Electronic Supporting Information

Synthesis, characterization, photophysical properties, and catalytic activity of an SCS bis(N-heterocyclic thione) (SCS-NHT) Pd pincer complex.

Ginger E. Tyson[a,c], Kenan Tokmic[b], Casey S. Oian[b], Daniel Rabinovich*[b], Henry U. Valle[a,c], T. Keith Hollis,*[a,c] John T. Kelly[c], Kristina A. Cuellar[c], Louis E. McNamara[c], Nathan I. Hammer*[c], Charles Edwin Webster,*[a,d] Allen G. Oliver*[e], Min Zhang[a]

[a]Department of Chemistry, Mississippi State University, Mississippi State, MS 39762
[b]Department of Chemistry, University of North Carolina at Charlotte, Charlotte, NC 28223.
[c]Department of Chemistry and Biochemistry, The University of Mississippi, University, MS 38677.
[d]Department of Chemistry, The University of Memphis, Memphis, TN 38152.
[e]Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA.

Table of Contents

Catalysis experimental details……S2

Figures S1-S5. NMR Spectra of **2** and **3**……S3-S7
Figures S6-S11. ^{1}H NMR spectra of DMSO titrations……S8-S13

Figure S12. ESI-TOF MS for complex **3**……S14

Figures S13-S14. Absorbance data in solid state and solution for complex **3**……S15-S16
Figures S15. Emission spectra in solution for complex **3**……S17

Figure S16. Lifetime measurements for complex **3**……S18

Figure S17. Photostability of complex **3**……S19

Figure S18. Raman spectra of complex **3** and computational simulation……S20

Crystallographic Reports

Compound **2**……S21-S28

Complex **3**……S28-S36

Figure S19. 3-D representations of various B3LYP DFT computed geometries……S37

Figure S20. Free energy diagram for the proposed mechanism for the isomerization of **3P**……S38

Table S8. Raw and relative energies……S39

DFT Computational Output……S40-51

Figure S21. ESI-MS of catalytic trial……S53

Catalysis

All reactions were carried out in air and no attempts to eliminate moisture were made. GC/MS yields were determined using toluene as an internal standard.

2-methyl 3-phenyl methyl ester: Iodobenzene (0.14 g, 0.69 mmol), methyl methacrylate (0.14 g, 1.4 mmol), Et_3N (0.07g, 0.69 mmol), complex **3** (10.9 mg, 2 mol %), and DMF (1.0 mL) were combined and heated at 80 ^oC for 52 h. GC/MS Calc: 176 m/z; Found: 176 m/z.

Butyl-3-phenylacrylate: Iodobenzene (0.14 g, 0.69 mmol), *n*-butyl acrylate (0.18 g, 1.4 mmol), Et_3N (0.07g, 0.69 mmol), complex **3** (10.9 mg, 2 mol %), and DMF (1.0 mL) were combined and heated at 80 ^oC for 52 h. GC/MS Calc: 218 m/z. Found: 218 m/z.

Biphenyl: Iodobenzene (25 mg, 0.12 mmol), phenylboronic acid (23 mg, 0.19 mmol), Cs_2CO_3 (20 mg, 0.25 mmol), complex **3** (1.3 mg, 2 mol %), and dioxane (1.0 mL) were added to a vial and heated at 80 ^oC for 48h. GC/MS Calc: 154 m/z. Found: 154 m/z.

4-Phenyltoluene: Iodobenzene (25 mg, 0.12 mmol), p-tolylboronic acid (25 mg, 0.19 mmol), Cs_2CO_3 (20 mg, 0.25 mmol), complex **3** (1.3 mg, 2 mol %), and dioxane (1.0 mL) were added to a vial and heated at 80 ^oC for 48h. GC/MS Calc: 168 m/z. Found: 168 m/z.

Diphenylacetylene: Iodobenzene (25, 0.12 mmol), phenylacetylene (15 mg, 0.15 mmol), CuI (2 mol %), $CsCO_3$ (20 mg, 0.24 mmol), complex **3** (2 mol %), and DMSO (1.0 mL) were added to a vial and heated at 80 ^oC for 18 h. GC/MS Calc: 178 m/z. Found: 178 m/z.

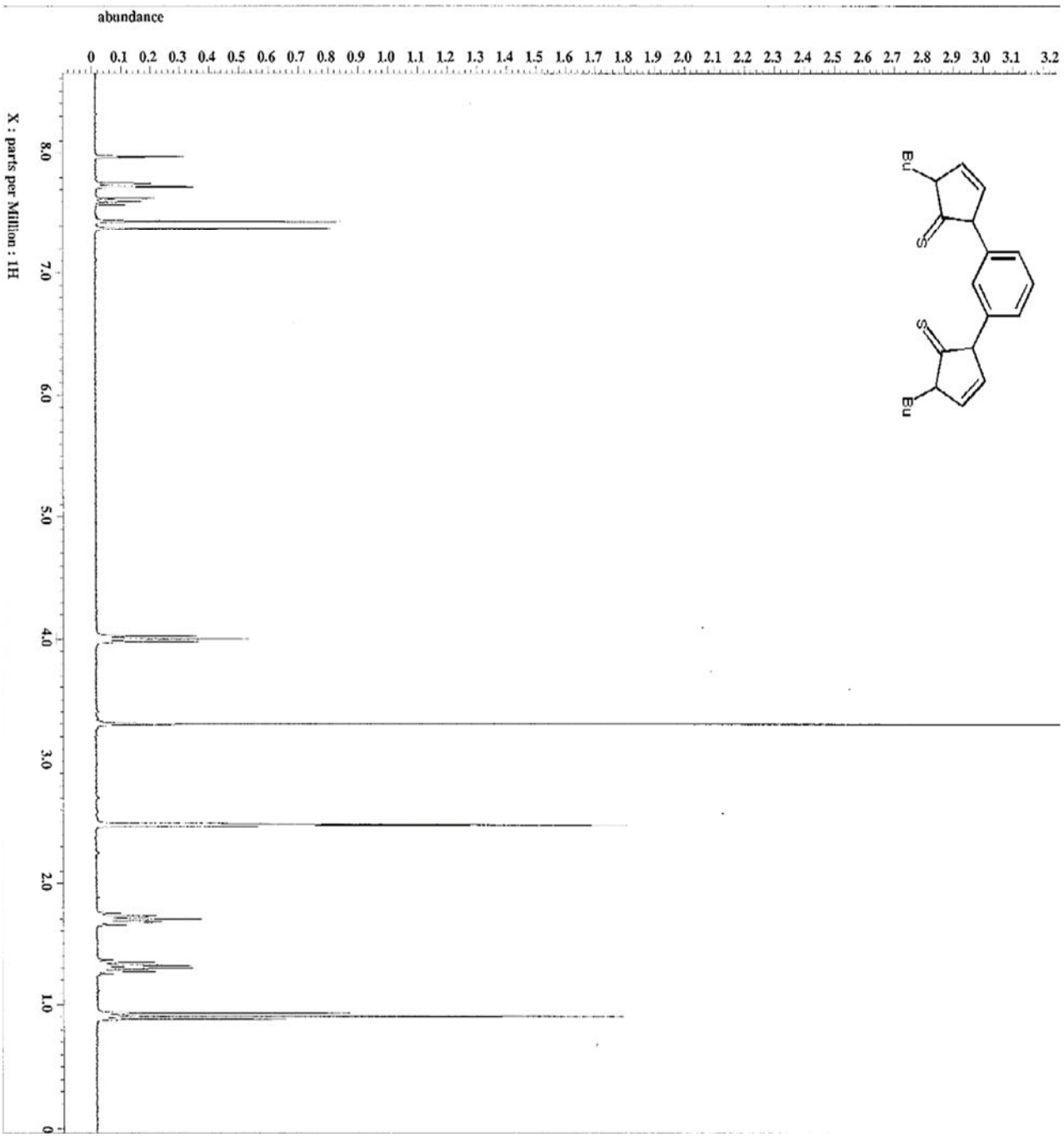

Figure S1. ^{1}H NMR spectra of ligand precursor **2** in DMSO-d_6.

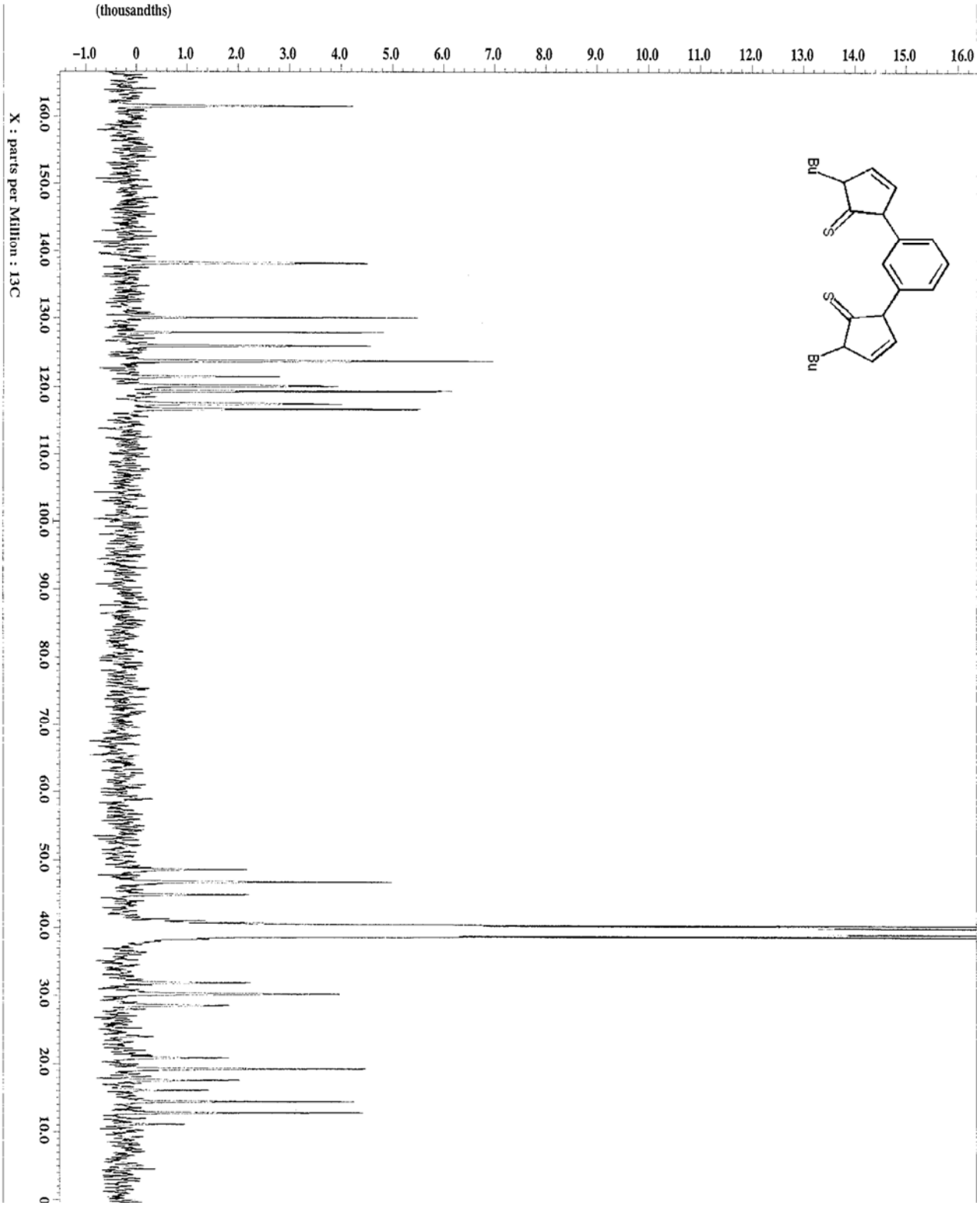

Figure S2. ^{1}H-coupled ^{13}C NMR of ligand precursor **2** in DMSO-d_6.

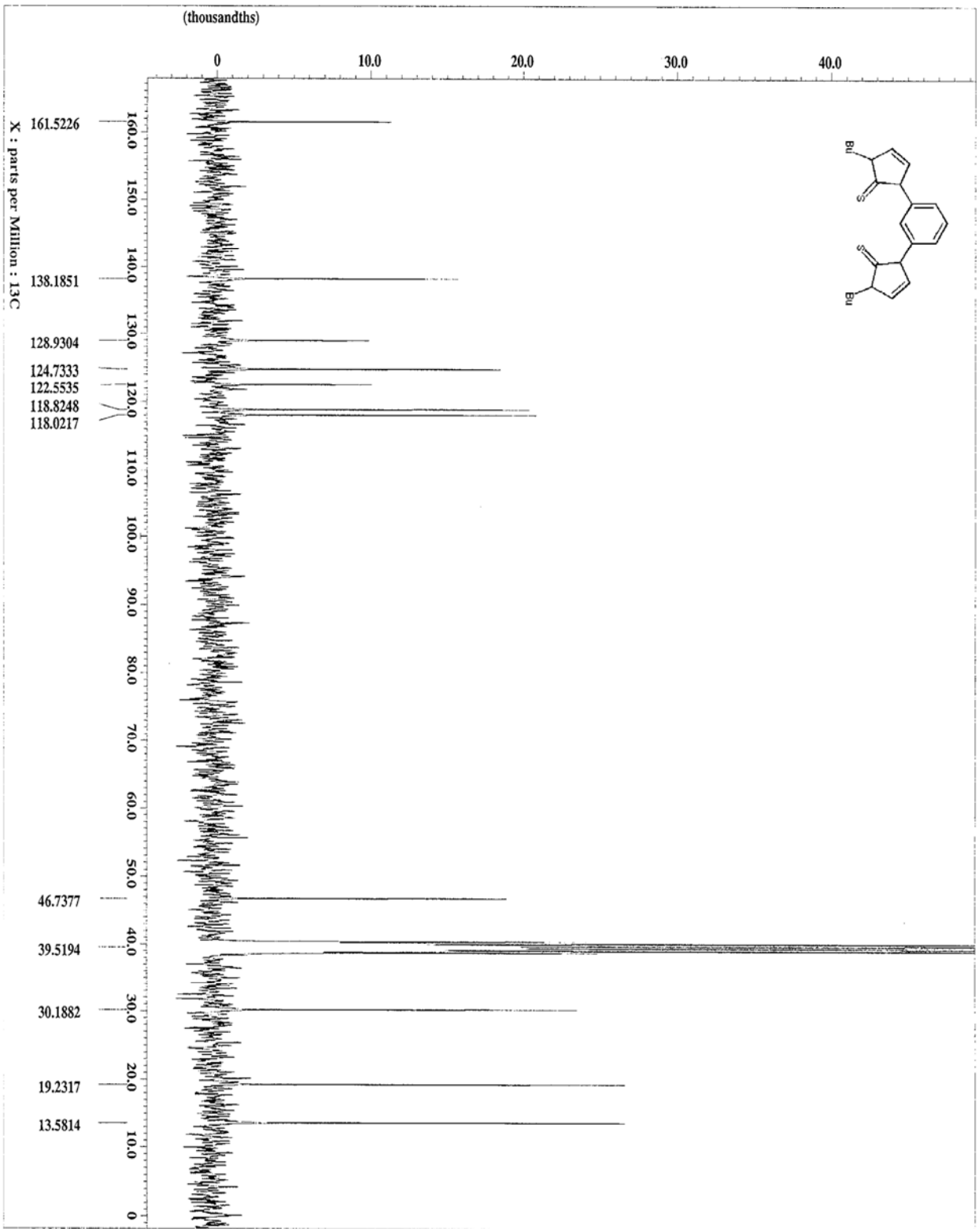

Figure S3. Decoupled ^{13}C of thione ligand precursor **2**.

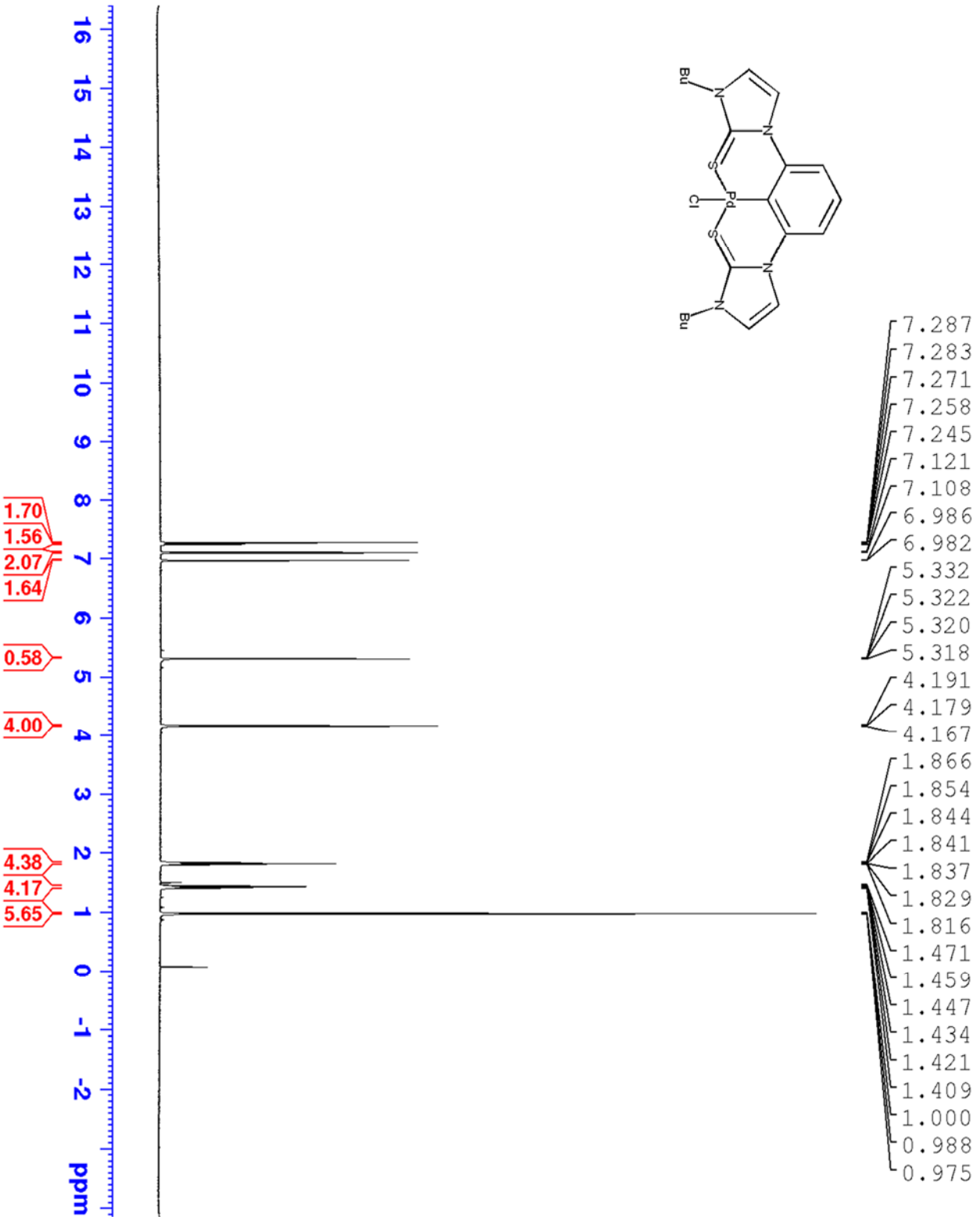

Figure S4. ^{1}H NMR of complex **3**.

