Electronic Supplementary Information for Dalton Transactions

A new chiral di-*N*-heterocyclic carbene (NHC) cyclophane ligand and its application in palladium enantioselective catalysis.

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Synthetic details:

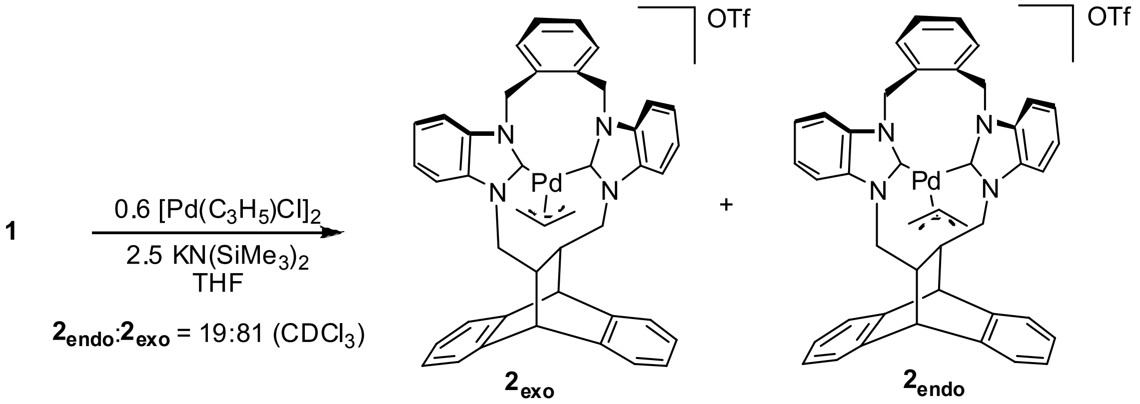
General Considerations.

Unless specified otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk or glovebox techniques. Glassware was oven dried before use. Acetonitrile (CH_3CN) and tetrahydrofuran (THF) were dried using a GlassContours drying column. $CDCl_3$, acetone-d_6, and DMSO-d_6 were purchased from Cambridge Isotopes and used as is. Chloro(allyl)palladium(II) dimer was purchased from Strem Chemicals Co. and used without further purification. Potassium bis(trimethylsilyl)amide ($KN(SiMe_3)_2$), α,α'-dibromo-*o*-xylene, potassium hydroxide (KOH), anhydrous potassium carbonate (K_2CO_3), ether, hexanes, THF, methanol (MeOH) and dioxane was purchased from Fisher Scientific and used without further purification. NMR spectra were recorded on a Varian INOVA spectrometer, operating at 500 MHz for ^1H and 125 MHz for ^{13}C. Chemical shifts are reported in ppm relative to tetramethylsilane, and were referenced to the residual ^1H signal of the solvent. Mass spectrometry was performed at the in-house facility of the Department of Chemistry at the University of Florida. Elemental analyses were performed at either the in-house facility of the Department of Chemistry at the University of Florida or Complete Analysis Inc., Parsippany, NJ. For HPLC analysis, a Shimadzu prominence system with a LC-20AT solvent delivery module, DGU-20A3 degasser, SPD-20A UV-vis detector (254 nm), and a CBM-20A system controller were used.

Synthesis of 1,1'-(α,α'-*o*-xylyl)-3,3'-*trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-(bibenzimidazolium)bis(trifluoromethanesulfonate) [DEAM-*o*-XYLBI][OTf]$_2$ (1).

To an oven dried 100 mL round bottom with a stir bar was added 2.00 g (3.77 mmol) of 9,10–dihydro–9,10–ethanoanthracene–11,12–diyldimethanediyl *bis*(trifluoromethanesulfonate)[1], 1.29 g (3.8 mmol) α,α'-di(*N*-benzimidazolyl)-*o*-xylene[2] and 50 mL of dry CH_3CN. The reaction was stirred under argon at reflux. After 16 hours, the reaction was cooled and then the CH_3CN was removed in vacuo and the resulting solids triturated with acetone (3x5 mL) until a pale yellow solid was obtained. Ethanol (50 mL, 200 proof) was then added and the reaction was gently heated while agitating the flask. After 10-15 minutes, a white precipitate formed. This material was filtered and washed with diethyl ether, leaving a powdery white solid (1.20 g, 36%). Anal. Calc. for $C_{42}H_{34}N_4S_2O_6F_6$: C, 58.07%; H, 3.95%; N, 6.45%. Found: C, 57.773%; H, 3.856%; N, 6.372%. ^{1}H NMR (499.80 MHz, acetone-*d$_6$*, @50 °C, δ: 8.88 (s, 2H, NC*H*N), 8.00 (d, *J* = 15 Hz, aromatic), 7.92 (dd, *J* = 5 Hz, *J* = 1 Hz, aromatic), 7.72 (ddd, *J* = 10 Hz, *J* = 5 Hz, *J* = 5 Hz, 2H, aromatic) 7.52 (d, *J* = 5 Hz, 2H, aromatic), 7.44 (d, *J* = 5 Hz, 2H, aromatic), 7.35 (dd, *J* = 5 Hz, *J* = 5 Hz, 3H, aromatic), 7.27-7.17 (m, 7H, aromatic), 5.93 (br s, 4H, NC*H*C), 4.86 (s, 2H, CC*H*C), 4.72 (d, *J* = 15 Hz, 2H, NC*H*$_2$CH), 3.35 (dd, *J* = 15 Hz, *J* = 10 Hz, 2H, NC*H*$_2$CH), 2.64 (d, *J* = 10 Hz, 2H, NCH$_2$C*H*). ^{13}C{^{1}H} NMR (125.69 MHz, acetone-*d$_6$*, 25 °C, δ): 142.61, (s, *C*CHC), 141.97 (br s, N*C*HN), 140.90 (s, CCH*C*), 135.28 (s, N*C*CH$_2$), 132.94 (s, N*C*CH), 132.47 (s, N*C*CH), 131.13 (s, aromatic), 128.53 (s, aromatic), 128.45 (s, aromatic), 127.65 (s, aromatic), 127.28 (s, aromatic), 125.84 (s, aromatic), 125.40 (s, aromatic), 122.15 (q, *J* = 534 Hz, *C*F$_3$), 114.50 (s, CHCH$_2$N*C*CH), 113.43 (br s, CCH$_2$N*C*CH), 53.36 (br s, N*C*H$_2$CH), 49.52 (s, C*C*HC), 48.44 (s, NCH$_2$*C*H), 45.96 (s, N*C*H$_2$C).

Synthesis of (1,1'-(α,α'-*o*-xylyl)-3,3'-trans-9,10-dihydro-9,10-ethanoanthracene-11,12-bis(benzimidazolidine-2-ylidene)palladium(II)(η^3-allyl) triflate, [(DEAM-*o*-XYLBI)Pd(η^3-C$_3$H$_5$)][OTf] (2).



Three solutions were prepared in a glovebox: (A) 476 mg (0.549 mmol) **1** in 2 mL THF, (B) 276 mg (1.38 mmol) KN(SiMe$_3$)$_2$ in 2 mL THF and (C) 120 mg (0.327 mmol) [Pd(C$_3$H$_5$)Cl]$_2$ in 2 mL THF. Solution A was vigorously stirred for 2 minutes and then all three solutions were chilled to -35 °C. After the solutions were at -35 °C, solution B was added to a vigorously stirring solution of A. After five minutes the combined AB solution was rechilled to -35 °C. Solution C was then added to solution AB and the final ABC solution was stirred. After 2-3 minutes solution ABC was placed in a -35 °C refrigerator overnight. The solution was then brought outside the oven and stirred for an additional 3 hours at room temperature. A white precipitate formed and was filtered. Crystals were grown in a vial on the benchtop by a slow diffusion of hexanes into 3:1 THF/CHCl$_3$ solution of **2** to provide long colorless needles in 37% yield (184 mg). Anal. Calc. for C$_{44}$H$_{37}$N$_4$SPdO$_3$F$_3$: C, 61.08%; H, 4.31%; N, 6.48%. Found: C, 60.97%; H, 4.35%; N, 6.38%. Due to the mixture of isomers (*endo*:*exo* 19:81), only some resonances can be assigned. The assignments are made according to the key below in CDCl$_3$ at 499.80 MHz (^{1}H). ^{13}C{^{1}H} NMR (125.69 MHz, CDCl$_3$, 25 °C, δ): 187.72, 186.87, 141.96, 141.66, 141.47, 141.30, 140.25, 140.19, 139.97, 135.75, 134.78, 134.69, 134.58, 134.53, 134.10, 133.37, 133.32, 133.26, 133.00, 132.58, 129.28, 128.92, 127.09, 126.96, 126.62, 126.56, 126.43, 125.75, 125.60, 125.14, 125.09, 124.78, 124.69, 124.31, 124.27, 124.11, 124.04, 123.90, 123.79, 119.72, 117.72, 112.21, 111.84, 111.17, 111.03, 109.62, 109.24, 109.10, 60.76, 57.00, 56.63, 50.45, 49.91, 49.50, 48.82, 48.75, 48.43, 43.18, 43.11. MS(HR–ESI-FTICR+):Calc. for [C$_{43}$H$_{37}$N$_4$Pd]$^+$: m/z 715.2063 M$^+$, Found m/z 715.2132.

Assignment key.

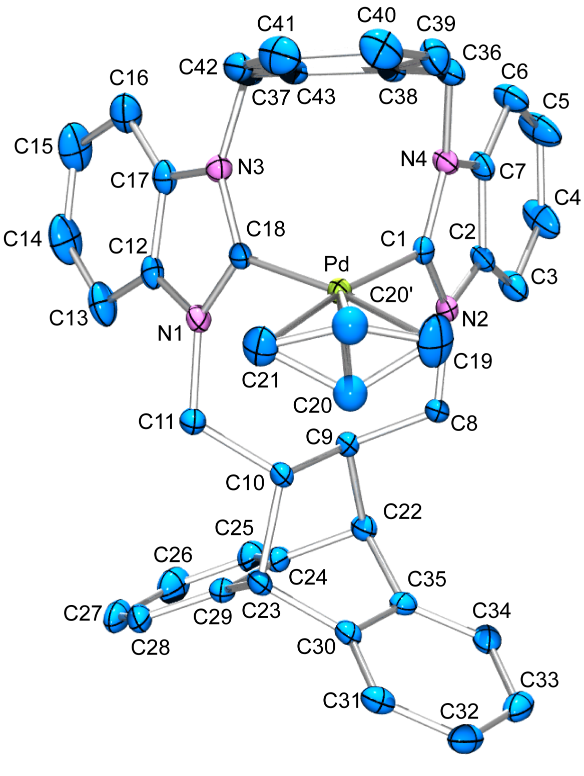
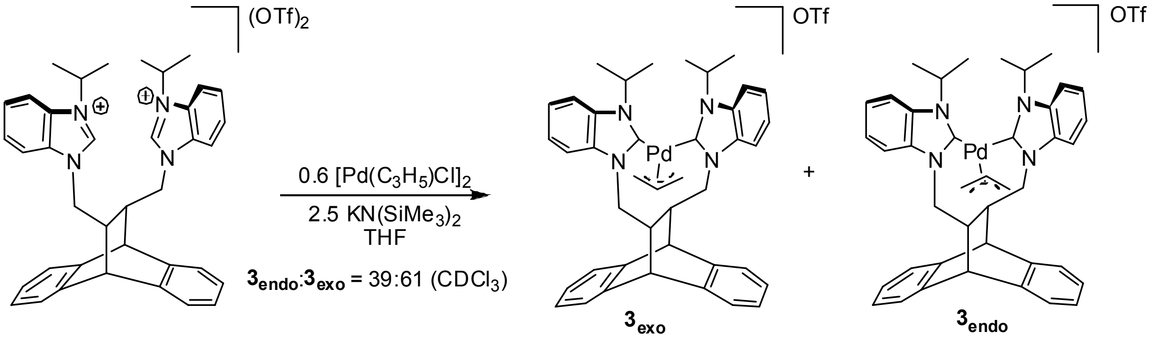


Table S1: Key for proton assignments for **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)**.

C#	Ppm	ppm
26	7.15-7.52	7.15-7.52
27	7.15-7.52	7.15-7.52
28	7.15-7.52	7.15-7.52
23	4.38	4.35
31	7.51	7.15-7.52
32	7.42	7.15-7.52
33	7.44	7.15-7.52
34	7.15	7.15-7.52
22	4.24	4.24
25	7.15-7.52	7.15-7.52
9	1.11	1.36
8	4.13, 3.10	3.26, 4.34
10	3.12	3.46
11	3.59, 4.15	3.61, 4.18
21	1.30, 3.58	2.56, 3.41
20	5.1	3.71
19	1.08, 3.92	2.19, 3.26
37	5.99	5.95
36	6.08	6.11
42	7.41	7.15-7.52
41	7.43	7.15-7.52
40	7.43	7.15-7.52
39	7.45	7.15-7.52
6	7.83	7.15-7.52
5	7.43	7.15-7.52
4	7.41	7.15-7.52
3	7.22	7.15-7.52
13	5.99	7.15-7.52
14	6.97	7.15-7.52
15	7.21	7.15-7.52
16	7.60	7.15-7.52
	exo	*endo*

Synthesis of *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-bis(1-*iso*propyl-benzimidazolidine-2-ylidene) palladium (II) (η^3-allyl) triflate, [(DEAM-IBY)Pd(η^3-C_3H_5)][OTf] (3).



3$_{\mathbf{exo}}$ **3**$_{\mathbf{endo}}$

Two solutions were prepared in a glovebox: (A) 200 mg (0.235 mmol) *trans*-1,1'-[9,10-dihydro-9,10-ethanoanthracene-11,12-diyldimethane]*bis*(3-isopropyl-1H-benzimidazol-3-ium) *bis*(trifluoromethansulfonate)[3] and 171 mg (0.526 mmol) Cs_2CO_3 in 2 mL THF, (B) 47 mg (0.128 mmol) [Pd(C_3 in 3 mL THF. Solution A was stirred for 2 minutes and B was added at room temperature. Solution AB was then stirred for 16 h at room temperature and then removed from the glovebox. The solution was filtered through a medium fritted funnel and the filtrate was dropped into 35 mL of hexanes. The precipitate was filtered leaving **3** as a white solid in 94% yield (187 mg). Complex 3 is isolated as a mixture of isomers (*endo*: *exo* 39:61), thus not all resonances can be assigned. Calc. for $C_{42}H_{42}N_4SPdO_3F_3$: C, 59.61%; H, 5.00%; N, 6.62%. Found: C, 59.49%; H, 5.03%; N, 6.76%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 7.81-7.74 (m, aromatic), 7.52-7.47 (m, aromatic), 7.29-7.09 (m, aromatic), 5.70 (*endo*, sept, J = 6 Hz, 0.67H, CH(CH_3)$_2$), 5.46 (*exo*, sept, J = 6 Hz, 1H, CH(CH_3)$_2$), 5.22 (*exo*, sept, J = 6 Hz, 1H, CH(CH_3)$_2$), 5.12 (*endo*, sept, J = 6 Hz, 0.67H, CH(CH_3)$_2$), 4.95-4.81 (1 *exo* and 1 *endo*, m, 1.67H, PdCHCH$_2$ (*exo*), PdCHCH_2 (*endo*)), 4.64 (*endo*, s, 0.67H, CCHC), 4.59

(*exo*, s, 1H, $\mathrm{CC}H\mathrm{C}$), 4.42 (*endo*, dd, J = 6 Hz, J = 9 Hz, 0.67H, $\mathrm{NCH_2C}H$), 4.27-4.14 (1 *exo* and 2 *endo*, m, 2.34H, $\mathrm{PdCHC}H_2$ (*exo*), $\mathrm{NC}H_2$(*endo*), $\mathrm{NC}H_2$ (*endo*)), 4.08 (*endo*, s, 0.67H, $\mathrm{CC}H\mathrm{C}$), 3.94 (*exo*, s, 1H, $\mathrm{CC}H\mathrm{C}$), 3.84-3.63 (3 *exo* and 3 *endo*, m, 5.01H, $\mathrm{PdCHC}H_2$ (2 *exo* and 2 *endo*), $\mathrm{PdC}H\mathrm{CH_2}$ (*endo*), $\mathrm{NC}H_2$ (*exo*)), 3.38 (*exo*, dd, J = 9 Hz, J = 12 Hz, 1H, $\mathrm{NCH_2C}H$), 3.12 (*exo*, d, J = 12 Hz, 1H, $\mathrm{NC}H_2$), 2.97 (*exo*, d, J = 9 Hz, 1H, $\mathrm{NC}H_2$), 2.57 (*endo*, d, J = 12 Hz, 0.67H, $\mathrm{NC}H_2$), 2.41 (*exo*, d, J = 12 Hz, 1H, $\mathrm{NC}H_2$), 2.39 (*endo*, d, J = 12 Hz, 0.67H, $\mathrm{NC}H_2$), 2.00 (1*exo* and 1 *endo*, m, 1.67H, $\mathrm{NCH_2C}H$ (*exo* and *endo*)), 1.87 (*endo*, d, J = 9 Hz, 2H, $\mathrm{CH(C}H_3)_2$), 1.81 (1 *endo* and 2 *exo*, d, J = 6 Hz, 8H, $\mathrm{CH(C}H_3)_2$), 1.71 (*endo*, d, J = 6 Hz, 3H, $\mathrm{CH(C}H_3)_2$), 1.58 (*exo*, d, J = 6 Hz, 3H, $\mathrm{CH(C}H_3)_2$), 1.49 (*endo*, d, J = 6 Hz, 2H, $\mathrm{CH(C}H_3)_2$), 1.21 (*exo*, d, J = 9 Hz, 3H, $\mathrm{CH(C}H_3)_2$), 1.08 (1 *exo* and 1 *endo*, d, J = 6 Hz, 1.67H, $\mathrm{PdCHC}H_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125.69 MHz, $\mathrm{CDCl_3}$, 25 °C, δ): 186.17 (*exo* $\mathrm{N}C\mathrm{N}$), 185.76 (*endo* $\mathrm{N}C\mathrm{N}$), 185.08 (*endo* $\mathrm{N}C\mathrm{N}$), 185.03 (*exo* $\mathrm{N}C\mathrm{N}$), 144.23 (*exo* $\mathrm{CCH}C$), 144.20 (*endo* $\mathrm{CCH}C$), 143.99 (*exo* $\mathrm{CCH}C$), 138.19 (*exo* $\mathrm{CCH}C$), 138.14 (*endo* $\mathrm{CCH}C$), 138.02 (*endo* $\mathrm{CCH}C$), 137.94 (*exo* $\mathrm{CCH}C$), 137.93 (*endo* $\mathrm{CCH}C$), 136.53 (*exo* $\mathrm{N}C\mathrm{CH}$), 136.45 (*endo* $\mathrm{N}C\mathrm{CH}$), 135.64 (*exo* $\mathrm{N}C\mathrm{CH}$), 135.61 (*endo* $\mathrm{N}C\mathrm{CH}$), 132.13 (*exo* $\mathrm{N}C\mathrm{CH}$), 132.03 (*endo* $\mathrm{N}C\mathrm{CH}$), 131.73 (*endo* $\mathrm{N}C\mathrm{CH}$), 131.54 (*exo* $\mathrm{N}C\mathrm{CH}$), 126.94, 126.87, 126.65, 126.59, 126.54, 126.52, 126.47, 125.91, 125.80, 125.24, 125.17, 124.05, 124.01, 123.95, 123.89, 123.80, 123.68, 123.59, 123.55, 123.53, 122.78, 122.09, 121.75, 119.27, 118.62, 113.32 (*endo* $\mathrm{NC}C\mathrm{H}$), 113.28 (*exo* $\mathrm{NC}C\mathrm{H}$), 112.35 (*endo* $\mathrm{NC}C\mathrm{H}$), 112.31 (*exo* $\mathrm{NC}C\mathrm{H}$), 111.27 (*endo* $\mathrm{NC}C\mathrm{H}$), 111.21 (*exo* $\mathrm{NC}C\mathrm{H}$), 110.03 (*endo* $\mathrm{NC}C\mathrm{H}$), 109.92 (*exo* $\mathrm{NC}C\mathrm{H}$), 62.15 (*endo* $\mathrm{PdCH}C\mathrm{H_2}$), 62.14 (*endo* $\mathrm{PdCH}C\mathrm{H_2}$), 61.60 (*exo* $\mathrm{PdCH}C\mathrm{H_2}$), 59.59 (*exo* $\mathrm{PdCH}C\mathrm{H_2}$), 56.71 (*exo* $C\mathrm{H(CH_3)_2}$), 56.32 (*endo* $C\mathrm{H(CH_3)_2}$), 56.01 (*endo* $C\mathrm{H(CH_3)_2}$), 54.85 (*exo* $C\mathrm{H(CH_3)_2}$), 54.61, 54.21 (2 signals), 53.93, 50.16, 49.58, 49.50, 49.35, 47.12, 47.07, 46.03, 45.96, 44.79, 44.61, 21.38 (2 signals, $CH(CH_3)_2$), 21.29 ($CH(CH_3)_2$), 21.18 ($CH(CH_3)_2$), 21.16 (2 signals, $CH(CH_3)_2$), 21.11 ($CH(CH_3)_2$), 21.00 ($CH(CH_3)_2$). MS(HR–ESI-FTICR+):Calc. for $[C_{41}H_{42}N_4Pd]^+$: m/z 697.2532, Found m/z 697.2551.

