Switchable Cyclopalladation of Substrates Containing Two Directing Groups: on the Way to Non-symmetrical [2.2]-Dipalladaparacyclophanes

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Supporting Information

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Experimental and computational details

Materials and methods

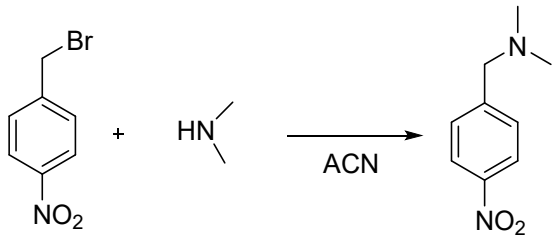
All the chemicals and solvents were purchased from Acros Organics, Sigma-Aldrich or Fluorochem and used as received. Palladium(II) acetate (recrystallized) was purchased from Sigma-Aldrich. High resolution mass spectra were recorded on a MALDI LTQ Orbitrap XL equipped with nitrogen UV laser (337 nm, 60 Hz, 8-20 μJ) in positive ion mode. The NMR spectra were recorded on a Bruker Avance III 400 MHz or on a Bruker Ascend 500 MHz instruments. Chemical shifts δ are referenced to TMS (δ = 0 ppm) or solvent residual peaks $\delta(CD_2Cl_2)$ = 5.35 ppm (^{1}H); δ(CD*3*CN) = 1.94 ppm (^{1}H)/1.3 ppm (^{13}C). FT-IR spectra were measured on Nicolet (Thermo Scientific) iS50 spectrophotometer using ATR (diamond) technique.

DFT calculations

All calculations were performed using the B3LYP density functional theory method as implemented in Gaussian16[1] with the D3 dispersion term using the Becke-Johnson damping function.[2] The basis set was a combination of the SDD pseudopotential model for palladium[3] and 6-311++G** for all other atoms. The final energies include solvation free energies in CH_2Cl_2 determined by single-point calculation for the optimized structures using the SMD model.[4] Graphics were processed using software CYLview.[5]

Synthesis and characterization of the compounds

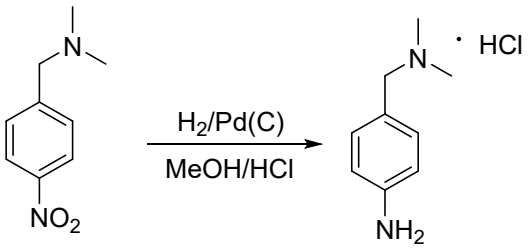
N, *N*-dimethyl-1-(4-nitrofenyl)methanamine



To the solution of 10,8 g (0,05 mol) 4-nitrobenzylbromide dissolved in 50 ml of acetonitrile in 250 ml reaction flask was added 50 ml of dimethylamine (50 % water solution). Reaction

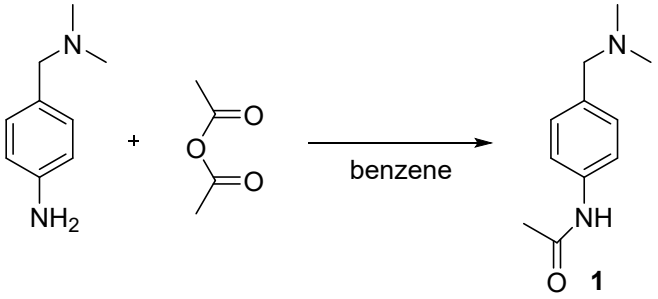
mixture was stirred for additional 1 hour at room temperature. Furthermore, 100 ml of water was added and formed solution was extracted by 2x150 ml of dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated to dryness giving (8,7 g, 96 %) of *N*,*N*-dimethyl-4-nitrobenzylamine, which was used in the next step of synthesis without further purification.

4-[(Dimethylamino)methyl]aniline hydrochloride[6]



To 250 ml reaction flask was added 8,7 g (0,048 mol) *N*,*N*-dimethyl-4-nitrobenzylamine, 100 ml of methanol and 12 ml of HCl (37 %). After dissolution of starting material the 0,5 g Pd–C (5 %) was added and the mixture was hydrogenated using a balloon filled with hydrogen for 24 h. The reaction mixture was filtered and residual solvent evaporated to dryness. The residue was triturated by 30 ml of methanol, filtered and washed by cold methanol 5 ml) giving 6,01 g (67 %) of yellowish solid.

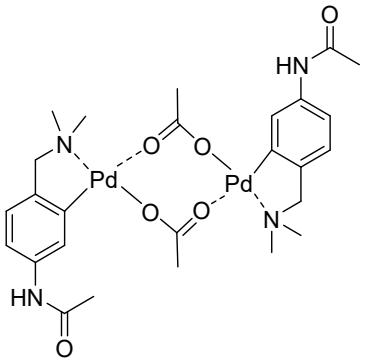
***N*-(4-((dimethylamino)methyl)phenyl) acetamide**[7] **1**



To 6,01 g (0,04 mol) of 4-[(dimethylamino)methyl]aniline hydrochloride was added 30 ml of saturated solution of NaOH. The solution was extracted by 2x100 ml of dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was dissolved in benzene (20 ml) followed by addition of acetanhydride (6 ml). After 15 minutes of stirring, the reaction mixture was alkalized by 10 ml of saturated NaOH and extracted 2 x 100 ml of chloroform. The organic phase was dried over Na_2SO_4 and evaporated to dryness. The crude product was recrystallized (benzene:petrolether; 1:1) giving 5,3 g (69 %) of white crystals.

^{1}H NMR (500 MHz, $CDCl_3$): 8,00 (s; 1H); 7,45 (d; J = 8.3 Hz; 2H); 7,22 (d; J = 8,3 Hz; 2H); 3,36 (s; 2H); 2,21 (s; 6H); 2,13 (s; 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): 168,6; 136,9; 134,7; 129,5; 119,9; 63,7; 45,2; 24,3.

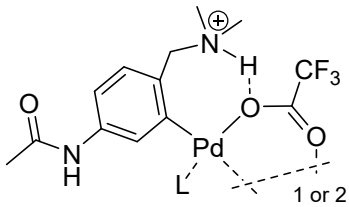
Complex 2



N-(4-((Dimethylamino)methyl)phenyl)acetamide **1** (20 mg; 0.1 mmol) and $Pd(OAc)_2$ (23.3 mg, 0.1 mmol) were dissolved in DCM (1 ml) and stirred for 24 hours at room temperature. The product was precipitated by addition of hexane (1 ml), filtered and washed by hexane yielding 24.3 mg (68 %) of yellow-green crystals with m. p. 196-197 °C.

^{1}H NMR (500 MHz, CD_3CN): δ 8.16 (s; 1H); 7.33 (dd; J = 8.2; 1.8 Hz; 1H); 6.84 (d; J = 1.8 Hz; 1H); 6.81 (d; J = 7.8 Hz; 1H); 3.54 (d; J = 13.4 Hz; 1H); 3.19 (d; J = 14.1 Hz; 1H); 2.71 (s; 3H); 2.03 (s; 3H); 2.00 (s; 3H); 1.98 (s; 3H). **^{13}C{1H} NMR** (125 MHz, CD_3CN): δ 181.2; 169.2; 145.1; 144.0; 135.8; 123.4; 122.2; 116.6; 72.6; 52.7; 51.7; 24.7; 24.3. **FT-IR** (ATR, diamond): $\tilde{\nu}$ (cm^{-1}) 3455, 3293, 3090, 2922, 2841, 1663, 1538, 1387, 1308, 1256, 1040, 854

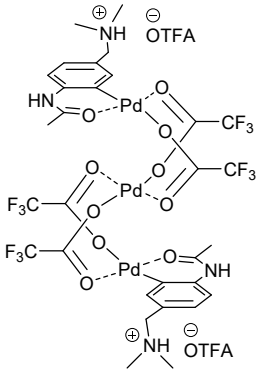
Complex 2a-TFA



Trifluoroacetic acid (5 equiv.) was added to the solution of **2** in dichloromethane or acetonitrile. Evaporation to dryness gave **2a-TFA** in quantitative manner. M.p.128-130 °C decomp

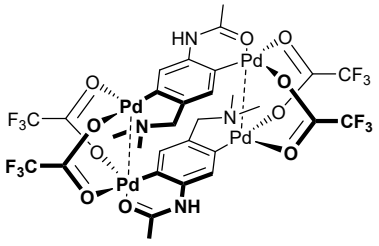
^{1}H NMR (500 MHz, CD_3CN): δ 8.31 (s; 1H); 7.28 (dd; J = 8.1; 1.7 Hz; 1H); 7.13 (s; 1H); 6.90 (d; J = 8.1 Hz; 1H); 3.94 (s; 2H); 2.75 (s; 6H); 2.03 (s; 3H). **^{13}C{1H} NMR** (125 MHz, CD_3CN): δ 169.5; 160.56 (q, J = 36 Hz); 144.3; 143.6; 136.6; 124.7; 123.1; 117.7; 117.2 (q, J = 290 Hz); 73.4; 52.9; 24.3 **FT-IR** (ATR, diamond): $\tilde{\nu}$ (cm^{-1}) 3291, 1778, 1669, 1583, 1200, 1150, 854, 731. **Anal. Found:** C, 35.87; H, 3.50; N, 5.75.

Complex 4



Trifluoroacetic acid (40 µl, 0.5 mmol) was added to the solution of *N*-(4-((dimethylamino)methyl)phenyl)acetamide **1** (20 mg; 0.1 mmol) in DCM (1 ml). After 15 minutes of stirring the $Pd(OAc)_2$ (23.3 mg, 0.1 mmol) was added. The brownish oil was formed within 15 minutes. Trituration and washing by hexane followed by diethylether gave 35.6 mg (50 %) of yellow-brown solid with m. p. 192–193 °C.
FT-IR (ATR, diamond): $\tilde{\nu}$ (cm^{-1}) 3288, 3198, 3132, 3068, 2767, 1670, 1542, 1420, 1193, 983, 809 **Anal. Calcd for** $C_{34}H_{32}F_{18}N_4O_{14}Pd_3$: C, 29.55; H, 2.33; N, 4.05. Found: C, 30.40; H, 2.51; N, 4.15.

Complex 5



N-(4-((Dimethylamino)methyl)phenyl)acetamide **1** (20 mg; 0.1 mmol) and $Pd(OAc)_2$ (23.3 mg, 0.1 mmol) were dissolved in DCM (1 ml) and stirred for 1 hour at room temperature. Next, TFA (40 µl; 0.5 mmol) and $Pd(OAc)_2$ (23.3 mg, 0.1 mmol) were added to the reaction mixture and stirred for further 24 hours. The precipitated product

was filtered and washed by DCM yielding 45 mg (70 %) of yellow crystals with m. p. 261–262 °C.

^{1}H NMR (400 MHz, CD_3CN): δ11.82 (s, 2H); 6.77 (s; 2H); 6.73 (s; 2H); 3.90 (s; 4H); 2.71 (s; 12H); 2.24 (s,6H). **^{13}C{1H} NMR** (125 MHz, CD_3CN): *δ* 166.9; 161.3 (q, J = 31.2 Hz); 144.7; 140.2; 130.6; 128.8; 122.5; 118.1 (q, J = 294 Hz); 114.8; 73.2; 52.5; 21.0 **FT-IR** (ATR, diamond): ṽ (cm^{-1}) 3291, 3164, 1677, 1516, 1445, 1225, 1187, 1142, 990, 861, 786. **Anal. Calcd for** $C_{30}H_{28}F_{12}N_4O_{10}Pd_4$: C, 28.64; H, 2.24; N, 4.45. Found: C, 28.28; H, 2.43; N, 4.09.

Experimental data

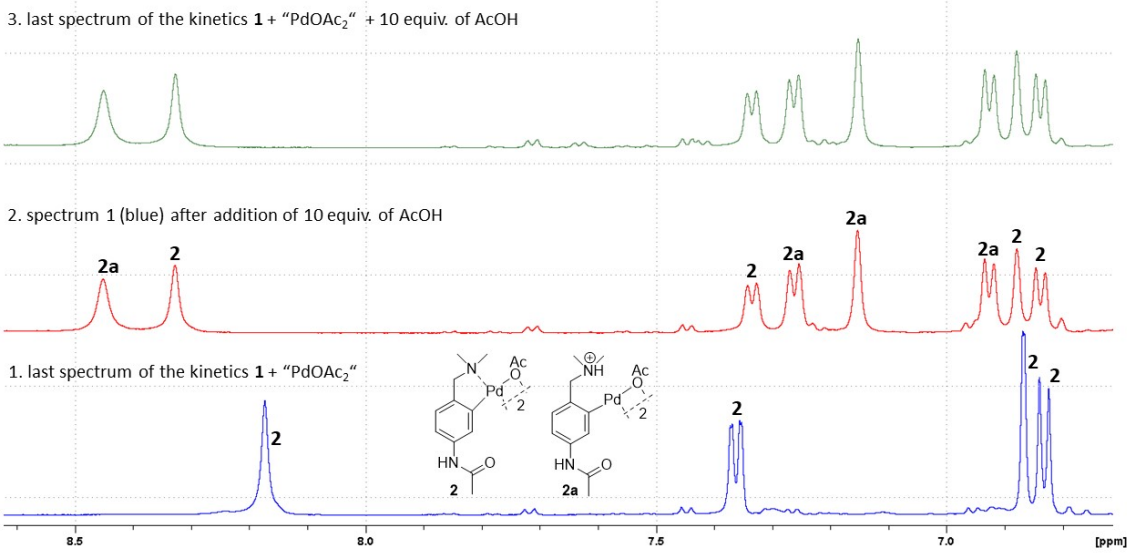


Figure S1. The comparison of aromatic regions of ^{1}H NMR spectra measured in CD_3CN illustrating influence of additional acetic acid to compound **2**.

