Supplementary Information

Csp^3–H Bond Activation Mediated by a Pd(II) Complex under Mild Conditions

Hanah Na,[a,b,#] Andrew J. Wessel,[c,#] SeoungTae Kim,[d,e,#] Mu-Hyun Baik,[d,e,*] and Liviu M. Mirica[a,*]

[a] Department of Chemistry, University of Illinois at Urbana-Champaign, 600 S. Mathews Avenue, Urbana, Illinois, 61801

[b] Center for Advanced Specialty Chemicals, Korea Research Institute of Chemical Technology (KRICT), Ulsan 44412, Republic of Korea

[c] Department of Chemistry, Washington University, St. Louis, Missouri, 63130-4899

[d] Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

[e] Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon 34141, Republic of Korea

[#] These authors contributed equally.

[*] Email: mbaik2805@kaist.ac.kr

[*] Email: mirica@illinois.edu

Table of contents

1. General specifications

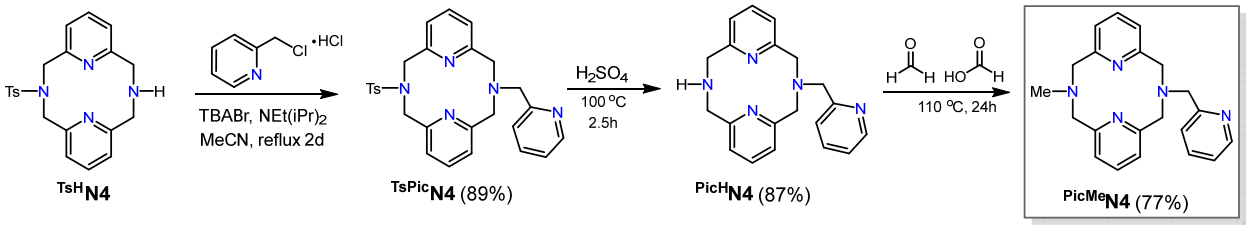
Materials. Reactions were performed in ambient conditions unless otherwise stated. Solvents were purified prior to use by passing through a column of activated alumina using an M Braun solvent purification system. All starting materials and reagents, unless otherwise specified, were obtained from commercial sources and used without further purification.

Physical Methods. ^{1}H-NMR spectra (300.121 MHz) were recorded on a Varian Mercury-300 spectrometer or a Varian Unity Inova-500 spectrometer. EPR spectra were recorded on a JEOL JES-FA X-band (9.2GHz) EPR spectrometer at 77K. EPR spectra simulation and analysis were performed using Bruker WINEPR SimFonia program, version 1.25. ESI-MS experiments were performed using a Thermo FT or Bruker Maxis Q-TOF mass spectrometer with an electrospray ionization source. Elemental analyses were carried out by Intertek Pharmaceutical Service. Cyclic voltammetry (CV) experiments were performed with a BASi EC Epsilon electrochemical workstation or a CHI 660D Electrochemical Analyzer. Electrochemical-grade Bu_4NClO_4 (Fluka) was used as the supporting electrolyte. Electrochemical measurements were performed under a blanket of nitrogen, and the analyzed solutions were de-aerated by purging with nitrogen. A glassy carbon disk electrode (d = 1.6 mm) was used as the working electrode, and either a Ag/AgCl wire electrode or a non-aqueous reference electrode (BASi) was used as the reference electrode. The reference electrodes were calibrated against ferrocene, Cp_2Fe (Fc). *Caution! Perchlorate salts are potentially explosive and should be handled with appropriate care and only in small quantities.*

2. Synthesis

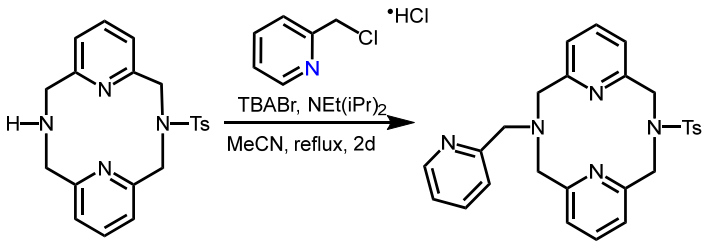
Reactions were performed in ambient conditions unless otherwise stated. Solvents were purified prior to use by passing through a column of activated alumina using an MBraun solvent purification system. All starting materials and reagents, unless otherwise specified, were obtained from commercial sources and used without further purification. The starting material *N*-(tosyl)-2,11-diaza[3,3](2,6)pyridinophane (^{TsH}N4) was synthesized following our previously published procedure.[1]

Synthesis of ligands



Scheme S1. Synthesis of ^{PicCH3}N4 ligand

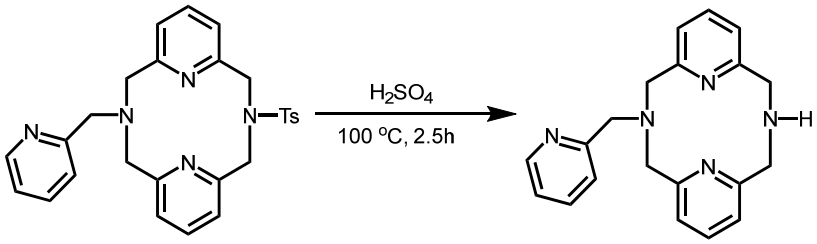
Synthesis of ^{TsPic}N4



Under N_2, ^{TsH}N4 (1.96 g, 4.97 mmol) was suspended in diisopropylethylamine (1.75 mL, 14.4 mmol) and MeCN (200 mL) in a 500 mL round bottom flask. To this, 2-(chloromethyl)pyridine hydrochloride (1.12 g, 8.67 mmol) and a catalytic amount of tetrabutylammonium bromide (0.020 g) was added, and the resulting solution was refluxed for two days. After cooling with ice bath, the solution was basified with NaOH solution until a pH of 13 was reached. Then the aqueous layer was extracted with CH_2Cl_2 (3 × 500 mL), the combined organic layer was dried with K_2CO_3, and the solvent was removed by rotary evaporation. The resulting tan-colored solid was dried under a vacuum. Yield: ^{TsPic}N4 (2.16 g, 89%).^{1}H NMR (300 MHz, CD_3CN): 8.548 (d, 2 H), 7.830 (d, 2 H), 7.795 (m, 4 H), 7.454 (d, 2 H), 7.248 (m, 3 H), 6.8995 (d of d, 4 H), 4.437 (s, 4 H), 4.127 (s, 2 H), 3.856 (s, 4 H), 2.467 (s, 3 H).^{13}C (125 MHz, CD_3CN): 155.553, 154.772, 143.589, 137.205,

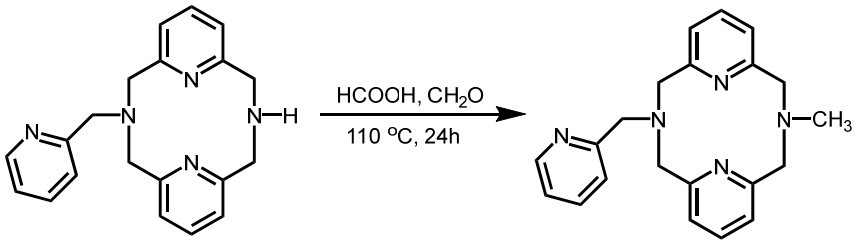
136.850, 135.996, 135.692, 129.965, 129.696, 127.277, 126.964, 123.237, 121.060, 56.541, 54.208, 21.505. ESI-MS (*m*/*z*): $[M + H]^+$ calcd for $C_{27}H_{27}N_5O_2S$, 486.1885; found, 486.1909.

Synthesis of ^{PicH}N4



Under N_2, ^{TsPic}N4 (2.98 g, 6.14 mmol) was dissolved in 90% sulfuric acid (65 mL). This mixture was refluxed at 100 °C for 2.5 hours. After cooling, the solution was diluted with 50 mL of DI water. In an ice bath, a saturated solution of NaOH was added to basify until the pH of 13 was reached. The resulting solution was extracted with CH_2Cl_2 (3 × 500 mL), the combined organic layer was dried with K_2CO_3, and filtered. The filtrate was concentrated to give a white solid. Yield: ^{PicH}N4 (1.77 g, 87%).^{1}H NMR (300 MHz, $CDCl_3$): 8.586 (d, 2 H), 7.740 (m, 4 H), 7.209 (m, 1 H), 7.058 (t, 2 H), 6.693 (d, 2H), 6.478 (d, 2 H), 4.182 (s, 2 H), 3.963 (s, 4 H), 3.905 (s, 4 H); ^{13}C (125 MHz, $CDCl_3$): 159.348, 158.667, 136.374, 135.621, 120.611, 119.649, 55.892 54.588. ESI-MS (*m*/*z*): $[M + H]^+$ calcd for $C_{20}H_{21}N_5$, 332.1797; found, 332.1870.

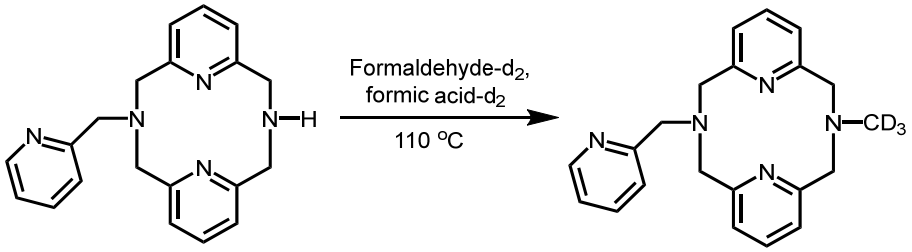
Synthesis of ^{PicCH3}N4



Under N_2, ^{PicH}N4 (1.77 g, 5.34 mmol) was dissolved in concentrated formic acid (150 mL) and 40% formaldeyde solution (15 mL). This mixture was stirred and refluxed at 110 °C for 24 hours. After 24 hours, the reaction mixture was removed from the heat and 15 mL of 1 M HCl solution was stirred in. The solution was stirred for an additional 30 minutes. The solution was then concentrated to dryness via rotary evaporation, and the residue was basified using KOH. The basic aqueous fraction was extracted with DCM, and organic layers were combined and dried with K_2CO_3. The organic layer was then concentrated to dryness to give a white residue. This residue was purified

by hot heptane extraction (3 × 500 mL) or soxhlet extraction with heptane (500 mL). The solution was concentrated under reduced pressure to yield a white powder. Yield: ^{PicCH3}N4 (1.4 g, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): 8.61 (dt, *J* = 4.9, 1.4 Hz, 1H), 7.76 (dd, *J* = 6.3, 1.7 Hz, 2H), 7.22 (ddd, *J* = 6.1, 4.8, 2.5 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.80 – 6.75 (m, 4H), 4.18 (s, 2H), 4.00 (s, 4H), 3.84 (s, 4H), 2.72 (s, 3H); ^{1}H NMR (300 MHz, CD_3CN): 8.564 (d, 2 H), 7.689 (m, 4 H), 7.182 (m, 3 H), 6.806 (d of d, 4 H), 4.145 (s, 2 H), 4.001 (s, 4 H), 3.852 (s, 4 H), 2.694 (s, 3 H). ^{13}C (125 MHz, $CDCl_3$): 159.62, 157.45, 157.03, 149.17, 136.43, 135.33, 123.25, 122.51, 122.38, 122.14, 77.18, 76.93, 76.67, 66.09, 65.71, 63.63, 49.07. ESI-MS (*m*/*z*): $[M + H]^+$ calcd for $C_{21}H_{23}N_5$, 346.1952; found, 346.2029.

Synthesis of ^{PicCD3}N4



Under N_2, ^{PicH}N4 (600 mg, 1.1 mmol), 20% formaldehyde-d_2 in D_2O (1.8 mL, 6 mmol) and formic acid-d_2 (0.9 mL, 25 mmol) was refluxed overnight. After cooling, 37% HCl (0.55 mL) was added to the reaction mixture, and the solvent removed under reduced pressure. The residue was basified with aqueous NaOH and extracted with DCM. The organic layer was dried over anhydrous K_2CO_3, filtered, and concentrated in vacuo to dryness. The tan crude was purified via hot heptane extraction to yield a white powder. Yield: ^{PicCD3}N4 (412 mg, 65%). Note: The starting material ^{PicH}N4 was carefully dried to make sure no H_2O is present. To ensure no H_2O was present, D_2O was added to the ^{PicH}N4 and left to dry under reduced pressure. ^{1}H NMR (300 MHz, $CDCl_3$): 8.48 (d, *J* = 4.9 Hz, 2H), 7.64 (dd, *J* = 5.0, 2.3 Hz, 3H), 7.10 (dt, *J* = 5.5, 2.6 Hz, 2H), 7.01 (s, 3H), 6.68 – 6.64 (m, 6H), 3.87 (d, *J* = 6.7 Hz, 2H), 3.70 (d, *J* = 7.3 Hz, 2H). *Note*: We observed partial extra deuteration of the aliphatic –CH_2– backbone of the ligand, as suggested by ESI-MS and ^{2}H-NMR, although we washed ^{PicH}N4 ligand with D_2O prior to the reaction. We suspect that the deuterium exchange occurs during the acidic methylation, as picolyl pyridine may act as a weak base to aid the exchange reaction under this condition.

Synthesis of [(^{PicCH2}N4)Pd^{II}]BF$_4$ (**1**)

The ^{PicCH3}N4 (30.8 mg, 0.09 mmol) and [(MeCN)$_4$Pd^{II}](BF$_4$)$_2$, (40.0 mg, 0.09 mmol) were added to a 20 mL vial with 1 mL of MeCN and the color immediately changed from two white solids to a yellow solution. The reaction was stirred in the dark overnight. The solution mixture was concentrated down to a yellow oil. Pentane was added to this yellow oil which was stirred for two days to precipitate. The solid was filtered off using a pipet filter, rinsed with more pentane, dried under vacuum, and weighed. Additional purification through crystallization was achieved, and yellow-orange crystals were obtained by adding two equivalents of Na(BPh$_4$)$_2$ to solution of MeCN and complex with diethyl ether diffusion at room temperature (22.2 mg, 40.0%). ^{1}H NMR (500 MHz, CD$_3$CN): 8.52 (dt, *J* = 5.3, 1.8 Hz, 1H), 7.97 (tq, *J* = 7.7, 1.5 Hz, 1H), 7.56 – 7.45 (m, 2H), 7.31 (ddt, *J* = 9.6, 7.6, 1.6 Hz, 2H), 6.87 (dd, *J* = 7.6, 2.5 Hz, 2H), 6.79 (dd, *J* = 7.6, 2.5 Hz, 2H), 4.48 (d, *J* = 2.3 Hz, 2H), 4.41 (dd, *J* = 14.8, 2.5 Hz, 2H), 4.04 (d, *J* = 16.1 Hz, 2H), 4.01 (s, 1H), 3.97 (s, 2H), 3.95-3.97 (3H). ^{13}C NMR (151 MHz, CD$_3$CN): 161.34, 153.11, 149.91, 139.52, 138.78, 136.82, 126.66, 125.93, 125.78, 123.09, 123.05, 122.85, 122.81, 122.50, 66.11, 65.00, 64.97, 62.03, 58.01. ESI-MS (*m*/*z*): calcd for [C$_{21}$H$_{22}$N$_5$Pd]$^+$ 450.0913; found, 450.0912. Elemental analysis: found 39.90%; H, 3.29%; N, 10.83%; C$_{21}$H$_{23}$B$_2$F$_8$N$_5$Pd: C, 40.33%; H, 3.71%; N, 11.20%.

Synthesis of [(^{PicCH3}N4)Pd^{II}(OAc)]OAc (**2**)

The ^{PicCH3}N4 (20 mg, 0.058 mmol) and Pd^{II}(OAc)$_2$, (13 mg, 0.058 mmol) were added to a 20 mL vial with 8 mL of THF and the color immediately changed from to a dark green. The reaction was stirred overnight. The resulting solid was filtered off using a pipet filter (cotton plug), and washed with THF. Collected THF solution was concentrated and pentane was added to precipitate a green solid. Yield: 14.2 mg, 43 %. ^{1}H NMR (499 MHz, CD$_3$CN) δ 8.47 (d, *J* = 5.7 Hz, 1H), 8.16 (td, *J* = 7.8, 1.6 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 4.92 (s, 4H), 4.22 (t, *J* = 13.2 Hz, 4H), 3.89 (d, *J* = 13.2 Hz, 2H), 2.76 (s, 3H), 1.88 (d, *J* = 1.3 Hz, 3H), 1.76 (s, 3H). ^{13}C NMR (126 MHz, CD$_3$CN) δ 177.19, 150.29, 142.14, 140.31, 139.33, 126.52, 125.97, 124.89, 123.58, 123.54, f123.52, 123.43, 70.60, 68.74, 64.94, 54.75, 48.64, 23.28, 22.63. Attempts to obtain analytically pure solid samples of **2** were not successful, likely to the slow C-H activation process occurring during the isolation of the product.

3. NMR spectra

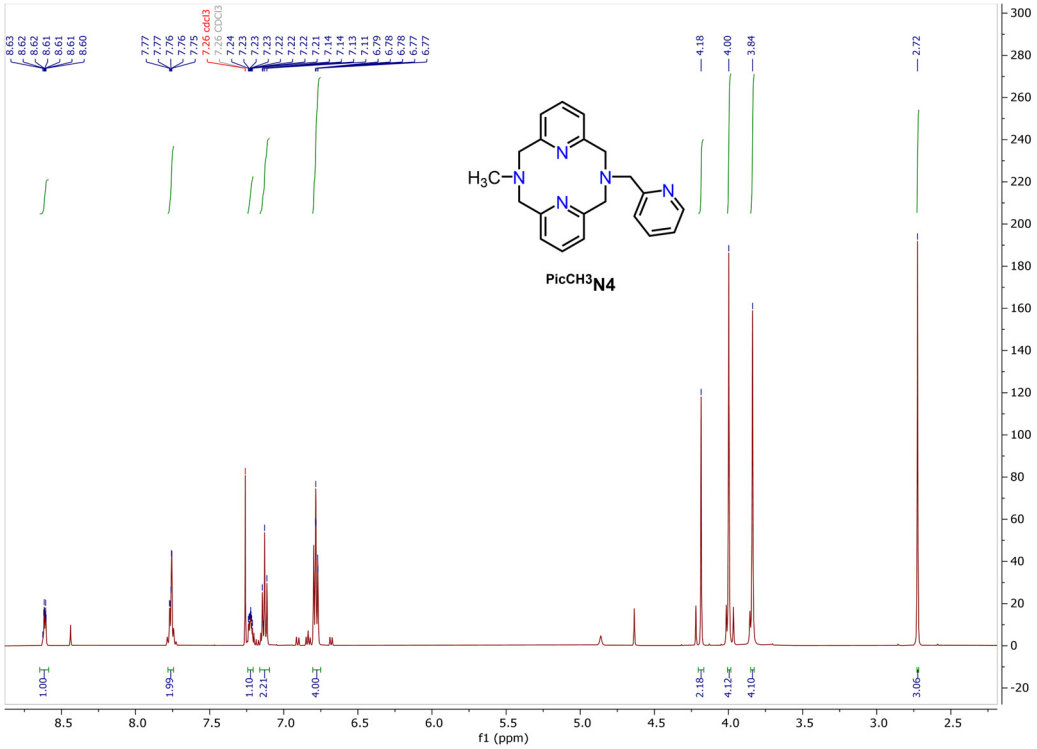


Figure S1. ^{1}H NMR spectrum of ^{PicCH3}N4, recorded at 500 MHz in $CDCl_3$.

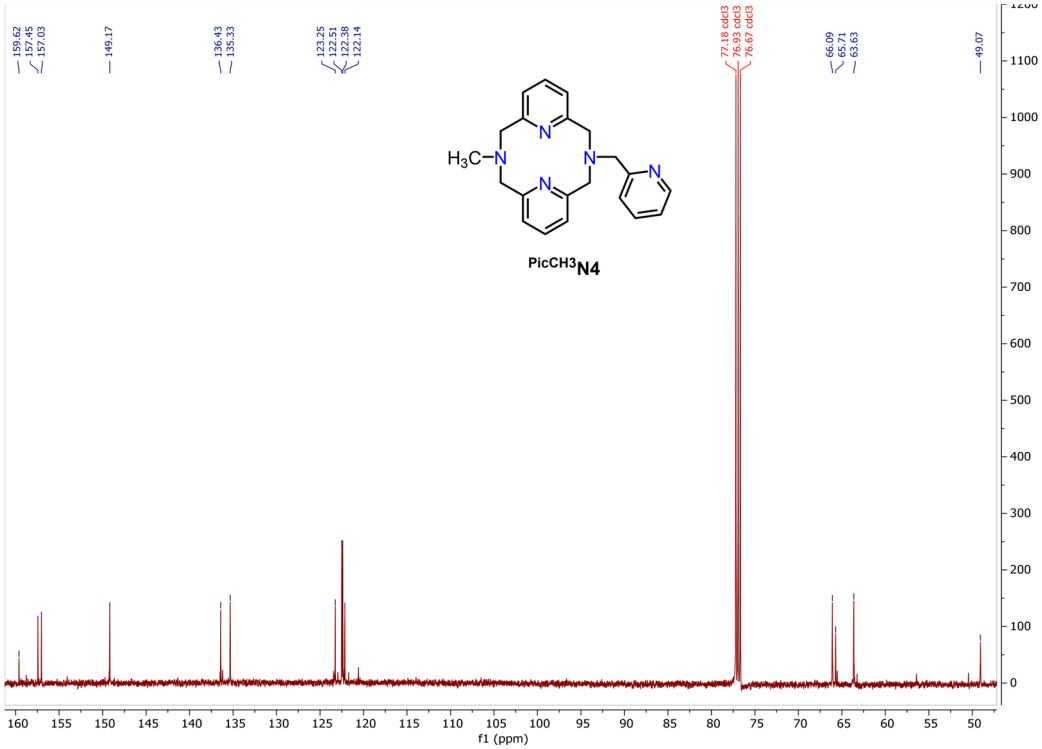


Figure S2. ^{13}C NMR spectrum of ^{PicCH3}N4, recorded at 126 MHz in $CDCl_3$.