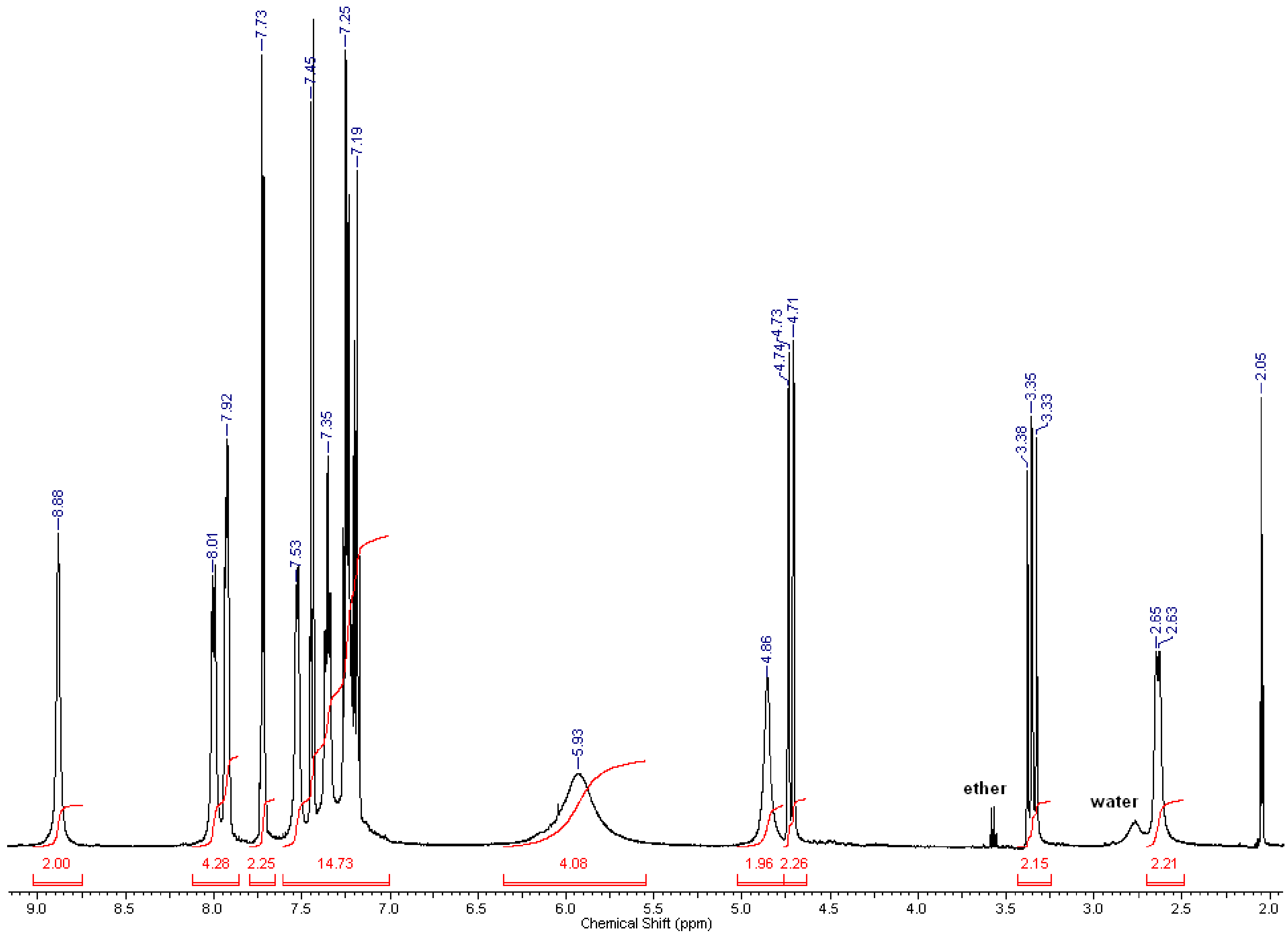


Figure S1: ^{1}H NMR spectrum of **[DEAM-*o*-XYLBI][OTf]$_2$** (**1**) in acetone-d_6 @ 50 °C.

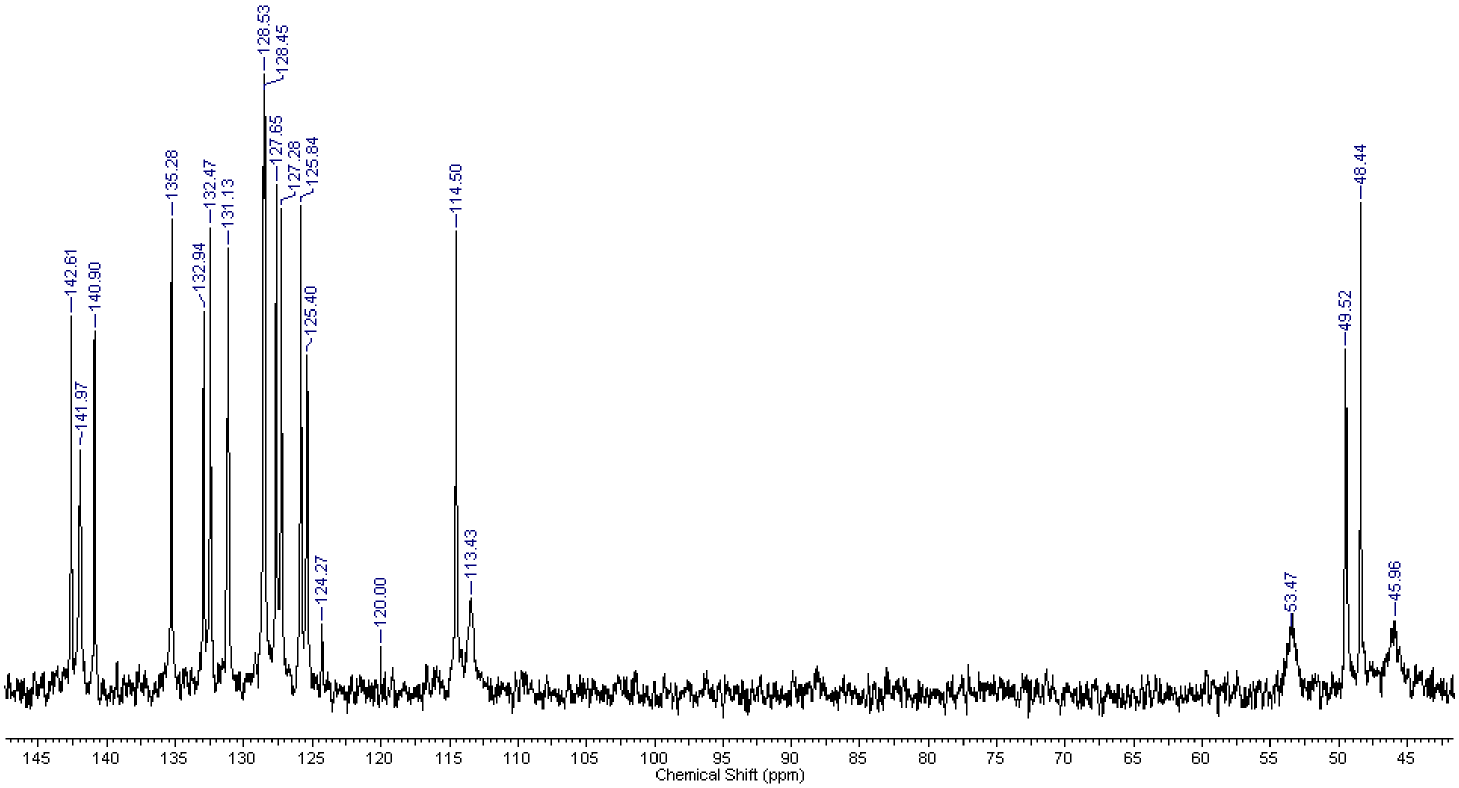


Figure S2: $^{13}C\{^1H\}$ NMR spectrum **[DEAM-*o*-XYLBI][OTf]$_2$** (**1**) in acetone-d_6 @ 25 °C.

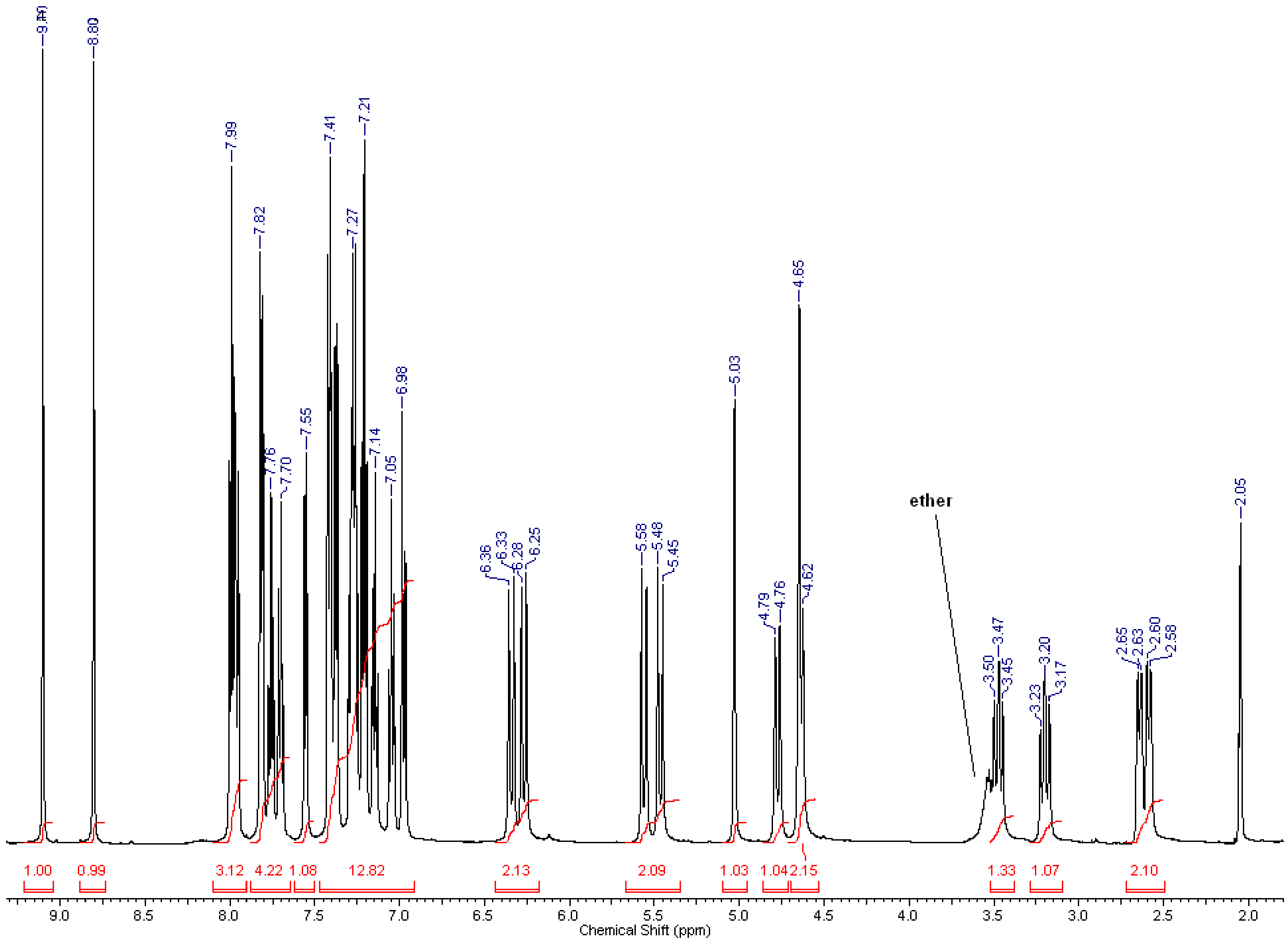


Figure S3: ^{1}H NMR spectrum of **[DEAM-*o*-XYLBI][OTf]$_2$** (**1**) in acetone-d_6 @ -60 °C.

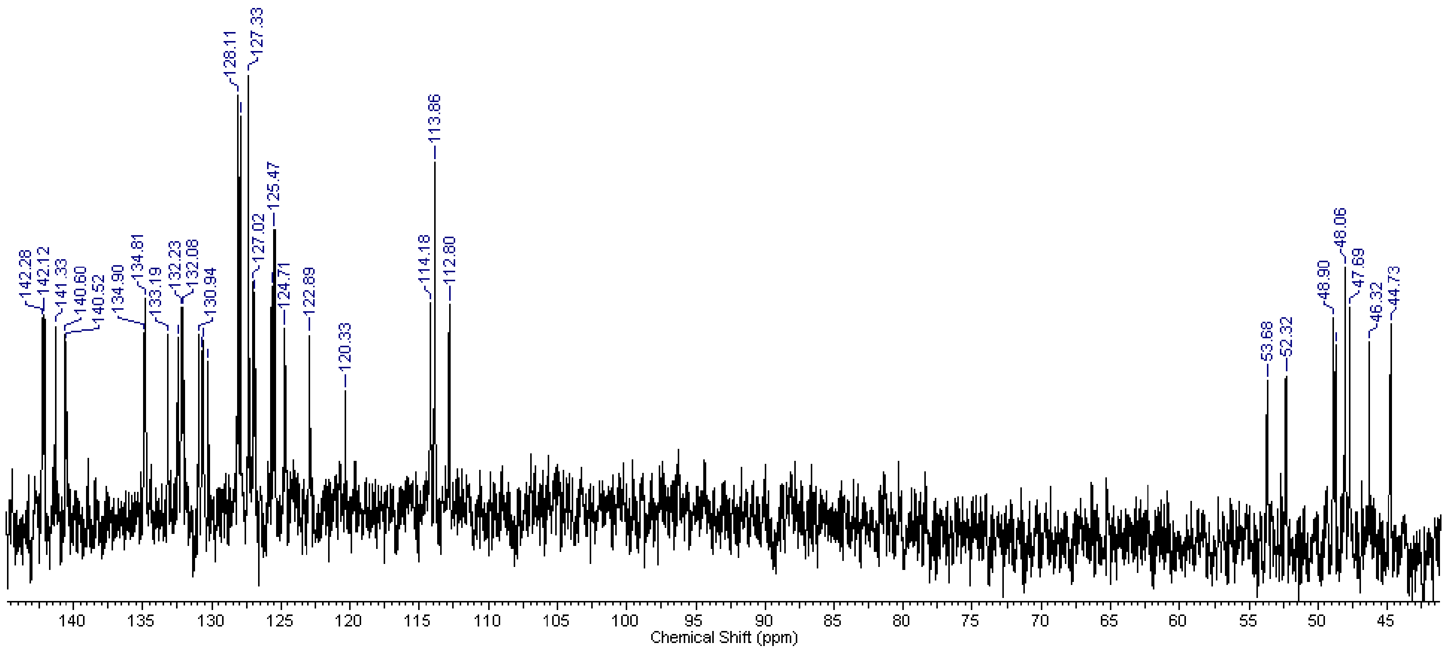


Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum **[DEAM-*o*-XYLBI][OTf]$_2$** (**1**) in acetone-d_6 @ -60 °C.

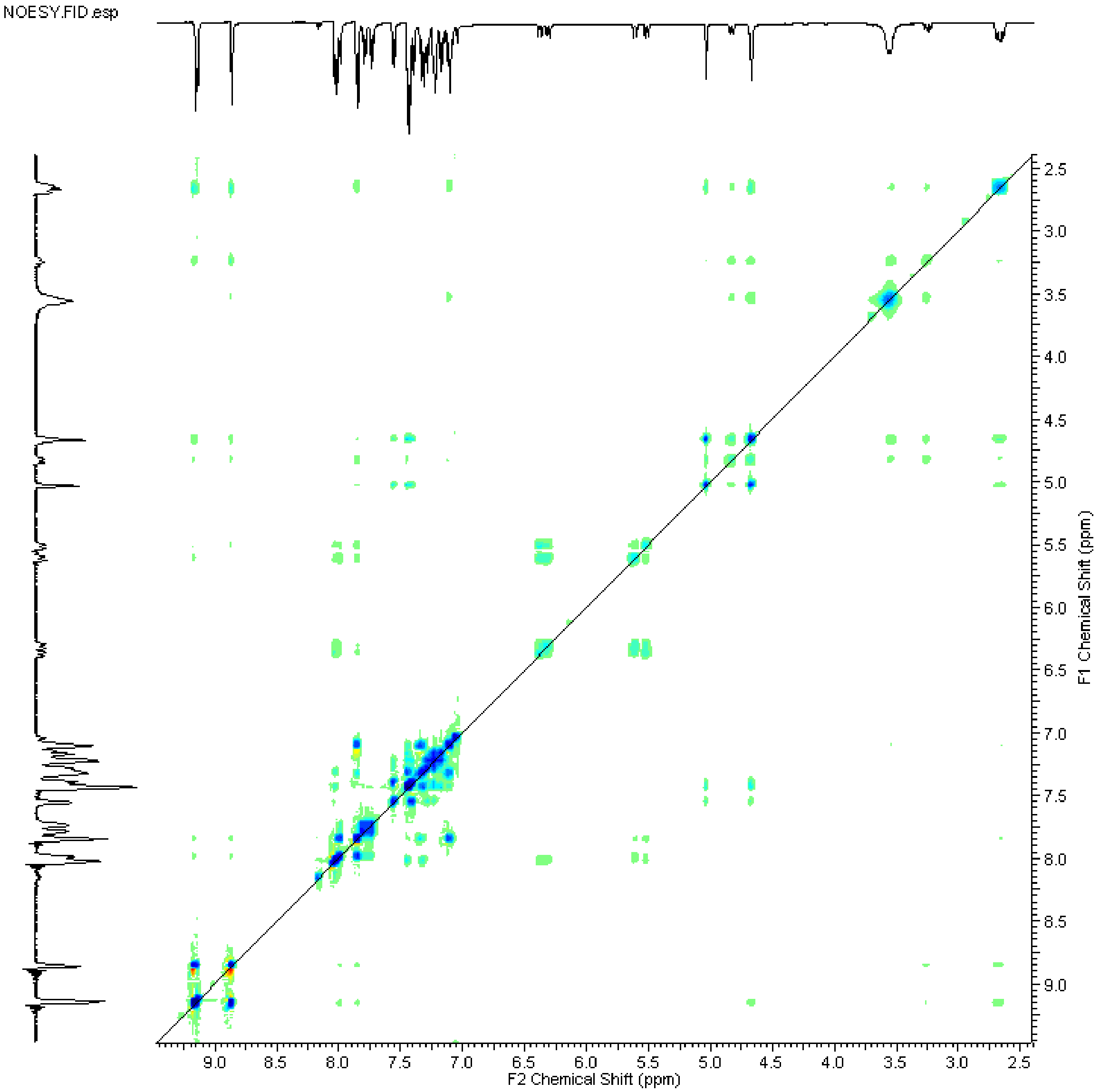


Figure S5: 2-D NOESY NMR spectrum of **[DEAM-*o*-XYLBI][OTf]$_2$ (1)** in acetone-d_6 @ -60 °C.