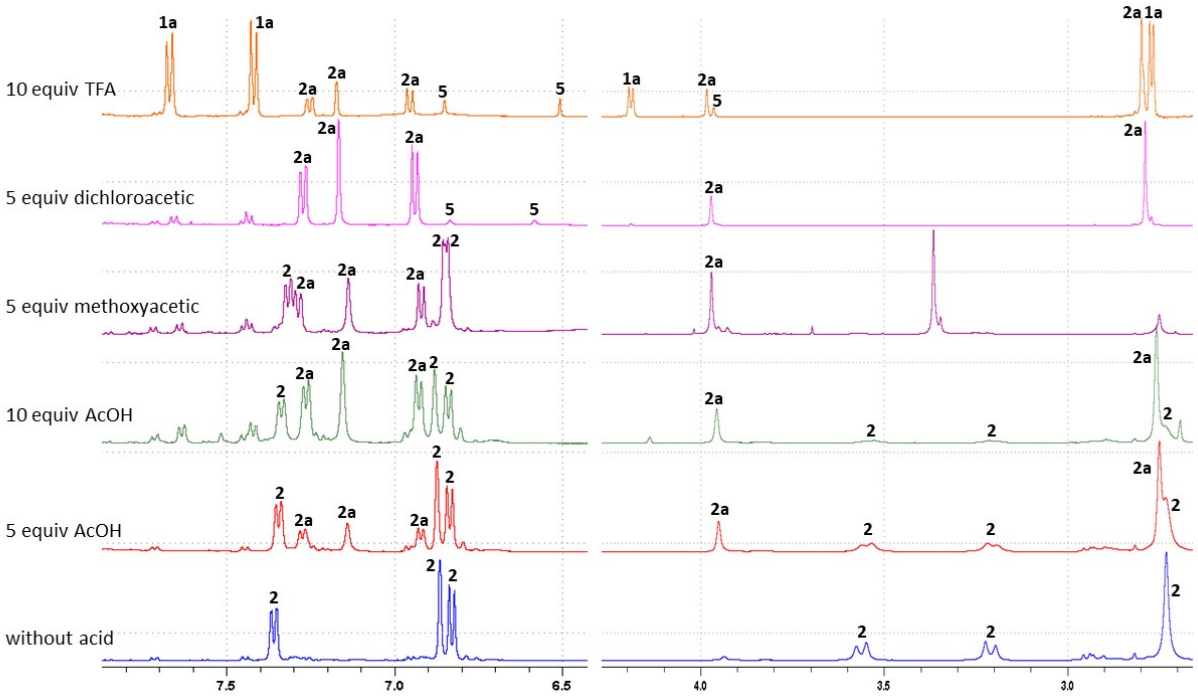


Figure S2. Comparison of aromatic region of the last spectra of the time-conversion experiments in acetonitrile showing distribution of complexes **2**, **2a** and **5** in dependence of amount and nature of additional acetic acids.

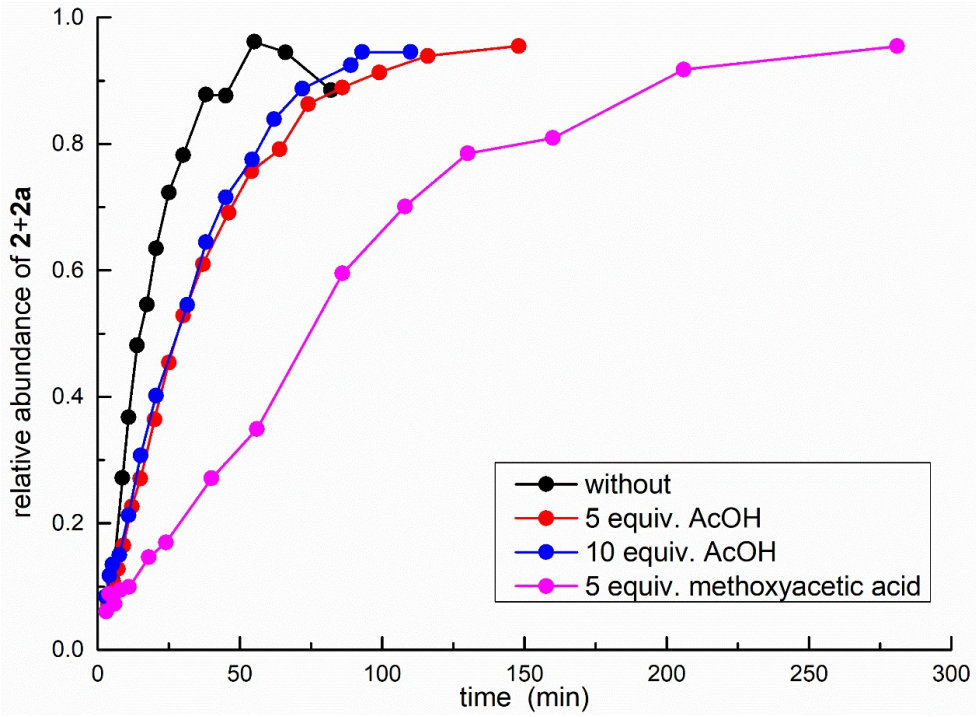


Figure S3. ^{1}H NMR time-conversion traces for C–H activation of **1** with palladium(II)acetate in presence of various amount and nature of acetic acids in CD_3CN.

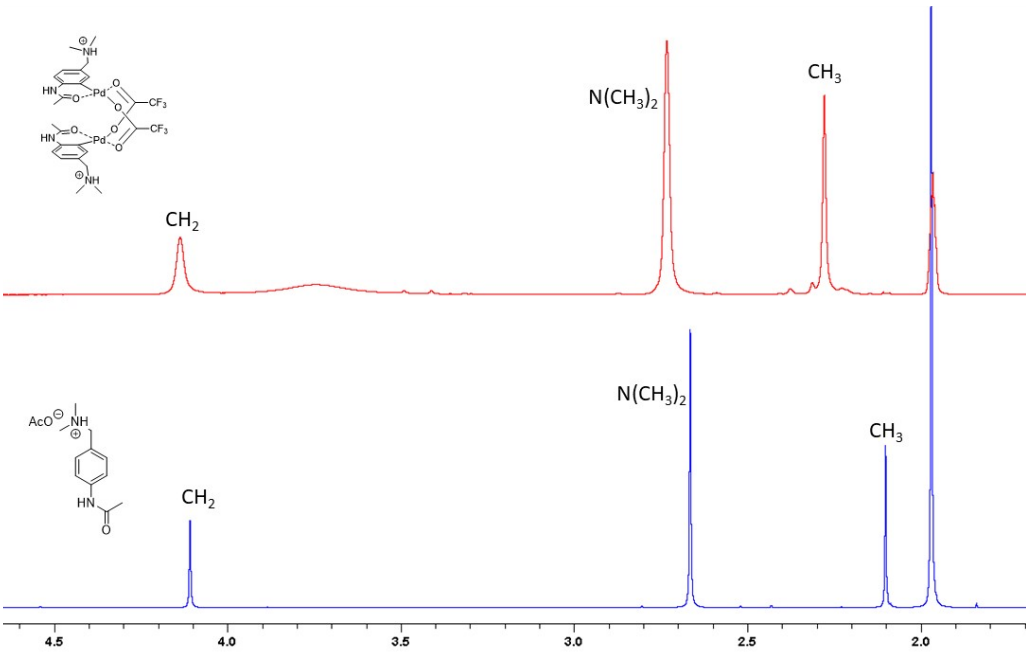


Figure S4. Comparison of ^{1}H NMR spectra of protonated **1** and complex **4** measured immediately after its dissolution in CD_3CN.

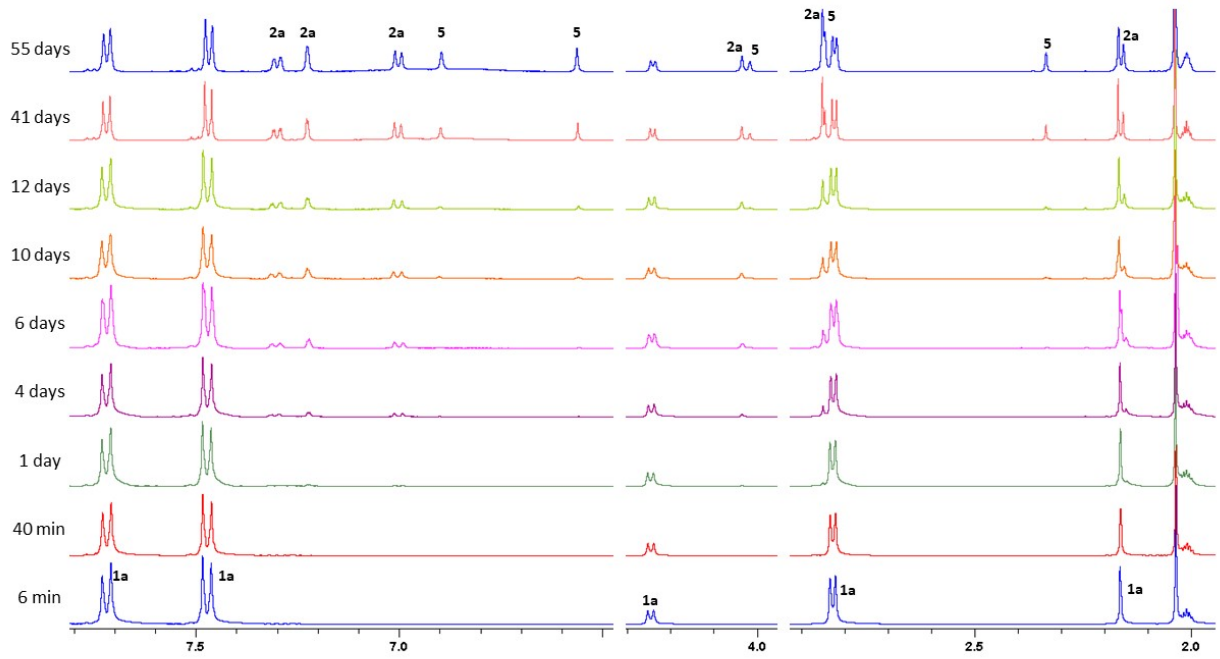


Figure S5. The ^{1}H NMR spectral changes for the reaction of **1** with "$Pd(OAc)_2$" in the presence of 5 equivalents of TFA in acetonitrile.

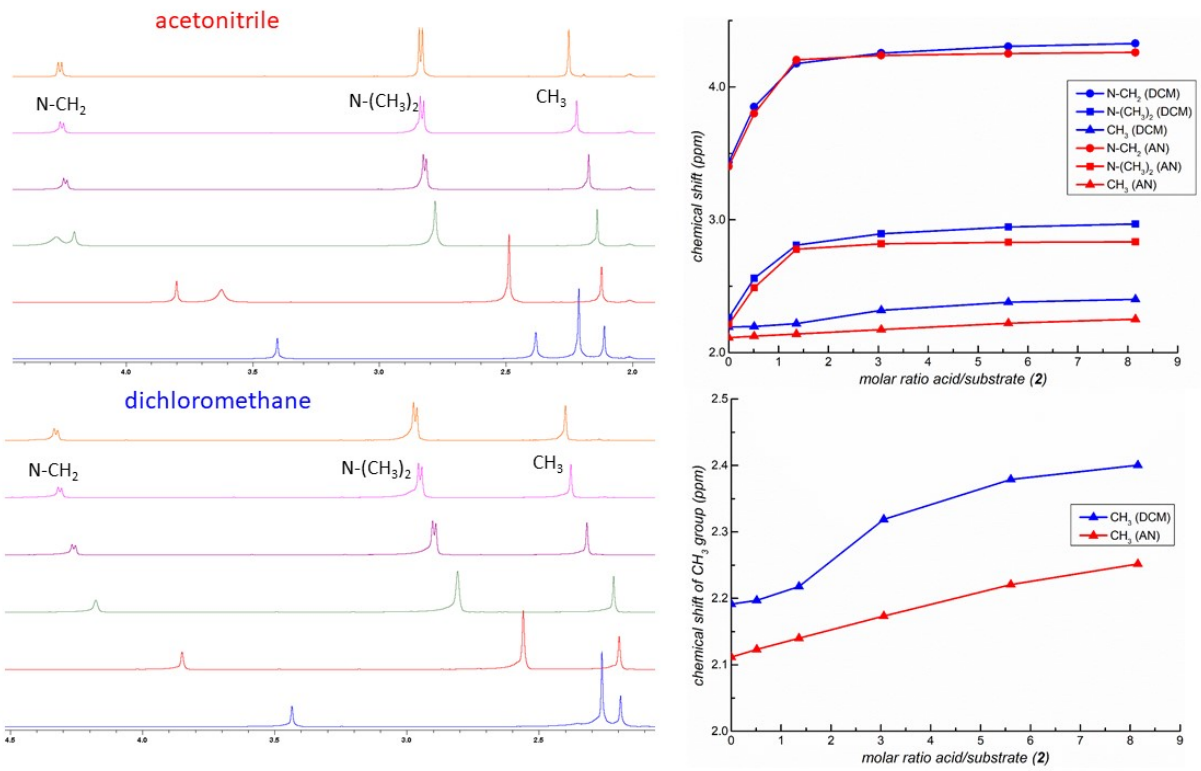


Figure S6. The ^{1}H NMR titration of **1** with TFA in CD_3CN and CD_2Cl_2.

Crystallography

The X-ray data for colorless crystals of **2** and **5**·3Et_2O were obtained at 150K using Oxford Cryostream low-temperature device with a Bruker D8-Venture diffractometer equipped with Mo (Mo/K_α radiation; λ = 0.71073 Å) microfocus X-ray (IμS) source, Photon CMOS detector and Oxford Cryosystems cooling device was used for data collection. Obtained data were treated by XT-version 2014/5 and SHELXL-2017/1 software implemented in APEX3 v2016.9-0 (Bruker AXS) system.[8] $R_{int} = \sum | F_o^2 - F_{o,mean}^2 | / \sum F_o^2$, $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$ for all data, $R(F) = \sum | |F_o| - |F_c| | / \sum |F_o|$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$ for all data. Crystallographic data for all structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 2241934-2241935. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

The frames for all complexes were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The structures were solved and refined using the Bruker SHELXTL Software Package.

Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, most of the hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors Hiso(H) = 1.2 Ueq (pivot atom) or of 1.5Ueq (methyl). H atoms in methyl, methylene moieties and C-H in aromatic rings were placed with C-H distances of 0.96, 0.97 and 0.93 Å. Hydrogen atoms in N-H bonds were refined freely. In **5**, the disordered trifluormethyl groups were split into two positions and treated with ISOR and DFIX instructions.

Table S1: Experimental details for **2**

Crystal data	
Chemical formula	$C_{26}H_{36}N_4O_6Pd_2$
M_r	713.39
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	150
a, *b*, *c* (Å)	18.3312 (13), 11.1332 (7), 15.7306 (12)
β (°)	111.275 (2)
V (Å^3)	2991.6 (4)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	1.25
Crystal size (mm)	0.39 × 0.28 × 0.08
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.458, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	38675, 3447, 2854
R_{int}	0.070
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.057, 1.08
No. of reflections	3447
No. of parameters	180
No. of restraints	150
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.72, −0.64

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.5-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2016*/6 (Sheldrick, 2016), *PLATON* (Spek, 2009).

Table S2: Hydrogen-bond geometry (Å, º) for **2**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O2^{i}	0.79 (3)	2.17 (3)	2.940 (3)	166 (3)

Symmetry code: (i) −*x*+1/2, *y*−1/2, −*z*+3/2.

