

Supporting Information
for
**Molecular Switching through Chalcogen Bond-Induced Isomerization of Binuclear
(Diaminocarbene)Pd^{II} Complexes**

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NMR spectra

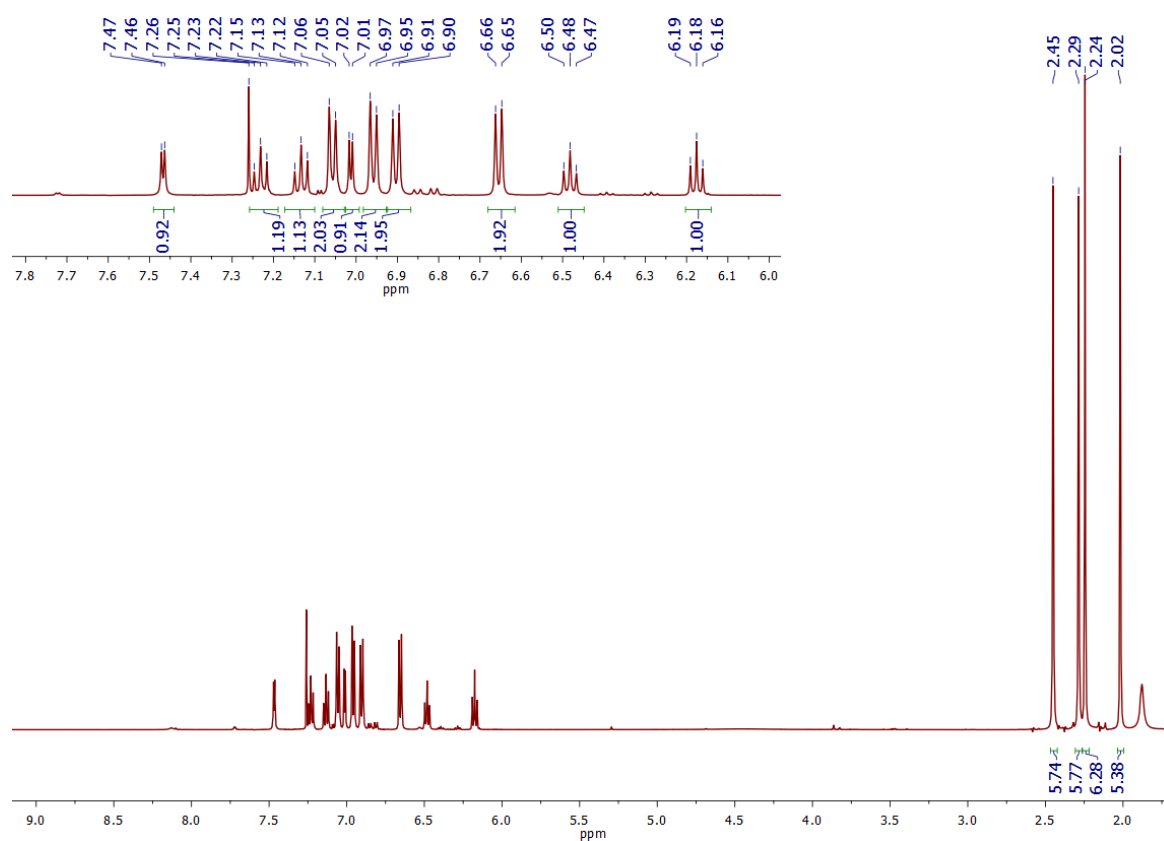


Figure S1. The ¹H NMR spectrum of **4a** with traces of **4b** in CDCl₃.

