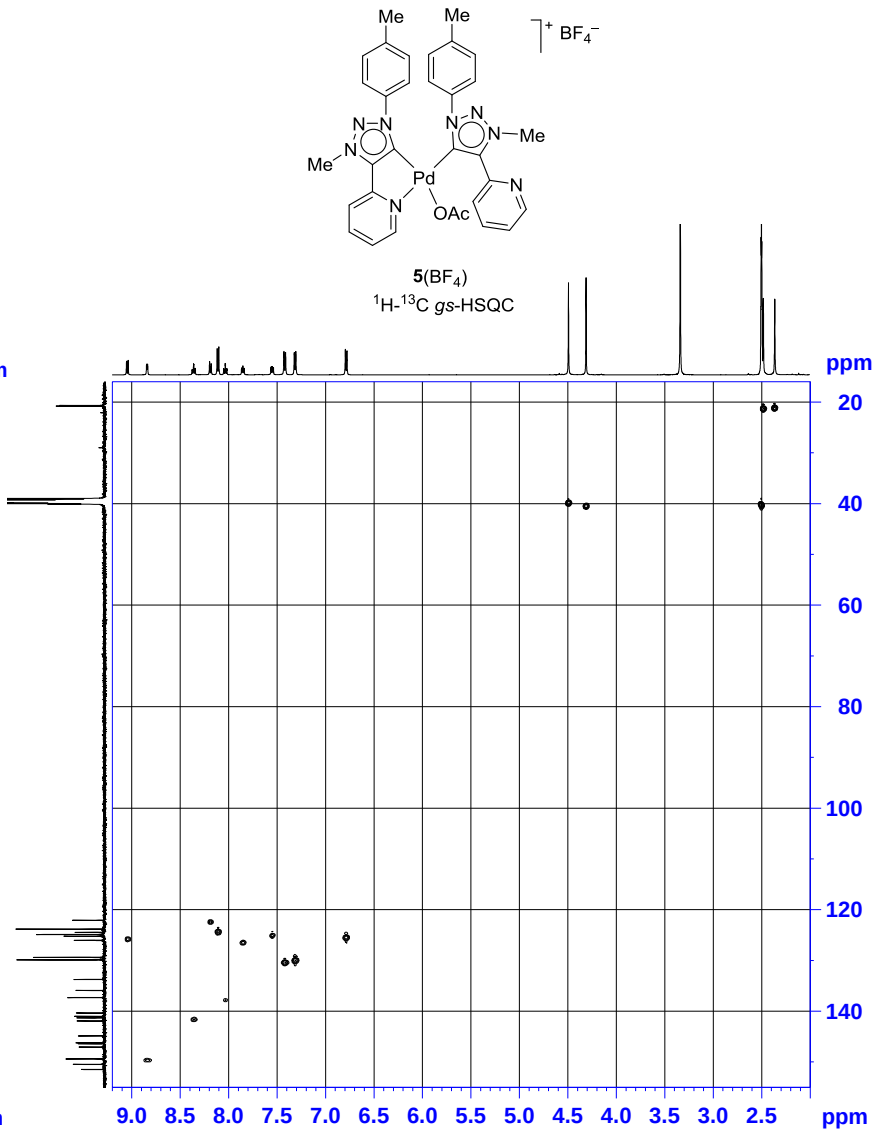
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Me
Me
N
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N
N
Me
Pd
N
OAc
N
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