Supplementary Information

A Nickel Pincer Model of the Active Site of Lactate Racemase: Ligand Participation in Hydride Transfer

Tao Xu,[a] Matthew D. Wodrich,[a,b] Rosario Scopelliti,[a] Clemence Corminboeuf,[b] and Xile Hu[a]

[a]Laboratory of Inorganic Synthesis and Catalysis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne CH-1015, Switzerland; and [b]Laboratory for Computational Molecular Design, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne CH-1015, Switzerland.

Experimental Section

A. Chemicals and Reagents

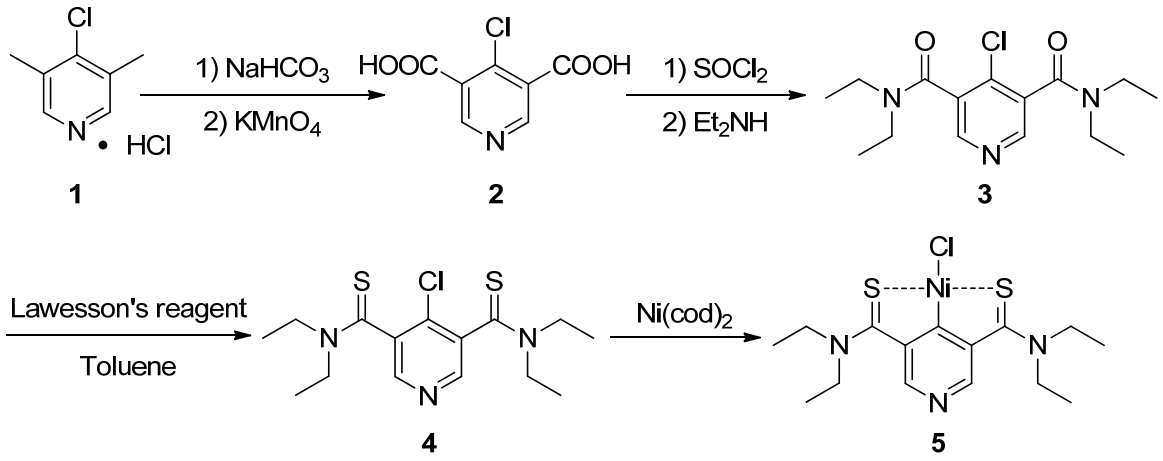
All manipulations were carried out under an inert N_2(g) atmosphere using glovebox techniques. Solvents were purified using a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to the glovebox without exposure to air. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., and were degassed and stored over activated 3Å molecular sieves. All other reagents were purchased from commercial sources. Liquid compounds were degassed by standard freeze-pump-thaw procedures prior to use.

B. Physical Methods

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer. The chemical shifts (δ) are given in parts per million relative to internal standard d8-THF (3.62 and 1.79 ppm). IR spectra were recorded on solid samples on a Varian 800 FT-IR spectrometer using attenuated total reflection (ATR) sampling techniques. Elemental analyses were performed on a Carlo Erba EA 1110 CHN instrument at EPFL. X-ray diffraction studies were carried out in the EPFL Crystallographic Facility. Data collection was performed at low temperature using four-circle kappa diffractometers equipped with CCD detectors. Data were reduced and then corrected for absorption. Solution, refinement and geometrical calculations for all crystal structures were performed by the SHELX software package.

C. Synthetic Methods and Characterization data

1 Synthesis of complex 5 from compound 1.



4-Chloro-3,5-dimethylpyridine hydrochloric acid salt (**1**, 7 g, 39.5 mmol, synthesized according to the literature)[1] was dissolved in water (30 mL) and Et_2O (30 mL), then $NaHCO_3$ (3.65 g, 1.1 eq) in water (20 mL) was added slowly. The mixture was stirred for 15 min and then extracted with ether (30 mL) three times. The combined organic phases were concentrated. The residue was purified by column chromatography on SiO_2 to yield the product 4-chloro-3,5-dimethylpyridine (4.3 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 8.28 (s, 2H), 2.36 (s, 6H) ppm.

Potassium permanganate (10.1 g, 2.1 eq) was added in 100 mL of water and heated to 80°C. Once the $KMnO_4$ was dissolved, 4-chloro-3,5-dimethylpyridine (4.3 g, 30.5 mmol) was added slowly.[2] After this addition, the temperature was raised to 100°C. The mixture was stirred until the purple color disappeared. When the temperature came down to 80°C, another part of $KMnO_4$ (10.1 g, 2.1 eq) was added carefully. The mixture was then heated to 100°C. After 3 h, the purple color again disappeared. After cooling to room temperature, it was filtrated. The liquid layer was concentrated to about 40 mL, then concentrated sulfuric acid (98%, 4 mL) was added slowly. The precipitate was filtered and dried in vacuo to give the dicarboxylic acid as a white solid **2** (3g, 49%). ^{1}H NMR (400 MHz, CD_3OD, 25°C): δ 9.00 (s, 2H) ppm. HRMS: m/z (ESI) calculated $[M+H]^+$: 201.9907, measured: 201.9903.

To the dicarboxylic acid **2** (1.6 g, 8 mmol) in dry DCM (40 mL), $SOCl_2$ (2 mL) and DMF (0.2 mL) were added at room temperature. The mixture was heated to reflux for 2.5 h and concentrated to dryness. Dry toluene (10 mL) was added and concentrated again. Then the residue was dissolved in dry DCM (40 mL), Et_2NH (1.2 g, 2 eq) and triethylamine (1.8 g, 2.2 eq) were added. The mixture was stirred overnight. It was quenched by water and extracted with DCM. The combined organic phases were concentrated. The residue was purified by column chromatography (DCM / MeOH =10:1) on SiO_2 to yield the product **3** (1.7 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ 8.50 (s, 2H), 3.81 (bs, 2H), 3.40 (bs, 2H), 3.17 (bs, 4H), 1.28 (t, J = 7.2 Hz, 6H), 1.10 (t, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ 164.5, 147.7, 136.6, 133.1, 42.9, 39.3, 14.1, 12.5 ppm. HRMS: m/z (ESI) calculated $[M+Na]^+$: 334.1298, measured: 334.1302.

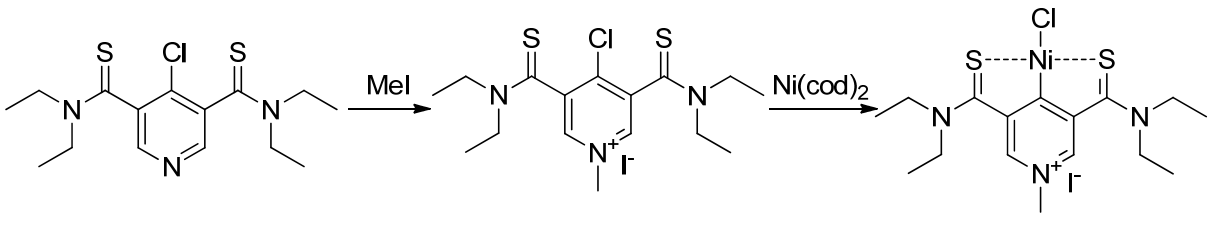
The mixture of dicarboxamide **3** (0.45 g, 1.4 mmol) and Lawesson's reagent [2,4-bis(4-methoxyphenyl)-2,4-dithioxo-1,3,2,4-dithiadiphosphetane] (0.32 g, 0.55 eq) in toluene (5 mL) was stirred for 2 h at 60°C. Then another part of Lawesson's reagent (0.32 g, 0.55 eq) was added and stirred for an additional 3 h. After concentration, the residue was subjected to column chromatography on SiO_2 to yield the crude product which was further purified by recrystallization to give product **4** (0.29 g, 58%). ^{1}H NMR (400 MHz, MeOD, 25°C): δ 8.39

(s, 2H), 4.52-3.84 (m, 2H), 3.95-3.84 (m, 2H), 3.58-3.42 (m, 4H), 1.41 (t, J = 7.2 Hz, 6H), 1.21 (t, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (100 MHz, MeOD, 25°C): δ 192.7, 147.8, 140.8, 134.8, 49.6, 47.9, 14.7, 11.8 ppm. HRMS: m/z (ESI) calculated $[M+H]^+$: 344.1022, measured: 344.1033.

Compound **4** (69 mg, 0.2 mmol) was dissolved in benzene (10 mL) and $Ni(cod)_2$ (55 mg, 0.2 mmol, 1 eq) was added. The mixture turned black. After stirring at 100°C for 20 h, the reaction was cooled to room temperature and filtered to give a black red solid. This solid was put in benzene (10 mL) and stirred for another 2 h. The product was obtained after filtration as a dark red powder solid **5** (55 mg, 69%) that was suitable for elemental analysis. Further recrystallization was made in DMF/Et_2O to give the crystal for X-ray diffraction study. Anal. Calcd for $C_{15}H_{22}ClN_3NiS_2$: C, 44.75; H, 5.51; N, 10.44. Found: C, 44.76, H, 5.70, N, 10.26. ^{1}H NMR (400 MHz, DMSO, 25°C): δ 8.36 (s, 2H,), 4.22-4.00 (m, 8H), 1.56-1.38 (m, 12H) ppm. ^{13}C NMR (100 MHz, DMSO, 25°C): δ 196.4, 186.0, 144.5, 144.0, 51.2, 50.4, 13.4, 10.9 ppm.

Crystallographic details of complex 5. A total of 29852 reflections ($-13 \le h \le 13$, $-12 \le k \le 13$, $-29 \le l \le 29$) were collected at T = 120(2) K in the range of 2.26 to 30.00° of which 11108 were unique (R_{int} = 0.0517); $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The structure was solved by the Direct method. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 0.628 and -0.575 eÅ^{-3}, respectively. The absorption coefficient was 1.339 mm^{-1}. The least squares refinement converged normally with residuals of $R(F)$ = 0.0619, $wR(F^2)$ = 0.1047 and a GOF = 1.119 ($I > 2\sigma(I)$). $C_{16.50}H_{25.50}N_{3.50}S_2ClNiO_{0.50}$, Mw = 439.18, space group P-1, triclinic, a = 9.6962(6), b = 9.7447(7), c = 21.021(2) Å, α =86.499(8)°, β = 84.034(7)°, γ = 89.455(6)°, V = 1971.7(3) Å^3, Z = 4, ρ_{calcd} = 1.479 Mg/m^3. CCDC-1486993 contain(s) the supplementary crystallographic data for this work. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

2 Synthesis of complex 7 from compound 4.



4 **6** **7**

Compound **4** (0.66 g, 2 mmol) was dissolved in benzene (3 mL) and CH_3I (1.8 mL) was added. After stirring at 100°C overnight, the reaction was cooled to room temperature and filtered to give the salt as a yellow solid (**6**, 0.85 g, 92%) with some impurity, all of which was directly used in the next step. ^{1}H NMR (400 MHz, CD_3OD, 25°C): δ 9.00 (s, 2H,), 4.39 (s, 3H), 4.38-4.31 (m, 2H), 4.08-4.00 (m, 2H), 3.79-3.70 (m, 2H), 3.64-3.56 (m, 2H), 1.43 (t, J = 7.2 Hz, 6H), 1.31 (t, J = 7.2 Hz, 6H) ppm. HRMS: m/z (ESI) calculated $[M-I]^+$: 358.1178, measured: 358.1180.

Compound **6** (97 mg, 0.2 mmol) was dissolved in benzene (25 mL) and $Ni(cod)_2$ (55 mg, 0.2 mmol, 1 eq) was added. The mixture turned black immediately. After stirring at room temperature for 20 h, the reaction was filtered to give a black solid. This solid was put in benzene (10 mL) and stirred for another 2 h. The product was obtained after filtration as a black powder solid **7** (95 mg, 87%). Further recrystallization was made in DMF/Et_2O to give crystals that were suitable for X-ray diffraction study and elemental analysis. Anal. Calcd for $C_{16}H_{25}ClIN_3NiS_2$: C, 35.29; H, 4.63; N, 7.72. Found: C, 35.33, H, 4.72, N, 7.86. ^{1}H NMR (400 MHz, DMSO, 25°C): δ 8.22 (s, 2H,), 4.22 (s, 3H), 4.19-4.05 (m, 8H), 1.54-1.36 (m, 12H) ppm. ^{13}C NMR (100 MHz, DMSO, 25°C): δ 197.9, 193.7, 145.0, 138.5, 52.7, 51.8, 49.3, 14.2, 11.7 ppm.