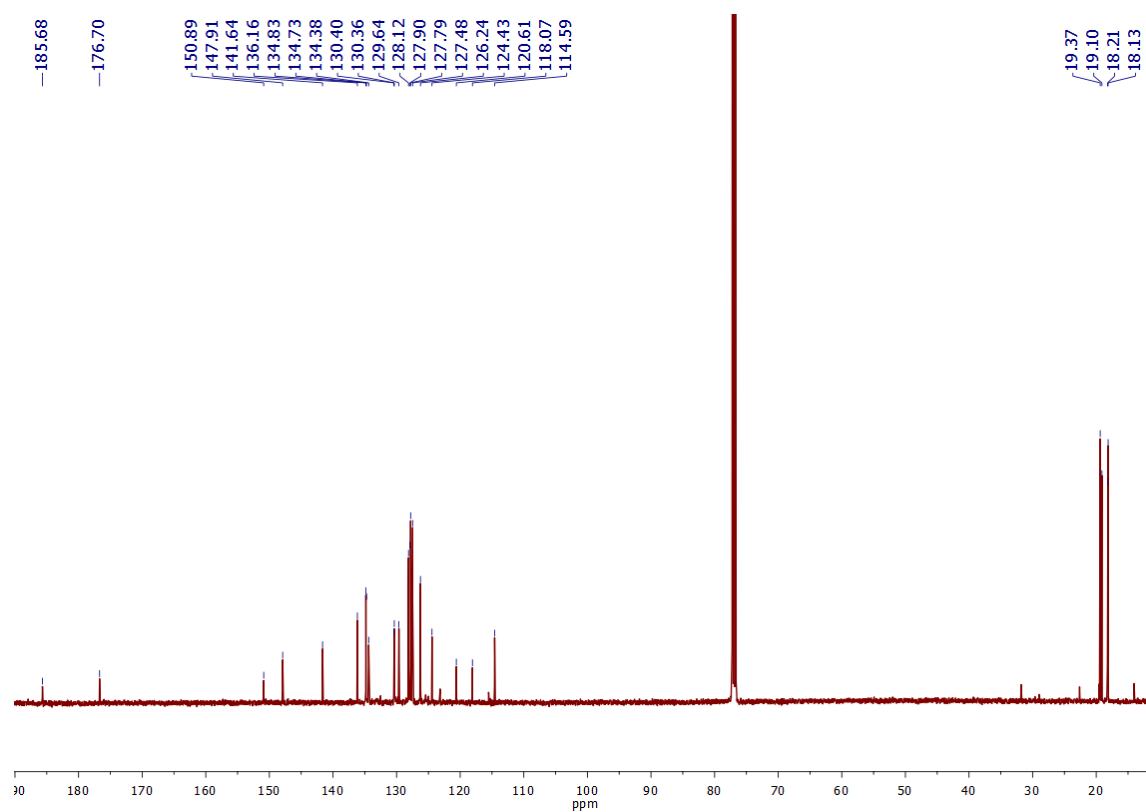


Figure S2. The ¹³C NMR spectrum of **4a** with traces of **4b** in CDCl₃.

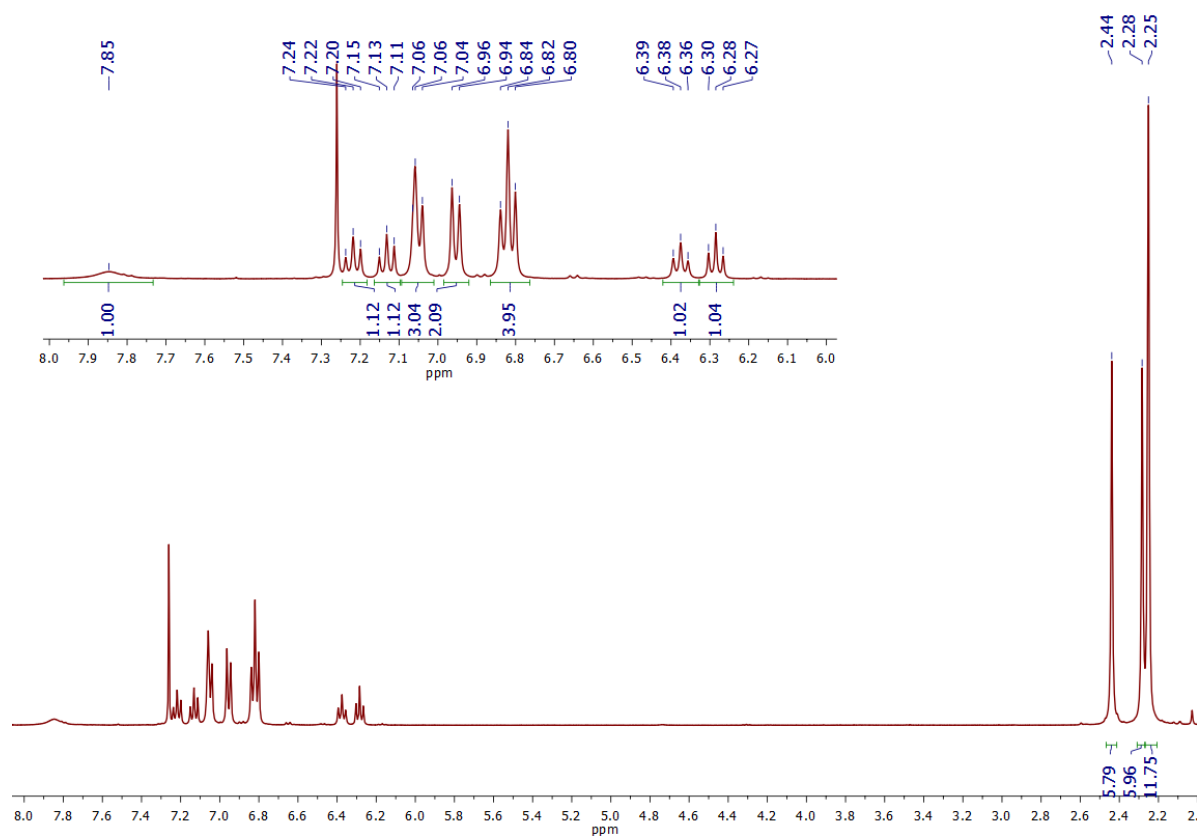


Figure S3. The ¹H NMR spectrum of **4b** with traces of **4a** in CDCl₃.

