Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Synthesis and Characterization of Pt(II) and Au(I) Complexes with *N*-Oxy-Heterocyclic Carbene Ligands (NOHCs)

Alice Benin,[a,b] Joshua Immanuel Kollar,[b] Tim Riesebeck,[b] Felix Wurl,[b] Claudia Graiff,[c] Thomas Strassner[b] and Cristina Tubaro[a]

[a] Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35131, Padova, Italy.

[b] Physikalische Organische Chemie, Technische Universität Dresden, Bergstrasse 66, 01062 Dresden, Germany.

[c] Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma, Parco Area delle Scienze 17/A, 43124 Parma, Italy.

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General considerations

The reactions in this work were performed with Schlenk techniques under an inert argon atmosphere (99.999%). Dimethylformamide (DMF) was dried over activated molecular sieves (3 Å) and degassed by freeze-pump-thaw cycles. Dichloromethane, isohexane, ethyl acetate and tetrahydrofuran were distilled before use; other solvents were used without further purifications. Column chromatography was carried out using silica gel 60 (230–400 mesh). Chemicals were obtained from suppliers and were used without further purification.

NMR spectra were recorded on a Bruker Avance 300 MHz (300 MHz for ^{1}H, 75 MHz for ^{13}C) spectrometer or on Avance 300P and Avance III 600 Bruker (600 MHz for ^{1}H, 151 MHz for ^{13}C and 129 MHz for ^{195}Pt) spectrometers. All the spectra have been recorded at 298 K.

The chemical shift values (δ) are reported in units of ppm relative to the residual of the deuterated solvent; the ^{195}Pt NMR spectra were referenced externally by using K_2PtCl_4 in D_2O ($\delta = -1617.2$ ppm in D_2O for $PtCl_4^{2-}$). All coupling constants (*J)* are reported in Hertz. The multiplicities of the signals are reported using the following abbreviations: singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br).

The following experiments have been carried out: ^{1}H NMR, ^{13}C{^{1}H} NMR,^{195}Pt{^{1}H} NMR, COSY (COrrelation SpectroscopY), HMQC (*H*eteonuclear *M*ultiple *Q*uantum *C*oherence), HMBC (*H*eteronuclear *M*ultiple *B*ond *C*oherence) and NOESY (*N*uclear *O*verhauser *E*nhancement *S*pectroscopY).

HRMS measurements were carried out with a Q-Exactive hybrid quadrupole-Orbitrapt mass spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts, USA). MS conditions were as followed: electrospray ionization in positive mode, resolution 70 000, AGC target 1 x 10^{6}, max injection time of 50 ms, scan range 150–2000 amu, capillary voltage 3.5 kV and RF voltage at 50 V, capillary temperature 320°C and probe temperature 350°C; nitrogen was used as shealth gas at 11 psi.

Calibration was performed with a standard solution purchased by Thermo Fisher Scientific (Pierces ESI positive Ion Calibration Solution). The software for analysis of MS data was Xcalibur 3.1 (Thermo Fisher Scientific). Otherwise, HR-ESI mass spectra were recorded on a Waters Xevo G2-XS QTOF mass spectrometer.

Absorption spectra were measured on a Perkin Elmer Lambda 365 UV-vis spectrometer in dichloromethane ($5x10^{-5}$ M) solutions, with a quartz cuvette (cell length of 1 cm). The spectra were recorded with a scan speed of 600 nm/min.

Melting points were measured by a Wagner and Munz PolyTherm A system and were not corrected. Cyclic voltammetry and differential scanning voltammetry experiments were carried out using a Biologic SP-150 potentiostat in degassed, anhydrous DMF 0.5 mM solutions with 0.1M supporting electrolyte ($N(^nBu)_4ClO_4$), employing a platinum wire counter electrode, a glassy carbon working electrode and a Ag/Ag^+ pseudo reference electrode. The measurements were conducted with a sweep rate of 100 mV/s and internally referenced against Fc/Fc^+, whereas the DPV measurements were carried out with a sweep rate of 50 mV/s.

The Gaussian16[1] package was used for all quantum chemical calculations employing the hybrid functional PBE0[2,3] and the 6-311G*[4–6] basis set. Platinum was described through the LANL2TZ ECP and basis set[7–10]. Dispersion forces were employed by using the D3 dispersion correction with Becke-Johnson damping (D3BJ).[11,12] All given structures were verified as true minima by vibrational frequency analysis and the absence of negative eigenvalues. Calculated geometries were visualized with GaussView.[13]

The synthesized Pt(II)-NOHC complexes were surprisingly difficult to purify, thus no reproducibly correct elemental analyses could be obtained.

NMR spectra

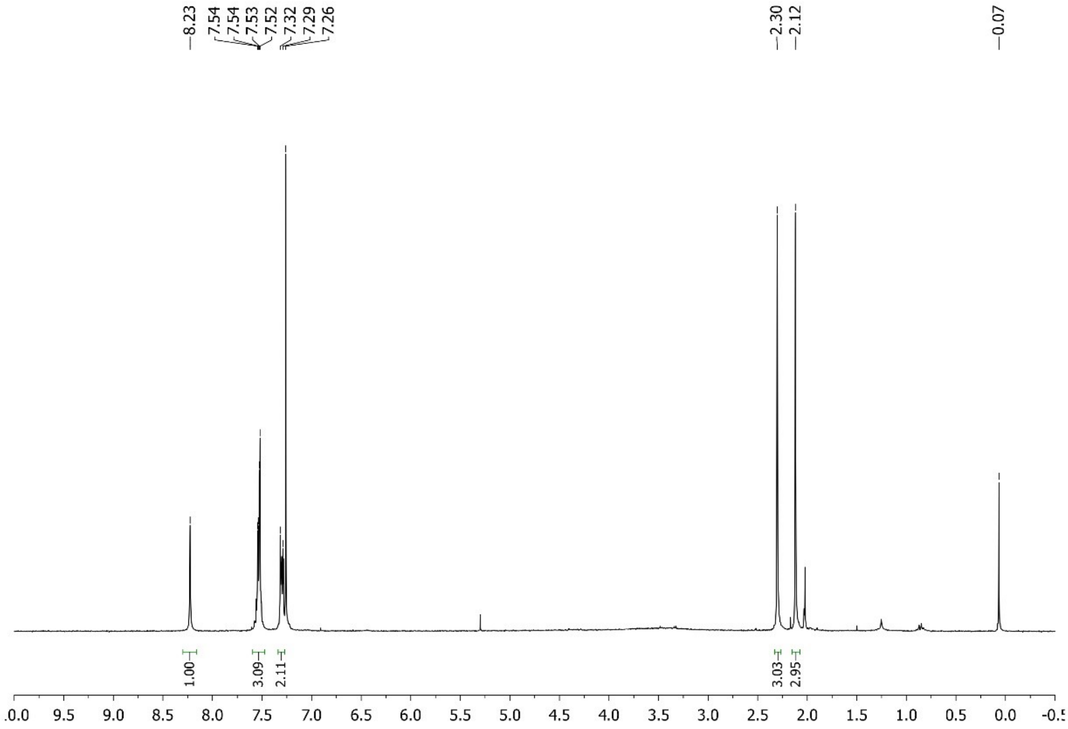


Figure S1. ^1H NMR ($CDCl_3$, 25°C) of compound **1**.

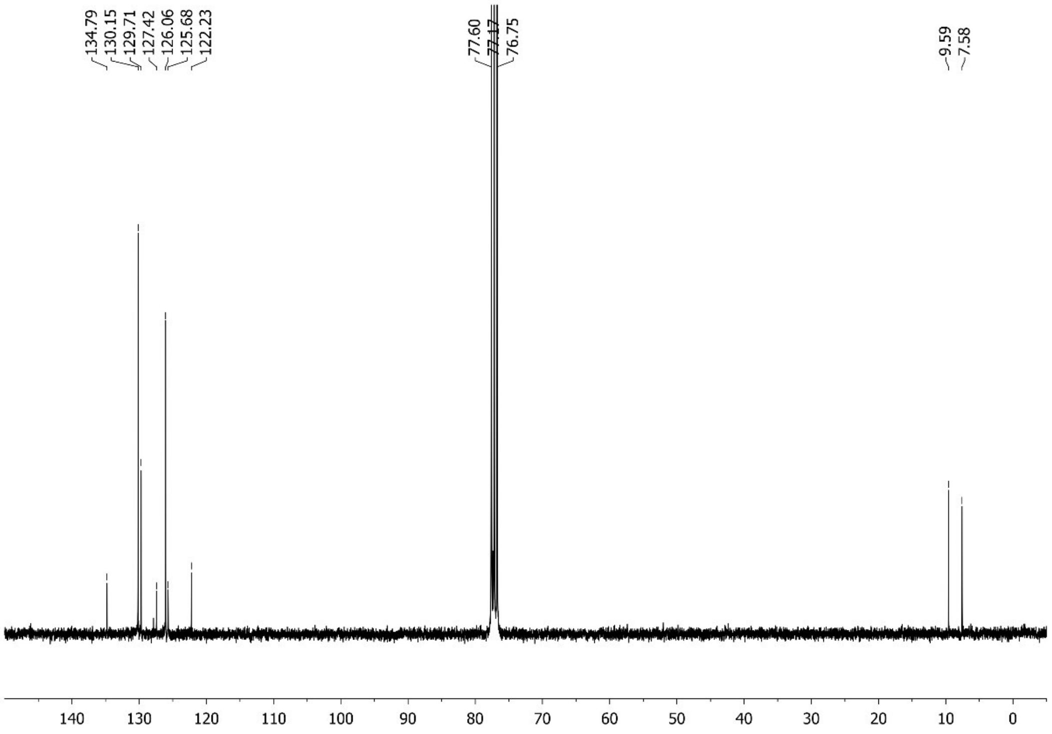


Figure S2. $^{13}C\{^1H\}$-NMR ($CDCl_3$, 25°C) of compound **1**.

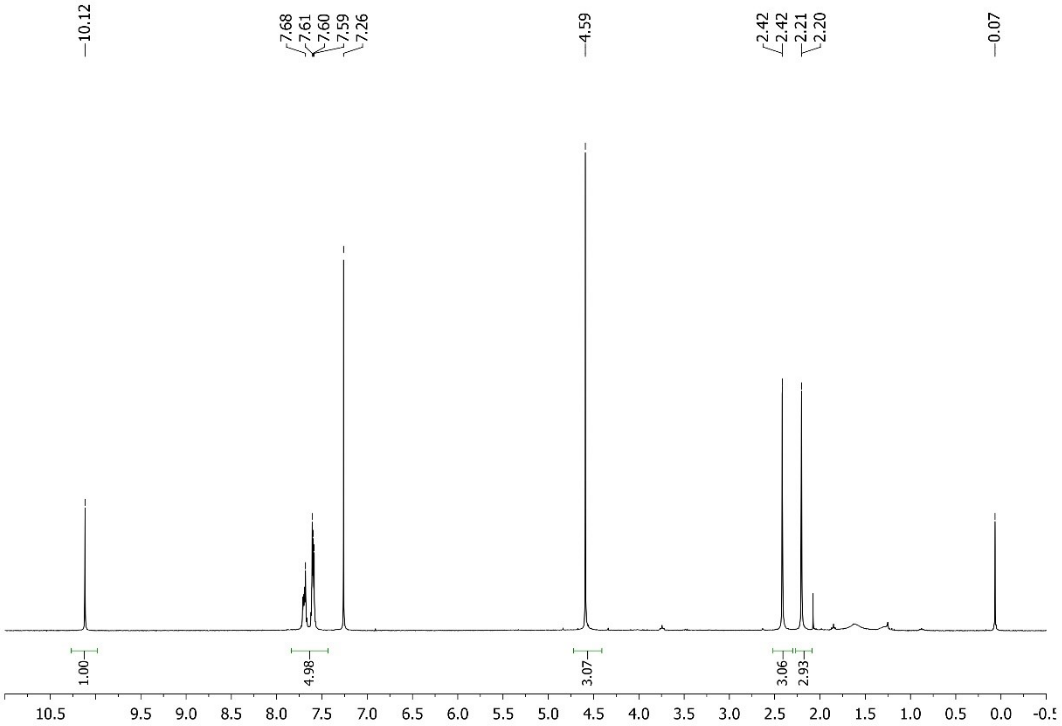


Figure S3. ^{1}H NMR (CDCl$_3$, 25°C) of compound **2**.