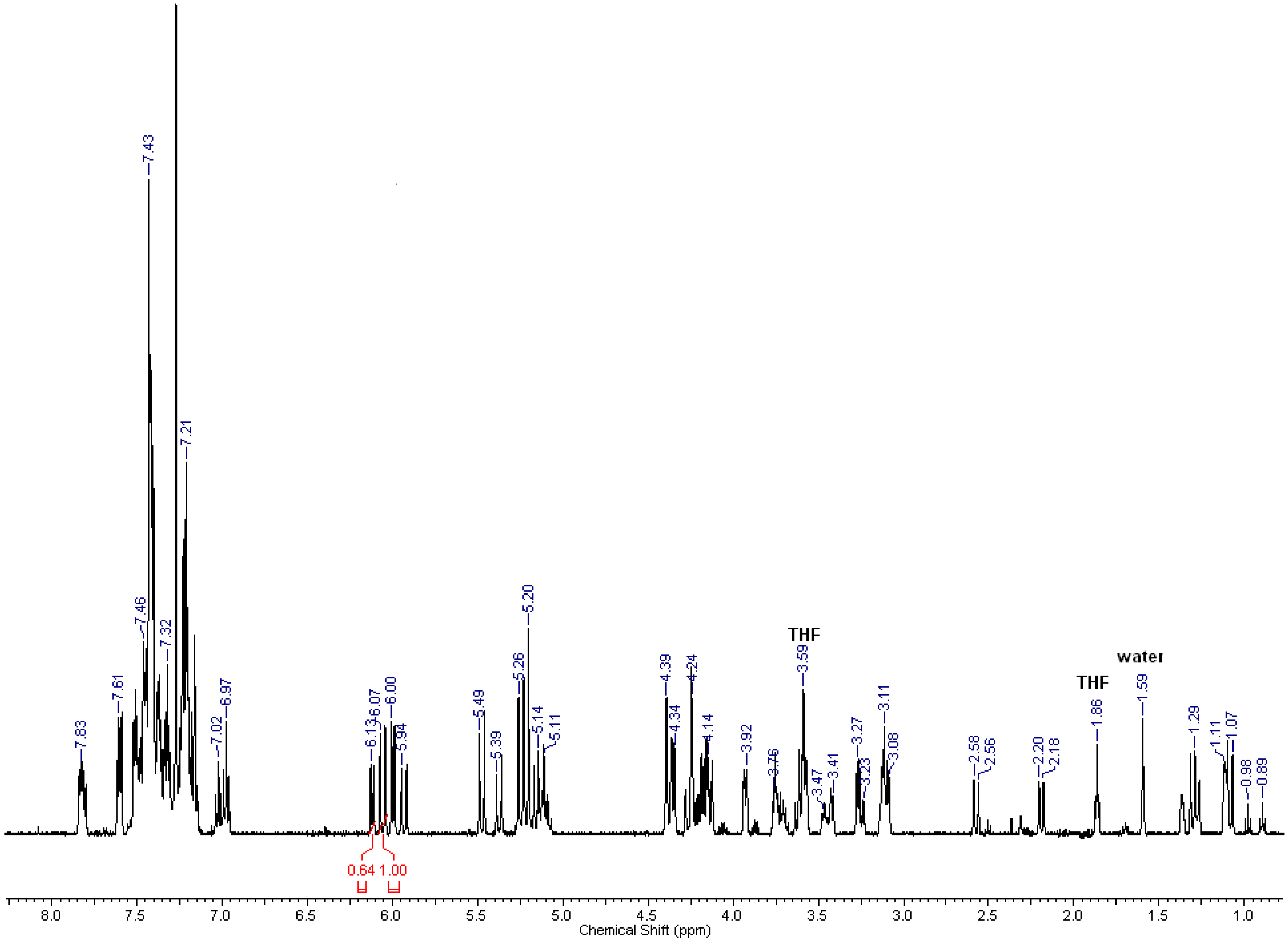


Figure S6: ^{1}H NMR spectrum of **[(DEAM-*o*-XYLBI)Pd(η^3-C$_3$H$_5$)][OTf] (2)** in CDCl$_3$ upon isolation.

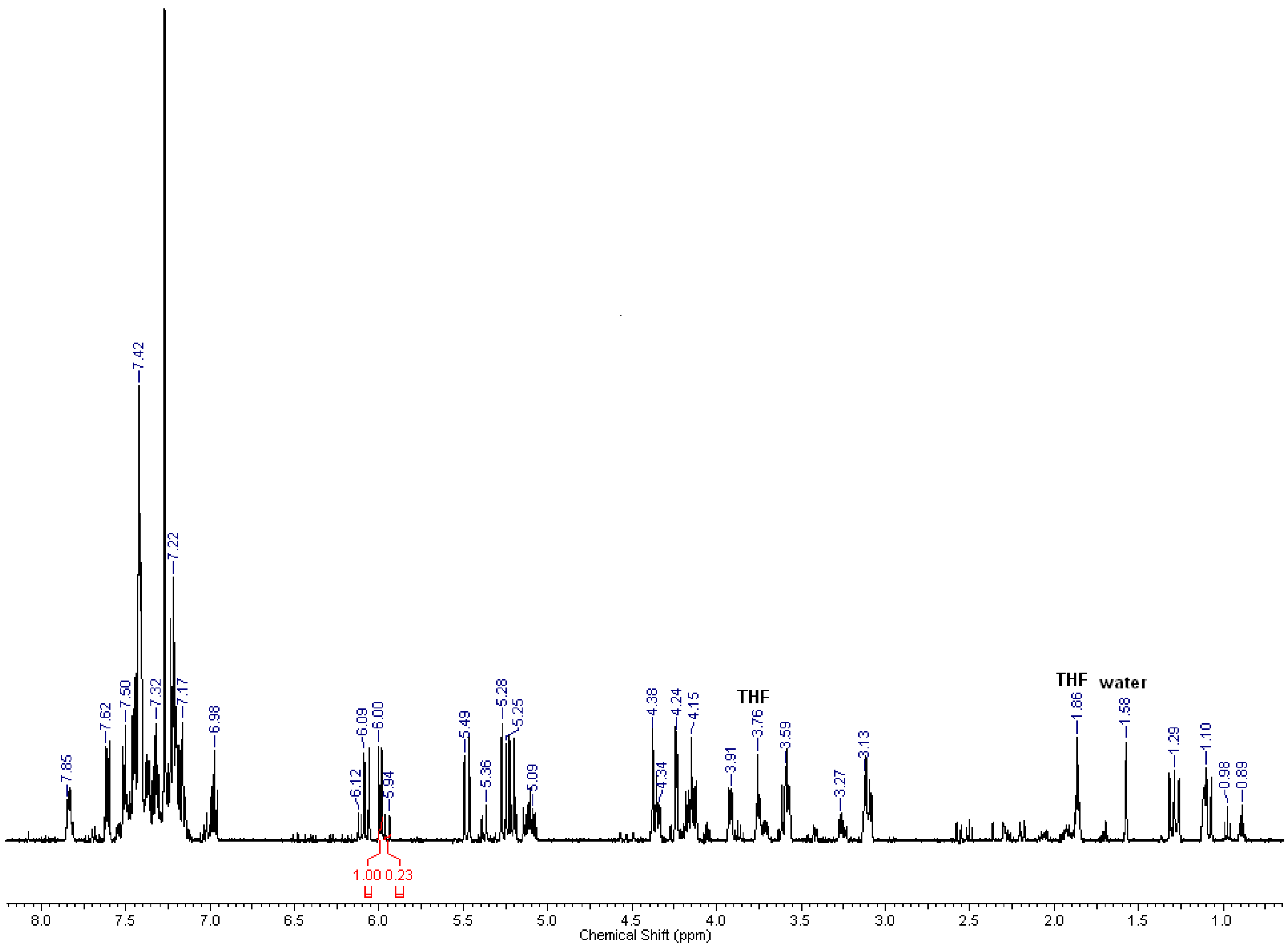


Figure S7: ^{1}H NMR spectrum of **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)** in $CDCl_3$ 18 h after isolation.

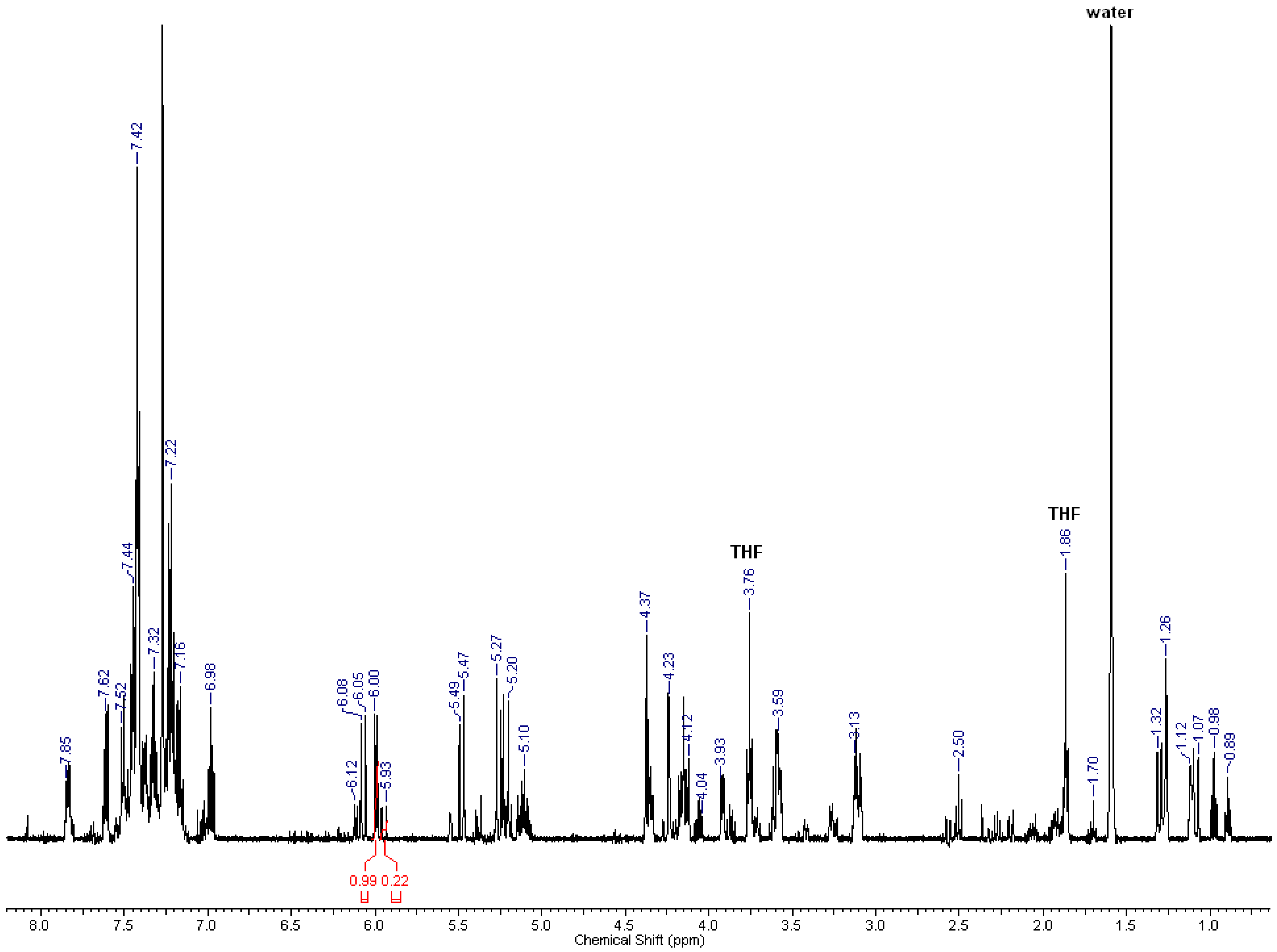


Figure S8: ^{1}H NMR spectrum of **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)** in $CDCl_3$ after 10 days.

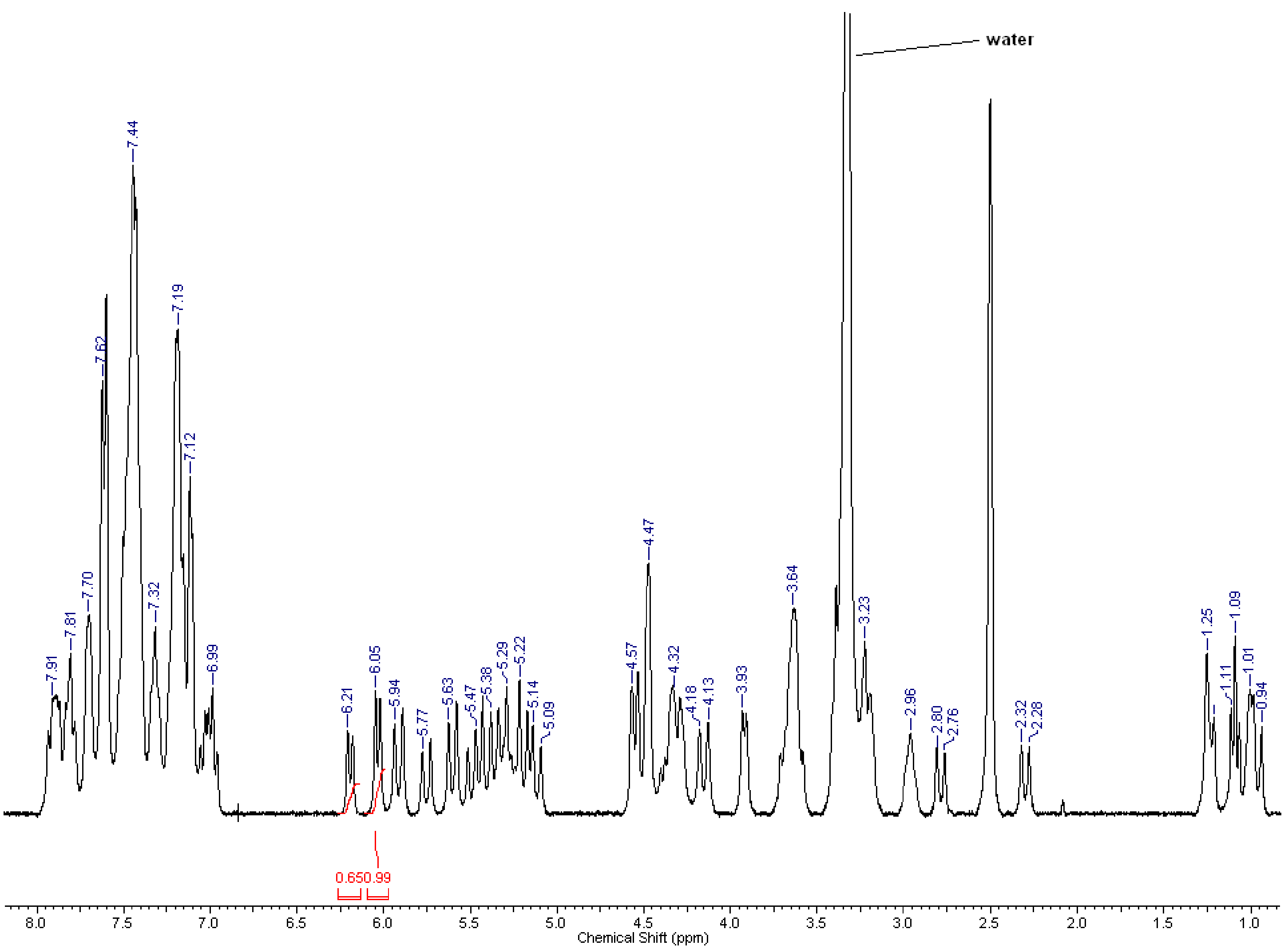


Figure S9: ^{1}H NMR spectrum of **[(DEAM-*o*-XYLBI)Pd(η^3-C$_3$H$_5$)][OTf] (2)** in DMSO-d_6 immediately after isolation.

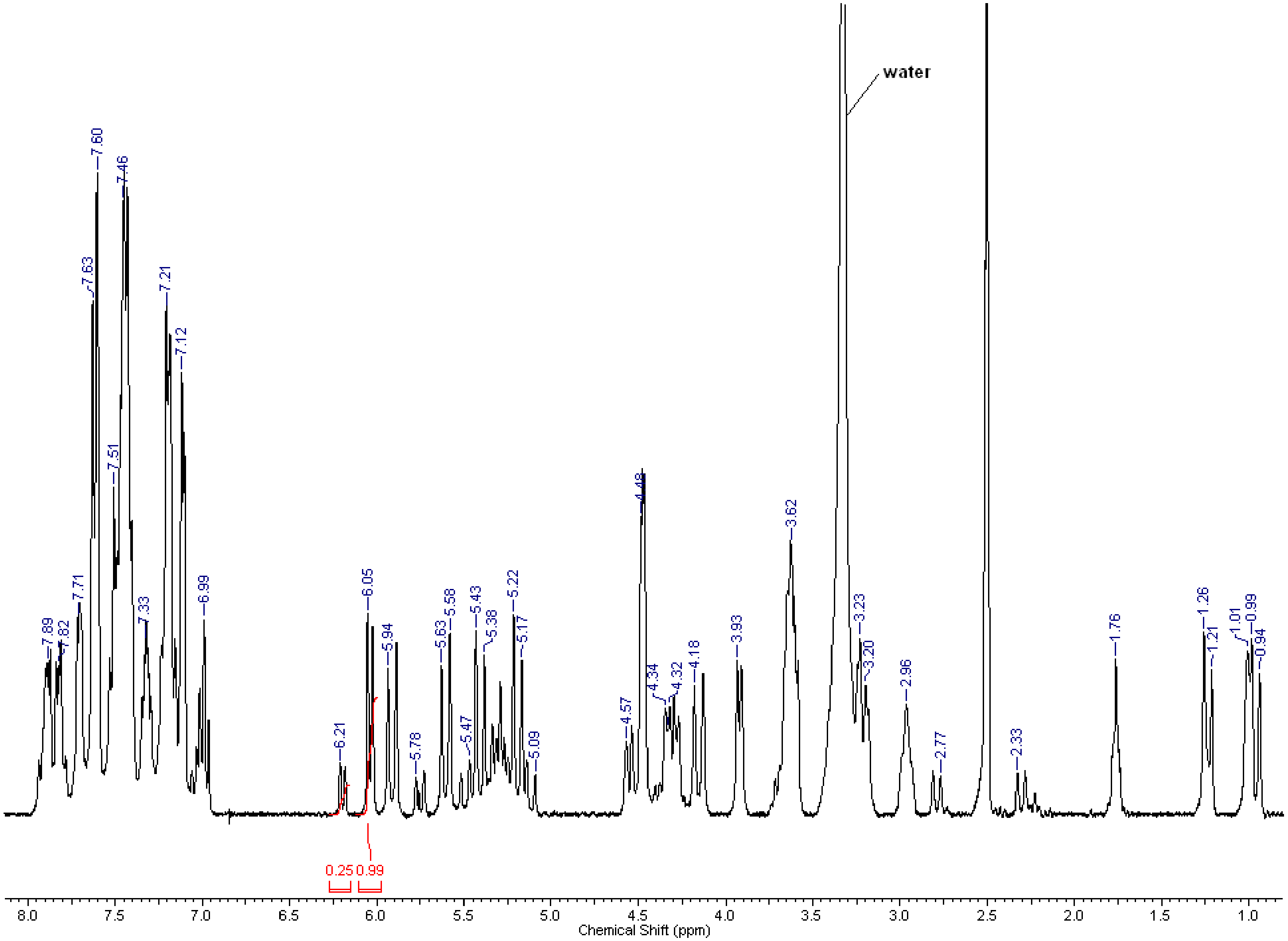


Figure S10: ^{1}H NMR spectrum of **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)** in DMSO-d_6 after 24 h.