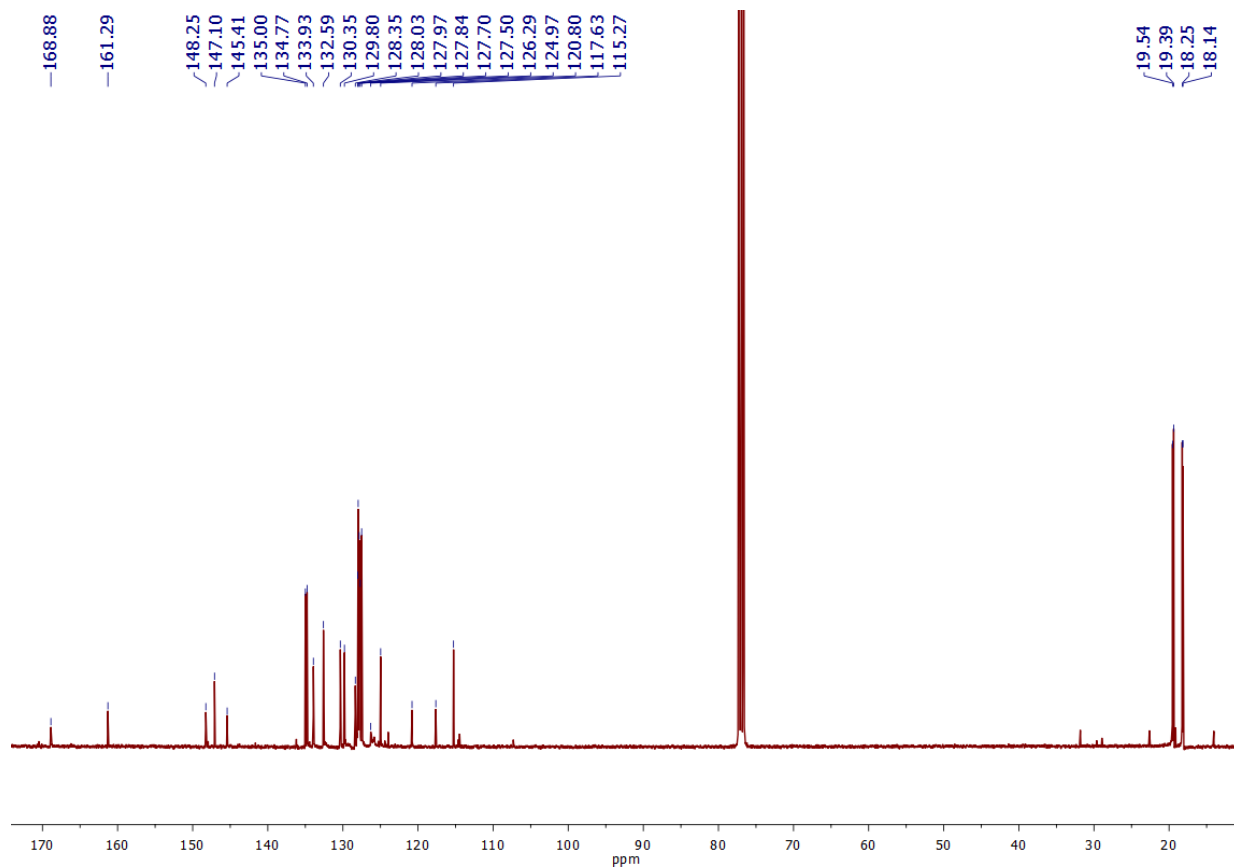


Figure S4. The ¹³C NMR spectrum of **4b** with traces of **4a** in CDCl₃.