Crystallographic details of complex 7. A total of 14265 reflections ($-12 \le h \le 8$, $-14 \le k \le 15$, $-21 \le l \le 22$) were collected at T = 139.99 (10) K in the range of 4.44 to 75.37° of which 4275 were unique (R_{int} = 0.0365); $Cu_{K\alpha}$ radiation (λ = 1.54184 Å). The structure was solved by the Direct method. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 1.293 and -0.868 eÅ^{-3}, respectively. The absorption coefficient was 15.983 mm^{-1}. The least squares refinement converged normally with residuals of $R(F)$ = 0.0316, $wR(F^2)$ = 0.0832 and a GOF = 1.042 ($I > 2\sigma(I)$). $C_{16}H_{25}N_3S_2ClNiI$, Mw = 544.57, space group $P2_1/c$, monoclinic, a = 9.90168(16), b = 12.10351(18), c = 17.9225(3) Å, α =90°, β = 103.0346(16)°, γ = 90°, V = 2092.58(6) Å^3, Z = 4, ρ_{calcd} = 1.729 Mg/m^3. CCDC-1486994 contain(s) the supplementary crystallographic data for this work. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

D. Computational Details

The geometries of relevant compounds were optimized at the M06/def2-SVP level in implicit acetonitrile solvent [SMD solvation model [3]] using the "ultrafine" grid in

Gaussian09.[4] Structures were confirmed to be minima or transition states on the potential energy surface via examination of vibrational frequencies (zero imaginary frequencies for minima, one for transition states). Reported free energies include unscaled free energy corrections determined at the same theoretical level. The M06 free energies were complemented by single point computations on the optimized M06 geometries using a density-dependent dispersion correction appended to the PBE0 functional (PBE0-dDsC) with the TZ2P basis set as implemented in ADF. The reported PBE0-dDsC free energies include solvation corrections (in acetonitrile) determined at the same theoretical level using COSMO-RS, also as implemented in ADF.[5,6] Hirshfeld-I charges were determined at the M06/def2-SVP level using an in-house modified version of QChem.[7] DORI maps were computed on a grid with a modified version of DGrid[8] and Paraview[9] was used to visualize the results.

E. Dehydrogenation of alcohol mediated by nickel complexes and isolation of 10

A solution of a Ni complex (0.02 mmol), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), alcohol or lithium alkoxide (1 equiv. or 5 equiv.) in solvent (1 mL) was stirred at 100^{o}C for 10 h under nitrogen atmosphere. Then water was added to quench the reaction. The reaction was separated by adding EtOAc. Decane (20 μL) was added as an internal standard and the reaction was detected by GC-MS. The yields of products were conducted using standard equations which were drawn according the ratios of the pure products in different amounts to the internal standard. The different trials are summarized in Table S1.

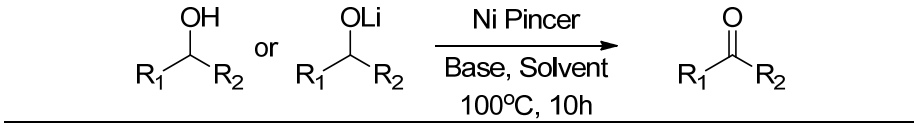
The reaction (Table S1, Entry 6) was cooled to room temperature after 3 h. After removing the solvent in vacuo, DCM (4 mL) and water (4 mL) were added. The organic layer was extracted by water three times (4 mL). The combined aqueous layer was concentrated. The residue was purified by preparative TLC using a solvent mixture (hexane / DCM / MeOH = 5:5:2 v/v/v) as eluent to afford compound **10** (1.9 mg, 21%) with some impurities. Further purification led to decomposition of the compound.

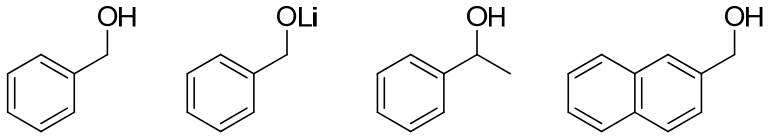
Compound **10** can also be prepared by another procedure: In the NMR tube, to complex **7** (4 mg) in CD_3CN (0.5 mL), HCl in dioxane (25 uL, 4M) was added. The tube was put in an oil bath at 50^{o}C until the reaction completely finished (detected by NMR). The solution was concentrated to give compound **10** in quantitative yield.

^{1}H NMR (400 MHz, CD_3OD, 25°C): δ 8.90 (d, J = 1.2 Hz, 2H,), 8.35 (t, J = 1.2 Hz, 1H), 4.38 (s, 3H), 4.14 (q, J = 7.2 Hz, 4H), 3.63 (q, J = 7.2 Hz, 4H), 1.39 (t, J = 7.2 Hz, 6H), 1.24 (t, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CD_3OD, 25°C): δ 190.3, 144.4, 142.1, 137.4, 50.2, 47.7, 14.1, 11.3 ppm. HRMS: m/z (ESI) calculated $[M\text{-}I]^+$: 324.1568, measured: 324.1570. m/z (ESI negative) calculated $[I]^-$: 126.9039, measured: 126.9052.

For the reaction with deuterium benzyl alcohol (α,α-D_2-**8**), the calculated $[M\text{-}I]^+$ for D-**10** is 325.1625, measured 325.1626. From the ^{1}H NMR, the deuterium percent at the C4 position is above 97%, while at the C2 position it is 17% (See Figure S6).

Table S1. The alcohol oxidation mediated by Ni pincer complexes.[a]





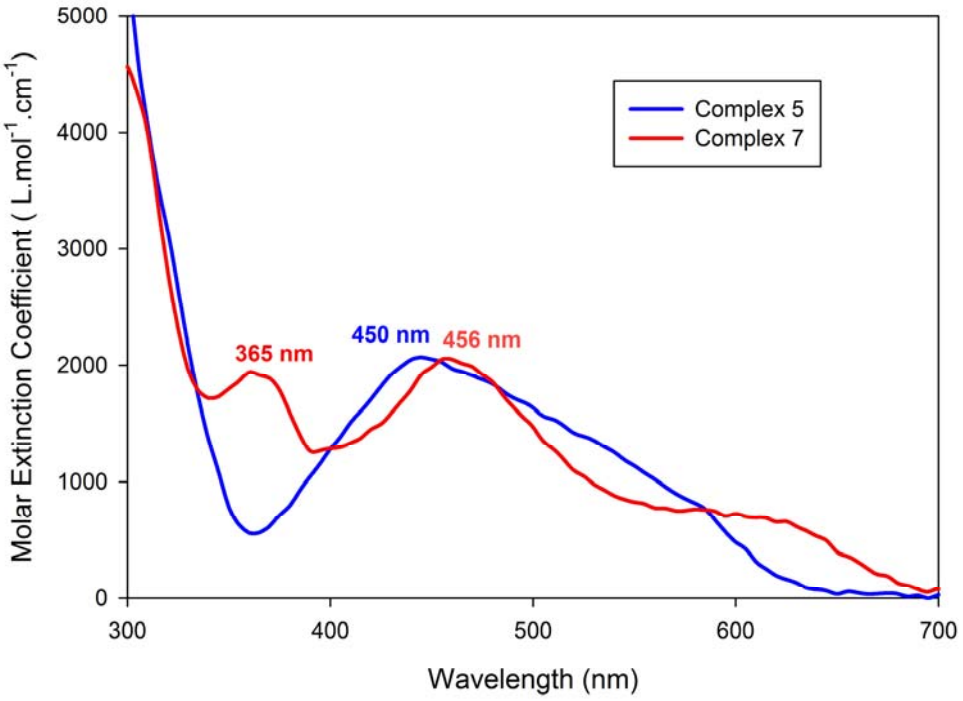
8 **11** **12** **13**

Entry	Nickel Pincer	Alcohol (equiv.)	Base (equiv.)	Solvent	Yield[b]
1	**7**	**8** (5)	---	DMF	11%
2	**7**	**8** (5)	NMI (5)	DMF	14%
3	**7**	**8** (5)	DBU (5)	DMF	38%
4	**7**	**8** (5)	DBU (5)	DMSO	48%
5	**7**	**8** (5)	DBU (5)	CH_3CN	62%
6	**7**	**8** (1)	DBU (1)	CH_3CN	64%
7	**7**	**11** (1)	---	CH_3CN	25%
8	**7**	**11** (5)	---	CH_3CN	0
9[c]	**7**	**12** (1)	DBU (1)	CH_3CN	49%
10	**7**	**13** (1)	DBU (1)	CH_3CN	53%
11	**5**	**8** (1)	DBU (1)	CH_3CN	8%
12	**5**	**8** (5)	DBU (5)	CH_3CN	10%
13	$NiCl_2$	**8** (1)	DBU (1)	CH_3CN	5%

[a] The reactions were conducted on a 0.02 mmol scale in solvent (1.0 mL) under N_2. [b] The yields were determined by GC using *n*-decane as the internal standard. [c] While (*S*)-1-phenylethanol was used, it gave the same result, with no detected racemization of (*S*)-1-phenylethanol.

Table S2. Computed electronic energies, free energy corrections, and solvation corrections for relevant compounds.

Compound	M06/def2-SVP Electronic Energy (hartree)	M06/def2-SVP Free Energy Correction (hartree)	PBE0-dDsC/TZ2P//M06/def2-SVP Electronic Energy (hartree)	COSMO-RS Solvation Correction (kcal/mol)
5	-3512.350072	0.300993	-11.561404	-27.074
7	-3552.045998	0.337850	-12.228410	-63.399
DBU	-422.170761	0.181025	-6.254432	-6.163
H+-DBU	-422.650126	0.192071	-6.224073	-48.548
H+-DBU-Cl-	-882.848194	0.189994	-6.559690	-26.837
8 - Benzylalcohol	-346.279951	0.100982	-4.414223	-7.895
9 - Benzaldehyde	-345.082472	0.078790	-4.082740	-5.995
$\mathbf{11_A}$	-4320.543994	0.670656	-22.963765	-60.781
$\mathbf{11_{TS(A\rightarrow B)}}$	-4320.494164	0.661847	-22.910974	-68.551
$\mathbf{11_B}$	-3552.790903	0.347103	-12.599371	-34.363
$\mathbf{12_A}$	-4320.538049	0.669142	-22.957083	-60.780
$\mathbf{12_{TS(A\rightarrow B)}}$	-4320.510811	0.667431	-22.925478	-63.530
$\mathbf{12_B}$	-3552.786132	0.345321	-12.596798	-33.212
$\mathbf{13_A}$	-3437.641631	0.449738	-16.314187	-63.747
$\mathbf{13_{A'}}$	-3437.622227	0.450525	-16.304460	-54.437
$\mathbf{13_{TS(A'\rightarrow B)}}$	-3437.605502	0.447836	-16.285389	-54.563
$\mathbf{13_B}$	-3092.520962	0.345714	-12.199366	-54.261
$\mathbf{14_A}$	-4280.839826	0.624949	-22.272158	-33.660
$\mathbf{14_{TS(A\rightarrow B)}}$	-4280.787435	0.624789	-22.207968	-45.396
$\mathbf{14_B}$	-3513.056528	0.307958	-11.784275	-67.500
$\mathbf{15_A}$	-4280.835218	0.626082	-22.269875	-33.828
$\mathbf{15_{TS(A\rightarrow B)}}$	-4280.785969	0.622856	-22.201770	-44.913
$\mathbf{15_B}$	-3513.055434	0.307536	-11.794228	-60.509
$\mathbf{16_A}$	-3397.945340	0.410571	-15.646973	-26.859
$\mathbf{16_{A'}}$	-3397.920687	0.410857	-15.624194	-22.916
$\mathbf{16_{TS(A'\rightarrow B)}}$	-3397.904362	0.405873	-15.604145	-23.665
$\mathbf{16_B}$	-3052.822461	0.307953	-11.521827	-21.749