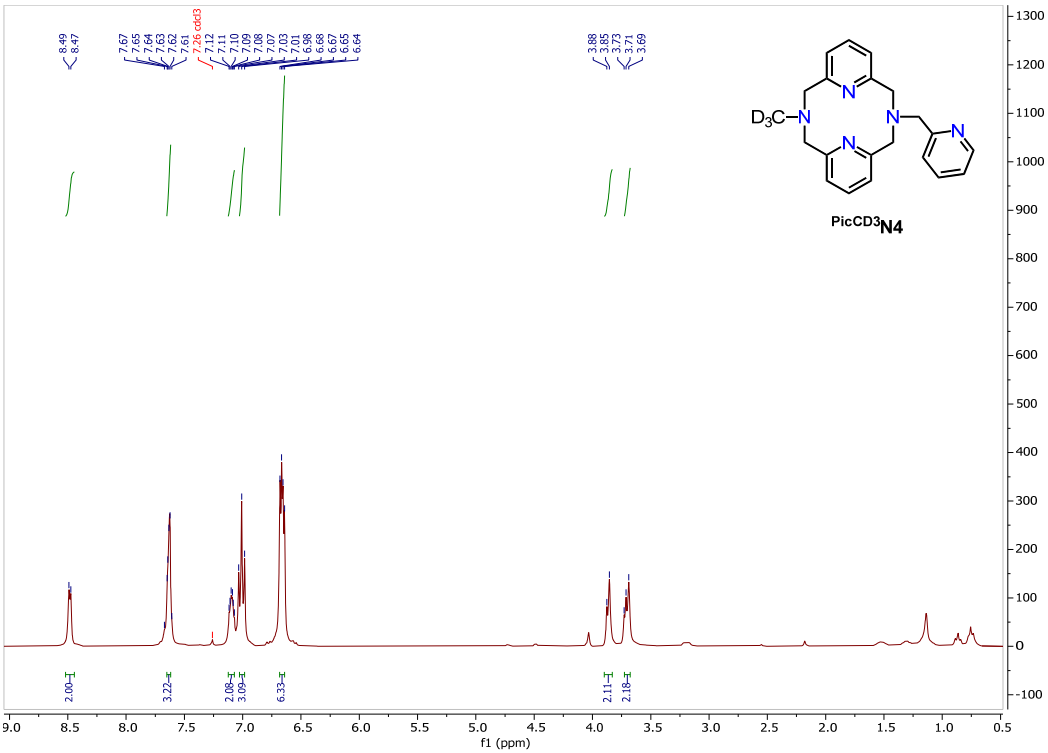


Figure S3. ^{1}H NMR spectrum of ^{PicCD3}N4 recorded at 300 MHz in $CDCl_3$, showing the absence of CH_3 peak.

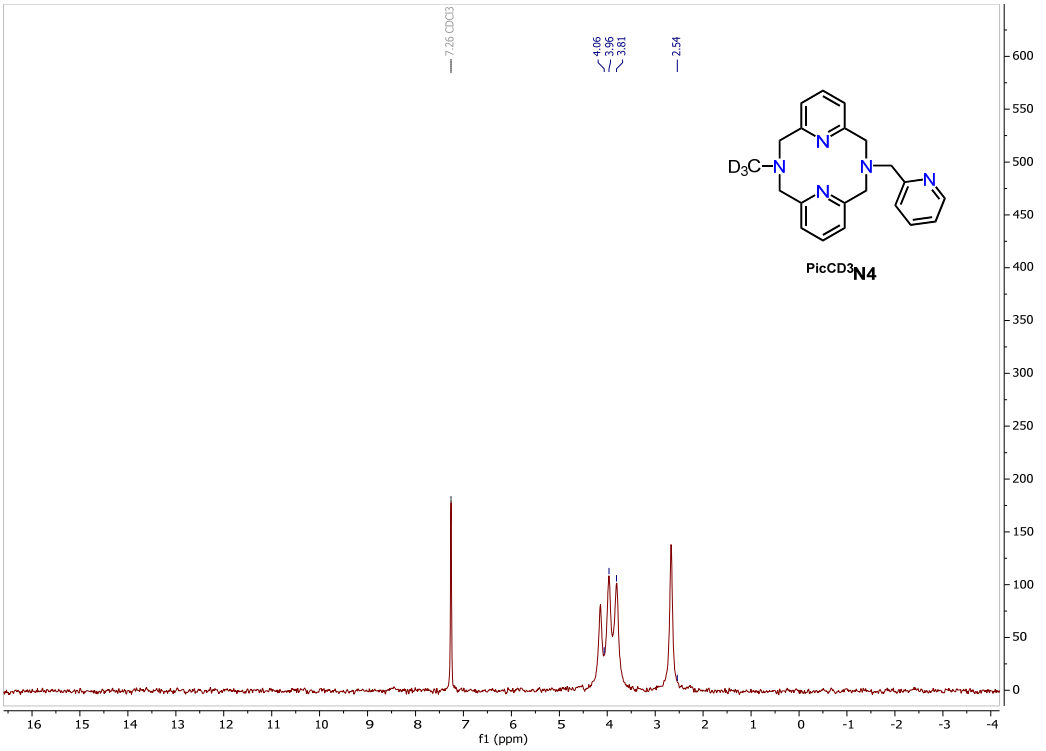


Figure S4. ^{2}H NMR spectrum of ^{PicCD3}N4, recorded at 500 MHz in $CHCl_3$, showing deuteration of aliphatic $–CH_2–$ groups of the pyridinophane macrocycle (at ~4 ppm).

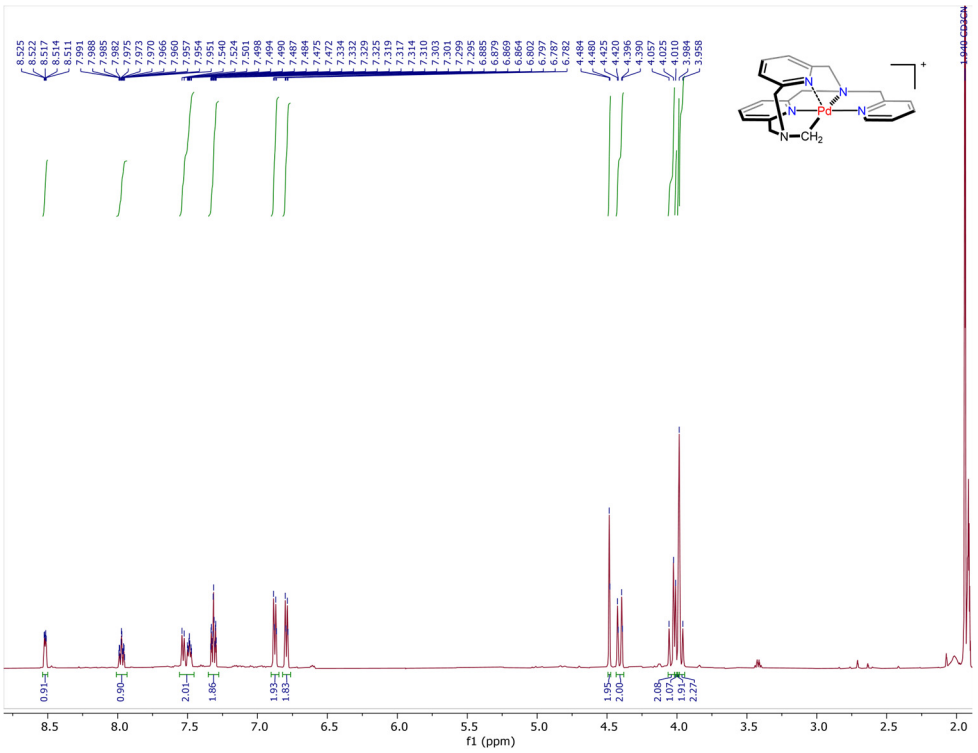


Figure S5. ^{1}H NMR spectrum of [(^{PicCH2}N4)Pd^{II}]BF$_4$ (**1**) recorded at 500 MHz in CD$_3$CN.

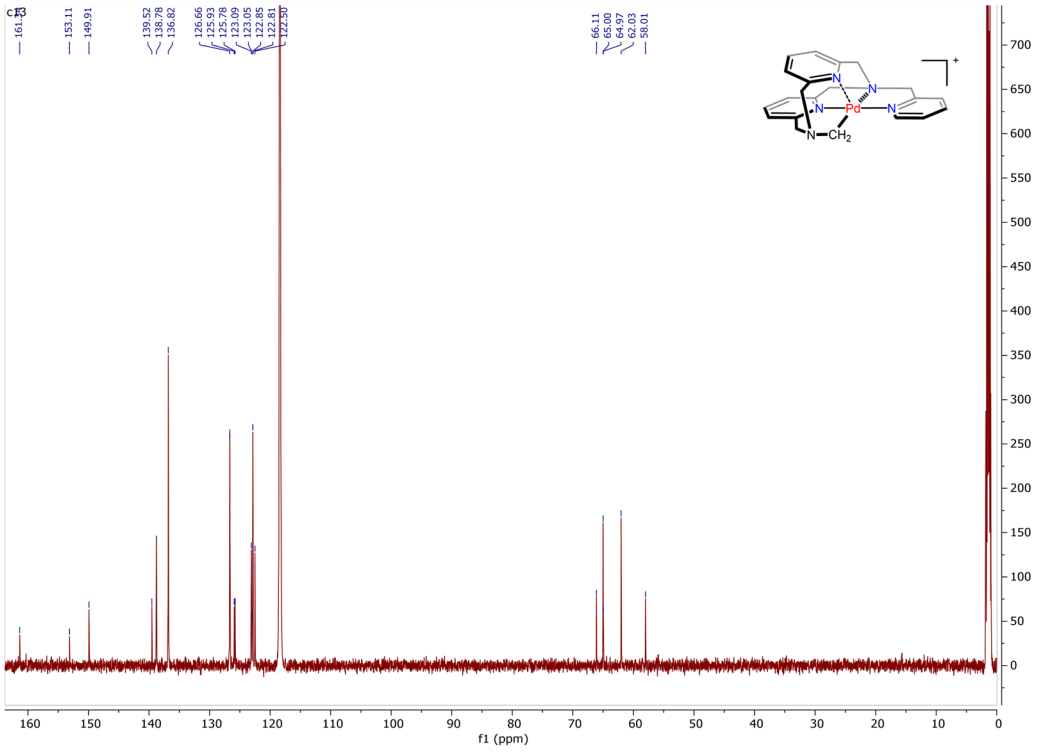


Figure S6. ^{13}C NMR spectrum of [(^{PicCH2}N4)Pd^{II}]BF$_4$ (**1**) recorded at 151 MHz in CD$_3$CN.

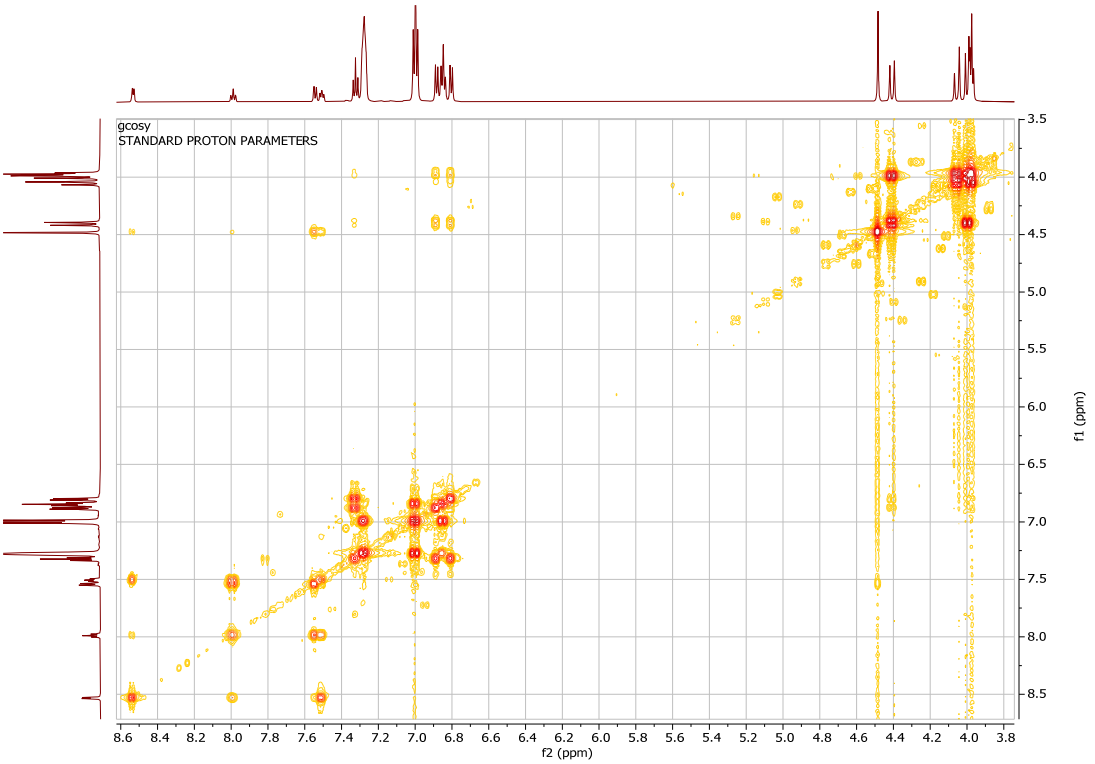


Figure S7. ^{1}H–^{1}H gCOSY NMR spectrum of [(^{PicCH2}N4)Pd^{II}]BF$_4$ (**1**).

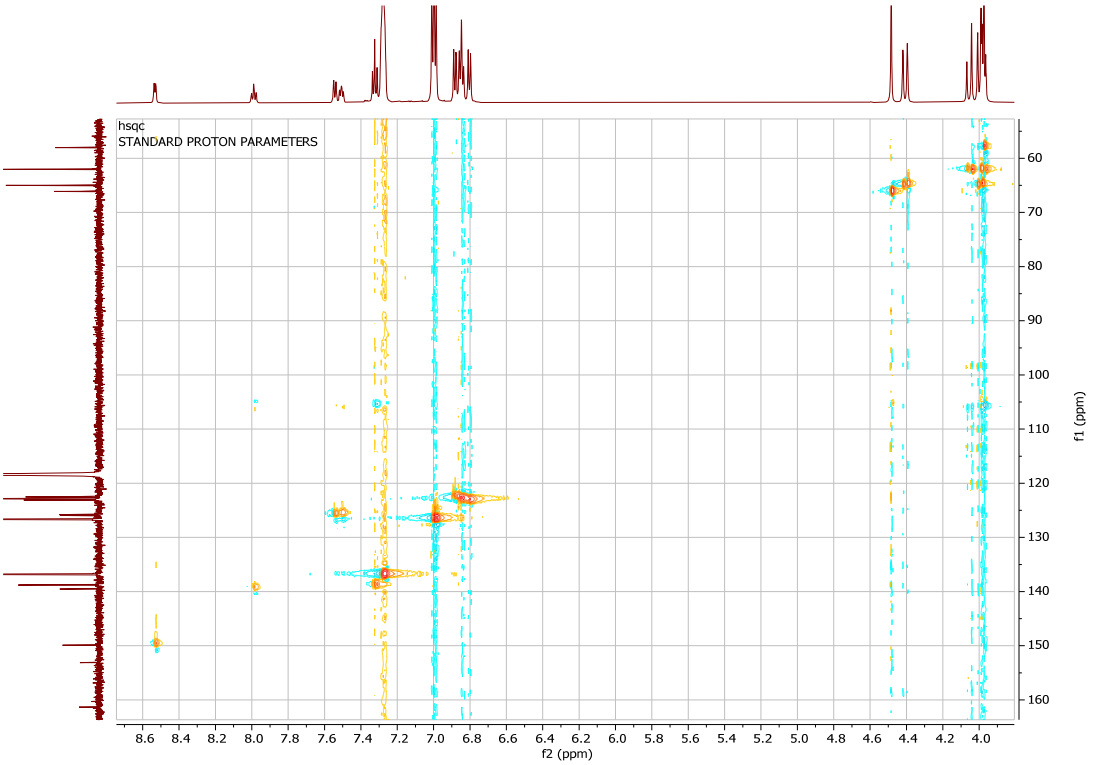


Figure S8. ^{1}H–^{13}C HSQC NMR spectrum of [(^{PicCH2}N4)Pd^{II}]BF$_4$ (**1**).

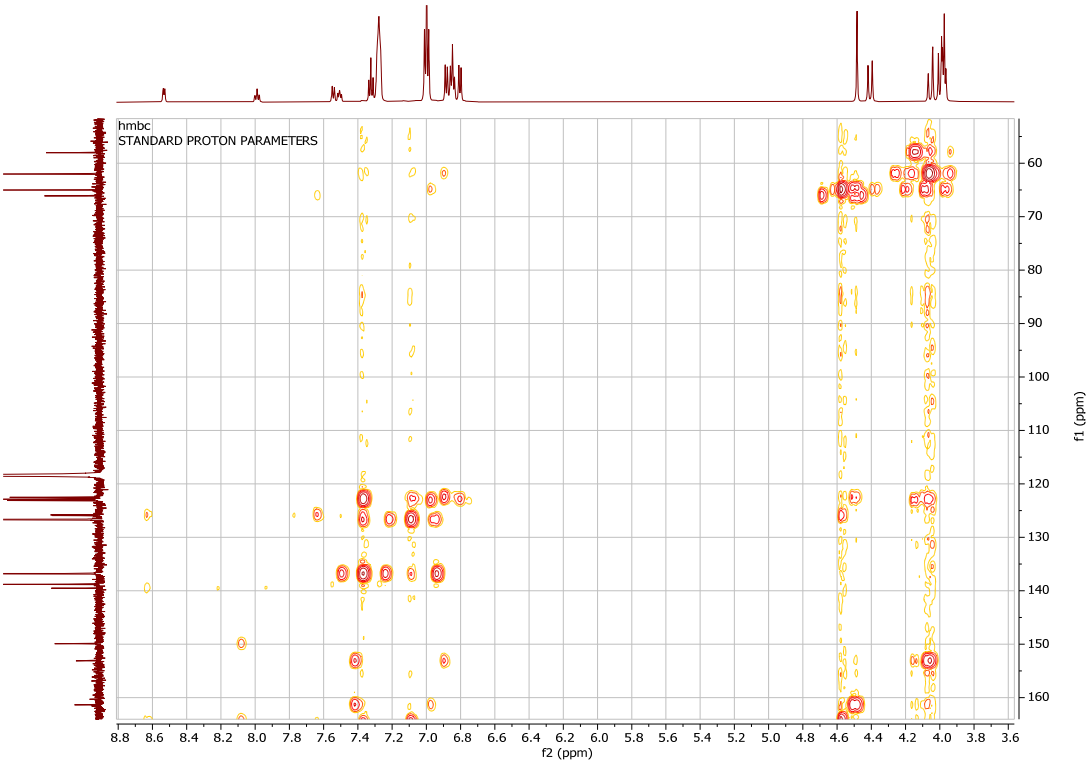


Figure S9. $^{1}H–^{13}C$ HMBC NMR spectrum of [(^{PicCH2}N4)Pd^{II}]BF_4 (**1**).

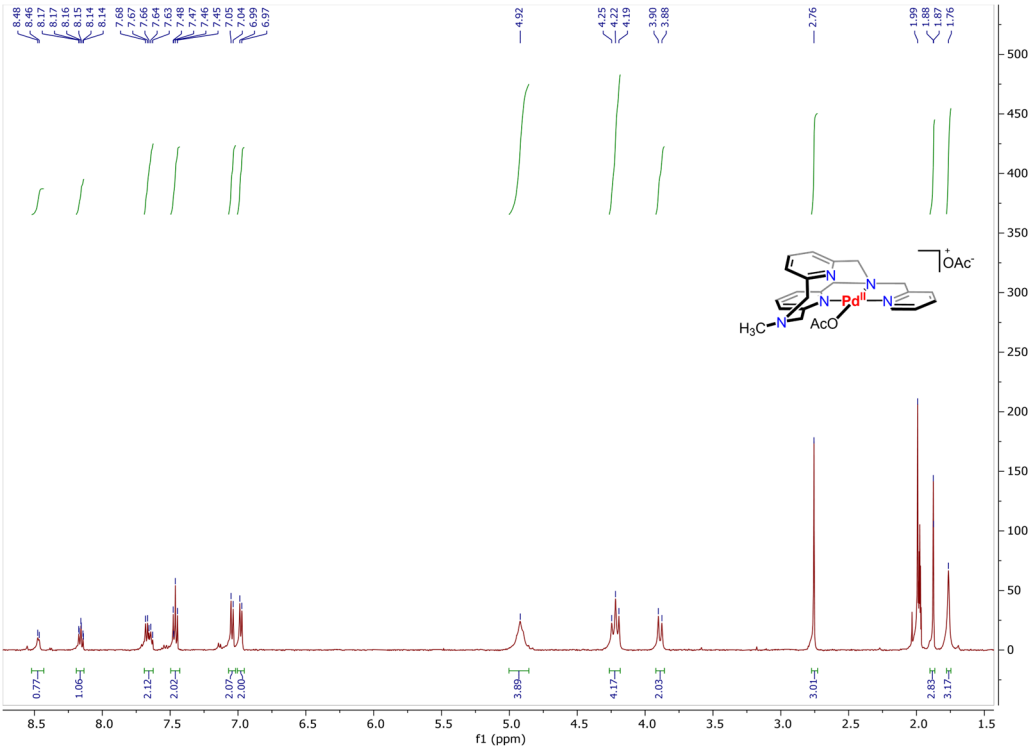


Figure S10. ^{1}H NMR spectrum of [(^{PicCH3}N4)Pd^{II}(OAc)]OAc (**2**) recorded at 500 MHz in CD_3CN.