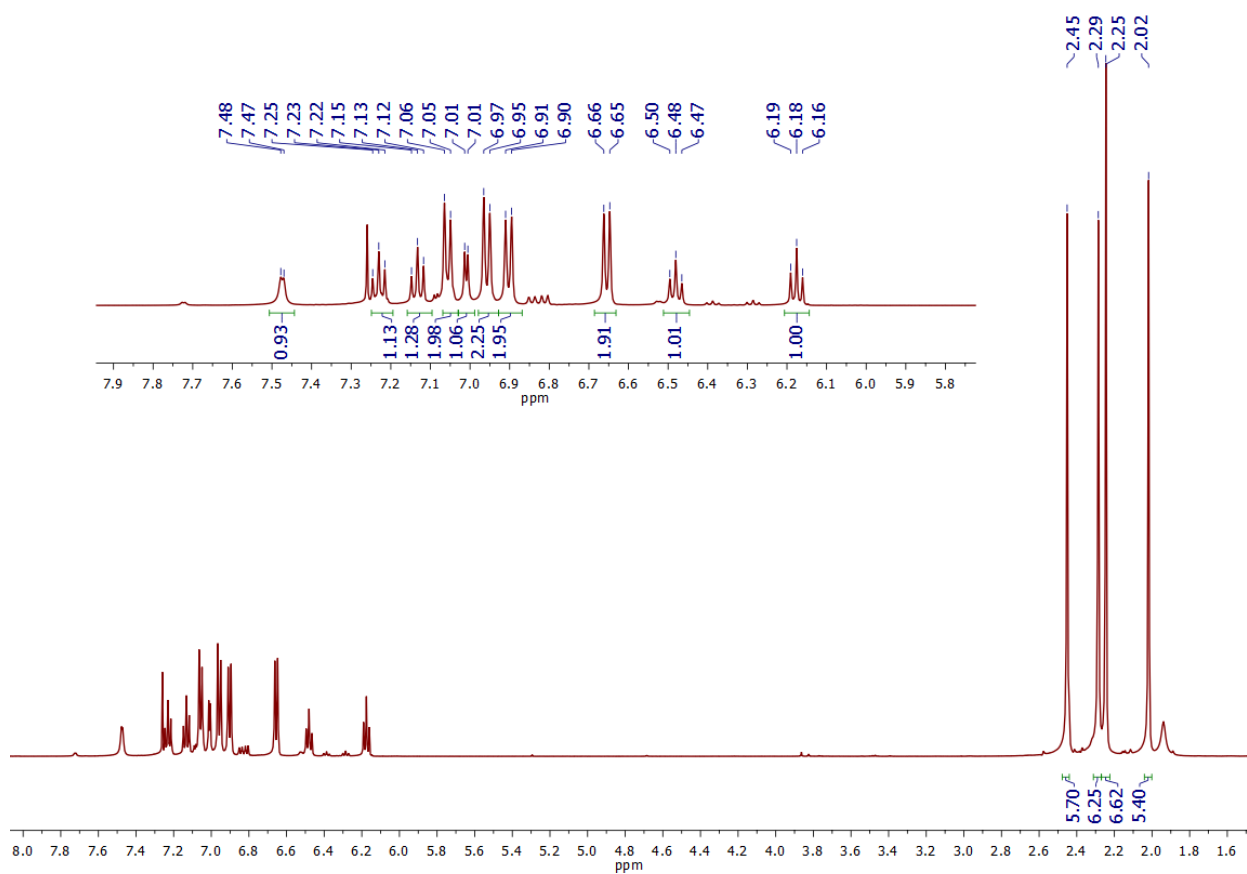


Figure S5. The ¹H NMR spectrum of **5a** with traces of **5b** in CDCl₃.

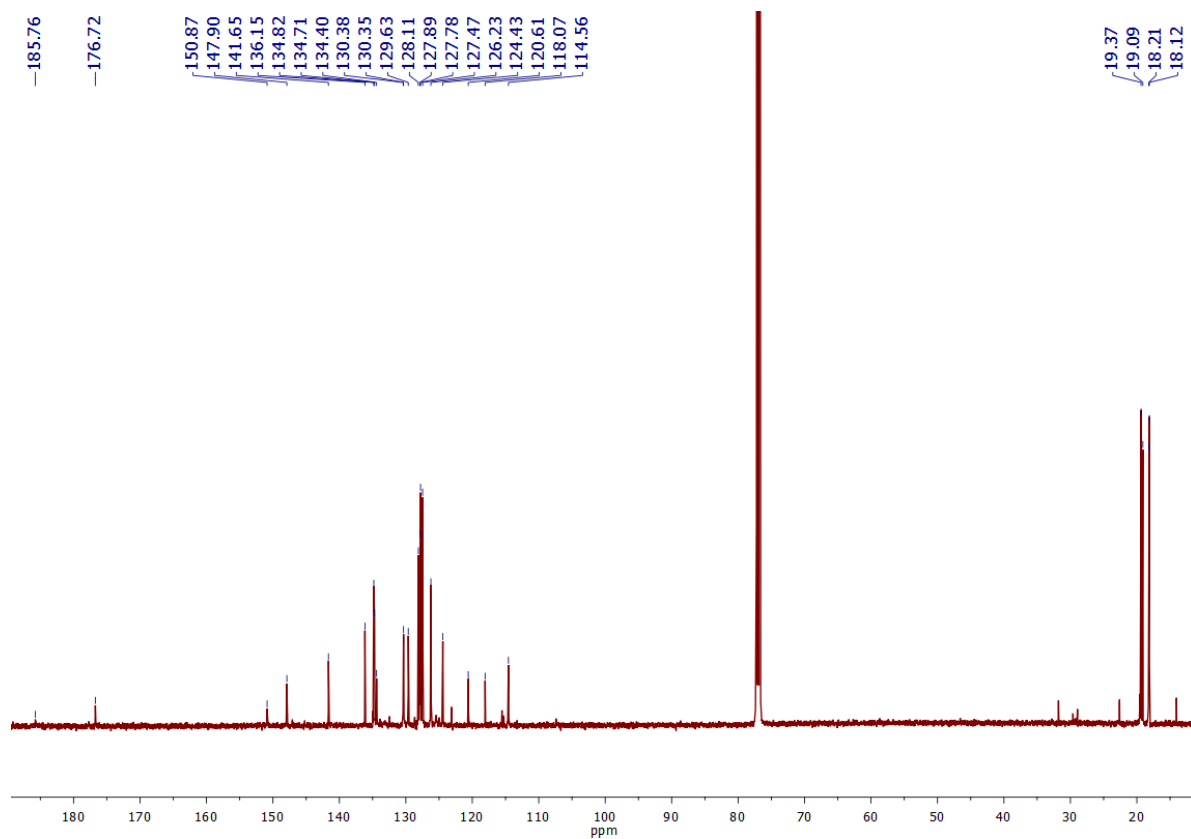


Figure S6. The ¹³C NMR spectrum of **5a** with traces of **5b** in CDCl₃.