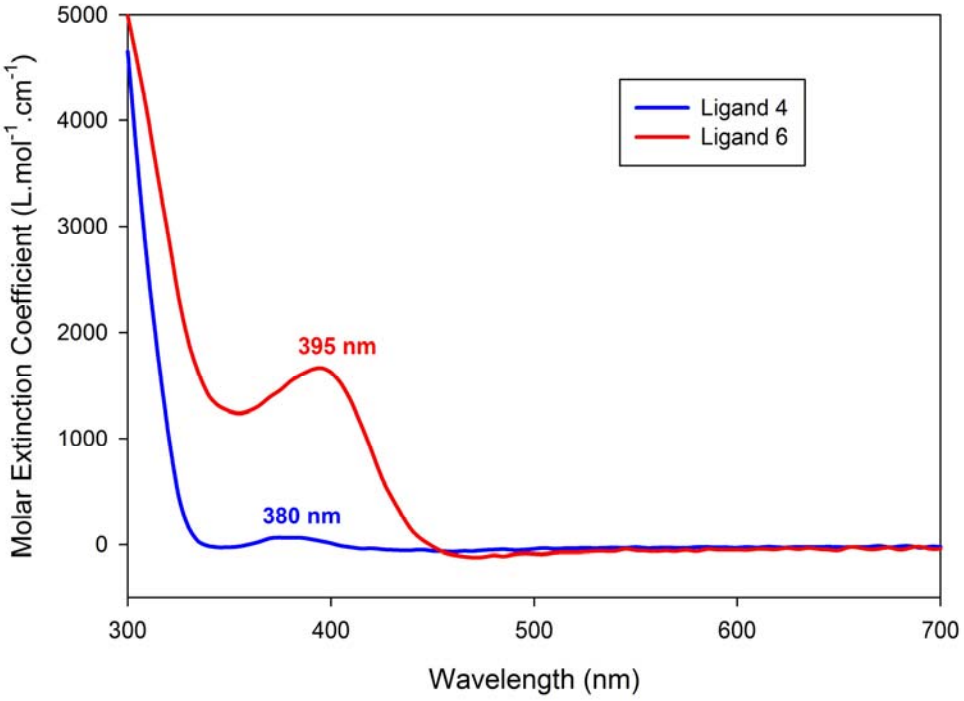


Figure S1. UV-Vis spectra. (top) UV-Vis spectra of complex **5** and complex **7** in CH_3CN. Concentration: 30 μM (**5**) and 40 μM (**7**). (bottom) UV-Vis spectra of ligand **4** and ligand **6** (bottom). Concentration: 120 μM (**4**) and 60 μM (**6**).

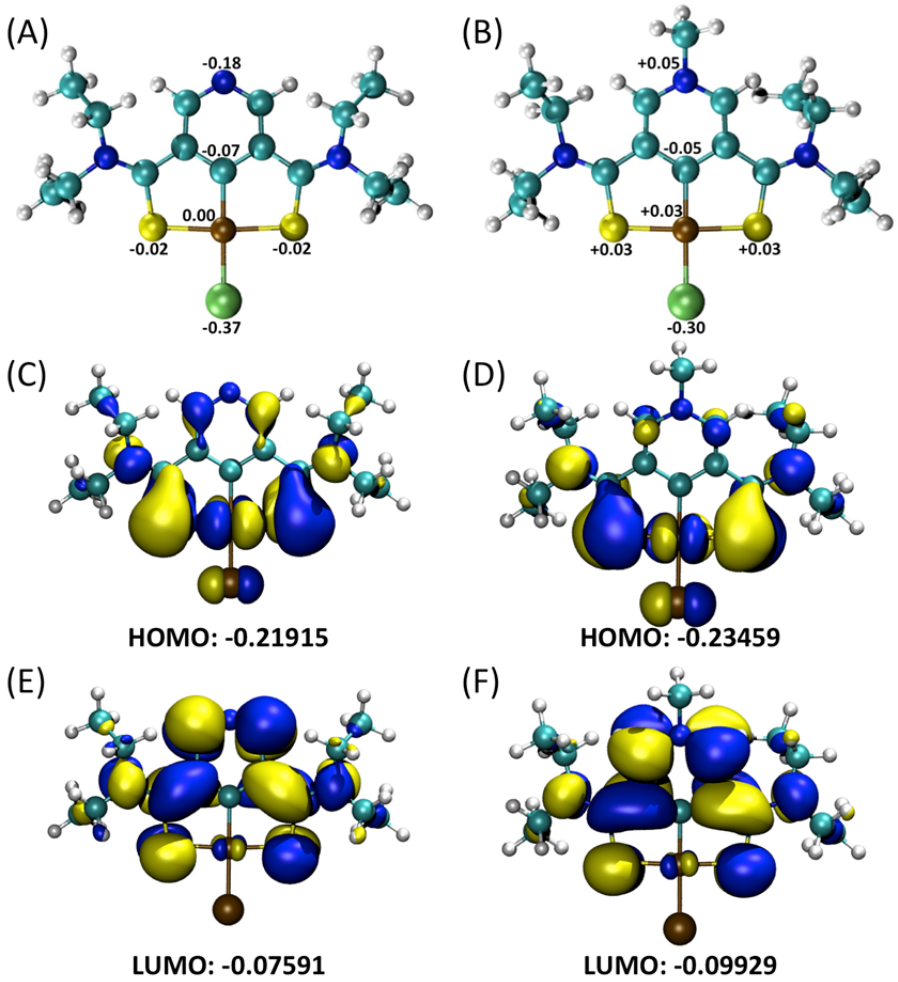


Figure S2. **Electronic structures.** Hirshfeld-I charges (A,B) and frontier orbitals (C-F) of complexes **5** (A, C, E) and **7** (B, D, F) computed at the M06/def2-SVP level. Molecular orbital energies given in atomic units.

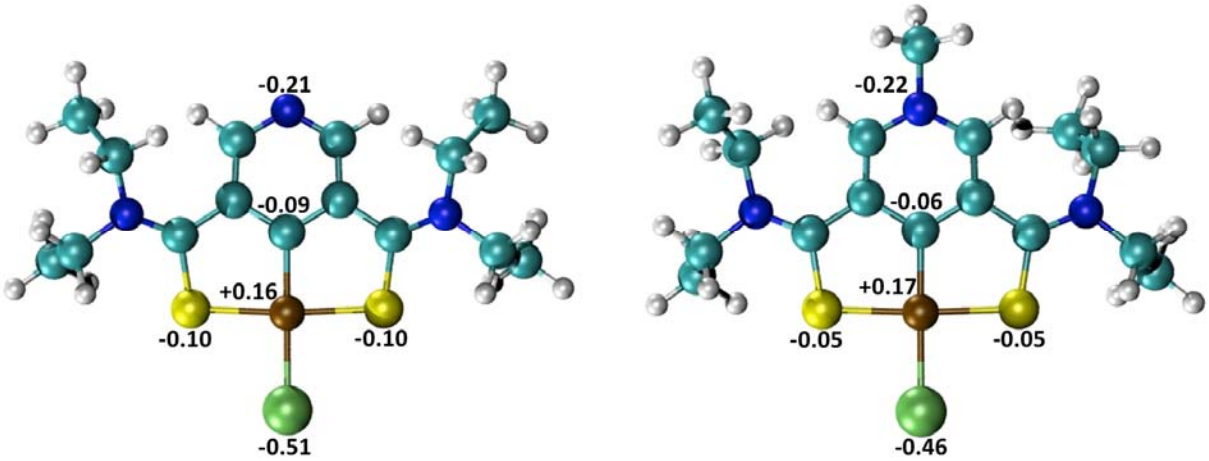


Figure S3. **Mulliken charges (M06/def2-SVP)**. The charges for **5** (left) and for **7** (right).

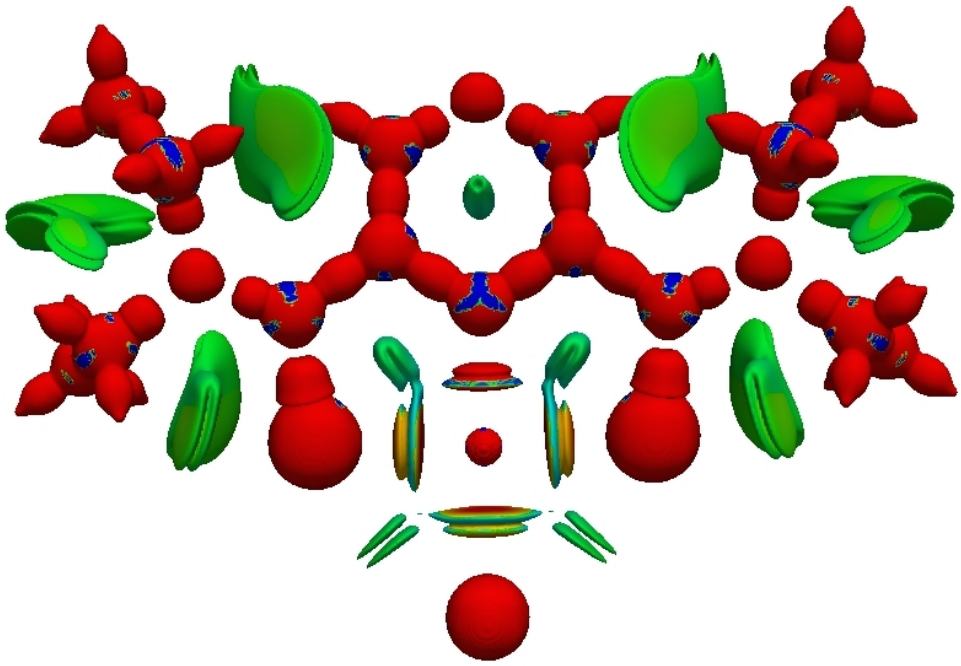


Figure S4. DORI = 0.9 isosurface for **5**. The isosurface is color coded with $sgn(\lambda_2)\rho(\mathbf{r})$ ranging from -0.01 au (red) to 0.01 au (blue).