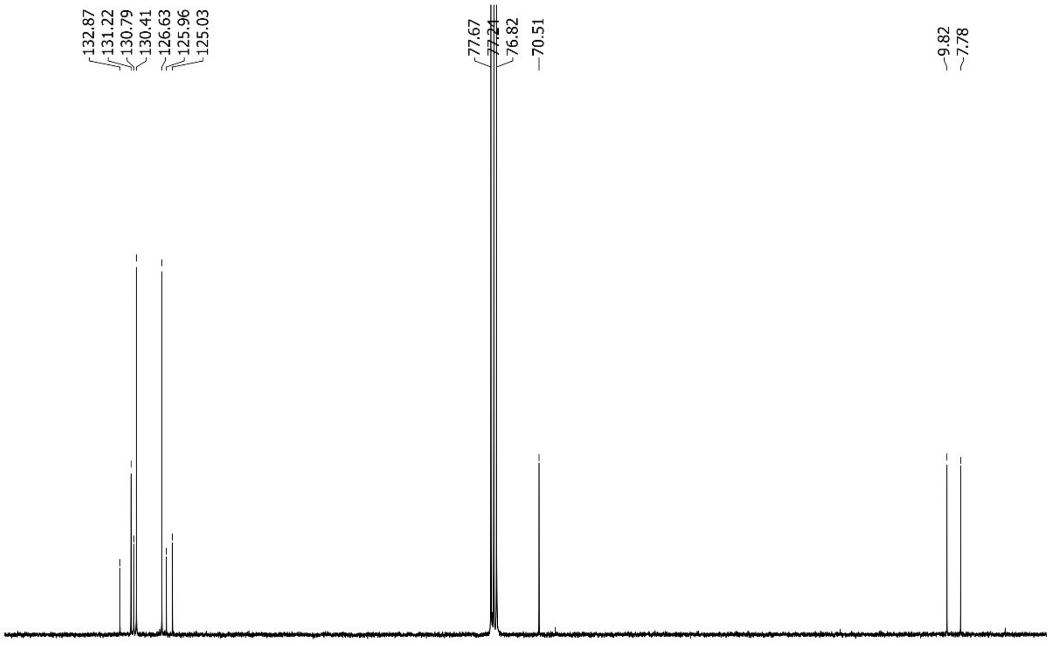


Figure S4. ^{13}C{^{1}H}-NMR (CDCl$_3$, 25°C) of compound **2**.

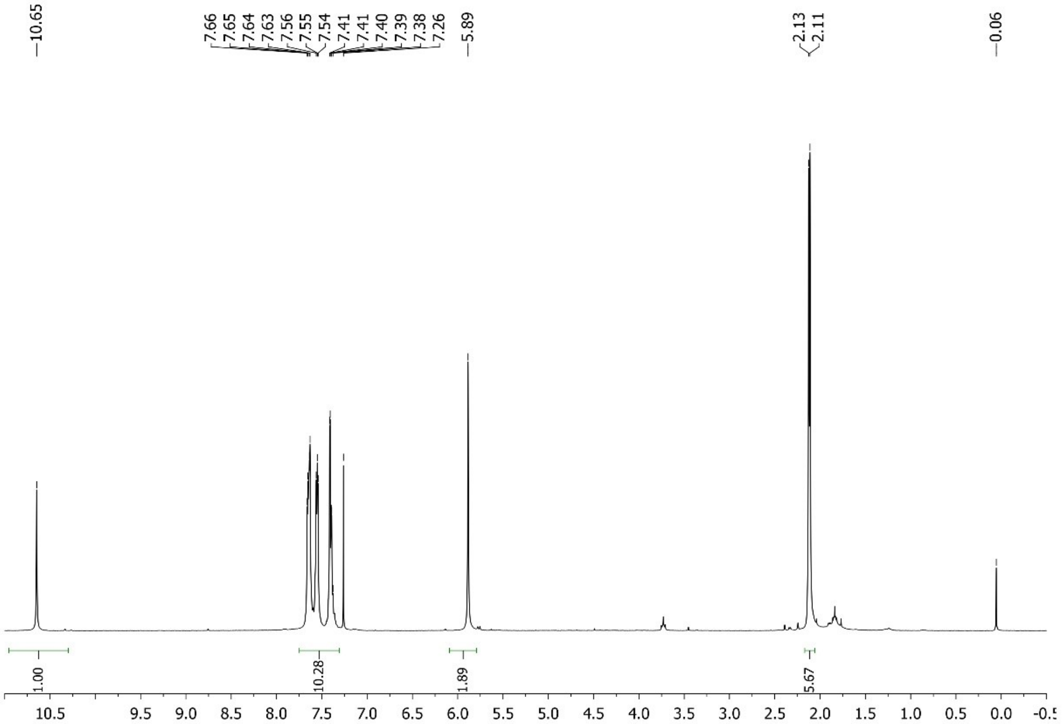


Figure S5. ^1H NMR ($CDCl_3$, 25°C) of compound **3**.

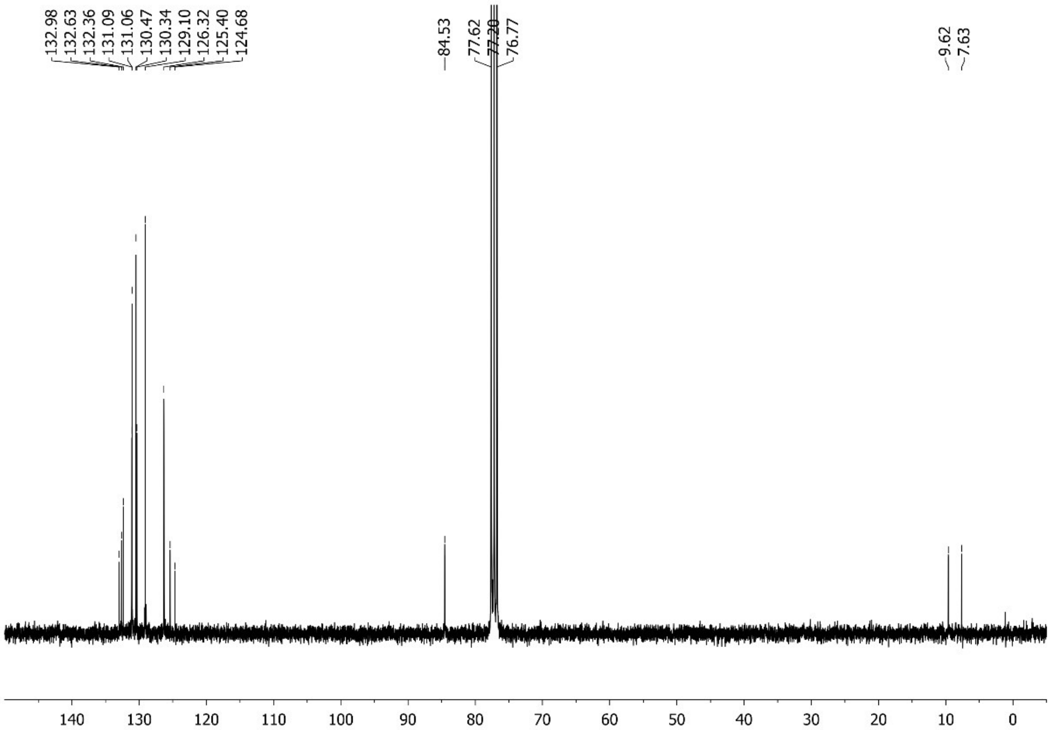


Figure S6. $^{13}C\{^1H\}$-NMR ($CDCl_3$, 25°C) of compound **3**.

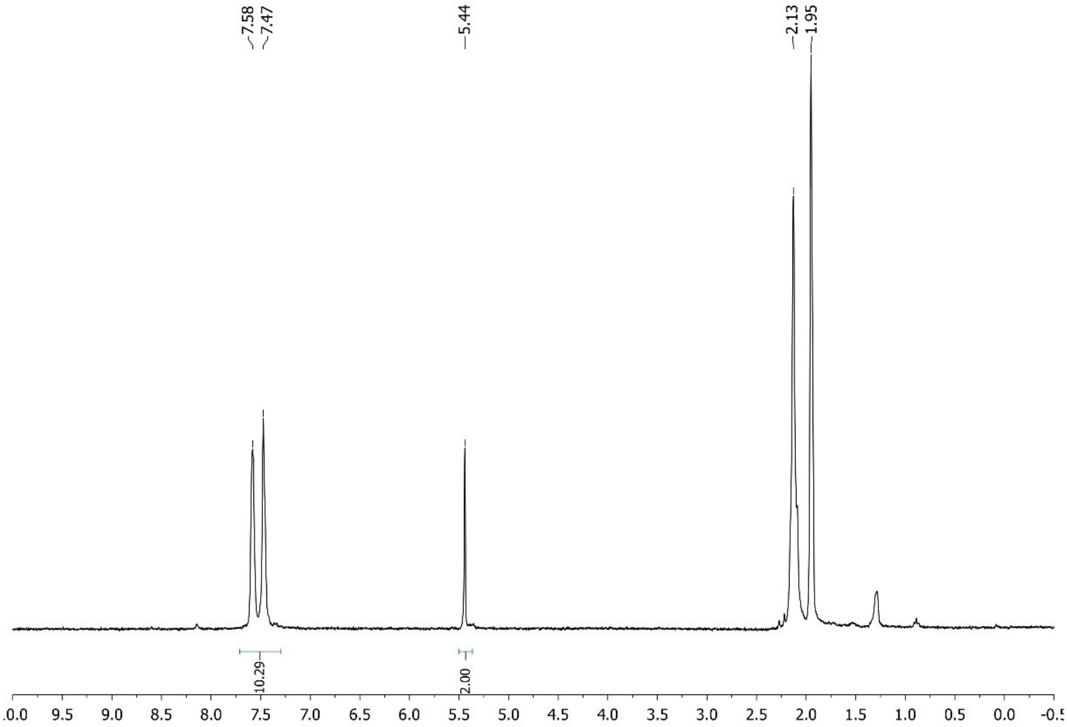


Figure S7. ^1H NMR (CD_3CN, 25°C) of compound **4**.

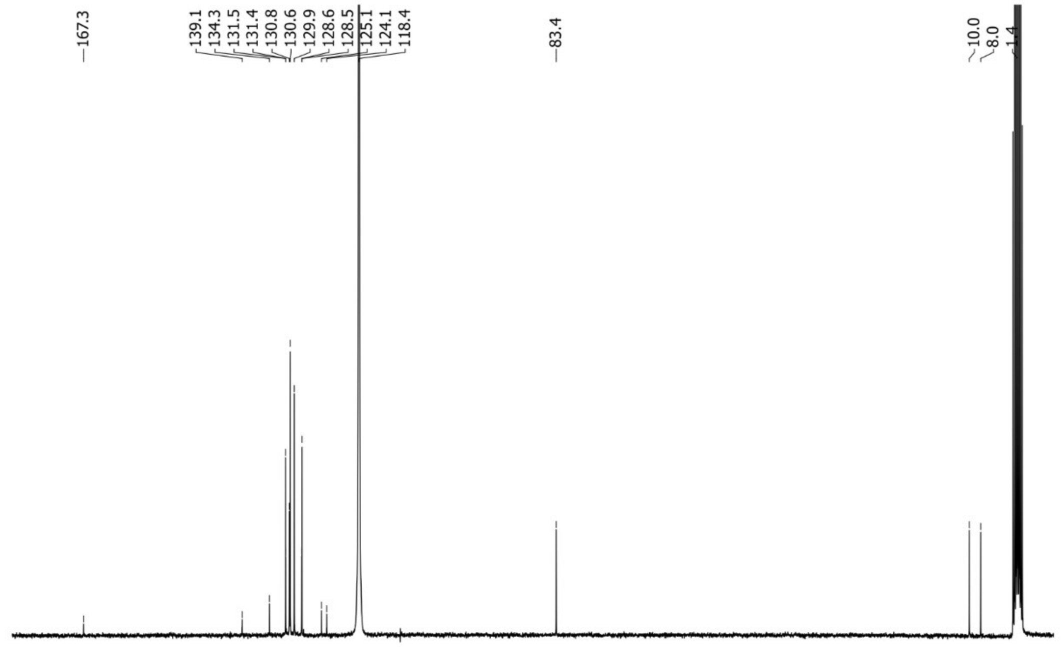


Figure S8. $^{13}C\{^1H\}$-NMR (CD_3CN, 25°C) of compound **4**.