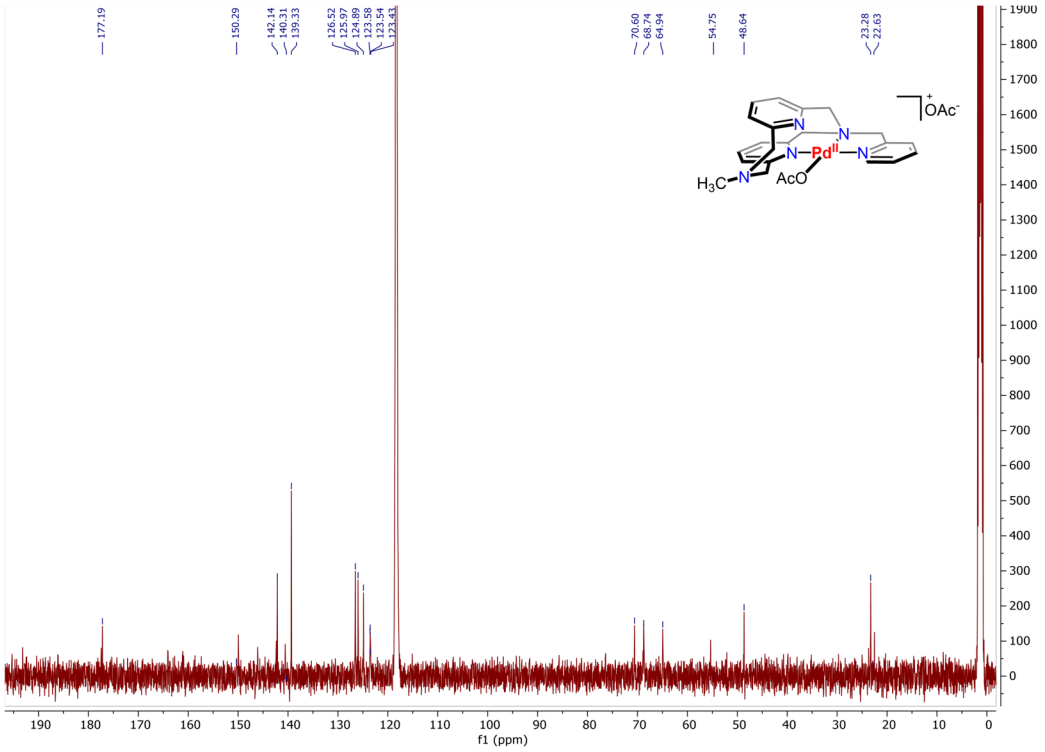


Figure S 11. ^{13}C NMR spectrum of [(^{PicCH3}N4)Pd^{II}(OAc)]OAc (**2**) recorded at 151 MHz in CD_3CN.

4. Cyclic voltammograms of Pd complexes

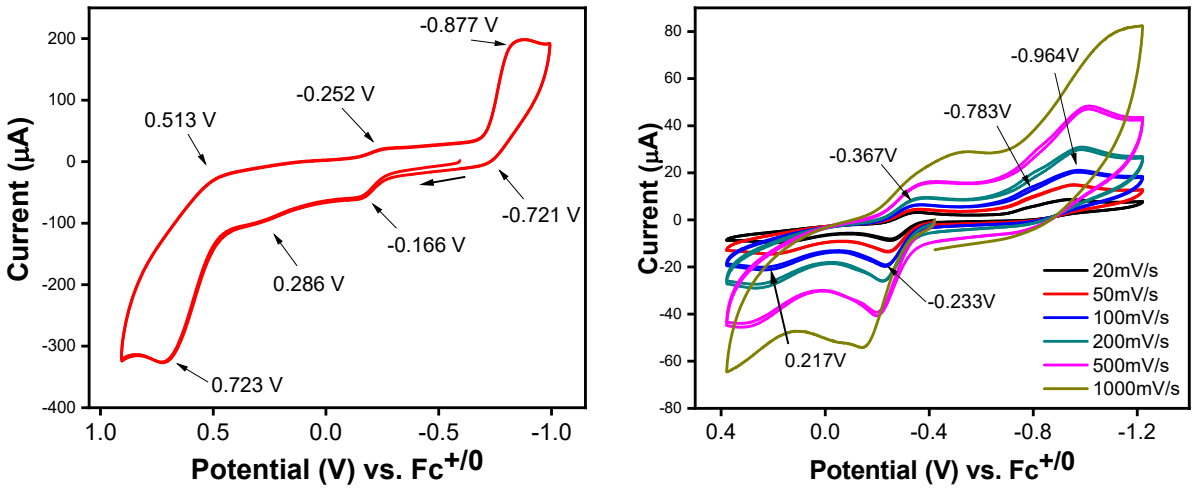


Figure S12. Cyclic voltammograms of [(^{PicCH2}N4)Pd^{II}]BF$_4$ (**1**), recorded at room temperature in 0.1 M Bu$_4$NClO$_4$ MeCN at 100 mV/s scan rate (left) and variable scan rate (right).

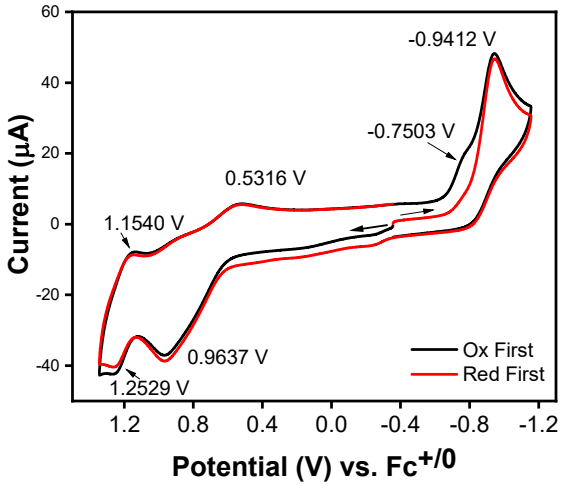


Figure S13. Cyclic voltammograms of *in-situ* generated [(^{PicCH3}N4)Pd^{II}]BF$_4$ (pre-activation), recorded at room temperature in 0.1 M Bu$_4$NClO$_4$ MeCN at scan rate 100 mV/s.

5. C–H activation studies

General procedures for the C–H activation studies in presence or absence of acetate: KIE determination and Eyring analysis

All kinetic experiments were monitored by ^{1}H and ^{2}H NMR spectroscopy. In a N_2-filled glove box, a solution of 5 mg of ^{PicCH3}N4 and 1 equiv NaOAc (or without any acetate) in 0.6 mL of MeCN-d_3 was added into a J. Young NMR tube containing 1 μL of tetramethylsilane as an internal standard. A ligand-only NMR was taken as a background at this point. Then, to the ligand solution 1 equiv of $[(MeCN)_4Pd^{II}](BF_4)_2$ dissolved in 0.1 mL MeCN-d_3 was injected, to generate a solution with a final concentration of 20 mM in Pd complex. The NMR tubes were taken out of the box and then kept at 63 °C and mixed vigorously to form a homogeneous solution, and then periodically monitored by a ^{1}H NMR array until no additional changes were observed. The average product yields and initial rates from at least three independent experiments were determined by NMR integration.

A similar procedure was performed for ^{2}H NMR studies. A solution of 5 mg of ^{PicCD3}N4 in 0.6 mL of MeCN was added to a J. Young tube, along with 1 equiv of NaOAc. The internal standard used was 1 μL of benzene-d_6. The ^{2}H NMR was taken initially for the ligand-only solution. Four-hundred scans were compiled with a one second delay time for each of the ^{2}H NMR spectra. The J. Young tube was brought back into a glovebox and 1 equiv of $[(MeCN)_4Pd^{II}](BF_4)_2$ dissolved in 0.1 mL MeCN was added, to generate a solution with a final concentration of 20 mM in Pd complex. The tubes were kept at 63 °C and mixed vigorously to form a homogeneous solution, and then monitored by the ^{2}H NMR array. For determining the product yield and the initial rate values, the methylene peak at ~4.5 ppm for ^{1}H NMR and ^{2}H NMR was integrated. The average product yields and the initial rates from at least three independent experiments were determined by NMR integration. Data fitting and analysis was performed with the software OriginPro.

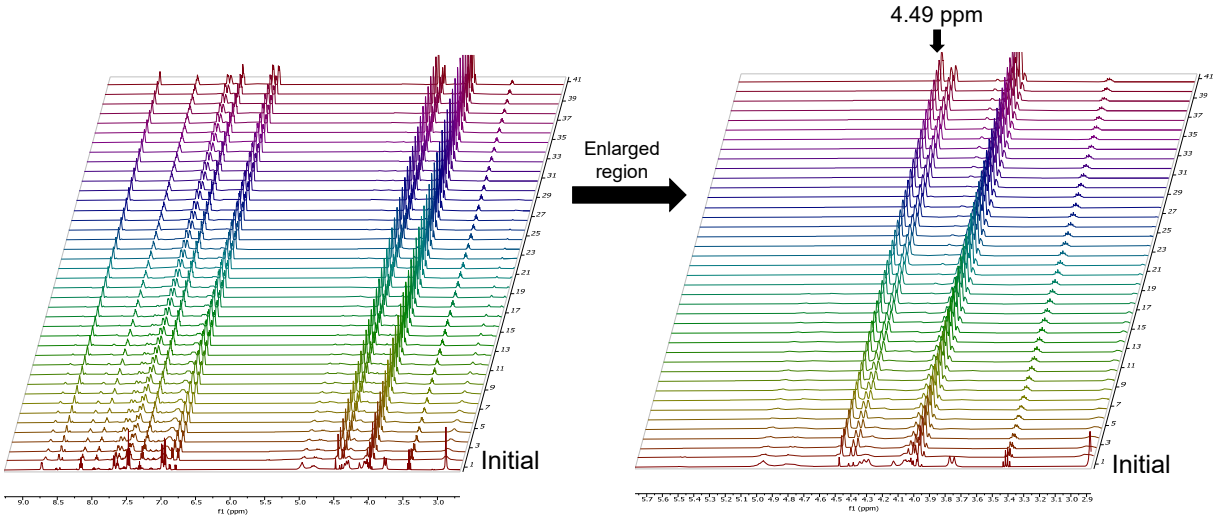


Figure S14. Representative time-resolved ^{1}H NMR spectra of reaction between $^{PicCH3}N4$ and $[Pd(MeCN)_4](BF_4)_2$ in the presence of NaOAc at 63 °C. Peak at 4.49 ppm was integrated for yield determination.

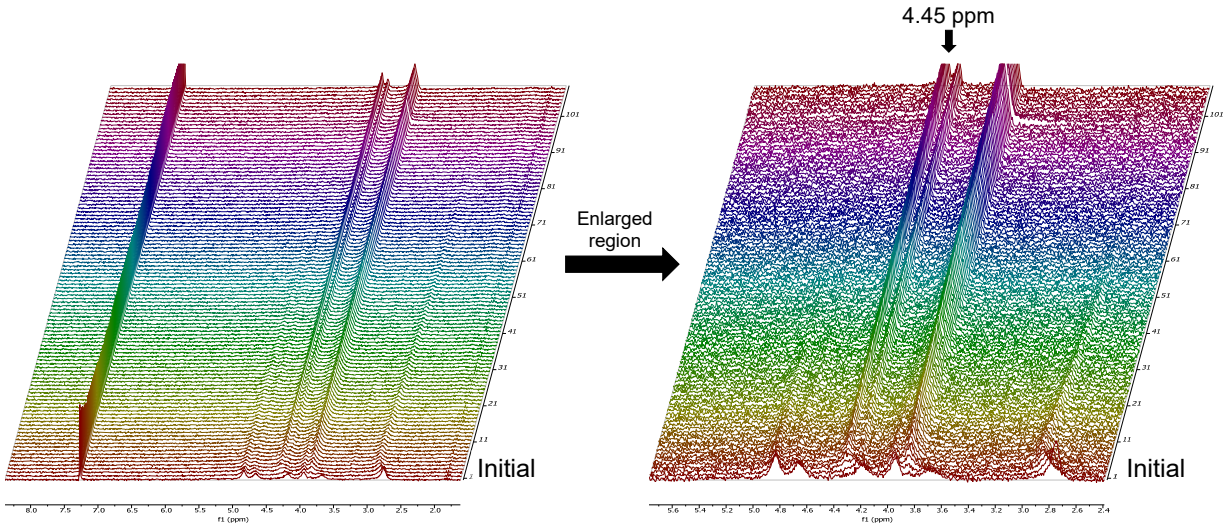


Figure S15. Representative time-resolved ^{2}H NMR spectra of reaction between $^{PicCD3}N4$ and $[Pd(MeCN)_4](BF_4)_2$ in the presence of NaOAc at 63 °C. Peak at 4.45 ppm was integrated for yield determination.

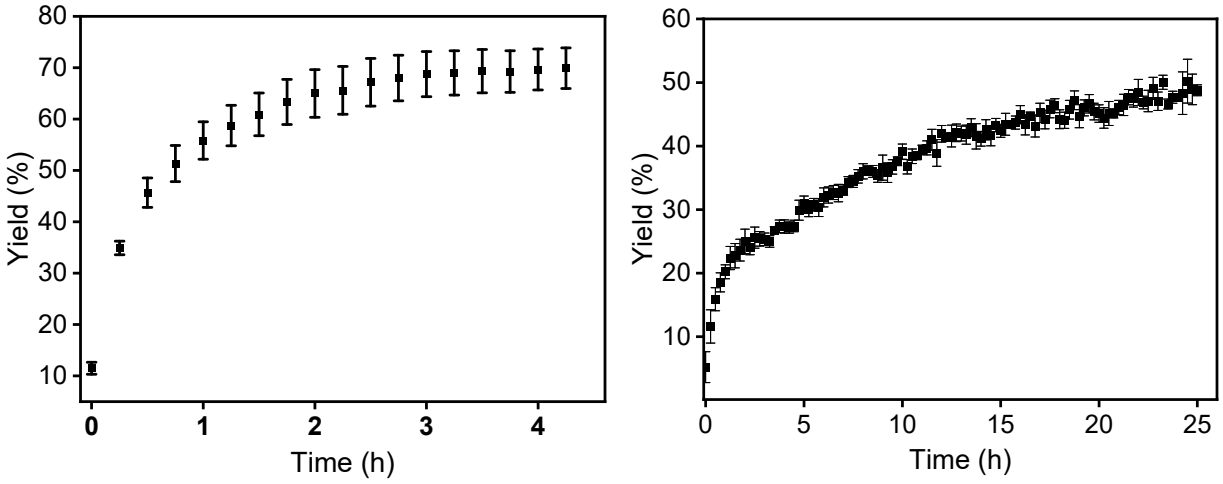


Figure S16. Representative kinetic traces for the reaction of (left) ^{PicCH3}N4 or (right) ^{PicCD3}N4 and $[Pd(MeCN)_4](BF_4)_2$ in the presence of NaOAc (collected at 63 °C), showing the formation of the C-H activated product, as monitored by ^{1}H NMR (left) and ^{2}H NMR (right). Initial rate analysis was performed to obtain the KIE value for this transformation. Note: The reaction of PicCD3N4 with [Pd(MeCN)4](BF4)2 takes longer times to reach completion, thus the initial rate method was employed.

Table S1. Initial rates for C-H activated product formation, obtained for $[(^{PicCH3}N4)Pd^{II}]^{2+}$ and $[(^{PicCD3}N4)Pd^{II}]^{2+}$ in MeCN in the presence of NaOAc at 63 °C, and KIE value and standard error determination.[2]

Complex	Initial rate (M h^{-1})	Average (standard error)	KIE (standard error)[2]
$[(^{Pic\mathbf{CH3}}N4)Pd^{II}]^{2+}$	0.015	0.0153 (0.0003)	**2.28 (0.39)**
	0.0152		
	0.0156		
$[(^{Pic\mathbf{CD3}}N4)Pd^{II}]^{2+}$	0.006	0.0067 (0.0011)	
	0.0061		
	0.008		

Eyring analysis

The plot of ln(k/T) as a function of 1/T was fitted according to the expression:

$$\ln\frac{k}{T} = -\frac{\Delta H^{\ddagger}}{R}\cdot\frac{1}{T} + \ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}$$

The enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation were extracted from the slope and intercept, respectively.

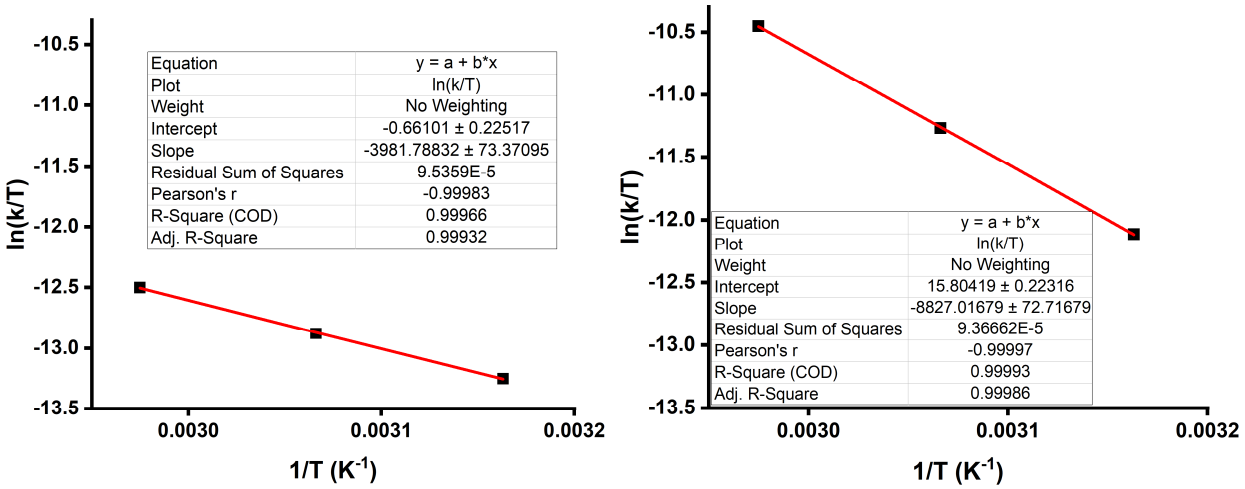


Figure S17. Eyring plots for the generation of **1** obtained from initial rate analysis (left) in absence of NaOAc and (right) in presence of NaOAc.

Effect of additives

General procedure for the C–H activation study with various additives

All experiments were monitored by NMR spectroscopy. In N_2-filled glove box, a solution of 5 mg of ^{PicCH3}N4 along with corresponding 1 equiv of additive in 0.6 mL of MeCN-d_3 was added into an NMR tube containing 1 μL of tetramethylsilane as an internal standard. A ligand-only NMR was taken as a background at this point. To this solution 6.4 mg of $[(MeCN)_4Pd^{II}](BF_4)_2$ (1 equiv) dissolved in 0.1 mL MeCN-d_3 was injected in the glovebox. The reaction mixtures were mixed vigorously fully to form homogeneous solutions and the ^{1}H NMR was taken to obtain an initial spectrum. The additive was then added and the sample was then kept at a constant temperature and periodically monitored by a ^{1}H NMR at different time points.

Table S2. Conditions for C–H Activation reaction

Additive	Equiv.	$^{PicCH3/CD3}$N4 H/D	Temp. (°C)	Time (h)	Formation of **1** (%)
Control	NA	H	25	60	40% [a]
	NA	H	50	24	39% [a]
	NA	H	70	24	Decomp.
	NA	D	25	25	Decomp.
NaOAc	1	H	25	73	43%
	1	H	63	3	82%
	1	D	63	24	80%
1,8-bis(dimethylamino)napthalene	1	H	25	24	0% [b]
Lithium Hexamethyldisilazide	1	H	25	0.5	Decomp.
Tetramethylammonium mesylamide	1	H	25	0.5	Decomp.
CsOPiv	1	H	25	60	0% [b]
	1	H	63	24	6%
AgOAc	1	H	25	60	0% [b]
	1	H	63	24	7%
TBAOAc	1	H	25	48	0% [b]
	1	H	63	48	0% [b]
	0.5	H	63	3	80%
$Pd(OAc)_2$ [c]	1	H	25	60	0% [b]
	1	H	63	24	0% [b]
$Pd(TFA)_2$ [c]	1	H	25	24	0% [b]

[a] The formation of up to 40% of protonated ^{PicCH3}N4 ligand was observed by NMR. [b] Other palladium product observed other than starting material or **1**. [c] All trials were run with $[(MeCN)_4Pd^{II}](BF_4)_2$ as the Pd source except for those with additive with alternative palladium sources: $Pd(OAc)_2$ and $Pd(TFA)_2$. NA: Not Applicable.

6. X-ray structure Characterization

General information: Suitable crystals were mounted on MiTeGen cryoloops in random orientations in a Bruker Kappa Apex-II CCD X-ray diffractometer equipped with an Oxford Cryostream LT device and a fine focus Mo Kα radiation X-ray source (λ = 0.71073 Å). Preliminary unit cell constants were determined with a set of 36 narrow frame scans. Typical data sets consist of combinations of ω and φ scan frames with a typical scan width of 0.5° and a counting time of 15−30 s/frame at a crystal-to-detector distance of 4.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages (Bruker Analytical X-Ray, Madison, WI, 2008) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of xyz centroids of reflections from the complete data sets. Collected data were corrected for systematic errors using SADABS (Bruker Analytical X-Ray, Madison, WI, 2008) based on the Laue symmetry using equivalent reflections. Crystal data and intensity data collection parameters are listed in Tables S3 and S4. Structure solutions and refinement were carried out using the SHELXTL-PLUS software package. The structures were solved by direct methods and refined successfully in specified crystal systems and space groups. Full matrix least-squares refinements were carried out by minimizing $\Sigma w(Fo^2-Fc^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. Typically, the hydrogen atoms were treated using the appropriate riding model. The deposition numbers CCDC 2226270 (**1**) and -2226271 (**2**) at the Cambridge Crystallographic Data Centre CCDC contain the supplementary crystallographic data. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

X-ray structure determination of [(^{PicCH2}N4)Pd^{II}]BF_4 (1).