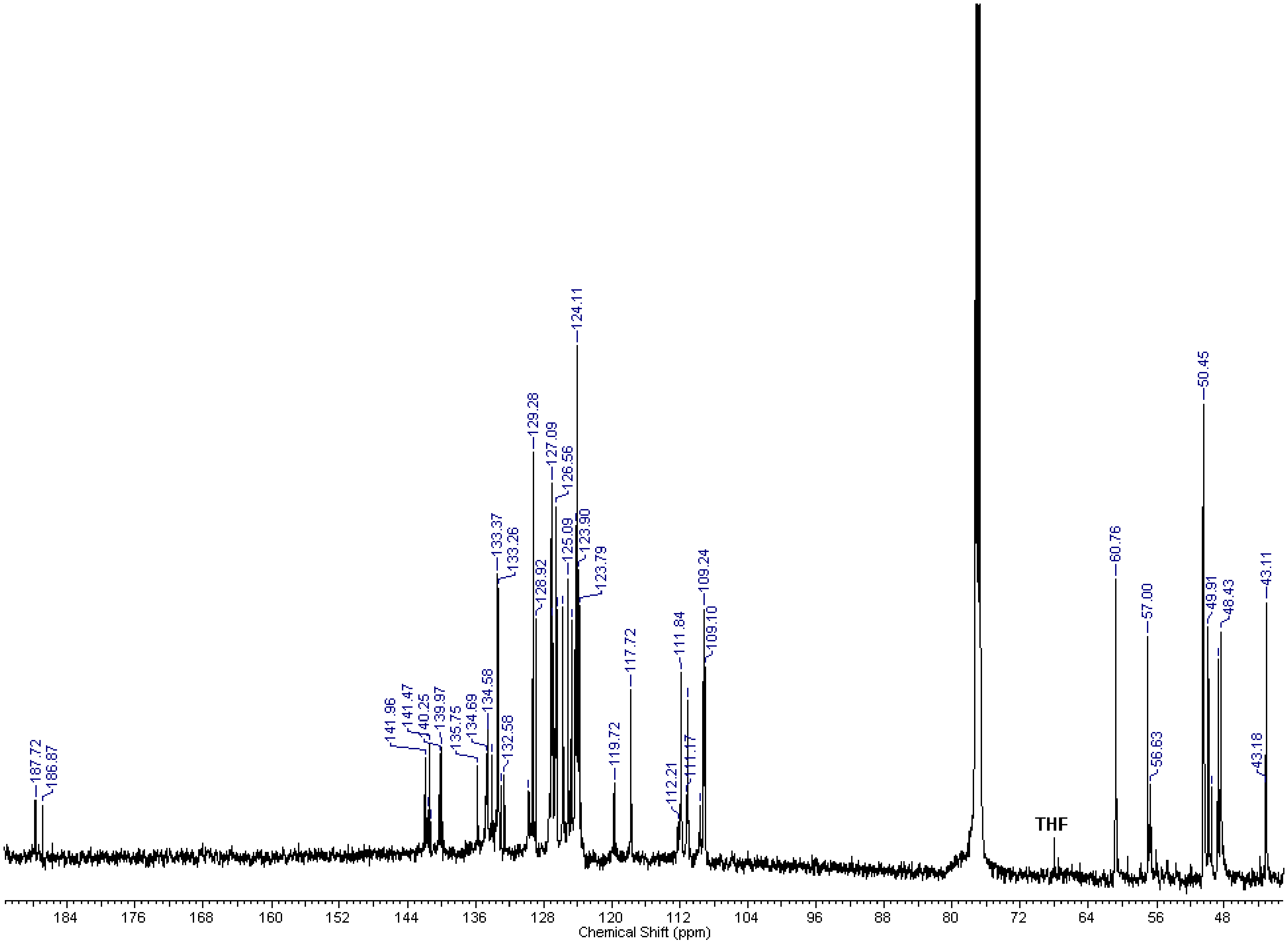


Figure S11: $^{13}C\{^1H\}$ NMR spectrum **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)** in $CDCl_3$.

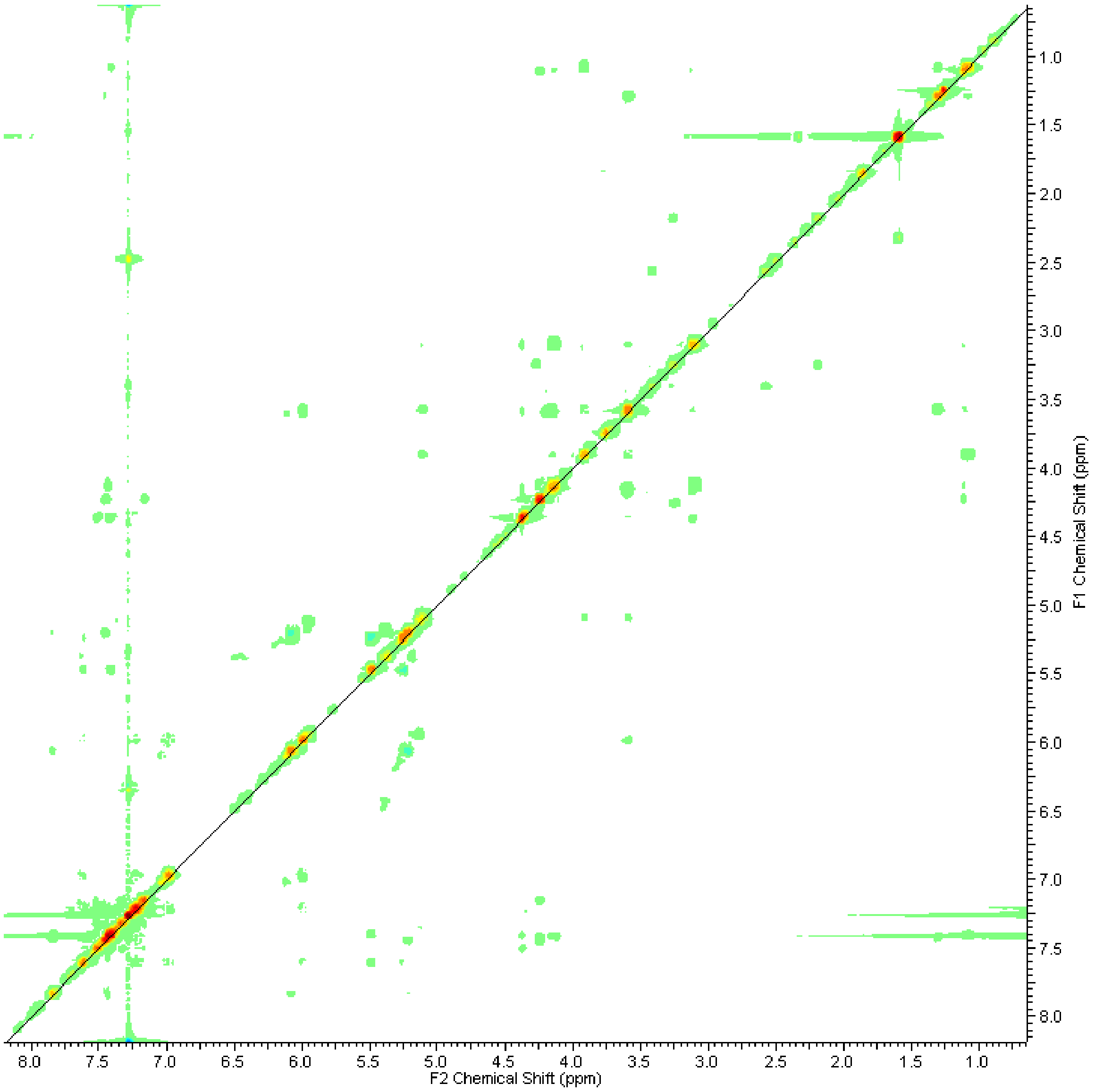


Figure S12: 2-D NOESY NMR spectrum of **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)** in $CDCl_3$.

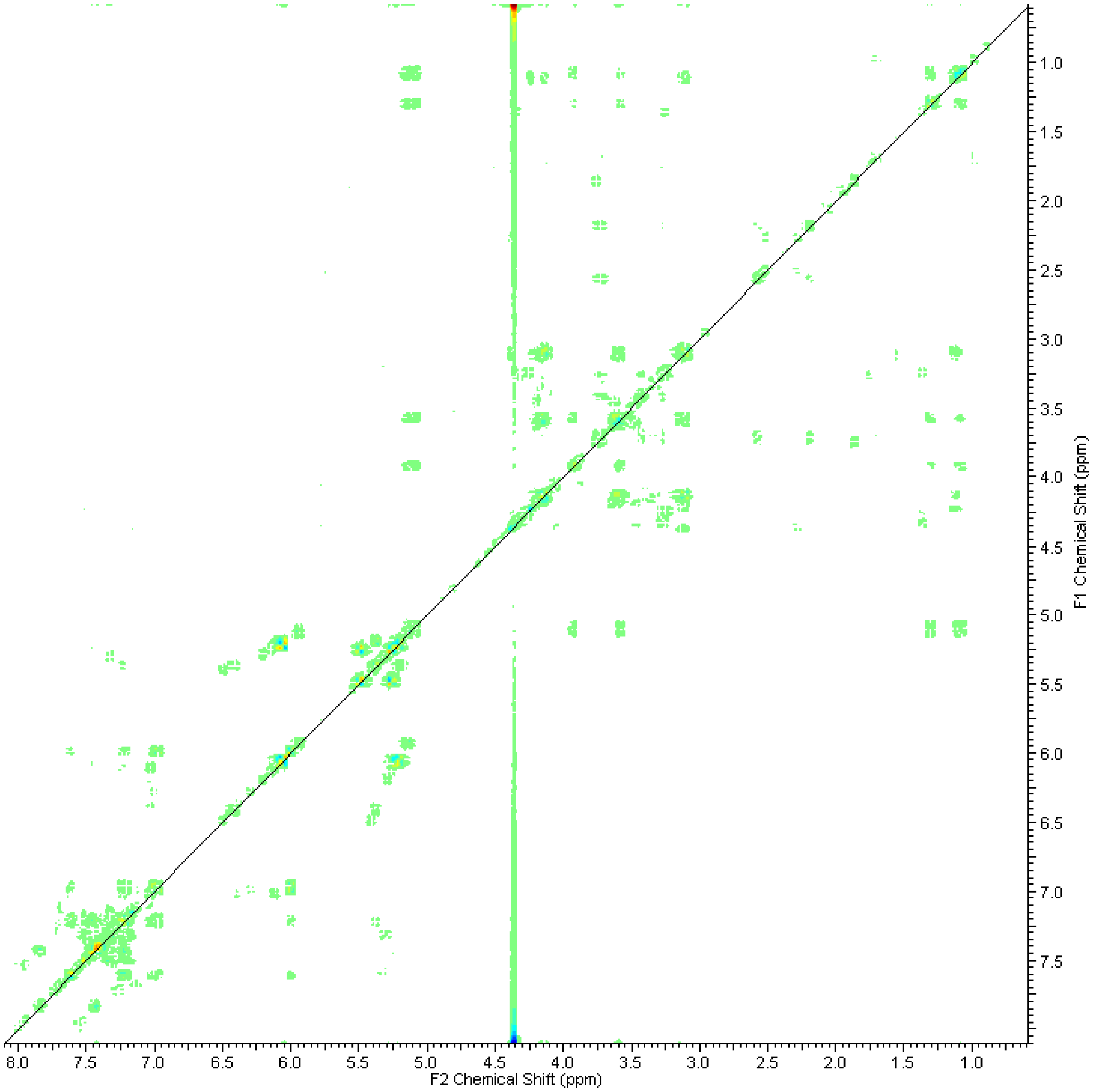


Figure S13: gdqCOSY NMR spectrum of **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)** in $CDCl_3$.

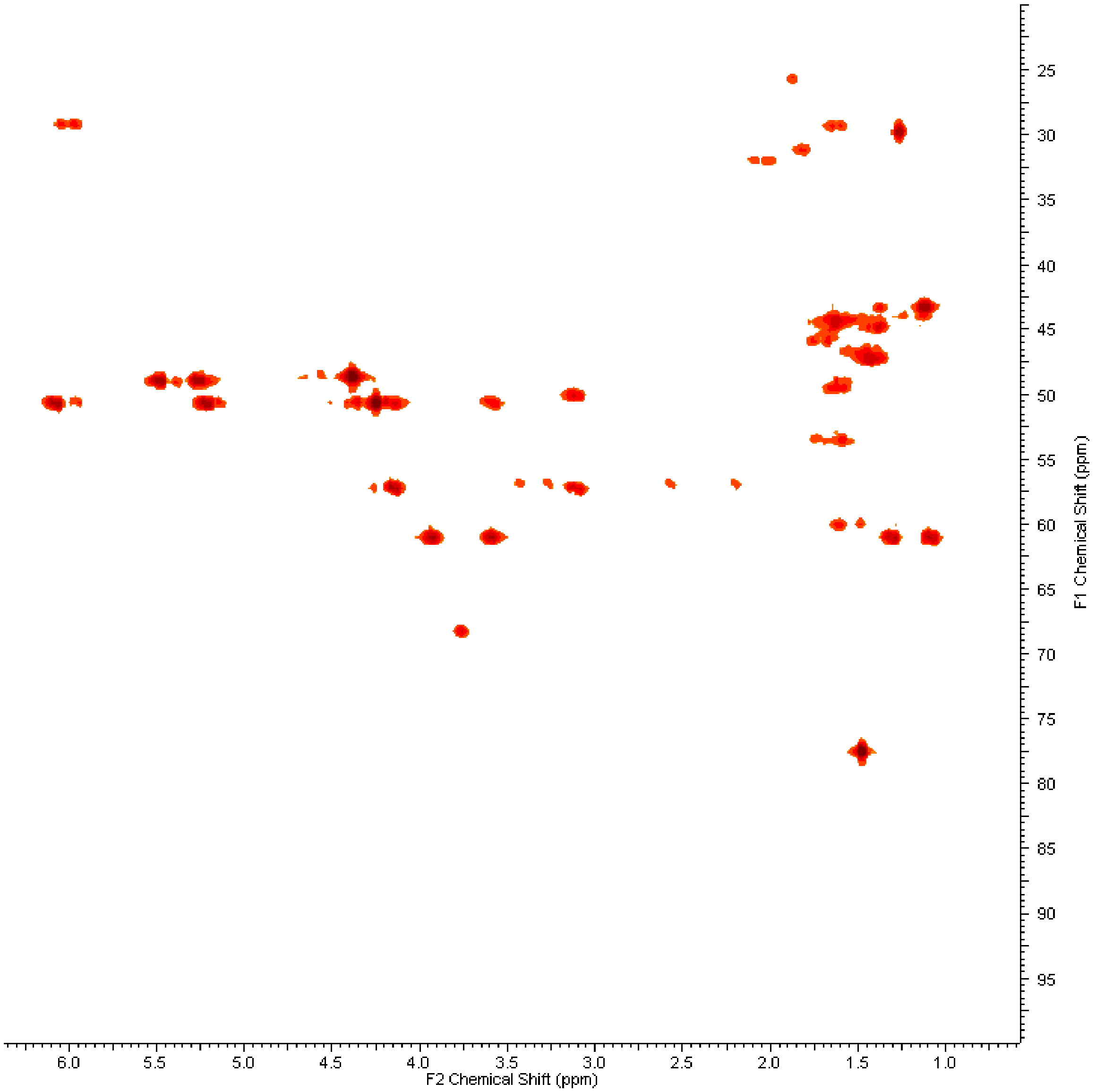


Figure S14: gHMQC-aliphatic NMR spectrum of **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)** in $CDCl_3$.

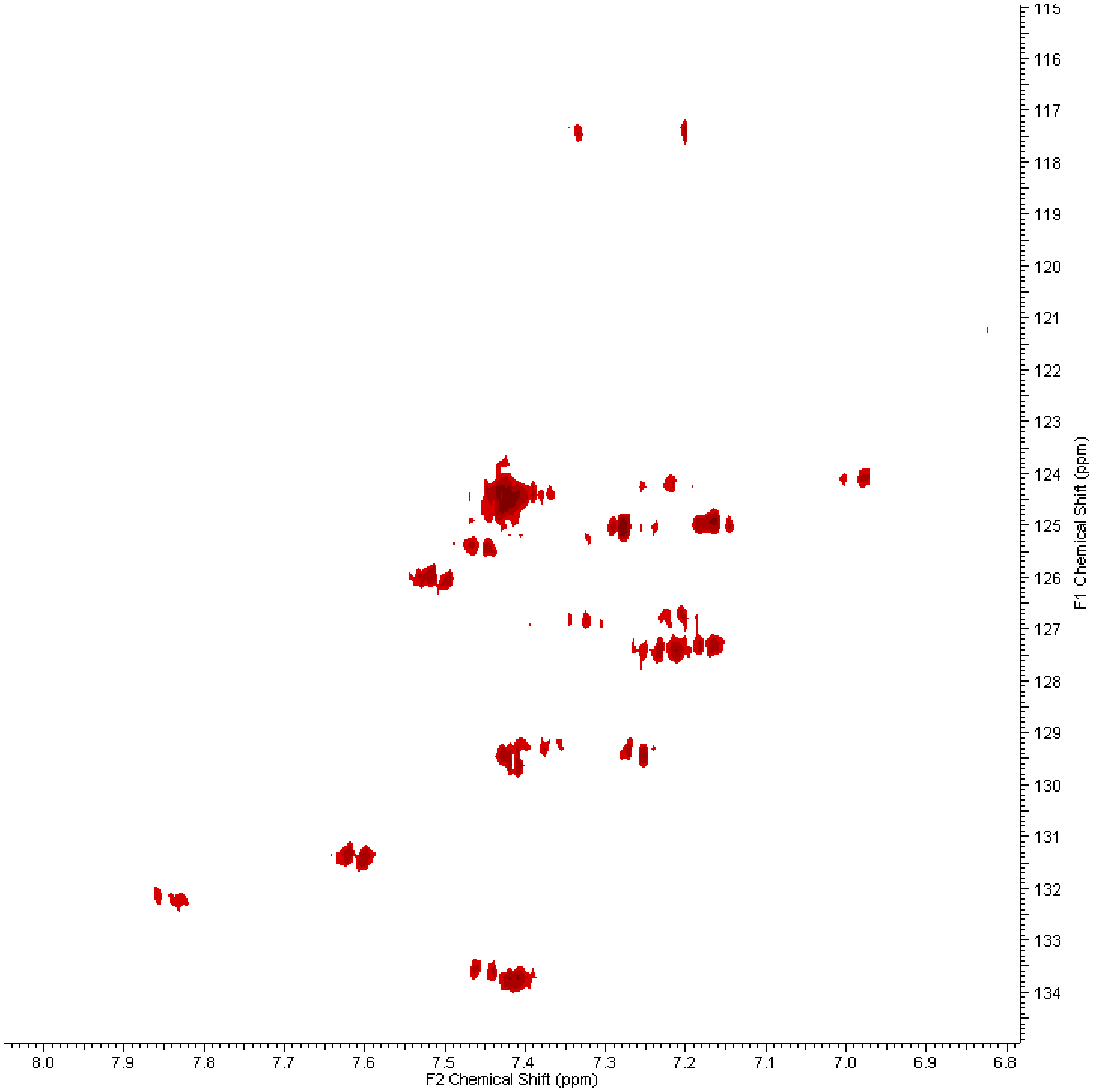


Figure S15: gHMQC-aromatic NMR spectrum of **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)** in $CDCl_3$.