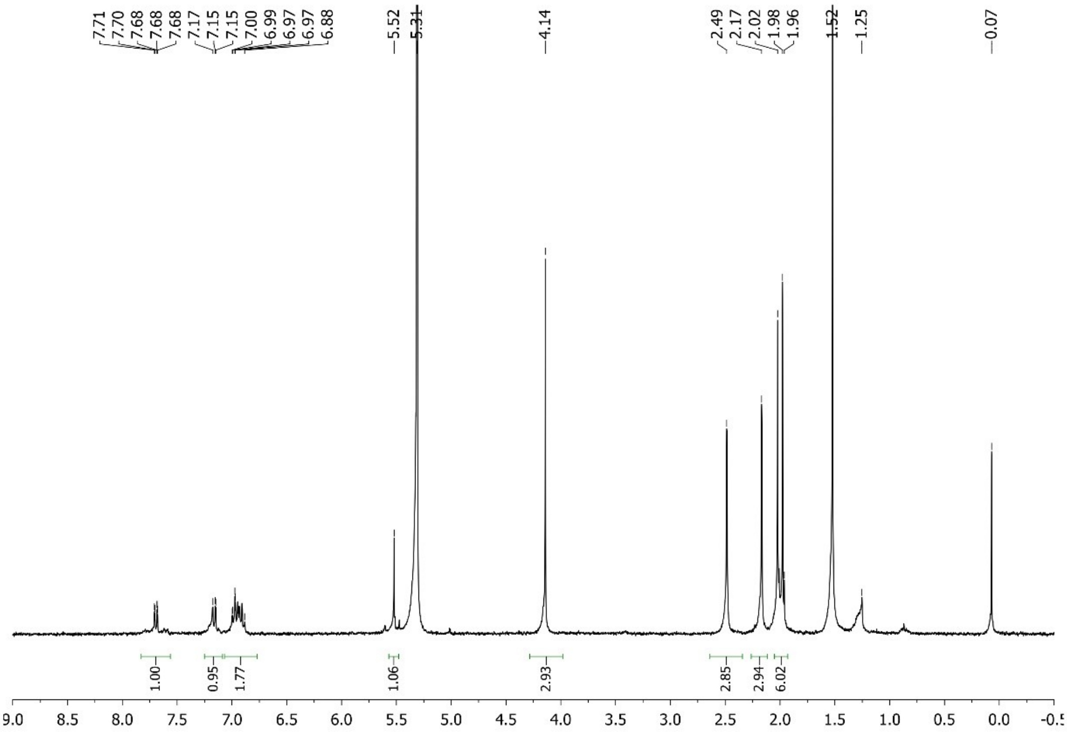


Figure S9. ^{1}H NMR (CD_2Cl_2, 25°C) of compound **5**.

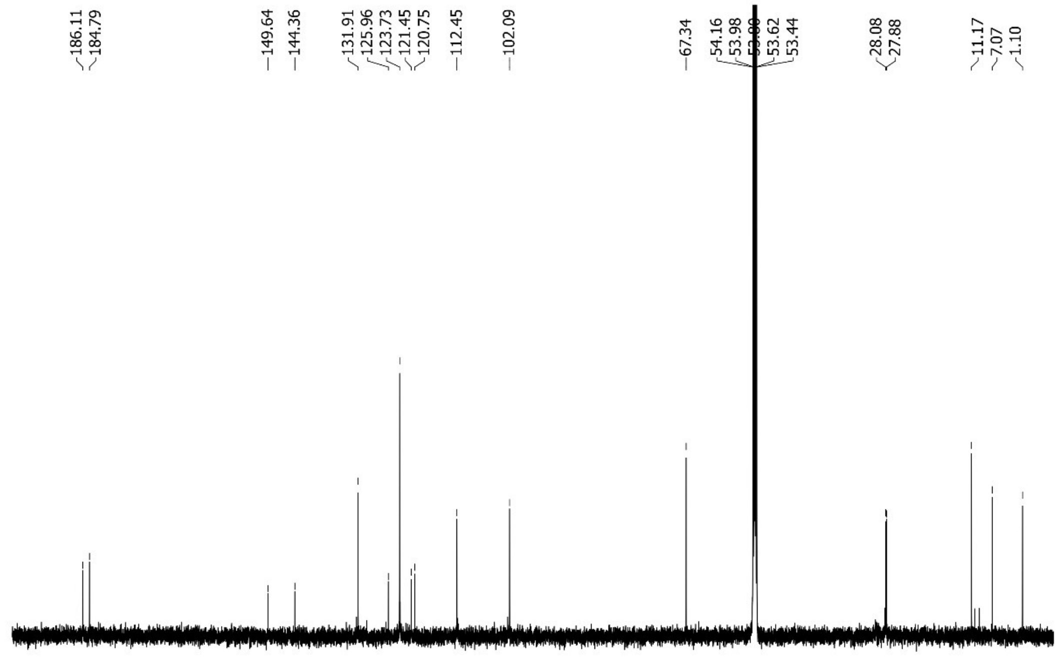


Figure S10. $^{13}C\{^{1}H\}$-NMR (CD_2Cl_2, 25°C) of compound **5**.

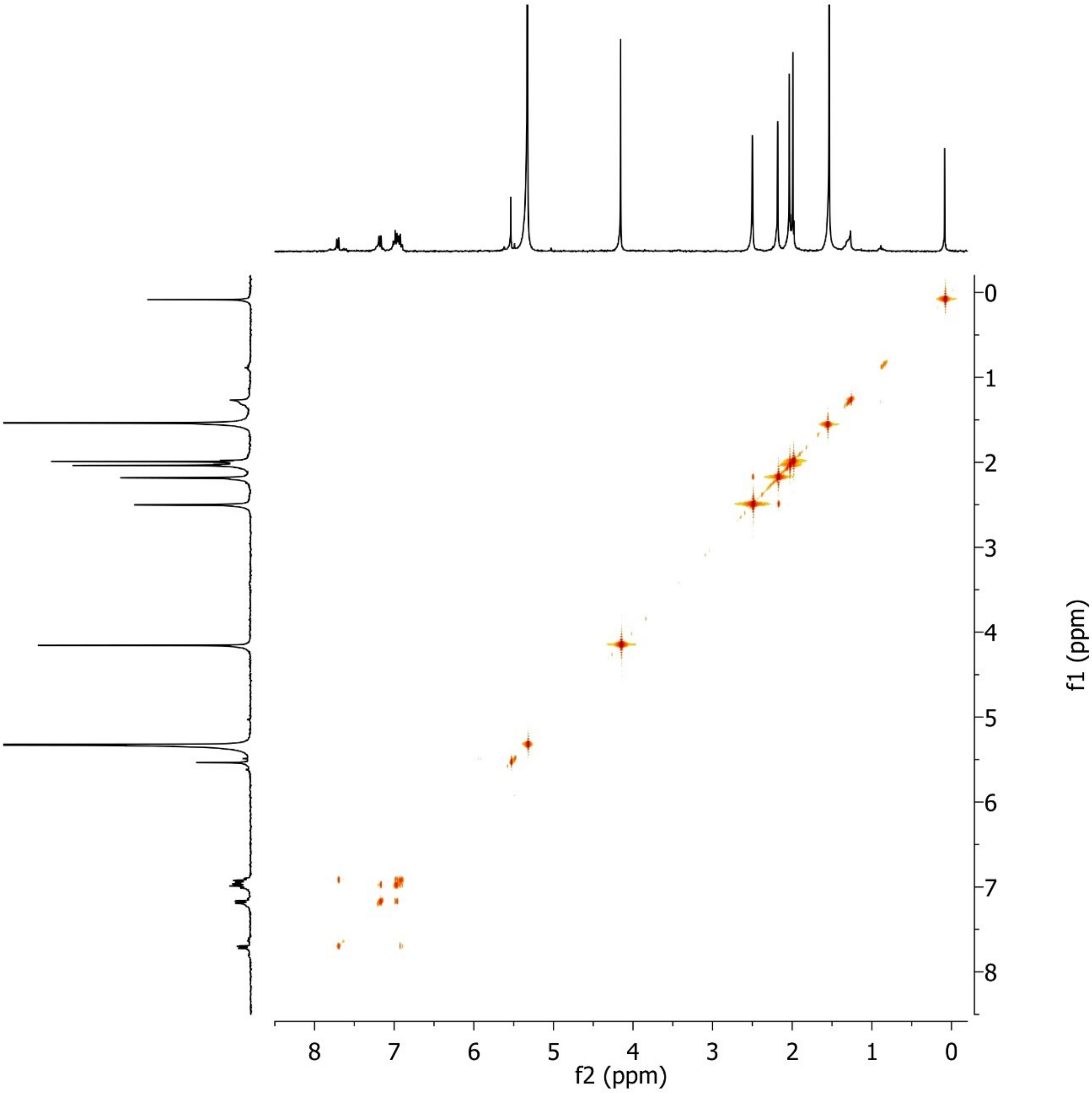


Figure S11. COSY spectrum of compound **5** (CD_2Cl_2, 25°C).

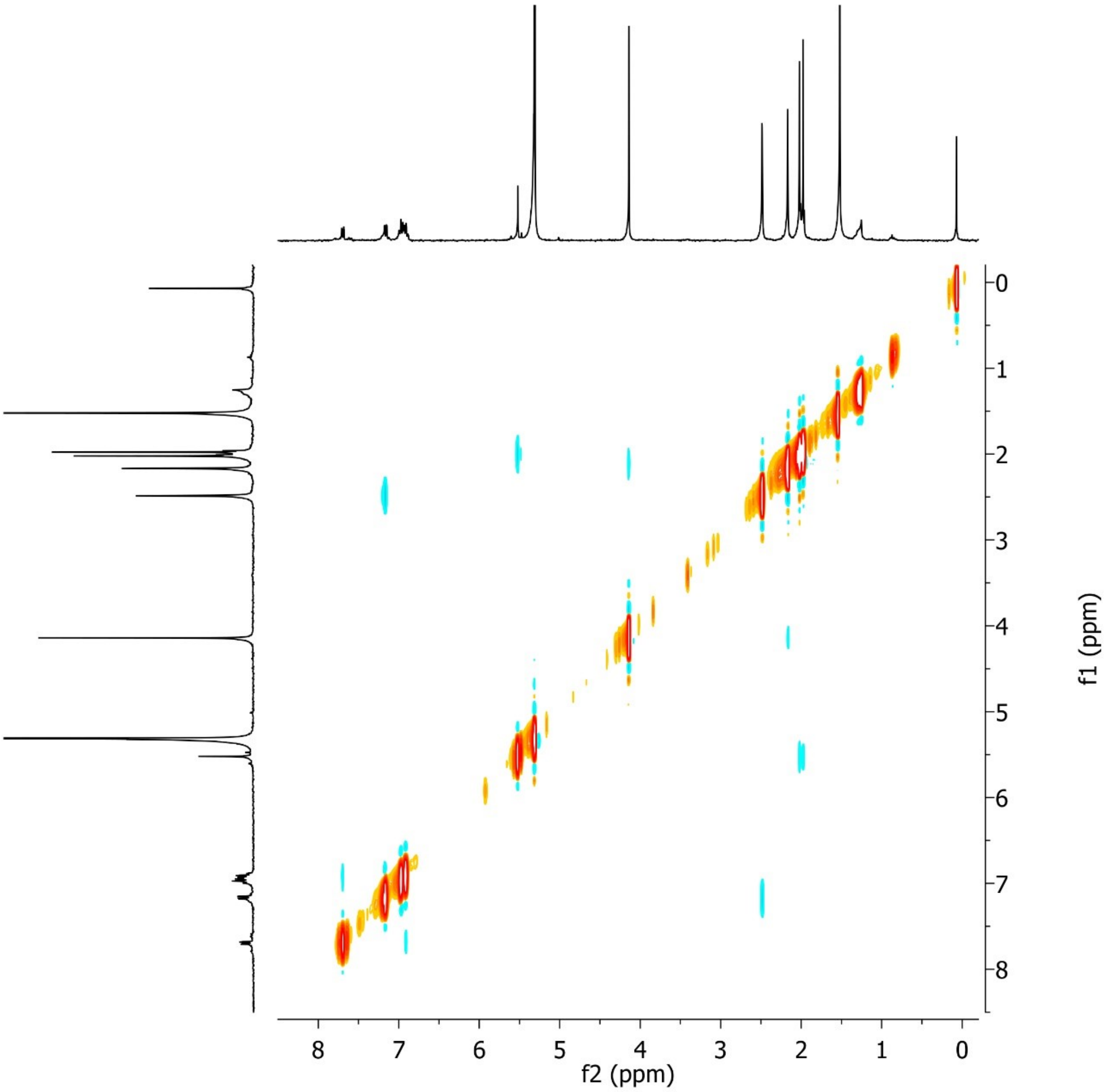


Figure S12. NOESY spectrum of compound **5** (CD_2Cl_2, 25°C).