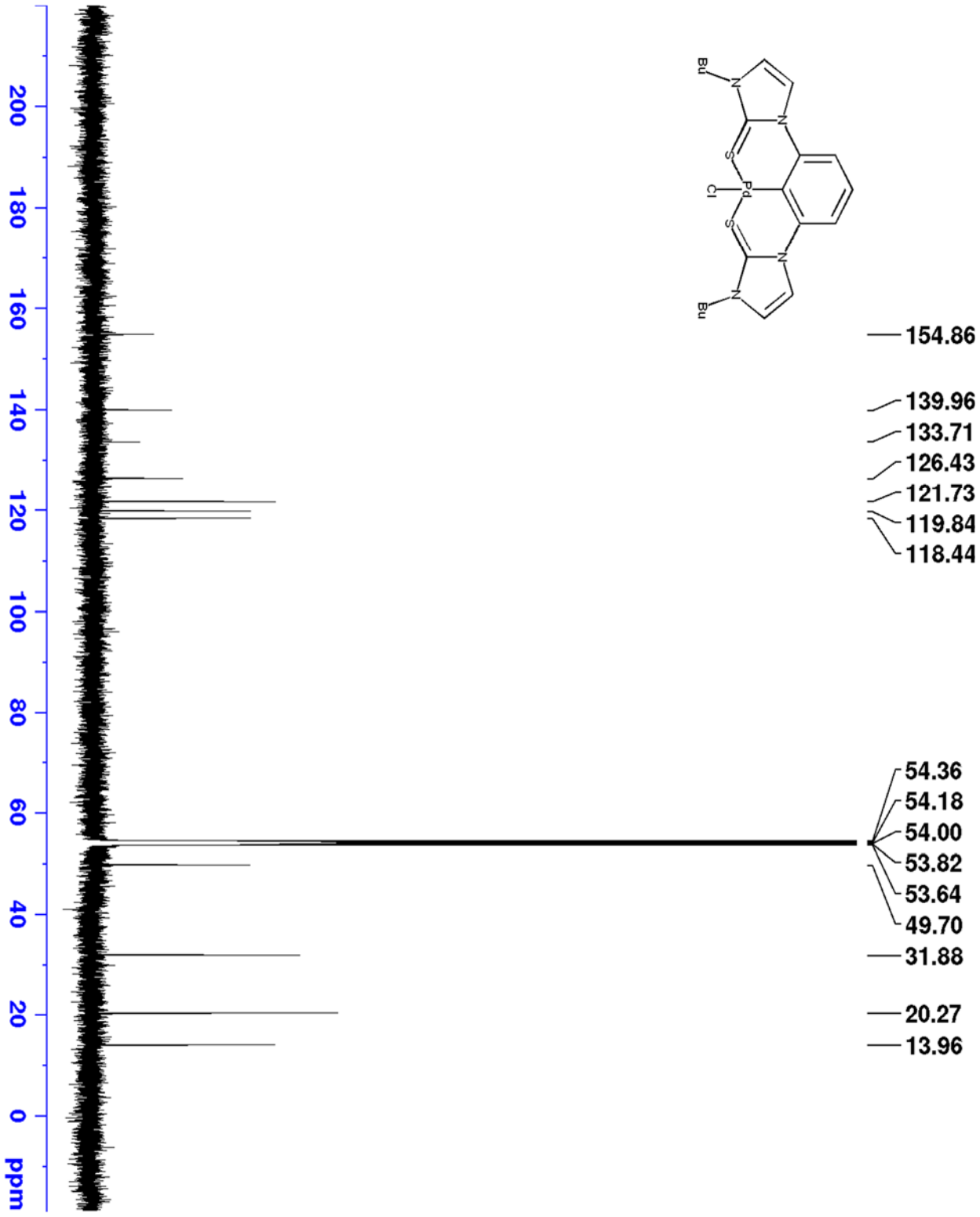

Figure S5. ^{13}C NMR of complex **3**.

DMSO Titrations

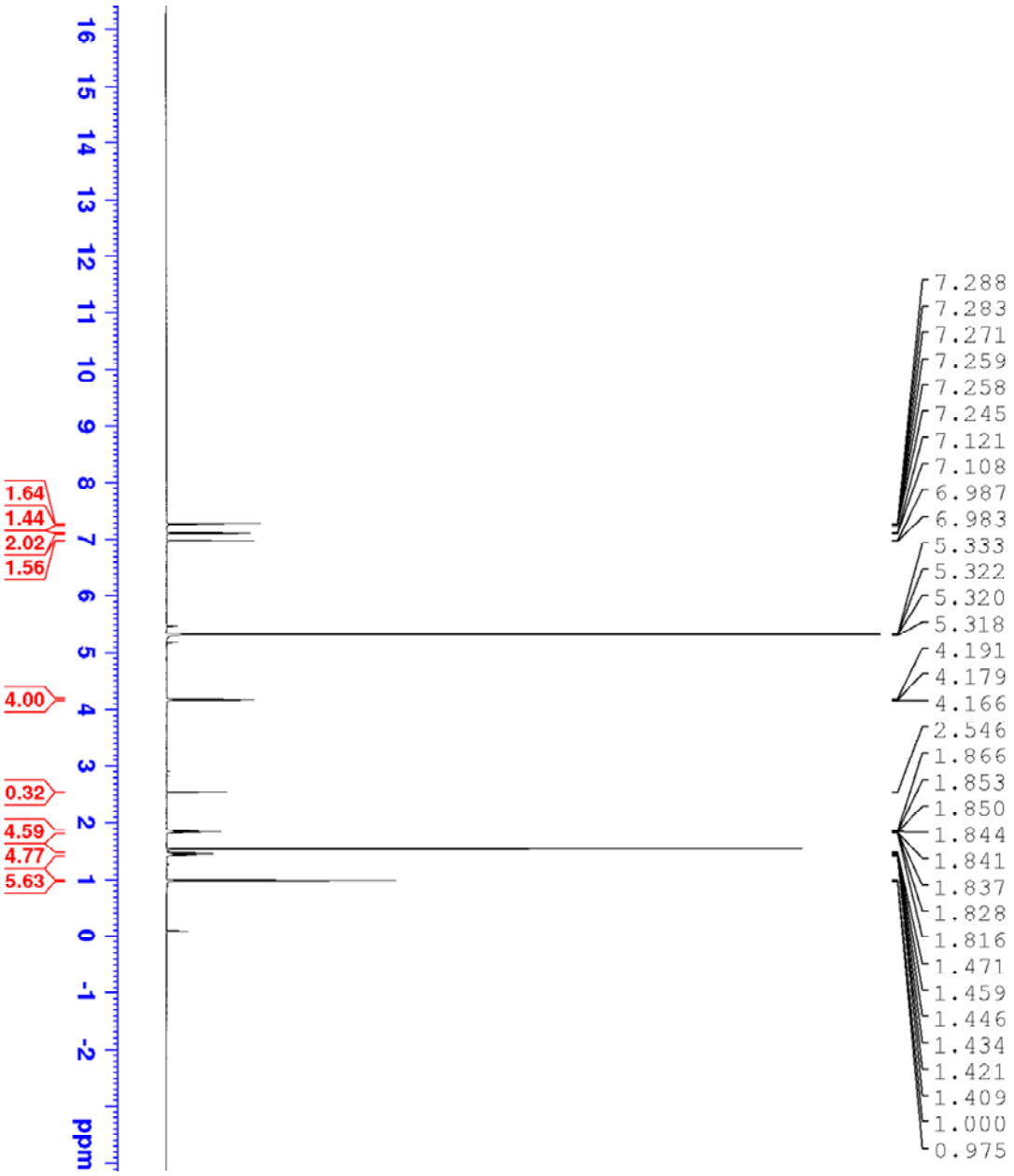

Figure S6. ^{1}H NMR of complex **3** in CD_2Cl_2 with 0.1 equiv. DMSO.

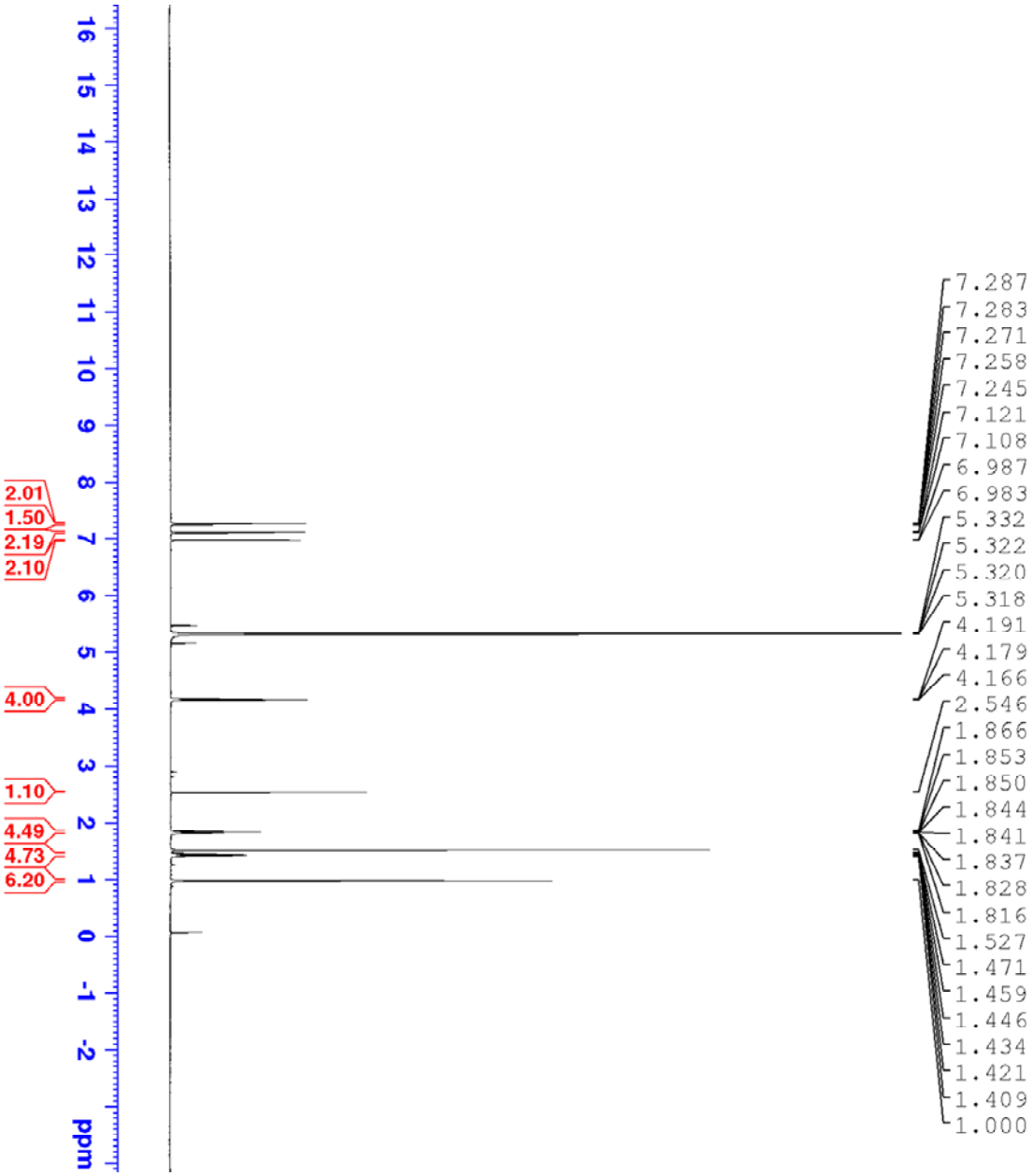

Figure S7. ^{1}H NMR of complex **3** in CD_2Cl_2 with 0.3 equiv. DMSO.

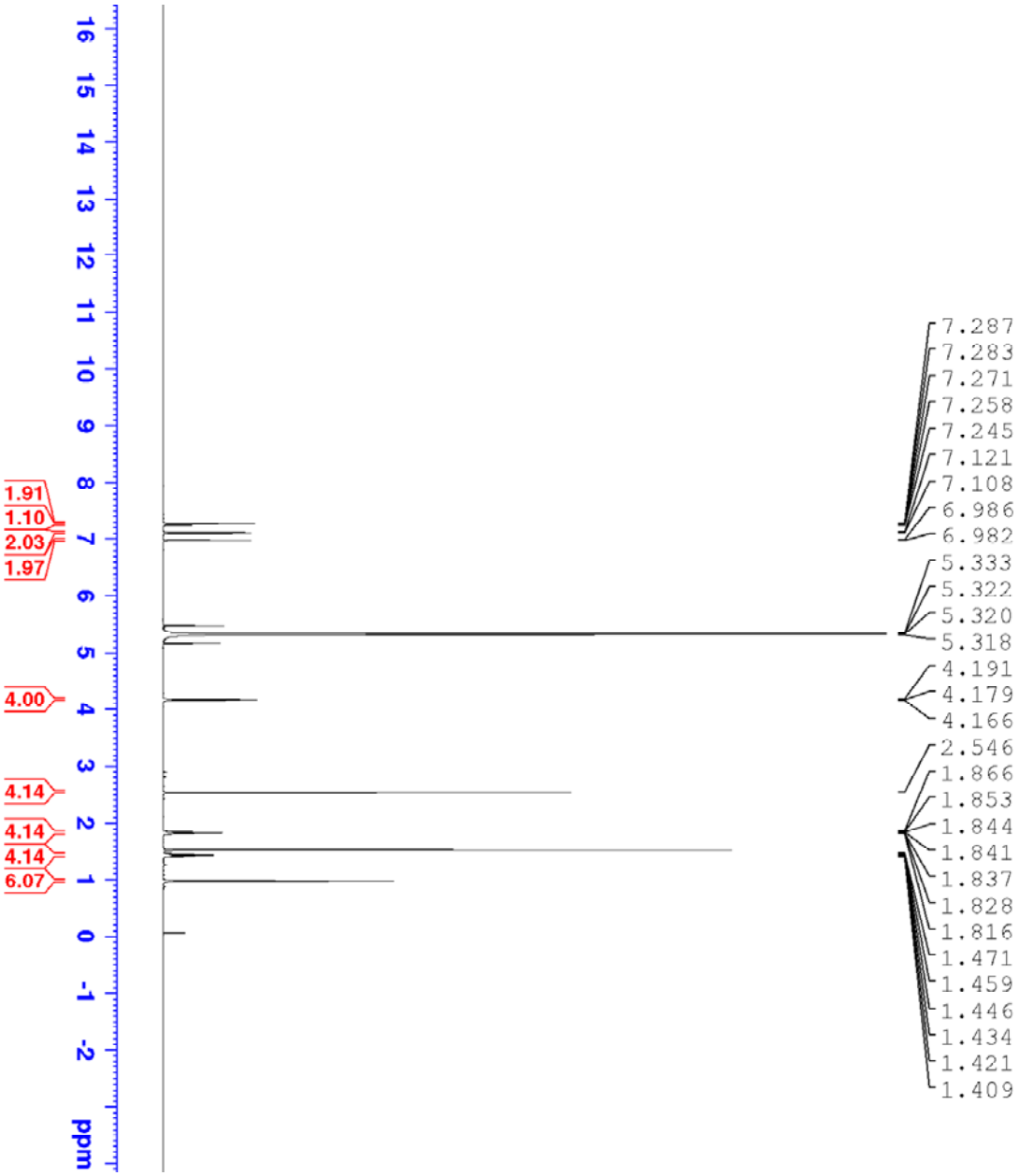

Figure S8. ^{1}H NMR of complex **3** in CD_2Cl_2 with 0.5 equiv. DMSO.

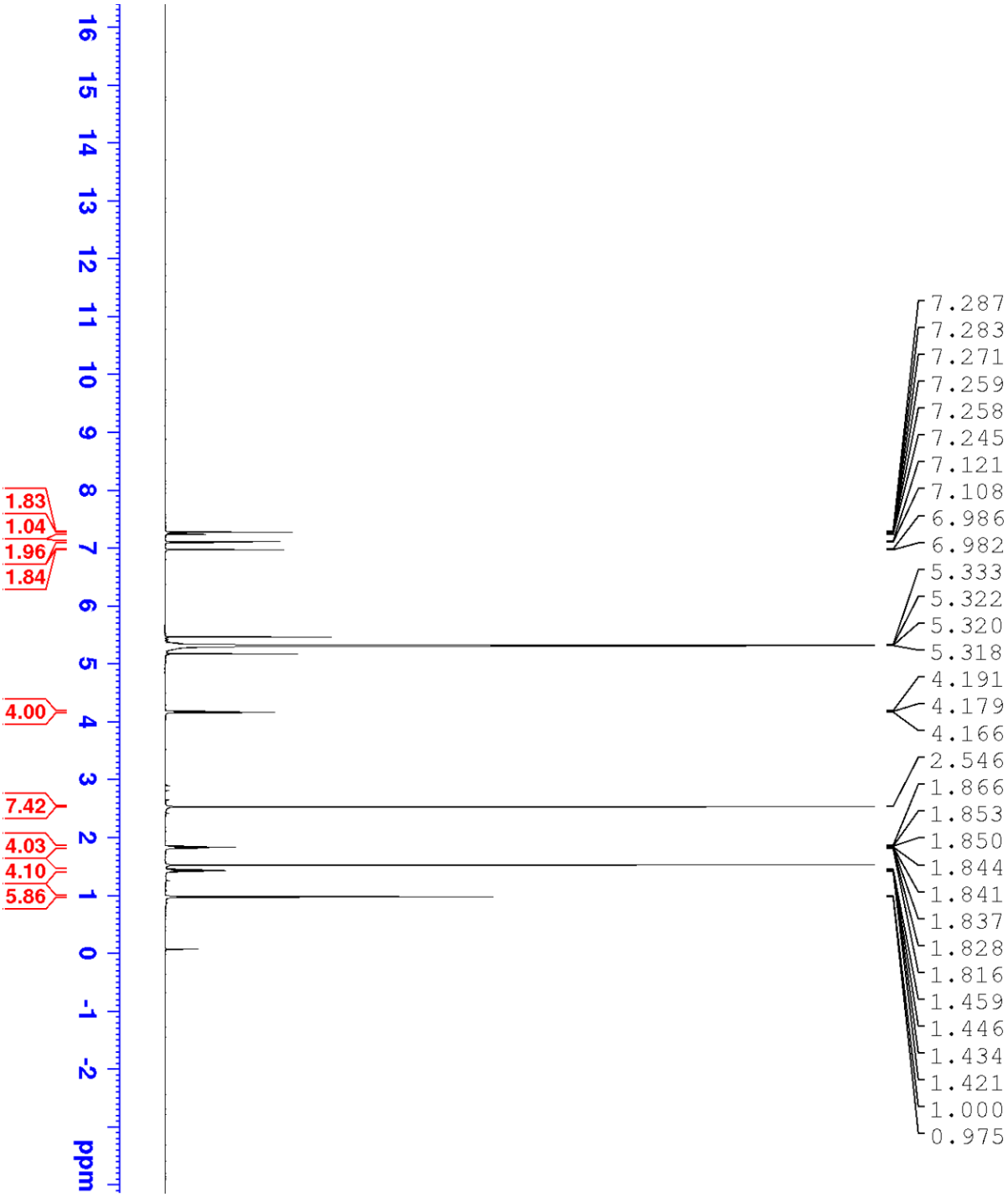

Figure S9. ^{1}H NMR of complex **3** in CD_2Cl_2 with 1.0 equiv. DMSO.