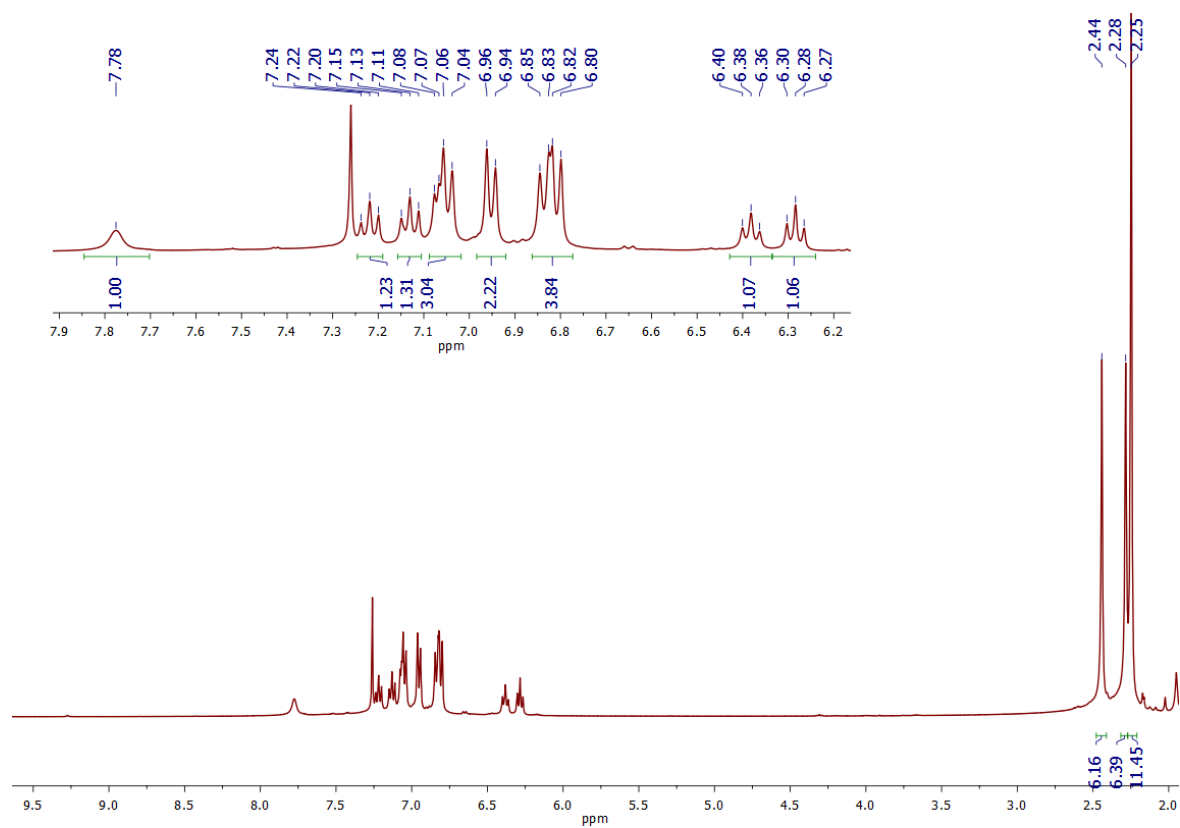


Figure S7. The ¹H NMR spectrum of **5b** with traces of **5a** in CDCl₃.