Table S3: Experimental details for **5**

Crystal data

Chemical formula	$C_{30}H_{28}F_{12}N_4O_{10}Pd_4 \cdot 3(C_4H_{10}O)$
M_r	1480.52
Crystal system, space group	Trigonal, *R*-3:*H*
Temperature (K)	150
a, *c* (Å)	22.9077 (10), 23.8452 (12)
V (Å^3)	10836.6 (11)
Z	9
Radiation type	Mo *K*α
μ (mm^{-1})	1.58
Crystal size (mm)	0.41 × 0.16 × 0.14
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.640, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	47233, 4987, 3833
R_{int}	0.076
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.627
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.121, 1.11
No. of reflections	4987
No. of parameters	274
No. of restraints	339
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 81.8462P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.47, −1.06

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.5-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2019*/1 (Sheldrick, 2019), *PLATON* (Spek, 2009).

Table S4: Hydrogen-bond geometry (Å, º) for **5**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.92 (1)	2.02 (1)	2.932 (5)	173 (6)
N1—H1···F3^{A}b^{i}	0.92 (1)	2.91 (5)	3.418 (11)	116 (4)

Symmetry code: (i) $y-1/3$, $-x+y+1/3$, $-z+4/3$.

Spectra

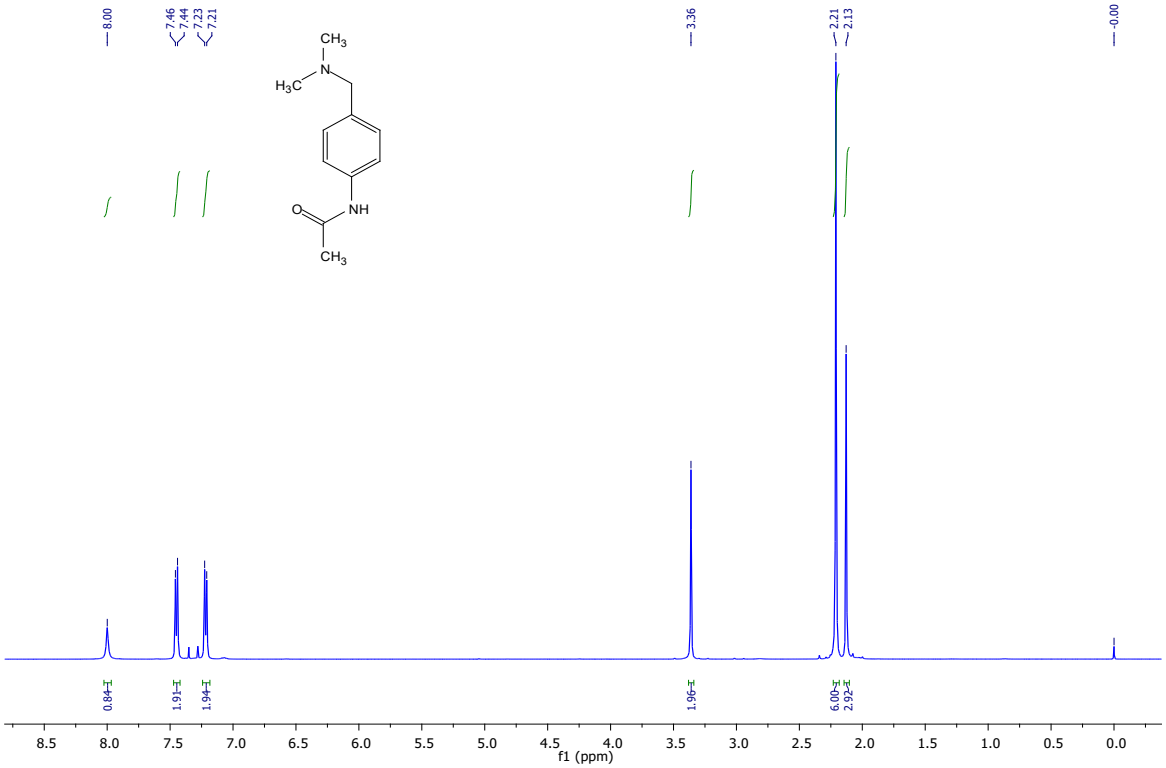


Figure S7. ^{1}H NMR ($CDCl_3$) of compound **1**.

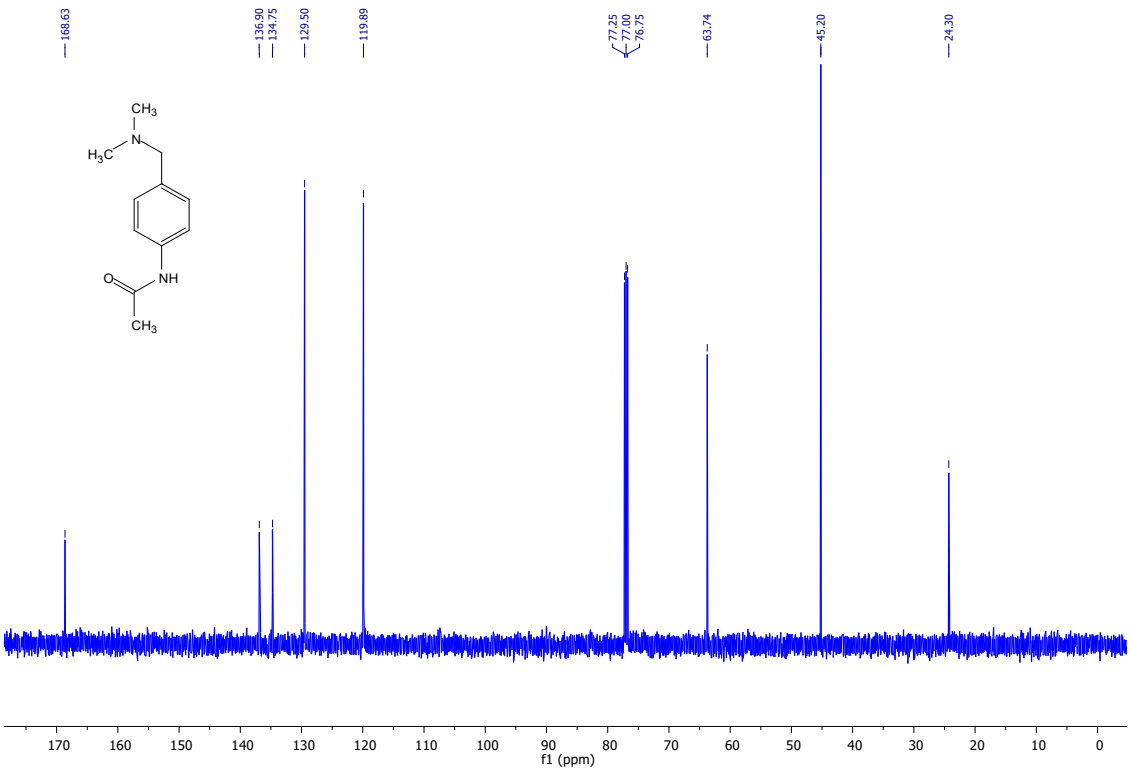


Figure S8. ^{13}C NMR ($CDCl_3$) of compound **1**.

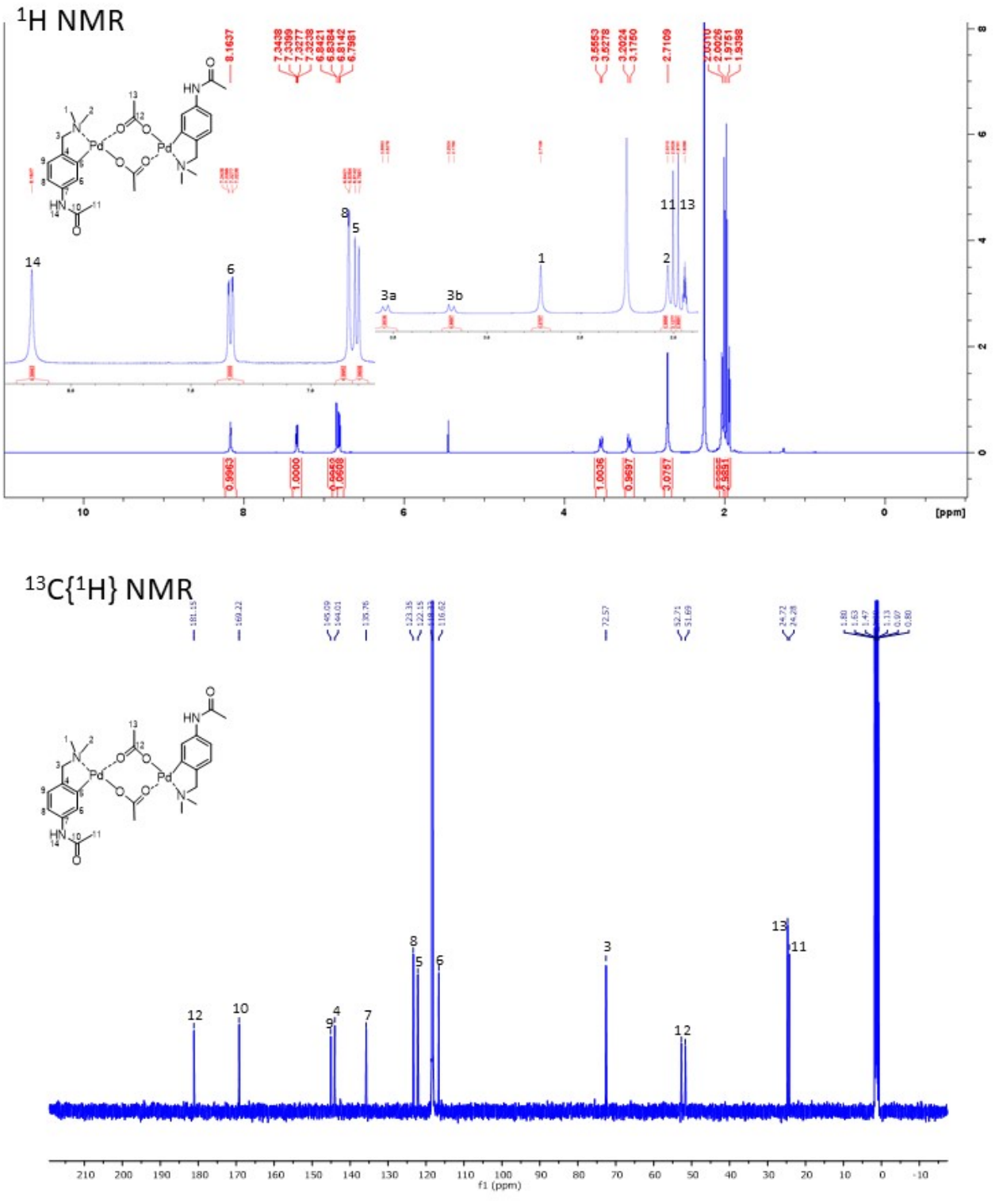


Figure S9. ^{1}H and ^{13}C NMR spectra (CD_3CN) of compound **2** with signal assignment..

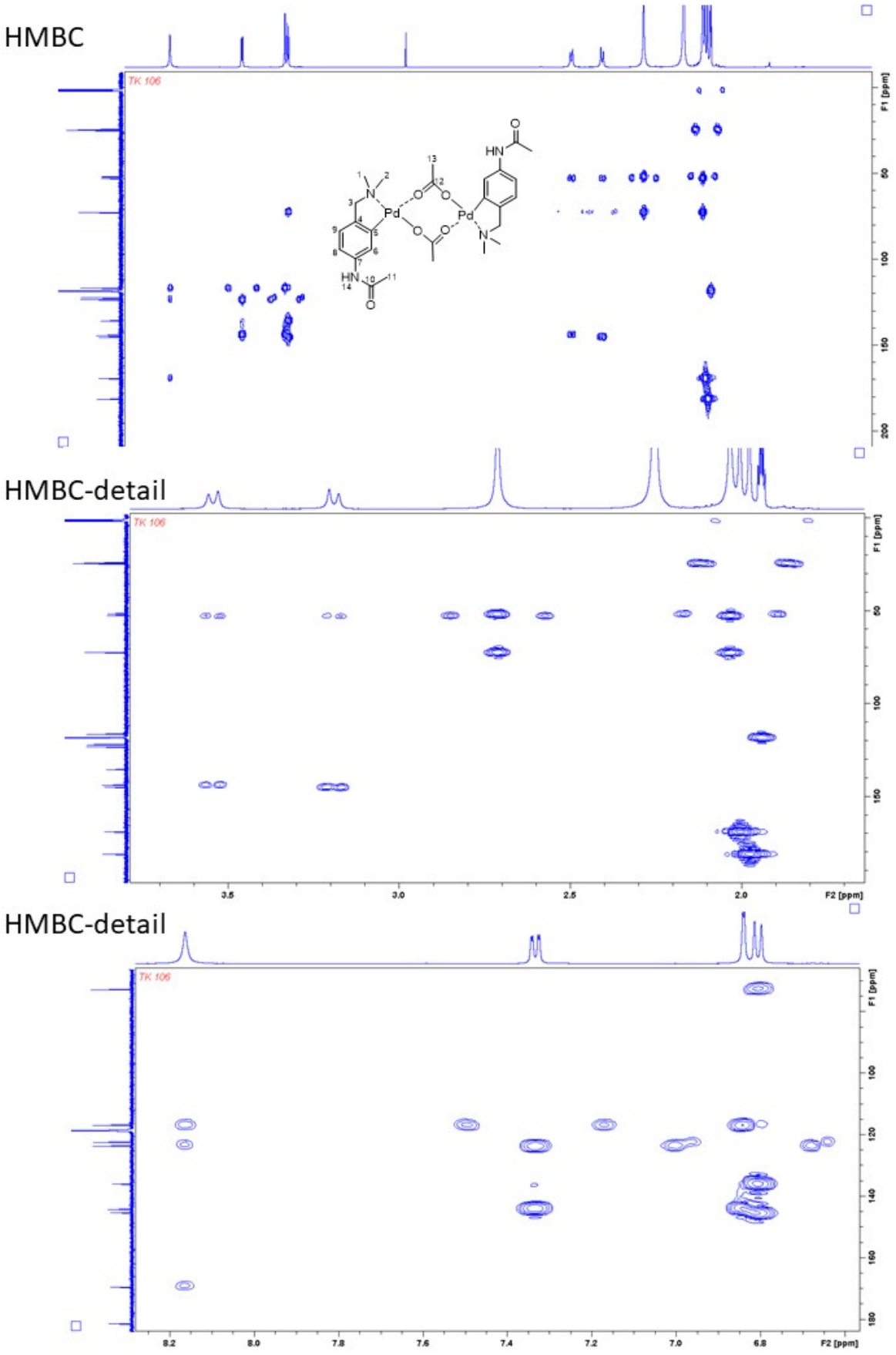


Figure S10. ^{1}H- ^{13}C HMBC NMR spectra (CD_3CN) of compound **2**.