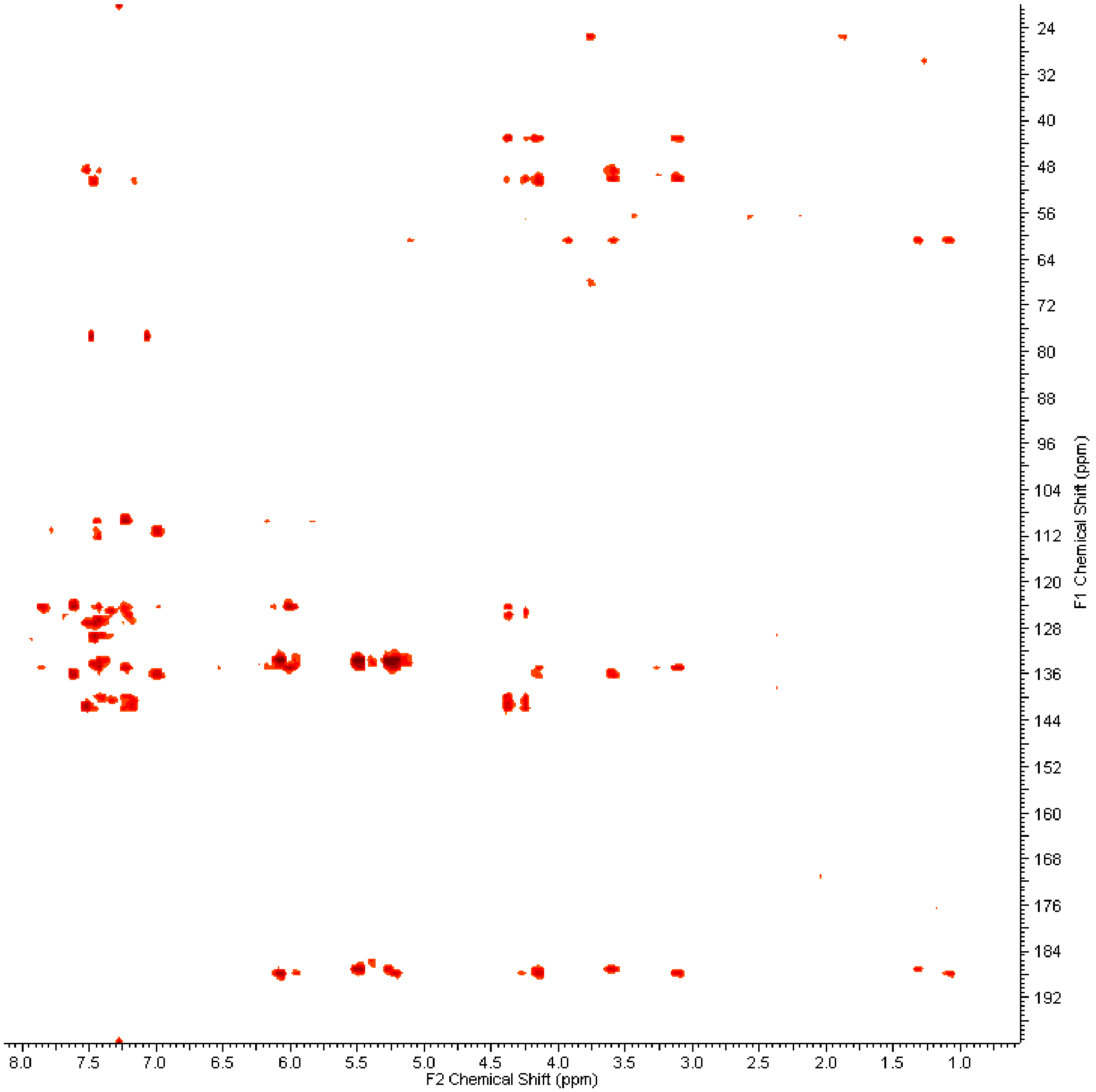


Figure S16: gHMBC NMR spectrum of **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)** in $CDCl_3$.

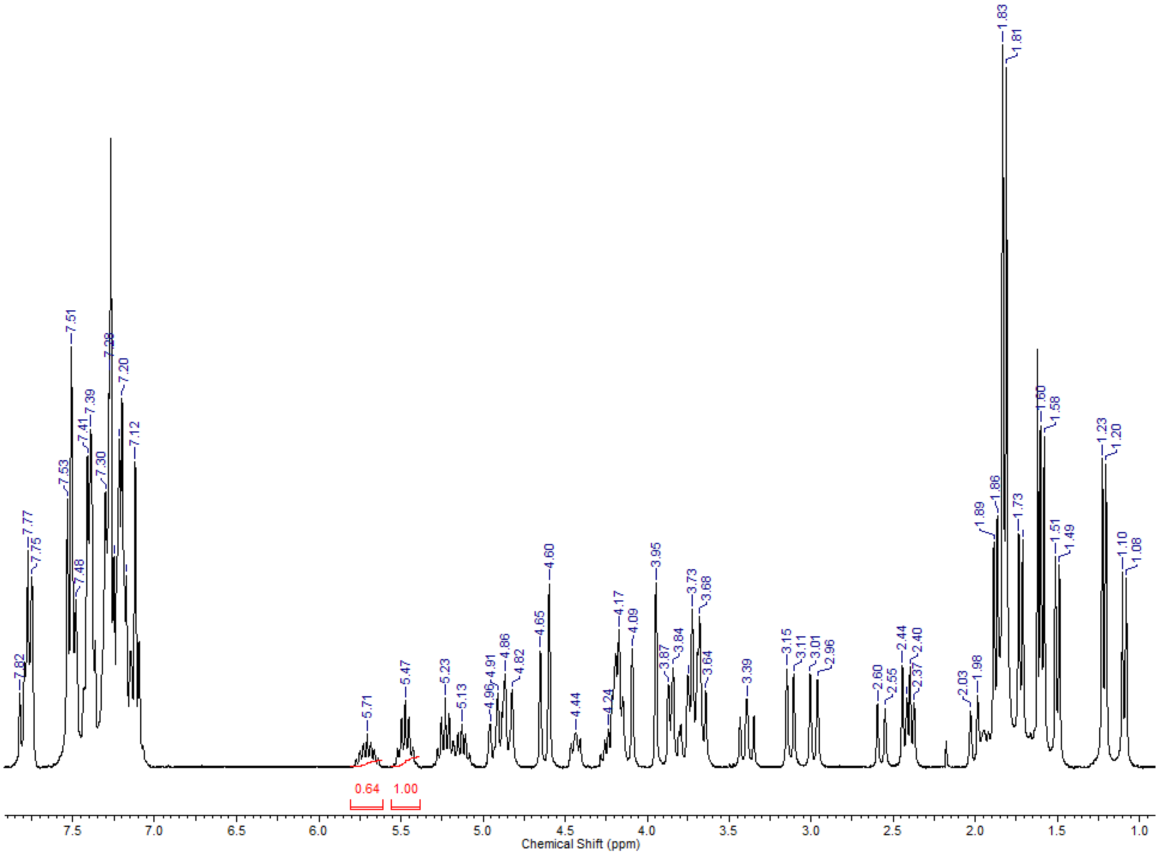


Figure S17: ^{1}H NMR spectrum of **[(DEAM-IBY)Pd(η^3-C_3H_5)][OTf] (3)** in $CDCl_3$.

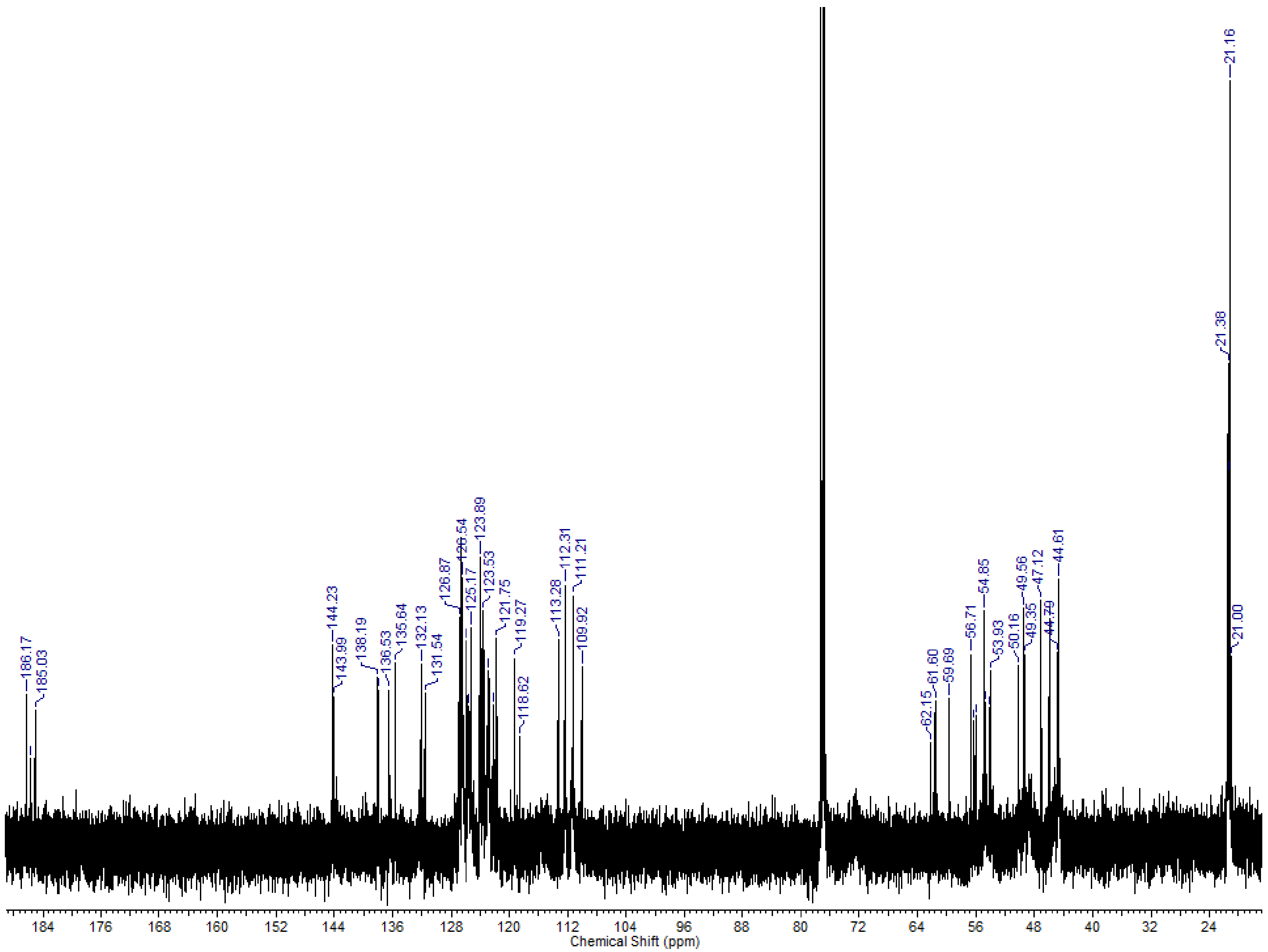


Figure S18: $^{13}C\{^1H\}$ NMR spectrum of **[(DEAM-IBY)Pd(η^3-C_3H_5)][OTf]** **(3)** in $CDCl_3$.

X-Ray Crystallography Details for [DEAM-*o*-XYLBI][OTf]$_2$ (1):

Data were collected at 100 K on a Bruker DUO system equipped with an APEX II area detector and a graphite monochromator utilizing MoK$_\alpha$ radiation (λ = 0.71073 Å). Cell parameters were refined using up to 9999 reflections. A hemisphere of data was collected using the ω-scan method (0.5° frame width). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in *SHELXTL6,* and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The asymmetric unit consists of the dication, two triflate anions, an acetone solvent molecule in a general position, another acetone disordered around a 2-fold rotation axis of symmetry, and a disordered hexane molecule. All solvent molecules were disordered and could not be modeled properly, thus program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. The 9,10-dihydroethanoanthracene-11,12-dyl fragment is disordered, and was refined in two parts with their site occupation factors dependently refined. The H1 and H26 on C1 and C26, respectively, were obtained form a Difference Fourier map and refined freely. One of the triflate anions (S2) is also disordered and O5, O6 and the CF$_3$ groups were refined in two positions and their site occupation factors were dependently refined. A total of 529 parameters were refined in the final cycle of refinement using 5802 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 5.84% and 16.28%, respectively. Refinement was done using F^2.

P. van der Sluis & A.L. Spek (1990). SQUEEZE, Acta Cryst. A46, 194-201

SHELXTL6 (2000). Bruker-AXS, Madison, Wisconsin, USA.

Spek, A.L. (1990). PLATON, Acta Cryst. A46, C-34

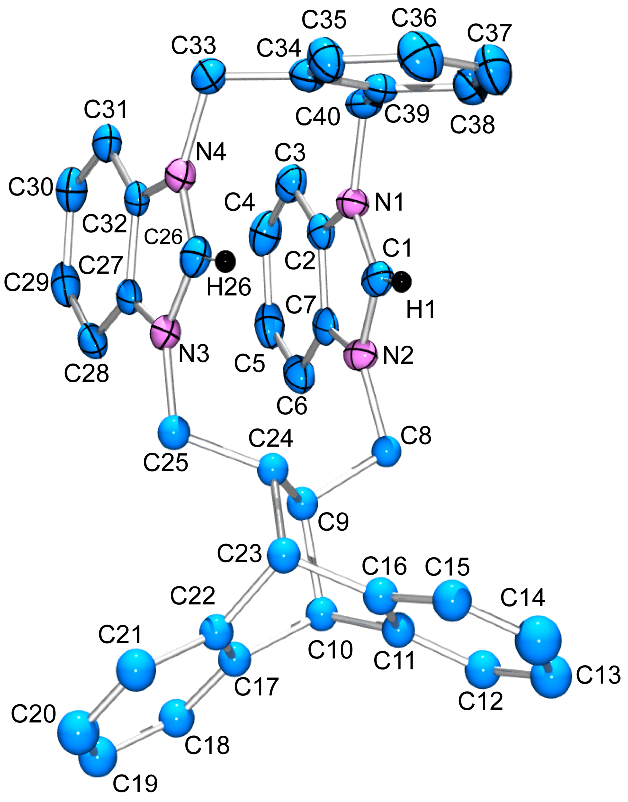


Figure S19. Molecular Structure of **[DEAM-*o*-XYLBI][OTf]$_2$** (**1**) with ellipsoids drawn at the 50% probability level. Hydrogen atoms and OTf counter ions have been omitted for clarity.

Table S2. Crystal data, structure solution and refinement for **[DEAM-*o*-XYLBI][OTf]$_2$ (1)**.

identification code	mj29
empirical formula	$C_{42}H_{34}N_4F_6O_6S_2$
formula weight	868.85
T (K)	100(2)
λ (Å)	0.71073
crystal system	monoclinic
space group	C2/c
a (Å)	31.103(2)
b (Å)	11.8780(9)
c (Å)	28.914(2)
α (deg)	90
β (deg)	115.714(2)
γ (deg)	90
V (Å^3)	9624.4(12)
Z	8
ρ_{calcd} (Mg mm^{-3})	1.199
crystal size (mm^3)	0.22 x 0.15 x 0.10
abs coeff (mm^{-1})	0.179
F(000)	3584
θ range for data collection	1.45 to 25.00
limiting indices	$-35 \leq h \leq 36, -13 \leq k \leq 14, -34 \leq \ell \leq 34$
no. of reflns collcd	43338
no. of ind reflns (R_{int})	8481 (0.0453)
completeness to $\theta = 27.45°$	100 %
absorption corr	Numerical
refinement method	Full–matrix least–squares on F^2
data / restraints / parameters	8481 / 0 / 529
$R1$,[a] $wR2$[b] [I > 2σ]	0.0584, 0.1628[5802]
$R1$,[a] $wR2$[b] (all data)	0.0806, 0.1724
GOF[c] on F^2	1.106
largest diff. peak and hole	0.863 and –0.583 eÅ^{-3}

$R1 = \sum(||F_o| - |F_c||) / \sum|F_o|$

$wR2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$

$S = [\sum[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w = 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **[DEAM-*o*-XYLBI][OTf]$_2$ (1)**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	**X**	**Y**	**Z**	**U(eq)**
F1	1230(1)	585(2)	3648(1)	55(1)
S1	716(1)	916(1)	4150(1)	42(1)
O1	293(1)	837(2)	3669(1)	56(1)
F2	1571(1)	104(2)	4447(1)	64(1)
O2	698(1)	310(2)	4573(1)	56(1)
F3	1010(1)	-928(2)	3888(1)	77(1)
O3	918(1)	2012(2)	4272(1)	47(1)
C41	1153(1)	134(3)	4028(1)	48(1)
S2	2054(1)	7406(1)	2973(1)	39(1)
O4	2193(1)	8482(2)	2857(1)	47(1)
O5	2361(2)	6838(4)	3386(2)	39(1)
O6	1759(2)	6718(3)	2498(2)	44(1)
C42	1570(3)	7889(8)	3138(4)	58(2)
F4	1369(2)	7016(4)	3251(2)	66(1)
F5	1230(2)	8436(4)	2785(2)	69(2)
F6	1776(2)	8509(4)	3565(2)	67(1)
O5'	2403(2)	7024(6)	3537(3)	44(2)
O6'	2011(2)	6559(4)	2628(2)	36(2)
C42'	1523(3)	7540(8)	3018(4)	41(2)
F4'	1359(2)	6532(5)	3125(2)	55(2)
F5'	1176(2)	7846(6)	2550(2)	79(2)
F6'	1538(3)	8284(6)	3380(3)	84(2)
N1	2187(1)	8590(2)	1784(1)	24(1)
N2	2125(1)	6769(2)	1684(1)	26(1)
N3	1785(1)	7567(2)	410(1)	27(1)
N4	1814(1)	9349(2)	610(1)	25(1)
C1	1888(1)	7721(2)	1644(1)	26(1)
C2	2649(1)	8182(2)	1940(1)	25(1)
C3	3088(1)	8731(2)	2130(1)	31(1)
C4	3478(1)	8053(3)	2236(1)	38(1)
C5	3437(1)	6878(3)	2166(1)	39(1)

C6	3004(1)	6341(3)	1983(1)	33(1)
C7	2608(1)	7025(2)	1871(1)	26(1)
C8	1876(3)	5653(6)	1574(3)	21(2)
C9	1798(3)	5257(6)	1029(3)	24(2)
C10	1671(3)	3965(5)	968(2)	24(2)
C11	1217(3)	3848(5)	1024(2)	25(2)
C12	1156(3)	3213(5)	1398(2)	30(2)
C13	716(3)	3241(6)	1405(3)	38(2)
C14	351(3)	3907(6)	1064(3)	45(2)
C15	418(2)	4513(5)	703(2)	32(1)
C16	844(2)	4489(5)	671(2)	27(2)
C17	1573(3)	3695(5)	409(2)	25(1)
C18	1838(2)	2985(5)	250(2)	31(1)
C19	1706(3)	2808(5)	-275(3)	35(2)
C20	1302(2)	3381(5)	-621(2)	39(2)
C21	1035(2)	4111(5)	-471(2)	34(2)
C22	1177(2)	4275(5)	54(2)	25(1)
C23	971(2)	5105(5)	296(2)	25(1)
C24	1390(3)	5910(6)	597(3)	22(2)
C25	1526(3)	6492(6)	209(3)	24(2)
C8'	1961(3)	5619(8)	1554(3)	23(3)
C9'	1895(4)	5219(8)	1036(4)	25(3)
C10'	1823(3)	3910(6)	1006(3)	23(2)
C11'	1364(3)	3696(6)	1048(3)	22(2)
C12'	1309(3)	3135(7)	1435(3)	29(2)
C13'	866(4)	3059(7)	1437(3)	35(2)
C14'	459(3)	3550(8)	1049(3)	43(2)
C15'	522(3)	4135(8)	643(3)	44(2)
C16'	970(3)	4204(7)	663(3)	30(2)
C17'	1764(3)	3559(6)	480(3)	25(2)
C18'	2074(3)	2889(6)	379(3)	30(2)
C19'	1978(3)	2655(6)	-127(3)	42(2)
C20'	1557(3)	3127(6)	-523(3)	37(2)
C21'	1251(3)	3834(7)	-426(3)	37(2)
C22'	1362(3)	4024(6)	85(3)	26(2)
C23'	1093(3)	4818(7)	267(3)	28(2)

C24'	1469(4)	5773(8)	582(4)	30(3)
C25'	1628(4)	6427(8)	219(3)	26(3)
C26	1534(1)	8456(2)	438(1)	29(1)
C27	2258(1)	7915(2)	570(1)	26(1)
C28	2665(1)	7333(2)	622(1)	32(1)
C29	3079(1)	7954(3)	793(1)	34(1)
C30	3091(1)	9100(3)	902(1)	35(1)
C31	2691(1)	9680(2)	855(1)	31(1)
C32	2272(1)	9053(2)	687(1)	25(1)
C33	1651(1)	10460(2)	705(1)	30(1)
C34	1348(1)	10343(2)	992(1)	29(1)
C35	867(1)	10561(2)	732(1)	34(1)
C36	574(1)	10485(3)	979(1)	42(1)
C37	761(1)	10180(3)	1488(1)	42(1)
C38	1241(1)	9944(2)	1750(1)	33(1)
C39	1544(1)	10029(2)	1512(1)	26(1)
C40	2064(1)	9786(2)	1818(1)	30(1)

Table S4. Bond lengths (in Å) for **[DEAM-*o*-XYLBI][OTf]$_2$** (**1**).