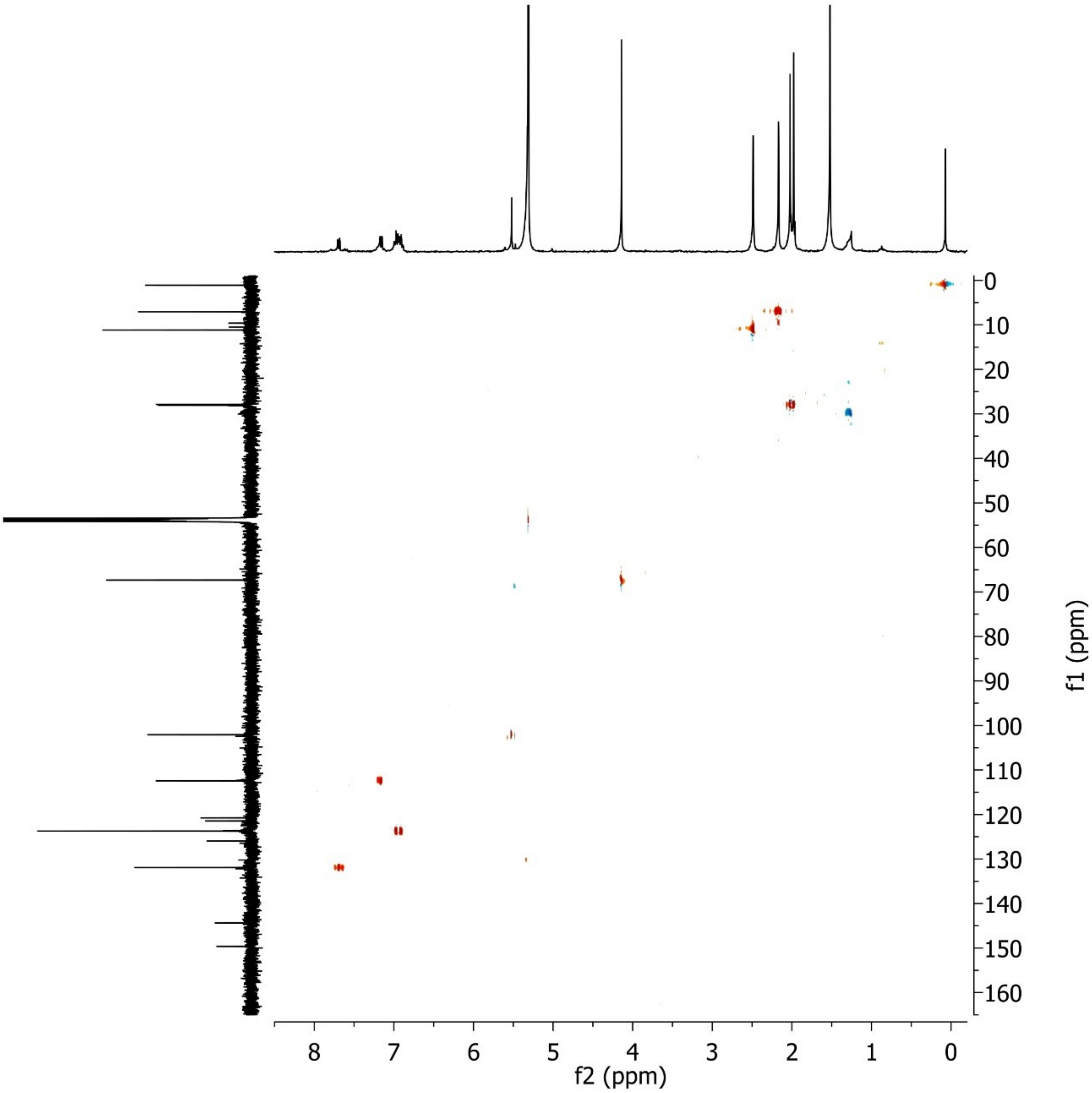


Figure S13. HSQC spectrum of compound **5** (CD_2Cl_2, 25°C).

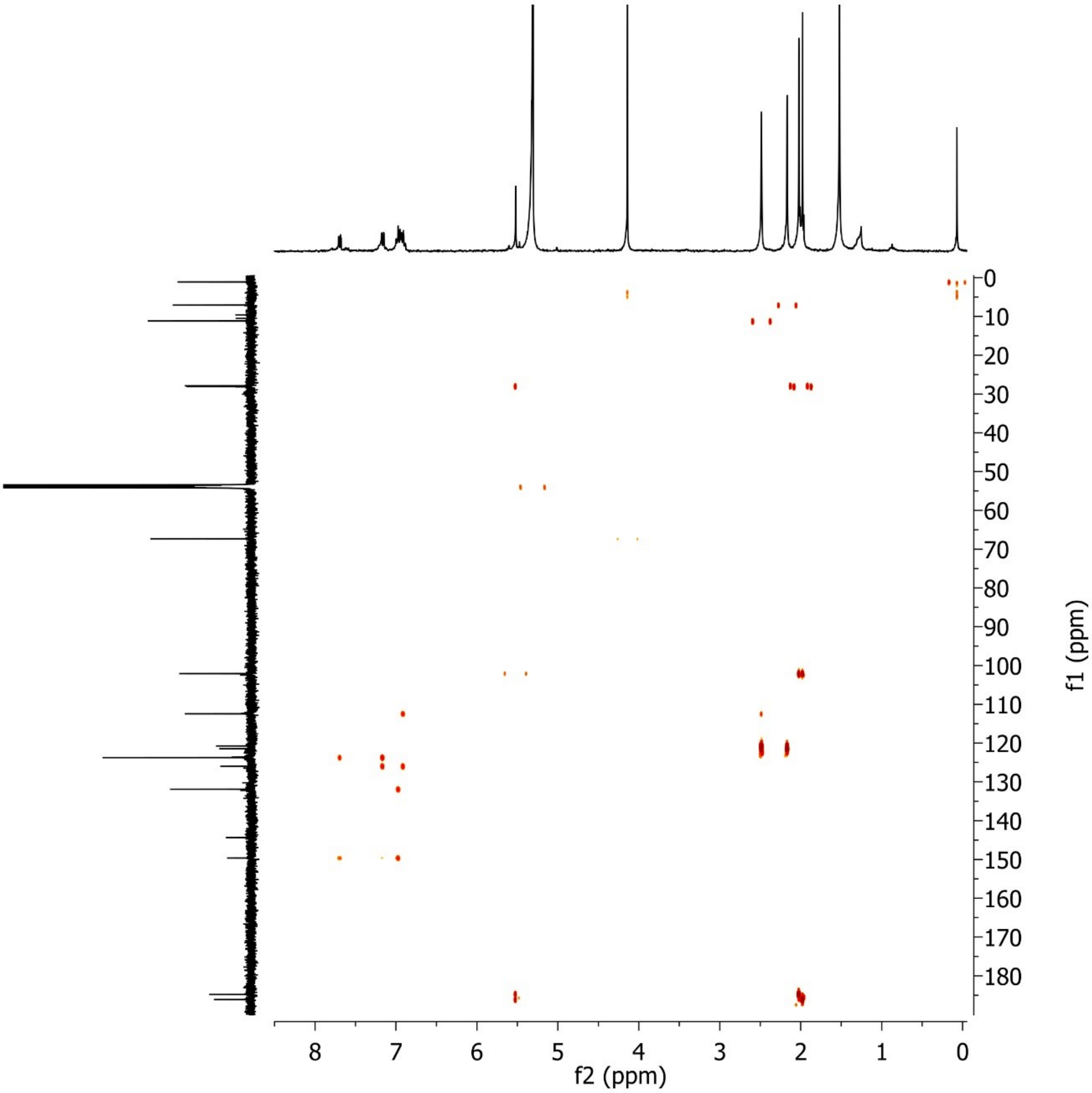


Figure S14. HMBC spectrum of compound **5** (CD_2Cl_2, 25°C).

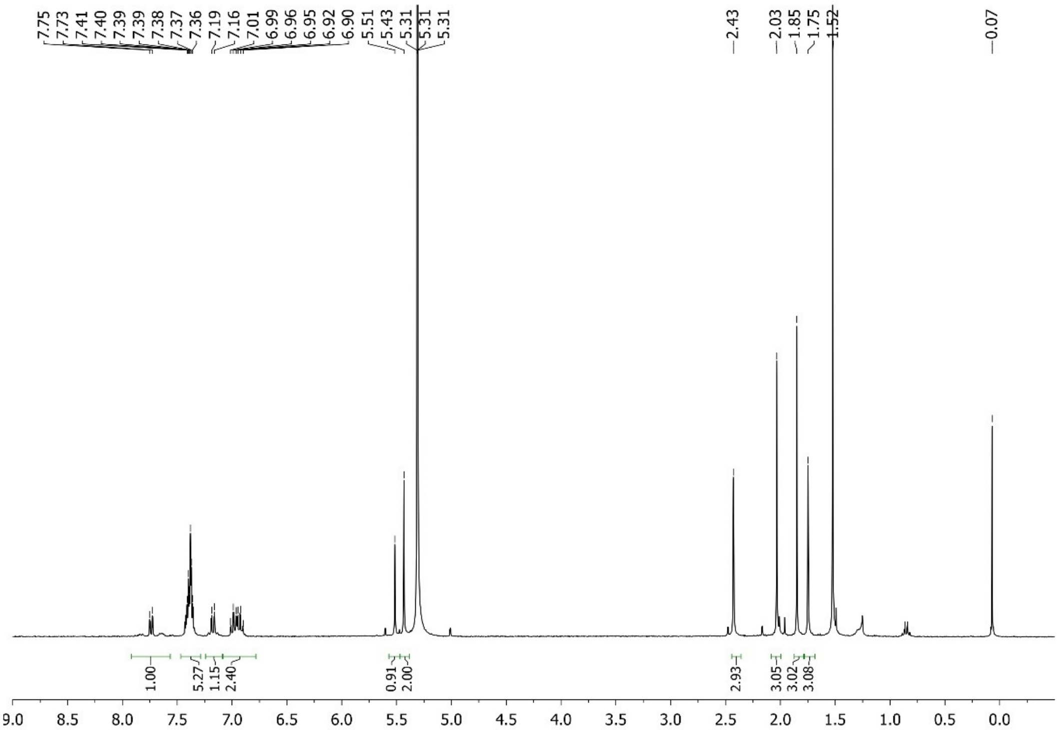


Figure S15. ^1H NMR (CD_2Cl_2, 25°C) of compound **6**.

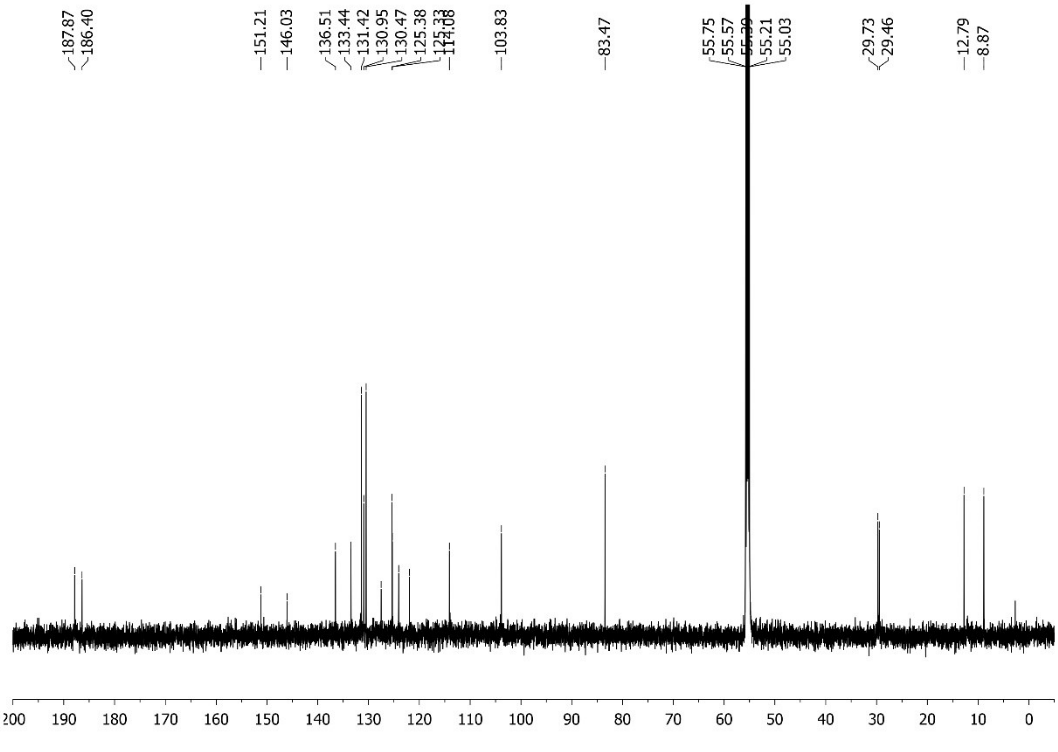


Figure S16. $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 25°C) of compound **6**.