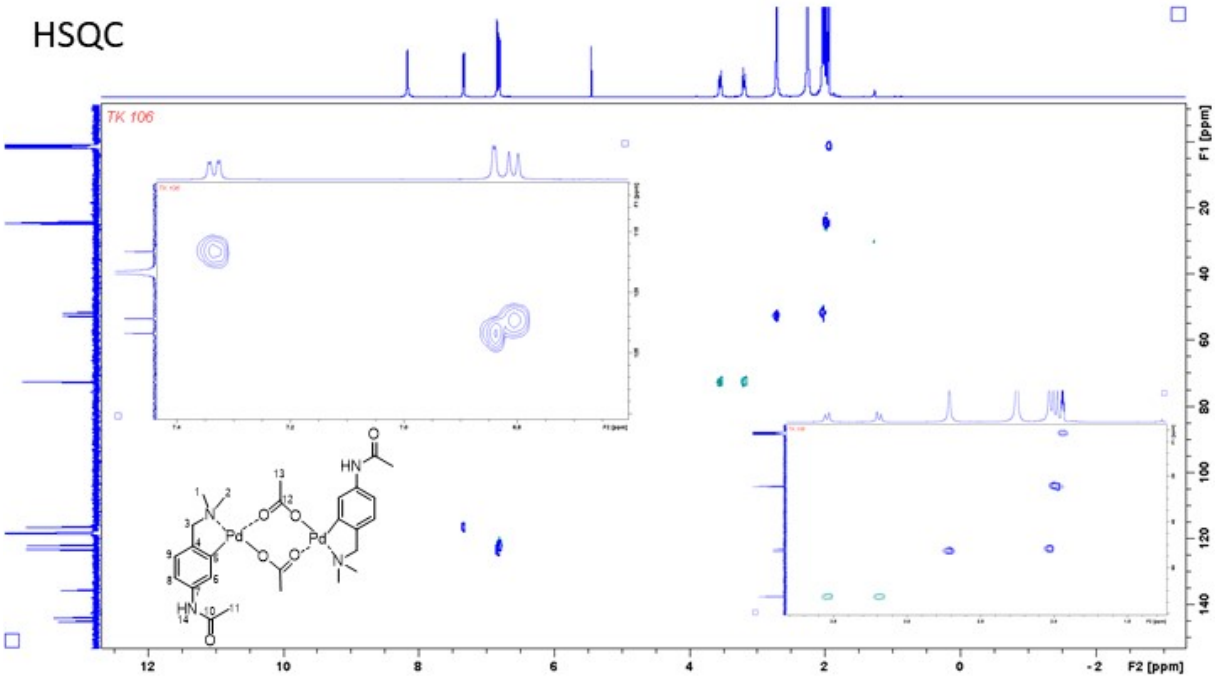


Figure S11. ^{1}H- ^{13}C HSQC NMR spectra (CD_3CN) of compound **2**.

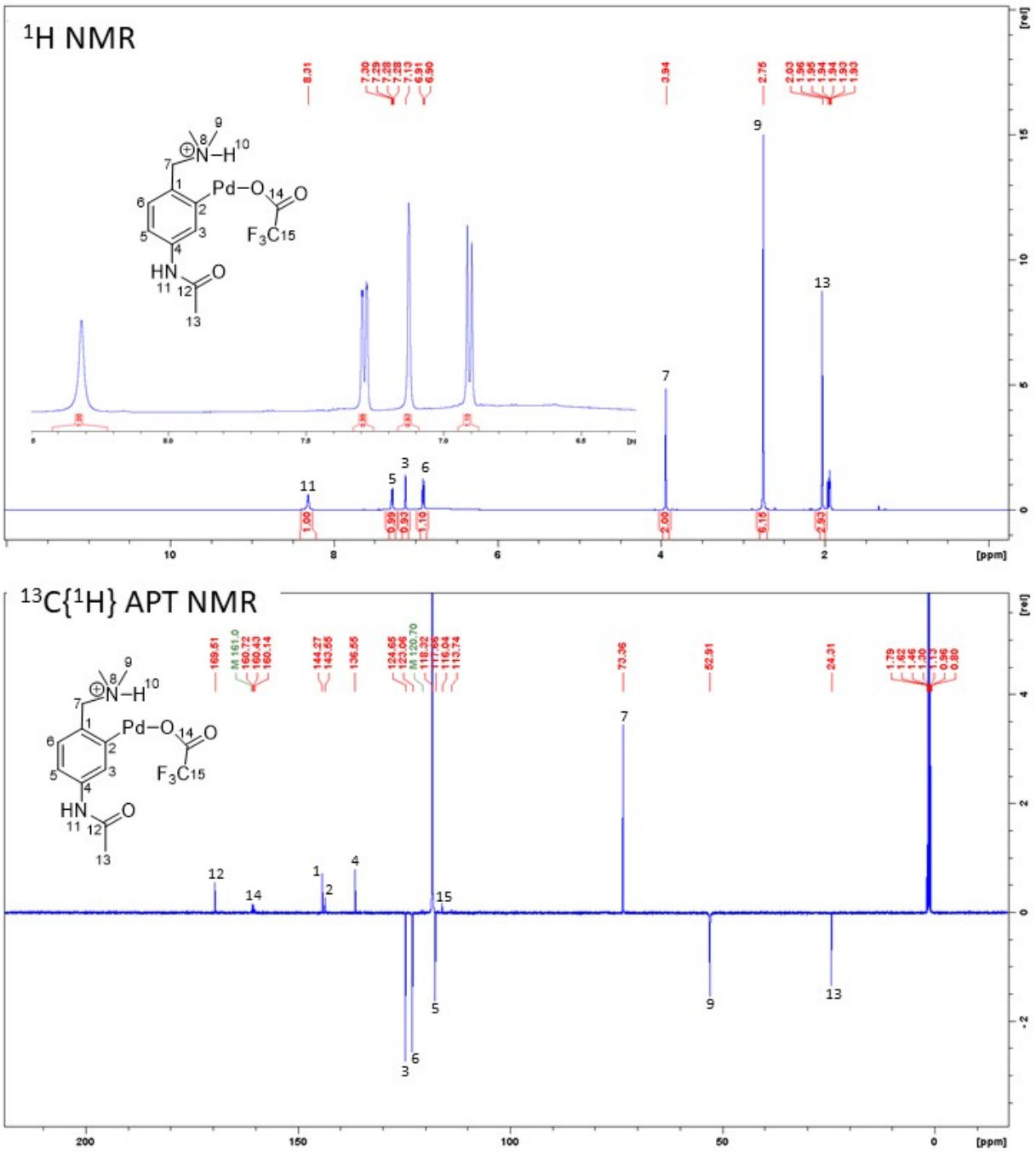


Figure S12. ^{1}H and ^{13}C NMR spectra (CD_3CN) of compound **2a-TFA** with signal assignment..

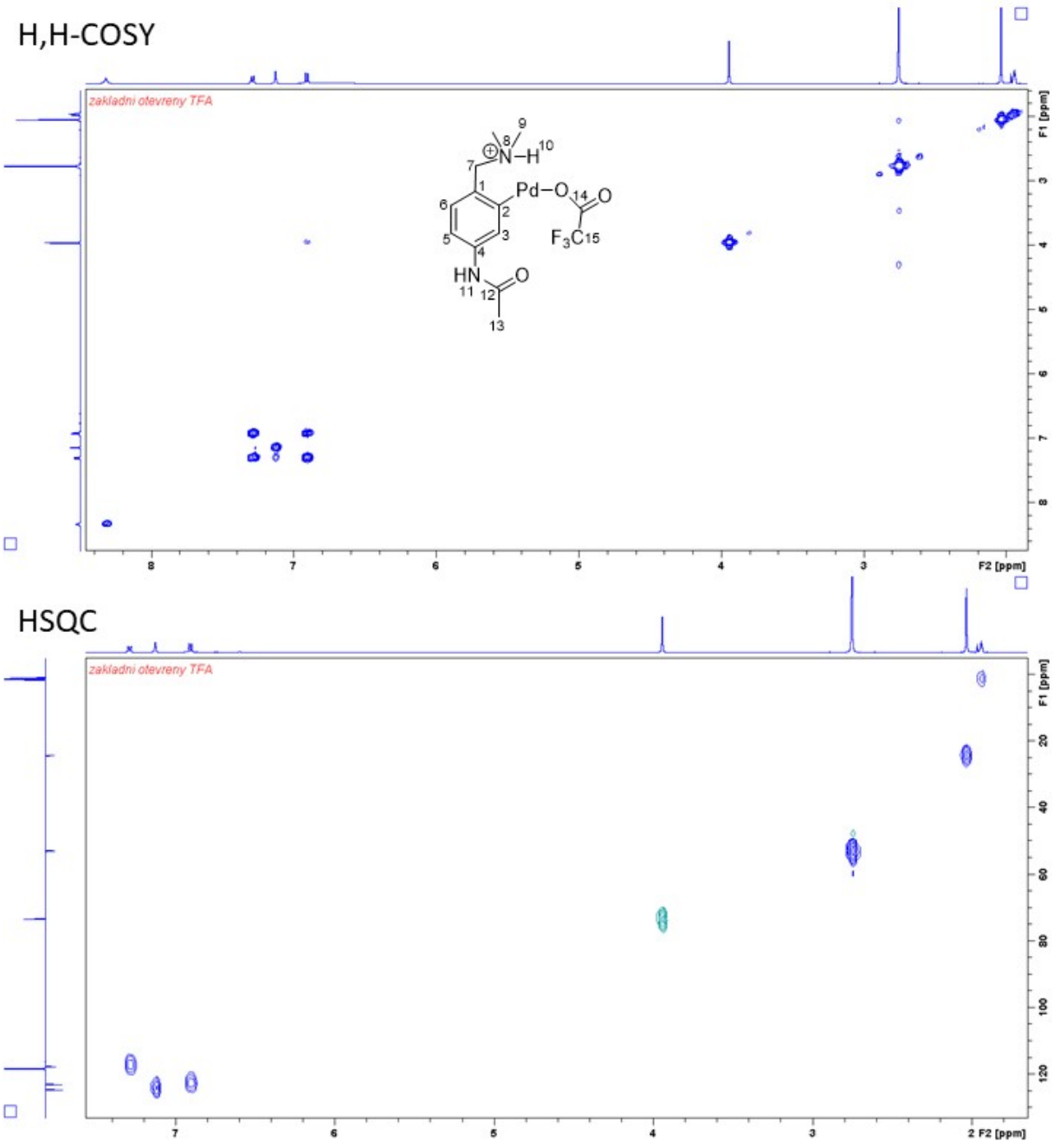


Figure S13. H,H-cosy and ^{1}H- ^{13}C HSQC NMR spectra (CD_3CN) of compound **2a-TFA**.

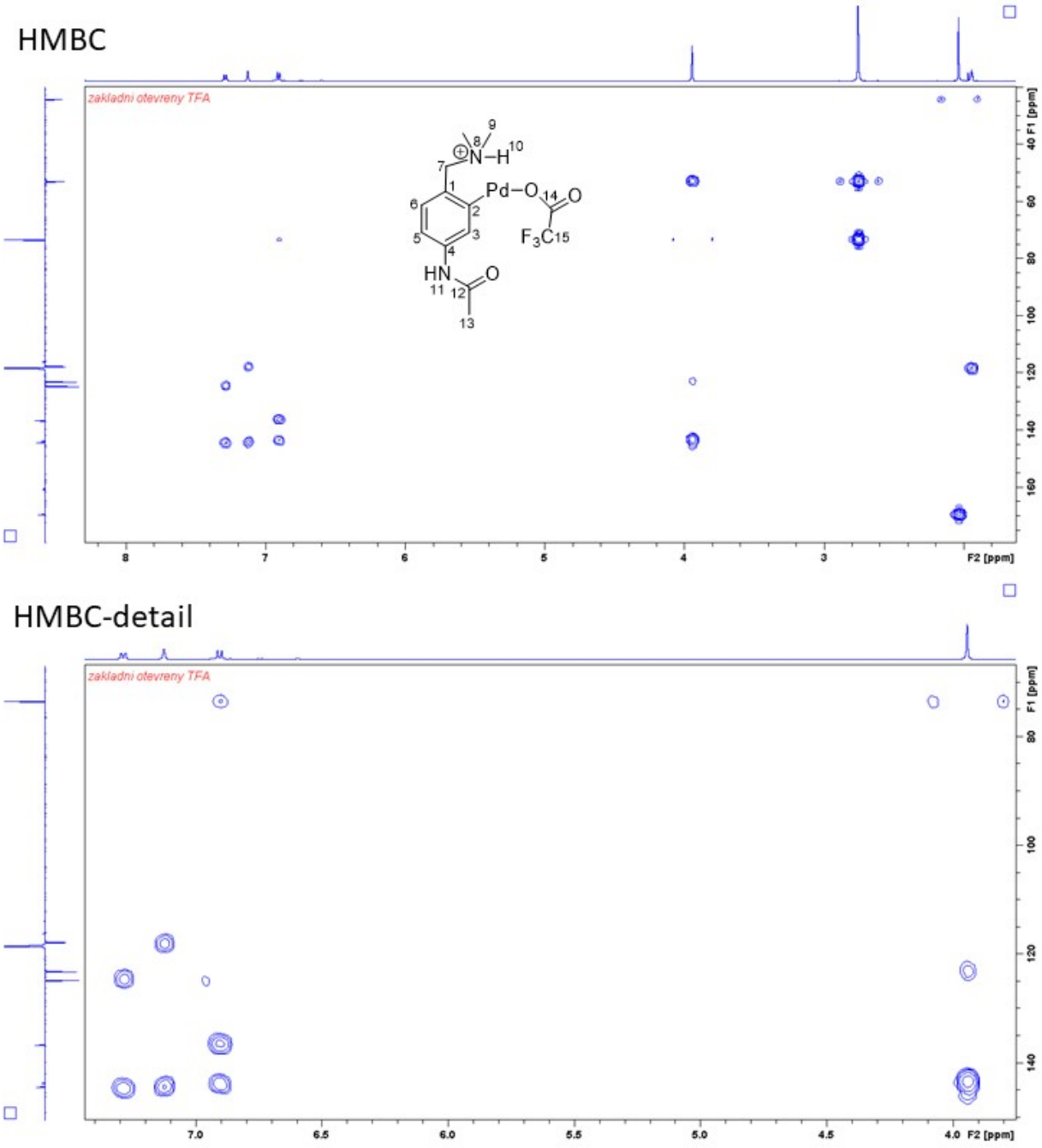


Figure S14. ^{1}H- ^{13}C HMBC NMR spectra (CD_3CN) of compound **2a-TFA**.