Table S3. Crystal data and structure refinement for [(^{PicCH2}N4)Pd^{II}]BF_4 (**1**) **(lm8414)**

Identification code	l8414/lt/x8/AJW-N5Pd	
Empirical formula	C_{21} H_{22} B F_4 N_5 Pd	
Formula weight	537.64	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	a = 8.2212(6) Å	α = 75.751(4)°.
	b = 11.0718(9) Å	β = 89.961(5)°.
	c = 12.3446(11) Å	γ = 68.232(4)°.
Volume	1006.29(15) Å^3	
Z	2	
Density (calculated)	1.774 Mg/m^3	
Absorption coefficient	0.979 mm^{-1}	
F(000)	540	
Crystal size	0.234 x 0.231 x 0.082 mm^3	
Theta range for data collection	2.054 to 31.484°.	
Index ranges	-12≤h≤12, -16≤k≤16, -18≤l≤18	
Reflections collected	29820	
Independent reflections	6601 [R(int) = 0.0397]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8623 and 0.7767	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6601 / 21 / 290	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0245, wR2 = 0.0497	
R indices (all data)	R1 = 0.0260, wR2 = 0.0503	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.684 and -0.771 e.Å^{-3}	

Table S4. Bond length (Å) and angles (°) for [(^{PicCH2}N4)Pd^{II}]BF_4 (**1**)

Pd1—C7	2.017 (2)	C8—C9	1.385 (3)
Pd1—N1	2.0633 (17)	C8—H8	0.9500
Pd1—N2	2.0695 (18)	C9—C10	1.382 (4)
Pd1—N4	2.1677 (16)	C9—H9	0.9500
Pd1—N3	2.5495 (16)	C10—C11	1.382 (3)
N1—C5	1.339 (3)	C10—H10	0.9500
N1—C1	1.354 (3)	C11—C12	1.385 (3)
N2—C8	1.341 (3)	C11—H11	0.9500
N2—C12	1.361 (3)	C12—C13	1.506 (3)
N3—C19	1.339 (3)	C13—H13A	0.9900
N3—C15	1.344 (3)	C13—H13B	0.9900
N4—C21	1.473 (3)	C14—C15	1.512 (3)
N4—C13	1.481 (3)	C14—H14A	0.9900
N4—C14	1.492 (3)	C14—H14B	0.9900
N5—C7	1.431 (3)	C15—C16	1.382 (3)
N5—C6	1.444 (3)	C16—C17	1.394 (3)
N5—C20	1.475 (3)	C16—H16	0.9500
C1—C2	1.382 (3)	C17—C18	1.382 (4)
C1—C21	1.522 (3)	C17—H17	0.9500
C2—C3	1.386 (3)	C18—C19	1.391 (3)
C2—H2	0.9500	C18—H18	0.9500
C3—C4	1.380 (3)	C19—C20	1.523 (3)
C3—H3	0.9500	C20—H20A	0.9900
C4—C5	1.384 (3)	C20—H20B	0.9900
C4—H4	0.9500	C21—H21A	0.9900
C5—C6	1.525 (3)	C21—H21B	0.9900
C6—H6A	0.9900	F1—B1	1.377 (3)
C6—H6B	0.9900	F2—B1	1.395 (3)
C7—H7A	0.9900	F3—B1	1.399 (3)
C7—H7B	0.9900	F4—B1	1.385 (3)

C7—Pd1—N1	92.67 (8)	C10—C9—C8	119.2 (2)
C7—Pd1—N2	104.11 (8)	C10—C9—H9	120.4
N1—Pd1—N2	162.35 (6)	C8—C9—H9	120.4

C7—Pd1—N4	166.28 (7)	C9—C10—C11	118.8 (2)
N1—Pd1—N4	82.85 (7)	C9—C10—H10	120.6
N2—Pd1—N4	81.99 (7)	C11—C10—H10	120.6
C7—Pd1—N3	89.68 (7)	C10—C11—C12	119.2 (2)
N1—Pd1—N3	77.90 (6)	C10—C11—H11	120.4
N2—Pd1—N3	107.19 (6)	C12—C11—H11	120.4
N4—Pd1—N3	76.72 (6)	N2—C12—C11	122.18 (19)
C5—N1—C1	120.19 (17)	N2—C12—C13	117.06 (18)
C5—N1—Pd1	127.94 (14)	C11—C12—C13	120.68 (19)
C1—N1—Pd1	111.86 (13)	N4—C13—C12	110.35 (16)
C8—N2—C12	117.82 (19)	N4—C13—H13A	109.6
C8—N2—Pd1	129.46 (15)	C12—C13—H13A	109.6
C12—N2—Pd1	112.04 (14)	N4—C13—H13B	109.6
C19—N3—C15	118.61 (18)	C12—C13—H13B	109.6
C19—N3—Pd1	110.44 (12)	H13A—C13—H13B	108.1
C15—N3—Pd1	100.38 (12)	N4—C14—C15	109.83 (16)
C21—N4—C13	114.22 (17)	N4—C14—H14A	109.7
C21—N4—C14	113.59 (17)	C15—C14—H14A	109.7
C13—N4—C14	110.68 (17)	N4—C14—H14B	109.7
C21—N4—Pd1	104.31 (12)	C15—C14—H14B	109.7
C13—N4—Pd1	104.17 (12)	H14A—C14—H14B	108.2
C14—N4—Pd1	109.12 (12)	N3—C15—C16	122.40 (19)
C7—N5—C6	115.65 (17)	N3—C15—C14	114.12 (18)
C7—N5—C20	118.36 (17)	C16—C15—C14	122.92 (18)
C6—N5—C20	115.93 (17)	C15—C16—C17	118.49 (19)
N1—C1—C2	120.6 (2)	C15—C16—H16	120.8
N1—C1—C21	118.49 (17)	C17—C16—H16	120.8
C2—C1—C21	120.8 (2)	C18—C17—C16	119.12 (19)
C1—C2—C3	119.0 (2)	C18—C17—H17	120.4
C1—C2—H2	120.5	C16—C17—H17	120.4
C3—C2—H2	120.5	C17—C18—C19	118.7 (2)
C4—C3—C2	119.86 (19)	C17—C18—H18	120.6
C4—C3—H3	120.1	C19—C18—H18	120.6
C2—C3—H3	120.1	N3—C19—C18	122.16 (19)
C3—C4—C5	118.6 (2)	N3—C19—C20	115.59 (18)
C3—C4—H4	120.7	C18—C19—C20	121.8 (2)

C5—C4—H4	120.7	N5—C20—C19	114.40 (17)
N1—C5—C4	121.37 (19)	N5—C20—H20A	108.7
N1—C5—C6	119.02 (18)	C19—C20—H20A	108.7
C4—C5—C6	119.58 (19)	N5—C20—H20B	108.7
N5—C6—C5	117.48 (17)	C19—C20—H20B	108.7
N5—C6—H6A	107.9	H20A—C20—H20B	107.6
C5—C6—H6A	107.9	N4—C21—C1	113.30 (16)
N5—C6—H6B	107.9	N4—C21—H21A	108.9
C5—C6—H6B	107.9	C1—C21—H21A	108.9
H6A—C6—H6B	107.2	N4—C21—H21B	108.9
N5—C7—Pd1	110.08 (13)	C1—C21—H21B	108.9
N5—C7—H7A	109.6	H21A—C21—H21B	107.7
Pd1—C7—H7A	109.6	F1—B1—F4	110.8 (2)
N5—C7—H7B	109.6	F1—B1—F2	109.98 (19)
Pd1—C7—H7B	109.6	F4—B1—F2	110.15 (18)
H7A—C7—H7B	108.2	F1—B1—F3	108.85 (18)
N2—C8—C9	122.7 (2)	F4—B1—F3	109.38 (19)
N2—C8—H8	118.7	F2—B1—F3	107.7 (2)
C9—C8—H8	118.7		

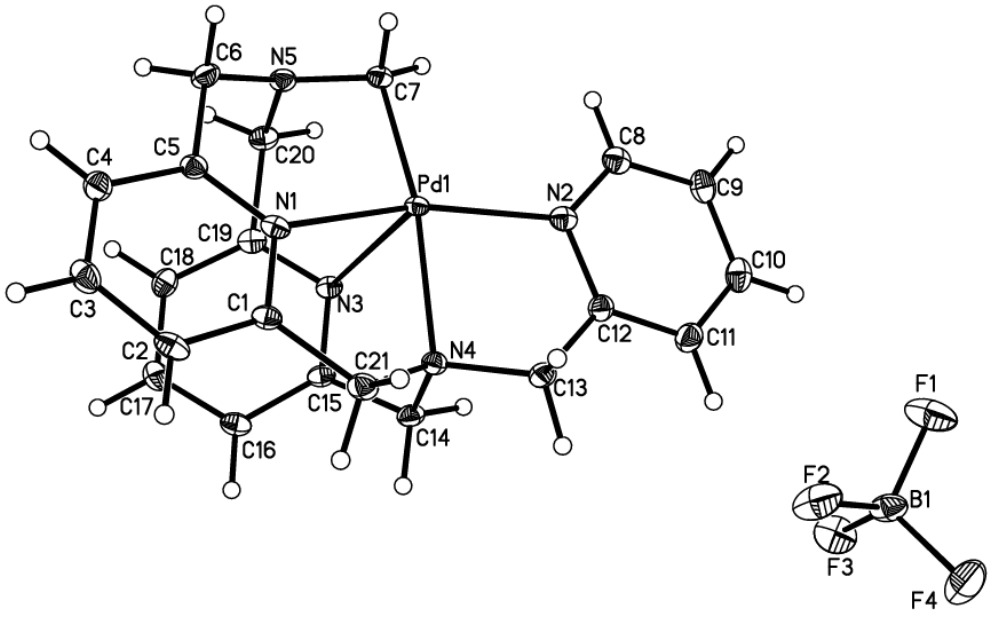


Figure S18. Projection view of of [(^{PicCH2}N4)Pd^{II}]BF$_4$ (**1**) with 50% probability thermal ellipsoids.

X-ray structure determination of [(^{PicCH3}N4)Pd^{II}OAc]OAc (2)

Table S5. Crystal data and structure refinement for [(^{PicCH3}N4)Pd^{II}OAc]OAc (**2**)

Identification code	l7317/lt/x8/AW-N5PdOac	
Empirical formula	C_{31} H_{41} N_5 O_7 Pd	
Formula weight	702.09	
Temperature	99(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.9182(3) Å	α = 90°.
	b = 19.5779(9) Å	β = 94.348(2)°.
	c = 20.2624(9) Å	γ = 90°.
Volume	3132.1(2) Å^3	
Z	4	
Density (calculated)	1.489 Mg/m^3	
Absorption coefficient	0.647 mm^{-1}	
F(000)	1456	
Crystal size	0.598 x 0.102 x 0.097 mm^3	
Theta range for data collection	1.448 to 35.995°.	
Index ranges	-8≤h≤12, -32≤k≤31, -32≤l≤32	
Reflections collected	108458	
Independent reflections	14216 [R(int) = 0.0562]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7471 and 0.6516	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14216 / 3 / 402	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0655	
R indices (all data)	R1 = 0.0624, wR2 = 0.0739	
Largest diff. peak and hole	0.660 and -1.056 e.Å^{-3}	

Table S6. Bond length (Å) and angles (°) for [(^{PicCH3}N4)Pd^{II}OAc]OAc (**2**)

Pd1—N3	1.9940 (12)	C15—C16	1.5027 (19)
Pd1—O1	2.0191 (10)	C15—H15A	0.9900
Pd1—N4	2.0220 (12)	C15—H15B	0.9900
Pd1—N1	2.0432 (12)	C16—C17	1.383 (2)
O1—C21	1.2990 (18)	C17—C18	1.387 (2)
O2—C21	1.2256 (19)	C17—H17	0.9500
N1—C1	1.3468 (19)	C18—C19	1.386 (2)
N1—C5	1.3589 (18)	C18—H18	0.9500
N2—C12	1.3342 (19)	C19—C20	1.381 (2)
N2—C8	1.3474 (19)	C19—H19	0.9500
N3—C20	1.3470 (18)	C20—H20	0.9500
N3—C16	1.3529 (19)	C21—C22	1.512 (2)
N4—C7	1.5036 (18)	C22—H22A	0.9800
N4—C15	1.5060 (18)	C22—H22B	0.9800
N4—C6	1.5070 (17)	C22—H22C	0.9800
N5—C23	1.470 (2)	C23—H23A	0.9800
N5—C13	1.4723 (19)	C23—H23B	0.9800
N5—C14	1.4747 (19)	C23—H23C	0.9800
C1—C2	1.392 (2)	O1S—C1S	1.424 (2)
C1—C14	1.516 (2)	O1S—C4S	1.428 (2)
C2—C3	1.386 (2)	C1S—C2S	1.520 (3)
C2—H2	0.9500	C1S—H1SA	0.9900
C3—C4	1.386 (2)	C1S—H1SB	0.9900
C3—H3	0.9500	C2S—C3S	1.540 (3)
C4—C5	1.3820 (19)	C2S—H2SA	0.9900
C4—H4	0.9500	C2S—H2SB	0.9900
C5—C6	1.506 (2)	C3S—C4S	1.518 (3)
C6—H6A	0.9900	C3S—H3SA	0.9900
C6—H6B	0.9900	C3S—H3SB	0.9900
C7—C8	1.506 (2)	C4S—H4SA	0.9900
C7—H7A	0.9900	C4S—H4SB	0.9900
C7—H7B	0.9900	O3—C24	1.2384 (19)
C8—C9	1.386 (2)	O4—C24	1.281 (2)
C9—C10	1.393 (2)	C24—C25	1.512 (2)
C9—H9	0.9500	C25—H25A	0.9800

C10—C11	1.380 (2)	C25—H25B	0.9800
C10—H10	0.9500	C25—H25C	0.9800
C11—C12	1.399 (2)	O5—C26	1.298 (2)
C11—H11	0.9500	O5—H5	0.8400
C12—C13	1.508 (2)	O6—C26	1.225 (2)
C13—H13A	0.9900	C26—C27	1.503 (2)
C13—H13B	0.9900	C27—H27A	0.9800
C14—H14A	0.9900	C27—H27B	0.9800
C14—H14B	0.9900	C27—H27C	0.9800

N3—Pd1—O1	90.14 (5)	N4—C15—H15A	109.6
N3—Pd1—N4	84.13 (5)	C16—C15—H15B	109.6
O1—Pd1—N4	171.82 (5)	N4—C15—H15B	109.6
N3—Pd1—N1	167.46 (5)	H15A—C15—H15B	108.1
O1—Pd1—N1	102.01 (5)	N3—C16—C17	120.72 (13)
N4—Pd1—N1	83.46 (5)	N3—C16—C15	116.21 (12)
C21—O1—Pd1	116.03 (9)	C17—C16—C15	122.90 (13)
C1—N1—C5	119.48 (12)	C16—C17—C18	119.33 (14)
C1—N1—Pd1	130.38 (10)	C16—C17—H17	120.3
C5—N1—Pd1	110.02 (9)	C18—C17—H17	120.3
C12—N2—C8	118.02 (13)	C19—C18—C17	119.55 (14)
C20—N3—C16	119.99 (12)	C19—C18—H18	120.2
C20—N3—Pd1	127.21 (10)	C17—C18—H18	120.2
C16—N3—Pd1	112.79 (9)	C20—C19—C18	118.69 (14)
C7—N4—C15	107.75 (11)	C20—C19—H19	120.7
C7—N4—C6	112.84 (11)	C18—C19—H19	120.7
C15—N4—C6	110.75 (11)	N3—C20—C19	121.61 (14)
C7—N4—Pd1	116.47 (9)	N3—C20—H20	119.2
C15—N4—Pd1	105.89 (8)	C19—C20—H20	119.2
C6—N4—Pd1	102.90 (8)	O2—C21—O1	124.79 (14)
C23—N5—C13	108.70 (11)	O2—C21—C22	121.68 (14)
C23—N5—C14	108.89 (12)	O1—C21—C22	113.53 (13)
C13—N5—C14	112.61 (12)	C21—C22—H22A	109.5
N1—C1—C2	120.22 (13)	C21—C22—H22B	109.5
N1—C1—C14	119.96 (12)	H22A—C22—H22B	109.5
C2—C1—C14	119.78 (13)	C21—C22—H22C	109.5

C3—C2—C1	120.25 (14)	H22A—C22—H22C	109.5
C3—C2—H2	119.9	H22B—C22—H22C	109.5
C1—C2—H2	119.9	N5—C23—H23A	109.5
C2—C3—C4	118.81 (14)	N5—C23—H23B	109.5
C2—C3—H3	120.6	H23A—C23—H23B	109.5
C4—C3—H3	120.6	N5—C23—H23C	109.5
C5—C4—C3	118.80 (14)	H23A—C23—H23C	109.5
C5—C4—H4	120.6	H23B—C23—H23C	109.5
C3—C4—H4	120.6	C1S—O1S—C4S	104.62 (13)
N1—C5—C4	121.88 (13)	O1S—C1S—C2S	105.68 (14)
N1—C5—C6	115.99 (12)	O1S—C1S—H1SA	110.6
C4—C5—C6	122.13 (13)	C2S—C1S—H1SA	110.6
C5—C6—N4	110.51 (11)	O1S—C1S—H1SB	110.6
C5—C6—H6A	109.5	C2S—C1S—H1SB	110.6
N4—C6—H6A	109.5	H1SA—C1S—H1SB	108.7
C5—C6—H6B	109.5	C1S—C2S—C3S	103.28 (14)
N4—C6—H6B	109.5	C1S—C2S—H2SA	111.1
H6A—C6—H6B	108.1	C3S—C2S—H2SA	111.1
N4—C7—C8	112.17 (11)	C1S—C2S—H2SB	111.1
N4—C7—H7A	109.2	C3S—C2S—H2SB	111.1
C8—C7—H7A	109.2	H2SA—C2S—H2SB	109.1
N4—C7—H7B	109.2	C4S—C3S—C2S	103.97 (14)
C8—C7—H7B	109.2	C4S—C3S—H3SA	111.0
H7A—C7—H7B	107.9	C2S—C3S—H3SA	111.0
N2—C8—C9	122.93 (14)	C4S—C3S—H3SB	111.0
N2—C8—C7	115.43 (12)	C2S—C3S—H3SB	111.0
C9—C8—C7	121.47 (13)	H3SA—C3S—H3SB	109.0
C8—C9—C10	118.68 (14)	O1S—C4S—C3S	106.07 (15)
C8—C9—H9	120.7	O1S—C4S—H4SA	110.5
C10—C9—H9	120.7	C3S—C4S—H4SA	110.5
C11—C10—C9	118.52 (14)	O1S—C4S—H4SB	110.5
C11—C10—H10	120.7	C3S—C4S—H4SB	110.5
C9—C10—H10	120.7	H4SA—C4S—H4SB	108.7
C10—C11—C12	119.25 (15)	O3—C24—O4	122.80 (16)
C10—C11—H11	120.4	O3—C24—C25	119.46 (16)
C12—C11—H11	120.4	O4—C24—C25	117.74 (14)

N2—C12—C11	122.37 (14)	C24—C25—H25A	109.5
N2—C12—C13	116.82 (13)	C24—C25—H25B	109.5
C11—C12—C13	120.73 (14)	H25A—C25—H25B	109.5
N5—C13—C12	112.03 (12)	C24—C25—H25C	109.5
N5—C13—H13A	109.2	H25A—C25—H25C	109.5
C12—C13—H13A	109.2	H25B—C25—H25C	109.5
N5—C13—H13B	109.2	C26—O5—H5	109.5
C12—C13—H13B	109.2	O6—C26—O5	124.62 (15)
H13A—C13—H13B	107.9	O6—C26—C27	121.26 (15)
N5—C14—C1	112.07 (12)	O5—C26—C27	114.07 (14)
N5—C14—H14A	109.2	C26—C27—H27A	109.5
C1—C14—H14A	109.2	C26—C27—H27B	109.5
N5—C14—H14B	109.2	H27A—C27—H27B	109.5
C1—C14—H14B	109.2	C26—C27—H27C	109.5
H14A—C14—H14B	107.9	H27A—C27—H27C	109.5
C16—C15—N4	110.18 (11)	H27B—C27—H27C	109.5
C16—C15—H15A	109.6		

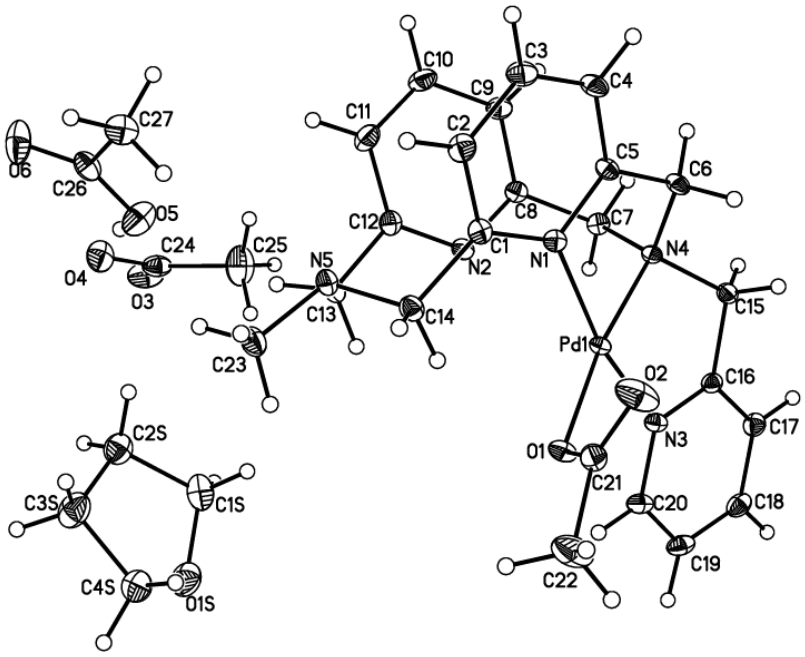


Figure S19. Projection view of of [(^{PicCH3}N4)Pd^{II}OAc]OAc (**2**) with 50% probability thermal ellipsoids.