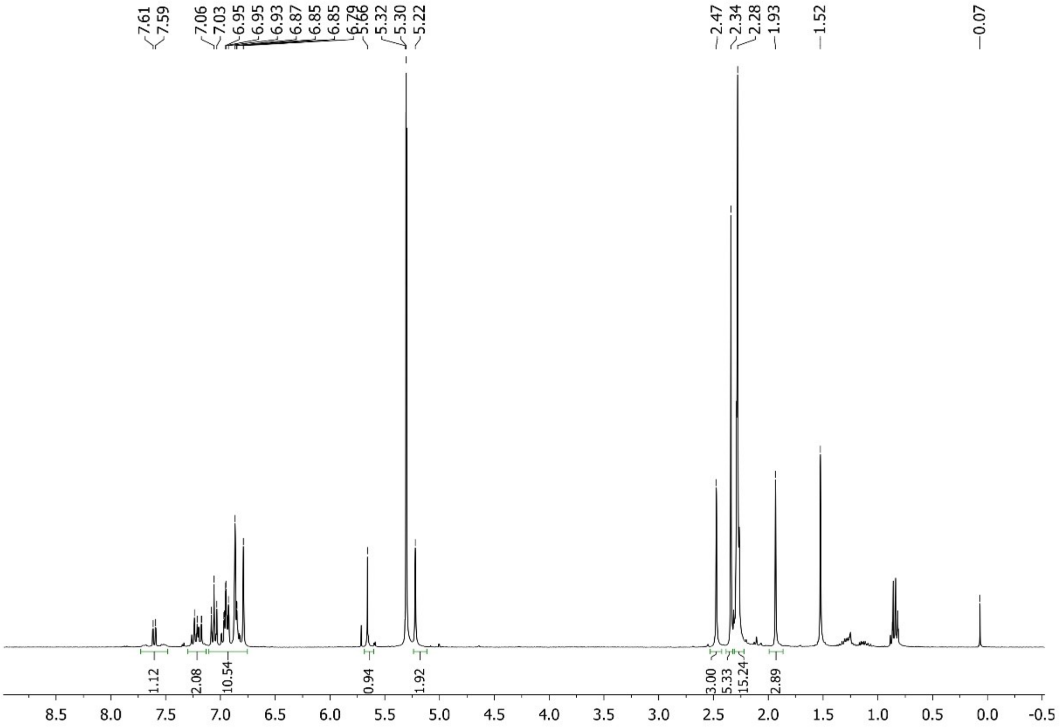


Figure S17. ^{1}H NMR (CD_2Cl_2, 25°C) of compound **7**.

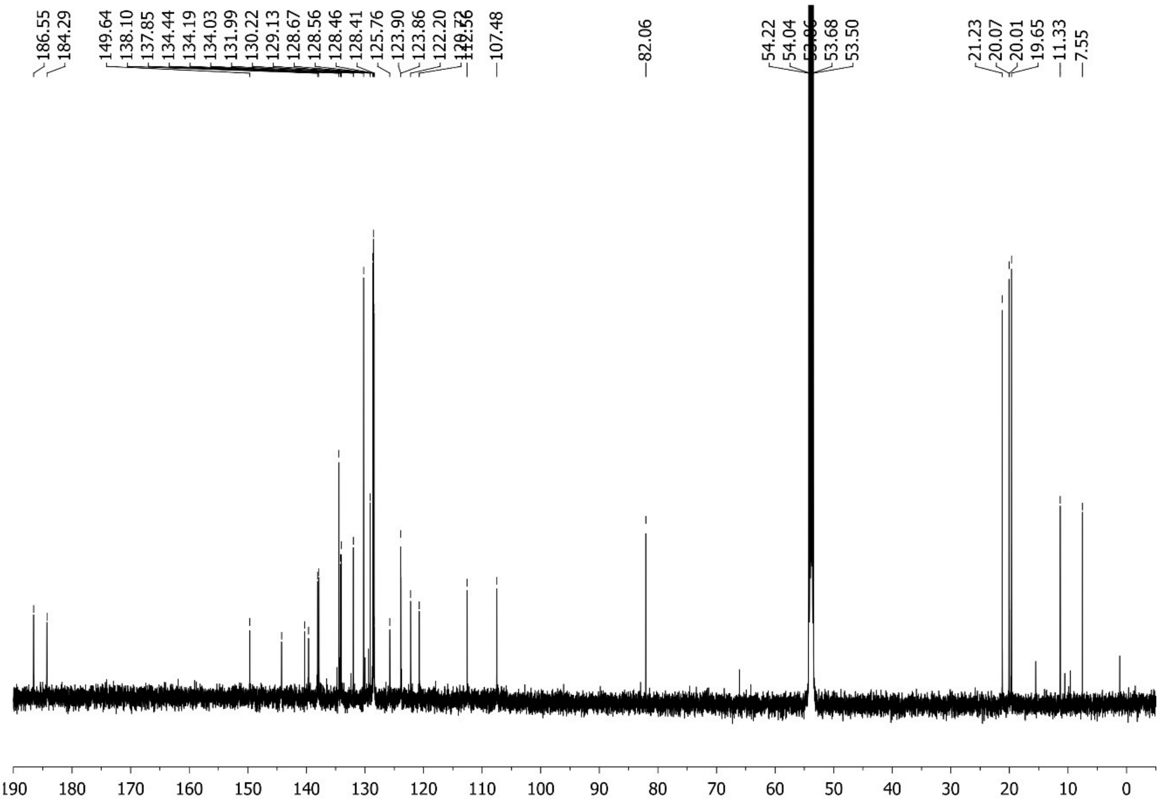


Figure S18. $^{13}C\{^1H\}$-NMR (CD_2Cl_2, 25°C) of compound **7**.

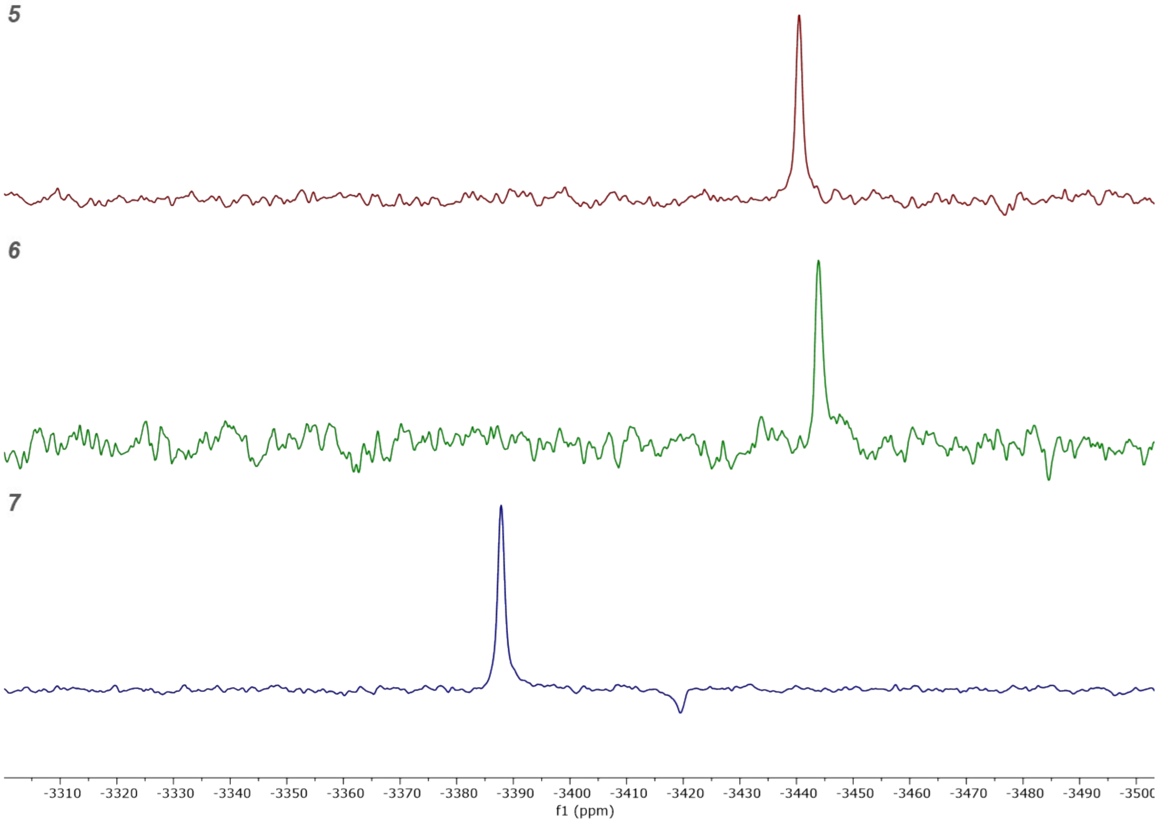


Figure S19. ^{195}Pt NMR spectra (129 MHz, CD_2Cl_2, 25°C) of complexes **5**-**7**.

Solid state structure determination

Preliminary examination and data collection for single crystals of **5** and **7** were carried out on a Bruker D8 VENTURE (KAPPA goniometer, PHOTON detector) single crystal-diffractometer equipped with an Oxford Cryosystem (Cryostream 800) cooling system at the window of a sealed x-ray tube using monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) (Incoatec IµS3.0 microfocus source equipped with multilayer optics).

Idealized geometries were assigned to the hydrogen atoms. Intensity data were extracted using the APEX3 suite[14] including the SAINT software package.[15] The reflections were merged and corrected from Lorentz, polarization and decay effects and absorption correction was applied based on multiple scans.[16] The structure was solved by a combination of dual space,[17] direct methods with the aid of difference Fourier synthesis and were refined against all data using SHELXTL-XTMP.[18] Hydrogen atoms were assigned to ideal positions using the SHELXTL-XTMP riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(Fo^2-Fc^2)^2$ with the SHELXTL-XTMP weighting scheme. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography.[19] All calculations were performed with the APEX3 suite[14] including SAINT software package,[15] the SHELX program package[20] and PLATON.[21]

Complex **4** crystallographic data were collected on a Bruker D8 Venture Photon II single-crystal diffractometer working with monochromatic Mo-Kα radiation and equipped with an area detector. The structures were solved by direct methods and refined against F2 with SHELXL-2014/7 with anisotropic thermal parameters for all non-hydrogen atoms.[20,22] For the visualization Mercury[23] was used.

Table S1. Collected X-Ray data.