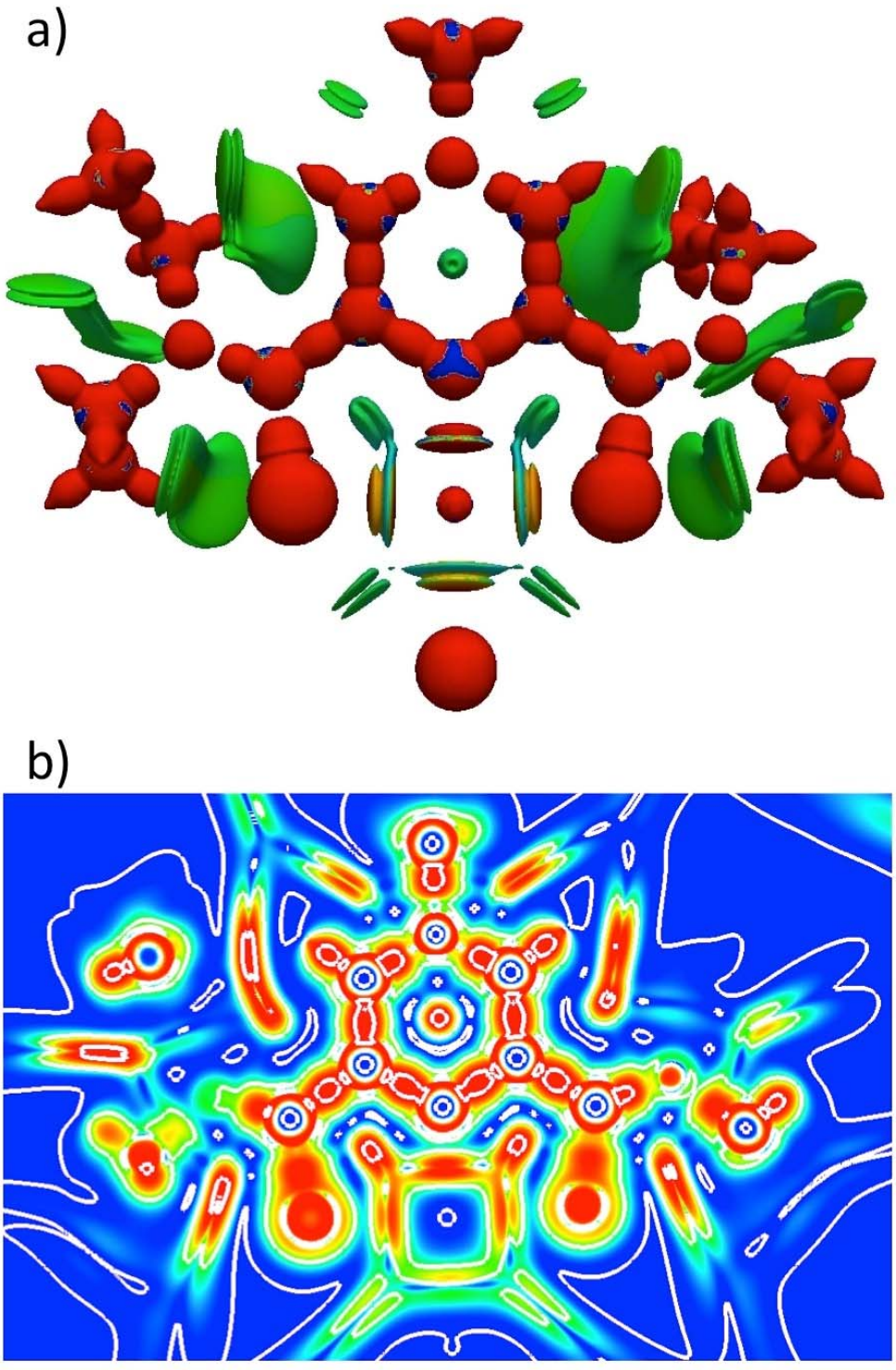
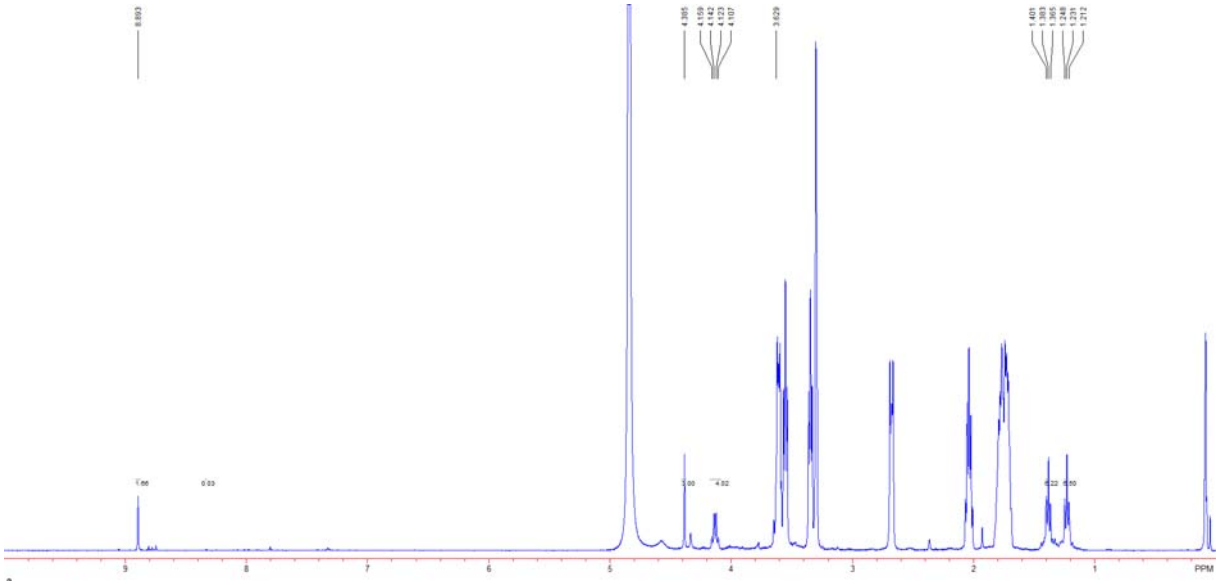
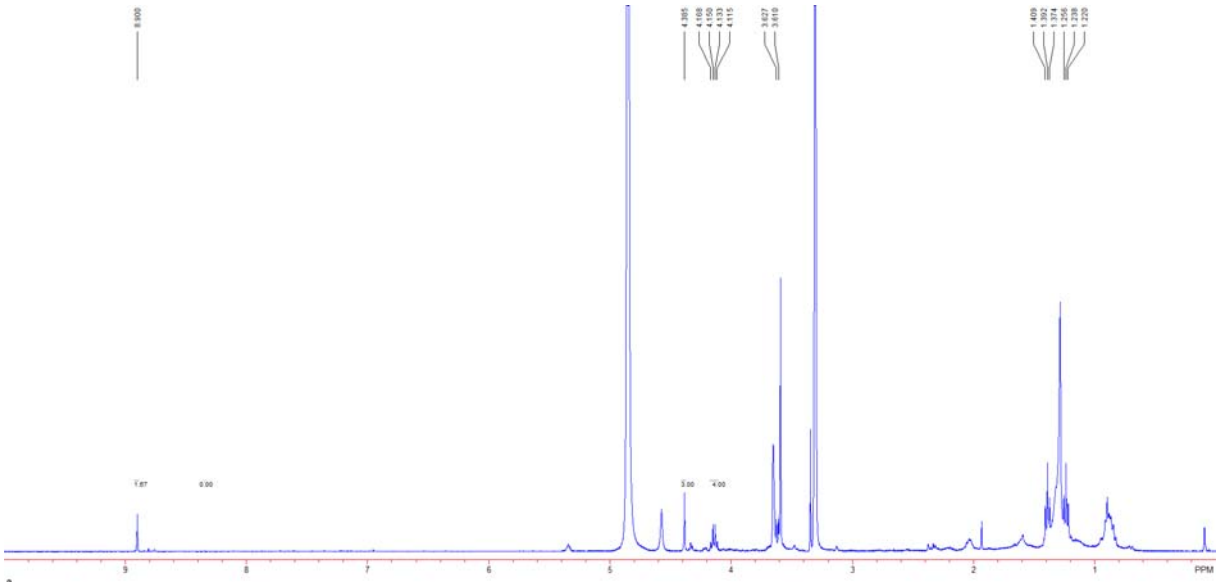


Figure S5. a) DORI = 0.9 isosurface for **7**. The isosurface is color coded with $\mathrm{sgn}(\lambda_2)\rho(\mathbf{r})$ ranging from -0.01 au (red) to 0.01 au (blue). b) DORI map in the plane of the pyrdinium ring of **7**. Isocontour lines of $DORI[\rho] \in \{0.01, 0.50, 0.99\}$ are plotted in white and DORI values range from 0 (blue) to 1 (red).


8.893
4.385
4.159
4.145
4.133
4.107
3.629
1.401
1.393
1.365
1.248
1.238
1.212
PPM


8.900
4.385
4.168
4.159
4.133
4.115
3.627
3.610
1.409
1.392
1.374
1.256
1.238
1.220
PPM

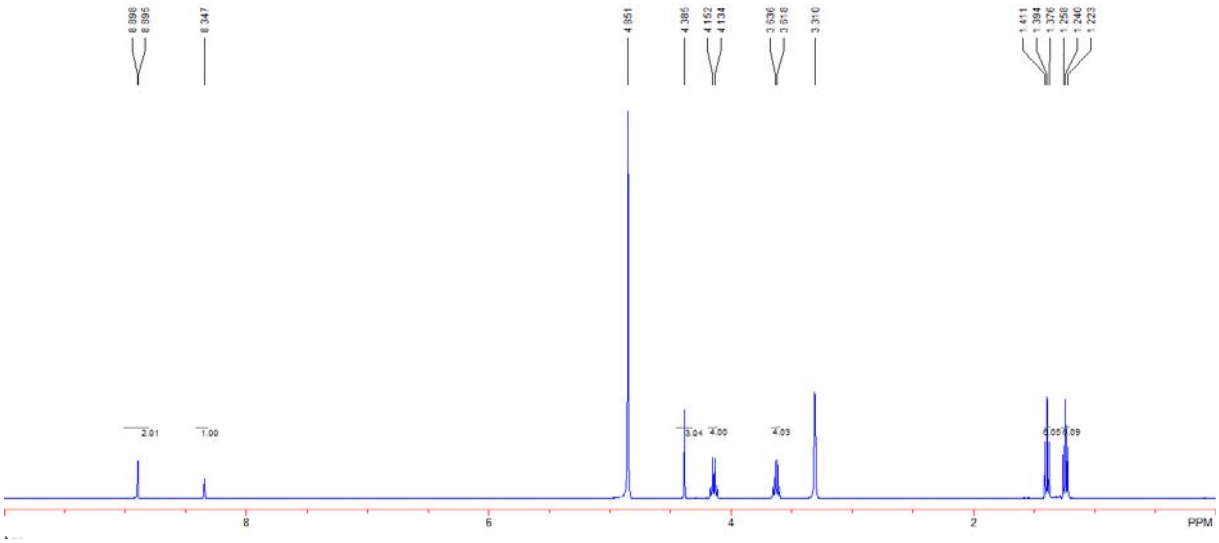

8.896
8.895
8.347
4.951
4.385
4.152
4.134
3.536
3.518
3.310
1.411
1.394
1.376
1.258
1.240
1.223
2.01
1.00
3.04
4.00
4.03
PPM

Figure S6. ^{1}H NMR spectra indicating the formation of deuterated 10. (a) The ^{1}H NMR spectrum of the crude aqueous layer from the dehydrogenation reaction using α,α-D_2-benzyl alcohol (top). (b) The ^{1}H NMR spectrum of deuterium compound **10** after preliminary purification (middle). (c) The ^{1}H NMR spectrum of compound **10** (bottom).

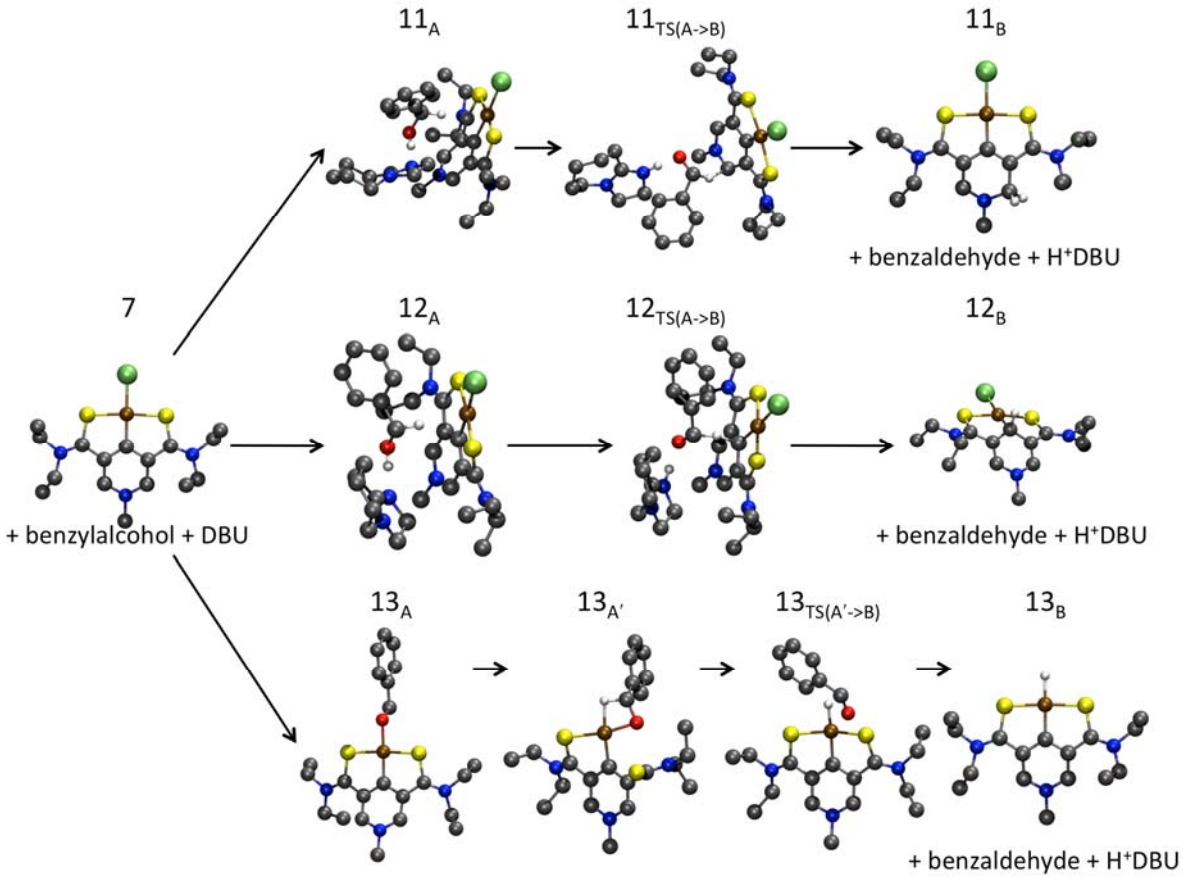


Figure S7. 3D representations of M06/def2-SVP optimized geometries of selected points in the potential mechanisms of **7**.