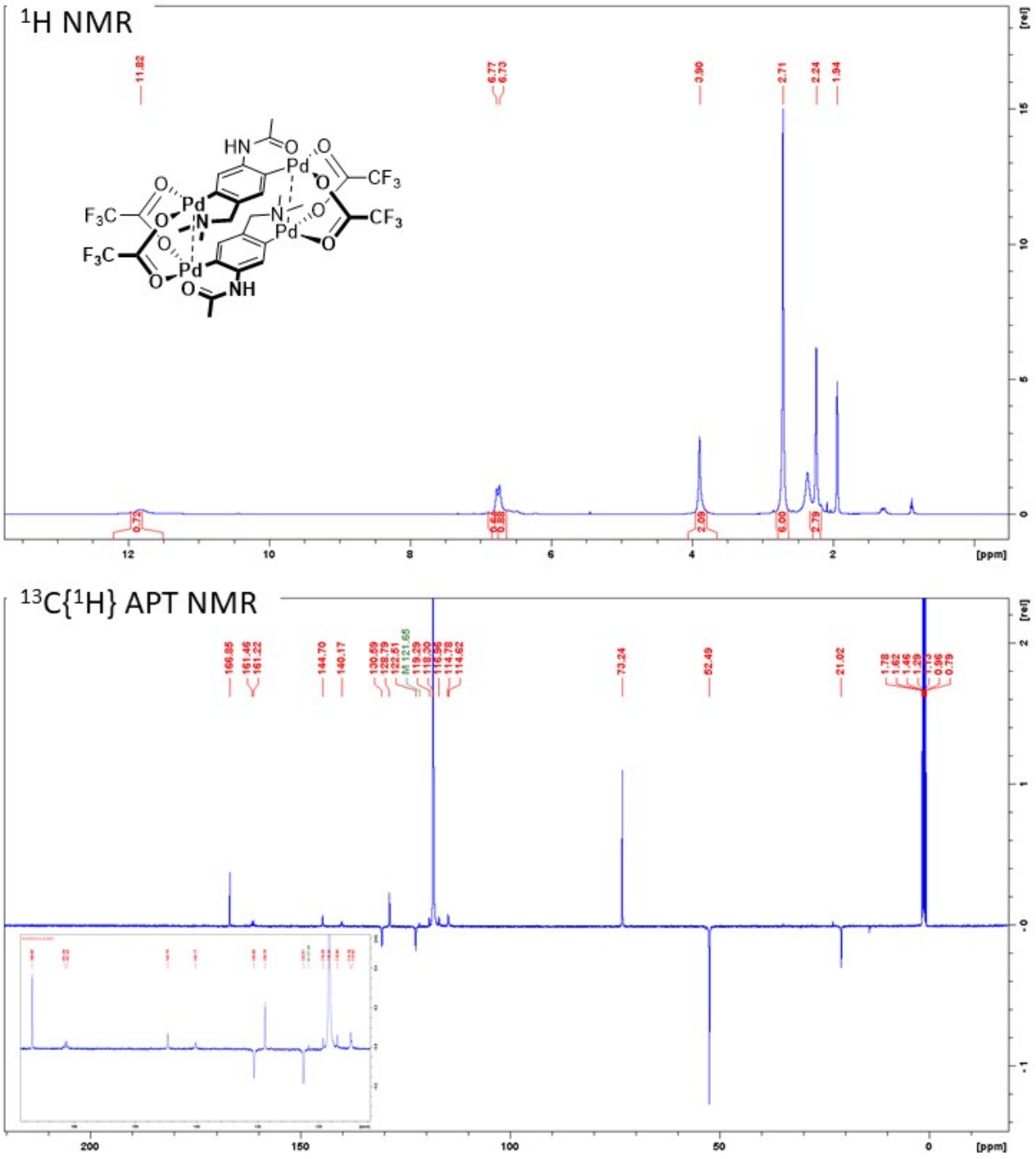


Figure S15. ^{1}H and ^{13}C NMR spectra (CD_3CN) of compound **5**.

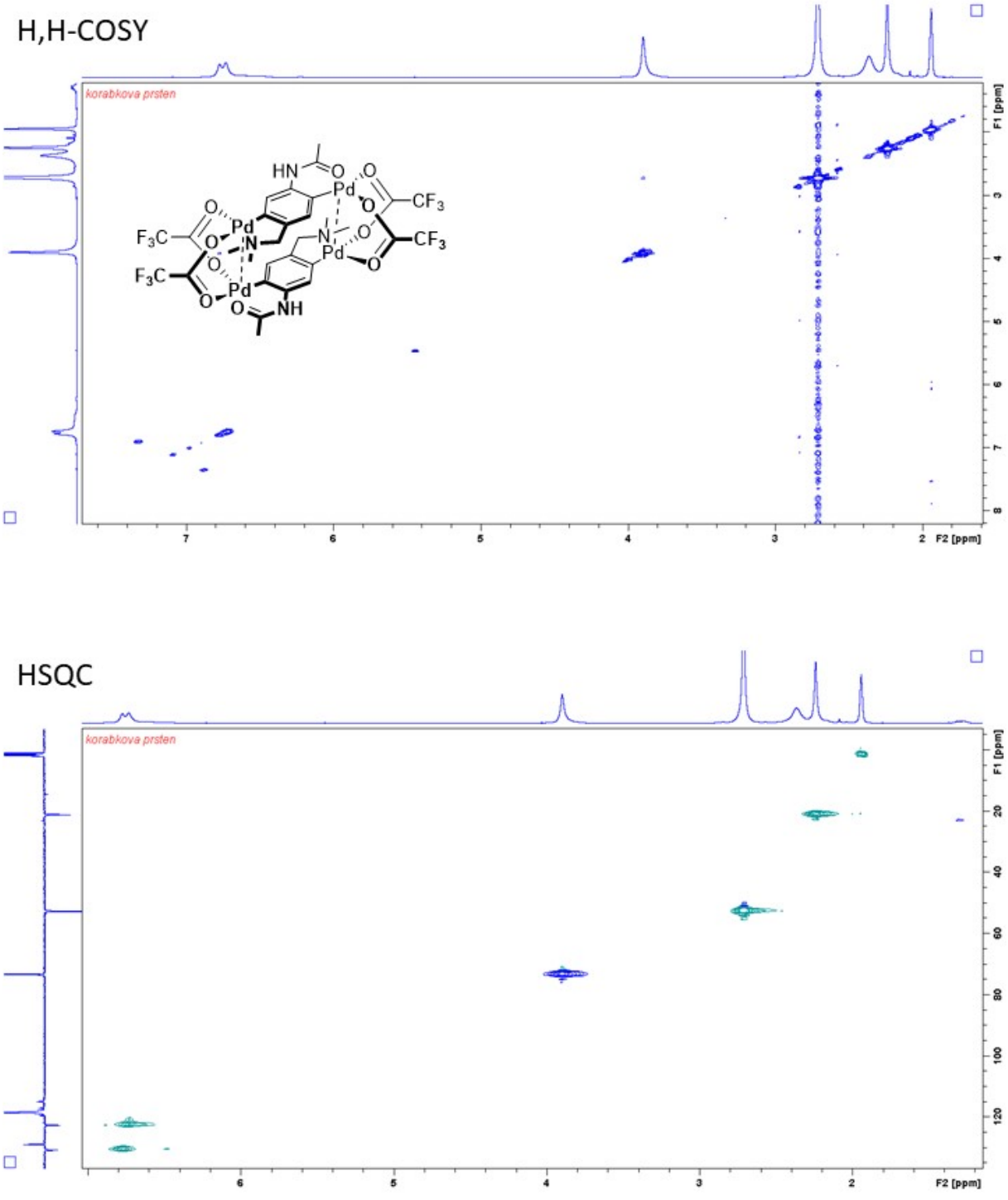


Figure S16. H,H-cosy and ^{1}H- ^{13}C HSQC NMR spectra (CD_3CN) of compound **5**.

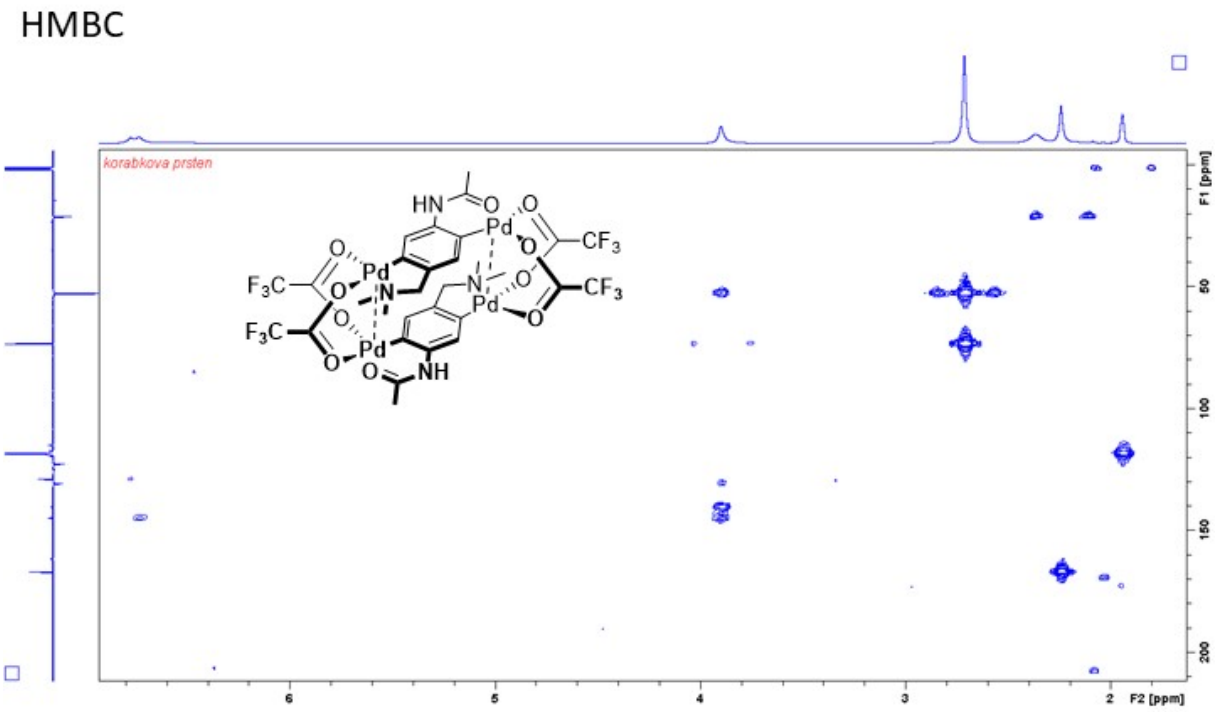


Figure S17. ^{1}H- ^{13}C HMBC NMR spectra (CD_3CN) of compound **5**.

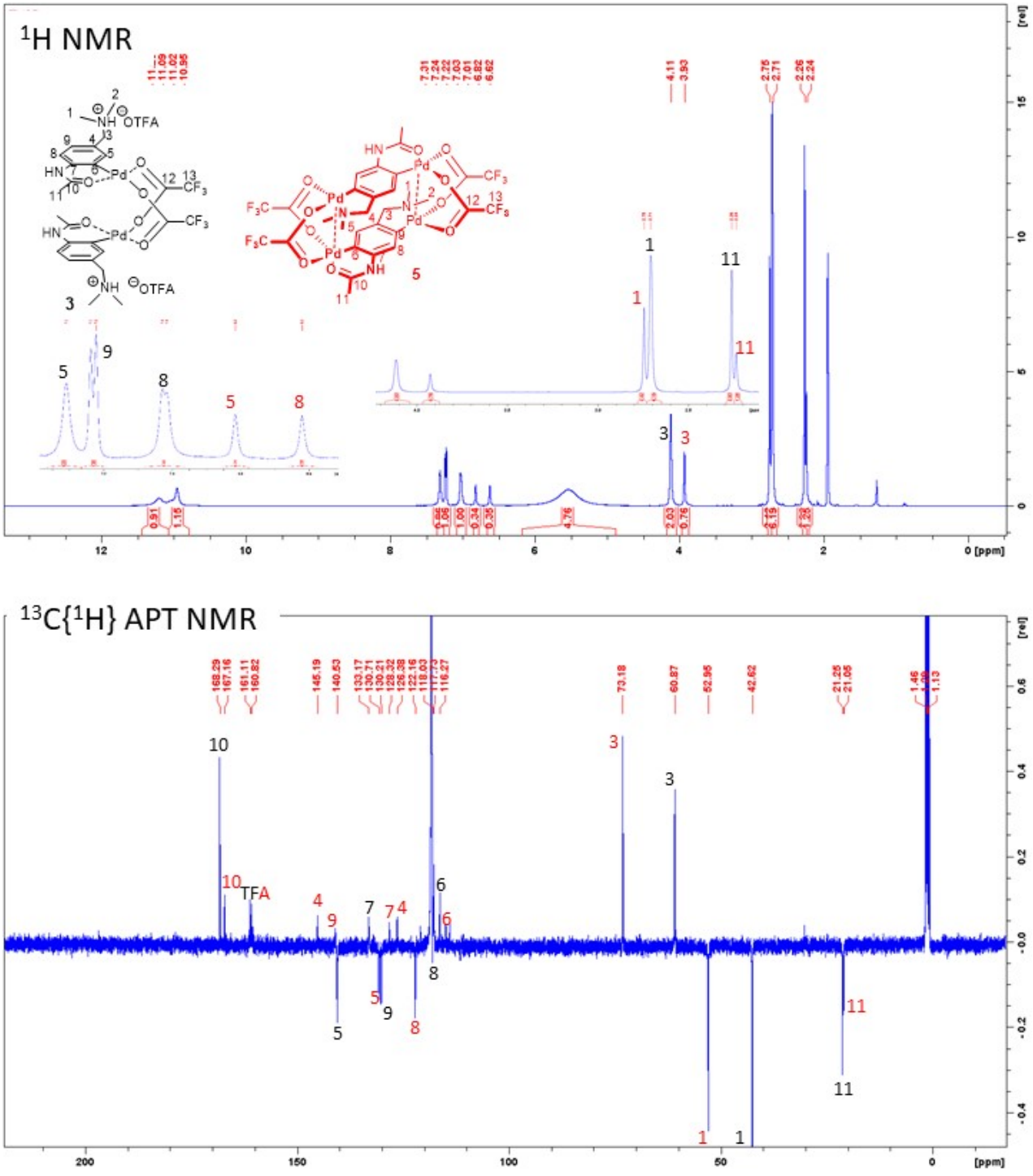


Figure S18. ^{1}H and ^{13}C NMR spectra (CD_3CN) of reaction mixture containing compounds **3** and **5** with signal assignment.