Complex	**4**	**5**	**7**
Formula	$C_{18}H_{18}AuBrN_2O$	$C_{17}H_{20}N_2O_3Pt$	$C_{39}H_{40}N_2O_3Pt$
Formula weight	698.09	495.43	779.81
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P 2_1/n	P -1	P -1
a/Å	11.184(3)	7.4545(9)	7.0873(4)
b/Å	14.559(5)	10.2906(12)	15.5352(10)
c/Å	11.536(4)	11.2348(13)	15.6123(10)
α/°	90.00	79.217(4)	73.911(2)
β/°	105.929(14)	84.616(4)	87.614(2)
γ/°	90.00	74.004(4)	87.428(2)
Volume/Å^3	1806.26	813.02(17)	1649.20(18)
T (K)	200	150	150
Z	4	2	2
D_{calc}/g·cm^{-3}	2.042	2.024	1.570
F(000)	1048	476.0	780.0
μ(Mo-Kα)/mm^{-1}	10.362	8.645	4.294
Reflections collected	76346	38885	234359
Unique reflections	4522	4064	8196
Observed reflections [I >	4021 [Rint =	3994 [Rint = 0.0435]	7946 [Rint = 0.0314]

2σ(I)]	0.0590,]		
R [I > 2σ(I)]	*R*1 = 0.0324, *wR*2 = 0.0918	*R*1 = 0.0274, *wR*2 = 0.0648	*R*1 = 0.0147, *wR*2 = 0.0410
R [all data]	*R*1 = 0.0382, *wR*2 = 0.0961	*R*1 = 0.0279, *wR*2 = 0.0651	*R*1 = 0.0156, *wR*2 = 0.0417

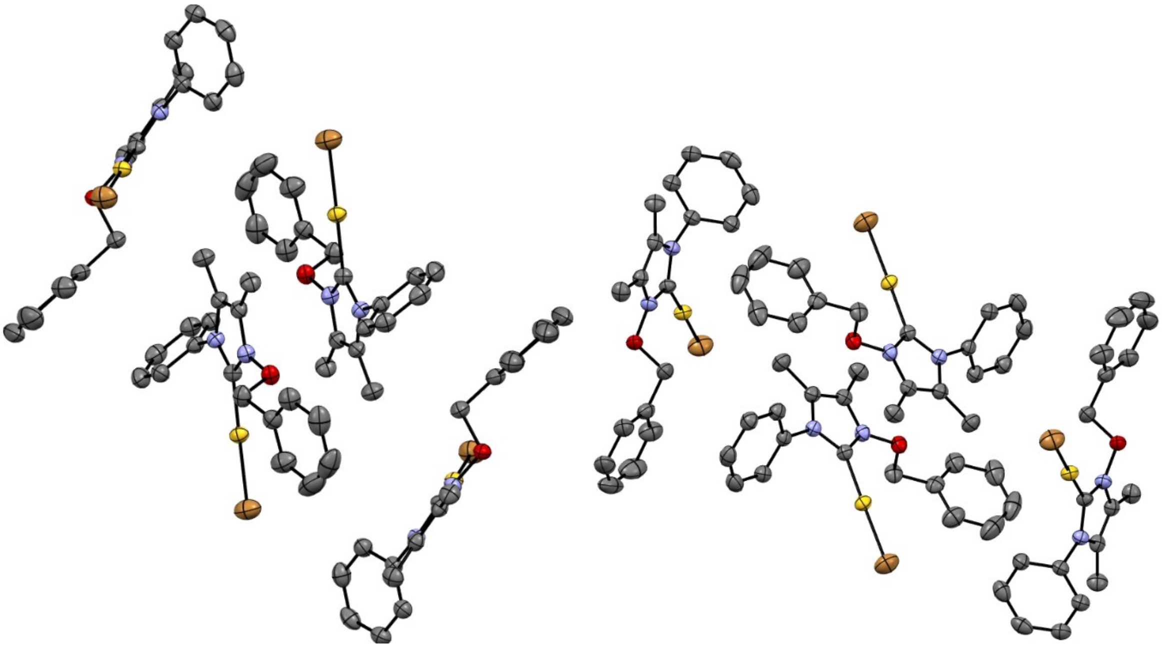


Figure S20. ORTEP views of complex **4** crystallization cell structure (hydrogens have been omitted for clarity). Ellipsoids are drawn at their 50% probability.

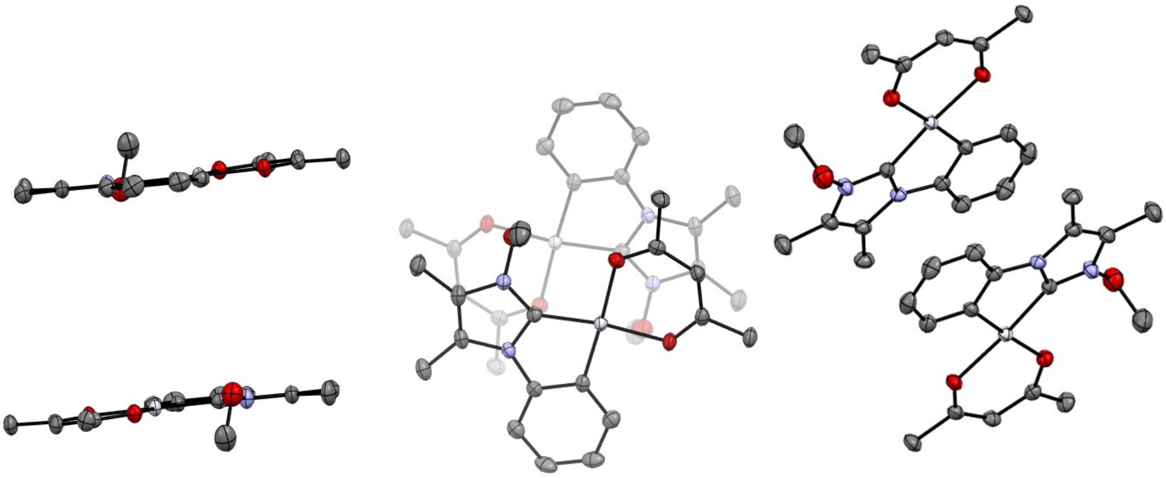


Figure S21. ORTEP views of complex **5** crystallization cell structure (hydrogens have been omitted for clarity). Ellipsoids are drawn at their 50% probability.

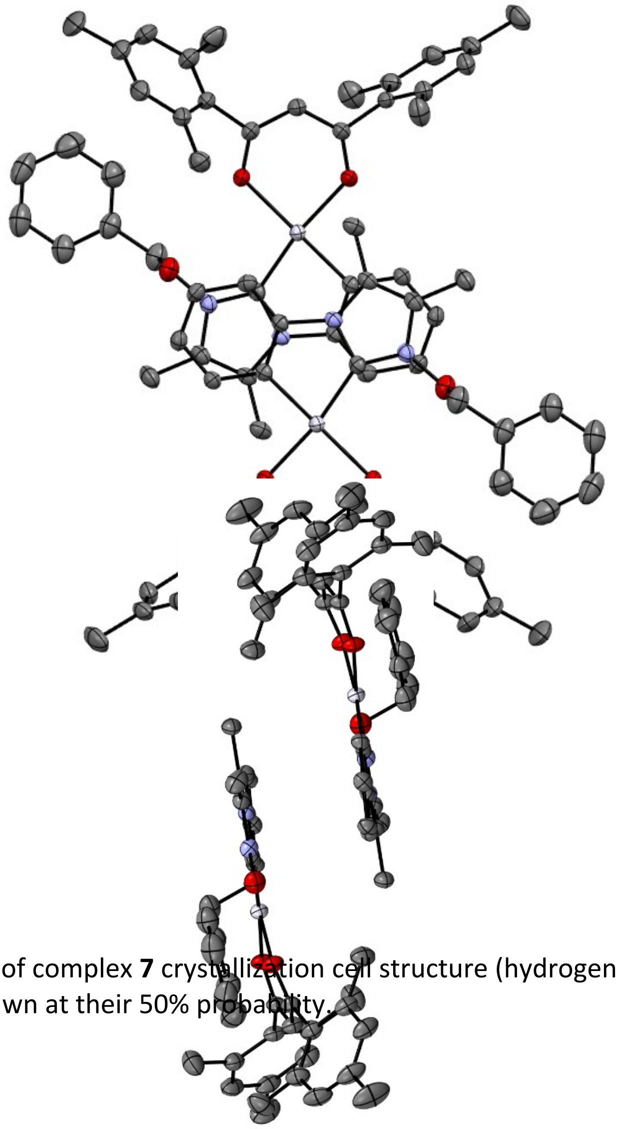


Figure S22. ORTEP views of complex **7** crystallization cell structure (hydrogens have been omitted for clarity). Ellipsoids are drawn at their 50% probability.

Photophysical properties

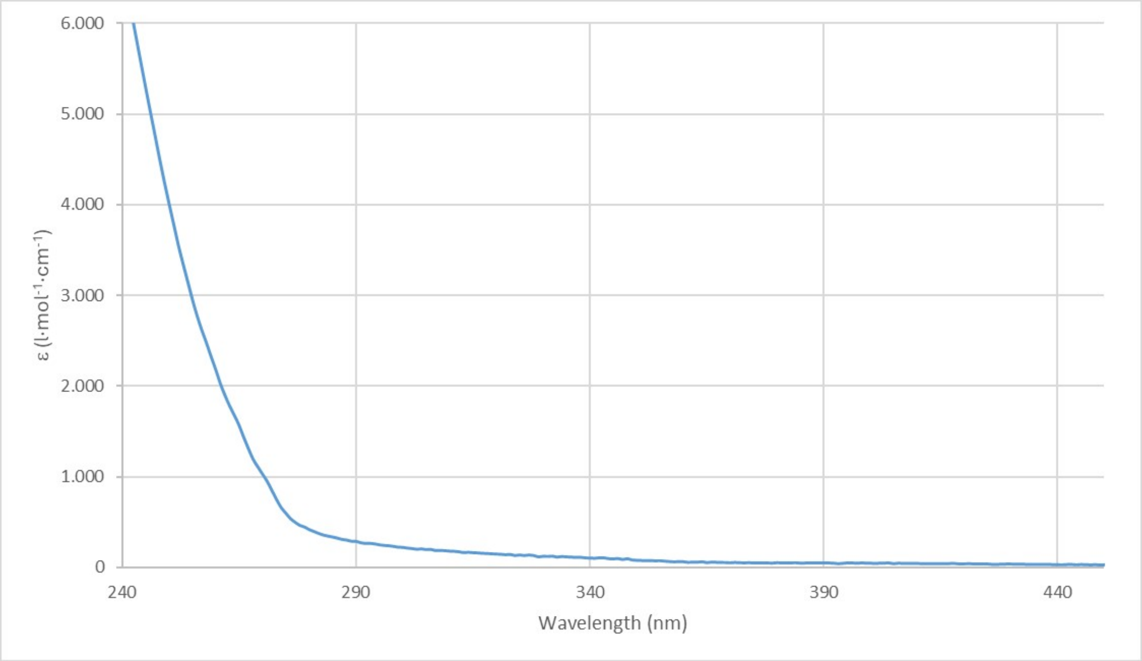


Figure S23. Absorption spectra of compound **3** recorded in CH_2Cl_2 solutions (5·10-5 M) at room temperature. Cuvette length d = 1 cm.

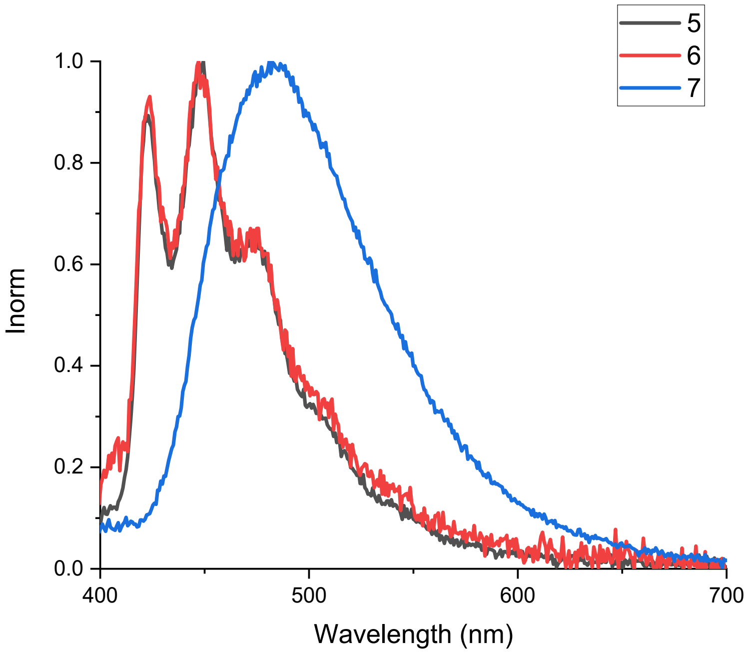


Figure S24. Normalized emission spectra of compounds **5**-**7** (2 wt % emitter load in a PMMA matrix on a quartz glass substrate at room temperature; λ_{exc}= 320 nm, N_2 atmosphere).