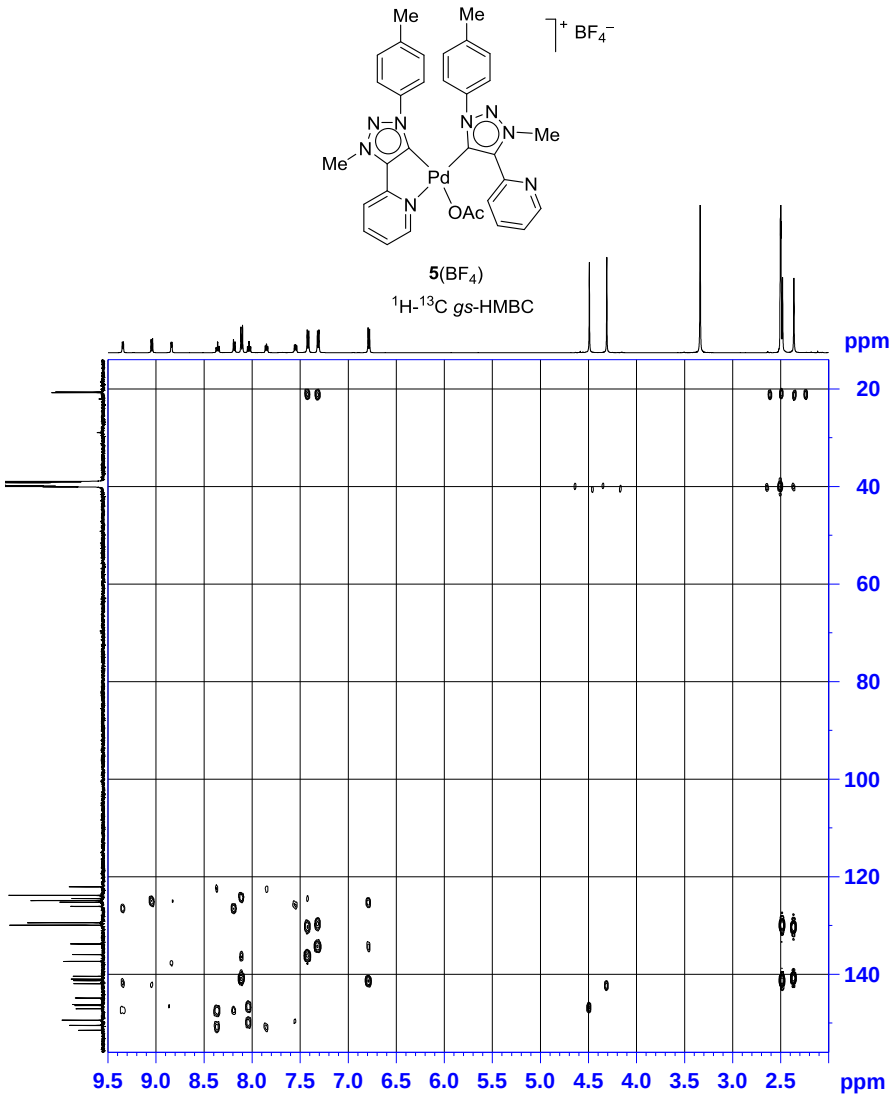
ppm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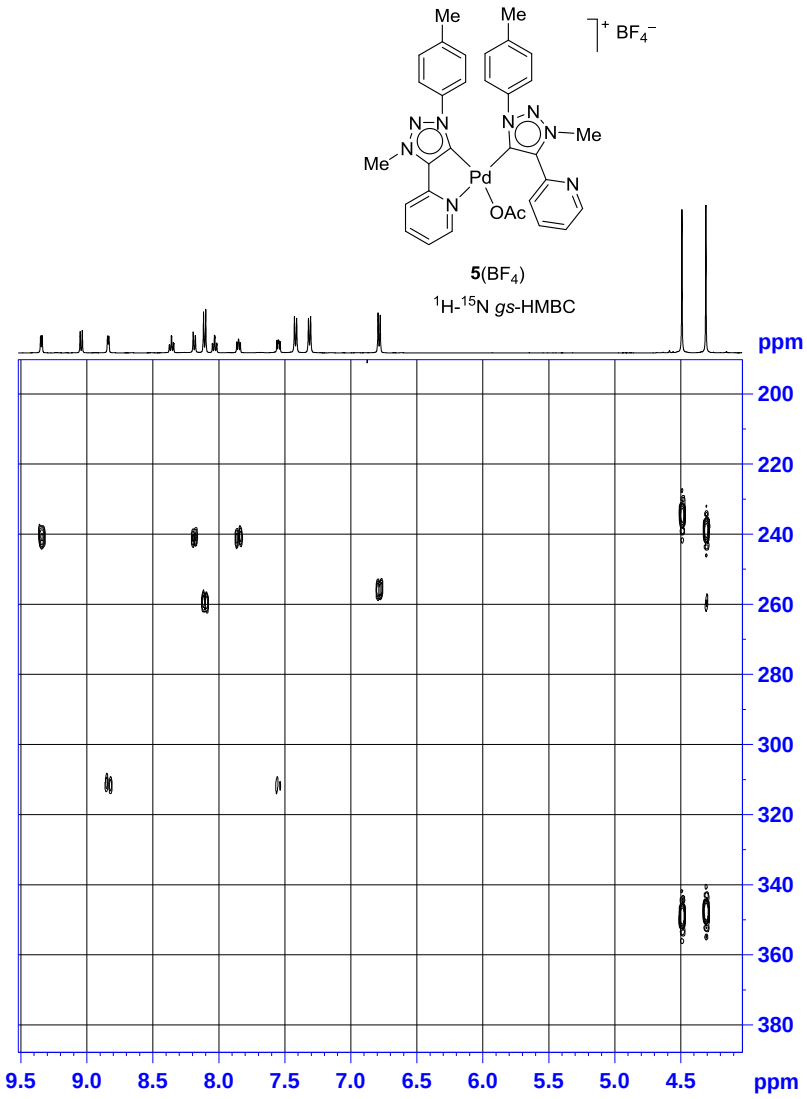
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ppm