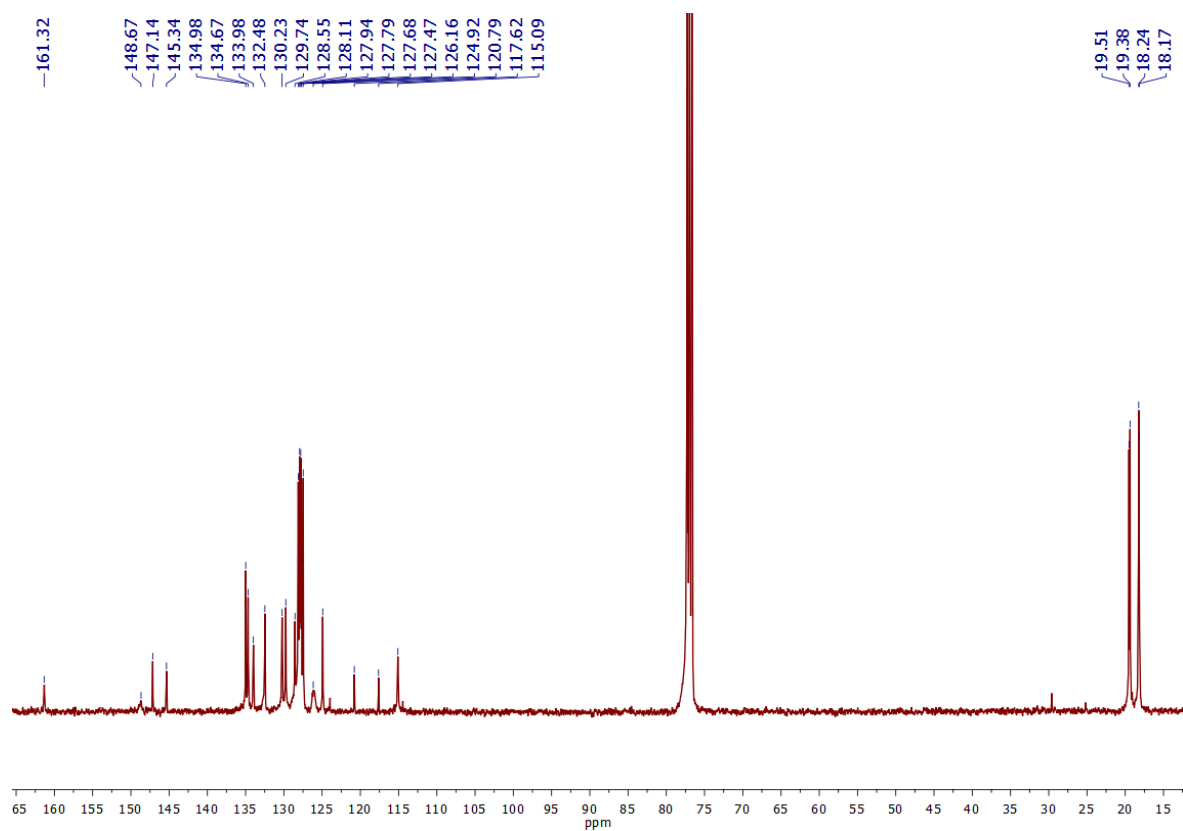


Figure S8. The ¹³C NMR spectrum of **5b** with traces of **5a** in CDCl₃.

Table S1. Crystal data and structure refinement for **4b**, **5b**

Identification code	4b	5b
Empirical formula	C ₄₀ H ₃₉ Br ₂ Cl ₃ N ₆ Pd ₂ S	C ₃₉ H ₃₈ I ₂ N ₆ Pd ₂ S
Formula weight	1114.80	1089.41
Temperature/K	100(2)	100.01(10)
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c
a/Å	8.15286(19)	16.6540(4)
b/Å	18.9330(4)	16.7752(3)
c/Å	28.0248(7)	15.3610(3)
α/°	90	90
β/°	95.618(2)	111.854(3)
γ/°	90	90
Volume/Å ³	4305.07(17)	3983.08(17)
Z	4	4
ρ _{calc} /cm ³	1.720	1.817
μ/mm ⁻¹	2.963	2.541
F(000)	2200.0	2112.0
Crystal size/mm ³	0.2 × 0.2 × 0.2	0.3 × 0.25 × 0.25
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.462 to 55	5.636 to 55
Index ranges	-10 ≤ h ≤ 10, -24 ≤ k ≤ 24, -36 ≤ l ≤ 36	-21 ≤ h ≤ 21, -21 ≤ k ≤ 21, -18 ≤ l ≤ 19
Reflections collected	57722	23322
Independent reflections	9898 [R _{int} = 0.0369, R _{sigma} = 0.0258]	9143 [R _{int} = 0.0284, R _{sigma} = 0.0369]
Data/restraints/parameters	9898/0/495	9143/0/459
Goodness-of-fit on F ²	1.072	1.064
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0264, wR ₂ = 0.0573	R ₁ = 0.0287, wR ₂ = 0.0629
Final R indexes [all data]	R ₁ = 0.0334, wR ₂ = 0.0600	R ₁ = 0.0373, wR ₂ = 0.0673
Largest diff. peak/hole / e Å ⁻³	0.71/-0.86	0.98/-1.48
CCDC number	2263952	2263951

Table S2. Cartesian atomic coordinates of optimized equilibrium model structures.

Atom	X	Y	Z
4a			
C	-3.046958	-2.768404	1.514888
C	-2.435341	-2.609449	0.257444
C	-3.011257	-3.153911	-0.905268
C	-4.211622	-3.852766	-0.788942
C	-4.827944	-4.024355	0.446401
C	-4.244952	-3.479084	1.585518
N	-1.174831	-2.020032	0.176124
C	-0.899109	-0.794988	0.063862
Pd	-2.018181	0.878278	-0.073994
Br	-3.409643	2.940133	-0.245902

C	-2.343696	-2.973194	-2.232975
C	-2.422586	-2.180269	2.741896
N	-0.082506	1.713247	-0.012011
C	0.367706	3.007558	0.016166
N	1.668665	3.259086	0.057601
C	1.969803	4.598769	0.095405
C	0.880486	5.396768	0.086455
S	-0.585036	4.455553	0.019150
Pd	2.814421	1.560722	0.036739
Br	4.948785	2.763496	0.079168
C	3.930293	-0.040249	-0.019680
N	4.779609	-0.837594	-0.065626
C	5.821391	-1.745568	-0.127797
C	6.387887	-2.185706	1.076713
C	7.421977	-3.113409	0.984022
C	7.865171	-3.568238	-0.253764
C	7.289421	-3.096500	-1.428951
C	6.249549	-2.171669	-1.393234
C	5.894478	-1.662089	2.386461
C	5.610624	-1.634008	-2.632205
C	0.907259	0.802972	0.006531
N	0.517639	-0.478857	0.026450
C	1.436033	-1.588196	0.056620
C	1.853985	-2.076564	1.298488
C	2.667375	-3.209915	1.307650
C	3.045816	-3.825363	0.119690
C	2.618532	-3.313252	-1.100558
C	1.799106	-2.185119	-1.154756
C	1.500666	-1.370581	2.570143
C	1.373848	-1.602955	-2.466612
C	-3.769725	-0.005984	-0.142588
N	-4.911888	-0.246465	-0.188038
C	-6.277950	-0.453032	-0.151737
C	-6.947738	-0.712589	-1.354406
C	-8.322524	-0.919094	-1.279737
C	-8.986151	-0.867764	-0.057943
C	-8.288361	-0.605577	1.117128
C	-6.912646	-0.394605	1.097749
C	-6.193608	-0.754743	-2.643730
C	-6.117090	-0.121973	2.333170
H	-4.660392	-4.276730	-1.688380
H	-5.761299	-4.579911	0.520940
H	-4.719796	-3.609942	2.559123
H	-2.321384	-1.915588	-2.537892
H	-2.870722	-3.530584	-3.017307
H	-1.299799	-3.318845	-2.210288
H	-1.391405	-2.536993	2.882601
H	-2.997002	-2.443541	3.638701
H	-2.372420	-1.081520	2.688523
H	3.013875	4.894218	0.125190
H	0.836435	6.479553	0.105410
H	7.883349	-3.479139	1.900529