Cyclic and differential pulse voltammograms

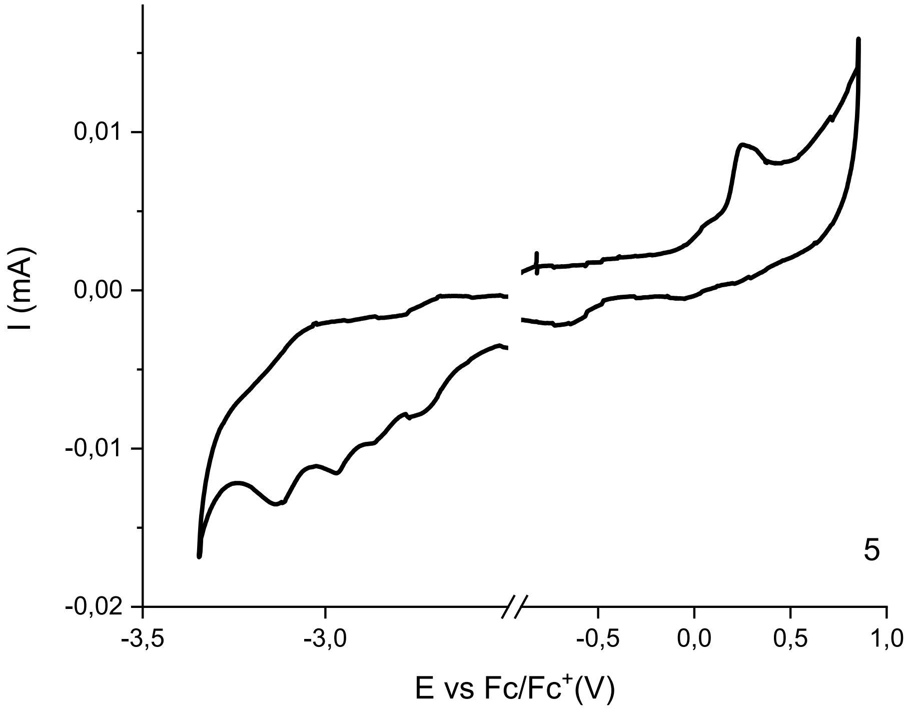


Figure S25. Cyclic voltammogram of complex **5**, referenced internally versus Fc/Fc⁺.

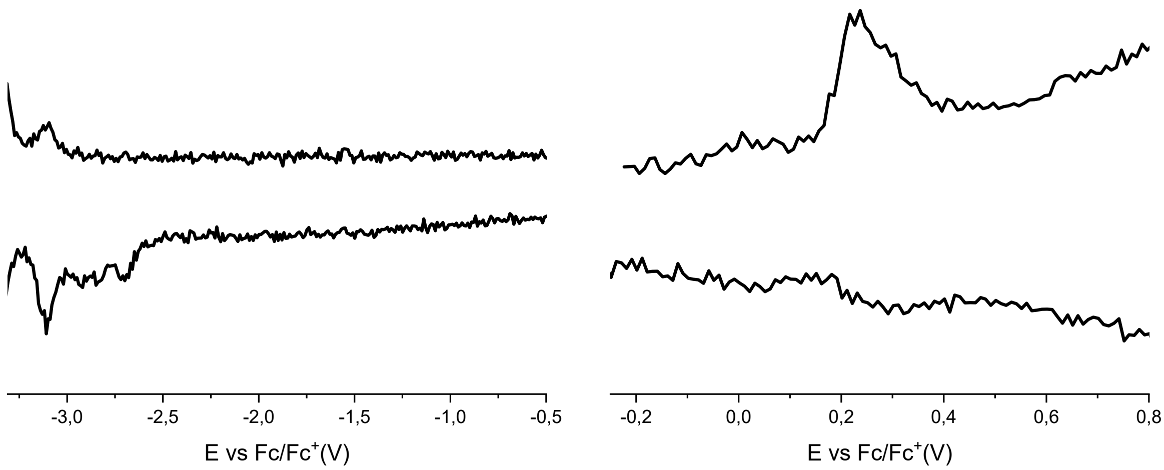


Figure S26. Differential pulse voltammograms for the reductive (left) and the oxidative (right) events of complex **5**, referenced internally versus Fc/Fc⁺.

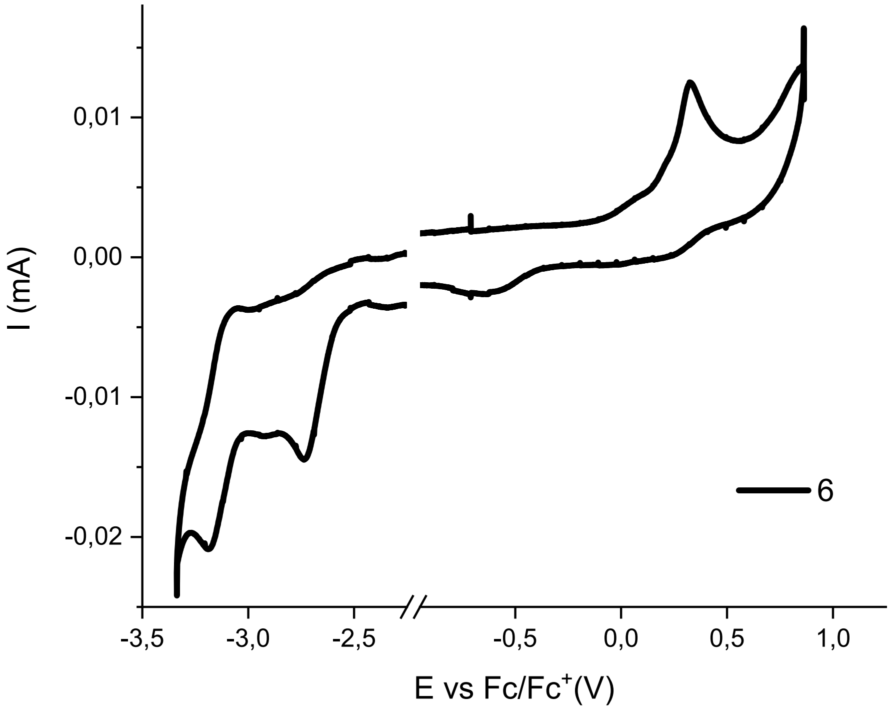


Figure S27. Cyclic voltammogram of complex **6**, referenced internally versus Fc/Fc⁺.

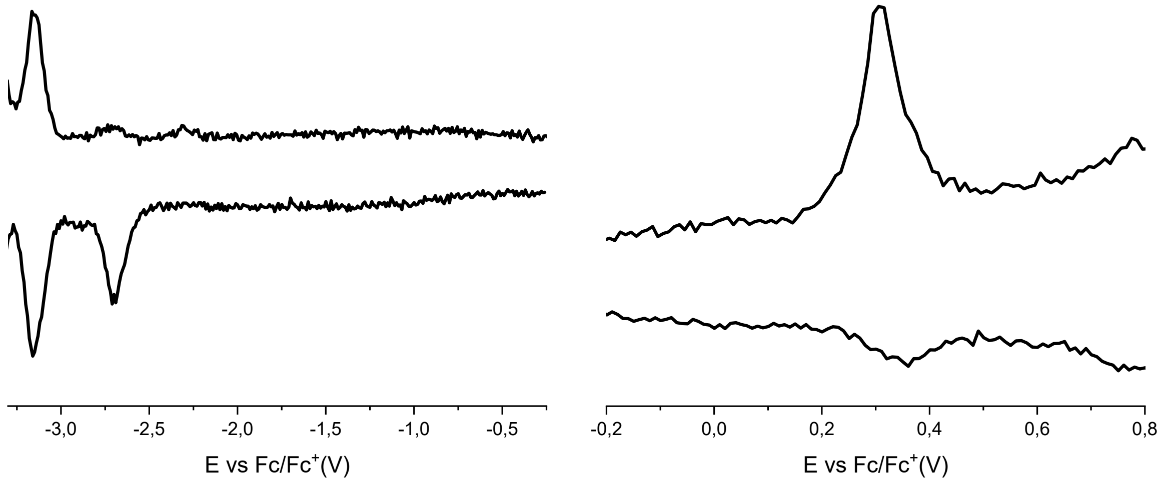


Figure S28. Differential pulse voltammograms for the reductive (left) and the oxidative (right) events of complex **6**, referenced internally versus Fc/Fc⁺.

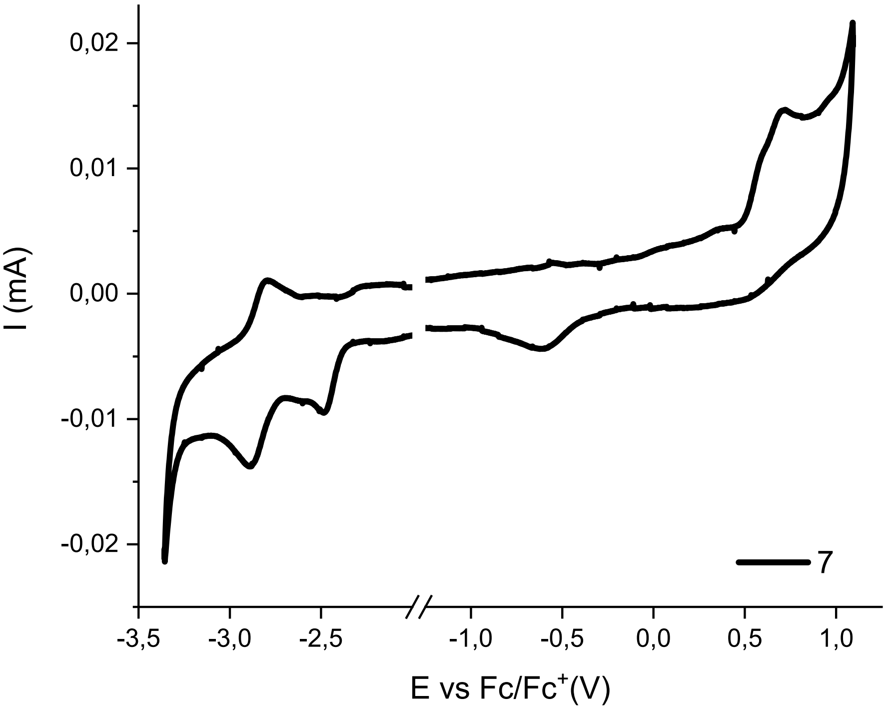


Figure S29. Cyclic voltammogram of complex **7**, referenced internally versus Fc/Fc⁺.

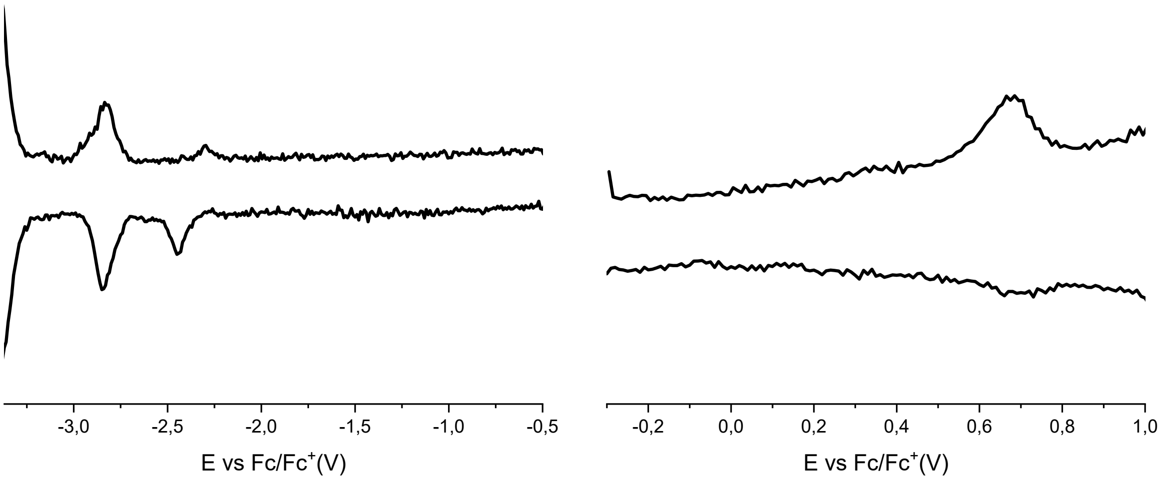
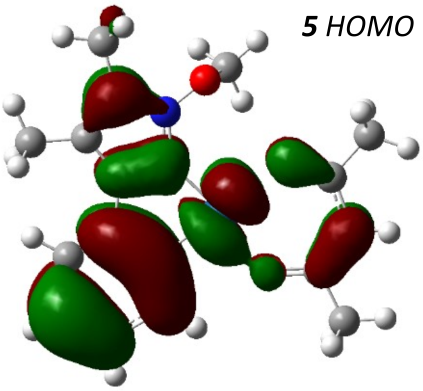
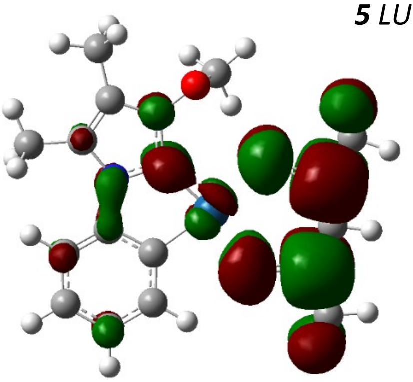
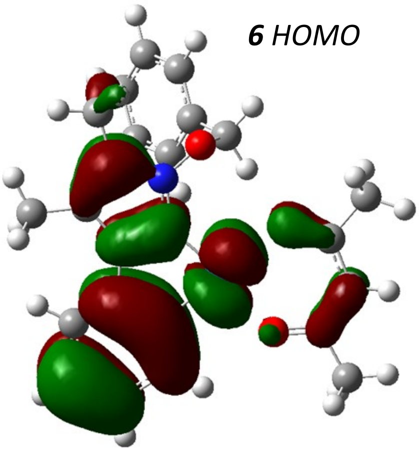


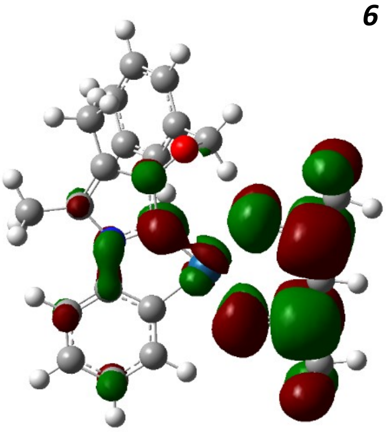
Figure S30. Differential pulse voltammograms for the reductive (left) and the oxidative (right) events of complex **7**, referenced internally versus Fc/Fc⁺.