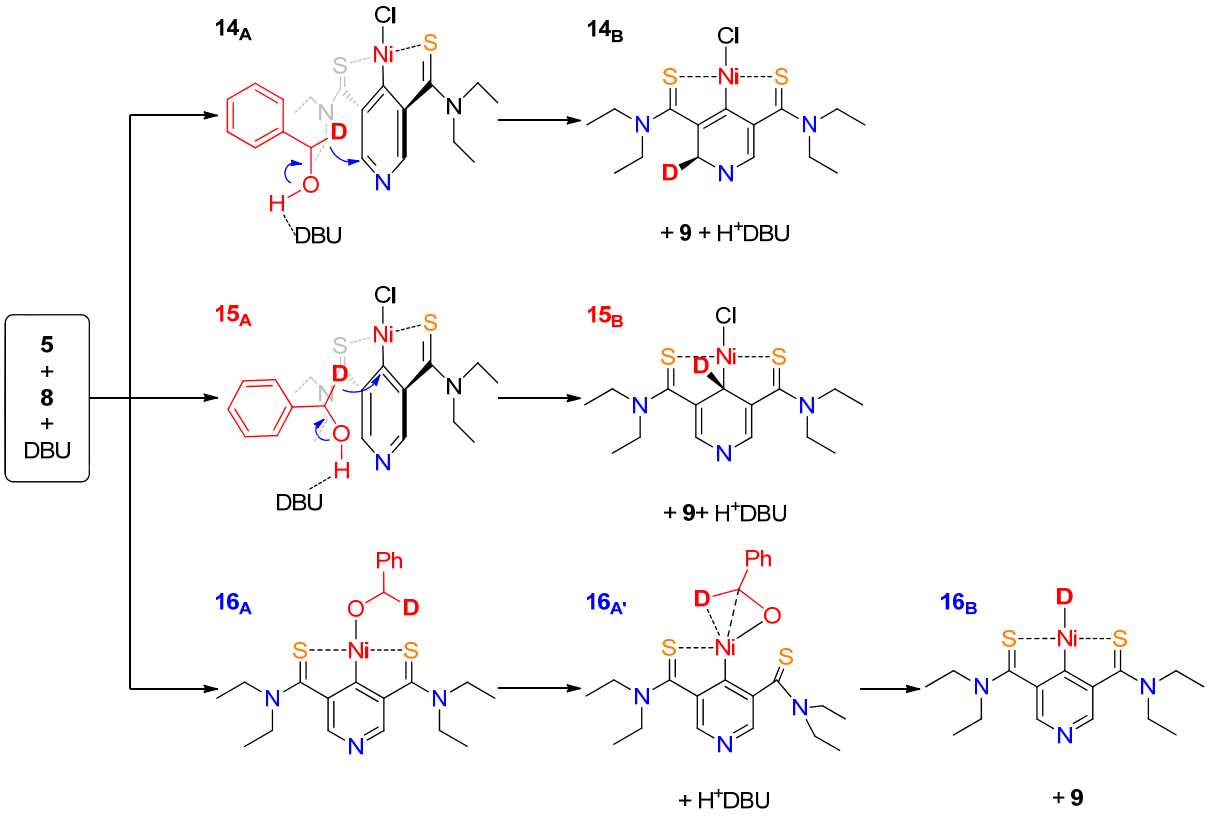


Figure S8. Potential mechanisms for the transformation of benzyl-alcohol to benzaldehyde utilizing **5**.

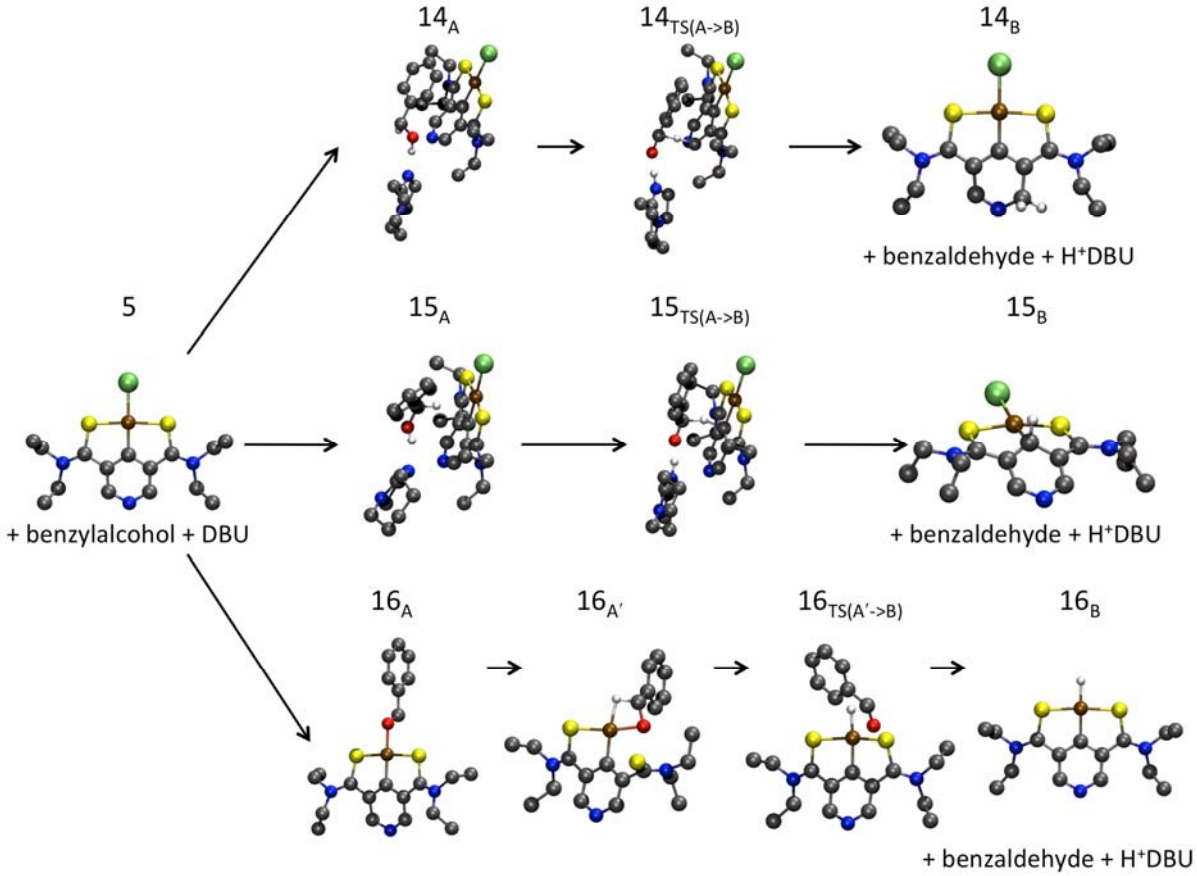


Figure S9. 3D representations of M06/def2-SVP optimized geometries of selected points in the potential mechanisms of **5**.

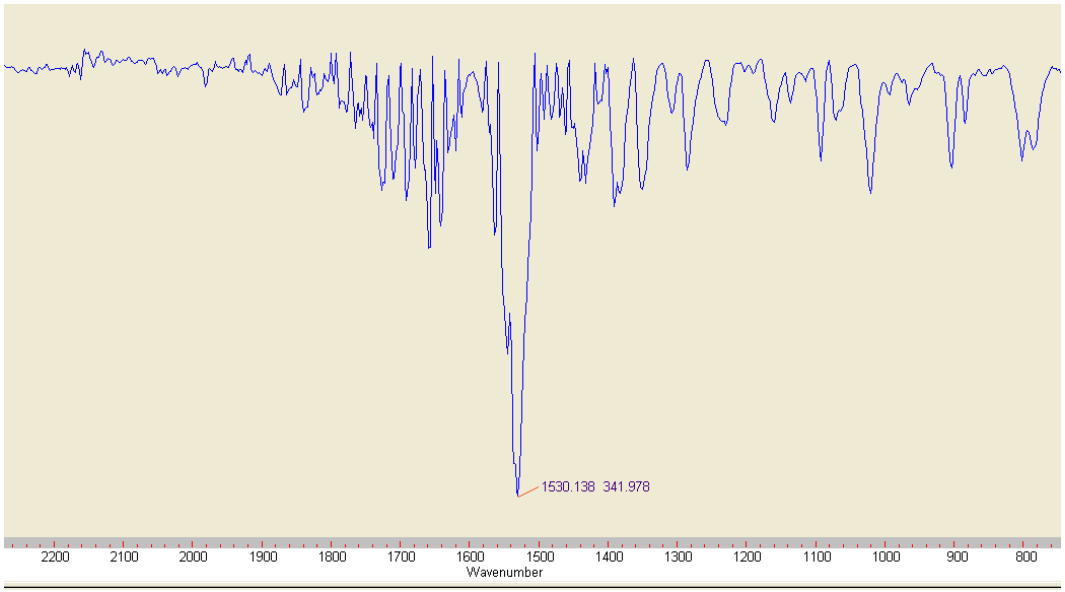


Figure S10. The IR spectrum of complex **5** collected in the solid-state.