Bond	Distance	Bond	Distance
F1-C41	1.334(4)	N4-C32	1.389(3)
S1-O3	1.422(2)	N4-C33	1.481(3)
S1-O2	1.440(2)	C2-C7	1.387(4)
S1-O1	1.444(2)	C2-C3	1.393(4)
S1-C41	1.805(4)	C3-C4	1.376(4)
F2-C41	1.338(4)	C4-C5	1.409(4)
F3-C41	1.340(4)	C5-C6	1.372(4)
S2-O5	1.343(5)	C6-C7	1.390(4)
S2-O6'	1.383(5)	C8-C9	1.559(10)
S2-O4	1.435(2)	C9-C24	1.549(11)
S2-O6	1.517(4)	C9-C10	1.576(9)
S2-O5'	1.582(7)	C10-C11	1.497(9)
S2-C42'	1.717(9)	C10-C17	1.543(8)
S2-C42	1.855(10)	C11-C16	1.393(9)
C42-F5	1.283(9)	C11-C12	1.398(9)
C42-F4	1.324(9)	C12-C13	1.375(11)
C42-F6	1.338(11)	C13-C14	1.384(11)
C42'-F6'	1.356(12)	C14-C15	1.355(9)
C42'-F5'	1.364(10)	C15-C16	1.371(9)
C42'-F4'	1.388(11)	C16-C23	1.494(8)
N1-C1	1.329(3)	C17-C18	1.390(8)
N1-C2	1.393(3)	C17-C22	1.396(9)
N1-C40	1.485(3)	C18-C19	1.405(8)
N2-C1	1.327(3)	C19-C20	1.398(9)
N2-C7	1.393(4)	C20-C21	1.394(9)
N2-C8'	1.449(9)	C21-C22	1.398(8)
N2-C8	1.497(7)	C22-C23	1.504(8)
N3-C26	1.337(4)	C23-C24	1.543(9)
N3-C27	1.398(4)	C24-C25	1.527(10)
N3-C25'	1.465(9)	C8'-C9'	1.499(13)
N3-C25	1.486(7)	C9'-C24'	1.548(14)
N4-C26	1.325(4)	C9'-C10'	1.568(12)

C10'-C11'	1.507(11)	C28-C29	1.377(4)
C10'-C17'	1.510(10)	C29-C30	1.395(4)
C11'-C12'	1.373(10)	C30-C31	1.376(4)
C11'-C16'	1.386(11)	C30-H30A	0.9500
C12'-C13'	1.385(13)	C31-C32	1.393(4)
C13'-C14'	1.404(13)	C31-H31A	0.9500
C14'-C15'	1.447(11)	C33-C34	1.507(4)
C15'-C16'	1.372(12)	C33-H33A	0.9900
C16'-C23'	1.540(10)	C33-H33B	0.9900
C17'-C18'	1.375(11)	C34-C35	1.378(4)
C17'-C22'	1.390(10)	C34-C39	1.405(4)
C18'-C19'	1.389(10)	C35-C36	1.385(4)
C19'-C20'	1.426(12)	C35-H35A	0.9500
C20'-C21'	1.386(12)	C36-C37	1.376(4)
C21'-C22'	1.385(10)	C36-H36A	0.9500
C22'-C23'	1.499(11)	C37-C38	1.380(4)
C23'-C24'	1.600(12)	C38-C39	1.391(4)
C24'-C25'	1.548(13)	C39-C40	1.498(4)
C27-C32	1.390(4)	C1-H1	0.94(3)
C27-C28	1.392(4)	C26-H26	0.95(3)

Table S5. Bond angles in (°) for **[DEAM-*o*-XYLBI][OTf]$_2$** (**1**).

Bond Angle	**Angle**	**Bond Angle**	**Angle**
O3-S1-O2	115.01(14)	C42'-S2-C42	16.2(4)
O3-S1-O1	114.77(15)	F5-C42-F4	106.1(7)
O2-S1-O1	115.48(14)	F5-C42-F6	110.8(8)
O3-S1-C41	103.26(15)	F4-C42-F6	106.9(7)
O2-S1-C41	102.59(16)	F5-C42-S2	115.7(7)
O1-S1-C41	103.17(16)	F4-C42-S2	110.2(7)
F1-C41-F2	107.8(3)	F6-C42-S2	106.8(6)
F1-C41-F3	106.5(3)	F6'-C42'-F5'	109.9(7)
F2-C41-F3	108.3(3)	F6'-C42'-F4'	106.4(7)
F1-C41-S1	111.9(2)	F5'-C42'-F4'	104.0(7)
F2-C41-S1	110.8(2)	F6'-C42'-S2	113.9(7)
F3-C41-S1	111.3(2)	F5'-C42'-S2	108.9(6)
O5-S2-O6'	94.8(3)	F4'-C42'-S2	113.3(6)
O5-S2-O4	119.0(2)	C1-N1-C2	108.4(2)
O6'-S2-O4	115.1(2)	C1-N1-C40	126.7(2)
O5-S2-O6	116.8(3)	C2-N1-C40	124.7(2)
O6'-S2-O6	28.8(2)	C1-N2-C7	108.3(2)
O4-S2-O6	113.13(18)	C1-N2-C8'	131.3(4)
O5-S2-O5'	15.2(3)	C7-N2-C8'	120.3(4)
O6'-S2-O5'	110.0(3)	C1-N2-C8	121.3(4)
O4-S2-O5'	110.8(3)	C7-N2-C8	130.3(4)
O6-S2-O5'	130.7(3)	C8'-N2-C8	11.4(5)
O5-S2-C42'	108.5(4)	C26-N3-C27	107.8(2)
O6'-S2-C42'	109.1(4)	C26-N3-C25'	130.1(5)
O4-S2-C42'	109.4(3)	C27-N3-C25'	122.0(5)
O6-S2-C42'	84.0(4)	C26-N3-C25	118.0(4)
O5'-S2-C42'	101.6(4)	C27-N3-C25	134.1(4)
O5-S2-C42	105.8(3)	C25'-N3-C25	12.2(5)
O6'-S2-C42	125.2(4)	C26-N4-C32	108.6(2)
O4-S2-C42	98.3(3)	C26-N4-C33	124.2(2)
O6-S2-C42	99.2(4)	C32-N4-C33	127.2(2)
O5'-S2-C42	95.5(4)	N2-C1-N1	110.2(3)

C7-C2-C3	122.2(3)	C21-C22-C23	126.8(5)
C7-C2-N1	106.4(2)	C16-C23-C22	108.4(5)
C3-C2-N1	131.4(3)	C16-C23-C24	108.6(5)
C4-C3-C2	115.7(3)	C22-C23-C24	104.1(5)
C3-C4-C5	122.1(3)	C25-C24-C23	107.6(5)
C6-C5-C4	122.0(3)	C25-C24-C9	115.2(7)
C5-C6-C7	116.1(3)	C23-C24-C9	109.9(6)
C2-C7-C6	122.0(3)	N3-C25-C24	112.3(5)
C2-C7-N2	106.7(2)	N2-C8'-C9'	116.0(7)
C6-C7-N2	131.3(3)	C8'-C9'-C24'	114.0(8)
N2-C8-C9	108.7(5)	C8'-C9'-C10'	108.9(7)
C24-C9-C8	112.2(6)	C24'-C9'-C10'	109.0(7)
C24-C9-C10	108.5(6)	C11'-C10'-C17'	109.3(6)
C8-C9-C10	109.2(6)	C11'-C10'-C9'	106.3(7)
C11-C10-C17	109.2(5)	C17'-C10'-C9'	106.3(6)
C11-C10-C9	106.3(5)	C12'-C11'-C16'	119.0(8)
C17-C10-C9	104.2(5)	C12'-C11'-C10'	127.2(7)
C16-C11-C12	120.8(7)	C16'-C11'-C10'	113.6(6)
C16-C11-C10	113.2(5)	C11'-C12'-C13'	120.7(8)
C12-C11-C10	126.0(6)	C12'-C13'-C14'	121.6(9)
C13-C12-C11	117.9(6)	C13'-C14'-C15'	117.1(8)
C12-C13-C14	121.1(7)	C16'-C15'-C14'	119.1(8)
C15-C14-C13	119.9(7)	C15'-C16'-C11'	122.4(7)
C14-C15-C16	121.2(6)	C15'-C16'-C23'	125.0(7)
C15-C16-C11	118.9(5)	C11'-C16'-C23'	112.6(7)
C15-C16-C23	127.4(5)	C18'-C17'-C22'	121.4(7)
C11-C16-C23	113.7(6)	C18'-C17'-C10'	125.7(7)
C18-C17-C22	121.2(6)	C22'-C17'-C10'	112.9(7)
C18-C17-C10	126.6(6)	C17'-C18'-C19'	119.3(7)
C22-C17-C10	112.2(5)	C18'-C19'-C20'	118.0(8)
C17-C18-C19	120.7(6)	C21'-C20'-C19'	123.2(8)
C20-C19-C18	116.9(6)	C22'-C21'-C20'	116.2(8)
C21-C20-C19	123.5(6)	C21'-C22'-C17'	121.9(7)
C20-C21-C22	118.3(6)	C21'-C22'-C23'	124.1(8)
C17-C22-C21	119.4(6)	C17'-C22'-C23'	113.8(6)
C17-C22-C23	113.5(5)	C22'-C23'-C16'	108.7(6)

C22'-C23'-C24'	105.3(6)
C16'-C23'-C24'	105.6(6)
C25'-C24'-C9'	112.4(8)
C25'-C24'-C23'	109.8(7)
C9'-C24'-C23'	109.1(7)
N3-C25'-C24'	111.2(7)
N4-C26-N3	110.4(3)
C32-C27-C28	121.7(3)
C32-C27-N3	106.6(2)
C28-C27-N3	131.7(3)
C29-C28-C27	116.0(3)
C28-C29-C30	122.2(3)
C31-C30-C29	122.1(3)
C30-C31-C32	115.9(3)
N4-C32-C27	106.6(2)
N4-C32-C31	131.4(2)
C27-C32-C31	122.1(3)
N4-C33-C34	111.4(2)
C35-C34-C39	119.8(3)
C35-C34-C33	118.2(2)
C39-C34-C33	122.0(3)
C34-C35-C36	120.6(3)
C37-C36-C35	120.1(3)
C36-C37-C38	119.7(3)
C37-C38-C39	121.2(3)
C38-C39-C34	118.5(3)
C38-C39-C40	118.9(2)
C34-C39-C40	122.5(2)
N1-C40-C39	112.8(2)
N2-C1-H1	122.9(16)
N1-C1-H1	126.8(16)
N4-C26-H26	125.2(17)
N3-C26-H26	124.3(17)

Table S6. Anisotropic displacement parameters ($Å^2 x10^3$) for **[DEAM-*o*-XYLBI][OTf]$_2$ (1)**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ...+ 2 h k a^* b^* U^{12}]$.

	U^{11}	**U^{22}**	**U^{33}**	**U^{23}**	**U^{13}**	**U^{12}**
F1	72(1)	55(1)	60(1)	3(1)	49(1)	2(1)
S1	38(1)	62(1)	29(1)	-5(1)	17(1)	-14(1)
O1	34(1)	94(2)	35(1)	-1(1)	11(1)	-14(1)
F2	47(1)	86(2)	53(1)	17(1)	18(1)	9(1)
O2	43(1)	95(2)	32(1)	7(1)	18(1)	-20(1)
F3	112(2)	41(1)	94(2)	-3(1)	59(2)	-7(1)
O3	46(1)	54(1)	44(1)	-12(1)	23(1)	-7(1)
C41	56(2)	46(2)	44(2)	8(2)	22(2)	-6(2)
S2	63(1)	25(1)	40(1)	0(1)	33(1)	0(1)
O4	63(2)	30(1)	44(1)	8(1)	21(1)	-5(1)
N1	29(1)	21(1)	22(1)	-1(1)	9(1)	0(1)
N2	31(1)	22(1)	22(1)	1(1)	8(1)	0(1)
N3	35(1)	24(1)	25(1)	1(1)	16(1)	-1(1)
N4	29(1)	24(1)	24(1)	2(1)	13(1)	2(1)
C1	29(2)	26(2)	20(1)	2(1)	8(1)	-1(1)
C2	28(2)	30(2)	18(1)	2(1)	10(1)	1(1)
C3	33(2)	35(2)	25(1)	2(1)	12(1)	-3(1)
C4	30(2)	48(2)	34(2)	6(1)	14(1)	-3(1)
C5	38(2)	51(2)	36(2)	10(1)	23(2)	14(2)
C6	40(2)	34(2)	27(2)	4(1)	17(1)	8(1)
C7	33(2)	33(2)	13(1)	3(1)	10(1)	1(1)
C26	31(2)	32(2)	24(1)	7(1)	12(1)	2(1)
C27	37(2)	27(1)	17(1)	3(1)	14(1)	2(1)
C28	48(2)	29(2)	25(1)	1(1)	20(1)	8(1)
C29	35(2)	46(2)	27(2)	6(1)	18(1)	10(1)
C30	34(2)	45(2)	32(2)	2(1)	18(1)	-1(1)
C31	40(2)	32(2)	25(1)	1(1)	18(1)	-3(1)
C32	32(2)	26(1)	19(1)	2(1)	15(1)	1(1)
C33	37(2)	25(1)	29(2)	5(1)	16(1)	4(1)
C34	38(2)	21(1)	29(2)	0(1)	16(1)	4(1)
C35	38(2)	37(2)	29(2)	4(1)	16(1)	11(1)

C36	35(2)	46(2)	46(2)	1(2)	18(2)	12(2)
C37	43(2)	49(2)	42(2)	-2(2)	27(2)	4(2)
C38	44(2)	29(2)	31(2)	-1(1)	20(1)	3(1)
C39	33(2)	18(1)	30(1)	-2(1)	15(1)	2(1)
C40	39(2)	19(1)	29(2)	-1(1)	13(1)	0(1)

X-Ray Crystallography Details for [(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2):

Data were collected at 100 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoK_α radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in *SHELXTL6,* and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The asymmetric unit consists of the Pd complex cation, a triflate anion and a thf molecule disordered against a chloroform solvent molecule. The C19-C21 allyl group is disordered with the middle CH unit occupying two positions. The disordered parts were refined with dependent occupation factors; major to minor ration refined to 0.78(1) to 0.22(1), respectively. The thf molecule site occupation factor was fixed at 0.7 while that of the chloroform molecule was fixed at 0.3. A total of 552 parameters were refined in the final cycle of refinement using 9418 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 2.48% and 6.46%, respectively. Refinement was done using F^2.

SHELXTL6 (2000). Bruker-AXS, Madison, Wisconsin, USA.

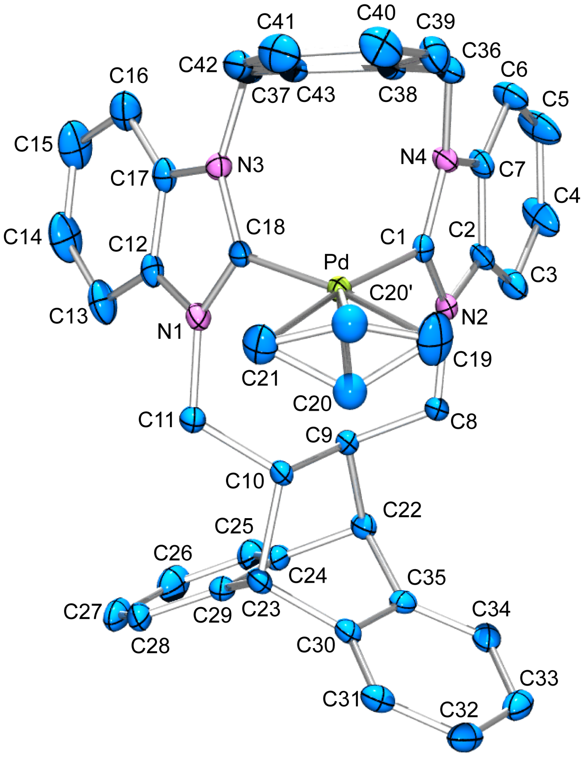


Figure S20. Molecular Structure of **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)** with ellipsoids drawn at the 50% probability level. Hydrogen atoms and OTf counter ion have been omitted for clarity.

Table S7. Crystal data, structure solution and refinement for **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)**.

identification code	mj28
empirical formula	$C_{47}H_{43}ClN_4Pd F_3O_4S$
formula weight	958.76
T (K)	100(2)
λ (Å)	0.71073
crystal system	monoclinic
space group	P2(1)
a (Å)	10.7929(10)
b (Å)	18.7805(17)
c (Å)	11.1768(10)
α (deg)	90
β (deg)	108.9260(10)
γ (deg)	90
V (Å^3)	2143.0(3)
Z	2
ρ_{calcd} (Mg mm^{-3})	1.486
crystal size (mm^3)	0.28 x 0.22 x 0.09
abs coeff (mm^{-1})	0.607
F(000)	982
θ range for data collection	1.93 to 27.50
limiting indices	$-13 \leq h \leq 14$, $-24 \leq k \leq 24$, $-13 \leq \ell \leq 14$
no. of reflns collcd	19749
no. of ind reflns (R_{int})	9600 (0.0149)
completeness to $\theta = 27.45°$	99.8 %
absorption corr	Numerical
refinement method	Full–matrix least–squares on F^2
data / restraints / parameters	9600 / 4 / 552
$R1$,[a] $wR2$[b] [I > 2σ]	0.0248, 0.0646
$R1$,[a] $wR2$[b] (all data)	0.0255, 0.0650
GOF[c] on F^2	1.043
largest diff. peak and hole	1.047 and –0.742 eÅ^{-3}

$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$

$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_o^2)+(m*p)^2+n*p]$, $p = [\max(F_o^2,0)+ 2* F_c^2]/3$, m & n are constants.