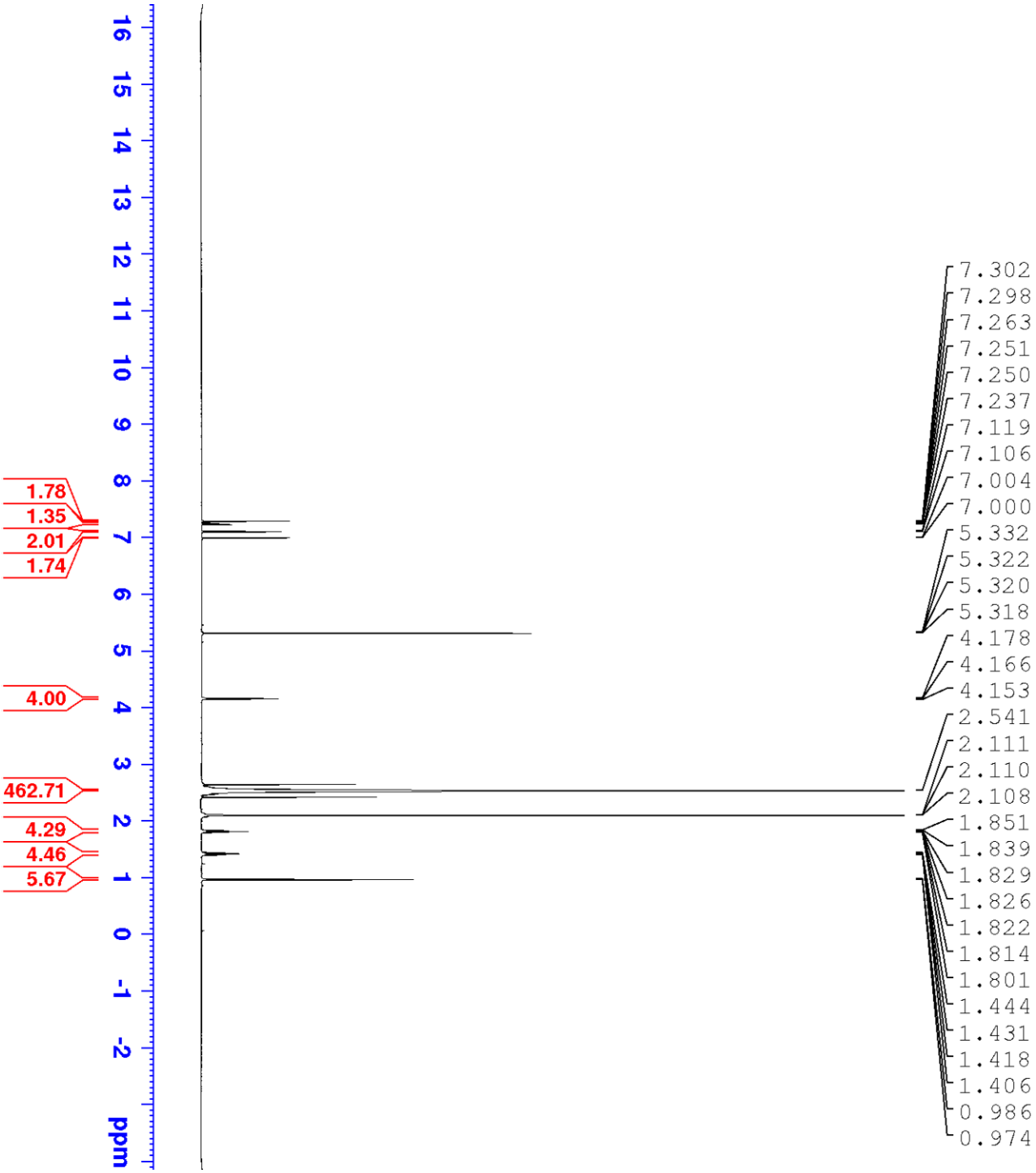

Figure S10. ^{1}H NMR of complex **3** in CD_2Cl_2 with 25.0 equiv. of DMSO.

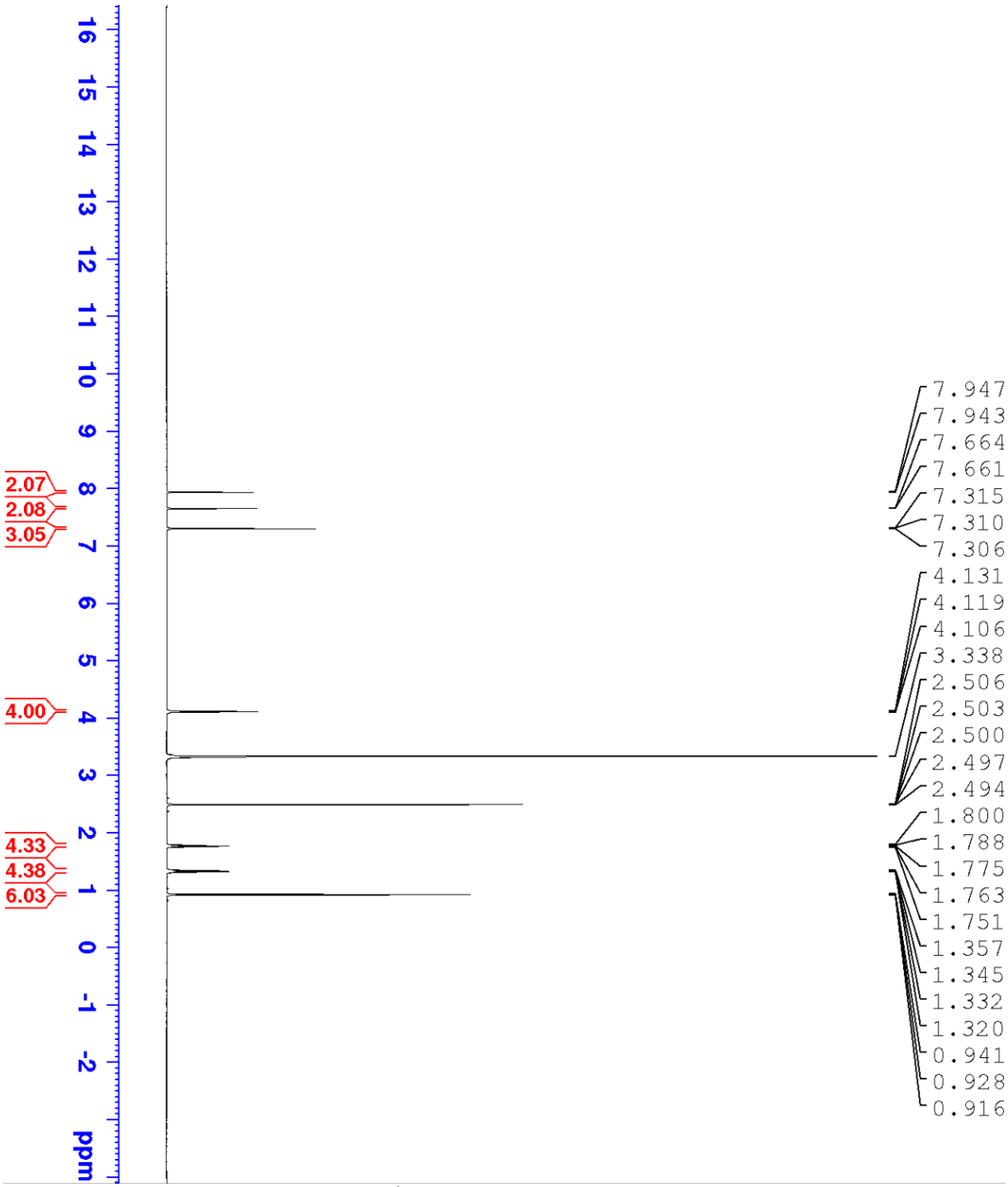

Figure S11. ^{1}H NMR of complex **3** in DMSO-d_6.

ESI-TOF MS Data

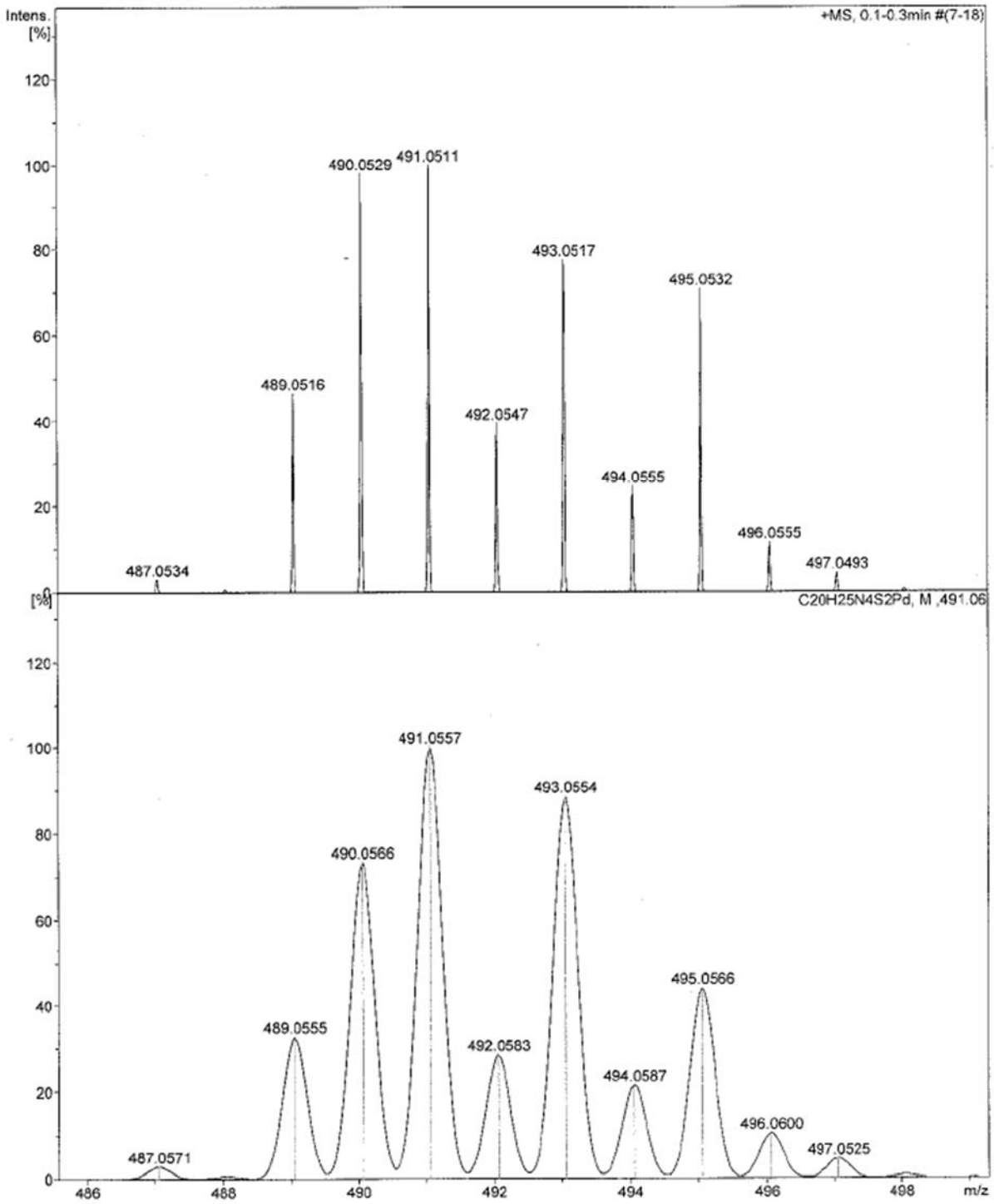

Figure S12. Experimental (top) vs. theoretical (bottom) ESI-TOF MS for $[M\text{-}Cl]^+$

Photophysical Data

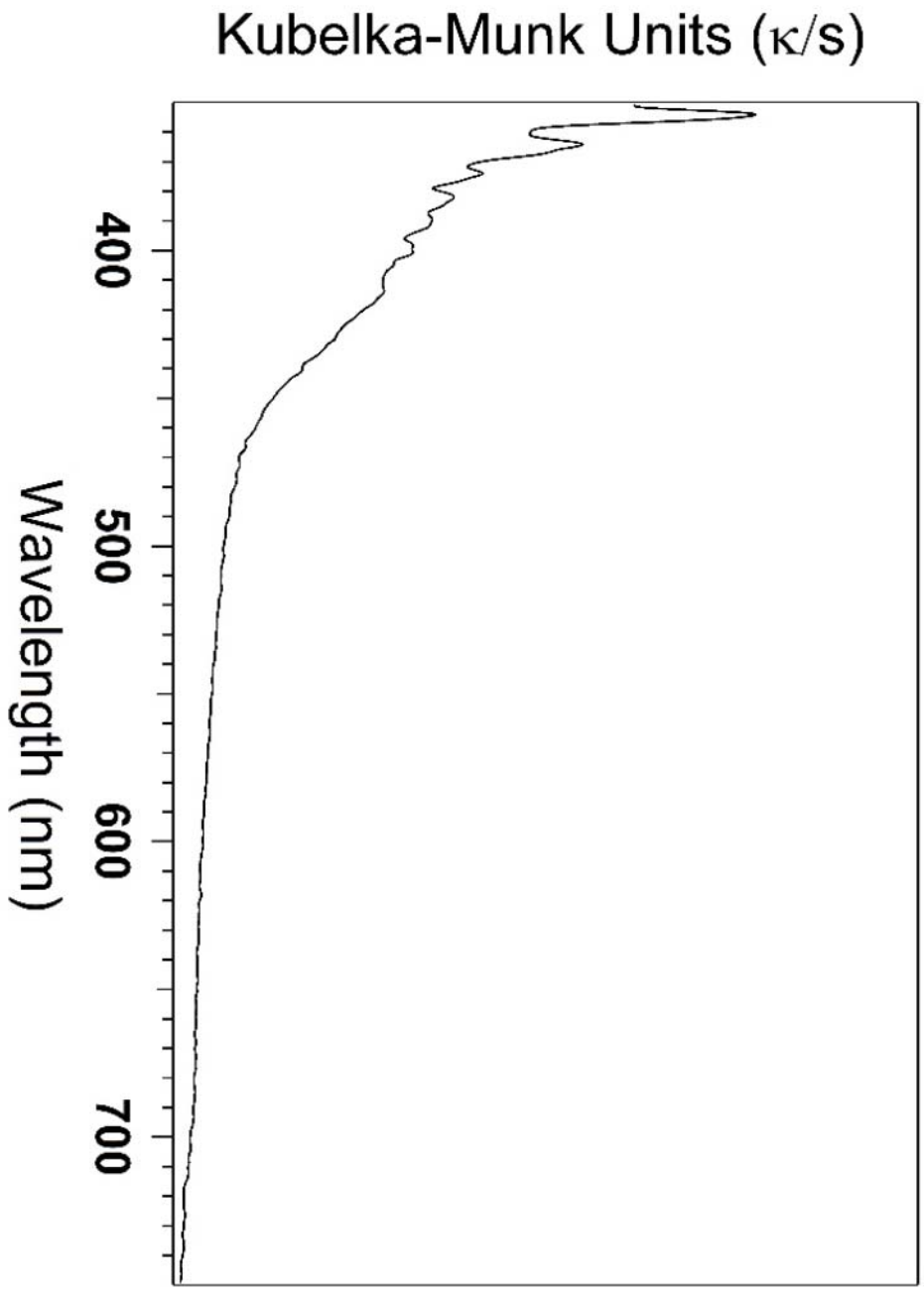

Figure S13. Diffuse Reflectance of complex **3**.

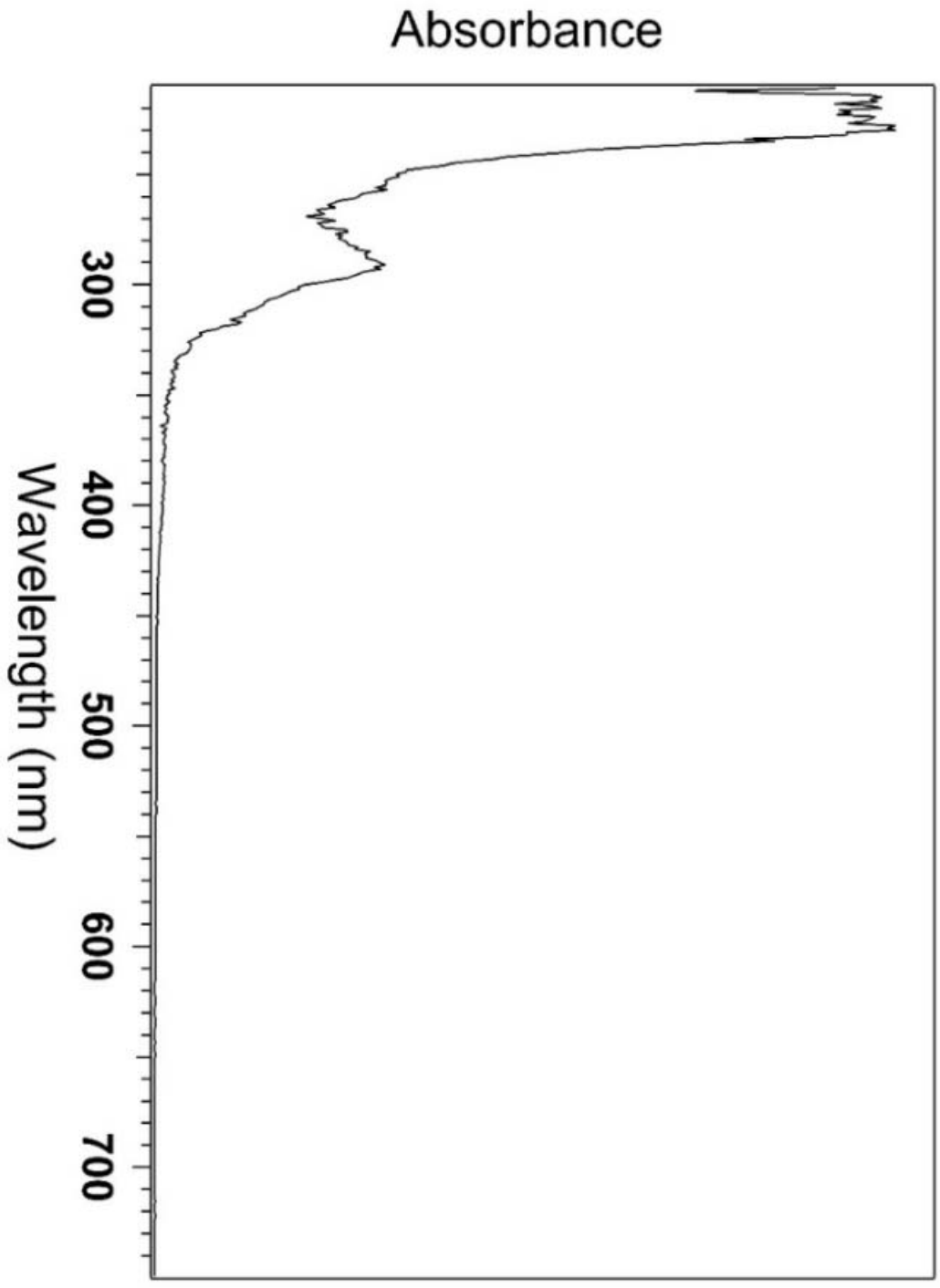

Figure S146. Solution state UV/Vis of complex **3**.