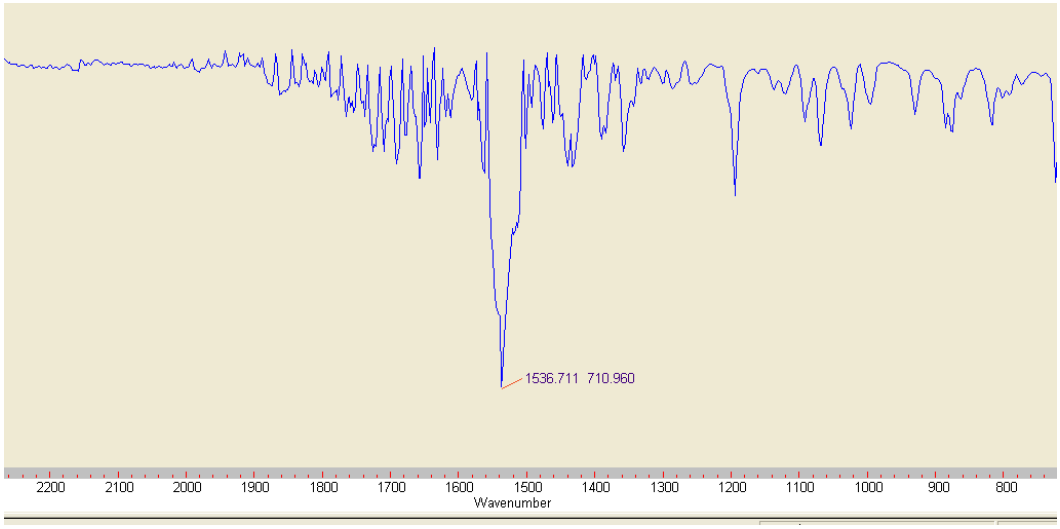
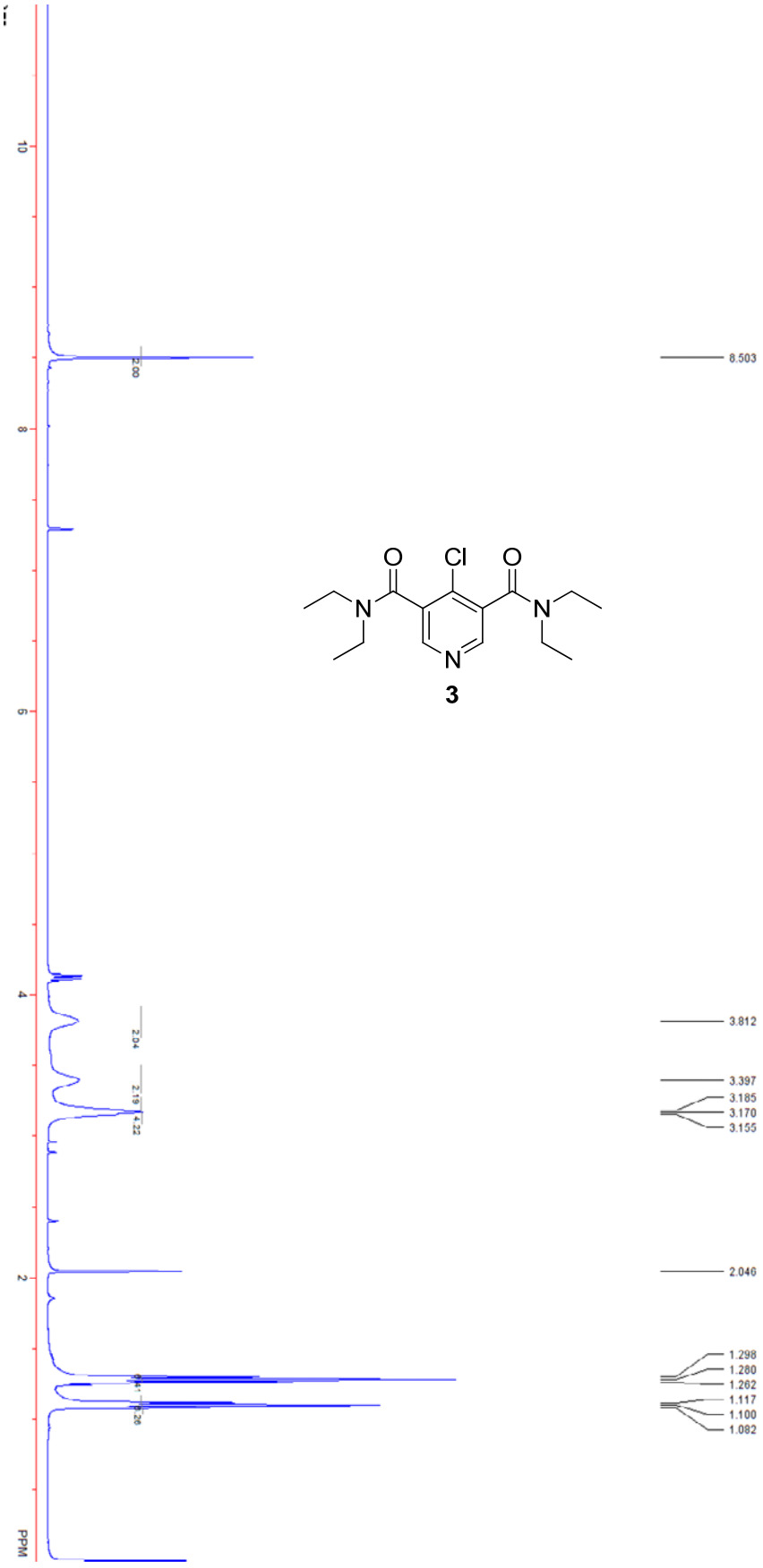


Figure S11. The IR spectrum of complex **7** collected in the solid-state.



3

Figure S12. The ^{1}H NMR spectrum of compound **3**.

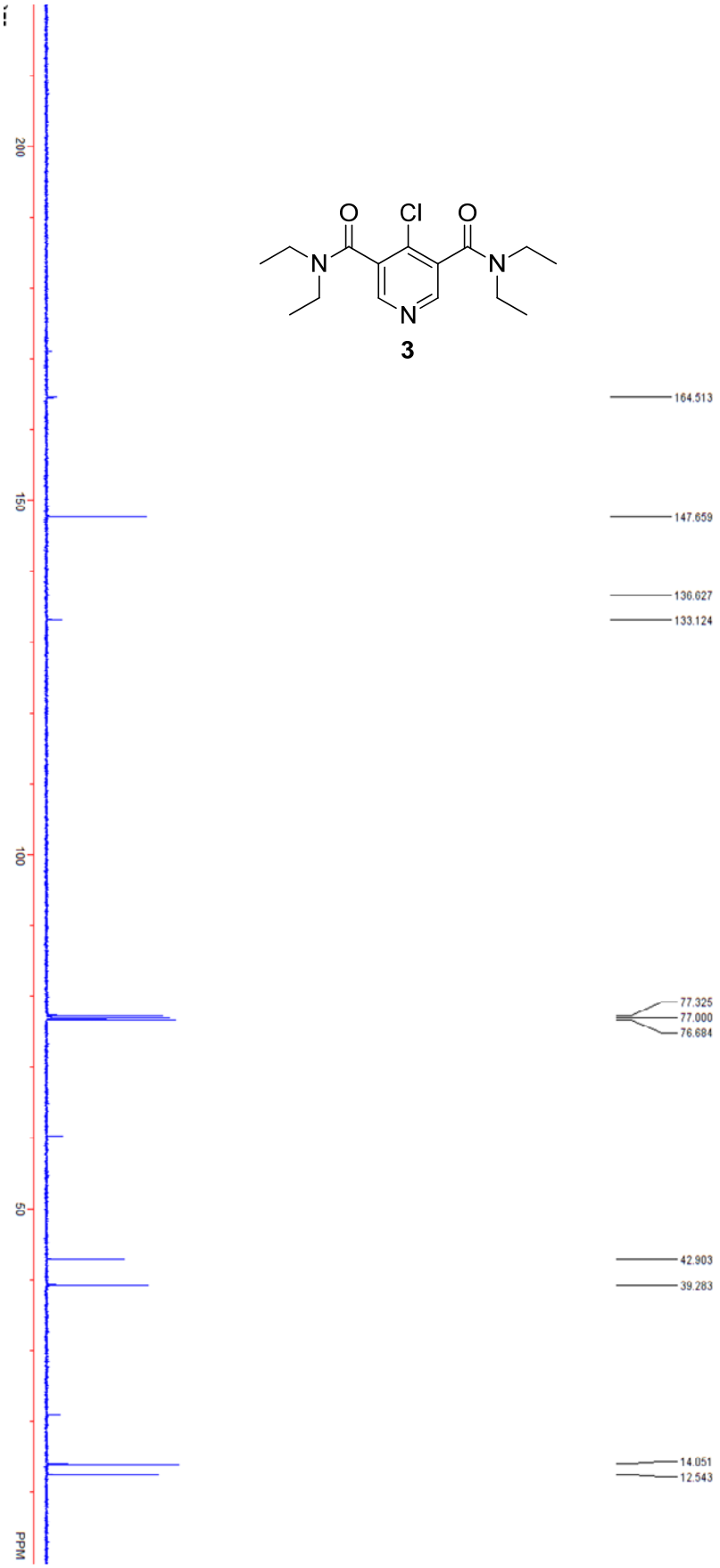
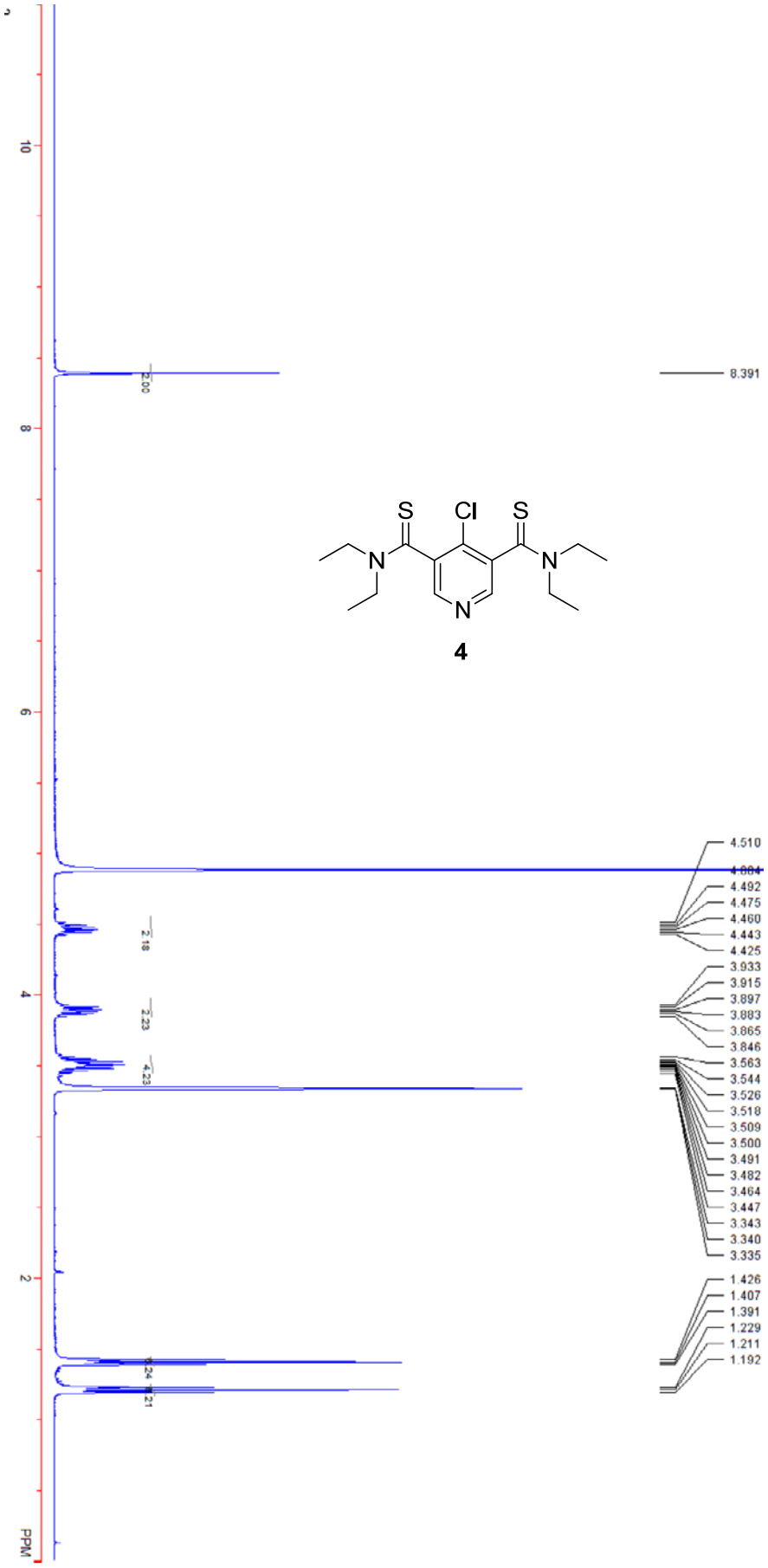


Figure S13. The ^{13}C NMR spectrum of compound **3**.



S Cl S
N N
N

4

Figure S14. The ^{1}H NMR spectrum of compound **4**.