H	8.674928	-4.293977	-0.303742
H	7.647849	-3.448254	-2.395660
H	5.973456	-0.566367	2.435995
H	6.468821	-2.082954	3.218980
H	4.833576	-1.909757	2.544678
H	6.076940	-2.054731	-3.529725
H	5.695404	-0.538777	-2.684108
H	4.536185	-1.870622	-2.662108
H	3.002370	-3.612436	2.264150
H	3.685879	-4.706566	0.144075
H	2.915182	-3.797143	-2.031770
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H	0.324970	-1.280291	-2.460216
H	1.503208	-2.330065	-3.277448
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H	-10.061658	-1.031865	-0.020983
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H	-5.440816	-1.557338	-2.636762
H	-5.652704	0.186118	-2.820495
H	-6.867888	-0.927252	-3.489565
H	-6.761961	-0.081847	3.217965
H	-5.573037	0.831372	2.259011
H	-5.359638	-0.905188	2.495629
5a			
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C	2.642117	2.390418	1.188548
C	3.179916	3.385278	0.351989
C	4.481453	3.822054	0.587018
C	5.227186	3.313825	1.645016
C	4.664099	2.362671	2.487240
N	1.329714	1.974757	0.937973
C	0.985254	0.848465	0.492716
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C	2.376199	3.917513	-0.792302
C	2.796831	0.832134	3.180544
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C	-0.452175	-2.834045	0.327716
N	-1.759677	-3.052612	0.302514
C	-2.090893	-4.366419	0.536706
C	-1.026629	-5.170094	0.754605
S	0.459713	-4.268035	0.648856
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I	-5.255045	-2.503165	-0.124417
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C	-7.213315	4.396416	-0.526381
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H	2.889425	4.755982	-1.279443
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H	5.827220	-0.181835	2.015348

4b

C	6.193056	-2.230152	-1.185775
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C	7.071636	-3.195324	1.307120
C	7.562062	-3.737918	0.123730
C	7.131508	-3.255635	-1.108160
N	4.734956	-0.740170	-0.017862
C	3.909392	0.082529	-0.023849
Pd	2.801735	1.685918	-0.013809
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C	5.588510	-1.553105	2.534697
C	5.710420	-1.679852	-2.488368
C	0.939288	0.835984	-0.029840
N	-0.075653	1.804963	-0.026799
C	0.330648	3.120229	-0.009177
S	-0.665514	4.530430	0.002360
C	0.786454	5.504056	0.024173
C	1.892174	4.728602	0.021064
N	1.621074	3.378542	0.001980
N	0.511337	-0.381426	-0.038244
C	1.386106	-1.503597	-0.034063
C	1.770753	-2.065394	-1.257760
C	2.585312	-3.196995	-1.229893
C	2.992496	-3.754995	-0.023044
C	2.577421	-3.191118	1.178401
C	1.761571	-2.060423	1.195051
C	1.330923	-1.455814	-2.550255
C	1.309438	-1.447293	2.481705
Pd	-1.571527	-0.621840	-0.040329
Br	-1.579601	-3.106583	-0.046765
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C	-4.370213	2.247681	-1.243477
C	-5.764482	2.241947	-1.213379
C	-6.457262	2.231712	-0.006973
C	-5.752622	2.216785	1.192583
C	-4.358041	2.219464	1.208431
C	-3.618685	2.239262	-2.538423
C	-3.591498	2.174635	2.493575