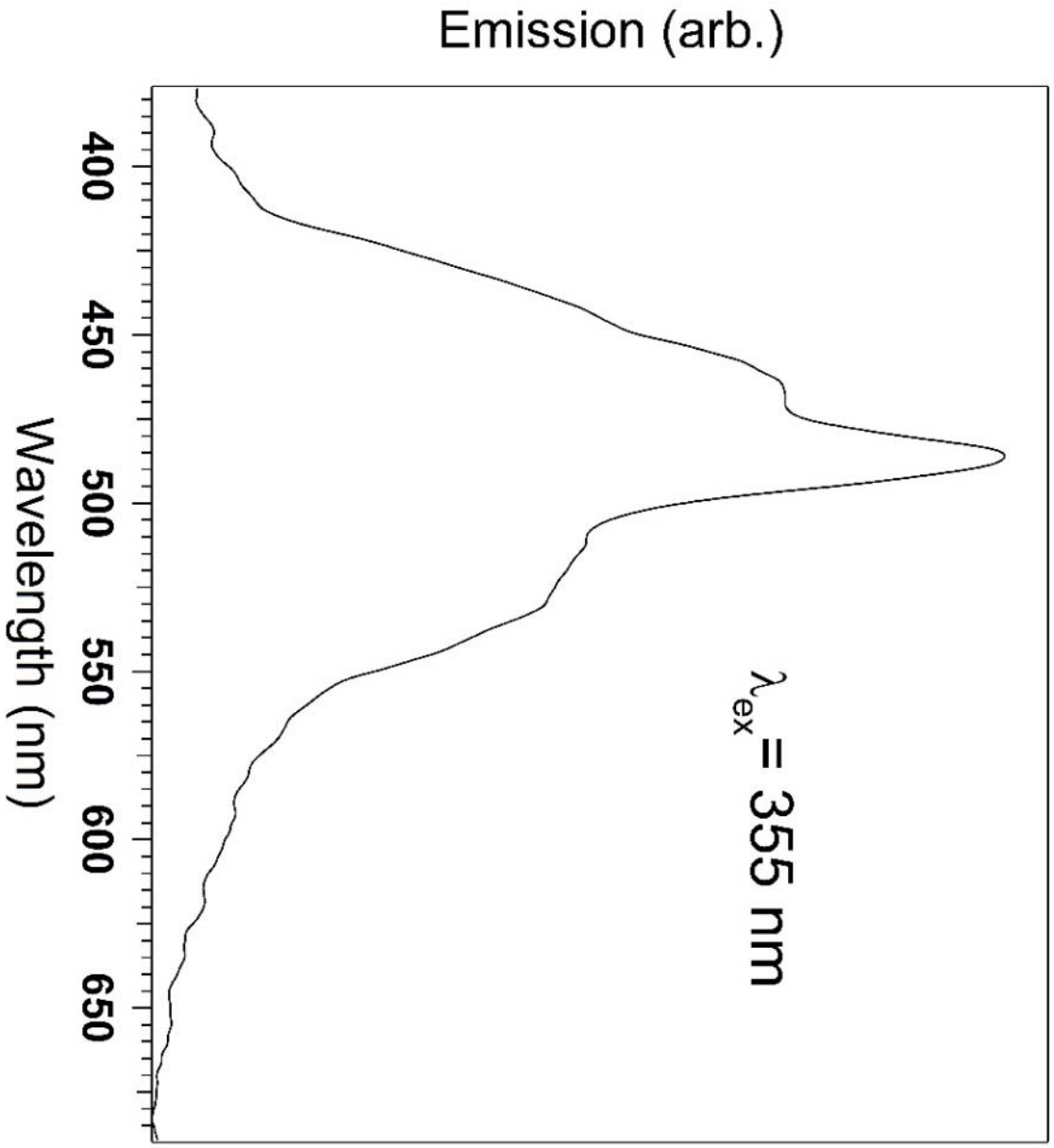

Figure S15. Solution state emission of complex **3**.

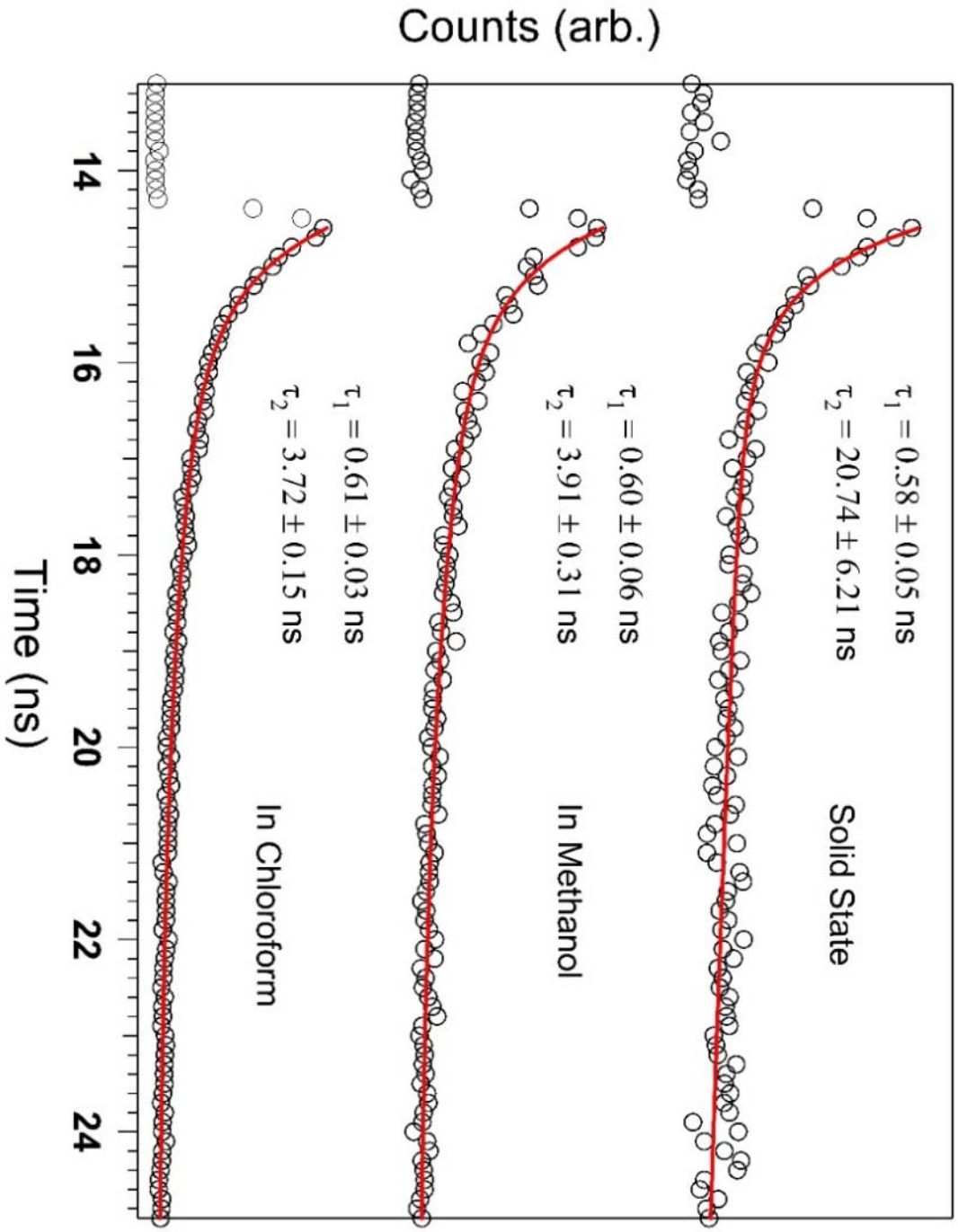

Figure S167. Emission lifetime in solution and solid state of complex **3**.

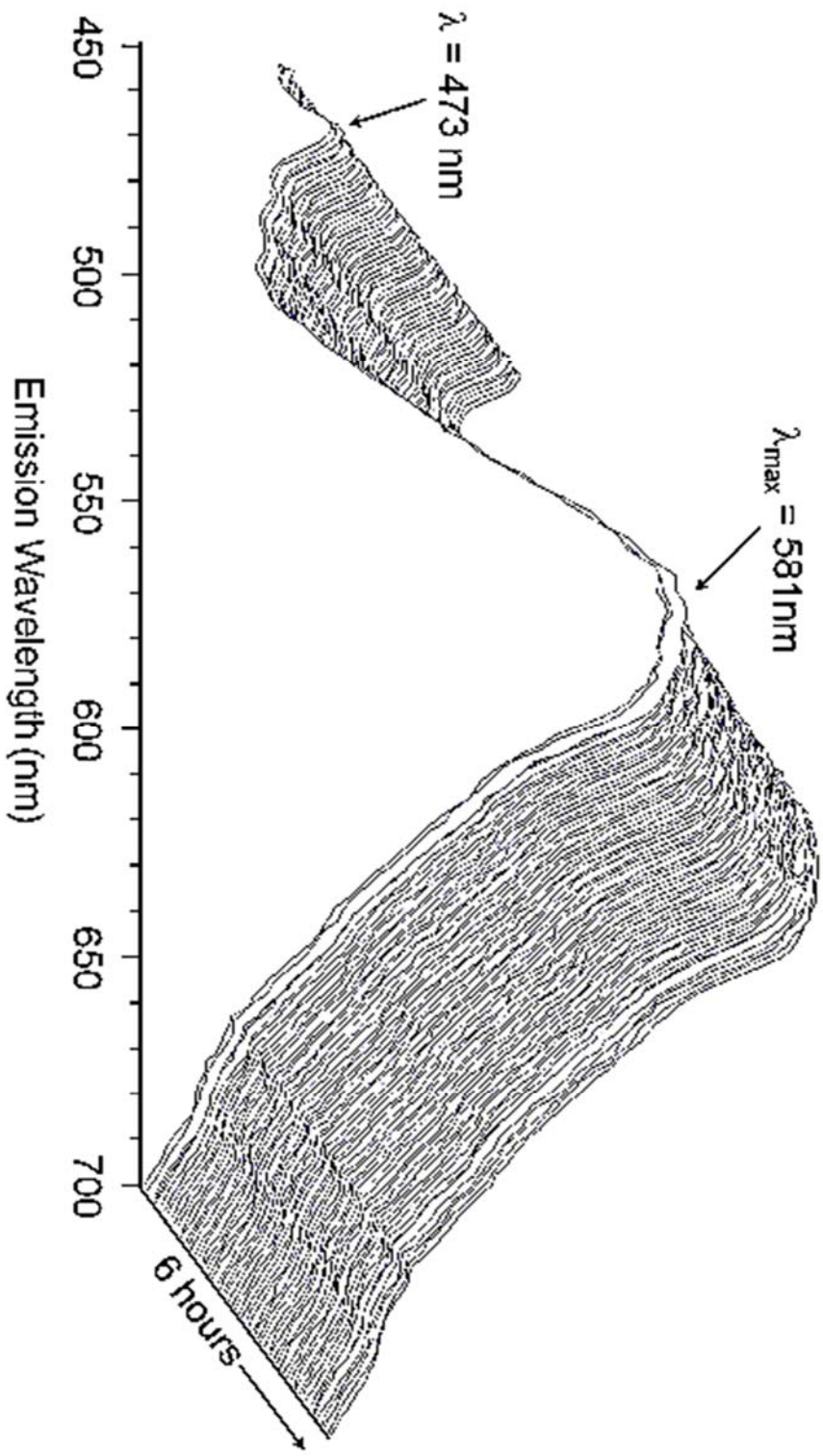

Figure S17. Photostability of complex **3**.

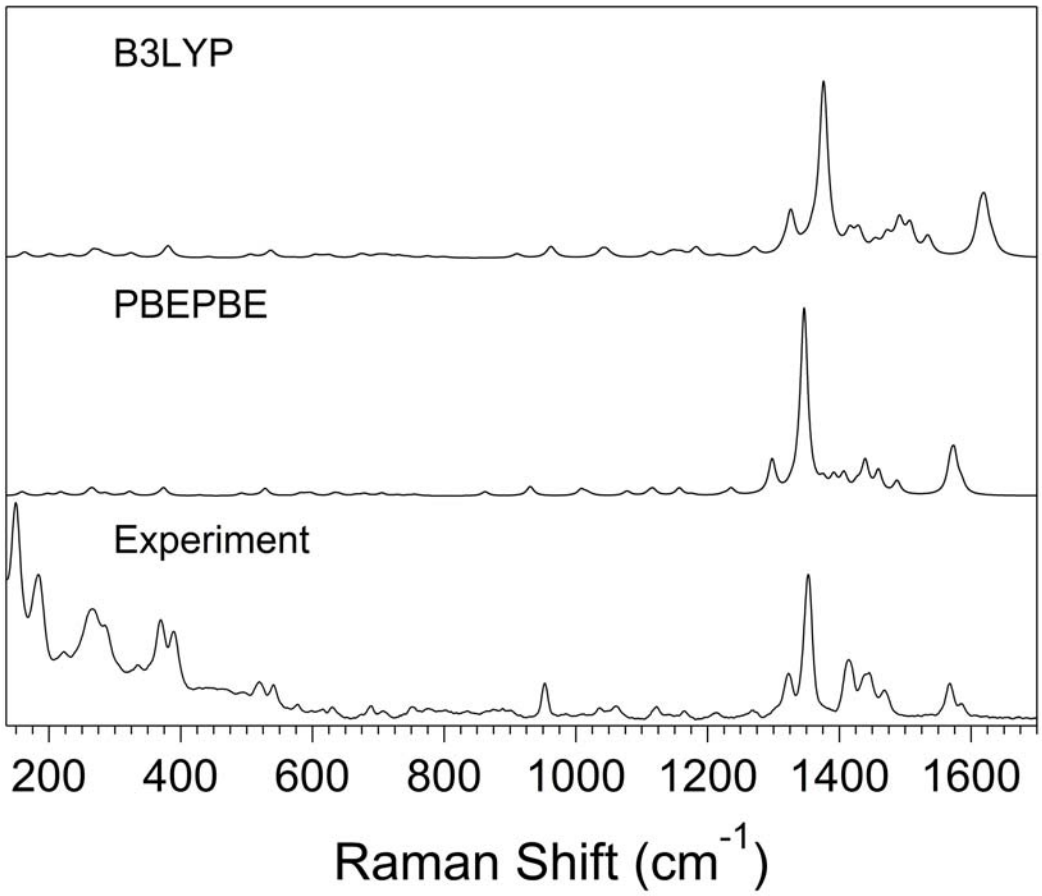

Figure S18. Raman Spectrum of complex **3** and computational simulation.

X-ray Crystallography Data

Experimental for crystal data

1,3-bis(3'-butylimidazole-2'-thione)benzene:

A suitable crystal was selected and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at 296.15 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the XL [3] refinement package using Least Squares minimization.

Crystal Data for $C_{20}H_{26}N_4S_2$ (M =386.57): monoclinic, space group $P2_1/c$ (no. 14), a = 22.212(2) Å, b = 6.9974(6) Å, c = 26.698(2) Å, β = 92.585(2)°, V = 4145.4(6) Å^3, Z = 8, T = 296.15 K, μ(MoKα) = 0.268 mm^{-1}, $Dcalc$ = 1.239 g/mm^3, 64400 reflections measured (1.836 ≤ 2Θ ≤ 54.294), 9135 unique (R_{int} = 0.0626) which were used in all calculations. The final R_1 was 0.0395 (I > 2σ(I)) and wR_2 was 0.0946 (all data).

chloro[1,3-bis(3'-butylimidazole-2'-thione-κ-*S*)benzene-κ-*C*]palladium(II)•½CH_2Cl_2:

A suitable crystal was selected and mounted on a 200 μm mitogen loop on a Bruker APEX-II CCD diffractometer. The crystal was kept at 120.04 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

Crystal Data for $C_{20}H_{25}N_4S_2ClPd$•½CH_2Cl_2 (M =569.91): monoclinic, space group C2/c (no. 15), a = 31.218(4) Å, b = 9.2969(11) Å, c = 18.482(3) Å, β = 120.004(3)°, V = 4645.2(11) Å^3, Z = 8, T = 120.04 K, μ(Mo Kα) = 1.225 mm^{-1}, $Dcalc$ = 1.6297 g/mm^3, 41942 reflections measured (3.02 ≤ 2Θ ≤ 54.58), 5207 unique reflections (R_{int} = 0.0379, R_{sigma} = 0.0208) which were used in all calculations. The final R_1 was 0.0227 (I>=2σ(I)) and wR_2 was 0.0526 (all data).

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.

[2] L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, in preparation (2013)

[3] SHELX, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122

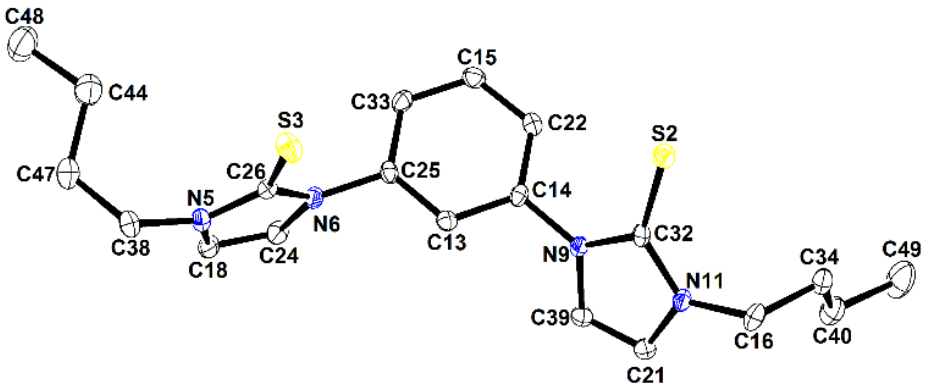

Table S1. Crystal data and structure refinement for 1,3-bis(3'-butylimidazole-2'-thione)benzene.