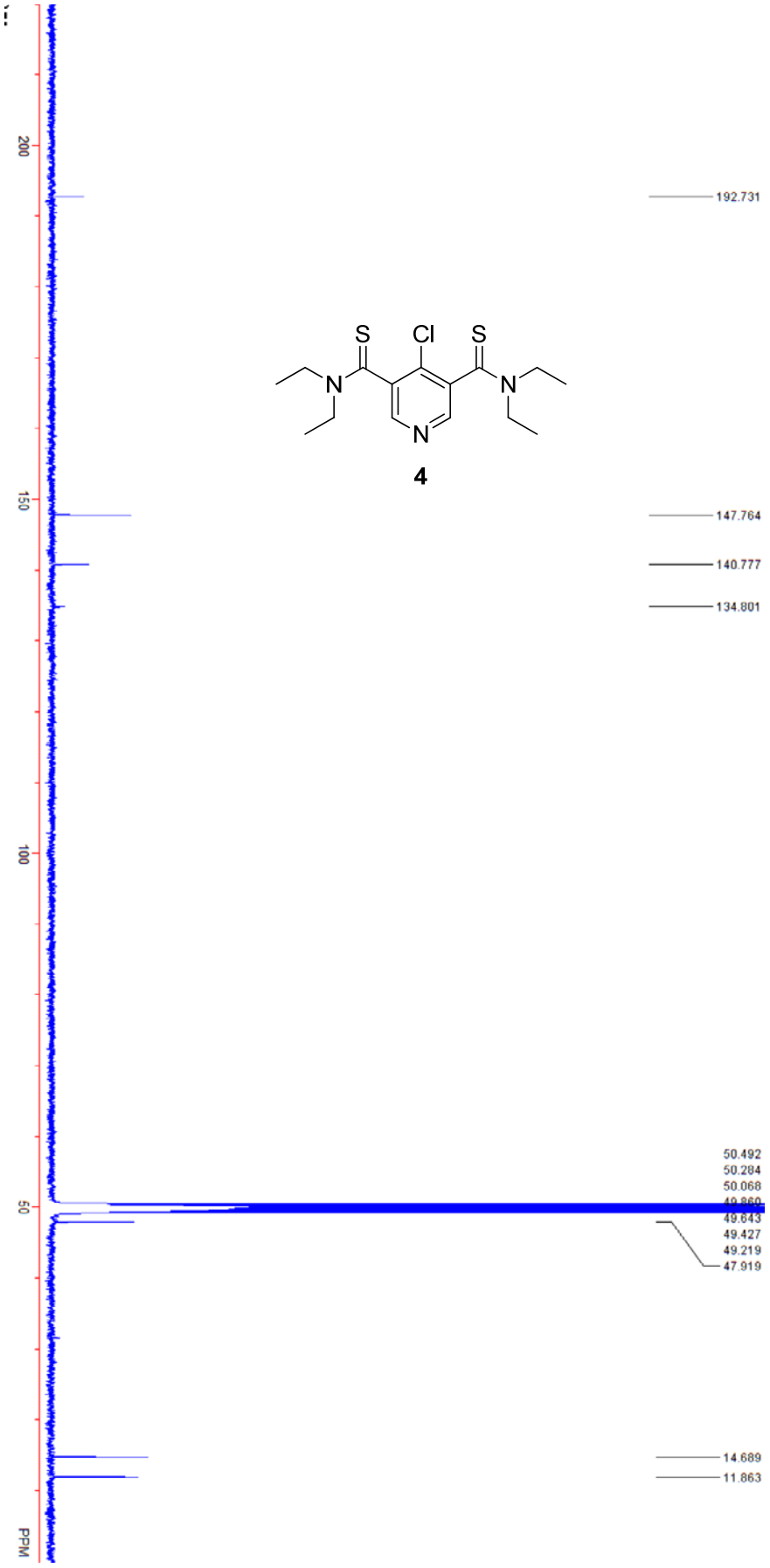


Figure S15. The ^{13}C NMR spectrum of compound **4**.

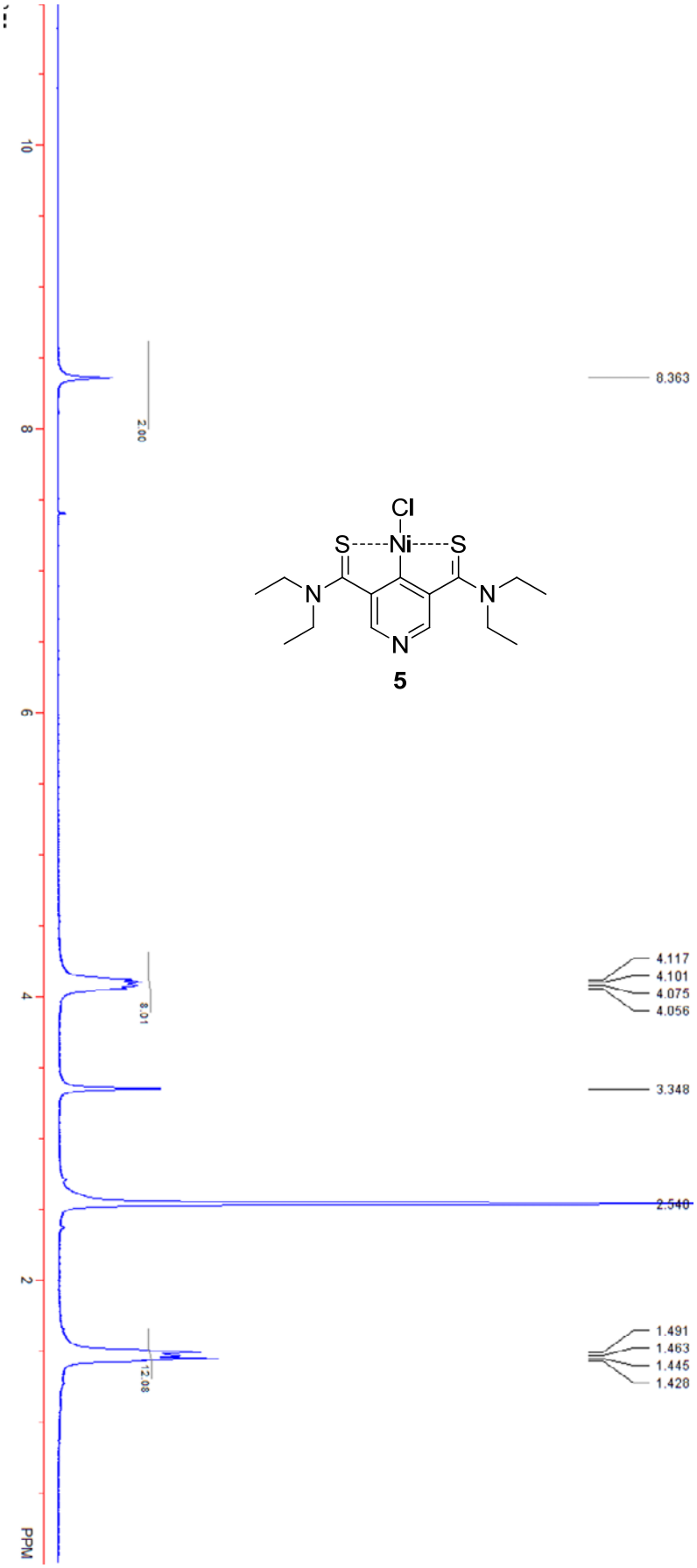


Figure S16. The ^{1}H NMR spectrum of compound **5**.

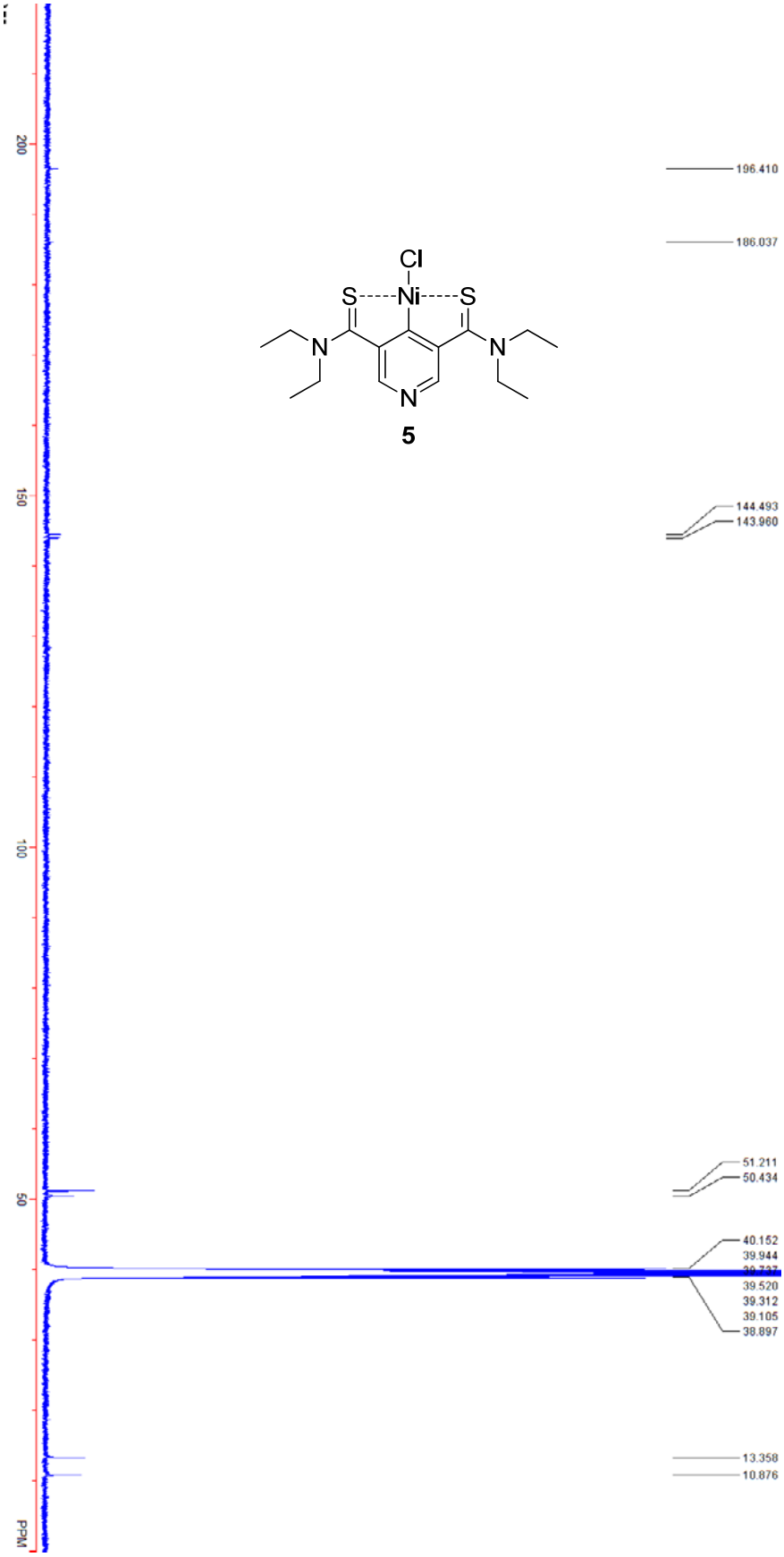


Figure S17. The ^{13}C NMR spectrum of compound **5**.

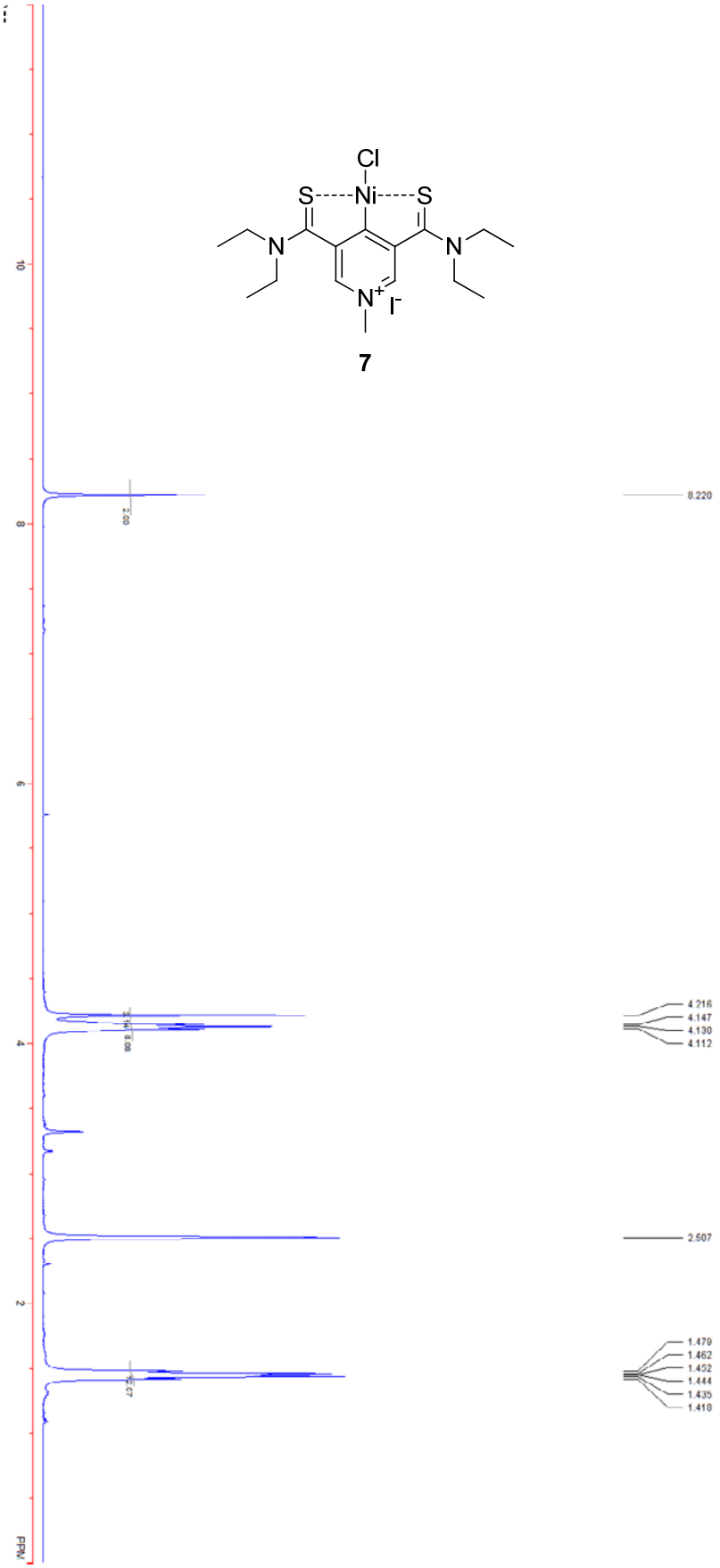


Figure S18. The ^{1}H NMR spectrum of compound **7**.