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	X	Y	Z	U(eq)
Pd1	7504(1)	5174(1)	692(1)	15(1)
S1	7681(1)	9518(1)	2898(1)	22(1)
F1	8595(2)	9857(1)	1064(2)	53(1)
F2	9751(2)	9082(1)	2360(2)	54(1)
F3	9833(2)	10172(2)	2924(2)	69(1)
O1	7063(2)	10204(2)	2768(2)	39(1)
O2	8347(2)	9298(1)	4175(2)	32(1)
O3	6926(2)	8971(1)	2086(2)	38(1)
O4	5771(7)	7617(3)	4785(5)	107(2)
N1	5494(2)	5205(1)	2054(2)	18(1)
N2	8089(2)	6562(1)	2091(2)	17(1)
N3	7219(2)	4636(1)	3180(2)	16(1)
N4	9583(2)	5794(1)	3033(2)	16(1)
C1	8539(2)	5902(1)	1977(2)	16(1)
C2	8842(2)	6884(1)	3222(2)	19(1)
C3	8764(2)	7548(1)	3739(3)	27(1)
C4	9686(2)	7688(2)	4912(3)	34(1)
C5	10634(3)	7186(2)	5529(3)	36(1)
C6	10727(2)	6524(1)	5007(2)	26(1)
C7	9798(2)	6388(1)	3829(2)	19(1)
C8	6977(2)	6918(1)	1168(2)	18(1)
C9	5628(2)	6758(1)	1316(2)	17(1)
C10	4854(2)	6173(1)	376(2)	17(1)
C11	4473(2)	5506(1)	967(2)	22(1)
C12	5305(2)	5066(1)	3208(2)	19(1)
C13	4276(2)	5215(2)	3660(2)	31(1)
C14	4397(3)	4964(2)	4861(3)	38(1)
C15	5495(3)	4579(2)	5579(3)	38(1)
C16	6539(3)	4446(2)	5132(2)	30(1)
C17	6417(2)	4696(1)	3937(2)	20(1)
C18	6662(2)	4942(1)	2032(2)	16(1)

C19	8183(3)	5317(2)	-920(2)	36(1)
C20	6919(3)	5072(2)	-1332(3)	24(1)
C20'	7593(11)	4692(7)	-1053(11)	27(3)
C21	6505(3)	4464(1)	-862(2)	25(1)
C22	4803(2)	7463(1)	1068(2)	18(1)
C23	3558(2)	6501(1)	-547(2)	18(1)
C24	3475(2)	7281(1)	1167(2)	19(1)
C25	2946(2)	7552(1)	2056(2)	26(1)
C26	1715(3)	7318(2)	2044(3)	31(1)
C27	1029(3)	6814(2)	1163(3)	30(1)
C28	1570(2)	6533(1)	291(2)	24(1)
C29	2795(2)	6773(1)	285(2)	19(1)
C30	3983(2)	7130(1)	-1157(2)	18(1)
C31	3849(2)	7192(1)	-2432(2)	23(1)
C32	4337(2)	7800(1)	-2850(2)	26(1)
C33	4979(2)	8322(1)	-1991(2)	26(1)
C34	5137(2)	8254(1)	-708(2)	21(1)
C35	4633(2)	7659(1)	-295(2)	17(1)
C36	10557(2)	5219(2)	3263(2)	21(1)
C37	8484(2)	4267(1)	3639(2)	23(1)
C38	10105(2)	4559(1)	2487(2)	19(1)
C39	10732(2)	4356(1)	1627(2)	25(1)
C40	10386(3)	3737(2)	928(3)	29(1)
C41	9385(3)	3312(1)	1057(3)	30(1)
C42	8755(2)	3504(1)	1901(2)	23(1)
C43	9115(2)	4118(1)	2647(2)	19(1)
C44	9035(3)	9666(2)	2280(3)	37(1)
C45	5646(7)	6865(5)	4950(8)	81(1)
C46	7061(7)	6600(5)	5631(7)	81(1)
C47	7345(9)	7237(5)	6564(9)	81(1)
C48	6987(9)	7956(8)	5928(10)	81(1)
C49	7390(20)	7214(3)	6297(6)	74(6)
Cl1	6281(5)	6577(2)	5484(4)	67(1)
Cl2	6752(6)	8028(3)	5678(6)	67(1)
Cl3	7662(4)	7138(2)	7902(4)	67(1)

Table S9. Bond lengths (in Å) for **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)**.

Bond	Distance	Bond	Distance
Pd1-C1	2.034(2)	C6-C7	1.395(3)
Pd1-C18	2.036(2)	C8-C9	1.547(3)
Pd1-C20	2.151(3)	C9-C10	1.562(3)
Pd1-C19	2.171(2)	C9-C22	1.569(3)
Pd1-C21	2.179(2)	C10-C11	1.533(3)
Pd1-C20'	2.181(12)	C10-C23	1.569(3)
S1-O2	1.4340(19)	C12-C13	1.390(3)
S1-O1	1.436(3)	C12-C17	1.397(3)
S1-O3	1.436(2)	C13-C14	1.388(4)
S1-C44	1.830(3)	C14-C15	1.398(5)
F1-C44	1.335(4)	C15-C16	1.396(4)
F2-C44	1.327(4)	C16-C17	1.380(3)
F3-C44	1.327(4)	C19-C20'	1.322(13)
O4-C45	1.436(10)	C19-C20	1.370(4)
O4-C48	1.635(13)	C20-C21	1.391(4)
N1-C18	1.361(3)	C20'-C21	1.331(12)
N1-C12	1.394(3)	C22-C24	1.511(3)
N1-C11	1.463(3)	C22-C35	1.519(3)
N2-C1	1.352(3)	C23-C30	1.508(3)
N2-C2	1.399(3)	C23-C29	1.517(3)
N2-C8	1.466(3)	C24-C25	1.393(3)
N3-C18	1.355(3)	C24-C29	1.397(3)
N3-C17	1.398(3)	C25-C26	1.396(4)
N3-C37	1.468(3)	C26-C27	1.394(4)
N4-C1	1.357(3)	C27-C28	1.392(4)
N4-C7	1.399(3)	C28-C29	1.399(3)
N4-C36	1.470(3)	C30-C31	1.390(3)
C2-C3	1.390(3)	C30-C35	1.403(3)
C2-C7	1.392(3)	C31-C32	1.399(4)
C3-C4	1.390(4)	C32-C33	1.390(4)
C4-C5	1.396(4)	C33-C34	1.394(3)
C5-C6	1.392(4)	C34-C35	1.386(3)

C36-C38	1.500(4)
C37-C43	1.504(3)
C38-C39	1.396(3)
C38-C43	1.408(3)
C39-C40	1.382(4)
C40-C41	1.387(4)
C41-C42	1.378(4)
C42-C43	1.402(3)
C45-C46	1.550(11)
C46-C47	1.550(11)
C47-C48	1.516(15)
C49-Cl3	1.727(9)
C49-Cl1	1.727(9)
C49-Cl2	1.727(9)

Table S10. Bond angles in (°) for **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)**.

Bond Angle	Angle	Bond Angle	Angle
C1-Pd1-C18	84.18(8)	C1-N4-C36	127.33(18)
C1-Pd1-C20	135.16(10)	C7-N4-C36	120.85(18)
C18-Pd1-C20	134.9(1)	N2-C1-N4	106.08(19)
C1-Pd1-C19	104.31(9)	N2-C1-Pd1	123.42(15)
C18-Pd1-C19	171.42(9)	N4-C1-Pd1	128.68(16)
C20-Pd1-C19	36.95(11)	C3-C2-C7	122.2(2)
C1-Pd1-C21	172.33(9)	C3-C2-N2	132.0(2)
C18-Pd1-C21	103.38(9)	C7-C2-N2	105.84(19)
C20-Pd1-C21	37.48(10)	C2-C3-C4	116.1(2)
C19-Pd1-C21	68.1(1)	C3-C4-C5	121.6(2)
C1-Pd1-C20'	137.5(3)	C6-C5-C4	122.5(3)
C18-Pd1-C20'	136.8(3)	C5-C6-C7	115.6(2)
C20-Pd1-C20'	26.5(3)	C2-C7-C6	122.0(2)
C19-Pd1-C20'	35.4(3)	C2-C7-N4	106.20(19)
C21-Pd1-C20'	35.5(3)	C6-C7-N4	131.8(2)
O2-S1-O1	115.21(11)	N2-C8-C9	114.82(18)
O2-S1-O3	114.94(12)	C8-C9-C10	112.46(18)
O1-S1-O3	115.29(13)	C8-C9-C22	108.47(17)
O2-S1-C44	102.44(13)	C10-C9-C22	108.98(17)
O1-S1-C44	103.14(13)	C11-C10-C9	116.43(19)
O3-S1-C44	103.20(14)	C11-C10-C23	107.35(17)
C45-O4-C48	111.6(7)	C9-C10-C23	109.51(17)
C18-N1-C12	111.25(18)	N1-C11-C10	116.01(19)
C18-N1-C11	125.26(18)	C13-C12-N1	132.2(2)
C12-N1-C11	122.97(17)	C13-C12-C17	121.6(2)
C1-N2-C2	111.13(18)	N1-C12-C17	106.14(18)
C1-N2-C8	126.13(19)	C14-C13-C12	116.6(3)
C2-N2-C8	122.73(19)	C13-C14-C15	121.8(2)
C18-N3-C17	111.59(18)	C16-C15-C14	121.3(3)
C18-N3-C37	127.45(18)	C17-C16-C15	116.8(3)
C17-N3-C37	120.96(18)	C16-C17-C12	121.9(2)
C1-N4-C7	110.75(18)	C16-C17-N3	132.4(2)

C12-C17-N3	105.62(19)
N3-C18-N1	105.40(18)
N3-C18-Pd1	128.35(15)
N1-C18-Pd1	124.94(16)
C20'-C19-C20	43.3(5)
C20'-C19-Pd1	72.7(5)
C20-C19-Pd1	70.74(15)
C19-C20-C21	123.8(3)
C19-C20-Pd1	72.31(15)
C21-C20-Pd1	72.34(15)
C19-C20'-C21	133.3(10)
C19-C20'-Pd1	71.9(5)
C21-C20'-Pd1	72.1(5)
C20'-C21-C20	42.8(5)
C20'-C21-Pd1	72.3(5)
C20-C21-Pd1	70.18(15)
C24-C22-C35	108.62(18)
C24-C22-C9	107.10(17)
C35-C22-C9	105.04(18)
C30-C23-C29	108.54(18)
C30-C23-C10	105.59(17)
C29-C23-C10	105.96(18)
C25-C24-C29	120.6(2)
C25-C24-C22	126.0(2)
C29-C24-C22	113.3(2)
C24-C25-C26	119.2(2)
C27-C26-C25	120.4(2)
C28-C27-C26	120.3(2)
C27-C28-C29	119.5(2)
C24-C29-C28	119.9(2)
C24-C29-C23	113.37(19)
C28-C29-C23	126.6(2)
C31-C30-C35	120.5(2)
C31-C30-C23	125.7(2)
C35-C30-C23	113.69(19)
C30-C31-C32	119.0(2)
C33-C32-C31	120.2(2)
C32-C33-C34	120.9(2)
C35-C34-C33	119.1(2)
C34-C35-C30	120.3(2)
C34-C35-C22	126.7(2)
C30-C35-C22	112.79(19)
N4-C36-C38	115.20(16)
N3-C37-C43	114.95(18)
C39-C38-C43	118.9(2)
C39-C38-C36	119.0(2)
C43-C38-C36	122.0(2)
C40-C39-C38	121.1(2)
C39-C40-C41	120.1(2)
C42-C41-C40	119.7(2)
C41-C42-C43	121.2(2)
C42-C43-C38	119.0(2)
C42-C43-C37	119.1(2)
C38-C43-C37	121.8(2)
F3-C44-F2	107.1(3)
F3-C44-F1	108.3(3)
F2-C44-F1	107.4(2)
F3-C44-S1	111.1(2)
F2-C44-S1	111.6(2)
F1-C44-S1	111.2(2)
O4-C45-C46	105.1(7)
C45-C46-C47	91.8(6)
C48-C47-C46	114.0(8)
C47-C48-O4	92.2(9)
Cl3-C49-Cl1	110.2(8)
Cl3-C49-Cl2	113.6(9)
Cl1-C49-Cl2	106.5(8)

Table S11. Anisotropic displacement parameters ($Å^2$ x10^3) for **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ...+ 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd1	13(1)	17(1)	13(1)	1(1)	3(1)	-2(1)
S1	23(1)	23(1)	21(1)	-1(1)	8(1)	0(1)
F1	71(1)	60(1)	44(1)	18(1)	40(1)	22(1)
F2	49(1)	68(1)	59(1)	17(1)	34(1)	28(1)
F3	53(1)	74(1)	92(2)	-13(2)	40(1)	-31(2)
O1	52(1)	30(1)	45(1)	10(1)	31(1)	14(1)
O2	37(1)	36(1)	20(1)	-2(1)	8(1)	0(1)
O3	33(1)	38(1)	34(1)	-7(1)	-2(1)	-7(1)
O4	172(6)	85(4)	48(3)	11(3)	15(3)	-13(4)
N1	14(1)	16(1)	23(1)	2(1)	6(1)	0(1)
N2	13(1)	16(1)	20(1)	2(1)	2(1)	-2(1)
N3	16(1)	17(1)	15(1)	1(1)	4(1)	-1(1)
N4	13(1)	16(1)	19(1)	-1(1)	2(1)	0(1)
C1	14(1)	16(1)	19(1)	2(1)	7(1)	-2(1)
C2	11(1)	19(1)	23(1)	-1(1)	1(1)	-1(1)
C3	16(1)	19(1)	40(1)	-3(1)	3(1)	0(1)
C4	23(1)	26(1)	44(2)	-17(1)	2(1)	-1(1)
C5	23(1)	35(2)	38(2)	-15(1)	-7(1)	2(1)
C6	18(1)	26(1)	27(1)	-5(1)	-3(1)	2(1)
C7	14(1)	17(1)	24(1)	-3(1)	3(1)	-2(1)
C8	13(1)	18(1)	21(1)	6(1)	1(1)	-1(1)
C9	14(1)	16(1)	19(1)	3(1)	3(1)	-1(1)
C10	11(1)	15(1)	23(1)	2(1)	2(1)	-1(1)
C11	14(1)	18(1)	32(1)	7(1)	4(1)	1(1)
C12	19(1)	16(1)	24(1)	-4(1)	8(1)	-4(1)
C13	24(1)	34(1)	40(1)	-8(2)	18(1)	-6(2)
C14	34(1)	52(2)	37(1)	-12(1)	24(1)	-10(1)
C15	42(2)	56(2)	22(1)	-6(1)	18(1)	-15(1)
C16	31(1)	37(1)	20(1)	-2(1)	7(1)	-9(1)
C17	20(1)	20(1)	20(1)	-4(1)	8(1)	-6(1)
C18	13(1)	13(1)	19(1)	0(1)	2(1)	-2(1)

C19	45(1)	46(2)	21(1)	-5(1)	19(1)	-14(1)
C21	29(1)	28(1)	17(1)	-5(1)	6(1)	-6(1)
C22	16(1)	17(1)	19(1)	0(1)	4(1)	1(1)
C23	12(1)	18(1)	21(1)	1(1)	1(1)	0(1)
C24	17(1)	19(1)	22(1)	6(1)	7(1)	2(1)
C25	25(1)	27(1)	28(1)	4(1)	11(1)	3(1)
C26	32(1)	33(1)	36(1)	8(1)	20(1)	6(1)
C27	21(1)	30(1)	44(2)	16(1)	17(1)	4(1)
C28	15(1)	20(1)	34(1)	8(1)	6(1)	0(1)
C29	15(1)	18(1)	24(1)	6(1)	5(1)	3(1)
C30	11(1)	20(1)	21(1)	2(1)	2(1)	1(1)
C31	16(1)	28(1)	21(1)	1(1)	2(1)	4(1)
C32	21(1)	35(1)	23(1)	9(1)	8(1)	8(1)
C33	22(1)	26(1)	32(1)	12(1)	12(1)	7(1)
C34	16(1)	18(1)	28(1)	3(1)	7(1)	4(1)
C35	13(1)	19(1)	19(1)	4(1)	4(1)	4(1)
C36	15(1)	19(1)	26(1)	-1(1)	1(1)	2(1)
C37	16(1)	30(1)	19(1)	9(1)	1(1)	5(1)
C38	14(1)	19(1)	22(1)	2(1)	2(1)	2(1)
C39	19(1)	26(1)	30(1)	-1(1)	10(1)	-1(1)
C40	27(1)	32(1)	29(1)	-6(1)	11(1)	6(1)
C41	30(1)	21(1)	32(1)	-7(1)	2(1)	2(1)
C42	18(1)	18(1)	28(1)	4(1)	0(1)	-1(1)
C43	15(1)	19(1)	20(1)	4(1)	2(1)	2(1)
C44	38(2)	40(2)	41(2)	4(1)	22(1)	3(1)
C45	60(2)	113(4)	85(3)	-16(2)	45(2)	-6(2)
C46	60(2)	113(4)	85(3)	-16(2)	45(2)	-6(2)
C47	60(2)	113(4)	85(3)	-16(2)	45(2)	-6(2)
C48	60(2)	113(4)	85(3)	-16(2)	45(2)	-6(2)
Cl1	75(2)	56(1)	72(1)	5(1)	27(1)	13(1)
Cl2	75(2)	56(1)	72(1)	5(1)	27(1)	13(1)
Cl3	75(2)	56(1)	72(1)	5(1)	27(1)	13(1)

Variable Temperature NMR Details:

Activation parameters for rotation have been measured in acetone-d_6, DMSO-d_6, and $CDCl_3$ by line-shape analysis[4,5] using ^1H NMR spectroscopy in the temperature range -60 to 120 °C. The temperature was raised incrementally in steps of 5-15 °C, and 5 minutes were allowed for temperature equilibration before shimming at each temperature. The reading of the thermocouple was corrected according to a methanol standard.

All the exchange processes exhibited equal populations and thus the rates were calculated according to the following equations:

1. slow exchange limit:

$$k=\pi(\Delta W)$$

Where $\Delta W = W - W_o$, W=width at half-height and $k \ll v_1 - v_2$, v=frequency in Hz of the exchanging protons.

2. coalescence temperature:

$$k=\pi(v_1-v_2)/(\text{sqrt}2)$$

3. fast exchange limit:

$$k==\pi(v_1-v_2)^2 /2(W-W_f)$$

Where $k \gg v_1-v_2$

Error Treatment

1. The temperature was measured and maintained by a thermocouple controlled by the console unit. Errors in fluctuation of temperature were accounted for by generating a calibration curve over the temperature range.

2. Digital resolution is 0.137 Hz. The measurement of peak frequency is ± 1 Hz.

3. The standard errors on the slope and intercept for the Eyring plots were calculated and then all the errors were propagated (page 112, reference 4).

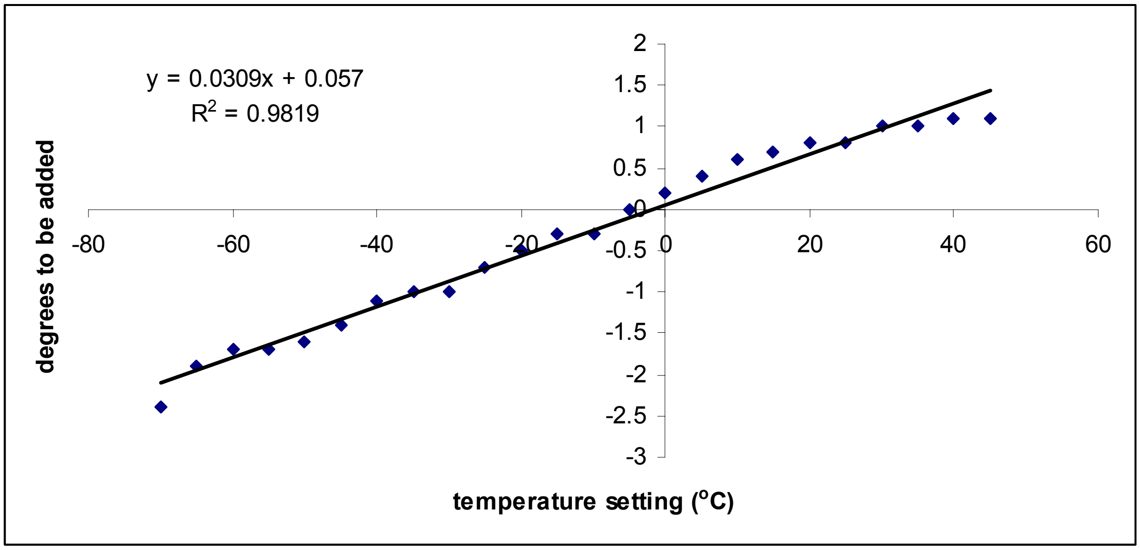


Figure S21. Temperature calibration curve for the INOVA 500.