Identification code	Kmtb
Empirical formula	$C_{20}H_{26}N_4S_2$
Formula weight	386.57
Temperature/K	296.15
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	22.212(2)
b/Å	6.9974(6)
c/Å	26.698(2)
α/°	90
β/°	92.585(2)
γ/°	90
Volume/Å^3	4145.4(6)
Z	8
ρ_{calc}mg/mm^3	1.239
m/mm^{-1}	0.268
F(000)	1648.0
Crystal size/mm^3	0.145 × 0.132 × 0.129
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	1.836 to 54.294°
Index ranges	-28 ≤ h ≤ 28, -8 ≤ k ≤ 8, -34 ≤ l ≤ 34
Reflections collected	64400
Independent reflections	9135[R(int) = 0.0626]
Data/restraints/parameters	9135/0/472
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.0837
Final R indexes [all data]	R_1 = 0.0601, wR_2 = 0.0946
Largest diff. peak/hole / e Å^{-3}	0.52/-0.45

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1,3-bis(3'-butylimidazole-2'-thione)benzene. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S1	3895.0(2)	1663.0(7)	6727.0(2)	21.44(11)
S2	3083.7(2)	6162.7(6)	4387.2(2)	18.36(11)
S3	1139.6(2)	772.6(7)	3159.1(2)	22.28(12)
S4	1814.9(2)	7300.9(7)	5571.2(2)	20.03(11)
N5	1306.9(7)	-3090(2)	3058.5(6)	16.9(3)
N6	2130.6(6)	-1543(2)	3241.9(5)	14.5(3)
N7	1606.7(7)	5060(2)	4747.6(5)	16.0(3)
N8	1834.0(6)	3410(2)	5418.3(5)	14.9(3)
N9	3301.0(6)	2307(2)	4447.6(5)	14.2(3)
N10	2907.6(7)	-672(2)	6634.7(5)	16.8(3)
N11	3452.2(6)	3798(2)	5153.5(5)	15.3(3)
N12	3727.2(7)	-2186(2)	6852.1(5)	17.1(3)
C1	1474.2(8)	6656(3)	4405.6(7)	20.5(4)
C2	795.6(15)	6827(6)	4275.0(14)	22.7(9)
C3	427.5(18)	7423(6)	4714.8(16)	36.5(12)

C4	-246(2)	7624(8)	4595.5(19)	39.1(12)
C2A	861(2)	7556(8)	4471(2)	25.8(13)
C3A	350(3)	6180(9)	4386(2)	42.8(17)
C4A	-258(3)	6943(11)	4459(3)	46.4(17)
C13	2706.9(8)	438(2)	3841.9(6)	13.6(3)
C14	3129.1(7)	1878(2)	3937.5(6)	13.0(3)
C15	3229.6(8)	2346(3)	3054.7(7)	17.6(4)
C16	3464.0(8)	5301(3)	5539.3(7)	19.2(4)
C17	2166.8(9)	1616(3)	6907.6(7)	20.0(4)
C18	1770.7(8)	-4423(3)	3094.7(7)	17.8(4)
C19	3510.4(8)	-413(3)	6740.7(6)	16.0(4)
C20	3266.1(9)	-3525(3)	6817.0(7)	20.1(4)
C21	3578.3(8)	1889(3)	5238.9(7)	18.6(4)
C22	3392.4(8)	2833(3)	3546.2(6)	15.2(4)
C23	1742.0(9)	3031(3)	6799.1(7)	21.7(4)
C24	2281.4(8)	-3463(3)	3207.8(7)	17.2(4)
C25	2554.8(8)	-31(2)	3347.6(6)	13.5(4)
C26	1524.4(8)	-1300(3)	3150.3(6)	15.5(4)
C27	1624.1(9)	3152(3)	4607.6(7)	20.3(4)
C28	1953.9(8)	2847(3)	5928.5(6)	14.5(4)
C29	2758.0(9)	-2588(3)	6682.8(7)	21.6(4)
C30	1630.9(8)	3645(3)	6311.5(7)	18.1(4)
C31	2479.9(8)	831(2)	6521.4(7)	15.8(4)
C32	3281.6(7)	4091(3)	4663.2(6)	14.2(4)
C33	2809.5(8)	907(3)	2953.7(7)	16.5(4)
C34	4036.0(8)	6500(3)	5542.8(7)	20.8(4)
C35	2381.5(8)	1433(2)	6029.9(7)	15.2(4)
C36	4356.1(8)	-2622(3)	6998.4(7)	22.0(4)
C37	1763.8(8)	2127(3)	5020.4(7)	19.0(4)
C38	674.7(8)	-3561(3)	2935.6(7)	21.6(4)
C39	3481.2(8)	951(3)	4804.9(7)	18.1(4)
C40	4610.7(9)	5370(3)	5660.5(7)	25.3(4)
C41	1742.8(8)	5247(3)	5246.1(6)	14.3(4)
C42	4426.8(9)	-3446(3)	7527.0(7)	21.9(4)
C43	4189.6(9)	-2176(3)	7934.6(7)	25.1(4)
C44	751.2(10)	-2853(3)	2001.3(8)	33.1(5)
C46	4297(1)	-3053(3)	8454.0(7)	28.3(5)
C47	575.7(9)	-4264(3)	2398.0(8)	27.9(5)
C48	595.7(11)	-3597(4)	1474.4(8)	42.2(6)
C49	5168.8(10)	6633(4)	5696.2(9)	41.2(6)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 1,3-bis(3'-butylimidazole-2'-thione)benzene. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
S1	20.6(2)	15.1(2)	28.5(3)	2.8(2)	-0.52(19)	-1.50(19)
S2	22.3(2)	12.9(2)	19.5(2)	-1.42(18)	-4.05(18)	2.33(18)
S3	17.7(2)	15.1(2)	33.8(3)	1.7(2)	-1.6(2)	1.37(18)

S4	27.5(3)	13.4(2)	18.9(2)	0.67(18)	-2.49(19)	0.10(19)
N5	16.7(8)	15.7(8)	18.1(8)	0.3(6)	-2.5(6)	-3.7(6)
N6	15.8(7)	12.7(7)	14.7(7)	-1.2(6)	-3.2(6)	-0.2(6)
N7	17.8(8)	16.3(8)	13.6(7)	2.8(6)	-1.0(6)	0.9(6)
N8	16.9(7)	13.6(7)	13.9(7)	1.8(6)	-2.0(6)	1.2(6)
N9	16.2(7)	13.1(7)	13.0(7)	-0.4(6)	-2.9(6)	-1.3(6)
N10	21.5(8)	11.8(8)	16.5(8)	2.1(6)	-4.4(6)	0.3(6)
N11	15.4(7)	17.3(8)	13.0(7)	-2.1(6)	-1.1(6)	-3.1(6)
N12	21.6(8)	15.5(8)	14.0(7)	1.8(6)	-0.4(6)	4.1(6)
C1	24(1)	21.3(10)	16.4(9)	9.2(8)	0.7(7)	1.6(8)
C13	14.1(8)	11.8(8)	14.8(8)	0.1(7)	0.7(7)	1.7(7)
C14	13.2(8)	12.5(8)	13.1(8)	-3.1(7)	-1.7(6)	2.8(7)
C15	19.8(9)	16.9(9)	16.3(9)	1.3(7)	4.0(7)	-1.3(7)
C16	20.1(9)	23.1(10)	14.4(9)	-7.0(8)	-1.0(7)	0.5(8)
C17	28.4(10)	17.6(9)	13.8(9)	2.5(7)	-1.3(8)	-2.0(8)
C18	24.8(10)	11.8(9)	16.5(9)	-2.4(7)	-2.5(7)	0.3(7)
C19	21.9(9)	15.3(9)	10.8(8)	0.1(7)	-0.4(7)	2.4(7)
C20	31.6(11)	11.2(9)	17.2(9)	-0.1(7)	-1.9(8)	0.3(8)
C21	21.2(9)	17.3(9)	16.8(9)	3.3(7)	-3.5(7)	-3.1(8)
C22	13.8(8)	13.6(9)	18.3(9)	-1.1(7)	0.3(7)	-1.7(7)
C23	28.5(10)	19.7(10)	17.3(9)	-0.4(8)	5.6(8)	1.3(8)
C24	20.9(9)	12.5(9)	17.8(9)	-2.0(7)	-2.8(7)	3.7(7)
C25	12.7(8)	9.6(8)	17.9(9)	-1.5(7)	-2.2(7)	0.4(7)
C26	17.6(9)	16.1(9)	12.7(8)	1.7(7)	-2.0(7)	-3.2(7)
C27	25.6(10)	18.6(10)	16.4(9)	-2.4(8)	-1.1(7)	1.1(8)
C28	15.9(8)	13.7(9)	13.7(8)	3.3(7)	-1.8(7)	-4.3(7)
C29	28.8(11)	15.0(9)	20.3(10)	1.1(8)	-5.5(8)	-4.9(8)
C30	17.7(9)	15.7(9)	21.0(9)	2.6(7)	1.3(7)	0.3(7)
C31	17.6(9)	10.8(9)	18.5(9)	3.0(7)	-4.6(7)	-2.0(7)
C32	10.9(8)	15.7(9)	15.7(9)	-3.0(7)	-1.1(7)	-2.3(7)
C33	20.0(9)	16.7(9)	12.7(8)	-2.8(7)	-1.0(7)	1.4(7)
C34	24.9(10)	19(1)	18.1(9)	-3.1(8)	-4.2(8)	-3.4(8)
C35	16.0(9)	13.5(9)	16.2(9)	0.8(7)	0.1(7)	-2.3(7)
C36	21.7(10)	22.3(10)	22.2(10)	0.9(8)	2.6(8)	7.6(8)
C37	23.1(10)	15.1(9)	18.6(9)	-2.5(7)	-1.8(7)	1.7(8)
C38	17.4(9)	23(1)	24.1(10)	0.0(8)	-1.4(8)	-7.6(8)
C39	21.9(9)	13.6(9)	18.4(9)	3.6(7)	-3.6(7)	-1.1(7)
C40	20.8(10)	33.0(12)	21.6(10)	-3.4(9)	-2.8(8)	-2.6(9)
C41	12.0(8)	15.0(9)	15.9(9)	2.3(7)	-0.2(7)	0.1(7)
C42	22.5(10)	20.5(10)	22.3(10)	1.3(8)	-2.0(8)	7.2(8)
C43	27.6(11)	23.9(11)	23.8(10)	0.7(8)	1.5(8)	2.9(9)
C44	30.4(12)	40.7(13)	28.0(11)	-0.6(10)	-1.0(9)	-9.7(10)
C46	30.1(11)	34.1(12)	20.9(10)	-1.6(9)	1.1(8)	-2.7(9)
C47	23.1(10)	31.0(12)	29.2(11)	-1.9(9)	-5.1(8)	-8.2(9)
C48	35.2(13)	65.2(18)	26.0(12)	-2.9(12)	0.7(10)	-16.0(12)
C49	26.4(12)	64.7(18)	32.4(12)	-9.8(12)	-0.6(9)	-16.4(12)

Table S4. Bond Lengths for 1,3-bis(3'-butylimidazole-2'-thione)benzene.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C19	1.6864(19)	C2	C3	1.519(6)
S2	C32	1.6760(18)	C3	C4	1.522(6)
S3	C26	1.6843(19)	C2A	C3A	1.498(8)
S4	C41	1.6829(18)	C3A	C4A	1.474(9)
N5	C18	1.390(2)	C13	C14	1.392(2)
N5	C26	1.361(2)	C13	C25	1.387(2)
N5	C38	1.465(2)	C14	C22	1.391(2)
N6	C24	1.389(2)	C15	C22	1.388(2)
N6	C25	1.436(2)	C15	C33	1.391(3)
N6	C26	1.368(2)	C16	C34	1.522(3)
N7	C1	1.464(2)	C17	C23	1.389(3)
N7	C27	1.387(2)	C17	C31	1.383(3)
N7	C41	1.358(2)	C18	C24	1.341(3)
N8	C28	1.431(2)	C20	C29	1.340(3)
N8	C37	1.394(2)	C21	C39	1.341(3)
N8	C41	1.377(2)	C23	C30	1.383(3)
N9	C14	1.430(2)	C25	C33	1.382(2)
N9	C32	1.376(2)	C27	C37	1.340(3)
N9	C39	1.392(2)	C28	C30	1.392(3)
N10	C19	1.368(2)	C28	C35	1.390(2)
N10	C29	1.388(2)	C31	C35	1.386(2)
N10	C31	1.440(2)	C34	C40	1.522(3)
N11	C16	1.471(2)	C36	C42	1.526(3)
N11	C21	1.382(2)	C38	C47	1.524(3)
N11	C32	1.362(2)	C40	C49	1.522(3)
N12	C19	1.359(2)	C42	C43	1.518(3)
N12	C20	1.388(2)	C43	C46	1.526(3)
N12	C36	1.466(2)	C44	C47	1.512(3)
C1	C2	1.536(4)	C44	C48	1.525(3)
C1	C2A	1.517(5)			

Table S5. Bond Angles for 1,3-bis(3'-butylimidazole-2'-thione)benzene.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C18	N5	C38	124.37(15)	N12	C19	N10	104.97(15)
C26	N5	C18	110.43(15)	C29	C20	N12	107.30(16)
C26	N5	C38	125.20(16)	C39	C21	N11	107.88(16)
C24	N6	C25	124.57(15)	C15	C22	C14	119.46(16)
C26	N6	C24	110.28(15)	C30	C23	C17	120.57(18)
C26	N6	C25	125.14(15)	C18	C24	N6	107.18(16)
C27	N7	C1	124.98(15)	C13	C25	N6	119.40(16)
C41	N7	C1	124.57(16)	C33	C25	N6	119.18(15)
C41	N7	C27	110.44(15)	C33	C25	C13	121.41(16)
C37	N8	C28	123.86(15)	N5	C26	S3	128.24(14)
C41	N8	C28	126.38(15)	N5	C26	N6	104.88(15)
C41	N8	C37	109.70(14)	N6	C26	S3	126.88(14)

C32	N9	C14	125.24(14)	C37	C27	N7	107.56(16)
C32	N9	C39	110.20(14)	C30	C28	N8	120.58(16)
C39	N9	C14	124.47(15)	C35	C28	N8	118.54(16)
C19	N10	C29	110.17(15)	C35	C28	C30	120.83(16)
C19	N10	C31	125.23(15)	C20	C29	N10	107.17(17)
C29	N10	C31	124.48(15)	C23	C30	C28	119.41(17)
C21	N11	C16	125.34(15)	C17	C31	N10	118.85(16)
C32	N11	C16	124.12(15)	C17	C31	C35	121.45(17)
C32	N11	C21	110.45(15)	C35	C31	N10	119.68(16)
C19	N12	C20	110.39(15)	N9	C32	S2	127.83(13)
C19	N12	C36	124.93(16)	N11	C32	S2	127.50(14)
C20	N12	C36	124.67(16)	N11	C32	N9	104.67(15)
N7	C1	C2	111.63(19)	C25	C33	C15	119.35(16)
N7	C1	C2A	113.7(2)	C16	C34	C40	114.01(16)
C3	C2	C1	113.7(3)	C31	C35	C28	118.57(17)
C2	C3	C4	115.0(4)	N12	C36	C42	112.47(15)
C3A	C2A	C1	113.2(4)	C27	C37	N8	107.21(16)
C4A	C3A	C2A	116.1(5)	N5	C38	C47	112.31(16)
C25	C13	C14	118.62(16)	C21	C39	N9	106.79(16)
C13	C14	N9	118.38(15)	C49	C40	C34	112.61(19)
C22	C14	N9	120.75(15)	N7	C41	S4	126.85(14)
C22	C14	C13	120.83(16)	N7	C41	N8	105.08(15)
C22	C15	C33	120.33(17)	N8	C41	S4	128.01(13)
N11	C16	C34	112.75(15)	C43	C42	C36	114.65(16)
C31	C17	C23	119.17(17)	C42	C43	C46	111.77(17)
C24	C18	N5	107.23(16)	C47	C44	C48	111.61(19)
N10	C19	S1	126.99(14)	C44	C47	C38	114.73(17)
N12	C19	S1	128.03(14)				

Table S6. Torsion Angles for 1,3-bis(3'-butylimidazole-2'-thione)benzene.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
N5	C18	C24	N6	0.1(2)	C25	N6	C24	C18	-178.72(16)
N5	C38	C47	C44	-59.7(2)	C25	N6	C26	S3	-2.2(3)
N6	C25	C33	C15	-178.71(16)	C25	N6	C26	N5	178.57(15)
N7	C1	C2	C3	67.9(4)	C25	C13	C14	N9	-177.71(15)
N7	C1	C2A	C3A	-59.7(5)	C25	C13	C14	C22	0.2(3)
N7	C27	C37	N8	-0.1(2)	C26	N5	C18	C24	-0.2(2)
N8	C28	C30	C23	177.93(16)	C26	N5	C38	C47	112.0(2)
N8	C28	C35	C31	-177.38(15)	C26	N6	C24	C18	0.0(2)
N9	C14	C22	C15	178.09(16)	C26	N6	C25	C13	94.3(2)
N10	C31	C35	C28	178.15(15)	C26	N6	C25	C33	-86.6(2)
N11	C16	C34	C40	-62.0(2)	C27	N7	C1	C2	78.0(3)
N11	C21	C39	N9	0.8(2)	C27	N7	C1	C2A	108.3(3)
N12	C20	C29	N10	0.1(2)	C27	N7	C41	S4	176.18(14)
N12	C36	C42	C43	-57.8(2)	C27	N7	C41	N8	-1.2(2)
C1	N7	C27	C37	179.52(17)	C28	N8	C37	C27	176.55(16)
C1	N7	C41	S4	-2.5(3)	C28	N8	C41	S4	6.7(3)

C1	N7	C41	N8	-179.91(15)	C28	N8	C41	N7	-176.00(15)
C1	C2	C3	C4	179.4(3)	C29	N10	C19	S1	179.49(14)
C1	C2A	C3A	C4A	178.1(5)	C29	N10	C19	N12	0.19(19)
C2	C1	C2A	C3A	32.2(5)	C29	N10	C31	C17	82.9(2)
C2A	C1	C2	C3	-32.2(5)	C29	N10	C31	C35	-95.8(2)
C13	C14	C22	C15	0.3(3)	C30	C28	C35	C31	0.0(3)
C13	C25	C33	C15	0.3(3)	C31	N10	C19	S1	-4.3(3)
C14	N9	C32	S2	-2.5(3)	C31	N10	C19	N12	176.43(15)
C14	N9	C32	N11	176.77(15)	C31	N10	C29	C20	-176.46(16)
C14	N9	C39	C21	-177.29(16)	C31	C17	C23	C30	0.2(3)
C14	C13	C25	N6	178.56(15)	C32	N9	C14	C13	-126.29(18)
C14	C13	C25	C33	-0.5(3)	C32	N9	C14	C22	55.8(2)
C16	N11	C21	C39	175.88(16)	C32	N9	C39	C21	-0.5(2)
C16	N11	C32	S2	3.0(3)	C32	N11	C16	C34	-82.6(2)
C16	N11	C32	N9	-176.28(15)	C32	N11	C21	C39	-0.8(2)
C16	C34	C40	C49	-176.08(17)	C33	C15	C22	C14	-0.4(3)
C17	C23	C30	C28	-0.7(3)	C35	C28	C30	C23	0.6(3)
C17	C31	C35	C28	-0.5(3)	C36	N12	C19	S1	1.7(3)
C18	N5	C26	S3	-178.99(14)	C36	N12	C19	N10	-179.02(15)
C18	N5	C26	N6	0.24(19)	C36	N12	C20	C29	178.91(16)
C18	N5	C38	C47	-67.7(2)	C36	C42	C43	C46	-177.79(17)
C19	N10	C29	C20	-0.2(2)	C37	N8	C28	C30	-133.35(18)
C19	N10	C31	C17	-92.8(2)	C37	N8	C28	C35	44.1(2)
C19	N10	C31	C35	88.5(2)	C37	N8	C41	S4	-176.19(14)
C19	N12	C20	C29	0.0(2)	C37	N8	C41	N7	1.15(19)
C19	N12	C36	C42	117.47(19)	C38	N5	C18	C24	179.43(16)
C20	N12	C19	S1	-179.42(14)	C38	N5	C26	S3	1.3(3)
C20	N12	C19	N10	-0.12(19)	C38	N5	C26	N6	-179.42(15)
C20	N12	C36	C42	-61.3(2)	C39	N9	C14	C13	50.0(2)
C21	N11	C16	C34	101.1(2)	C39	N9	C14	C22	-127.91(19)
C21	N11	C32	S2	179.73(14)	C39	N9	C32	S2	-179.23(14)
C21	N11	C32	N9	0.45(19)	C39	N9	C32	N11	0.05(19)
C22	C15	C33	C25	0.1(3)	C41	N7	C1	C2	-103.5(3)
C23	C17	C31	N10	-178.30(16)	C41	N7	C1	C2A	-73.1(3)
C23	C17	C31	C35	0.4(3)	C41	N7	C27	C37	0.8(2)
C24	N6	C25	C13	-87.1(2)	C41	N8	C28	C30	43.4(3)
C24	N6	C25	C33	91.9(2)	C41	N8	C28	C35	-139.17(18)
C24	N6	C26	S3	179.09(14)	C41	N8	C37	C27	-0.7(2)
C24	N6	C26	N5	-0.16(19)	C48	C44	C47	C38	-175.74(19)

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1,3-bis(3'-butylimidazole-2'-thione)benzene.