7. Computational Details

All density functional theory (DFT) calculations were carried out employing the Jaguar 9.1 quantum chemistry program.[2] Electronic exchange and correlation energy contribution to the total electronic energy was approximated with B3LYP hybrid functional[3-4] along with Grimme's D3 dispersion correction (B3LYP-D3).[5] All intermediate and transition state geometries were optimized with 6-31G** basis set for main group atoms.[5-7] Pd were described by Los Alamos relativistic effective core potentials (ECP) and its corresponding LACVP basis set.[8-10] While these basis sets are adequate for obtaining accurate geometries, more reliable energies and EPR parameters were obtained from single point calculations using Dunning's correlation-consistent triple-ζ basis set, cc-pVTZ(-f)[11] for main group and larger LACV3P** for Pd.[12] The zero-point energy (ZPE), entropic and solvation contributions to the Gibbs energy are obtained from the same level of theory as the geometry optimizations (B3LYP-D3/6-31G**/LACVP) at 298 K. The solvation calculations utilized self-consistent reaction field (SCRF) approach on the gas phase geometry to model the solvation shell of dielectric constant ε = 37.5.[13]

The free energy in the solution phase G(sol) reported in these studies were calculated as follows:

G(sol) = G(gas) + G(solv)

G(gas) = H(gas) -TS(gas)

H(gas) = H(SCF) + ZPE

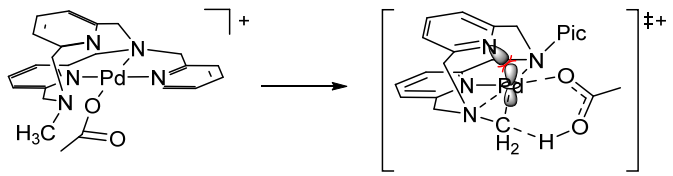
G(gas) = free energy in gas phase; G(solv) = free energy of solvation as computed using the continuum solvation model (the entropy of the solvent is implicitly included in this model); H(gas) = enthalpy in gas phase; S(gas) = entropy in gas phase; H(SCF) = Self-consistent field energy, i.e. electronic energy as computed from the SCF procedure; ZPE = zero point energy

Concerted Metalation Deprotonation (CMD)

The alternative C–H activation process through CMD is examined using computation as shown in Figure S21. The calculation results reveal that the CMD requires 37.1 kcal/mol energy which is insurmountable barrier in the reaction condition.

Computed energy components for DFT-optimized structures

	E(SCF)/(eV)	ZPE/(kcal/mol)	S(gas)/(cal/mol)	G(solv)/(kcal/mol)
	cc-pVTZ(-f)/LACV3P	6-31G**/LACVP	6-31G**/LACVP	6-31G**/LACVP
Acetonitrile	-3613.765	28.48	57.933	-8.12
Acetate	-6220.609	30.19	68.821	-74.42
Acetic_acid	-6236.253	38.91	68.415	-8.65
^{PicCH3}**N4**	-29611.291	258.038	154.782	-14.29
Protonated_ligand	-29622.475	267.545	155.647	-50.12
2	-39277.109	293.46	179.961	-51.93
A1	-36663.151	291.3	177.269	-136.22
A2	-33048.153	261.71	148.704	-145.28
A3	-33047.718	260.49	149.913	-145.39
A3-TS'	-33047.296	259.03	148.733	-143.17
A3-TS	-33047.474	259.35	148.824	-146.18
A4	-33047.651	259.96	151.343	-147.15
A4-TS	-33047.414	259.4	148.312	-144.86
A5	-33047.883	260.36	147.31	-142.48
A5-TS	-62660.918	519.121	248.162	-121.41
A6	-39276.208	291.67	182.838	-49.73
A6-TS	-39276.211	291.38	178.049	-48.98
A7	-39276.864	293.17	186.392	-45.60
1	-33040.394	253.37	148.982	-42.53
2-TS	-39275.593	289.8	175.591	-47.45



2 (0.00) **2-TS** (37.08)

Figure S20. A calculated concerted metalation deprotonation (CMD) process in which the Pd-bound acetate promotes C(sp^3)-H bond activation.

Cartesian Coordinates of the Optimized Geometries

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Acetonitrile

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C	5.192547321	-1.964493513	-1.168555737
N	5.192404270	-1.964488864	-2.328603983
C	5.192533493	-1.964498043	0.292607397
H	6.218322277	-1.964491606	0.672552407
H	4.679591656	-2.852859020	0.672375560
H	4.679596424	-1.076132774	0.672359109

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Acetate

==========

O	-2.456018686	1.513437748	-2.469693422
O	-2.186069250	3.280153990	-1.057450175
C	-2.767987967	2.616344690	-1.952748060
C	-4.058975220	3.291466713	-2.551501036
H	-3.779957771	3.921880722	-3.409461498
H	-4.769812107	2.540175200	-2.919814110
H	-4.549242973	3.942715883	-1.816123486

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Acetic_acid

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O	-2.573490620	1.402518630	-2.169728756
O	-2.093296528	3.391219139	-1.224385619
C	-2.838555336	2.572801113	-2.010340214
C	-3.996449947	3.315481186	-2.629037857
H	-3.622177362	4.149710178	-3.229981422
H	-4.574927330	2.633948565	-3.251428127
H	-4.628551960	3.738858461	-1.842954993
H	-1.374032021	2.842638493	-0.868989706

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PicCH3N4

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N	-1.047486186	0.517344534	-4.663683891
N	1.692094326	0.505089521	-2.408634901
N	-4.142249107	-0.445642620	-4.113167286
C	0.182006344	0.085517049	-4.352771759
C	-1.923623085	-0.361342013	-5.165124416
C	0.793186367	0.567080677	-1.237172127
C	1.092832685	1.066067219	-3.634379387
C	-3.367320538	0.091637798	-5.245789528
C	-3.769048691	0.147207782	-2.810504198
C	-5.590637684	-0.390928835	-4.337996960
C	-2.579147577	-0.534166813	-2.154435873
C	-0.417586654	-0.332237303	-1.379125476
C	-2.580770016	-1.914235353	-1.924727201
H	-3.453664541	-2.501300335	-2.188498974
C	-1.442038655	-2.502083540	-1.381090522
C	-0.328755468	-1.703565359	-1.124908209
H	0.599961996	-2.130291939	-0.758512020
H	1.379782438	0.248029321	-0.368008643
H	0.442050755	1.596695900	-1.049790621
H	1.918455958	1.329322577	-4.307110786
C	0.612227976	-1.217633247	-4.618947983
H	1.610914946	-1.520776868	-4.323340893
C	-0.279965162	-2.109044790	-5.209833622
C	-1.579992890	-1.682345271	-5.468783855
H	-2.330457687	-2.362200737	-5.860486984
H	-3.824382782	-0.293235540	-6.164420605

H	-3.538858891	1.218590617	-2.898344040
H	-4.635203362	0.050468702	-2.146635056
H	-3.390565157	1.192903519	-5.285501480
H	-6.030607700	0.605806649	-4.172827244
H	-5.775536537	-0.658430636	-5.385624409
C	-6.309852123	-1.388675809	-3.449990749
C	-5.930818081	-2.739451647	-3.472192287
C	-6.589341164	-3.638510466	-2.640766382
C	-7.907947063	-1.801245093	-1.855903983
C	-7.604772091	-3.160128593	-1.809072375
H	-5.117945194	-3.050046206	-4.120427132
H	-6.317285061	-4.690637589	-2.635400772
H	-8.687174797	-1.390470266	-1.216083288
H	-8.143264771	-3.821393013	-1.137303710
N	-7.280457497	-0.922992289	-2.652894735
H	0.022888027	-3.129117727	-5.431004047
H	-1.411975265	-3.570656776	-1.184766769
N	-1.535336971	0.244002208	-1.842171669
C	2.964792013	1.150106549	-2.097171783
H	3.421338320	0.664420128	-1.228139758
H	3.652540684	1.038695931	-2.941624641
H	2.872485876	2.229496002	-1.871580839
H	0.519529939	1.986099958	-3.442640066

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Protonated_ligand

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N	-0.936240315	0.506787539	-4.798796654
N	0.715972662	1.293849707	-2.501402855
N	-4.117844105	-0.268848121	-4.155380726
C	0.291620284	0.010754540	-4.570031166
C	-1.897929072	-0.332349211	-5.189271927
C	0.842759728	0.124881372	-1.548700333
C	1.223100781	0.995287955	-3.907760859
C	-3.312948227	0.210507482	-5.283225060
C	-3.781062126	0.376524538	-2.874244690
C	-5.568435669	-0.339900732	-4.409223080
C	-2.724512100	-0.414094597	-2.129344940
C	-0.506584227	-0.581630349	-1.487331986
C	-2.976212025	-1.713338494	-1.669738650
H	-3.963651419	-2.142646313	-1.799273491
C	-1.942592263	-2.436852694	-1.082532883
C	-0.663922787	-1.874618053	-1.005379915
H	0.176470205	-2.433676720	-0.605896473
H	1.632999182	-0.543034911	-1.897954345
H	1.137342334	0.515706360	-0.571018100
H	2.251602173	0.637399673	-3.821545362
C	0.639263093	-1.317659497	-4.787246227
H	1.648069620	-1.671285033	-4.596920967
C	-0.360136360	-2.189048529	-5.237451077
C	-1.645978212	-1.696760535	-5.413398743
H	-2.461536407	-2.349571705	-5.705807209
H	-3.771876097	-0.155995175	-6.206989288
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H	-5.710131645	-0.653110206	-5.447669506
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C	-6.809690952	-3.623032093	-2.936301947
C	-7.147753239	-1.790502667	-1.431619763
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H	-6.880478859	-4.676906109	-3.189500570
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H	-7.687392235	-3.826493263	-0.964096010
N	-6.636663437	-0.903985560	-2.297183037
H	-0.135286242	-3.235272646	-5.420365334
H	-2.116501808	-3.443294525	-0.714280725
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H	1.211498737	1.947297096	-4.442050457
H	-0.340383381	1.368784666	-2.580522299

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N	-3.693683863	-0.206020370	-3.813885212
C	0.263440639	-0.011747099	-4.770107746
C	-1.869542480	-0.708310187	-5.452190876
C	0.922103405	-0.827017486	-1.907551289
C	1.095316648	0.771630526	-3.775975466
C	-3.366711855	-0.597226560	-5.226763725
C	-3.753393650	-1.375292659	-2.864780188
C	-4.967514038	0.583524644	-3.710508585
C	-2.426243544	-2.087359905	-2.744362116
C	-0.181708708	-1.793176293	-2.316736937
C	-2.242643356	-3.402489185	-3.169881344
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C	-0.947726846	-3.925368309	-3.132915974
C	0.100432552	-3.103060961	-2.728631258
H	1.125825882	-3.459932327	-2.746477842
H	1.899613380	-1.239628911	-2.219006300
H	0.939343750	-0.792968750	-0.812531829
H	2.160711288	0.539433837	-3.961646318
C	0.852271795	-0.880013704	-5.691491604
H	1.933533907	-0.952450991	-5.732963562
C	0.051225618	-1.663943887	-6.515949249
C	-1.333595634	-1.604443789	-6.369689465
H	-1.988382101	-2.250365257	-6.944758415
H	-3.864599943	-1.536623120	-5.497065067
H	-4.045438290	-0.964932442	-1.894080520
H	-4.540734291	-2.059502363	-3.207723379
H	-3.756448984	0.189221919	-5.880491734
H	-5.064692974	1.179244757	-4.623327255
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N	-3.700627804	2.105564594	-2.311677456
H	0.498828799	-2.345084429	-7.232889175
H	-0.756699860	-4.946124554	-3.450239658
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H	0.897361934	1.394524813	-0.487571388

H	2.373758793	1.538532138	-1.473381877
H	0.930311143	2.533595562	-1.839712262
H	0.943641603	1.836596847	-3.972215414
O	-1.029079556	2.899168015	-3.201198816
C	-1.320369601	3.797998667	-4.127612591
O	-2.176368952	3.649260998	-4.994538307
C	-0.484708369	5.061771393	-4.004898548
H	-0.764780998	5.600163937	-3.093513966
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A1

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N	-3.596498251	-2.157777786	-2.829760790
C	-0.077289566	-1.009353399	-4.782787800
C	-2.002515316	-2.352634430	-4.736511230
C	0.715454578	-0.230757281	-1.780819535
C	0.579679132	0.231685117	-4.247869492
C	-3.385972738	-2.660902262	-4.180044651
C	-3.135205269	-3.039681673	-1.753343701
C	-4.872484207	-1.502652407	-2.605239630
C	-1.618655205	-3.019219160	-1.677825809
C	0.245482892	-1.664543867	-1.731370211
C	-0.832841098	-4.173347473	-1.732960582
H	-1.297587633	-5.154360294	-1.755372286
C	0.555482566	-4.036577225	-1.780910730
C	1.111610532	-2.755969524	-1.808308244
H	2.184457302	-2.613248587	-1.891775608
H	1.803915620	-0.167523056	-1.899350643
H	0.447084665	0.260351002	-0.842087686
H	1.670811415	0.122502051	-4.229964256
C	0.591632187	-1.911608219	-5.598101139
H	1.623685598	-1.728131175	-5.876619339
C	-0.081562713	-3.054525852	-6.027048588
C	-1.372686267	-3.283225775	-5.566159725
H	-1.897100091	-4.197894096	-5.822636127
H	-3.535792112	-3.749310970	-4.244026661
H	-3.538232803	-2.659706354	-0.809038222
H	-3.501289368	-4.071666241	-1.872323275
H	-4.124562740	-2.219776630	-4.858052731
H	-5.741533279	-2.178941965	-2.662669659
H	-4.862589836	-1.086804152	-1.589965105
C	-5.077460289	-0.376971632	-3.597538710
C	-6.330752373	-0.153540358	-4.170693398
C	-6.500747204	0.858945370	-5.111404419
C	-4.176099300	1.366914630	-4.871669292
C	-5.397794724	1.631667972	-5.474436760
H	-7.161716938	-0.789083481	-3.882298708
H	-7.472121239	1.030678391	-5.564672470
H	-3.292433739	1.942106485	-5.122774124
H	-5.472533226	2.420549393	-6.214685917
N	-4.018923759	0.386185825	-3.954810858
H	0.410177648	-3.775703430	-6.672453880
H	1.193635821	-4.913902283	-1.825461149
N	-1.078189611	-1.797524333	-1.627431393
C	0.395371526	2.024518490	-2.621573925
H	0.029762521	2.305591106	-1.635089517
H	1.480520010	2.178397417	-2.659698486
H	-0.083713643	2.650915623	-3.375094652
H	0.348662615	1.074194551	-4.908897877

C	-2.996676207	2.572139263	-1.071900964
N	-2.629022121	1.794571757	-1.846042752
C	-3.451650143	3.547163725	-0.092428215
H	-3.298910618	3.152673721	0.917032480
H	-4.516258717	3.751091003	-0.242444515
H	-2.888269424	4.478524685	-0.205933124

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A2

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N	-1.132691860	0.050220773	-4.438726425
Pd	-2.201097012	1.319531441	-3.343755484
N	-0.080918640	1.807250857	-2.613436699
N	-3.745837688	-0.079845652	-3.696860552
C	0.209469393	0.101851851	-4.438639164
C	-1.836932063	-0.927190125	-5.057215691
C	0.142305985	1.025561571	-1.318881154
C	0.803290725	1.289250851	-3.717965126
C	-3.345408916	-0.791924477	-4.964110374
C	-3.843629599	-1.037961483	-2.500064611
C	-4.988401890	0.749774277	-3.800424337
C	-2.474037170	-1.392261386	-1.949276567
C	-0.482983172	-0.355778694	-1.363735199
C	-1.877505302	-2.652321339	-1.970231891
H	-2.435163498	-3.536939383	-2.262387991
C	-0.524938762	-2.739030838	-1.614838123
C	0.203667015	-1.572620630	-1.356469870
H	1.273079515	-1.612640262	-1.173495173
H	1.218962312	0.988884151	-1.114911199
H	-0.339360237	1.603165388	-0.526545644
H	1.802993298	1.055355668	-3.332387924
C	0.933621764	-0.862004995	-5.136306763
H	2.017745495	-0.825981498	-5.152775288
C	0.236871481	-1.868335247	-5.807728291
C	-1.161562562	-1.912368774	-5.764902115
H	-1.711019278	-2.698536873	-6.271870136
H	-3.839488745	-1.767295361	-5.035661697
H	-4.410039902	-0.507246435	-1.731856227
H	-4.416630745	-1.914654851	-2.818843603
H	-3.689052820	-0.185524717	-5.808813095
H	-5.012356281	1.192262411	-4.801395893
H	-5.885637283	0.129927069	-3.688073635
C	-4.958619118	1.861476302	-2.766665936
C	-6.119947433	2.365564585	-2.195182562
C	-6.035574913	3.440844536	-1.307540655
C	-3.657025814	3.416977406	-1.593041539
C	-4.785886288	3.978417873	-1.005410314
H	-7.079600334	1.922807932	-2.441200495
H	-6.934988976	3.845909595	-0.854717016
H	-2.660483360	3.782669544	-1.374425054
H	-4.679416656	4.812608242	-0.321123838
N	-3.739049911	2.387006521	-2.452620745
H	0.782896638	-2.627712727	-6.358779430
H	-0.029029846	-3.704605579	-1.599878788
N	-1.802051187	-0.309586495	-1.551595569
C	0.246290237	3.238542318	-2.368217945
H	-0.367932498	3.610597610	-1.546903610
H	1.301220894	3.364205360	-2.093966722
H	0.034500781	3.819374323	-3.267216206
H	0.917665541	2.094550133	-4.452046394

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A3

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N	-1.145040154	0.172655001	-4.485486031
Pd	-2.445680857	1.468777657	-3.430503607
N	0.592894256	1.735643387	-2.560651779
N	-3.763715267	-0.145512298	-3.598651171
C	0.197758108	0.169796854	-4.549643040
C	-1.854292154	-0.849246204	-5.042328835
C	0.673917234	0.881211102	-1.364531040
C	1.065949798	1.222442746	-3.825562716
C	-3.356911182	-0.841688037	-4.859329700
C	-3.654304981	-1.007975101	-2.355735064
C	-5.130299568	0.472085088	-3.676020145
C	-2.228681326	-1.303655267	-1.925061822
C	-0.161261514	-0.392649174	-1.433047771
C	-1.744027734	-2.606225729	-1.814086199
H	-2.390357018	-3.459393740	-1.995200753
C	-0.402097583	-2.784621716	-1.467539430
C	0.409679562	-1.663531899	-1.300174832
H	1.466742754	-1.772484064	-1.078748345
H	1.726926565	0.619092345	-1.212123156
H	0.364944547	1.481464505	-0.504162014
H	2.046449661	0.760001242	-3.673398018
C	0.868002892	-0.806088150	-5.293781757
H	1.951297879	-0.778933406	-5.353086472
C	0.150993824	-1.810096383	-5.933162689
C	-1.233928561	-1.850179553	-5.776603222
H	-1.823730826	-2.650326967	-6.211244106
H	-3.750380754	-1.865053654	-4.873413563
H	-4.163506985	-0.458650231	-1.559320807
H	-4.209605217	-1.934528708	-2.542408228
H	-3.812614441	-0.302503407	-5.696039677
H	-5.281136990	0.825498164	-4.700788021
H	-5.903180599	-0.275205910	-3.462492228
C	-5.222383022	1.650727630	-2.735620737
C	-6.403142452	2.027424097	-2.109202623
C	-6.417132854	3.177402258	-1.315808177
C	-4.088300705	3.477636337	-1.801802874
C	-5.243924618	3.914681911	-1.163557649
H	-7.300272465	1.431815147	-2.243119001
H	-7.331789970	3.487858772	-0.820713460
H	-3.148865938	4.009005070	-1.704563856
H	-5.214371681	4.812269211	-0.556064188
N	-4.080289841	2.374352694	-2.572542906
H	0.663622499	-2.571258307	-6.512983322
H	0.009440463	-3.783617496	-1.361182451
N	-1.464439034	-0.228101358	-1.688841701
C	-0.203791991	2.876783371	-2.592684507
H	-0.442864150	3.258786678	-1.600475669
H	0.194185659	3.663196087	-3.240729809
H	1.221379399	2.064415693	-4.510815620
H	-1.276996017	2.738027096	-3.112826586

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A3-TS'

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N	-0.581815600	-0.634359837	-3.684191704
Pd	-1.772421122	1.100165129	-3.785248280
N	0.648811996	1.682030797	-2.454795837
N	-3.429806948	-0.404246360	-3.663828611
C	0.677135289	-0.723199010	-3.229308844
C	-1.332917452	-1.755099535	-3.875051737
C	0.124102756	1.764242768	-1.079192519
C	1.461873293	0.541398346	-2.845197201
C	-2.774066687	-1.575913668	-4.316247940
C	-3.895512342	-0.676480651	-2.271808624