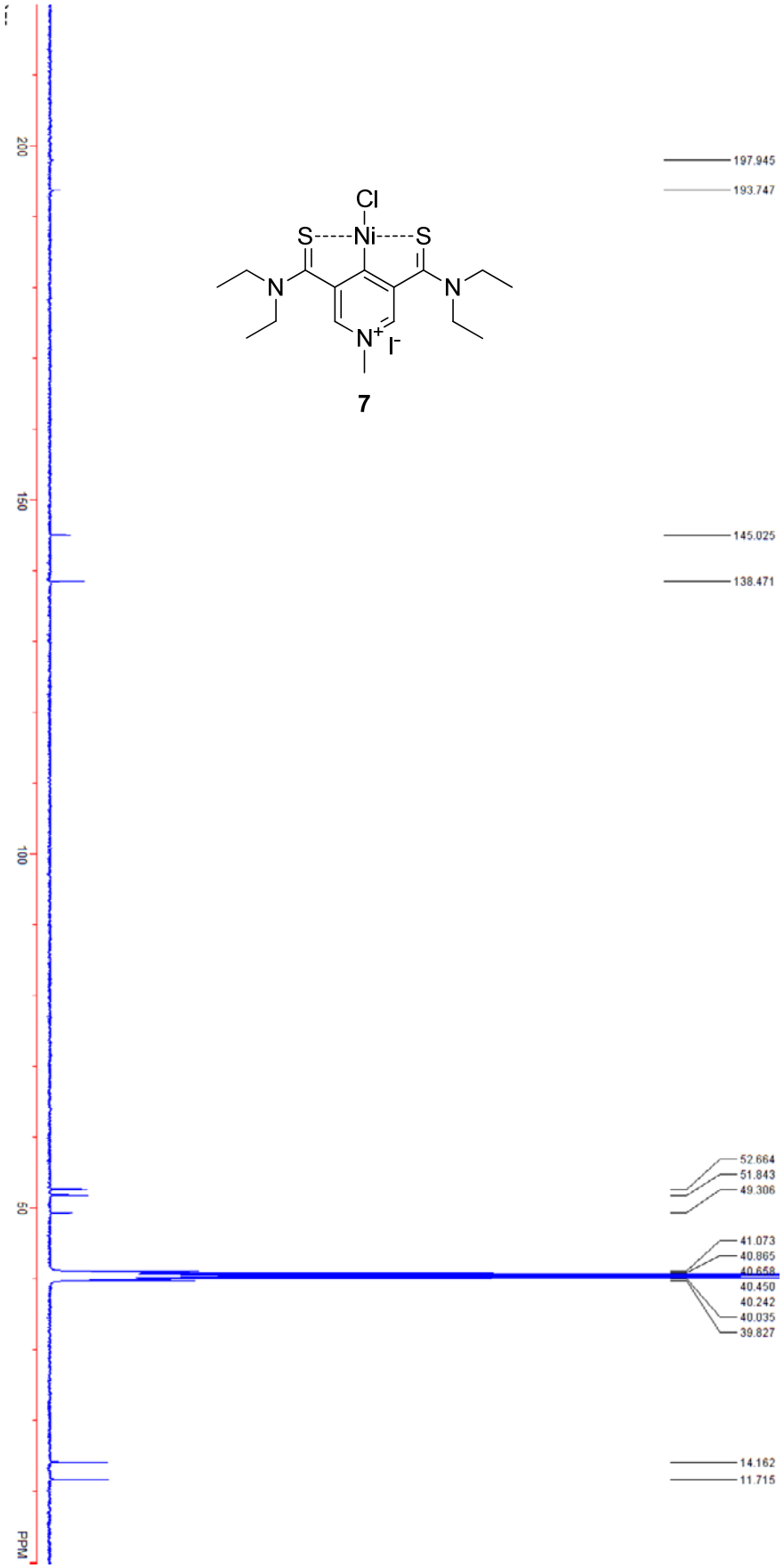
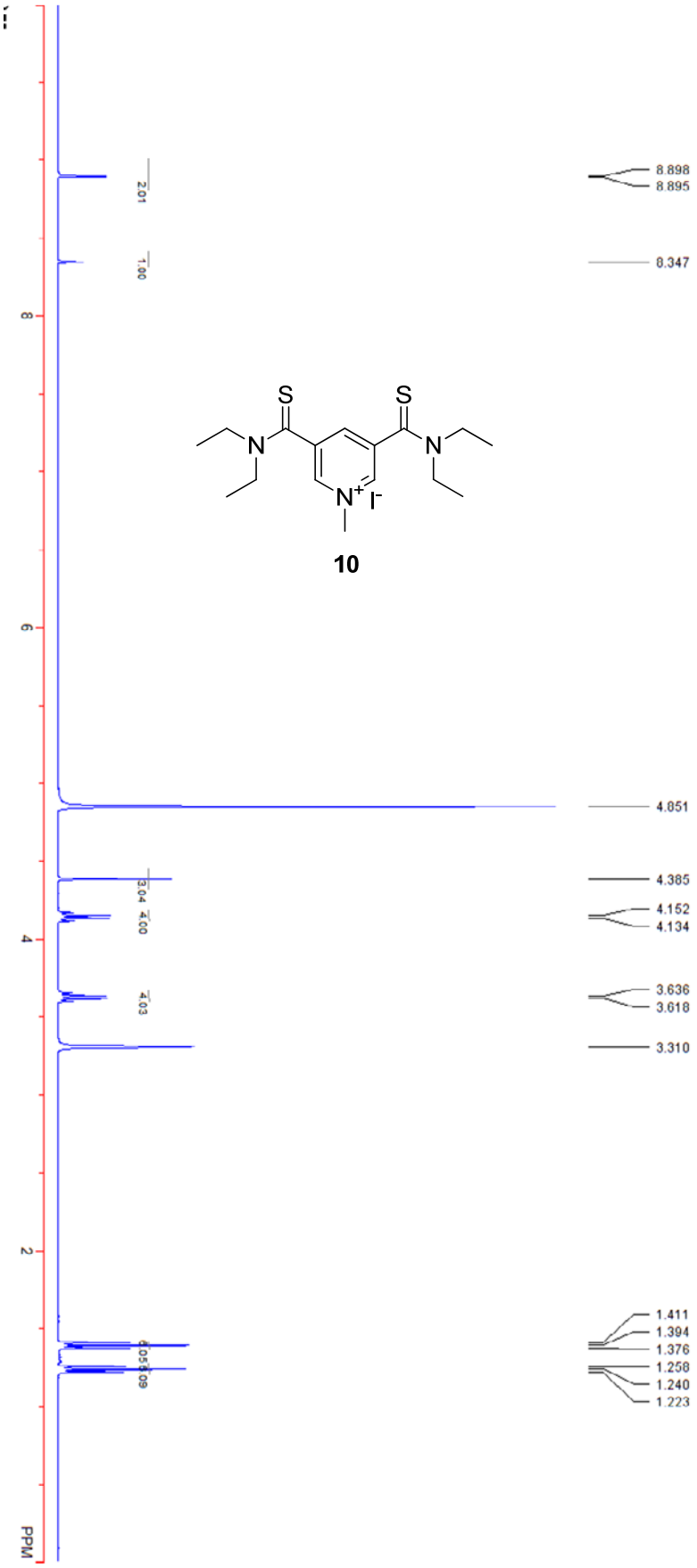


Figure S19. The ^{13}C NMR spectrum of compound **7**.



10

Figure S20. The ^{1}H NMR spectrum of compound **10**.

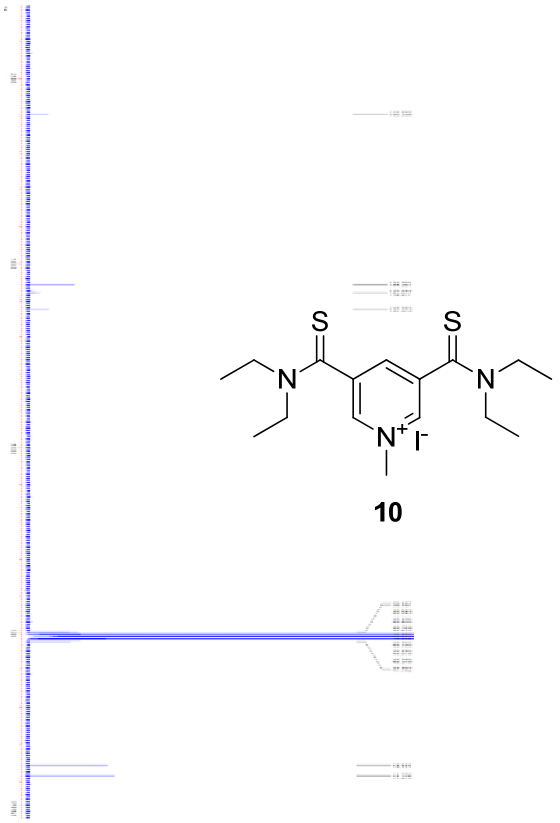


Figure S21. The ^{13}C NMR spectrum of compound **10**.

References

1. Hoglund IPJ, et al. (2006) Structure−Activity Relationship of Quinoline Derivatives as Potent and Selective α_{2C}-Adrenoceptor Antagonists. *J Med Chem* 49(21): 6351-6363.
2. Shi Q, et al. (2007) Synthesis and crystal structure of metal-organic frameworks $[Ln_2(pydc\text{-}3,5)_3(H_2O)_9]_n 3nH_2O$ (Ln = Sm, Eu, Gd, Dy; pydc-3,5 = pyridine-3,5-dicarboxylate) along with the photoluminescent property of its europium one. *J Molecular Structure* 837(1-3): 185-189.
3. Marenich AV, Cramer CJ, Truhlar DJ (2009) Ionic Recognition by 7-Nitro-1,3,5-triaza Adamantane: First Thermodynamic Study. *J Phys Chem B* 113(14): 4775-4780.
4. Frisch MJ, et al. (2009) *Gaussian 09, Revision D.01* (Gaussian, Inc., Wallingford CT).
5. Guera CF, Snijders JG, Te Velde G, Baerends EJ (1998) Towards an order-N DFT method. *Theor Chem Acc* 99(6): 391-403.
6. Te Velde G, et al. (2001) Chemistry with ADF. *J Comput Chem* 22(9): 931-967.
7. Shao Y, et al. (2006) Advances in methods and algorithms in a modern quantum chemistry program package. *Phys Chem Chem Phys* 8: 3172-3191.
8. Kohout M (2011) *DGrid* (Radebeul, Version 4.6).
9. Henderson A, Ahrens J, Law C (2004) *The Paraview Guide* (Kitware Clifton Park, NY).