Atom	***x***	***Y***	***z***	**U(eq)**
H1AA	1692	6466	4094	25
H1AB	1621	7859	4563	25

H1BC	1495	6195	4056	25
H1BD	1788	7647	4460	25
H2A	733	7774	4002	27
H2B	645	5579	4148	27
H3A	584	8662	4844	44
H3B	489	6468	4986	44
H4A	-323	8789	4399	59
H4B	-459	7700	4909	59
H4C	-391	6512	4402	59
H2AA	848	8081	4814	31
H2AB	808	8633	4232	31
H3AA	362	5686	4039	51
H3AB	418	5081	4615	51
H4AA	-265	7576	4786	70
H4AB	-550	5894	4445	70
H4AC	-363	7868	4193	70
H13	2527	-209	4110	16
H15	3406	2999	2786	21
H16A	3430	4701	5873	23
H16B	3111	6147	5480	23
H17	2241	1193	7243	24
H18	1733	-5764	3048	21
H20	3304	-4859	6877	24
H21	3711	1338	5550	22
H22	3681	3810	3615	18
H23	1526	3581	7062	26
H24	2673	-3996	3256	21
H27	1550	2662	4279	24
H29	2368	-3132	6630	26
H30	1337	4602	6239	22
H33	2699	572	2617	20
H34A	4005	7530	5795	25
H34B	4065	7113	5211	25
H35	2602	891	5768	18
H36A	4599	-1439	6981	26
H36B	4515	-3550	6758	26
H37	1807	778	5039	23
H38A	424	-2413	2985	26
H38B	542	-4564	3168	26
H39	3527	-382	4752	22
H40A	4573	4687	5982	30
H40B	4660	4401	5395	30
H42A	4213	-4687	7534	26
H42B	4860	-3697	7605	26
H43A	3752	-1969	7870	30
H43B	4392	-916	7925	30
H44A	1190	-2604	2037	40

H44B	538	-1629	2051	40
H46A	4103	-4310	8463	43
H46B	4126	-2218	8706	43
H46C	4731	-3196	8527	43
H47A	811	-5452	2358	34
H47B	144	-4589	2340	34
H48A	711	-2645	1227	63
H48B	161	-3835	1437	63
H48C	815	-4790	1420	63
H49A	5193	7380	5387	62
H49B	5529	5831	5741	62
H49C	5144	7500	5983	62

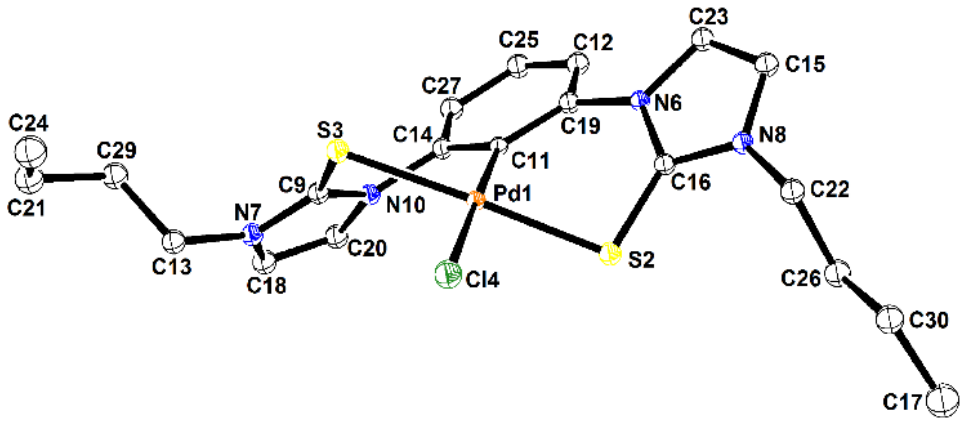

Table S8. Crystal data and structure refinement for chloro[1,3-bis(3'-butylimidazole-2'-thione-κ-*S*)benzene-κ-*C*]palladium(II)•½CH_2Cl_2.

Identification code	get1146
Empirical formula	$C_{20.5}H_{26}Cl_2N_4PdS_2$
Formula weight	569.91
Temperature/K	120.04
Crystal system	monoclinic

Space group	C2/c
a/Å	31.218(4)
b/Å	9.2969(11)
c/Å	18.482(3)
α/°	90
β/°	120.004(3)
γ/°	90
Volume/Å^3	4645.2(11)
Z	8
ρ_{calc}mg/mm^3	1.6297
m/mm^{-1}	1.225
F(000)	2309.0
Crystal size/mm^3	0.226 × 0.097 × 0.042
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection	3.02 to 54.58°
Index ranges	-40 ≤ h ≤ 40, -11 ≤ k ≤ 11, -23 ≤ l ≤ 23
Reflections collected	41942
Independent reflections	5207 [R_{int} = 0.0379, R_{sigma} = 0.0208]
Data/restraints/parameters	5207/0/269
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0227, wR_2 = 0.0497
Final R indexes [all data]	R_1 = 0.0298, wR_2 = 0.0526
Largest diff. peak/hole / e Å^{-3}	0.90/-1.02

Table S9. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for chloro[1,3-bis(3'-butylimidazole-2'-thione-κ-*S*)benzene-κ-*C*]palladium(II)•½CH_2Cl_2. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*X*	*y*	*z*	U(eq)

Pd1	3672.40(5)	8735.26(16)	4715.41(9)	9.49(5)
S2	4390.85(18)	7546.7(6)	5047.0(3)	13.29(10)
S3	2938.17(18)	9908.4(5)	4417.7(3)	13.56(11)
Cl4	4008.16(18)	9235.0(6)	6178.6(3)	18.85(11)
N6	4190.5(6)	8613.6(18)	3512.6(10)	11.4(3)
N7	2162.1(6)	8043.9(19)	3954(1)	13.6(3)
N8	4974.8(6)	8453.2(18)	4440.3(10)	12.3(3)
C9	2547.9(7)	8522(2)	3884.9(12)	12.0(4)
N10	2585.8(6)	7629.9(18)	3338.5(10)	11.7(3)
C11	3399.8(7)	8281(2)	3504.5(12)	10.6(4)
C12	3451.9(7)	8145(2)	2216.7(12)	13.8(4)
C13	1951.7(7)	8773(2)	4411.7(13)	15.3(4)
C14	2902.7(7)	7861(2)	2991.3(12)	11.2(4)
C15	4941.8(8)	9038(2)	3724.1(13)	15.8(4)
C16	4514.6(7)	8201(2)	4311.0(12)	11.0(4)
C17	6377.1(9)	5436(3)	6626.8(14)	25.9(5)
C18	1962.0(7)	6830(2)	3462.1(13)	16.0(4)
C19	3667.3(7)	8364(2)	3078.0(12)	11.0(4)
C20	2224.1(7)	6570(2)	3081.6(13)	15.5(4)
C21	1276.8(8)	10460(3)	4267.4(15)	21.6(5)
C22	5431.2(7)	8320(2)	5252.2(12)	13.8(4)
C23	4460.9(7)	9141(2)	3149.6(13)	14.6(4)
C24	1613.4(9)	11617(3)	4851.8(16)	26.4(5)
C25	2955.1(8)	7815(2)	1742.2(13)	16.2(4)
C26	5637.7(7)	6811(2)	5487.7(13)	15.6(4)
C27	2678.8(7)	7659(2)	2133.6(13)	14.7(4)
C29	1498.4(8)	9644(2)	3815.4(13)	17.4(4)
C30	6112.2(8)	6874(2)	6339.0(13)	19.1(4)

Cl1	212.2(3)	9845.8(12)	1958.0(5)	56.2(2)
C1	0	8761(5)	2500	52.1(12)

Table S10. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for chloro[1,3-bis(3'-butylimidazole-2'-thione-κ-*S*)benzene-κ-*C*]palladium(II)•½CH_2Cl_2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd1	7.89(7)	12.96(8)	7.99(8)	-2.09(6)	4.23(6)	-0.73(6)
S2	10.3(2)	19.2(3)	10.8(2)	1.09(19)	5.56(19)	4.38(19)
S3	11.7(2)	12.7(2)	16.7(2)	-1.30(19)	7.5(2)	-2.95(19)
Cl4	13.4(2)	33.9(3)	11.0(2)	-8.3(2)	7.42(19)	-7.2(2)
N6	10.8(8)	14.7(9)	9.0(7)	-0.7(7)	5.2(6)	1.0(7)
N7	10.8(8)	15.5(9)	14.9(8)	0.2(7)	6.8(7)	1.4(7)
N8	8.6(8)	15.3(9)	12.5(8)	-0.2(6)	4.9(7)	0.9(6)
C9	9.0(9)	13.4(10)	12.1(9)	1.7(7)	4.1(7)	2.6(8)
N10	9.1(8)	13.6(8)	12.2(8)	-1.7(6)	5.1(7)	-0.8(7)
C11	12.2(9)	8.5(9)	9.6(9)	1.8(7)	4.4(8)	1.5(7)
C12	14.1(9)	16.8(10)	13.0(9)	0.5(8)	8.7(8)	-0.4(8)
C13	14.4(10)	20.1(11)	14.4(10)	0.9(9)	9.5(8)	1.7(8)
C14	10.5(9)	10.0(9)	13.4(9)	0.8(7)	6.3(8)	0.7(7)
C15	15(1)	20.5(11)	15.9(10)	-2.1(8)	10.7(8)	1.2(8)
C16	9.9(9)	11.0(9)	11.8(9)	0.3(7)	5.2(8)	0.2(7)
C17	30.6(13)	23.1(13)	20.2(12)	9.9(10)	9.7(10)	4.6(10)
C18	11.7(9)	16.2(10)	19.5(10)	-3.6(8)	7.1(8)	0.6(8)
C19	9.3(9)	11.0(9)	11.0(9)	-0.2(7)	3.8(8)	0.7(7)
C20	12.3(10)	14(1)	18.1(10)	-3.5(8)	6.1(8)	-1.8(8)
C21	18.0(11)	22.8(12)	27.7(12)	-0.1(9)	14.2(10)	-3.5(10)
C22	8.0(9)	17.2(10)	13.3(9)	-0.6(8)	3.2(8)	-0.5(8)
C23	14.8(10)	19.3(11)	13.1(10)	-2.4(8)	9.5(8)	1.2(8)

C24	29.0(13)	29.4(13)	29.5(13)	-6.7(10)	21.1(11)	-9.7(10)
C25	15.5(10)	20.2(11)	10.9(9)	0.3(8)	5.1(8)	-2.9(8)
C26	13.1(10)	16.6(10)	15.8(10)	1.6(8)	6.3(8)	-0.7(8)
C27	9.7(9)	16.9(10)	14.6(10)	-0.1(8)	3.8(8)	-2.9(8)
C29	15.8(10)	18.2(11)	17.7(10)	0.8(8)	7.9(9)	-1.0(8)
C30	16.4(10)	20.2(11)	16.5(10)	3.3(9)	5.1(9)	0.7(9)
Cl1	34.8(4)	99.2(7)	33.5(4)	-4.4(4)	16.4(3)	-9.4(4)
C1	35(2)	53(3)	54(3)	-0	12(2)	0

Table S11. Bond Lengths for chloro[1,3-bis(3'-butylimidazole-2'-thione-κ-*S*)benzene-κ-*C*]palladium(II)•½CH_2Cl_2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	S2	2.2917(6)	N10	C20	1.391(3)
Pd1	S3	2.3419(6)	C11	C14	1.410(3)
Pd1	Cl4	2.4068(6)	C11	C19	1.408(3)
Pd1	C11	2.0017(19)	C12	C19	1.399(3)
S2	C16	1.702(2)	C12	C25	1.381(3)
S3	C9	1.707(2)	C13	C29	1.521(3)
N6	C16	1.362(2)	C14	C27	1.389(3)
N6	C19	1.433(2)	C15	C23	1.340(3)
N6	C23	1.404(2)	C17	C30	1.521(3)
N7	C9	1.349(2)	C18	C20	1.341(3)
N7	C13	1.470(3)	C21	C24	1.514(3)
N7	C18	1.387(3)	C21	C29	1.526(3)
N8	C15	1.386(3)	C22	C26	1.514(3)
N8	C16	1.354(2)	C25	C27	1.383(3)
N8	C22	1.469(2)	C26	C30	1.531(3)
C9	N10	1.357(3)	Cl1	$C1^1$	1.767(3)

N10 C14 1.439(2)

[1]-X,+Y,1/2-Z

Table S12. Bond Angles for chloro[1,3-bis(3'-butylimidazole-2'-thione-κ-*S*)benzene-κ-*C*]palladium(II)•½CH_2Cl_2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S3	Pd1	S2	177.911(19)	C19	C11	C14	113.56(17)
Cl4	Pd1	S2	88.540(18)	C25	C12	C19	120.19(18)
Cl4	Pd1	S3	89.955(18)	C29	C13	N7	110.50(16)
C11	Pd1	S2	90.53(6)	C11	C14	N10	120.79(17)
C11	Pd1	S3	90.96(6)	C27	C14	N10	115.02(17)
C11	Pd1	Cl4	178.84(6)	C27	C14	C11	124.19(18)
C16	S2	Pd1	101.36(7)	C23	C15	N8	107.68(17)
C9	S3	Pd1	96.67(7)	N6	C16	S2	128.61(15)
C19	N6	C16	125.63(16)	N8	C16	S2	124.47(15)
C23	N6	C16	108.52(16)	N8	C16	N6	106.88(16)
C23	N6	C19	125.31(16)	C20	C18	N7	107.31(18)
C13	N7	C9	125.41(17)	C11	C19	N6	121.59(17)
C18	N7	C9	109.71(17)	C12	C19	N6	115.20(17)
C18	N7	C13	124.62(17)	C12	C19	C11	123.15(18)
C16	N8	C15	109.49(16)	C18	C20	N10	107.29(18)
C22	N8	C15	125.41(16)	C29	C21	C24	113.62(18)
C22	N8	C16	124.55(16)	C26	C22	N8	115.34(17)
N7	C9	S3	127.43(16)	C15	C23	N6	107.42(18)
N10	C9	S3	126.02(15)	C27	C25	C12	119.15(19)
N10	C9	N7	106.46(17)	C30	C26	C22	108.33(17)
C14	N10	C9	125.16(17)	C25	C27	C14	119.55(18)
C20	N10	C9	109.22(16)	C21	C29	C13	112.34(18)
C20	N10	C14	125.10(17)	C26	C30	C17	113.78(19)

C14	C11	Pd1	121.35(14)	Cl1	C1	Cl1[1]	110.4(3)
C19	C11	Pd1	125.07(14)				

[1]-X,+Y,1/2-Z

Table S13. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for chloro[1,3-bis(3'-butylimidazole-2'-thione-κ-*S*)benzene-κ-*C*]palladium(II)•½CH_2Cl_2.

Atom	*X*	*y*	*z*	U(eq)
H12	3647.8(7)	8224(2)	1957.3(12)	16.6(5)
H13a	1858.3(7)	8050(2)	4701.3(13)	18.3(5)
H13b	2203.1(7)	9419(2)	4839.1(13)	18.3(5)
H15	5211.4(8)	9315(2)	3653.3(13)	19.0(5)
H17a	6453(6)	5069(9)	6207(5)	38.9(8)
H17b	6685(3)	5563(4)	7160(5)	38.9(8)
H17c	6164(3)	4748(6)	6699(10)	38.9(8)
H18	1689.6(7)	6283(2)	3405.3(13)	19.3(5)
H20	2172.4(7)	5804(2)	2706.2(13)	18.6(5)
H21a	1199.4(8)	9766(3)	4592.3(15)	25.9(6)
H21b	962.0(8)	10909(3)	3846.6(15)	25.9(6)
H22a	5686.9(7)	8944(2)	5248.0(12)	16.5(5)
H22b	5366.3(7)	8687(2)	5691.0(12)	16.5(5)
H23	4327.6(7)	9505(2)	2598.0(13)	17.5(5)
H24a	1716(5)	12260(11)	4547(3)	39.6(8)
H24b	1436(2)	12171(12)	5071(8)	39.6(8)
H24c	1906(3)	11169(3)	5316(6)	39.6(8)
H25	2805.2(8)	7697(2)	1154.5(13)	19.4(5)
H26a	5393.2(7)	6172(2)	5517.4(13)	18.7(5)
H26b	5710.3(7)	6424(2)	5061.6(13)	18.7(5)
H27	2338.0(7)	7416(2)	1817.9(13)	17.7(5)
H29a	1591.4(8)	10339(2)	3511.7(13)	20.9(5)

H29b	1245.2(8)	8989(2)	3398.5(13)	20.9(5)
H30a	6029.5(8)	7222(2)	6760.7(13)	22.9(5)
H30b	6340.4(8)	7581(2)	6310.0(13)	22.9(5)
H1a	272.335248	8136(5)	2901.444273	62.5(14)
H1b	-272.335248	8136(5)	2098.555727	62.5(14)

Table S14. Atomic Occupancy for chloro[1,3-bis(3'-butylimidazole-2'-thione-κ-*S*)benzene-κ-*C*]palladium(II)•½CH_2Cl_2.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
H1a	0.500000	H1b	0.500000		

Number of restraints - 0, number of constraints - 43.