C	-4.478804111	0.252950788	-4.496798515
C	-2.811556816	-0.481047899	-1.220112681
C	-0.886342049	0.696875870	-0.656782150
C	-2.753232002	-1.233693600	-0.046096936
H	-3.488197565	-2.005531073	0.158318624
C	-1.716438770	-0.975885332	0.850980937
C	-0.754848957	-0.011388449	0.537450850
H	0.076962143	0.180776224	1.207839012
H	0.985244811	1.736550689	-0.404602796
H	-0.331381708	2.753887892	-0.969397545
H	2.133412123	0.284071922	-2.021648884
C	1.286466837	-1.968542337	-3.060691595
H	2.313696861	-2.021293879	-2.713855505
C	0.559667468	-3.125602961	-3.316438913
C	-0.778066397	-3.016018867	-3.700591803
H	-1.385571599	-3.900288582	-3.859513998
H	-3.337000608	-2.498867750	-4.131740570
H	-4.709061623	0.024898183	-2.059260845
H	-4.317875862	-1.686157942	-2.205286741
H	-2.780321121	-1.401411891	-5.397213459
H	-4.207440853	0.113986902	-5.548149109
H	-5.461070061	-0.211543590	-4.351575851
C	-4.546185017	1.741922021	-4.227010250
C	-5.743865967	2.446663618	-4.256562710
C	-5.737308025	3.832366467	-4.087546349
C	-3.359068394	3.725567341	-3.842984915
C	-4.523979187	4.483255863	-3.876853943
H	-6.674106121	1.912695527	-4.417718410
H	-6.666615963	4.391914845	-4.115841866
H	-2.394256353	4.190500259	-3.676915169
H	-4.469860554	5.557409286	-3.739087105
N	-3.366856337	2.392155886	-4.015539169
H	1.016398549	-4.101559162	-3.185283661
H	-1.642638803	-1.539434910	1.776000977
N	-1.923431039	0.480975986	-1.478234172
C	0.091340341	2.416829348	-3.469298601
H	-0.389487416	3.340156555	-3.154838085
H	0.779034674	2.551320314	-4.302704334
H	-0.957501233	1.806375504	-4.884155273
H	2.094455957	0.835300386	-3.691620588

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A3-TS

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N	-0.625691533	-0.551009595	-3.548896074
Pd	-1.892873049	1.164931059	-3.901174784
N	0.782935977	1.688121200	-2.195108414
N	-3.444273233	-0.281767517	-3.508688450
C	0.655364752	-0.649614096	-3.137933254
C	-1.370585203	-1.684112787	-3.643568754
C	0.404236555	1.531110883	-0.761716723
C	1.499136090	0.600772202	-2.884428740
C	-2.846131802	-1.560547829	-3.984673262
C	-3.859761238	-0.301659256	-2.064046860
C	-4.578736305	0.194121137	-4.360030174
C	-2.688921452	-0.405152470	-1.107632041
C	-0.640063763	0.456972778	-0.505593717
C	-2.557267189	-1.466191530	-0.208779782
H	-3.330453634	-2.223927736	-0.130660132
C	-1.407783985	-1.536578774	0.579306126
C	-0.412734061	-0.573725998	0.409849077
H	0.512566745	-0.624156356	0.975301623
H	1.328642011	1.312678099	-0.219158217
H	0.040312394	2.503495932	-0.420618981

H	2.363321543	0.321910262	-2.276927471
C	1.267504454	-1.886200666	-2.937835217
H	2.305289030	-1.931160450	-2.624016285
C	0.535164773	-3.054783583	-3.130599499
C	-0.812501729	-2.946596622	-3.454520226
H	-1.434867382	-3.830148935	-3.549755812
H	-3.390639544	-2.424994946	-3.584137440
H	-4.391133308	0.636738956	-1.880511165
H	-4.564699173	-1.127974629	-1.907365441
H	-2.948280811	-1.592109203	-5.074406147
H	-4.382925034	-0.122117244	-5.389436722
H	-5.526785851	-0.262339979	-4.051495075
C	-4.671734810	1.704626560	-4.341650963
C	-5.885885715	2.373265266	-4.438532352
C	-5.896861553	3.767501593	-4.513635159
C	-3.503329277	3.734328270	-4.372129917
C	-4.686147213	4.456788063	-4.485753536
H	-6.811441422	1.807385683	-4.460987091
H	-6.837133408	4.303957939	-4.591629505
H	-2.538448095	4.223966122	-4.343691826
H	-4.649519444	5.538697720	-4.547124386
N	-3.494423389	2.389045477	-4.299046040
H	0.996854961	-4.026817322	-2.988994837
H	-1.276927829	-2.343986988	1.292959213
N	-1.767810702	0.562805116	-1.212799430
C	0.402129978	2.720479250	-2.893616676
H	-0.181741491	3.499850035	-2.416331768
H	0.883620024	2.927821636	-3.840616226
H	-0.834191978	2.223174572	-4.332961082
H	1.873765588	0.995589554	-3.833424091

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N	-0.649399698	-0.435971767	-3.591384411
Pd	-1.900878668	1.170215845	-4.078388214
N	0.750377536	1.630089283	-1.925054550
N	-3.444638252	-0.197954208	-3.366514683
C	0.662317216	-0.442472994	-3.266541719
C	-1.360652447	-1.586866975	-3.511579752
C	0.748324513	0.973068237	-0.593333006
C	1.349756837	0.895757258	-3.085773706
C	-2.865998030	-1.523899436	-3.736785173
C	-3.812808752	-0.076256953	-1.916274786
C	-4.606577396	0.211600110	-4.218436241
C	-2.664456129	-0.373789102	-0.975818574
C	-0.496684641	0.108244188	-0.376270354
C	-2.705364704	-1.463934064	-0.105028279
H	-3.593725920	-2.083949566	-0.038876295
C	-1.579307675	-1.749662876	0.670386493
C	-0.436271518	-0.969875515	0.512782454
H	0.473196477	-1.193218827	1.062454104
H	1.651421905	0.363259941	-0.521394432
H	0.819910288	1.759334087	0.164183736
H	2.411696911	0.759488344	-2.869580746
C	1.341385245	-1.627409339	-2.999923944
H	2.400824547	-1.606615663	-2.766405344
C	0.638082266	-2.833396912	-3.017529964
C	-0.735077620	-2.803623676	-3.234197617
H	-1.325418234	-3.712705374	-3.184189081
H	-3.351053715	-2.342576742	-3.190253735
H	-4.160861969	0.950384676	-1.768250227
H	-4.650506020	-0.753859878	-1.705860496
H	-3.059678555	-1.690860987	-4.801315308

H	-4.464286327	-0.221970022	-5.213683128
H	-5.551422119	-0.182275727	-3.824653864
C	-4.679764271	1.718721151	-4.376409531
C	-5.890965939	2.391678810	-4.480807781
C	-5.892283916	3.763457537	-4.743382454
C	-3.495225430	3.704514742	-4.761699677
C	-4.676301003	4.427364349	-4.892632484
H	-6.822137833	1.846445203	-4.366981506
H	-6.830365658	4.302238941	-4.831770420
H	-2.524158716	4.170630932	-4.869740486
H	-4.634003162	5.489566326	-5.106301785
N	-3.496586084	2.381953716	-4.505276680
H	1.146846414	-3.772033930	-2.821722507
H	-1.583116770	-2.586165428	1.362377644
N	-1.589071631	0.426746428	-1.064407706
C	0.111603998	2.732140541	-2.095754147
H	-0.368897945	3.207453012	-1.246484280
H	0.077671647	3.194821835	-3.074789286
H	-0.849598110	2.090114594	-4.746243954
H	1.239841104	1.525845766	-3.970055580

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N	-0.604912937	-0.538059354	-3.637155533
Pd	-1.816865325	1.161766887	-3.919798136
N	0.658152044	1.676957369	-2.231128931
N	-3.475923777	-0.325858384	-3.479498625
C	0.684712350	-0.589925349	-3.251769066
C	-1.350195408	-1.673323035	-3.668095112
C	0.402987033	1.390362620	-0.803903878
C	1.442463756	0.719467282	-3.031195164
C	-2.839125156	-1.574536562	-3.984148026
C	-3.929954052	-0.395416737	-2.065625906
C	-4.549528599	0.216947943	-4.358668327
C	-2.771312475	-0.467719555	-1.093739033
C	-0.699753821	0.370589733	-0.529611707
C	-2.716791868	-1.419141173	-0.074792340
H	-3.529312134	-2.125070810	0.064374268
C	-1.592527390	-1.449023724	0.751011431
C	-0.551979303	-0.553703547	0.507795334
H	0.350972235	-0.572743177	1.110164285
H	1.346505046	1.050070643	-0.369866192
H	0.154438391	2.341890574	-0.324346989
H	2.382761955	0.513370156	-2.515741587
C	1.320461988	-1.804754138	-3.011753321
H	2.364732981	-1.821557999	-2.717918396
C	0.593064547	-2.988293409	-3.130987644
C	-0.764621675	-2.915662766	-3.428010464
H	-1.374136090	-3.812593460	-3.461221933
H	-3.348287344	-2.466035843	-3.596145630
H	-4.500731945	0.518660724	-1.869613171
H	-4.608353138	-1.247716188	-1.924690723
H	-2.952045918	-1.593958855	-5.073249340
H	-4.327770233	-0.075709671	-5.390036583
H	-5.530251026	-0.205822691	-4.108035564
C	-4.601826191	1.733160853	-4.309126377
C	-5.803919792	2.427096844	-4.390382767
C	-5.794465542	3.822175741	-4.446554661
C	-3.403220415	3.750258207	-4.319970608
C	-4.573781490	4.493756294	-4.416642666
H	-6.738950729	1.877155781	-4.416887760
H	-6.727169037	4.373274803	-4.513595104
H	-2.430187941	4.225541592	-4.295515537

H	-4.520440102	5.575608253	-4.465833187
N	-3.415766716	2.404461145	-4.261687279
H	1.068114281	-3.947387218	-2.950284958
H	-1.517241955	-2.175080776	1.554518223
N	-1.796047568	0.432679236	-1.288195848
C	-0.008254875	2.622370720	-2.859719753
H	-0.658328295	3.268684864	-2.279031992
H	0.363352329	2.976554394	-3.810535908
H	-0.978369772	1.833123207	-5.003855228
H	1.677889943	1.190697908	-3.989800453

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A5

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N	-0.578164458	-0.656663537	-3.692109108
Pd	-1.749532580	1.087239981	-3.721443892
N	0.668751895	1.676666737	-2.475907087
N	-3.448425531	-0.439678520	-3.725341797
C	0.689706147	-0.732148588	-3.263189793
C	-1.324525237	-1.774651170	-3.893116236
C	0.242476597	1.710001826	-1.073624253
C	1.468815088	0.555470765	-2.945559263
C	-2.783642530	-1.622942686	-4.317958355
C	-3.913949013	-0.605084121	-2.324573040
C	-4.449772358	0.240564361	-4.579159737
C	-2.826267004	-0.395175815	-1.282389164
C	-0.861194789	0.720723689	-0.688291252
C	-2.831378937	-1.101740003	-0.081566676
H	-3.607316732	-1.833703399	0.117354110
C	-1.820143104	-0.860088229	0.847718596
C	-0.811423779	0.049688131	0.533186853
H	0.009615860	0.228491783	1.220031857
H	1.117996693	1.526672244	-0.445238650
H	-0.094419882	2.729496241	-0.855119526
H	2.226849318	0.321733415	-2.193801403
C	1.312509179	-1.971231818	-3.108942986
H	2.344287872	-2.018553972	-2.775654554
C	0.590108573	-3.132775784	-3.367457628
C	-0.751211762	-3.032368422	-3.740157604
H	-1.352025867	-3.921365738	-3.900990486
H	-3.323059797	-2.549818993	-4.084825993
H	-4.692140102	0.145071104	-2.145919561
H	-4.382917404	-1.587009192	-2.183056355
H	-2.803661823	-1.505666971	-5.406946659
H	-4.133614540	0.134879351	-5.622410774
H	-5.445219040	-0.212899446	-4.493329525
C	-4.529111862	1.726878166	-4.258312702
C	-5.730308056	2.423594952	-4.342665672
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C	-3.393154621	3.704727888	-3.716820717
C	-4.560926437	4.453433990	-3.801593781
H	-6.641749382	1.888501406	-4.588586807
H	-6.682501793	4.353714466	-4.185803890
H	-2.446205854	4.170612335	-3.471319675
H	-4.528275490	5.521886349	-3.619495392
N	-3.379033327	2.378410339	-3.934735537
H	1.055205584	-4.106438637	-3.248473883
H	-1.802222013	-1.395400047	1.792012215
N	-1.875749469	0.524488986	-1.549752355
C	-0.059623949	2.371621847	-3.407206297
H	-0.508183599	3.289637566	-3.030151367
H	0.422750324	2.476190805	-4.376246929
H	-1.573300362	1.279141665	-5.224563599
H	2.003250360	0.870043397	-3.849623442

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A5-TS

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N	-1.381760359	-0.409820586	-5.316318512
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N	0.443329334	0.653233409	-3.318601370
N	-2.204581499	1.637818694	-7.162618160
C	-1.150334835	-1.119873047	-4.203523159
C	-2.482983112	-0.623784900	-6.082745552
C	-0.317826927	1.631353259	-2.536525726
C	0.026405592	-0.737421572	-3.284878969
C	-2.784496784	0.281174958	-7.271446228
C	-3.052201271	2.612497807	-6.434384346
C	-1.700084686	2.224665642	-8.421893120
C	-3.028314829	2.423226357	-4.933197975
C	-1.707573891	1.965719700	-3.076969862
C	-4.180785656	2.490956783	-4.152025700
H	-5.144528866	2.676780224	-4.614900112
C	-4.067160606	2.302634001	-2.774990320
C	-2.814894915	2.022295475	-2.229673862
H	-2.698933601	1.839225054	-1.166283011
H	-0.409511596	1.255355477	-1.513661742
H	0.279757529	2.547928333	-2.486658573
H	-0.250736654	-0.999147117	-2.260103703
C	-1.971226692	-2.192317486	-3.863497257
H	-1.768749237	-2.766729355	-2.965131760
C	-3.058932066	-2.496513367	-4.680274487
C	-3.332229614	-1.687876105	-5.780629635
H	-4.207403660	-1.864181757	-6.397389412
H	-3.874860048	0.328649998	-7.396010399
H	-2.658098698	3.611410618	-6.652224541
H	-4.082727432	2.580679178	-6.813453674
H	-2.396887064	-0.177432597	-8.195818901
H	-1.457119584	1.437011003	-9.140320778
H	-2.474474430	2.807791948	-8.930329323
C	-0.474823296	3.089215517	-8.197108269
C	-0.171156093	4.112343311	-9.096486092
C	1.006255269	4.839838982	-8.951615334
C	1.521616340	3.509599209	-7.031699181
C	1.871179342	4.533686161	-7.899198055
H	-0.850717962	4.300456524	-9.919769287
H	1.250499964	5.631829262	-9.652643204
H	2.162403584	3.224393129	-6.205139637
H	2.800863504	5.072006226	-7.751976967
N	0.375933915	2.813328028	-7.172035694
H	-3.710409164	-3.330402613	-4.437451839
H	-4.945955753	2.348381281	-2.139230490
N	-1.818663478	2.197242498	-4.393031120
C	1.163857818	1.081555009	-4.416148663
H	1.545718431	2.097317696	-4.311842918
H	1.900142550	0.370734841	-4.782773972
H	0.728005230	0.361503869	-6.707408905
H	0.889977038	-1.359584570	-3.543696165
N	-1.883007765	-0.768999636	-10.121249199
C	-2.876831293	-1.082082272	-10.962788582
C	-0.674505711	-1.310226679	-10.300434113
C	-3.437079430	1.929998040	-11.713695526
N	-3.918591022	1.155285954	-10.549649239
C	-4.155336380	-0.271162868	-10.825444221
C	-5.132652760	1.777654648	-10.020874977
C	0.410579175	-0.782653868	-9.390925407
N	1.546209097	-0.120675400	-10.056910515
C	1.259573579	1.157145858	-10.758231163

C	2.596824646	0.203391492	-9.063890457
C	-2.726452112	-2.067323685	-11.939614296
C	-0.431931555	-2.297479391	-11.258021355
C	-2.074340105	1.516886830	-12.245249748
H	-4.169008255	1.898076892	-12.540850639
H	-3.374554634	2.976520061	-11.390486717
H	-4.783859253	-0.424305528	-11.721279144
H	-4.731195450	-0.671564519	-9.980381012
H	0.821282923	-1.636767507	-8.848526955
H	-0.062620766	-0.133462757	-8.637055397
C	0.159104317	1.136341214	-11.796103477
H	1.008104324	1.946206212	-10.034280777
H	2.200309515	1.451550007	-11.238687515
H	3.496097326	0.502696216	-9.613846779
H	2.293791533	1.060716271	-8.436206818
C	2.916203499	-0.942291021	-8.138617516
C	0.382013291	0.625682533	-13.078567505
N	-1.029863358	1.617635846	-11.406753540
C	-1.933704734	1.031397820	-13.547370911
H	1.363212943	0.251055866	-13.352178574
C	-0.679668248	0.596264839	-13.976803780
H	-0.542715013	0.217613444	-14.985391617
H	-2.794788837	0.977650523	-14.206133842
H	-3.549388409	-2.310555696	-12.604887009
C	-1.489941001	-2.703293562	-12.067554474
H	-1.346414924	-3.476235867	-12.816963196
H	0.564562798	-2.711322784	-11.372181892
C	3.751559973	-1.985591769	-8.545857430
N	2.305225134	-0.943749070	-6.937346458
C	3.962493658	-3.065118790	-7.691121578
H	4.214373112	-1.946208477	-9.526559830
C	3.322638988	-3.072220802	-6.451651096
H	4.608206749	-3.886631012	-7.986126900
C	2.506048918	-1.992133737	-6.127220154
H	1.982889771	-1.972757936	-5.174566746
H	3.450957537	-3.892429829	-5.753065586
H	-5.981322765	1.772211194	-10.728199959
H	-5.453891754	1.253141880	-9.113572121
H	-4.930283070	2.821797609	-9.756989479

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N	-0.362429351	-1.051359057	-3.369601965
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N	-3.187973261	-0.581661224	-3.137609005
C	0.928246379	-1.218806863	-3.040784359
C	-1.208923817	-2.105449438	-3.404361725
C	0.957163811	1.371877432	-1.007107377
C	1.849654317	0.004412189	-2.904471636
C	-2.669777632	-1.845260859	-3.709862232
C	-3.472216368	-0.641431510	-1.677098274
C	-4.327349663	-0.048062466	-3.929962635
C	-2.254379272	-0.484910101	-0.781163216
C	-0.158492848	0.485288262	-0.444110662
C	-2.172837734	-1.162886143	0.436631709
H	-2.973214149	-1.829859853	0.739607751
C	-1.047447085	-0.980159938	1.237209082
C	-0.016084930	-0.157349959	0.785386801
H	0.890947819	-0.027642809	1.367183328
H	1.879138470	1.169213533	-0.453355879
H	0.698406160	2.421173573	-0.826672196
H	2.669024706	-0.264017016	-2.231170177

C	1.448930264	-2.494640589	-2.822611570
H	2.497642994	-2.611026525	-2.567883492
C	0.607789278	-3.600113869	-2.911300659
C	-0.743343294	-3.399890184	-3.184499502
H	-1.439170837	-4.231542110	-3.213173389
H	-3.273508787	-2.702398777	-3.390949249
H	-4.148906231	0.190328866	-1.455164552
H	-4.016314507	-1.556996703	-1.427026391
H	-2.774276972	-1.767499208	-4.798839569
H	-4.672143936	0.854627669	-3.414170980
H	-3.928092480	0.294645458	-4.888791084
C	-5.488785267	-1.000238419	-4.161991596
C	-6.255503178	-0.879774988	-5.326020718
C	-7.337418556	-1.738794684	-5.509839058
C	-6.779777050	-2.748374939	-3.412710190
C	-7.608201981	-2.696051121	-4.532557487
H	-6.004743576	-0.129094258	-6.070062637
H	-7.951152325	-1.668324351	-6.403009892
H	-6.954076290	-3.486549139	-2.632485390
H	-8.435658455	-3.390311003	-4.635540962
N	-5.741858959	-1.922479987	-3.219912291
H	0.992589772	-4.600269794	-2.736958027
H	-0.961313069	-1.496023297	2.188648939
N	-1.274321795	0.347722501	-1.175983667
C	0.431895733	1.916274309	-3.344653845
H	0.096875995	2.893277407	-2.999825001
H	0.837390423	1.928228140	-4.355337620
H	-1.444298625	1.030329347	-4.904152870
H	2.297239065	0.201688945	-3.886402369
O	-2.369069815	2.596964836	-3.423980236
O	-2.666703939	2.358866453	-5.655580521
C	-2.832895517	2.967268705	-4.594874859
C	-3.628875256	4.259538174	-4.531348228
H	-4.425855637	4.170925617	-3.788019896
H	-2.973603487	5.074122906	-4.209375381
H	-4.047567368	4.486445904	-5.511363983

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A6-TS

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N	-0.356585383	-1.032710075	-3.358029366
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N	-3.183595896	-0.581152439	-3.145115137
C	0.933891058	-1.194015503	-3.026796103
C	-1.194747567	-2.092889071	-3.407554388
C	0.923346221	1.372439742	-0.968013346
C	1.843548894	0.036471155	-2.874049902
C	-2.656362295	-1.841294169	-3.717237949
C	-3.481165886	-0.643284261	-1.686866522
C	-4.318313599	-0.051407274	-3.943179607
C	-2.261533976	-0.524422705	-0.788975537
C	-0.172666430	0.449387729	-0.427213758
C	-2.156315804	-1.268923163	0.387460321
H	-2.944969893	-1.960661888	0.664196372
C	-1.021007419	-1.118141890	1.181141496
C	-0.004425842	-0.260183305	0.762035668
H	0.909170628	-0.152913272	1.338121176
H	1.846758485	1.188425422	-0.409855723
H	0.634895325	2.412451744	-0.780396521
H	2.661088467	-0.231074363	-2.197961569
C	1.464220166	-2.468030453	-2.822504997
H	2.513276815	-2.578769684	-2.567035198
C	0.631561041	-3.578653097	-2.924939394