C	-3.528483	-0.800139	-0.031121
N	-4.640503	-1.155963	-0.012949
C	-5.942085	-1.619275	0.036284
C	-6.535393	-1.782935	1.296469
C	-7.842231	-2.262392	1.321475
C	-8.517163	-2.554748	0.140685
C	-7.899076	-2.371714	-1.092275
C	-6.592813	-1.897390	-1.173659
C	-5.781278	-1.435808	2.539517
C	-5.896134	-1.676825	-2.477328
H	7.423277	-3.567223	2.268768
H	8.295321	-4.541531	0.162435
H	7.528947	-3.674515	-2.031923
H	5.779726	-0.470661	2.566022
H	6.040551	-2.004829	3.424450
H	4.497937	-1.681925	2.600662
H	4.623824	-1.812714	-2.599773
H	6.204371	-2.175882	-3.331071
H	5.904400	-0.600371	-2.564813
H	0.724287	6.586101	0.037905
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H	2.896446	-3.646227	-2.173996
H	3.638918	-4.632544	-0.018756
H	2.882904	-3.635542	2.126606
H	1.770397	-0.457710	-2.701736
H	0.238435	-1.328957	-2.580877
H	1.625726	-2.082752	-3.400578
H	0.216645	-1.320064	2.501024
H	1.747232	-0.448769	2.635127
H	1.595216	-2.072395	3.336453
H	-6.310030	2.251624	-2.158064
H	-7.545998	2.231463	-0.001515
H	-6.288631	2.206445	2.142905
H	-2.861260	3.035354	-2.575661
H	-4.299602	2.373185	-3.387694
H	-3.080869	1.290594	-2.687795
H	-3.036865	1.229258	2.599626
H	-4.262805	2.267572	3.356015
H	-2.844714	2.979818	2.551090
H	-8.331921	-2.404076	2.284444
H	-9.538736	-2.928428	0.181455
H	-8.434693	-2.599707	-2.013251
H	-4.837353	-1.995699	2.611427
H	-6.375840	-1.655106	3.433164
H	-5.518566	-0.365889	2.555283
H	-5.616039	-0.619625	-2.601772
H	-6.537082	-1.960314	-3.319461
H	-4.966503	-2.260442	-2.544177
<hr/>			
5b			
C	5.891534	-2.480243	-1.255643
C	5.469044	-2.021440	0.000483
C	5.923344	-2.548901	1.217061

C	6.816199	-3.614764	1.147114
C	7.238230	-4.113484	-0.081092
C	6.784302	-3.548126	-1.268334
N	4.551848	-0.986929	0.036872
C	3.786471	-0.107402	0.038499
Pd	2.767485	1.556550	0.036049
I	5.201570	2.762912	-0.074715
C	5.456429	-1.979393	2.517170
C	5.395941	-1.837269	-2.509819
C	0.865148	0.786689	0.059775
N	-0.104434	1.798049	0.058822
C	0.356282	3.096461	0.055666
S	-0.589414	4.540914	0.063153
C	0.895175	5.461554	0.058909
C	1.972397	4.647230	0.049619
N	1.656420	3.305525	0.047119
N	0.388617	-0.411308	0.054673
C	1.209634	-1.574705	0.034128
C	1.556044	-2.129700	-1.205152
C	2.288143	-3.316647	-1.207004
C	2.652756	-3.933656	-0.015604
C	2.287422	-3.367303	1.200702
C	1.557793	-2.179560	1.248878
C	1.158898	-1.461263	-2.482881
C	1.165021	-1.560826	2.552364
Pd	-1.708135	-0.568320	0.032474
I	-1.937775	-3.324312	0.016553
C	-1.496638	1.451781	0.043238
N	-2.290681	2.433483	0.035508
C	-3.688647	2.370213	0.017103
C	-4.357848	2.390274	-1.218177
C	-5.751957	2.363291	-1.212086
C	-6.465043	2.334543	-0.018668
C	-5.782786	2.344882	1.192946
C	-4.389235	2.369262	1.234537
C	-3.584131	2.396623	-2.500153
C	-3.649453	2.350011	2.535966
C	-3.677330	-0.617711	0.000368
N	-4.827631	-0.815472	-0.025552
C	-6.192550	-1.033134	-0.052753
C	-6.868451	-1.136777	1.170936
C	-8.251733	-1.285521	1.117371
C	-8.917185	-1.339167	-0.103341
C	-8.208617	-1.268630	-1.298583
C	-6.824368	-1.118935	-1.301314
C	-6.116924	-1.079777	2.460969
C	-6.028672	-1.044716	-2.563581
H	7.186270	-4.051216	2.074066
H	7.935465	-4.948778	-0.113277
H	7.130475	-3.932521	-2.227009
H	5.707297	-0.912045	2.600892
H	5.916046	-2.503915	3.361981

H	4.363627	-2.054810	2.619140
H	4.300918	-1.905588	-2.591482
H	5.834306	-2.313872	-3.393398
H	5.648681	-0.767344	-2.538524
H	0.872056	6.545271	0.060847
H	3.019072	4.934118	0.042954
H	2.566468	-3.763295	-2.162281
H	3.230954	-4.856946	-0.034802
H	2.562797	-3.855229	2.136447
H	1.649186	-0.482583	-2.602145
H	0.074269	-1.275421	-2.520466
H	1.427273	-2.078941	-3.348422
H	0.079929	-1.381814	2.603514
H	1.650721	-0.584321	2.702771
H	1.442318	-2.207204	3.393722
H	-6.282212	2.362706	-2.165816
H	-7.553877	2.293522	-0.033236
H	-6.337207	2.331319	2.132689
H	-2.827991	3.194700	-2.515424
H	-4.249622	2.539703	-3.360227
H	-3.040084	1.451353	-2.650870
H	-3.117300	1.397889	2.686318
H	-4.336699	2.484693	3.380087
H	-2.888386	3.142030	2.583575
H	-8.808237	-1.362226	2.050864
H	-9.999654	-1.451941	-0.123831
H	-8.731628	-1.333521	-2.252135
H	-5.334704	-1.851582	2.503057
H	-6.789400	-1.227283	3.313002
H	-5.612240	-0.109941	2.587100
H	-5.519388	-0.074023	-2.659238
H	-6.671179	-1.179450	-3.440546
H	-5.245702	-1.816507	-2.589598