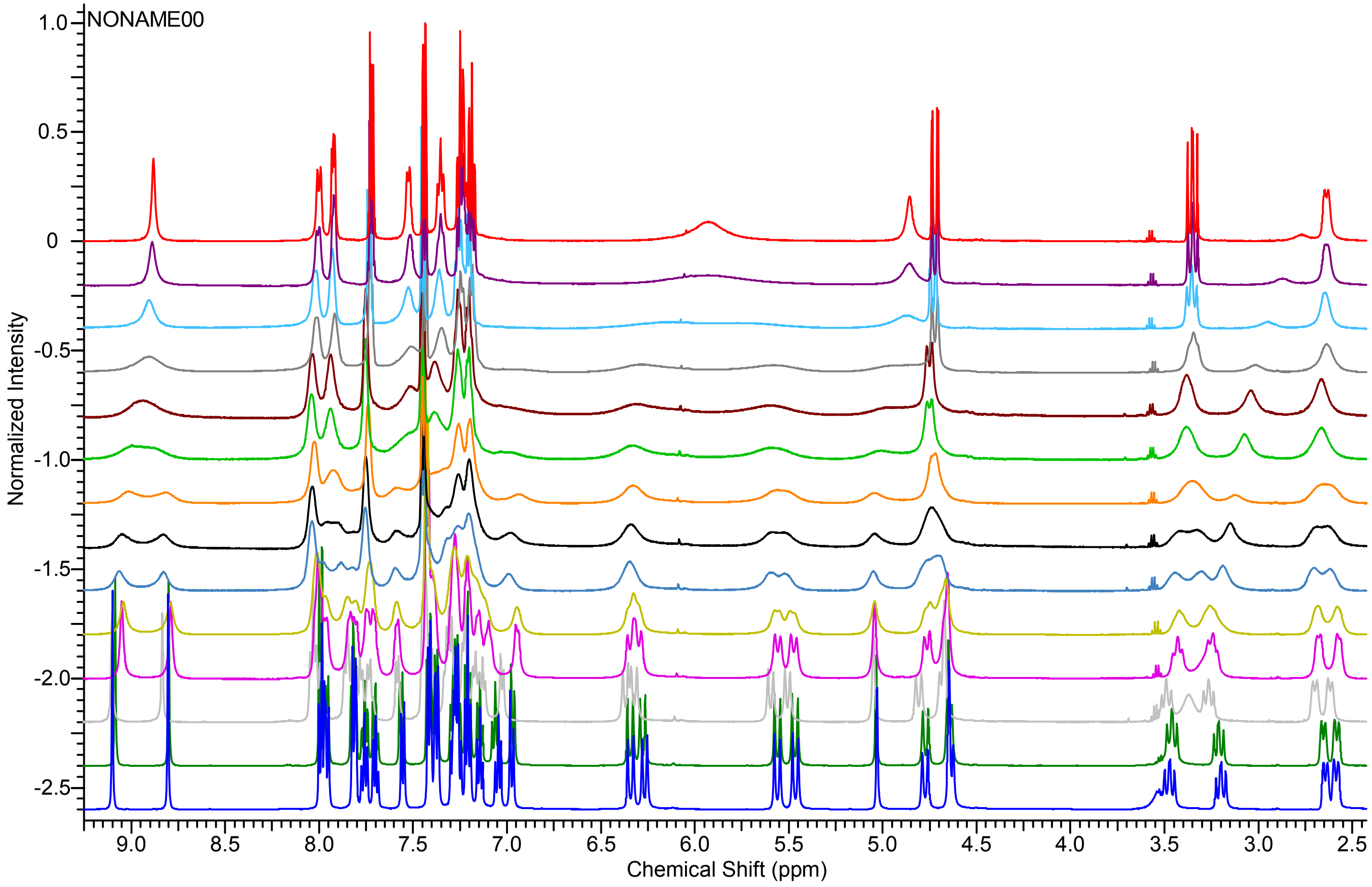


Figure S22. Variable temperature NMR of **[DEAM-*o*-XYLBI][OTf]$_2$ (1)** in acetone-d$_6$. Temperatures (°C) from top to bottom; 50, 35, 25, 15, 10, 5, 0, -5, -10, -15, -25, -35, -50, -60.

Table S12. Rate constant determinations by monitoring the resonance at 5.9 ppm on the INOVA 500 in acetone-*d*$_6$. Data correlates to the arene ring flipping motion.

Temp, °C (probe)	Temp, °C (calibrated)	Temp (K)	W (Hz)	**k (1/s)**	**ΔG‡ (kcal/mol)**	Ln(k/T)	1/T
-60	-61.8	211.4	17.5				
-50	-51.5	221.7	20.0	**7.9**	**11.9**	-3.34013	0.004511
-35	-36.0	237.1	27.0	**29.8**	**12.2**	-2.07257	0.004217
-25	-25.7	247.4	44.0	**83.3**	**12.2**	-1.08927	0.004041
0	0.1	273.2	93.0	**237.2**	**13.0**	-0.14137	0.00366
5	5.2	278.4	100.5	**260.8**	**13.2**	-0.06535	0.003592
10	10.4	283.5	135.5	**370.7**	**13.2**	0.268146	0.003527
15	15.5	288.7	145.5	**402.1**	**13.4**	0.331474	0.003464
25	25.8	299.0		**888.6**	**13.5**	1.089246	0.003345
35	36.1	309.3	226.0	**1164.9**	**13.8**	1.326117	0.003233
50	51.6	324.8	95.0				

Notes: ΔG‡ calculated from –RT[Ln(k/T)+Ln(h/κ)], coalescence temperature is 25 °C

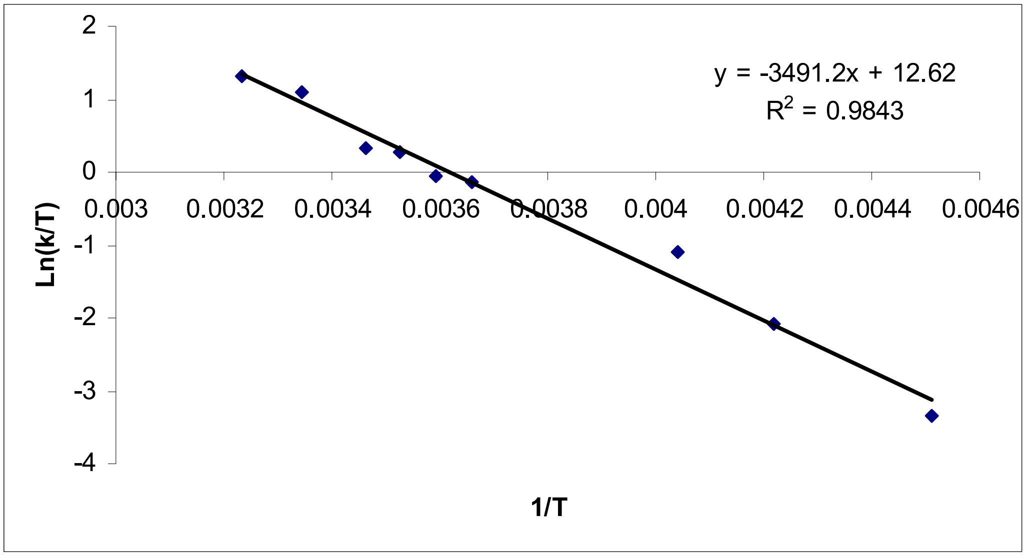


Figure S23. Eyring plot for the arene ring flipping motion.

ΔG‡=ΔH‡-TΔS‡, T=298 K

ΔG‡=13.6 ± 0.3 kcal/mol, ΔH‡ = 6.9 ± 0.3 kcal/mol ΔS‡= -22.1 ± 1.2 cal/mol

Table S13. Rate constant determinations by monitoring the resonance at 8.8 ppm on the INOVA 500 in acetone-*d*$_6$. Data correlates to the benzimidazole ring rotation motion.

Temp, °C (probe)	Temp, °C (calibrated)	Temp (K)	W (Hz)	**k (1/s)**	**$\Delta G^\ddagger$ (kcal/mol)**	Ln(k/t)	1/t
-60	-61.8	211.4	2.95				
-50	-51.5	221.7	3.20	**0.8**	**12.9**	-5.64272	0.004511
-35	-36.0	237.1	5.70	**8.6**	**12.8**	-3.31226	0.004217
-25	-25.7	247.4	11.00	**25.3**	**12.8**	-2.28074	0.004041
-15	-15.4	257.7	21.00	**56.7**	**12.9**	-1.51409	0.00388
-10	-10.3	262.9	34.00	**97.5**	**12.9**	-0.99144	0.003804
-5	-5.1	268.1	52.50	**155.7**	**12.9**	-0.54347	0.003731
0	0.1	273.2	81.00	**245.2**	**13.0**	-0.10815	0.00366
5	5.2	278.4		**333.2**	**13.0**	0.179871	0.003592
10	10.4	283.5	89.50	**446.0**	**13.1**	0.452977	0.003527
15	15.5	288.7	78.00	**521.7**	**13.3**	0.591743	0.003464
25	25.8	299	35.00	**1428.0**	**13.2**	1.563653	0.003345
35	36.1	309.3	20.50	**3448.1**	**13.1**	2.411301	0.003233
50	51.6	324.8	10.25				

Notes: $\Delta G^\ddagger$ calculated from $-RT[\mathrm{Ln}(k/T)+\mathrm{Ln}(h/\kappa)]$, coalescence temperature is 5 °C

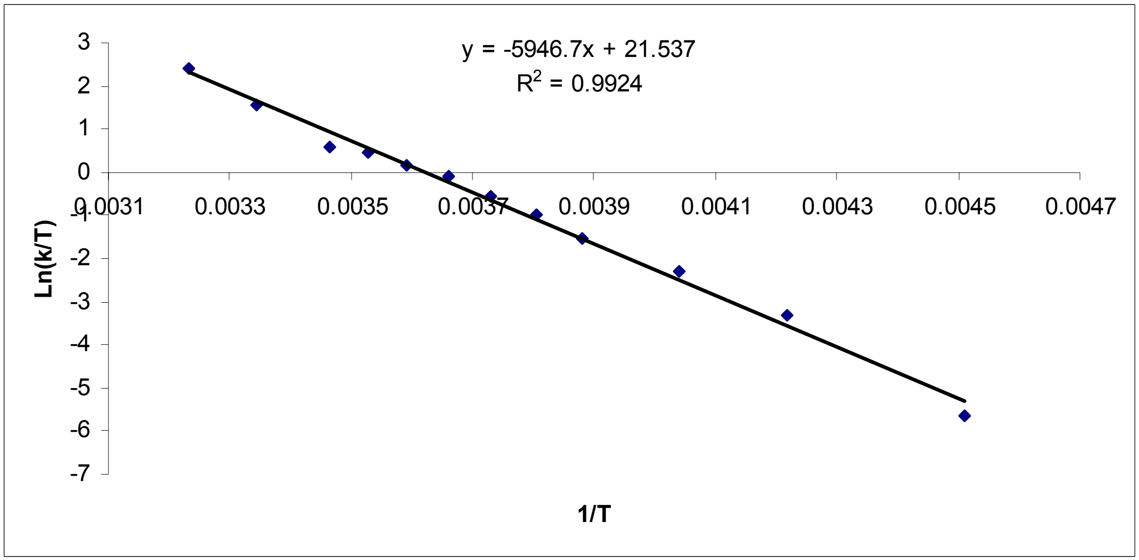


Figure S24. Eyring plot for the benzimidazole ring rotation motion.

$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, T=298 K

$\Delta G^\ddagger = 13.1 \pm 0.3$ kcal/mol, $\Delta H^\ddagger = 11.8 \pm 0.3$ kcal/mol $\Delta S^\ddagger = -4.4 \pm 1.2$ cal/mol

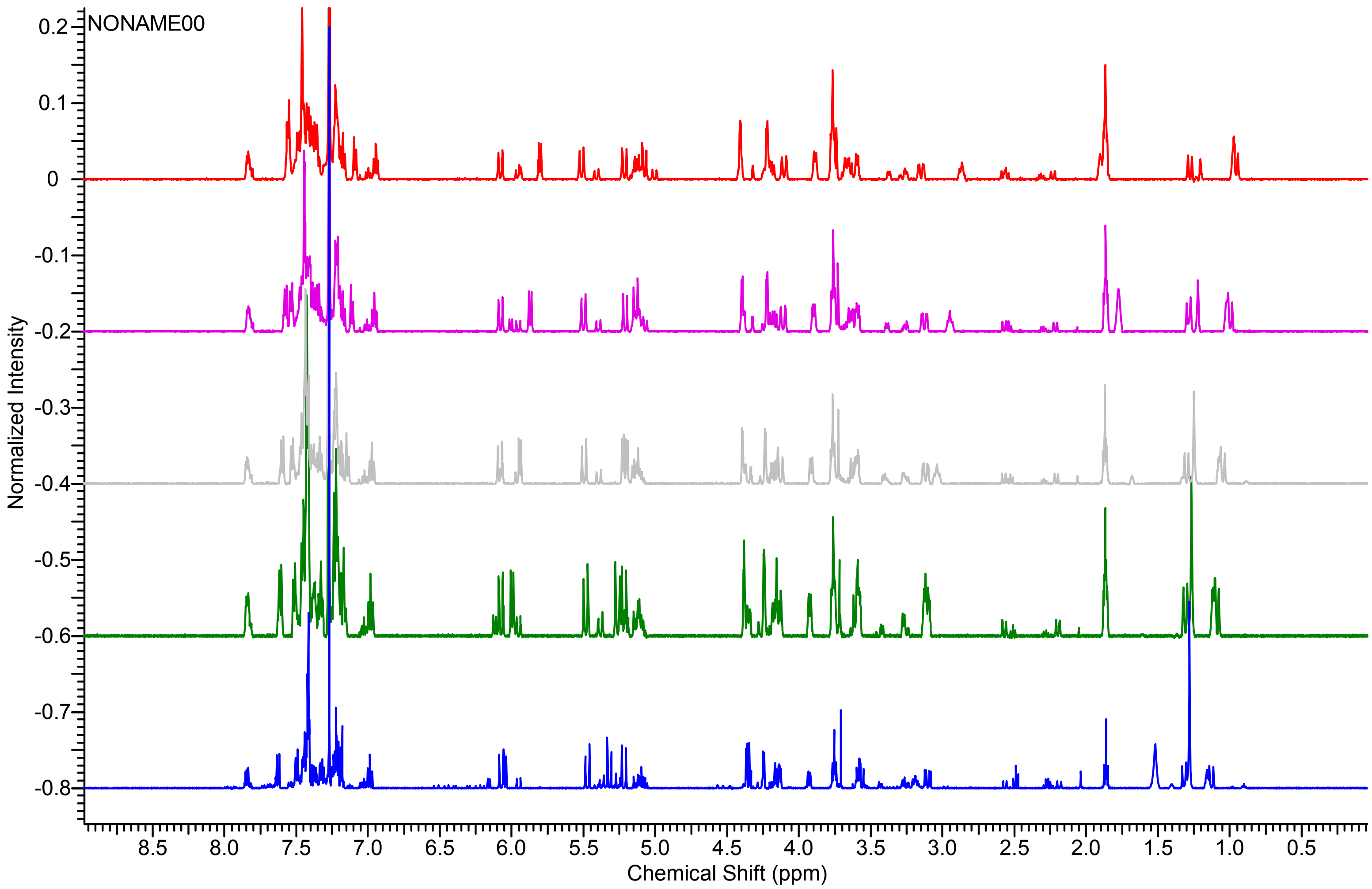


Figure S25. Variable temperature NMR of **[(DEAM-*o*-XYLBI)Pd(η^3-C_3H_5)][OTf] (2)** in $CDCl_3$. Temperatures (°C) from top to bottom; 50, 25, 0, -25, -50.

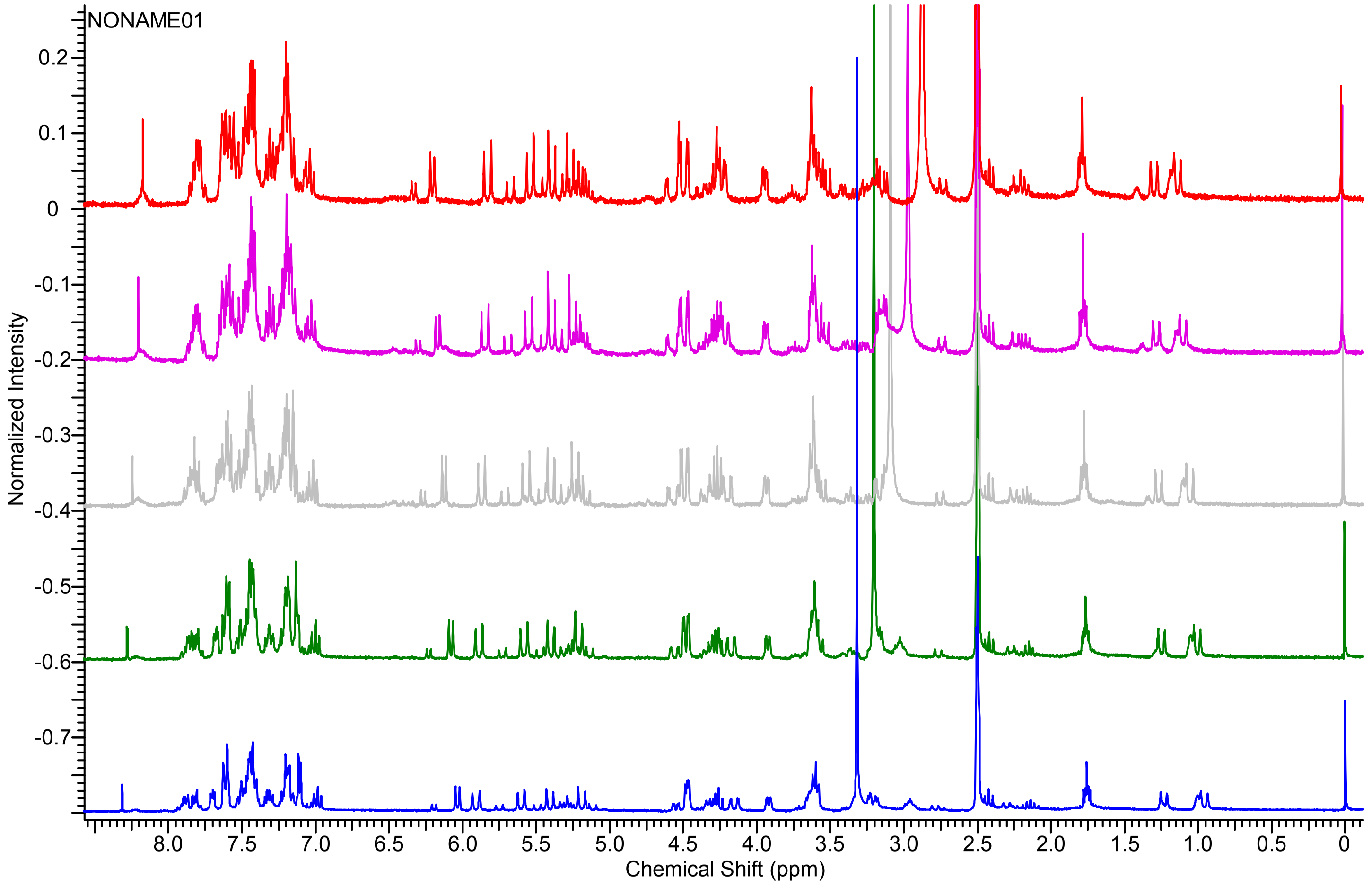


Figure S26. Variable temperature NMR of **[(DEAM-*o*-XYLBI)Pd(η^3-C$_3$H$_5$)][OTf] (2)** in DMSO-d_6. Temperatures (°C) from top to bottom; 120, 100, 75, 50, 25.

General catalytic details

1,4 conjugate addition of phenylboronic acid to 2-cyclohexen-1-one

To a 20 mL glass vial was added 95 mg (1.5 eq.) phenylboronic acid, 30 mg (*S*,*S*)-**2** and base (either 17 mg KOH (33 mol%) or 84 mg K_2CO_3 (50 mol%)) on the benchtop. Solvent that was degassed with argon for 20 minutes was then added (either 2.2 mL 10:1 THF:H_2O or 2.5 mL 4:1 dioxane:MeOH). Finally, 100 μL 2-cyclohexen-1-one was added. The reaction was allowed to stir at the appropriate temperature and time (50 °C/ 24 h, 25 °C/48 h). 1 mL of a saturated solution of sodium bicarbonate was then added. The product was then extracted with 2x5 mL diethyl ether. The solvent was removed in vacuo leaving the crude product as an oil. 5 mL of hexanes was then added to the oil. The final solution was filtered and hexanes removed in vacuo leaving the purified product. The yield was measured by ^{1}H NMR spectroscopy and the % enantiomeric excess determined by HPLC. HPLC conditions: Column diacel IA, 98:2 hexanes:isopropanol, λ=254 nm, 0.5 mL/min. biphenyl, 7.4 min; (*R*)-3-Phenylcyclohexanone, 16.8 min; (*S*)-3-Phenylcyclohexanone, 19.3 min.

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