C	-0.720200539	-3.385855436	-3.199416876
H	-1.409606576	-4.222261906	-3.238908529
H	-3.256809950	-2.701718807	-3.401697874
H	-4.135025501	0.206899256	-1.466253996
H	-4.048664093	-1.547486782	-1.448774934
H	-2.755749941	-1.762915134	-4.806576729
H	-4.651623726	0.865687490	-3.445370674
H	-3.919838190	0.267595589	-4.910907745
C	-5.492290974	-0.992681563	-4.155541420
C	-6.315660954	-0.820026636	-5.273523331
C	-7.406381607	-1.669787407	-5.441095829
C	-6.749810219	-2.770422459	-3.420020819
C	-7.630819798	-2.670036554	-4.494827747
H	-6.100684643	-0.037157513	-5.995298862
H	-8.063554764	-1.559455037	-6.298529625
H	-6.887040138	-3.541139603	-2.664360523
H	-8.463778496	-3.358917236	-4.587871075
N	-5.701393127	-1.953776360	-3.243597507
H	1.023300409	-4.577610970	-2.760080576
H	-0.915564001	-1.685422540	2.100874424
N	-1.297233462	0.340715259	-1.149369955
C	0.411898017	1.940715671	-3.306017876
H	0.069310732	2.911721468	-2.950561523
H	0.830405235	1.971687078	-4.311209202
H	-1.442682028	1.058729887	-4.915941715
H	2.295381069	0.247034103	-3.851171732
O	-2.416539669	2.600757122	-3.471248150
O	-2.560135126	2.288631916	-5.701263428
C	-2.808800697	2.933533669	-4.672701359
C	-3.613955259	4.218675613	-4.719547272
H	-4.339718342	4.245967388	-3.903922558
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H	-4.112361431	4.311162472	-5.684070110

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A7

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N	-0.786544323	-0.526346624	-3.553239346
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N	-3.614146233	-0.100712769	-3.367957830
C	0.490766883	-0.721046090	-3.200161695
C	-1.615405440	-1.580793142	-3.714172125
C	0.382740110	1.626215100	-0.913681507
C	1.384049177	0.495922744	-2.900117874
C	-3.067795038	-1.297543406	-4.046180725
C	-3.912480116	-0.326621771	-1.917762160
C	-4.809283257	0.430040330	-4.088660717
C	-2.673546553	-0.410556346	-1.047016025
C	-0.625056505	0.543087304	-0.531267524
C	-2.423422098	-1.503069162	-0.212624714
H	-3.140422583	-2.314847708	-0.140552580
C	-1.228067875	-1.535898566	0.505224705
C	-0.299154550	-0.510424674	0.327299595
H	0.663170815	-0.534898043	0.829560101
H	1.307712078	1.480676770	-0.345229864
H	-0.018964591	2.609667540	-0.652617276
H	2.174572468	0.170752198	-2.216117382
C	1.022875547	-2.007306814	-3.095105648
H	2.065150976	-2.137962103	-2.821101904
C	0.197835699	-3.105008841	-3.316439867
C	-1.147945166	-2.887980461	-3.606336117
H	-1.834032536	-3.718783617	-3.733438253
H	-3.668681145	-2.193813324	-3.838286400

H	-4.522175789	0.519166946	-1.589760184
H	-4.525483131	-1.226125360	-1.789059877
H	-3.136740685	-1.114802837	-5.125607491
H	-5.111669064	1.346154571	-3.574443579
H	-4.470866203	0.702860773	-5.093624592
C	-5.984096527	-0.524657369	-4.166093349
C	-6.237234592	-1.268708825	-5.323487759
C	-7.306174278	-2.163430214	-5.330330372
C	-7.755074501	-1.494124770	-3.073037863
C	-8.082453728	-2.282251596	-4.179973602
H	-5.614737988	-1.142598152	-6.204617500
H	-7.529368877	-2.750316143	-6.216591835
H	-8.343416214	-1.556156635	-2.159506798
H	-8.925425529	-2.964147568	-4.136606216
N	-6.732730389	-0.632377982	-3.055269957
H	0.587620616	-4.114616394	-3.230014324
H	-1.007440805	-2.368892193	1.166189194
N	-1.809511542	0.607741356	-1.147946358
C	-0.059850764	2.416061163	-3.227460146
H	-0.385908991	3.362325907	-2.788688898
H	0.443547398	2.557818174	-4.188463211
H	-2.145699739	2.078930140	-5.728109837
H	1.875636220	0.795043886	-3.834640741
O	-2.868406057	3.290171146	-3.943180561
O	-2.653065681	2.834056854	-6.130351067
C	-3.091549873	3.582891464	-5.125062943
C	-3.891990185	4.780898094	-5.534759045
H	-4.879836082	4.447897911	-5.870947838
H	-4.009784222	5.454822063	-4.687230110
H	-3.410648823	5.287387371	-6.373856544

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1

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N	-1.075199127	0.094438627	-4.464340210
Pd	-2.259872675	1.515815735	-3.340083838
N	0.414132327	1.674081206	-2.553094625
N	-3.794940233	-0.145178378	-3.646666288
C	0.260144234	0.037047554	-4.488769054
C	-1.820057034	-0.890333652	-5.012926102
C	0.444101006	0.863281250	-1.324873805
C	1.048153400	1.123084903	-3.731717825
C	-3.340433359	-0.793396831	-4.895326138
C	-3.794721127	-1.047507524	-2.453163624
C	-5.053304672	0.623326719	-3.756424904
C	-2.388478994	-1.375911951	-1.975399733
C	-0.340534210	-0.447141469	-1.415722847
C	-1.854402184	-2.664615393	-2.001616955
H	-2.470869303	-3.514315605	-2.278107166
C	-0.502577066	-2.828438520	-1.687948585
C	0.276563764	-1.702315331	-1.423130870
H	1.343247771	-1.792067051	-1.241227388
H	1.491143703	0.647971153	-1.083958983
H	0.033719700	1.477615118	-0.518395126
H	2.019339085	0.700324357	-3.453310728
C	0.922662556	-0.983192146	-5.173040867
H	2.007860184	-1.004361749	-5.195168972
C	0.172989026	-1.976706028	-5.795889378
C	-1.218135357	-1.945285678	-5.692708492
H	-1.827687502	-2.734019995	-6.121580124
H	-3.775395393	-1.796601176	-5.016459465
H	-4.319248199	-0.514293969	-1.655149221
H	-4.356757641	-1.965584993	-2.677380562
H	-3.699012518	-0.183925942	-5.731946468

H	-5.095133781	1.048641324	-4.764935017
H	-5.942086697	-0.012454848	-3.633270502
C	-5.111489773	1.783138633	-2.766930342
C	-6.301459312	2.121408463	-2.128839731
C	-6.342826843	3.241517067	-1.297240019
C	-4.023333073	3.589894772	-1.776410818
C	-5.183984280	3.993489742	-1.122490287
H	-7.186660767	1.513418674	-2.285960913
H	-7.263628006	3.516647577	-0.792730629
H	-3.091296673	4.133117676	-1.661507964
H	-5.169138908	4.872693062	-0.487767816
N	-3.981778145	2.513246298	-2.577850580
H	0.665097415	-2.785836697	-6.326855183
H	-0.054548942	-3.817515850	-1.692954063
N	-1.653949738	-0.312457055	-1.623045683
C	-0.635136008	2.604938269	-2.760830164
H	-0.894241750	3.125349760	-1.833594084
H	-0.384533405	3.308387995	-3.560918570
H	1.246678233	1.945606232	-4.430617332

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2-TS

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N	-1.150872827	-0.167095721	-4.412861824
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N	-3.832481384	-0.190909401	-3.524997234
C	0.187190816	-0.216199934	-4.500260353
C	-1.892528296	-1.254024267	-4.725597858
C	0.520314276	1.204868197	-1.578168154
C	1.024913073	0.978972495	-4.020789623
C	-3.391448021	-1.163511276	-4.567004681
C	-3.803539991	-0.756605268	-2.121933460
C	-5.180797577	0.357721716	-3.849772453
C	-2.395050526	-1.008210897	-1.633591771
C	-0.303363502	-0.059569661	-1.362145782
C	-1.905586600	-2.286570072	-1.357197165
H	-2.563074589	-3.148976803	-1.403227448
C	-0.551734984	-2.426539421	-1.046536684
C	0.272672564	-1.301060915	-1.077807426
H	1.340510726	-1.386098981	-0.900457740
H	1.573275447	1.005098820	-1.348732471
H	0.175639540	1.987281084	-0.896690130
H	2.005338907	0.595882356	-3.717883110
C	0.832665622	-1.342105627	-5.010964394
H	1.915446639	-1.350933313	-5.086347103
C	0.079875804	-2.448632002	-5.391867161
C	-1.301631093	-2.413551092	-5.220977306
H	-1.919717431	-3.272750616	-5.459047794
H	-3.817816019	-2.151734352	-4.370995998
H	-4.271837234	-0.001196277	-1.485397816
H	-4.410931587	-1.663964152	-2.100923538
H	-3.810343742	-0.822209716	-5.520812035
H	-5.437235832	1.061351657	-3.052890539
H	-5.071235180	0.966187537	-4.752470970
C	-6.309792995	-0.643748820	-4.062277794
C	-7.477864742	-0.203298658	-4.696124554
C	-8.526771545	-1.101206422	-4.871485710
C	-7.172162533	-2.760562897	-3.807238340
C	-8.373620033	-2.412164211	-4.418250084
H	-7.559328556	0.822753787	-5.043484688
H	-9.444746971	-0.786504209	-5.358639717
H	-7.009394646	-3.772992611	-3.443913698
H	-9.162908554	-3.147038221	-4.536458015

N	-6.157251835	-1.901774406	-3.627573013
H	0.564541161	-3.336899996	-5.785456181
H	-0.137832910	-3.405020714	-0.821868539
N	-1.614873409	0.077724069	-1.572188735
C	-0.460509807	2.751969337	-3.288183212
H	-0.795784354	3.331192255	-2.430147648
H	-0.047289107	3.412693977	-4.057667732
H	1.193632364	1.645626664	-4.876291752
C	-3.451373577	4.035028458	-3.774424553
O	-3.722772360	2.906429052	-3.206007242
O	-2.410316706	4.234006405	-4.443867683
C	-4.482335567	5.126350880	-3.607869864
H	-5.296760082	4.948678017	-4.318365097
H	-4.903553486	5.101124763	-2.601142168
H	-4.038312912	6.099042416	-3.818845749
H	-1.622451663	2.914240837	-4.157102585

Vibrational Frequencies (in cm^{-1}) of the Optimized Geometries

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Acetonitrile

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386.47 386.62 932.39 1061.24 1061.28 1420.16

1482.72 1483.05 2378.66 3058.52 3135.65 3136.10

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Acetate

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52.38 426.26 585.83 627.07 861.01 990.43

1021.74 1320.31 1375.74 1480.18 1494.11 1758.12

2990.68 3053.72 3078.41

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Acetic_acid

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89.37 422.57 541.31 583.80 677.23 866.46

1003.28 1069.83 1218.41 1354.62 1421.91 1482.70

1488.33 1857.10 3066.02 3132.70 3184.88 3755.76

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PicCH3N4

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15.97 23.60 51.34 57.85 72.35 78.52

97.09 104.04 122.95 174.52 193.88 208.45

245.71 250.11 261.50 267.06 295.42 323.40

345.33 352.54 376.10 395.59 403.59 418.62

427.78 438.36 444.48 456.28 471.33 519.30

560.47 574.25 612.86 628.09 637.20 647.29

682.37 687.88 745.46 750.73 764.43 771.21

778.31 783.78 827.25 836.57 850.17 875.01

888.82 910.77 914.12 925.32 926.77 942.96

962.04 975.66 986.31 989.11 995.91 998.82

1010.85 1011.26 1013.81 1015.14 1019.66 1024.47

1051.84 1075.19 1116.30 1119.99 1122.34 1140.49

1148.21 1151.21 1165.07 1184.12 1186.62 1192.92

1210.86 1222.69 1248.54 1255.15 1256.01 1269.78

1276.46 1282.96 1287.06 1302.70 1310.75 1326.08

1334.49 1340.83 1357.97 1371.64 1381.28 1397.73

1412.31 1420.71 1470.07 1471.37 1480.68 1486.72

1488.62 1489.98 1496.87 1498.62 1502.13 1502.42

1510.74 1514.91 1520.69 1521.99 1628.07 1635.16

1638.70 1644.27 1645.51 1647.15 2939.06 2970.47

2983.23 2991.07 3001.95 3017.87 3057.75 3059.47

3064.70 3069.62 3071.90 3082.12 3110.35 3162.61

3177.98 3178.39 3183.00 3198.60 3199.56 3205.21

3212.03 3213.25 3216.83

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Protonated_ligand

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14.99 24.39 37.21 48.81 60.67 85.04
97.55 101.43 125.89 180.50 200.44 217.38
229.43 239.36 255.63 286.98 298.46 323.21
341.78 371.61 383.23 411.57 418.10 421.94
428.22 444.88 448.32 469.72 488.47 525.69
553.69 566.52 609.57 626.35 627.75 646.12
650.45 687.37 740.63 749.03 769.15 773.31
777.21 789.97 816.19 832.06 857.28 875.08
884.47 914.37 922.96 929.07 935.46 938.98
946.72 969.38 979.34 983.60 987.17 1001.49
1013.02 1013.72 1015.38 1016.15 1018.26 1024.00
1027.14 1076.56 1086.57 1115.72 1121.38 1123.45
1148.85 1149.98 1163.42 1187.28 1190.17 1196.21
1198.71 1219.91 1235.97 1246.71 1255.02 1260.51
1274.72 1285.10 1289.44 1312.81 1313.85 1314.06
1336.89 1348.91 1353.12 1368.62 1380.08 1390.63
1409.77 1428.92 1434.84 1469.95 1475.43 1475.87
1481.77 1491.04 1493.01 1499.29 1502.55 1504.85
1509.94 1511.00 1514.70 1519.22 1521.64 1536.01
1627.88 1628.93 1632.85 1646.41 1652.25 1656.30
2873.53 2990.32 3004.72 3017.70 3079.41 3086.53
3088.57 3095.27 3100.40 3102.70 3139.74 3158.01
3174.37 3175.16 3181.50 3188.94 3194.12 3197.57
3203.08 3207.08 3210.93 3216.71 3220.04 3225.64

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2

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26.29 40.47 42.11 48.65 61.52 67.88
76.33 78.85 86.79 100.20 127.43 131.53
157.53 192.67 195.35 201.84 206.02 212.58
235.42 246.62 252.91 259.85 277.35 293.90
297.59 310.47 321.44 341.76 355.56 388.97
412.63 417.14 422.74 437.03 457.04 461.34
468.39 482.50 497.45 514.99 522.40 559.01
578.68 612.25 616.20 643.84 648.80 665.88
671.97 683.95 692.55 737.86 742.86 749.20
775.55 781.34 788.17 812.88 824.29 841.87
880.74 892.77 916.92 919.28 927.42 928.01
953.60 962.82 965.52 975.93 991.88 1005.67
1012.76 1015.47 1018.84 1020.02 1021.47 1029.70
1042.37 1044.07 1052.89 1063.34 1073.26 1079.64
1091.30 1103.35 1125.78 1136.50 1142.65 1157.40
1171.31 1196.27 1198.61 1204.95 1218.02 1235.19
1236.95 1244.87 1259.64 1267.96 1276.16 1287.71
1292.12 1307.45 1310.74 1318.44 1326.38 1338.93
1344.14 1356.01 1385.62 1397.87 1399.28 1406.35
1422.70 1427.51 1468.68 1471.66 1478.60 1478.86
1484.14 1485.48 1487.61 1489.76 1497.23 1500.33
1502.22 1504.25 1510.88 1511.95 1519.91 1521.94
1625.66 1629.48 1633.87 1646.43 1657.77 1661.81
1733.21 2943.25 2947.17 2962.42 3037.99 3046.66
3052.96 3058.65 3074.28 3093.15 3103.21 3106.90
3110.44 3113.42 3126.00 3148.83 3172.68 3191.46
3199.76 3204.44 3207.81 3213.03 3216.05 3219.00
3224.23 3224.29 3235.63

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A1

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22.38 33.01 36.75 46.14 58.82 64.12
78.67 89.96 102.10 133.46 151.70 164.16
184.13 191.46 204.17 208.19 218.85 226.51
241.92 254.51 265.59 268.26 284.17 291.03
301.77 314.91 334.15 342.57 393.72 407.95
412.24 415.78 428.23 432.28 447.99 459.01
463.69 468.23 486.79 501.27 517.54 546.24
568.01 619.16 635.66 647.50 656.55 661.32
683.92 727.69 746.98 747.74 774.51 783.95

787.44 812.70 826.03 842.47 868.66 894.57
913.96 923.21 934.39 943.94 950.01 965.31
969.95 983.72 984.91 993.68 1011.77 1019.49
1021.42 1025.25 1031.54 1037.24 1037.83 1039.54
1044.41 1048.65 1049.62 1088.98 1098.82 1122.89
1139.68 1143.03 1165.71 1169.03 1187.75 1197.91
1198.27 1205.46 1211.96 1229.46 1246.55 1250.35
1252.74 1268.30 1279.41 1285.57 1294.77 1304.73
1309.45 1323.51 1337.86 1344.44 1372.32 1391.59
1401.07 1405.94 1410.73 1420.91 1436.75 1460.50
1460.72 1470.55 1473.68 1479.83 1481.61 1484.02
1489.02 1496.06 1500.98 1503.94 1508.74 1510.51
1514.18 1515.90 1524.08 1621.03 1625.33 1634.20
1647.59 1653.86 1656.80 2391.32 2983.13 3001.94
3007.24 3049.47 3052.77 3058.00 3058.16 3059.74
3081.70 3092.67 3099.36 3122.39 3143.77 3144.67
3144.72 3186.79 3199.95 3207.08 3209.36 3210.11
3218.26 3218.99 3219.17 3223.74 3227.28 3236.18

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A2

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42.34 66.29 72.73 85.08 98.89 104.01
145.83 176.63 191.47 195.34 209.89 221.24
239.46 254.56 263.85 271.78 277.15 290.29
323.07 327.37 336.98 359.51 409.54 423.50
427.60 431.40 438.37 455.53 466.58 480.11
486.10 496.64 524.44 536.99 581.15 623.17
640.42 655.22 658.31 667.27 670.42 729.26
739.92 748.75 772.10 784.08 787.87 798.50
818.23 827.42 842.04 862.53 914.00 921.78
934.03 939.87 948.29 960.80 969.71 980.67
989.07 993.51 1018.11 1020.42 1025.72 1034.24
1040.43 1041.55 1043.75 1063.31 1070.94 1082.64
1096.62 1103.86 1113.99 1126.14 1146.80 1158.65
1189.83 1193.53 1206.55 1209.46 1219.36 1235.02
1243.13 1246.81 1262.43 1270.95 1285.44 1290.83
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1381.05 1389.97 1395.14 1408.87 1419.65 1464.92
1469.42 1475.09 1476.94 1478.15 1485.50 1496.30
1497.99 1501.28 1504.55 1507.26 1513.69 1517.56
1521.41 1619.85 1626.89 1630.69 1639.00 1652.19
1656.81 3043.96 3052.07 3057.55 3061.68 3062.44
3076.35 3100.89 3108.68 3113.11 3130.93 3134.87
3142.20 3169.58 3202.89 3208.81 3212.93 3213.11
3221.53 3221.54 3222.85 3228.33 3228.46 3240.23

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A3

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41.06 54.16 61.57 79.84 89.19 99.63
134.22 169.83 184.86 186.79 207.21 230.02
239.93 246.60 256.81 264.68 281.42 306.11
326.23 339.38 359.48 397.37 408.42 422.57
427.18 434.25 458.87 461.18 470.19 488.28
499.38 506.68 524.50 540.40 561.99 604.98
636.18 643.27 665.16 669.61 683.24 726.66
738.49 740.38 764.82 781.24 786.14 812.17
824.07 836.65 868.27 880.60 913.88 923.60
931.92 951.71 954.33 959.79 973.96 981.39
984.21 993.63 1019.17 1029.07 1029.41 1033.74
1037.11 1040.88 1047.14 1051.26 1071.25 1084.14
1085.34 1104.89 1129.21 1144.48 1146.63 1199.88
1202.35 1206.32 1209.32 1219.73 1232.29 1240.25
1248.24 1255.94 1267.41 1270.07 1288.85 1291.54
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1370.76 1388.95 1399.48 1404.11 1407.03 1429.03
1445.40 1471.47 1473.26 1475.59 1480.04 1484.25
1485.99 1498.21 1499.26 1501.32 1505.49 1513.23
1521.21 1620.09 1624.53 1627.36 1642.26 1650.48

1656.75 2154.03 3053.04 3055.34 3059.76 3063.69
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3124.16 3182.31 3203.07 3209.02 3209.85 3213.93
3216.50 3221.64 3223.46 3226.79 3229.15 3240.59

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-581.32 36.23 48.30 65.61 81.44 87.33
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308.54 341.74 356.90 375.86 391.74 424.21
436.56 447.71 452.99 461.10 463.61 483.05
494.27 512.34 526.71 541.68 553.69 607.71
640.78 643.40 658.43 670.73 677.93 714.80
733.46 738.75 748.87 765.06 779.02 786.54
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975.38 985.54 987.13 999.91 1015.76 1031.37
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1095.32 1111.57 1117.80 1129.30 1141.72 1147.69
1152.73 1203.37 1206.71 1209.26 1221.12 1233.93
1241.47 1246.20 1254.94 1258.56 1267.46 1271.78
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1370.10 1376.58 1396.15 1398.59 1407.73 1425.85
1442.33 1472.87 1476.10 1478.27 1481.42 1487.12
1489.39 1494.48 1501.65 1503.72 1508.39 1522.04
1530.14 1621.28 1626.01 1633.46 1643.73 1651.17
1658.94 2088.02 3049.75 3051.51 3058.07 3058.40
3069.97 3099.60 3103.17 3108.99 3119.53 3121.93
3129.65 3206.10 3208.91 3213.42 3216.26 3218.76
3221.92 3223.46 3223.69 3228.48 3228.93 3239.13