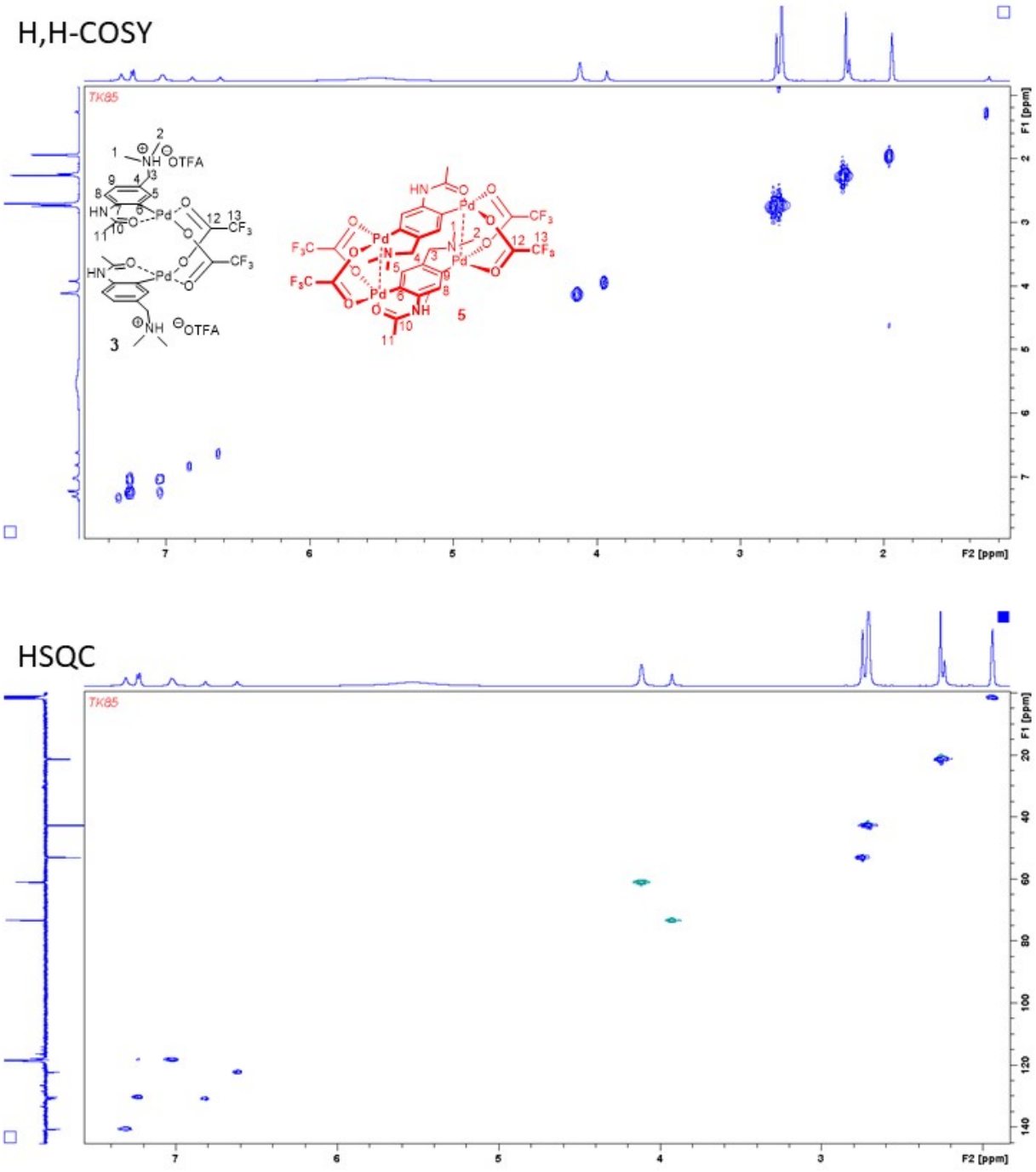


Figure S19. H,H-cosy and ^{1}H- ^{13}C HSQC NMR spectra (CD_3CN) of reaction mixture containing compounds **3** and **5**.

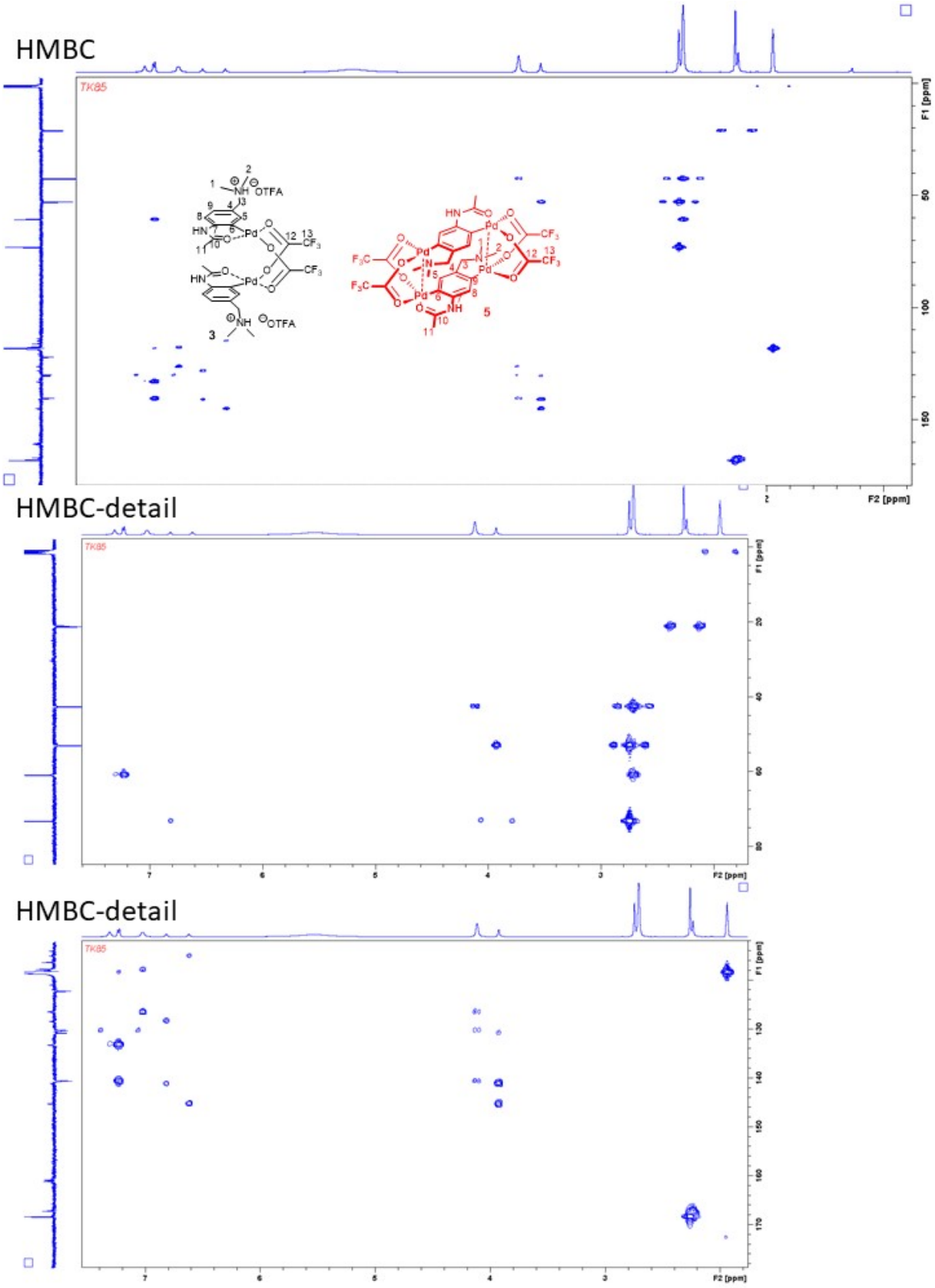


Figure S20. ^{1}H- ^{13}C HMBC NMR spectra (CD_3CN) of reaction mixture containing compounds **3** and **5**.

IR spectra

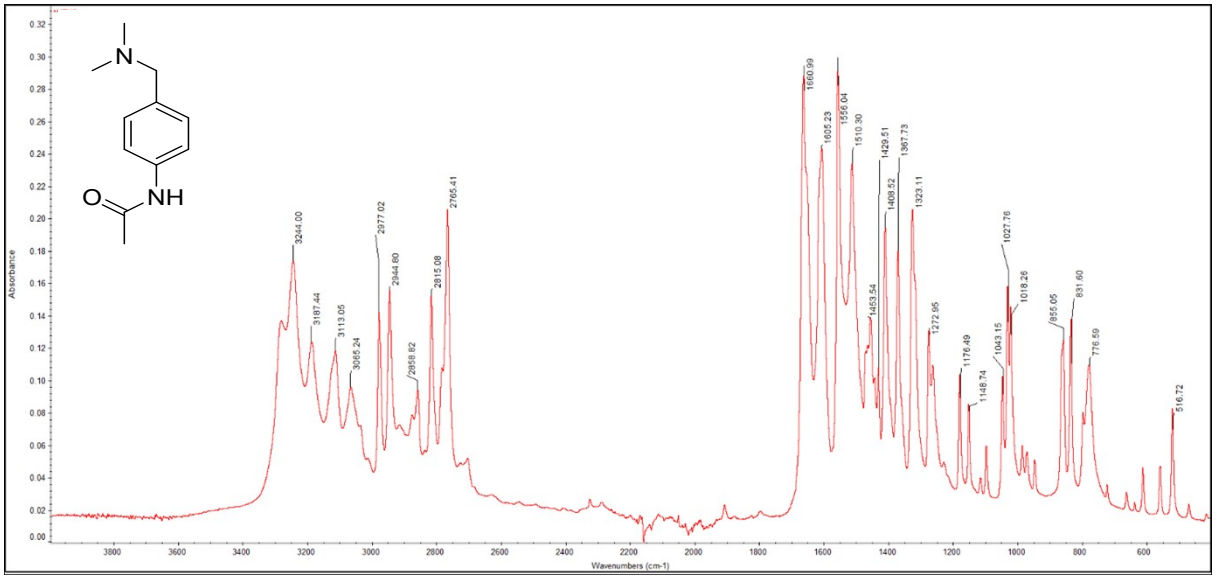


Figure S21. IR (ATR,diamond) of **1**.

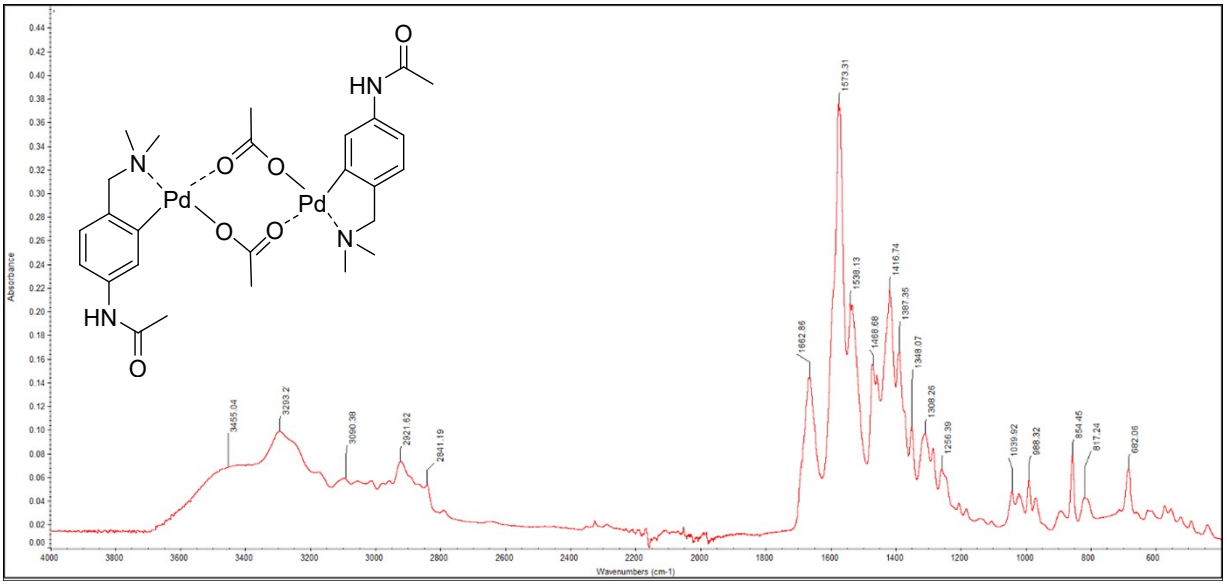


Figure S22. IR (ATR,diamond) of complex **2**.

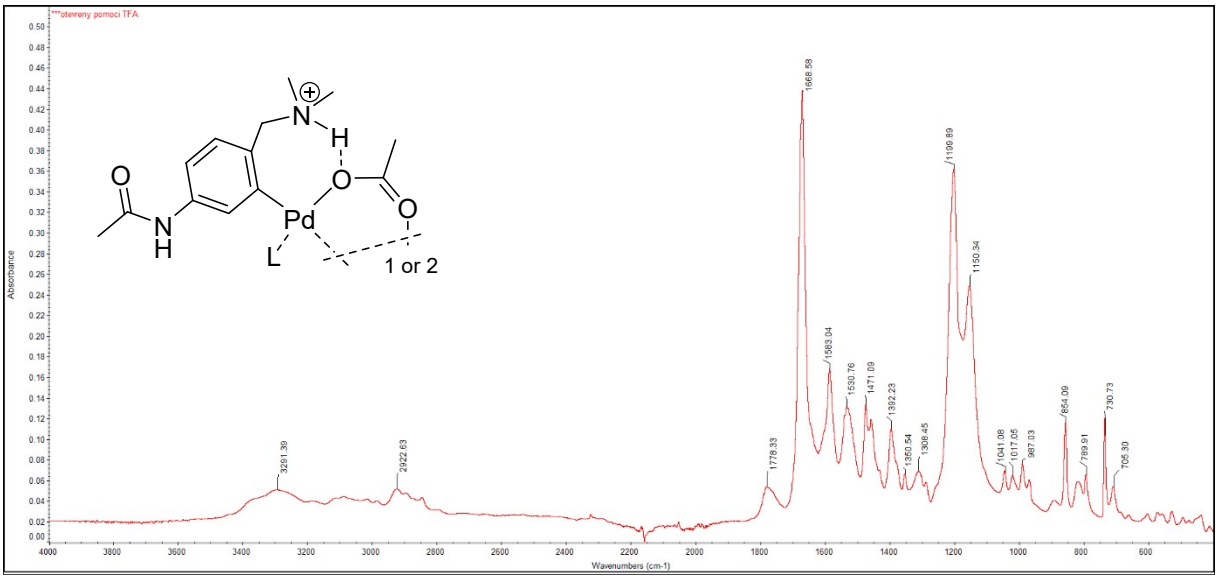


Figure S23. IR (ATR,diamond) of complex **2a-TFA.**.