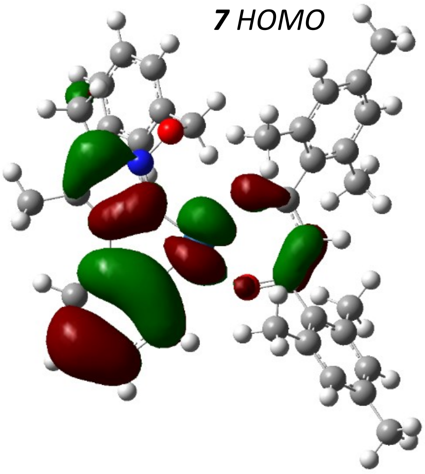
Quantum chemistry


5 *HOMO*


5 *LUMO*


6 *HOMO*


6 *LUMO*


7 *HOMO*

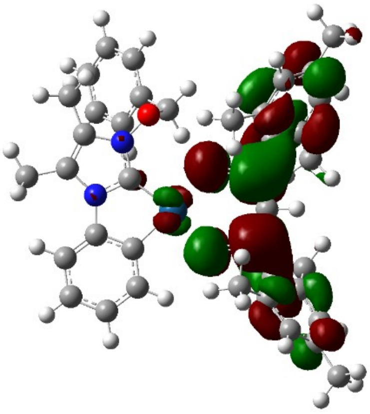

7 *LUMO*

Figure S31. Calculated frontier molecular orbitals for the ground state (isovalue=0.03). PBE/6-311G* level of theory with LANL2TZ ECP for platinum and inclusion of dispersion forces as D3BJ.

XYZ Coordinates

Complex 5

C	4.60280700	1.90427600	-0.01397400
C	3.64631400	-2.98498100	-0.13497000
C	-0.54918500	1.80137900	0.03348300
H	3.20883600	-3.54263100	-0.96692800
C	-0.11622600	3.12106900	0.08985900
C	3.91296300	-0.49849100	-0.09092500
C	-1.03078500	4.17160800	0.13640600
O	2.35256700	1.30278900	0.00852300
C	-2.39471900	3.91598500	0.12816500
C	-3.42119200	-0.54833500	-0.09142200
C	-1.14756700	-0.62381100	-0.07046100
C	-3.05335900	-1.85848200	-0.14750000
C	3.53476400	0.84691400	-0.03320000
Pt	0.60099300	0.19048500	-0.02665800
H	-3.92813300	2.41918800	0.06694500
H	5.61049300	1.49069100	-0.05858200
H	4.50048100	2.50234400	0.89567400
H	0.95070800	3.31823800	0.09720700
N	-2.24133300	0.18754100	-0.03789400
H	4.73185600	-2.97877200	-0.23639600
H	4.45419700	2.58099800	-0.85971600
H	-0.67334300	5.19643200	0.17981200
N	-1.66539500	-1.85980000	-0.12647600
H	4.97541400	-0.70589000	-0.12370200
O	1.78738400	-1.57540400	-0.06731300
H	-3.10722900	4.73387900	0.16553600
C	-2.86228500	2.60493800	0.07164500
H	3.38184700	-3.51733500	0.78372100
C	3.05089000	-1.60310100	-0.09719500
C	-1.93716900	1.57445700	0.02350400
O	-0.94310500	-2.99935100	-0.25095600
C	-4.78519500	0.03269100	-0.09128900
H	-4.98869100	0.59907400	0.82198500
H	-4.94461800	0.69879600	-0.94388600
H	-5.52548800	-0.76573100	-0.15387400
C	-3.82508700	-3.11826400	-0.24044300
H	-3.69080500	-3.74498600	0.64678600
H	-4.89009300	-2.90733200	-0.34009300
H	-3.51168700	-3.70710800	-1.10622600
C	-0.42436900	-3.41224900	1.01473000
H	0.10506200	-4.34021100	0.80523900
H	0.27273300	-2.66649400	1.39468200
H	-1.24021500	-3.59305100	1.72121100

Complex 6

C	5.29943400	-1.08802200	1.01150900
C	1.94677200	-4.29536000	-0.80957300
C	1.22657000	1.94616200	0.22260000
H	1.55025000	-4.32197200	-1.82757300
C	2.27170200	2.69088900	0.75668600

C	3.48740200	-2.53119800	0.06846200
C	2.13862200	4.06299100	0.96176500
O	3.20639900	-0.20271300	0.50015000
C	0.95580500	4.71002400	0.63337600
C	-2.25390800	1.91662900	-1.06216900
C	-0.55147700	0.44909600	-0.71061300
C	-2.69885300	0.67988700	-1.41625100
C	3.89905300	-1.26441000	0.49507100
Pt	1.24484600	0.00170200	-0.14788200
H	-1.02657400	4.50939500	-0.15726200
H	5.87771300	-2.01200200	0.99411600
H	5.25994500	-0.70876600	2.03628900
H	3.19622400	2.18275300	1.00997700
N	-0.94372000	1.75136900	-0.62554600
H	2.83200000	-4.92902900	-0.74980500
H	5.81189200	-0.33203500	0.41049500
H	2.96624400	4.62867900	1.38004200
N	-1.63560200	-0.18220600	-1.18808200
H	4.21666800	-3.32936900	0.13099500
O	1.23696400	-2.08472400	-0.57233900
H	0.85206700	5.77882500	0.79142500
C	-0.11053900	3.99263400	0.09581700
H	1.17435300	-4.70736800	-0.15298700
C	2.21866300	-2.86736800	-0.42068500
C	0.04075900	2.62897100	-0.09963500
O	-1.72620600	-1.51119800	-1.43634300
C	-2.98053700	3.20794300	-1.10584900
H	-3.08977800	3.64861400	-0.11063300
H	-2.48022000	3.93950600	-1.74666000
H	-3.98324300	3.05011900	-1.50436800
C	-3.99468800	0.20116500	-1.94682300
H	-4.55220000	-0.35791600	-1.19042100
H	-4.60809200	1.04289400	-2.27011800
H	-3.84351100	-0.45955600	-2.80351500
C	-1.78183800	-2.28072900	-0.20327500
H	-1.92668200	-3.29573900	-0.57458300
H	-0.80310000	-2.21597300	0.27074900
C	-2.88730800	-1.84331600	0.70145500
C	-2.64800900	-0.86447100	1.66624900
C	-4.17514500	-2.36063000	0.56477000
C	-3.68311500	-0.39709500	2.46599600
H	-1.64351400	-0.46573300	1.78213400
C	-5.20938300	-1.90314400	1.37045800
H	-4.36663900	-3.12631100	-0.18261200
C	-4.96461700	-0.91460100	2.31809500
H	-3.48670700	0.36897800	3.20938300
H	-6.20668200	-2.31795300	1.26144800
H	-5.77257600	-0.55412300	2.94729900

Complex 7

C	0.25322500	-2.96312100	-0.06359700
C	-0.75085800	-3.88466100	0.21053600
C	-2.46042800	1.26769000	-0.00462700
C	-0.47309900	-5.24989800	0.25621300
O	-1.99328000	-1.06761800	0.19144000
C	0.81568000	-5.71170000	0.02935900
C	3.83110000	-2.37365300	-0.86732800

C	1.93434800	-1.16813900	-0.53471300
C	4.14781100	-1.05944100	-1.03288300
C	-2.79132700	-0.08048700	0.17050400
Pt	0.04693400	-0.99587400	-0.16208100
H	2.84604800	-5.18719100	-0.41876600
H	-1.75702600	-3.52125500	0.39413100
N	2.47561800	-2.41658300	-0.55570400
H	-1.27024400	-5.95533700	0.47226300
N	2.96686400	-0.35967000	-0.82015800
H	-3.28237900	1.97270000	-0.02407600
O	-0.10114500	1.10888200	-0.26061300
H	1.03242100	-6.77457600	0.06598900
C	1.84513000	-4.81415400	-0.24654300
C	-1.17160900	1.78161700	-0.19945000
C	1.54893700	-3.46126100	-0.29030800
O	2.87676100	0.98557600	-0.96317600
C	4.71776800	-3.55672700	-0.97509900
H	4.78361600	-4.10576800	-0.03119200
H	4.38044400	-4.25336900	-1.74784500
H	5.72647000	-3.23478200	-1.23612500
C	5.42290600	-0.37848700	-1.35210800
H	5.89734400	0.02825800	-0.45439600
H	6.11941400	-1.07296400	-1.82376800
H	5.25213900	0.45241000	-2.03936900
C	2.78230500	1.65454000	0.32470000
H	2.65253600	2.69757800	0.03583900
H	1.86779400	1.31640800	0.81016200
C	4.00127000	1.43221800	1.15769700
C	4.06569900	0.33510500	2.01657600
C	5.11172500	2.26702100	1.03885500
C	5.22831500	0.06431000	2.72705200
H	3.19841400	-0.31150500	2.12047400
C	6.27101900	2.00631500	1.75688600
H	5.06586500	3.12412400	0.37241600
C	6.33272700	0.89856600	2.59642600
H	5.27006700	-0.79561500	3.38803500
H	7.12814700	2.66567500	1.66213300
H	7.23967000	0.69127100	3.15594000
C	-4.23381700	-0.44353000	0.30241500
C	-4.96779000	-0.07488000	1.43328800
C	-4.82780600	-1.19164200	-0.72669800
C	-6.30734000	-0.45396900	1.51356500
C	-6.16934100	-1.53275200	-0.61237900
C	-6.92769800	-1.17411200	0.50090200
H	-6.87737000	-0.18135600	2.39898100
H	-6.63720900	-2.10040400	-1.41401100
C	-0.99128300	3.24883700	-0.40790700
C	-1.37010900	4.17729400	0.56857300
C	-0.37397000	3.67675100	-1.59841500
C	-1.13091900	5.53182500	0.33553000
C	-0.17548300	5.03728400	-1.79434600
C	-0.54467300	5.98300300	-0.83886300
H	-1.40955100	6.25164800	1.10207700
H	0.28444000	5.37156300	-2.72196800
C	-4.34562000	0.69564100	2.56332100
H	-3.31978200	0.37593800	2.75926200
H	-4.30910300	1.76796700	2.34776700
H	-4.92179300	0.56634900	3.48219200

C	-4.03910500	-1.61053100	-1.93380300
H	-3.47813400	-0.77202400	-2.35743600
H	-3.30393200	-2.37795300	-1.67946000
H	-4.69622400	-2.00636900	-2.71068700
C	-8.37560600	-1.55725900	0.59188700
H	-8.97159500	-1.03262500	-0.16209600
H	-8.51639100	-2.62911400	0.42398600
H	-8.79426600	-1.31467200	1.57097300
C	-2.00501700	3.76950000	1.86857900
H	-3.09673800	3.74125300	1.78533400
H	-1.68555700	2.77950000	2.19715000
H	-1.76151500	4.48694700	2.65579200
C	0.05561600	2.70131100	-2.65729400
H	0.93621500	2.13638400	-2.34380700
H	-0.72480700	1.96421600	-2.86629100
H	0.28738700	3.22307700	-3.58835000
C	-0.32586900	7.44612500	-1.08808300
H	0.67388100	7.64009300	-1.48680500
H	-1.04414000	7.83185100	-1.81940500
H	-0.44237000	8.03156500	-0.17343500

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