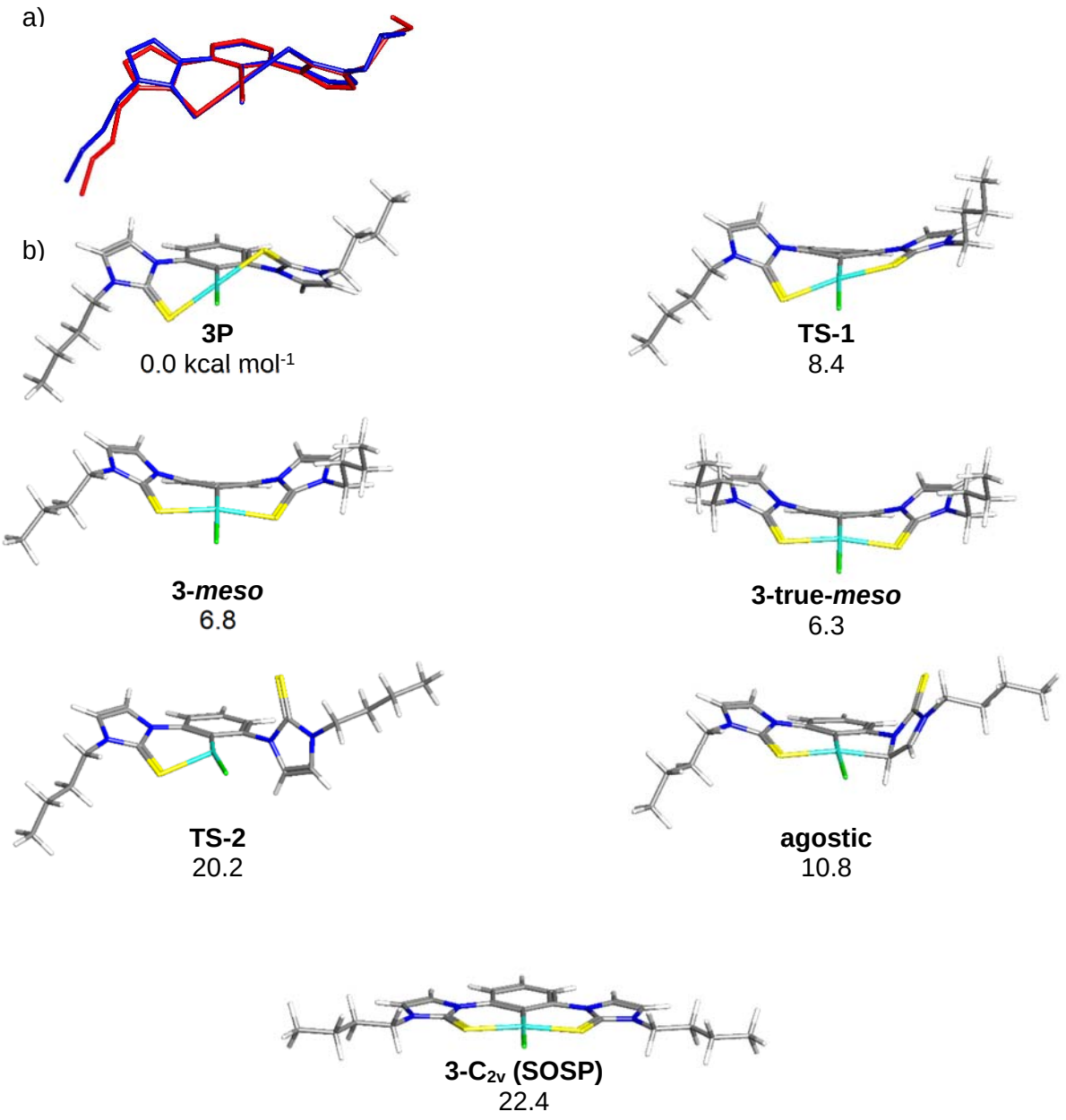

Figure S19. 3-D representations of various B3LYP DFT computed geometries: a) Overlay of molecular geometries of complex **3**, experimental molecular geometry from X-ray structure (in red) and computed gas-phase B3LYP geometry (in blue). Hydrogen atoms are omitted for clarity. The conformations of the butyl chains from the X-ray structure are anti on the left and gauche on the right. For the B3LYP structures, this conformation is 0.5 kcal mol^{-1} higher in energy than the conformer in **3P**. b) 3-D representations of various B3LYP DFT computed geometries for **3P**, **TS-1**, **3-*meso***, **3-true-*meso***, **TS-2**, **agnostic**, and **3-C_{2v} (SOSP)**. Relative free energies are given in kcal mol^{-1}.

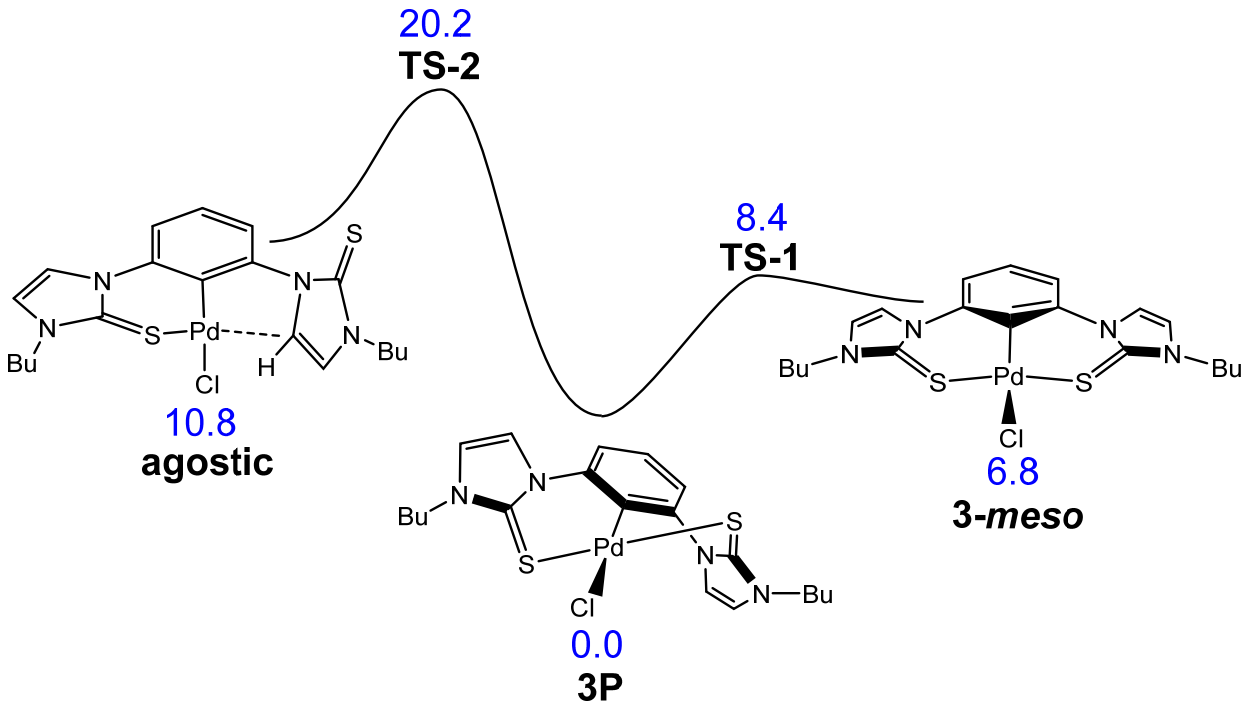

Figure S20. Free energy diagram for the proposed mechanism for the isomerization of **3P** (through **TS-1**) to produce **3-*meso*** and the decoordination of the thione sulfur (through **TS-2**) to produce the **agostic** complex.

Table S8. Raw and relative energies (absolute energies in Hartrees, relative energies in kcal mol^{-1})

	E_e	$G^{(\circ/\ddagger)}$	$\Delta G^{(\circ/\ddagger)}$
3P-PBEPBE	-1156.98662144	-1156.634569	0.00
TS-1-PBEPBE	-1156.97591994	-1156.621960	7.91
3-*meso*-PBEPBE	-1156.97751377	-1156.624815	6.12
3P-B3LYP	-1158.22739497	-1157.862455	0.00
TS-1-B3LYP	-1158.21484437	-1157.849058	8.41
3-*meso*-B3LYP	-1158.21595819	-1157.851581	6.82
3-true-*meso*-B3LYP	-1158.21528842	-1157.852411	6.30
3-compare-Xray	-1158.22611895	-1157.861689	0.48
TS-2-B3LYP	-1158.19185311	-1157.830303	20.18
TS-3-B3LYP	-1158.20739467	-1157.842472	12.54
3-C_{2v}-(SOSP)-B3LYP	-1158.19274217	-1157.826820	22.36

DFT Computational Output

```
3P-B3LYP
Pd    0.000000  0.000000  0.665938
S     1.362797 -1.966866  0.672132
S    -1.362797  1.966866  0.672132
Cl    0.000000  0.000000  3.087440
N    -0.293173 -2.457621 -1.501525
N     0.000000  4.186932 -0.191943
N     0.000000 -4.186932 -0.191943
C    -0.348146  2.880085 -0.367385
N     0.293173  2.457621 -1.501525
C     0.000000  0.000000 -1.370055
C    -0.094842 -1.195140 -3.536682
C    -0.444460  5.026244  0.924925
C     0.130372  1.179371 -2.135343
C    -0.861379 -4.579804 -1.206525
C     0.348146 -2.880085 -0.367385
C     3.584637 -7.266024  1.604779
C     0.861379  4.579804 -1.206525
C    -0.130372 -1.179371 -2.135343
C     1.052243  3.507331 -2.014238
C    -2.235744  6.578929  1.846687
C     0.444460 -5.026244  0.924925
C    -1.052243 -3.507331 -2.014238
C    -3.584637  7.266024  1.604779
C     0.000000  0.000000 -4.242068
C     1.793562 -5.706803  0.663488
C     0.094842  1.195140 -3.536682
C    -1.793562  5.706803  0.663488
C     2.235744 -6.578929  1.846687
H    -0.123392 -2.141811 -4.070780
H    -0.500849  4.377005  1.805930
H     0.343592  5.768876  1.097734
H    -1.282536 -5.573660 -1.240246
H     3.877188 -7.878564  2.466437
H     3.546076 -7.923073  0.725424
H     4.379847 -6.528589  1.434172
H     1.282536  5.573660 -1.240246
H     1.685826  3.378235 -2.877452
H    -1.466362  7.339658  2.049696
H    -2.297393  5.956009  2.750846
H     0.500849 -4.377005  1.805930
H    -0.343592 -5.768876  1.097734
H    -1.685826 -3.378235 -2.877452
H    -3.877188  7.878564  2.466437
H    -3.546076  7.923073  0.725424
H    -4.379847  6.528589  1.434172
H     0.000000  0.000000 -5.328873
H     1.722496 -6.318080 -0.248899
H     2.548185 -4.931912  0.470062
H     0.123392  2.141811 -4.070780
H    -1.722496  6.318080 -0.248899
H    -2.548185  4.931912  0.470062
```

```
H     1.466362 -7.339658  2.049696
H     2.297393 -5.956009  2.750846
    el energy= -1158.22739497
          zpe= -1157.799866
    th energy= -1157.770852
  th enthalpy= -1157.769908
  free energy= -1157.862455

TS-1-B3LYP (3P to 3-meso)
Pd   -0.009194 -0.642768 -0.495855
S    -2.388139 -0.734549 -0.739873
S     2.278697 -1.030476 -0.447801
Cl   -0.109773 -2.991217 -1.129332
N    -2.199463  1.477949  0.887964
N     4.426588  0.594514 -0.477867
N    -3.925607  0.207726  1.330292
C     3.061746  0.483985 -0.481121
N     2.556984  1.761746 -0.521286
C     0.091916  1.375415 -0.114561
C    -1.244814  3.475048  0.023243
C     5.363642 -0.531644 -0.432611
C     1.182171  2.212637 -0.475528
C    -3.950135  1.262557  2.232255
C    -2.847194  0.340412  0.503991
C    -8.106599 -1.589778 -0.867575
C     4.782984  1.929849 -0.474852
C    -1.077529  2.101724  0.236364
C     3.643170  2.653840 -0.493725
C     6.617366 -2.211908  1.008308
C    -4.894156 -0.889695  1.262683
C    -2.876670  2.047462  1.965884
C     6.920188 -2.710001  2.426234
C    -0.205856  4.211068 -0.531175
C    -6.004436 -0.645413  0.233402
C     1.009185  3.582087 -0.757682
C     5.650114 -1.020283  0.993274
C    -6.998203 -1.813544  0.167402
H    -2.200065  3.943736  0.246114
H     4.937991 -1.337401 -1.040844
H     6.284615 -0.195181 -0.924205
H    -4.710650  1.339505  2.995167
H    -8.799465 -2.439713 -0.895593
H    -8.691699 -0.688989 -0.637975
H    -7.687835 -1.466835 -1.874854
H     5.815728  2.245484 -0.453457
H     3.518690  3.719538 -0.435198
H     7.557094 -1.930312  0.508440
H     6.187833 -3.032806  0.415660
H    -4.330379 -1.796539  1.015037
H    -5.310468 -1.011376  2.269894
H    -2.507448  2.934252  2.456755
H     7.609189 -3.563333  2.407532
H     7.381194 -1.921481  3.036251
H     6.003070 -3.032118  2.936264
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H    -0.334225  5.262492 -0.773992
H    -6.534129  0.286169  0.483893
H    -5.543075 -0.494656 -0.752264
H     1.815920  4.164883 -1.186918
H     6.066628 -0.189613  1.582775
H     4.700991 -1.304887  1.466186
H    -7.447393 -1.971059  1.160150
H    -6.452837 -2.737822 -0.073055
    el energy= -1158.21484437
          zpe= -1157.787602
    th energy= -1157.759426
  th enthalpy= -1157.758482
  free energy= -1157.849058
```