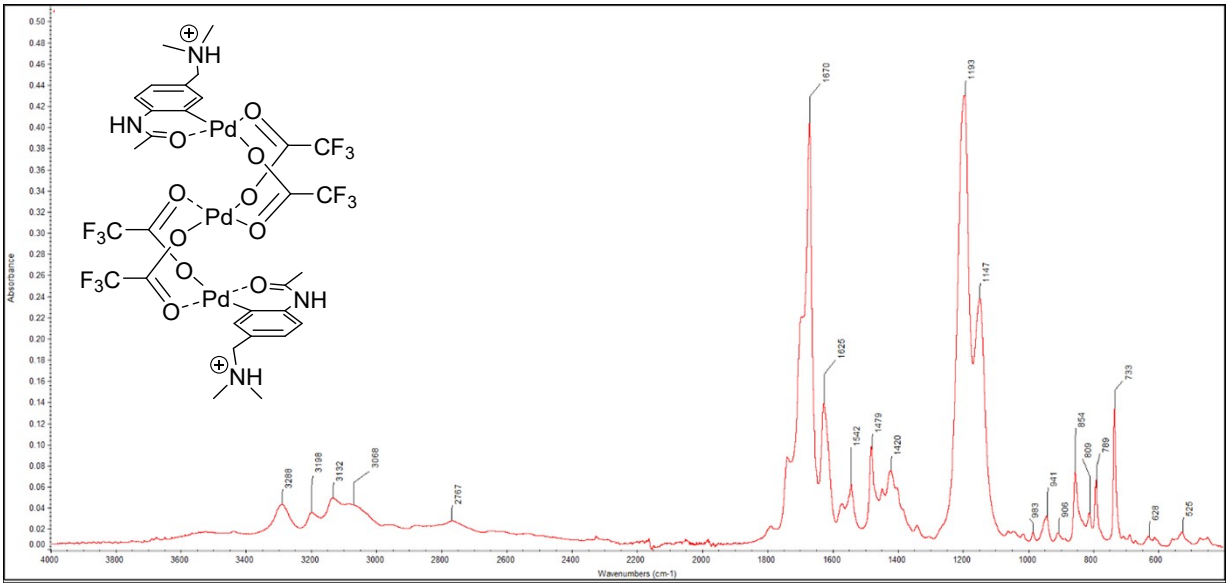


Figure S24. IR (ATR,diamond) of complex **3**.

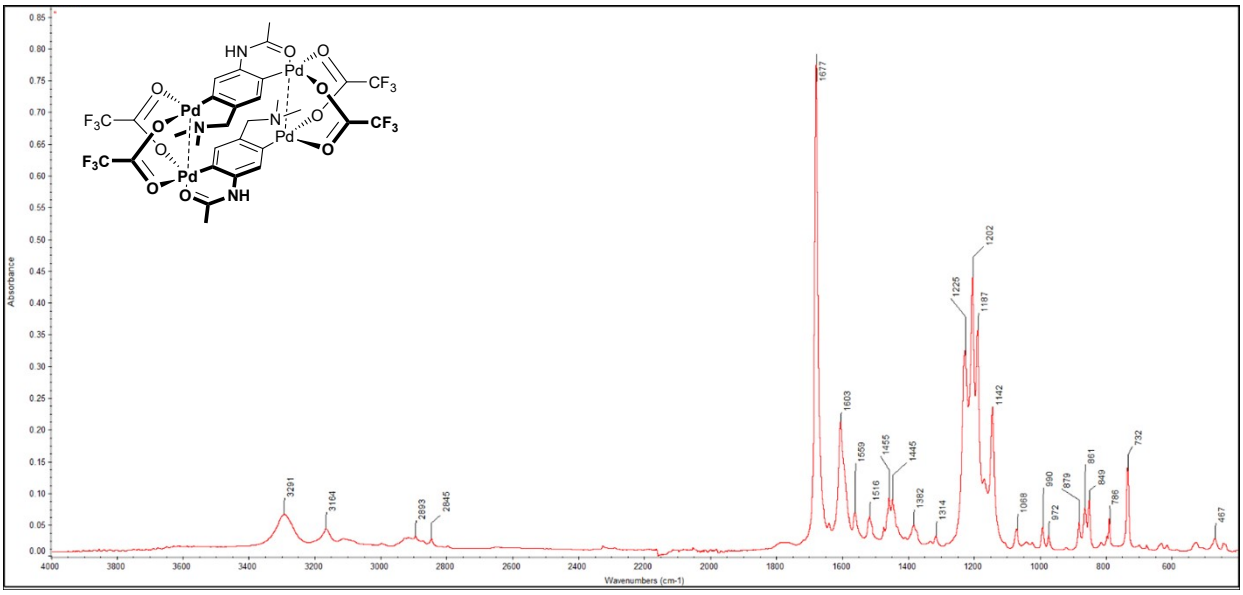
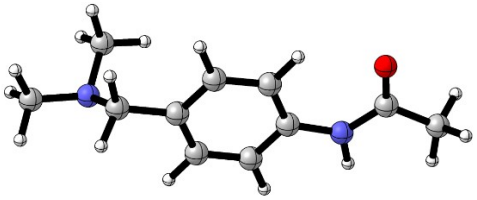


Figure S25. IR (ATR,diamond) of complex **5.**

Coordinates



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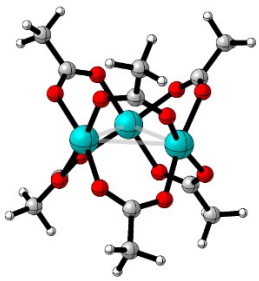
C	2.2787900	0.2548250	1.3014930
C	2.1924740	0.2485080	-0.0823140
C	0.9694050	0.0276040	-0.7271800
N	1.3137910	0.0565190	3.4876110
C	0.3896550	-0.1008770	4.4843150
O	-0.8050170	-0.2948030	4.2811910
C	0.8863540	0.0245020	-2.2348360
N	1.2735580	1.3086930	-2.8306790
C	1.3979160	1.1864870	-4.2787870
C	0.9520400	-0.0145550	5.8857430
C	0.3354360	2.3693130	-2.4781520
H	-1.1181030	-0.3490040	-0.4115810
H	-0.9776610	-0.3485540	2.0515580
H	3.2347530	0.4266430	1.7861100
H	3.0851240	0.4215050	-0.6730480
H	-0.1353110	-0.2616120	-2.5414700
H	1.5646190	-0.7353870	-2.6347350
H	0.4446370	0.9085400	-4.7645130
H	1.7276440	2.1384990	-4.7017500
H	2.1408180	0.4238100	-4.5251650
H	-0.6863720	2.1643470	-2.8467770
H	0.2882560	2.4865800	-1.3941510
H	0.6718960	3.3142110	-2.9110210
H	2.2655840	0.2116820	3.7904280
H	2.0328450	0.1315410	5.9146470
H	0.4656180	0.8142290	6.4062540
H	0.7007490	-0.9339200	6.4198080



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$Pd_3(OAc)_6$ 0 1 scf done: -1755.430651 Sum of electronic and thermal Free Energies -1755.187691 imag. freq.: 0

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Pd	1.4345810	-0.3637780	4.0551670
O	1.9928640	-0.8781070	5.9465490
C	2.1588090	-0.0852080	6.9184810
O	1.8061870	1.1275530	6.9681540
Pd	0.4950240	2.1517230	5.7772790
O	-0.7027340	3.5805770	4.9323940
C	-1.4247720	3.5224140	3.8973250
O	-1.7655230	2.4738660	3.2749410
Pd	-1.6069850	0.5681170	3.9776410
O	-1.7516510	-1.3756550	4.5717210
C	-0.8713580	-2.2694480	4.4058030
C	-1.2851620	-3.6902320	4.6812370
O	-1.1385200	0.0373480	2.0569540
O	-2.5949670	1.0356430	5.7074040
C	-2.1320270	1.3022440	6.8528970
O	-0.9389180	1.6235130	7.1254010
C	-3.0921020	1.2030890	8.0079890
O	0.3284500	-2.0856190	4.0534170
O	2.9374870	1.0155480	3.8935700
C	2.9101510	2.2675280	4.0642130
O	2.0017750	2.9284620	4.6465370
C	4.0617960	3.0508630	3.4930000
C	2.8167920	-0.6476160	8.1501130
C	-1.9594760	4.8260450	3.3674610
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H	-0.0255390	0.9875050	-0.3631540
H	4.1754150	4.0037060	4.0077980
H	4.9801180	2.4668720	3.5547260
H	3.8497940	3.2416350	2.4362710
H	-2.1467070	4.7530290	2.2966230
H	-2.9098910	5.0300000	3.8709460
H	-1.2690830	5.6400680	3.5851790
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H	3.4003770	0.1246790	8.6510890
H	2.0278750	-0.9766710	8.8338490
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H	-0.7231420	-4.3763120	4.0478960
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H	-2.7492030	1.8028650	8.8496510
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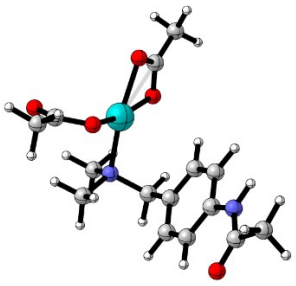

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imag. freq.: 0

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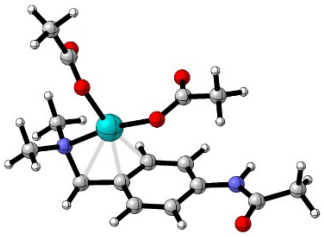
C	2.3869330	0.0550820	1.2981450
C	2.3648160	-0.0538550	-0.0835660
C	1.1570820	-0.0096370	-0.7894620
N	1.3034310	0.3185780	3.4183280
C	0.3186310	0.4787380	4.3575960
O	-0.8758720	0.5380470	4.0856250
C	1.1399970	-0.0980270	-2.2904960
N	1.3127560	1.2262620	-2.9897990
C	1.3342060	0.9820400	-4.4554580
C	0.8141100	0.5866670	5.7820020
Pd	3.2037420	1.9734280	-2.5197510
O	2.4604880	3.5487670	-1.4857610
C	2.2301560	4.6603140	-2.1214660
C	1.7091890	5.7638500	-1.2206260
C	0.1933780	2.1431850	-2.6697130
O	5.3222180	2.2114660	-2.3439980
C	5.4934040	1.1153420	-2.9677800
O	4.4481660	0.4782340	-3.3423810
C	6.8576960	0.6009190	-3.2808880
O	2.3714730	4.8256920	-3.3337060
H	7.1604160	0.9955810	-4.2562970
H	7.5744740	0.9426170	-2.5336730
H	6.8512920	-0.4880560	-3.3374790
H	2.1780460	5.7266560	-0.2363540
H	1.8742270	6.7378380	-1.6814980
H	0.6321920	5.6195740	-1.0851680
H	-0.9752640	0.1407870	-0.5825040
H	-0.9488240	0.3356440	1.8722570
H	3.3318610	0.0234210	1.8305390
H	3.2979580	-0.1720730	-0.6221670
H	0.1903230	-0.5177640	-2.6383900
H	1.9464000	-0.7396660	-2.6457240
H	0.3897840	0.5217620	-4.7649750
H	1.4632500	1.9307230	-4.9733870
H	2.1592280	0.3152120	-4.7009110
H	-0.7513840	1.6609290	-2.9407140

H	0.1968390	2.3799500	-1.6105660
H	0.3136810	3.0572320	-3.2465980
H	2.2500110	0.2837550	3.7719530
H	1.8924480	0.4564000	5.8812880
H	0.5370600	1.5694390	6.1722510
H	0.3038040	-0.1659680	6.3871790



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imag. freq.: 0

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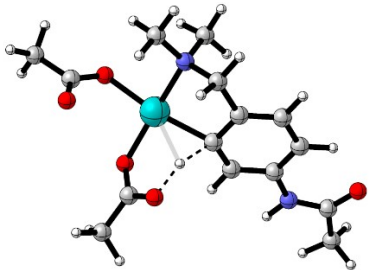
C	1.6160790	-0.4843220	1.9754670
C	2.6496280	-0.2471510	1.0796340
C	2.4095220	0.4462570	-0.1342050
C	1.0788820	0.8452860	-0.4128200
N	-0.6395970	-0.2338620	2.6954970
C	-1.9600120	0.1578690	2.7292250
C	-2.6467540	-0.1112480	4.0468830
Pd	3.2317400	2.2868340	0.9067350
O	4.0179890	4.1765960	1.1753910
C	5.2210210	4.3544590	1.6238780
O	6.0243460	3.4622680	1.9043980
C	3.5045370	0.6148210	-1.1783640
N	4.4348150	1.6865630	-0.6792280
C	5.7398020	1.1299390	-0.2516780
O	1.7789790	2.7400060	2.2581070
C	1.8862310	2.3983640	3.5037370
O	2.8607610	1.8441800	4.0159970
C	0.6667850	2.7633080	4.3356890
C	4.6325590	2.7649000	-1.6716140
C	5.5771290	5.8209170	1.8104440
O	-2.5266420	0.7020830	1.7918820
H	0.8599680	3.7200350	4.8315050
H	-0.2254960	2.8707440	3.7188900
H	0.5037630	2.0109610	5.1090960
H	5.1481870	6.1640520	2.7572180
H	6.6593280	5.9460710	1.8530040
H	5.1564490	6.4346070	1.0122410
H	0.8691660	1.3475830	-1.3500770
H	-0.9482240	0.9550470	0.2639390
H	1.8207020	-0.9923520	2.9098940
H	3.6382850	-0.6311930	1.2973950
H	3.0688990	0.9351410	-2.1225600

H	4.0596810	-0.3089180	-1.3455630
H	6.2571820	0.7144420	-1.1235150
H	6.3263790	1.9212870	0.2067980
H	5.5784400	0.3431510	0.4826640
H	5.1226170	2.3599570	-2.5634810
H	3.6675780	3.1895450	-1.9441990
H	5.2566660	3.5412860	-1.2332870
H	-0.2931260	-0.6718140	3.5391440
H	-2.1918700	-0.9334350	4.6019090
H	-2.5858860	0.7939880	4.6596030
H	-3.6990940	-0.3272670	3.8632670



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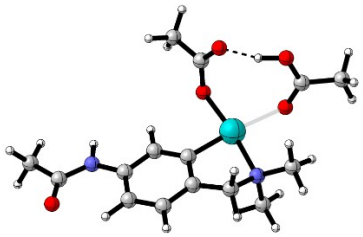
C	1.1946330	-0.0158820	2.0993770
C	2.4101820	0.0367050	1.4055520
C	2.3969000	0.0741380	0.0042980
C	1.1981210	0.0390480	-0.7102820
N	3.6703620	0.0494760	2.0324420
C	3.9751470	0.0406090	3.3681580
O	3.1298060	0.0234860	4.2567960
Pd	0.8346220	0.9840270	-2.5889160
O	0.4478070	2.2244170	-4.2000760
C	0.1664160	1.6598090	-5.3336420
O	0.0097860	0.4480680	-5.5050760
C	-1.2696560	0.1846890	-0.8081450
N	-1.0613050	1.3173540	-1.7714310
C	-2.1271530	1.2996910	-2.7998740
C	5.4543070	0.0535910	3.6793730
O	2.6634330	0.4442920	-3.4279210
C	2.8941960	-0.7997390	-3.3241400
O	2.2049010	-1.5725310	-2.5890330
C	4.0245670	-1.3815530	-4.1239690
C	-1.0759560	2.6218970	-1.0647230
C	0.0569200	2.6382900	-6.4909690
H	3.5963170	-1.8816170	-4.9982640
H	4.7034280	-0.6011470	-4.4638890
H	4.5587210	-2.1290260	-3.5362950
H	-0.4074920	3.5737280	-6.1739970
H	1.0656650	2.8709510	-6.8472090
H	-0.5079480	2.1968040	-7.3124080