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A3-TS

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-140.86 40.28 57.60 64.83 74.87 88.51
112.09 142.68 164.89 185.30 196.55 203.85
225.61 230.74 244.60 259.74 277.51 285.81
302.13 335.24 339.89 366.88 407.60 416.93
429.88 432.99 453.30 458.47 464.80 475.35
491.34 508.21 527.89 548.40 575.34 603.83
641.47 649.14 657.72 670.20 694.32 726.08
735.11 744.28 747.94 773.87 785.33 788.17
814.28 829.60 846.21 870.63 887.95 894.86
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1029.35 1031.49 1034.79 1038.33 1039.83 1049.13
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1240.15 1246.79 1263.29 1269.41 1270.52 1285.03
1292.78 1295.34 1310.57 1321.24 1334.95 1348.41
1352.49 1385.94 1397.38 1404.29 1410.27 1432.55
1473.54 1477.44 1480.55 1482.54 1484.33 1487.19
1498.07 1500.29 1501.64 1505.57 1508.32 1519.47
1620.36 1623.41 1629.43 1641.22 1649.86 1657.15
1658.32 2026.49 3045.88 3047.91 3056.42 3081.73
3084.45 3098.96 3108.39 3113.75 3138.07 3140.31
3188.55 3203.96 3209.45 3210.22 3212.78 3216.21
3222.92 3223.18 3227.42 3232.42 3249.30 3303.93

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A4

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40.58 55.13 66.54 75.33 82.21 99.11
124.78 126.54 173.00 188.18 197.66 203.42
234.78 239.65 251.08 264.76 286.55 290.51
317.49 339.97 354.37 402.52 409.67 426.12
433.64 448.32 460.18 468.51 471.04 490.22
511.50 521.24 558.57 567.72 590.24 639.89
643.57 651.70 663.39 671.96 686.26 707.18

737.44 742.41 749.11 780.49 784.50 790.73

811.46 826.93 844.68 862.23 885.46 897.14

919.06 927.30 939.42 947.35 961.51 967.27

970.79 987.87 994.32 1000.74 1009.33 1021.09

1030.40 1032.19 1035.86 1038.32 1043.40 1051.18

1064.26 1084.80 1098.93 1119.71 1131.99 1142.66

1147.95 1202.25 1204.40 1205.33 1209.12 1228.56

1238.63 1244.78 1261.04 1266.84 1268.22 1276.78

1288.54 1305.74 1311.09 1320.89 1334.76 1341.01

1347.68 1379.16 1389.15 1399.88 1410.61 1432.49

1470.78 1479.55 1484.63 1486.60 1488.16 1490.49

1498.52 1501.57 1502.72 1509.36 1512.42 1518.68

1618.07 1621.79 1630.70 1639.64 1652.91 1658.21

1720.30 2042.41 3041.70 3046.23 3052.52 3085.69

3099.27 3100.60 3105.76 3110.34 3144.22 3163.08

3181.40 3201.66 3209.34 3209.90 3212.24 3216.44

3222.04 3222.64 3226.79 3231.94 3249.34 3302.85

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A4-TS

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-137.78 42.52 50.54 65.49 80.02 83.13

113.87 155.18 165.56 186.53 201.38 209.87

224.36 232.45 244.06 256.75 275.20 286.42

307.46 342.39 346.88 397.34 403.46 422.49

429.61 438.29 454.74 460.11 468.89 483.09

505.07 519.50 542.95 560.59 563.57 603.59

642.98 647.43 660.19 671.60 690.16 727.29

731.15 743.74 768.64 776.48 786.97 791.02

809.88 817.59 830.38 843.09 878.85 891.45

916.83 925.81 938.13 956.82 963.36 970.23

975.23 982.08 990.27 1003.43 1007.29 1016.59

1030.68 1030.73 1033.23 1039.76 1041.81 1043.43

1050.81 1086.24 1116.44 1125.30 1135.47 1144.71

1149.56 1202.13 1206.32 1207.12 1211.94 1231.58

1239.99 1245.41 1263.06 1265.32 1268.91 1281.56

1292.60 1293.78 1309.49 1319.36 1337.06 1351.47

1355.09 1380.67 1392.97 1399.12 1410.89 1432.25

1473.16 1476.39 1479.60 1485.06 1486.52 1487.99

1496.23 1501.00 1501.93 1504.20 1509.16 1519.39

1618.85 1620.36 1622.24 1631.32 1644.80 1652.53

1657.28 2111.91 3035.30 3043.01 3050.72 3081.04

3087.39 3093.59 3096.74 3104.34 3134.69 3147.70

3185.28 3204.30 3211.24 3211.27 3212.75 3218.15

3222.85 3223.31 3227.73 3230.00 3241.63 3306.37

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A5

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38.32 48.85 70.43 92.22 95.00 113.35

173.55 180.18 183.55 205.63 223.26 233.86

238.59 251.67 260.19 279.03 295.92 307.05

344.08 357.01 385.29 405.93 426.62 435.73

448.13 456.18 464.98 466.38 484.30 501.37

514.60 522.56 540.30 545.48 604.81 641.02

645.61 659.83 669.95 679.69 726.47 727.70

732.43 741.92 763.35 778.63 785.71 813.04

816.50 837.23 837.51 852.34 880.53 900.36

913.94 926.71 937.01 957.71 964.93 967.84

979.55 985.20 987.14 1000.98 1018.08 1033.46

1035.07 1035.46 1040.76 1042.28 1047.96 1082.38

1090.71 1114.44 1127.81 1134.18 1142.45 1144.17

1153.28 1206.85 1207.17 1207.82 1223.25 1228.00

1239.69 1241.69 1255.43 1257.28 1265.51 1272.96

1294.65 1295.72 1307.44 1316.56 1339.47 1354.51

1371.81 1374.81 1392.39 1397.66 1409.37 1425.00

1442.81 1472.04 1475.02 1479.40 1482.89 1485.05

1488.54 1494.34 1501.75 1503.51 1508.96 1521.28

1534.81 1620.94 1624.08 1626.75 1647.40 1649.63

1656.54 2123.23 3041.66 3044.01 3047.80 3064.05

3067.74 3092.21 3095.27 3101.01 3121.22 3124.41
3128.04 3208.14 3209.71 3212.51 3215.32 3216.97
3220.02 3222.17 3225.06 3226.50 3227.78 3239.12

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A5-TS

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-55.19 18.94 29.96 38.03 43.72 46.19
48.86 50.58 55.14 62.77 72.75 78.85
85.59 91.76 95.88 101.51 103.13 108.06
112.91 117.26 130.52 154.97 176.22 182.10
183.46 204.68 208.42 222.06 223.96 233.16
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274.76 290.98 300.99 303.60 310.21 314.59
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399.13 399.64 404.73 414.97 422.40 426.99
428.19 435.29 438.80 446.07 456.86 460.47
465.54 469.14 473.00 488.91 507.47 520.03
527.65 530.09 545.38 550.67 559.52 575.69
606.95 617.42 637.81 642.35 644.51 645.76
655.43 661.41 668.72 670.08 684.90 692.76
695.99 728.03 736.74 738.01 740.73 748.58
763.36 768.78 778.65 780.36 781.63 785.33
792.86 810.47 818.17 833.27 836.65 841.32
847.70 866.95 878.83 890.89 891.53 898.97
902.38 911.34 914.53 921.42 922.91 934.48
935.30 946.35 950.34 954.80 966.33 967.52
969.05 970.27 975.65 982.90 986.65 989.94
996.23 1004.87 1013.14 1015.38 1016.86 1019.06
1020.43 1023.86 1024.32 1027.35 1027.68 1028.16
1028.98 1029.23 1030.22 1044.82 1049.49 1051.97
1081.52 1085.75 1093.69 1105.73 1118.61 1119.95
1121.85 1128.83 1133.71 1136.60 1139.73 1143.45
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1199.08 1202.41 1203.99 1205.71 1217.56 1220.04
1222.80 1233.90 1238.07 1238.91 1241.70 1251.60
1252.39 1258.01 1266.22 1269.17 1270.22 1275.86
1277.44 1290.66 1292.13 1295.95 1298.93 1306.11
1309.46 1315.55 1320.08 1326.97 1329.57 1335.38
1350.87 1358.86 1361.08 1374.28 1378.47 1380.49
1395.04 1402.62 1403.27 1411.04 1415.37 1425.18
1427.61 1443.14 1444.99 1462.68 1471.65 1473.14
1476.43 1478.71 1479.29 1481.42 1484.24 1487.51
1489.76 1492.21 1492.57 1496.37 1497.55 1498.74
1500.39 1501.70 1503.85 1504.27 1509.86 1518.81
1519.66 1520.62 1524.37 1526.45 1532.68 1615.46
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2947.69 2957.92 2959.08 2960.02 2967.83 2985.54
3016.93 3031.78 3039.46 3042.73 3053.74 3057.40
3066.02 3067.46 3067.62 3073.22 3074.43 3087.33
3098.22 3107.74 3111.84 3112.88 3118.19 3121.36
3178.93 3194.06 3195.09 3204.34 3204.47 3204.59
3205.49 3206.29 3211.57 3212.46 3212.64 3215.61
3215.97 3216.88 3217.83 3220.34 3222.54 3222.64
3224.00 3230.50 3235.47

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20.53 23.72 46.96 47.79 51.71 56.58
59.96 61.82 73.55 91.11 125.76 144.19
159.05 168.38 179.24 187.66 197.88 204.73
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312.66 343.65 349.91 387.45 415.39 420.52
439.53 449.05 460.46 468.79 474.67 476.26
512.22 519.25 521.62 541.70 547.09 550.24
614.59 616.41 623.19 644.06 661.83 665.69
687.93 697.77 705.25 731.55 741.07 759.71
770.50 777.83 788.17 810.90 814.92 822.36

841.52 853.33 889.86 903.52 915.96 920.09
929.44 947.91 956.93 964.34 966.64 977.30
988.67 992.42 999.86 1015.27 1020.53 1020.95
1022.52 1023.10 1033.13 1034.16 1042.14 1065.99
1078.54 1096.04 1112.20 1124.24 1132.16 1137.00
1138.93 1143.86 1193.41 1201.02 1202.47 1210.99
1221.60 1235.25 1246.49 1252.27 1258.31 1272.70
1277.16 1296.08 1307.13 1309.90 1320.69 1322.97
1339.06 1346.59 1373.18 1380.10 1390.21 1396.82
1398.57 1413.66 1425.10 1432.86 1471.19 1475.74
1476.85 1478.30 1479.43 1486.00 1488.27 1488.70
1493.44 1501.09 1502.39 1512.49 1522.34 1523.36
1628.26 1629.20 1631.54 1647.47 1649.92 1654.08
1683.98 2107.21 3046.94 3050.11 3059.85 3063.57
3066.41 3069.45 3092.76 3107.89 3110.65 3112.58
3113.93 3115.52 3135.56 3173.29 3180.56 3191.40
3200.02 3201.46 3205.49 3207.39 3210.20 3212.18
3219.92 3219.96 3222.45

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A6-TS

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-39.90 17.47 35.58 48.06 50.46 52.90
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158.93 165.48 178.32 184.05 193.65 201.91
228.51 240.81 245.39 263.38 284.67 303.93
312.89 341.74 348.96 388.67 414.83 421.29
437.88 448.47 459.76 468.58 473.94 476.80
507.65 511.94 519.49 541.82 547.82 551.85
614.15 615.60 624.71 643.89 655.65 661.77
667.76 698.50 705.31 731.43 741.45 757.95
771.71 777.17 788.19 810.74 816.72 838.13
840.51 849.87 889.54 902.44 914.85 919.39
929.27 955.16 957.43 964.71 967.54 977.43
989.37 992.89 1001.04 1015.66 1019.89 1021.76
1022.28 1022.82 1032.39 1036.28 1041.75 1066.29
1078.27 1095.52 1113.04 1124.96 1132.00 1137.71
1138.47 1143.87 1193.30 1200.40 1201.86 1209.29
1220.62 1234.04 1245.90 1252.16 1258.58 1273.31
1277.52 1296.13 1307.80 1311.71 1323.56 1337.29
1340.72 1346.34 1371.76 1380.02 1390.97 1395.91
1400.63 1412.97 1423.41 1431.70 1471.20 1475.54
1476.89 1477.67 1478.92 1486.59 1489.91 1490.35
1493.87 1501.22 1502.27 1512.96 1520.95 1524.26
1628.49 1629.66 1631.80 1648.64 1649.26 1653.82
1655.64 2003.98 3048.03 3050.36 3060.57 3062.97
3067.98 3068.65 3094.62 3107.17 3109.59 3110.50
3111.40 3116.26 3139.87 3174.01 3181.56 3191.04
3199.70 3202.14 3202.73 3205.88 3210.41 3212.91
3220.02 3220.88 3223.27

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A7

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17.41 22.46 35.88 44.76 52.99 54.43
58.86 68.05 70.57 72.75 104.23 120.79
138.76 153.15 163.09 190.00 191.21 208.02
218.35 222.62 245.37 250.15 262.35 278.49
306.39 334.40 388.44 401.67 412.90 419.98
431.61 437.80 449.88 457.97 466.83 472.73
476.13 506.18 532.36 543.75 551.61 559.86
586.38 610.85 616.33 639.29 651.37 653.62
670.06 693.21 730.19 743.31 768.73 771.00
779.33 784.50 796.36 800.96 813.94 829.72
853.78 888.43 895.41 903.59 913.31 920.32
923.85 949.45 957.44 960.49 969.94 987.84
991.43 999.18 1010.22 1012.81 1015.73 1020.42
1022.56 1025.33 1033.75 1035.68 1071.48 1074.91
1086.07 1094.86 1111.24 1126.87 1135.92 1140.89
1143.16 1192.24 1194.60 1195.62 1202.44 1218.19

1235.73 1247.05 1248.92 1260.78 1270.81 1274.97
1284.45 1296.11 1308.96 1317.35 1322.30 1342.59
1355.68 1366.04 1376.58 1384.36 1389.57 1392.89
1405.99 1411.91 1432.09 1434.25 1470.91 1471.80
1474.39 1474.62 1477.63 1482.93 1485.21 1487.12
1489.28 1498.11 1499.42 1506.92 1509.89 1517.09
1628.96 1631.02 1632.65 1642.26 1644.20 1652.76
1727.09 3021.87 3041.79 3056.96 3057.20 3061.30
3064.04 3069.53 3070.18 3098.64 3116.78 3118.47
3124.06 3143.16 3145.29 3173.47 3187.63 3192.18
3192.84 3198.16 3203.01 3203.13 3208.27 3213.74
3218.90 3219.30 3300.23

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37.67 60.69 68.17 76.70 90.87 98.50
136.41 152.34 179.34 192.33 201.01 218.52
236.94 247.14 256.31 264.99 283.93 299.50
334.85 340.57 402.63 409.51 421.13 430.85
434.92 446.12 459.75 465.97 482.80 500.56
514.17 540.72 553.37 560.17 602.96 633.74
641.17 659.91 665.91 687.24 726.38 736.93
749.69 761.85 776.34 779.94 787.77 805.61
825.18 834.85 875.72 879.72 913.19 914.65
922.95 948.70 955.70 960.29 975.39 982.41
987.02 995.76 1009.78 1014.60 1016.39 1022.92
1024.29 1031.23 1035.25 1083.03 1091.59 1113.43
1121.44 1127.91 1136.58 1138.69 1148.58 1184.67
1192.41 1198.37 1200.10 1214.79 1232.39 1235.09
1243.12 1256.95 1264.04 1269.07 1286.61 1300.05
1310.30 1321.38 1336.65 1348.70 1362.64 1369.04
1384.62 1390.45 1401.52 1407.24 1428.91 1467.51
1469.40 1474.94 1479.15 1482.65 1484.69 1494.12
1496.14 1497.63 1500.15 1505.85 1514.45 1622.94
1626.21 1630.64 1639.82 1651.44 1656.16 3011.52
3017.56 3022.21 3040.33 3046.77 3057.10 3081.68
3089.53 3094.44 3106.51 3116.18 3127.75 3193.06
3197.44 3201.93 3202.70 3206.65 3210.32 3214.03
3216.97 3217.78 3230.16

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-1019.80 6.52 25.37 38.81 46.06 56.87
59.80 63.63 73.75 83.69 99.65 134.69
142.62 151.92 171.21 179.62 188.24 199.16
205.67 230.13 244.18 260.74 269.20 279.07
294.56 311.45 323.39 329.30 387.87 409.28
413.77 421.06 431.71 444.23 463.59 467.86
472.09 480.05 502.42 519.65 529.55 542.86
562.97 613.30 617.07 622.51 642.88 654.56
672.72 699.60 703.57 733.19 741.94 754.10
768.66 775.79 779.81 786.39 802.91 809.33
832.07 840.33 886.21 905.96 912.94 917.93
927.89 951.25 957.90 961.28 966.20 972.09
987.47 997.18 1007.54 1014.57 1016.27 1019.71
1020.42 1022.74 1035.92 1039.22 1041.25 1069.40
1077.40 1086.83 1102.35 1115.42 1126.43 1136.16
1139.53 1191.98 1193.70 1196.03 1204.81 1221.39
1224.51 1238.61 1244.90 1253.99 1270.16 1277.49
1282.36 1299.02 1309.66 1314.20 1325.93 1337.20
1343.66 1368.36 1381.96 1387.33 1393.23 1398.28
1406.10 1415.15 1422.86 1431.04 1468.74 1471.09
1473.36 1474.87 1478.50 1484.43 1488.31 1491.85
1495.14 1498.06 1501.18 1507.45 1516.07 1523.14
1595.95 1629.82 1630.00 1633.22 1643.23 1649.00
1655.22 1710.25 3039.96 3057.03 3057.19 3065.72
3066.34 3076.90 3082.68 3093.57 3110.43 3119.05
3119.68 3140.63 3143.83 3176.54 3182.52 3190.27
3190.45 3194.04 3200.24 3204.08 3206.72 3210.56
3215.02 3220.87 3221.82

[(^{PicCH2})N4Pd^{III}]$^{2+}$

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Pd	11.090089	8.733966	6.124636
N	10.873363	7.989617	8.095336
N	10.629816	9.237492	4.127956
N	10.577143	10.631544	7.332801
N	8.825380	8.656999	6.223964
N	13.246926	9.524160	7.610511
C	9.590712	7.667330	8.374082
C	9.209643	7.382732	9.679850
H	8.167049	7.135295	9.893495
C	10.161450	7.447811	10.693307
H	9.881160	7.231889	11.727312
C	11.461815	7.829014	10.387454
H	12.224462	7.939139	11.162498
C	11.787393	8.109761	9.063009
C	13.186716	8.562461	8.692897
H	13.664015	8.995024	9.585248
H	13.781013	7.677745	8.404492
C	13.136331	9.080083	6.331390
H	13.533865	8.068358	6.149938
H	13.356798	9.832752	5.561353
C	11.436802	9.792464	3.216581
H	12.474384	9.969336	3.515043
C	10.993665	10.134130	1.947295
H	11.690413	10.573835	1.231095
C	9.660019	9.905233	1.626368
H	9.273517	10.174370	0.640310
C	8.820590	9.339368	2.579781
H	7.765363	9.149957	2.367396
C	9.331405	8.999476	3.828468
C	8.468537	8.301740	4.849621
H	7.403557	8.501004	4.628148
H	8.618023	7.214279	4.729889
C	8.344278	9.990561	6.607366
H	7.330579	9.928433	7.044660
H	8.257428	10.596826	5.687725
C	9.261647	10.725606	7.551589
C	8.775748	11.472872	8.622323
H	7.698524	11.532428	8.796660
C	9.686322	12.100216	9.466962
H	9.336114	12.682604	10.322904
C	11.051121	11.943563	9.244847
H	11.792871	12.380599	9.918187
C	11.466791	11.177478	8.157601
C	12.942603	10.910939	7.907261
H	13.277800	11.525621	7.055041
H	13.516713	11.222229	8.792852
C	8.599563	7.618242	7.236104
H	8.704885	6.636720	6.741048
H	7.573702	7.663235	7.646662

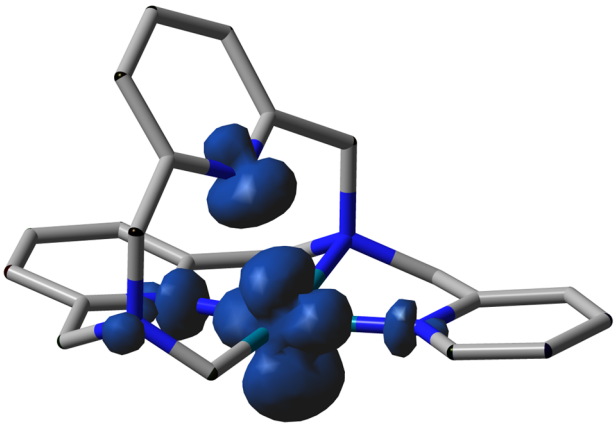
Complex	$[(^{PicCH2})N4Pd^{III}]^{2+}$
Spin Density	
	Pd 0.682 3N 0.238
***g* values (expt)**	2.056; 2.083; 2.277
***g* values (calcd)**	2.073; 2.107; 2.312
A_N values (G, expt)	18; 19; 5
A_N values (G, calcd)	9; 22; 5

Figure S21. DFT-calculated spin density and EPR parameters for the $[(^{PicCH2})N4Pd^{III}]^{2+}$ complex.

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