3-*meso*-B3LYP

```
Pd    0.077933 -0.570932 -0.560386
S    -2.236891 -0.954940 -0.332034
S     2.367042 -0.784793 -1.097571
Cl    0.035677 -2.887020 -1.320035
N    -2.318289  1.661189  0.586365
N     4.433063  0.691865 -0.102246
N    -3.988657  0.404520  1.252403
C     3.113658  0.605665 -0.449187
N     2.553708  1.820256 -0.168230
C     0.069879  1.446702 -0.164721
C    -1.241524  3.550053 -0.386900
C     5.389328 -0.419136 -0.160804
C     1.204119  2.274065 -0.388378
C    -4.176284  1.659609  1.808602
C    -2.843226  0.401616  0.505691
C    -7.845918 -2.256392 -0.645013
C     4.692787  1.947182  0.424510
C    -1.130320  2.196213 -0.029121
C     3.534417  2.647378  0.390791
C     6.324389 -2.482007  1.001858
C    -4.879111 -0.746600  1.419835
C    -3.140750  2.436374  1.411690
C     6.292894 -3.371155  2.250238
C    -0.119805  4.260807 -0.792395
C    -5.901512 -0.886469  0.284747
C     1.116057  3.629214 -0.746390
C     5.345855 -1.302764  1.092195
C    -6.815862 -2.103801  0.480151
H    -2.215333  4.032166 -0.373977
H     5.159268 -1.005223 -1.056444
H     6.383035  0.023497 -0.300376
H    -5.012816  1.875318  2.456788
H    -8.484273 -3.133195 -0.480954
H    -8.498151 -1.375132 -0.710499
H    -7.353472 -2.379277 -1.618323
H     5.673189  2.220710  0.785821
H     3.301424  3.638281  0.744574
H     7.346447 -2.103606  0.844158
H     6.079478 -3.086229  0.116083
```

```
H    -4.244517 -1.638274  1.479501
H    -5.380736 -0.622523  2.387289
H    -2.881195  3.448276  1.675946
H     6.995600 -4.208361  2.157507
H     6.564980 -2.804392  3.150883
H     5.291531 -3.790949  2.410343
H    -0.204548  5.293557 -1.119788
H    -6.504789  0.031931  0.225312
H    -5.361535 -0.976296 -0.667569
H     2.016406  4.173755 -1.018012
H     5.576817 -0.688478  1.975493
H     4.321840 -1.677589  1.219840
H    -7.336236 -2.021462  1.446966
H    -6.199442 -3.012723  0.539024
    el energy= -1158.21595819
          zpe= -1157.788490
    th energy= -1157.759529
  th enthalpy= -1157.758585
  free energy= -1157.851581

3-true-meso-B3LYP
Pd   -0.243749  0.948912  0.000000
S    -0.493825  1.176166  2.335046
S    -0.493825  1.176166 -2.335046
Cl   -2.298012  2.261996  0.000000
N     1.796605 -0.381477  2.466845
N     0.558949 -0.421980 -4.277302
N     0.558949 -0.421980  4.277302
C     0.648507  0.110954 -3.021589
N     1.796605 -0.381477 -2.466845
C     1.608597  0.057316  0.000000
C     3.787791 -0.086948  1.193071
C    -0.560524 -0.209136 -5.200866
C     2.383263 -0.097552 -1.181725
C     1.631214 -1.271802  4.497648
C     0.648507  0.110954  3.021589
C    -4.074366 -1.871717  5.677887
C     1.631214 -1.271802 -4.497648
C     2.383263 -0.097552  1.181725
C     2.396460 -1.255325 -3.380893
C    -2.900512 -0.913072 -5.908808
C    -0.560524 -0.209136  5.200866
C     2.396460 -1.255325  3.380893
C    -4.074366 -1.871717 -5.677887
C     4.496251 -0.034283  0.000000
C    -1.726747 -1.174867  4.955215
C     3.787791 -0.086948 -1.193071
C    -1.726747 -1.174867 -4.955215
C    -2.900512 -0.913072  5.908808
H     4.318591 -0.088181  2.141239
H    -0.887826  0.829596 -5.087653
H    -0.160320 -0.321406 -6.215821
H     1.743024 -1.818807  5.422217
H    -4.900578 -1.659320  6.367550
```

```
H    -4.461437 -1.782271  4.654737
H    -3.772316 -2.916745  5.830073
H     1.743024 -1.818807 -5.422217
H     3.286575 -1.808988 -3.131114
H    -2.555792 -0.996707 -6.951309
H    -3.244492  0.123681 -5.780508
H    -0.160320 -0.321406  6.215821
H    -0.887826  0.829596  5.087653
H     3.286575 -1.808988  3.131114
H    -4.900578 -1.659320 -6.367550
H    -3.772316 -2.916745 -5.830073
H    -4.461437 -1.782271 -4.654737
H     5.581200  0.027609  0.000000
H    -2.059435 -1.064033  3.914883
H    -1.370001 -2.209343  5.071420
H     4.318591 -0.088181 -2.141239
H    -1.370001 -2.209343 -5.071420
H    -2.059435 -1.064033 -3.914883
H    -3.244492  0.123681  5.780508
H    -2.555792 -0.996707  6.951309
    el energy= -1158.21528842
          zpe= -1157.787998
    th energy= -1157.758917
  th enthalpy= -1157.757973
  free energy= -1157.852411

TS-2-B3LYP
Pd    0.172738 -0.787261 -0.005706
S     2.436310 -0.917373  0.340363
S    -3.115342  1.033079 -1.631971
Cl   -0.224139 -3.129350 -0.225350
N     2.463182  1.796122 -0.345371
N    -3.876388 -0.569512  0.482418
N     4.261298  0.679980 -0.912738
C    -3.045865  0.369234 -0.076957
N    -2.126036  0.662561  0.922667
C     0.171159  1.182452  0.321072
C     0.972468  3.480110  0.574539
C    -4.995672 -1.200188 -0.215732
C    -1.068102  1.633624  0.801281
C     4.442533  1.989737 -1.326537
C     3.044088  0.560706 -0.311887
C     8.073931 -1.988711  1.071033
C    -3.502787 -0.832396  1.794800
C     1.182736  2.144874  0.195416
C    -2.421411 -0.068879  2.078285
C    -7.478498 -1.119313 -0.768411
C     5.222795 -0.413080 -1.101676
C     3.325022  2.680696 -0.991072
C    -8.809946 -0.381555 -0.585700
C    -0.274549  3.887969  1.041983
C     6.144313 -0.621741  0.106678
C    -1.313684  2.961591  1.143870
C    -6.317983 -0.447921 -0.021921
```

```
C     7.142655 -1.764593 -0.125958
H     1.787547  4.198149  0.531220
H    -4.724228 -1.235037 -1.275585
H    -5.067946 -2.231183  0.151913
H     5.336082  2.301920 -1.846477
H     8.774208 -2.810168  0.877398
H     8.665444 -1.089789  1.290333
H     7.504543 -2.241738  1.974815
H    -4.025410 -1.560824  2.397143
H    -1.812820  0.008832  2.966225
H    -7.584458 -2.159608 -0.424087
H    -7.233953 -1.175406 -1.839327
H     4.641380 -1.318433 -1.309702
H     5.802217 -0.170064 -1.999942
H     3.044565  3.701539 -1.193230
H    -9.619766 -0.880052 -1.133106
H    -9.100109 -0.338465  0.472894
H    -8.744125  0.650911 -0.953585
H    -0.431430  4.924443  1.328662
H     6.684652  0.313398  0.316437
H     5.529904 -0.839298  0.991396
H    -2.304175  3.257938  1.479735
H    -6.550170 -0.386545  1.052459
H    -6.187989  0.582226 -0.380387
H     7.741970 -1.550141 -1.023899
H     6.589378 -2.690735 -0.339608
    el energy= -1158.19185311
          zpe= -1157.765567
    th energy= -1157.736676
  th enthalpy= -1157.735731
  free energy= -1157.830303

agostic-B3LYP
Pd   -0.104606 -0.785425 -0.430107
S    -2.395038 -0.998272 -0.043350
S     3.924721  2.147810  0.815572
Cl    0.043446 -3.212470 -0.610912
N    -2.413988  1.791430  0.316945
N     3.595022 -0.484265  0.116639
N    -4.165003  0.710635  1.087301
C     3.247152  0.871461 -0.027773
N     2.213568  0.880170 -0.941448
C    -0.111531  1.244175 -0.469744
C    -1.017287  3.513797 -0.656062
C     4.653709 -0.972546  1.008517
C     1.118371  1.808597 -0.889542
C    -4.349919  2.049314  1.383380
C    -2.971329  0.544451  0.441606
C    -7.947778 -2.208614 -0.565929
C     2.780819 -1.263008 -0.629932
C    -1.163223  2.160454 -0.292566
C     1.876437 -0.454023 -1.304745
C     7.126874 -1.493705  1.279509
C    -5.109225 -0.365460  1.405806
```

```
C    -3.267500  2.719018  0.925011
C     8.509054 -1.531254  0.617355
C     0.203058  4.003134 -1.108519
C    -6.042658 -0.710272  0.238590
C     1.303652  3.150464 -1.201936
C     6.027466 -1.002418  0.327910
C    -7.014138 -1.844288  0.594060
H    -1.866085  4.189440 -0.611876
H     4.666556 -0.306914  1.877263
H     4.351303 -1.972162  1.341030
H    -5.221831  2.398986  1.916175
H    -8.629424 -3.020439 -0.284240
H    -8.559728 -1.349199 -0.871113
H    -7.377953 -2.540370 -1.443519
H     2.874061 -2.339980 -0.675114
H     1.482608 -0.657293 -2.298489
H     6.869718 -2.497146  1.651471
H     7.160087 -0.838212  2.162238
H    -4.517849 -1.239604  1.700902
H    -5.680347 -0.034115  2.281263
H    -3.003012  3.757426  1.026288
H     9.275229 -1.881930  1.319733
H     8.517851 -2.205058 -0.249806
H     8.807887 -0.534605  0.266898
H     0.294943  5.050307 -1.384768
H    -6.604549  0.189616 -0.053158
H    -5.433143 -1.001128 -0.627581
H     2.278367  3.510813 -1.514074
H     5.980734 -1.652971 -0.558351
H     6.264826  0.008890 -0.027992
H    -7.612581 -1.554613  1.471621
H    -6.438506 -2.732243  0.894049
    el energy= -1158.20776625
          zpe= -1157.780814
    th energy= -1157.751736
  th enthalpy= -1157.750792
  free energy= -1157.845212

3-C2v-(SOSP)-B3LYP
Pd    0.000000  0.000000  0.755404
S     0.000000  2.268947  1.175187
S     0.000000 -2.268947  1.175187
Cl    0.000000  0.000000  3.217197
N     0.000000  2.586516 -1.605203
N     0.000000 -4.435311 -0.374000
N     0.000000  4.435311 -0.374000
C     0.000000 -3.066658 -0.317089
N     0.000000 -2.586516 -1.605203
C     0.000000  0.000000 -1.324204
C     0.000000  1.185790 -3.518505
C     0.000000 -5.284629  0.823929
C     0.000000 -1.208657 -2.112746
C     0.000000  4.833120 -1.693827
C     0.000000  3.066658 -0.317089
```

```
C     0.000000  9.126845  1.525743
C     0.000000 -4.833120 -1.693827
C     0.000000  1.208657 -2.112746
C     0.000000 -3.718159 -2.452094
C     0.000000 -7.618662  1.799066
C     0.000000  5.284629  0.823929
C     0.000000  3.718159 -2.452094
C     0.000000 -9.126845  1.525743
C     0.000000  0.000000 -4.218475
C     0.000000  6.780841  0.511211
C     0.000000 -1.185790 -3.518505
C     0.000000 -6.780841  0.511211
C     0.000000  7.618662  1.799066
H     0.000000  2.085656 -4.110387
H     0.879687 -5.015654  1.423364
H    -0.879687 -5.015654  1.423364
H     0.000000  5.869165 -1.992501
H     0.000000  9.696605  2.462840
H     0.886505  9.429079  0.952257
H    -0.886505  9.429079  0.952257
H     0.000000 -5.869165 -1.992501
H     0.000000 -3.679030 -3.522386
H     0.879010 -7.353513  2.404295
H    -0.879010 -7.353513  2.404295
H     0.879687  5.015654  1.423364
H    -0.879687  5.015654  1.423364
H     0.000000  3.679030 -3.522386
H     0.000000 -9.696605  2.462840
H    -0.886505 -9.429079  0.952257
H     0.884376  7.039456 -0.089958
H    -0.884376  7.039456 -0.089958
H     0.886505 -9.429079  0.952257
H     0.000000  0.000000 -5.305260
H     0.000000 -2.085656 -4.110387
H    -0.884376 -7.039456 -0.089958
H     0.884376 -7.039456 -0.089958
H    -0.879010  7.353513  2.404295
H     0.879010  7.353513  2.404295
    el energy= -1158.19274217
          zpe= -1157.766083
    th energy= -1157.738221
  th enthalpy= -1157.737277
  free energy= -1157.826820
```

```
3P-PBEPBE
Pd     0.000000  0.000000  0.638652
S      1.337389 -1.952755  0.683810
S     -1.337389  1.952755  0.683810
Cl     0.000000  0.000000  3.056565
N     -0.291450 -2.462100 -1.524725
N      0.000000  4.193094 -0.196555
N      0.000000 -4.193094 -0.196555
C     -0.341998  2.874070 -0.370300
N      0.291450  2.462100 -1.524725
C      0.000000  0.000000 -1.383735
C     -0.089877 -1.200778 -3.565295
C     -0.440084  5.014680  0.934657
C      0.128854  1.184908 -2.157192
C     -0.841106 -4.599865 -1.225642
C      0.341998 -2.874070 -0.370300
C      3.624910 -7.167965  1.699044
C      0.841106  4.599865 -1.225642
C     -0.128854 -1.184908 -2.157192
C      1.031510  3.524205 -2.046566
C     -2.252338  6.514684  1.907748
C      0.440084 -5.014680  0.934657
C     -1.031510 -3.524205 -2.046566
C     -3.624910  7.167965  1.699044
C      0.000000  0.000000 -4.274186
C      1.814032 -5.661596  0.706833
C      0.089877  1.200778 -3.565295
C     -1.814032  5.661596  0.706833
C      2.252338 -6.514684  1.907748
H     -0.107828 -2.156904 -4.100610
H     -0.464079  4.348324  1.817304
H      0.339174  5.780579  1.100467
H     -1.256053 -5.604991 -1.259878
H      3.919636 -7.769583  2.577119
H      3.622263 -7.837530  0.818731
H      4.408968 -6.405716  1.536453
H      1.256053  5.604991 -1.259878
H      1.661676  3.400180 -2.923221
H     -1.491902  7.298251  2.101301
H     -2.276912  5.878766  2.814587
H      0.464079 -4.348324  1.817304
H     -0.339174 -5.780579  1.100467
H     -1.661676 -3.400180 -2.923221
H     -3.919636  7.769583  2.577119
H     -3.622263  7.837530  0.818731
H     -4.408968  6.405716  1.536453
H      0.000000  0.000000 -5.369052
H      1.780440 -6.283415 -0.210327
H      2.556790 -4.860369  0.524856
H      0.107828  2.156904 -4.100610
H     -1.780440  6.283415 -0.210327
H     -2.556790  4.860369  0.524856
H      1.491902 -7.298251  2.101301
H      2.276912 -5.878766  2.814587
```

```
    el energy= -1156.98662144
          zpe= -1156.570626
    th energy= -1156.540814
  th enthalpy= -1156.539870
  free energy= -1156.634569

TS-1-PBEPBE (3P to 3-meso)
Pd   -0.010621 -0.616184 -0.483468
S    -2.363845 -0.750097 -0.709499
S     2.250172 -1.033173 -0.380373
Cl   -0.113132 -2.960382 -1.144131
N    -2.194178  1.485257  0.916191
N     4.425327  0.569582 -0.513416
N    -3.929729  0.202277  1.347650
C     3.050579  0.473369 -0.478021
N     2.557604  1.765267 -0.554075
C     0.092856  1.381922 -0.110838
C    -1.240772  3.496828  0.072730
C     5.339717 -0.573870 -0.452673
C     1.189457  2.225084 -0.475800
C    -3.971242  1.264530  2.243429
C    -2.835583  0.333954  0.525704
C    -8.038732 -1.626126 -0.959505
C     4.797519  1.901233 -0.578159
C    -1.075612  2.113126  0.266555
C     3.657361  2.643636 -0.598235
C     6.569188 -2.252105  1.015995
C    -4.890269 -0.900717  1.262037
C    -2.890336  2.059123  1.983414
C     6.873906 -2.722537  2.444378
C    -0.199469  4.239489 -0.483250
C    -5.972685 -0.667267  0.198098
C     1.015972  3.606252 -0.733334
C     5.628560 -1.037352  0.983282
C    -6.958225 -1.843282  0.107887
H    -2.202383  3.965988  0.308775
H     4.882729 -1.390698 -1.041802
H     6.269335 -0.268526 -0.967024
H    -4.745340  1.339603  3.004243
H    -8.730641 -2.485512 -1.009215
H    -8.639726 -0.722627 -0.745743
H    -7.588596 -1.499049 -1.961117
H     5.841930  2.205773 -0.600024
H     3.548974  3.720823 -0.578678
H     7.515968 -2.002579  0.495132
H     6.110618 -3.081672  0.442226
H    -4.306866 -1.811518  1.029183
H    -5.335666 -1.023515  2.266018
H    -2.522703  2.952912  2.480694
H     7.544689 -3.599962  2.442780
H     7.364282 -1.925789  3.034226
H     5.947441 -3.009175  2.974981
H    -0.326875  5.302219 -0.713040
H    -6.517824  0.270046  0.428785
```

```
H    -5.477623 -0.518169 -0.781371
H     1.824623  4.199733 -1.165928
H     6.070791 -0.197130  1.555339
H     4.669189 -1.292100  1.472966
H    -7.436081 -2.002932  1.095868
H    -6.395940 -2.771268 -0.116185
    el energy= -1156.97591994
          zpe= -1156.559972
    th energy= -1156.531101
  th enthalpy= -1156.530156
  free energy= -1156.621960
```

3-*meso*-PBEPBE

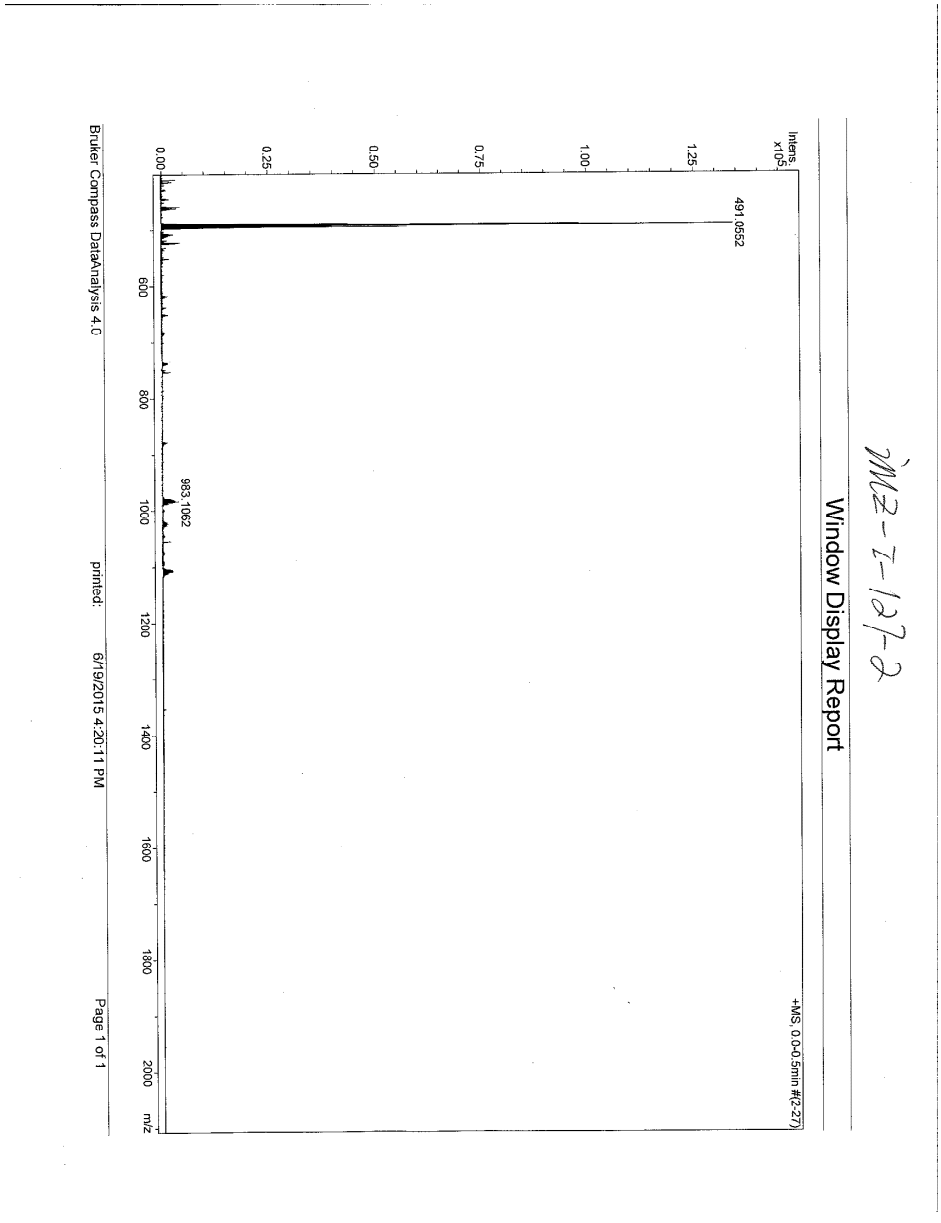
```
Pd    0.073919 -0.538245 -0.566736
S    -2.212142 -0.951710 -0.316378
S     2.343708 -0.810248 -1.053117
Cl    0.014344 -2.842549 -1.378632
N    -2.308371  1.677116  0.603466
N     4.445962  0.671125 -0.109557
N    -3.981849  0.404762  1.273520
C     3.111988  0.588279 -0.439125
N     2.566216  1.824306 -0.172756
C     0.076910  1.453263 -0.167814
C    -1.232571  3.577175 -0.360597
C     5.380185 -0.459175 -0.156569
C     1.220521  2.284455 -0.386145
C    -4.181541  1.663733  1.822195
C    -2.827288  0.404053  0.523438
C    -7.781891 -2.298017 -0.682818
C     4.726621  1.936519  0.386787
C    -1.125450  2.212717 -0.014363
C     3.566876  2.654166  0.353152
C     6.245802 -2.550133  1.016105
C    -4.862197 -0.755275  1.430081
C    -3.142553  2.452106  1.421588
C     6.174769 -3.436579  2.266540
C    -0.105072  4.289392 -0.769065
C    -5.865775 -0.907610  0.277098
C     1.134081  3.649909 -0.734333
C     5.301256 -1.340650  1.098904
C    -6.767992 -2.138426  0.457848
H    -2.214006  4.063357 -0.341984
H     5.142774 -1.047174 -1.061348
H     6.392436 -0.035891 -0.289871
H    -5.026912  1.876155  2.473372
H    -8.416739 -3.189114 -0.532326
H    -8.448191 -1.418185 -0.753674
H    -7.271433 -2.410282 -1.656839
H     5.721790  2.206629  0.734007
H     3.343925  3.658853  0.699580
H     7.287509 -2.200783  0.863936
H     5.987231 -3.150794  0.121628
H    -4.210107 -1.646432  1.496290
H    -5.382052 -0.638861  2.398695
```

```
H    -2.881609  3.471294  1.690559
H     6.853734 -4.303521  2.181463
H     6.459795 -2.874188  3.175173
H     5.151424 -3.824798  2.420249
H    -0.188615  5.330939 -1.095595
H    -6.483204  0.010272  0.206339
H    -5.303403 -0.991276 -0.673048
H     2.042528  4.194140 -1.014270
H     5.543113 -0.727724  1.990178
H     4.256938 -1.687722  1.217235
H    -7.304127 -2.065547  1.426013
H    -6.135777 -3.045996  0.522622
    el energy= -1156.97751377
          zpe= -1156.561320
    th energy= -1156.531687
  th enthalpy= -1156.530743
  free energy= -1156.624815
```

As can be seen in Figure S21 below the primary component present in the ESI-MS data collected on aliquots during the catalytic run was $[M\text{-}Cl]^+$ (m/z = 491) of the SCS-NHT Pd complex with a matching isotope envelope. Small amounts (<100 times the intensity of the 491 peak) of the $[2M - 2Cl]^+$ peak (m/z = 982) and variously charged multiples were observed in concentrated samples, but this level was attributed to formation in the droplet during the ionization in the mass spectral experiment. Collection of the ESI-MS data on suitably diluted samples dramatically diminished these peaks, which is consistent with their formation during ionization.

Figure S21. Representative ESI-MS data collected on aliquots during a catalytic Suzuki reaction trial.

a. Illustrative mass spectrum upto ~2000 amu.



b. Expansion of the vertical scale upto 2000 amu.