H	-0.9415500	0.0043580	1.9400080
H	1.1947880	-0.0432980	3.1773000
H	3.3434400	0.0970540	-0.5266780
H	1.4657710	-0.7475060	-1.8033400
H	-2.1487400	0.3909390	-0.1906130
H	-1.4669360	-0.7058080	-1.4089020
H	-3.1037840	1.3845990	-2.3109380
H	-1.9840330	2.1386580	-3.4760670
H	-2.0744640	0.3684080	-3.3599660
H	-2.0650000	2.7891910	-0.6240210
H	-0.3222020	2.6268710	-0.2801360
H	-0.8576570	3.4127790	-1.7805360
H	4.4583070	0.0674970	1.3990480
H	5.6908050	-0.8273870	4.2808560
H	6.0880570	0.0609220	2.7917040
H	5.6753510	0.9364690	4.2841320



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Prod-amine 0 1 scf done: -1198.955412 Sum of electronic and thermal Free Energies -1198.653785 imag. freq.: 0

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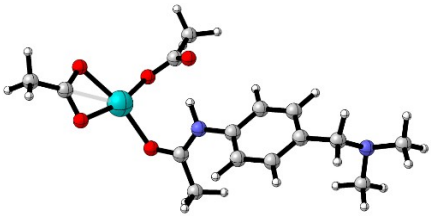
C	1.2037130	0.0316610	2.1076000
C	2.4241320	0.0447040	1.4464750
C	2.4560480	0.0278160	0.0401040
C	1.2623070	0.0016120	-0.6734100
N	-1.1910050	-0.0082390	2.1407540
C	-2.4915980	-0.0698830	1.7245390
C	-3.5126140	-0.0710590	2.8414780
Pd	4.1965980	0.1700540	2.2997130
O	6.2800700	0.4043910	3.0906770
C	7.1108700	-0.4890990	3.2874320
O	6.7980230	-1.7374700	3.5226200
C	3.8169520	0.0086330	-0.5876420
N	4.7852840	0.6907720	0.3345320
C	6.1668620	0.2744090	0.0069640
O	3.3870600	-0.2847810	4.1599130
C	3.6103050	-1.4151730	4.7071650
O	4.4562960	-2.2538700	4.3121850
C	2.7453980	-1.7532910	5.8998110
C	4.6718860	2.1642440	0.1868220
C	8.5833850	-0.2171350	3.2535790
O	-2.8298150	-0.1280240	0.5454740
H	3.3022010	-2.3548430	6.6189920

H	2.3582070	-0.8519920	6.3747040
H	1.8968040	-2.3482590	5.5455480
H	9.0487830	-0.5662050	4.1779500
H	9.0281000	-0.7809720	2.4283360
H	8.7711370	0.8454060	3.1145700
H	1.2793680	-0.0028350	-1.7588320
H	-0.8923910	-0.0385060	-0.5749930
H	1.1737090	0.0460680	3.1918960
H	5.7947290	-1.8750420	3.7115740
H	3.8465460	0.4882360	-1.5719250
H	4.1647900	-1.0208610	-0.7035720
H	6.3811420	0.4933260	-1.0452980
H	6.8667720	0.8210280	0.6352200
H	6.2754590	-0.7952000	0.1834420
H	4.9825790	2.4592340	-0.8223790
H	3.6410700	2.4704750	0.3532380
H	5.3137460	2.6504700	0.9202340
H	-1.0510070	0.0356150	3.1408080
H	-3.0768950	0.0688450	3.8321060
H	-4.2383570	0.7230900	2.6528840
H	-4.0497120	-1.0230870	2.8210750



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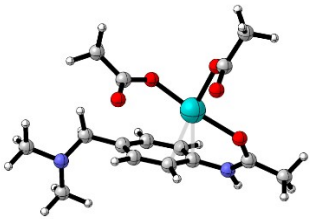
Pre-amide 0 1 scf done: -1198.912475 Sum of electronic and thermal Free Energies -1198.615181 imag. freq.: 0

C	0.0876680	0.0805770	-0.0732980
C	0.1172370	0.1511060	1.3172720
C	1.3434840	0.1467760	1.9800280
C	2.5454840	0.1014370	1.2730340
C	2.4971960	0.0605280	-0.1251750
C	1.2820950	0.0469870	-0.7981240
C	3.8753650	0.0996980	1.9897830
N	4.6709240	-1.0977630	1.7002580
C	4.0410340	-2.3026290	2.2304280
N	-1.1433910	0.0932500	-0.7906860
C	-2.1797780	-0.7230360	-0.6147480
O	-3.2452420	-0.5960840	-1.2870240
Pd	-3.7607520	1.0079420	-2.4586870
O	-2.7102160	0.2973640	-4.0371390
C	-1.4698590	0.6423470	-4.1692480
O	-0.8131490	1.2521850	-3.3121630
C	-2.1366200	-1.8440360	0.3776520
O	-4.6454430	2.7255870	-3.2479460
C	-5.2632740	2.9342380	-2.1474950
O	-5.0593640	2.0948640	-1.2072130
C	-6.1944830	4.0827660	-1.9850930

C	-0.8550800	0.2606230	-5.4962890
C	6.0283300	-0.9518360	2.2141380
H	-0.9597660	1.1112520	-6.1774080
H	-5.9040150	4.9032780	-2.6417180
H	-7.2013510	3.7543860	-2.2628040
H	-6.2131060	4.4108320	-0.9452720
H	0.2080020	0.0538510	-5.3692820
H	-1.3607660	-0.5971120	-5.9392490
H	-2.5537790	-1.5026690	1.3287950
H	-2.7643330	-2.6527840	0.0045710
H	-1.1222470	-2.2003450	0.5497080
H	-0.8070750	0.2140880	1.8777240
H	1.3624200	0.1875030	3.0635990
H	3.4219030	0.0270160	-0.6897570
H	-1.1679930	0.6981350	-1.6294710
H	1.2475700	0.0135830	-1.8803830
H	4.4595970	0.9664570	1.6667200
H	3.7040960	0.2110260	3.0748540
H	4.6442340	-3.1752440	1.9698330
H	3.9351890	-2.2709660	3.3302470
H	3.0477940	-2.4317410	1.7966620
H	6.6176970	-1.8333530	1.9508250
H	6.5025030	-0.0744640	1.7676420
H	6.0560350	-0.8374620	3.3130660



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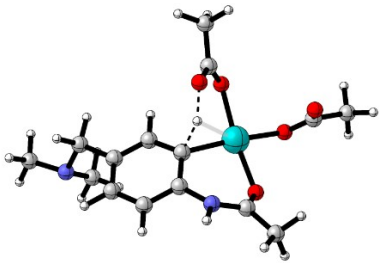
Int-amide 0 1 scf done: -1198.904558 Sum of electronic and thermal Free Energies -1198.607180

imag. freq.: 0

C	0.2185460	0.2686890	-0.3320290
C	-0.2122890	-0.0870790	0.9405550
C	0.7132560	-0.6459690	1.8322700
C	2.0325360	-0.8796300	1.4644660
C	2.4532670	-0.5423480	0.1769230
C	1.5447630	0.0435560	-0.7362820
C	-1.6596730	0.0898600	1.3373650
N	-2.2069850	1.3870470	0.9470150
C	-1.6308000	2.4710810	1.7352630
N	3.8290370	-0.6781460	-0.1767980
C	4.2727580	-1.2382380	-1.3123310
C	5.7340500	-1.1563890	-1.6160900
Pd	1.4997110	-2.1702920	-1.6438320
O	1.5880900	-3.9651230	-2.6127620
C	1.6835910	-3.9479360	-3.9124860
O	1.6466610	-2.9453510	-4.6209360
O	3.5067420	-1.8166810	-2.1196720

O	-0.3356180	-2.7045940	-1.0279670
C	-1.3965220	-2.2336590	-1.6210000
O	-1.3980910	-1.3957530	-2.5187750
C	-2.6816290	-2.8551360	-1.1046730
C	1.8836460	-5.3348040	-4.5018130
C	-3.6625860	1.3879360	1.0380710
H	-2.5908600	-3.1681740	-0.0643770
H	2.9535110	-5.5659660	-4.4841400
H	-3.5081280	-2.1535850	-1.2211610
H	-2.8962340	-3.7424490	-1.7089060
H	1.3630380	-6.0962850	-3.9200460
H	1.5426200	-5.3514190	-5.5372940
H	6.0708040	-2.1110310	-2.0207010
H	5.8849030	-0.3900060	-2.3823210
H	6.3209870	-0.8948730	-0.7354970
H	4.5148750	-0.3205780	0.4770060
H	1.9060370	0.4749330	-1.6626750
H	-0.4725020	0.7247100	-1.0267460
H	0.3895640	-0.9137070	2.8319860
H	2.7353370	-1.3206820	2.1607870
H	-2.2483110	-0.6832460	0.8347140
H	-1.7640840	-0.0852080	2.4224250
H	-2.0240220	3.4282760	1.3856540
H	-1.8614330	2.3738410	2.8117460
H	-0.5451860	2.4857000	1.6196870
H	-4.0501890	2.3519330	0.7004910
H	-4.0743910	0.6067900	0.3949520
H	-4.0241410	1.2154870	2.0680380



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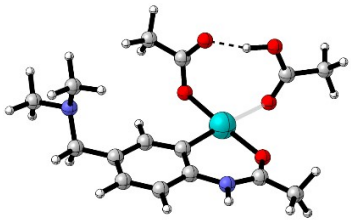
TSamide 0 1 scf done: -1198.884800 Sum of electronic and thermal Free Energies -1198.592022 imag. freq.: 1 (-1219.3635)

C	2.9151570	0.7609540	-0.6634160
C	2.8967530	2.1390110	-0.4057500
C	1.7506130	2.7614730	0.0636010
C	0.5940390	2.0119160	0.2972760
C	0.5897560	0.6177930	0.1113590
C	1.7653310	0.0296950	-0.4040450
N	-0.5612900	2.7257790	0.6960680
C	-1.8101660	2.5351780	0.2393840
O	-2.1409020	1.5677070	-0.4867240
Pd	-1.2761100	-0.2893890	-0.2777850
O	-0.5867150	-2.1716170	0.1911300
C	-0.0246580	-2.2398240	1.3329740

C	0.2556060	-3.6060150	1.8906300
C	-2.8479740	3.5494610	0.6050550
O	-3.0460270	-1.1175640	-0.9420900
C	-3.9661370	-1.3343290	-0.0558910
C	-5.2151930	-1.9893500	-0.6234320
O	-3.8734850	-1.0766570	1.1481530
O	0.2938930	-1.2199620	2.0102790
H	1.2518810	-3.6306170	2.3342870
H	-6.0715200	-1.8003270	0.0246680
H	-0.4719210	-3.8038950	2.6835680
H	0.1581270	-4.3696330	1.1210830
H	-5.4230080	-1.6370610	-1.6349590
H	-5.0492370	-3.0705120	-0.6719260
H	-3.3001920	3.9328580	-0.3123210
H	-3.6322310	3.0501890	1.1793540
H	-2.4400240	4.3759980	1.1864260
H	-0.3980220	3.5958080	1.1881570
H	0.2039970	-0.1658890	1.1119730
H	1.7813010	-1.0425860	-0.5647920
H	3.7860360	2.7294440	-0.5941740
H	1.7346440	3.8335100	0.2253700
C	4.1647550	0.1031170	-1.1978030
H	4.9955030	0.3035250	-0.5149180
H	4.0185920	-0.9906250	-1.2203690
N	4.5443480	0.6176360	-2.5168510
C	5.8802500	0.1600810	-2.8841890
C	3.5686160	0.2479680	-3.5379880
H	3.8648160	0.6766440	-4.4979160
H	3.4841280	-0.8470740	-3.6585340
H	2.5828470	0.6382290	-3.2785230
H	6.1634760	0.5900820	-3.8477700
H	6.6042700	0.4871740	-2.1339790
H	5.9430830	-0.9398590	-2.9685320



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Prod-amide 0 1 scf done: -1198.937772 Sum of electronic and thermal Free Energies -1198.638695 imag. freq.: 0

C	-0.0130780	-0.0053600	0.0067310
C	0.0094870	-0.0542190	1.4012240
C	1.2209940	-0.0413010	2.0781960
C	2.4287600	0.0433410	1.3739700
C	2.4367410	0.1148870	-0.0292790
C	1.2003210	0.0687910	-0.6808800
N	3.5994120	0.0502810	2.1738090
C	4.8781270	-0.0168570	1.7979340
O	5.2549010	-0.0394490	0.6018010

Pd	4.1159640	0.2919560	-1.0605380
O	6.0743260	0.4294900	-2.1066760
C	6.7219010	1.4570150	-2.3282500
C	8.2061280	1.4290500	-2.5251270
C	-1.3179580	-0.0355940	-0.7574040
N	-1.4118200	1.0169680	-1.7718550
C	-1.4333530	2.3463760	-1.1725330
C	5.9191130	-0.0735350	2.8747180
O	3.0568720	0.6376110	-2.7928800
C	2.9948510	1.8208910	-3.2758290
O	3.6990840	2.7874020	-2.9035330
C	1.9480830	2.0252790	-4.3450120
O	6.1892060	2.6509340	-2.4192570
C	-2.5733840	0.8112240	-2.6276890
H	1.8242690	1.1237200	-4.9457480
H	8.6776820	2.1625910	-1.8670260
H	8.5978500	0.4346640	-2.3221830
H	8.4365960	1.7147700	-3.5553400
H	0.9940030	2.2290240	-3.8473750
H	2.2010610	2.8756120	-4.9778220
H	6.4701100	-1.0127810	2.7823550
H	6.6264470	0.7453350	2.7264650
H	5.4870310	-0.0054060	3.8728640
H	3.4361310	0.0598660	3.1725950
H	5.1659400	2.6270160	-2.4760960
H	1.1764330	0.1139290	-1.7603040
H	-0.9185290	-0.1018880	1.9604070
H	1.2413130	-0.0928430	3.1624240
H	-2.1573540	0.0242380	-0.0412810
H	-1.4113200	-0.9957070	-1.2755950
H	-2.5964470	1.5770040	-3.4068800
H	-2.5117470	-0.1680330	-3.1088650
H	-3.5270910	0.8619220	-2.0705380
H	-1.4685360	3.1021610	-1.9606050
H	-2.3075870	2.4949250	-0.5120930
H	-0.5293330	2.5093210	-0.5833510

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